Titel…

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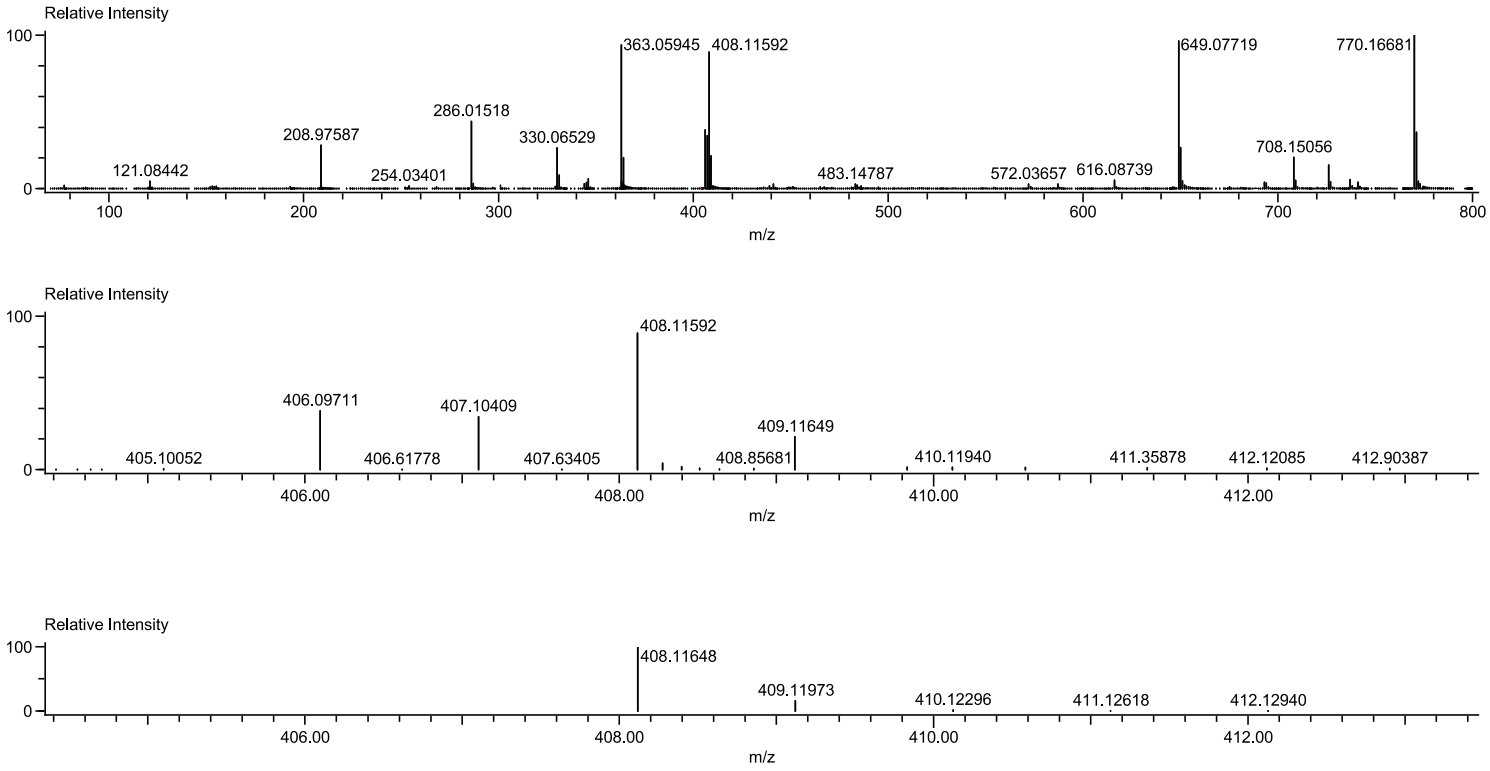
1. Mass spectra

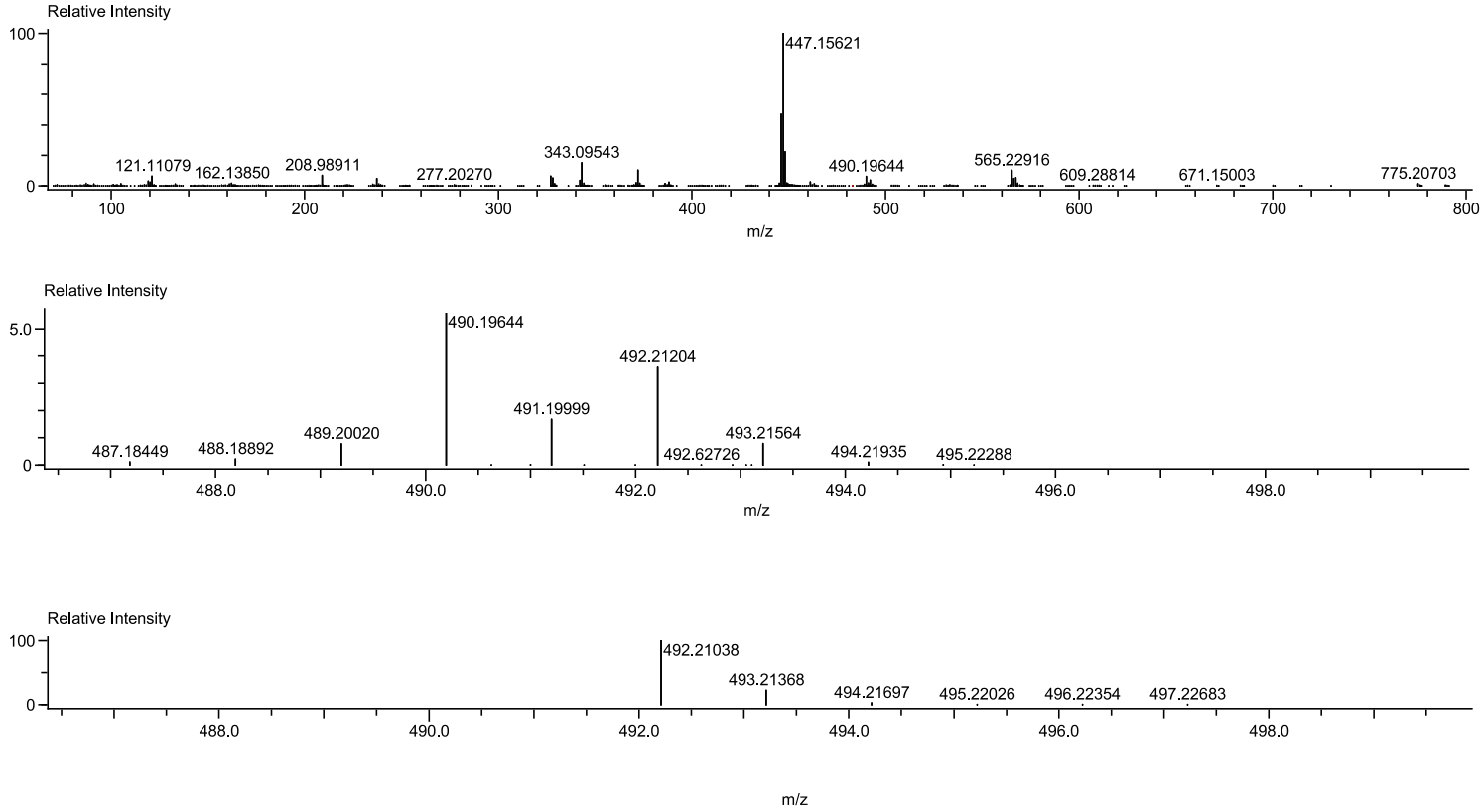
1.1 Ph_2BiNMe_2 (**1**)



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	$^{12}C_{14}{}^{1}H_{17}{}^{209}Bi_{1}{}^{14}N_{1}$	7.5

Figure S1.1. HR-CI(+) Mass spectrum of Ph_2BiNMe_2 (**1**) as $[M + H]^+$. Top: Whole spectrum. Middle: High resolution extract. Bottom: Calculated isotope pattern.

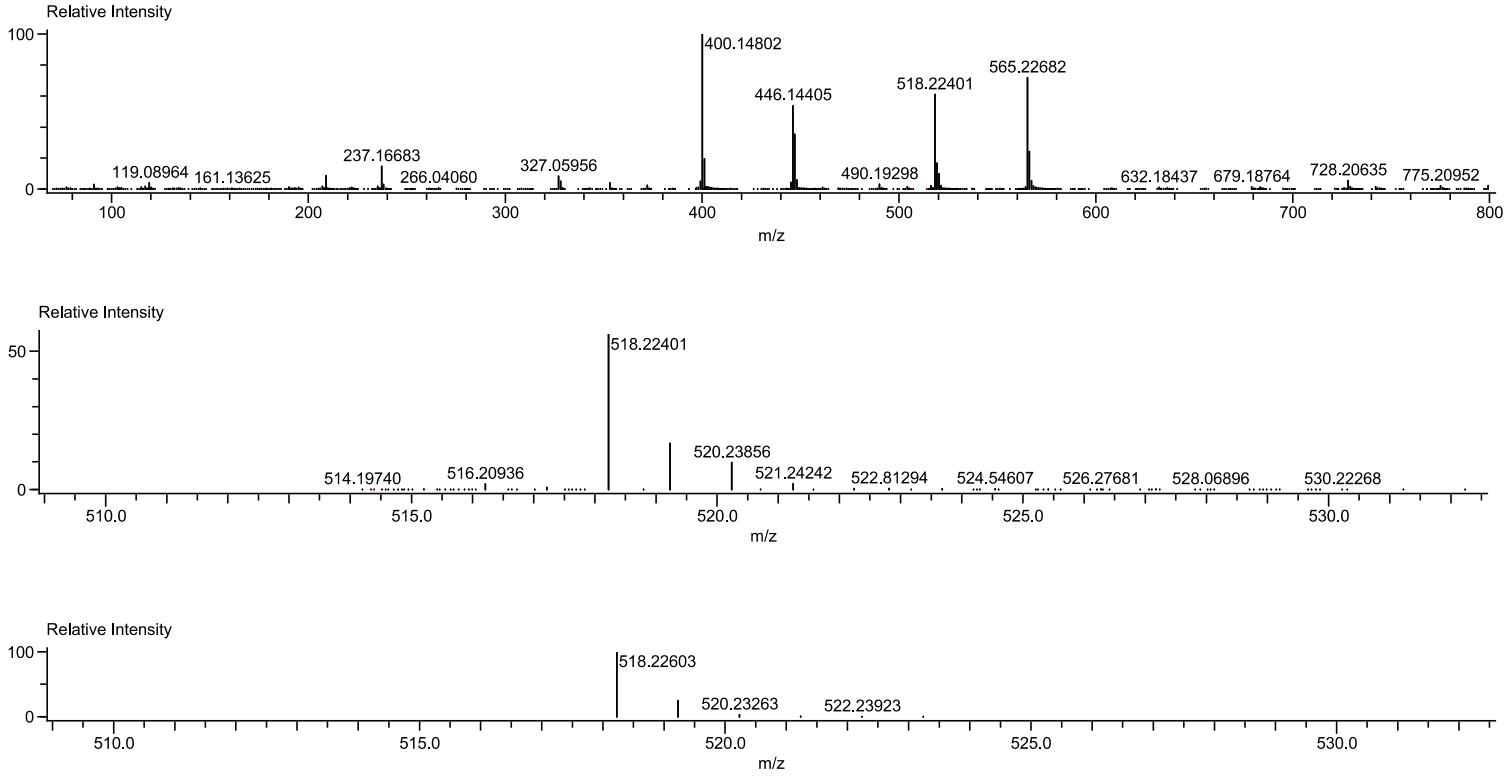
1.2 Mes_2BiNMe_2 (**2**)



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-CI(+) Mass spectrum of Mes_2BiNMe_2 (**2**) as $[M + H]^+$. Top: Whole spectrum. Middle: High resolution extract. Bottom: Calculated isotope pattern.

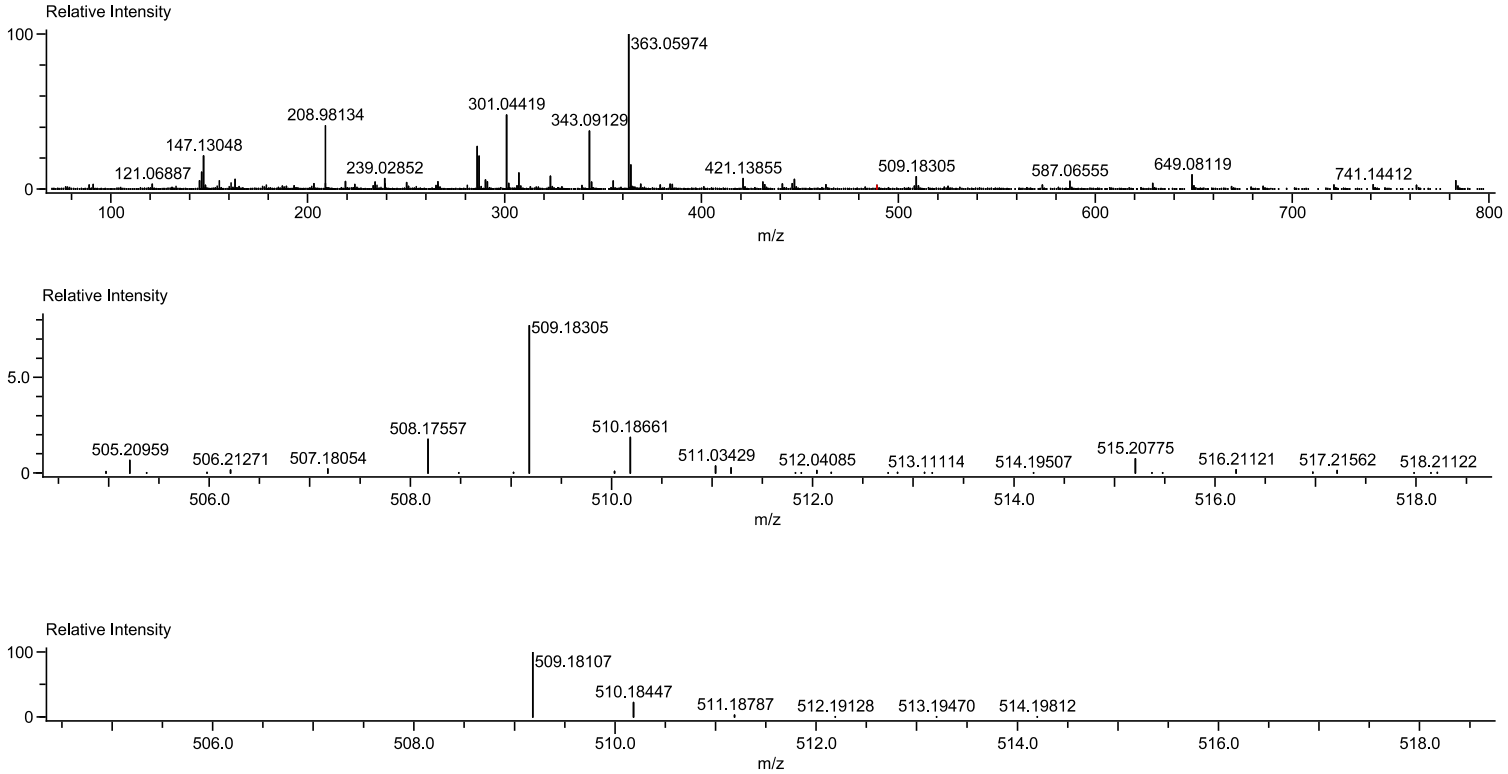
1.3 $Mes_2BiNHtBu$ (**3**)



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-CI(+) Mass spectrum of $Mes_2BiNHtBu$ (**3**) as $[M - H]^+$. Top: Whole spectrum. Middle: High resolution extract.

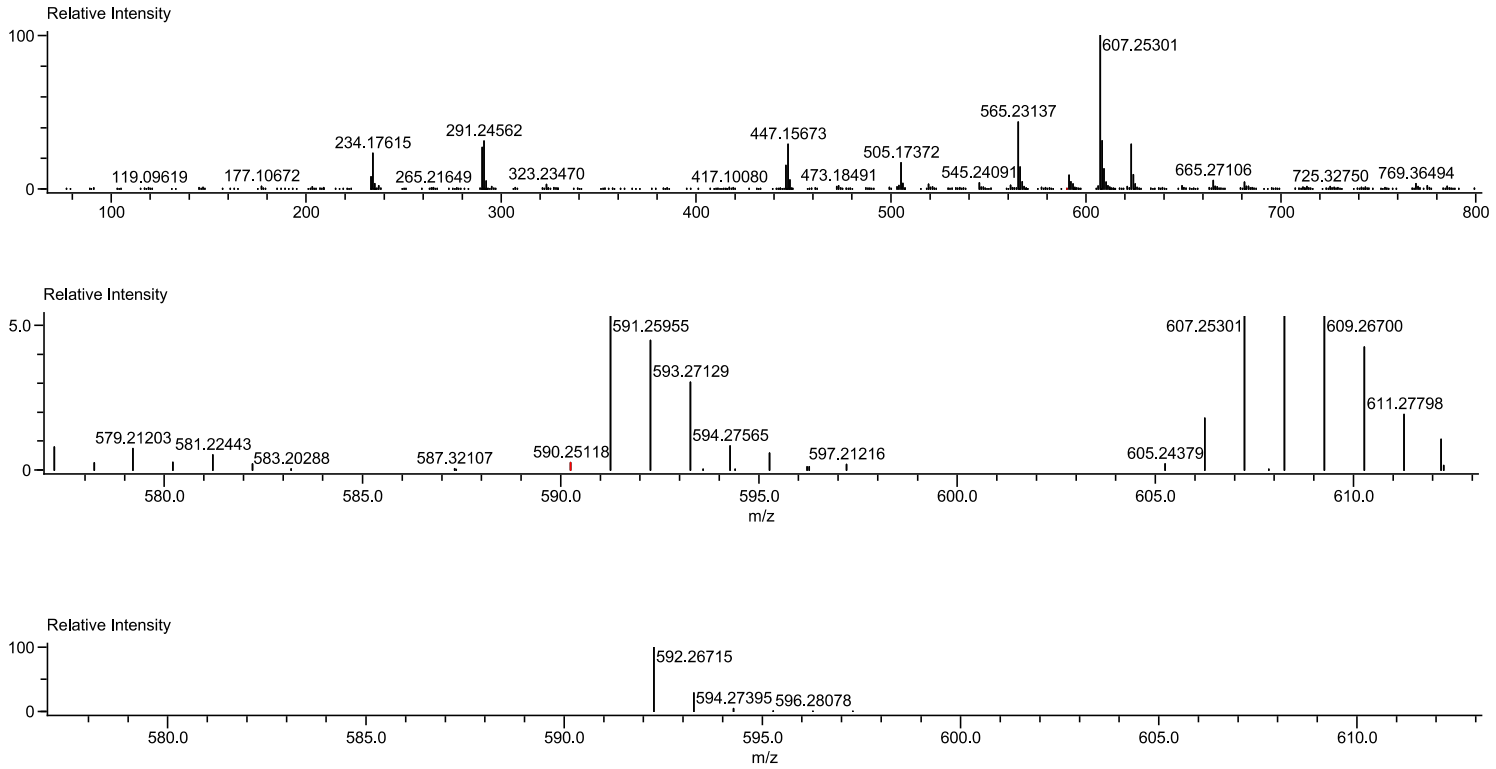
1.4 $Ph_2BiPtBu_2$ (**4**)



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	$^{12}C_{20}{}^{1}H_{29}{}^{209}Bi_{1}{}^{31}P_{1}$	8.5

Figure S1.4. HR-CI(+) Mass spectrum of $Ph_2BiPtBu_2$ (**4**) as $[M + H]^+$. Top: Whole spectrum. Middle: High resolution extract. Bottom: Calculated isotope pattern.

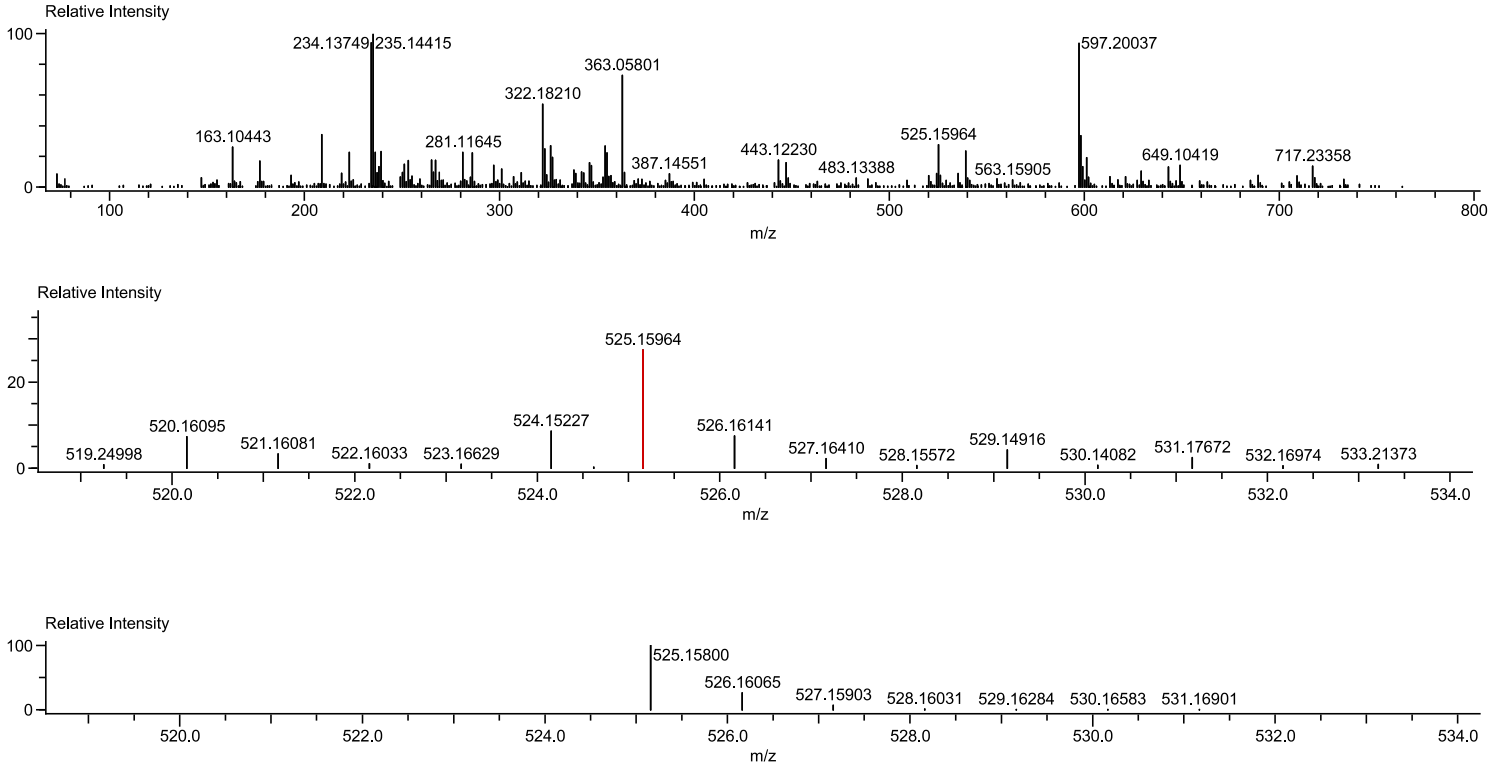
1.5 $Mes_2BiPtBu_2$ (**5**)



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-CI(+) Mass spectrum of $Mes_2BiPtBu_2$ (**5**) as $[M]^+$. Top: Whole spectrum. Middle: High resolution extract. Bottom: Calculated isotope pattern.

