

–Supporting Information for–

**Borenum-catalyzed hydroborations of silyl-substituted alkenes and  
alkynes by a readily available N-heterocyclic carbene borane**

Anne Boussonnière, Xiangcheng Pan, Steven J. Geib and Dennis P. Curran\*

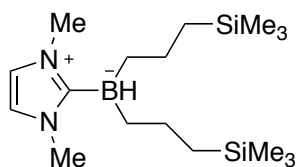
Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260,  
USA

E-mail: curran@pitt.edu

**Table of Contents**

General remarks .....	2
Experimental procedures and compound characterization data .....	3
Copies of $^1\text{H}$ , $^{11}\text{B}$ and $^{13}\text{C}$ NMR spectra of products .....	13
Figures S1–S3, X-ray Diagrams .....	50

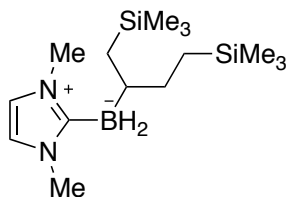
**General Remarks.** Chemicals and solvents were purchased from commercial suppliers and used as received, except as follows.  $\text{CH}_2\text{Cl}_2$  was dried by passing through an activated alumina column. Reactions were carried out under argon gas with magnetic stirring. Thin layer chromatography (TLC) was performed on Merck 60 F254 silica gel and flash column chromatography was performed with 230–400 mesh silica gel purchased from Sorbent Technologies as the stationary phase. The melting points reported were measured with a Mel-Temp II apparatus and were uncorrected. IR spectra were recorded with a Nicolet Avatar 360 FT-IR spectrometer as thin films ( $\text{CH}_2\text{Cl}_2$ ) on NaCl plates. Chemical shifts are given in ppm. Unless otherwise noted, the NMR spectra were recorded in  $\text{CDCl}_3$ . Chloroform ( $\delta = 7.27$  ppm) was used as internal standard in  $^1\text{H}$  NMR spectra, whereas  $\text{CDCl}_3$  ( $\delta = 77.16$  ppm) was used as internal standard in  $^{13}\text{C}$  NMR spectra.  $^{11}\text{B}$  chemical shifts are relative to  $\text{Et}_2\text{O}\cdot\text{BF}_3$ . Coupling constants ( $J$ ) are given in Hertz (Hz). The terms m, s, d, t, q, quint., sept. represent multiplet, singlet, doublet, triplet, quadruplet, quintuplet, septet, respectively. The term br means that the signal is broad. The signal of carbon atoms connected to the boron atom can almost never be seen in the  $^{13}\text{C}$  NMR spectra due to the quadrupole broadening and the coupling with the boron atom. Low and high resolution mass spectra (LRMS and HRMS) were obtained on a Micromass Inc. Autospec instrument with E-B-E geometry. X-ray diffractions were recorded by the Chemistry Department X-ray Diffraction Facility of the University of Pittsburgh (Dr. Steven J. Geib).



5

**1,3-Dimethylimidazol-2-ylidene bis(3-(trimethylsilyl)propyl)borane 5:** To a solution of diMe-Imd-BH<sub>3</sub> (60 mg, 0.55 mmol, 1 equiv) in CH<sub>2</sub>Cl<sub>2</sub> (1 mL) in a 10 mL flask was added I<sub>2</sub> (14 mg, 0.05 mmol, 0.1 equiv) at room temperature. Once bubbling was over, allyltrimethylsilane (0.2 mL, 1.2 mmol, 2.2 equiv) was added in one portion. The reaction was monitored by <sup>11</sup>B NMR. The solvent was evaporated and the crude oil was characterized. An attempt to purify the product by flash chromatography resulted in decomposition.

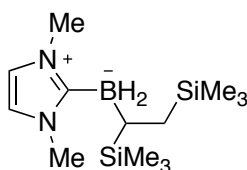
Analysis of the crude product: <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>) δ 5.62 (s, 2H, =CH(N)), 3.20 (s, 6H, *N*-CH<sub>3</sub>), 2.33 (bq, 1H, *J*<sub>H-B</sub> = 82.7 Hz, BH; in <sup>11</sup>B decoupled <sup>1</sup>H NMR, quint, *J* = 5.6 Hz), 1.81-1.70 (m, 2H, CH<sub>2</sub>), 1.58-1.45 (m, 2H, CH<sub>2</sub>), 1.20-1.08 (m, 2H, CH<sub>2</sub>), 0.97-0.86 (m, 6H, CH<sub>2</sub>), 0.13 (s, 18H, TMS); <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>): δ 119.6 (=CH(N)), 35.7 (N-CH<sub>3</sub>), 26.2 (CH<sub>2</sub>), 21.6 (CH<sub>2</sub>), -1.0 (TMS); <sup>11</sup>B NMR (128.4 MHz, C<sub>6</sub>D<sub>6</sub>) δ -19.1 (d, *J*<sub>B-H</sub> = 82.7 Hz).



6

**1,3-Dimethylimidazol-2-ylidene 1,4-bis(trimethylsilyl)butan-2-ylborane 6:** To a solution of diMe-Imd-BH<sub>3</sub> (30 mg, 0.27 mmol, 1 equiv) in CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL) in a 10 mL flask was added Tf<sub>2</sub>NH (15 mg, 0.05 mmol, 0.2 equiv) at room temperature. Once bubbling was over, 1,4-

Bis(trimethylsilyl)-2-butene<sup>1</sup> (80 mg, 0.39 mmol, 1.4 equiv) was added in one portion. The reaction was monitored by <sup>11</sup>B NMR. The crude compound was purified by chromatography (flash chromatography, SiO<sub>2</sub>, hexanes : ethyl acetate = 85 : 15 to 75 : 25) to give the title compound (49 mg, 59 %) as a colorless oil. IR (thin film, CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>)  $\nu$  = 3136, 2950, 2896, 2275, 1476, 1243, 1072, 833; <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  5.71 (s, 2H, =CH(N)), 3.21 (s, 6H, N-CH<sub>3</sub>), 2.12 (bdd, 1H,  $J_{\text{H-B}}$  = 33.5, 86.5 Hz, BH<sub>2</sub>), 1.79 (bdd, 1H,  $J_{\text{H-B}}$  = 33.5, 86.5 Hz, BH<sub>2</sub>), 1.57-1.50 (m, 1H, CH<sub>2</sub>), 1.47-1.40 (m, 1H, CH<sub>2</sub>), 1.10 (dd,  $J$  = 4.8, 14.0 Hz, 1H, CH<sub>2</sub>), 0.99-0.92 (bm, 1H, CH-B), 0.92 (ddd,  $J$  = 4.5, 12.2, 14.4 Hz, 1H, CH<sub>2</sub>), 0.84 (dd,  $J$  = 7.6, 14.0 Hz, 1H, CH<sub>2</sub>), 0.67 (ddd, 5.0, 12.2, 14.4 Hz, 1H, CH<sub>2</sub>), 0.32 (s, 9H, TMS), 0.08 (s, 9H, TMS); <sup>13</sup>C NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  119.3 (=CH(N)), 118.3 (=CH(N)), 35.3 (N-CH<sub>3</sub>), 35.1 (CH<sub>2</sub>), 24.8 (CH<sub>2</sub>), 16.1 (CH<sub>2</sub>), 0.45 (TMS), -1.3 (TMS); <sup>11</sup>B NMR (106.5 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  -23.7 (t,  $J_{\text{B-H}}$  = 85.7 Hz); HRMS (ESI) calcd. for C<sub>15</sub>H<sub>35</sub><sup>11</sup>BN<sub>2</sub>Si<sub>2</sub> ([M-H]<sup>+</sup>): 309.2354, found: 309.2361.



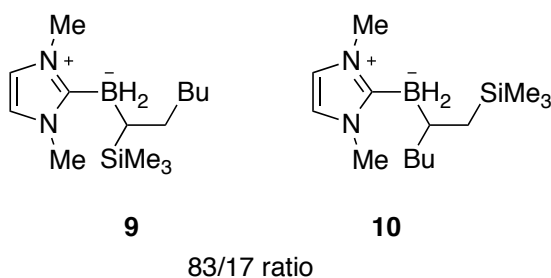
**8**

**1,3-Dimethylimidazol-2-ylidene 1,2-bis(trimethylsilyl)ethaneborane 8:** To a solution of diMe-Imd-BH<sub>3</sub> (60 mg, 0.55 mmol, 1 equiv) in CH<sub>2</sub>Cl<sub>2</sub> (1 mL) in a 10 mL flask was added Tf<sub>2</sub>NH (31 mg, 0.11 mmol, 0.2 equiv) at room temperature. Once bubbling was over, (Z)-1,2-bis(trimethylsilyl)ethene<sup>2</sup> (210 mg, 1.2 mmol, 2.2 equiv) was added in one portion. The reaction was monitored by <sup>11</sup>B NMR. The crude compound was purified by chromatography (flash chromatography, SiO<sub>2</sub>, hexanes : ethyl acetate = 85 : 15 to 75 : 25) to give the title compound (61

<sup>1</sup> Watabe, H.; Terao, J.; Kambe, N. *Org. Lett.* **2001**, 3, 1733-1735.

<sup>2</sup> Obora, Y.; Moriya, H.; Tokunaga, M.; Tsuji, Y. *Chem. Commun.* **2003**, 2820-2821.

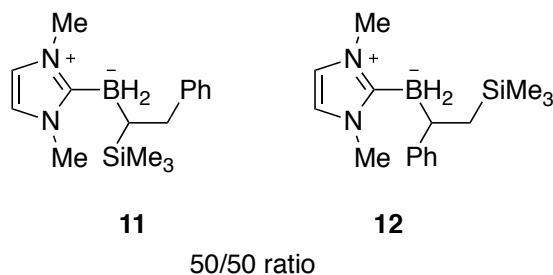
mg, 39 %) as a colorless oil. IR (thin film, CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>)  $\nu$  = 2951, 2893, 2284, 1477, 1239, 1090, 834; <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  5.63 (s, 2H, =CH(N)), 3.14 (s, 6H, N-CH<sub>3</sub>), 2.00 (bq, 2H,  $J_{\text{H-B}}$  = 86.5 Hz, BH<sub>2</sub>), 1.12 (bd, 1H,  $J$  = 14.7 Hz, CH<sub>2</sub>), 0.73 (bs, 1H, CH<sub>2</sub>), 0.32 (s, 9H, TMS), 0.05 (s, 9H, TMS), -0.12 (bs, 1H, CH-B); <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  119.4 (=CH(N)), 35.4 (N-CH<sub>3</sub>), 18.0 (CH<sub>2</sub>), -0.6 (TMS), -1.1 (TMS); <sup>11</sup>B NMR (128.4 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  -25.4 (t,  $J_{\text{B-H}}$  = 86.5 Hz); HRMS (ESI) calcd. for C<sub>13</sub>H<sub>31</sub><sup>11</sup>BN<sub>2</sub>Si<sub>2</sub> ([M-H]<sup>+</sup>): 281.2041, found: 281.2037.



**1,3-Dimethylimidazol-2-ylidene 1-(trimethylsilyl)hex-1-ylborane 9 and 1,3-dimethylimidazol-2-ylidene 1-(trimethylsilyl)hex-2-ylborane 1:** To a solution of diMe-Imd-BH<sub>3</sub> (150 mg, 1.36 mmol, 1 equiv) in CH<sub>2</sub>Cl<sub>2</sub> (2.5 mL) in a 10 mL flask was added I<sub>2</sub> (35 mg, 0.14 mmol, 0.1 equiv) at room temperature. Once bubbling was over, (Z)-1-(trimethylsilyl)-1-hexene<sup>3</sup> (266 mg, 1.7 mmol, 1.25 equiv) was added in one portion. The reaction was monitored by <sup>11</sup>B NMR. The crude compound was purified by chromatography (flash chromatography, SiO<sub>2</sub>, hexanes : ethyl acetate = 80 : 20 to 60 : 40) to give the title compounds (178 mg, 49 % as a mixture of two regioisomers in a 83:17 ratio) as a colorless oil. A second flash chromatography again produced mostly mixed fractions, but the pure major regioisomer **9** was isolated in small quantity. IR (thin film, CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>)  $\nu$  = 3138, 2952, 2869, 2281, 1476, 1235, 1088, 856, 830; <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  5.65 (s, 2H, =CH(N)), 3.14 (s, 6H, N-CH<sub>3</sub>), 2.26-1.69 (bm, 2H, BH<sub>2</sub>), 1.80 (bs,

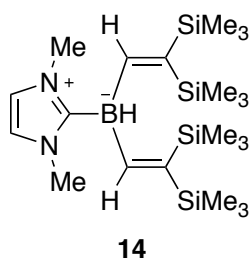
<sup>3</sup> Miura, K.; Inoue, G.; Sasagawa, H.; Kinoshita, H.; Ichikawa, J.; Hosomi, A. *Org. Lett.* **2009**, *11*, 5066-5069.

2H,  $CH_2$ ), 1.50-1.26 (m, 6H,  $CH_2$ ), 0.91 (t, 3H,  $J = 6.9$  Hz,  $CH_3$ ), 0.46 (s, 9H, TMS), -0.06 (bs, 1H,  $CH-B$ );  $^{13}C$  NMR (125 MHz,  $C_6D_6$ ):  $\delta$  119.2 ( $=CH(N)$ ), 35.3 (N- $CH_3$ ), 33.33 ( $CH_2$ ), 33.30 ( $CH_2$ ), 32.3 ( $CH_2$ ), 23.3 ( $CH_2$ ), 14.5 ( $CH_3$ ), -0.3 (TMS);  $^{11}B$  NMR (160.5 MHz,  $C_6D_6$ )  $\delta$  -27.0 (t,  $J_{B-H} = 86.1$  Hz); HRMS (ESI) calcd. for  $C_{14}H_{31}^{11}BN_2Si$  ( $[M-H]^+$ ): 265.2271, found: 265.2276.



**1,3-Dimethylimidazol-2-ylidene 2-phenyl-1-(trimethylsilyl)ethyl borane 11 and 1,3-Dimethylimidazol-2-ylidene 1-phenyl-2-(trimethylsilyl)ethyl borane 12:** Iodine (25.4 mg, 0.1 mmol) was added to a solution of diMe-Imd-BH<sub>3</sub> (110.0 mg, 1.0 mmol) and (*Z*)-trimethyl(styryl)silane<sup>3</sup> (211.2 mg, 1.2 mmol) in  $CH_2Cl_2$  (1 mL). The solution was charged to a small vial and stirred for 2 d. The solvent was evaporated and the crude product was purified by flash column chromatography to ~1:1 mixture of two regioisomers (205.5 mg, 72%) as colorless liquid.  $^1H$  NMR (400 MHz,  $C_6D_6$ ,  $^{11}B$  decoupled) one regioisomer:  $\delta$  5.44 (s, 2H,  $=CH-N$ ), 2.93 (s, 6H, N- $CH_3$ ), 0.49 (s, 9H, TMS); another regioisomer:  $\delta$  5.53 (s, 2H,  $=CH-N$ ), 2.82 (s, 6H, N- $CH_3$ ), 0.27 (s, 9H, TMS); overlapping peaks: 7.09–6.95 (m, 5H, aromatic *H*), 3.25 (brs, 1H, B-*CH*), 2.55 (t,  $J = 11.2$  Hz, 1H, B-*CH*), 2.34 (brs, 2H,  $CH_2$ ), 2.30–1.55 (m, 4H,  $CH_2 + BH_2$ );  $^{13}C$  NMR (75 MHz,  $CDCl_3$ )  $\delta$  156.7 (aromatic C), 147.2 (aromatic C), 127.7 (aromatic C), 127.3 (aromatic C), 127.2 (aromatic C), 126.4 (aromatic C), 124.1 (aromatic C), 122.1 (aromatic C), 119.8 ( $=CH-N$ ), 119.6 ( $=CH-N$ ), 38.3 ( $CH_2$ ), 35.7 (N- $CH_3$ ), 35.4 (N- $CH_3$ ), 24.5 ( $CH_2$ ), -0.4 (TMS), -1.5 (TMS);  $^{11}B$  NMR (128.4 MHz,  $C_6D_6$ )  $\delta$  -21.0 (t,  $J_{B-H} = 90$  Hz) and -27.0 (t,  $J_{B-H} =$

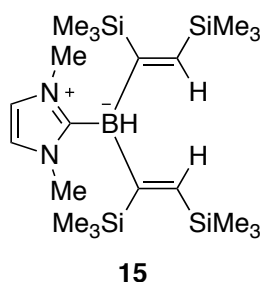
86 Hz); IR (thin film, CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>) 3169, 3136, 3057, 3019, 2949, 2890, 2286, 1596, 1574, 1480, 1450, 1237, 1110, 862, 833; HRMS (ESI) m/z (M<sup>+</sup>-H ) calculated for C<sub>16</sub>H<sub>26</sub><sup>11</sup>BN<sub>2</sub>Si 285.1958, found 285.1965.



**1,3-Dimethylimidazol-2-ylidene bis(2,2-di(trimethylsilyl)vinyl)borane 14:** To a solution of diMe-Imd-BH<sub>3</sub> (30 mg, 0.27 mmol, 1 equiv) in CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL) in a 10 mL flask was added Tf<sub>2</sub>NH (15 mg, 0.05 mmol, 0.2 equiv) at room temperature. Once bubbling was over, bis(trimethylsilyl)acetylene (140 mg, 0.82 mmol, 3 equiv) was added in one portion. The reaction was monitored by <sup>11</sup>B NMR. The crude compound was purified by chromatography (flash chromatography, SiO<sub>2</sub>, hexanes : ethyl acetate = 100 : 0 to 90 : 10) to give the title compound (55 mg, 44 %) as a white solid. mp 84–86 °C; IR (thin film, CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>) ν = 2949, 2895, 2335, 1482, 1240, 1036, 836; <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>) δ 7.93 (d, 2H, *J* = 6.4 Hz, =CH(B)), 5.54 (s, 2H, =CH(N)), 3.09 (s, 6H, *N*-CH<sub>3</sub>), 3.08 (bq, 1H, *J*<sub>H-B</sub> = 86.8 Hz, BH), 0.37 (s, 18H, TMS), 0.33 (s, 18H, TMS); <sup>13</sup>C NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>): δ 147.5 (=C(TMS)<sub>2</sub>), 120.3 (=CH(N)), 36.7 (*N*-CH<sub>3</sub>), 2.9 (TMS), 1.5 (TMS); <sup>11</sup>B NMR (160.5 MHz, C<sub>6</sub>D<sub>6</sub>) δ -19.3 (t, *J*<sub>B-H</sub> = 86.8 Hz); HRMS (ASAP) calcd. for C<sub>21</sub>H<sub>48</sub><sup>11</sup>BN<sub>2</sub>Si<sub>4</sub> ([M-H]<sup>+</sup>): 450.2909, found: 450.2923.

