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Ge(II) cation catalyzed hydroboration of aldehydes and ketones

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Experimental section

All experiments and manipulations were carried out in an atmosphere of dry dinitrogen using either standard schlenk or glove box [GP(Concept)-T2, Jacomex] techniques. Solvents were dried using conventional procedures. [(*t*-Bu)$_2$ATI]GeCl (**1**)[S1] and [(*i*-Bu)$_2$ATI]GeCl (**2**)[S2] were prepared according to literature procedures. AgOTf, $NaBH_4$ and LiI were purchased from Sigma-Aldrich, and were used without any further purification. $GaCl_3$ and HBPin were purchased from Alfa Aesar and used without any further purification. All the aldehydes (except solid aldehydes) and ketones were distilled over anhydrous $MgSO_4$ prior to use. Melting points were measured in sealed glass capillaries using Unitech sales digital melting point apparatus, and the reported melting points are uncorrected. Elemental analyses were carried out on a Perkin-Elmer CHN analyzer. ^{1}H, ^{13}C, and ^{19}F spectra were recorded on a 300 MHz / 400 MHz Bruker Topspin NMR spectrometer using dry $CDCl_3$. Chemical shifts (δ) are expressed in ppm. The referencing was done internally with respect to the residual solvent (for ^{1}H NMR) and solvent resonances (for ^{13}C NMR). In the case ^{19}F NMR spectroscopic studies, $CFCl_3$ was used as an external standard.

Synthesis of [(*t*-Bu)$_2$ATIGeOTf] (3). A solution of compound **1** (1.00 g, 2.95 mmol) in dichloromethane (40 mL) was transferred to a suspension of AgOTf (0.76 g, 2.95 mmol) in dichloromethane (30 mL) at -78 ºC. Then, the reaction mixture was brought to room temperature, stirred for 30 min, filtered through a G4 frit, and the filtrate was reduced under reduced pressure to afford compound **3** as a yellow solid. Washing this solid with hexane and drying under reduced pressure afforded an analytically pure sample of compound **3**. Yield: 1.12 g, 84%. Mp: 119 °C. Anal. Calcd for $C_{16}H_{23}F_3GeN_2O_3S$ (M = 453.06): C, 42.42; H, 5.12; N, 6.18 Found: C, 42.67; H, 5.43; N, 5.94. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.83 (s, 18H, C(CH_3)$_3$), 7.16 (t, $^3J_{HH}$ = 8.7 Hz, 1H, C*H*), 7.54-7.67 (m, 4H, C*H*). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 31.30 (C(*C*H$_3$)$_3$), 57.80 (*C*(CH$_3$)$_3$), 121.52 (C_4), 121.88 (*C*F$_3$), 127.65 ($C_{2,6}$), 135.91 ($C_{3,5}$), 160.48 ($C_{1,7}$). ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$): δ -78.06.

Synthesis of [(*i*-Bu)$_2$ATIGeOTf] (4). A dichloromethane solution (40 mL) of compound **2** (1.00 g, 2.95 mmol) was transferred to a suspension of AgOTf (0.76 g, 2.95 mmol) in dichloromethane (30 mL) at -78 ºC. Then, the reaction mixture was brought to room temperature, stirred for 30 minutes, filtered through a G4 frit, and the solvent from the filtrate was removed under reduced pressure to result compound **4** as a yellow solid. Washing with hexane and drying for long time under reduced pressure gave the analytically pure sample of this compound. Single crystals suitable for X-ray diffraction analysis were obtained from its solution in a mixture of dichloromethane and toluene at -40 °C. Yield: 1.21 g, 88%. Mp: 101 °C. Anal. Calcd for $C_{16}H_{23}F_3GeN_2O_3S$ (M = 453.06): C, 42.42; H, 5.12; N, 6.18 Found: C, 42.19; H, 5.23; N, 6.01. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.06 (d, $^3J_{HH}$ = 6.6 Hz, 12H, $CH(CH_3)_2$), 2.19-2.30 (m, 2H, $CH(CH_3)_2$), 3.74 (d, $^3J_{HH}$ = 7.2 Hz, 4H, CH_2), 7.16 (t, $^3J_{HH}$ = 9.6 Hz, 1H, CH), 7.24 (d, $^3J_{HH}$ = 11.4 Hz, 2H, CH), 7.63 (t, $^3J_{HH}$ = 9 Hz, 2H, CH). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 21.06 ($CH(CH_3)_2$), 28.10 ($CH(CH_3)_2$), 54.22 (CH_2), 118.20 (C_4), 121.86 (CF_3), 127.81 ($C_{2,6}$), 137.73 ($C_{3,5}$), 160.55 ($C_{1,7}$). $^{19}F\{^1H\}$ NMR (282 MHz, $CDCl_3$): δ -77.97.

Synthesis of [(*i*-Bu)$_2$ATIGe][GaCl$_4$] (5). A solution of $GaCl_3$ (0.52 g, 2.95 mmol) in dichloromethane (10 mL) was transferred to a solution of compound **2** (1.00 g, 2.95 mmol) in dichloromethane (20 mL) at -78 ºC. Then, the reaction mixture was allowed to stir for 1h at ambient temperature. Removal of solvent under reduced pressure resulted in a yellow solid of compound **5**. Washing with hexane and drying *in vacuo* produced an analytically pure sample of compound **5**. Single crystals suitable for the X-ray diffraction analysis were grown by cooling its solution in dichloromethane and toluene at -40 °C. Yield: 1.43 g, 94%. Mp: 84 °C. Anal. Calcd for $C_{15}H_{23}Cl_4GaGeN_2$ (M = 515.53): C, 34.95; H, 4.50; N, 5.43 Found: C, 34.71; H, 4.64; N, 5.21. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.09 (d, $^3J_{HH}$ = 6.6 Hz, 12H, $CH(CH_3)_2$), 2.21-2.34 (m, 2H, $CH(CH_3)_2$), 3.98 (d, $^3J_{HH}$ = 7.2 Hz, 4H, CH_2), 7.61-7.71 (m, 3H, CH), 7.96-8.03 (m, 2H, CH). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 21.24 ($CH(CH_3)_2$), 28.39 ($CH(CH_3)_2$), 55.16 (CH_2), 121.52 (C_4), 133.28 ($C_{2,6}$), 138.39 ($C_{3,5}$), 159.45 ($C_{1,7}$).

Synthesis of [(*t*-Bu)$_2$ATIGeI] (6). Compound **3** (1.00 g, 2.21 mmol) and lithium iodide (0.89 g, 6.62 mmol) were mixed in dichloromethane (40 mL) at room temperature. The resulting mixture was stirred for 2 days, filtered through a G4 frit, and the solvent from the filtrate was removed *in vacuo* to yield compound **6** as a yellow solid. Washing with hexane and drying under reduced pressure gave an analytically pure sample of this compound. Single crystals suitable for X-ray diffraction analysis were grown from its solution in dichloromethane and toluene at -40 °C. Yield: 0.87 g, 92%. Mp: 137 °C. Anal. Calcd for $C_{15}H_{23}GeIN_2$ (M = 430.90): C, 41.81; H, 5.38; N, 6.50 Found: C, 42.05; H, 5.47; N, 6.39. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.83 (s, 18H, $C(CH_3)_3$), 6.93 (t, $^3J_{HH}$ = 9.0 Hz, 1H, CH), 7.30-7.43

(m, 4H, C*H*). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 30.11 ($C(CH_3)_3$), 57.82 ($C(CH_3)_3$), 121.22 (C_4), 125.03 ($C_{2,6}$), 135.51 ($C_{3,5}$), 161.18 ($C_{1,7}$).

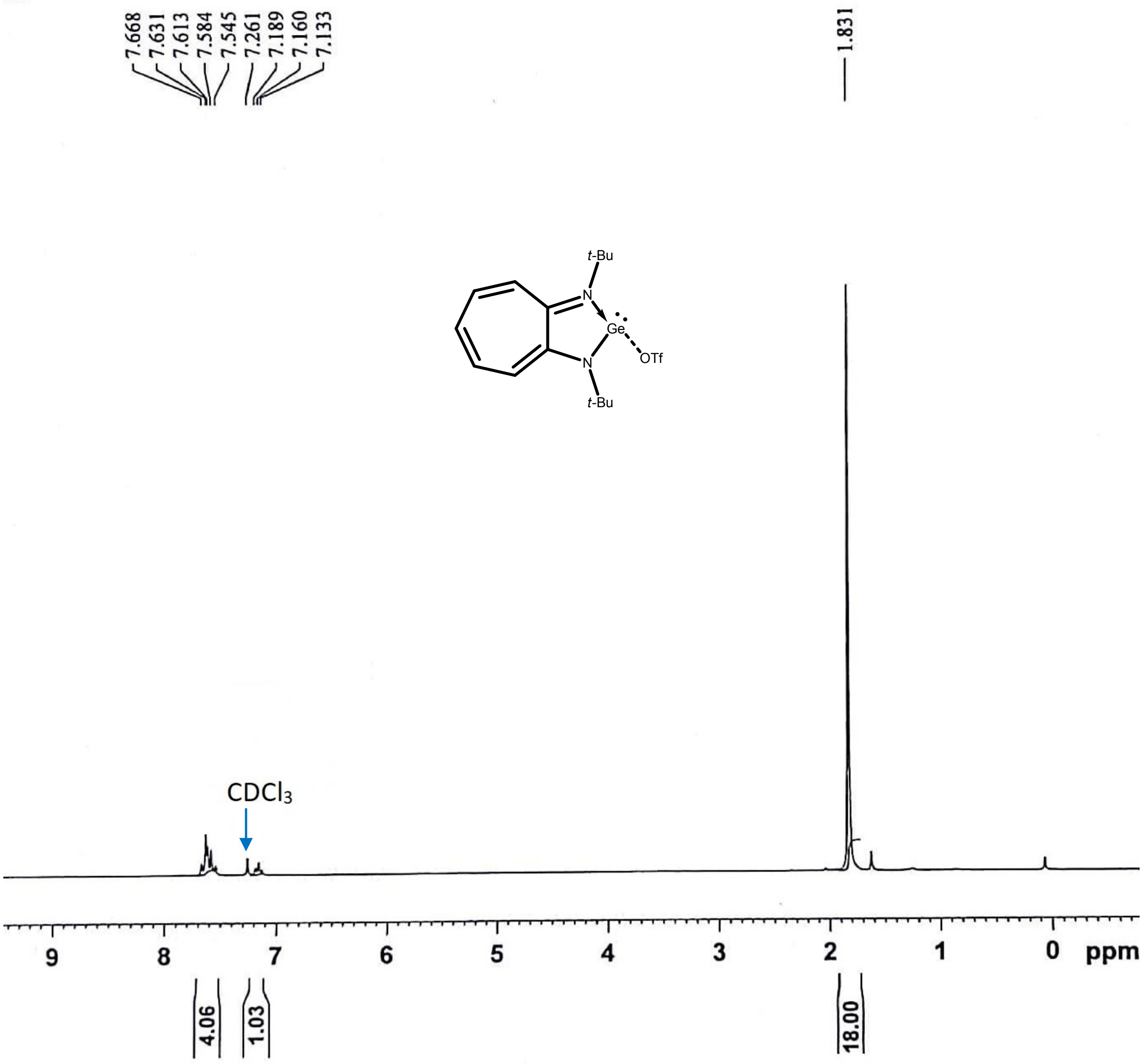
Synthesis of [(*i*-Bu)$_2$ATIGeI] (7). To compound **4** (1.00 g, 2.21 mmol) and lithium iodide (0.89 g, 6.62 mmol) in a Schlenk flask, dichloromethane (20 mL) was added at room temperature. The resulting mixture was stirred for 2 days, and the solvent was removed under reduced pressure to yield an orange solid. This solid was extracted using toluene (60 mL) and filtered through a G4 frit. Removal of solvent from the filtrate afforded compound **7** as a yellow solid. Washing using hexane and drying through a vacuum pump afforded an analytically pure sample of compound **7**. Single crystals suitable for X-ray diffraction analysis were grown from its toluene solution at -40 °C. Yield: 0.84 g, 90%. Mp: 125 °C. Anal. Calcd for $C_{15}H_{23}GeIN_2$ (M = 430.90): C, 41.81; H, 5.38; N, 6.50 Found: C, 41.98; H, 5.26; N, 6.28. ^1H NMR (300 MHz, $CDCl_3$): δ 1.05 (d, $^3J_{HH}$ = 6.6 Hz, 12H, $CH(CH_3)_2$), 2.19-2.32 (m, 2H, $CH(CH_3)_2$), 3.55 (d, $^3J_{HH}$ = 7.2 Hz, 4H, CH_2), 6.88-6.99 (m, 3H, C*H*), 7.35 (t, $^3J_{HH}$ = 9 Hz, 2H, C*H*). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 21.22 ($CH(CH_3)_2$), 28.02 ($CH(CH_3)_2$), 54.50 (CH_2), 117.65 (C_4), 124.89 ($C_{2,6}$), 137.27 ($C_{3,5}$), 161.47 ($C_{1,7}$).

Synthesis of [(*t*-Bu)$_2$ATIGe(H)BH$_3$] (11). To a solution of compound **1** (0.40 g, 1.17 mmol) in THF (25 ml), $NaBH_4$ (0.05 g, 1.28 mmol) was added and stirred for 24 h at room temperature. After that, THF was removed under reduced pressure to get a red solid. It was extracted into toluene and filtered through a G4 frit with Celite. Removal of toluene from the filtrate afforded compound **11** as a red solid. Washing it using hexane and drying through a vacuum pump afforded an analytically pure sample of compound **11**. Single crystals suitable for X-ray diffraction analysis were grown from its toluene solution at -40 °C. Yield: 0.371 g, 99%. ^1H NMR (500 MHz, C_6D_6): δ 1.38 (s, 18H, $C(CH_3)_3$), 6.00-6.03 (m, 1H, C*H*), 6.44-6.47 (m, 4H, C*H*) 7.72 (bs, 1H, Ge*H*). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6): δ 28.70 ($C(CH_3)_3$), 56.91 ($C(CH_3)_3$), 118.23 (C_4), 121.11 ($C_{2,6}$), 136.58 ($C_{3,5}$), 160.32 ($C_{1,7}$). $^{11}B\{^1H\}$ (128 MHz, C_6H_6): δ -31.01 (s, BH_3).

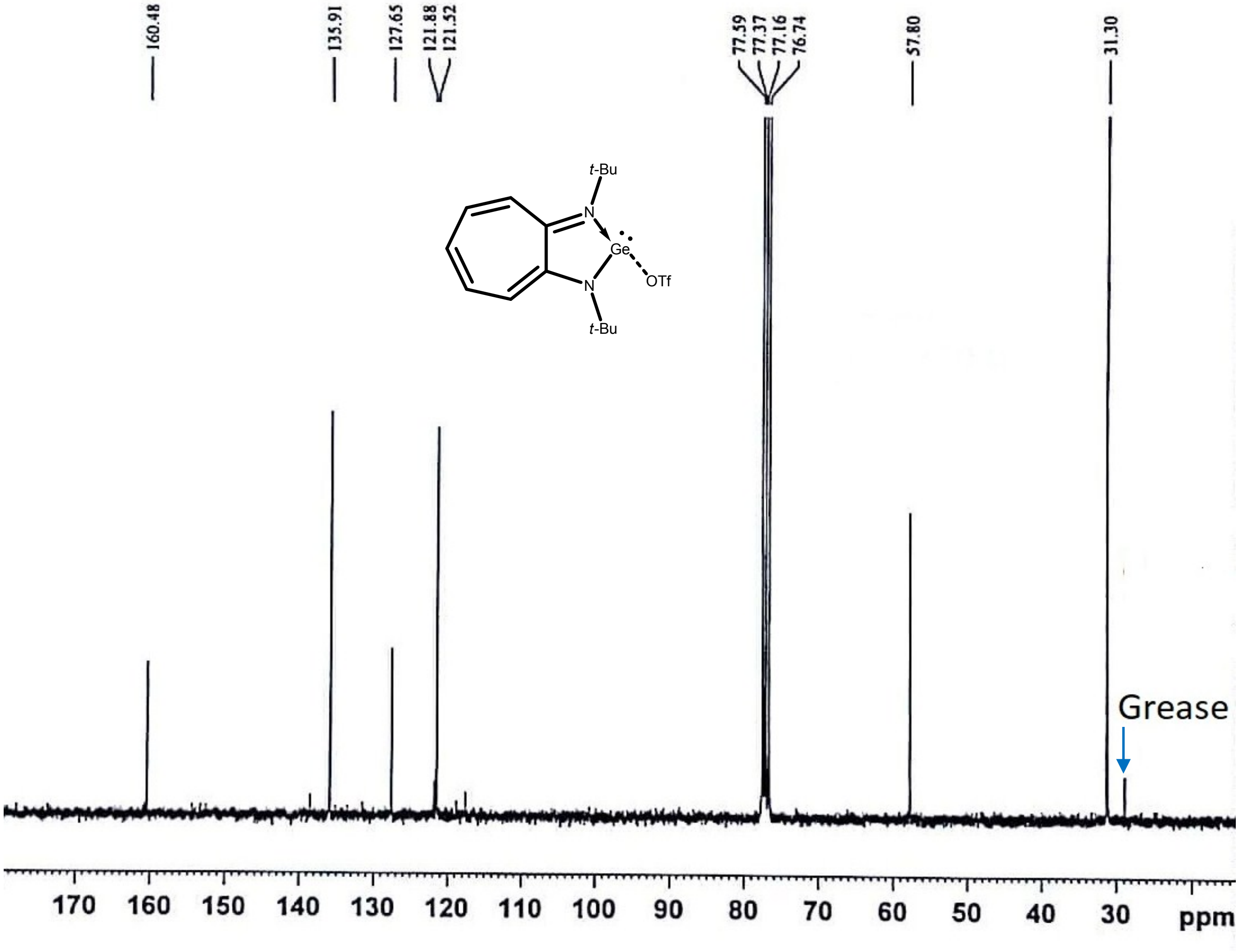
General procedure for the catalytic hydroboration of carbonyl compounds: Aldehydes/ketones (1 mmol), pinacolborane (1.1 mmol), and [(*i*-Bu)$_2$ATI]GeOTf (**4**) (1 mol% - 5 mol%) (for details, see Table 2) were taken in a Schlenk flask. This reaction mixture was stirred at room temperature/elevated temperature for the required time period (for details, see Table 2). Progress of the reactions was monitored by ^1H NMR spectroscopy (for details, see the footnote of Table 1).

