
Über die Darstellung 2,6-Di-*iso*-propylphenyl
substituierter Bismutverbindungen und neuer
bismuthaltiger Interpnictogenverbindungen

Kumulative Dissertation

zur Erlangung des Doktorgrades der Naturwissenschaften

(Dr. rer. nat.)

am Fachbereich Chemie
der Philipps-Universität Marburg

vorgelegt von

Tobias Dunaj, M.Sc.

geboren in Böblingen

Marburg (Lahn) 2023

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„Über die Darstellung 2,6-Di-*iso*-propylphenyl substituierter Bismutverbindungen und neuer bismuthaltiger Interpnictogenverbindungen“

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Lebenslauf

Die persönlichen Daten sind nicht Teil der elektronischen Version dieser Dissertation.

Danksagung

Die persönlichen Daten sind nicht Teil der elektronischen Version dieser Dissertation.

„Life before death. Strength before weakness. Journey before destination.“

- Brandon Sanderson

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Abkürzungsverzeichnis

Ad	Adamantyl-
AN	Akzeptor Nummer (vgl. GBM)
Bbt	2,6-(CH(SiMe ₃))-4-(C(SiMe ₃) ₃)C ₆ H ₂
BDE	Bindungsdissoziationsenergie
<i>t</i> Bu	<i>tert</i> -Butyl
CAAC	Zyklische(Alkyl)(Amino)Carbene
CCDC	Cambridge Crystallographic Data Centre
CDC	Carbodicarben
Cp	Cyclopentadienid
Cy	Cyclohexyl-
DABCO	1,4-Diazabicyclo[2.2.2]octan
DCM	Dichlormethan
DFT	Density Functional Theory
Dipp	2,6-Di- <i>iso</i> -propylphenyl
DTBAA	Di- <i>tert</i> -butylaminoarsan
DTBAP	Di- <i>tert</i> -butylaminophosphan
DTBASb	Di- <i>tert</i> -butylaminostiban
FIA	Fluorid-Ionen Affinität
GBM	<i>Gutmann-Beckett</i> -Methode
Ph	Phenyl
<i>i</i> Pr	<i>iso</i> -Propyl
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Occupied Molecular Orbital
Me	Methyl
MeCN	Acetonitril
Mes	2,4,6-Trimethylphenyl
Mes*	2,4,6-Tri- <i>tert</i> -butylphenyl
MOCVD	Metal Organic Chemical Vapour Deposition
MOVPE	Metal Organic Vapour Phase Epitaxy
NBO	Natural Bond Order
NHC	<i>N</i> -heterozyklisches Carben
NMR	Nuclear Magnetic Resonanz
NON ^R	[O(SiMe ₂ NR) ₂] ²⁻

OTf	Triflat (OSO_2CF_3)
py	Pyridin
TBA	<i>tert</i> -Butylarsan
TBP	<i>tert</i> -Butylphosphan
Ter ^{Ar}	2,5-Diarylphenyl
TFT	α - α - α -Trifluortoluol
THF	Tetrahydrofuran
TP ⁻	Trispyrazolborat
Trip	2,4,6-Tri- <i>iso</i> -propylphenyl
UDMHy	Unsymmetrisches Dimethylhydrazin (Me_2NNH_2)
Xyl	Xylyl

1 Einleitung

1.1 Bismut - Ein Element im Trend

Bismut, das schwerste in großen Mengen vorhandene Element der 15. Gruppe, und seine Verbindungen zeigen viele besondere Eigenschaften, welche in den letzten Jahren zu einem stark gesteigerten Interesse an bismuthaltigen Verbindungen und Materialien geführt haben. So zeigen sowohl die meisten Verbindungen des Schwermetalls Bismut, als auch Bismut in elementarer Form, eine geringe Toxizität. Dies gilt vor allem im Vergleich zu den leichteren Pnictogenen Antimon und Arsen, oder anderen Schwermetallen, wie zum Beispiel Blei.^[1-3]

Die geringe Toxizität macht Bismutverbindungen attraktiv für den Einsatz als Pigmente in der Kosmetikindustrie oder als aktive Bestandteil von Medizinprodukten. So wird das schwer lösliche BiOCl als Weißpigment mit perlmuttartigem Glanz in Mascara oder Lippenstiften eingesetzt.^[4] Der aktive Wirkstoff im, vor allem in den USA verkauften, bismuthaltigen Medikament *Pepto-Bismol* ist Bismutsubsalicylat (Abbildung 1.1 a.).^[5,6] *Pepto-Bismol* wird bei Magenbeschwerden oral eingenommen. Des Weiteren wird Bismutsubgallat (Abbildung 1.1 b.; Handelsname: *Devrom*) als internes Deodorant gegen den Geruch von Stuhl sowie Flatulenzen eingesetzt.^[7,8] Durch die sehr geringe Toxizität sind sogar Anwendungen am Auge möglich. So wird Bibrocathol (Abbildung 1.1 c.; Handelsnamen: *Noviform*, *Posiformin*) in Form einer Augensalbe als Antiseptikum verwendet.^[9]

Organische Bismutverbindungen zeigen vielversprechende Reaktivität als homogene Katalysatoren. Die Wahl geeigneter Substituten verschafft hier Zugang zu vielen verschiedenen Oxidationsstufen (+I, +II, +III, +V), was an eine typische Eigenschaft von Übergangsmetallen erinnert. Dies ermöglicht den Einsatz von Bismutverbindungen in der Redoxkatalyse.^[10] In Ein-Elektronen-Prozessen kann

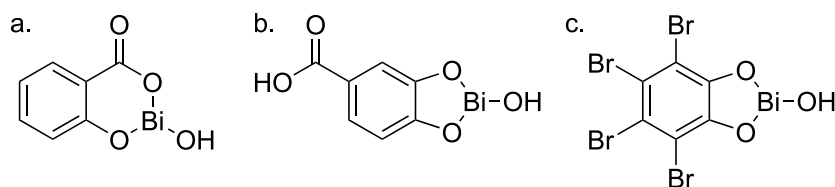


Abbildung 1.1: Struktur einiger in Medikamenten eingesetzter Bismutverbindungen. a. Bismutsubsalicylat (*Pepto-Bismol*). b. Bismutsubgallate (*Devrom*). c. Bibrocathol (*Noviform*).

das II/III-Redoxpaar, zum Beispiel in der katalytischen Dehydrokupplung von TEMPO und Silanen (Abbildung 1.2 a.) oder der Zyklisomerisierung von δ -Iodo-Olefinen, eingesetzt werden.^[11–13] Des Weiteren können transiente Bi(II)-Spezies als Radikalstarter in der radikalischen Polymerisationen verwendet werden.^[14–16] Für Zwei-Elektronen-Prozesse sind in der Literatur katalytische Reaktionen sowohl für das I/III- als auch das III/V-Redoxpaar beschrieben. In ersterem Fall zum Beispiel in der Transfer-Hydrierung von Azoaren- und Nitroarenverbindungen (Abbildung 1.2 b.)^[17] oder der Hydrodefluorierung von Polyfluorarenverbindungen.^[18] Mittels eines III/V Redoxpaar können dagegen zum Beispiel fluorierte Arylverbindungen oder Aryltriflate aus Arylboronsäureestern dargestellt werden (Abbildung 1.2 c.).^[19,20]

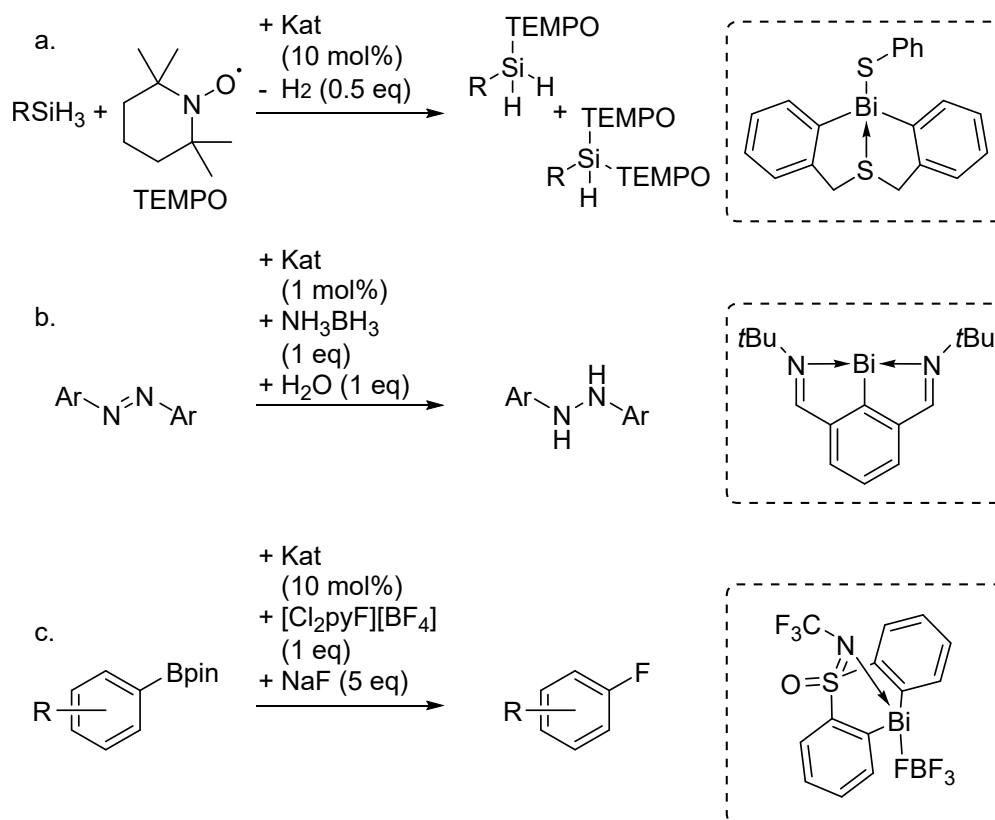


Abbildung 1.2: Katalytische Redoxreaktion mit Organobismut-Katalysatoren (rechts) in verschiedenen Oxidationsstufen. a. Katalytische Kopplung von Silanen und TEMPO; Bi-Redoxpaar II/III. b. Transferhydrierung von Azoarenen; Bi-Redoxpaar I/III. c. Darstellung von Fluoroarene Verbindungen aus Boronsäureestern; Bi-Redoxpaar III/V.

Auch in technischen Anwendungen sind bismuthaltige Materialien gefragt. So wird im *SOHIO*-Prozess Acrolein aus Propen und Sauerstoff, oder Acrylnitril aus Propen, Sauerstoff und Ammoniak dargestellt. Die Reaktion in der Multi-Millionen-Tonnen Produktion erfolgt dabei durch einen heterogenen Katalysator auf Bismut-Molybdat-Basis.^[21] In der Forschung finden $\text{Bi}[\text{VO}_4]$ und die Bismutoxyhalogenide $\text{Bi}_x\text{O}_y\text{X}_z$ ($X = \text{F}, \text{Cl}, \text{Br}, \text{I}$) Verwendung als Photokatalysatoren.^[22,23] Diese können in der Wasserspaltung,^[24–26] bei der CO_2 Reduktion,^[27–29] der N_2 Fixierung^[30] oder der Zersetzung von organischen Verbindungen und damit potentiell zur Wasseraufbereitung^[31–34] genutzt werden. Im Kontext dieser Arbeit soll auch das Potential von bismuthaltigen 13/15-Halbleitern nicht unerwähnt bleiben. Wird eine Legierung aus Galliumarsenid (GaAs) und Galliumbismutid (GaBi) dargestellt ($\text{GaAs}_{1-x}\text{Bi}_x$), so verringert sich die Bandlücke des Halbleitermaterials im Vergleich zum GaAs um ungefähr 88 meV pro % Bismut im Material.^[35–40] In theoretischen Rechnungen konnte gezeigt werden, dass $\text{GaAs}_{1-x}\text{Bi}_x$ ($x \approx 10\%$) ein vielversprechendes Material zum Bau effizienter Laser mit einer Emissionswellenlänge von $1.55\ \mu\text{m}$ sein könnte.^[41–43] Die Bandlücke ist dabei gleichzeitig wenig temperaturempfindlich, was ein Vorteil gegenüber konventionell verwendeten quaternären 13/15-Halbleitern ist, die mit $1.55\ \mu\text{m}$ emittieren. Diese müssen bei Verwendung üblicherweise gekühlt werden.^[40,44,45] Durch das Einbringen von Bismut in GaAs steigt außerdem die Energie der *Spin-Orbit-Kopplung*, was emissionslose Elektron-Loch-Rekombinationen unterdrückt.^[36,41] Licht mit Wellenlängen von 1.3 oder $1.55\ \mu\text{m}$ wird genutzt, um Informationen weite Distanzen in Glasfaserkabeln zu transferieren. Die genannten Eigenschaften von $\text{GaAs}_{0.9}\text{Bi}_{0.1}$ machen es daher zu einem potentiell attraktiven Material für die technische Anwendung in der Telekommunikationsbranche. Da es sich bei $\text{GaAs}_{0.9}\text{Bi}_{0.1}$ um ein metastabiles Material handelt, ist die Darstellung von Halbleitern mit hohem Bismut-Anteil und guter Qualität bis heute problematisch.^[46] Bei üblichen Prozesstemperaturen der *MOVPE* (siehe Kapitel 1.4) beginnt sich bereits sehr wenig eingebrachtes Bismut in Form von elementarem Bismut aus dem Material zu separieren.^[47–51] Aufgrund dessen konnten *via MOVPE* für $\text{GaAs}_{1-x}\text{Bi}_x$ bisher maximale Werte von nur $x = 7\%$ erreicht werden.^[52] Ein Ansatz, um mittels *MOVPE* höhere Einbauraten zu erreichen, ist die Senkung der Prozesstemperatur. Dafür ist es nötig neue bismuthaltige Präkursoren zu entwickeln, die sich bereits bei tieferen Temperaturen wie gewünscht zersetzen.

1.2 Bismutverbindungen

1.2.1 Bismut im Kontext der Pnictogene

Als Pnictogene werden die Elemente der 15. Gruppe bezeichnet. Nach dem künstlich erzeugten, nicht stabilen und damit chemisch nicht weiter relevanten, Moscovium^[53] ist Bismut das schwerste Element der Pnictogene. Bismut ist ein anisotopes Element, wobei das einzige natürlich vorkommende Isotop, ²⁰⁹Bi, nicht stabil ist und sich mittels α -Zerfall langsam in ²⁰⁵Tl umwandelt.^[54] Durch die sehr lange Halbwertszeit von etwa $2 \cdot 10^{19}$ Jahren, und damit etwa drei Zerfällen in einhundert Milliarden Jahren pro einer Milliarde Atome, kann die Radioaktivität bei der Arbeit mit bismuthaltigen Verbindungen oder Materialien vernachlässigt werden.^[55]

Beim Gang durch die Gruppe der Pnictogene steigt der metallische Charakter der Elemente zusehends. Während es sich beim grauen Arsen und Antimon noch um Halbmetalle handelt, liegt Bismut metallisch vor. Da alle drei Elemente wenig duktil sind, werden sie auch als *Sprödmetalle* bezeichnet.^[56] Der zunehmend metallische Charakter zeigt sich auch in den gebildeten Allotropen der Pnictogene. Stickstoff tritt als einziges Pnictogen unter Normalbedingungen als zweiatomiges Gas (N₂) auf. Auch für den Phosphor ist ein kinetisch stabiles, molekulares Allotrop bekannt. Dabei handelt es sich um den weißen Phosphor, welcher aus diskreten P₄-Tetraedern aufgebaut ist. Unter dem Einfluss von Licht, erhöhten Temperaturen oder unter Druck wandelt sich der weiße Phosphor in thermodynamisch stabilere Allotrope wie den roten, violetten oder schwarzen Phosphor um. Im Falle des Arsens ist das zum P₄ isomorphe gelbe Arsen sehr instabil und wandelt sich unter dem Einfluss von Licht innerhalb weniger Minuten in graues Arsen um. Auch ohne den Einfluss von Licht kann gelbes Arsen bei tiefen Temperaturen (-70 °C) nur kurzfristig gelagert werden.^[57,58] Für Antimon und Bismut sind keine Modifikationen mit diskreten Molekülen bekannt. Die Strukturen von grauem Arsen, grauem Antimon und grauem Bismut ähneln einander stark. Dabei werden im Festkörper sesselförmig gewellte, übereinander gestapelte Schichten gebildet. Die Stapelung erfolgt so, dass jedes Atom von drei Atomen der eigenen und drei Atomen der nächsten Schicht koordiniert wird, woraus sich eine Koordinationszahl von 3+3 ergibt. Der zunehmende metallische Charakter wird zum Beispiel beim Gang vom grauen Arsen zum Bismut im Verhältnis der Atomabstände innerhalb einer Schicht und zwischen zwei Schichten deutlich. Dieser sinkt von 1.240 (As)

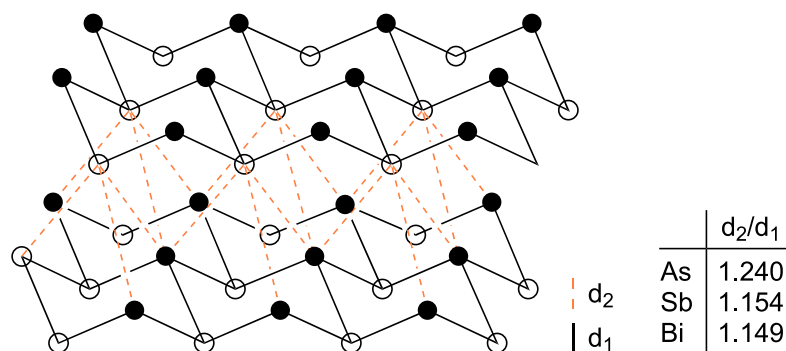


Abbildung 1.3: Schematischer Ausschnitt der Struktur von grauem Arsen, grauem Antimon und grauem Bismut.^[56]

bis zu 1.149 (Bi) (Abbildung 1.3).^[56]

Die Pnictogene zeigen Präferenzen zur Ausbildung verschiedener Oxidationsstufen. Trends für die bevorzugten Oxidationsstufen lassen sich zum Beispiel beim Blick auf die beschriebenen Halogenide erkennen. Während für alle Pnictogene in der Oxidationsstufe +3 alle Halogenide der Form EX_3 ($E = P\text{-}Bi$, $X = F\text{-}I$) darstellbar sind, ist dies für die Oxidationsstufe +5 nicht der Fall. Der zugrunde liegende Trend innerhalb der Periode lässt sich gut anhand der Pentachloride beobachten. So ist PCl_5 ein stabiler Feststoff, der bei 150 °C sublimiert werden kann.^[56] Das schwerere $AsCl_5$ ist dagegen nur noch metastabil und zersetzt sich schon bei -50 °C in $AsCl_3$ und Cl_2 .^[59] Für das schwerere Antimon liegt dagegen $SbCl_5$ bei Raumtemperatur als stabile Flüssigkeit vor, während $BiCl_5$ nicht dargestellt werden kann.^[56] Der Trend innerhalb der Gruppe lässt sich durch zwei Effekte, den *inert-pair-Effekt* und die *d-Elektronen-Kontraktion*, erklären. Ersterer besagt, dass bei steigender Ordnungszahl innerhalb einer Periode die Tendenz der beiden Elektronen im s-Orbital zur Ausbildung chemischer Bindungen sinkt. Das Elektronenpaar wird inert. Der Effekt kann durch das Auftreten relativistischer Effekte in Atomen mit hoher Protonenzahl und der daraus resultierenden hohen elektrostatischen Anziehung des Kerns auf die Elektronen im Atom erklärt werden. Da die Elektronen in den s-Orbitalen die höchste Aufenthaltswahrscheinlichkeit in der Nähe des Kerns haben, wirkt die elektrostatische Anziehung auf diese besonders stark. Daraus resultiert eine energetische Absenkung und Kontraktion der s-Orbitale. Ähnlich verhält es sich mit den p-Orbitalen. Auch diese kontrahieren und senken sich energetisch ab, wenn auch nicht so stark wie die s-Orbitale. Das Resultat ist

nun, dass die Energiedifferenz zwischen s- und p-Orbitalen für schwere Elemente steigt. Da die s-Orbitale energetisch sehr tief liegen nehmen sie nun eher nicht an chemischen Bindungen teil. Durch die Kontraktion der s- und p-Orbitale nimmt die effektive Ladung, die auf d- und f-Elektronen wirkt, ab, was zu einer Expansion der d- und f-Orbitale führt. Der *inert-pair-Effekt* erklärt demnach, warum schwerere Hauptgruppenelemente eher zu niedrigen Oxidationsstufen neigen.^[56,60–62] Dass das Arsen vom Trend abweicht und auch zu einer Valenz von drei neigt, kann mit der *d-Orbital Kontraktion* erklärt werden. In der vierten Periode liegen die 3d-Orbitale energetisch tiefer als die 4p-Orbitale, weshalb nach dem *Aufbauprinzip*, zunächst diese mit Elektronen befüllt werden. Da die d-Orbitale diffuser als s- oder p-Orbitale sind, wird die Kernladung auf letztere etwas weniger effektiv abgeschirmt. Wieder ist die Kontraktion der s-Orbitale stärker als die der p-Orbitale, was zu einer erhöhten Energiedifferenz im p-Block der vierten Periode führt. Weitere Ergebnisse des Effektes sind zum Beispiel die höheren Elektronegativitäten der Elemente Gallium und Germanium im Vergleich zu Aluminium und Silizium oder erhöhte Ionisationsenergien aller p-Block Elemente der 4. Periode.^[63–66]

Neben den Halogenverbindungen, zeigen auch die Wasserstoffverbindungen der Form EH_3 einige Trends auf. So nimmt die Stabilität der Verbindungen vom NH_3 zum BiH_3 deutlich ab. Während NH_3 , PH_3 und AsH_3 noch bei Raumtemperatur lagerbare Gase darstellen, können SbH_3 und BiH_3 nur *in situ* erzeugt werden und zersetzen sich bei Raumtemperatur oder unter dem Einfluss von Licht zu den Elementen. Gleichwohl sind alle Verbindungen schon seit langem in der Literatur bekannt und selbst das extrem labile BiH_3 wurde bereits 1918 erstmals beschrieben.^[67,68] Die Standardbildungsenthalpie gibt an, wie viel Wärme bei der Bildung von Verbindungen aus den Elementen frei wird. Während die Bildung von NH_3 noch exotherm ist, ist diese im Falle des PH_3 und AsH_3 schon leicht, und vor allem für SbH_3 und BiH_3 deutlich, endotherm. (Tabelle 1, links).^[69,70] Ähnlich verhält es sich bei der Standardbildungsenthalpie von organischen Verbindungen. Diese wurde für Verbindungen der Form EMe_3 ($\text{E} = \text{P}, \text{As}, \text{Sb}, \text{Bi}$) kalorimetrisch bestimmt (Tabelle 1, rechts). Auch hier ist die Bildung von Verbindungen der schweren Elemente deutlich weniger begünstigt, und im Falle des BiMe_3 deutlich endotherm (Tabelle 1, rechts).^[71–74] Aus der Standardbildungsenthalpie der Verbindungen EH_3 und EMe_3 kann die mittlere Energie eines E-H- beziehungsweise E-C-Bindungsbruchs berechnet werden. Hierbei zeigt sich, dass Bismut die labilsten E-H- sowie E-C-Bindungen ausbildet.^[69–74] Beim Vergleich von Alkyl-

Tabelle 1: Standardbildungsenthalpien von Verbindungen der Form EH_3 und EMe_3 ($\text{E} = \text{N}, \text{P}, \text{As}, \text{Sb}, \text{Bi}$) und mittlere Energie des E-H- beziehungsweise E-C-Bindungsbruch (\emptyset BDE).^[69–74]

EH_3	ΔH_f^0 [kJ · mol ⁻¹]	\emptyset BDE [kJ · mol ⁻¹]	EMe_3	ΔH_f^0 [kJ · mol ⁻¹]	\emptyset BDE [kJ · mol ⁻¹]
NH_3	-46	391			
PH_3	5	321	PMe_3	-126	273
AsH_3	66	279	AsMe_3	-15	214
SbH_3	145	256	SbMe_3	6	208
BiH_3	278	209	BiMe_3	157	141

und Arylbismutanen zeigt sich, dass letztere eine etwas stabilere Bi-C-Bindung ausbilden, wobei die mittlere Dissoziationsenergie einer Bi-C-Bindung im Ph_3Bi kalorimetrisch zu $194 \text{ kJ} \cdot \text{mol}^{-1}$ bestimmt wurde.^[75]

1.2.2 Organobismutverbindungen

Abgeleitet von der Stammverbindung, dem Bismutan (BiH_3), werden Bismutverbindungen mit organischen Resten als primäre (RBiH_2), sekundäre (R_2BiH) oder ternäre Bismutane (R_3Bi) bezeichnet (Abbildung 1.4, links). Dies steht in Analogie mit den leichteren Pnictogenen Phosphor, Arsen und Antimon. Im Gegensatz zu den leichteren Vertretern sind primäre und sekundäre Stibane und Bismutane instabil und neigen zur Zersetzung, wobei die Bismutane nochmals deutlich labiler sind als die entsprechenden Stibane. Während selbst einige primäre Stibane isolierbar sind ($(\text{Me}_3\text{CCH}_2)\text{SbH}_2$,^[77] $(\text{Me}_3\text{SiCH}_2)\text{SbH}_2$,^[78] $(2,6\text{-Trip}_2\text{C}_6\text{H}_3)_2\text{SbH}_2$ ^[79]), sind bisher keine isolierbaren primären Bismutane beschrieben. Über die erste definierte Reaktion eines *in situ* dargestellten primären Bismutans, dem MeBiH_2 , wurde dagegen schon 1961 berichtet, wobei Zersetzung zu BiH_3 , welches sich wiederum in die Elemente zersetzt, und BiMe_3 beobachtet wurde.^[80] Im Falle der sekundären Bismutane konnte im Jahr 2000 mit $(\text{Ter}^{\text{Mes}})_2\text{BiH}$ die erste, bei Raumtemperatur stabile Verbindung isoliert werden (Abbildung 1.4, rechts).^[76] Die Zersetzung wird dabei durch die Verwendung sterisch sehr anspruchsvoller Substituenten unterdrückt. Sekundäre Bismutane mit kleineren Substituenten konnten zuvor schon spektroskopisch identifiziert werden. Beispiele sind hier Mes_2BiH ,

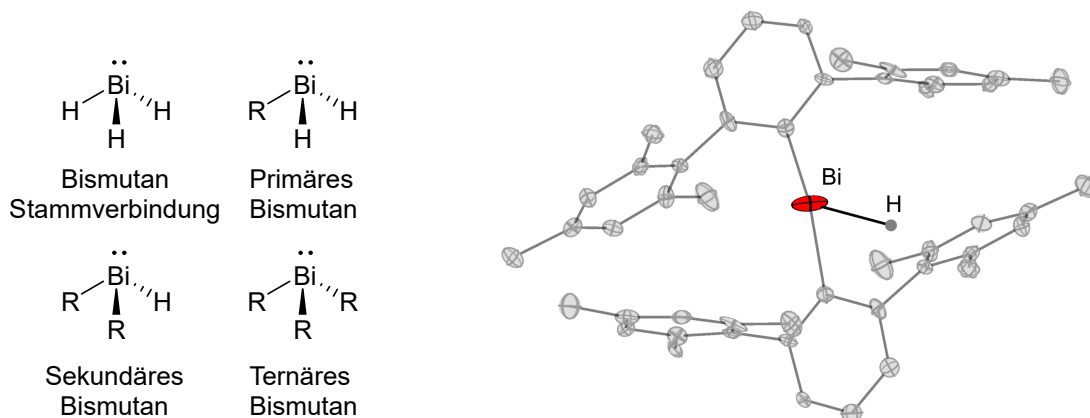


Abbildung 1.4: Links: Bismutan als Stammverbindung und Namensgeber für die Verbindungsklasse der Bismutane. Rechts: Erstes isoliertes und strukturell charakterisiertes sekundäres Bismutan.^[76] An Kohlenstoff gebundene Wasserstoffatome sind aus Gründen der Übersichtlichkeit nicht dargestellt. Die Schwingungsellipsoide sind mit 50 % Aufenthaltswahrscheinlichkeit gezeigt.

$((\text{Me}_3\text{Si})_2\text{HC})_2\text{BiH}$ oder $(\text{F}_5\text{C}_2)_2\text{BiH}$, welche sich jedoch zwischen $-30\text{ }^\circ\text{C}$ und $0\text{ }^\circ\text{C}$ unter Freisetzung von H_2 zum Dibismutan zersetzen.^[81–83] Die entsprechenden Antimonverbindungen, zum Beispiel das Me_2SbH , sind dagegen verhältnismäßig stabil und oft unter Inertbedingungen lagerbar.^[84] Ternäre Bismutane sind, je nach verwendeten Substituenten, üblicherweise kinetisch stabil. Die meisten Vertreter der Form R_3Bi ($\text{R} = \text{Alkyl-}, \text{Aryl-}$) können unter Ausschluss von Licht und Sauerstoff bei Raumtemperatur gelagert werden.

Wie in Abschnitt 1.2.1 beschrieben, ist die Bi-C-Bindung schwächer als die E-C-Bindung der leichteren Pnictogene. Trotz alledem sind viele homoleptische Bismutane synthetisch einfach zugänglich. So werden diese üblicherweise durch Umsatz eines Metallorganischen Reagenz mit BiX_3 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) erhalten.^[1] Die Struktur der Verbindungen ist stark durch das sterisch aktive, freie Elektronenpaar geprägt. Durch die deutliche energetische Absenkung des s-Orbitals nimmt dieses kaum an der Bildung der bindenden und antibindenden Orbitale teil (*inert-pair-Effekt*, siehe Abschnitt 1.2.1). Das freie Elektronenpaar befindet sich also in einem Orbital mit beinahe ausschließlich s-Charakter. Da hauptsächlich die p-Orbitale zu den Bindungen beisteuern, zeigen Bismutane mit kleinen Resten (zum Beispiel BiMe_3 oder Ph_3Bi) einen C-Bi-C-Bindungswinkel von etwas über 90° .^[85–92] Für sterisch anspruchsvolle Reste kann der Bindungswinkel allerdings deutlich aufgeweitet sein. So liegt er im $((2,4,6\text{-Ph})\text{C}_6\text{H}_2)_3\text{Bi}$ zwischen $103.7(4)$ und $109.4(4)^\circ$.^[93]

Ähnlich zu den leichteren Pnictanen, können Bismutane über ihr freies Elektronenpaar mit *Lewis*-Säuren Donor-Akzeptor-Komplexe bilden. So sind einige Übergangsmetallkomplexe mit BiR_3 -Substituenten, zum Beispiel $[\text{Fe}(\text{BiPh}_3)(\text{Cp})(\text{CO})_2][\text{BF}_4]$ oder $[\text{Cr}(\text{Bi}t\text{Bu}_3)(\text{CO})_5]$ (Abbildung 1.5 a., b.), beschrieben.^[94,95] Die Anzahl der beschriebenen Verbindungen ist allerdings deutlich geringer als im Falle der leichteren Pnictane. Auch die Stabilität von Bismutan-Addukten und Gruppe 13-Verbindungen ist begrenzt. So konnte bei der Reaktion von GaMe_3 und Me_3E ($\text{E} = \text{N}, \text{P}, \text{As}, \text{Sb}, \text{Bi}$) einzig im Falle der Bismutverbindung keine Adduktbildung beobachtet werden.^[96] Die Stabilität von Addukten der Form $\text{R}_3\text{E-AlR}'_3$ ($\text{E} = \text{N}, \text{P}, \text{As}, \text{Sb}, \text{Bi}$; $\text{R} = \text{SiMe}_3, i\text{Pr}$; $\text{R}' = \text{Et}, t\text{Bu}$) wurde mittels experimenteller und theoretischer Methoden im Detail untersucht, wobei sich die dative Bi-Al-Bindung als am schwächsten herausstellte (Abbildung 1.5 c.).^[97]

Einige Trialkylbismutane reagieren an Luft pyrophor.^[1] Durch kontrollierte Reaktionen mit Sauerstoff können jedoch auch gezielt Alkoxybismutane dargestellt

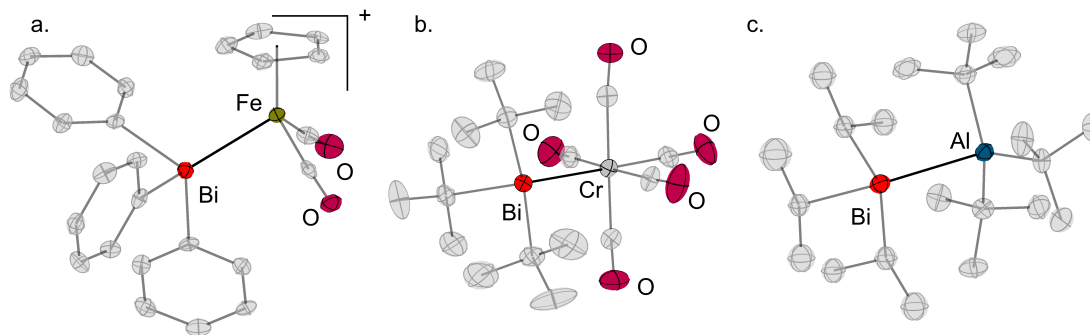


Abbildung 1.5: Bismutane als Donor in den Übergangsmetallkomplexen $[\text{Fe}(\text{BiPh}_3)(\text{Cp})(\text{CO})_2][\text{BF}_4]$ (ohne Gegenion dargestellt) und $[\text{Cr}(\text{Bi}t\text{Bu}_3)(\text{CO})_5]$. Außerdem die 13/15-Verbindung $i\text{Pr}_3\text{BiAl}t\text{Bu}_3$.^[94,95,97] Wasserstoffatome sind aus Gründen der Übersichtlichkeit nicht dargestellt. Die Schwingungsellipsoide sind mit 50 % Aufenthaltswahrscheinlichkeit gezeigt.

werden. So reagieren zum Beispiel Me_3Bi oder Et_3Bi bei kontrollierter Zugabe von O_2 zu $\text{Me}_2\text{Bi}(\text{OMe})$ beziehungsweise $\text{Et}_2\text{Bi}(\text{OEt})$.^[98,99] Bei diesen Reaktionen zeigt sich außerdem die Neigung von Organobismutverbindungen nicht die Oxidationsstufe +V auszubilden. Im Gegensatz dazu werden Triarylbismutane bei Raumtemperatur üblicherweise nicht durch Luftsauerstoff oxidiert und sind im Allgemeinen auch über längere Zeit an Luft lagerbar.^[1] Auch bei der Reaktion mit Dihalogenen oder Halogenierungsreagenzien zeigen Trialkyl- und Triarylbismutane teilweise unterschiedliche Reaktivitäten. So kann bei der Reaktion von R_3Bi ($\text{R} = \text{Alkyl}$) mit X_2 oder X_2 -Übertragungsreagenzien ($\text{X} = \text{Cl-I}$) die oxidierte Bi(V) -Verbindung BiR_3X_2 üblicherweise nicht isoliert werden und zersetzt sich zu R_2BiX , einer Bi(III) -Verbindung, und R-X . Die Oxidation mit anschließender reduktiver Eliminierung von R-X ist eine praktikable Methode zur Darstellung von Me_2BiCl , $i\text{Pr}_2\text{BiBr}$, $t\text{Bu}_2\text{BiBr}$ oder $t\text{Bu}_2\text{BiI}$.^[100–103] Wird bei sehr tiefen Temperaturen gearbeitet, kann nach Umsatz von BiMe_3 mit Thionylchlorid Me_3BiCl_2 isoliert werden. Bei Raumtemperatur zersetzt sich die Verbindung allerdings wie zuvor beschrieben.^[104] Im Falle von Aryl-Substituenten sind Verbindungen der Form Ar_3BiX_2 für $\text{X} = \text{Cl, Br}$ im Allgemeinen bei Raumtemperatur stabil. So können zum Beispiel Ph_3BiCl_2 , $\text{Mes}_3\text{BiCl}_2$ oder Ph_3BiBr_2 durch Umsetzung von R_3Bi mit SOCl_2 oder Br_2 dargestellt werden.^[105–107] Die entsprechenden Iodverbindungen können nicht isoliert werden und zersetzen sich auch für die Aryl-Verbindungen zu R_2BiI und R-I . So kann zum Beispiel Ph_2BiI durch Umsatz von Ph_3Bi mit I_2

erhalten werden.^[108] Auch mit Halogenwasserstoffsäuren können ternäre Bismutane reagieren, wobei mit einem Äquivalent HX Verbindungen der Form R_2BiX entstehen. Im Gegensatz zur Reaktion mit den Dihalogeniden ist die Tendenz zur Spaltung der C_{Aryl} -Bindung höher als die der C_{Alkyl} -Bindung. So kann zum Beispiel Ph_2BiMe mit zwei äquivalenten HX ($X = Cl, Br$) umgesetzt und als Edukt zur Darstellung von $MeBiCl_2$ oder $MeBiBr_2$ genutzt werden.^[109] Verbindungen der Form $R_{3-n}BiX_n$ ($R = Aryl-, Alkyl;$ $X = Cl, Br, I;$ $n = 1, 2$) können am atomökonomischsten, und meist auch apparativ am wenigsten aufwendig, mittels Redistributionsreaktionen dargestellt werden. Dafür wird ein ternäres Bismutan in der richtigen Stöchiometrie mit einem Bismuttrihalogenid umgesetzt. So können zum Beispiel Ph_2BiCl , $(p\text{-MePh})BiBr_2$ oder $(o\text{-(H}_2\text{C}_2\text{)C}_6\text{H}_4)_2BiI$ aus R_3Bi und BiX_3 dargestellt werden.^[110–112] Alkyl- oder Arylhalidobismutane liegen meist in Form von Feststoffen vor, wobei die Struktur im Festkörper von sekundären Wechselwirkungen der Halogenid-Substituenten und den Bi-Atomen bestimmt wird. Für Verbindungen mit sehr großen Substituenten können diese Wechselwirkungen unterdrückt werden, was zur Bildung von Monomeren im Festkörper führt. Beispiele sind hier $(Ter^{Mes})_2BiCl$ oder $(2,4,6\text{-(CF}_3\text{)C}_6\text{H}_2)_2BiCl$.^[76,113] Für die Dihalogenide werden durch Verwendung großer Reste meist kleine Aggregate gebildet, so zum Beispiel Dimere im Falle des $(Ter^{Mes})BiCl_2$ ^[114] oder $(2,4,6\text{-PhC}_6\text{H}_2)BiCl_2$ ^[115]. Mit kleineren Substituten bilden Verbindungen der Form R_2BiX ($X = F, Cl, Br, I$) im Festkörper meist eindimensionale polymere Stränge mit alternierenden Bismut- und Halogenatomen. Die Stärke der sekundären Wechselwirkung zwischen Bismut- und Halogenatom kann dabei stark variieren, was eine Auswirkung auf die inter- und intramolekularen Bi-X-Abstände hat. Für eine sehr starke Wechselwirkung kann die inter- und intramolekulare Bindungslänge sogar ununterscheidbar werden. Beispiele hierfür sind die Strukturen von Me_2BiBr oder Ph_2BiCl (Abbildung 1.6 a.).^[116,117] In anderen Fällen können sich die Abstände deutlich unterscheiden. So zum Beispiel im Mes_2BiBr . Hier ist der intermolekulare Bi-Br-Abstand über 0.9 \AA größer als der intramolekulare Abstand.^[118] In Verbindungen der Form $RBiX_2$ bilden sich für kleine Substituenten meist auch eindimensionale polymere Stränge mit verbrückenden Halogenid-Substituenten ($EtBiI_2$, $MesBiBr_2$).^[119,120] Im Falle sehr kleiner Substituenten können sich auch zweidimensionale Flächen mit verbrückenden Bi- und X-Atomen bilden, so zum Beispiel im $MeBiCl_2$ (Abbildung 1.6 b.).^[109]

Bei der Umsetzung von Organohalidobismutanen mit Reduktionsmitteln bilden

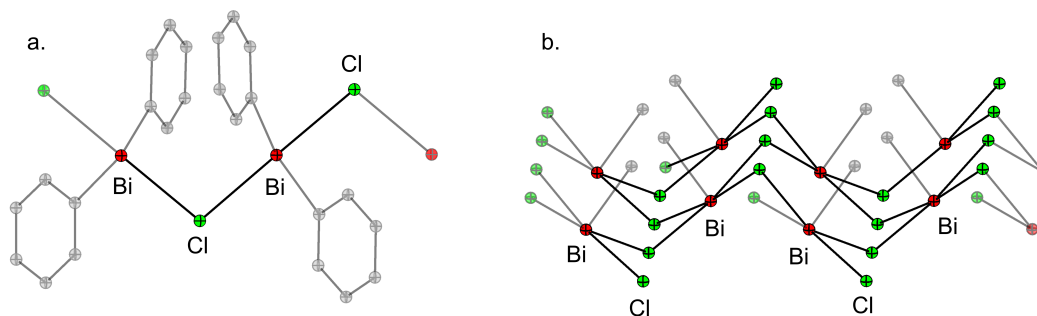


Abbildung 1.6: Polymere Stränge des Ph_2BiCl (a.) und polymere Fläche des MeBiCl_2 (b.) im Festkörper.^[109,117] Wasserstoffatome sind aus Gründen der Übersichtlichkeit nicht dargestellt. Die Schwingungsellipsoide sind mit 50 % Aufenthaltswahrscheinlichkeit gezeigt.

sich meist Verbindungen mit Bi-Bi-Bindungen. Auf diese Weise können aus Verbindungen der Form R_2BiX ($\text{R} = \text{Alkyl, Aryl}$; $\text{X} = \text{Halogen}$) Dibismutane, also Bi(II)-Verbindungen, erhalten werden.^[82,121–124] Ein weiterer Zugang zu Dibismutanen ist die Oxidation metallierter Bismutverbindungen der Form R_2BiM ($\text{M} = \text{Alkali-metall}$) mit 1,2-Dihalidoethan.^[81,125–128] Meist ist Ersterer allerdings synthetisch weniger aufwendig. Durch den Einsatz sterisch anspruchsvoller Liganden konnte die Dimerisierung der reduzierten Bismut-Spezies in einigen Fällen unterdrückt werden, wobei radikalische Bi(II)-Verbindungen erhalten werden. Für das im Festkörper als Dibismutan vorliegende $((2,2,5,5(\text{Me}_3\text{Si})_4\text{C}_4\text{H}_4)\text{Bi})_2$ (Abbildung 1.7 a.) lässt sich so in Lösung die Bildung des entsprechenden Monomeren Bismutanylradikals beobachten.^[122] Weiterhin konnte durch Verwendung eines sterisch anspruchsvollen NON^{Dipp} -Liganden ($\text{NON}^{\text{R}} = [\text{O}(\text{SiMe}_2\text{NR})_2]^{2-}$) die Dimerisierung auch im Festkörper unterdrückt, die Radikalspezies also auch im Festkörper erhalten, werden.^[129] Bi(II)-Verbindungen können mit Element-Element-Bindungen reagieren. So ließen sich in der Vergangenheit alle Chalkogenide (O, S, Se, Te) aktivieren, wobei ein (Poly-)Chalkogenid in die Bi-Bi-Bindung insertiert wird.^[130–133] Im Falle des radikalischen $\text{Bi}(\text{NON}^{\text{Dipp}})$ konnte außerdem eine Reaktion mit P_4 beobachtet werden wobei sich ein P_4 -Butterfly-Komplex mit zwei $\text{Bi}(\text{NON}^{\text{Dipp}})$ Substituenten bildet.^[134]

Mit Reduktionsmitteln können aus Verbindungen der Form RBiX_2 Bi(I)-Verbindungen erhalten werden. Werden keine extrem sterisch anspruchsvollen Substituenten verwendet, bilden sich hier meist zyklische Verbindungen der Form $(\text{RBi})_n$ mit zentralem Bi_n -Zyklus, so zum Beispiel im Falle von $((\text{Me}_3\text{C}(\text{H}_2\text{C}))\text{Bi})_n$

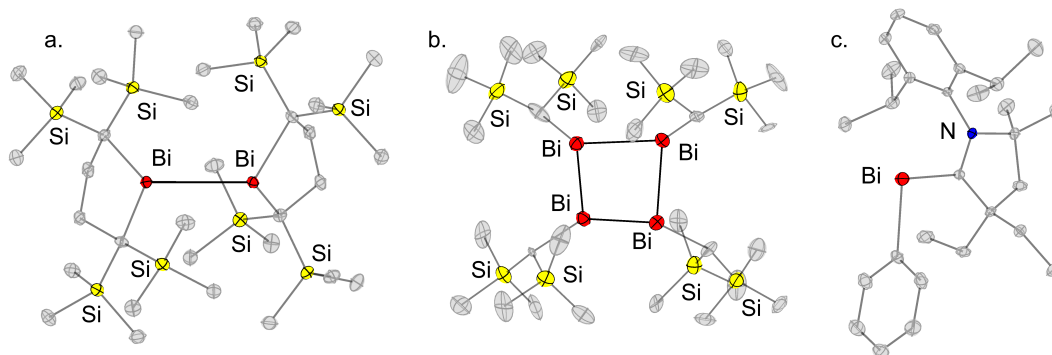


Abbildung 1.7: Molekülstrukturen von $((2,2,5,5(\text{Me}_3\text{Si})_4\text{C}_4\text{H}_4)\text{Bi})_2$ (a.), $(((\text{Me}_3\text{Si})_2\text{HC})\text{Bi})_4$ und des CAAC stabilisierten Bismutenidene BiPh (c.) im Festkörper.^[122,138,143] Wasserstoffatome sind aus Gründen der Übersichtlichkeit nicht dargestellt. Die Schwingungsellipsoide sind mit 50 % Aufenthaltswahrscheinlichkeit gezeigt.

oder $(((\text{Me}_3\text{Si})_2\text{HC})\text{Bi})_n$, wobei Ringe verschiedener Größen ($n = 3-5$) in Lösung in einem dynamischen Gleichgewichten vorliegen (Abbildung 1.7 b.).^[135-138] Sterisch anspruchsvolle Reste können zur Bildung kleinerer Aggregate führen, wobei auf diese Weise Dibismutenene mit Bi=Bi-Doppelbildung dargestellt werden können. So zum Beispiel im Falle des $(\text{Ter}^{\text{Ar}}\text{Bi})_2$ ($\text{Ar} = \text{Mes}, \text{Dipp}$).^[114,139] Auch Monomere Bi(I)-Spezies konnten isoliert werden. Diese werden als Bismutenidene bezeichnet und können durch geeignete Substituenten stabilisiert werden. Realisiert wurde dies unter anderem durch chelatisierenden Liganden mit N-Donor-Funktionen. Auf diese Weise konnte eine Reihe von Bi(I)-Verbindungen mit verschiedenen $(2,6-(\text{CH}=\text{NR})_2-\text{C}_6\text{H}_3)$ -Substituenten dargestellt werden.^[18,140-142] Auch durch starke σ -Donor-Liganden, namentlich einem Zyklisches(Alkyl)(Amino)Carben (CAAC), kann das Bismutenidene BiPh stabilisiert werden (Abbildung 1.7 c.).^[143]

1.2.3 Ionische Bismutverbindungen

Bismut kann sowohl in der Oxidationsstufe +3 als auch +5 Zentralatom, in sowohl Kationen als auch Anionen sein. Im Folgenden werden dabei ausgewählte Verbindungen genauer beleuchtet. Anionen mit Bismut in der Oxidationsstufe +5 werden Bismutate genannt. In der Literatur beschrieben sind hier zum Beispiel die Alkalimetallsalze des, dem $[\text{PF}_6]^-$ -Anion isoelektrischen, $[\text{BiF}_6]^-$ -Anions.^[144] Auch zwei Verbindungen mit sechs organischen Substituenten, $[\text{Li}(\text{THF})_4][\text{BiMe}_6]$ (Abbildung 1.8 a.) und $[\text{Li}(\text{THF})_4][\text{BiPh}_6]$, konnten in der Vergangenheit isoliert werden. Diese sind jedoch labil und zersetzen sich bei Raumtemperatur rasch.^[145,146] Salze von Bismut(V)-Kationen der Form $[\text{BiR}_4]^+$ werden Bismutonium-Salze genannt, wobei das Bismutonium-Kation isoelektrisch zum Ammonium-Kation ist. Salze von Bismutonium-Kationen wurden erfolgreich als Starter für die kationische Polymerisation von Epoxiden verwendet.^[147] Dargestellt werden können die Verbindungen ausgehend von Bi(V)- oder Bi(III)-Verbindungen. So zum Beispiel das Tosylat des $[\text{BiPh}_4]^+$ -Kations durch Reaktion von BiPh_5 mit *p*-Toluolsulfonsäure, oder $[\text{BiMe}_4][\text{OTf}]$ durch Umsetzung von BiMe_3 mit dem Methylierungsreagenz MeOTf .^[146,148]

Im Falle der Anionen mit Bi(III)-Zentrum sind viele Verbindungen mit $[\text{BiX}_{3+n}]^{n-}$ -Anionen ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}; n = 1-3$) beschrieben. Für $n = 1$ zum Beispiel im $[\text{FeCp}_2][\text{BiCl}_4]$, wobei in dieser Verbindung das Bismut durch sein sterisch aktives, freies Elektronenpaar eine wippenartige Koordination zeigt.^[150] In der Vergangenheit war es außerdem möglich Salze mit zweifach negativ geladenen

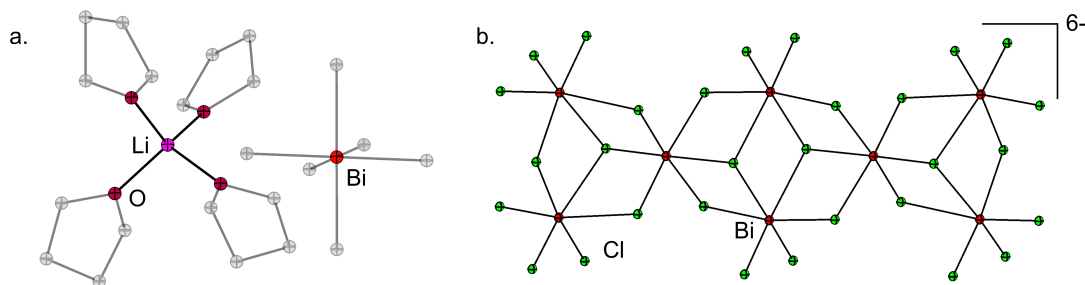


Abbildung 1.8: Molekülstrukturen $[\text{Li}(\text{THF})_4][\text{BiMe}_6]$ (a.) und des Anions der Verbindung $[\text{NEt}_4]_6[\text{Bi}_8\text{Cl}_{30}]$ (b.).^[146,149] Wasserstoffatome und Fehlordnungen sind aus Gründen der Übersichtlichkeit nicht dargestellt. Die Schwingungsellipsoide sind mit 50 % Aufenthaltswahrscheinlichkeit gezeigt.

$[\text{BiX}_5]^{2-}$ -Anionen ($X = \text{Cl}/\text{Br}, \text{Br}, \text{I}$) zu erhalten.^[151] Dreifach negativ geladene Anionen der Form $[\text{BiX}_6]^{3-}$ sind dagegen deutlich verbreiteter. Durch sekundäre Wechselwirkungen der freien Elektronenpaare von Halogenid-Substituenten und weiteren BiX_n -Einheiten können polymere Anionen gebildet werden. Diese haben dann die Allgemeine Form $[\text{Bi}_n\text{X}_m]^{(m-3n)-}$ ($X = \text{Cl}, \text{Br}, \text{I}$), wobei die größten beschriebenen Anionen bis zu acht Bismutatome enthalten. So sind zum Beispiel die Salze $[\text{PPh}_4]_4[\text{Bi}_8\text{I}_{28}]$ oder $[\text{NEt}_4]_6[\text{Bi}_8\text{Cl}_{30}]$ (Abbildung 1.8 b.) realisiert worden.^[149,152]

Durch formale Abstraktion eines R-Substituenten eines ternären Bismutans werden Kationen der allgemeinen Form $[\text{R}_2\text{Bi}]^+$ erhalten. Diese haben sechs Valenzelektronen und werden im Folgenden als Bismutenium-Kationen bezeichnet. Mit sechs Valenzelektronen sind Bismutenium-Kationen Elektronenmangel-Verbindungen und haben eine analoge Struktur wie, die in der Literatur sehr intensiv untersuchten, elektrisch neutralen Singulett-Carbene.^[153–155] In den Singulett-Carbenen werden die sechs Valenzelektronen wie folgt verteilt: Vier bilden die beiden C-R-Bindungen aus, während die restlichen beiden Elektronen sich in einem der beiden verbliebenen Valenzorbitale befinden. Damit haben Singulett-Carbene zugleich ein freies Elektronenpaar (meist das HOMO) und ein leeres Orbital (meist das LUMO). Damit der Singulett-Zustand dem Grundzustand entspricht, muss die Energiedifferenz zwischen HOMO und LUMO in Carbenen etwa $170 \text{ kJ}\cdot\text{mol}^{-1}$ betragen. Ist dies nicht der Fall werden stattdessen die beiden verbliebenen Valenzorbitale einfach besetzt, was einem Triplett-Grundzustand entspricht.^[156] Ein hoher HOMO-LUMO-Abstand kann durch den Einsatz von σ -Akzeptoren, π -Donoren und einem kleinen R-C-R Winkel erreicht werden. So ist zum Beispiel in der Verbindungsklasse der N-heterozyklischen-Carben (NHCs) der HOMO-LUMO-Abstand besonders groß.^[157–159] Der elektronische Grundzustand von Kationen der Form $[\text{Ph}_2\text{E}]^+$ ($E = \text{P}, \text{As}, \text{Sb}, \text{Bi}$) wurde mittels DFT-Rechnungen im Detail untersucht. Dabei wurde für alle Kationen ein Singulett-Grundzustand gefunden. Der energetische Abstand zwischen HOMO und LUMO liegt bei den untersuchten Verbindungen bei Werten zwischen 273.1 ($E = \text{Bi}$) und $301.2 \text{ kJ}\cdot\text{mol}^{-1}$ ($E = \text{P}$). Mittels NBO-Analyse konnte des Weiteren gezeigt werden, dass sich das freie Elektronenpaar am Pnictogen in einem Orbital mit vorwiegend s-Charakter befindet und dieser in der Reihe von Phosphor bis Bismut von 64% auf 86% steigt. Das LUMO stellt ein Pnictogen-zentriertes leeres Orbital mit beinahe ausschließlich p-Charakter (P: 99% ; As-Bi: 100%) dar.

Daraus resultiert für das zentrale Pnictogenatom in allen Fällen eine gewinkelte Geometrie.^[153]

Durch das leere, energetisch tief liegende p-Orbital stellen Bismutenium-Kationen gute *Lewis*-Säuren dar, wodurch Gegenionen oder elektrisch neutrale *Lewis*-Basen koordiniert werden können. So bildet zum Beispiel das $[\text{Me}_2\text{Bi}(\text{SbF}_6)]$ im Festkörper eindimensionale Stränge mit verbrückenden $[\text{SbF}_6]^-$ -Anionen aus und im $[(i\text{Pr}_2\text{N})_2\text{Bi}(\text{BPh}_4)]$ koordinieren zwei Phenyl-Substituenten des $[\text{BPh}_4]^-$ -Anions durch Bi- π -Wechselwirkungen (Abbildung 1.9).^[160,161] Über das erste Donor-freie Bismutenium-Kation wurde erst 2018 in der Literatur berichtet. Es hat die Summenformel $[(\text{Ter}^{\text{Mes}})_2\text{Bi}][\text{B}(3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3)_4]$. Die Koordination des Anions wird hier durch sterisch anspruchsvolle Aryl-Reste und ein schwach koordinierendes Borat-Anion verhindert.^[153] Im Vergleich zu den Donor-freien Verbindungen sind für Bismutenium-Kationen mit Donoren wie THF, Pyridin oder Phosphanchalkogenide mehr Beispiele beschrieben. Diese haben die allgemeine Form $[\text{R}_2\text{Bi}(\text{D})_n(\text{A})]$ oder $[\text{R}_2\text{Bi}(\text{D})_n][\text{A}]$ (D = Donor; A = Anion), wobei bis zu fünf Substituenten an das Bismutzentrum gebunden sein können. Am häufigsten wird in der Literatur über die Bildung von Verbindungen mit zwei Donoren berichtet. Ein Beispiel ist hier das $[\text{Ph}_2\text{Bi}(\text{OP}(\text{NMe}_3))_2][\text{BF}_4]$.^[162] Des Weiteren sind einzelne Verbindungen mit nur einem Donoren, zum Beispiel $[(\text{H}_2\text{C}_2(\text{C}_6\text{H}_4)_2)\text{Bi}(\text{SPMe}_3)(\text{SbF}_6)]$, beschrieben.^[163] Einige Verbindungen mit fünf Donoren haben die Form $[\text{BiX}_2(\text{py})_5][\text{B}(3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3)_4]$ (X = Cl, Br, I), wobei das freie Elektronpaar am Bismut nicht mehr stereoaktiv ist.^[164] In Abbildung 1.10 sind die Molekülstrukturen der Kationen einiger hier aufgeführten Verbindungen gezeigt. An dieser Stelle soll außerdem erwähnt sein, dass einige Addukte von Bismutenium-Kationen und Pnictogenen beschrieben sind. Auf diese wird in Kapitel 1.3.1 genauer eingegangen.

Die Stärke der *Lewis*-Acidität bezieht sich, anders als im Falle des Säure-Base-Konzepts nach *Brønsted*, nicht auf eine universelle Skala. Um dennoch *Lewis*-Acidität mittels einer Skala zu quantifizieren wurden verschiedene theoretische und experimentelle Verfahren entwickelt. Zwei Verfahren, welche die Bindungsstärke eines Säure-Base-Addukts als Kriterium für die *Lewis*-Acidität heranziehen, werden im Folgenden kurz beschrieben. Bei der *Fluorid-Ionen-Affinität (FIA)* dient die Bindungsenthalpie von *Lewis*-Säure und einem Fluorid-Ion als Skala.^[165–167] Werte für die *FIA* werden dabei meist mittels theoretischen Verfahren erhalten. Ein experimentelles, apparativ wenig aufwendiges Verfahren ist die *Gutmann-*

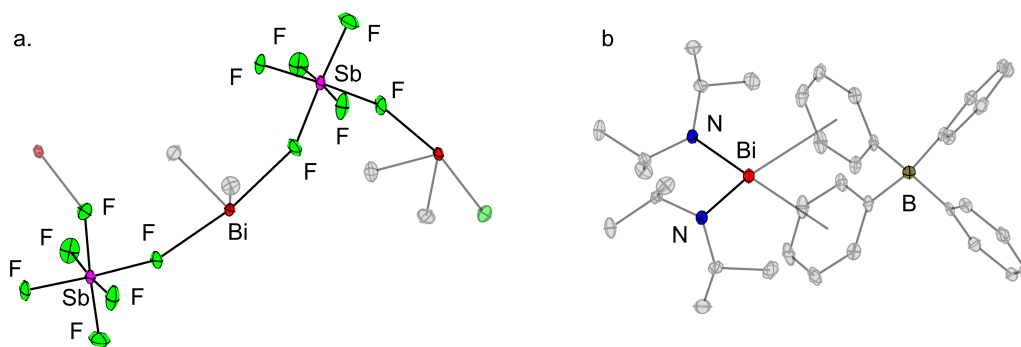


Abbildung 1.9: Eindimensional polymerer Strang von $[\text{Me}_2\text{Bi}(\text{SbF}_6)]$ (a.) und Molekülstruktur von $[(i\text{Pr}_2\text{N})_2\text{Bi}(\text{BPh}_4)]$ mit Koordination des π -Systems des Anion im Kristall.^[160,161] Wasserstoffatome sind aus Gründen der Übersichtlichkeit nicht dargestellt. Die Schwingungsellipsoide sind mit 50 % Aufenthaltswahrscheinlichkeit gezeigt.

Beckett-Methode (GBM).^[168,169] Hier wird die *Lewis*-Säure zusammen mit einem äquivalent OPEt_3 in Lösung gebracht. Die Koordination des freien Elektronenpaares am Sauerstoff führt dabei zum Abzug von Elektronendichte am Phosphor und einer magnetischen Entschirmung des Phosphorkerns. Es wird nun angenommen, dass die chemische Verschiebung im ^{31}P -NMR-Spektrum abhängig von der Stärke der Donor-Akzeptor-Bindung ist. Aus der Verschiebung wird im Anschluss die *Akzeptor-Nummer (AN)* berechnet, wobei diese nach Definition für OPEt_3 in *n*Hexan bei 0 und für $\text{OPEt}_3\cdot\text{SbCl}_5$ bei 100 liegt. Ein Problem der *GBM* ist, dass sie sich nur auf die Affinität von *Lewis*-Säuren zu der harten *Lewis*-Base OPEt_3 beschränkt. Weiche *Lewis*-Säuren zeigen deshalb immer vergleichsweise geringe *AN*s.^[167,170] Um auch für weiche *Lewis*-Säuren eine aussagekräftige Aciditätsskala aufzustellen, kann eine modifizierte Version der *GBM* verwendet werden, wobei als Base SPMe_3 oder SePMe_3 verwendet werden.^[163]

Durch die Einführung der positiven Ladung erhöht sich die Acidität des *Lewis*-sauren Bismuts in Bismutenium-Kationen stark. So steigt die *AN* im Falle der traditionellen *GBM* (OPEt_3) von 20 für Ph_3Bi auf 64 für $[(\text{H}_2\text{C}_2(\text{C}_6\text{H}_3)_2)\text{Bi}(\text{THF})_2(\text{SbF}_6)]$ (gemessen in CD_2Cl_2).^[112] Sie ist damit jedoch geringer als für härtere *Lewis*-saure Referenzverbindungen wie $\text{Bi}(\text{OTf})_3$ ($AN = 105$ in CD_2Cl_2) oder $\text{B}(\text{C}_6\text{F}_5)_3$ ($AN = 76$ bis 82 in C_6D_6 , Toluol- d_8 , CD_2Cl_2 , CDCl_3).^[112,171–174] Wird dagegen mit SPMe_3 eine weiche *Lewis*-Säure verwendet, übersteigt die *AN* von $[(\text{H}_2\text{C}_2(\text{C}_6\text{H}_3)_2)\text{Bi}(\text{SPMe}_3)(\text{SbF}_6)]$ (96, in CD_2Cl_2) die der Referenzverbindungen $\text{Bi}(\text{OTf})_3$ (52, in CD_2Cl_2) und $\text{B}(\text{C}_6\text{F}_5)_3$

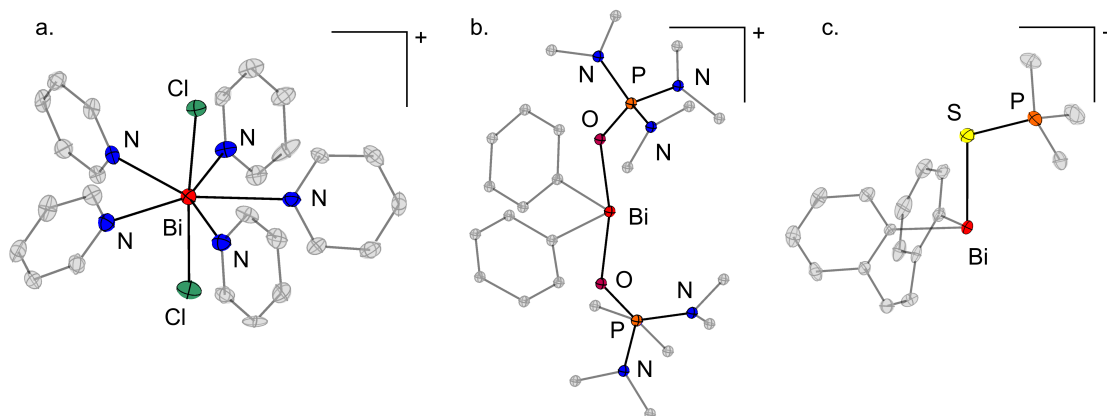


Abbildung 1.10: Molekülstrukturen der Kationen $[\text{BiCl}_2(\text{py})_5][\text{B}(3,5\text{-(CF}_3)_2\text{-C}_6\text{H}_3)_4]$ (a.), $[\text{Ph}_2\text{Bi}(\text{OP}(\text{NMe}_3)_2)[\text{BF}_4]$ (b.) und $[(\text{H}_2\text{C}_2(\text{C}_6\text{H}_4)_2)\text{Bi}(\text{SPMe}_3)(\text{SbF}_6)]$.^[162–164] im Festkörper. Wasserstoffatome sind aus Gründen der Übersichtlichkeit nicht dargestellt. Die Schwingungsellipsoide sind mit 50 % Aufenthaltswahrscheinlichkeit gezeigt.

(42, in CD_2Cl_2).^[163] Auch die *FIA* eines Bismutenium-Kations wurde in der Vergangenheit ermittelt. So wird für das Donor-freie $[(\text{Ter}^{\text{Mes}})_2\text{Bi}]^+$ -Kation mittels DFT-Rechnungen in der Gasphase eine *FIA* von 602 berechnet, was deutlich höher ist als die *FIA* der Referenzverbindungen $\text{B}(\text{C}_6\text{F}_5)_3$ (448) oder SbF_5 (496).^[175,176] Der Vergleich der *Lewis*-Acidität von Bismutenium-Kationen und Referenzverbindung wie $\text{B}(\text{C}_6\text{F}_5)_3$ zeigt die Grenzen verschiedener *Lewis*-Aciditätsskalen auf. So ist die *FIA* von kationischen Verbindungen in der Gasphase verglichen mit neutralen Verbindungen oft stark erhöht.^[167] Ein Problem der traditionellen *GBM* ist, dass sie sich nur auf die Affinität von *Lewis*-Säuren zu der harten *Lewis*-Base OPEt_3 beschränkt. Weiche *Lewis*-Säuren zeigen deshalb immer vergleichsweise geringe *AN*s.^[167,170] Auch Eigenschaften wie Ladung oder sterische Effekte haben einen Einfluss auf die *AN*, welcher im Wert nicht reflektiert wird.^[167,177,178] Trotz ihrer Unzulänglichkeiten bieten sowohl die *FIA* als auch die *GBM* eine Möglichkeit die *Lewis*-Acidität in einer Skala zu quantifizieren und die Reaktivität verschiedener Verbindungen und Verbindungsklassen als *Lewis*-Säure abzuschätzen.

Mittels starker σ -Donor-Liganden wie *N*-heterozyklischen-Carbenen (NHCs), Zyklischen(Alkyl)(Amino)Carbenen (CAACs), Carbodicarbenen (CDCs) oder Trispyrazolborat (Tp^-) lassen sich kationische Bi(III)-Verbindungen mit bemerkenswerten strukturellen Eigenschaften und Reaktivitäten darstellen. Die

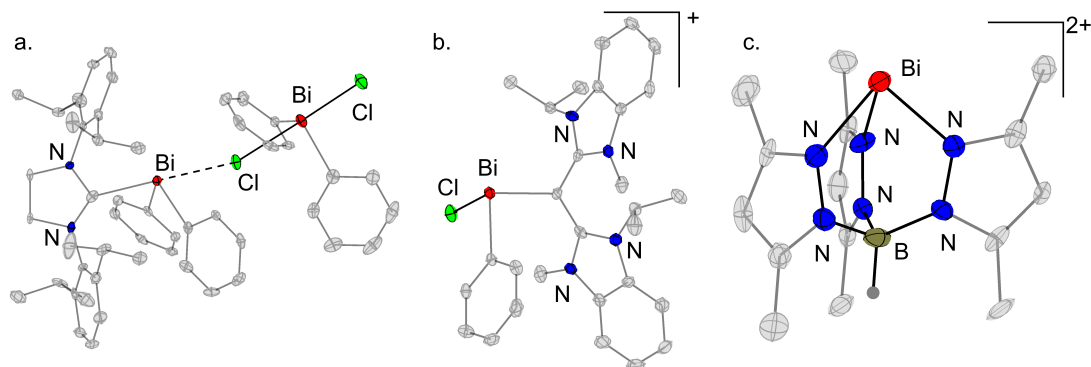


Abbildung 1.11: Molekülstrukturen von $[(\text{NHC})\text{BiPh}_2][\text{BiPh}_2\text{Cl}_2]$ (a.), des Kations der Verbindung $[(\text{CDC})\text{BiPhCl}][\text{SbF}_6]$ mit dativer C=Bi-Doppelbindung und des Dikations in $[(\text{Tp})\text{Bi}][\text{B}(\text{C}_6\text{F}_5)_4]_2$.^[180,181] Wasserstoffatome sind aus Gründen der Übersichtlichkeit nicht dargestellt. Die Schwingungsellipsoide sind mit 50 % Aufenthaltswahrscheinlichkeit gezeigt.

erste beschriebene kationische NHC-stabilisierte Bismutverbindung hat die Form $[(\text{NHC})\text{BiBr}_2][\text{AlBr}_4]$.^[179] Seitdem wurden auch NHC-stabilisierte Kationen mit organischen Substituenten beschrieben. So kann $[(\text{NHC})\text{BiPh}_2][\text{BiPh}_2\text{Cl}_2]$ aus zwei Äquivalenten Ph_2BiCl und einem Äquivalent eines NHCs dargestellt werden (Abbildung 1.11 a.).^[180] Auch die analoge, CAAC-stabilisierte Verbindung konnte auf diese Weise synthetisiert werden ($[(\text{CAAC})\text{BiPh}_2][\text{BiPh}_2\text{Cl}_2]$).^[180] Die erste Verbindung mit einer dativen C=Bi-Doppelbindung wurde durch Verwenden von CDC Liganden synthetisiert. Beispiele sind hier die Kationen in den Verbindungen $[(\text{CDC})\text{BiPhCl}][\text{SbF}_6]$ (Abbildung 1.11 b.) oder $[(\text{CDC})\text{BiPh}][\text{SbF}_6]_2$.^[180] In der Verbindung $[(\text{Tp})\text{Bi}][\text{B}(\text{C}_6\text{F}_5)_4]_2$ ist das zweifach positiv geladene Kation in der Lage die Hydrosilylierung von Olefinen zu katalysieren (Abbildung 1.11 c.).^[181] Durch Verwenden von CAAC-Liganden kann außerdem ein Bismut-Kation in der Formalen Oxidationsstufe +1 stabilisiert werden ($[(\text{CAAC})_2\text{Bi}][\text{OTf}]$). Mit zwei freien Elektronenpaaren am Bismut handelt es sich bei dem Kation der Verbindung formal also um ein schweres Analogon der Verbindungsklasse der Carbene.^[182]

1.3 Interpnictogenverbindungen

Als Interpnictogenverbindungen werden Verbindungen bezeichnet, in denen es Einfach- oder Mehrfachbindungen zwischen verschiedenen Pnictogenatomen gibt. Handelt es sich dabei um genau zwei Pnictogene, so spricht man von binären Verbindungen. Im einfachsten Fall besteht eine molekulare Verbindung oder eine Legierung ausschließlich aus Pnictogenen. Bekannt sind hier zum Beispiel definierte Verbindungen wie $\text{P}\equiv\text{N}$, P_3N_5 oder AsP_3 .^[183–185] Des Weiteren sind Legierungen aus Bismut und Antimon mit der Zusammensetzung $\text{Bi}_x\text{Sb}_{1-x}$ bekannt, welche für verschiedene Bi/Sb Verhältnisse unterschiedliche Eigenschaften haben können. So ist zum Beispiel $\text{Bi}_{0,9}\text{Sb}_{0,1}$ ein topologischer Isolator.^[186]

In der Literatur sind sehr viele Interpnictogenverbindungen mit organischen Resten beschrieben. Vom Stickstoff, als leichtestem Pnictogen, sind mit Abstand die meisten Interpnictogenverbindungen dargestellt worden. So sind zum Beispiel alle Verbindungen der Form $\text{E}(\text{NMe}_2)_3$ ($\text{E} = \text{P}, \text{As}, \text{Sb}, \text{Bi}$) bekannt. Anhand dieser Verbindungen zeigt sich die Sonderstellung des Bismuts bei den Interpnictogenverbindungen. Handelt es sich für $\text{E} = \text{P-Sb}$ noch um, unter Inertbedingungen, stabile Verbindungen, ist $\text{Bi}(\text{NMe}_2)_3$ empfindlich gegenüber Licht und Temperatur.^[187–190] Für den Phosphor nimmt die Zahl an Verbindungen zu den schwereren Pnictogenen stark ab. Erhält man für Verbindungen mit P-As-Einfachbindung 161 Treffer in der *CCDC Datenbank* (Stand November 2020), sind es im Falle von P-Sb- noch 102 und für P-Bi-Einfachbindungen nur noch 46 Treffer. Für Verbindungen mit einer As-Sb- oder As-Bi-Einfachbindung nimmt die Zahl mit 5 beziehungsweise 7 Treffern nochmals deutlich ab. Für die schweren Pnictogene Sb und Bi sind dabei zusätzlich viele der beschriebenen Einfachbindungen dative Bindungen, wobei ein ER_3 -Fragment ($\text{E} = \text{P}, \text{As}, \text{Sb}, \text{Bi}$) mit seinem freien Elektronenpaar an ein *Lewis-acides* schwereres Pnictogen bindet. In den folgenden Kapiteln werden einige Interpnictogenverbindungen, mit besonderem Augenmerk auf Verbindungen des Bismuts, vorgestellt.

1.3.1 Lewis-Säure-Base-Addukte

Vor allem von den schwereren, *Lewis*-saureren Elementen, Antimon und Bismut, sind einige Addukte beschrieben. Im Falle der dativen Bi-N-Bindungen sind in der Literatur sehr viele Verbindungen beschrieben, wobei sowohl Verbindungen mit inter- als auch intramolekularer Bi-N-Koordination bekannt sind. Die einfachsten Vertreter sind Addukte aus einem Amin und einem Bismuttrihalogenid, wie zum Beispiel das DABCO·BiI₃-Addukt.^[191] Des Weiteren zeigen Aryl-Substituenten mit *o*-(CH₂NR₂)-Substituenten oft intramolekulare Bi-N-Wechselwirkungen. Für dieses Strukturmotiv sind eine Vielzahl an Verbindungen mit tridentaten NCN-, CNC- und NNN-Liganden in der Literatur beschrieben. Beispiele für Komplexe mit polydentaten Liganden sind in Abbildung 1.12 gezeigt.^[192–195]

Im Falle des Phosphors gibt es deutlich weniger Verbindungen mit dativer Bi-P-Bindung. Wieder sind inter- und intramolekulare Donor-Akzeptor-Komplexe beschrieben, welche in den einfachsten Fällen Phosphan-Addukte von Bismut(pseudo)halogeniden sind. Bekannt sind hier zum Beispiel Me₃PBiBr₃ und Et₃PBiBr₃, welche im Festkörper Aggregate bilden.^[196,197] Auch Addukte mit chelatisierenden Liganden sind beschrieben. Diese haben die allgemeine Form ((H₂C)_n(Ph₂P)₂)BiX₂ (n = 1, 2; X = Cl, Br, OTf). Im Festkörper bilden sich meist Dimere die, außer in einem Fall, durch Halogenid-Ionen verbrückt sind.^[196,198,199] Des Weiteren sind Donor-Akzeptor-Verbindungen mit [(*i*Pr₂P)₂N]⁻-Anionen beschrieben. Dabei ist es sowohl möglich BiCl₃ zu koordinieren, als auch eine

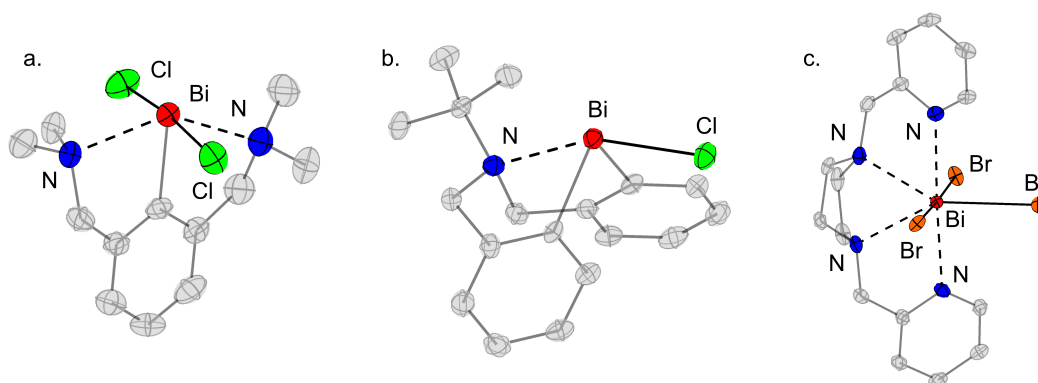


Abbildung 1.12: Verbindungen mit tridentaten NCN-, CNC- und NNN-Chelatliganden mit dativer Bi-N-Bindung.^[192–194] Wasserstoffatome sind aus Gründen der Übersichtlichkeit nicht dargestellt. Die Schwingungsellipsoide sind mit 50 % Aufenthaltswahrscheinlichkeit gezeigt.

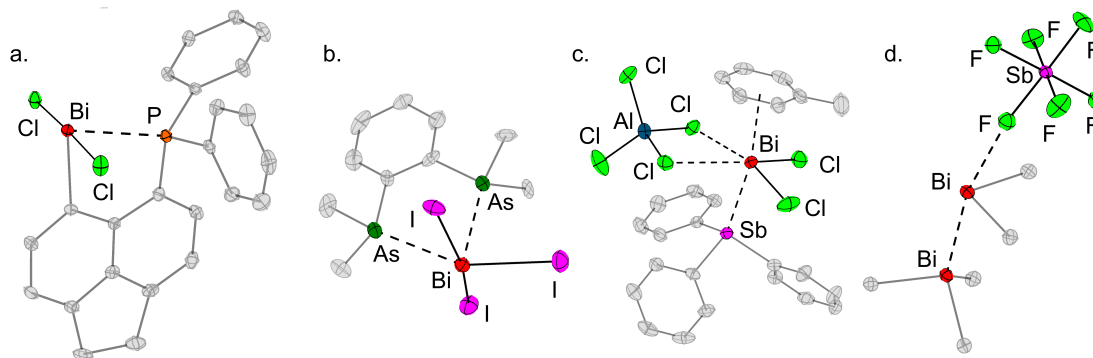


Abbildung 1.13: a. Verbindung mit intramolekularer dativer P-Bi-Bindung mit Acenaphthyl-Rückgrat.^[203] b. Addukt eines Arsan-Chelat Liganden mit BiI_3 .^[206] c. Addukt eines Stibanes der Form $[(\text{Ph}_3\text{Sb})(\text{BiCl}_2)(\text{AlCl}_4)]$.^[204] d. Addukt von BiMe_3 und $[\text{BiMe}_2(\text{SbF}_6)]$.^[160] Wasserstoffatome sind aus Gründen der Übersichtlichkeit nicht dargestellt. Die Schwingungsellipsoide sind mit 50 % Aufenthaltswahrscheinlichkeit gezeigt.

Bi_4 -Kette zu stabilisieren.^[200] Ein Beispiel für Verbindungen mit intramolekularer Donor-Akzeptor-Bindung sind Acenaphthalene-substituierte Verbindungen, wobei eine Verbindung in Abbildung 1.13 a. gezeigt ist.^[201–203]

Auch für Verbindungen mit Bi-As-Bindungen sind einige Verbindungen mit dativer Bi-As-Bindung beschrieben. So sind zum Beispiel Addukte des AsPh_3 mit $\text{BiPh}(\text{OTf})_2$ oder $\text{BiCl}_2(\text{OTf})$ beschrieben.^[204,205] Des Weiteren ist ein Komplex des BiI_3 mit dem bidentaten 1,2- $(\text{Me}_2\text{As})_2\text{C}_6\text{H}_4$ -Liganden beschrieben (Abbildung 1.13 b.).^[206]

Sogar Strukturen zweier Addukte des SbPh_3 sind beschrieben. Es handelt sich dabei um Verbindungen der Form $[(\text{Ph}_3\text{Sb})\text{BiCl}_{3-n}(\text{AlCl}_4)_n]$ ($n = 1, 2$), wobei das $[\text{AlCl}_4]^-$ -Anion mit zwei Cl-Substituenten an das Bismutzentrum koordiniert ist (Abbildung 1.13 c.).^[204]

Obwohl es sich im eigentlichen Sinne nicht um eine Interpnictogenverbindung handelt, soll an dieser Stelle auch erwähnt sein, dass ein *Lewis*-Säure-Base-Addukt eines Bismutans mit einem Bismutenium-Kation in der Literatur beschrieben wurde. Es handelt sich dabei um folgende Verbindung: $[\text{Me}_2\text{Bi}(\text{BiMe}_3)(\text{SbF}_6)]$ (Abbildung 1.13 d.). In Lösung zeigt die Verbindung dynamisches Verhalten, wobei die Methylgruppen zwischen den Bismutatomen migrieren können. Im Festkörper ist die Migration eingefroren und die Verbindung kann als klassisches Addukt beschrieben werden.^[160]

1.3.2 Binäre bismuthaltige Interpnictogenverbindungen

In der Literatur sind sehr viele Bismutanamine beschrieben, weshalb in diesem Abschnitt nur ausgewählte Beispiele besprochen werden. So können einige homoleptische Bismuttrisamine der Form $\text{Bi}(\text{NR}_2)_3$ mit verschiedenen Alkyl-, Aryl- oder Silyl-Resten dargestellt werden.^[207,210–214] Besitzen die Verbindungen sehr kleine Reste, können Wechselwirkungen zwischen dem freien Elektronenpaar des Stickstoffs und Bismut-Atomen ausgebildet werden. So bildet $\text{Bi}(\text{NMe}_2)_3$ im Festkörper eindimensionale Stränge, wobei jedes Bismutatome von sechs Stickstoffatomen umgeben ist (Abbildung 1.14 a).^[207] Einige homoleptische Verbindungen zeigen interessante Eigenschaften und Reaktivitäten. So kann zum Beispiel $\text{Bi}(\text{NMe}_2)_3$ als Präkursor zur Darstellung von Bi_2Te_3 mittels des *MOCVD*-Verfahren verwendet werden.^[215] Des Weiteren können Aryl-substituierte Verbindungen der Form $\text{Bi}(\text{NAr}_2)_3$ als Kopplungsreagenzien zur Darstellung von Hydrazin-Derivaten, Diphosphanen oder Diarsanen verwendet werden.^[211] Homo- und heteroleptische Verbindungen mit Bi-NR_2 -Fragmenten können mit aciden E-H-Einheiten reagieren, wobei unter Abspaltung von HNR_2 eine Bi-E-Bindung ($\text{E} = \text{C}, \text{O}, \text{N}, \text{Sb}$) gebildet wird.^[211,216–221] Auf diese Weise kann zum Beispiel das Triscyclopentadienylbismut (Cp_3Bi) aus $\text{Bi}(\text{NMe}_2)_3$ und CpH dargestellt werden.^[216] Diese Reaktivität macht

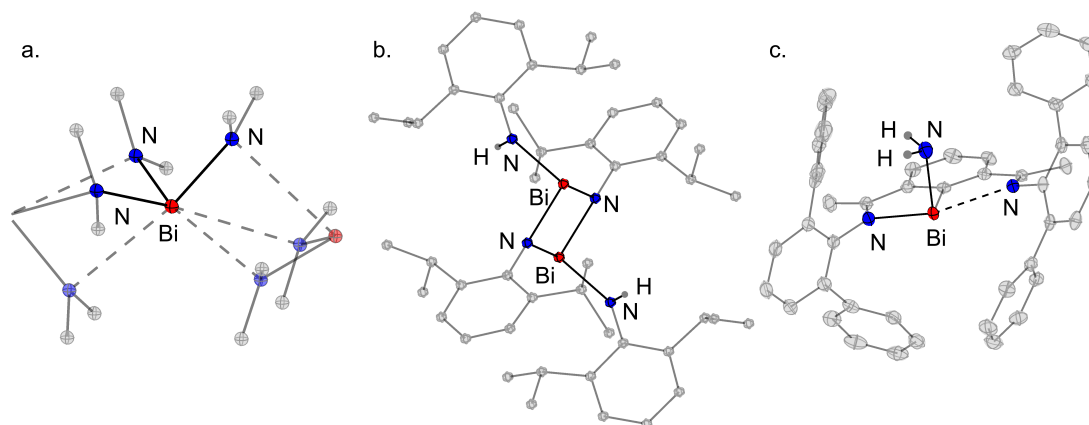


Abbildung 1.14: Molekülstrukturen einiger Bismutanamine im Festkörper. a. Ausschnitt des eindimensionalen Stranges in $\text{Bi}(\text{NMe}_2)_3$. b. Zyklische Verbindung mit zentralem Bi_2N_2 -Vierring und terminalen NHDipp -Substituenten. c. Bismutanamine mit NH_2 -Substituenten.^[207–209] Wasserstoffatome sind aus Gründen der Übersichtlichkeit nicht dargestellt. Die Schwingungsellipsoide sind mit 50 % Aufenthaltswahrscheinlichkeit gezeigt.

Bismutanamine zu Bausteinen für die Darstellung weiter funktionalisierter Bismutane. Auch heterozyklische Bismutanamine, meist mit zentralen Bi_2N_2 -Ringen oder Porphyrin-Substituenten mit zentralem Bismutatome, sind bekannt.^[208,214,222–229] Gemeinsam haben die meisten beschriebenen Bismutanamine, dass die Stickstoffatome nicht durch Protonen substituiert sind. Für primäre und sekundäre Bismutanamine sind nur sehr wenige Beispiele beschrieben. Allen gemeinsam ist dabei, dass sie durch sterisch sehr anspruchsvolle Reste stabilisiert sind. Vertreter sind zum Beispiel $\text{Bi}(\text{NH}(\text{Mes}^*))_3$, $\text{Bi}(\text{NH}(\text{Ter}^{\text{Mes}})_n\text{Cl}_{3-n})$ ($n = 1, 2$) oder das heterozyklische $(\text{DippN})_2(\text{Bi}(\text{NH}(\text{Dipp}))_2)$ (Abbildung 1.14 b.).^[208,224,230] Die erste Verbindung mit einem NH_2 -Substituenten am Bismut wurde erst 2022 beschrieben, wobei diese durch sterisch anspruchsvolle Reste am Bismut kinetisch stabilisiert ist (Abbildung 1.14 c.). Bemerkenswert ist auch die Darstellung der genannten Verbindung. Der NH_2 -Substituent wurde hier durch radikalische Aktivierung einer N-H-Bindung des als Edukt eingesetzten NH_3 eingebracht.^[209]

Die erste in der Literatur beschriebene Verbindung, in der ein PR_2 -Substituent an ein Bismutatome gebunden ist, wurde erst 1999 dargestellt und hat die Form $\text{Li}[\text{Bi}((\text{PtBu})_2\text{PtBu})_2]$.^[234] Seitdem sind einige Struktur motive, die eine Bi-P-Bindung beinhalten, realisiert worden. So konnte auch ein neutrales homoleptisches Tris(phosphanyl)bismutan dargestellt werden, wobei drei P_4tBu_3

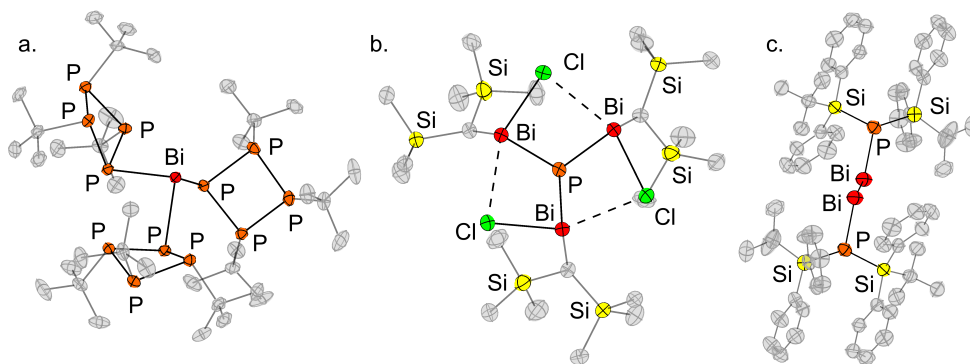


Abbildung 1.15: Molekülstrukturen einiger Bismutanylphosphane im Festkörper. a. Homoleptisches Trisphosphanylbismutan der Form $\text{Bi}(\text{P}_4t\text{Bu}_3)_3$. b. Homoleptisches Trisbismutan mit drei $\text{Bi}(\text{Cl})(\text{CH}(\text{SiMe}_3)_2)$ -Substituenten. c. Durch sterisch anspruchsvollen $\text{P}(\text{Si}(t\text{BuPh}_2)_2)$ -Substituenten stabilisiertes Dibismutene.^[231–233] Wasserstoffatome sind aus Gründen der Übersichtlichkeit nicht dargestellt. Die Schwingungsellipsoide sind mit 50 % Aufenthaltswahrscheinlichkeit gezeigt.

Ringe an das zentrale Bismutatatom gebunden sind (Abbildung 1.15 a.).^[231] Auch ist *vice versa* ein Tris(bismutanyl)phosphan beschrieben ($((\text{Me}_3\text{Si})_2\text{CH})\text{ClBi})_3\text{P}$, Abbildung 1.15 b.).^[232] Des Weiteren konnten heterozyklische Verbindungen wie $(\text{Ter}^{\text{Mes}}\text{P})_2(\text{BiCl})_2$, welches einen zentralen Bi_2P_2 -Ring aufweist, dargestellt werden.^[235] Auch terminale Bismutanylphosphane sind beschrieben. Bei der ersten beschriebenen Verbindung handelt es sich um $(\text{NON}^{\text{Dipp}})\text{BiPCy}_2$.^[134] Da es sich genau genommen hier um eine ternäre Interpnictogenverbindung handelt, wird diese in Abschnitt 1.3.3 genauer diskutiert. Des Weiteren konnte mit $((t\text{BuPh}_2\text{Si})_2\text{P})_2\text{Bi}$ ein Bismuten mit zentraler $\text{Bi}=\text{Bi}$ -Doppelbindungen durch Verwendung sterisch anspruchsvoller Silylphosphane realisiert werden (Abbildung 1.15 c.).^[233]

Der erste Versuch zur Darstellung eines terminalen Bismutanylarsans der Form $\text{R}_2\text{Bi-AsR}'_2$ erfolgte 1986 während der Untersuchung der Austauschreaktion verschiedener Tetramethyldipnictane der Form Me_4E_2 ($\text{E} = \text{As}, \text{Sb}, \text{Bi}$). Dabei konnte bei der Reaktion von Me_4Bi_2 und Me_4As_2 in C_6D_6 die Bildung von $\text{Me}_2\text{BiAsMe}_2$ beobachtet werden, wobei die drei Verbindungen in einem Gleichgewicht vorliegen. Das Gleichgewicht liegt hier jedoch deutlich auf der Seite der symmetrischen Verbindungen ($K = 9 \cdot 10^{-3}$).^[236] Die erste isolierbare Verbindung mit einer Bi-As -Einfachbindung wurde von *von Hänisch* und Mitarbeitern dargestellt. Dafür wurde $((\text{Me}_3\text{Si})_2\text{CH})\text{BiCl}_2$ mit einem Silylarsan, oder wahlweise einem Silylarsanid, umgesetzt, wobei in beiden Reaktionen Verbindungen mit einem ähnlichen Strukturmotiv, einer zentralen BiAsBi -Kette, erhalten wurden. In den Verbindungen der Form $((\text{Me}_3\text{Si})_2\text{CH})\text{ClBi}_2\text{AsR}$ ($\text{R} = \text{Si}(i\text{Pr})_3, \text{Si}(t\text{Bu})_2\text{Ph}$) findet man eine intramolekulare Wechselwirkung zwischen einem Chlor-Substituenten und einem Bismutatatom, was zur Bildung eines AsBi_2Cl -Vierrings führt.^[237] Wird dagegen $\text{As}(\text{SiMe}_3)_3$ umgesetzt, kann eine Verbindung mit zentraler As_2 -Hantel erhalten werden. Die Hantel ist von vier Bismutanyl-Substituenten der Form $((\text{Me}_3\text{Si})_2\text{CH})\text{ClBi}$, welche mittels sekundärer Wechselwirkungen zwischen Chlor und Bismut einen Bi_4Cl_4 -Ring bilden, koordiniert (Abbildung 1.16 a.).^[237] Auch ein, dem P_4 isolobales, Tetrahedran der Form $[\text{Mo}]_2\text{AsBi}$ ($[\text{Mo}] = \text{MoCp}(\text{CO})_2$), mit zentraler Bi-As -Bindung, konnte kürzlich dargestellt werden (Abbildung 1.16 b.). Für die sehr kurze Bi-As -Bindung wurde mittels DFT-Rechnungen eine Bindungsordnung von 1.35 bestimmt.^[238] Wird das $[\text{Mo}]_2\text{AsBi}$ -Tetrahedran mit einem Oxidationsmittel umgesetzt, kann eine dikationische Verbindung mit käfigartiger Struktur erhalten werden. For-

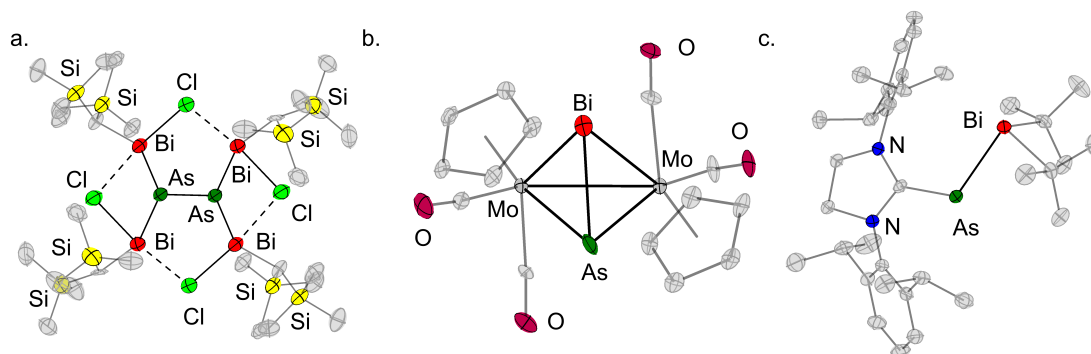


Abbildung 1.16: Molekülstrukturen einiger Bismutanylphosphane im Festkörper. a. Verbindung mit zentraler As₂-Hantel und vier Bismutanyl-Substituenten. b. [Mo]AsBi-Tetrahedran ([Mo] = MoCp(CO)₂). c. NHC-stabilisiertes Arseniden mit Bi(*t*Bu)₂-Substituent.^[237,238,240] Wasserstoffatome sind aus Gründen der Übersichtlichkeit nicht dargestellt. Die Schwingungsellipsoide sind mit 50 % Aufenthaltswahrscheinlichkeit gezeigt.

mal handelt es sich hierbei um eine Verbindung, in der zwei kantenverknüpfte [Mo]₂AsBi-Tetraeder vorliegen, wobei ein zentraler, planarer Bi₂As₂-Ring mit alternierenden Bi- und As-Atomen gebildet wird.^[239] Eine weitere bemerkenswerte Struktur mit Bi-As-Einfachbindung ist das NHC-stabilisierte Bismutanylarseniden der Form (NHC)AsBi(*t*Bu)₂, welche durch eine Salzmetathesereaktion zugänglich ist (Abbildung 1.16 c.).^[240]

Die erste in der Literatur erwähnte binäre Verbindung mit einer Bi-Sb-Einfachbindung ist Me₂BiSbMe₂, welche analog zu Me₂BiAsMe₂ dargestellt und untersucht wurde. Die Bildung der Verbindung wurde beim Lösen von Me₄Bi₂ und Me₄Sb₂ in C₆D₆ beobachtet. Ähnlich wie im Falle der entsprechenden Arsenverbindung liegen alle drei Verbindungen in Lösung in einem Gleichgewicht vor. Das Gleichgewicht ist, im Gegensatz zur Arsenverbindung, jedoch nicht in Richtung der symmetrischen Verbindungen verschoben und die Gleichgewichtskonstante beträgt $K = 1.2$ (Abbildung 1.17 a.).^[236] Auch eine Verlängerung der Alkyl-Substituenten führt zur Ausbildung eines Gleichgewichts mit ähnlicher Gleichgewichtskonstante. So liegt diese für die Reaktion von n Pr₄Bi₂ und Me₄Sb₂ zu n Pr₂BiSbMe₂ bei $K = 0.7$.^[241] Durch die Ausbildung der Gleichgewichte konnten die Verbindungen R₂BiSbMe₂ (R = Me, Pr) nicht isoliert werden. Die erste isolierbare Verbindung mit einer Bi-Sb-Bindung ist (Bbt)Bi=Sb(Bbt) (Bbt = 2,6-(CH(SiMe₃))-4-(C(SiMe₃)₃)C₆H₂), wobei diese eine Bi=Sb-Doppelbindung

aufweist (Abbildung 1.17 b.). Dargestellt wird die Verbindung aus (Bbt)BiBr₂ und (Bbt)SbH₂ in Anwesenheit von DBU. Die Verbindung wird durch die sterisch sehr anspruchsvollen Reste kinetisch stabilisiert, was die Ausbildung eines Gleichgewichts, analog zu den Verbindungen mit kleineren Resten, unterdrückt. Erst ab einer Temperatur von 70 °C kann in Lösung die Bildung des Dibismutens und des Distibenes beobachtet werden.^[242] Kürzlich, 2020, wurde über die ersten isolierbaren Bismutanylstibane mit einer Bi-Sb-Einfachbindung berichtet, wobei der Bruch der Bi-Sb-Bindung und damit die Ausbildung des Gleichgewichts, durch Verwendung von Bis(silylamino)naphthalene-Substituenten, unterdrückt wird.^[221] Da es sich bei den Verbindungen eigentlich um ternäre Interpnictogenverbindungen handelt, werden diese in Kapitel 1.3.3 genauer beleuchtet. Des Weiteren kann, analog zum Arsen, ein Tetraederan mit zentralem [Mo]₂BiSb-Tetraeder ([Mo] = MoCp(CO)₂) dargestellt werden.^[238] Auch dieses lässt sich oxidieren,

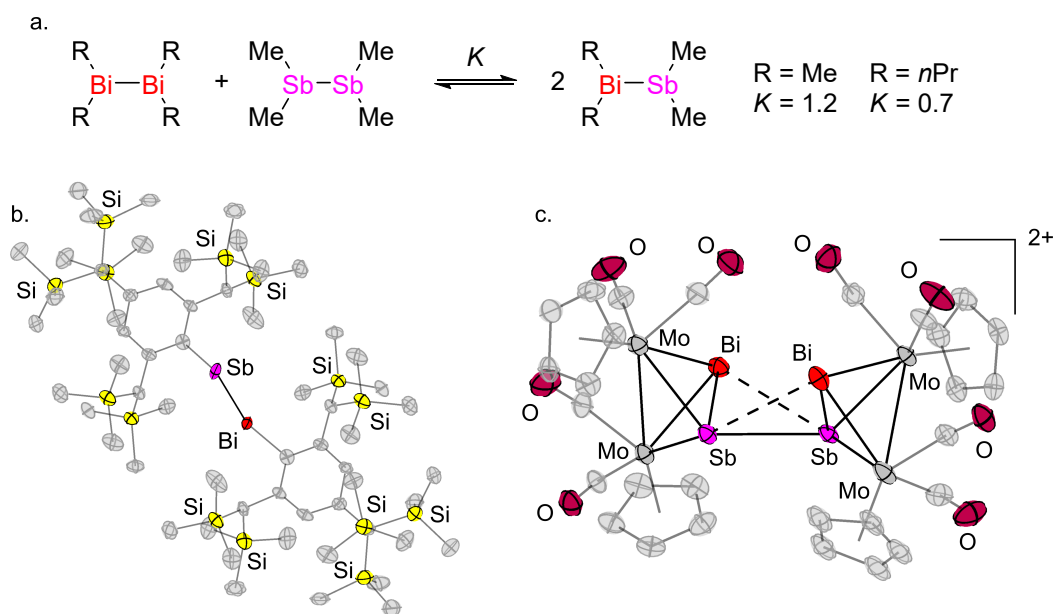


Abbildung 1.17: a. Gleichgewicht zwischen Dibismutan, Distiban und Bismutanylstiban für Me- oder *n*Pr-Reste am Bismut. b. Molekülstruktur im Festkörper eines Bismutanylstiban mit Bi=Sb Doppelbindung und extrem sterisch anspruchsvollen Bbt-Substituenten an Bi und Sb. c. Nach Oxidation des [Mo]₂BiSb-Tetraeders ([Mo] = MoCp(CO)₂) erhaltenes dikationisches Dimer mit zentralem Bi₂Sb₂-*butterfly*-Motiv.^[236,239,241,242] Wasserstoffatome sind aus Gründen der Übersichtlichkeit nicht dargestellt. Die Schwingungsellipsoide sind mit 50 % Aufenthaltswahrscheinlichkeit gezeigt.

wobei ein dikationisches Dimer gebildet wird. Jedoch wird nun kein zentraler, planarer Ring, sondern ein *butterfly*-artiges Bi_2Sb_2 -Motiv ausgebildet (Abbildung 1.17 c.). In der Molekülstruktur im Festkörper sind die beiden Bi-Sb-Bindungen zwischen den beiden Tetraedern allerdings deutlich verlängert.^[239]

1.3.3 Multinäre Interpnictogenverbindungen

Als multinäre Interpnictogenverbindungen werden Verbindungen bezeichnet, in denen mindestens drei verschiedene Pnictogenatome aneinander gebunden sind. Wie zuvor bei den binären Verbindungen beschrieben, sind auch hier Verbindungen mit den leichteren Pnictogenen deutlich intensiver untersucht worden. In diesem Kapitel werden zunächst multinäre Verbindungen der leichteren Elemente (N, P, As, Sb) und im Anschluss bismuthaltige Interpnictogenverbindungen diskutiert.

Im Falle der ternären Interpnictogenverbindungen sind für die Elementkombination mit N, P und E (E = As, Sb) sehr viele Struktur motive beschrieben. Für die Elemente N, P und As konnten Verbindungen mit allen Reihenfolgen der Elemente, also N-P-As, N-As-P oder P-N-As, realisiert werden. Es werden eine Vielzahl von Struktur motiven ausgebildet, darunter Ketten, Heterozyklen oder käfigartige Verbindungen. Einige Beispiele für Verbindungen dieser Art sind in Abbildung 1.18 gezeigt.^[243–245] Für einige Verbindungen wurden dabei interessante Reaktivitäten beobachtet. So kann zum Beispiel der in Abbildung 1.18 b. gezeigte AsN_2P -Heterozyklus mit Magnesium zum Diradikaloid umgesetzt werden. Das Diradikaloid ist nun in der Lage kleine Moleküle wie zum Beispiel CS_2 oder Isonitrile

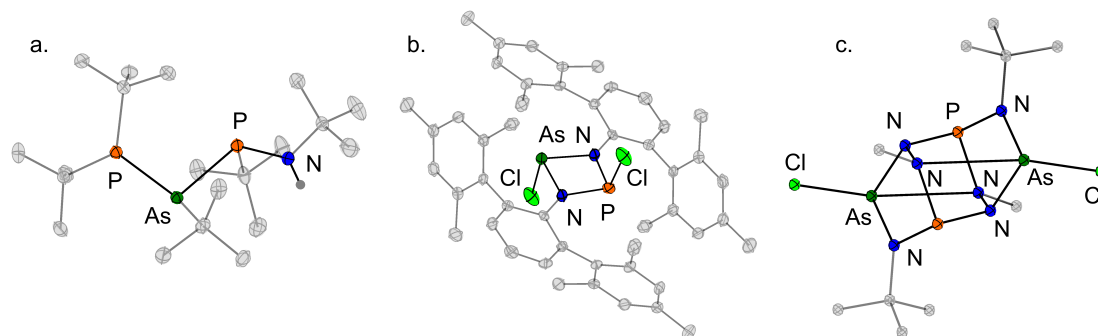


Abbildung 1.18: Molekülstrukturen einer kettenförmigen (a.), zyklischen (b.) und käfigartigen Verbindung (c.) mit N-P-As-Motiv.^[243–245] Wasserstoffatome sind aus Übersichtsgründen nicht und alle Schwingungsellipsoide mit einer Aufenthaltswahrscheinlichkeit von 50 % dargestellt.

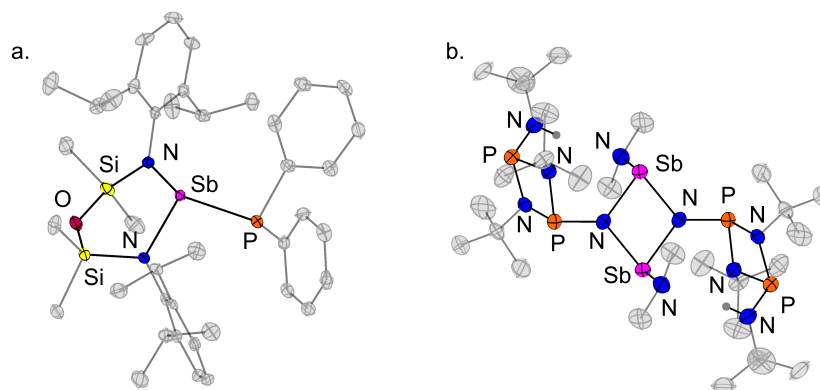


Abbildung 1.19: Molekülstrukturen für Verbindungen mit N-Sb-P (d.) und P-N-Sb (e.) Kettenmotiv.^[247,248] Kohlenstoffgebundene Wasserstoffatome sind aus Übersichtsgründen nicht und alle Schwingungsellipsoide mit einer Aufenthaltswahrscheinlichkeit von 50 % dargestellt.

zu aktivieren.^[244,246] Für die Elementkombination N-P-Sb sind auch einige Verbindungen untersucht worden, wobei wieder kettenförmige, zyklische und auch käfigartige Motive beschrieben sind. Auch diese zeigen teilweise interessante Reaktivitäten. So kann das in Abbildung 1.19 a. gezeigte Molekül als Katalysator für die Hydrophosphanierung von Isocyanaten genutzt werden.^[247]

Für die Elementkombinationen mit nur einem der beiden leichtesten Pnictogene (N, P) sind deutlich weniger Verbindungen beschrieben. Im Falle der Elementkombination N-As-Sb wird in der Literatur hauptsächlich von substituierten

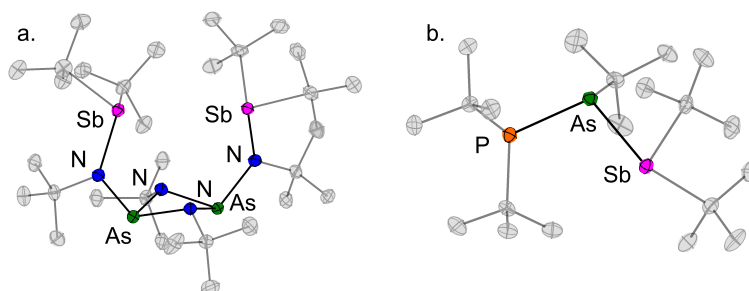


Abbildung 1.20: Molekülstrukturen eines zweifach $\text{Sb}(t\text{Bu})_2$ -substituierten Bis(amino)diazadiarsetidine (a.), und von $t\text{Bu}_2\text{PAs}(t\text{Bu})\text{SbtBu}_2$ (b.). Wasserstoffatome sind aus Übersichtsgründen nicht und alle Schwingungsellipsoide mit einer Aufenthaltswahrscheinlichkeit von 50 % dargestellt.^[243,249]

Bis(amino)diazadiarsetidinen berichtet.^[249] Der Name der genannten Verbindungsklasse leitet sich aus der Heterozyklennomenklatur ab, wobei ein *Etidine* einem stickstoffhaltigen gesättigten Vierring entspricht. *Diaza* beziehungsweise *diarsa* bedeutet, dass im Ring je zwei Atome nicht Kohlenstoff- sondern Stickstoff- beziehungsweise Arsenatomen entsprechen. Der Ring ist des Weiteren mit je einem Amin-Substituenten am Arsen funktionalisiert. Eine Beispielverbindung, in der die Amin-Funktionen wiederum je mit einer $\text{Sb}(t\text{Bu})_2$ -Einheit substituiert ist, ist in Abbildung 1.20 a. gezeigt. Für die Kombination P-As-Sb sind nur zwei Verbindungen strukturell charakterisiert. Beide sind *tert*-Butyl-substituierte Ketten, wobei die Verbindungen eine zentrale As-P-Sb- oder P-As-Sb-Kette aufweisen.^[243,250] Letztere Kette, mit einer, in der Literatur äußerst selten beschriebenen As-Sb-Bindung, ist in Abbildung 1.20 b. gezeigt.

Für die vier leichtesten Pnictogene sind des Weiteren fünf verschiedene quaternäre Verbindungen strukturell charakterisiert. Hier bilden alle vier Pnictogene eine Kette, einen Zyklus oder käfigartige Strukturen. Eine kettenförmige Verbindung mit zentraler P-As-N-Sb-Kette (Abbildung 1.21 b.) konnte dabei durch Reaktion von $\text{Li}(\text{N}(\text{Mes}^*)\text{As}=\text{P}(\text{Mes}^*))$ mit SbCl_3 dargestellt werden. Bemerkenswert ist, dass die im Edukt vorhandene $\text{As}=\text{P}$ -Doppelbindung auch in der quaternären Verbindung erhalten bleibt.^[252] Es ist außerdem eine weitere kettenförmige quaternäre Verbindung beschrieben. Diese hat ein zentrales P-As-Sb-N-Motiv und

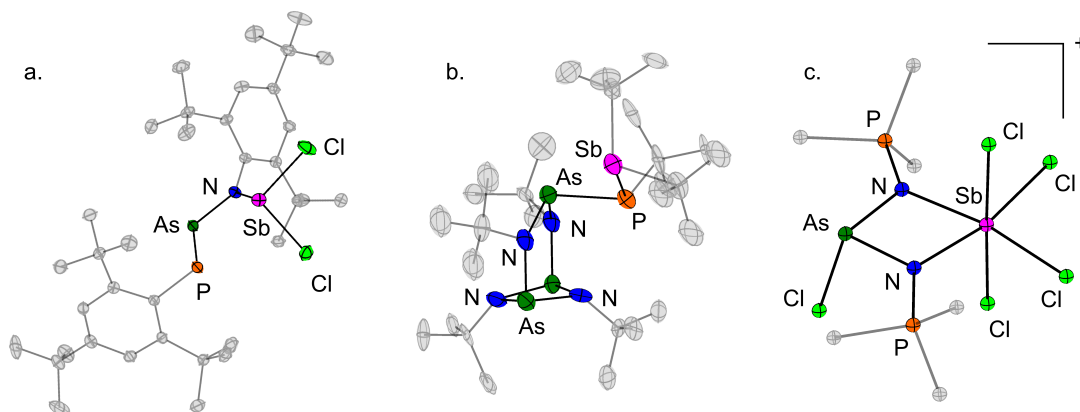


Abbildung 1.21: Molekülstrukturen dreier quaternärer Interpnictogenverbindungen der leichtesten Elemente N, P, As und Sb.^[251–253] Wasserstoffatome sind aus Übersichtsgründen nicht und alle Schwingungsellipsoide mit einer Aufenthaltswahrscheinlichkeit von 50 % dargestellt.

ist, bis auf ein Proton am Stickstoff, ausschließlich durch *tert*-Butyl-Gruppen substituiert. Die Verbindung konnte durch Reaktion zweier binärer Bausteine, $\text{LiAs}(t\text{Bu})\text{PtBu}_2$ und $\text{ClSb}(t\text{Bu})\text{NH}t\text{Bu}$, in einer Salzmetathesereaktion dargestellt werden.^[243] Auch im Falle der quaternären Verbindungen sind zwei funktionalisierte Bis(amino)diazadiarsetidine beschrieben. Wieder können diese durch Einsatz eines lithiierten binären Baustein dargestellt werden.^[251] Eine der beiden käfigartigen Verbindungen ist in Abbildung 1.21 b. gezeigt. Außerdem ist eine kationische, heterozyklische Verbindung beschrieben. Der zentrale Zyklus wird von Stickstoffatomen zweier Phosphaniminito-Substituenten ($\text{Me}_3\text{P}=\text{N}^-$), einem AsCl - und einem SbCl_4 -Fragment gebildet. Das Kation ist in Abbildung 1.21 c. gezeigt. Dargestellt wird die Verbindung durch eine Kondensationsreaktion aus dem zweifach positiv geladenen $[(\text{Me}_3\text{P}=\text{NAsCl})_2]^{2+}$ mit zentralem N_2As_2 -Zyklus und SbCl_5 , wobei AsCl_3 abgespalten wird.^[253]

Bismuthaltige, ternäre Interpnictogenverbindungen sind bisher sehr wenig untersucht. Im Falle der Verbindungen mit einer N-Bi-P-Kette zeigen einige Verbindungen bemerkenswerte Reaktivitäten. So kann die in Abbildung 1.22 a. gezeigte Verbindung mit zentralem P_4 -*butterfly*-Motiv durch Reaktion eines $(\text{NON}^{\text{Dipp}})\text{Bi}(\text{II})$ -Radikals mit P_4 dargestellt werden. Die Insertion des P_4 ist des Weiteren reversibel und in Lösung kann, unter Rückbildung des $\text{Bi}(\text{II})$ -Radikals, P_4 wieder abgegeben werden.^[134] In einer strukturell ähnlichen

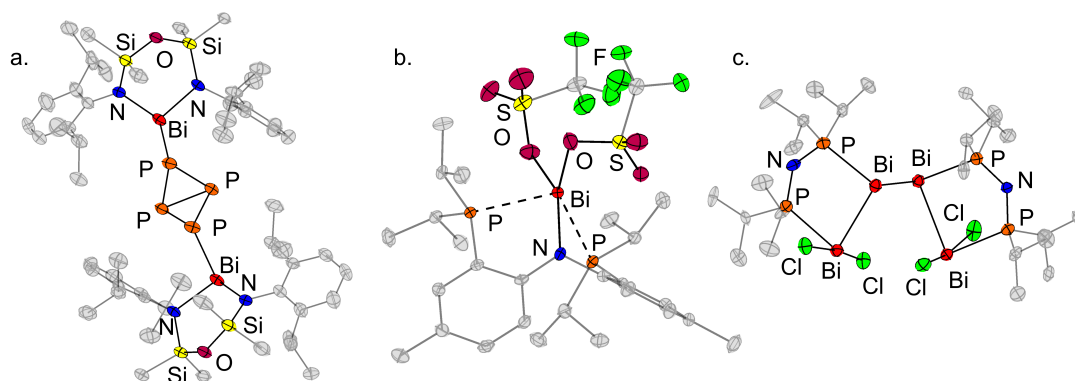


Abbildung 1.22: Molekülstrukturen dreier Interpnictogenverbindungen mit N-P-Bi-Motiv. a. $((\text{NON}^{\text{Dipp}})\text{Bi})_2\text{P}_4$. b. Komplex mit PNP-*Pincer*-Ligand. c. Durch $(i\text{Pr}_2\text{P})_2\text{N}$ -Substituenten stabilisierte Bi_4 -Kette.^[134,200,254] Wasserstoffatome sind aus Übersichtsgründen nicht und alle Schwingungsellipsoide mit einer Aufenthaltswahrscheinlichkeit von 50 % dargestellt.

Verbindung, $\text{NON}^{\text{R}}\text{BiPCy}$ ($\text{R} = t\text{Bu}, \text{Dipp}$), konnten außerdem die ersten terminalen Bismutanylphosphane überhaupt dargestellt werden.^[134] Mit einem $\text{Bi}(\text{N}(\text{SiMe}_3)_2)$ -funktionalisierten Bis(amino)diazadiphosphetidine ist außerdem eine käfigartige Verbindung beschrieben.^[255] Auch sind Donor-Akzeptor Komplexe mit N-P-Bi-Motiv untersucht worden. Das zentrale, *Lewis*-saure Bi-Atom wird dabei in zwei Verbindungen von negativ geladenen NNN- oder PNP-*Pincer*-Liganden koordiniert, wobei hier nur auf die zweite Struktur eingegangen wird. In der in Abbildung 1.22 b. gezeigten Verbindung ist ein PNP-*Pincer*-Ligand an ein *Lewis*-saurer Bi-Zentralatom gebunden. Die abgebildete Verbindung kann durch Umsetzung der entsprechenden Chlorverbindung mit $\text{Ag}[\text{OTf}]$ erhalten werden. In DCM zeigt die Verbindung eine Dissoziation der beiden schwach koordinierenden $[\text{OTf}]^-$ -Anionen, wobei das gebildete zweifach positiv geladene Kation nicht stabil ist und sich langsam zersetzt. Als ein Zersetzungsprodukt kann hier die Bildung der ursprünglichen Dichlorverbindung beobachtet werden, was auf eine Reaktion mit dem als Lösemittel verwendeten DCM hinweist.^[254] Des Weiteren konnten auch nach Reaktion von $(i\text{Pr}_2\text{P})_2\text{NH}$ mit BiCl_3 je nach Reaktionsbedingungen verschiedene Verbindungen mit N-P-Bi-Motiv dargestellt werden. Eine neutrale Verbindung mit zentraler, durch $(i\text{Pr}_2\text{P})_2\text{N}$ -Substituenten stabilisierter, Bi_4 -Kette ist in Abbildung 1.22 c. gezeigt.^[200]

Für Verbindungen mit N-As-Bi-Motiv sind nur zwei Verbindungen strukturell

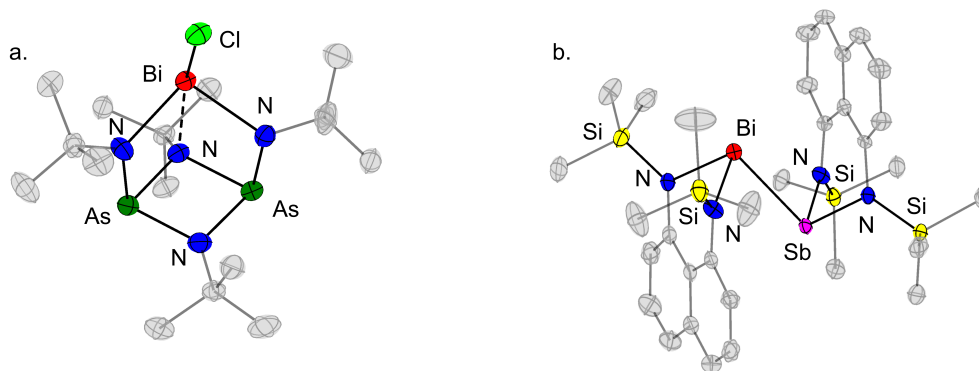


Abbildung 1.23: Molekülstrukturen im Festkörper von Verbindungen mit N-As-Bi-Käfigstruktur (a.) und einer der ersten beschriebenen Verbindungen mit Bi-Sb-Einfachbindung und Bis(silylamino)naphthalene-Substituenten (b.).^[221,251] Wasserstoffatome sind aus Übersichtsgründen nicht und alle Schwingungsellipsoide mit einer Aufenthaltswahrscheinlichkeit von 50 % dargestellt.

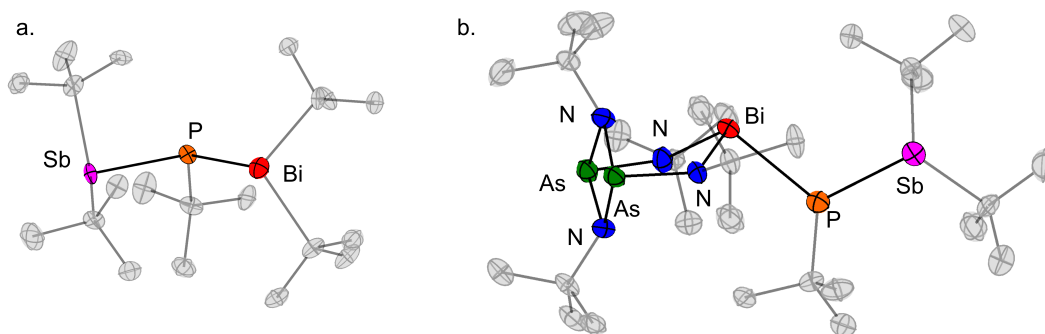


Abbildung 1.24: Molekülstrukturen im Festkörper von einer Verbindung mit zentraler Sb-P-Bi-Kette (a.) und der ersten quaternären Interpnictogenverbindung (b.).^[103,251] Wasserstoffatome sind aus Übersichtsgründen nicht und alle Schwingungsellipsoide mit einer Aufenthaltswahrscheinlichkeit von 50 % dargestellt.

charakterisiert, wobei beide auf dem Bis(amino)diazadiarsetidine-Gerüst beruhen. Eine der beiden Verbindungen ist isostrukturell zu der in Abbildung 1.20 a. gezeigten Verbindung mit N-As-Sb-Motiv. Die andere zeigt zwischen den beiden Amin-Funktionen eine BiCl-Einheit und ist in Abbildung 1.23 a. gezeigt.^[249,251] Im Falle der Verbindungen die ein N-Sb-Bi-Motiv enthalten sind zwei Struktur motive bekannt. Die erste zeigt einen zentralen N_2BiSb -Heterozyklus und ist isostrukturell zu der in Abbildung 1.18 b. gezeigten Verbindung. Dargestellt wird die Verbindung aus $(Sb(Ter^{Mes}N)_2)MgCl$ und $BiCl_3$ unter Abspaltung von $MgCl_2$. Bei den Verbindungen mit dem zweiten Strukturmotiv handelt es sich um die ersten isolierbaren Verbindungen mit einer Bi-Sb-Einfachbindung überhaupt. Beide Schweratome sind dabei von Bis(silylamino)naphthalene-Substituenten koordiniert, wobei die Stabilität der Bi-Sb-Bindung in den Verbindungen auf attraktiven dispersiven Wechselwirkungen zwischen den Substituenten zurück zu führen ist. Die Verbindungen zeigen interessante Reaktivität und sind in der Lage elementaren Schwefel zu aktivieren, wobei formal ein S_1 -Fragment in die Bi-Sb-Bindung insertiert wird.^[221] Eine der Verbindungen mit Bi-Sb-Bindung ist in Abbildung 1.23 b. gezeigt.

Für ternäre Verbindungen die ein Bismut- und kein N-Atom enthalten sind nur zwei Verbindungen mit dem gleichen Motiv strukturell charakterisiert. Beide sind kettenförmige *tert*-Butyl-substituierte Moleküle mit zentraler P-As-Bi- oder Sb-P-Bi-Kette (Abbildung 1.24 a.).^[103,243] Eine ternäre Verbindung, die alle drei schweren Pnictogene, also As, Sb und Bi, in einer Kette enthält, ist dagegen noch nicht beschrieben.

Des Weiteren ist eine quintärnere Verbindung, die alle Pnictogene von Stickstoff bis Bismut enthält, beschrieben. Um diese darzustellen, wurde die in Abbildung 1.23 a. gezeigte Verbindung mit N-As-Bi-Motiv mit einem binären lithiierten Bausteins, $\text{LiP}(t\text{Bu})\text{Sb}t\text{Bu}_2$, umgesetzt, wobei in einer Salzmetathesereaktion eine Bi-P-Bindung geknüpft wird. Die einzige beschriebene quinternäre Interpnictogenverbindung ist in Abbildung 1.24 b. gezeigt.

1.4 Das MOVPE-Verfahren

Die Abkürzung *MOVPE* steht für *Metal-Organic-Vapor-Phase-Epitaxy*. Sie bezeichnet ein Verfahren, in dem ein Material durch Zersetzung von Präkursormolekülen in der Gasphase über einem geeigneten Substrat schichtweise abgeschieden werden kann. Genau genommen ist das Verfahren eine spezielle Form des *MOCVD*-Verfahrens (*Metal-Organic-Chemical-Vapor-Deposition*), wobei in der *MOVPE* die Schichten epitaktisch, also mit gleicher Orientierung der Kristallstruktur des Substrats, gewachsen werden. In der Praxis werden die beiden Begriffe jedoch oft synonym verwendet. Die *MOVPE* ermöglicht das Wachsen von hochreinen Schichten, wobei deren Qualität, Zusammensetzung und Dicke sehr gut durch Einstellen der Prozessbedingungen kontrollierbar ist. Verwendet wird das *MOVPE*-Verfahren zum Beispiel für die Herstellung blauer LEDs (GaN , $(\text{Ga},\text{In})\text{N}$), hoch effizienter Solarzellen ($(\text{Ga},\text{In})\text{P}$, GaAs , $(\text{Ga},\text{In})(\text{AsP})$, $(\text{Ga},\text{In})\text{As}$), Transistoren (GaAs , InP) oder Infrarotdetektoren ($(\text{Hg},\text{Cd})\text{Te}$).^[256–262]

Während des Prozesses werden zunächst Präkursor-Moleküle in die Gasphase überführt und mittels eines Trägergases, beispielsweise N_2 oder H_2 , in kontrollierten Mengen in die Reaktionskammer und damit in die Nähe eines heißen Substrats geleitet. Durch die hohe Temperatur zersetzt sich der Präkursor über oder auf dem Substrat. Entstehende organische Fragmente werden im Anschluss mit dem Trägergas fortgetragen oder binden an den so entstehenden Film des abzuscheidenden Materials. Bindende Fragmente können im Anschluss entweder desorbiert und fortgetragen oder als Defekte in das abzuscheidende Material eingebaut werden. Die genauen Mechanismen von Zersetzung der Präkursoren über dem Transport der Präkursoren zur Substratoberfläche bis hin zur Desorption der organischen Reste sind komplex und stark von den Prozessbedingungen abhängig.^[262] Im Rahmen dieser Arbeit werden deshalb nur ausgewählte Teilbereiche wie ein grundlegendes Model zum Transport von Präkursormolekülen zum Substrat und einige Präkursoren für die Elemente der Gruppe 15 diskutiert.

1.4.1 Das *Boundary-Layer-Model*

Die Kinetik und Thermodynamik des Transports von Präkursor-Molekülen aus der Gasphase zum Substrat kann durch das stark vereinfachte *Boundary-Layer-Model* beschrieben werden. Die Oberfläche des Substrats wird hier als eine, durch eine Grenzschicht, von der Gasphase im Reaktor getrennte Phase betrachtet. Die Gasphase ist im Vergleich mit der Oberfläche und der Grenzschicht mit Präkursor-Molekülen übersättigt. Das resultierende chemische Potential liefert die Triebkraft für die Diffusion von Präkursor-Molekülen zum Substrat.^[262,263] Die Wachstumsrate des abzuscheidenden Materials ist von der Temperatur abhängig und kann grob in drei Bereiche unterteilt werden. Bei tieferen Temperaturen ist sie hauptsächlich durch die Zersetzungsgeschwindigkeit der Präkursoren bestimmt, wodurch bei Erhöhung der Temperaturen und schnellerer Zersetzung die Wachstumsrate steigt. Im mittleren Temperaturregime ist der bestimmende Faktor hauptsächlich die Diffusionsgeschwindigkeit von Präkursor-Molekülen durch die Grenzschicht. Änderungen der Temperatur spielen für die Diffusionsgeschwindigkeit, und damit für die Wachstumsrate in diesem Temperaturregime, nur eine geringe Rolle. Durch hohe Desorptionsraten bei sehr hohen Temperaturen sinkt die Wachstumsrate im dritten Regime bei weiterer Erhöhung der Temperatur deutlich.^[262]

1.4.2 Präkursoren der 15. Gruppe

In der *MOVPE* verwendete Präkursoren müssen einige Anforderungen erfüllen. Um wirtschaftlich relevant zu sein, sollten die hochreinen Präkursoren zunächst möglichst günstig in der Herstellung beziehungsweise Aufreinigung, wenig toxisch und lagerstabil sein. Gleichzeitig müssen sie sich jedoch unter Prozesstemperaturen über dem Substrat in ausreichender Menge zersetzen. Des Weiteren müssen sie, falls es sich nicht um Gase handelt, zumindest einen gewissen Dampfdruck zeigen, um von einem Trägergas mitgetragen werden zu können. Im Allgemeinen steigt der Dampfdruck in molekularen Verbindungen bei Verringerung der molaren Masse, weshalb kleine organische Reste bevorzugt werden. Außerdem sollten die Präkursoren keine ungewünschten Reaktionen mit anderen, im Prozess simultan verwendeten Präkursoren in der Gasphase zeigen. Dies ist vor allem wichtig wenn multilaminäre Schichten, zum Beispiel 13/15-Halbleiter, aufgebaut werden. Zuletzt muss der Zersetzungsprozess über beziehungsweise auf dem Substrat wie gewünscht von statten gehen. Abgespaltene, organische Reste müssen unter gegebenen Prozessbe-

dingungen vom Substrat fortgetragen werden können. Ist dies nicht möglich, können gegebenenfalls unerwünschte Defekte im abgeschiedenen Material entstehen, oder die Oberfläche des Substrats passiviert werden.^[264] Einige Substituenten haben sich als besonders geeignet für die Verwendung in Präkursoren herausgestellt, wobei für viele Hauptgruppenelemente oft Wasserstoff- oder Alkyl-Substituenten verwendet werden. Bei der Zersetzung eines Präkursors mit E-H-Bindung können zum Beispiel H-Radikale entstehen. Diese können entweder zu gasförmigem H₂ rekombinieren oder mit organischen Resten in der Reaktionskammer beziehungsweise auf dem Substrat abreagieren. Bei den kleinen Alkylgruppen haben sich, je nach Element, vor allem Methyl-, Ethyl-, *iso*-Propyl-, *iso*-Butyl- oder *tert*-Butyl-Gruppen etabliert.^[262]

Im Falle der 15. Gruppe sind Verbindungen mit Wasserstoff der Form EH₃ (E = N, P, As, Sb, Bi) für alle Elemente bekannt, wobei allerdings nur NH₃, PH₃ und AsH₃ lagerstabil sind (Vergleich: Kapitel 1.2.1). Dies schließt die schwereren Hydride als geeignete Präkursoren aus. Bei Verwendung von NH₃ als Präkursor für 13/15-Halbleiter, muss der *MOVPE*-Prozess üblicherweise bei sehr hohen Temperaturen durchgeführt werden, um stabile Zwischenstufen bei der Zersetzung von NH₃-Addukten weiter zu konvertieren. In Prozessen, die bei tiefen Temperaturen stattfinden müssen, zum Beispiel die Darstellung multinärer stickstoffhaltiger 13/15-Halbleitern, ist NH₃ also gegebenenfalls ungeeignet. Üblicherweise werden in diesem Fall Hydrazin oder Hydrazin-Derivate, wie zum Beispiel das *Unsymmetrische Dimethylhydrazin* (Me₂NNH₂, *UDMHy*), eingesetzt, welche sich schon bei deutlich geringeren Temperaturen zersetzen.^[265] PH₃ und AsH₃ finden breite Verwendung als Präkursoren. Die beiden Verbindungen sind jedoch extrem giftige Gase, weshalb ihr Einsatz nach Möglichkeit zu vermeiden ist.^[266] Als leichter handhabbare Alternativen werden zum Beispiel *tert*-Butylphosphan (TBP) und *tert*-Butylarsan (TBA) eingesetzt.^[267] Wenngleich deutlich aufwendiger und damit teurer in der Herstellung, handelt es sich bei beiden Verbindungen um Flüssigkeiten mit hohem Dampfdruck. Durch die großen *tert*-Butyl-Reste, welche bei Zersetzung entweder durch β -H-Eliminierung flüchtiges Isobuten oder durch homolytischen E-C-Bindungsbruch *t*Bu'-Radikale bilden, werden nur geringe Mengen an Kohlenstoff-Defekten in die abzuschheidende Schicht eingebracht.^[268–272] Dagegen sind Me₃P und Me₃As als Präkursoren für die Darstellung hoch reiner 13/15-Halbleiter ungeeignet. Im Falle von Me₃As wird durch die Kombination aus einer relativ stabilen As-C-Bindung und einem

kleinen, kohlenstoffhaltigem Rest viel Kohlenstoff in die abzuscheidende Schicht eingebracht. Sollen Kohlenstoff-dotierte Materialien dargestellt werden, kann sich die Verbindung jedoch unter Umständen als Präkursor eignen.^[273] Im Falle des Antimons sind zwei *tert*-Butyl-substituierte Verbindungen, namentlich $t\text{BuSbH}_2$ und $t\text{Bu}_2\text{SbH}$, nicht lagerstabil, was deren kommerzielle Verwendung verhindert.^[274,275] Das stabilere $t\text{Bu}_3\text{Sb}$ ist durch seine hohe molare Masse relativ schwer flüchtig, was die Verwendung unattraktiv macht.^[276] In vielen Fällen wird als Antimon-Präkursor Me_3Sb verwendet. Durch die deutlich schwächere Sb-C-Bindung (siehe Kapitel 1.2.1) werden hier deutlich geringere Mengen von kohlenstoffhaltigen Verunreinigungen eingebracht als im Falle von Me_3P oder Me_3As . Sollen Defekte jedoch gänzlich vermieden werden, kann auf die deutlich weniger flüchtigen Verbindungen Et_3Sb oder $i\text{Pr}_3\text{Sb}$ zurückgegriffen werden.^[277,278] Für das schwerste Pnictogen Bismut werden aufgrund ihres Dampfdrucks hauptsächlich Me_3Bi oder Et_3Bi als Präkursoren eingesetzt. Hier unterscheiden sich die Einbauraten für Kohlenstoffdefekte bei der Verwendung verschiedener Trialkylbismutane wenig. Für die Darstellung von $\text{Ga}(\text{As},\text{Bi})$ wurden diese für Me_3Bi , Et_3Bi , $i\text{Pr}_3\text{Bi}$ und $t\text{Bu}_3\text{Bi}$ im Detail untersucht, wobei kein signifikanter Unterschied gefunden wurde.^[279] Auch Interpnictogenverbindungen können als Präkursoren im *MOVPE*-Verfahren eingesetzt werden. So werden $\text{P}(\text{NMe}_2)_3$, $\text{As}(\text{NMe}_2)_3$ oder $\text{Sb}(\text{NMe}_2)_3$ zum Dotieren von Halbleitern bei tiefen Prozesstemperaturen genutzt.^[280–284] Die NMe_2 -Reste verbleiben dabei nicht im Material. Kürzlich konnte gezeigt werden, dass Di-*tert*-butylaminoarsan ($t\text{Bu}_2\text{AsNH}_2$, (DTBAA)) und Di-*tert*-butylaminophosphan ($t\text{Bu}_2\text{PNH}_2$, DTBAP) als *single-source*-Präkursoren für den gleichzeitigen Einbau von Arsen beziehungsweise Phosphor und Stickstoff in multinäre 13/15-Halbleiterschichten geeignet sind.^[285–289] So zersetzen sich die Verbindungen schon bei tiefen Prozesstemperaturen und zeigen eine hohe Effizienz beim Einbau von Stickstoff (DTBAA: 4.2 %; DTBAP: 16 %). Im Falle des DTBAPs wird dabei sogar die Effizienz von UDMHy bei gleicher Prozesstemperatur übertroffen.^[285,286] In einer experimentellen und einer theoretischen Studie wurde die thermische Zersetzung von DTBAA untersucht.^[287,290] Mittels *in situ* Massenspektrometrie wurde die Bildung von $t\text{Bu}_2\text{AsH}$, Isobuten, Isobutan und NH_3 beobachtet. Die Bildung von Isobuten erfolgt wahrscheinlich durch Zersetzung *via* β -H Eliminierung. Isobutan kann durch verschiedene Mechanismen gebildet werden. Einer ist die homolytische Spaltung der As-C-Bindung und anschließender Reaktion des $t\text{Bu}\cdot$ -Radikals mit $\text{H}\cdot$ -Radikalen, welche wiederum selbst

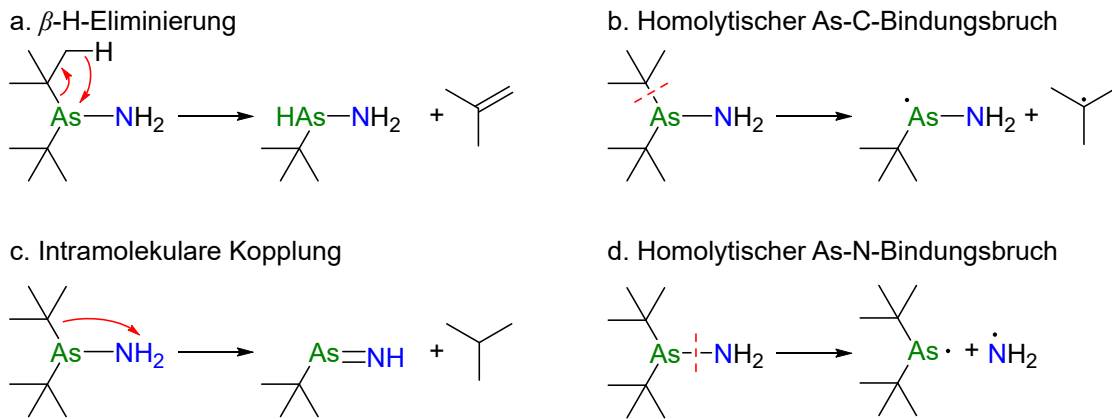


Abbildung 1.25: Initiale thermische Zersetzungskanäle von DTBAA in der Gasphase.

durch die Zersetzung des Präkursors oder durch Reaktion mit dem Trägergas H_2 entstehen. Außerdem kann als initialer Zersetzungsschritt eine intramolekulare Kopplungsreaktion mit N-H-Bindungsbruch stattfinden, wobei neben Isobutan noch $tBuAs=NH$ in der Gasphase entsteht. Zuletzt kann die Bildung von tBu_2AsH und NH_3 durch einen homolytischen As-N-Bindungsbruch und anschließender Reaktion mit H_2 oder H^\cdot -Radikalen erklärt werden. In Abbildung 1.25 sind die vier beschriebenen initialen Zersetzungsreaktionen von DTBAA dargestellt. Durch Wechselwirkungen mit anderen Präkursoren beim tatsächlichen Aufbau von 13/15-Halbleiterschichten können die Zersetzungsmechanismen nochmals deutlich komplexer werden.

Für Halbleiter der Zusammensetzung $GaAs_{1-x}Bi_x$ ($x \approx 10\%$) konnte mittels quantenchemischer Rechnungen gezeigt werden, dass sich diese als Materialien für Laser mit einer Emissionswellenlänge von $1.55\ \mu m$ eignen könnten.^[41–43] Damit wären sie geeignet für die Datenübertragung in Glasfaserkabeln. Durch die Separation von elementarem Bismut aus $GaAs_{1-x}Bi_x$, war es bei den zur Zersetzung von Trialkylbismut-Präkursoren benötigten Prozesstemperaturen bisher nicht möglich, mittels *MOVPE*, ausreichend große Einbauraten des Bismuts zu erreichen.^[47–52] Wie zuvor beschrieben, war es für die leichteren Pnictogene in der Vergangenheit möglich, durch Verwendung von Interpnictogenverbindungen, geringe Prozesstemperaturen zu erreichen. Auch für das Element Bismut wurde mit $Bi(NMe_2)_3$ bereits eine Interpnictogenverbindung im *MOCVD*-Verfahren erprobt. Hierbei konnten in Verbindung mit $Te(SiMe_3)_2$ Filme aus Bi_2Te_3 schon bei Raumtemperatur

abgeschieden werden. Jedoch macht der geringe Dampfdruck des als Feststoff vorliegenden $\text{Bi}(\text{NMe}_2)_3$ seine Verwendung problematisch.^[187,215] Das Beispiel zeigt allerdings, dass bismuthaltige Interpnictogenverbindungen durchaus Potential für die Anwendung in der *MOVPE* haben, wenn prozessbedingt tiefe Temperaturen notwendig sind. Dafür müssen allerdings neue, flüchtigere und bestenfalls flüssige Präkursoren entwickelt werden.

2 Motivation

Ziel dieser Arbeit ist die Darstellung bismuthaltiger Interpnictogenverbindungen für die anschließende Verwendung als Präkursoren im *MOVPE*-Verfahren. Während in der Literatur viele Interpnictogenverbindungen mit Elementkombinationen der leichteren Elemente Stickstoff, Phosphor und Arsen bekannt sind, beschränkt sich die Zahl der Verbindungen die eine Bi-N, -P, -As oder -Sb-Bindung aufweisen auf bedeutend weniger Beispiele (siehe Abbildung 2.1). In vorangegangenen Arbeiten der Arbeitsgruppe von *Hänisch* konnten einige Interpnictogenverbindungen dargestellt werden, die nur durch *tert*-Butyl-Gruppen oder Wasserstoff substituiert sind. Die Wahl der Substituenten machen diese Verbindungen attraktiv für den Einsatz als Präkursoren im *MOVPE*-Verfahren. Durch Verwendung von Di-*tert*-butylaminoarsan (DTBAA) oder Di-*tert*-butylaminophosphan (DTBAP) als *single-source*-Präkursoren für den gleichzeitigen Einbau von Arsen, beziehungsweise Phosphor und Stickstoff, konnten zum Beispiel $\text{GaE}_{1-x}\text{N}_x$ Halbleiterschichten aufgebaut werden. Beide Präkursoren zeigen mit bis zu 4.2 % ($\text{E} = \text{As}$) beziehungsweise 16 % ($\text{E} = \text{P}$) Stickstoff im abgeschiedenen Material sehr hohe Stickstoffeinbauraten.^[285,286] Gleichzeitig entstehen nur wenige, durch Kohlenstoffeinbau verursachte Defektstellen in der abgeschiedenen Schicht. Dies ist vermutlich auf die schon im Präkursor existierende E-N-Bindung, die Verwendung von *t*Bu-Gruppen und das Fehlen von N-C-Bindungen zurück zu führen.^[287] Für die Halbleiterindustrie ist auch der Einbau von Antimon- oder Bismutatomen in Halbleiterschichten relevant. Aufgrund der deutlich geringeren Stabilität von Verbindungen der schwereren Elemente, erfüllt die entsprechende Antimonverbindung, Di-*tert*-butylaminostiban (DTBASb), nicht die Voraussetzungen zur Eignung als Präkursor. Selbst bei tiefen Temperaturen oder unter dem Einfluss von Licht neigt diese zur Kondensationsreaktionen unter Abspaltung von Ammoniak. Die entsprechende Bismutverbindung ist dagegen gänzlich unbekannt. Des Weiteren zeigen Alkylbismutverbindungen im Allgemeinen, und *tert*-Butylsubstituierte Verbindungen im Speziellen, eine hohe Labilität gegenüber Licht und Wärme. Während Me_3Bi bei Raumtemperatur gelagert werden kann, zersetzt sich tBu_3Bi schon bei $-60\text{ }^\circ\text{C}$ langsam.^[291] Arylbismutane sind dagegen erheblich stabiler gegenüber Licht und Wärme. Aufgrund dessen ist der Ansatz dieser Arbeit zunächst Interpnictogenverbindungen darzustellen, die Aryl-Substituenten am Bismut tragen. An den leichteren Pnictogenen werden weiterhin hauptsächlich *tert*-

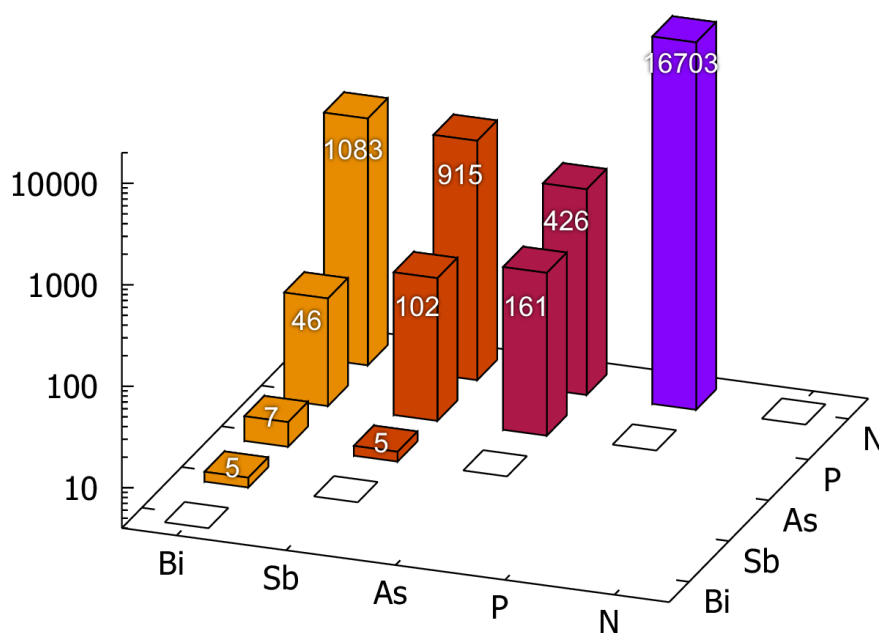


Abbildung 2.1: Anzahl Treffer von Verbindungen mit E¹-E²-Bindung nach Suche in der CCDC-Datenbank (Stand November 2020).

Butyl- oder Wasserstoff-Substituenten verwendet, um die positiven Eigenschaften für die MOVPE zu erhalten. Als Aryl-Substituenten sollen Phenyl- (Ph), Mesityl- (Mes) und 2,6-Di-*iso*-propylphenyl- (Dipp) verwendet werden. Dabei soll auch der Einfluss des sterischen Anspruchs der Substituenten auf die Eigenschaften der Verbindungen untersucht werden. Während die als Edukte benötigten Diarylhalidobismutane mit Ph- oder Mes-Substituenten bereits in der Literatur beschrieben sind, wurde der Dipp-Substituent im Rahmen dieser Arbeit in die Bismut Chemie eingeführt. Dafür soll zunächst die Darstellung von Verbindungen der Form $\text{Dipp}_{3-n}\text{BiX}_n$ ($X = (\text{Pseudo-})\text{Halogenid}$, $n = 1-3$) untersucht werden. Außerdem soll der Einfluss des Dipp-Substituenten auf die Eigenschaften und Reaktivität der erhaltenen Bismutane untersucht werden, wofür prototypische Bismutverbindungen wie ein Dibismutan oder ein Bismutenium-Kation dargestellt werden sollen. Mit den Ph-, Mes- und Dipp-substituierten Diarylhalidobismutanen als Edukte sollten im Anschluss Interpnictogenverbindungen mit terminalen Diarylbismut-Einheiten dargestellt und untersucht werden, inwieweit Bi-N, Bi-P, Bi-As und Bi-Sb-Bindungen aufgebaut werden können. Nachdem binäre Interpnictogenver-

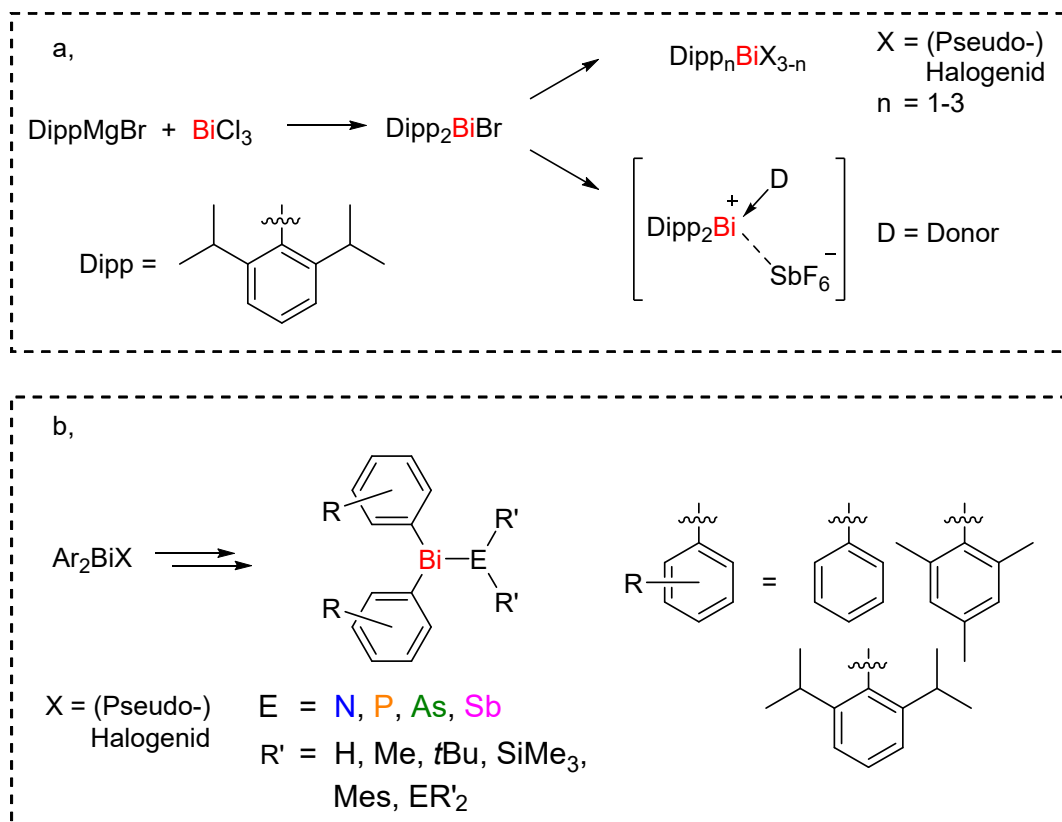


Abbildung 2.2: a. Darstellung von Dipp-substituierten Bismutverbindungen. b. Darstellung von Interpnictogenverbindungen mit Bi-N, -P, -As und -Sb Einfachbindungen.

bindungen erfolgreich dargestellt werden können, soll außerdem die Darstellung multinärer Interpnictogenverbindungen untersucht werden. Zuletzt sollen Interpnictogenverbindungen mit terminalen Dimethylbismutanyl-Substituenten, welche keine β -H-Atome aufweisen, dargestellt werden. Diese könnten sich als geeignete Präkursoren für die *MOVPE* herausstellen.

3 Kumulativer Teil

European Journal of Inorganic Chemistry **2021**, 2021, 870-878.

2,6-Diisopropylphenyl-Substituted Bismuth Compounds: Synthesis, Structure and Reactivity

Tobias Dunaj, Kevin Dollberg, Christian Ritter, Fabian Dankert, Carsten von Hähnisch

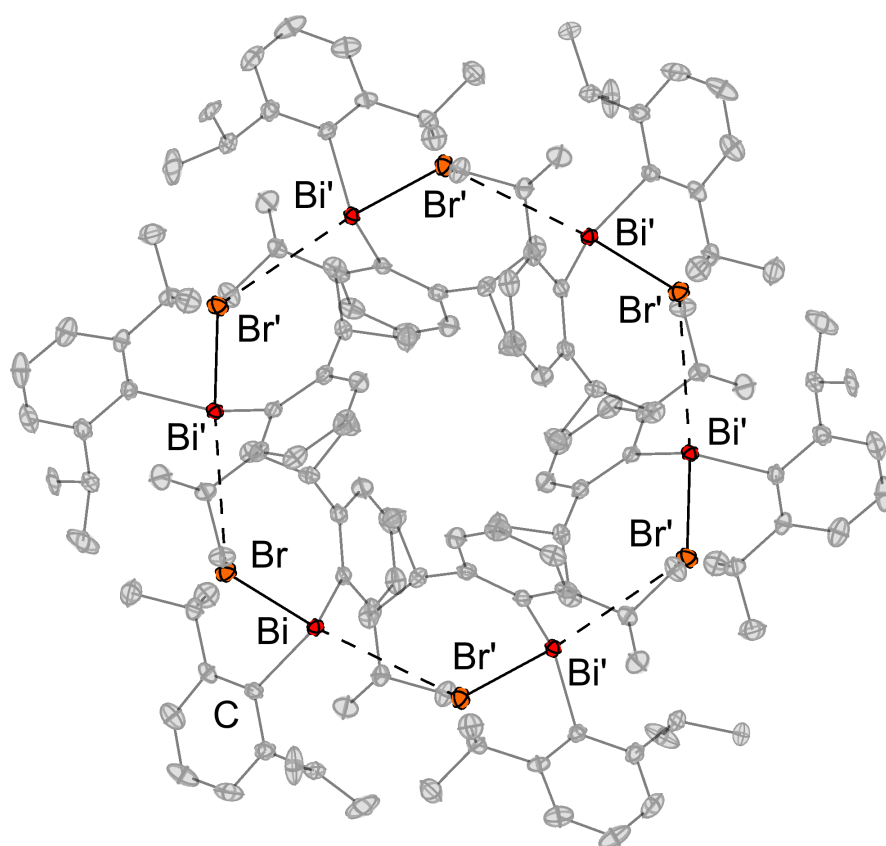


Abbildung 3.1: Struktur des Hexamers von Dipp_2BiBr im Einkristall. Wasserstoffatome sind aus Übersichtsgründen nicht und alle Schwingungsellipsoide mit einer Aufenthaltswahrscheinlichkeit von 50 % dargestellt. Moleküle die zu mit einem Apostroph markierten Atom gehören wurden durch $1/3+x, 2/3x+y, 2/3z; 1xy, 1x, z; 4/3x, 2/3y, 2/3z; 1y, xy, z; 1/3+xy, 1/3+x, 2/3z$ symmetriegeneriert.

Im Rahmen dieser Publikation wurde der Dipp-Substituent erstmalig in die Bismut-Chemie eingeführt. Dabei wurde durch Umsetzung zweier Äquivalente des *Grignard*-Reagenz $\text{DippMgBr}\cdot\text{THF}$ mit BiCl_3 zunächst das Diarylbromobismutan Dipp_2BiBr erhalten. Davon ausgehend konnte durch einen Halogenidaustausch auch das entsprechende Iodobismutan Dipp_2BiI dargestellt werden. Über einen Umweg, das $\text{Dipp}_2\text{BiOTf}$, welches nach Reaktion von Dipp_2BiBr und AgOTf erhalten wurde, konnte sowohl das entsprechende Fluorid (Dipp_2BiF), als auch das Chlorid (Dipp_2BiCl) dargestellt werden. Dafür wurde $\text{Dipp}_2\text{BiOTf}$ mit NaCl beziehungsweise NaF umgesetzt. Die Strukturen der fünf Verbindungen im Festkörper wurden mittels Einkristallröntgenstrukturanalyse untersucht, wobei abhängig vom (Pseudo-)Halogenid unterschiedliche Struktur motive realisiert werden. So werden mit dem leichtesten Halogen, Fluor, in der Kristallstruktur von Dipp_2BiF eindimensionale Ketten mit alternierenden Bi- und F-Atomen gebildet. Für die schwereren Halogene Chlor und Brom bilden sich dagegen Aggregate, genauer Hexamere, welche deutlich schwächere intermolekulare Bi-X-Wechselwirkungen zeigen. Überraschenderweise zeigt das Dipp_2BiI keine intermolekulare Bi-I-Wechselwirkungen. Stattdessen werden Dimere mit kurzen Bi-Bi-Abständen gebildet. Dies weist vermutlich auf attraktive dispersive Wechselwirkungen zwischen den Bismutatomen hin. Mit dem Triflat-Substituenten bilden sich im Festkörper Dimere. Die Sauerstoffatome zweier Triflat-Anionen verbrücken dabei zwei Dipp_2Bi -Fragmente. Im Anschluss wurde die Reaktivität der dargestellten Verbindungen der Form Dipp_2BiX untersucht. Nach Reduktion mit $\text{Na}[\text{BHEt}_3]$ konnte das Dibismutan Dipp_4Bi_2 erhalten werden. Dieses zeigt, wie für Dibismutane üblich, starke Thermochromie, wobei sich der bei Raumtemperatur dunkel braune Feststoff beim Abkühlen intensiv rosa färbt. In Umsetzungen mit S_8 wurde die Reaktivität des Dibismutanes in der Aktivierung von Element-Element-Bindungen untersucht. Es wurde die Insertion von Polysulfiden in die Bi-Bi-Bindung beobachtet und zwei Verbindungen der Form $(\text{Dipp}_2\text{Bi})_2\text{S}_n$ ($n = 3, 5$) konnten *via* Einkristallröntgendiffraktometrie identifiziert werden. Des Weiteren wurden erste Versuche zur Darstellungen von Interpnictogenverbindungen präsentiert, wobei die Verbindung $\text{Dipp}_2\text{BiPtBu}_2$ über verschiedene Syntheserouten zugänglich war. Zunächst *via* Salzmetathesereaktion von Dipp_2BiBr und LiPtBu_2 in *n*Pentan und außerdem *via* SiMe_3F Abspaltung nach Reaktion von Dipp_2BiF und $\text{PtBu}_2(\text{SiMe}_3)$ in TFT (α - α - α -Trifluorotoluol). Die Diarylbismut-Plattform ist also zum Aufbau bismuthaltiger Interpnictogenverbindungen geeignet.

Eigener Anteil:

Die Darstellung des Dipp_2BiF , die Optimierung der Reaktionsbedingungen für die SiMe_3F -Abstraktion und das Sammeln einiger analytischer Daten für das Dipp_2BiF und das $\text{Dipp}_2\text{BiPtBu}_2$ wurden von Kevin Dollberg im Rahmen eines Forschungspraktikums unter meiner Anleitung durchgeführt. Christian Ritter gab mir essentielle Hilfestellung bei der Verfeinerung der Kristallstruktur des Dipp_2BiF und der Lösemittelmoleküle in der Elementarzelle. Die Aufnahme der Einkristalldaten des Dipp_2BiI erfolgte durch Fabian Dankert. Die Aufnahme aller Massenspektren, Elementaranalysen, einiger NMR-Spektren und das Sammeln einiger Einkristalldaten wurden durch die Serviceabteilungen der Philipps-Universität Marburg durchgeführt. Alle weiteren Synthesen, die Auswertung der analytischen Daten, sowie das Lösen und Verfeinern aller Kristallstrukturen wurde von mir durchgeführt. Des Weiteren wurde das Sammeln der Einkristalldaten von Dipp_2BiCl , $(\text{Dipp}_2\text{Bi})_2\text{S}_3$ und $(\text{Dipp}_2\text{Bi})_2\text{S}_5$ mit entsprechender Probenvorbereitung von mir durchgeführt. Das Manuskript wurde durch mich mit Unterstützung von Prof. Dr. Carsten von Hänisch erstellt.

Dalton Transactions **2022**, 51, 7551-7560.

Binary interpnictogen compounds bearing diaryl bismuth fragments bound to all lighter pnictogens

Tobias Dunaj, Kevin Dollberg, Carsten von Hähnisch

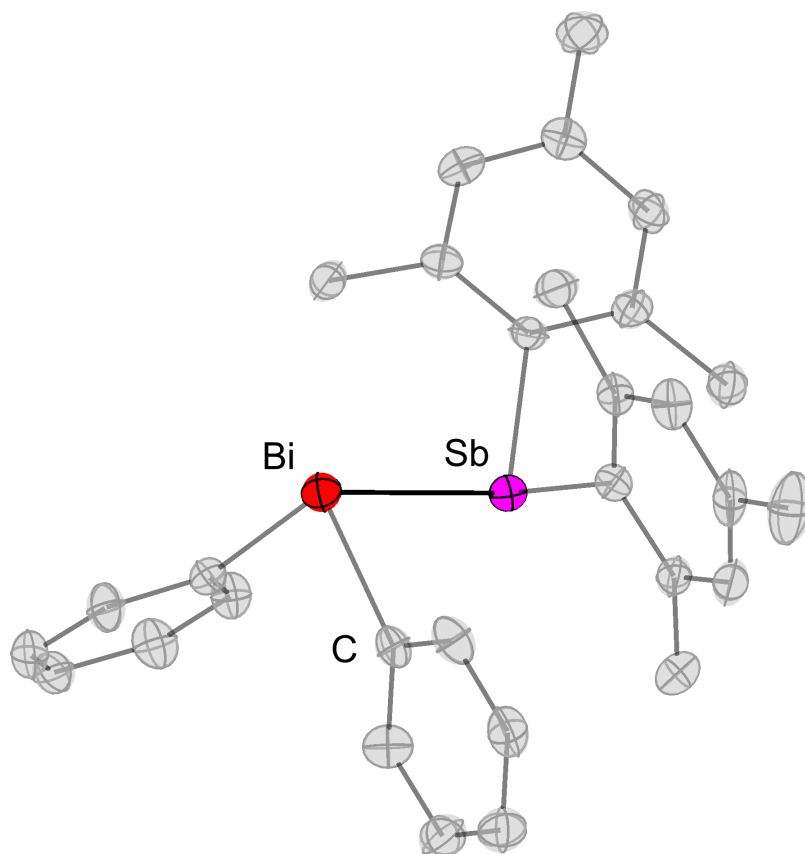


Abbildung 3.2: Struktur von $\text{Ph}_2\text{BiSbMes}_2$ im Einkristall. Wasserstoffatome sind aus Überichtsgründen nicht und alle Schwingungsellipsoide mit einer Aufenthaltswahrscheinlichkeit von 50 % dargestellt.

In dieser Publikation wird über die Darstellung und Charakterisierung binärer bismuthaltiger Interpnictogenverbindungen berichtet. Dabei wurden, ausgehend von den einfach zugänglichen Diarylhalidobismutanen Ph_2BiCl und Mes_2BiCl , Verbindungen mit einer Bi-N, -P, -As oder -Sb-Einfachbindung dargestellt. Die Bismutanamine $\text{Ph}_2\text{BiNMe}_2$ und $\text{Mes}_2\text{BiNMe}_2$ waren durch Reaktion mit LiNMe_2 zugänglich. Interessanterweise bildet $\text{Ph}_2\text{BiNMe}_2$ im Festkörper eindimensionale polymere Stränge mit alternierenden Bi- und N-Atomen, während für $\text{Mes}_2\text{BiNMe}_2$ mit den größeren Substituenten nur Monomere gebildet werden. Beide Verbindungen konnten in Kondensationsreaktionen unter Abspaltung von HNMe_2 als Edukte für weitere Synthesen eingesetzt werden. So konnte nach Umsetzung von $\text{Mes}_2\text{BiNMe}_2$ mit NH_2tBu die Verbindung $\text{Mes}_2\text{BiNH}t\text{Bu}$, welche mit dem Proton am Stickstoff potentiell weiter funktionalisierbar ist, erhalten werden. Für beide Verbindungen der Form $\text{Ar}_2\text{BiNMe}_2$ war die Umsetzung mit Mes_2SbH erfolgreich, wobei Bi-Sb-Einfachbindungen aufgebaut werden konnten. Solche Verbindungen sind in der Regel instabil und neigen zu einem homolytischen Bi-Sb-Bindungsbruch, wobei durch Rekombination das entsprechende Dibismutan beziehungsweise Distiban erhalten wird. Auch die Bi-Bi- und Sb-Sb-Bindungen sind labil, weshalb die Bildung im Gleichgewicht mit der Rückbildung des ursprünglichen Bismutanylstibans steht. Im Falle des $\text{Ph}_2\text{BiSbMes}_2$ liegt das Gleichgewicht weit auf der Seite der gemischten Verbindung ($K_{\text{Ph}} = 76$), was eine Isolation des $\text{Ph}_2\text{BiSbMes}_2$ ermöglichte. Dagegen liegt die Gleichgewichtskonstante für $\text{Mes}_2\text{BiSbMes}_2$ bei $K_{\text{Mes}} = 1.1$, was eine Isolation verhinderte. Die Gleichgewichte wurden mittels temperaturabhängiger NMR-Spektroskopie untersucht, wobei sich herausstellte, dass diese weitestgehend unempfindlich gegenüber Temperaturänderungen sind. Daraus folgt, dass die Begünstigung des $\text{Ph}_2\text{BiSbMes}_2$ maßgeblich durch entropische Effekte bestimmt ist. Es war außerdem möglich, neue Bismutanylphosphane und -arsane der Form $\text{R}_2\text{BiEtBu}_2$ durch Umsetzung von R_2BiCl ($\text{R} = \text{Ph}, \text{Mes}$) und LiEtBu_2 ($\text{E} = \text{P}, \text{As}$) darzustellen. Vor allem die Bismutanylarsane sind seltene Vertreter von Verbindungen mit Bi-As-Einfachbindung. Des Weiteren wurden Bismutanylarsane und -phosphane mit funktionellen Trimethylsilyl-Substituenten dargestellt. Dafür wurde R_2BiCl mit Verbindungen der Form $\text{EtBu}(\text{SiMe}_3)_2$ ($\text{E} = \text{P}, \text{As}$) umgesetzt. Auf diese Weise konnten alle vier Verbindungen der allgemeinen Form $\text{Ar}_2\text{BiEtBu}(\text{SiMe}_3)$ ($\text{Ar} = \text{Ph}, \text{Mes}; \text{E} = \text{P}, \text{As}$) isoliert und charakterisiert werden.

Eigener Anteil:

Die erste Darstellung und das Sammeln der analytischen Daten für die Verbindung $\text{Me}_2\text{BiPtBu}_2$ wurde von Kevin Dollberg im Rahmen eines Forschungspraktikums unter meiner Anleitung durchgeführt. Die Aufnahme aller Massenspektren und Elementaranalysen sowie einiger NMR-Spektren wurden durch die Serviceabteilungen der Philips-Universität Marburg durchgeführt. Die Durchführung aller weiteren Synthesen, das Vorbereiten von Analyseproben und die Auswertung der analytischen Daten geschah durch mich. Des Weiteren wurden alle Einkristalldaten von mir gesammelt und alle Kristallstrukturen von mir gelöst und verfeinert. Das Manuskript wurde durch mich mit Unterstützung von Prof. Dr. Carsten von Hänisch erstellt.

Chemistry - A European Journal **2022**, *28*, e202202932.

Heavy Chains: Synthesis, Reactivity and Decomposition of Interpnictogen Chains with Terminal Diaryl Bismuth Fragments

Tobias Dunaj, Carsten von Hänisch

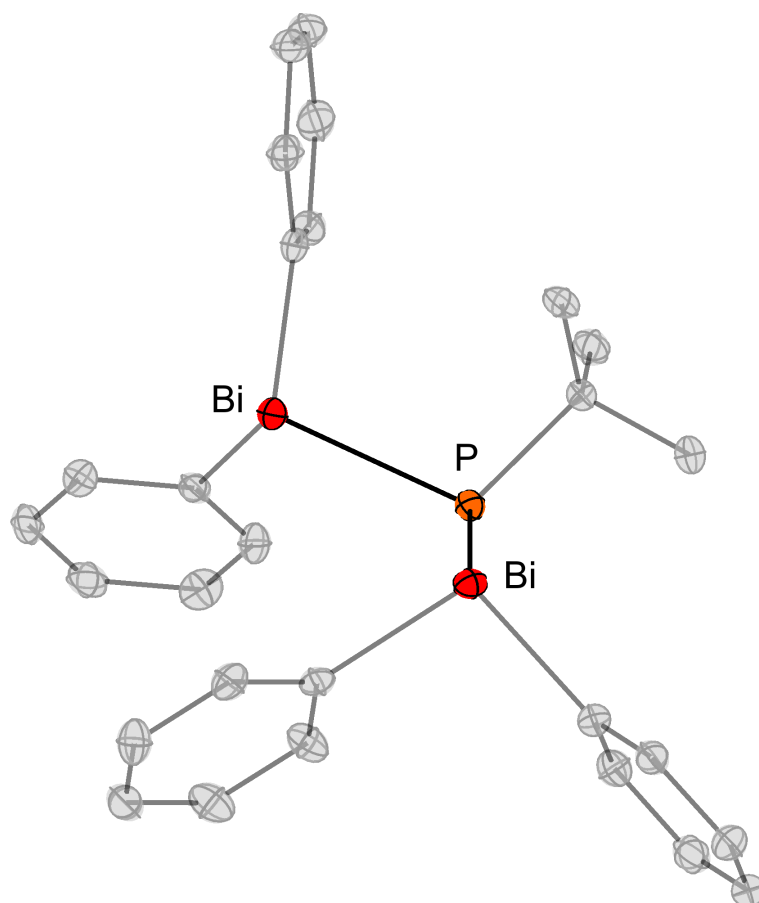


Abbildung 3.3: Struktur von $(\text{Ph}_2\text{Bi})_2\text{PtBu}$ im Einkristall. Wasserstoffatome sind aus Übersichtsgründen nicht und alle Schwingungsellipsoide mit einer Aufenthaltswahrscheinlichkeit von 50 % dargestellt.

In dieser Arbeit wurden kettenförmige Interpnictogenverbindungen mit drei aufeinanderfolgenden Pnictogenen und terminalen Diarylbismut-Fragmenten dargestellt. Durch Umsetzung von Diarylhalidobismutanen der Form R_2BiCl ($R = Ph, Mes$) mit lithiierten binären Interpnictogenverbindungen, namentlich $LiP(tBu)AsPtBu_2$, $LiP(tBu)SbPtBu_2$ und $LiAs(tBu)P(tBu)_2$, konnten sechs ternäre Interpnictogenverbindungen der allgemeinen Form $Ar_2BiE^1(tBu)E^2PtBu_2$ erhalten werden. Die Ketten zeigen dabei die zentralen Motive Bi-P-As, Bi-P-Sb und Bi-As-P. In Lösung zersetzten sich alle sechs Verbindungen innerhalb von Tagen. Im Falle der Bi-P-As-Kette wird ausschließlich die Bi-P-Bindung gespalten, was zur Bildung des entsprechenden Dibismutanes und $tBu_2AsP(tBu)P(tBu)AsPtBu$ mit zentraler As-P-P-As-Kette führt. Anschließend konnte die Verbindung auch gezielt durch den Umsatz von $LiP(tBu)AsPtBu_2$ mit 1,2-Dibromethan dargestellt werden. Im Falle der Bi-As-P-Kette wurde auch eine Spaltung der Bi-As-Bindung beobachtet. Wie erwartet wurde hier nach Rekombination der entstehenden Radikale, neben dem entsprechenden Dibismutan, das bereits in der Literatur beschriebene Molekül mit einer zentralen P-As-As-P-Kette erhalten. Im Falle der Bi-P-Sb-Ketten tritt sowohl ein Bindungsbruch der Bi-P- als auch der Sb-P-Bindung auf. Dies führt zu deutlich mehr Zersetzungsprodukten, wobei unter anderem das Dibismutan und Moleküle mit zentraler Bi-P-Bi- oder Sb-P-Sb-Kette identifiziert wurden. Auch eine symmetrische Verbindung mit zentraler Bi-P-Bi-Kette konnte selektiv dargestellt werden. Durch Umsatz von Ph_2BiCl und $Ph_2BiP(tBu)(SiMe_3)$ wurde $(Ph_2Bi)_2P(tBu)$ erhalten. Für die Mesityl-substituierten Verbindung konnte in einer analogen Reaktion, vermutlich aufgrund des höheren sterischen Anspruchs der Substituenten, keine Reaktion beobachtet werden. Die symmetrische Verbindung mit der zentralen Bi-P-Bi-Einheit neigt stark zur Zersetzung, was nach Lösen zur Entstehung von Ph_4Bi_2 und Polyphosphanen führt. Bei der Entstehung des Dibismutans wird formal eine Formeleinheit eines Phosphinidens („ $PtBu$ “) abgespalten, wodurch die Verbindung als maskiertes Phosphiniden betrachtet werden kann. Um ein möglicherweise bei der Zersetzung transient existierendes Phosphiniden, abzufangen wurde die Verbindung mit einem kleinen NHC, namentlich 1,3,4,5-tetramethylimidazol-2-ylidene (Me_2Ime) umgesetzt. Es konnte hierbei unter intensiver Rotfärbung der Reaktionslösung quantitativ die Bildung des entsprechenden NHC-stabilisierten Phosphinidens ($Me_2Ime=PtBu$) beobachtet werden. Dieses zersetzt sich wiederum im Anschluss unter Rückbildung des freien NHCs und P_4tBu_4 , was eine Isolation von

$\text{Me}_2\text{IME}=\text{PtBu}$ verhinderte. Zuletzt konnten symmetrische Verbindungen der Form $(\text{Ar}_2\text{Bi})_2\text{As}t\text{Bu}$ ($\text{Ar} = \text{Ph}, \text{Mes}$) mit zentraler Bi-As-Bi-Kette erhalten werden, wofür Ar_2BiCl und $\text{Ar}_2\text{BiAs}t\text{Bu}(\text{SiMe}_3)$ umgesetzt wurden. Die Bi-As-Bi-Ketten sind in Lösung deutlich weniger stabil als die Bi-P-Bi-Kette. Jedoch zeigt sich hier bei der Umsetzung mit Me_2IME keine Reaktion, was heißt, dass die Ketten unter diesen Reaktionsbedingungen nicht als Arsenidenüberträger reagieren.

Eigener Anteil:

Alle im Rahmen dieser Arbeit durchgeführten Synthesen wurden von mir durchgeführt. Des Weiteren wurden alle Proben zur Röntgenbeugung am Einkristall von mir vorbereitet und vermessen. Aus den erhaltenen Daten wurden alle Kristallstrukturen von mir gelöst und verfeinert. Die Aufnahme von Massenspektren, die Durchführung der Elementaranalysen, sowie die Messung einiger NMR-Spektren erfolgte durch die Serviceabteilungen der Philipps-Universität Marburg, wobei die Probenvorbereitung ausschließlich durch mich erfolgte. Das Manuskript wurde von mir in Zusammenarbeit mit Prof. Dr. Carsten von Hänisch verfasst.

Zeitschrift für anorganische und allgemeine Chemie

Manuskript vorläufig angenommen.

**2,6-Diisopropylphenyl substituted Bismuth Halide and
Interpnictogen Compounds**

Tobias Dunaj, Marina Egorycheva, Ahmed Arebi, Kevin Dollberg, Carsten von
Hänisch

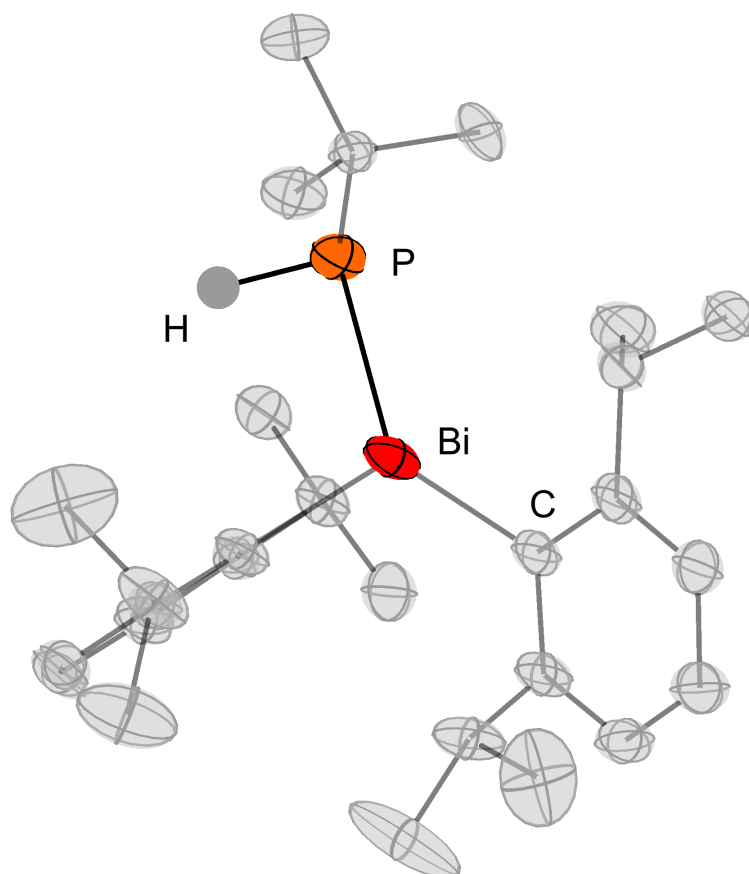


Abbildung 3.4: Struktur von $\text{Dipp}_2\text{BiPHtBu}$ im Einkristall. An Kohlenstoff gebundene Wasserstoffatome sind aus Übersichtsgründen nicht und alle Schwingungsellipsoide mit einer Aufenthaltswahrscheinlichkeit von 50 % dargestellt.

Im Rahmen dieser Publikation wurden weitere Dipp-substituierte Halidobismutane sowie bismuthaltige Interpnictogenverbindungen dargestellt. Durch Reaktion von Dipp_2BiBr mit $\text{DippMgBr}\cdot\text{THF}$ und einem Äquivalent CuCl konnte zunächst das sterisch überfrachtete Dipp_3Bi dargestellt werden. Der hohe sterische Anspruch der drei Dipp-Substituenten zeigt sich dabei zum Beispiel in sehr großen C-Bi-C-Bindungswinkeln oder der eingeschränkten Rotation um die Bi-C-Bindungen. Durch temperaturabhängige NMR-Spektroskopie und *line-shape-Analyse* konnte die Rotationsbarriere für die Drehung um die Bi-C-Bindungen zu $E_A = 62(3) \text{ kJ}\cdot\text{mol}^{-1}$ bestimmt werden. Dipp_3Bi wurde in einer Reaktion mit BiCl_3 erfolgreich als Edukt zur Darstellung von DippBiCl_2 verwendet. DippBiBr_2 konnte dagegen nach Reaktion von Dipp_2BiBr und BiBr_3 erhalten werden. Es wurden außerdem Versuche zur Darstellung von DippBiI_2 unternommen, wobei die Zielverbindung nicht als Reinstoff erhalten werden konnte. Jedoch konnte die Struktur nach Charakterisierung *via* Einkristallröntgenstrukturanalyse verifiziert werden. Es konnten auch Einkristalle der anderen beiden Verbindungen, DippBiCl_2 und DippBiBr_2 , erhalten werden, wobei sich ausgeprägte Unterschiede zwischen den verschiedenen Halogeniden zeigen. Für DippBiCl_2 wurde nach Kristallisation bei $5 \text{ }^\circ\text{C}$ aus Benzol im Festkörper die Bildung von Dimeren beobachtet, wohingegen bei $20 \text{ }^\circ\text{C}$ die Bildung eines eindimensionalen Koordinationspolymers beobachtet wird. Ein ähnlicher eindimensionaler polymerer Strang, welcher jedoch andere Verknüpfungen zeigt, wurde für DippBiBr_2 beobachtet. Im Falle des DippBiI_2 bilden sich im Festkörper Dimere, welche wiederum selbst eindimensionale Polymere Stränge bilden. Umsetzungen von DippBiBr_2 mit MeLi oder LiNMe_2 stellten sich als unselektiv heraus, wobei in der Reaktionslösung unter anderem die Bildungen von Dipp_2BiMe beziehungsweise $\text{Dipp}_2\text{BiNMe}_2$ beobachtet wurde. Beide Verbindungen lassen sich in guten Ausbeuten leicht durch Umsetzung von Dipp_2BiBr und MeLi beziehungsweise LiNMe_2 darstellen. Im Anschluss wurde die Reaktion von Dipp_2BiMe mit einem Äquivalent HCl untersucht, wobei gefunden wurde, dass sich MeBiCl_2 bildet. $\text{Dipp}_2\text{BiNMe}_2$ konnte durch Rühren in reinem NH_2tBu erfolgreich als Edukt für die Synthese von $\text{Dipp}_2\text{BiNH}t\text{Bu}$ eingesetzt werden. Des Weiteren konnte auch ein neues Bismutanylstibane erhalten werden. Für Letzteres wurde $\text{Dipp}_2\text{BiNMe}_2$ mit Mes_2SbH umgesetzt, wobei in einer Kondensationsreaktion unter Verlust von HNMe_2 , $\text{Dipp}_2\text{BiSbMes}_2$ dargestellt wurde. Wird $\text{Dipp}_2\text{BiSbMes}_2$ gelöst, kann die Einstellung eines Gleichgewichts mit Dipp_4Bi_2 und Mes_4Sb_2 beobachtet werden. Im Gegensatz zu den Bismutanylstibanen mit kleineren aroma-

tischen Resten am Bismut ($\text{Ph}_2\text{BiSbMes}_2$, $\text{Mes}_2\text{BiSbMes}_2$), stellen sich bei der Dipp-substituierten Verbindung Gleichgewichtskonzentrationen bei Raumtemperatur langsam, innerhalb von etwa 70 Minuten, ein. Zuletzt wurden außerdem neue Bismutanylphosphane, namentlich $\text{Dipp}_2\text{BiPtBu}(\text{SiMe}_3)$ und $\text{Dipp}_2\text{BiPH}t\text{Bu}$, dargestellt. In beiden Fällen wurde Dipp_2BiF mit $\text{PtBu}(\text{SiMe}_3)\text{R}$ ($\text{R} = \text{H}, \text{SiMe}_3$) umgesetzt. $\text{Dipp}_2\text{BiPH}t\text{Bu}$ ist das erste in der Literatur beschriebene Bismutanyl-substituierte sekundäre Phosphan. In den ^1H - und ^{31}P -NMR-Spektren lässt sich die erwartete $^1J_{\text{P-H}}$ Kopplung (167 Hz) beobachten. Des Weiteren zeigt das IR-Spektrum eine Bande für die P-H Schwingung bei 2272 cm^{-1} .

Eigener Anteil:

Die Verbindungen DippBiBr_2 , Dipp_2BiMe und $\text{Dipp}_2\text{BiSbMes}_2$ wurden erstmals von Marina Egorycheva im Rahmen einer Vertiefung unter meiner Anleitung, sowie von Kevin Dollberg im Rahmen einer Masterarbeit dargestellt. Teile der Proben für die Analytik der genannten Verbindungen wurden auch durch die beiden vorbereitet. Des Weiteren führte Marina Egorycheva die Versuche zur Umsetzungen von Dipp_2BiMe mit HCl durch. Ahmed Arebi konnte im Rahmen einer Vertiefung unter meiner Anleitung die Analytik von $\text{Dipp}_2\text{BiSbMes}_2$ und Dipp_3Bi vervollständigen. Massen- und NMR-Spektren wurden nach Vorbereitung der Proben durch mich oder von mir angeleitete Vertiefer*innen durch die Serviceabteilung der Philipps-Universität Marburg aufgenommen. Einkristalldaten für Dipp_2BiMe wurden durch die Serviceabteilung und für DippBiBr_2 von Roman-Malte Richter aufgenommen. Das Sammeln aller restlichen Einkristalldaten, sowie das Lösen und Verfeinern aller Kristallstrukturen wurde von mir durchgeführt. Auch alle anderen Verbindungen (DippBiCl_2 , DippBiI_2 , $\text{Dipp}_2\text{BiNMe}_2$, $\text{Dipp}_2\text{BiNH}t\text{Bu}$, $\text{Dipp}_2\text{BiPH}t\text{Bu}$ und $\text{Dipp}_2\text{BiPtBu}(\text{SiMe}_3)$) wurden von mir dargestellt und analytische Daten dieser Verbindungen wurden entweder von mir gesammelt oder Proben für die Serviceabteilung von mir präpariert. Das Manuskript wurde von mir mit Unterstützung von Prof. Dr. Carsten von Hänisch verfasst.

Chemistry - A European Journal
Manuskript eingereicht am 23.12.2022.

**Bismuth Cations: Fluoride Ion Abstraction, Isocyanide
Coordination, and Impact of Steric Bulk on Lewis Acidity**

Tobias Dunaj, Carsten von Hähnisch

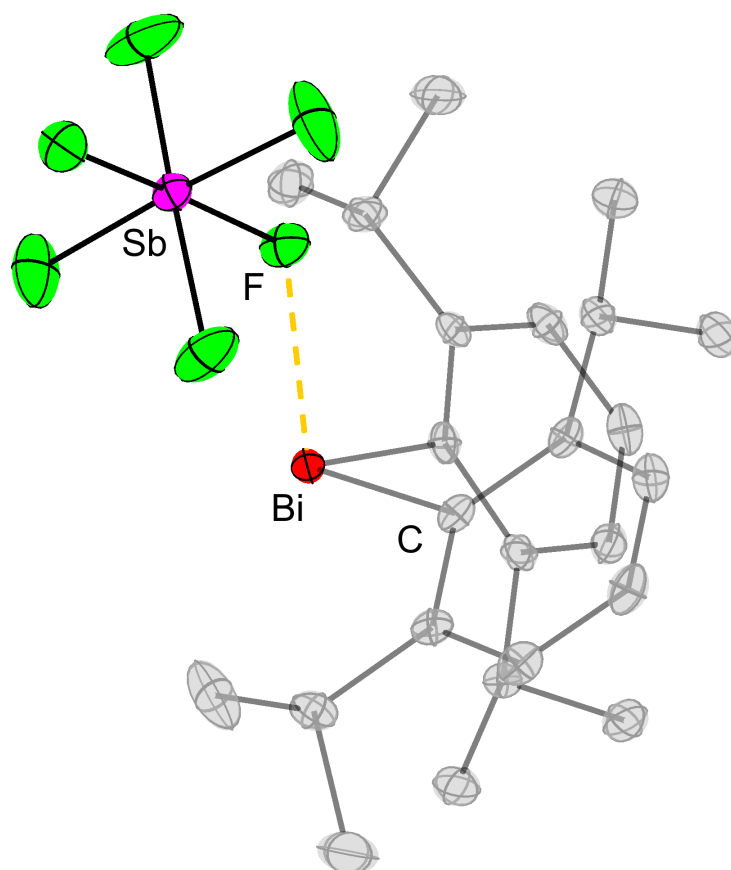


Abbildung 3.5: Struktur von $\text{Dipp}_2\text{BiSbF}_6$ im Einkristall. Wasserstoffatome sind aus Übersichtsgründen nicht und alle Schwingungsellipsoide mit einer Aufenthaltswahrscheinlichkeit von 50 % dargestellt.

In Rahmen dieser Arbeit wird über die Eigenschaften von Bismutenium-Kationen und die Evaluation derer *Lewis*-Acidität berichtet. Dabei wurde der Einfluss von sterischen Effekten durch einen Vergleich von $[\text{Me}_2\text{Bi}]^+$ und $[\text{Dipp}_2\text{Bi}]^+$ betrachtet. Es wurde zunächst die Darstellung einer Verbindung mit dem $[\text{Dipp}_2\text{Bi}]^+$ -Kation untersucht. In Umsetzungen von Dipp_2BiBr mit $\text{Ag}[\text{PF}_6]$ zeigte sich, dass das $[\text{PF}_6]^-$ -Anion nicht stabil gegenüber dem reaktiven Bismutenium-Kation ist und Zersetzung beobachtet wird. Zwei Zersetzungsprodukte, $[(\text{Dipp}_2\text{Bi})_2\text{F}(\text{PF}_6)]$ und Dipp_2BiF , konnten dabei identifiziert werden. Um zu zeigen, dass $[\text{Dipp}_2\text{Bi}(\text{PF}_6)]$ initial in der Lösung vorhanden war, wurde die labile Verbindung mit einem Donor abgefangen, wobei $[\text{Dipp}_2\text{Bi}(\text{OPeEt}_3)_2(\text{PF}_6)]$ isoliert und charakterisiert wurde. Nachdem sich $[\text{PF}_6]^-$ als Anion als zu labil herausgestellt hatte, wurde das stabilere $[\text{SbF}_6]^-$ -Anion verwendet. Nach Reaktion von Dipp_2BiBr und $\text{Ag}[\text{SbF}_6]$ und anschließender Kristallisation aus Toluol wurde $[\text{Dipp}_2\text{Bi}(\text{Toluol})(\text{SbF}_6)]$ als dunkelroter Feststoff erhalten. In der Verbindung koordiniert das Toluol-Molekül mit seinem π -System am Bismutenium-Kation. Um die donorfreie Verbindung zu erhalten, wurde die Verbindung aus TFT (α - α - α -Trifluorotoluol) umkristallisiert. Da jedoch $[\text{Dipp}_2\text{Bi}(\text{SbF}_6)]$ und das Toluol-Addukt in Lösung das gleiche Verhalten zeigen, wurde für Folgesynthesen meist das einfacher zugängliche Toluol-Addukt verwendet. Mit dem $[\text{SbF}_6]^-$ -Anion war es außerdem möglich eine Verbindung mit dem zuvor als Zersetzungsprodukt beobachteten Fluor-verbrückten $[(\text{Dipp}_2\text{Bi})_2\text{F}]^+$ -Kation zu isolieren. Dafür wurde $[\text{Dipp}_2\text{Bi}(\text{Toluol})(\text{SbF}_6)]$ mit einem Äquivalent Dipp_2BiF umgesetzt. Nach erfolgreicher Darstellung von $[\text{Dipp}_2\text{Bi}(\text{SbF}_6)]$ wurde nun der Einfluss der sterisch anspruchsvollen Dipp-Substituenten auf die *Lewis*-Acidität durch einen Vergleich mit $[\text{Me}_2\text{Bi}(\text{SbF}_6)]$ evaluiert. Dafür wurden die traditionelle und eine modifizierte Version der *Gutmann-Beckett*-Methode verwendet, wobei die Verschiebung des Signals eines Phosphanchalkogenids im ^{31}P -NMR-Spektrum als abhängig von der *Lewis*-Acidität eines Akzeptors angenommen wird. Für die Dipp-substituierten Verbindungen wurden Umsetzungen mit OPeEt_3 , SPMe_3 und SePMe_3 unternommen, wobei $[\text{Dipp}_2\text{Bi}(\text{OPeEt}_3)_2(\text{SbF}_6)]$, $[\text{Dipp}_2\text{Bi}(\text{SPMe}_3)(\text{SbF}_6)]$ und $[\text{Dipp}_2\text{Bi}(\text{SePMe}_3)(\text{SbF}_6)]$ isoliert und mittels NMR-Spektroskopie untersucht wurden. Durch Umsetzungen mit einem weiteren Äquivalent ChPMe_3 ($\text{Ch} = \text{S}, \text{Se}$) wurden Reaktionslösungen mit einem 1:2-Verhältnis aus Bismutenium-Kation und Phosphanchalkogenid hergestellt und *in situ* mittels NMR-Spektroskopie untersucht. Auch eine Lösung einer 1:1 Mischung aus $[\text{Dipp}_2\text{Bi}(\text{OPeEt}_3)_2(\text{SbF}_6)]$

und $[\text{Dipp}_2\text{Bi}(\text{SbF}_6)]$ wurde *in situ* untersucht. Für das Methyl-substituierte Bismutenium-Kation wurden alle sechs Reaktionslösungen, mit 1:1 und 1:2 Verhältnis von Donor und Akzeptor hergestellt und *in situ* mittels NMR-Spektroskopie untersucht. Dabei zeigte sich, dass die *Lewis*-Acidität der beiden Bismutenium-Kationen gegenüber SPMe_3 , SePMe_3 und dem 1:2 Verhältnis von Kation und OPEt_3 sehr ähnlich ausfallen. Ein signifikanter Unterschied konnte nur für ein 1:1 Verhältnis aus Kation und OPEt_3 beobachtet werden, wobei $[\text{Dipp}_2\text{Bi}(\text{SbF}_6)]$ eine größere Acidität zeigt. Mittels DFT Rechnungen wurde gezeigt, dass dies auf den sterischen Anspruch der Dipp-Substituenten zurückzuführen ist. Zeigt die Methyl-substituierte Verbindung erhebliche Wechselwirkungen zwischen Bismutenium-Kation und dem $[\text{SbF}_6]^-$ -Anion, ist die Wechselwirkung durch Blockieren der Koordinationsstelle am Bismut gegenüber des OPEt_3 Liganden gehemmt. Dies führt wiederum zu einer stärkeren Bi-O-Wechselwirkung und einer stärkeren Entschirmung des P-Atoms.

Neben der Untersuchung der *Lewis*-Acidität mittels der *Gutmann-Beckett*-Methode wurde auch untersucht, ob Isonitril-Liganden geeignete Sonden für die Evaluation der Acidität von Bismutenium-Kationen sein können. Dafür wurden im Falle des $[\text{Me}_2\text{Bi}(\text{SbF}_6)]$ einige Isonitril-Addukte, namentlich $[\text{Me}_2\text{Bi}(\text{CN}t\text{Bu})(\text{SbF}_6)]$, $[\text{Me}_2\text{Bi}(\text{CNAd})(\text{SbF}_6)]$, $[\text{Me}_2\text{Bi}(\text{CNXyl})(\text{SbF}_6)]$, $[\text{Me}_2\text{Bi}(\text{CNXyl})_2(\text{SbF}_6)]$, $[\text{Me}_2\text{Bi}(\text{CNCy})(\text{SbF}_6)]$ und $[\text{Me}_2\text{Bi}(\text{CN}n\text{Bu})(\text{SbF}_6)]$, dargestellt. Für den größeren Dipp-Substituenten wurde $[\text{Dipp}_2\text{Bi}(\text{CN}t\text{Bu})(\text{SbF}_6)]$ dargestellt und isoliert. Bei Koordination des Isonitrils zeigt sich eine Blauverschiebung der, der Schwingung der C-N-Dreifachbindung zugeordneten, Schwingungsbande. Die Blauverschiebung ist dabei im Falle des Dipp-Substituenten etwas geringer als im Falle der Methyl-Substituenten, was einer etwas besseren Rückbindung zugeschrieben wird. Für die Energien von für die Rückbindung relevanten, gefüllten Orbitalen (Dipp: HOMO-1 bis HOMO-5; Me: HOMO, HOMO-1) wurden mittels DFT-Rechnungen in Falle der Dipp-Substituenten höhere Energien gefunden als im Falle der Methylsubstituenten. Die schwächste Blauverschiebung wird bei $[\text{Me}_2\text{Bi}(\text{CNXyl})_2(\text{SbF}_6)]$ beobachtet, in welchem zwei Isonitril-Substituenten koordiniert sind.

Zuletzt wurde die Koordination von weiteren Donoren untersucht, wobei drei Verbindungen isoliert wurden. Dies sind die Phosphan-Addukte $[\text{Me}_2\text{Bi}(\text{PPh}_3)(\text{SbF}_6)]$ und $[\text{Me}_2\text{Bi}(\text{PCy}_3)(\text{SbF}_6)]$, sowie das Acetonitril-Addukt $[\text{Dipp}_2\text{Bi}(\text{MeCN})(\text{SbF}_6)]$.

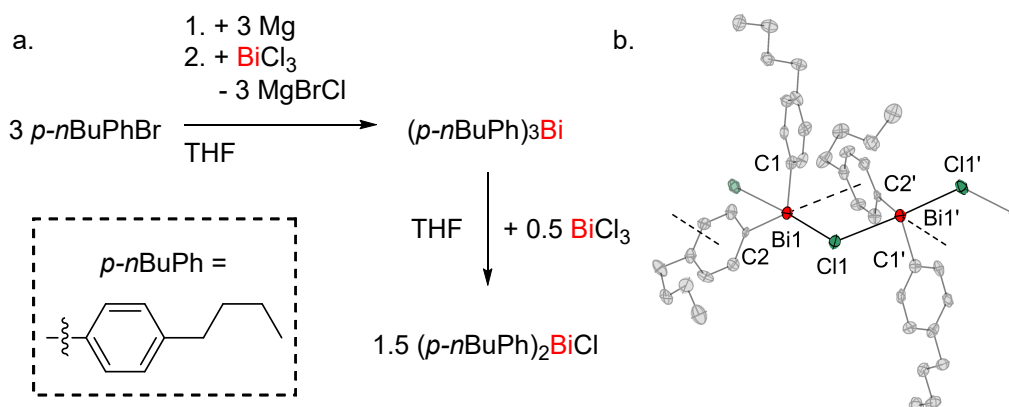
Eigener Anteil:

Diese Veröffentlichung stellt eine Kooperation zwischen der Arbeitsgruppe *Lichtenberg* und der Arbeitsgruppe *von Hänisch* dar, wobei die Anteile an dieser Arbeit, wie im Folgenden beschrieben, verteilt sind. Alle Verbindungen die das $[\text{Me}_2\text{Bi}]^+$ -Kation beinhalten wurden von Mitarbeitern des Arbeitskreis *Lichtenberg* dargestellt und charakterisiert. Dies schließt jegliche Analytik, wie die Aufnahme von NMR- und IR-Spektren, sowie das Sammeln von Daten für die Einkristallröntgendiffraktometrie ein. Die Mitarbeiter der Arbeitsgruppe *Lichtenberg* sind Johannes Schwarzmann, Jacqueline Ramler, Andreas Stoy und Sascha Reith. Des Weiteren wurden alle DFT Rechnungen, sowohl der Methyl- als auch der Dipp-substituierten Verbindungen von Prof. Dr. Crispin Lichtenberg durchgeführt und ausgewertet. Die Verbindungen mit Dipp-Substituenten wurden im Arbeitskreis *von Hänisch* dargestellt und charakterisiert. Die Untersuchungen der Verbindungen mit dem $[\text{PF}_6]^-$ -Anion, sowie die erstmalige Darstellung und das Sammeln einiger analytischer Daten für $[\text{Dipp}_2\text{Bi}(\text{SbF}_6)]$, $[\text{Dipp}_2\text{Bi}(\text{Toluol})(\text{SbF}_6)]$ und $[\text{Dipp}_2\text{Bi}(\text{OPEt}_2)_3(\text{SbF}_6)]$ wurden von Joel Nitzsche im Rahmen einer von mir betreuten Bachelorarbeit durchgeführt. Lena Völlinger konnte im Rahmen einer von mir betreuten Vertiefung weitere analytische Daten von $[\text{Dipp}_2\text{Bi}(\text{SbF}_6)]$ und $[\text{Dipp}_2\text{Bi}(\text{Toluol})(\text{SbF}_6)]$ sammeln, sowie die Addukte $[\text{Dipp}_2\text{Bi}(\text{CN}t\text{Bu})(\text{SbF}_6)]$ und $[\text{Dipp}_2\text{Bi}(\text{MeCN})(\text{SbF}_6)]$ erstmalig darstellen. Alle restlichen Dipp-substituierten Verbindungen wurden erstmals durch mich dargestellt. NMR-Spektren für die Dipp-substituierten Verbindungen wurden von mir, Joel Nitzsche, Lena Völlinger oder der Serviceabteilung der Philipps-Universität Marburg aufgenommen. Des Weiteren wurden Einkristalldaten von $[(\text{Dipp}_2\text{Bi})_2\text{F}(\text{PF}_6)]$, $[\text{Dipp}_2\text{Bi}(\text{OPEt}_3)_2(\text{PF}_6)]$, $[\text{Dipp}_2\text{Bi}(\text{Toluol})(\text{SbF}_6)]$, $[(\text{Dipp}_2\text{Bi})_2\text{F}(\text{SbF}_6)]$, $[\text{Dipp}_2\text{Bi}(\text{SPMe}_3)(\text{SbF}_6)]$, $[\text{Dipp}_2\text{Bi}(\text{SePMe}_3)(\text{SbF}_6)]$, $[\text{Dipp}_2\text{Bi}(\text{OPEt}_3)_2(\text{SbF}_6)]$, $[\text{Dipp}_2\text{Bi}(\text{CN}t\text{Bu})(\text{SbF}_6)]$ und $[\text{Dipp}_2\text{Bi}(\text{MeCN})(\text{SbF}_6)]$ nach Probenvorbereitung durch mich von mir gesammelt. Einkristalldaten von $[\text{Dipp}_2\text{Bi}(\text{SbF}_6)]$ wurden durch die Serviceabteilung der Philipps-Universität Marburg gesammelt. Alle Kristallstrukturen der Dipp-substituierten Verbindungen wurden von mir gelöst und verfeinert. Das Manuskript wurde in Kooperation von Johannes Schwarzmann, Prof. Dr. Crispin Lichtenberg, Prof. Dr. Carsten von Hänisch und mir verfasst.

4 Unveröffentlichte Ergebnisse

4.1 Darstellung flüssiger Bismutverbindungen

Im Rahmen dieser Arbeit konnten einige bismuthaltige Interpnictogenverbindungen mit terminalen Diarylbismut-Substituenten dargestellt werden. Bei allen dargestellten Verbindungen handelt es sich jedoch um Feststoffe mit geringem Dampfdruck, welche deshalb eher nicht für die Verwendung als Präkursor im *MOVPE*-Verfahren geeignet sind. Um flüssige Verbindungen zu erhalten und gleichzeitig nicht auf die Verwendung von Aryl-Substituenten verzichten zu müssen, wurde der *para-n*Butyl-Phenyl-Substituent (*p-n*BuPh) eingeführt. Nach Darstellung und Umsetzung von drei Äquivalenten (*p-n*BuPh)MgBr mit BiCl₃ wurde so erfolgreich (*p-n*BuPh)₃Bi erhalten. Die Verbindung liegt in Form einer blass gelben Flüssigkeit vor, deren Dampfdruck jedoch nicht ausreicht um sie mittels Destillation aufzureinigen. Allerdings zeigt schon das Rohprodukt eine sehr hohe Reinheit, weshalb dieses für weitere Reaktionen verwendet werden konnte. Nach Umsetzung von zwei Äquivalenten (*p-n*BuPh)₃Bi mit BiCl₃ konnte im Anschluss (*p-n*BuPh)₂BiCl in Form eines farblosen Feststoffs dargestellt werden (Abbildung 4.2 a.). Aus einer Lösung in Benzol wurden für die Einkristallröntgendiffraktometrie geeignete, nadelförmige Kristalle erhalten. Die Verbindung kristallisiert in der monoklinen Raumgruppe *P*2₁/*c* mit einem Molekül in der asymmetrischen Einheit, wobei ein-



dimensionale polymere Stränge mit alternierenden Bi-Cl-Bindungen entlang der kristallographischen b-Achse ausgebildet werden (Abbildung 4.2 b.). Die inter- und intramolekularen Bi-Cl-Bindungslängen sind mit 275.0(3) und 283.0(3) pm nahezu identisch. Jedes Bismutatom zeigt außerdem einen kurzen Abstand zum Zentroid eines Phenyl-Rings des nächsten Moleküls (Bi-ct: 369.3(1) pm), was zu einer quadratisch pyramidalen Koordination der Bismutatome führt. Die ^1H - und ^{13}C -NMR-Spektren zeigen die erwarteten Signale. Um eine Interpnictogenverbindung mit Bi-N-Bindung zu erhalten, wurde $(p\text{-}n\text{BuPh})_2\text{BiCl}$ mit LiNMe_2 umgesetzt. Dabei wurde $(p\text{-}n\text{BuPh})_2\text{BiNMe}_2$ in Form eines hochviskosen, farblosen Harzes erhalten. Sowohl das ^1H - als auch das ^{13}C -NMR-Spektrum des Rohprodukts zeigen die zu erwartenden Signale und sehr geringe Mengen an Nebenprodukten, was auf eine sehr selektive Reaktion hinweist. Eine vollständige Aufreinigung *via* Destillation war allerdings nicht möglich, da die Verbindungen auch unter Erwärmung bis zur Zersetzung keinen signifikanten Dampfdruck aufweisen. Aufgrund des geringen Dampfdrucks der Verbindungen mit $p\text{-}n\text{BuPh}$ -Substituenten wurde von weiteren Untersuchung mit selbigem abgesehen.

Nachdem die Verwendung von Aryl-Substituenten keinen Erfolg brachte, wurde schließlich die Darstellung bismuthaltiger Interpnictogenverbindungen mit Methyl-Substituenten am Bismut untersucht. Dafür wurde zunächst die Umsetzung von Me_2BiCl mit LiNMe_2 durchgeführt, wobei jedoch nur schwarzer Feststoff und nicht das gewünschte Produkt erhalten wurde. Umsetzungen mit LiPtBu_2 und LiAstBu_2 waren dagegen erfolgreich, wobei die beiden Verbindungen der Form $\text{Me}_2\text{BiEtBu}_2$ (E = P, As) erhalten wurden. Beide Verbindungen liegen in Form gelber Flüssigkeiten vor und können unter dynamischem Feinvakuum bei 60 °C destilliert werden.

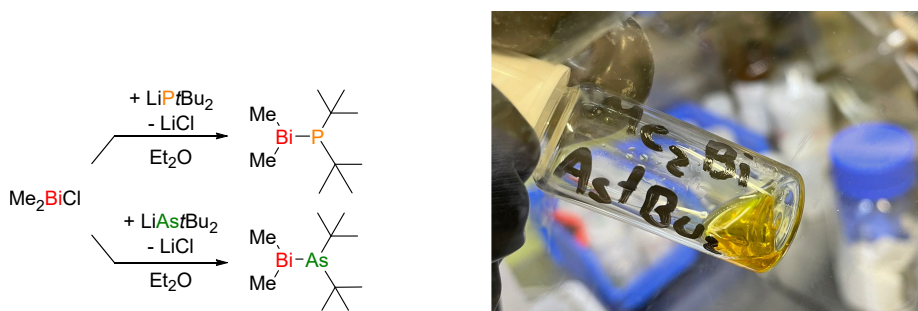


Abbildung 4.2: Links: Darstellung der flüssigen Interpnictogenverbindungen $\text{Me}_2\text{BiEtBu}_2$ (E = P, As). Rechts: Foto des $\text{Me}_2\text{BiAstBu}_2$ nach der Destillation.

Dies zeigt, dass die beiden Verbindungen bei erhöhten Temperaturen einen gewissen Dampfdruck zeigen. Jedoch zersetzen sich die beiden Verbindungen bei diesen Temperaturen innerhalb von wenigen Minuten, was die Ausbeute nach der Aufarbeitung stark verringert (15-19 %). Auch bei Raumtemperatur zersetzen sich die Verbindungen unter dem Einfluss von Licht innerhalb von Stunden. Unter Ausschluss von Licht ist die Zersetzung deutlich verlangsamt, wobei jedoch auch hier nach einigen Tagen deutliche Zersetzung in Form eines metallischen Niederschlags eintritt. Bei -40 °C und unter Ausschluss von Licht sind die Verbindungen allerdings lagerstabil und zeigen auch nach Monaten keine Anzeichen von Zersetzung. Die thermische Zersetzung der beiden Verbindungen wurde mittels TGA und DSC ($2\text{ K}\cdot\text{min}^{-1}$) genauer untersucht. Für $\text{Me}_2\text{BiPtBu}_2$ wird ein gradueller Gewichtsverlust der Probe schon ab etwa 35 °C beobachtet, was die beginnende Zersetzung impliziert. Der Gewichtsverlust endet bei einer Temperatur von etwa 175 °C , wobei etwa 20.2 % des ursprünglichen Gewichts verbleiben (Abbildung 4.3). Im Verlauf des Gewichtsverlusts werden dabei zwei endotherme Prozesse mit maximalem Wärmestrom bei 106 °C und 170 °C beobachtet. Bei beiden handelt es sich wahrscheinlich um die Verdampfung von Zersetzungsprodukten, wobei die erhaltenen

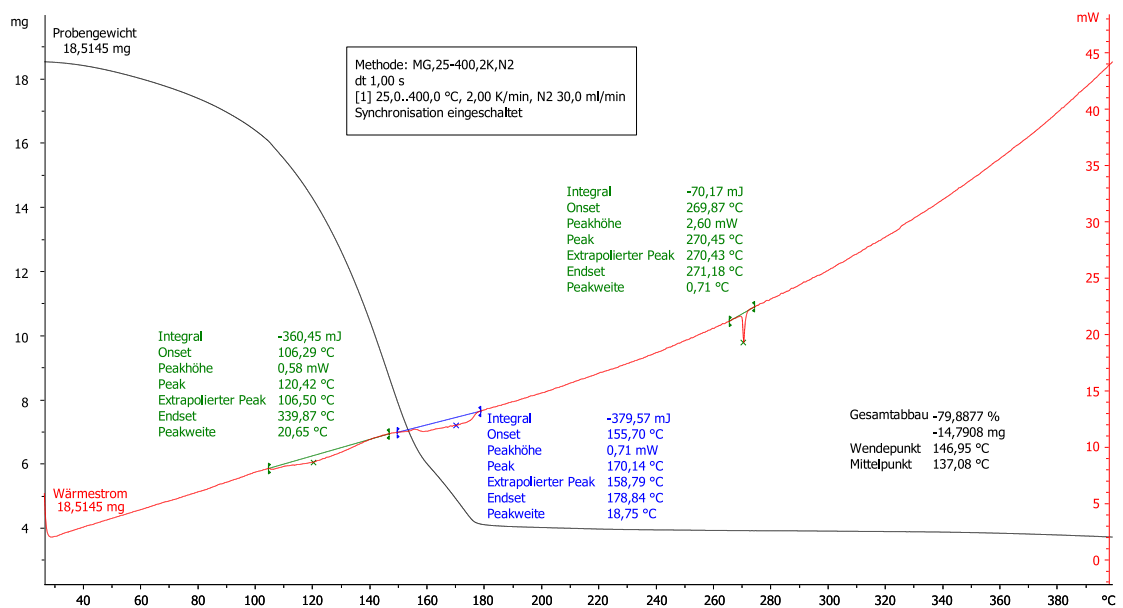


Abbildung 4.3: TGA (schwarz) und DSC (rot) von $\text{Me}_2\text{BiPtBu}_2$ mit einer Heizrate von $2\text{ K}\cdot\text{min}^{-1}$.

Temperaturen sehr gut mit den Siedepunkten von Me_3Bi (106 °C) und MePtBu_2 (170 °C) übereinstimmen.^[292,293] Des Weiteren wird ein endothermer Prozess ohne Gewichtsverlust bei 270 °C beobachtet. Da dies dem Schmelzpunkt von elementarem Bismut entspricht, ist davon auszugehen, dass es sich bei einem Teil der verbliebenen Masse um elementares Bismut handelt. Das eingesetzte $\text{Me}_2\text{BiPtBu}_2$ zersetzt sich also zu BiMe_3 , MePtBu_2 und elementarem Bismut. Im Rahmen dieser Arbeit wurde der verbliebene Feststoff nicht untersucht. Aufgrund dessen kann über die genau Zusammensetzung des Rückstands keine Aussage getroffen werden. Im Falle des $\text{Me}_2\text{BiAstBu}_2$ kann ein ähnlicher Kurvenverlauf beobachtet werden. Auch hier beginnt der Massenverlust schon bei etwa 35 °C und endet bei etwa 180 °C, wobei etwa 23.5 % der Masse der eingesetzten Probe verbleiben und ein endothermer Schmelzprozess bei 271 °C stattfindet, also elementares Bismut zurück bleibt. Auch hier wurde der verbliebene Feststoff nicht weiter untersucht.

4.2 Experimentaltteil

(*p-n*BuPh)₃Bi: Zu in 400 ml THF suspendierten Magnesiumspänen (1.95 g, 80.2 mmol) wurde *p-n*PhBr (18 g, 89.5 mmol) gelöst in 50 ml THF unter Reflux langsam hinzugegossen. Nach beendeter Zugabe und Rühren unter Reflux für eine weitere Stunde wurde die Reaktionslösung auf 0°C gekühlt und BiCl₃ (8.0 g, 25.3 mmol) in 50 ml THF wurde langsam zur Lösung getropft. Nach beendeter Zugabe wurde die Reaktionsmischung 16 h bei Raumtemperatur gerührt. Im Anschluss wurden feste Bestandteile mittels Filtration über Celite entfernt und die erhaltene Lösung wurde in ein Becherglas mit Eis überführt. Nach Trennung der Phasen und anschließender Extraktion der wässrigen Phase mit Ethylacetat (2 · 30 ml) wurden die organischen Phasen vereinigt und flüchtige Bestandteile unter vermindertem Druck entfernt. Der Rückstand wurde in 200 ml Ethylacetat aufgenommen und mit gesättigter wässriger NaCl Lösung gewaschen. Nach erneutem Entfernen von flüchtigen Bestandteilen wird (*p-n*BuPh)₃Bi in Form einer blass gelben Flüssigkeit erhalten.

Ausbeute: 95 %. ¹H NMR (300 MHz, C₆D₆): δ = 0.82 (t, ³J_{H-H} = 7.3, 9H, CH₃), 1.21 (m, ³J_{H-H} = 7.4, 6H, CH₂CH₃), 1.46 (m, ³J_{H-H} = 7.5, 6H, CH₂CH₂CH₃), 2.43 (t, ³J_{H-H} = 7.6, 6H, CH₂CH₂CH₂CH₃), 7.10 (d, ³J_{H-H} = 7.7, 4H, *m-CH*), 7.78 (d, ³J_{H-H} = 7.8, 4H, *m-CH*). ¹³C{¹H} NMR (75 MHz, C₆D₆): 14.2, 22.7, 33.9, 36.0, 131.1, 138.1, 142.5, 152.1. ; HRMS: LIFDI(+) *m/z* 608.28389 [(*p-n*Bu)₃Bi]⁺; calcd 608.28556.

(*p-n*BuPh)₂BiCl: Zu in 5 ml Et₂O gelöstem (*p-n*BuPh)₃Bi (1.35 g, 2.22 mmol) wurde bei 0 °C langsam BiCl₃ (0.35 g, 1.11 mmol) in 5 ml Et₂O hinzugegossen. Die Reaktionslösung wird im Anschluss für 16 h bei Raumtemperatur gerührt, wobei weißer Feststoff ausfällt. Der Feststoff wurde mittels Zentrifugation von der Lösung getrennt und mit 10 ml kaltem *n*Pentan gewaschen. Nach Entfernen flüchtiger Bestandteile wurde (*p-n*BuPh)₂BiCl in Form eines weißen Feststoffs erhalten.

Ausbeute: 82 %. ¹H NMR (300 MHz, C₆D₆): δ = 0.83 (t, ³J_{H-H} = 7.3, 9H, CH₃), 1.20 (m, ³J_{H-H} = 7.4, 6H, CH₂CH₃), 1.44 (m, ³J_{H-H} = 7.5, 6H, CH₂CH₂CH₃), 2.41 (t, ³J_{H-H} = 7.6, 6H, CH₂CH₂CH₂CH₃), 7.30 (d, ³J_{H-H} = 7.9, 4H, *m-CH*), 8.04 (d, ³J_{H-H} = 7.9, 4H, *m-CH*). ¹³C{¹H} NMR (75 MHz, C₆D₆): 14.1, 22.7, 33.8, 36.1, 132.4, 137.2, 143.8; HRMS: CI(+) *m/z* 475.18457 [(*p-n*Bu)₂Bi]⁺; calcd 475.18383.

(*p-n*BuPh)₂BiNMe₂: Zu einer auf -78 °C gekühlten Lösung von (*p-n*BuPh)₂BiCl (170 mg, 0.33 mmol) in 10 ml *n*Pentan wurde festes LiNMe₂ (17 mg, 0.33 mmol) hinzugegeben. Die Lösung wurde innerhalb von fünf Stunden auf 0°C aufgetaut und im Anschluss wurden feste Bestandteile durch Filtration abgetrennt. Flüchtige Bestandteile wurden unter vermindertem Druck entfernt, woraufhin (*p-n*BuPh)₂BiNMe₂ in Form eines farblosen harzigen Rückstandes erhalten wurde.

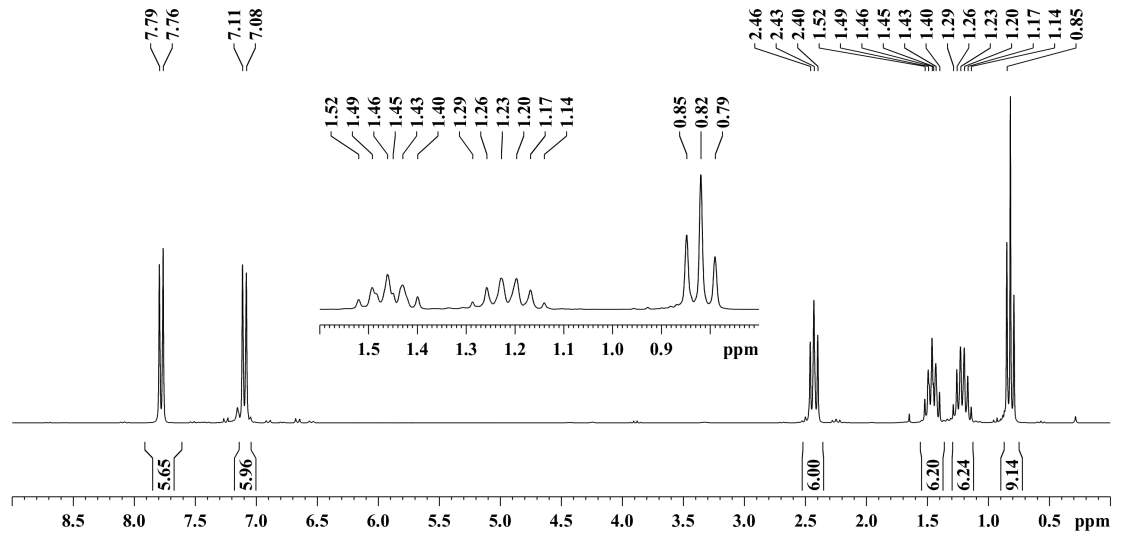
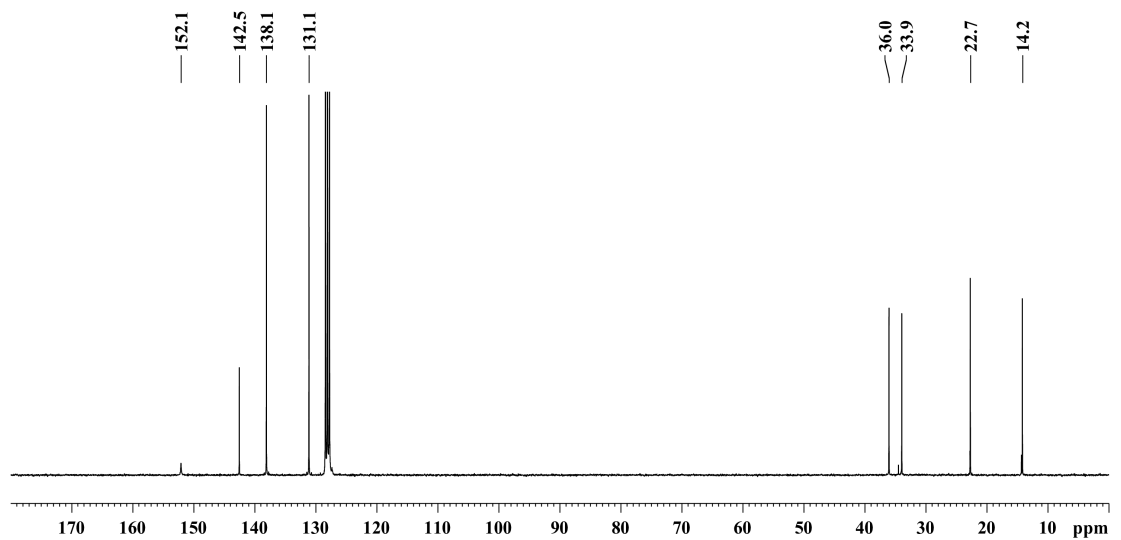
¹H NMR (300 MHz, C₆D₆): δ = 0.83 (t, ³J_{H-H} = 7.3, 9H, CH₃), 1.23 (m, ³J_{H-H} = 7.4, 6H, CH₂CH₃), 1.49 (m, ³J_{H-H} = 7.5, 6H, CH₂CH₂CH₃), 2.46 (t, ³J_{H-H} = 7.6, 6H, CH₂CH₂CH₂CH₃), 3.43 (s, N(CH₃)₂), 7.26 (d, ³J_{H-H} = 7.9, 4H, *m*-CH), 7.91 (d, ³J_{H-H} = 7.9, 4H, *m*-CH). ¹³C{¹H} NMR (75 MHz, C₆D₆): 14.2, 22.7, 33.9, 36.1, 48.0, 131.2, 136.9, 143.1, 165.9.

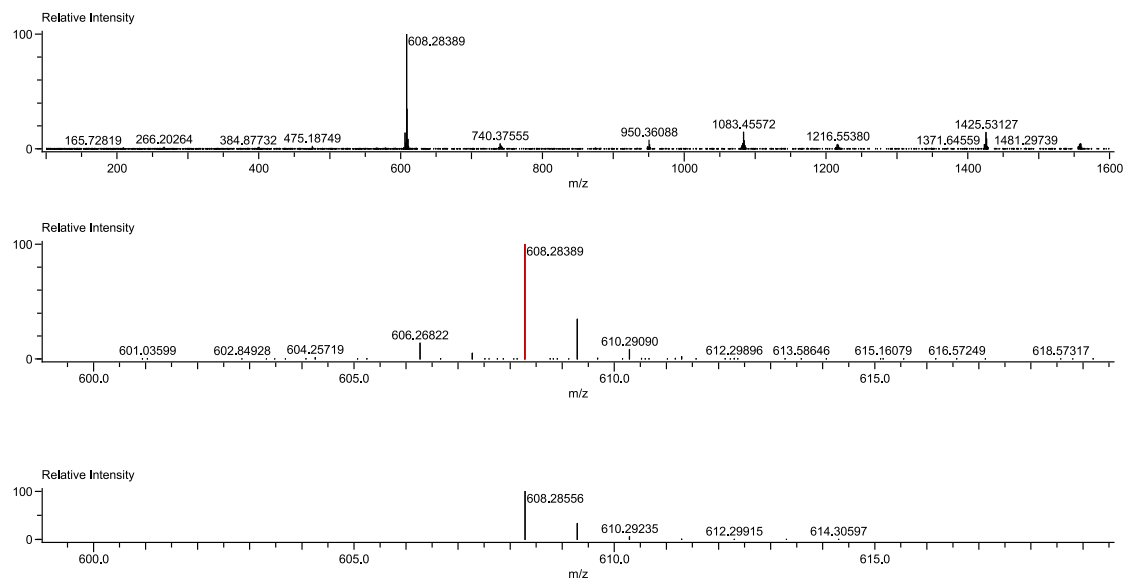
Allgemeine Synthese zur Darstellung von Me₂BiEtBu₂ (E = P, As): Me₂BiCl wurde in Diethylether suspendiert und auf -78 °C gekühlt, woraufhin festes LiEtBu₂ (E = P, As) portionsweise zugegeben wurde. Nach Erwärmen auf Raumtemperatur über 5 h wurden flüchtige Bestandteile unter vermindertem Druck entfernt und es wurden 20 ml *n*Pentan zum Rückstand gegeben. Feste Bestandteile wurden mittels Filtration abgetrennt und flüchtige Bestandteile unter vermindertem Druck entfernt. Nach anschließender Destillation bei 60 °C unter dynamischem Feinvakuum (<1·10⁻³ mbar) werden die Verbindungen Me₂BiEtBu₂ (E = P, As) in Form gelber Flüssigkeiten erhalten.