**Crystal structure of 14:** Crystals of pure product were obtained by vaporizing the solvent (CH<sub>2</sub>Cl<sub>2</sub>) of the solution of the complex. Crystals of **14** diffracted strongly but with reflections

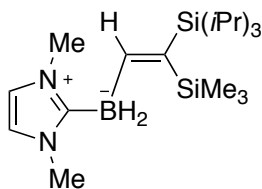
which were significantly aspherical. The structure was solved via direct methods readily showing all non-hydrogen atoms. Hydrogen atoms were calculated in idealized positions. The structure only refined to a RF value of 20.5% with most anisotropic displacement parameters appearing significantly anisotropic. Atom C6 required isotropic refinement. The program ROTAX indicates non-merohedral twinning ; however, refinement utilizing the twin law did not give significant improvement. Although bond lengths and angles should not be relied upon as being extremely accurate and anisotropic displacement parameters are behaving poorly, we are confident in the identities of atoms and their connectivity for the structure of **14**.



**1,3-Dimethylimidazol-2-ylidene bis(1,2-bis(trimethylsilyl)vinyl)borane 15:** To a solution of bis(trimethylsilyl)acetylene (0.69 g, 4 mmol, 2 equiv) in THF (10 mL) at 0°C was added BH<sub>3</sub>·THF (2 mL, 1M in THF, 2 mmol, 1 equiv) dropwise. The mixture was stirred for 1h at 0°C. In parallel, a solution of sodium bis-(trimethylsilyl) amide (2.3 mL, 1M in THF, 2.3 mmol, 1.15 equiv) was added to a suspension of the corresponding 1,3-dimethylimidazolium iodide<sup>35</sup> (0.5 g, 2.2 mmol, 1.1 equiv) in THF (10 mL) at −78 °C. The yellow mixture was stirred at −78 °C for 30 min, before slow addition of the tetra(trimethylsilyl)divinylborane solution by cannula at the same temperature. The resulting yellow mixture was stirred at −78 °C to room temperature for 18 h, and evaporated. The crude compound was purified by chromatography (flash chromatography, SiO<sub>2</sub>, hexanes : ethyl acetate = 100 : 0 to 90 : 10) to give the title compound (55 mg, 34 %) as a



white solid. mp 68–70 °C; IR (thin film, CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>)  $\nu$  = 3142, 2950, 2895, 2265, 1474, 1242, 1070, 840; <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  6.49 (bs, 2H, =CH), 5.64 (s, 2H, =CH(N)), 3.11 (s, 6H, *N*-CH<sub>3</sub>), 0.35 (s, 9H, TMS), 0.33 (s, 9H, TMS); <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  150.0 (=CH), 119.8 (=CH(N)), 36.2 (N-CH<sub>3</sub>), 2.17 (TMS), 1.75 (TMS); <sup>11</sup>B NMR (128.4 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  -13.7 (d,  $J_{\text{B-H}}$  = 81.3 Hz); HRMS (ASAP) calcd. for C<sub>21</sub>H<sub>48</sub><sup>11</sup>BN<sub>2</sub>Si<sub>4</sub> ([M-H]<sup>+</sup>): 450.2909, found: 450.2906.

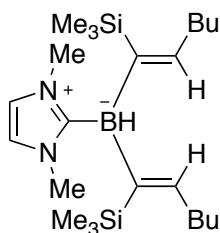


**18**

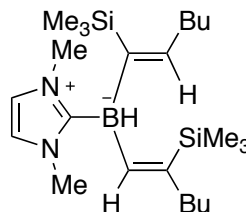
**1,3-Dimethylimidazol-2-ylidene (*E*)-(2-(triisopropylsilyl)-2-(trimethylsilyl)vinylborane 18:**

To a solution of diMe-Imd-BH<sub>3</sub> (240 mg, 2.2 mmol, 1 equiv) in CH<sub>2</sub>Cl<sub>2</sub> (4 mL) in a 25 mL flask was added Tf<sub>2</sub>NH (122 mg, 0.44 mmol, 0.2 equiv) at room temperature. Once bubbling was over, (triisopropylsilyl)(trimethylsilyl)acetylene<sup>4</sup> (835 mg, 3.3 mmol, 1.5 equiv) was added in one portion. The reaction was monitored by <sup>11</sup>B NMR. The crude compound was purified by chromatography (flash chromatography, SiO<sub>2</sub>, hexanes : ethyl acetate = 80 : 20 to 70 : 30) to give the title compound (306 mg, 38 %) as a white solid. mp 85–88 °C; IR (thin film, CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>)  $\nu$  = 3118, 2942, 2864, 2318, 1477, 1454, 1235, 1075, 838; <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  7.88 (t, 1H,  $J$  = 4.9 Hz, =CH(B)), 5.56 (s, 2H, =CH(N)), 3.10 (s, 6H, *N*-CH<sub>3</sub>), 2.66 (bq, 2H,  $J_{\text{H-B}}$  = 86.8 Hz, BH<sub>2</sub>), 1.47-1.38 (m, 3H, SiCH(CH<sub>3</sub>)<sub>2</sub>), 1.29 (d, 18H,  $J$  = 7.2 Hz, SiCH(CH<sub>3</sub>)<sub>2</sub>), 0.75 (s, 9H, TMS); <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  140.2 (=C(TMS)TIPS), 119.5 (=CH(N)), 35.5 (N-CH<sub>3</sub>), 19.9 (SiCH(CH<sub>3</sub>)<sub>2</sub>), 13.0 (SiCH(CH<sub>3</sub>)<sub>2</sub>), 3.3 (TMS); <sup>11</sup>B NMR (128.4 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  -26.1 (t,  $J_{\text{B-H}}$  = 86.8 Hz); HRMS (ASAP) calcd. for C<sub>19</sub>H<sub>42</sub><sup>11</sup>BN<sub>2</sub>Si<sub>2</sub> ([M-H]<sup>+</sup>): 365.2980, found: 365.3011.

<sup>4</sup> Nicolai, S.; Erard, S. P.; González, D. F. N.; Waser, J. R. M. *Org. Lett.* **2010**, *12*, 384-387.



**19**



**20**

**1,3-Dimethylimidazol-2-ylidene (*E*)-bis(1-(trimethylsilyl)-2-(butyl)vinyl)borane **19** and**

**1,3-Dimethylimidazol-2-ylidene (*E*)-(1-(trimethylsilyl)-2-(butyl)vinyl)-(Z)-(2-(trimethylsilyl)-2-(butyl)vinyl)borane **20**:**

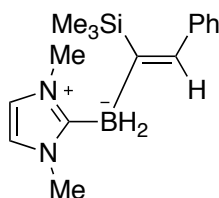
To a solution of diMe-Imd-BH<sub>3</sub> (110 mg, 1 mmol, 1 equiv) in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) in a 10 mL flask was added Tf<sub>2</sub>NH (56 mg, 0.2 mmol, 0.2 equiv) at room temperature. Once bubbling was over, 1-(trimethylsilyl)-1-hexyne (0.6 mL, 3 mmol, 3 equiv) was added in one portion. The reaction was monitored by <sup>11</sup>B NMR. The crude mixture was purified by chromatography (flash chromatography, SiO<sub>2</sub>, hexanes : ethyl acetate = 100 : 0 to 95 : 5) to give the the major isomer **19** ( 179 mg, 43 %) as a colorless oil and the minor isomer **20** (42 mg, 10 %) as a colorless oil. IR (mixture of two isomers, thin film, CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>)  $\nu$  = 3141, 2953, 2863, 2265, 1577, 1472, 1238, 1069, 830.

Major isomer **19**: <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  5.86 (bs, 2H, =CH), 5.68 (s, 2H, =CH(N)), 3.21 (s, 6H, N-CH<sub>3</sub>), 2.55-2.46 (m, 2H, CH<sub>2</sub>-CH=), 2.44-2.35 (m, 2H, CH<sub>2</sub>-CH=), 1.56-1.38 (m, 8H, CH<sub>2</sub>), 0.96 (t, 6H, *J* = 7.2 Hz, CH<sub>3</sub>), 0.39 (s, 18H, TMS); <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  146.3 (=CH), 119.6 (=CH(N)), 36.0 (N-CH<sub>3</sub>), 35.6 (CH<sub>2</sub>), 33.4 (CH<sub>2</sub>), 23.1 (CH<sub>2</sub>), 14.5 (CH<sub>3</sub>), 1.9 (TMS); <sup>11</sup>B NMR (128 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  -16.2 (d, *J*<sub>B-H</sub> = 77.9 Hz); HRMS (ASAP) calcd. for C<sub>23</sub>H<sub>47</sub><sup>11</sup>BN<sub>2</sub>Si<sub>2</sub> ([M-H]<sup>+</sup>): 417.3293, found: 417.3288.

Minor isomer **20**: <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>)  $\delta$  6.78 (d, 1H, *J* = 7.2 Hz, =CH(B)), 5.99 (bt, 1H, *J* = 6.5 Hz, =CH(*n*Bu)), 5.63 (s, 2H, =CH(N)), 3.21 (s, 6H, N-CH<sub>3</sub>), 2.55-2.36 (m, 4H, CH<sub>2</sub>-CH=), 1.71-1.36 (m, 8H, CH<sub>2</sub>), 1.00 (t, 3H, *J* = 7.3 Hz, CH<sub>3</sub>), 0.96 (t, 3H, *J* = 7.2 Hz, CH<sub>3</sub>), 0.39 (s, 9H,

TMS), 0.33 (s, 9H, TMS);  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  145.5 (=CH), 145.0 (=CH), 119.8 (=CH(N)), 36.0 (N-CH<sub>3</sub>), 35.5 (CH<sub>2</sub>), 34.8 (CH<sub>2</sub>), 33.4 (CH<sub>2</sub>), 23.4 (CH<sub>2</sub>), 23.1 (CH<sub>2</sub>), 14.48 (CH<sub>3</sub>), 14.46 (CH<sub>3</sub>), 2.1 (TMS), 1.6 (TMS);  $^{11}\text{B}$  NMR (128 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  -18.4 (d,  $J_{\text{B-H}}$  = 81.7 Hz);

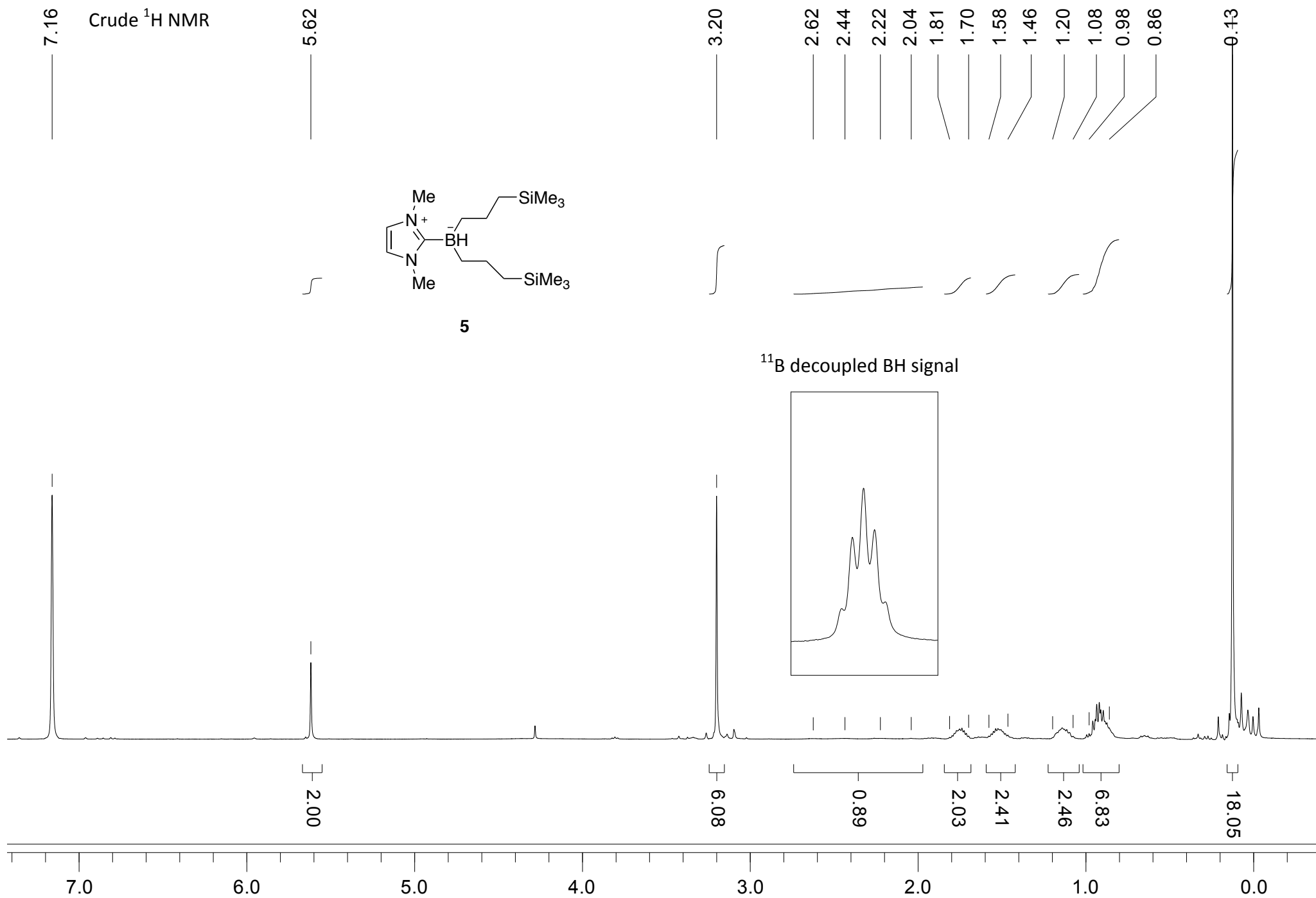
**Oxidation of 19 to hexanoic acid:** Direct oxidation **19** with NaOH, H<sub>2</sub>O<sub>2</sub> in methanol was not successful; the starting material remained intact. Reaction of **19** with BF<sub>3</sub>•Et<sub>2</sub>O (1.15 equiv) in CH<sub>2</sub>Cl<sub>2</sub> formed diMe-Imd-BF<sub>3</sub> with simultaneous liberation of the borane part of **19**. Subsequent addition of NaOH, H<sub>2</sub>O<sub>2</sub> and methanol and vigorous stirring provide hexanoic acid after acidic workup.



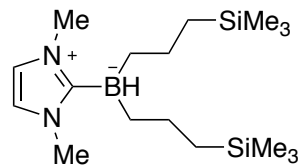
**22**

**1,3-Dimethylimidazol-2-ylidene (Z)-(2-phenyl-1-(trimethylsilyl)vinyl) borane 22:** Iodine (25.4 mg, 0.1 mmol) was added to a solution of diMe-Imd-BH<sub>3</sub> (110.0 mg, 1.0 mmol) and 1-phenyl-2-trimethylsilylacetylene (191.7 mg, 1.1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1 mL). The solution was charged to a small vial and stirred for 4 h. The solvent was evaporated and the crude product was purified by flash column chromatography to give the title compound (97.8 mg, 34%) as a white crystal. mp 110–114 °C; IR (thin film, CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>) 3172, 3143, 3067, 3016, 2953, 2893, 2320, 2282, 2239, 1573, 1477, 1439, 1401, 1233, 1102, 1082, 831, 788, 751, 727;  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  7.38–7.36 (m, 2H, aromatic *H*), 7.22–7.16 (m, 2H, aromatic *H*), 7.09–7.06 (m, 1H, aromatic *H*), 6.72 (brs, 1H, C=CH-B), 5.67 (s, 2H, =CH-N), 3.15 (s, 6H, N-CH<sub>3</sub>), 3.01–2.36 (q,

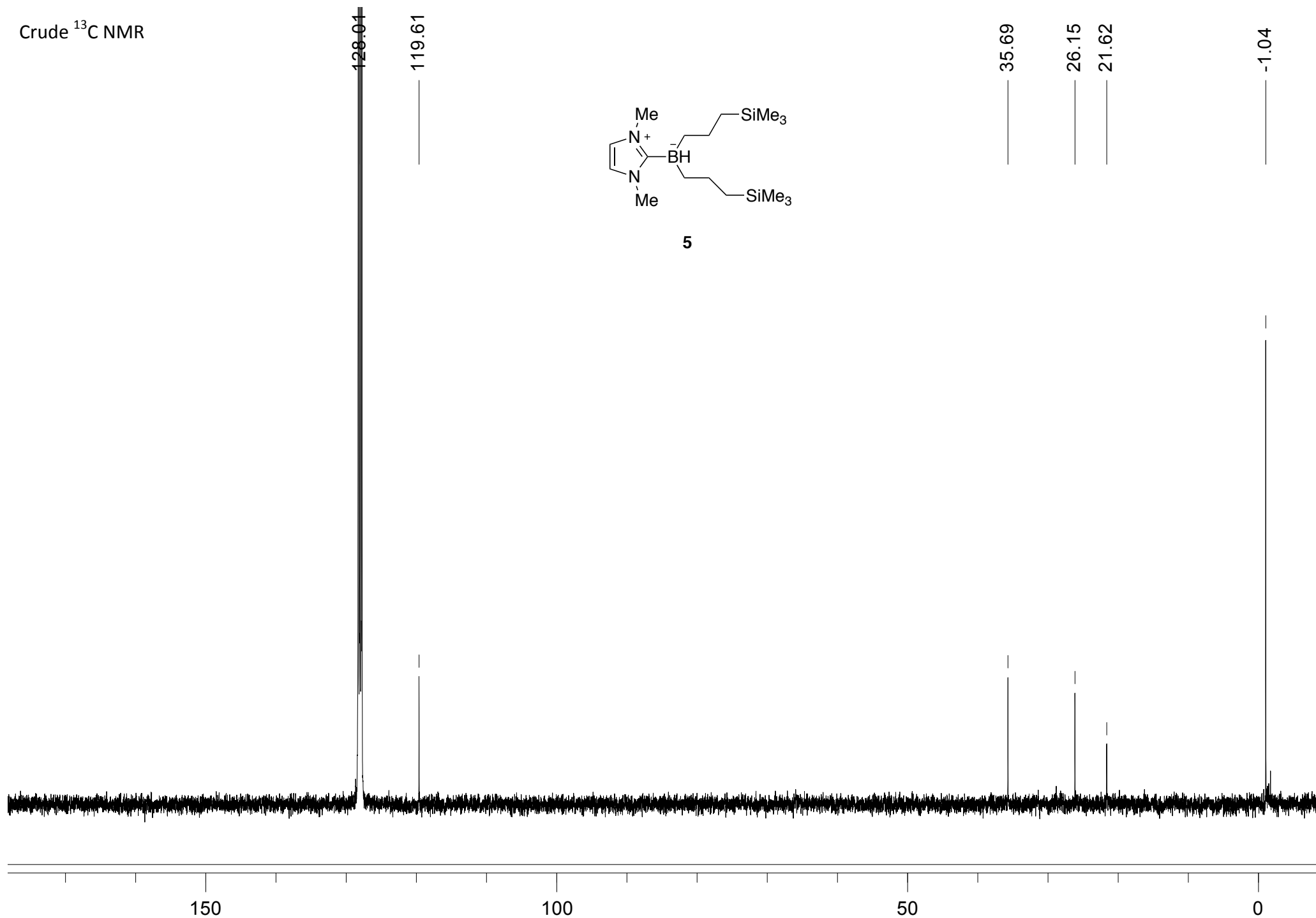
$J_{B-H} = 87$  Hz, 2H,  $BH_2$ ), 0.45 (s, 9H, TMS);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$  144.6 (aromatic C), 141.3 (=CH-C), 128.2 (aromatic CH), 127.3 (aromatic CH), 125.3 (aromatic CH), 120.2 (=CH-N), 36.0 (N-CH<sub>3</sub>), 1.0 (TMS);  $^{11}B$  NMR (160.5 MHz,  $C_6D_6$ )  $\delta$  -24.5 (t,  $J_{B-H} = 87$  Hz); HRMS (ESI)  $m/z$  ( $M^+ + Na$ ) calculated for  $C_{16}H_{25}^{11}BN_2NaSi$  307.1778, found 307.1764. Crystals of pure product were obtained by vaporizing the solvent ( $CH_2Cl_2$ ) of the solution of the complex.