NMR spectra of compounds 3-7

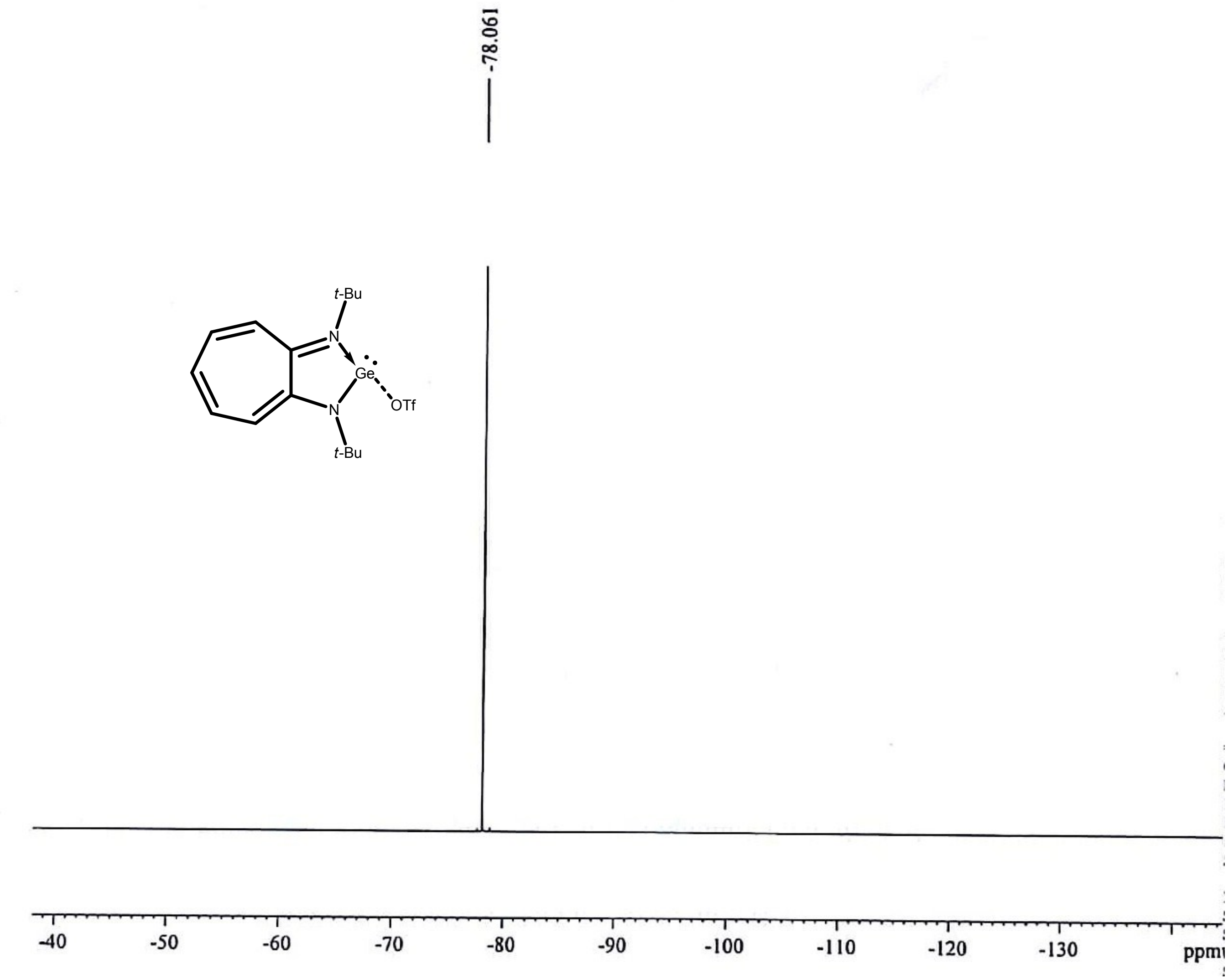
^{1}H NMR spectrum of compound **3**



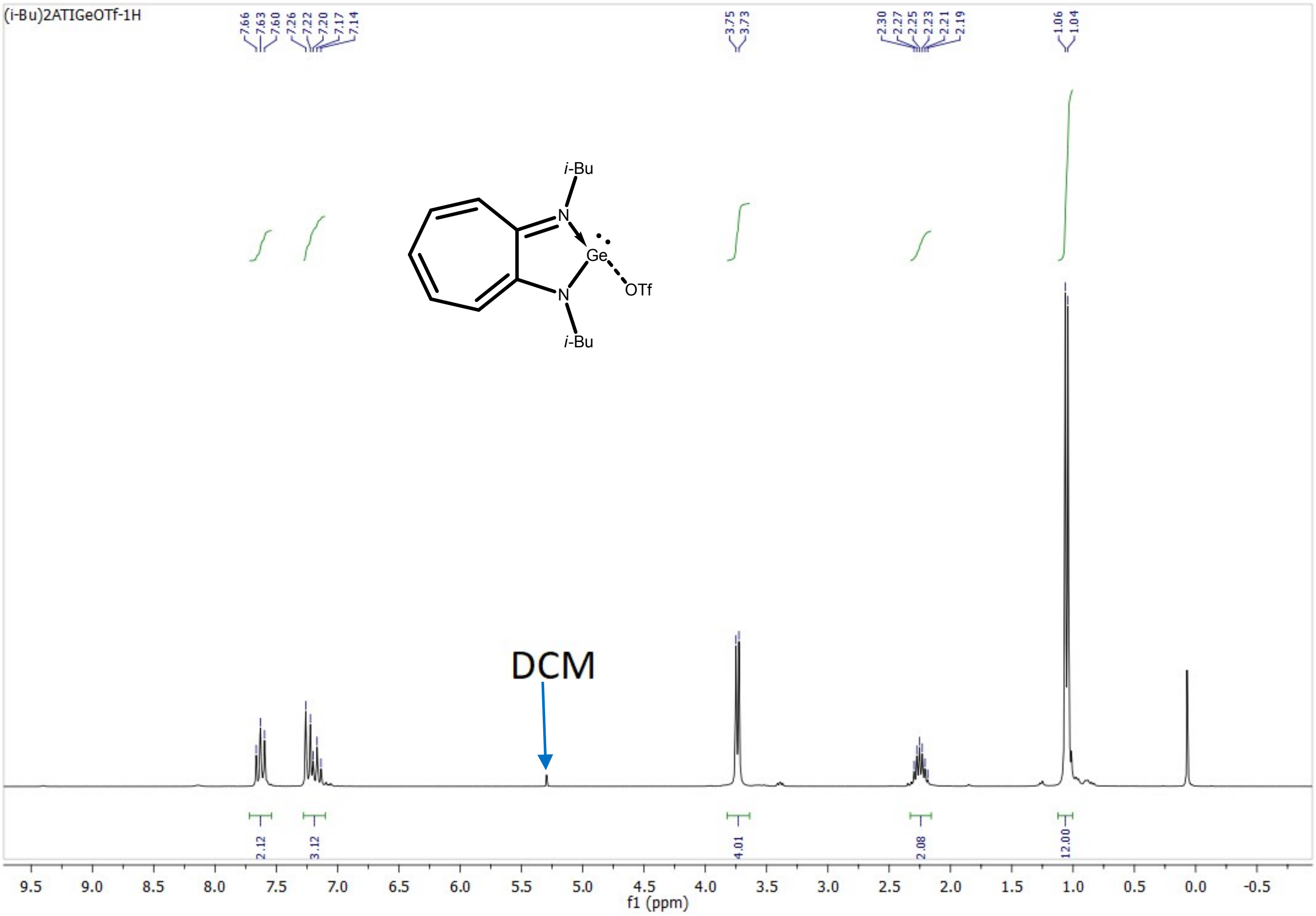
^{13}C NMR spectrum of compound **3**



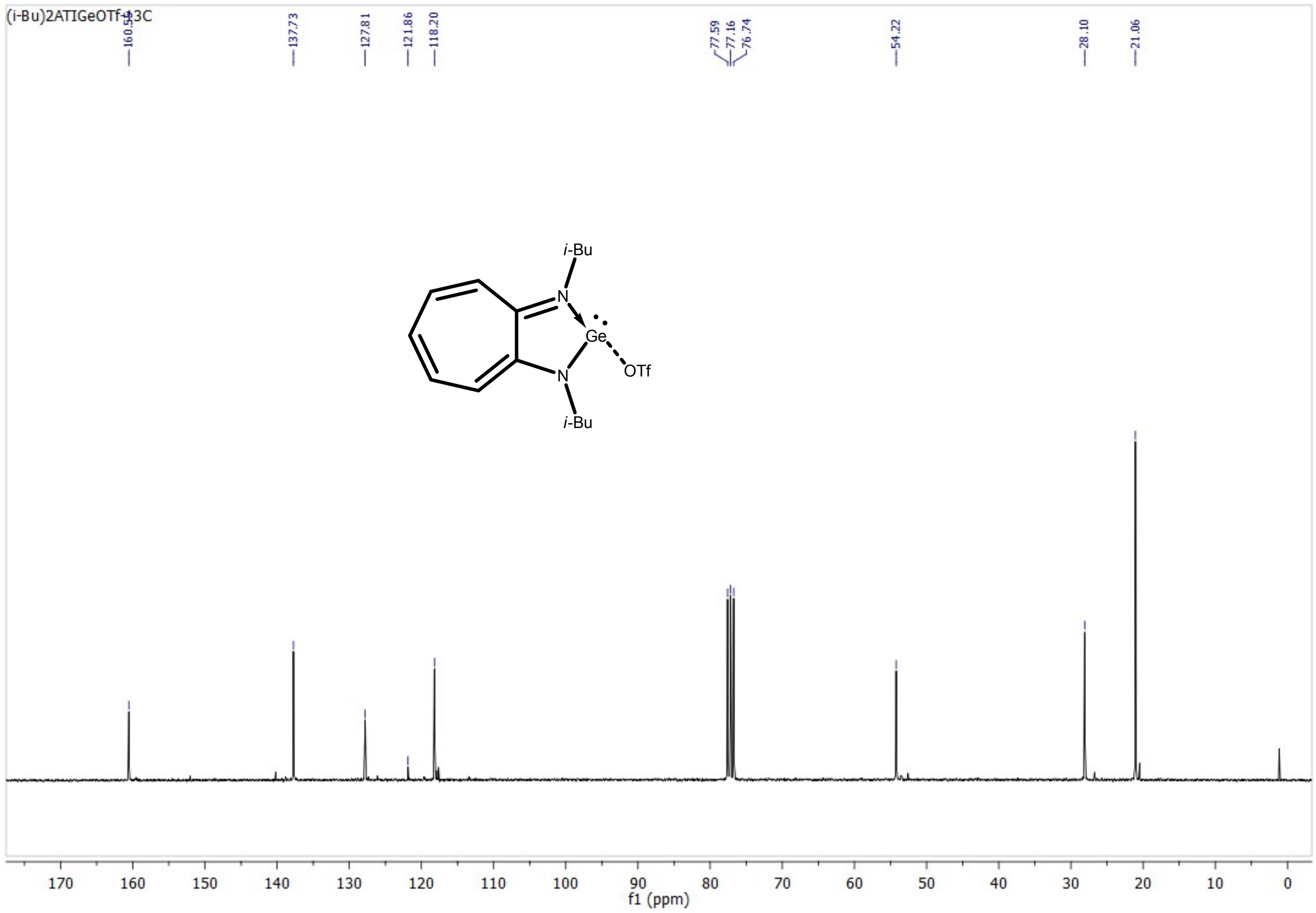
^{19}F NMR spectrum of compound **3**



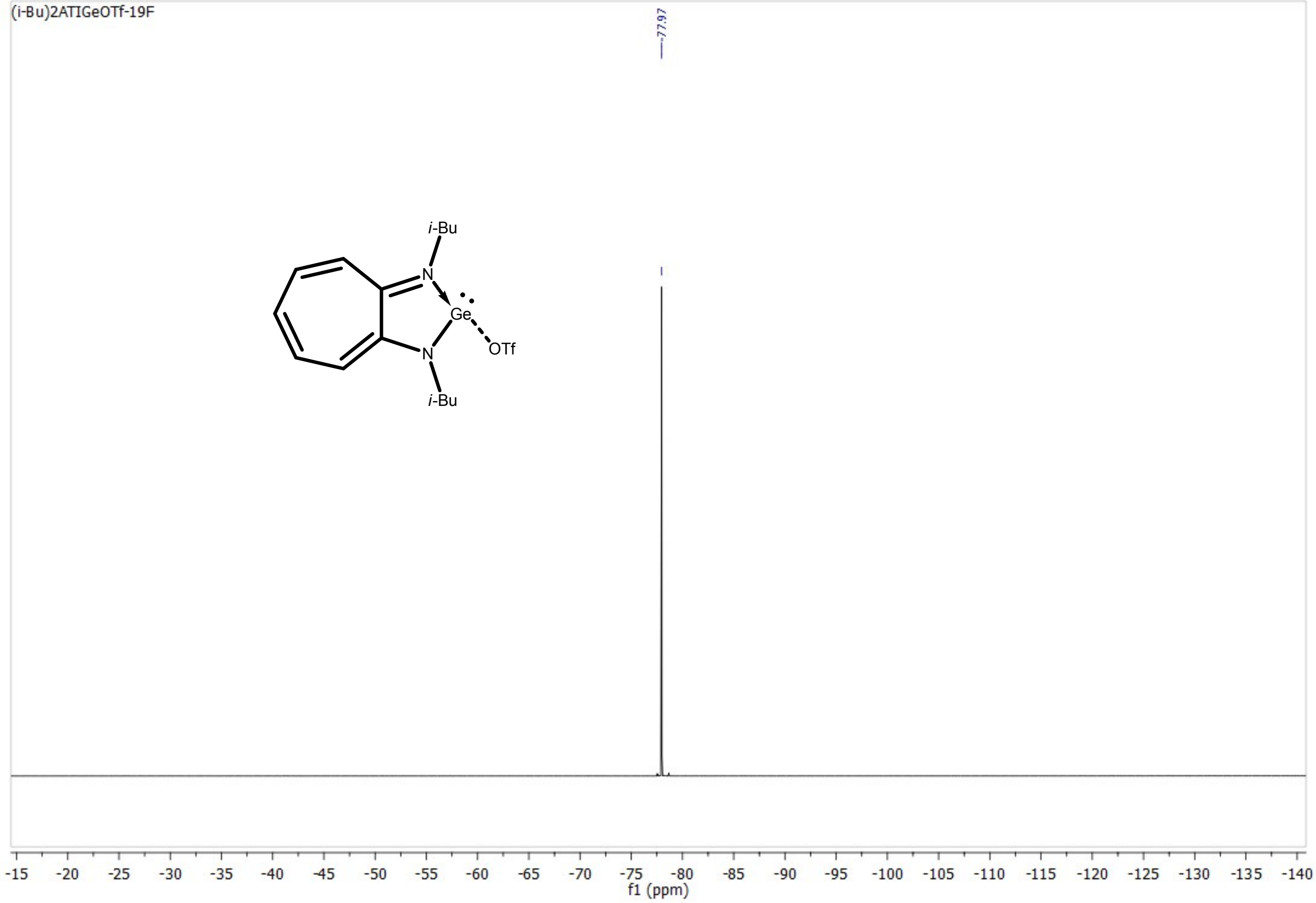
^{1}H NMR spectrum of compound **4**



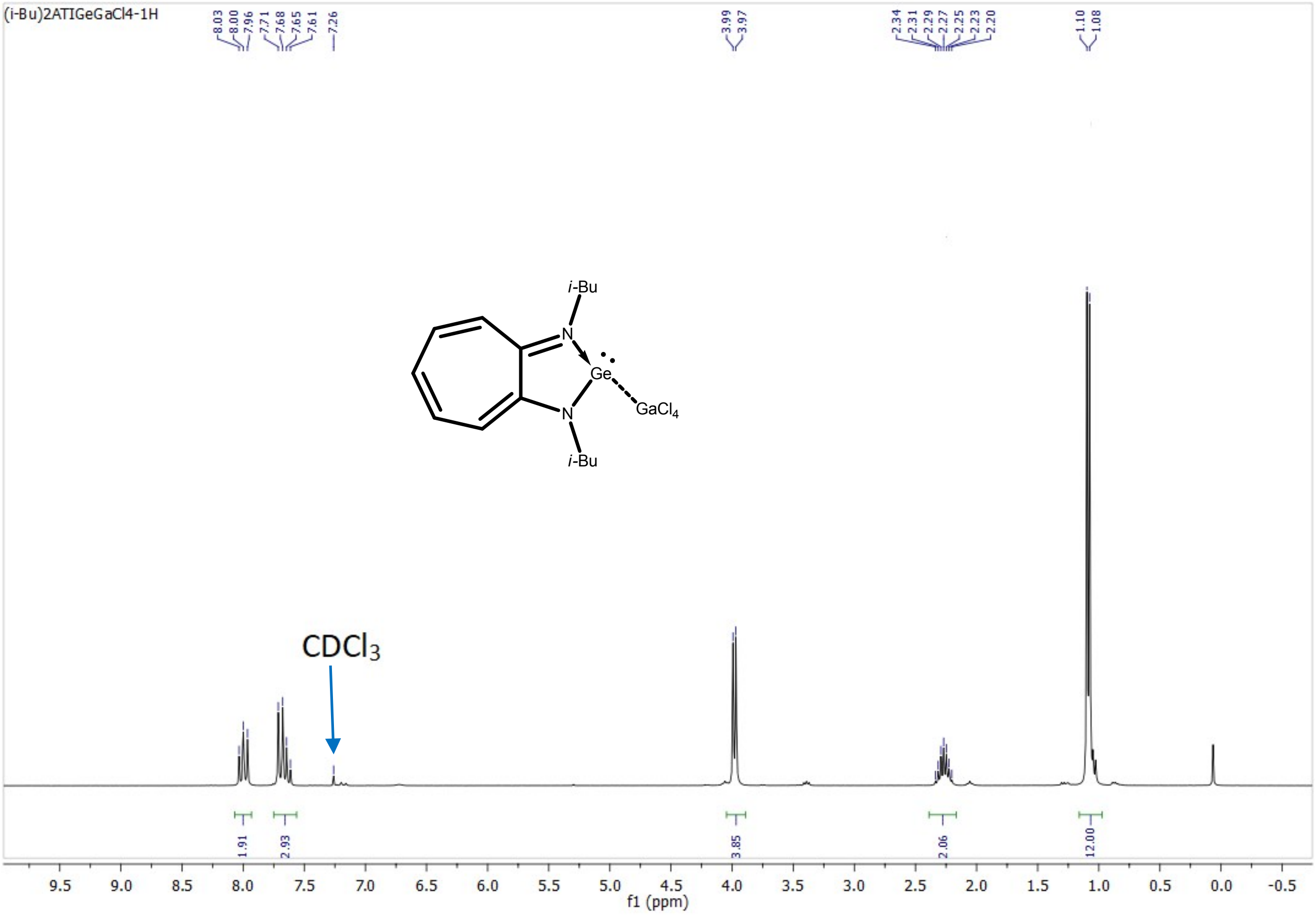
^{13}C NMR spectrum of compound **4**



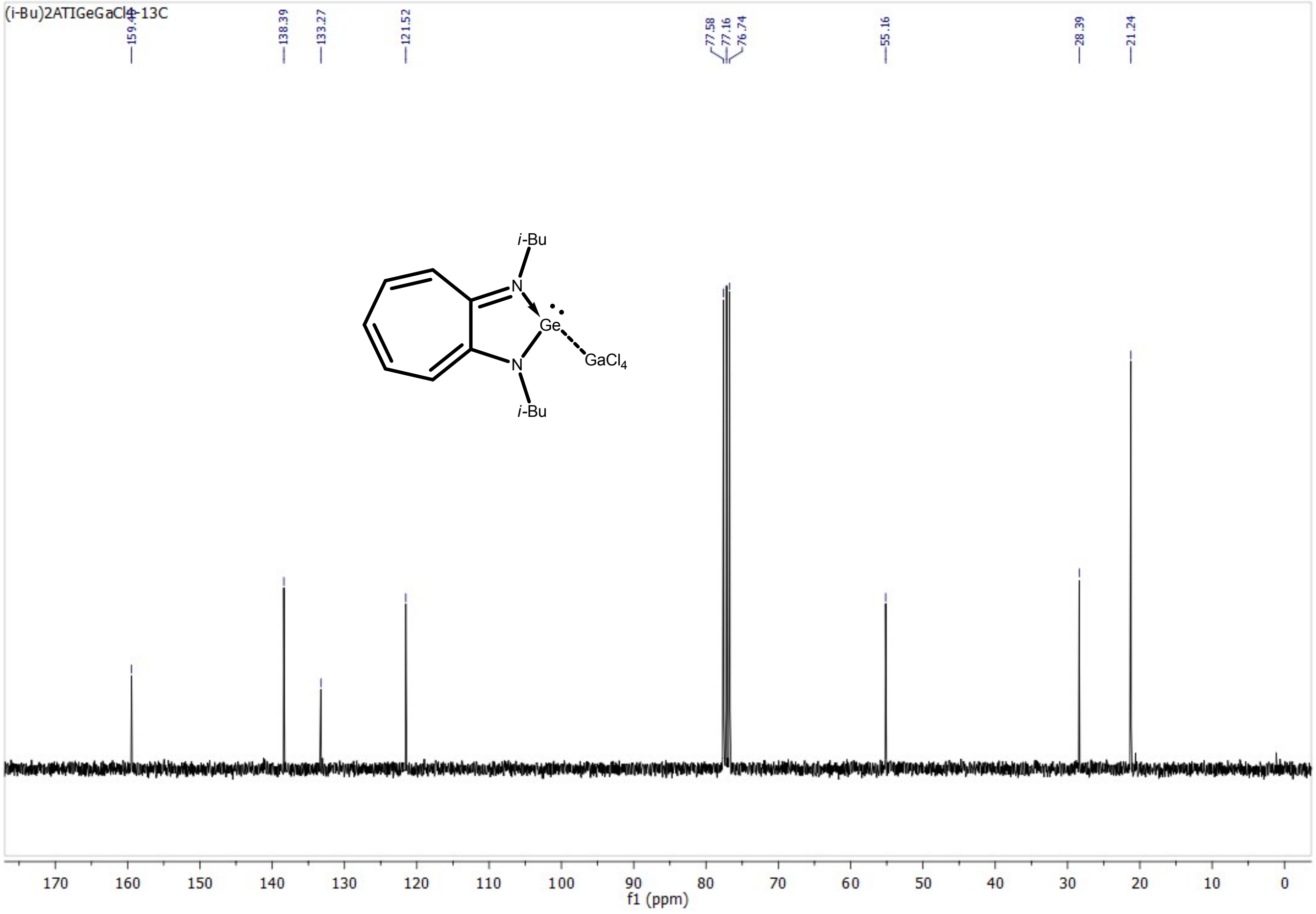
^{19}F NMR spectrum of compound **4**



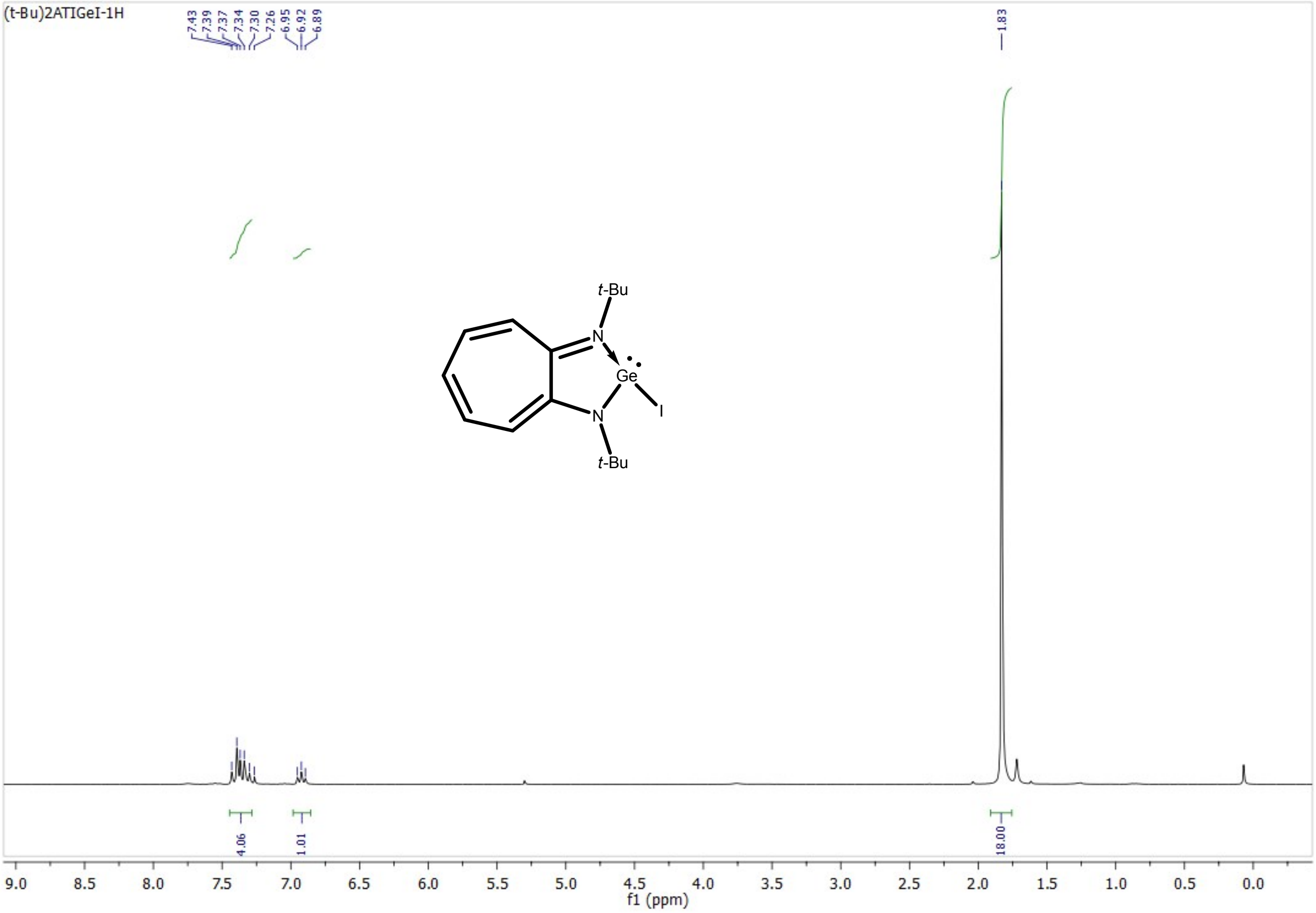
^{1}H NMR spectrum of compound **5**



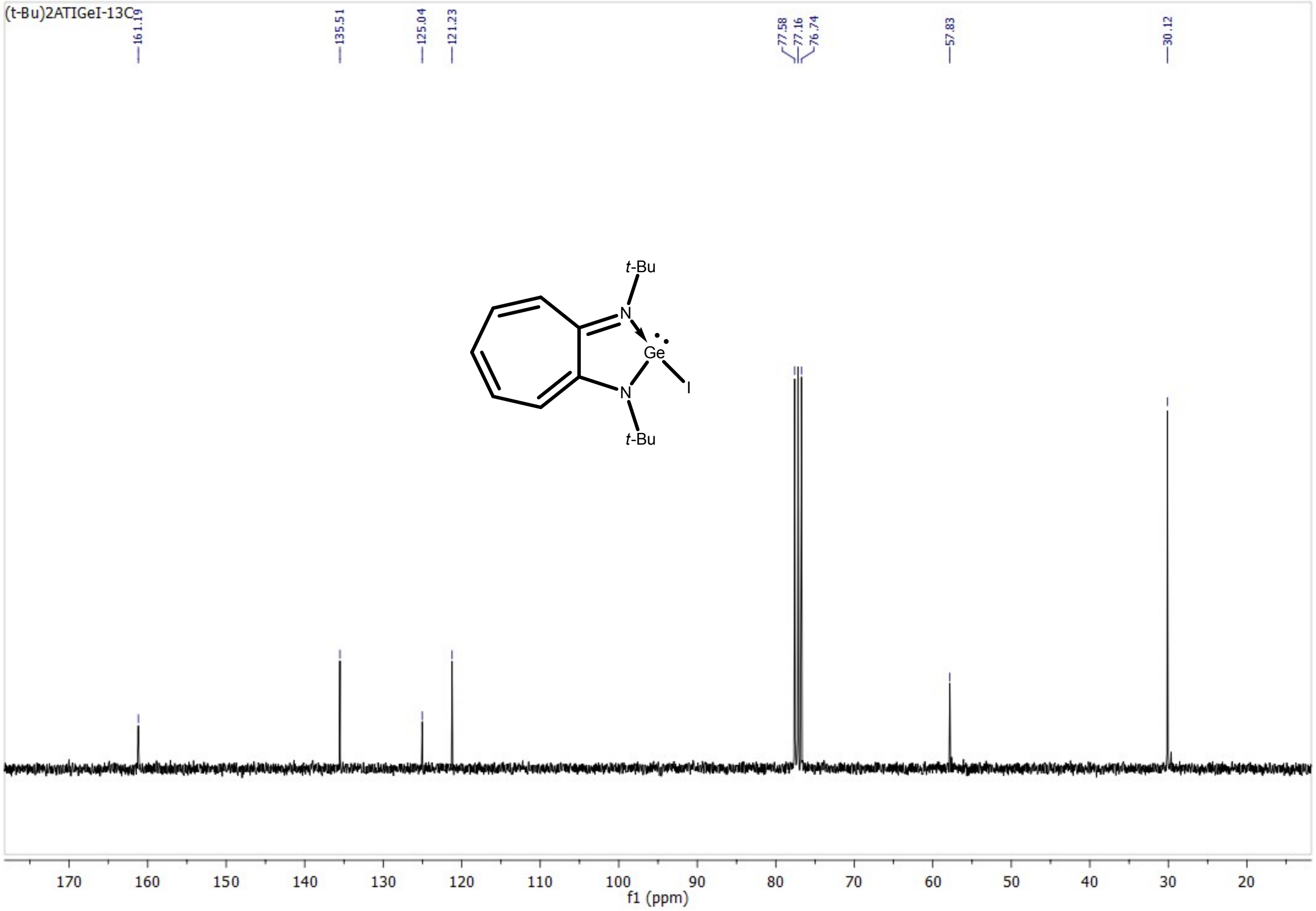
^{13}C NMR spectrum of compound **5**



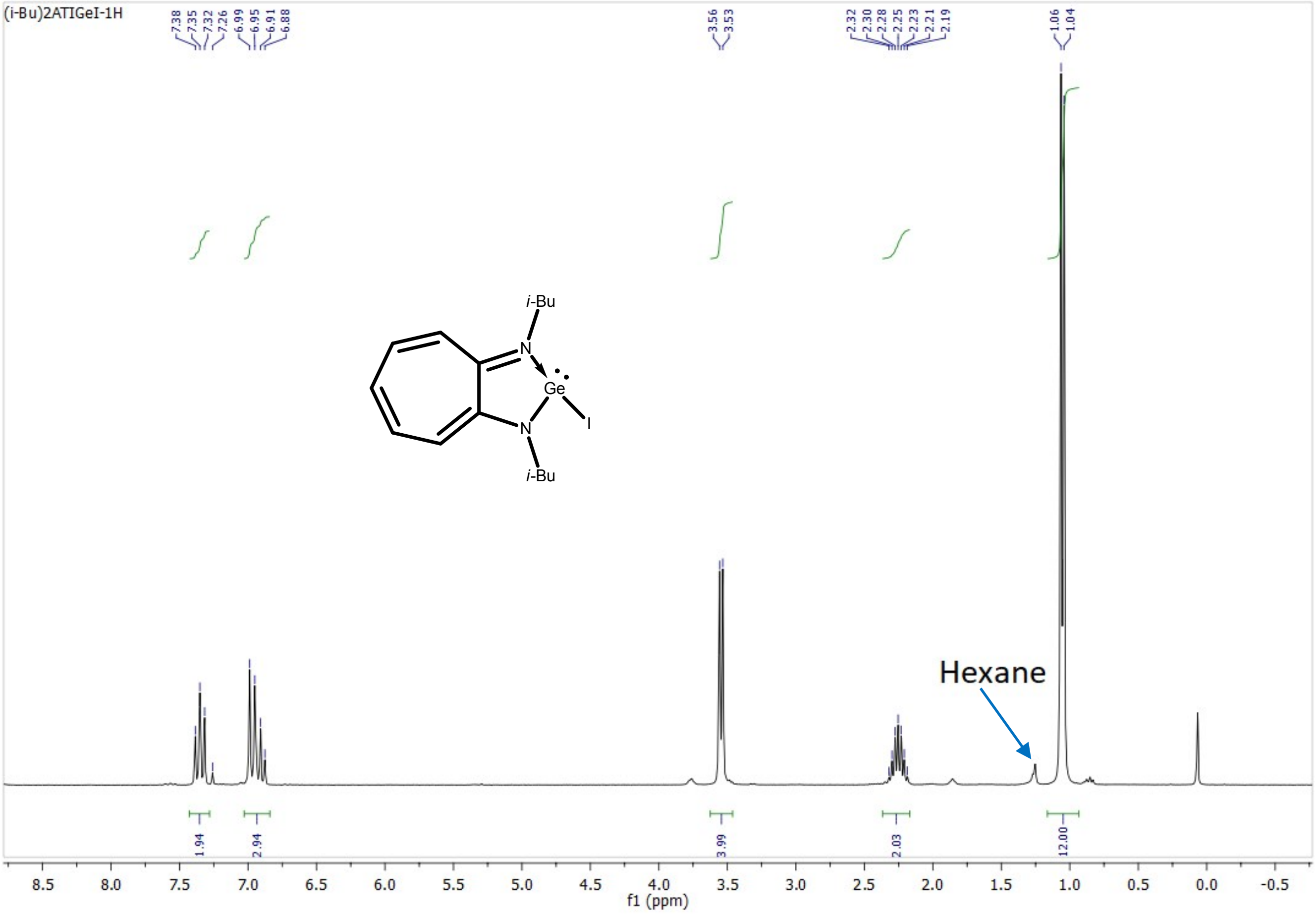
^{1}H NMR spectrum of compound **6**



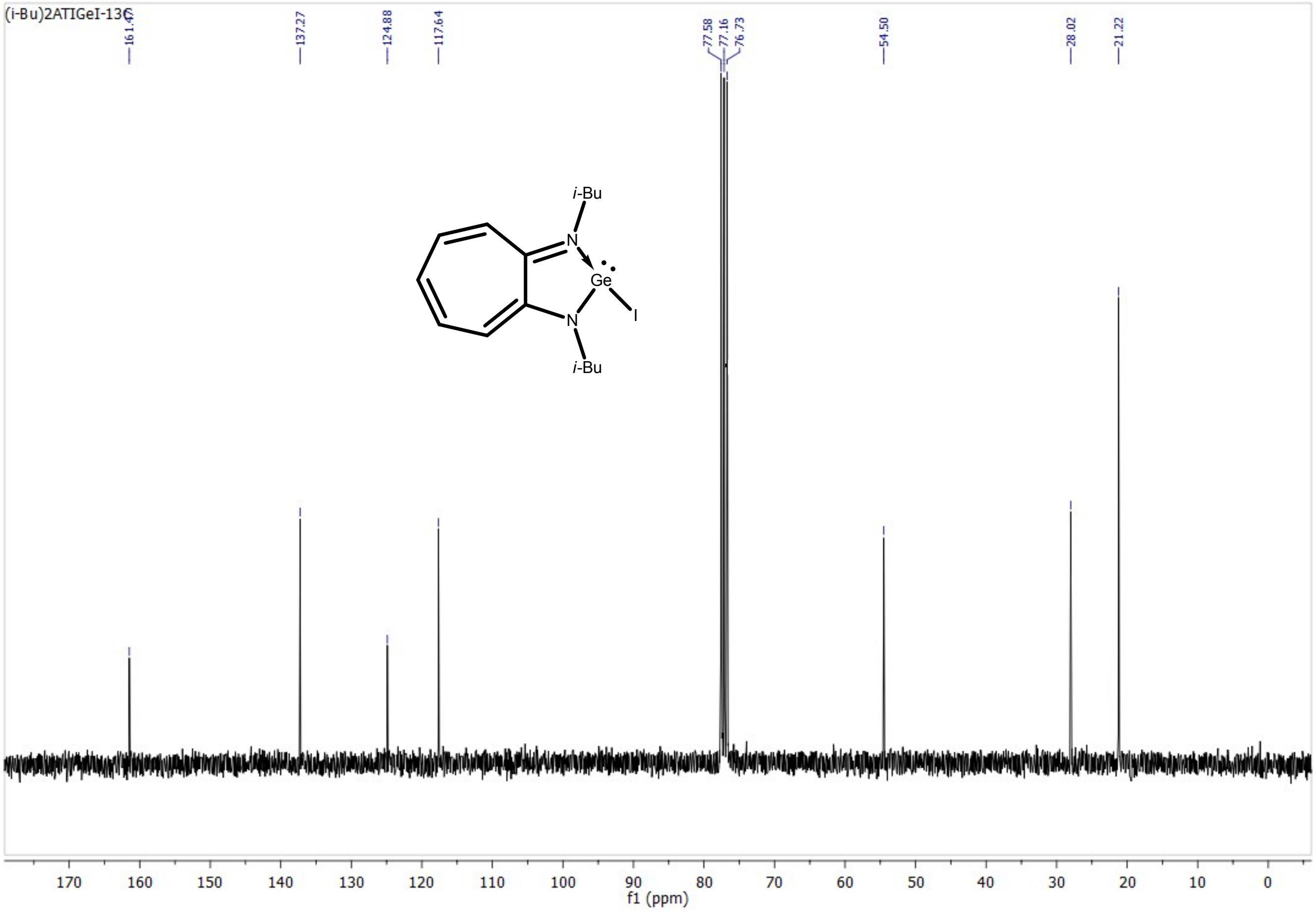
^{13}C NMR spectrum of compound **6**



^{1}H NMR spectrum of compound **7**



^{13}C NMR spectrum of compound **7**



Computational details

GAUSSIAN-09 programs were used for carrying out the computational studies on compound **4**.[S5-S6] The B3LYP level of theory was used for geometry optimization; (a) for germanium atom, LANL2DZ basis set with ECP core potential was used, and (b) 6-31+G* basis set was employed for the rest of the elements. Further, for the geometry optimization, coordinates obtained from single crystal X-ray diffraction studies were used. The optimized structure of compound **4** is shown in Figure S4; it was drawn through Chemcraft software using the optimized coordinates. The aforementioned level of theory and optimized coordinates were used for calculating the NPA[S7] charges.

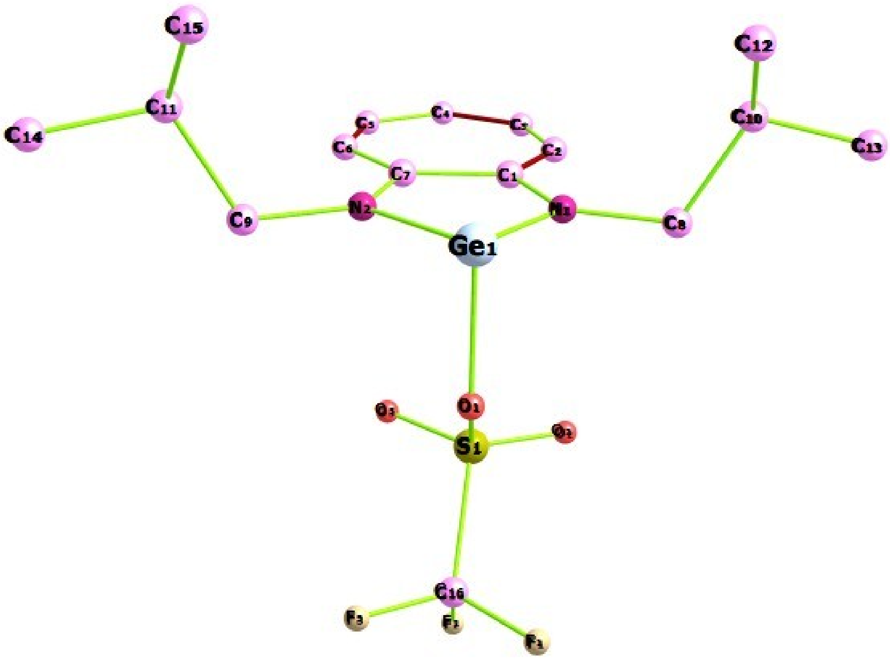


Figure S4: Optimized structure of compound 4. Hydrogen atoms are omitted for clarity.