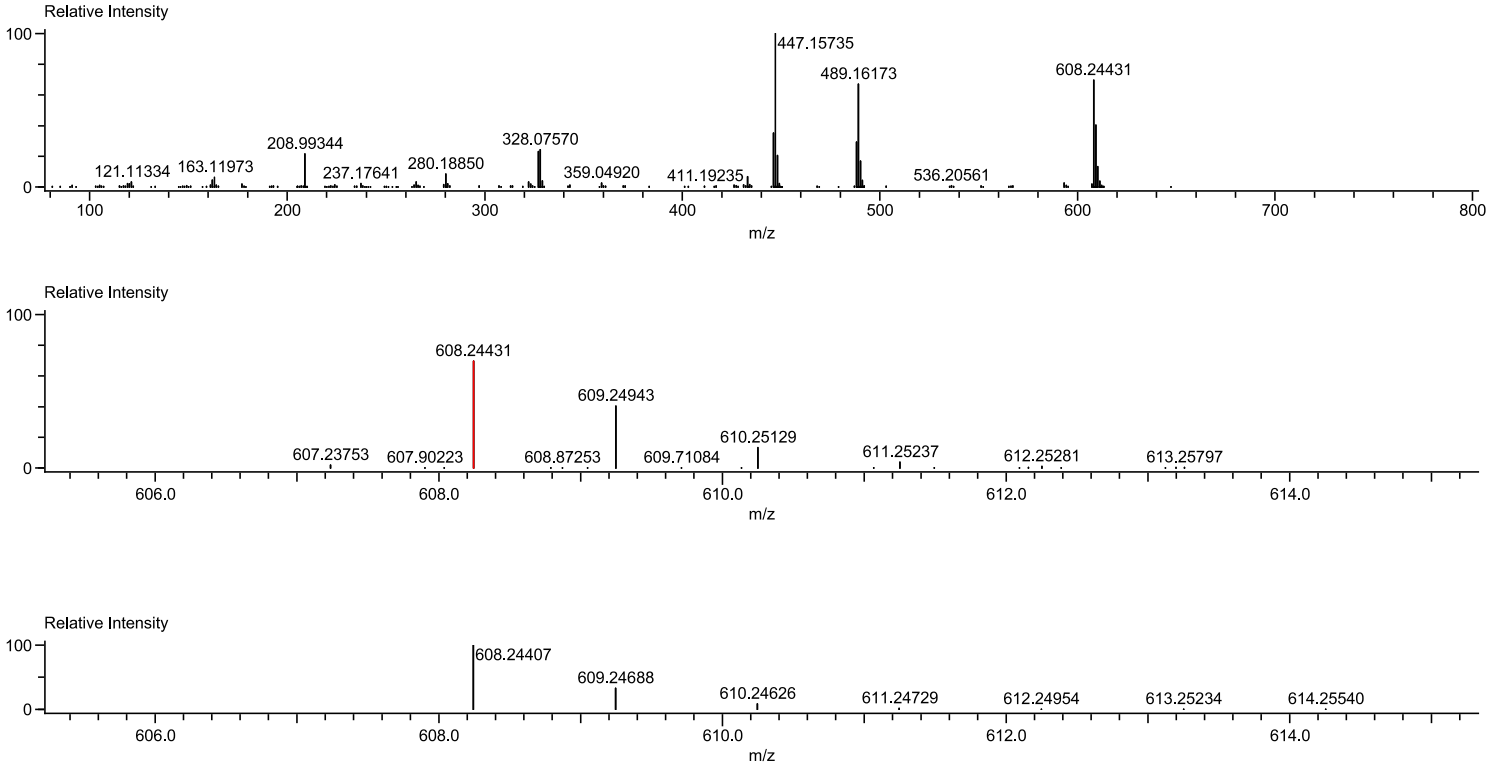
1.6 $Ph_2BiPtBu(SiMe_3)_3$ (**6**)



Mass	Intensity	Calc. Mass	Mass Difference [mDa]	Mass Difference [ppm]	Possible Formula	Unsaturation Number
525.15964	93633.23	525.15800	1.64	3.12	$^{12}C_{19}{}^{1}H_{29}{}^{209}Bi_1{}^{31}P_1{}^{28}Si_1$	8.5

Figure S1.6. HR-CI(+) Mass spectrum of $Ph_2BiPtBu(SiMe_3)$ (**6**) as $[M + H]^+$. Top: Whole spectrum. Middle: High resolution extract. Bottom: Calculated isotope pattern.

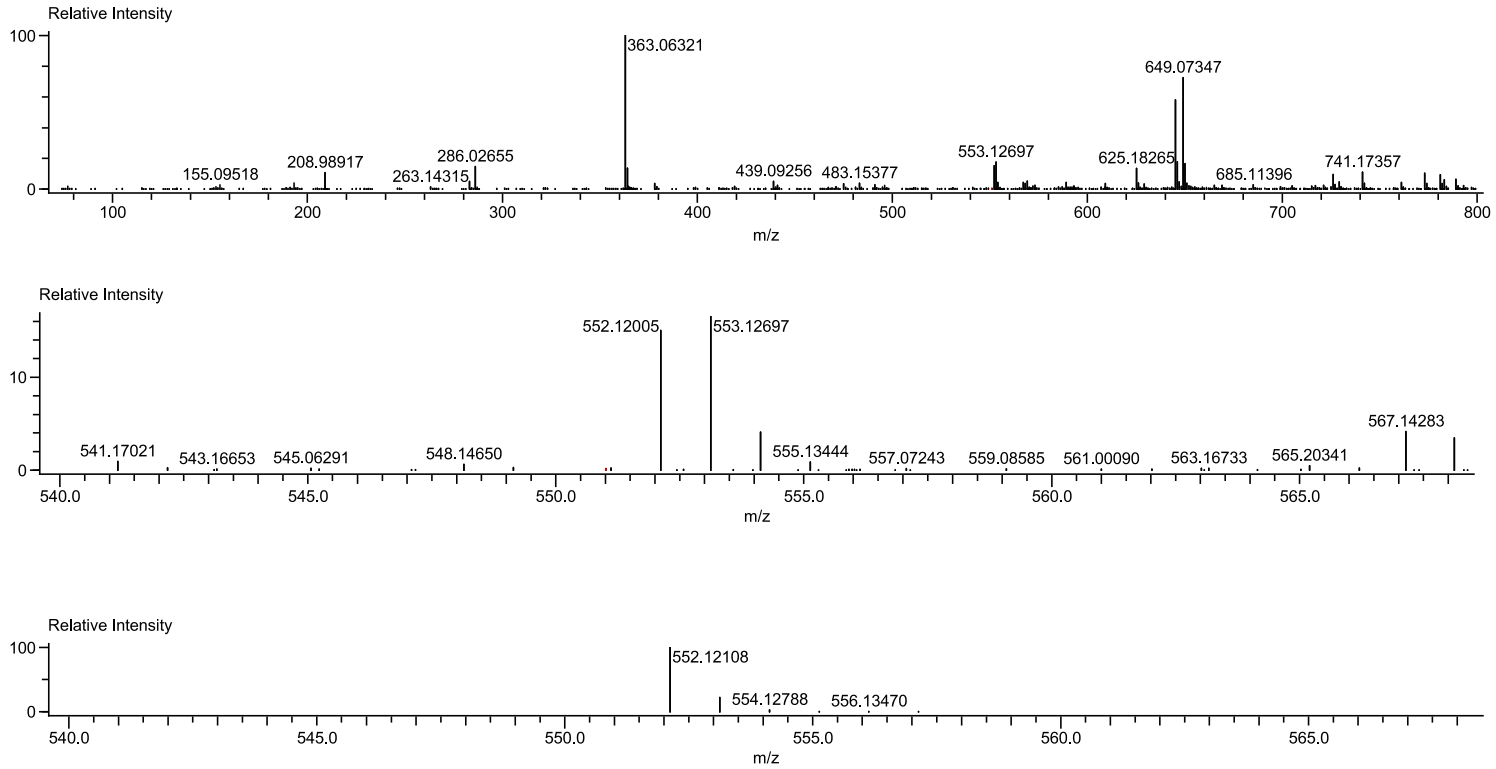
1.7 $Mes_2PtBu(SiMe_3)_3$ (**7**)



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-CI(+) Mass spectrum of $Mes_2BiPtBu(SiMe_3)$ (**7**) as $[M + H]^+$. Top: Whole spectrum. Middle: High resolution extract. Bottom: Calculated isotope pattern.

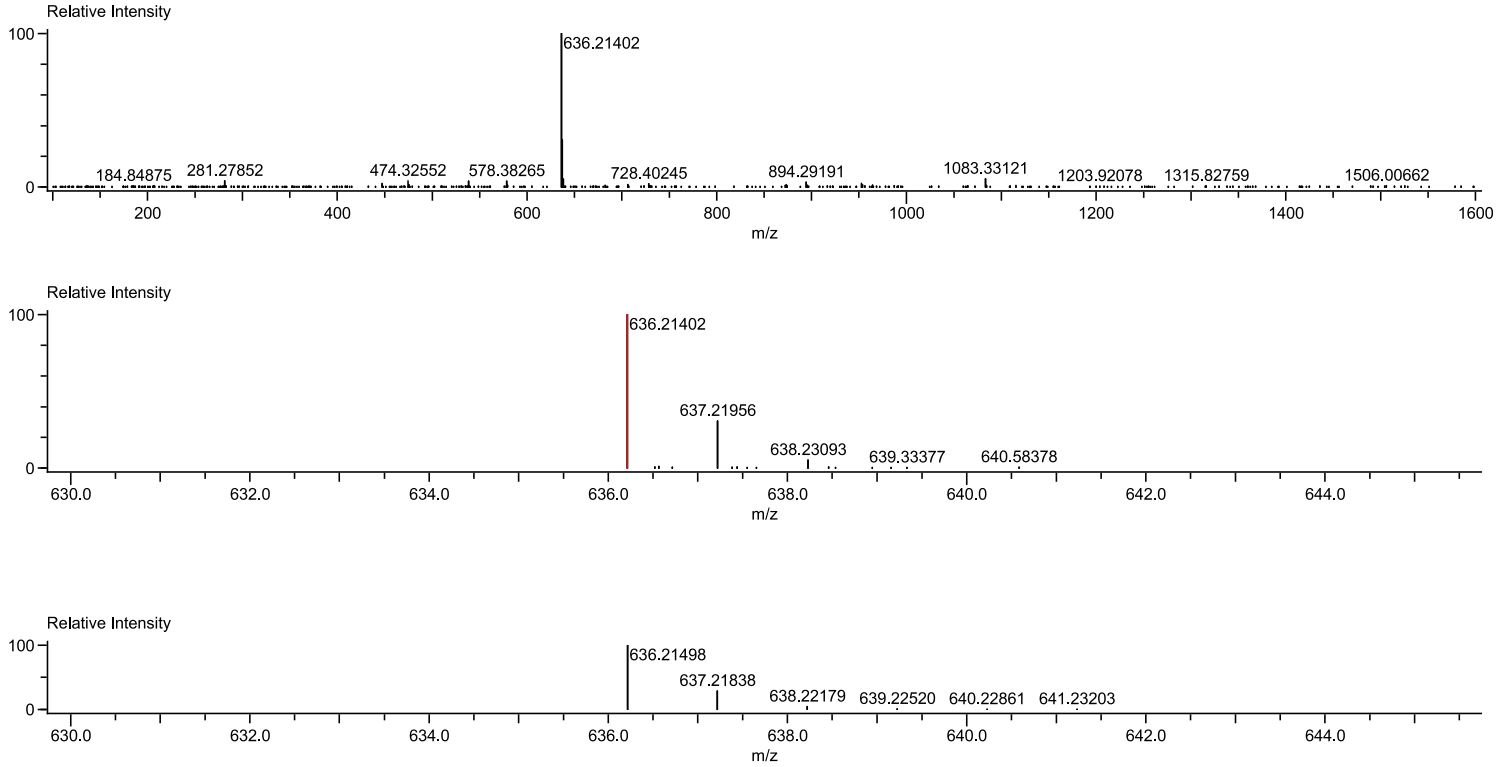
1.8 $Ph_2BiAstBu_2$ (**8**)



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-CI(+) Mass spectrum of Ph_2BiAst*t*Bu_2 (**8**) as $[M]^+$. Top: Whole spectrum. Middle: High resolution extract. Bottom: Calculated isotope pattern.

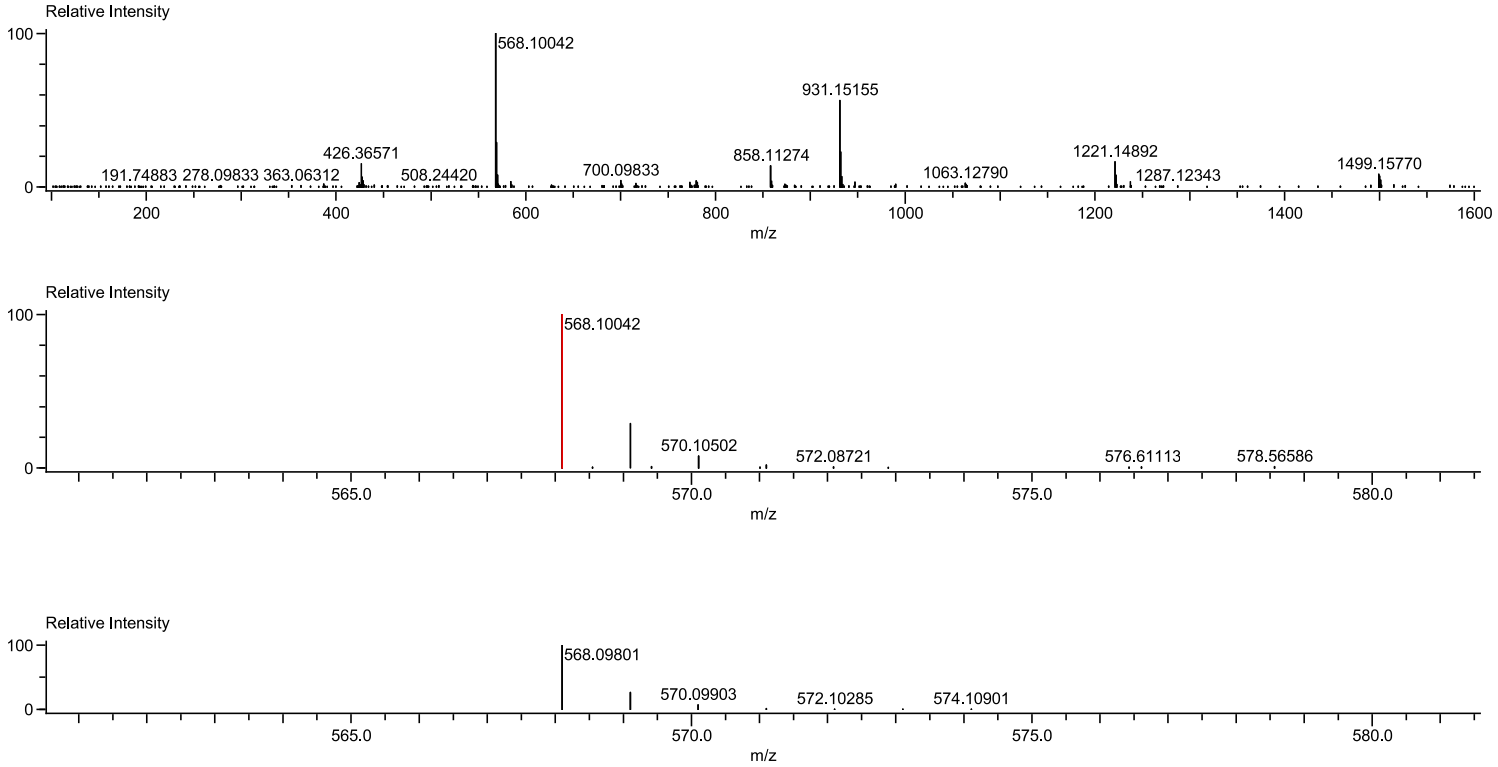
1.9 $Mes_2BiAstBu_2$ (**9**)



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 Mes_2BiAs*t*Bu_2 (**9**) as $[M]^+$. Top: Whole spectrum. Middle: High resolution extract. Bottom: Calculated isotope pattern.

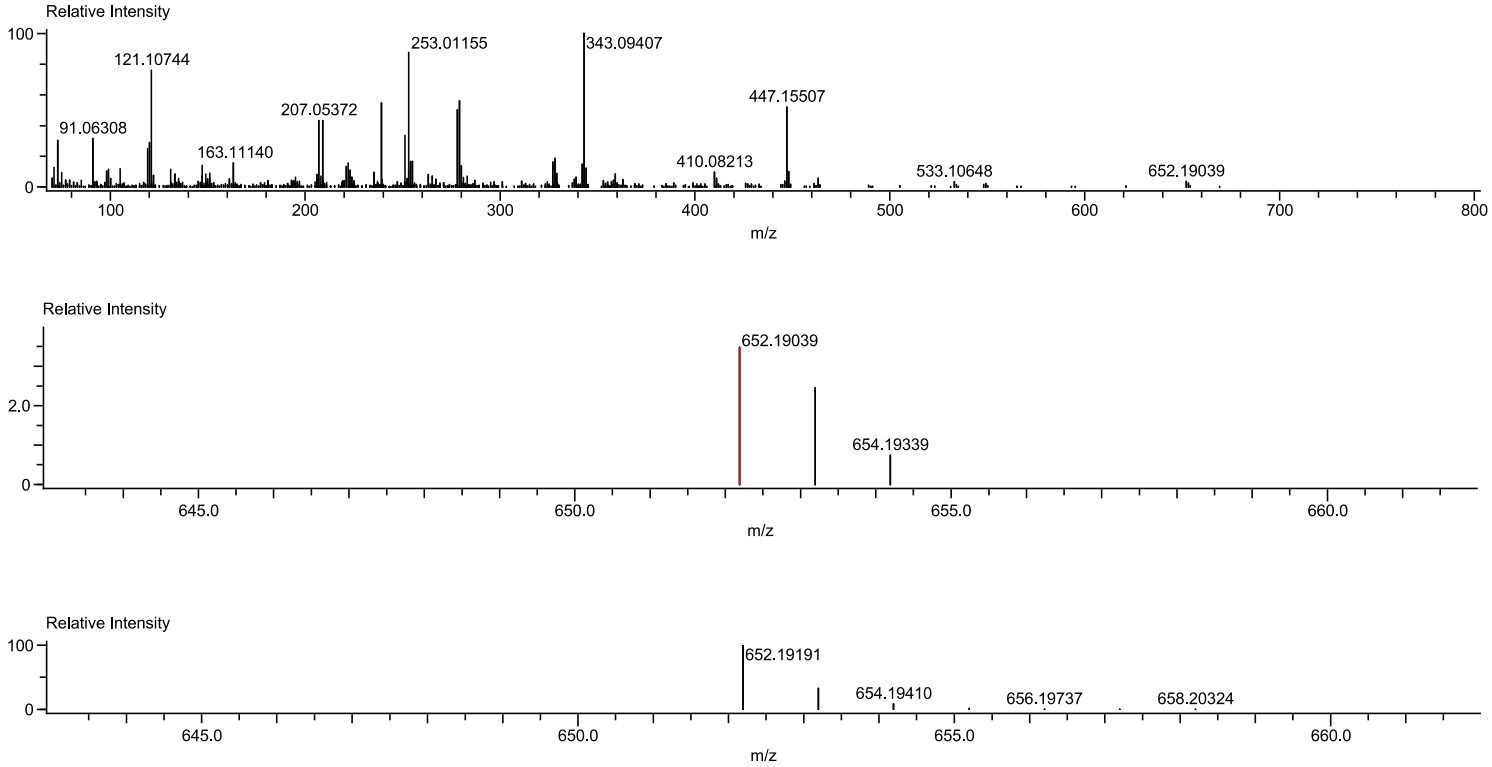
1.10 $Ph_2BiAstBu(SiMe_3)_3$ (**10**)



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 $Mes_2BiAstBu(SiMe_3)$ (**10**) as $[M]^+$. Top: Whole spectrum. Middle: High resolution extract. Bottom: Calculated isotope pattern.

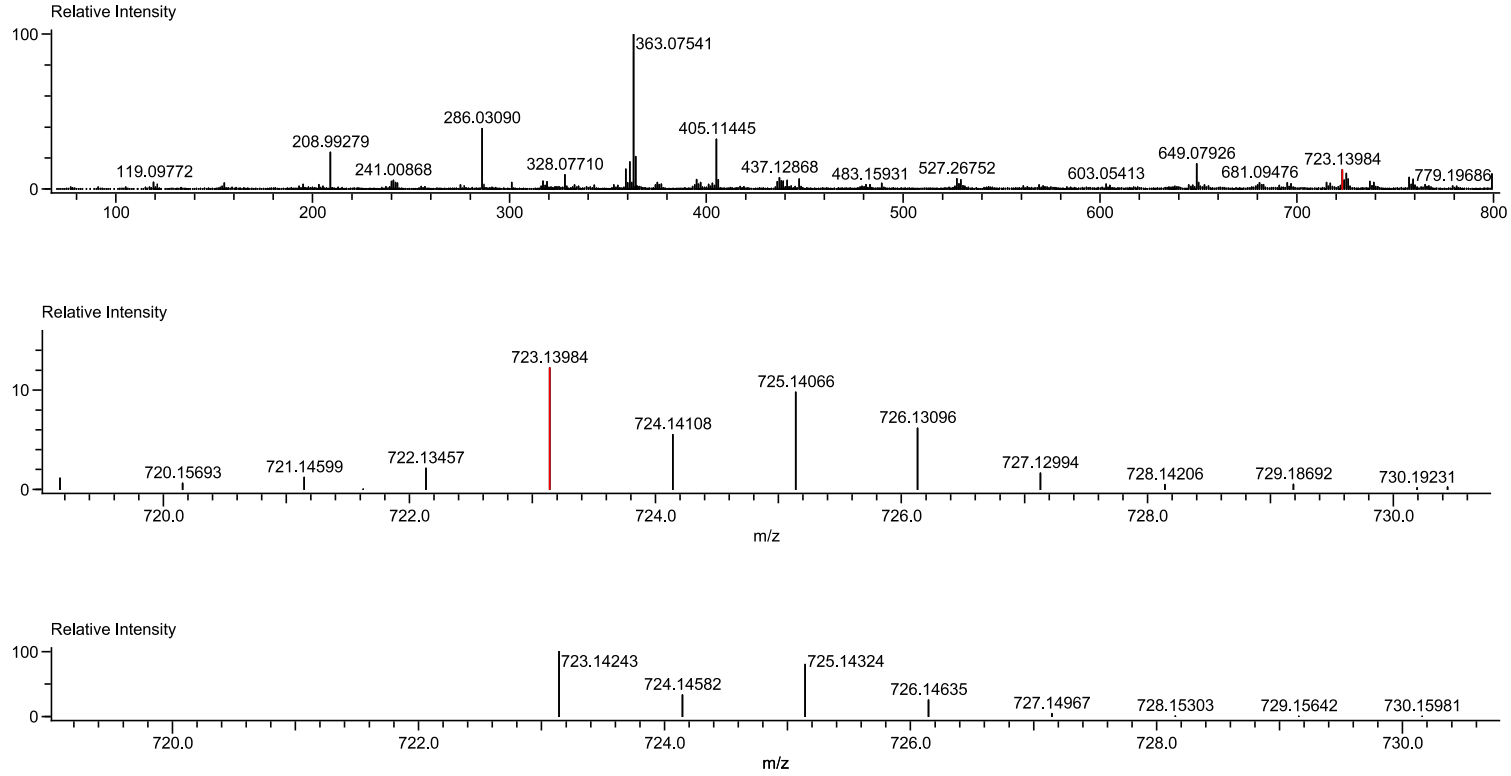
1.11 $Mes_2BiAstBu(SiMe_3)_3$ (**11**)



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-CI(+) Mass spectrum of $Mes_2BiAstBu(SiMe_3)$ (**11**) as $[M]^+$. Top: Whole spectrum. Middle: High resolution extract. Bottom: Calculated isotope pattern.

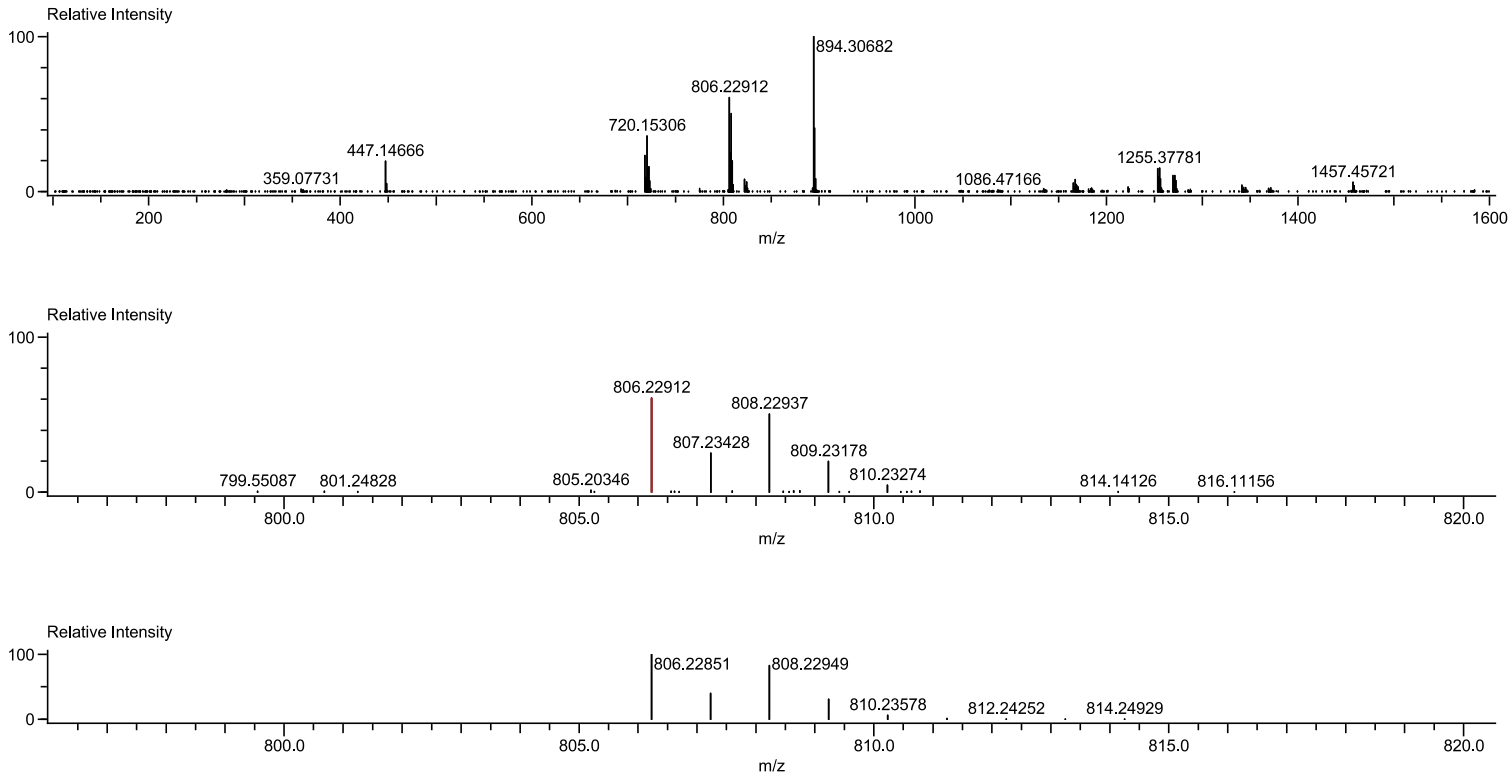
1.12 $Ph_2BiSbMes_2$



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-CI(+) Mass spectrum of $Ph_2BiSbMes_2$ (**12**) as $[M + H]^+$. Top: Whole spectrum. Middle: High resolution extract. Bottom: Calculated isotope pattern.