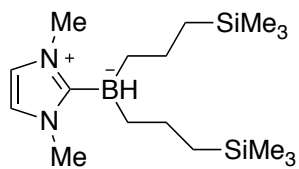
Crude  $^{13}\text{C}$  NMR



5



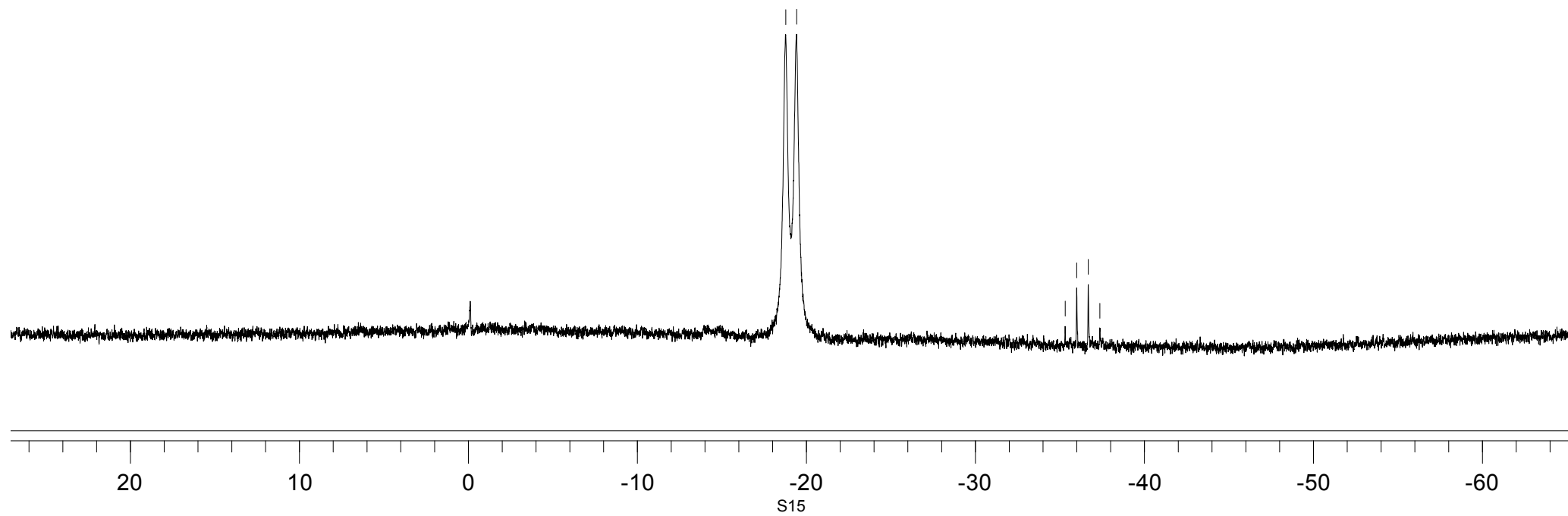
Crude  $^{11}\text{B}$  NMR



5

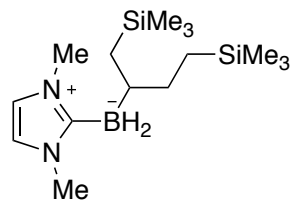
-18.78  
-19.42

-35.31  
-36.00  
-36.68  
-37.36

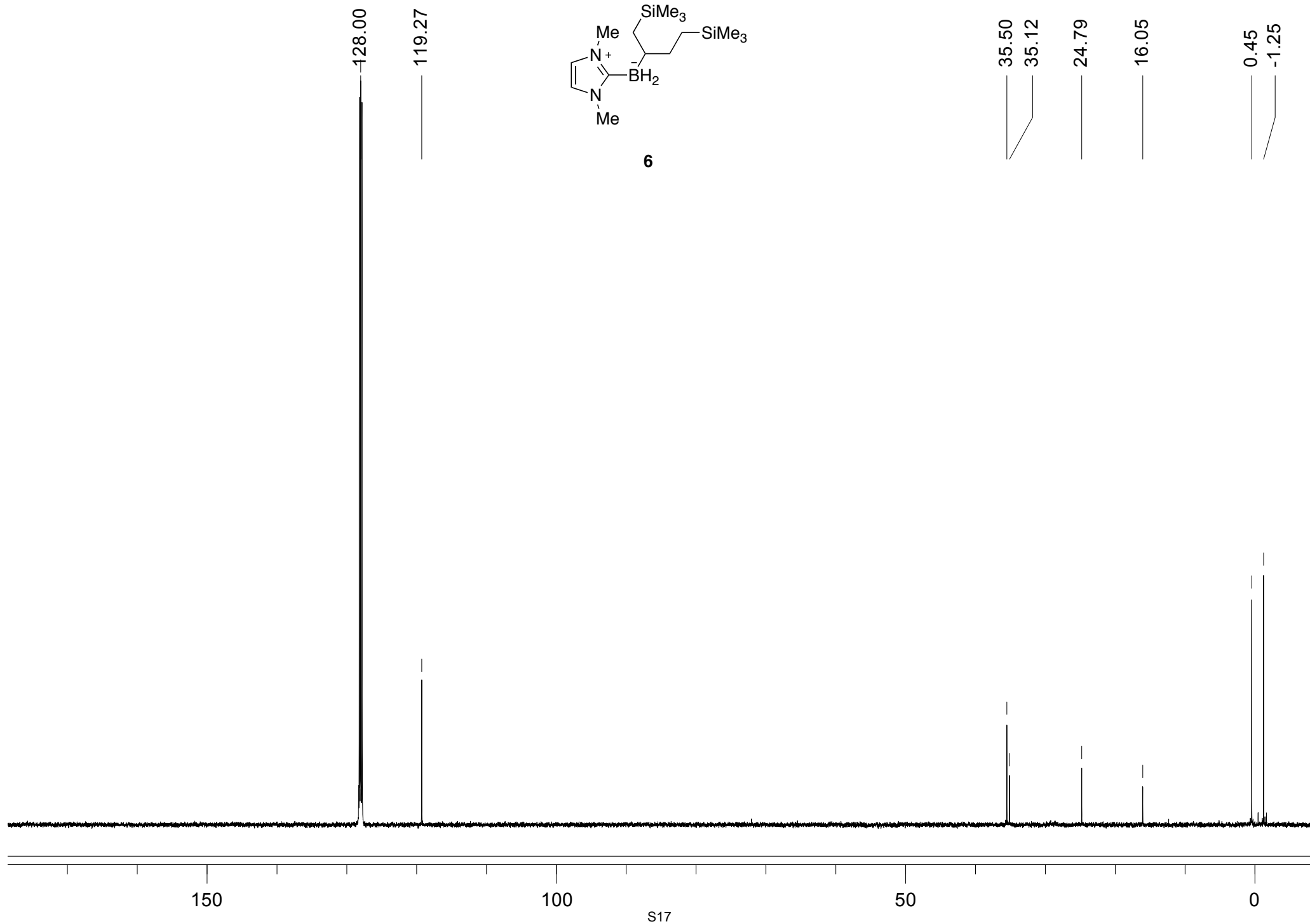


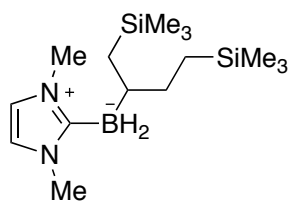






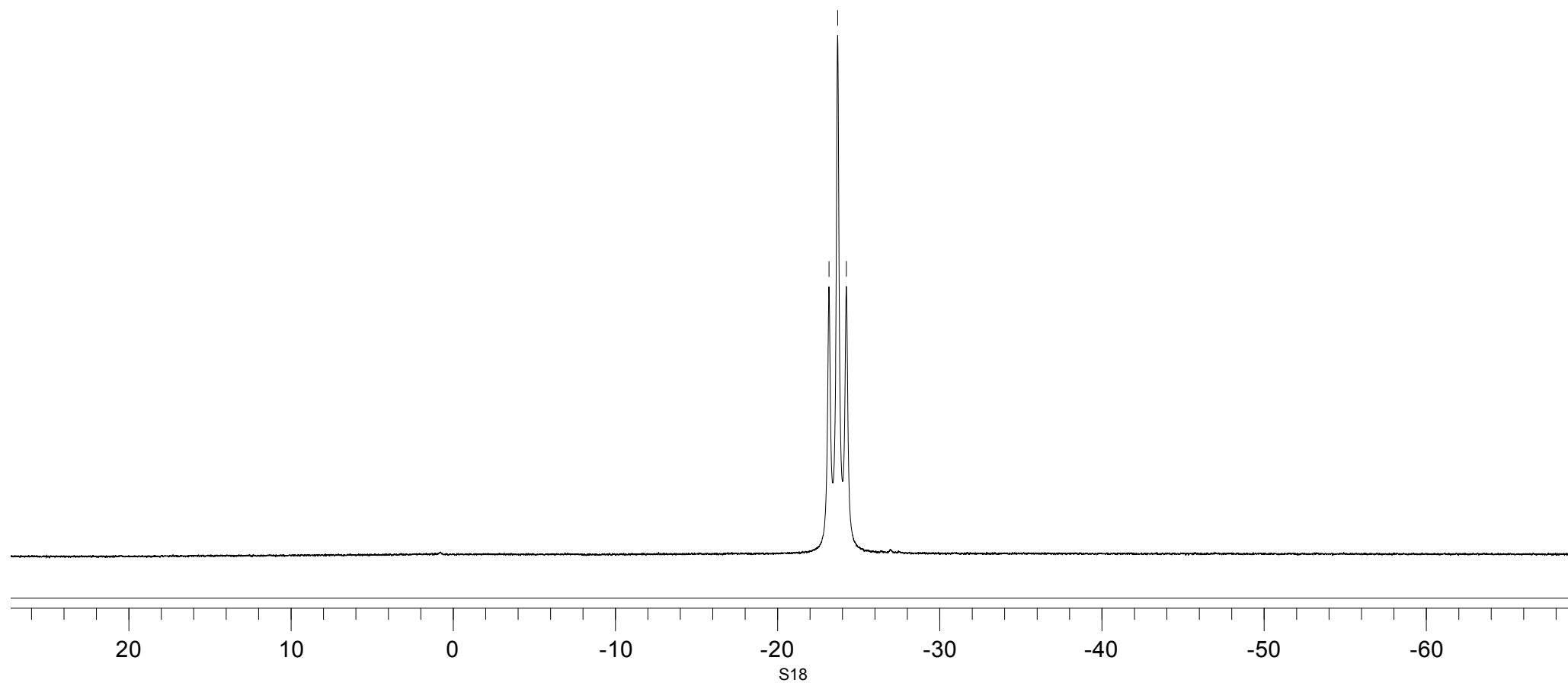
6

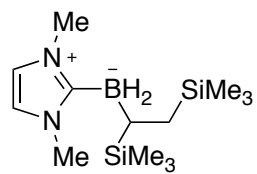




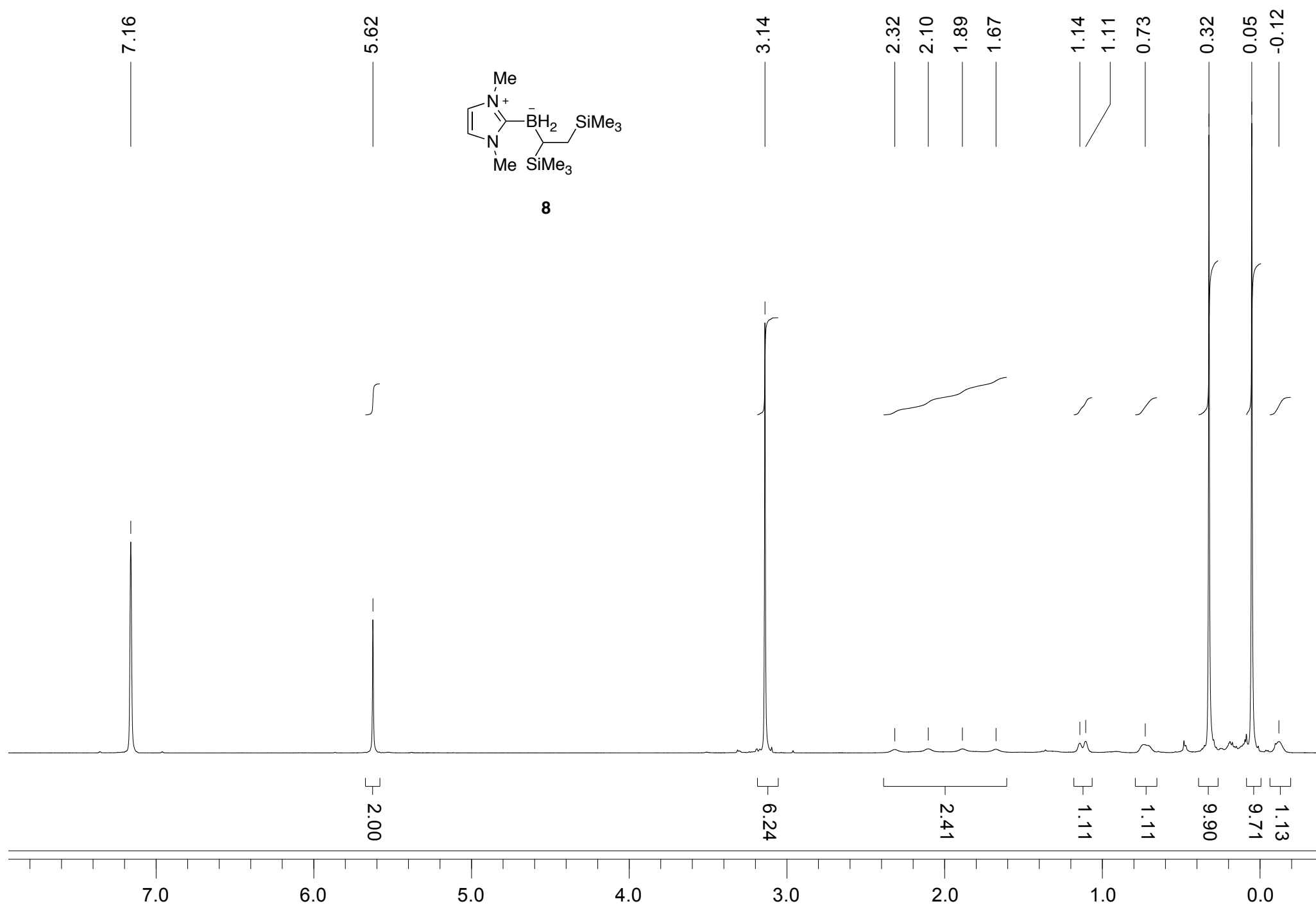
6

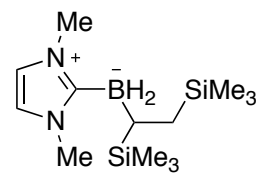
-23.17  
-23.71  
-24.24



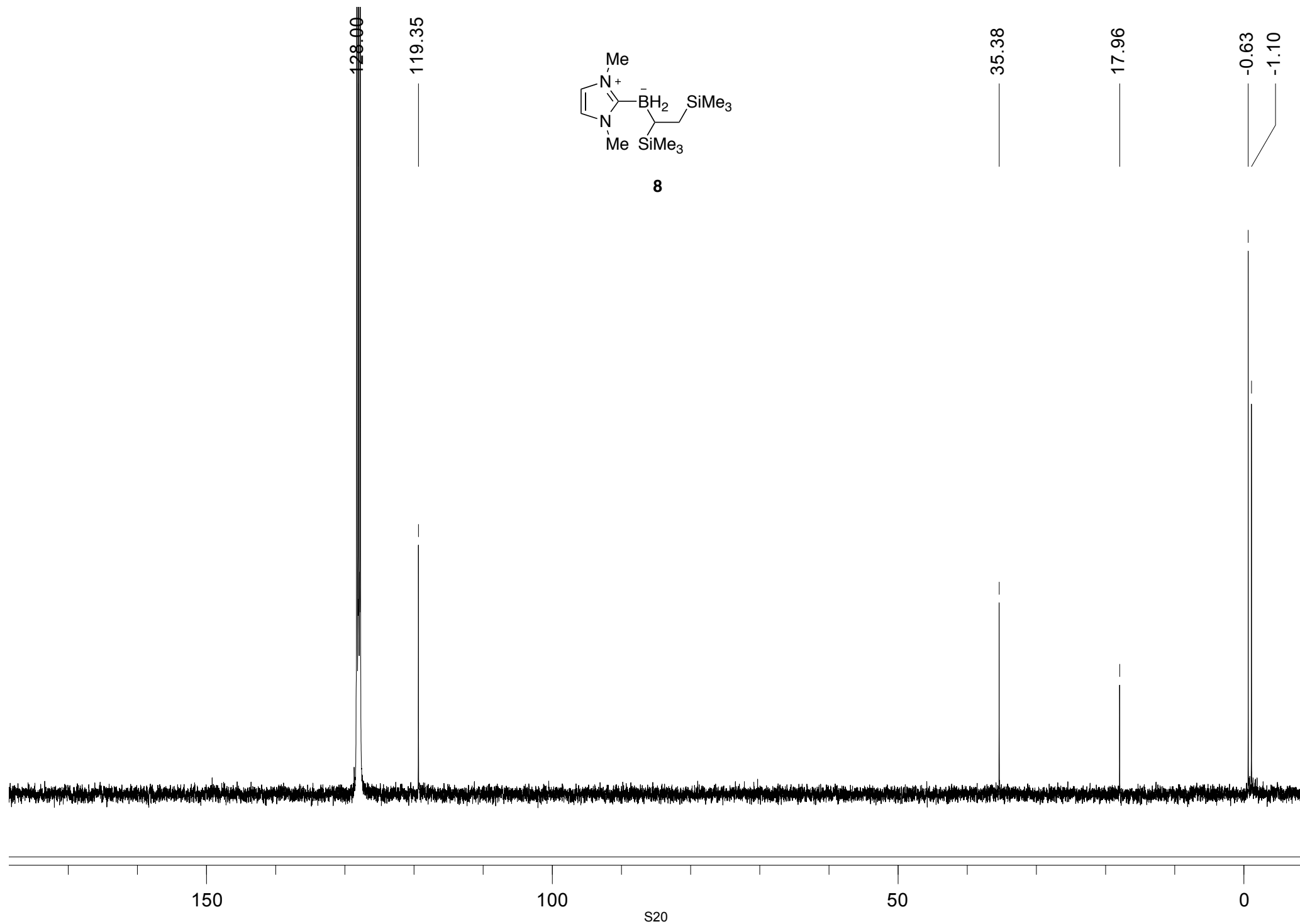


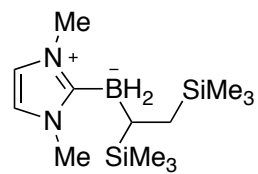
**8**



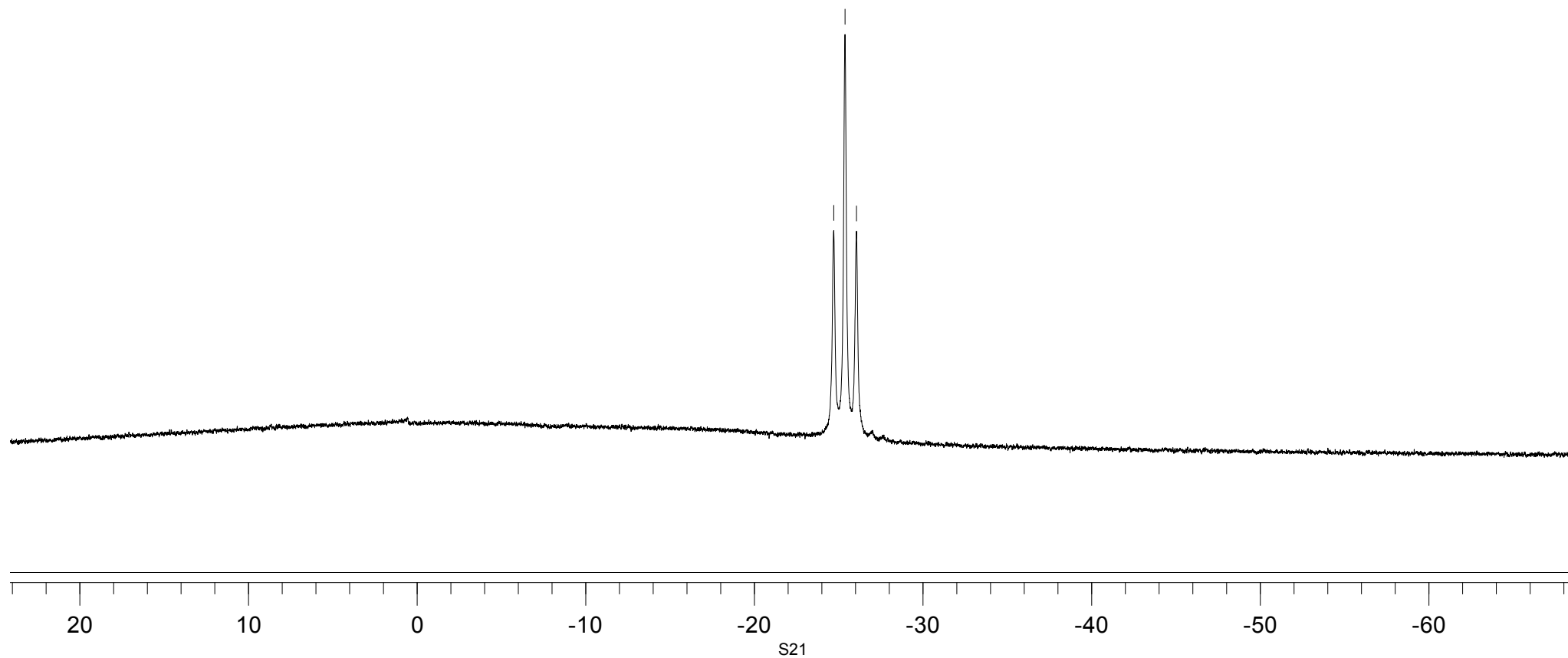
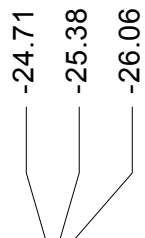


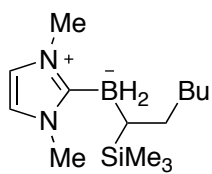
8



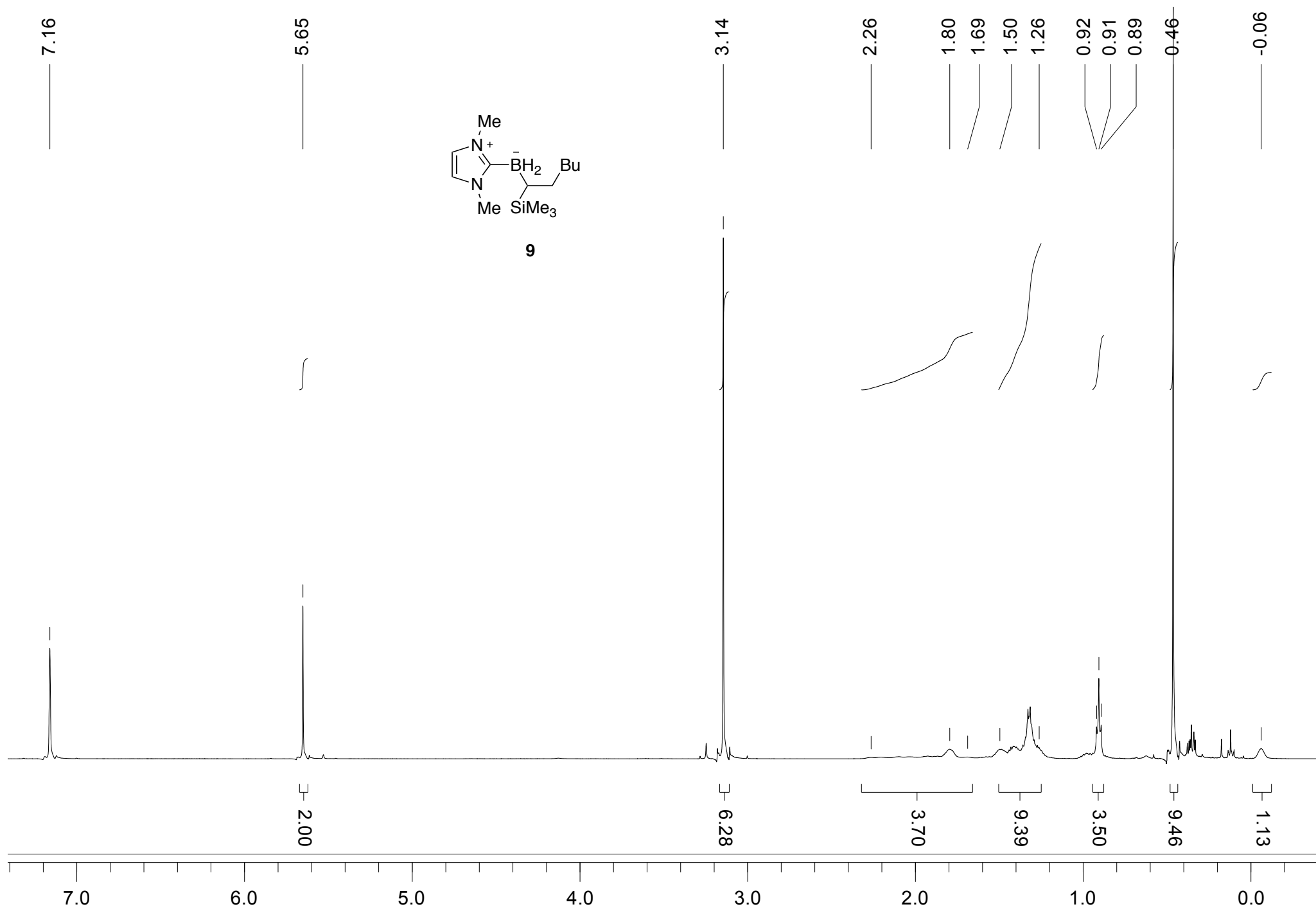