Me₂BiPtBu₂: Ausbeute: 15 %. ¹H NMR (300 MHz, C₆D₆): δ = 1.25 (d, ³J_{P-H} = 10.4, 18H, PC(CH₃)₃), 1.34 (d, ³J_{P-H} = 3.9, 6H, BiCH₃) ¹³C{¹H} NMR (75 MHz, C₆D₆): -4.9 (br, BiCH₃), 33.7 (d, ²J_{P-C} = 12.7, PC(CH₃)₃), 34.0 (d, ¹J_{P-C} = 26.0, PC(CH₃)₃); ³¹P{¹H} NMR (101 MHz, C₆D₆): 61.7 (br m) HRMS: CI(+) *m/z* 385.14861 [Me₂BiPtBu₂ + H]⁺; calcd 385.14977.

Me₂BiAstBu₂: Ausbeute: 19 %. ¹H NMR (300 MHz, C₆D₆): δ = 1.31 (s, 18H, AsC(CH₃)₃), 1.37 (s, 6H, BiCH₃) ¹³C{¹H} NMR (75 MHz, C₆D₆): -8.7 (br, BiCH₃), 33.8 (s, AsC(CH₃)₃), 33.9 (s, AsC(CH₃)₃); HRMS: CI(+) *m/z* 429.09846 [Me₂BiAstBu₂ + H]⁺; calcd 429.09761.

4.3 Analytische Daten

 $(p\text{-}n\text{BuPh})_3\text{Bi}$ Abbildung 4.4: $^1\text{H-NMR}$ -Spektrum (300 MHz) von $(p\text{-}n\text{BuPh})_3\text{Bi}$ in C_6D_6 bei 25 °C.Abbildung 4.5: $^{13}\text{C-NMR}$ -Spektrum (75 MHz) von $(p\text{-}n\text{BuPh})_3\text{Bi}$ in C_6D_6 bei 25 °C.



Mass	Intensity	Relative Intensity	Calc. Mass	Mass Difference [mDa]	Mass Difference [ppm]	Possible Formula	Unsaturation Number
608.28389	89298.05	100.00	608.28556	-1.67	-2.75	$^{12}\text{C}_{30}^{1}\text{H}_{30}^{209}\text{Bi}_1$	12.0

Abbildung 4.6: HR-LIFDI(+) Massenspektrum von $(p\text{-}n\text{BuPh})_3\text{Bi}$ beobachtet als $[\text{M}]^+$. Oben: Übersichtsspektrum. Mitte: Hochaufgelöster Ausschnitt. Unten: Berechnetes Isotopenmuster.

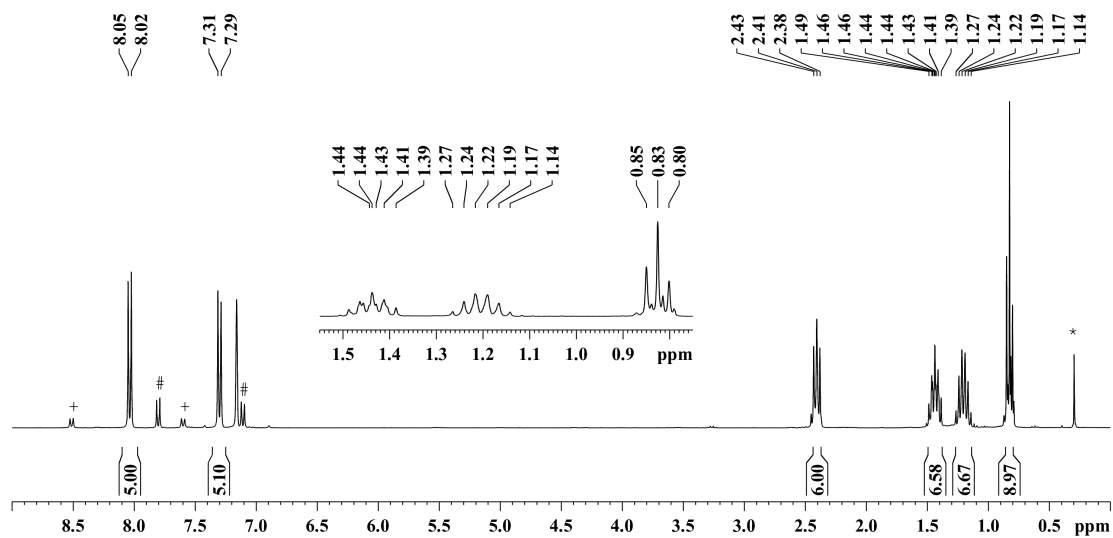
$(p\text{-}n\text{BuPh})_2\text{BiCl}$ 

Abbildung 4.7: ^1H -NMR-Spektrum (300 MHz) von $(p\text{-}n\text{BuPh})_2\text{BiCl}$ in C_6D_6 bei 25 °C. +: $(p\text{-}n\text{BuPh})_3\text{Bi}$; #: $(p\text{-}n\text{BuPh})\text{BiCl}_2$; *: Silikonschliffett.

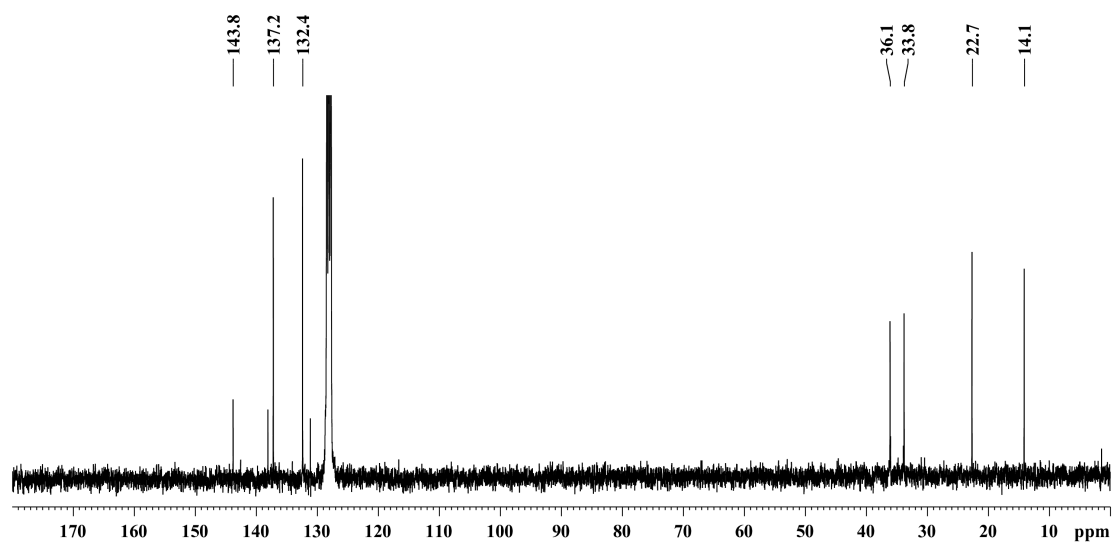


Abbildung 4.8: ^{13}C -NMR-Spektrum (75 MHz) von $(p\text{-}n\text{BuPh})_2\text{BiCl}$ in C_6D_6 bei 25 °C.

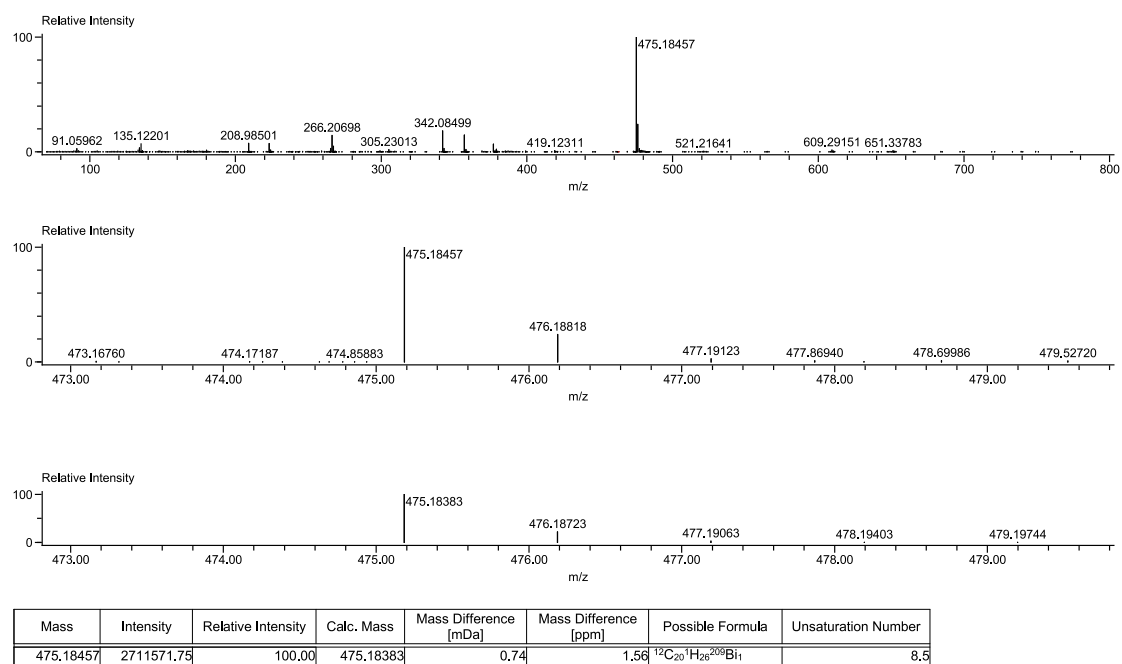


Abbildung 4.9: HR-Cl(+)-Massenspektrum von $(p\text{-}n\text{BuPh})_2\text{BiCl}$, wobei $[\text{M} - \text{Cl}]^+$ als größtes Fragment identifiziert wurde. Oben: Übersichtsspektrum. Mitte: Hochaufgelöster Ausschnitt. Unten: Berechnetes Isotopenmuster.

Tabelle 2: Ausgewählte kristallographische Daten der Strukturverfeinerung von $(p\text{-}n\text{BuPh})_2\text{BiCl}$.

Empirische Formel	$\text{C}_{20}\text{H}_{26}\text{BiCl}$	Strahlung	Mo $\text{K}\alpha$
Molmasse	510.84		($\lambda = 0.71073$)
Kristallfarbe, Habitus	farblos, Nadeln	2Θ Reichweite bei	5.22 bis
Temperatur [K]	100 K	der Datensammlung	58.948
Kristallsystem	monoklin	Gesammelte Reflexe	16656
Raumgruppe	$P2_1/c$	Unabhängige Reflexe	16656,
a [Å]	13.799(7)		[$R_{\text{int}} = 0.0511$,
b [Å]	9.099(2)		$R_{\text{sigma}} = 0.1458$]
c [Å]	15.467(5)	Daten/Restrain/ Parameter	16656/0/202
α [°]	90	Goodness-of-fit zu F^2	0.871
β [°]	101.30(4)	R Indices [Alle Daten]	$R_1 = 0.1428$,
γ [°]	90		$wR_2 = 0.1181$
Volumen [Å ³]	1904.3(13)	R Indices [$I \geq 2\sigma$]	$R_1 = 0.0492$,
Z	4		$wR_2 = 0.0944$
ρ_{calc} [g·cm ³]	1.782	Größte peak-hole	3.96/-2.54
μ [mm ⁻¹]	9.394	Differenz e Å ⁻³	
F(000)	984.0	Kommentar	verfeinert als
Kristallradius (equiv) [mm]	0.0427		nicht-merohedri-
Diffraktormeter	Stoe IPDS 2T		scher Zwilling

$(p\text{-}n\text{BuPh})_2\text{BiNMe}_2$

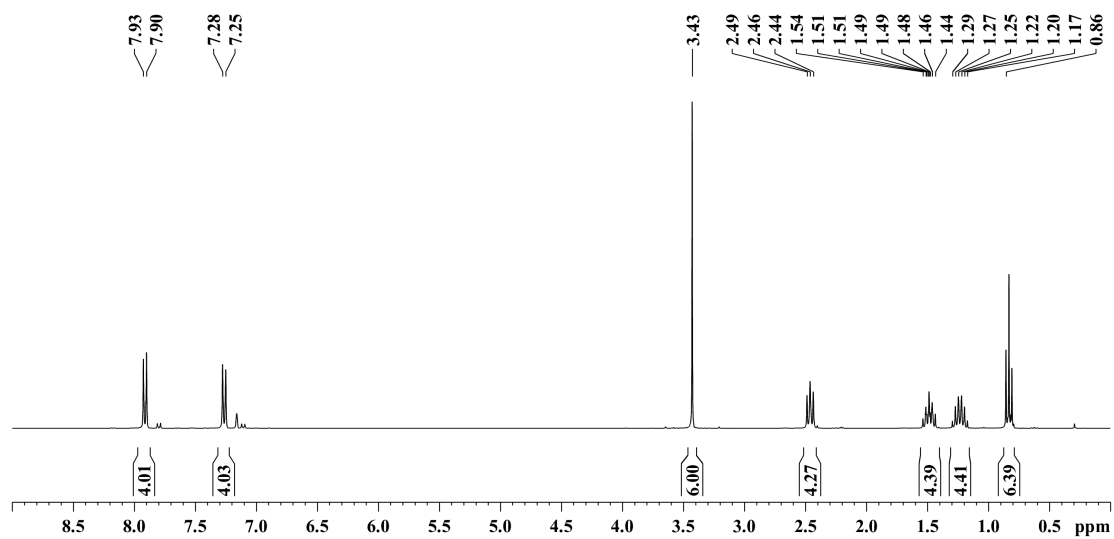


Abbildung 4.10: ^1H -NMR-Spektrum (300 MHz) von $(p\text{-}n\text{BuPh})_2\text{BiNMe}_2$ in C_6D_6 bei 25 °C.

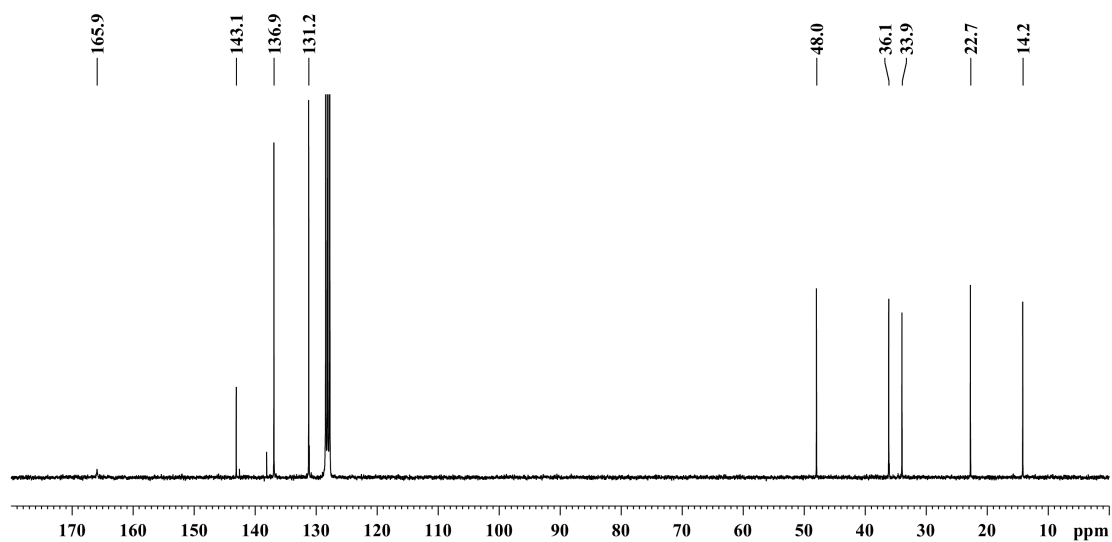
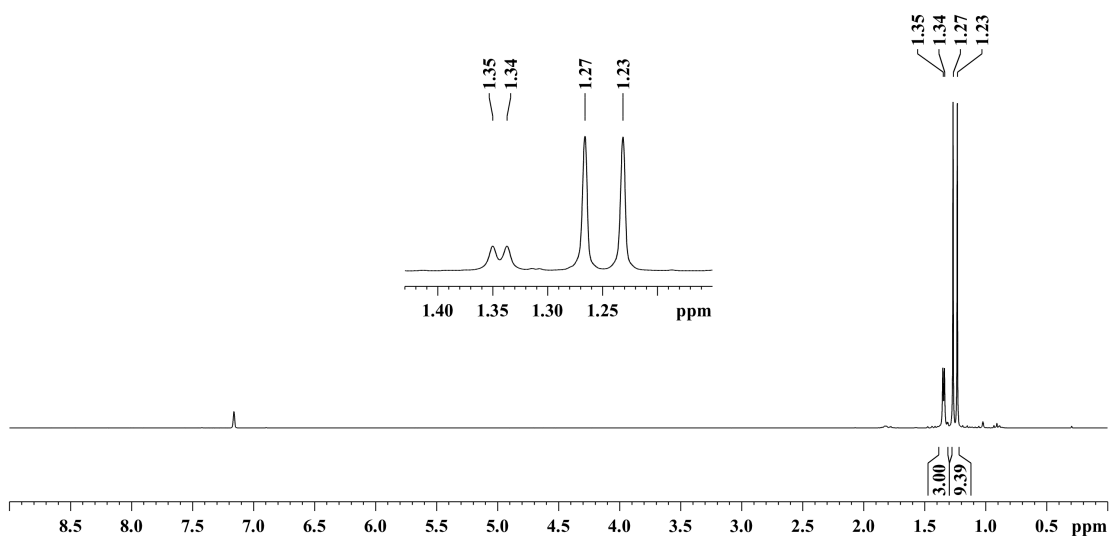
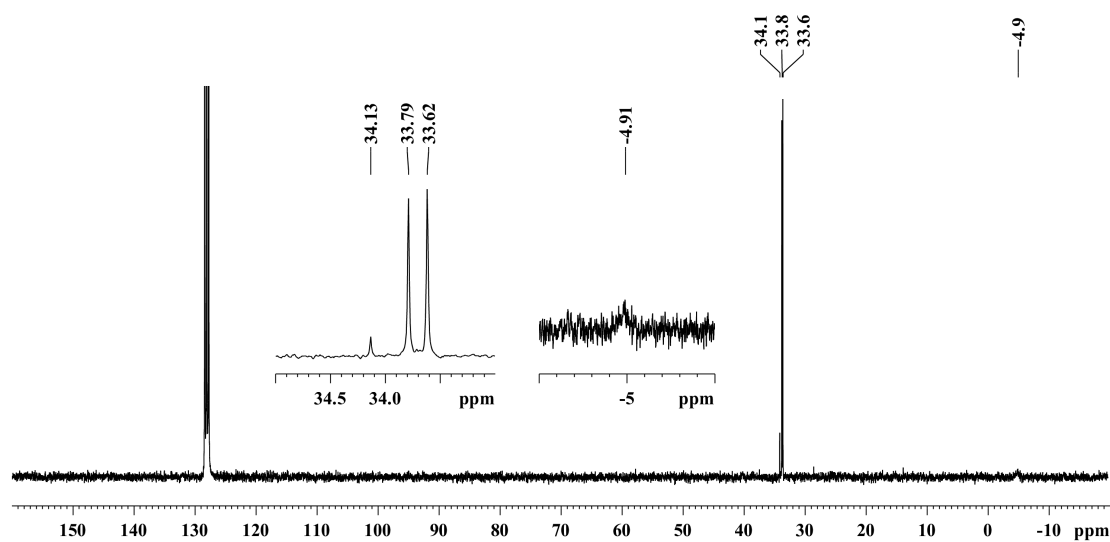


Abbildung 4.11: ^{13}C -NMR-Spektrum (75 MHz) von $(p\text{-}n\text{BuPh})_2\text{BiNMe}_2$ in C_6D_6 bei 25 °C.

Me₂BiPtBu₂Abbildung 4.12: ¹H-NMR-Spektrum (300 MHz) von Me₂BiPtBu₂ in C₆D₆ bei 25 °C.Abbildung 4.13: ¹³C-NMR-Spektrum (75 MHz) von Me₂BiPtBu₂ in C₆D₆ bei 25 °C.

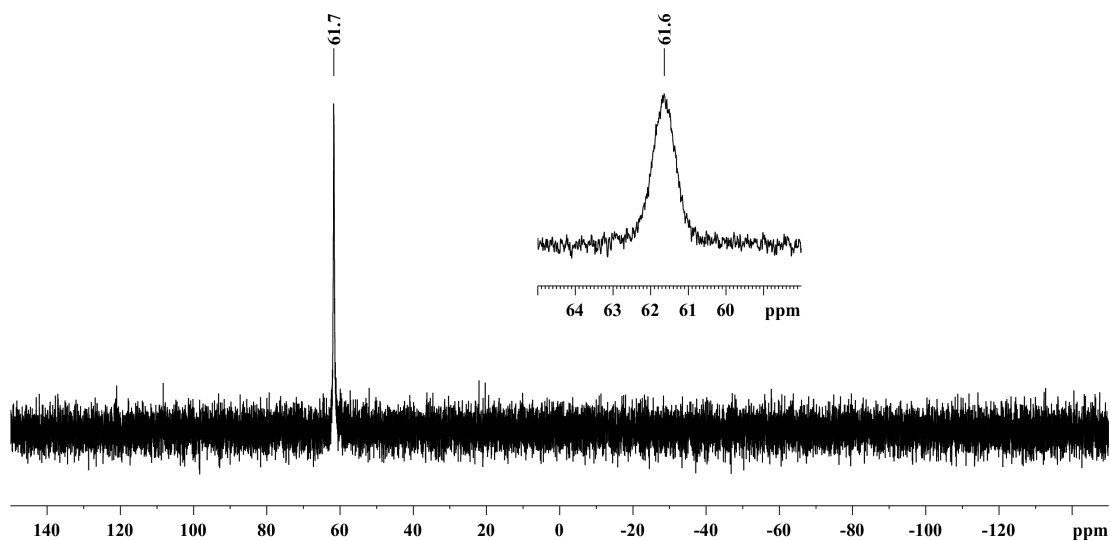
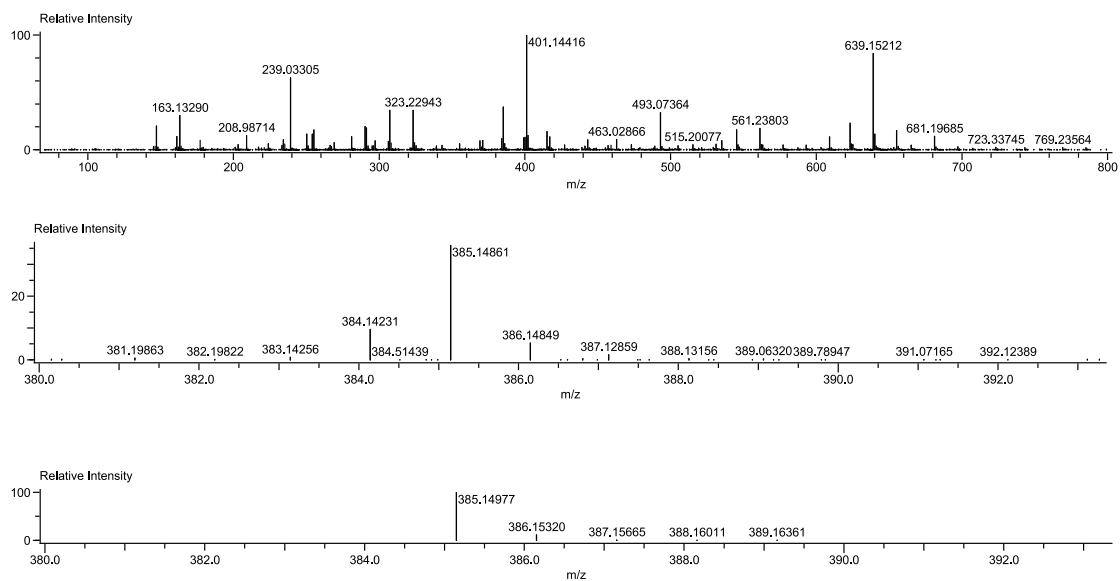
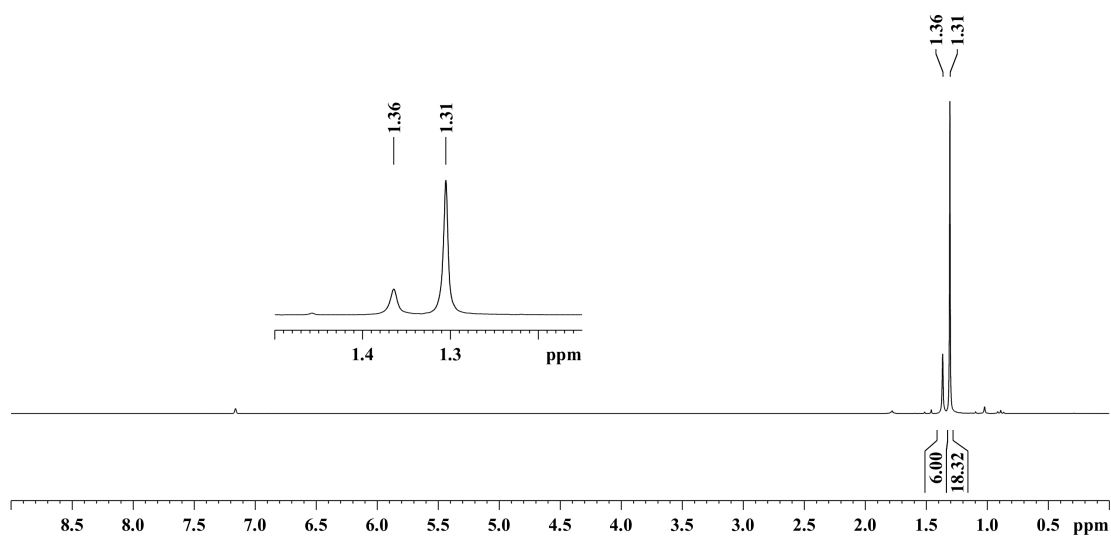
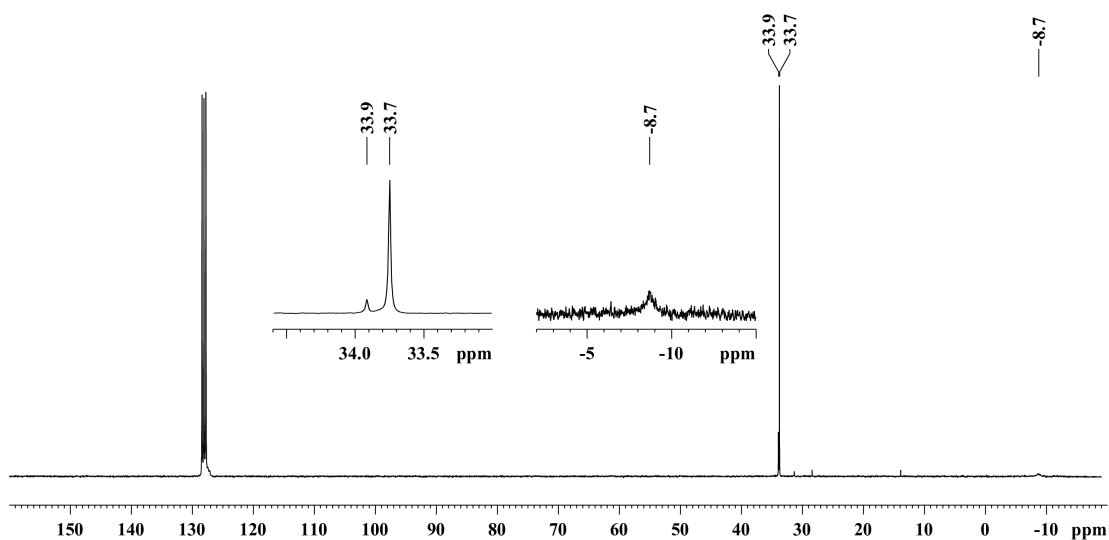


Abbildung 4.14: ^{31}P -NMR-Spektrum (75 MHz) von $\text{Me}_2\text{BiPtBu}_2$ in C_6D_6 bei 25 °C.



Mass	Intensity	Relative Intensity	Calc. Mass	Mass Difference [mDa]	Mass Difference [ppm]	Possible Formula	Unsaturation Number
385.14861	882863.50	37.16	385.14977	-1.16	-3.01	$^{12}\text{C}_{10}\text{H}_{25}^{209}\text{Bi}^{31}\text{P}_1$	0.5

Abbildung 4.15: HR-ESI(+)-Massenspektrum von $\text{Me}_2\text{BiPtBu}_2$ beobachtet als $[\text{M} + \text{H}]^+$. Oben: Übersichtsspektrum. Mitte: Hochaufgelöster Ausschnitt. Unten: Berechnetes Isotopenmuster.

Me₂BiAstBu₂**Abbildung 4.16:** ¹H-NMR-Spektrum (300 MHz) von Me₂BiAstBu₂ in C₆D₆ bei 25 °C.**Abbildung 4.17:** ¹³C-NMR-Spektrum (75 MHz) von Me₂BiAstBu₂ in C₆D₆ bei 25 °C.

4 Unveröffentlichte Ergebnisse

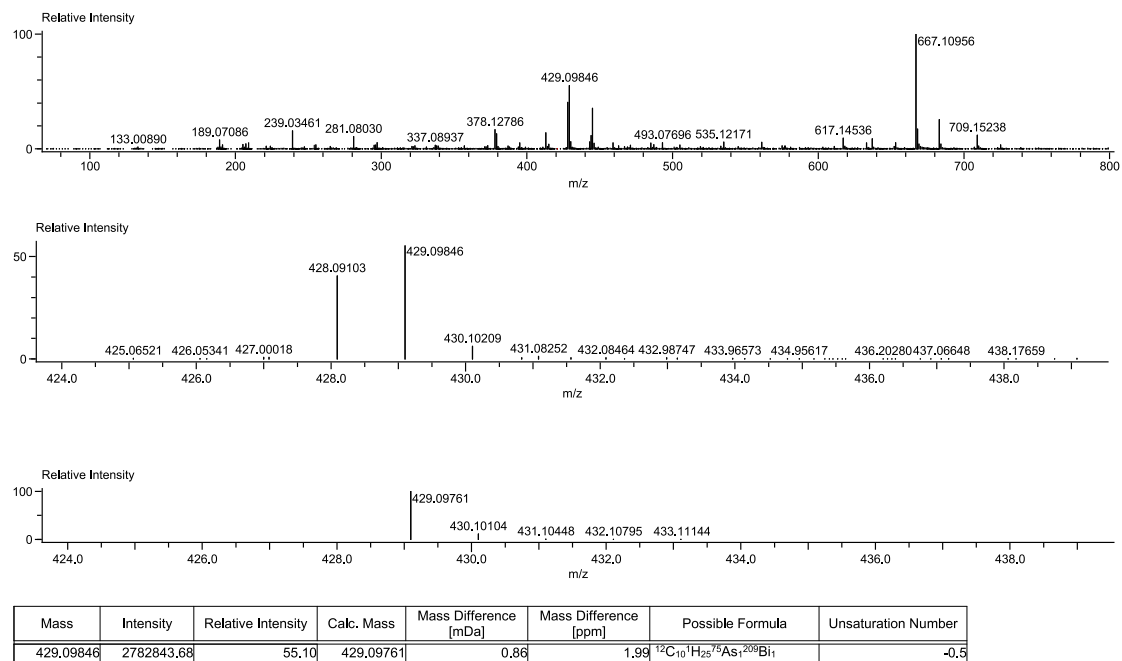


Abbildung 4.18: HR-CI(+) Massenspektrum von $\text{Me}_2\text{BiAstBu}_2$ beobachtet als $[\text{M} + \text{H}]^+$. Oben: Übersichtsspektrum. Mitte: Hochaufgelöster Ausschnitt. Unten: Berechnetes Isotopenmuster.

5 Zusammenfassung

Ziel der vorliegenden Dissertation war die Darstellung neuer Interpnictogenverbindungen mit terminalen Diarylbismut-Einheiten. Die Darstellung erfolgte aus Verbindungen der Form Ar_2BiX ($\text{X} = \text{F}, \text{Cl}, \text{Br}$), wobei als Aromaten Phenyl-, Mesityl- und 2,6-Di-*iso*-propylphenyl-Substituenten eingesetzt wurden, um den Einfluss des sterischen Anspruchs auf die Stabilität der Verbindungen zu untersuchen. Arylhalidobismutane mit Phenyl- und Mesityl-Substituenten sind weitestgehend in der Literatur beschrieben.^[118,294,295] Dagegen wurde der Dipp-Substituent im Rahmen dieser Arbeit in die Bismut-Chemie eingeführt. Die Ergebnisse dieser Arbeit werden im Folgenden deshalb in zwei Kapitel unterteilt. Zunächst wird über die Einführung des Dipp-Substituenten in die Bismut-Chemie berichtet, anschließend über den Aufbau neuer bismuthaltiger Interpnictogenverbindungen.

5.1 Einführung des Dipp-Substituenten in die Bismut-Chemie

Ein Ziel der Arbeit war die Einführung des Dipp-Substituenten in die Bismut-Chemie. Dabei wurde die Darstellung und Struktur im Festkörper von Verbindungen der Form $\text{Dipp}_n\text{BiX}_{3-n}$ ausführlich untersucht ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}, \text{OTf}, \text{SbF}_6$; $n = 1-3$). Durch Umsetzung von zwei Äquivalenten des *Grignard*-Reagenz $\text{DippMgBr} \cdot \text{THF}$ mit BiCl_3 in THF wurde dabei zunächst Dipp_2BiBr erhalten.

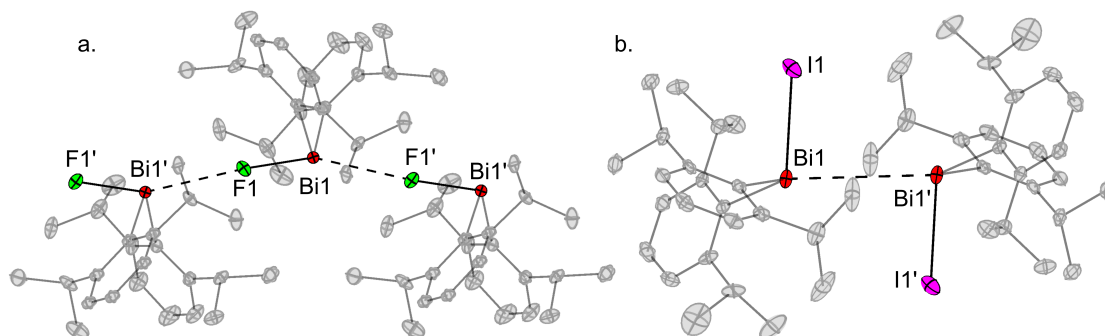


Abbildung 5.1: Molekülstrukturen von Dipp_2BiF (a.) und Dipp_2BiI (b.) im Festkörper. Wasserstoffatome sind aus Gründen der Übersichtlichkeit nicht dargestellt. Moleküle die zu mit Apotrop markierten Atomen gehören wurden symmetriegeneriert. Die Schwingungsellipsoide sind mit 50 % Aufenthaltswahrscheinlichkeit gezeigt.

Ausgehend vom Dipp_2BiBr konnte Dipp_2BiI (Abbildung 5.1 b.) mittels Halogenidenaustausch durch Reaktion mit CaI_2 gewonnen werden. Die entsprechenden Halidobismutane des Fluors und Chlors waren hingegen so nicht zugänglich. Hierfür musste zunächst mit $\text{Dipp}_2\text{BiOTf}$ ein geeignetes Zwischenprodukt dargestellt werden. Dieses wurde durch Umsatz von Dipp_2BiBr und AgOTf dargestellt. Triebkraft für die Reaktion ist dabei die Bildung des schwer löslichen AgBr . Aus $\text{Dipp}_2\text{BiOTf}$ und NaF , beziehungsweise NaCl , konnten im Anschluss Dipp_2BiF (Abbildung 5.1 a.) und Dipp_2BiCl dargestellt werden. Alternativ konnte Dipp_2BiF auch aus der Reaktion von Dipp_2BiI und AgF erhalten werden, was jedoch eine etwas schlechtere Ausbeute lieferte. Alle erwähnten Verbindungen konnten in reiner Form isoliert und mittels NMR-Spektroskopie, IR-Spektroskopie, Massenspektrometrie und Einkristallstrukturanalyse charakterisiert werden. Eine Übersicht zur Synthese der Diarylhalidobismutane ist in Abbildung 5.2 gegeben.

Anhand der erhaltenen Verbindungen konnten einige Trends für die Dipp -substituierten Halidobismutane herausgearbeitet werden. So unterscheiden sich diese zum Beispiel bei der Aggregation im Festkörper. Im Falle des leichtesten Halogens Fluor werden im Festkörper eindimensionale Stränge mit alternierenden Bi- und F-Atomen gebildet. Durch sekundäre Wechselwirkungen ist der intermolekulare Bi-F-Abstand deutlich kleiner als die Summe der *van der Waals*-Radien von Bi und F.^[296,297] Für die schwereren Halogene Cl und Br bildet sich ein kleineres Aggregat, genauer Hexamere aus. Der intermolekulare Bi-X-Abstand ist nun allerdings sehr nah an der Summe der *van der Waals*-Radien,^[296,297] was auf schwache Wechselwirkungen schließen lässt. Das Dipp_2BiI dagegen zeigt keine

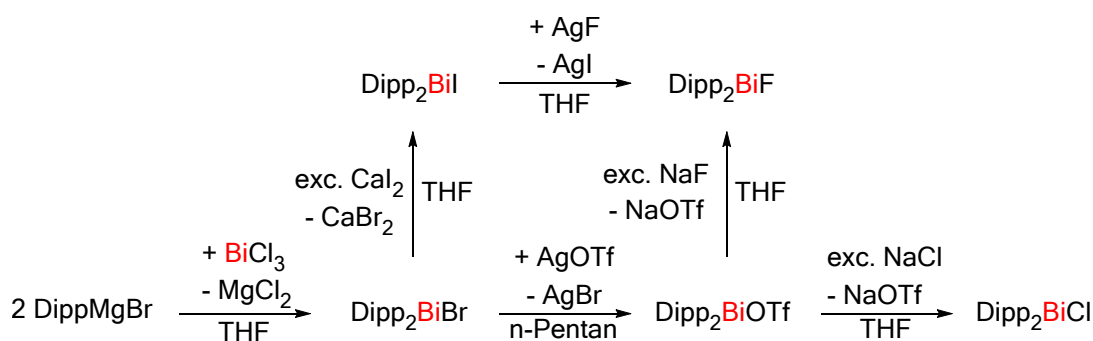


Abbildung 5.2: Reaktionsschema zur Darstellung von Dipp_2BiBr und Folgeumsetzungen zu den Verbindungen der Form Dipp_2BiX ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}, \text{OTf}$).

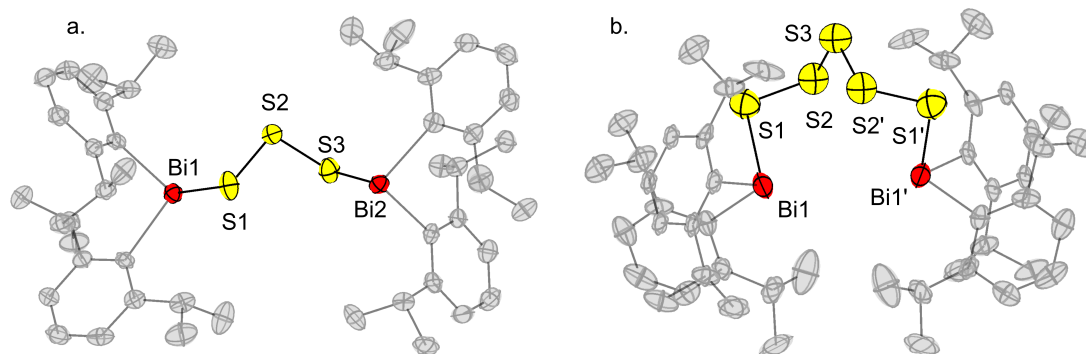


Abbildung 5.3: Molekülstrukturen von $(\text{Dipp}_2\text{Bi})_2\text{S}_3$ (a.) und $(\text{Dipp}_2\text{Bi})_2\text{S}_5$ (b.) im Festkörper. Wasserstoffatome sind aus Gründen der Übersichtlichkeit nicht dargestellt. Mit Apostroph markierte Atomen wurden symmetriegeneriert. Die Schwingungsellipsoide sind mit 50 % Aufenthaltswahrscheinlichkeit gezeichnet.

sekundären Bi-I-Wechselwirkungen. Stattdessen werden Dimere gebildet, die kurze Bi-Bi-Abstände zeigen, was auf disperse Bi-Bi-Wechselwirkungen hinweist. Ein weiterer interessanter Trend zeigt sich in der chemischen Verschiebung des *ipso*-C-Atoms im ^{13}C -NMR-Spektrum. Diese ist stark von der Elektronegativität des gebundenen (Pseudo-)Halogenids abhängig. Wird für $\text{X} = \text{I}$ noch ein Signal bei 174.5 ppm beobachtet, so ist es im Falle von $\text{X} = \text{F}$ zu einem Wert von 191.1 ppm verschoben. Für $\text{X} = \text{OTf}$ ist das Signal sogar bis auf 207.6 ppm verschoben.

Es wurde außerdem die Reaktivität von Dipp_2BiBr untersucht. Mit MeLi wird wie erwartet Dipp_2BiMe gebildet. Durch Umsetzung mit $\text{Li}[\text{BHET}_3]$, einem Hydrierungsreagenz, wird unter Freisetzung von H_2 das Dibismutan Dipp_4Bi_2 gebildet.

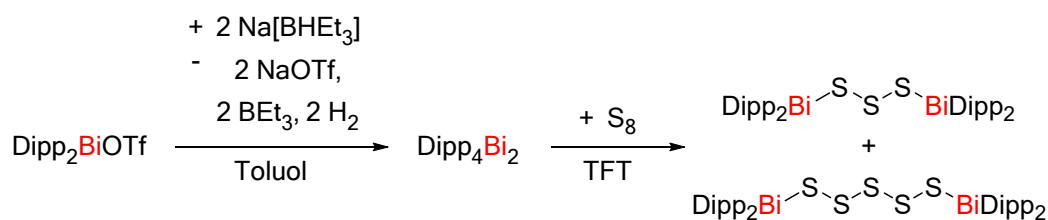


Abbildung 5.4: Reaktionsschema zur Darstellung von Dipp_4Bi_2 und Folgeumsetzung mit elementarem Schwefel.

Wie für Dibismutane üblich ist Dipp_4Bi_2 in der Lage Ch-Ch-Bindungen zu aktivieren. So konnten nach Reaktion mit elementarem Schwefel zwei Verbindungen der Reaktionsmischung als $(\text{Dipp}_2\text{Bi})_2\text{S}_3$ und $(\text{Dipp}_2\text{Bi})_2\text{S}_5$ identifiziert werden (Abbildung 5.3 und 5.4).

Für viele bismuthaltige Zielverbindungen finden Bismutane der Form R_3Bi als Edukte Verwendung. Im Falle von $\text{R} = \text{Dipp}$ wurde deshalb auch die Synthese von Dipp_3Bi untersucht. Durch Umsatz von Dipp_2BiBr , $\text{DippMgBr} \cdot \text{THF}$ und einem Äquivalent CuCl in THF konnte nach zweitägigem Rühren unter Rückfluss Dipp_3Bi erhalten werden (Abbildung 5.6 a.). Der hohe sterische Anspruch der drei Dipp -Substituenten wird dabei zum Beispiel durch die eingeschränkte Drehbarkeit um die Bi-C-Bindung erkennbar. Mittels *line-shape-Analyse* konnte durch temperaturabhängige ^{13}C -NMR-Spektroskopie die Aktivierungsenergie für die Rotation um die Bi-C-Bindung berechnet werden ($E_A = 62(3) \text{ kJ} \cdot \text{mol}^{-1}$). Durch Umsetzung des Dipp_3Bi mit zwei äquivalenten BiCl_3 wurde im Anschluss DippBiCl_2 erfolgreich dargestellt. Die Verbindungen kann Donor-Akzeptor-Komplexe mit dem π -System von Aromaten ausbilden, wobei sich, bei Kristallisation aus Benzol bei 5°C , ein Dimer des $\text{DippBiCl}_2 \cdot \text{C}_6\text{H}_6$ -Addukt im Festkörper bildet (Abbildung 5.6 b.). DippBiBr_2 war durch Umsetzung von Dipp_2BiBr und BiBr_3 zugänglich. Das DippBiBr_2 bildet eindimensionale Stränge im Festkörper, wobei die beiden Br-Atome und der Dipp -Substituent verbrückend wirken, sodass jedes Bi-Atom verzerrt oktaedrisch umgeben ist. Analog zur Darstellung des Dipp_2BiI wurde für die Darstellung des DippBiI_2 eine Halogenidionenaustausch-Reaktion untersucht.

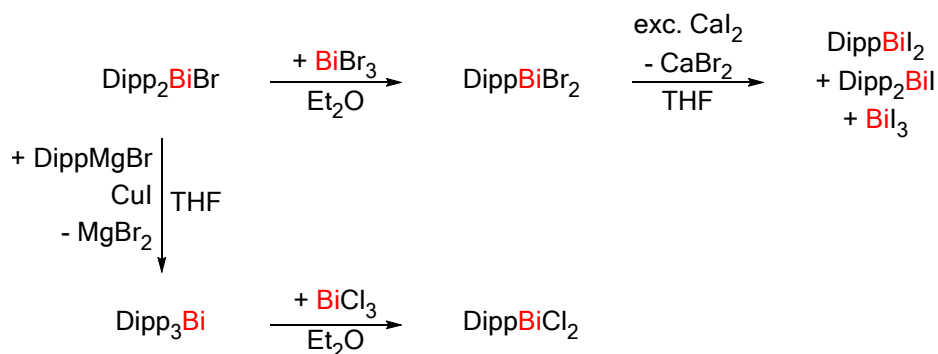


Abbildung 5.5: Reaktionsschema zur Umsetzung von Dipp_2BiBr zu Dipp_3Bi und Folgeumsetzungen zu den Verbindungen der Form DippBiX_2 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$).

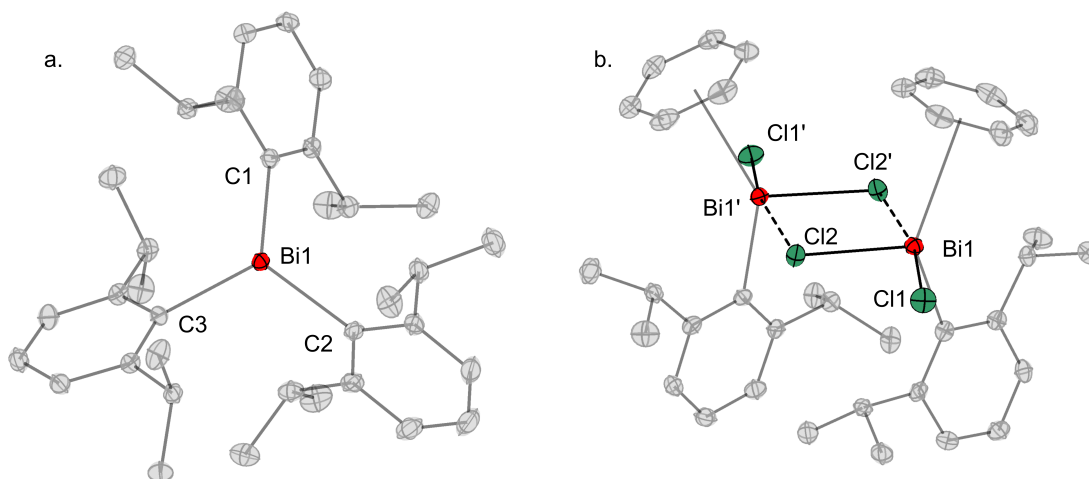


Abbildung 5.6: Molekülstrukturen von Dipp_3Bi (a.) und dem Dimer des $\text{DippBiCl}_2 \cdot \text{C}_6\text{H}_6$ (b.) im Festkörper. Wasserstoffatome sind aus Gründen der Übersichtlichkeit nicht dargestellt. Moleküle die zu mit Apostroph markierten Atomen gehören wurden symmetriegeneriert. Die Schwingungsellipsoide sind mit 50 % Aufenthaltswahrscheinlichkeit gezeigt.

Leider war es nicht möglich die Zielverbindung in reiner Form zu erhalten, da als Nebenprodukt immer Dipp_2BiI , welches nicht abgetrennt werden konnte, gebildet wird. Trotzdem konnten Einkristalle von DippBiI_2 erhalten und die Struktur im Festkörper aufgeklärt werden. Hier bilden sich Dimere mit kurzen intermolekularen Bi-I-Abständen, die wiederum einen eindimensionalen Strang bilden, in dem längere Bi-I-Abstände zwischen den Dimeren beobachtet werden. Auch das DippBiBr_2 wurde mit MeLi umgesetzt. Hierbei wurde nicht nur die Bildung von DippBiMe_2 beobachtet, sondern auch die Bildung von Dipp_2BiMe und BiMe_3 , was die besondere Stabilität der Diarylbismut-Einheit herausstellt.

Nachdem mit dem Triflat-Anion ein schwach gebundener Substituent an das Diarylbismut-Fragment koordiniert werden konnte, sollte nun das freie Dipp-substituierte Bismutenium-Kation, $[\text{Dipp}_2\text{Bi}]^+$, in Form einer salzartigen Verbindung dargestellt werden. Im Folgenden sollte dann die Eigenschaft des Dipp-Substituenten als Aryl-Substituent intermediärer Größe auf die *Lewis*-Acidität eines Bismutenium-Kations untersucht werden. In ersten Versuchen wurde dafür Dipp_2BiBr mit $\text{Ag}[\text{PF}_6]$ umgesetzt, wobei sich jedoch zeigte, dass das $[\text{PF}_6]^-$ -Anion nicht inert genug ist um die Verbindung $[\text{Dipp}_2\text{Bi}(\text{PF}_6)]$ zersetzungsfrei darzustellen. Als Zersetzungsprodukte konnten dabei $[\text{((Dipp}_2\text{Bi})_2\text{F)}(\text{PF}_6)]$

und Dipp_2BiF identifiziert werden. Zuletzt konnte das zumindest transient existierende $[\text{Dipp}_2\text{Bi}(\text{PF}_6)]$ durch einen Donor, OPEt_3 , abgefangen werden, wobei $[\text{Dipp}_2\text{Bi}(\text{OPEt}_3)_2(\text{PF}_6)]$ erhalten wurde.

Nachdem sich also gezeigt hatte, dass $[\text{PF}_6]^-$ kein geeignetes Anion ist, wurde mit $[\text{SbF}_6]^-$ ein stabileres Anion verwendet. Nun war es möglich durch Umsetzung von Dipp_2BiBr und $\text{Ag}[\text{SbF}_6]$ in Toluol das Toluol-Addukt $[\text{Dipp}_2\text{Bi}(\text{SbF}_6)(\text{Toluol})]$ zu erhalten (Abbildung 5.8 a.). Die Donor-freie Verbindung $[\text{Dipp}_2\text{Bi}(\text{SbF}_6)]$ konnte durch Umkristallisation aus TFT (α - α - α -Trifluorotoluol) erhalten werden. Mit dem $[\text{SbF}_6]^-$ -Anion war es des Weiteren möglich die zuvor als Zersetzungsprodukt erhaltene Verbindung $[\text{((Dipp}_2\text{Bi})_2\text{F})(\text{SbF}_6)]$ gezielt darzustellen und zu isolieren

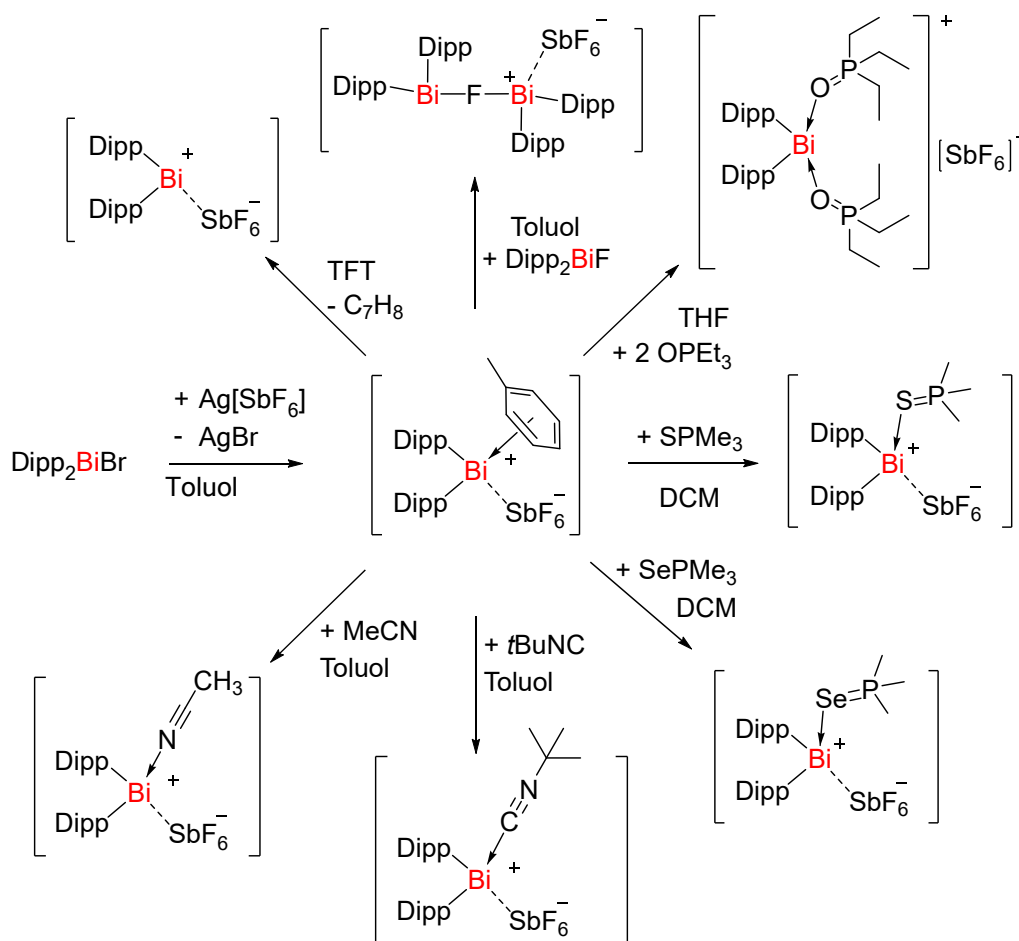


Abbildung 5.7: Reaktionsschema zur Darstellung von $[\text{Dipp}_2\text{Bi}(\text{SbF}_6)(\text{Toluol})]$ und Folgeumsetzung mit verschiedenen Donoren.

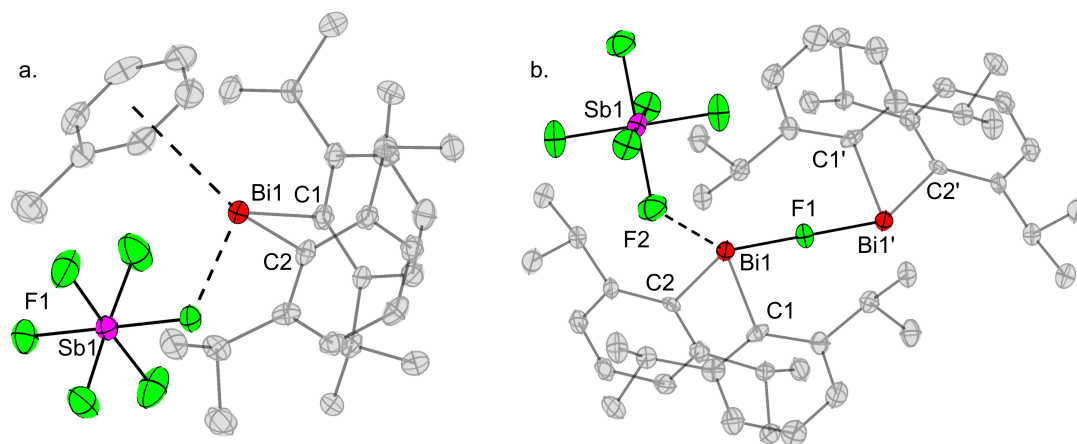


Abbildung 5.8: Molekülstrukturen von $[\text{Dipp}_2\text{Bi}(\text{SbF}_6)]$ (a.) und $[(\text{Dipp}_2\text{Bi})_2\text{F}(\text{SbF}_6)]$ (b.) im Festkörper. Wasserstoffatome sind aus Gründen der Übersichtlichkeit nicht dargestellt. Moleküle die zu mit Apostroph markierten Atomen gehören wurden symmetriegeneriert. Die Schwingungsellipsoide sind mit 50 % Aufenthaltswahrscheinlichkeit gezeigt.

(Abbildung 5.8 b.). Des Weiteren wurden Umsetzungen mit Phosphanchalkogeniden, genauer OPEt_3 , SPMe_3 und SePMe_3 , durchgeführt um die *Lewis*-Acidität der Verbindung mittels der originalen und einer modifizierten Version der *Gutmann-Beckett*-Methode zu untersuchen.^[163,168,169] In Kooperation mit der Arbeitsgruppe *Lichtenberg*, welche mit $[\text{Me}_2\text{Bi}(\text{SbF}_6)]$ arbeitet, wurde dabei die *Lewis*-Acidität in Abhängigkeit der Größe der Reste untersucht. Es zeigte sich, dass sich die *Acceptor Number* (*AN*) von $[\text{Dipp}_2\text{Bi}(\text{SbF}_6)]$ und $[\text{Me}_2\text{Bi}(\text{SbF}_6)]$ gegenüber den weichen *Lewis*-Säuren, SPMe_3 und SePMe_3 , stark ähneln. Gegenüber einem Äquivalent OPEt_3 zeigt sich dagegen eine erhöhte *Lewis*-Acidität des $[\text{Dipp}_2\text{Bi}(\text{SbF}_6)]$. Mittels DFT-Rechnungen konnte gezeigt werden, dass dies vermutlich auf die Abschirmung der anderen Seite des Bismutatoms durch die großen Dipp-Substituenten zurückzuführen ist, welche die Koordination des $[\text{SbF}_6]^-$ -Anions verhindern und damit die Bi-O-Donor-Akzeptor-Bindung stärken. Zuletzt konnten außerdem zwei Donor-Akzeptor-Komplexe mit einem Nitril (MeCN) und einem Isonitrile ($t\text{BuCN}$) dargestellt werden. Die Darstellung von $[\text{Dipp}_2\text{Bi}(\text{SbF}_6)](\text{C}_7\text{H}_8)$ und die anschließende Umsetzung mit Donoren ist schematisch in Abbildung 5.7 zusammengefasst.

5.2 Darstellung von Interpnictogenverbindungen

Als Edukte zur Darstellung von Interpnictogenverbindungen wurde stets von Verbindungen der Form Ar_2BiX ($\text{Ar} = \text{Ph}, \text{Mes}, \text{Dipp}$; $\text{X} = \text{F}, \text{Cl}, \text{Br}$) ausgegangen, wobei Dipp_2BiF und Dipp_2BiBr wie in Kapitel 5.1 beschrieben, dargestellt wurden. Zunächst wurden Interpnictogenverbindungen mit dem leichtesten Pnictogen Stickstoff und damit einer Bi-N-Bindung dargestellt. Nach Umsetzung von Ar_2BiX mit LiNMe_2 wurden Verbindungen der Form $\text{Ar}_2\text{BiNMe}_2$ ($\text{Ar} = \text{Ph}, \text{Mes}, \text{Dipp}$) erhalten. Im Festkörper bildet $\text{Ph}_2\text{BiNMe}_2$, analog zu den Diarylhalidobismutanen, eindimensionale Stränge mit alternierenden Bi- und N-Atomen. Die Bismutatome werden innerhalb der Stränge vom freien Elektronenpaar des Stickstoffs und dem π -System eines Aromaten verbrückt (Abbildung 5.9 a.). Die Verbindungen $\text{Mes}_2\text{BiNMe}_2$ und $\text{Dipp}_2\text{BiNMe}_2$ mit den sterisch anspruchsvolleren Substituenten zeigen dagegen keine intermolekularen Wechselwirkungen und bilden Monomere. Nachdem die Darstellung der Bismutanamine mit LiNMe_2 erfolgreich durchgeführt werden konnte, sollten im Anschluss Verbindungen mit Substituenten zur weiteren Funktionalisierung am Stickstoff dargestellt werden. Die Zielverbindungen haben dabei die Form $\text{Ar}_2\text{BiNH}t\text{Bu}$. Nachdem Reaktionen von Ar_2BiX und $\text{LiNH}t\text{Bu}$ nicht den gewünschten Erfolg brachten, konnten über eine alternative Route $\text{Mes}_2\text{BiNH}t\text{Bu}$ und $\text{Dipp}_2\text{BiNH}t\text{Bu}$ (Abbildung 5.9 b.) dargestellt werden. Dies gelang im Falle der Mes-substituierten Verbindung durch Reaktion von

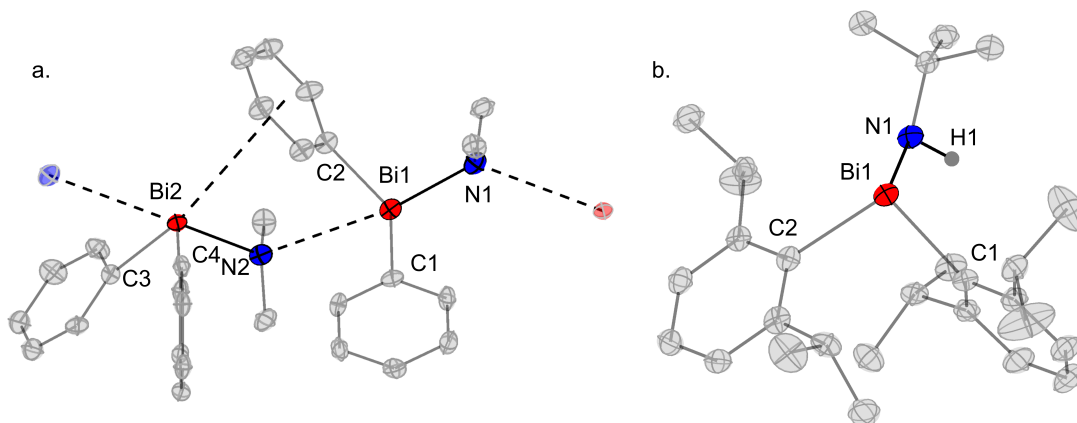


Abbildung 5.9: Molekülstrukturen von $\text{Ph}_2\text{BiNMe}_2$ (a.) und $\text{Dipp}_2\text{BiNH}t\text{Bu}$ (b.) im Festkörper. Wasserstoffatome sind aus Gründen der Übersichtlichkeit nicht dargestellt. Die Schwingungselipsoide sind mit 50 % Aufenthaltswahrscheinlichkeit gezeigt.

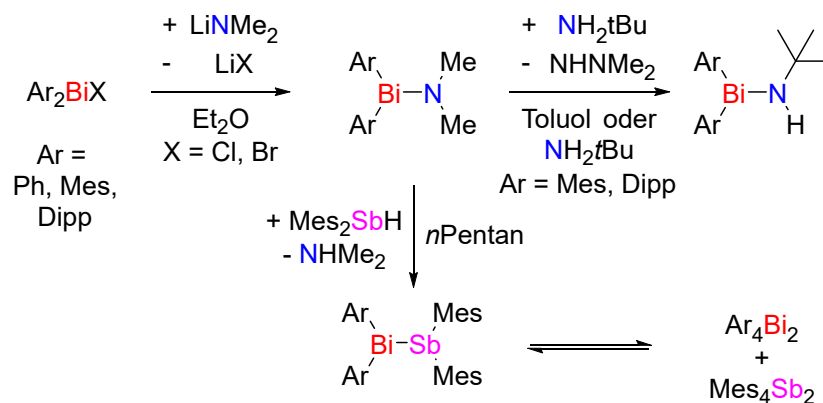


Abbildung 5.10: Reaktionsschema zur Darstellung der Bismutanamine $\text{Ar}_2\text{BiNMe}_2$ und Folgeumsetzungen mit NH_2tBu und Mes_2SbH .

$\text{Mes}_2\text{BiNMe}_2$ mit einem Überschuss NH_2tBu in Toluol. Für die Dipp-Verbindung wurde hingegen NH_2tBu selbst als Lösemittel verwendet. Ein Reaktionsschema für die Darstellung der Bismutanamine ist in Abbildung 5.10 dargestellt.

Durch Umsetzung eines Bismutanamins mit einem sekundären Stiban konnten 2020 die ersten isolierbaren Verbindungen mit einer Bi-Sb-Einfachbindung durch *Chitnis* und Mitarbeiter dargestellt werden.^[221] Unter ähnlichen Bedingungen wur-

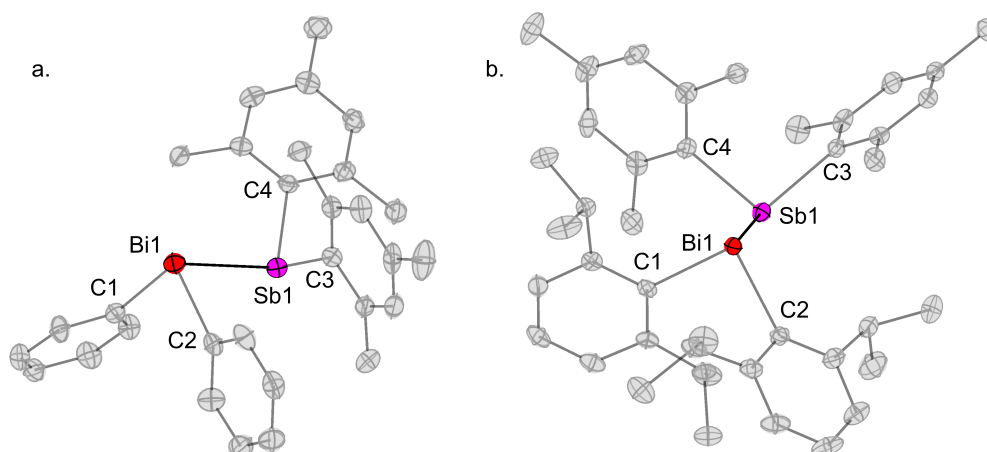


Abbildung 5.11: Molekülstrukturen von $\text{Ph}_2\text{BiSbMes}_2$ (a.) und $\text{Dipp}_2\text{BiSbMes}_2$ (b.) im Festkörper. Wasserstoffatome sind aus Gründen der Übersichtlichkeit nicht dargestellt. Die Schwingungsellipsoide sind mit 50 % Aufenthaltswahrscheinlichkeit gezeigt.

den nun die Verbindungen der Form $\text{Ar}_2\text{BiNMe}_2$ mit Mes_2SbH umgesetzt (Abbildung 5.10). Unter Abspaltung von NHMe_2 sollte so eine Bi-Sb-Bindung aufgebaut werden. In allen drei Reaktionen konnten die entstandenen Bismutanylstibane neben Ar_4Bi_2 und Mes_4Sb_2 mittels NMR-Spektroskopie nachgewiesen werden. Im Falle von $\text{Ar} = \text{Ph}$ und Dipp konnten die erhaltenen Bismutanylstibane isoliert und unter anderem mittels Röntgenstrukturanalyse untersucht werden (Abbildung 5.11). Nach Auflösen der isolierten Bismutanylstibane in C_6D_6 lässt sich erneut die Bildung von Ar_4Bi_2 und Mes_4Sb_2 beobachten, was auf ein Gleichgewicht zwischen den drei Verbindungen hindeutet. Dies konnte auch durch eine Gegenreaktion verifiziert werden, wobei nach Auflösen von Mes_4Bi_2 und Mes_4Sb_2 in Toluol- d_8 die Bildung von $\text{Mes}_2\text{BiSbMes}_2$ beobachtet wird. Die Gleichgewichtskonstanten wurden dabei zu $K_{\text{Ph}} = 76$, $K_{\text{Mes}} = 1.1$ und $K_{\text{Dipp}} = 7.8$ ermittelt. Durch temperaturabhängige NMR-Spektroskopie wurde gezeigt, dass die Lage des Gleichgewichts maßgeblich durch entropische Effekte kontrolliert ist.

Nach der erfolgreichen Darstellung einiger Bismutanamine wurden nun Verbindungen mit einer Bi-P- oder Bi-As-Einfachbindung dargestellt. Für den Aufbau einer Bi-P-Bindung wurde erneut die Salzmetathesereaktion als Ansatz gewählt, wobei nach Umsatz von Ar_2BiX mit LiPtBu_2 drei Bismutanylphosphane, nämlich $\text{Ph}_2\text{BiPtBu}_2$, $\text{Mes}_2\text{BiPtBu}_2$ und $\text{Dipp}_2\text{BiPtBu}_2$, erhalten wurden. Im Gegensatz zum $\text{Ph}_2\text{BiNMe}_2$ liegen alle Bismutanylphosphane im Festkörper als Monomere vor. Durch die Salzmetathese-Route war es erneut nicht möglich Bismutanylphos-

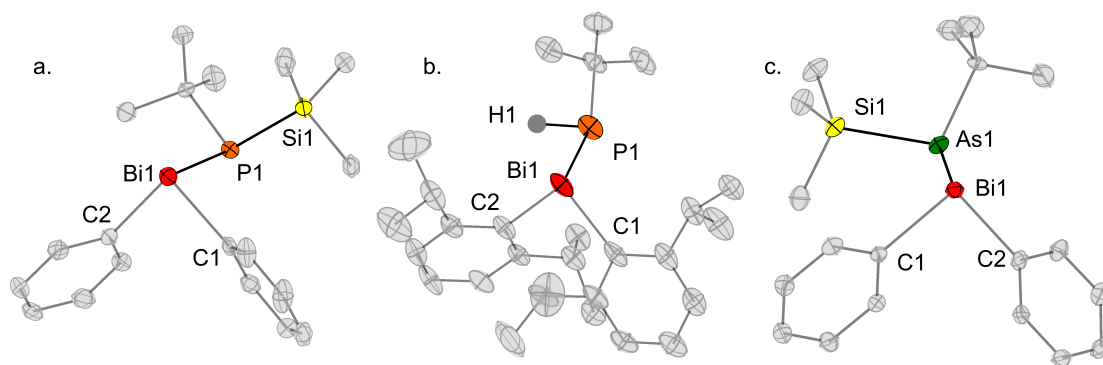


Abbildung 5.12: Molekülstrukturen von $\text{Ph}_2\text{BiPtBu}(\text{SiMe}_3)$ (a.), $\text{Dipp}_2\text{BiPtBu}$ (b.) und $\text{Ph}_2\text{BiAsPtBu}(\text{SiMe}_3)$ (c.) im Festkörper. Wasserstoffatome sind aus Gründen der Übersichtlichkeit nicht dargestellt. Die Schwingungsellipsoide sind mit 50 % Aufenthaltswahrscheinlichkeit gezeigt.

phane mit funktionellen Gruppen darzustellen, weshalb ein neuer Reaktionspfad mit sanfteren Reaktionsbedingungen untersucht wurde. Es stellte sich dabei heraus, dass eine Bi-P-Bindung *via* Trimethylsilylhalogenid-Eliminierung aufgebaut werden kann. Dabei zeigte sich, dass die Reaktion am schnellsten und selektivsten im ungewöhnlichen Lösemittel TFT von statten geht. Auf diese Weise konnten aus Ar_2BiX und $\text{PtBu}(\text{SiMe}_3)_2$ nun $\text{Ph}_2\text{BiPtBu}(\text{SiMe}_3)$ (Abbildung 5.12, a.), $\text{Mes}_2\text{BiPtBu}(\text{SiMe}_3)$ und $\text{Dipp}_2\text{BiPtBu}(\text{SiMe}_3)$, welche mit SiMe_3 eine funktionelle Gruppe enthalten, dargestellt werden. Durch Reaktion mit $\text{PHtBu}(\text{SiMe}_3)$ konnte eine weitere Verbindung, namentlich $\text{Dipp}_2\text{BiPHtBu}$ (Abbildung 5.12 b.), isoliert werden. Die Verbindung wurde unter anderem *via* Einkristallröntgendiffraktometrie und IR-Spektroskopie untersucht. Im IR-Spektrum kann eine Bande bei 2272 cm^{-1} der P-H Schwingung zugeordnet werden.

Durch analoge Reaktionsführung konnten auch einige Bismutanylarsane darge-

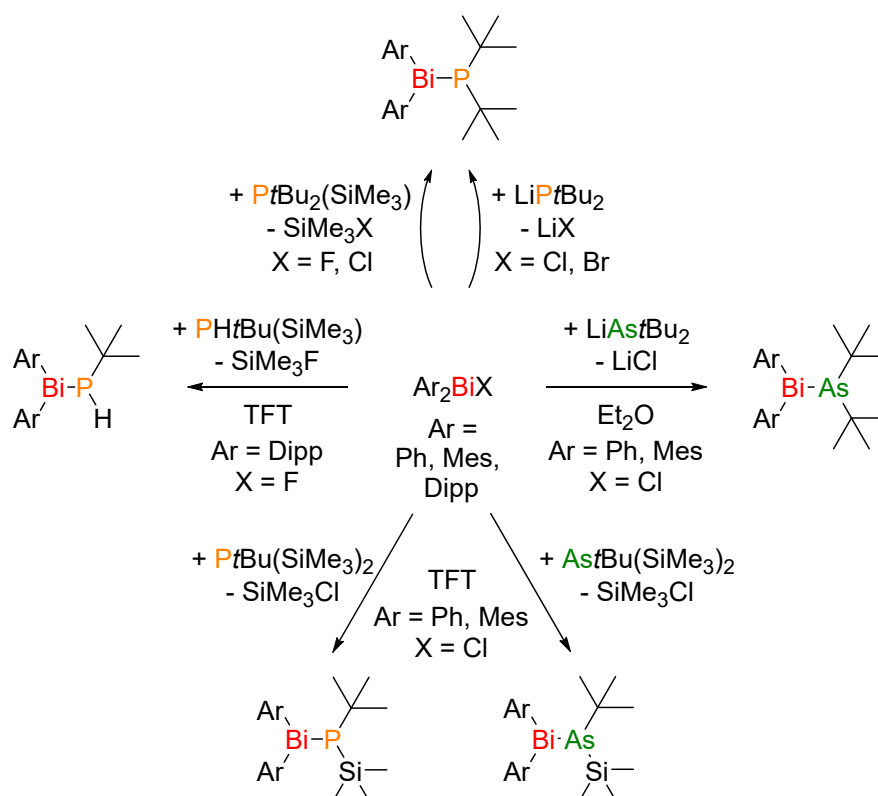


Abbildung 5.13: Reaktionsschema zur Darstellung binärer Interpnictogenverbindungen mit Bi-P- oder Bi-As-Bindung.

stellt werden. Die Diarylhalidobismutane wurden zunächst mit LiAstBu_2 umgesetzt, wobei $\text{Ph}_2\text{BiAstBu}_2$ und $\text{Mes}_2\text{BiAstBu}_2$ isoliert werden konnten. Außerdem wurden $\text{Ph}_2\text{BiAstBu}(\text{SiMe}_3)$ (Abbildung 5.12 c.) und $\text{Mes}_2\text{BiAstBu}(\text{SiMe}_3)$ mit funktionellen Silyl-Gruppen durch Umsatz von Ar_2BiCl mit $\text{AstBu}(\text{SiMe}_3)_2$ erhalten. Sowohl die Salzmetathese-Reaktion als auch die SiMe_3X Eliminierung sind also geeignet um sowohl Bi-P- als auch Bi-As-Bindungen aufzubauen.

Nachdem nun eine Bi-P- beziehungsweise Bi-As-Bindung durch die SiMe_3X Eliminierung aufgebaut werden konnte, wurden im Anschluss die Umsetzungen von $\text{Ar}_2\text{BiEtBu}(\text{SiMe}_3)$ ($\text{Ar} = \text{Ph}, \text{Mes}; \text{E} = \text{P}, \text{As}$) mit einem weiteren Äquivalent Ar_2BiX untersucht. Dabei konnte im Falle von $\text{E} = \text{P}$ das gewünschte $\text{Ph}_2\text{BiP}(t\text{Bu})\text{BiPh}_2$ (Abbildung 5.14 a.) mit einer zentralen Bi-P-Bi-Kette dargestellt werden. Die Verbindung ist labil und zersetzt sich in Lösung innerhalb von Stunden unter Verlust einer „ PtBu “-Einheit zum Tetraphenyldibismutan. Für $\text{E} = \text{As}$ konnten sowohl für den Phenyl- als auch für den Mesityl-Substituenten am Bismut Zielverbindungen mit zentraler Bi-As-Bi-Kette erhalten werden (Abbildung 5.14 b.). Ähnlich wie die Bi-P-Bi-Ketten sind auch die Verbindungen mit Bi-As-Bi-Kette labil und zersetzen sich in Lösung zum entsprechenden Dibismutan. Im Falle von $\text{Ar} = \text{Ph}$ war es hierbei möglich ein weiteres Zerset-

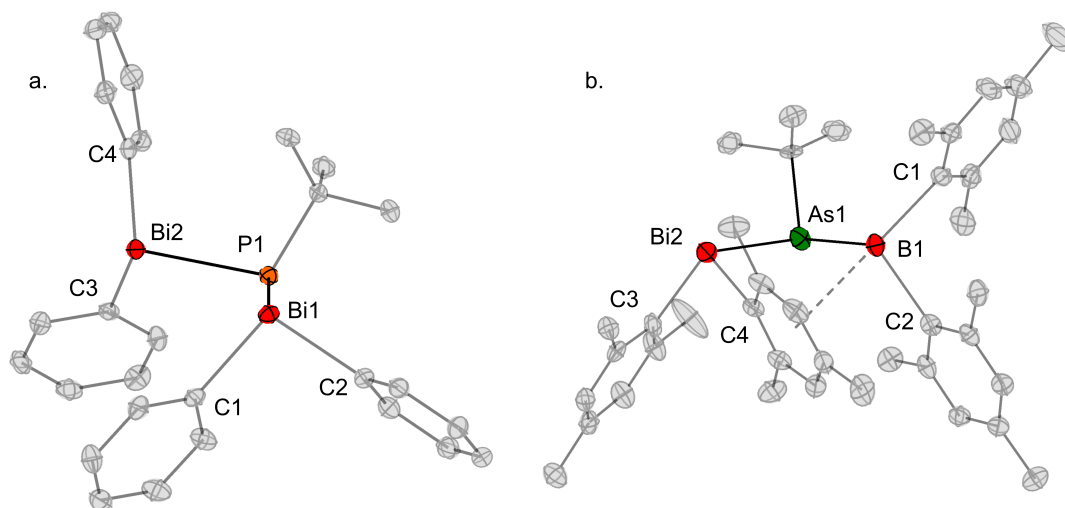


Abbildung 5.14: Molekülstrukturen von $\text{Ph}_2\text{BiP}(t\text{Bu})\text{BiPh}_2$ (a.) und $\text{Mes}_2\text{BiAs}(t\text{Bu})\text{BiMes}_2$ (b.) im Festkörper. Wasserstoffatome sind aus Gründen der Übersichtlichkeit nicht dargestellt. Die Schwingungsellipsoide sind mit 50 % Aufenthaltswahrscheinlichkeit gezeigt.

zungsprodukt *via* Röntgenstrukturanalyse zu identifizieren. Dabei handelt es sich um eine Verbindung mit zentraler Bi-As-As-Bi-Kette, welche der folgenden Summenformel entspricht: $\text{Ph}_2\text{BiAs}(t\text{Bu})\text{As}(t\text{Bu})\text{BiPh}_2$. Formal wurde in eine Bi-As-Bindung der Ausgangsverbindung ein „AstBu“-Fragment inseriert, was uns veranlasste das Potential der Dreierketten als Pnictogeniden-Übertragungsreagenzien zu untersuchen. Als Pnictogeniden-Akzeptor wurde ein sterisch wenig anspruchsvolles *N*-heterozyklisches Carben (1,3,4,5-tetramethylimidazol-2-ylidene, Me_2IME) gewählt. Bei Zugabe von Me_2IME zu einer Lösung von $\text{Ph}_2\text{BiP}(t\text{Bu})\text{BiPh}_2$ konnte schon bei der Zugabe eine intensive Rotfärbung beobachtet werden. Durch Untersuchung der Reaktionslösung *via* NMR-Spektroskopie wurde die Bildung von $\text{Me}_2\text{IME}=\text{PtBu}$ beobachtet. Auch wenn $\text{Me}_2\text{IME}=\text{PtBu}$ im Anschluss nicht isoliert werden konnte, zeigt die Reaktion, dass $\text{Ph}_2\text{BiP}(t\text{Bu})\text{BiPh}_2$ tatsächlich als Phosphiniden-Übertragungsreagenz eingesetzt werden kann. Für die Dreierketten mit dem schwereren Zentralatom Arsen war im Gegensatz dazu keine Reaktion mit Me_2IME zu beobachten. Es war also mit analoger Reaktionsführung nicht möglich ein Arseniden-Fragment zu übertragen.

Nachdem symmetrische Dreierketten durch Abstraktion von Me_3SiCl dargestellt werden konnten, wurde im Anschluss die Umsetzung mit Verbindungen der Form

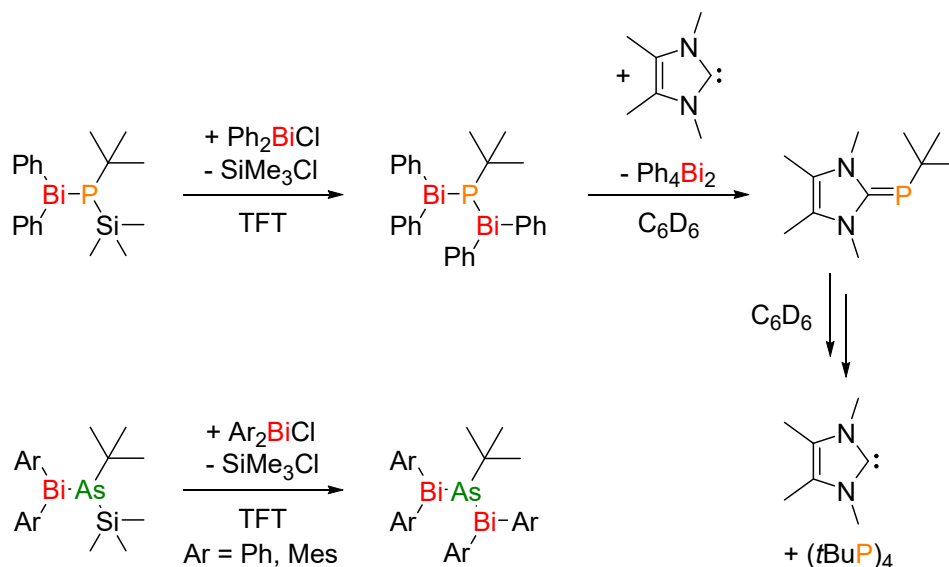


Abbildung 5.15: Reaktionsschema zur Darstellung von Interpnictogenverbindungen mit zentraler Bi-E-Bi-Kette (E = P, As) und Reaktion von $(\text{Dipp}_2\text{Bi})_2\text{PtBu}$ mit Me_2IME .

$t\text{Bu}_2\text{EX}$ ($\text{E} = \text{P}, \text{As}, \text{Sb}$; $\text{X} = \text{F}, \text{Cl}$) untersucht, um so ternäre Interpnictogenverbindungen aufzubauen. Dabei konnte jedoch in keinem Fall eine Reaktion beobachtet werden. Um dennoch ternäre Interpnictogenverbindungen zu erhalten, wurde erneut auf Salzmetathesereaktionen zurückgegriffen und die Verbindungen Ar_2BiCl ($\text{Ar} = \text{Ph}, \text{Mes}$) wurden mit $\text{LiE}^1(t\text{Bu})\text{E}^2t\text{Bu}_2$ ($\text{E}^1 = \text{P}, \text{As}$; $\text{E}^2 = \text{P}, \text{As}, \text{Sb}$) umgesetzt. Mit einem zentralen Phosphoratom wurden dabei vier Verbindungen der Form $\text{Ar}_2\text{BiP}(t\text{Bu})\text{E}^2t\text{Bu}_2$ ($\text{Ar} = \text{Ph}, \text{Mes}$; $\text{E}^2 = \text{As}, \text{Sb}$) erhalten (Abbildung 5.17 a. und b.). Im Falle des zentralen As-Atoms wurden zwei Verbindungen der Form $\text{Ar}_2\text{BiAs}(t\text{Bu})\text{PtBu}_2$ ($\text{Ar} = \text{Ph}, \text{Mes}$) erfolgreich dargestellt (Abbildung 5.17 c.). Die ternären Dreierketten sind bedeutend stabiler als die Verbindungen mit symmetrischer Bi-E-Bi-Zentraleinheit, zersetzen sich jedoch auch in Lösung innerhalb von mehreren Tagen unter Bildung definierter Zersetzungsprodukte, wobei sich die Mes-substituierten Verbindungen in allen Fällen langsamer zersetzen als die Ph-substituierten. Je nach Kettenmotiv unterscheiden sich die Zersetzungsprodukte. In den Verbindungen mit Bi-P-As- und Bi-As-P-Kette wird die Bildung eines Dibismutanes und einer $t\text{Bu}_2\text{PAs}(t\text{Bu})\text{As}(t\text{Bu})\text{PtBu}_2$ beziehungsweise einer $t\text{Bu}_2\text{AsP}(t\text{Bu})\text{P}(t\text{Bu})\text{As}t\text{Bu}_2$ -Kettenverbindung beobachtet. Dies deutet auf eine homolytische Spaltung der Bi-E-Bindung mit anschließender Rekombination

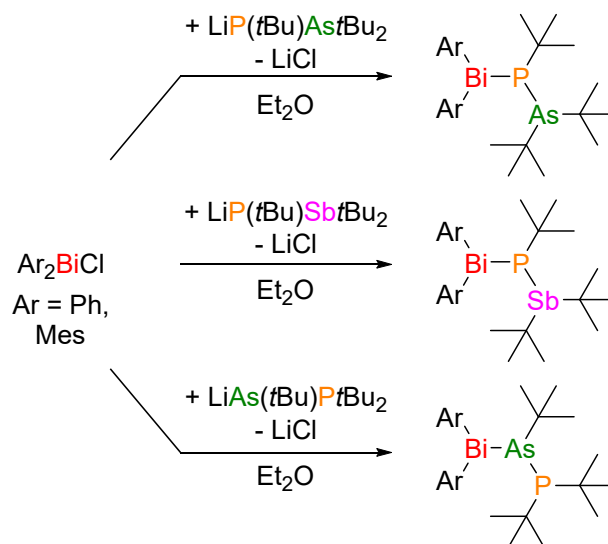


Abbildung 5.16: Reaktionsschema zur Darstellung ternärer bismuthaltiger Interpnictogenverbindungen aus Ar_2BiCl ($\text{Ar} = \text{Ph}, \text{Mes}$) und $\text{LiE}^1(t\text{Bu})\text{E}^2t\text{Bu}_2$ ($\text{E}^1 = \text{P}, \text{As}$; $\text{E}^2 = \text{P}, \text{As}, \text{Sb}$).

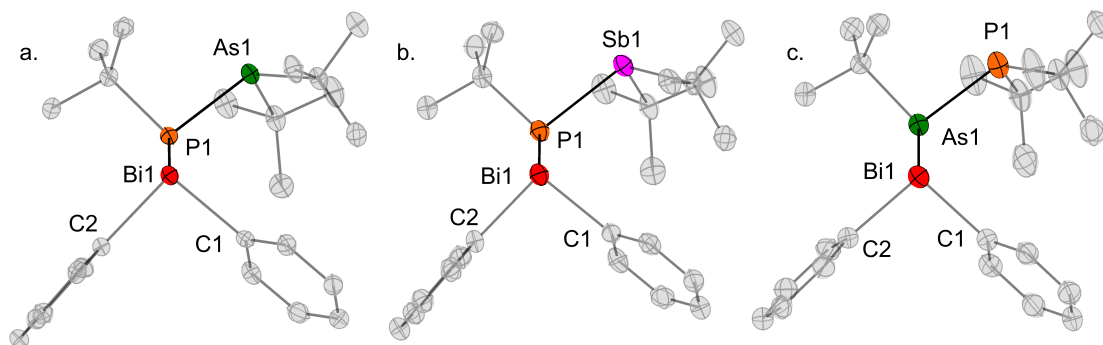


Abbildung 5.17: Molekülstrukturen von $\text{Ph}_2\text{BiP}(t\text{Bu})\text{As}t\text{Bu}_2$ (a.), $\text{Ph}_2\text{BiP}(t\text{Bu})\text{Sb}t\text{Bu}_2$ und $\text{Ph}_2\text{BiAs}(t\text{Bu})\text{P}t\text{Bu}_2$ (c.) im Festkörper. Wasserstoffatome sind aus Gründen der Übersichtlichkeit nicht dargestellt. Die Schwingungsellipsoide sind mit 50 % Aufenthaltswahrscheinlichkeit gezeigt.

der entstanden Radikale hin. Im Falle der Bi-P-Sb-Ketten werden deutlich mehr Zersetzungsprodukte, unter anderem auch die symmetrischen Bi-P-Bi- und Sb-P-Sb-Ketten, beobachtet. Neben dem Bi-P-Bindungsbruch findet also außerdem ein Sb-P-Bindungsbruch statt.

Nachdem nun einige binäre und ternäre Interpnictogenverbindungen, welche jedoch alle als Feststoffe mit niedrigem Dampfdruck vorliegen, dargestellt werden konnten, sollten nun flüchtige und im besten Fall flüssige Interpnictogenverbindungen dargestellt werden. Dafür wurde zunächst versucht die Kristallisationseigenschaften der Aryl-substituierten Verbindungen durch Einführung eines *para-n*-Butyl-Phenyl-Substituenten (*p-n*BuPh) zu verschlechtern. Es konnte bei der Umsetzung von (*p-n*BuPh)MgBr und BiCl_3 erfolgreich (*p-n*BuPh) $_3$ Bi in Form einer blass gelben Flüssigkeit erhalten werden. Auch die anschließende Umsetzung mit BiCl_3 zum (*p-n*BuPh) $_2$ BiCl war erfolgreich. Bei weiter Umsetzung mit LiNMe_2 wurde ein hoch viskoses Rohprodukt, welches sich nicht weiter aufreinigen ließ und keinen hohen Dampfdruck zeigt, erhalten. Aufgrund dessen wurde von der Verwendung von Aryl-Substituenten abgesehen und Me_2BiCl als Edukt eingesetzt. Nun konnten durch Umsetzung mit LiEtBu_2 ($\text{E} = \text{P}, \text{As}$) die gewünschten Produkte $\text{Me}_2\text{BiP}t\text{Bu}_2$ und $\text{Me}_2\text{BiAs}t\text{Bu}_2$ in Form gelber Flüssigkeiten erhalten werden (Abbildung 5.18). Beide Produkte zeigen einen gewissen Dampfdruck und können bei 60°C destilliert werden. Jedoch zersetzten sich die Verbindungen bei diesen Temperaturen schnell, was zu großen Ausbeuteverlusten bei der Destillation führt.

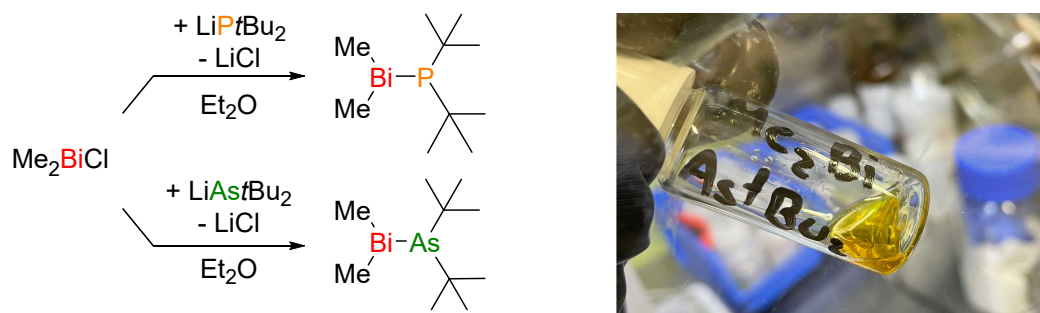


Abbildung 5.18: Links: Darstellung der flüssigen Interpnictogenverbindungen $\text{Me}_2\text{BiEtBu}_2$ (E = P, As). Rechts: Foto des $\text{Me}_2\text{BiAs}^t\text{Bu}_2$ nach der Destillation.

Des Weiteren ist die Lagerstabilität der Verbindungen für den Einsatz als *MOV-PE*-Präkursoren zu gering. Lassen sich beide Verbindungen bei -40°C noch ohne Zersetzung lagern, lässt sich schon nach wenigen Tagen bei Raumtemperatur unter Ausschluss von Licht die Bildung von schwarzem Feststoff beobachten. Um in Zukunft für die chemische Industrie relevante bismuthaltige Interpnictogen-Präkursoren zu erhalten, sind weitere Modifikationen an den Zielverbindungen nötig.

6 Summary

The goal of this work is the preparation of new interpnictogen compounds with terminal diaryl bismuth groups. These are prepared from compounds with the general formula Ar_2BiX ($\text{X} = \text{Hal}$), whereby Phenyl, Mesityl and 2,6-di-*iso*-propylphenyl substituents are used for the investigation of steric effects on the stability of the prepared compounds. Most aryl halido bismuthanes with phenyl and mesityl substituents are already described in the literature.^[118,294,295] In contrast, the Dipp substituent is introduced as a substituent for bismuth in the course of this work. Because of that, the summary is split into two subsections. First, the introduction of the Dipp substituent to bismuth chemistry is discussed. Afterwards, a report about the preparation of interpnictogen compounds follows.

6.1 Introduction of the Dipp Substituent to Bismuth Chemistry

One goal of this work was the introduction of the Dipp substituent into bismuth chemistry. In doing so, the preparation and structure in the solid state of compounds of the form $\text{Dipp}_n\text{BiX}_{3-n}$ was studied in detail ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}, \text{OTf}, \text{SbF}_6$; $n = 1-3$). Through reaction of two equivalents of the *Grignard*-reagent $\text{DippMgBr}\cdot\text{THF}$ with BiCl_3 in THF, Dipp_2BiBr was obtained initially. Starting from Dipp_2BiBr , Dipp_2BiI (Figure 6.1) was obtained *via* halide ion exchange by reaction with CaI_2 . The corresponding halidobismuthanes of fluorine and chlorine were not accessible *via* halide exchange from the bromide. Rather, a detour *via*

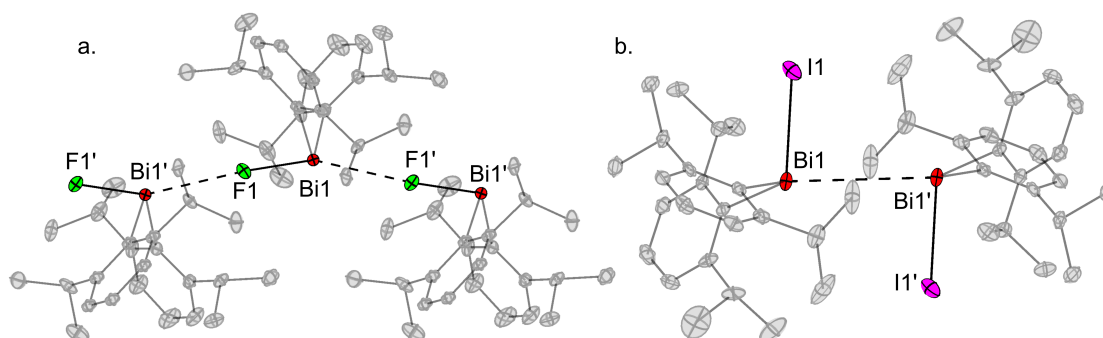


Figure 6.1: Molecular structure of Dipp_2BiF (a.) and Dipp_2BiI (b.) in the solid state. Hydrogen atoms are omitted for clarity and ellipsoids are shown at the 50 % probability level.

Dipp₂BiOTf had to be taken, which was prepared from Dipp₂BiBr and AgOTf. The driving force for this reaction is the formation of the poorly soluble AgBr. Through addition of NaF or NaCl to Dipp₂BiOTf, Dipp₂BiF (Figure 6.5) and Dipp₂BiCl were obtained, subsequently. Alternatively, Dipp₂BiF can also be prepared from Dipp₂BiI and AgF, which however, gives somewhat poorer yields. All compounds mentioned were isolated in pure form and analysed by NMR spectroscopy, IR spectroscopy, mass spectrometry and single crystal X-ray diffraction. An overview for the synthesis of the diaryl halido bismuthanes is given in Figure 6.2.

Based on the characteristics of the obtained compounds, some trends for the Dipp-substituted halido bismuthanes are worked out. For the different halides, the degree of aggregation in the solid state changes. In case of the lightest halogen, fluorine, one-dimensional polymeric strands with alternating bismuth and fluorine atoms are formed in the solid state. Due to secondary interactions, the intermolecular Bi-F distance is significantly smaller than the sum of the *van der Waals* radii of Bi and F.^[296,297] For the heavier halogens Cl and Br, a smaller aggregate, more precisely a hexamer, is formed. However, the intermolecular Bi-X distance is now very close to the sum of the *van der Waals* radii,^[296,297] which is indicative of weak interactions. In contrast, Dipp₂BiI does not show any secondary Bi-I interactions. Instead, dimers with short Bi-Bi distances are formed, which presumably indicates dispersive Bi-Bi interactions. Another interesting trend is reflected in the chemical shift of the *ipso*-carbon atom in the ¹³C NMR spectrum, which depends very much on the electronegativity of the bound (pseudo)halide. A signal is observed at 174.5 ppm for X = I, which is shifted significantly to

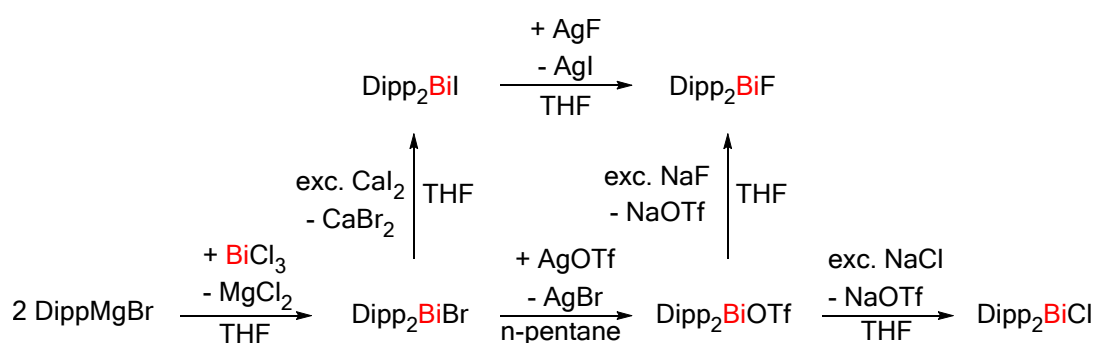


Figure 6.2: Reaction scheme for the preparation of Dipp₂BiBr and subsequent reactions to compounds of the form Dipp₂BiX (X = F, Cl, Br, I, OTf).

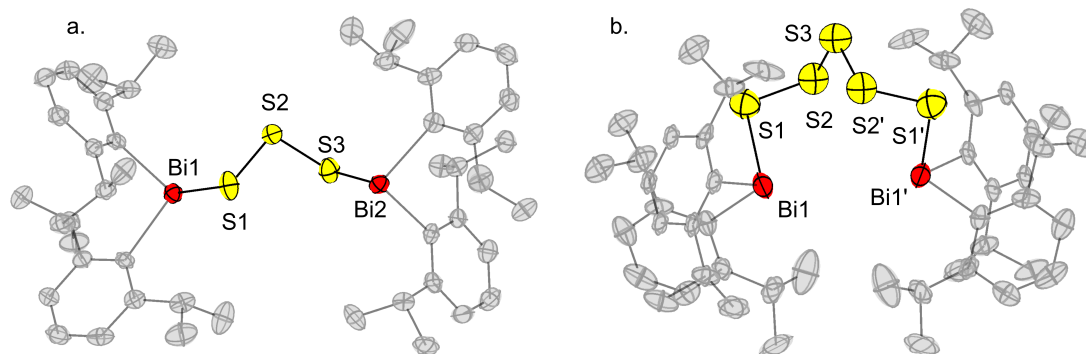


Figure 6.3: Molecular structure of $(\text{Dipp}_2\text{Bi})_2\text{S}_3$ (a.) and $(\text{Dipp}_2\text{Bi})_2\text{S}_5$ (b.) in the solid state. Hydrogen atoms are omitted for clarity and ellipsoids are shown at the 50 % probability level.

191.1 ppm for $X = \text{F}$. For $X = \text{OTf}$ the signal is shifted even more towards lower field and a resonance at 207.6 ppm is observed.

Moreover, the reactivity of Dipp_2BiBr was studied. In a reaction with MeLi the expected Dipp_2BiMe is formed. By reaction with $\text{Li}[\text{BHEt}_3]$, a hydrogenating agent, the dibismuthane Dipp_4Bi_2 is formed under release of H_2 . As is common for dibismuthanes, Dipp_4Bi_2 is able to activate S-S bonds. After the reaction with elemental sulphur, two compounds present in the reaction mixture, namely $(\text{Dipp}_2\text{Bi})_2\text{S}_3$ and $(\text{Dipp}_2\text{Bi})_2\text{S}_5$, were identified *via* single crystal X-ray diffraction (Figure 6.3 and 6.4).

Bismuthanes of the form R_3Bi are versatile educts for the preparation of many different bismuth compounds. In the case of $\text{R} = \text{Dipp}$, the synthesis of Dipp_3Bi was therefore also investigated. After reaction of Dipp_2BiBr with additional

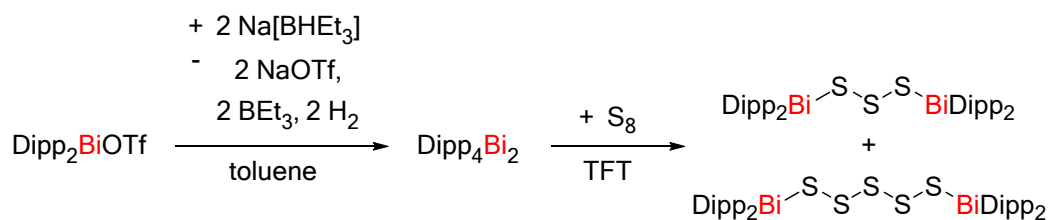


Figure 6.4: Reaction scheme for the preparation of Dipp_4Bi_2 and a follow up reaction with elemental sulphur.

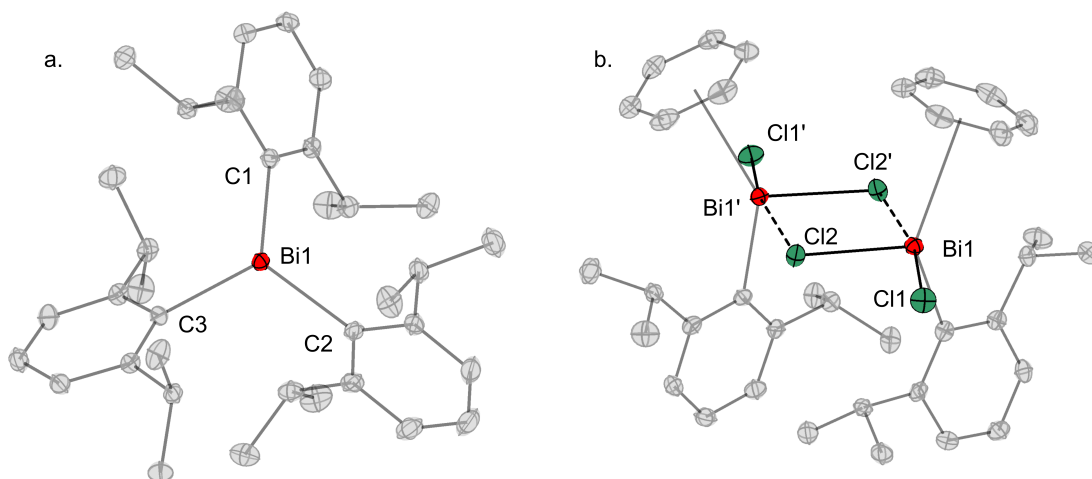


Figure 6.6: Molecular structure of Dipp_3Bi (a.) and $\text{DippBiCl}_2\cdot\text{toluene}$ (b.) in the solid state. Hydrogen atoms are omitted for clarity and ellipsoids are shown at the 50 % probability level.

in pure form. Rather, a mixture of Dipp_2BiMe and BiMe_3 was obtained, which signifies the particular stability of the diaryl bismuth unit.

With the triflate anion a weakly coordinating substituent was bound to the Dipp_2Bi -fragment. Now the free Dipp substituted bismuthenium cation, $[\text{Dipp}_2\text{Bi}]^+$, was to be prepared. In the following, the property of the Dipp substituent as an aryl substituent of intermediate size on the *Lewis* acidity of a bismuthenium cation was to be investigated. For this purpose, Dipp_2BiBr was reacted with $\text{Ag}[\text{PF}_6]$ in first attempts. It turned out that the $[\text{PF}_6]^-$ anion is not inert enough to stabilise the bismuthenium cation and the compound $[\text{Dipp}_2\text{Bi}(\text{PF}_6)]$, although initially formed, decomposes. Two decomposition products were identified, namely $[(\text{Dipp}_2\text{Bi})_2\text{F}(\text{PF}_6)]$ and Dipp_2BiF . At last it was possible to intercept the labile $[\text{Dipp}_2\text{Bi}(\text{PF}_6)]$ with a donor (OPEt_3) to give $[\text{Dipp}_2\text{Bi}(\text{OPEt}_3)_2(\text{PF}_6)]$.

After it had been shown that $[\text{PF}_6]^-$ is not a suitable anion, the more stable $[\text{SbF}_6]^-$ anion was used in following experiments. After reaction of Dipp_2BiBr and $\text{Ag}[\text{SbF}_6]$ in toluene it was now possible to obtain the toluene adduct of the desired product $[\text{Dipp}_2\text{Bi}(\text{SbF}_6)(\text{toluene})]$. The donor-free compound, $[\text{Dipp}_2\text{Bi}(\text{SbF}_6)]$, was obtained by recrystallization from the less π -donating aromatic solvent TFT (α - α - α -trifluorotoluene). With the $[\text{SbF}_6]^-$ anion it was also possible to prepare and

isolate $[\text{((Dipp}_2\text{Bi)}_2\text{F)(SbF}_6\text{)}]$, which was previously observed as decomposition product, by addition of one equivalent of Dipp_2BiF to $[\text{Dipp}_2\text{Bi(SbF}_6\text{)}]$. Furthermore, reactions with phosphane chalcogenides, more precisely OPeEt_3 , SPMe_3 and SePMe_3 were performed to examine the *Lewis* acidity of the bismuthenium cation. Therefore, *Lewis* acidity was investigated using the original and a modified version of the *Gutmann-Beckett* method.^[163,168,169] In cooperation with the *Lichtenberg* group from the Philipps-university of Marburg, where the bismuthenium cation $[\text{Me}_2\text{Bi(SbF}_6\text{)}]$ with small substituents is investigated, the correlation of *Lewis* acidity and steric demand of the substituents was to be examined *via* experimental and theoretical means. It turned out that the *acceptor number* (*AN*) of

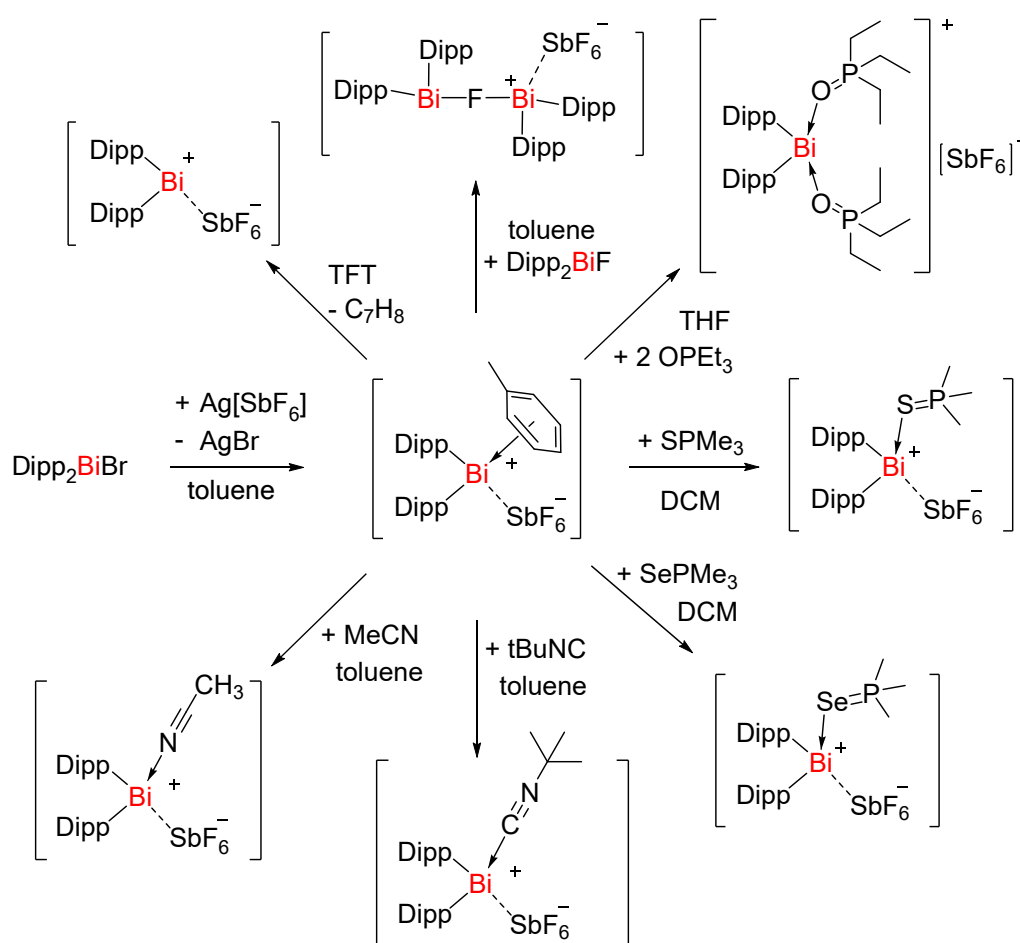


Figure 6.7: Reaction scheme for the preparation of $[\text{Dipp}_2\text{Bi(SbF}_6\text{)}(\text{toluene})]$ and follow up reactions with several different donors.

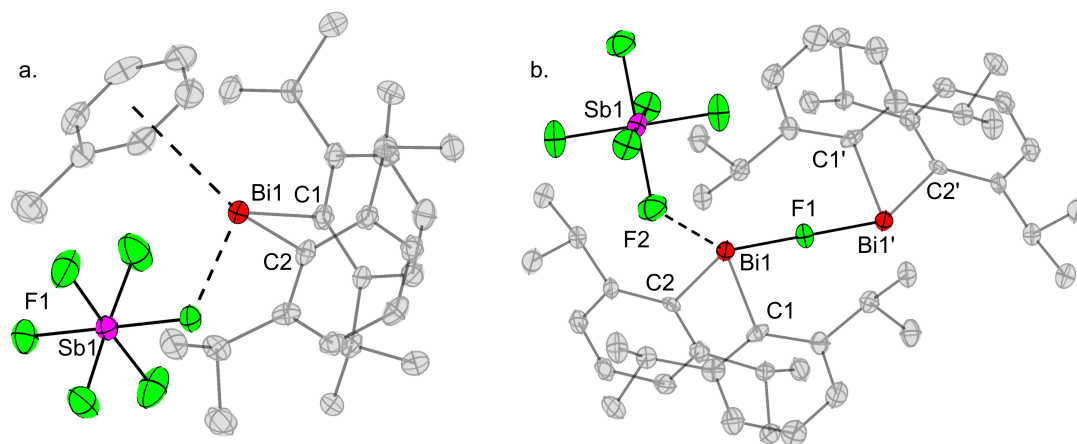


Figure 6.8: Molecular structure of $[\text{Dipp}_2\text{Bi}(\text{SbF}_6)]$ (a.) and $[(\text{Dipp}_2\text{Bi})_2\text{F}(\text{SbF}_6)]$ (b.) in the solid state. Hydrogen atoms are omitted for clarity and ellipsoids are shown at the 50 % probability level.

$[\text{Dipp}_2\text{Bi}(\text{SbF}_6)]$ and $[\text{Me}_2\text{Bi}(\text{SbF}_6)]$ with the soft *Lewis* acids SPMe_3 and SePMe_3 are very similar. However, with the harder OPEt_3 , there is an increased *Lewis* acidity observed for $[\text{Dipp}_2\text{Bi}(\text{SbF}_6)]$, with the sterically more demanding Dipp substituents. Using DFT calculations, it could be shown that this is probably due to shielding of the coordination site on the other side of the bismuth atom. Due to the large Dipp substituents coordination of the $[\text{SbF}_6]^-$ anion is inhibited, thus the Bi-O bond on the other side is strengthened. At last, two more donor-acceptor complexes with a C-N triple bond were prepared. Through reaction of the bismuthenium cation with acetonitrile or *tert*-butylisonitrile, the adducts $[\text{Dipp}_2\text{Bi}(\text{MeCN})(\text{SbF}_6)]$ and $[\text{Dipp}_2\text{Bi}(\text{CN}t\text{Bu})(\text{SbF}_6)]$ were obtained.

6.2 Preparation of Interpnictogen Compounds

All educts used for preparation of interpnictogen compounds have the general formula Ar_2BiX ($\text{Ar} = \text{Ph}, \text{Mes}, \text{Dipp}$; $\text{X} = \text{F}, \text{Cl}, \text{Br}$). The preparation of Dipp_2BiF and Dipp_2BiBr is described in the previous chapter 6.1. Initially interpnictogen compounds with the lightest representative nitrogen and thus bearing a Bi-N bond, were prepared. To achieve this, Ar_2BiX was reacted with LiNMe_2 , resulting in the formation of compounds with the general formula $\text{Ar}_2\text{BiNMe}_2$ ($\text{Ar} = \text{Ph}, \text{Mes}, \text{Dipp}$). In the solid state $\text{Ph}_2\text{BiNMe}_2$ forms one-dimensional polymeric strands with alternating Bi and N atoms, analogously to the diaryl halido bismuthanes. The bismuth atoms are coordinated from the lone pair of a nitrogen atom of the next and the aromatic π -system of the previous molecule (Figure 6.9). On the other hand, the compounds $\text{Mes}_2\text{BiNMe}_2$ and $\text{Dipp}_2\text{BiNMe}_2$ with the sterically more demanding substituents do not show any intermolecular interactions of bismuth and thus, form monomers. After the successful preparation of the bismuthaneamines with LiNMe_2 , compounds with functional groups for potential further functionalization at the nitrogen atom were to be prepared. The target compounds have the general formula $\text{Ar}_2\text{BiNH}t\text{Bu}$. After reactions of Ar_2BiX and $\text{LiNH}t\text{Bu}$ did not lead to sufficient success, an alternative route had to be taken, which succeeded in case of $\text{Mes}_2\text{BiNH}t\text{Bu}$ and $\text{Dipp}_2\text{BiNH}t\text{Bu}$ (Figure 6.9). To access the Mes substituted compound, $\text{Mes}_2\text{BiNMe}_2$ was reacted with an excess of NH_2tBu in toluene,

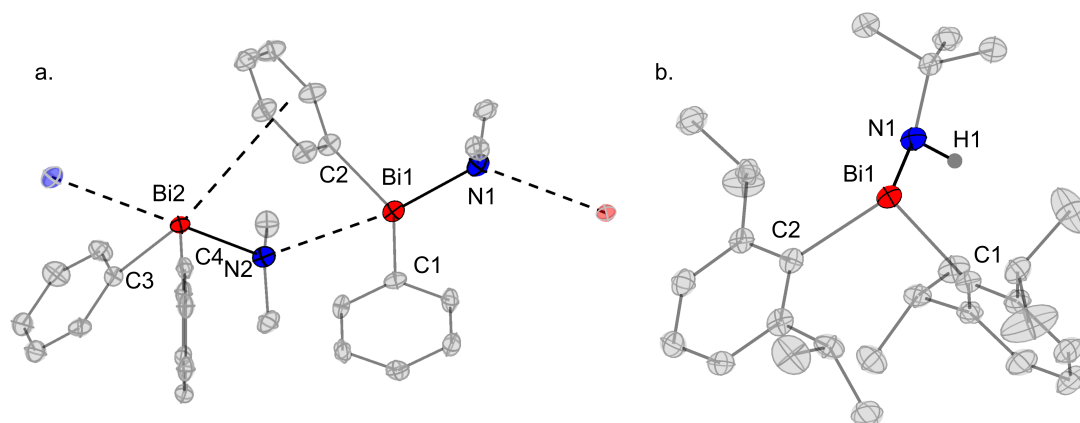


Figure 6.9: Molecular structure of $\text{Ph}_2\text{BiNMe}_2$ (a.) and $\text{Dipp}_2\text{BiNH}t\text{Bu}$ (b.) in the solid state. Hydrogen atoms bound to carbon are omitted for clarity and ellipsoids are shown at the 50 % probability level.

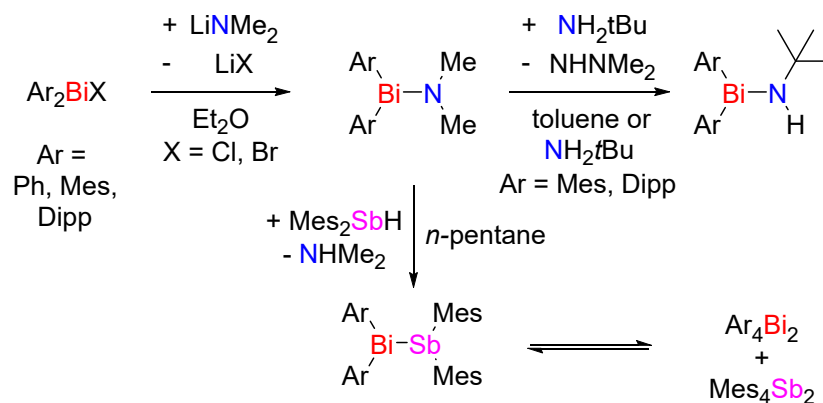


Figure 6.10: Reaction scheme for the preparation of bismuthaneamines with the general formula $\text{Ar}_2\text{BiNMe}_2$. Moreover, the reaction of these with NH_2tBu or Mes_2SbH .

leading to the elimination of NHMe_2 . For the Dipp compound on the other hand, pure NH_2tBu has to be used as a solvent and the reaction has to be run a lot longer for complete consumption of the educt. The reaction scheme for the preparation of the bismuthaneamines is shown in Figure 6.10.

By reacting a bismuthaneamine with a secondary stibane, the first isolable compounds bearing a Bi-Sb single bond have been prepared in 2020.^[221] In a sim-

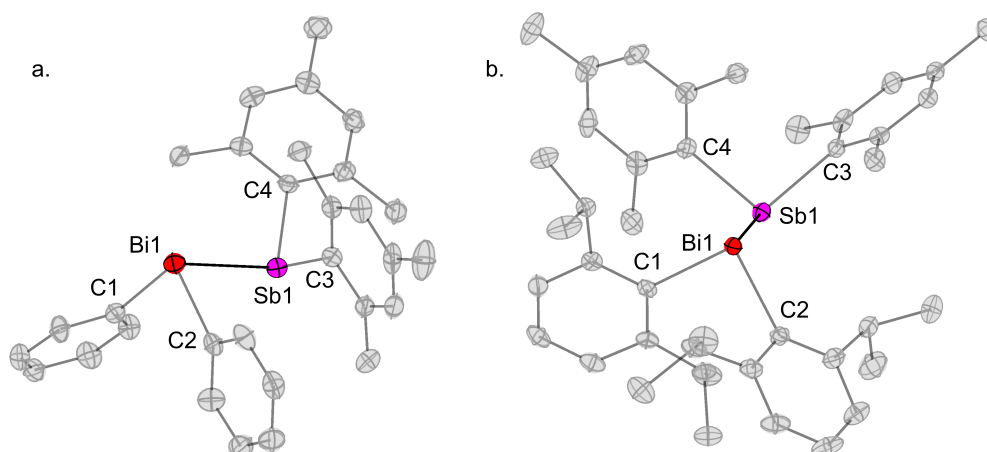


Figure 6.11: Molecular structure of $\text{Ph}_2\text{BiSbMes}_2$ (a.) and $\text{Dipp}_2\text{BiSbMes}_2$ (b.) in the solid state. Hydrogen atoms are omitted for clarity and ellipsoids are shown at the 50 % probability level.

ilar reaction, the previously prepared bismuthaneamines of the form $\text{Ar}_2\text{BiNMe}_2$ ($\text{Ar} = \text{Ph}, \text{Mes}, \text{Dipp}$) were reacted with Mes_2SbH (Figure 6.10). In this reaction a Bi-Sb bond is formed in a condensation reaction under elimination of NHMe_2 . In all three performed reactions it was possible to identify the targeted bismuthanyl stibanes in addition to Ar_4Bi_2 and Mes_4Sb_2 by NMR spectroscopy. In the case of $\text{Ar} = \text{Ph}$ and Dipp , the obtained Bismuthanyl stibane could also be isolated and, among other things, be examined *via* single crystal X-ray diffraction (Figure 6.11). After dissolving the isolated bismuthanyl stibanes in C_6D_6 again, the formation of Ar_4Bi_2 and Mes_4Sb_2 is observed, suggesting an equilibrium between the three compounds. The equilibrium hypothesis could in turn be verified by the reverse experiment, where Mes_4Bi_2 and Mes_4Sb_2 were dissolved in toluene- d_8 and the formation of $\text{Mes}_2\text{BiSbMes}_2$ is observed again. The equilibrium constants for the scrambling reaction with the symmetrical compounds as educts are determined to $K_{\text{Ph}} = 76$, $K_{\text{Mes}} = 1.1$, and $K_{\text{Dipp}} = 7.8$. Temperature-dependent NMR spectroscopy also showed that the equilibrium, which is shifted far towards $\text{Ph}_2\text{BiSbMes}_2$, is mostly controlled by entropic effects.

After the successful preparation of some bismuthaneamines and bismuthanyl stibanes, compounds with a Bi-P single bond were to be prepared. For the construction of a Bi-P bond, salt metathesis reaction was chosen as the first approach again. After conversion of the three educts of the form Ar_2BiX with LiPtBu_2 , three bismuthanyl phosphanes $\text{Ph}_2\text{BiPtBu}_2$, $\text{Mes}_2\text{BiPtBu}_2$, and $\text{Dipp}_2\text{BiPtBu}_2$ were

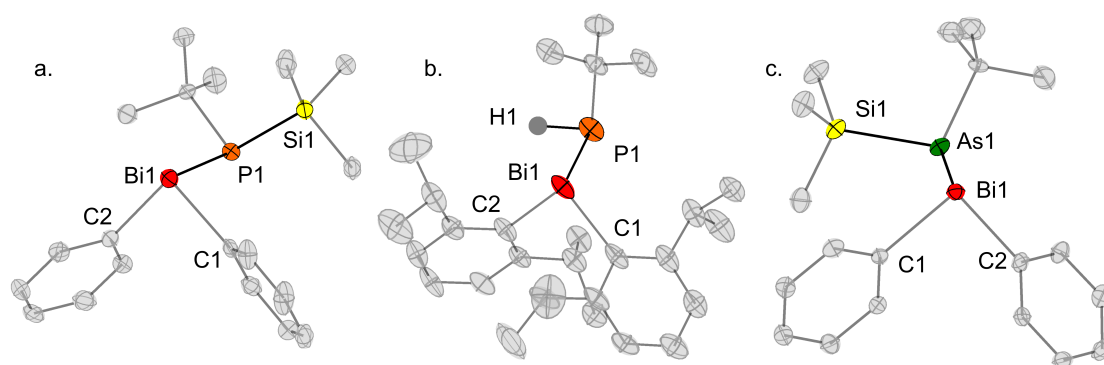


Figure 6.12: Molecular structure of $\text{Ph}_2\text{BiPtBu}(\text{SiMe}_3)$ (a.), $\text{Dipp}_2\text{BiPtBu}$ (b.) and $\text{Ph}_2\text{BiAsPtBu}(\text{SiMe}_3)$ (c.) in the solid state. Hydrogen atoms bound to carbon are omitted for clarity and ellipsoids are shown at the 50 % probability level.

obtained (Figure 6.13). In contrast to $\text{Ph}_2\text{BiNMe}_2$, all bismuthanyl phosphanes are monomers in the solid state. The clean preparation of bismuthanyl phosphanes bearing functional groups was again not possible *via* the salt metathesis route. Because of that, a new reaction path with less harsh reaction conditions was examined. It turned out, that Bi-P bonds can be formed *via* trimethylsilyl halide elimination, with the reaction taking place fastest and most selectively in the unusual solvent TFT. Through this synthetic pathway, $\text{Ph}_2\text{BiPtBu}(\text{SiMe}_3)$, $\text{Mes}_2\text{BiPtBu}(\text{SiMe}_3)$ and $\text{Dipp}_2\text{BiPtBu}(\text{SiMe}_3)$ have been prepared. With SiMe_3 , they feature a group which can be potentially used for further functionalisation. By reaction of Dipp_2BiF and $\text{P}t\text{Bu}(\text{SiMe}_3)$ another compound, namely $\text{Dipp}_2\text{BiPH}t\text{Bu}$ was prepared and examined *via* single-crystal X-ray diffraction and IR spectroscopy. In the IR spectrum, an intense band at 2272 cm^{-1} can be assigned to the P-H vibration.

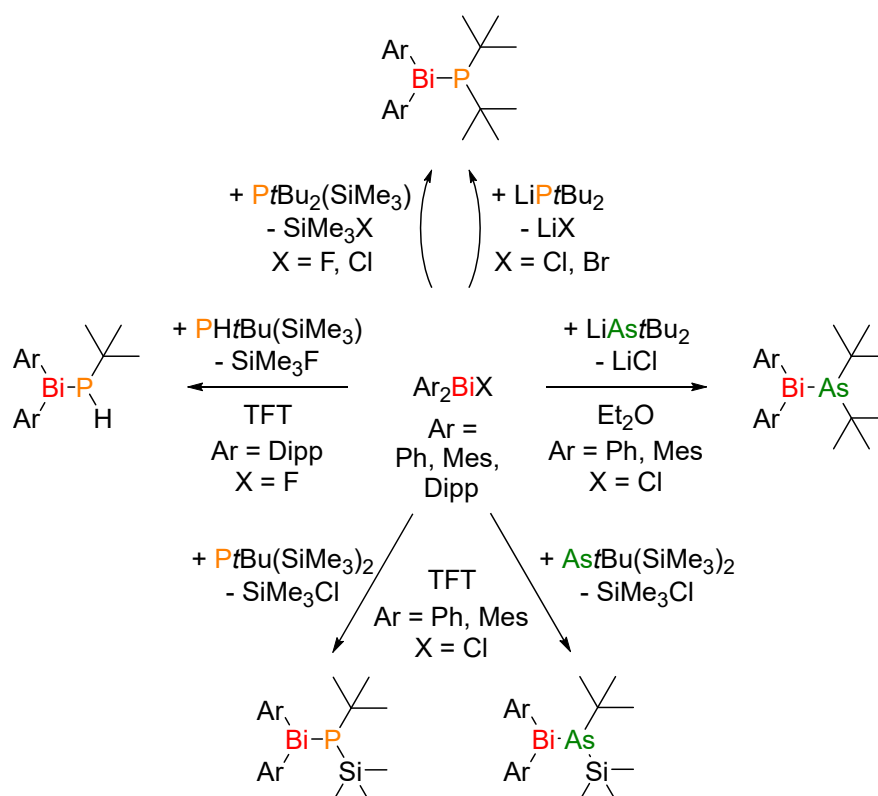


Figure 6.13: Reaction scheme for the preparation of binary interpnictogen compounds bearing Bi-P or Bi-As bonds.

It was also possible to prepare multiple bismuthanyl arsanes through reactions under similar conditions (Figure 6.13). First compounds bearing no functional groups were prepared by reaction of Ar_2BiCl and LiAstBu , where $\text{Ph}_2\text{BiAstBu}_2$ and $\text{Mes}_2\text{BiAstBu}_2$ have been obtained. In addition, $\text{Ph}_2\text{BiAstBu}(\text{SiMe}_3)$ and $\text{Mes}_2\text{BiAstBu}(\text{SiMe}_3)$ with functional silyl groups were prepared *via* reaction of Ar_2BiCl with $\text{AstBu}(\text{SiMe}_3)_2$. It was shown, that salt metathesis reaction as well as SiMe_3Cl elimination are suitable for the formation of both, Bi-P and Bi-As, bonds.

Now that compounds with a single Bi-P or Bi-As bond had been prepared by the SiMe_3X elimination, the follow up reactions of $\text{Ar}_2\text{BiEtBu}(\text{SiMe}_3)$ ($\text{Ar} = \text{Ph}, \text{Mes}$; $\text{E} = \text{P}, \text{As}$) with an additional equivalent of Ar_2BiCl were investigated. In the case of $\text{E} = \text{P}$ the desired $\text{Ph}_2\text{BiP}(t\text{Bu})\text{BiPh}_2$ with a central Bi-P-Bi chain was successfully prepared. However, the compound is very labile and decomposes within hours under loss of one “*PtBu*” unit to the tetraphenyldibismuthane in solution. For $\text{E} = \text{As}$ target compounds with the central Bi-As-Bi chain were prepared successfully for two aromatic substituents ($\text{Ar} = \text{Ph}, \text{Mes}$). Similar to the Bi-P-Bi chain, the compounds with the central Bi-As-Bi chain are labile and decompose in solution to the corresponding dibismuthanes respectively. In the

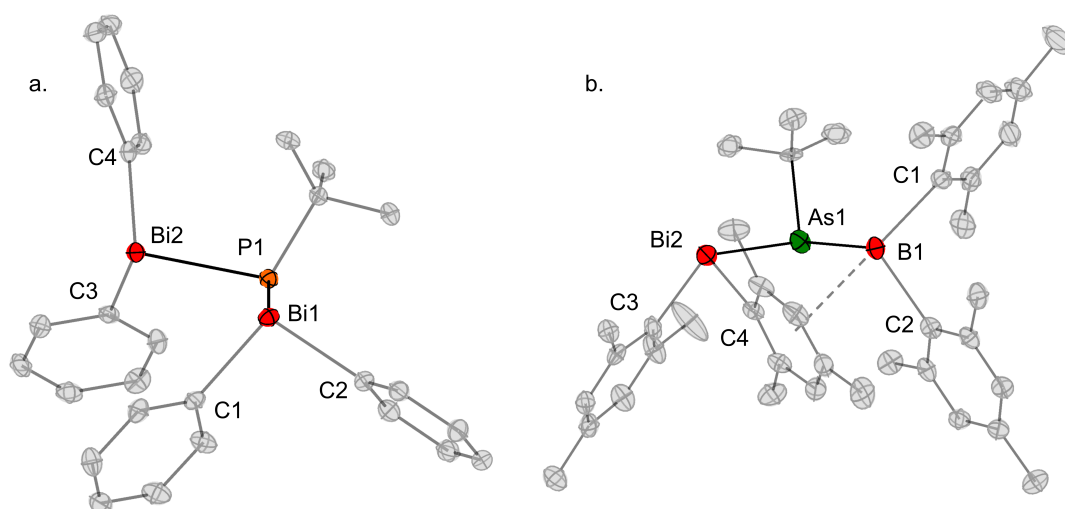


Figure 6.14: Molecular structure of $\text{Ph}_2\text{BiP}(t\text{Bu})\text{BiPh}_2$ (a.) and $\text{Mes}_2\text{BiAs}(t\text{Bu})\text{BiMes}_2$ (b.) in the solid state. Hydrogen atoms are omitted for clarity and ellipsoids are shown at the 50 % probability level.

case of Ar = Ph an additional decomposition product was identified *via* single crystal X-ray diffraction. The compound turned out to have a central Bi-As-As-Bi chain and the following sum formula: $\text{Ph}_2\text{BiAs}(t\text{Bu})\text{As}(t\text{Bu})\text{BiPh}_2$. Formally, this compound represents the Bi-As-Bi chain molecule with an additional “AstBu“ fragment inserted into one Bi-As bond. This prompted us to investigate the potential of the three membered chains as pnictogenidene transfer reagents. A small *N*-heterocyclic carbene (1,3,4,5-tetramethylimidazol-2-ylidene, Me_2IME) was chosen as pnictogenidene acceptor. When adding a solution of Me_2IME to a solution of $\text{Ph}_2\text{BiP}(t\text{Bu})\text{BiPh}_2$ the reaction mixture immediately takes on an intense red colour. The reaction mixture was analysed *via* NMR spectroscopy, where the formation of $\text{Me}_2\text{IME}=\text{PtBu}$ was confirmed. Even though $\text{Me}_2\text{IME}=\text{PtBu}$ could not be isolated afterwards, the initial reaction confirms, that $\text{Ph}_2\text{BiP}(t\text{Bu})\text{BiPh}_2$ can indeed be used as a phosphinidene transfer agent. In contrast, there was no reaction observed upon addition of Me_2IME to the Bi-As-Bi chain molecules. Hence, it was not possible to observe an arsenidene fragment transfer.

After some symmetrical three membered chains had been prepared by abstraction of Me_3SiCl , similar reaction of $\text{Ar}_2\text{BiEtBu}(\text{SiMe}_3)$ with compounds of the form $t\text{Bu}_2\text{EX}$ (E = P, As, Sb; X = F, Cl) for the preparation of ternary interpnictogen

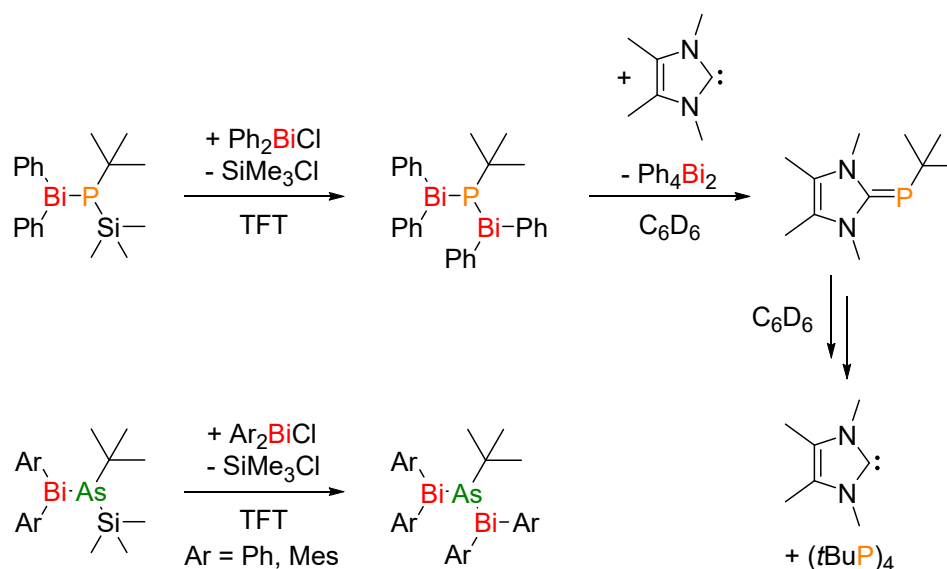


Figure 6.15: Reaction scheme for the preparation of interpnictogen compounds with a central Bi-E-Bi chain (E = P, As) and reaction of $(\text{Dipp}_2\text{Bi})_2\text{PtBu}$ with Me_2IME .

togen compounds where attempted under similar conditions. However, no reaction of the two educts was observed in any case. In order to nevertheless obtain ternary interpnictogen compounds, salt metathesis reactions were used again and the compounds Ar_2BiCl ($\text{Ar} = \text{Ph}, \text{Mes}$) were reacted with $\text{LiE}^1(t\text{Bu})\text{E}^2t\text{Bu}_2$ ($\text{E}^1 = \text{P}, \text{As}; \text{E}^2 = \text{P}, \text{As}, \text{Sb}$). In case of a central phosphorus atom, four compounds with the general formula $\text{Ar}_2\text{BiP}(t\text{Bu})\text{E}^2t\text{Bu}_2$ ($\text{Ar} = \text{Ph}, \text{Mes}; \text{E}^2 = \text{As}, \text{Sb}$) have been prepared. In the case of a central As atom, two compounds of the form $\text{Ar}_2\text{BiAs}(t\text{Bu})\text{PtBu}_2$ ($\text{Ar} = \text{Ph}, \text{Mes}$) were prepared. The ternary three membered chains are all much more stable than the compounds with the symmetrical Bi-E-Bi central unit. Nevertheless, they also decompose in solution within days and the formation of decomposition products is observed. In all cases, the Mes-substituted compounds decompose significantly slower than the Ph-substituted ones. The decomposition products depend mainly on the chain motif and not the aromatic substituents, hence the decomposition products differ between the chains. For the Bi-As-P and Bi-P-As chains only two decomposition products are observed. These are the corresponding dibismuthanes and a $t\text{Bu}_2\text{PAs}(t\text{Bu})\text{As}(t\text{Bu})\text{PtBu}_2$ or $t\text{Bu}_2\text{AsP}(t\text{Bu})\text{P}(t\text{Bu})\text{As}t\text{Bu}_2$ chain compound respectively. This indicates a homolytic cleavage of the Bi-E bond with subsequent recombination of the result-

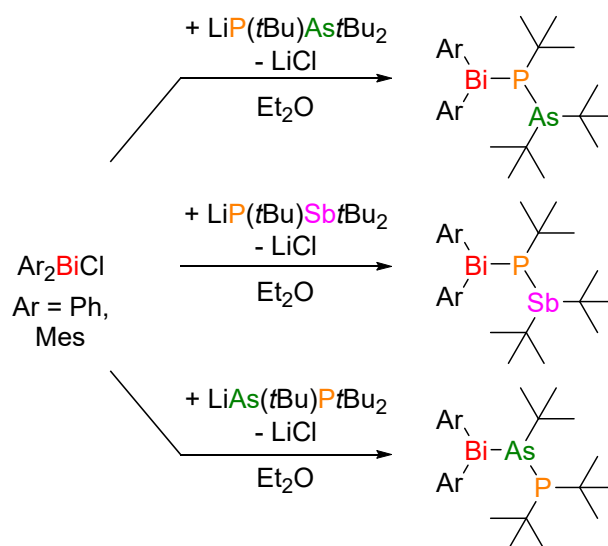


Figure 6.16: Reaction scheme for the preparation of ternary bismuth containing interpnictogen compounds from Ar_2BiCl ($\text{Ar} = \text{Ph}, \text{Mes}$) and $\text{LiE}^1(t\text{Bu})\text{E}^2t\text{Bu}$ ($\text{E}^1 = \text{P}, \text{As}; \text{E}^2 = \text{P}, \text{As}, \text{Sb}$).

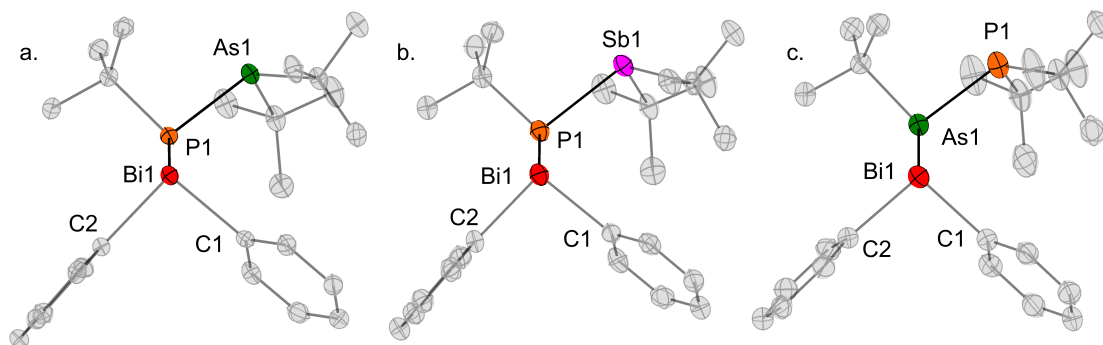


Figure 6.17: Molecular structure of $\text{Ph}_2\text{BiP}(t\text{Bu})\text{As}(t\text{Bu})_2$ (a.), $\text{Ph}_2\text{BiP}(t\text{Bu})\text{Sb}(t\text{Bu})_2$ and $\text{Ph}_2\text{BiAs}(t\text{Bu})\text{P}(t\text{Bu})_2$ (c.) in the solid state. Hydrogen atoms are omitted for clarity and ellipsoids are shown at the 50 % probability level.

ing radicals. In the case of the Bi-P-Sb chains, significantly more decomposition products are observed, including the symmetrical Bi-P-Bi and Sb-P-Sb chains. Hence, in addition to the Bi-P bond rupture the P-Sb bond is also broken during decomposition.

After some binary and ternary interpnictogen compounds, which are all solids with low vapour pressure, had been prepared, new binary compounds which should be liquids and, in the best case, show a high vapour pressure, were to be prepared. In first attempts compounds with aryl substituents and worse crystallization properties have been prepared. Therefore, the *para*-nbutyl-phenyl (*p*-nBuPh) substituent was introduced. Through the reaction of (*p*-nBuPh)MgBr and BiCl_3 , (*p*-nBuPh) $_3\text{Bi}$ was successfully obtained in the form of a pale yellow liquid. The subsequent reaction with BiCl_3 to form (*p*-nBuPh) $_2\text{BiCl}$ was also successful. However, after further reaction with LiNMe_2 only a highly viscous raw product was obtained, which could not be further purified and did not have a high enough vapour pressure for distillation. Because of this, the use of aryl substituents was stopped and a methyl substituted bismuthane, namely Me_2BiCl , was used as the starting material. Reaction with LiEtBu_2 ($\text{E} = \text{P}, \text{As}$) gave the desired products $\text{Me}_2\text{BiEtBu}_2$ in the form of yellow liquids (Figure 6.18). Both products have a vapour pressure to some extent and can be distilled under dynamic fine vacuum at 60°C . However, the compounds also decomposed within minutes at these temperatures, leading to large losses in yield during the distillation. Furthermore, the storage stability of the compounds is limited and too low for the usage as

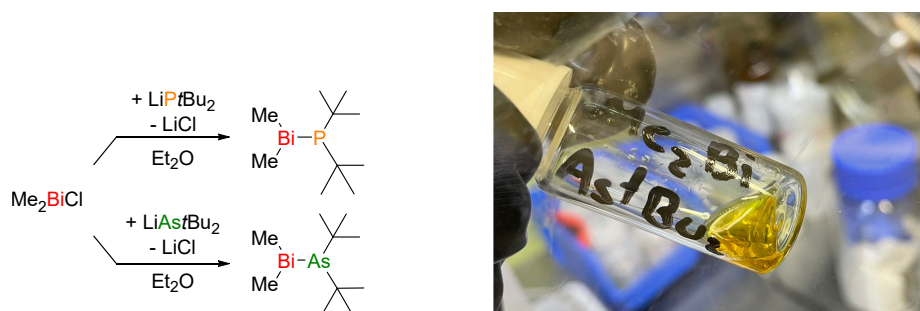


Figure 6.18: Left: Reaction scheme for the preparation of liquid interpnictogen compounds with methyl substituents at bismuth ($\text{Me}_2\text{BiEt}^t\text{Bu}_2$ ($\text{E} = \text{P}, \text{As}$)). Right: Picture of liquid $\text{Me}_2\text{BiAs}^t\text{Bu}_2$ after purification by distillation.

MOVPE precursors. Even with the exclusion of light, formation of black solid is observed after days at room temperature. However, both compounds can be stored at $-40\text{ }^\circ\text{C}$ without noticeable decomposition for months. In order to obtain precursors relevant to the chemical industry, further modifications of the target compounds may be necessary in the future.

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8 Anhang

An dieser Stelle sind die im Rahmen dieser Dissertation entstandenen Publikationen, inklusive deren Anhänge, in chronologischer Reihenfolge aufgeführt. Die Urheberrechte der Veröffentlichungen liegen bei den entsprechenden Verlagen.

- 1.) Tobias Dunaj, Kevin Dollberg, Christian Ritter, Dr. Fabian Dankert, Prof. Dr Carsten von Hänisch *Eur. J. Inorg. Chem.*, **2021**, 2021, 870-878. „2,6-Diisopropylphenyl-Substituted Bismuth Compounds: Synthesis, Structure, and Reactivity“
- 2.) Tobias Dunaj, Kevin Dollberg, Prof. Dr Carsten von Hänisch, *Dalton Trans.*, **2022**, 51, 7551-7560. „Binary interpnictogen compounds bearing diaryl bismuth fragments bound to all lighter pnictogens“
- 3.) Tobias Dunaj, Prof. Dr. Carsten von Hänisch, *Chem. Eur. J.*, **2022**, 28, e202202932. „Heavy Chains: Synthesis, Reactivity and Decomposition of Interpnictogen Chains with Terminal Diaryl Bismuth Fragments“
- 4.) Tobias Dunaj, Marina Egorycheva, Ahmed Arebi, Kevin Dollberg, Carsten von Hänisch, *Z. Anorg. Allg. Chem.*, Manuskript vorläufig angenommen. „2,6-Diisopropylphenyl substituted Bismuth Halide and Interpnictogen Compounds“
- 5.) Tobias Dunaj, Johannes Schwarzmann, Jacqueline Ramler, Andreas Stoy, Sascha Reith, Joel Nitzsche, Lena Völlinger, Carsten von Hänisch and Crispin Lichtenberg, *Chem. Eur. J.*, Manuskript eingereicht am 23.12.2022. „Bismuth Cations: Fluoride Ion Abstraction, Isocyanide Coordination, and Impact of Steric Bulk on Lewis Acidity“

VIP Very Important Paper

2,6-Diisopropylphenyl-Substituted Bismuth Compounds:
Synthesis, Structure, and ReactivityTobias Dunaj,^[a] Kevin Dollberg,^[a] Christian Ritter,^[a] Fabian Dankert,^[a] and
Carsten von Hänisch^{*[a]}

The 2,6-diisopropylphenyl (Dipp) substituent is introduced to diaryl bismuth chemistry. Dipp₂BiBr (**1-Br**) was prepared by a Grignard reaction and subsequently used as precursor for synthesis of the other diaryl halido bismuthanes Dipp₂BiX (**1-X**, X=F, Cl, I) and the corresponding triflate Dipp₂BiOTf (**1-OTf**). Moreover, 1,1,2,2-tetrakis(2,6-diisopropylphenyl)dibismuthane (**2**) was prepared. All isolated compounds were characterized via single crystal X-ray diffraction analysis, NMR spectroscopy, IR

spectroscopy, and elemental analysis. Furthermore, the reactivity of a dibismuthane towards elemental sulfur was investigated, and the formed dibismuthanyl tri- and pentasulfide (**3a**, **3b**) were characterized by single crystal X-ray analysis. Functionalization of the diaryl halido bismuthanes with LiPtBu₂ or tBu₂PTMS (TMS=SiMe₃) gives access to the interpnictogen compound Dipp₂Bi–PtBu₂ (**4**), which shows a rare example of a covalent Bi–P bond.

Introduction

Diaryl halido bismuthanes can be prepared *via* salt metathesis,^[1–4] or redistribution reactions of two equivalents of a triaryl bismuthane and a bismuth trihalides.^[1,5–10] Moreover, diaryl bismuth halides of the heavier halogens can be prepared *via* halogen exchange reactions with alkaline or earth alkaline metal halides and diaryl bismuth halides of lighter halogens.^[1,11,12] It is common for bismuth halides to show secondary bonding interactions between bismuth and halogen atoms of neighboring molecules in the solid state.^[8–10,12–14] The tendency for intermolecular interactions lowers when sterically more demanding substituents are employed.^[2,4] Consequently, steric demand greatly influences the solid state structure of substituted halido bismuthanes. Most dialkyl and diaryl halido bismuthanes with low steric bulk around the bismuth center form one dimensional polymeric chains with alternating bismuth and halide atoms.^[9,10,12–14] Sterically shielded dialkyl and diaryl halido bismuthanes form monomers,^[2,4] dimers^[8] or oligomers.^[12] The monomeric, 2,6-dimesitylphenyl (Ter) substituted, chloro bismuthane (Ter₂BiCl) and the polymeric, mesityl substituted, bromo bismuthane (Mes₂BiBr) are shown in Figure 1 as examples.

Through reaction of a diaryl or dialkyl halido bismuthane with alkali and alkaline earth metals dibismuthanes are

obtained *via* reductive coupling.^[3,15–17] Another reaction pathway towards dibismuthanes is the reaction with hydride sources. Here, a secondary bismuthane is produced in the first reaction step, decomposing to the corresponding dibismuthane under elimination of dihydrogen.^[18–22] Such dibismuthanes are known to react with element-element bonds and have successfully been used for the activation of chalcogens^[16,23–26] and even white phosphorus.^[19] It was shown recently, that dibismuthanes are also suitable as catalysts in dehydrocoupling reactions.^[22]

Recently, we showed that interpnictogen compounds are useful as precursors for the preparation of doped semiconductors *via* MOCVD processes.^[27–31] Using aryl substituents at bismuth, could give access to interpnictogen compounds that prove useful as precursors.

In this report, the 2,6-diisopropylphenyl-substituent (Dipp) is introduced to diaryl bismuthane chemistry. Diaryl halido bismuthanes of all halides (X=F, Cl, Br, I) and the corresponding triflate compound (Dipp₂BiOTf) were prepared and their structures were examined. The 1,1,2,2-tetrakis(2,6-diisopropylphenyl)dibismuthane was obtained and its reactivity towards elemental sulfur was investigated. Moreover, an interpnictogen compound with a Bi–P bond was obtained by functionalization of the diaryl halido bismuthanes with LiPtBu₂ or tBu₂PTMS (TMS=SiMe₃).

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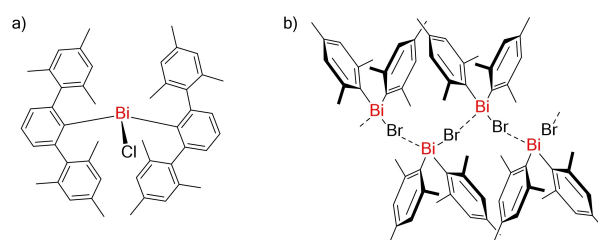


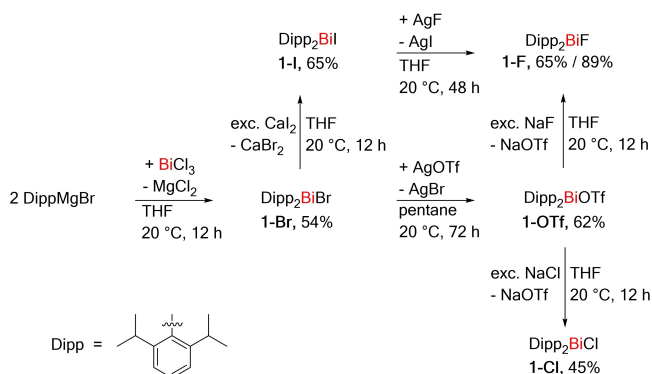
Figure 1. (a) Monomeric Ter₂BiCl. (b) Polymeric Mes₂BiBr.^[4,9]

Results and Discussion

Synthesis of the diaryl halido bismuthanes Dipp_2BiX ($\text{X}=\text{F}$, Cl , Br , I) and $(\text{Dipp}_2\text{Bi})_2$

It is reported in the literature, that chlorobis(2,4,6-triisopropylphenyl)bismuthane can be prepared from the corresponding Grignard reagent, 2,4,6-triisopropylphenylmagnesium bromide, and BiCl_3 .^[1] Applying this synthetic protocol, 2,6-diisopropylphenylmagnesium bromide was reacted with BiCl_3 in THF. The reaction did not yield the expected chloro bismuthane as reported for the 2,4,6-triisopropylphenyl substituent. Rather the corresponding bromo-bis(2,6-diisopropylphenyl)bismuthane (**1-Br**) was obtained as an orange solid in 54% yield. This is probably due to halide exchange with MgBrCl , produced during the reaction. This reaction can easily be performed in a gram scale. Repeating the reaction on a milligram scale using BiBr_3 , gives a better yield of 67%. Halide exchange reactions are well known in aryl and alkyl bismuth chemistry and often applied to obtain iodo bismuthanes.^[1,11,12,21,32] Consequently, the (2,6-diisopropylphenyl)iodobismuthane (**1-I**) was prepared by the reaction of **1-Br** with CaI_2 in THF at 20 °C and obtained as deep red crystals from pentane solution in 65% yield. The compounds **1-Br** and **1-I** show thermochromism, becoming pale yellow upon cooling to liquid nitrogen temperatures. Moreover, solutions of **1-Br** and **1-I** are yellow, opposed to the orange or red bulk material. Obtaining the chloro-(2,6-diisopropylphenyl)bismuthane **1-F** from **1-Br** via halide exchange reaction was neither possible with the sodium, nor the silver halides. Using **1-I** in the reaction with silver fluoride, **1-F** can be obtained as colorless solid in 66% yield. The solution to obtain the chloro bismuthane, and **1-F** in higher yield, was the reaction of **1-Br** with silver triflate. The corresponding (2,6-diisopropylphenyl)triflatobismuthane **1-OTf** was obtained as a yellow solid in 62% yield. Using **1-OTf** as precursor, reaction with NaF or NaCl respectively, gave access to **1-F** and also **1-Cl**. Compound **1-F** was obtained in 89% and **1-Cl** in 45% yield (see Scheme 1 for an overview of the herein synthesized bismuthanes).

Upon reaction of the sterically shielded Ter_2BiCl with a hydride source, the first stable molecular secondary bismuthane



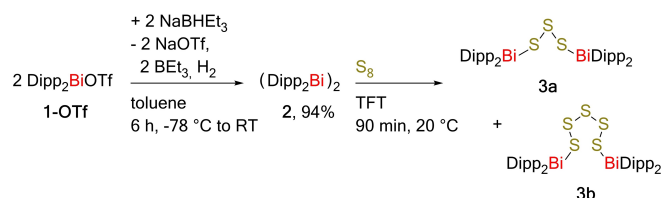
Scheme 1. Synthesis of **1-F**, **1-Cl**, **1-Br** and **1-OTf**.

was isolated by Power et al.^[4] For sterically less shielded halido bismuthanes, dibismuthanes are obtained in similar reactions.^[18–20] Reaction of **1-Br** or **1-OTf** with NaBHET_3 , at $-50\text{ }^\circ\text{C}$ in toluene gives a red solution that turns black upon warming to room temperature. After work up of the reaction mixture, the 1,1,2,2-tetrakis(2,6-diisopropylphenyl)dibismuthane (**2**) is obtained as black, light sensitive solid in 94% yield. The red color at the start of the reaction, might be due to thermochromic behavior or indicate formation of the hydride Dipp_2BiH , decomposing to **2** at higher temperature. However, the assumed bismuth hydride intermediate could not be isolated or spectroscopically characterized due to lack of thermal stability. The same behavior was observed in the literature for the reaction of Mes_2BiCl with LiBH_4 or LiAlH_4 , or the reaction of $(\text{C}_2\text{F}_5)_2\text{BiBr}$ and Bu_3SnH .^[21,22] Compound **2** shows intense thermochromism, turning bright pink upon cooling to liquid nitrogen temperatures. Diluted solutions of **2** are yellow, turning black upon concentrating the solution.

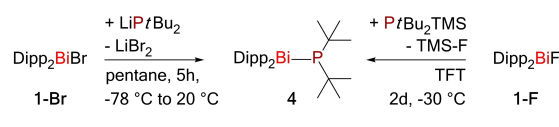
Reaction of **2** with sulfur

Aryl substituted dibismuthanes are known to react with elemental sulfur, leading to the insertion of a sulfur atom into the Bi–Bi bond.^[16,24,25] Reaction of **2** with $1/8 \text{ S}_8$ in α,α,α -trifluorotoluene (TFT) did not lead to complete conversion of the dibismuthane, even after stirring for 12 hours. In the next experiment, **2** and $2/8 \text{ S}_8$ were stirred for 90 minutes in TFT. Complete consumption of the black compound **2** was indicated by a color change of the reaction mixture, turning yellow. After workup, cooling of a concentrated solution in pentane gave crystals of a dibismuthanyl tri- (**3a**) and a pentasulfide (**3b**) both of which were suitable for single crystal X-ray diffraction analysis (see Scheme 2). Due to the stoichiometry in the reaction, **3a** and **3b** must be side products, assuming complete consumption of **2**. The insertion of S_n -chains ($n=1, 3, 5$) into a Bi–Bi single bond is known in the literature for bis(amidodimethyl)disiloxane substituted dibismuthanes, with n being depended on steric bulk of the ligands.^[23] For solely aryl or alkyl substituted dibismuthanes, only the insertion of one

a. Formation of Dibismuthane **2** and reaction with sulfur.



b. Formation of the phospha-bismuthane **4**.



Scheme 2. (a) Synthesis of **3a** and **3b** via reaction of **2** with elemental sulfur. (b) Synthesis of **4** via salt elimination and via silyl-halide abstraction.

sulfur atom into the Bi–Bi bond is reported so far.^[16,24,25] The reaction of **2** with sulfur shows, that the insertion of a S_3 or S_5 unit is also possible for solely aryl substituted dibismuthanes. The obtained mixture of compounds was examined *via* 1H NMR spectroscopy, showing at least two different Dipp substituted compounds. Unfortunately, the 1H NMR spectrum of the bulk does not give insights, which signal sets corresponds to the found species. It can also not be excluded, that one species might correspond to a single sulfur “ S_1 ”-bridged species. So far, it was not possible to obtain **3a** or **3b** in analytically pure form.

Functionalization with phosphanes

With the earliest mention of a bismuth phosphide complex in 1999, examples for covalent Bi–P bonds are very rare in the literature.^[10,19,33–37] The formation of the Bi–P bond is realized by the reaction of a halido bismuthane and either a lithium phosphide or silyl phosphane. Upon reaction of **1-Br** with $LiPtBu_2$ in pentane, the phosphabismuthane $Dipp_2BiPtBu_2$ (**4**) was obtained. Reaction of **1-Br** with $PtBu_2TMS$ ($TMS = SiMe_3$) did not yield the desired product as no reaction was observed, even after several days. Using **1-F** though, reaction with $PtBu_2TMS$ proceeds smoothly *via* formation of Me_3SiF and **4** (see Scheme 2). Red, light and temperature sensitive, crystals, suitable for single crystal X-ray diffraction, were obtained from a pentane solution at $-32^\circ C$. The successful synthesis of **4** shows that the compounds **1-X** are indeed useful starting materials for the formation of new binary group 15 compounds containing bismuth. For application in MOCVD processes, the metal organic compounds have to be volatile. This is not the case for compound **4**. Nevertheless, the insights gained by the synthesis of **4** will be of use in the preparation of bismuth containing interpnictogen compounds bearing smaller substituents. A more detailed analysis of such binary precursor molecules of group 15 elements will be published soon.

Spectroscopic data analysis

The 1H NMR spectra of all compounds **1-X** ($X = F, Cl, Br, I, OTf$) and **4** show one set of signals corresponding to a Dipp substituent indicating C_s symmetry for the compounds **1-X** and **4**. From heavier to the lighter halogens, the aromatic signals of the Dipp substituent are shifted towards a lower field. The aromatic protons of **1-OTf** show an even stronger low field shift. The chemical shift of the ipso-carbon atom in the ^{13}C NMR spectra of compounds **1-X** show the same trend (**1-I**: $\delta = 174.5$; **1-Br**: $\delta = 181.9$; **1-Cl**: $\delta = 185.6$; **1-F**: $\delta = 191.1$; **1-OTf**: 207.6). This strong deshielding indicates a trend in group electronegativity of the Bi–X fragment, lowest in **1-I** and highest in **1-OTf**. The deshielding effect corresponds well with literature known diaryl halido and triflato bismuthanes.^[1,5,38–40] The ^{19}F NMR chemical shift of **1-F** ($\delta = -215.5$) in C_6D_6 is considerably high field shifted compared to literature known diaryl or dialkyl fluoro bismuthanes ($\delta = -171.9$ to -188.7).^[21,41,42] This indicates a stronger shielding of the fluorine nucleus compared to literature known

compounds. The bismuth atoms of the R_2BiF compounds described in the literature are either coordinated by an intramolecular lewis-base or NMR spectra were recorded in donating solvents like acetonitrile.^[21,41,42] To exclude, that the high field shift in the ^{19}F NMR spectrum is attributed to the use of a donor free deuterated solvent, spectra of **1-F** were also measured using CD_3CN as a solvent. The chemical shift in the ^{19}F NMR spectrum ($\delta = -213.1$ ppm) is almost identical to that in C_6D_6 , indicating no coordination of CD_3CN to the bismuth centre due to the steric demand of the Dipp substituents. Compound **4** shows the expected signals for the Dipp substituents in the 1H and ^{13}C NMR-spectra. The ^{31}P NMR spectrum shows a broadened signal at 84.3 ppm, matching well to other literature known dialkyl phosphabismuthanes.^[10,19,36]

In the MS spectra, a signal corresponding to the ionized molecular species was observed for **1-Br**, **1-I** and **1-OTf**, although only of low intensity. For **2** and **4** signals corresponding to fragments arising from Bi–Bi or Bi–P bond cleavage are observed. The main signals in all recorded spectra correspond to the fragments $Dipp_2Bi^+$ and $DippBi^+$, showing that cleavage of the Bi–X bond is favored, compared to the Bi–C bond.

The IR spectra of the isolated components show the expected bands for the Dipp substituent. For **1-OTf** additional bands for SO stretching modes are identified at 1332, 1100 and 975 cm^{-1} . Moreover, bands for the stretching vibrations of the CF_3 group are observed at 1190 and 1160 cm^{-1} . The positions of the SO bands fits to a covalently bound triflate anion.^[43–47] This was confirmed by single crystal X-ray diffraction.

Single crystal X-ray analysis

Compound **1-F** crystallizes in the monoclinic space group $P2_1/c$ with $Z = 4$. The intramolecular Bi1–F1 bond length has a value of 211.5(3) pm. Moreover, a secondary bonding interaction between the fluoride atom and a bismuth atom of a neighboring molecule with a Bi1–F1' distance of 304.6(3) pm is observed. This value is clearly smaller than the sum of the van der Waals radii (354 pm).^[48,49] This results in one dimensional polymer strings of alternating Bi and F atoms along the crystallographic *c*-axis (Figure 2) with alternating short and long Bi–F distances. There are only few structurally described dialkyl or diaryl fluoro bismuthanes in the literature,^[21,41,42] with **1-F** being the first donor free compound. To the best of our knowledge, **1-F** shows the shortest intramolecular Bi–F bond of a Bi(III) compound so far. Like **1-F**, the compounds $(C_2F_5)_2BiF$ -acetone^[21] and $[MeO-(C_2H_4)-N(CH_2C_6H_4)_2]BiF$ ^[42] form polymer chains in the solid state. Due to less steric demand, the intra- and intermolecular Bi–F bond lengths in $(C_2F_5)_2BiF$ -acetone are almost equal in length (222.9(2) and 226.2(2) pm).^[21] Thus the intramolecular Bi–F bond length in **1-F** is shorter, while the intermolecular bond length is much longer. In $[MeO-(C_2H_4)-N(CH_2C_6H_4)_2]BiF$, the Bi atom is coordinated intramolecularly by N and O leading to longer intra- and intermolecular Bi–F bond lengths of 221.3(4) and 358.8(5) pm,^[42] compared to **1-F**. With an Bi1–F1–Bi1' angle of $175.8(1)^\circ$, the fluorine atoms in **1-F** are almost linearly coordinated. The

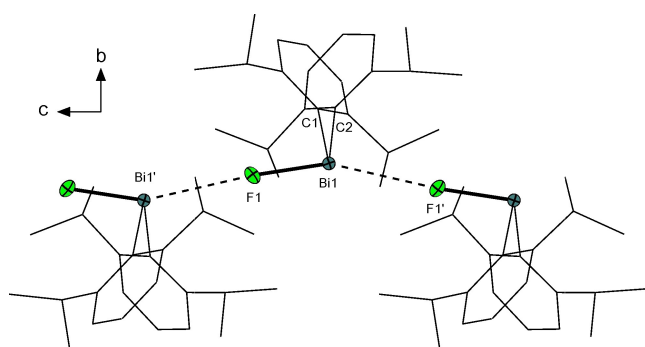


Figure 2. Molecular structure of **1-F** in the solid state. Hydrogen atoms are omitted and Dipp substituents are shown as wire model for clarity. Ellipsoids are shown at a 50% probability level. Molecules corresponding to atoms labelled with an apostrophe are symmetry generated using $x, 1/2 - y, 1/2 + z$ and $x, 1/2 - y, -1/2 + z$. Selected bond lengths (pm) and angles (deg): Bi1-F1 211.5(3); Bi1-F1' 304.6(3); Bi1-C1 228.6(6); Bi1-C2 229.3(6); C1-Bi1-C2 97.2(2); F1-Bi1-C1 92.0(2); F1-Bi1-C2 96.4(2); Bi1-F1-Bi1' 175.8(1); F1-Bi1-Bi1' 158.3(1).

F1-Bi1-F1' angle is 158.3(1)°, which results in a seesaw coordination of the bismuth atom. The F1-Bi1-C1 angle is slightly larger compared to the F1-Bi1-C2 angle (96.4(2)° vs. 92.0(2)°). This is most likely a consequence of steric repulsion of the isopropyl group of one Dipp substituent and the fluorine atom.

The compounds **1-Cl** and **1-Br** crystallize isostructural in the trigonal space group $R\bar{3}$ with $Z=18$ and do not form one-dimensional strings. Instead, hexamers containing a ring of alternating Bi and X (X=Cl, Br) atoms are formed (Figure 3). The Bi-Cl bond length of 255.15(9) pm in **1-Cl** is longer than in the monomeric (2,6-Mes₂H₃C₆)₂BiCl (248.3(3) pm),^[4] but smaller than

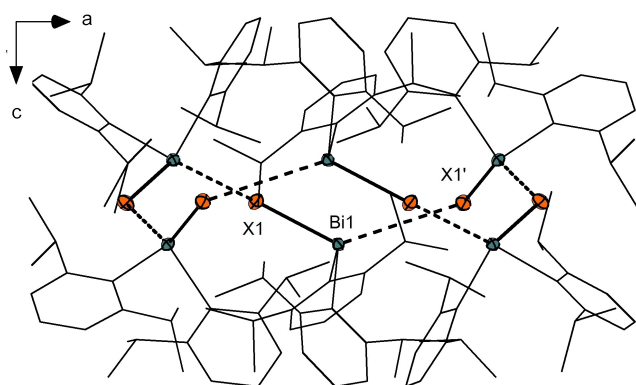


Figure 3. Structure of the hexamer formed by **1-Br** in the solid state with view along the crystallographic and b -axis. Hydrogen atoms are omitted and the Dipp substituents are shown as wire model for clarity. Ellipsoids are shown at a 50% probability level. Molecules not labelled or corresponding to atoms labelled with an apostrophe are symmetry generated using $1/3 + x, 2/3 - x + y, 2/3 - z; 1 - x, y, z; 4/3 - x, 2/3 - y, 2/3 - z; 1 - y, x - y, z; 1/3 + x - y, -1/3 + x, 2/3 - z$. Compound **1-Cl** crystallizes isostructural. Selected bond lengths (pm) and angles (deg) for **1-Br**: Bi1-Br1 270.19(6); Bi1-Br1' 387.71(7); Bi1-C1 229.2(3); Bi1-C2 228.2(3); C1-Bi1-Br1 110.31(7); C2-Bi1-Br1 92.66(7); C1-Bi1-C2 96.8(1); Bi1-Br1-Bi1' 129.35(2); Br1-Bi1-Br1' 134.13(2). Selected bond lengths (pm) and angles (deg) for **1-Cl**: Bi1-Cl1 255.15(9); Bi1-Cl1' 387.7(1); Bi1-C1 228.1(4); Bi1-C2 229.4(3); C1-Bi1-Cl1 92.84(8); C2-Bi1-Cl1 108.60(8); C1-Bi1-C2 96.3(1); Bi1-Cl1-Bi1' 131.49(3); Cl1-Bi1-Bi1' 134.90(3).

in polymeric Ph₂BiCl (274.6(4) pm).^[13] With 387.7(1) pm, the intermolecular Bi-Cl' distance is far larger than in Ph₂BiCl (276.3(3) pm)^[13] and even slightly larger than the sum of the van der Waals radii (382 pm).^[48,49] Hence, it is questionable, whether the formation of oligomers in the solid state can be traced to coulomb interactions between molecules or if they play no decisive role in structure formation. The intramolecular Bi-Br bond length of 270.19(6) pm in **1-Br** corresponds well to the literature known in Mes₂BiBr (269.6(2) pm).^[9] Contrary, the intermolecular Bi-Br' distance of 387.71(7) pm is elongated compared to Mes₂BiBr (379.5(3) pm),^[9] but still beneath the sum of van der Waals radii (390 pm).^[48,49] As in **1-F**, the long intermolecular Bi-X distances are attributed to the steric demand of the two Dipp substituents around the Bi atom. With 131.49(3)° (**1-Cl**) and 129.35(2)° (**1-Br**), the Bi-X-Bi' bond angles are significantly smaller than in the previously discussed **1-F**. Same holds true for the Br-Bi-Br' angles. With 134.90(3)° (**1-Cl**) and 134.13(2)° (**1-Br**), the X-Bi-X' angle in the seesaw coordinated bismuth atom also becomes smaller, compared to **1-F**. Similarly to **1-F**, the steric demand of the Dipp substituent leads to one large C-Bi-X angle (**1-Cl**: 108.60(8)° vs. 92.84(8)°; **1-Br**: 110.21(6)° vs. 92.66(7)°). As expected, this effect becomes more pronounced for the heavier and larger halides. The orange **1-Br** shows thermochromism, yielding a pale yellow solid upon cooling to liquid nitrogen temperatures. Investigation *via* temperature dependent powder X-ray diffraction and cooling to up to -170 °C did not show phase transitions. The XRD patterns can be found in the supplementary information.

Compound **1-I** crystallizes in the monoclinic space group $P2_1/n$ with $Z=4$. The Bi-I bond length of 289.74(4) pm corresponds well with other donor free dialkyl and diaryl iodo bismuthanes, forming weak intermolecular bonds (278.5–286.9 pm).^[10,21,38] In contrast to the other halogen compounds **1-X** (X=F, Cl, Br) and many literature-known diaryl or dialkyl iodo bismuthanes,^[10,12,21] **1-I** does not show secondary intermolecular interactions of bismuth and halogen atoms. Rather, dimers with short Bi-Bi' contacts of 396.54(4) pm are formed in the solid state (see Figure 4). The Bi-Bi' distance in this dimer is considerably shorter than the sum of the van der Waals radii (414 pm).^[48] Short intermolecular Bi-Bi' distances in the solid state are not unheard of in the literature. Reported dimeric compounds with short Bi-Bi contacts in the crystal structure include Me₃Bi (389.9(1) pm),^[50] (m-(C₂H₄)C₆H₃)₃Bi (395.94(5) pm)^[51] or [Ph-(C₂H₄)-N(CH₂C₆H₄)₂]BiCl (397.39(9) pm).^[42] It was shown *via* coupled cluster and dispersion corrected DFT methods, that the secondary bonding interaction in Me₃Bi is dispersion-dominated.^[50] The weak interaction within dimers of the pnictogen trihalides was also subject of a theoretical study. It is reported that binding interactions in these compounds are dispersion dominated, but also show significant ionic contribution.^[52] Consequently, it can be assumed that the Bi-Bi interaction in **1-I** is also mostly dispersion dominated. Using the Bi-Bi bond length in the dibismuthane **2** for the calculation of the ratio between the Bi-Bi distance in **1-I** and a Bi-Bi single bond, a value of 1.31 is obtained. According to Breunig et al., compounds with short Pn-Pn contacts, where this ratio is lower than 1.4, show thermochromism.^[52] This also holds true for **1-I**,

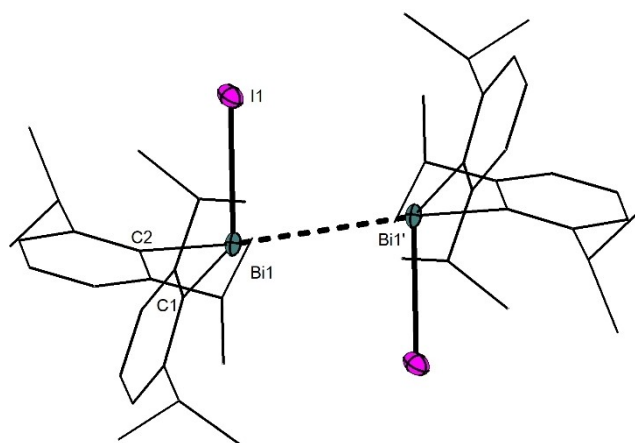


Figure 4. Molecular structure of the **1-I** dimer in the solid state. Hydrogen atoms are omitted and Dipp substituents are shown as wire model for clarity. Ellipsoids are shown at a 50% probability level. Molecules corresponding to atoms labelled with an apostrophe are symmetry generated using $1-x, 1-y, 1-z$. Selected bond lengths (pm) and angles (deg): Bi1-I1 289.74(4); Bi1-C1 229.8(2); Bi1-C2 229.3(3); Bi1-Bi1' 396.54(4); C1-Bi1-I1 111.67(7); C2-Bi1-I1 95.70(6); C1-Bi1-C2 96.20(9); I1-Bi1-Bi1' 85.29(1).

changing color from deep red at room temperature to pale yellow at liquid nitrogen temperatures.

Compound **1-OTf** crystallizes in the monoclinic space group $P2_1/n$ with $Z=4$. The Bi–O bond length of 231.9(1) pm is significantly shorter than in the corresponding Ph_2BiOTf (253.1(6) pm).^[39] The literature known Ph_2BiOTf forms one

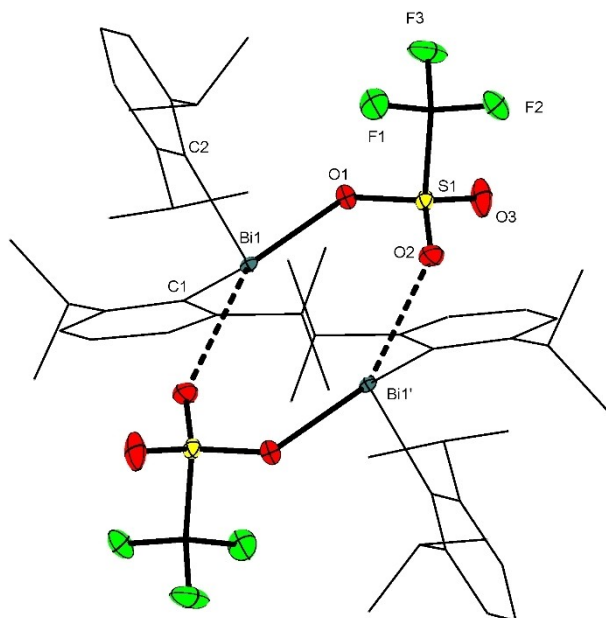


Figure 5. Molecular structure of the **1-OTf** dimer in the solid state. Hydrogen atoms are omitted and Dipp substituents are shown as wire model for clarity. Ellipsoids are shown at a 50% probability level. Molecules corresponding to atoms labelled with an apostrophe are symmetry generated using $1-x, 1-y, 1-z$. Selected bond lengths (pm) and angles (deg): Bi1-O1 231.9(1); Bi1-C1 226.7(2); Bi1-C2, 226.8(2); Bi1-O2' 349.8(2); C1-Bi1-O1 99.66(5); C2-Bi1-O1 90.49(5); C1-Bi1-C2 97.61(6); O1-Bi1-O2' 150.39(4).

dimensional polymers with multiple inter- and intramolecular short contacts, explaining the elongation of the Bi–O bond. Contrary, **1-OTf** forms dimers *via* intermolecular secondary bonding interactions of a second oxygen atom of a triflate anion and a neighboring bismuth atom (Figure 5). This bridging motif is known for several bismuth compounds with examples including $\text{Mes}(o\text{-(Me}_2\text{N(CH}_2)_6\text{H}_4)\text{BiOTf}$ or $(o\text{-(tBuO)}_2\text{C}_6\text{H}_3)\text{BiOTf}_2$.^[44,54] The intermolecular Bi–O distance of 349.8(2) pm is slightly shorter than the sum of the van der Waals radii (359 pm).^[48,49] The formation of a dimeric structure with fewer but shorter Bi–O contacts is caused by steric shielding of the Bi atoms through the bulky Dipp substituents. As in the previous compounds, the Bi atom is coordinated by four substituents in a seesaw manner with an O1–Bi1–O2' angle of 150.39(4)°.

Compound **2** crystallizes in the monoclinic space group $C2/c$ with $Z=4$ with half a molecule representing the asymmetric unit (Figure 6). With 302.02(2) pm, the Bi–Bi bond length is similar to related compounds like $(\text{Ph}_2\text{Bi})_2$ (299.0(2) pm) or $(\text{Mes}_2\text{Bi})_2$ (308.7(3) pm) described in the literature.^[20,55] The Bi–C distances and the angles around the bismuth center correspond well with the previously discussed compounds. Compound **2** shows intense thermochromism, turning bright pink when cooled to liquid nitrogen temperatures.

An inseparable mixture of products was obtained by reaction of **2** with sulfur. Two species, the trisulfide and the pentasulfide, were identified *via* single crystal X-ray analysis after choosing crystals from the mixture mechanically. Due to similar color and habitus, bulk material of **3a** and **3b** could not be obtained separately. The trisulfide **3a** crystallizes in the monoclinic space group $P2_1/c$ with $Z=4$ (Figure 7) and the

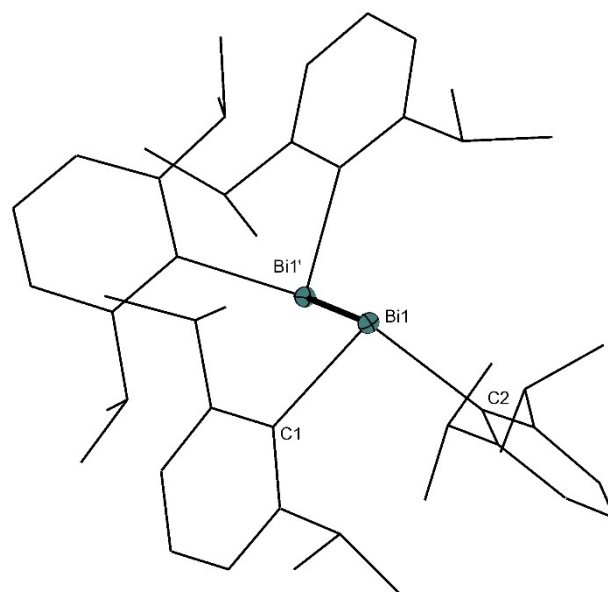


Figure 6. Molecular structure of **2** in the solid state. Hydrogen atoms are omitted and Dipp substituents are shown as wire model for clarity. Ellipsoids are shown at a 50% probability level. Molecules corresponding to atoms labelled with an apostrophe are symmetry generated using $1-x, y, 3/2-z$. Selected bond lengths (pm) and angles (deg): Bi1-Bi1' 302.02(2); Bi1-C1 231.8(2); Bi1-C2 232.2(2); C1-Bi1-Bi1' 91.14(5); C2-Bi1-Bi1' 111.66(6); C1-Bi1-C2 94.97(8).

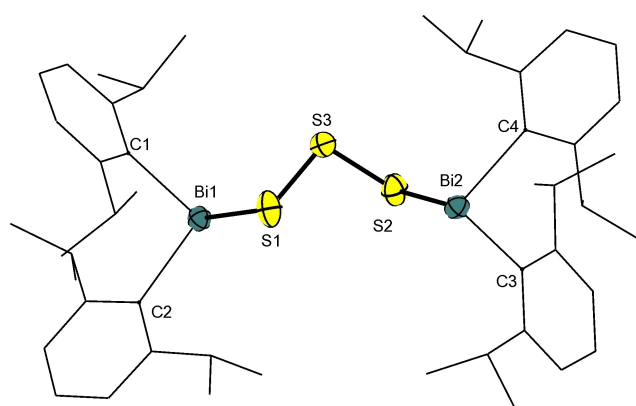


Figure 7. Molecular structure of **3a** in the solid state. Hydrogen atoms are omitted and Dipp substituents are shown as wire model for clarity. Atoms labelled with an apostrophe are symmetry generated using $1-x, y, 3/2-z$. Ellipsoids are shown at a 50% probability level. Selected bond lengths (pm) and angles (deg) for **3a**: Bi1-S1 258.6(1); Bi2-S2 258.8(1); Bi1-C1 228.3(3); Bi1-C2 229.6(4); Bi2-C3 228.5(4); Bi2-C4 229.9(4); S1-S3 204.7(2); S2-S3 206.1(2); C1-Bi1-S1 94.3(1); C2-Bi1-S1 108.2(1); C1-Bi1-C2 93.8(1); Bi1-S1-S3 93.9(6); C3-Bi2-S2 90.7(1); C4-Bi2-S2 110.2(1); C3-Bi2-C4 95.3(1); Bi2-S2-S3 97.4(6); S1-S3-S2 106.9(9).

pentasulfide **3b** in the orthorhombic space group $Pbcn$ with $Z=4$ with only half a molecule representing the asymmetric unit (Figure 8). Within the standard deviation, the S–S bond lengths and S–S–S angles in **3a** and **3b** correspond well with the average bond lengths and angles in elemental S_8 .^[56–58] With a bond length of 258.6(1) pm and 258.8(1) pm, the Bi–S bond length in **3a** fit in with other literature known Bi–S bonds of compounds with an $(Ar_2Bi)_2S_n$ ($n=1, 3, 5$; (252–260 pm)) structure.^[20,59] In comparison, the Bi–S bond of **3b** (260.1(2) pm) is slightly longer. An example for a longer Bi–S bond than in **3b** is described in one compound of the form $RBi-(S_5)_2-BiR$ ($R=o-(CH_2NMe_2)_2C_6H_3$) showing a twelve membered Bi_2S_{10} ring,

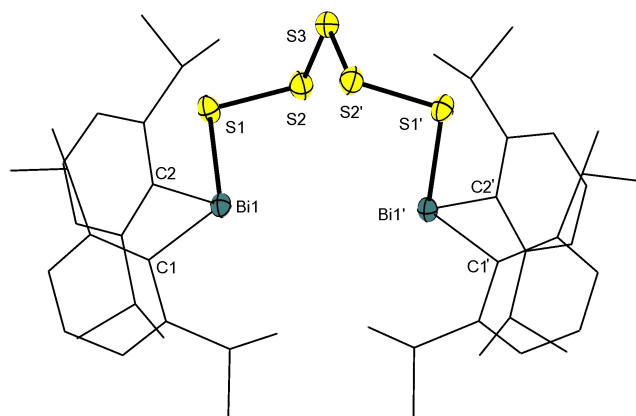


Figure 8. Molecular structure of **3b** in the solid state. Hydrogen atoms are omitted and Dipp substituents are shown as wire model for clarity. Atoms labelled with an apostrophe are symmetry generated using $1-x, y, 3/2-z$. Ellipsoids are shown at a 50% probability level. Selected bond distances (pm) and angles (deg) for **3b**: Bi1-S1 260.1(2); Bi1-C1 228.1(6); Bi1-C2 229.5(5); S1-S2 204.3(2); S2-S3 206.3(2); C1-Bi1-S1 90.2(2); C2-Bi1-S1 104.5(1); C1-Bi1-C2 94.6(2); Bi1-S1-S2 101.11(8); S1-S2-S3 107.74(9); S2-S3-S2' 105.95(7).

stabilized by NCN-type pincer ligands at the bismuth atoms (Bi–S: 275–277 pm). The authors ascribe the elongated bond length to a polarized Bi–S bond, with the positive charge at the bismuth atoms being stabilized by the pincer ligand.^[60] The C–Bi–S angles around the bismuth atom are similar as in the previously discussed Dipp substituted structures ($Dipp_2BiX$, $X=Cl, Br$) with each Bi atom showing one small (**3a**: 94.3(1)°, 90.7(1)°; **3b**: 90.2(2)°) and one larger (**3a**: 108.2(1)°, 110.2(1)°; **3b**: 104.5(1)°) angle due to steric repulsion of the polysulfide chain and one Dipp substituent. The Bi–Bi' distance in **3b** is 442.40(5) pm, far larger than the sum of the van der Waals radii (414 pm),^[49] indicating no interaction between the bismuth atoms.

Compound **4** crystallizes in the triclinic space group $P\bar{1}$ with two molecules in the asymmetric unit (Figure 9). The Bi–P bond in **4** (269.80(7) pm and 270.14(7) pm) is slightly elongated compared to most literature known neutral phosphabismuthanes (258.9(2)–269.5(7) pm).^[10,19,33–37] The elongation is most likely a result of the sterically shielding Dipp substituents. The steric demand also reflects in the large C1–Bi1–P1–C3 torsion angles of 106.97 (9) °.

Conclusion

The Dipp substituent is introduced to diaryl bismuth chemistry. The respective diaryl halido bismuthanes **1-X** ($X=F, Cl, Br, I$) were prepared and fully characterized. Their solid state structures were examined *via* single crystal X-ray diffraction and it was shown that the solid state structure is strongly depended

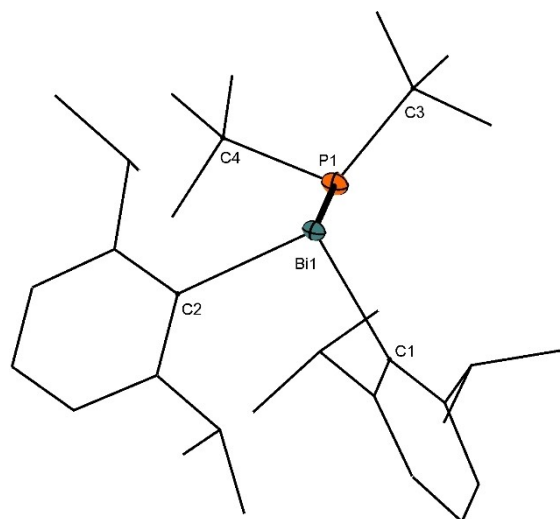


Figure 9. Molecular structure of **4** in the solid. One of two molecules of the asymmetric unit are shown. Hydrogen atoms are omitted and Dipp and *t*Bu substituents are shown as wire model for clarity. Ellipsoids are shown at a 50% probability level. Selected bond lengths (pm) and angles (deg) for **4**: Bi1-P1 269.80(7); Bi1A-P1A 270.14(7); Bi1-C1 232.1(2); Bi1A-C1A 233.8(2); Bi1-C2 230.5(2); Bi1A-C2A 231.4(2); P1-C3 192.0(2); P1A-C3A 191.2(2); P1-C4 190.6(2); P1A-C3A 190.4(2); C1-Bi1-C2 95.09(7); C1A-Bi1A-C2A 95.91(7); C1-Bi1-P1 108.5(5); C1A-Bi1A-P1A 107.99(5); C2-Bi1-P1 104.01(5); C2A-Bi1A-P1A 104.52(5); C3-P1-C4 109.03(9); C3A-P1A-C4A 109.34(9); C3-P1-Bi1 95.69(6); C3A-P1A-Bi1A 95.71(7); C4-P1-Bi1 102.58(6); C4A-P1A-Bi1A 103.55(7).

on the respective halogen atom attached to the bismuth center. While **1-F** forms one dimensional polymers, hexamers are formed in the solid state by **1-Cl** and **1-Br**. Compound **1-I** shows a dimeric structure in the solid state. Surprisingly, no secondary interaction between iodine and bismuth was observed. Rather short intermolecular Bi–Bi contacts are formed. Furthermore, the corresponding triflate compound **1-OTf** was prepared, fully characterized, and successfully used as a precursor for the synthesis of **1-F** and **1-Cl**. *Via* reaction of **1-Br** and sodium superhydride, the dibismuthane **2** was obtained. Its reactivity towards elemental sulfur was studied, leading to a mixture of products. In contrast to previously reported reactions of purely aryl- or alkyl- substituted dibismuthanes with sulfur, an S_n -chain ($n=3, 5$) was inserted into the Bi–Bi bond, rather than a single sulfur atom.^[16,24,25] The dibismuthanyl tri- and pentasulfide (**3a**, **3b**), were characterized *via* single crystal X-ray analysis. The ability of **2** to activate element-element bonds should be further examined to activate other chalcogens or even P_4 . The diaryl halido bismuthanes were further functionalized to compound **4** under formation of a covalent Bi–P bond. The reaction proceeds either *via* salt metathesis or trimethylsilyl fluoride abstraction. Compounds similar to **4** bearing a bismuth-pnictogen-bond could prove useful as single-source-precursors in MOCVD processes. Even though **4** is not volatile enough to be of use in MOCVD processes, its synthesis gives insides for the preparation of interpnictogen compounds containing bismuth. Systematic investigation of interpnictogen compounds with diaryl and dialkyl bismuth fragments and a higher vapor pressure as well as their application in MOCVD processes will be subject to future research.

Experimental Section

General Procedure. All manipulations were carried out under argon atmosphere and exclusion of light using standard Schlenk technique. All solvents used in the reactions and for crystallizations were dried *via* standard techniques, distilled, and stored under argon.^[61] Solvents were never stored longer than three weeks before use. DippBr, used for the preparation of DippMgBr-THF, $t\text{Bu}_2\text{PLi}$ and $t\text{Bu}_2\text{PTMS}$ were prepared according to literature known procedures.^[62–64] The 2,6-Disopropylaniline (TCl), $t\text{Bu}_2\text{PH}$ (Aldrich), $n\text{-BuLi}$ in hexane (Aldrich), Me_3SiCl (Aldrich), Mg (ITW), CaI_2 (Aldrich), AgOTf (Aldrich), NaF (Aldrich), NaCl (ITW), NaBH Et_3 in toluene (Alfa Aesar) and sulfur (Strem) were used as received. BiCl_3 (Strem) was freshly sublimed under reduced pressure before use in synthesis. NMR spectra were recorded using a Bruker Avance II 300 MHz and a Bruker Avance III 500 MHz spectrometer. The IR-spectra were recorded on a Bruker FT-IR spectrometer using the attenuated total reflectance (ATR) mode. For mass spectrometry (CI), a Jeol AccuTOF GCv was used. Elemental analysis was performed on a Vario MicroCube.

Synthesis of Dipp $_2$ BiBr (1-Br). BiCl_3 (6.00 g, 19.02 mmol) are dissolved in 50 ml THF and added dropwise to a solution of DippMgBr-THF (15.0 g, 44.43 mmol) in 50 ml THF at 0 °C. The reaction mixture is allowed to warm to room temperature and stirred overnight. After removal of volatile components under reduced pressure, the solid residue is suspended in pentane and filtered. Through concentration of the solution and cooling to –32 °C, **1-Br** is obtained as crystalline orange solid. Yield 54%. Elemental analysis for $\text{C}_{24}\text{H}_{34}\text{BiBr}$ calcd: C, 47.15; H, 5.61; found: C,

47.38; H, 5.61; ^1H NMR (500 MHz, C_6D_6) δ : 7.41 (d, $^3J_{\text{H-H}}=7.6$ Hz, 4H, *m-CH*), 7.24 (t, $^3J_{\text{H-H}}=7.6$ Hz, 2H, *p-CH*), 3.31 (sept, $^3J_{\text{H-H}}=6.6$ Hz, 4H, $\text{CH}(\text{CH}_3)_2$), 1.11 (d, $^3J_{\text{H-H}}=6.6$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 1.06 (d, $^3J_{\text{H-H}}=6.6$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, C_6D_6) δ : 181.9 (s, Bi–C), 156.5 (s, *m-C*), 129.5 (s, *p-C*), 127.9 (s, *o-C*), 38.9 (s, $\text{CH}(\text{CH}_3)_2$), 25.1 (s, $\text{CH}(\text{CH}_3)_2$), 24.4 (s, $\text{CH}(\text{CH}_3)_2$); IR (cm^{-1}): 3045 (w), 2958 (m) 2923 (w) 2861 (w), 1568 (w), 1458 (w), 1446 (w), 1413 (w), 1382 (w), 1363 (w), 1344 (w), 1259 (w), 1234 (w), 1176 (w), 1098 (w), 1043 (w), 1001 (w), 928 (w), 796 (s), 728 (m); HR-MS: Cl^+ m/z 611.1515 $[\text{M}+\text{H}]^+$; calcd 611.1726

Synthesis of Dipp $_2$ BiI (1-I). Compound **1-Br** (200 mg, 0.32 mmol) and CaI_2 (566 mg, 1.93 mmol) were suspended in 20 ml THF and stirred over 12 h at room temperature. After removal of volatiles under reduced pressure and 40 ml of pentane were added to the remaining solid. The solution was filtered and the filtrate was concentrated. By cooling to –32 °C, red crystals of **1-I** were obtained. Yield 62%. Elemental analysis for $\text{C}_{24}\text{H}_{34}\text{BiI}$ calcd: C, 43.78; H, 5.21; found: C, 43.78; H, 5.22; ^1H NMR (300 MHz, C_6D_6) δ : 7.36 (d, $^3J_{\text{H-H}}=7.6$ Hz, 4H, *m-CH*), 7.21 (t, $^3J_{\text{H-H}}=7.6$ Hz, 2H, *p-CH*), 3.32 (sept, $^3J_{\text{H-H}}=7$ Hz, 4H, $\text{CH}(\text{CH}_3)_2$), 1.11 (d, $^3J_{\text{H-H}}=6.6$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 1.06 (d, $^3J_{\text{H-H}}=6.7$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6) δ : 174.5 (s, Bi–C), 156.7 (s, *m-C*), 130.1 (s, *p-C*), 127.8 (s, *o-C*), 41.0 (s, $\text{CH}(\text{CH}_3)_2$), 25.6 (s, $\text{CH}(\text{CH}_3)_2$), 24.9 (s, $\text{CH}(\text{CH}_3)_2$); IR (cm^{-1}): 3040 (w), 2958 (m), 2924 (w), 2863 (w), 1569 (w), 1457 (m), 1444 (m), 1411 (w), 1382 (w), 1360 (w), 1260 (m), 1233 (w), 1097 (m), 1045 (m), 1019 (m), 998 (m), 798 (s), 728 (m); HR-MS: Cl^+ m/z 657.1437 $[\text{M}-\text{H}]^+$; calcd 657.1431

Synthesis of Dipp $_2$ BiOTf (1-OTf). Compound **1-Br** (2.2 g, 3.53 mmol) and AgOTf (1.00 g, 3.89 mmol) are suspended in 150 ml pentane and stirred over 72 h at room temperature. After removal of the solvent under reduced pressure, the remaining solid is suspended with 150 ml of toluene and filtered. Volatiles are removed under reduced pressure and the remaining yellow solid is washed two times with 20 ml pentane. Crystals suitable for X-ray diffraction were grown from a pentane/toluene mixture at 5 °C. Yield 62%. Elemental analysis for $\text{C}_{25}\text{H}_{34}\text{BiF}_3\text{O}_3\text{S}$ calcd: C, 44.12; H, 5.04; found: C, 44.02; H, 4.94; ^1H NMR (500 MHz, C_6D_6) δ : 7.62 (d, $^3J_{\text{H-H}}=7.6$ Hz, 4H, *m-CH*), 7.31 (t, $^3J_{\text{H-H}}=6.6$ Hz, 2H, *p-CH*), 2.76 (sept, $^3J_{\text{H-H}}=6.6$ Hz, 4H, $\text{CH}(\text{CH}_3)_2$), 1.06 (d, $^3J_{\text{H-H}}=6.6$ Hz, 24H, $\text{CH}(\text{CH}_3)_2$); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, C_6D_6) δ : 207.6 (s, Bi–C), 156.5 (s, *m-C*), 130.3 (s, *p-C*), 129.7 (s, *o-C*), 37.2 (s, $\text{CH}(\text{CH}_3)_2$), 23.9 (s, $\text{CH}(\text{CH}_3)_2$); IR (cm^{-1}): 3046 (w), 2996 (w) 2927 (w) 2868 (w), 1569 (w), 1462 (w), 1441 (w), 1388 (w), 1332 (m), 1190 (s), 1160 (m), 1100 (m), 1028 (w), 975 (s), 931 (w), 802 (w), 756 (w), 720 (w), 628 (s), 584 (w), 529 (w), 512 (w); HR-MS: Cl^+ m/z 531.2472 $[\text{M}-\text{OTf}]^+$; calcd 531.2464

Synthesis of Dipp $_2$ BiF (1-F). Compound **1-OTf** (400 mg, 0.59 mmol) and NaF (172 mg, 2.94 mmol) are suspended in 20 ml THF and stirred 12 h at room temperature. After removal of volatiles under reduced pressure, the remaining solid is taken up in 40 ml of toluene. The solution is filtered and all volatiles of the filtrate are removed under reduced pressure. The remaining residue is washed with cold pentane to obtain **1-F** as colorless solid. Crystals suitable for single crystal X-ray diffraction analysis are obtained from a solution of **1-F** in a pentane/ethanol mixture and cooling to –32 °C. Yield 89%. Elemental analysis for $\text{C}_{24}\text{H}_{34}\text{BiF}$ calcd: C, 52.36; H, 6.23; found: C, 51.96; H, 6.30; ^1H NMR (300 MHz, C_6D_6) δ : 7.45 (d, $^3J_{\text{H-H}}=7.6$ Hz, 4H, *m-CH*), 7.30 (t, $^3J_{\text{H-H}}=7.6$ Hz, 2H, *p-CH*), 3.24 (sept, $^3J_{\text{H-H}}=6.7$ Hz, 4H, $\text{CH}(\text{CH}_3)_2$), 1.12 (br s, 24H, $\text{CH}(\text{CH}_3)_2$); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, C_6D_6) δ : 191.1 (d, $^2J_{\text{C-F}}=15.3$ Hz, (s, Bi–C)), 156.4 (s, *m-C*), 129.5 (s, *p-C*), 128.2 (s, *o-C*), 35.9 (s, $\text{CH}(\text{CH}_3)_2$), 25.0 (s, $\text{CH}(\text{CH}_3)_2$), 24.4 (s, $\text{CH}(\text{CH}_3)_2$); ^{19}F NMR (280 MHz, C_6D_6) δ : –215.5 (s, Bi–F); ^1H NMR (250 MHz, CD_3CN) δ : 7.56 (d, $^3J_{\text{H-H}}=7.6$ Hz, 4H, *m-CH*), 7.41 (t, $^3J_{\text{H-H}}=7.6$ Hz, 2H, *p-CH*), 3.13 (sept, $^3J_{\text{H-H}}=6.6$ Hz, 4H, $\text{CH}(\text{CH}_3)_2$), 1.07 (d, $^3J_{\text{H-H}}=6.6$ Hz, 24H, $\text{CH}(\text{CH}_3)_2$); ^{19}F NMR (235 MHz, CD_3CN) δ :

–213.1 (s, Bi–F); IR (cm⁻¹): 3047 (w), 2962 (m), 2923 (m), 2865 (w), 1569 (w), 1460 (m), 1447 (m), 1417 (w), 1381 (m), 1357 (w), 1261 (w), 1236 (m), 1194 (w), 1177 (w), 1160 (w), 1146(w), 1098 (w), 1046 (m), 1013 (m), 1006 (w), 929 (w), 797 (s), 729 (s), 633 (m), 495 (w), 446 (m), 412 (m); HR-MS: Cl(+) m/z 531.2457 [M–F]⁺; calcd 531.2464

Synthesis of Dipp₂BiCl (1-Cl). Compound 1-OTf (90 mg, 0.13 mmol) and NaCl (77 mg, 1.32 mmol) is suspended in 10 ml THF and stirred over 12 h at room temperature. After removal of volatiles under reduced pressure, the remaining solid is taken up in 20 ml pentane. The solution is filtered and all volatiles are removed under reduced pressure. The remaining residue is washed with cold pentane to obtain 1-Cl as a yellow solid. Crystals suitable for single crystal X-ray diffraction analysis are obtained from an oversaturated solution of 1-Cl in pentane at room temperature. Yield 45%. Elemental analysis for C₂₄H₃₄BiCl calcd: C, 50.84; H, 6.04; found: C, 50.60; H, 6.04; ¹H NMR (500 MHz, C₆D₆) δ: 7.43 (d, ³J_{H-H} = 7.6 Hz, 4H, *m*-CH), 7.26 (t, ³J_{H-H} = 7.6 Hz, 2H, *p*-CH), 3.29 (sept, ³J_{H-H} = 6.7 Hz, 4H, CH(CH₃)₂), 1.12 (d, ³J_{H-H} = 6.6 Hz, 12H, CH(CH₃)₂), 1.07 (d, ³J_{H-H} = 6.7 Hz, 12H, CH(CH₃)₂); ¹³C{¹H} NMR (125 MHz, C₆D₆) δ: 185.6 (s, Bi–C), 156.6 (s, *m*-C), 129.5 (s, *p*-C), 128.3 (s, *o*-C), 38.0 (s, CH(CH₃)₂), 25.2 (s, CH(CH₃)₂), 24.4 (s, CH(CH₃)₂); IR (cm⁻¹): 3046 (w), 2961 (m), 2923 (w), 2862 (w), 1569 (w), 1458 (w), 1446 (w), 1413 (w), 1382 (w), 1363 (w), 1259 (s), 1084 (s), 1013 (s), 928 (w), 865 (w), 793 (s), 728 (m), 701 (m), 661 (w), 495 (w)

Synthesis of (Dipp₂Bi)₂ (2). A 1 M solution of NaBHET₃ (0.64 ml, 0.64 mmol) in toluene is added to a solution of 1-Br (400 mg, 0.64 mmol) in 50 ml toluene cooled to –78 °C. The reaction mixture is allowed to warm to room temperature over six hours, turning red at –50 °C and black at –30 °C. After separation of precipitate via filtration, volatiles are evaporated under reduced pressure. The remaining residue is washed with acetonitrile and 2 is obtained as a dark brown solid. Black crystals of 2 suitable for single crystal X-ray diffraction where grown from a mixture of toluene and diethyl ether at –32 °C. Yield 94%. Elemental analysis for C₄₈H₆₈Bi₂ calcd: C, 54.23; H, 6.45; found: C, 54.12; H, 6.58; ¹H NMR (300 MHz, C₆D₆) δ: 7.08–7.21 (m, 12H, *m*-CH, *p*-CH), 3.23 (sept, ³J_{H-H} = 6.7 Hz, 8H, CH(CH₃)₂), 1.14 (d, ³J_{H-H} = 6.8 Hz, 24H, CH(CH₃)₂), 0.89 (d, ³J_{H-H} = 6.8 Hz, 24H, CH(CH₃)₂); ¹³C{¹H} NMR (125 MHz, C₆D₆) δ: 156.3 (s, *m*-C), 128.9 (s, *p*-C), 125.5 (s, *o*-C), 44.3 (s, CH(CH₃)₂), 25.7 (s, CH(CH₃)₂), 24.8 (s, CH(CH₃)₂); IR (cm⁻¹): 3038 (w), 2952 (m), 2920 (w), 2861 (w), 1565 (w), 1455 (w), 1381 (w), 1360 (w), 1291 (w), 1234 (w), 1174 (w), 1157 (w), 1043 (w), 995 (w), 907 (w) 794 (s), 725 (s); HR-MS: Cl(+) m/z 531.2443 [0.5 M]⁺; calcd 531.2464

Reaction of 2 with elemental sulfur. Compound 2 (100 mg, 0.09 mmol) is dissolved in 5 ml trifluorotoluene and elemental sulfur (6 mg, 0.19 mmol) is added at room temperature. After stirring for 90 minutes, volatiles are removed under reduced pressure and the remaining solid is extracted with 15 ml pentane. The solution is concentrated and cooled to –32 °C. Orange crystals of 3a and 3b were obtained after one week.

Synthesis of Dipp₂BiPtBu₂ (4). a.) To a solution of compound 1-Br (150 mg, 0.24 mmol) in 10 ml of pentane, cooled to –78 °C, LiPtBu₂ (36.6 mg, 0.24 mmol) is added. The reaction mixture is allowed to reach 0 °C in the course of 5 hours under continuous stirring. After filtration, all volatiles of the filtrate are removed under reduced pressure. The red compound 4 is obtained in crystalline form from a solution of the remaining solid in pentane at –32 °C. Yield 32%. b.) Compound 1-F (100 mg, 0.18 mmol) was dissolved in 5 ml of TFT, cooled to –30 °C and 0.018 ml of PtBu₂TMS (40 mg, 0.18 mmol) in 2 ml TFT are added. The solution was stirred for two days at –30 °C. After removal of all volatiles under reduced pressure, the remaining solid is taken up in 0.5 ml pentane and compound 2 is obtained in the form of red crystals at –32 °C. Yield 45%. Elemental

analysis for C₃₂H₅₂BiP₁ calcd: C, 56.80; H, 7.75; found: C, 56.44; H, 7.12; ¹H NMR (300 MHz, C₆D₆) δ: 7.19–7.27 (m, 6H, *m*-CH), 3.57–3.74 (m, 4H, *p*-CH), 1.38 (d, ³J_{P-H} = 10.6 Hz, 18H, P-C(CH₃)₃), 1.19 (d, ³J_{H-H} = 6.6 Hz, 12H, CH(CH₃)₂), 1.12 (d, ³J_{H-H} = 6.6 Hz, 12H, CH(CH₃)₂); ¹³C{¹H} NMR (125 MHz, C₆D₆) δ: 156.4 (s, *m*-C), 129.1 (s, *p*-C), 126.0 (s, *o*-C), 41.1 (s, CH(CH₃)₂), 41.0 (s, CH(CH₃)₂), 35.4 (d, ¹J_{P-C} = 44.0 Hz, P-C(CH₃)₃), 33.9 (d, ²J_{P-C} = 13.7 Hz, P-C(CH₃)₃), 25.4 (s, CH(CH₃)₂), 25.0 (s, CH(CH₃)₂); ³¹P{¹H} NMR (122 MHz, C₆D₆) δ: 85.4 (s); IR (cm⁻¹): 3046 (w), 2990(m), 2959 (m), 2928 (m), 2885 (m), 2858 (m), 1568 (w), 1459 (m), 1445 (m), 1409 (w), 1382 (m), 1381(m), 1360 (m), 1308 (w), 1229 (w), 1165 (w), 1148(w), 1044 (w), 1012 (w), 996 (w), 926 (w), 796 (s), 724 (s), 592 (w), 557 (w), 492 (w), 462 (w), 424 (w); 145.1148 [M–Dipp₂Bi]⁺; calcd 145.1146

X-ray diffraction analysis. Single crystal X-ray diffraction analysis was conducted using a Bruker D8 Quest and a Stoe IPDS 2 diffractometer. The diffractometers use Mo–Kα (λ = 0.71073 Å) radiation and respective X-ray optics. Structures were solved via intrinsic phasing using SHELXT-2015. Structure refinement was performed via full-matrix-least-squares against F2 using SHELXL-2015. All structures were solved and refined using the OLEX2 platform.^{65–68}

Deposition Numbers 2012037 (1-F), 2012042 (1-Cl), 2012043 (1-Br), 2012038 (1-I), 2012040 (1-OTf), 2012044 (2), 2012039 (3a), 2012041 (3b), and 2032570 (4) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

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Conflict of Interest

The authors declare no conflict of interest.

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Supporting Information

2,6-Diisopropylphenyl-Substituted Bismuth Compounds: Synthesis, Structure, and Reactivity

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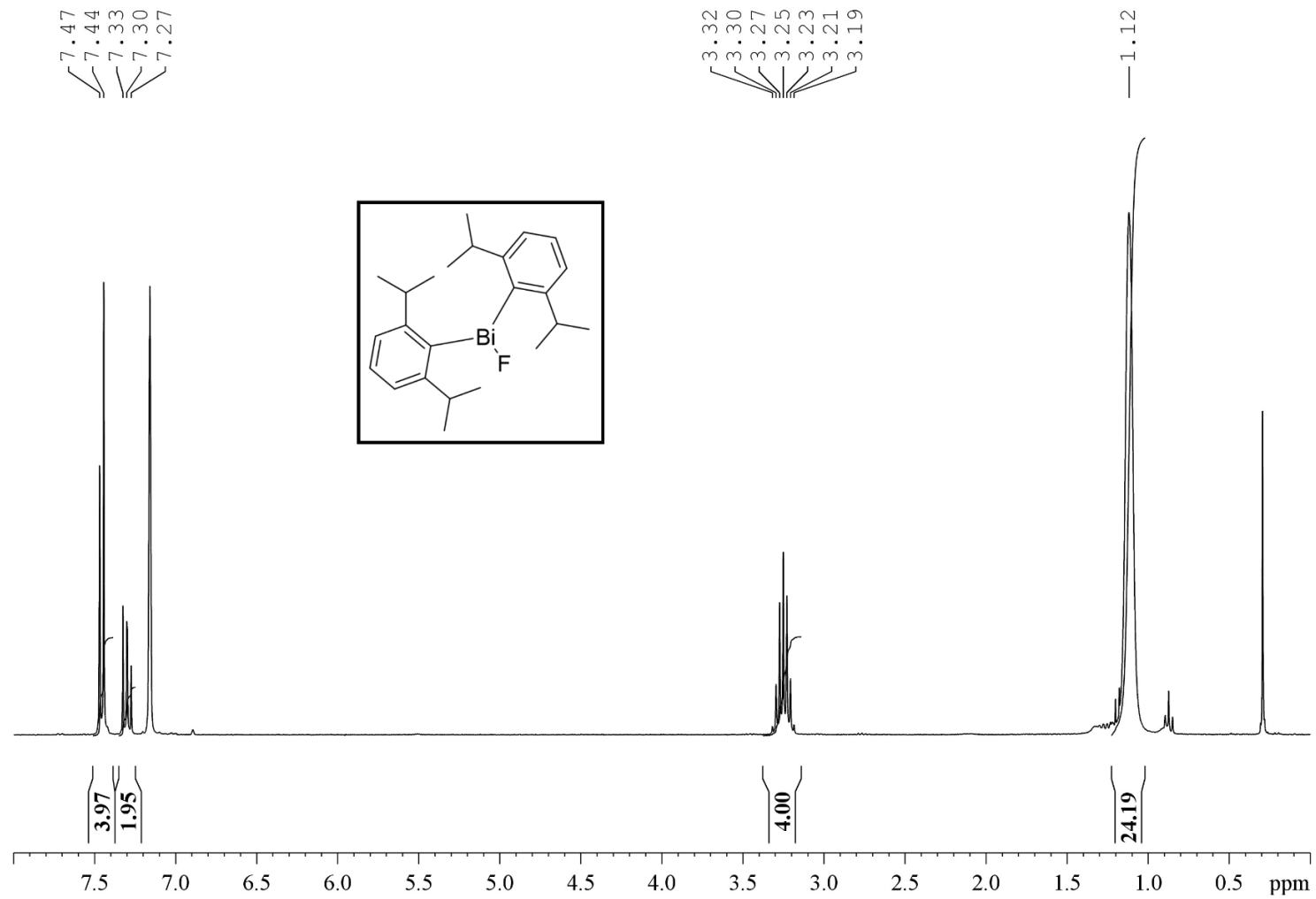


Figure S1: ^1H NMR spectrum (300 MHz) of **1-F** in C_6D_6 at room temperature.

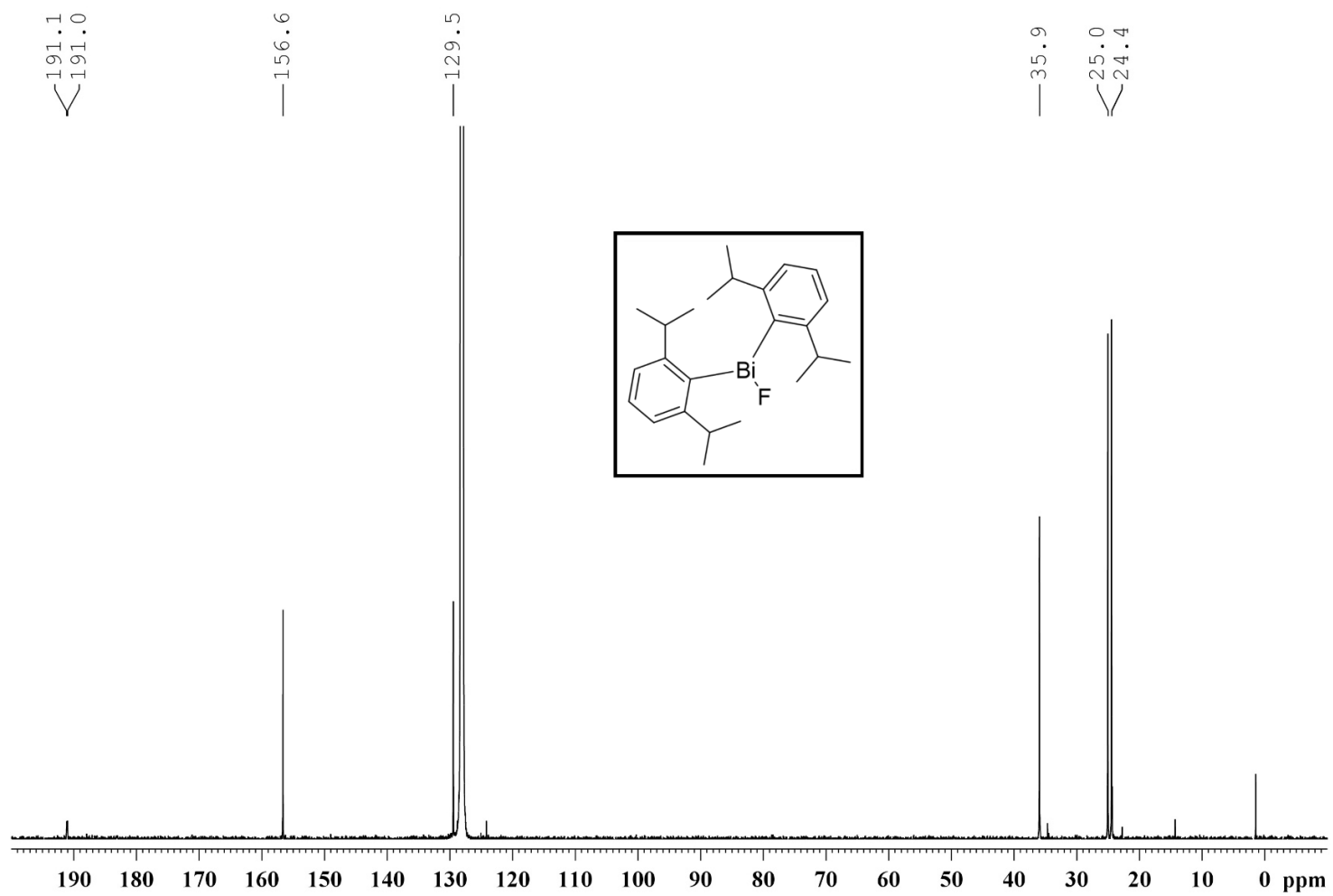


Figure S2: ^{13}C NMR (125 MHz) of **1-F** in C_6D_6 at room temperature.

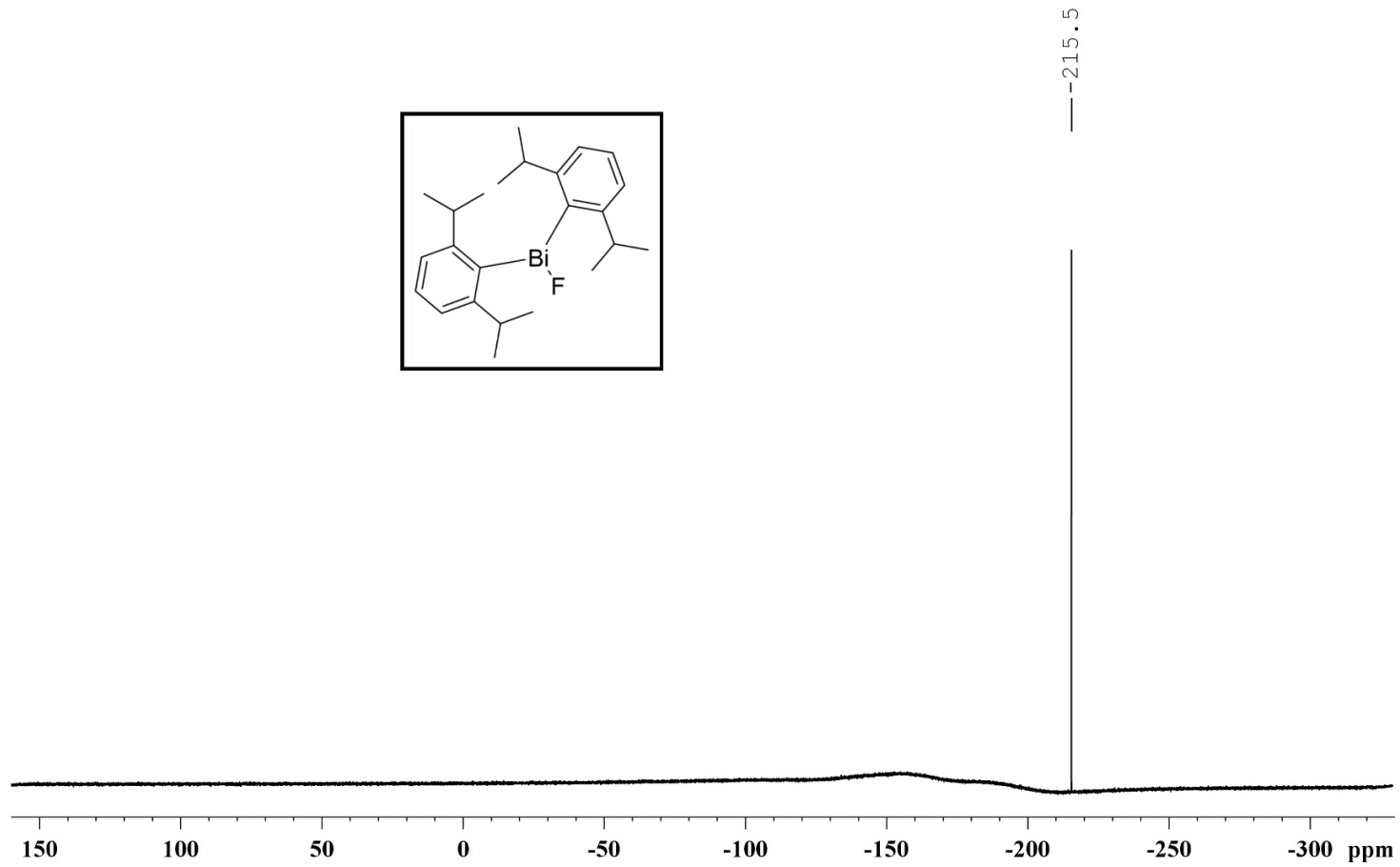


Figure S3: ^{19}F NMR (280 MHz) of **1-F** in C_6D_6 at room temperature.