1.13 $Mes_2BiSbMes_2$



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 $Mes_2BiSbMes_2$ (**13**) as $[M]^+$, Mes_4Bi_2 as $[M]^+$ (m/z = 894.30507) and Mes_4Sb_2 as $[M]^+$ (m/z = 718.15194).Top: Whole spectrum. Middle: High resolution extract of $Mes_2BiSbMes_2$ (**13**). Bottom: Calculated isotope pattern for $Mes_2BiSbMes_2$ (**13**).

2. NMR spectra

2.1 Ph_2BiNMe_2

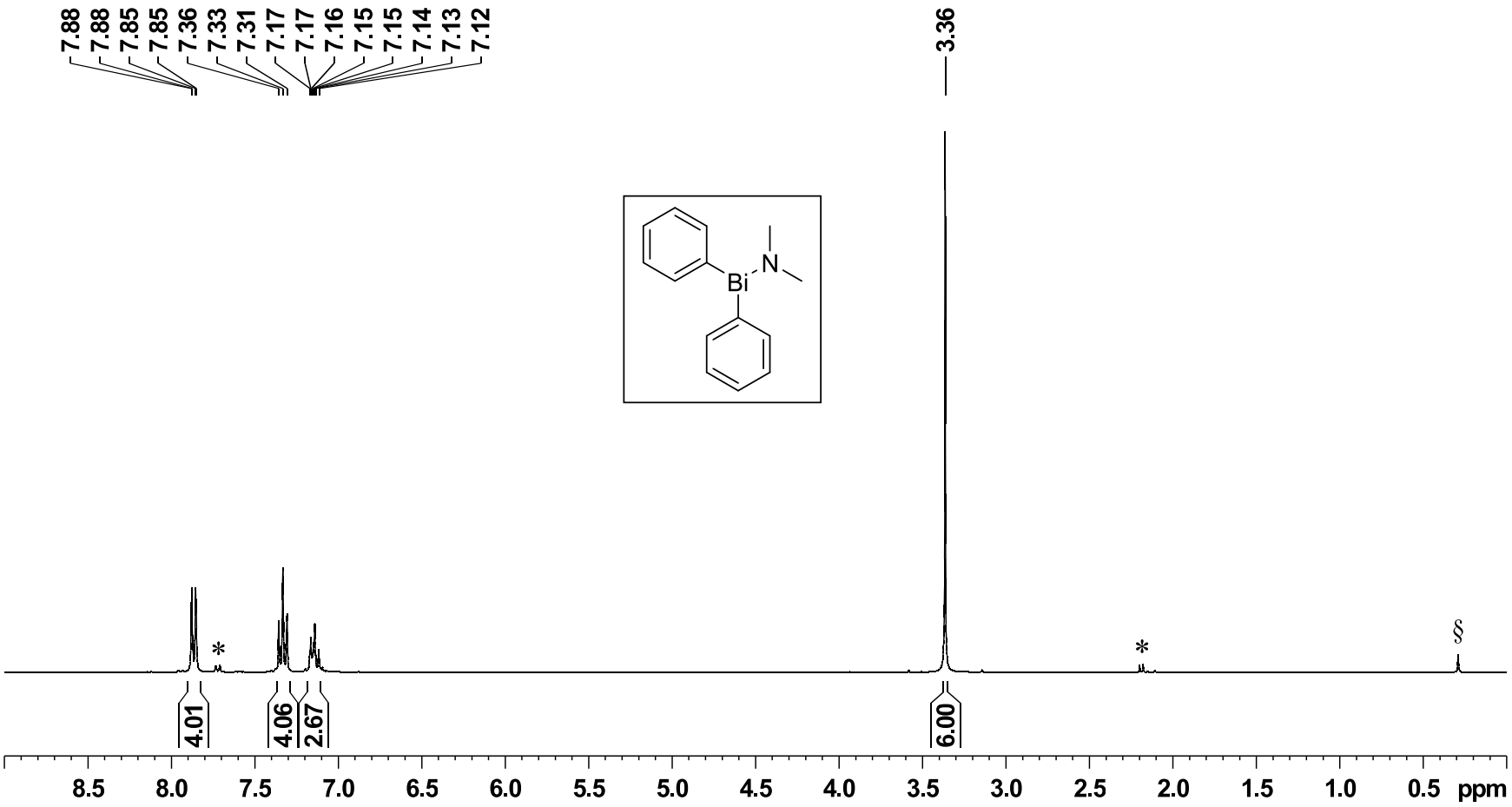


Figure S2.1.1: ^{1}H NMR spectrum (300 MHz) of **1** in C_6D_6 at room temperature (* = Unknown impurity, § = Silicon grease).

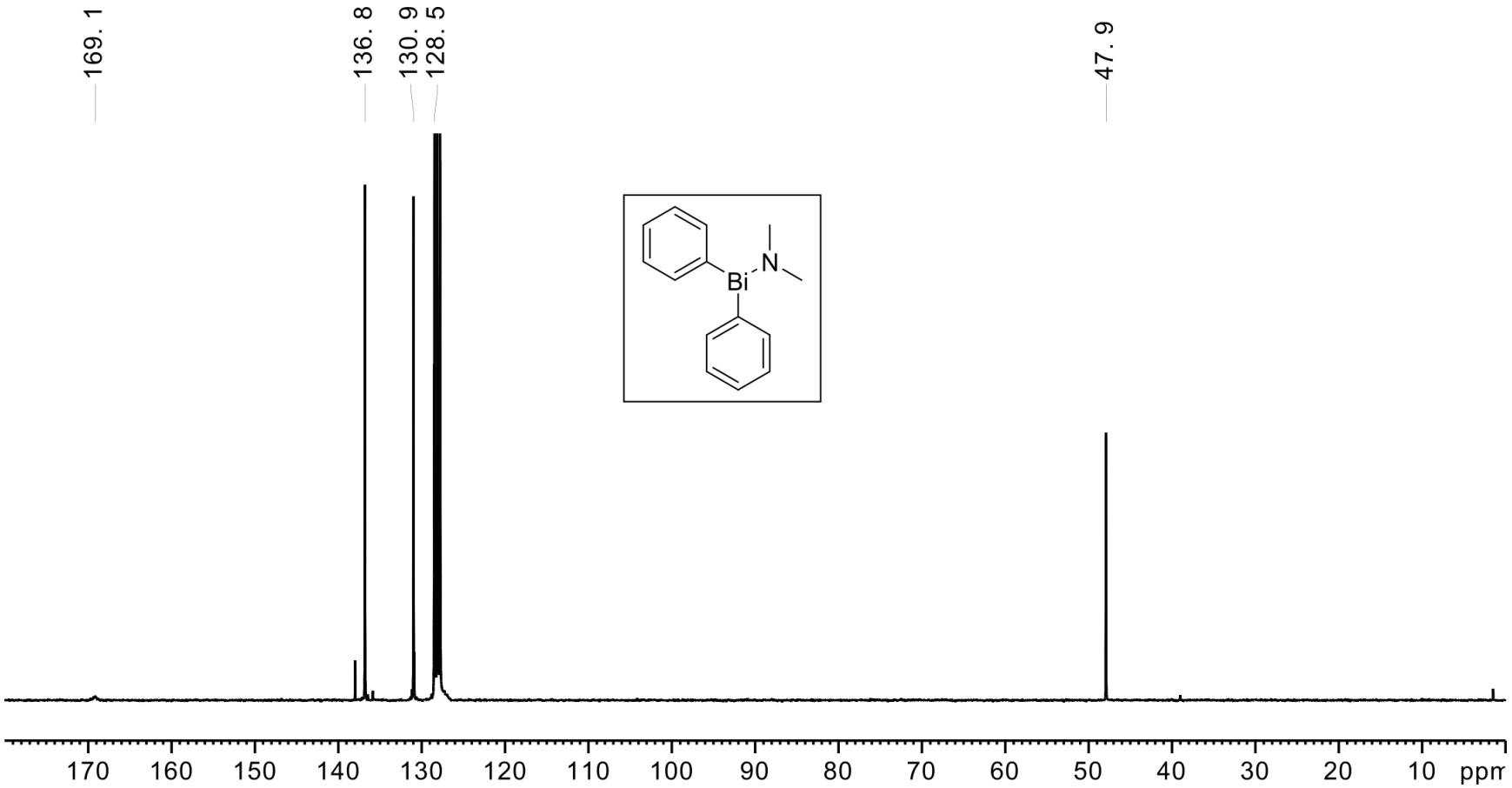


Figure S2.1.2: ^{13}C NMR spectrum (75 MHz) of **1** in C_6D_6 at room temperature.

2.2 Mes_2BiNMe_2

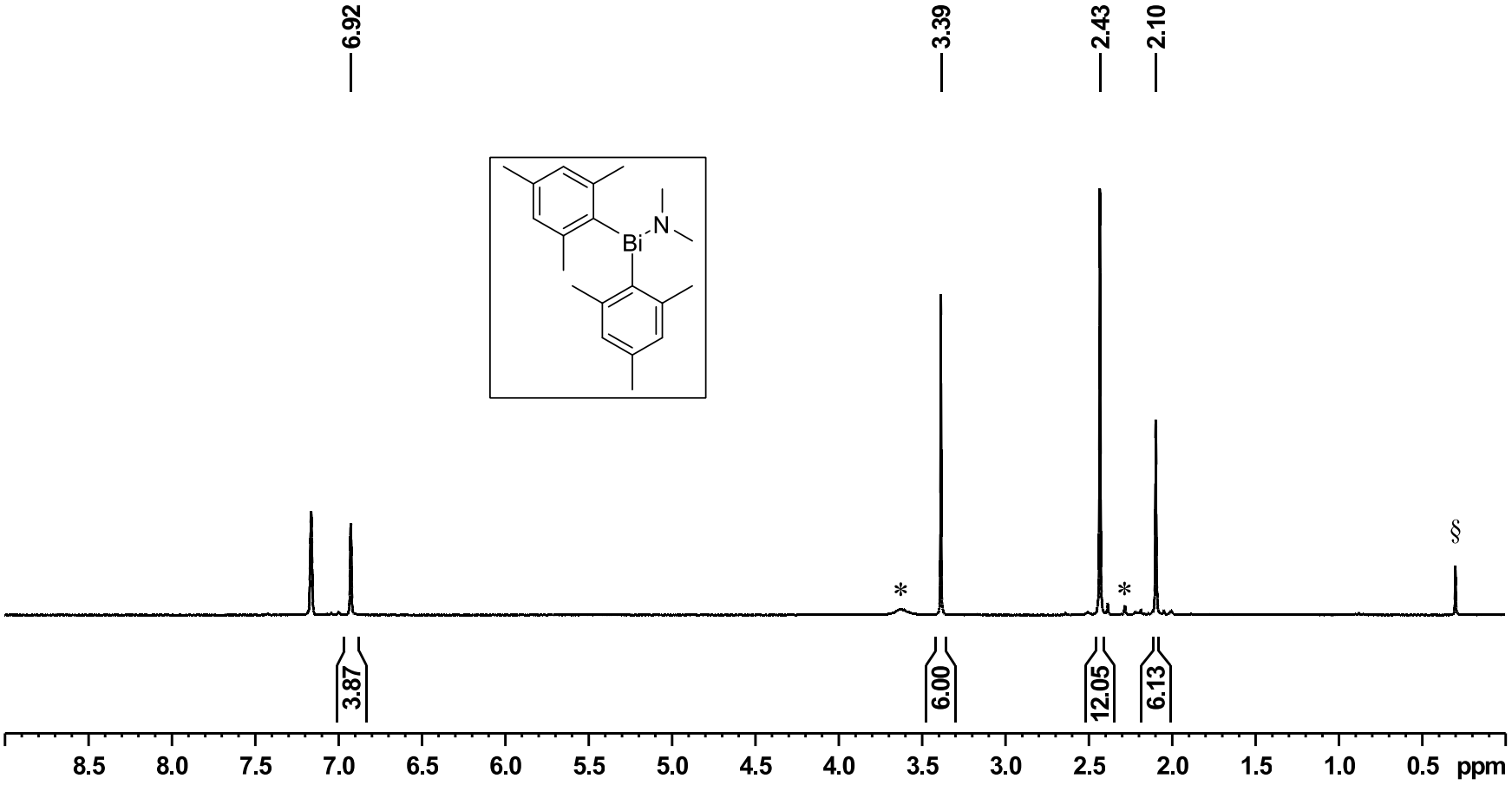


Figure S2.2.1: ^1H NMR spectrum (300 MHz) of **2** in C_6D_6 at room temperature (* = Unknown impurity, § = Silicon grease).

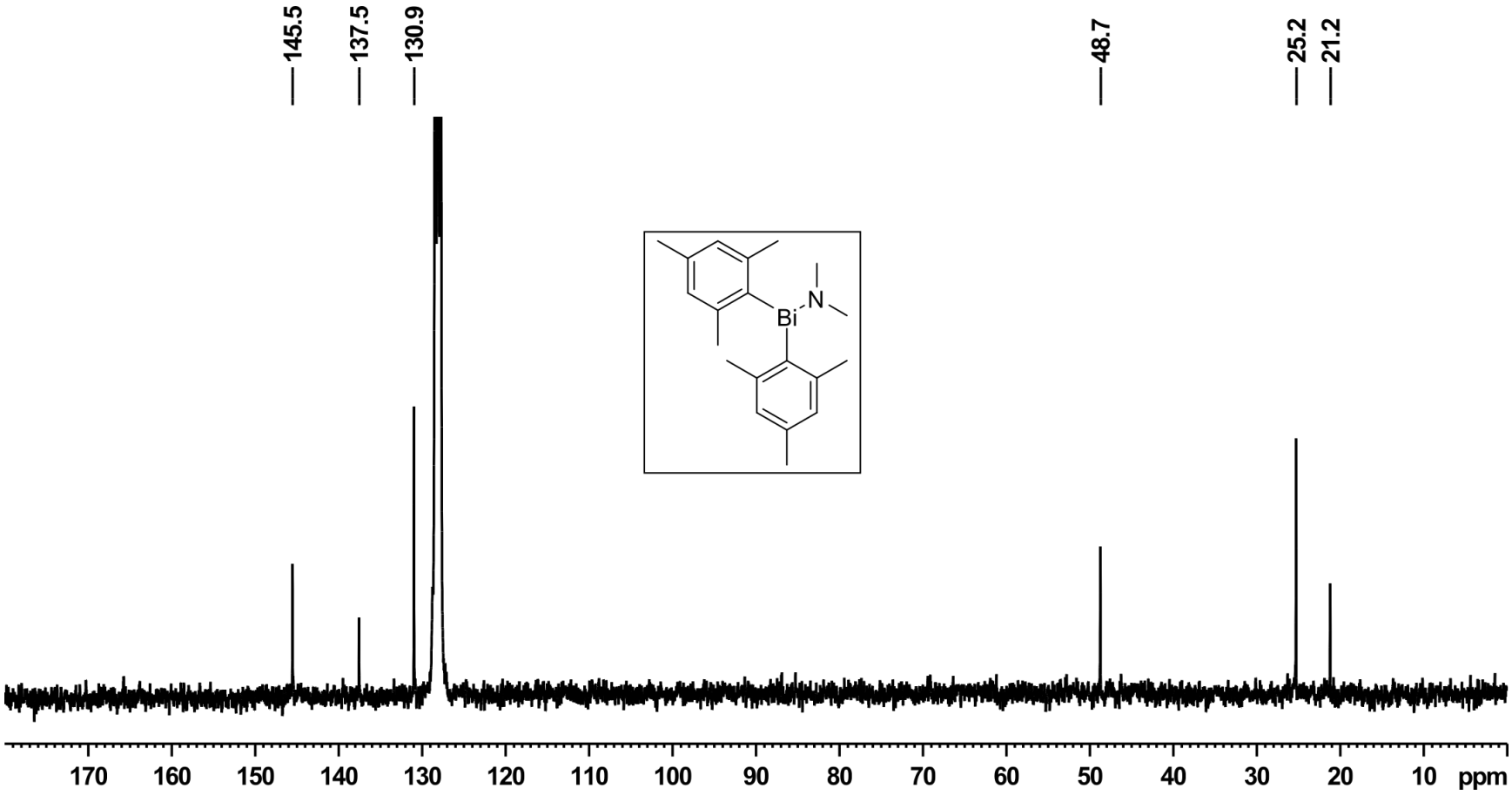


Figure S2.2.2: ^{13}C NMR spectrum (75 MHz) of **2** in C_6D_6 at room temperature.

2.3 $Mes_2BiNHtBu$

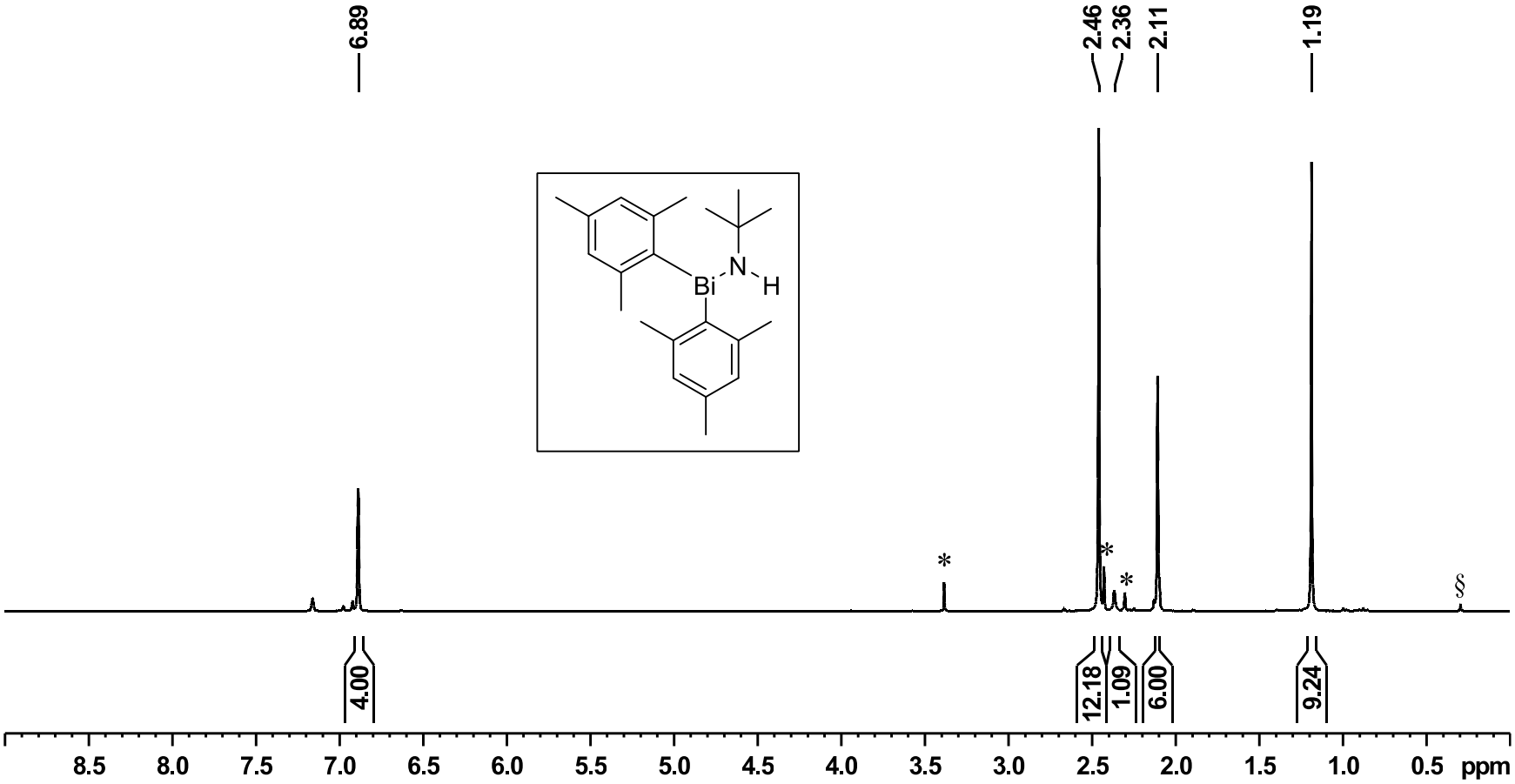


Figure S2.3.1: ^1H NMR spectrum (300 MHz) of **3** in C_6D_6 at room temperature (* = Mes_2BiNMe_2 (**2**), § = Silicon grease).

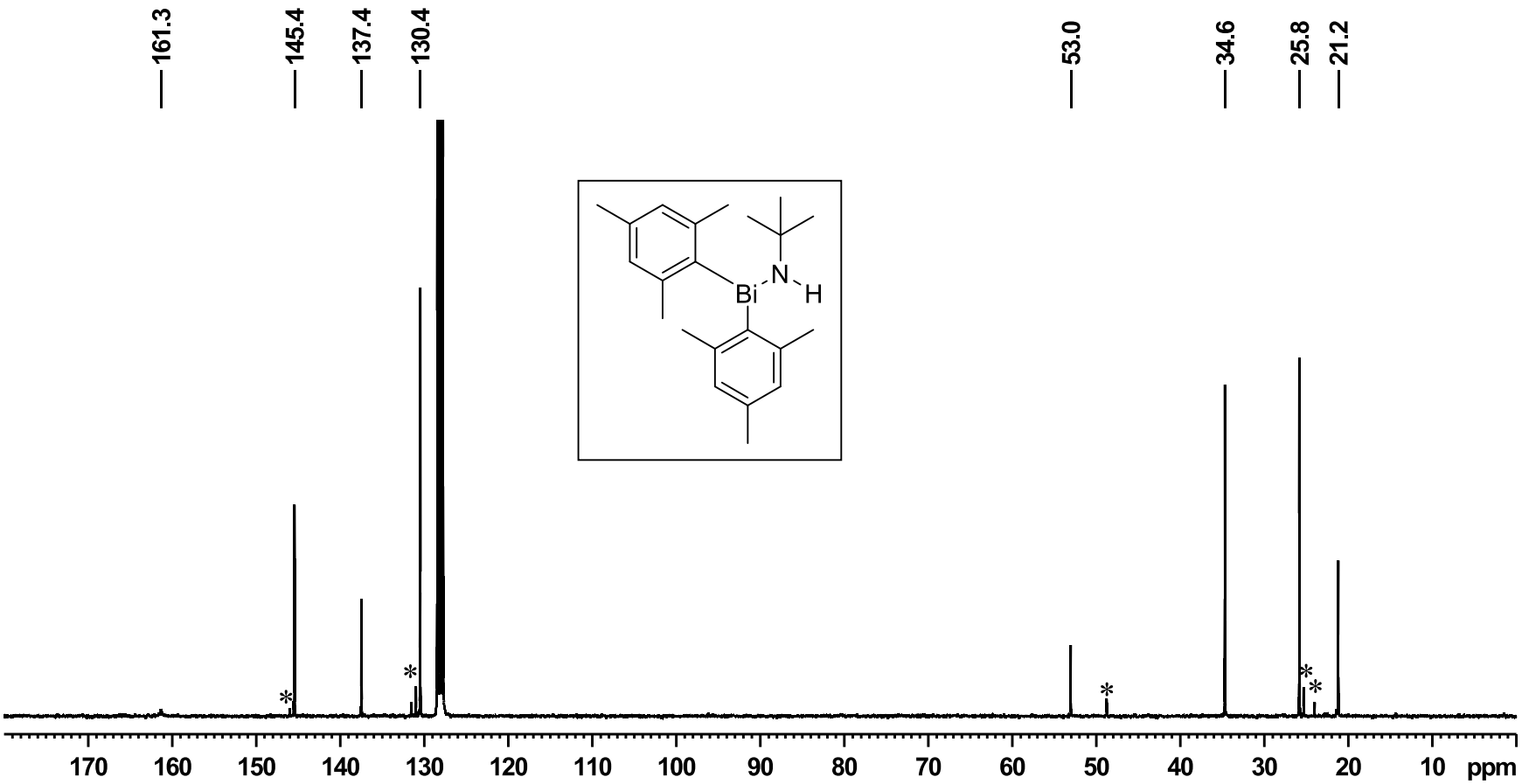


Figure S2.3.2: ^{13}C NMR spectrum (75 MHz) of **3** in C_6D_6 at room temperature (* = Mes_2BiNMe_2 (**2**)).