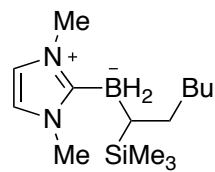
8



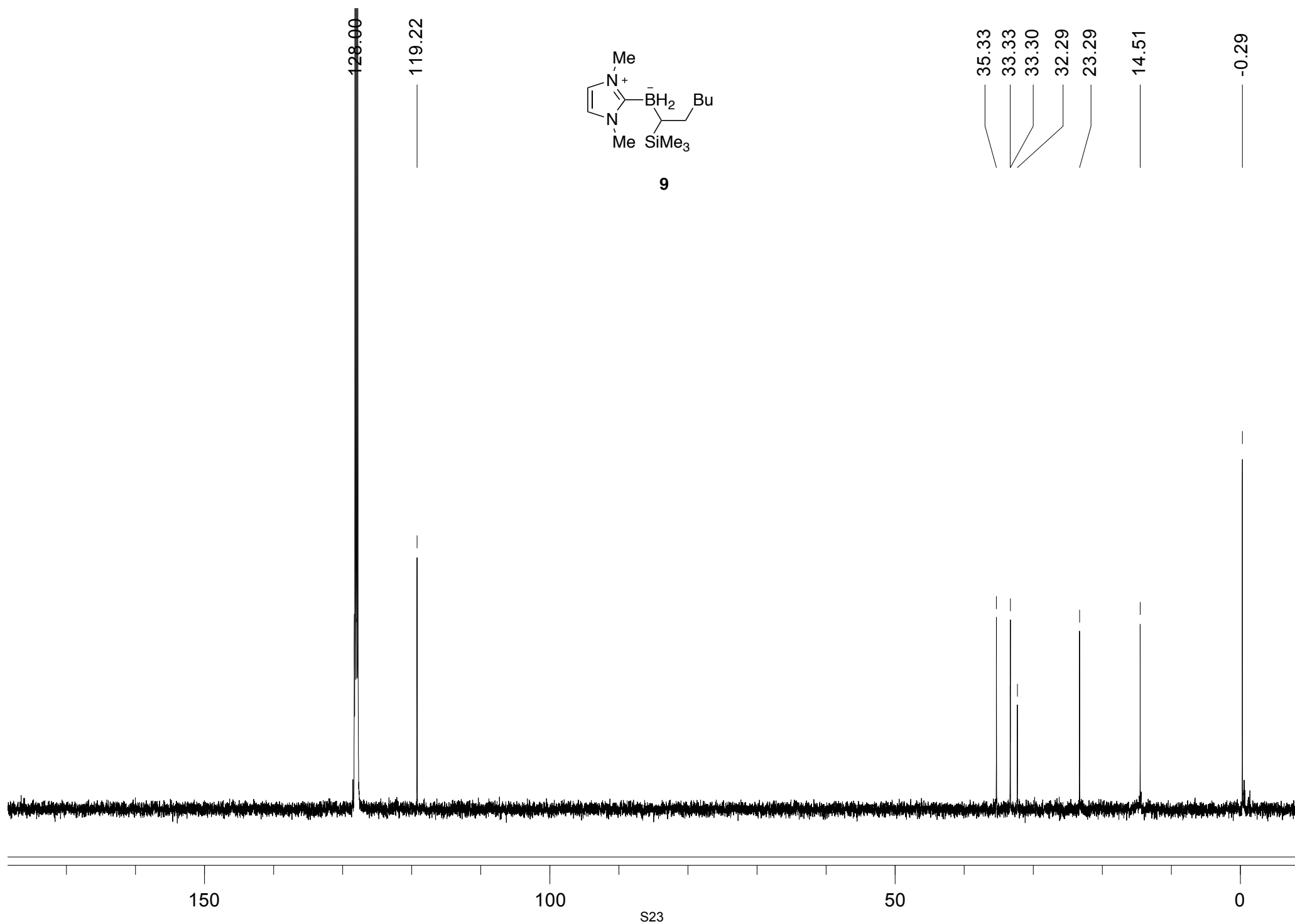


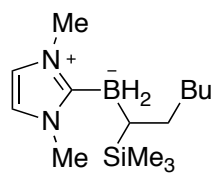
**9**





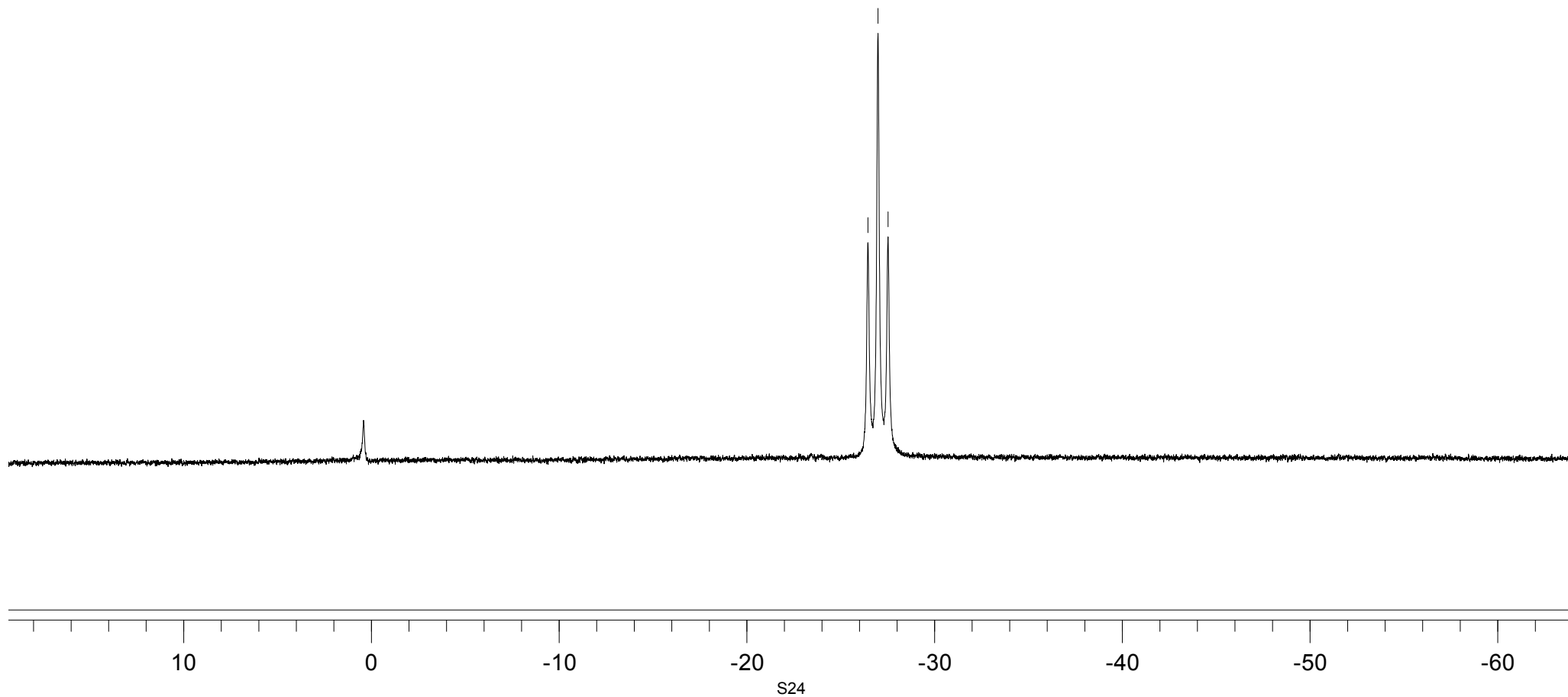
9





**9**

-26.45  
-26.99  
-27.52





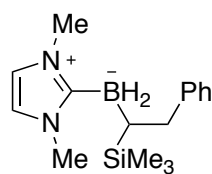
XP-109-36, 1H, C6D6, pdt, 400A, 6/13/2012

7.085  
7.067  
7.021  
7.003  
6.977  
6.966  
6.948

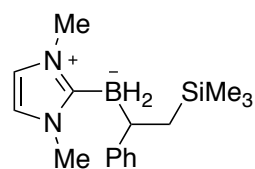
5.530  
5.441

3.263  
3.234  
2.930  
2.822  
2.578  
2.547  
2.519  
2.349  
1.739  
1.723  
1.703  
1.688  
1.677  
1.570  
1.555

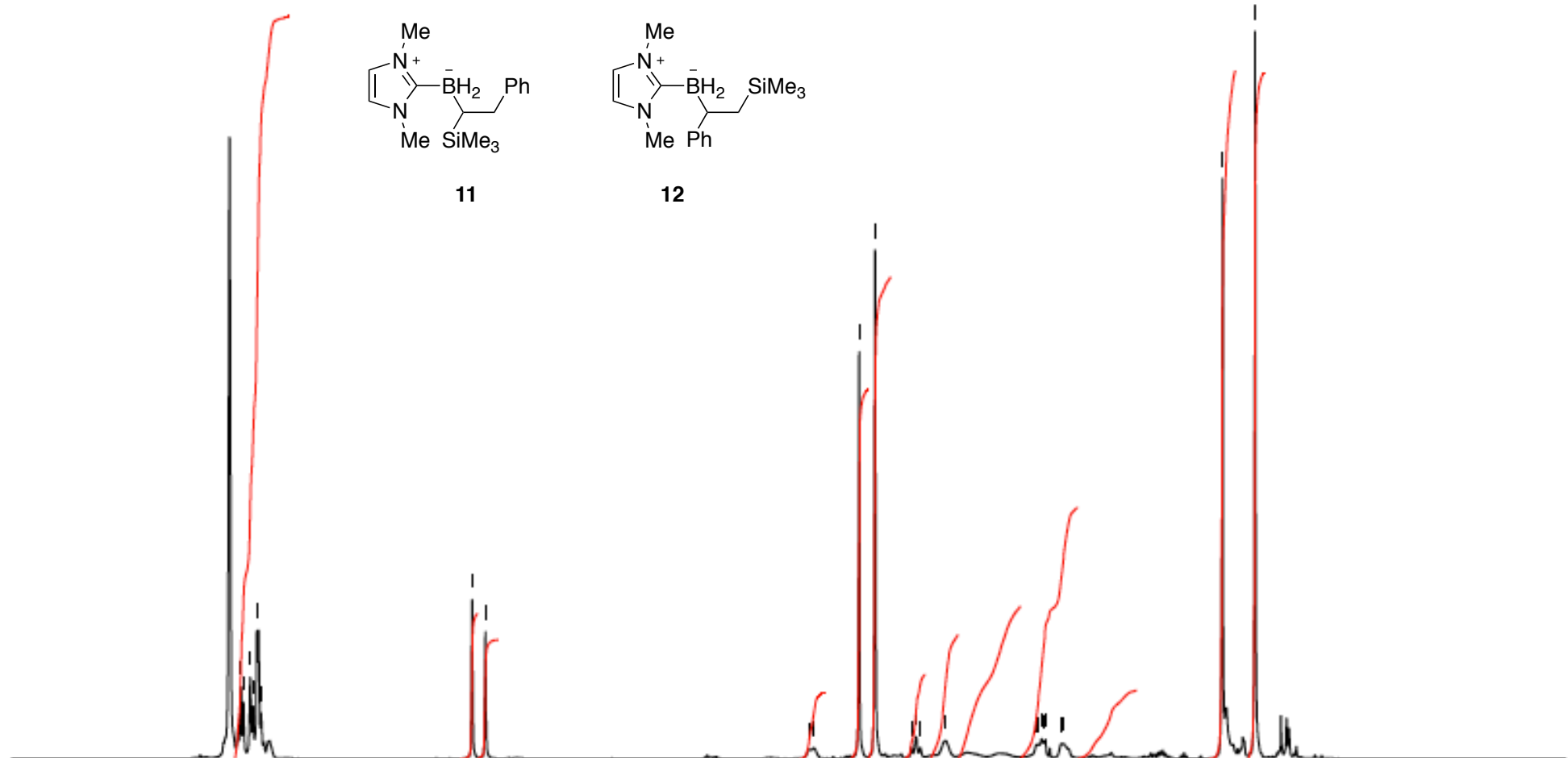
0.487  
0.268



11



12



8

12.45

6

2.44  
2.00

5

4

S25

1.11

6.20

8.08

1.42

2.08

2.56

4.22

1.15

11.54

11.50

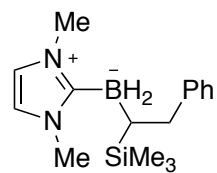
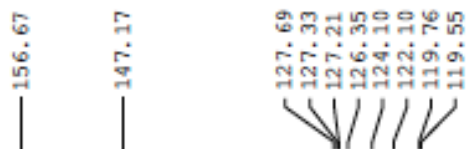
0