Coordinates for the optimized geometry of compound 4

32	0.000645000	-0.001577000	-1.534785000
8	1.744075000	-0.094276000	-0.765609000
8	1.923365000	-1.625511000	1.215408000
8	1.720203000	0.873986000	1.552344000
7	-0.875928000	-1.236600000	-0.191374000
7	-0.739091000	1.324860000	-0.193639000
16	2.181074000	-0.263280000	0.755869000
6	-1.609237000	-0.660457000	0.752450000
6	-2.358512000	-1.447973000	1.684930000
1	-2.281781000	-2.515940000	1.525516000
6	-3.146023000	-1.086674000	2.763117000
1	-3.591167000	-1.917632000	3.304135000
6	-3.447015000	0.190481000	3.261340000
1	-4.097871000	0.226042000	4.130532000
6	-2.994039000	1.425949000	2.774013000
1	-3.334543000	2.299872000	3.323226000
6	-2.171800000	1.698387000	1.695438000
1	-1.968334000	2.750742000	1.543253000
6	-1.525705000	0.834441000	0.753771000
6	-0.741245000	-2.692636000	-0.377720000
1	-0.565584000	-3.154766000	0.598087000
1	0.178012000	-2.844692000	-0.952946000
6	-0.426339000	2.752037000	-0.372325000

1	0.497469000	2.792448000	-0.960002000
1	-0.186483000	3.183664000	0.604109000
6	-1.919685000	-3.382436000	-1.113049000
1	-2.838173000	-3.193846000	-0.539761000
6	-1.515155000	3.589703000	-1.092969000
1	-2.435221000	3.539999000	-0.494088000
6	-2.128545000	-2.843772000	-2.534773000
1	-2.390244000	-1.780012000	-2.547709000
1	-2.945633000	-3.380983000	-3.025674000
1	-1.229774000	-2.983034000	-3.147777000
6	-1.660697000	-4.897625000	-1.122699000
1	-0.751275000	-5.139798000	-1.684667000
1	-2.493403000	-5.422714000	-1.599711000
1	-1.547136000	-5.300057000	-0.110289000
6	-1.048308000	5.053238000	-1.137978000
1	-0.845831000	5.450226000	-0.137350000
1	-1.815571000	5.682728000	-1.598168000
1	-0.134034000	5.157481000	-1.733558000
6	-1.835027000	3.061297000	-2.497646000
1	-2.579525000	3.701161000	-2.980696000
1	-2.245781000	2.045767000	-2.479653000
1	-0.942377000	3.058349000	-3.135133000
6	4.041922000	-0.078178000	0.501027000
9	4.480667000	-1.034280000	-0.315027000

9	4.631628000	-0.190014000	1.690065000
9	4.303582000	1.120052000	-0.022380000

X-ray crystal structure determination of compounds 4-7 and 11

X-ray data of these compounds were collected on a Bruker SMART APEX CCD diffractometer using Mo Kα radiation (λ = 0.71073 Å). The crystals were covered with Paratone-N and loaded on a glass fiber. The data were collected under a steady flow of cold dinitrogen or at room temperature. SAINT was used for the integration of data and SADABS was used for applying an empirical absorption correction.[S3] The structures were solved by direct methods and refined by full matrix least-squares on F^2 using SHELXTL.[S4] All non-hydrogen atoms were refined anisotropically; the positions of hydrogen atoms were fixed according to a riding model and were refined isotropically. The important crystallographic data for compounds **4-7** and **11** are given in Tables S1 and S2, respectively.

Table S1. Crystal data and structure refinement parameters for compounds 4-7

	4	**5**	**6**	**7**
Empirical formula	$C_{16}H_{23}F_3GeN_2O_3S$	$C_{15}H_{23}Cl_4GaGeN_2$	$C_{15}H_{23}GeIN_2$	$C_{15}H_{23}GeIN_2$
Formula weight	453.04	515.48	430.86	430.86
Temperature, K	200(2)	100(2)	298(2)	175(2)
Wavelength, Å	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P2_1/c$
Unit cell dimensions	a = 15.057(3) Å b = 16.433(3) Å c = 16.648(3) Å β = 93.621(4)°	a = 10.6849(16) Å b = 19.510(3) Å c = 10.8848(16) Å β = 109.004(3)°	a = 8.7656(7) Å b = 17.3579(15) Å c = 11.8312(10) Å β = 107.5640(10)°	a = 13.175(3) Å b = 16.047(4) Å c = 8.182(2) Å β = 90.806(5)°
Volume, Å^3	4111.0(13)	2145.4(6)	1716.2(2)	1729.7(7)
Z	8	4	4	4
Density (calculated), Mg/m^3	1.464	1.596	1.668	1.655
Absorption coefficient, mm^{-1}	1.635	3.154	3.574	3.547
F(000)	1856.0	1032.0	848.0	848.0
Crystal size, mm^3	0.543 x 0.281 x 0.124	0.486 x 0.273 x 0.152	0.532 x 0.321 x 0.283	0.431 x 0.291 x 0.211
θ range for data collection, °	1.36 to 25.00	2.09 to 25.00	2.56 to 25.00	1.55 to 25.00

Limiting indices	-17 ≤ h ≤ 16, -19 ≤ k ≤ 18, -19 ≤ l ≤ 13	-11 ≤ h ≤ 12, -20 ≤ k ≤ 23, -12 ≤ l ≤ 10	-10 ≤ h ≤ 10, -20 ≤ k ≤ 17, -13 ≤ l ≤ 14	-15 ≤ h ≤ 14, -19 ≤ k ≤ 14, -9 ≤ l ≤ 9
Reflections collected	21356	11126	8839	8911
Independent reflections	7243 [R_{int} = 0.0552]	3779 [R_{int} = 0.0308]	3022 [R_{int} = 0.0205]	3053 [R_{int} = 0.0437]
Absorption correction	Semi-empirical	Semi-empirical	Semi-empirical	Semi-empirical
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/ parameters	7233/0/477	3769/0/212	3015/0/178	3050/0/176
Goodness-of-fit on F^2	1.031	1.046	1.104	1.164
Final R indices [I>2σ(I)]	R_1 = 0.0446, wR^2 = 0.1013	R_1 = 0.0324, wR^2 = 0.0774	R_1 = 0.0422, wR^2 = 0.1226	R_1 = 0.0560, wR^2 = 0.1123
R indices (all data)	R_1 = 0.0714, wR_2 = 0.1103	R_1 = 0.0389, wR_2 = 0.0801	R_1 = 0.0506, wR_2 = 0.1350	R_1 = 0.0666, wR_2 = 0.1165
Largest diff. peak and hole, e.Å^{-3}	0.374 and -0.310	0.506 and -0.293	1.547 and -0.566	1.158 and -0.842

Table S2. Crystal data and structure refinement parameters for compound 11

	11
Empirical formula	$C_{15}H_{26}BGeN_2$
Formula weight	317.80
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	a = 9.538(4) Å b = 10.012(4) Å c = 17.299(7) Å
Volume	1652.0(11) Å^3
Z	4
Density (calculated)	1.278 Mg/m^3
Absorption coefficient	1.844 mm^{-1}
F(000)	668
Crystal size	0.562 x 0.31 x 0.16 mm^3
Theta range for data collection	2.350 to 24.992°
Index ranges	$-6 \le h \le 11$, $-11 \le k \le 11$, $-20 \le l \le 19$
Reflections collected	7791
Independent reflections	2893 [R(int) = 0.0439]

Completeness to theta = 24.992°	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.745 and 0.509
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2893 / 0 / 179
Goodness-of-fit on F^2	1.036
Final R indices [I>2sigma(I)]	R1 = 0.0298, wR2 = 0.0698
R indices (all data)	R1 = 0.0321, wR2 = 0.0707
Largest diff. peak and hole	0.552 and -0.222 e.Å^{-3}

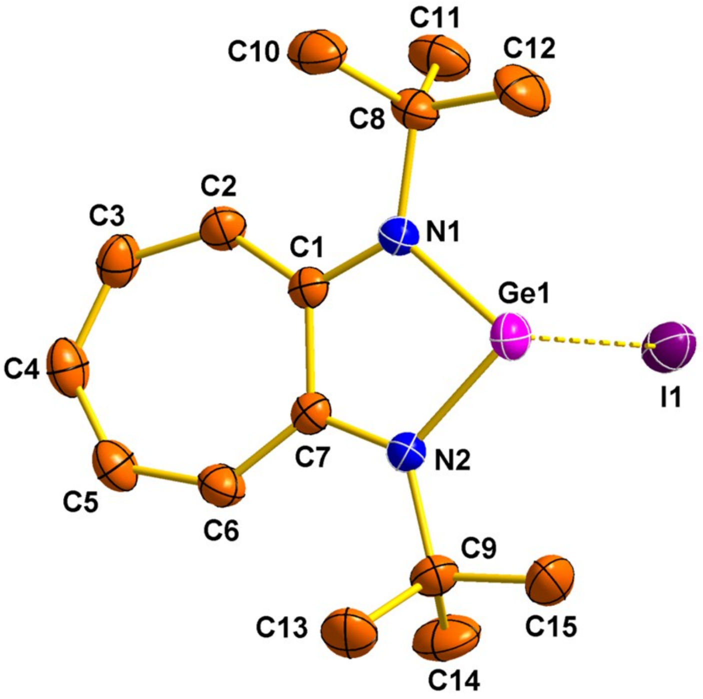


Figure S1: Molecular structure of compound 6. Thermal ellipsoids are shown at the 30% probability level and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge1···I1 3.154(7), Ge1-N1 1.936(4), Ge1-N2 1.937(4); N1-Ge1-N2 82.10(2), N1-Ge1-I1 95.20(1), N2-Ge1-I1 94.11(1), C1-N1-Ge1 115.40(3), C7-N2-Ge1 115.50(3).

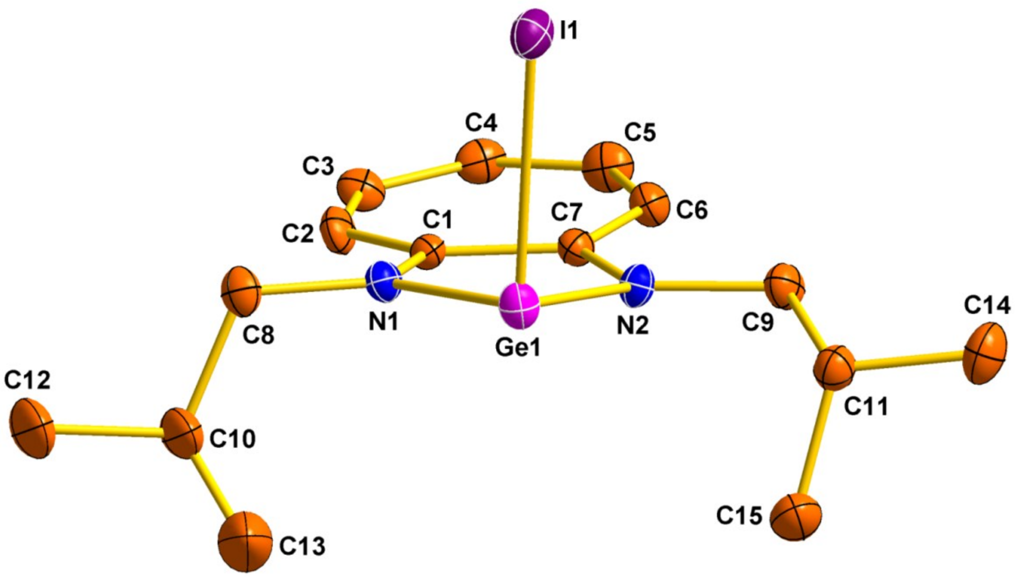


Figure S2: Molecular structure of compound 7. Thermal ellipsoids are shown at the 30% probability level and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ge1-I1 2.795(1), Ge1-N1 1.939(5), Ge1-N2 1.948(5); N1-Ge1-N2 80.70(2), N1-Ge1-I1 96.97(2), N2-Ge1-I1 96.20(2), C1-N1-Ge1 117.10(4), C7-N2-Ge1 115.90(4).

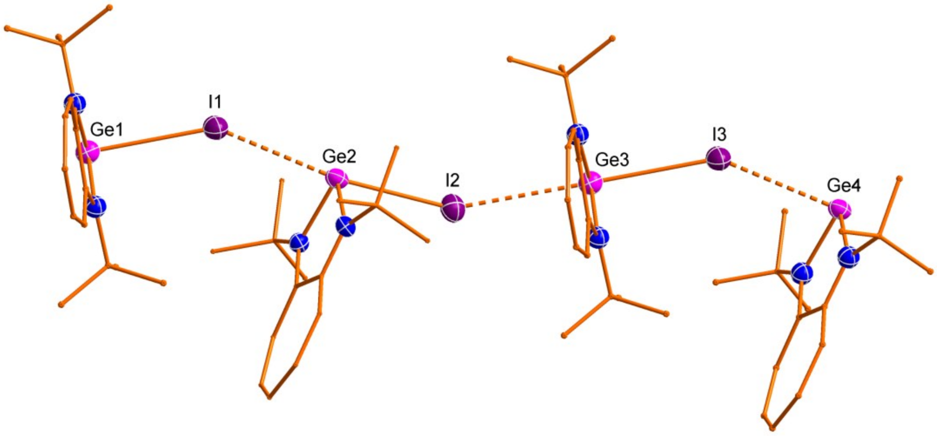
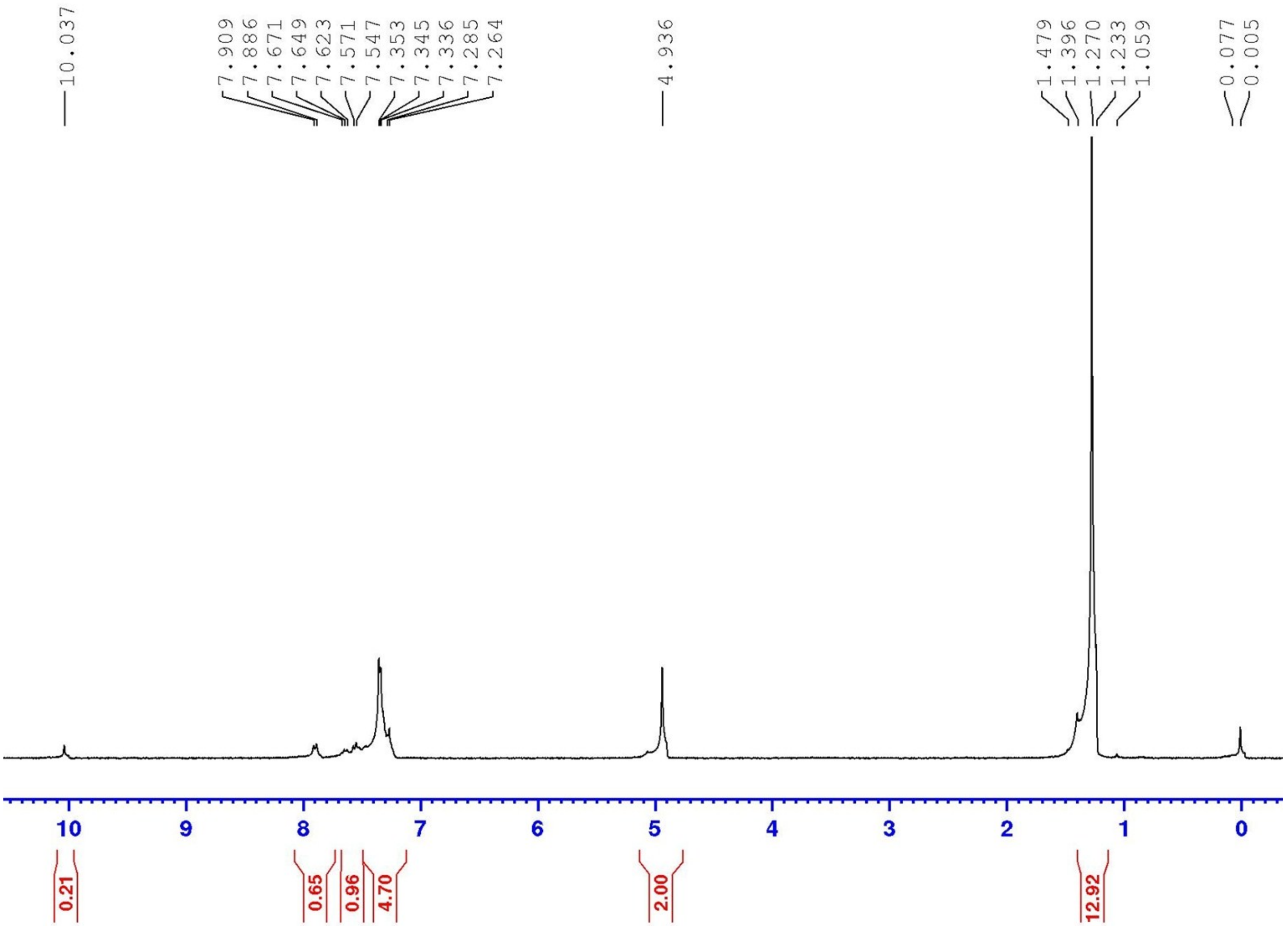


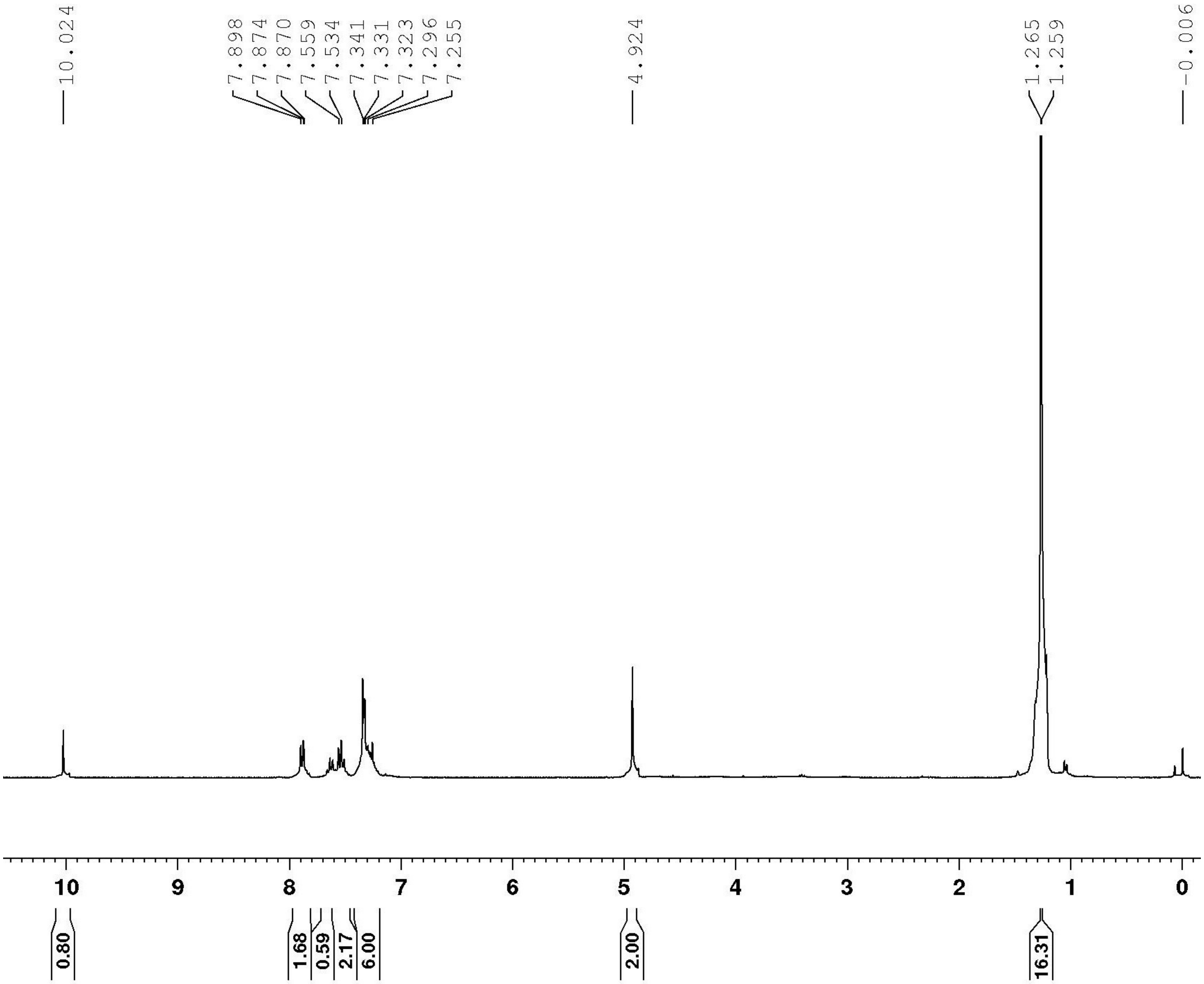
Figure S3: Intermolecular interactions in compound 6. Selected bond lengths (Å) and angles (deg): Ge2···I1 3.406(7); Ge1-I1-Ge2 142.77(2), I1-Ge2-I2 171.84(2).

^{1}H NMR spectra for the entries in Table 1

Entry 1



Entry 3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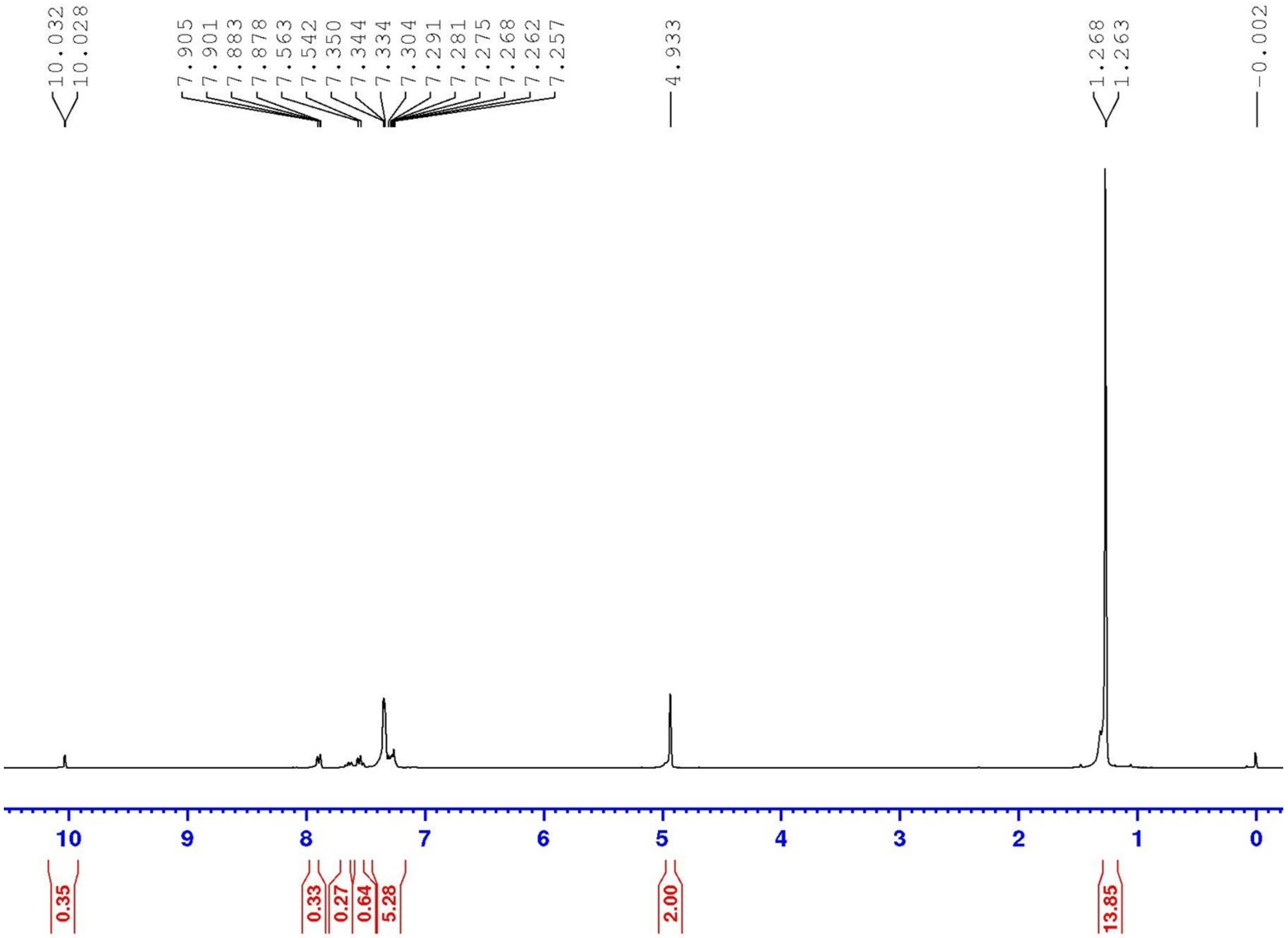
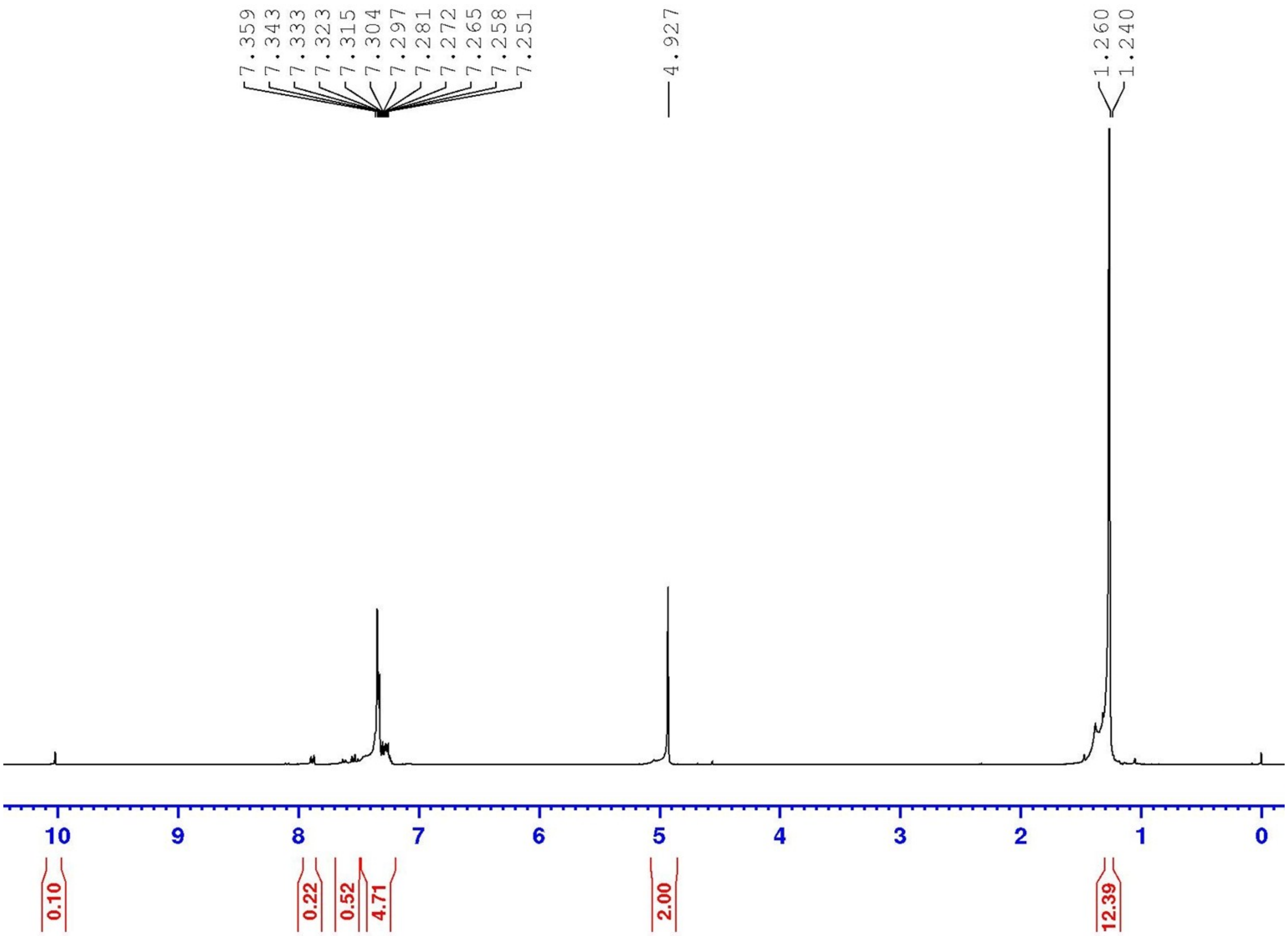
7.898
7.874
7.870
7.559
7.534
7.341
7.331
7.323
7.296
7.255
4.924
1.265
1.259
-0.006
10
9
8
7
6
5
4
3
2
1
0
0.80
1.68
0.59
2.17
6.00
2.00
16.31

Entry 4


10.032
10.028
7.905
7.901
7.883
7.878
7.563
7.542
7.350
7.344
7.334
7.304
7.291
7.281
7.275
7.268
7.262
7.257
4.933
1.268
1.263
-0.002
10
9
8
7
6
5
4
3
2
1
0
0.35
0.33
0.27
0.64
5.28
2.00
13.85

Entry 5



7.359
7.343
7.333
7.323
7.315
7.304
7.297
7.281
7.272
7.265
7.258
7.251
4.927
1.260
1.240
10
9
8
7
6
5
4
3
2
1
0
0.10
0.22
0.52
4.71
2.00
12.39

NMR data for the hydroborylated products in Table 2

^{n}PrOBpin: Hydroborylated product of propionaldehyde

^{1}H NMR (400 MHz, CDCl$_3$): δ 0.78 (t, $^{3}J_{HH}$ = 8 Hz, 3H, CH$_2$CH_3), 1.11 (s, 12H, Bpin-CH_3), 1.42-1.47 (m, 2H, CH_2CH$_3$), 3.66 (t, $^{3}J_{HH}$ = 6.4 Hz, 2H, OCH_2); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 9.92 (OCH$_2$CH$_2$CH$_3$), 24.43 (Bpin-CH$_3$), 24.73 (OCH$_2$CH$_2$CH$_3$), 66.33 (OCH$_2$CH$_2$CH$_3$), 82.35 (Bpin-C).