2.4 $Ph_2BiPtBu_2$ (**4**)

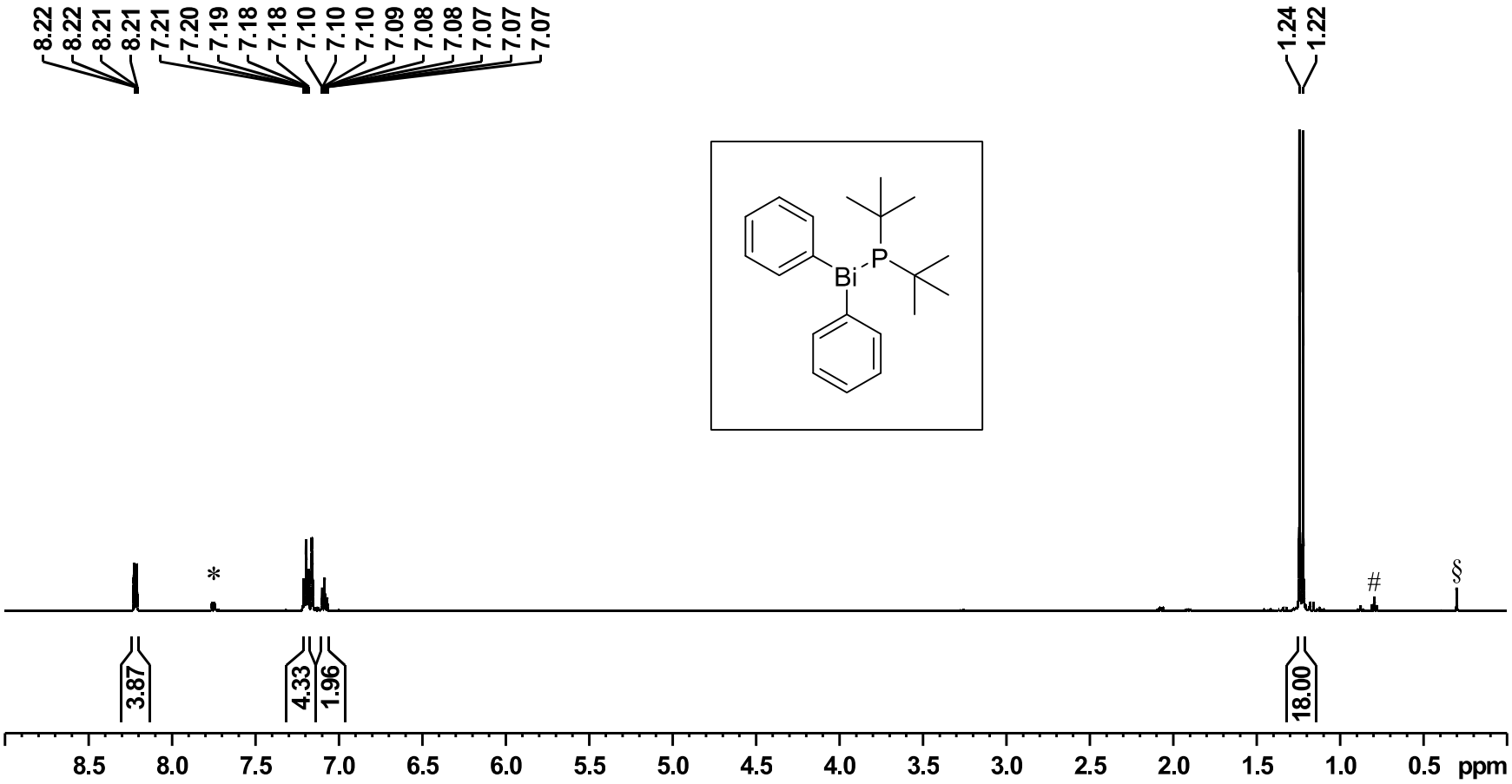


Figure S2.4.1: ^{1}H NMR spectrum (500 MHz) of **4** in C_6D_6 at room temperature (* = Unknown impurity, # = pentane, § = Silicon grease).

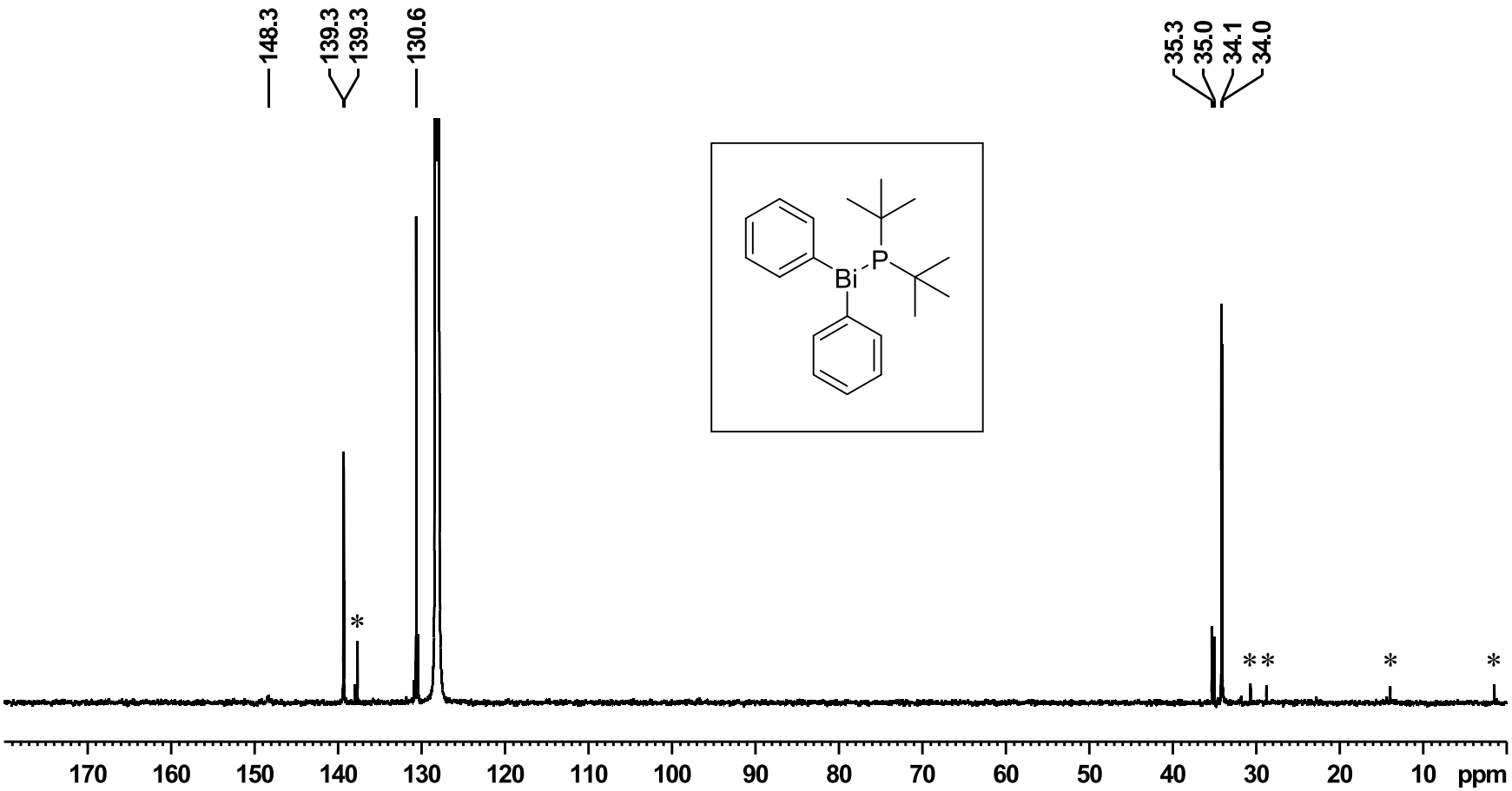


Figure S2.4.2: ^{13}C NMR spectrum (125 MHz) of **4** in C_6D_6 at room temperature (* = Unknown impurity).

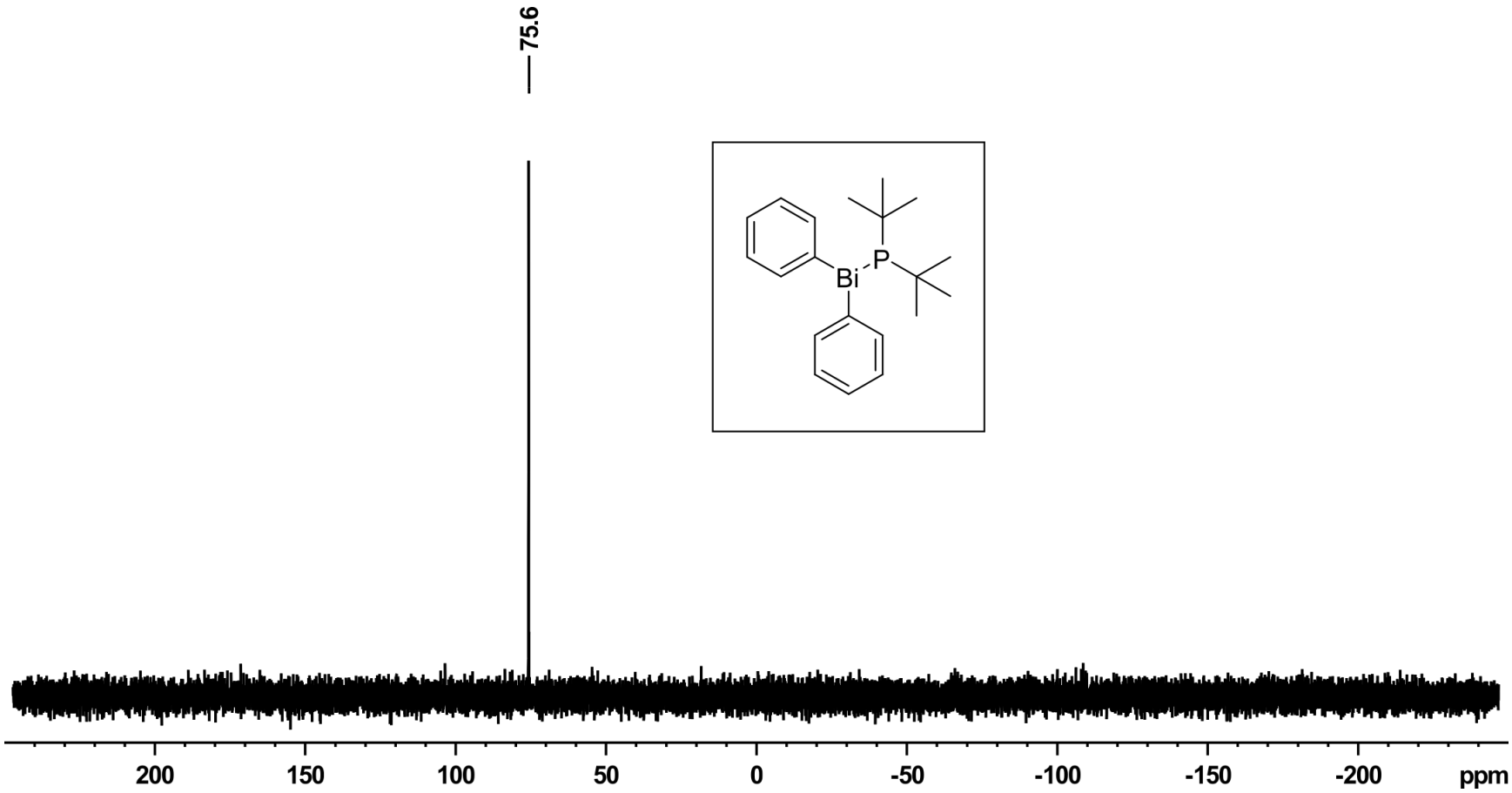


Figure S2.4.3: $^{13}P\{^{1}H\}$ NMR spectrum (200 MHz) of **4** in C_6D_6 at room temperature.

2.5 $Mes_2BiPtBu_2$ (**5**)

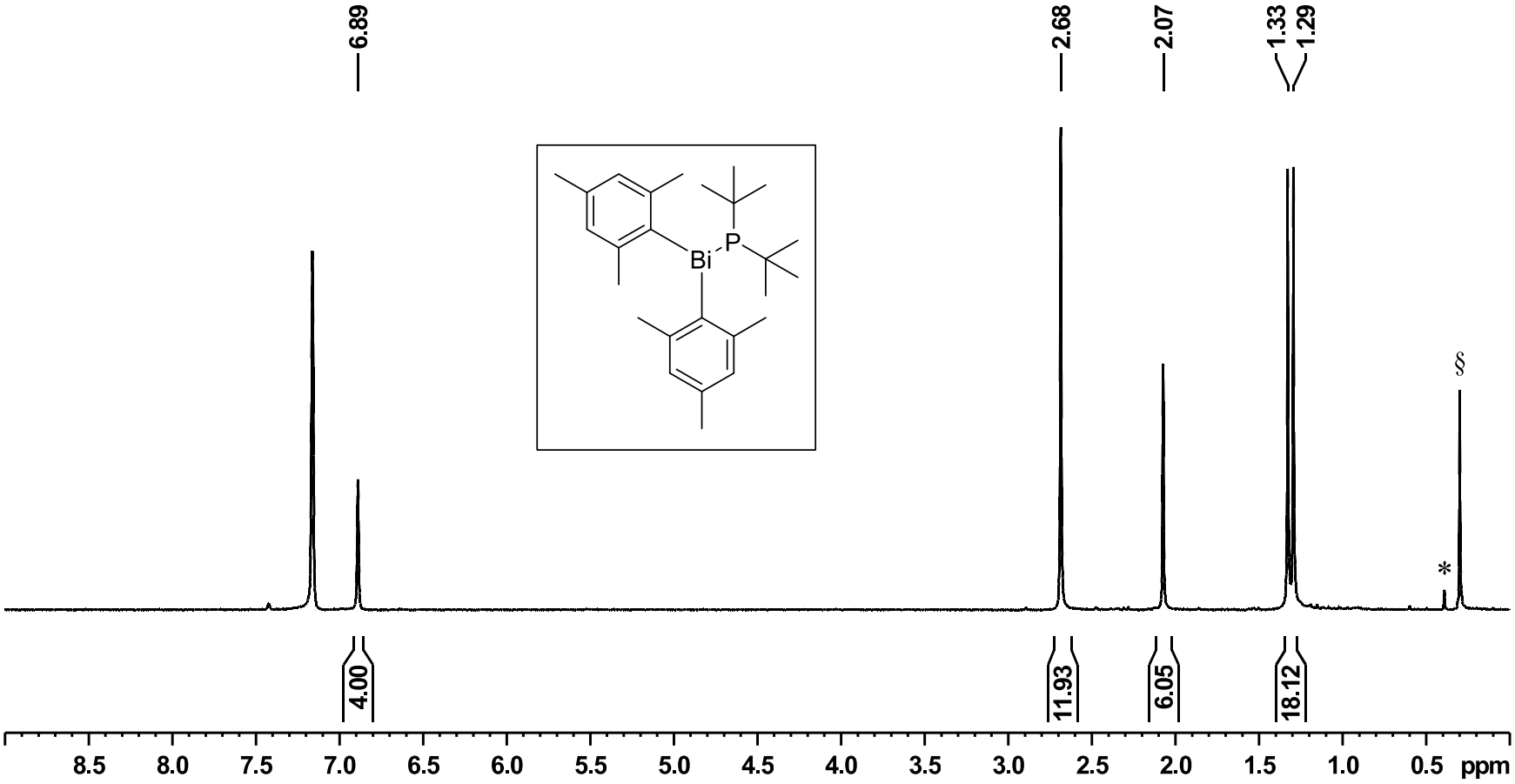


Figure S2.5.1: ^1H NMR spectrum (500 MHz) of **5** in C_6D_6 at room temperature (* = Unknown impurity, § = Silicon grease).

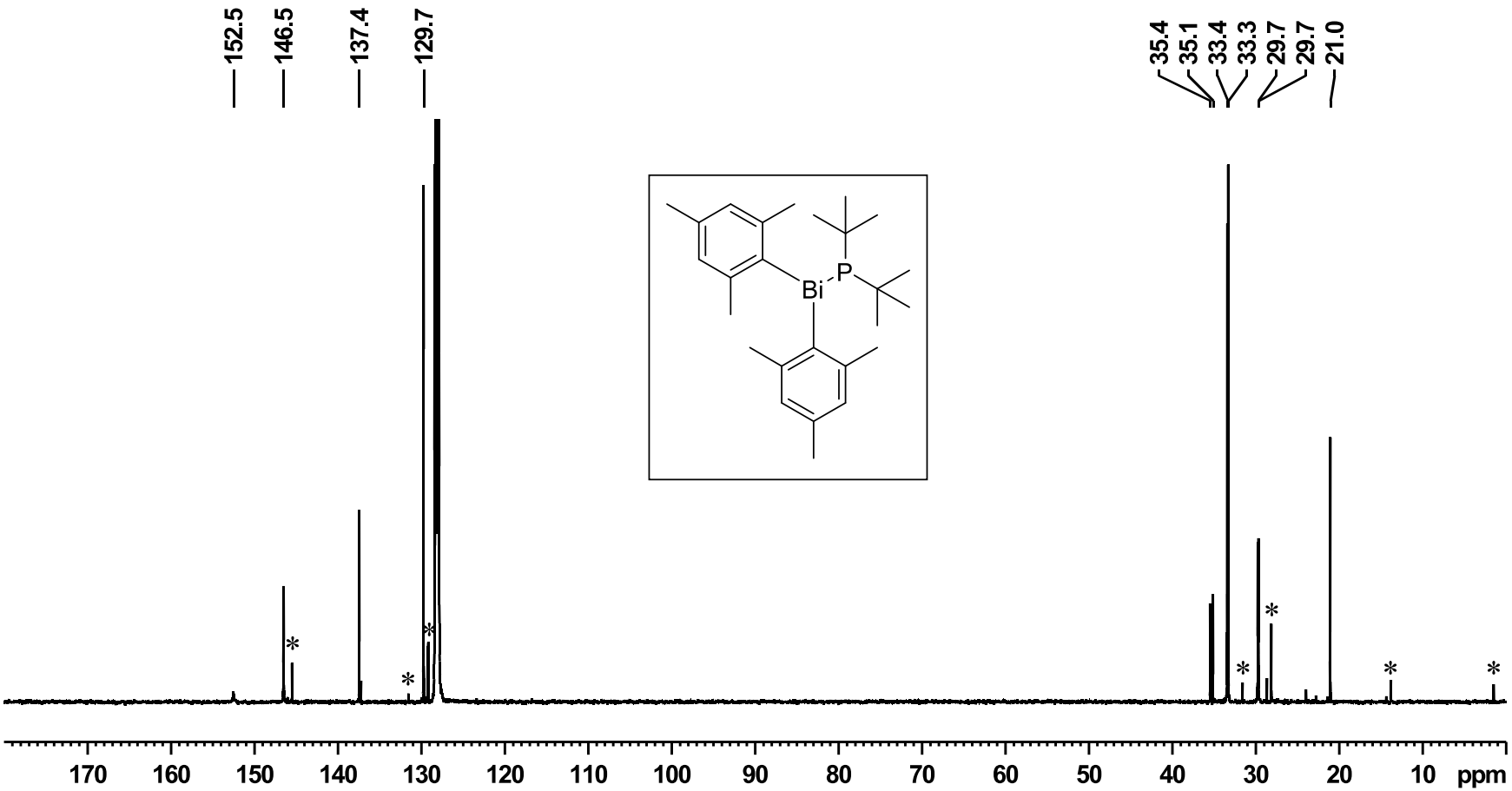


Figure S2.5.2: ^{13}C NMR spectrum (125 MHz) of **5** in C_6D_6 at room temperature (* = Unknown impurity).

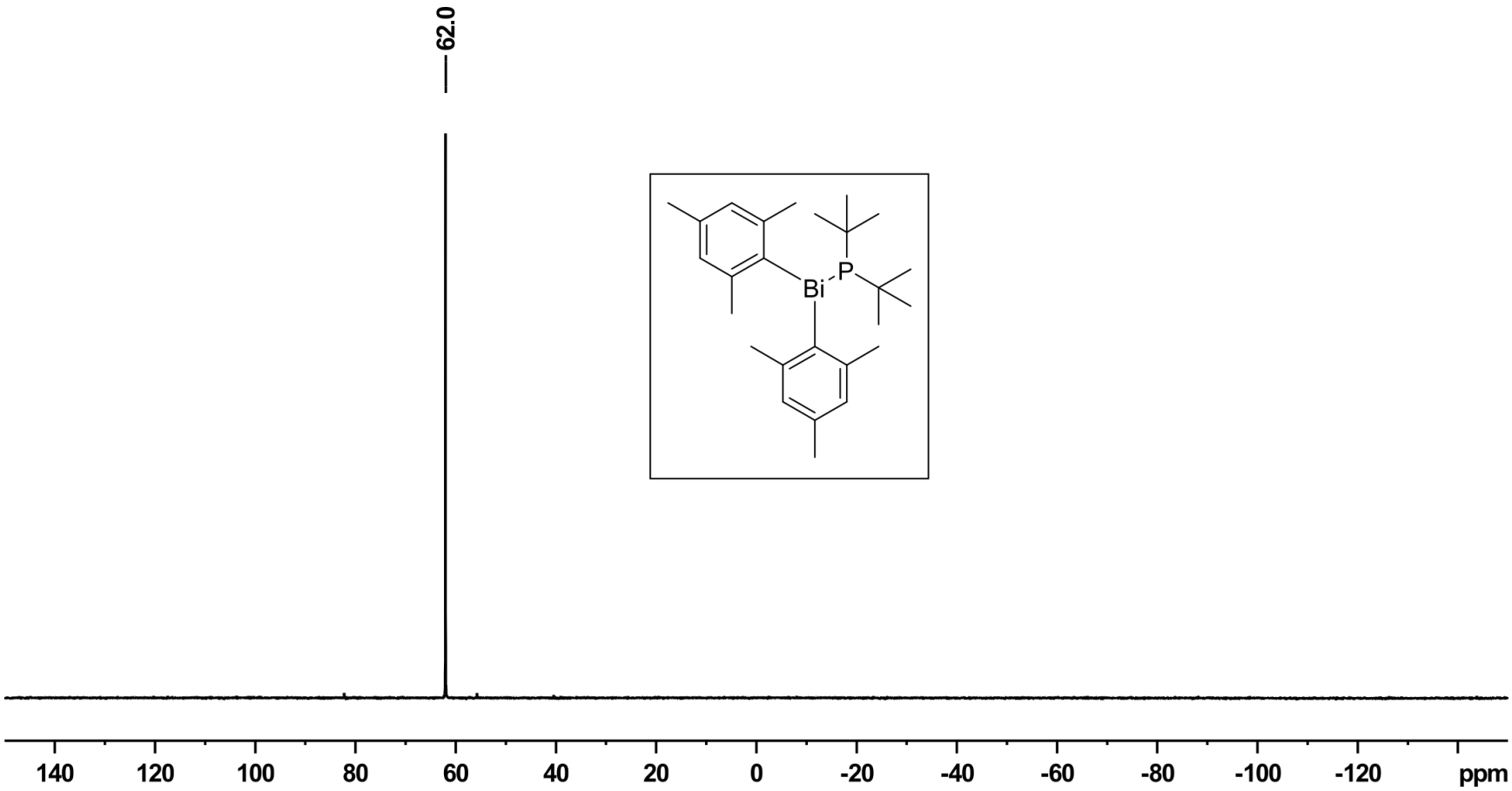


Figure S2.5.3: $^{31}P\{^{1}H\}$ NMR spectrum (125 MHz) of **5** in C_6D_6 at room temperature.

2.6 $Ph_2BiPtBu(SiMe_3)_3$ (**6**)

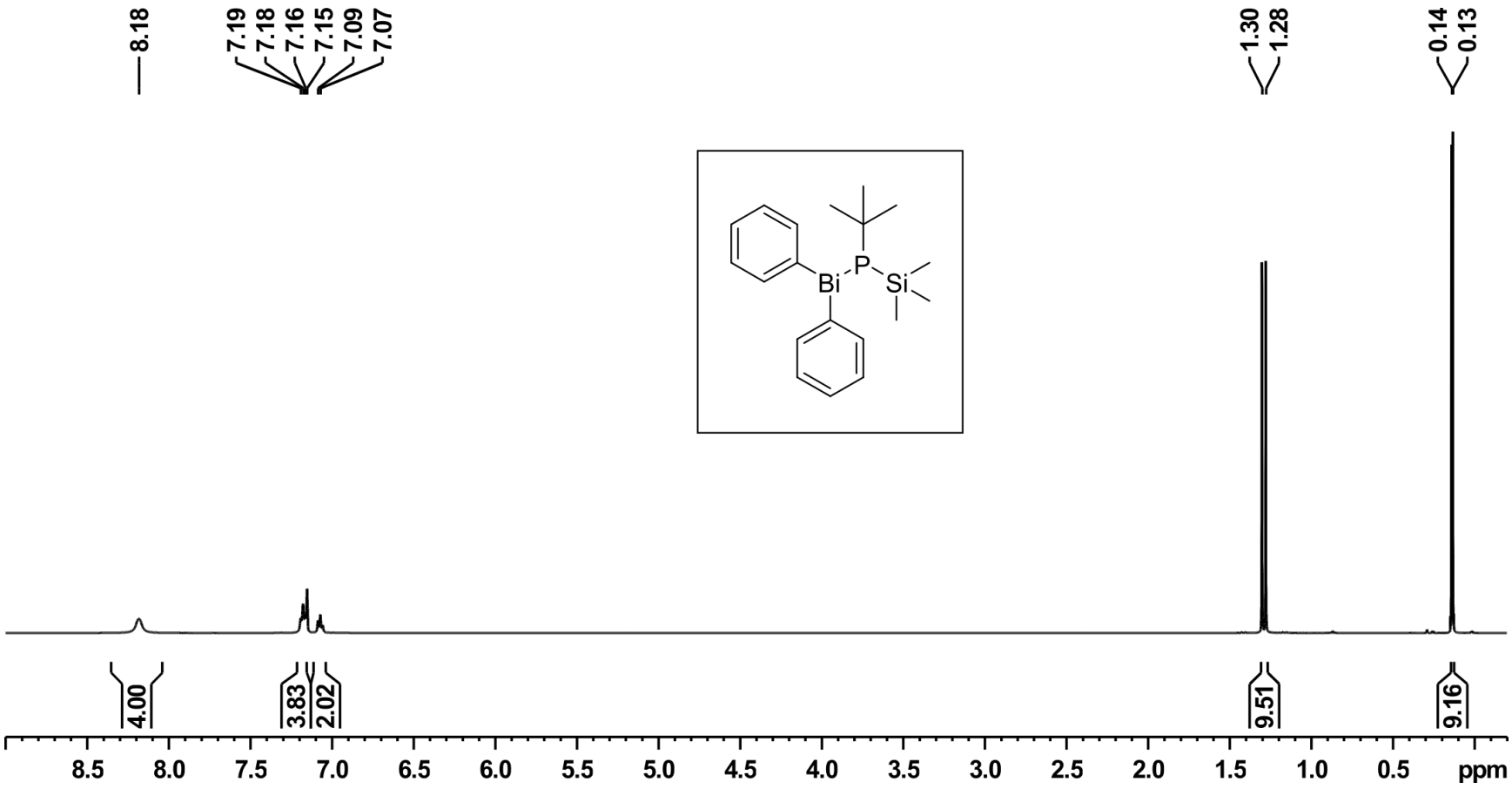


Figure S2.6.1: ^1H NMR spectrum (500 MHz) of **6** in C_6D_6 at room temperature.