-1

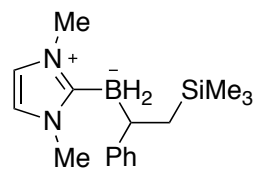
ppm



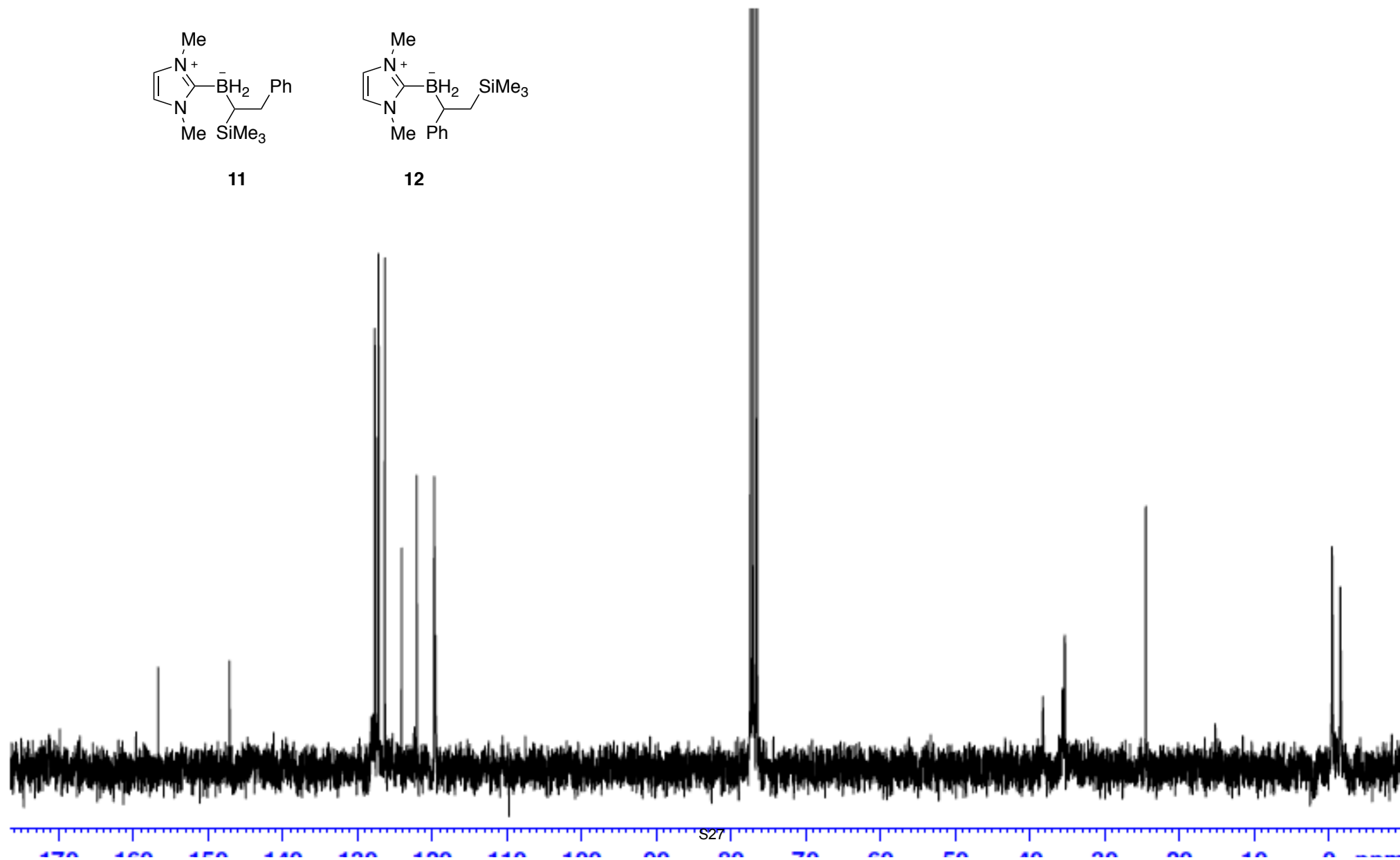
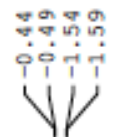
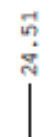
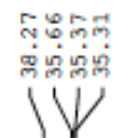
XP-109-36,  $^{13}\text{C}$ , pdt,  $\text{CDCl}_3$ , 301B, 9/10/2012