^{n}BuOBpin: Hydroborylated product of butyraldehyde

^{1}H NMR (400 MHz, CDCl$_3$): δ 0.79 (t, $^{3}J_{HH}$ = 7.2 Hz, 3H, CH$_2$CH$_2$CH_3), 1.12 (s, 12H, Bpin-CH_3), 1.22-1.27 (m, 2H, CH$_2$CH_2CH$_3$), 1.40-1.43 (m, 2H, CH_2CH$_2$CH$_3$), 3.69 (t, $^{3}J_{HH}$ = 6.4 Hz, 2H, OCH_2); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 13.59 (OCH$_2$CH$_2$CH$_2$CH$_3$), 18.65 (OCH$_2$CH$_2$CH$_2$CH$_3$), 24.45 (Bpin-CH$_3$), 33.45 (OCH$_2$CH$_2$CH$_2$CH$_3$), 64.45 (OCH$_2$CH$_2$CH$_2$CH$_3$), 82.37 (Bpin-C).

$C_6H_5CH_2$OBpin: Hydroborylated product of benzaldehyde

^{1}H NMR (400 MHz, CDCl$_3$): δ 1.24 (s, 12H, Bpin-CH_3), 4.92 (s, 2H, OCH_2), 7.23-7.32 (m, 5H, Ar-H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 24.63 (Bpin-CH$_3$), 66.69 (OCH$_2$), 82.94 (Bpin-C), 126.74, 127.38, 128.29, 139.28 (Ar-C).

2-NO$_2$PhOBpin: Hydroborylated product of 2-nitrobenzaldehyde

^{1}H NMR (400 MHz, CDCl$_3$): δ 1.29 (s, 12H, Bpin-CH_3), 5.36 (s, 2H, OCH_2), 7.45 (t, $^{3}J_{HH}$ = 8 Hz,1H, Ar-H), 7.68 (t, $^{3}J_{HH}$ = 8 Hz, 1H, Ar-H), 7.86 (d, $^{3}J_{HH}$ = 8 Hz, 1H, Ar-H), 8.13 (d, $^{3}J_{HH}$ = 8 Hz, 1H, Ar-H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 24.71 (Bpin-CH$_3$), 63.92 (OCH$_2$), 83.44 (Bpin-C), 124.83, 127.89, 127.95, 134.03, 136.21 (Ar-C).

3-NO$_2$PhOBpin: Hydroborylated product of 3-nitrobenzaldehyde

^{1}H NMR (400 MHz, CDCl$_3$): δ 1.27 (s, 12H, Bpin-CH_3), 5.00 (s, 2H, OCH_2), 7.50 (t, $^{3}J_{HH}$ = 8 Hz, 1H, Ar-H), 7.67 (d, $^{3}J_{HH}$ = 8 Hz, 1H, Ar-H), 8.13 (d, $^{3}J_{HH}$ = 7.2 Hz, 1H, Ar-H), 8.23 (s, 1H, Ar-H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 24.57 (Bpin-CH$_3$), 65.50 (OCH$_2$), 83.31 (Bpin-C), 121.51, 122.34, 129.28, 132.59, 141.36 (Ar-C).

4-ClPhCH$_2$OBpin: Hydroborylated product of 4-chlorobenzaldehyde

^{1}H NMR (400 MHz, CDCl$_3$): δ 1.25 (s, 12H, Bpin-C*H*$_3$), 4.87 (s, 2H, OC*H*$_2$), 7.27 (bs, 4H, Ar-*H*); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 24.93 (Bpin-*C*H$_3$), 65.99 (O*C*H$_2$), 83.12 (Bpin-*C*), 128.17, 128.47, 133.16, 137.82 (Ar-*C*).

4-BrPhCH$_2$OBpin: Hydroborylated product of 4-bromobenzaldehyde

^{1}H NMR (400 MHz, CDCl$_3$): δ 1.26 (s, 12H, Bpin-C*H*$_3$), 4.87 (s, 2H, OC*H*$_2$), 7.22 (d, $^3J_{\mathrm{HH}}$ = 8 Hz, 2H, Ar-*H*), 7.45 (d, $^3J_{\mathrm{HH}}$ = 8 Hz, 2H, Ar-*H*); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 24.67 (Bpin-*C*H$_3$), 66.02 (O*C*H$_2$), 83.13 (Bpin-*C*), 121.26, 128.48, 131.43, 138.33 (Ar-*C*).

4-MePhCH$_2$OBpin: Hydroborylated product of 4-methylbenzaldehyde

^{1}H NMR (400 MHz, CDCl$_3$): δ 1.26 (s, 12H, Bpin-C*H*$_3$), 2.33 (s, 3H, C*H*$_3$), 4.88 (s, 2H, OC*H*$_2$), 7.13 (d, $^3J_{\mathrm{HH}}$ = 8 Hz, 2H, Ar-*H*), 7.24 (d, $^3J_{\mathrm{HH}}$ = 8 Hz, 2H, Ar-*H*); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 21.14 (*C*H$_3$), 24.63 (Bpin-*C*H$_3$), 66.60 (O*C*H$_2$), 82.91 (Bpin-*C*), 126.87, 128.96, 136.27, 136.97 (Ar-*C*).

4-MeOPhCH$_2$OBpin: Hydroborylated product of 4-methoxybenzaldehyde

^{1}H NMR (400 MHz, CDCl$_3$): δ 1.25 (s, 12H, Bpin-C*H*$_3$), 3.78 (s, 3H, OC*H*$_3$), 4.84 (s, 2H, OC*H*$_2$), 6.85 (d, $^3J_{\mathrm{HH}}$ = 8 Hz, 2H, Ar-*H*), 7.27 (d, $^3J_{\mathrm{HH}}$ = 8 Hz, 2H, Ar-*H*); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 24.66 (Bpin-*C*H$_3$), 55.28 (O*C*H$_3$), 66.49 (O*C*H$_2$), 82.94 (Bpin-*C*), 113.73, , 128.57, 131.52, 159.10 (Ar-*C*).

2,4,6-(CH$_3$)$_3$PhCH$_2$OBpin: Hydroborylated product of mesitaldehyde

^{1}H NMR (400 MHz, CDCl$_3$): δ 1.21 (s, 12H, Bpin-C*H*$_3$), 2.21 (s, 3H, C*H*$_3$), 2.34 (s, 6H, C*H*$_3$), 4.92 (s, 2H, OC*H*$_2$), 6.79 (s, 2H, Ar-*H*); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 19.40 (*C*H$_3$), 20.94 (*C*H$_3$), 24.61 (Bpin-*C*H$_3$), 61.17 (O*C*H$_2$), 82.70 (Bpin-*C*), 128.88, 132.19, 137.48, 137.66 (Ar-*C*).

(CH$_3$)$_2$CHOBpin: Hydroborylated product of acetone

^{1}H NMR (400 MHz, CDCl$_3$): δ 1.18 (d, $^3J_{\mathrm{HH}}$ = 6 Hz, 6H, (C*H*$_3$)$_2$), 1.22 (s, 12H, Bpin-C*H*$_3$), 4.29-4.32 (m, 1H, C*H*(CH$_3$)$_2$); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 24.69 ((*C*H$_3$)$_2$), 25.01 (Bpin-*C*H$_3$), 67.43 (*C*H(CH$_3$)$_2$), 82.55 (Bpin-*C*).

$(CH_3CH_2CH_2)(CH_3)CHOBpin$: Hydroborylated product of 2-pentanone

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.83 (t, $^3J_{HH}$ = 8 Hz, 3H, CH_2CH_3), 1.11 (d, $^3J_{HH}$ = 8 Hz, 3H, (CH_3)), 1.18 (s, 12H, Bpin-CH_3), 1.23-1.33 (m, 2H, $(CH_2)_2CH_3$), 1.40-1.45 (m, 2H, $(CH_2)_2CH_3$), 4.09-4.11 (m, 1H, $CHCH_3$); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 13.96 ($CH_2CH_2CH_3$), 18.71 ($CH_2CH_2CH_3$), 22.61 ($CH_2CH_2CH_3$), 24.52 (Bpin-CH_3), 24.58 (Bpin-CH_3), 40.39 ($CHCH_3$), 70.61 ($OCHCH_3$), 82.37 (Bpin-*C*).

$(CH_3)(Ph)CHOBpin$: Hydroborylated product of acetophenone

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.18 (s, 6H, Bpin-CH_3), 1.21 (s, 6H, Bpin-CH_3), 1.47 (d, $^3J_{HH}$ = 9 Hz, 3H, CH_3), 5.21-5.23 (m, 1H, $CH(CH_3)_2$) 7.20-7.33 (m, 4H, Ar-*H*); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 24.55 (Bpin-CH_3), 24.60 (Bpin-CH_3), 25.48 (CH_3), 72.60 ($CHCH_3$), 82.73 (Bpin-*C*), 125.36, 127.13, 128.22, 144.62 (Ar-*C*).

$(CH_3)(4\text{-}FPh)CHOBpin$: Hydroborylated product of 4-fluoroacetophenone

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.20 (s, 6H, Bpin-CH_3), 1.23 (s, 6H, Bpin-CH_3), 1.46 (d, $^3J_{HH}$ = 6.6 Hz, 3H, CH_3), 5.21-5.23 (m, 1H, $CH(CH_3)_2$) 6.98 (t, $^3J_{HH}$ = 8 Hz, 2H, Ar-*H*), 7.31-7.33 (m, 2H, Ar-*H*); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 24.53 (Bpin-CH_3), 24.59 (Bpin-CH_3), 25.43 (CH_3), 72.04 ($CHCH_3$), 82.83 (Bpin-*C*), 114.87, 115.08, 127.04, 127.12, 140.43, 160.78, 163.21 (Ar-*C*).

$(CH_3)(4\text{-}ClPh)CHOBpin$: Hydroborylated product of 4-chloroacetophenone

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.20 (s, 6H, Bpin-CH_3), 1.23 (s, 6H, Bpin-CH_3), 1.45 (d, $^3J_{HH}$ = 6.4 Hz, 3H, CH_3), 5.17-5.22 (m, 1H, $CH(CH_3)_2$) 7.28 (s, 4H, Ar-*H*); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 24.65 (Bpin-CH_3), 24.70 (Bpin-CH_3), 25.50 (CH_3), 72.10 ($CHCH_3$), 83.01 (Bpin-*C*), 126.92, 128.47, 132.89, 143.24 (Ar-*C*).

$(CH_3)(4\text{-}MePh)CHOBpin$: Hydroborylated product of 4-methylacetophenone

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.20 (s, 6H, Bpin-CH_3), 1.22 (s, 6H, Bpin-CH_3), 1.46 (d, $^3J_{HH}$ = 6.4 Hz, 3H, CH_3), 5.20-5.22 (m, 1H, $CH(CH_3)_2$) 7.11 (d, $^3J_{HH}$ = 8 Hz, 2H, Ar-*H*), 7.24 (d, $^3J_{HH}$ = 8 Hz, 2H, Ar-*H*); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 21.12 (CH_3), 24.59 (Bpin-CH_3), 24.62 (Bpin-CH_3), 25.49 (CH_3), 72.48 ($CHCH_3$), 82.71 (Bpin-*C*), 125.35, 128.90, 136.66, 141.71 (Ar-*C*).

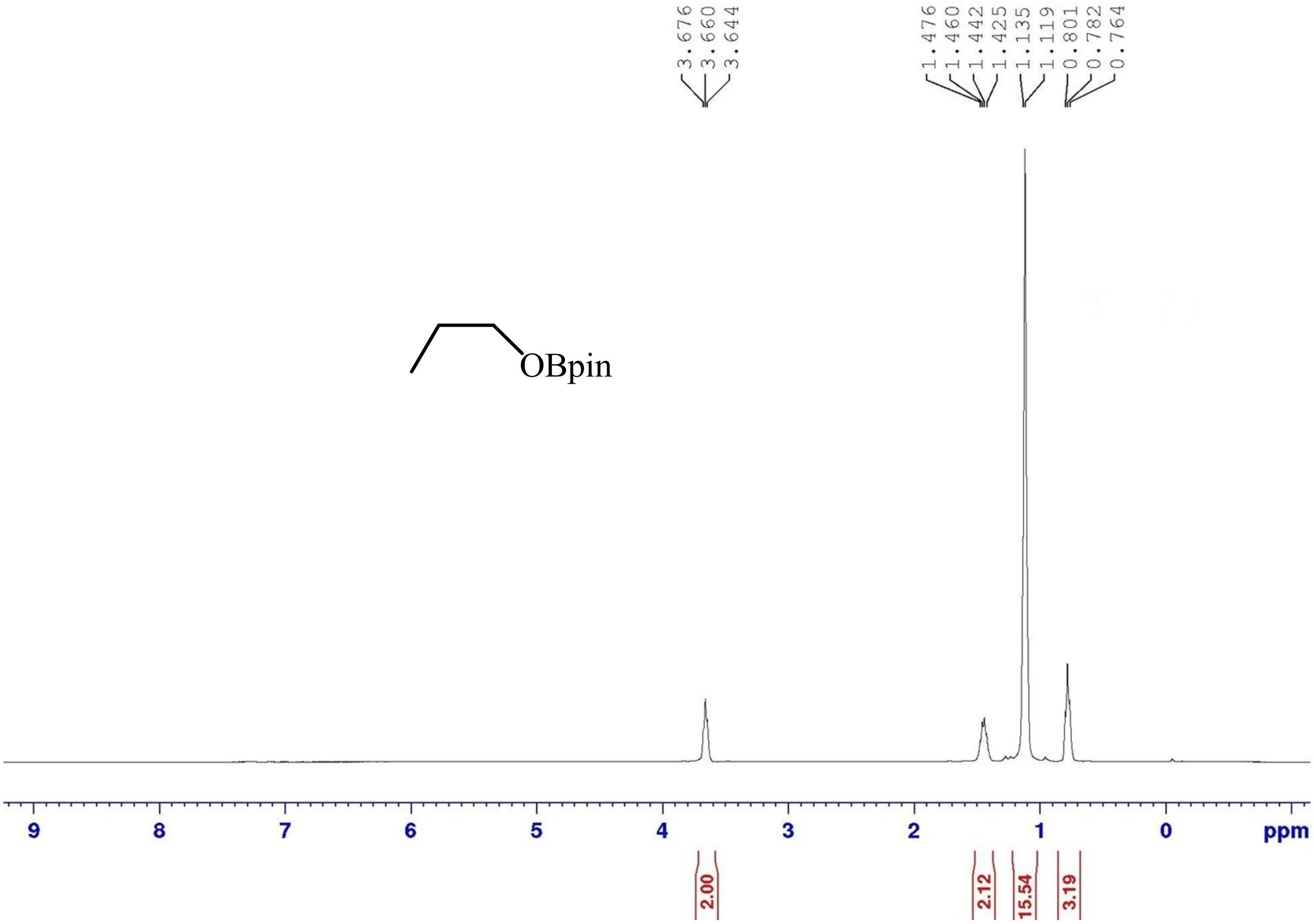
$(C_6H_5)_2CHOBpin$: Hydroborylated product of Benzophenone

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.18 (s, 12H, Bpin-C*H*$_3$), 6.16 (s, 1H, C*H*(CH_3)$_2$) 7.21 (d, $^3J_{HH}$ = 8 Hz, 2H, Ar-*H*), 7.28 (t, $^3J_{HH}$ = 8 Hz, 4H, Ar-*H*), 7.37 (d, $^3J_{HH}$ = 8 Hz, 4H, Ar-*H*); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 24.61 (Bpin-*C*H$_3$), 77.99 (*C*HCH$_3$), 83.07 (Bpin-*C*), 126.58, 127.37, 128.31, 143.20 (Ar-*C*).

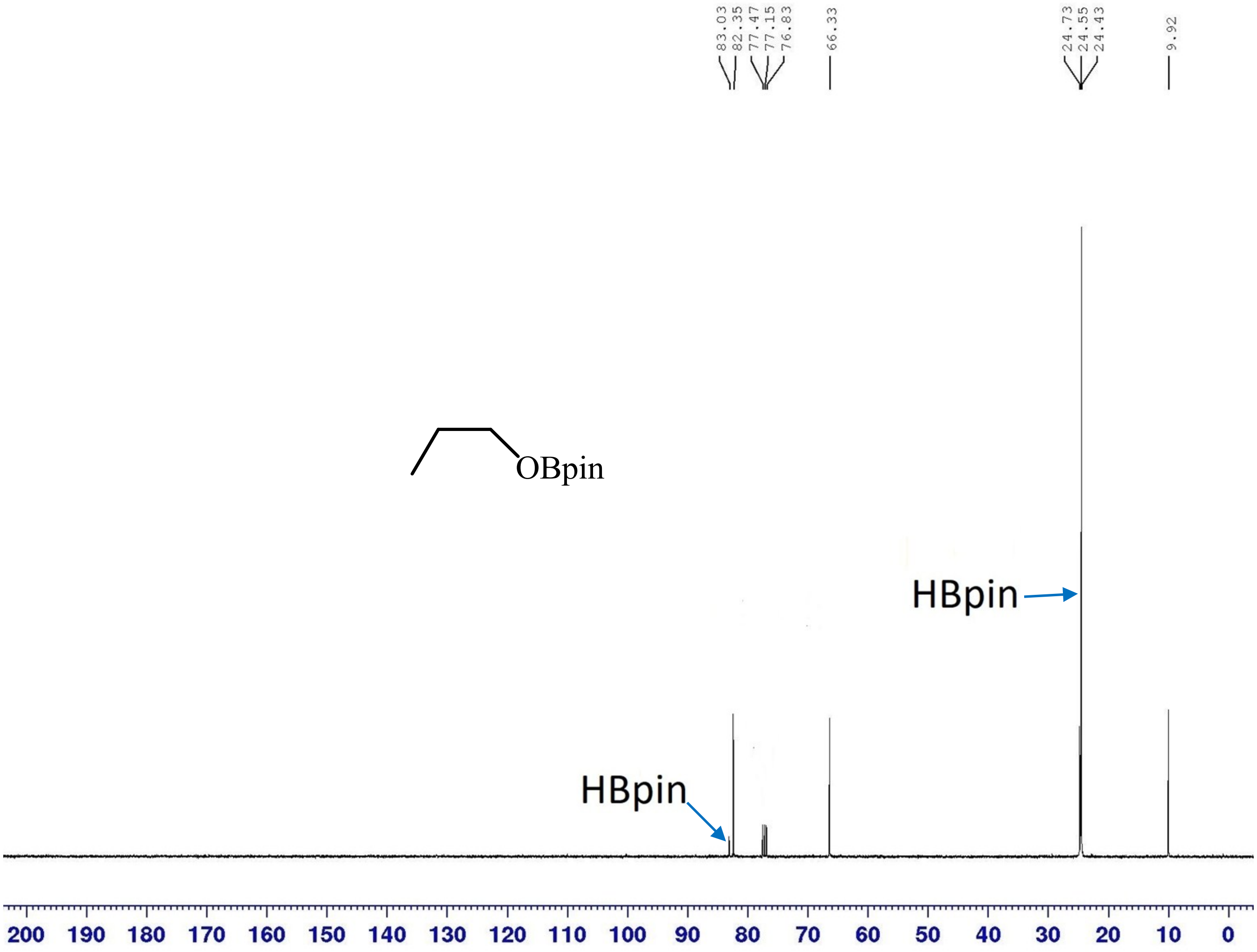
^{1}H and ^{13}C NMR spectra of the hydroborylated products in Table 2*

**In the ^{1}H NMR spectra of hydroborylated aldehydes, the peak for the methyl protons of pinacolborane (which was used in slight excess) is overlapping with the peak due to the methyl protons of the OBpin moiety of the hydroborylated aldehyde. Therefore, the integration for the latter is greater than the expected value of 12.*

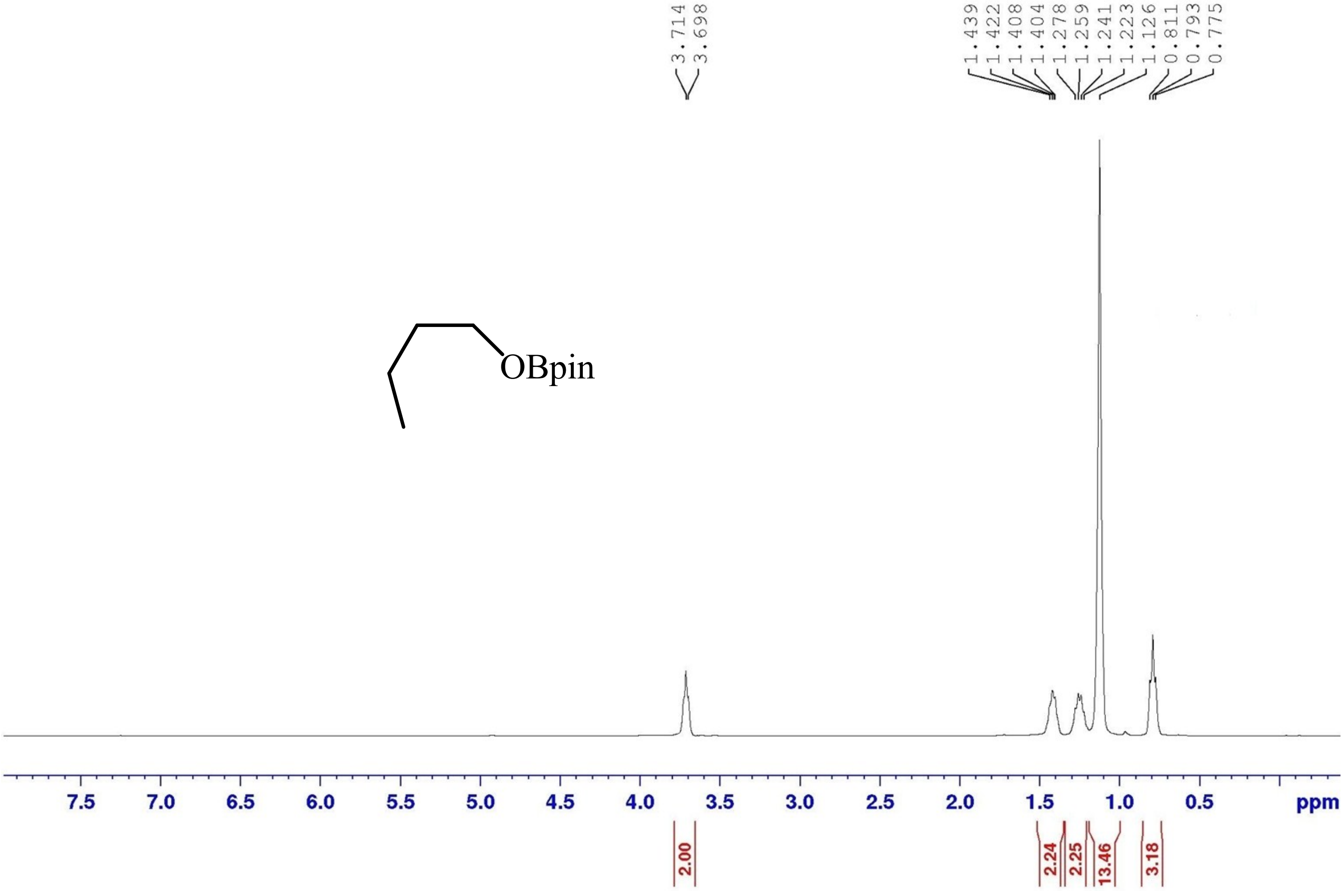
^{1}H NMR spectrum of the hydroborylated product of propionaldehyde



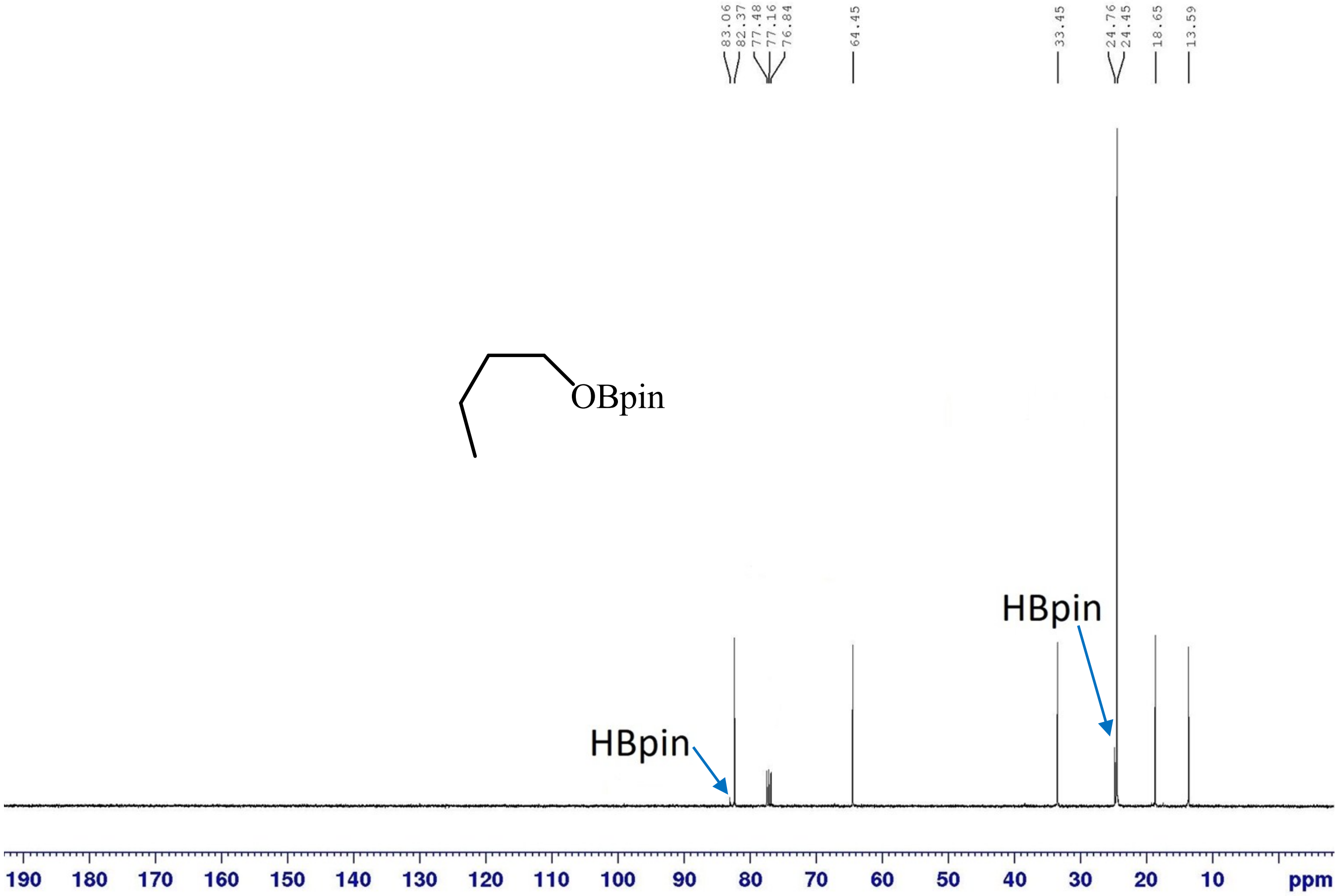
^{13}C NMR spectrum of the hydroborylated product of propionaldehyde