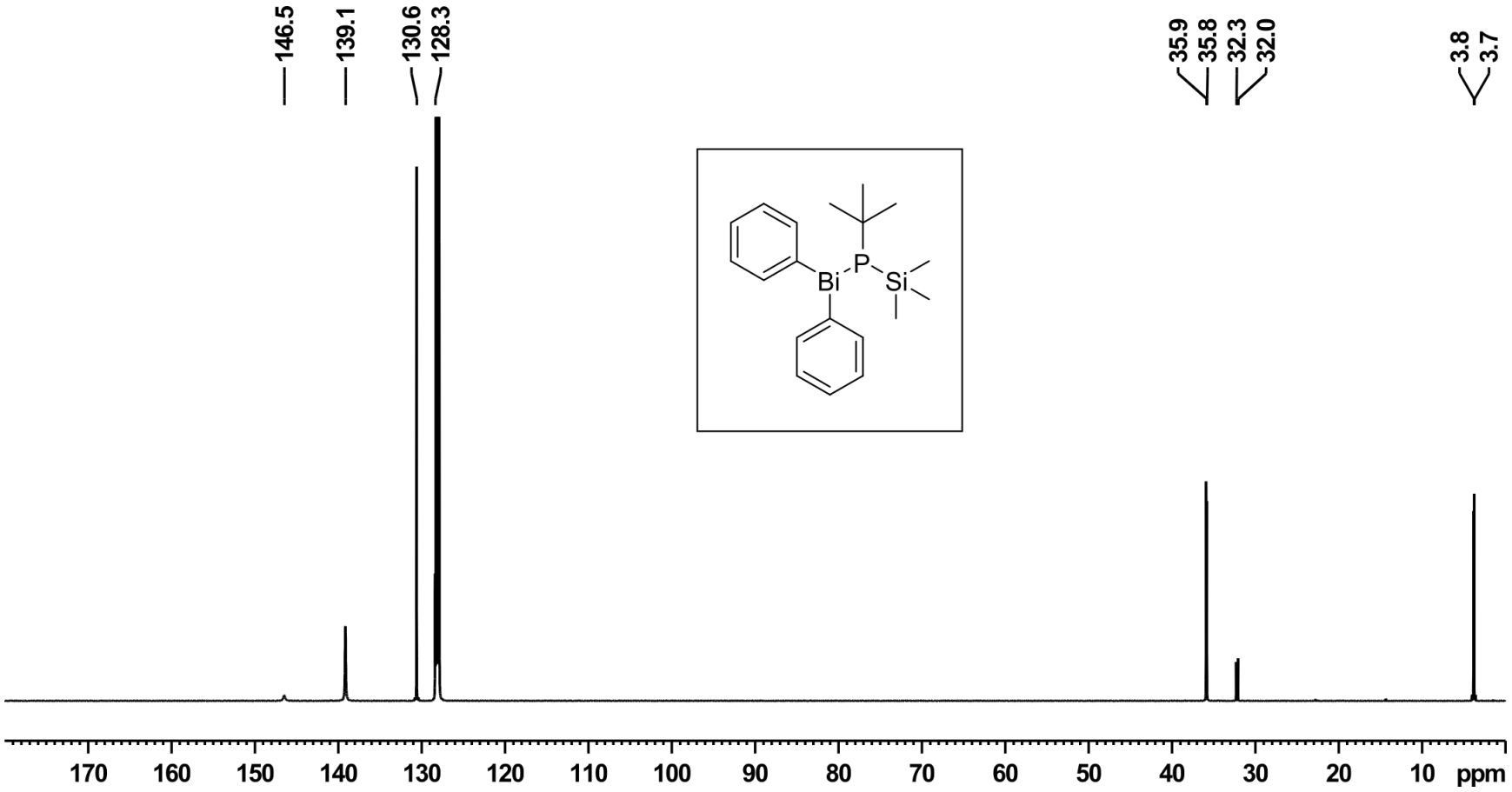


Figure S2.6.2: ^{13}C NMR spectrum (125 MHz) of **6** in C_6D_6 at room temperature.

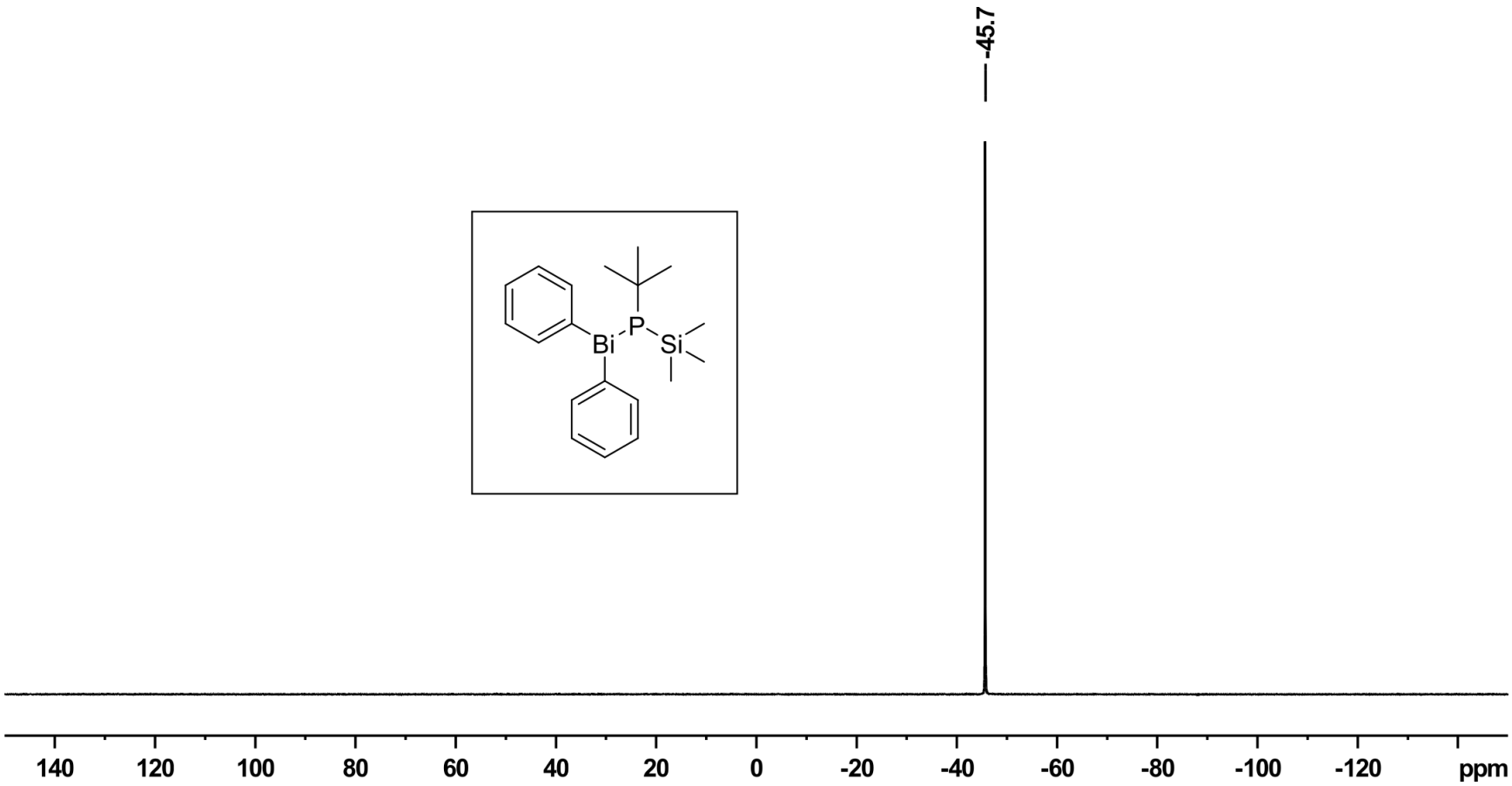


Figure S2.6.3: $^{31}P\{^{1}H\}$ NMR spectrum (200 MHz) of **6** in C_6D_6 at room temperature.

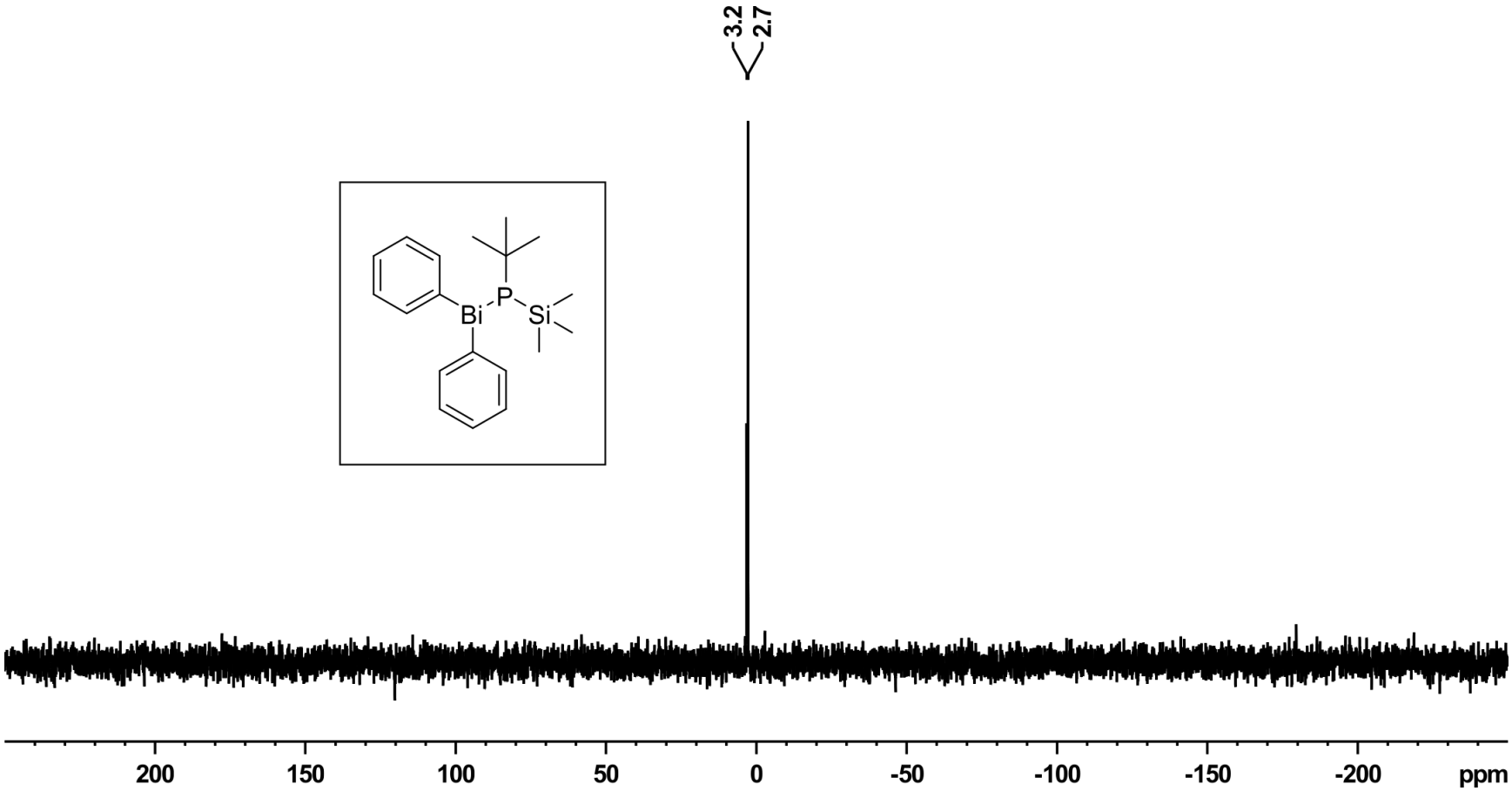


Figure S2.6.4: ^{29}Si-DEPT NMR spectrum (99 MHz) of **6** in C_6D_6 at room temperature.

2.7 $Mes_2BiPtBu(SiMe_3)_3$ (**7**)

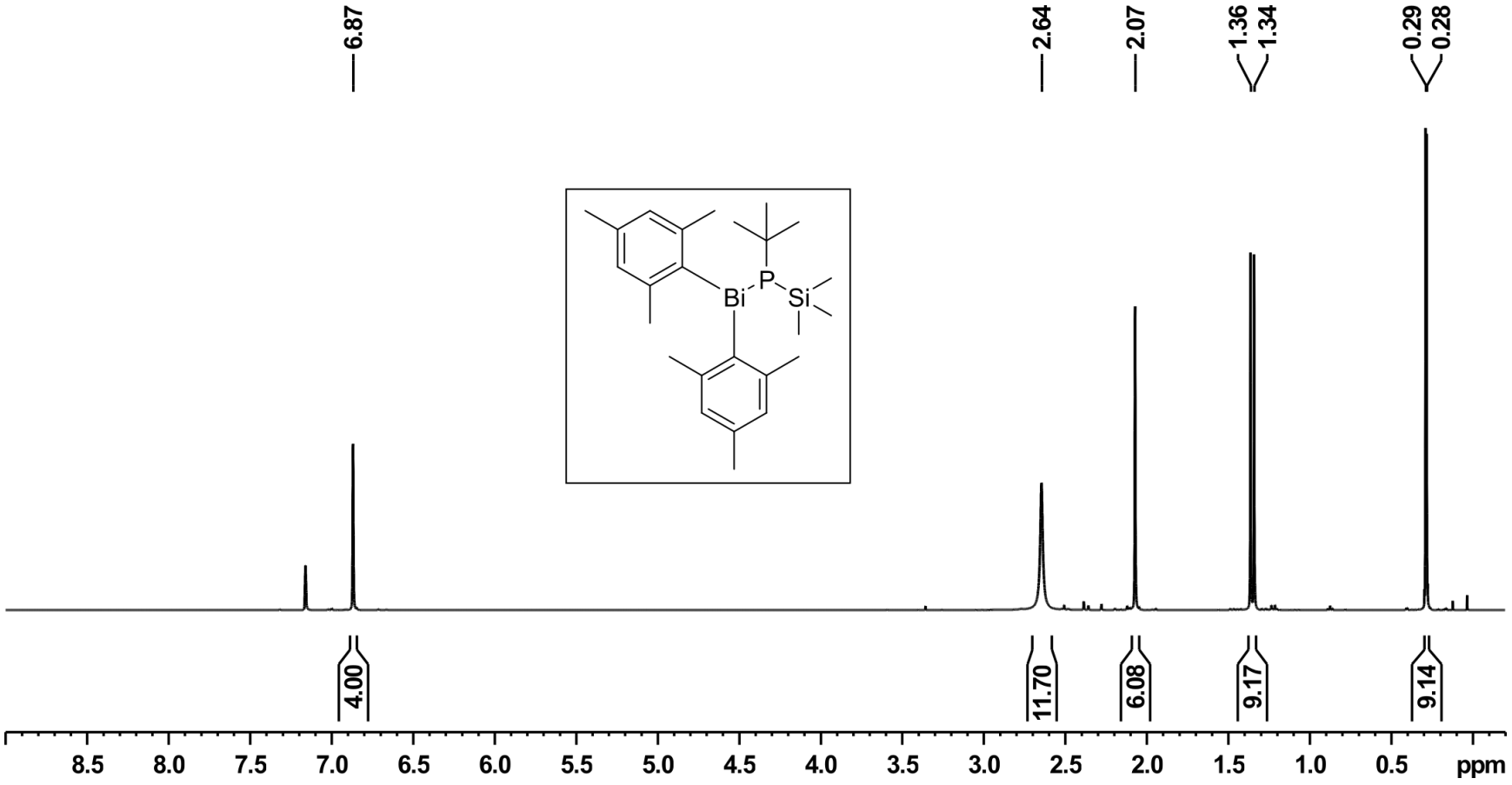


Figure S2.7.1: ^1H NMR spectrum (500 MHz) of **7** in C_6D_6 at room temperature.

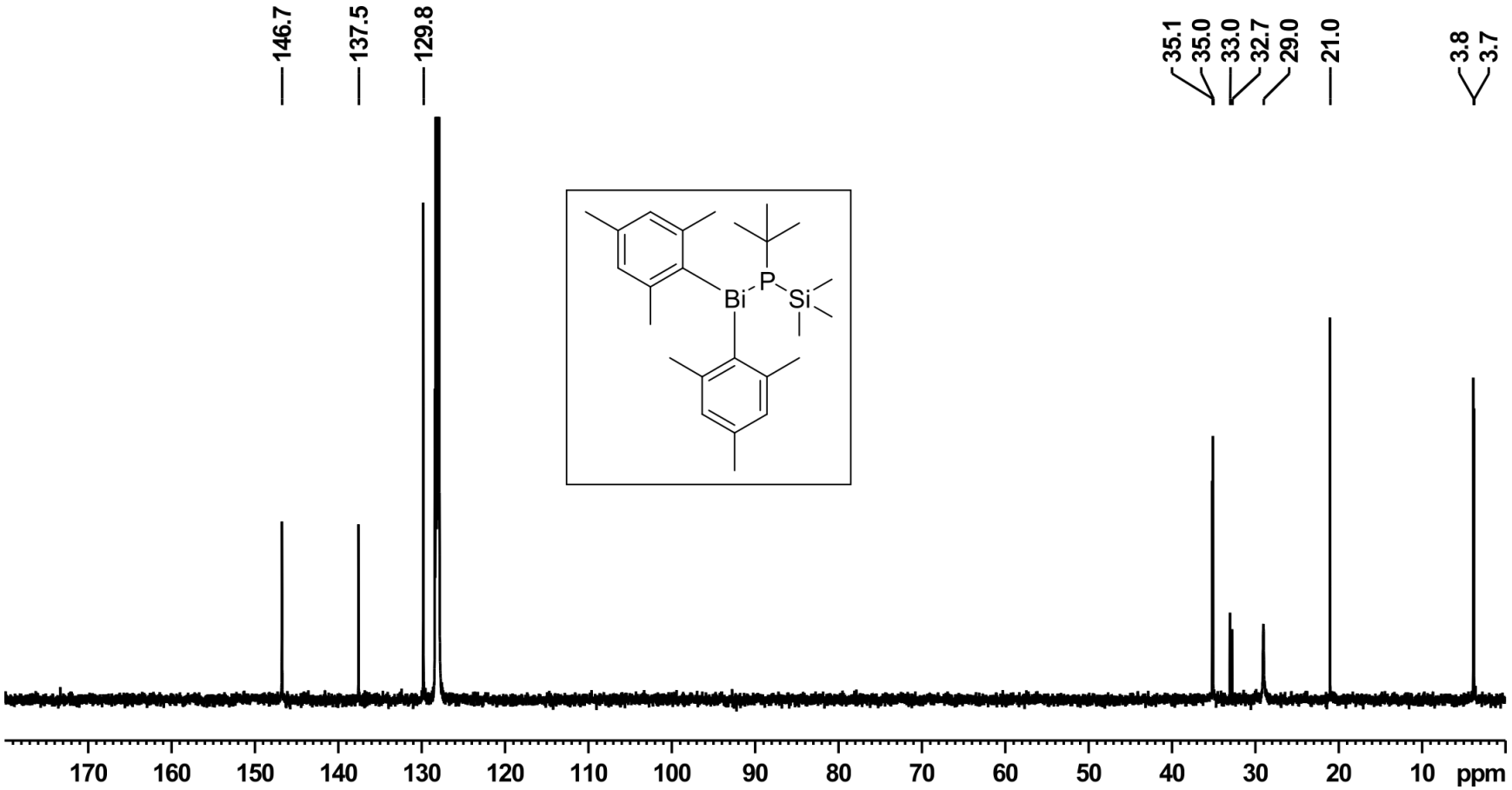


Figure S2.7.2: ^{13}C NMR spectrum (125 MHz) of **7** in C_6D_6 at room temperature.

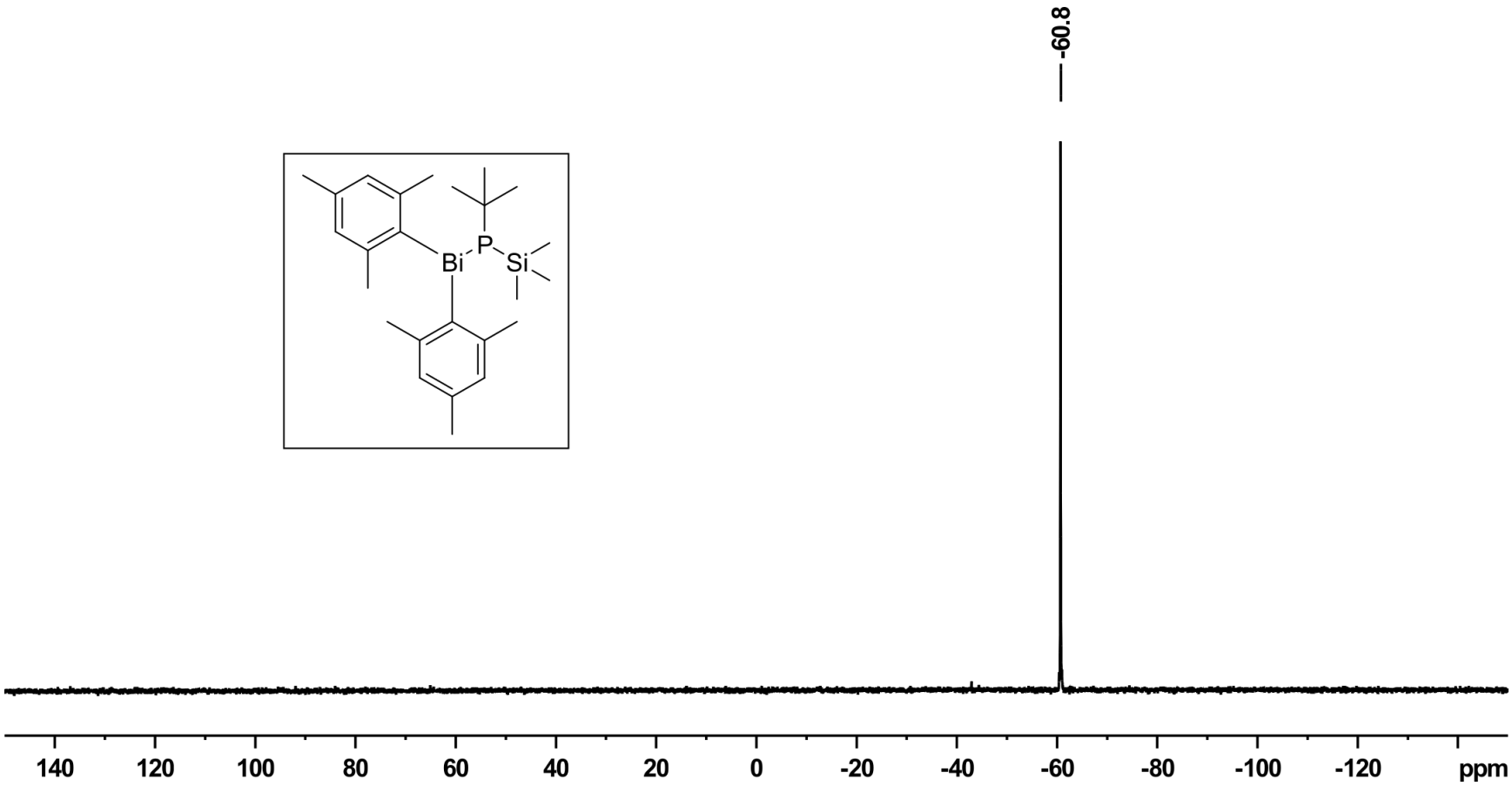


Figure S2.7.3: ^{31}P NMR spectrum (200 MHz) of **7** in C_6D_6 at room temperature.

