

## Supporting Information

### **Iridium-catalyzed selective arylation of B(6)-H of 3-Aryl-*o*-carboranes with arylboronic acid via direct B-H activation**

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## Context

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## General information

1a<sup>1</sup> and 4a-4g<sup>1</sup> were synthesized according to literature methods. Other materials were purchased from Acros, J&K and Aladdin, and used as received unless otherwise specified. The THF was dried and freshly distilled over sodium/benzophenone before used. All reactions under standard conditions were monitored by thin-layer chromatography (TLC) on gel F254 plates. The silica gel (200-300 meshes) is used for column chromatography, and the distillation range of petroleum ether is 60-90 °C. <sup>1</sup>H NMR, <sup>13</sup>C{<sup>1</sup>H} and <sup>11</sup>B{<sup>1</sup>H} NMR spectra were recorded on the Bruker 500 MHz instruments. All <sup>1</sup>H NMR and <sup>13</sup>C{<sup>1</sup>H} NMR spectra data are reported in ppm relative to tetramethylsilane (TMS) as internal standard, and <sup>11</sup>B{<sup>1</sup>H} NMR spectra data are referenced to external BF<sub>3</sub>•Et<sub>2</sub>O. HRMS data were measured with ESI techniques.

## Experimental

### Typical procedure for synthesis of 1a, 4a-4h (Take 1a as an example):

To a 10 ml dried flask were sequentially added *o*-carborane (14.4 mg, 0.1 mmol), THF (1 ml), iodobenzene (22.3 μl, 0.2 mmol), Pd(OAc)<sub>2</sub> (1.2 mg, 0.005 mmol), 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (IPrHCl, L1) (4.3 mg, 0.01 mmol) and Ag<sub>2</sub>CO<sub>3</sub> (27.5 mg, 0.1 mmol) under an argon atmosphere. After the reaction was stirred at 25 °C for 24 h, the mixture was filtered through a short silica gel column using ethyl acetate as eluent. After evaporation of the solvent, the residue was purified by column chromatography on 200-300 mesh silica gel with *n*-hexane as eluent to gave the 2a with 42% yield (9.2 mg).

### General procedure for synthesis of 3a-3p, 5a-5g, (Take 3a as an example):

To a 10 ml dried flask were sequentially added 3-Ph-*o*-carborane (22 mg, 0.1 mmol), THF (1 ml), phenylboronic acid (48 mg, 0.4 mmol), [Cp\*IrCl<sub>2</sub>]<sub>2</sub> (8 mg, 0.01 mmol), AgSbF<sub>6</sub> (34 mg, 0.1 mmol), AgBF<sub>4</sub> (80 mg, 0.4 mmol), CsF (45 mg, 0.3 mmol) and H<sub>2</sub>O (7.2 mg, 0.4 mmol) under an air atmosphere. After the reaction was stirred at 25 °C for 24 h, the mixture was filtered through a short silica gel column using ethyl acetate as eluent. After evaporation of the solvent, the residue was purified by column

chromatography on 200-300 mesh silica gel with *n*-hexane as eluent to gave the 1a with 82% yield (24.2 mg).

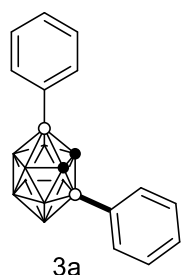
**Procedure for synthesis of 6a in 1 mmol scale:**

To a 50 ml dried flask were sequentially added 3-Ph-*o*-carborane (220 mg, 1 mmol), THF (10 ml), phenylboronic acid (480 mg, 4 mmol), [Cp\*IrCl<sub>2</sub>]<sub>2</sub> (80 mg, 0.1 mmol), AgSbF<sub>6</sub> (340 mg, 1 mmol), AgBF<sub>4</sub> (800 mg, 4 mmol), CsF (450 mg, 3 mmol) and H<sub>2</sub>O (72 mg, 4 mmol) under an air atmosphere. After the reaction was stirred at 25 °C for 24h, the mixture was filtered through a short silica gel column using ethyl acetate as eluent. After evaporation of the solvent, the residue was purified by column chromatography on 200-300 mesh silica gel with n-hexane as eluent to gave the 1a with 67% yield (198.3 mg).