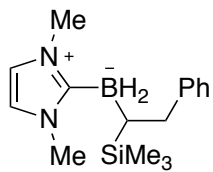
11



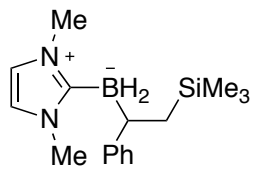
12



XP-109-36, pdt, 11B, C6D6, 400A, 6/13/2012

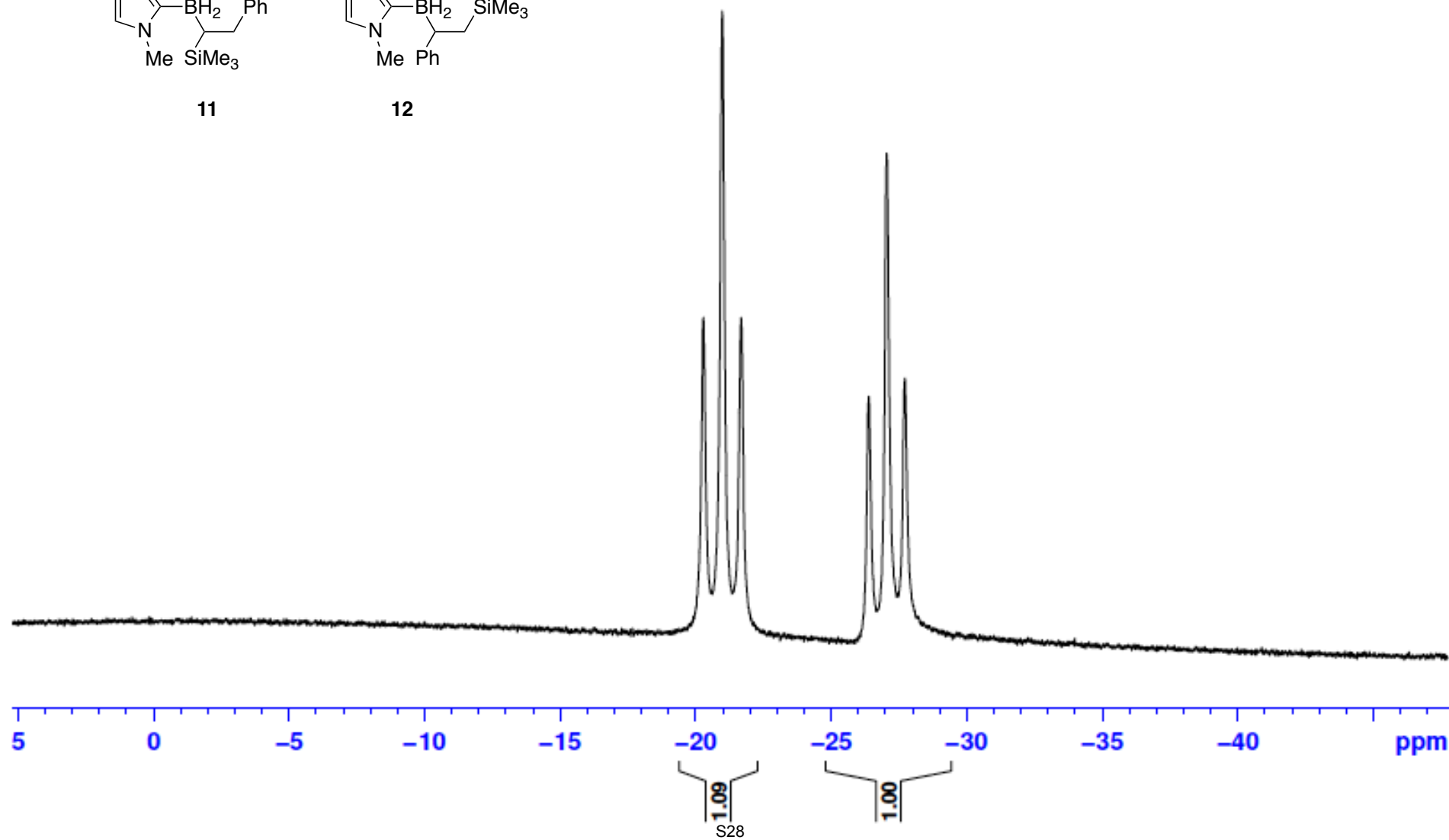


11



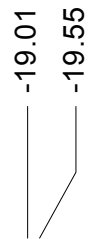
12

-20.28  
-20.97  
-21.67  
  
-26.38  
-27.04  
-27.71

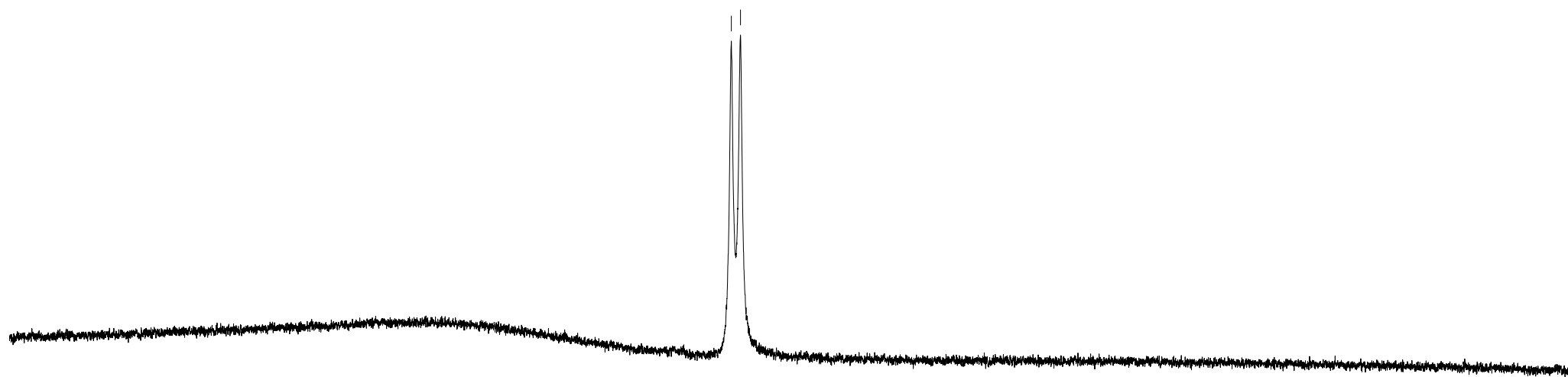


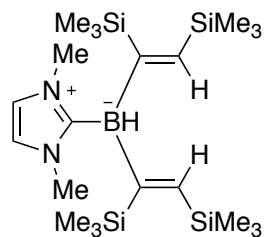




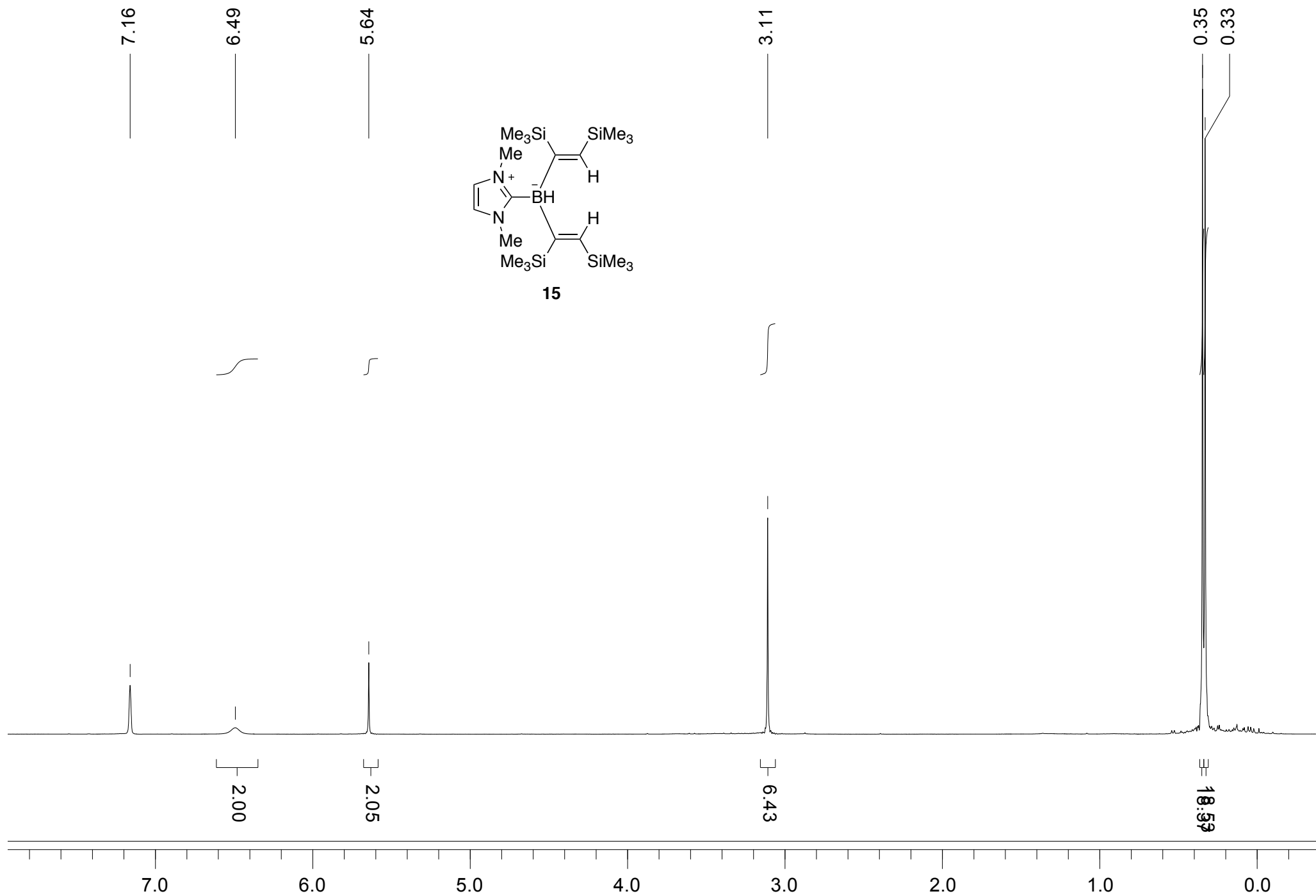


S31





**15**

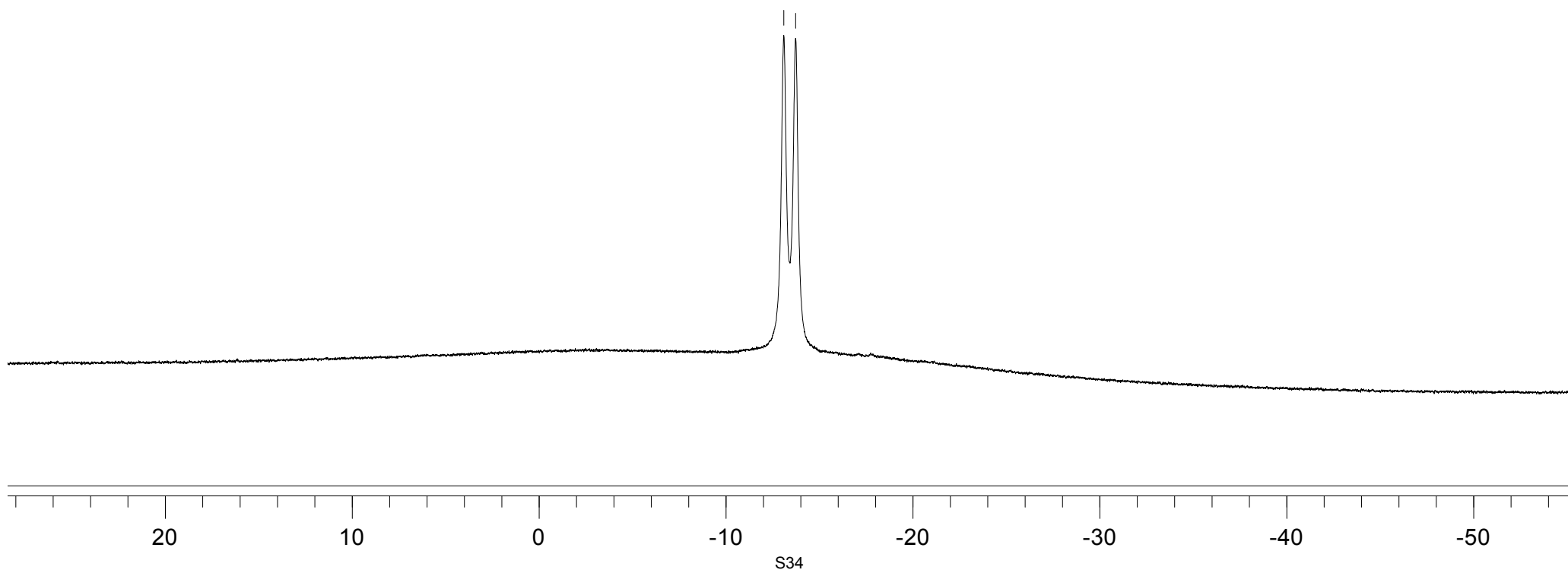




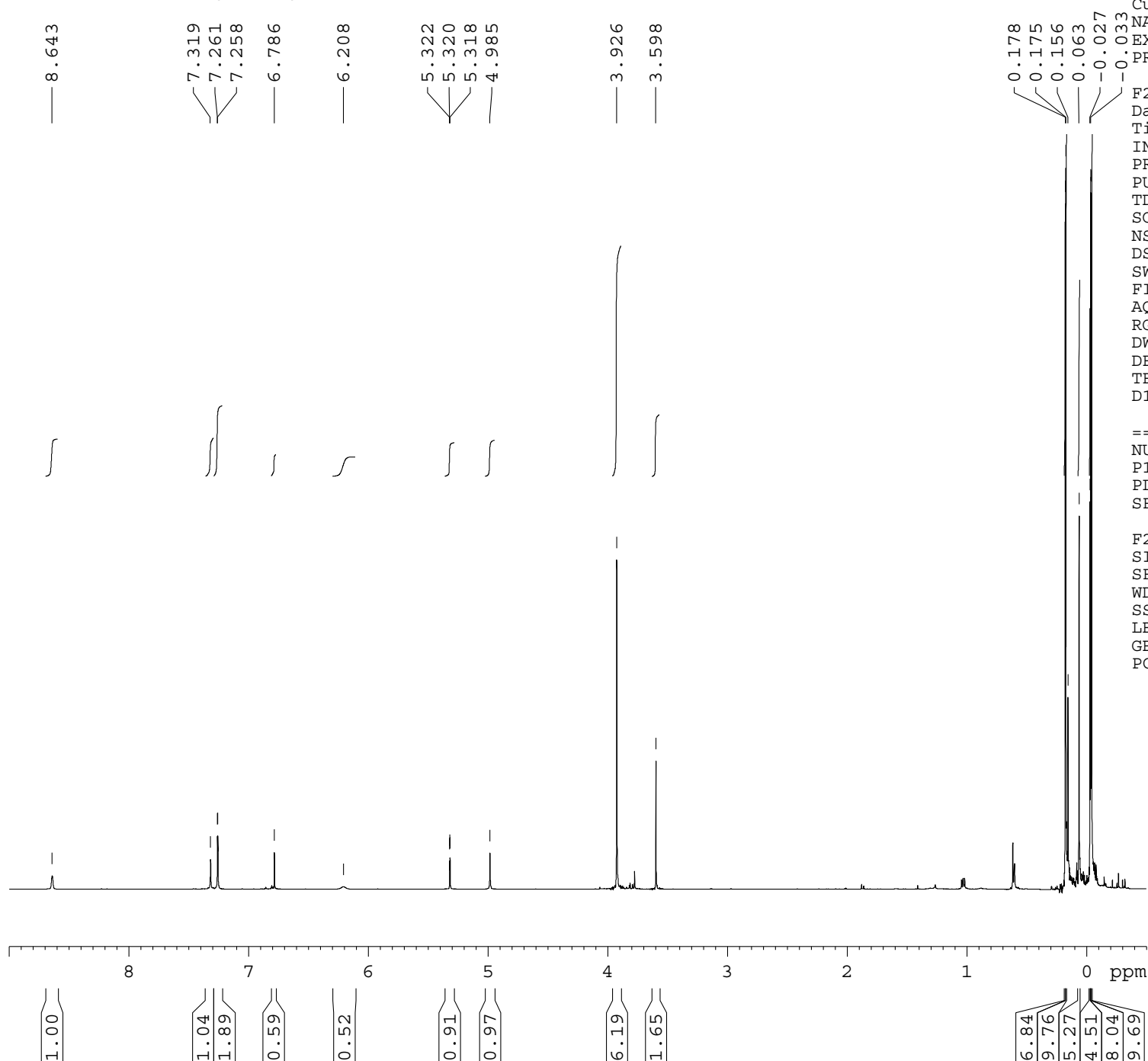




S34



AB104.60-+HNTf2, 500, 15 + triflimide



Current Data Parameters  
NAME AB104.60-+HNTf2  
EXPNO 2  
PROCNO 1

F2 - Acquisition Parameters  
Date\_ 20120612  
Time\_ 10.26  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zg30  
TD 65536  
SOLVENT CD2Cl2  
NS 8  
DS 2  
SWH 10330.578 Hz  
FIDRES 0.157632 Hz  
AQ 3.1719923 sec  
RG 32  
DW 48.400 usec  
DE 6.50 usec  
TE 296.8 K  
D1 1.00000000 sec

===== CHANNEL f1 =====  
NUC1 1H  
P1 10.20 usec  
PLW1 18.74300003 W  
SFO1 500.1630887 MHz

F2 - Processing parameters  
SI 65536  
SF 500.1600192 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00

AB104.60-+HNTf2, 500, 15 + triflimide

— 50.63

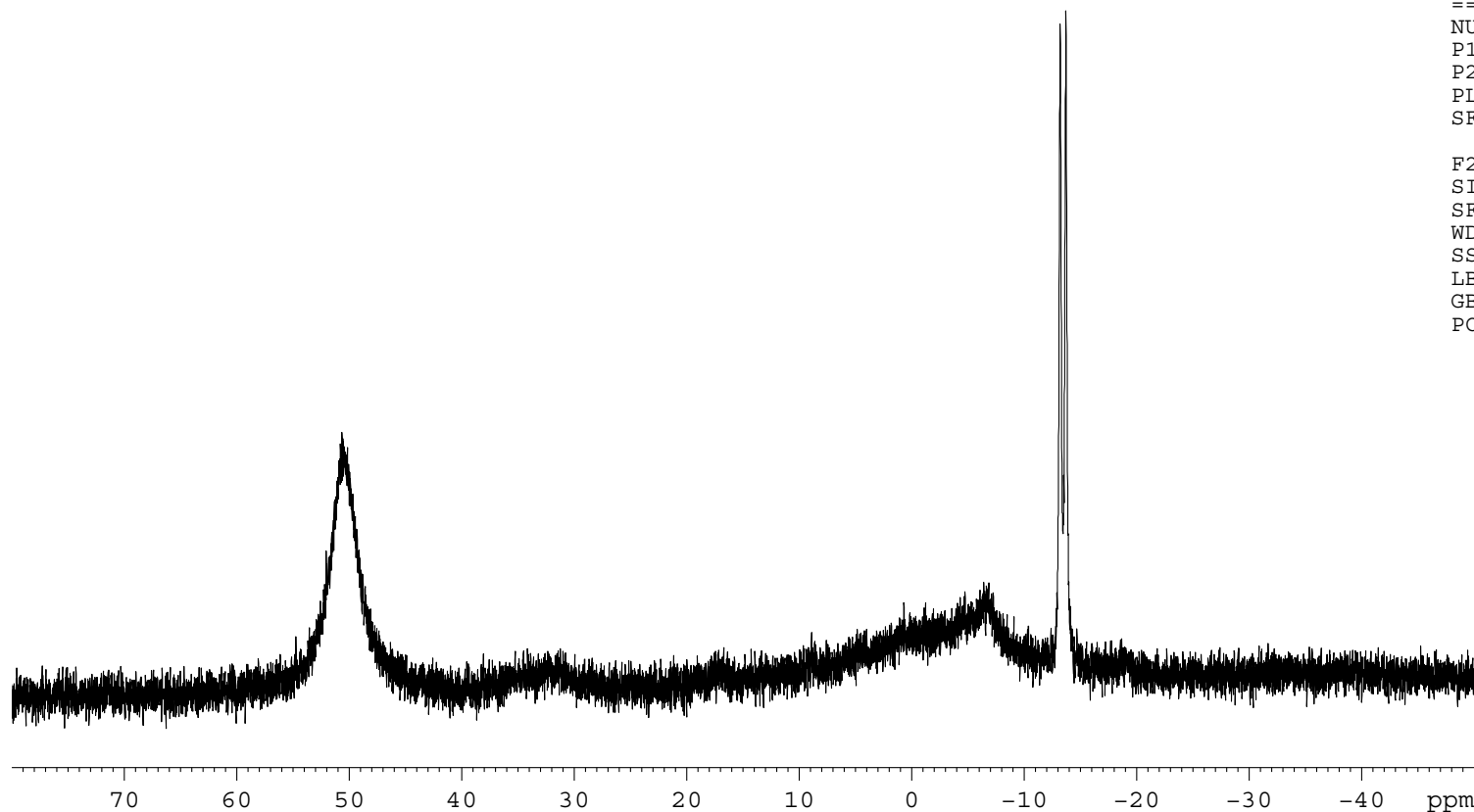
— -13.22  
— -13.73

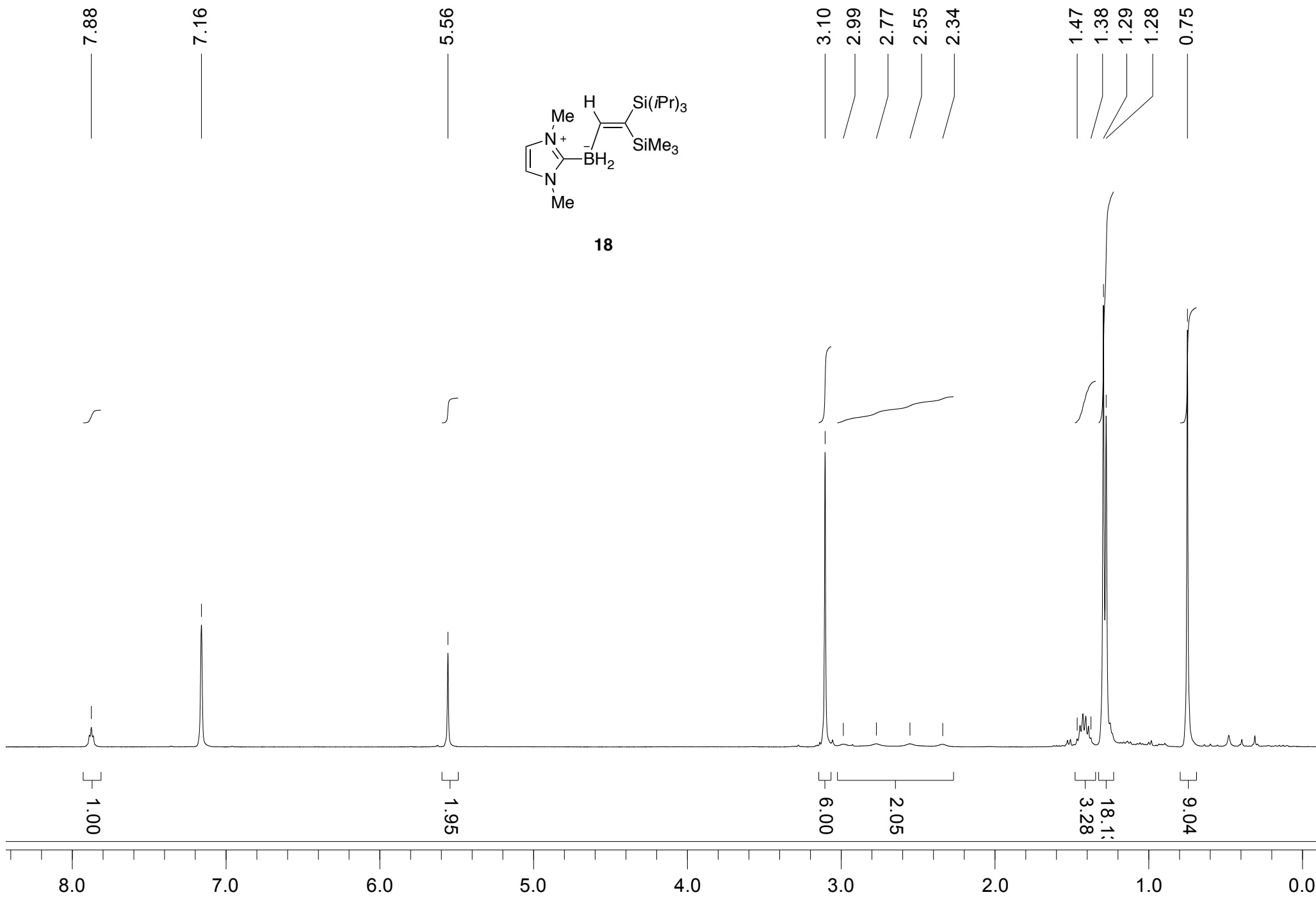
Current Data Parameters  
NAME AB104.60-+HNTf2  
EXPNO 1  
PROCNO 1

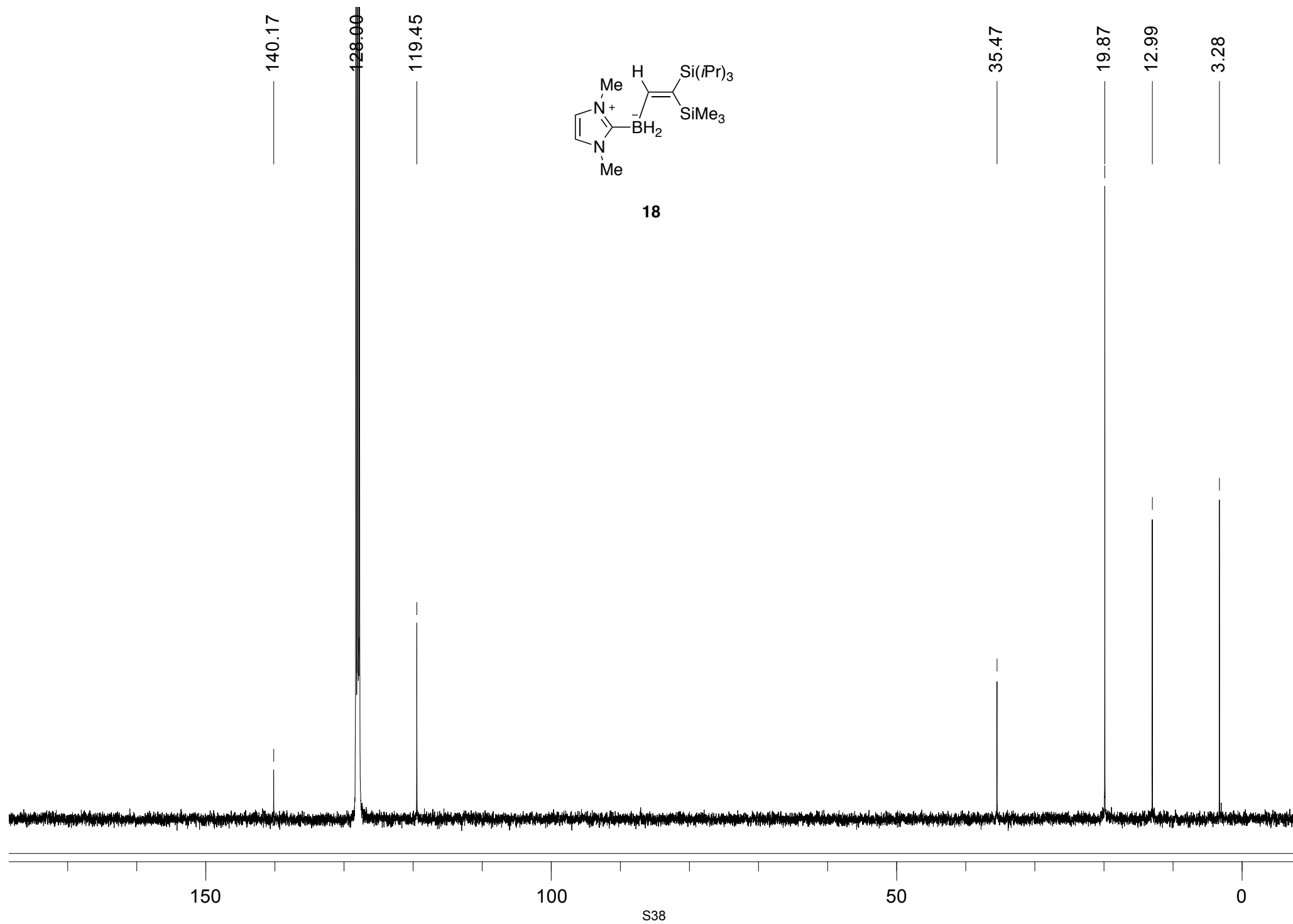
F2 - Acquisition Parameters  
Date\_ 20120612  
Time 10.21  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zgbs  
TD 65536  
SOLVENT CD2Cl2  
NS 24  
DS 2  
SWH 32051.281 Hz  
FIDRES 0.489064 Hz  
AQ 1.0224116 sec  
RG 57  
DW 15.600 usec  
DE 6.50 usec  
TE 296.8 K  
D1 1.00000000 sec

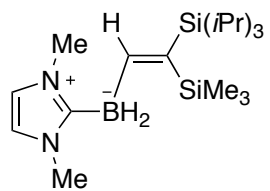
===== CHANNEL f1 =====  
NUC1 11B  
P1 8.50 usec  
P2 17.00 usec  
PLW1 109.64779663 W  
SFO1 160.4712044 MHz

F2 - Processing parameters  
SI 32768  
SF 160.4712040 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.40