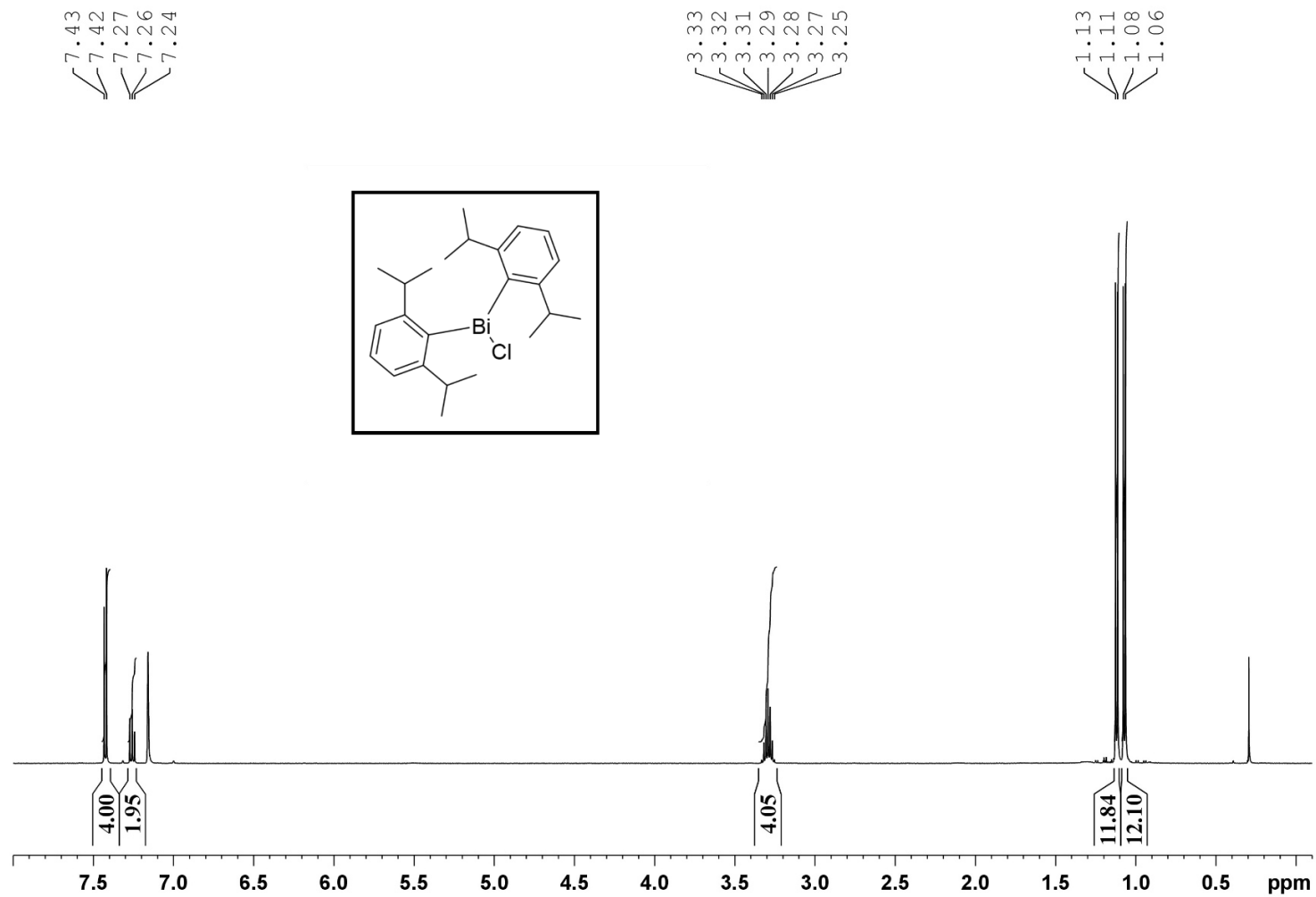


Figure S4: ^1H NMR (500 MHz) of **1-Cl** in C_6D_6 at room temperature.

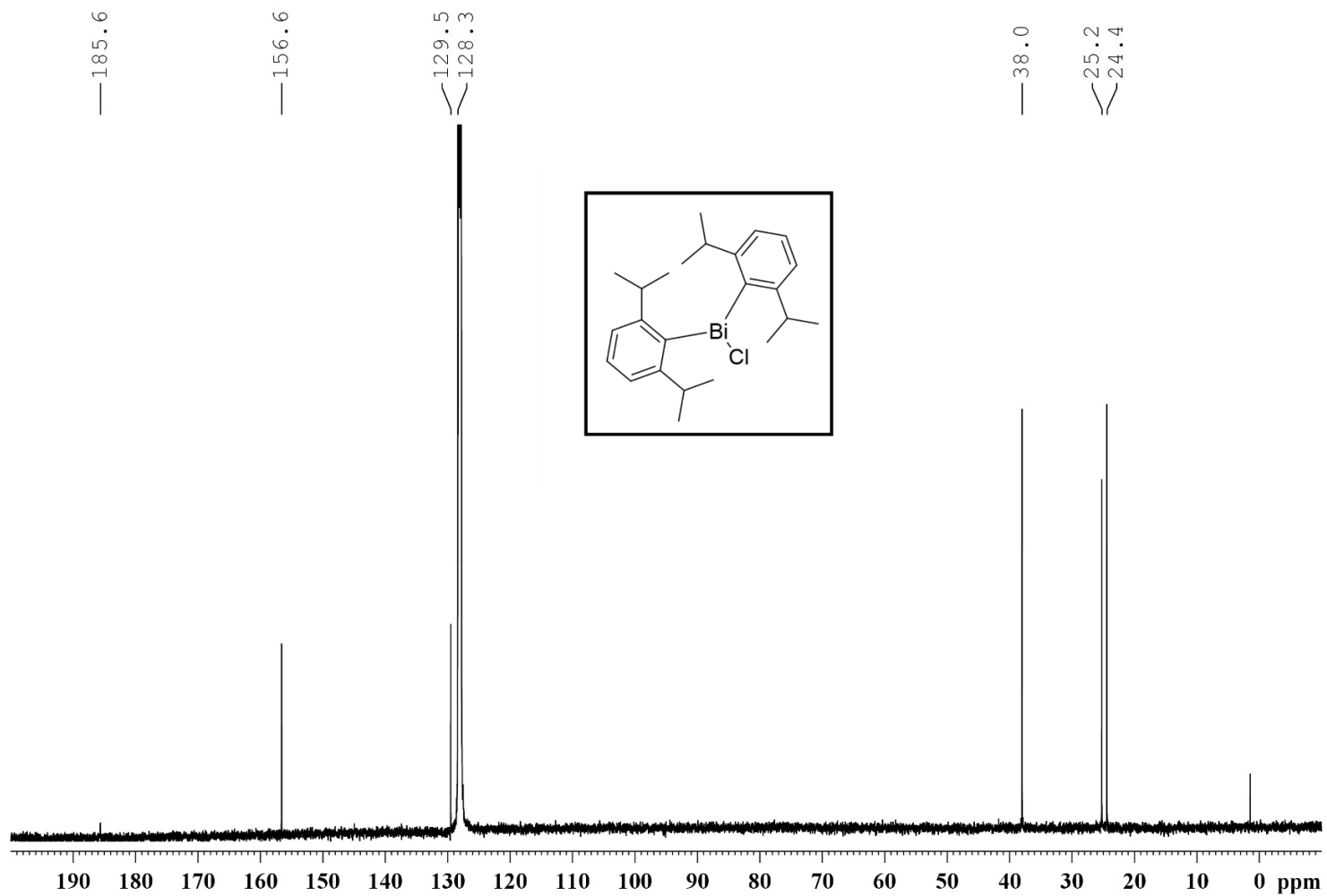


Figure S5: ^{13}C NMR (125 MHz) of 1-Cl in C_6D_6 at room temperature.

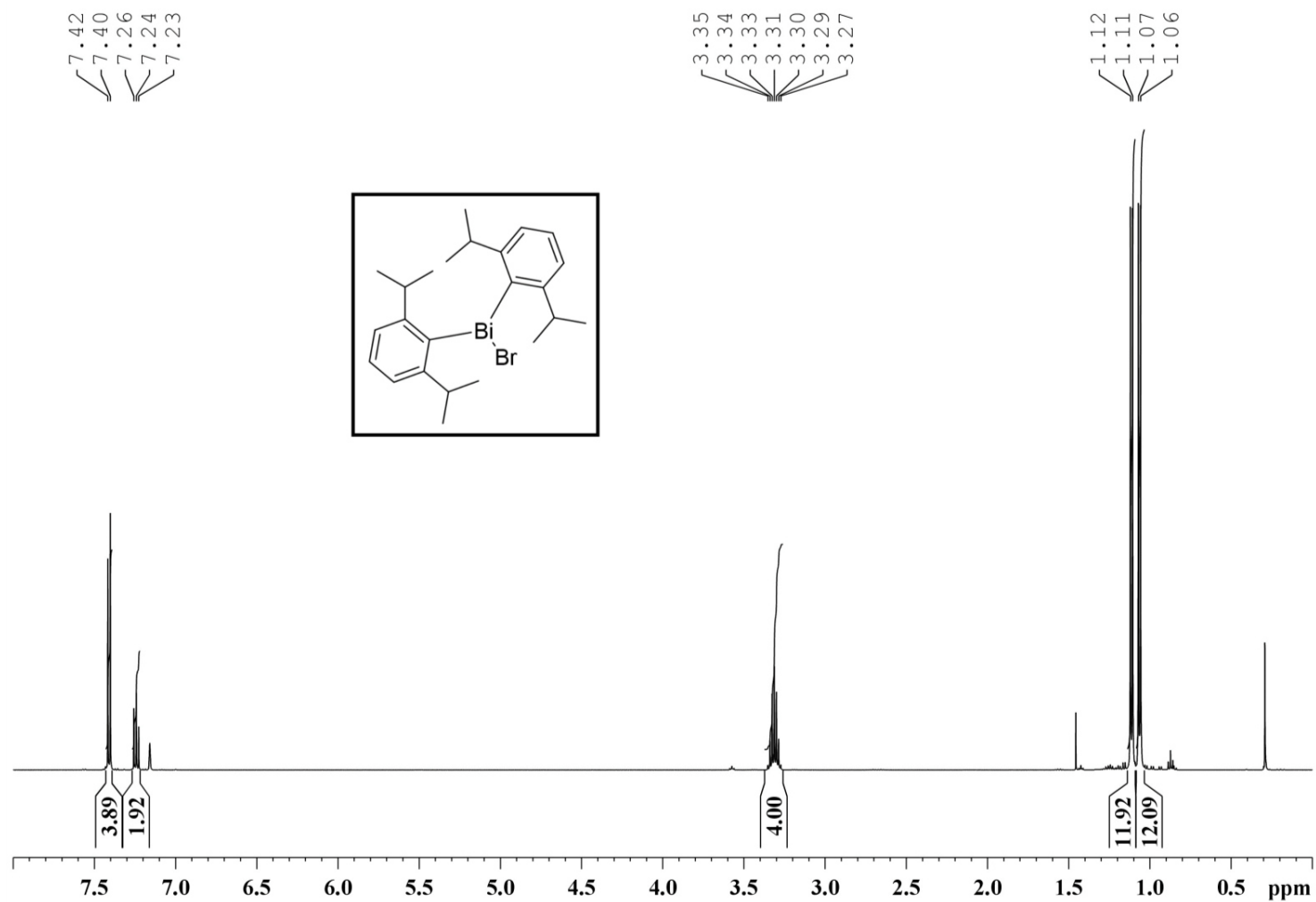


Figure S6: ^1H NMR (500MHz) of **1-Br** in C_6D_6 at room temperature.

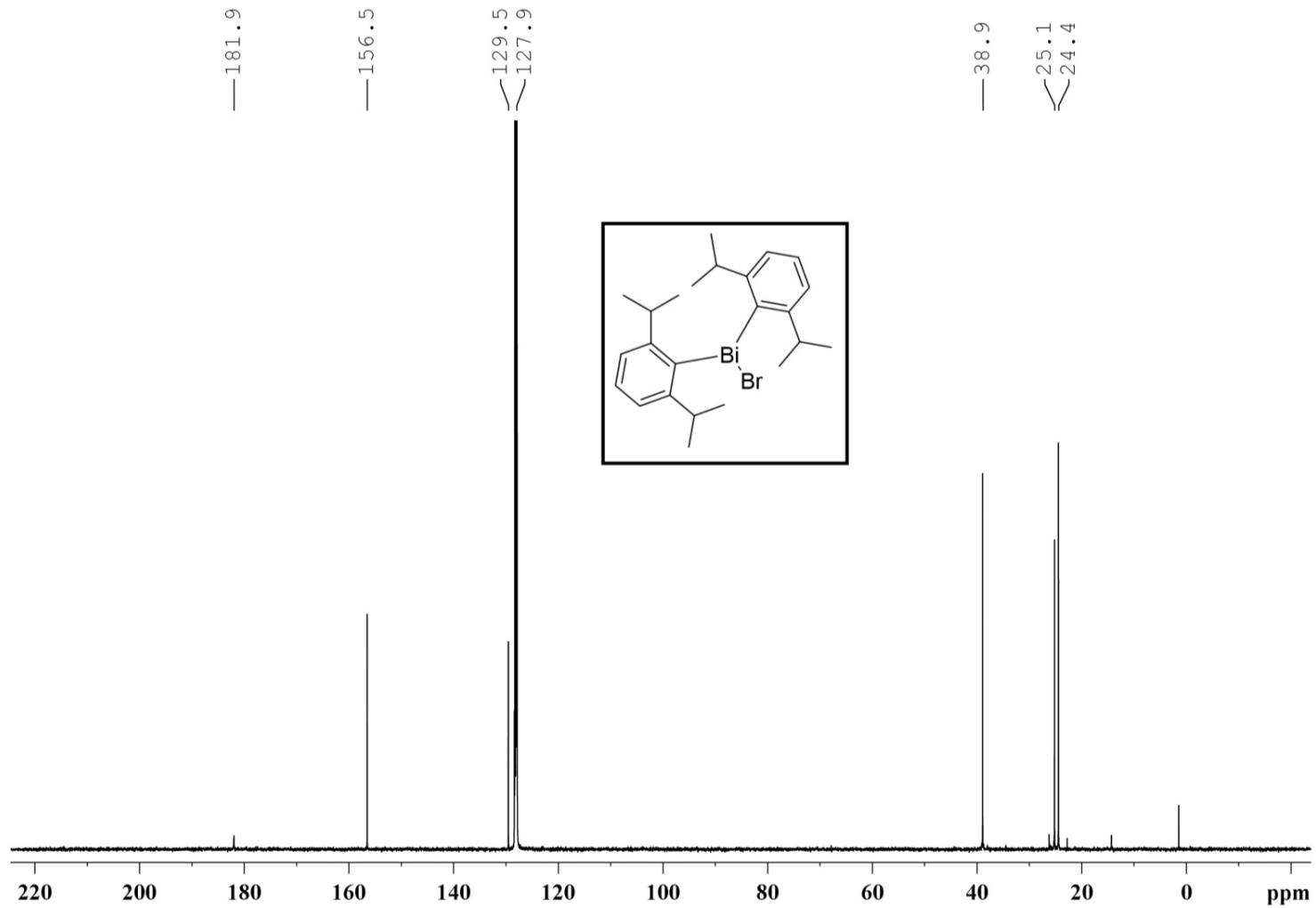


Figure S7: ^{13}C NMR (125 MHz) of **1-Br** in C_6D_6 at room temperature.

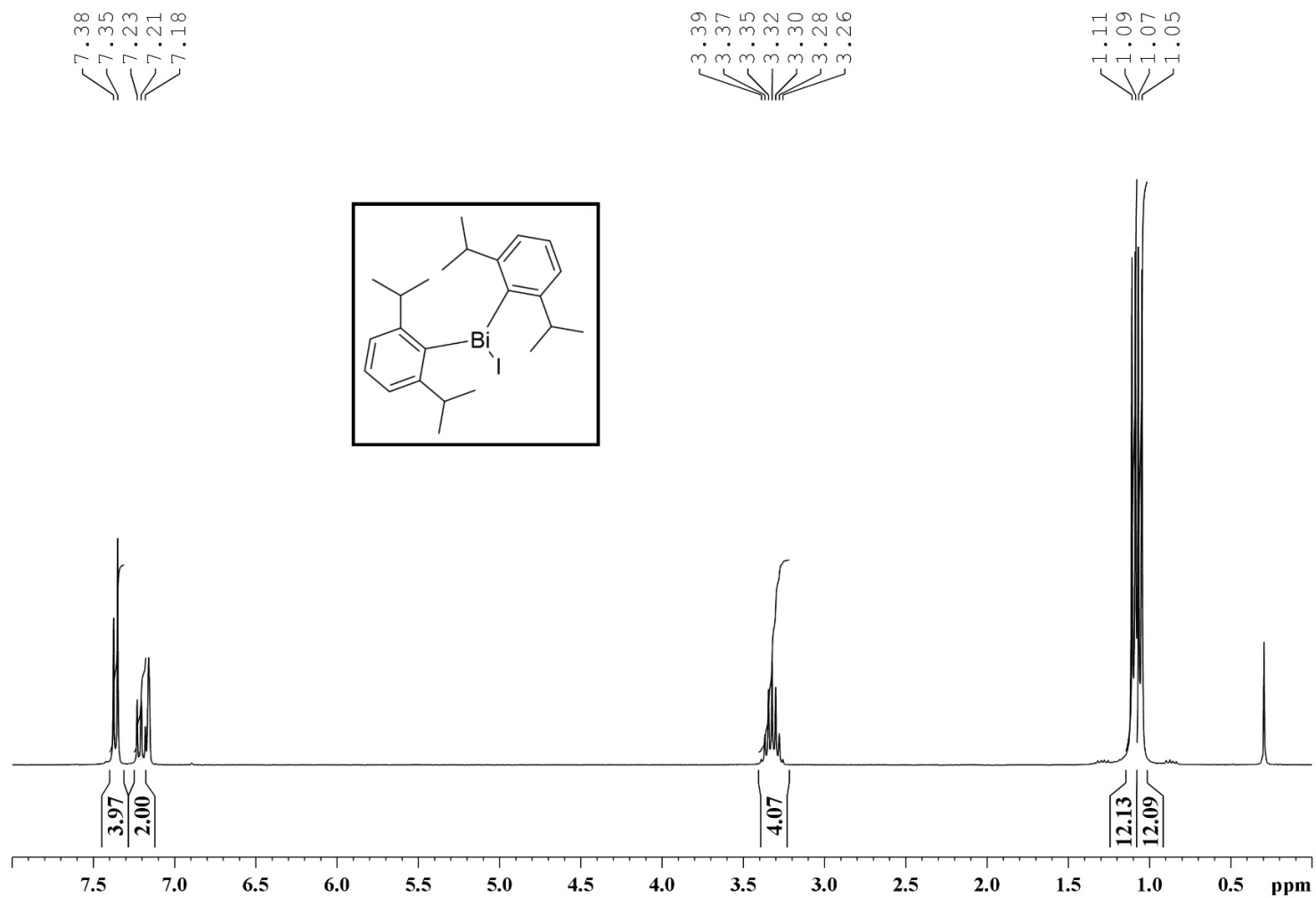


Figure S8: ^1H NMR (300 MHz) of **1-I** in C_6D_6 at room temperature.

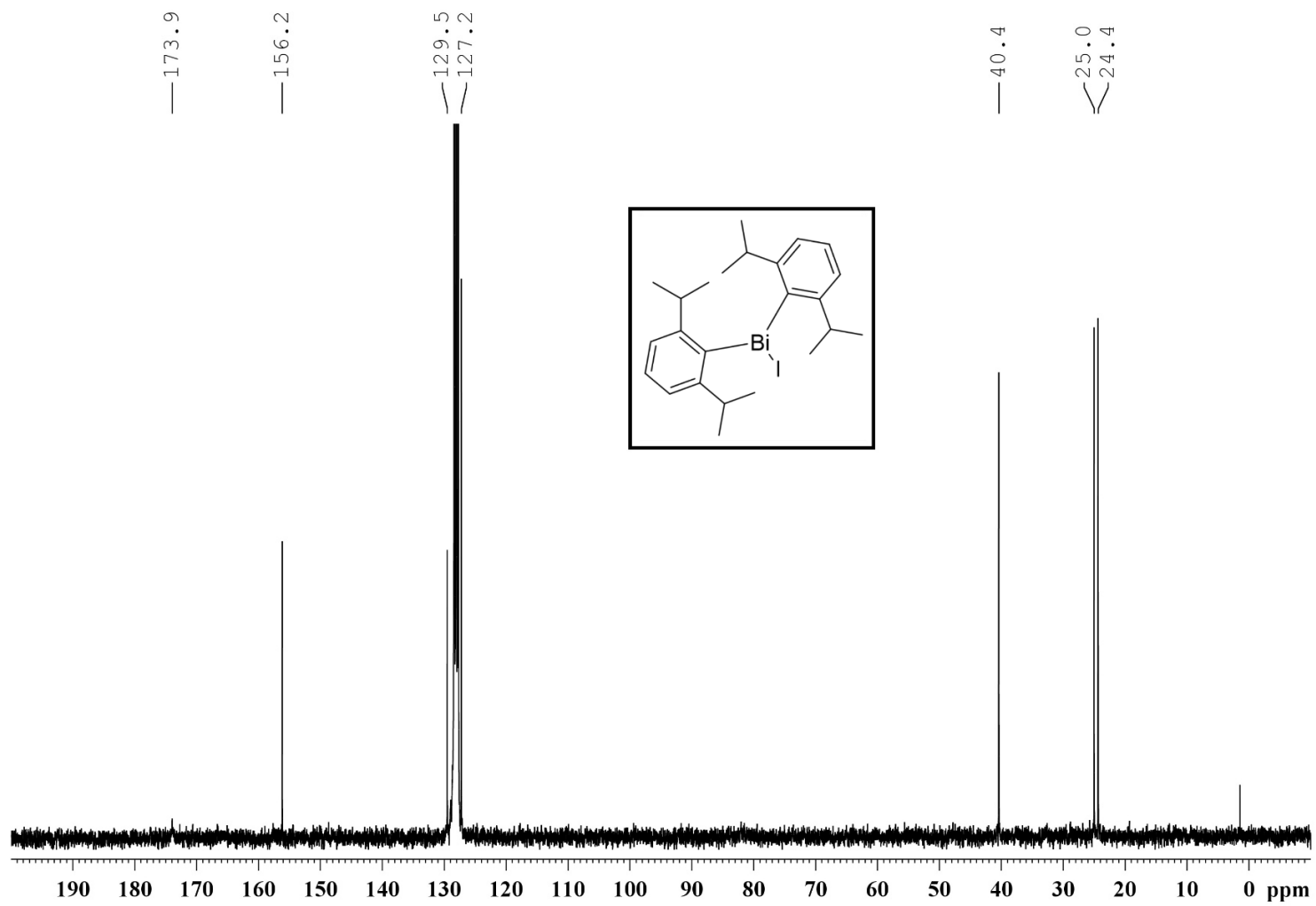


Figure S9: ^{13}C NMR (75 MHz) of **1-I** in C_6D_6 at room temperature.

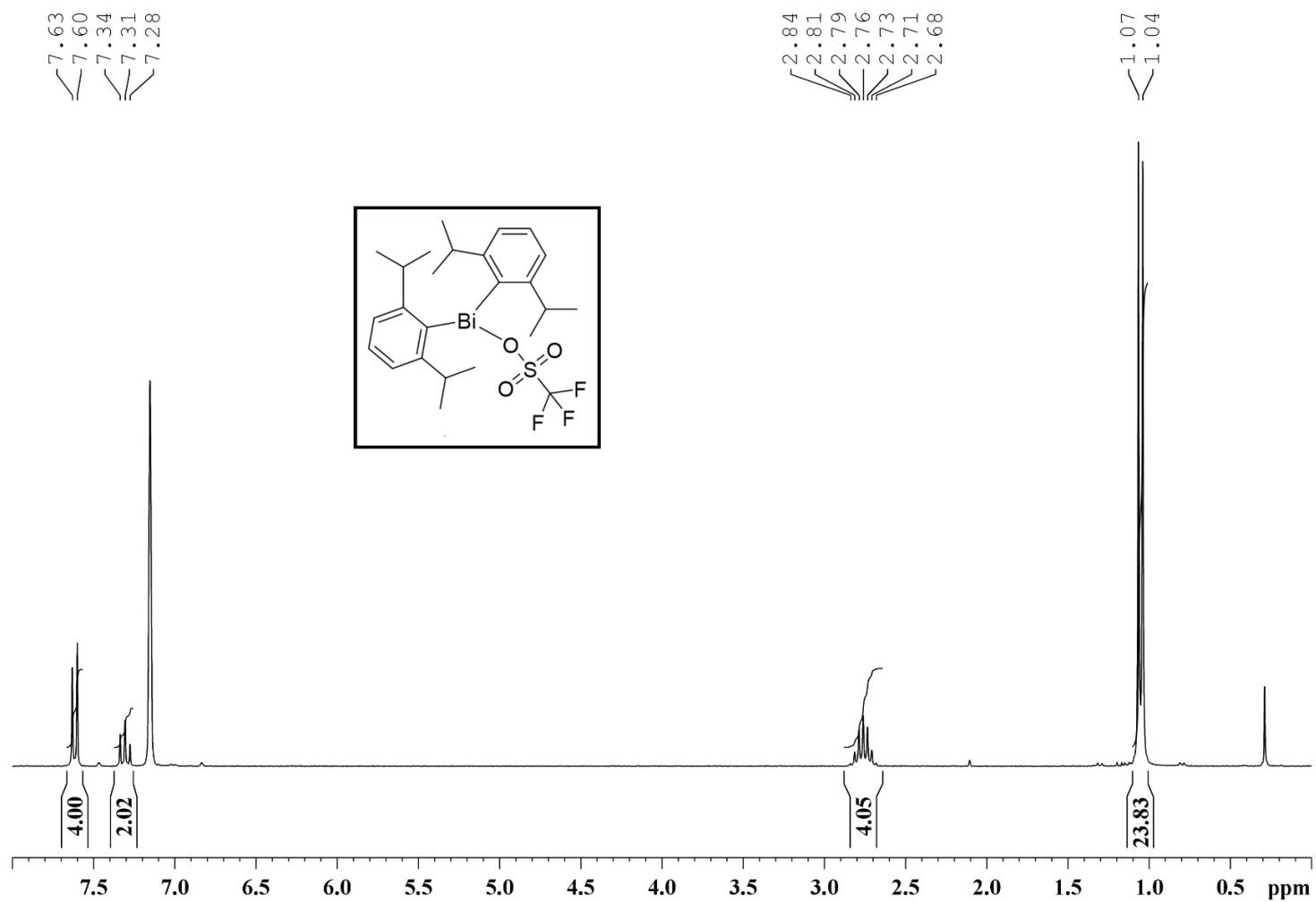


Figure S10: ^1H NMR (250 MHz) of **1-OTf** in C_6D_6 at room temperature.

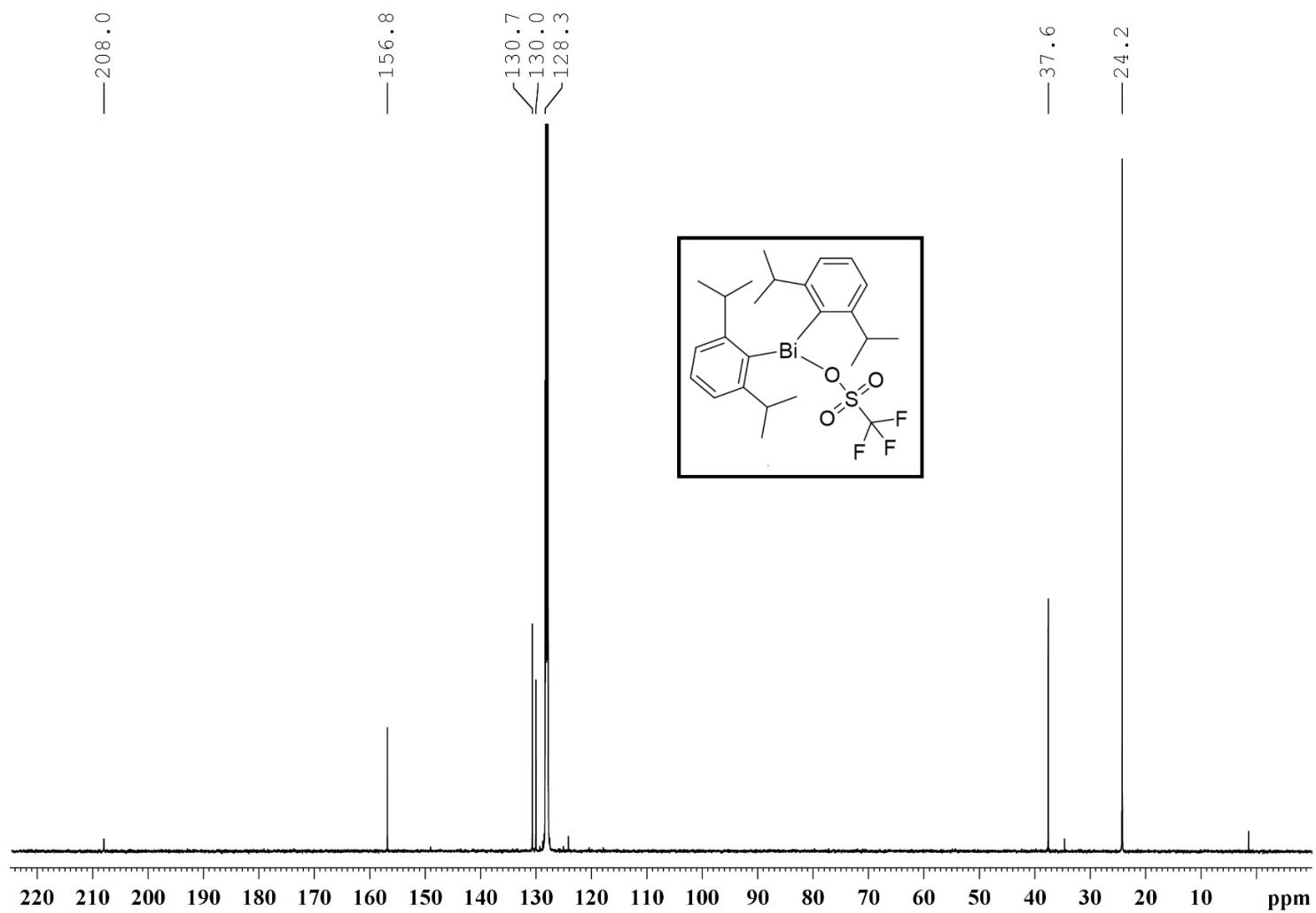


Figure S11: ^{13}C NMR (125 MHz) of **1-OTf** in C_6D_6 at room temperature

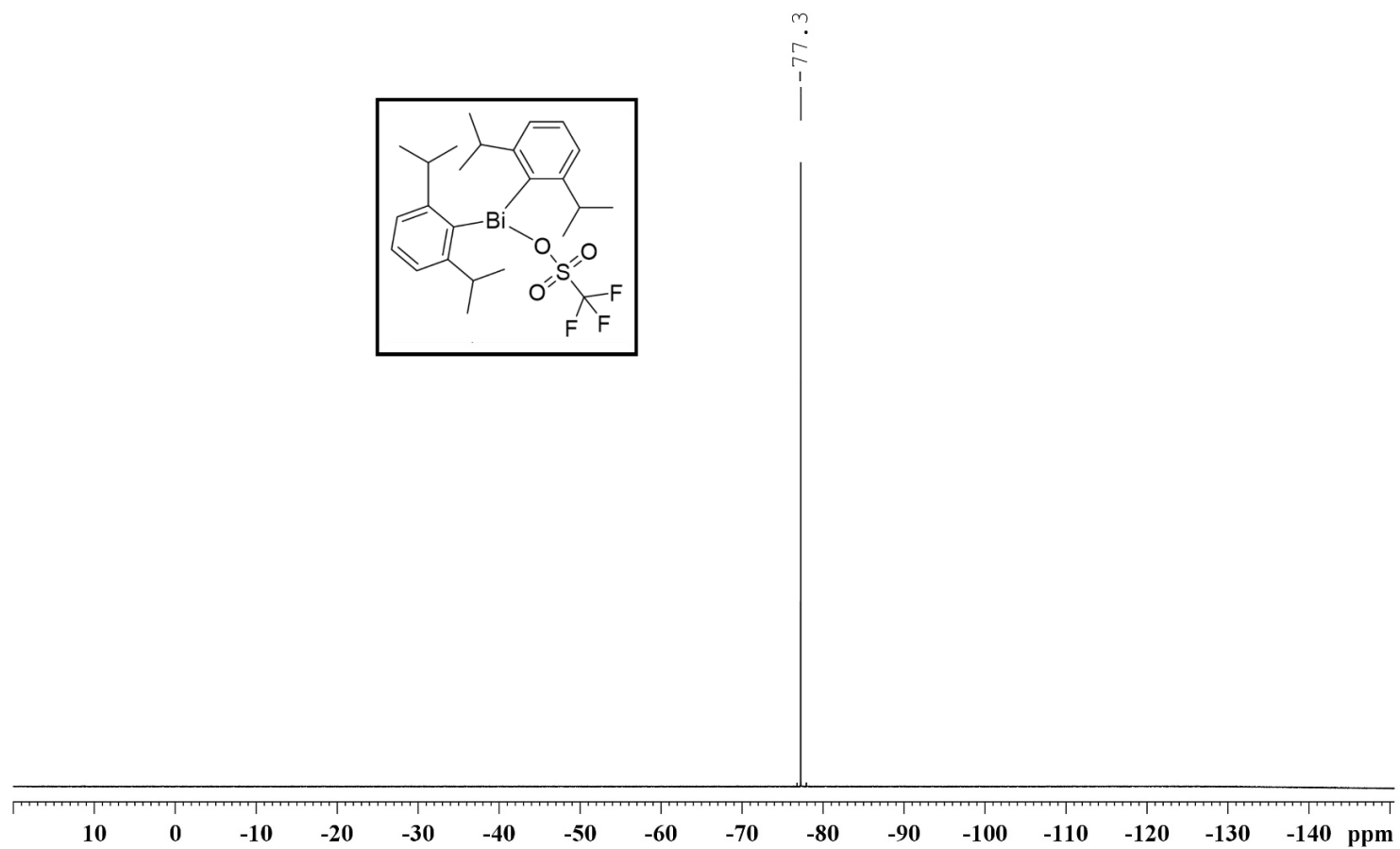


Figure S12: ^{19}F NMR (280MHz) of 1-OTf in C_6D_6 at room temperature.

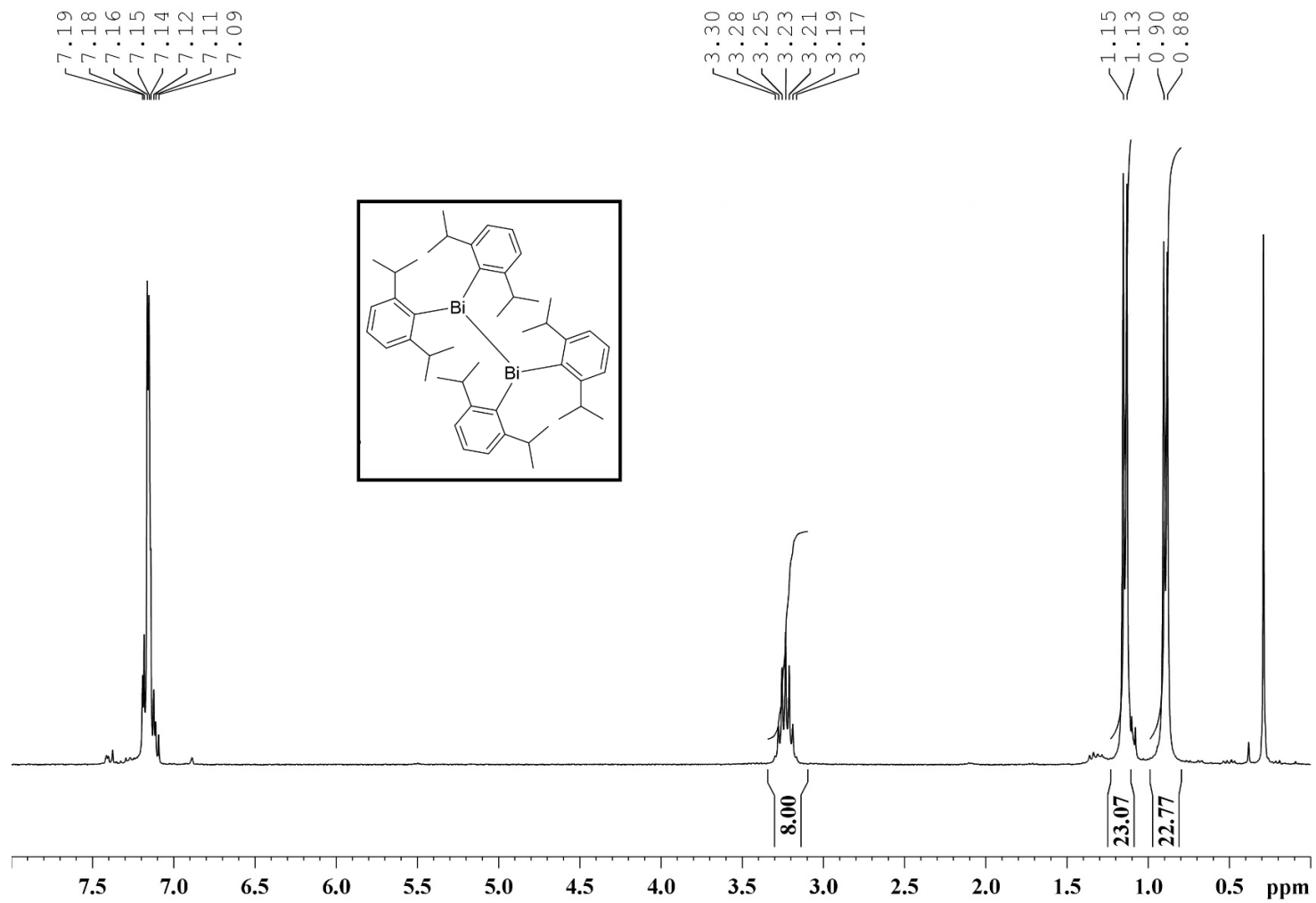


Figure S13: ^1H NMR of **2** (300 MHz) in C_6D_6 at room temperature.

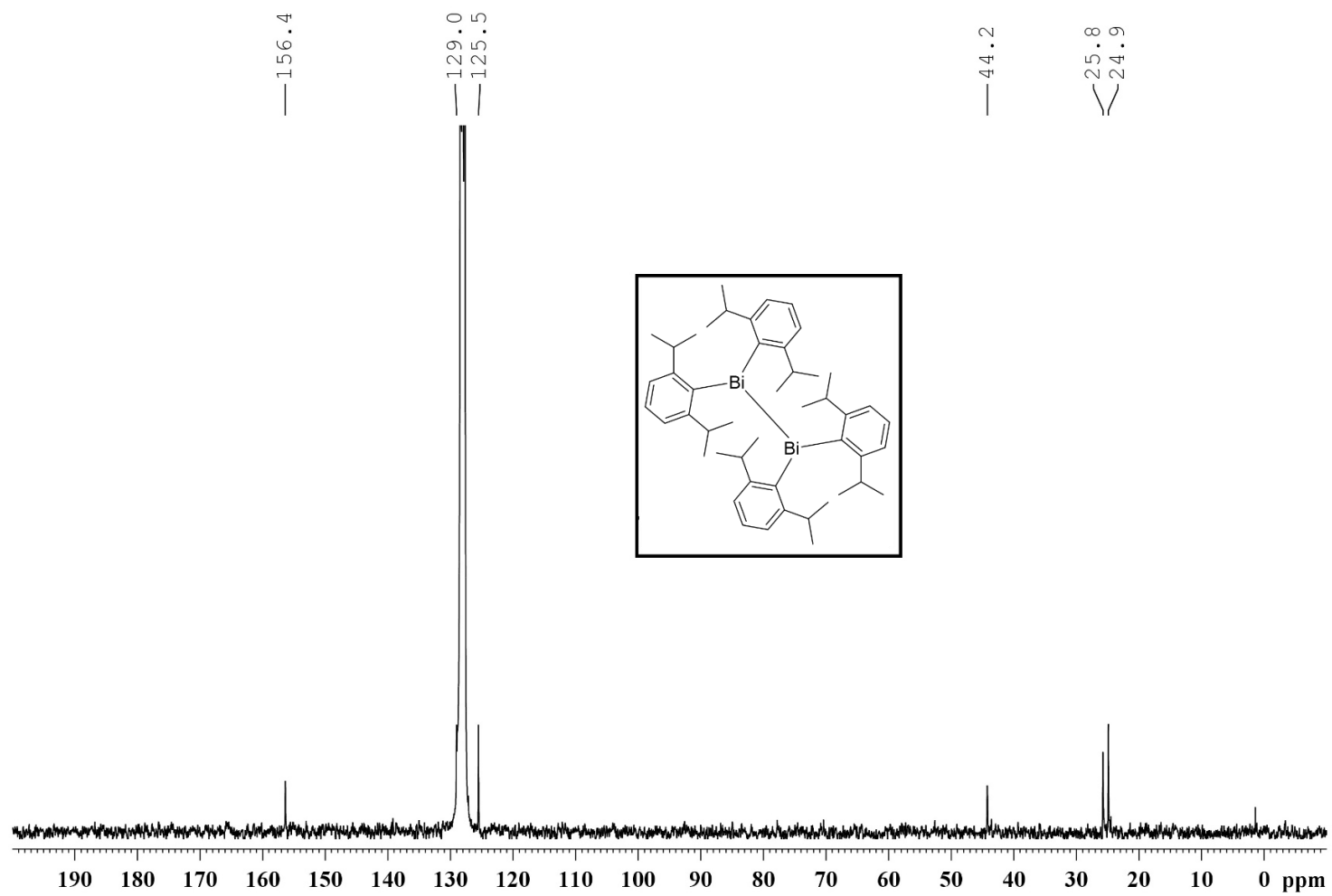


Figure S14: ^{13}C NMR of **2** in (75 MHz) C_6D_6 at room temperature.

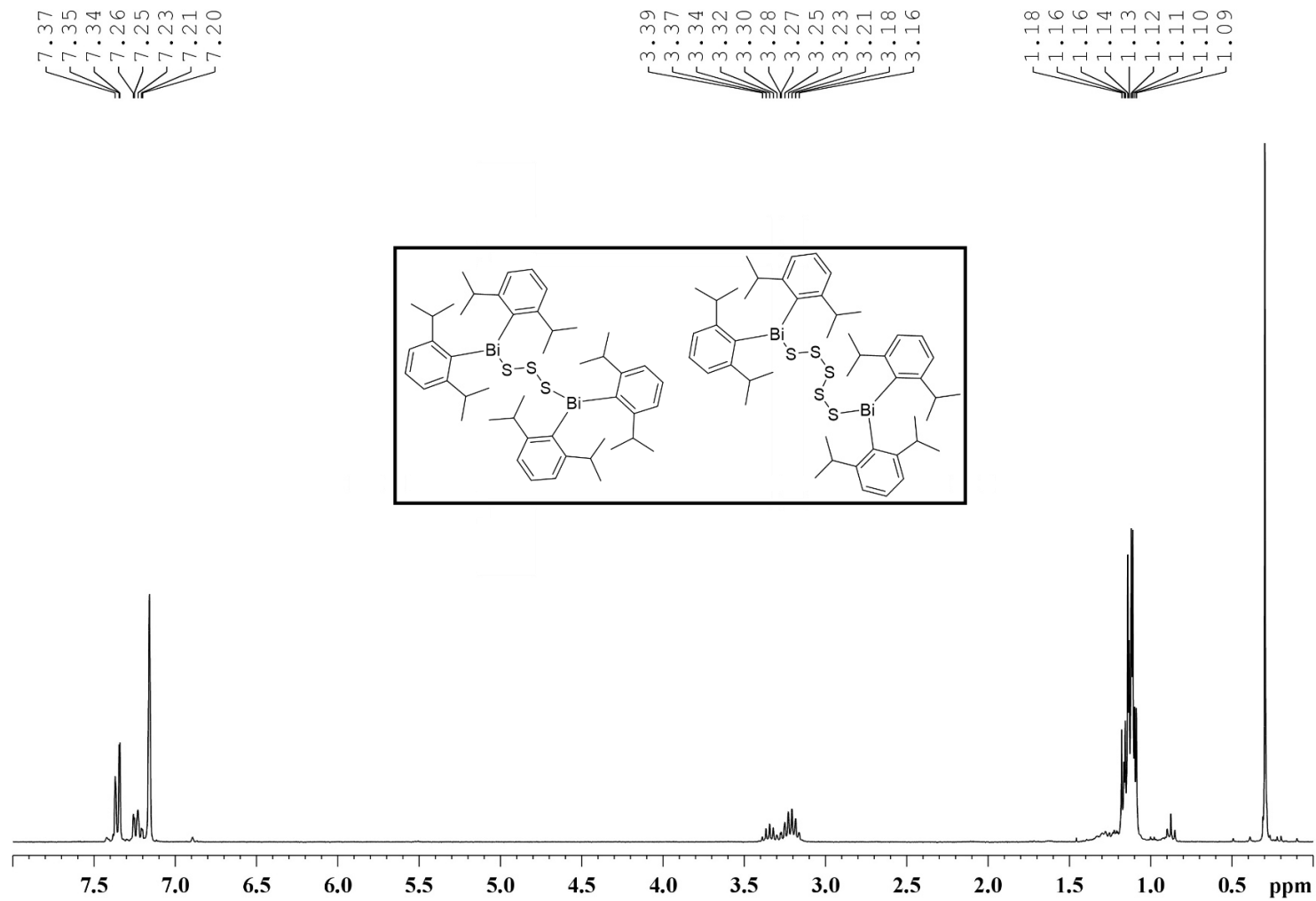


Figure S15: ^1H NMR (300 MHz) of a mixture of **3a** and **3b** in C_6D_6 at room temperature.

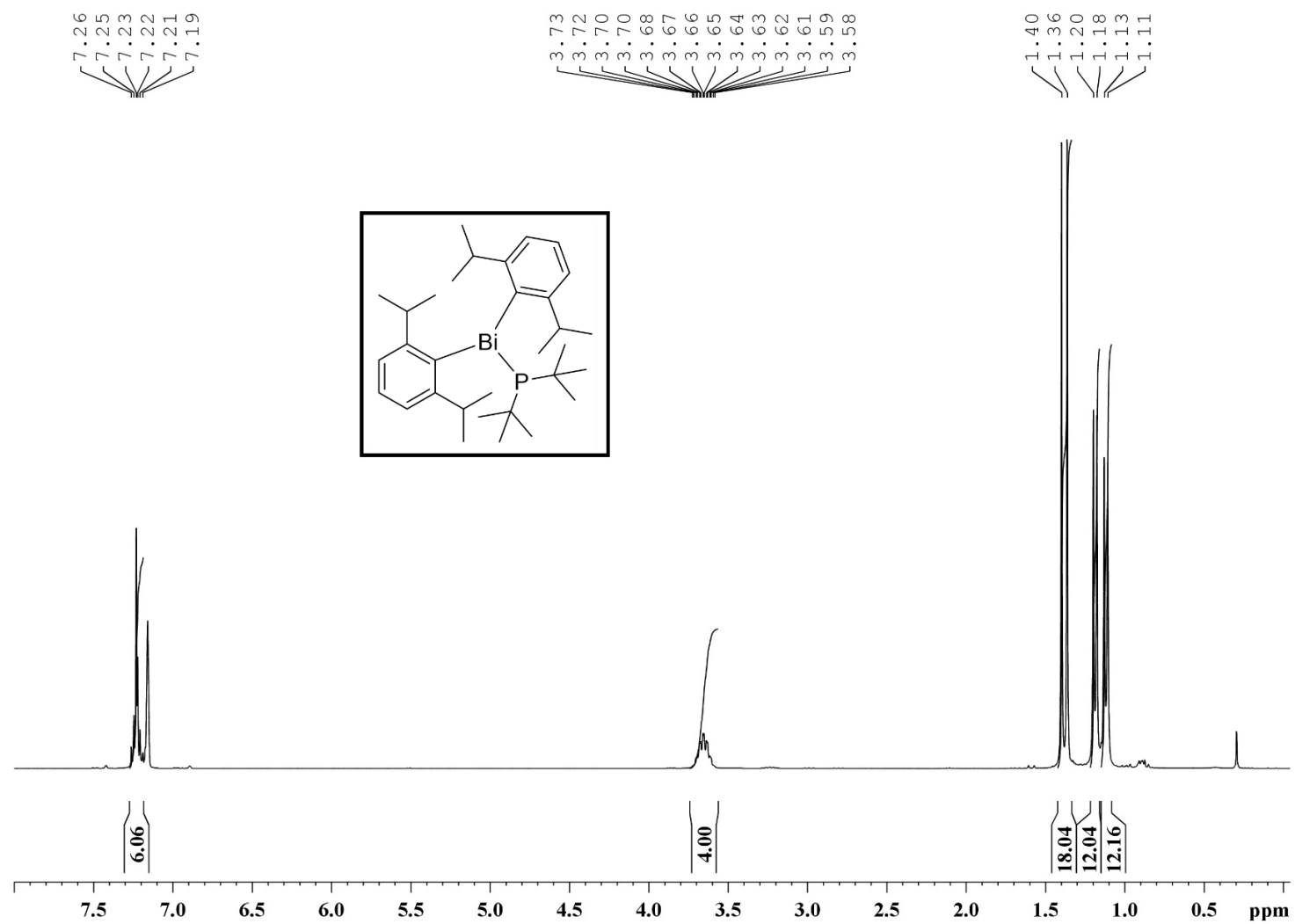


Figure S16: ^1H NMR (300 MHz) of **4** in C_6D_6 at room temperature.

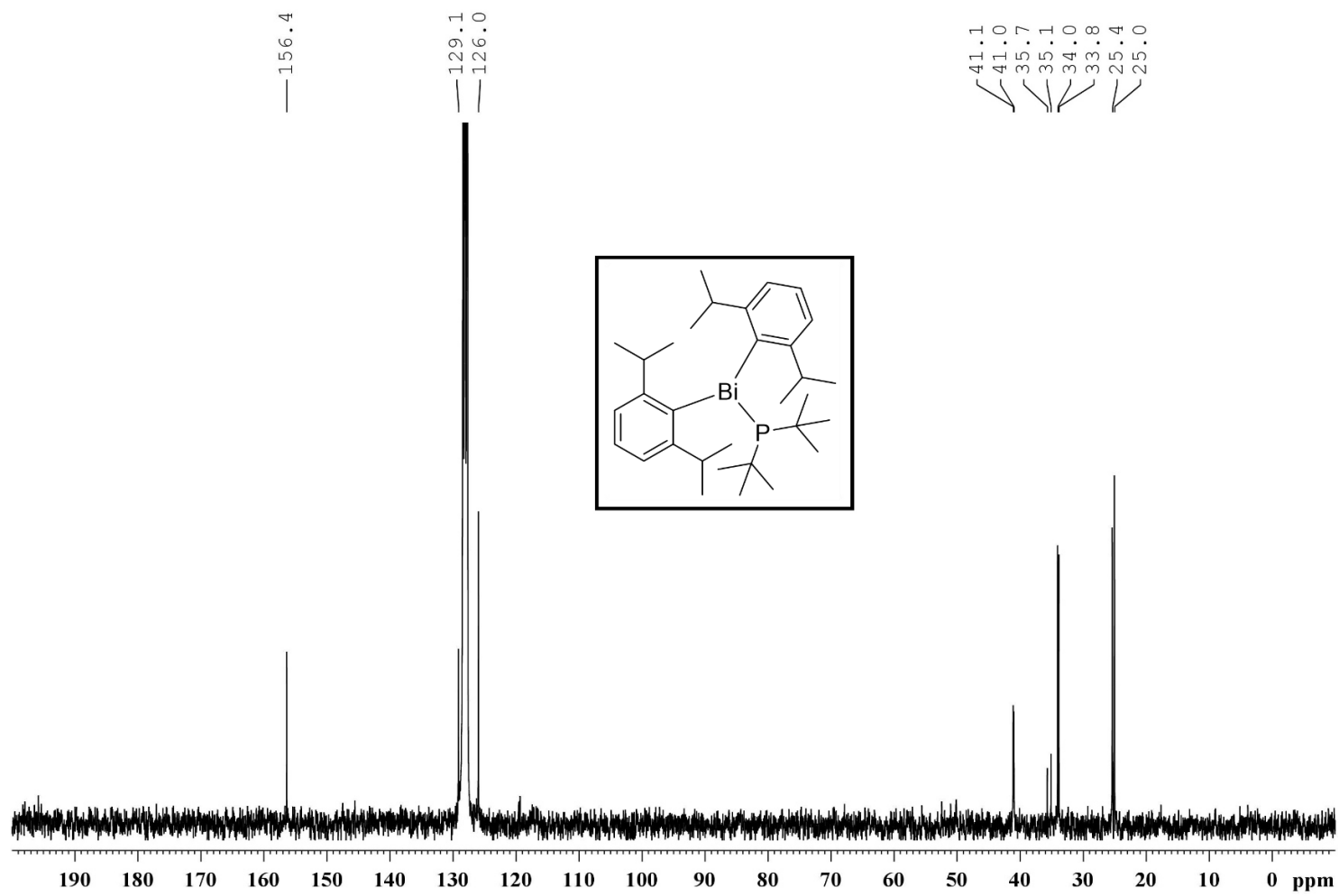


Figure S17: ^{13}C NMR (300 MHz) of **4** in C_6D_6 at room temperature.

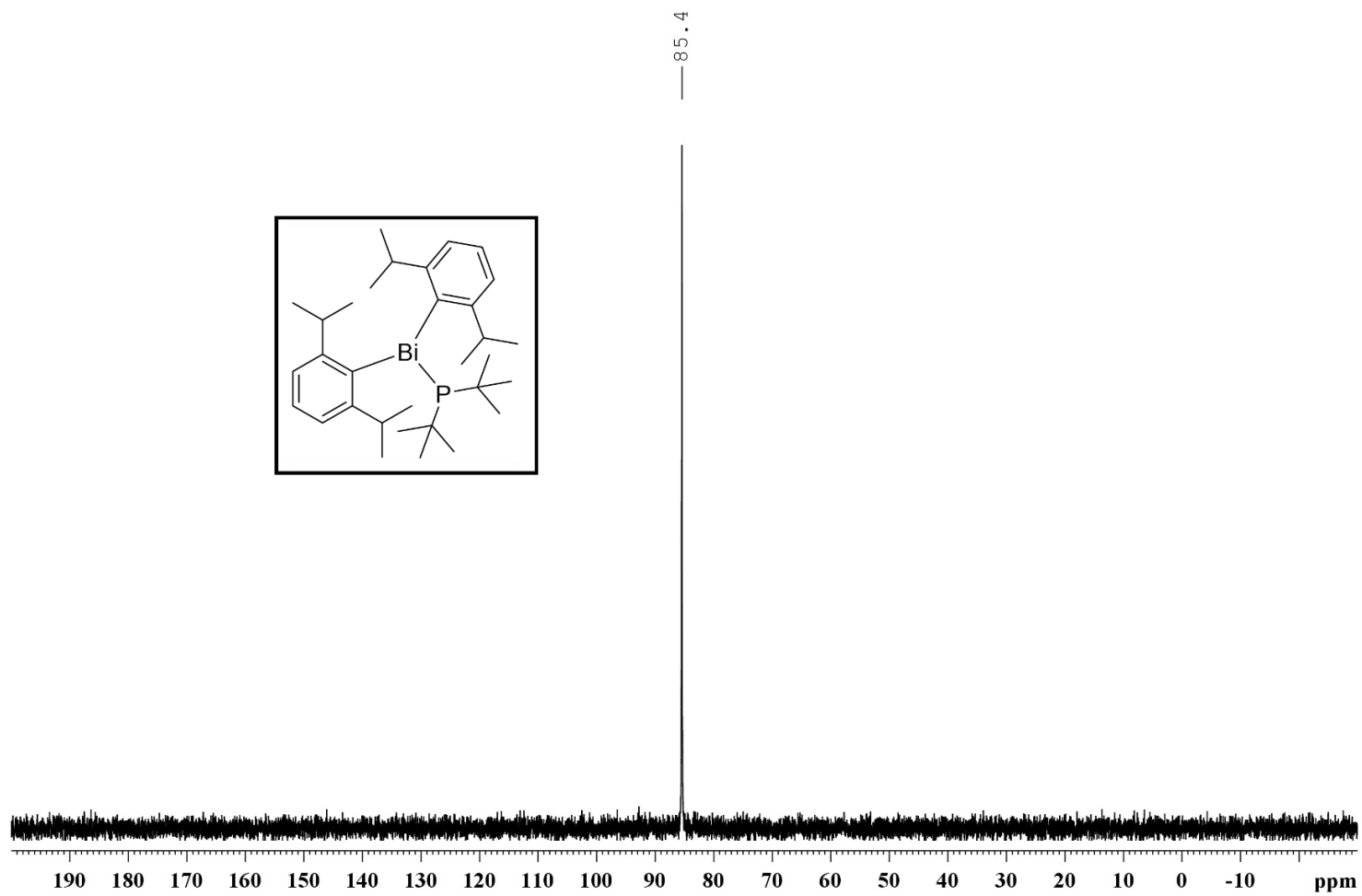


Figure S18: $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz) of **4** in C_6D_6 at room temperature.

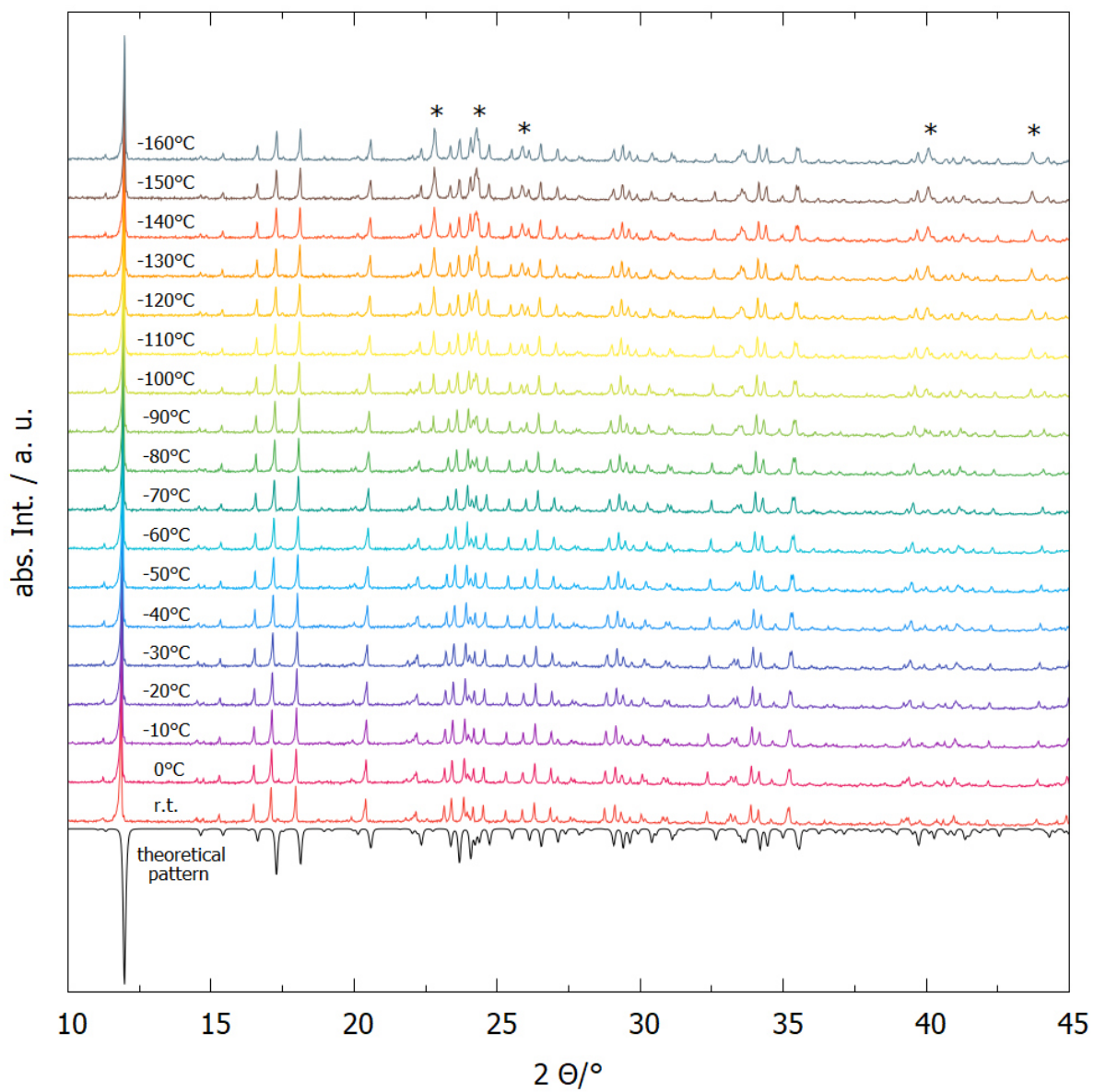


Figure S20: XRD patterns of 1-Br at different temperatures. Black: Theoretical pattern; *: ice.

Table S1. Selected crystal structure data of the structure determinations of compounds**1-F·0.5C₂H₅OH, 1-Cl and 1-Br**

Compound	1-F·0.5C₂H₅OH	1-Cl	1-Br
Empirical formula	C ₂₄ H ₃₇ BiFO _{0.5}	C ₂₄ H ₃₄ BiCl	C ₂₄ H ₃₄ BiBr
Formula weight	573.52	566.94	611.40
Crystal color, habit	colorless, needle	yellow, prism	orange, prism
Temperature/K	100.0	100.0	100.0
Crystal system	monoclinic	trigonal	trigonal
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>R</i> $\bar{3}$	<i>R</i> $\bar{3}$
<i>a</i> /Å	11.2574(8)	18.3705(6)	18.448(1)
<i>b</i> /Å	22.456(2)	18.3705(6)	18.448(1)
<i>c</i> /Å	10.1186(7)	36.776(1)	36.980(2)
α /°	90	90	90
β /°	95.537(2)	90	90
γ /°	90	120	120
Volume/Å ³	2546.0(3)	10748.2(8)	10899(1)
Z	4	18	18
ρ_{calc} /cm ³	1.496	1.577	1.677
μ /mm ⁻¹	6.941	7.499	8.934
F(000)	1132.0	5004.0	
Crystal size/mm ³	0.261x0.126x0.055	-	0.386x0.304x0.162
Crystal radius(equiv)/mm	-	0.0813	-
Diffractometer	Bruker D8 Quest	Stoe IPDS 2	Bruker D8 Quest
Radiation	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)
2 θ range for data collection/°	4.432 to 52.00	2.79 to 52.00	5.1 to 66.28
Reflections collected	40403	32650	55075
Independent reflections	4995 [<i>R</i> _{int} = 0.0810, <i>R</i> _{sigma} = 0.0524]	4681 [<i>R</i> _{int} = 0.0215, <i>R</i> _{sigma} = 0.0117]	4758 [<i>R</i> _{int} = 0.0301, <i>R</i> _{sigma} = 0.0130]
Data/restraint/parameters	4995/12/270	4681/4/264	4758/6/264
Goodness-of-fit on <i>F</i> ²	1.062	1.057	1.093
Final R indexes [all data]	<i>R</i> ₁ = 0.0618, <i>wR</i> ₂ = 0.0677	<i>R</i> ₁ = 0.0236, <i>wR</i> ₂ = 0.0564	<i>R</i> ₁ = 0.0180, <i>wR</i> ₂ = 0.0477
Final R indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0398, <i>wR</i> ₂ = 0.0646	<i>R</i> ₁ = 0.0203, <i>wR</i> ₂ = 0.0554	<i>R</i> ₁ = 0.0163, <i>wR</i> ₂ = 0.0471
Largest diff. peak/hole/ e Å ⁻³	1.23/-2.69	1.02/-0.40	1.57/-0.66
CCDC	2012037	2012042	2012043

Table S2. Selected crystal structure data of the structure determinations of compounds **1-I**, **1-OTf** and **2**

Compound	1-I	1-OTf	2
Empirical formula	C ₂₄ H ₃₇ BiI	C ₂₅ H ₃₄ BiF ₃ O ₃ S	C ₄₈ H ₆₈ Bi ₂
Formula weight	658.39	680.56	1062.98
Crystal color, habit	red, block	yellow, block	black, block
Temperature/K	100.0	100.0	100.0
Crystal system	monoclinic	monoclinic	monoclinic
Space group	<i>P2₁/n</i>	<i>P2₁/n</i>	<i>C2/c</i>
a/Å	11.7948(5)	11.8830(5)	23.554(1)
b/Å	14.3303(6)	15.0695(7)	11.7678(8)
c/Å	14.5291(6)	14.7993(7)	16.831(1)
α/°	90	90	90
β/°	97.443(2)	95.158(1)	109.036(2)
γ/°	90	90	90
Volume/Å ³	2435.2(2)	2639.4(2)	4409.9(5)
Z	4	4	4
ρ _{calc} /cm ³	1.796	1.713	1.601
μ/mm ⁻¹	8.514	6.803	8.000
F(000)	1256.0	1336.0	2088.0
Crystal size/mm ³	0.269x0.221x0.158	0.467x0.208x0.198	0.273x0.176x0.087
Diffractionmeter	Bruker D8 Quest	Bruker D8 Quest	Bruker D8 Quest
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	4.496 to 51.99	5.008 to 56.00	4.997 to 52.00
Reflections collected	42757	60468	35354
Independent reflections	4776 [R _{int} = 0.0453, R _{sigma} = 0.0211]	6364 [R _{int} = 0.0307, R _{sigma} = 0.0155]	4332 [R _{int} = 0.0464, R _{sigma} = 0.0257]
Data/restraint/parameters	4776/0/244	6364/0/307	235/0/4332
Goodness-of-fit on F ²	1.021	1.057	1.034
Final R indexes [all data]	R ₁ = 0.0215, wR ₂ = 0.0333	R ₁ = 0.0141, wR ₂ = 0.0305	R ₁ = 0.0202, wR ₂ = 0.0339
Final R indexes [I ≥ 2σ(I)]	R ₁ = 0.0169, wR ₂ = 0.0322	R ₁ = 0.0125, wR ₂ = 0.0300	R ₁ = 0.0142, wR ₂ = 0.0320
Largest diff. peak/hole/ e Å ⁻³	0.60/-0.75	0.74/-0.61	0.49/-0.70
CCDC	2012038	2012040	2012044

Table S3. Selected crystal structure data of the structure determinations of compounds **3a**, **3b** and **4**

Compound	3a	3b	4
Empirical formula	C ₄₈ H ₆₈ Bi ₂ S ₃	C ₄₈ H ₆₈ Bi ₂ S ₅	C ₃₂ H ₅₂ Bi ₁ P ₁
Formula weight	1159.17	1223.28	676.68
Crystal color, habit	yellow, block	yellow, plate	red, block
Temperature/K	100.0	100.0	100.0
Crystal system	monoclinic	orthorhombic	triclinic
Space group	<i>P2₁/c</i>	<i>Pbcn</i>	<i>P</i> $\bar{1}$
a/Å	13.810(1)	15.0507(4)	9.2709(5)
b/Å	19.786(2)	19.7682(7)	18.1689(9)
c/Å	17.850(1)	16.8491(5)	19.122(1)
α /°	90	90	79.347(2)
β /°	100.067(6)	90	89.517(2)
γ /°	90	90	82.730(2)
Volume/Å ³	4802.2(6)	5013.0(3)	3139.6(3)
Z	4	4	4
ρ_{calc} /cm ³	1.603	1.621	1.432
μ /mm ⁻¹	7.479	7.249	5.684
F(000)	2280.0	2408.0	1368.0
Crystal size/mm ³	-	-	0.415×0.226×0.177
Crystal radius(equiv)/mm	0.0596	0.466	-
Diffractometer	Stoe IPDS 2	Stoe IPDS 2	Bruker D8 Quest
Radiation	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)
2 θ range for data collection/°	2.996 to 55.00	3.402 to 51.996	4.43 to 54.994
Reflections collected	43825	25403	71075
Independent reflections	11030 [R _{int} = 0.0349, R _{sigma} = 0.0412]	4933 [R _{int} = 0.0507, R _{sigma} = 0.0374]	14356 [R _{int} = 0.0277, R _{sigma} = 0.0209]
Data/restraint/parameters	11030/5/526	4933/0/257	14356/0/642
Goodness-of-fit on F ²	0.899	1.041	1.024
Final R indexes [all data]	R ₁ = 0.0511, wR ₂ = 0.0680	R ₁ = 0.0709, wR ₂ = 0.0799	R ₁ = 0.0168, wR ₂ = 0.0359
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0305, wR ₂ = 0.0650	R ₁ = 0.0380, wR ₂ = 0.0729	R ₁ = 0.0202, wR ₂ = 0.0368
Largest diff. peak/hole/ e Å ⁻³	1.92/-0.95	1.33/-0.53	2.66/-1.22
CCDC	2012039	2012041	2032570

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7551Binary interpnictogen compounds bearing diaryl
bismuth fragments bound to all lighter pnictogens†Tobias Dunaj,  Kevin Dollberg  and Carsten von Hänisch *

Multiple interpnictogen compounds with covalent single bonds between a diarylbismuth fragment and all lighter pnictogens were prepared from the corresponding diarylhalido bismuthanes. The aminobismuthanes $\text{Ph}_2\text{BiNMe}_2$ (**1**) and $\text{Mes}_2\text{BiNMe}_2$ (**2**) (Mes = 2,4,6-trimethylphenyl-) have been obtained via a salt metathesis reaction and compound **2** was successfully reacted with $t\text{BuNH}_2$ in a condensation reaction to yield $\text{Mes}_2\text{BiNHtBu}$ (**3**). The bismuthanyl phosphanes $\text{Ar}_2\text{BiPtBu}_2$ (Ar = Ph: **4** and Ar = Mes: **5**) and arsanes $\text{Ar}_2\text{BiAs}t\text{Bu}_2$ (Ar = Ph: **8** and Ar = Mes: **9**) were also obtained via salt metathesis. Through a trimethylsilyl halide abstraction reaction of the diaryl halido bismuthanes and $\text{EtBu}(\text{SiMe}_3)_2$ (E = P and As), the bismuthanyl phosphanes $\text{Ar}_2\text{BiPtBu}(\text{SiMe}_3)$ (Ar = Ph: **6**; Ar = Mes: **7**) and the arsanes $\text{Ar}_2\text{BiAs}t\text{Bu}(\text{SiMe}_3)$ (Ar = Ph: **10**; Ar = Mes: **11**) have been prepared. Bismuthanyl stibanes were accessed via a condensation reaction of Mes_2SbH with **1** or **2**, respectively. The compound $\text{Ph}_2\text{BiSbMe}_2$ (**12**), which has different substituents at the bismuth and antimony atoms, was isolated and fully characterised. In contrast, the isolation of $\text{Mes}_2\text{BiSbMe}_2$ (**13**) was not possible due to a dynamic equilibrium with Mes_4Bi_2 and Mes_4Sb_2 which was investigated via low-temperature $^1\text{H-NMR}$ spectroscopy in solution. The isolated compounds with a single bond between bismuth and the heavy pnictogens arsenic and antimony are rare examples of their kind. All isolated compounds (**1–12**) were characterised by NMR and IR spectroscopy, mass spectrometry, elemental analysis and single crystal X-ray diffraction.

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Introduction

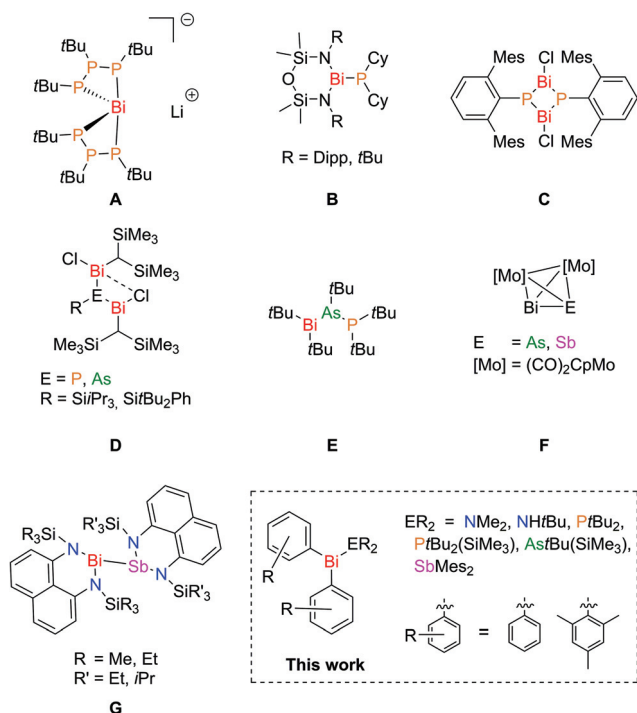
Homoleptic bismuthanetriamines have been known since the 1960s.¹ However, since then only few additional bismuthane triamines were described in the 1970s and 1980s^{2,3} and their potential use in atomic layer deposition (ALD) has been studied.⁴ Moreover, homoleptic hexaaryl bismuthane triamines have been used in E–E (E = pnictogens) coupling reactions recently.⁵ Most heteroleptic alkyl or aryl bismuthanetriamines of the form $\text{RBi}(\text{NR}'_2)_2$ reported in the literature have an intramolecular amine moiety acting as a donor ligand.⁶ Besides one entry ($\text{Ph}_2\text{Bi-NHDipp}$; Dipp = 2,6-diisopropylphenyl-) in the CCDC structure database, bismuthanetriamines of the general formula R_2BiNR_2 (R = alkyl, aryl, H) are unknown in the literature.⁷ However, it should also be mentioned that there are two patents, which claim the preparation of two other compounds, $\text{Me}_2\text{BiNMe}_2$ ⁸ and $\text{Ph}_2\text{BiN}i\text{Pr}_2$.⁹

Interpnictogen compounds containing a Bi–E bond (E = P, As, and Sb) are very scarce in the literature. For a long time, these compounds were restricted to coordination compounds of bismuth halides or bismuthanes and tertiary phosphanes.¹⁰ More recently, coordination compounds with arsanes^{11,12} and stibanes¹² have been prepared. The first compound featuring a PR_2 -fragment bound to a bismuth centre was not isolated until 1999 (Scheme 1, **A**).¹³ Since then, multiple structural motifs bearing covalent Bi–P single bonds have been realised. Some exemplary compounds are shown in Scheme 1 (**B–D**).^{14–18}

The first spectroscopically observed compounds with a Bi–As or Bi–Sb single bond were $\text{Me}_2\text{BiEMe}_2$ (E = As and Sb). However, these compounds undergo a dismutation reaction and are in equilibrium with the corresponding dibismuthane and diarsane or distibane, respectively, and thus, are not isolable. In the arsenic case, the equilibrium strongly disfavours the mixed compound, while the equilibrium constant in the antimony case is close to unity.¹⁹ The first isolated compounds with covalent Bi–As single bonds have the general formula $\text{RAs}(\text{BiClR}')_2$ (R = $\text{Si}i\text{Pr}_3$, $\text{Si}t\text{Bu}_2\text{Ph}$; R' = $\text{CH}(\text{SiMe}_3)_2$) and feature an arsenic atom bridging two bismuth atoms (Scheme 1, **D**).¹⁴ Moreover, a compound where an As_2 fragment is bound to four Bi atoms has been isolated and structurally characterised.¹⁴ In 2021, the first terminal bismuthanyl arsane was realised in the ternary interpnictogen compound $t\text{Bu}_2\text{BiAs}(t\text{Bu})\text{PtBu}_2$ (Scheme 1, **E**).²⁰

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† Electronic supplementary information (ESI) available. CCDC 2151498–2151509. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d2dt00472k>



Scheme 1 Examples for isolated compounds containing Bi–P (A–D),^{13–18} Bi–As (D–F)^{14,15,20} and Bi–Sb (F–G)^{21,23} single bonds. Moreover, the goal of this work is shown.

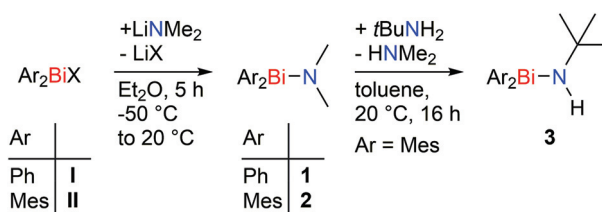
In 2020, the first isolable bismuthanyl stibanes with a thermally stable Bi–Sb single bond were prepared (Scheme 1, G). The authors ascribe the lack of a disproportionation reaction partially to the attractive dispersion effects of the sophisticated bis(silylamino)naphthalene ligands at the Bi and Sb centres.²¹ It should also be mentioned that a Bi–Sb double bond stabilised by very bulky substituents has been reported before.²² Moreover, Scheer and co-workers reported about compounds consisting of $[\text{Mo}]_2\text{BiE}$ -tetrahedra ($[\text{Mo}] = [\text{Mo}(\text{CO})_2\text{Cp}]$; $E = \text{Sb}$ and As) where a bond order of around 1.5 is ascribed for the Bi–E bond (Scheme 1, F).²³

Herein, we report the synthesis and characterisation of multiple interpnictogen compounds prepared from diphenyl or dimesityl halido bismuthanes, featuring Bi–E bonds to all lighter pnictogens, including compounds with rare arsenic- and antimony–bismuth bonds ($E = \text{N, P, As}$ and Sb). All isolated compounds were characterised by NMR and IR spectroscopy, mass spectrometry and elemental analysis. Moreover, the equilibrium of (dimesitylbismuthanyl)dimesitylstibane and the corresponding dibismuthane and distibane has been investigated *via* low temperature ¹H NMR spectroscopy.

Results and discussion

Preparation of bismuthanamines

The reaction of chloro diphenylbismuthane (**I**) or chloro dimesitylbismuthane (**II**) with LiNMe_2 in diethylether at -50°C proceeds smoothly and gives the 1,1-diaryl-*N,N*-dimethyl-



Scheme 2 Synthesis of the bismuthanamines 1–3.

bismuthanamines **1** and **2** in good yields (Scheme 2). Crystals suitable for single crystal X-ray diffraction were obtained from a toluene (**1**) or a pentane solution (**2**), respectively, at -32°C .

Compound **1** crystallises in the triclinic space group $P\bar{1}$ with two molecules in the asymmetric unit. The bismuth atom of each molecule shows a short intermolecular contact with a nitrogen atom of the following, and the π -system of a phenyl ring from the previous molecule. As a result, a one-dimensional polymer string is formed in the solid state, where each bismuth atom is coordinated fivefold and shows a square pyramidal coordination geometry (Fig. 1a). The intramolecular Bi–N bond lengths in **1** are 223.6(4) and 223.8(4) pm, respectively. This fits well with the literature known compounds like $\text{Bi}(\text{NMe}_2)_3$,²⁴ $\text{Bi}(\text{NPh}_2)_3$,³ or $\text{Bi}(\text{N}(\text{SiMe}_3)_2)_3$.⁴ The intermolecular Bi–N distances are 312.8(4) and 315.9(4) pm, which are significantly smaller than the sum of their van der Waals-

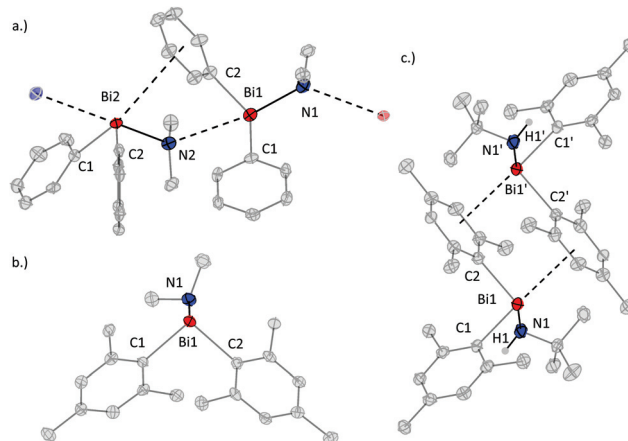


Fig. 1 Molecular structures of **1** (a, top left), **2** (b, bottom, left) and **3** (c, right) in the solid state. Hydrogen atoms at carbon are omitted for clarity. Ellipsoids are shown at a 50% probability level. (a) Selected bond lengths (pm) and angles ($^\circ$) of **1**: Bi1–N1 223.6(4); Bi2–N2 223.8(4); Bi1–N2 315.8(4); Bi2–N1 312.8(4); Bi1–C1 224.6(4); Bi1–C2 226.4(6); Bi2–C3 224.1(4); Bi1–C4 226.0(4); C1–Bi1–C2 97.1(2); N1–Bi1–C1 96.6(1); N1–Bi1–C2 95.7(2); Bi1–N1–Bi2 121.5(1); N1–Bi1–N2 170.1(1); C3–Bi2–C4 97.3(1); N2–Bi2–C3 95.5(2); N2–Bi2–C4 94.5(2); Bi2–N2–Bi1 118.8(1); N2–Bi2–N1 170.3(1). (b) Selected bond lengths (pm) and angles ($^\circ$) of **2**: Bi1–N1 220.8(4); Bi1–C1 226.9(4); Bi1–C2 228.0(4); C1–Bi1–C2 97.3(1); N1–Bi1–C1 94.6(1); N1–Bi1–C2 102.4(1). (c) Molecules corresponding to atoms labelled with an apostrophe are symmetry generated using $1 - x$, $1 - y$ and $1 - z$. Selected bond lengths (pm) and angles ($^\circ$) of **3**: Bi1–N1 219.8(3); Bi1–C1 226.8(3); Bi1–C2 227.3(3); C1–Bi1–C2 98.7(1); N1–Bi1–C1 90.7(1); N1–Bi1–C2 100.6(1).

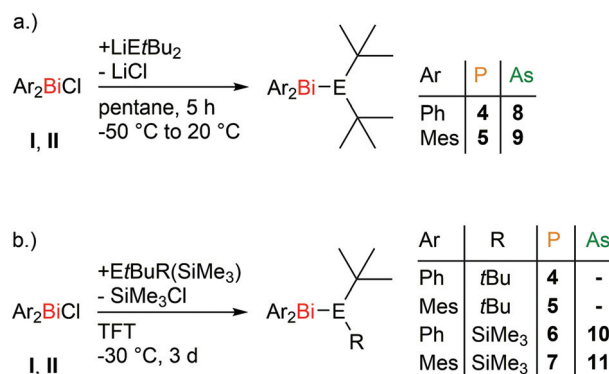
radii (362 pm)²⁵ and similar to those in Bi(NMe₂)₃ (319(2)–322(2) pm) where the central bismuth atom shows sixfold coordination.²⁴ The distances between the bismuth atom and a centroid of the coordinating phenyl ring are 381.79(2) pm and 367.27(2) pm, which is well within the range of an attractive Bi– π interaction.²⁶ Contrary to **1**, no intermolecular short contacts are observed in **2**, which crystallises in the monoclinic space group *P*2₁/*c* (Fig. 1b). This is probably due to the larger steric demand of the mesityl substituent. The steric demand of the aryl substituents does not seem to have a large impact on the intramolecular Bi–N bond. At 220.9(4) pm, the Bi–N bond in **2** is even a little shorter than in **1**.

In previous works we were able to prepare interpnictogen compounds of lighter pnictogens with functionalisable NH*t*Bu substituents.^{15,20,27} Using the same approaches, the reactions of **I** and **II** with LiNH*t*Bu or NH₂*t*Bu were attempted. These either did not proceed at all or were unselective. However, a reaction of **2** with an excess *t*BuNH₂ at 20 °C in toluene proceeds in a selective manner. By elimination of dimethylamine, *N-tert-butyl-1,1-dimesitylbismuthanamine* (**3**) is obtained in a yield of 46%. The proton of the secondary amine shows a chemical shift of 2.37 ppm in the ¹H NMR spectrum and the NH bond is confirmed further by the IR spectrum; a band at 3277 cm^{−1} is observed. Compound **3** crystallises in the triclinic space group *P* $\bar{1}$ with *Z* = 2. The Bi–N bond length is 219.3(5) pm which fits well with the previously discussed bismuthanamines. The bismuth centre shows a π -interaction to a Mes substituent of a neighbouring molecule and *vice versa*, leading to the formation of dimers through Bi– π interactions (Fig. 1c). The distance between bismuth and the centroid of the coordinating Mes substituent is 364.2(3) pm, which corresponds well with the Bi– π interaction in **1** and is well within the range of bonding Bi– π -interactions.²⁶

Preparation of bismuthanyl phosphanes and arsanes

In a previous work, we presented the preparation of Dipp₂BiPtBu₂ (Dipp = 2,6-diisopropylphenyl-), one of the few examples of compounds with a covalent Bi–P bond.²⁸ Using a similar approach, **I** or **II** react with LiPtBu₂ in pentane at –50 °C, which gives the desired di-*tert*-butyl(diarylbi-muthanyl)phosphanes **4** and **5** in yields of 70% and 75% (Scheme 3a). Alternatively, **4** and **5** are accessed by a reaction of **I** or **II** and PtBu₂(SiMe₃) in α,α,α -trifluorotoluene (TFT), where a Bi–P bond is formed *via* the elimination of trimethylsilyl chloride. This gives yields of 65% and 61% (Scheme 3b). Both compounds are fairly stable against light and temperature and show no visible decomposition after several hours of exposure to light and ambient temperature. However, decomposition with the formation of a black solid is observed after several days at ambient temperatures or exposure to light with **4** decomposing faster than **5**.

Compounds **4** and **5** show singlets in the ³¹P NMR spectra at 75.6 ppm (**4**) and 61.7 ppm (**5**), which is in a similar shift range as Dipp₂BiPtBu₂ (84.3 ppm).²⁸ Crystals of **4** and **5** suitable for single crystal X-ray diffraction were obtained from a concentrated solution in pentane at –32 °C (**4**) and in benzene



Scheme 3 Synthesis of the bismuthanyl phosphanes **4–7** and the bismuthanyl arsanes **8–11** via salt metathesis or trimethyl silyl halide elimination. TFT = α,α,α -trifluorotoluene.

at 5 °C (**5**), respectively. Compound **4** crystallises in the monoclinic space group *P*2₁/*n* (Fig. 2a). The Bi–P bond length of 265.07(9) pm fits well to other literature known bismuthanyl phosphanes like (Cy₂P)Bi{(NR)₂(SiMe₂)₂O} (**B**, Cy = Cyclohexyl; R = *t*Bu: 264.65(7) pm; R = Dipp: 265.03(4) pm)¹⁷ or SitBuPh₂P (BiClCH(SiMe₃)₂) (**D**) (262.6(2) pm; 265.1(2) pm),¹⁵ even though the coordination spheres of bismuth and phosphorus are vastly different in most of the reference compounds. The bond length of the structurally similar Dipp₂BiPtBu₂ (269.80(7) and 270.14(7) pm) is considerably longer than in **4**, due to the large Dipp substituents.²⁸

Compound **5** crystallises with two molecules in the asymmetric unit (Fig. 2b). With 267.2(1) and 268.4(1) pm, the Bi–P bond length is intermediate between **4** and Dipp₂BiPtBu₂, reflecting the rising steric demand from the phenyl to the Dipp substituent.

As all carbon substituted compounds were readily prepared, we attempted the preparation of bismuthanyl phosphanes

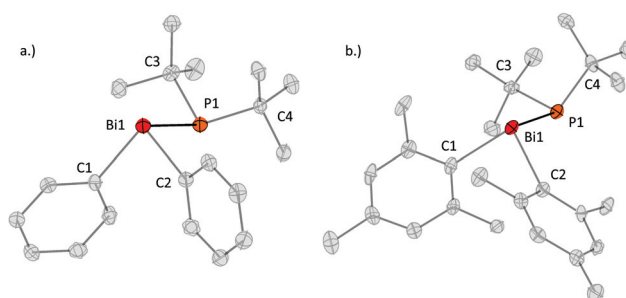


Fig. 2 Molecular structures of **4** (a, left) and one of the two molecules of the asymmetric unit of **5** (b, right) in the solid state. Hydrogen atoms are omitted for clarity. Ellipsoids are shown at a 50% probability level. (a) Selected bond lengths (pm) and angles (°) of **4**: Bi1–P1 265.08(8); Bi1–C1 225.3(3); Bi1–C2 225.7(3); C1–Bi1–C2 93.6(1); P1–Bi1–C1 93.20(8); P1–Bi1–C2 96.55(8). (b) Selected bond lengths (pm) and angles (°) of **5**: Bi1–P1 267.2(1); Bi2–P2 268.4(1); Bi1–C1 227.5(4); Bi1–C2 229.9(4); Bi2–C5 227.8(4); Bi2–C6 231.4(4); C1–Bi1–C2 93.7(1); P1–Bi1–C1 102.8(1); P1–Bi1–C2 107.6(1); C5–Bi2–C6 94.9(1); P2–Bi2–C5 100.7(1); P2–Bi2–C6 107.6(1).

bearing functional groups at the phosphorus atom. As trimethylsilyl chloride elimination has proven to be a powerful tool in the formation of Bi–P bonds under mild conditions, we wanted to replace one *tert*-butyl group with an additional trimethylsilyl substituent. The reaction of **I** and **II** with $\text{PtBu}(\text{SiMe}_3)_2$ in TFT at -30°C proceeds smoothly and the desired *tert*-butyl(diarylbi-muthanyl)(trimethylsilyl)phosphanes **6** and **7** are obtained in 53% and 55% yield (Scheme 3b). The two compounds show similar stability under the influence of light and temperature as **4** and **5**.

The ^{31}P NMR spectra of **6** and **7** show singlet signals with resonances at -45.8 ppm (**6**) and -60.0 ppm (**7**), respectively. Crystals of **6** and **7** suitable for single crystal X-ray diffraction were obtained from concentrated solutions in pentane at -32°C . The molecular structures of **6** and **7** in the solid state are shown in Fig. 3. The Bi–P bond in **6** has a length of 262.1(1) pm and is shorter than the bond in the structurally similar compound **4** (265.07(9) pm).

This might be due to the lower cone angle of the SiMe_3 substituent in **6** compared to a *t*Bu group in **4**.²⁹ Compound **7** shows disorder in the solid state with respect to an exchange of the *t*Bu and the SiMe_3 substituent. The two domains have an occupancy of 73 and 27% after free refinement. As a result, the Bi–P bond lengths need to be interpreted with care. However, with 268.6(5) and 263(2) pm, respectively, they fit well with the previously reported data of **4–6**.

Examples of compounds with covalent Bi–As bonds are very rare in the literature. In fact, only five compounds have been structurally characterised so far.^{14,20,23} Reaction of **I** and **II** with $\text{LiAs}t\text{Bu}_2$ in pentane at -50°C leads to the formation of the corresponding (diarylbi-muthanyl)di-*tert*-butylarsanes **8** and **9** in good yields (Scheme 3). Compounds **8** and **9** can be handled at ambient temperature and exposure to light for several minutes with noticeable decomposition starting within

hours. Crystals suitable for single crystals X-ray diffraction were obtained from pentane at -32°C . The molecular structures of **8** and **9** in the solid state are shown in Fig. 4. Compound **8** crystallises isomorphically to **4** in the monoclinic space group $P2_1/n$. The length of the Bi–As single bond is 273.15(7) pm, which fits well with the other literature known Bi–As bonds (264(2)–275.75(9) pm).^{14,20,23}

Compound **9** crystallises in the monoclinic space group $P2_1/n$ with only one molecule in the asymmetric unit. With 278.15(8) pm, the Bi–As bond in **9** is significantly elongated compared to **8**, due to the larger aromatic substituents. To the best of our knowledge, it is the longest covalent Bi–As single bond reported so far.

As in the bismuthanyl phosphanes, we wanted to introduce functional silyl substituents to the bismuthanyl arsanes. Therefore, **I** and **II** were reacted with $\text{As}t\text{Bu}(\text{SiMe}_3)_2$ in TFT at -32°C (Scheme 3). The reaction proceeds smoothly and the corresponding (diarylbi-muthanyl)(*tert*-butyl)(trimethylsilyl)arsanes **10** and **11** are obtained in yields of 38% and 53%.

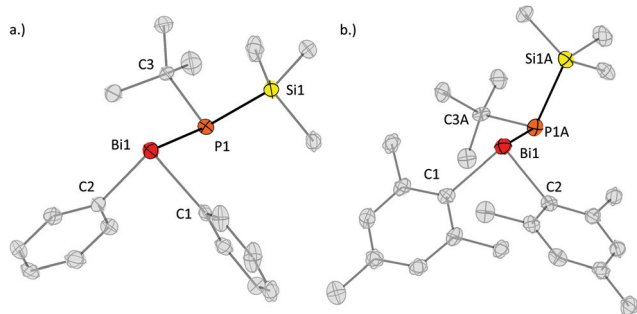


Fig. 3 Molecular structures of **6** (a, left) and **7** (b, right) in the solid state. Hydrogen atoms are omitted and disorder in compound **7** is not shown for clarity. Disordered atoms are labelled with the suffixes A and B. Ellipsoids are shown at a 50% probability level. (a) Selected bond lengths (pm) and angles ($^\circ$) of **6**: Bi1–P1 262.1(1); Bi1–C1 224.8(4); Bi1–C2 225.2(4); P1–Si1 226.7(2); C1–Bi1–C2 93.1(1); P1–Bi1–C1 90.9(1); P1–Bi1–C2 96.1(1). (b) Selected bond lengths (pm) and angles ($^\circ$) of **7**: Bi1–P1A 268.6(6); Bi1–P1B 263(2); Bi1–C1 227.6(3); Bi1–C2 230.0(3); P1A–Si1A 227.4(5); P1B–Si1B 226.8(2); C1–Bi1–C2 94.0(1); P1A–Bi1–C1 98.2(1); P1B–Bi1–C1 105.8(1); P1A–Bi1–C2 106.8(1); P1B–Bi1–C2 104.8(4).

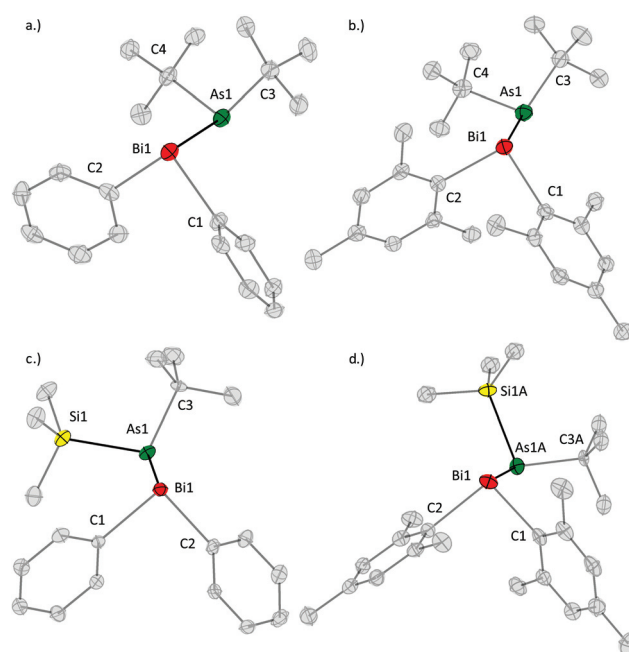


Fig. 4 Molecular structures of **8** (a, top left), **9** (b, top right), **10** (c, bottom left), and **11** (d, bottom right) in the solid state. Hydrogen atoms are omitted and disorder in compound **11** is not shown for clarity. Disordered atoms are labelled with the suffixes A and B. Ellipsoids are shown at a 50% probability level. (a) Selected bond lengths (pm) and angles ($^\circ$) of **8**: Bi1–As1 273.15(7); Bi1–C1 225.5(6); Bi1–C2 225.7(6); C1–Bi1–C2 93.9(2); As1–Bi1–C1 92.7(2); As1–Bi1–C2 94.9(2). (b) Selected bond lengths (pm) and angles ($^\circ$) of **9**: Bi1–As1 278.15(6); Bi1–C1 229.8(4); Bi1–C2 228.3(3); C1–Bi1–C2 94.5(1); As1–Bi1–C1 106.94(9); As1–Bi1–C2 101.78(1); (c) selected bond lengths (pm) and angles ($^\circ$) of **10**: Bi1–As1 272.27(4); Bi1–C1 224.1(4); Bi1–C2 225.7(4); As1–Si1 237.2(1); C1–Bi1–C2 92.2(1); As1–Bi1–C1 97.9(1); As1–Bi1–C2 94.0(1). (d) Selected bond lengths (pm) and angles ($^\circ$) of **11**: Bi1–As1A 277.6(5); Bi1–As1B 271.9(8); Bi1–C1 227.3(4); Bi1–C2 229.1(4); As1A–Si1A 239.9(8); As1B–Si1B 240(2); C1–Bi1–C2 94.5(1); As1A–Bi1–C1 97.6(1); As1B–Bi1–C1 104.3(1); As1A–Bi1–C2 107.0(1); As1B–Bi1–C2 105.8(2).

Their stability against light and temperature is similar to that of **8** and **9**.

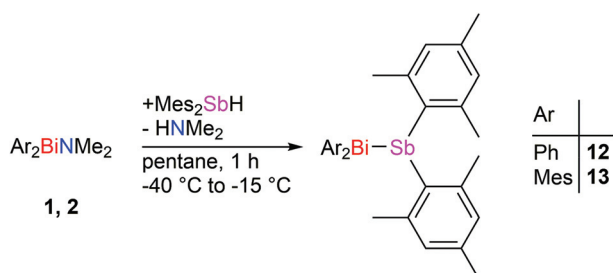
Compound **10** crystallises in the monoclinic space group $C2/c$ (Fig. 4). The Bi–As bond length is 270.26(7) pm and slightly shorter than that in the previously discussed compound **8**. This behaviour is similar to those of compounds **4** and **6** and might again be traced to the lower cone angle of SiMe_3 compared to $t\text{Bu}$.²⁹ Compound **11** crystallizes in the space group $P2_1/c$ (Fig. 4).

Similar to **7**, compound **11** shows a disorder of the $t\text{Bu}$ and the SiMe_3 substituents with an occupancy of 60% and 40% of the two domains after free refinement. Again, the bond lengths and distances have to be interpreted with care. The Bi–As bond lengths in the two domains are 271.9(8) and 277.6(5) pm. The large difference probably results from the disorder in the solid state.

Preparation of bismuthanyl stibanes

The preparation of bismuthanyl stibanes with simple alkyl substituents at the bismuth and antimony atoms was attempted in the past. However, in the compounds obtained, bismuthanyl stibanes undergo a redistribution reaction and an equilibrium with the corresponding dibismuthane and distibane is observed.^{19,30} Only very recently, the first isolable bismuthanyl stibanes bearing highly sophisticated bis(silylamino) naphthalene substituents have been reported in the literature.^{21–23} Chitnis and colleagues showed that the Bi–Sb bonds can be formed by the reaction of a bismuthanamine and an antimony hydride.²¹ In a similar approach, we reacted **1** and Mes_2SbH in pentane at $-40\text{ }^\circ\text{C}$, which gave (diphenylbismuthanyl)dimesitylstibane (**12**) and small amounts of the corresponding distibane and dibismuthane (Scheme 4). After crystallisation, orange crystals of **12** were isolated by manually separating them from crystalline side products.

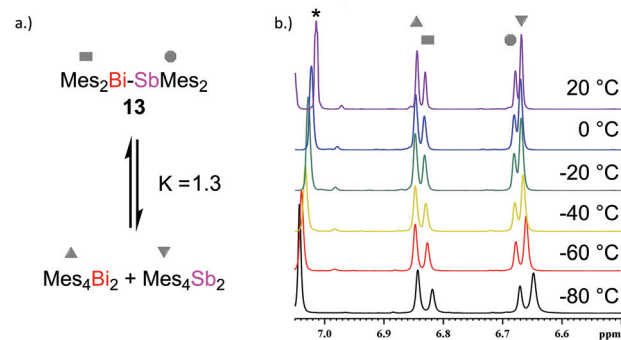
Upon dissolving the pure crystals of **12**, the NMR spectrum shows small signals for the dibismuthane Ph_4Bi_2 and the distibane Mes_4Sb_2 , indicating an equilibrium that lies far on the side of the bismuthanyl stibane. The equilibrium constant is calculated to be $K = [\text{Ph}_2\text{BiSbMes}_2]^2 / [\text{Ph}_4\text{Bi}_2]^{-1} [\text{Mes}_4\text{Sb}_2]^{-1} = 76$ at $20\text{ }^\circ\text{C}$ in toluene- d_8 . The equilibrium was further investigated at different temperatures from $-80\text{ }^\circ\text{C}$ to $+20\text{ }^\circ\text{C}$. No significant dependence on temperature was observed. Using the obtained equilibrium constants at different temperatures, we



Scheme 4 Synthesis of the bismuthanyl stibanes **12** and **13**.

were able to calculate the reaction enthalpy ($\Delta H_r^\circ = 0.6(2)\text{ kJ mol}^{-1}$), reaction entropy ($\Delta S_r^\circ = 37.8(9)\text{ J mol}^{-1}\text{ K}^{-1}$) and reaction free energy at $20\text{ }^\circ\text{C}$ ($\Delta G_r^\circ = -10.47(5)\text{ kJ mol}^{-1}$) (ESI, Table S1 and Fig. S3.1†). As expected from the low temperature dependence of the equilibrium, ΔH_r° is close to zero. Crystals of **12** suitable for single crystal X-ray diffraction were obtained from a pentane solution at $-32\text{ }^\circ\text{C}$. Compound **12** crystallises in the triclinic space group $P\bar{1}$ with one molecule in the asymmetric unit (Fig. 5). The Bi–Sb bond length is 292.57(4) pm. This is slightly shorter than that in the bis(silylamino)naphthalene substituted compounds prepared by Chitnis and co-workers (297.64(7)–297.75(9) pm),²¹ which is probably due to the lower steric strain in **12**. In fact, these bond lengths are in the region of the previously reported $\text{BbtBi}=\text{SbBbt}$ ($\text{Bbt} = o,o\text{-}(\text{CH}(\text{SiMe}_3)_2)_2p\text{-CH}(\text{SiMe}_3)\text{-C}_6\text{H}_2$) featuring a formal Bi–Sb double bond (297.2(5) pm).²²

Upon the reaction of **2** and Mes_2SbH , the formation of **13** is observed, indicated by the colour change of the reaction mixture from yellow to orange and new signals arising in the NMR spectra. Besides **13**, large signals corresponding to Mes_4Sb_2 ³¹ and Mes_4Bi_2 ³² are observed as well. Hence, an equilibrium reaction is observed. Due to the dynamic equilibrium, isolation of the pure compound **13** was not possible. The equilibrium was confirmed by mass spectrometry (LIFDI+) of a toluene solution of a mixture of Mes_4Bi_2 and Mes_4Sb_2 , where signals corresponding to the dibismuthane, distibane and bismuthanyl stibane were observed. Moreover, temperature dependent NMR-spectroscopy of a mixture of Mes_4Bi_2 and Mes_4Sb_2 in toluene- d_8 was performed, further verifying the equilibrium. The equilibrium constant at $20\text{ }^\circ\text{C}$ is $K = 1.1$, which means that it does not lie on the side of the bismuthanyl stibane, as in **12**. Compound **13** rather behaves similar to literature known compounds $\text{Me}_2\text{BiSbMe}_2$ ($K = 1.2$) or $n\text{Pr}_2\text{BiSbMe}_2$ ($K = 0.7$).^{19,30} Low temperature NMR spectroscopy indicates that the equilibrium is not influenced by temperature (Scheme 5). Again, we were able to extract the reaction enthalpy ($\Delta H_r^\circ = -0.6(2)\text{ kJ mol}^{-1}$), reaction entropy ($\Delta S_r^\circ = -2.1(8)\text{ J mol}^{-1}\text{ K}^{-1}$) and reaction free energy at $20\text{ }^\circ\text{C}$ ($\Delta G_r^\circ =$



Scheme 5 (a) Equilibrium reaction of **13** and Mes_4Bi_2 and Mes_4Sb_2 . (b) Excerpt from the aromatic region of the ^1H NMR spectra of a mixture of Mes_4Bi_2 and Mes_4Sb_2 in toluene- d_8 at different temperatures. *toluene- d_8 .

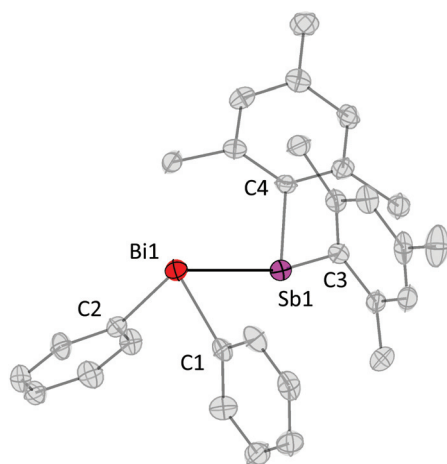


Fig. 5 Molecular structure of **12** in the solid state. Hydrogen atoms are omitted for clarity. Ellipsoids are shown at a 50% probability level. Selected bond lengths (pm) and angles ($^{\circ}$): Bi1–Sb1 292.56(3); Bi1–C1 224.0(4); Bi1–C2 225.6(4); Sb1–C3 216.6(5); Sb1–C4 217.2(4); C1–Bi1–C2 95.1(2); C1–Bi1–Sb1 85.0(1), C2–Bi1–Sb1 94.9(1); C3–Sb1–C4 101.8(1); C3–Sb1–Bi1 88.5(1); C4–Sb1–Bi1 110.1(1).

$-0.03(5)\text{kJ mol}^{-1}$) (ESI, Table S1 and Fig. S3.2†). The equilibrium constants of **12** and **13** are rather different, even though the substitution pattern of both compounds is electronically and sterically very similar which should lead to Bi–Sb bonds of similar strength. As a result, the equilibria are likely driven by reaction entropy which is close to zero for the equilibrium of compound **13** but significantly positive for the formation of the mixed substituted compound **12**.

In conclusion, we showed an alternative pathway for the stabilization of labile Bi–Sb bonds *via* different substituents at the bismuth and antimony atoms rather than by dispersive interactions of the substituents, as is the case of compounds presented by Chitnis.²¹

Conclusions

In this work, we report on the preparation of multiple binary interpnictogen compounds featuring covalent single bonds of bismuth to all lighter pnictogens. Several synthetic pathways for the preparation of the interpnictogen compounds were realized. Bismuthanamines **1** and **2**, bismuthanyl phosphanes **4** and **5**, and bismuthanyl arsanes **8** and **9** were prepared *via* salt metathesis from the corresponding diaryl bismuthane chlorides and LiNMe_2 , LiPtBu_2 , or LiAstBu_2 , respectively. Moreover, the bismuthanyl phosphanes **6** and **7** and the bismuthanyl arsanes **10** and **11** bearing a trimethylsilyl substituent for potential further functionalisation have been prepared from diaryl halido bismuthanes and $\text{EtBu}(\text{SiMe}_3)_2$ ($\text{E} = \text{P}$ and As). Upon reaction of **1** and $t\text{BuNH}_2$, the NH functionalized compound **3** was obtained. In a similar reaction of **1** or **2** and Mes_2SbH , the bismuthanyl stibanes **12** and **13** were obtained by a condensation reaction with the release of dimethylamine.

Compounds **12** and **13** are two of the few examples of compounds with a covalent Bi–Sb single bond, with **12** being isolable and with this an even rarer example of its kind. Both **12** and **13** form an equilibrium with the dibismuthane and distibane in solution. For **12**, this equilibrium strongly favours the bismuthanyl stibane ($K = 76$ at $20\text{ }^{\circ}\text{C}$), whereas the equilibrium constant is close to 1 for **13** ($K = 1.1$ at $20\text{ }^{\circ}\text{C}$). The equilibrium reaction was confirmed by mass spectrometry of a mixture of Mes_4Bi_2 and Mes_4Sb_2 in toluene and ^1H NMR spectroscopy of the same mixture in toluene- d_8 ; compound **13** was observed in both cases. By temperature dependent ^1H NMR measurements, the reaction enthalpy and reaction entropy of the equilibria of **12** and **13** were calculated. Some of the prepared compounds still bear functional groups in the form of protons or trimethylsilyl substituents. These species will be used as educts in the preparation of ternary or quaternary interpnictogen compounds in future experiments.

Experimental

General procedure

All manipulations were carried out under an argon atmosphere and exclusion of light using the standard Schlenk technique. All solvents used in the reactions and for crystallisations were dried *via* standard techniques, distilled and stored under argon.³³ The solvents were never stored longer than three weeks before use. The obtained products often contained systematic impurities with educts or hydrolysed products and hence have to be re-crystallised to obtain high purity compounds suitable for elemental analysis. The yields given below always refer to the purified and not the raw products. Ph_2BiCl ,³⁴ Mes_2BiCl ,³⁵ LiPtBu_2 ,³⁶ $\text{PtBu}_2\text{SiMe}_3$,³⁷ $\text{PtBu}(\text{SiMe}_3)_2$,³⁸ LiAstBu_2 ,³⁹ $\text{AstBu}(\text{SiMe}_3)_2$,⁴⁰ Mes_2SbH ,⁴¹ Mes_4Bi_2 ²⁸ and Mes_4Sb_2 ⁴² were prepared according to the literature procedures. The NMR spectra were recorded using a Bruker Avance II 300 MHz or a Bruker Avance III 500 MHz spectrometer. If not otherwise specified, the spectra were measured at 300 K. The IR spectra were recorded using a Bruker FT-IR spectrometer in the attenuated total reflectance (ATR) mode. For mass spectrometry, a Jeol AccuTOF GCv (CI, LIFDI) was used. The FD-emitters were purchased from Linden Chromaspec GmbH. Elemental analysis was performed using an Elementar Vario MicroCube.

General procedure for the syntheses of $\text{Ph}_2\text{BiNMe}_2$ (**1**) and $\text{Mes}_2\text{BiNMe}_2$ (**2**)

LiNMe_2 (1 eq.) was added to a solution of **I** (1.00 g, 2.5 mmol) in 100 ml of diethylether or **II** (6.43 g, 13.3 mmol) in 200 ml of diethylether, cooled to $-50\text{ }^{\circ}\text{C}$. The suspensions were allowed to warm to room temperature over the course of five hours. After evaporation of the solvent under reduced pressure, the remaining solids are taken up in 100 (**1**) or 300 ml (**2**) of toluene, respectively. The suspension is filtered and the filtrate is dried under reduced pressure. The raw product is further purified by suspension in pentane and an additional filtration.

The obtained filtrate is concentrated and stored at $-32\text{ }^{\circ}\text{C}$. After one week, analytically pure materials of **1** and **2** are obtained.

Ph₂BiNMe₂ (1): Yield 30%.

Elemental analysis for C₁₄H₁₆BiN₁ calcd: C, 41.29; H, 3.96; N, 3.44; found: C, 41.00; H, 3.98; N, 3.65.

¹H NMR (300 MHz, C₆D₆) δ : 7.85–7.90 (m, 4H, *o*-CH), 7.30–7.37 (m, 4H, *m*-CH), 7.14–7.19 (m, 2H, *p*-CH), 3.37 (s, 6H, N(CH₃)₂).

¹³C{¹H} NMR (75 MHz, C₆D₆) δ : 169.1 (s, 1C, Bi-C), 136.8 (s, 4C, *o*-CH), 130.9 (s, 4C, *m*-CH), 128.5 (s, 4C, *p*-CH), 47.9 (s, 6H, N(CH₃)₂).

IR (cm⁻¹) $\tilde{\nu}$: 3056 (w), 3044 (w), 3034 (w), 1565 (w), 1478 (w), 1424 (m), 1326 (w), 1299 (w), 1259 (w), 1182 (w), 1153 (w), 1054 (w), 1013 (w), 995 (m), 851 (w), 721 (s), 691 (s), 448 (s), 434 (m).

HR-MS: CI(+) *m/z* 408.11592 [Ph₂BiNMe₂ + H]⁺; calcd 408.11648.

Mes₂BiNMe₂ (2): Yield 57%.

Elemental analysis for C₂₀H₂₈BiN₁ calcd: C, 48.88; H, 5.74; N, 2.85; found: C, 49.05; H, 5.61; N, 2.72.

¹H NMR (300 MHz, C₆D₆) δ : 6.92 (s, 4H, *m*-CH), 3.39 (s, 6H, N(CH₃)₂), 2.43 (s, 12H, *o*-C(CH₃)₃), 2.10 (s, 6H, *p*-C(CH₃)₃).

¹³C{¹H} NMR (75 MHz, C₆D₆) δ : 168.5 (s, 2C, Bi-C, found *via* HMBC), 145.5 (s, 4C, *o*-CCH₃), 137.5 (s, 4C, *p*-CCH₃), 130.9 (s, 4C, *m*-CCH₃), 48.7 (s, 2C, N(CH₃)₂), 25.2 (s, 4C, *o*-CCH₃), 21.2 (s, 2C, *p*-CCH₃).

IR (cm⁻¹) $\tilde{\nu}$: 3010 (w), 2960 (m), 2942 (m), 2912 (m), 2854 (m), 2831 (m), 2800 (m), 2750 (s), 1592 (w), 1553 (w), 1458 (w), 1422 (s), 1400 (s), 1375 (m), 1287 (m), 1260 (m), 1236 (m), 1134 (s), 1088 (m), 1041 (s), 1023 (s), 1003 (m), 905 (s), 844 (s), 780 (m), 576 (m), 538 (m), 483 (m).

HR-MS: CI(+) *m/z* 492.21204 [Mes₂BiNMe₂ + H]⁺; calcd 492.21038.

Mes₂BiNHtBu (3): Compound **2** (500 mg, 1.02 mmol) is dissolved in 10 ml of toluene and 1.1 ml of NH₂tBu (744 mg, 10.20 mmol) is added at room temperature. The reaction mixture is stirred at room temperature for 16 h. Volatiles are removed under reduced pressure and the remaining highly viscous liquid is taken up in 15 ml of pentane. After filtration, the filtrate is concentrated in around 5 ml of solvent and left at $-32\text{ }^{\circ}\text{C}$ for two days. The precipitate is removed from the mother liquor, which is concentrated further to 2 ml. After storage at $-32\text{ }^{\circ}\text{C}$, **3** is obtained as a crystalline pale yellow solid in 46% yield.

Elemental analysis for C₂₂H₃₂BiN₁ calcd: C, 50.87; H, 6.21; N, 2.70; found: C, 50.60; H, 5.73; N, 2.95.

¹H NMR (300 MHz, C₆D₆) δ : 6.89 (s, 4H, *m*-CH), 2.46 (s, 12H, *o*-CCH₃), 2.36 (s, 1H, NH), 2.11 (s, 6H, *p*-CCH₃), 1.19 (s, 9H, NHC(CH₃)₃).

¹³C{¹H} NMR (75 MHz, C₆D₆) δ : 161.3 (s, 2C, Bi-C), 145.4 (s, 4C, *o*-CCH₃), 137.4 (s, 4C, *p*-CCH₃), 130.4 (s, 4C, *m*-CCH₃), 53.0 (s, C, NC(CH₃)₃), 34.6 (s, 3C, NC(CH₃)₃), 25.8 (s, 4C, *o*-CCH₃), 21.2 (s, 2C, *p*-CCH₃).

IR (cm⁻¹) $\tilde{\nu}$: 3277 (w), 3008 (w), 2952 (m), 2934 (m), 2915 (m), 2859 (w), 2727 (w), 1593 (w), 1553 (w), 1444 (s), 1399 (m), 1378 (m), 1356 (m), 1286 (m), 1261 (s), 1091 (m), 1023 (m), 1005

(m), 931 (w), 911 (m), 845 (s), 801 (w), 749 (w), 595 (w), 575 (s), 535 (s), 442 (w).

HR-MS: CI(+) *m/z* 518.22401 [M + H]⁺; calcd 518.22601.

General procedure for the syntheses of Ph₂BiEtBu₂ (E = P: 4; E = As: 8) and Mes₂BiEtBu₂ (E = P: 5; E = As: 9) *via* salt metathesis

LiEtBu₂ (1 eq.) was added to a suspension of **I** (**4**: 300 mg, 0.75 mmol; **8**: 600 mg, 1.51 mmol) or **II** (**5**: 300 mg, 0.62 mmol; **9**: 280 mg, 0.58 mmol) in 10–50 ml of pentane, cooled to $-50\text{ }^{\circ}\text{C}$. The suspension is allowed to warm to room temperature over the course of five hours. The reaction mixture is filtered and the yellow filtrate is concentrated and stored at $-32\text{ }^{\circ}\text{C}$. After one week, pale yellow crystals of **3** or yellow crystals of **4**, **7** or **8** are obtained, respectively.

General procedure for the syntheses of Ph₂BiPtBu₂ (4), Mes₂BiPtBu₂ (5), Ph₂BiEtBu(SiMe₃) (E = P: 6; E = As: 10) and Mes₂BiEtBu(SiMe₃) (E = P: 7; E = As: 11) *via* trimethylsilyl chloride elimination

Compound **I** (**4**: 50 mg, 0.13 mmol; **6**: 500 mg, 0.10 mmol; **10**: 400 mg; 1.00 mmol) or **II** (**5**: 50 mg, 0.10 mmol; **7**: 1.20 g; 2.49 mmol; **11**: 620 mg, 1.28 mmol) is suspended in 10–40 ml of α,α,α -trifluorotoluene, cooled to $-30\text{ }^{\circ}\text{C}$ and PtBu₂(SiMe₃) (1 eq.) or EtBu(SiMe₃)₂ (E = P, As; 1 eq.) is added. The resulting suspensions are stirred for three days at $-30\text{ }^{\circ}\text{C}$. After evaporation of the solvent under reduced pressure, the remaining yellow to orange solid is taken up in 10–50 ml of pentane. The remaining solids are removed *via* filtration and the obtained solution is concentrated. After one week of storage at $-32\text{ }^{\circ}\text{C}$, crystalline material of **4–7** or **10–11** is obtained.

Ph₂BiPtBu₂ (4): Salt metathesis: Yield 70%; Trimethylsilyl halide elimination: 65%.

Elemental analysis for C₂₀H₂₈BiP₁ calcd: C, 47.25; H, 5.55; found: C, 47.28; H, 5.62.

¹H NMR (500 MHz, C₆D₆) δ : 8.19–8.22 (m, 4H, *o*-CH), 7.17–7.22 (m, 4H, *m*-CH), 7.06–7.10 (m, 2H, *p*-CH), 1.23 (d, ³J_{P-H} = 10.7 Hz, 18H, PC(CH₃)₃).

¹³C{¹H} NMR (125 MHz, C₆D₆) δ : 148.3 (s, 2C Bi-C), 139.3 (d, ³J_{P-C} = 4.7 Hz, 4C, *o*-CH), 130.6 (s, 4C, *m*-CH), 127.8 (found *via* HMQC, 2C, *p*-CH), 35.1 (d, ¹J_{P-C} = 38.1 Hz, 2C, PC(CH₃)₃), 34.1 (d, ²J_{P-C} = 13.4 Hz, 6C, PC(CH₃)₃).

³¹P{¹H} NMR (200 MHz, C₆D₆) δ : 75.6 (s, 1P).

IR (cm⁻¹) $\tilde{\nu}$: 3056 (w), 3048 (w), 3037 (m), 2989 (w), 2974 (w), 2947 (m), 2932 (m), 2884 (m), 2852 (m), 1569 (m), 1465 (m), 1453 (m), 1427 (m), 1360 (m), 1165 (m), 1055 (m), 1012 (m), 995 (m), 807 (s), 772 (s), 694 (s), 643 (w), 450 (m), 443 (m).

HR-MS: CI(+) *m/z* 509.18305 [Ph₂BiPtBu₂ + H]⁺; calcd 509.18107.

Mes₂BiPtBu₂ (5): Salt metathesis: Yield 75%; Trimethylsilyl halide elimination: 61%.

Elemental analysis for C₂₆H₄₀BiP₁ calcd: C, 52.70; H, 6.80; found: C, 52.30; H, 6.82.

¹H NMR (500 MHz, C₆D₆) δ : 6.89 (s, 4H, *m*-CH), 2.68 (s, 12H, *o*-CCH₃), 2.07 (s, 6H, *p*-CCH₃), 1.31 (d, ³J_{P-H} = 8.4 Hz, 18H, P PC(CH₃)₃).

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, C_6D_6) δ : 152.5 (br s, 2C, Bi-C), 146.5 (s, 4C *o*- CCH_3), 137.4 (s, 2C *p*- CCH_3), 129.7 (s, 4C *m*-CH), 35.3 (d, $^1J_{\text{P-C}} = 42.2$ Hz, 2C, $\text{PC}(\text{CH}_3)_3$), 33.3 (d, $^2J_{\text{P-C}} = 13.4$ Hz, 6C, $\text{PC}(\text{CH}_3)_3$), 29.7 (s, 2C *o*- CCH_3), 29.6 (s, 2C *o*- CCH_3), 21.0 (s, 2C *p*- CCH_3).

$^{31}\text{P}\{^1\text{H}\}$ NMR (200 MHz, C_6D_6) δ : 62.0 (s, 1P).

IR (cm^{-1}) $\tilde{\nu}$: 3011 (w), 2996 (w), 2970 (w), 2936 (w), 2916 (m), 2888 (w), 2856 (m), 1458 (m), 1441 (m), 1361 (m), 1286 (w), 1168 (m), 1020 (w), 1001 (w), 941 (w), 879 (w), 844 (s), 806 (m), 699 (w), 578 (w), 539 (m), 465 (w), 412 (m).

HR-MS: CI^+ m/z 592.26483 [$\text{Mes}_2\text{BiPtBu}_2$] $^+$; calcd 592.26715.

Ph₂BiPtBu(SiMe₃) (6): Yield 53%.

Elemental analysis for $\text{C}_{19}\text{H}_{28}\text{Bi}_1\text{P}_1\text{Si}_1$ calcd: C, 43.51; H, 5.38; found: C, 43.41; H, 5.34.

^1H NMR (500 MHz, C_6D_6) δ : 8.18 (br, 4H, *o*-CH), 7.18 (t, $^3J_{\text{H-H}} = 7.3$ Hz, 4H, *m*-CH), 7.07 (t, $^3J_{\text{H-H}} = 7.4$, 2H, *p*-CH), 1.29 (d, $^3J_{\text{P-H}} = 11.7$, 9H, $\text{PC}(\text{CH}_3)_3$), 0.14 (d, $^3J_{\text{P-H}} = 3.8$ Hz, 9H, $\text{PSi}(\text{CH}_3)_3$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, C_6D_6) δ : 146.6 (br s, 2C, Bi-C), 139.1 (s, 4C, *o*-CH), 130.6 (s, 4C, *m*-CH), 128.4 (s, 2C, *p*-CH), 35.8 (d, $^2J_{\text{P-C}} = 11.0$, 3C, $\text{PC}(\text{CH}_3)_3$), 32.1 (d, $^1J_{\text{P-C}} = 29.2$, 1C, $\text{PC}(\text{CH}_3)_3$), 3.9 (d, $^2J_{\text{P-C}} = 9.9$, 3C, $\text{PSi}(\text{CH}_3)_3$).

$^{31}\text{P}\{^1\text{H}\}$ NMR (125 MHz, C_6D_6) δ : -45.7 (s, 1P).

^{29}Si -DEPT NMR (100 MHz, C_6D_6) δ : 2.9 (d, $^1J_{\text{P-Si}} = 50.4$, 1Si).

IR (cm^{-1}) $\tilde{\nu}$: 3056 (w), 3054 (m), 3033 (w), 3008 (w), 2961 (w), 2941 (m), 2924 (m), 2887 (m), 2884 (m), 2851 (m), 1567 (m), 1470 (m), 1456 (m), 1427 (s), 1459 (m), 1326 (m), 1242 (m), 1165 (m), 1053 (m), 1012 (m), 995 (s), 831 (m), 720 (s), 692 (s), 628 (m), 447 (m), 440 (m).

HR-MS: CI^+ m/z 525.15964 [$\text{Ph}_2\text{BiPtBu}(\text{SiMe}_3) + \text{H}$] $^+$; calcd 525.15800.

Mes₂BiPtBu(SiMe₃) (7): Yield 55%.

Elemental analysis for $\text{C}_{26}\text{H}_{40}\text{Bi}_1\text{P}_1\text{Si}_1$ calcd: C, 49.34; H, 6.62; found: C, 49.09; H, 6.34.

^1H NMR (500 MHz, C_6D_6) δ : 6.87 (s, 4H, *m*-CH), 2.64 (br s, 12H, *o*- $\text{C}(\text{CH}_3)_3$), 2.07 (s, 6H, *p*- $\text{C}(\text{CH}_3)_3$), 1.35 (d, $^3J_{\text{P-H}} = 11.2$ Hz, 9H, $\text{PC}(\text{CH}_3)_3$), 0.28 (d, $^3J_{\text{P-H}} = 3.38$ Hz, 9H, $\text{PSi}(\text{CH}_3)_3$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, C_6D_6) δ : (1C, Bi-C, not found), 146.7 (s, 2C, *o*- CCH_3), 137.5 (s, 1C, *p*- CCH_3), 129.8 (s, 2C, *m*-CH), 35.1 (d, $^2J_{\text{P-C}} = 11.6$ Hz, 3C, $\text{PC}(\text{CH}_3)_3$), 32.9 (d, $^1J_{\text{P-C}} = 33.0$ Hz, 1C, $\text{PC}(\text{CH}_3)_3$), 29.0 (s, 2C, *o*- CCH_3), 29.0 (s, 2C, *o*- CCH_3), 21.0 (s, 2C, *p*- CCH_3), 3.8 (d, $^2J_{\text{P-C}} = 9.9$ Hz, 3C, $\text{PSi}(\text{CH}_3)_3$).

$^{31}\text{P}\{^1\text{H}\}$ NMR (200 MHz, C_6D_6) δ : -60.4 (s, 1P).

^{29}Si -DEPT NMR (99 MHz, C_6D_6) δ : 2.21 (d, $^1J_{\text{P-Si}} = 56.5$ Hz, 1Si).

IR (cm^{-1}) $\tilde{\nu}$: 3010 (w), 2963 (m), 2941 (m), 2916 (m), 2885 (m), 2852 (m), 1457 (m), 1441 (m), 1401 (w), 1387 (w), 1372 (w), 1358 (w), 1287 (m), 1262 (w), 1241 (m), 1164 (m), 1024 (w), 1000 (w), 831 (s), 746 (m), 697 (w), 683 (w), 630 (m), 576 (w), 541 (w), 535 (w), 446(w).

HR-MS: CI^+ m/z 608.24431 [$\text{Mes}_2\text{BiPtBu}(\text{SiMe}_3) + \text{H}$] $^+$; calcd 608.24407.

Ph₂BiAstBu₂ (8): Yield 61%.

Elemental analysis for $\text{C}_{20}\text{H}_{28}\text{Bi}_1\text{As}_1$ calcd: C, 43.49; H, 5.11; found: C, 43.81; H, 5.16.

^1H NMR (300 MHz, C_6D_6) δ : 8.20–8.26 (m, 4H, *o*-CH), 7.16–7.21 (m, 4H, *m*-CH), 7.05–7.11 (m, 2H, *p*-CH), 1.28 (s, 18H).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6) δ : 146.0 (found *via* HMQC, s, 2C, Bi-C), 139.7 (s, 4C, *o*-CH), 130.7 (s, 4C, *m*-CH), 127.8 (found *via* HMQC, 2C, *p*-CH), 35.8 (s, 2C, $\text{AsC}(\text{CH}_3)_3$), 34.1 (s, 6C, $\text{AsC}(\text{CH}_3)_3$).

IR (cm^{-1}) $\tilde{\nu}$: 3057 (w), 3045 (w), 2971 (w), 2924 (w), 2850 (w), 1569 (w), 1471 (m), 1427 (m), 1361 (w), 1180 (w), 1154 (m), 1055 (w), 1012 (w), 995 (m), 850 (m), 811 (s), 722 (s), 692 (s), 552 (w), 530 (w), 447 (m).

HR-MS: CI^+ m/z 552.12005 [$\text{Ph}_2\text{BiAstBu}_2$] $^+$; calcd 552.12108.

Mes₂BiAstBu₂ (9): Yield 75%.

Elemental analysis for $\text{C}_{26}\text{H}_{40}\text{Bi}_1\text{As}_1$ calcd: C, 49.06; H, 6.33; found: C, 49.37; H, 6.52.

^1H NMR (500 MHz, C_6D_6) δ : 6.89 (s, 4H, *m*-CH), 2.64 (s, 12H, *o*- CCH_3), 2.07 (s, 6H, *p*- CCH_3), 1.34 (s, 18H, $\text{AsC}(\text{CH}_3)_3$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, C_6D_6) δ : 151.4 (br s, 2C Bi-C), 146.4 (s, 4C, *o*- CCH_3), 137.4 (s, 2C, *p*- CCH_3), 129.5 (s, 4C, *m*-CH), 35.8 (s, 2C, $\text{AsC}(\text{CH}_3)_3$), 33.3 (s, 6C, $\text{AsC}(\text{CH}_3)_3$), 30.3 (s, 4C, *o*- CCH_3), 21.0 (s, 2C, *p*- CCH_3).

IR (cm^{-1}) $\tilde{\nu}$: 3010 (w), 2998 (w), 2925 (w), 2873 (w), 2849 (m), 1457 (s), 1399 (s), 1362 (m), 1286 (m), 1154 (s), 1012 (w), 1001 (w), 941 (w), 877 (w), 843 (s), 802 (w), 698 (w), 576 (w), 537 (m), 418 (m).

HR-MS: LIFDI(+) m/z 636.21402 [$\text{Mes}_2\text{BiAstBu}_2$] $^+$; calcd 636.21498.

Ph₂BiAstBu(SiMe₃) (10): Yield 38%.

Elemental analysis for $\text{C}_{19}\text{H}_{28}\text{As}_1\text{Bi}_1\text{Si}_1$ calcd: C, 40.15; H, 4.97; found: C, 40.06; H, 4.73.

^1H NMR (500 MHz, C_6D_6) δ : 8.30–8.34 (m, 2H, *o*-CH), 8.09–8.13 (m, 2H, *o*-CH), 7.20–7.25 (m, 2H, *m*-CH), 7.14–7.10 (m, 1H, *p*-CH), 7.09–7.13 (m, 2H, *m*-CH), 7.01–7.06 (m, 1H, *p*-CH), 1.39 (s, 9H, $\text{AsC}(\text{CH}_3)_3$), 0.18 (s, 9H, $\text{AsSi}(\text{CH}_3)_3$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, C_6D_6) δ : 145.1 (br s, 1C Bi-C), 143.4 (br s, 1C Bi-C), 139.9 (s, 2C, *o*-CH), 139.3 (s, 2C, *o*-CH), 130.7 (s, 2C, *m*-CH), 130.6 (s, 2C, *m*-CH), 127.9 (found *via* HMBC, s, 2C, *p*-CH), 36.1 (s, 3C, $\text{AsC}(\text{CH}_3)_3$), 32.9 (s, 1C, $\text{AsC}(\text{CH}_3)_3$), 3.7 (s, 3C, $\text{AsSi}(\text{CH}_3)_3$).

^{29}Si -DEPT NMR (125 MHz, C_6D_6) δ : 3.2 (s, 1Si).

IR (cm^{-1}) $\tilde{\nu}$: 3054 (m), 3033 (w), 3011 (w), 2961 (w), 2947 (w), 2938 (w), 2919 (w), 2877 (w), 2846 (w), 1566 (w), 1471 (w), 1459 (w), 1427 (m), 1360 (m), 1242 (m), 1153 (m), 1055 (m), 1012 (m), 995 (m), 830 (s), 744 (w), 691 (s), 621 (s), 448 (m), 436 (m).

HR-MS: LIFDI(+) m/z 568.10042 [$\text{Ph}_2\text{BiAstBu}(\text{SiMe}_3)$] $^+$; calcd 568.09801.

Mes₂BiAstBu(SiMe₃) (11): Yield 53%.

Elemental analysis for $\text{C}_{25}\text{H}_{40}\text{Bi}_1\text{As}_1\text{Si}_1$ calcd: C, 46.01; H, 6.18; found: C, 46.12; H, 6.15.

^1H NMR (500 MHz, C_6D_6) δ : 6.88 (s, 2H, *m*-CH), 6.87 (s, 2H, *m*-CH), 2.67 (s, 6H, *o*- $\text{C}(\text{CH}_3)_3$), 2.55 (s, 6H, *o*- $\text{C}(\text{CH}_3)_3$), 2.09 (s, 3H, *p*- $\text{C}(\text{CH}_3)_3$), 2.06 (s, 3H, *p*- $\text{C}(\text{CH}_3)_3$), 1.42 (s, 9H, $\text{AsC}(\text{CH}_3)_3$), 0.29 (s, 9H, $\text{AsSi}(\text{CH}_3)_3$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, C_6D_6) δ : 150.6 (br s, 1C Bi-C), 147.2 (br s, 1C Bi-C), 146.7 (s, 2C, *o*-CCH₃), 146.5 (s, 2C, *o*-CCH₃), 137.5 (s, 1C, *p*-CCH₃), 137.4 (s, 1C, *p*-CCH₃), 129.5 (s, 2C, *m*-CH), 129.4 (s, 2C, *m*-CH), 35.3 (s, 3C, AsC(CH₃)₃), 33.3 (s, 1C, AsC(CH₃)₃), 30.0 (s, 2C, *o*-CCH₃), 29.4 (s, 2C, *o*-CCH₃), 21.0 (s, 2C, *p*-CCH₃), 3.6 (s, 3C, AsSi(CH₃)₃).

^{29}Si -DEPT NMR (99 MHz, C_6D_6) δ : 2.5 (s, 1Si).

IR (cm^{-1}) $\tilde{\nu}$: 3007 (w), 2960 (m), 2939 (m), 2918 (m), 2874 (m), 2848 (m), 1457 (m), 1438 (m), 1399 (w), 1370 (m), 1359 (w), 1287 (m), 1240 (s), 1153 (m), 1023 (w), 1012 (w), 998 (w), 798 (s), 743 (m), 685 (m), 624 (m), 576 (w), 536 (w).

HR-MS: CI(+) m/z 652.19039 [$\text{Mes}_2\text{BiAsfBu}(\text{SiMe}_3)^+$]; calcd 652.19191.

Ph₂BiSbMes₂ (12): Mes₂SbH (54 mg, 0.13 mmol, 1 eq.) is dissolved in 3 ml of pentane at $-40\text{ }^\circ\text{C}$ and a solution of Ph₂BiNMe₂ (48 mg, 0.13 mmol, 1 eq.) in 7 ml of pentane is added dropwise. After complete addition, the solution is slowly warmed to $-15\text{ }^\circ\text{C}$ under the observation of a colour change from yellow to orange and the precipitation of a little colourless solid. The mixture is filtered at $-15\text{ }^\circ\text{C}$ and the solution is concentrated and stored at $-32\text{ }^\circ\text{C}$. After a week of storage, compound 12 is obtained as orange crystals next to colourless crystals which are removed mechanically. The colourless crystals are identified as the distibane Mes₄Sb₂ via NMR spectroscopy and comparison with an authentic sample. Yield 57%.

Elemental analysis for C₃₀H₃₂Bi₁Sb₁ calcd: C, 49.82; H, 4.46; found: C, 50.27; H, 4.53.

^1H NMR (500 MHz, toluene-*d*₈) δ : 7.80–7.85 (m, 4H, Bi-*o*-CH), 7.08–7.13 (m, 6H, Bi-*m*-CH, Bi-*p*-CH), 6.67 (s, 4H, Sb-*m*-CH), 2.20 (s, 12H, Sb-*o*-C(CH₃)₃), 2.14 (s, 6H, Sb-*p*-C(CH₃)₃).

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, toluene-*d*₈) δ : 147.2 (found via HMQC, s, 2C, Bi-C), 145.0 (s, 4C, Sb-*o*-CCH₃), 139.4 (s, 4C, Bi-*o*-CH), 137.7 (s, 2C, Sb-*p*-C(CH₃)₃), 133.7 (s, 2C, Sb-C), 130.8 (s, 4C, Bi-*m*-CH), 128.6 (s, 4C, Sb-*m*-CH), 127.5 (s, 2C, Bi-*p*-CH), 28.1 (s, 4C, Sb-*o*-CCH₃), 34.1 (s, 2C, Sb-*p*-CCH₃).

IR (cm^{-1}) $\tilde{\nu}$: 3046 (w), 3009 (w), 2958 (m), 2908 (w), 2858 (w), 1595 (w), 1567 (w), 1442 (m), 1425 (m), 1371 (m), 1322 (m), 1286 (w), 1185 (w), 1153 (w), 1052 (w), 1010 (m), 982 (m), 901 (w), 849 (s), 720 (s), 691 (s), 577 (w), 553 (m), 538 (w), 440 (m).

HR-MS: CI(+) m/z 723.13984 [Ph₂BiSbMes₂ + H]⁺; calcd 723.14243.

Investigations on the equilibrium reaction of Mes₄Bi₂, Mes₄Sb₂ and Mes₂BiSbMes₂ (13)

Mes₄Bi₂ and Mes₄Sb₂ are dissolved in 0.5 ml of toluene-*d*₈. Almost immediately, an equilibrium is reached which is confirmed by NMR experiments right after filling the NMR tube compared to NMR spectra taken several hours later. For analysis of the temperature dependent behaviour, the sample is cooled to $-80\text{ }^\circ\text{C}$ and slowly warmed to room temperature. ^1H NMR-spectra are recorded in 10 K steps.

^1H NMR (500 MHz, toluene-*d*₈) δ : 6.83 (s, 4H, Bi-*m*-CH), 6.68 (s, 4H, Sb-*m*-CH), 2.45 (s, 12H, Sb-*o*-C(CH₃)₃), 2.40 (s, 12H, Bi-*o*-C(CH₃)₃), 2.15 (s, 6H, Sb-*p*-C(CH₃)₃), 2.12 (s, 6H, Bi-*p*-C(CH₃)₃).

$^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, toluene-*d*₈) δ : 152.2 (found via HMQC, s, 2C, Bi-C), 146.0 (s, 4C, Bi-*o*-C(CH₃)₃), 145.1 (s, 2C,

Sb-*o*-CCH₃), 137.6 (s, 2C, Bi-*p*-CCH₃), 137.3 (s, 2C, Sb-*o*-CCH₃), 133.9 (s, 2C, Sb-C), 129.2 (s, 4C, Sb-*m*-CH), 129.0 (found via HMQC, 2C, Bi-*m*-CH), 30.2 (s, 4C, Bi-*o*-C(CH₃)₃), 27.8 (s, 4C, Sb-*o*-C(CH₃)₃), 21.0 (s, 2C, Bi-*p*-C(CH₃)₃), 20.8 (s, 2C, Sb-*p*-C(CH₃)₃).

HR-MS: LIFDI(+) m/z 806.22851 [$\text{Mes}_2\text{BiSbMes}_2^+$]; calcd 806.22851; 894.30682 [$\text{Mes}_4\text{Bi}_2^+$]; calcd 894.30507; 718.15091 [$\text{Mes}_4\text{Sb}_2^+$]; calcd 718.15194.

X-ray diffraction analysis

Single crystal X-ray diffraction analysis was conducted using a Stoe IPDS 2 and an IPDS 2T diffractometer. The diffractometers used Mo-K α ($\lambda = 0.71073\text{ \AA}$) radiation and respective X-ray optics. Structures were solved via intrinsic phasing using SHELXT-2015. Structure refinement was performed via full-matrix-least-squares against F^2 using SHELXL-2015. All structures were solved and refined using the OLEX2 platform.⁴³

The crystal structure of compound 6 shows disorder of the whole molecule with a second site occupation of around 1.5%. Because of the low occupation, only the P and Bi atoms could be refined.

Author contributions

This work was conceived by Tobias Dunaj and Carsten von Hänisch; investigations and experiments were performed by Tobias Dunaj and Kevin Dollberg. The project was supervised by Carsten von Hänisch and the manuscript was written by Tobias Dunaj and Carsten von Hänisch.

Conflicts of interest

There are no conflicts to declare.

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2. NMR spectra

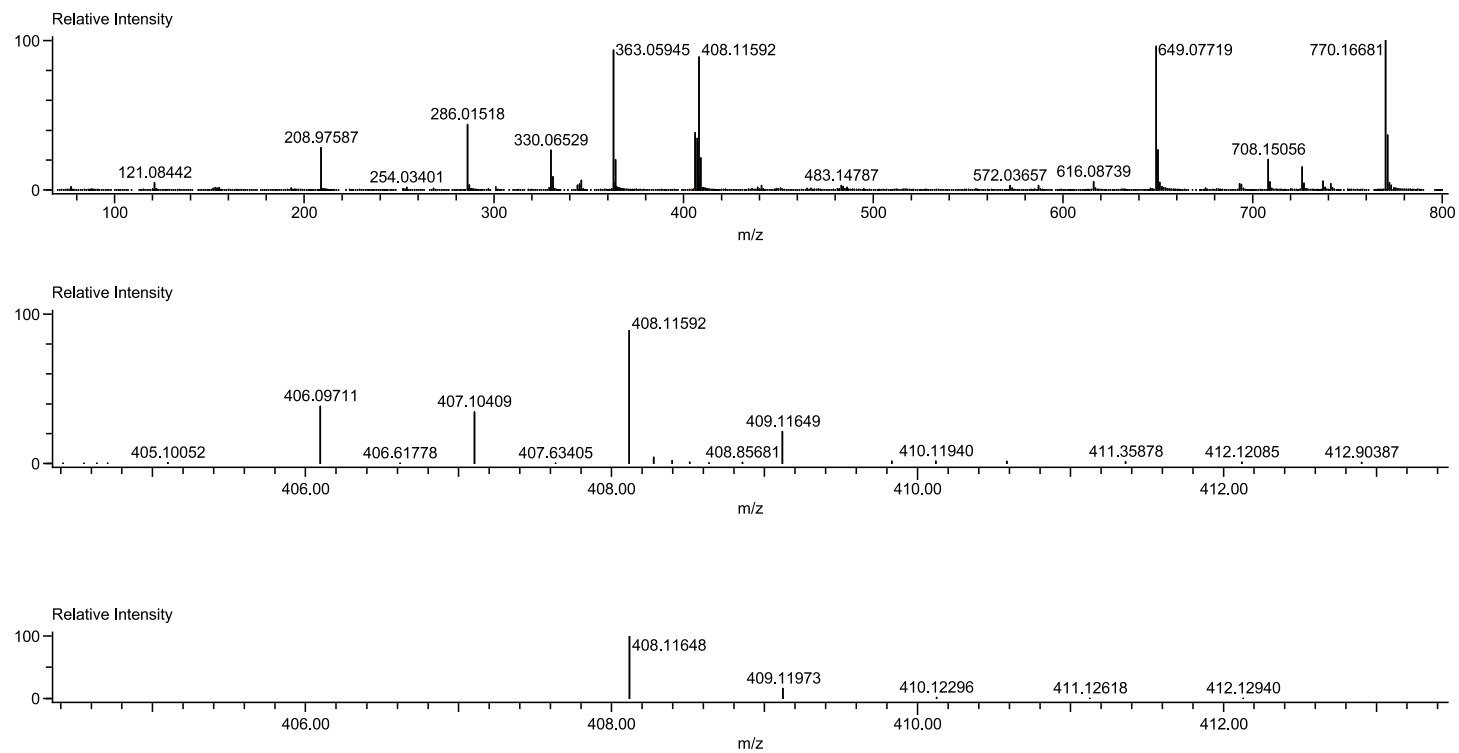
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1. Mass spectra

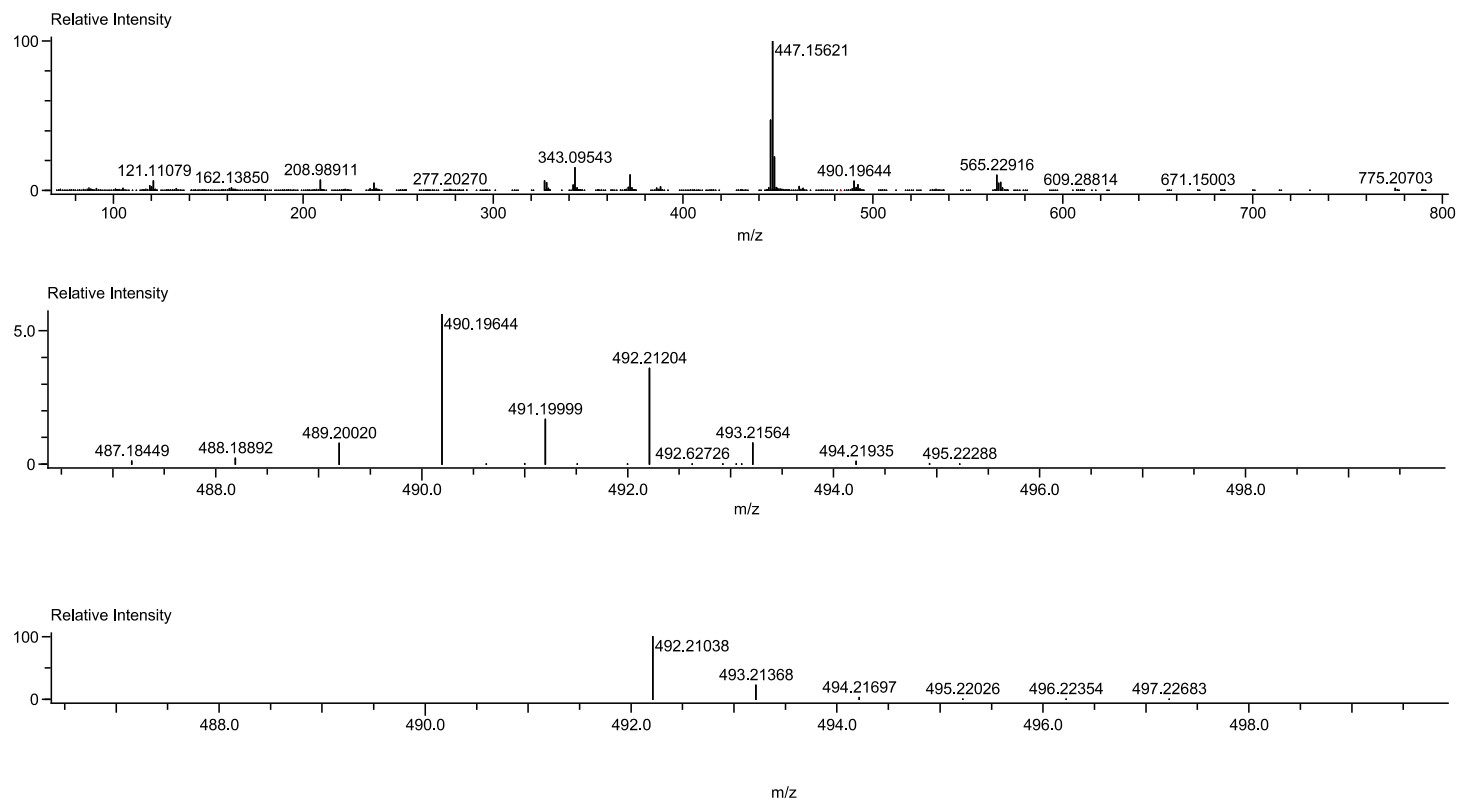
1.1 Ph₂BiNMe₂ (1)



Mass	Intensity	Relative Intensity	Calc. Mass	Mass Difference [mDa]	Mass Difference [ppm]	Possible Formula	Unsaturation Number
408.11592	6511205.94	88.73	408.11648	-0.56	-1.37	¹² C ₁₄ ¹ H ₁₇ ²⁰⁹ Bi ¹⁴ N ₁	7.5

Figure S1.1. HR-Cl(+)-Mass spectrum of Ph₂BiNMe₂ (1) as [M + H]⁺. Top: Whole spectrum. Middle: High resolution extract. Bottom: Calculated isotope pattern.

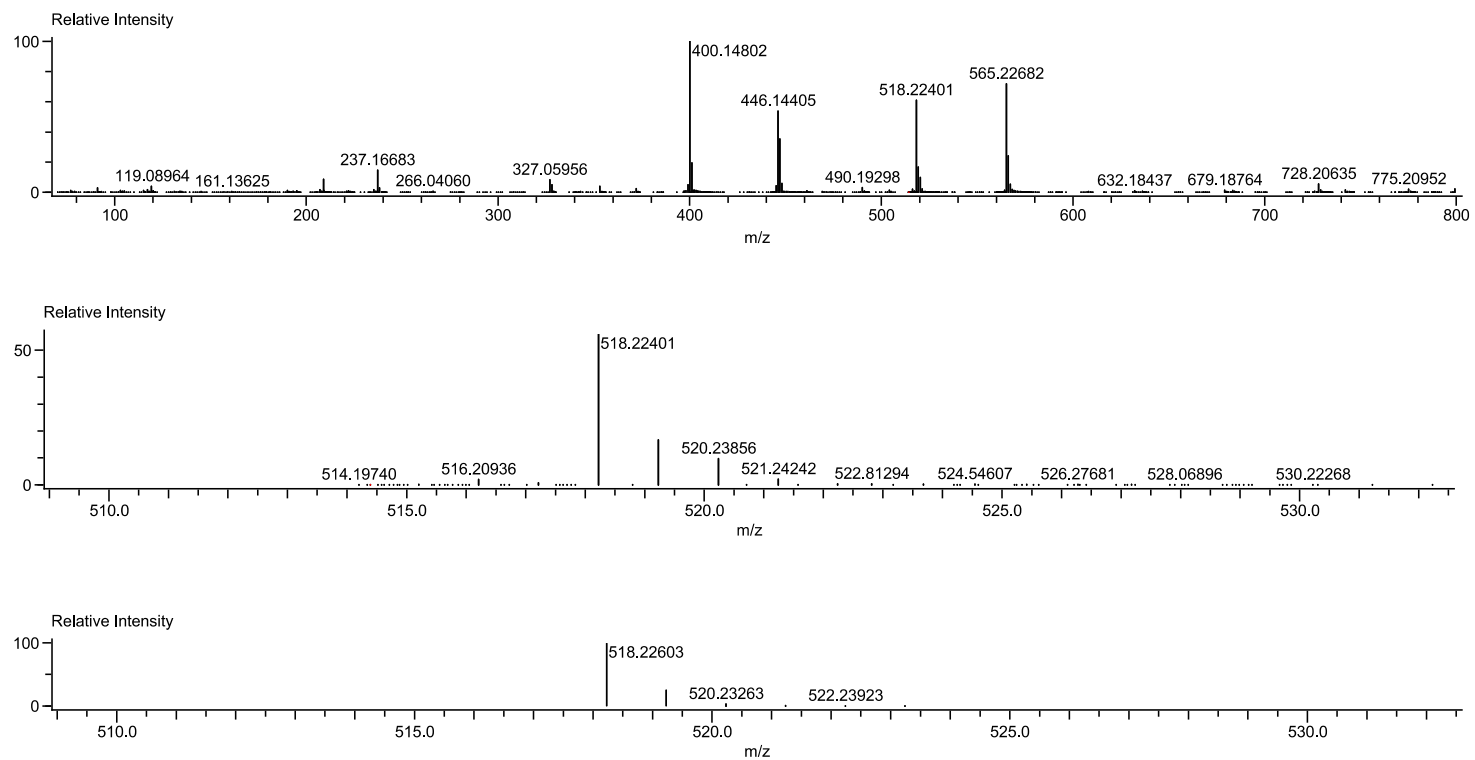
1.2 Mes₂BiNMe₂ (2)



Mass	Intensity	Relative Intensity	Calc. Mass	Mass Difference [mDa]	Mass Difference [ppm]	Possible Formula	Unsaturation Number
492.21204	165139.39	3.59	492.21038	1.66	3.37	¹² C ₂₀ ¹ H ₂₉ ²⁰⁹ Bi ₁ ¹⁴ N ₁	7.5

Figure S1.2. HR-Cl(+)⁺ Mass spectrum of Mes₂BiNMe₂ (2) as [M + H]⁺. Top: Whole spectrum. Middle: High resolution extract. Bottom: Calculated isotope pattern.

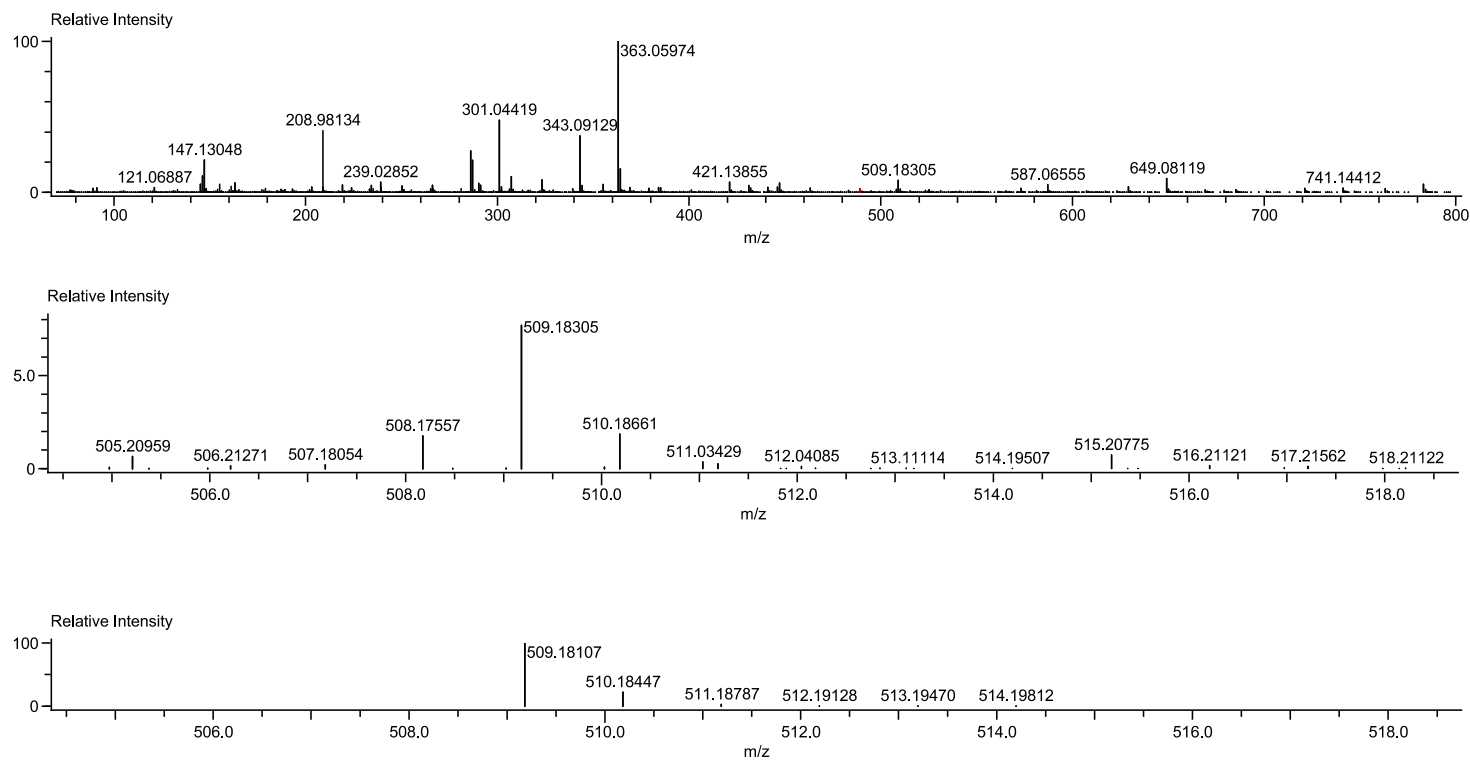
1.3 Mes₂BiNHtBu (3)



Mass	Intensity	Relative Intensity	Calc. Mass	Mass Difference [mDa]	Mass Difference [ppm]	Possible Formula	Unsaturation Number
518.22401	5854050.42	60.96	518.22603	-2.02	-3.90	¹² C ₂₂ ¹ H ₃₁ ²⁰⁹ Bi ₁ ¹⁴ N ₁	8.5

Figure S1.3. HR-Cl(+)⁺ Mass spectrum of Mes₂BiNHtBu (3) as [M - H]⁺. Top: Whole spectrum. Middle: High resolution extract.

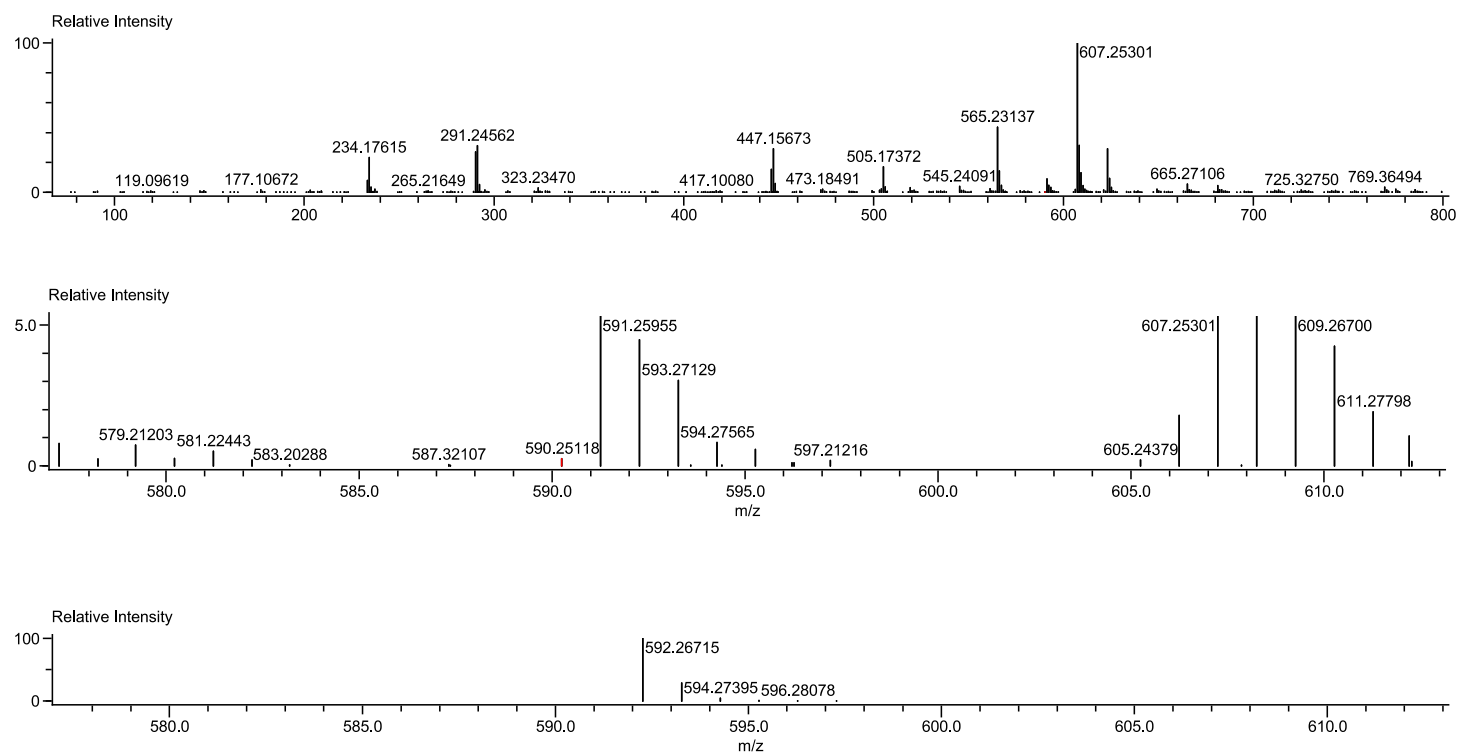
1.4 Ph₂BiPtBu₂ (4)



Mass	Intensity	Relative Intensity	Calc. Mass	Mass Difference [mDa]	Mass Difference [ppm]	Possible Formula	Unsaturation Number
509.18305	346895.41	7.68	509.18107	1.98	3.89	¹² C ₂₀ ¹ H ₂₉ ²⁰⁹ Bi ³¹ P ₁	8.5

Figure S1.4. HR-Cl(+)⁺ Mass spectrum of Ph₂BiPtBu₂ (4) as [M + H]⁺. Top: Whole spectrum. Middle: High resolution extract. Bottom: Calculated isotope pattern.

1.5 Mes₂BiPtBu₂ (5)



Mass	Intensity	Relative Intensity	Calc. Mass	Mass Difference [mDa]	Mass Difference [ppm]	Possible Formula	Unsaturation Number
592.26483	49003.65	4.47	592.26715	-2.31	-3.91	¹² C ₂₆ ¹ H ₄₀ ²⁰⁹ Bi ₁ ³¹ P ₁	9.0

Figure S1.5. HR-Cl(+)
Mass spectrum of Mes₂BiPtBu₂ (5) as [M]⁺. Top: Whole spectrum. Middle: High resolution extract. Bottom: Calculated isotope pattern.

1.6 Ph₂BiP*t*Bu(SiMe₃)₃ (**6**)

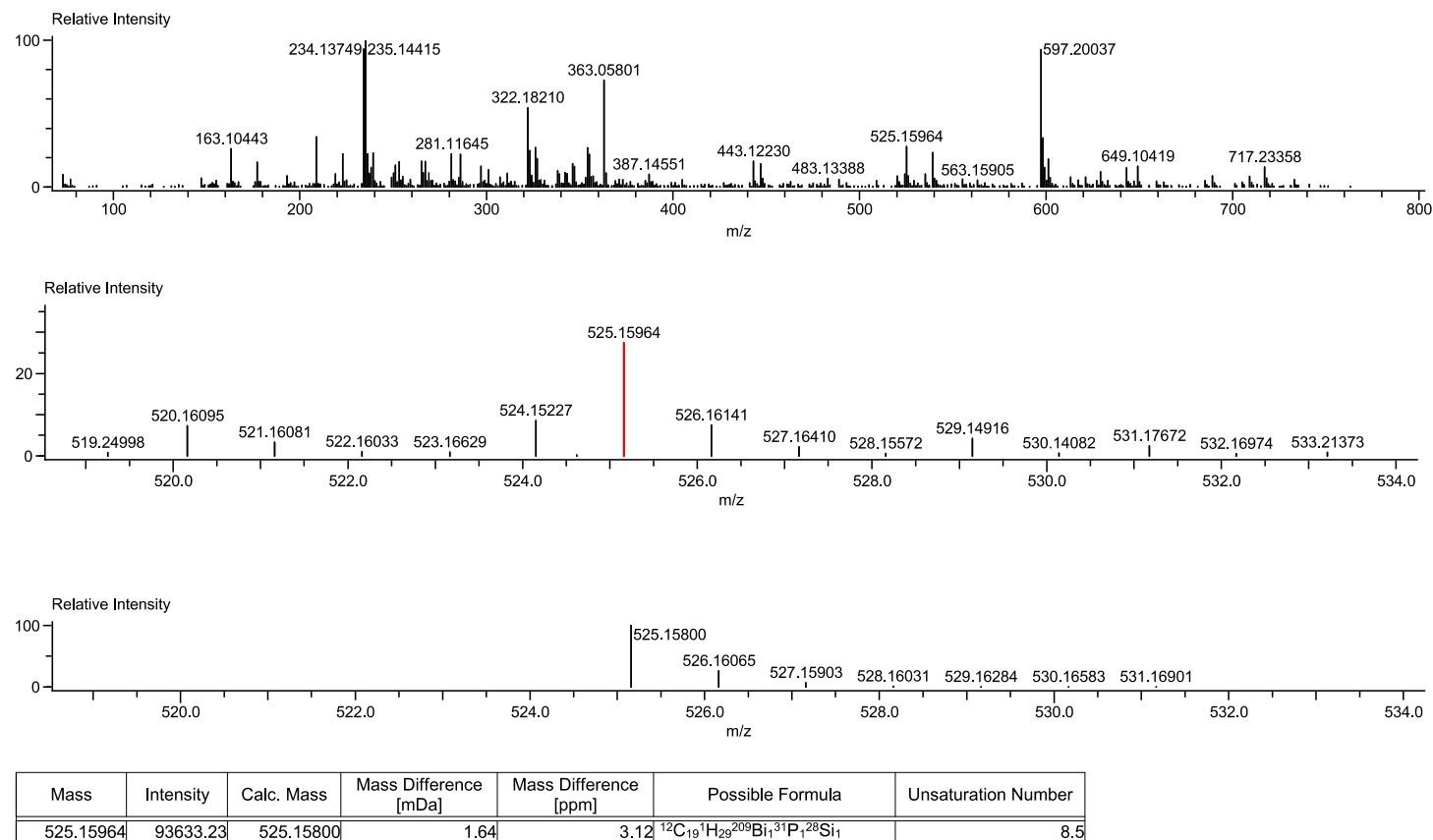
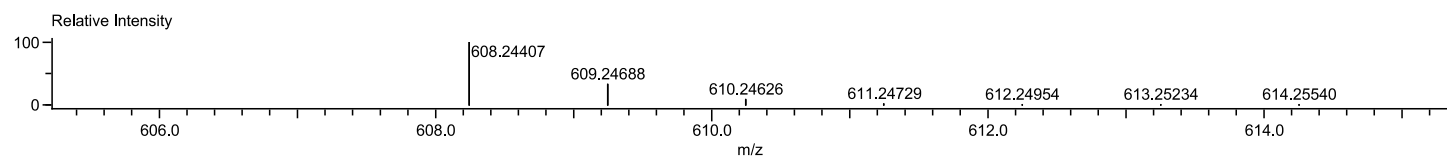
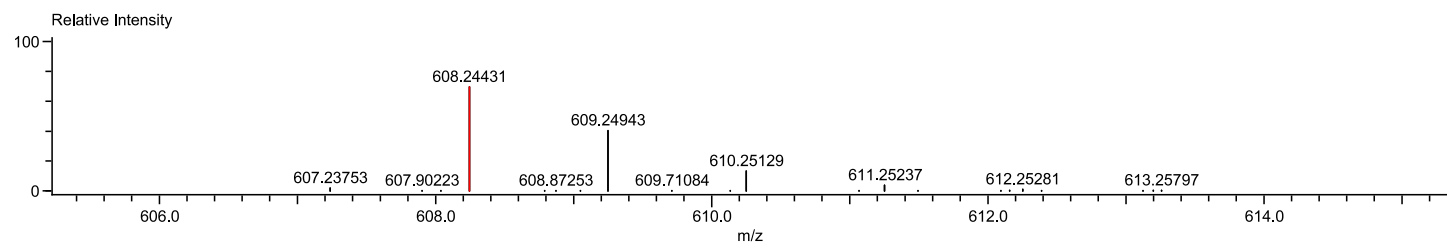
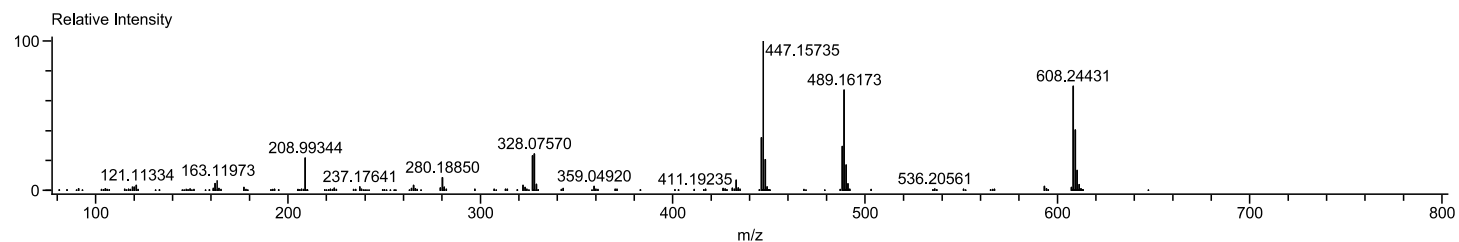


Figure S1.6. HR-Cl(+)⁺ Mass spectrum of Ph₂BiP*t*Bu(SiMe₃)₃ (**6**) as [M + H]⁺. Top: Whole spectrum. Middle: High resolution extract. Bottom: Calculated isotope pattern.

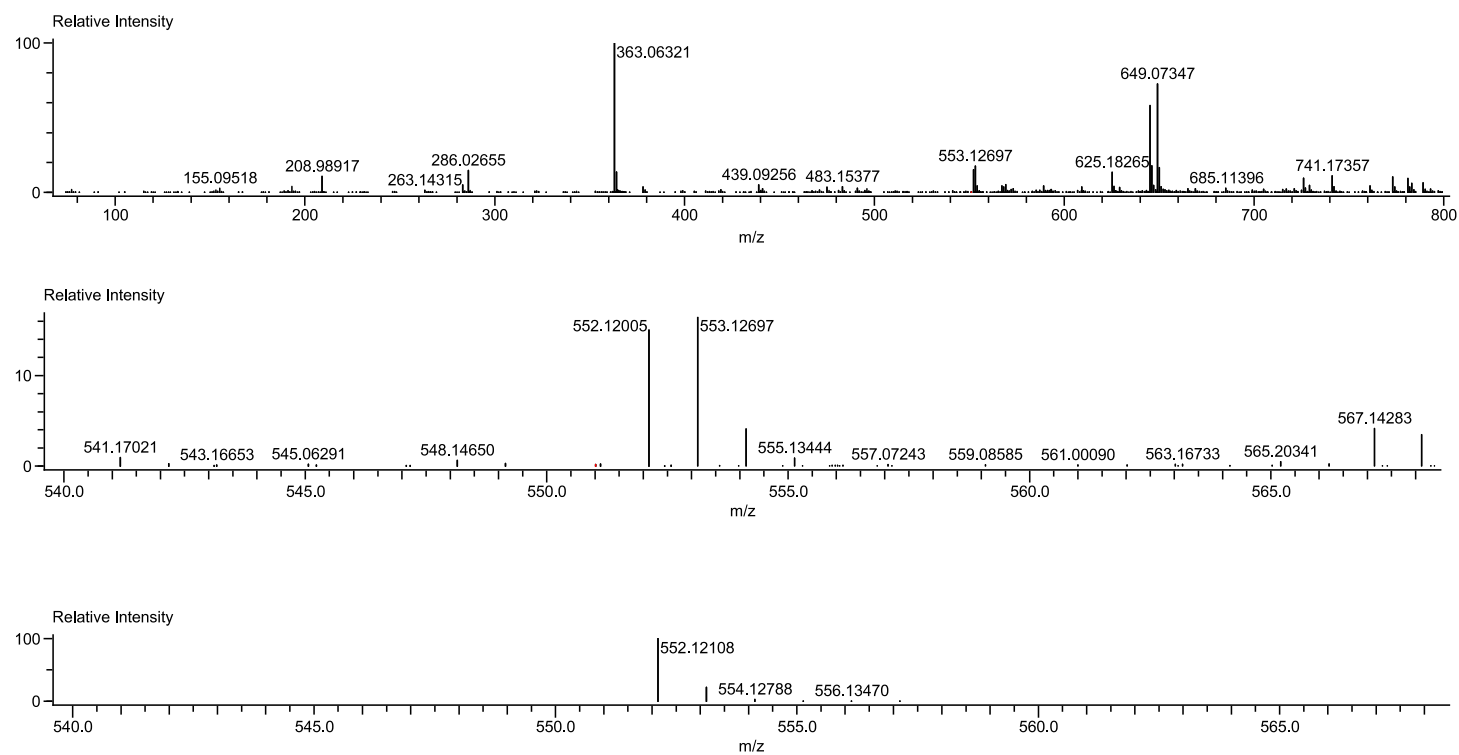
1.7 Mes₂PfBu(SiMe₃)₃ (7)



Mass	Intensity	Relative Intensity	Calc. Mass	Mass Difference [mDa]	Mass Difference [ppm]	Possible Formula	Unsaturation Number
608.24431	194777.28	69.57	608.24407	0.24	0.40	¹² C ₂₅ ¹ H ₄₀ ²⁰⁹ Bi ₁ ³¹ P ₁ ²⁸ Si ₁	9.0

Figure S1.7. HR-Cl(+)⁺ Mass spectrum of Mes₂PfBu(SiMe₃)₃ (7) as [M + H]⁺. Top: Whole spectrum. Middle: High resolution extract. Bottom: Calculated isotope pattern.

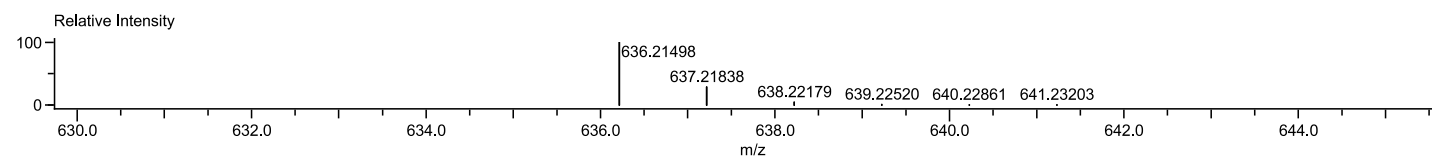
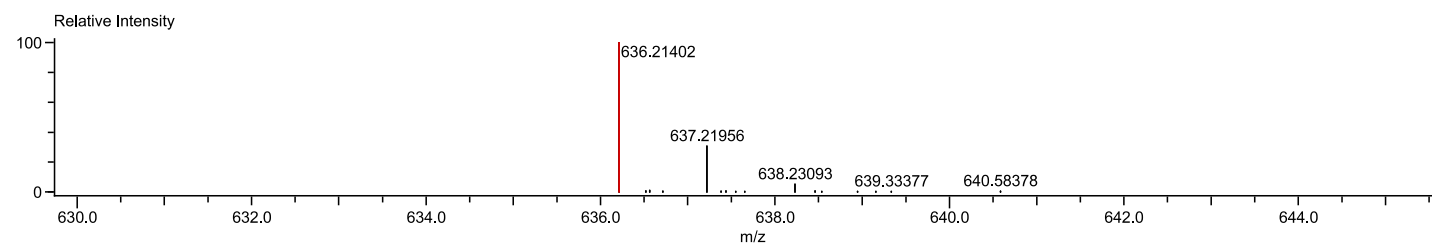
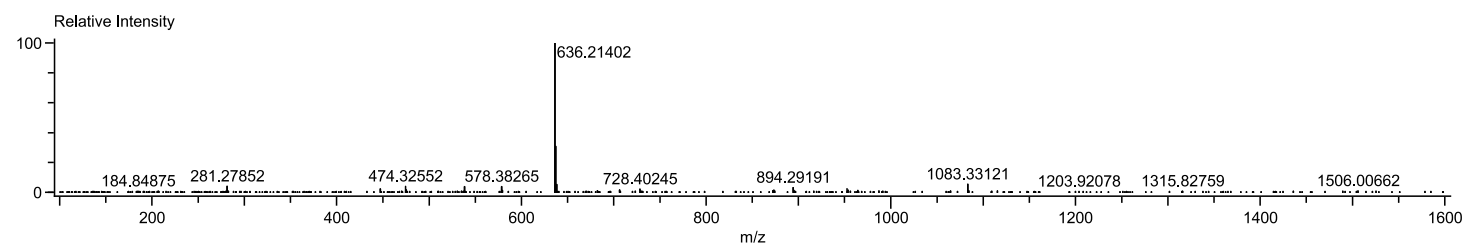
1.8 Ph₂BiAstBu₂ (8)



Mass	Intensity	Relative Intensity	Calc. Mass	Mass Difference [mDa]	Mass Difference [ppm]	Possible Formula	Unsaturation Number
552.12005	173278.54	15.01	552.12108	-1.03	-1.87	¹² C ₂₀ ¹ H ₂₈ ⁷⁵ As ₁ ²⁰⁹ Bi ₁	8.0

Figure S1.8. HR-Cl(+)⁺ Mass spectrum of Ph₂BiAstBu₂ (8) as [M]⁺. Top: Whole spectrum. Middle: High resolution extract. Bottom: Calculated isotope pattern.

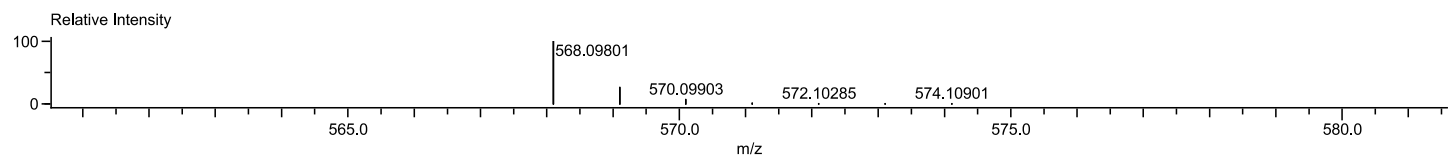
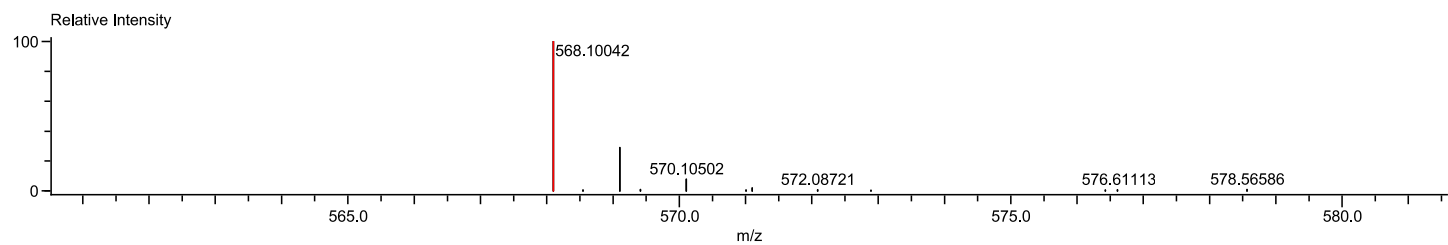
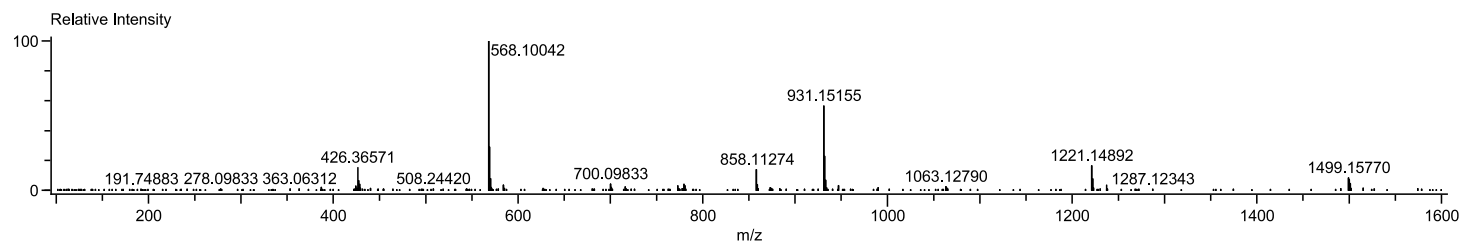
1.9 Mes₂BiAstBu₂ (9)



Mass	Intensity	Relative Intensity	Calc. Mass	Mass Difference [mDa]	Mass Difference [ppm]	Possible Formula	Unsaturation Number
636.21402	29785.36	100.00	636.21498	-0.96	-1.52	¹² C ₂₆ ¹ H ₄₀ ⁷⁵ As ₁ ²⁰⁹ Bi ₁	8.0

Figure S1.9. HR-LIFDI(+) Mass spectrum of Mes₂BiAstBu₂ (9) as [M]⁺. Top: Whole spectrum. Middle: High resolution extract. Bottom: Calculated isotope pattern.

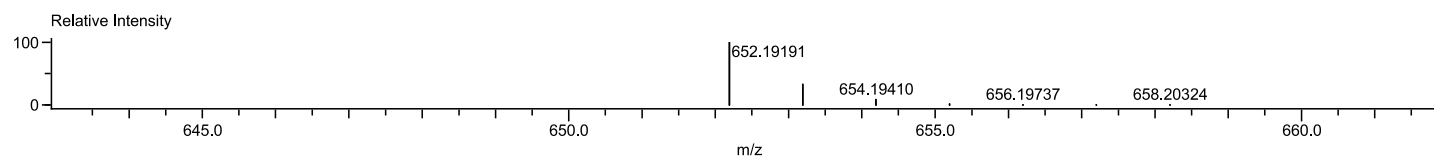
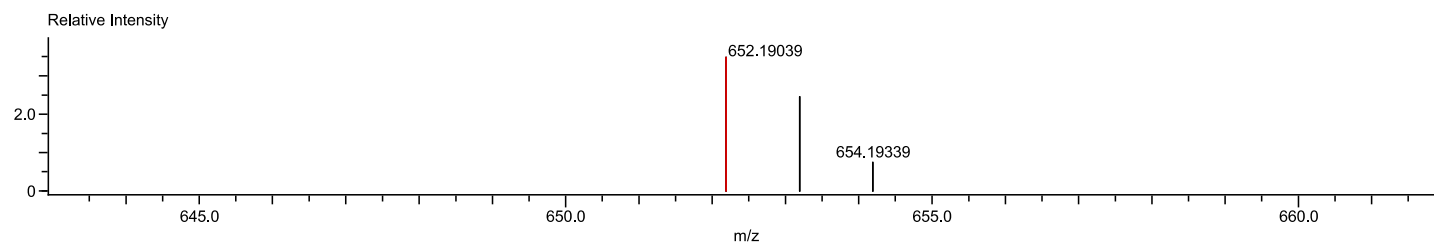
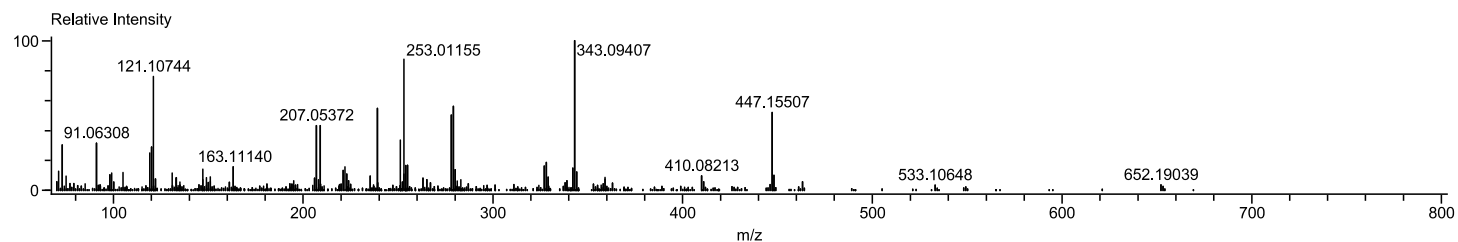
1.10 Ph₂BiAsfBu(SiMe₃)₃ (**10**)



Mass	Intensity	Relative Intensity	Calc. Mass	Mass Difference [mDa]	Mass Difference [ppm]	Possible Formula	Unsaturation Number
568.10042	71038.63	100.00	568.09801	2.41	4.25	¹² C ₁₉ ¹ H ₂₈ ⁷⁵ As ₁ ²⁰⁹ Bi ₁ ²⁸ Si ₁	8.0

Figure S1.10. HR-LIFDI(+) Mass spectrum of Mes₂BiAsfBu(SiMe₃) (**10**) as [M]⁺. Top: Whole spectrum. Middle: High resolution extract. Bottom: Calculated isotope pattern.

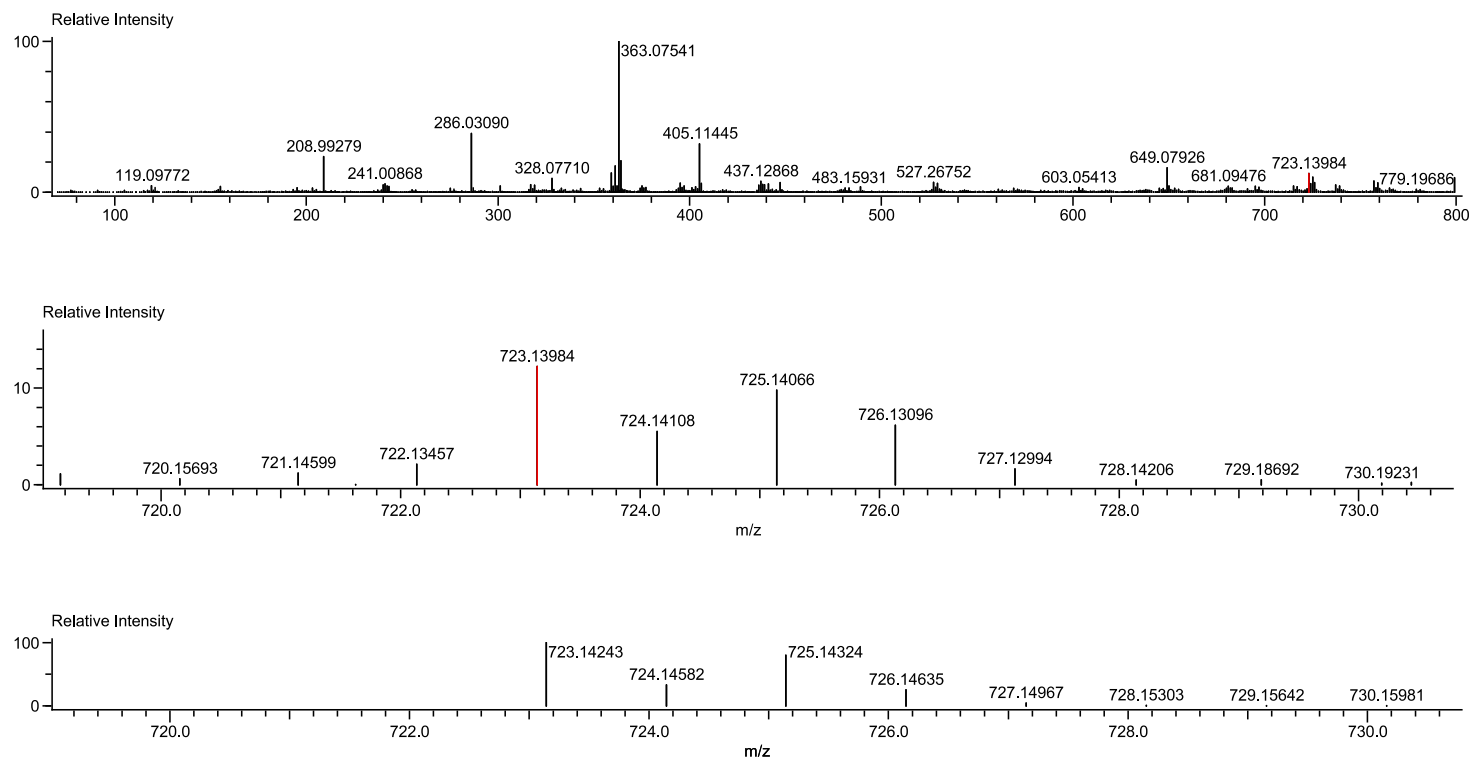
1.11 Mes₂BiAsfBu(SiMe₃)₃ (**11**)



Mass	Intensity	Relative Intensity	Calc. Mass	Mass Difference [mDa]	Mass Difference [ppm]	Possible Formula	Unsaturation Number
652.19039	7122.62	3.48	652.19191	-1.52	-2.33	¹² C ₂₅ ¹ H ₄₀ ⁷⁵ As ₁ ²⁰⁹ Bi ₁ ²⁸ Si ₁	8.0

Figure S1.11. HR-Cl(+)
Mass spectrum of Mes₂BiAsfBu(SiMe₃)₃ (**11**) as [M]⁺. Top: Whole spectrum. Middle: High resolution extract. Bottom: Calculated isotope pattern.

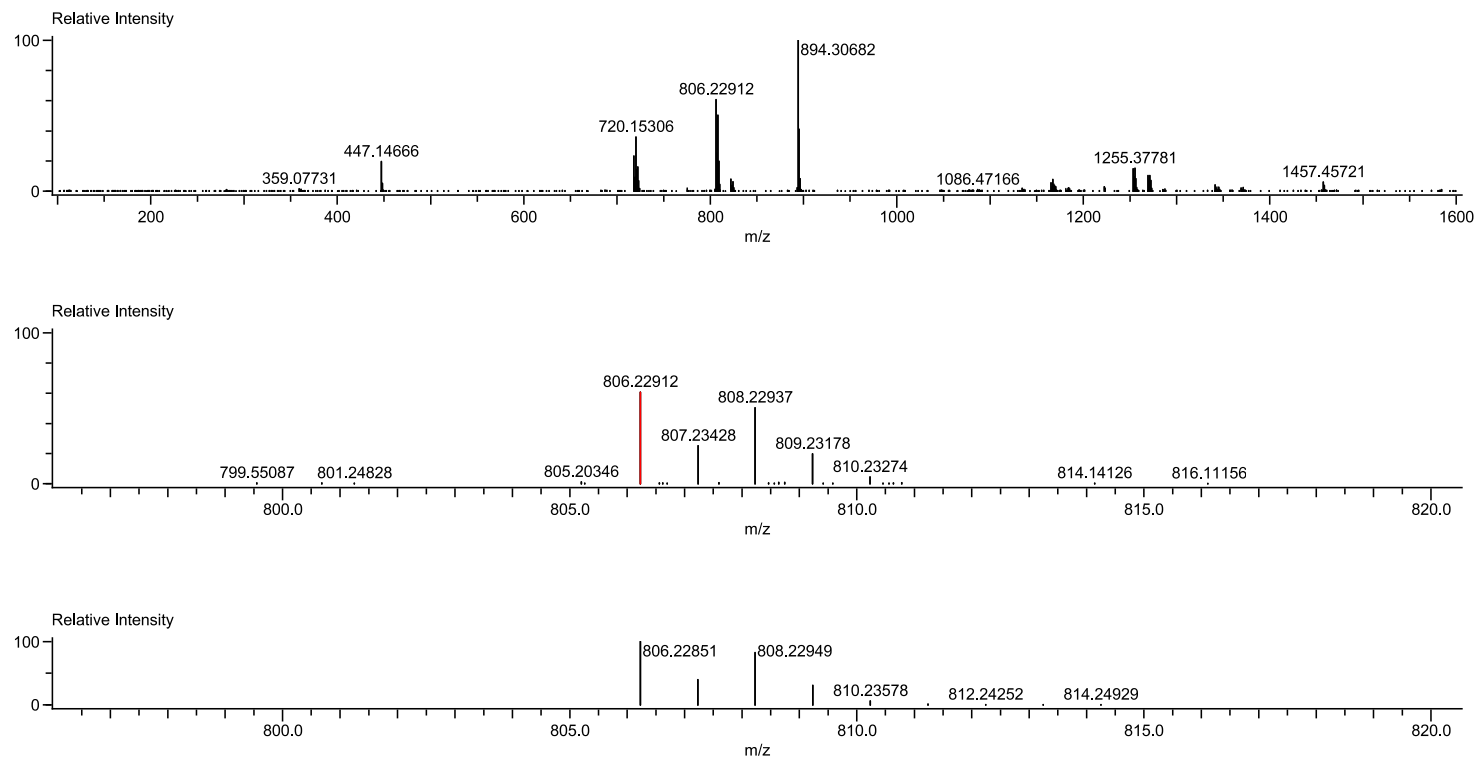
1.12 Ph₂BiSbMes₂



Mass	Intensity	Relative Intensity	Calc. Mass	Mass Difference [mDa]	Mass Difference [ppm]	Possible Formula	Unsaturation Number
723.13984	806359.27	12.20	723.14243	-2.59	-3.58	¹² C ₃₀ ¹ H ₃₃ ²⁰⁹ Bi ₁ ¹²¹ Sb ₁	15.5

Figure S1.12. HR-Cl(+). Mass spectrum of Ph₂BiSbMes₂ (**12**) as [M + H]⁺. Top: Whole spectrum. Middle: High resolution extract. Bottom: Calculated isotope pattern.

1.13 Mes₂BiSbMes₂



Mass	Intensity	Relative Intensity	Calc. Mass	Mass Difference [mDa]	Mass Difference [ppm]	Possible Formula	Unsaturation Number
806.22912	36062.66	60.53	806.22851	0.61	0.76	¹² C ₃₆ ¹ H ₄₄ ²⁰⁹ Bi ₁ ¹²¹ Sb ₁	16.0

Figure S1.13. HR-LIFDI(+) Mass spectrum of a mixture of Mes₂BiSbMes₂ (**13**) as [M]⁺, Mes₄Bi₂ as [M]⁺ (m/z = 894.30507) and Mes₄Sb₂ as [M]⁺ (m/z = 718.15194). Top: Whole spectrum. Middle: High resolution extract of Mes₂BiSbMes₂ (**13**). Bottom: Calculated isotope pattern for Mes₂BiSbMes₂ (**13**).

2. NMR spectra

2.1 Ph₂BiNMe₂

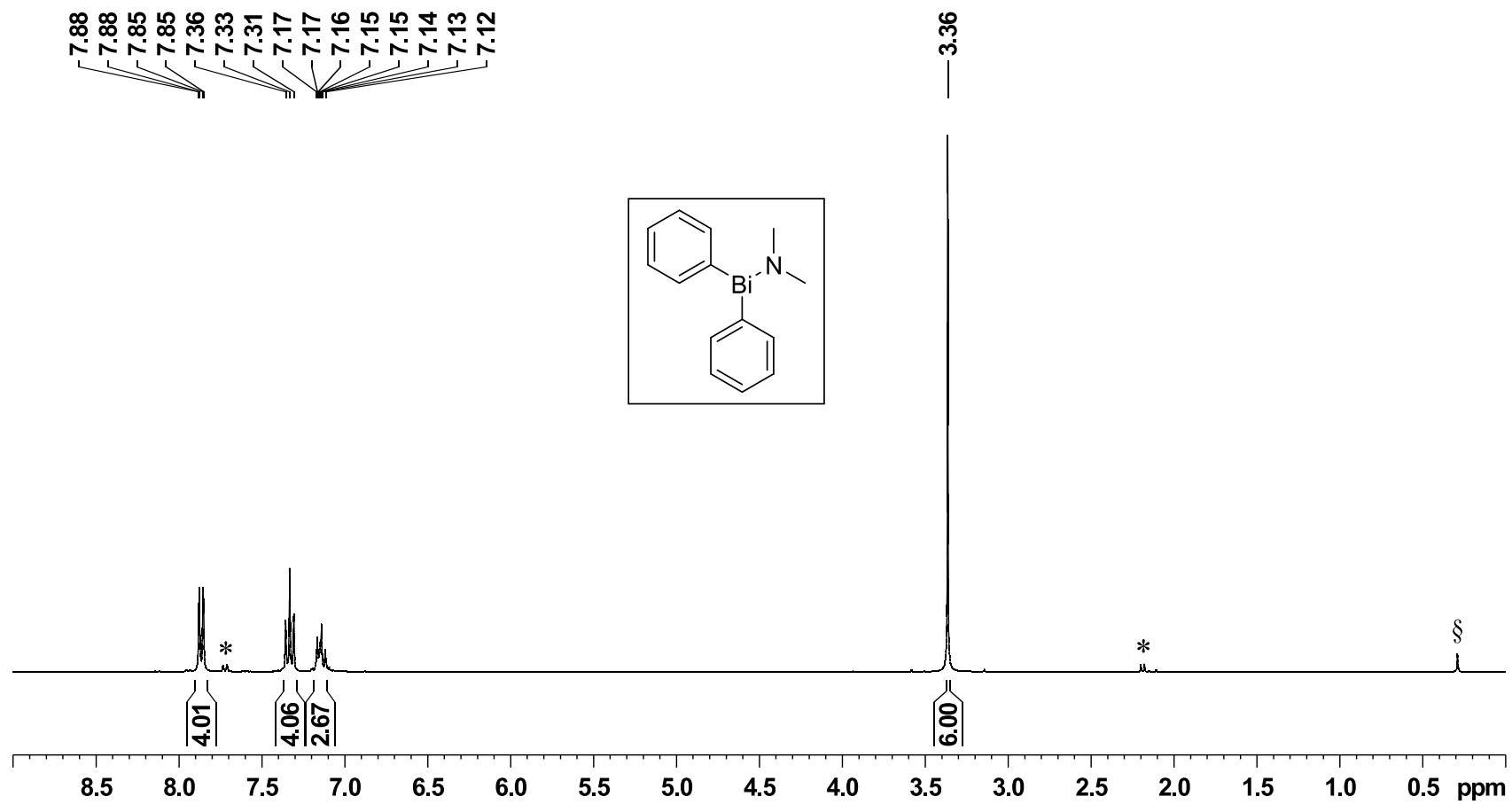


Figure S2.1.1: ¹H NMR spectrum (300 MHz) of **1** in C₆D₆ at room temperature (* = Unknown impurity, § = Silicon grease).

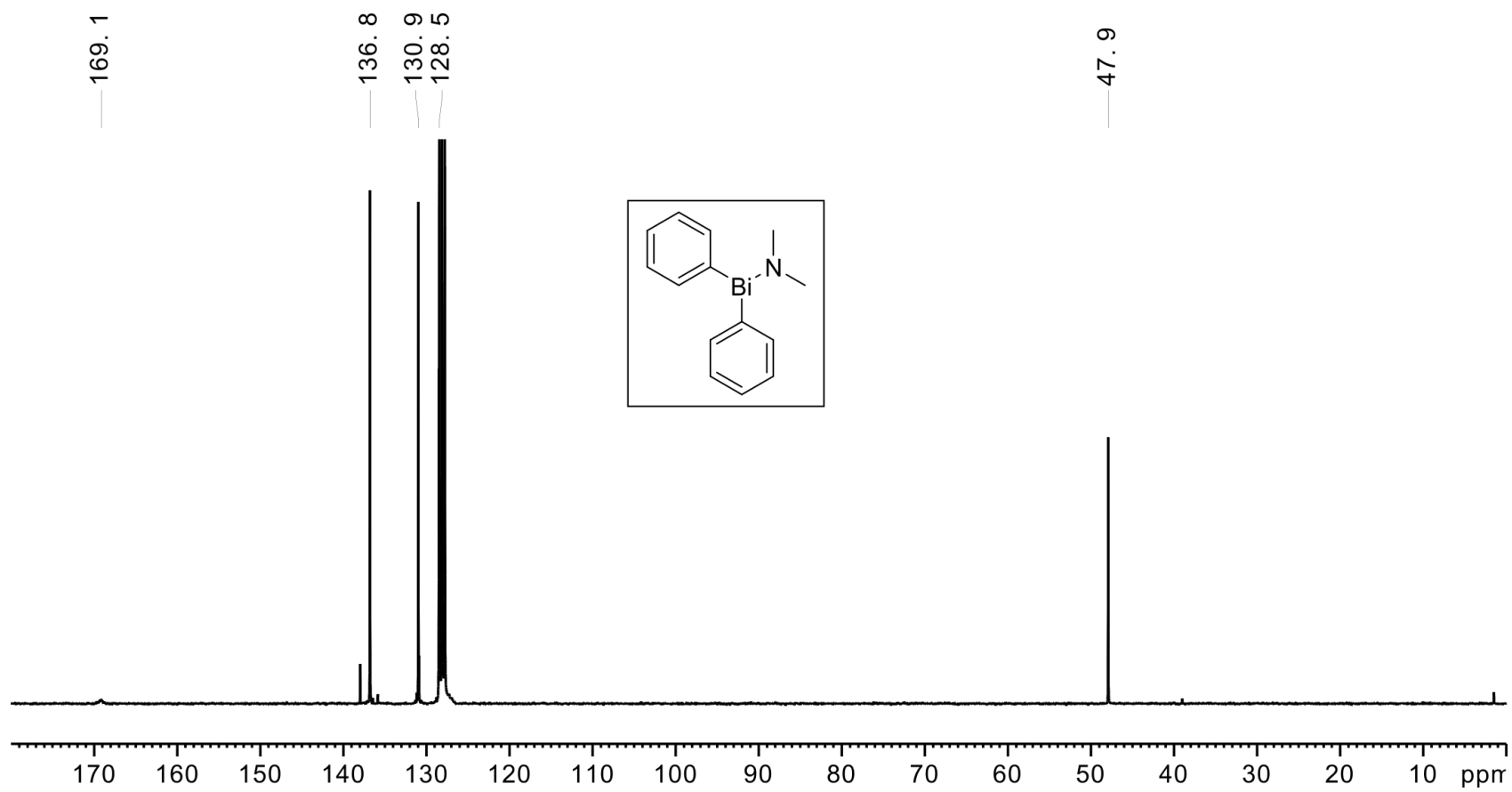


Figure S2.1.2: ^{13}C NMR spectrum (75 MHz) of **1** in C_6D_6 at room temperature.

2.2 Mes₂BiNMe₂

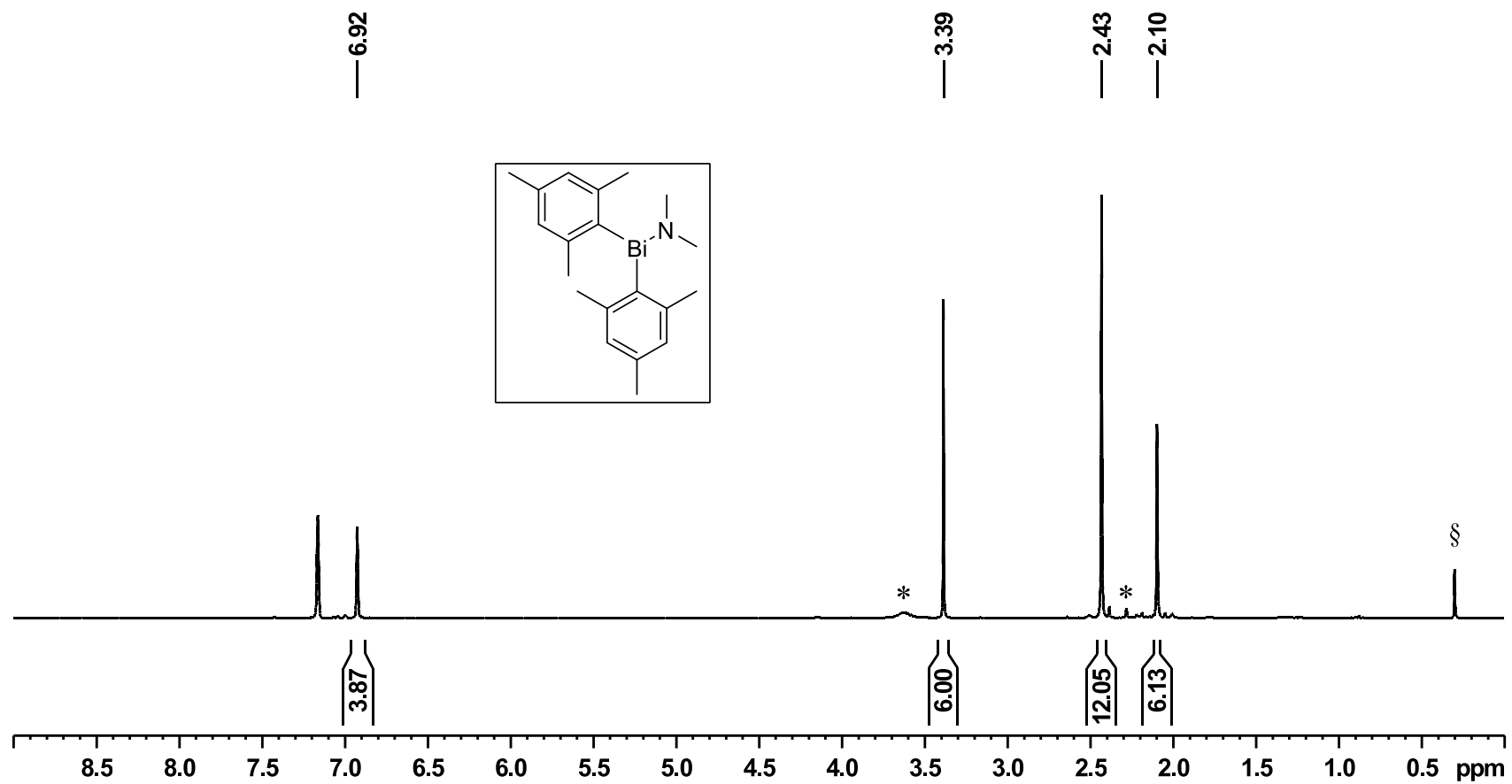


Figure S2.2.1: ¹H NMR spectrum (300 MHz) of 2 in C₆D₆ at room temperature (* = Unknown impurity, § = Silicon grease).

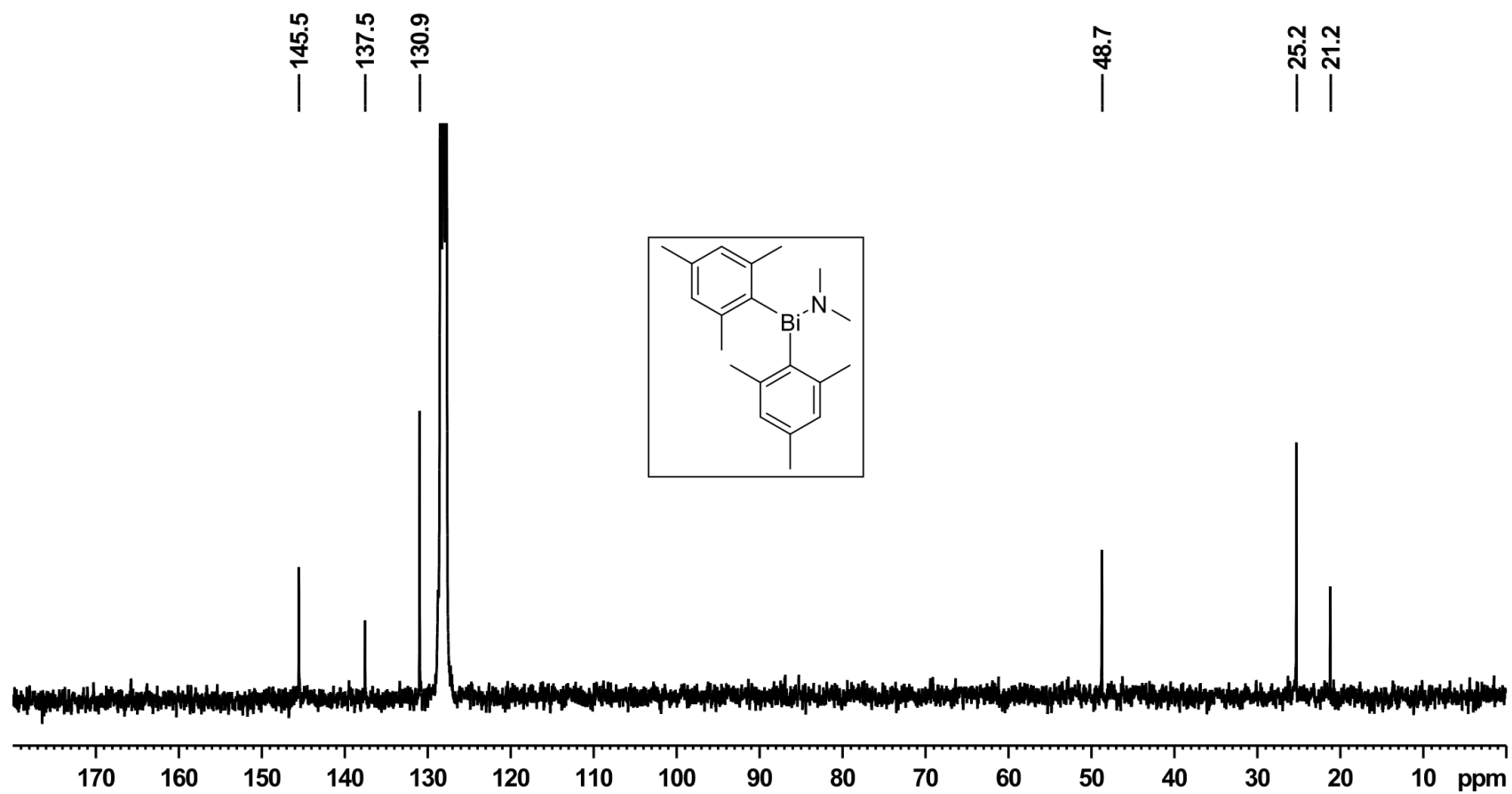


Figure S2.2.2: ^{13}C NMR spectrum (75 MHz) of **2** in C_6D_6 at room temperature.

2.3 Mes₂BiNH*t*Bu

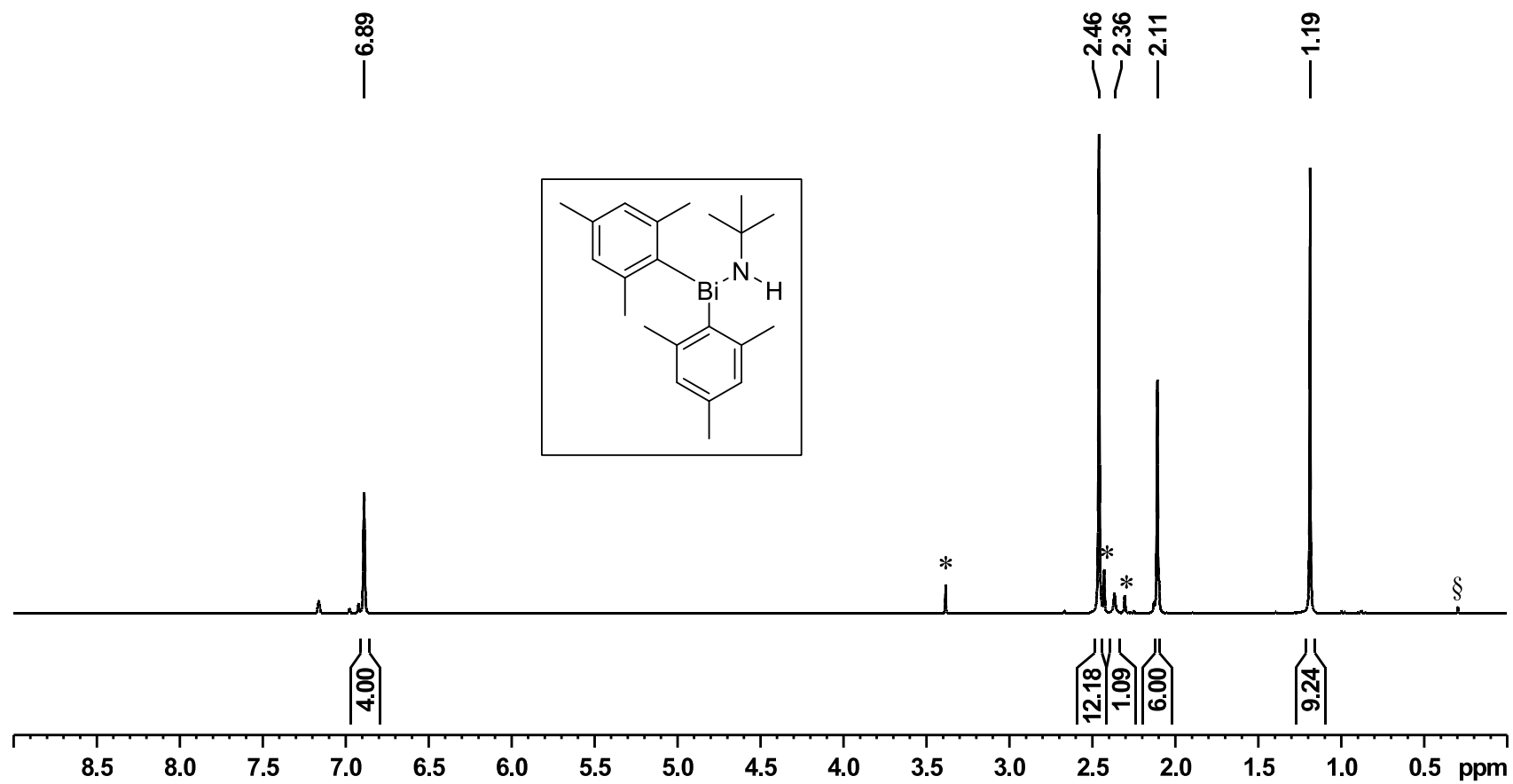


Figure S2.3.1: ¹H NMR spectrum (300 MHz) of **3** in C₆D₆ at room temperature (* = Mes₂BiNMe₂ (**2**), § = Silicon grease).

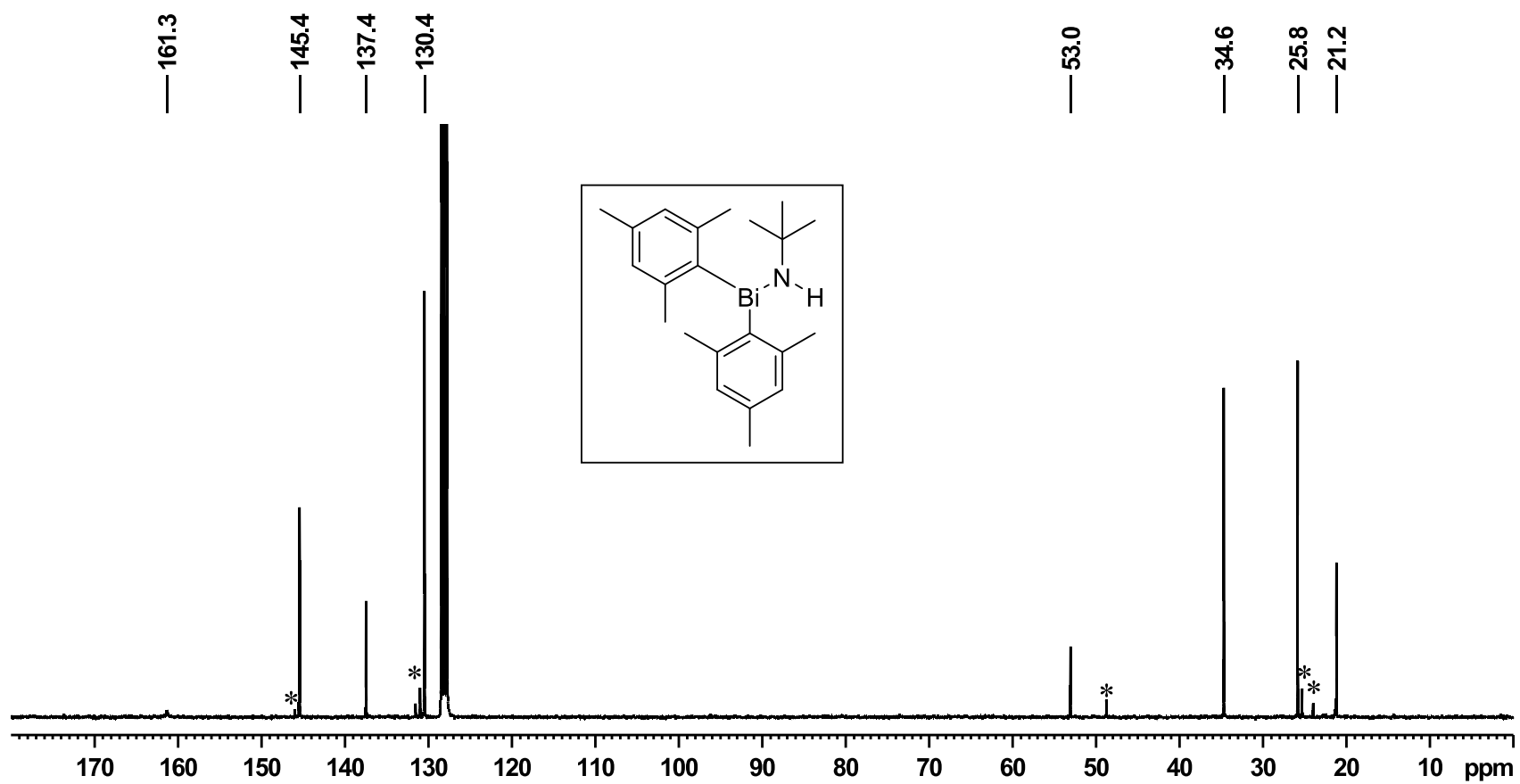


Figure S2.3.2: ^{13}C NMR spectrum (75 MHz) of **3** in C_6D_6 at room temperature (* = $\text{Mes}_2\text{BiNMe}_2$ (**2**)).

2.4 Ph₂BiPtBu₂ (4)

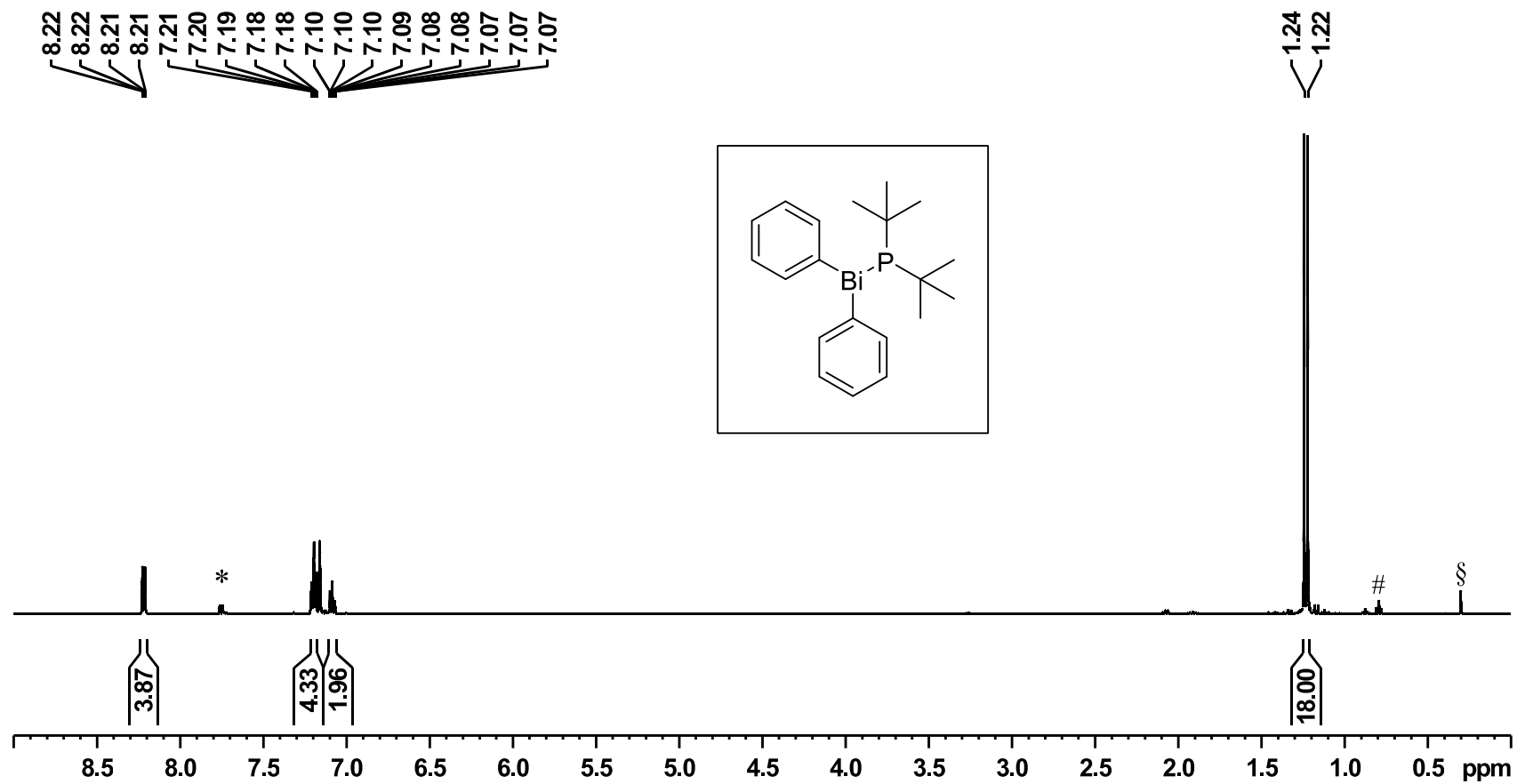


Figure S2.4.1: ¹H NMR spectrum (500 MHz) of 4 in C₆D₆ at room temperature (* = Unknown impurity, # = pentane, § = Silicon grease).