**Reference:**

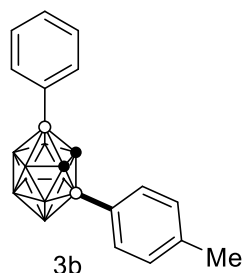
1.Xu, T.-T.; Cao, K.; Zhang, C.-Y.; Wu, J.; Ding, L.-F.; Yang, J., Old key opens the lock in carborane: The in situ NHC-Palladium catalytic system for selective arylation of B(3, 6)-H bonds of *o*-carboranes via B-H activation. *Org. Lett.* 2019, 21, 9276-9279.

**Spectroscopic data for products**



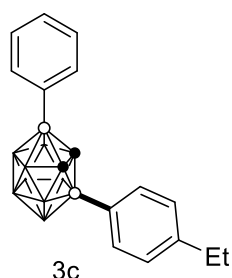
**3a:** 24.2 mg. Yield 82%. White solid (Melting point: 151.1°C). Purified by column chromatography with *n*-hexane as eluent.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm ): δ 7.63-7.61 (m, 4H), 7.44-7.40 (m, 2H), 7.38-7.35 (m, 4H), 3.85 (s, 2H, Cage C-H); <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>, ppm): δ 133.1, 129.8, 128.3, 59.1; <sup>11</sup>B{<sup>1</sup>H} NMR (160 MHz, CDCl<sub>3</sub>, ppm ): δ -2.2 (2B), -3.8 [2B, B(3, 6)-Ph], -11.3 (2B), -12.9 (4B); HRMS: calculated for C<sub>14</sub>B<sub>10</sub>H<sub>19</sub><sup>-</sup> (M-H)<sup>-</sup> 297.2422, found 297.2420.



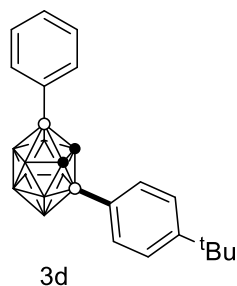
**3b:** 15.8 mg. Yield 51%. White solid (Melting point: 110.2°C). Purified by column chromatography with *n*-hexane as eluent.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.62-7.61 (m, 2H), 7.51-7.50 (d, 2H,  $J = 5$  Hz), 7.43-7.40 (m, 1H), 7.38-7.35 (m, 2H), 7.19-7.18 (d, 2H,  $J = 5$  Hz), 3.83 (s, 2H, Cage C-H), 2.36 (s, 3H,  $-\text{CH}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  139.9, 133.1, 129.7, 129.0, 128.3, 59.1, 21.3;  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  -2.3 (2B), -3.7 [2B, B(3)-Ph & B(6)-Ph], -11.4 (2B), -13.0 (4B); HRMS: calculated for  $\text{C}_{15}\text{H}_{22}\text{B}_{10}^-$  (M-H) $^-$  311.2579, found 311.2584.



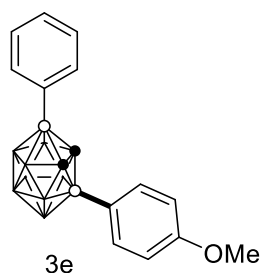
**3c:** 22 mg. Yield 68%. White solid (Melting point: 108.3°C). Purified by column chromatography with *n*-hexane as eluent.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.62-7.61 (m, 2H), 7.54-7.53 (d, 2H,  $J = 5$  Hz), 7.43-7.40 (m, 1H), 7.37-7.35 (m, 2H), 7.21-7.20 (m, 2H), 3.83 (s, 2H, Cage C-H), 2.67-2.64 (q, 2H,  $J = 5$  Hz,  $-\text{CH}_2-$ ), 1.25-1.22 (m, 3H,  $-\text{CH}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  146.2, 133.2, 129.7, 128.3, 127.9, 59.1, 28.7, 15.4;  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  -2.3 (2B), -3.7 [2B, B(3)-Ph & B(6)-Ph], -11.4 (2B), -13.0 (4B); HRMS: calculated for  $\text{C}_{16}\text{H}_{24}\text{B}_{10}^-$  (M-H) $^-$  325.2735, found 325.2748.