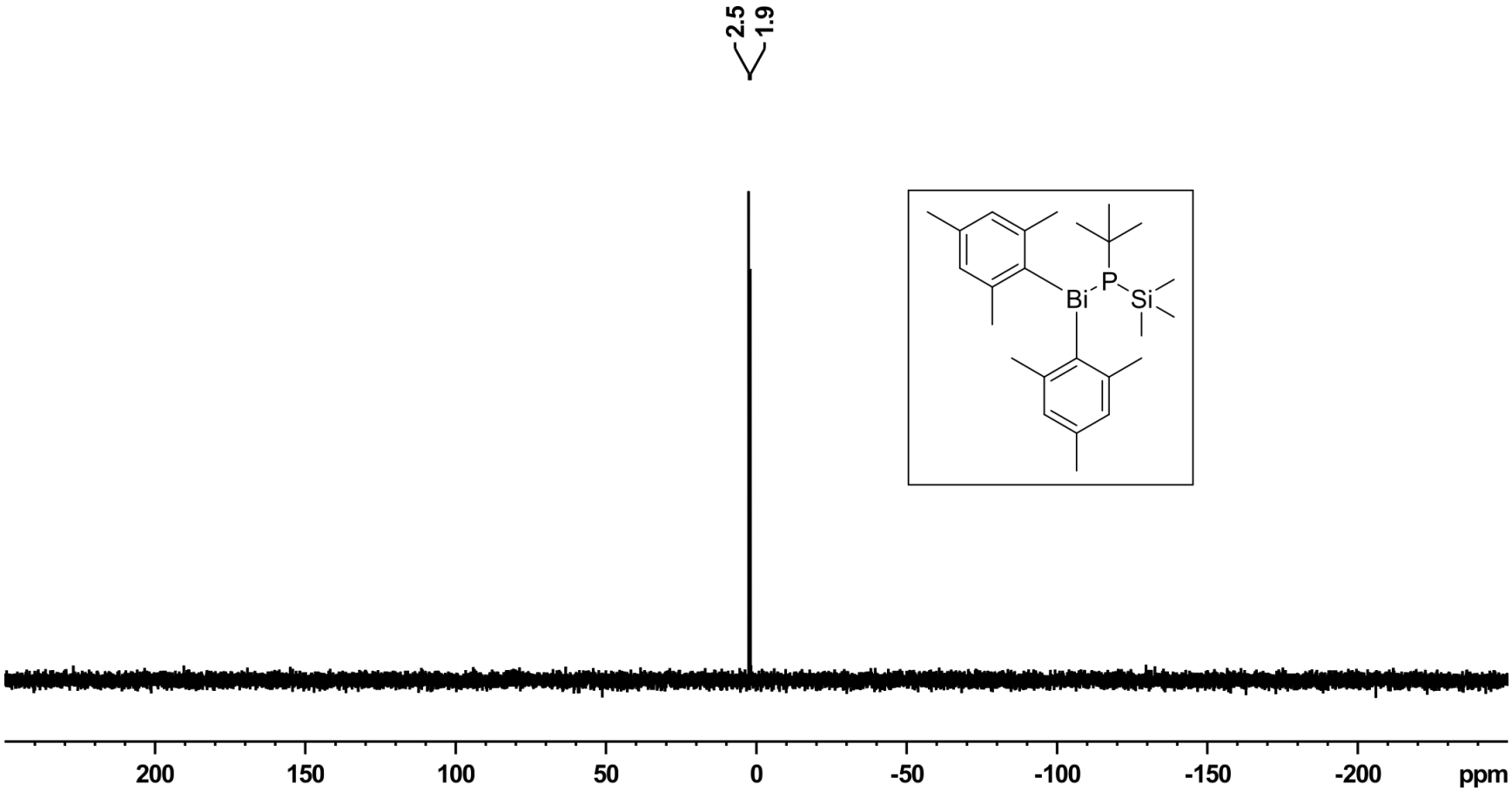


Figure S2.7.4: ^{29}Si NMR spectrum (99 MHz) of **7** in C_6D_6 at room temperature.

2.8 $Ph_2BiAstBu_2$ (**8**)

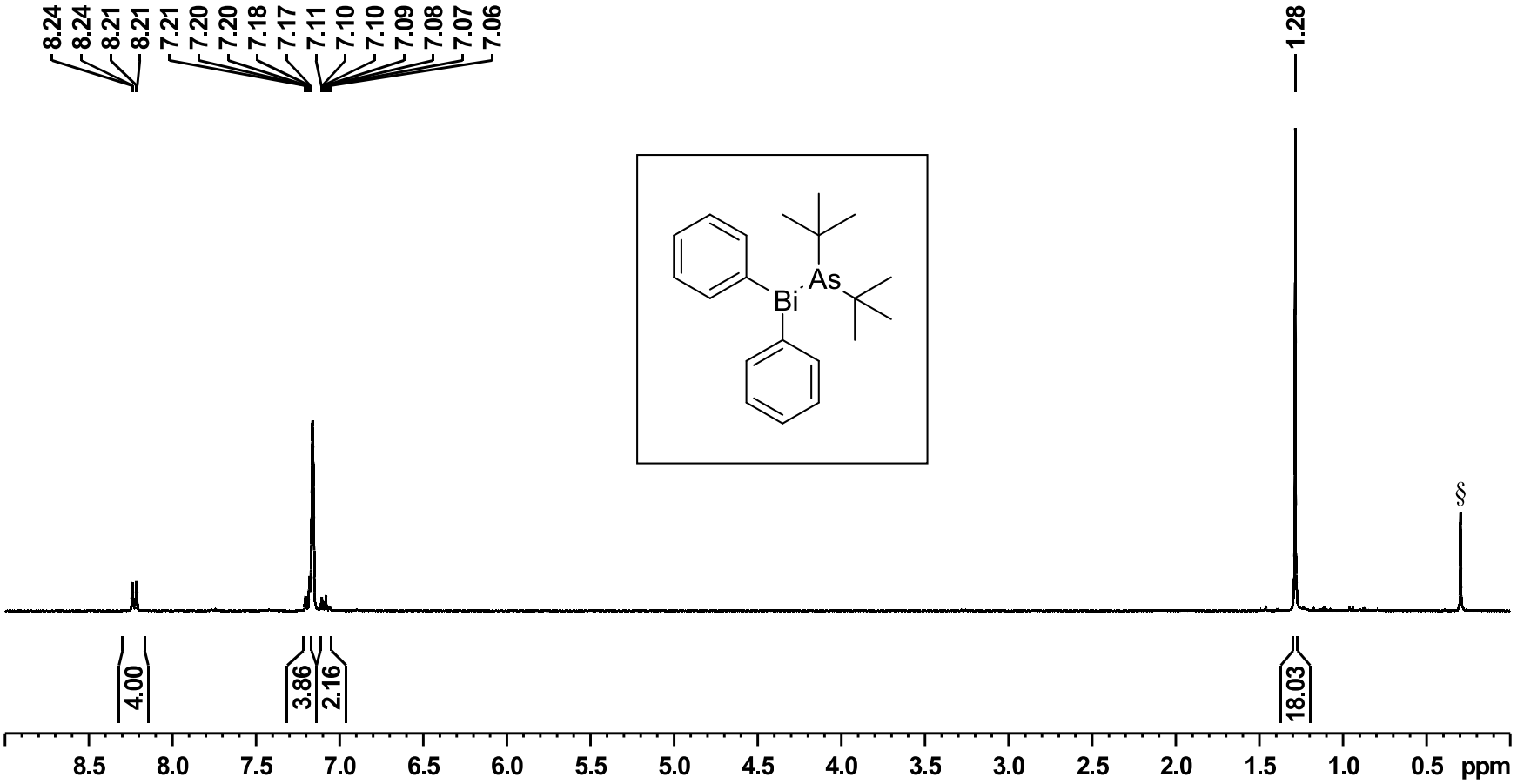


Figure S2.8.1: ^1H NMR spectrum (300 MHz) of **8** in C_6D_6 at room temperature (§ = Silicon grease).

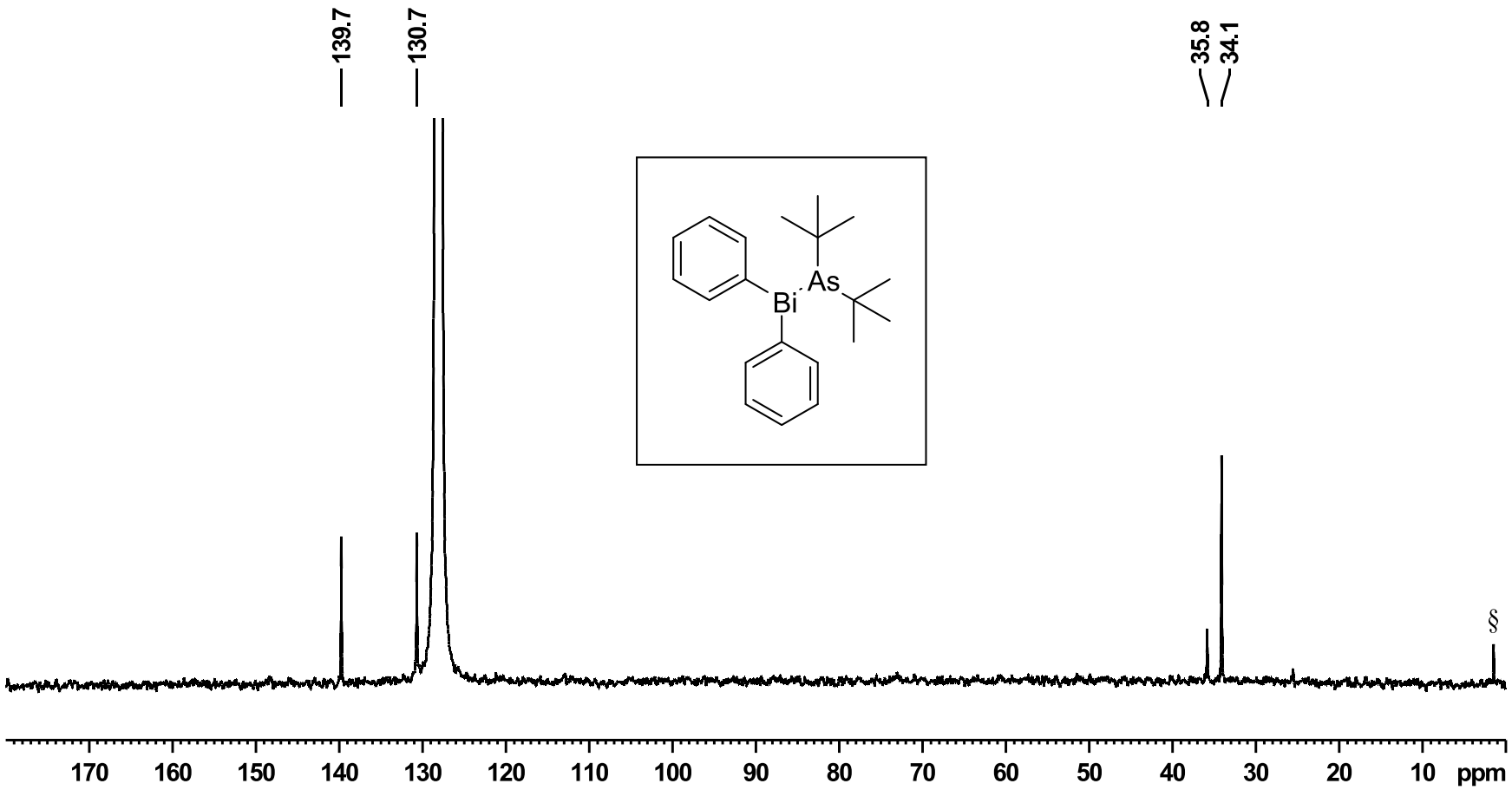


Figure S2.8.2: ^{13}C NMR spectrum (75 MHz) of **8** in C_6D_6 at room temperature (§ = Silicon grease).

2.9 $Mes_2BiAstBu_2$ (**9**)

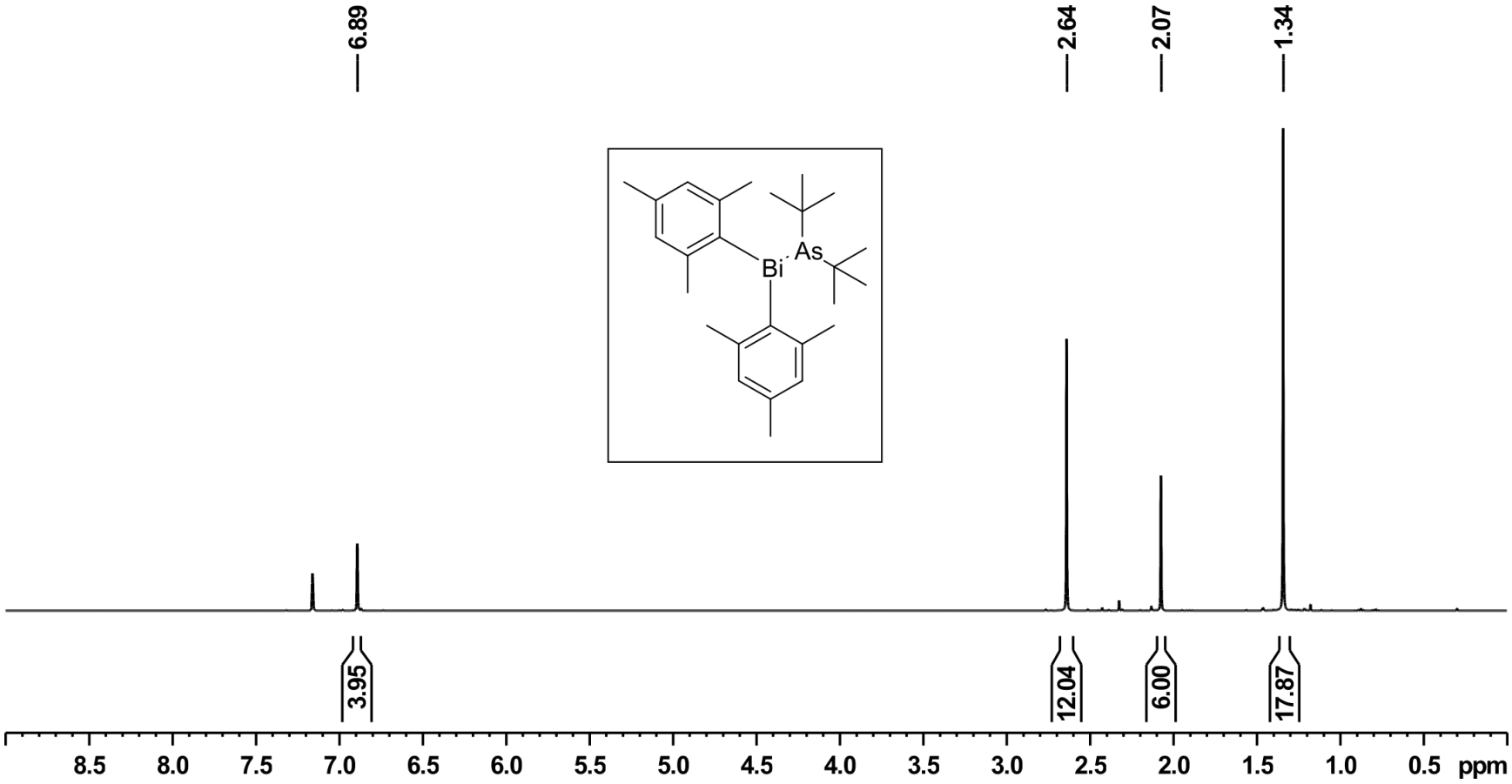


Figure S2.9.1: ^1H NMR spectrum (500 MHz) of **9** in C_6D_6 at room temperature.

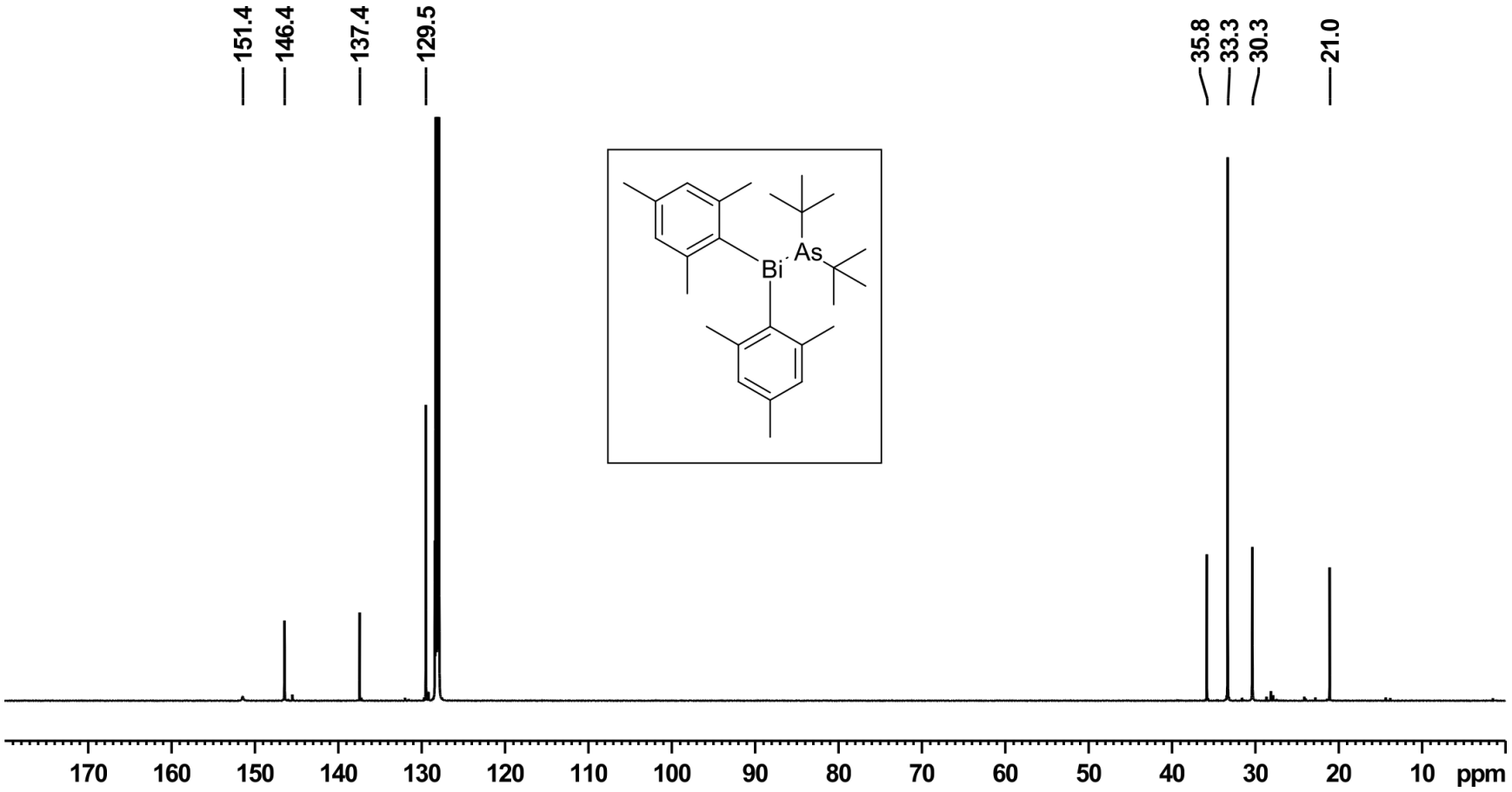


Figure S2.8.2: ^{13}C NMR spectrum (125 MHz) of **9** in C_6D_6 at room temperature.

2.10 $Ph_2BiAstBu(SiMe_3)_3$ (**10**)

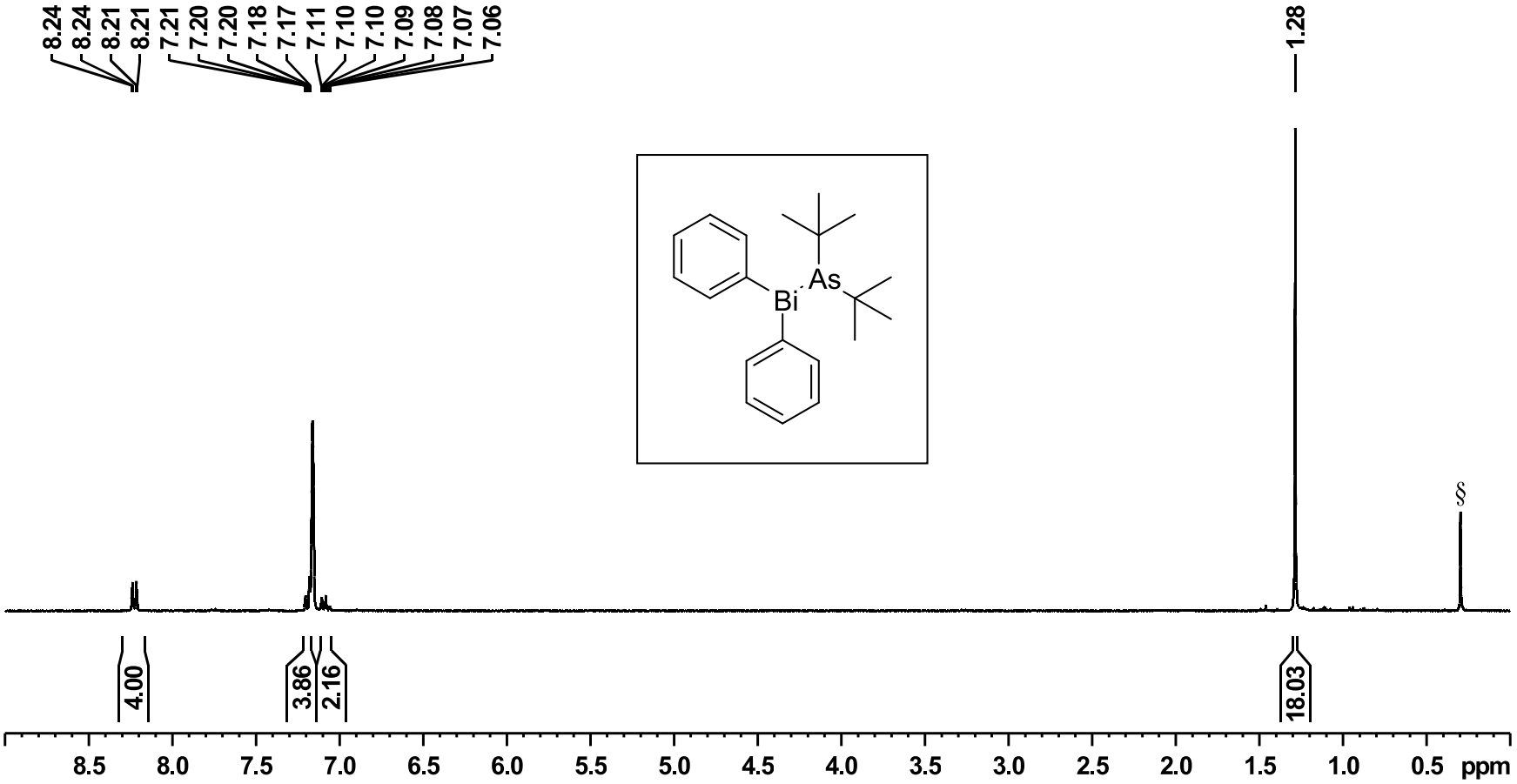


Figure S2.10.1: ^1H NMR spectrum (500 MHz) of **10** in C_6D_6 at room temperature (§ = Silicon grease).

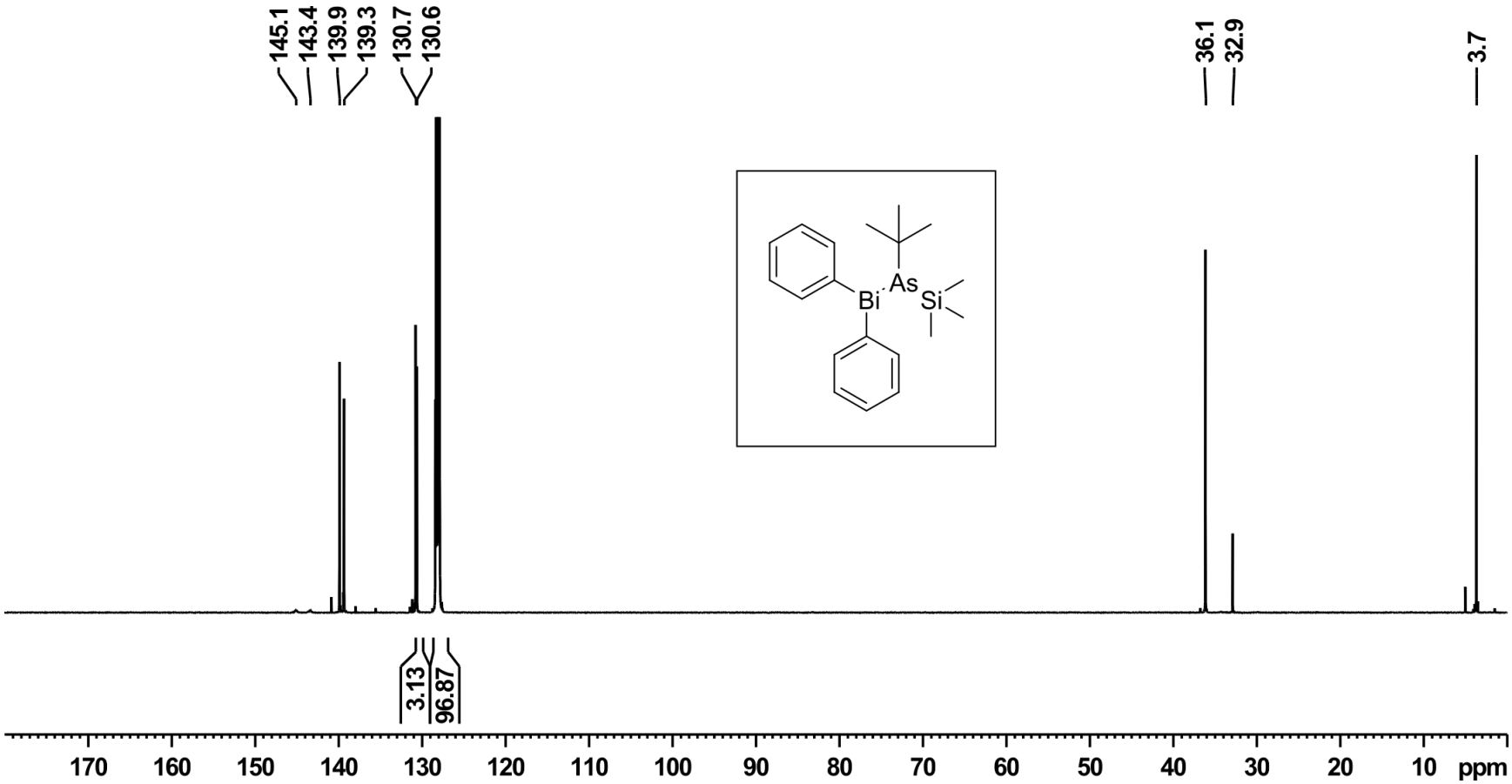


Figure S2.10.2: ^{13}C NMR spectrum (125 MHz) of **10** in C_6D_6 at room temperature.