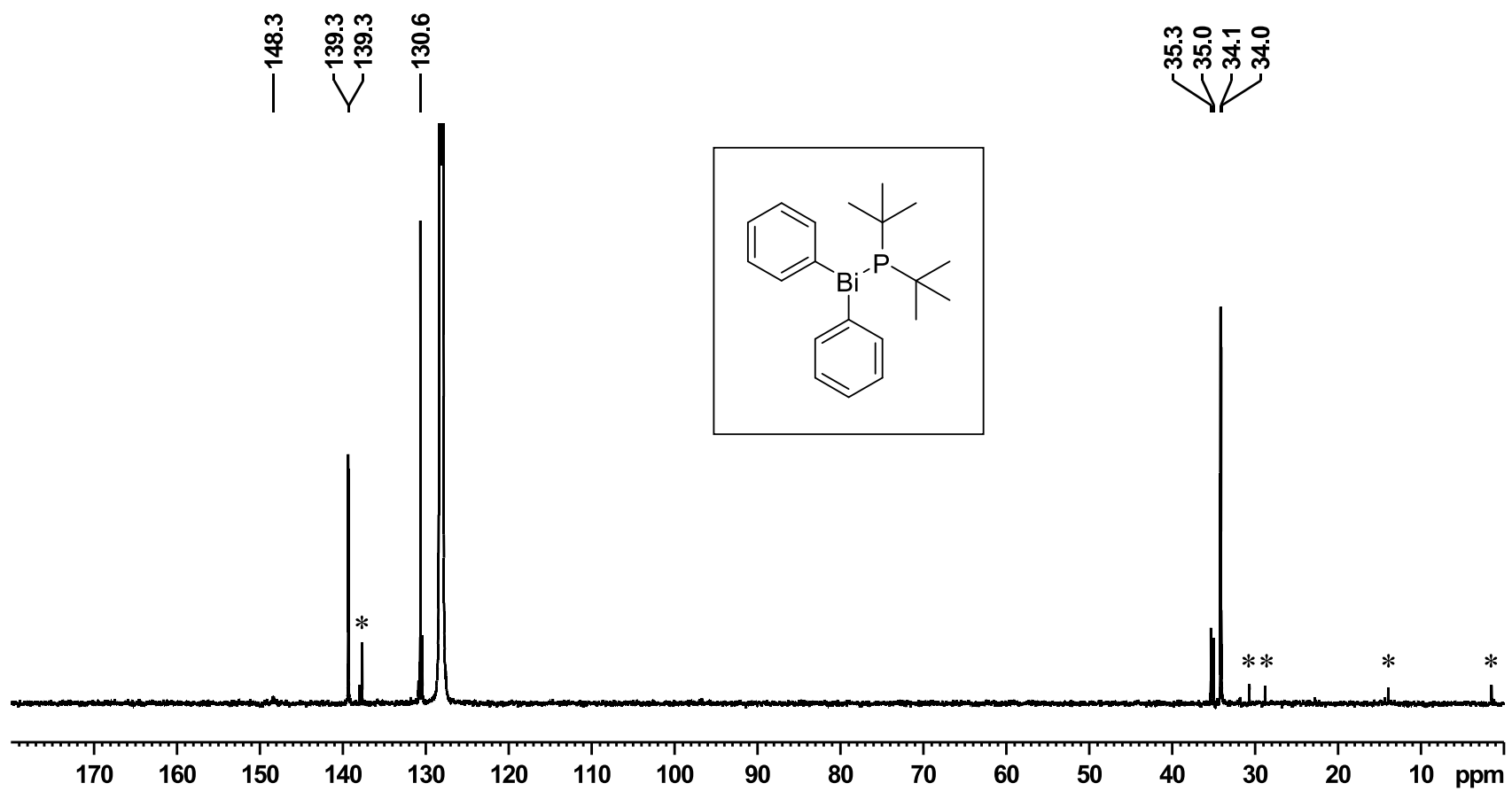


Figure S2.4.2: ^{13}C NMR spectrum (125 MHz) of **4** in C_6D_6 at room temperature (* = Unknown impurity).

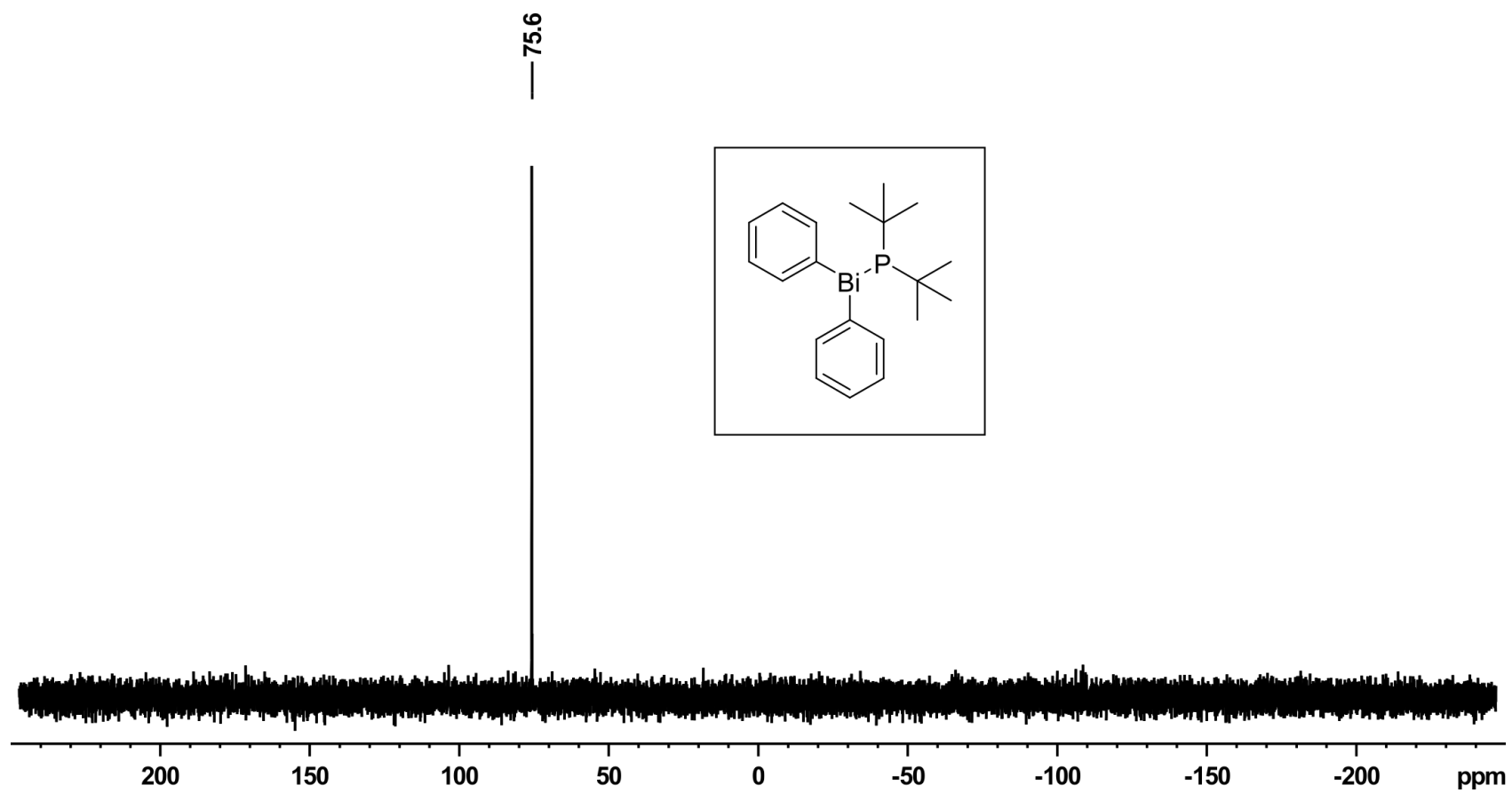


Figure S2.4.3: $^{13}\text{P}\{^1\text{H}\}$ NMR spectrum (200 MHz) of **4** in C_6D_6 at room temperature.

2.5 Mes₂BiPtBu₂ (**5**)

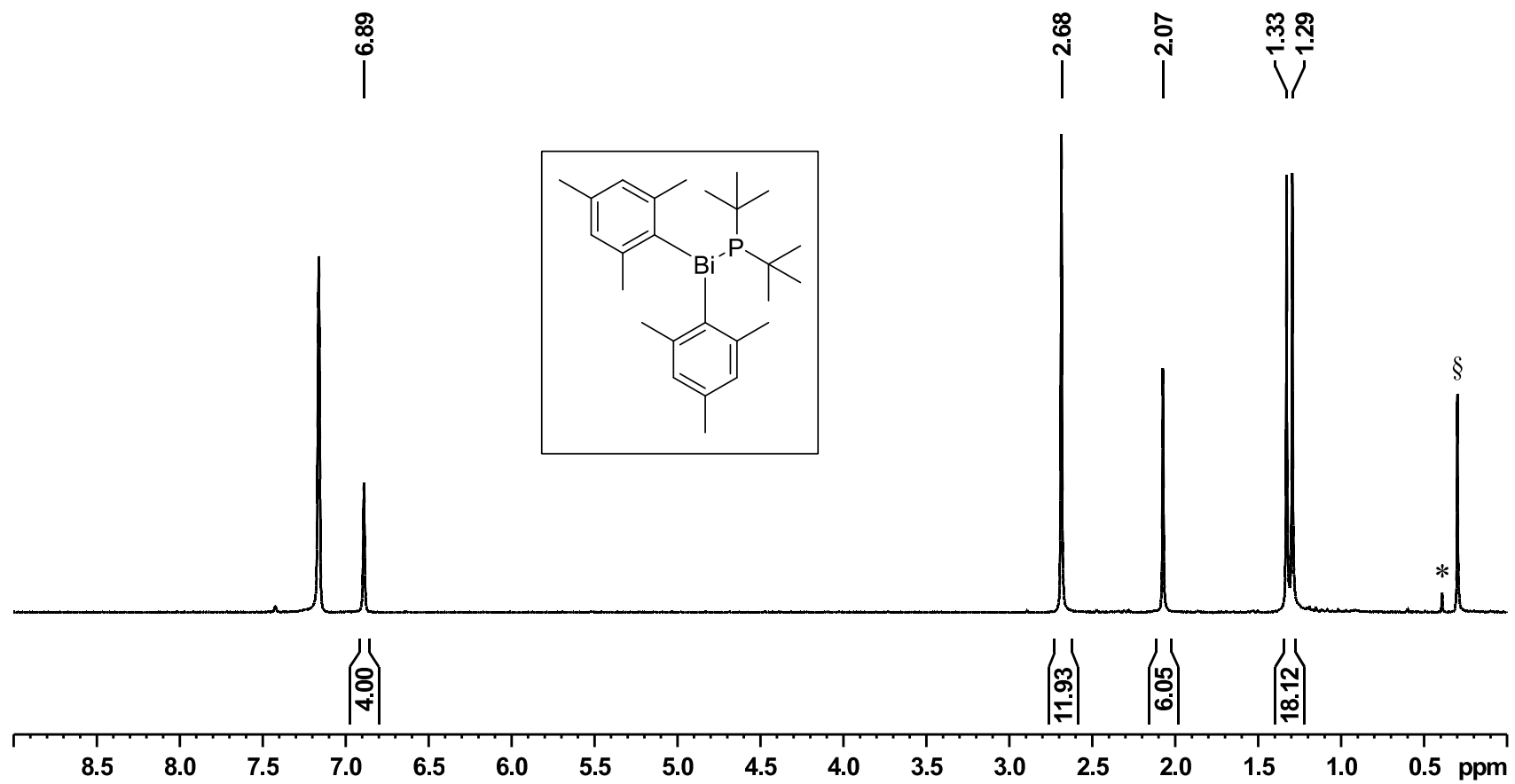


Figure S2.5.1: ¹H NMR spectrum (500 MHz) of **5** in C₆D₆ at room temperature (* = Unknown impurity, § = Silicon grease).

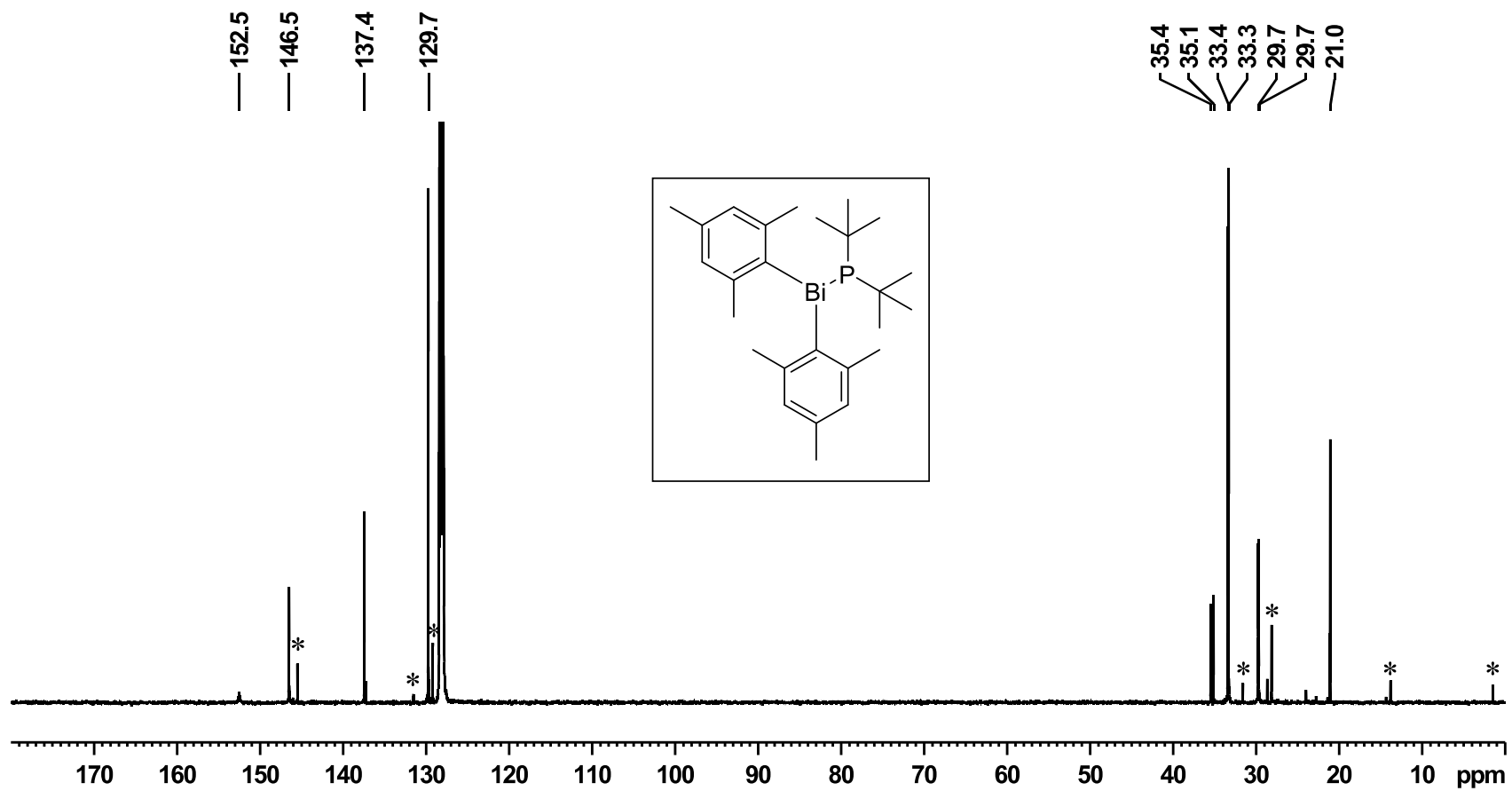


Figure S2.5.2: ^{13}C NMR spectrum (125 MHz) of **5** in C_6D_6 at room temperature (* = Unknown impurity).

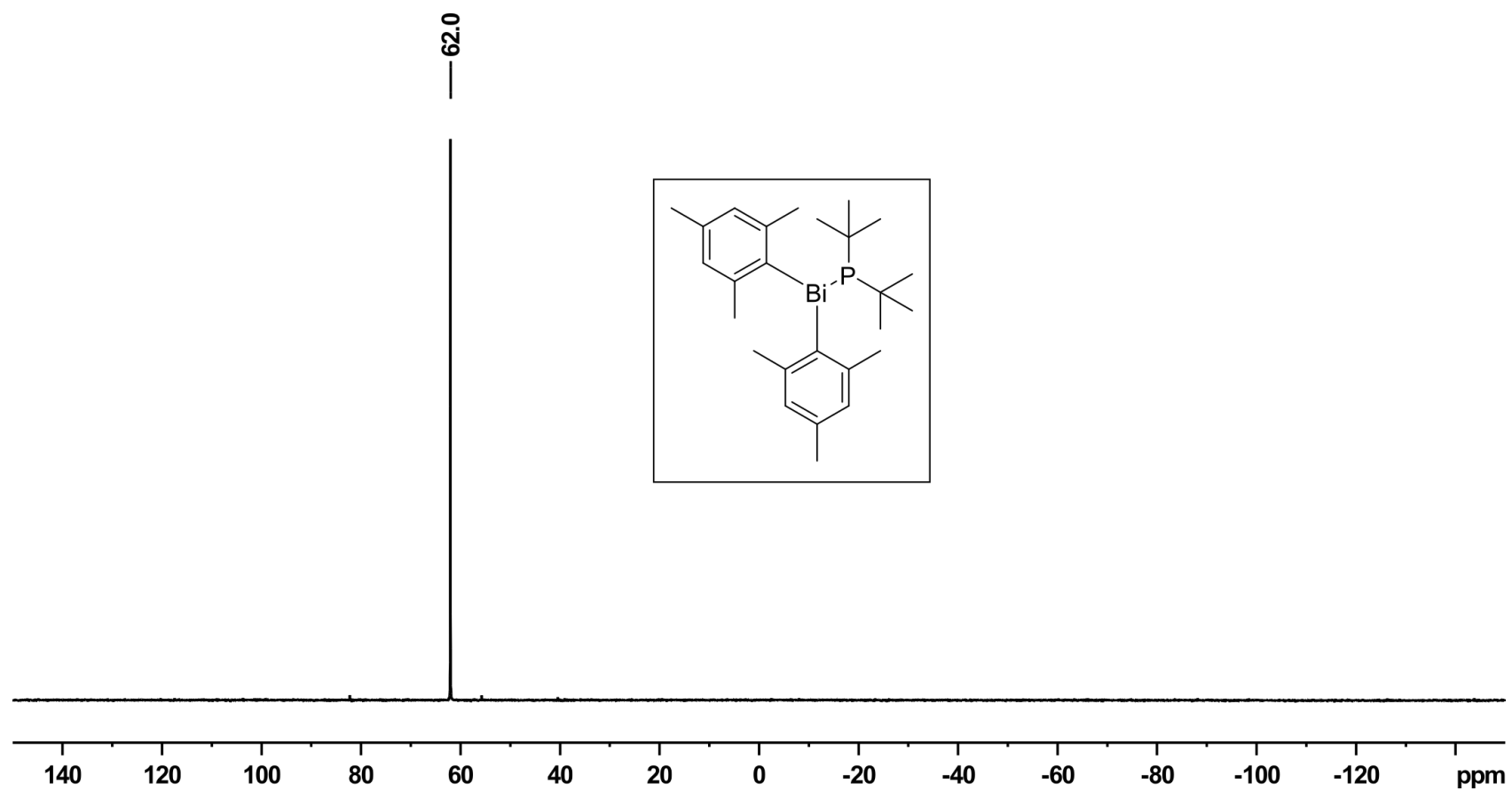


Figure S2.5.3: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (125 MHz) of **5** in C_6D_6 at room temperature.

2.6 Ph₂BiPtBu(SiMe₃)₃ (**6**)

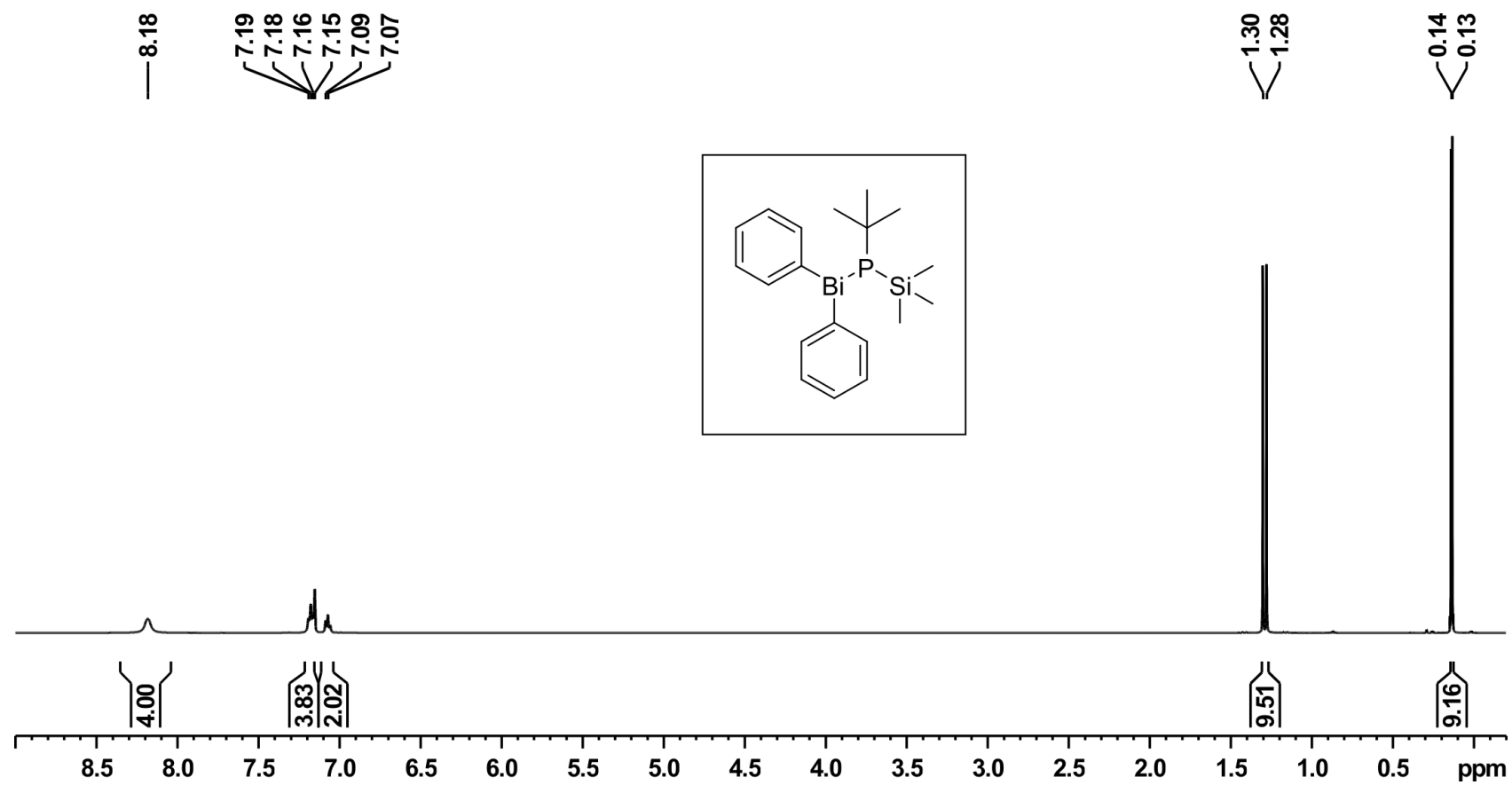


Figure S2.6.1: ¹H NMR spectrum (500 MHz) of **6** in C₆D₆ at room temperature.

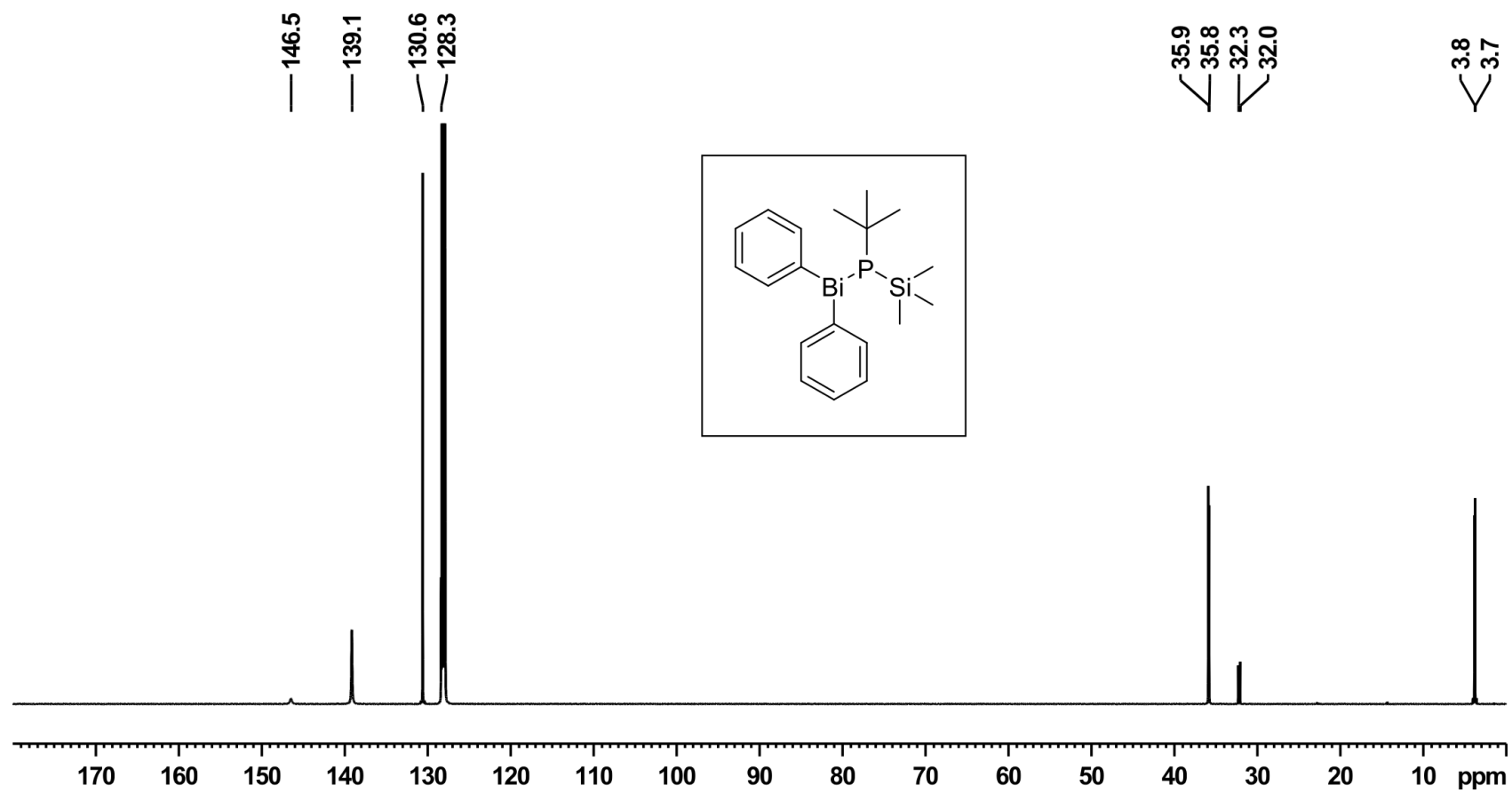


Figure S2.6.2: ^{13}C NMR spectrum (125 MHz) of **6** in C_6D_6 at room temperature.

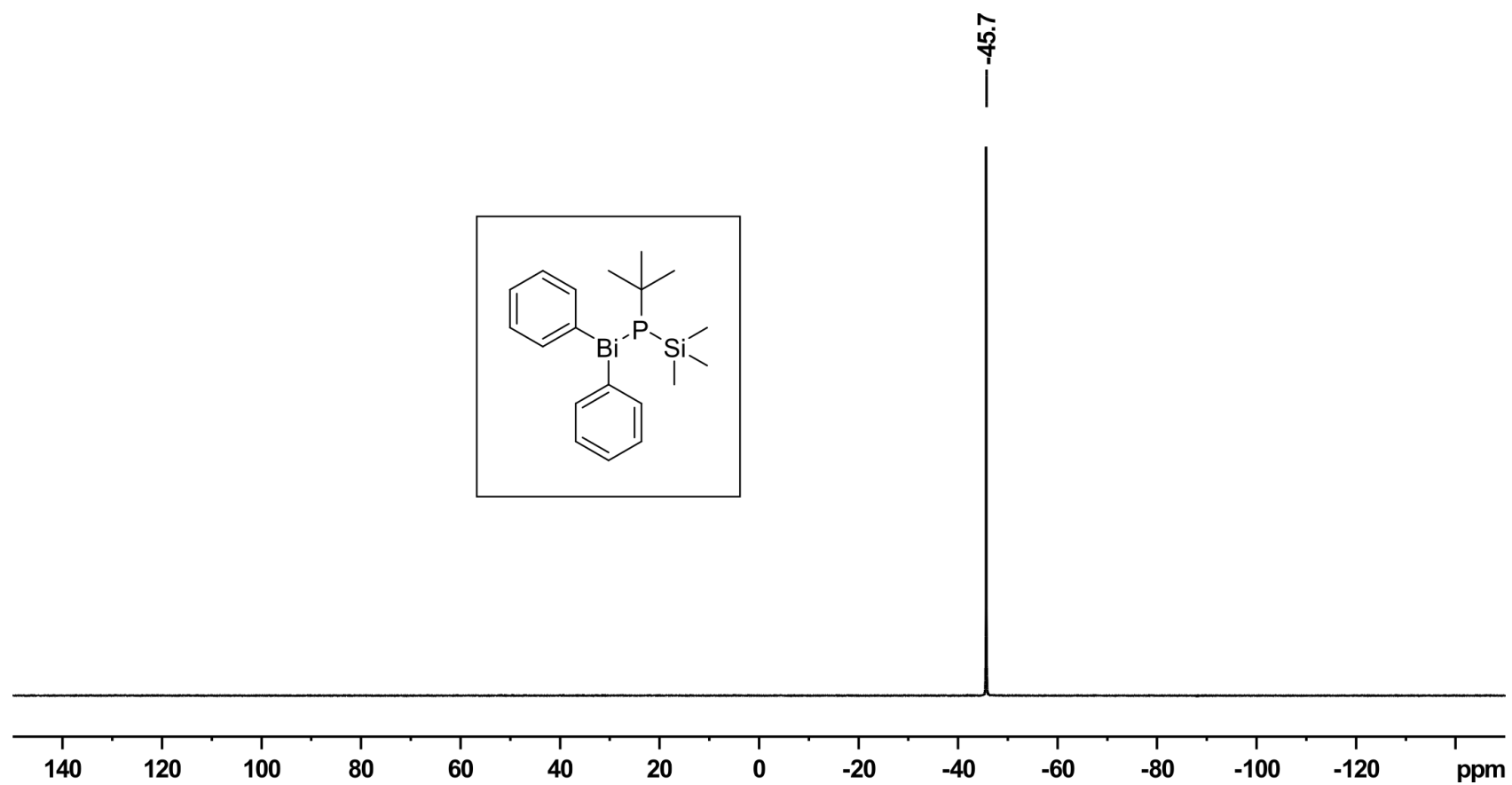


Figure S2.6.3: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (200 MHz) of **6** in C_6D_6 at room temperature.

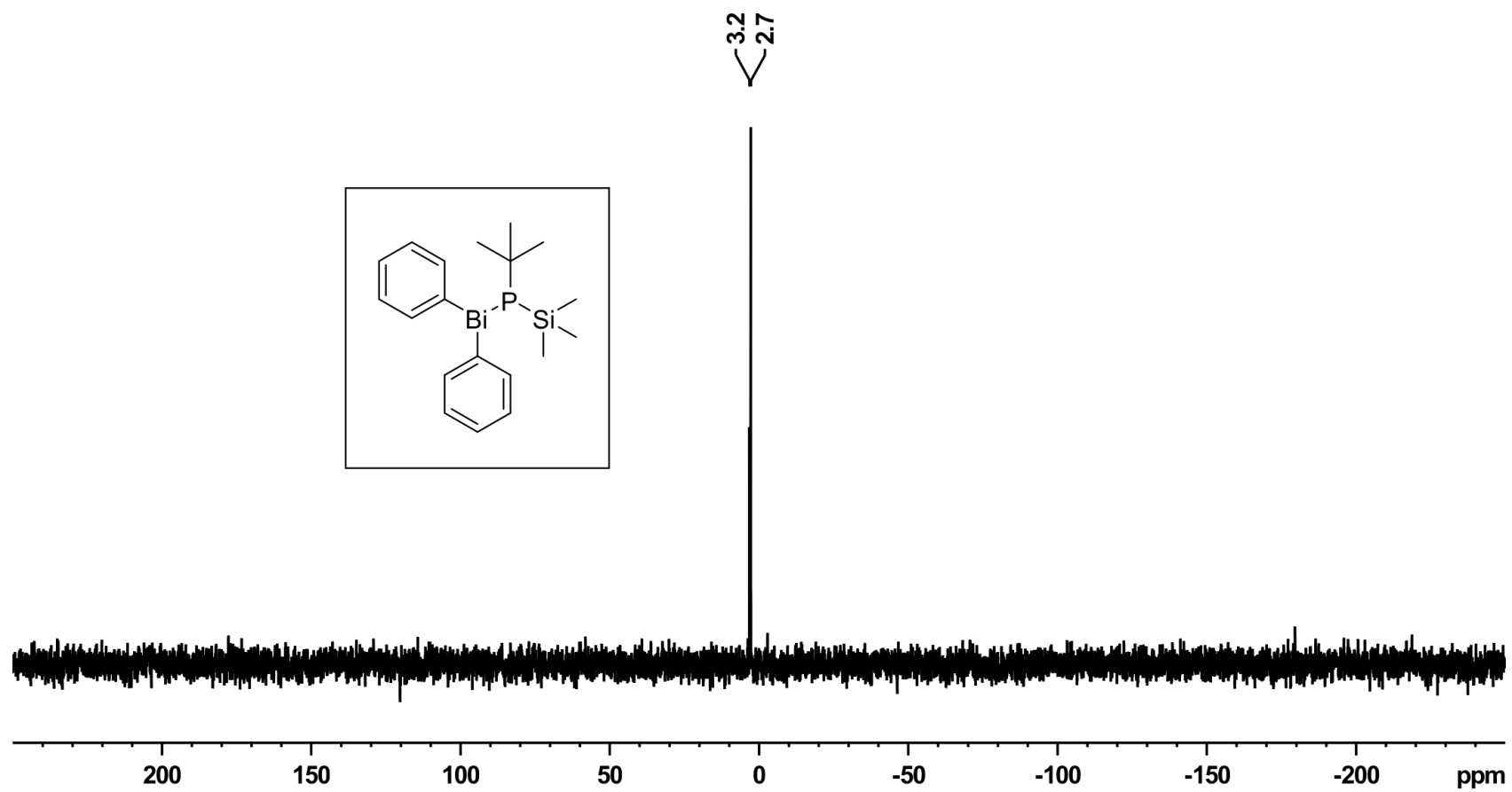


Figure S2.6.4: ^{29}Si -DEPT NMR spectrum (99 MHz) of **6** in C_6D_6 at room temperature.

2.7 Mes₂BiPtBu(SiMe₃)₃ (**7**)

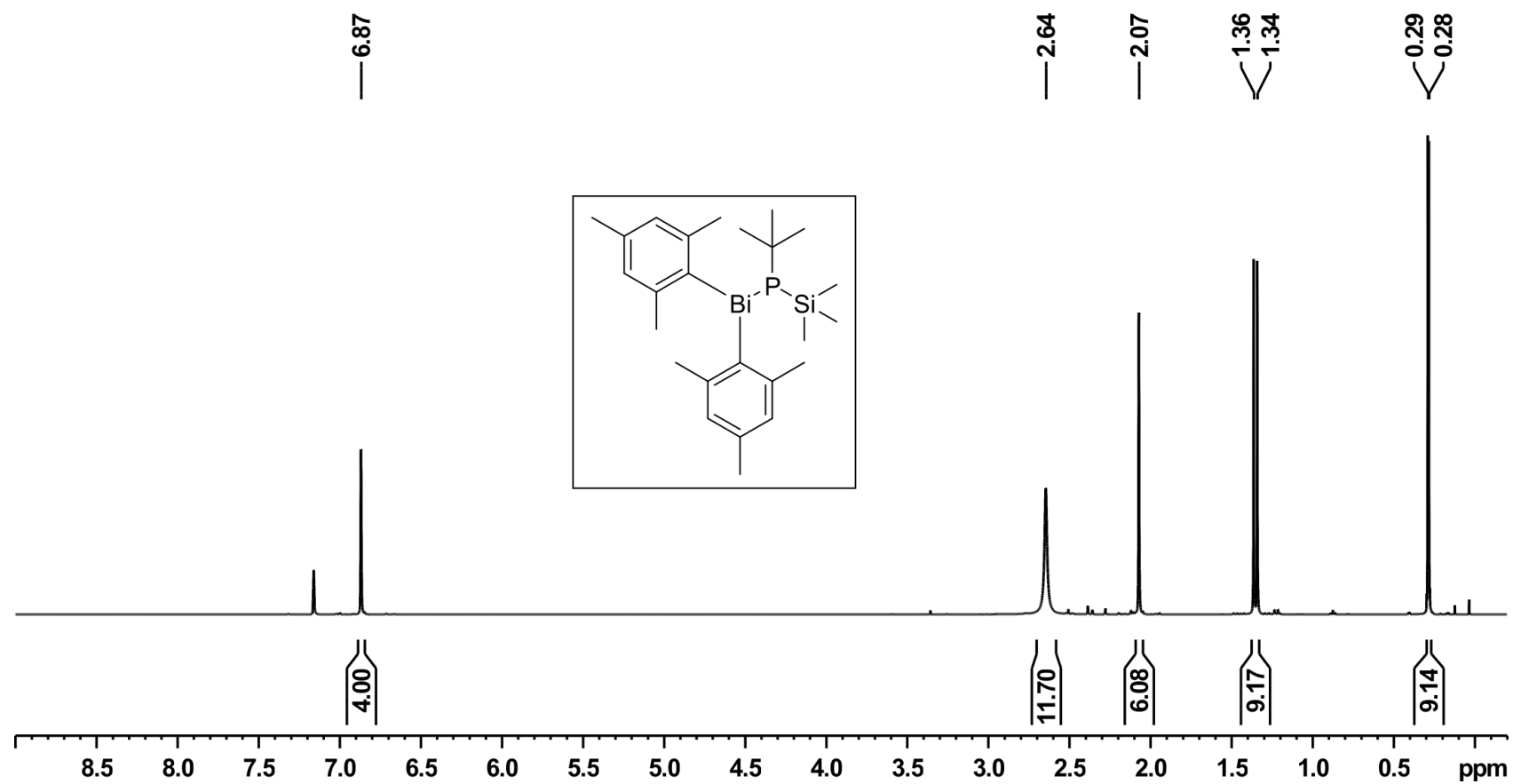


Figure S2.7.1: ¹H NMR spectrum (500 MHz) of **7** in C₆D₆ at room temperature.

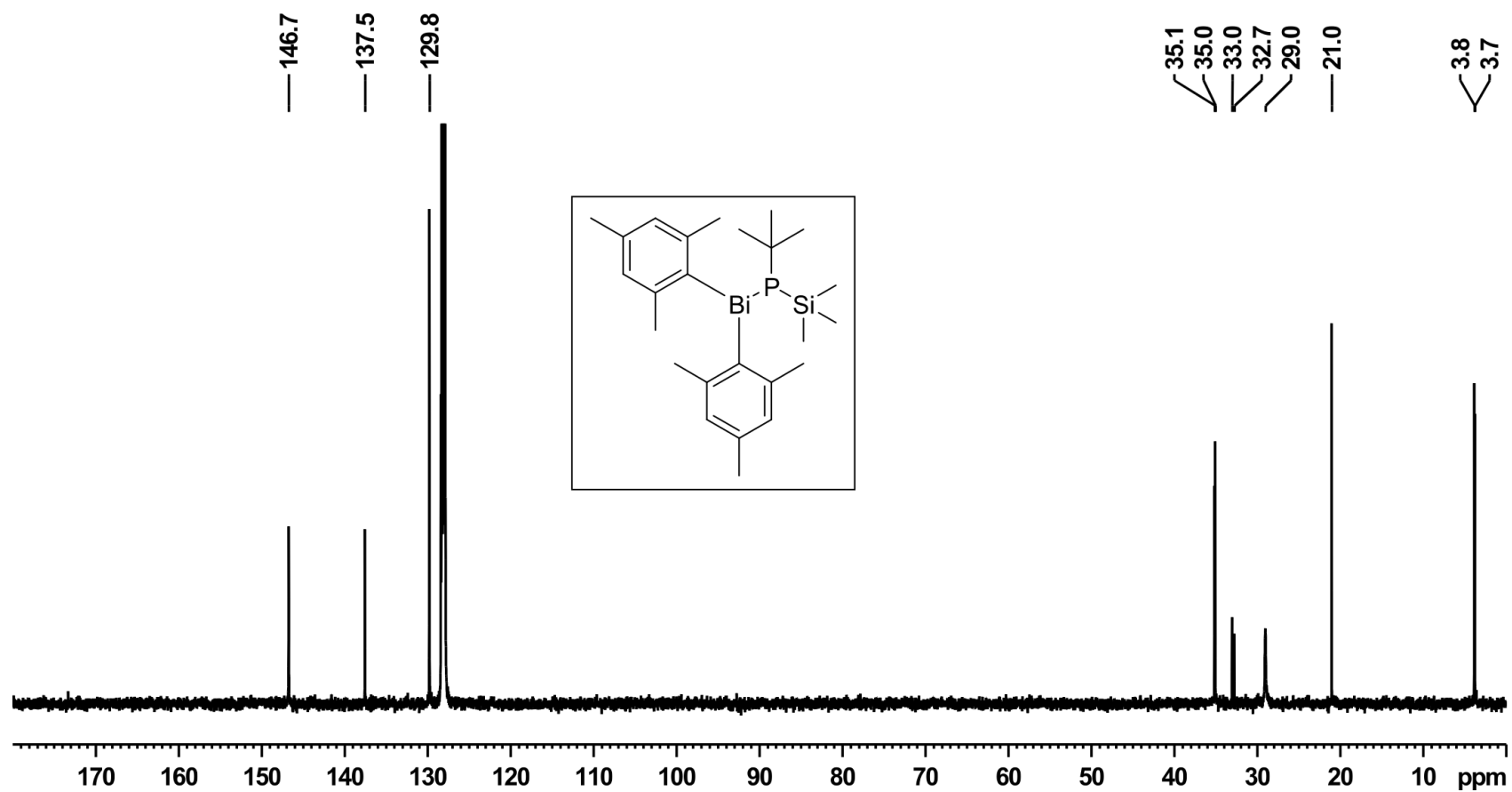


Figure S2.7.2: ^{13}C NMR spectrum (125 MHz) of 7 in C_6D_6 at room temperature.

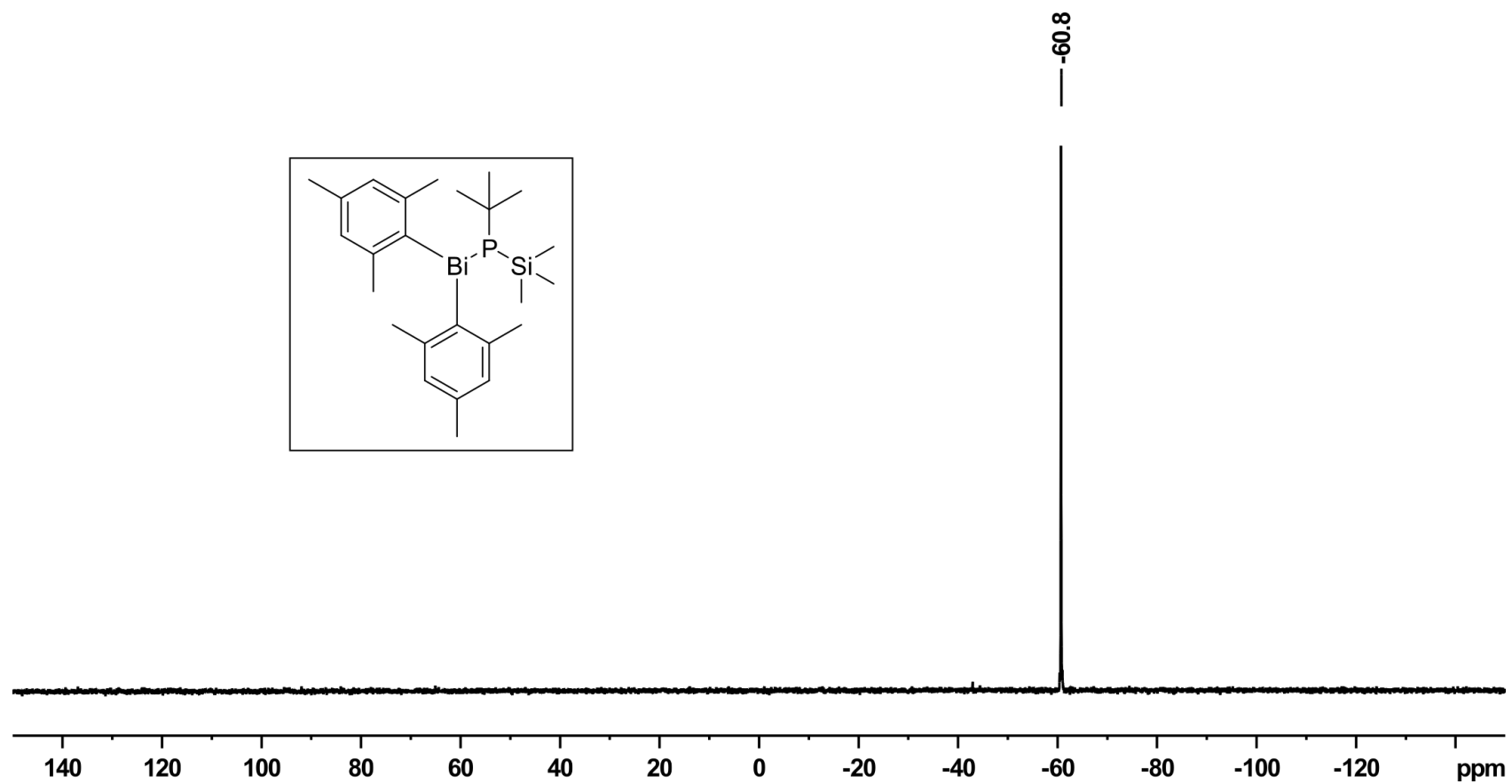


Figure S2.7.3: ^{31}P NMR spectrum (200 MHz) of 7 in C_6D_6 at room temperature.

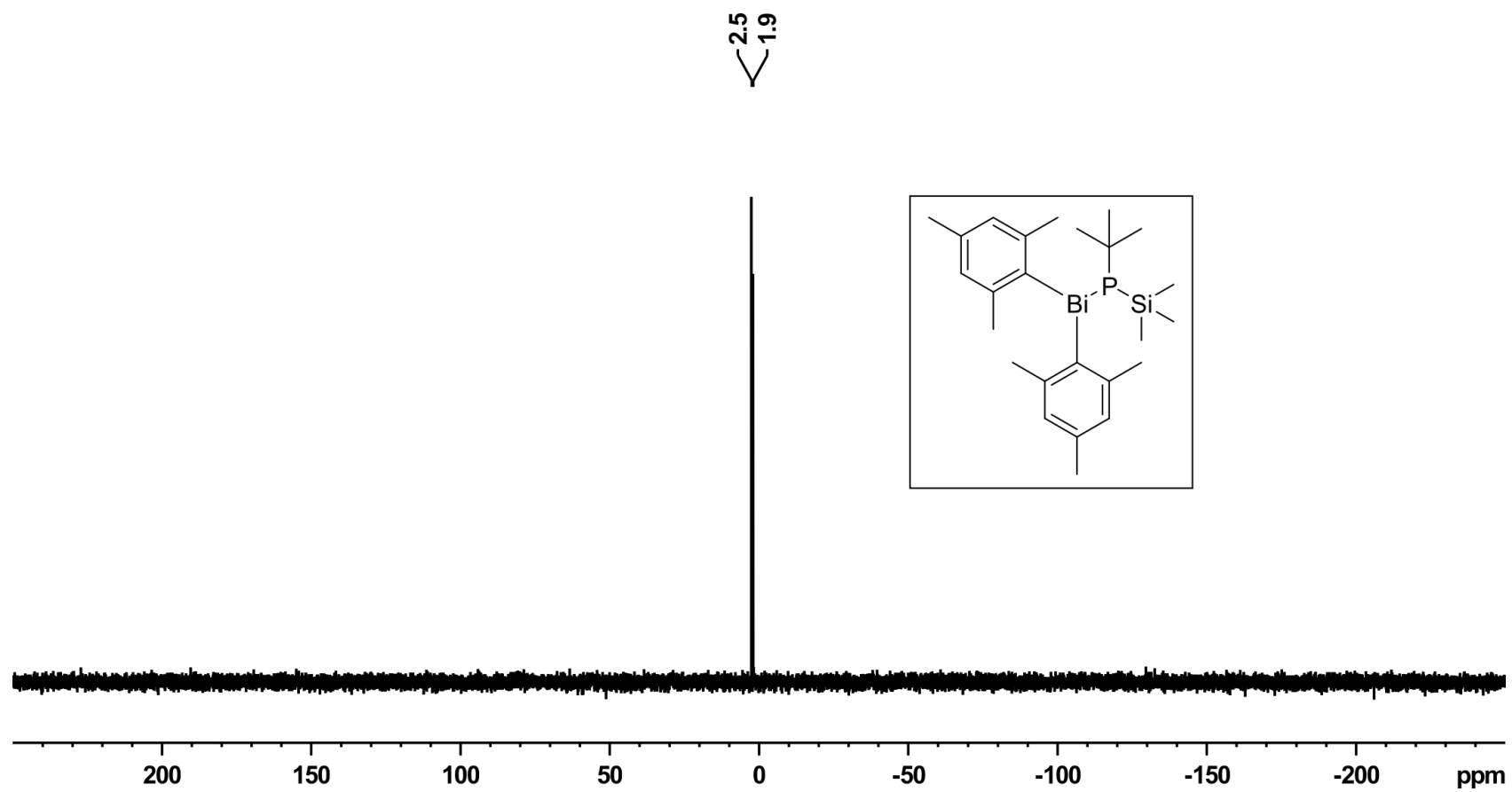


Figure S2.7.4: ^{29}Si NMR spectrum (99 MHz) of 7 in C_6D_6 at room temperature.

2.8 Ph₂BiAs*t*Bu₂ (**8**)

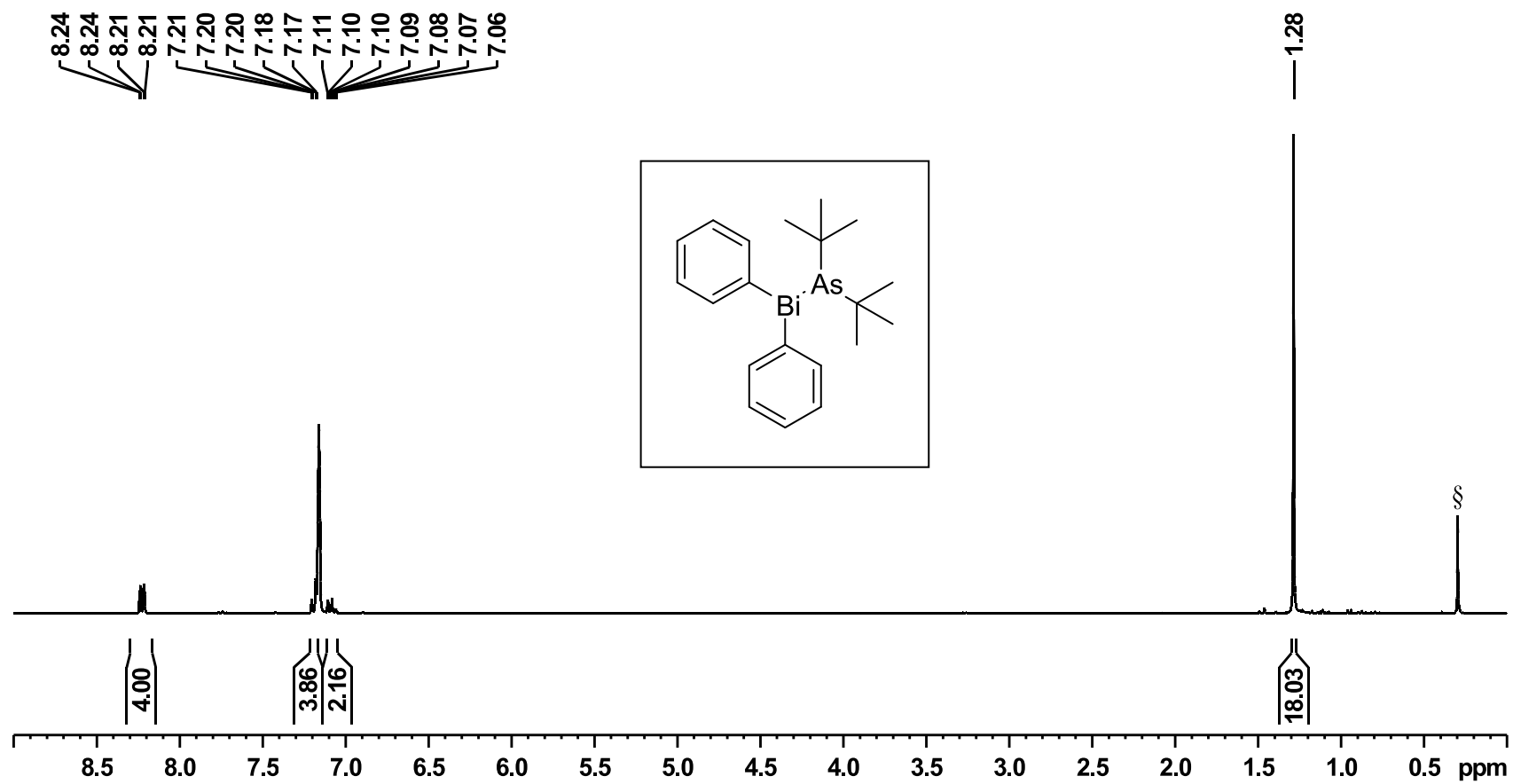


Figure S2.8.1: ¹H NMR spectrum (300 MHz) of **8** in C₆D₆ at room temperature (§ = Silicon grease).

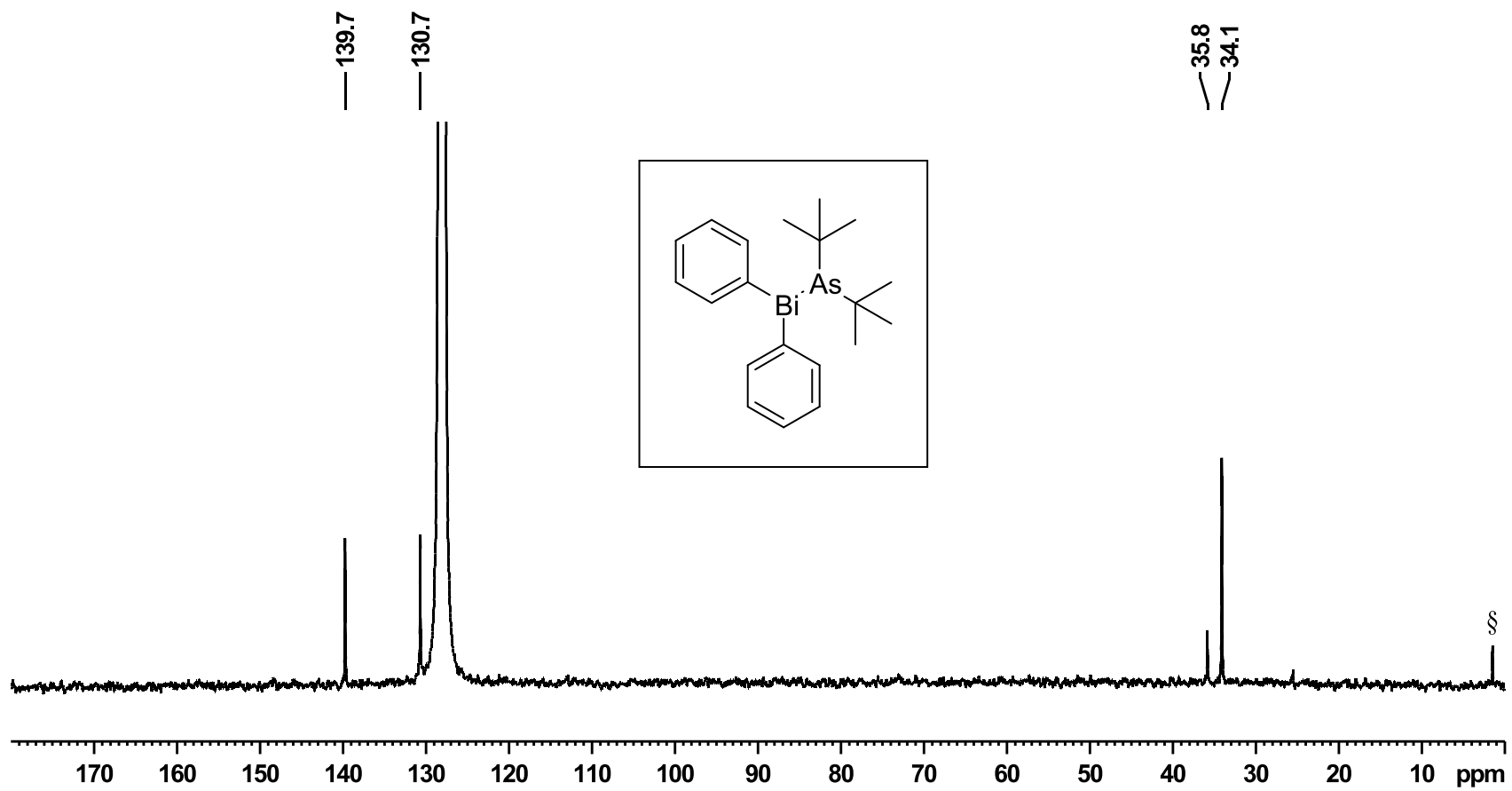


Figure S2.8.2: ^{13}C NMR spectrum (75 MHz) of **8** in C_6D_6 at room temperature (§ = Silicon grease).

2.9 Mes₂BiAstBu₂ (**9**)

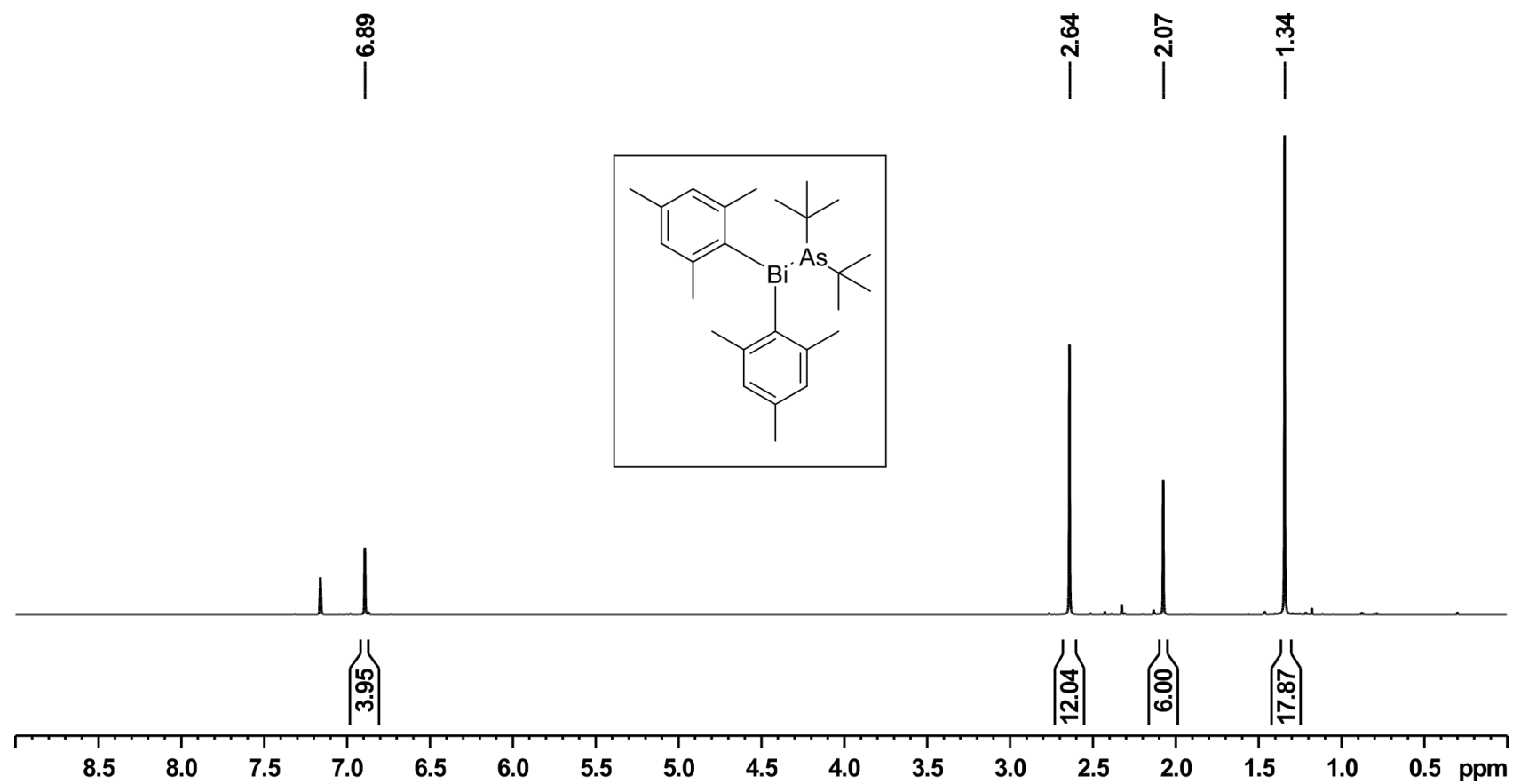


Figure S2.9.1: ¹H NMR spectrum (500 MHz) of **9** in C₆D₆ at room temperature.

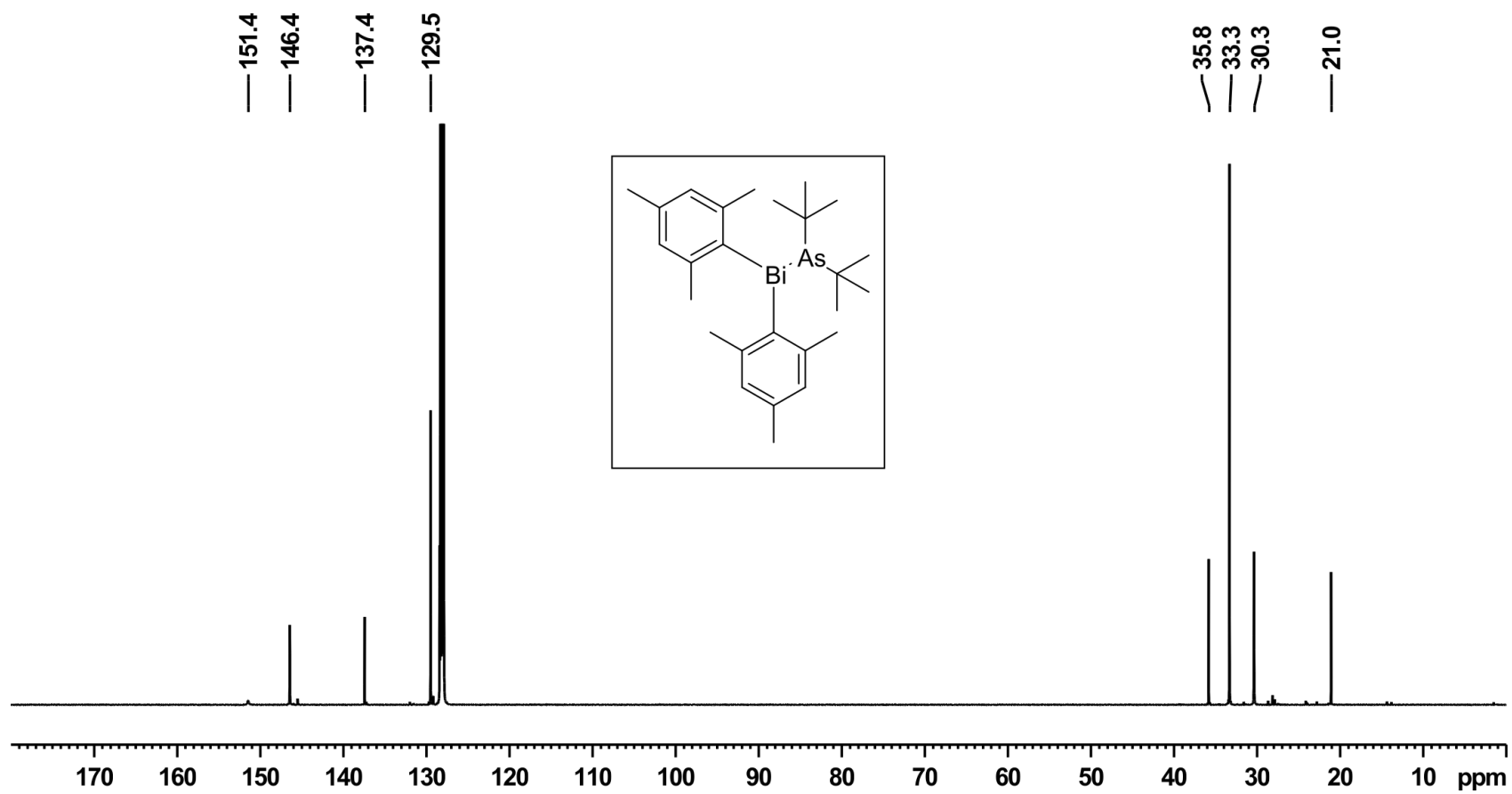


Figure S2.8.2: ^{13}C NMR spectrum (125 MHz) of **9** in C_6D_6 at room temperature.

2.10 Ph₂BiAstBu(SiMe₃)₃ (**10**)

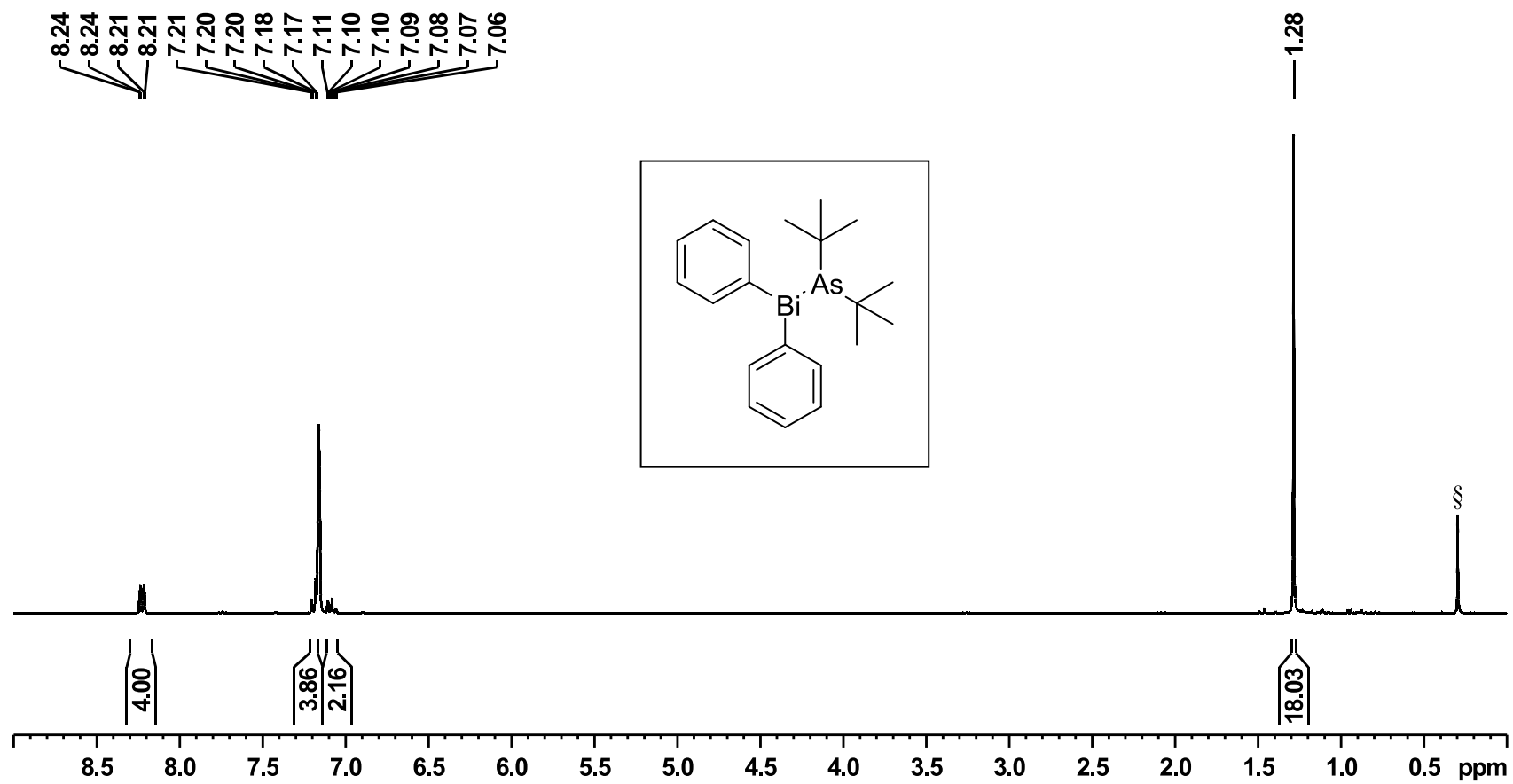


Figure S2.10.1: ¹H NMR spectrum (500 MHz) of **10** in C₆D₆ at room temperature (§ = Silicon grease).

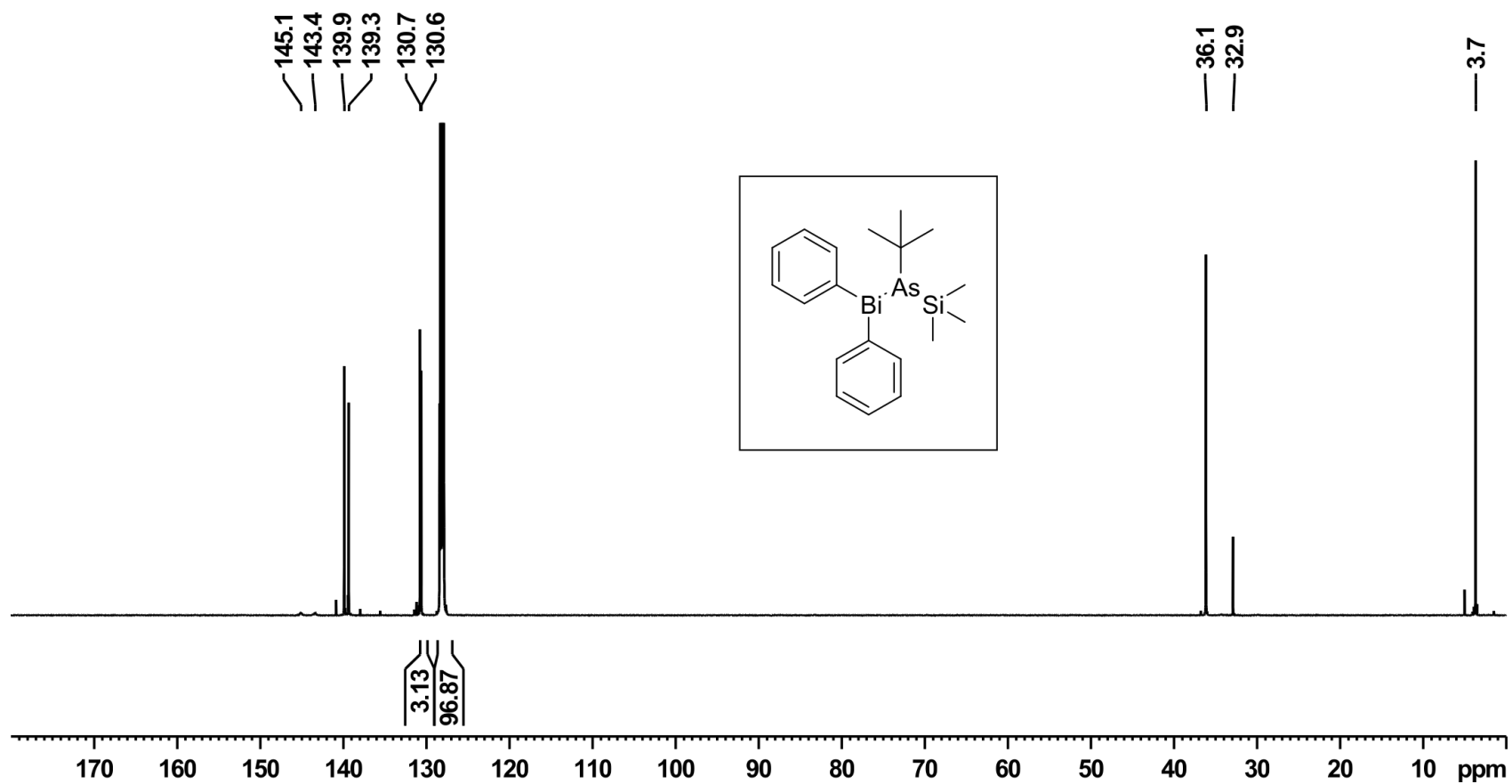


Figure S2.10.2: ^{13}C NMR spectrum (125 MHz) of **10** in C_6D_6 at room temperature.

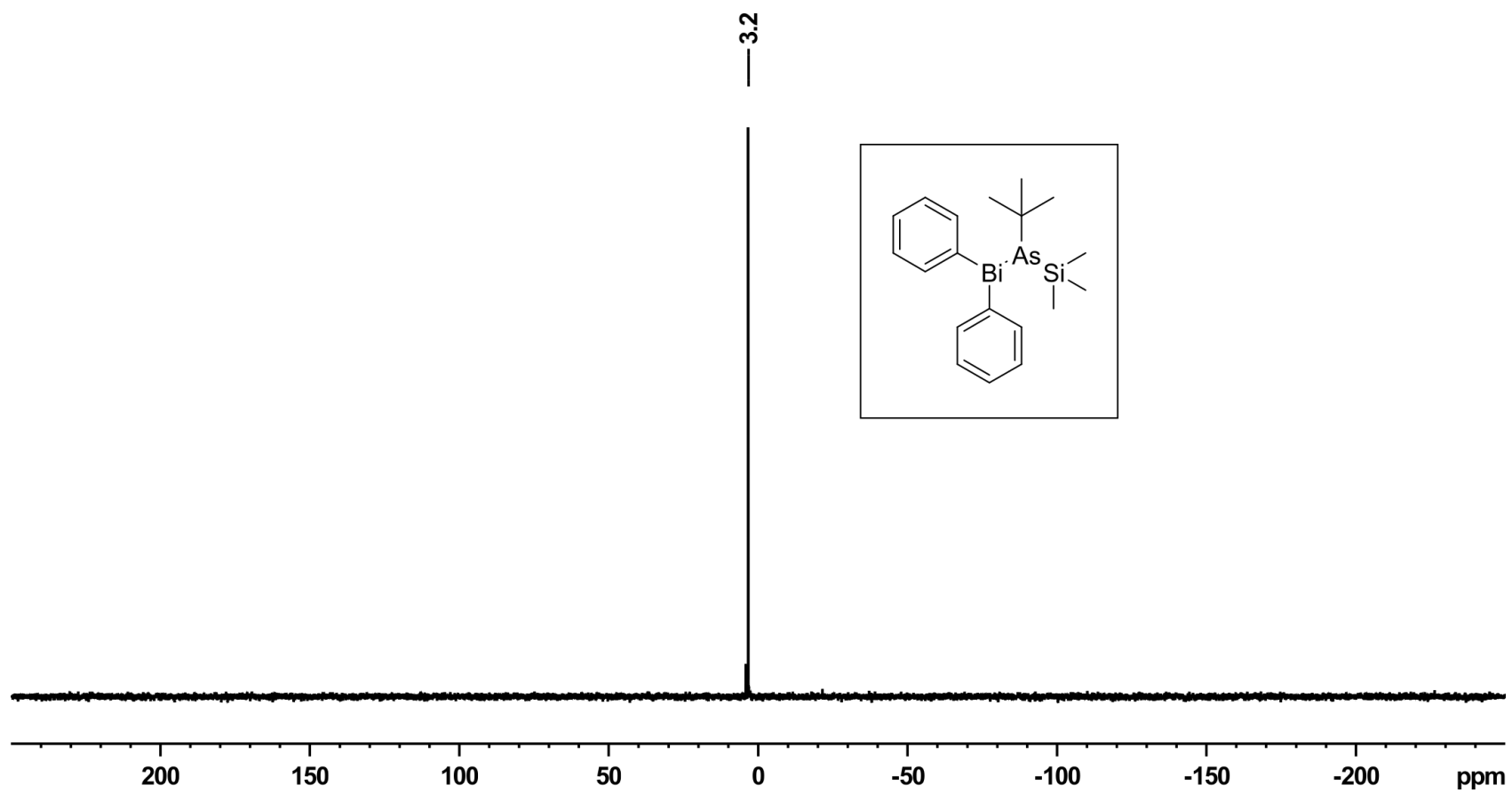


Figure S2.10.3: ^{29}Si NMR spectrum (99 MHz) of **10** in C_6D_6 at room temperature.

2.11 Mes₂BiAstBu(SiMe₃)₃ (**11**)

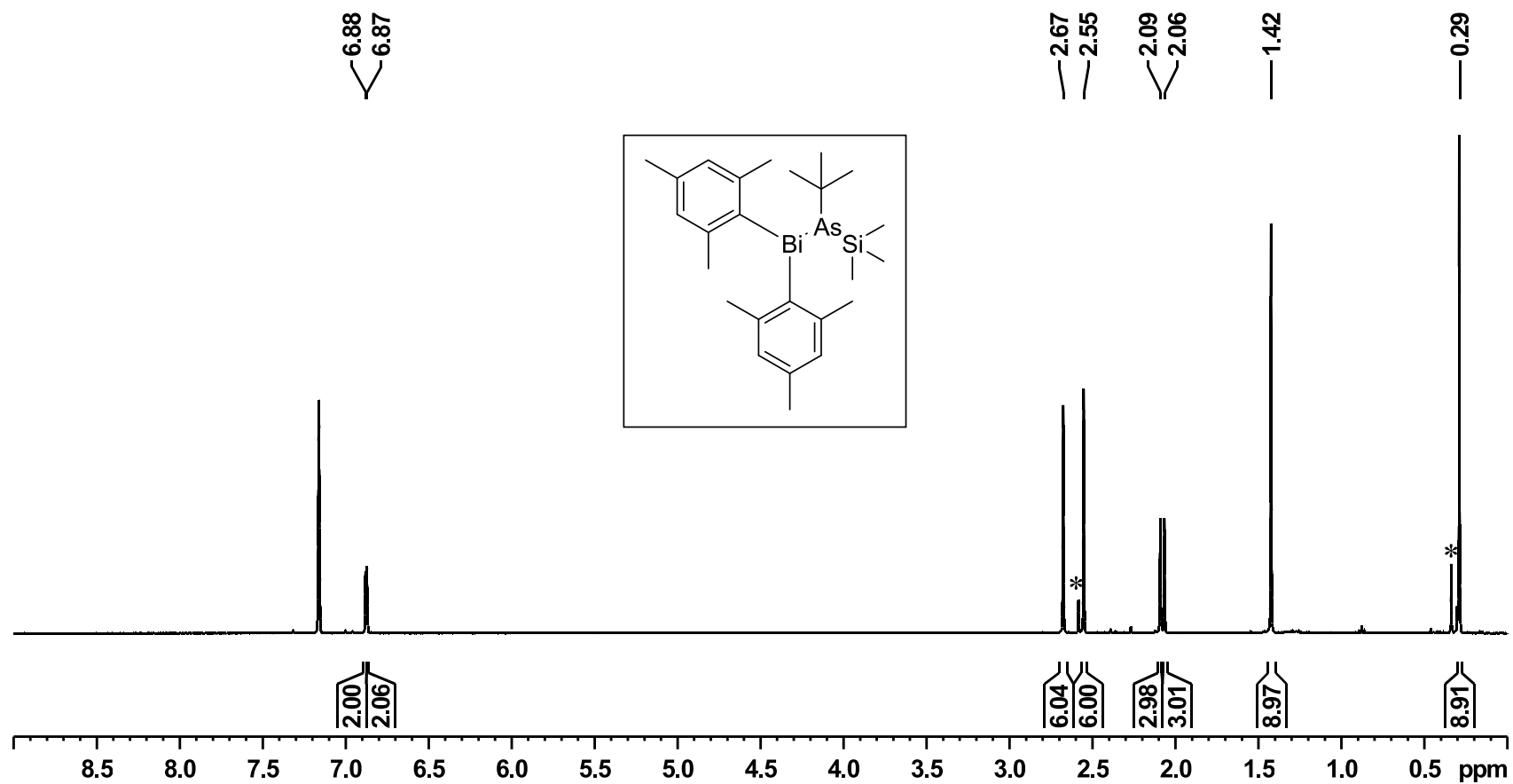


Figure S2.11.1: ¹H NMR spectrum (500 MHz) of **11** in C₆D₆ at room temperature (* = Unknown impurity).

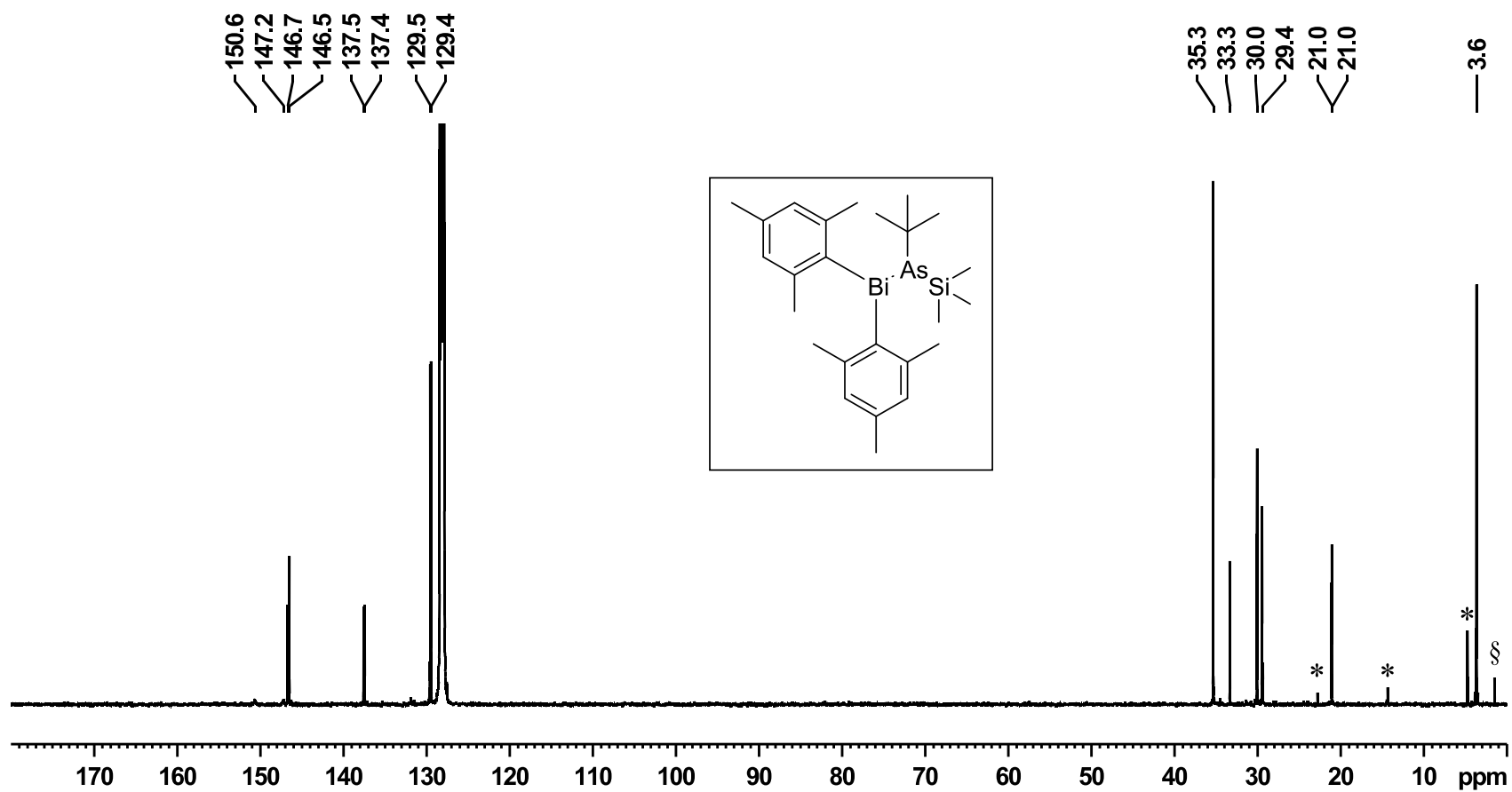


Figure S2.11.2: ^{13}C NMR spectrum (125 MHz) of **11** in C_6D_6 at room temperature (* = Unknown impurity, § = Silicon grease).

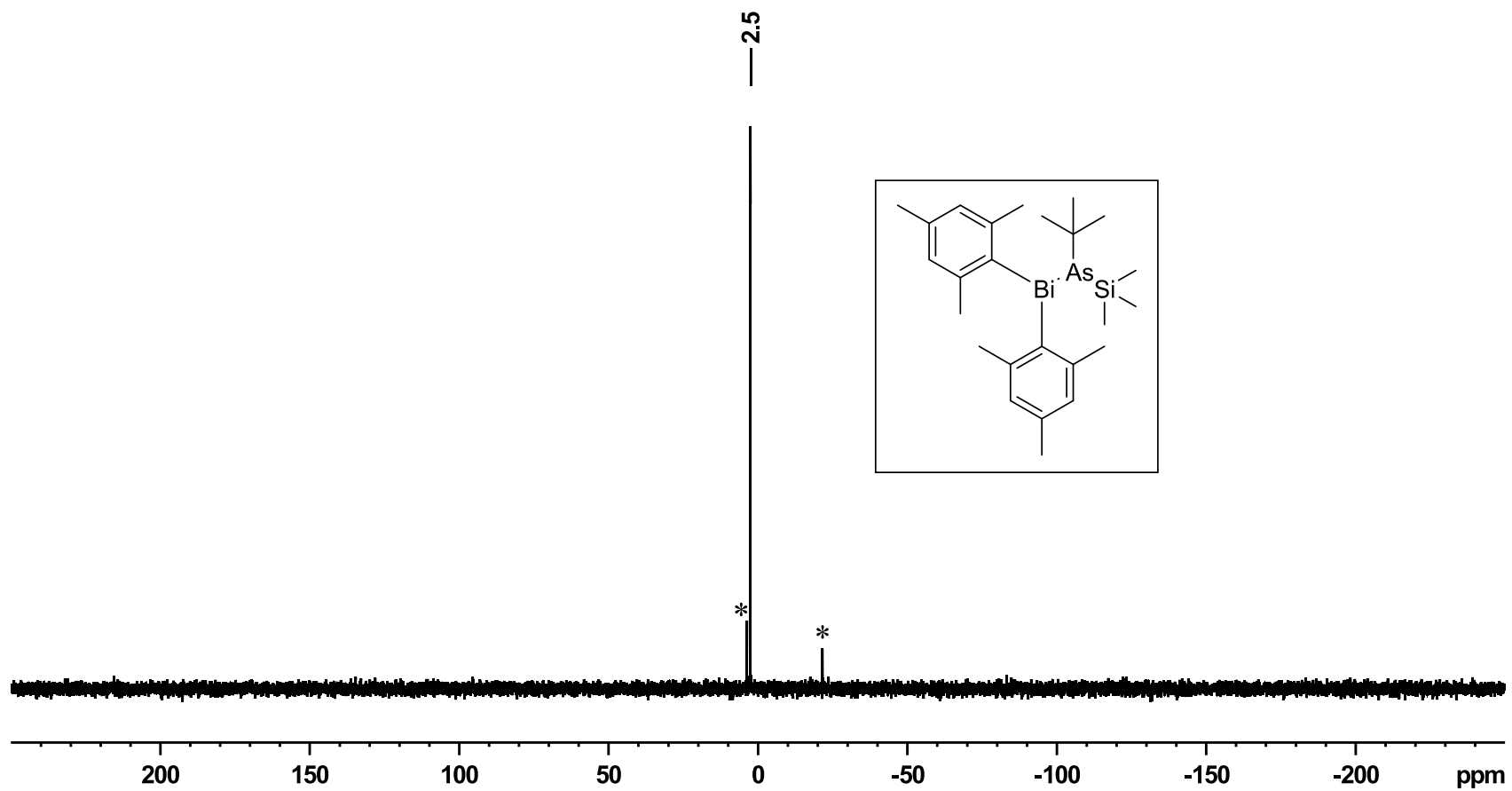


Figure S2.11.1: ^{29}Si NMR spectrum (99 MHz) of **11** in C_6D_6 at room temperature (* = Unknown impurity).

2.12 Ph₂BiSbMes₂ (**12**)

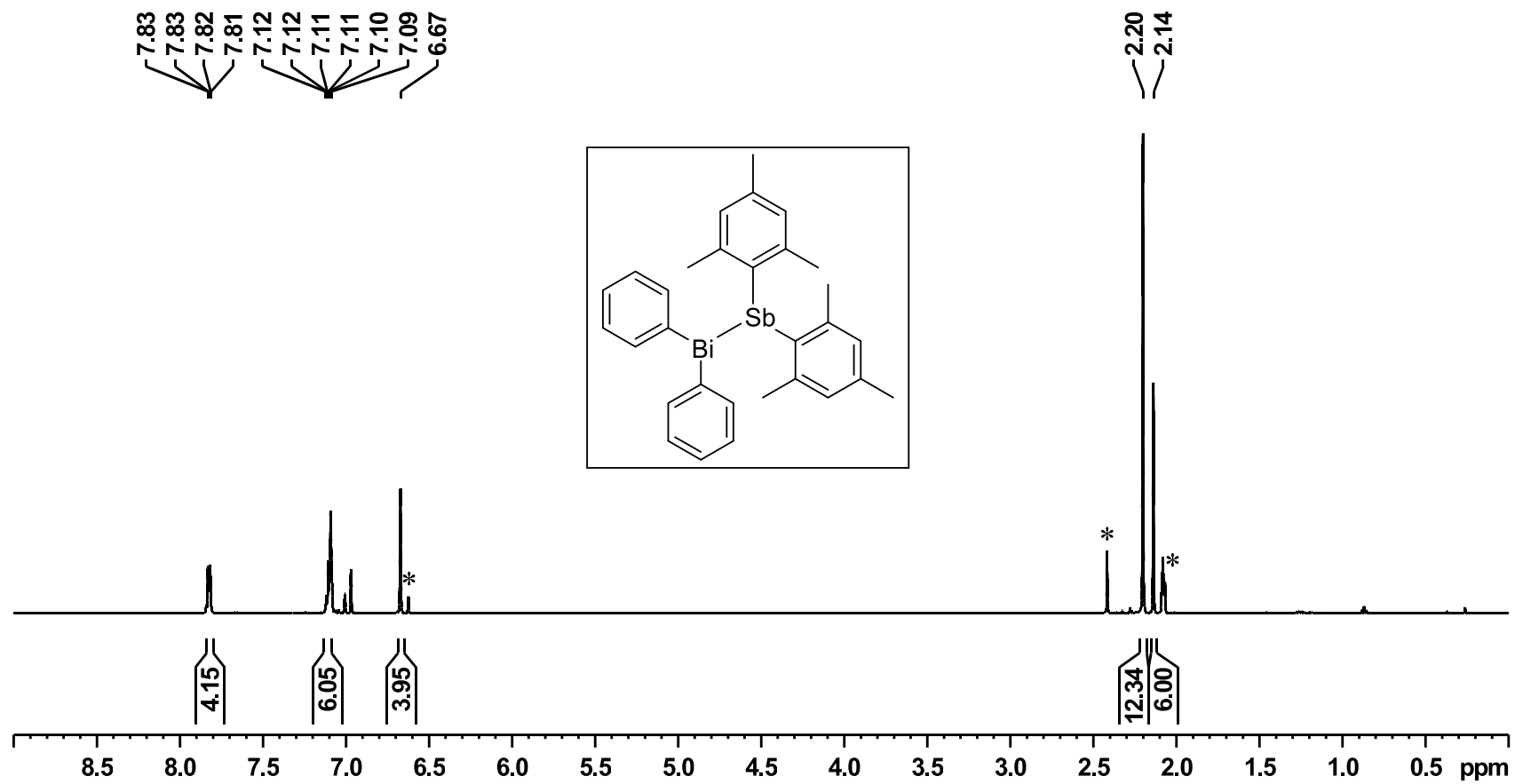


Figure S2.12.1: ¹H NMR spectrum (500 MHz) of **12** in toluene-d₈ at room temperature (* = Mes₄Sb₂).

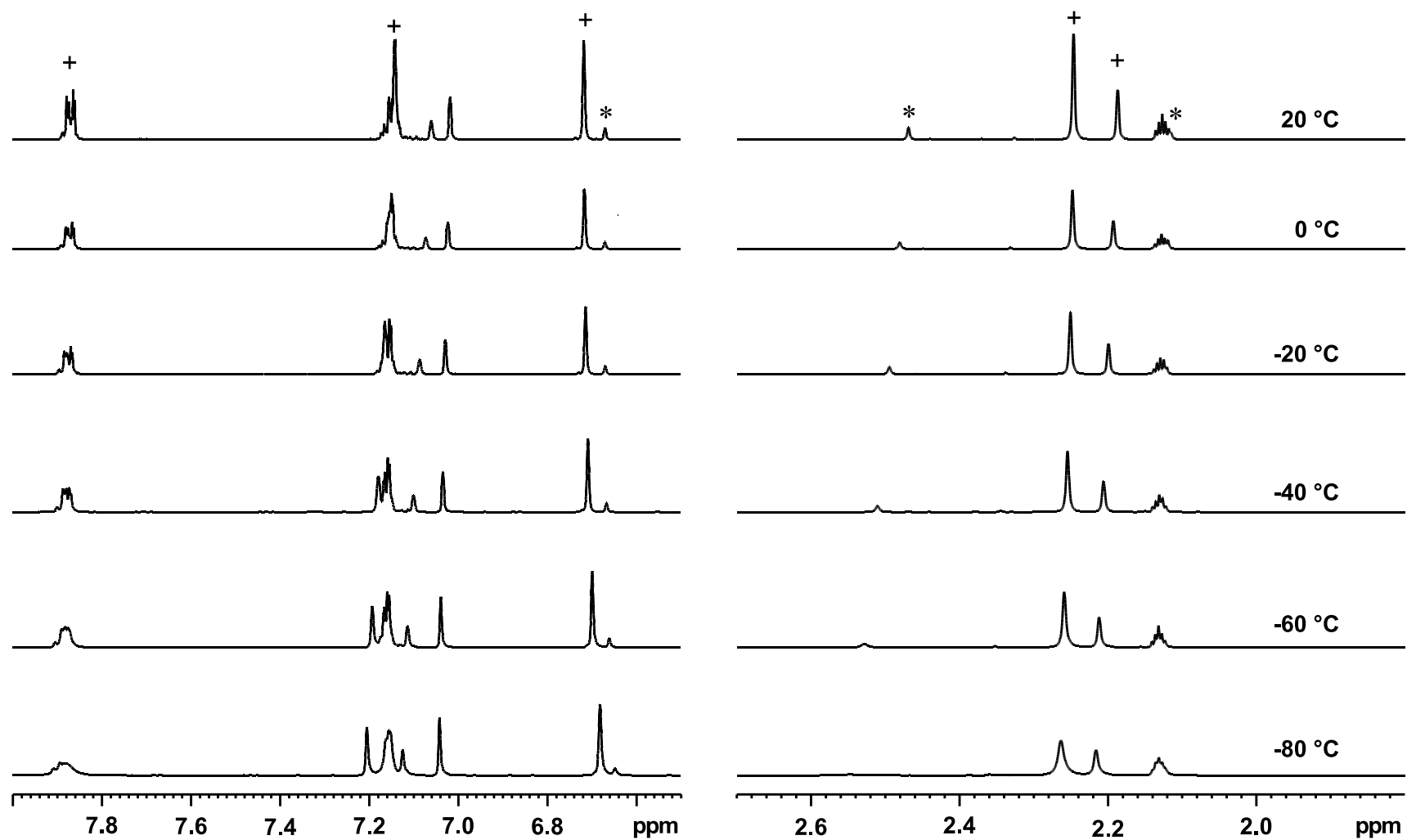


Figure S2.12.2: Excerpts of the temperature dependent ^1H NMR spectra (500 MHz) of **12** in toluene-d_8 (+ = **12**, * = Mes_4Sb_2).

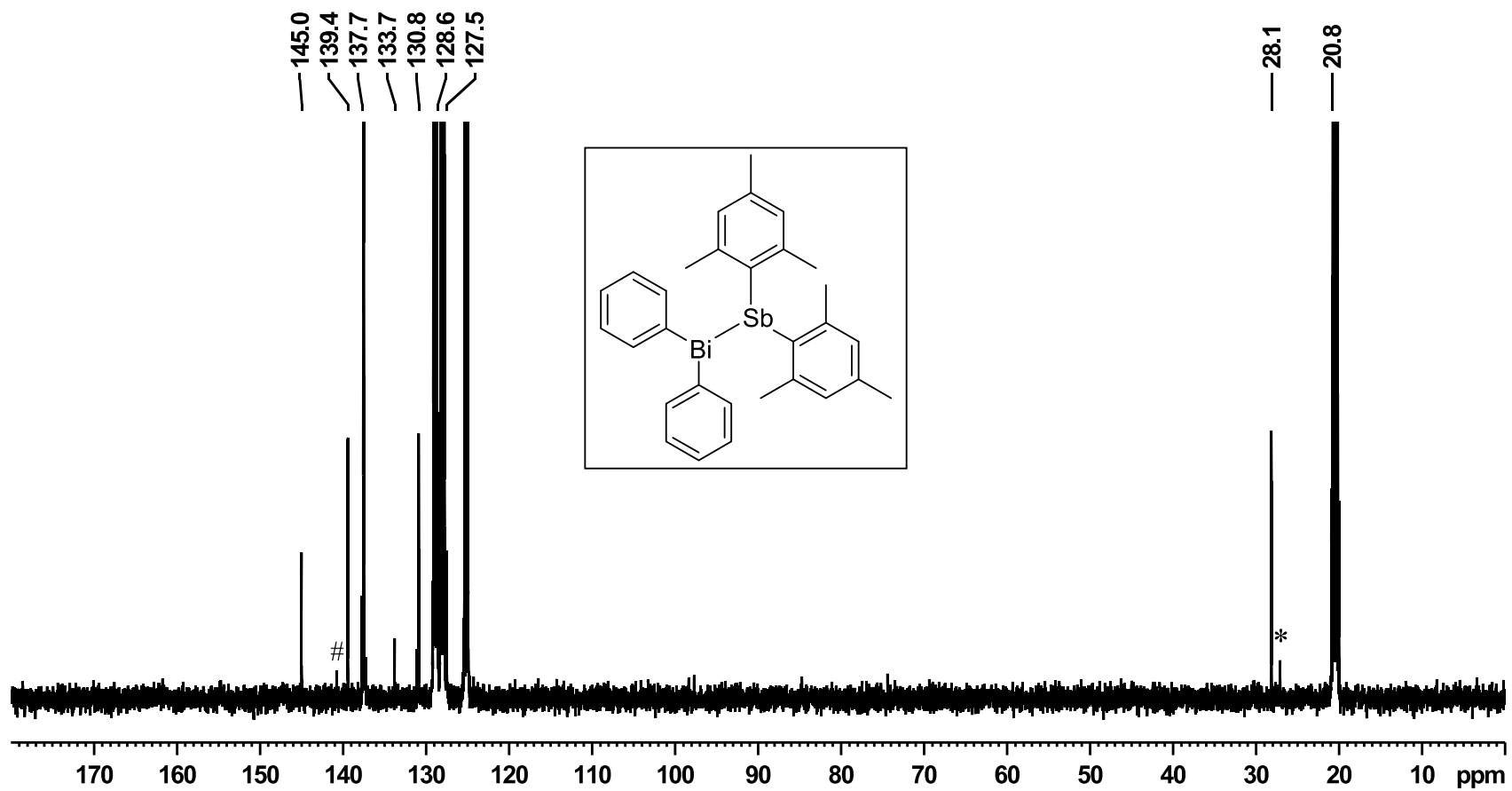


Figure S2.12.3: ^{13}C NMR spectrum (125 MHz) of 12 in toluene- d_8 at room temperature (* = Mes_4Sb_2 , # = Ph_4Bi_2).

2.12 Mes₂BiSbMes₂ (**13**)

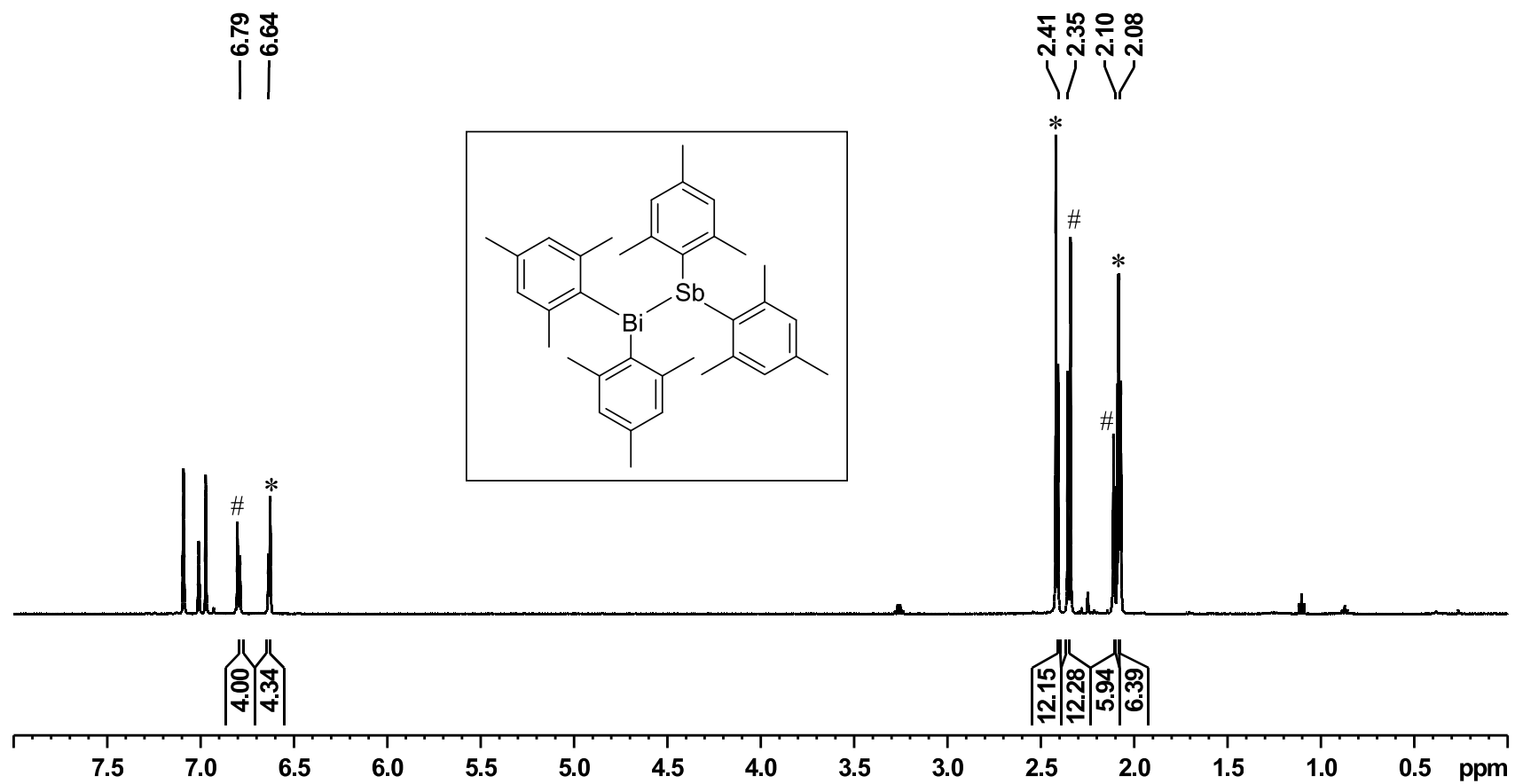


Figure S2.13.1: ¹H NMR spectrum (500 MHz) of **13** in toluene-d₈ at room temperature (* = Mes₄Sb₂, # = Mes₄Bi₂).

<

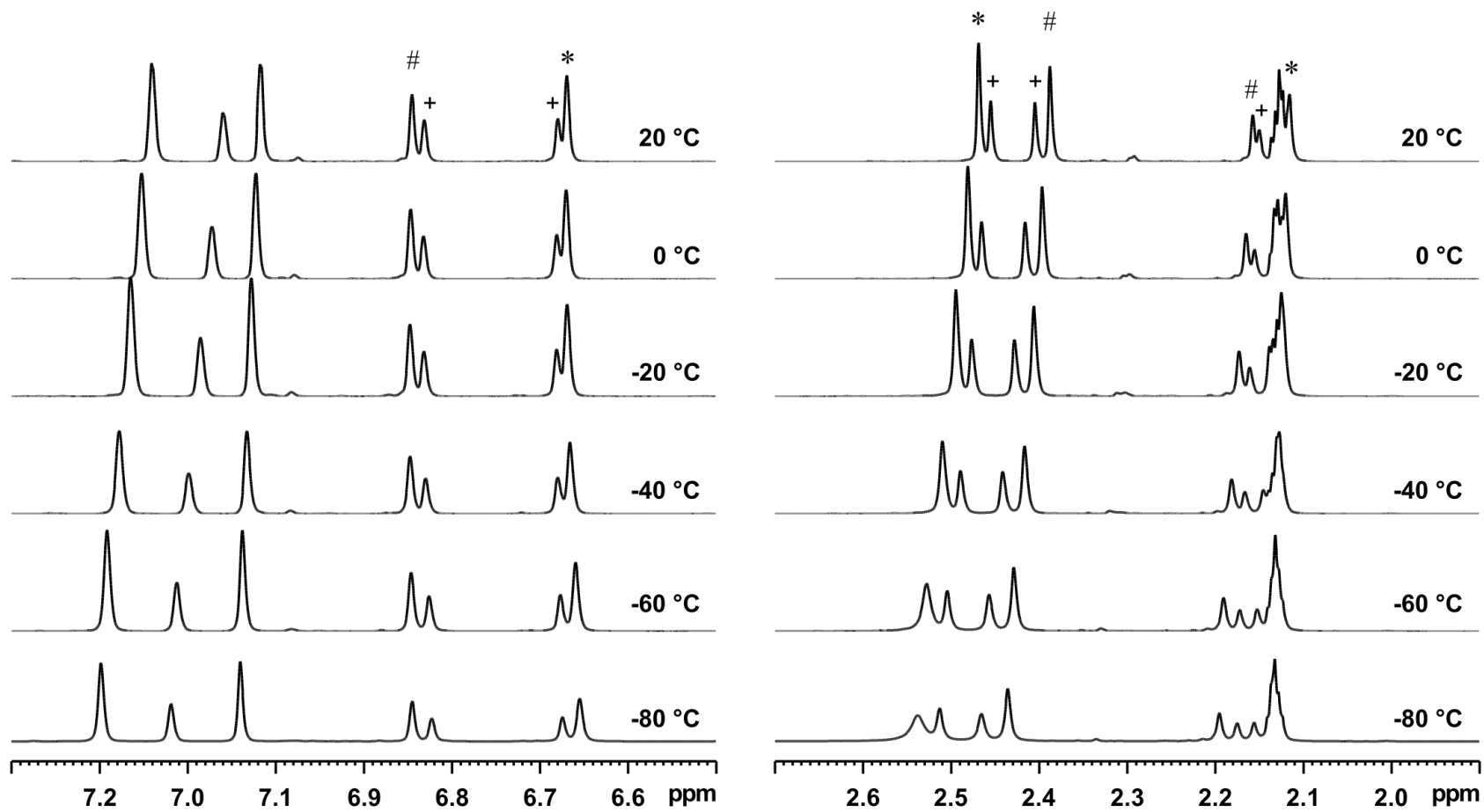


Figure S2.13.2: Excerpts of the temperature dependent ¹H NMR spectra (500 MHz) of **13** in toluene-d₈ at room temperature (+ = **13**,

* = Mes₄Sb₂, # = Mes₄Bi₂).

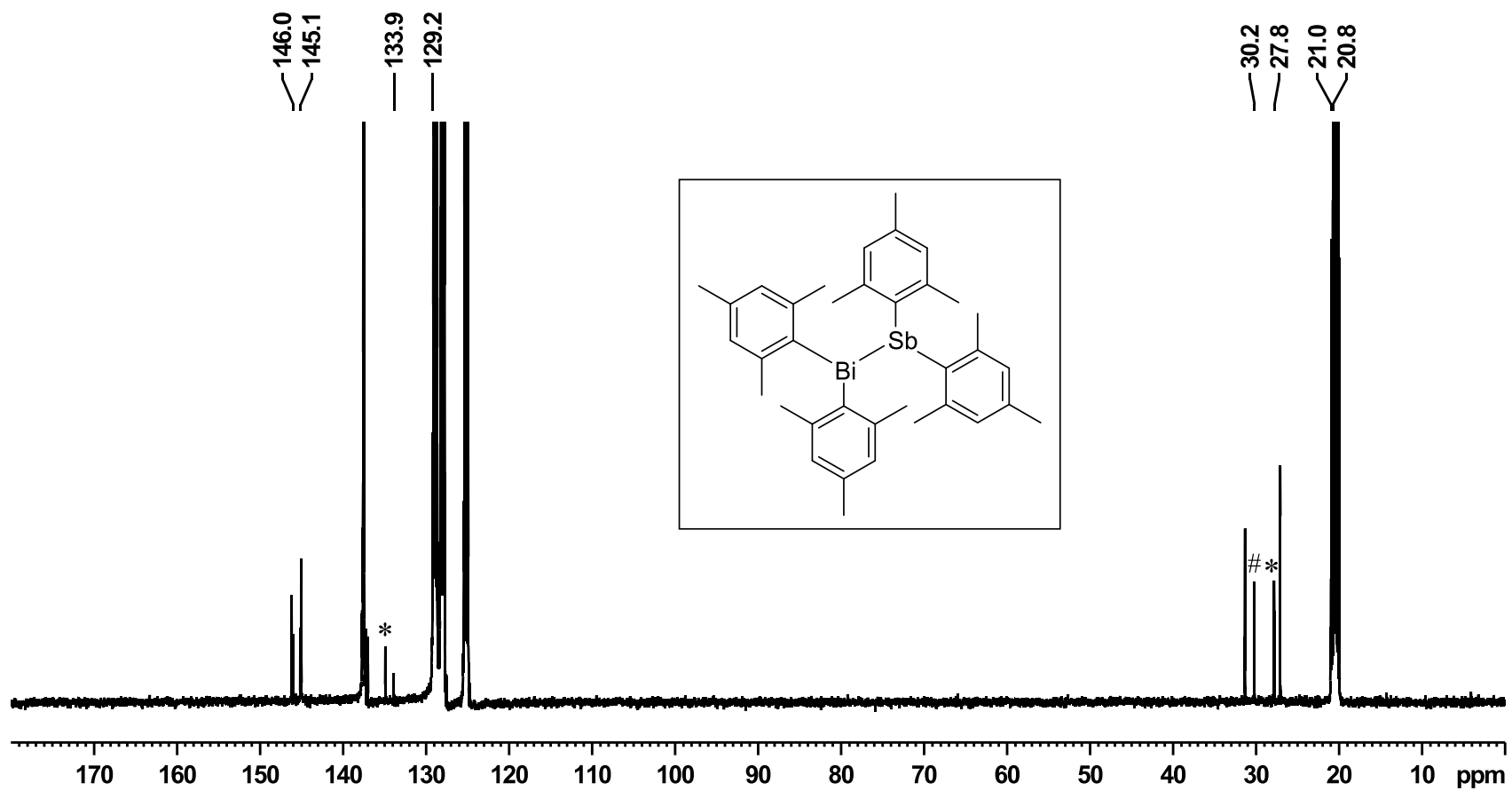


Figure S2.13.3: ^{13}C NMR spectrum (125 MHz) of **13** in toluene- d_8 at room temperature (* = Mes $_4$ Sb $_2$, # = Mes $_4$ Bi $_2$).

3. Calculation of ΔH_r° , ΔS_r° and ΔG_r (20 °C) for the equilibria of **12** and **13**

Table S1. Equilibrium constants for the dismutation of **12** and **13** two Mes_4Sb_2 and the corresponding disbimuthine at different temperatures. Equilibrium constants were obtained *via* integration of NMR signals using the *dcon* implementation in *TopSpin 4.0.7*.

T (K ⁻¹)	T ⁻¹ (K ⁻¹)	12		13	
		K	ln K	K	ln K
193	0.00518	64.811	4.1285	1.154	0,1291
213	0.00469	64.811	4.1715	1.154	0,1432
233	0.00429	68.117	4.2212	1.077	0,0744
253	0.00395	67.864	4.2175	1.039	0,0386
273	0.00366	72.382	4.2820	0.987	-0,0132
293	0.00341	76.357	4.3354	1.049	0,0476

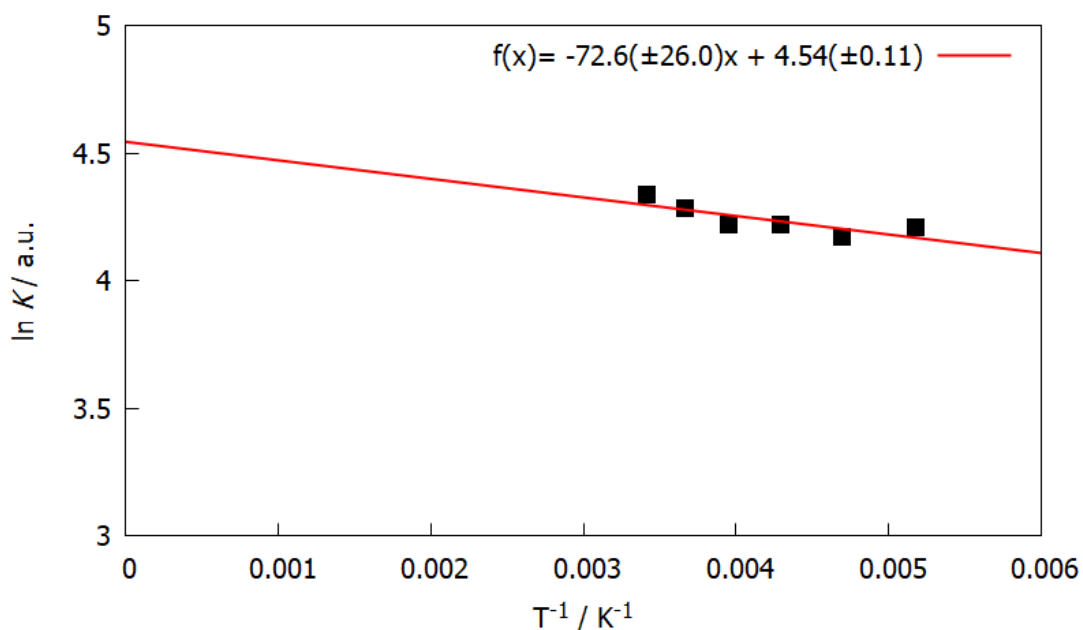


Figure S3.1: *van't Hoff* plot of the natural logarithmic of the equilibrium constant in the equilibrium of **12** and Mes_4Sb_2 and Ph_4Bi_2 against the reciprocal temperature with a fitted linear regression $f(x)$.

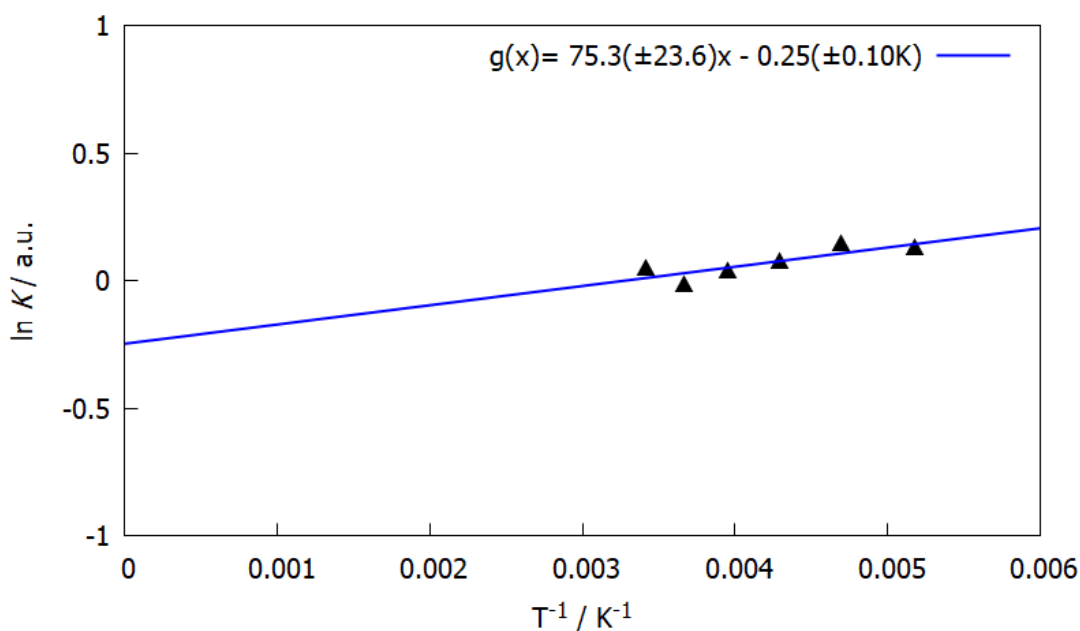


Figure S3.2: *van't Hoff* plot of the natural logarithmic of the equilibrium constant in the equilibrium of **13** and Mes₄Sb₂ and Mes₄Bi₂ against the reciprocal temperature with a fitted linear regression $g(x)$.

Calculation of reaction entropy, reaction enthalpy and free reaction energy at 20 °C:

12:

$$\Delta H_r^\theta = 72.6 \text{ K} \cdot 8.314 \text{ J} \cdot \text{mol}^{-1} \text{K}^{-1} = 603 \text{ J} \cdot \text{mol}^{-1} = 0.603 \text{ KJ} \cdot \text{mol}^{-1}$$

$$\Delta(\Delta H_r^\theta) = \pm 26.0 \text{ K} \cdot 8.314 \text{ J} \cdot \text{mol}^{-1} \text{K}^{-1} = 216 \text{ J} \cdot \text{mol}^{-1} = \pm 0.216 \text{ KJ} \cdot \text{mol}^{-1}$$

$$\Delta S_r^\theta = 4.54 \cdot 8.314 \text{ J} \cdot \text{mol}^{-1} \text{K}^{-1} = 37.78 \text{ J} \cdot \text{mol}^{-1} \text{K}^{-1}$$

$$\Delta(\Delta S_r^\theta) = \pm 0.11 \text{ K} \cdot 8.314 \text{ J} \cdot \text{mol}^{-1} \text{K}^{-1} = \pm 0.92 \text{ J} \cdot \text{mol}^{-1} \text{K}^{-1}$$

$$\Delta G_r(20 \text{ }^\circ\text{C}) = 603 \text{ J} \cdot \text{mol}^{-1} - 293 \text{ K} \cdot 37.78 \text{ J} \cdot \text{mol}^{-1} \text{K}^{-1} = -10.47 \text{ KJ} \cdot \text{mol}^{-1}$$

$$\Delta(\Delta G_r(20 \text{ }^\circ\text{C})) = \pm 216 \text{ J} \cdot \text{mol}^{-1} - 293 \text{ K} \cdot 0.92 \text{ J} \cdot \text{mol}^{-1} \text{K}^{-1} = \pm 0.05 \text{ KJ} \cdot \text{mol}^{-1}$$

13:

$$\Delta H_r^\theta = -75.3 \text{ K} \cdot 8.314 \text{ J} \cdot \text{mol}^{-1} \text{K}^{-1} = -626 \text{ J} \cdot \text{mol}^{-1} = -0.626 \text{ KJ} \cdot \text{mol}^{-1}$$

$$\Delta(\Delta H_r^\theta) = \pm 23.6 \text{ K} \cdot 8.314 \text{ J} \cdot \text{mol}^{-1} \text{K}^{-1} = 196 \text{ J} \cdot \text{mol}^{-1} = \pm 0.196 \text{ KJ} \cdot \text{mol}^{-1}$$

$$\Delta S_r^\theta = -0.25 \cdot 8.314 \text{ J} \cdot \text{mol}^{-1} \text{K}^{-1} = -2.05 \text{ J} \cdot \text{mol}^{-1} \text{K}^{-1}$$

$$\Delta(\Delta S_r^\theta) = \pm 0.10 \text{ K} \cdot 8.314 \text{ J} \cdot \text{mol}^{-1} \text{K}^{-1} = \pm 0.83 \text{ J} \cdot \text{mol}^{-1} \text{K}^{-1}$$

$$\Delta G_r(20 \text{ }^\circ\text{C}) = -626 \text{ J} \cdot \text{mol}^{-1} - 293 \text{ K} \cdot -2.05 \text{ J} \cdot \text{mol}^{-1} \text{K}^{-1} = -0.03 \text{ KJ} \cdot \text{mol}^{-1}$$

$$\Delta(\Delta G_r(20 \text{ }^\circ\text{C})) = \pm(196 \text{ J} \cdot \text{mol}^{-1} - 293 \text{ K} \cdot 0.92 \text{ J} \cdot \text{mol}^{-1} \text{K}^{-1}) = \pm 0.05 \text{ KJ} \cdot \text{mol}^{-1}$$

4. Crystallographic data

Table S2. Selected crystal structure data of the structure determinations of compounds **1**, **2** and **3**

Compound	1	2	3
Empirical formula	C ₁₄ H ₁₆ Bi ₁ N ₁	C ₂₀ H ₂₈ Bi ₁ N ₁	C ₂₂ H ₃₂ Bi ₁ N ₁
Formula weight	407.26	491.41	519.46
Crystal color, habit	colorless, needle	yellow, needle	colorless, block
Temperature/K	100.0	100.0	100.0
Crystal system	triclinic	monoclinic	triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> /Å	9.3621(3)	8.075(3)	9.5236(5)
<i>b</i> /Å	9.725(3)	8.710(3)	9.9232(5)
<i>c</i> /Å	14.8523(6)	26.474(12)	13.0242(6)
α /°	80.019(3)	90	96.380(4)
β /°	78.242(3)	93.97(4)	104.891(4)
γ /°	88.274(3)	90	115.291(4)
Volume/Å ³	1307.51(9)	1857.7(13)	1040.56(10)
Z	4	4	2
ρ_{calc} /cm ³	2.069	1.757	1.658
μ /mm ⁻¹	13.458	9.488	8.475
F(000)	760.0	952.0	508.0
Crystal size/mm ³	-	-	-
Crystal radius(equiv)/mm	0.0569	0.0669	0.0701
Diffractometer	Stoe IPDS 2T	Stoe IPDS 2	Stoe IPDS 2
Radiation	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)
2 θ range for data collection/°	4.240 to 58.358	3.084 to 58.342	3.344 to 58.302
Reflections collected	15578	22828	16312
Independent reflections	7042 [R _{int} = 0.0220, R _{sigma} = 0.0269]	4997 [R _{int} = 0.0357, R _{sigma} = 0.0317]	5617 [R _{int} = 0.0236, R _{sigma} = 0.0291]
Data/restraint/parameters	7042/0/293	4997/0/207	5617/1/230
Goodness-of-fit on <i>F</i> ²	1.029	0.971	1.004
Final R indexes [all data]	R1 = 0.0407, wR2 = 0.0639	R1 = 0.0389, wR2 = 0.0665	R1 = 0.0312, wR2 = 0.0568
Final R indexes [<i>I</i> ≥2 σ (<i>I</i>)]	R1 = 0.0270, wR2 = 0.0591	R1 = 0.0268, wR2 = 0.0640	R1 = 0.0245, wR2 = 0.0554
Largest diff. peak/hole/ e Å ⁻³	1.83/-1.55	1.99/-0.81	1.29/-0.83
CCDC	2151498	2151502	2151499

Table S3. Selected crystal structure data of the structure determinations of compounds **4**, **5** and **6**.

Compound	4	5	6
Empirical formula	C ₂₀ H ₂₈ Bi ₁ P ₁	C ₂₆ H ₄₀ Bi ₁ P ₁	C ₁₉ H ₂₈ Bi ₁ P ₁ Si ₁
Formula weight	508.37	592.53	524.45
Crystal color, habit	colorless, block	yellow, needle	colorless, needle
Temperature/K	100.0	100.0	100.0
Crystal system	monoclinic	monoclinic	triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> /Å	6.3994(3)	17.2923(13)	6.2419(3)
<i>b</i> /Å	18.2817(10)	9.4485(5)	8.9902(4)
<i>c</i> /Å	16.9616(9)	31.273(2)	19.3583(10)
α /°	90	90	77.940(4)
β /°	95.753(4)	96.938(6)	88.394(4)
γ /°	90	90	75.687(4)
Volume/Å ³	1974.38(18)	5072.1(6)	1029.04(9)
Z	4	8	2
ρ_{calc} /cm ³	1.710	1.552	1.693
μ /mm ⁻¹	9.007	7.024	8.699
F(000)	984.0	2352.0	508.0
Crystal size/mm ³	-	-	0.0853
Crystal radius(equiv)/mm	0.0705	0.0492	
Diffractionmeter	Stoe IPDS 2T	Stoe IPDS 2T	Stoe IPDS 2
Radiation	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)
2 θ range for data collection/°	4.456 to 57.00	3.318 to 55.828	4.304 to 52.00
Reflections collected	24622	33120	15780
Independent reflections	5012 [<i>R</i> _{int} = 0.0277, <i>R</i> _{sigma} = 0.0158]	12063 [<i>R</i> _{int} = 0.0309, <i>R</i> _{sigma} = 0.0370]	4036 [<i>R</i> _{int} = 0.0246, <i>R</i> _{sigma} = 0.0264]
Data/restraint/parameters	5012/0/205	12063/0/529	4036/0/205
Goodness-of-fit on <i>F</i> ²	1.047	1.012	1.011
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0284, <i>wR</i> ₂ = 0.0475	<i>R</i> ₁ = 0.0521, <i>wR</i> ₂ = 0.0695	<i>R</i> ₁ = 0.0267, <i>wR</i> ₂ = 0.0523
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0214, <i>wR</i> ₂ = 0.0475	<i>R</i> ₁ = 0.0300, <i>wR</i> ₂ = 0.0630	<i>R</i> ₁ = 0.0215, <i>wR</i> ₂ = 0.0523
Largest diff. peak/hole/ e Å ⁻³	0.95/-0.75	1.65/-1.13	3.17/-0.37
CCDC	2151505	2151506	2151500

Table S4. Selected crystal structure data of the structure determinations of compounds**7, 8 and 9**

Compound	7	8	9
Empirical formula	C ₂₅ H ₄₀ Bi ₁ P ₁ Si ₁	C ₂₀ H ₂₈ Bi ₁ As ₁	C ₂₆ H ₄₀ Bi ₁ As ₁
Formula weight	608.61	552.32	638.48
Crystal color, habit	yellow, block	colorless, needle	yellow, block
Temperature/K	100.0	100.0	100.0
Crystal system	monoclinic	monoclinic	monoclinic
Space group	<i>P2₁/c</i>	<i>P2₁/n</i>	<i>P2₁/n</i>
<i>a</i> /Å	10.1342(10)	6.3753(3)	10.010(2)
<i>b</i> /Å	8.4111(10)	18.4967(9)	8.3035(19)
<i>c</i> /Å	31.257(3)	17.0593(7)	30.855(6)
α /°	90	90	90
β /°	98.857(8)	95.766(3)	97.675(16)
γ /°	90	90	90
Volume/Å ³	2632.6(5)	2001.49(16)	2541.7(9)
Z	4	4	4
$\rho_{\text{calc}}/\text{cm}^3$	1.536	1.833	1.663
μ/mm^{-1}	6.812	10.446	8.238
F(000)	1208.0	1056.0	1248.0
Crystal radius(equiv)/mm	0.1573	-	-
		0.0293	0.0696
Diffractometer	Stoe IPDS 2T	Stoe IPDS 2	Stoe IPDS 2
Radiation	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)
2 θ range for data collection/°	4.068 to 53.37	3.256 to 51.992	2.664 to 51.998
Reflections collected	31860	12090	23780
Independent reflections	5563 [R_{int} = 0.0265, R_{sigma} = 0.0176]	3927 [R_{int} = 0.0354, R_{sigma} = 0.0412]	4994 [R_{int} = 0.0281, R_{sigma} = 0.0182]
Data/restraint/parameter s Goodness-of-fit on F^2	5563/14/323 0.993	3927/0/205 0.999	4994/0/265 1.071
Final R indexes [all data]	R_1 = 0.0265, wR_2 = 0.0499	R_1 = 0.0538, wR_2 = 0.0717	R_1 = 0.0284, wR_2 = 0.0641
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0195, wR_2 = 0.0482	R_1 = 0.0325, wR_2 = 0.0671	R_1 = 0.0238, wR_2 = 0.0629
Largest diff. peak/hole/ e Å ⁻³	0.99/-0.28	1.47/-0.59	1.79/-0.50
CCDC	2151503	2151508	2151502

Table S5. Selected crystal structure data of the structure determinations of compounds **10**, **11** and **12**

Compound	10	11	12
Empirical formula	C ₁₉ H ₂₈ Bi ₁ As ₁ Si ₁	C ₂₅ H ₄₀ Bi ₁ As ₁ Si ₁	C ₃₀ H ₃₂ Bi ₁ Sb ₁
Formula weight	568.40	652.56	723.28
Crystal color, habit	colorless, needle	yellow, block	yellow, block
Temperature/K	100.0	100.0	100.0
Crystal system	monoclinic	monoclinic	triclinic
Space group	C2/c	<i>P</i> 2 ₁ /c	<i>P</i> $\bar{1}$
a/Å	40.1899(18)	10.1538(3)	9.8036(4)
b/Å	6.1680(2)	8.4878(2)	11.5319(5)
c/Å	17.2741(7)	31.1727(10)	13.3134(5)
α /°	90	90	77.045(3)
β /°	103.327(3)	98.745(2)	76.373(3)
γ /°	90	90	65.976(3)
Volume/Å ³	4166.8(3)	2655.34(13)	1317.59(10)
Z	4	4	2
ρ_{calc} /cm ³	1.812	1.632	1.823
μ /mm ⁻¹	10.092	7.930	7.709
F(000)	2176.0	1280.0	692.0
Crystal size/mm ³	-	-	-
Crystal radius(equiv)/mm	0.0972	0.1738	0.0453
Diffractometer	Stoe IPDS 2	Stoe IPDS 2T	Stoe IPDS 2T
Radiation	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)
2 θ range for data collection/°	4.814 to 58.458	4.058 to 55.952	3.192 to 58.51
Reflections collected	19382	15324	16609
Independent reflections	5619 [R _{int} = 0.0321, R _{sigma} = 0.0249]	6248 [R _{int} = 0.0280, R _{sigma} = 0.0300]	7091 [R _{int} = 0.0268, R _{sigma} = 0.0367]
Data/restraint/parameters	5619/0/205	6248/25/304	7091/0/295
Goodness-of-fit on F^2	1.056	1.049	1.026
Final R indexes [all data]	R ₁ = 0.0402, wR ₂ = 0.0796	R ₁ = 0.0371, wR ₂ = 0.0668	R ₁ = 0.0456, wR ₂ = 0.0762
Final R indexes [$I \geq 2\sigma(I)$]	R ₁ = 0.0301, wR ₂ = 0.0733	R ₁ = 0.0282, wR ₂ = 0.0641	R ₁ = 0.0318, wR ₂ = 0.0719
Largest diff. peak/hole/ e Å ⁻³	1.95/-2.14	1.02/-0.58	1.64/-1.68
CCDC	2151504	2151509	2151507

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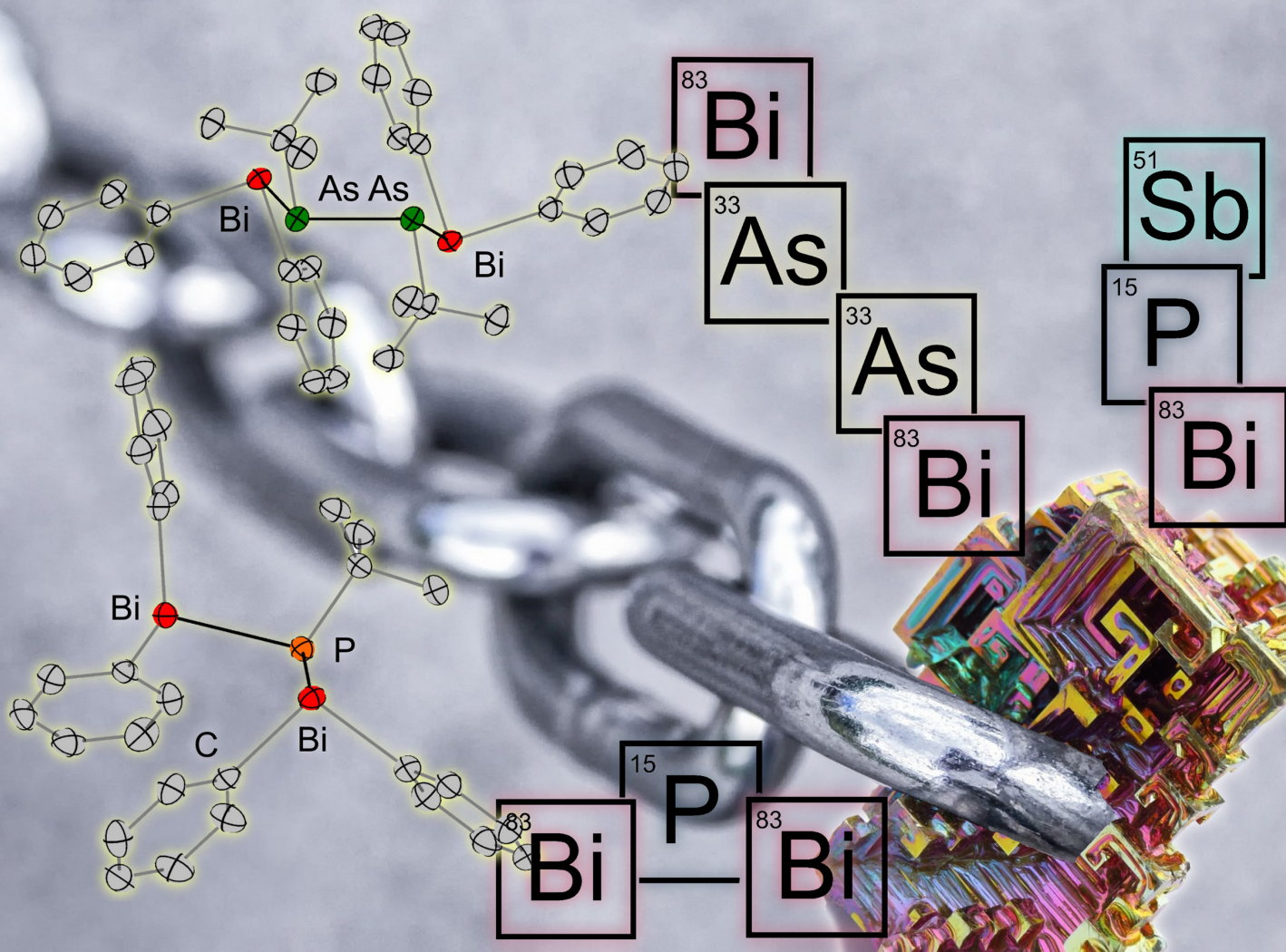
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Heavy Chains: Synthesis, Reactivity and Decomposition of Interpnictogen Chains
with Terminal Diaryl Bismuth Fragments



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Heavy Chains: Synthesis, Reactivity and Decomposition of Interpnictogen Chains with Terminal Diaryl Bismuth Fragments

Tobias Dunaj^[a] and Carsten von Hänisch^{*[a]}

Abstract: In this work, we report the preparation of multiple interpnictogen chain compounds with three consecutive pnictogen atoms and terminal Ar_2Bi fragments ($\text{Ar} = \text{Ph}, \text{Mes}$). Symmetrical compounds of the form $\text{Ar}_2\text{Bi}-\text{E}(\text{tBu})-\text{Bi}_2\text{Ar}$ (**1**: $\text{Ar} = \text{Ph}, \text{E} = \text{P}$; **2**: $\text{Ar} = \text{Ph}, \text{Mes}, \text{E} = \text{As}$) as well as ternary interpnictogen compounds of the form $\text{Ar}_2\text{Bi}-\text{E}^1(\text{tBu})-\text{E}^2\text{tBu}_2$ ($\text{Ar} = \text{Ph}, \text{Mes}$; **4**: $\text{E}^1 = \text{P}, \text{E}^2 = \text{As}$; **5**: $\text{E}^1 = \text{P}, \text{E}^2 = \text{Sb}$; **6**: $\text{E}^1 = \text{As}, \text{E}^2 = \text{P}$) were prepared. The decomposition in solution at room temperature and under the influence of light was studied for

compounds **1–6**. The reactivity of **1_{ph}** and **2_{ph}** with the small N-heterocyclic carbene 1,3,4,5-tetramethylimidazol-2-ylidene (Me_2Ime) was also studied. In the case of **1_{ph}**, the formation and consecutive decomposition of $\text{Me}_2\text{Ime}=\text{PtBu}$ (**8**) was observed in solution. Hence, it was shown that **1_{ph}** can react as a “masked phosphinidene”. In the case of **2_{ph}**, no reaction with Me_2Ime was observed. All isolated compounds were analysed by NMR and IR spectroscopy, mass spectrometry, elemental analysis and single-crystal X-ray diffraction.

Introduction

Compounds with bonds between at least two different pnictogen atoms are called interpnictogen compounds. However, the incorporation of the heaviest pnictogen bismuth, remains underexplored. Only a few interpnictogen compounds with a Bi–P or Bi–As single bonds are known today. The first isolatable compound with an R_2P^- fragment bound to bismuth was only prepared in 1999, and the first terminal bismuthanyl phosphane ($\text{R}_2\text{Bi}-\text{PR}_2$) in 2016.^[1,2] In 2011, the first bismuthanyl arsanes were reported; they feature an arsenic atom bridging two bismuthanyl fragments and have the general formula $\text{R}^1\text{As}(\text{BiR}^2\text{Cl})_2$ ($\text{R}^1 = \text{Si}(\text{Pr})_3, \text{Si}(\text{tBu})_2\text{Ph}$; $\text{R}^2 = \text{CH}(\text{SiMe}_3)_2$).^[3] Ternary interpnictogen molecules have also been realized, for example, chain molecules of the form $\text{tBu}_2\text{E}^1-\text{E}^2(\text{tBu})-\text{E}^3\text{tBu}_2$ ($\text{E} = \text{P}, \text{As}, \text{Sb}$), in which several permutations were realized.^[4,5] Ternary interpnictogen compounds including bismuth are rare and mostly restricted to systems including nitrogen.^[1,6–9] Only two ternary compounds without nitrogen are known, $\text{tBu}_2\text{Bi}-\text{P}(\text{tBu})-\text{Sb}(\text{tBu})_2$ ^[10] and $\text{tBu}_2\text{Bi}-\text{As}(\text{tBu})-\text{PtBu}_2$.^[5] Created by using sophisticated strategies, multiple quaternary compounds of the lighter pnictogens N, P, As and Sb are described in the literature.^[5,11,12]

However, there are no quaternary interpnictogen compounds including a bismuth atom. It should be noted, however, that a compound featuring all five pnictogen atoms N, P, As, Sb and Bi, was reported recently.^[12] The Bi–P and Bi–N bonds in this quinary compound are stabilized by an intramolecular N-donor bond. The heaviest pnictogen, bismuth, still remains the critical element in the preparation of multinary interpnictogen compounds.

In a recent publication, we could show, that diarylbismuth chlorides are effective precursors for the synthesis of interpnictogen compounds bearing Bi–N, –P, –As, and even –Sb bonds.^[13] We present here a systematic study of the preparation of interpnictogen compounds featuring terminal diarylbismuthanyl fragments and a chain of three pnictogen atoms by using the diarylbismuth platform. The obtained chains feature either central P or As atoms with two diarylbismuthanyl substituents or chains of the type $\text{Ar}_2\text{Bi}-\text{E}^1(\text{tBu})-\text{E}^2\text{tBu}_2$ ($\text{Ar} = \text{Ph}, \text{Mes}$; $\text{E}^1 = \text{P}; \text{E}^2 = \text{As}, \text{Sb}$; $\text{E}^1 = \text{As}; \text{E}^2 = \text{P}$) were realized. Moreover, decomposition of the compounds was studied in solution and the symmetric dibismuthanyl phosphanes and arsanes were examined on their usability as pnictogenidene transfer reagents.

Results and Discussion

Synthesis of the chain molecules

In a previous publication, we reported the synthesis of binary interpnictogen compounds, containing silyl functions. These were prepared from Ar_2BiCl ($\text{Ar} = \text{Ph}, \text{Mes}$) and $\text{tBuE}(\text{SiMe}_3)_2$ ($\text{E} = \text{P}, \text{As}$) by elimination of trimethylsilyl chloride in α, α, α -trifluorotoluene (TFT) and had the general formula $\text{Ar}_2\text{Bi}-\text{EtBu}(\text{SiMe}_3)$ ($\text{Ar} = \text{Ph}, \text{Mes}$; $\text{E} = \text{P}, \text{As}$).^[13] For further functionalization by trimethylsilyl chloride elimination, these were reacted

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Compounds **4** and **5** with the central P atom give the expected signals in the IR spectra and the HR-LIFDI(+) or HR-Cl(+) mass spectra. The ^1H NMR spectra show one set of signals corresponding to the phenyl (4_{Ph} , 5_{Ph}) or Mesityl (4_{Mes} , 5_{Mes}) substituents at the bismuth atom and a doublet signal for the *tert*-butyl substituent at the phosphorus atom (4_{Ph} : $^3J_{\text{P-H}} = 11.4$ Hz; 4_{Mes} : $^3J_{\text{P-H}} = 11.1$; 5_{Ph} : $^3J_{\text{P-H}} = 11.4$ Hz; 5_{Mes} : $^3J_{\text{P-H}} = 10.8$ Hz). Moreover, a singlet signal for the *tert*-butyl group is assigned to the arsenic or antimony atom respectively, indicating free rotation around the Bi–P and the P–E axes. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra show singlet signals at 10.6 ppm (4_{Ph}), 8.9 ppm (4_{Mes}), –5.8 ppm (5_{Ph}) and –10.0 ppm (5_{Mes}) while the proton coupled spectra show multiplets at the respective chemical shifts. The phenyl substituted compounds 4_{Ph} and 5_{Ph} both show a slight downfield shift compared to their mesityl substituted counterparts 4_{Mes} and 5_{Mes} . As expected, the chemical shifts of **4** and **5** fit well to $t\text{Bu}_2\text{BiP}(t\text{Bu})\text{Sb}(t\text{Bu})_2$ (–1.83 ppm).^[10]

After compound 4_{Mes} was left in a sealed NMR tube in C_6D_6 for one day, new signals start to rise in the ^{31}P NMR spectra, which keep growing over the following days (Figure 1). The ^1H NMR spectrum shows rising signals corresponding to Mes_4Bi_2 and also new signals in the aliphatic region. This new species was identified as compound **7**, which was confirmed by its targeted preparation through the reaction of $t\text{Bu}_2\text{As–P}(t\text{Bu})\text{Li}$ with dibromoethane and comparison of the NMR spectra. In similar reactions, the preparation of hydrazines, diphosphanes and diarsanes under precipitation of elemental bismuth was recently reported.^[14] Moreover, for $\text{Me}_2\text{Bi–AsMe}_2$, an equilibrium with Me_4Bi_2 and Me_4As_2 has been found, which is predominantly on the side of dibismuthane and diarsane.^[15] Hence, we wanted to examine if 4_{Mes} decomposes thoroughly to Ph_4Bi_2 and **7**, or if these three compounds exist in equilibrium. Therefore, Ph_4Bi_2 and **7** were dissolved in a sealed NMR tube in C_6D_6 and the mixture was observed over several days, where no formation of 4_{Mes} was observed. Leading to the assumption that the equilibrium of the reaction of 4_{Mes} to **7** and Ph_4Bi_2 is largely on the side of the products. However, time-dependent NMR spectra show that this equilibrium is reached very slowly.

Surprisingly, 5_{Ph} shows a different decomposition pathway compared to 4_{Mes} . The Bi–P–Sb chain is scrambled, and the formation of the symmetrical compounds 1_{Ph} and $(t\text{Bu}_2\text{Sb})_2\text{PtBu}$ ^[4] are observed after one day at room temperature. Moreover, there is also dibismuthane and $(t\text{BuP})_4$ present in solution. The decomposition of 5_{Mes} proceeds similar to 5_{Ph} , however 5_{Mes} is significantly more stable and faint signals for $(t\text{Bu}_2\text{Sb})_2\text{PtBu}$ and $(t\text{BuP})_4$ are only observed after several days. A faint signal at 14.7 ppm, similar in shift to 1_{Ph} (13.6 ppm), might correspond to $(\text{Mes}_2\text{Bi})_2\text{PtBu}$, which could not be obtained through trimethylsilyl chloride abstraction (see section “Synthesis of the chain molecules”).

Compound 6_{Ph} and 6_{Mes} also show the expected signals in the NMR, IR spectra, as well as in the HR-LIFDI(+) mass spectra. Contrary to **4** and **5** though, compounds 6_{Ph} and 6_{Mes} with the central arsenic atom show two sets of signals for the aryl substituents and the terminal PtBu_2 group in the ^1H and the ^{13}C NMR spectra, indicating a hindered rotation around the Bi–As or the As–P axes. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra show singlet signals at 70.9 ppm (6_{Ph}) and 75.8 (6_{Mes}), which is in agreement with similar compounds of the form $t\text{Bu}_2\text{E}^1\text{As}(t\text{Bu})\text{PtBu}_2$ ($\text{E}^1 = \text{P}$ (72.7 ppm), As (70.6 ppm), Sb (67.2 ppm), Bi (66.0 ppm)).^[5] Immediately after preparation of the NMR samples in C_6D_6 from clean product, traces of Ph_4Bi_2 or Mes_4Bi_2 are observed in the ^1H and ^{13}C NMR spectra. Moreover, a new, broad signal is observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (75.6 ppm), which was identified as the symmetrical diarsane $t\text{Bu}_2\text{PAs}(t\text{Bu})\text{As}(t\text{Bu})\text{PtBu}_2$.^[5] The compounds 6_{Ph} and 6_{Mes} decompose in a similar way to 4_{Ph} and 4_{Mes} ; however, they show faster decomposition, probably due to the more labile Bi–As bond.

Compound **7** also shows the expected signals in the IR spectrum and the HR-LIFDI(+) mass spectrum. The ^1H NMR spectrum shows a singlet for the $\text{As}(t\text{Bu})_2$ group and a deceptively simple pseudo triplet signal for the $t\text{BuP}$ fragment, which is actually a limit case for an $\text{X}_9\text{AA}'\text{X}'_9$ system, where the following condition is met: $J_{\text{A-A}'} \gg (J_{\text{A-X}} - J_{\text{A}'\text{X}'})$.^[16,17] Due to the nature of the multiplet, only a value for the sum of the $^3J_{\text{P-H}} + ^4J_{\text{P-H}}$ coupling constant (15.3 Hz) can be obtained. Analogue

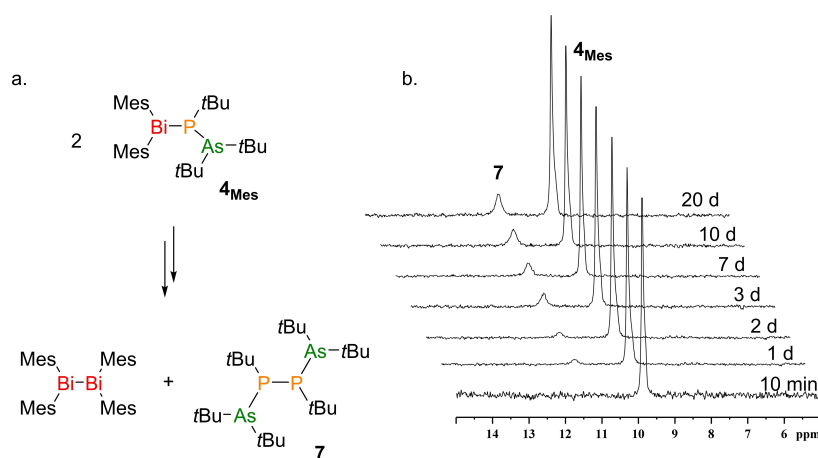


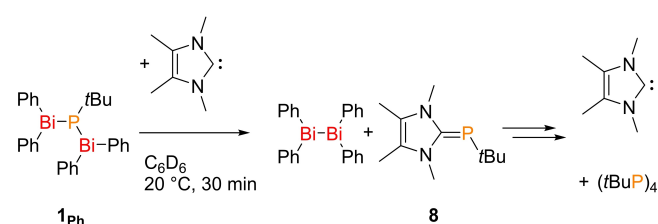
Figure 1. a) Reaction scheme for the decomposition of 4_{Mes} to the dibismuthane Mes_4Bi_2 and the diphosphane **7**. b) ^{31}P NMR spectra of a solution of 4_{Mes} in C_6D_6 over several days at room temperature.

$X_nAA'X_n'$ systems and pseudo triplets are encountered in the ^{13}C NMR spectrum. In the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, a very broad signal at 10.2 ppm is observed.

Pnictogenidene transfer reaction

The reductive cleavage of Bi–E (E = N, P, As, Sb) bonds under formation of a reduced bismuth species and formation of an E–E bond has been reported before. Examples include the reversible activation of P_4 by a dibismuthane under formation of a compound with a butterfly type structural motif,^[11] the formation of hydrazines, diphosphanes or diarsanes from trisaminobismuthanes and secondary phosphanes or arsanes under precipitation of elemental bismuth,^[14] or the equilibrium reaction of bismuthanyl stibanes.^[13] In the formation of $\mathbf{3}_{\text{ph}}$, a mechanism, where two Bi–As bonds are cleaved and a transient arsenidene fragment is transferred to another equivalent of $\mathbf{2}_{\text{ph}}$ is imaginable. It should be noted however, that this transfer of R–As unit is a formal description of this reaction, since the mechanistic pathway is unknown. Nevertheless, the potential of $\mathbf{1}_{\text{ph}}$ and $\mathbf{2}_{\text{ph}}$ as possible pnictogenidene transfer reagents was examined. To intercept a possibly transient pnictogenidene, the small N-heterocyclic carbene Me_2Ime (1,3,4,5-tetramethylimidazol-2-ylidene) was added to solutions of $\mathbf{1}_{\text{ph}}$ or $\mathbf{2}_{\text{ph}}$ in C_6D_6 (Scheme 3).

Upon addition of the carbene to $\mathbf{1}_{\text{ph}}$, the reaction mixture immediately turned dark red and $\mathbf{1}_{\text{ph}}$ is not observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum anymore. Rather, three compounds are identified from the reaction mixture, namely $(\text{tBuP})_3$ (~21%), $(\text{tBuP})_4$ (~9%) and, a singlet for a new compound with a chemical shift of –31.1 ppm (~70%). The ^{31}P NMR chemical shift matches the high level theoretical calculation of –35.4 ppm reported for $\text{Me}_2\text{Ime}=\text{PtBu}$ (**8**) very well.^[18] Moreover, the expected signals for **8** are also observed in the ^1H and ^{13}C NMR spectra and cross signals from the *tert*-butyl group and the carbene C atom are observed by $^1\text{H},^{13}\text{C}$ HMBC measurements, confirming the successful phosphinidene transfer. Compound **8** decomposes to the free carbene and $(\text{tBuP})_4$ over the course of hours, which is in agreement with the decomposition of a structurally similar compound bearing *iso*-propyl instead of methyl groups at the nitrogen atom.^[19] Due to the decomposition, isolation of **8** was not possible. Nevertheless, the reaction of $\mathbf{1}_{\text{ph}}$ with Me_2Ime indicates that compound $\mathbf{1}_{\text{ph}}$ can indeed be considered a “masked phosphinidene”.



Scheme 3. Phosphinidene transfer from $\mathbf{1}_{\text{ph}}$ to Me_2Ime with formation and consecutive decomposition of **8** in C_6D_6 .

Upon addition of Me_2Ime to a solution of $\mathbf{2}_{\text{ph}}$, no drastic change of colour was observed. The reaction mixture in C_6D_6 showed no indication of a formation of the $\text{Me}_2\text{Ime}=\text{As}t\text{Bu}$ adduct in the ^1H or the $^1\text{H},^1\text{H}$ NOESY NMR spectra. Surprisingly, the two educts did not seem to react at all. Although $\mathbf{1}_{\text{ph}}$ and $\mathbf{2}_{\text{ph}}$ are structurally very similar, they seem to behave different in the reaction with Me_2Ime .

Single-crystal X-ray analysis

Crystals of the compounds $\mathbf{1}_{\text{ph}}$ and $\mathbf{2}_{\text{ph}}$ suitable for single-crystal X-ray diffraction were obtained from a solution in *n*-pentane at -32°C . Compound $\mathbf{1}_{\text{ph}}$ crystallizes in the monoclinic space group $P2_1/c$ with one molecule in the asymmetric unit (Figure 2). The Bi–P distances in $\mathbf{1}_{\text{ph}}$ are 261.86(1) and 266.26(6) pm and fit quite well to other bismuthanylphosphanes like $\text{Ar}_2\text{Bi}-\text{PtBuR}$ (Ar = Ph, Mes, Dipp; R = *t*Bu, SiMe₃: 262.1(1)–269.80(7) pm),^[13,20] $t\text{Bu}_2\text{BiP}(\text{tBu})\text{SbtBu}_2$ (262.5(3) pm),^[10] $(\text{Cl}((\text{SiMe}_3)_2\text{CH})\text{Bi})_2\text{P}(\text{Si}t\text{Bu}_{3-x}\text{Ph}_x)$ ($x = 1, 2$; 262.6(2)–265.1(2) pm)^[3,21] or $(\text{Cy}_2\text{P})\text{Bi}((\text{NR})_2(\text{SiMe}_2)_2\text{O})$ (Cy = cyclohexyl; R = *t*Bu, Dipp: 264.65(7) and 265.03(4) pm).^[11] With $90.05(3)^\circ$, the Bi1–P1–Bi2 angle in $\mathbf{1}_{\text{ph}}$ is significantly smaller than in the structurally similar $(\text{Cl}((\text{SiMe}_3)_2\text{CH})\text{Bi})_2\text{P}(\text{Si}t\text{Bu}_{3-x}\text{Ph}_x)$ ($x = 1, 2$; $99.19(4)$ – $96.66(6)^\circ$), where one chlorine atom acts as a bridging ligand for the Bi atoms.^[3,21] However, it is still larger than in the $(\text{ClBiP}(\text{Mes}_2\text{C}_6\text{H}_4))_2$ ($85.83(2)^\circ$) with a P_2Bi_2 core.^[22] The Bi1–P1–Bi2 angle in $\mathbf{1}_{\text{ph}}$ is so small, that the distance of the two bismuth atoms (373.61(6) pm) is far smaller than the sum of the van der Waals radii (414 pm),^[23] which might indicate some attractive dispersive interaction between the two bismuth atoms.

Compound $\mathbf{2}_{\text{ph}}$ crystallizes in the monoclinic space group $C2/c$ with one molecule in the asymmetric unit (Figure 2). The Bi–As bond lengths are 273.6(1) and 275.1(1) pm. Again, this fits well to other described covalent Bi–As single bonds (264(2)–283.77(1) pm)^[3,5,13,24,25] The Bi–As–Bi angle is $90.97(4)^\circ$, which is in a similar range than the Bi–P–Bi angle in $\mathbf{1}_{\text{ph}}$. The Bi–Bi distance (391.2(1) pm) is smaller than the sum of van der Waals radii (414 pm)^[23] but larger than in $\mathbf{1}_{\text{ph}}$ (373.61(6) pm). This larger Bi–Bi distance could be an explanation for the lower reactivity of $\mathbf{2}_{\text{ph}}$ compared to $\mathbf{1}_{\text{ph}}$ mentioned above.

Next to crystals of $\mathbf{2}_{\text{ph}}$ and Ph_4Bi_2 , crystals of another habitus were obtained from the same mother liquor. This proved to be compound $\mathbf{3}_{\text{ph}}$ which also crystallizes in the monoclinic space group $C2/c$, however, only with half a molecule in the asymmetric unit (Figure 3). Formally, an *As**t*Bu fragment was inserted into one Bi–As bond under formation of a Bi–As–As–Bi chain. A Bi–As–As–Bi motive can only be found in one other literature known compound, $(\text{Cl}(\text{SiMe}_3)_2\text{CHBi})_2\text{As}_2$, where an As_2 fragment is bound to four bismuth atoms.^[3] The Bi–As bond length of 272.19(3) pm in $\mathbf{3}_{\text{ph}}$ is slightly shorter than in compound $\mathbf{2}_{\text{ph}}$ but still fits well to the other described Bi–As bonds.^[3,5,13,24,25] The As–As bond length of 243.42(6) pm is similar to model compounds like $(\text{tBuAs})_4$ (244.2(1)–244.4(1) pm)^[26] or the before mentioned $((\text{Me}_3\text{Si})_2\text{CH})\text{ClBi}(\text{As})_2$ (245.0(3) pm).^[3] Looking along the As–As axis, the two diphenylbismuthanyl

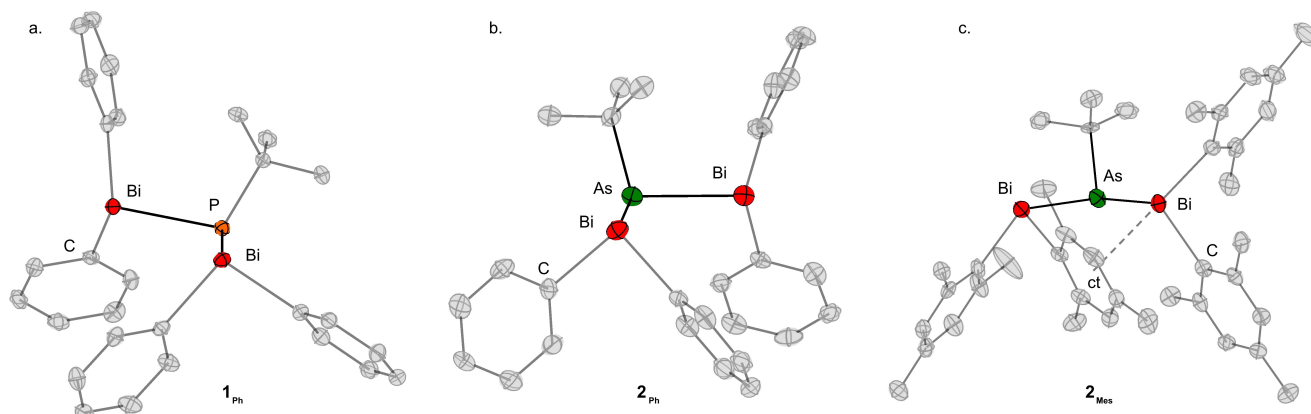


Figure 2. Molecular structure of a) 1_{Ph} , b) 2_{Ph} and c) 2_{Mes} in the solid state. Hydrogen atoms are omitted and disorder is not shown for clarity. Ellipsoids are shown at the 50% probability level. Selected bond lengths [pm] and angles [°] for 1_{Ph} : Bi1–P1 261.86(6); Bi2–P1 266.26(6); Bi1–C1 225.6(3); Bi1–C2 225.6(3); Bi2–C3 225.4(2); Bi2–C4 225.5(2); Bi1–Bi2 373.61(6); Bi1–P1–Bi2 90.05(2); C1–Bi1–P1 87.98(6); C2–Bi1–P1 96.42(7); C1–Bi1–C2 96.94(9); C3–Bi2–P1 94.40(7); C4–Bi2–P1 101.65(6); C3–Bi2–C4 93.79(9). Selected bond lengths [pm] and angles [°] for 2_{Ph} : Bi1–As1 273.6(1); Bi2–As1 275.1(1); Bi1–C1 226(1); Bi1–C2 227(2); Bi2–C3 226(1); Bi2–C4 227(1); Bi1–Bi2 391.2(1); Bi1–As1–Bi2 90.97(4); C1–Bi1–As1 95.7(3); C2–Bi1–As1 93.5(4); C1–Bi1–C2 90.3(5); C3–Bi2–As1 99.0(3); C4–Bi2–As1 95.2(4); C3–Bi2–C4 92.3(5). Selected bond lengths [pm] and angles [°] for 2_{Mes} : Bi1–As1 276.53(5); Bi2–As1 276.87(6); Bi1–C1 229.7(4); Bi1–C2 228.9(6); Bi2–C3 227.6(7); Bi2–C4 227.9(6); Bi1–ct 355.42(3); Bi1–As1–Bi2 91.59(2); C1–Bi1–As1 100.8(1); C2–Bi1–As1 106.2(1); C1–Bi1–C2 98.3(2); C3–Bi2–As1 107.1(1); C4–Bi2–As1 95.3(1); C3–Bi2–C4 95.3(2).

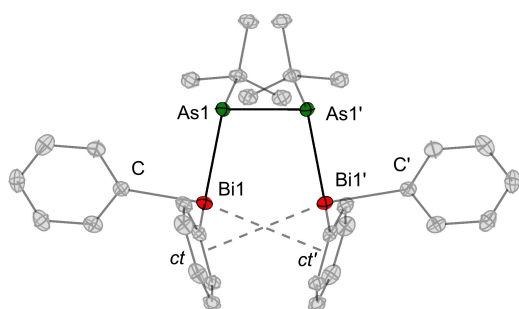


Figure 3. Molecular structure of 3_{Ph} in the solid state. Hydrogen atoms are omitted for clarity. Ellipsoids are shown at the 50% probability level. Atoms labelled with an apostrophe were symmetry generated by using $1-x, y, \frac{3}{2}+z$. Selected bond lengths [pm] and angles [°] for 3_{Ph} : Bi1–As1 272.19(3); Bi1–C1 2.263(3); Bi1–C2 2.272(3); Bi1–Ct 372.47(4); As1–As1' 243.42(6); Bi1–As1–As1' 107.021(8).

fragments are almost in an eclipsed arrangement with a Bi–As–As–Bi torsion angle of $29.81(2)^\circ$. This is in stark contrast to $(Cl(SiMe_3)_2CHBi)_2As_2$, where this torsion angle is 89.0° .^[3] One phenyl substituent at the bismuth atom shows a short contact to the symmetry generated bismuth atom of the same molecule (Bi–ct: 372.47(4) pm). This distance is indicative of an attractive Bi– π interaction.^[27,28] This Bi– π interaction might explain the nearly eclipsed arrangement of the diphenylbismuthanyl substituents. The intramolecular Bi–Bi distance is 424.43(4) pm, which is far larger than the sum of van der Waals radii (414 pm) indicative of no attractive interaction between the bismuth atoms.^[23]

Compound 2_{Mes} crystallizes in the triclinic space group $P\bar{1}$ with one molecule in the asymmetric unit (Figure 2). The Bi–As distances are 276.53(5) and 276.87(6) pm, which is about 2 pm longer than in 2_{Ph} . This slight elongation of the Bi–As bond for the larger Mes group compared to the Ph substituent is

consistent with compounds of the form $Ar_2BiPtBuR$ ($Ar = Ph, Mes$; $R = tBu, SiMe_3$).^[13] The Bi–As–Bi angle is $91.58(1)^\circ$ which is only slightly expanded compared to 2_{Ph} . Contrary to 1_{Ph} or 2_{Ph} , compound 2_{Mes} shows an intramolecular Bi– π interaction of one Bi-atom and one mesityl substituent of the other Bi atom. With 355.42(3) pm, the Bi1–ct distance is pretty small and well within a bonding interaction.^[27,28]

The compounds 4_{Ph} , 5_{Ph} and 6_{Ph} crystallize isostructural in the triclinic space group $P\bar{1}$ with one molecule in the asymmetric unit (Figure 4). In compound 4_{Ph} the Bi–P distance is 262.40(7) pm and fits well to the bond lengths in 1_{Ph} (261.86(6) and 266.26(8) pm) and the other previously mentioned reference compounds.^[1,3,10,13,20,21] The As–P bond has a length of 235.40(7) pm, which is in the usual range for covalent As–P single bonds.^[4,5,29–31] The Bi–P–As angle around the central phosphorus atom is $113.58(3)^\circ$, much larger than the angle around the central P atom in compound 1_{Ph} ($90.05(3)^\circ$).

In 5_{Ph} , the Bi–P bond length of 262.5(1) pm is very similar to that of 4_{Ph} (262.40(7) pm) or the structurally very similar $tBu_2Bi-P(tBu)-SbtBu_2$ (262.5(3) pm).^[10] Same holds true for the P–Sb bond (5_{Ph} : 255.3(1) pm; $tBu_2BiP(tBu)SbtBu_2$: 253.9(3) pm).^[10] With $111.15(3)^\circ$, the Bi–P–Sb angle is slightly larger than in $tBu_2BiP(tBu)SbtBu_2$ ($107.9(1)^\circ$),^[10] which might be explained by packing effects. Compared to 4_{Ph} and 1_{Ph} , the Bi–P–E angle ($E = As, Sb, Bi$) is intermediate, showing a trend towards lower angles around the central pnictogen atoms for heavier substituents. This trend is also observed for the completely *tert*-butyl substituted compounds with the general formula $tBu_2E^1P(tBu)E^2tBu_2$ ($E^1, E^2 = As, Sb, Bi$).^[4,10]

Compound 6_{Ph} represents the structural isomer of compound 4_{Ph} . Despite the large *tBu* and *PtBu* substituents at the arsenic atom, the Bi–As distance of 271.91(4) pm is on the shorter end of Bi–As single bonds. Nonetheless, it fits well to 2_{Ph} , 2_{Mes} , 3_{Ph} and other compounds described in the literature

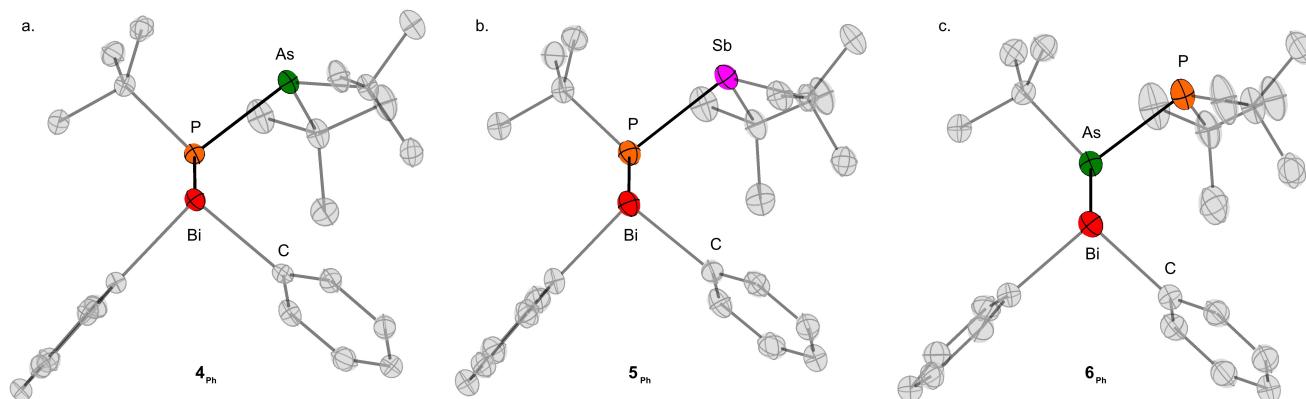


Figure 4. Molecular structure of a) 4_{ph} , b) 5_{ph} and c) 6_{ph} in the solid state. Hydrogen atoms are omitted and disorder is not shown for clarity. Ellipsoids are shown at the 50% probability level. Selected bond lengths [pm] and angles [°] for 4_{ph} : Bi1–P1 262.40(7); Bi1B–P1B (260(5)); Bi1–C1 224.7(2); Bi1–C2 225.2(2); P1–As1 235.40(7); C1–Bi1–C2 92.43(9); P1–Bi1–C1 95.25(7); P1–Bi1–C2 94.90(7); Bi1–P1–As1 113.58(3). Selected bond lengths [pm] and angles [°] for 5_{ph} : Bi1–P1 262.5(1); Bi1B–P1B 262(2); Bi1–C1 224.9(4); Bi1–C2 225.6(4); P1–Sb1 255.3(1); C1–Bi1–C2 92.6(1); P1–Bi1–C1 94.6(1); P1–Bi1–C2 94.9(1); Bi1–P1–Sb1 111.15(3). Selected bond lengths [pm] and angles [°] for 6_{ph} : Bi1–As1 271.91(4); Bi1B–As1B 271(1); Bi1–C1 225.2(4); Bi1–C2 225.2(3); As1–P1 236.0(1); C1–Bi1–C2 93.3(1); As1–Bi1–C1 94.6(1); As1–Bi1–C2 94.8(1); Bi1–As1–P1 113.15(3).

(271.7(9)–282.61(1) pm).^[3,5,13,24,25] With 236.0(1) pm, the As–P distance is similar to compound 4_{ph} (235.40(7) pm). The same similarity applies to the Bi–As–P angle of 113.15(3)° (4_{ph} , Bi–P–As: 113.58(3)°).

Of the three corresponding mesityl substituted compounds, only 4_{Mes} and 6_{Mes} crystallize isostructural in the space group $P\bar{1}$ with half a molecule of toluene in the asymmetric unit (Figure 5). With 270.18(6) pm, the Bi–P bond in 4_{Mes} is significantly elongated compared to 4_{ph} (262.40(7) pm). The same applies to the Bi–P–As angle, which rises to 119.07(3)° (4_{ph} : 113.58(3)°). This is caused by the larger steric demand of the Mes substituent. The elongation of 8 pm is significantly larger than in the previously reported model compounds $\text{Ph}_2\text{BiPtBu}_2$ (265.08(8) pm) and $\text{Mes}_2\text{BiPtBu}_2$ (267.2(1) pm).^[13] The

P–As bond length is 234.42(7), the same length as in 4_{ph} (235.40(7) pm) within the margin of error.

Different to 4_{Mes} and 6_{Mes} , compound 5_{Mes} was crystallized from *n*-pentane and the asymmetric unit accommodates a highly disordered *n*-pentane molecule and two molecules of 5_{Mes} (Figure 5). The Bi–P distances are 267.18(7) and 268.25(7) pm, which is slightly shorter than in 4_{Mes} (270.18(6) pm) and larger than in the phenyl substituted compound 5_{ph} (262.5(1) pm). With distances of 256.02(7) and 256.65(8) pm, the P–Sb bond is slightly longer than in 5_{ph} (255.3(1) pm) or $t\text{Bu}_2\text{BiP}(t\text{Bu})\text{Sb}t\text{Bu}_2$ (253.9(3) pm).^[4] Surprisingly, the Bi–P–Sb angles in 5_{Mes} (102.09(2) and 101.83(3)°) are much smaller than in 5_{ph} (111.15(3)°) or $t\text{Bu}_2\text{BiP}(t\text{Bu})\text{Sb}t\text{Bu}_2$ (107.9(1)°). As a result, the Bi–Sb distances are 406.91(5) and 407.49(5) pm,

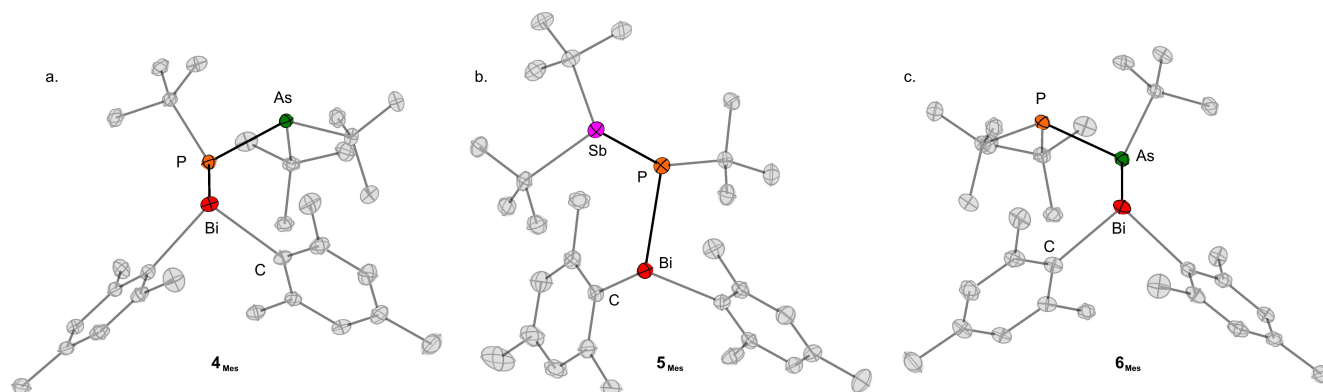


Figure 5. Molecular structures of a) 4_{Mes} , b) one molecule of the asymmetric unit of 5_{Mes} and c) 6_{Mes} in the solid state. Hydrogen atoms are omitted and disorder is not shown for clarity. Ellipsoids are shown at the 50% probability level. Selected bond lengths [pm] and angles [°] for 4_{Mes} : Bi1–P1 270.18(6); Bi1–C1 227.8(3); Bi1–C2 230.4(3); P1–As1 234.42(7); C1–Bi1–C2 96.15(9); P1–Bi1–C1 106.16(7); P1–Bi1–C2 106.05(6); Bi1–P1–As1 119.06(3). Selected bond lengths [pm] and angles [°] for 5_{Mes} : Bi1–P1 267.18(7); Bi2–P2 268.25(7); Bi1–C1 228.0(3); Bi2–C6 228.4(3); Bi1–C2 229.0(3); Bi2–C7 229.3(3); P1–Sb1 256.02(7); P2–Sb2 256.65(8); C1–Bi1–C2 93.4(1); C6–Bi2–C7 92.50(9); P1–Bi1–C1 100.74(7); P2–Bi2–C6 101.71(7); P1–Bi1–C2 106.88(7); P2–Bi2–C7 105.08(7); Bi1–P1–Sb1 102.09(2); Bi2–P2–Sb2 101.83(3). Selected bond lengths [pm] and angles [°] for 6_{Mes} : Bi1–As1 279.60(2); Bi1–C1 227.7(2); Bi1–C2 230.2(3); As1–P1 234.62(6); C1–Bi1–C2 96.55(8); As1–Bi1–C1 105.14(6); As1–Bi1–C2 106.26(6); Bi1–As1–P1 117.59(2).

which is slightly smaller than the sum of the van der Waals radii (413 pm).^[23]

As mentioned above, **6**_{Mes} crystallize isomorphous to **4**_{Mes}. The Bi–As distance of 279.60(4) pm corresponds to an elongation of 8 pm compared to **6**_{Ph} (271.91(4) pm). This elongation is similar to the effect observed in the Bi–P bond length of **4**_{Ph} and **4**_{Mes}. The Bi–As bond length in **6**_{Mes} still fits to reference compounds though (271.7(9)–282.61(1) pm)^[3,5,13,24,25] The P–As bond (234.62(6) pm), is slightly shorter than in **6**_{Ph} (236.0(1) pm), while the angle around the central arsenic atom (117.59(2)°) is slightly larger (**6**_{Ph}: 113.15(3)°).

Conclusion

In this work, we have reported the preparation and characterization of multiple interpnictogen chain compounds, with three consecutive pnictogen atoms. All compounds contain terminal diarylbismuth fragments, making them rare examples of interpnictogen compounds containing bismuth. Symmetrical compounds of the form Ar₂Bi–E(tBu)–Bi₂Ar (Ar = Ph, Mes; E = P, As; **1**_{Ph}–**2**_{Mes}) have been prepared. Compound **1**_{Ph} shows potential in a phosphinidene transfer reaction, in which a “PtBu” fragment was successfully transferred to an N-heterocyclic carbene (Me₂Ime) with formation of the corresponding dibismuthane and Me₂Ime=PtBu (**8**), which was identified by NMR spectroscopy. The mechanism of the phosphinidene transfer will be investigated in future research in our group. Moreover, ternary interpnictogen compounds of the form Ar₂Bi–E¹(tBu)–E²tBu₂ (Ar = Ph, Mes; **4**: E¹ = P, E² = As; **5**: E¹ = P, E² = Sb; **6**: E¹ = As, E² = P) have been prepared, and their decomposition in solution was studied in detail. All isolated compounds were analysed by NMR and IR spectroscopy, mass spectrometry, single-crystal X-ray diffraction and elemental analysis.

Experimental Section

General procedure: All manipulations were carried out under argon and with the exclusion of light by using standard Schlenk technique. All solvents used in the reactions and for crystallisation were dried by using standard techniques, distilled and stored under argon. Solvents were never stored longer than three weeks before use. Obtained products often contain systematic impurities with educts or hydrolysed product and because of that have to be recrystallized to obtain high purity compounds suitable for elemental analysis. The given yields always refer to the purified and not the raw products. Ph₂BiCl, Mes₂BiCl, Ar₂BiEtBu(SiMe₃) (Ar = Ph, Mes, E = P, As), tBu₂E¹E²(tBu)Li (E¹ = P, As; E² = P, As, Sb) were prepared according to literature procedures.^[5,10,13,32,33] NMR spectra were recorded using a Bruker Avance III HD 250 MHz, a Bruker Avance II 300 MHz, a Bruker Avance III 500 MHz or a Avance III HD 500 MHz spectrometer at 300 K. The IR spectra were run on a Bruker FTIR spectrometer using the attenuated total reflectance (ATR) mode. For mass spectrometry, a Jeol AccuTOF GCv (CI, LIFDI) was used. The FD emitters were purchased from Linden Chromaspec GmbH. Elemental analysis was performed on an Elementar Vario MicroCube.

(Ph₂Bi)₂P(tBu) (**1**_{Ph}): Ph₂BiCl (646 mg, 1.62 mmol, 1.0 equiv.) is suspended in 20 mL of TFT and a solution of Ph₂BiPtBu(SiMe₃) (850 mg, 1.62 mmol, 1.0 equiv.) in 20 mL TFT is added at 0 °C. The reaction mixture is stirred for 15 min, whereupon the reaction mixture clears up. Volatiles are removed under reduced pressure, and the remaining solid is taken up in 20 mL of *n*-pentane and remaining solids are removed by filtration. Volatiles are removed under reduced pressure, and the remaining solid was washed with cold *n*-pentane, which left **1**_{Ph} in the form of a pale yellow solid. Yield 21%. Elemental analysis for C₂₈H₂₉Bi₂P calcd: C 41.29, H 3.59; found: C 41.32, H 3.68; ¹H NMR (500 MHz, C₆D₆): δ = 8.04–8.20 (brm, 4H, *o*-CH), 7.67–7.78 (brm, 4H, *o*-CH), 7.17–7.25 (brm, 4H, *m*-CH), 7.06–7.11 (brm, 2H, *p*-CH), 6.93–7.02 (brm, 6H, *m*-CH, *p*-CH), 1.32 (d, ³J_{P-H} = 10.9 Hz, 9H, PC(CH₃)₃); ¹³C{¹H} NMR (125 MHz, C₆D₆): δ = 151.6 (s, 2C, Bi-C), 148.7 (s, 2C, Bi-C), 139.2 (s, 4C, *o*-C), 139.1 (s, 4C, *o*-C), 130.7 (s, 4C, *m*-C), 130.4 (s, 4C, *m*-C), 127.7 (s, 4C, *p*-C, found by HMBC), 36.7 (d, ²J_{P-C} = 11.4 Hz, 3C, PC(CH₃)₃), 33.1 (d, ¹J_{P-C} = 42.1 Hz, 1C, PC(CH₃)₃); ³¹P{¹H} NMR (202 MHz, C₆D₆): δ = 13.6 (s, 1P, Bi–P–Bi); IR (cm⁻¹): 3053 (w), 3031 (w), 2961 (w), 2941 (w), 2919 (w), 2849 (w), 1566 (w), 1471 (m), 1427 (m), 1258 (s), 1165 (w), 1085 (s), 1011 (s), 994 (s), 864 (w), 793 (s), 720 (s), 692 (s), 447 (m), 439 (m); HRMS: LIFDI(+) *m/z* 814.16042 [(Ph₂Bi)₂P(tBu)]⁺; calcd: 814.16145.

(Ph₂Bi)₂As(tBu) (**2**_{Ph}): Ph₂BiCl (140 mg, 0.35 mmol, 1.0 equiv.) is suspended in 5 mL of TFT, and a solution of Ph₂BiAs(tBu)(SiMe₃) (185 mg, 0.35 mmol, 1.0 equiv.) in 5 mL TFT is added at 0 °C. The reaction mixture is stirred for 15 min, whereupon the reaction mixture clears. Volatiles are removed under reduced pressure, 20 mL of *n*-pentane are added and remaining solids are removed by filtration. Volatiles are removed under reduced pressure again and the remaining solid is washed with cold *n*-pentane, leaving **2**_{Ph} in the form of a pale brown solid. Yield: 25%. Elemental analysis for C₂₈H₂₉As₂Bi₂ calcd: C 39.18, H 3.41; found: C 38.63, H 3.49; ¹H NMR (500 MHz, C₆D₆): δ = 8.09–8.14 (m, 4H, *o*-CH), 7.74–7.77 (m, 4H, *o*-CH), 7.17–7.21 (m, 4H, *m*-CH), 7.08–7.10 (m, 2H, *p*-CH), 6.94–7.01 (m, 6H, *m*-CH, *p*-CH), 1.39 (s, 9H, AsC(CH₃)₃); ¹³C{¹H} NMR (125 MHz, C₆D₆): δ = 149.5 (s, 2C, Bi-C), 147.3 (s, 2C, Bi-C), 139.8 (s, 4C, *o*-C), 139.4 (s, 4C, *o*-C), 130.8 (s, 4C, *m*-C), 130.6 (s, 4C, *m*-C), 127.6 (s, 4C, *p*-C), 36.7 (s, 3C, AsC(CH₃)₃), 33.5 (s, 1C, AsC(CH₃)₃); IR (cm⁻¹): 3054 (w), 3033(m), 3007 (m), 2931 (w), 2875 (w), 2843 (w), 1564 (w), 1470 (m), 1425 (s), 1359 (w), 1325 (m), 1297 (w), 1185 (w), 1151 (m), 1054 (w), 1010 (w), 994 (s), 906 (m), 852 (w), 841 (w), 720 (s), 691 (s), 640 (m), 615 (m), 446 (m), 436 (s); HRMS: LIFDI(+) *m/z* 858.11007 [(Ph₂Bi)₂As(tBu)]⁺; calcd 858.10929.

(Mes₂Bi)₂As(tBu) (**2**_{Mes}): Mes₂BiCl (74 mg, 0.15 mmol, 1.0 equiv.) is suspended in 2 mL of TFT and a solution of Mes₂BiAs(tBu)(SiMe₃) (100 mg, 0.15 mmol, 1.0 equiv.) in 2 mL TFT is added at 20 °C. The reaction mixture is stirred for 45 min, and volatiles are removed under reduced pressure. 20 mL of *n*-pentane are added and remaining solids are removed by filtration. Volatiles are removed under reduced pressure again and the remaining solid is washed with cold *n*-pentane, leaving **2**_{Mes} in the form of a pale yellow solid. Yield: 47%. Elemental analysis for C₄₀H₅₃As₂Bi₂ calcd: C 46.79, H 5.20; found: C 46.48, H 5.11; ¹H NMR (500 MHz, C₆D₆): δ = 6.92 (s, 4H, *m*-CH), 6.68 (s, 4H, *m*-CH), 2.64 (s, 12H, *o*-C(CH₃)₃), 2.47 (s, 12H, *o*-C(CH₃)₃), 2.09 (s, 6H, *p*-C(CH₃)₃), 1.95 (s, 6H, *p*-C(CH₃)₃), 1.47 (s, 9H, AsC(CH₃)₃); ¹³C{¹H} NMR (125 MHz, C₆D₆): δ = 155.6 (s, 2C, Bi-C, found by HMBC), 153.2 (s, 2C, Bi-C, found by HMBC), 146.3 (s, 4C, *o*-C(CH₃)₃), 146.2 (s, 4C, *o*-C(CH₃)₃), 137.4 (s, 2C, *p*-C(CH₃)₃), 137.1 (s, 2C, *p*-C(CH₃)₃), 129.6 (s, 4C, *m*-CH), 129.4 (s, 4C, *m*-CH), 35.1 (s, 3C, AsC(CH₃)₃), 30.8 (s, 4C, *o*-C(CH₃)₃), 30.3 (s, 4C, *o*-C(CH₃)₃), 30.0 (s, 1C, AsC(CH₃)₃), 21.1 (s, 2C, *p*-C(CH₃)₃), 20.9 (s, 2C, *p*-C(CH₃)₃); IR (cm⁻¹): 3008 (w), 2954 (m), 2917 (m), 2879 (m), 2849 (m), 2726 (w), 1592 (w), 1553 (w), 1440 (s), 1399 (w), 1286 (m), 1240 (w), 1152 (m), 1024 (m), 999 (m), 943 (w), 922 (w), 842 (s), 744 (w), 698 (m), 625 (w), 576 (w), 534 (m), 492 (w);

HRMS: LIFDI(+) m/z 1026.29705 [(Mes₂Bi)₂AstBu]⁺; calcd 1026.29709.

Ph₂BiP(tBu)AsfBu₂ (4_{ph}): Solid tBu₂AsP(tBu)Li·THF (161 mg, 0.45 mmol, 1.0 equiv.) is slowly added to a suspension of Ph₂BiCl (180 mg, 0.45 mmol, 1.0 equiv.) in 15 mL of diethyl ether at −50 °C. After complete addition, the reaction mixture is allowed to warm to room temperature over 5 h. Volatiles are removed under reduced pressure, and the remaining solid is taken up in 20 mL of *n*-pentane. After removal of black and colourless precipitate by filtration, a yellow solution is obtained. The solution is concentrated and stored at −32 °C which gives yellow crystals of **4_{ph}**. Yield: 76% (first batch). Elemental analysis for C₂₄H₃₇As₂Bi₂P₁ calcd: C 45.01, H 5.82; found: C 45.39, H 5.97; ¹H NMR (300 MHz, C₆D₆): δ = 8.22 (d, ³J_{H-H} = 7.4 Hz, 4H, *o*-CH), 7.20 (t, ³J_{H-H} = 7.3 Hz, 4H, *m*-CH), 7.07 (t, ³J_{H-H} = 7.3 Hz, 2H, *p*-CH), 1.36 (d, ³J_{P-H} = 12.0 Hz, 9H, PC(CH₃)₃), 1.34 (s, 18H, AsC(CH₃)₃); ¹³C{¹H} NMR (75 MHz, C₆D₆): δ = 149.4 (d, ²J_{P-C} = 8.3 Hz, 2C, Bi-C), 138.5 (d, ³J_{P-C} = 3.9 Hz, 4C, *o*-C), 130.1 (s, 4C, *m*-C), 127.7 (s, 4C, *p*-C, found by HMQC), 37.3 (brs, 2C, AsC(CH₃)₃), 34.6 (d, ²J_{P-C} = 12.3 Hz, 3C, PC(CH₃)₃), 33.8 (d, ¹J_{P-C} = 34.1 Hz, 1C, PC(CH₃)₃), 32.5 (d, ³J_{P-C} = 32.5 Hz, 6C, AsC(CH₃)₃); ³¹P{¹H} NMR (101 MHz, C₆D₆): δ = 10.6 (s, 1P, Bi-P-As); IR (cm⁻¹): 3057 (w), 3034 (w), 2982 (m), 2955 (m), 2927 (m), 2875 (m), 2848 (m), 1568 (m), 1470 (m), 1456 (m), 1428 (s), 1384 (w), 1355 (s), 1326 (w), 1302 (w), 1238 (w), 1161 (s), 1052 (w), 1013 (m), 995 (s), 931 (w), 807 (w), 721 (s), 694 (s), 453 (s), 436 (m); HRMS: LIFDI(+) m/z 640.16431 [Ph₂BiP(tBu)AsfBu₂]⁺; calcd 640.16527.

Mes₂BiP(tBu)AsfBu₂ (4_{Mes}): Solid tBu₂AsP(tBu)Li·THF (221 mg, 0.62 mmol, 1.0 equiv.) is added slowly to a suspension of Mes₂BiCl (300 mg, 0.62 mmol, 1.0 equiv.) in 20 mL of diethyl ether at −50 °C. After complete addition, the reaction mixture is allowed to warm to room temperature over 5 h. Volatiles are removed under reduced pressure, and the remaining solid is taken up in 20 mL of *n*-pentane. After removal of solids by filtration an orange solution is obtained. Volatiles are again removed under reduced pressure and the crude product is recrystallized from 1 mL of toluene at −32 °C. Yield: 55% (first batch). Elemental analysis for C₃₀H₄₉As₂Bi₂P₁·0.5 C₅H₈ calcd: C 52.21, H 6.93; found: C 52.66, H 6.66; ¹H NMR (300 MHz, C₆D₆): δ = 6.88 (s, 4H, *m*-CH), 2.65 (s, 12H, *o*-C(CH₃)), 2.06 (s, 6H, *p*-C(CH₃)), 1.47 (s, 18H, AsC(CH₃)₃), 1.46 (d, ³J_{P-H} = 11.6 Hz, 9H, PC(CH₃)₃); ¹³C{¹H} NMR (75 MHz, C₆D₆): δ = 154.5 (s, 2C, Bi-C), 145.9 (s, 4C, *o*-C(CH₃)), 137.1 (s, 2C, *p*-C(CH₃)), 129.6 (s, 4C, *m*-CH), 37.9 (brs, 2C, AsC(CH₃)₃), 34.1 (d, ¹J_{P-C} = 39.0 Hz, 1C, PC(CH₃)₃), 33.9 (d, ²J_{P-C} = 12.4 Hz, 3C, PC(CH₃)₃), 33.9 (d, ³J_{P-C} = 2.2 Hz, 6C, AsC(CH₃)₃), 28.8 (d, ⁴J_{P-C} = 7.7 Hz, 4C, *o*-C(CH₃)), 20.6 (s, 2C, *p*-C(CH₃)); ³¹P{¹H} NMR (101 MHz, C₆D₆): δ = 9.9 (s, 1P, Bi-P-As); IR (cm⁻¹): 3006 (w), 2985 (s), 2965 (s), 2939 (s), 2920 (s), 2875 (s), 2848 (s), 2764 (w), 2730 (w), 2724 (w), 1493 (w), 1454 (s), 1437 (s), 1400 (m), 1384 (w), 1373 (m), 1356 (s), 1288 (m), 1261 (w), 1158 (s), 1114 (w), 1107 (w), 1080 (m), 1017 (m), 1007 (w), 1002 (m), 996 (m), 942 (w), 842 (s), 805 (m), 730 (s), 695 (m), 576 (w), 539 (m), 491 (s), 465 (m) 419 (w); HRMS: Cl(+) m/z 725.26789 [Mes₂BiP(tBu)AsfBu₂ + H]⁺; calcd 725.26699.

Ph₂BiP(tBu)SbtBu₂ (5_{ph}): Solid tBu₂SbP(tBu)Li·0.2 Et₂O (260 mg, 0.75 mmol, 1.0 equiv.) is slowly added to a suspension of Ph₂BiCl (300 mg, 0.75 mmol, 1.0 equiv.) in 20 mL of diethyl ether at −50 °C. After complete addition, the reaction mixture is allowed to warm to room temperature over 5 h. Volatiles are removed under reduced pressure, and the remaining solid is taken up in 20 mL of *n*-pentane. After removal of black and colourless precipitate by filtration, a yellow solution is obtained. The solution is concentrated and stored at −32 °C which gives yellow crystals of **5_{ph}**. Yield: 77% (first batch). Elemental analysis for C₂₄H₃₇Bi₂P₁Sb₁ calcd: C 41.94, H 5.43; found: C 42.57, H 5.60; ¹H NMR (300 MHz, C₆D₆): δ = 8.22 (d, ³J_{H-H} = 7.4 Hz, 4H, *o*-CH), 7.20 (t, ³J_{H-H} = 7.4 Hz, 4H, *m*-CH), 7.07 (t, ³J_{H-H} = 7.4 Hz, 2H, *p*-CH), 1.41 (s, 18H, SbC(CH₃)₃), 1.40 (d, ³J_{P-H} = 11.5 Hz, 9H, PC(CH₃)₃); ¹³C{¹H} NMR (75 MHz, C₆D₆): δ = 148.8 (brs, 2C, Bi-C),

138.9 (s, ³J_{P-C} = 4.0 Hz, 4C, *o*-C), 130.5 (s, 4C, *m*-C), 128.1 (s, 2C, *p*-C, found by HMQC), 36.1 (d, ²J_{P-C} = 11.5 Hz, 3C, PC(CH₃)₃), 33.8 (d, ³J_{P-C} = 2.2 Hz, 6C, SbC(CH₃)₃), 33.8 (d, ¹J_{P-C} = 36.6 Hz, 1C, PC(CH₃)₃), 32.8 (brs, 2C, SbC(CH₃)₃); ³¹P{¹H} NMR (101 MHz, C₆D₆): δ = −5.8 (s, 1P, Bi-P-Sb); IR (cm⁻¹): 3057 (w), 3034 (w), 3016 (w), 2975 (m), 2915 (w), 2840 (s), 1567 (m), 1463 (m), 1456 (m), 1456 (s), 1428 (s), 1355 (s), 1053 (s), 1145 (s), 1151 (m), 1052 (w), 1013 (m), 995 (s), 930 (w), 845 (w), 800 (w), 721 (s), 693 (s), 644 (w), 453 (s); 435 (m); HRMS: LIFDI (+) m/z 686.14698 [Ph₂BiP(tBu)SbtBu₂]⁺; calcd 686.14749.

Mes₂BiP(tBu)SbtBu₂ (5_{Mes}): Solid tBu₂SbP(tBu)Li·0.2 Et₂O (214 mg, 0.62 mmol, 1.0 equiv.) is added slowly to a suspension of Mes₂BiCl (300 mg, 0.62 mmol, 1.0 equiv.) in 20 mL of diethyl ether at −30 °C. After complete addition, the reaction mixture is allowed to warm to room temperature over 6 h. Volatiles are removed under reduced pressure, and the remaining solid is taken up in 20 mL of *n*-pentane. After removal of solids by filtration, the orange solution is concentrated and stored at −32 °C. After one week, orange-red crystals of **5_{Mes}** are obtained. Yield: 67% (first batch). Elemental analysis for C₃₀H₄₉Bi₂P₁Sb₁·0.5 C₅H₁₂ calcd: C 48.34, H 6.87; found: C 48.79, H 6.76; ¹H NMR (500 MHz, C₆D₆): δ = 6.86 (s, 4H, *m*-CH), 2.64 (s, 12H, *o*-C(CH₃)), 2.06 (s, 6H, *p*-C(CH₃)), 1.55 (s, 18H, SbC(CH₃)₃), 1.42 (d, ³J_{P-H} = 10.8 Hz, 9H, PC(CH₃)₃); ¹³C{¹H} NMR (125 MHz, C₆D₆): δ = 152.9 (brs, 2C, Bi-C), 146.4 (s, 4C, *o*-C(CH₃)), 137.5 (s, 2C, *p*-C(CH₃)), 129.9 (s, 4C, *m*-CH), 34.9 (d, ²J_{P-C} = 12.6 Hz, 3C, PC(CH₃)₃), 34.6 (d, ¹J_{P-C} = 43.1 Hz, 1C, PC(CH₃)₃), 34.2 (s, 6C, SbC(CH₃)₃), 33.2 (brs, 2C, SbC(CH₃)₃), 29.0 (d, ⁴J_{P-C} = 8.2 Hz, 4C, *o*-C(CH₃)), 21.0 (s, 2C, *p*-C(CH₃)); ³¹P{¹H} NMR (202 MHz, C₆D₆): δ = −10.0 (s, 1P, Bi-P-As); IR (cm⁻¹): 3012 (s), 2946 (s), 2916 (s), 2843 (s), 1593 (w), 1554 (w), 1454 (s), 1370 (m), 1357 (s), 1288 (m), 1259 (w), 1236 (w), 1146 (s), 1025 (m), 999 (m), 941 (w), 844 (s), 799 (m), 698 (w), 671 (m), 577 (w), 518 (m); HRMS: LIFDI(+) m/z 770.24196 [Mes₂BiP(tBu)SbtBu₂]⁺; calcd 770.24139.

Ph₂BiAs(tBu)PtBu₂ (6_{ph}): Solid tBu₂PAs(tBu)Li·Et₂O (270 mg, 0.75 mmol, 1.0 equiv.) is slowly added to a suspension of Ph₂BiCl (300 mg, 0.75 mmol, 1.0 equiv.) in 20 mL of diethyl ether at −50 °C. After complete addition, the reaction mixture is allowed to warm to room temperature over 5 h. Volatiles are removed under reduced pressure, and the remaining solid is taken up in 20 mL of *n*-pentane. After removal of black and colourless precipitate by filtration, a yellow solution is obtained. The solution is concentrated and stored at −32 °C which gives yellow crystals of **6_{ph}**. Yield: 50% (first batch). Elemental analysis for C₂₄H₃₇As₂Bi₂P₁ calcd: C 45.01, H 5.82; found: C 45.14, H 5.74; ¹H NMR (500 MHz, C₆D₆): δ = 8.25 (d, ³J_{H-H} = 6.9 Hz, 2H, *o*-CH), 8.22 (d, ³J_{H-H} = 6.9 Hz, 2H, *o*-CH), 7.21 (t, ³J_{H-H} = 7.4 Hz, 2H, *m*-CH), 7.18 (t, ³J_{H-H} = 7.4 Hz, 2H, *m*-CH), 7.08 (t, ³J_{H-H} = 7.6 Hz, 1H, *p*-CH), 7.06 (t, ³J_{H-H} = 7.6 Hz, 1H, *p*-CH), 1.42 (s, 9H, AsC(CH₃)₃), 1.34 (d, ³J_{P-H} = 11.3 Hz, 9H, PC(CH₃)₃); 1.24 (d, ³J_{P-H} = 11.7 Hz, 9H, PC(CH₃)₃); ¹³C{¹H} NMR (125 MHz, C₆D₆): δ = 149.0 (brs, 1C, Bi-C), 147.9 (brs, 1C, Bi-C), 139.5 (s, 2C, *o*-C), 138.7 (s, 2C, *o*-C), 130.7 (s, 2C, *m*-C), 130.6 (s, 2, *m*-C), 127.7 (s, 2C, *p*-C, found by HMQC), 36.8 (d, 1C, ¹J_{P-C} = 41.7 Hz, PC(CH₃)₃), 35.0 (d, 1C, ²J_{P-C} = 12.1 Hz, AsC(CH₃)₃), 34.7 (d, 3C, ³J_{P-C} = 6.6 Hz, AsC(CH₃)₃), 34.1 (d, 1C, ¹J_{P-C} = 28.6 Hz, PC(CH₃)₃), 33.9 (d, 3C, ²J_{P-C} = 14.6 Hz, PC(CH₃)₃), 32.8 (d, 3C, ²J_{P-C} = 13.4 Hz, PC(CH₃)₃), ³¹P{¹H} NMR (101 MHz, C₆D₆): δ = 70.9 (s, 1P, Bi-As-P); IR (cm⁻¹): 3058 (w), 2982 (w), 2952 (m) 2939 (s), 2884 (s), 2851 (s), 1568 (m), 1466 (m), 1428 (m), 1383 (m) 1355 (s), 1326 (w), 1302 (w), 1241 (w), 1204 (w), 1156 (s), 1054 (m), 1013 (m), 995 (m), 984 (m), 934 (w), 807 (m), 727 (s), 721 (s), 694 (s), 643 (w), 587 (w), 564 (w), 468 (w), 452 (s), 435 (m), 413 (w); HRMS: LIFDI(+) m/z 640.16498 [Ph₂BiAs(tBu)PtBu₂]⁺; calcd 640.16527.

Mes₂BiAs(tBu)PtBu₂ (6_{Mes}): Solid tBu₂PAs(tBu)Li·Et₂O (297 mg, 0.83 mmol, 1.0 equiv.) is added slowly to a suspension of Mes₂BiCl (400 mg, 0.83 mmol, 1.0 equiv.) in 20 mL of diethyl ether at −50 °C. After complete addition, the reaction mixture is allowed to warm to room temperature over 5 h. Volatiles are removed under reduced

pressure, and the remaining solid is taken up in 20 mL of *n*-pentane. After removal of solids by filtration, an orange solution is obtained. Volatiles are again removed under reduced pressure and the crude product is recrystallized from 1 mL of toluene at -32°C . Yield: 63% (first batch). Elemental analysis for $\text{C}_{30}\text{H}_{49}\text{As}_2\text{Bi}_2\text{P}_1\cdot 0.5\text{C}_7\text{H}_8$ calcd: C 52.21, H 6.93; found: C 52.84, H 6.78; ^1H NMR (300 MHz, C_6D_6): $\delta = 6.89$ (s, 4H, *m*-CH), 2.66 (s, 6H, *m*-C(CH_3)), 2.58 (s, 6H, *m*-C(CH_3)), 2.07 (s, 3H, *p*-C(CH_3)), 2.06 (s, 3H, *p*-C(CH_3)), 1.47 (s, 9H, $\text{AsC}(\text{CH}_3)_3$), 1.46 (d, $^3J_{\text{P-H}} = 11.6$ Hz, 9H, $\text{PC}(\text{CH}_3)_3$), 1.34 (d, $^3J_{\text{P-H}} = 11.7$ Hz, 9H, $\text{PC}(\text{CH}_3)_3$); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, C_6D_6): $\delta = 155.5$ (s, Bi-C, 1 C, found by HMBC), 153.9 (s, Bi-C, 1C, found by HMBC), 146.4 (s, 2C *o*-C(CH_3)), 145.9 (s, 2C, *o*-C(CH_3)), 137.6 (s, 1C, *p*-C(CH_3)), 137.2 (s, 1C, *p*-C(CH_3)), 129.9 (s, 2C, *m*-CH), 129.8 (s, 2C, *m*-CH), 37.0 (d, 1C, $^1J_{\text{P-C}} = 41.7$ Hz, $\text{PC}(\text{CH}_3)_3$), 35.4 (d, 1C, $^2J_{\text{P-C}} = 14.5$ Hz, $\text{AsC}(\text{CH}_3)_3$), 34.9 (d, 1C, $^1J_{\text{P-C}} = 33.3$ Hz, $\text{PC}(\text{CH}_3)_3$), 34.0 (d, 3C, $^2J_{\text{P-C}} = 15.3$ Hz, $\text{PC}(\text{CH}_3)_3$), 33.8 (d, 3C, $^3J_{\text{P-C}} = 6.8$ Hz, $\text{AsC}(\text{CH}_3)_3$), 33.2 (d, 3C, $^2J_{\text{P-C}} = 13.3$ Hz, $\text{PC}(\text{CH}_3)_3$), 29.8 (s, 2C, *m*-C(CH_3)), 29.4 (s, 2C, *m*-C(CH_3)), 21.0 (s, 1C, *p*-C(CH_3)), 20.9 (s, 1C, *p*-C(CH_3)); ^{31}P NMR (280 MHz, C_6D_6): $\delta = 75.8$ (s, 1P, Bi-As-P); IR (cm^{-1}): 3006 (w), 2985 (s), 2965 (s), 2939 (s), 2920 (s), 2874 (s), 2847 (s), 2765 (w), 2725 (w), 1493 (w), 1454 (s), 1436 (s), 1400 (m), 1383 (w), 1372 (m), 1355 (s), 1288 (m), 1158 (s), 1080 (m), 1017 (m), 1001 (m), 996 (m), 942 (w), 842 (s), 804 (m), 730 (s), 694 (m), 576 (w), 539 (m), 491 (s), 465 (m), 429 (w), 419 (w); HRMS: LIFDI(+) *m/z* 724.26048 [$\text{Mes}_2\text{BiAs}(\text{tBu})\text{PtBu}_2$] $^+$; calcd 724.25917.

tBu₂AsP(tBu)P(tBu)AsPtBu₂ (7): Compound tBu₂AsP(tBu)Li-TfH (600 mg, 1.68 mmol, 2 equiv.) was dissolved in 20 mL Et₂O and cooled to -40°C and 1,2-dibromethane (158 mg, 0.84 mmol, 1.0 equiv.) in 20 mL Et₂O was added dropwise over 30 min. After stirring for an additional 30 min at -40°C , the reaction mixture was warmed to room temperature, and volatiles were removed under reduced pressure. Afterwards, 40 mL of *n*-pentane were added, and the remaining solids were removed by filtration. The clear filtrate was concentrated and stored at -32°C . After one week, 7 is obtained in the form of colourless crystals. Yield 58%. Elemental analysis for $\text{C}_{24}\text{H}_{54}\text{As}_2\text{P}_2$ calcd: C 51.99, H 9.82; found: C 52.21, H 9.49; ^1H NMR (500 MHz, C_6D_6): $\delta = 1.55$ (s, 36H, $\text{AsC}(\text{CH}_3)_3$), 1.52 (m, $^3J_{\text{P-H}} + ^4J_{\text{P-H}} = 15.3$ Hz, 18H, $\text{PC}(\text{CH}_3)_3$); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, C_6D_6): $\delta = 39.4$ (s, 4C, $\text{AsC}(\text{CH}_3)_3$), 36.4 (m, 2C, $^1J_{\text{P-C}} + ^2J_{\text{P-C}} = 20.2$ Hz, $\text{PC}(\text{CH}_3)_3$), 33.7 (m, 12C, $^3J_{\text{P-C}} + ^4J_{\text{P-C}} = 4.4$ Hz, $\text{AsC}(\text{CH}_3)_3$), 33.6 (m, 6C, $^2J_{\text{P-C}} + ^3J_{\text{P-C}} = 20.9$ Hz, $\text{PC}(\text{CH}_3)_3$); $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, C_6D_6): $\delta = 10.2$ (brs, 2P, As-P-P-As); IR (cm^{-1}): 2982 (m), 2964 (m), 2932 (m), 2874 (s), 2850 (s), 2703 (w), 1471 (m), 1455 (m), 1440 (m), 1384 (m), 1356 (s), 1191 (w), 1149 (s), 1008 (m), 935 (w), 802 (m), 565 (w), 534 (w), 518 (w), 421 (w); HRMS: LIFDI(+) *m/z* 554.21435 [tBu₂AsP(tBu)P(tBu)AsPtBu₂] $^+$; calcd 554.21327.

Pnictogenidene transfer reactions

Me₂IIme = PtBu (8): Compound 1_{ph} (15 mg, 0.02 mmol, 1.0 equiv.) was dissolved in 0.5 mL C_6D_6 and the Me₂IIme (4 mg, 0.02 mmol, 1.0 equiv.) was added at room temperature, whereupon the solutions turned dark red. The obtained solution was analysed by NMR spectroscopy after 10 min, 1 day, and 4 days. NMR data of compound 8: ^1H NMR (300 MHz, C_6D_6): $\delta = 3.38$ (s, 6H, NCH_3), 1.67 (d, $^3J_{\text{P-H}} = 11.1$ Hz, 9H, $\text{PC}(\text{CH}_3)_3$), 1.33 (s, 6H, CCH_3); ^{13}C NMR (300 MHz, C_6D_6): $\delta = 171.0$ ($\text{N}_2\text{C}=\text{P}$, found by HMBC); 122.7 (d, $^3J_{\text{P-C}} = 3.5$ Hz, 2C, $\text{N}-\text{C}-\text{CH}_3$), 36.5 (d, $^2J_{\text{P-C}} = 17.1$ Hz, 3C, $\text{PC}(\text{CH}_3)_3$), 34.9 (d, $^3J_{\text{P-C}} = 12.1$ Hz, 2C, NCH_3), 31.8 (d, $^1J_{\text{P-C}} = 44.6$ Hz, 2C, $\text{PC}(\text{CH}_3)_3$), 8.9 (s, 2C, CCH_3); $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, C_6D_6): $\delta = -31.1$ (s, 1P, $\text{C}=\text{PC}(\text{CH}_3)_3$).

X-ray diffraction analysis: Single-crystal X-ray diffraction analysis was conducted using a Stoe IPDS 2 and an IPDS 2T diffractometer. The diffractometers use $\text{MoK}\alpha$ ($\lambda = 0.71073$ Å) radiation and respective X-ray optics. Structures were solved by intrinsic phasing using SHELXT-2015. Structures were refined through full-matrix-least-

squares against F^2 using SHELXL-2015. All structures were solved and refined by using the OLEX2 platform.

Deposition Numbers 2207778 (1_{ph}), 2207783 (2_{ph}), 2207779 (3_{ph}), 2207780 (2_{Mes}), 2207777 (4_{ph}), 2207781 (4_{Mes}), 2207782 (5_{ph}), 2207787 (5_{Mes}), 2207784 (6_{ph}), 2207785 (6_{Mes}) and 2207786 (7) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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Supporting Information

**Heavy Chains: Synthesis, Reactivity and Decomposition of
Interpnictogen Chains with Terminal Diaryl Bismuth
Fragments**

Tobias Dunaj and Carsten von Hänisch*

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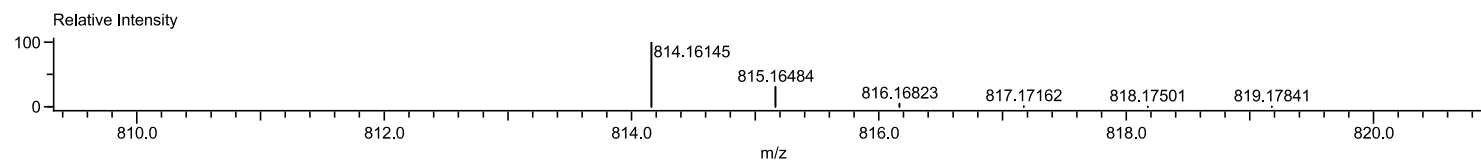
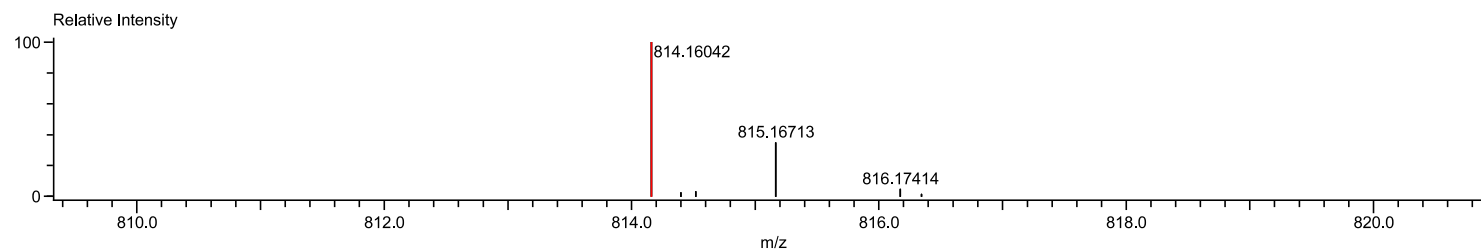
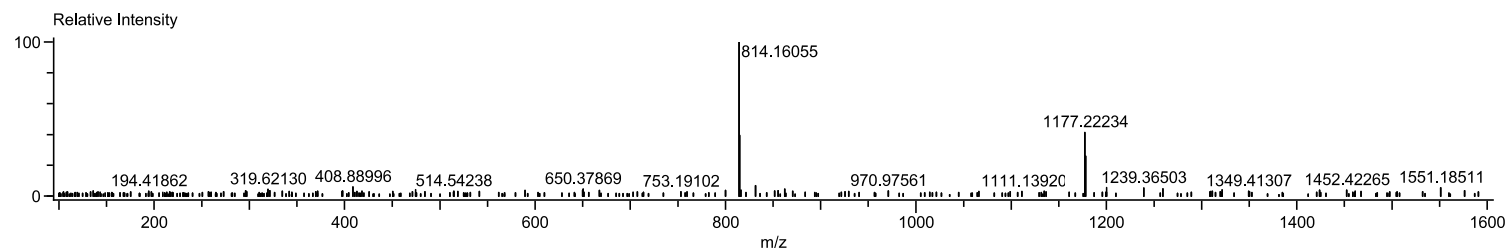
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3. Crystallographic Data

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1. Mass spectra

1.1 Ph₂BiP(*t*Bu)BiPh₂ (1_{Ph})



Mass	Intensity	Relative Intensity	Calc. Mass	Mass Difference [mDa]	Mass Difference [ppm]	Possible Formula	Unsaturation Number
814.16042	13495.56	100.00	814.16145	-1.03	-1.27	¹² C ₂₈ ¹ H ₂₉ ²⁰⁹ Bi ₂ ³¹ P ₁	17.0

Figure S1.1. HR-LIFDI(+) Mass spectrum of Ph₂BiP(*t*Bu)BiPh₂ (1_{Ph}) as [M]⁺. Top: Whole spectrum. Middle: High resolution extract. Bottom: Calculated isotope pattern.

1.2 Ph₂BiAs(*t*Bu)BiPh₂ (**2Ph**)

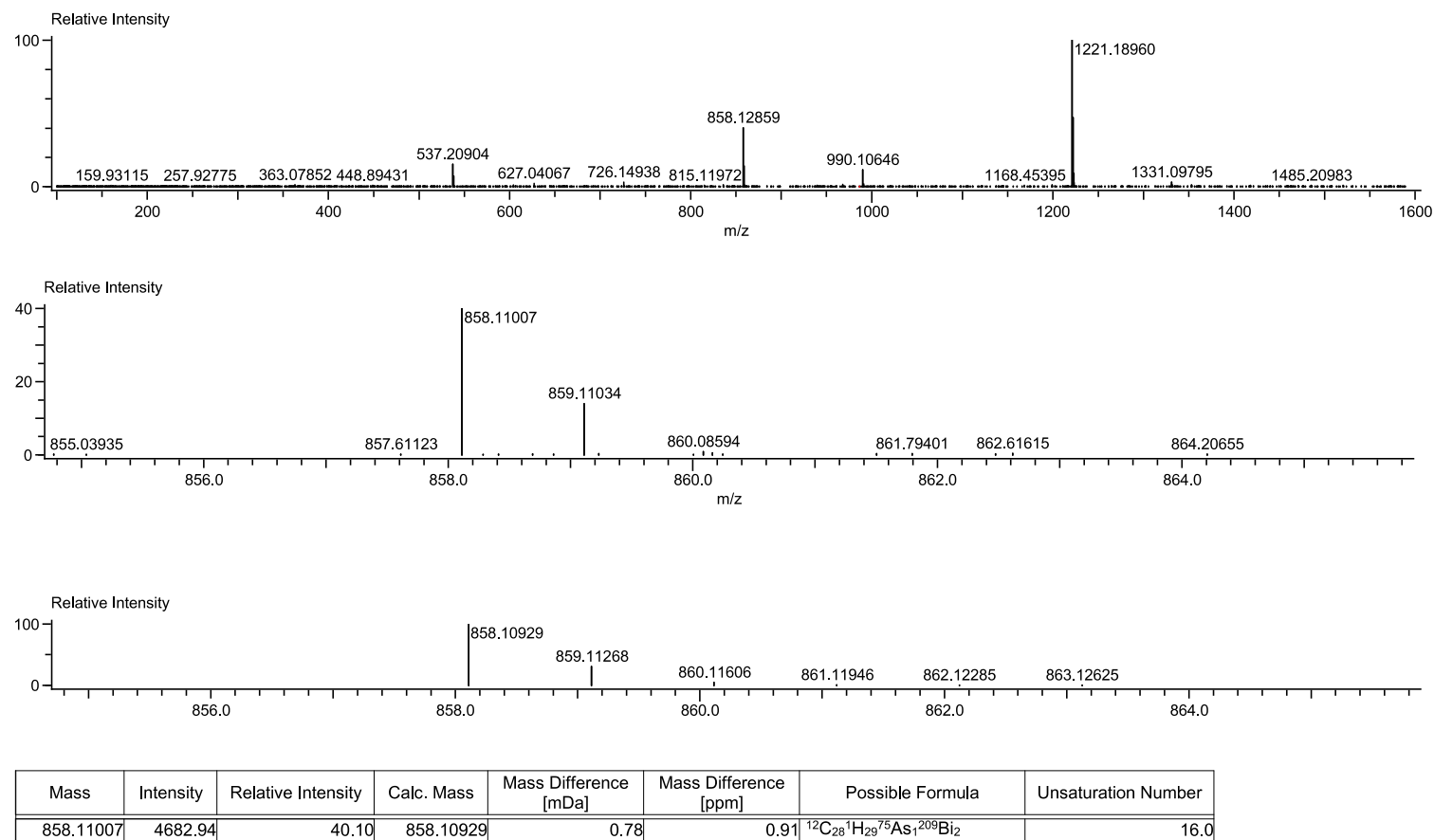


Figure S1.2. HR-LIFDI(+) Mass spectrum of Ph₂BiAs(*t*Bu)BiPh₂ (**2Ph**) as [M + H]⁺. Top: Whole spectrum. Middle: High resolution extract. Bottom: Calculated isotope pattern.

1.3 Ph₂BiAs(*t*Bu)As(*t*Bu)BiPh₂ (**3Ph**)

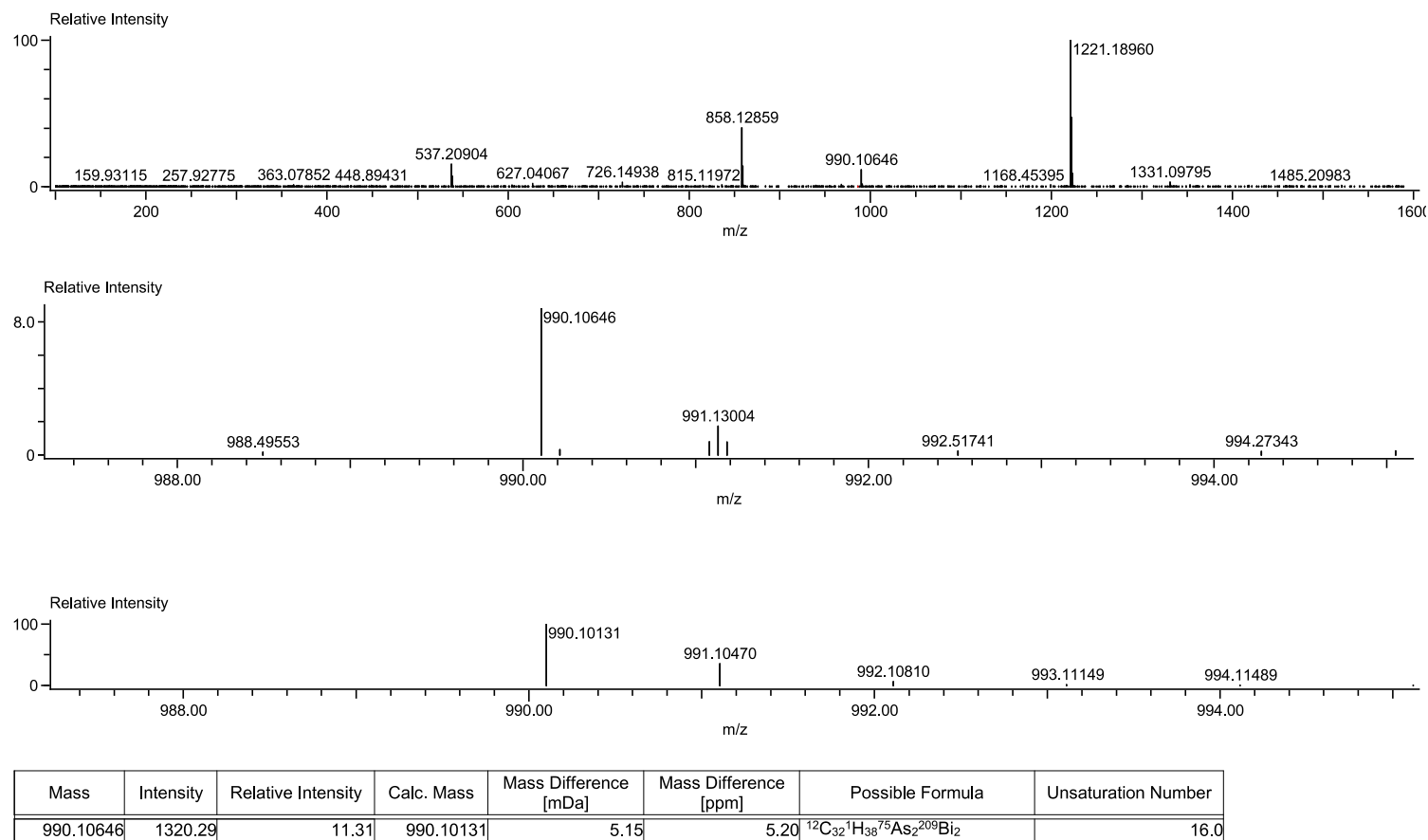


Figure S1.3. HR-LIFDI(+) Mass spectrum of Ph₂BiAs(*t*Bu)As(*t*Bu)BiPh₂ (**3Ph**) as [M]⁺. Top: Whole spectrum. Middle: High resolution extract. Bottom: Calculated isotope pattern.