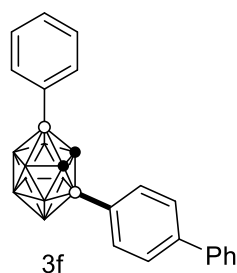
**3d:** 27.5 mg. Yield 65%. White solid (Melting point: 150.4°C). Purified by column chromatography with *n*-hexane as eluent.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.61-7.60 (m, 2H), 7.57-7.55 (m, 2H), 7.43-7.39 (m, 3H), 7.38-7.35 (m, 2H), 3.84 (s, 2H, Cage C-H), 1.32 (s, 9H, - $\text{CH}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  153.0, 133.1, 129.7, 128.2, 125.3, 59.1, 34.7, 31.2;  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  -2.3 (2B), -3.7 [2B, B(3)-Ph & B(6)-Ph], -11.4 (2B), -13.0 (4B); HRMS: calculated for  $\text{C}_{18}\text{H}_{28}\text{B}_{10}^-$  (M-H) $^-$  353.3048, found 353.3040.



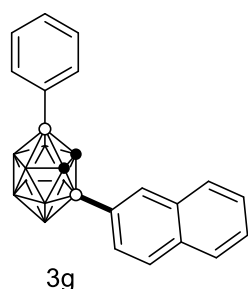
**3e:** 12.5 mg. Yield 38%. White solid (Melting point: 119.4°C). Purified by column chromatography with *n*-hexane/EtOAc=20:1 as eluent.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.62-7.61 (m, 2H), 7.55-7.53 (m, 2H), 7.43-7.41 (m, 1H), 7.38-7.35 (m, 2H), 6.91-6.89 (m, 2H), 3.82 (m, 5H, Cage C-H & - $\text{OCH}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  161.0, 134.6, 133.1, 129.7, 128.3, 113.9, 59.1, 55.2;  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  -2.2 (2B), -3.5 [2B, B(3)-Ph & B(6)-Ph], -11.3 (2B), -12.9 (4B);  $\text{C}_{15}\text{H}_{22}\text{B}_{10}\text{O}^-$  (M-H) $^-$  327.2528, found 327.2522.



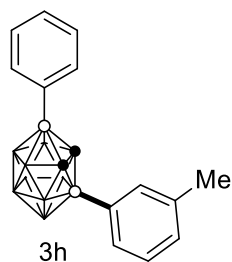
**3f:** 26.9 mg. Yield 72%. White solid (Melting point: 141.9°C). Purified by column chromatography with *n*-hexane as eluent.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.70-7.69 (m, 2H), 7.64-7.63 (m, 2H), 7.61-7.58 (m, 4H), 7.47-7.41 (m, 3H), 7.39-7.36 (m, 3H), 3.89 (s, 2H, Cage C-H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  142.7, 140.4, 133.6, 133.1, 129.8, 128.9, 128.3, 127.7, 127.1, 127.0, 59.1;  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  -2.2 (2B), -3.7 [2B, B(3)-Ph & B(6)-Ph], -11.3 (2B), -12.9 (4B); HRMS: calculated for  $\text{C}_{20}\text{H}_{24}\text{B}_{10}^-$  (M-H) $^-$  373.2735, found 373.2747.



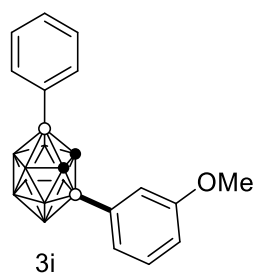
**3g:** 26 mg. Yield 75%. White solid (Melting point: 87.1°C). Purified by column chromatography with *n*-hexane as eluent.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  8.11 (s, 1H), 7.85-7.83 (m, 3H), 7.68-7.64 (m, 3H), 7.53-7.50 (m, 2H), 7.45-7.42 (m, 1H), 7.39-7.36 (m, 2H), 3.95 (s, 2H, Cage C-H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  133.8, 133.2, 132.8, 129.8, 129.3, 128.3, 128.0, 127.8, 127.0, 126.6, 59.2;  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  -2.1 (2B), -3.6 [2B, B(3)-Ph & B(6)-Ph], -11.2 (2B), -12.8 (4B); HRMS: calculated for  $\text{C}_{18}\text{H}_{22}\text{B}_{10}^-$  (M-H) $^-$  347.2579, found 347.2567.