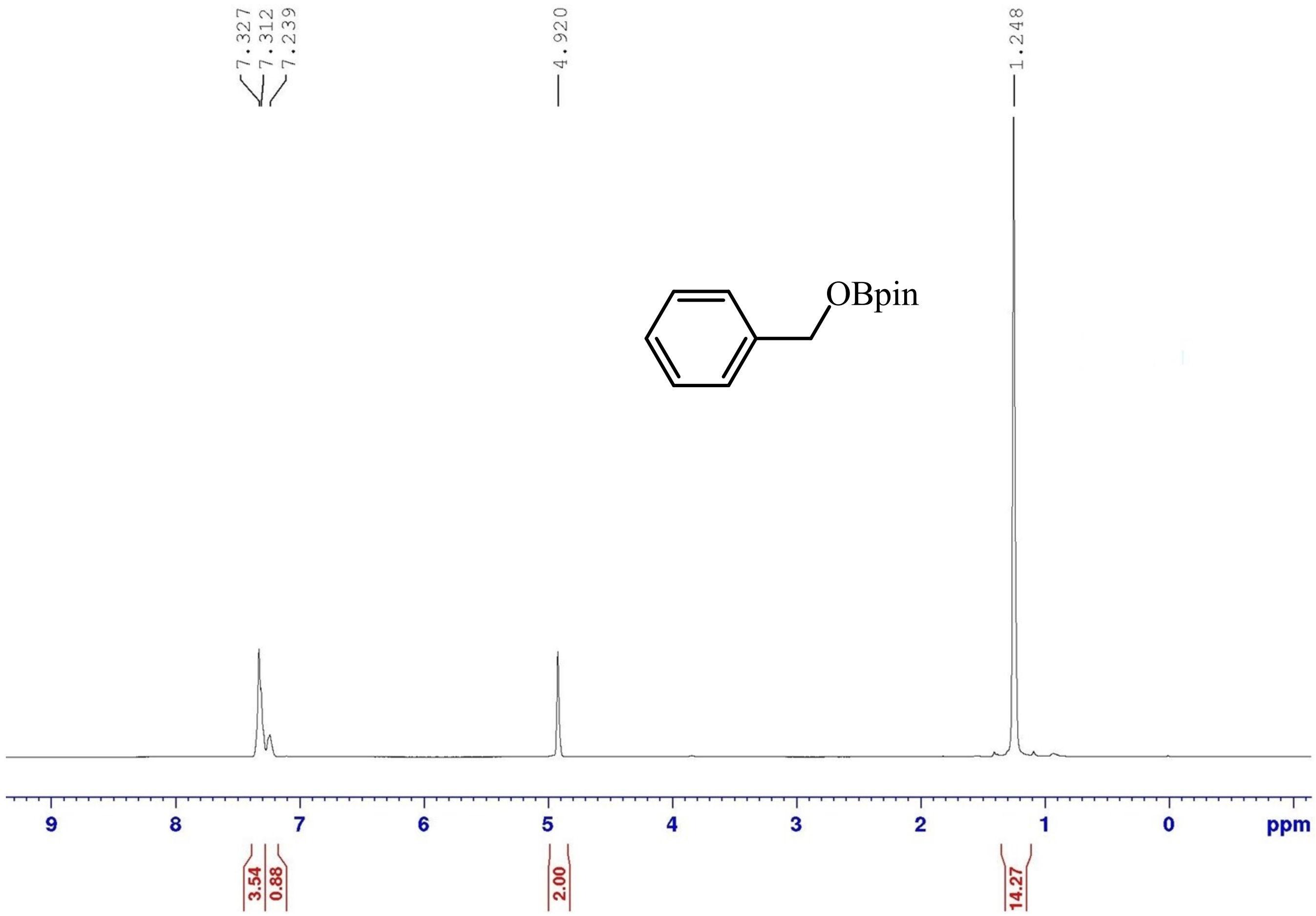
^{1}H NMR spectrum of the hydroborylated product of *n*-butyraldehyde



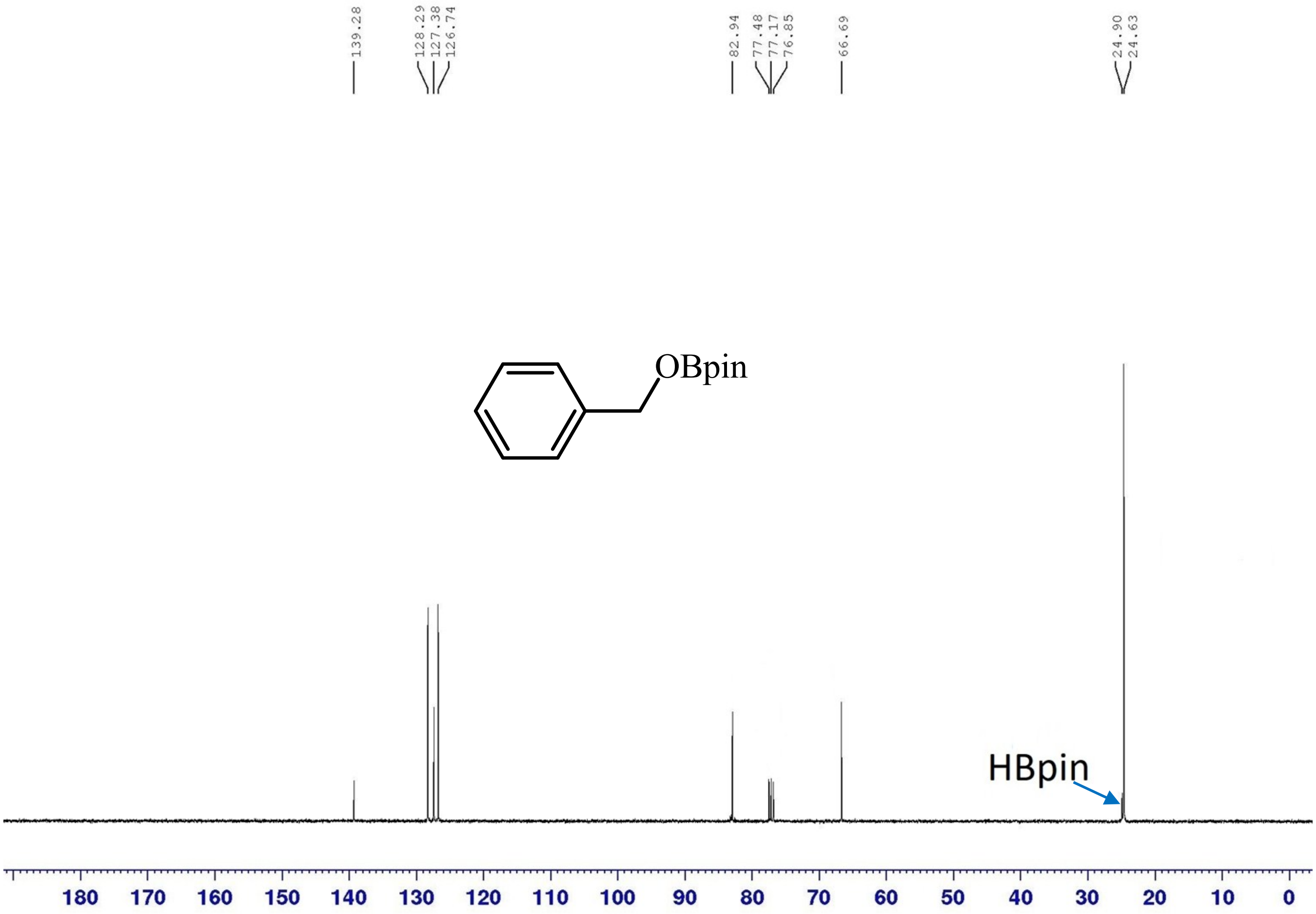
^{13}C NMR spectrum of the hydroborylated product of *n*-butyraldehyde



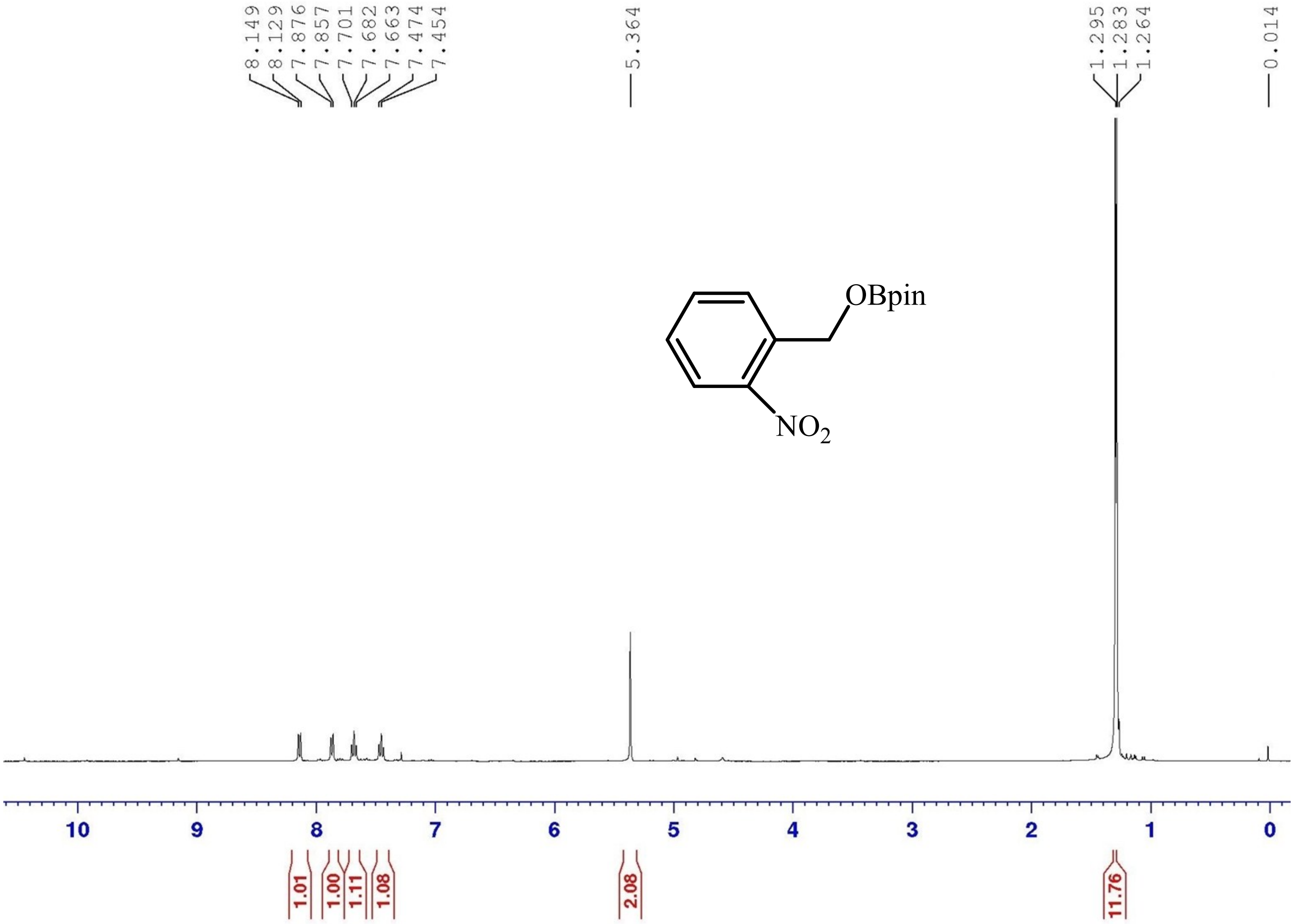
^{1}H NMR spectrum of the hydroborylated product of benzaldehyde



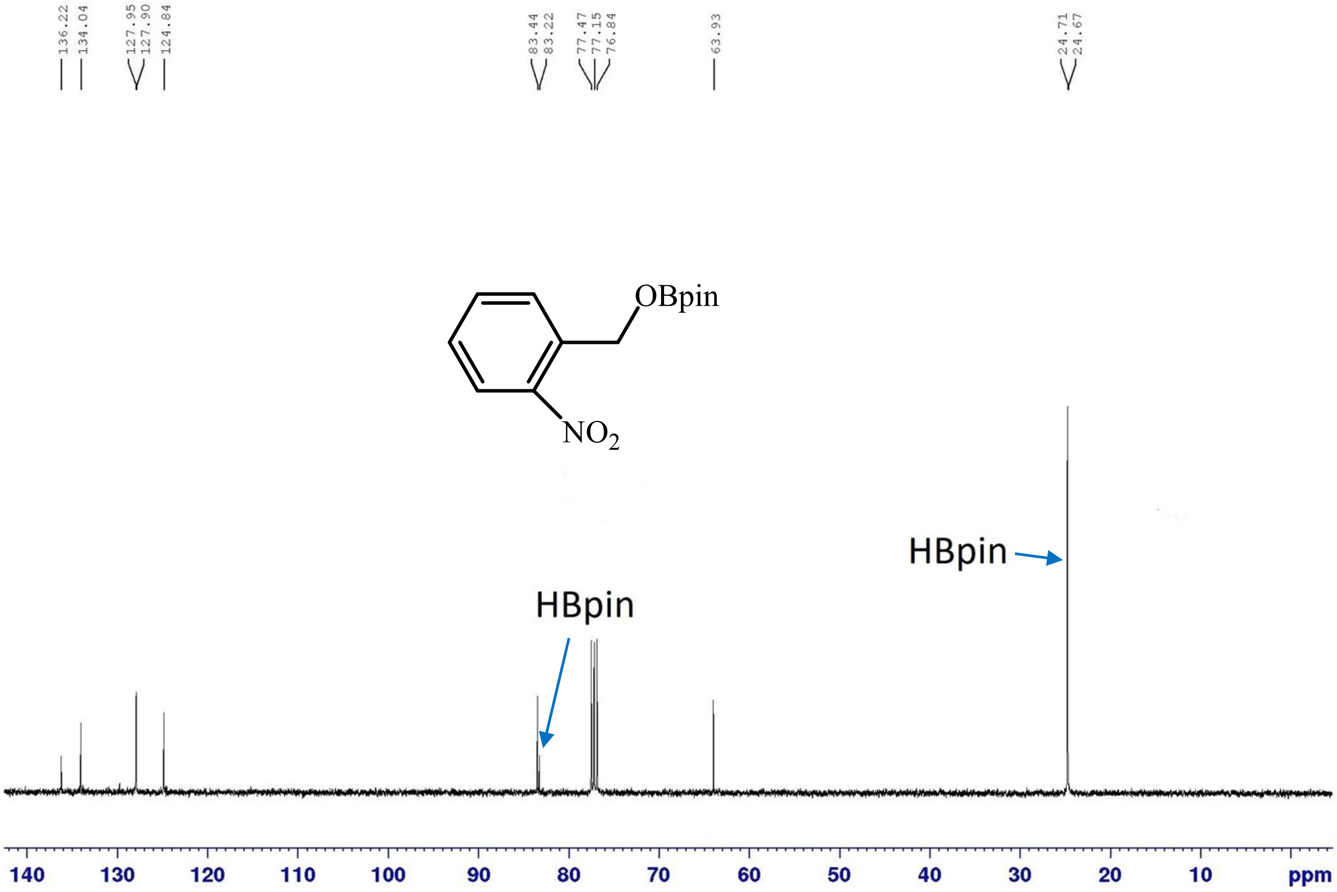
^{13}C NMR spectrum of the hydroborylated product of benzaldehyde



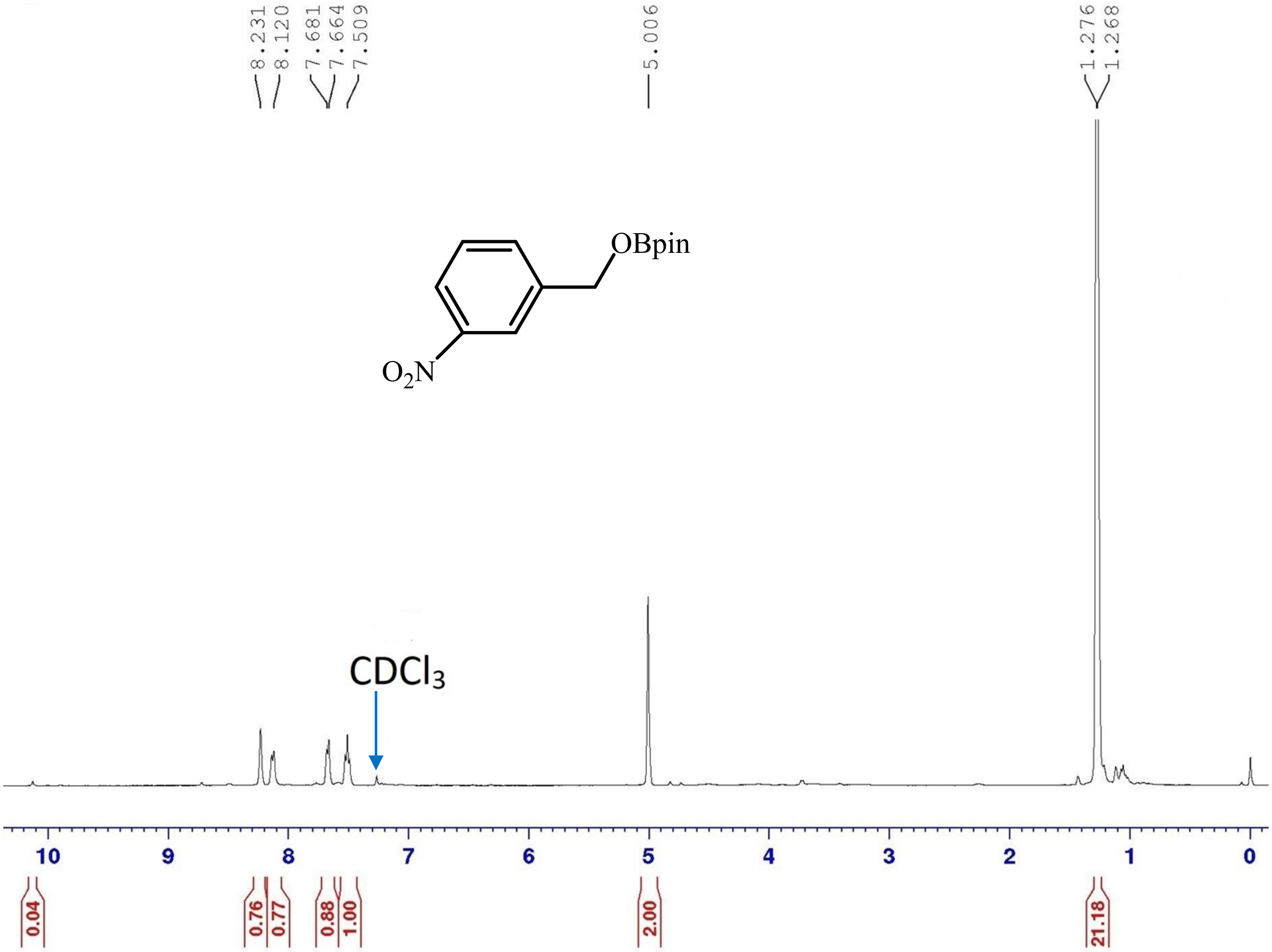
^{1}H NMR spectrum of the hydroborylated product of 2-nitrobenzaldehyde



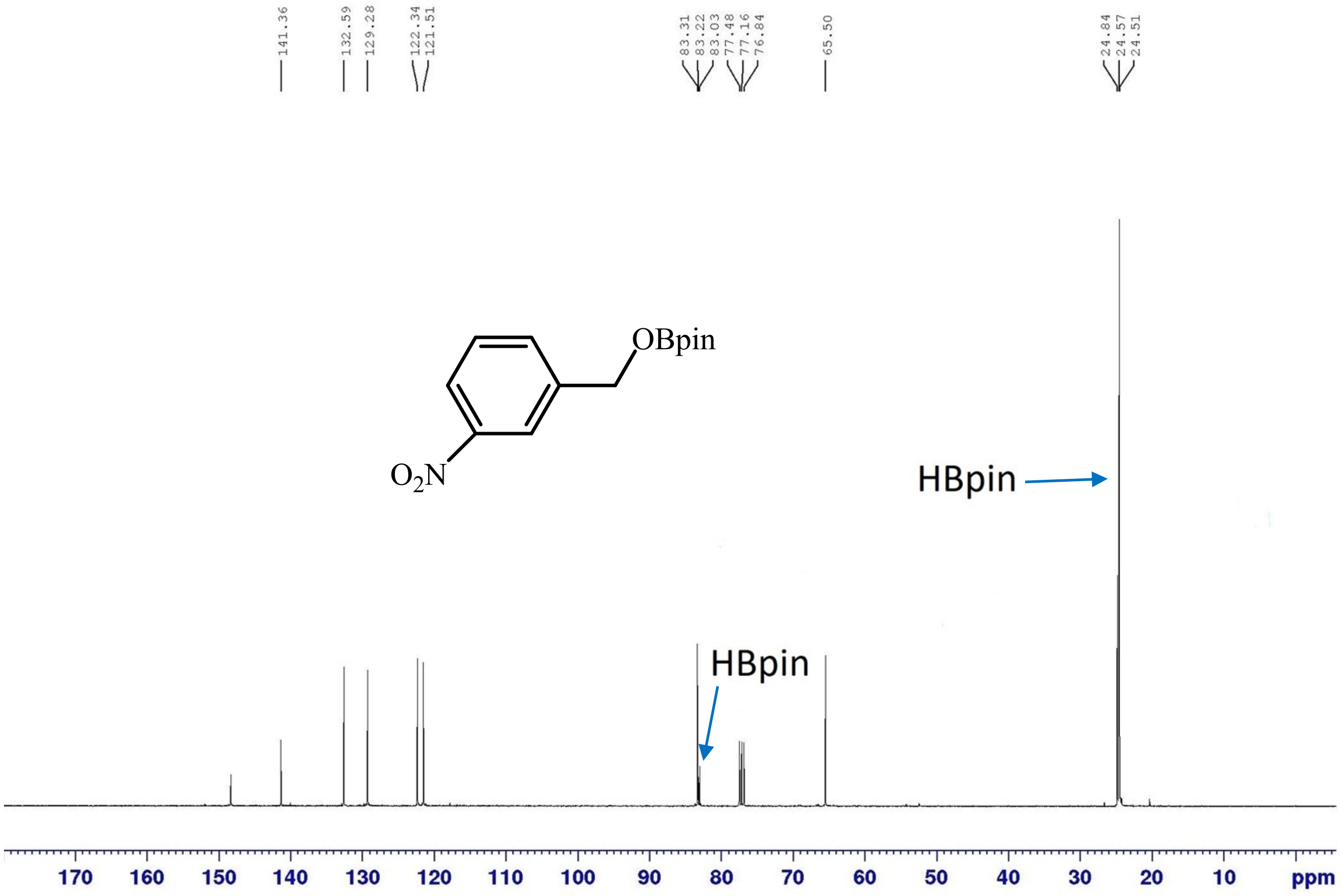
^{13}C NMR spectrum of the hydroborylated product of 2-nitrobenzaldehyde



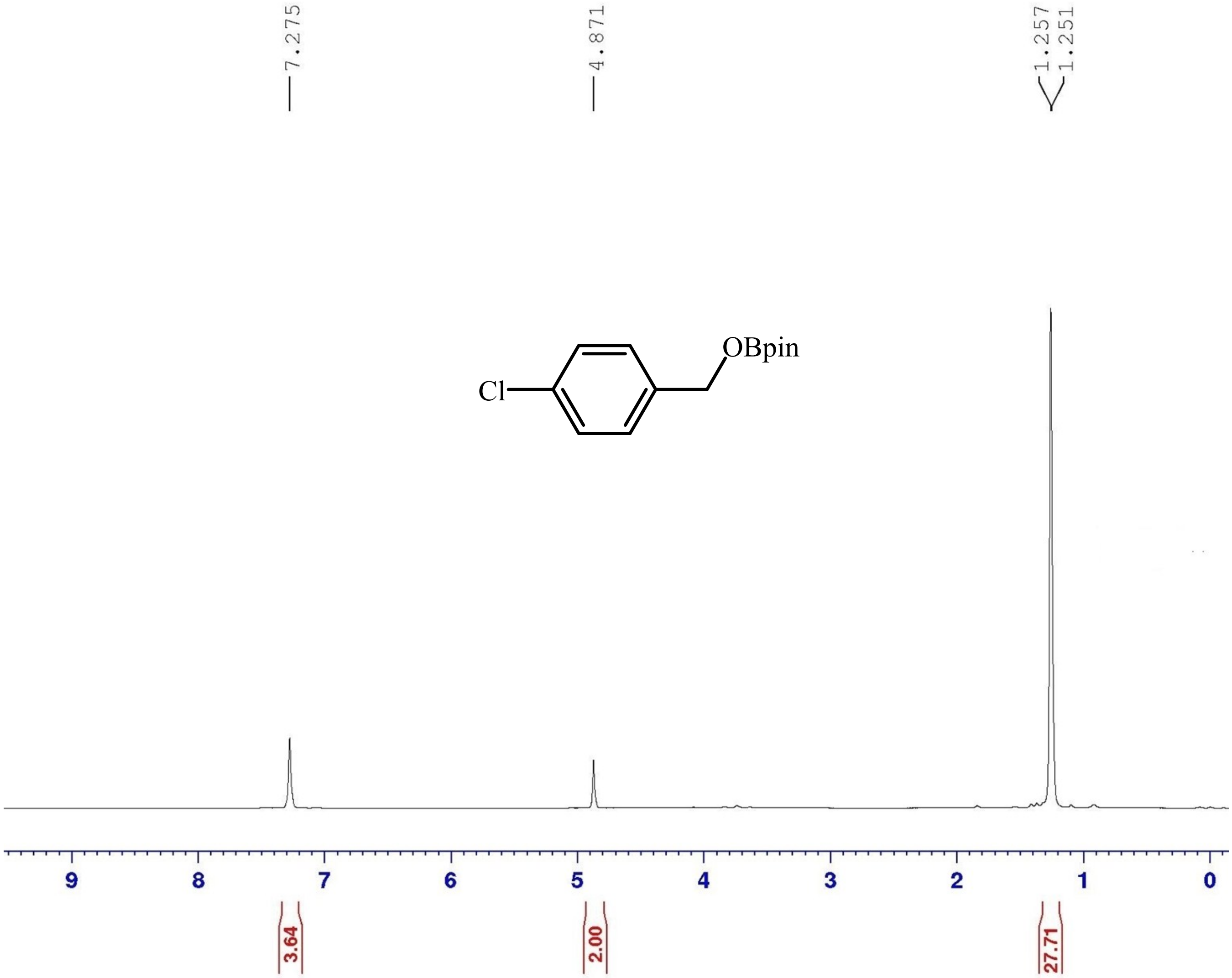
^{1}H NMR spectrum of the hydroborylated product of 3-nitrobenzaldehyde



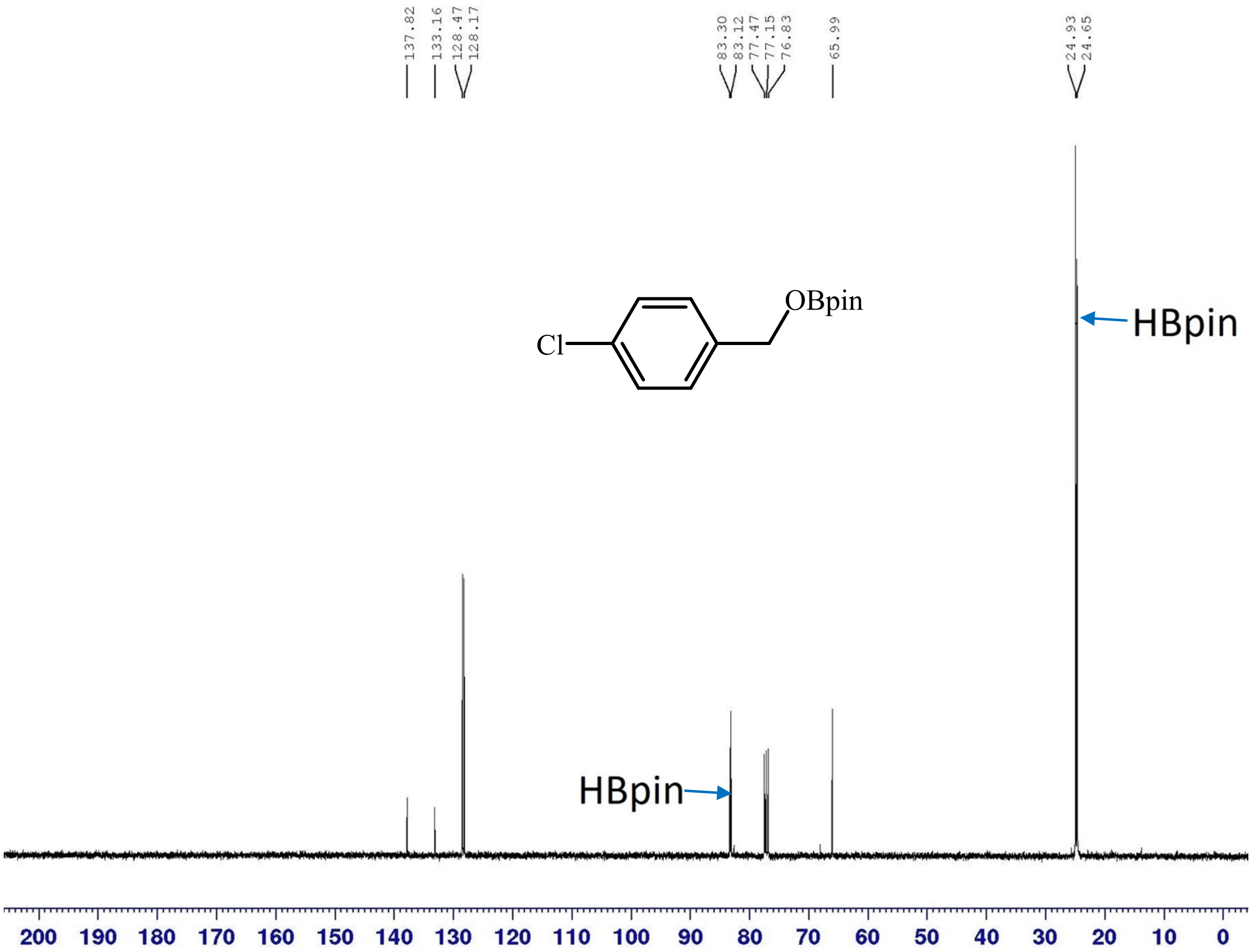
^{13}C NMR spectrum of the hydroborylated product of 3-nitrobenzaldehyde