1.4 Mes₂BiAs(*t*Bu)BiMes₂ (2Mes)

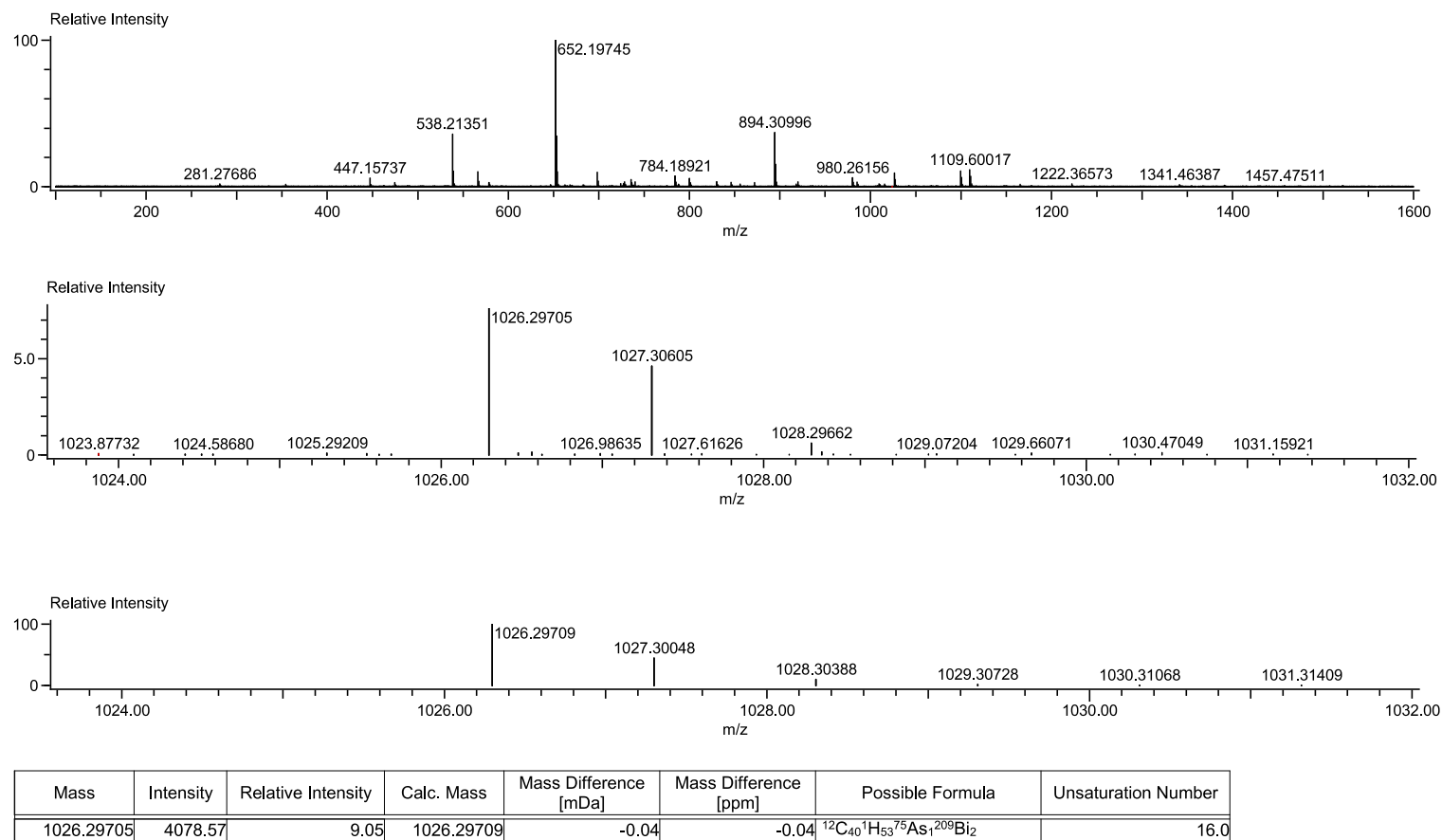


Figure S1.4. HR-LIFDI(+) Mass spectrum of Mes₂BiAs(*t*Bu)BiMes₂ (2Mes) as [M]⁺. Top: Whole spectrum. Middle: High resolution extract. Bottom: Calculated isotope pattern.

1.5 Ph₂BiP(*t*Bu)As*t*Bu₂ (4Ph)

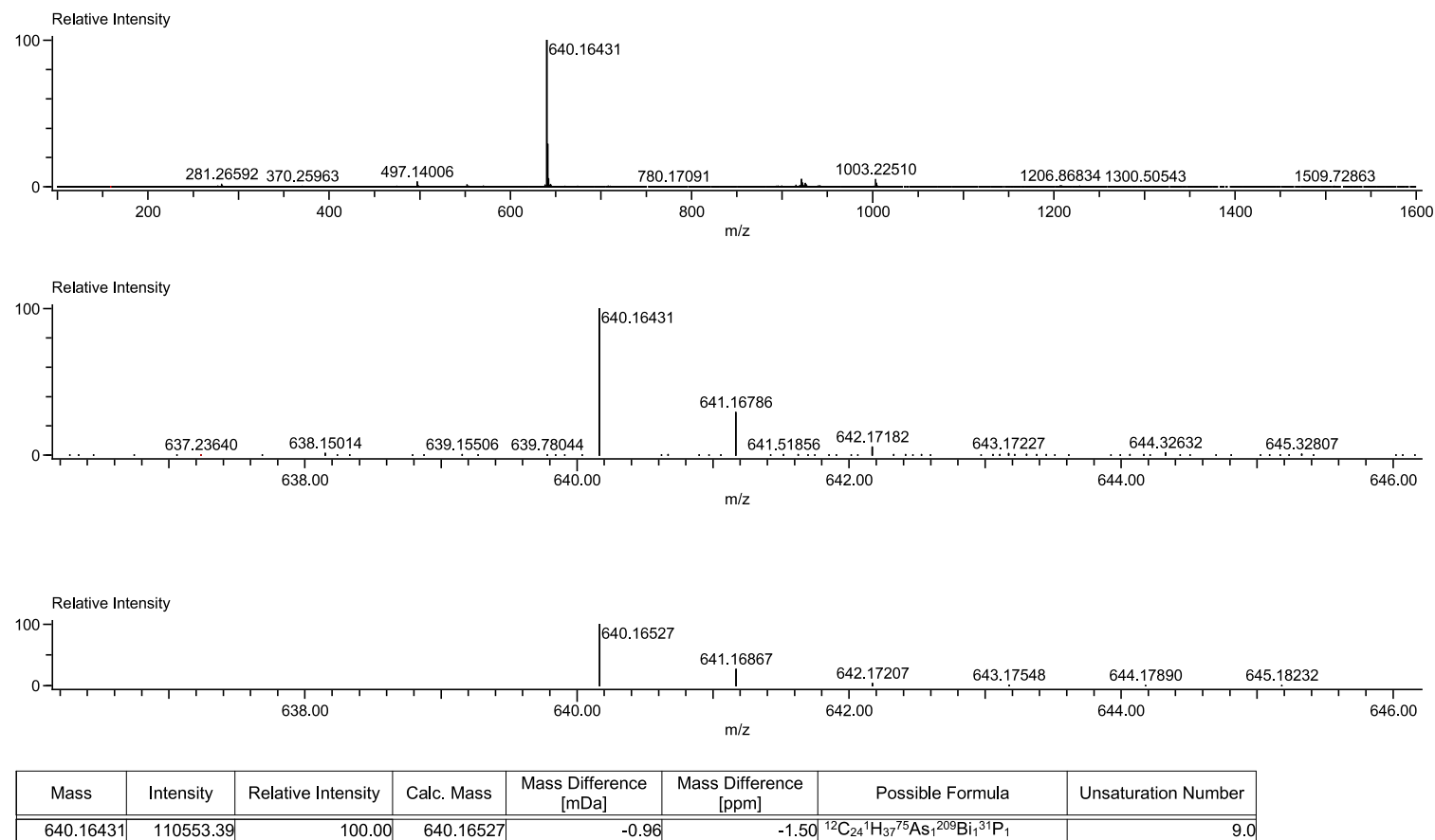


Figure S1.5. HR-LIFDI(+) Mass spectrum Ph₂BiP(*t*Bu)As*t*Bu₂ (4Ph) as [M]⁺. Top: Whole spectrum. Middle: High resolution extract. Bottom: Calculated isotope pattern.

1.6 Mes₂BiP(*t*Bu)As*t*Bu₂ (4Mes)

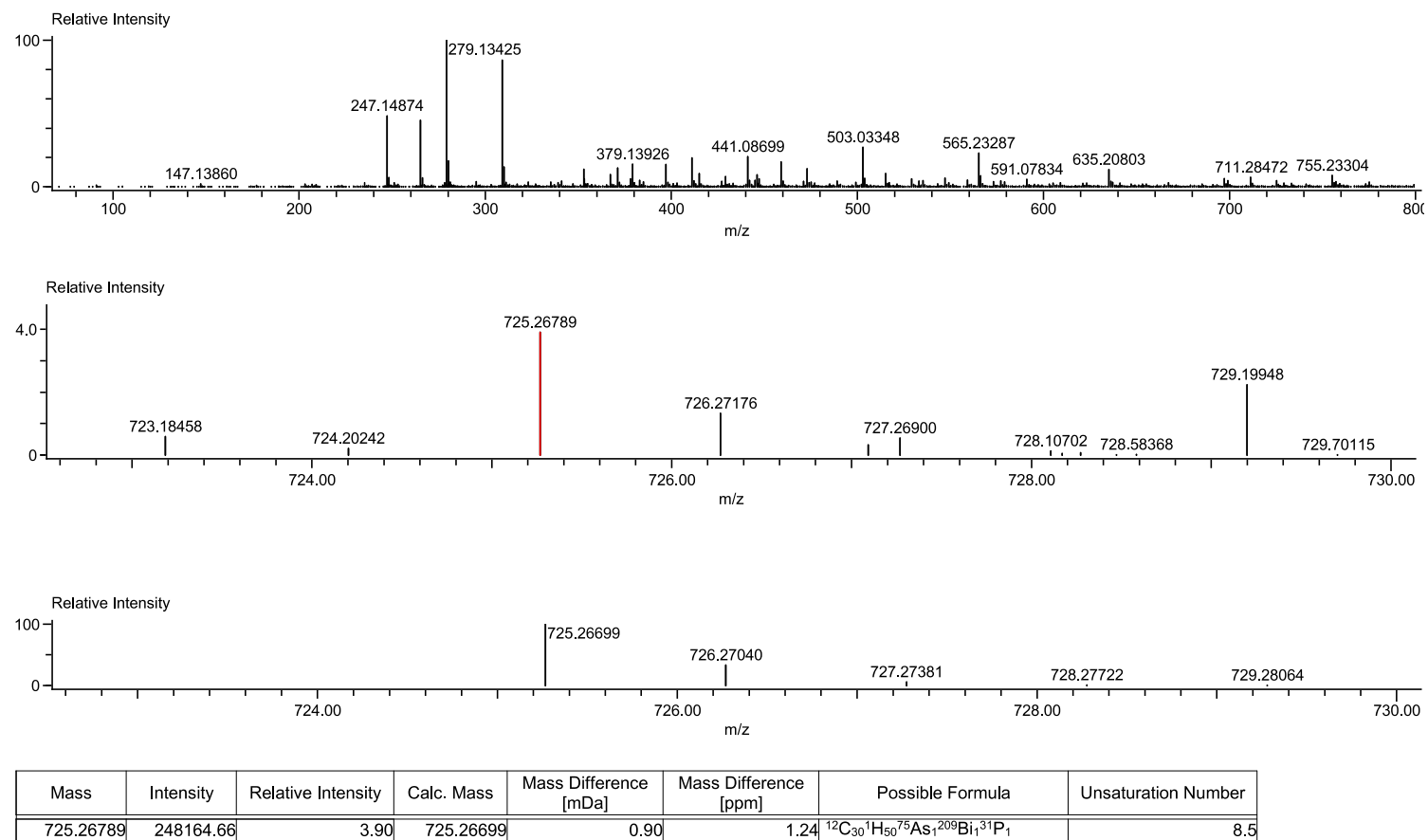


Figure S1.6. HR-Cl(+)
Mass spectrum of Mes₂BiP(*t*Bu)As*t*Bu₂ (4Mes) as [M+H]⁺. Top: Whole spectrum. Middle: High resolution extract. Bottom: Calculated isotope pattern.

1.7 Ph₂BiP(*t*Bu)Sb*t*Bu₂ (**5Ph**)

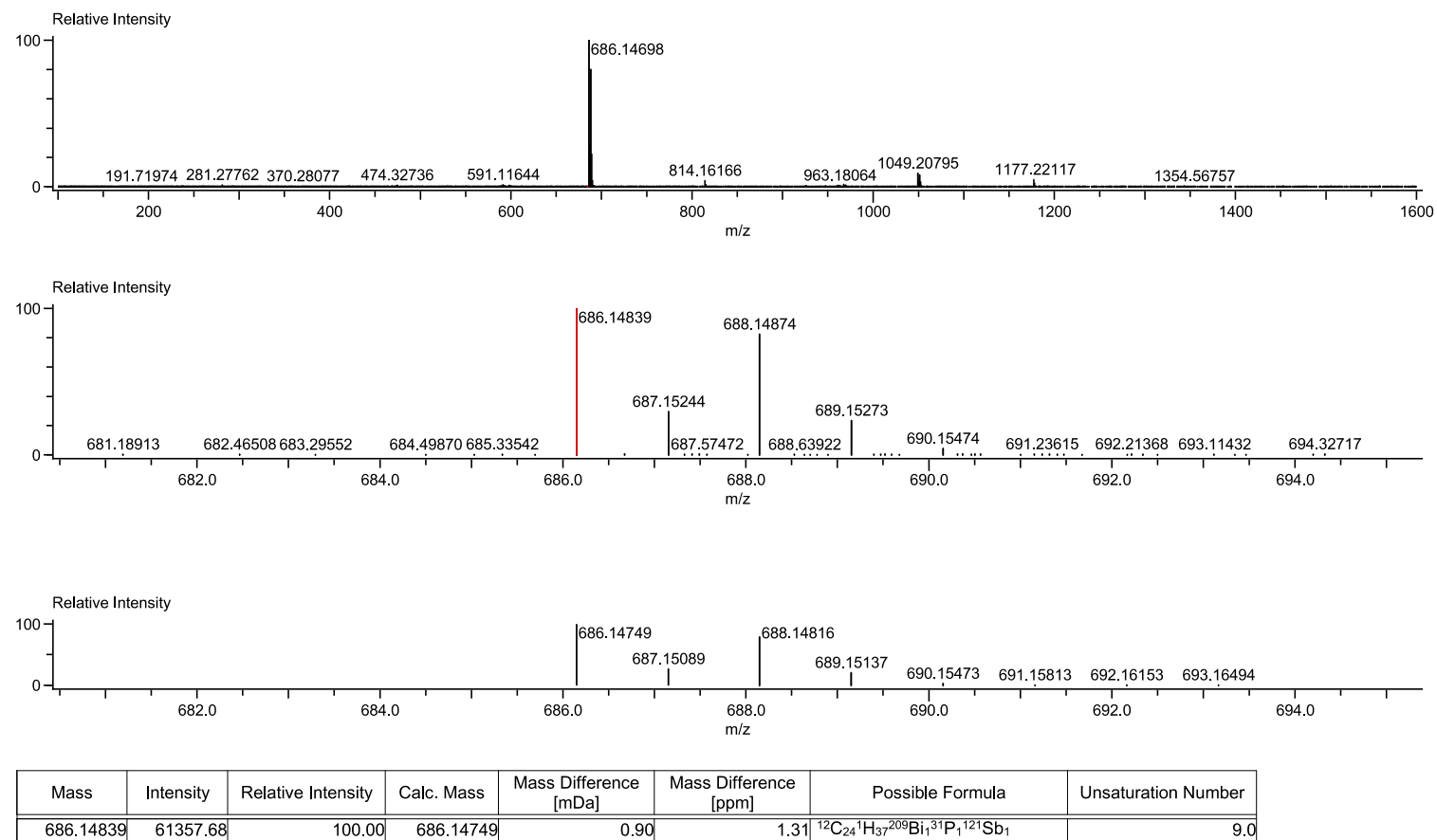


Figure S1.7. HR-LIFDI(+) Mass spectrum of Ph₂BiP(*t*Bu)Sb*t*Bu₂ (**5Ph**) as [M]⁺. Top: Whole spectrum. Middle: High resolution extract. Bottom: Calculated isotope pattern.

1.8 Mes₂BiP(*t*Bu)Sb*t*Bu₂ (5Mes)

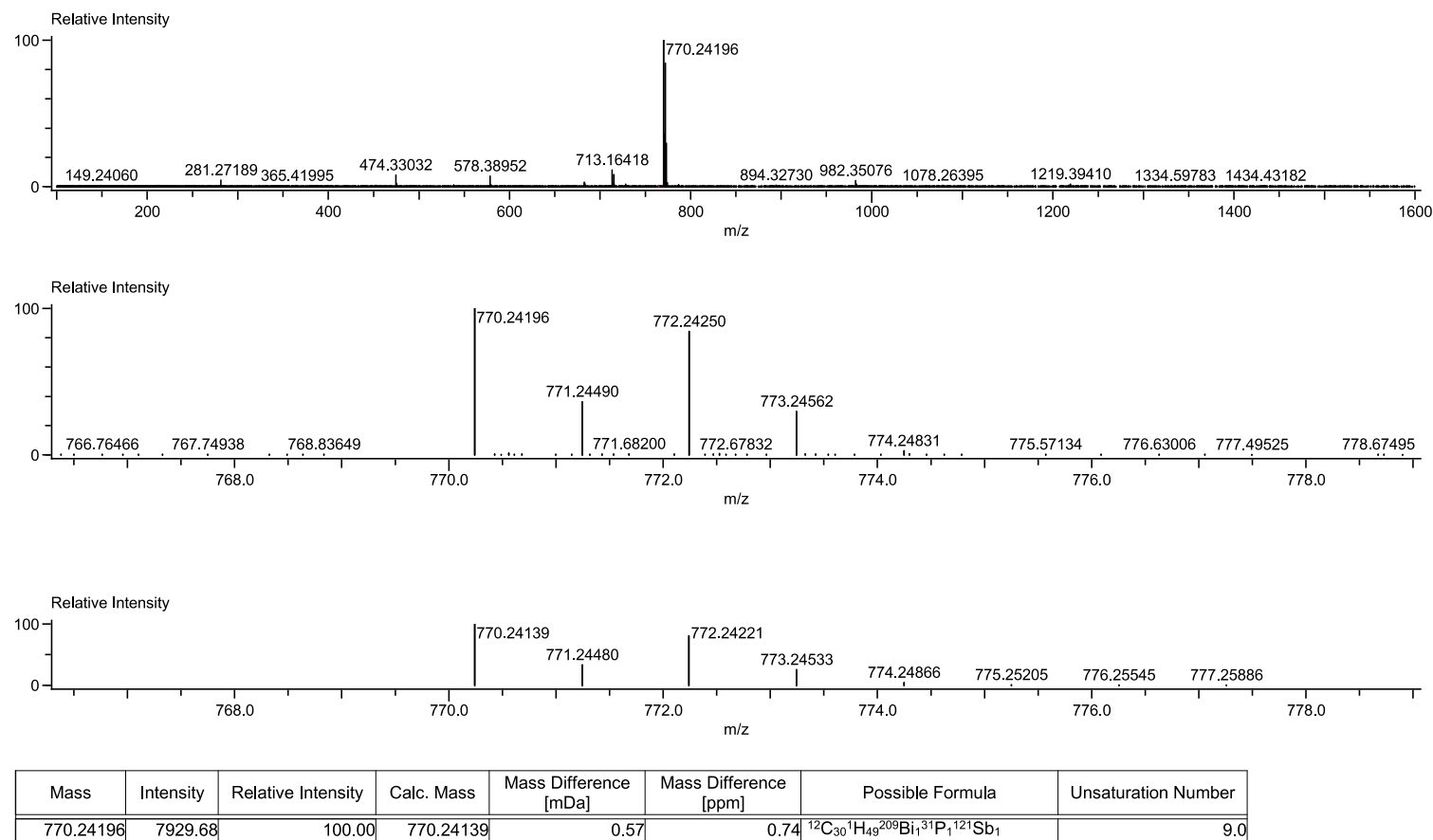


Figure S1.8. HR-LIFDI(+) Mass spectrum of Mes₂BiP(*t*Bu)Sb*t*Bu₂ (5Mes) as [M]⁺. Top: Whole spectrum. Middle: High resolution extract. Bottom: Calculated isotope pattern.

1.9 Ph₂BiAs(*t*Bu)P*t*Bu₂ (**6Ph**)

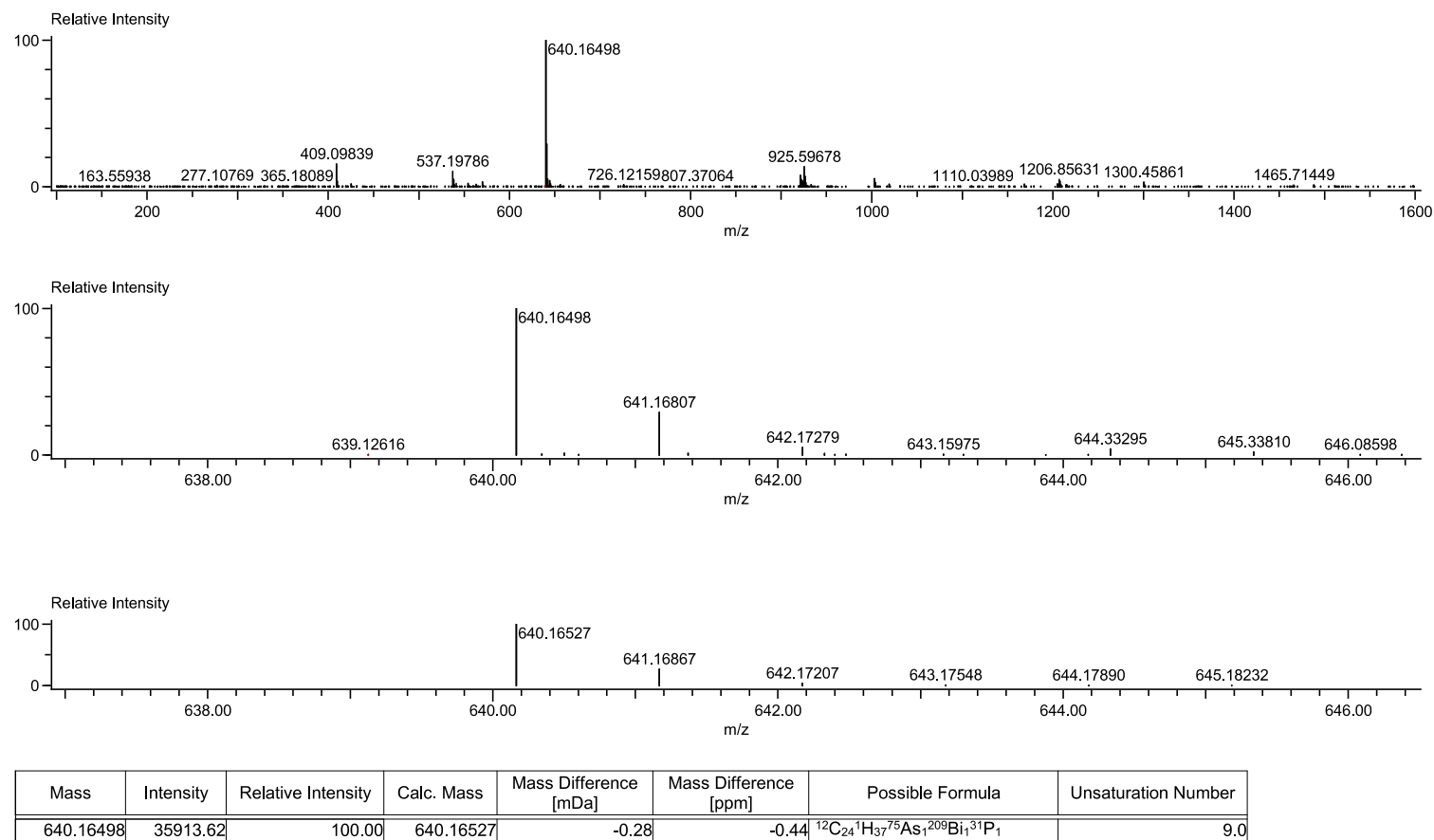


Figure S1.9. HR-LIFDI(+) Mass spectrum of Ph₂BiAs(*t*Bu)P*t*Bu₂ (**6Ph**) as [M]⁺. Top: Whole spectrum. Middle: High resolution extract. Bottom: Calculated isotope pattern.

1.10 Mes₂BiAs(*t*Bu)P*t*Bu₂ (6Mes)

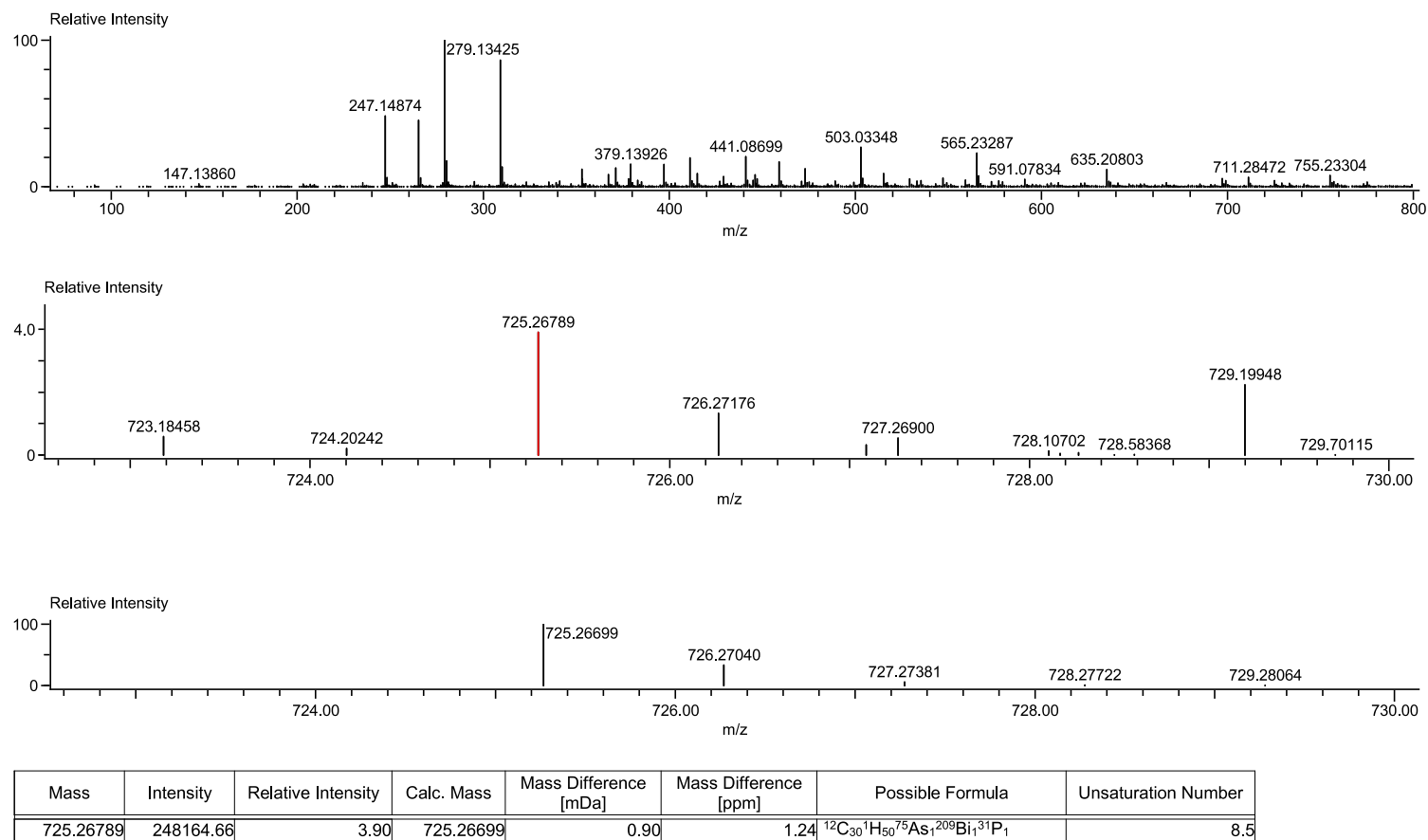


Figure S1.10. HR-LIFDI(+) Mass spectrum of Mes₂BiAs(*t*Bu)P*t*Bu₂ (6Mes) as [M+H]⁺. Top: Whole spectrum. Middle: High resolution extract. Bottom: Calculated isotope pattern.

1.11 *t*Bu₂AsP(*t*Bu)P(*t*Bu)As*t*Bu₂ (7)

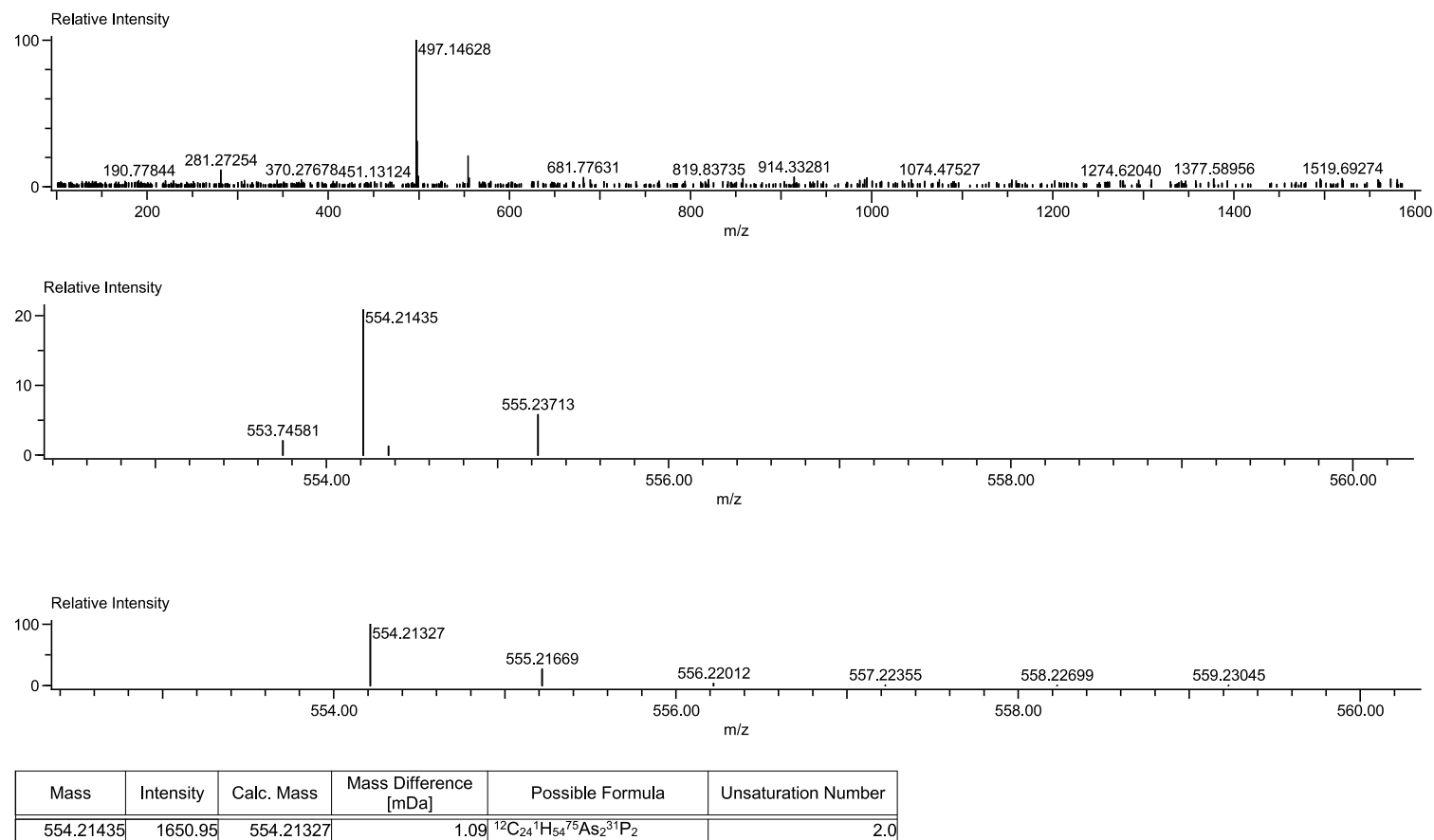


Figure S1.11. HR-LIFDI(+) Mass spectrum of *t*Bu₂AsP(*t*Bu)P(*t*Bu)As*t*Bu₂ (7) as [M]⁺. Top: Whole spectrum. Middle: High resolution extract. Bottom: Calculated isotope pattern.

2. NMR spectra

2.1 Ph₂BiP(*t*Bu)BiPh₂ (**1Ph**)

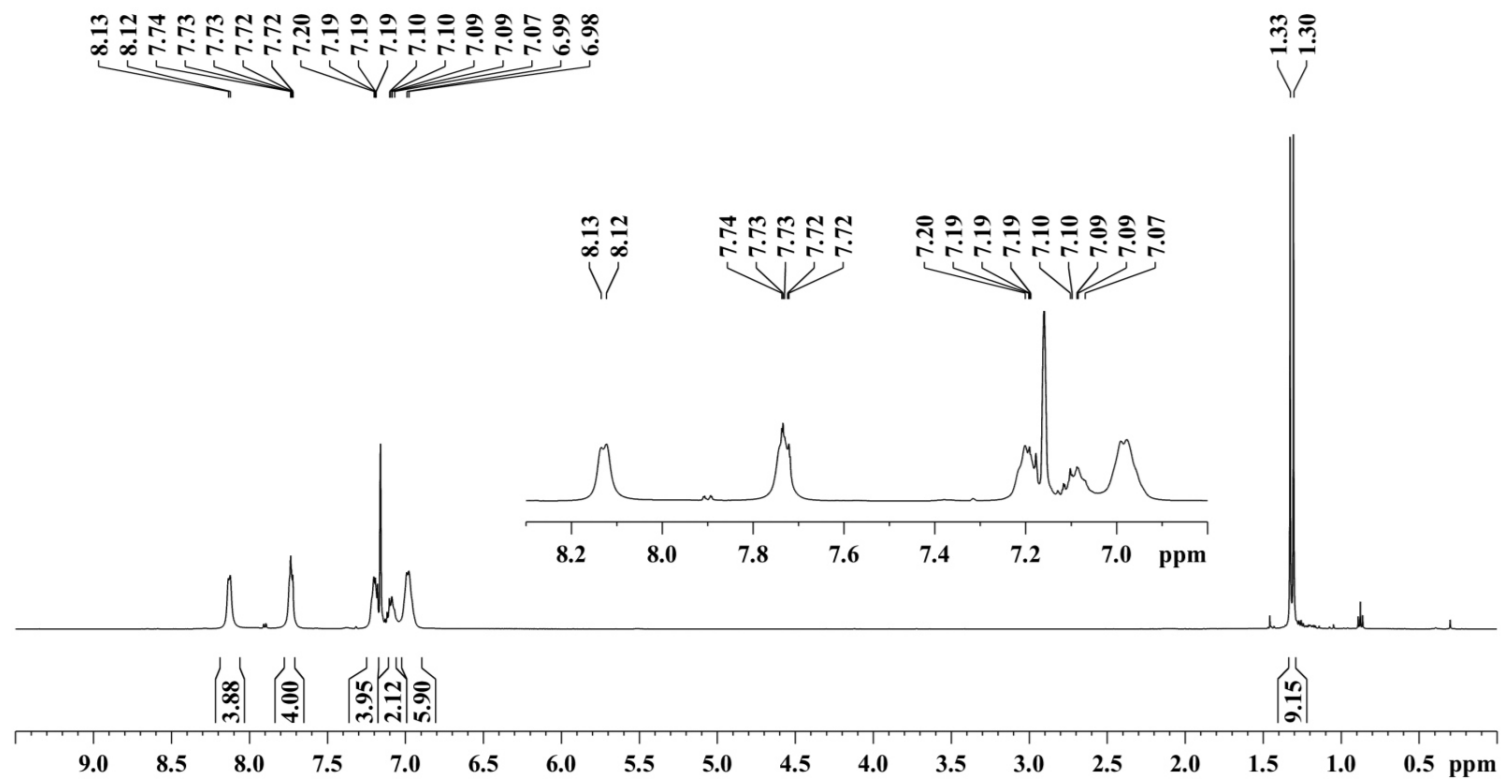


Figure S2.1.1: ¹H NMR spectrum (500 MHz) of **1Ph** in C₆D₆ at room temperature.

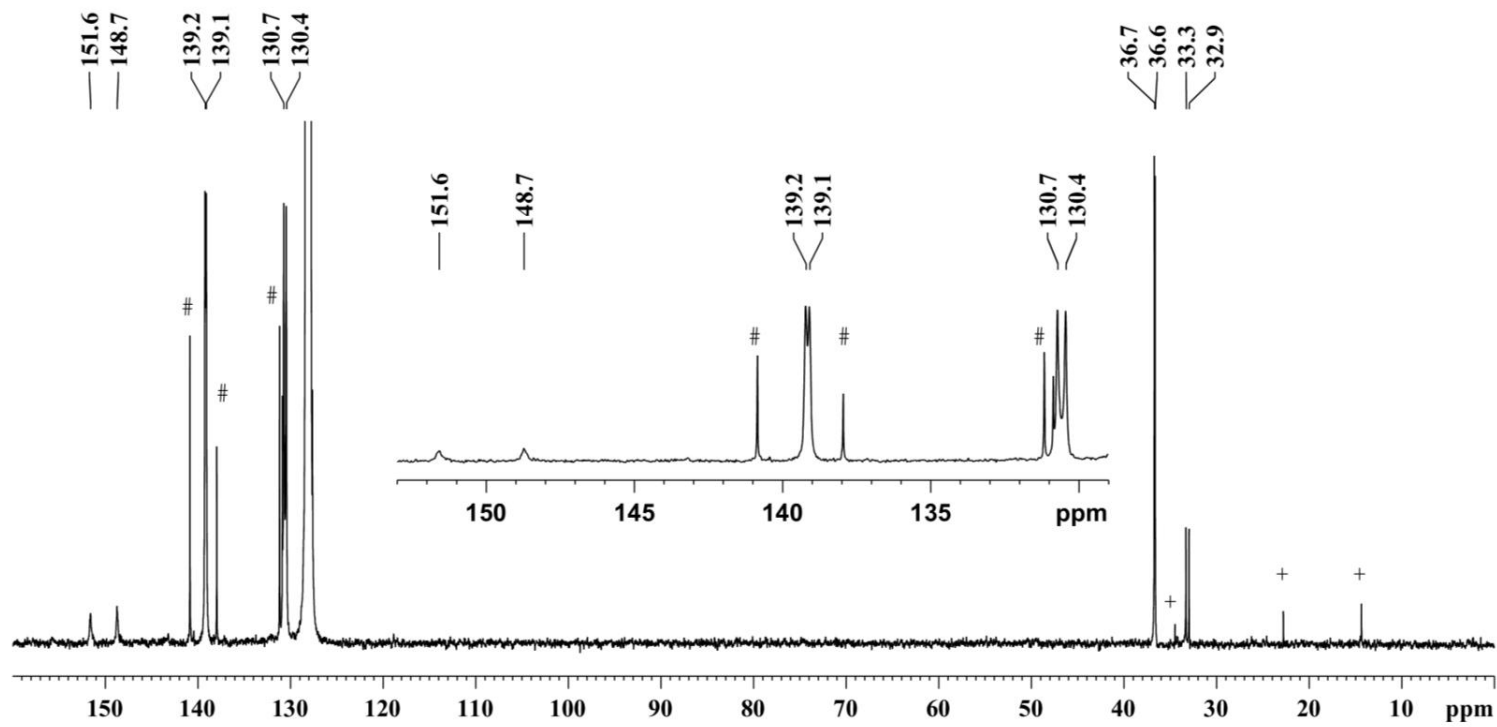


Figure S2.1.2: ^{13}C NMR spectrum (125 MHz) of **1Ph** in C_6D_6 at room temperature (# = Ph_4Bi_2 , + = *n*pentane).

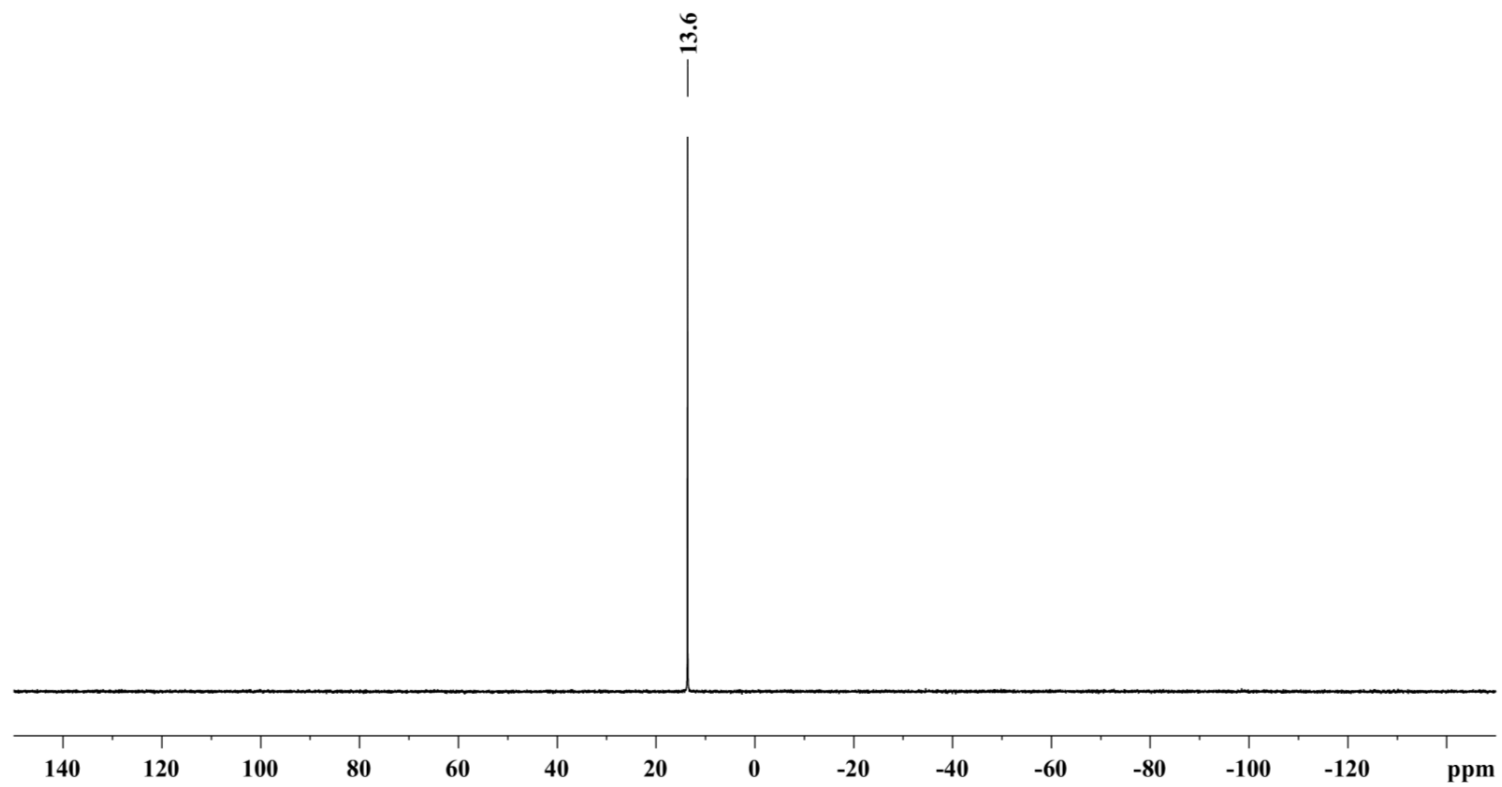


Figure S2.1.3: ^{31}P NMR spectrum (202 MHz) of **1Ph** in C_6D_6 at room temperature.

2.2 Ph₂BiAs(*t*Bu)BiPh₂ (**2Ph**)

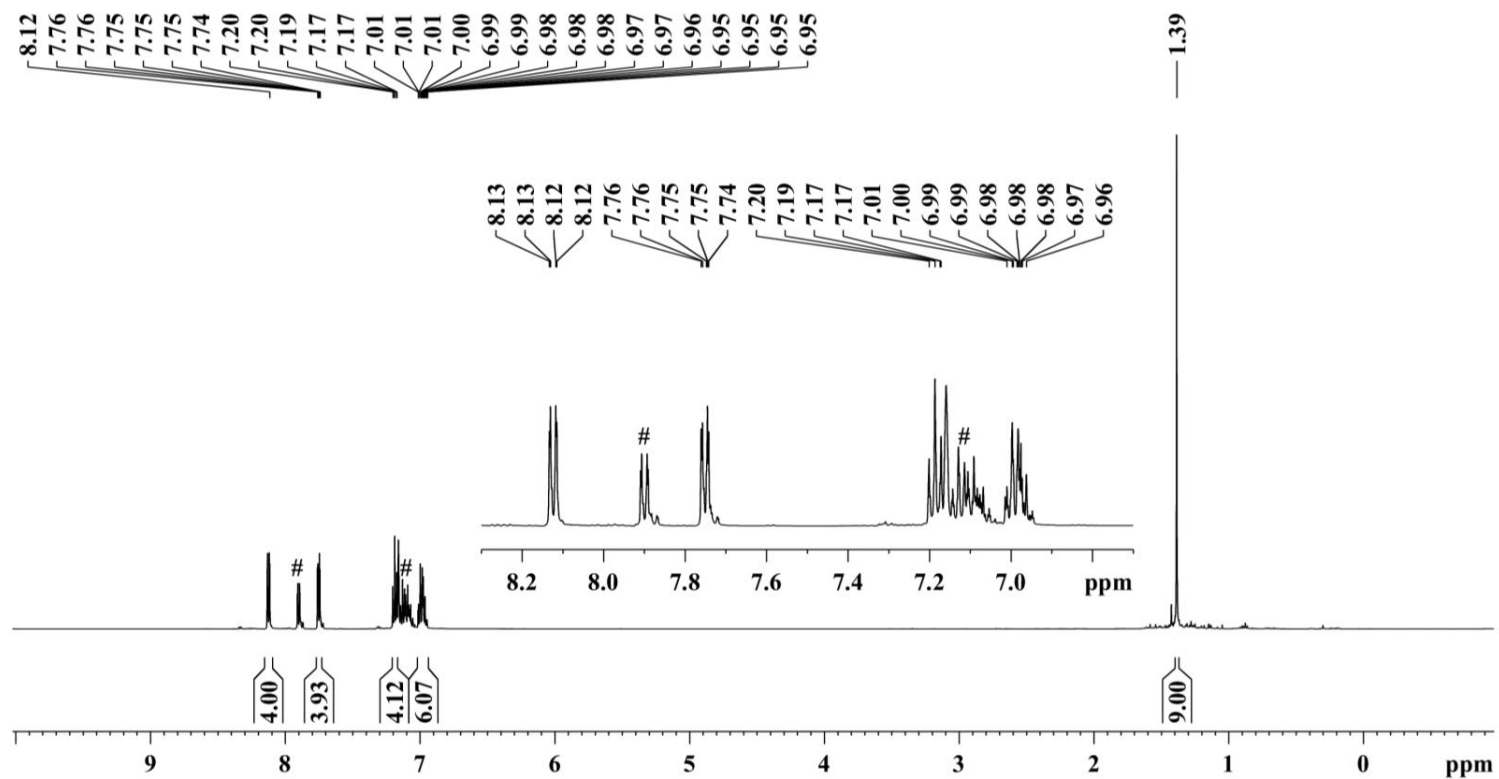


Figure S2.2.1: ¹H NMR spectrum (500 MHz) of **2Ph** in C₆D₆ at room temperature (# = Ph₄Bi₂).

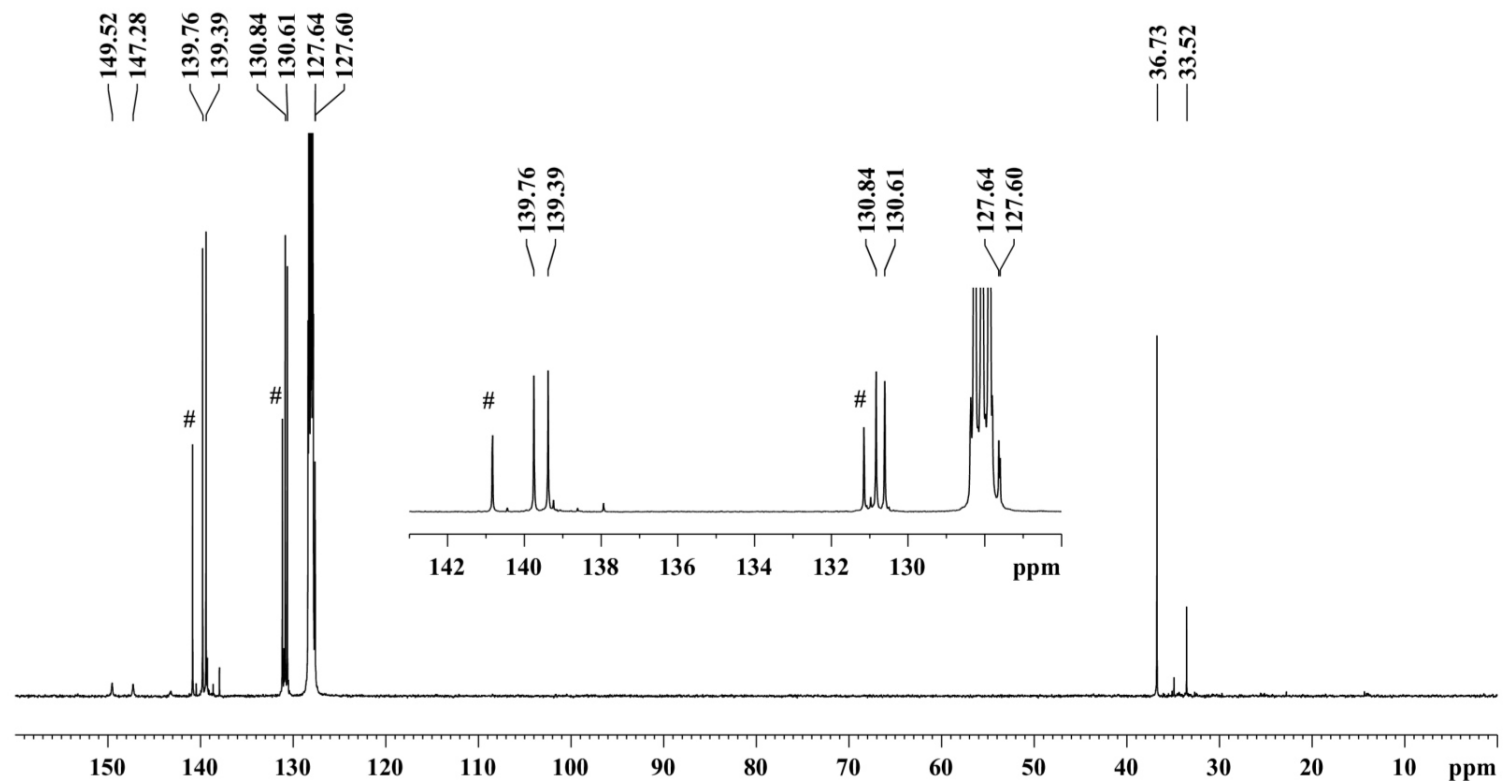


Figure S2.2.2: ^{13}C NMR spectrum (125 MHz) of **2Ph** in C_6D_6 at room temperature (# = Ph_4Bi_2).

2.3 Mes₂BiAs(*t*Bu)BiMes₂ (**2**_{Mes})

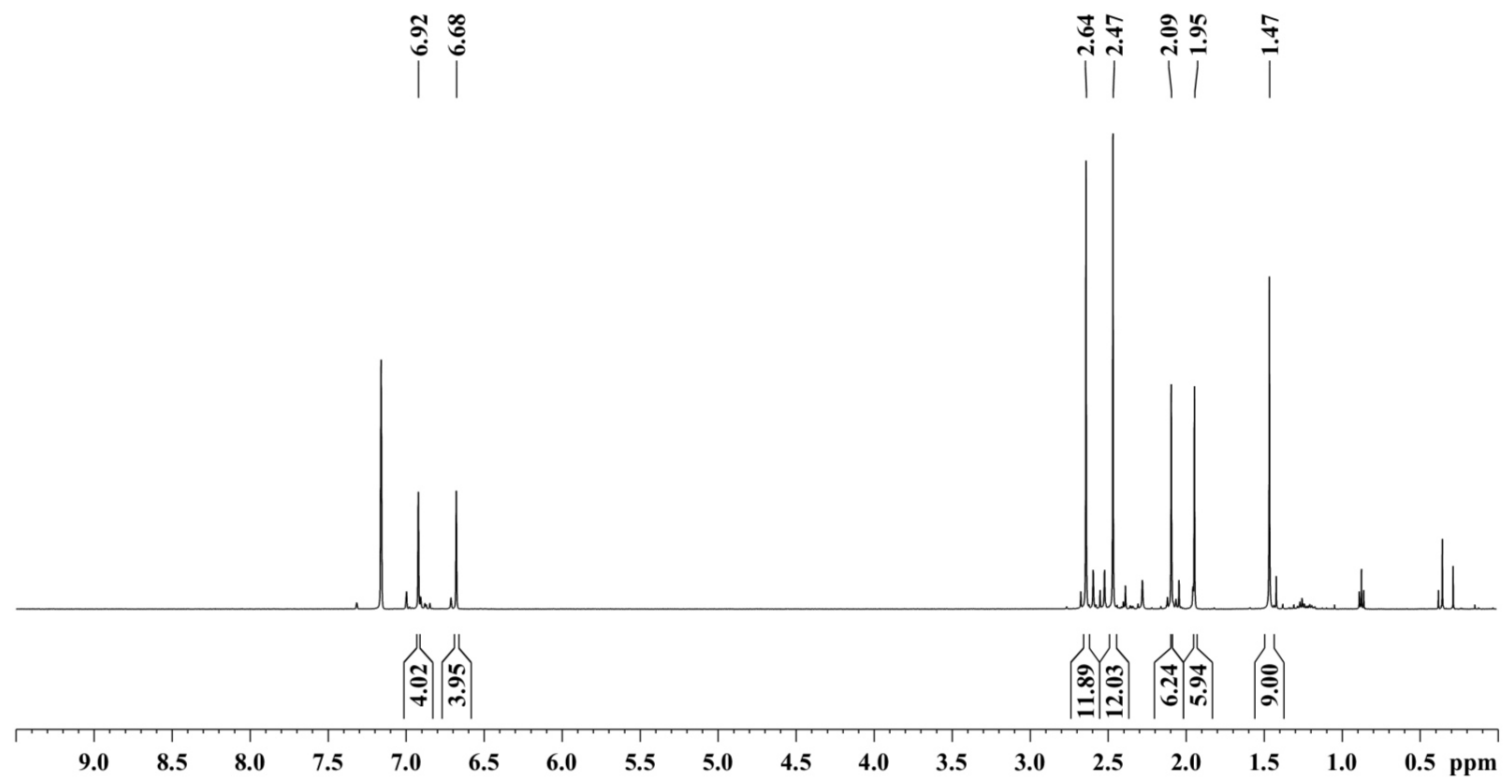


Figure S2.3.1: ¹H NMR spectrum (500 MHz) of **2**_{Mes} in C₆D₆ at room temperature.

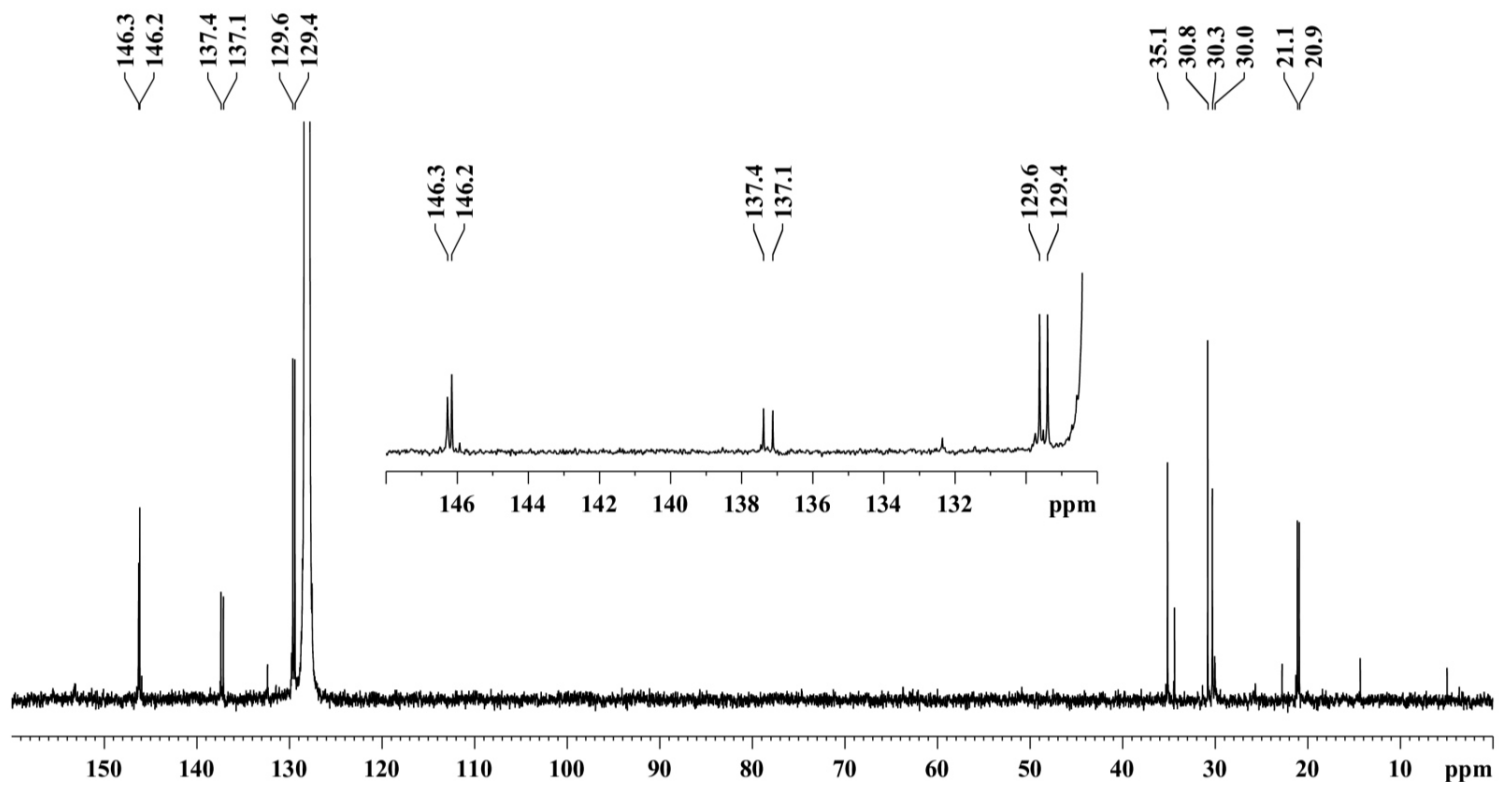


Figure S2.3.2: ^{13}C NMR spectrum (125 MHz) of **2Mes** in C_6D_6 at room temperature.

2.4 Ph₂BiP(*t*Bu)As*t*Bu₂ (**4Ph**)

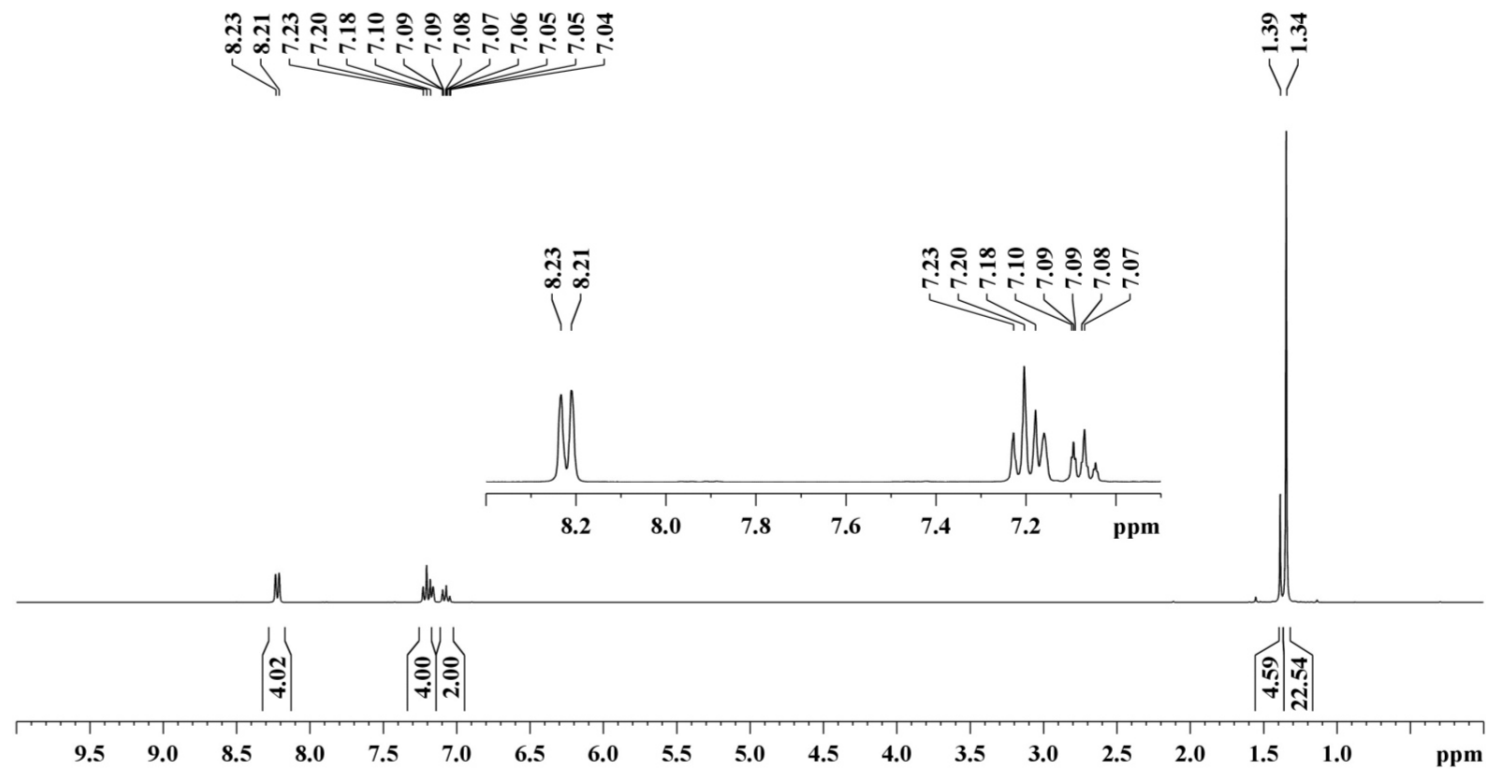


Figure S2.4.1: ¹H NMR spectrum (300 MHz) of **4Ph** in C₆D₆ at room temperature.

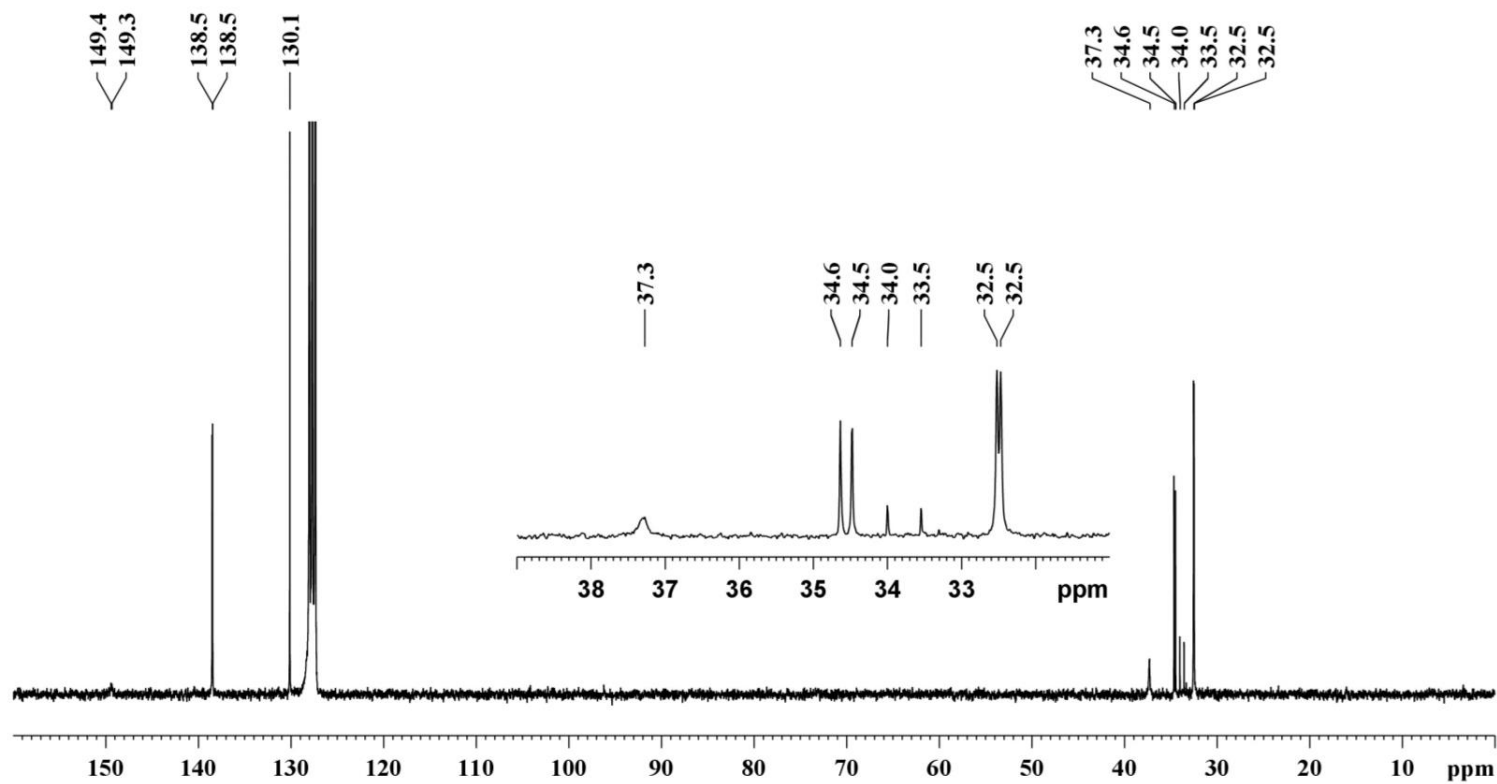


Figure S2.4.2: ^{13}C NMR spectrum (75 MHz) of **4Ph** in C_6D_6 at room temperature.

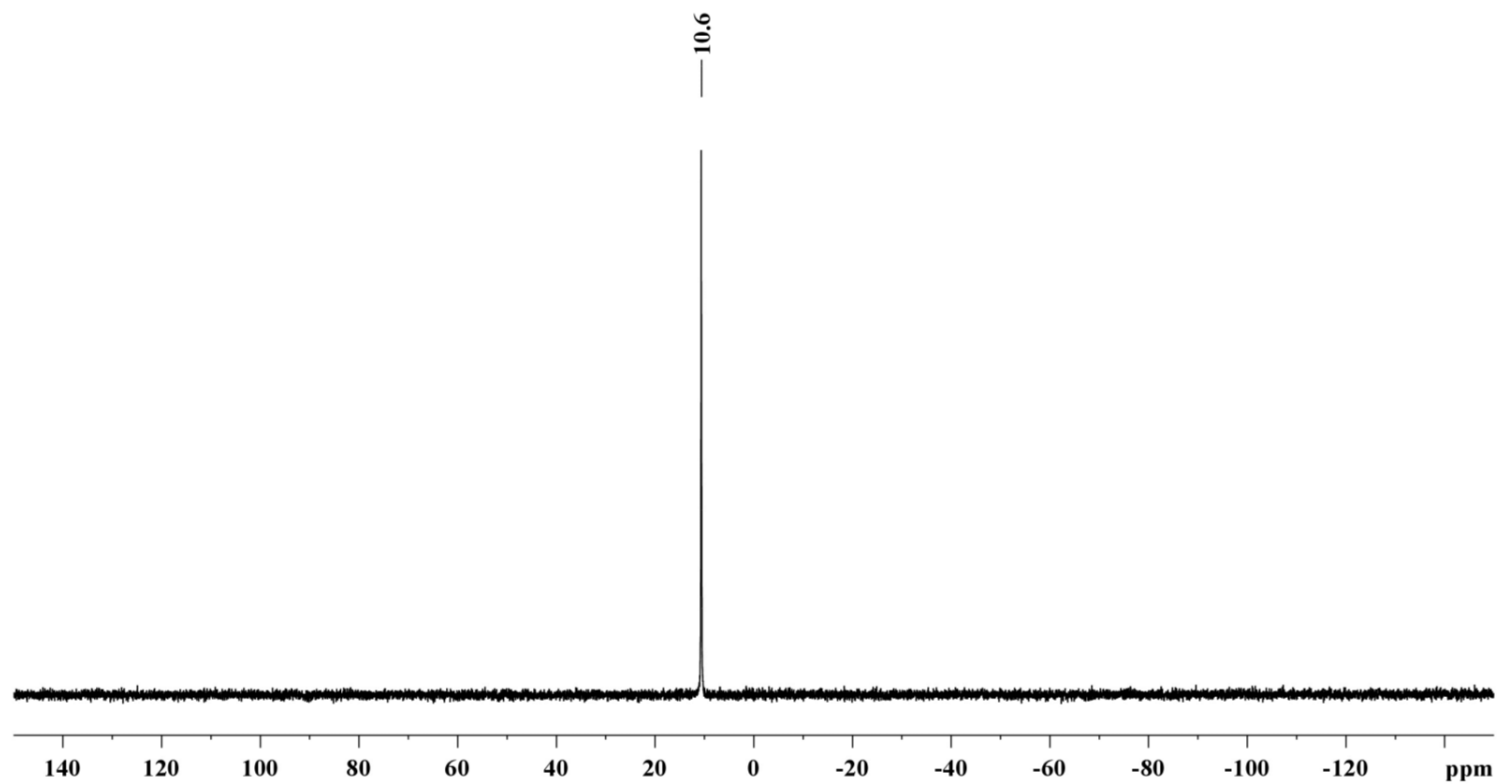


Figure S2.4.3: ^{31}P NMR spectrum (101 MHz) of **4Ph** in C_6D_6 at room temperature.ink

2.5 Mes₂BiP(*t*Bu)As*t*Bu₂ (**4Mes**)

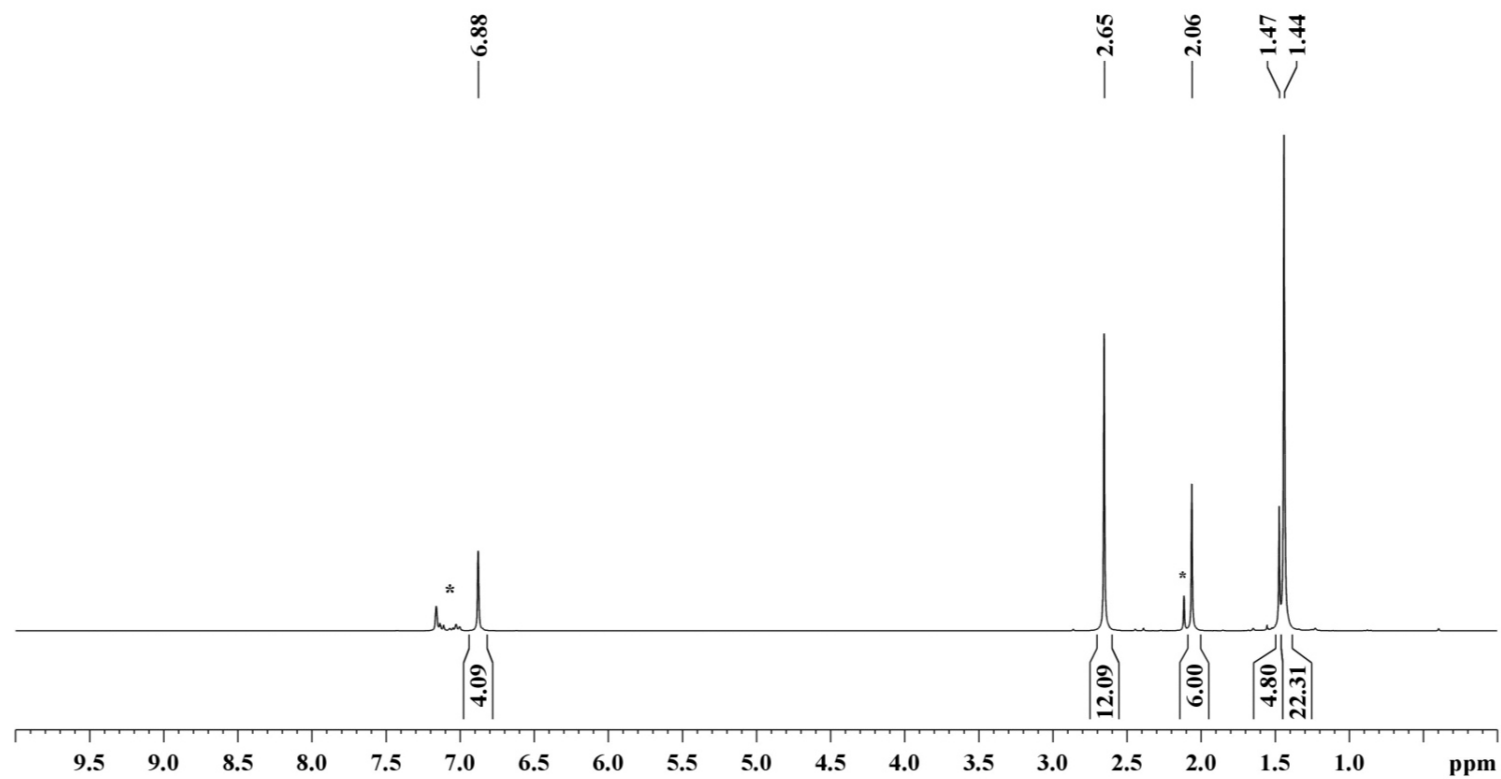


Figure S2.5.1: ¹H NMR spectrum (300 MHz) of **4Mes** in C₆D₆ at room temperature (* = toluene).

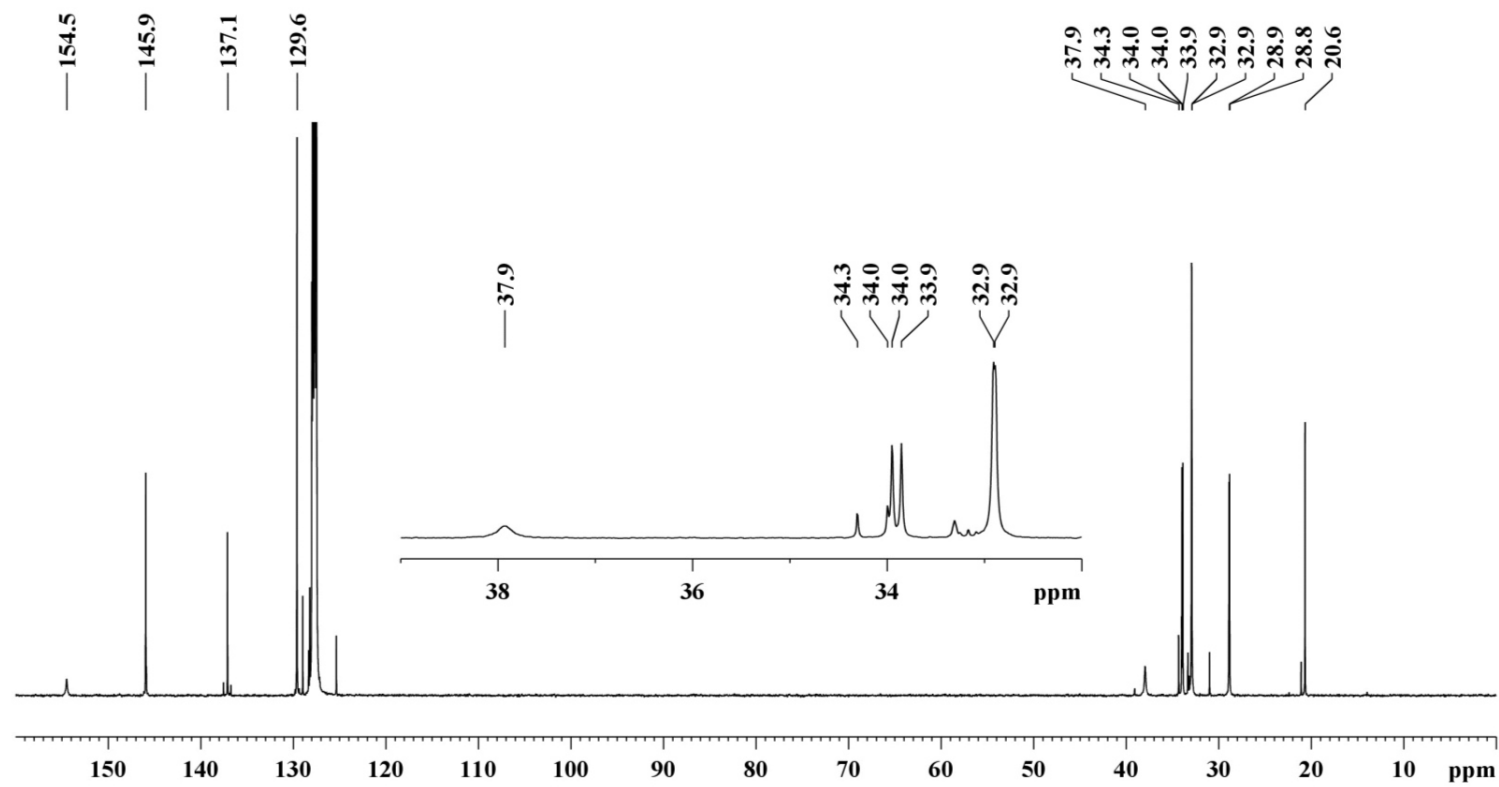


Figure S2.5.2: ^{13}C NMR spectrum (125 MHz) of **4Mes** in C_6D_6 at room temperature.

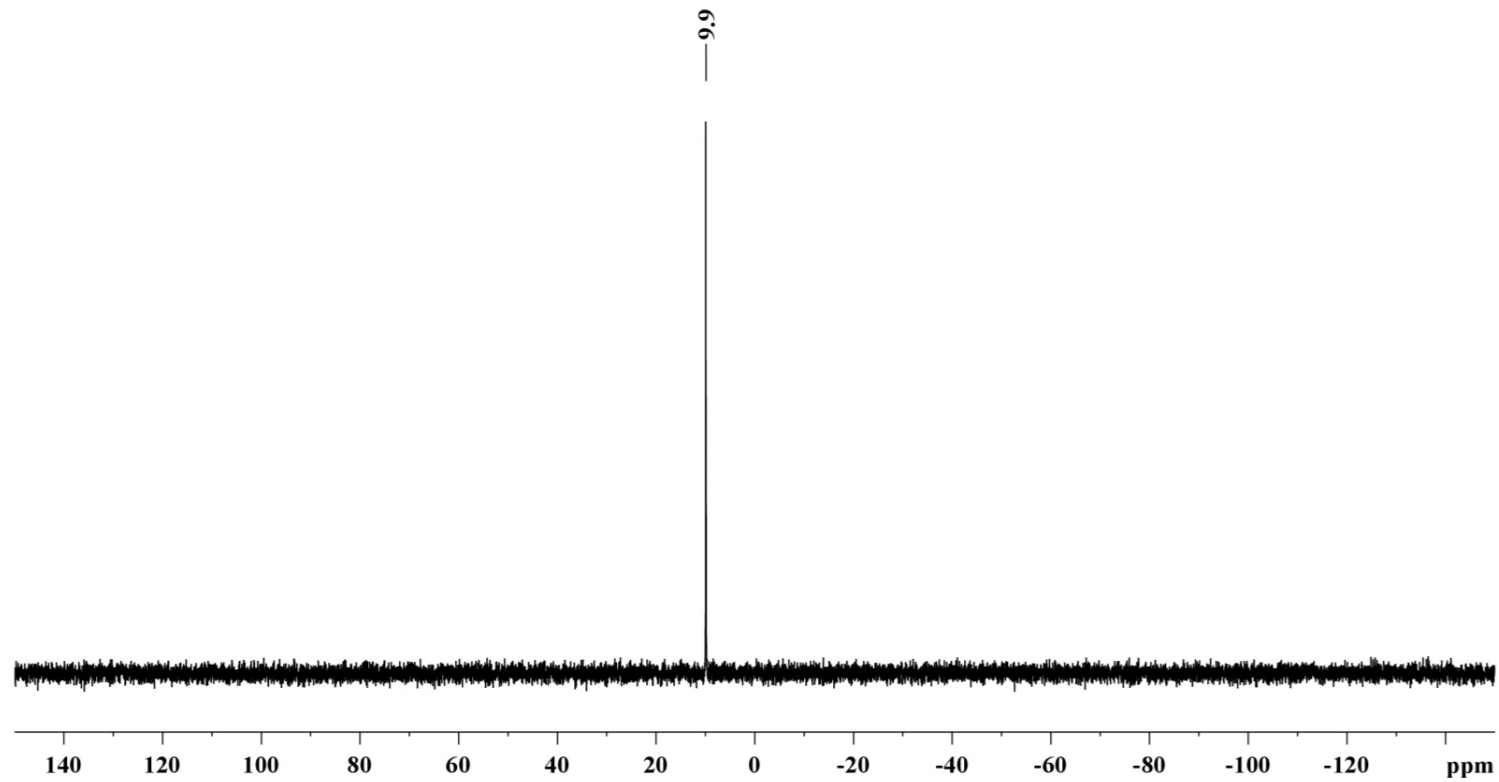


Figure S2.5.3: ^{31}P NMR spectrum (101 MHz) of **4Mes** in C_6D_6 at room temperature.

2.6 Ph₂BiP(*t*Bu)SbtBu₂ (**5Ph**)

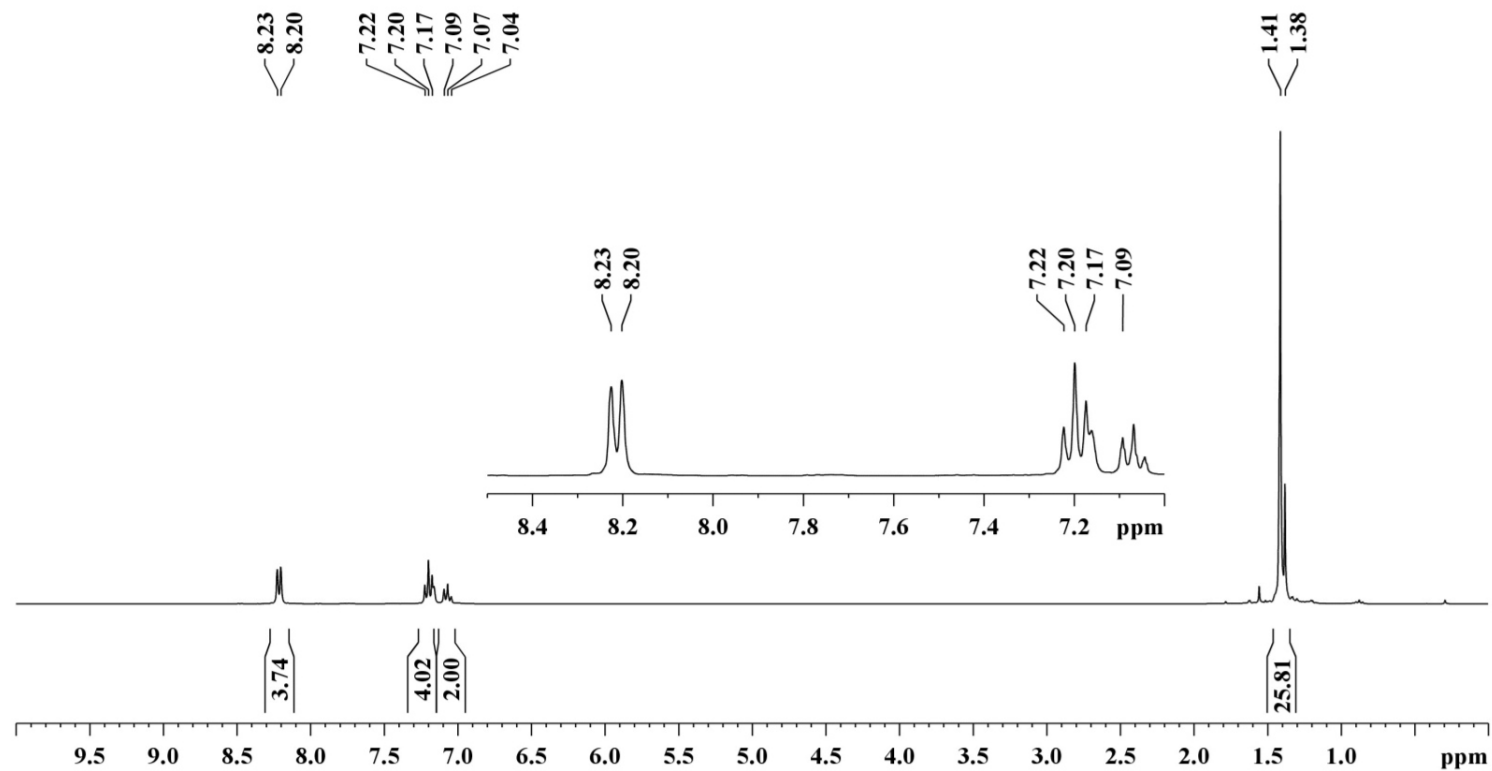


Figure S2.6.1: ¹H NMR spectrum (300 MHz) of **5Ph** in C₆D₆ at room temperature.

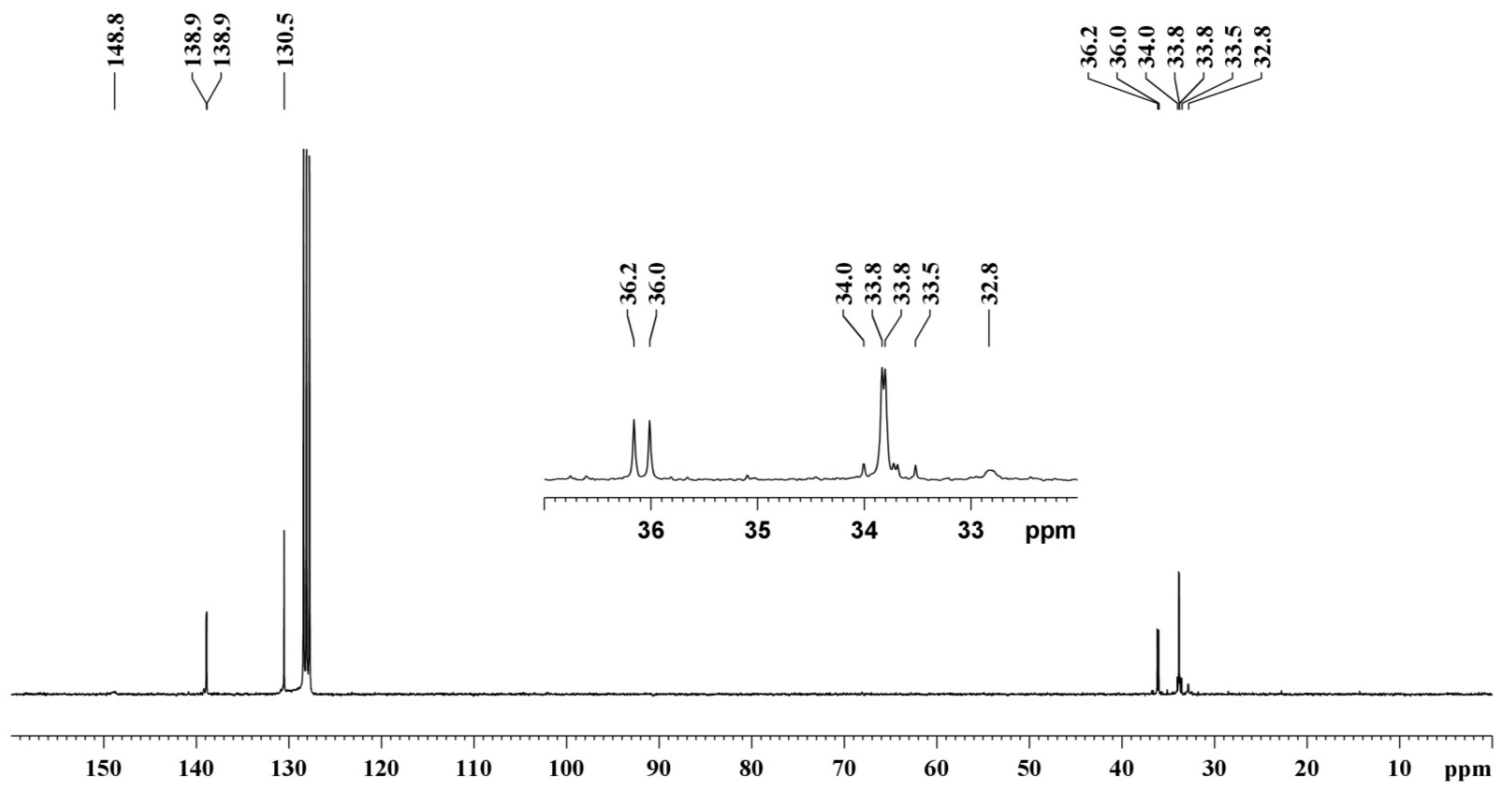


Figure S2.6.2: ^{13}C NMR spectrum (125 MHz) of **5Ph** in C_6D_6 at room temperature.

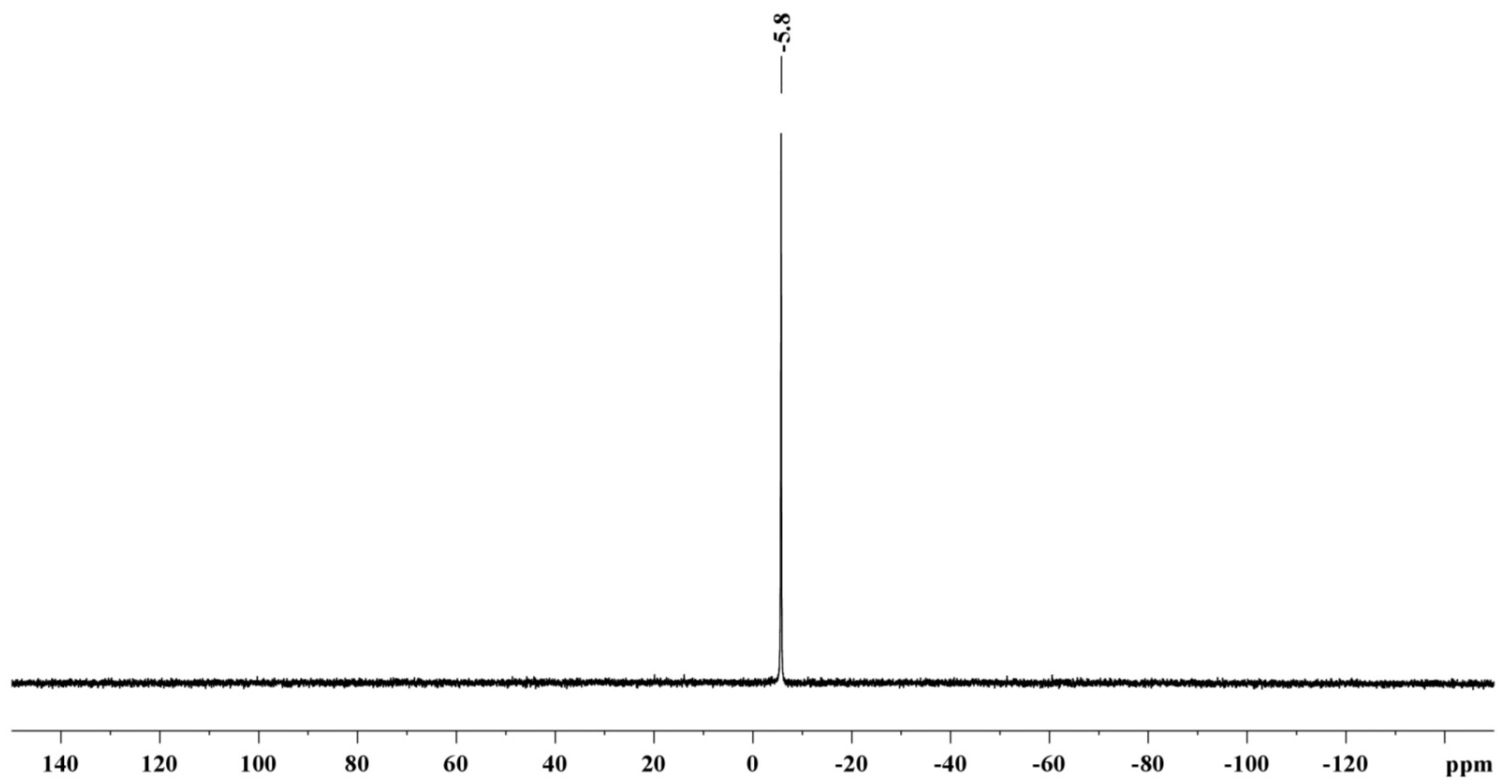


Figure S2.6.3: $^{13}\text{P}\{^1\text{H}\}$ NMR spectrum (202 MHz) of **5Ph** in C_6D_6 at room temperature.

2.7 Mes₂BiP(*t*Bu)Sb*t*Bu₂ (**5Mes**)

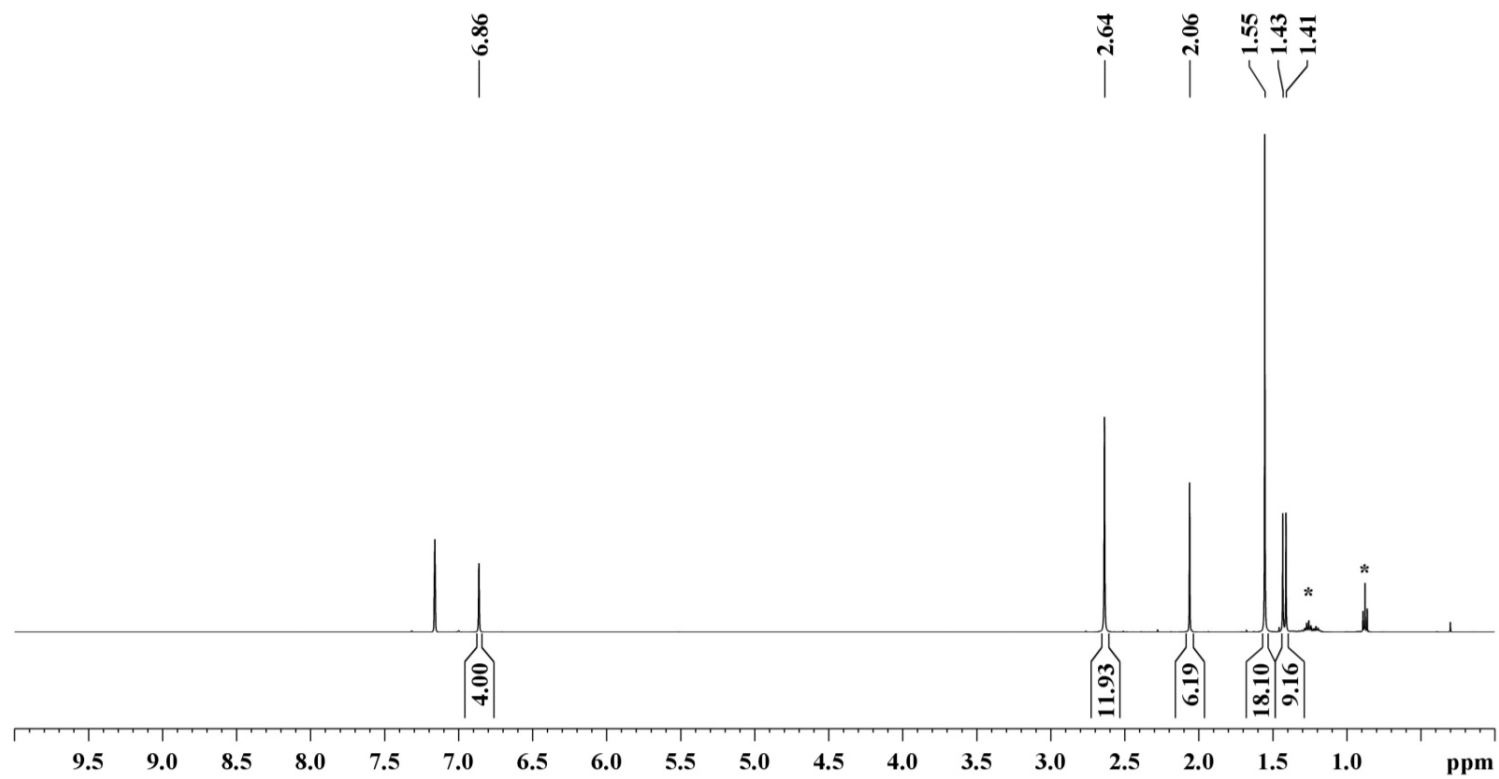


Figure S2.7.1: ¹H NMR spectrum (500 MHz) of **5Mes** in C₆D₆ at room temperature (* = *n*pentane).

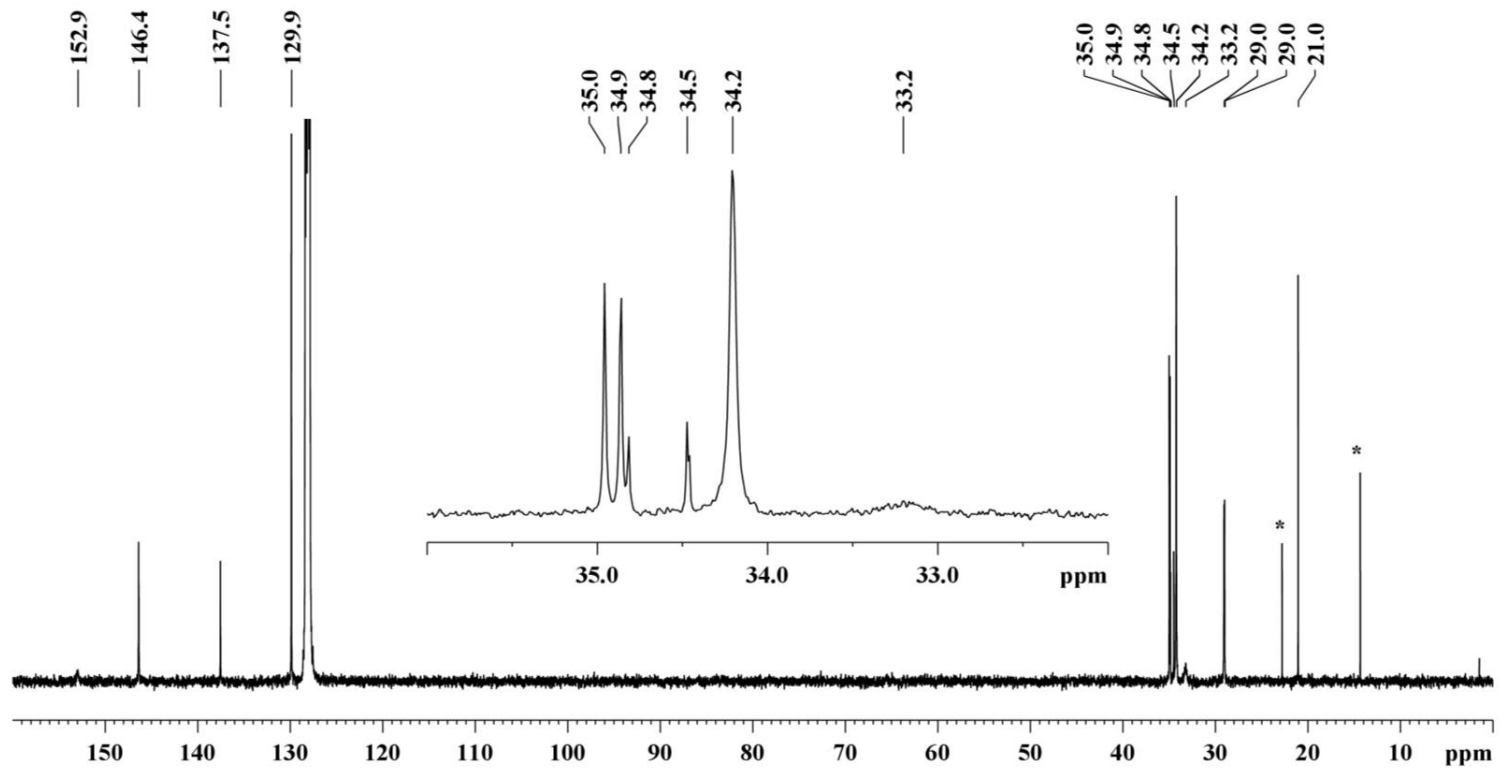


Figure S2.7.2: ^{13}C NMR spectrum (125 MHz) of **5Mes** in C_6D_6 at room temperature (* = *n*-pentane).

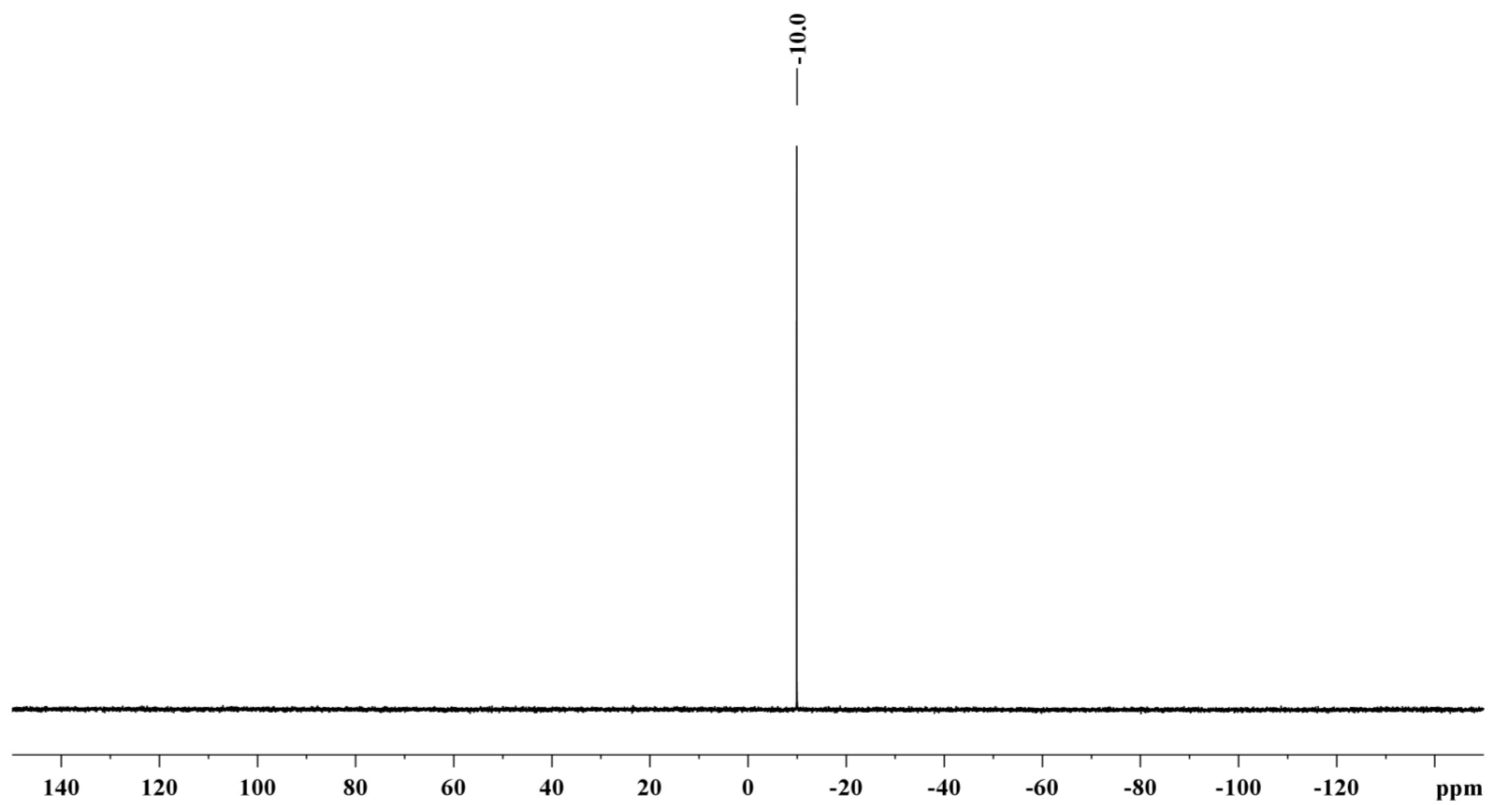


Figure S2.7.3: ^{31}P NMR spectrum (202 MHz) of **5**_{Mes} in C_6D_6 at room temperature.

2.8 Ph₂BiAs(*t*Bu)P*t*Bu₂ (**6Ph**)

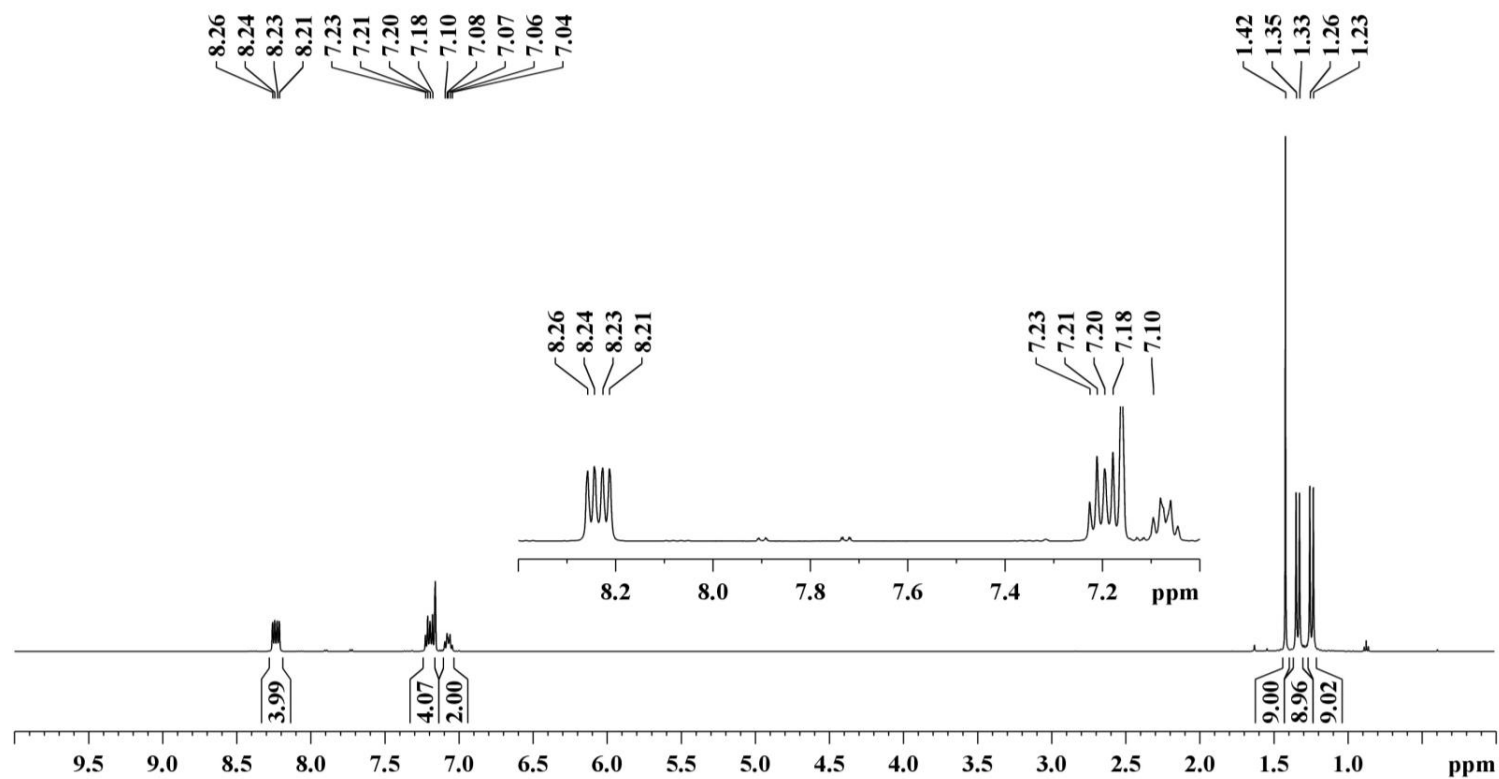


Figure S2.8.1: ¹H NMR spectrum (500 MHz) of **6Ph** in C₆D₆ at room temperature.

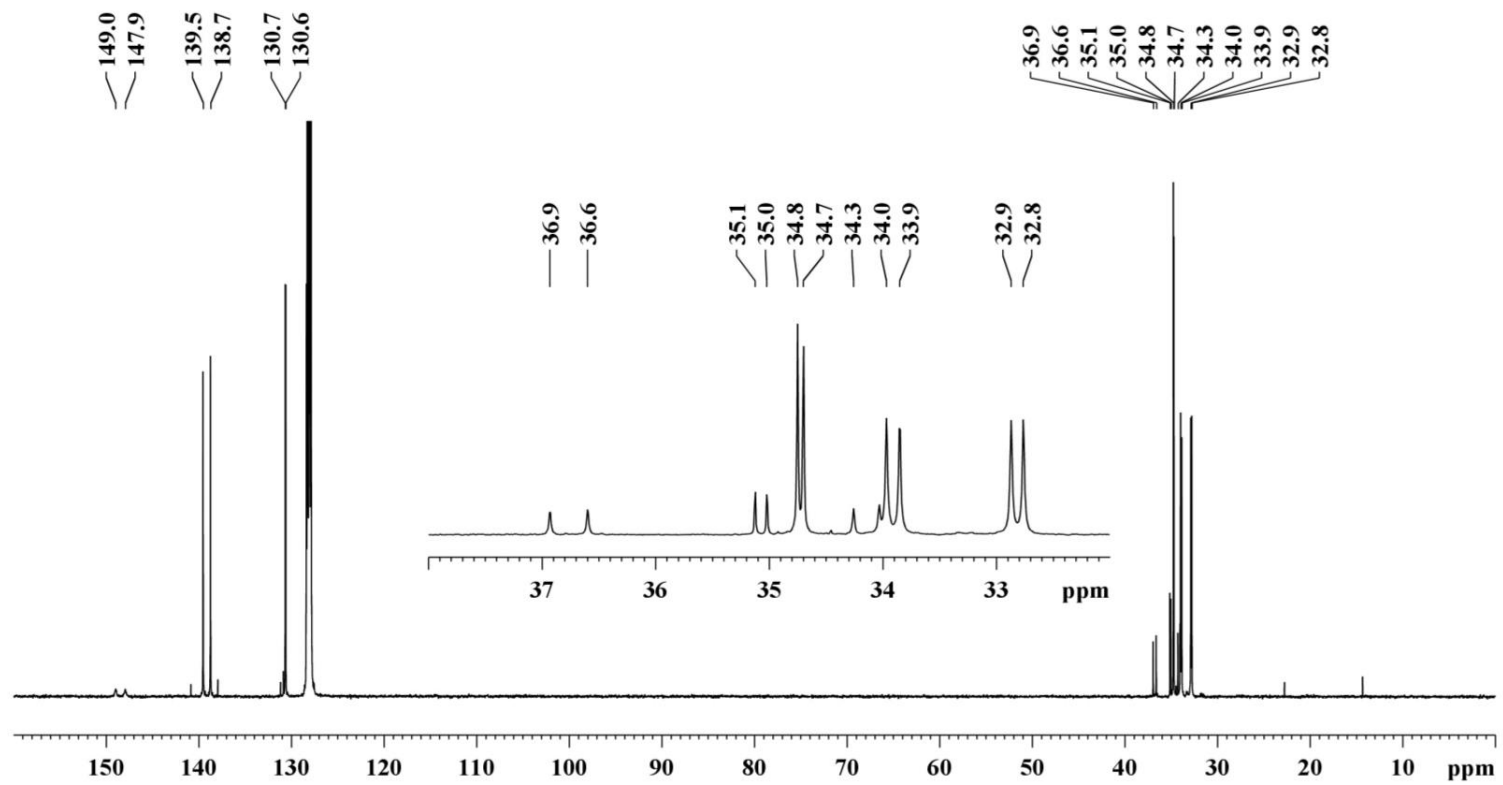


Figure S2.8.2: ^{13}C NMR spectrum (125 MHz) of **6Ph** in C_6D_6 at room temperature.

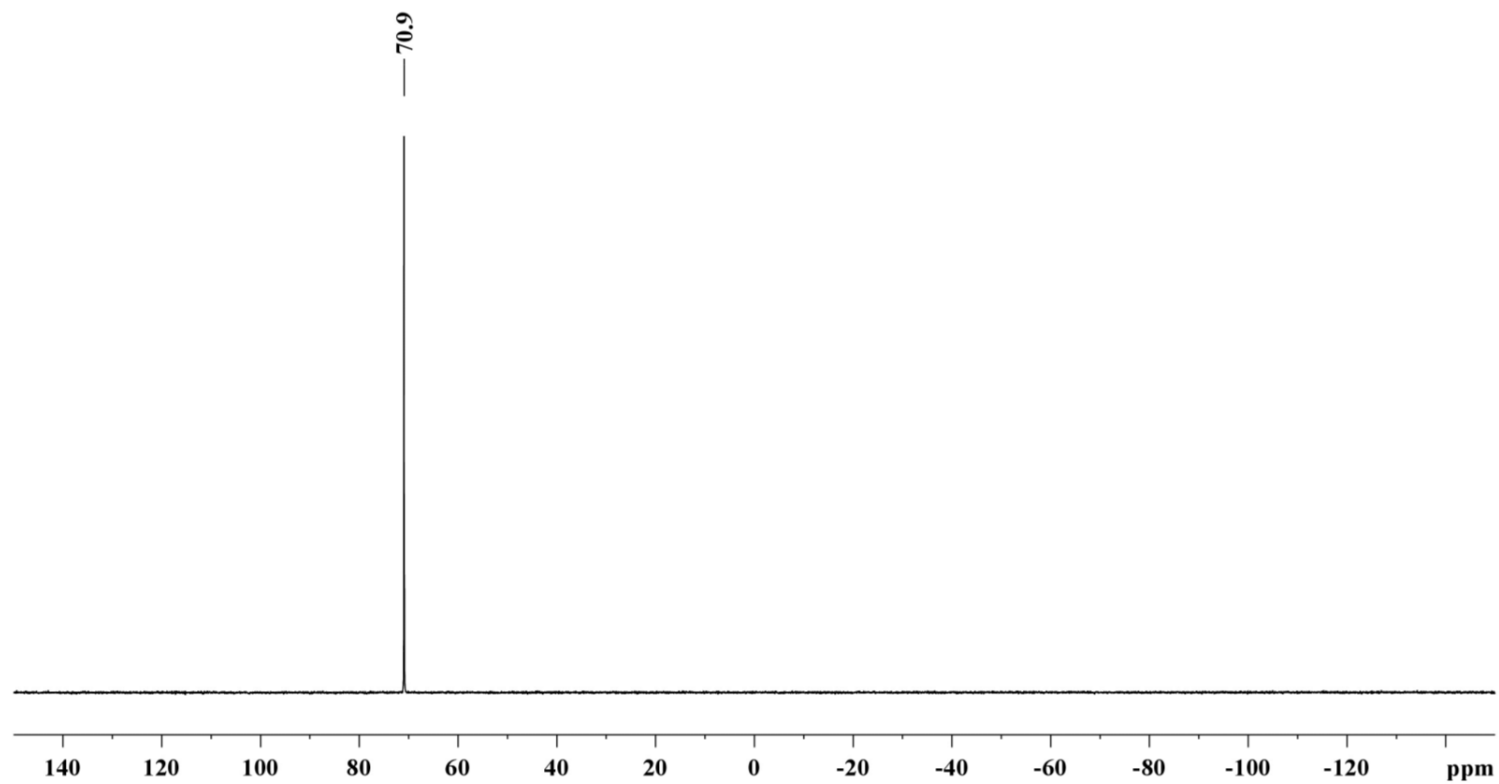


Figure S2.8.3: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (101 MHz) of **6Ph** in C_6D_6 at room temperature.

2.9 Mes₂BiAs(*t*Bu)P*t*Bu₂ (**6Mes**)

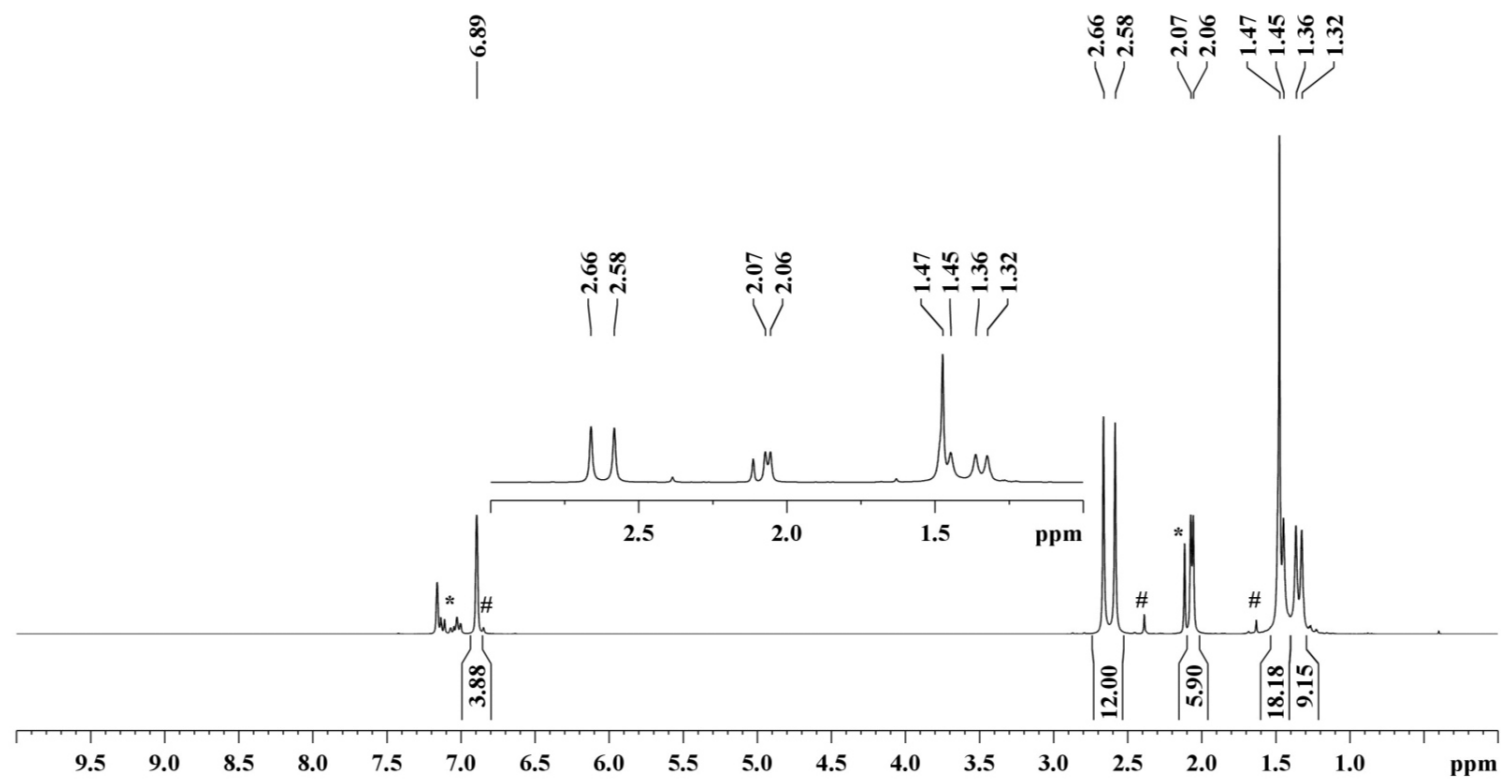


Figure S2.9.1: ¹H NMR spectrum (300 MHz) of **6Mes** in C₆D₆ at room temperature (# = toluene; * = Mes₄Bi₂).

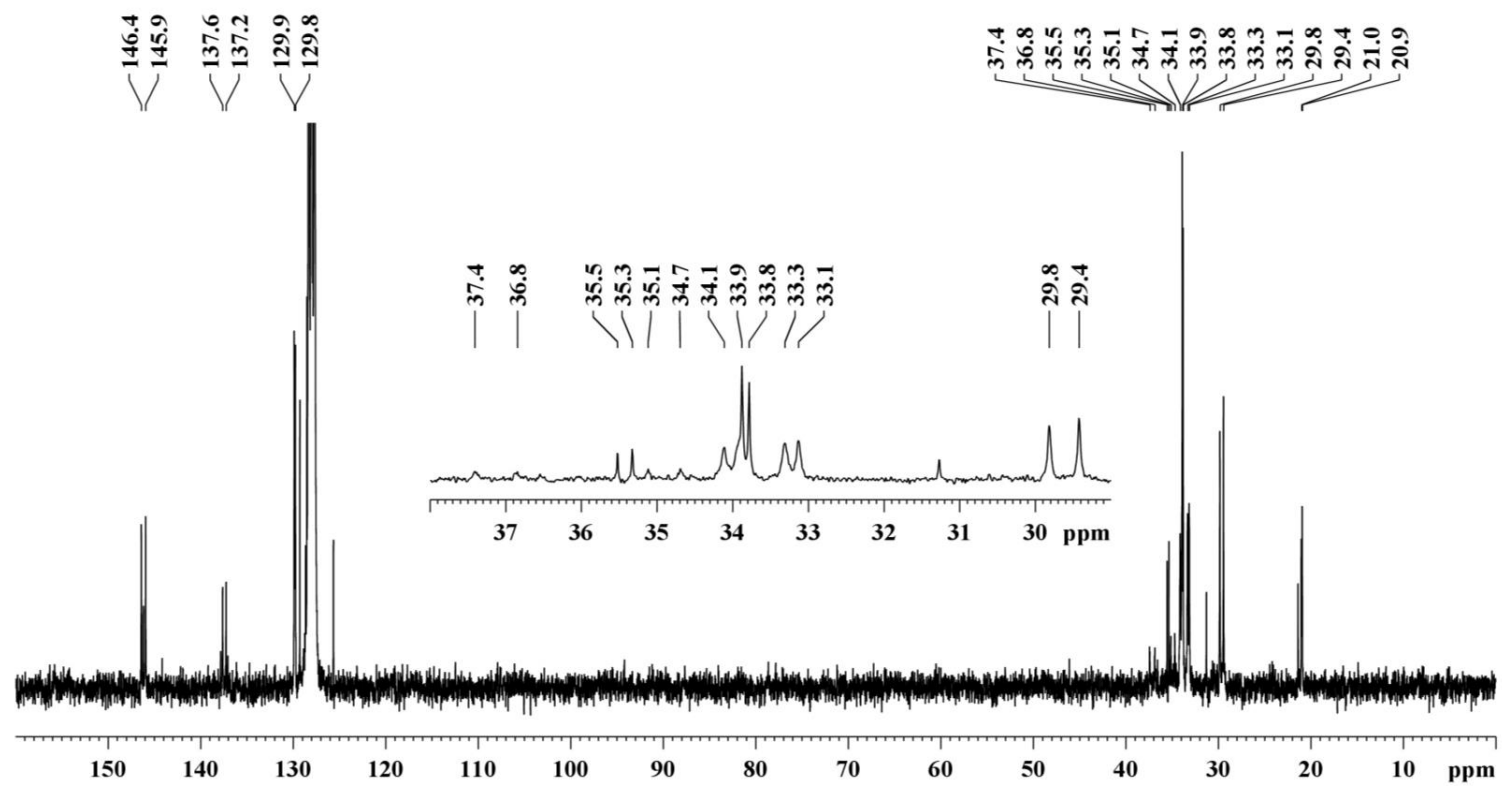


Figure S2.9.2: ^{13}C NMR spectrum (125 MHz) of **6**Mes in C_6D_6 at room temperature.

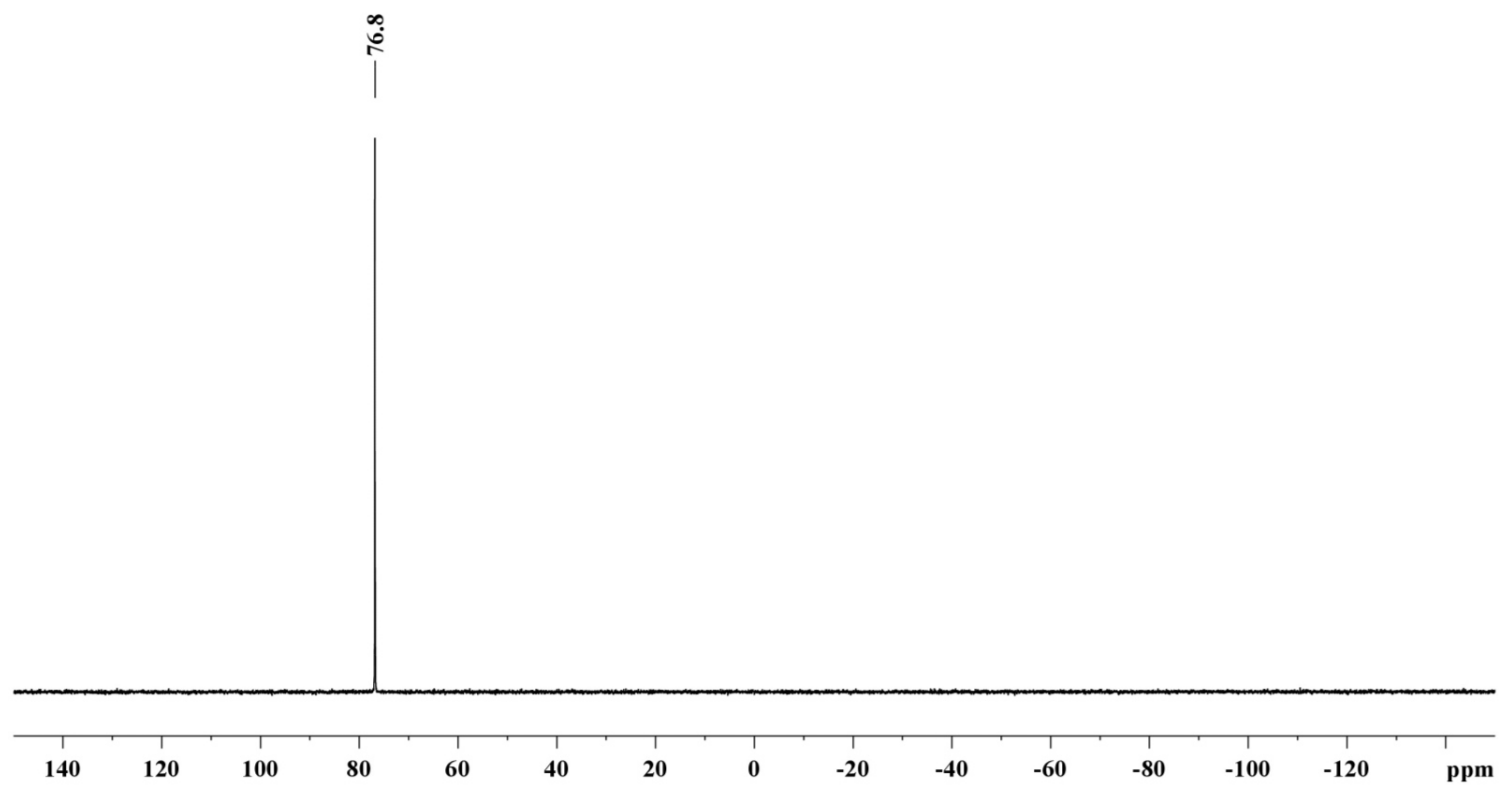


Figure S2.9.3: ^{31}P NMR spectrum (101 MHz) of **6Mes** in C_6D_6 at room temperature.

2.10 $t\text{Bu}_2\text{AsP}(t\text{Bu})\text{P}(t\text{Bu})\text{As}t\text{Bu}_2$ (**7**)

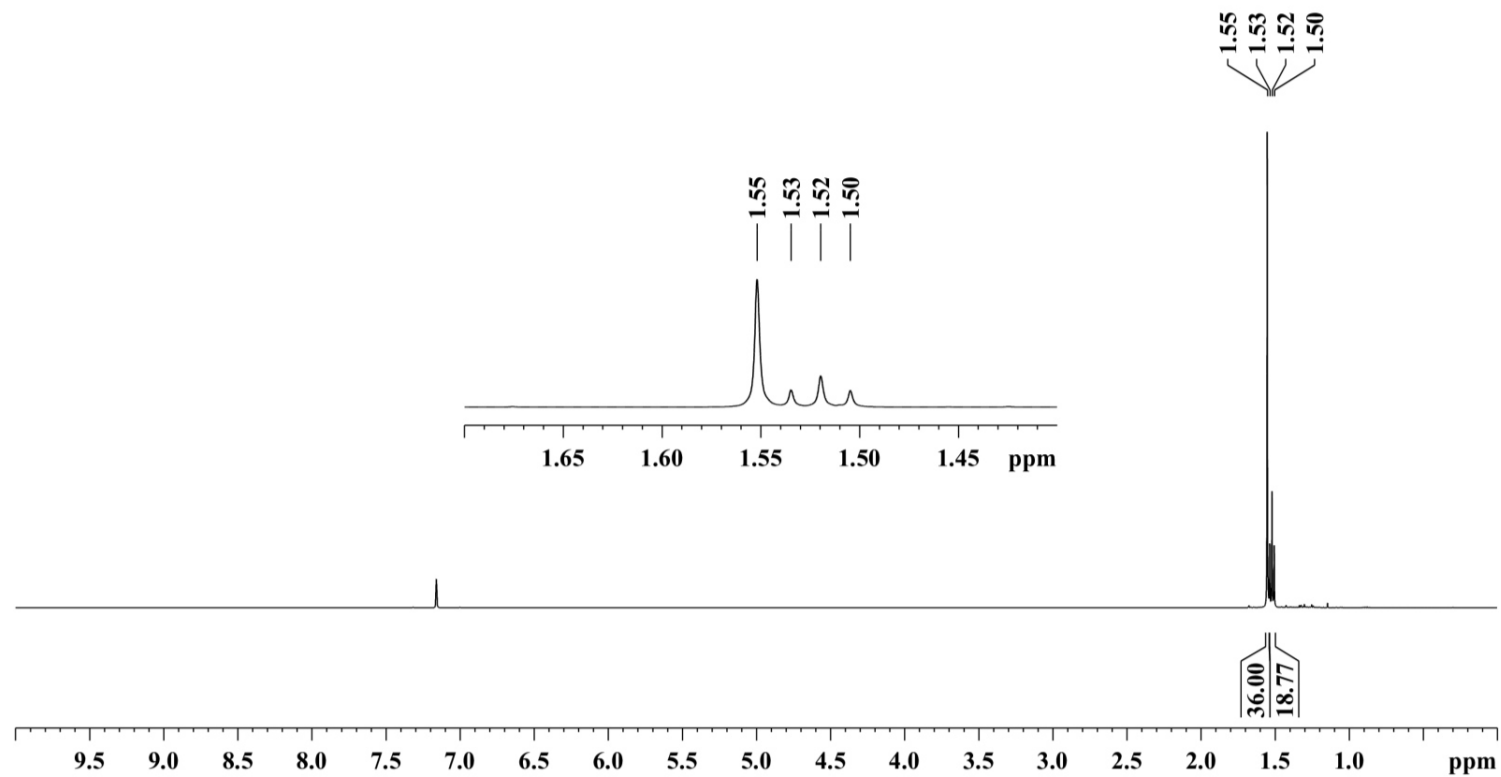


Figure S2.10.1: ^1H NMR spectrum (500 MHz) of **7** in C_6D_6 at room temperature.

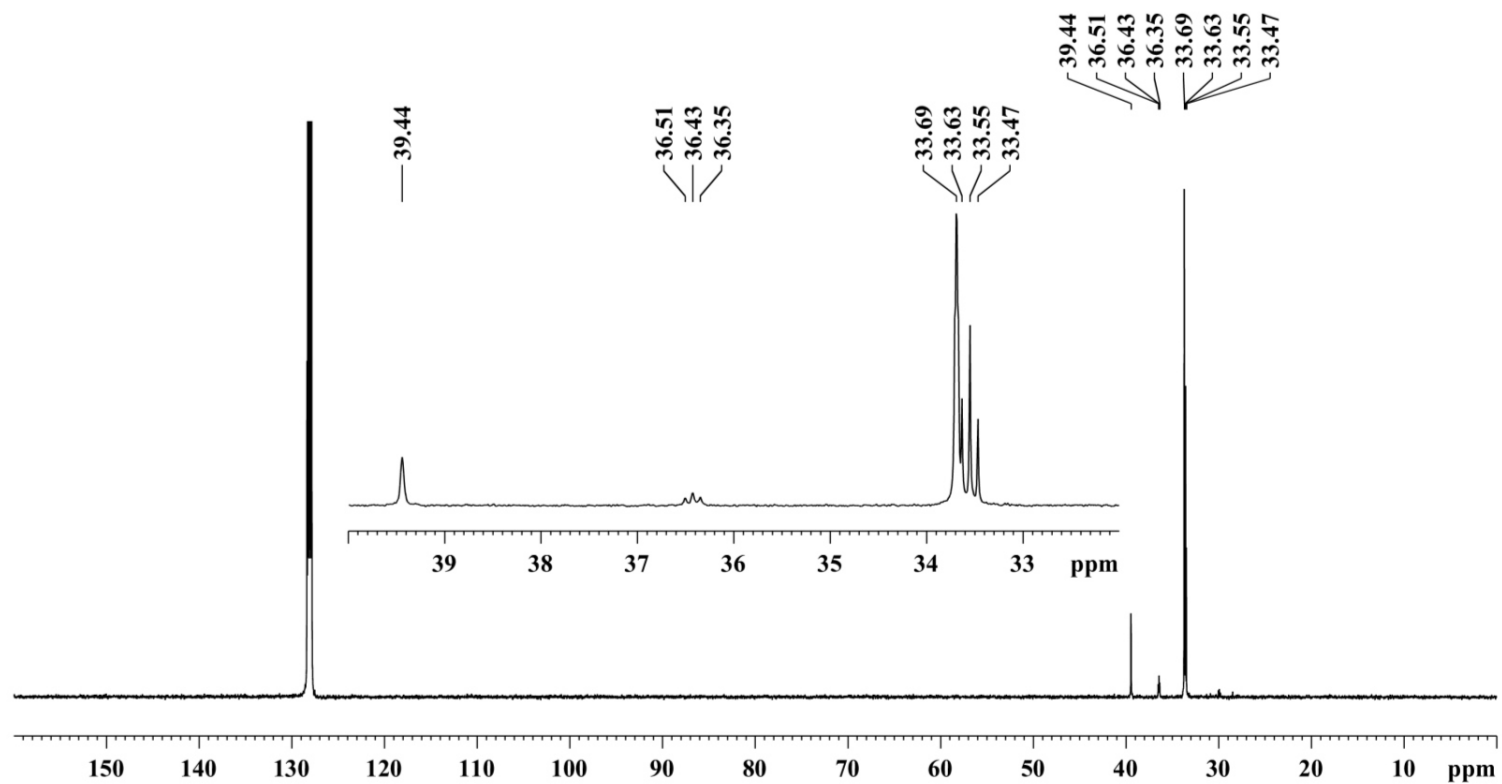


Figure S2.10.2: ^{13}C NMR spectrum (125 MHz) of **7** in C_6D_6 at room temperature.

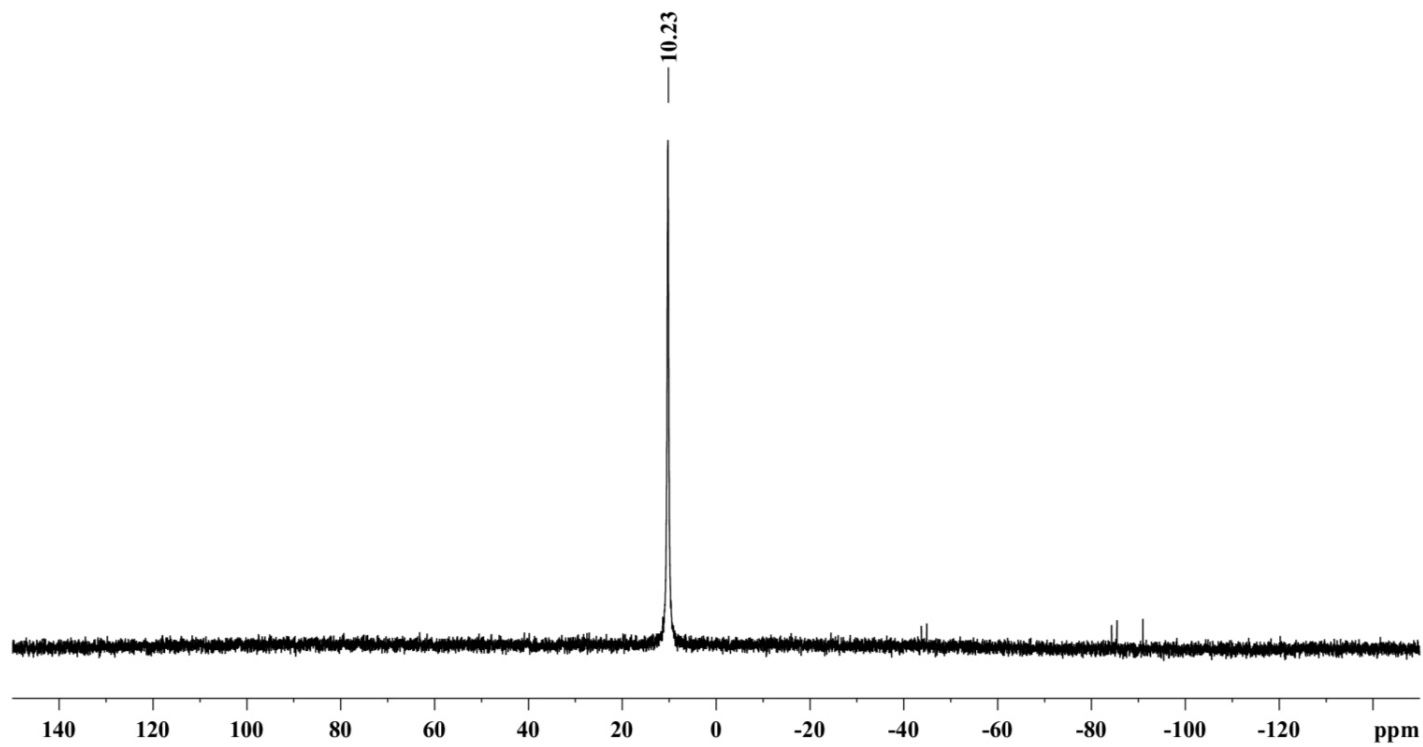


Figure S2.10.3: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (202 MHz) of **7** in C_6D_6 at room temperature.

2.11 Me₄NHC=PtBu (**8**)

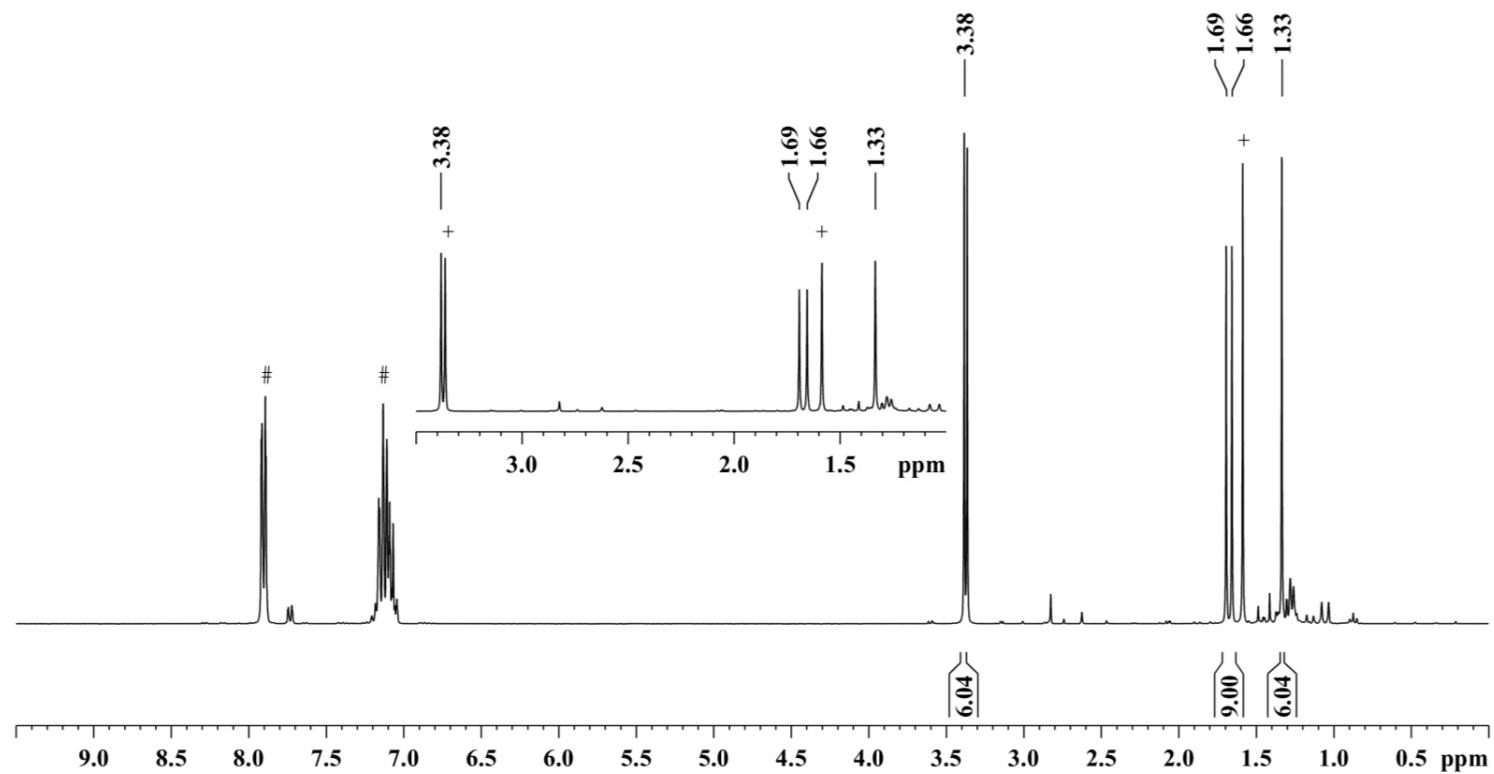


Figure S2.11.1: ¹H NMR spectrum (300 MHz) of **8** in the reaction mixture of **1Ph** and Me₄NHC in C₆D₆ at room temperature after one hour (# = Ph₄Bi₂, + = Me₄NHC).

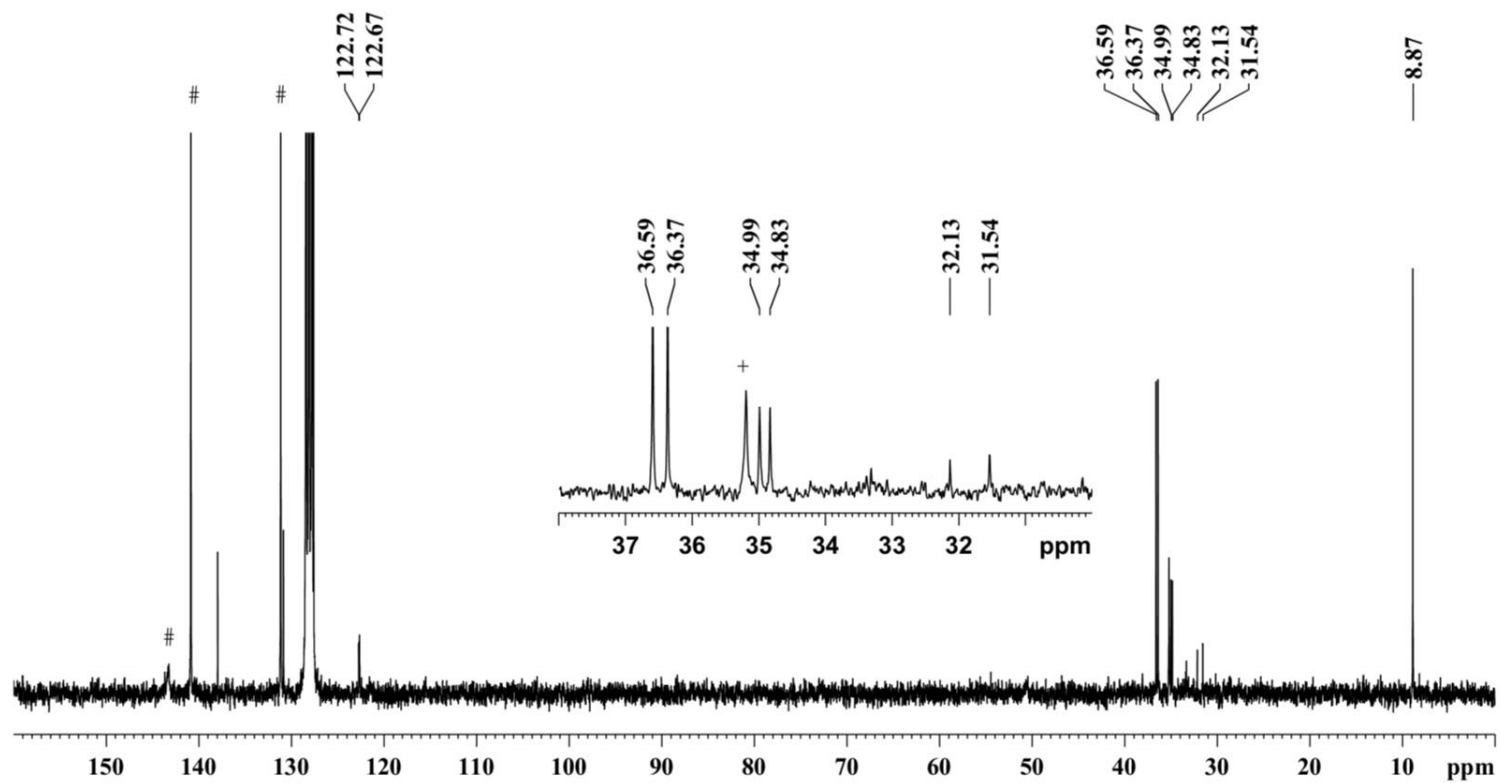


Figure S2.11.2: ^{13}C NMR spectrum (75 MHz) of **8** in the reaction mixture of **1_{Ph}** and Me_4NHC in C_6D_6 at room temperature after one hour (# = Ph_4Bi_2 , + = Me_4NHC).

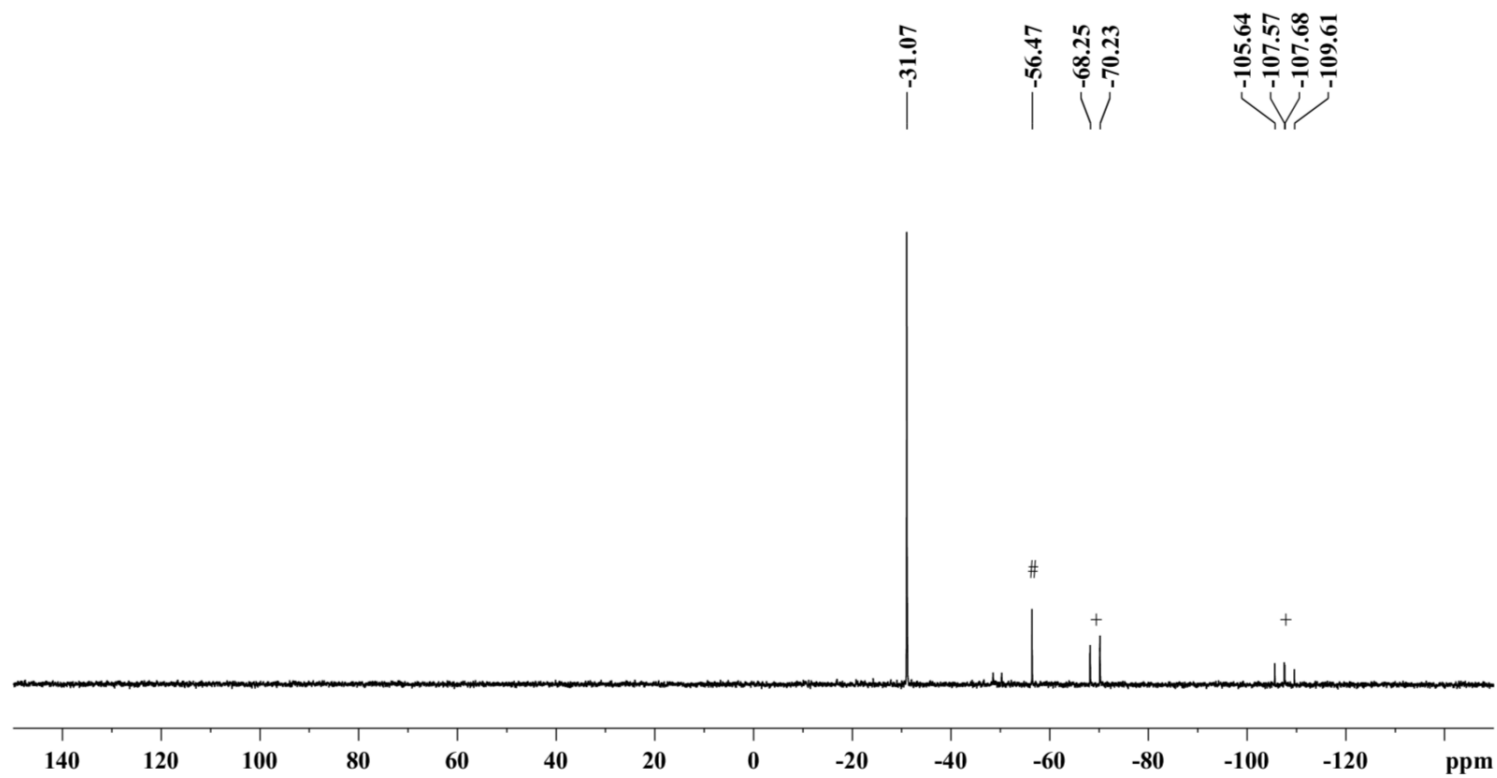


Figure S2.11.3: ^{31}P NMR spectrum (101 MHz) of **8** in the reaction mixture of **1_{Ph}** and Me_4NHC in C_6D_6 at room temperature after one hour (# = $(t\text{BuP})_4$, + = $(t\text{BuP})_3$).

3. Crystallographic data

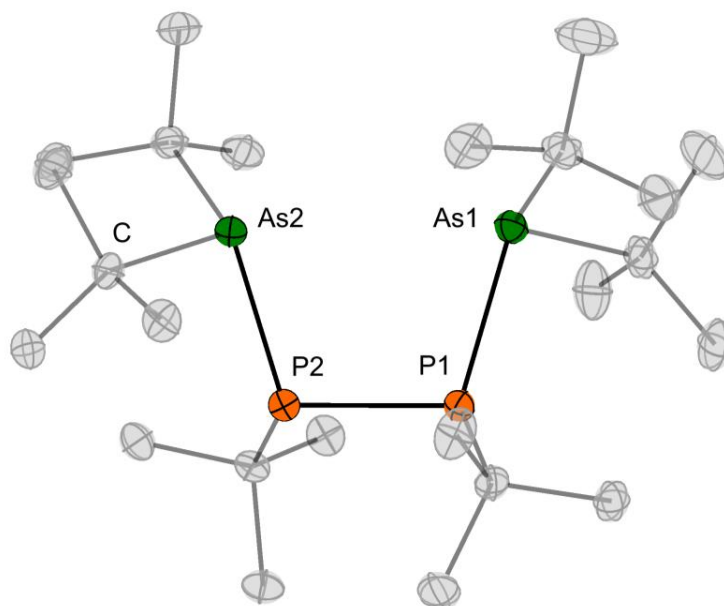


Figure S3.1. Molecular structure of **7** in the solid state. Hydrogen atoms are omitted for clarity. Ellipsoids are shown at a 50% probability level. Selected bond lengths (pm) and angles (deg): As1-P1 235.21(4); P2-As2 234.03(4); P1-P2 209.2(5); As1-As2 360.99(6); As1-P1-P2 106.04(2); As2-P2-P1 106.91(2).

Table S1. Selected crystal structure data of the structure determinations of compounds**1_{Ph}**, **2_{Ph}** and **3_{Ph}**.

Compound	1_{Ph}	2_{Ph}	3_{Ph}
Empirical formula	C ₂₈ H ₂₉ Bi ₂ P	C ₂₈ H ₂₉ AsBi ₂	C ₃₂ H ₃₈ As ₂ Bi ₂
Formula weight	814.44	858.39	990.42
Crystal color, habit	yellow, needle	yellow, plate	yellow block
Temperature/K	100	100	100
Crystal system	monoclinic	monoclinic	monoclinic
Space group	<i>P2₁/c</i>	<i>C2/c</i>	<i>C2/c</i>
a/Å	20.6337(6)	46.0158(15)	10.3530(5)
b/Å	6.3041(2)	6.01450(10)	17.7360(10)
c/Å	21.1064(5)	21.0777(8)	17.2405(9)
α/°	90	90	90
β/°	109.906(2)	116.710(3)	99.383(4)
γ/°	90	90	90
Volume/Å ³	2581.42(13)	5211.0(3)	3123.4(3)
Z	4	8	4
ρ _{calc} /cm ³	2.096	2.188	2.106
μ/mm ⁻¹	13.690	14.763	13.374
F(000)	1512.0	3168.0	1848.0
Crystal radius(equiv)/mm	0.0596	0.0535	0.0732
Diffractometer	Stoe IPDS 2T	Stoe IPDS 2	Stoe IPDS 2T
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	3.922 to 58.286	3.864 to 51.99	4.594 to 58.428
Reflections collected	33020	26808	19554
Independent reflections	6958 [R _{int} = 0.0492, R _{sigma} = 0.0255]	5122 [R _{int} = 0.1555, R _{sigma} = 0.0871]	4205 [R _{int} = 0.0642, R _{sigma} = 0.0333]
Data/restraint/parameters	6958/0/283	5122/0/284	4205/0/167
Goodness-of-fit on F ²	1.056	1.061	1.101
Final R indexes [all data]	R ₁ = 0.0233, wR ₂ = 0.0365	R ₁ = 0.0833, wR ₂ = 0.1775	R ₁ = 0.0287, wR ₂ = 0.0623
Final R indexes [I ≥ 2σ(I)]	R ₁ = 0.0184, wR ₂ = 0.0353	R ₁ = 0.0663, wR ₂ = 0.1703	R ₁ = 0.0252, wR ₂ = 0.0607
Largest diff. peak/hole/ e Å ⁻³	0.76/-1.46	5.36/-2.87	2.03/-1.98
CCDC	2207778	2207783	2207779

Table S2. Selected crystal structure data of the structure determinations of compounds**2_{Mes}, 4_{Ph} and 4_{Mes}.**

Compound	2_{Mes}	4_{Ph}	4_{Mes}
Empirical formula	C ₂₄ H ₅₃ AsBi ₂	C ₂₄ H ₃₇ AsBiP	C ₃₀ H ₄₉ AsBiP · 0.5 C ₇ H ₈
Formula weight	1026.70	640.40	770.63
Crystal color, habit	orange, block	yellow, block	orange, block
Temperature/K	100	100	100
Crystal system	triclinic	triclinic	triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> /Å	11.8078(4)	9.8418(3)	9.254(3)
<i>b</i> /Å	11.8199(4)	11.1811(4)	10.1222(3)
<i>c</i> /Å	16.4792(5)	12.4310(4)	17.9526(5)
α /°	104.028(3)	107.124(3)	96.392(2)
β /°	92.801(3)	99.967(3)	92.994(2)
γ /°	119.584(2)	98.677(3)	95.782(2)
Volume/Å ³	1901.35(12)	1257.61(8)	1655.92(9)
Z	2	2	2
ρ_{calc} /cm ³	1.793	1.691	1.546
μ /mm ⁻¹	10.131	8.386	6.383
F(000)	984.0	624.0	770.0
Crystal radius(equiv)/mm	0.0786	0.0976	0.0746
Diffractometer	Stoe IPDS 2T	Stoe IPDS 2	Stoe IPDS 2T
Radiation	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)
2 θ range for data collection/°	4.016 to 58.52	4.302 to 58.412	4.072 to 58.374
Reflections collected	26540	24481	24952
Independent reflections	10242 [R _{int} = 0.0630, R _{sigma} = 0.0488]	6759 [R _{int} = 0.0461, R _{sigma} = 0.0339]	8913 [R _{int} = 0.0563, R _{sigma} = 0.0410]
Data/restraint/parameters	10242/0/385	6759/0/267	8913/57/376
Goodness-of-fit on <i>F</i> ²	1.016	1.022	1.031
Final R indexes [all data]	R ₁ = 0.0457, wR ₂ = 0.0712	R ₁ = 0.0252, wR ₂ = 0.0483	R ₁ = 0.0298, wR ₂ = 0.0554
Final R indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	R ₁ = 0.0314, wR ₂ = 0.0662	R ₁ = 0.0208, wR ₂ = 0.0477	R ₁ = 0.0237, wR ₂ = 0.0536
Largest diff. peak/hole/ e Å ⁻³	2.36/-1.21	1.53/-0.64	1.50/-1.19
CCDC	2207780	2207777	2207781

Table S3. Selected crystal structure data of the structure determinations of compounds**5_{Ph}**, **5_{Mes}** and **6_{Ph}**.

Compound	5_{Ph}	5_{Mes}	6_{Ph}
Empirical formula	C ₂₄ H ₃₇ BiPSb	C ₃₀ H ₃₇ BiPSb · 0.5 C ₅ H ₁₂	C ₂₄ H ₃₇ AsBiP
Formula weight	687.23	789.43	640.40
Crystal color, habit	yellow, block	orange block	yellow, block
Temperature/K	100	100	100
Crystal system	triclinic	triclinic	triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> /Å	9.9116(3)	13.9567(3)	9.8068(4)
<i>b</i> /Å	11.1939(4)	16.1148(4)	11.2231(4)
<i>c</i> /Å	12.5804(4)	16.6377(3)	12.6555(5)
α /°	106.707(3)	82.409(2)	108.242(3)
β /°	99.931(3)	86.409(2)	100.936(3)
γ /°	100.072(3)	67.030(2)	97.882(3)
Volume/Å ³	1279.02(8)	3414.8(1)	1269.70(9)
Z	2	4	2
ρ_{calc} /cm ³	1.784	1.536	1.675
μ /mm ⁻¹	7.995	6.000	8.306
F(000)	660.0	1554.0	624.0
Crystal radius(equiv)/mm	0.1077	0.1095	0.1082
Diffractometer	Stoe IPDS 2	Stoe IPDS 2T	Stoe IPDS 2
Radiation	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)
2 θ range for data collection/°	3.478 to 58.268	3.484 to 58.424	3.498 to 58.484
Reflections collected	24897	81230	19352
Independent reflections	6879 [R _{int} = 0.0570, R _{sigma} = 0.0372]	18412 [R _{int} = 0.0640, R _{sigma} = 0.0366]	6715 [R _{int} = 0.0429, R _{sigma} = 0.0391]
Data/restraint/parameter s Goodness-of-fit on <i>F</i> ²	6879/0/268 1.058	18412/56/665 1.060	6715/0/272 0.995
Final R indexes [all data]	R ₁ = 0.0353, wR ₂ = 0.0802	R ₁ = 0.0305, wR ₂ = 0.0612	R ₁ = 0.0391, wR ₂ = 0.0660
Final R indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	R ₁ = 0.0319, wR ₂ = 0.0791	R ₁ = 0.0247, wR ₂ = 0.0591	R ₁ = 0.0288, wR ₂ = 0.0636
Largest diff. peak/hole/ e Å ⁻³	1.89/-1.70	2.80/-0.91	1.31/-1.01
CCDC	2207782	2207787	2207784

Table S4. Selected crystal structure data of the structure determinations of compounds**6_{Mes}** and **7**.

Compound	6_{Mes}	7
Empirical formula	C ₃₀ H ₄₉ AsBiP · 0.5 C ₇ H ₈	C ₂₄ H ₅₄ As ₂ P ₂
Formula weight	770.63	554.45
Crystal color, habit	orange, block	colorless, block
Temperature/K	100	100
Crystal system	triclinic	monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>
a/Å	9.2597(3)	8.6863(2)
b/Å	10.1372(4)	22.8897(7)
c/Å	17.8641(7)	14.9250(4)
α /°	95.798(3)	90
β /°	93.662(3)	92.297(2)
γ /°	96.167(3)	90
Volume/Å ³	1653.9(1)	2965.11(14)
Z	2	4
ρ_{calc} /cm ³	1.547	1.242
μ /mm ⁻¹	6.391	2.370
F(000)	770.0	1176.0
Crystal radius(equiv)/mm	0.1268	0.1225
Diffractometer	Stoe IPDS 2T	Stoe IPDS 2
Radiation	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)
2 θ range for data collection/°	4.066 to 58.43	3.26 to 58.436
Reflections collected	32296	47886
Independent reflections	8915 [R_{int} = 0.0604, R_{sigma} = 0.0362]	7968 [R_{int} = 0.0513, R_{sigma} = 0.0358]
Data/restraint/parameters	8915/0/365	7968/0/271
Goodness-of-fit on F^2	1.088	0.969
Final R indexes [all data]	R_1 = 0.0222, wR_2 = 0.0508	R_1 = 0.0369, wR_2 = 0.0572
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0199, wR_2 = 0.0501	R_1 = 0.0239, wR_2 = 0.0551
Largest diff. peak/hole/ e Å ⁻³	1.30/-1.16	0.67/-0.19
CCDC	2207785	2207786

2,6-Diisopropylphenyl substituted Bismuth Halide and Interpnictogen Compounds

Tobias Dunaj,^[a] Marina Egorycheva^[a], Ahmed Arebi^[a], Kevin Dollberg^[a], Carsten von Hänisch^{*[a]}

Dedication ((optional))

Abstract: Herein, we report about the preparation of several new 2,6-diisopropylphenyl (Dipp) substituted (halido-) bismuthanes, namely, Dipp_3Bi (**1**) and compounds of the form DippBiX_2 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$; **2-4**). The compounds **2-4** show a variety of structural motifs in their solid state structures. Reactivity of **2** towards the nucleophiles LiNMe_2 and MeLi was examined, where mostly scrambling reactions with a preference for two Dipp substituents at bismuth were observed. Therefore, the compounds $\text{Dipp}_2\text{BiNMe}_2$ (**5**) and Dipp_2BiMe (**6**) are the main products of these reactions. Moreover, new interpnictogen compounds with Bi-N, -P, and -Sb single bonds were prepared. Compound **5** was successfully used as precursor for the preparation of $\text{Dipp}_2\text{BiNHtBu}$ (**7**) and $\text{Dipp}_2\text{BiSbMes}_2$ (**8**), one of very few isolated compounds with a Bi-Sb single bond. Moreover, bismuthanyl phosphanes bearing functional groups ($\text{Dipp}_2\text{BiPtBu}(\text{SiMe}_3)$ (**9**), $\text{Dipp}_2\text{BiPHtBu}$ (**10**)) have been prepared. Compound **10** is the first isolated secondary phosphane with a bismuthanyl substituent. All isolated compounds were analyzed via IR and NMR spectroscopy, mass spectrometry, elemental analysis and single crystal X ray diffraction.

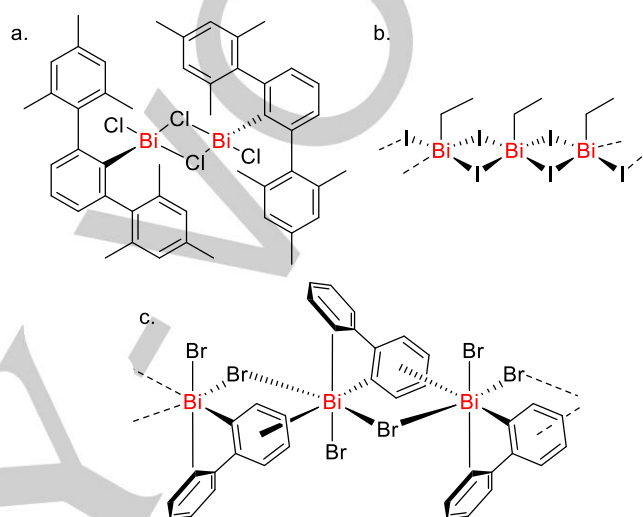


Figure 1. a. Dimeric $(2,6\text{-Mes}_2(\text{C}_6\text{H}_3))\text{BiCl}_2$. b. Polymeric EtBi_2 . c. Polymeric $(2\text{-PhC}_6\text{H}_4)\text{BiBr}_2$ with Bi- π interactions.^[6,5,14]

Introduction

Aryl or alkyl dihalido bismuthanes can be prepared *via* salt metathesis from BiX_3 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) and metallogenic nucleophiles,^[1a,1b,2,1c-p,3,1q-t,4,1u,5] scrambling reactions of BiR_3 and BiX_3 ($\text{X} = \text{Cl}, \text{Br}$)^[6,3,7-11] or oxidation of BiR_3 with I_2 and subsequent reductive elimination of R-I .^[12,4] Halido bismuthanes show a tendency towards intermolecular secondary bonding interactions and thus compounds of the form RBiX_2 show a rich variety of structural motifs in their solid state structures. For large substituents, mostly dimeric compounds with bridging halogenide atoms are known (Figure 1, a.).^[5,13,2] For smaller substituents, one dimensional chains are often observed (Figure 1, b.).^[14,5,15,16a,17,16b,6] If aryl groups are present, Bi- π -interactions can have significant influence on the solid state structures, for example in compounds of the form $(2\text{-PhC}_6\text{H}_4)_n\text{BiX}_{3-n}$ ($n = 1, 2$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$) (Figure 1, c.).^[6]

In the past, we were able to introduce the 2,6-diisopropylphenyl substituent into Bi chemistry and successfully prepared compounds of the form Dipp_2BiX ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$), which showed diverse structural motifs depending on the halogenides.^[18] The Dipp_2Bi group also enabled the formation of a compound with a Bi-P bond, either *via* salt metathesis or trimethylsilylfluoride abstraction.^[18] Additionally, we could show that diaryl halido bismuthanes are in general suitable precursors for the preparation of interpnictogen compounds with Bi-N, Bi-P, Bi-As and Bi-Sb single bonds.^[19] So far bismuth containing interpnictogen compounds with hydrogen atoms at the pnictogen atoms have only been isolated in case of bismuthaneamines and are quite rare.^[19,20] For the heavier pnictogens only one secondary bismuthanyl phosphanes has been observed spectroscopically (Figure 2, b.).^[21] The first isolable and solution stable compounds with a Bi-Sb single bond have only been reported very recently in 2020, using sophisticated bis(silylamino)naphthalene ligands.^[22] In a previous report we demonstrated, that bismuthanyl stibanes with simpler substituents can also be isolated, even though these are not completely stable in solution and are in an equilibrium with the corresponding dibismuthane and distibane.^[19]

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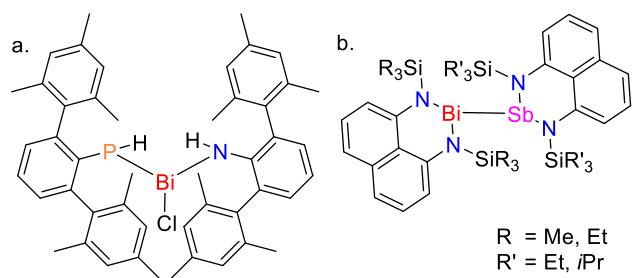


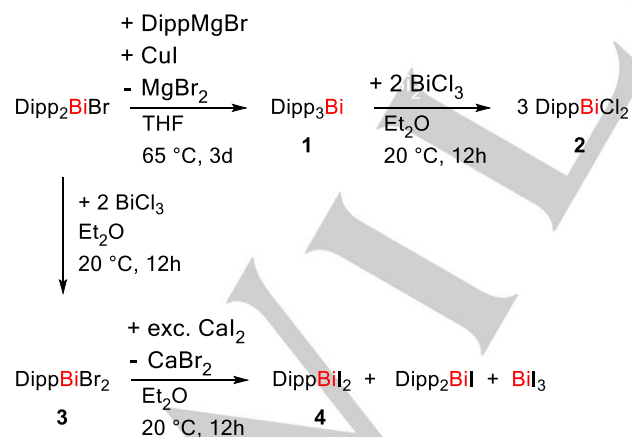
Figure 2. a. First spectroscopically detected secondary bismuthanyl phosphane. b. First isolated bismuthanyl stibanes.^[21,19]

In this report, we investigate the preparation and solid state structures of new Dipp substituted bismuthanes, namely Dipp_3Bi , DippBiCl_2 , DippBiBr_2 and DippBiI_2 . Moreover the reactivity of DippBiBr_2 towards simple nucleophiles (LiNMe_2 , MeLi) was investigated. From the isolated $\text{Dipp}_2\text{BiNMe}_2$, a new bismuthanyl stibane ($\text{Dipp}_2\text{BiSbMes}_2$) was prepared and its behavior in solution investigated. Additionally, new Dipp substituted bismuthanyl phosphanes bearing functional groups ($\text{Dipp}_2\text{BiP}t\text{Bu}(\text{SiMe}_3)$, $\text{Dipp}_2\text{BiPH}t\text{Bu}$) were isolated and characterized.

Results and Discussion

Synthesis of 2,6-diisopropylphenyl dihalido bismuthanes:

Triaryl bismuthanes are suitable starting materials for the synthesis of organo bismuth dihalides (R_2BiX_2) either *via* a scrambling reaction of Ar_3Bi and BiX_3 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) or reaction of Ar_3Bi with two equivalents of I_2 .^[6,3,7–11,4,12] Hence, the preparation of the corresponding Dipp_3Bi (**1**) as versatile starting material was attempted (Scheme 1).



Scheme 1. Synthesis of Dipp_3Bi (**1**), DippBiCl_2 (**2**), DippBiBr_2 (**3**) and DippBiI_2 (**4**).

Similar to the preparation of literature known Tripp_3Bi ^[23], Dipp_3Bi (**1**) was obtained in the form of a pale yellow solid from the reaction of Dipp_2BiBr and $\text{DippMgBr}\cdot\text{THF}$ in the presence of one equivalent of CuCl and heating to reflux in THF for two days. Pale yellow crystals of **1**, suitable for single crystal X-ray diffraction are obtained from a solution in *n*-pentane at -32°C . Compound **1** crystallizes in the monoclinic space group $P2_1/c$ with one molecule in the asymmetric unit (Figure 3a.). Due to the three sterically demanding substituents, all C-Bi-C angles ($105.64(7)$ - $107.19(7)^\circ$) are very large and the angle sum around bismuth of $318.4(2)^\circ$ is far larger than in compounds like Ph_3Bi ($281.0(3)$ - $283.2(3)^\circ$)^[24–30] or Mes_3Bi ($307.5(7)^\circ$, $308(1)^\circ$)^[31,32] and comparable to other triaryl bismuthanes with sterically very demanding substituents like $((2,4,6\text{-CF}_3)\text{C}_6\text{H}_2)_3\text{Bi}$ ($318(1)^\circ$)^[33] or $((2,4,6\text{-Ph})\text{C}_6\text{H}_2)_3\text{Bi}$ ($317(1)^\circ$).^[7] The Bi-C distances however, are very similar to Ph_3Bi or Mes_3Bi .^[24–32] The influence of three sterically demand substituents is also observed in the NMR spectra of compound **1**, where extremely broad signals are obtained in the ^1H and ^{13}C NMR spectra at room temperature. This is caused by hindered rotation around the Bi-C and the *o*-C-CH axes and was further examined *via* temperature dependent ^1H and ^{13}C NMR spectroscopy (see Supporting Informations). At low temperature, rotation around the Bi-*i*-C and the *o*-C-CH axes is slow and the *m*-CH and *o*-CCH(CH_3)₂ groups give two sets of signals respectively. Moreover, the *o*-CH(CH_3)₂ gives four sets. Upon warming, coalescence is observed for all mentioned signals. In the ^1H NMR spectra, the septets have a very defined coalescence temperature of 0°C , whereas the *m*-CH and *o*-CH(CH_3)₂ give very broad signals over a large temperature range from 10 to 60°C and -10 to 80°C respectively. As the splitting of the *m*-CH and *o*-CCH(CH_3)₂ groups is only dependent on rotation around the Bi-C axis, the rotational barrier was calculated *via* line shape analysis of the singlet signals in the ^{13}C NMR spectra, which gives an activation energy of $62(3) \text{ kJ}\cdot\text{mol}^{-1}$ (see Supporting Informations). Starting from **1**, preparation of compounds DippBiX_2 was attempted. Reaction of Dipp_3Bi and two equivalents of BiCl_3 gives DippBiCl_2 (**2**) as a pale yellow solid. Crystals suitable for single crystal X-ray diffraction were obtained from a solution of **2** in benzene at 0°C or 20°C , where crystals of different habitus (0°C : blocks, **2a**; 20°C : needles, **2b**) were obtained. At 0°C , the benzene adduct **2a** crystallizes in the orthorhombic space group $Pbcn$ with one molecule in the asymmetric unit (Figure 3b.). **2a** forms dimers, where two Cl atoms are bridging two bismuth atoms, forming a planar square with two long and two short Bi-Cl contacts. The other two chlorine atoms are within the plane formed by the square. The Dipp substituents are both on the same face of said square. On the other side, the Bi centers are in close proximity to benzene molecules, which are coordinated *via* a Bi- π interaction, making the bismuth center fivefold coordinated. Similar dimer motifs, without benzene, are formed by compounds, which have large substituents, namely $(2,6\text{-Mes}_2\text{H}_3\text{C}_6)\text{BiCl}_2$ ^[5] and $(2,4,6\text{-Ph}_3\text{H}_2\text{C}_6)\text{BiCl}_2$.^[13] The intramolecular Bi-Cl bond lengths in **2a** are 250.4 and 253.4 pm , fitting well to the reference compounds $((2,6\text{-Mes}_2\text{H}_3\text{C}_6)\text{BiCl}_2$: $249.5(6)$ - $254.3(7) \text{ pm}$; $(2,4,6\text{-Ph}_3\text{H}_2\text{C}_6)\text{BiCl}_2$: $252.9(1)$ - $253.0(1) \text{ pm}$).^[5,13] The intermolecular Bi-Cl distance is 319.1 pm , which is well within the sum of van der Waals radii of

formation of one dimensional polymers, made up of the dimers (Figure 4c). Between two dimers, the Bi-I distance is 377.7(1)-393.6(1) pm, again lower than the sum of van der Waals radii (405 pm) indicating a very weak secondary interaction.

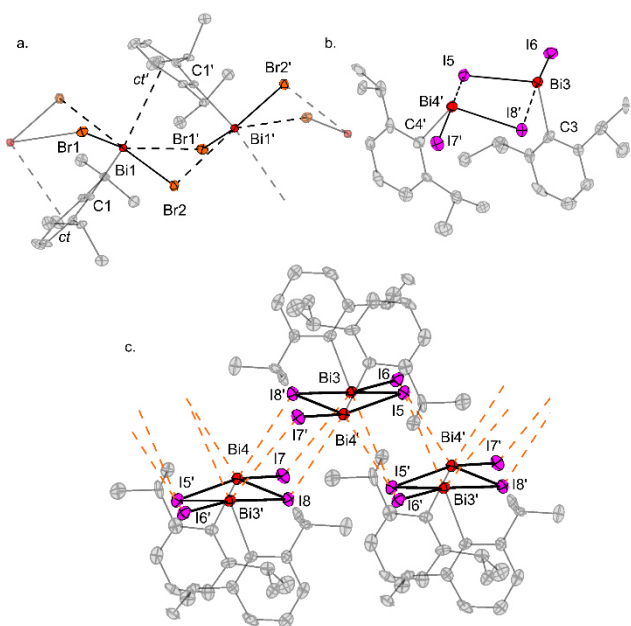
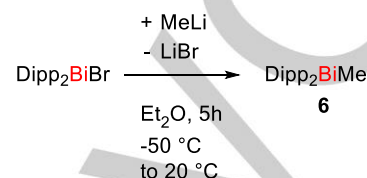


Figure 4. Molecular structures of **3** (a., top left), a dimer of **4** (b., top right) and the polymer of dimers of **4** (c., bottom) in the solid state. Hydrogen atoms are omitted for clarity. Ellipsoids are shown at a 50% probability level. Molecules corresponding to atoms labelled with an apostrophe are symmetry generated using, 1/2-x, 1/2-y, 1-z (**3**, top left), 2-x, 1-y, 1-z (**4**, top right) 2-x, 1-y, 1-z, 2-x 1-y 2-z and x, y, 1+z (**4** bottom). a. Selected bond lengths and angles: Bi1-Br1 265.65(5); Bi1-Br2 270.52(5); Bi1-C1 227.8(4); Bi1-Br1' 355.68(6); Bi1-Br2' 328.27(5); Bi1-ct' 364.22(4); Br1-Bi1-Br3 96.95(2); Br1-Bi1-C1 95.5(1); Br2-Bi1-C1 96.6(2). b. and c. Selected bond lengths and angles: Bi1-I1 285.9(1); Bi1-I2 286.7(1); Bi1-C1 229(1); Bi1-I4 352.9(1); Bi3-I4' 3817(1); Bi3-I1' 439.0(1); Bi2-I3 287.4(1); Bi2-I4 287.5(1); Bi2-C2 229(1); Bi2-I2 355.8(1); Bi2-I3 377.5(1); Bi2-I2' 421.4(1); Bi3-I5 286.9(1); Bi3-I6 287.5(1); Bi3-C3 228(1); Bi3-I8' 352.4(1); Bi3-I5' 393.0(1); Bi3-I7' 410.6(1); Bi4-I7 285.6(1); Bi4-I8 287.8(1); Bi4-C4 228(1); Bi4-I5' 3595(1); Bi4-I6 389.3(1); Bi4-I8 390.3(1); I1-Bi1-I2 95.11(3); I1-Bi1-C1 95.8(3); I2-Bi1-C1 106.6(3); I3-Bi2-I4 101.54(3); I3-Bi2-C2 93.0(3); I4-Bi2-C2 103.0(3); I5-Bi3-I6 97.79(3); I5-Bi3-C3 106.0(3); I6-Bi3-C3 92.0(3); I7-Bi4-I8 98.35(3); I7-Bi4-C4 93.4(3); I8-Bi4-C4 105.0(3);

Reactivity of 2,6-diisopropylphenyl dibromo bismuthanes:

As we successfully prepared interpnictogen compounds with two aryl substituents at the bismuth before, ^[18,19] synthesis of $\text{DippBi}(\text{NMe}_2)_2$ was attempted and **3** was reacted with two equivalents of LiNMe_2 in diethylether at -50°C . NMR spectra of the reaction mixture revealed, that even though the target compound may be identified in the reaction mixture, the reaction is not selective and $\text{Dipp}_2\text{BiNMe}_2$ (**5**) is identified as the main product (For the targeted preparation of **5** see the following section). Hence, $\text{DippBi}(\text{NMe}_2)_2$ could not be isolated. To further investigate its reactivity, **3** was reacted with, MeLi. In NMR spectra of the reaction mixture, only one product, namely Dipp_2BiMe (**6**) was identified. Again, it seems that a scrambling reaction has taken place and that DippBiMe_2 , which may have existed in

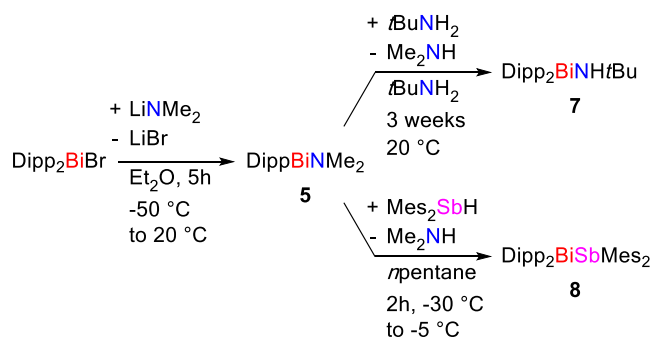
solution, decomposed to **6** and BiMe_3 . This is consistent with the decomposition of PhBiMe_2 to Ph_2BiMe and BiMe_3 , described in the literature.^[37] Compound **6** can easily be prepared in better yields through reaction of Dipp_2BiBr and MeLi in Et_2O (Scheme 2). Crystals of **6**, suitable for single crystal X-ray diffraction were obtained from a solution in nheptane at -32°C . There are two molecules in the asymmetric unit of a cell with the space group $P2_1/n$ (See Supporting Information). In the crystal structure, all Bi-C distances and C-Bi-C bond angles are in the usual range for Bi-C bonds. Moreover, IR and NMR spectra show signals in the expected range.



Scheme 2. Synthesis of Dipp_2BiMe (**6**).

In an attempt to further functionalize Dipp_2BiMe and prepare a bismuthane with three different substituents, we tried to exchange one Dipp substituent for a chloride atom to get to DippBiMeCl . It is described in the literature, that hydrogen halides cleave $\text{Bi-C}_{\text{aryl}}$ rather than $\text{Bi-C}_{\text{alkyl}}$ bonds.^[36,15,38] In a similar attempt, compound **6** was dissolved in diethylether and reacted with one equivalent of HCl in dioxane. Investigation of the reaction mixture *via* NMR spectroscopy and mass spectrometry revealed however, that the target compound was not obtained. Rather, compound **6** is still present in solution and formation of MeBiCl_2 is observed, leading to the assumption, that selective cleavage of only one Dipp substituent is not possible. All of the performed reactions discussed within this section seem to strongly favor products with two aryl substituents at the bismuth, rather than one. Subsequently, further functionalization with the Dipp_2Bi platform was attempted.

Synthesis of new Interpnictogen compounds. Preparation of Interpnictogen compounds from Ar_2BiCl ($\text{Ar} = \text{Ph}, \text{Mes}$) was successful in the past and compounds containing Bi-E bonds ($\text{E} = \text{N}, \text{P}, \text{As}, \text{Sb}$) have been prepared.^[19,18] Subsequently, we want to prepare the corresponding Dipp substituted interpnictogen compounds. In a reaction of Dipp_2BiBr and LiNMe_2 compound **5** (observed as a decomposition product in the previous section) was obtained in the form of pale yellow crystals. Compound **5** crystalizes in the triclinic space group $P\bar{1}$ with two independent molecules in the asymmetric unit (Figure 5a). In contrast to $\text{Ph}_2\text{BiNMe}_2$ and similar to $\text{Mes}_2\text{BiNMe}_2$, **5** does not show any intramolecular Bi-N interaction. The Bi-N distances are 220.8(3) and 222.3(3) pm, which is very similar to $\text{Ph}_2\text{BiNMe}_2$ (223.6(4) and 223.8(4) pm), $\text{Mes}_2\text{BiNMe}_2$ (220.8(4) pm) or $\text{Mes}_2\text{BiNHfBu}$ (219.8(3) pm).^[19] The NMR spectra show the expected signals with a singlet for the NMe_2 substituent at 3.44 ppm in the ^1H NMR spectrum.



Scheme 3. Synthesis of $\text{Dipp}_2\text{BiNMe}_2$ (5), $\text{Dipp}_2\text{BiNHtBu}$ (7) and $\text{Dipp}_2\text{BiSbMes}_2$ (8).

In a previous report, we were able to prepare a secondary bismuthane amine through reaction of a dimethylamino bismuthane with an excess of $t\text{BuNH}_2$ in toluene and subsequent elimination of Me_2NH . The same reaction was attempted again for 5. However, this did not lead to any desired product. Only after using pure $t\text{BuNH}_2$ as solvent and stirring for three weeks at room temperature and under ambient light, complete conversion to $\text{Dipp}_2\text{BiNHtBu}$ (7) is observed. If the reaction mixture is stirred without ambient light, no reaction is observed, hinting at a homolytic Bi-N bond cleavage in the first step and subsequently a radical mechanism. This is also in agreement with the studies on the decomposition of tris(diaryl)aminobismuthanes by the *Lichtenberg* group.^[39] Compound 7 shows a singlet at 2.35 ppm in the ^1H NMR spectrum for the NH group. Moreover, a very faint band in the IR spectrum at 3295 cm^{-1} for the N-H bond is observed. Both values are very similar to the structurally related $\text{Mes}_2\text{BiNHtBu}$ (^1H NMR(C_6D_6) $\delta_{\text{NH}} = 2.36$; $\nu = 3277\text{ cm}^{-1}$). Crystals suitable for single crystal X-ray diffraction were obtained from $n\text{pentane}$ at -32°C . Compound 7 crystallizes in the monoclinic space group $P2_1/n$ with one molecule in the asymmetric unit (Figure 5b). The Bi-N distance of 218.8(2) pm is in agreement with that of 5 (220.8(3) and 222.3(3) pm) and the previously discussed reference compounds.

Through a similar reaction and Me_2NH elimination, compounds with Bi-Sb bonds can be formed. With this method *Chitnis* and coworkers prepared the first isolable compound with a Bi-Sb single bond only recently.^[22] For smaller aryl substituted bismuthanes, compounds of the form $\text{Ar}_2\text{BiSbMes}_2$ have been prepared and fast equilibria between the bismuthanyl stibane, the dibismuthane and the distibane were observed in solution.^[19] Preparation of a bismuthanyl stibane was attempted through reaction of 5 and Mes_2SbH , where $\text{Dipp}_2\text{BiSbMes}_2$ (8) was obtained. Besides 8 the corresponding dibismuthane Dipp_4Bi_2 and the distibane Mes_4Sb_2 are observed in the reaction mixture via NMR spectroscopy and mass spectrometry. Through fast work up at low temperatures, it is possible to isolate 8 through crystallization from $n\text{pentane}$ at -32°C . Compound 8 crystallizes in the triclinic space group $P\bar{1}$ with one molecule in the asymmetric unit (Figure 6). The Bi-Sb distance is 294.64(6) pm, which is slightly longer than in the structurally similar $\text{Ph}_2\text{BiSbMes}_2$ (292.56(3) pm)^[19] but shorter than in the

bis(silylamino)naphthalene substituted bismuthanyl stibanes prepared by *Chitnis* and coworkers (297.64(7)–297.75(9) pm).^[22] We attribute this to the lower steric bulk of 8.

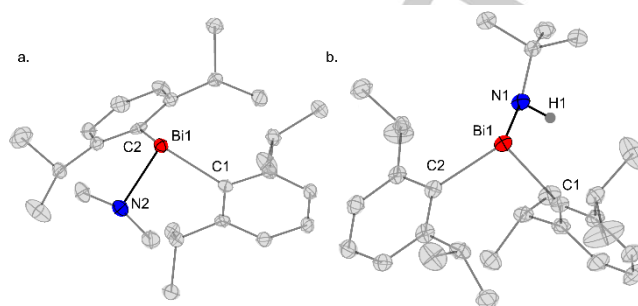


Figure 5. Molecular structures of 6 (a., left) and 7 (b., right) in the solid state. Hydrogen atoms at carbon are omitted for clarity. Ellipsoids are shown at a 50% probability level. a. Selected bond lengths and angles: Bi1-N1 222.3(3); Bi1-C1 228.4(3); Bi1-C2 229.3(3); Bi2-N2 221.0(3); Bi2-C3 229.3(3); Bi2-C4 229.3(3); N1-Bi1-C1 96.0(1); N1-Bi1-C2 107.3(1); C1-Bi1-C2 91.9(2); N2-Bi2-C3 97.1(1); N2-Bi2-C4 106.9(1). b. Selected bond lengths and angles: Bi1-N1 218.8(2); Bi1-C1 227.7(3); Bi1-C2 229.5(3); N1-Bi1-C1 91.03(9); N1-Bi1-C2 103.18(9); C1-Bi1-C2 95.76(9).

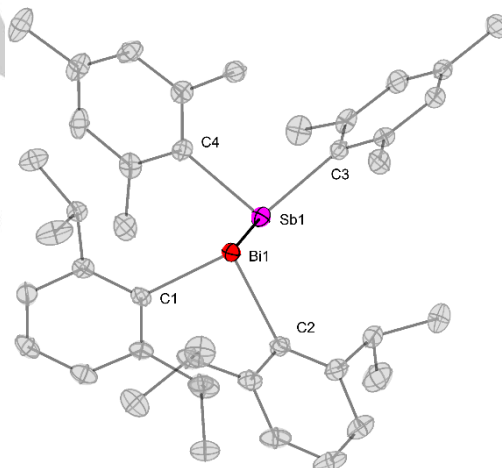
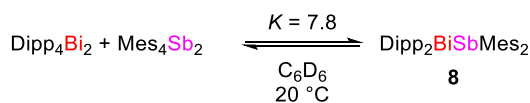


Figure 6. Molecular structures of 8 in the solid state. Hydrogen atoms at carbon are omitted for clarity. Ellipsoids are shown at a 50% probability level. Selected bond lengths and angles: Bi1-Sb1 294.63(2); Bi1-C1 230.0(2); Bi1-C2 231.2(2); Sb1-C3 218.0(2); Sb1-C4 218.5(2); Sb1-Bi1-C1 85.36(6); Sb1-Bi1-C2 110.68(6); C1-Bi1-C2 96.54(8); Bi1-Sb1-C3 112.22(6); Bi1-Sb1-C4 90.45(6); C3-Sb1-C4 99.01(9).

In contrast to the bismuthanyl stibanes with the smaller aryl substituents, equilibrium concentrations of 8, Dipp_4Bi_2 and Mes_4Sb_2 are not reached virtually immediately upon solvation. Rather, it takes around 70 minutes at room temperature ($K = 7.8$) until equilibrium concentrations are reached (Figure 7). At first glance, these results are surprising, as one might expect faster homolytic bond cleavage for a sterically more strained system. However, the naphthyl substituted compounds prepared by *Chitnis* are sterically even more demanding and ultimately stable against

Bi-Sb bond cleavage. In his reports this is partially attributed to attractive dispersive interactions of the ligands.^[22,40] A similar stabilizing effect might be accountable for reaching equilibrium between **8** and the dipnictanes, which is slower than observed for $\text{Ph}_2\text{BiSbMes}_2$ or $\text{Mes}_2\text{BiSbMes}_2$.



Scheme 4. Equilibrium reaction of Dipp_4Bi_2 , Mes_4Sb_2 and $\text{Dipp}_2\text{BiSbMes}_2$ (**8**).

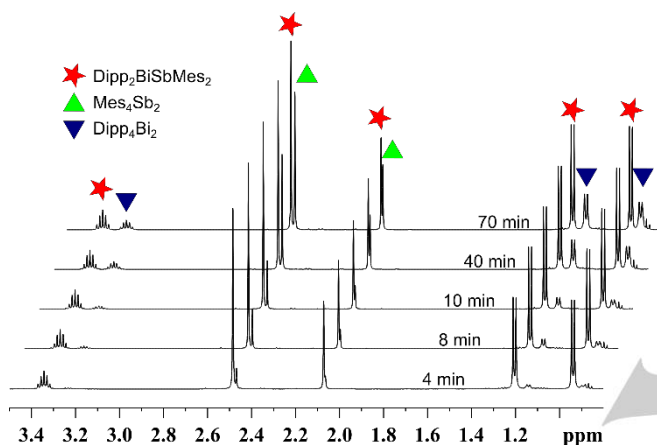
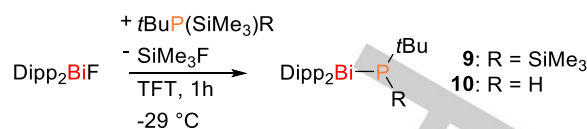


Figure 7. Excerpts from ^1H NMR spectra after dissolving pure crystalline **8** in C_6D_6 at room temperature after certain amounts of time.

For the smaller aryl substituents, it was possible to prepare compounds with a Bi-P bond and an additional functional group, in the form of a Me_3Si substituent. This was also attempted for the Dipp compound and $\text{Dipp}_2\text{BiP}t\text{Bu}(\text{SiMe}_3)$ (**9**) was prepared from Dipp_2BiF and $\text{P}t\text{Bu}(\text{SiMe}_3)_2$ (Scheme 3). Compound **9** crystallizes in the triclinic space group $P\bar{1}$ with two molecules in the asymmetric unit (Figure 8a). One molecule shows a disorder with respect to the $t\text{Bu}$ and the SiMe_3 group with an occupancy of 82 % and 18 % of the two domains. The Bi-P distances are 267.0(1) and 267.6(4) pm, which fits well to other literature known compounds like $\text{Ar}_2\text{BiP}t\text{BuR}$ ($\text{Ar} = \text{Ph}, \text{Mes}, \text{R} = t\text{Bu}, \text{SiMe}_3$)^[19,18] or $(\text{Cy}_2\text{P})\text{Bi}\{(\text{NR})_2(\text{SiMe}_2)_2\text{O}\}$ ($\text{Cy} = \text{Cyclohexyl}; \text{R} = t\text{Bu}: 264.65(7)$ pm; $\text{R} = \text{Dipp}: 265.03(4)$ pm).^[41] Moreover, the $^{31}\text{P}\{^1\text{H}\}$ and $^{29}\text{Si}\{^1\text{H}\}$ NMR chemical shifts of -45.5 ppm and 2.4 ppm ($^1J_{\text{P-Si}} = 56.7$ Hz) respectively fit well to the similar bismuthanyl silyl phosphanes.^[19] As the introduction of a silyl substituent worked well, we also attempted the preparation of a secondary bismuthanyl phosphane. Therefore, Dipp_2BiF was reacted with $t\text{BuPH}(\text{SiMe}_3)$, and, under abstraction of SiMe_3F , $\text{Dipp}_2\text{BiPH}t\text{Bu}$ (**10**) was obtained in the form of a light sensitive yellow solid (Scheme 3). It is the first isolated secondary bismuthanyl phosphane and only the second spectroscopically detected one.^[21]



Scheme 3. Synthesis of $\text{Dipp}_2\text{BiP}t\text{Bu}(\text{SiMe}_3)$ (**9**) and $\text{Dipp}_2\text{BiPH}t\text{Bu}$ (**10**).

In the ^{31}P NMR spectrum, compound **10** shows a doublet of multiplets, with a $^1J_{\text{P-H}}$ coupling constant of 168 Hz, which is in agreement with the spectroscopically observed reference compound $(2,6\text{-Mes}_2\text{C}_6\text{H}_3)\text{NH}(\text{BiCl})\text{PH}(2,6\text{-Mes}_2\text{C}_6\text{H}_3)$ (^{31}P (DCM-d_2) δ : -64.6 , $^1J_{\text{P-H}} = 187$ Hz).^[21] In the IR spectrum, a band for the P-H bond is observed at 2272 cm^{-1} , which is also in the usual range for P-H vibrations. Crystals, suitable for single crystal x-ray diffraction, were obtained from a saturated solution in n pentane (Figure 8b). Compound **10** crystallizes in the orthorhombic space group $Iba2$ with one molecule in the asymmetric unit. The Bi-P distance is 265.9(4) pm and in agreement with **9**, $\text{Ar}_2\text{BiP}t\text{BuR}$ ($\text{Ar} = \text{Ph}, \text{Mes}, \text{R} = t\text{Bu}, \text{SiMe}_3$)^[19,18] or $(\text{Cy}_2\text{P})\text{Bi}\{(\text{NR})_2(\text{SiMe}_2)_2\text{O}\}$ ($\text{Cy} = \text{Cyclohexyl}; \text{R} = t\text{Bu}: 264.65(7)$ pm; $\text{R} = \text{Dipp}: 265.03(4)$ pm).^[41]

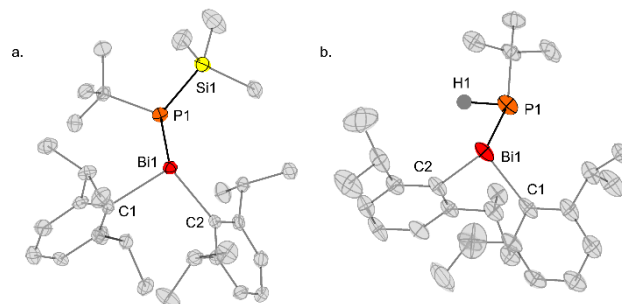


Figure 8. Molecular structures of **9** (a., left) and **10** (b., right) in the solid state. Hydrogen atoms at carbon are omitted for clarity. Ellipsoids are shown at a 50% probability level. a. Bi1-P1 267.0(1); Bi1-C1 230.1(4); Bi1-C2 230.5(4); P1-Si1 227.7(2) Bi2-P2A 267.6(3); Bi2-C3 230.4(4); Bi2-C4 233.4(4); P2A-Si2A 226.9(5); P1-Bi1-C1 100.9(1); P1-Bi1-C2 107.0(1); C1-Bi1-C2 96.3(1); C3-Bi1-P2A 99.4(1); C4-Bi2-P2A 106.4(2); C3-Bi2-C4 97.3(2). Selected bond lengths and angles: b. Selected bond lengths and angles: Bi1-P1 265.7(2); Bi-C1 230(1); Bi-C2 228.8(8); P1-Bi1-C1 110.0(2); P1-Bi1-C2 90.9(3); C1-Bi1-C2 94.1(5).

Conclusions

Herein, we report about the preparation of multiple new 2,6-diisopropylphenyl (Dipp) substituted bismuthanes. Dipp_3Bi (**1**) was successfully prepared and used as precursor for the preparation of compounds of the form DippBiX_2 ($\text{X} = \text{Cl}, \text{Br}, \text{I}; \mathbf{2-4}$). The compounds **2-4** show a variety of structural motifs in their solid state structures due to intermolecular secondary bonding interactions between bismuth, the halides and, in some cases, the π -systems of the next molecules or aromatic solvents. The reactivity of **2-4** against nucleophiles ($\text{MeLi}, \text{LiNMe}_2$) was examined, where mostly scrambling reactions with a preference

for two Dipp substituents at the bismuth were observed. Moreover, new interpnictogen compounds of the form $\text{Dipp}_2\text{BiER}^1\text{R}^2$ were prepared. Through salt metathesis, $\text{Dipp}_2\text{BiNMe}_2$ (**5**) was obtained and successfully used as precursor for the preparation of $\text{Dipp}_2\text{BiNHfBu}$ (**7**) and $\text{Dipp}_2\text{BiSbMes}_2$ (**8**), the former being one of very few isolated compounds with a Bi-Sb single bond. In solution, **8** shows an equilibrium with Dipp_4Bi_2 and Mes_4Sb_2 which was examined *via* time dependent NMR spectroscopy, where equilibrium concentrations were reached after 70 minutes. Moreover, new bismuthanyl phosphanes of the form $\text{Dipp}_2\text{BiP}^t\text{BuR}$ (R = SiMe_3 (**9**); R = H (**10**)) have been prepared. Compound **10** is the first isolated secondary phosphane bearing a bismuthanyl substituent. All isolated compounds were analyzed *via* IR and NMR spectroscopy, mass spectrometry and single crystal X-ray diffraction.

Experimental Section

General Procedure. Unless otherwise specified, all manipulations were carried out under argon atmosphere and exclusion of light using standard Schlenk technique. All solvents used in the reactions and for crystallisations were dried *via* standard techniques, distilled and stored under argon. Solvents were never stored longer than three weeks before use. Obtained products often contain systematic impurities with educts or hydrolysed product and because of that have to be recrystallized to obtain high purity compounds suitable for elemental analysis. The given yields always refer to the purified and not the raw products. For Compound **2** elemental analysis always showed to low values for carbon and hydrogen, even after multiple recrystallization cycles. This might be due to BiCl_3 formation during crystallization. Dipp_2BiX (X = F, Br), $\text{DippMgBr}\cdot\text{THF}$, $t\text{BuP}(\text{SiMe}_3)_2$, $t\text{BuPH}(\text{SiMe}_3)$ and Mes_2SbH were prepared according to literature procedures.^[18,42] BiCl_3 , BiBr_3 and $t\text{BuNH}_2$ were sublimed or distilled prior to use. MeLi (1.6 M in Et_2O) and LiNMe_2 were bought and used as received. NMR spectra were recorded using a Bruker Avance III HD 250 MHz, a Bruker Avance II 300 MHz, a Bruker Avance III 500 MHz or a Avance III HD 500 MHz spectrometer at 300 K. The IR-spectra were run on a Bruker FT-IR spectrometer using the attenuated total reflectance (ATR) mode. For mass spectrometry, a Jeol AccuTOF GCv (CI, LIFDI) was used. The FD-emitters were purchased from Linden ChromSpec GmbH. Elemental analysis was performed on an Elementar Vario MicroCube.

Synthesis of Dipp_3Bi (1**).** Solid $\text{DippMgBr}\cdot\text{THF}$ (1.03 g, 3.05 mmol, 1.0 eq) is slowly added to a suspension of CuCl (302 mg, 3.05 mmol, 1.0 eq) suspended in 30 ml THF and the reaction mixture is warmed to room temperature. Afterwards, solid Dipp_2BiBr (1.90 g, 3.05 mmol, 1.0 eq) is added in small portions. The reaction mixture is heated to reflux and, after stirring for 2 days, cooled back to room temperature. The residue obtained after removal of the solvent *in vacuo* consists of CuCl , compound **1** as well as Dipp_2BiBr and various unidentified by-products. Subsequently, 40 ml *n*-pentane are added and remaining solids are removed *via* filtration. After concentration and storage at -32°C for one week, an orange precipitate is obtained. The precipitate is washed with acetonitrile until the remaining Dipp_3Bi is obtained as pale yellow solid. Yield 21%. Elemental analysis for $\text{C}_{36}\text{H}_{51}\text{Bi}$ calcd: C, 62.41; H, 7.42; found: C, 62.21; H, 7.29; ^1H NMR (500 MHz, toluene- d_8) δ : 7.09–7.35 (br m, 6H, *m-CH*), 7.16 (t, $^3J_{\text{H-H}} = 7.4$ Hz, 3H, *p-CH*), 3.34 (sept, $^3J_{\text{H-H}} = 6.7$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 0.45–1.82 (br m, 36H, $\text{CH}(\text{CH}_3)_2$); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, toluene- d_8) δ : 162.4 (br s, 3C Bi-C), 156.9 (br s, 3C, *m-C*), 155.3 (br s, 3C, *m-C*), 129.2 (s, 3C, *p-C*), 125.8 (br s, 3C, *o-C*), 124.3 (br s, 3C, *o-C*), 42.2 (br s, 3C, $\text{CH}(\text{CH}_3)_2$), 38.1 (br s, 3C, $\text{CH}(\text{CH}_3)_2$), 23.4–26.9 (br m, 6C, $\text{CH}(\text{CH}_3)_2$); IR (cm^{-1}): 3038 (w); 2964 (m); 2950 (s); 2927 (m); 2864 (w); 1566 (w); 1458 (m); 1446 (m);

1408 (w); 1382 (w); 1360 (m); 1341 (w); 1314 (w); 1228 (w); 1175 (w); 1145 (w); 1100 (w); 1087 (w); 1048 (w); 1020 (w); 995 (w); 925 (w); 796 (s); 729 (s); 501 (w); 442 (w); HR-MS: Cl^+ m/z 692.38014 [Dipp_3Bi^+]; calcd 692.37946.

Synthesis of DippBiCl_2 (2**).** Dipp_3Bi (125 mg, 0.18 mmol, 1.0 eq) was dissolved in 5 ml Et_2O and BiCl_3 (113 mg, 0.36 mmol, 2.0 eq) in 5 ml Et_2O are added dropwise over 30 minutes at room temperature. After stirring for 4 days, evaporation of volatiles under reduced pressure and washing of the remaining solid with a mixture of *n*-pentane and diethylether, DippBiCl_2 is obtained as a yellow solid. Yield 87%. ^1H NMR (500 MHz, CD_3CN) δ : 8.06 (d, $^3J_{\text{H-H}} = 7.7$ Hz, 2H, *m-CH*), 7.62 (t, $^3J_{\text{H-H}} = 7.7$ Hz, 1H, *p-CH*), 3.73 (sept, $^3J_{\text{H-H}} = 6.6$ Hz, 2H, $\text{CH}(\text{CH}_3)_2$), 1.31 (d, $^3J_{\text{H-H}} = 6.6$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CD_3CN) δ : 222.6 (s, 1C Bi-C), 160.0 (s, 2C, *m-C*), 131.4 (s, 1C, *p-C*), 130.8 (s, 2C, *o-C*), 36.0 (s, 2C, $\text{CH}(\text{CH}_3)_2$), 25.4 (s, 4C, $\text{CH}(\text{CH}_3)_2$); IR (cm^{-1}): 3044 (w); 2950 (w); 2924 (w); 2848 (w); 1568 (w); 1461 (m); 1447 (m); 1383 (w); 1362 (w); 1348 (w); 1233 (w); 1181 (w); 1148 (w); 1115 (w); 1100 (w); 1083 (w); 1045 (w); 998 (w); 925 (w); 796 (s); 726 (s); 695 (w); 497 (w); 465 (w); HR-MS: Cl^+ m/z 440.05070 [DippBiCl_2^+]; calcd 440.0511.

Synthesis of DippBiBr_2 (3**).** Dipp_2BiBr (0.61 g, 0.98 mmol, 1.0 eq) is dissolved in 15 ml Et_2O and BiBr_3 (0.44 g, 0.98 mmol, 1.0 eq) in 15 ml Et_2O is added dropwise over 30 minutes at 0°C . After stirring for additional 30 minutes at 0°C , the solution is warmed to room temperature and stirred for 12 hours. Little participating solid was removed *via* filtration and volatiles were evaporated under reduced pressure. After washing of the remaining solid with *n*-pentane, **3** is obtained as an orange solid. Yield 91%. Elemental analysis for $\text{C}_{12}\text{H}_{17}\text{Bi}$ calcd: C, 27.19; H, 3.23; found: C, 27.28; H, 3.24; ^1H NMR (300 MHz, CD_3CN) δ : 8.06 (d, $^3J_{\text{H-H}} = 7.7$ Hz, 2H, *m-CH*), 7.63 (t, $^3J_{\text{H-H}} = 7.7$ Hz, 1H, *p-CH*), 3.75 (sept, $^3J_{\text{H-H}} = 6.6$ Hz, 2H, $\text{CH}(\text{CH}_3)_2$), 1.33 (d, $^3J_{\text{H-H}} = 6.6$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CD_3CN) δ : 216.1 (s, 1C, Bi-C), 159.9 (s, 2C, *m-C*), 131.2 (s, 1C, *p-C*), 130.9 (s, 2C, *o-C*), 37.7 (s, 2C, $\text{CH}(\text{CH}_3)_2$), 25.5 (s, 4C, $\text{CH}(\text{CH}_3)_2$); IR (cm^{-1}): 3115 (m), 3009 (m), 2935 (w), 2889 (w), 2836 (w), 2820 (w), 2207 (w), 2194 (w), 2140 (w), 2086 (w), 1953 (w), 1648 (w), 1421 (w), 1391 (w), 1328 (w), 1248 (w), 1059 (w), 936 (m), 831 (m), 774 (m), 763 (m), 660 (m), 522 (s); HR-MS: Cl^+ m/z 530.95639 [$\text{DippBi}^{79}\text{Br}^{81}\text{Br} + \text{H}^+$]; calcd 530.95586.

Synthesis of $\text{Dipp}_2\text{BiNMe}_2$ (5**).** Dipp_2BiBr (320 mg, 0.51 mmol, 1.0 eq), is dissolved in 15 ml Et_2O and cooled to 0°C . After portion wise addition of solid LiNMe_2 (31 mg, 0.62 mmol, 1.2 eq) over 15 minutes, the reaction mixture is slowly warmed to room temperature over 5 hours. All volatiles are removed under reduced pressure and the product is taken up in 20 ml of *n*-pentane and solids are removed *via* filtration. After concentration and storage at -32°C , **5** is obtained in the form of colourless crystals. Yield 95%. Elemental analysis for $\text{C}_{26}\text{H}_{40}\text{BiN}$ calcd: C, 54.25; H, 7.00; N, 2.43; found: C, 54.54; H, 7.04; N, 2.84; ^1H NMR (500 MHz, C_6D_6) δ : 7.26 (m, $^3J_{\text{H-H}} = 7.6$ Hz, 4H, *m-CH*), 7.30 (m, $^3J_{\text{H-H}} = 7.6$ Hz, 2H, *p-CH*), 3.54 (sept, $^3J_{\text{H-H}} = 6.7$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$), 3.44 (s, 6H, $\text{N}(\text{CH}_3)_2$), 1.52 (d, $^3J_{\text{H-H}} = 6.7$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 1.14 (d, $^3J_{\text{H-H}} = 6.7$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, C_6D_6) δ : 173.2 (s, 2C, Bi-C), 156.1 (s, 4C, *m-C*), 129.1 (s, 2C, *p-C*), 126.4 (s, 4C, *o-C*), 49.4 (s, 2C, $\text{N}(\text{CH}_3)_2$), 37.1 (s, 2C, $\text{CH}(\text{CH}_3)_2$), 25.0 (s, 2C, $\text{CH}(\text{CH}_3)_2$), 24.9 (s, 2C, $\text{CH}(\text{CH}_3)_2$); IR (cm^{-1}): 3051 (w), 3039 (w), 2952 (s), 2920 (s), 2862 (s), 1568 (w), 1455 (s), 1445 (s), 1412 (m), 1380 (s), 1361 (s), 1302 (w), 1260 (w), 1232 (w), 1178 (w), 1156 (w), 1116 (w), 1099 (m), 1046 (m), 1003 (w), 926 (s), 793 (m), 720 (s), 500.18 (w), 447.08(m); HR-MS: Cl^+ m/z 574.28492 [$\text{Dipp}_2\text{BiNMe}_2 - \text{H}^+$]; calcd 574.28863.

Synthesis of Dipp_2BiMe (6**).** Dipp_2BiBr (1.00 g, 1.64 mmol, 1.0 eq) is dissolved in 10 ml Et_2O cooled to -50°C and 1.03 ml of a 1.6 M solution of MeLi (1.64 mmol, 1.0 eq) in Et_2O was added dropwise. Afterwards, the mixture is slowly warmed to room temperature over 5 hours. After

evaporation at reduced pressure, 15 ml of *n*pentane are added and black solids are removed *via* filtration. The filtrate was concentrated and, after storage at $-32\text{ }^{\circ}\text{C}$ for one week, **6** was obtained as crystalline colourless solid. Yield 46%. Elemental analysis for $\text{C}_{25}\text{H}_{37}\text{Bi}$ calcd: C 54.94; H, 6.82; found: C, 54.94; H, 6.80; ^1H NMR (300 MHz, C_6D_6) δ : 7.13-7.24 (m, 6H, *m-CH*, *p-CH*), 3.18 (sept, $^3J_{\text{H-H}} = 6.7\text{ Hz}$, 4H, $\text{CH}(\text{CH}_3)_2$), 1.73 (s, 3H, BiCH_3), 1.10 (d, $^3J_{\text{H-H}} = 6.6\text{ Hz}$, 12H, $\text{CH}(\text{CH}_3)_2$), 1.08 (d, $^3J_{\text{H-H}} = 6.6\text{ Hz}$, 12H, $\text{CH}(\text{CH}_3)_2$); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, C_6D_6) δ : 159.9 (s, 2C *Bi-C*), 155.8 (s, 4C *m-C*), 128.9 (s, 2C *p-C*), 124.8 (s, 4C, *o-C*), 40.0 (s, 2C $\text{CH}(\text{CH}_3)_2$), 25.5 (s, 4C $\text{CH}(\text{CH}_3)_2$), 24.7 (s, 4C, $\text{CH}(\text{CH}_3)_2$), *B-CH*₃ not observed; IR (cm^{-1}): 3051 (w), 3039 (w), 2952 (s), 2920 (m), 2862 (m), 1567 (w), 1455 (m), 1445 (m), 1411 (w), 1380 (m), 1360 (m), 1301 (w), 1260 (w), 1232 (w), 1177 (w), 1156 (w), 1116 (w), 1100 (w), 1046 (m), 1003 (w), 926 (w), 793 (s), 720 (s), 500 (w), 447 (m); HR-MS: Cl^+ *m/z* 547.27849 [$\text{Dipp}_2\text{BiMe} + \text{H}$] $^+$; calcd 547.27773.

Synthesis of $\text{Dipp}_2\text{BiNHtBu}$ (7**):** Compound **5** (300 mg, 0.52 mmol, 1.0 eq) is dissolved in 2 ml of dry *t*BuNH₂ and stirred for 3 weeks at room temperature under ambient light. Volatiles are removed under reduced pressure and the highly viscous remains are taken up in 5 ml of *n*pentane. Black solids are removed *via* filtration and the remaining yellow filtrate is concentrated and stored at $-32\text{ }^{\circ}\text{C}$. After two days, pale yellow crystals of **7** are obtained. Yield 57%. Elemental analysis for $\text{C}_{28}\text{H}_{44}\text{BiN}$ calcd: C, 55.71; H, 7.35; N, 2.32; found: C, 56.10; H, 7.16; N, 2.39; ^1H NMR (500 MHz, C_6D_6) δ : 7.20-7.27 (m, 6H, *m-CH*, *p-CH*), 3.60 (sept, $^3J_{\text{H-H}} = 6.7\text{ Hz}$, 4H, $\text{CH}(\text{CH}_3)_2$), 2.35 (s, 1H, *NH*), 1.25 (s, 9H, $\text{NC}(\text{CH}_3)_3$), 1.34 (d, $^3J_{\text{H-H}} = 6.7\text{ Hz}$, 12H, $\text{CH}(\text{CH}_3)_2$); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, C_6D_6) δ : 165.2 (s, 1C *Bi-C*), 156.1 (s, 4C, *m-C*), 129.0 (s, 2C, *p-C*), 126.1 (s, 2C, *o-C*), 52.9 (s, 1C, $\text{NC}(\text{CH}_3)_3$), 37.2 (s, 4C, $\text{CH}(\text{CH}_3)_2$), 34.8 (s, 3C, $\text{NC}(\text{CH}_3)_3$), 25.3 (s, 4C, $\text{CH}(\text{CH}_3)_2$), 24.9 (s, 4C, $\text{CH}(\text{CH}_3)_2$); IR (cm^{-1}): 3295 (w) 3132 (w) 3040 (w) 2949 (s) 2921 (s) 2863 (m) 1567 (m) 1458 (s) 1446 (s) 1415 (w) 1382 (m) 1360 (s) 1234 (w) 1203 (s) 1177 (m) 1159 (w) 1145 (w) 1101 (w) 1048 (w) 1017 (w) 1004 (w) 936 (w) 912 (w) 796 (s) 752 (w) 729 (s) 675 (w) 531 (w) 494 (w) 440 (w); HR-MS: Cl^+ *m/z* 442.19332 [DippBiNHtBu] $^+$; calcd 442.19473; *m/z* 530.23613 [$\text{Dipp}_2\text{Bi} - \text{H}$] $^+$; calcd 530.23861.

Synthesis of $\text{Dipp}_2\text{BiSbMes}_2$ (8**):** To a suspension of Mes_2SbH (91.6 mg, 0.25 mmol, 1.0 eq) in 3 ml *n*pentane cooled to $-30\text{ }^{\circ}\text{C}$ compound **5** (150 mg, 0.25 mmol, 1.0 eq) dissolved in 3 ml *n*pentane is added and the reaction mixture is slowly warmed to $-5\text{ }^{\circ}\text{C}$. After concentration and storage at $-32\text{ }^{\circ}\text{C}$ red crystals of **8** are obtained. Yield 34%. Elemental analysis for $\text{C}_{42}\text{H}_{56}\text{BiSb}$ calcd: C, 56.58; H, 6.33; found: C, 54.54; H, 6.31; ^1H NMR (300 MHz, C_6D_6) δ : 7.19-7.48 (m, 6H, *Bi-m-CH*, *Bi-p-CH*), 6.68 (s, 4H, *Sb-m-CH*), 3.35 (sept, $^3J_{\text{H-H}} = 7.0\text{ Hz}$, 4H, $\text{CH}(\text{CH}_3)_2$), 2.49 (s, 12H, *o-CH*₃), 2.08 (s, 12H, *p-CH*₃), 1.21 (d, $^3J_{\text{H-H}} = 7.0\text{ Hz}$, 12H, $\text{CH}(\text{CH}_3)_2$), 0.95 (d, $^3J_{\text{H-H}} = 7.0\text{ Hz}$, 12H, $\text{CH}(\text{CH}_3)_2$); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, C_6D_6) δ : 157.4 (br s, 2C, *Bi-C*), 155.9 (s, 4C *Bi-m-C*), 145.3 (s, 4C, *Sb-o-CCH*₃), 137.5 (s, 2C, *Sb-p-CCH*₃), 133.0 (s, 2C, *Sb-p-CCH*₃), 128.6 (s, 4C, *Sb-m-CH*), 128.4 (s, 2C, *Bi-p-C*), 125.1 (s, 4C, *Bi-o-C*), 42.7 (s, 4C, *Bi-CH}(\text{CH}_3)_2), 27.5 (s, 4C, *Sb-o-CCH*₃), 25.1 (s, 4C, *Bi-CH}(\text{CH}_3)_2), 24.6 (s, 4C, *Bi-CH}(\text{CH}_3)_2), 20.4 (s, 2C, *Sb-p-CCH*₃); IR (cm^{-1}): 3043 (w); 3013 (w); 2959 (m); 2913 (m); 2860 (m); 1551 (w); 1456 (w); 1443 (s); 1407 (s); 1380 (w); 1359 (m); 1286 (m); 1229 (w); 1174 (w); 1157 (w); 1044 (m); 1025 (w); 995 (w); 923 (w); 848 (s); 793 (s); 725 (s); 703 (m); 579 (w); 541 (m); 496 (w); HR-MS: LIFDI^+ *m/z* 890.32154 [$\text{Dipp}_2\text{BiSbMes}_2$] $^+$; calcd 890.32241.***

Synthesis of $\text{Dipp}_2\text{BiP}^t\text{Bu}(\text{SiMe}_3)$ (9**):** Dipp_2BiF (150 mg, 0.27 mmol, 1.0 eq) is suspended in 5 ml of TFT, cooled to $-29\text{ }^{\circ}\text{C}$ and *t*BuP(SiMe₃)₂ (63 mg, 0.27 mol, 1 eq) in 1 ml TFT are added. The suspension is allowed to warm to room temperature over the course of two hours and volatiles are removed under reduced pressure. The remains are dissolved in 10 ml *n*pentane and stored at $-32\text{ }^{\circ}\text{C}$, whereupon **9** is obtained in the form of pale yellow crystals. Yield 41%. Elemental analysis for $\text{C}_{31}\text{H}_{52}\text{BiP}_1\text{Si}_1$

calcd: C, 53.74; H, 7.57; found: C, 53.40; H, 6.97; ^1H NMR (500 MHz, C_6D_6) δ : 7.18-7.25 (m, 6H, *m-CH*, *p-CH*), 7.30 (m, $^3J_{\text{H-H}} = 7.6\text{ Hz}$, 2H, *p-CH*), 3.52 (sept, $^3J_{\text{H-H}} = 6.6\text{ Hz}$, 2H, $\text{CH}(\text{CH}_3)_2$), 3.51 (sept, $^3J_{\text{H-H}} = 6.6\text{ Hz}$, 2H, $\text{CH}(\text{CH}_3)_2$), 1.32 (d, $^3J_{\text{P-H}} = 11.4\text{ Hz}$, 9H, $\text{PC}(\text{CH}_3)_3$), 1.17 (d, $^3J_{\text{H-H}} = 6.6\text{ Hz}$, 12H, $\text{CH}(\text{CH}_3)_2$), 1.11 (d, $^3J_{\text{H-H}} = 6.5\text{ Hz}$, 12H, $\text{CH}(\text{CH}_3)_2$), 0.41 (d, $^3J_{\text{P-H}} = 3.3\text{ Hz}$, 9H, $\text{PSi}(\text{CH}_3)_3$); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, C_6D_6) δ : 156.5 (s, 4C *m-C*), 148.7 (s, 2C, *Bi-C*, found *via* HMBC), 129.1 (s, 2C *p-C*), 126.1 (s, 4C, *o-C*), 40.8 (br s, 4C, $\text{CH}(\text{CH}_3)_2$), 35.7 (d, $^2J_{\text{P-H}} = 11.9\text{ Hz}$, 3C, $\text{PC}(\text{CH}_3)_3$), 33.9 (d, $^1J_{\text{P-C}} = 34.8\text{ Hz}$, 1C, $\text{PC}(\text{CH}_3)_3$), 25.4 (s, 4C, $\text{CH}(\text{CH}_3)_2$), 25.2 (s, 4C, $\text{CH}(\text{CH}_3)_2$), 4.83 (d, $^2J_{\text{P-H}} = 9.5\text{ Hz}$, 3C, $\text{PSi}(\text{CH}_3)_3$); $^{31}\text{P}\{^1\text{H}\}$ NMR (121 MHz, C_6D_6) δ : -45.1 (s, 1P, *Bi-P-Si*); $^{29}\text{Si-DEPT}$ NMR (100 MHz, C_6D_6) δ : 2.4 (d, $^1J_{\text{P-Si}} = 56.7\text{ Hz}$, 1Si, *Bi-P-Si*); IR (cm^{-1}): 3040 (w); 2957 (s); 2922 (s); 2899 (m); 2863 (m); 1569 (w); 1459 (w); 1445 (s); 1409 (w); 1382 (s); 1360 (s); 1338 (w); 1306 (w); 1243 (w); 1231 (w); 1175 (m); 1147 (w); 1045 (w); 996 (w); 927 (m); 836 (w); 793 (s); 726 (s); 592 (w); 495 (w); HR-MS: Cl^+ *m/z* 692.33549 [$\text{Dipp}_2\text{BiP}^t\text{Bu}(\text{SiMe}_3)$] $^+$; calcd 692.33797.