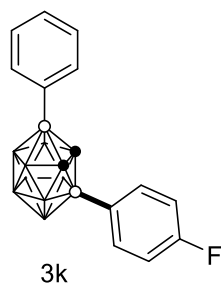
**3h:** 19.9 mg. Yield 64%. White solid (Melting point: 178.8°C). Purified by column chromatography with *n*-hexane as eluent.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.63-7.62 (m, 2H), 7.44-7.41 (m, 3H), 7.38-7.35 (m, 2H), 7.25-7.22 (m, 2H), 3.84 (s, 2H, Cage C-H), 2.37 (s, 3H,  $-\text{CH}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  133.9, 133.1, 130.5, 130.2, 129.8, 128.3, 59.1, 21.4;  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  -2.3 (2B), -3.8 [2B, B(3)-Ph & B(6)-Ph], -11.4 (2B), -13.0 (4B); HRMS: calculated for  $\text{C}_{15}\text{H}_{22}\text{B}_{10}^-$  (M-H) $^-$  311.2579, found 311.2583.



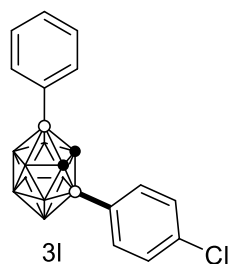
**3i:** 25.3mg. Yield 77%. White solid (Melting point: 150.4°C). Purified by column chromatography with *n*-hexane/EtOAc=20:1 as eluent.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.62-7.61 (m, 2H), 7.44-7.41 (m, 1H), 7.38-7.36 (m, 2H), 7.31-7.28 (m, 1H), 7.17-7.16 (m, 2H), 6.96-6.94 (m, 1H), 3.84-3.83 (m, 5H, Cage C-H &  $-\text{OCH}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  159.3, 133.1, 129.8, 129.5, 128.3, 125.2, 119.2, 114.8, 59.1, 55.3;  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  -2.3 (2B), -3.9 [2B, B(3)-Ph & B(6)-Ph], -11.3 (2B), -12.9 (4B); HRMS: calculated for  $\text{C}_{15}\text{H}_{22}\text{B}_{10}\text{O}^-$  (M-H) $^-$  327.2528, found 327.2527.



**3k:** 31.1 mg. Yield 98%. White solid (Melting point: 148.2°C). Purified by column chromatography with *n*-hexane as eluent.

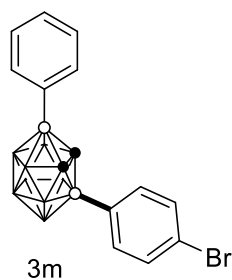
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.62-7.58 (m, 4H), 7.44-7.41 (m, 1H), 7.38-7.36 (m, 2H), 7.08-7.04 (m, 2H), 3.82 (s, 2H, Cage C-H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  164.1 ( $J=200\text{Hz}$ ), 135.1 ( $J=12.5\text{Hz}$ ), 133.1, 129.8, 128.3, 115.4 ( $J=12.5\text{Hz}$ ), 59.1;  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  -2.1 (2B), -3.9 [2B, B(3)-Ph & B(6)-Ph], -11.3 (2B), -13.0 (4B); HRMS: calculated for  $\text{C}_{14}\text{H}_{19}\text{B}_{10}\text{F}^-$  (M-H) $^-$  315.2328, found 315.2330.



**3l:** 32.3mg. Yield 98%. White solid (Melting point: 152.7°C). Purified by column chromatography with *n*-hexane as eluent.

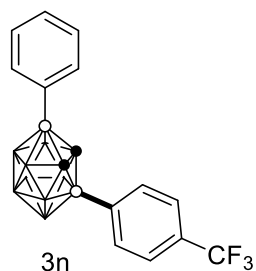
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.62-7.61 (m, 2H), 7.55-7.54 (d, 2H,  $J=5\text{ Hz}$ ), 7.44-7.42 (m, 1H), 7.38-7.34 (m, 4H), 3.82 (s, 2H, Cage C-H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  136.3, 134.4, 133.1, 129.9, 128.5, 128.3, 59.0;  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  -2.2 (2B), -4.4 [2B, B(3)-Ph & B(6)-Ph], -11.4 (2B), -13.0 (4B); HRMS: calculated for  $\text{C}_{14}\text{H}_{19}\text{B}_{10}\text{Cl}^-$  (M-H) $^-$  331.2076, found 331.2063.