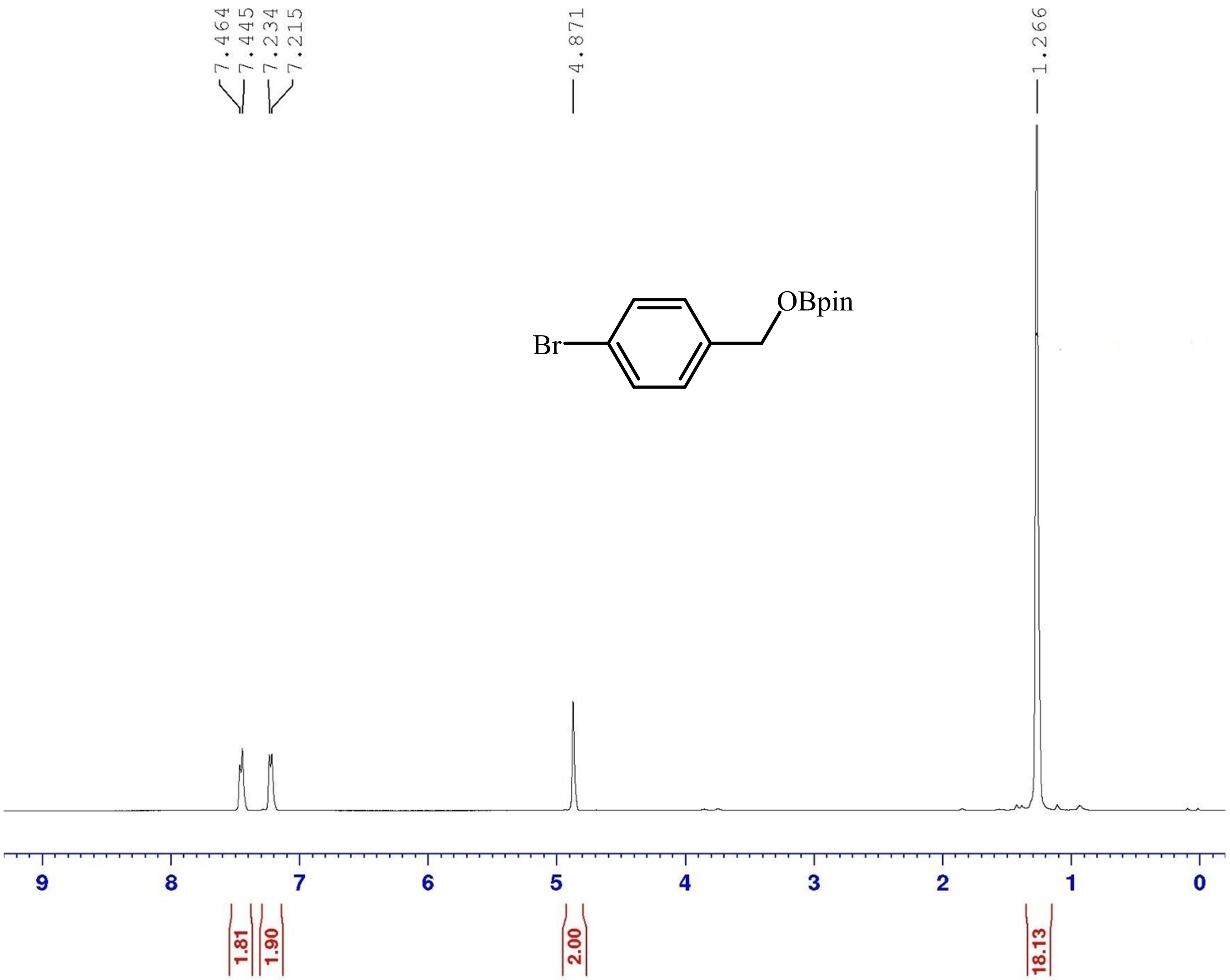
^{1}H NMR spectrum of the hydroborylated product of 4-chlorobenzaldehyde



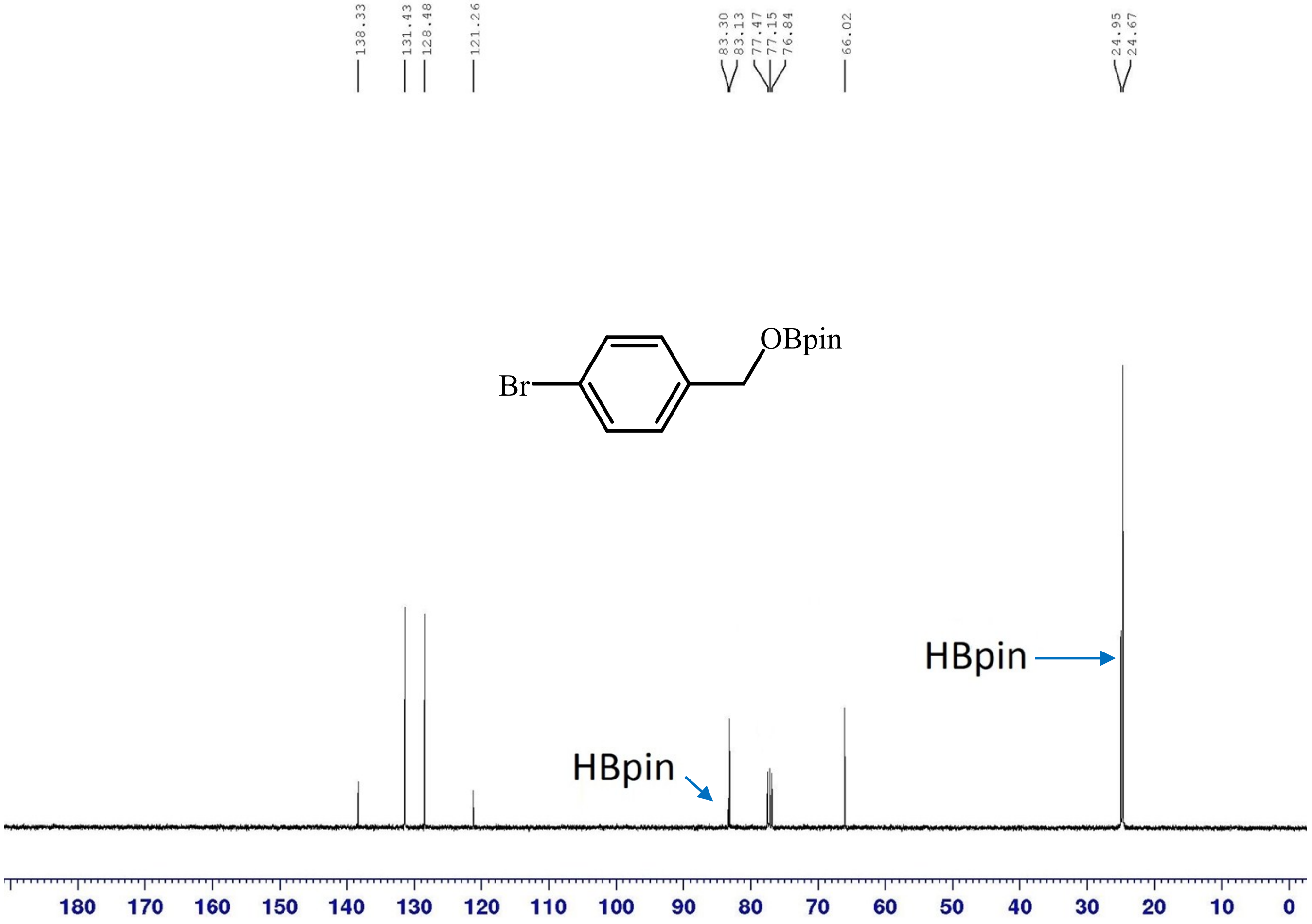
^{13}C NMR spectrum of the hydroborylated product of 4-chlorobenzaldehyde



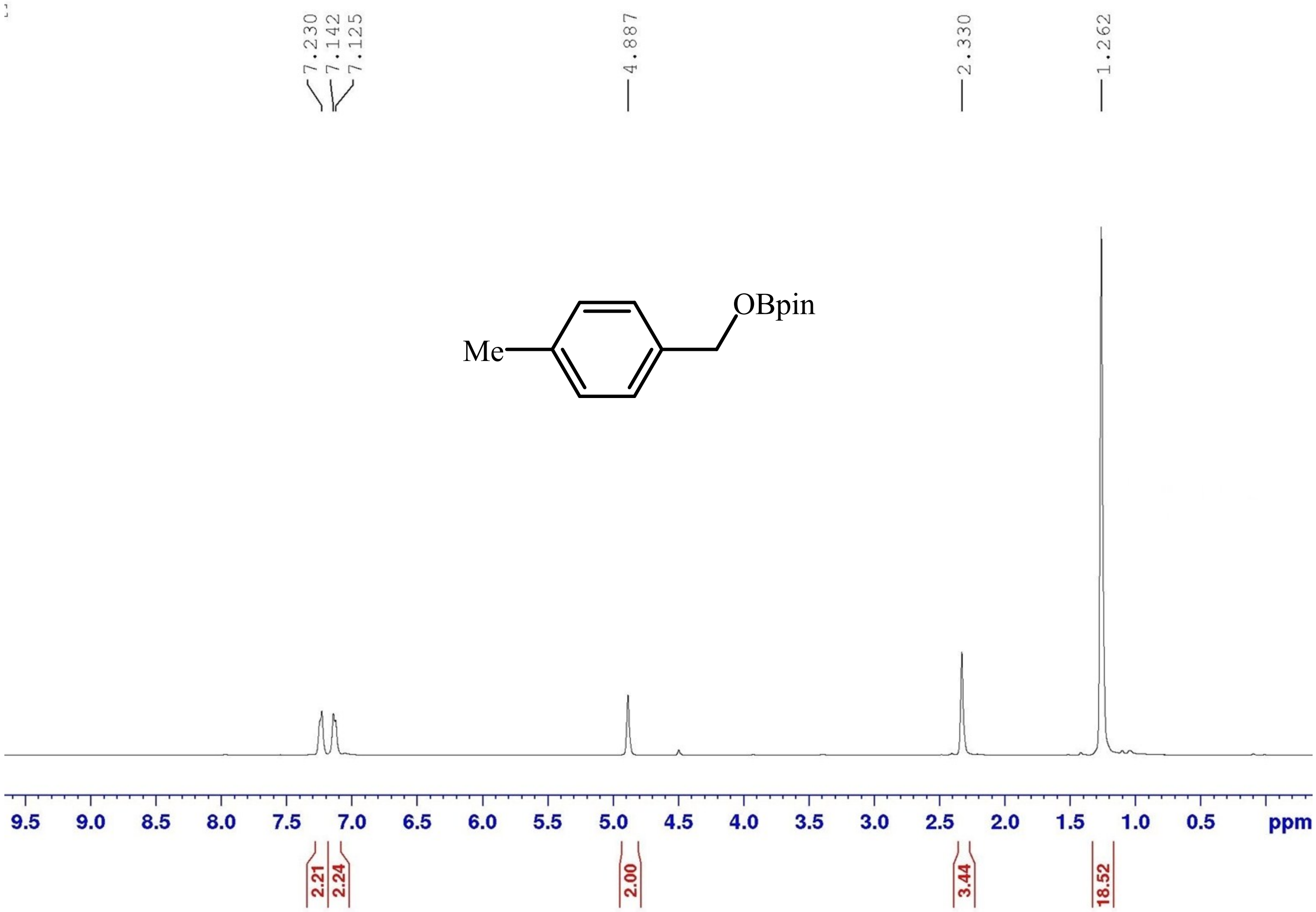
^{1}H NMR spectrum of the hydroborylated product of 4-bromobenzaldehyde



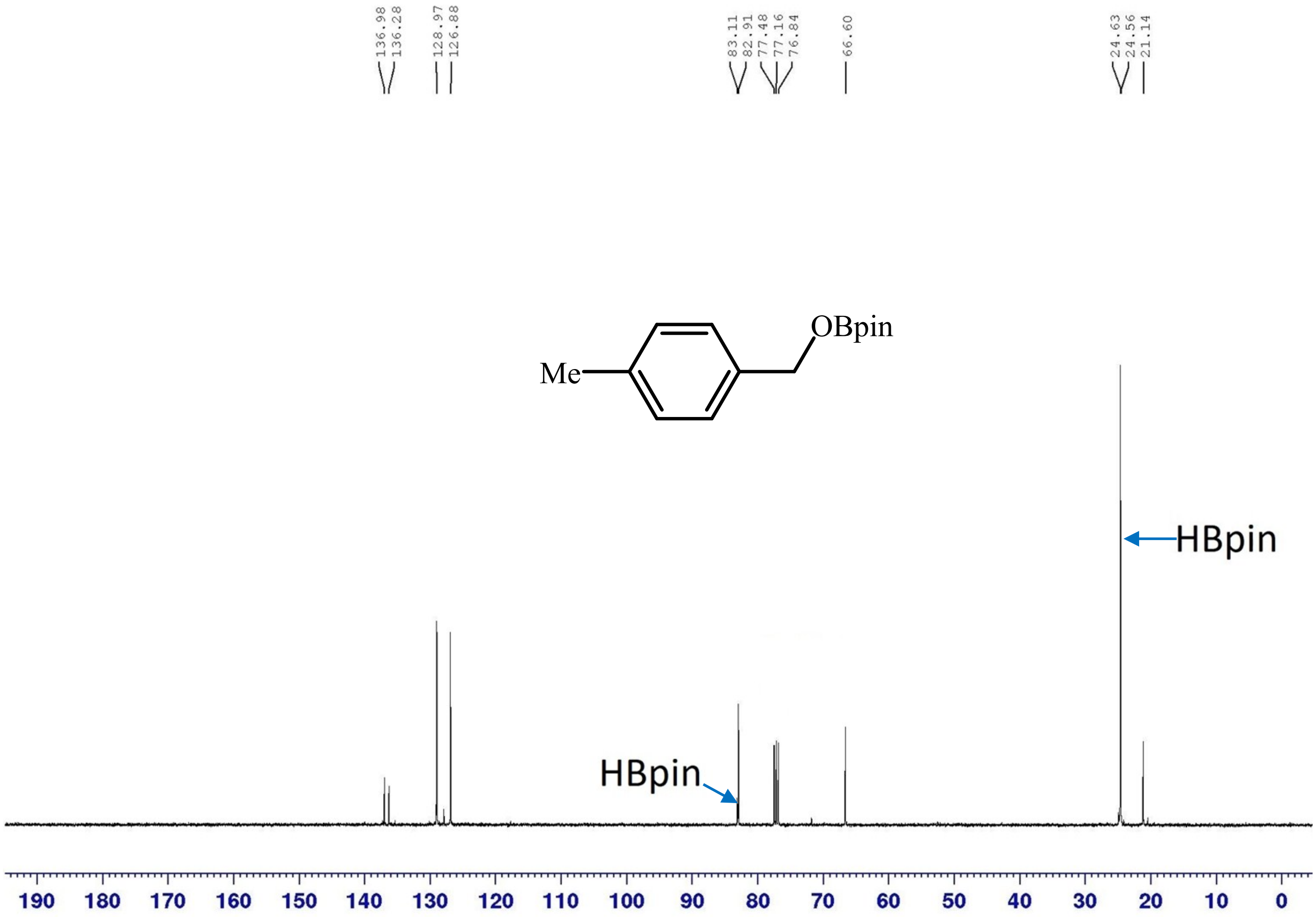
^{13}C NMR spectrum of the hydroborylated product of 4-bromobenzaldehyde



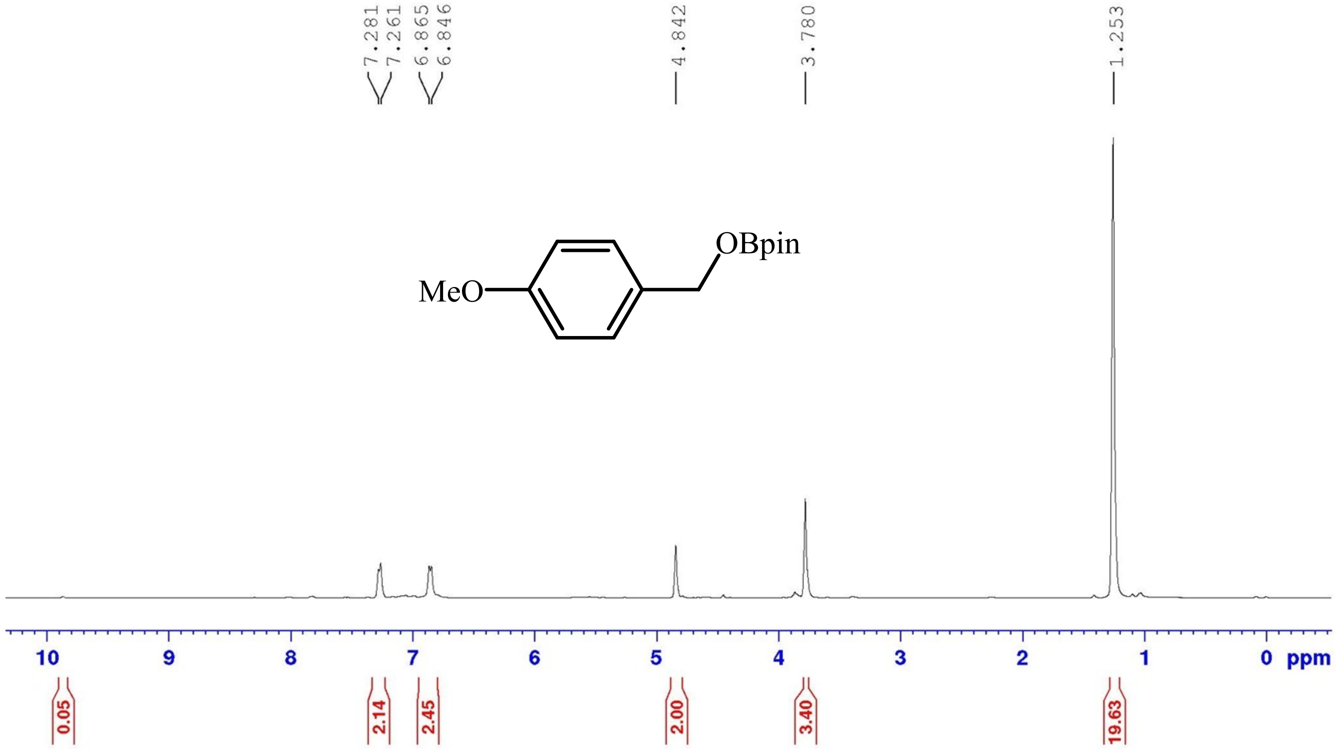
^{1}H NMR spectrum of the hydroborylated product of 4-methylbenzaldehyde



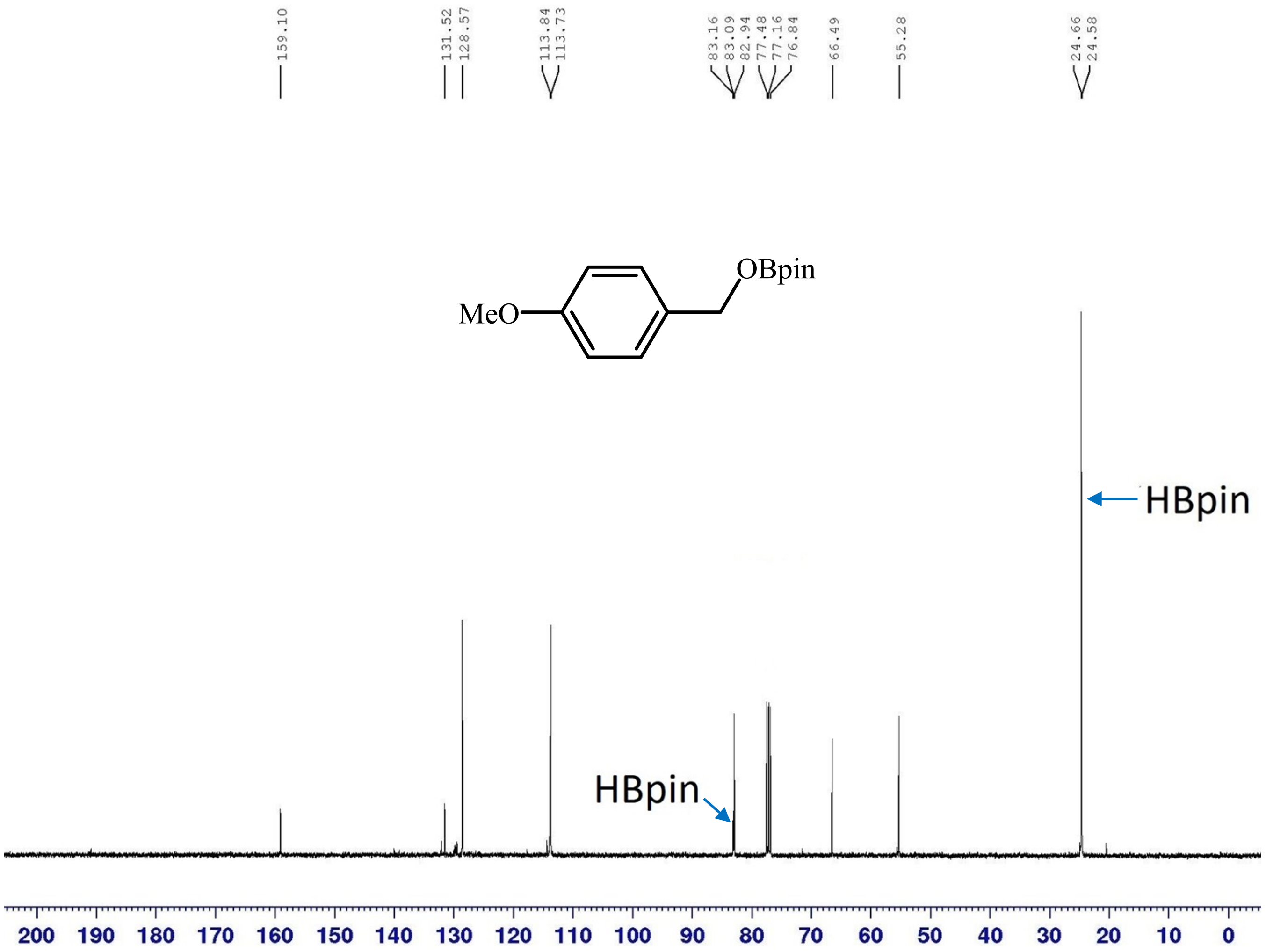
^{13}C NMR spectrum of the hydroborylated product of 4-methylbenzaldehyde



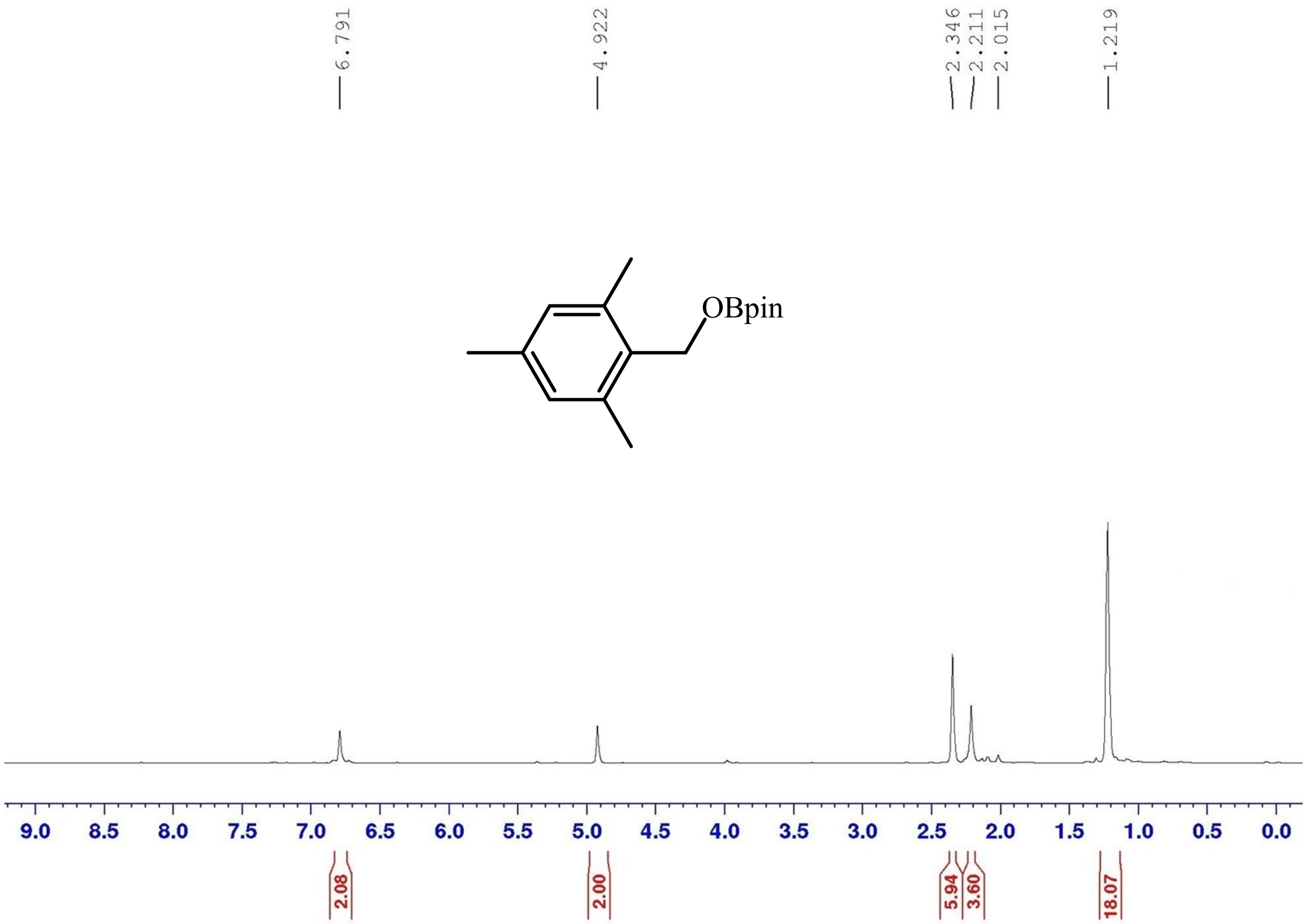
^{1}H NMR spectrum of the hydroborylated product of 4-methoxybenzaldehyde



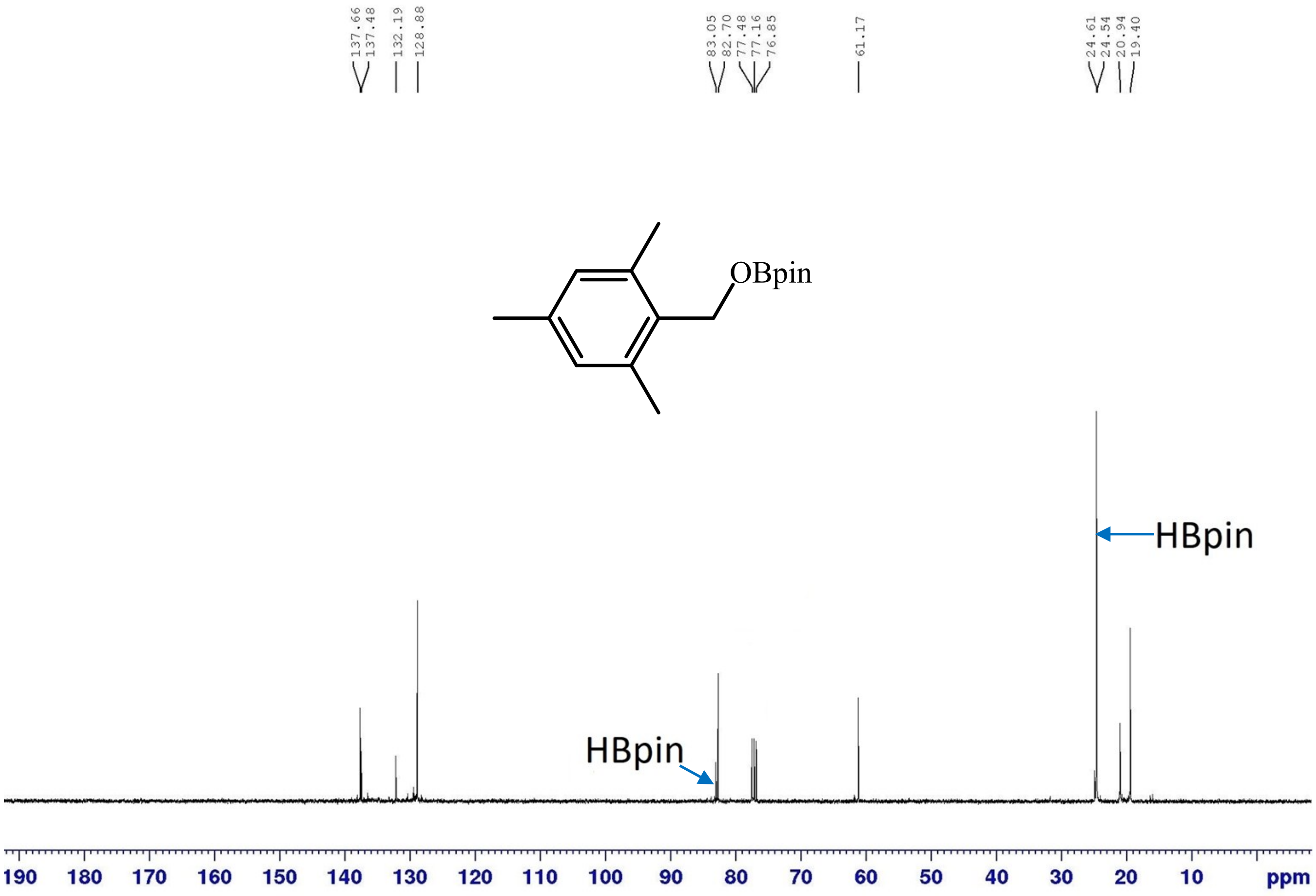
^{13}C NMR spectrum of the hydroborylated product of 4-methoxybenzaldehyde