Synthesis of $\text{Dipp}_2\text{BiPH}^t\text{Bu}$ (10**):** Dipp_2BiF (50 mg, 0.09 mmol, 1 eq) is suspended in 5 ml of TFT, cooled to $-29\text{ }^{\circ}\text{C}$ and *t*BuPH(SiMe₃) (15 mg, 0.09 mol, 1 eq) in 0.5 ml TFT are added. The suspension is allowed to warm to $5\text{ }^{\circ}\text{C}$ over the course of two hours and volatiles are removed under reduced pressure. The remains are dissolved in 0.1 ml *n*pentane and stored at $-32\text{ }^{\circ}\text{C}$, whereupon **10** is obtained in the form of pale yellow crystals. Yield 53%. Elemental analysis for $\text{C}_{28}\text{H}_{44}\text{BiP}_1$ calcd: C, 54.19; H, 7.15; found: C, 53.99; H, 6.87; ^1H NMR (500 MHz, C_6D_6) δ : 7.26-7.18 (m, 6H, *m-CH*, *p-CH*), 3.56 (d, $^1J_{\text{P-H}} = 166.7\text{ Hz}$, 1H, *PH*), 3.47 (sept, $^3J_{\text{H-H}} = 6.6\text{ Hz}$, 1H, $\text{CH}(\text{CH}_3)_2$), 3.46 (sept, $^3J_{\text{H-H}} = 6.6\text{ Hz}$, 1H, $\text{CH}(\text{CH}_3)_2$), 3.22 (sept, $^3J_{\text{H-H}} = 6.7\text{ Hz}$, 1H, $\text{CH}(\text{CH}_3)_2$), 1.32 (d, $^3J_{\text{P-H}} = 10.8\text{ Hz}$, 9H, $\text{P}(\text{CH}_3)_3$), 1.22 (d, $^3J_{\text{H-H}} = 6.7\text{ Hz}$, 6H, $\text{CH}(\text{CH}_3)_2$), 1.22 (d, $^3J_{\text{H-H}} = 6.7\text{ Hz}$, 6H, $\text{CH}(\text{CH}_3)_2$), 1.07 (d, $^3J_{\text{H-H}} = 6.7\text{ Hz}$, 6H, $\text{CH}(\text{CH}_3)_2$), 1.02 (d, $^3J_{\text{H-H}} = 6.7\text{ Hz}$, 6H, $\text{CH}(\text{CH}_3)_2$); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, C_6D_6) δ : 159.1 (br s, 1C, *Bi-C*), 156.2 (s, 2C, *m-C*), 155.7 (s, 2C, *m-C*), 153.7 (br s, 1C, *Bi-C*), 129.0 (s, 1C, *p-C*), 129.0 (s, 1C, *p-C*), 125.4 (s, 2C *o-C*), 125.4 (s, 2C *o-C*), 42.9 (s, 1C, $\text{CH}(\text{CH}_3)_2$), 42.8 (s, 1C, $\text{CH}(\text{CH}_3)_2$), 41.1 (s, 1C, $\text{CH}(\text{CH}_3)_2$), 41.0 (s, 1C, $\text{CH}(\text{CH}_3)_2$), 34.4 (d, $^3J_{\text{P-H}} = 11.4\text{ Hz}$, 3C, $\text{PC}(\text{CH}_3)_3$), 28.9 (d, $^2J_{\text{P-H}} = 24.8\text{ Hz}$, 3C, $\text{PC}(\text{CH}_3)_3$), 25.5 (s, 1C, $\text{CH}(\text{CH}_3)_2$), 25.5 (s, 1C, $\text{CH}(\text{CH}_3)_2$), 25.4 (s, 1C, $\text{CH}(\text{CH}_3)_2$), 25.0 (s, 1C, $\text{CH}(\text{CH}_3)_2$); $^{31}\text{P}\{^1\text{H}\}$ (100 MHz, C_6D_6) δ : -34.5 (s, 1P); $^{31}\text{P}\{^1\text{H}\}$ (100 MHz, C_6D_6) δ : -34.5 (m, $^1J_{\text{P-H}} = 166.7\text{ Hz}$, $^3J_{\text{P-H}} = 10.8\text{ Hz}$, 1P); IR (cm^{-1}): 3051 (w); 3037 (w); 2956 (s); 2921 (s); 2889 (m); 2860(m); 2272 (w, *P-H*); 1568 (m); 1456 (s); 1445 (s); 1411 (w); 1381 (m); 1359 (s); 1339 (w); 1310 (w); 1292 (w); 1260 (w); 1232 (w); 1196 (w); 1172 (m); 1146 (w); 1118 (w); 1101 (w); 1046 (w); 1025 (w); 1015 (w); 1000 (m); 927 (w); 828 (w); 809 (m); 796 (s); 728 (s); 636 (w); 591 (w); 576 (w); 496 (w); 445 (w); HR-MS: LIFDI^+ *m/z* 620.30013 [$\text{Dipp}_2\text{BiPH}^t\text{Bu}$] $^+$; calcd 620.29845.

X-ray diffraction analysis. Single crystal x-ray diffraction analysis was conducted using a Stoe IPDS 2, Stoe IPDS 2T, Stoe StadiVari or a Bruker D8 Quest diffractometer. The diffractometers use Mo-K α ($\lambda = 0.71073\text{ \AA}$) radiation and respective X-ray optics. Structures were solved *via* intrinsic phasing using SHELXT-2015. Structure refinement was performed *via* full-matrix-least-squares against F^2 using SHELXL-2015. All structures were solved and refined using the OLEX2 platform. Deposition Numbers 2234536 (**1**), 2234534 (**2a**), 2234543 (**2b**), 2234533 (**3**), 2234538 (**4**), 2234535 (**5**), 2234537 (**6**), 2234539 (**7**), 2234541 (**8**), 2234542 (**9**) and 2234540 (**10**), contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Acknowledgements

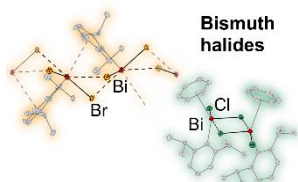
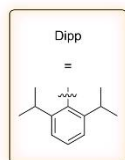
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Keywords: bismuth • antimony • phosphorus • organometallic chemistry • interpnictogen compounds

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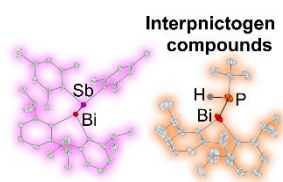
Entry for the Table of Contents

FULL PAPER

**Bismuth halides**

Dipp

=

**Interpnictogen compounds***Author(s), Corresponding Author(s)****Page No. – Page No.****Title**

Herein, we report about the preparation of multiple new 2,6 diisopropylphenyl (Dipp) substituted (halido-) bismuthanes, namely, Dipp_3Bi and compounds of the form DippBiX_2 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$). Reactivity of DippBiCl_2 towards nucleophiles (MeLi , LiNMe_2) was examined, where mostly scrambling reactions with a preference for two Dipp substituents at bismuth were observed. Moreover, new interpnictogen compounds with Bi-N, -P, and even -Sb single bonds were prepared and isolated.

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1. Mass spectra

1.1 Dipp₃Bi (1)

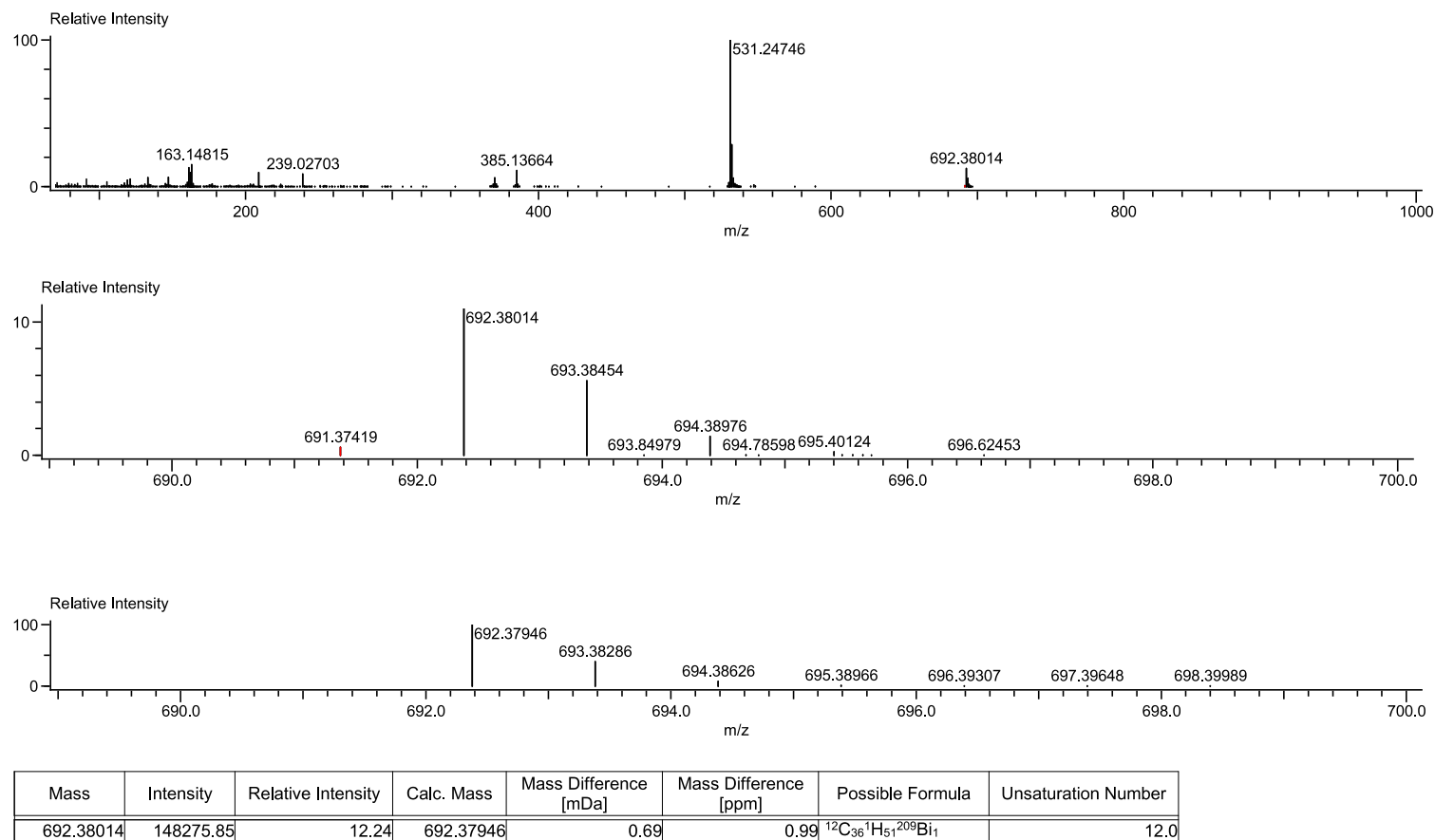


Figure S1.1. HR-Cl(+)-Mass spectrum of Dipp₃Bi (1) as [M]⁺. Top: Whole spectrum. Middle: High resolution extract. Bottom: Calculated isotope pattern.

1.2 DippBiCl₂ (2)

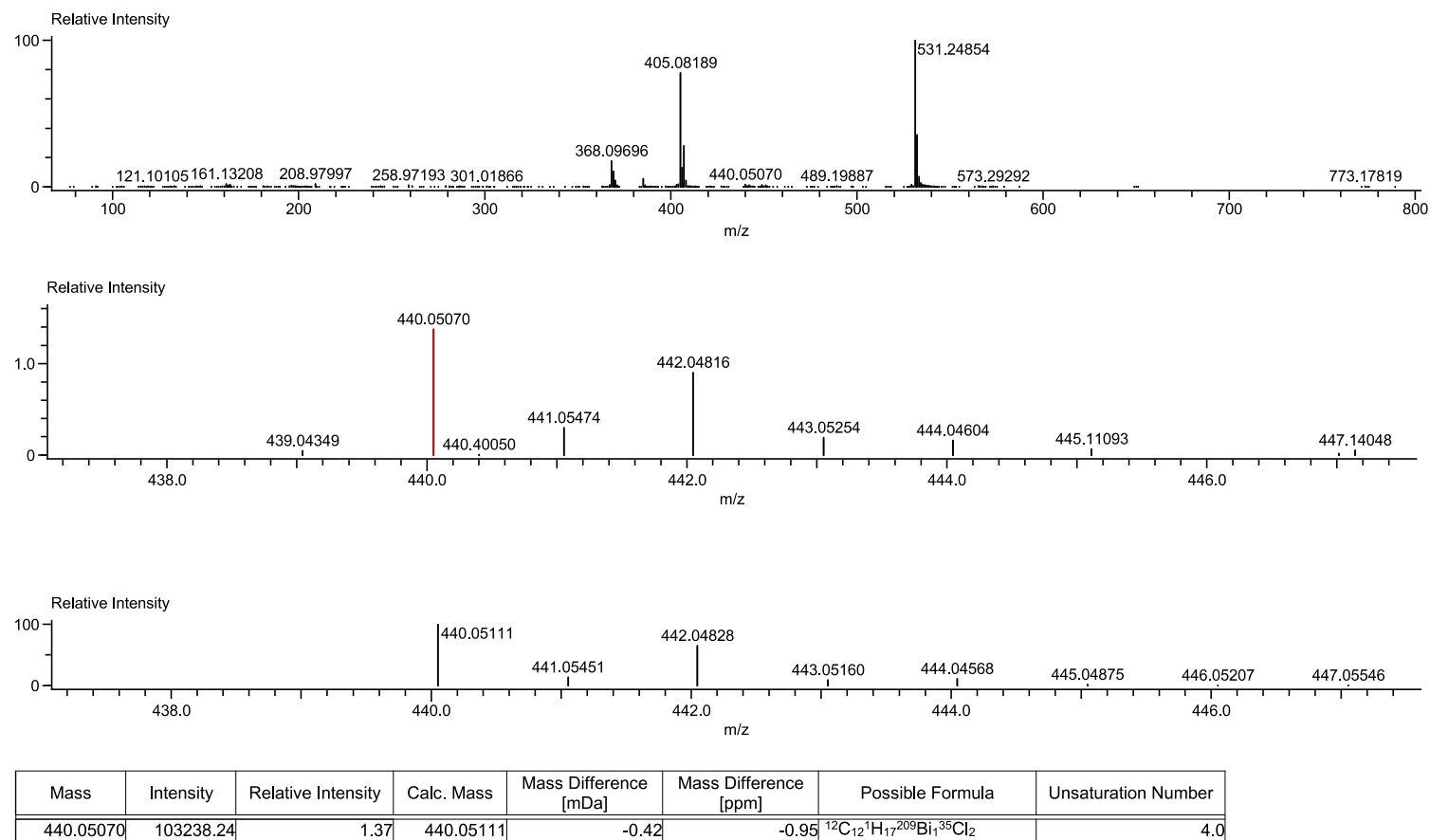


Figure S1.2. HR-Cl(+)⁺ Mass spectrum of DippBiCl₂ (2) as [M]⁺. Top: Whole spectrum. Middle: High resolution extract. Bottom: Calculated isotope pattern.

1.3 DippBiBr₂ (3)

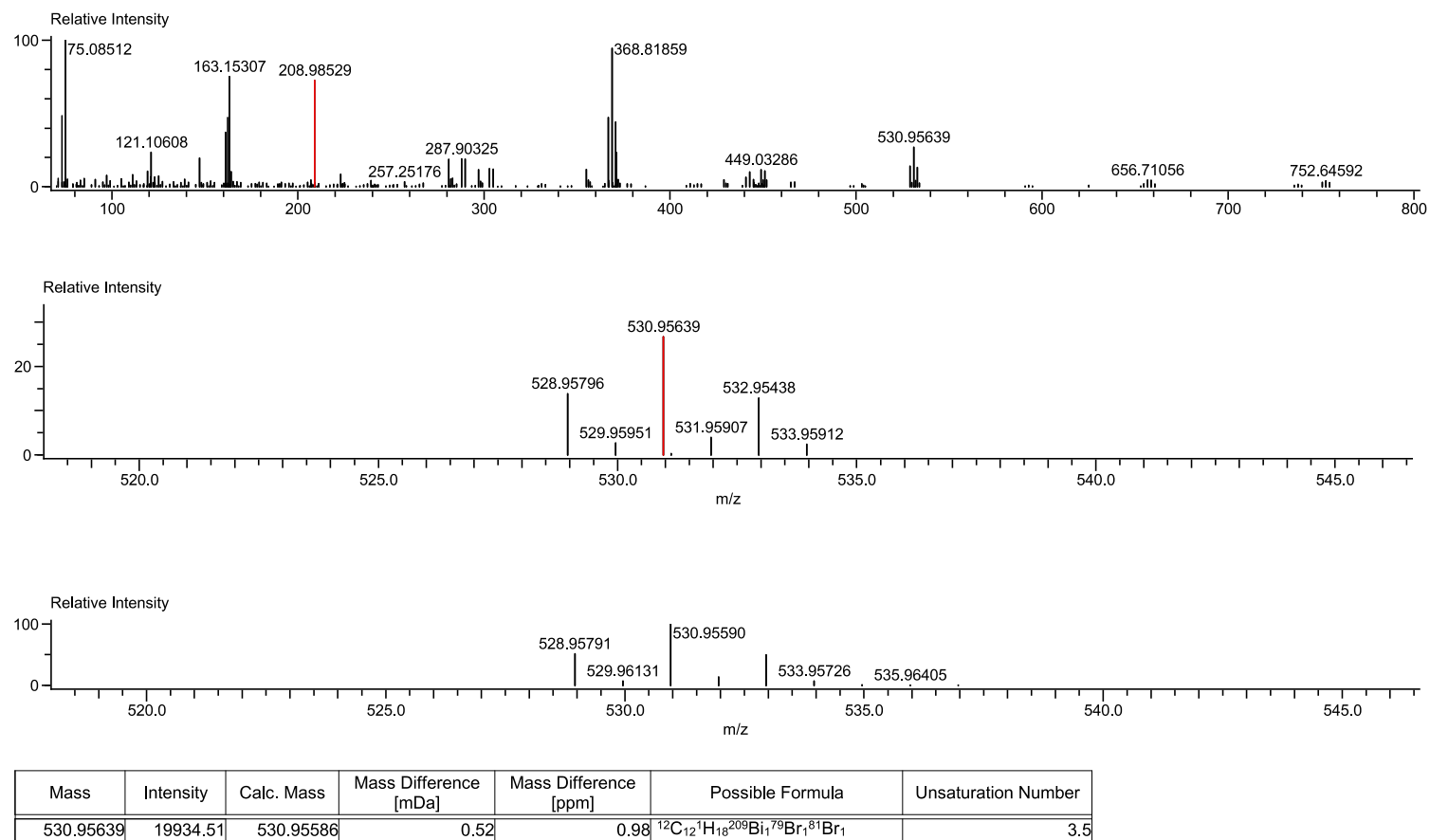
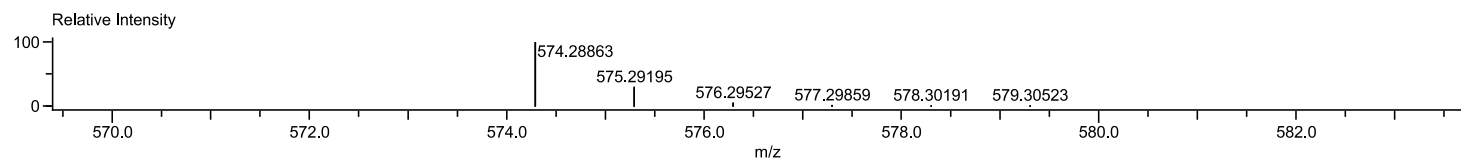
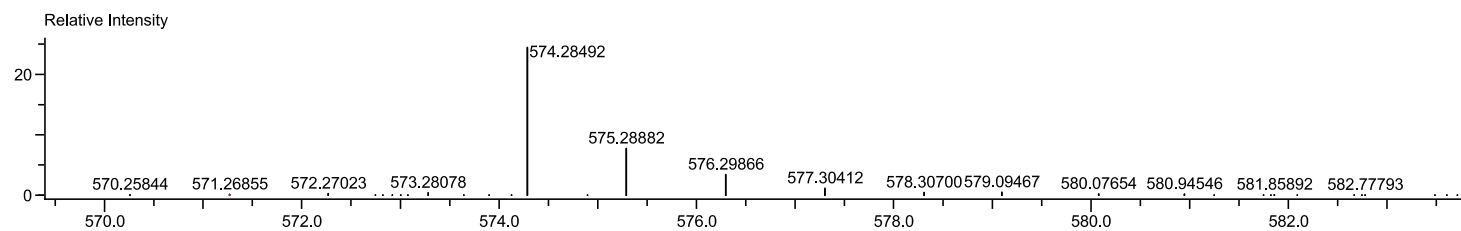
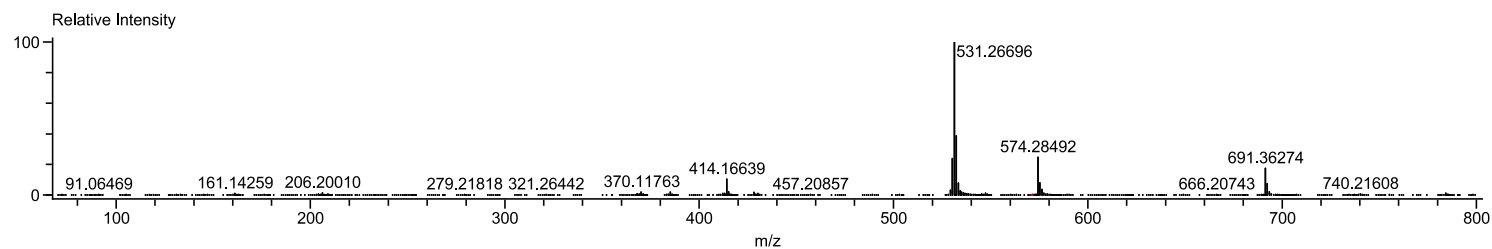


Figure S1.3. HR-Cl(+)⁺ Mass spectrum of DippBiBr₂ (3) as [M + H]⁺. Top: Whole spectrum. Middle: High resolution extract. Bottom: Calculated isotope pattern.

1.4 Dipp₂BiNMe₂ (5)



Mass	Intensity	Relative Intensity	Calc. Mass	Mass Difference [mDa]	Mass Difference [ppm]	Possible Formula	Unsaturation Number
574.28492	3138031.37	24.38	574.28863	-3.72	-6.47	¹² C ₂₆ ¹ H ₃₉ ²⁰⁹ Bi ₁ ¹⁴ N ₁	8.5

Figure S1.4. HR-Cl(+)⁺ Mass spectrum of Dipp₂BiNMe₂ (6) as [M - H]⁺. Top: Whole spectrum. Middle: High resolution extract. Bottom: Calculated isotope pattern.

1.5 Dipp₂BiMe (6)

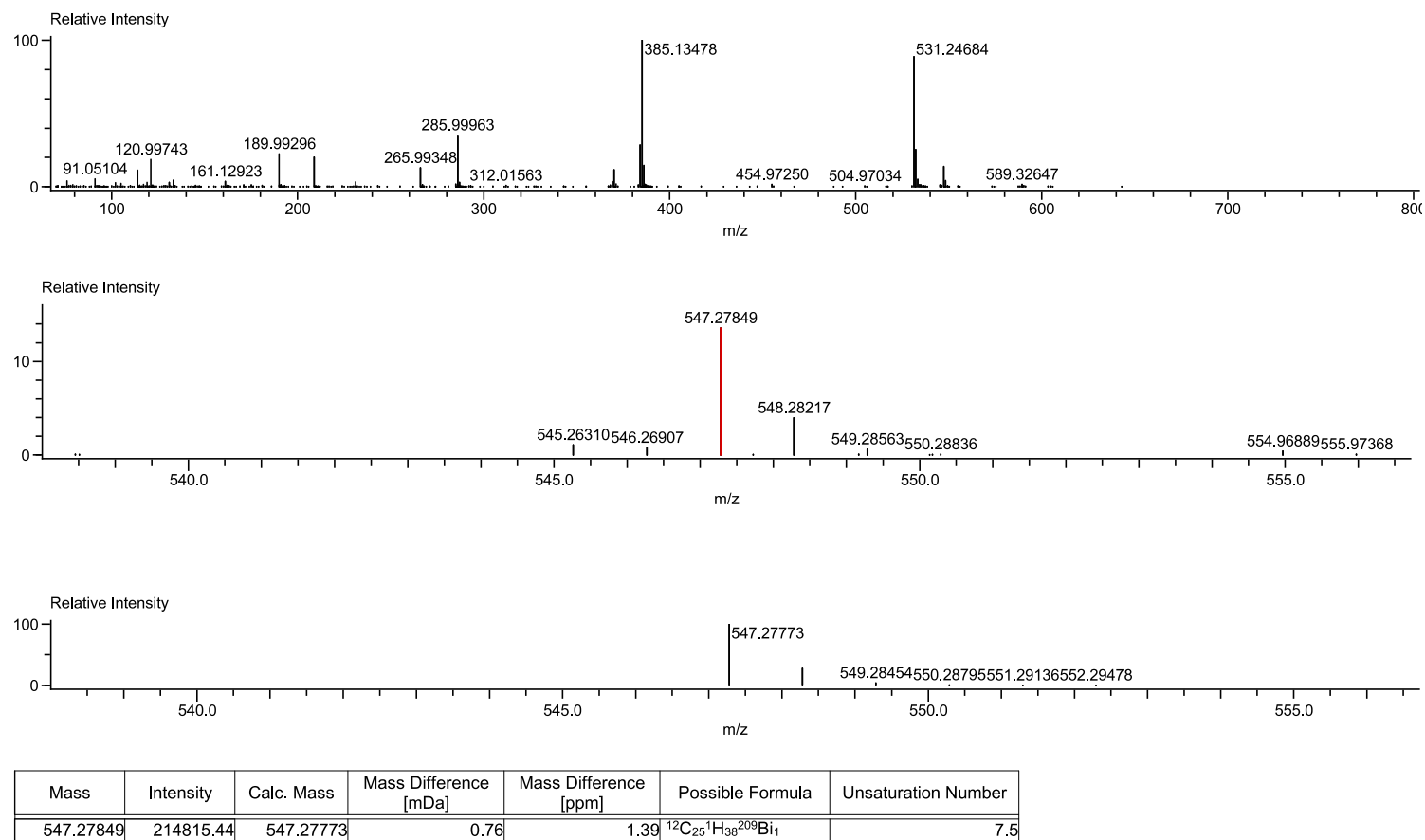
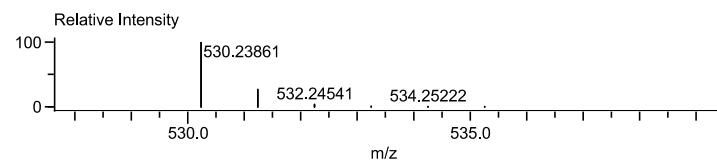
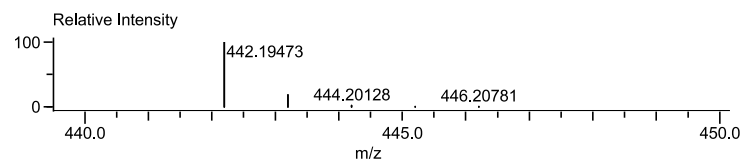
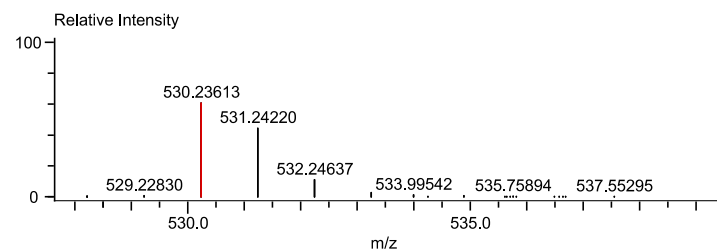
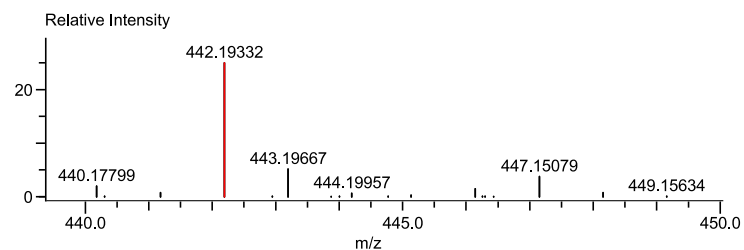
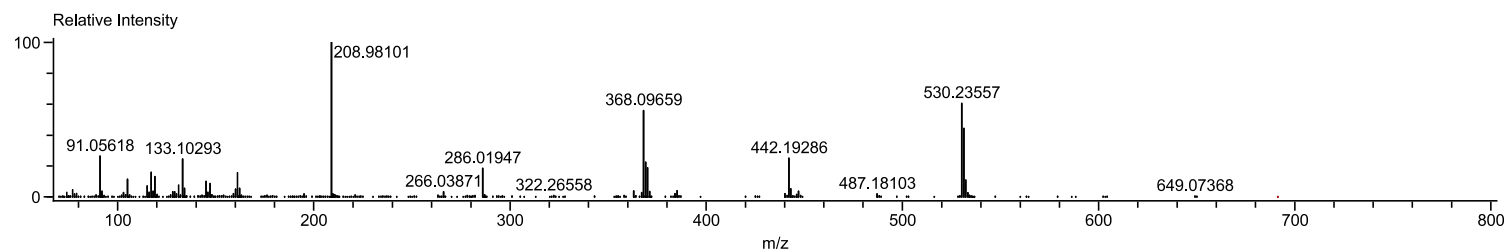


Figure S1.5. HR-Cl(+)⁺ Mass spectrum of Dipp₂BiMe (6) as [M + H]⁺. Top: Whole spectrum. Middle: High resolution extract. Bottom: Calculated isotope pattern.

1.6 Dipp₂BiNH*t*Bu (7)



Mass	Intensity	Relative Intensity	Calc. Mass	Mass Difference [mDa]	Mass Difference [ppm]	Possible Formula	Unsaturation Number
442.19332	313036.15	24.95	442.19473	-1.42	-3.20	¹² C ₁₆ ¹ H ₂₇ ²⁰⁹ Bi ₁ ¹⁴ N ₁	4.5

Mass	Intensity	Relative Intensity	Calc. Mass	Mass Difference [mDa]	Mass Difference [ppm]	Possible Formula	Unsaturation Number
530.23613	760145.83	60.60	530.23861	-2.47	-4.67	¹² C ₂₄ ¹ H ₃₃ ²⁰⁹ Bi ₁	9.0

Figure 1.6. HR-Cl(+)⁺ Mass spectrum of Dipp₂BiNH*t*Bu (5) as [M - Dipp]⁺ and [M - *t*BuNH₂]⁺. Top: Whole spectrum. Middle: High resolution extracts. Bottom: Calculated isotope patterns.

1.7 Dipp₂BiSbMes₂ (**8**)

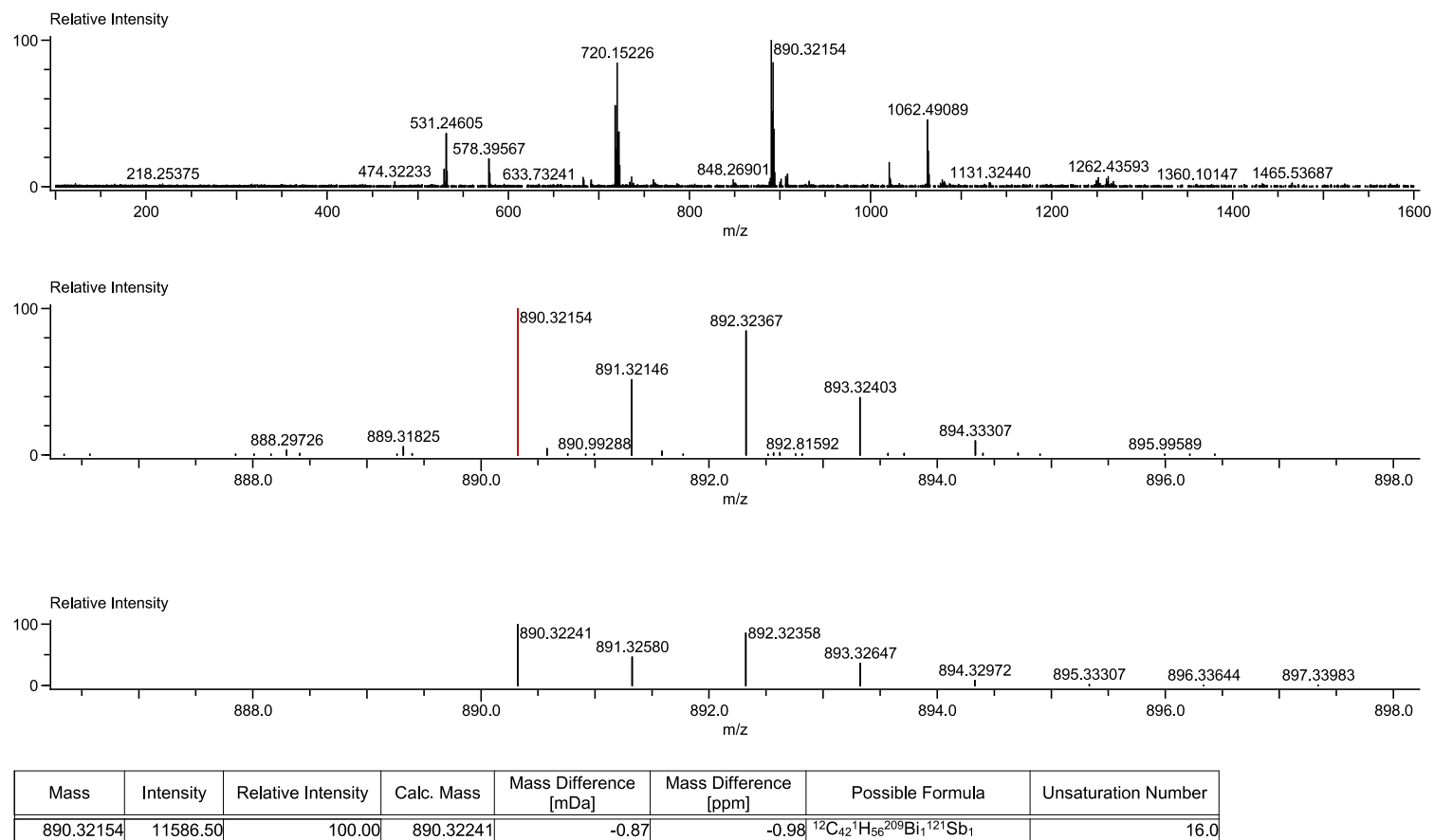


Figure S1.7. HR-LIFDI(+) Mass spectrum of a solution of Dipp₂BiSbMes₂ (**8**) as [M]⁺, Dipp₄Bi₂ as [M]⁺ (m/z = 1062.49089) and Mes₄Sb₂ as [M]⁺ (m/z = 718.15210). Top: Whole spectrum. Middle: High resolution extract of Dipp₂BiSbMes₂ (**8**). Bottom: Calculated isotope pattern for Dipp₂BiSbMes₂ (**8**).

1.8 Dipp₂BiP*t*Bu(SiMe₃) (9)

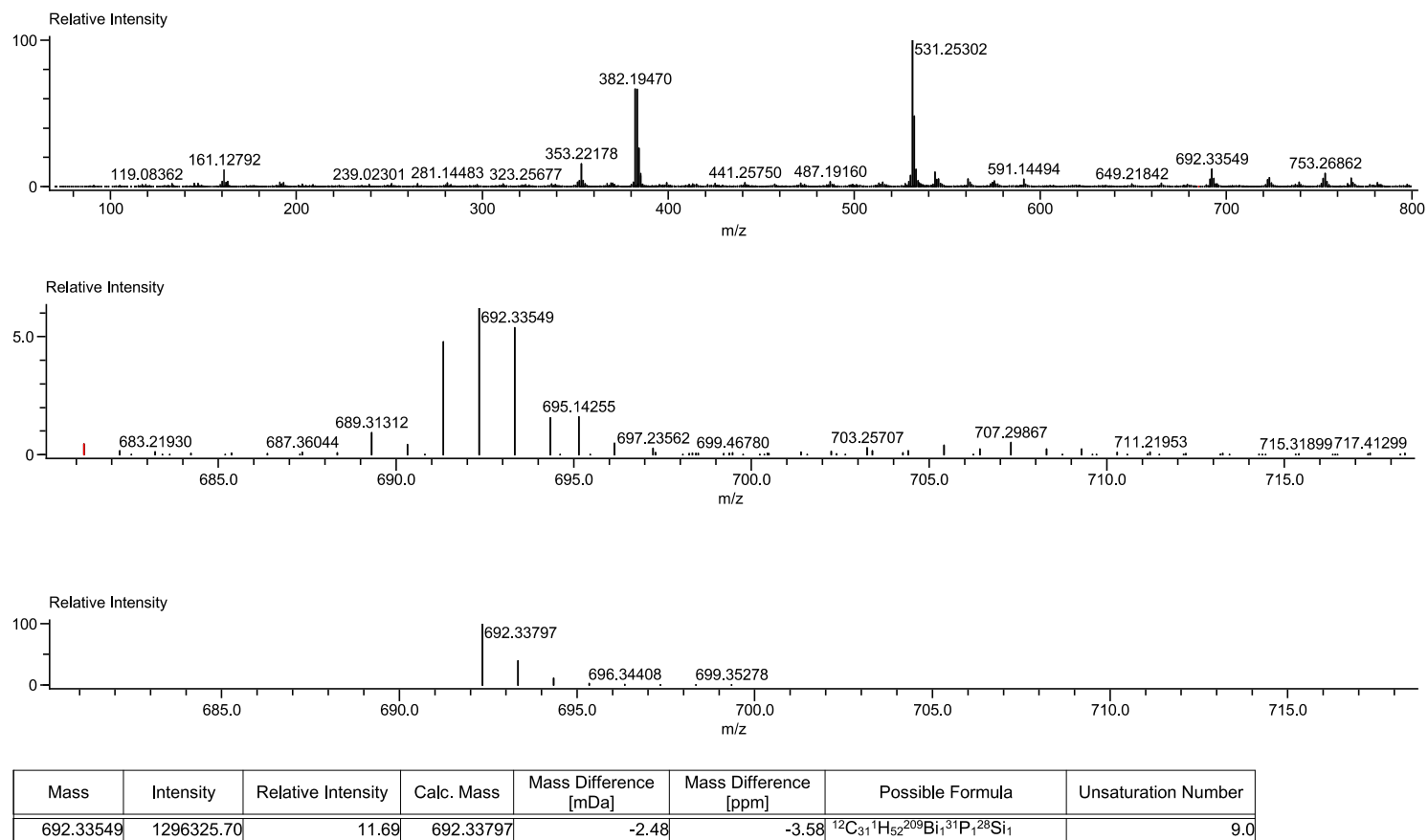
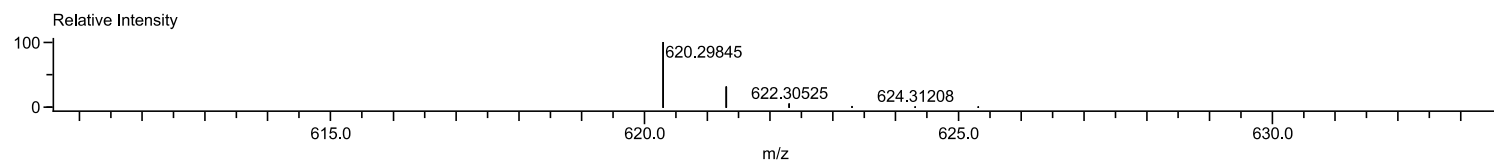
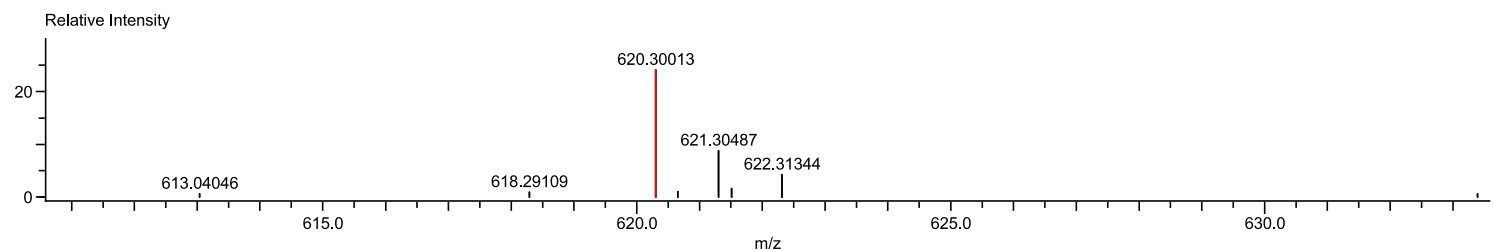
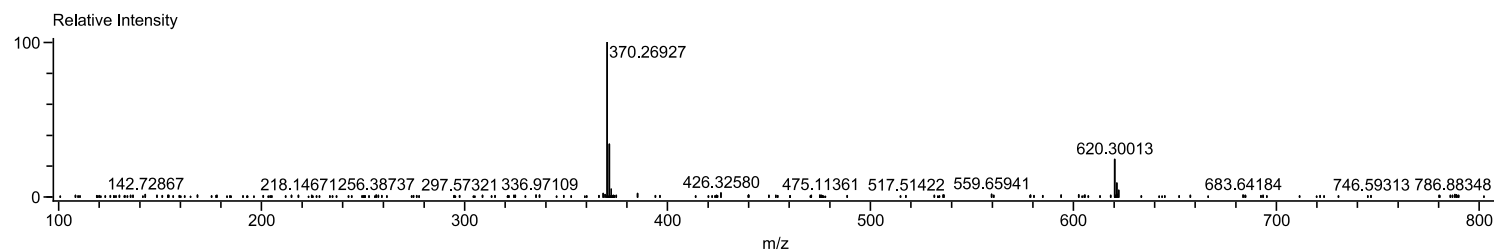


Figure S1.8. HR-Cl(+)⁺ Mass spectrum of Dipp₂BiP*t*Bu(SiMe₃) (9) as [M]⁺. Top: Whole spectrum. Middle: High resolution extract. Bottom: Calculated isotope pattern.

1.9 Dipp₂BiPHtBu (10)



Mass	Intensity	Relative Intensity	Calc. Mass	Mass Difference [mDa]	Mass Difference [ppm]	Possible Formula	Unsaturation Number
620.30013	16284.97	24.06	620.29845	1.69	2.72	¹² C ₂₈ ¹ H ₄₄ ²⁰⁹ Bi ₁ ³¹ P ₁	9.0

Figure S1.9. HR-LIFDI(+) Mass spectrum of Dipp₂BiPHtBu (10) as [M]⁺. Top: Whole spectrum. Middle: High resolution extract. Bottom: Calculated isotope pattern.

2. NMR spectra

2.1 Dipp₃Bi (1)

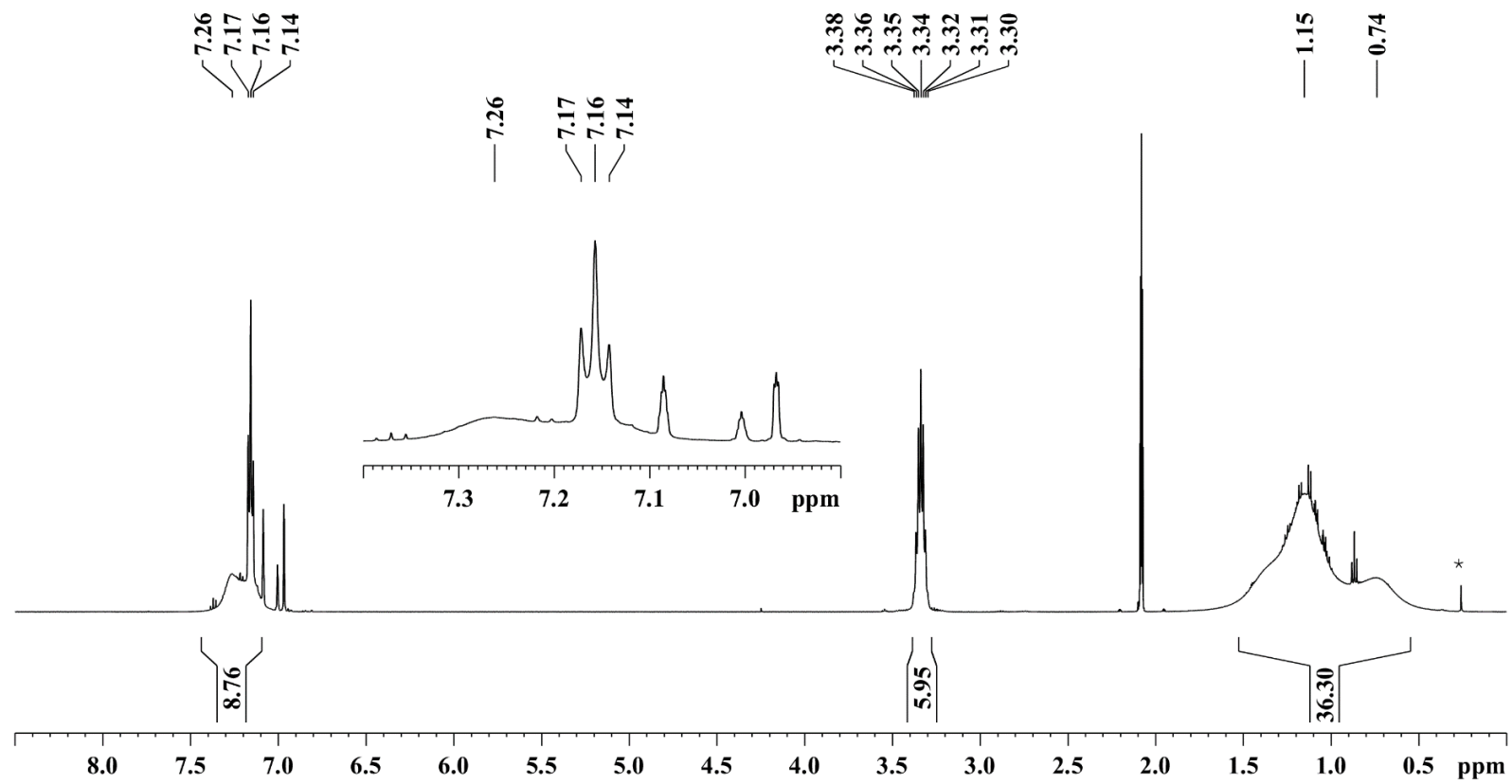


Figure S2.1.1: ¹H NMR spectrum (500 MHz) of **1** in toluene-d₈ at room temperature (* = silicon grease).

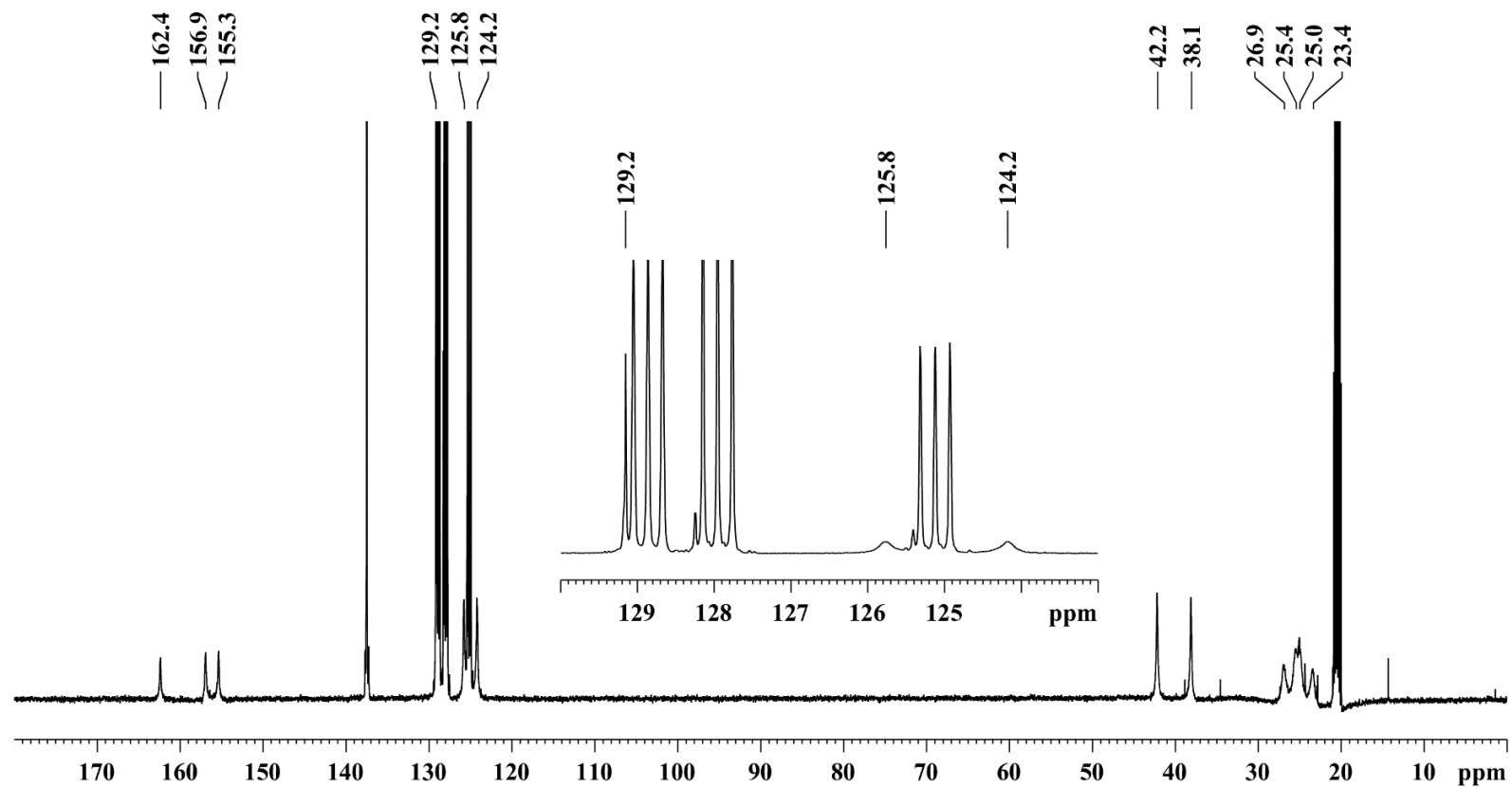


Figure S2.1.2: ^{13}C NMR spectrum (125 MHz) of **1** in tol-d_8 at room temperature.

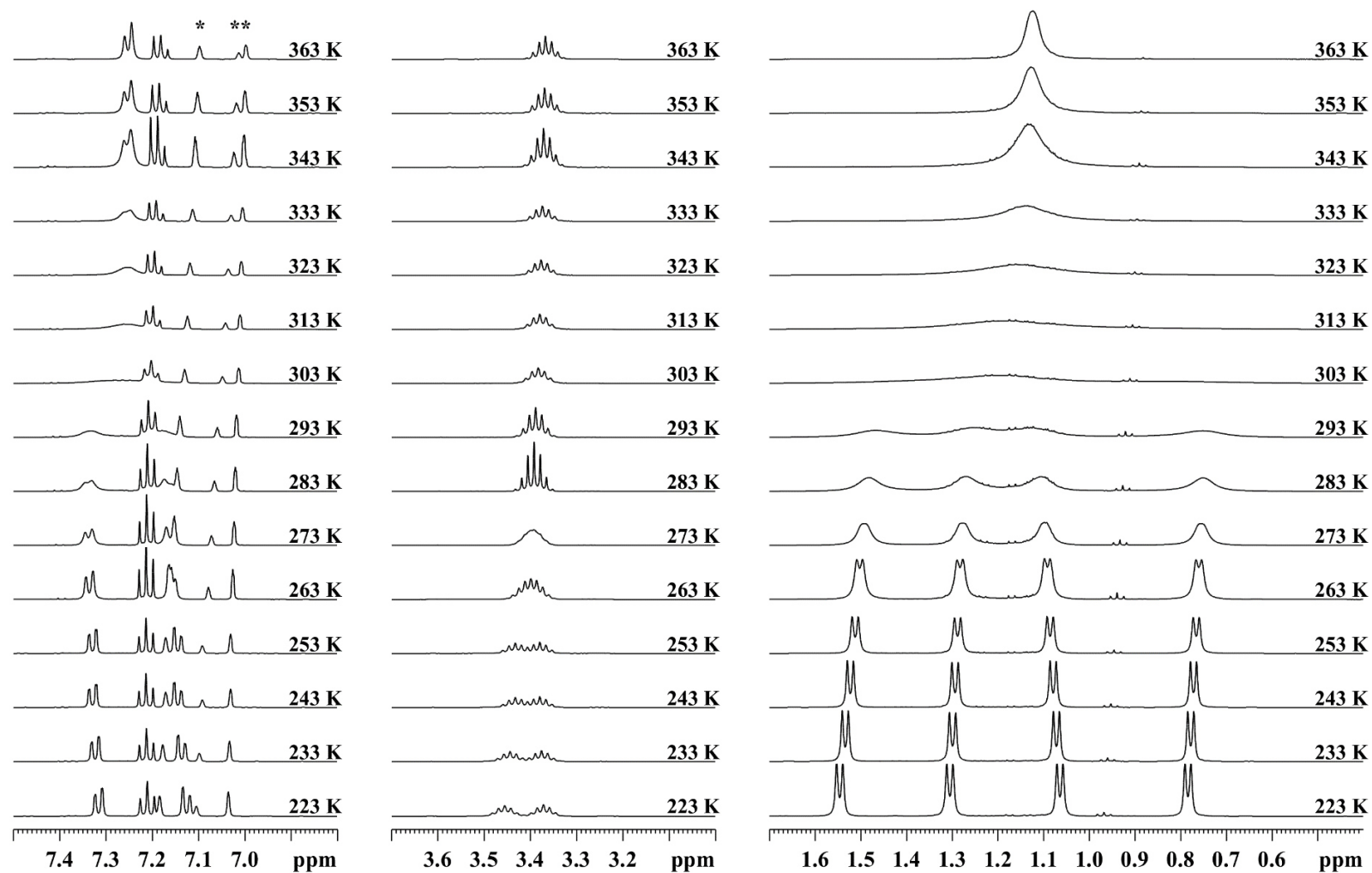


Figure S2.1.3: Excerpts of the temperature dependent ^1H NMR spectra (500 MHz) of **1** in tol-d_8 (* = tol-d_8).

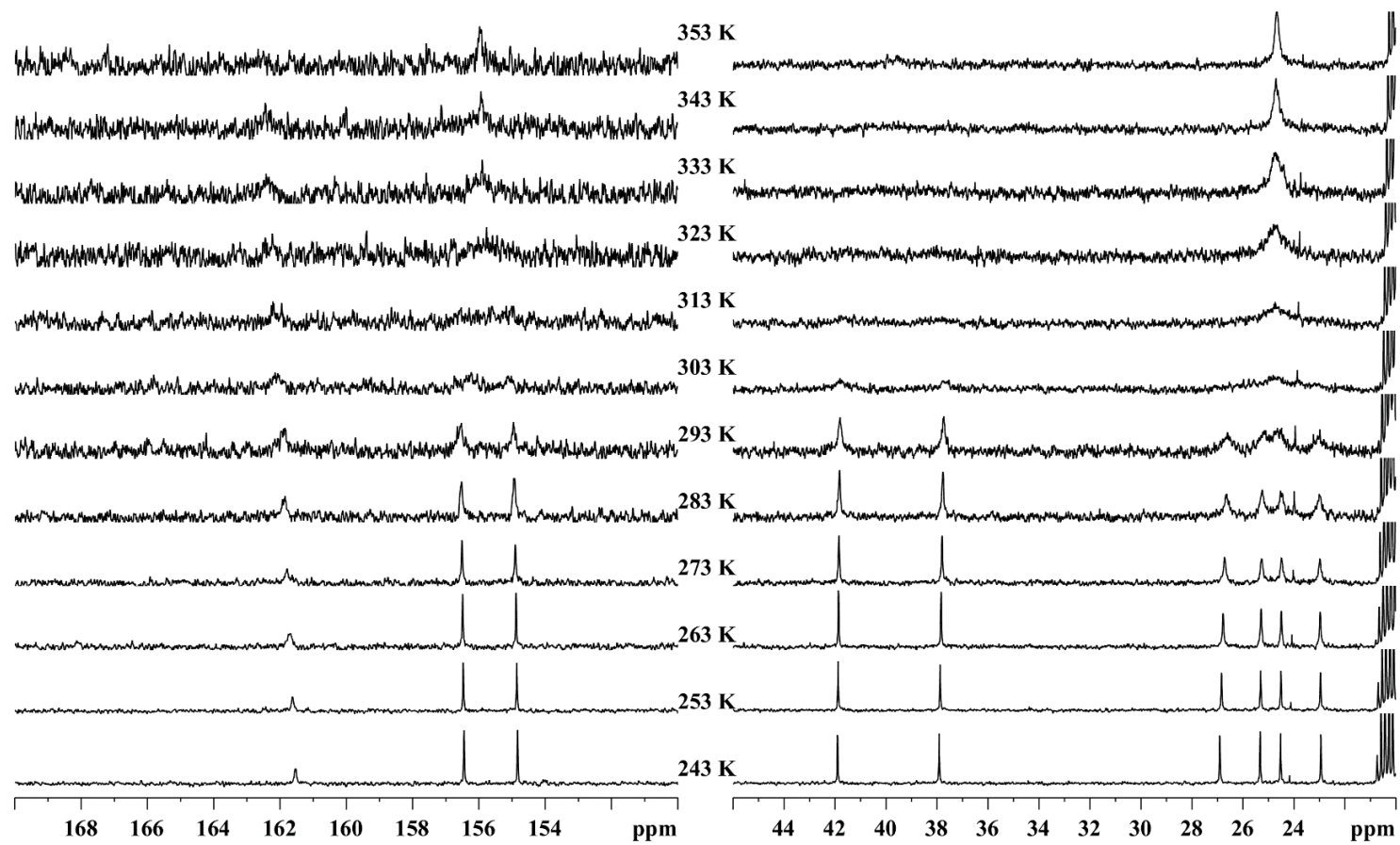


Figure S2.1.4: Excerpts of the temperature dependent ^{13}C NMR spectra (125 MHz) of **1** in toluene- d_8 .

2.2 DippBiCl₂ (**2**)

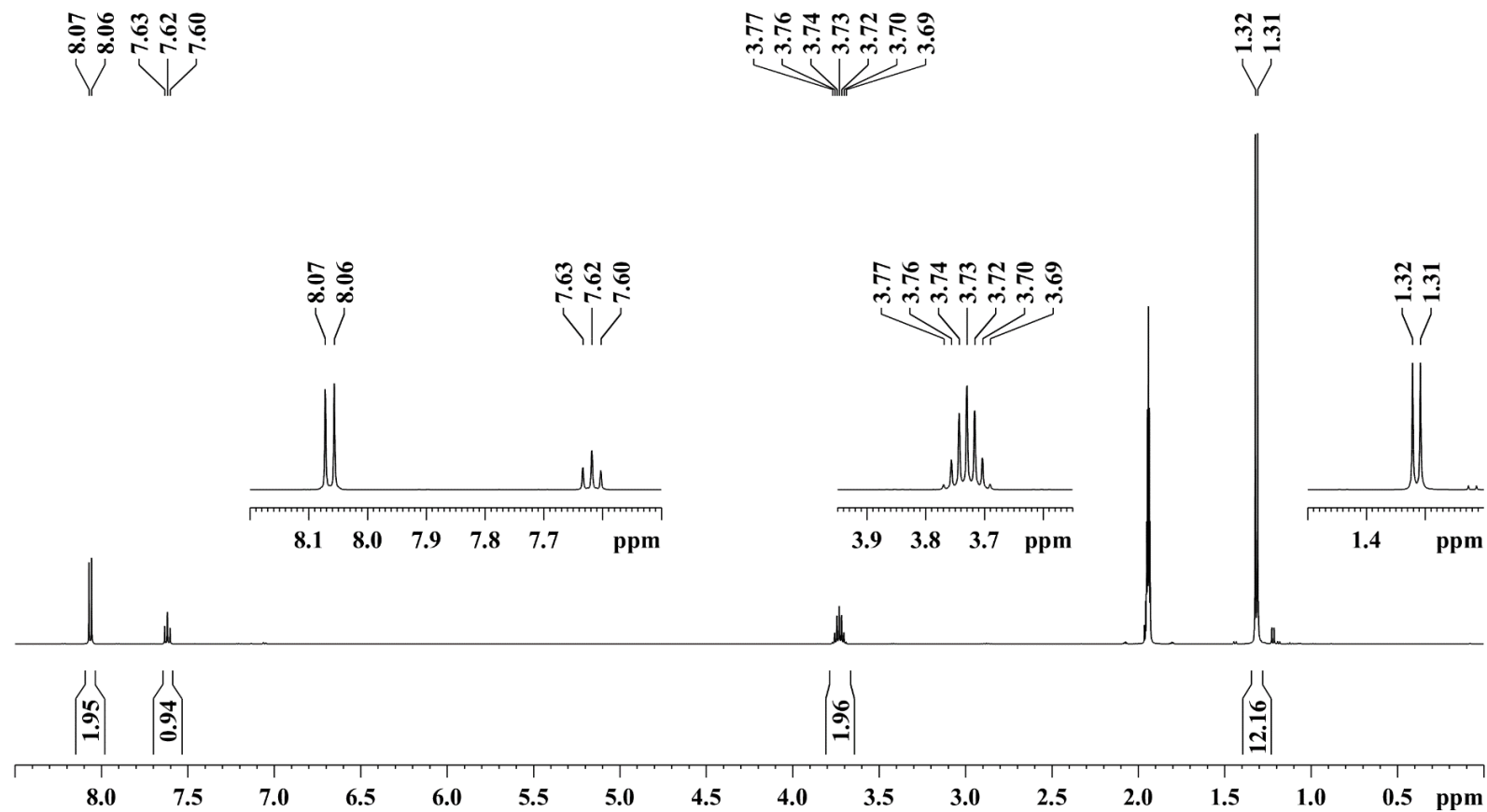


Figure S2.2.1: ¹H NMR spectrum (500 MHz) of **2** in CD₃CN at room temperature.

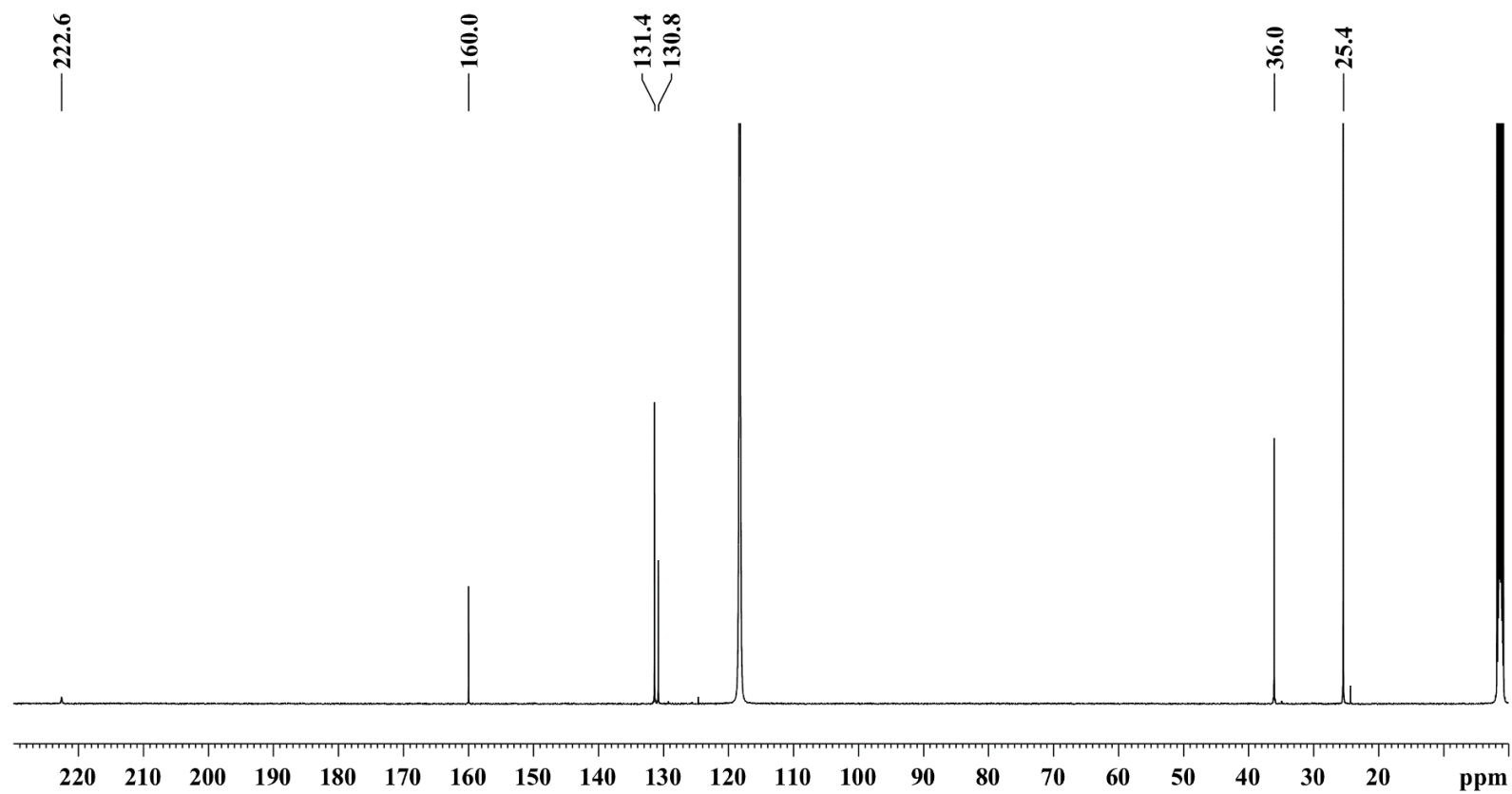


Figure S2.2.2: ^{13}C NMR spectrum (125 MHz) of **2** in CD_3CN at room temperature.

2.3 DippBiBr₂ (**3**)

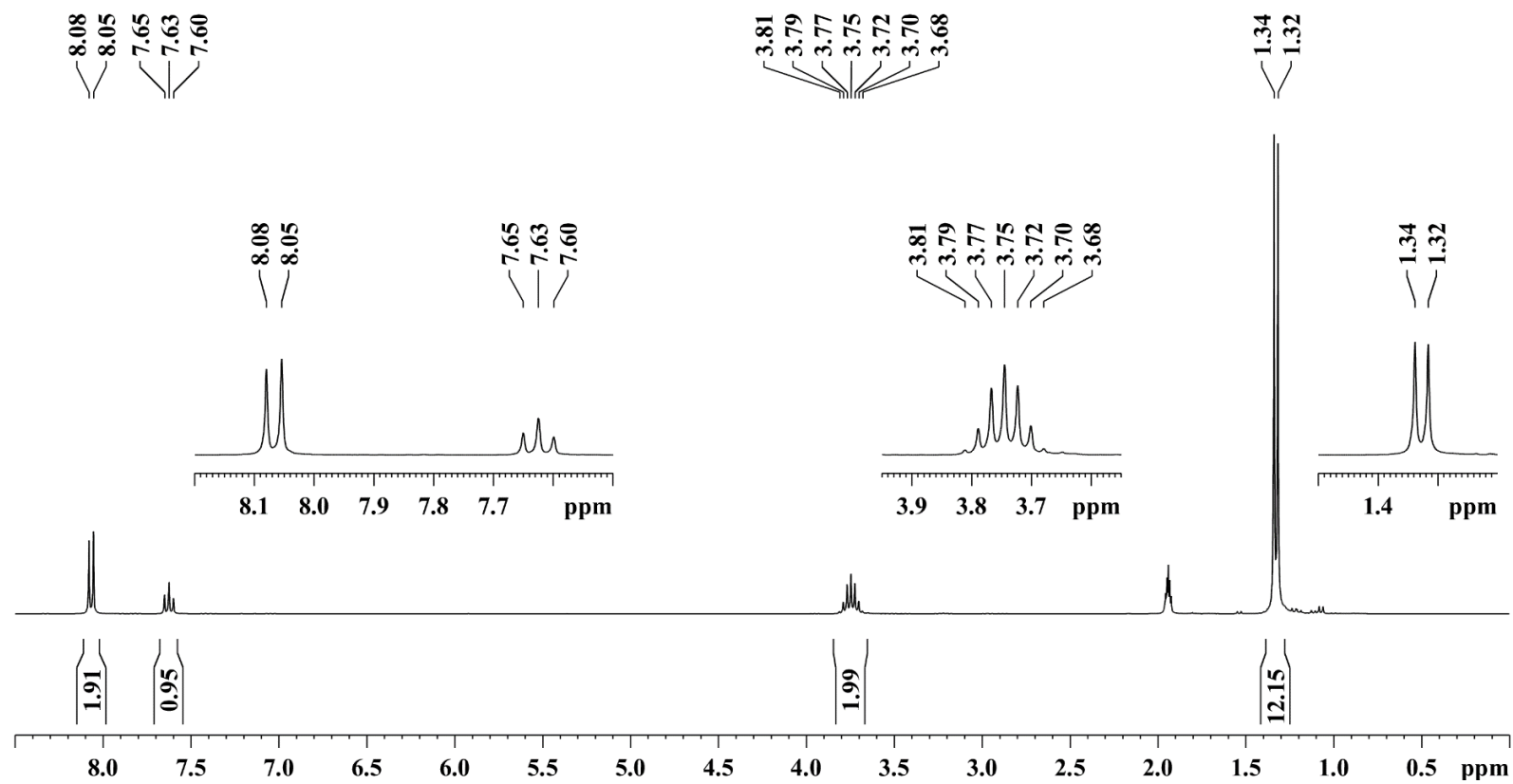


Figure S2.3.1: ¹H NMR spectrum (300 MHz) of **3** in CD₃CN at room temperature.

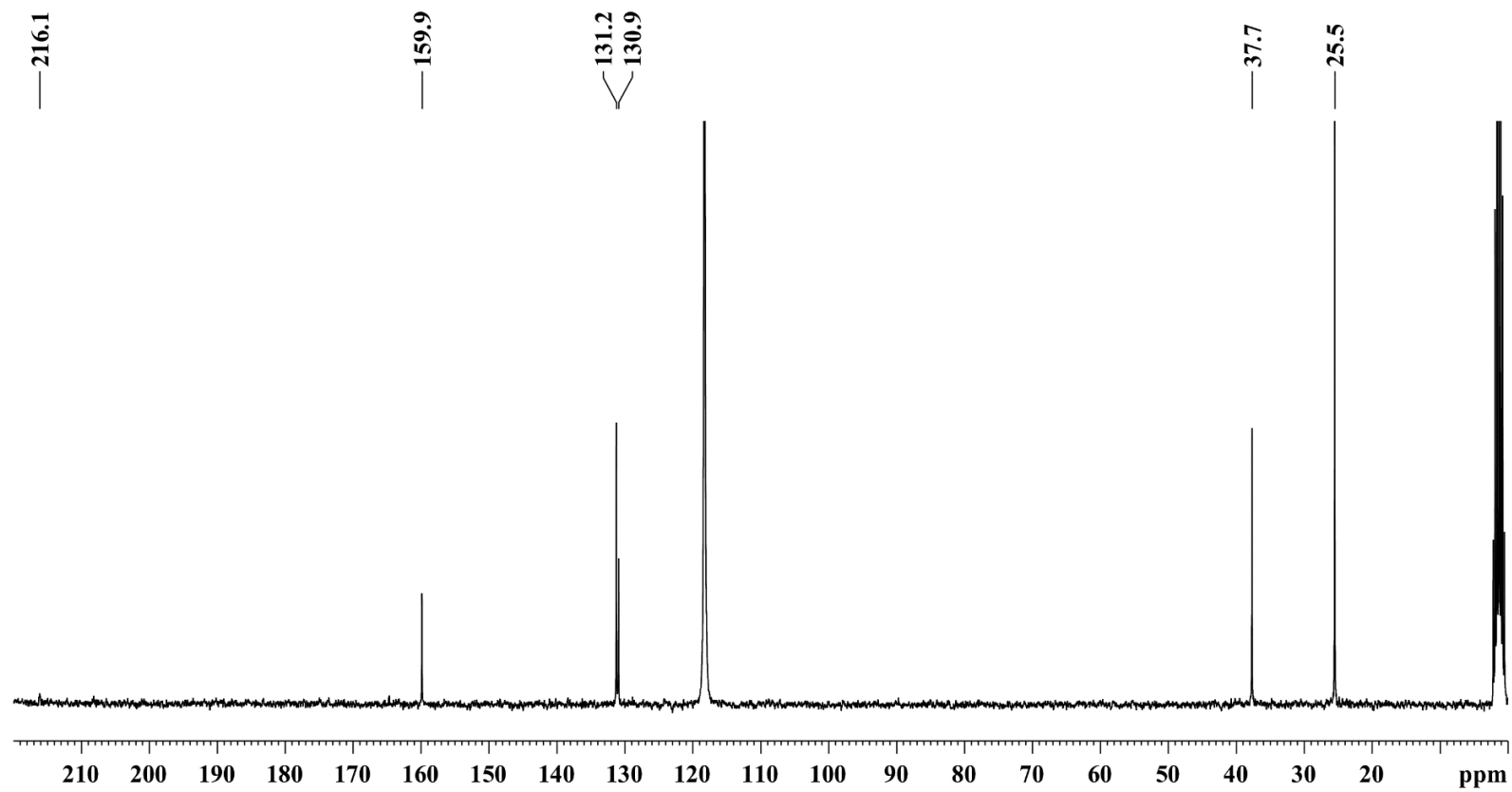


Figure S2.3.2: ^{13}C NMR spectrum (75 MHz) of **3** in CD_3CN at room temperature.

2.4 DippBil₂ (4)

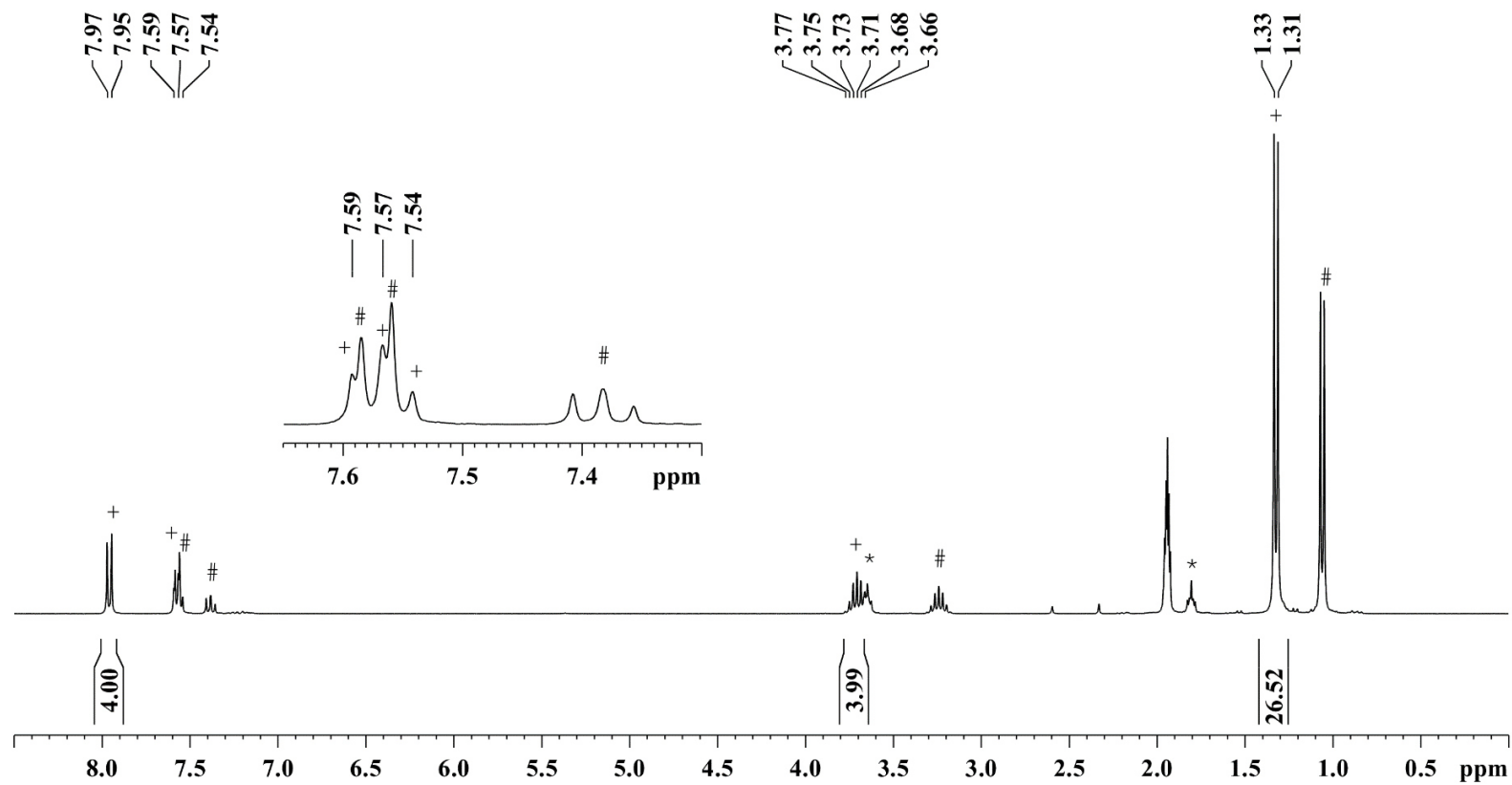


Figure S2.4.1: ¹H NMR spectrum (300 MHz) of 4 in CD₃CN at room temperature (+ = DippBil₂; # = Dipp₂Bil; * = THF).

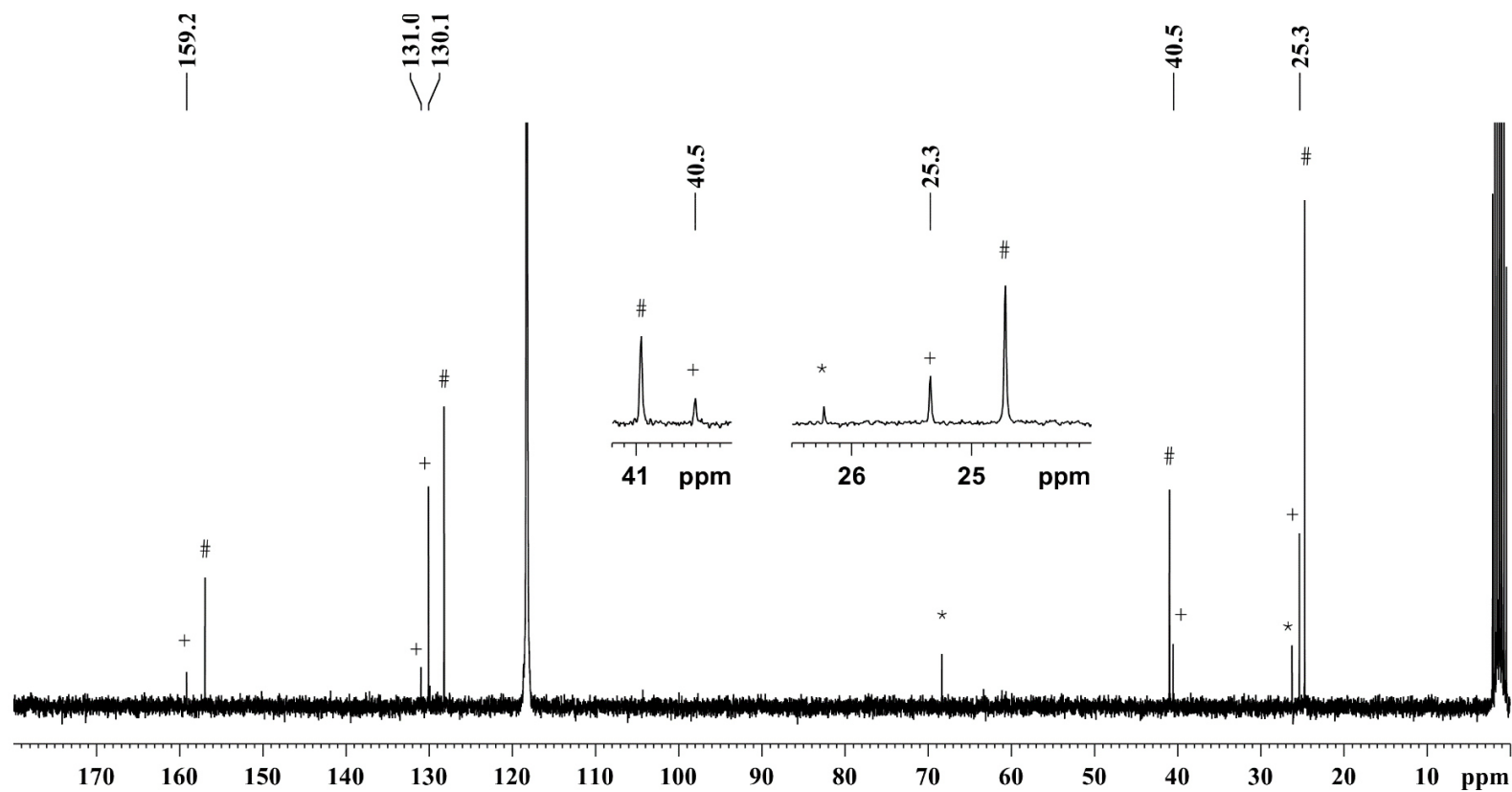


Figure S2.4.2: ^{13}C NMR spectrum (75 MHz) of **4** in CD_3CN at room temperature (+ = DippBil₂; # = Dipp₂Bil; * = THF).

2.5 Dipp₂BiNMe₂ (**5**)

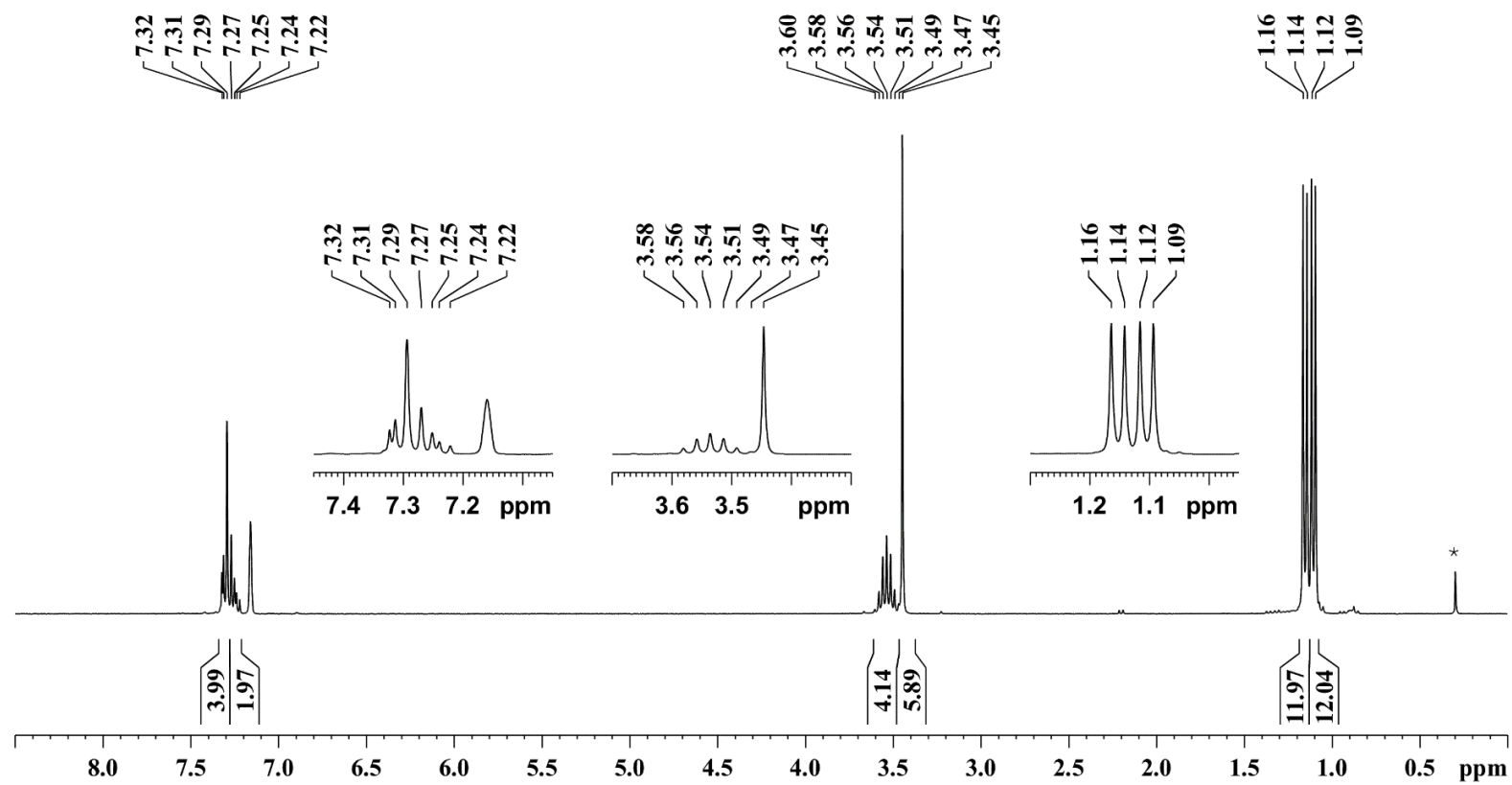


Figure S2.5.1: ¹H NMR spectrum (500 MHz) of **5** in C₆D₆ at room temperature (* = silicon grease).

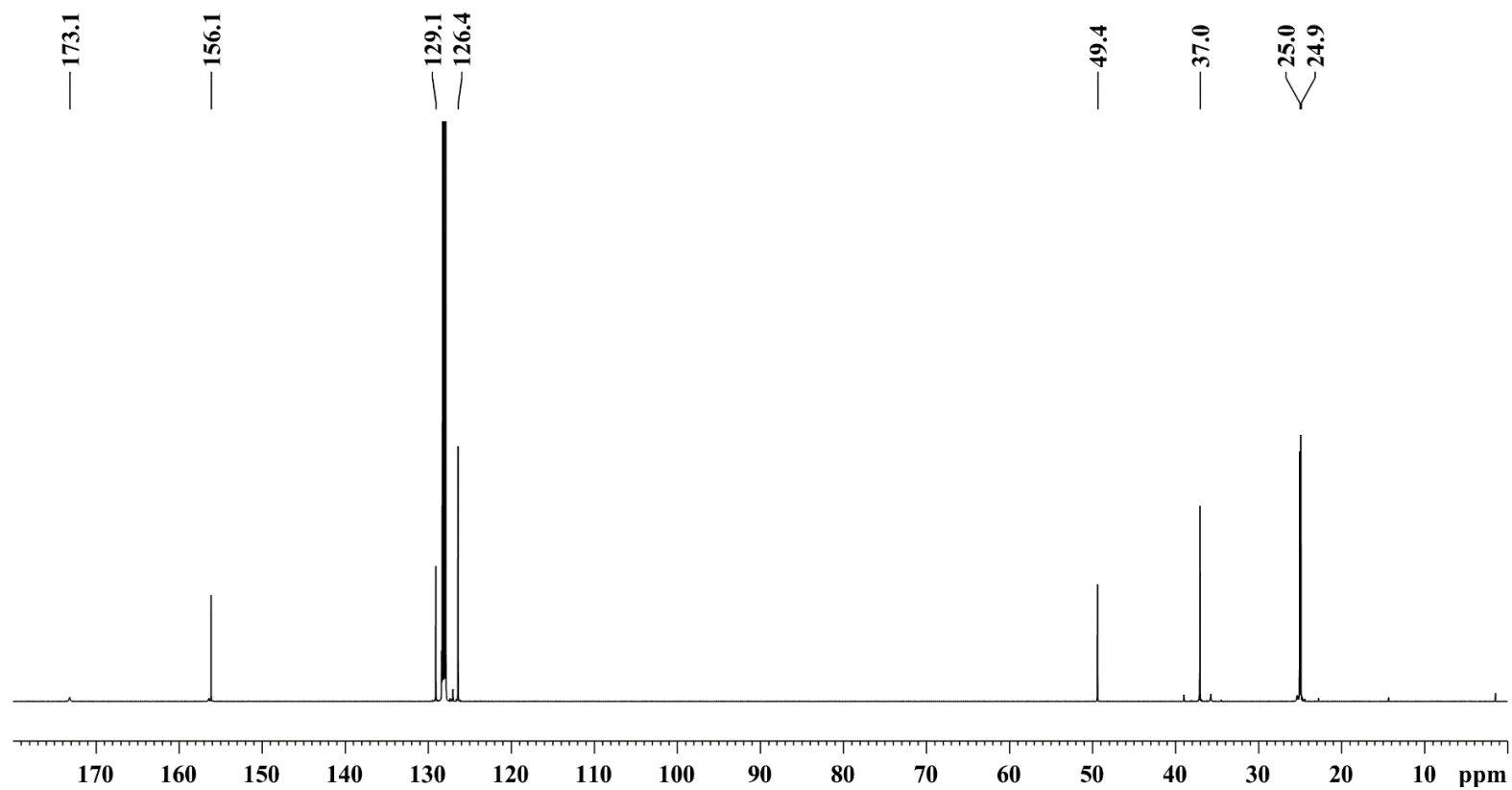


Figure S2.5.2: ^{13}C NMR spectrum (125 MHz) of **5** in C_6D_6 at room temperature.

2.6 Dipp₂BiMe (**6**)

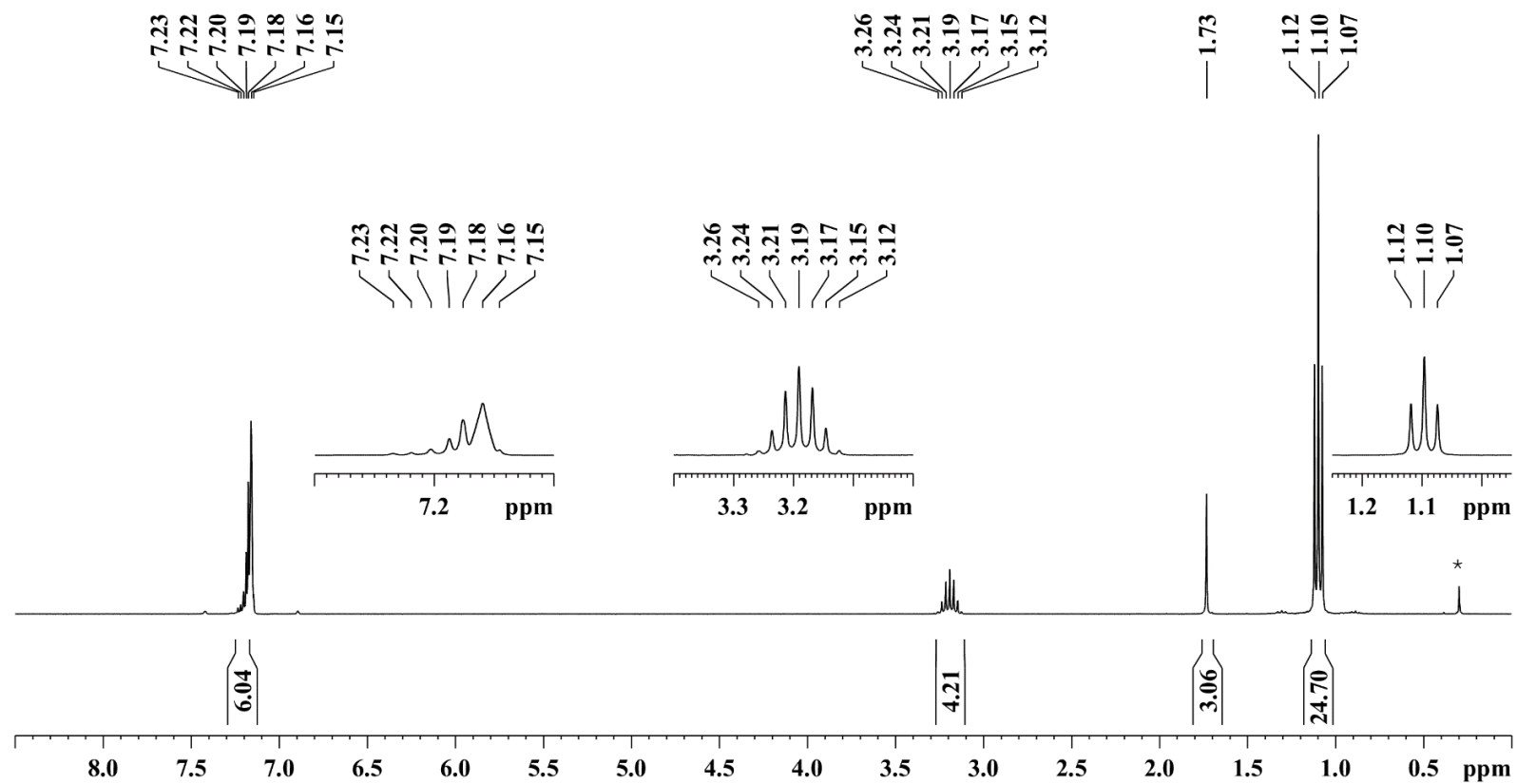


Figure S2.6.1: ¹H NMR spectrum (300 MHz) of **6** in C₆D₆ at room temperature (* = silicon grease).

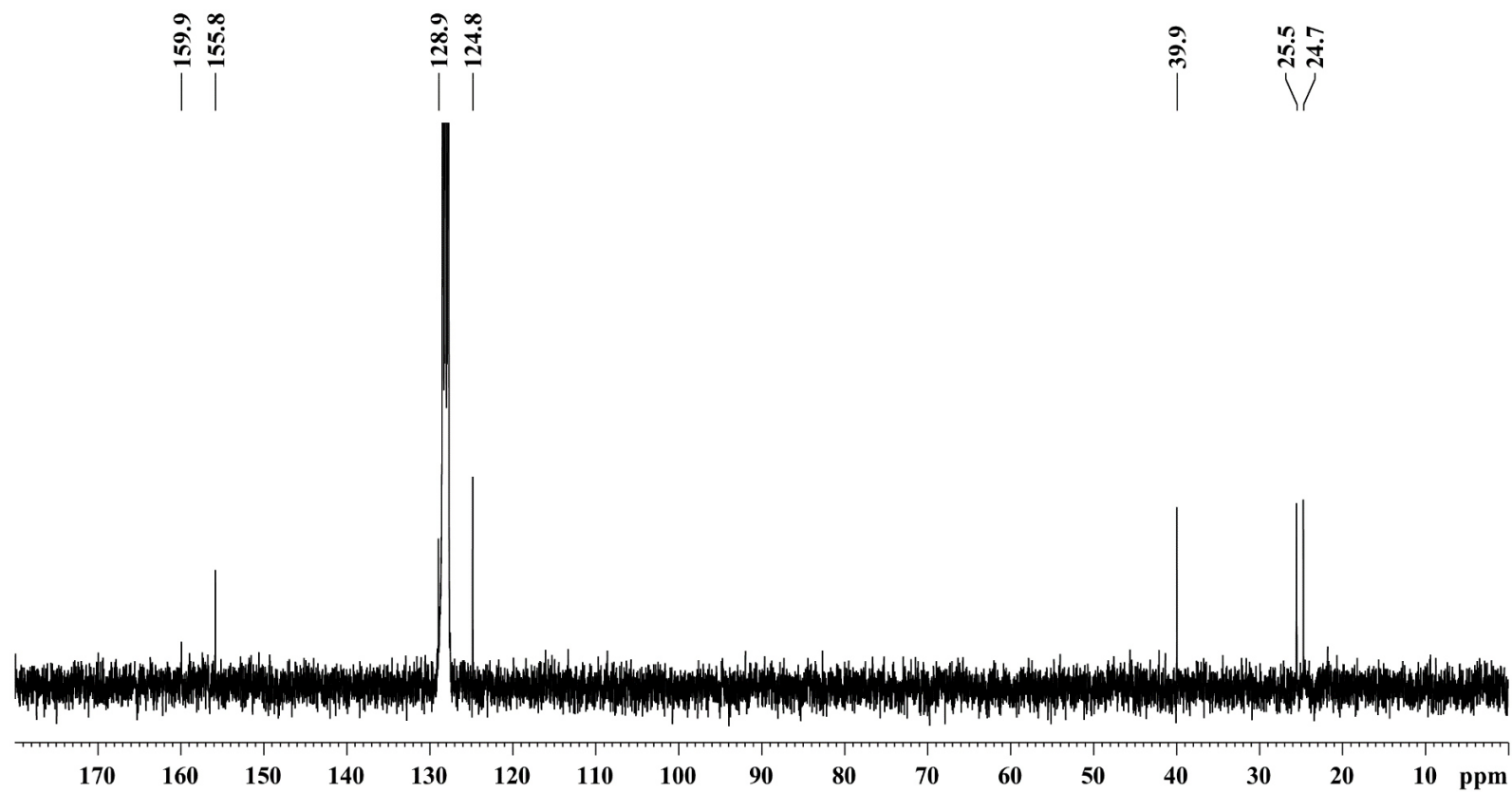


Figure S2.6.2: ^{13}C NMR spectrum (75 MHz) of **6** in C_6D_6 at room temperature.

2.7 Dipp₂BiNHtBu (7)

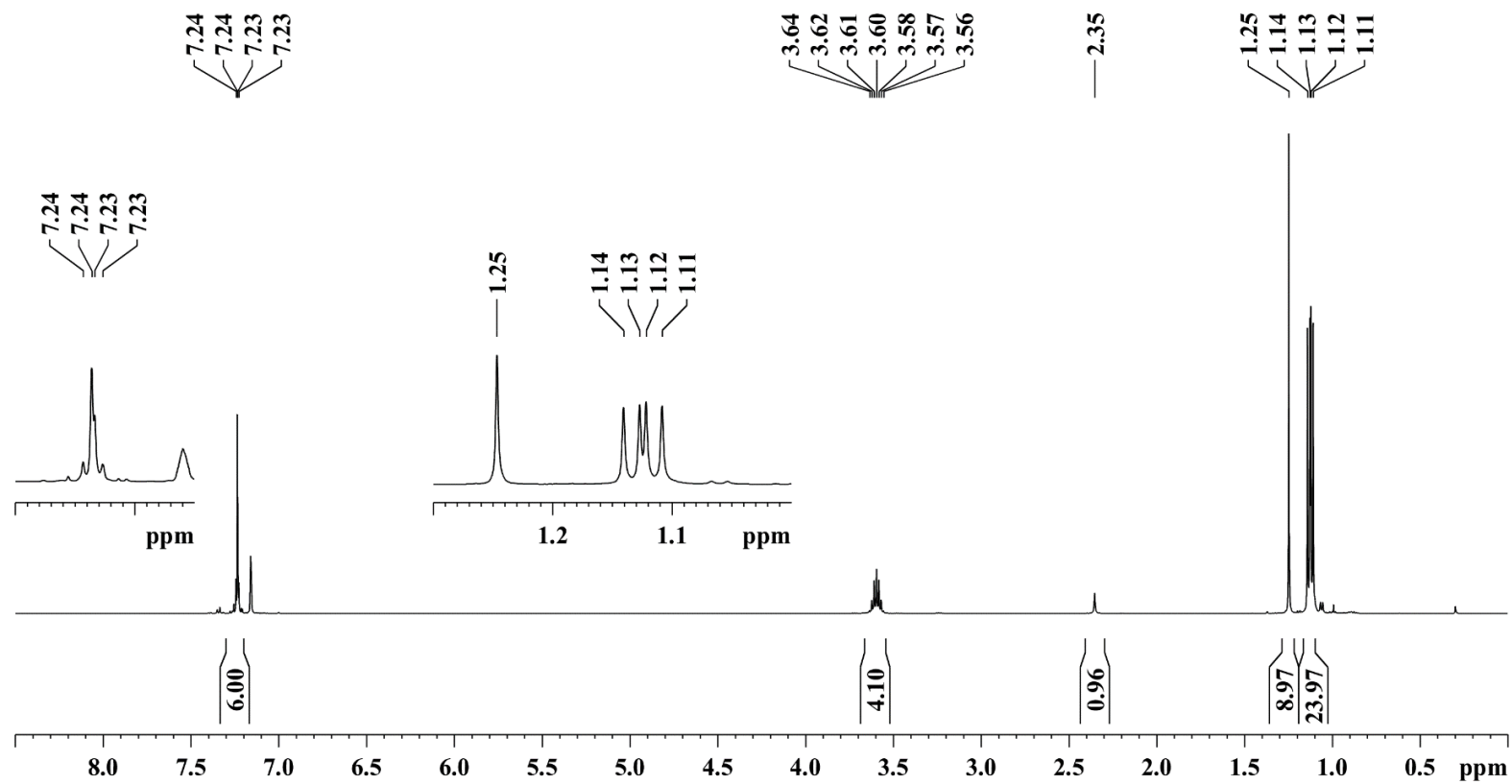


Figure S2.7.1: ¹H NMR spectrum (500 MHz) of 7 in C₆D₆ at room temperature.

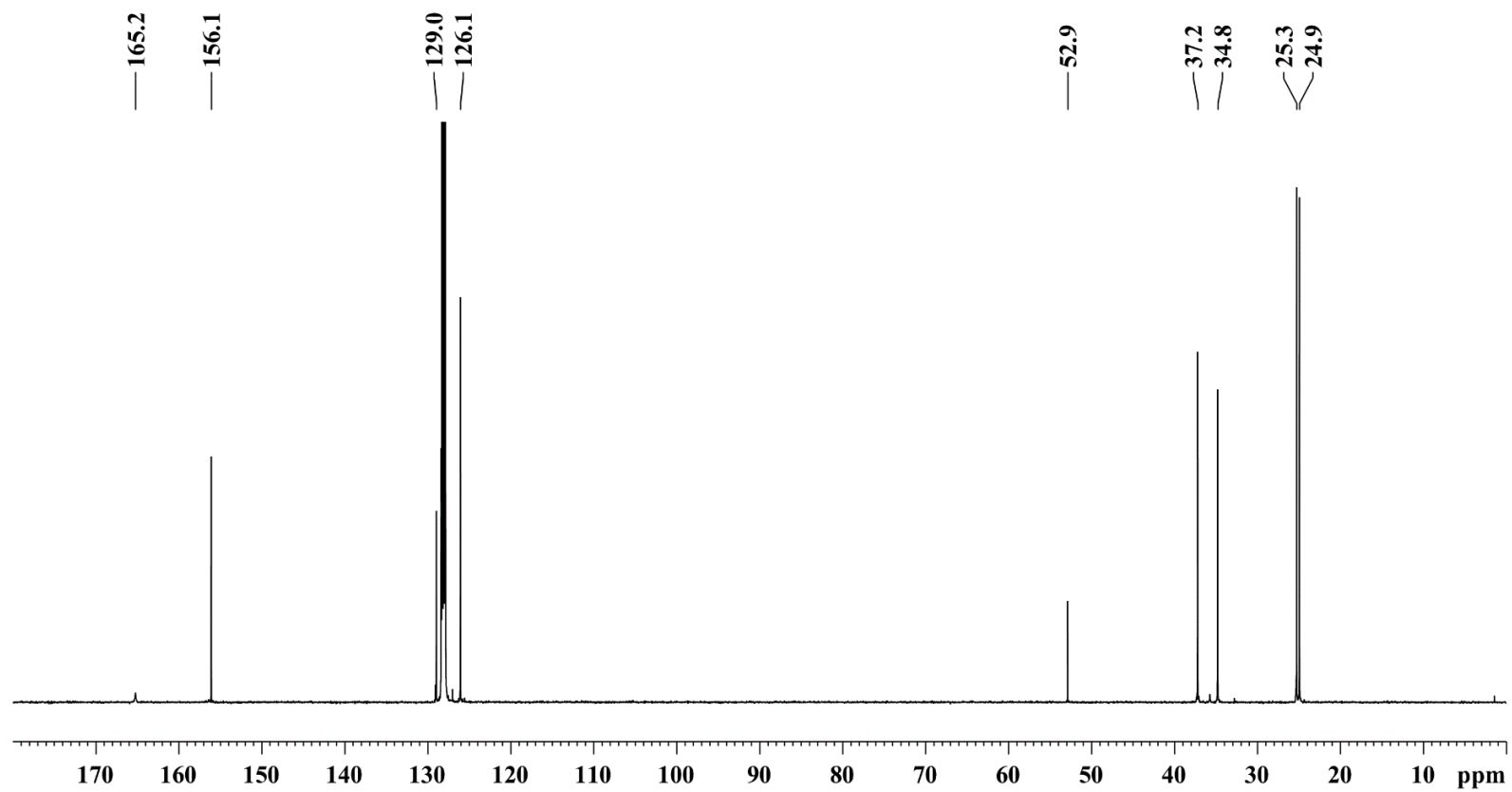


Figure S2.7.2: ^{13}C NMR spectrum (125 MHz) of **7** in C_6D_6 at room temperature.

2.8 Dipp₂BiSbMes₂ (**8**)

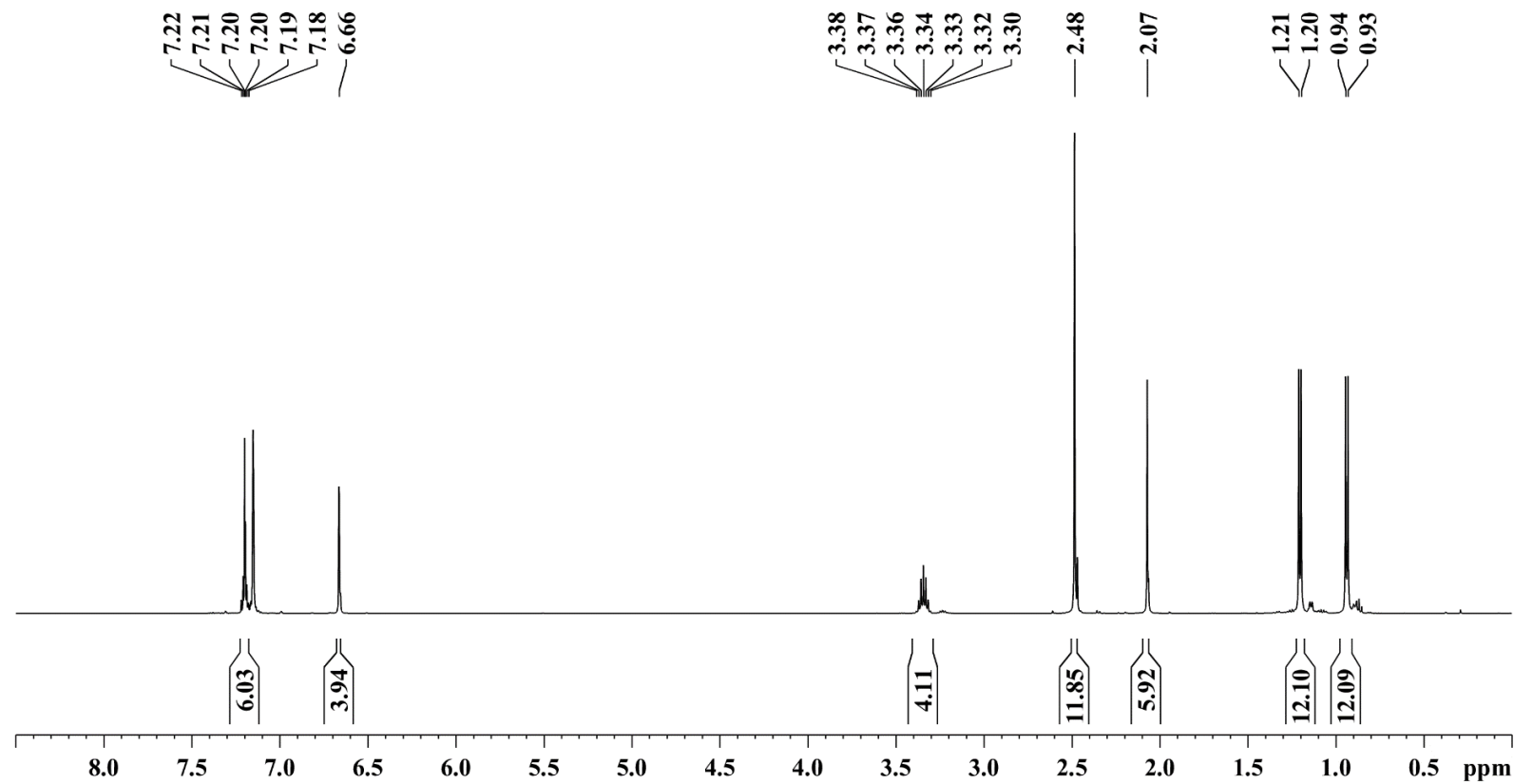


Figure S2.8.1: ¹H NMR spectrum (500 MHz) of **8** in C₆D₆ at room temperature (* = silicon grease).

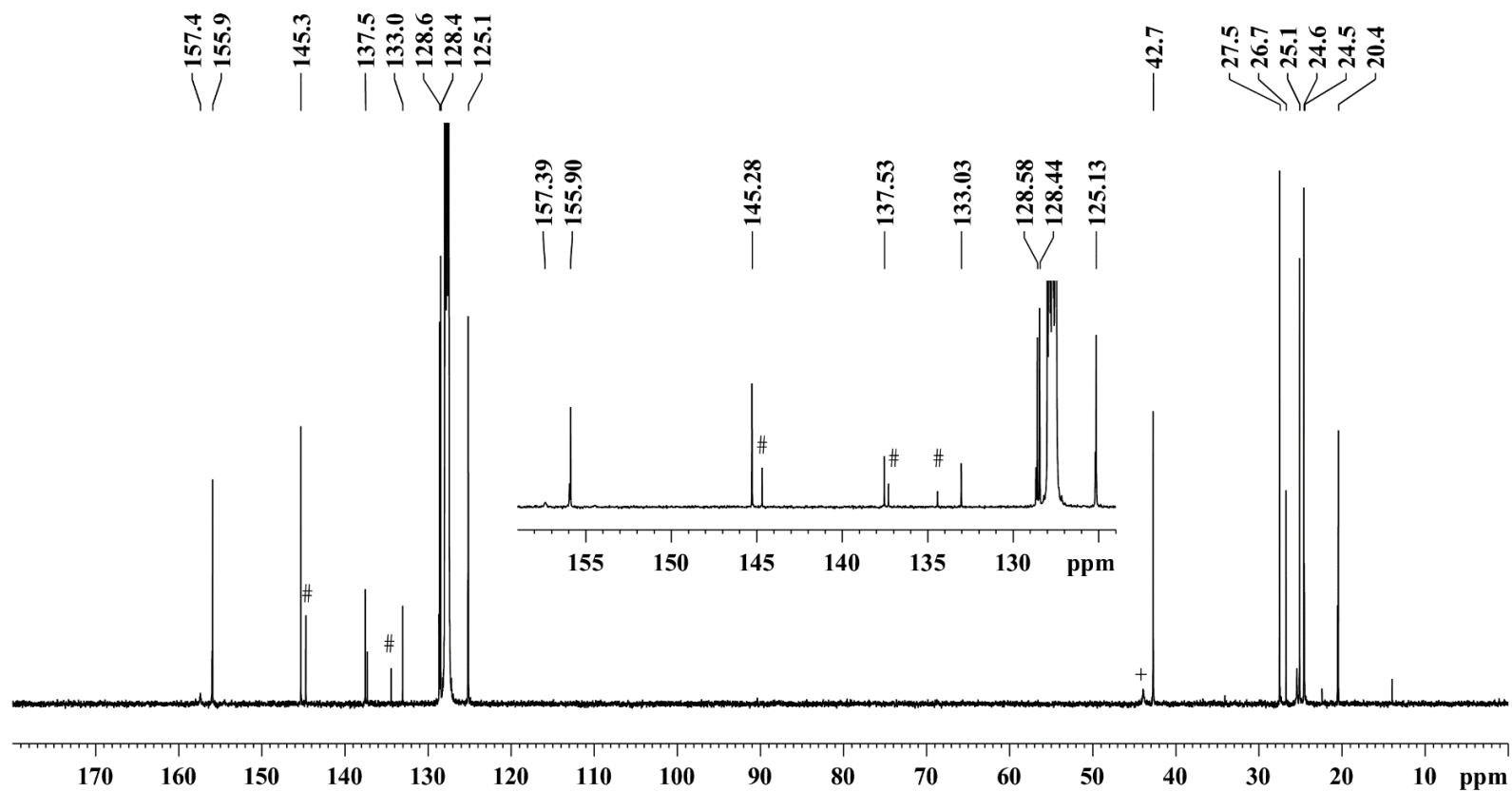


Figure S2.8.2: ^{13}C NMR spectrum (125 MHz) of **8** in C_6D_6 at room temperature (+ = Dipp_4Bi_2 ; # = Mes_4Sb_2).

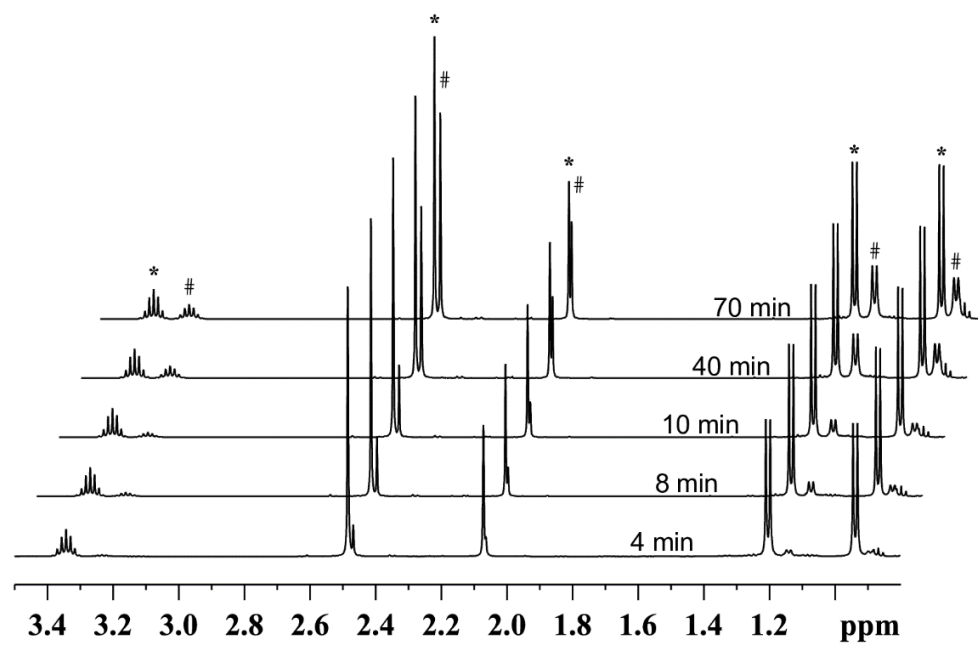


Figure S2.8.3: Excerpts of time dependent ¹H NMR spectra (500 MHz) of **7** in C₆D₆ at room temperature (* = **8**, + = Dipp₄Bi₂, # = Mes₄Sb₂).

2.9 Dipp₂BiPtBu(SiMe₃) (**9**)

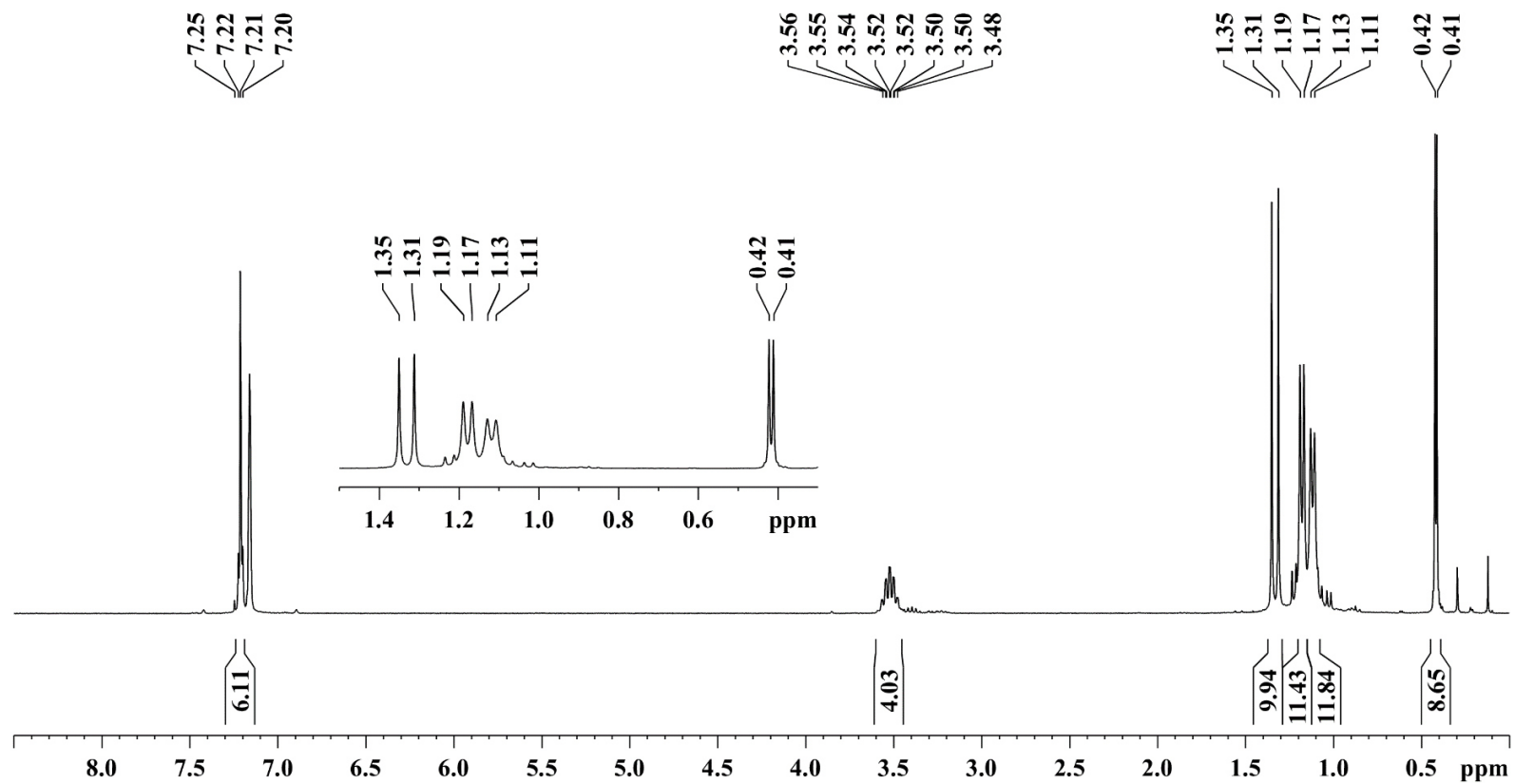


Figure S2.9.1: ¹H NMR spectrum (300 MHz) of **9** in C₆D₆ at room temperature.

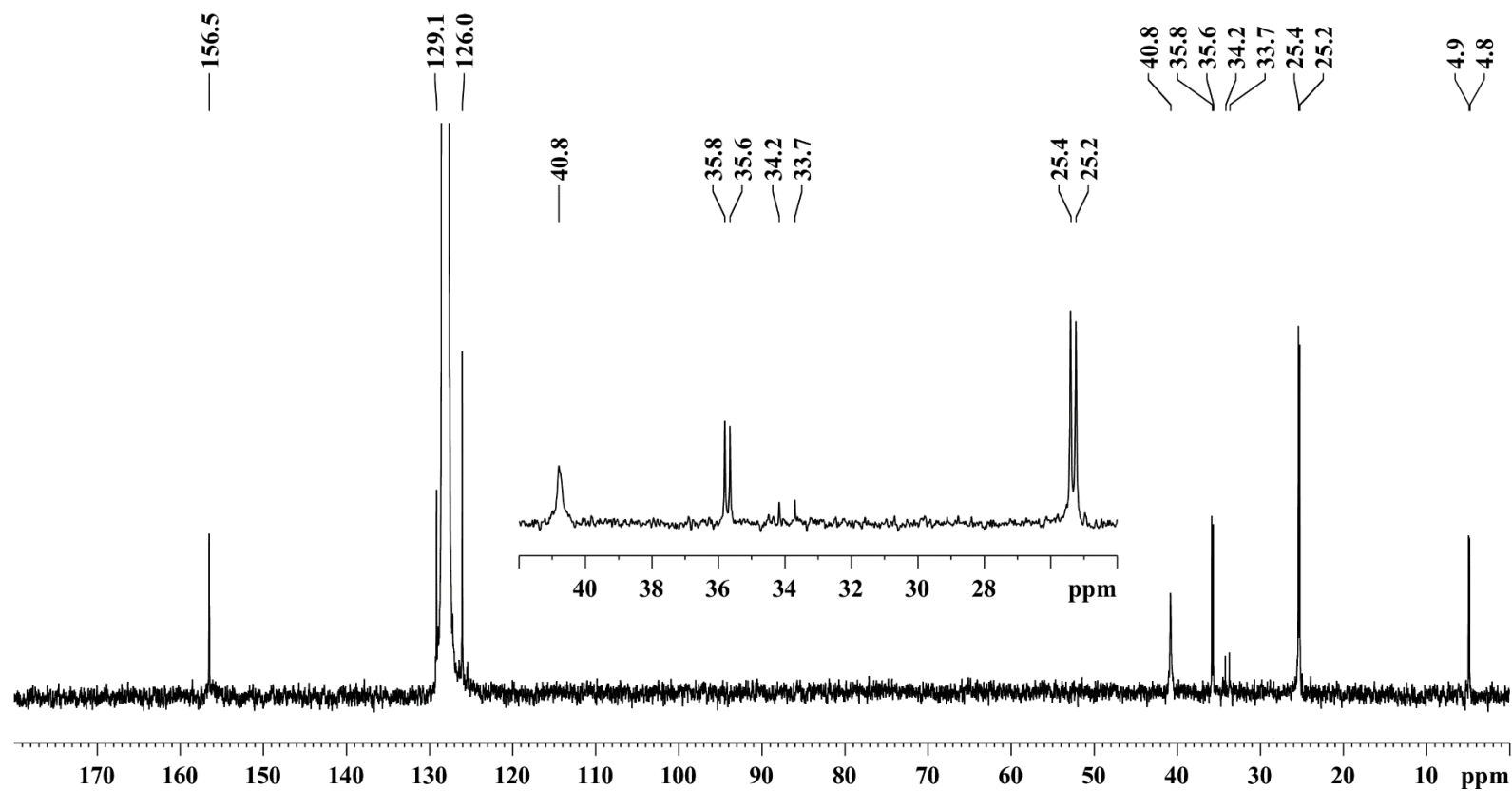


Figure S2.9.2: ^{13}C NMR spectrum (75 MHz) of **9** in C_6D_6 at room temperature.

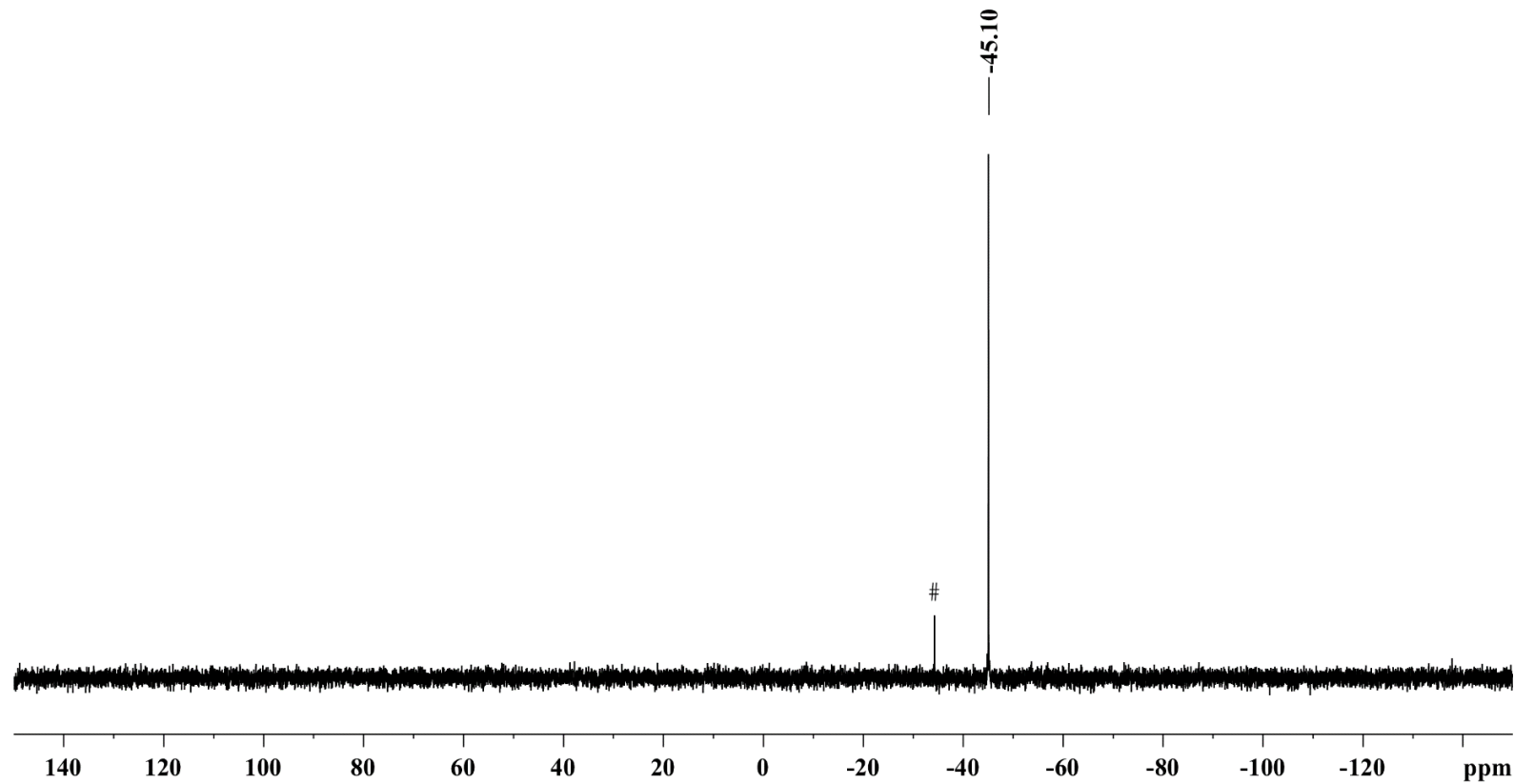


Figure S2.9.3: ^{31}P NMR spectrum (121 MHz) of **9** in C_6D_6 at room temperature (# = unknown impurity).

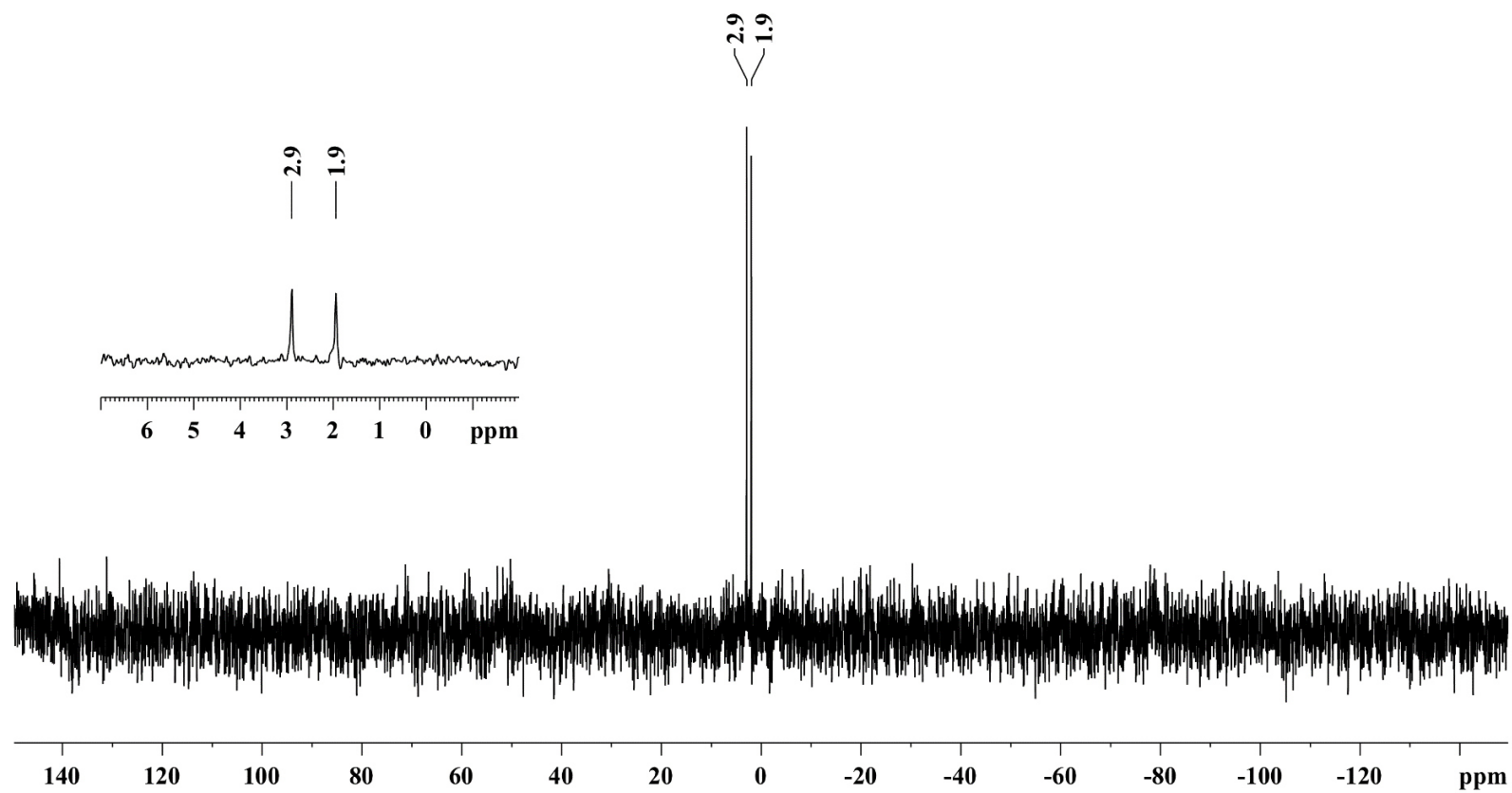


Figure S2.9.4: ^{29}Si NMR spectrum (60 MHz) of **9** in C_6D_6 at room temperature.

2.10 Dipp₂BiPHtBu (**10**)

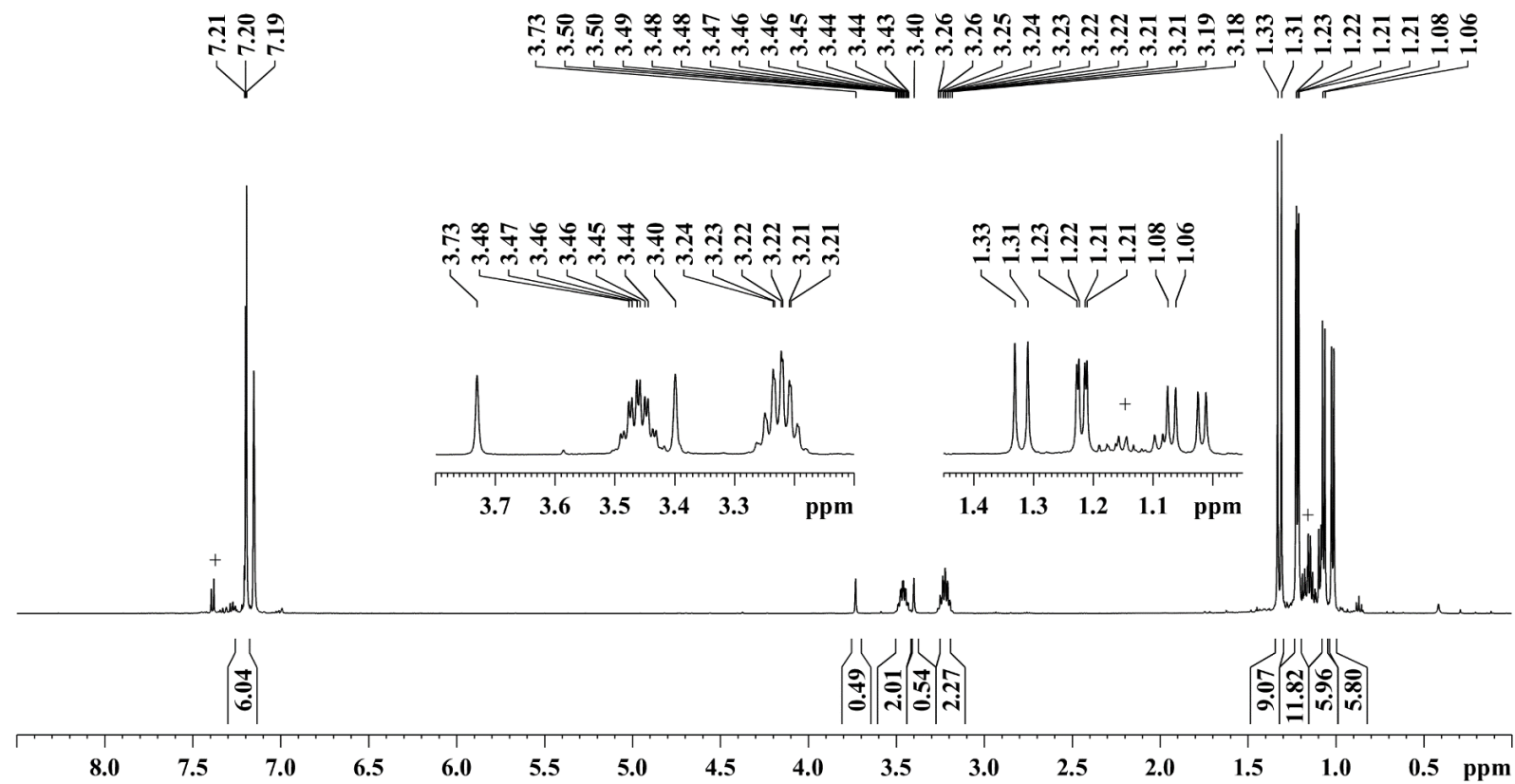


Figure S2.10.1: ¹H NMR spectrum (500 MHz) of **10** in C₆D₆ at room temperature (+ = unknown impurity).

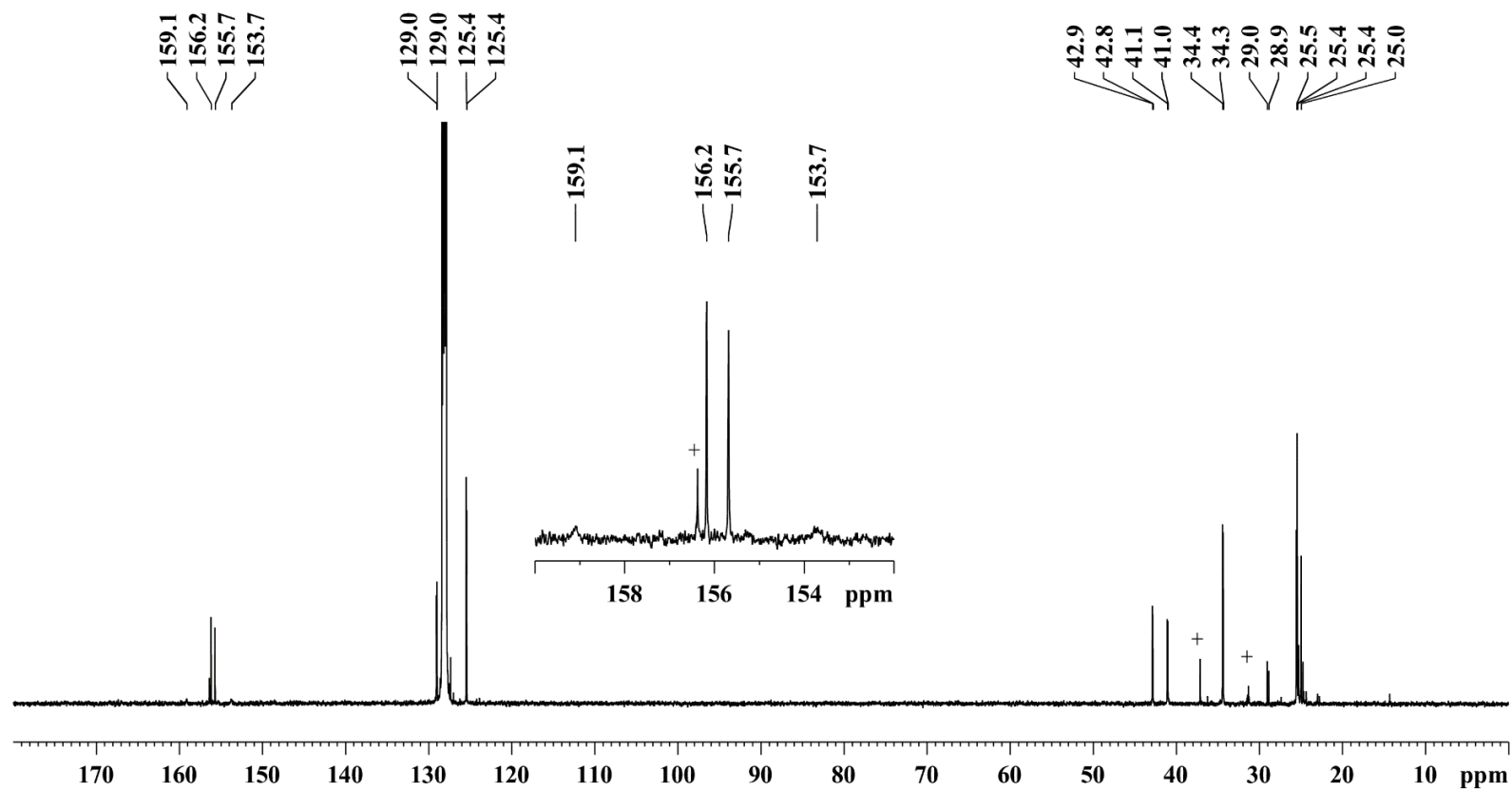


Figure S2.10.2: ^{13}C NMR spectrum (125 MHz) of **10** in C_6D_6 at room temperature (+ = unknown impurity).

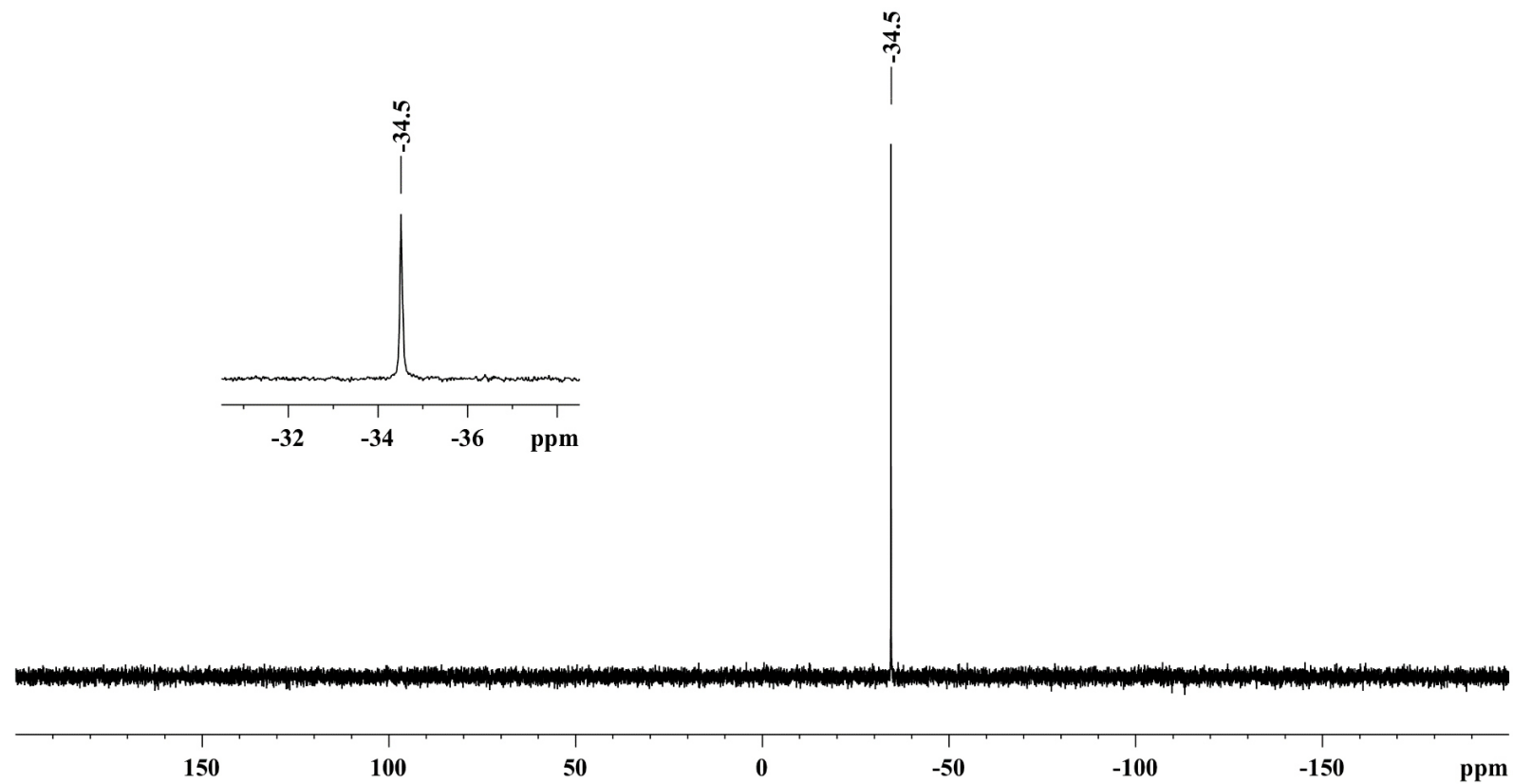


Figure S2.10.3: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (101 MHz) of **10** in C_6D_6 at room temperature.

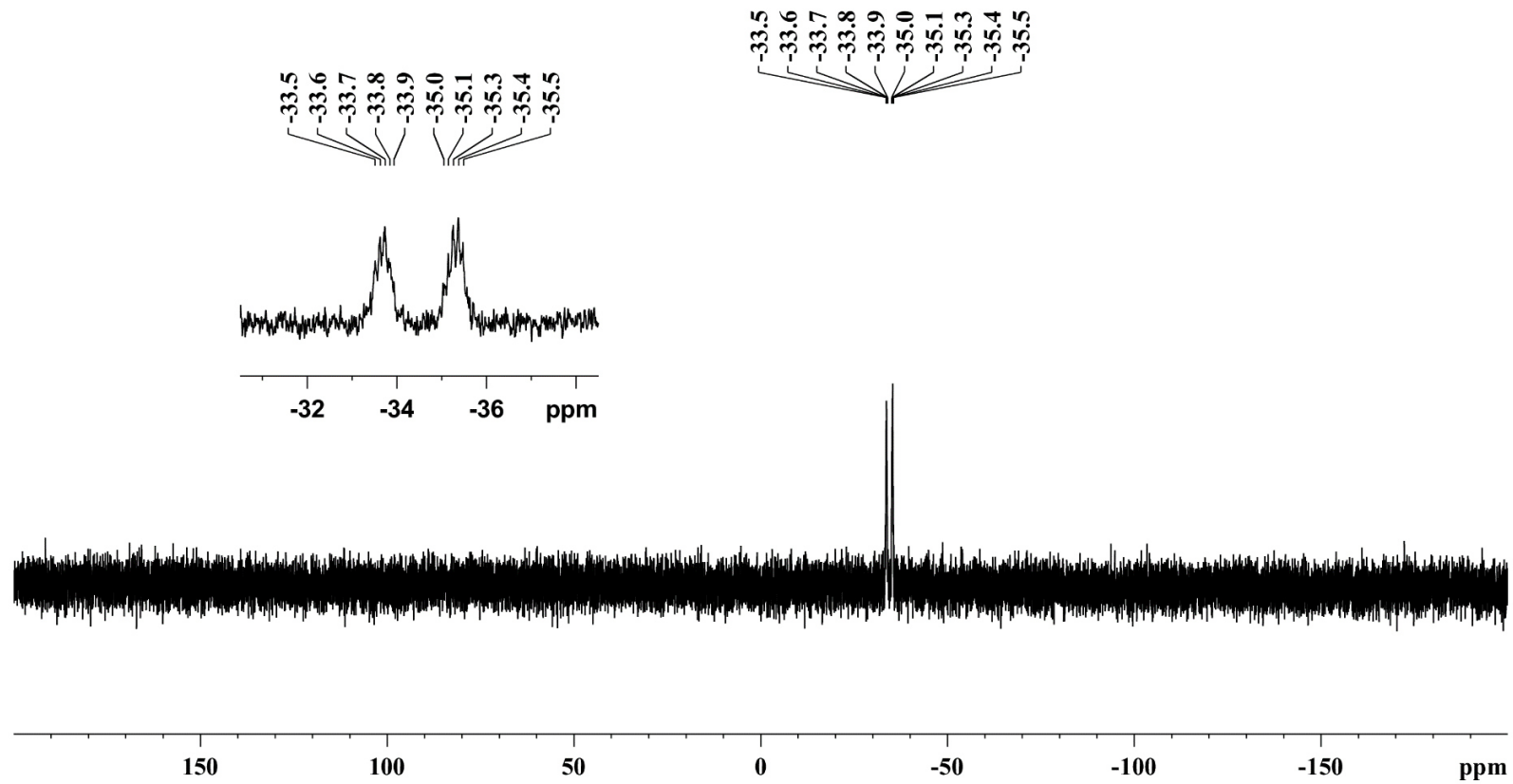


Figure S2.10.4: ^{31}P NMR spectrum (101 MHz) of **10** in C_6D_6 at room temperature.

2. Selected IR spectra

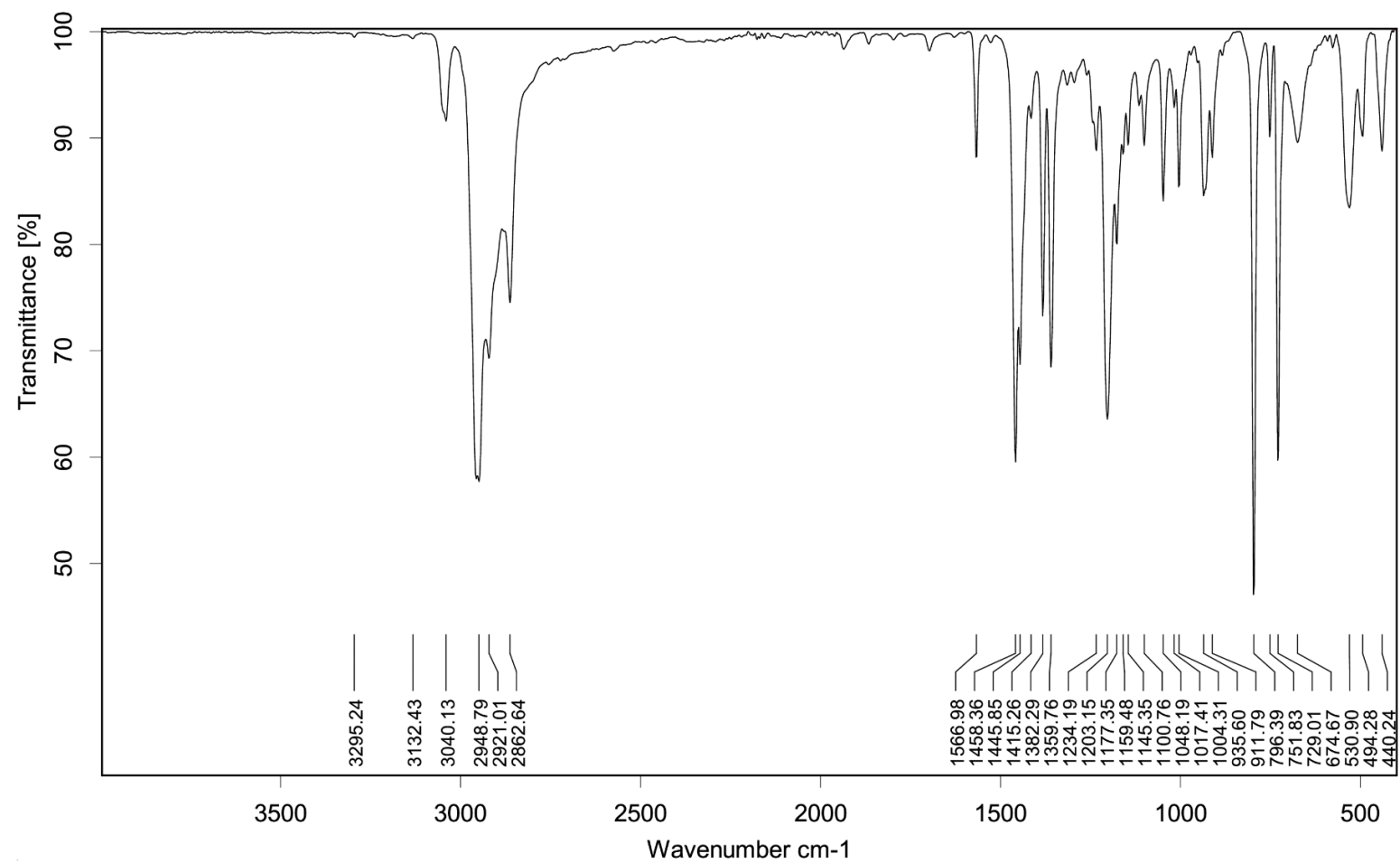


Figure S3.1: IR Spectrum of solid **7** at room temperature.

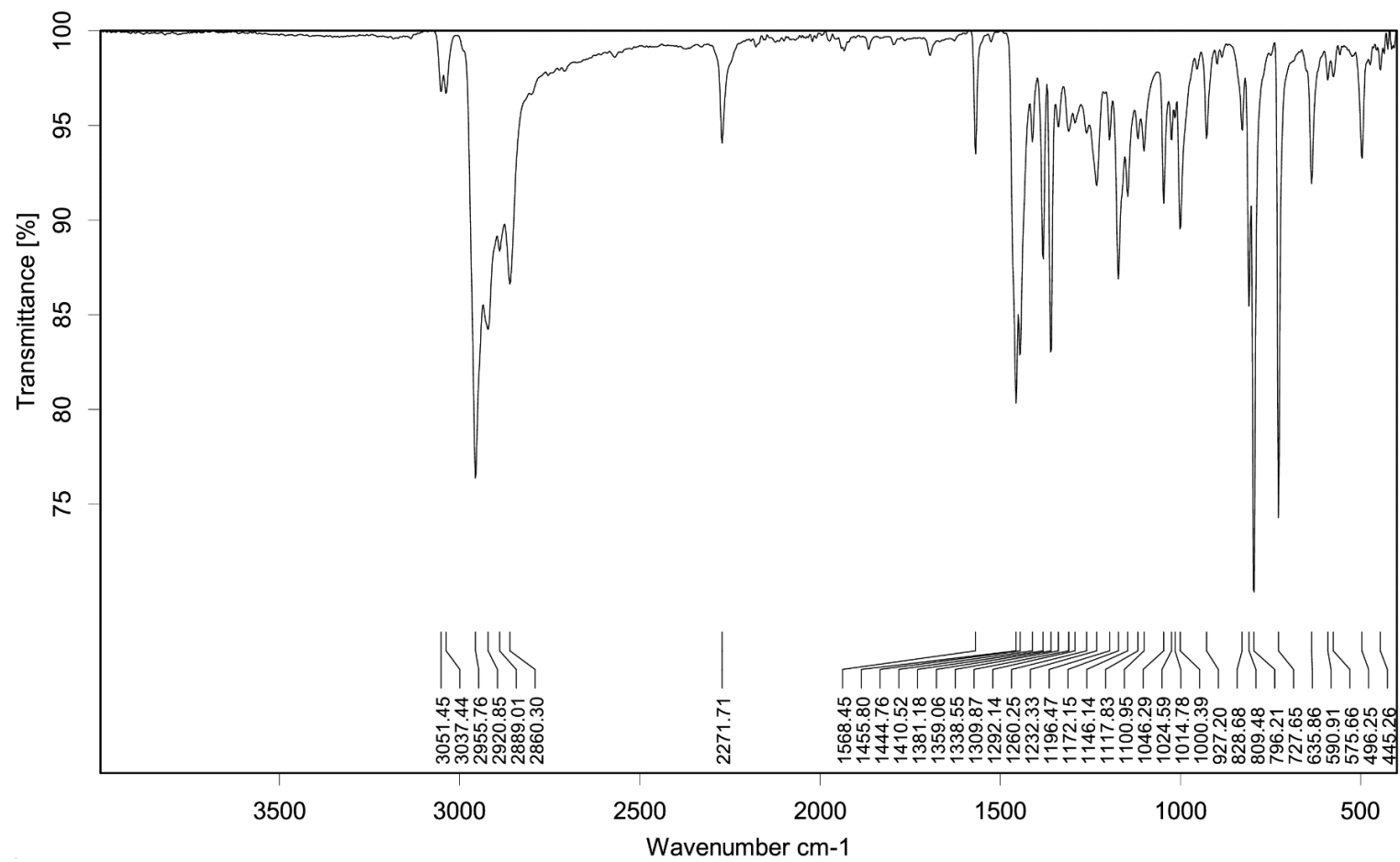


Figure S3.2: IR Spectrum of solid **10** at room temperature.

4. Calculation of the Rotational barrier around the Bi-C axis of Dipp₃Bi

Table 4. FWHM of the signals from temperature dependent ¹³C-MNR spectra used for the calculation of the rate constant k ($k = \pi \cdot (\text{FWHM}_T - \text{FWHM}_{243\text{K}})$) and subsequent calculation of the rotational barrier.

		<i>m</i>-CH		
T (K ⁻¹)	T ⁻¹ (K ⁻¹)	FWHM (Hz)	k	ln(k)
243	0.00412	2.918	0.000	-
253	0.00395	3.234	0.994	-0.006
263	0.00380	4.012	3.437	1.235
273	0.00366	6.323	10.697	2.370
283	0.00353	10.852	24.925	3.216
293	0.00341	18.713	49.621	3.904
		<i>o</i>-CCH(CH₃)₂		
T (K ⁻¹)	T ⁻¹ (K ⁻¹)	FWHM (Hz)	k	ln(k)
243	0.00412	3.527	0.000	-
253	0.00395	3.821	0,924	-0.0794
263	0.00380	4.521	3,123	1.1387
273	0.00366	6.948	10,747	2.3747
283	0.00353	11.389	24,699	3.2068
293	0.00341	20.039	51,872	3.9488
		Mittelwert		
T (K ⁻¹)	T ⁻¹ (K ⁻¹)		k	ln(k)
243	0.00412		0.000	-
253	0.00395		0.959	-0.043
263	0.00380		3.280	1.187
273	0.00366		10.722	2.372
283	0.00353		24.812	3.211
293	0.00341		50.747	3.927

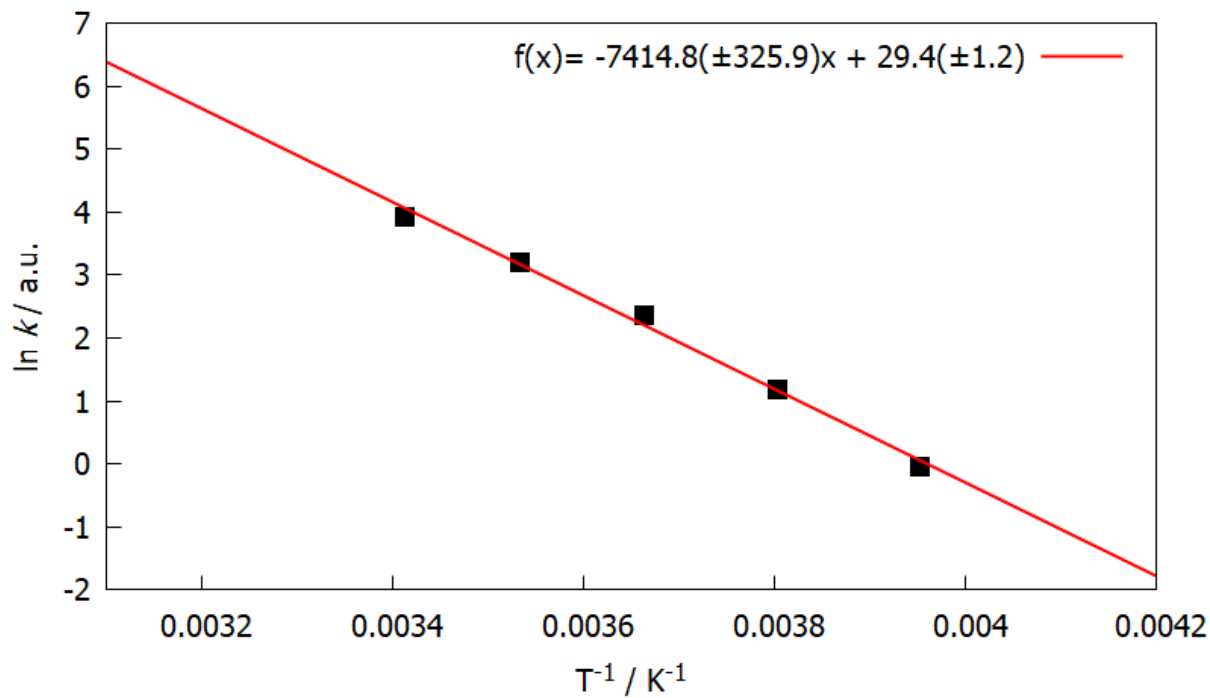


Figure S4: Arrhenius plot of the natural logarithmic of the rate constant for the rotation around the Bi-C axis in Dipp_3Bi against the reciprocal temperature with a linear regression $f(x)$.

Calculation of the rotational barrier E_A mit $k = A \cdot \exp(E_A \cdot (RT)^{-1})$

$$E_A = -(-7414.8 \text{ K} \cdot 8.314 \text{ J} \cdot \text{mol}^{-1} \text{K}^{-1}) = 61650 \text{ J} \cdot \text{mol}^{-1} = 62 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta E_A = -(\pm 325.9 \text{ K} \cdot 8.314 \text{ J} \cdot \text{mol}^{-1} \text{K}^{-1}) = \pm 2709 \text{ J} \cdot \text{mol}^{-1} = \pm 3 \text{ kJ} \cdot \text{mol}^{-1}$$

5. Experimental

Preparation of DippBiI₂

DippBiBr₂ (160 mg, 0.30 mmol) and CaI₂ (310 mg, 1.05 mmol) are dissolved in THF and stirred over 16 hours at room temperature. After removal of volatiles under reduced pressure, 20 ml of toluene are added and undissolved solids are removed *via* filtration. After removing all volatiles a red product mixture of DippBiI₂ (75 %) and Dipp₂BiI (25 %) is obtained which could not be separated. Nevertheless, all signals in the ¹H and ¹³C NMR spectra were identified and are assigned to Dipp₂BiI and DippBiI₂. Crystals of DippBiI₂ suitable for single crystal x-ray diffraction were obtained from *n*-pentane at – 32 °C.

DippBiI₂: ¹H NMR (300 MHz, CD₃CN) δ: 7.96 (d, ³J_{H-H} = 7.7 Hz, 2H, *m*-CH), 7.57 (t, ³J_{H-H} = 7.7 Hz, 1H, *p*-CH), 3.71 (sept, ³J_{H-H} = 6.6 Hz, 2H, CH(CH₃)₂), 1.32 (d, ³J_{H-H} = 6.6 Hz, 12H, CH(CH₃)₂); ¹³C{¹H} NMR (75 MHz, CD₃CN) δ: (s, 1C, Bi-C, not found), 159.2 (s, 2C, *m*-C), 131.0 (s, 1C, *p*-C), 130.1 (s, 2C, *o*-C), 40.5 (s, 2C, CH(CH₃)₂), 25.3 (s, 4C CH(CH₃)₂);

Dipp₂BiI: ¹H NMR (300 MHz, CD₃CN) δ: 7.57 (d, ³J_{H-H} = 7.7 Hz, 4H, *m*-CH), 7.38 (t, ³J_{H-H} = 7.7 Hz, 2H, *p*-CH), 3.24 (sept, ³J_{H-H} = 6.7 Hz, 2H, CH(CH₃)₂), 1.06 (d, ³J_{H-H} = 6.7 Hz, 12H, CH(CH₃)₂); ¹³C{¹H} NMR (75 MHz, CD₃CN) δ: (s, 2C, Bi-C, not found), 157.0 (s, 4C, *m*-C), 129.9 (s, 2C, *p*-C), 128.2 (s, 4C, *o*-C), 41.0 (s, 4C, CH(CH₃)₂), 24.7 (s, 8C CH(CH₃)₂);

6. Crystallographic data

6.1 Crystallographic data for Compound 5

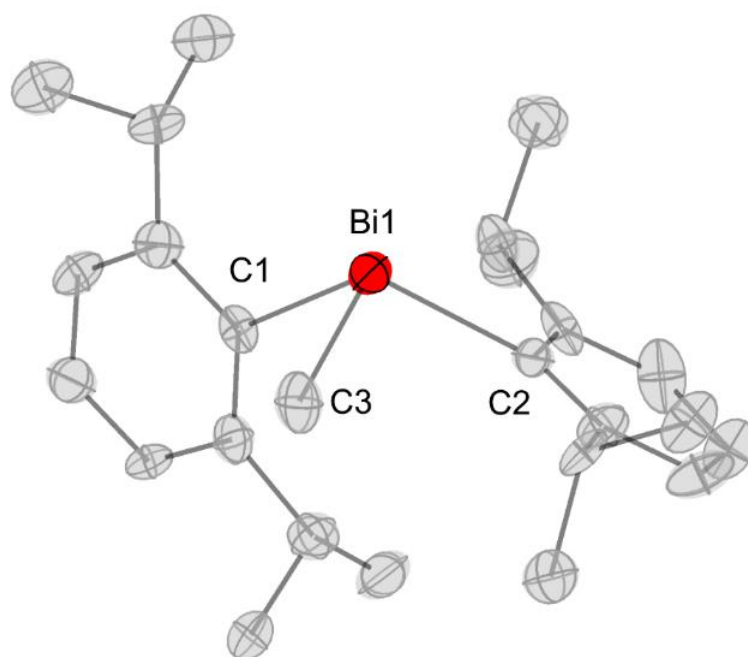


Figure S5: Molecular structure of **5** in the solid state. Hydrogen atoms are omitted for clarity. Ellipsoids are shown at a 50% probability level. Selected bond lengths (pm) and angles (deg): Bi1-C1 230.5(8); Bi1-C2 231.7(9); Bi1-C3 229.0(8); Bi2-C4 231.8(8); Bi2-C5 231.6(9); Bi2-C6 225.9(8); C1-Bi1-C2 100.4(3); C1-Bi1-C3 90.7(3); C2-Bi1-C3 105.1(3); C4-Bi2-C5 95.4(3); C4-Bi2-C6 94.8(3); C5-Bi2-C6 106.7(3).

Table S6.1. Selected crystal structure data of the structure determinations of compounds **1**, **2a** and **2b**

Compound	1	2a	2b
Empirical formula	C ₃₆ H ₅₁ Bi ₁	C ₁₂ H ₁₇ Bi ₁ Cl ₂ ·C ₆ H ₆	C ₁₂ H ₁₇ Bi ₁ Cl ₂ 0.25·C ₆ H ₆
Formula weight	692.74	519.24	460.66
Crystal color, habit	colorless, block	colorless, block	yellow, needle
Temperature/K	100	100	100
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	<i>P2₁/c</i>	<i>Pbcn</i>	<i>P2₁/n</i>
a/Å	11.0970(4)	20.7964(19)	9.9100(3)
b/Å	16.9565(5)	11.6107(12)	23.7933(5)
c/Å	17.9213(6)	15.4920(14)	13.2292(4)
α/°	90	90	90
β/°	107.578(3)	90	104.089(2)
γ/°	90	90	90
Volume/Å ³	3214.72(19)	3740.7(6)	3025.50(15)
Z	4	8	8
ρ _{calc} /cm ³	1.431	1.844	2.023
μ/mm ⁻¹	5.505	9.705	11.984
F(000)	1400.0	1984.0	1732.0
Crystal radius(equiv)/mm	0.1732	0.0794	0.0513
Diffractometer	Stoe IPDS 2T	Stoe IPDS 2	Stoe IPDS 2
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	3.384 to 58.446	4.018 to 58.344	3.424 to 58.498
Reflections collected	61628	34351	39872
Independent reflections	8679 [<i>R</i> _{int} = 0.0589, <i>R</i> _{sigma} = 0.0266]	5030 [<i>R</i> _{int} = 0.0589, <i>R</i> _{sigma} = 0.0266]	8153 [<i>R</i> _{int} = 0.0669, <i>R</i> _{sigma} = 0.0403]
Data/restraint/parameters	8679/0/346	5030/0/194	8153/0/306
Goodness-of-fit on <i>F</i> ²	1.072	0.901	0.955
Final R indexes [all data]	<i>R</i> ₁ = 0.0225, <i>wR</i> ₂ = 0.0407	<i>R</i> ₁ = 0.0430, <i>wR</i> ₂ = 0.0510	<i>R</i> ₁ = 0.0436, <i>wR</i> ₂ = 0.0733
Final R indexes [<i>I</i> ≥ 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0191, <i>wR</i> ₂ = 0.0395	<i>R</i> ₁ = 0.0215, <i>wR</i> ₂ = 0.0479	<i>R</i> ₁ = 0.0300, <i>wR</i> ₂ = 0.0692
Largest diff. peak/hole/ e Å ⁻³	1.48/-1.06	1.32/-0.68	1.83/-1.96
CCDC	2234536	2234534	2234543

Table S6.2. Selected crystal structure data of the structure determinations of compounds **3**, **4** and **5**.

Compound	3	4	5
Empirical formula	C ₁₂ H ₁₇ Bi ₁ Br ₂	C ₁₂ H ₁₇ Bi ₁ I ₂	C ₂₆ H ₄₀ Bi ₁ N ₁
Formula weight	530.05	624.03	575.57
Crystal color, habit	yellow, needle	red, needle	yellow, block
Temperature/K	100	100	100
Crystal system	orthorhombic	monoclinic	triclinic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> /Å	8.3307(2)	22.1504(4)	10.0981(3)
<i>b</i> /Å	9.5095(3)	29.8689(4)	14.9933(5)
<i>c</i> /Å	17.9469(5)	9.4719(2)	17.6121(6)
α /°	90	90	72.420(3)
β /°	90	90.017(2)	89.591(3)
γ /°	90	90	77.807(3)
Volume/Å ³	1421.77(7)	6266.68(19)	2480.06(15)
Z	4	16	4
ρ_{calc} /cm ³	2.476	2.646	1.541
μ /mm ⁻¹	17.991	15.168	7.120
F(000)	968.0	4448.0	1144.0
Crystal size/mm ³	0.714 0.083 0.081	-	-
Crystal radius(equiv)/mm	-	0.0581	0.0874
Diffractometer	Bruker D8 Quest	Stoe IPDS 2T	Stoe IPDS 2
Radiation	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)
2 θ range for data collection/°	5.392 to 56.588	3.29 to 55.97	3.174 to 58.426
Reflections collected	25338	74487	48120
Independent reflections	3534 [<i>R</i> _{int} = 0.0469, <i>R</i> _{sigma} = 0.0300]	15002 [<i>R</i> _{int} = 0.1593, <i>R</i> _{sigma} = 0.0792]	13318 [<i>R</i> _{int} = 0.0208, <i>R</i> _{sigma} = 0.0392]
Data/restraint/parameters	3534/0/141	15002/12/558	13318/0/525
Goodness-of-fit on <i>F</i> ²	1.038	1.026	0.868
Final R indexes [all data]	<i>R</i> ₁ = 0.0188, <i>wR</i> ₂ = 0.0325	<i>R</i> ₁ = 0.0663, <i>wR</i> ₂ = 0.1474	<i>R</i> ₁ = 0.0507, <i>wR</i> ₂ = 0.0526
Final R indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0166, <i>wR</i> ₂ = 0.0321	<i>R</i> ₁ = 0.0557, <i>wR</i> ₂ = 0.1387	<i>R</i> ₁ = 0.0208, <i>wR</i> ₂ = 0.0476
Largest diff. peak/hole/ e Å ⁻³	0.45/-0.56	2.86/-4.15	1.50/-0.58
Flack	0.323(7)		
Comment	Refined as inversion twin		
CCDC	2234533	2234538	2234535

Table S6.3. Selected crystal structure data of the structure determinations of compounds **6**, **7** and **8**.

Compound	6	7	8
Empirical formula	C ₂₅ H ₃₇ Bi ₁	C ₂₈ H ₄₄ Bi ₁ N ₁	C ₄₂ H ₅₆ Bi ₁ Sb ₁
Formula weight	546.52	603.62	891.59
Crystal color, habit	colorless, block	colorless, block	orange, block
Temperature/K	100	100	100
Crystal system	monoclinic	monoclinic	monoclinic
Space group	<i>P2₁/n</i>	<i>P2₁/n</i>	<i>P2₁/c</i>
a/Å	17.2060(9)	10.8514(8)	12.8727(3)
b/Å	9.7812(4)	17.3355(9)	12.36450(10)
c/Å	29.0109(19)	15.4407(10)	23.6698(5)
α/°	90	90	90
β/°	104.996(5)	108.827(5)	91.187(2)
γ/°	90	90	90
Volume/Å ³	4716.1(5)	2749.2(3)	3766.58(12)
Z	8	4	4
ρ _{calc} /cm ³	1.539	1.458	1.572
μ/mm ⁻¹	7.483	6.426	5.409
F(000)	2160.0	1208.0	1768.0
Crystal radius(equiv)/mm	0.0701	0.1181	0.0759
Diffractometer	Stoe StadiVari	Stoe IPDS 2	Stoe IPDS 2T
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	4.832 to 51.998	3.646 to 58.668	3.716 to 58.444
Reflections collected	33360	34185	35407
Independent reflections	9183 [<i>R</i> _{int} = 0.0667, <i>R</i> _{sigma} = 0.0803]	7429 [<i>R</i> _{int} = 0.0494, <i>R</i> _{sigma} = 0.0361]	10164 [<i>R</i> _{int} = 0.0536, <i>R</i> _{sigma} = 0.0373]
Data/restraint/parameters	9183/0/487	7429/1/286	10164/0/411
Goodness-of-fit on <i>F</i> ²	0.966	0.957	1.017
Final R indexes [all data]	<i>R</i> ₁ = 0.1040, <i>wR</i> ₂ = 0.1189	<i>R</i> ₁ = 0.0372, <i>wR</i> ₂ = 0.0494	<i>R</i> ₁ = 0.0359, <i>wR</i> ₂ = 0.0491
Final R indexes [<i>I</i> ≥ 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0521, <i>wR</i> ₂ = 0.01055	<i>R</i> ₁ = 0.0219, <i>wR</i> ₂ = 0.0471	<i>R</i> ₁ = 0.0238, <i>wR</i> ₂ = 0.0462
Largest diff. peak/hole/ e Å ⁻³	1.69/-0.80	1.32/-0.68	0.99/-0.80
CCDC	2234537	2234539	2234541

Table S6.4. Selected crystal structure data of the structure determinations of compounds **9** and **10**.

Compound	9	10
Empirical formula	C ₃₁ H ₅₂ Bi ₁ P ₁ Si ₁	C ₂₈ H ₄₄ Bi ₁ P ₁
Formula weight	692.76	620.58
Crystal color, habit	yellow, block	yellow, block
Temperature/K	100	100
Crystal system	triclinic	orthorhombic
Space group	<i>P</i> $\bar{1}$	<i>Iba</i> 2
a/Å	9.3894(3)	17.4710(4)
b/Å	18.2825(6)	19.2474(5)
c/Å	19.2785(6)	16.8395(5)
α /°	79.629(3)	90
β /°	88.991(2)	90
γ /°	82.088(3)	90
Volume/Å ³	3224.24(18)	5662.6(3)
Z	4	8
ρ_{calc} /cm ³	1.427	1.456
μ /mm ⁻¹	5.571	6.295
F(000)	1400.0	2480.0
Crystal radius(equiv)/mm	0.0571	0.0649
Diffractometer	Stoe IPDS 2T	Stoe IPDS 2T
Radiation	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)
2 θ range for data collection/°	4.296 to 58.522	4.232 to 58.532
Reflections collected	48648	31785
Independent reflections	17371 [R_{int} = 0.1023, R_{sigma} = 0.0794]	7634 [R_{int} = 0.0937, R_{sigma} = 0.0572]
Data/restraint/parameters	17371/26/692	7634/13/286
Goodness-of-fit on F^2	1.004	1.018
Final R indexes [all data]	R_1 = 0.0649, wR_2 = 0.0813	R_1 = 0.0678, wR_2 = 0.0884
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0376, wR_2 = 0.0733	R_1 = 0.0412, wR_2 = 0.0790
Largest diff. peak/hole/ e Å ⁻³	1.43/-1.72	1.56/-1.57
Flack parameter		0.006(8)
CCDC	2234542	2234540

Bismuth Cations: Fluoride Ion Abstraction, Isocyanide Coordination, and Impact of Steric Bulk on Lewis Acidity

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Abstract: The molecular compound [BiDipp₂(SbF₆)], containing the bulky, donor-free bismuth cation [BiDipp₂]⁺ has been synthesized and fully characterized (Dipp = 2,6-*i*-Pr₂-C₆H₃). Using its methyl analog [BiMe₂(SbF₆)] as a second reference point, the impact of steric bulk on bismuth-based Lewis acidity has been investigated in a combined experimental (Gutmann-Beckett method and modified Gutmann-Beckett method) and theoretical approach (DFT calculations). Reactivity studies of the bismuth cations towards (PF₆)⁻ and neutral Lewis bases such as isocyanides C≡NR' have revealed facile fluoride ion abstraction and straightforward Lewis pair formation, respectively. The first examples of compounds featuring bismuth-bound isocyanides have been isolated and fully characterized.

Introduction

The transformation of neutral bismuth species into cationic congeners has granted access to compounds featuring remarkable structural properties and reactivity patterns.^[1] This includes low-coordinate and low-valent compounds (such as [Bi(2,6-Mes₂C₆H₃)₂][B(3,5-(CF₃)₂-C₆H₃)₄] (Mes = 2,4,6-Me₃C₆H₂) and [Bi(cAAC)₂][OTf)],^[2,3] species with an unusual coordination chemistry (such as a pentagonal bipyramidal coordination geometry with a stereochemically inactive lone pair at bismuth),^[4] ring-strained coordination entities,^[5-7] and new structural motifs such as bisma-alkene species and Bi → Bi donor-acceptor bonding.^[8,9] It can be anticipated that such uncommon structural properties inevitably lead to unforeseen reactivity patterns. Remarkable examples include CH activation reactions,^[5,7,6] the activation of small molecules such as CO,^[10] reversible one-electron transfer at bismuth,^[10,11] the controlled living radical polymerization of activated α-olefins,^[12] the catalytic hydrosilylation of olefins and carbonyl compounds,^[13,14] and the exploitation of bismuth redox platforms in the fluorination, triflation, and nonaflation of arylboronic esters.^[15] These findings initiated investigations towards a more detailed understanding of bismuth-based Lewis acidity. As a result, the ability of bismuth(III) species to adopt formal charges ranging from +1 to +3,^[9,16,13,14,1] to bear multiple Lewis acidic binding sites that can reversibly be occupied by Lewis bases,^[13] and to act as exceptionally strong and soft Lewis acids has been uncovered.^[17] Smart ligand design including the use of chelating ligands and the control of the ligand bite angle can be exploited to significantly

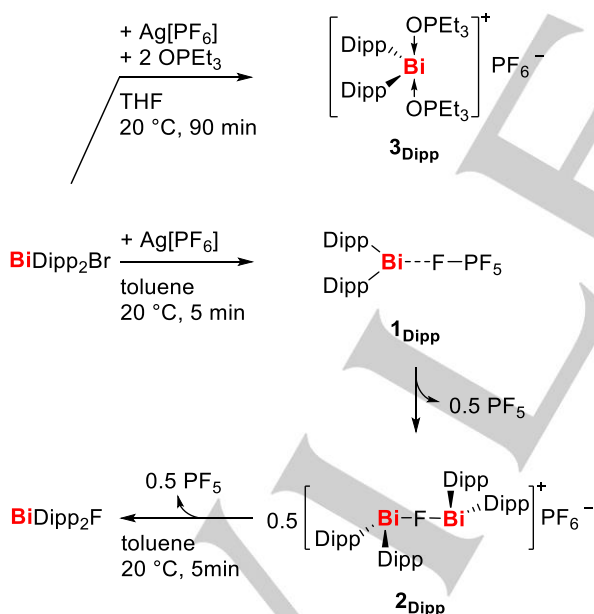
increase the Lewis acidity of bismuth cations.^[18,19] In addition, facets such as inversed solvent effects (where the increase of the solvent polarity increases the Lewis acidity) have been reported.^[4] The use of steric bulk for the stabilization of cationic bismuth species is well documented.^[1] However, the impact of steric factors on the Lewis acidity of bismuth cations has not been investigated in detail, quantified, and rationalized to so far. While often receiving less attention, the choice of the counteranion can also be a decisive factor in the design of cationic species, since they can considerably influence the solubility, coordination number, and stability of the cationic species.^[20] However, the stability and potential degradation pathways of weakly coordinating anions in the coordination sphere of bismuth cations has only received little attention to date.^[21] Here, we report the investigation of compounds featuring the structural motif [BiR₂]⁺ (R = Me, Dipp), evaluating steric factors, the stability of [PnF₆] anions (Pn = P, Sb), and the coordination of Lewis bases in the context of bismuth-based Lewis acidity.

Results and Discussion

In past experiments, donor-free [BiMe₂(SbF₆)] (**I**) was successfully synthesized.^[8] In this report, we want to prepare donor-free bismuthenium cations with larger aryl substituents to investigate the influence of electronic and steric effects of an intermediate-sized aryl substituent on the properties of the bismuthenium atoms. A compound with large terphenyl substituents, has previously been reported in the literature (Bi[(2,6-Mes-C₆H₃)₂][B(3,5-(CF₃)₂-C₆H₃)₄]).^[2] However, due to the extreme steric demand of the terphenyl substituent, the crowded bismuth center may not be suitable as a Lewis acid towards donors of considerable size. As a result, [BiDipp₂]⁺ was chosen as the target cation (Dipp = 2,6-*i*-Pr₂-C₆H₃). In first attempts BiDipp₂Br was reacted with Ag[PF₆] in toluene. Upon addition of the silver salt, the reaction mixture immediately turns dark red, indicating the possible formation of the desired [BiDipp₂(PF₆)] (**1**_{Dipp}). Upon fast workup, a dark red solid can be obtained. The crude product supposedly consists mainly of **1**_{Dipp}, however upon attempted purification or storage under inert atmosphere, the solid decomposes to an inhomogeneous mixture of black and yellow color over few days. If the reaction mixture is not worked up fast enough, slow precipitation of an orange solid is observed. The

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orange precipitate represents a mixture of compounds, none of which could be isolated so far. However, $[(\text{BiDipp}_2)_2\text{F}(\text{PF}_6)]$ ($\mathbf{2}_{\text{Dipp}}$) and literature-known BiDipp_2F could be identified by single-crystal X-ray analysis and NMR spectroscopy, respectively. Thus, we suggest the initial formation of short-lived $[\text{BiDipp}_2(\text{PF}_6)]$ ($\mathbf{1}_{\text{Dipp}}$), which readily decomposes *via* a stepwise and facile fluoride ion abstraction from $[\text{PF}_6]^-$ (Scheme 1, bottom). The structural analysis of $\mathbf{2}_{\text{Dipp}}$ reveals two crystallographically distinct molecules in the solid state. While the Bi–F bond lengths in these molecules are similar to each other and in the range of 2.275(4) - 2.296(4) Å, the Bi–F–Bi angle varies dramatically, indicating a bent geometry in one case ($144.0(2)^\circ$) and a linear coordination in the other (180° , F atom located on an inversion center). This is a rare case of an organobismuth(III) compound with a bridging fluorido ligand (*cf.* $[\text{Bi}(\text{C}_2\text{F}_5)_2\text{F}(\text{OCMe}_2)]_\infty$, Bi–F–Bi, 138°)^[22] and demonstrates that the linear and bent arrangements are similar in energy, paralleling previous findings in bismuth(V) and mixed bismuth(III/V) chemistry.^[23,24] In a similar reaction, Me_2BiCl (\mathbf{II}) was reacted with $\text{Ag}[\text{PF}_6]$ in toluene, which gave a complex mixture of products according to ^1H and ^{19}F NMR spectroscopy, none of which could unambiguously be identified. While bismuth cations with neutral donor ligands and $[\text{PF}_6]^-$ counteranions such as $[\text{BiPh}_2(\text{NC}_5\text{H}_5)_2]^+$ are accessible,^[25] our results indicate that $[\text{PF}_6]^-$ is not a suitable anion for the preparation of donor-free organobismuth cations. These experimental findings are in line with previously reported theoretical calculations, which assigned a fluoride ion affinity (FIA) of 602 to $[\text{Bi}(2,6\text{-Mes}_2\text{C}_6\text{H}_3)_2]^+$ (level of theory: B3PW91/6-311+G(2df,p)),^[26] surpassing the FIA of 384 found for PF_5 (level of theory: DLPNO-CCSD(T)/aug-cc-pVQZ).^[27]



Scheme 1. Reaction of Dipp_2BiBr and $\text{Ag}[\text{PF}_6]$ to $\mathbf{1}_{\text{Dipp}}$ and subsequent fluoride transfer from $[\text{PF}_6]^-$ under formation of $\mathbf{2}_{\text{Dipp}}$ and BiDipp_2F . In the presence of OPEt_3 , BiDipp_2Br reacts with $\text{Ag}[\text{PF}_6]$ to form $\mathbf{3}_{\text{Dipp}}$.

In order to obtain indications of the *in-situ*-formation of $\mathbf{1}_{\text{Dipp}}$ in solution we attempted to trap reactive intermediates with OPEt_3 , which subsequently yielded $[\text{BiDipp}_2(\text{OPEt}_3)_2][\text{PF}_6]$ ($\mathbf{3}_{\text{Dipp}}$) as a colorless crystalline solid. Crystals suitable for single-crystal X-ray diffraction were obtained from a mixture of toluene and *n*-pentane at -32°C (Figure 1). In $\mathbf{3}_{\text{Dipp}}$, the bismuth atom shows a

bisphenoidal coordination geometry with an O–Bi–O angle of ($165.84(7)^\circ$). The Bi–O lengths of 2.4389(16) and 2.4357(16) Å are slightly longer than those in similar Bi(III) phosphanoxide adducts of the general form $[\text{BiAr}_2(\text{OPR}_3)_2][\text{A}]$ (Ar = Ph, Mes; R = Ph, NMe₂; $[\text{A}]^- = [\text{BF}_4]^-$, $[\text{PF}_6]^-$; Bi–O, 2.317(5) Å - 2.41(1) Å).^[25] The Bi–O bond elongation in $\mathbf{3}_{\text{Dipp}}$ was assigned to the sterically demanding Dipp substituents.

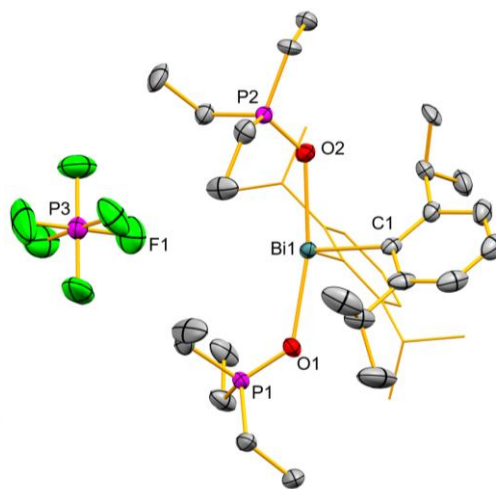


Figure 1. Molecular structure of $\mathbf{3}_{\text{Dipp}}$ in the solid state. Displacement ellipsoids are drawn at 50% probability level. H-Atoms are omitted and one of the Dipp ligands is shown as wireframe for clarity. Selected bond lengths (Å) and angles (°): Bi1–O1 2.4359(16), Bi1–O2 2.4389(16), Bi–C1 2.285(2), Bi–C2 2.326(5), O1–Bi1–O2 165.84(7), C1–Bi1–C2 92.3(2), C1–Bi1–O1 104.37(8), C1–Bi1–O2 88.12(8).

To obtain the donor-free $[\text{BiDipp}_2]^+$ cation, we exchanged the $[\text{PF}_6]^-$ anion for $[\text{SbF}_6]^-$, which already proved to be a suitable strategy in the preparation of $[\text{BiMe}_2(\text{SbF}_6)]$.^[8] Upon addition of $\text{Ag}[\text{SbF}_6]$ to a toluene solution of BiDipp_2Br , the reaction mixture turned dark red. After removal of solids, concentration and storage at -32°C , dark red crystals were obtained and identified as $[\text{BiDipp}_2(\text{tol})(\text{SbF}_6)]$ ($\mathbf{4}\text{-tol}_{\text{Dipp}}$; Scheme 2). For the $[\text{SbF}_6]^-$ anion, no hints for fluoride abstraction could be observed, indicating that the FIA of the $[\text{BiDipp}_2]^+$ cation in toluene solution lays in between those of PF_5 (384) and SbF_5 (496).^[27]

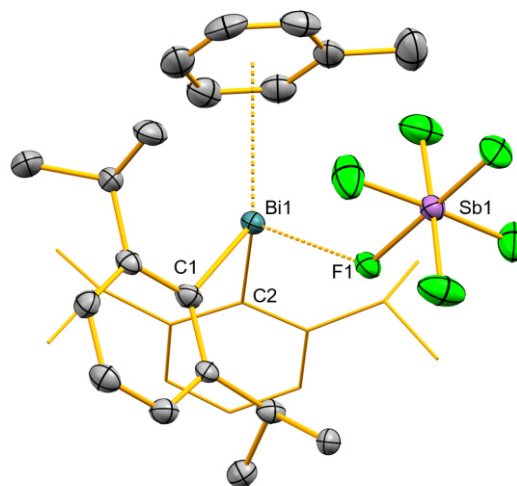
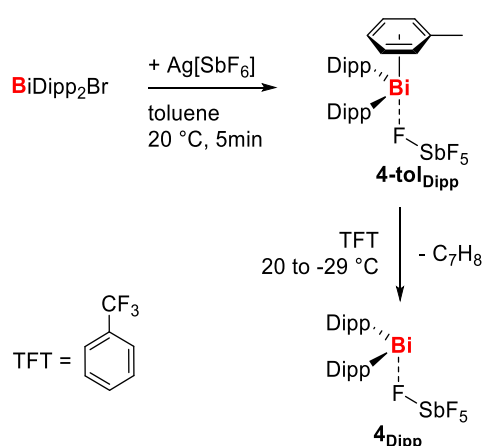


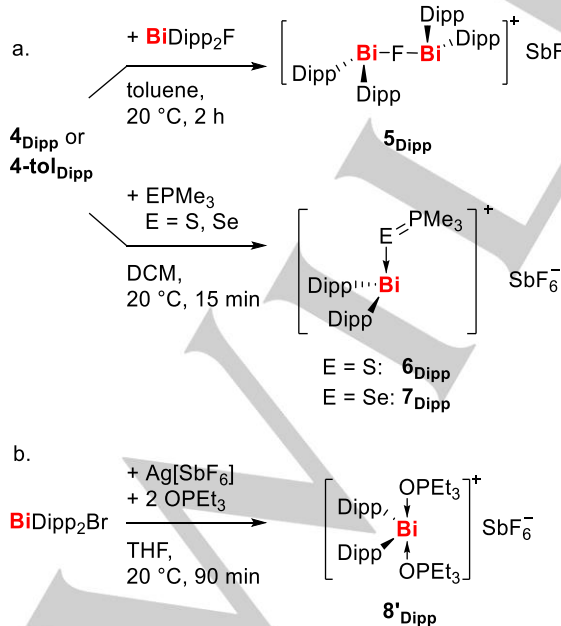
Figure 2. Crystal structure of $\mathbf{4}\text{-tol}_{\text{Dipp}}$, displacement ellipsoids drawn at 50% probability level, H-Atoms omitted and one of the Dipp ligands is shown as wireframe for clarity. Selected bond lengths (Å) and angles (°): Bi1–C1 2.259(8), Bi1–C2 2.257(7), Bi1–F1 2.491(4), Sb1–F1 1.918(6), C1–Bi1–C2 94.4(3), C1–Bi1–F1 86.6(2), C2–Bi1–F1 104.1(2).

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Compound **4-tol_{Dipp}** crystallizes in the monoclinic space group $P2_1$, forming a monomeric ion pair in the solid state. The Bi atom shows a bisphenoidal coordination sphere with two Dipp substituents in the equatorial positions, an η_6 -coordinated toluene molecule, and the $[\text{SbF}_6]^-$ anion coordinated *via* one fluorine atom. The distance of the Bi atom and the centroid of the aromatic toluene ring is 3.2301(3) Å, which is in the range of bonding Bi–arene π -interactions^[28] and similar to the Bi–*ct* distances in $\text{BiCl}_3 \cdot \text{C}_6\text{H}_5\text{Me}$ (3.04 and 3.09 Å)^[29] or $[\text{Bi}(\text{NMe}_2)_2(\text{BPh}_4)]$ (3.228(5) Å).^[21] The Bi–F1 distance is 2.488(5) Å, far below the sum of van der Waals radii (3.54 Å),^[30,31] similar to that in cationic $[\text{BiMe}_2(\text{SbF}_6)]$ (**1**) (2.451(3) and 2.452(3) Å),^[8] and significantly longer than that in neutral BiDipp_2F (2.115(3) Å).^[32] In return, the Sb1–F1 bond in **4-tol_{Dipp}** (1.930(7) Å) is elongated compared to the other Sb–F bonds (1.851(7)–1.871(6) Å).



Scheme 2. Reaction of BiDipp_2Br and $\text{Ag}[\text{SbF}_6]$ in toluene under formation of **4-tol_{Dipp}** and subsequent recrystallization from TFT (α, α, α -trifluorotoluene) to the donor free **4_{Dipp}**.



Scheme 3. a. Preparation of **5_{Dipp}**, **6_{Dipp}** and **7_{Dipp}** from **4-tol_{Dipp}** or **4_{Dipp}**. b. Preparation of **8'_{Dipp}**.

The donor free compound **4_{Dipp}** was obtained by recrystallization of **4-tol_{Dipp}** from a less π -donating aromatic solvent, namely α, α, α -trifluorotoluene (TFT). Compound **4_{Dipp}** crystallizes in the monoclinic space group $P2_1/n$ with one molecule in the asymmetric unit (Figure 3). In the solid state, dimers are formed through weak interactions of Bi and an F atom of the $[\text{SbF}_6]^-$ anion in the neighboring molecule, which corresponds to a decrease in nuclearity when compared to the parent compound $[\text{BiMe}_2(\text{SbF}_6)]_\infty$ (**1**) _{∞} that forms a coordination polymer with weakly bound μ_2 - $(\text{SbF}_6)^-$ bridging ligands in the solid state. As a result, the bismuth atom in **4_{Dipp}** shows a bisphenoidal coordination sphere with one short Bi1...F1 distance of 2.459(2) Å, similar to that in **4-tol_{Dipp}**, and a longer Bi1...F2' distance of 3.208(2) Å, the latter being 9% under the sum of the van der Waals radii (3.54 Å).^[30,31] The compounds **4_{Dipp}** and **4-tol_{Dipp}** show all expected signals in the ^1H - and ^{13}C -NMR spectra, with equal chemical shifts in DCM-d_2 or C_6D_6 , indicating no coordination of the toluene molecule in solution. As obtaining **4-tol_{Dipp}** requires less steps and shows the same behaviour in solution as **4_{Dipp}**, the former was used for most subsequent reactions. For compounds of the form BiDipp_2X (X = I, Br, Cl, F, OTf), the NMR chemical shift of the bismuth-bound carbon atoms could be correlated to the group electronegativity of X, and a low-field shift from 174.5 (X = I) to 207.6 (X = OTf) was observed.^[32] In case of **4_{Dipp}**, a chemical shift of 238.1 ppm (C_6D_6) or 237.6 (DCM- d_2) is observed, corresponding to an even lower field. In the ^{19}F NMR spectrum, a very broad signal at 120.8 ppm (C_6D_6) or 122.9 (DCM- d_2) is observed, hinting at the formation of a solvent-separated ion pair in solution

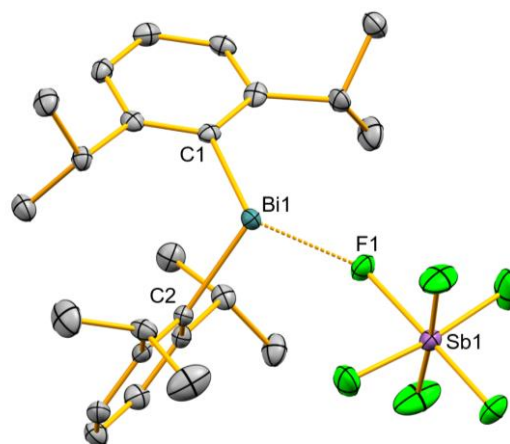


Figure 3. Crystal structure of **4_{Dipp}**, displacement ellipsoids drawn at 50% probability level, H-Atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Bi1–C1 2.257(2), Bi1–C2 2.260(2), Bi–F1 2.4593(15), Sb1–F1 1.9438(14), C1–Bi1–C2 97.86(9), C1–Bi1–F1 103.61(7), C2–Bi1–F1 91.19(7)

As **2_{Dipp}** was not isolable due to decomposition of the $[\text{PF}_6]^-$ anion, we attempted to reproduce the $[(\text{BiDipp})_2\text{F}]^+$ structural motif with an $[\text{SbF}_6]^-$ anion. Upon reaction of **4-tol_{Dipp}** with BiDipp_2F in toluene, $[(\text{BiDipp})_2\text{F}(\text{SbF}_6)]$ (**5_{Dipp}**) precipitates as an orange solid (Scheme 3). Compound **5_{Dipp}** crystallizes in the triclinic space group $P\bar{1}$ with half a molecule of **5_{Dipp}** in the asymmetric unit. The central fluorine atom and the antimony atom of the $[\text{SbF}_6]^-$ anion occupy inversion centers in the unit cell (Figure 4), which results in a perfectly linear coordination of the fluorine atom. Only recently, cationic Bi(V) compounds with a bridging fluoride motif have been isolated. One example, $[(\text{BiF}(\text{m-}t\text{Bu}_3\text{C}_6\text{H}_3)_3)_2\text{F}][\text{B}(\text{3,5-}(\text{CF}_3)_2\text{C}_6\text{H}_3)_4]$, also shows a linearly coordinated fluorine atom.^[23]

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However, **5**_{Dipp} is the first isolated cationic dinuclear Bi(III) compound with a bridging F⁻ anion and can be viewed as a structural excerpt of the one dimensional polymeric chains formed by BiDipp₂F in the solid state.^[32] The Bi1–F1 distance of 2.2755(4) Å in **5**_{Dipp} is somewhat longer than that in the neutral compounds BiDipp₂F (2.115(3) Å)^[32] or Bi(C₂F₅)₂F-acetone (2.229(2) and 2.262(2) Å)^[22] and very similar to that in the dinuclear Bi(V) compound described by Cornella and coworkers (2.2820(3) Å).^[23] Again, there are weak directional bonding interactions between the bismuth cation and the anion in the solid state (according to distance criteria), and the Bi1⋯F2 distance of 2.872(4) Å is clearly below the sum of van der Waals radii (3.54 Å).^[30,31]

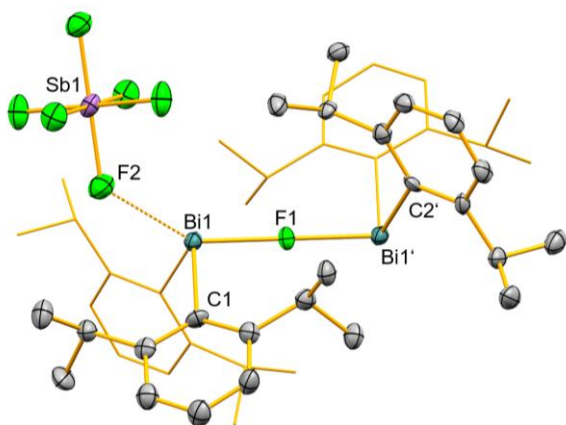


Figure 4. Crystal structure of **5**_{Dipp}, displacement ellipsoids drawn at 50% probability level, H-Atoms omitted and second Dipp shown as wireframe for clarity. Selected bond lengths (Å) and angles (°): Bi–C1 2.287(6), Bi–C2 2.285(6), Bi1–F1 2.2755(4), C1–Bi1–C2 96.0(2), C1–Bi1–F1 101.65(16), C2–Bi1–F1 93.17(16).

The above findings indicate that the fluoride ion affinity of (BiDipp₂)⁺ in the condensed phase lays in between that of PF₅ and SbF₅. As the fluoride ion affinity is used as a measure of Lewis acidity, we wanted to further investigate the Lewis acidity experimentally. For this, the Gutmann Beckett method (GBM) uses the ³¹P-NMR chemical shift of coordinated OPET₃. Recently, we proposed a Lewis acidity scale which uses the softer donors SPMe₃ or SePMe₃ as probes while otherwise relying on the same principles as the GBM, thereby creating a possibility to evaluate the softness and strength of Lewis acids.^[17,33,34] Along these lines, **4**-to**1**_{Dipp} was reacted with EPMe₃ (E = S, Se) to give [BiDipp₂(EPMe₃)(SbF₆)] (E = S (**6**_{Dipp}), E = Se (**7**_{Dipp})) in good yields of 92 % (**6**_{Dipp}) and 59 % (**7**_{Dipp}). Moreover, the preparation of the *mono*-OPET₃-adduct [BiDipp₂(OPET₃)(SbF₆)] (**8**_{Dipp}) was attempted for an evaluation *via* the original GBM, but only the *bis*-OPET₃-adduct [BiDipp₂(OPET₃)₂(SbF₆)] (**8'**_{Dipp}) could be isolated (for a more detailed discussion, see DFT section). The compounds **6**_{Dipp} and **7**_{Dipp} crystallize isomorphically in the space group *P2₁/c* with one molecule in the asymmetric unit (Figure 5). The Bi1–S1 bond length in **6**_{Dipp} is 2.6700(8) Å, only slightly longer than that in neutral diaryl bismuth sulfides ((Ar₂Bi)₂S_n (Ar = Mes, Dipp; n = 1, 3, 5): 2.520(7) – 2.601(2) Å; Ph₂Bi-SPh: 2.588(1) Å),^[32,35] and close to that in [Bi(aryl)₂(SPMe₃)](SbF₆) (2.611(2) Å), where a DFT study and NBO analysis suggested the interpretation of the Bi–S interaction as a regular covalent bond.^[17] An analogous situation is found for compound **7**_{Dipp} (Bi1–Se1, 2.7687(5) Å), when compared to the previously reported

compound [Bi(aryl)₂(SePMe₃)](SbF₆) (Bi–Se, 2.7222(4) Å).^[17] The F atoms in the [SbF₆]⁻ anion are disordered with an occupancy of 49% and 51% for **6**_{Dipp} and 54% and 46% for the two domains in **7**_{Dipp}. The shortest Bi–F distance in **6**_{Dipp} is 3.132(7) Å and similarly 3.180(4) Å in **7**_{Dipp}. This is only slightly shorter than the intermolecular contact in **4**_{Dipp} (3.208(2) Å) and indicative of weak Bi–F interactions.

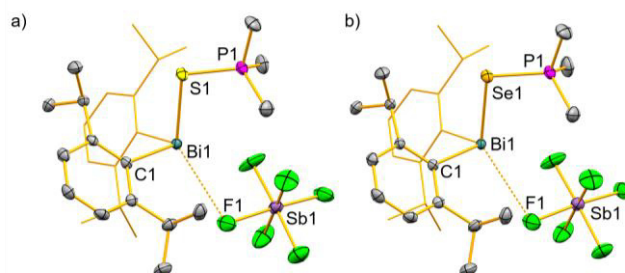


Figure 5. Crystal structure of **6**_{Dipp} and **7**_{Dipp}, displacement ellipsoids drawn at 50% probability level, H-Atoms omitted and second Dipp shown as wireframe for clarity. a) Selected bond lengths (Å) and angles (°) of **6**_{Dipp}: Bi1–S1 2.6699(7), Bi1–C1 2.277(3), Bi1–C2 2.287(3), S1–P1 2.022(1), C1–Bi1–C2 95.87(9), C1–Bi1–S1 90.02(7), C2–Bi1–S1 106.13(7), Bi1–S1–P1 99.09(4). b) Selected bond lengths (Å) and angles (°) of **7**_{Dipp}: Bi1–Se1 2.7689(2), Bi1–C1 2.283(2), Bi1–C2 2.289(2), Se1–P1 2.1755(7), C1–Bi1–C2 95.90(8), C1–Bi1–Se1 89.85(5), C2–Bi1–Se1 106.63(6), Bi1–S1–P1 95.65(2).

In order to evaluate the impact of steric factors on bismuth-based Lewis acidity, the Gutmann Beckett method and modified versions thereof were applied to compound [BiDipp₂(SbF₆)] (**4**_{Dipp}) with its bulky Dipp ligands and compound [BiMe₂(SbF₆)] (**1**) bearing methyl groups, i.e. ligands with a very low steric profile. Acceptor numbers (AN) for **4**_{Dipp} and [BiMe₂(SbF₆)] (**1**) were determined through the ³¹P-NMR shifts obtained from the analysis of isolated compounds or from *in situ* experiments and calculated according to formulae (1) to (3) for the respective donor.^[17,33,34]

$$\text{OPET}_3: \text{AN} = 2.21 \cdot (\delta_p - 41.0) \quad (1)$$

$$\text{SPMe}_3: \text{AN} = 6.41 \cdot (\delta_p - 29.2) \quad (2)$$

$$\text{SePMe}_3: \text{AN} = 5.71 \cdot (\delta_p - 7.8) \quad (3)$$

While the limitations and the theoretical background of the Gutmann Beckett method have been discussed on a few instances, the method still provides an experimental evaluation of Lewis acidity in a straightforward approach without the necessity for a special experimental setup.^[17,36] According to the Gutmann Beckett approach, low acceptor numbers are caused by weak interactions between the donor (OPET₃, SPMe₃, SePMe₃) and the acceptor and indicate a low Lewis acidity. On the other hand, high acceptor numbers are the result of stronger interactions between the donor and the acceptor, indicating a higher Lewis acidity. The results obtained for [BiDipp₂(SbF₆)] (**4**_{Dipp}) and [BiMe₂(SbF₆)] (**1**) are summarized in Table 1. In order to compare the ability of these compounds to bind not only one but two donors, experiments with two equivalents of the Lewis base were also performed. As a trend, the acceptor numbers of compound **4**_{Dipp} are greater than those of **1** (with a few exceptions where similar acceptor numbers were determined). Thus, the increase of steric bulk increases rather than decreases the Lewis acidity. The most prominent difference is found for the Lewis acidity towards OPET₃ (entries 1,2), where **1** gives results that are in line with previous findings,^[6,17,18,37] but **4**_{Dipp} shows a very pronounced Lewis acidity that even surpasses that of a tricationic bismuth species^[19] and bismuth cations, in which the Lewis acidity has been increased by

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tuning of the ligand bite angle.^[18] While acceptor numbers in experiments with two equivalents of a donor are expectedly smaller than in cases of a 1:1 stoichiometry, these results indicate that the simultaneous and considerable activation of two Lewis bases at the bismuth centers of **4**_{Dipp} and **I** is possible.

Table 1. Acceptor numbers (ANs) of compounds [BiR₂(SbF₆)] (R = Me, Dipp) according to the Gutmann-Beckett method and variations thereof.

Entry	Donor	Eq.	Acceptor	AN
1	OPEt ₃	1	[BiMe ₂ (SbF ₆)]	67.2
2	OPEt ₃	1	[BiDipp ₂ (SbF ₆)]	87.3
3	OPEt ₃	2	[BiMe ₂ (SbF ₆)]	51.1
4	OPEt ₃	2	[BiDipp ₂ (SbF ₆)]	52.4
5	SPhMe ₃	1	[BiMe ₂ (SbF ₆)]	94.4
6	SPhMe ₃	1	[BiDipp ₂ (SbF ₆)]	94.2
7	SPhMe ₃	2	[BiMe ₂ (SbF ₆)]	52.6
8	SPhMe ₃	2	[BiDipp ₂ (SbF ₆)]	60.6
9	SePhMe ₃	1	[BiMe ₂ (SbF ₆)]	76.2
10	SePhMe ₃	1	[BiDipp ₂ (SbF ₆)]	81.8
11	SePhMe ₃	2	[BiMe ₂ (SbF ₆)]	46.3
12	SePhMe ₃	2	[BiDipp ₂ (SbF ₆)]	47.3

To further elucidate the Lewis acidic properties of compounds [BiR₂(SbF₆)] (R = Me, Dipp), DFT calculations were performed at the B3LYP / 6-311++G(d,p) [H,C,O,F,P,S,Se] LanL2DZ [Sb,Bi] level of theory using the D3 version of Grimme's dispersion model (for details see Supp. Inf.). The most striking difference between the Gutmann-Beckett parameters of these compounds is the higher Lewis acidity of the sterically more demanding species towards one equivalent of OPEt₃ (Table 1, entries 1, 2, see discussion above). The geometry-optimized structures of [BiR₂(OPEt₃)(SbF₆)] (R = Me, Dipp) revealed that the bulky Dipp substituents effectively shield the bismuth atom, resulting in a solvent-separated ion pair, while a contact ion pair is formed for the compound featuring a BiMe₂⁺ core (Figure 6). Thus, the lower coordination number as such and the absence of a weakly bound ligand in *trans*-position to the spectroscopic probe OPEt₃ result in a significantly higher acceptor number for **8**_{Dipp}. The addition of the first and the second equivalent of EPR'₃ (E = O, S, Se; R' = Me, Et) to [BiR₂(SbF₆)] (R = Me (**I**), Dipp (**4**_{Dipp})) is exothermic and exergonic in all reactions that were studied (Table 2). Thus, the formation of compounds [BiR₂(EPR'₃)₂(SbF₆)] can be expected in all cases, when two equivalents of the base are present. A more detailed analysis reveals that the energy gain in the second addition is larger for the compounds with the BiMe₂⁺ core (entries 3,6,9) than for those with a BiDipp₂⁺ core (entries 12,15,18), which was ascribed to the absence of strong steric repulsion in the former cases. When studying the trends of the energy gain for the addition of the second equivalent of a Lewis base in the BiMe₂⁺ and BiDipp₂⁺ series (entries 3,6,9 and 12,15,18), it is relatively small for the softer Lewis bases S/SePhMe₃ in the compounds featuring bulky Dipp substituents (entries 15,18). This was

ascribed to stronger covalent contributions to Bi–S/SePhMe₃ bonding when compared to Bi–OPEt₃ bonding. Covalent contributions are more sensitive to changes in interatomic distances, which are relevant in the sterically encumbered complexes [BiDipp₂(EPhMe₃)(SbF₆)] (E = S (**6**_{Dipp}), Se (**7**_{Dipp})). Significantly larger covalent contributions to Bi–S/SePhMe₃ (as compared to Bi–OPEt₃) can be anticipated due to the differences in electronegativity of the donor atoms (O–Se) and were confirmed by distance criteria and atoms-in-molecules analyses (i.e. electron localization function; for details including a discussion of differences in the Laplacian of the electron density, the ratio of potential over kinetic energy density, and the total energy density at the bond critical points see Supp. Inf.). These findings are in

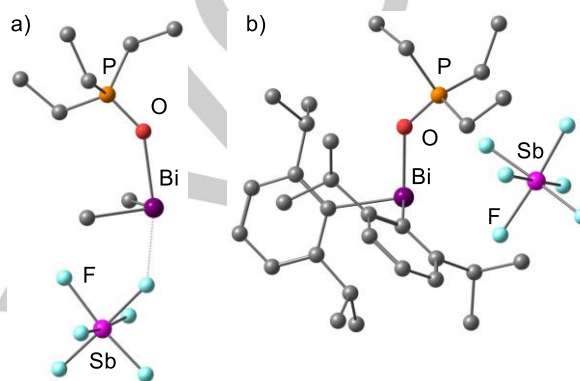
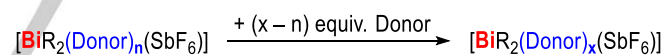


Figure 6. Geometry-optimized structures of [BiR₂(OPEt₃)(SbF₆)], as obtained from DFT calculations. a) R = Me (**8**_{Me}); b) R = Dipp (**8**_{Dipp}).

Table 2. Reaction enthalpies and Gibbs energies for adduct formation of the cationic species [BiR₂(Donor)_n(SbF₆)] (R = Me, Dipp; n = 0, 1) with donors EPR'₃ (E = O, S, Se; R' = Et, Me) to give compounds [BiR₂(Donor)_x(SbF₆)] (x = 1, 2).



Entry	R	Donor	n	x	ΔH [kcal·mol ⁻¹]	ΔG [kcal·mol ⁻¹]
1	Me	OPEt ₃	0	1	-29.7	-18.3
2	Me	OPEt ₃	0	2	-66.5	-42.7
3	Me	OPEt ₃	1	2	-36.8	-24.5
4	Me	SPhMe ₃	0	1	-19.9	-10.4
5	Me	SPhMe ₃	0	2	-51.3	-29.8
6	Me	SPhMe ₃	1	2	-31.5	-19.1
7	Me	SePhMe ₃	0	1	-21.2	-11.8
8	Me	SePhMe ₃	0	2	-56.5	-32.7
9	Me	SePhMe ₃	1	2	-35.3	-20.9
10	Dipp	OPEt ₃	0	1	-33.1	-19.2
11	Dipp	OPEt ₃	0	2	-62.3	-34.5
12	Dipp	OPEt ₃	1	2	-29.2	-15.4

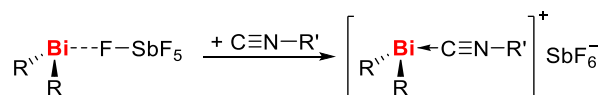
13	Dipp	SPMe ₃	0	1	-24.3	-12.9
14	Dipp	SPMe ₃	0	2	-45.9	-19.1
15	Dipp	SPMe ₃	1	2	-21.6	-6.1
16	Dipp	SePMe ₃	0	1	-27.1	-15.1
17	Dipp	SePMe ₃	0	2	-48.3	-21.3
18	Dipp	SePMe ₃	1	2	-21.3	-6.2

line with the ligand exchange reactions $2 [\text{BiDipp}_2(\text{EPR}'_3)][\text{SbF}_6] \rightleftharpoons [\text{BiDipp}_2(\text{SbF}_6)] + [\text{BiDipp}_2(\text{EPR}'_3)_2][\text{SbF}_6]$ becoming increasingly endergonic with increasing softness of the Lewis base ($\Delta G = +3.8 \text{ kcal}\cdot\text{mol}^{-1}$ (E=O, R'=Et), $+6.8 \text{ kcal}\cdot\text{mol}^{-1}$ (E=S, R'=Me), $+9.0 \text{ kcal}\cdot\text{mol}^{-1}$ (E=Se, R'=Me)). Thus, the fact that compound $[\text{BiDipp}_2(\text{OPeEt}_3)_2][\text{SbF}_6]$ (**8'**_{Dipp}) was reproducibly crystallized from solutions containing $[\text{BiDipp}_2(\text{SbF}_6)]$ and OPeEt_3 in a 1:1 stoichiometry can be attributed to favourable intermolecular interactions of this species in the solid state.

In order to explore the reactivity of **4**_{Dipp} and **I** towards Lewis bases, we turned our attention to isocyanides, which represent important chemical building blocks with relevance for fields such as medicinal chemistry, fragrance, and total synthesis.^[38] In addition to the rich portfolio of organic compounds that can be derived from isocyanides, their coordination chemistry towards main group metals has been investigated in some detail.^[39] In contrast, only little is known about the chemistry of isocyanides with heavy main group Lewis acids in general and group 15 species in specific. For instance, the insertion of isocyanides into Bi–B and Bi–N bonds has been reported, exploiting the high reactivity of boryl anions^[40] and ring-strained BiC₂N cycles.^[10] For transition metal stabilized phosphinidenes and arsinidenes, the coordination of CN*t*Bu could be observed, while less bulky isocyanides underwent subsequent insertion reactions.^[41] Simple Lewis acid/base adducts between bismuth compounds and isocyanides have not been reported to date.

Reaction of **4**_{Dipp} and **I** with CN*t*Bu gave **9**_{Dipp} and **9**_{Me} as isolable Lewis acid/base adducts (Scheme 4). In light of the previously reported importance of steric bulk for the stability of adducts between phosphinidenes and arsinidenes and isocyanides,^[41] the steric bulk of both, the bismuth cation and the isocyanide CNR', was modified stepwise. The synthesis of **10**_{Me} with R' = adamantyl confirmed the accessibility of adducts with sufficient steric bulk, but also compounds **11**_{Me}–**13**_{Me} with R' = xylyl, cyclohexyl, and *n*-butyl could readily be isolated. In all cases that bear aliphatic substituents in the isocyanide, even an excess of this substrate led to the isolation of the mono-adducts, albeit the reversible exchange of isocyanide ligands was apparent from NMR spectroscopic analyses of reactions with a Bi/isocyanide ratio of 1:2. Only in the case of R' = xylyl, the mono-adduct **11**_{Me} and the bis-adduct **11'**_{Me} could be obtained from reactions with a 1:1 and a 1:2 stoichiometry, respectively.

The ¹H and ¹³C NMR spectroscopic analyses of the isocyanide adducts **9**–**13** revealed similar trends for all compounds: the signals assigned to the protons of the bismuth-bound isocyanides are slightly shifted towards lower field, while the CNR' carbon atom experiences a strong up-field shift ($\Delta\delta \approx 70 \text{ ppm}$, for all formed monoadducts), when compared to the free compounds.^[42] The resonances corresponding to the bismuth-bound methyl groups, however, show a considerable upfield shift compared to the starting material **I** and are in most cases close to those of the neutral chlorido species BiMe₂Cl (**II**) (see Table 3).



R = Dipp, Me

R' = Ad, Xyl, Cy, *t*Bu, *n*Bu

Scheme 4. Synthesis of isonitrile adducts with $[\text{BiR}_2(\text{SbF}_6)]$.

Table 3. ¹H- and ¹³C-NMR chemical shifts of bismuth bound methyl groups and isocyanide carbon atoms.

Compound	¹ H-NMR (Me) δ [ppm]	¹³ C-NMR (Me) δ [ppm]	¹³ C-NMR (CNR') δ [ppm]
BiMe ₃ (II)	1.11	-6.82	-
BiMe ₂ Cl (III)	1.80	34.66	-
$[\text{BiMe}_2(\text{SbF}_6)]$ (I)	2.28	64.38	-
$[\text{BiMe}_2(\text{CN}i\text{Bu})(\text{SbF}_6)]$ (9 _{Me})	1.85	30.01	82.52
$[\text{BiDipp}_2(\text{CN}i\text{Bu})(\text{SbF}_6)]$ (9 _{Dipp})	0.98 ^[b]	-	- ^[a]
$[\text{BiMe}_2(\text{CNAd})(\text{SbF}_6)]$ (10 _{Me})	1.85	27.25	82.41
$[\text{BiMe}_2(\text{CNXyl})(\text{SbF}_6)]$ (11 _{Me})	2.00	30.82	98.25
$[\text{BiMe}_2(\text{CNXyl})_2(\text{SbF}_6)]$ (11' _{Me})	1.84	24.40	119.76
$[\text{BiMe}_2(\text{CNCy})(\text{SbF}_6)]$ (12 _{Me})	1.84	31.00	84.23
$[\text{BiMe}_2(n\text{BuNC})(\text{SbF}_6)]$ (13 _{Me})	1.89	22.75	- ^[a]

[a] Signal could not be detected due to signal broadening. [b] Measured in C₆D₆.

The IR spectroscopic analysis of compounds **9**–**13** revealed a considerable blue-shift of the CN stretching frequency in all cases of mono-adducts ($\Delta\tilde{\nu} = 80\text{--}108 \text{ cm}^{-1}$), indicating ligand to metal σ -donation to be dominant (Table 4).

A closer analysis of all mono-adducts with aliphatic isocyanides reveals that the coordination to the $[\text{BiMe}_2(\text{SbF}_6)]$ complex fragment results in a blue-shift by 93 to 108 cm^{-1} and for CN*t*Bu in specific, in a blue-shift of 106 cm^{-1} . In contrast, coordination of this ligand to the $[\text{BiDipp}_2(\text{SbF}_6)]$ complex fragment shifts the CN stretching frequency by only 80 cm^{-1} . This was tentatively ascribed to weak, but significant electron back-donation from the complex fragment $[\text{BiR}_2(\text{SbF}_6)]$ to the isocyanide, which appears to be more pronounced in the case of R = Dipp. This is supported by DFT calculations and molecular orbital analyses of $[\text{BiR}_2(\text{SbF}_6)]$, which reveal occupied orbitals relevant for back-donation to be higher in energy for R = Dipp (HOMO-1 to HOMO-5) than for R = Me (HOMO, HOMO-1) by up to 1.2 eV (for details see Supp. Inf.). It should be noted that for the Dipp-substituted species, some of these orbitals contain significant contributions by the π -electron cloud of a Dipp ligand that can contribute to back-donation. In the *bis*-isocyanide adduct **12'**_{Me}, an expectedly smaller blue shift of $\Delta\tilde{\nu} = 55 \text{ cm}^{-1}$ is observed.

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Table 4. Wavenumbers of the C≡N vibration in compounds [BiR₂(C≡NR')_n(SbF₆)] as determined by FT-IR spectroscopy in the solid state.

Compound	complex (C≡N) [cm ⁻¹]	free isocyanide (C≡N) [cm ⁻¹]
[BiMe ₂ (CN <i>t</i> Bu)(SbF ₆)] (9 _{Me})	2242	2136
[BiDipp ₂ (CN <i>t</i> Bu)(SbF ₆)] (9 _{Dipp})	2216	2136
[BiMe ₂ (CNAd)(SbF ₆)] (10 _{Me})	2229	2121
[BiMe ₂ (CNXyl)(SbF ₆)] (11 _{Me})	2203	2120
[BiMe ₂ (CNXyl) ₂ (SbF ₆)] (11' _{Me})	2175	2120
[BiMe ₂ (CNCy)(SbF ₆)] (12 _{Me})	2239	2136
[BiMe ₂ (CN <i>n</i> Bu)(SbF ₆)] (13 _{Me})	2243	2150

Single-crystal X-Ray diffraction of four *mono*-adducts (**9**_{Me}, **9**_{Dipp}, **11**_{Me}, **12**_{Me}) and the *bis*-adduct (**11'**_{Me}) were performed and confirm the connectivity suggested based on spectroscopic data. All compounds show a bisphenoidal coordination geometry around the central bismuth atom, with the isocyanide ligand and the [SbF₆]⁻ counter ion (weak Bi⋯F contact) occupying the axial positions. Selected structural parameters of these compounds are summarized in Table 5.