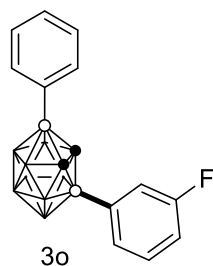
**3m**: 34.6 mg. Yield 92%. White solid (Melting point: 151.5°C). Purified by column chromatography with *n*-hexane as eluent.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.62-7.61 (m, 2H), 7.51-7.47 (m, 4H), 7.45-7.42 (m, 1H), 7.39-7.36 (m, 2H), 3.82 (s, 2H, Cage C-H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  134.6, 133.1, 131.5, 129.9, 128.3, 58.9;  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  -2.0 (2B), -3.7 [2B, B(3)-Ph & B(6)-Ph], -11.2 (2B), -12.9 (4B); HRMS: calculated for  $\text{C}_{14}\text{H}_{19}\text{B}_{10}\text{Br}^-$  (M-H) $^-$  375.1580, found 375.1577.



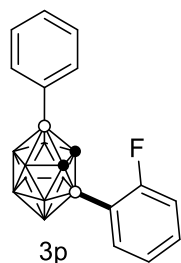
**3n**: 26.6 mg. Yield 73%. White solid (Melting point: 111.1°C). Purified by column chromatography with *n*-hexane as eluent.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.75-7.74 (d, 2H,  $J = 5$  Hz), 7.63-7.62 (d, 4H,  $J = 5$  Hz), 7.45-7.42 (m, 1H), 7.39-7.37 (m, 2H), 3.86 (s, 2H, Cage C-H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  133.3 ( $J = 50\text{Hz}$ ), 131.9 ( $J = 25\text{Hz}$ ), 129.9, 128.3, 124.9 ( $J = 12.5\text{Hz}$ ), 124.8, 123.0, 58.9;  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  -2.0 (2B), -4.7 [2B, B(3)-Ph & B(6)-Ph], -11.3 (2B), -12.9 (4B); HRMS: calculated for  $\text{C}_{15}\text{H}_{19}\text{B}_{10}\text{F}_3^-$  (M-H) $^-$  365.2296, found 365.2300.



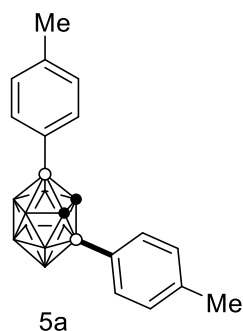
**3o**: 22.5 mg. Yield 71%. White solid (Melting point: 114.5°C). Purified by column chromatography with *n*-hexane as eluent.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.63-7.61 (m, 2H), 7.44-7.42 (m, 1H), 7.39-7.30 (m, 5H), 7.13-7.09 (m, 1H), 3.84 (s, 2H, Cage C-H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm): 161.8, 133.1, 130.1 ( $J = 12.5\text{Hz}$ ), 129.9, 128.6 ( $J = 12.5\text{Hz}$ ), 128.3, 119.9 ( $J = 25\text{Hz}$ ), 116.8 ( $J = 25\text{Hz}$ ), 59.0;  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  -2.1 (2B), -3.7 [1B, B(3)-Ph], -4.6 [1B, B(6)-Ph], -11.3 (2B), -13.0 (4B); HRMS: calculated for  $\text{C}_{14}\text{H}_{19}\text{B}_{10}\text{F}^-$  (M-H) $^-$  315.2328, found 315.2328. HRMS: calculated for  $\text{C}_{14}\text{H}_{19}\text{B}_{10}\text{F}^-$  (M-H) $^-$  315.2328, found 315.2328.



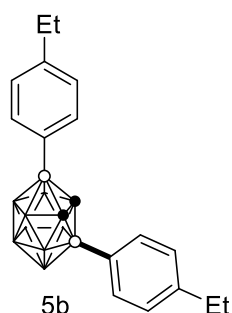
**3p**: 29.9 mg. Yield 94%. White solid (Melting point: 117.2°C). Purified by column chromatography with *n*-hexane as eluent.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.86-7.84 (m, 1H), 7.64-7.63 (m, 2H), 7.45-7.37 (m, 4H), 7.24-7.21 (t, 1H,  $J = 10$  Hz), 7.03-6.99 (m, 1H), 4.18 (s, 2H, Cage C-H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  164.9 ( $J = 200\text{Hz}$ ), 137.9 ( $J = 12.5\text{Hz}$ ), 133.0, 131.8 ( $J = 12.5\text{Hz}$ ), 129.7, 128.3, 124.7 ( $J = 12.5\text{Hz}$ ), 115.1 ( $J = 12.5\text{Hz}$ ), 58.3;  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  -2.6 (2B), -4.4 [1B, B(3)-Ph], -6.1 [1B, B(6)-Ph], -10.6 (2B), -12.1 (4B); HRMS: calculated for  $\text{C}_{14}\text{H}_{19}\text{B}_{10}\text{F}^-$  (M-H) $^-$  315.2328, found 315.2324.