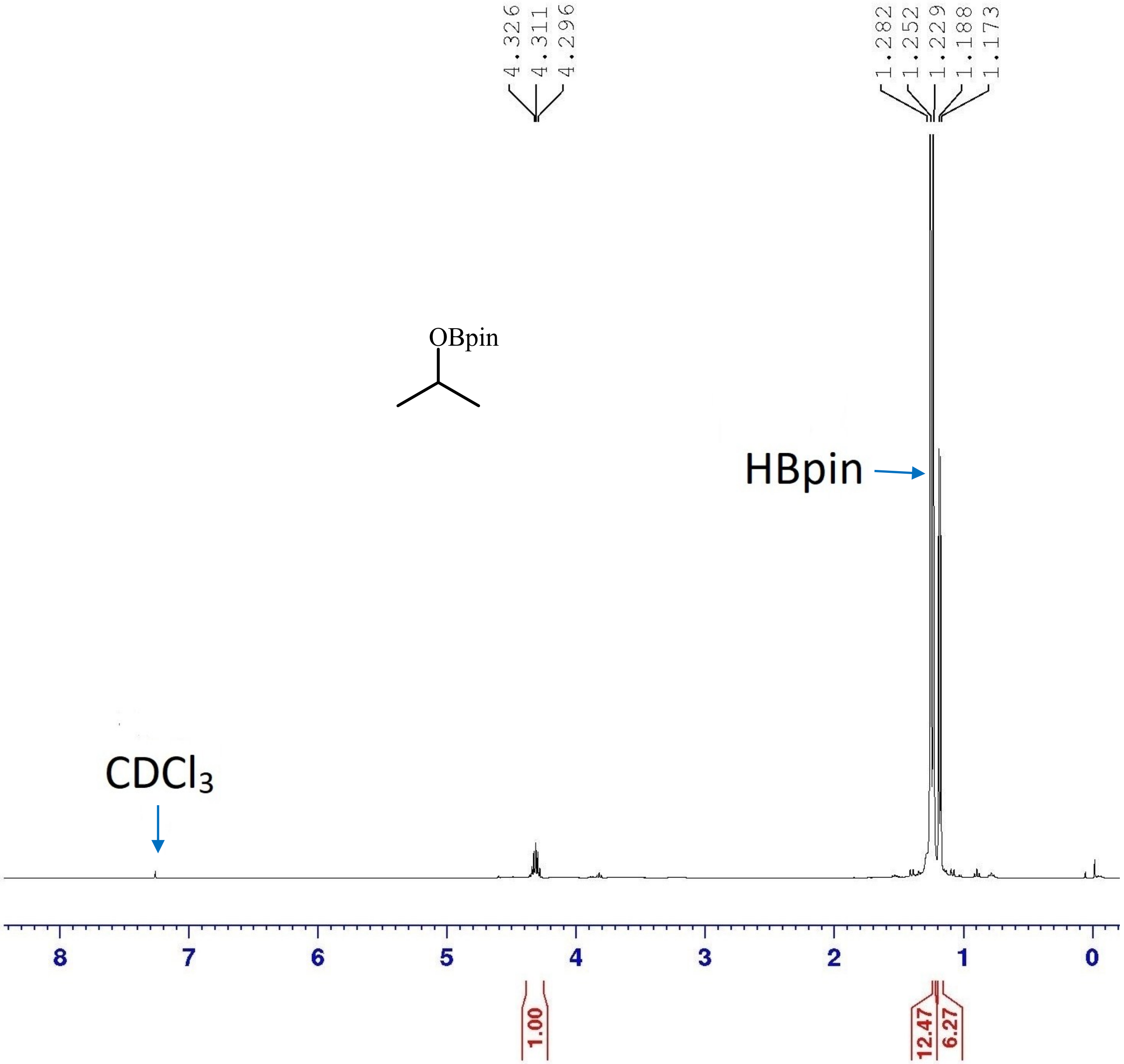
^{1}H NMR spectrum of the hydroborylated product of mesitaldehyde



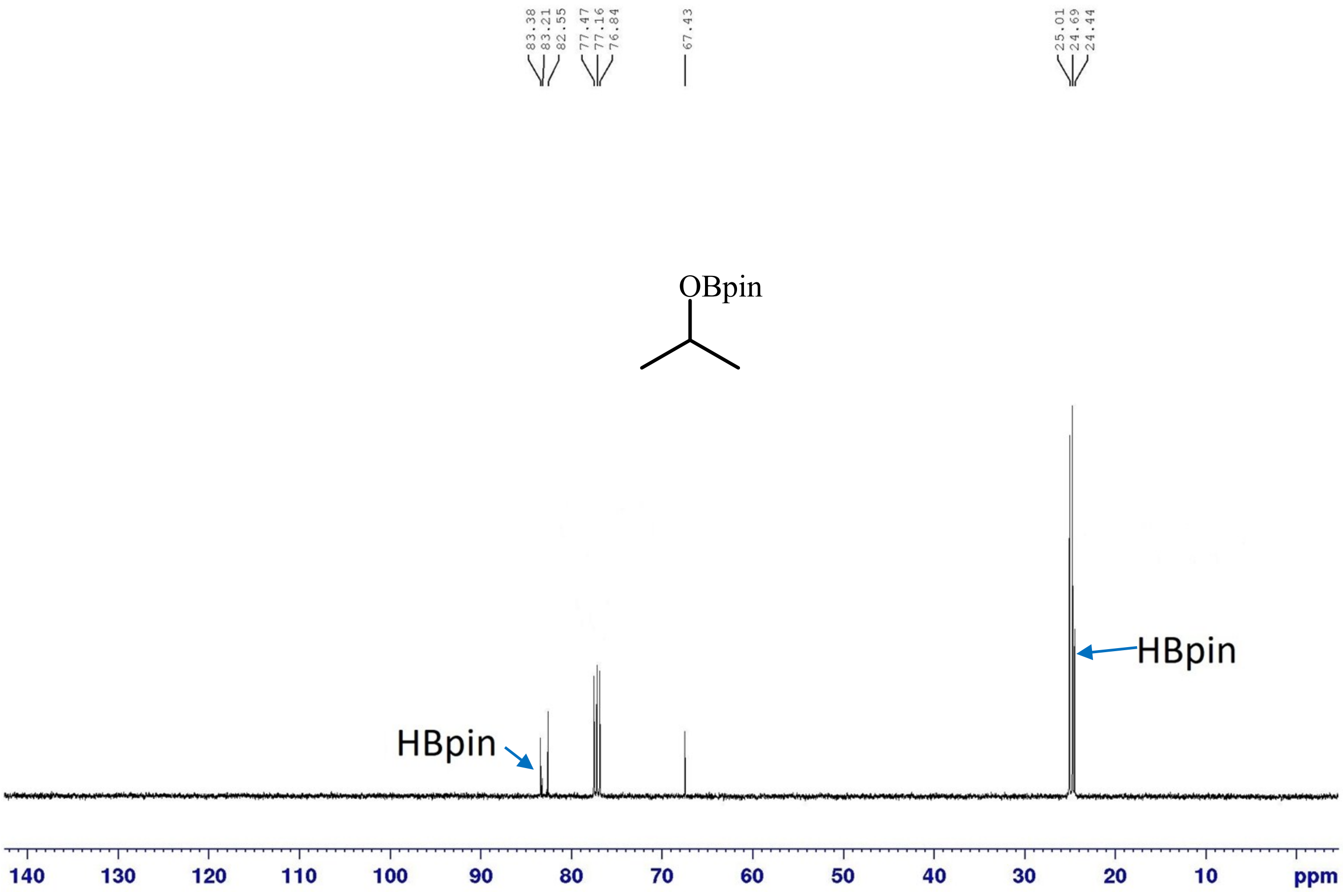
^{13}C NMR spectrum of the hydroborylated product of Mesitaldehyde



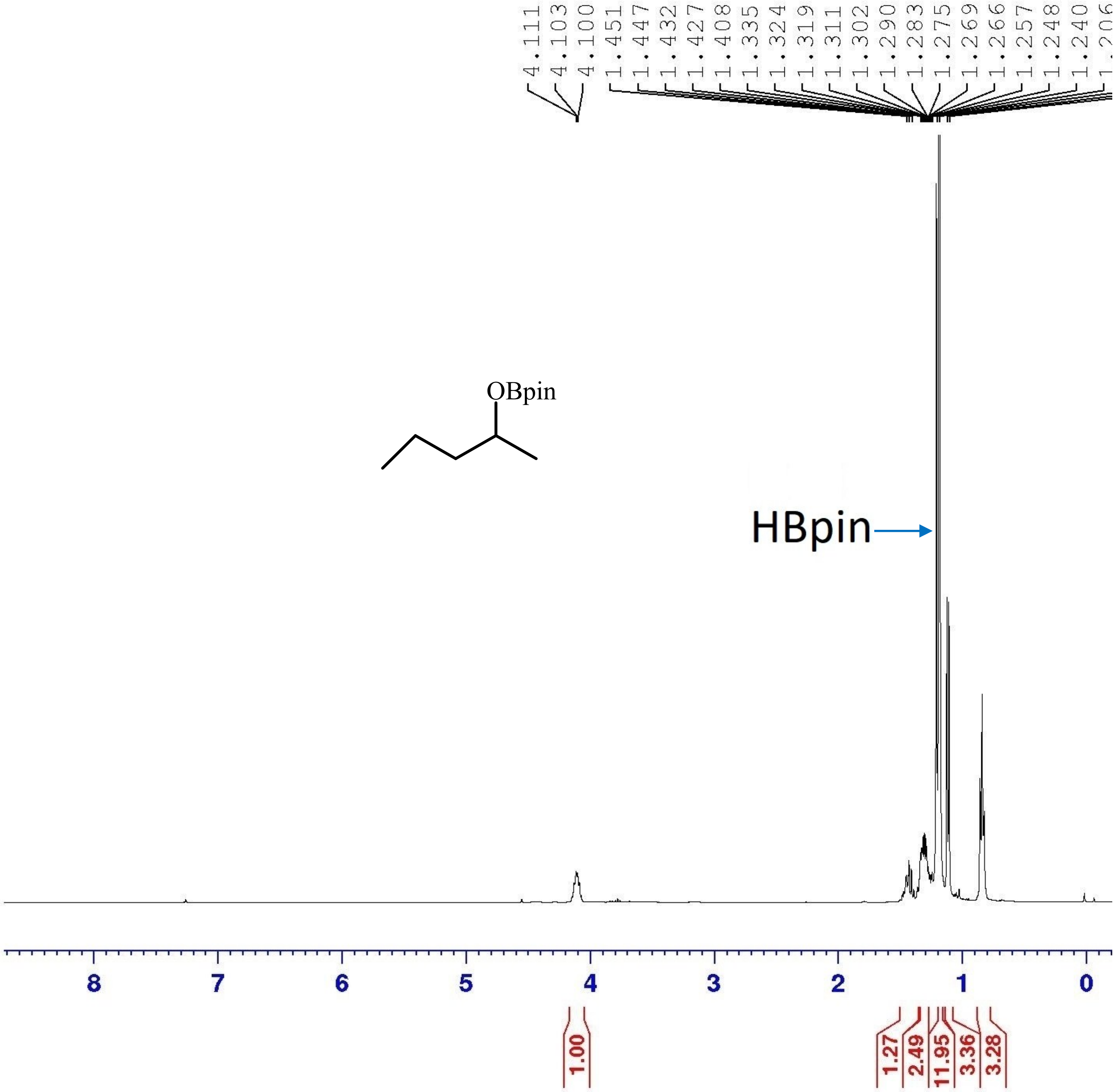
^{1}H NMR spectrum of the hydroborylated product of acetone



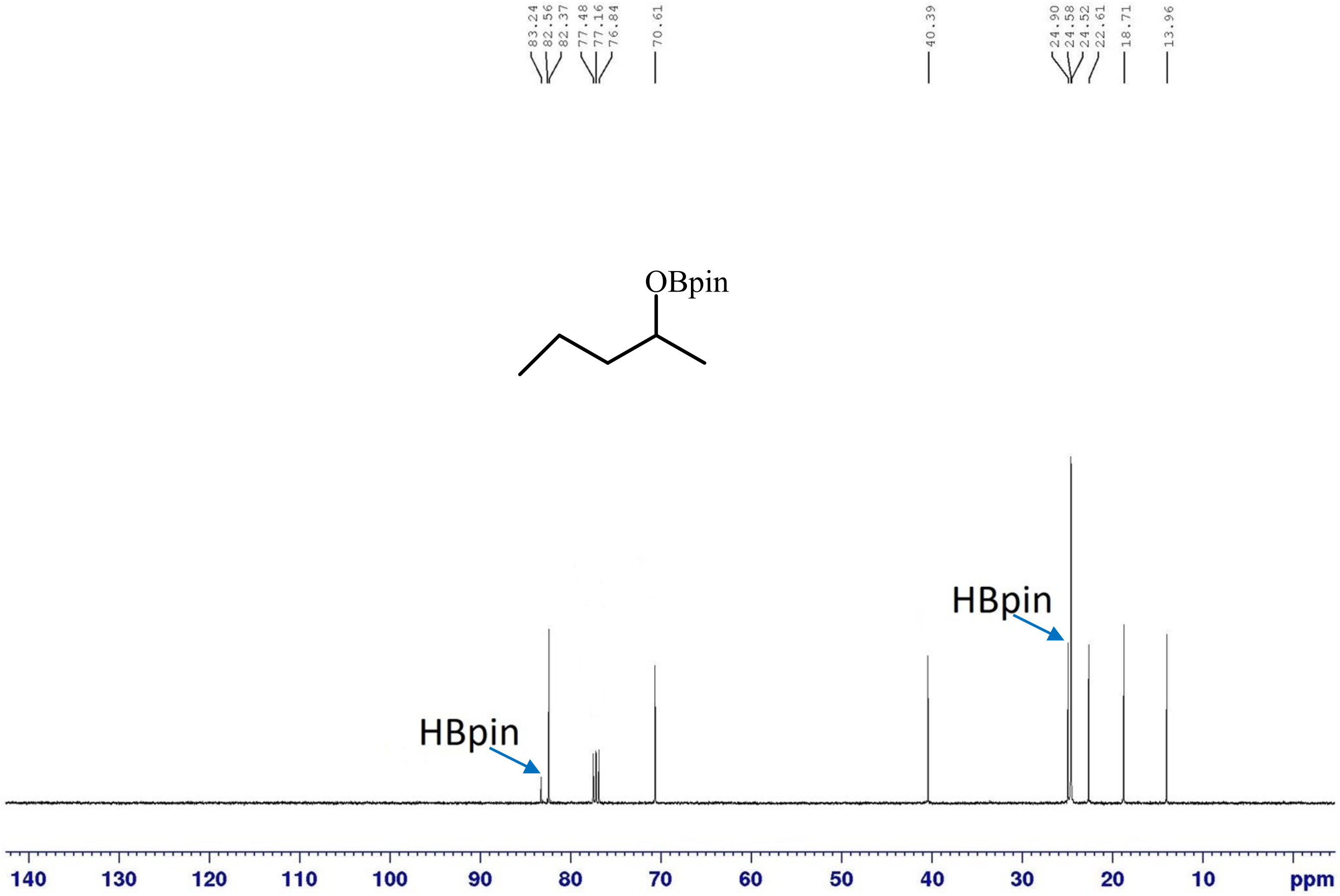
^{13}C NMR spectrum of the hydroborylated product of acetone



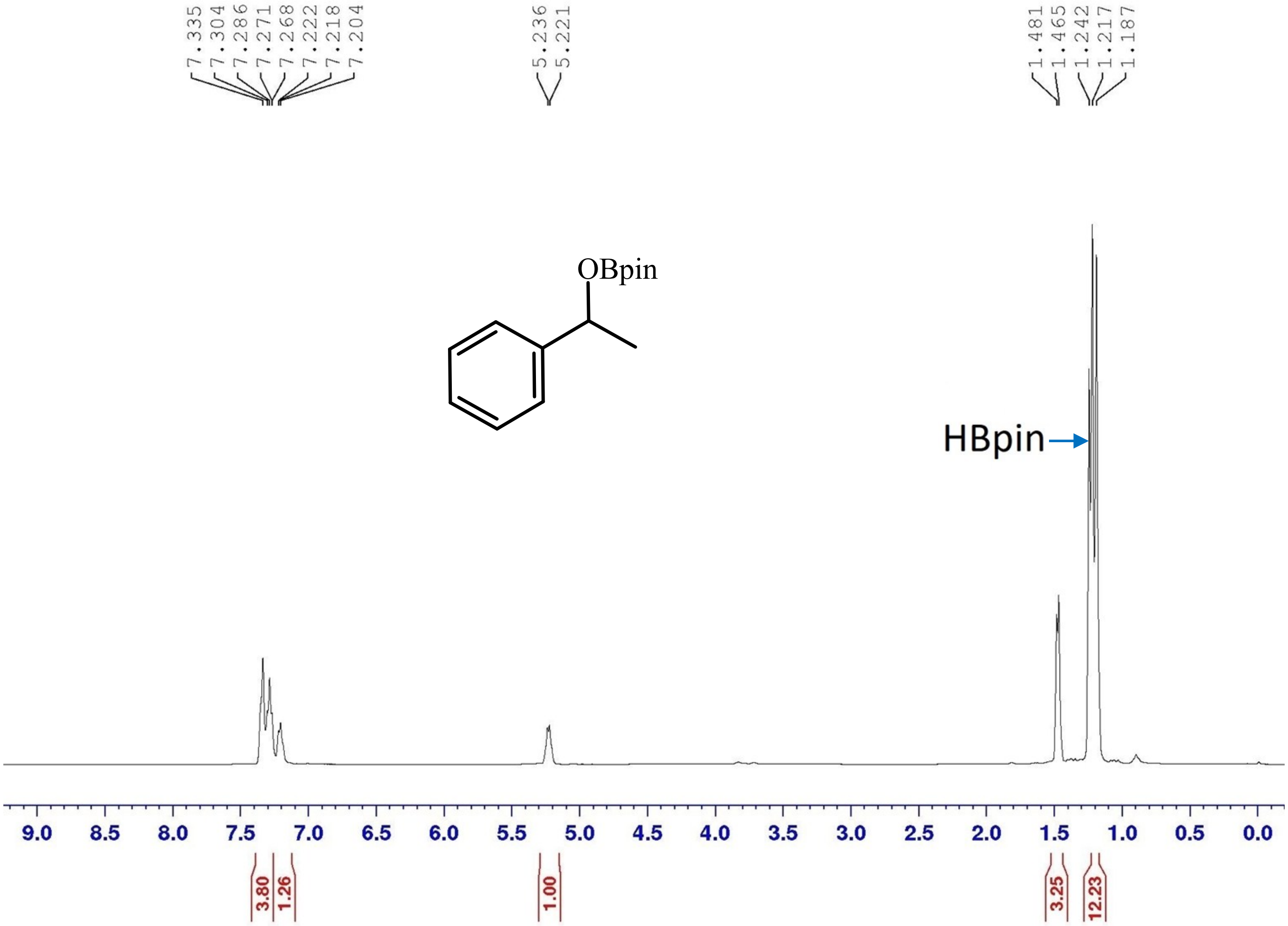
^{1}H NMR spectrum of the hydroborylated product of 2-pentanone



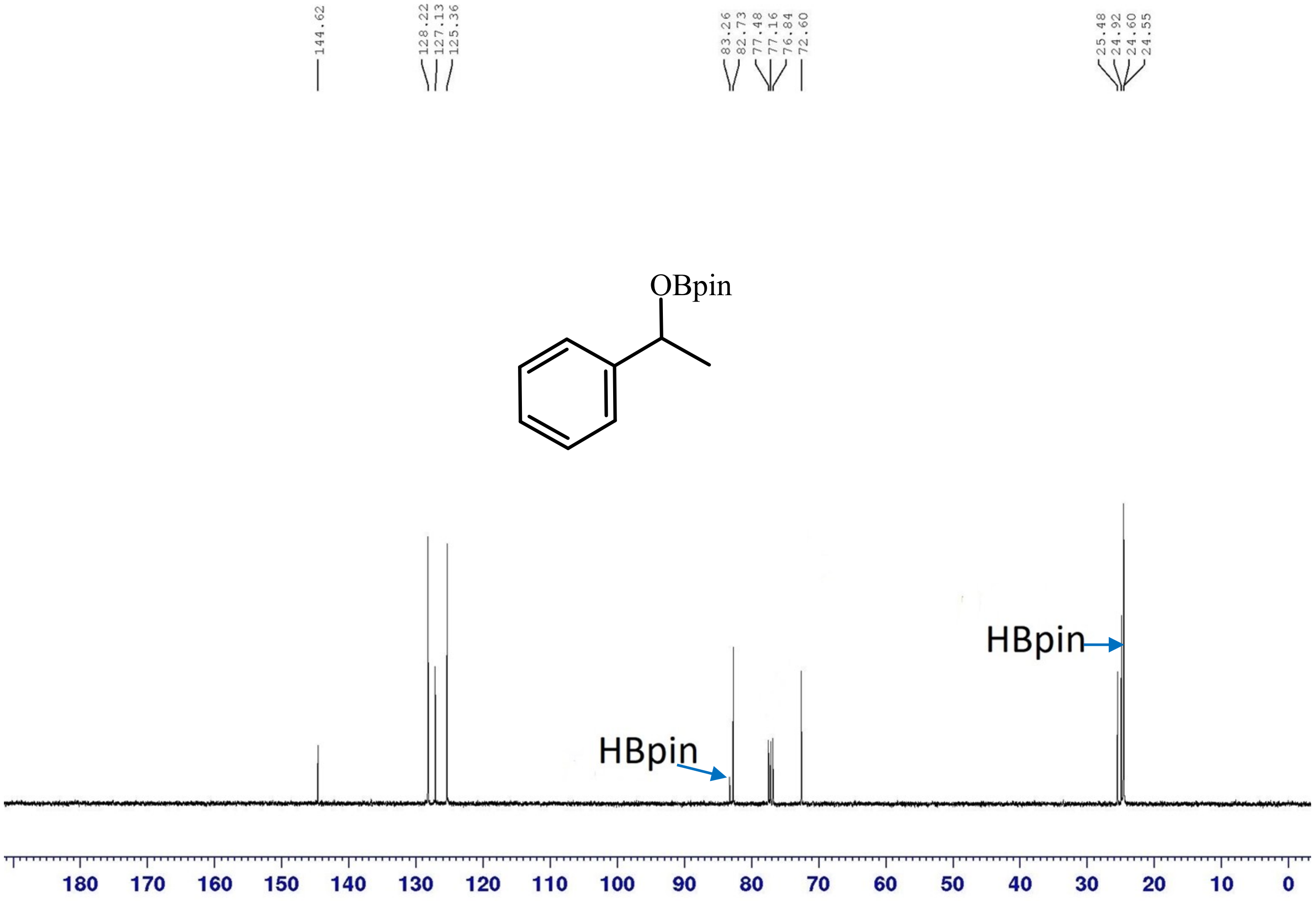
^{13}C NMR spectrum of the hydroborylated product of 2-pentanone



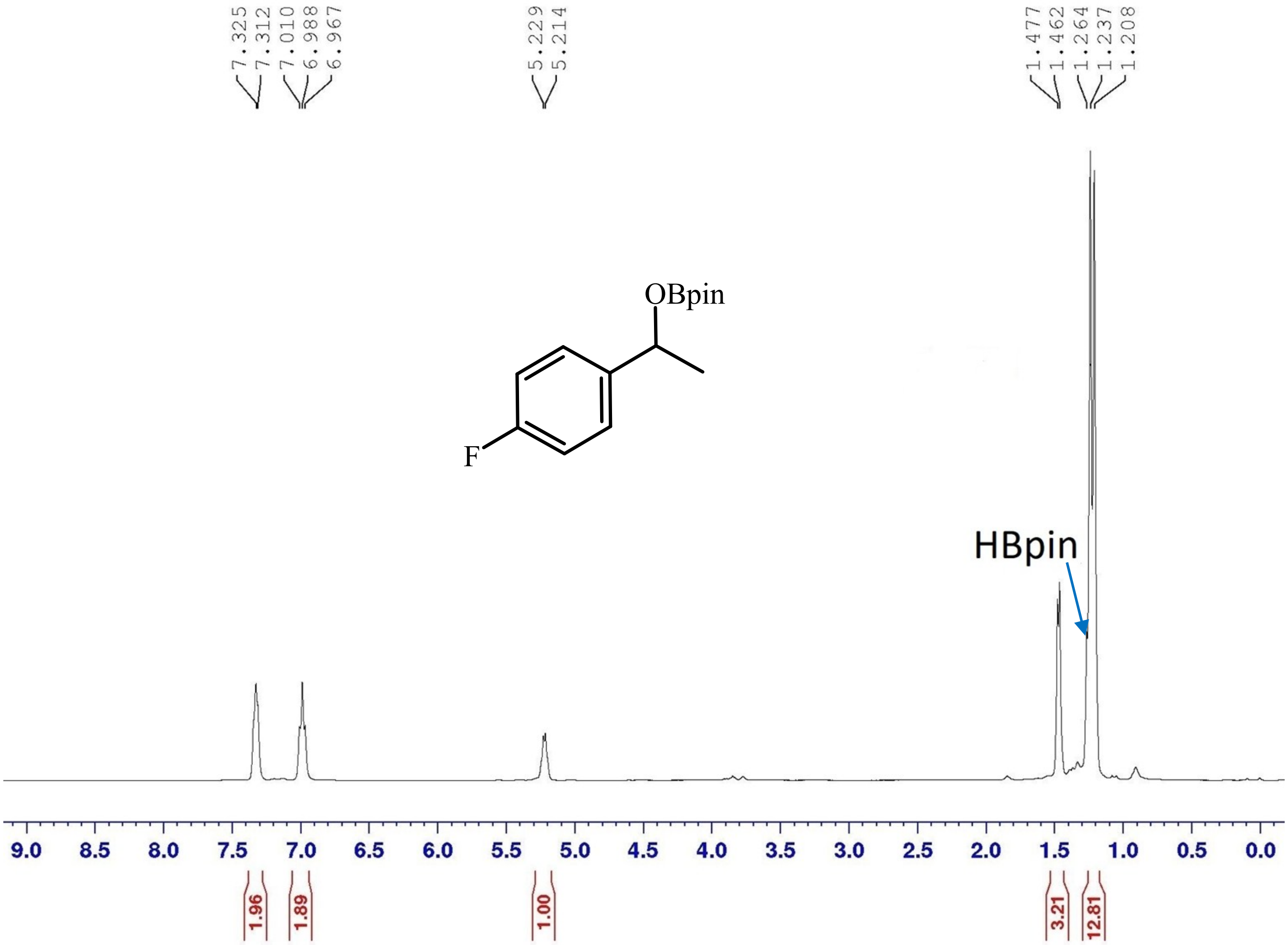
^{1}H NMR spectrum of the hydroborylated product of acetophenone



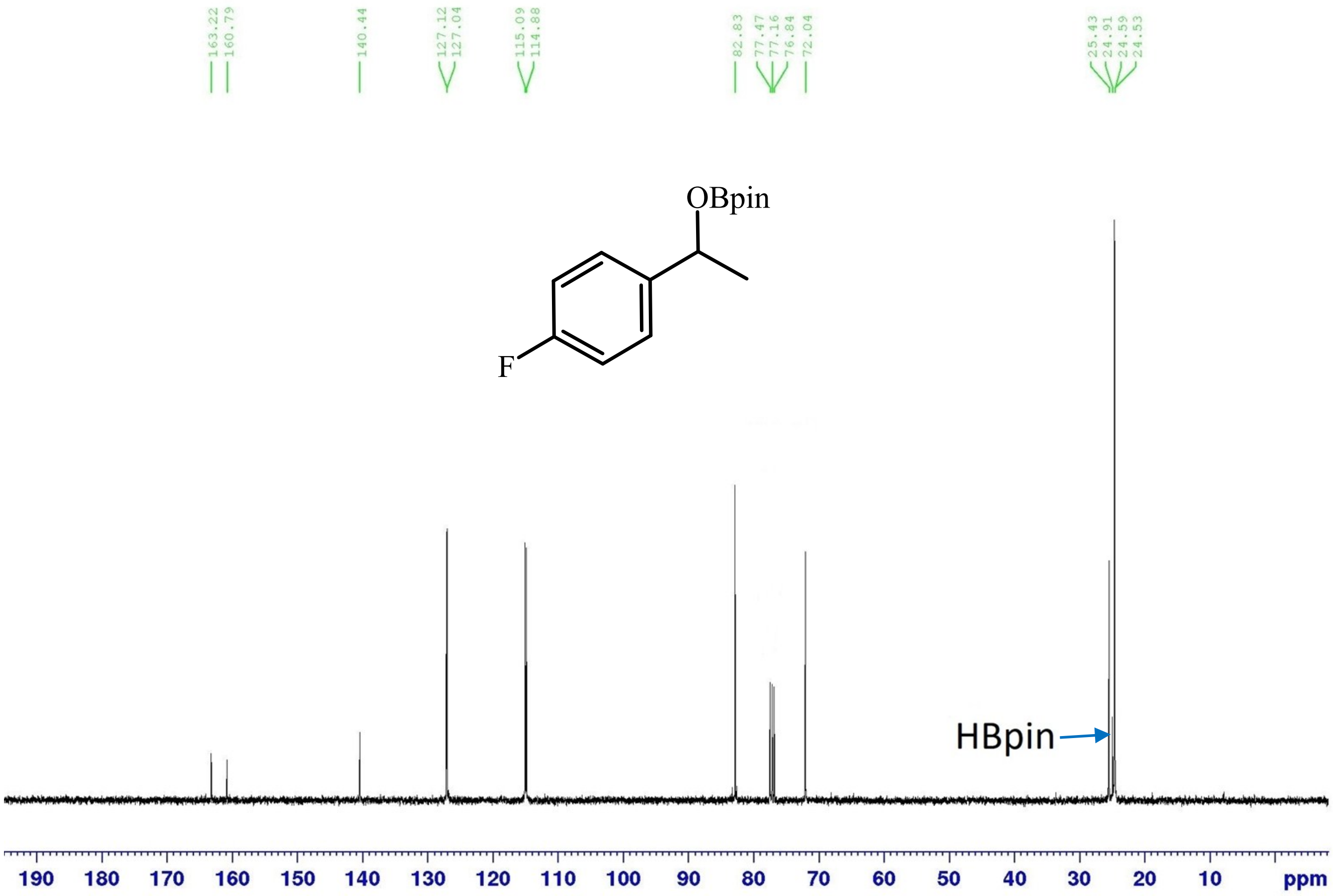
^{13}C NMR spectrum of the hydroborylated product of acetophenone