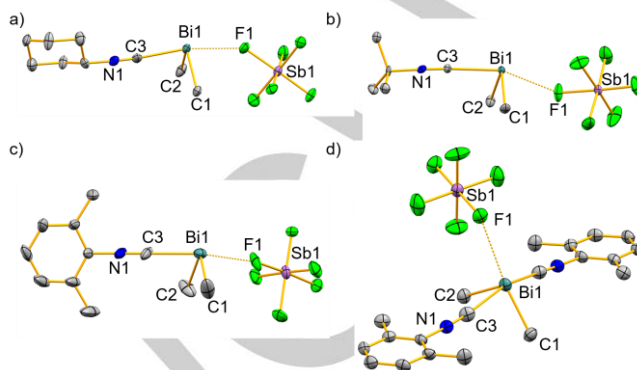
The bismuth–carbon bond lengths of the BiMe₂/BiDipp₂ unit are similar to those in the respective starting material.^[8] In the *mono*-adducts, the dative carbon–bismuth bond is significantly longer, but they are similar dative C→Bi bonds that have been reported for carbene ligands bound to bismuth (2.3545(5)–2.489(6) Å).^[43] The fourth coordination site at the bismuth atom is occupied by one fluorine atom of the (SbF₆)⁻ anion, corresponding to a Bi⋯F interaction based on distance criteria (sum of Bi/F van-der-Waals radii, 3.54 Å).^[30] The Bi⋯F distances reflect the electronic and steric parameters of the [BiR₂(CNR')]⁺ cations, as they are significantly larger for species with bulky ligands (R = Dipp: 3.15(1) Å) and shorter for compounds with more weakly σ-donating isonitriles (R' = Xyl; 2.540(7) Å).

Table 5. Selected bond lengths of the isocyanide adducts and parent compounds.

Compound	Bi–CH ₃ / Dipp [Å]	Bi–C [Å]	Bi⋯F [Å]
[BiMe ₂ (SbF ₆)] (I)	2.215(5) 2.223(5)	-	2.451(3) 2.452(3)
[BiDipp ₂ (SbF ₆)] (4 _{Dipp})	2.257(2) 2.260(2)	-	2.4593(15)
[BiMe ₂ (CN <i>t</i> Bu)(SbF ₆)] (9 _{Me}) ^[a]	2.2345 2.226	2.369	2.725(5)
[BiDipp ₂ (CN <i>t</i> Bu)(SbF ₆)] (9 _{Dipp}) ^[b]	2.27(2) 2.28(2)	2.36(2)	3.15(1)
[BiMe ₂ (CNXyl)(SbF ₆)] (11 _{Me})	2.230(6) 2.198(7)	2.391(7)	2.540(7)
[BiMe ₂ (CNXyl) ₂ (SbF ₆)] (11' _{Me})	2.244(5) 2.229(5)	2.568(5) 2.562(5)	3.264(3)

[BiMe ₂ (CNCy)(SbF ₆)] (12 _{Me})	2.225(8) 2.220(8)	2.382(9)	2.696(5)
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[a] two molecules in the asymmetric unit. [b] crystallized as a non-merohedral twin.

**Figure 7.** Crystal structure of a) **12**_{Me}, b) **9**_{Me}, c) **11**_{Me}, d) **11'**_{Me}, displacement ellipsoids drawn at 50% probability level, H-Atoms omitted for clarity. Selected bond lengths are shown in Table 5.

The coordination of two isocyanide ligands in **11'**_{Me} results in a distorted square pyramidal coordination geometry around bismuth ($\tau_5 = 0.19$) with one methyl group in the apical position, when weak Bi⋯F contacts are taken into account. The bismuth–methyl bond lengths are similar to those of the *mono*-adducts and [BiMe₂(SbF₆)], i.e. the coordination of the isocyanide has very little influence on the length of covalent bismuth–carbon bonds. The dative bismuth–carbon bonds are significantly longer than those in the *mono*-adduct [BiMe₂(XylNC)(SbF₆)] (**11**_{Me}), so the RNC–Bi bond weakening upon introduction of a second isocyanide ligand is clearly reflected by distance criteria in the solid state. The increase in coordination number (as compared to the *mono*-isocyanide-adducts) results in an elongation of the bismuth⋯fluorine distance (3.264(3) Å).

The straightforward Lewis pair formation presented here not only gives access to bismuth-bound isocyanides, but could be extended to generate isolable phosphane and nitrile adducts of **4**_{Dipp} and **I** (Supp. Inf.).

Conclusion

In conclusion, we have synthesized the donor-free bismuth cation [BiR₂(SbF₆)] with bulky aryl ligands (R = Dipp = 2,6-*i*Pr₂-C₆H₃). The Lewis acidity of this compound (R = Dipp) and its methyl analog (R = Me) have been investigated, revealing a remarkable impact of steric bulk: according to Gutmann-Beckett analyses combined with DFT calculations, the steric profile of [BiDipp₂(SbF₆)] boosts its Lewis acidity compared to [BiMe₂(SbF₆)] by protecting one lobe of the vacant p-orbital in the cationic complex fragment [BiDipp₂]⁺, a phenomenon that is most pronounced towards the hard donor OPt₃. The weakly coordinating anion (PF₆)⁻ is shown to be unsuitable for the stabilization of bismuth cations [BiR₂]⁺ due to stepwise fluoride ion abstraction, yielding the unprecedented structural motif [R₂Bi–F–BiR₂]⁺ with a remarkable flexibility of the Bi–F–Bi angle. Reactions of [BiR₂(SbF₆)] with Lewis bases resulted in facile Lewis pair formation. This gave access to the first set of compounds featuring isocyanide ligands CNR' in the coordination sphere of

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softly Lewis acidic bismuth cations, offering prospects for functionalization in subsequent reactions. It is anticipated that these results will facilitate and stimulate the design of Lewis acids and the application of cationic bismuth species as reagents and catalysts in chemical synthesis.

Experimental Section

All Experiments were, if not stated otherwise, conducted under an atmosphere of dry argon using Schlenk- and glovebox techniques. Solvents were degassed and purified according to standard laboratory procedures. NMR spectra were recorded on Bruker Avance spectrometers operating at 400 or 500 MHz with respect to ^1H . ^1H - and ^{13}C -NMR chemical shifts are reported relative to SiMe_4 using the residual signal of the deuterated solvent as a secondary standard. ^{19}F and ^{31}P NMR chemical shifts are reported relative to CFCl_3 and 85% aqueous H_3PO_4 , respectively, as external standards. Infrared spectra were recorded on a Bruker Alpha P spectrometer. Elemental analyses were performed on a vario MICRO cube. Single-crystals suitable for X-ray diffraction were coated with polyisobutylene or perfluorinated polyether oil in a glovebox, transferred to a nylon loop and then transferred to the goniometer of a diffractometer equipped with either a molybdenum ($\lambda = 0.71073 \text{ \AA}$) or copper ($\lambda = 1.54184 \text{ \AA}$) X-Ray tube. The structure was solved using intrinsic phasing methods and expanded using Fourier techniques.^[44] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factors calculations. All hydrogen atoms were assigned to idealized geometric positions.

Deposition Numbers 2232014 (for **4-tol**_{Dipp}), 2232015 (for **11'**_{Me}), 2232016 (for **5**_{Dipp}), 2232017 (for **3**_{Dipp}), 2232018 (for **11**_{Me}), 2232019 (for **8'**_{Dipp}), 2232020 (for **7**_{Dipp}), 2232021 (for **9**_{Me}), 2232022 (for **14**_{Me}), 2232023 (for **6**_{Dipp}), 2232024 (for **9**_{Dipp}), 2232025 (for **12**_{Me}), 2232026 (for **4**_{Dipp}), 2232027 (for **2**_{Dipp}), 2232028 (for **16**_{Dipp}) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

General procedure to determine the acceptor numbers: [$\text{BiMe}_2(\text{SbF}_6)$] (30 mg, 0.06 mmol, 1 eq) was dissolved in dichloromethane (5 mL). One equivalent of the modified Gutmann-Beckett reagents (OPEt_3 , SPMe_3 , SePMe_3) was added as well as a capillary filled with 85% aqueous H_3PO_4 . After addition the yellow solution quickly turned colourless. Without further purification ^1H - (to ensure the formation of a monoadduct) and ^{31}P -NMR spectra were measured. The acceptor numbers were calculated using the ^{31}P -NMR chemical shifts and the following formulas: OPEt_3 : $AN = 2.21 \cdot (\delta_p - 41.0)$; SPMe_3 : $AN = 6.41 \cdot (\delta_p - 29.2)$; SePMe_3 : $AN = 5.71 \cdot (\delta_p - 7.8)$

Attempted preparation of [$\text{BiDipp}_2(\text{PF}_6)$] **1**_{Dipp}: Dipp_2BiBr (200 mg, 0.33 mmol) was dissolved in 6 ml toluene and solid $\text{Ag}[\text{PF}_6]$ (83 mg, 0.33 mmol) was added in small batches under constant stirring. After the removal of precipitates via filtration and of volatiles via reduced pressure, a red solid was obtained. The solid supposedly consists mainly of **1**_{Dipp}. However, upon storage under inert atmosphere or attempted purification decomposition of **1**_{Dipp} to unidentified products, **2**_{Dipp} and Dipp_2BiF was observed. **Yield:** 80 % (278 mg, 0.26 mmol). $^1\text{H NMR}$ (300 MHz, tol-d_6) δ : 1.06 (d, $^3J_{\text{H-H}} = 6.4 \text{ Hz}$, 24H, $\text{o-CCH}(\text{CH}_3)_2$), 2.71 (sept, $^3J_{\text{H-H}} = 6.4 \text{ Hz}$, 4H, $\text{o-CCH}(\text{CH}_3)_2$), 7.42 (t, $^3J_{\text{H-H}} = 7.6 \text{ Hz}$, 2H, $p\text{-CH}$), 7.88 (d, $^3J_{\text{H-H}} = 7.6 \text{ Hz}$, 4H, $m\text{-CH}$) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, tol-d_6) δ = 24.7 (s, $\text{o-CCH}(\text{CH}_3)_2$), 38.1 (s, $\text{o-CCH}(\text{CH}_3)_2$), 130.0 (s, $\text{o-CCH}(\text{CH}_3)_2$), 132.7 (s, $p\text{-CH}$), 157.6 (s, $m\text{-CH}$), (Bi-C, not found) ppm; $^{31}\text{P}\{^1\text{H}\}$ -NMR (122 MHz, tol-d_6) δ = -139.8 (sept, $^1J_{\text{P-F}} = 730.1 \text{ Hz}$, PF_6), $^{19}\text{F NMR}$ (282 MHz tol-d_6) δ = -69.9 (d, $^1J_{\text{P-F}} = 728.6 \text{ Hz}$, PF_6)

[$\text{BiDipp}_2(\text{OPEt}_3)_2(\text{PF}_6)$] (**3**_{Dipp}): BiDipp_2Br (250 mg, 0.41 mmol) and triethylphosphaneoxide (88 mg, 0.82 mmol) were dissolved in 8 ml THF and AgPF_6 (104 mg, 0.41 mmol) in THF (6 mL) was added dropwise at

room temperature. After stirring for 90 minutes, precipitates were filtered off and all volatiles were removed under reduced pressure. The remaining colourless solid was recrystallized from a mixture of toluene and pentane and **3**_{Dipp} was obtained in the form of colorless crystals. **Yield:** 71 % (241 mg, 0.29 mmol). $^1\text{H-NMR}$ (300 MHz, C_6D_6) δ = 0.84 (dq, $^3J_{\text{H-H}} = 7.7 \text{ Hz}$, $^3J_{\text{P-H}} = 11.7 \text{ Hz}$, 18H, PCH_2CH_3), 1.09 (d, $^3J_{\text{H-H}} = 6.4 \text{ Hz}$, 24H, $\text{o-CCH}(\text{CH}_3)_2$), 1.58 (dq, $^3J_{\text{H-H}} = 7.7 \text{ Hz}$, $^2J_{\text{P-H}} = 11.7 \text{ Hz}$, 12H, PCl_2CH_3), 3.14 (sept, $^3J_{\text{H-H}} = 6.4 \text{ Hz}$, 4H, $\text{o-CCH}(\text{CH}_3)_2$), 7.33 (t, $^3J_{\text{H-H}} = 7.6 \text{ Hz}$, 2H, $p\text{-CH}$), 7.60 (d, $^3J_{\text{H-H}} = 7.6 \text{ Hz}$, 4H, $m\text{-CH}$) ppm; $^{13}\text{C}\{^1\text{H}\}$ -NMR (75 MHz, C_6D_6) δ = 5.6 (d, $^2J_{\text{P-C}} = 5.1 \text{ Hz}$, PCH_2CH_3), 19.0 (d, $^1J_{\text{P-C}} = 65.6 \text{ Hz}$, PCH_2CH_3), 25.0 (s, $\text{o-CCH}(\text{CH}_3)_2$), 37.5 (s, 4C, $\text{o-CCH}(\text{CH}_3)_2$), 129.4 (s, $\text{o-CCH}(\text{CH}_3)_2$), 129.9 (s, $p\text{-CH}$), 157.2 (s, $m\text{-CH}$), 206.0 (s, Bi-C) ppm; $^{31}\text{P}\{^1\text{H}\}$ -NMR (122 MHz, C_6D_6) δ = -142.4 (sept, $^1J_{\text{P-F}} = 712.1 \text{ Hz}$, PF_6), 66.3 (s, OPEt_3); **Elemental analysis:** calculated for $[\text{C}_{36}\text{H}_{64}\text{BiF}_6\text{O}_2\text{P}_3]$ (944.80 g/mol): C, 45.77; H, 6.83; found: C, 45.84; H, 6.90; **IR** (cm^{-1}) $\bar{\nu}$ = 3038.63 (w), 2965.56 (w), 2946.82 (w), 2923.95 (w), 2882.98 (w), 2865.05 (w), 1569.02 (w), 1457.91 (m), 1446.08 (w), 1409.99 (w), 1381.18 (w), 1359.59 (w), 1270.45 (w), 1237.22 (w), 1175.07 (w), 1146.71 (w), 1089.96 (w), 1069.81 (s), 1044.60 (s), 1033.49 (s), 984.84 (m), 921.66 (s), 872.89 (w), 794.35 (w), 780.44 (w), 725.66 (w), 555.56 (s), 447.72 (m); **HR-MS:** Cl^+ m/z 531.2461 [Dipp_2Bi^+]; calcd 531.2464; m/z 135.0966 [Et_3PO^+]; calcd 135.0939

[BiDipp_2][SbF_6] (**4**_{Dipp}): BiDipp_2Br (400 mg, 0.64 mmol) was dissolved in toluene (50 mL) and solid $\text{Ag}[\text{SbF}_6]$ (220 mg, 0.64 mmol) was added in small batches under constant stirring, whereupon the orange solution turned dark red. After stirring for 90 minutes, the solution was filtered and concentrated under reduced pressure. Storage at $-32 \text{ }^\circ\text{C}$ for two days yielded dark red crystals of **4-tol**_{Dipp}. **Yield:** 59 % (330 mg, 0.38 mmol). Crystalline **4**_{Dipp} was obtained by recrystallization from α,α -trifluorotoluene. $^1\text{H NMR}$ (500 MHz, C_6D_6) δ : 1.06 (d, $^3J_{\text{H-H}} = 6.4 \text{ Hz}$, 24H, $\text{o-CCH}(\text{CH}_3)_2$), 2.53 (sept, $^3J_{\text{H-H}} = 6.4 \text{ Hz}$, 4H, $\text{o-CCH}(\text{CH}_3)_2$), 7.51 (t, $^3J_{\text{H-H}} = 7.6 \text{ Hz}$, 2H, $p\text{-CH}$), 8.08 (d, $^3J_{\text{H-H}} = 7.6 \text{ Hz}$, 4H, $m\text{-CH}$) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, C_6D_6) δ : 23.9 (s, $\text{o-CCH}(\text{CH}_3)_2$), 38.8 (s, $\text{o-CCH}(\text{CH}_3)_2$), 130.3 (s, $\text{o-CCH}(\text{CH}_3)_2$), 134.3 (s, $p\text{-CH}$), 158.0 (s, $m\text{-CH}$), 238.1 (s, Bi-C) ppm; $^{19}\text{F NMR}$ (470 MHz) δ : -120.8 (br s, SbF_6) ppm; $^1\text{H NMR}$ (500 MHz, CD_2Cl_2) δ : 1.21 (d, $^3J_{\text{H-H}} = 6.4 \text{ Hz}$, 24H, $\text{o-CCH}(\text{CH}_3)_2$), 2.65 (sept, $^3J_{\text{H-H}} = 6.4 \text{ Hz}$, 4H, $\text{o-CCH}(\text{CH}_3)_2$), 8.00 (t, $^3J_{\text{H-H}} = 7.7 \text{ Hz}$, 2H, $p\text{-CH}$), 8.61 (d, $^3J_{\text{H-H}} = 7.7 \text{ Hz}$, 4H, $m\text{-CH}$) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CD_2Cl_2) δ : 24.0 (s, $\text{o-CCH}(\text{CH}_3)_2$), 39.6 (s, $\text{o-CCH}(\text{CH}_3)_2$), 131.0 (s, $\text{o-CCH}(\text{CH}_3)_2$), 135.3 (s, $p\text{-CH}$), 158.5 (s, $m\text{-CH}$), 237.6 (s, Bi-C) ppm; $^{19}\text{F NMR}$ (470 MHz) δ : -123.0 (br s, SbF_6) ppm; **Elemental analysis** calculated for $\text{C}_{24}\text{H}_{34}\text{BiF}_6\text{Sb}$ (767.27 g/mol): C, 37.57; H, 4.47; found: C, 37.28; H, 4.50; **IR** (cm^{-1}): 3046 (w), 2960 (m), 2927 (w), 2867 (w), 1570 (w), 1459 (m), 1447 (m), 1415 (w), 1384 (w), 1364 (w), 1343 (w), 1241 (w), 1177 (w), 1147 (w), 1046 (w), 1001 (w), 931 (s), 797 (s), 726 (s), 623 (s), 490 (w).

[$(\text{BiDipp}_2)_2\text{F}(\text{SbF}_6)$] (**5**_{Dipp}): Compound **4-tol** (40 mg, 0.05 mmol) was suspended in toluene (2 mL) and BiDipp_2F (26 mg, 0.05 mmol) in toluene (2 mL) was added, leading to the precipitation of an orange crystalline solid. After stirring for two hours and complete consumption of the dark red **4-tol**, liquids were removed by decanting with a syringe. The remaining solid was washed two times with pentane (5 mL) and dried under reduced pressure. **Yield:** 72% (44 mg, 0.03 mmol). $^1\text{H NMR}$ (500 MHz, CD_2Cl_2) δ = 1.08 (d, $^3J_{\text{H-H}} = 6.4 \text{ Hz}$, $\text{o-CCH}(\text{CH}_3)_2$) ppm, 2.72 (t, $^3J_{\text{H-H}} = 6.6 \text{ Hz}$, 4H, $\text{o-CCH}(\text{CH}_3)_2$), 7.73 (t, $^3J_{\text{H-H}} = 7.6 \text{ Hz}$, 2H, $p\text{-CH}$), 8.10 (d, $^3J_{\text{H-H}} = 7.6 \text{ Hz}$, 4H, $m\text{-CH}$) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CD_2Cl_2) δ = 24.4 (s, $\text{o-CCH}(\text{CH}_3)_2$), 38.0 (s, $\text{o-CCH}(\text{CH}_3)_2$), 130.6 (s, $\text{o-CCH}(\text{CH}_3)_2$), 132.6 (s, $p\text{-CH}$), 157.2 (s, $m\text{-CH}$), 215.8 (Bi-C, found via HMBC) ppm; $^{19}\text{F NMR}$ (282 MHz, CD_2Cl_2) δ = -122.3 (br s, SbF_6), -216.1 (br s, Bi-F) ppm; **Elemental analysis** calculated for $[\text{C}_{45}\text{H}_{68}\text{Bi}_2\text{F}_7\text{Sb}_1]$ (1317.77 g/mol): C 43.75; H 5.20; found: C 43.94; H 5.16; **IR** (cm^{-1}): 3046 (w), 2960 (m), 2927 (w), 2867 (w), 1570 (w), 1459 (m), 1447 (m), 1415 (w), 1384 (w), 1364 (w), 1343 (w), 1241 (w), 1177 (w), 1147 (w), 1046 (w), 1001 (w), 931 (w), 797 (m), 726 (s), 623 (s), 490 (w),

General procedure for the preparation of [$\text{BiDipp}_2(\text{EPMe}_3)$][SbF_6]: Compound **4-tol** (50 mg, 0.06 mmol) and EPMe_3 (E = S, Se, 0.06 mmol) were dissolved in DCM (3 mL) at room temperature. The yellow solution

was layered with *n*-pentane and stored at $-32\text{ }^{\circ}\text{C}$. After two days, yellow crystals of the products **6**_{Dipp} and **7**_{Dipp} were obtained.

[BiDipp₂(SPMe₃)] [SbF₆] (6**_{Dipp}):** Yield: 92% (47 mg, 0.05 mmol). **¹H-NMR** (500 MHz, CD₂Cl₂) $\delta = 1.11$ (d, $^3J_{\text{H-H}} = 6.6$ Hz, 24H, *o*-CCH(CH₃)₂), 2.15 (d, $^2J_{\text{P-H}} = 13.3$ Hz, 9H, SP(CH₃)₃), 2.92 (sept, $^3J_{\text{H-H}} = 6.6$ Hz, 4H, *o*-CCH(CH₃)₂), 7.51 (t, $^3J_{\text{H-H}} = 7.6$ Hz, 2H, *p*-CH), 7.69 (d, $^3J_{\text{H-H}} = 7.6$ Hz, 4H, *m*-CH) ppm; **¹³C{¹H}-NMR** (125 MHz, CD₂Cl₂) $\delta = 19.2$ (d, $^1J_{\text{P-C}} = 54.2$ Hz, SP(CH₃)₃), 24.7 (s, *o*-CCH(CH₃)₂), 40.6 (s, *o*-CCH(CH₃)₂), 129.4 (s, *o*-CCH(CH₃)₂), 130.4 (s, *p*-CH), 156.3 (s, *m*-CH), 183.1 (s, Bi-C) ppm; **³¹P-NMR** (202 MHz, CD₂Cl₂) $\delta = 43.9$ (s, SPMe₃) ppm; **Elemental analysis** calculated for [C₂₇H₄₃BiF₆P₁S₁Sb₁] (875.40 g/mol): C 37.05; H 4.95; S 3.66; found: C 36.67; H 5.13; S 3.54; **IR** (cm⁻¹): 3051 (w), 3008 (m), 2960 (w), 2922 (w), 2868 (w), 1569 (w), 1462 (w), 1442 (w), 1410 (w), 1384 (w), 1363 (w), 1342 (w), 1317 (w), 1300 (w), 1235 (w), 1181 (w), 1148 (w), 1048 (w), 1000 (w), 948 (s), 858 (w), 807 (m), 758 (w), 733 (w), 691 (w), 653 (s), 521 (w).

[BiDipp₂(SePMe₃)] [SbF₆] (7**_{Dipp}):** Yield: 59% (32 mg, 0.03 mmol). **¹H-NMR** (500 MHz, CD₂Cl₂) $\delta = 1.10$ (d, $^3J_{\text{H-H}} = 6.6$ Hz, 24H, *o*-CCH(CH₃)₂), 2.32 (d, $^2J_{\text{P-H}} = 13.5$ Hz, 9H, SeP(CH₃)₃), 2.95 (sept, $^3J_{\text{H-H}} = 6.6$ Hz, 4H, *o*-CCH(CH₃)₂), 7.48 (t, $^3J_{\text{H-H}} = 7.6$ Hz, 2H, *p*-CH), 7.65 (d, $^3J_{\text{H-H}} = 7.6$ Hz, 4H, *m*-CH) ppm; **¹³C{¹H}-NMR** (125 MHz, CD₂Cl₂) $\delta = 18.8$ (d, $^1J_{\text{P-C}} = 47.9$ Hz, SeP(CH₃)₃), 24.8 (s, *o*-CCH(CH₃)₂), 41.4 (s, *o*-CCH(CH₃)₂), 128.9 (s, *o*-CCH(CH₃)₂), 130.3 (s, *p*-CH), 156.2 (s, *m*-CH), 178.2 (s, Bi-C) ppm; **³¹P-NMR** (202 MHz, CD₂Cl₂) $\delta = 22.13$ (s, $^1J_{\text{P-Se}} = 485.1$ Hz, SePMe₃) ppm; **Elemental analysis** calculated for [C₂₇H₄₃BiF₆P₁Sb₁Se₁] (922.29 g/mol): C 35.16; H 4.70; found: C 35.17; H 4.79; **IR** (cm⁻¹): 2960 (m), 2920 (w), 2885 (w), 2867 (w), 1583 (w), 1569 (w), 1462 (w), 1441 (w), 1410 (w), 1383 (w), 1363 (w), 1297 (w), 1260 (w), 1235 (m), 1180 (w), 1150 (w), 1100 (w), 1048 (w), 1019 (w), 1000 (w), 947 (s), 857 (w), 806 (s), 758 (w), 733 (w), 652 (s), 641 (s), 503 (w), 494 (w).

[BiDipp₂(OPe₃)₂(SbF₆)] (8**_{Dipp}):** Dipp₂BiBr (162 mg, 0.26 mmol) and triethylphosphaneoxide (70 mg, 0.52 mmol) were dissolved in THF (8 mL). A solution of AgSbF₆ (90 mg, 0.26 mmol) in THF (6 mL) was added dropwise at room temperature. After stirring for 90 minutes, volatiles were removed. Toluene (20 mL) was added, and the suspension was filtered. The filtrate was concentrated and stored at $-32\text{ }^{\circ}\text{C}$ to give colorless crystals after 2 d, which were isolated by decantation and dried *in vacuo*. **Yield** 71% (196 mg, 0.19 mmol). **¹H-NMR** (300 MHz, C₆D₆) $\delta = 0.80$ (dt, $^3J_{\text{H-H}} = 7.7$ Hz, $^3J_{\text{P-H}} = 17.2$ Hz, 18H, PCH₂CH₃), 1.08 (d, $^3J_{\text{H-H}} = 6.4$ Hz, 24H, *o*-CCH(CH₃)₂), 1.49 (dq, $^3J_{\text{H-H}} = 7.6$ Hz, $^2J_{\text{P-H}} = 11.7$ Hz, 12H, PCH₂CH₃), 3.11 (sept, $^3J_{\text{H-H}} = 6.5$ Hz, 4H, *o*-CCH(CH₃)₂), 7.33 (t, $^3J_{\text{H-H}} = 7.6$ Hz, 2H, *m*-CH), 7.59 (d, $^3J_{\text{H-H}} = 7.6$ Hz, 4H, *p*-CH) ppm; **¹³C{¹H}-NMR** (125 MHz, C₆D₆) $\delta = 5.6$ (d, $^3J_{\text{P-C}} = 4.0$ Hz, PCH₂CH₃), 19.0 (d, $^2J_{\text{P-C}} = 65.6$ Hz, PCH₂CH₃), 25.0 (br s, *o*-CCH(CH₃)₂), 37.6 (s, *o*-CCH(CH₃)₂), 129.5 (s, *o*-CH), 129.9 (s, *p*-CH), 157.0 (s, *m*-CH), 205.6 (s, Bi-C), ppm; **³¹P{¹H}-NMR** (101 MHz, C₆D₆) $\delta = 65.3$ (s, 1P, OPe₃) ppm; **¹H-NMR** (500 MHz, CD₂Cl₂) $\delta = 1.09$ (d, $^3J_{\text{H-H}} = 6.4$ Hz, 24H, *o*-CCH(CH₃)₂), 1.11 (dt, $^3J_{\text{H-H}} = 7.7$ Hz, $^3J_{\text{P-H}} = 17.1$ Hz, 18H, PCH₂CH₃), 1.80 (dq, $^3J_{\text{H-H}} = 7.7$ Hz, $^2J_{\text{P-H}} = 11.6$ Hz, 12H, PCH₂CH₃), 2.96 (sept, $^3J_{\text{H-H}} = 6.4$ Hz, 4H, *o*-CCH(CH₃)₂), 7.55 (t, $^3J_{\text{H-H}} = 7.6$ Hz, 2H, *p*-CH), 7.79 (d, $^3J_{\text{H-H}} = 7.6$ Hz, 4H, *m*-CH) ppm; **¹³C{¹H}-NMR** (125 MHz, CD₂Cl₂) $\delta = 5.7$ (d, $^2J_{\text{P-C}} = 4.8$ Hz, PCH₂CH₃), 19.5 (d, $^1J_{\text{P-C}} = 65.6$ Hz, PCH₂CH₃), 24.6 (s, *o*-CCH(CH₃)₂), 37.4 (s, *o*-CCH(CH₃)₂), 130.1 (s, *o*-CH), 130.5 (s, *p*-CH), 156.6 (s, *m*-CH), 201.5 (s, Bi-C) ppm; **³¹P{¹H}-NMR** (202 MHz, CD₂Cl₂) $\delta = 65.2$ (s, 1P, OPe₃) ppm; **Elemental analysis** calculated for [C₃₆H₆₄BiF₆O₂P₂Sb₁] (1035.58 g/mol): C 41.75; H 6.23; found: C 41.77; H 6.44; **IR** (cm⁻¹): 3039 (w), 2964 (m), 2947 (w), 2924 (w), 2883 (w), 2865 (w), 1569 (w), 1458 (m), 1448 (w), 1410 (w), 1382 (w), 1360 (w), 1270 (w), 1237 (w), 1093 (m), 1070 (m), 1045 (m), 1032 (m), 985 (m), 928 (w), 796 (w), 778 (w), 768 (w), 726 (m), 650 (s), 446 (m), 406 (w).

[BiDipp₂(CNtBu)(SbF₆)] (9**_{Dipp}):** Compound **4-tol**_{Dipp} (30 mg, 35 μmol) is dissolved in 2 mL of toluene and CNtBu (2.9 mg, 35 μmol) in 0.2 mL of toluene is slowly added. Upon addition, the solution turns orange and some precipitating solids are removed *via* decanting the toluene solution. After evaporation of volatiles, **9**_{Dipp} is obtained as off white solid. **Yield:**

57% (17 mg, 20 μmol). **¹H-NMR** (500 MHz, C₆D₆) $\delta = 0.98$ (d, $^3J_{\text{H-H}} = 6.6$ Hz, 24H, *o*-CCH(CH₃)₂), 0.98 (s, 9H, C(CH₃)₃), 2.70 (sept, $^3J_{\text{H-H}} = 6.6$ Hz, 4H, *o*-CCH(CH₃)₂), 7.22 (t, $^3J_{\text{H-H}} = 7.6$ Hz, 2H, *p*-CH), 7.46 (d, $^3J_{\text{H-H}} = 7.6$ Hz, 4H, *m*-CH) ppm; **¹³C{¹H}-NMR** (125 MHz, C₆D₆) $\delta = 24.3$ (s, *o*-CCH(CH₃)₂), 28.9 (s, C(CH₃)₃), 60.8 (s, C(CH₃)₃, found *via* HMBC), 41.0 (s, *o*-CCH(CH₃)₂), 124.2 (s, *o*-CCH(CH₃)₂), 130.4 (s, *p*-CH), 156.3 (s, *m*-CH), 183.1 (s, Bi-C) ppm. **Elemental analysis** calculated for [C₂₉H₄₃BiF₆N₁Sb₁] (850.40 g/mol): C 40.96; H 5.10; N 1.65; found: C 39.77; H 4.80; N 2.36; **IR** (cm⁻¹): 3054 (w), 3043 (m), 2966 (w), 2929 (w), 2905 (w), 2866 (w), 2216 (w), 1570 (w), 1460 (w), 1446 (w), 1412 (w), 1376 (w), 1364 (w), 1342 (w), 1236 (m), 1183 (m), 1147 (w), 1046 (w), 1001 (w), 984 (w), 930 (w), 826 (w), 806 (w), 797 (w), 729 (w), 685 (w), 651 (s), 563 (w), 526 (w), 503 (w), 419 (w).

General procedure for the synthesis of [BiMe₂(SbF₆)] adducts: [BiMe₂(SbF₆)] was dissolved in benzene (typically 8 mL). A solution of the required isocyanide or phosphane in benzene (typically 4 mL) was added. The end of the reaction was determined by either a change in color or formation of a precipitate. Afterwards all volatiles were removed *in vacuo* and the remaining solid washed with pentane. Drying at 10^{-3} mbar yields the respective product. If there were any deviations from this procedure, this is noted below for the individual compounds.

[BiMe₂(CNtBu)(SbF₆)] (9**_{Me}):** [BiMe₂(SbF₆): 50 mg, 0.11 mmol, 1 eq.; *tert*-Butylisocyanide: 9 mg, 12 μL , 0.11 mmol, 1 eq. The synthesis was conducted in toluene, during the reaction the solution turned colorless. The crude product was recrystallized from dichloromethane/pentane. **Yield:** 45 mg (0.08 mmol, 72%) of an orange solid. **¹H-NMR** (500 MHz, CD₂Cl₂): $\delta = 1.58$ (s, 9H, CNC(CH₃)₃), 1.85 (s, 6H, Bi-CH₃), ppm. **¹³C{¹H}-NMR** (125 MHz, CD₂Cl₂): $\delta = 27.3$ (s, br, Bi-CH₃), 30.01 (s, CNC(CH₃)₃), 61.37 (s, br, CNC(CH₃)₃), 82.52 (s, br, CNC(CH₃)₃) ppm. **Elemental analysis:** calculated for [C₇H₁₅NBiSbF₆] (557.93 g/mol): C 15.07, H 2.71, N 2.51; found: C 14.89, H 2.83, N 2.42. **IR** (cm⁻¹): $\bar{\nu} = 2996$ (w, C-H), 2937 (w, C-H), 2242 (w, CN).

[BiMe₂(CNAd)(SbF₆)] (10**_{Me}):** [BiMe₂(SbF₆): 50 mg, 0.11 mmol, 1 eq.; Adamantylisocyanide: 20 mg, 0.12 mmol, 1.1 eq. During the reaction a colorless precipitate was formed. The crude product was dissolved in dichloromethane (2 mL) and layered with pentane (8 mL). After 18 h the liquid phase was removed and the remaining solid dried *in vacuo*. **Yield:** 58 mg (0.09 mmol, 87%) of a colorless solid. **¹H-NMR** (400 MHz, CD₂Cl₂): $\delta = 1.69$ (br d, $^2J_{\text{H-H}} = 13.2$ Hz, 3H, H-6^a, H-8^b, H-10^b), 1.74 (br d, $^2J_{\text{H-H}} = 13.2$ Hz, 3H, H-6^a, H-8^a, H-10^a), 1.85 (s, 6H, Bi-CH₃), 2.13 (d, $^3J_{\text{H-H}} = 2.8$ Hz, 6H, H-2, H-3, H-4), 2.19 (br s, 3H, H-5, H-7, H-9) ppm. **¹³C{¹H}-NMR** (101 MHz, CD₂Cl₂): $\delta = 27.5$ (br s, CH₃, Bi-CH₃), 29.1 (s, CH₂, C-6, C-8, C-10), 35.2 (s, CH, C-5, C-7, C-9), 42.7 (s, CH₂, C-2, C-3, C-4), 60.8 (s, C, C-1), 82.43 (br s, C, isocyanide CNR) ppm. **¹⁹F-NMR** (377 MHz, CD₂Cl₂): $\delta = -124.4$ (br s, SbF₆) ppm. **Elemental analysis:** calculated for [C₁₃H₂₁NBiSbF₆] (636.05 g/mol): C 24.55, H 3.33, N 2.20; found: C 24.31, H 3.12, N 2.38. **IR** (cm⁻¹): $\bar{\nu} = 2921$ (s, C-H), 2860 (s, C-H), 2229 (w, CN).

[BiMe₂(CNXyl)(SbF₆)] (11**_{Me}):** [BiMe₂(SbF₆): 100 mg, 0.21 mmol, 1 eq.; 2,6-Dimethylphenylisocyanide: 28 mg, 0.21 mmol, 1 eq. During the reaction a light red precipitate is formed. **Yield:** 91 mg (0.15 mmol, 71%) of a red solid. **¹H-NMR** (400 MHz, CD₂Cl₂): $\delta = 2.01$ (s, 6H, Bi-CH₃), 2.46 (s, 6H, *ortho*-phenyl CH₃), 7.24 (d, $^3J_{\text{H-H}} = 7.6$ Hz, 2H, *meta*-phenyl CH), 7.42 (t, $^3J_{\text{H-H}} = 7.8$ Hz, 1H, *para*-phenyl CH) ppm. **¹³C{¹H}-NMR** (101 MHz, CD₂Cl₂): $\delta = 18.8$ (s, CH₃, *ortho*-phenyl CH₃), 31.0 (br s, Bi-CH₃), 98.25 (s, br, C, isocyanide CNR), 123.4 (br s, C, *ipso*-phenyl C), 129.7 (s, CH, *meta*-phenyl CH), 132.7 (s, CH, *para*-phenyl CH), 137.4 (s, C, *ortho*-phenyl C) ppm. **Elemental analysis:** calculated for [C₁₁H₁₅NBiSbF₆] (605.98 g/mol): C 21.80, H 2.50, N 2.31; found: C 21.42, H 2.22, N 2.41. **IR** (cm⁻¹): $\bar{\nu} = 2928$ (w, C-H), 2203 (w, CN), 1590 (m, aromatic ring).

[BiMe₂(CNXyl)₂(SbF₆)] (11**_{Me}):** [BiMe₂(SbF₆): 50 mg, 0.11 mmol, 1 eq.; 2,6-Dimethylphenylisocyanide: 28 mg, 0.21 mmol, 2 eq. The synthesis was conducted in dichloromethane. During the reaction the solution turned dark red. **Yield:** 70 mg (0.09 mmol, 90%) of a red-violet solid. **¹H-NMR** (400 MHz, CD₂Cl₂): $\delta = 1.84$ (s, 6H, Bi-CH₃), 2.44 (s, 12H, *ortho*-phenyl

CH₃), 7.20 (d, ³J_{H-H} = 7.6 Hz, 4H, *meta*-phenyl CH), 7.32 (t, ³J_{H-H} = 7.7 Hz, 2H, *para*-phenyl CH) ppm. ¹³C{¹H}-NMR (101 MHz, CD₂Cl₂): δ = 18.9 (s, CH₃, *ortho*-phenyl CH₃), 24.4 (s, br, CH₃, Bi-CH₃), 119.76 (br s, C, isocyanide CNR), 125.0 (br s, C, *ipso*-phenyl C), 128.6 (s, CH, *meta*-phenyl CH), 131.1 (s, CH, *para*-phenyl CH), 136.4 (s, C, *ortho*-phenyl C) ppm. **Elemental analysis:** calculated for [C₂₀H₂₄N₂BiSbF₆] (737.16 g/mol): C 32.59, H 3.28, N 3.80; found: C 32.69, H 3.42, N 3.78. IR (cm⁻¹): $\bar{\nu}$ = 2924 (w, C-H), 2174 (m, CN), 1587 (w, aromatic ring).

[BiMe₂(CNCy)(SbF₆)] (12_{Me}): [BiMe₂(SbF₆): 50 mg, 0.11 mmol, 1 eq.; Cyclohexylisocyanide: 11 mg, 13 μL, 0.11 mmol, 1 eq. During the reaction the solution turned orange. **Yield:** 32 mg (0.05 mmol, 52%) of an orange solid. ¹H-NMR (400 MHz, CD₂Cl₂): δ = 1.37–1.58 (br m, 4H, 3,5-Cy CH₂), 1.63–1.82 (br m, 4H, 2,6-Cy CH₂), 1.84 (s, 6H, Bi-CH₃), 1.96–2.07 (br m, 2H, 4-Cy CH₂), 4.10 (sept, ³J_{H-H} = 4.1 Hz, 1H, 1-Cy CH) ppm. ¹³C{¹H}-NMR (101 MHz, CD₂Cl₂): δ = 23.1 (s, CH₃, 2,6-Cy CH₂), 24.8 (s, CH₂, 3,5-Cy CH₂), 31.1 (s, br, CH₃, Bi-CH₃), 32.0 (s, CH₂, 4-Cy CH₂), 56.2 (s, CH, 1-Cy CH), 84.2 (s, br, C, Isocyanide CNR) ppm. ¹⁹F-NMR (377 MHz, CD₂Cl₂): δ = -123.2 (br s, SbF₆) ppm. **Elemental analysis:** calculated for [C₉H₁₇NBiSbF₆] (583.97 g/mol): C 18.51, H 2.93, N 2.40; found: C 18.64, H 3.08, N 2.43. IR (cm⁻¹): $\bar{\nu}$ = 2938 (s, C-H), 2861 (s, C-H), 2239 (w, CN).

[BiMe₂(CN n Bu)(SbF₆)] (13_{Me}): [BiMe₂(SbF₆): 40 mg, 0.08 mmol, 1 eq.; *n*-Butylisocyanide: 7 mg, 9 μL, 0.08 mmol, 1 eq. The synthesis was conducted at 0 °C. **Yield:** 35 mg (0.06 mmol, 74%) of a dark red oil. ¹H-NMR (400 MHz, CD₂Cl₂): δ = 0.98 (dd, ³J_{H-H} = 7.4 Hz, 3H, H-4), 1.42–1.52 (sext, ³J_{H-H} = 7.5 Hz, 2H, H-3), 1.77–1.84 (quint, ³J_{H-H} = 7.2 Hz, 2H, H-2), 1.89 (s, 6 H, Bi-CH₃), 3.86 (dd, ³J_{H-H} = 6.6 Hz, 2H, H-1) ppm. ¹³C{¹H}-NMR (126 MHz, CD₂Cl₂): δ = 13.2 (s, CH₃, C-4), 19.8 (s, CH₂, C-3), 24.1 (s, CH₃, Bi-CH₃), 30.5 (s, CH₂, C-2), 44.11 (br s, CH₂, C-1) ppm [1]; **Elemental analysis:** calculated for [C₇H₁₅NBiSbF₆] (557.93 g/mol): C 15.07, H 2.71, N 2.51; found: C 15.35, H 2.844, N 2.57. IR (cm⁻¹): $\bar{\nu}$ = 2965 (s, C-H), 2879 (s, C-H), 2243 (w, CN). [1] The Signal corresponding to the isocyanide-carbon could not be detected due to signal broadening.

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Keywords: bismuth • cationic species • Lewis acidity • Lewis pair formation

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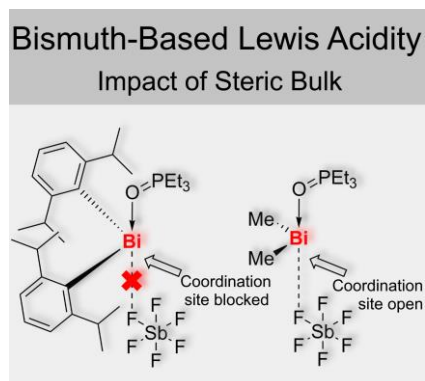
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Entry for the Table of Contents



The bismuth cation $[\text{BiDipp}_2]^+$, stabilized by an $[\text{SbF}_6]^-$ counteranion, has been synthesized, isolated and fully characterized (Dipp = 2,6-*i*-Pr₂-C₆H₃). A detailed comparison with $[\text{BiMe}_2(\text{SbF}_6)]$ highlights the impact of steric bulk on bismuth-based Lewis acidity. Differences in their Lewis acidity have been rationalized and their reactivity towards $[\text{PF}_6]^-$ as well as Lewis pair formations have been studied.

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1. Experimental

1.1 (Modified) Guttmann-Beckett Method

To quantify the Lewis acidity of [BiDipp₂(SbF₆)] (**4**_{Dipp}) and [BiMe₂(SbF₆)] (**I**) the traditional Guttmann-Beckett Method^[1] and modified versions, using SPMe₃ and SePMe₃ as donors, were used.^[2] Acceptor numbers (ANs) are derived from the ³¹P NMR chemical shifts of solutions containing the Lewis acid and the Lewis base EPR₃ (OPEt₃, SPMe₃, SePMe₃). The ANs are derived using the following formulae:

$$\text{OPEt}_3: \text{AN} = 2.21 \cdot (\delta_P - 41.0)$$

$$\text{SPMe}_3: \text{AN} = 6.41 \cdot (\delta_P - 29.2)$$

$$\text{SePMe}_3: \text{AN} = 2.21 \cdot (\delta_P - 7.8)$$

For the NMR spectroscopic experiments, solutions with 1:1 and 1:2 stoichiometries of **4**_{Dipp} or **I** and EPR₃ in CD₂Cl₂ were prepared. Three compounds, namely [BiDipp₂(OPEt₃)₂][SbF₆] (**8'**_{Dipp}), [BiDipp₂(SPMe₃)₂(SbF₆)] (**6**_{Dipp}) and [BiDipp₂(SePMe₃)₂(SbF₆)] (**7**_{Dipp}) were isolated and NMR experiments were performed subsequently. All other sample solutions were prepared *in situ* using the following protocols.

General protocol for the preparation of [BiMe₂(EPR₃)_x(SbF₆)] (x = 1, 2): Compound **I** (1 eq.) was dissolved in dichloromethane (5 mL). Subsequently 1 or 2 equivalents of the modified Guttmann-Beckett reagents (OPEt₃, SPMe₃, SePMe₃) were added as well as a capillary filled with 85% aqueous H₃PO₄. After addition the yellow solution quickly turned colourless. Without further purification ¹H- and ³¹P NMR spectra were measured.

[BiMe₂(SPMe₃)₂(SbF₆)] (6**_{Me}):** ¹H NMR (400 MHz, CD₂Cl₂): δ = 1.71 (s, 6H, Bi-CH₃), 2.06 (d, 9H, ²J_{P-H} = 13.4 Hz, P(CH₃)₃) ppm; ³¹P NMR (101 MHz, CD₂Cl₂): δ = 43.9 (s, SPMe₃) ppm.

[BiMe₂(SPMe₃)₂(SbF₆)] (6'**_{Me}):** ¹H NMR (400 MHz, CD₂Cl₂): δ = 1.81 (s, 6H, Bi-CH₃), 1.93 (d, 18H, ²J_{P-H} = 13.3 Hz, P(CH₃)₃) ppm; ³¹P NMR (101 MHz, CD₂Cl₂): δ = 37.4 (s, SPMe₃) ppm.

[BiMe₂(SePMe₃)₂(SbF₆)] (7**_{Me}):** ¹H NMR (400 MHz, CD₂Cl₂): δ = 2.01 (s, 6H, Bi-CH₃), 2.21 (d, 9H, ²J_{P-H} = 13.5 Hz, P(CH₃)₃) ppm; ³¹P NMR (101 MHz, CD₂Cl₂): δ = 21.1 (s, ¹J_{P-Se} = 495.3 Hz, SePMe₃) ppm.

[BiMe₂(SePMe₃)₂(SbF₆)] (7'**_{Me}):** ¹H NMR (400 MHz, CD₂Cl₂): δ = 1.85 (s, 6H, Bi-CH₃), 2.09 (d, 9H, ²J_{P-H} = 13.5 Hz, P(CH₃)₃) ppm; ³¹P NMR (101 MHz, CD₂Cl₂): δ = 15.9 (s, ¹J_{P-Se} = 573.2 Hz, SePMe₃) ppm.

[BiMe₂(OPEt₃)₂(SbF₆)] (8**_{Me}):** ¹H NMR (400 MHz, CD₂Cl₂): δ = 1.05-1.24 (m, 9H, PCH₂CH₃), 1.71 (s, 6H, Bi-CH₃), 1.75-1.91 (m, 6H, PCH₂CH₃) ppm; ³¹P NMR (101 MHz, CD₂Cl₂): δ = 71.4 (s, OPEt₃) ppm.

[BiMe₂(OPEt₃)₂(SbF₆)] (8'**_{Me}):** ¹H NMR (400 MHz, CD₂Cl₂): δ = 1.12 (dt, 18H, ³J_{H-H} = 6.7 Hz, ³J_{P-H} = 17.2 Hz PCH₂CH₃), 1.43 (s, 6H, Bi-CH₃), 1.74 (dq, 12H, ³J_{H-H} = 6.7 Hz, ²J_{P-H} = 11.6 Hz PCH₂CH₃ PCH₂CH₃) ppm; ³¹P NMR (101 MHz, CD₂Cl₂): δ = 64.1 (s, OPEt₃) ppm.

Protocol for the preparation of [BiDipp₂(EPRMe₃)₂(SbF₆)]: Compounds **6**_{Dipp} or **7**_{Dipp} (1 eq.) and one additional equivalent of EPRMe₃ (E = S, Se) were dissolved in CD₂Cl₂ and ¹H, ¹³C and ³¹P NMR spectra were measured.

[BiDipp₂(SPMe₃)₂(SbF₆)] (6'**_{Dipp}):** ¹H NMR (500 MHz, CD₂Cl₂): δ = 0.98 (d, ³J_{H-H} = 6.6 Hz, 24H, *o*-CCH(CH₃)₂), 1.85 (d, ²J_{P-H} = 13.1 Hz, 18H, SP(CH₃)₃), 2.81 (sept, ³J_{H-H} = 6.6 Hz, 4H, *o*-CCH(CH₃)₂), 7.39 (t, ³J_{H-H} = 7.6 Hz, 2H, *p*-CH), 7.57 (d, ³J_{H-H} = 7.6 Hz, 4H, *m*-CH) ppm; ¹³C NMR (125 MHz, CD₂Cl₂): δ = 20.7 (d, ¹J_{P-C} = 54.4 Hz, SP(CH₃)₃), 24.7 (s, *o*-CCH(CH₃)₂), 40.6 (s, *o*-CCH(CH₃)₂), 129.4 (s, *o*-CCH(CH₃)₂), 130.4 (s, *p*-CH), 156.3 (s, *m*-CH), 183.1 (s, Bi-C) ppm; ³¹P-NMR (202 MHz, CD₂Cl₂) δ = 38.7 (s, SPMe₃) ppm;

[BiDipp₂(SePMe₃)₂(SbF₆)] (7'**_{Dipp}):** ¹H NMR (500 MHz, CD₂Cl₂): δ = 1.10 (d, ³J_{H-H} = 6.6 Hz, 24H, *o*-CCH(CH₃)₂), 2.12 (d, ²J_{P-H} = 13.1 Hz, 18H, SeP(CH₃)₃), 2.95 (sept, ³J_{H-H} = 6.6 Hz, 4H, *o*-CCH(CH₃)₂), 7.47 (t, ³J_{H-H} = 7.6 Hz, 2H, *p*-CH), 7.64 (d, ³J_{H-H} = 7.6 Hz, 4H, *m*-CH) ppm; ¹³C NMR (125 MHz, CD₂Cl₂): δ = 21.0 (d, ¹J_{P-C} = 54.4 Hz, SP(CH₃)₃), 24.8 (s, *o*-CCH(CH₃)₂), 41.4 (s, *o*-CCH(CH₃)₂), 128.8 (s, *o*-CCH(CH₃)₂), 130.2 (s, *p*-CH), 156.2 (s, *m*-CH), 178.3 (s, Bi-C) ppm; ³¹P-NMR (202 MHz, CD₂Cl₂) δ = 16.1 (s, ¹J_{P-Se} = 587.8 Hz, SePMe₃) ppm;

Protocol for the preparation of [BiDipp₂(OPEt₃)₂(SbF₆)]: Compound **8'**_{Dipp} (1 eq.) and **4**_{Dipp-tol} (1 eq.) were dissolved in CD₂Cl₂ and ¹H, ¹³C and ³¹P NMR spectra were measured.

[BiDipp₂(OPMe₃)₂(SbF₆)] **8_{Dipp}:** ¹H-NMR (500 MHz, CD₂Cl₂) δ = 1.12 (d, ³J_{H-H} = 6.6 Hz, 24H, *o*-CCH(CH₃)₂), 1.13 (dt, ³J_{H-H} = 7.7 Hz, ²J_{P-H} = 16.6 Hz, 18H OP(CH₂CH₃)₃), 1.98 (dq, ³J_{H-H} = 7.7 Hz, ²J_{P-H} = 11.4 Hz, 12H OP(CH₂CH₃)₃), 2.94 (sept, ³J_{H-H} = 6.6 Hz, 4H, *o*-CCH(CH₃)₂), 7.59 (t, ³J_{H-H} = 7.6 Hz, 2H, *p*-CH), 7.83 (d, ³J_{H-H} = 7.6 Hz, 4H, *m*-CH) ppm;

¹³C{¹H}-NMR (125 MHz, CD₂Cl₂) δ = 5.5 (d, ²J_{P-C} = 5.7 Hz, OP(CH₂CH₃)₃), 19.0 (d, ¹J_{P-C} = 63.9 Hz, 3C, OP(CH₂CH₃)₃), 24.4 (s, 2C, *o*-CCH(CH₃)₂), 24.7 (s, 2C, *o*-CCH(CH₃)₂), 37.1 (s, 4C, *o*-CCH(CH₃)₂), 130.4 (s, 4C, *o*-CCH(CH₃)₂), 130.6 (s, 2C, *p*-CH), 156.6 (s, 4C, *m*-CH), 199.7 (s, 2C, Bi-C), ppm; ³¹P-NMR (202 MHz, CD₂Cl₂) δ = 80.5 (s, OPEt₃) ppm.

-6.0 ppm). The crystal structures of both compounds are similar to those of the isocyanide adducts and show a bisphenoidal coordination geometry around the bismuth atom. While the structure of **16_{Me}** only serves as a proof of connectivity, for **15_{Me}** bonding parameters can be discussed (monoclinic space group *C2/c*, *Z* = 8). The bismuth–methyl bonds (2.248(3)-2.253(3) Å) are slightly elongated compared to those in the starting material [BiMe₂(SbF₆)] (2.215(5)-2.223(5) Å).^[3] The bismuth center and the [SbF₆]⁻ counter ion form a contact ion pair with weak bismuth...fluorine interaction, judged on the basis of distance criteria (Bi...F, 2.942(2) Å).

Compound **16_{Dipp}** could be isolated from the reaction of **4_{Dipp-tol}** with acetonitrile. In the NMR spectra, all expected signals are observed. The signals corresponding to the MeCN fragment show a low-field shift in the ¹H and ¹³C NMR spectra compared to uncoordinated acetonitrile in C₆D₆.^[4] In the IR spectrum, two bands for the CN stretching mode are found at 2307 cm⁻¹ and 2275 cm⁻¹, ascribed to the C≡N stretching frequency and the combination band of CH₃ deformation and C–C stretching, which appears as an intense band due to Fermi resonance with the C≡N stretching.^[5] Compared to the free acetonitrile (2252 cm⁻¹), a blue-shift of 59 cm⁻¹ is observed. Crystals suitable for single-crystal X-ray diffraction were obtained from toluene at -32 °C. Compound **16_{Dipp}** crystallizes in the triclinic space group *P* $\bar{1}$ with two molecules in the asymmetric unit. The central bismuth atom shows several short contacts to fluorine atoms of two different SbF₆ anions with distances of 3.146(5)-3.820(5) Å. The Bi-N bond lengths are 2.388(7)-2.358(6) Å which is only slightly longer than in regular Bi-N single bonds (Mes₂BiNMe₂: 2.208(4) Å; Bi(NPh₂)₃ (2.167(2)-2.28(2) Å); Bi(N(SiMe₃)₂)₃ (2.199(8)-2.272(8))).^[6] In neutral donor acceptor complexes the Bi-N dative bond is significantly longer. Examples include intramolecular adducts like *o*-(*t*BuN)(C₆H₄)₂BiX (X = F-I; 2.559(4)-2.574(4)),^[7] or the acetonitrile adduct of Bi(N₃)₃ (2.81(1) Å).^[8] However, the Bi-N bond length is similar in the cationic bismuth(V) acetonitrile adduct [Bi(Ph)₃(MeCN)₂][P(CF₂CF₃)₃F₃]₂ (2.383(1) Å).^[9]

1.3 Evaluation of cation-anion interactions in solution

For many compounds described in this manuscript, we were not able to observe signals for the [SbF₆]⁻ anion in the ¹⁹F NMR spectra of the prepared samples. Notably, this was mostly the case, when the bismuth cation was shielded by donor ligands. In one particular case, namely **[BiDipp₂(SPMe₃)(SbF₆)]**, we observed a very broad (ca. 12000 Hz) multiplet of weak intensity in the ¹⁹F NMR spectrum at a chemical shift which can be expected for the SbF₆ anion (Figure S3). On the other hand, when the bismuth cation is less shielded, for example in **[BiDipp₂(SbF₆)]**, a slightly broadened signal (FWHM = 400 Hz) is observed. Under consideration of the ¹J_{Sb-F} coupling of the two naturally occurring antimony isotopes, ¹²¹Sb (*I* = 5/2) and ¹²³Sb (*I* = 7/2), we were able to simulate a spectrum which matches the experimental ¹⁹F NMR spectrum of **[BiDipp₂(SPMe₃)(SbF₆)]** very well (Figure S3). The simulation was performed using the *Daisy 3.5.2* implementation in *Topspin 4.0.7*.

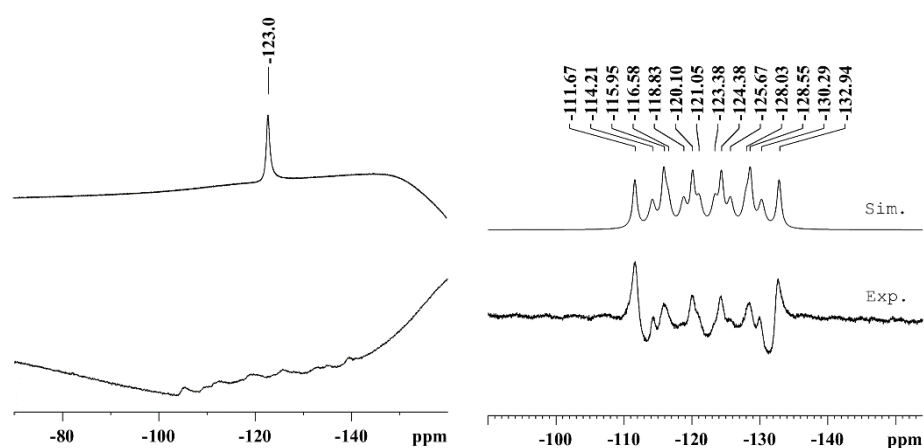


Figure S3. Left: Excerpts of ¹⁹F NMR spectra of **4-tolDipp** (top) and **6Dipp** (bottom) in CD₂Cl₂. Right: ¹⁹F NMR spectrum of **6Dipp** measured with a smaller sweep width (bottom) and simulated spectrum for an [SbF₆]⁻ anion with ¹J_{Sb-F} = 1920 Hz (¹²¹Sb) and 1040 Hz (¹²³Sb) (top).

The observed ¹J_{Sb-F} coupling constants of 1920 Hz (¹²¹Sb) and 1040 Hz (¹²³Sb) are in very good agreement with coupling constants observed for Ag[SbF₆] in acetonitrile.^[10] Due to the quadrupole momentum of the two antimony isotopes, the ¹J_{Sb-F} coupling should only be observed in a highly symmetrical environment. Hence, the SbF₆ anion should not interact significantly with the bismuthenium cation. In agreement with previous interpretations, we assign these observations to the formation of a solvent-separated ion pair.^[11] On the other hand, anion cation interactions lower the symmetry of the ion and subsequently, the ¹J_{Sb-F} coupling should not be observed anymore. This leads us to the assumption that **[BiDipp₂(SbF₆)]** exists as a contact ion pair in solution.

2. DFT Calculations

DFT calculations were performed with the Gaussian program using the 6-311++G(d,p) (H, C, N, O, F, P, S, Se),^[12] and the LaNL2DZ (Sb, Bi)^[13] basis set and the B3LYP functional.^[14] The D3 version of Grimme's dispersion model with the original D3 damping function was applied.^[15] Frequency analyses of the reported structures showed no imaginary frequencies for minimum structures. Thermodynamic parameters were calculated at a temperature of 298.15 K and a pressure of 1.00 atm. Cartesian coordinates of optimized structures are provided in xyz format.

Table S1. Enthalpies and Gibbs energies, imaginary frequencies, and reaction medium (gas phase vs. pyridine solvent model) of compounds investigated by DFT calculations.

compound	ΔH [hartree]	ΔG [hartree]
OPEt ₃	-654.215158	-654.264778
SPMe ₃	-859.299618	-859.340059
SePMe ₃	-2862.637117	-2862.679097
[BiMe ₂ (SbF ₆)] (1)	-689.992469	-690.054683
[BiMe ₂ (OPEt ₃)(SbF ₆)] (8 _{Me})	-1344.255018	-1344.348556
[BiMe ₂ (OPEt ₃) ₂ (SbF ₆)] (8' _{Me})	-1998.528827	-1998.65233
[BiMe ₂ (SPMe ₃)(SbF ₆)] (6 _{Me})	-1549.323742	-1549.411277
[BiMe ₂ (SPMe ₃) ₂ (SbF ₆)] (6' _{Me})	-2408.673523	-2408.781778
[BiMe ₂ (SePMe ₃)(SbF ₆)] (7 _{Me})	-3552.663372	-3552.752515
[BiMe ₂ (SePMe ₃) ₂ (SbF ₆)] (7' _{Me})	-6415.356736	-6415.464956
[BiDipp ₂ (SbF ₆)] (4 _{Dipp})	-1545.044085	-1545.156678
[BiDipp ₂ (OPEt ₃)(SbF ₆)] (8 _{Dipp})	-2199.311909	-2199.452020
[BiDipp ₂ (OPEt ₃) ₂ (SbF ₆)] (8' _{Dipp})	-2853.573620	-2853.741280
[BiDipp ₂ (SPMe ₃)(SbF ₆)] (6 _{Dipp})	-2404.382442	-2404.517340
[BiDipp ₂ (SPMe ₃) ₂ (SbF ₆)] (6' _{Dipp})	-3263.716410	-3263.867165
[BiDipp ₂ (SePMe ₃)(SbF ₆)] (7 _{Dipp})	-4407.724238	-4407.859885
[BiDipp ₂ (SePMe ₃) ₂ (SbF ₆)] (7' _{Dipp})	-7270.395338	-7270.548795

Theoretical analyses of bonding in [BiDipp₂(Donor)(SbF₆)] (Donor = OPEt₃, SPM₃, SePMe₃). The electron localization function (ELF) in the E2-Bi1-C3 plane of compounds [BiDipp₂(Donor)(SbF₆)] (Donor = OPEt₃, SPM₃, SePMe₃) was mapped (Figure S4). The ELF along the Bi–E bonds (E = O, S, Se) does not show a maximum in the region approximately at the midpoint between the atoms Bi and E, which is suggestive of ionic contributions. While the ELF shows low values in that region for E = O, they increase with increasing atomic number of E, suggesting an increase of the covalent contributions as the atom E in the Bi–E bond becomes heavier.

Further bonding analyses were performed using the quantum theory of atoms in molecules. The examination of a range of parameters at a bond critical point (critical point of type (3, -1)) such as the Laplacian of electron density ($\nabla^2\rho$), the ratio of the absolute value of the potential energy density and the kinetic energy density ($|V|/G$) and the total energy density (H) have been suggested to obtain information on the type of bonding (e.g.: ionic vs. dative vs. covalent).^[16,17] Values of these parameters found in certain ranges have been associated with the different types of bonding and have been suggested based on light atoms (i.e. second row elements).^[16,17] These values may change for heavier elements,^[16,17] but to the best of the authors' knowledge, there are no generally accepted ranges of values for bonding between a light(er) element of the second, third or fourth row and a heavy element of the sixth row as investigated in this work. Therefore, the ranges generally accepted for bonding between lighter elements are used here. Furthermore, these parameters can only give indications as part of a larger picture (i.e. not on their own). The data for compounds [BiDipp₂(Donor)(SbF₆)] (Donor = OPEt₃, SPM₃, SePMe₃) is summarized in Table S2. The Laplacian of electron density ($\nabla^2\rho$), is suggested to be negative for covalent bonds and positive for ionic bonds and is significantly positive for Bi–O bonding, but approaches zero for Bi–S/Se bonds. The ratio of the absolute value of the potential energy density and the kinetic energy density ($|V|/G$) is suggested to be >2 for covalent interactions and <1 for ionic interactions. For the molecules studied here, it ranges between 1 and 2 and increases with increasing atomic number of E. Differences in the the total energy density (H) appear too small to be discussed. Thus, as a trend, the parameters discussed here point towards the Bi–E bonding becoming more covalent with increasing atomic number of E.

Analysis of geometric parameters in geometry-optimized structures of [BiR₂(OPEt₃)_n(SbF₆)] (R = Me, Dipp; n = 1, 2). Results discussed in the main part suggest for the bulky compound [BiDipp₂(OPEt₃)(SbF₆)] interactions with a second Lewis base (in addition to the first molecule of OPEt₃ that is already present) is less favourable than in the case of [BiMe₂(OPEt₃)(SbF₆)]. This is further corroborated by an analysis of the geometric parameters in the geometry-optimized structures of [BiR₂(OPEt₃)_n(SbF₆)] (R = Me, Dipp; n = 1, 2) (Table S3). While the Bi–O bond length in [BiDipp₂(OPEt₃)(SbF₆)] (2.21 Å) is shorter than that in [BiMe₂(OPEt₃)(SbF₆)] (2.31 Å), the shortest Bi···F distance is

significantly larger ($R = \text{Dipp}: 3.10 \text{ \AA}$; $R = \text{Me}: 2.36 \text{ \AA}$). In line with these results, the compounds featuring two OPEt_3 ligands, $[\text{BiR}_2(\text{OPEt}_3)_2(\text{SbF}_6)]$, show shorter Bi–O bonds and a shorter Bi \cdots F distance in the case of $R = \text{Me}$.

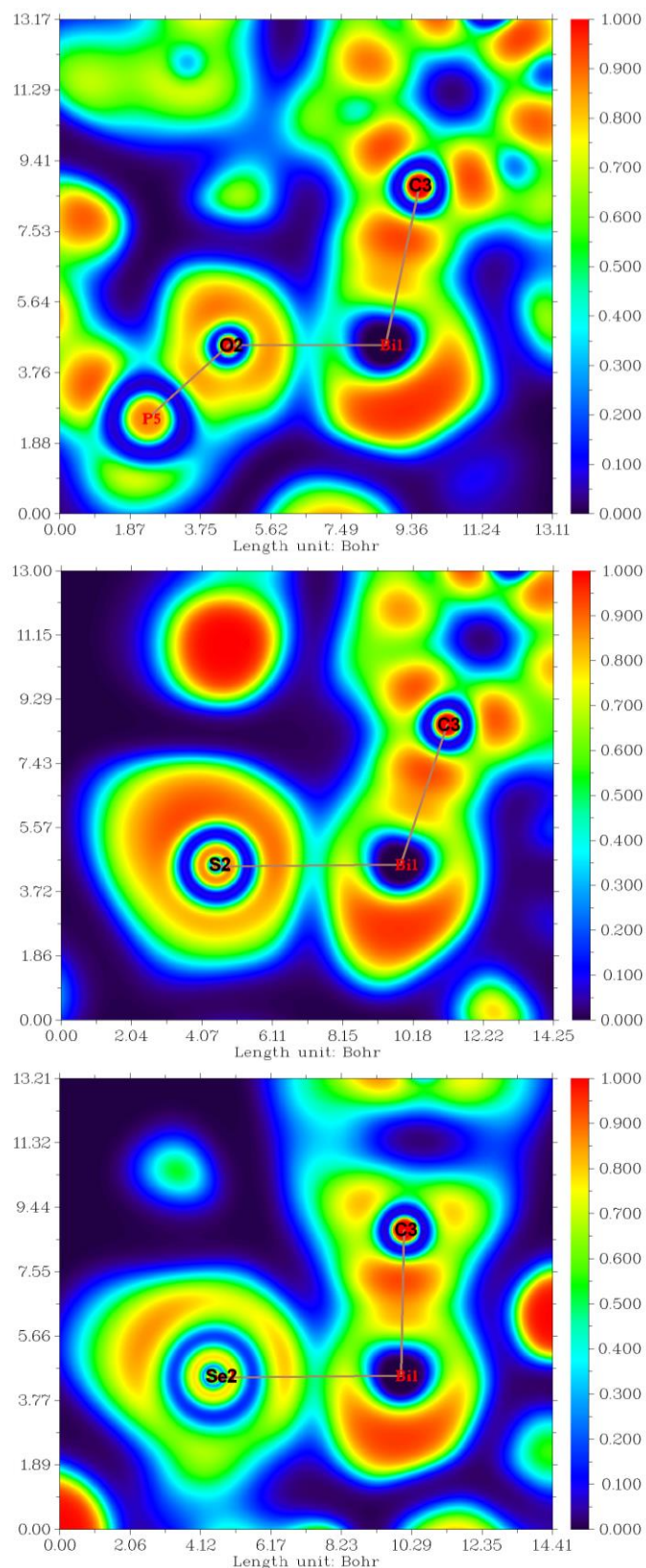


Figure S4. ELF plots of the E2-Bi1-C3 plane of compounds $[\text{BiDipp}_2(\text{OPEt}_3)(\text{SbF}_6)]$ (top), $[\text{BiDipp}_2(\text{SPMe}_3)(\text{SbF}_6)]$ (middle), and $[\text{BiDipp}_2(\text{SePMe}_3)(\text{SbF}_6)]$ (bottom).

Table S2. Parameters of bond critical points along the Bi–E axis of compounds [BiDipp₂(Donor)(SbF₆)] according to AIM analyses (Donor = OPEt₃, SPM₃, SePM₃).

E	$\nabla^2\rho$ [e/Å ⁵]	V /G	H [a.u.]
O (Et)	0.294	1.31	-0.012
S (Et)	0.0713	1.48	-0.0073
Se (Et)	0.0577	1.62	-0.0086

$\nabla^2\rho$ = Laplacian of electron density; V = Potential energy density; G = Kinetic energy density; H = Total energy density.

Table S3. Geometric parameters of structures obtained from geometry optimizations in DFT calculations.

compound	Bi···E1 [Å]	Bi···E2 [Å]	Bi···F [Å] ^a
[BiMe ₂ (OPEt ₃)(SbF ₆)] (8 _{Me})	2.31345	-	2.35922
[BiMe ₂ (OPEt ₃) ₂ (SbF ₆)] (8' _{Me})	2.34277	2.39242	2.92668
[BiDipp ₂ (OPEt ₃)(SbF ₆)] (8 _{Dipp})	2.20951	-	3.09895
[BiDipp ₂ (OPEt ₃) ₂ (SbF ₆)] (8' _{Dipp})	2.41336	2.43231	3.29597

a: shortest Bi···F distance

Molecular orbital analysis of [BiR₂(SbF₆)]. Compounds [BiR₂(SbF₆)] were analyzed in order to identify energetically high-lying molecular orbitals with a geometry making the candidates for back-donation into vacant, anti-bonding orbitals of isocyanide ligands (R = Me, Dipp). For compound [BiMe₂(SbF₆)], these orbitals are the HOMO (E = -0.3068 hartree) and the HOMO-2 (E = -0.3390 hartree). For compound [BiDipp₂(SbF₆)] these are the HOMO-1 (E = -0.2610 hartree), the HOMO-2 (E = -0.2628 hartree), the HOMO-3 (E = -0.2694 hartree), the HOMO-4 (E = -0.2942 hartree), and the HOMO-5 (E = -0.3127 hartree). Among these MOs of [BiDipp₂(SbF₆)], the HOMO-1, HOMO-2, and HOMO-3 also show contributions by p-type atomic orbitals of one Dipp ligand that are potentially relevant for back-bonding towards an isocyanide ligand.

3. NMR Spectra

3.1 [BiDipp₂(PF₆)] 1_{Dipp}

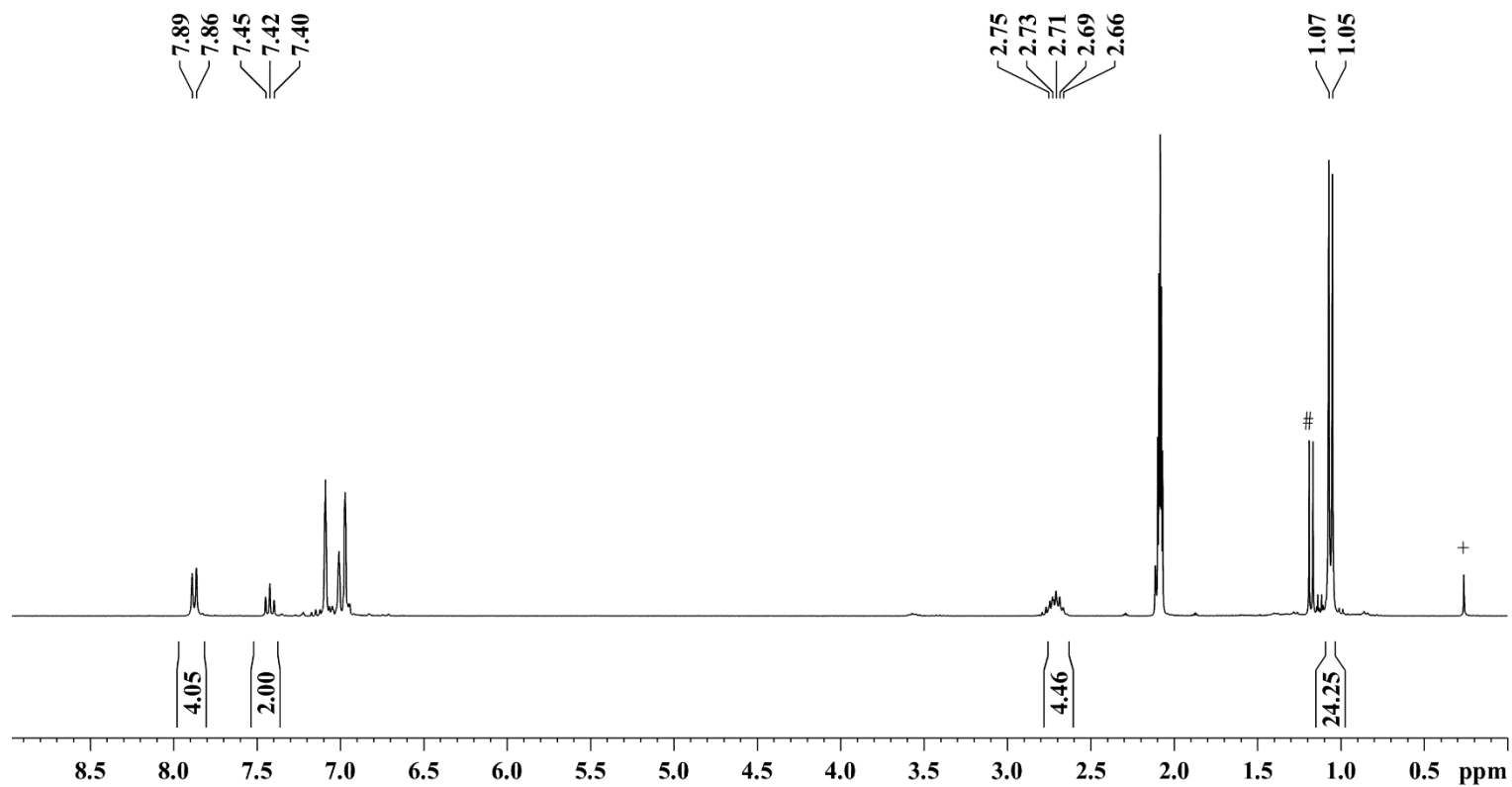


Figure S5. ¹H NMR spectrum (300 MHz) of 1_{Dipp} in toluene-d₈ at room temperature (# = hydrolysis; + = silicon grease).

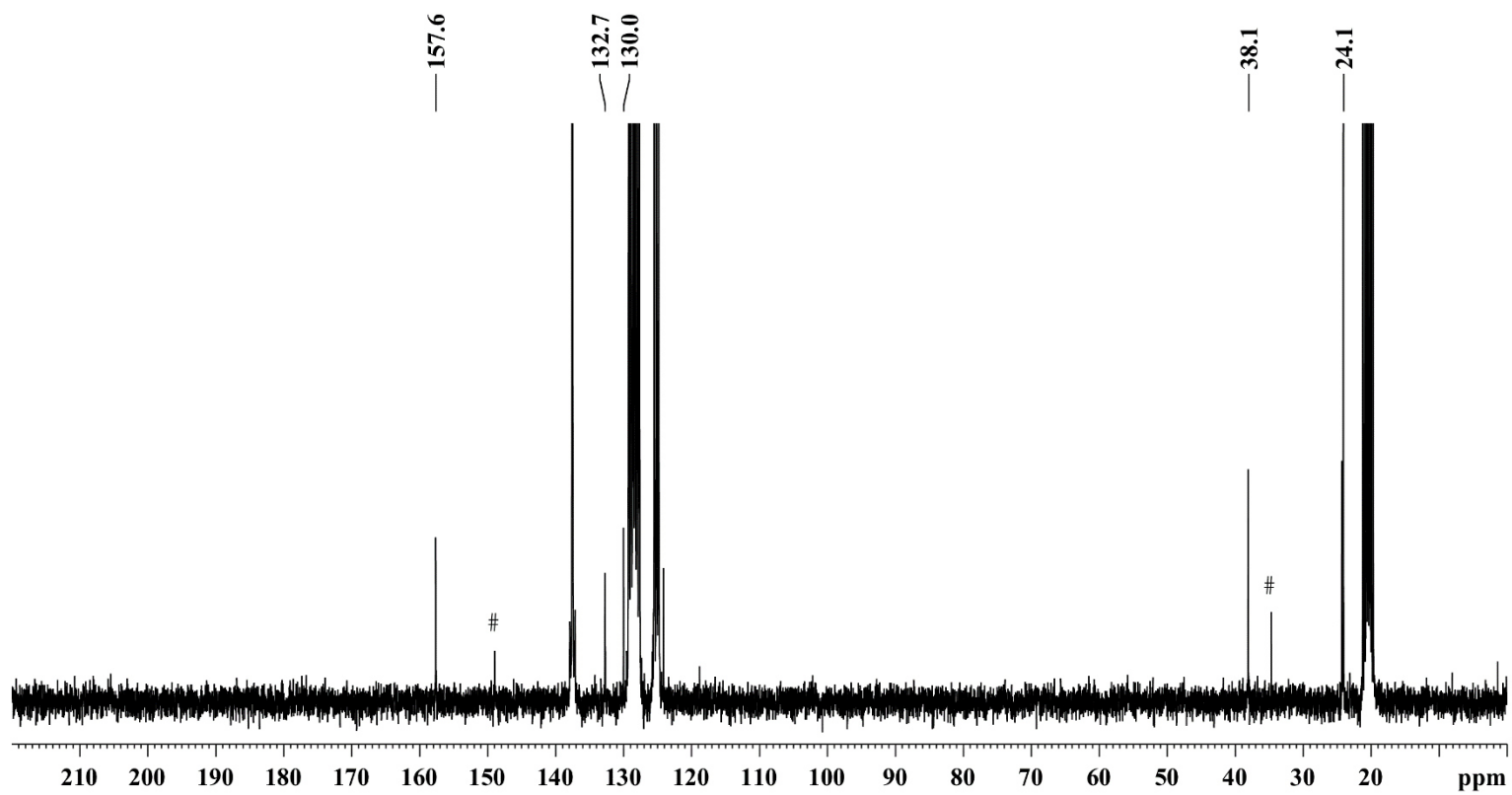


Figure S6. ^{13}C NMR spectrum (75 MHz) of $\mathbf{1}_{\text{Dipp}}$ in toluene- d_8 at room temperature (# = hydrolysis).

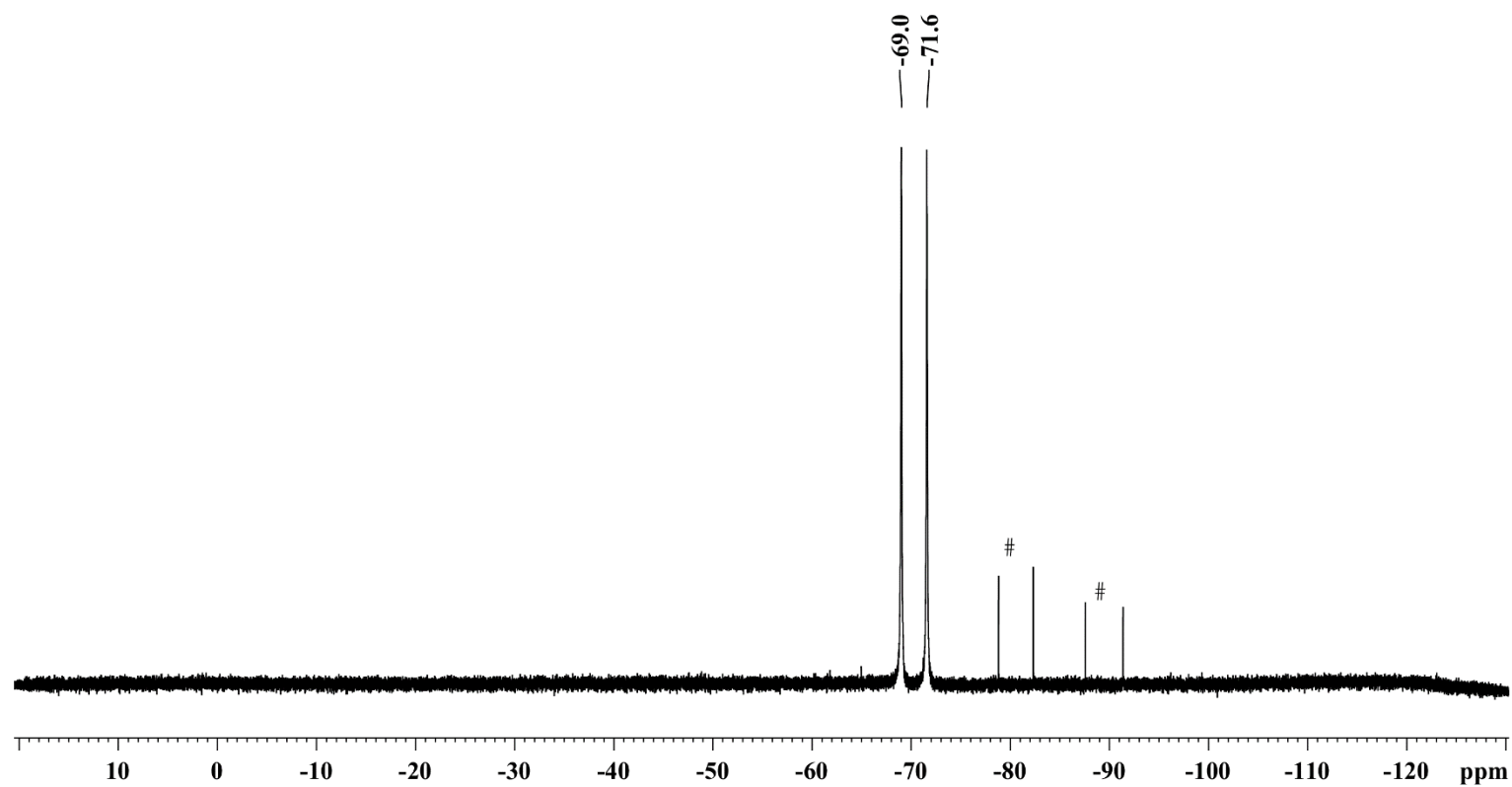


Figure S7. ^{19}F NMR spectrum (283 MHz) of **1**_{Dipp} in toluene- d_8 at room temperature (# = unknown side products).

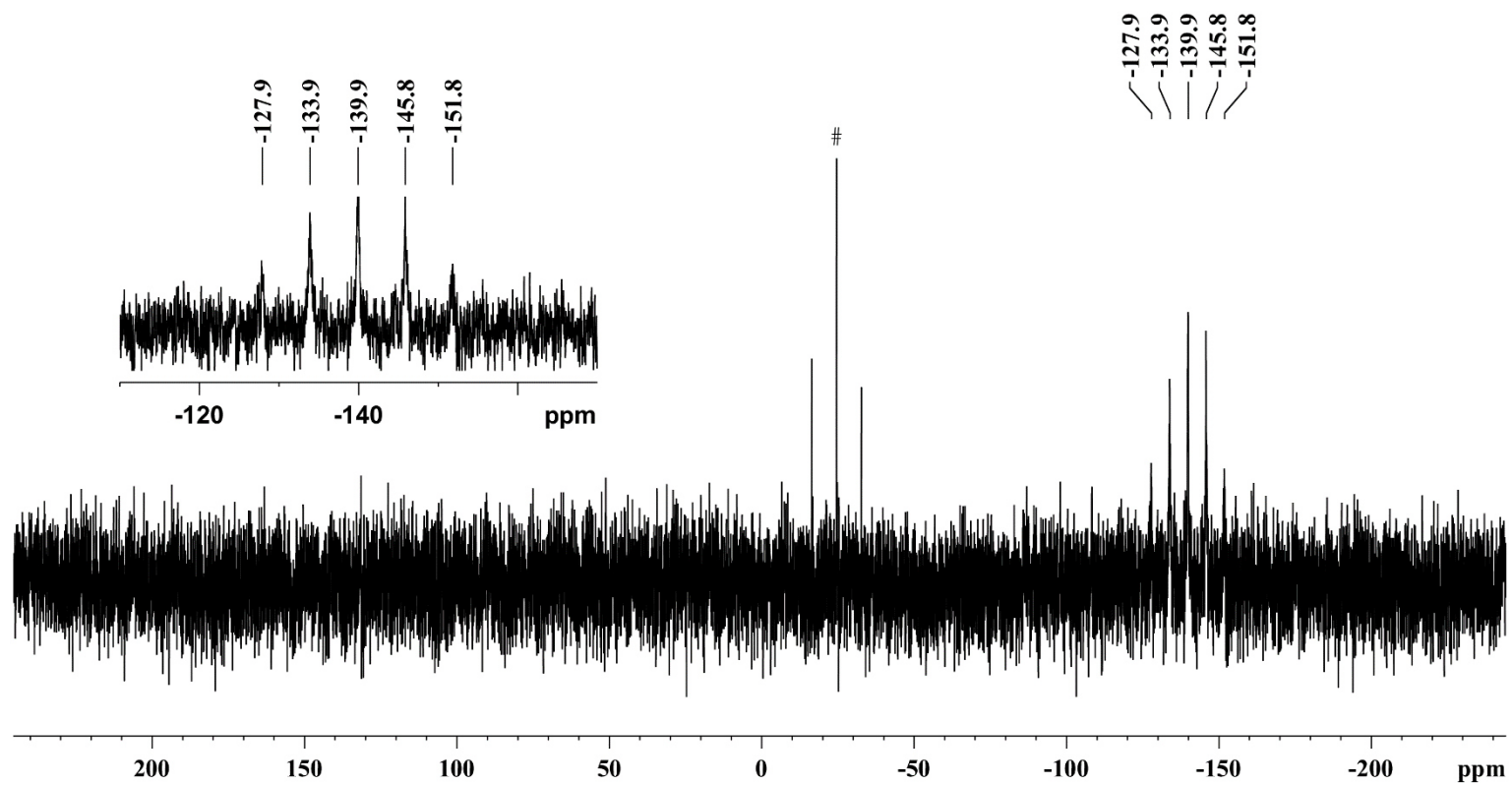


Figure S8. ^{31}P NMR spectrum (122 MHz) of 1_{Dipp} in toluene-d_8 at room temperature (# = unknown side products).

3.2 [BiDipp₂(OPe_t)₂(PF₆)] 3_{Dipp}

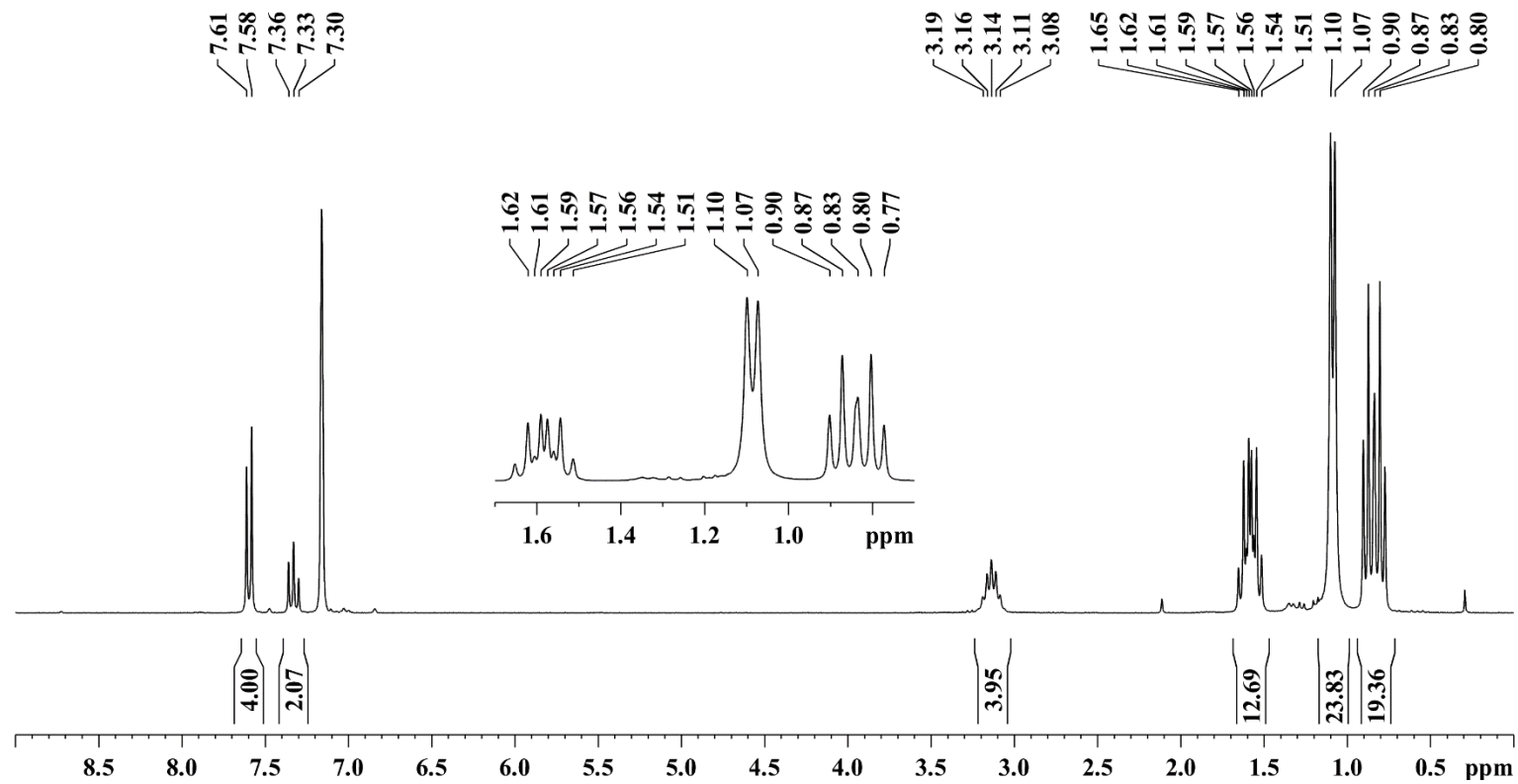


Figure S9. ¹H NMR spectrum (300 MHz) of 3_{Dipp} in C₆D₆ at room temperature.

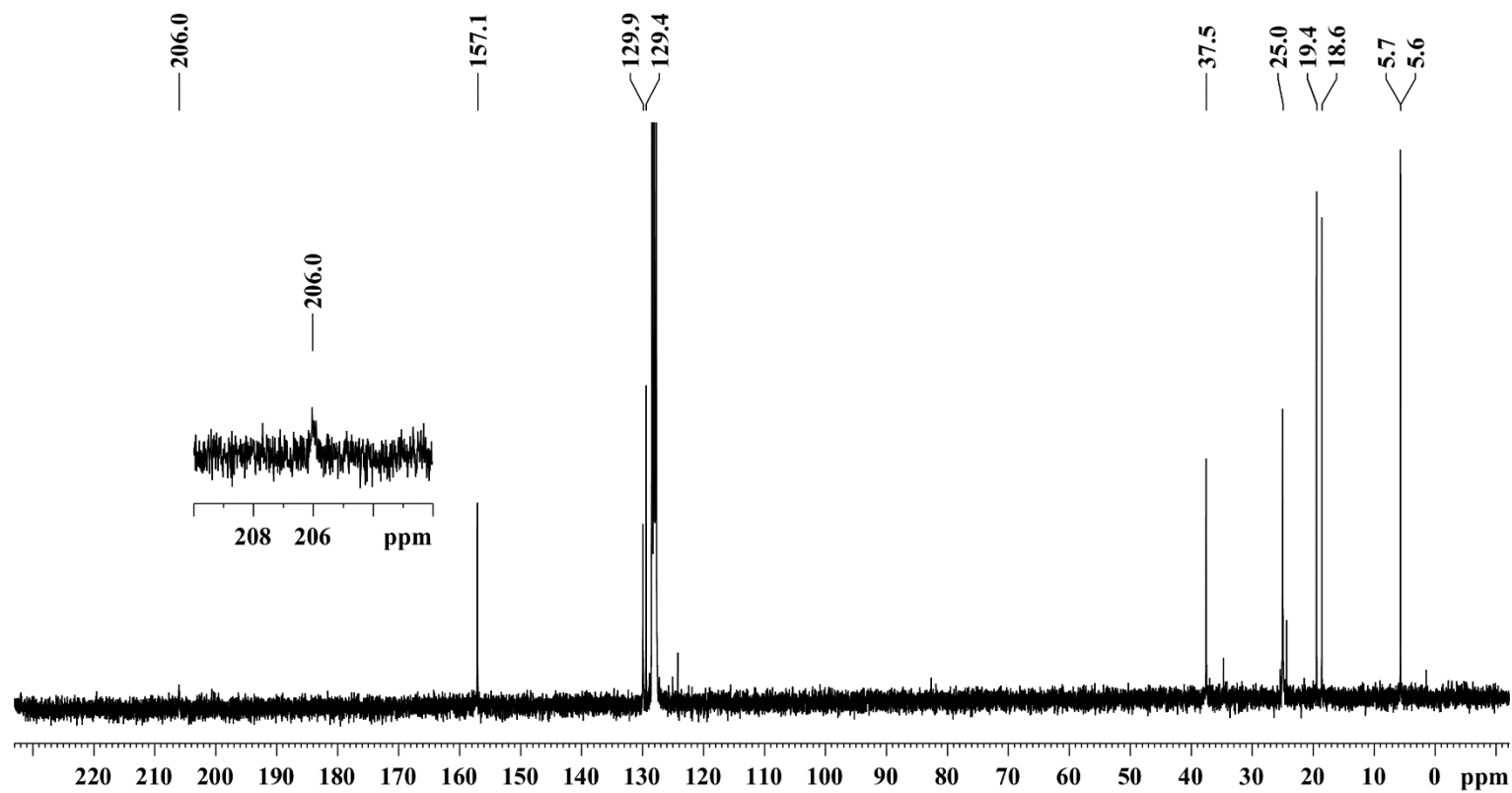


Figure S10. ^{13}C NMR spectrum (75 MHz) of 3DiPP in C_6D_6 at room temperature.

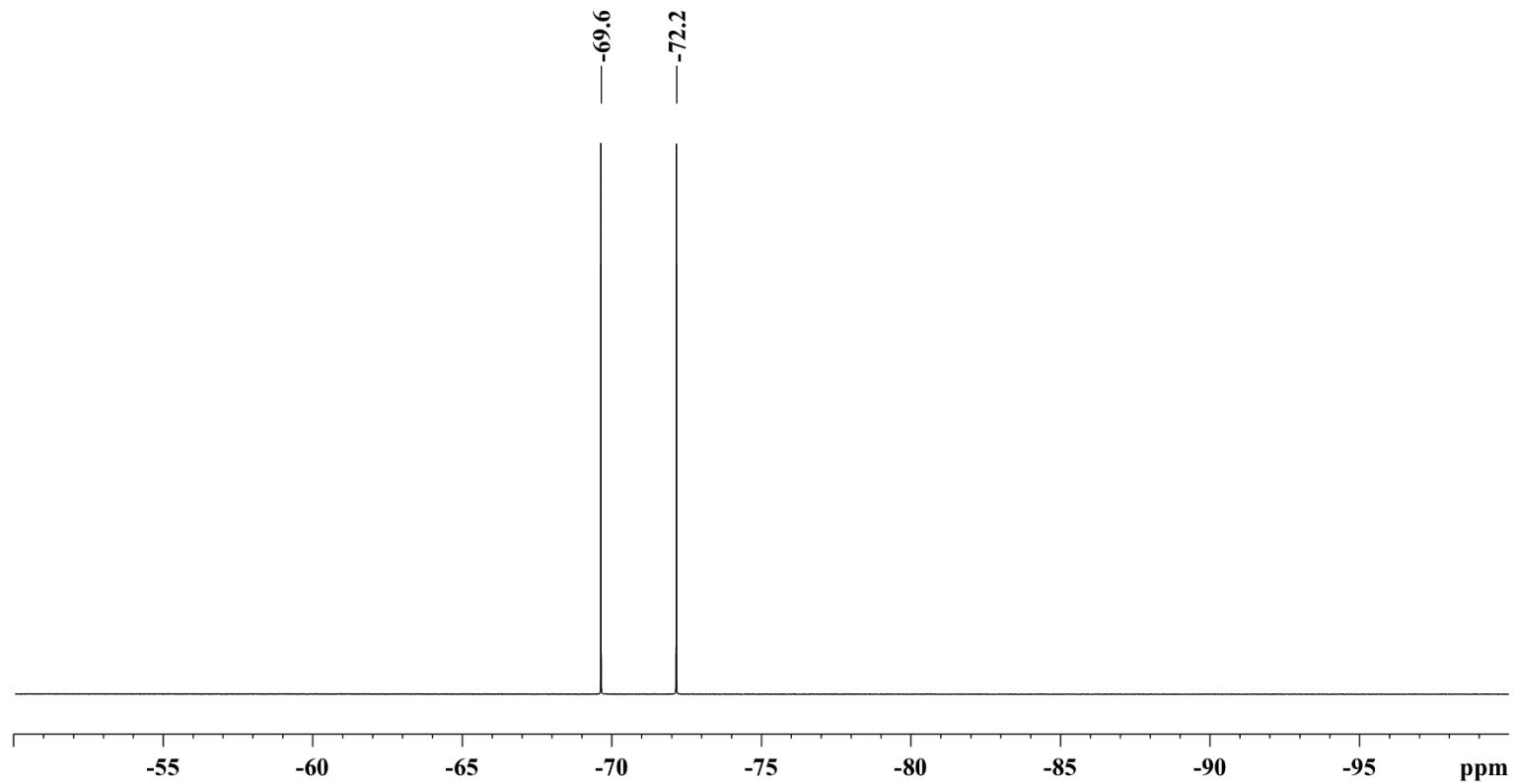


Figure S11. ^{19}F NMR spectrum (283 MHz) of **3_{Dipp}** in C_6D_6 at room temperature.

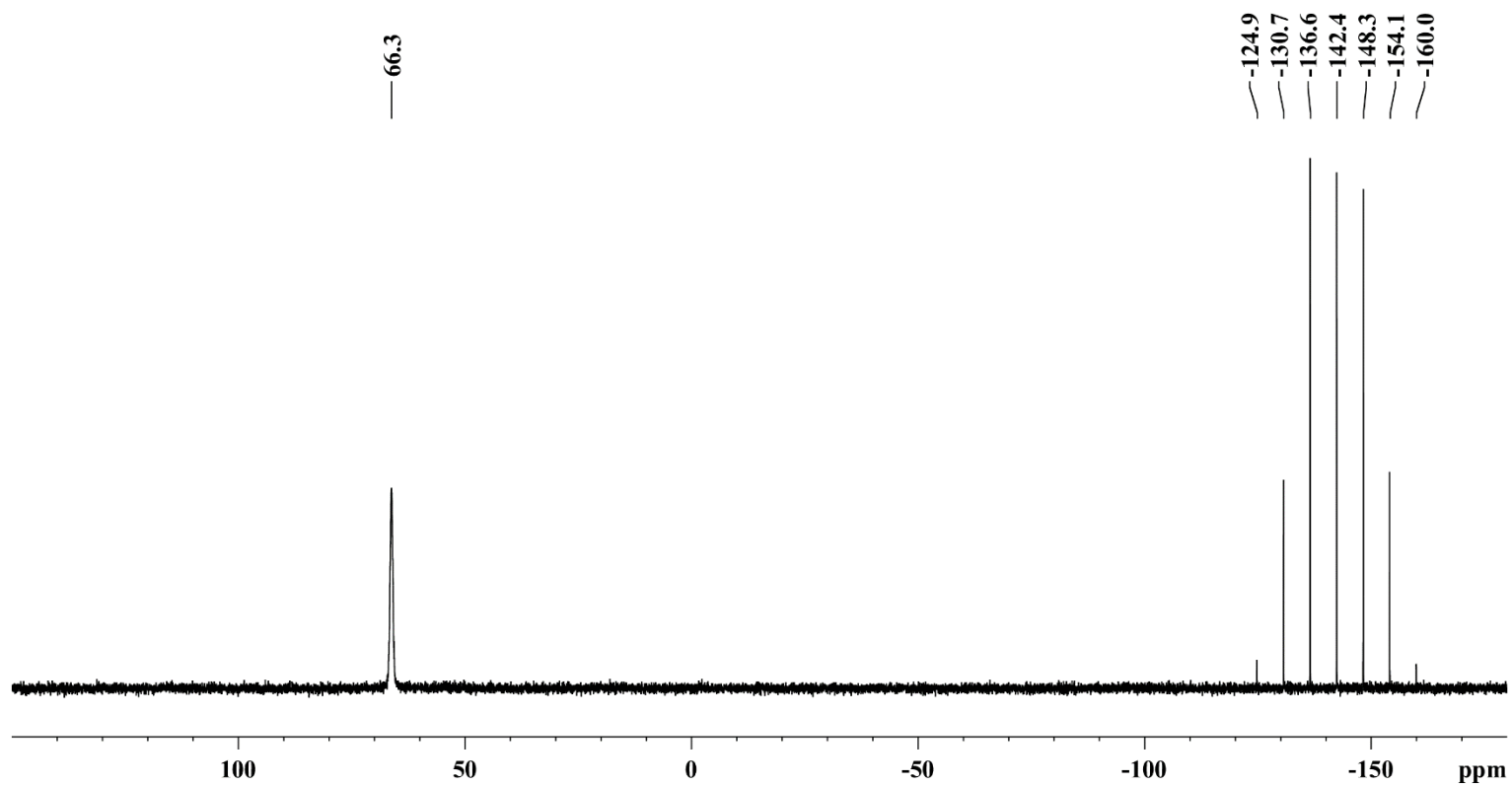


Figure S12. ^{31}P NMR spectrum (122 MHz) of 3_{Dipp} in C_6D_6 at room temperature.

3.3 [BiDipp₂(SbF₆)] 4_{Dipp}

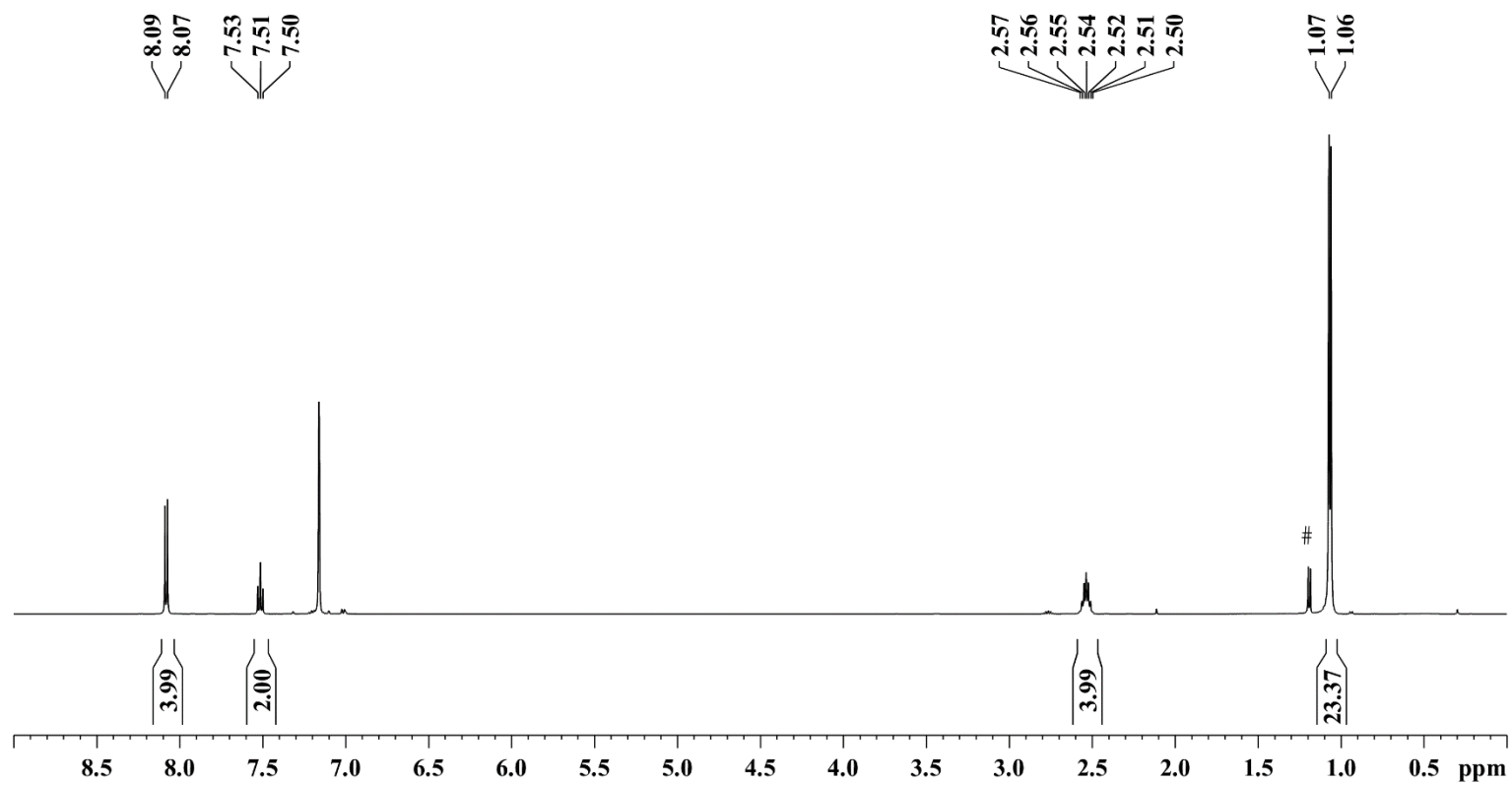


Figure S13. ¹H NMR spectrum (500 MHz) of 4_{Dipp} in C₆D₆ at room temperature (# = hydrolysis).

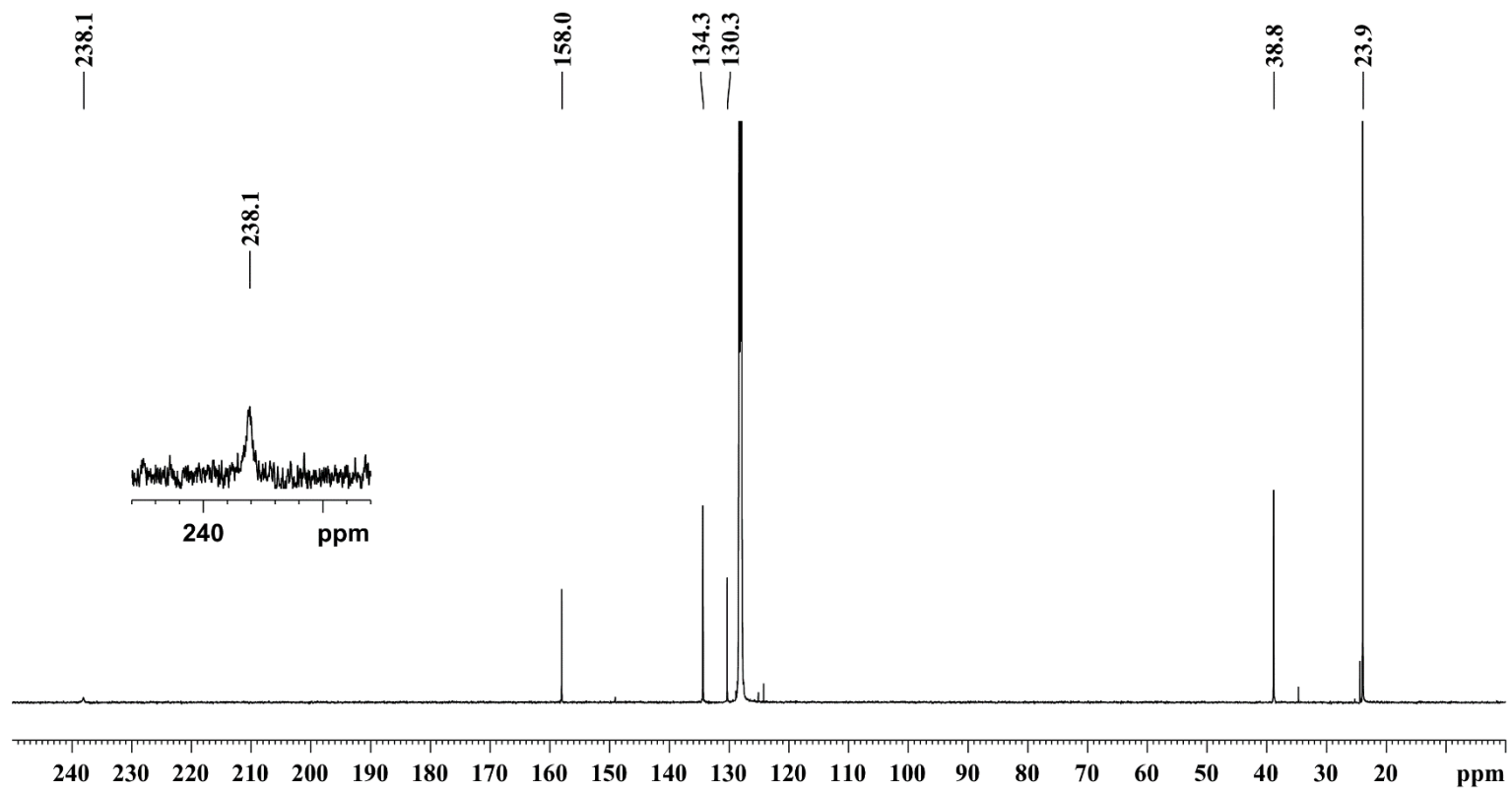


Figure S14. ^{13}C NMR spectrum (125 MHz) of 4Dipp in C_6D_6 at room temperature.

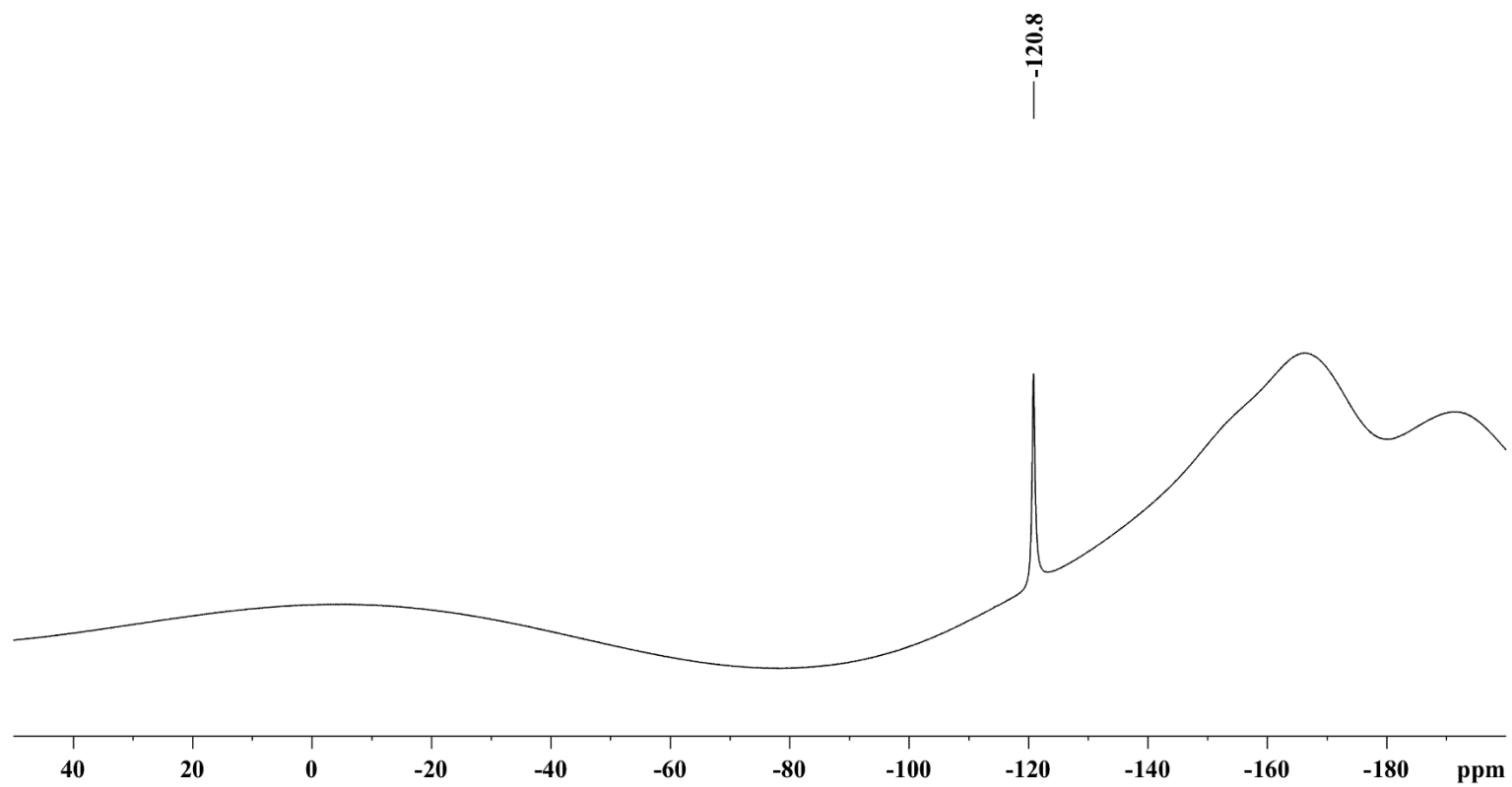


Figure S15. ^{19}F NMR spectrum (471 MHz) of 4_{Dipp} in C_6D_6 at room temperature.

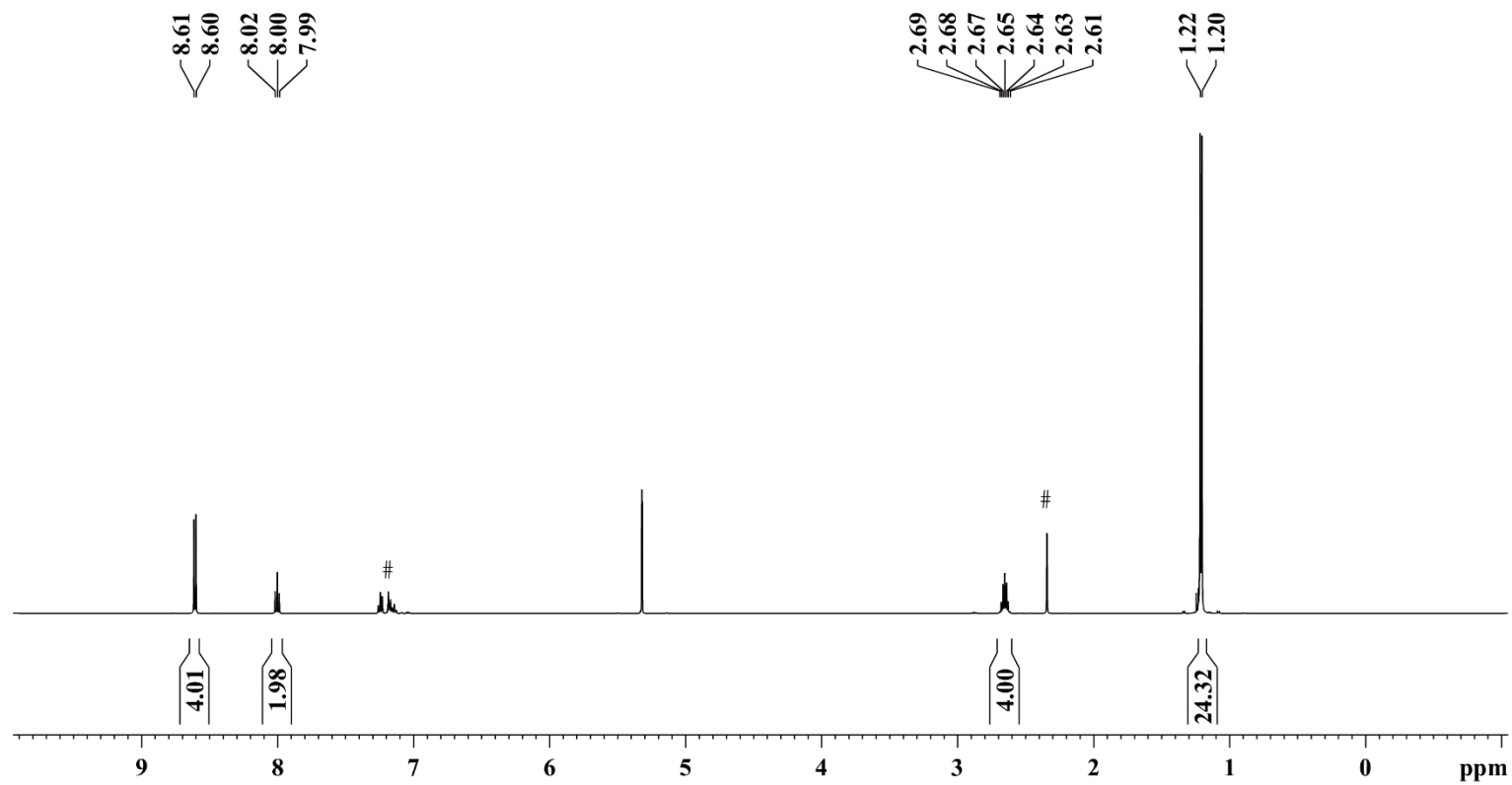


Figure S16. ^1H NMR spectrum (500 MHz) of **4_{Dipp}** in CD_2Cl_2 at room temperature (# = toluene).

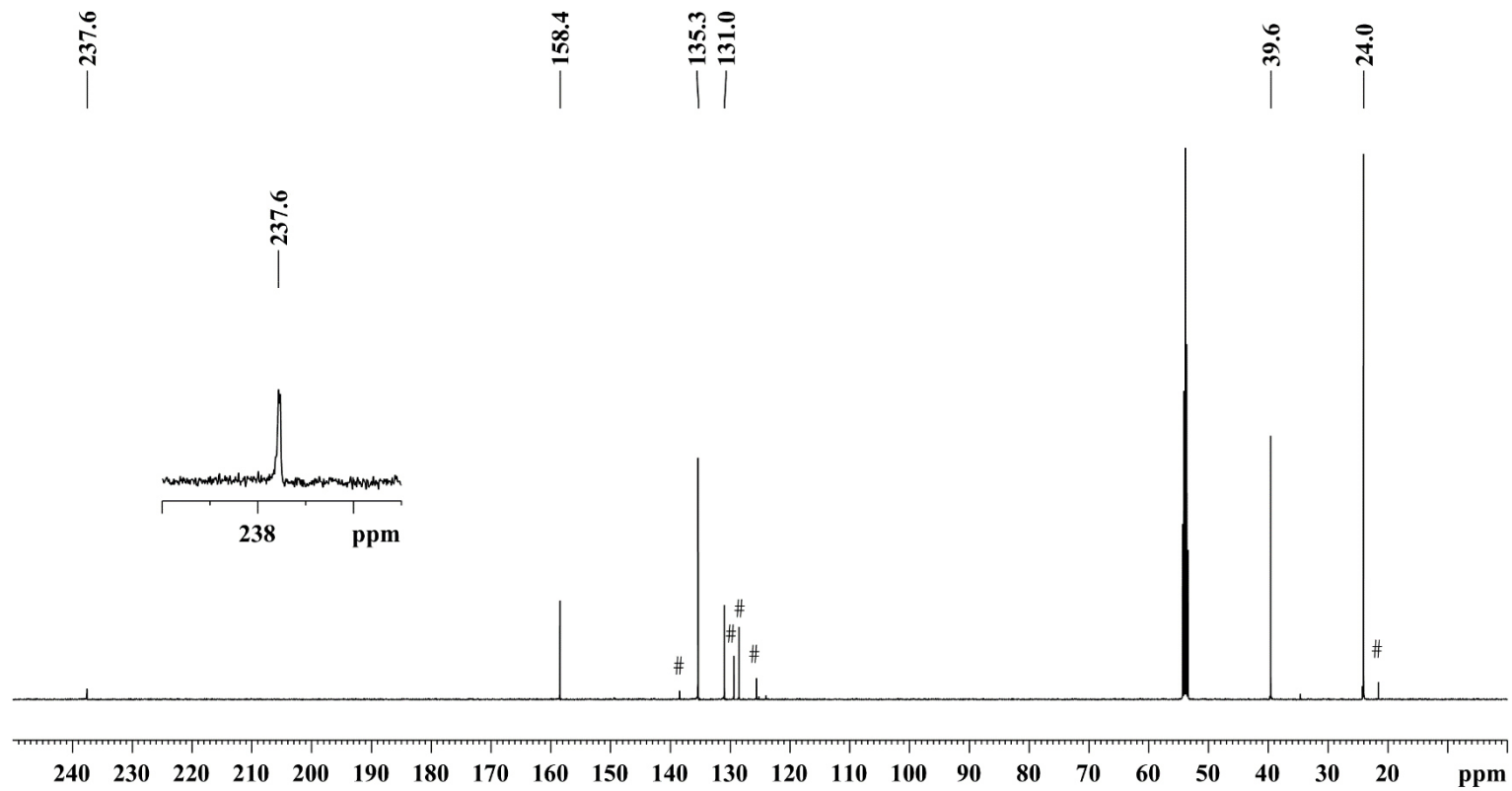


Figure S17. ^{13}C NMR spectrum (125 MHz) of 4DiPP in CD_2Cl_2 at room temperature (# = toluene).

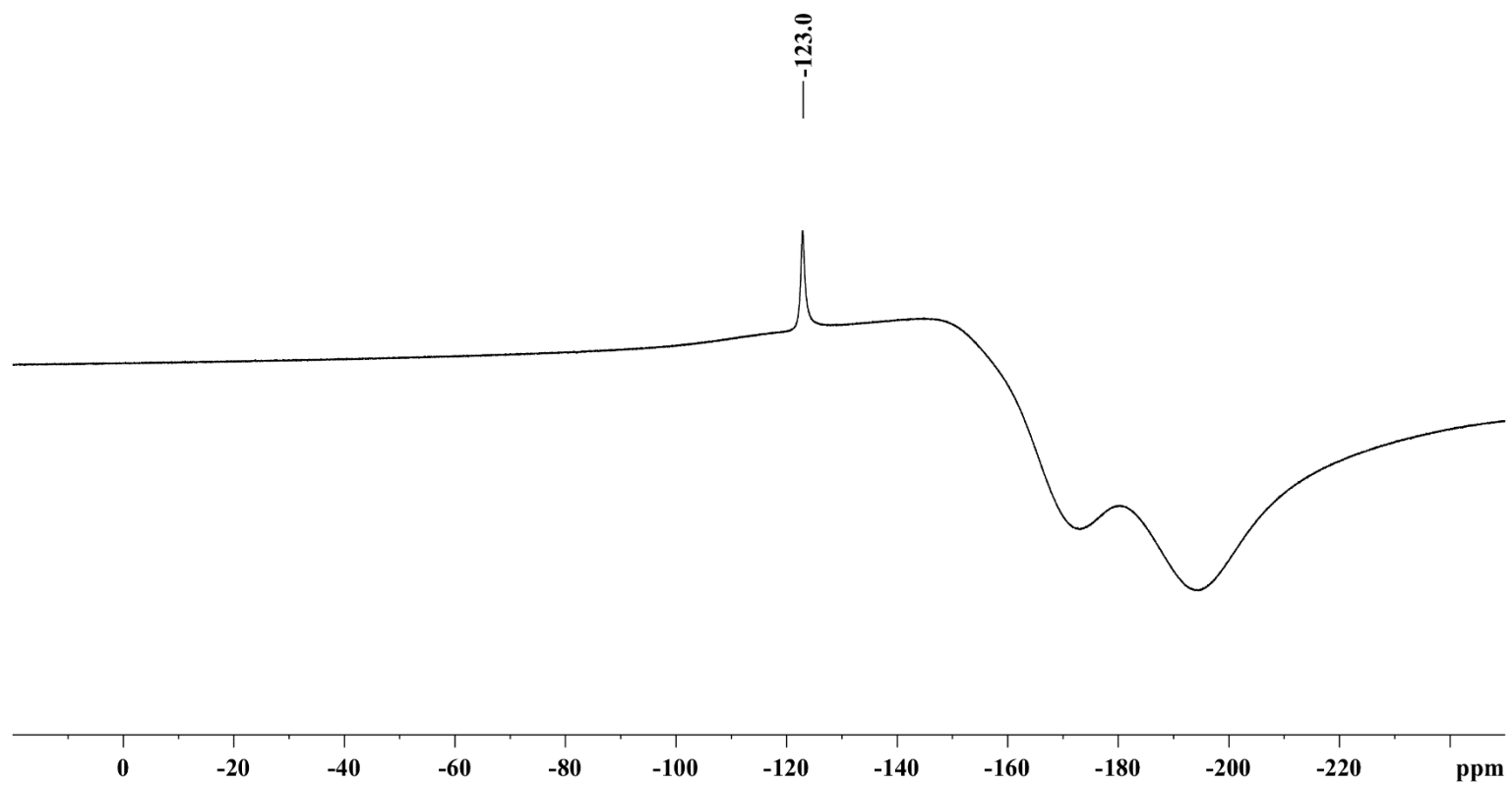


Figure S18. ^{19}F NMR spectrum (471 MHz) of 4_{Dipp} in CD_2Cl_2 at room temperature.

3.4 [(BiDipp)₂F][SbF₆] 5_{Dipp}

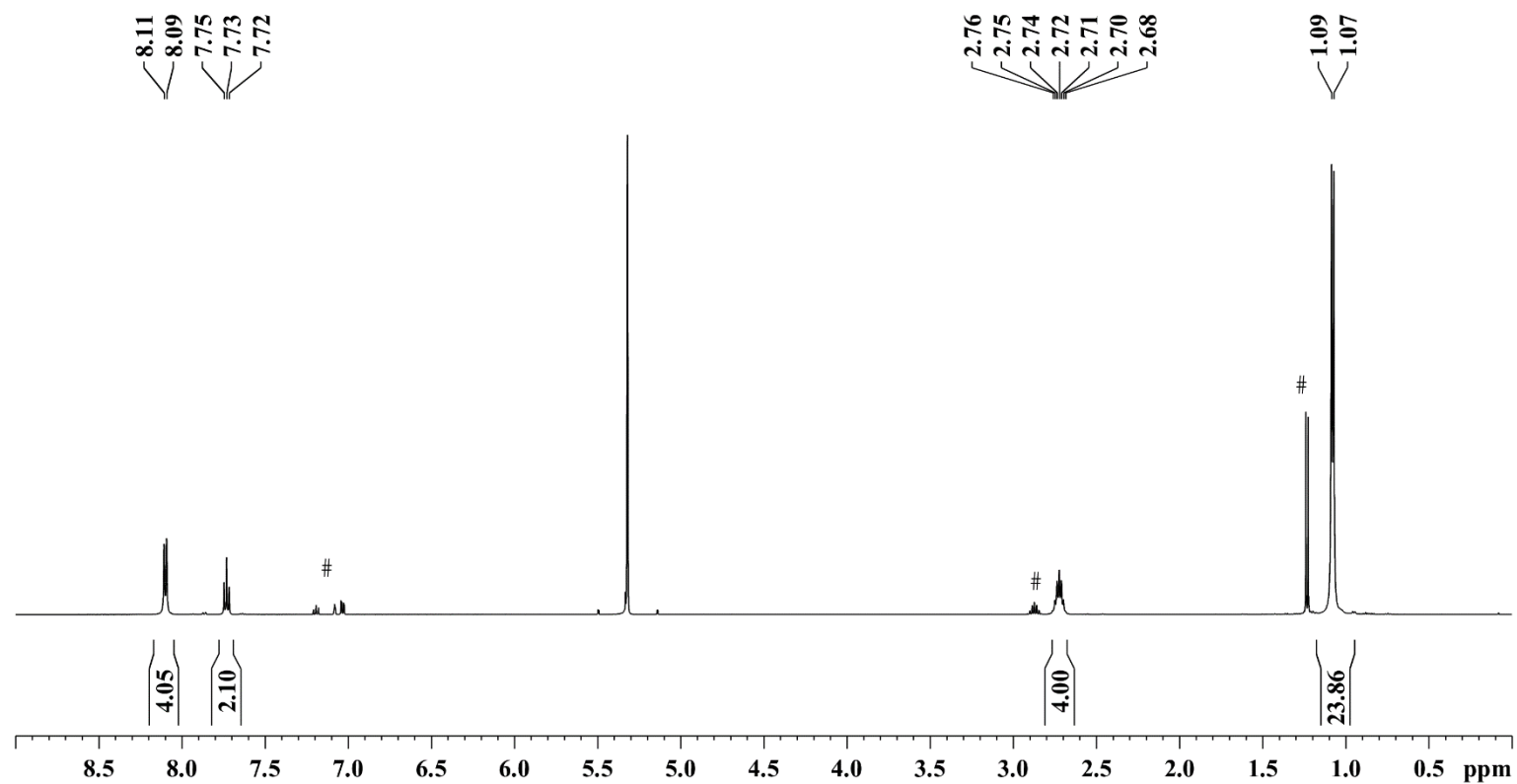


Figure S19. ¹H NMR spectrum (500 MHz) of **5_{Dipp}** in CD₂Cl₂ at room temperature (# = hydrolysis).

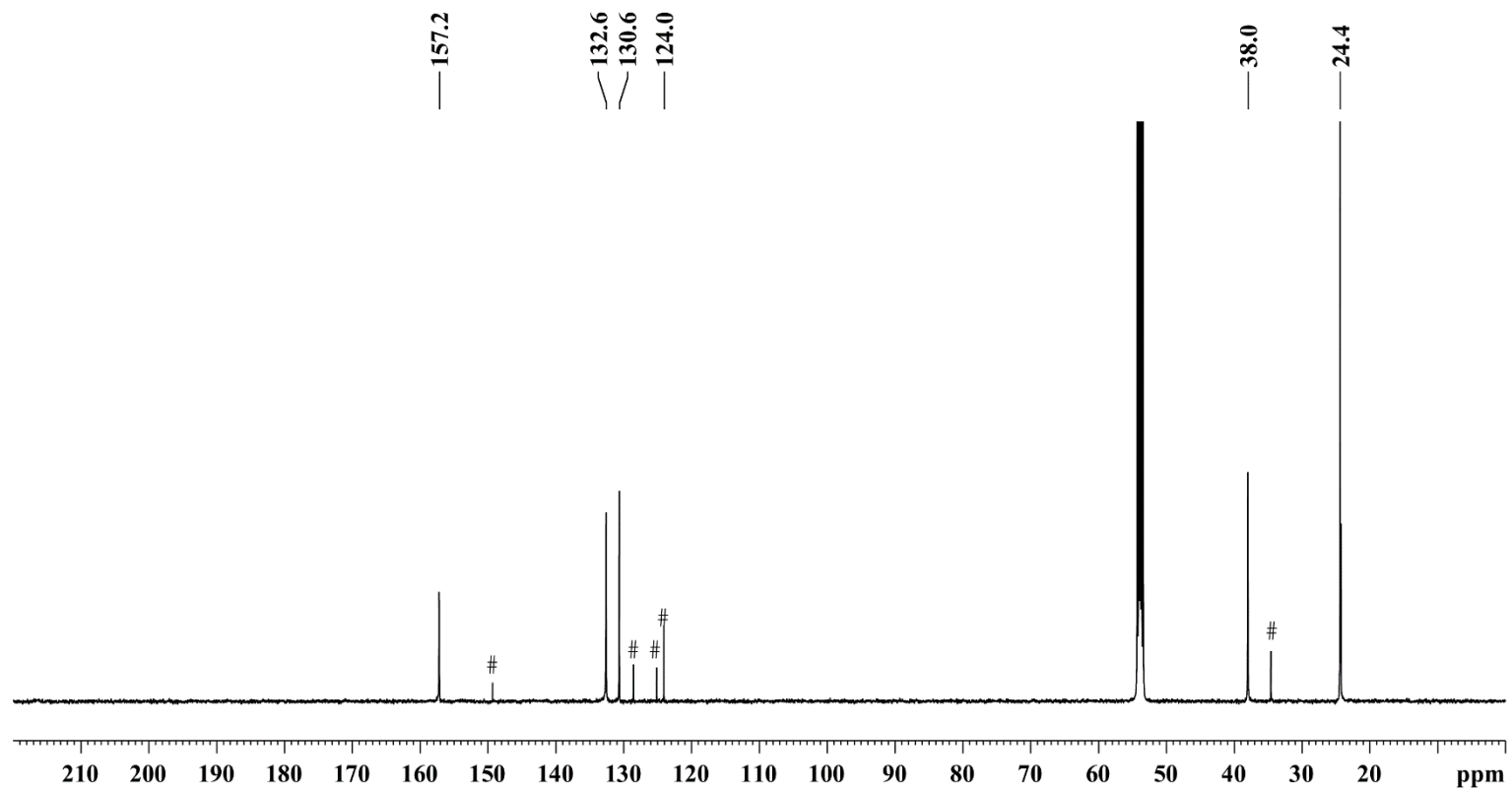


Figure S20. ^{13}C NMR spectrum (125 MHz) of **5**_{Dipp} in CD_2Cl_2 at room temperature (# = hydrolysis).

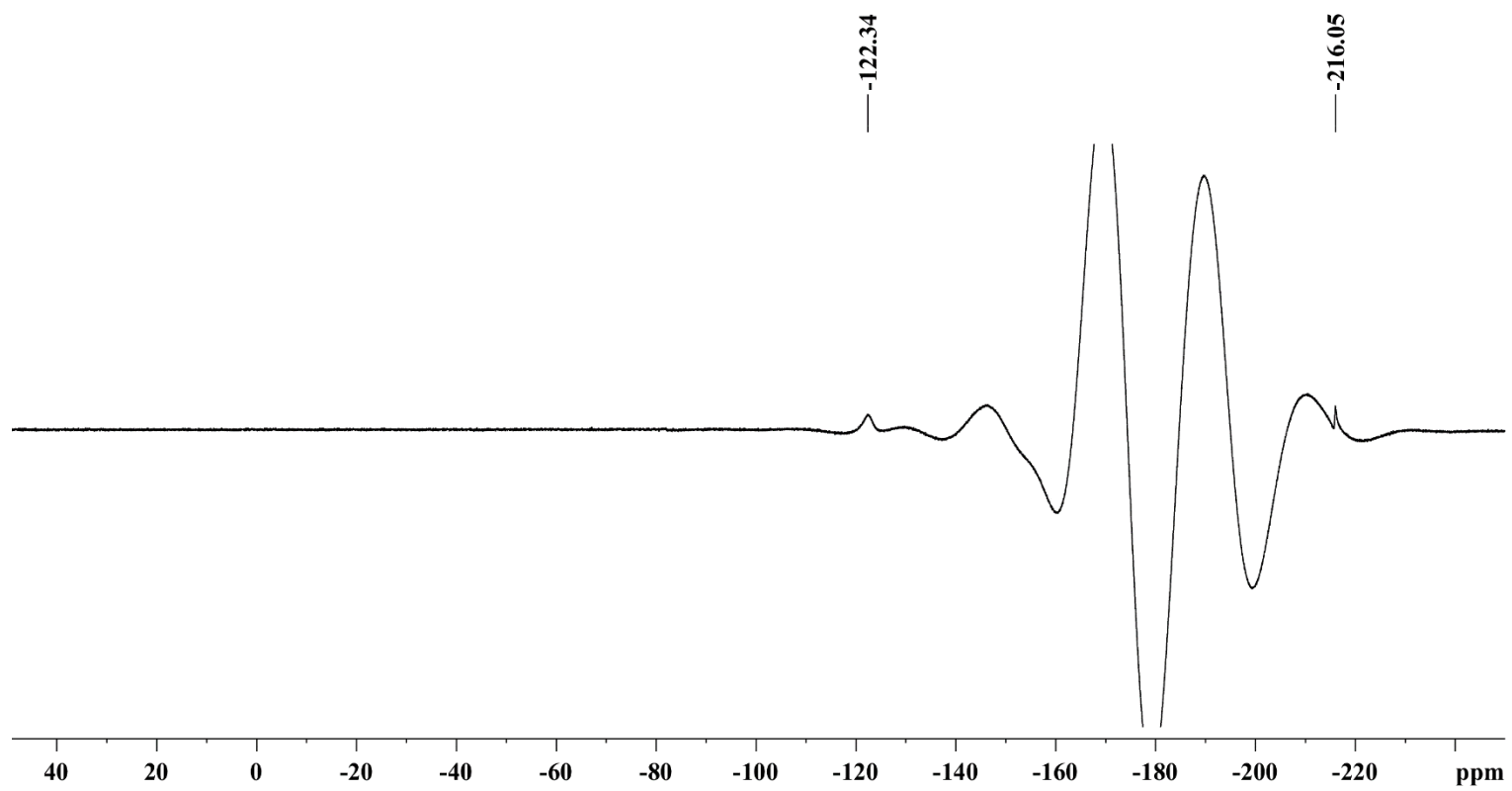


Figure S21. ^{19}F NMR spectrum (471 MHz) of 5_{Dipp} in CD_2Cl_2 at room temperature.

3.5. [BiDipp₂(SPMe₃)(SbF₆)] 6_{Dipp}

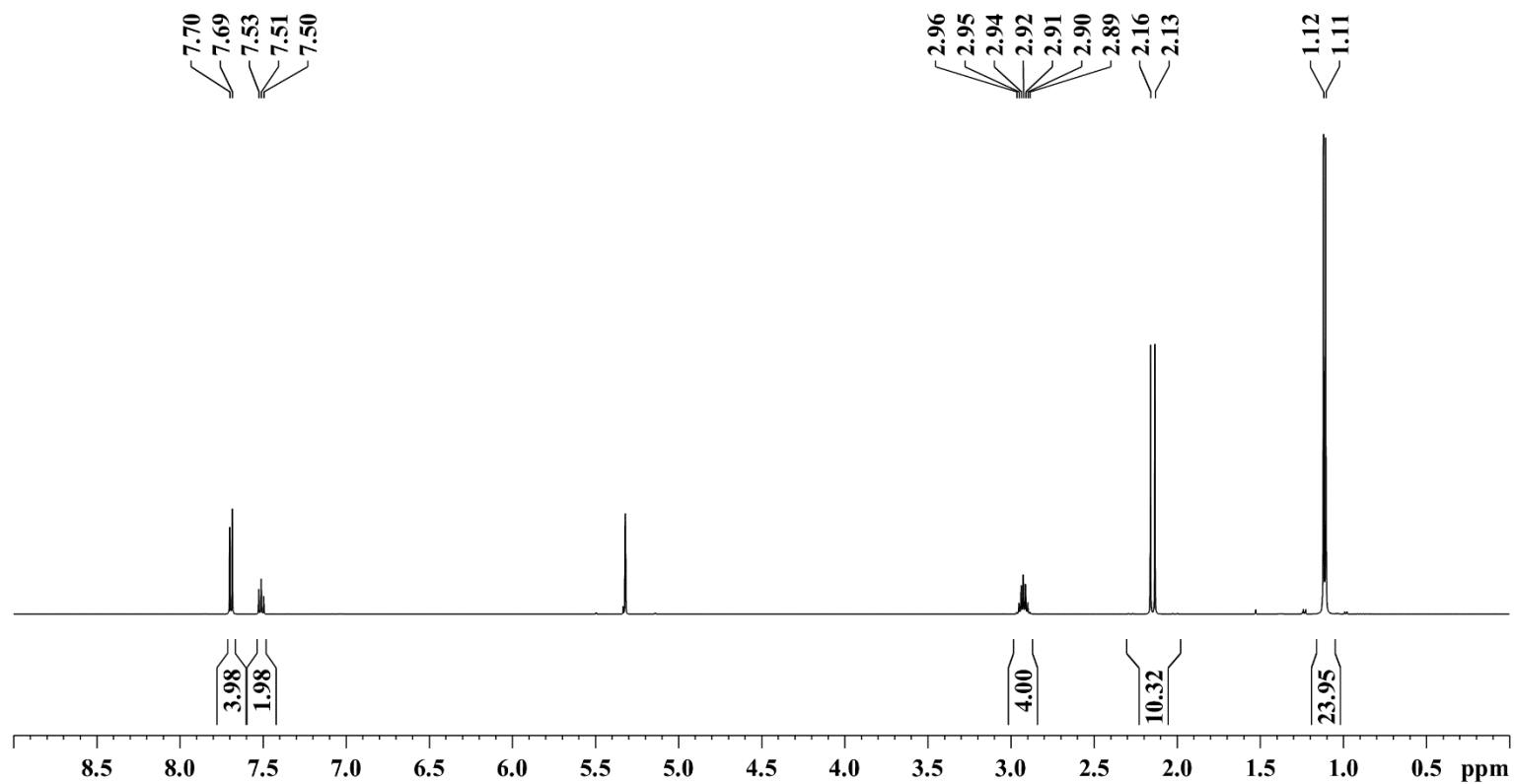


Figure S22. ¹H NMR spectrum (500 MHz) of 6_{Dipp} in CD₂Cl₂ at room temperature.

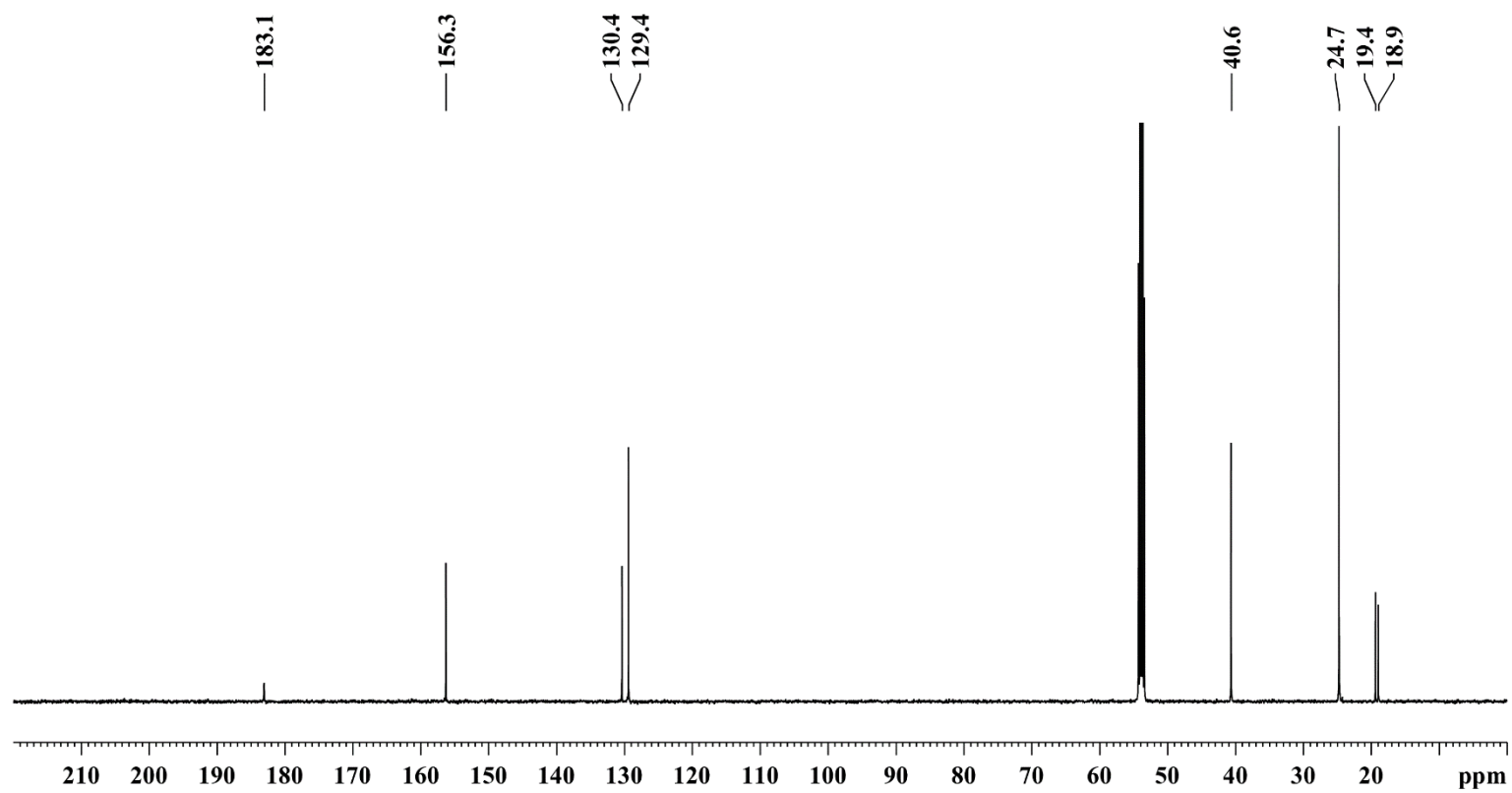


Figure S23. ^{13}C NMR spectrum (125 MHz) of 6_{Dipp} in CD_2Cl_2 at room temperature.

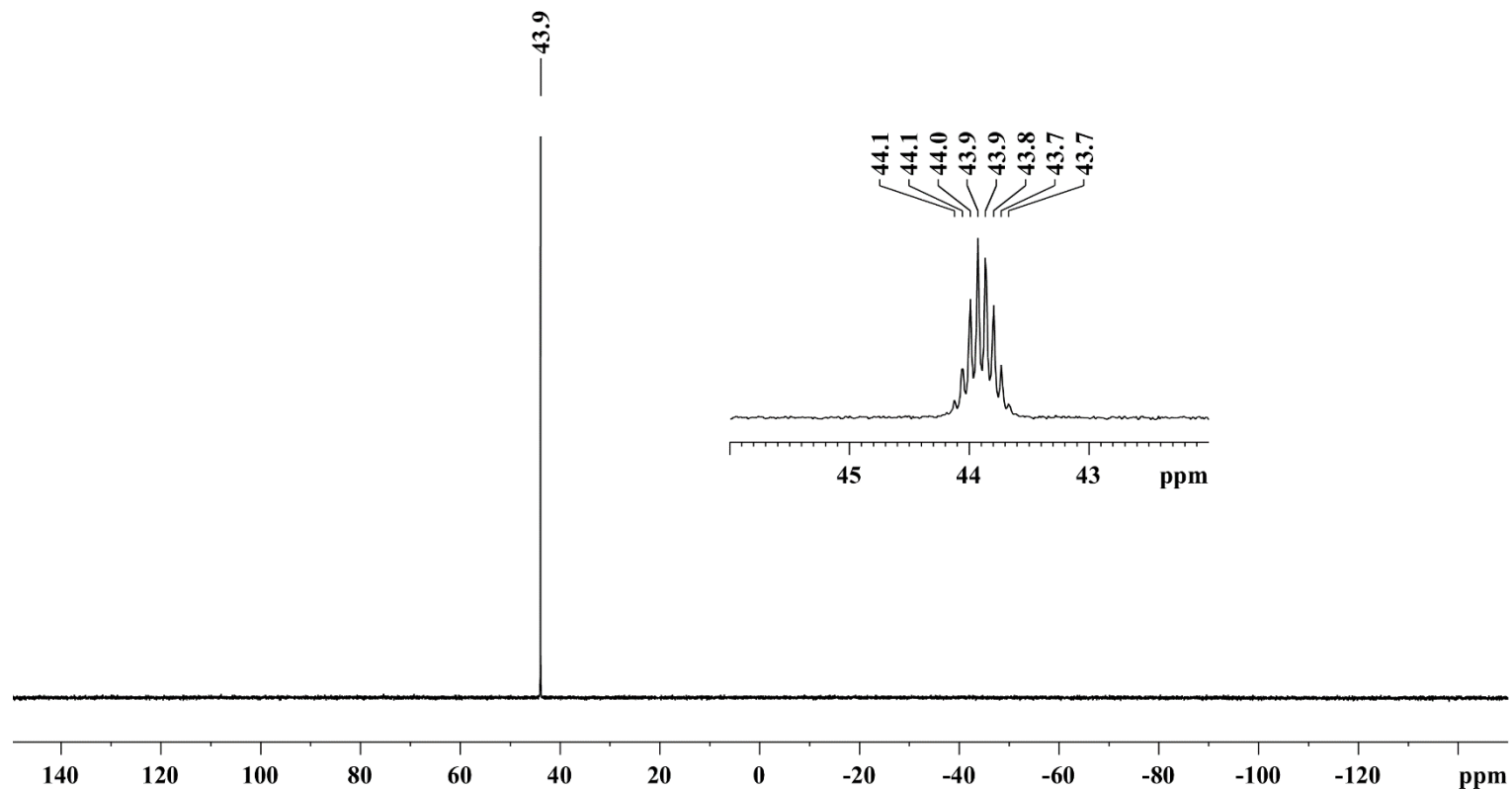


Figure S24. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (202 MHz) of **6_{Dipp}** in CD_2Cl_2 at room temperature (Excerpt: ^{31}P NMR signal).

3.6. [BiDipp₂(SPMe₃)₂(SbF₆)] 6'_{Dipp}

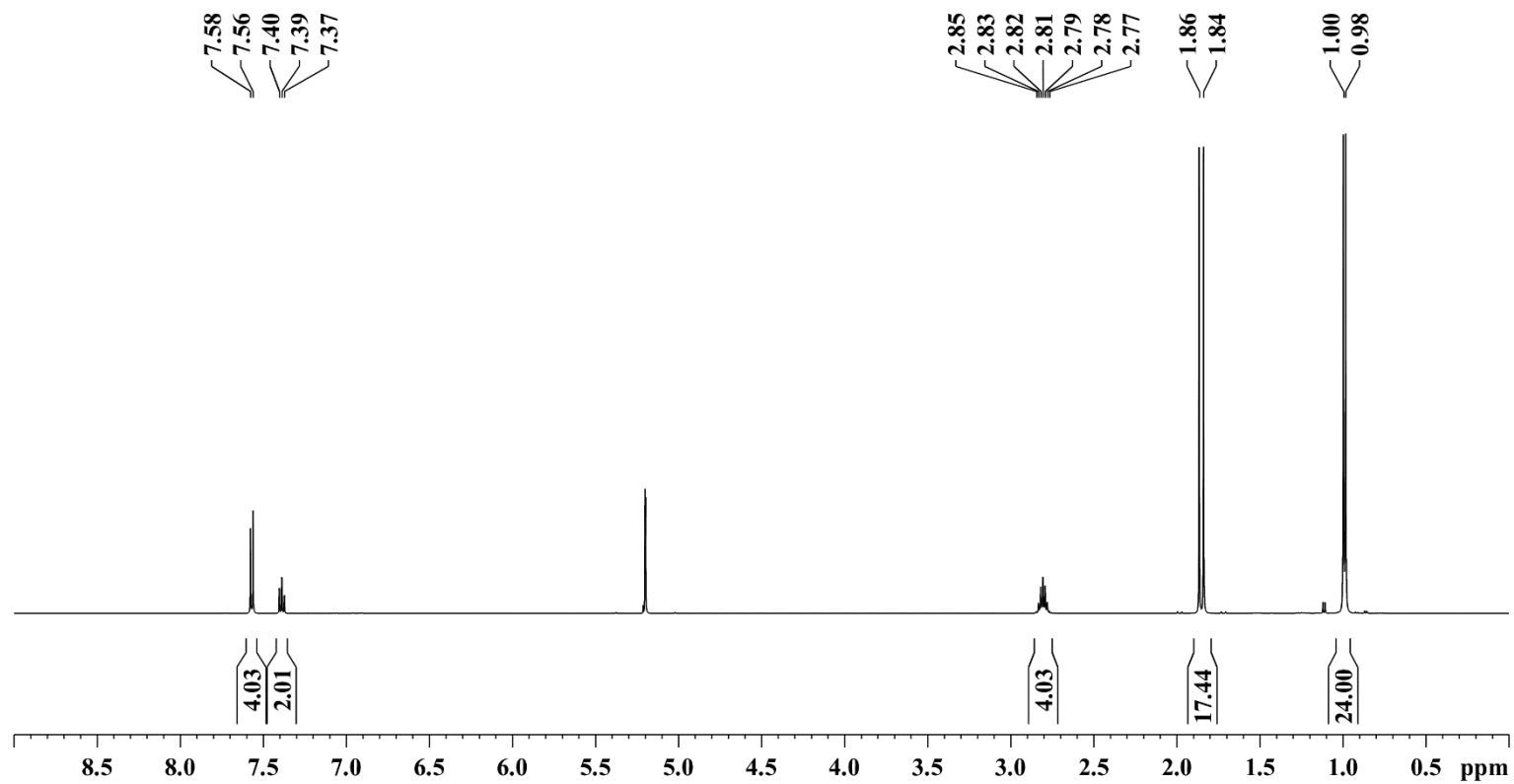


Figure S25. ¹H NMR spectrum (500 MHz) of 6'_{Dipp} in CD₂Cl₂ at room temperature.

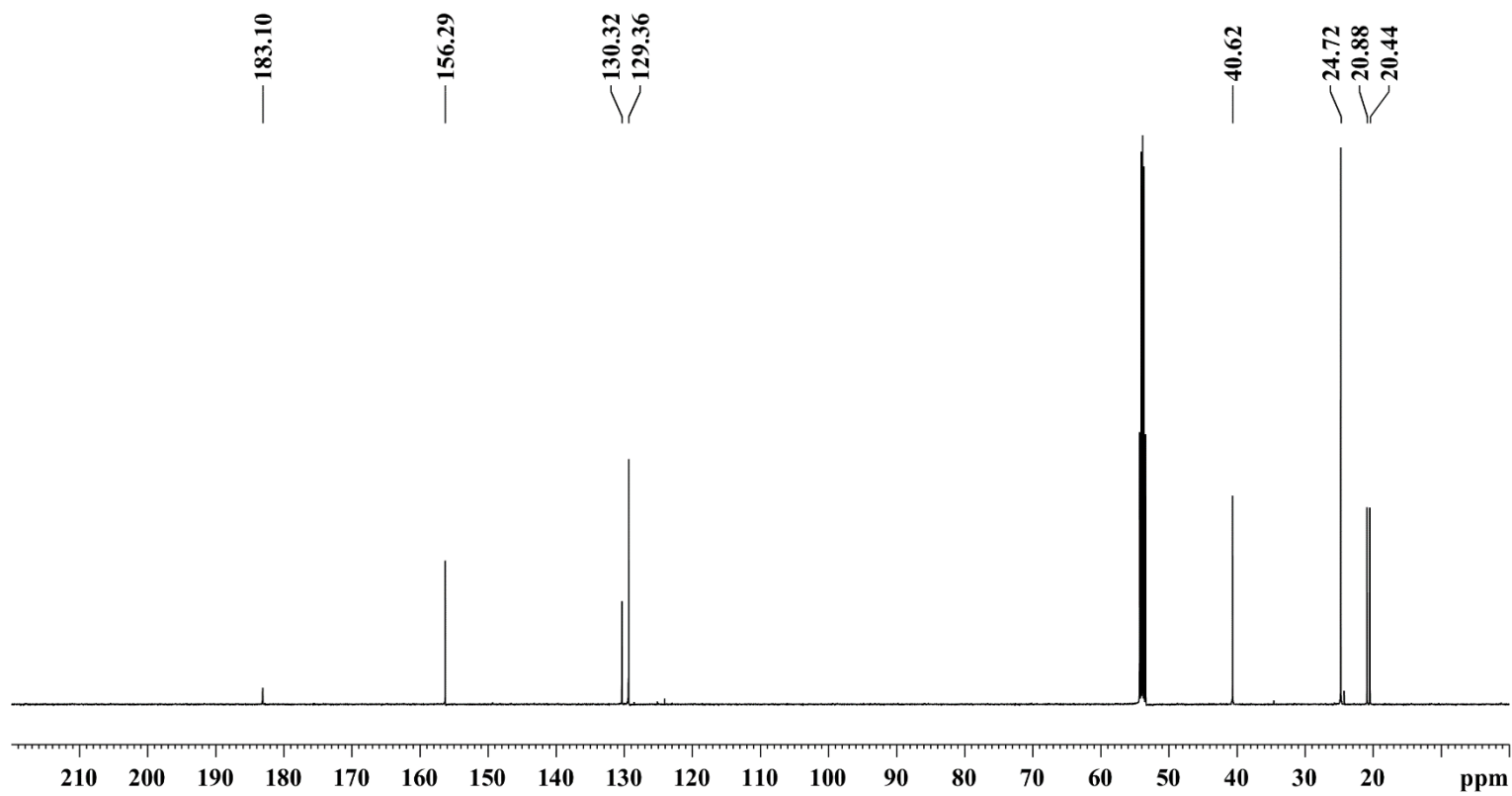


Figure S26. ^{13}C NMR spectrum (125 MHz) of 6^1_{Dipp} in CD_2Cl_2 at room temperature.

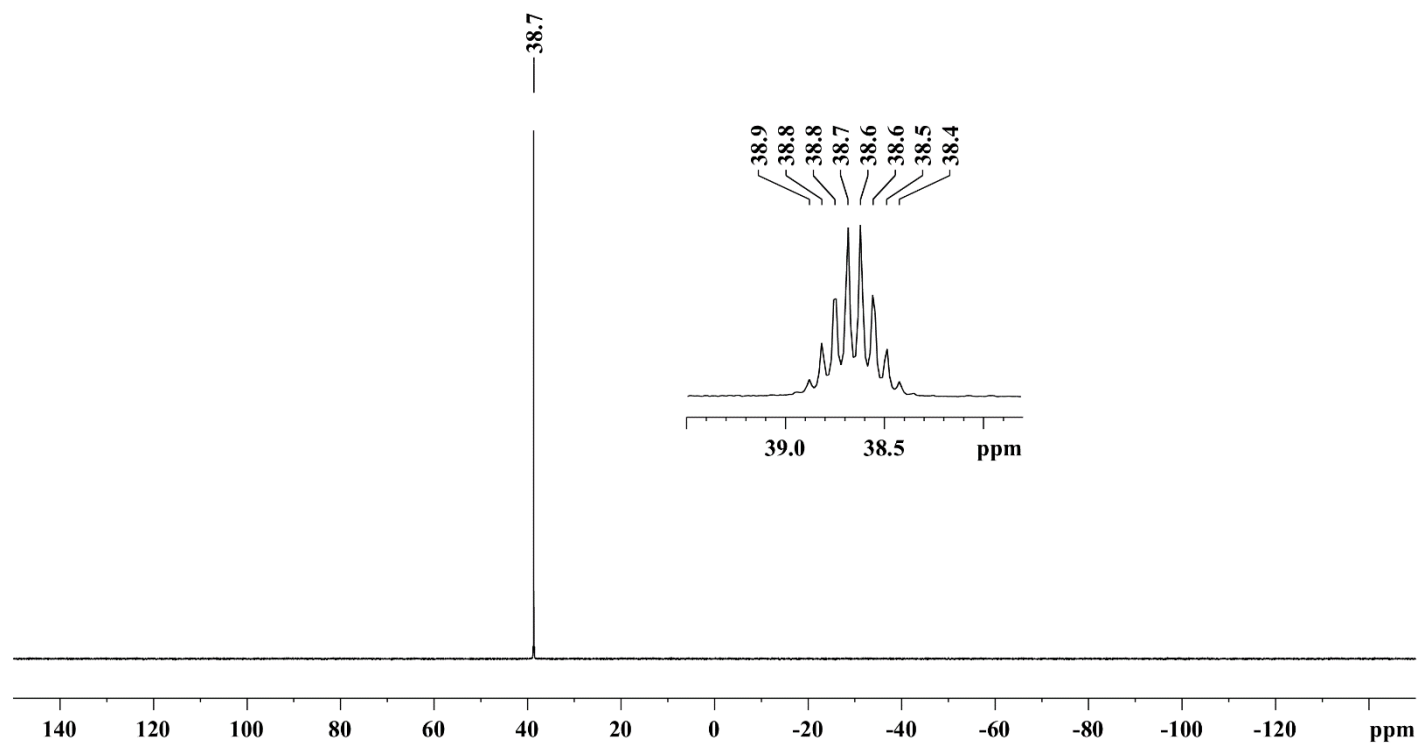


Figure S27. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (125 MHz) of $\mathbf{6}^{\text{Dipp}}$ in CD_2Cl_2 at room temperature (Excerpt: ^{31}P NMR signal).

3.7 [BiMe₂(SPMe₃)(SbF₆)] 6_{Me}

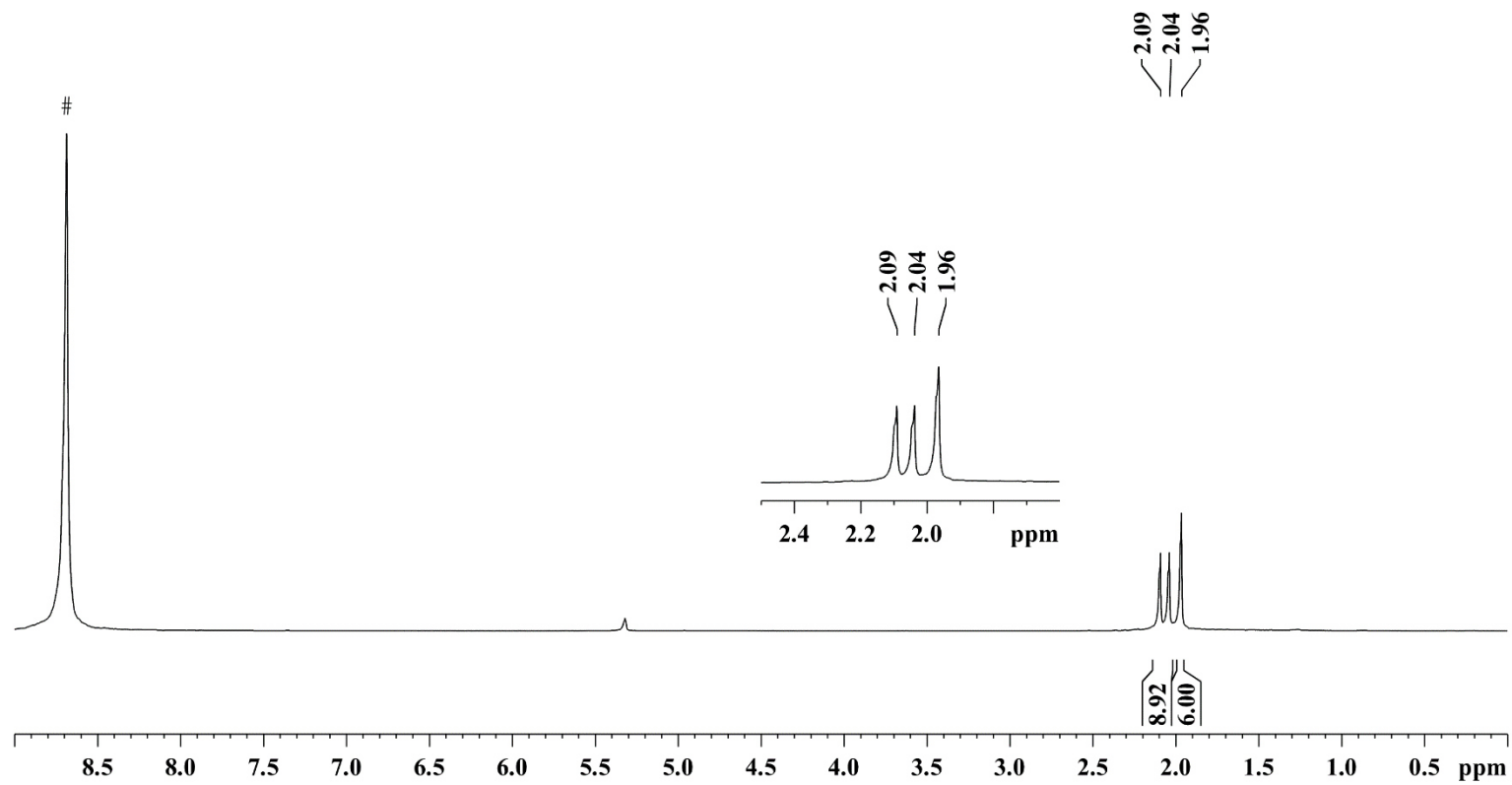


Figure S28. ¹H NMR spectrum (250 MHz) of 6_{Me} in CD₂Cl₂ at room temperature (# = capillary with 85% aqueous H₃PO₄).

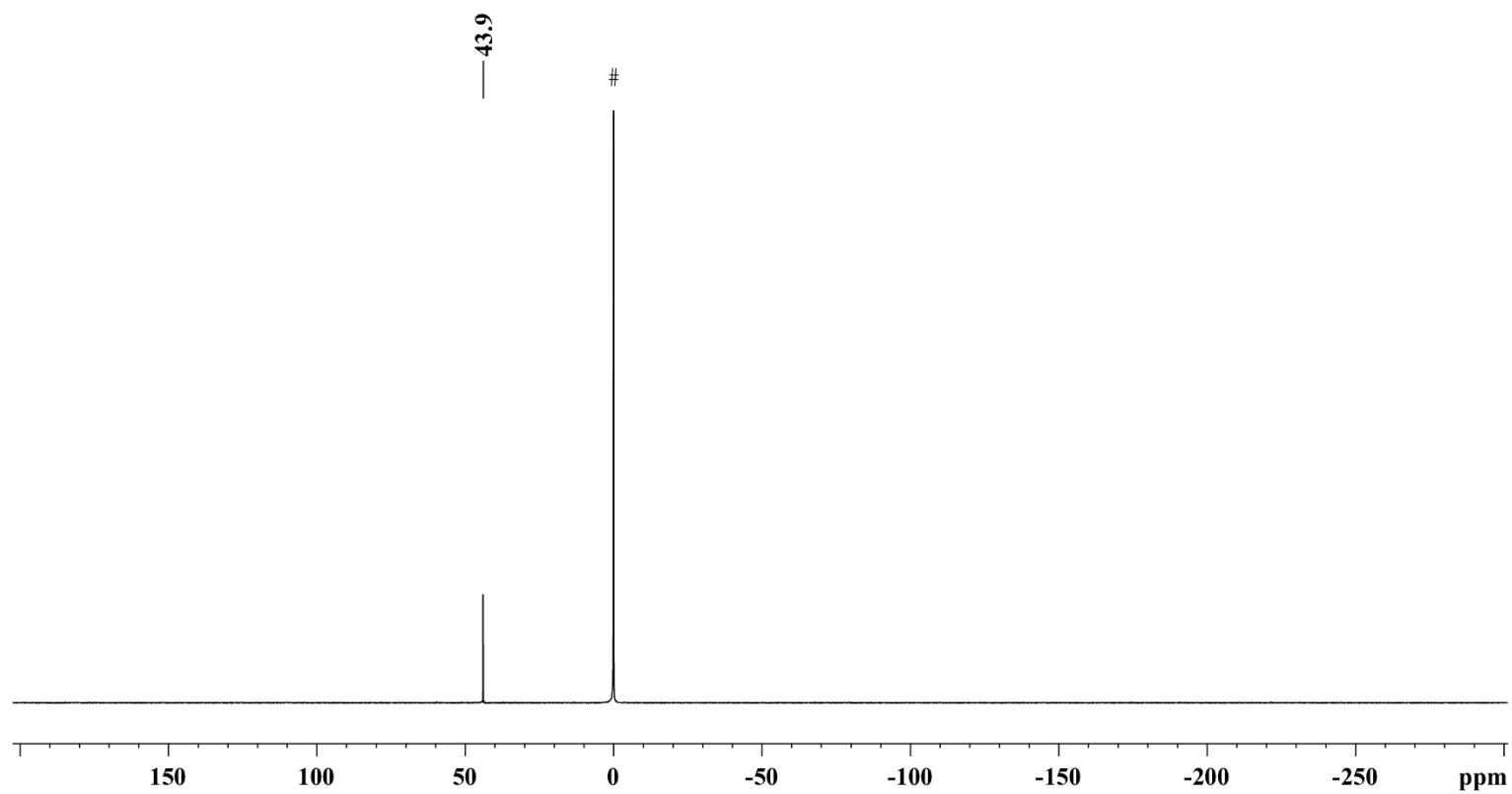


Figure S29. ^{31}P NMR spectrum (101 MHz) of **6_{Me}** in CD_2Cl_2 at room temperature (# = capillary with 85% aqueous H_3PO_4).

3.8 [BiMe₂(SPMe)₂(SbF₆)] 6'_{Me}

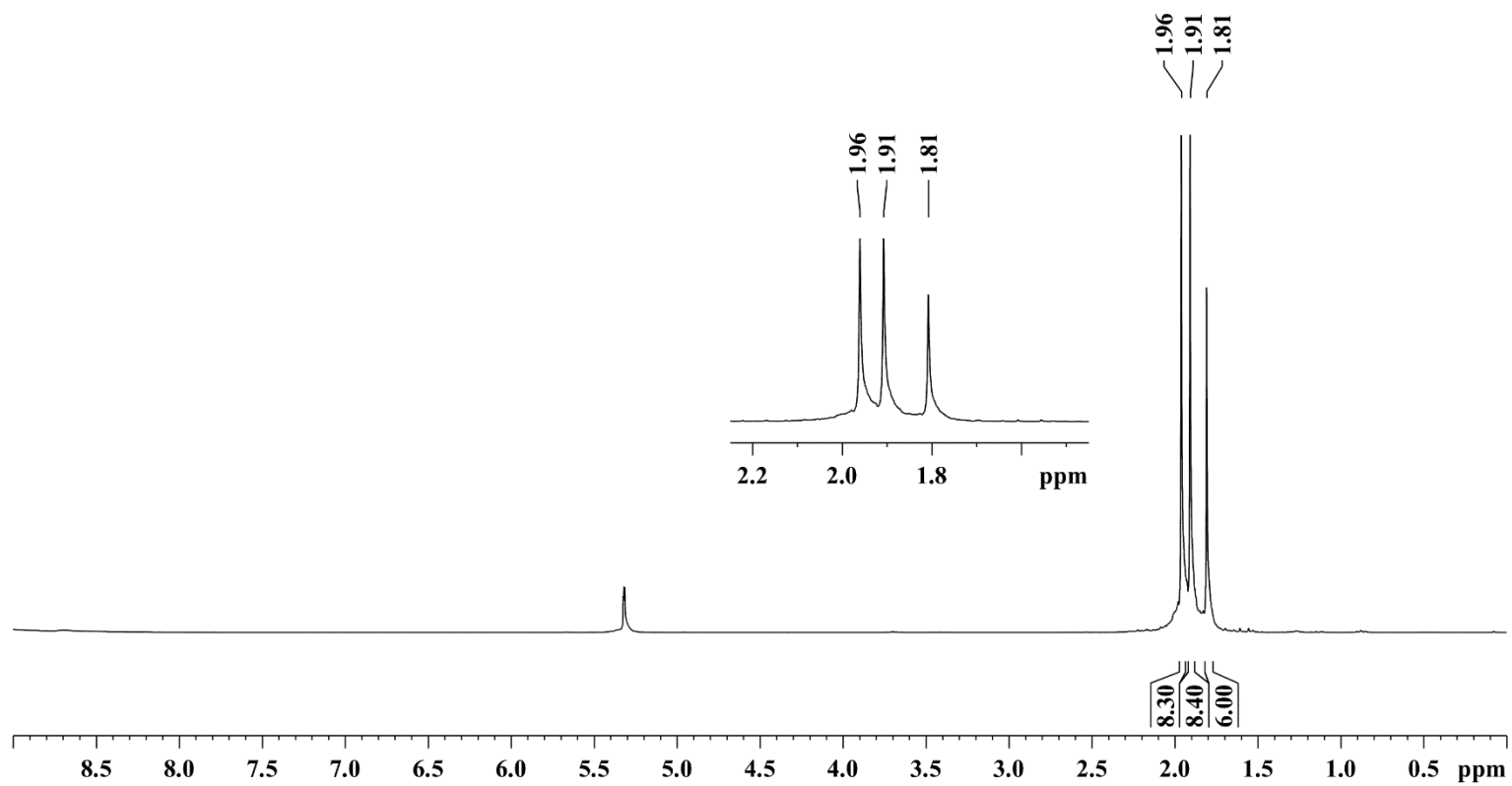


Figure S30. ¹H NMR spectrum (250 MHz) of 6'_{Me} in CD₂Cl₂ at room temperature.

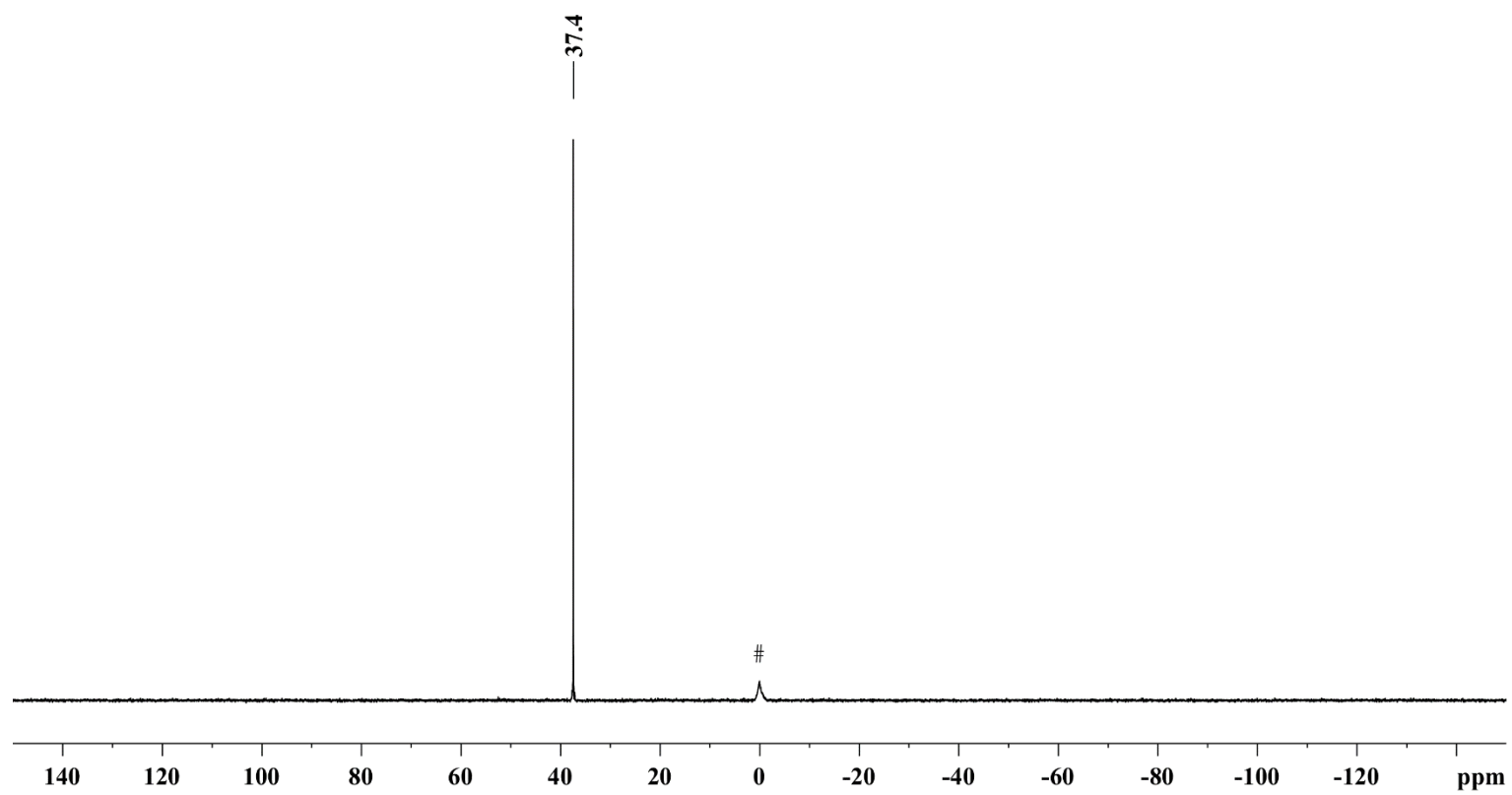


Figure S31. ^{31}P NMR spectrum (101 MHz) of **6'**_{Me} in CD_2Cl_2 at room temperature (# = capillary with 85% aqueous H_3PO_4).

3.9 [BiDipp₂(SePMe₃)(SbF₆)] 7_{Dipp}

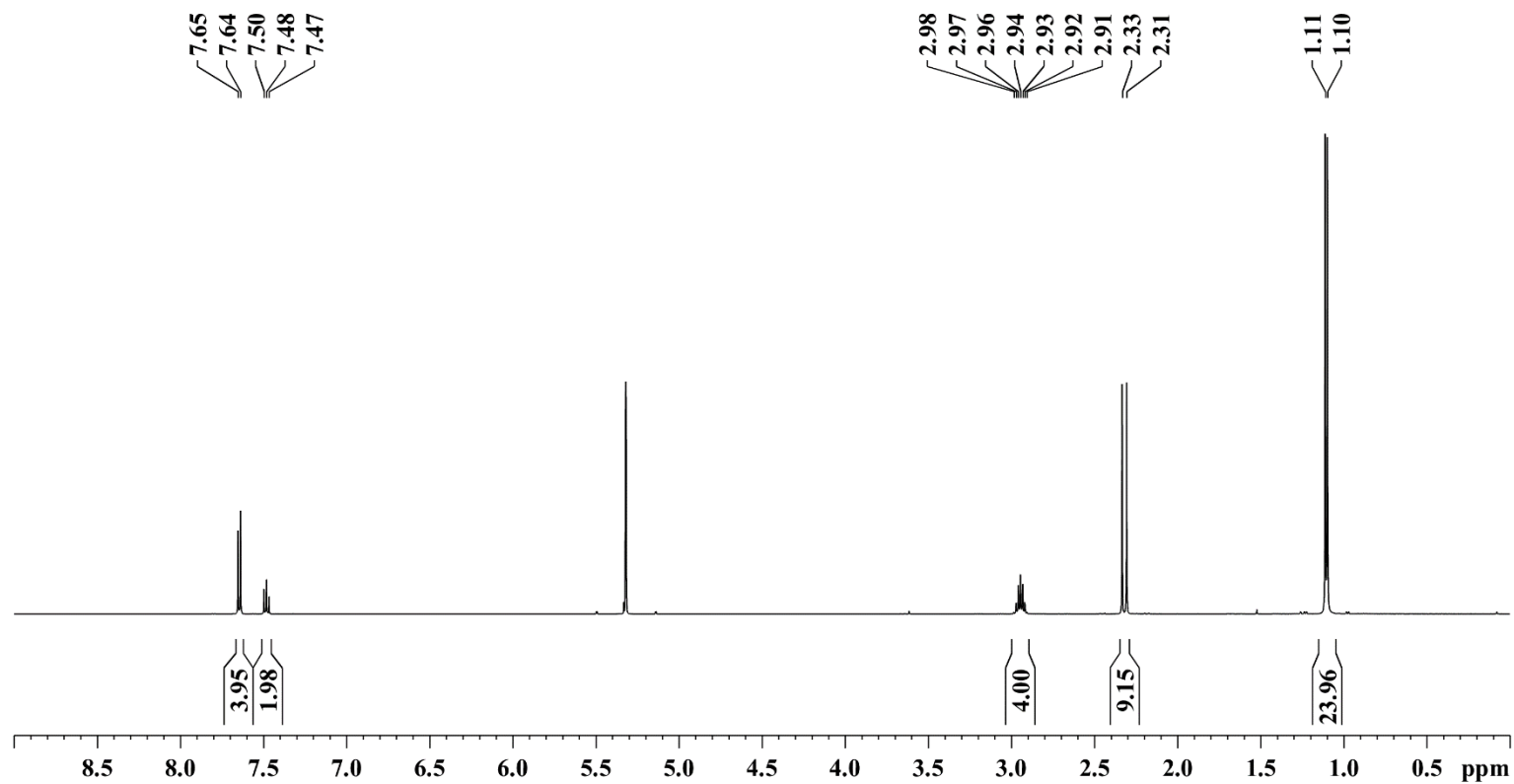


Figure S32. ¹H NMR spectrum (500 MHz) of 7_{Dipp} in CD₂Cl₂ at room temperature.

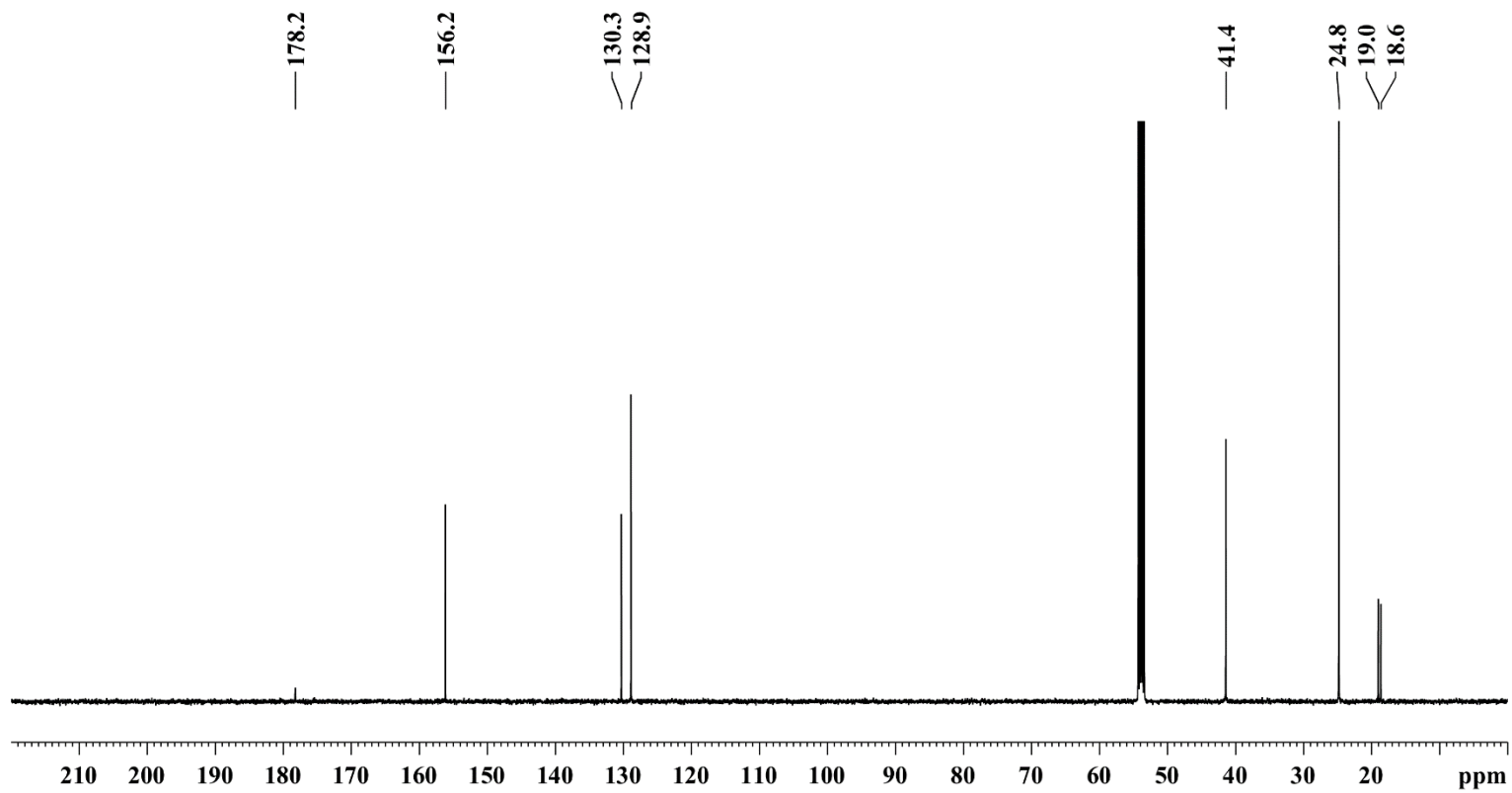


Figure S33. ^{13}C NMR spectrum (125 MHz) of **7_{Dipp}** in CD_2Cl_2 at room temperature.

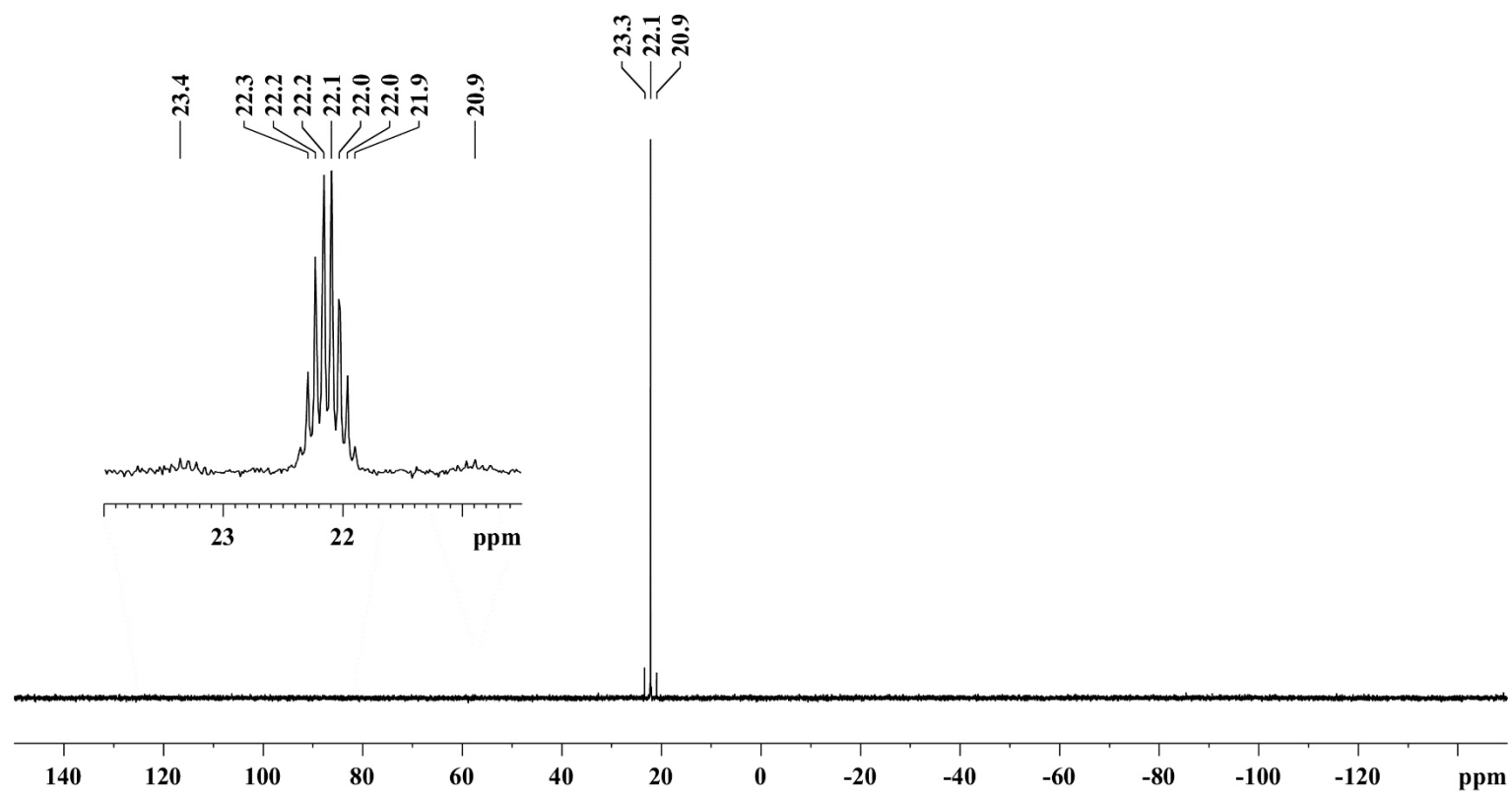


Figure S34. ^{31}P $\{^1\text{H}\}$ NMR spectrum (202 MHz) of 7_{Dipp} in CD_2Cl_2 at room temperature (Excerpt: ^{31}P NMR signal).

3.10 [BiDipp₂(SePMe₃)₂(SbF₆)] 7'_{Dipp}

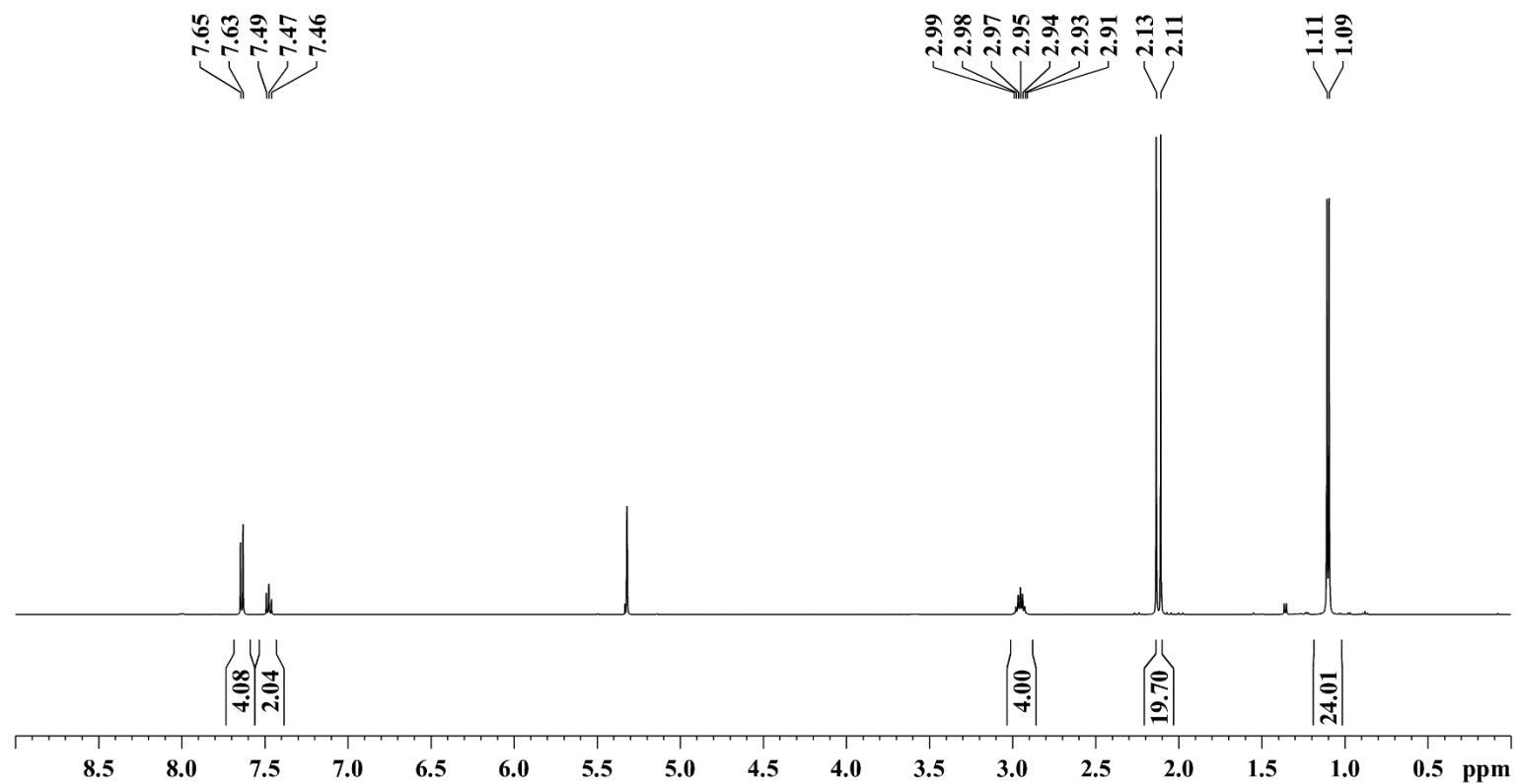


Figure S35. ¹H NMR spectrum (500 MHz) of 7'_{Dipp} in CD₂Cl₂ at room temperature.

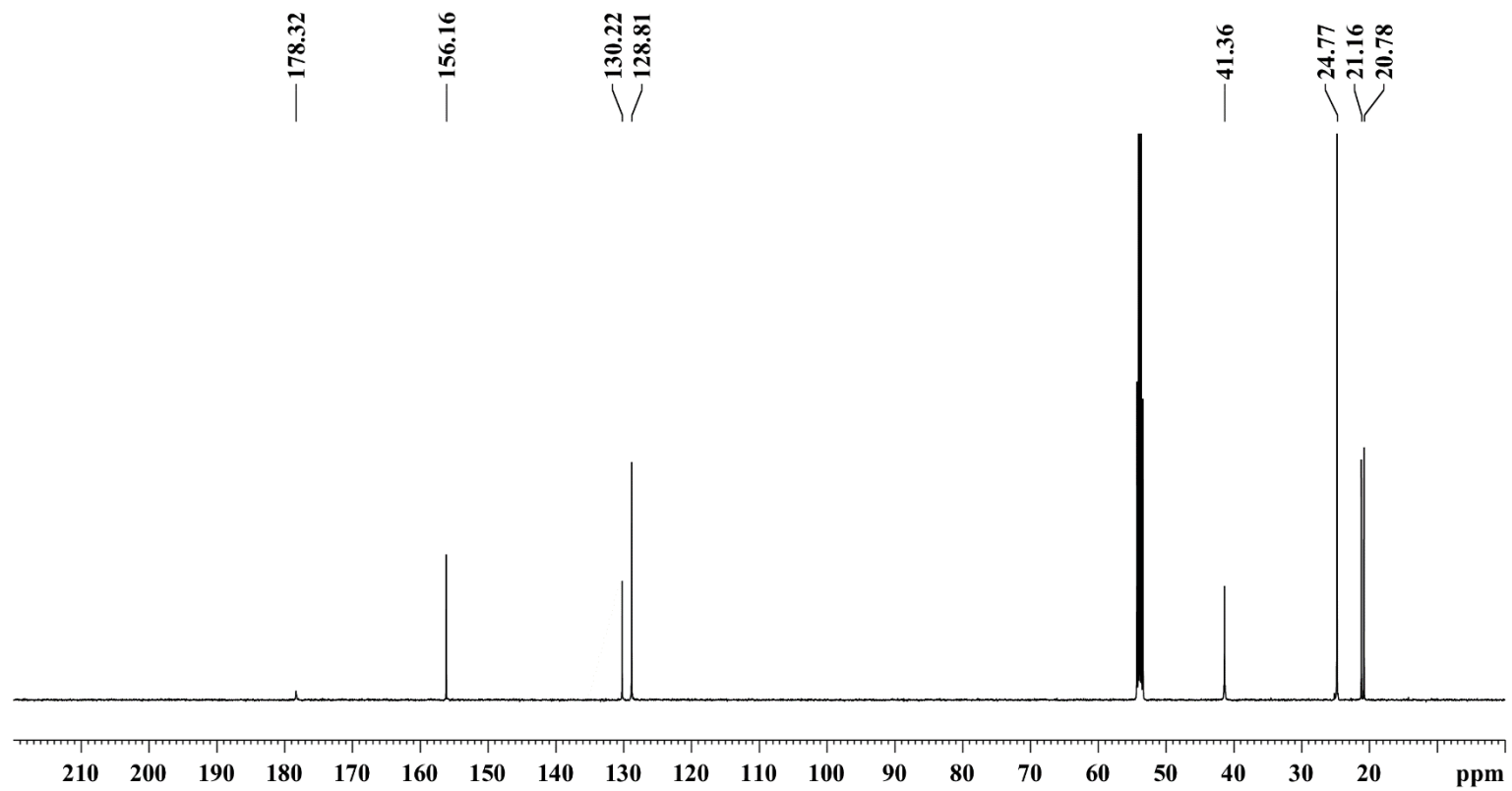


Figure S36. ^{13}C NMR spectrum (125 MHz) of 7^{Dipp} in CD_2Cl_2 at room temperature.

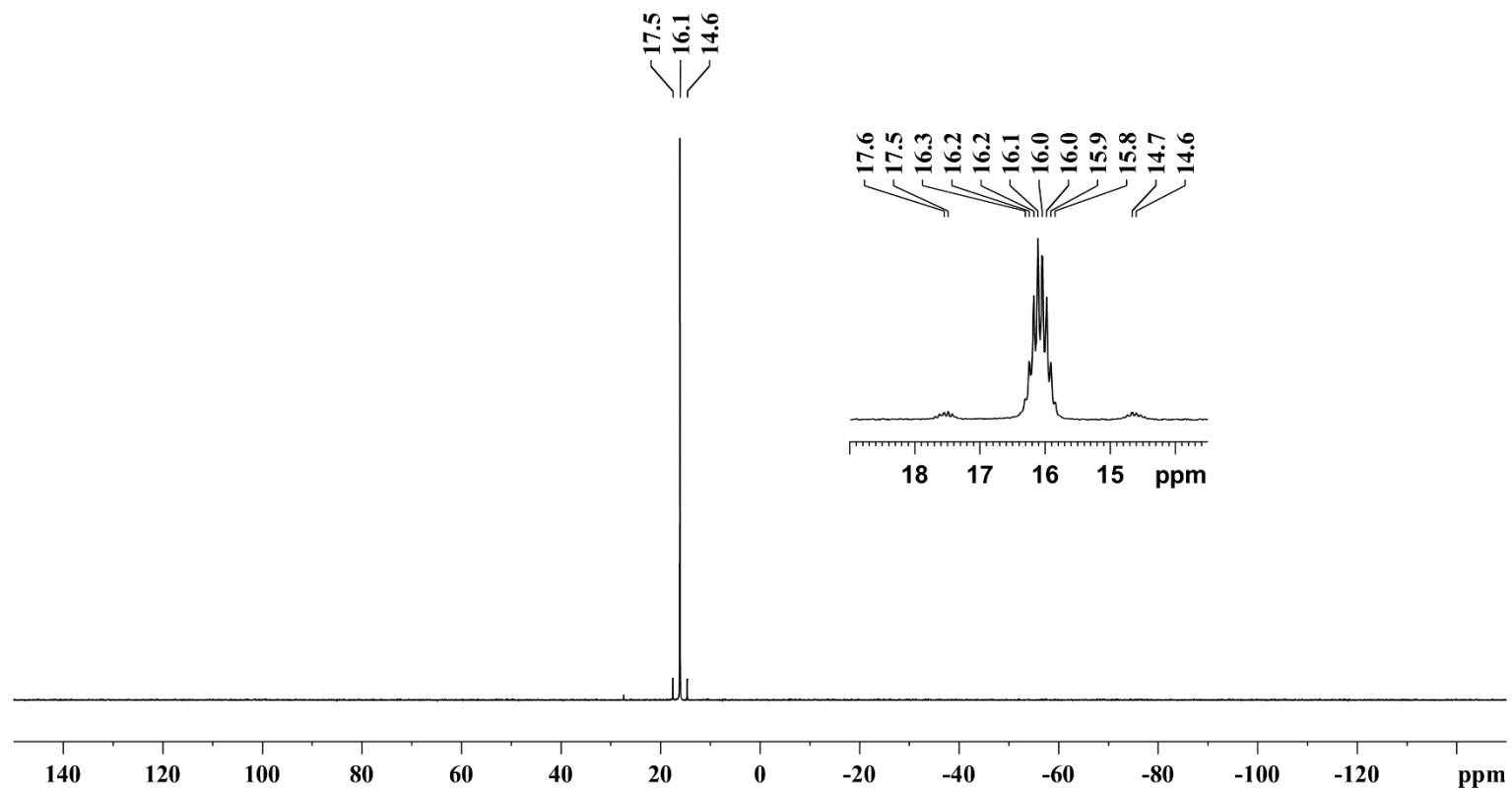


Figure S37. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (202 MHz) of $7'\text{Dipp}$ in CD_2Cl_2 at room temperature (excerpt: ^{31}P NMR signal).

3.11. $[\text{BiMe}_2(\text{SePMe}_3)_2(\text{SbF}_6)] \cdot 7\text{Me}$

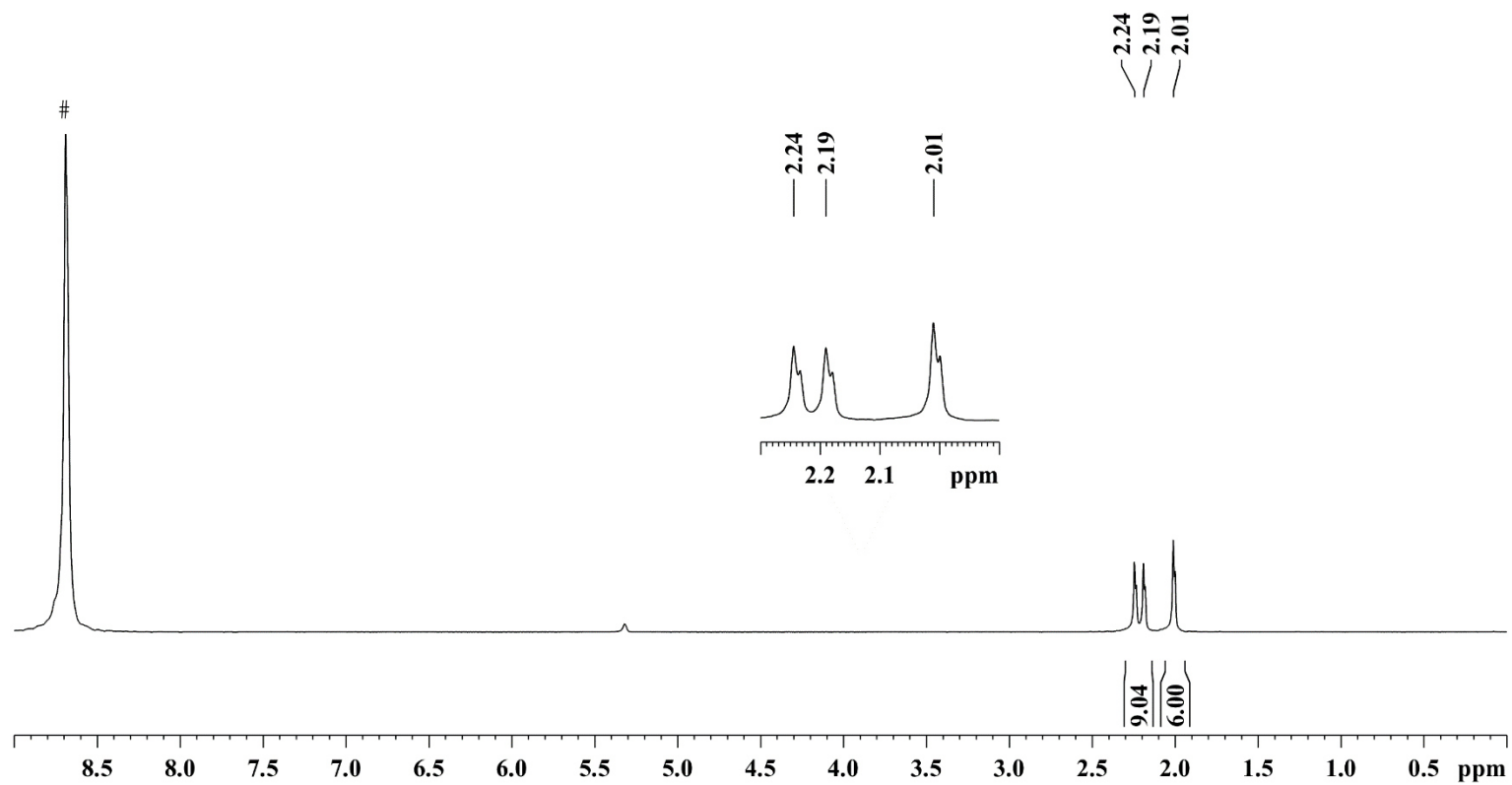


Figure S38. ^1H NMR spectrum (250 MHz) of 7Me in CD_2Cl_2 at room temperature (# = capillary with 85% aqueous H_3PO_4).

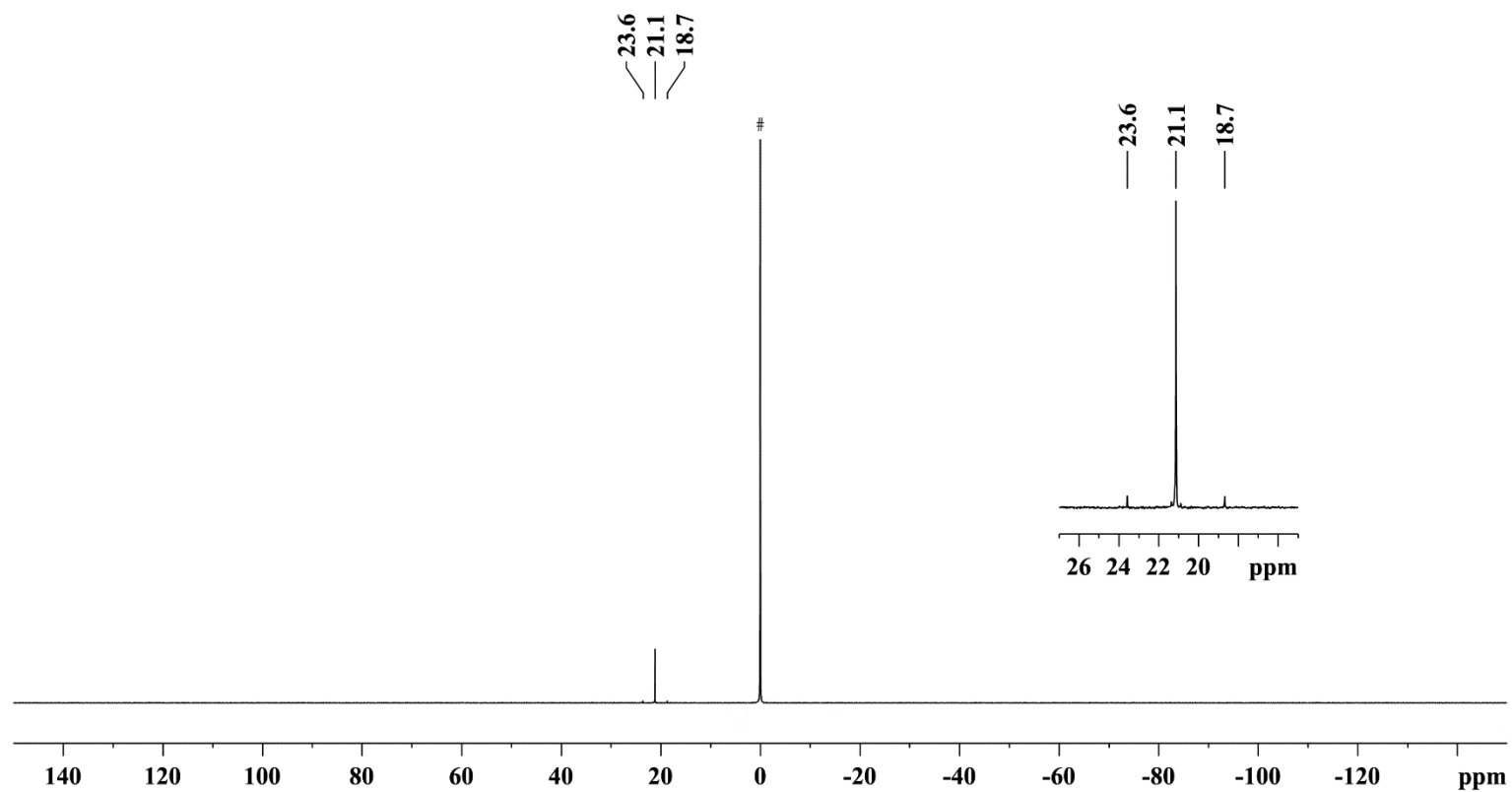


Figure S39. ^{31}P NMR spectrum (101 MHz) of 7_{Me} in CD_2Cl_2 at room temperature (# = capillary with 85% aqueous H_3PO_4).

3.12. $[\text{BiMe}_2(\text{SePMe}_3)_2(\text{SbF}_6)] \mathbf{7}'_{\text{Me}}$

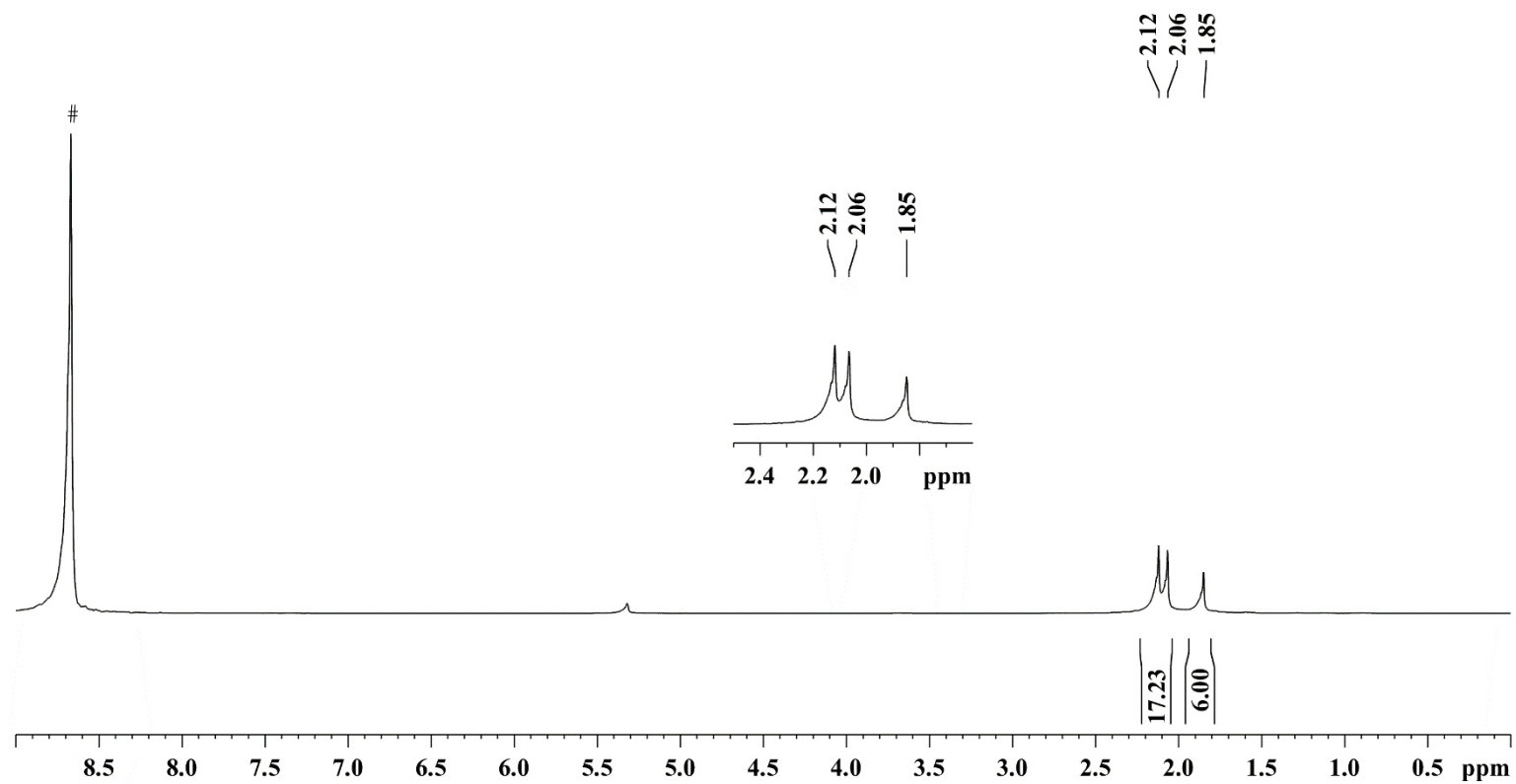


Figure S40. ^1H NMR spectrum (250 MHz) of $\mathbf{7}'_{\text{Me}}$ in CD_2Cl_2 at room temperature (# = capillary with 85% aqueous H_3PO_4).

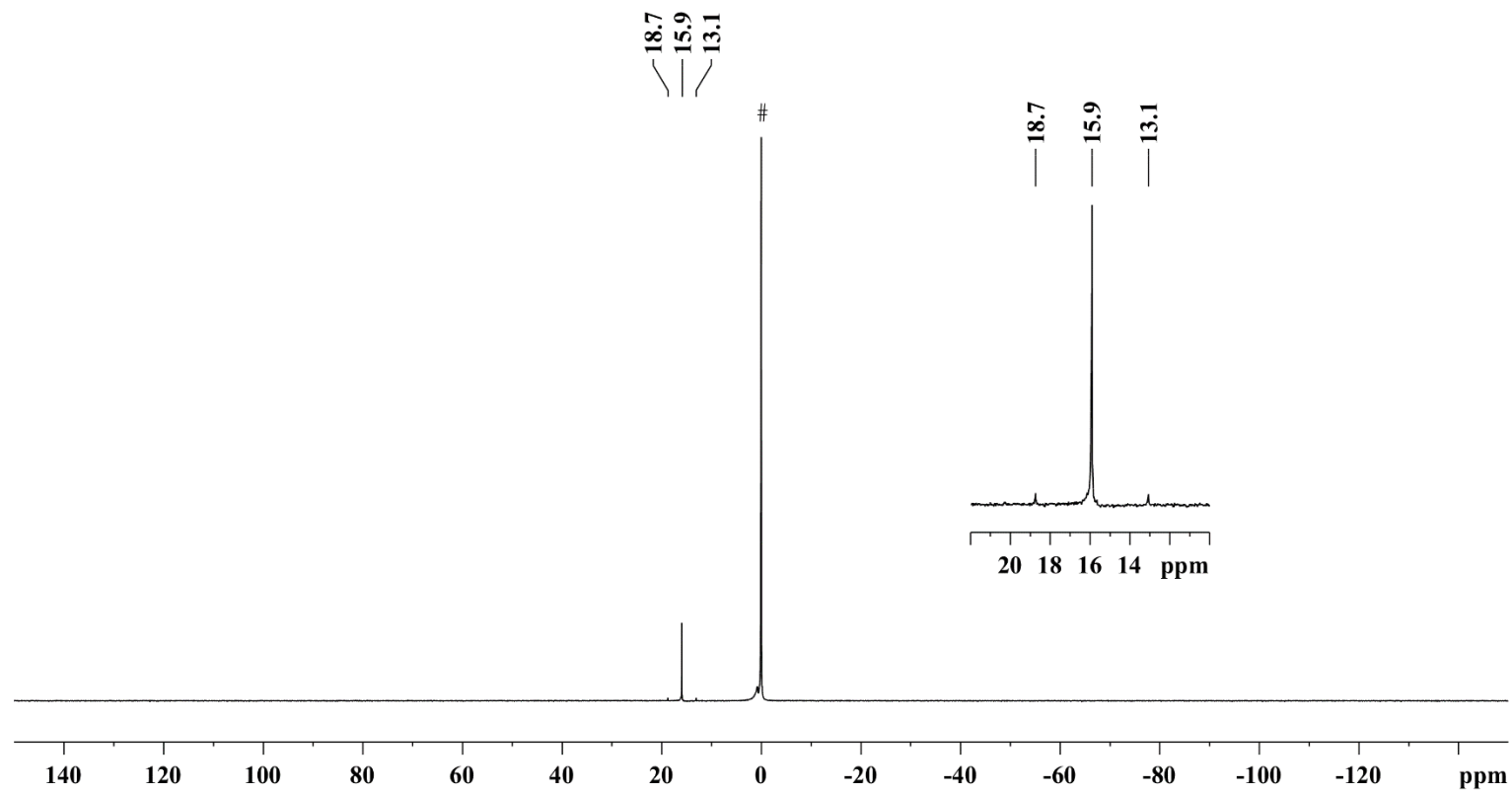


Figure S41. ^{31}P NMR spectrum (101 MHz) of $7'\text{Me}$ in CD_2Cl_2 at room temperature (# = capillary with 85% aqueous H_3PO_4).

3.13 [BiDipp₂(OPEt₃)(SbF₆)] 8_{Dipp}

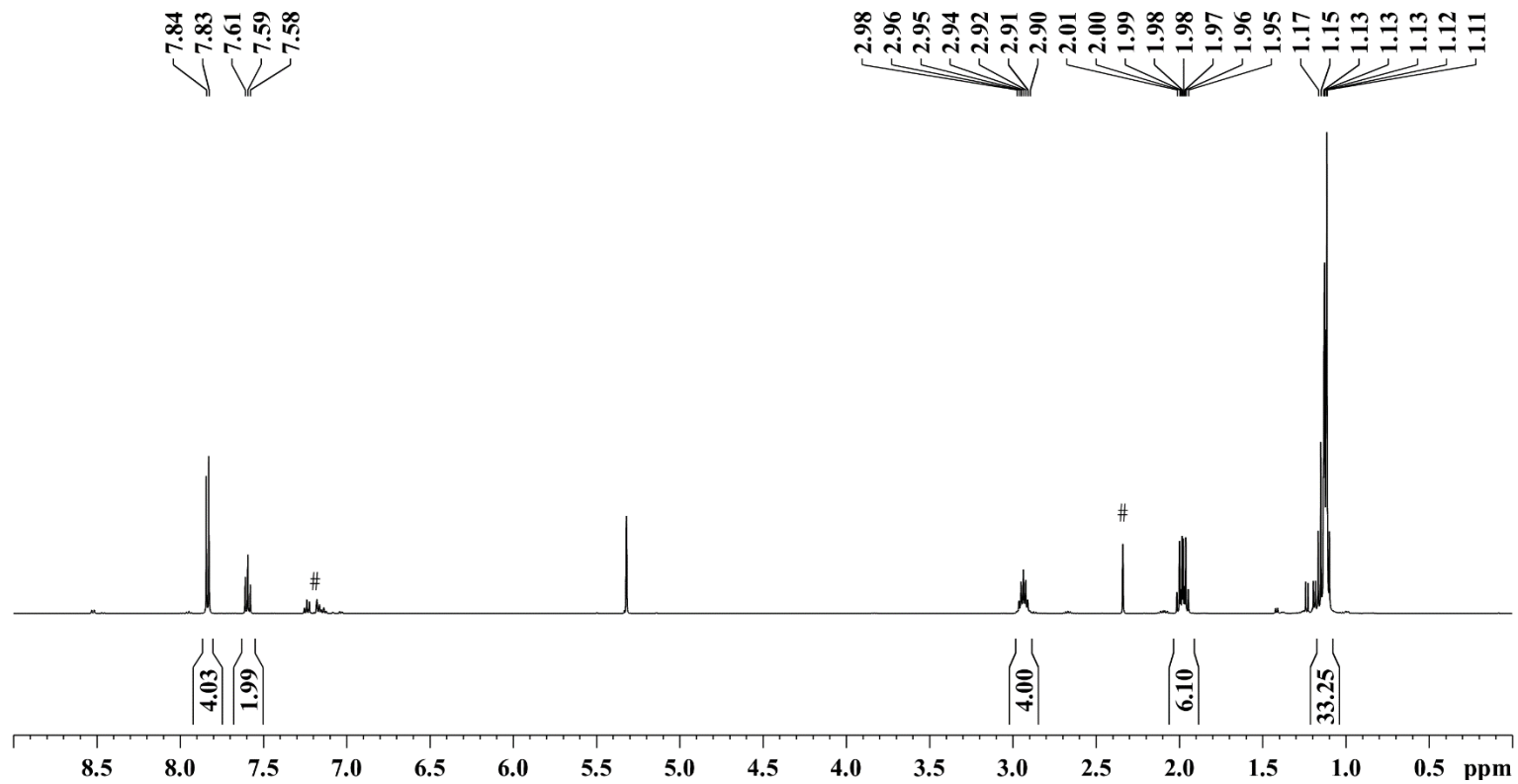


Figure S42. ¹H NMR spectrum (500 MHz) of 8_{Dipp} in CD₂Cl₂ at room temperature (# = toluene).