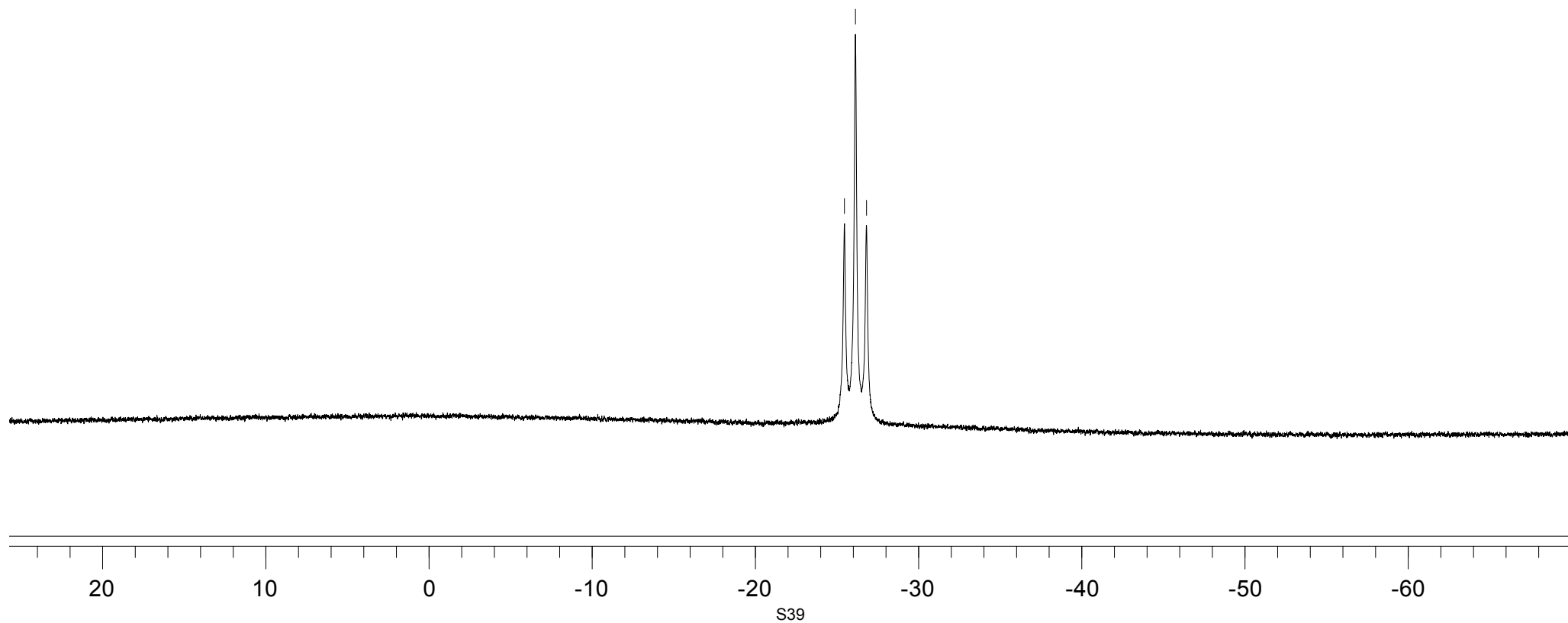


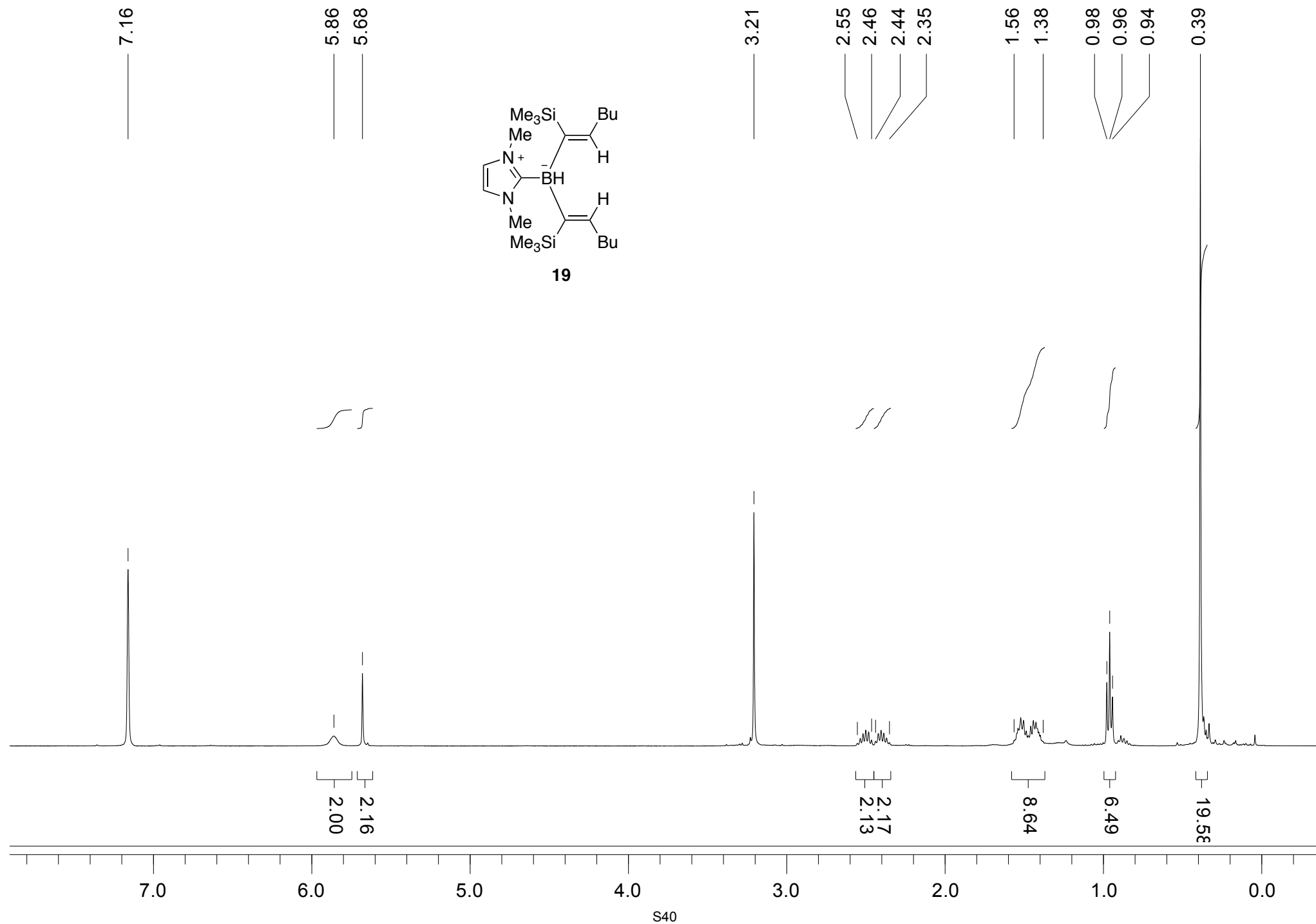




18

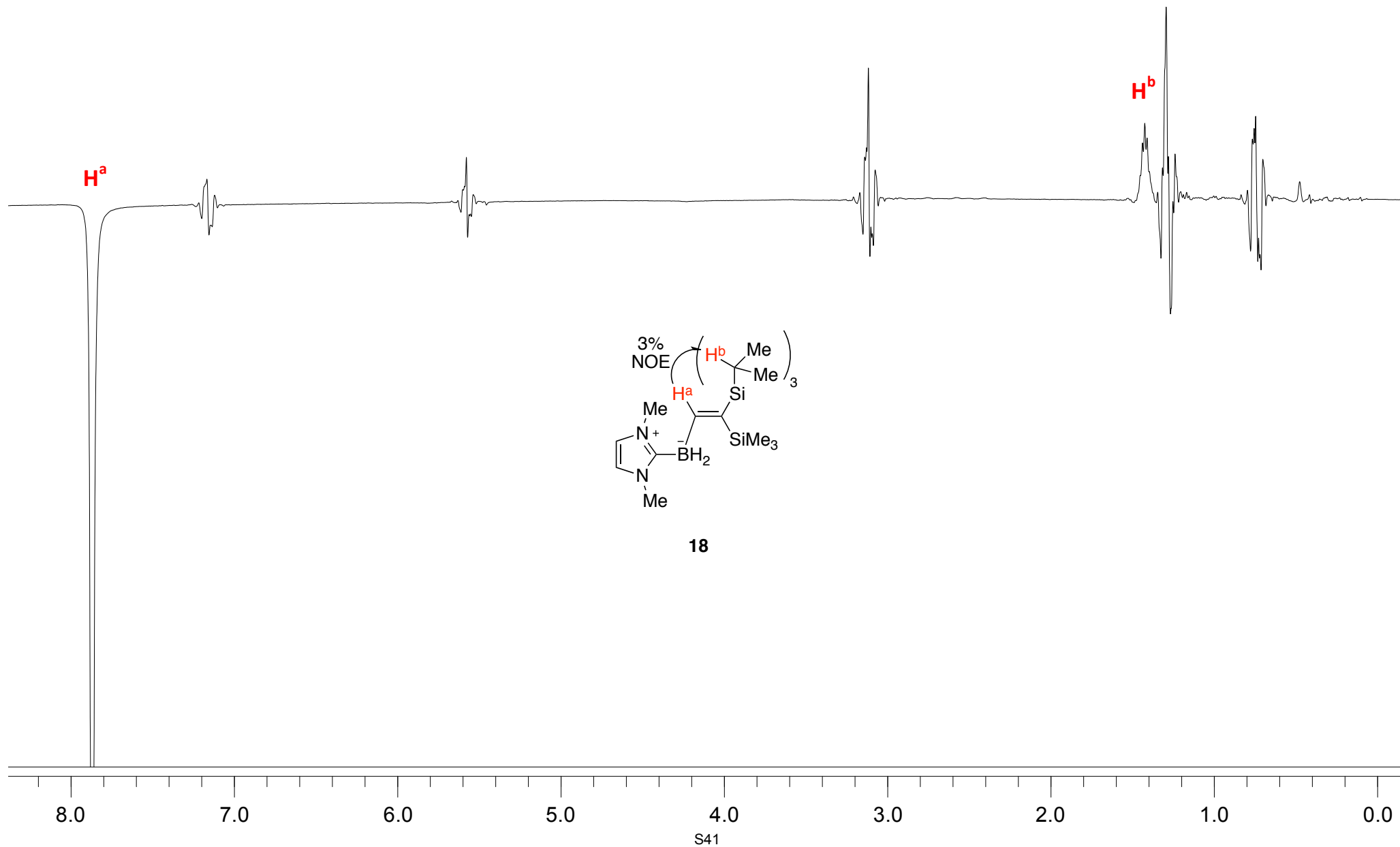
-25.46  
-26.13  
-26.81

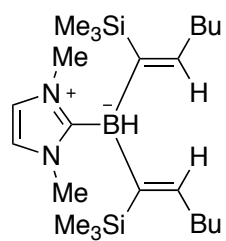




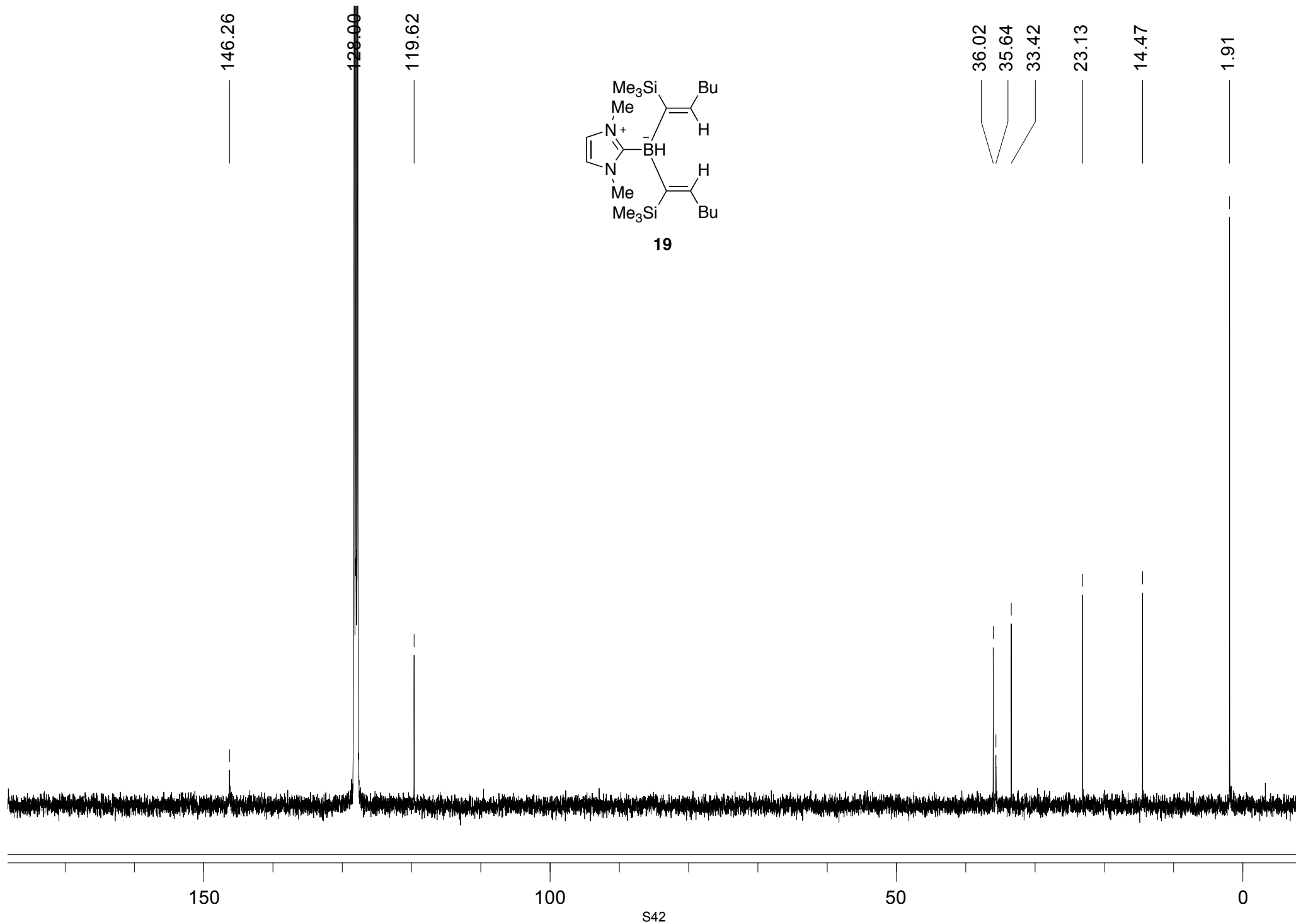


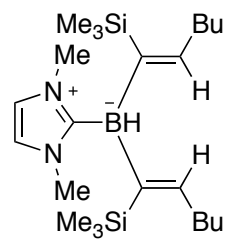
NOEdiff experiment – irradiation of proton H<sup>a</sup>