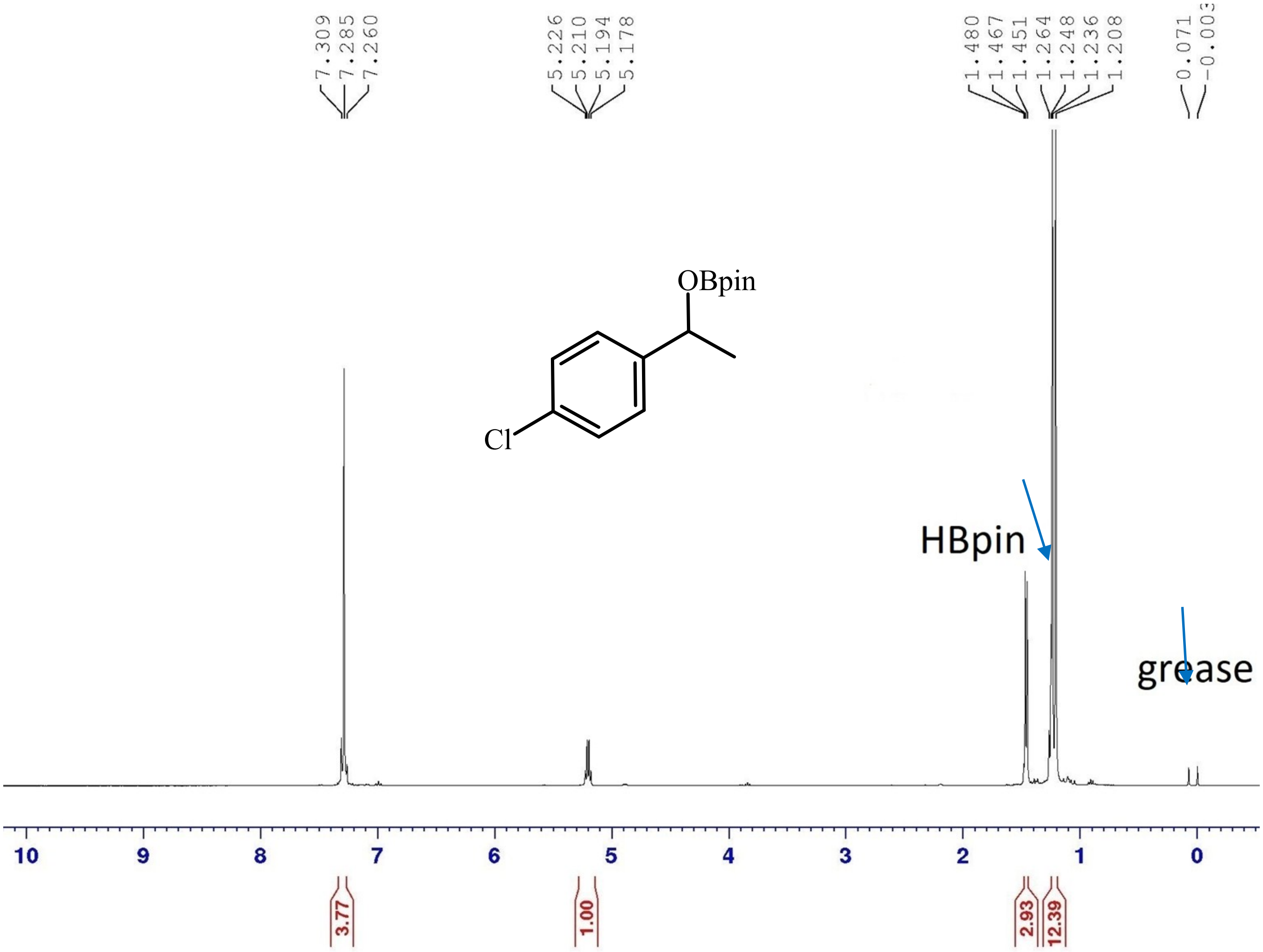
^{1}H NMR spectrum of the hydroborylated product of 4-floroacetophenone



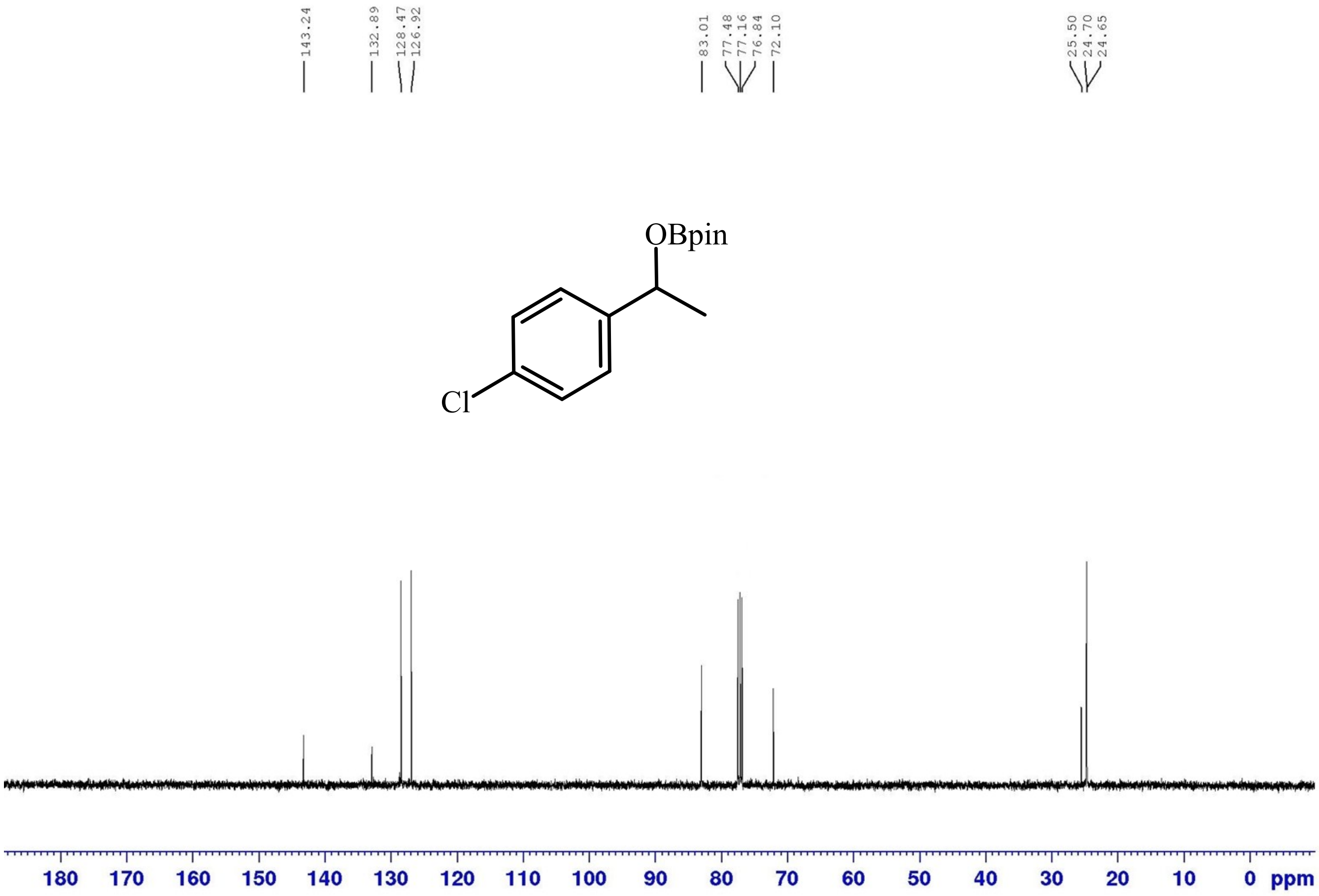
^{13}C NMR spectrum of the hydroborylated product of 4-floroacetophenone



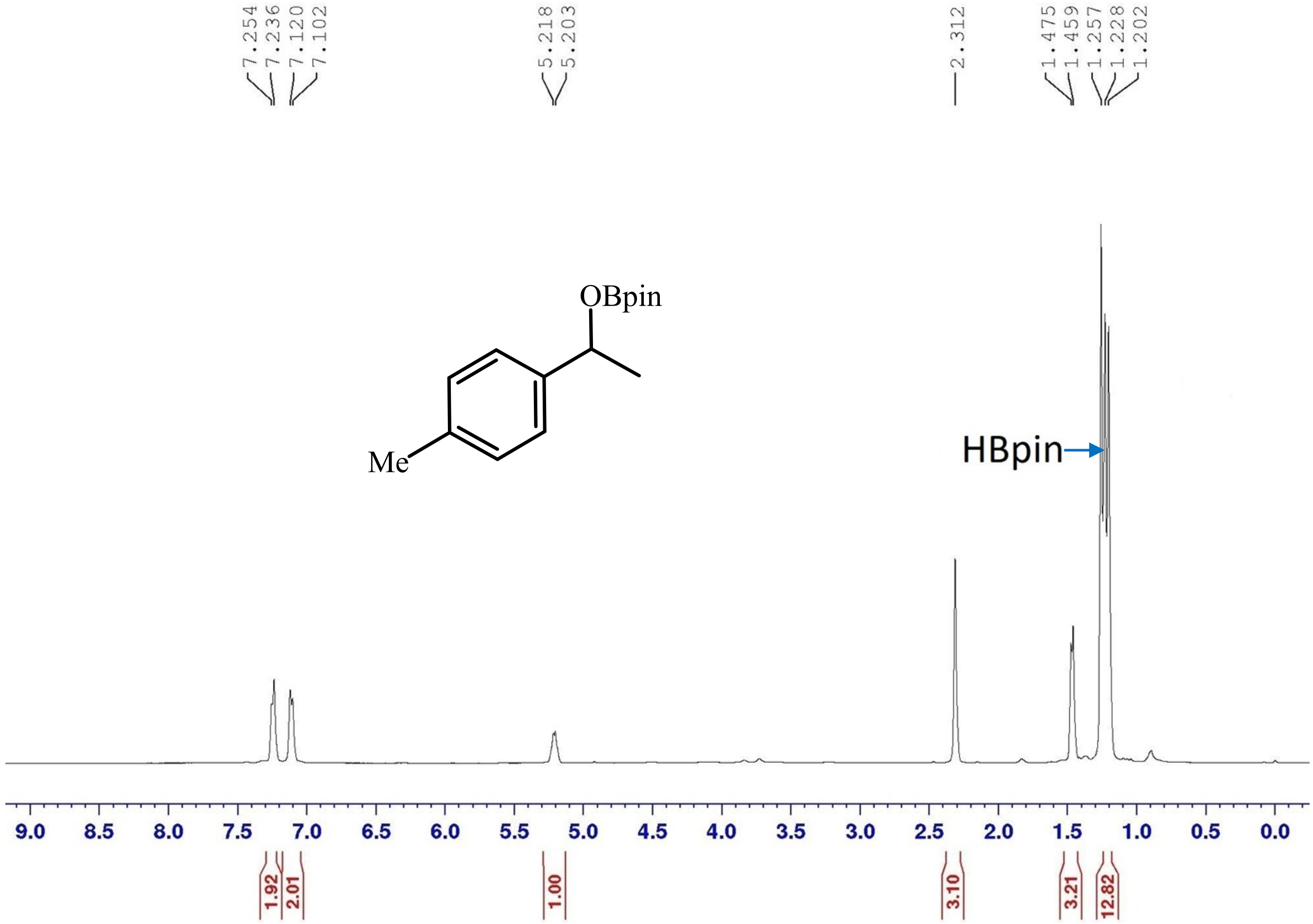
^{1}H NMR spectrum of the hydroborylated product of 4-chloroacetophenone



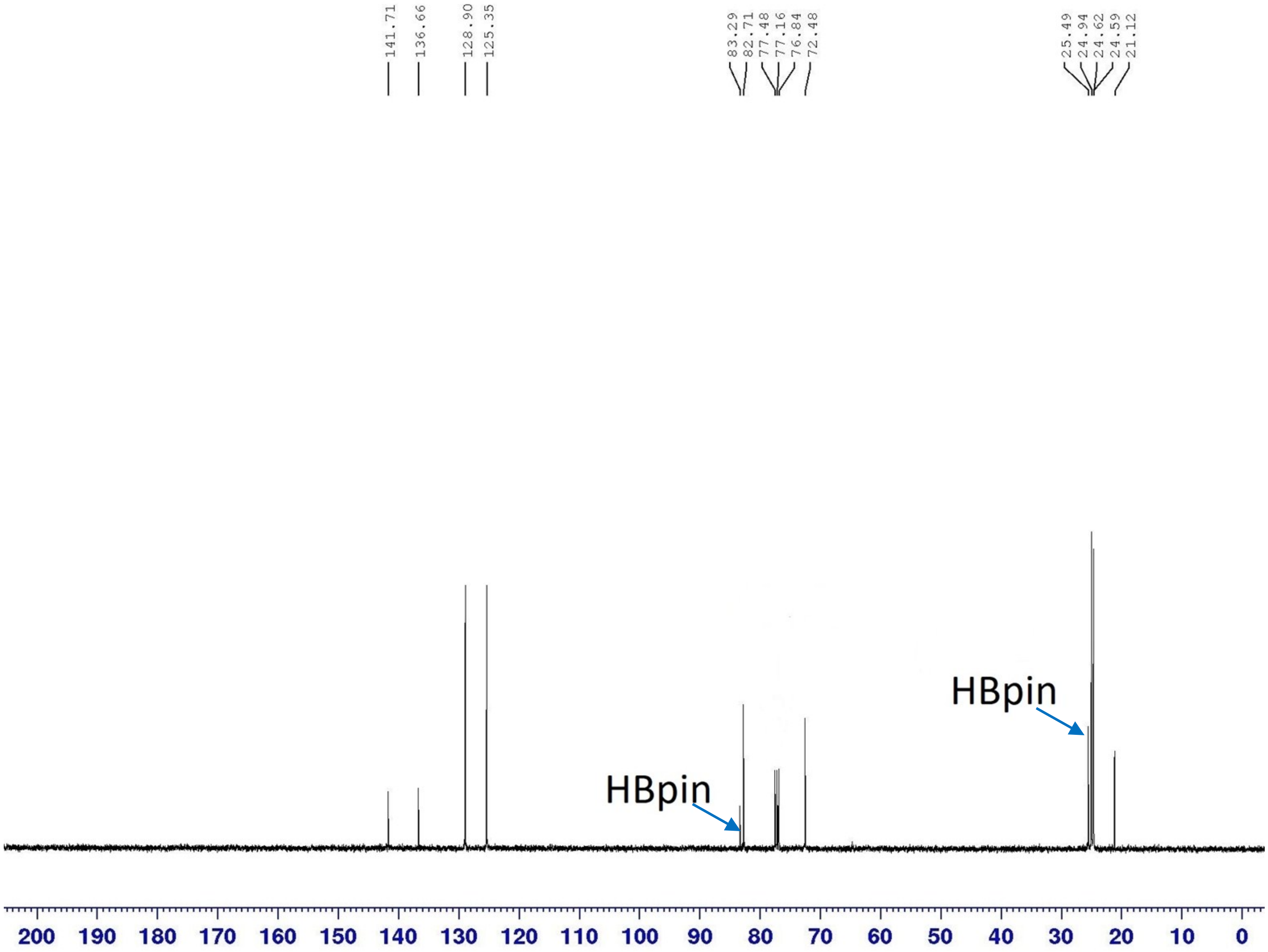
^{13}C NMR spectrum of the hydroborylated product of 4-chloroacetophenone



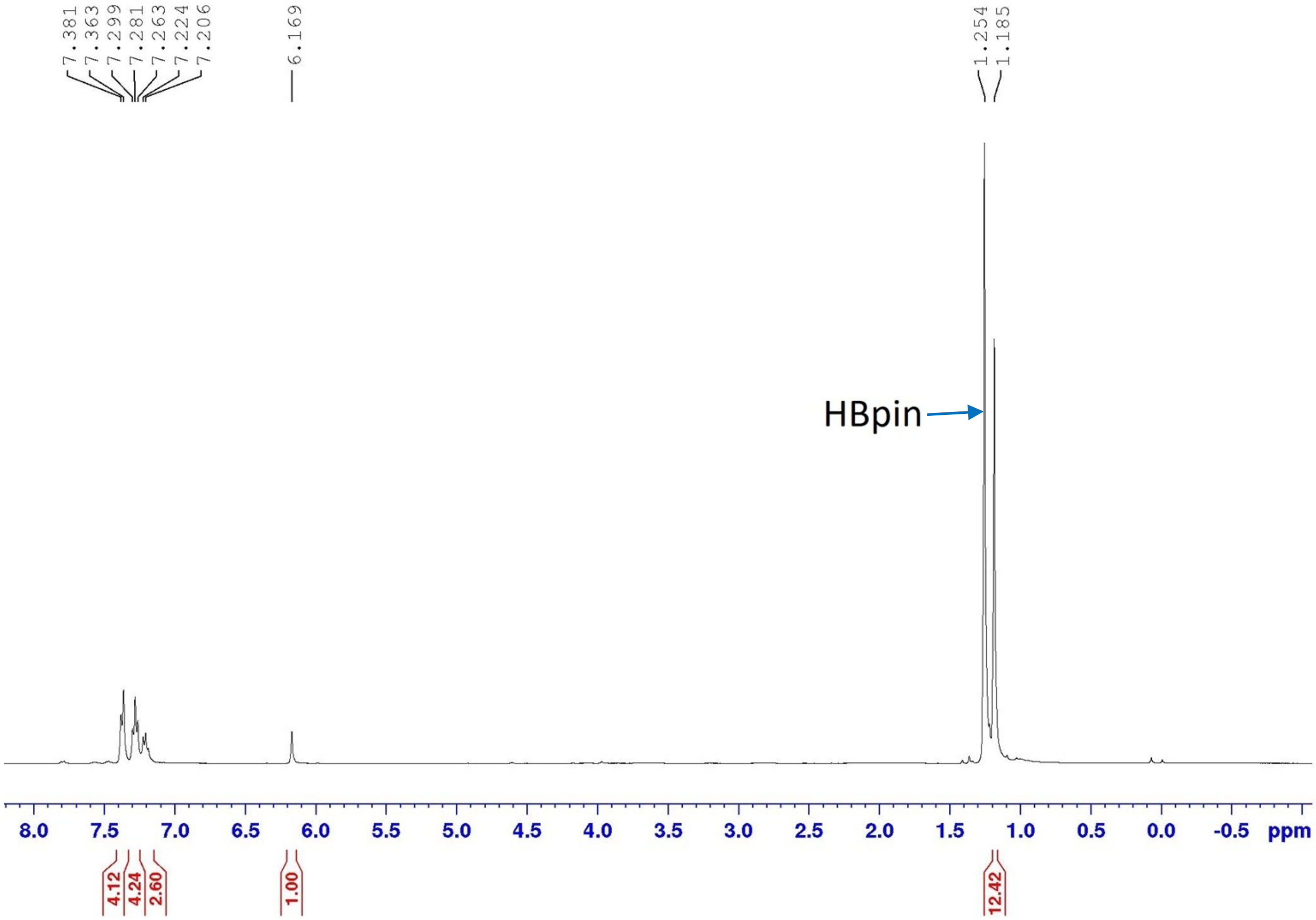
^{1}H NMR spectrum of the hydroborylated product of 4-methylacetophenone



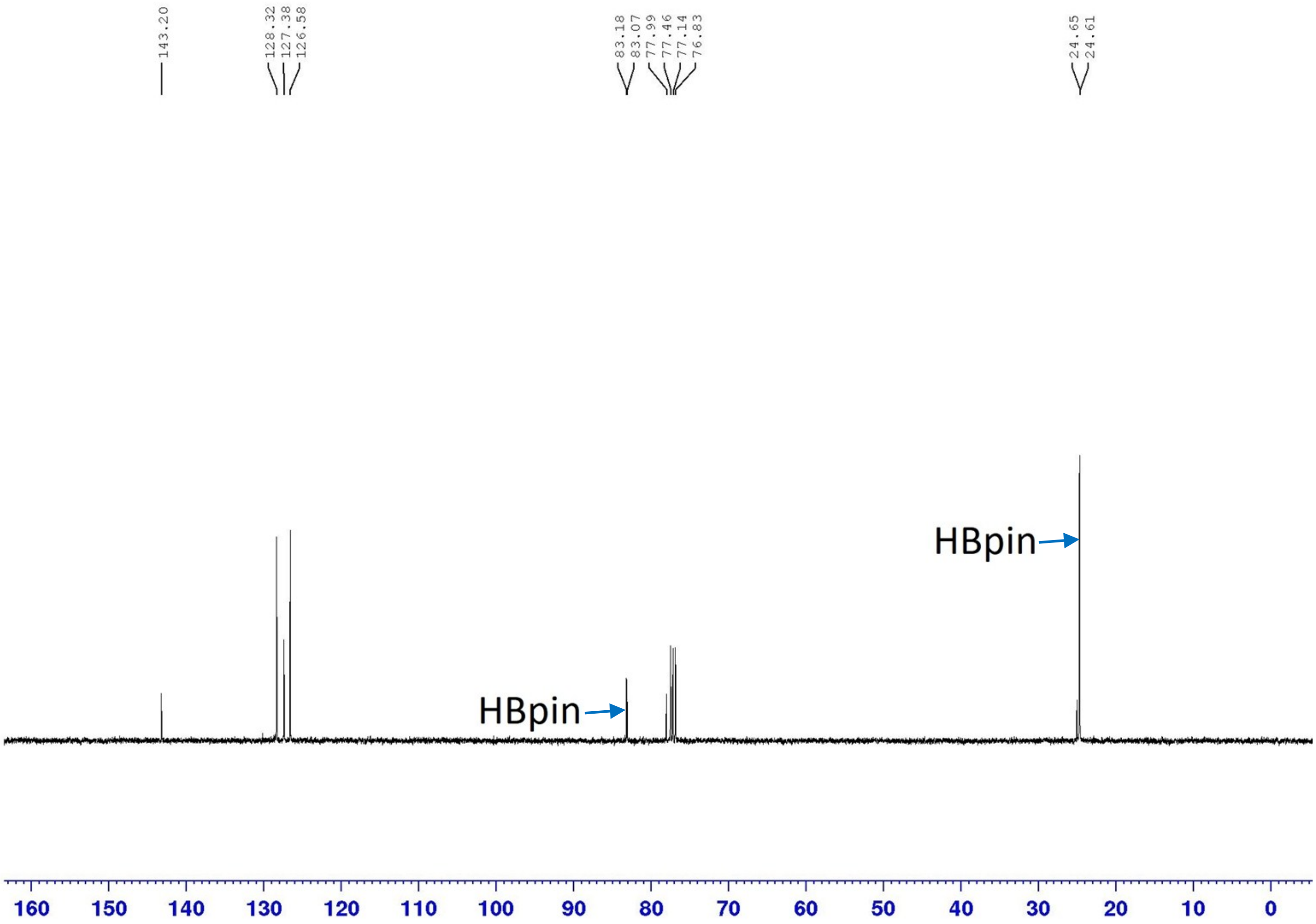
^{13}C NMR spectrum of the hydroborylated product of 4-methylacetophenone



^{1}H NMR spectrum of the hydroborylated product of benzophenone



^{13}C NMR spectrum of the hydroborylated product of benzophenone



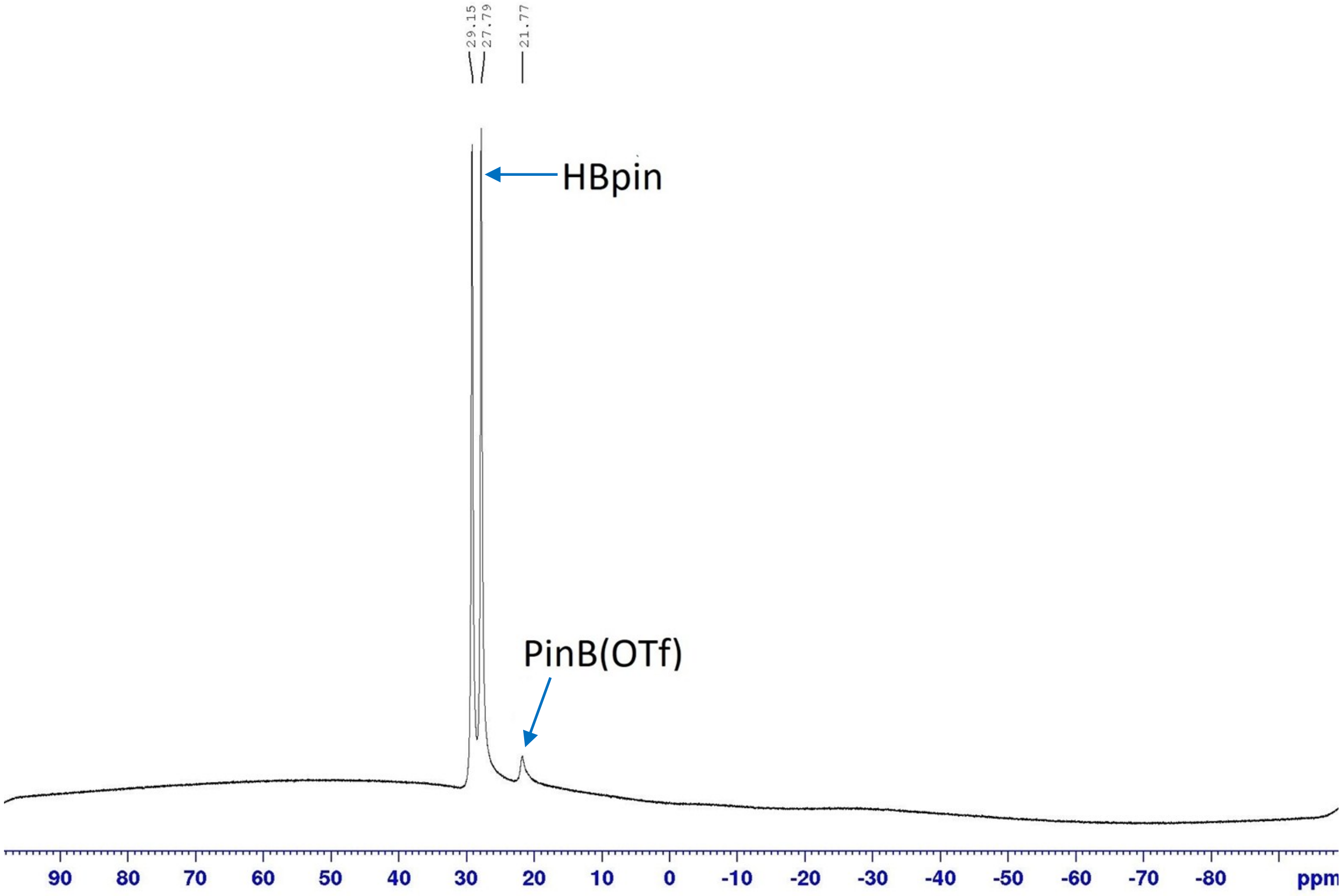


Figure S4: ^{11}B NMR spectrum for the reaction mixture containing compound 4 and HBpin (in a 1:1 molar ratio) in C_6D_6 (0.4 mL)

References

S1. R. K. Siwatch, S. Kundu, D. Kumar and S. Nagendran, *Oragnometallics*, 2011, **30**, 1998-2005.

S2. S. Sinhababu, R. K. Siwatch, G. Mukherjee, G. Rajaraman and S. Nagendran, *Inorg. Chem.*, 2012, **51**, 9240-9248.

S3. SAINT-NT, Version 6.04; Bruker AXS: Madison, WI, 2001.

S4. SHELXTL-NT, Version 6.10; Bruker AXS: Madison, WI, 2000.

S5. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B.Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao,H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N.Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian 09, Revision C.01; Gaussian, Inc.: Wallingford, CT, **2010**.

S6. F. Wheinhold, C. Landis, Valency and Bonding; Cambridge: Cambridge, **2005**.

S7. (a) A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.*, 1988, **88**, 899. (b) E. D. Glendening, A. E. Reed, J. E. Carpenter, Weinhold, F. NBO Version 3.1.