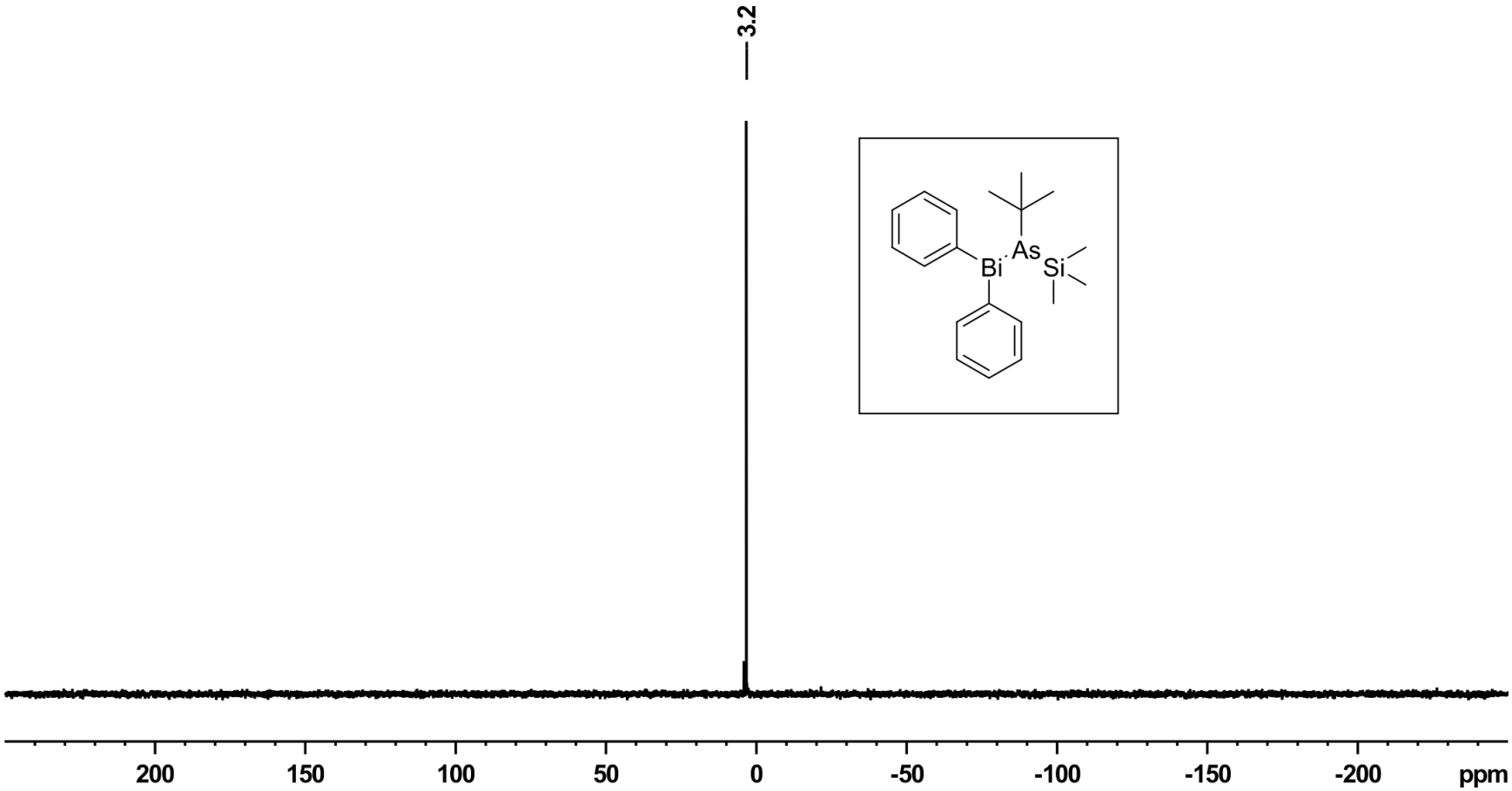


Figure S2.10.3: ^{29}Si NMR spectrum (99 MHz) of **10** in C_6D_6 at room temperature.

2.11 $Mes_2BiAstBu(SiMe_3)_3$ (**11**)

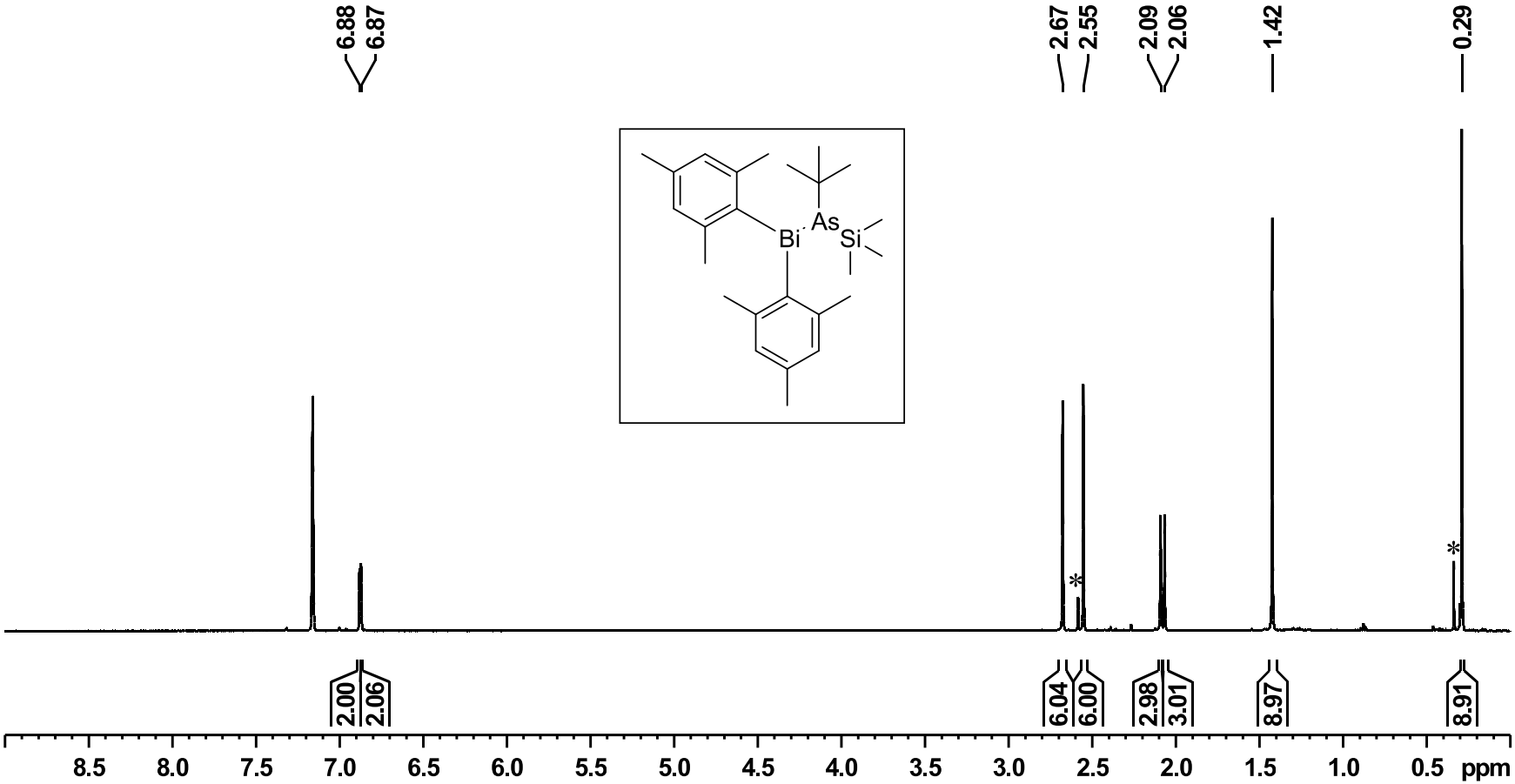


Figure S2.11.1: ^1H NMR spectrum (500 MHz) of **11** in C_6D_6 at room temperature (* = Unknown impurity).

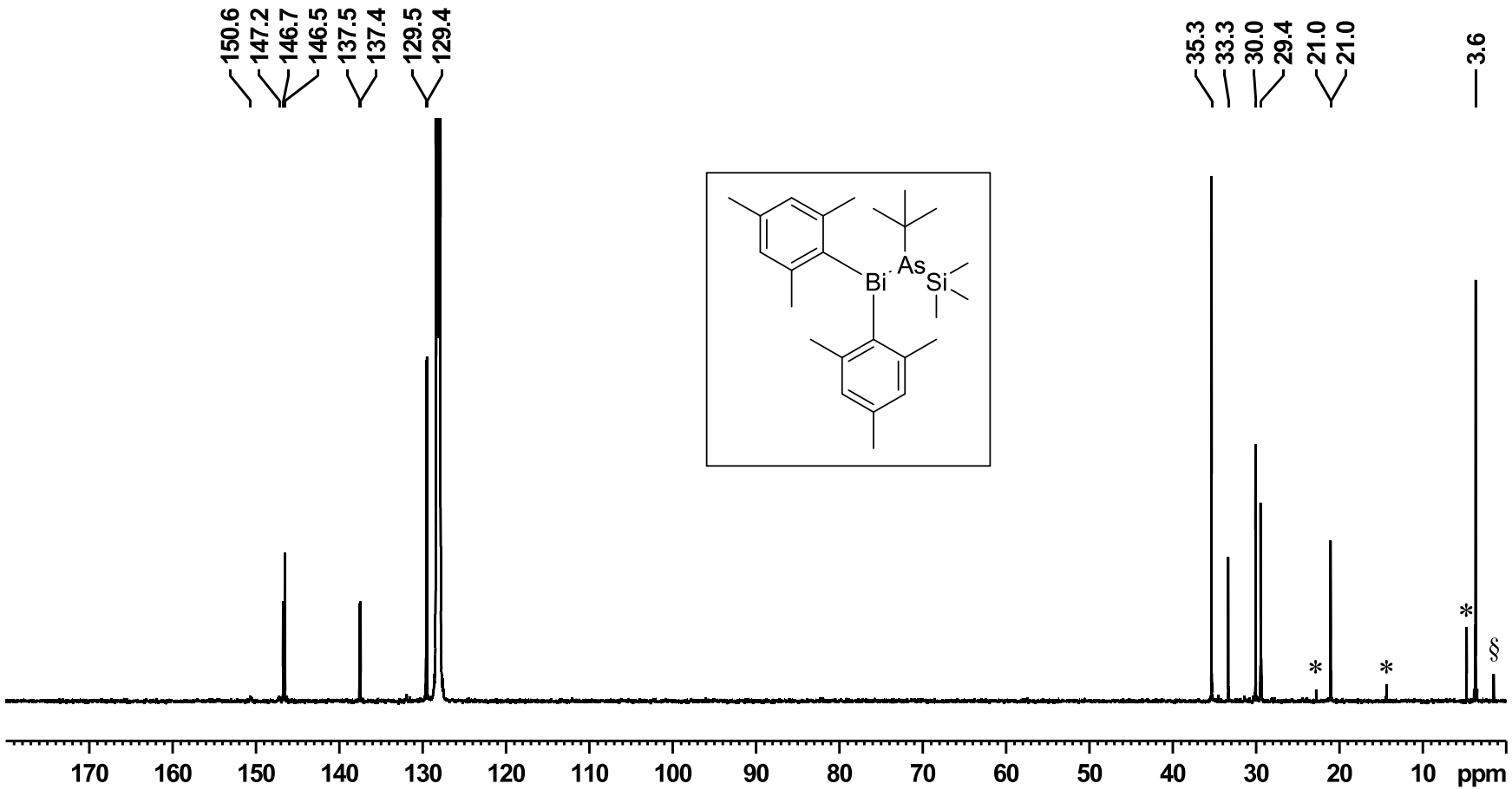


Figure S2.11.2: ^{13}C NMR spectrum (125 MHz) of **11** in C_6D_6 at room temperature (* = Unknown impurity, § = Silicon grease).

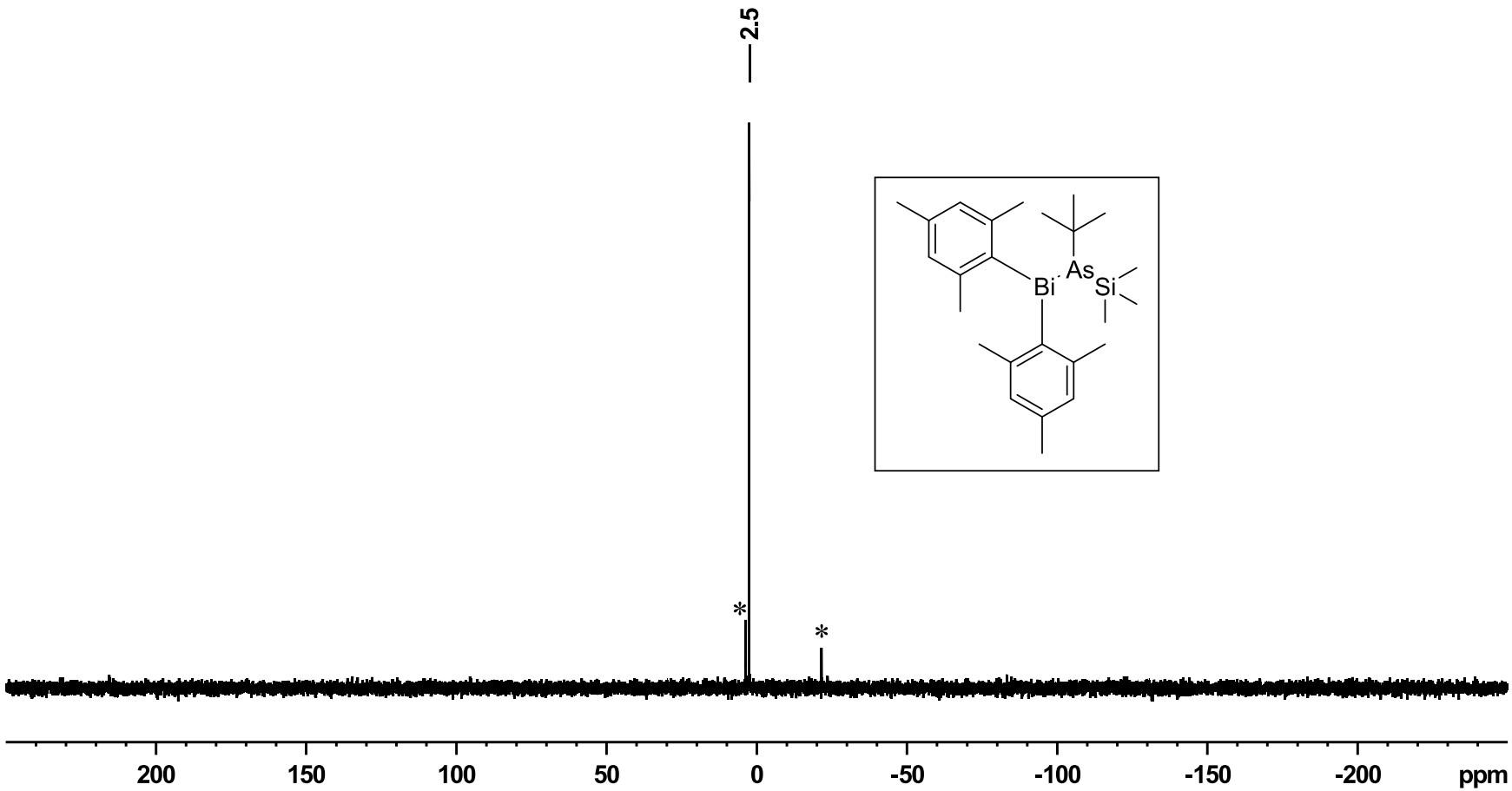


Figure S2.11.1: ^{29}Si NMR spectrum (99 MHz) of **11** in C_6D_6 at room temperature (* = Unknown impurity).

2.12 $Ph_2BiSbMes_2$ (**12**)

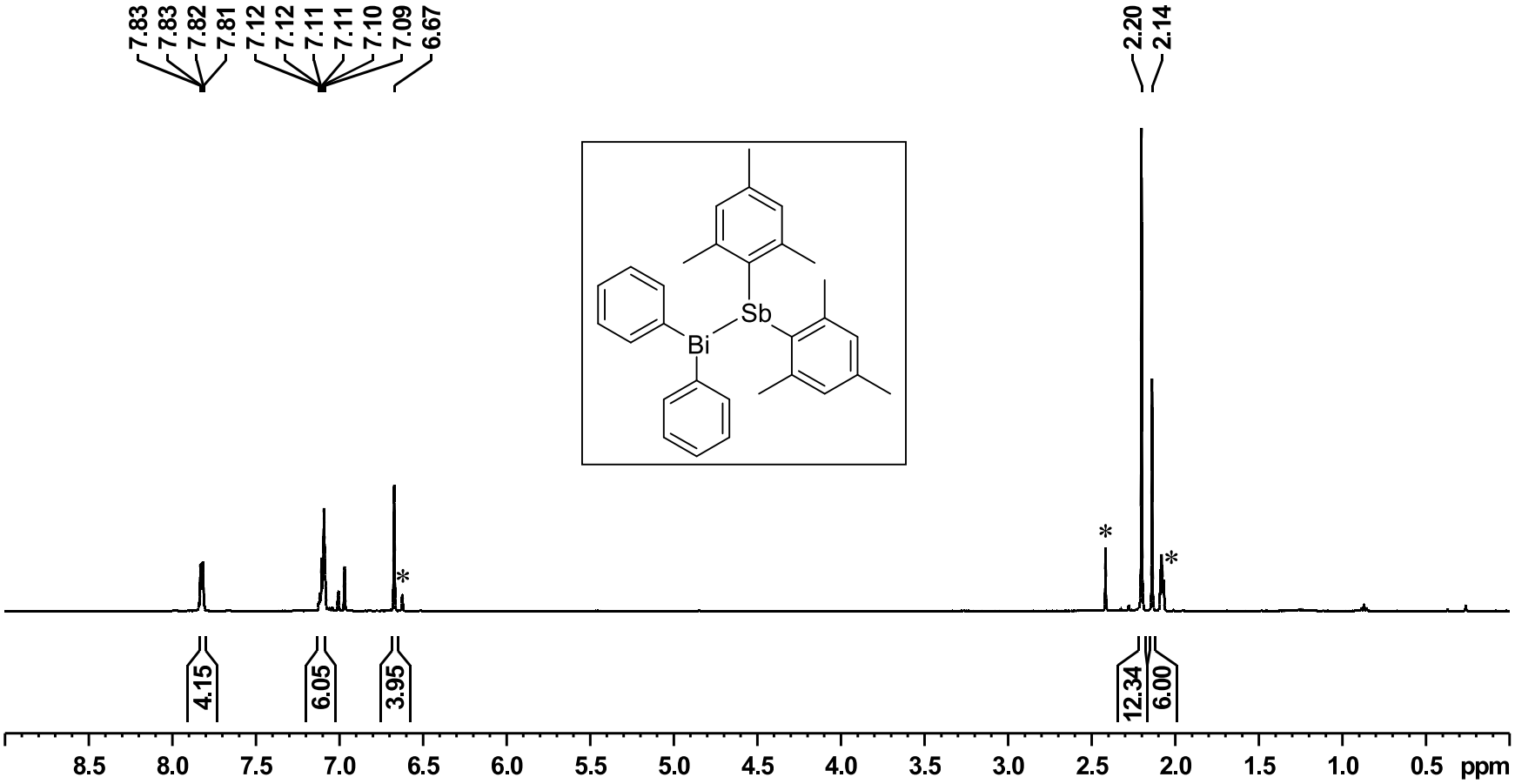


Figure S2.12.1: ^{1}H NMR spectrum (500 MHz) of **12** in toluene-d_8 at room temperature (* = Mes_4Sb_2).

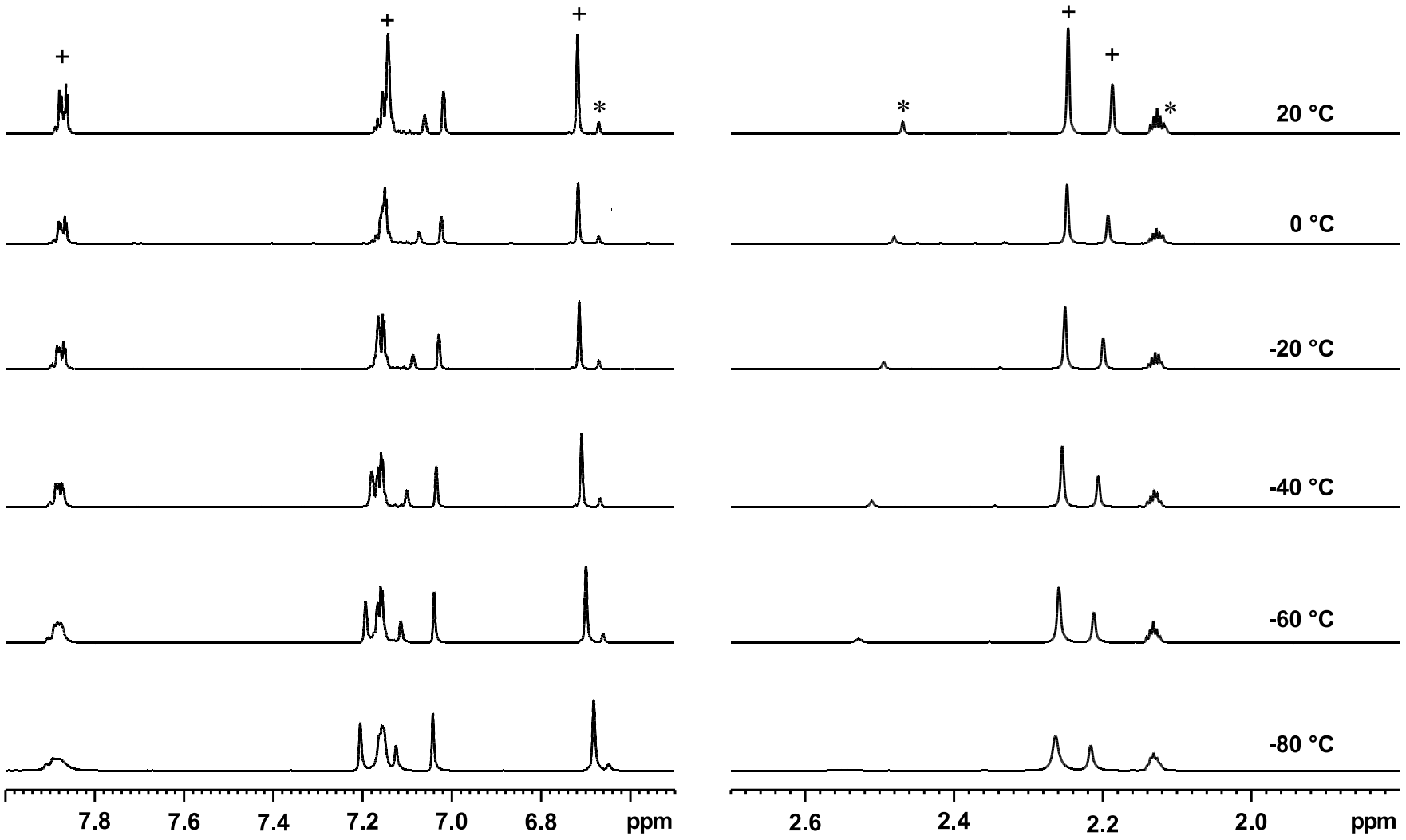


Figure S2.12.2: Excerpts of the temperature dependent ^{1}H NMR spectra (500 MHz) of **12** in toluene-d_8 (+ = **12**, * = Mes_4Sb_2).