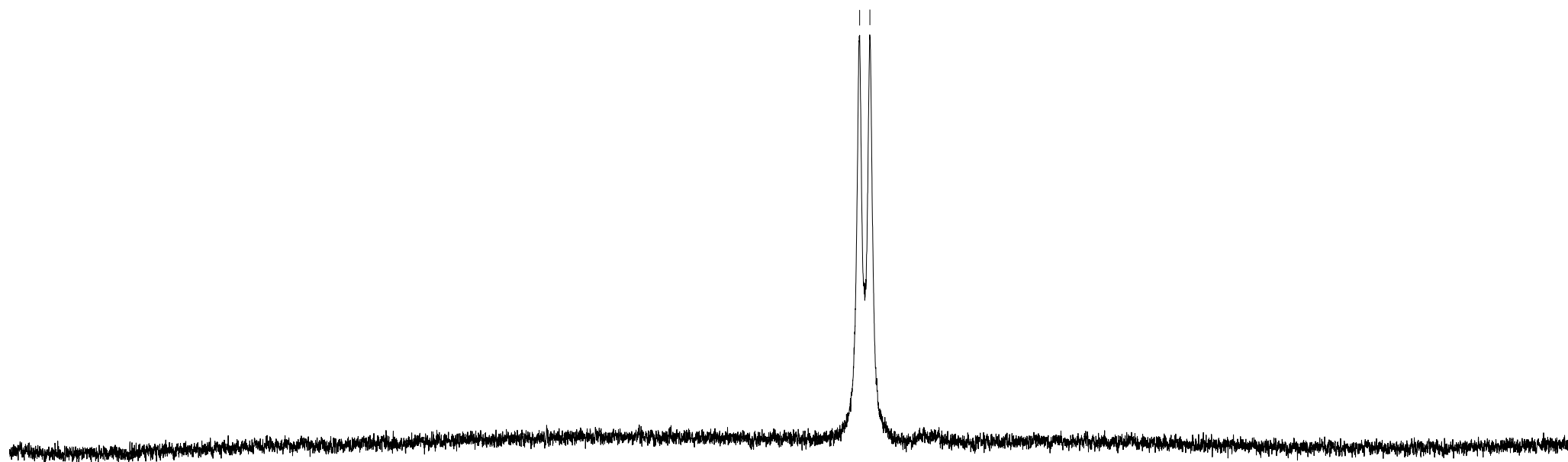
19



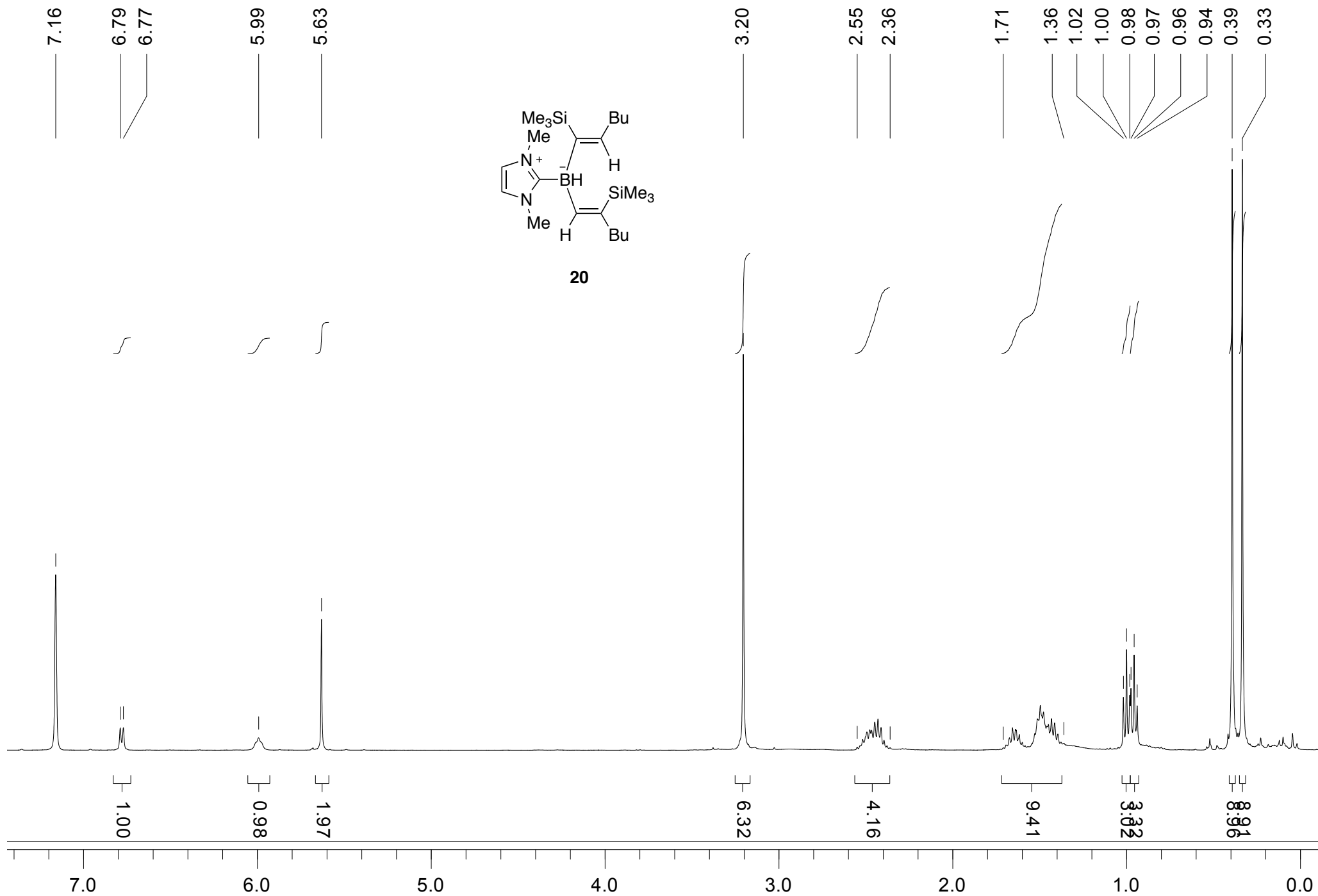


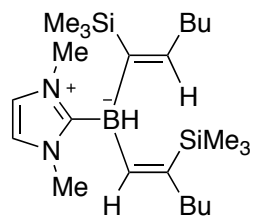
**19**

-15.94  
-16.55

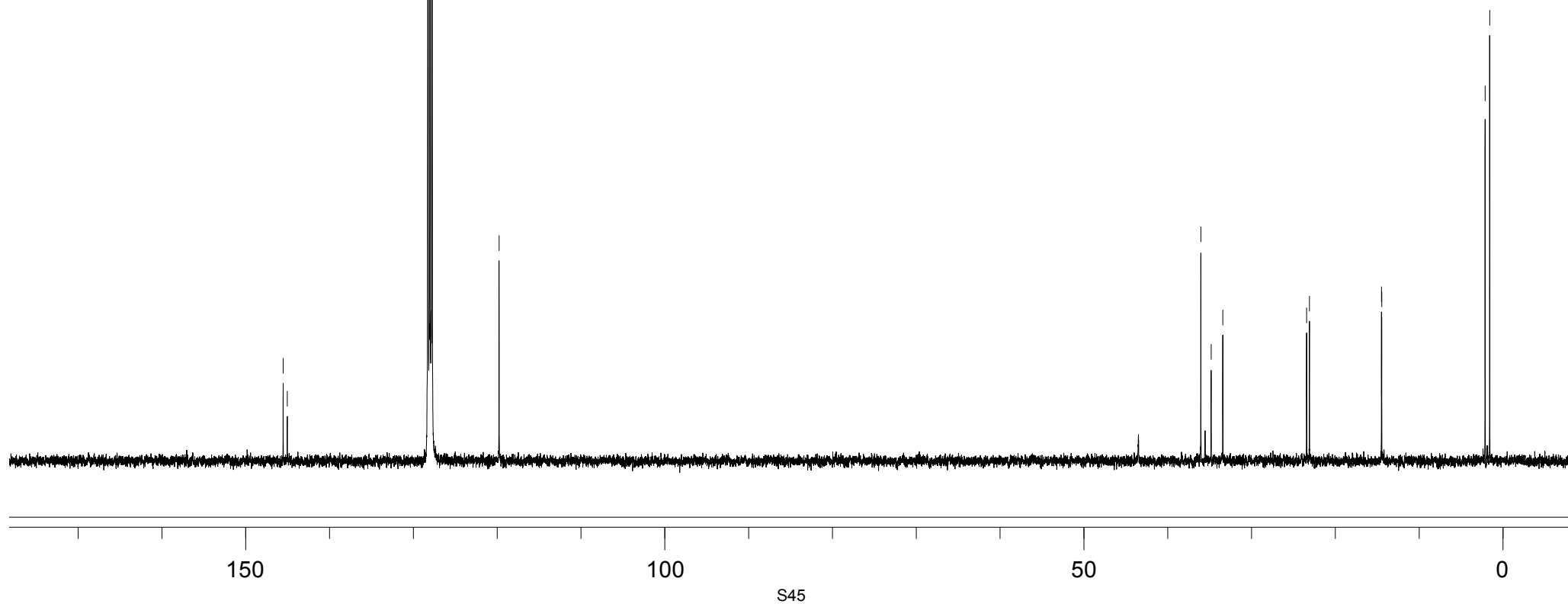


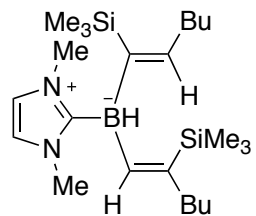
S43





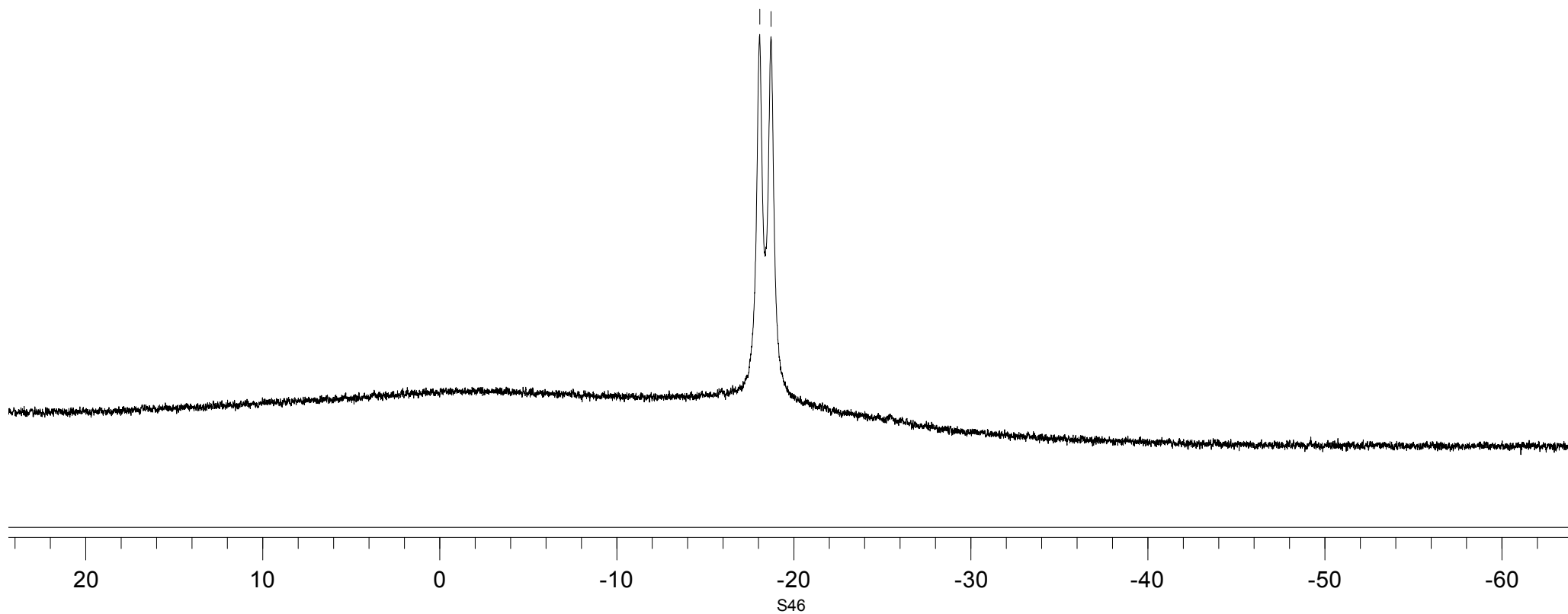
20



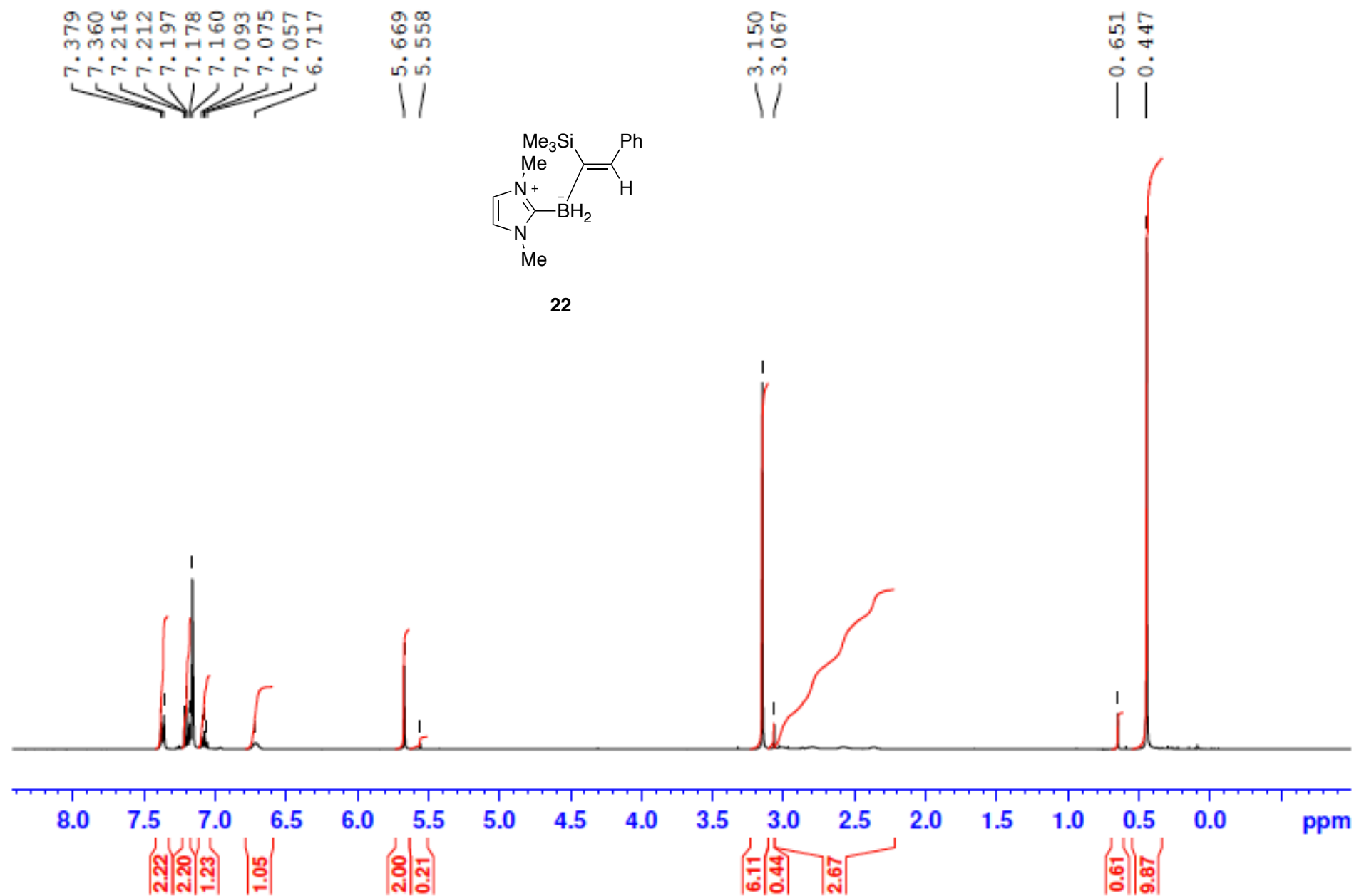


20

-18.08  
-18.71

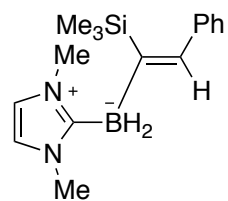


XP-109-16, pdt, 1H, C6D6, 400A, 5/16/2012



XP-109-16, pdt,  $^{13}\text{C}$ ,  $\text{CDCl}_3$ , 400A, 9/10/2012

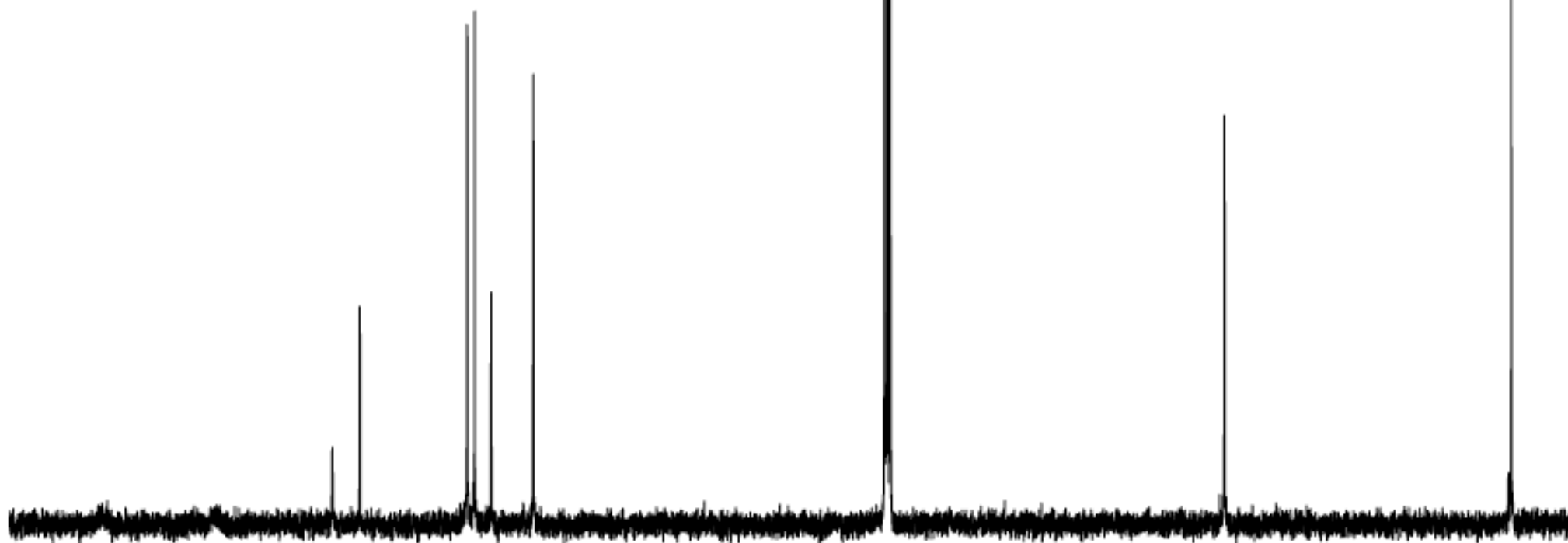
144.65  
141.32  
128.23  
127.30  
125.29  
120.15



22

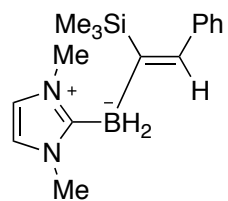
35.96

1.02



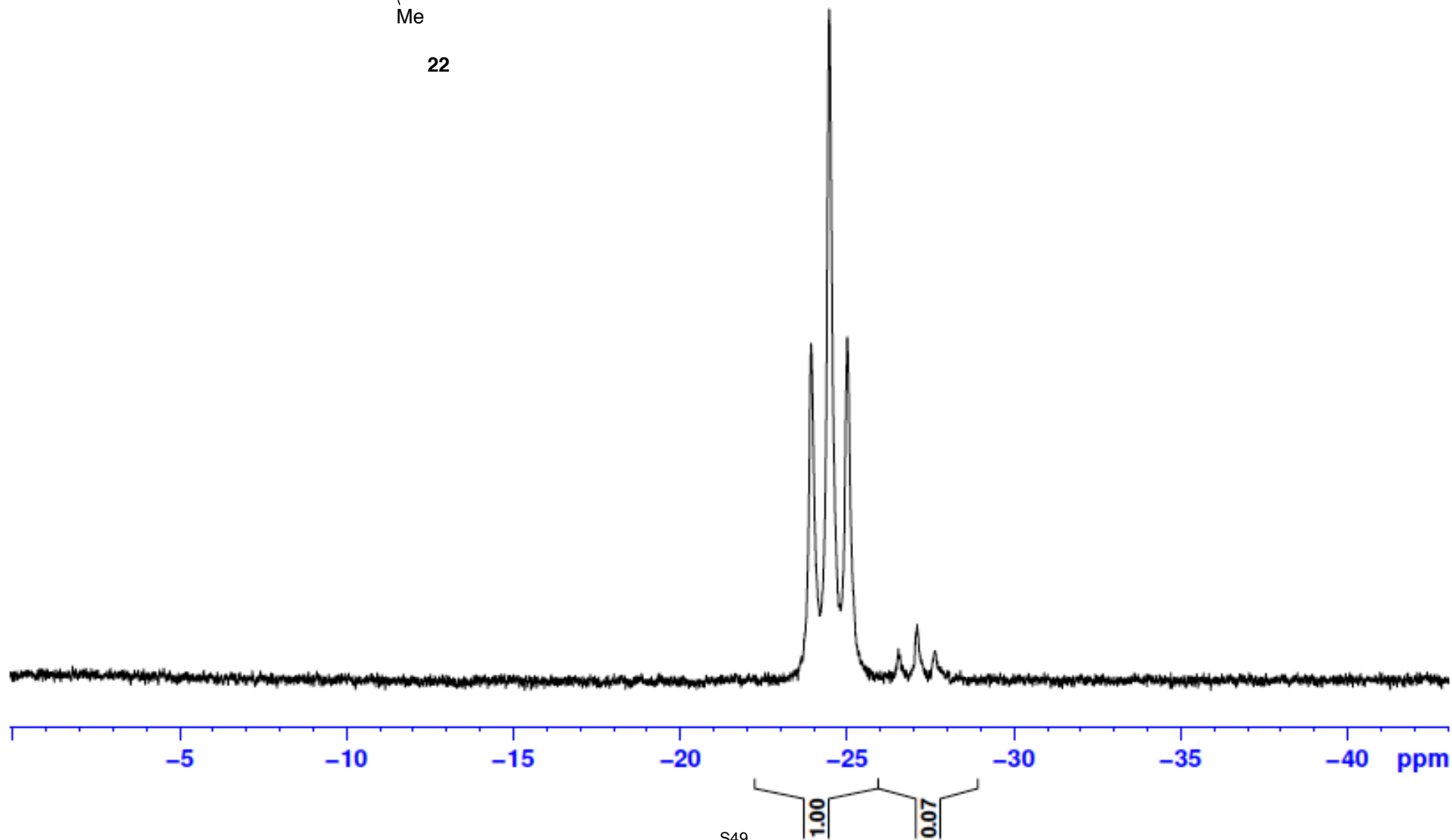


XP-109-16, 11B, pdt, C6D6, 500, 5/16/2012

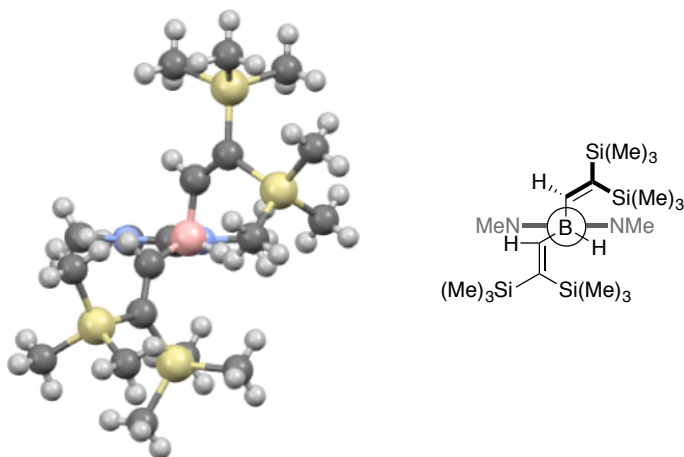


22

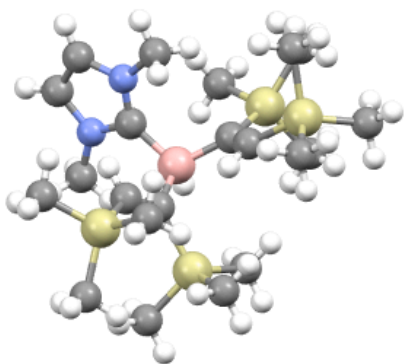
-23.92  
-24.46  
-25.00  
-26.53  
-27.09  
-27.62



**Figure S1.** Ball-and-stick representation of the X-ray crystal structure of rearranged 1,1-hydroboration product **14** (left) and a Newman projection of the B–C bond in a similar orientation (right).



**Figure S2.** Ball-and-stick representation of the X-ray crystal structure of rearranged 1,2-hydroboration product **15**.



Cif files of both crystal structures are available from the Cambridge Structural Database as personal communications from Stephen J. Geib, 2013, numbers 967,205 and 967,206.

**Figure S3.** ORTEP Diagram of Compound **22**