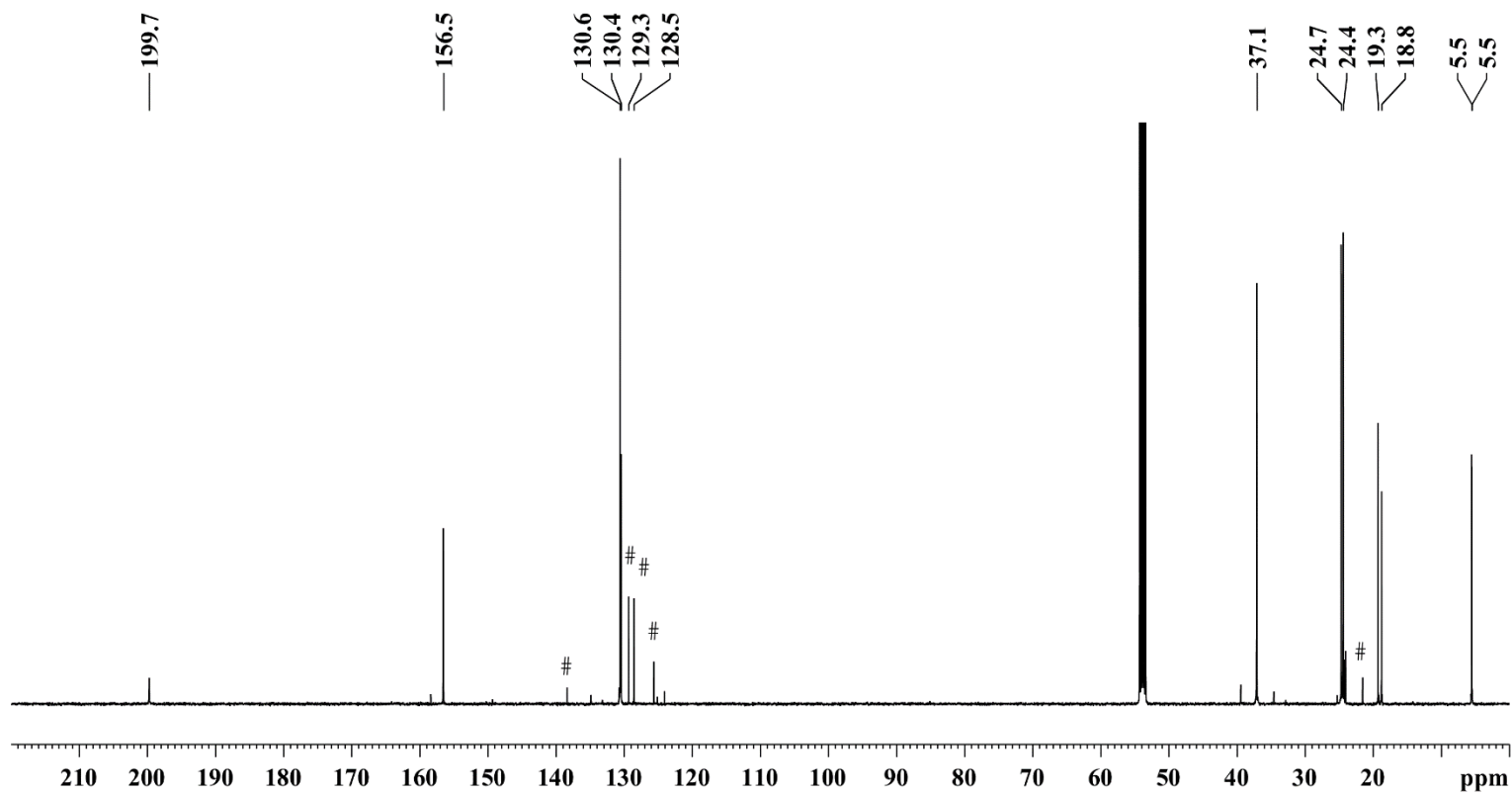


Figure S43. ^{13}C NMR spectrum (125 MHz) of **8_{Dipp}** in CD_2Cl_2 at room temperature (# = toluene).

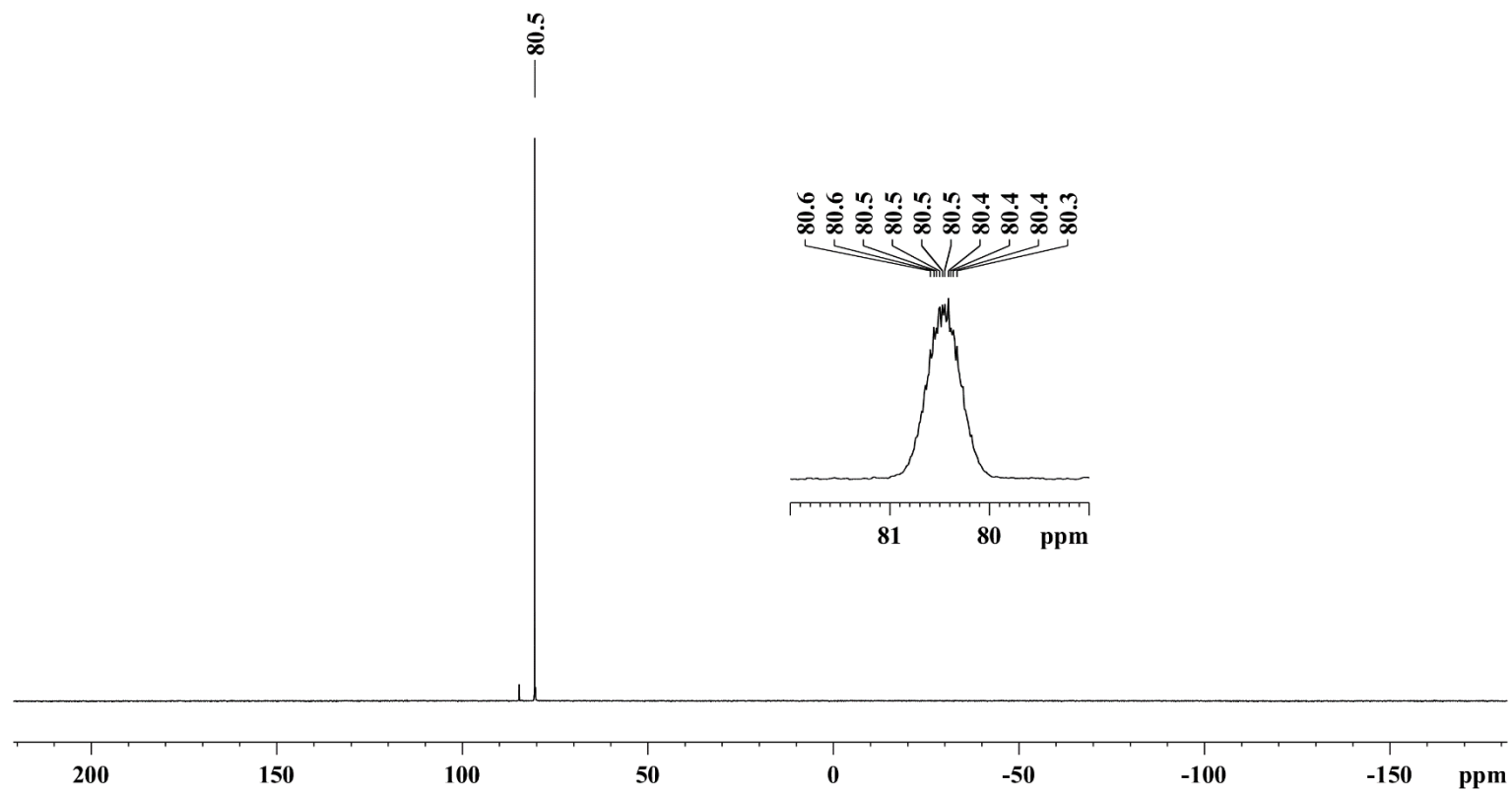


Figure S44. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (202 MHz) of **8_{Dipp}** in CD_2Cl_2 at room temperature (Excerpt: ^{31}P NMR signal).

[BiDipp₂(OPEt₃)₂(SbF₆)] 8'_{Dipp}

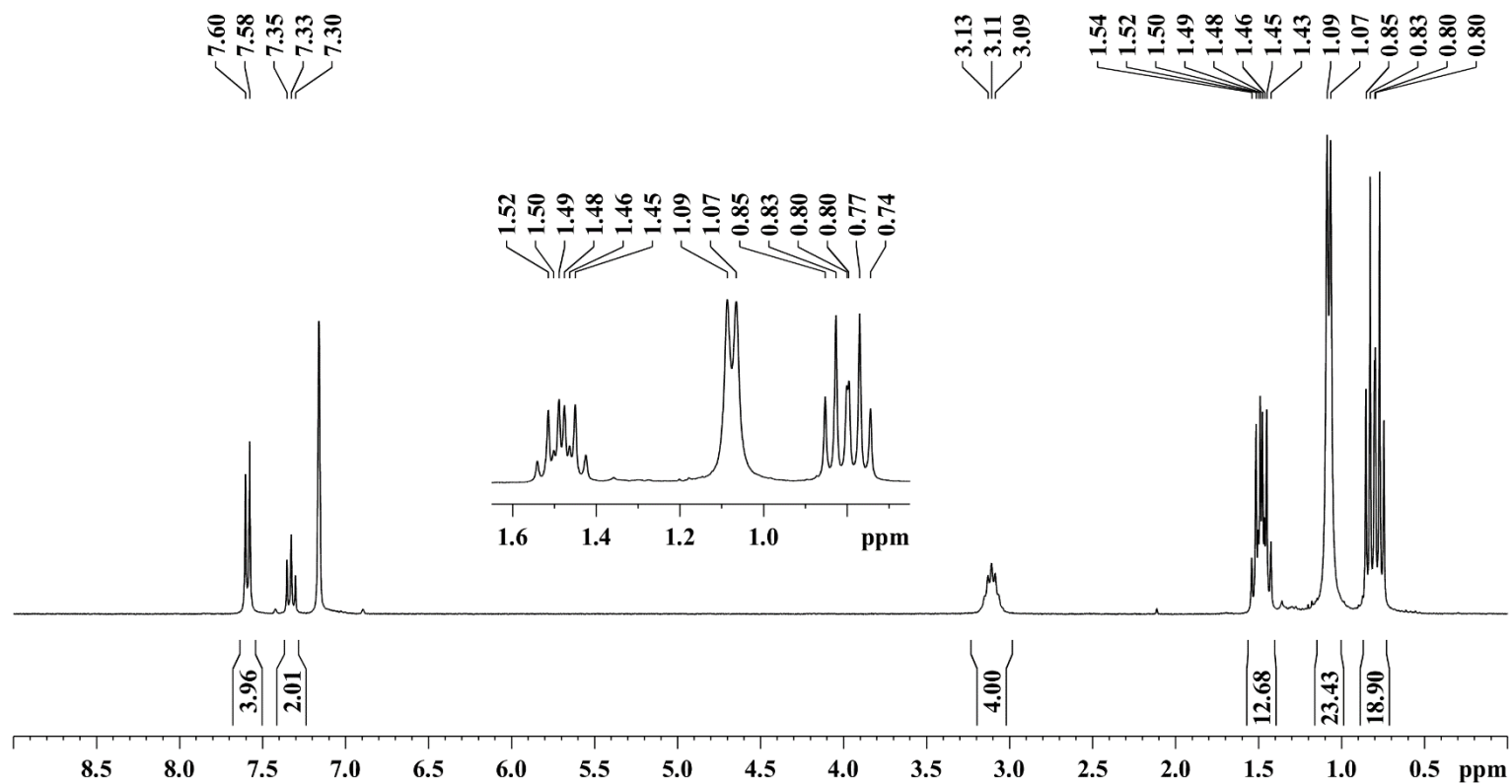


Figure S45. ¹H NMR spectrum (500 MHz) of 8'_{Dipp} in C₆D₆ at room temperature.

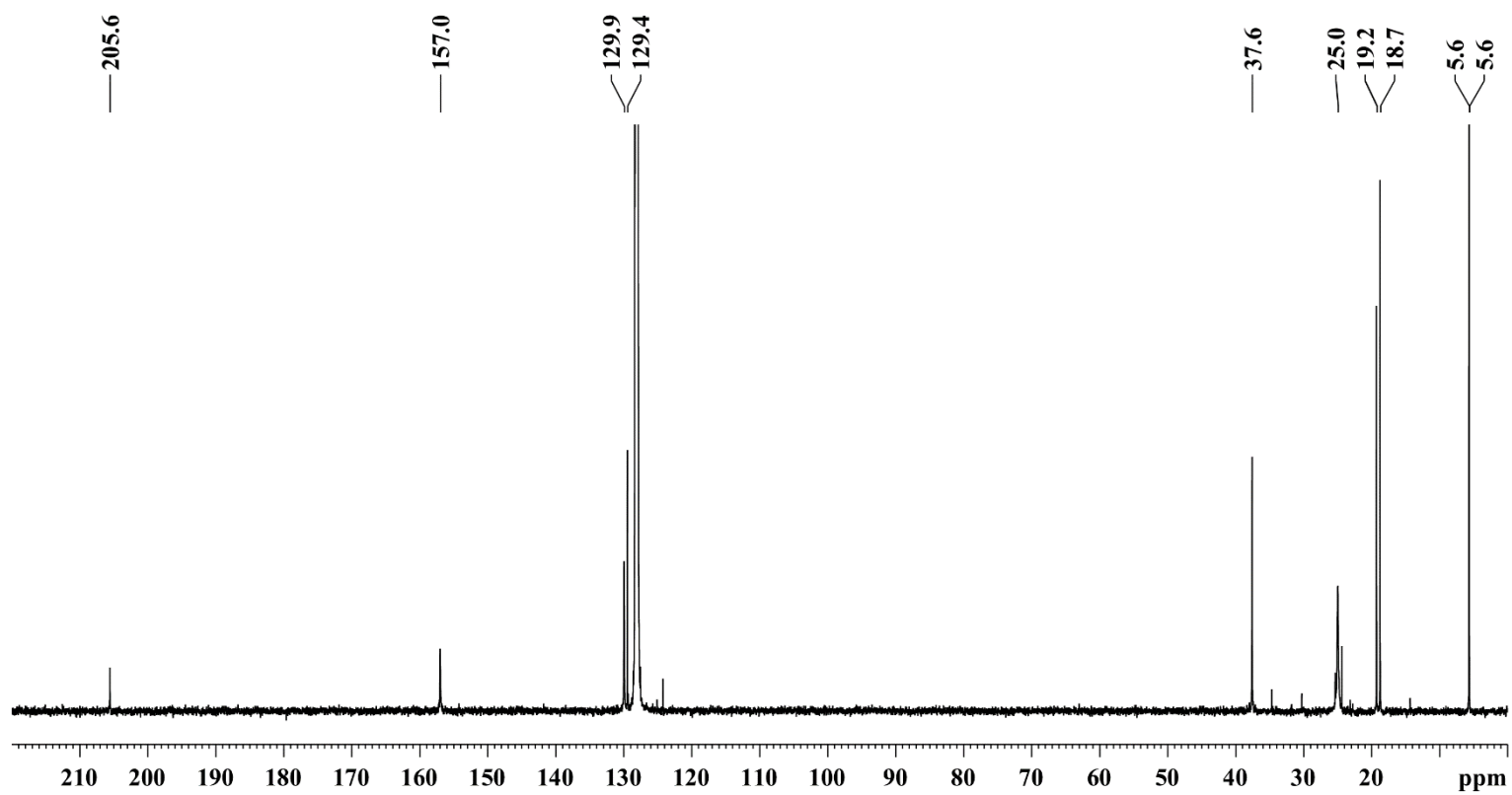


Figure S46. ^{13}C NMR spectrum (125 MHz) of $8'\text{Dipp}$ in C_6D_6 at room temperature.

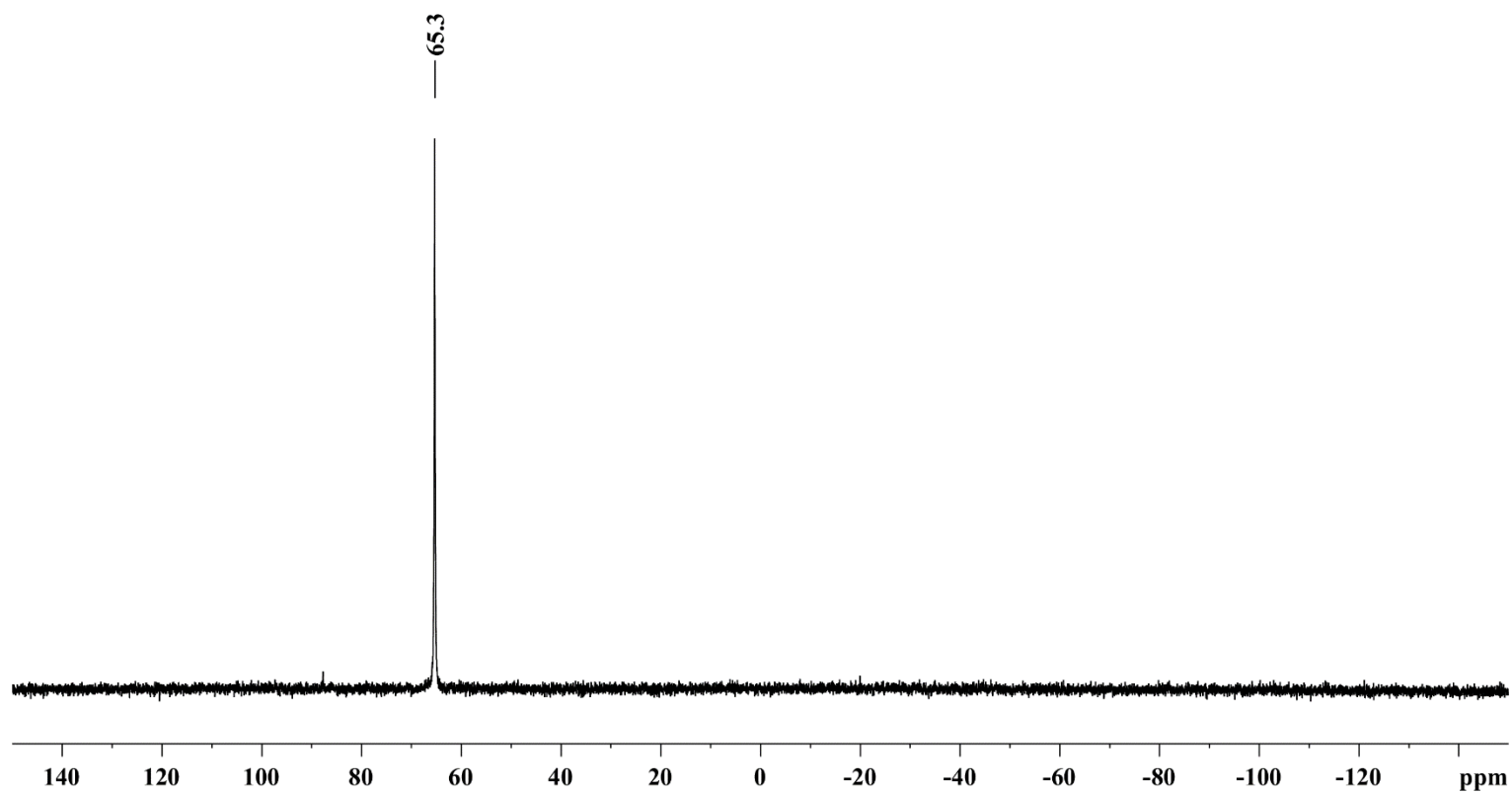


Figure S47. ^{31}P NMR spectrum (202 MHz) of $8'\text{Dipp}$ in C_6D_6 at room temperature.

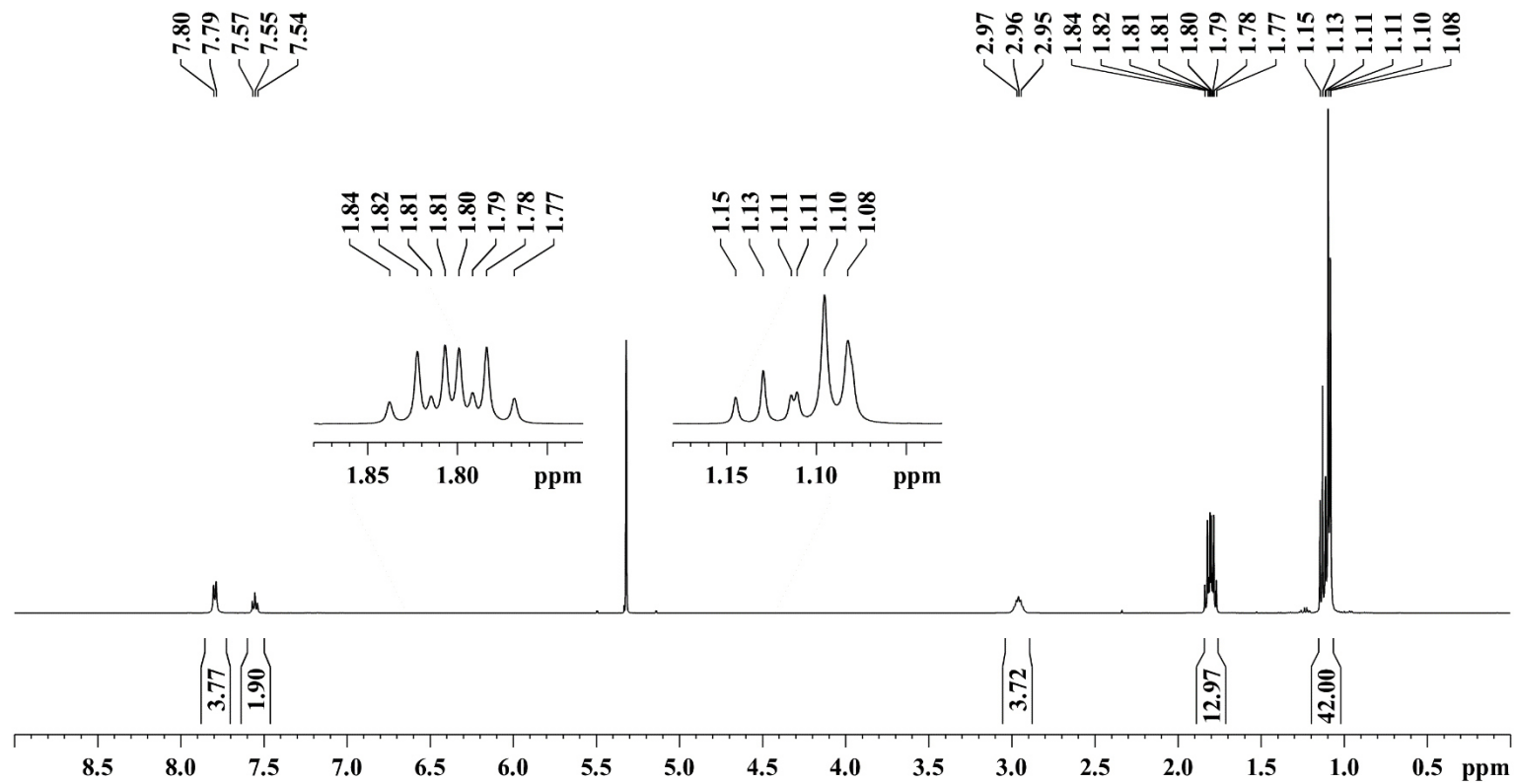


Figure S48. ^1H NMR spectrum (500 MHz) of $8'\text{Dipp}$ in CD_2Cl_2 at room temperature.

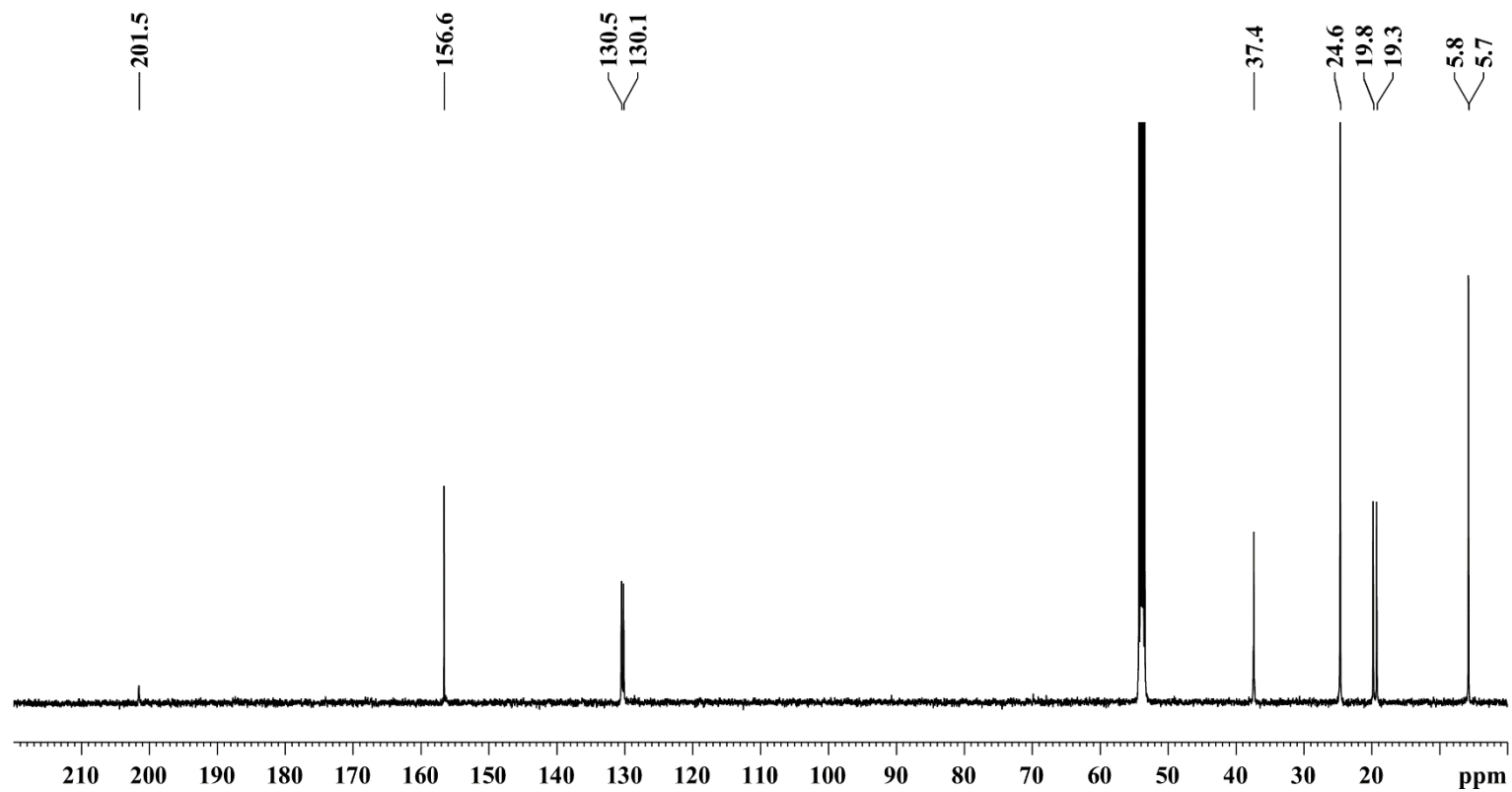


Figure S49. ^{13}C NMR spectrum (125 MHz) of $\mathbf{8}'_{\text{Dipp}}$ in CD_2Cl_2 at room temperature.

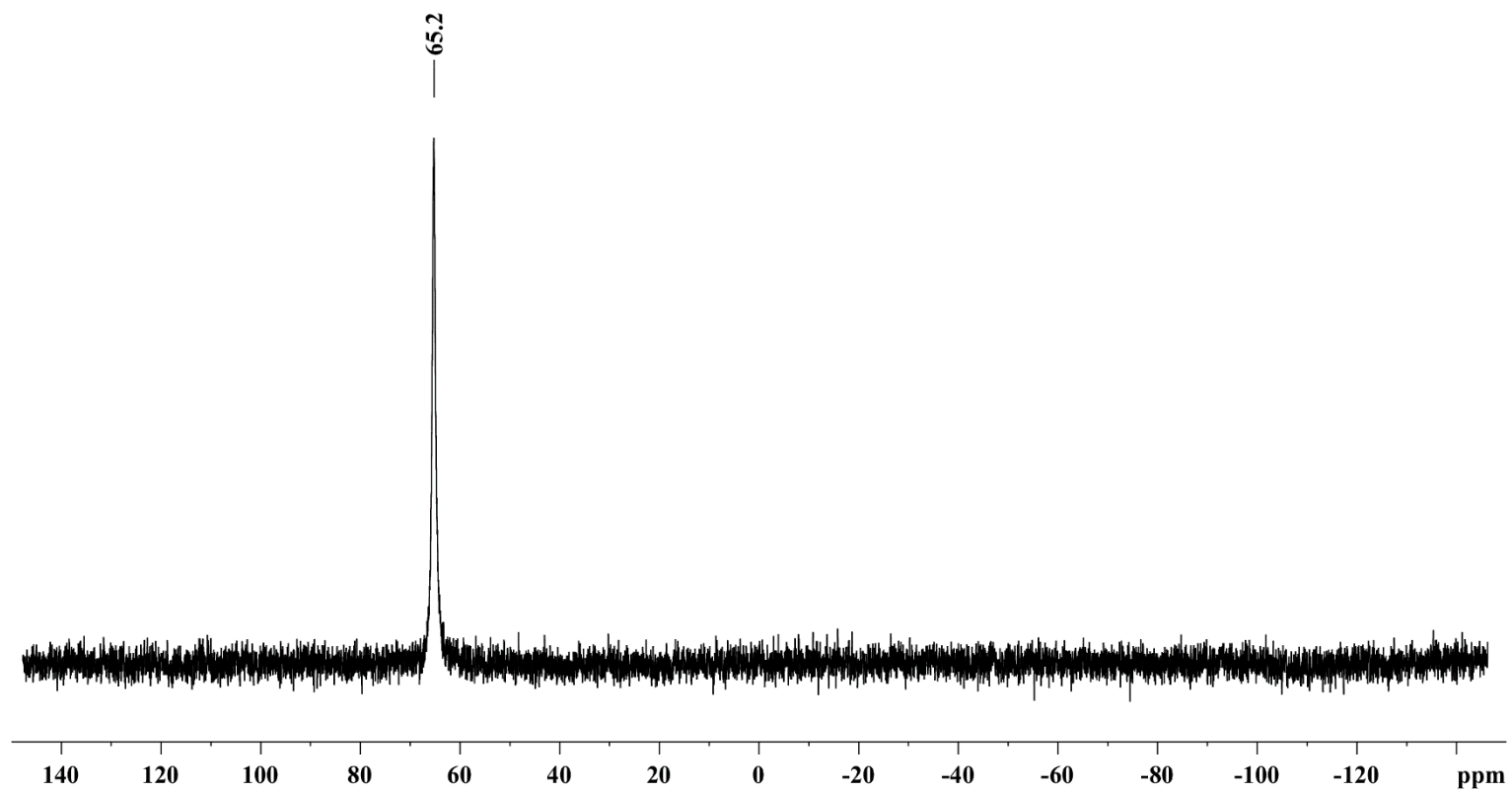


Figure S50. ^{31}P NMR spectrum (202 MHz) of $\mathbf{8}'_{\text{Dipp}}$ in CD_2Cl_2 at room temperature.

3.15. $[\text{BiMe}_2(\text{OPEt}_3)(\text{SbF}_6)] \cdot 8\text{Me}$

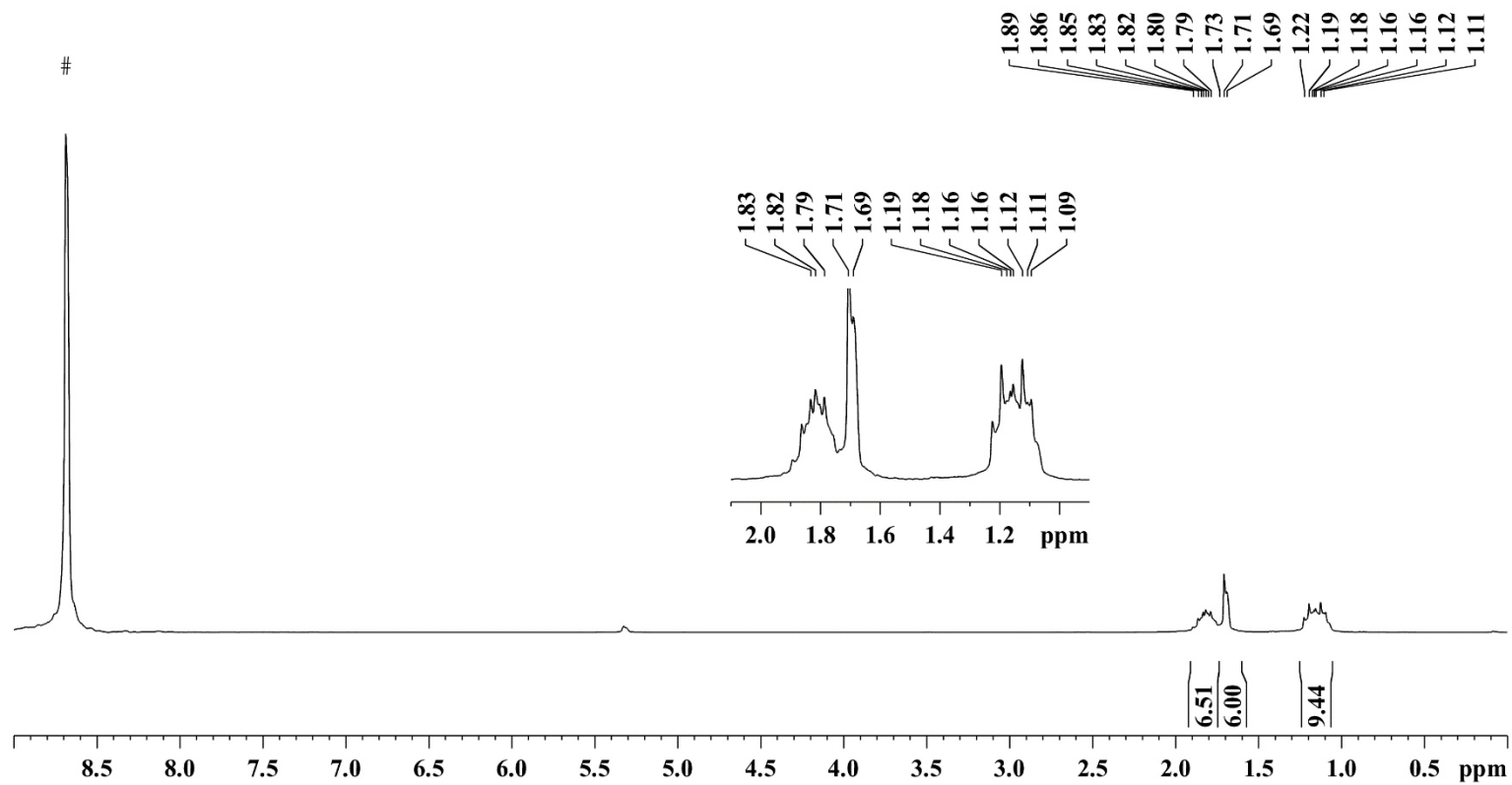


Figure S51. ^1H NMR spectrum (250 MHz) of 8Me in CD_2Cl_2 at room temperature (# = Capillary with 85% aqueous H_3PO_4).

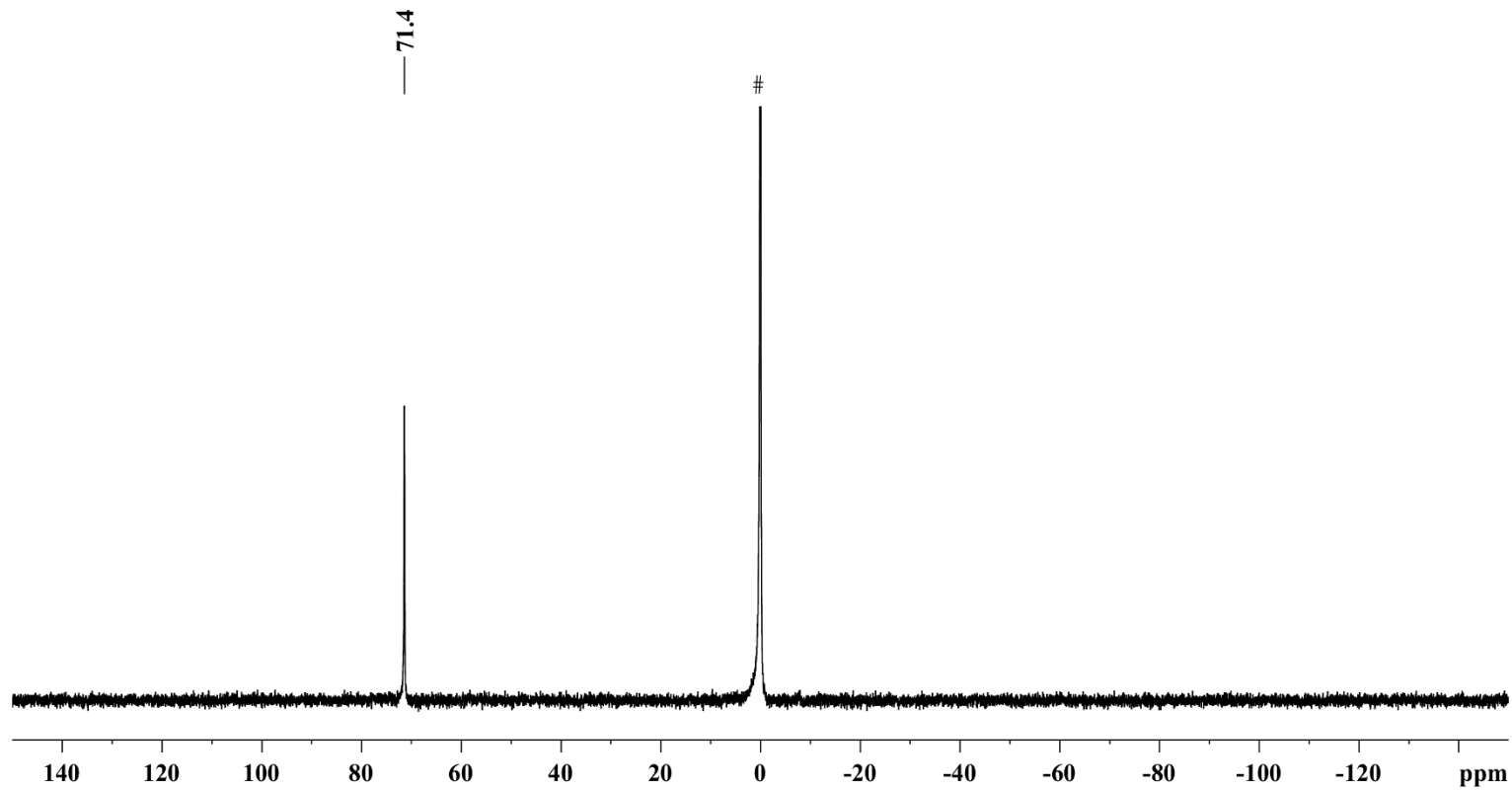


Figure S52. ^{31}P NMR spectrum (101 MHz) of $\mathbf{8}_{\text{Me}}$ in CD_2Cl_2 at room temperature (# = Capillary with 85% aqueous H_3PO_4).

3.16. $[\text{BiMe}_2(\text{OPEt}_3)_2(\text{SbF}_6)] \mathbf{8}'_{\text{Me}}$

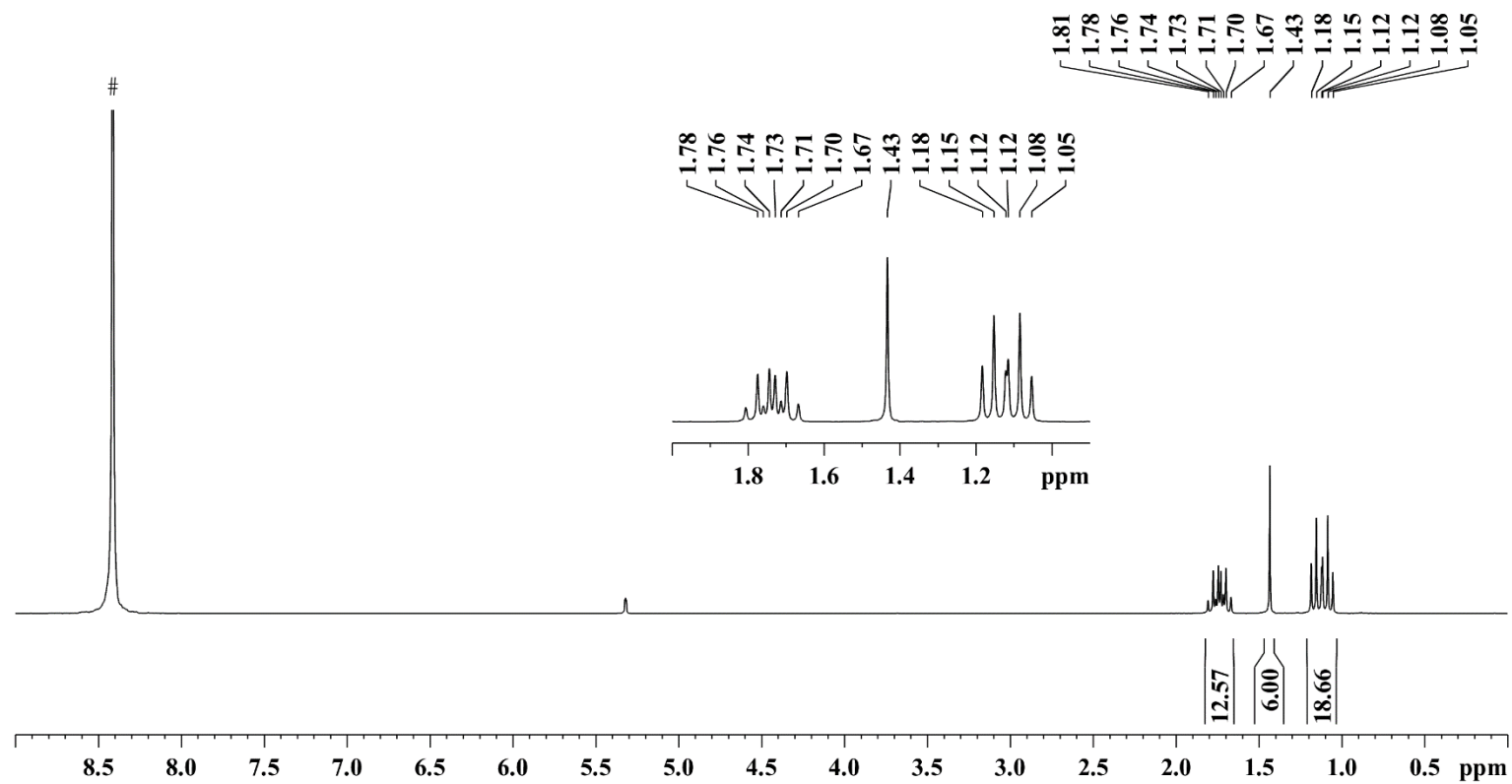


Figure S53. ^1H NMR spectrum (250 MHz) of $\mathbf{8}'_{\text{Me}}$ in CD_2Cl_2 at room temperature (# = Capillary with 85% aqueous H_3PO_4).

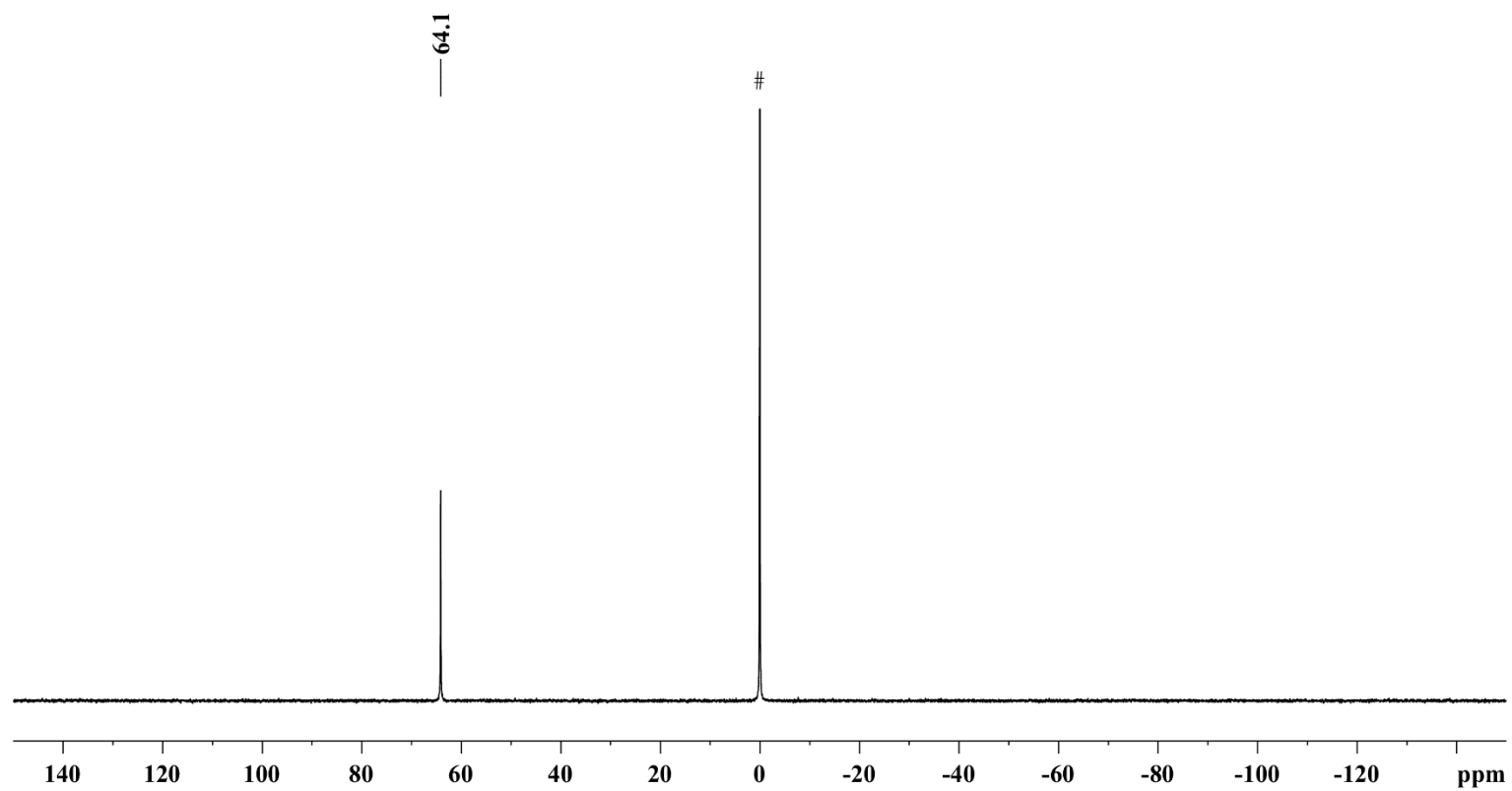


Figure S54. ^{31}P NMR spectrum (101 MHz) of $\mathbf{8}'_{\text{Me}}$ in in C_6D_6 at room temperature (# = Capillary with 85% aqueous H_3PO_4).

3.17 [BiDipp₂(CN*t*Bu)(SbF₆)] 9_{Dipp}

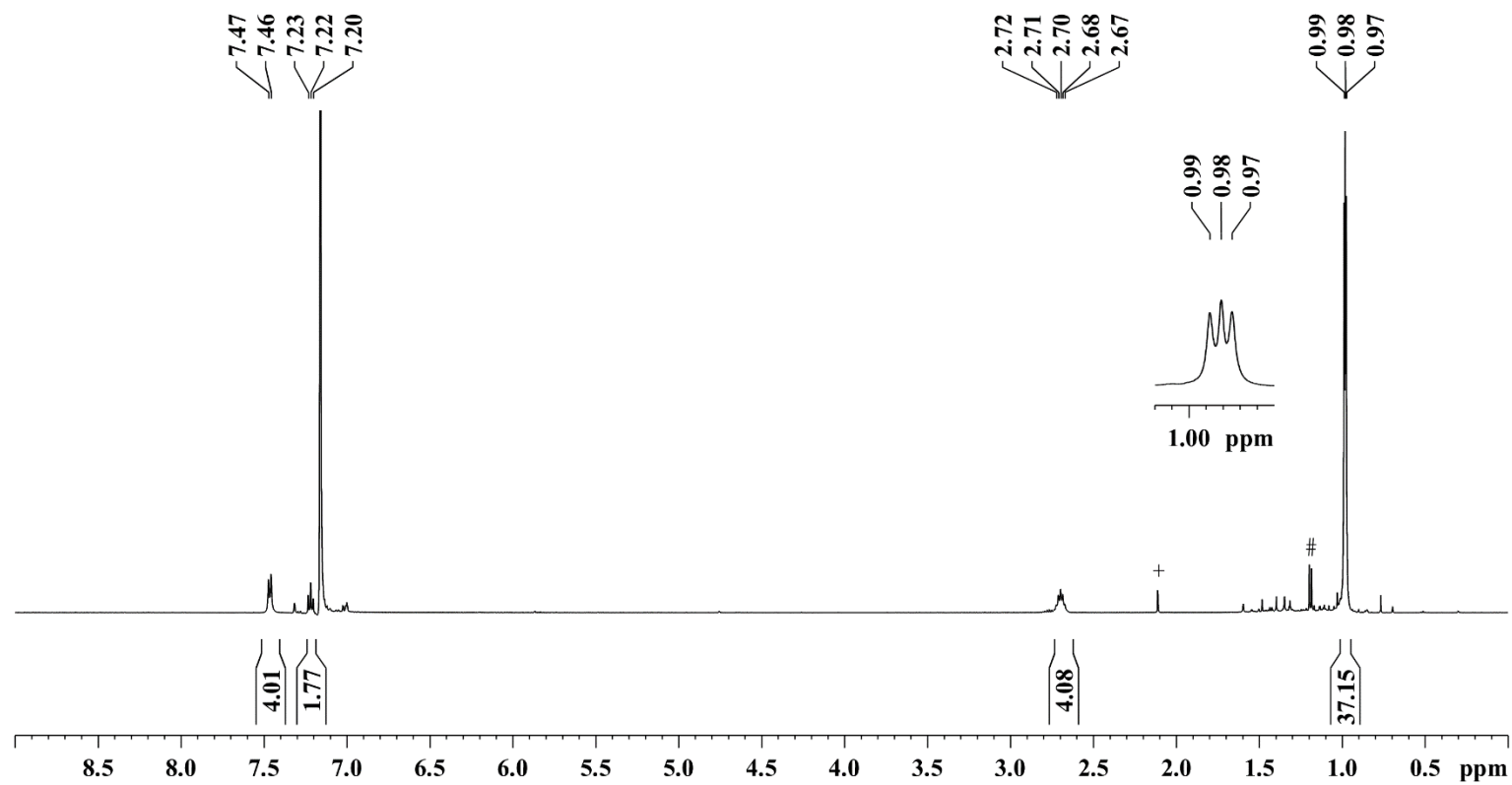


Figure S55. ¹H NMR spectrum (500 MHz) of 9_{Dipp} in in C₆D₆ at room temperature (# = hydrolysis; + = toluene) .

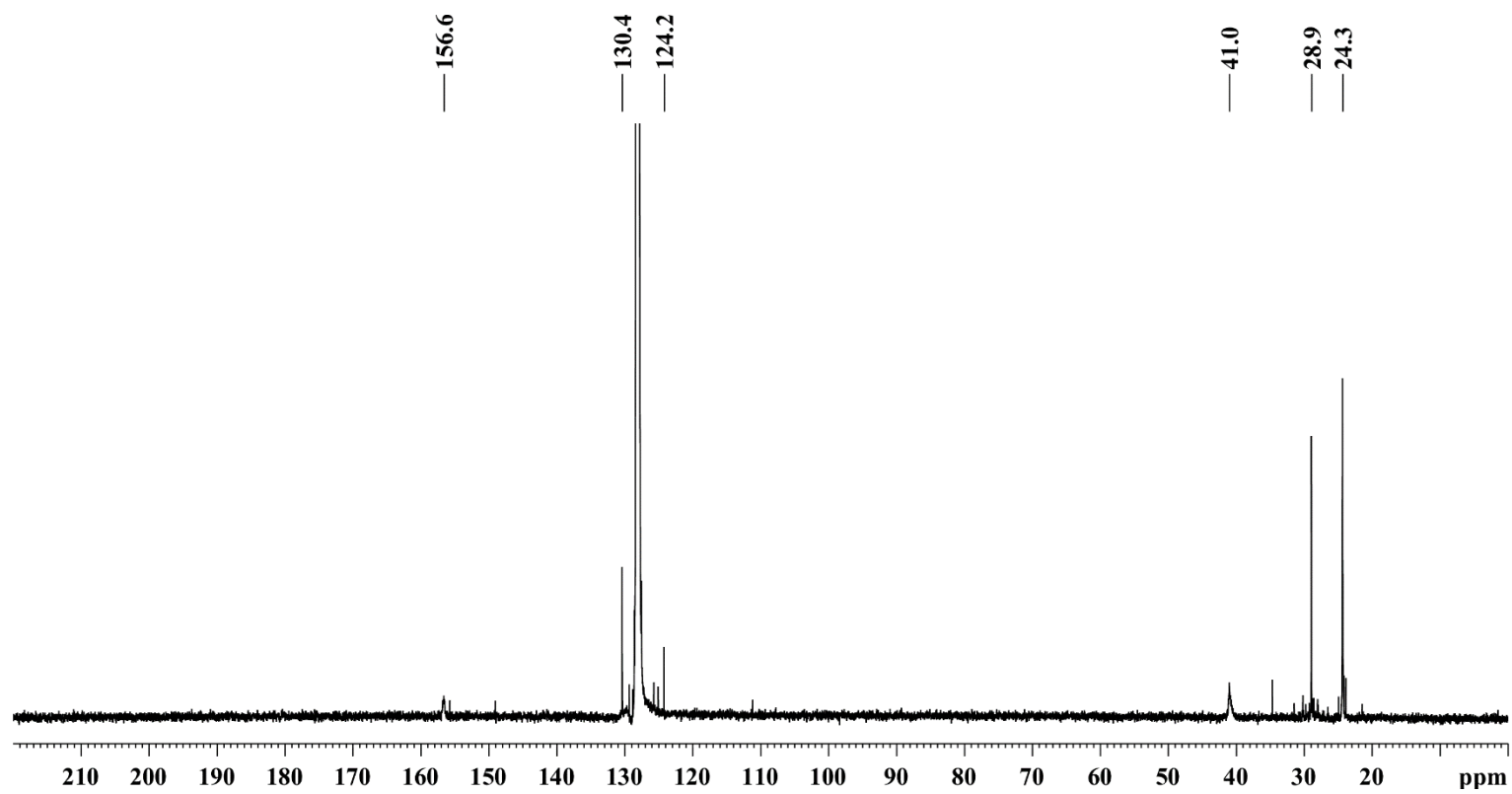


Figure S56. ^{13}C NMR spectrum (125 MHz) of **9**_{Dipp} in in C_6D_6 at room temperature.

3.18 [BiMe₂(CN*t*Bu)(SbF₆)] 9Me

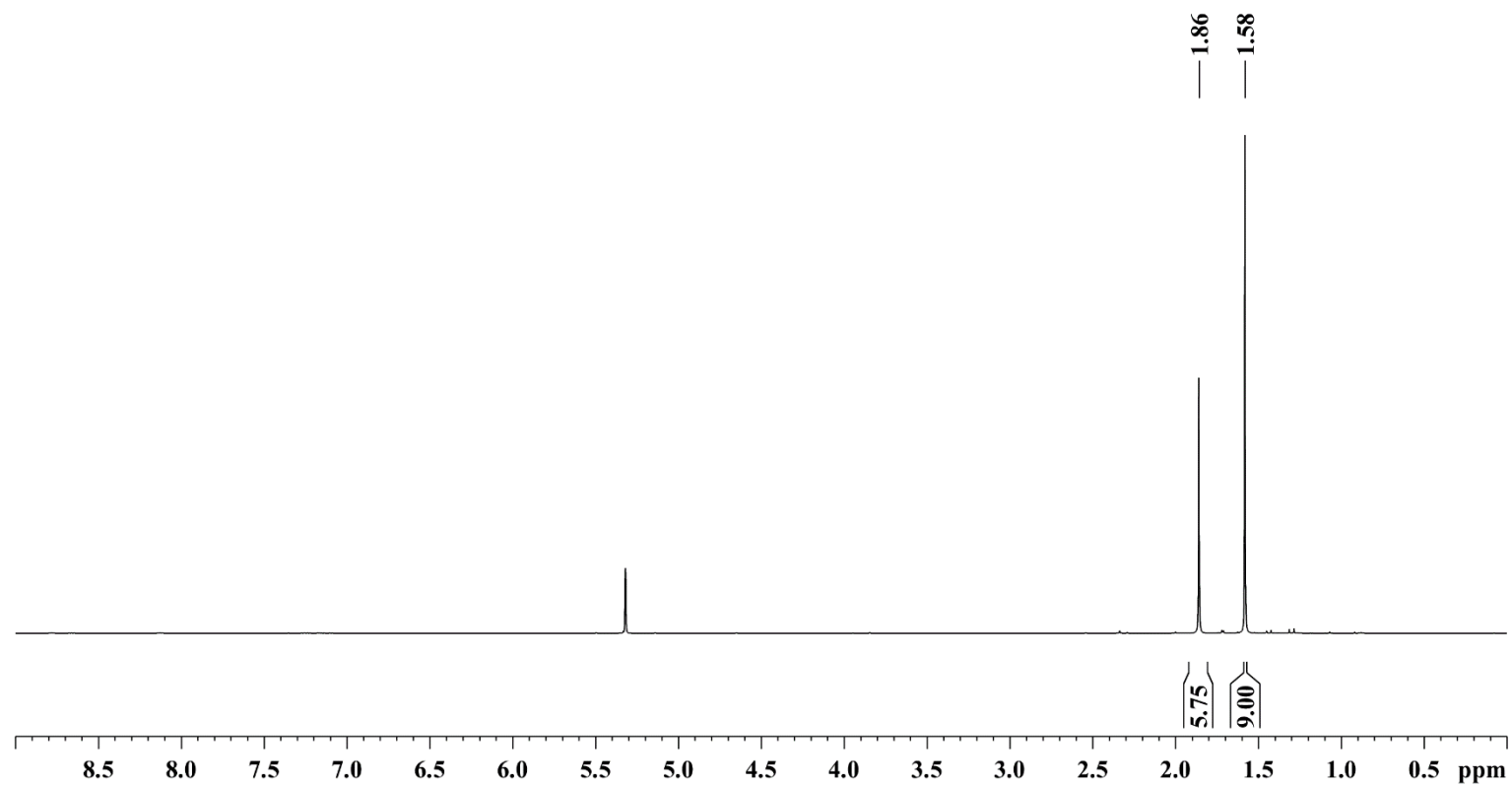


Figure S57. ¹H NMR spectrum (125 MHz) of 9Me in CD₂Cl₂ at room temperature.

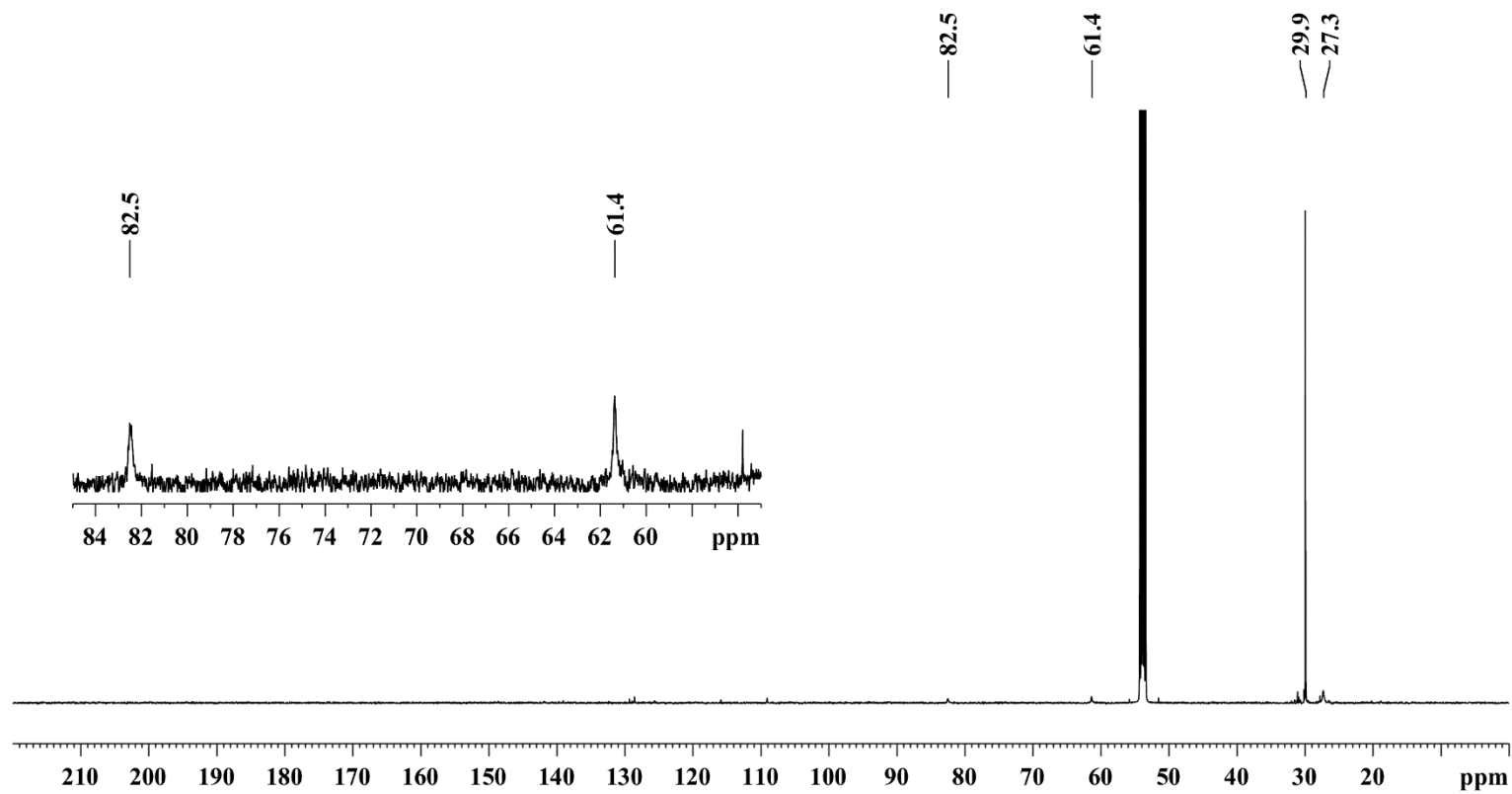


Figure S58. ^{13}C NMR spectrum (125 MHz) of **9Me** in CD_2Cl_2 at room temperature.

3.19 [BiMe₂(CNAd)(SbF₆)] 10_{Me}

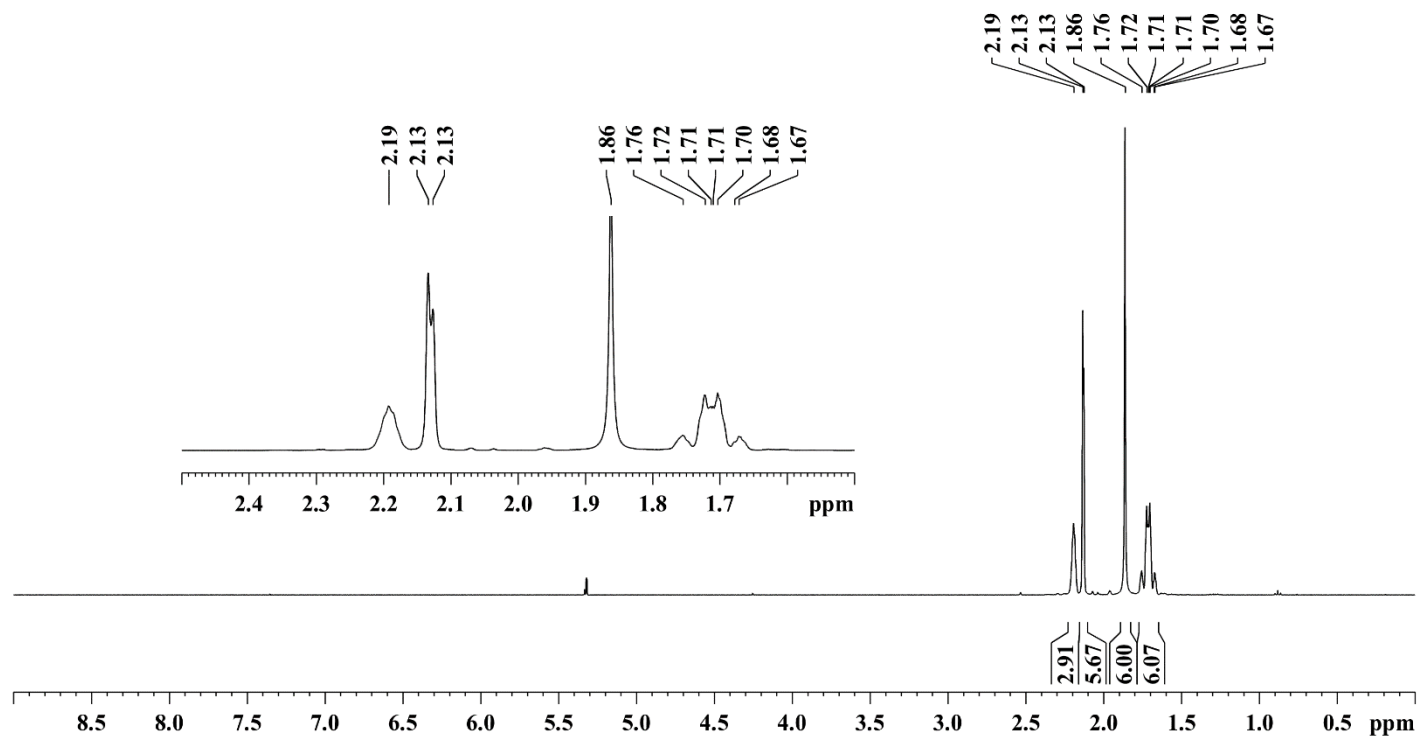


Figure S59. ¹H NMR spectrum (400 MHz) of 10_{Me} in in CD₂Cl₂ at room temperature.

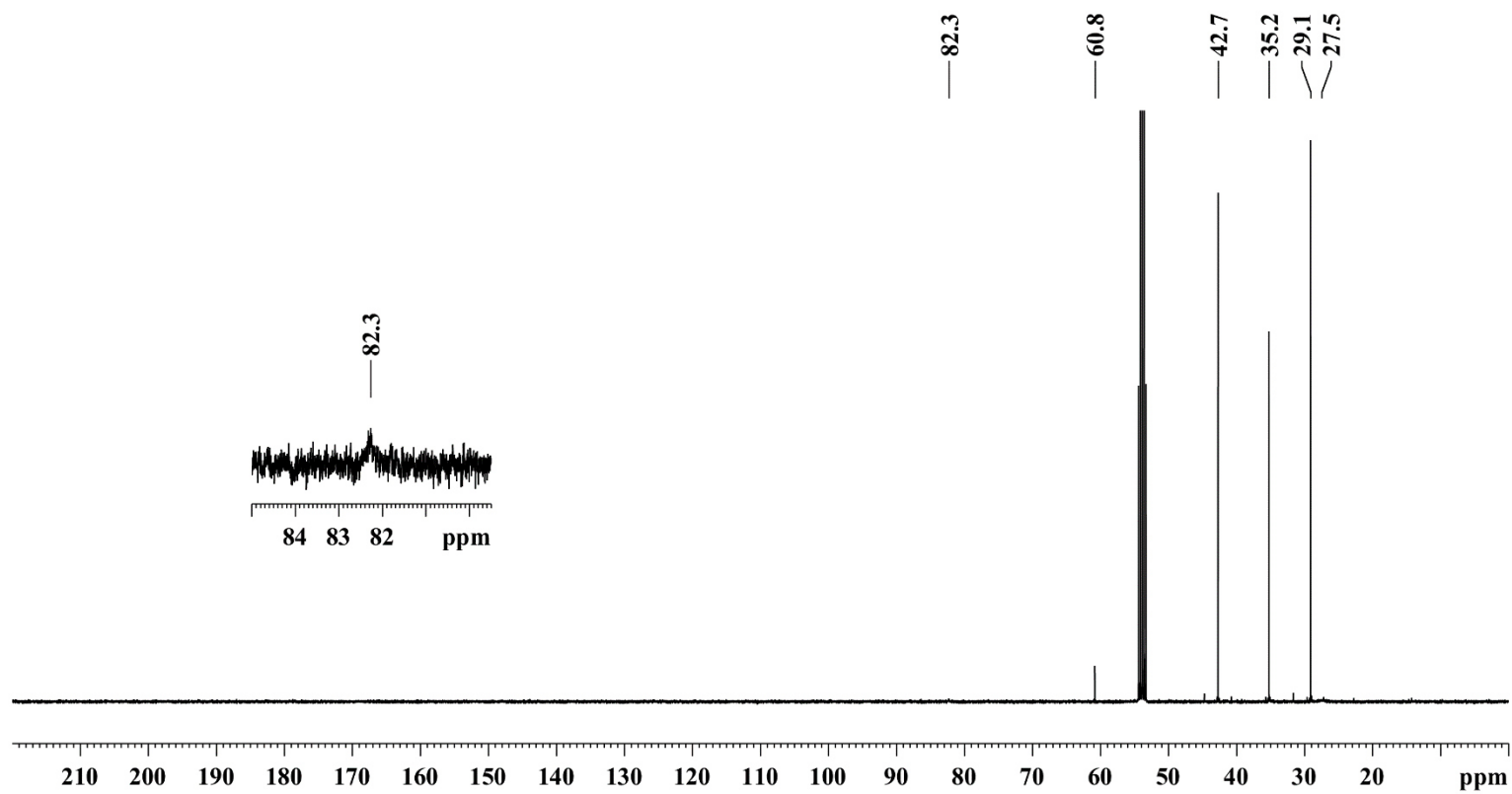


Figure S60. ^{13}C NMR spectrum (101 MHz) of **10**_{Me} in CD_2Cl_2 at room temperature.

3.20 [BiMe₂(CNXyl)(SbF₆)] 11_{Me}

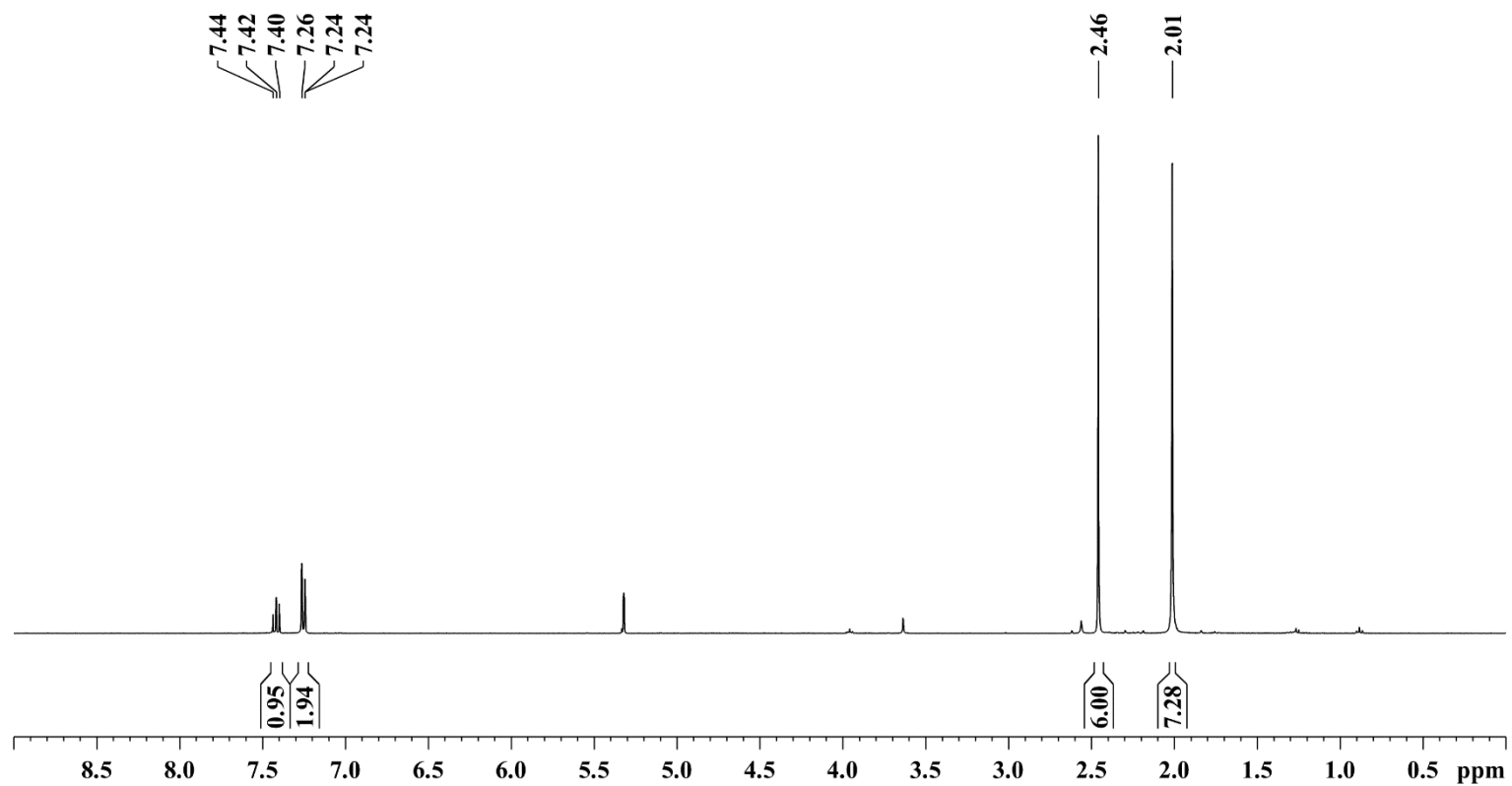


Figure S61. ¹H NMR spectrum (400 MHz) of 11_{Me} in in CD₂Cl₂ at room temperature.

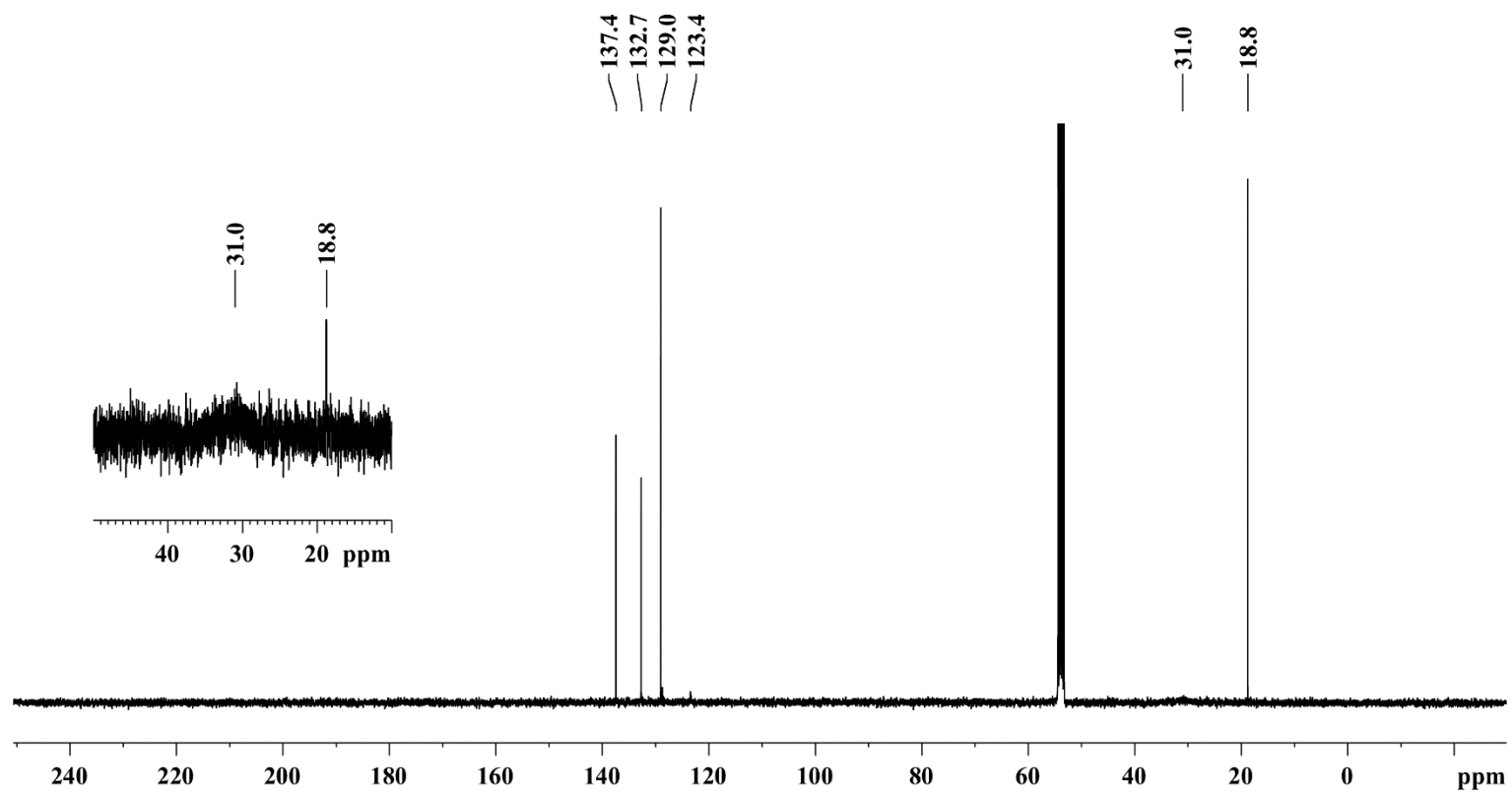


Figure S62. ^{13}C NMR spectrum (101 MHz) of **11Me** in CD_2Cl_2 at room temperature.

3.21 [BiMe₂(CNXyl)₂(SbF₆)] 11'_{Me}

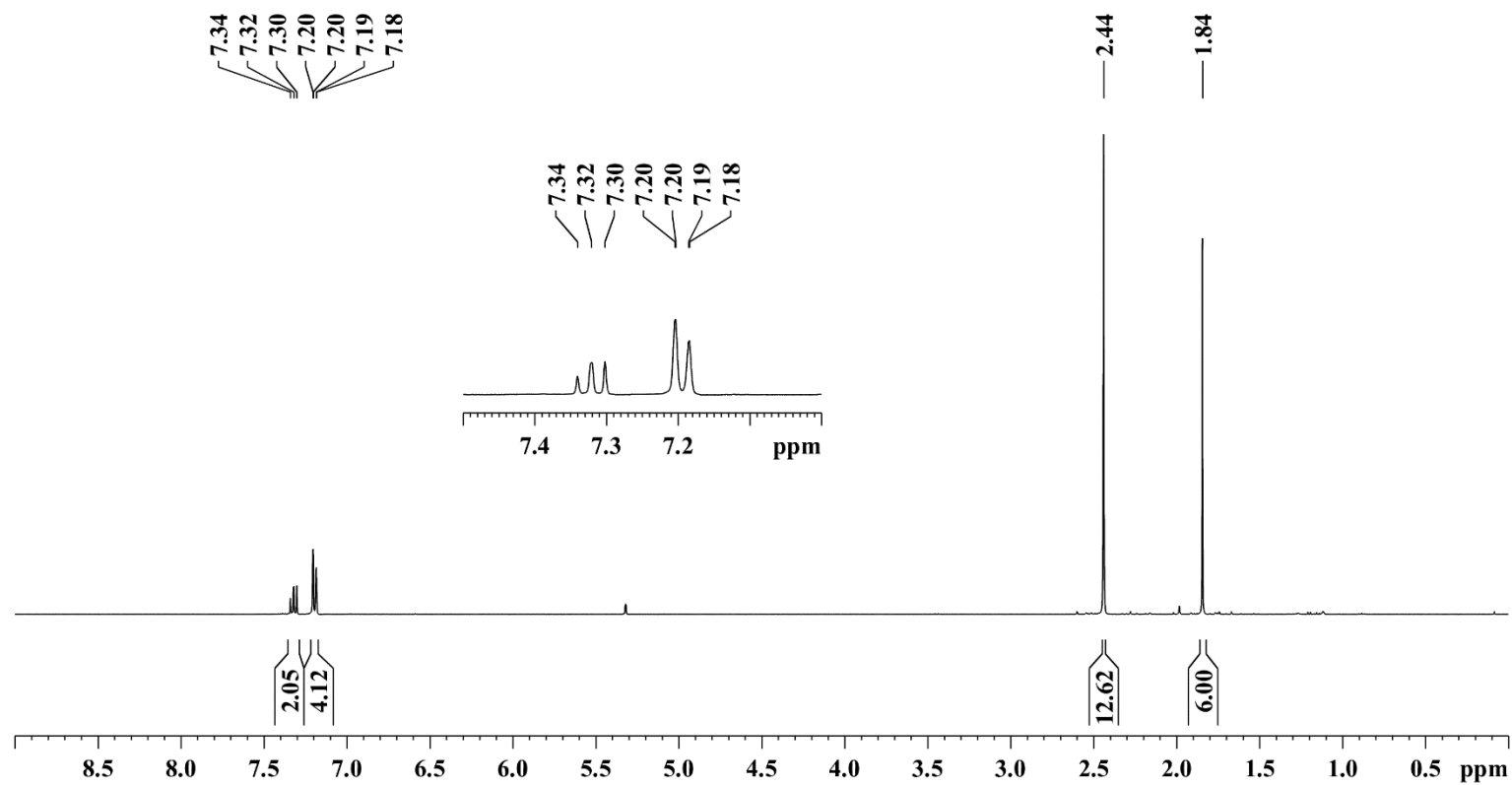


Figure S63. ¹H NMR spectrum (400 MHz) of 11'_{Me} in in CD₂Cl₂ at room temperature.

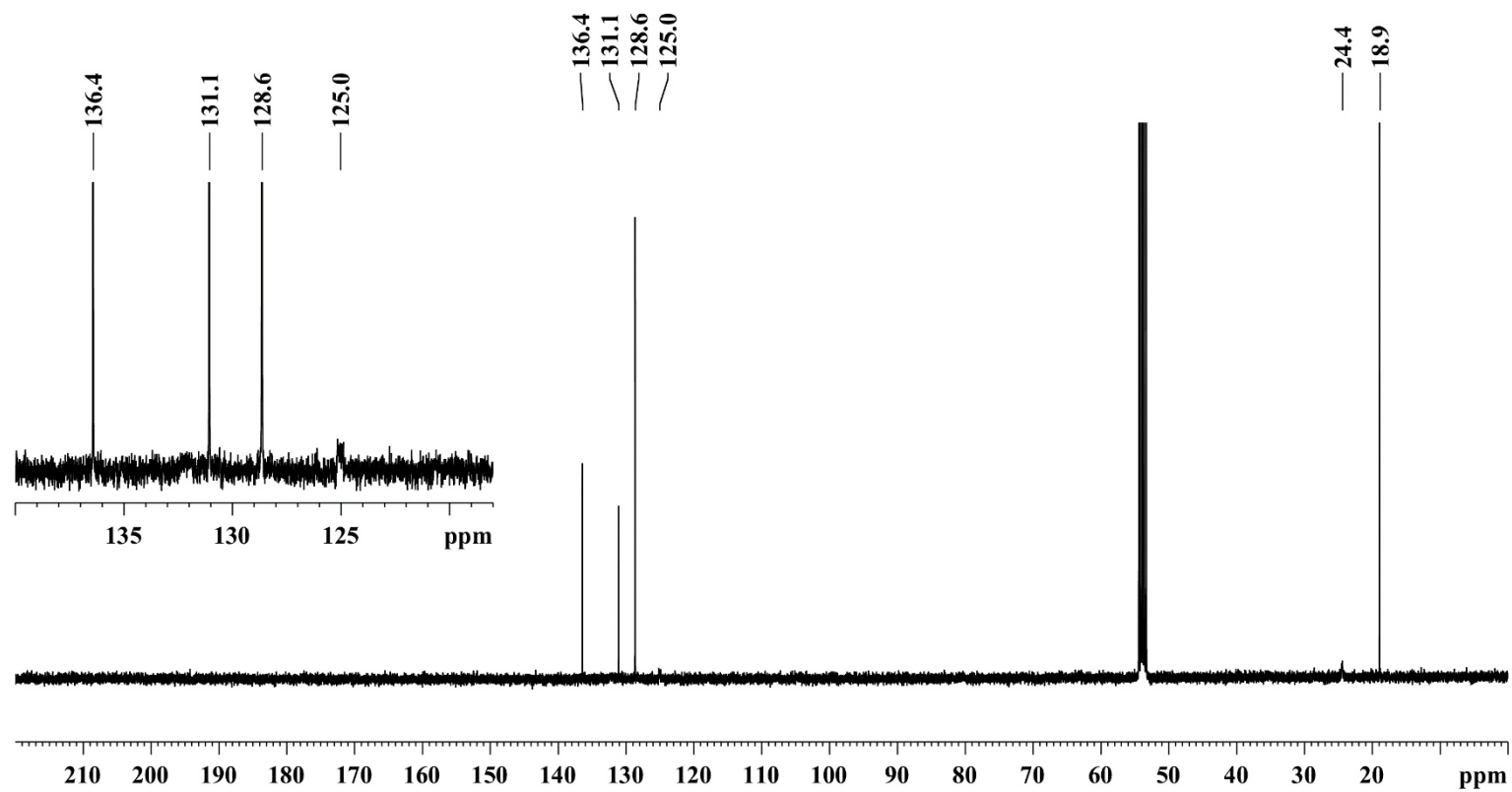


Figure S64. ^{13}C NMR spectrum (101 MHz) of $11'\text{Me}$ in CD_2Cl_2 at room temperature.

3.22 [BiMe₂(CNCy)(SbF₆)] 12_{Me}

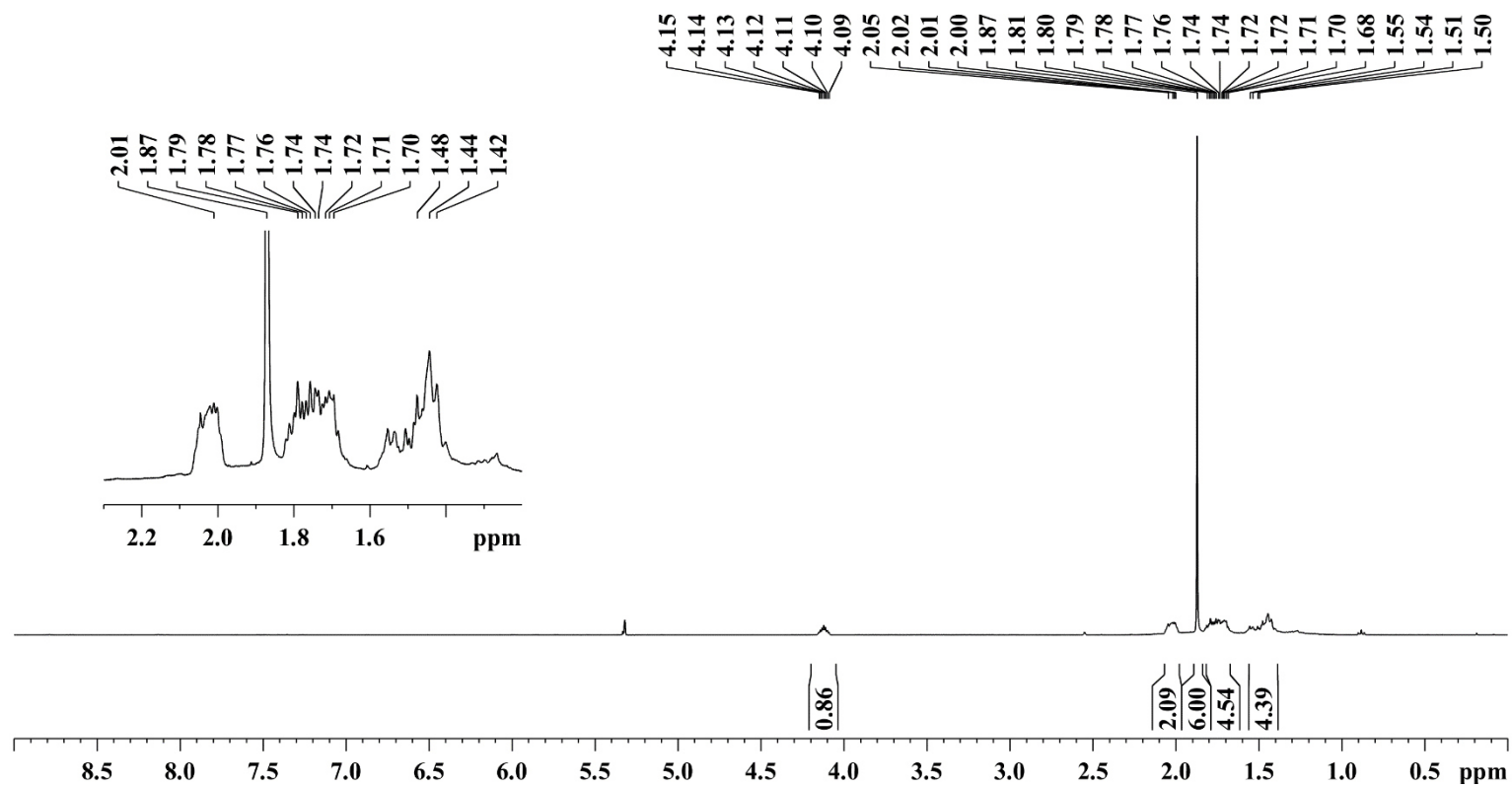


Figure S65. ¹H NMR spectrum (400 MHz) of 12_{Me} in CD₂Cl₂ at room temperature.

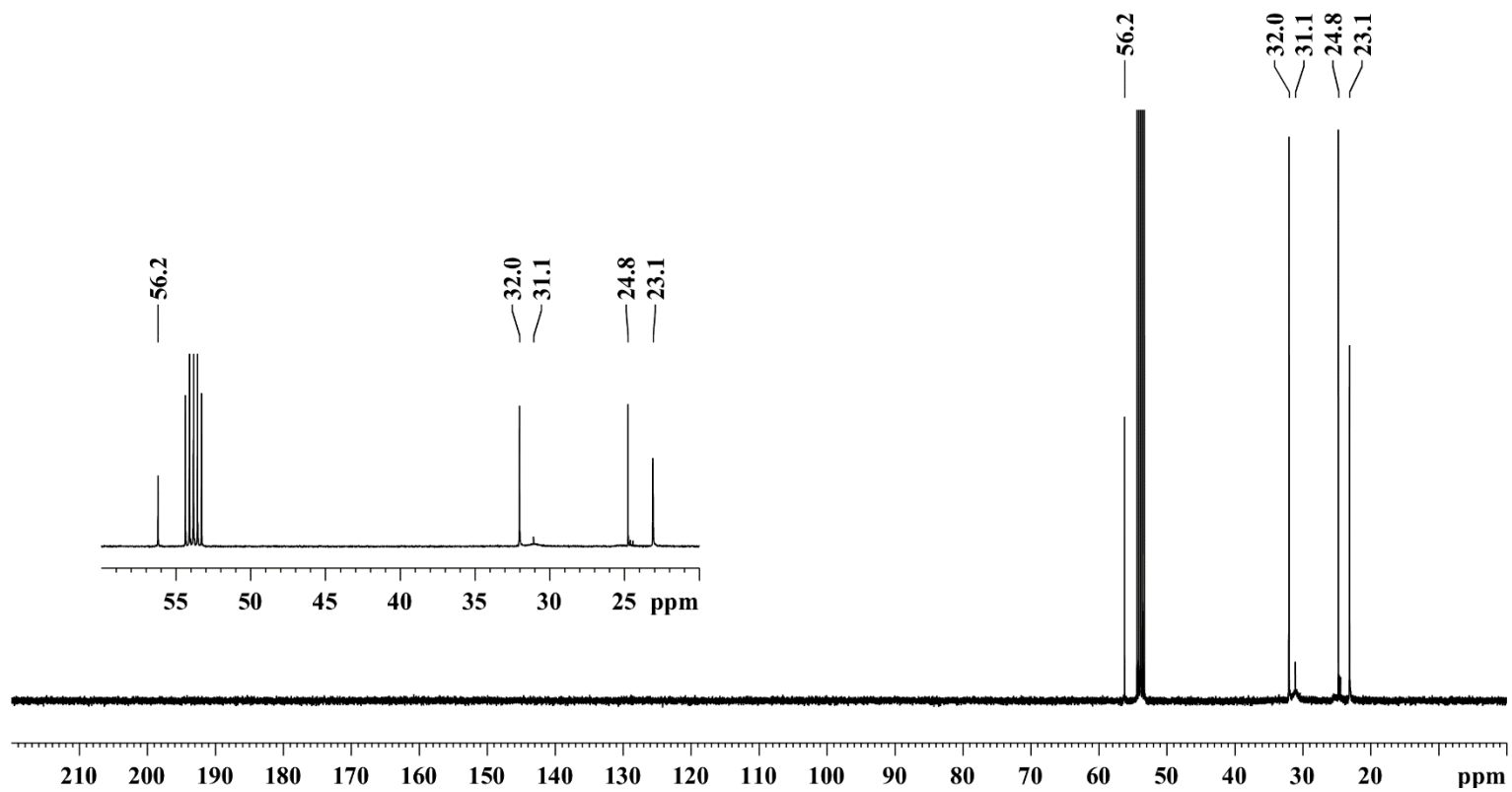


Figure S66. ^{13}C NMR spectrum (101 MHz) of **12**_{Me} in in CD_2Cl_2 at room temperature.

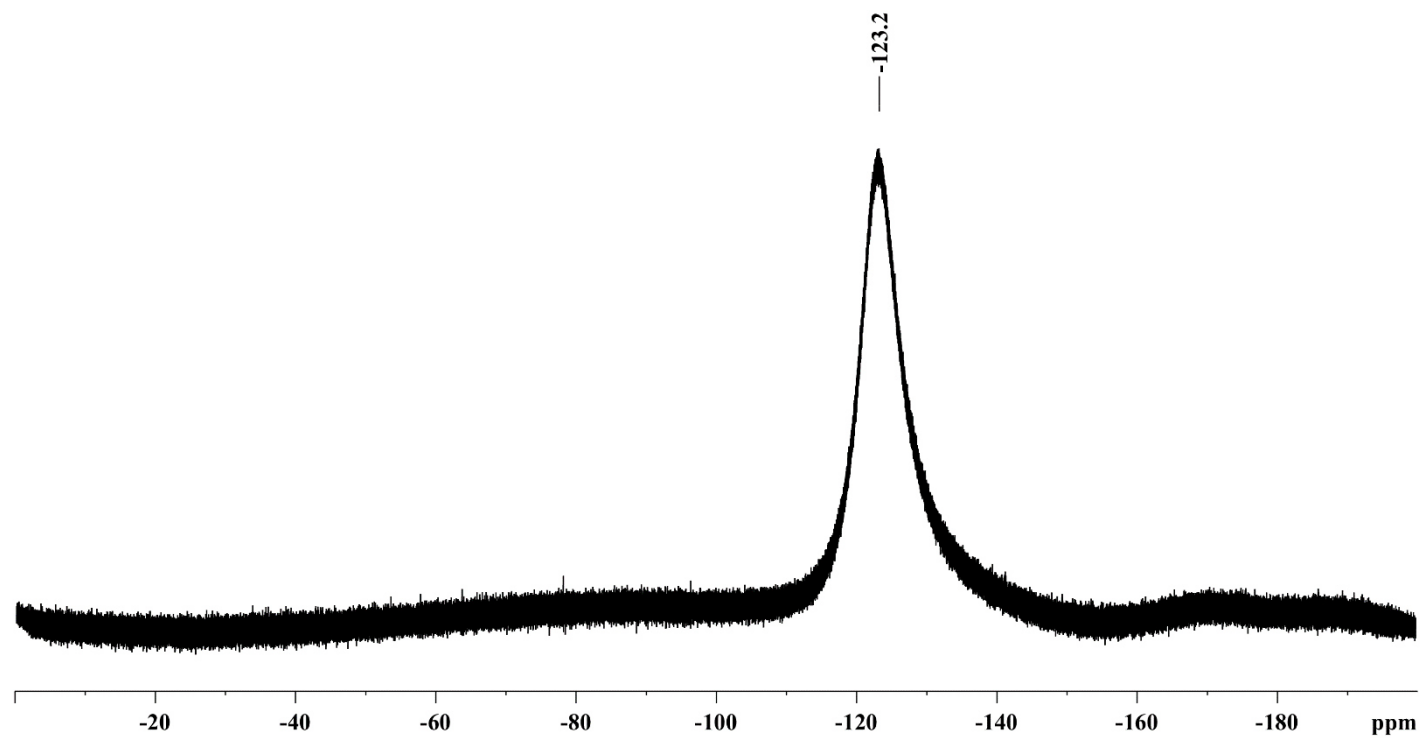


Figure S67. ^{19}F NMR spectrum (377 MHz) of **12_{Me}** in in CD_2Cl_2 at room temperature.

3.23. $[\text{BiMe}_2(\text{CN}n\text{Bu})(\text{SbF}_6)] \mathbf{13}_{\text{Me}}$

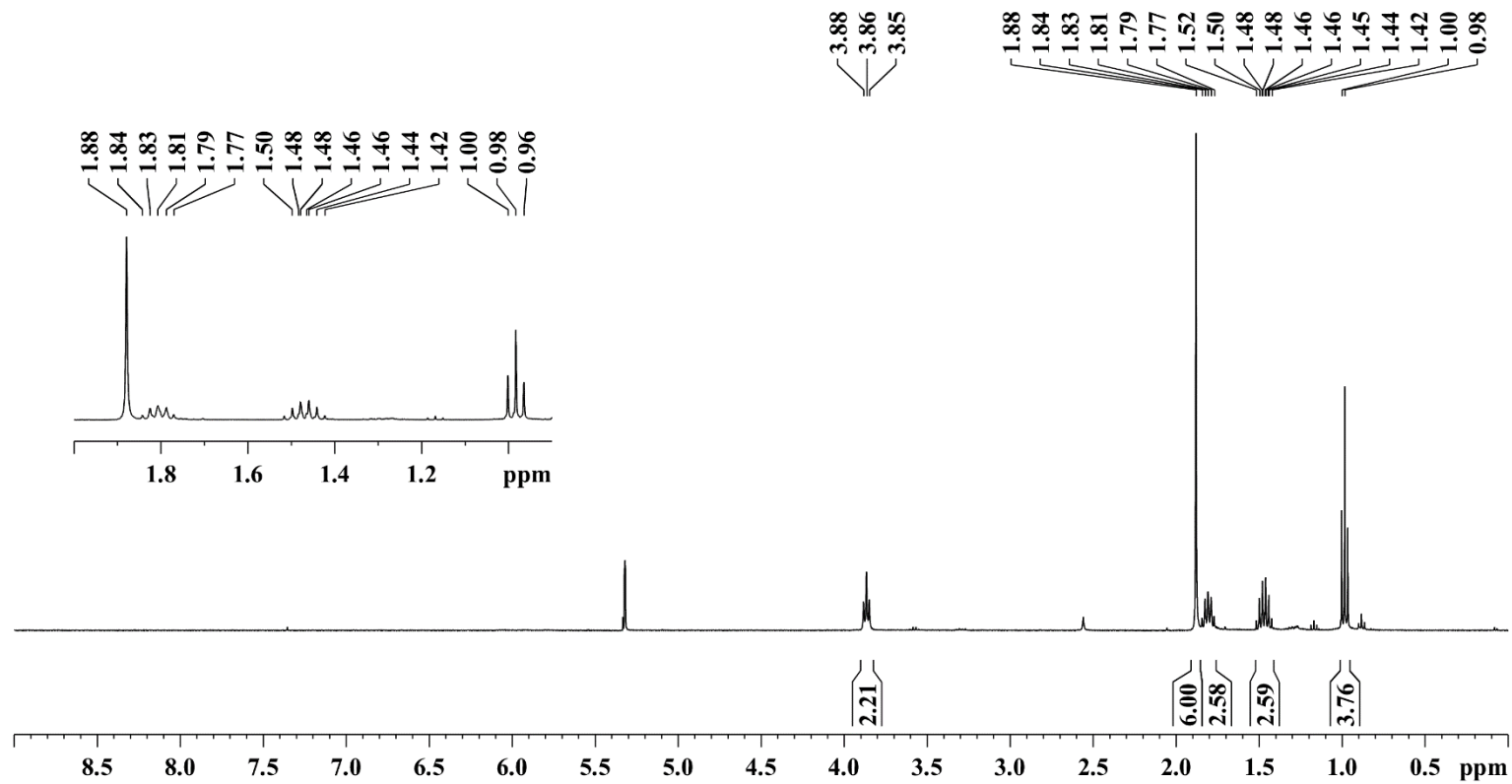


Figure S68. ^1H NMR spectrum (400 MHz) of $\mathbf{13}_{\text{Me}}$ in CD_2Cl_2 at room temperature.

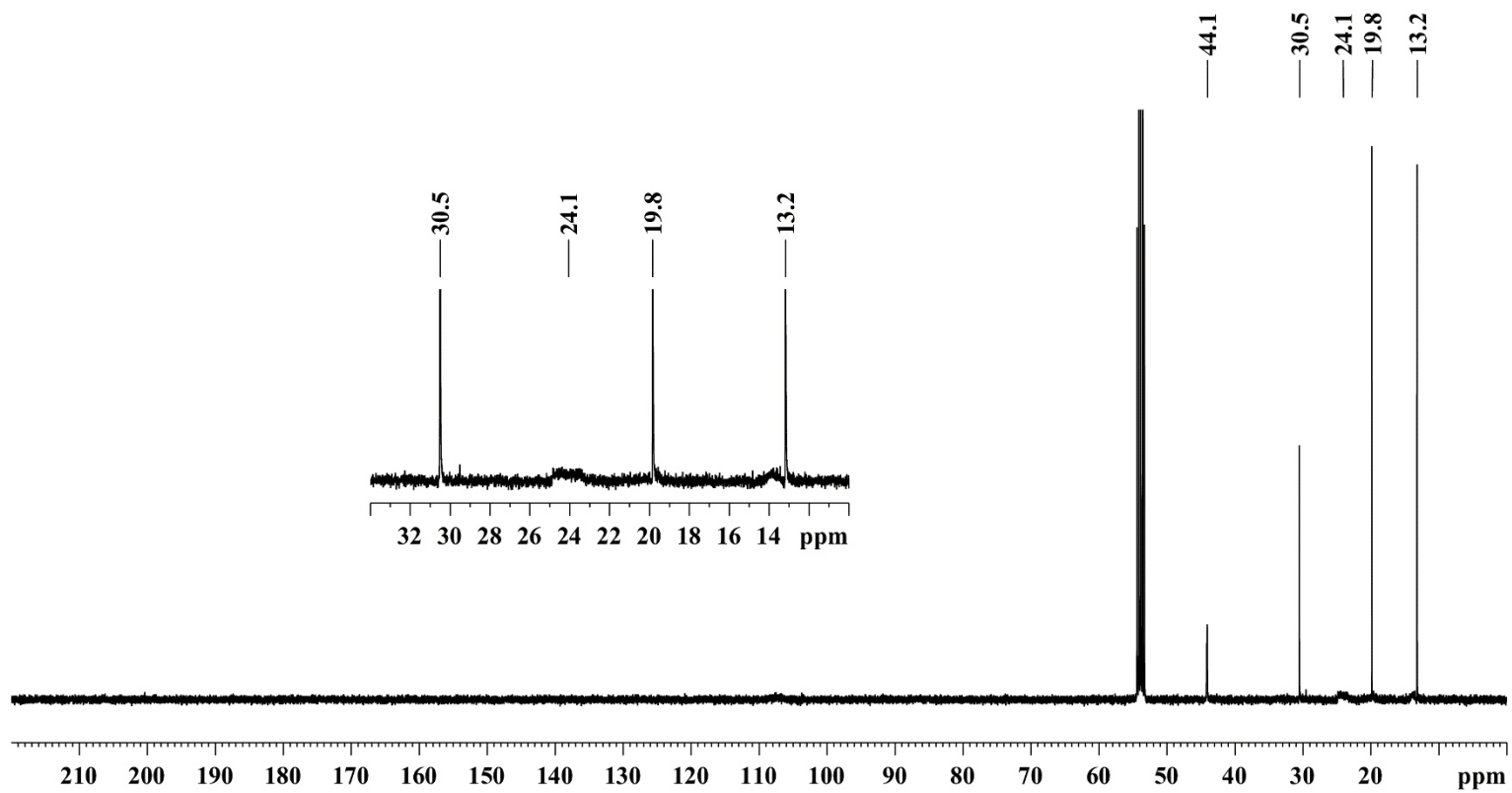


Figure S69. ^{13}C NMR spectrum (101 MHz) of ^{13}Me in in CD_2Cl_2 at room temperature.

3.24. [BiMe₂(PCy₃)(SbF₆)] 14_{Me}

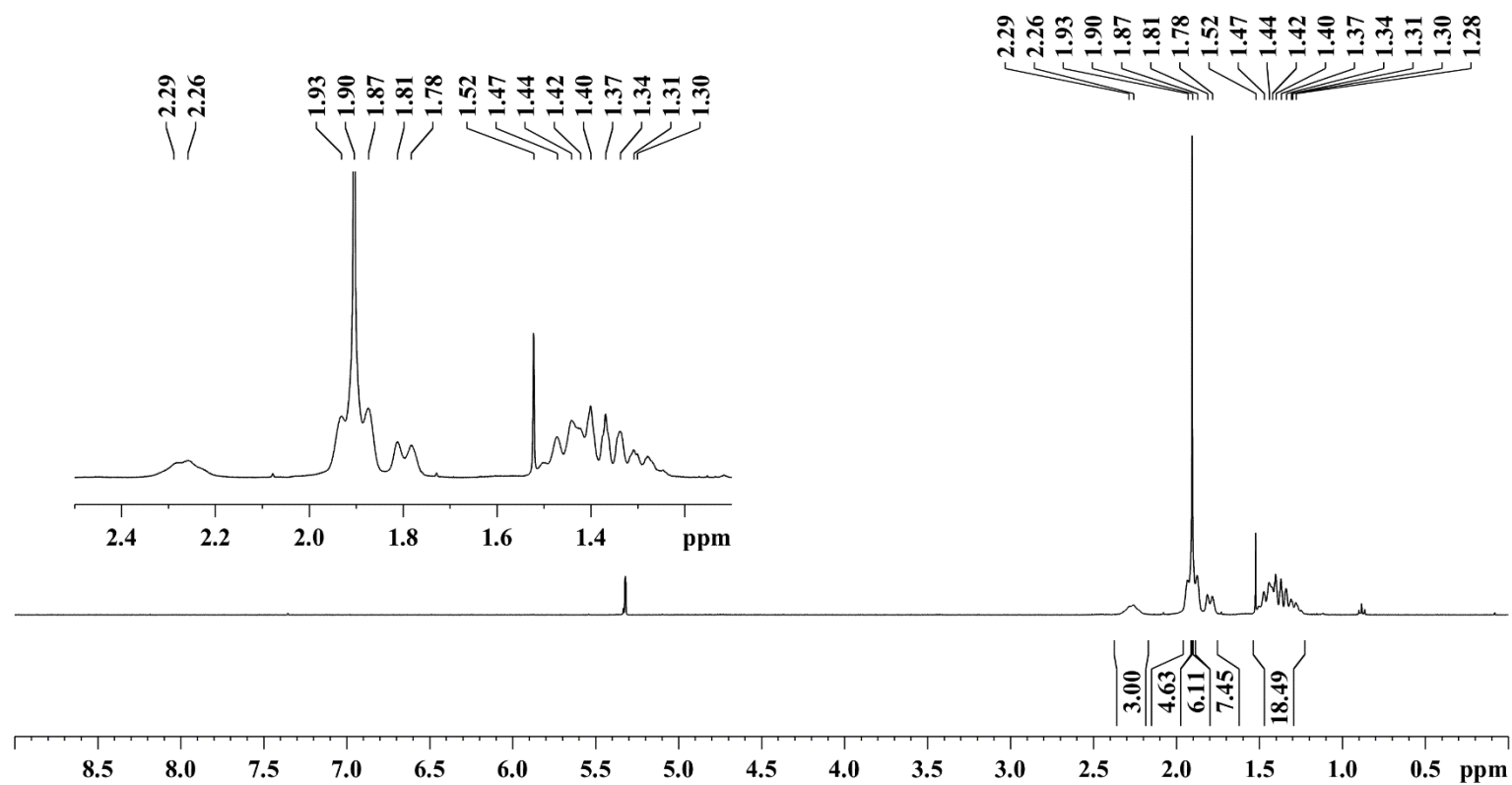


Figure S70. ¹H NMR spectrum (400 MHz) of 14_{Me} in in CD₂Cl₂ at room temperature.

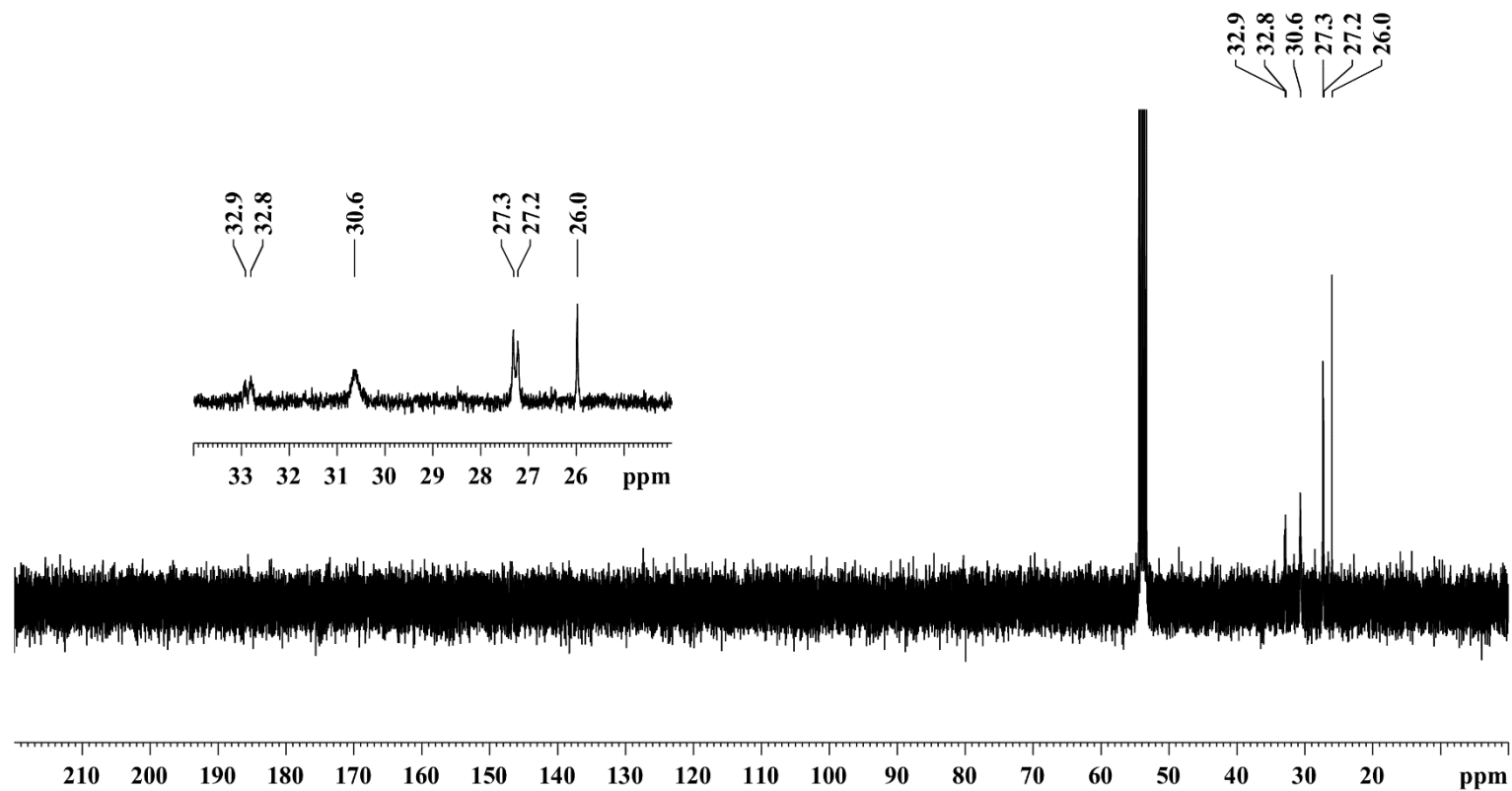


Figure S71. ^{13}C NMR spectrum (101 MHz) of **14**_{Me} in CD_2Cl_2 at room temperature.

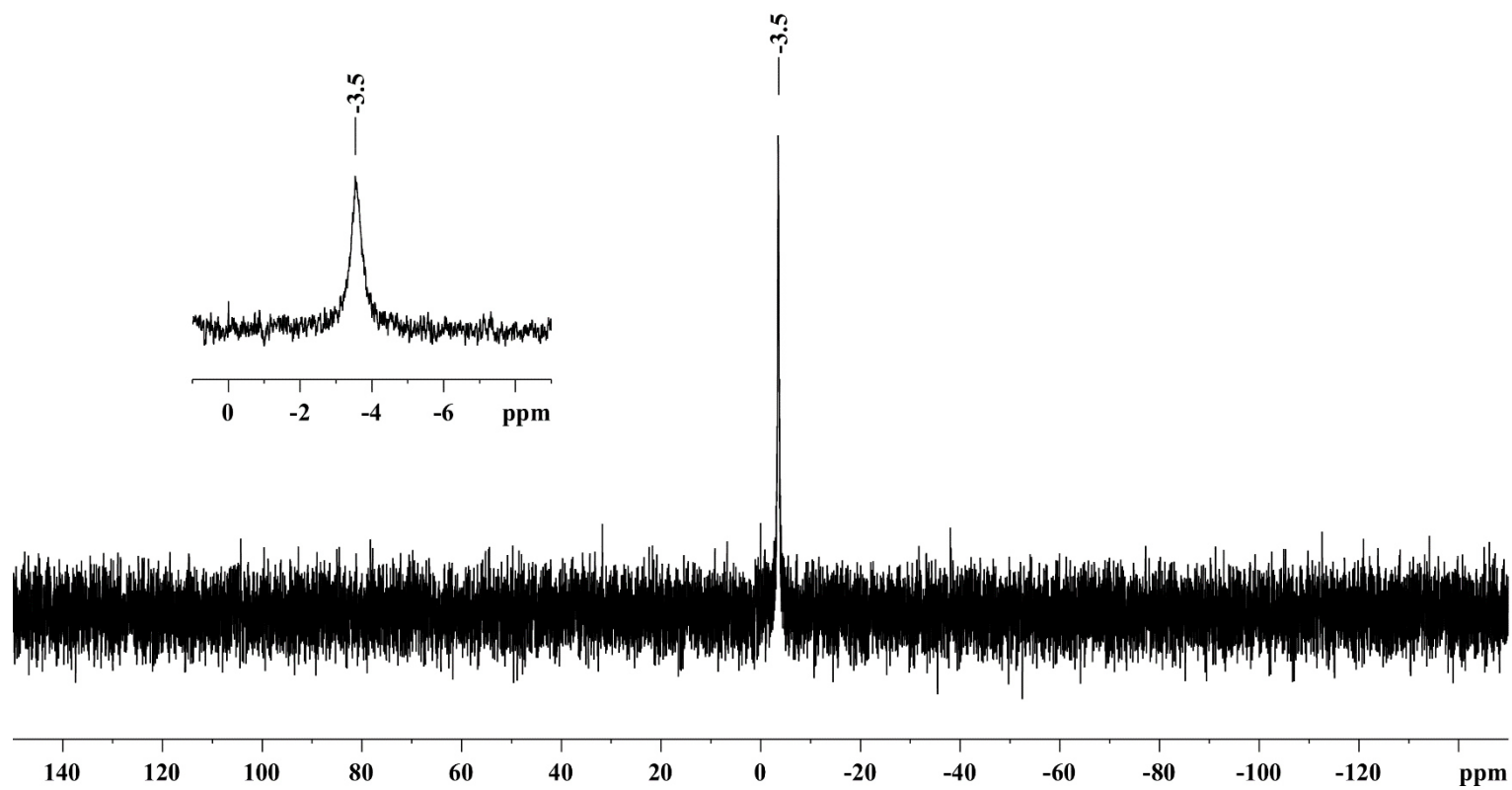


Figure S72. ^{31}P NMR spectrum (162 MHz) of **14**_{Me} in in CD_2Cl_2 at room temperature.

3.25. $[\text{BiMe}_2(\text{PPh}_3)(\text{SbF}_6)] \mathbf{15Me}$

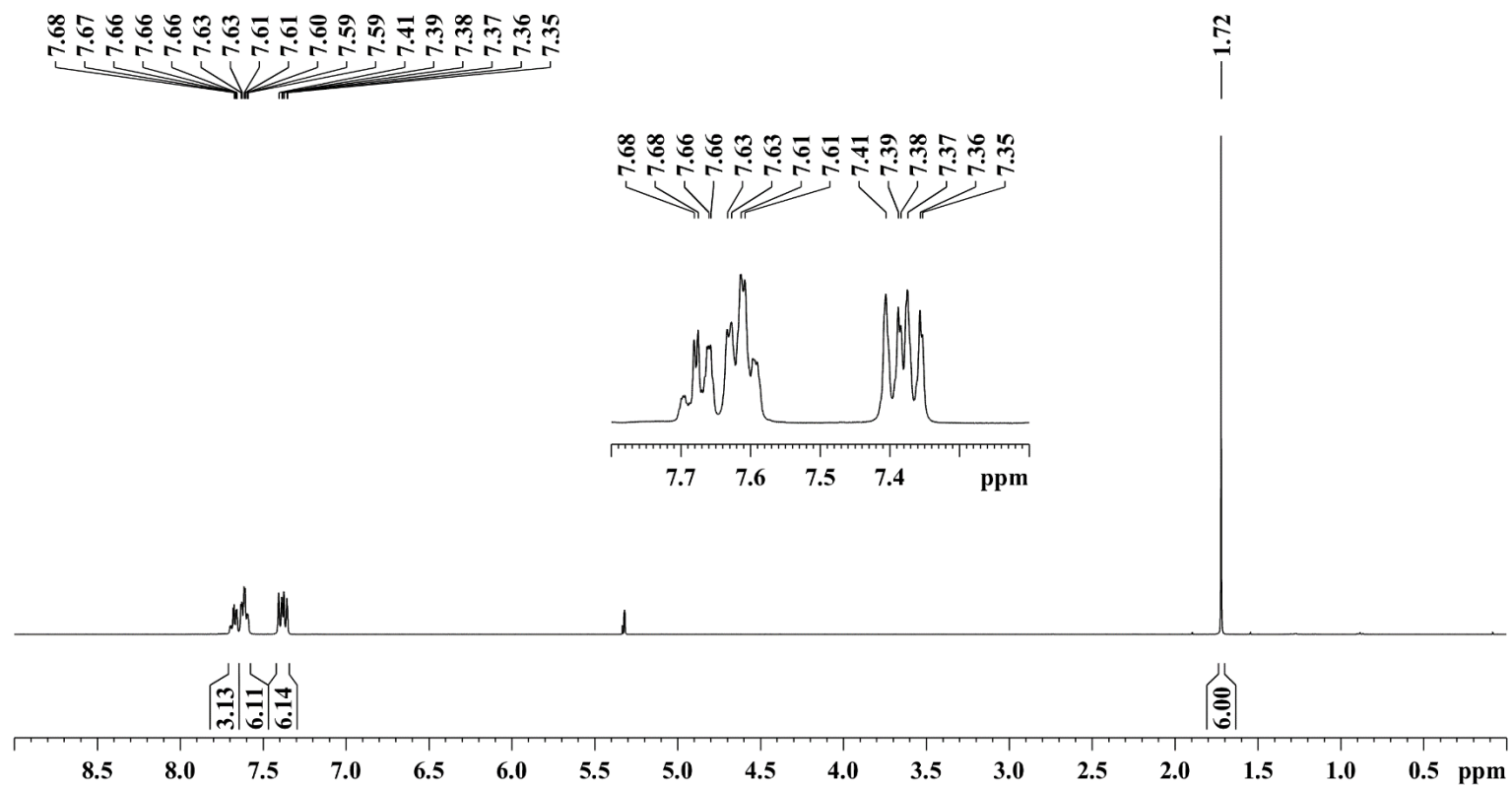


Figure S73. ^1H NMR spectrum (400 MHz) of $\mathbf{15Me}$ in CD_2Cl_2 at room temperature.

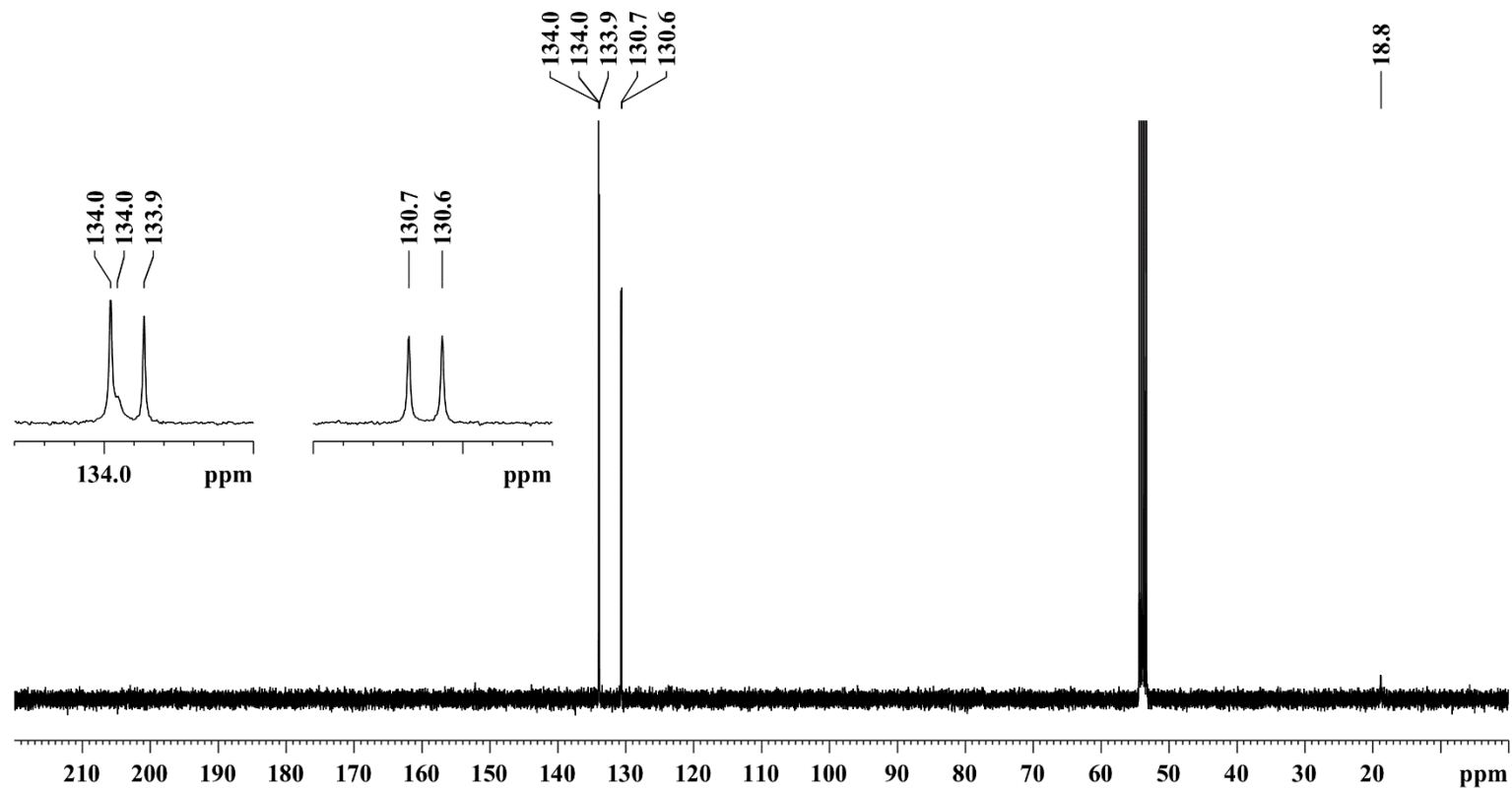


Figure S74. ^{13}C NMR spectrum (101 MHz) of 15_{Me} in CD_2Cl_2 at room temperature.

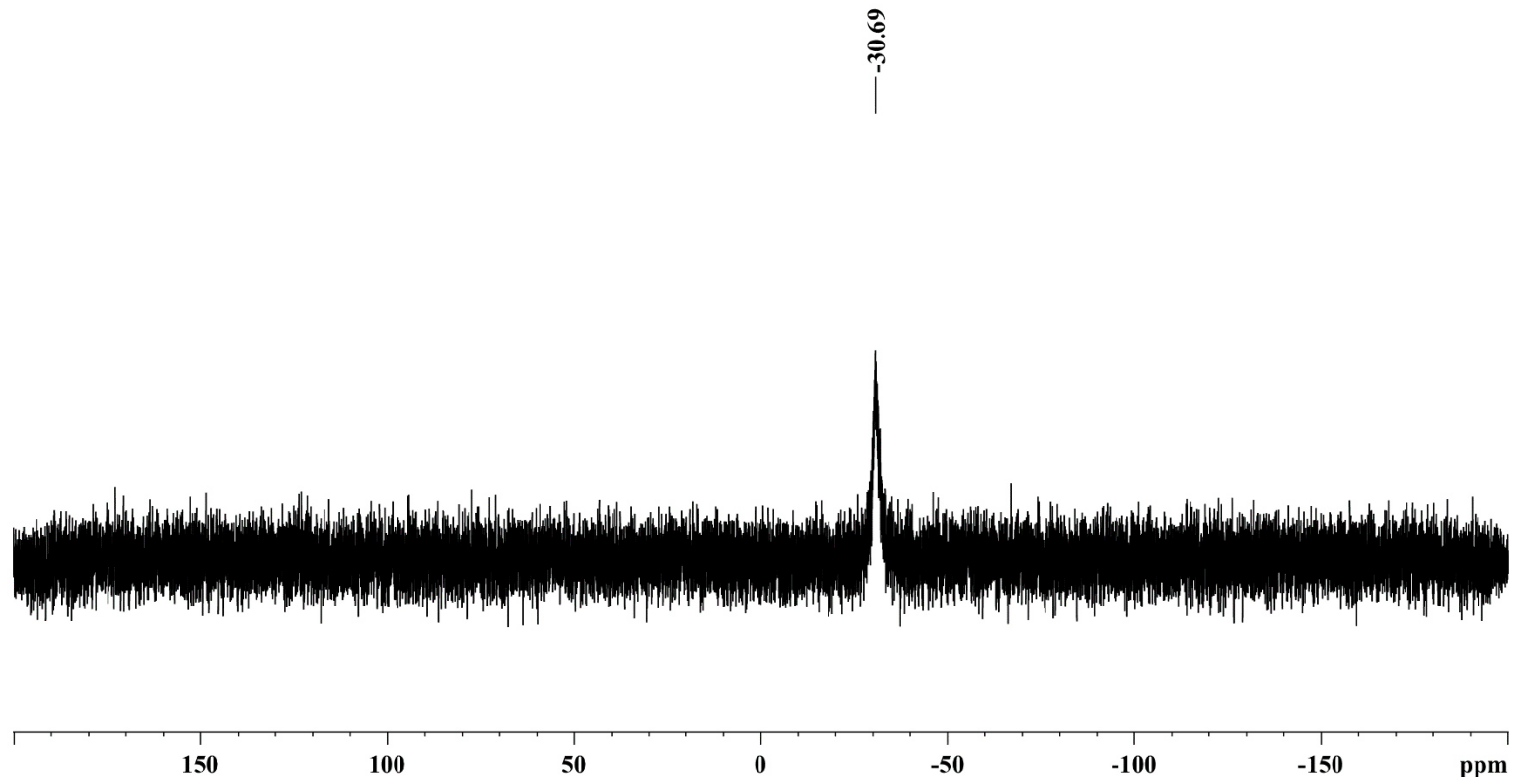


Figure S75. ^{31}P NMR spectrum (162 MHz) of 15M_e in in CD_2Cl_2 at room temperature.

3.26 [BiDipp₂(NCMe)(SbF₆)] 16_{Dipp}

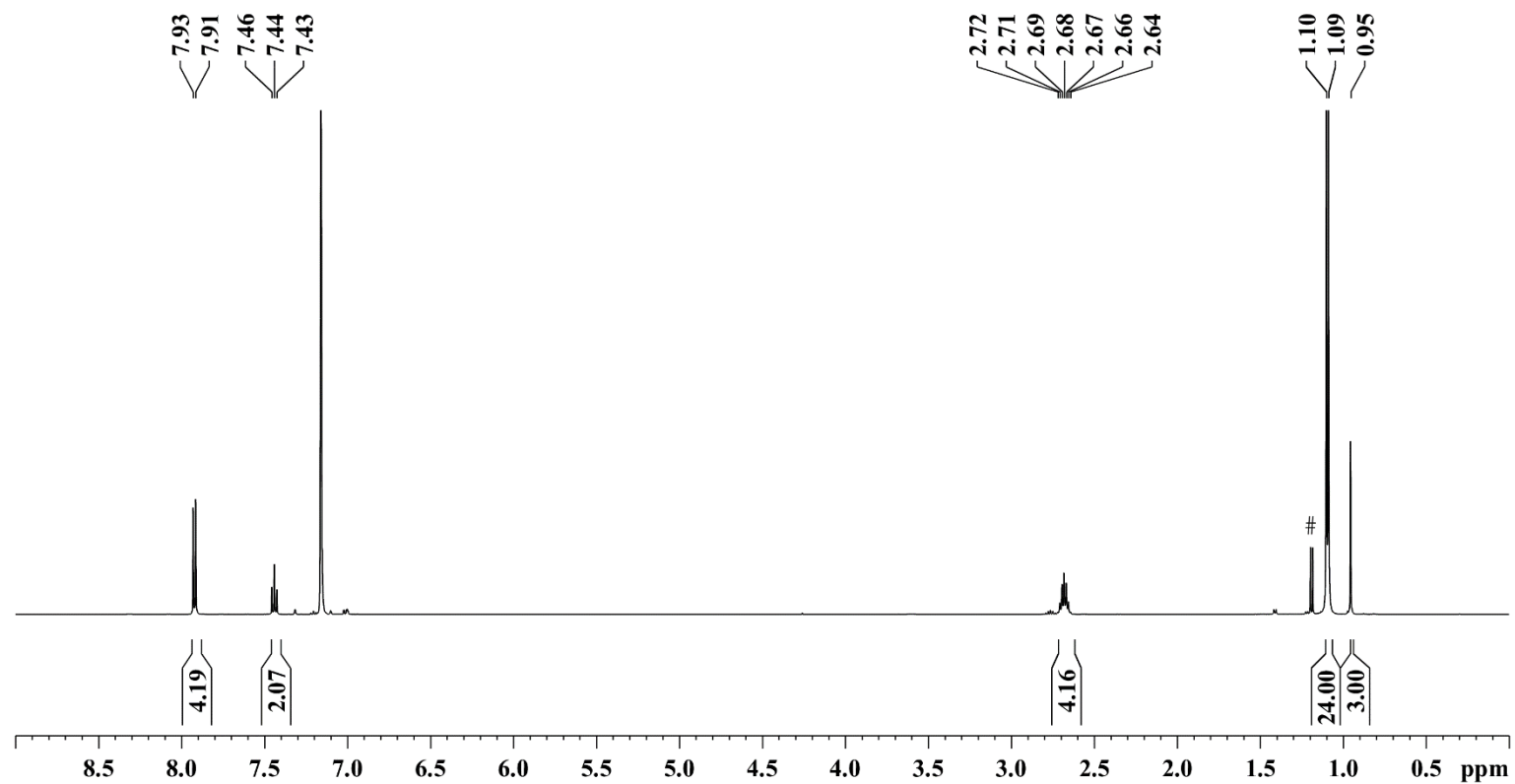


Figure S76. ¹H NMR spectrum (500 MHz) of 16_{Dipp} in in C₆D₆ at room temperature (# = hydrolysis).

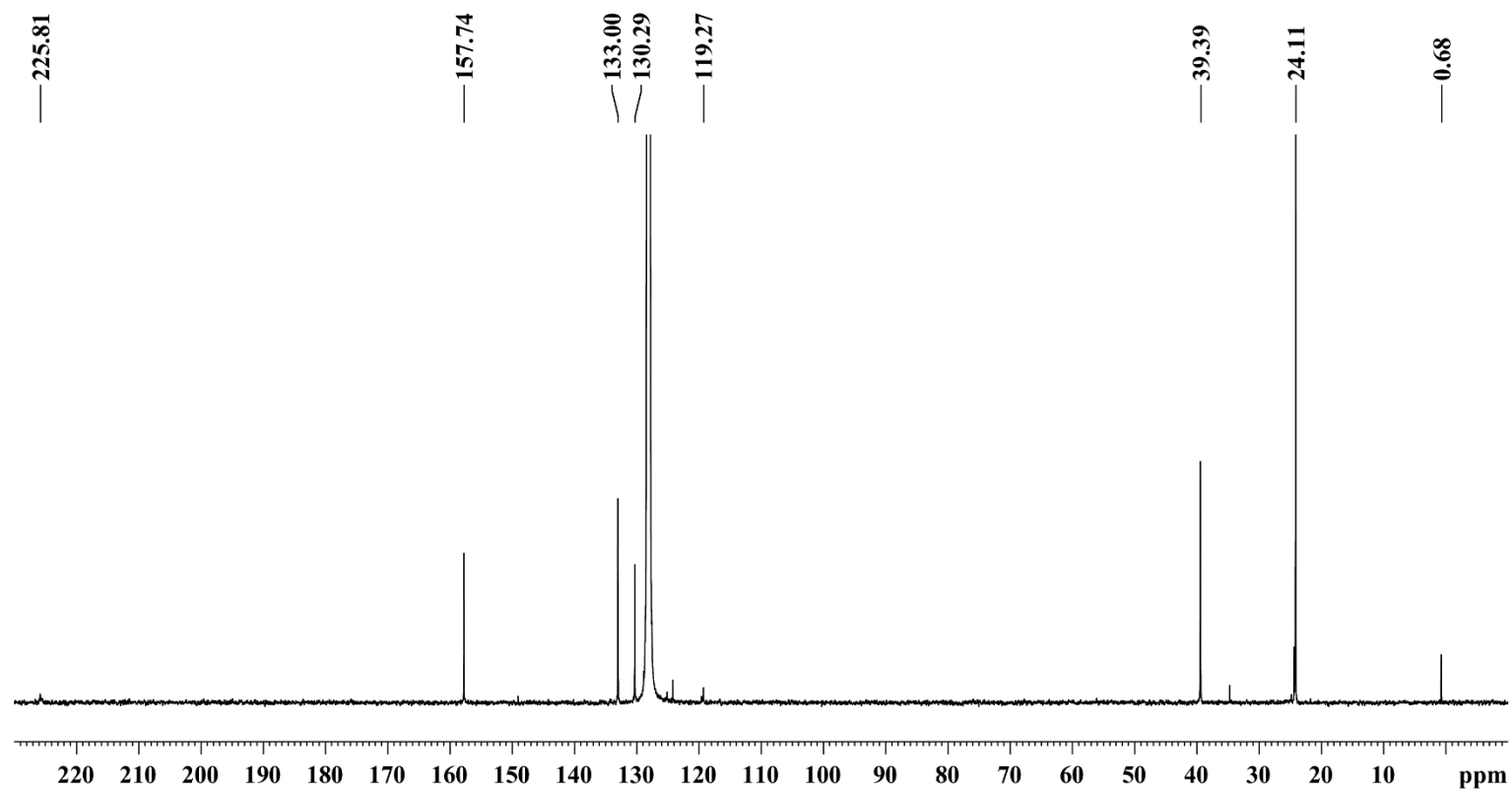


Figure S77: ^{13}C NMR spectrum (125 MHz) of **16**_{DiPP} in C_6D_6 at room temperature.

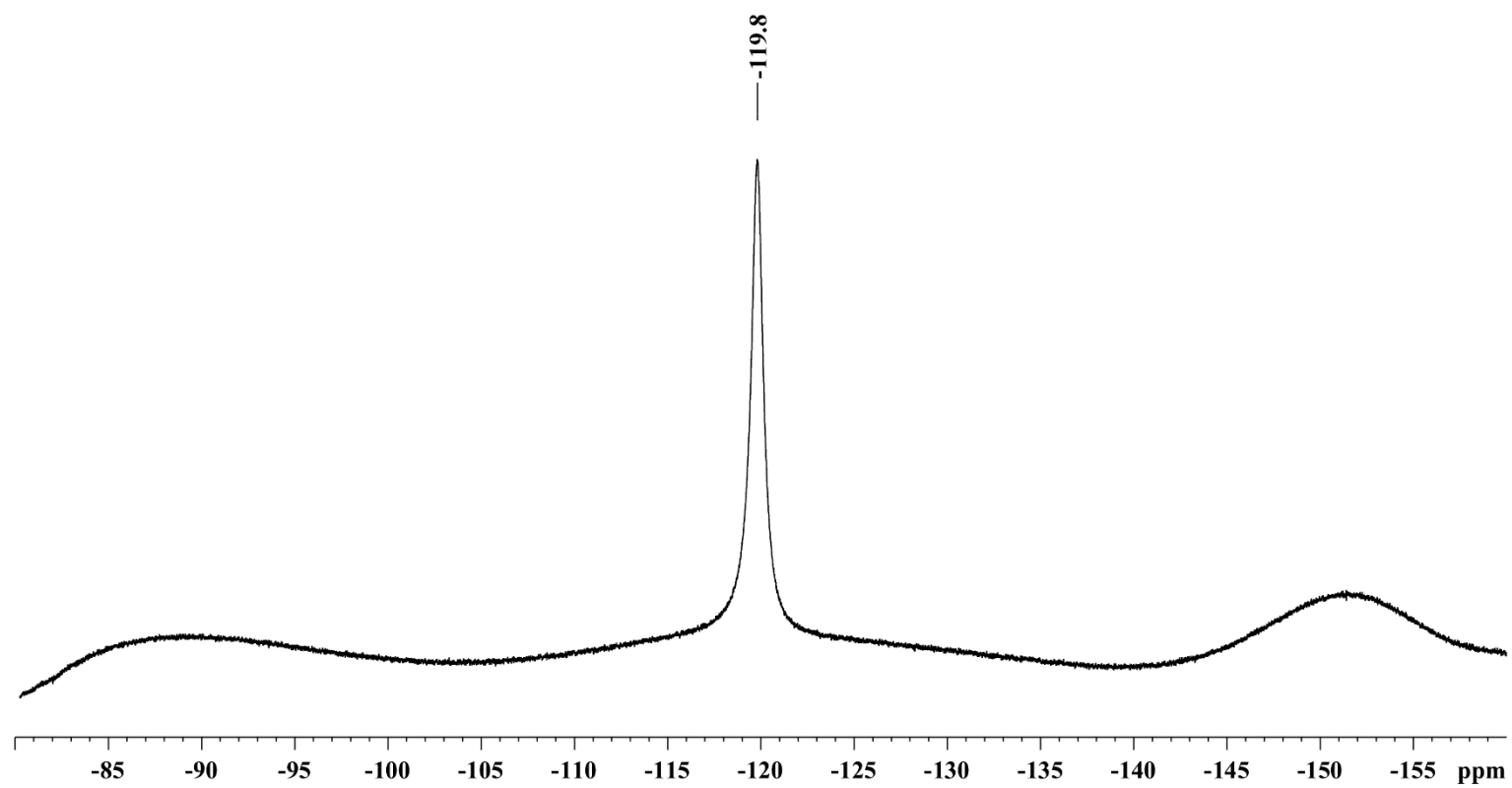


Figure S78. ^{19}F NMR spectrum (471 MHz) of 16_{Dipp} in in C_6D_6 at room temperature.

4. IR Spectra

4.1 [BiDipp₂(OPEt₃)₂(PF₆)] 3_{Dipp}

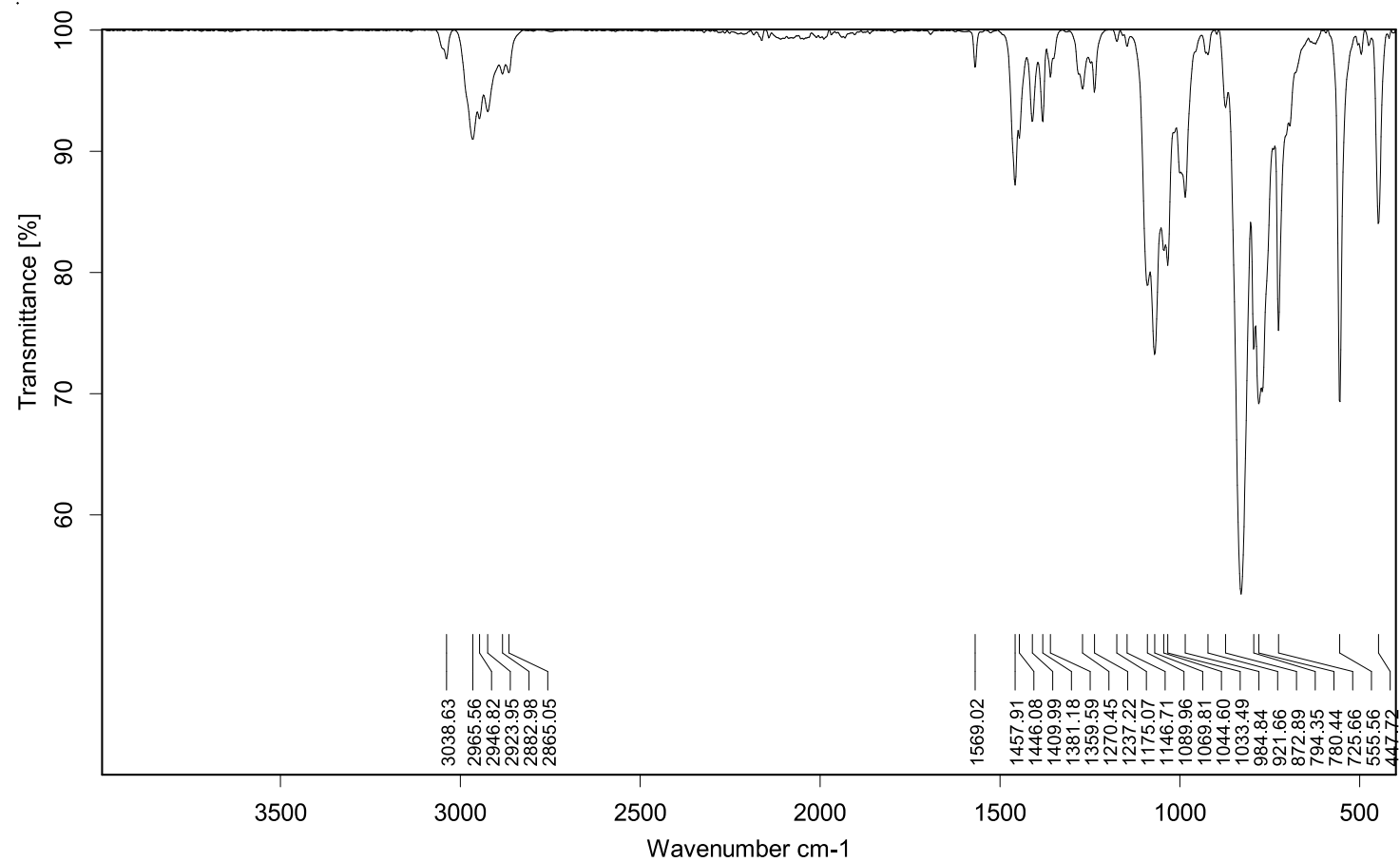


Figure S79. IR spectrum of solid **3_{Dipp}** at room temperature.

4.2 [BiDipp₂(SbF₆)] 4_{Dipp}

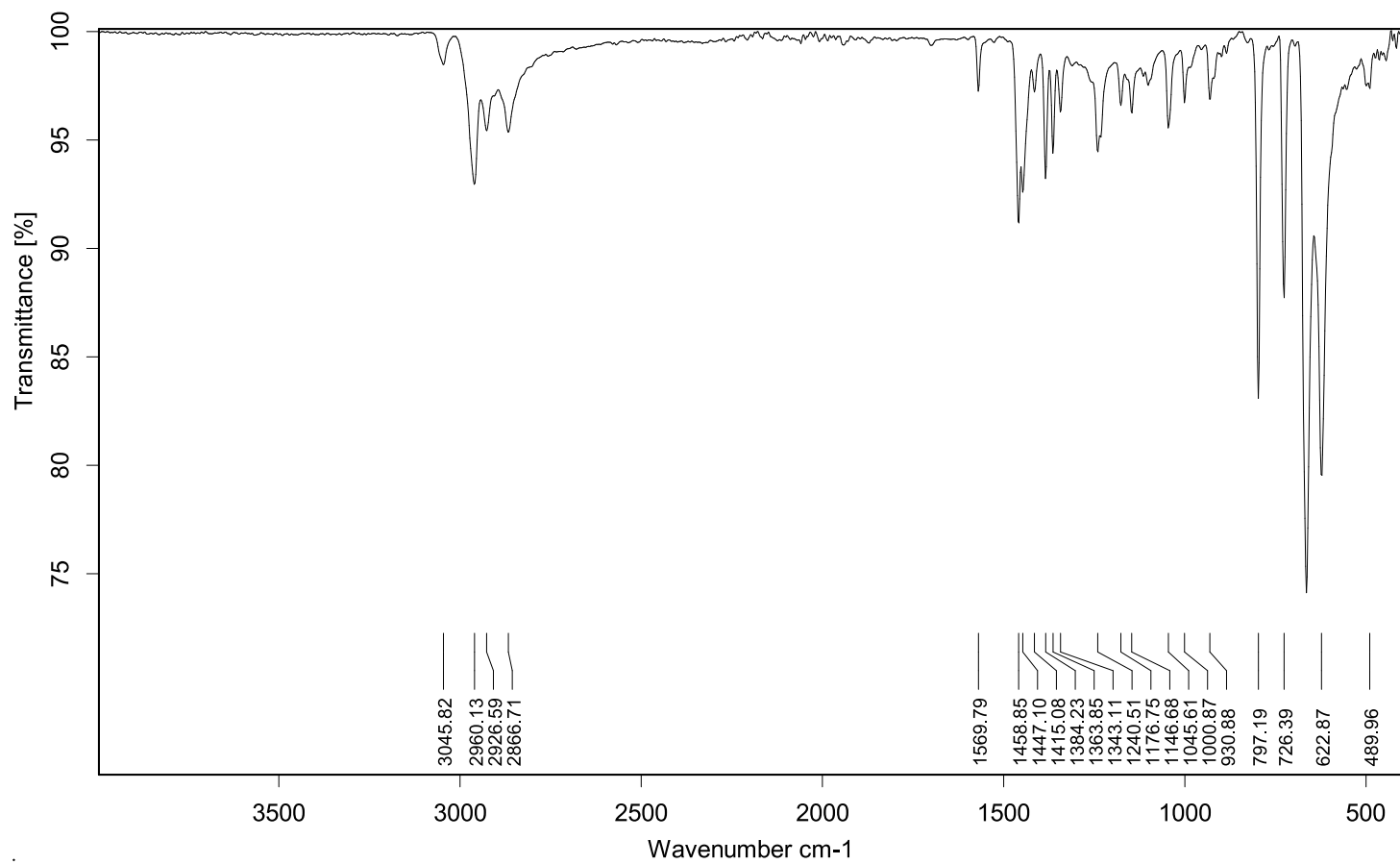


Figure S80. IR spectrum of solid 4_{Dipp} at room temperature.

4.3 [(BiDipp)₂F(SbF₆)] 5_{Dipp}

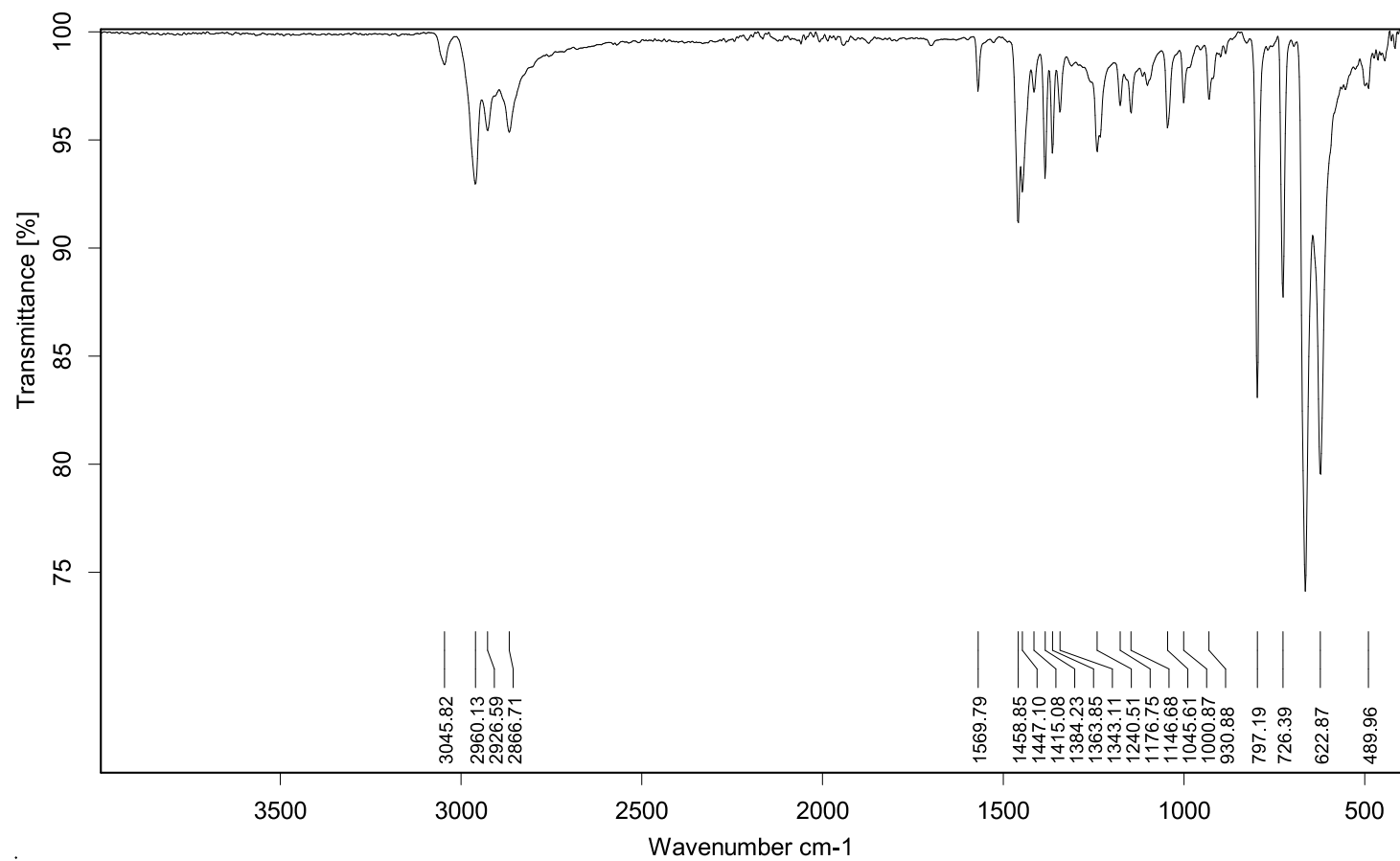


Figure S81. IR spectrum of solid 5_{Dipp} at room temperature

4.4 [BiDipp₂(SPMe₃)(SbF₆)] 6_{Dipp}

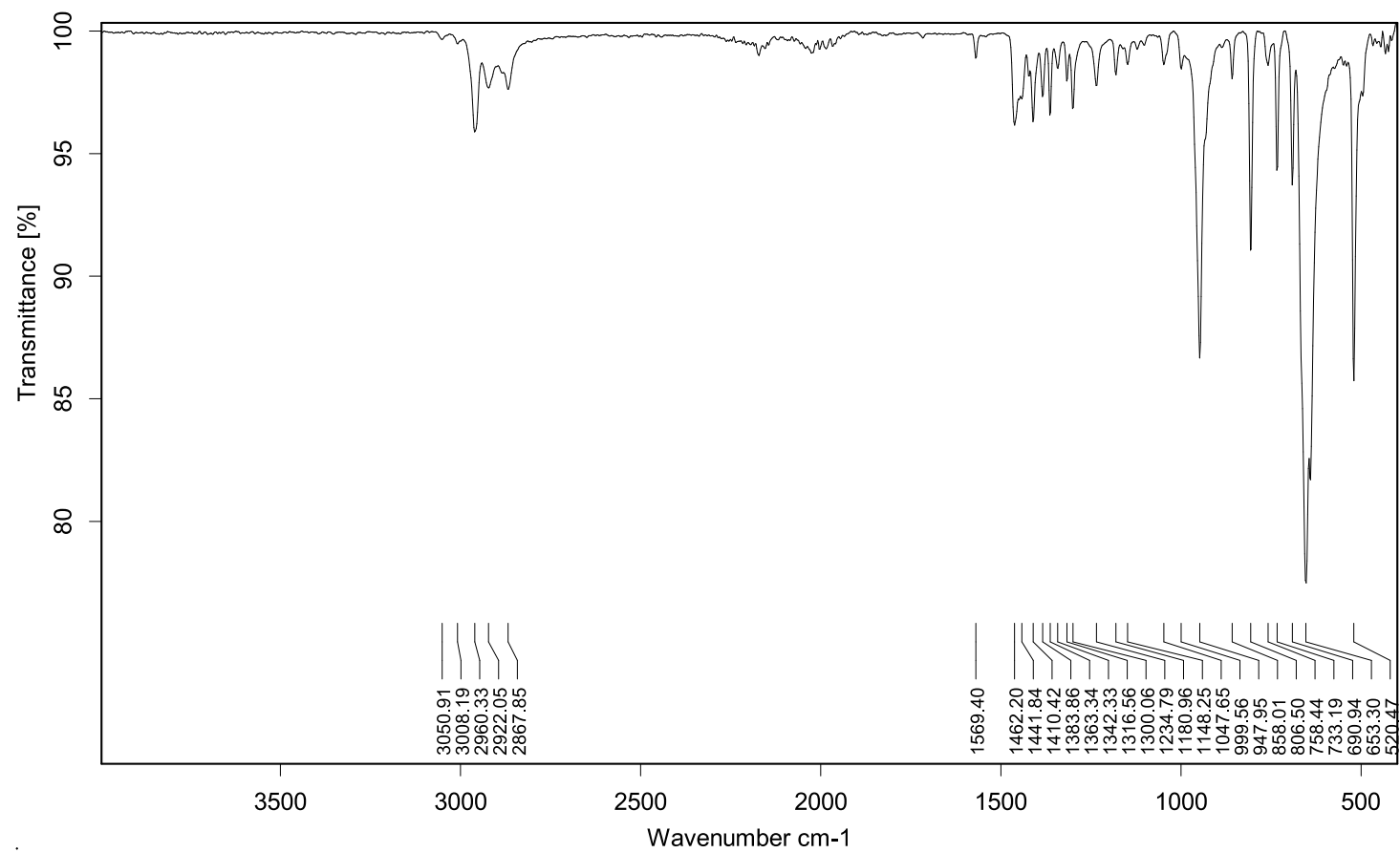


Figure S82. IR spectrum of solid **6_{Dipp}** at room temperature.

4.5 [BiDipp₂(SePMe₃)(SbF₆)] 7_{Dipp}

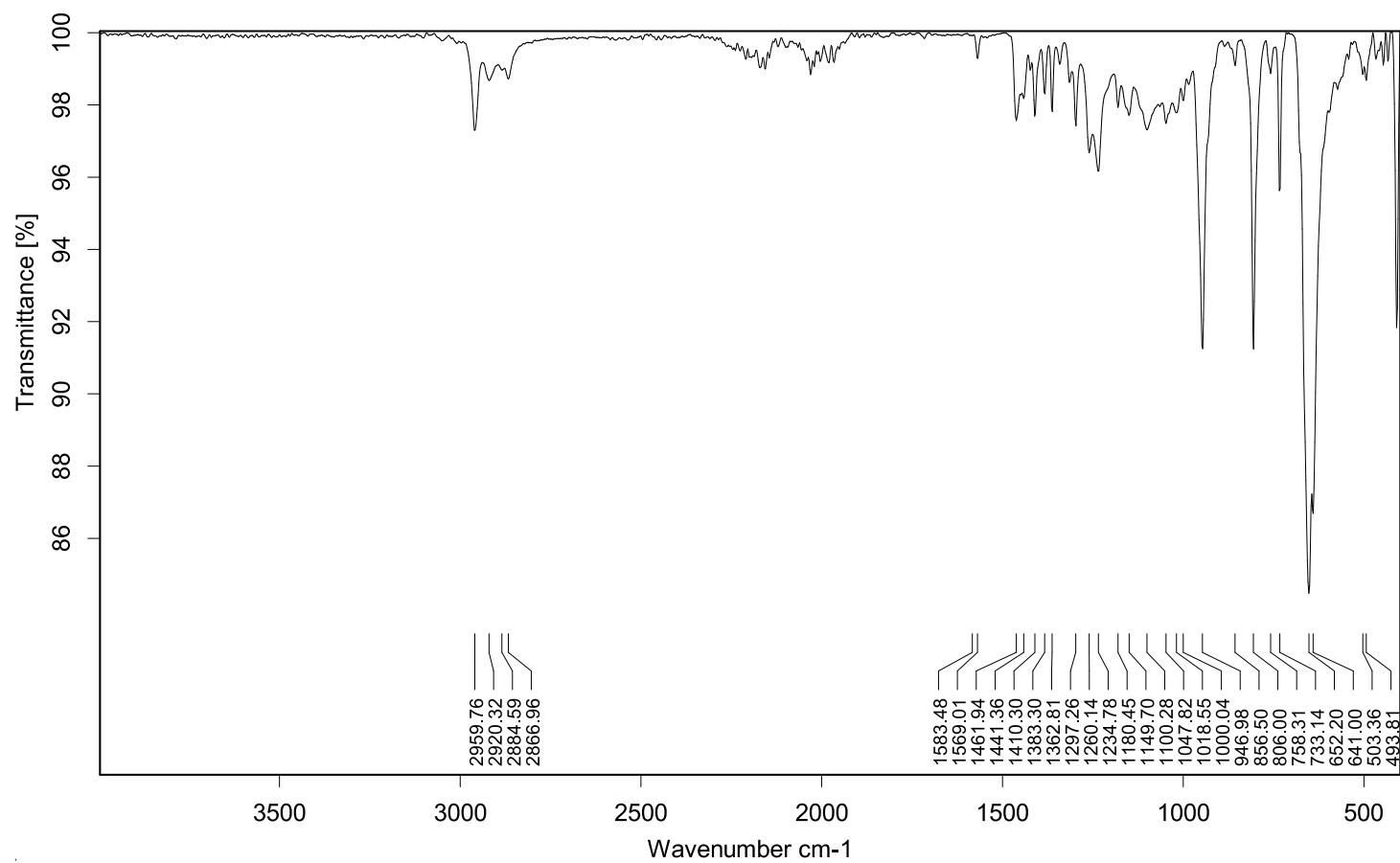


Figure S83. IR spectrum of solid 7_{Dipp} at room temperature.

4.6 [BiDipp₂(OPEt₃)₂(SbF₆)] 8'_{Dipp}

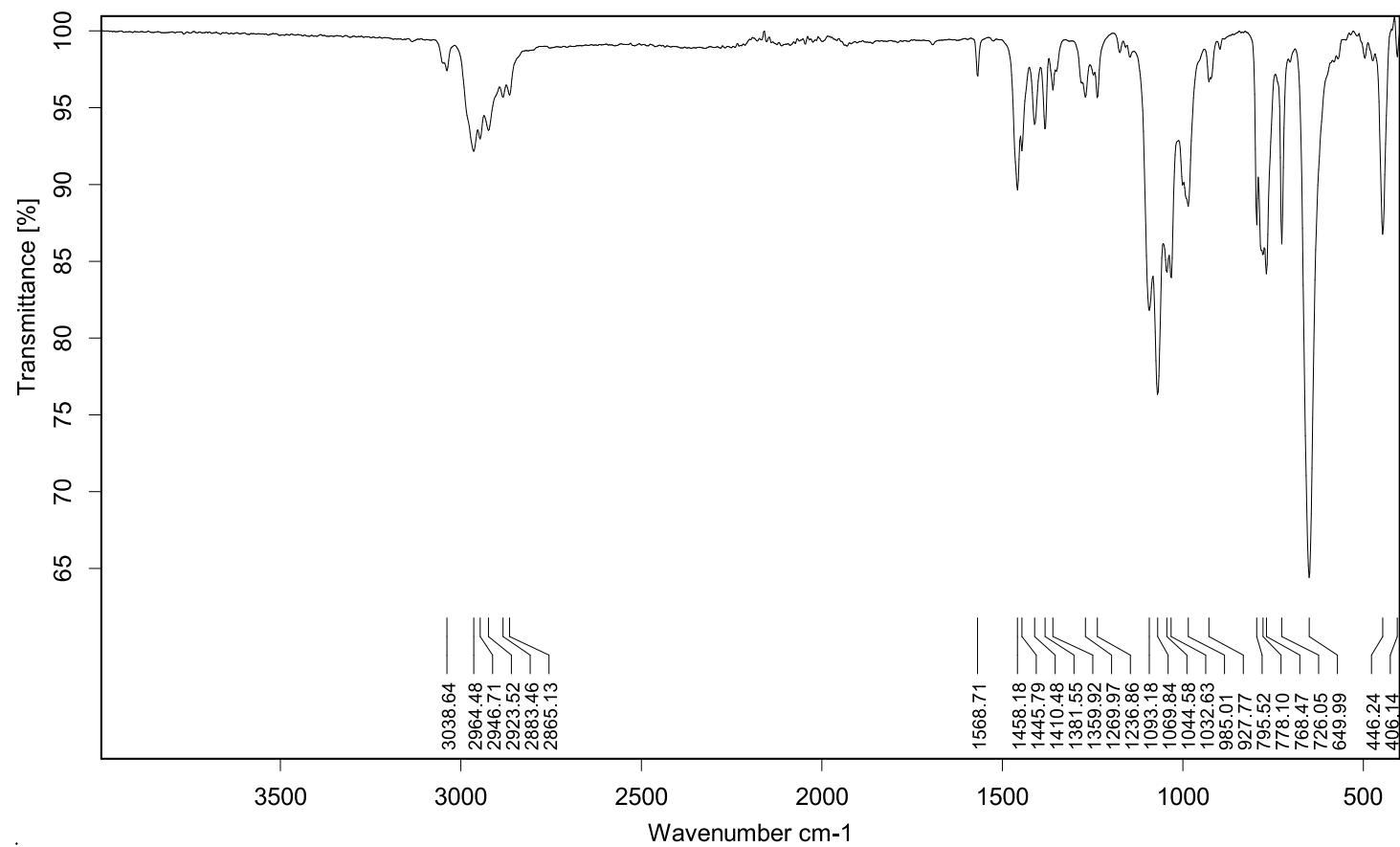


Figure S84. IR spectrum of solid 8'_{Dipp} at room temperature.

4.7 [BiDipp₂(CN*t*Bu)(SbF₆)] 9_{Dipp}

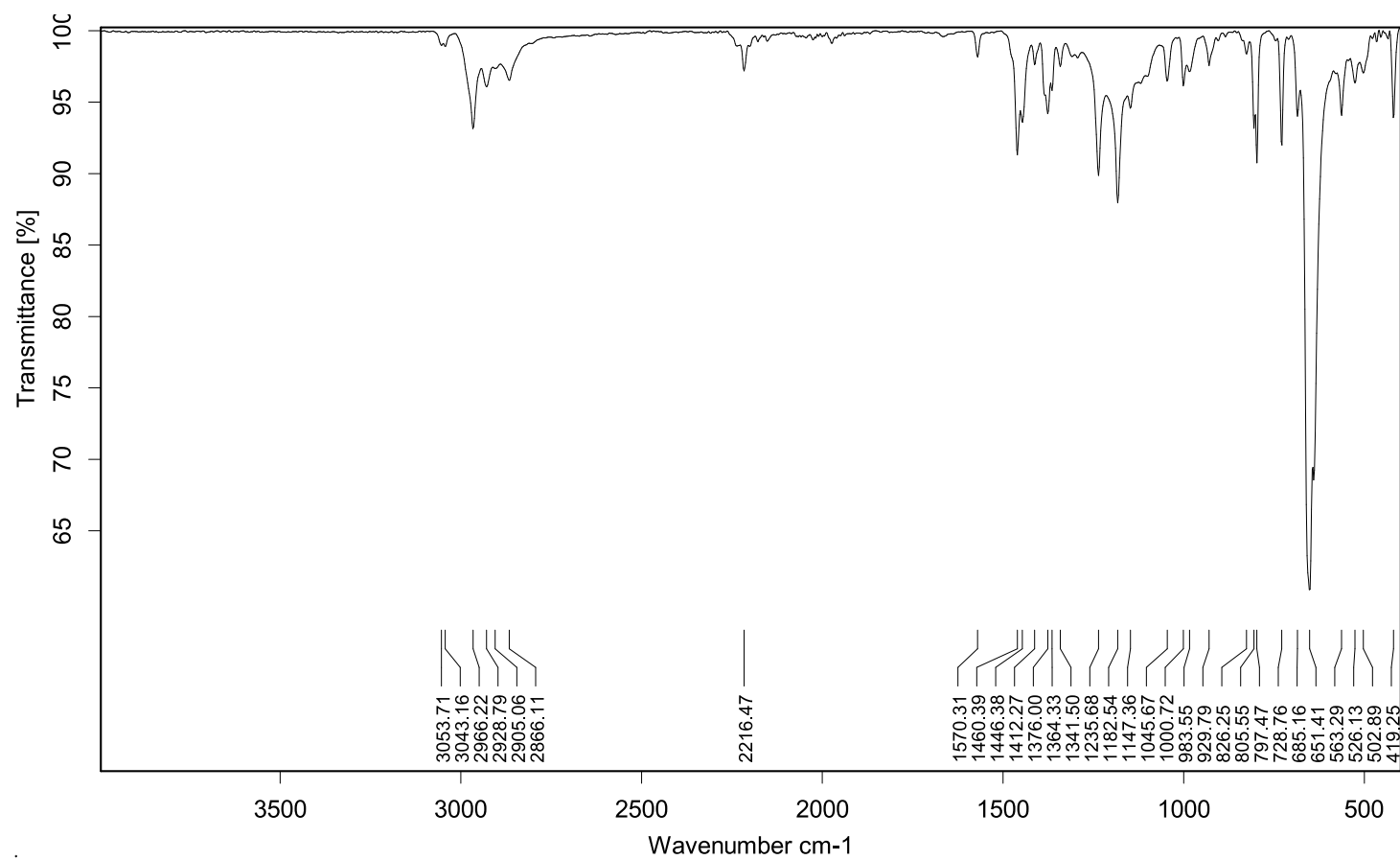


Figure S85. IR spectrum of solid **9_{Dipp}** at room temperature.

4.8 [BiMe₂(CN*t*Bu)(SbF₆)] 9Me

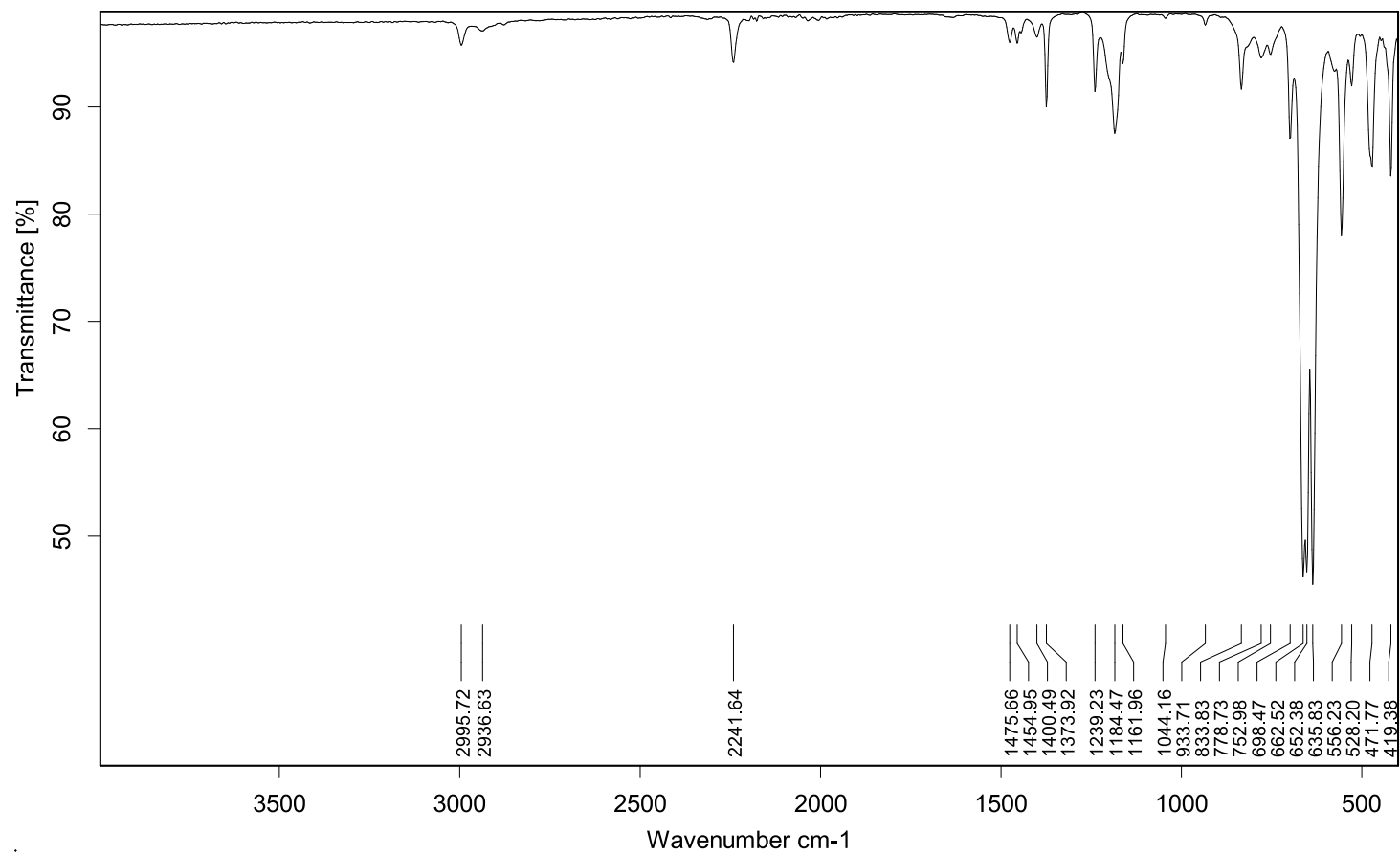


Figure S86. IR spectrum of solid 9Me at room temperature.

4.9 [BiMe₂(CNAd)(SbF₆)] 10_{Me}

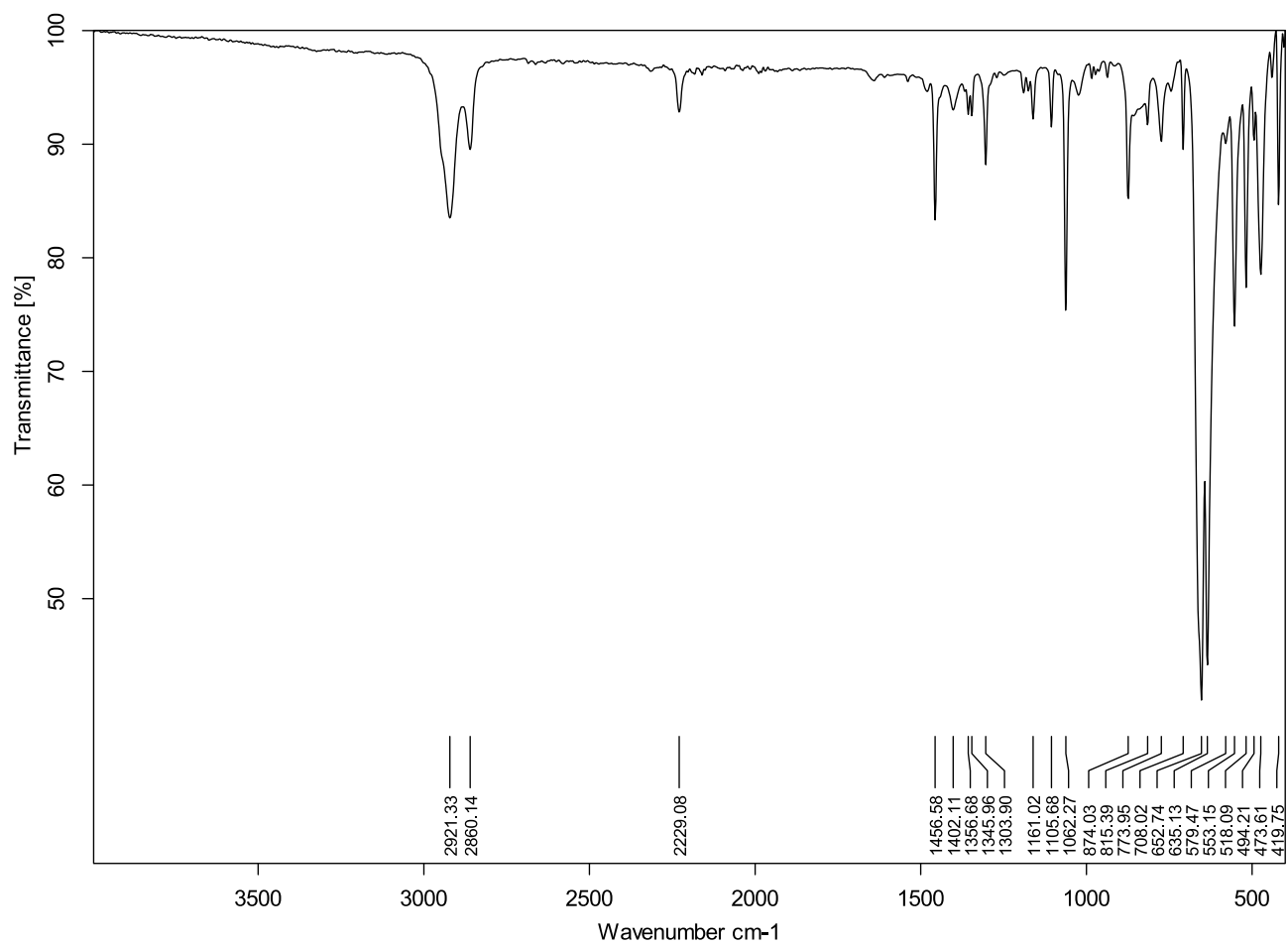


Figure S87. IR spectrum of solid **10_{Me}** at room temperature.

4.10 [BiMe₂(CNXyl)(SbF₆)] 11_{Me}

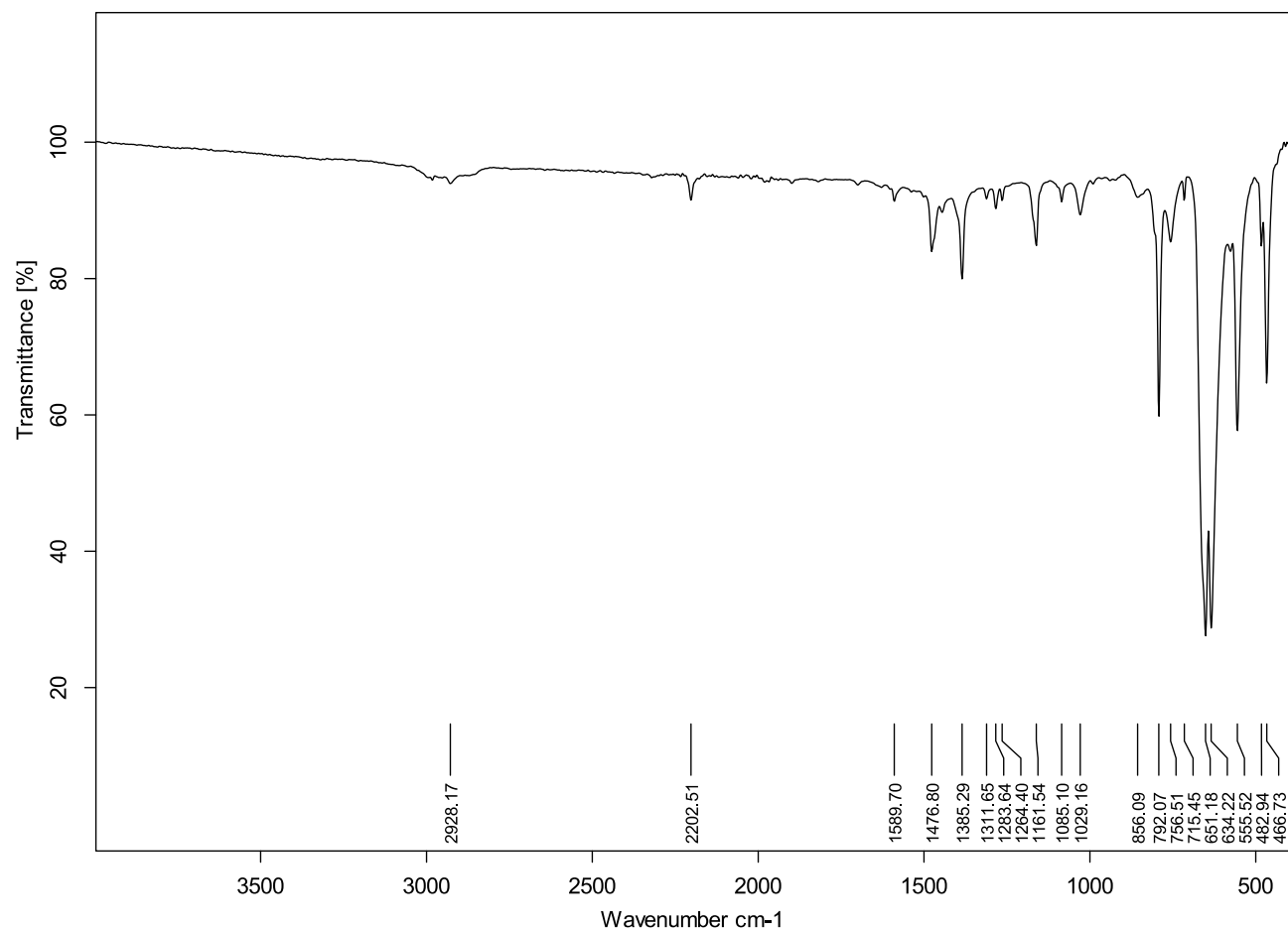


Figure S88. IR spectrum of solid **11_{Me}** at room temperature.

4.11 [BiMe₂(CNXyl)₂(SbF₆)] 11'_{Me}

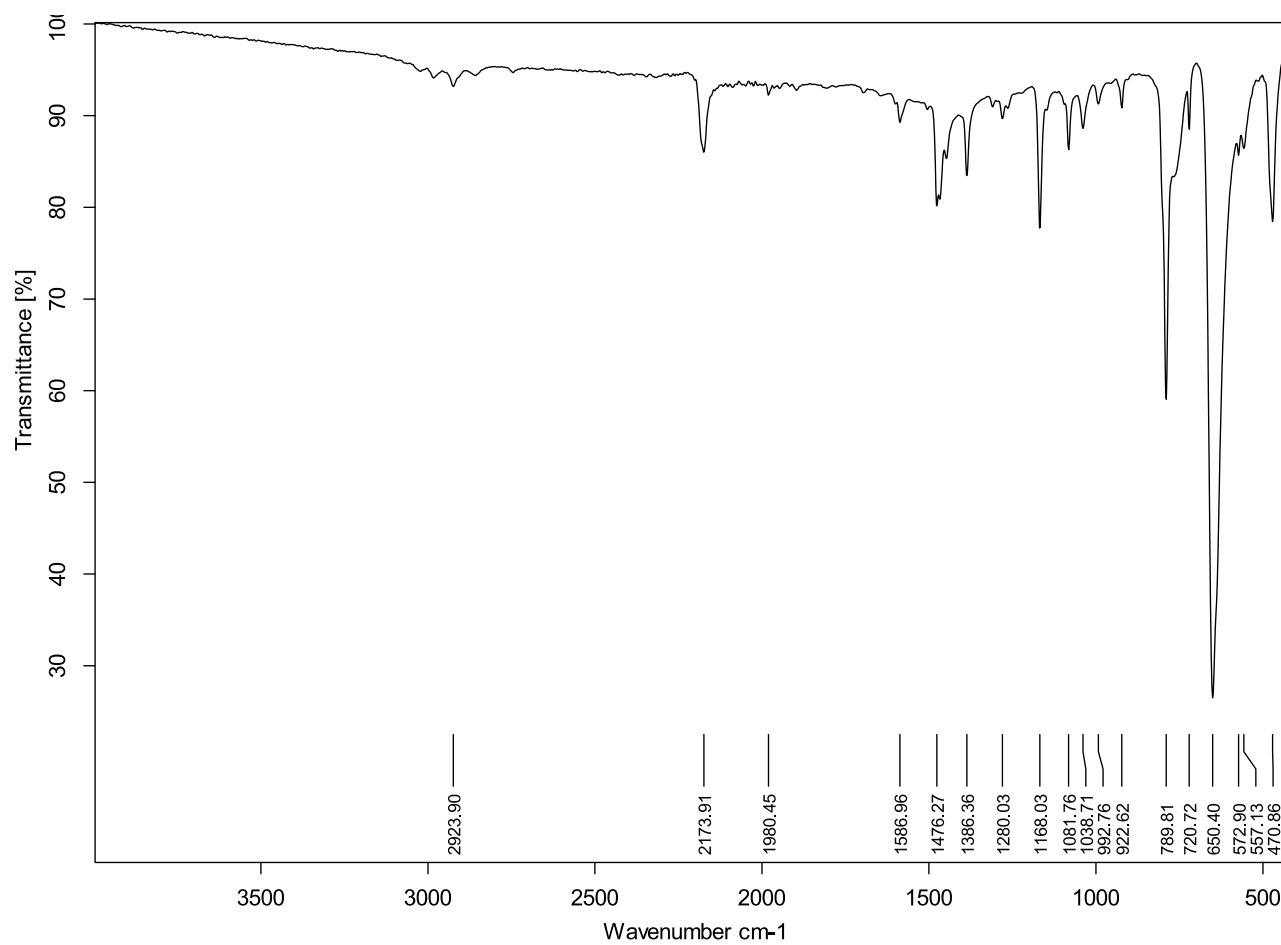


Figure S89. IR spectrum of solid 11'_{Me} at room temperature.

4.12 [BiMe₂(CNCy)(SbF₆)] 12_{Me}

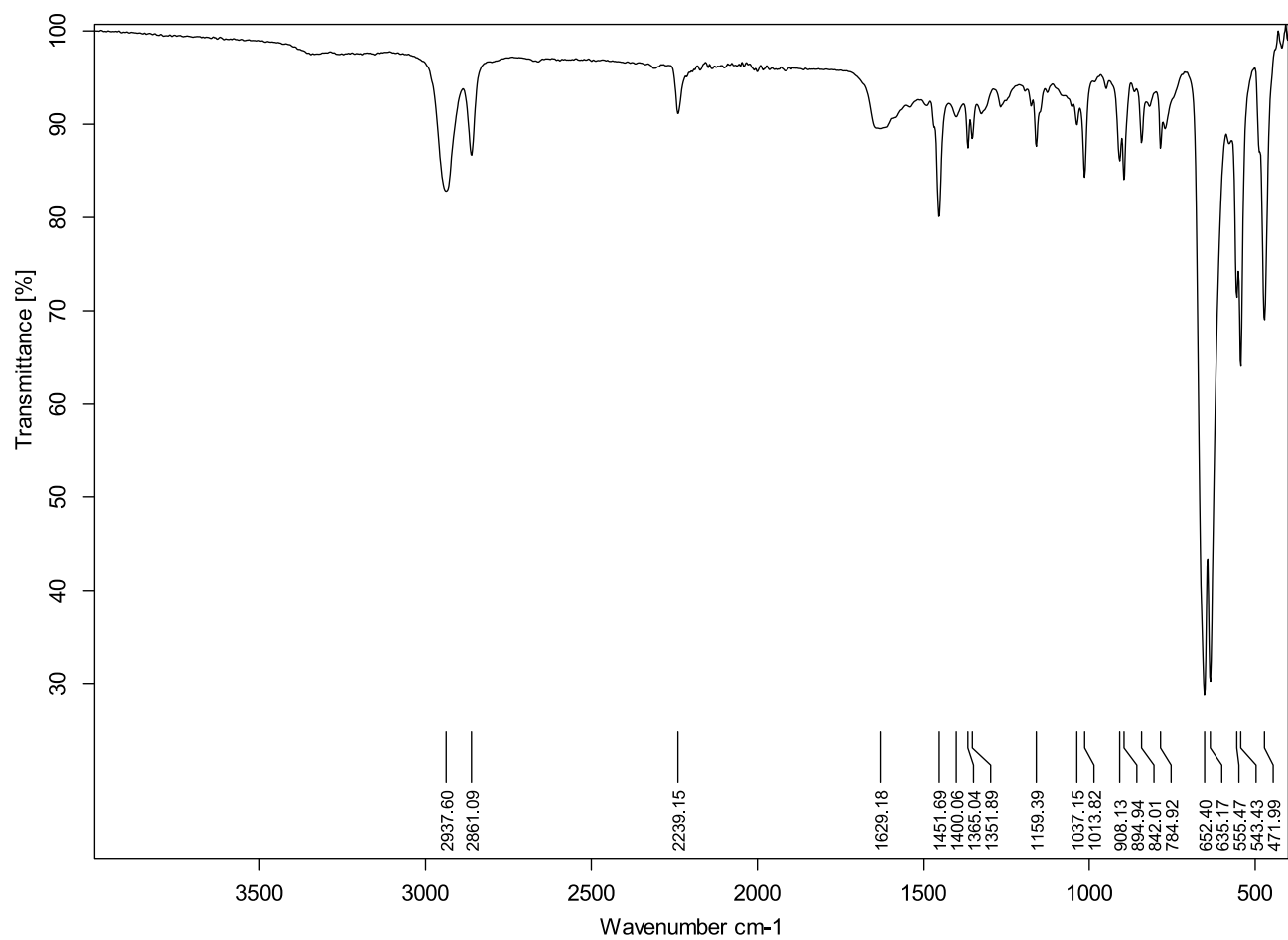


Figure S90. IR spectrum of solid **12_{Me}** at room temperature.

4.13 [BiMe₂(CN*n*Bu)(SbF₆)] 13_{Me}

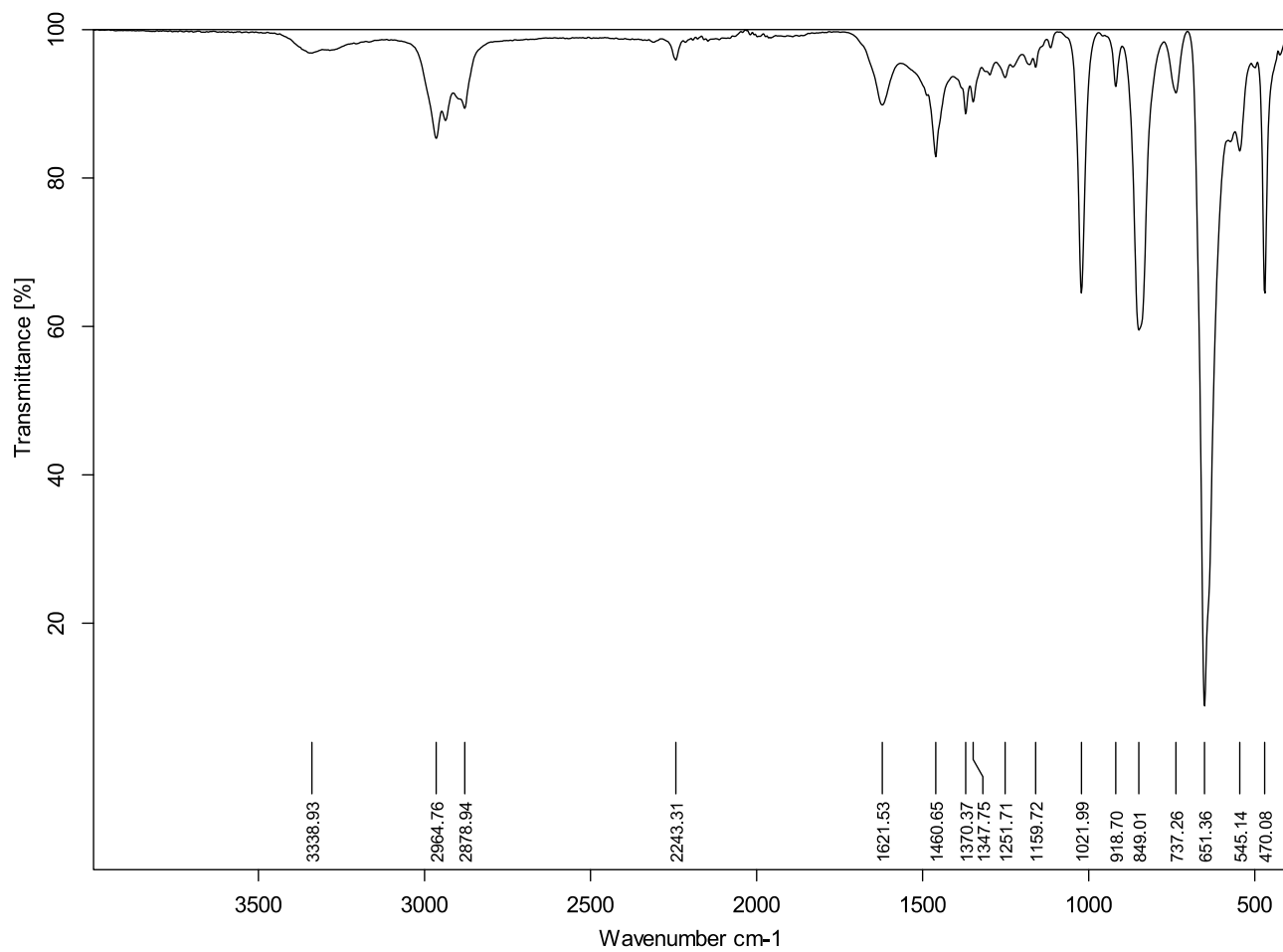


Figure S91. IR spectrum of solid 13_{Me} at room temperature.

4.14 [BiDipp₂(NCMe)(SbF₆)] 16_{Dipp}

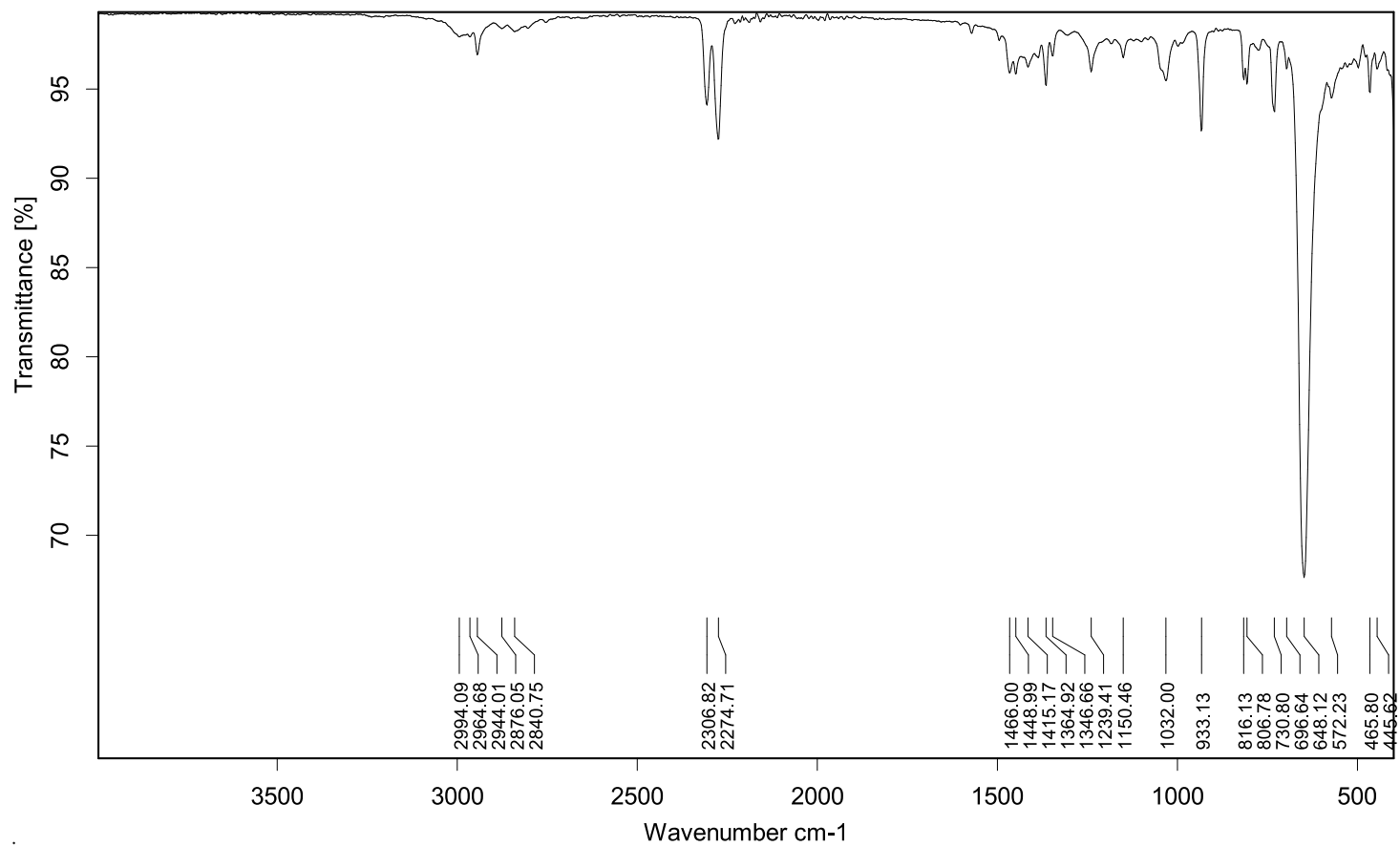


Figure S92. IR spectrum of solid 16_{Dipp} at room temperature.

5. Single crystal X-ray diffraction

The crystal structures of most compounds have been discussed in the text. Following here, are those that have not been discussed in the manuscript.

5.1 $[(\text{BiDipp})_2\text{F}][\text{PF}_6] \cdot 2\text{Dipp}$

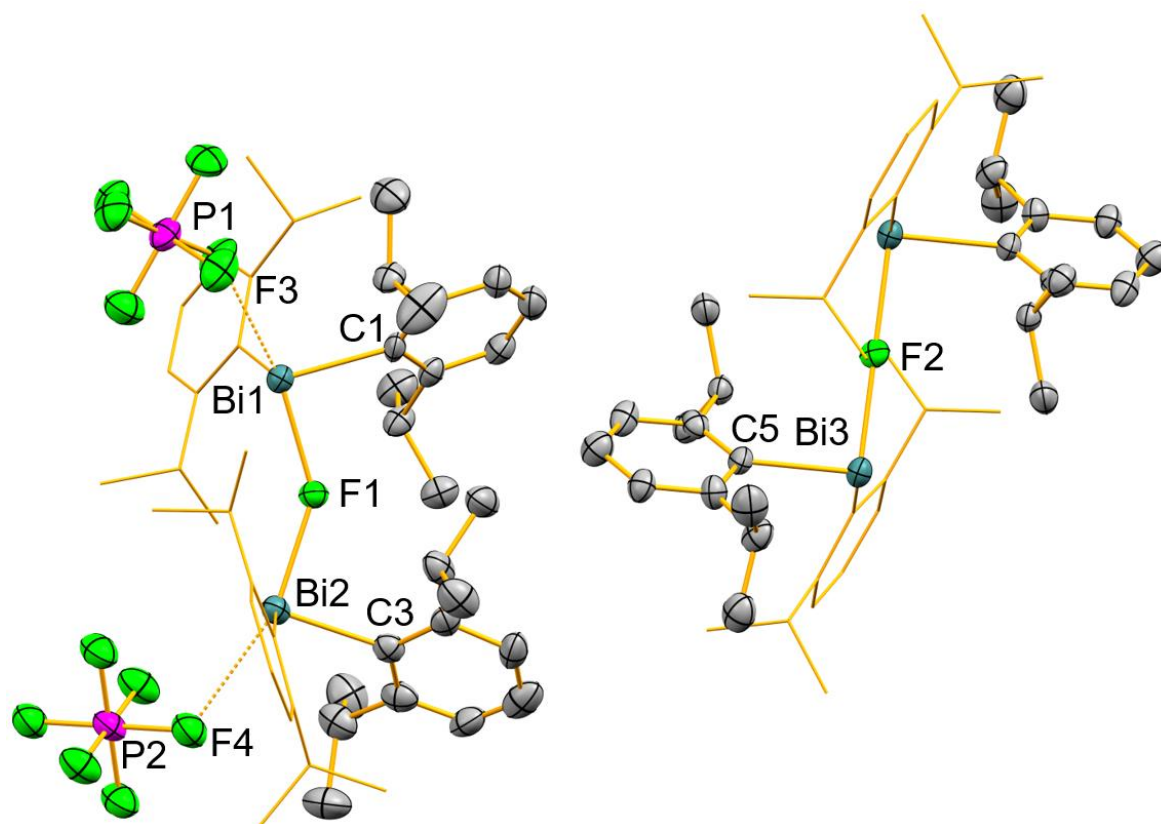


Figure S93. Molecular structure of 2_{Dipp} in the solid state, with the asymmetric unit containing two formula units (the bismuth atom that is not labelled is symmetry-generated). Hydrogen atoms and solvent molecules are omitted, second Dipp shown as wireframe for clarity. Ellipsoids are shown at a 50% probability level. Selected bond lengths (Å) and angles (deg): Bi1-F1 2.275(4); Bi2-F1 2.296(4); Bi3-F2 2.2770(3); Bi1-F3 2.717(5); Bi1-C1 2.268(8); Bi1-C2 2.277(8); Bi2-C3 2.268(8); Bi2-C4 2.294(8); Bi3-C5 2.283(8); Bi3-C6 2.278(8); Bi1-F1-Bi2 144.0(2); Bi3-F2-Bi3' 180.0.

5.2 [BiDipp₂(OPEt₃)₂(SbF₆)] 8'_{Dipp}

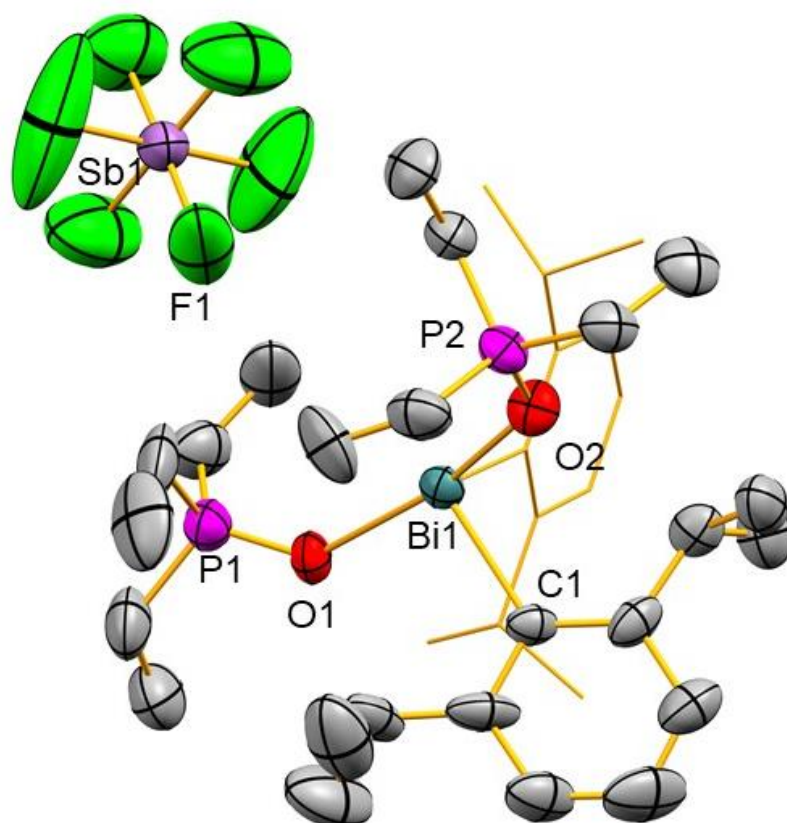


Figure S94. Molecular structure of **8'_{Dipp}** in the solid state. Hydrogen atoms and disordered atoms are omitted, second Dipp shown as wireframe for clarity. Ellipsoids are shown at a 50% probability level. Selected bond lengths (Å) and angles (deg): Bi1-F1 4.92(2); Bi1-C1 2.278(11); Bi1-C2 2.96(11); Bi1-O1 2.429(6); Bi1-O2 2.452(8); P1-O1 1.514(8); P2-O2 1.504(9); C1-Bi1-C2 94.9(4); O1-Bi1-O2 164.1(2); C1-Bi1-O1 86.8(4), C1-Bi1-O2 100.3(3); C2-Bi1-O1 104.8(3); C2-Bi1-O2 88.9(3).

5.3 [BiMe₂(PCy₃)(SbF₆)] 14_{Me}

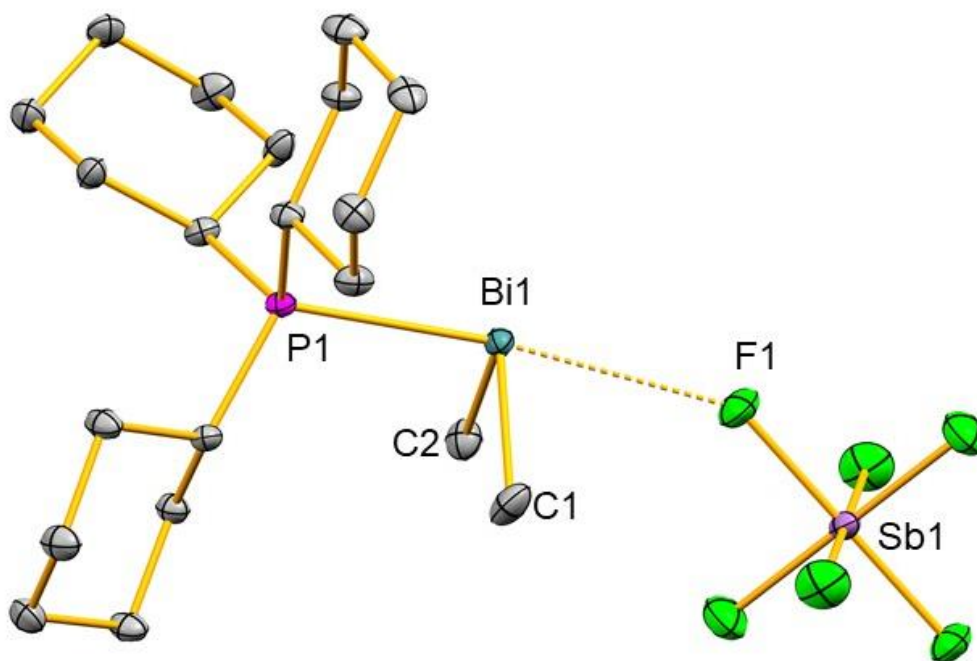


Figure S95. Molecular structure of **14_{Me}** in the solid state. Hydrogen atoms are omitted for clarity. Ellipsoids are shown at a 50% probability level. Selected bond lengths (Å) and angles (deg): Bi1-F1 2.942(2); Bi1-C1 2.248(3); Bi1-C2 2.253(3); Bi1-P1 2.6764(7); C1-Bi1-C2 95.5(1); C1-Bi1-P1 97.62(8); C2-Bi1-P1 92.88(9), P1-Bi1-F1 172.78(4).

5.4 [BiDipp₂(MeCN)(SbF₆)] 16_{Dipp}

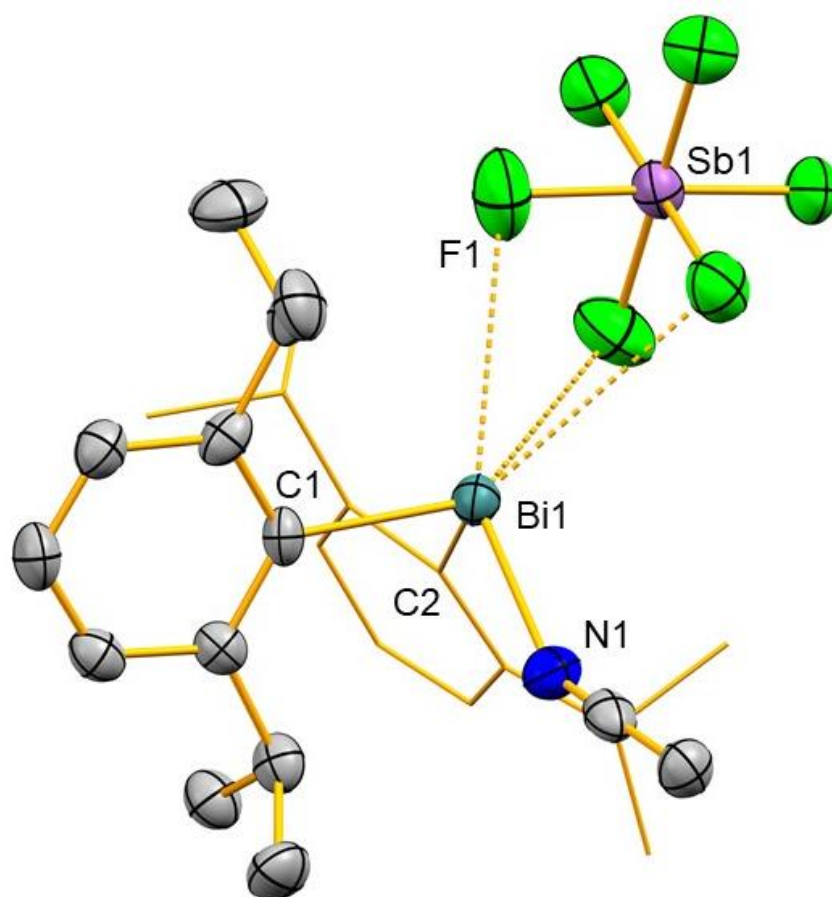


Figure S96. Molecular structure of one molecule of the asymmetric unit of **16_{Dipp}** in the solid state. Hydrogen atoms are omitted, second Dipp shown as wireframe for clarity. Ellipsoids are shown at a 50% probability level. Selected bond lengths (Å) and angles (deg): Bi1-N1 2.358(6); Bi1-C1 2.259(7); Bi1-C2 2.278(7); Bi2-N2 2.388(7); Bi2-C3 2.278(7); Bi2-C4 2.30(1); C1-Bi1-C2 95.5(3); C1-Bi1-N1 90.8(2); C2-Bi1-N1 104.5(2); Bi1-N1-C5 150.9(6); C3-Bi1-C4 95.2(3); C3-Bi2-N2 91.1(2); C4-Bi2-N2 104.9(3); Bi2-N2-C6 154.7(6).

Table S4. Selected crystal structure data of the structure determinations of compounds**2_{Dipp}**, **3_{Dipp}**, and **4_{Dipp}**.

Compound	2_{Dipp}	3_{Dipp}	4_{Dipp}
Empirical formula	C ₄₈ H ₆₈ Bi ₂ F ₇ P ₁ ·0.66 C ₇ H ₅ F ₃	C ₃₆ H ₆₄ Bi ₁ F ₆ O ₂ P ₃ 0.25 (C ₇ H ₈)	C ₂₄ H ₃₄ Bi ₁ F ₆ Sb
Formula weight	425.10	967.01	767.24
Crystal color, habit	orange, plate	colourless, plate	red, block
Temperature/K	100	100	100
Crystal system	triclinic	triclinic	monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>
a/Å	10.6120(3)	9.6454(5)	12.2580(8)
b/Å	17.0716(5)	12.2906(6)	14.9547(10)
c/Å	23.9432(8)	21.0269(10)	14.5409(9)
α /°	90.079(3)	102.1670(10)	90
β /°	91.020(3)	95.914(2)	95.8070(10)
γ /°	106.839(3)	110.8480(10)	90
Volume/Å ³	4150.9(2)	2233.5(2)	2651.9(3)
Z	3	2	4
ρ_{calc} /cm ³	1.531	1.439	1.922
μ /mm ⁻¹	6.436	4.109	7.697
F(000)	1874.0	981.0	1464.0
Crystal size/mm ³	-	0.272·0.221·0.102	0.245·0.151·0.112
Crystal radius(equiv)/mm	0.0447	-	-
Diffractionmeter	Stoe IPDS 2	Bruker D8 Quest	Bruker D8 Quest
Radiation	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)
2 θ range for data collection/°	3.008 to 51.992	4.04 to 56.794	4.582 to 51.996
Reflections collected	36843	106050	67368
Independent reflections	16303 [R_{int} = 0.438, R_{sigma} = 0.0592]	11151 [R_{int} = 0.0282, R_{sigma} = 0.0156]	5206 [R_{int} = 0.0255, R_{sigma} = 0.0106]
Data/restraint/parameters	16303/135/872	11151/151/677	5206/0/298
Goodness-of-fit on F^2	0.983	1.111	1.080
Final R indexes [all data]	R_1 = 0.0724, wR_2 = 0.1300	R_1 = 0.0248, wR_2 = 0.0579	R_1 = 0.0165, wR_2 = 0.0335
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0473, wR_2 = 0.1216	R_1 = 0.0228, wR_2 = 0.0579	R_1 = 0.0151, wR_2 = 0.0331
Largest diff. peak/hole/ e Å ⁻³	1.95/-1.59	2.19/-1.82	1.71/-0.43
CCDC	2232027	2232017	2232026

Table S5. Selected crystal structure data of the structure determinations of compounds**4-tol_{Dipp}**, **5_{Dipp}**, and **6_{Dipp}**.

Compound	4-tol_{Dipp}	5_{Dipp}	6_{Dipp}
Empirical formula	C ₃₁ H ₄₂ Bi ₁ F ₆ Sb ₁	C ₄₈ H ₆₈ Bi ₂ F ₇ Sb ₁	C ₂₇ H ₄₃ BiF ₆ P ₁ S ₁ Sb ₁
Formula weight	859.37	1317.73	875.37
Crystal color, habit	red, block	orange, block	yellow, block
Temperature/K	100	100	100
Crystal system	monoclinic	triclinic	monoclinic
Space group	<i>P2</i> ₁	<i>P</i> ₁ [−]	<i>P2</i> ₁ / <i>c</i>
<i>a</i> /Å	9.3675(3)	9.8561(9)	11.0048(5)
<i>b</i> /Å	17.5385(5)	11.1687(8)	15.5979(8)
<i>c</i> /Å	10.3409(3)	11.9630(9)	18.8944(8)
α /°	90	79.483(6)	90
β /°	109.099(2)	87.118(7)	97.514(3)
γ /°	90	68.888(6)	90
Volume/Å ³	1605.41(9)	1207.68(17)	3215.4(3)
Z	2	1	4
ρ_{calc} /cm ³	1.778	1.812	1.808
μ /mm ^{−1}	6.367	7.881	6.470
F(000)	832.0	636.0	1696.0
Crystal radius(equiv)/mm	0.0609	0.0263	0.0460
Diffractometer	Stoe IPDS 2	Stoe IPDS 2T	Stoe IPDS 2T
Radiation	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)
2 θ range for data collection/°	4.168 to 58.306	3.464 to 51.994	3.398 to 58.43
Reflections collected	18595	12574	40768
Independent reflections	8615 [R_{int} = 0.0368, R_{sigma} = 0.0644]	4746 [R_{int} = 0.0865, R_{sigma} = 0.0840]	8658 [R_{int} = 0.0698, R_{sigma} = 0.0415]
Data/restraint/parameters	8615/1/362	4746/0/274	8658/0/400
Goodness-of-fit on F^2	0.949	0.949	0.999
Final R indexes [all data]	R_1 = 0.0468, wR_2 = 0.643	R_1 = 0.0641, wR_2 = 0.0655	R_1 = 0.0420, wR_2 = 0.0457
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0325, wR_2 = 0.0618	R_1 = 0.0367, wR_2 = 0.0605	R_1 = 0.0258, wR_2 = 0.0425
Largest diff. peak/hole/ e Å ^{−3}	2.24/-1.12	1.15/-1.79	1.04/-0.91
Flack parameter	-0.037(5)	-	-
CCDC	2232014	2232016	2232023

Table S6. Selected crystal structure data of the structure determinations of compounds**7_{Dipp}**, **8'_{Dipp}**, and **9_{Dipp}**.

Compound	7_{Dipp}	8'_{Dipp}	9_{Dipp}
Empirical formula	C ₂₇ H ₄₃ BiF ₆ P ₁ Se ₁ Sb ₁	C ₃₆ H ₆₄ Bi ₁ F ₆ O ₂ P ₃	C ₂₉ H ₄₃ Bi ₁ F ₆ N ₁ Sb ₁
Formula weight	922.27	1058.57	942.50
Crystal color, habit	yellow, block	colourless, plate	colourless, block
Temperature/K	100	100	100
Crystal system	monoclinic	triclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /Å	11.0426(2)	9.7159(8)	9.3045(6)
<i>b</i> /Å	15.7506(4)	12.4237(11)	20.5292(15)
<i>c</i> /Å	18.8447(3)	21.4359(18)	20.2136(13)
α /°	90	102.431(7)	90
β /°	97.2990(10)	96.489(7)	101.592(5)
γ /°	90	110.531(6)	90
Volume/Å ³	3251.05(11)	2315.5(4)	3782.3(4)
Z	4	2	4
ρ_{calc} /cm ³	1.884	1.518	1.655
μ /mm ⁻¹	7.454	4.499	5.414
F(000)	1768.0	1053.0	1848.0
Crystal radius(equiv)/mm	1.546	0.0657	0.0391
Diffractometer	Stoe IPDS 2T	Stoe IPDS 2	Stoe IPDS 2
Radiation	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)
2 θ range for data collection/°	3.382 to 58.38	3.638 to 54	2.858 to 52.992
Reflections collected	55058	27430	35599
Independent reflections	8767 [R_{int} = 0.0567, R_{sigma} = 0.0287]	10064 [R_{int} = 0.1199, R_{sigma} = 0.0871]	35599 [R_{int} = 0.0394 R_{sigma} = 0.0973]
Data/restraint/parameters	8767/0/400	10064/42/496	35599/0/419
Goodness-of-fit on F^2	1.046	1.027	1.062
Final R indexes [all data]	R_1 = 0.0285, wR_2 = 0.0381	R_1 = 0.0915, wR_2 = 0.1878	R_1 = 0.1118, wR_2 = 0.02102
Final R indexes [$l \geq 2\sigma(l)$]	R_1 = 0.0206, wR_2 = 0.0364	R_1 = 0.0702, wR_2 = 0.1754	R_1 = 0.0754, wR_2 = 0.1951
Largest diff. peak/hole/ e Å ⁻³	0.95/-0.89	1.81/-1.93	1.87/-2.87
CCDC	2232020	2232019	2232024

Table S7. Selected crystal structure data of the structure determinations of compounds**9_{Me}, 11_{Me}, and 11'_{Me}.**

Compound	9_{Me}	11_{Me}	11'_{Me}
Empirical formula	C ₇ H ₁₅ BiF ₆ Sb	C ₁₁ H ₁₅ BiF ₆ NSb	C ₂₀ H ₂₄ BiF ₆ N ₂ Sb
Formula weight	557.93	605.97	737.14
Crystal color, habit	colourless, plate	colourless, plate	colourless, plate
Temperature/K	100	100	100
Crystal system	orthorhombic	triclinic	monoclinic
Space group	<i>Pca2</i> ₁	<i>P</i> ₁ [−]	<i>P2</i> ₁ / <i>c</i>
a/Å	11.7189(19)	6.907(3)	8.29140(10)
b/Å	14.906(2)	8.485(3)	14.0238(2)
c/Å	16.414(3)	14.452(4)	20.5318(3)
α/°	90	77.78(2)	90
β/°	90	83.17(2)	99.3270(10)
γ/°	90	88.92(2)	90
Volume/Å ³	2867.3(8)	821.9(5)	2355.81(6)
Z	8	2	4
ρ _{calc} /g/cm ³	2.585	2.449	2.078
μ/mm ^{−1}	14.184	12.383	24.102
F(000)	2016.0	552.0	1384.0
Crystal size/mm ³	0.239·0.215·0.150	0.075·0.075·0.64	
Crystal radius(equiv)/mm			
Diffractometer	Bruker Apex-II CCD	Bruker Apex-II CCD	Rigaku XtaLAB Synergy-R
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	CuKα (λ = 1.54184)
2θ range for data collection/°	4.422 to 57.478	4.912 to 52.142	7.666 to 136.476
Reflections collected	75005	21861	33255
Independent reflections	7421 [<i>R</i> _{int} = 0.0610, <i>R</i> _{sigma} = 0.0293]	3259 [<i>R</i> _{int} = 0.0520, <i>R</i> _{sigma} = 0.0316]	4299 [<i>R</i> _{int} = 0.0631, <i>R</i> _{sigma} = 0.0341]
Data/restraint/parameters	7421/1/300	3259/0/233	4299/0/278
Goodness-of-fit on <i>F</i> ²	1.099	1.081	0.953
Final R indexes [all data]	<i>R</i> ₁ = 0.0178, <i>wR</i> ₂ = 0.0404	<i>R</i> ₁ = 0.0336, <i>wR</i> ₂ = 0.0549	<i>R</i> ₁ = 0.0346, <i>wR</i> ₂ = 0.0939
Final R indexes [<i>I</i> ≥ 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0175, <i>wR</i> ₂ = 0.0605	<i>R</i> ₁ = 0.0292, <i>wR</i> ₂ = 0.0534	<i>R</i> ₁ = 0.0323, <i>wR</i> ₂ = 0.0916
Largest diff. peak/hole/ e Å ^{−3}	1.15/−1.79	0.88/−1.46	1.73/−2.40
Flack parameter	0.456(4)	-	
CCDC	2232021	2232018	2232015

Table S8. Selected crystal structure data of the structure determinations of compounds**12_{Me}**, **14_{Me}**, and **16_{Me}**.

Compound	12_{Me}	14_{Me}	16_{Dipp}
Empirical formula	C ₉ H ₁₇ BiF ₆ NSb	C ₂₀ H ₃₉ BiF ₆ PSb	C ₂₆ H ₃₇ BiF ₆ NSb
Formula weight	583.96	755.21	808.29
Crystal color, habit	colourless, plate	colourless, block	yellow, block
Temperature/K	100	100	100
Crystal system	monoclinic	monoclinic	triclinic
Space group	<i>P2₁/c</i>	<i>C2/c</i>	<i>P$\bar{1}$</i>
a/Å	7.359(2)	35.220(3)	11.3117(19)
b/Å	15.756(5)	9.7896(7)	15.749(3)
c/Å	13.496(3)	14.7211(11)	17.723(4)
α /°	90	90	111.516(17)
β /°	99.118(11)	100.835(2)	99.562(15)
γ /°	90	90	91.228(15)
Volume/Å ³	1544.9(7)	4985.2(6)	2884.8(10)
Z	4	8	4
ρ_{calc} /cm ³	2.511	2.012	1.861
μ /mm ⁻¹	13.169	8.247	7.081
F(000)	1064.0	2896.0	1552.0
Crystal size/mm ³	0.100 0.085 0.063	0.257 0.226 0.221	
Crystal radius(equiv)/mm			0.0391
Diffractometer	Bruker APEX-II CCD	Bruker X8-APEX II	Stoe IPDS 2
Radiation	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)
2 θ range for data collection/°	5.17 to 56.582	2.354 to 53.574	2.974 to 52.00
Reflections collected	8223	33253	26024
Independent reflections	3797 [R_{int} = 0.0435, R_{sigma} = 0.0729]	5323 [R_{int} = 0.0412, R_{sigma} = 0.0250]	11332 [R_{int} = 0.0439, R_{sigma} = 0.0690]
Data/restraint/parameters	3797/0/165	5323/0/266	11332/0/649
Goodness-of-fit on F^2	1.032	1.054	0.918
Final R indexes [all data]	R_1 = 0.0671, wR_2 = 0.0789	R_1 = 0.0209, wR_2 = 0.0446	R_1 = 0.0808, wR_2 = 0.0883
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0437, wR_2 = 0.0719	R_1 = 0.0181, wR_2 = 0.0437	R_1 = 0.0400, wR_2 = 0.0798
Largest diff. peak/hole/ e Å ⁻³	1.68/-1.18	1.23/-0.88	0.97/-1.04
CCDC	2232025	2232022	2232028

6. References

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