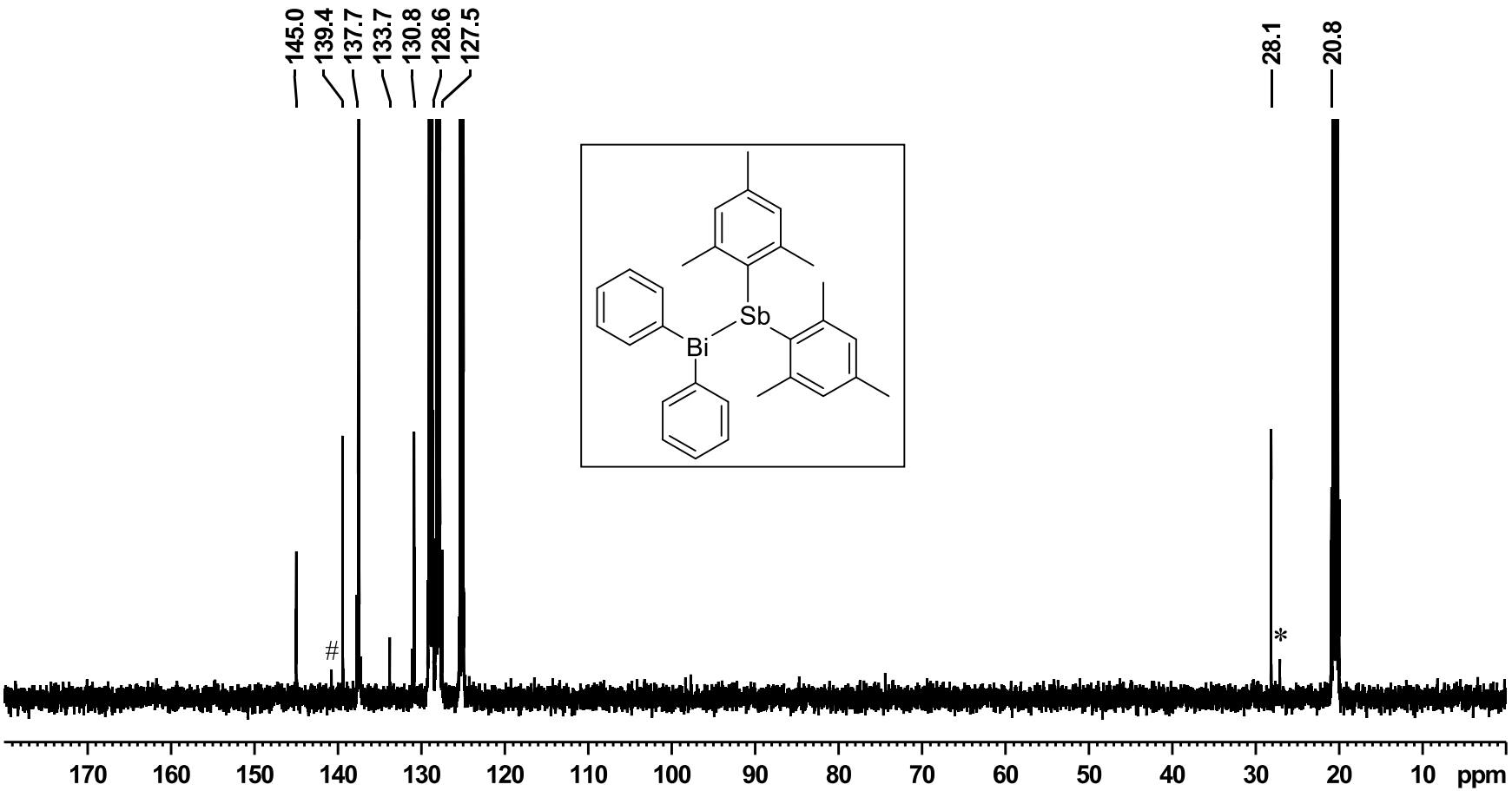


Figure S2.12.3: ^{13}C NMR spectrum (125 MHz) of **12** in toluene-d_8 at room temperature (* = Mes_4Sb_2, # = Ph_4Bi_2).

2.12 $Mes_2BiSbMes_2$ (**13**)

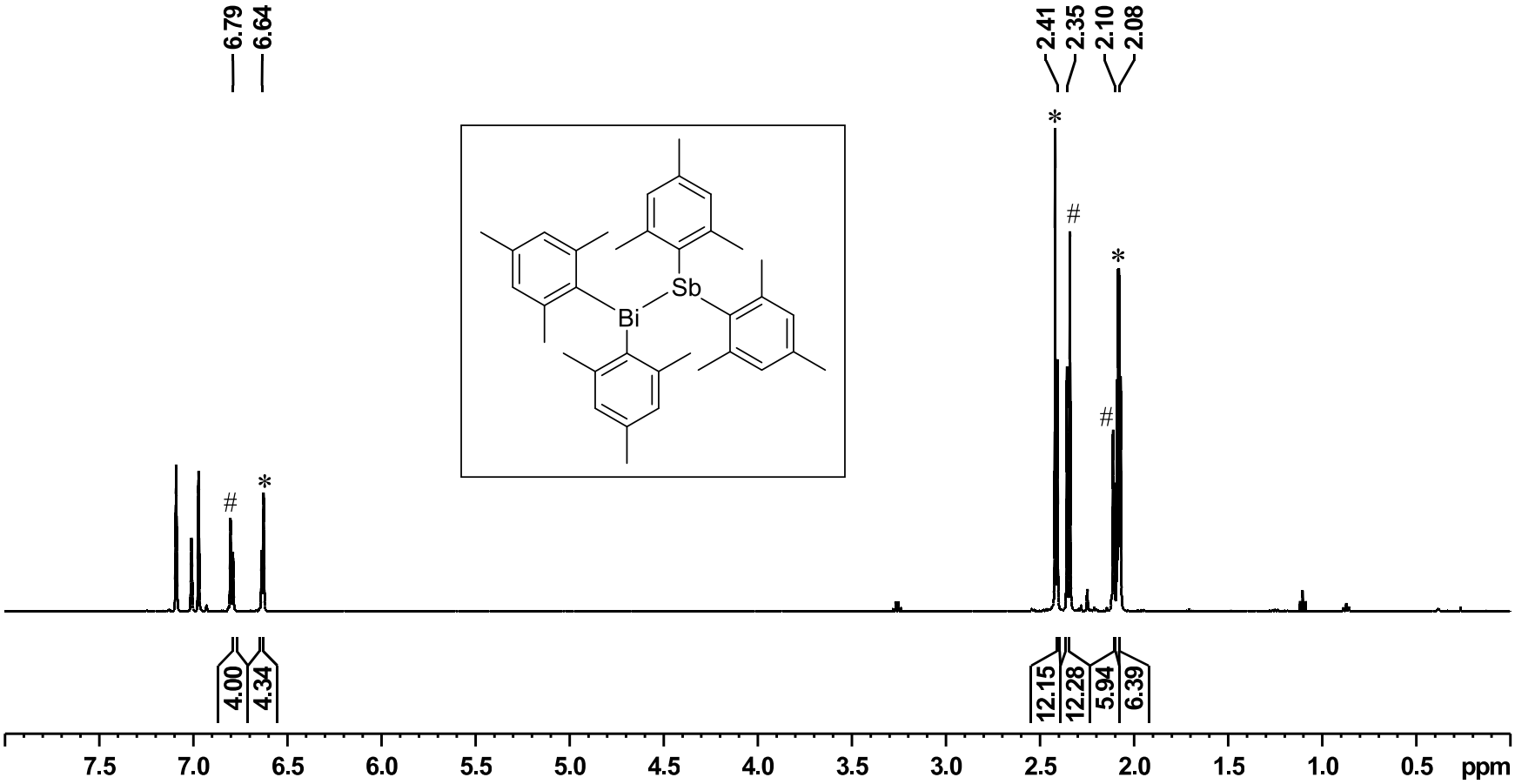


Figure S2.13.1: ^{1}H NMR spectrum (500 MHz) of **13** in toluene-d_8 at room temperature (* = Mes_4Sb_2, # = Mes_4Bi_2).

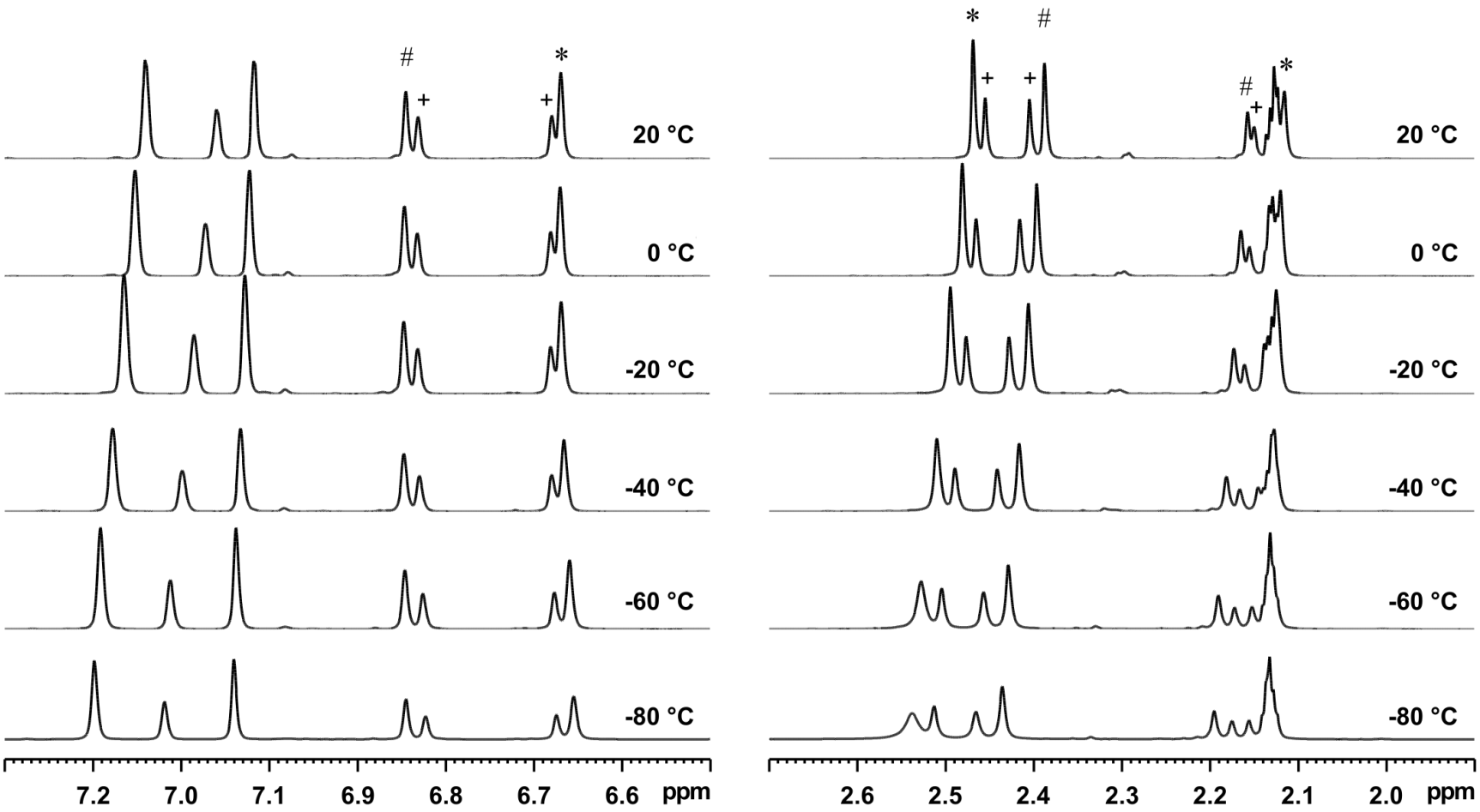


Figure S2.13.2: Excerpts of the temperature dependent ^{1}H NMR spectra (500 MHz) of **13** in toluene-d_8 at room temperature (+ = **13**, * = Mes_4Sb_2, # = Mes_4Bi_2).

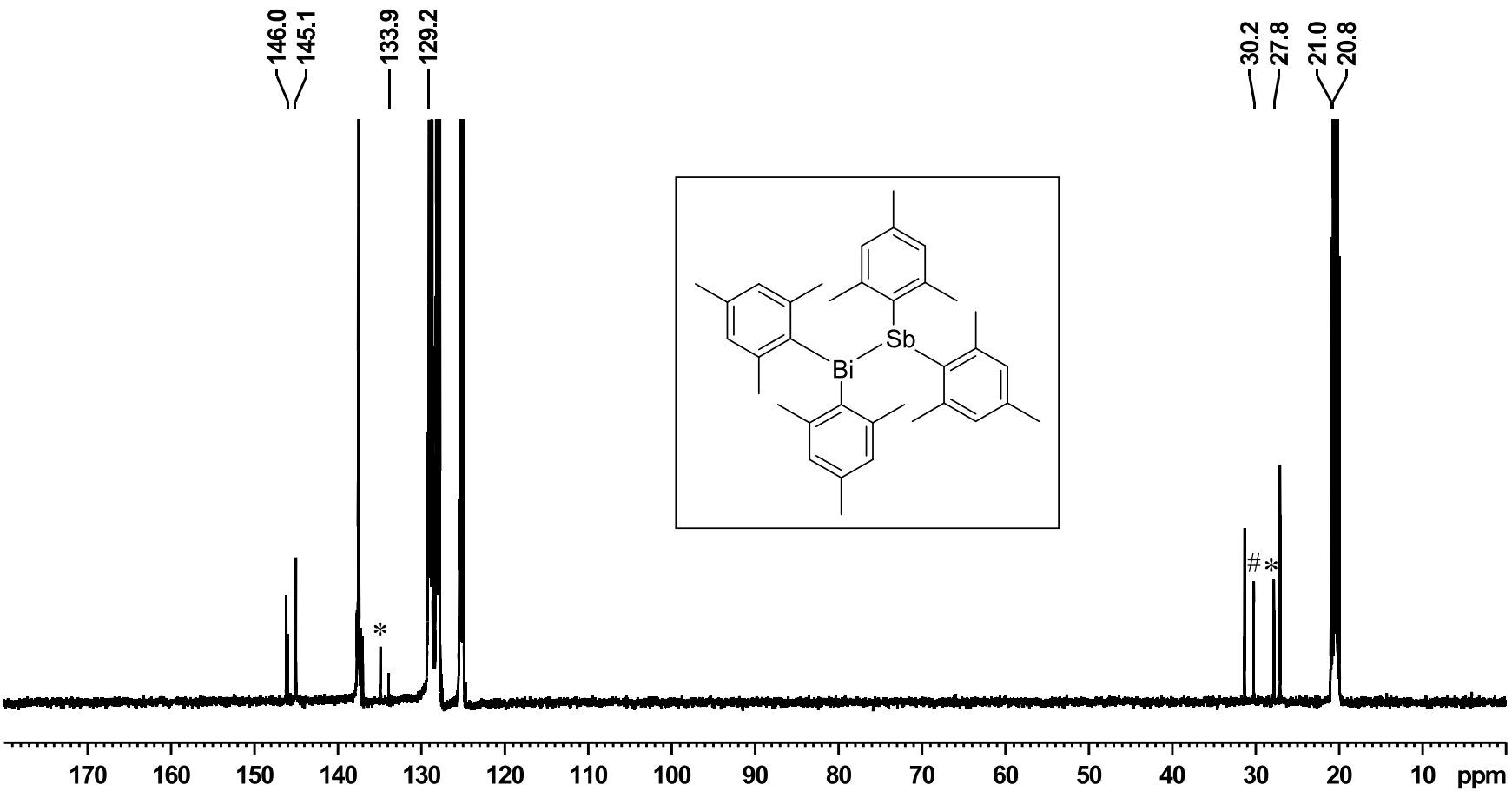


Figure S2.13.3: ^{13}C NMR spectrum (125 MHz) of **13** in toluene-d_8 at room temperature (* = Mes_4Sb_2, # = Mes_4Bi_2).

3. Calculation of ΔH_r^0, ΔS_r^0 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*.

		12		**13**	
T (K^{-1})	T^{-1} (K^{-1})	*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

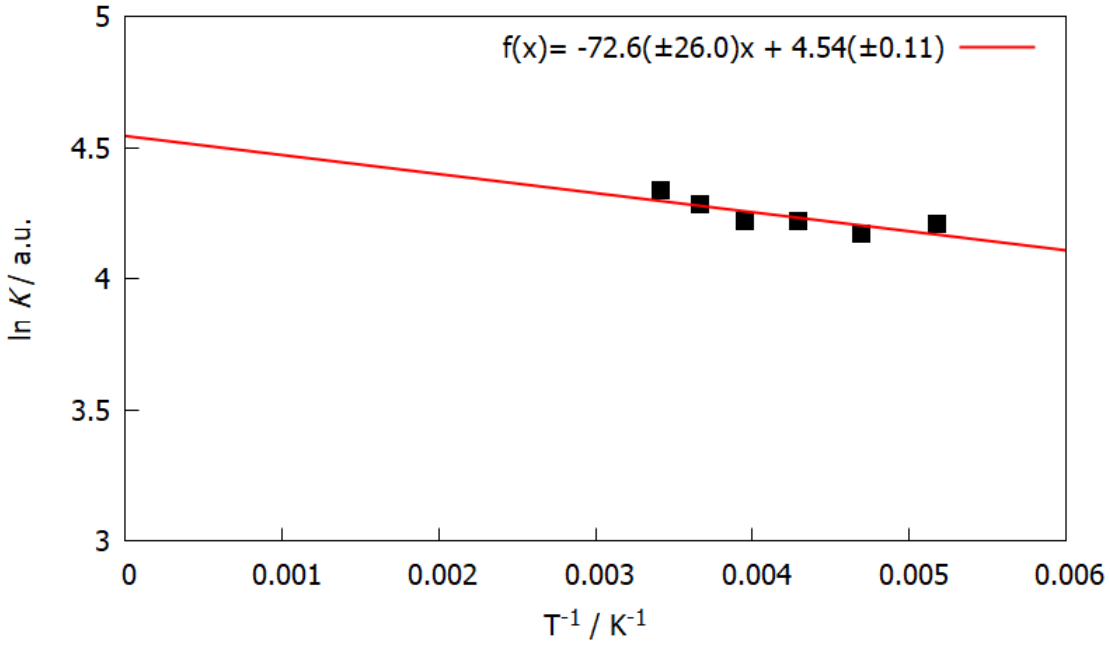


Figure S3.1: *van't Hoff* plot of the natural logarithmic of the equilibrium constant in the equilibrium of **12** and Mes_4Sb_2 and Ph_4Bi_2 against the reciprocal temperature with a fitted linear regression f(x).

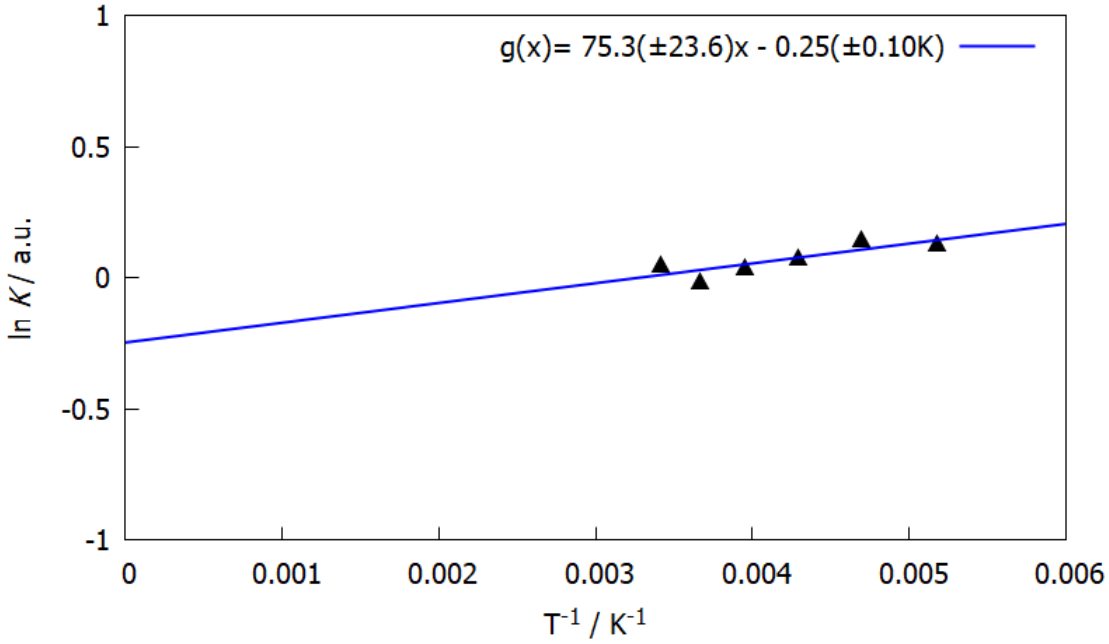


Figure S3.2: *van't Hoff* plot of the natural logarithmic of the equilibrium constant in the equilibrium of **13** and Mes_4Sb_2 and Mes_4Bi_2 against the reciprocal temperature with a fitted linear regression g(x).

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

12: ΔH_r^0 = 72.6 K · 8.314 J·mol^{-1}K^{-1} = 603 J·mol^{-1} = 0.603 KJ·mol^{-1}
$\Delta(\Delta H_r^0)$ = ±26.0 K · 8.314 J·mol^{-1}K^{-1} = 216 J·mol^{-1} = ±0.216 KJ·mol^{-1}

ΔS_r^0 = 4.54 · 8.314 J·mol^{-1}K^{-1} = 37.78 J·mol^{-1}K^{-1}
$\Delta(\Delta S_r^0)$ = ±0.11 K · 8.314 J·mol^{-1}K^{-1} = ±0.92 J·mol^{-1}K^{-1}

ΔG_r (20 °C) = 603 J·mol^{-1} - 293 K · 37.78 J·mol^{-1}K^{-1} = -10.47 KJ·mol^{-1}
$\Delta(\Delta G_r$ (20 °C)) = ±216 J·mol^{-1} - 293 K · 0.92 J·mol^{-1}K^{-1} = ±0.05 KJ·mol^{-1}

13: ΔH_r^0 = -75.3 K · 8.314 J·mol^{-1}K^{-1} = -626 J·mol^{-1} = -0.626 KJ·mol^{-1}
$\Delta(\Delta H_r^0)$ = ±23.6 K · 8.314 J·mol^{-1}K^{-1} = 196 J·mol^{-1} = ±0.196 KJ·mol^{-1}

ΔS_r^0 = -0.25 · 8.314 J·mol^{-1}K^{-1} = -2.05 J·mol^{-1}K^{-1}
$\Delta(\Delta S_r^0)$ = ±0.10 K · 8.314 J·mol^{-1}K^{-1} = ±0.83 J·mol^{-1}K^{-1}

ΔG_r (20 °C) = -626 J·mol^{-1} - 293 K · -2.05 J·mol^{-1}K^{-1} = -0.03 KJ·mol^{-1}
$\Delta(\Delta G_r$ (20 °C)) = ±(196 J·mol^{-1} - 293 K · 0.92 J·mol^{-1}K^{-1})= ±0.05 KJ·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	$C_{14}H_{16}Bi_1N_1$	$C_{20}H_{28}Bi_1N_1$	$C_{22}H_{32}Bi_1N_1$
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	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a/Å	9.3621(3)	8.075(3)	9.5236(5)
b/Å	9.725(3)	8.710(3)	9.9232(5)
c/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}g/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	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ 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 F^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≥2σ(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	$C_{20}H_{28}Bi_1P_1$	$C_{26}H_{40}Bi_1P_1$	$C_{19}H_{28}Bi_1P_1Si_1$
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	$P2_1/n$	$P2_1/c$	$P\bar{1}$
a/Å	6.3994(3)	17.2923(13)	6.2419(3)
b/Å	18.2817(10)	9.4485(5)	8.9902(4)
c/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}g/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	
Diffractometer	Stoe IPDS 2T	Stoe IPDS 2T	Stoe IPDS 2
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ 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 [R_{int} = 0.0277, R_{sigma} = 0.0158]	12063 [R_{int} = 0.0309, R_{sigma} = 0.0370]	4036 [R_{int} = 0.0246, R_{sigma} = 0.0264]
Data/restraint/parameters	5012/0/205	12063/0/529	4036/0/205
Goodness-of-fit on F^2	1.047	1.012	1.011
Final R indexes [all data]	R_1 = 0.0284, wR_2 = 0.0475	R_1 = 0.0521, wR_2 = 0.0695	R_1 = 0.0267, wR_2 = 0.0523
Final R indexes [I≥2σ(I)]	R_1 = 0.0214, wR_2 = 0.0475	R_1 = 0.0300, wR_2 = 0.0630	R_1 = 0.0215, wR_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	$C_{25}H_{40}Bi_1P_1Si_1$	$C_{20}H_{28}Bi_1As_1$	$C_{26}H_{40}Bi_1As_1$
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	*P*2$_1$/*c*	*P*2$_1$/*n*	*P*2$_1$/*n*
a/Å	10.1342(10)	6.3753(3)	10.010(2)
b/Å	8.4111(10)	18.4967(9)	8.3035(19)
c/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
ρ_{calc}g/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	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ 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/parameters	5563/14/323	3927/0/205	4994/0/265
Goodness-of-fit on F^2	0.993	0.999	1.071
Final R indexes [all data]	R_1 = 0.0265, wR_2 = 0.0499	R_1 = 0.0538, wR_2 = 0.0717	R1 = 0.0284, wR2 = 0.0641
Final R indexes [I≥2σ(I)]	R_1 = 0.0195, wR_2 = 0.0482	R_1 = 0.0325, wR_2 = 0.0671	R1 = 0.0238, wR2 = 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	$C_{19}H_{28}Bi_1As_1Si_1$	$C_{25}H_{40}Bi_1As_1Si_1$	$C_{30}H_{32}Bi_1Sb_1$
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	$P2_1/c$	$P\bar{1}$
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}g/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	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ 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	R1 = 0.0371, wR2 = 0.0668	R1 = 0.0456, wR2 = 0.0762
Final R indexes [I≥2σ(I)]	R_1 = 0.0301, wR_2 = 0.0733	R1 = 0.0282, wR2 = 0.0641	R1 = 0.0318, wR2 = 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