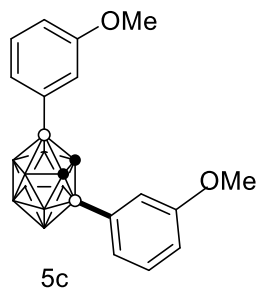
**5a:** 17.2 mg. Yield 53%. White solid (Melting point: 150.0°C). Purified by column chromatography with *n*-hexane as eluent.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.51-7.50 (d, 4H,  $J = 5$  Hz), 7.19-7.18 (d, 4H,  $J = 5$  Hz), 3.81 (s, 2H, Cage C-H), 2.36 (s, 6H,  $-\text{CH}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  139.8, 133.1, 129.0, 59.1, 21.3;  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  -2.3 (2B), -3.5 [2B, B(3, 6)-Ph], -11.5 (2B), -13.0 (4B); HRMS: calculated for  $\text{C}_{16}\text{H}_{24}\text{B}_{10}^-$  (M-H) $^-$  325.2735, found 352.2725.



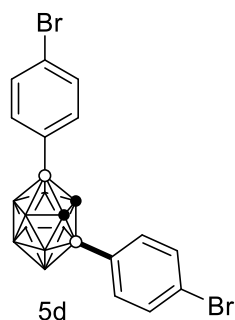
**5b:** 20.9mg. Yield 59%. White solid (Melting point: 99.1°C). Purified by column chromatography with *n*-hexane as eluent.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.54-7.53 (d, 4H,  $J = 5$  Hz), 7.21-7.20 (d, 4H,  $J = 5$  Hz), 3.82 (s, 2H, Cage C-H), 2.68-2.64 (m, 4H,  $-\text{CH}_2-$ ), 1.25-1.23 (m, 6H,  $-\text{CH}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  146.1, 133.2, 127.9, 59.1, 28.7, 15.4;  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  -2.4 (2B), -3.5 [2B, B(3)-Ph & B(6)-Ph], -11.5 (2B), -13.0 (4B); HRMS: calculated for  $\text{C}_{18}\text{H}_{28}\text{B}_{10}^-$  (M-H) $^-$  353.3048, found 353.3031.



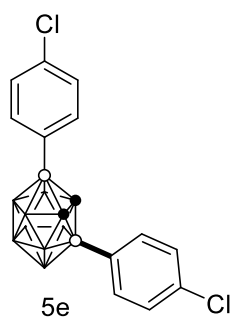
**5c:** 30.8 mg. Yield 67%. White solid (Melting point: 158.2°C). Purified by column chromatography with *n*-hexane/EtOAc=20:1 as eluent.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.41-7.36 (m, 3H), 7.27-7.26 (m, 3H), 7.07-7.05 (m, 2H), 3.94 (m, 8H, Cage C-H & -OCH<sub>3</sub>);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  159.3, 129.5, 125.2, 119.2, 114.8, 59.1, 55.2;  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  -2.3 (2B), -4.0 [2B, B(3)-Ph & B(6)-Ph], -11.4 (2B), -12.9 (4B); HRMS: calculated for  $\text{C}_{16}\text{H}_{24}\text{B}_{10}\text{O}_2^-$  (M-H)<sup>-</sup> 357.2634, found 357.2621.



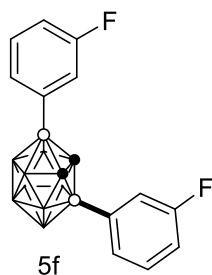
**5d:** 33.2mg. Yield 73%. White solid (Melting point: 175.2°C). Purified by column chromatography with *n*-hexane as eluent.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.52-7.50 (m, 4H), 7.48-7.46 (m, 4H), 3.79 (s, 2H, Cage C-H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  134.6, 131.5, 124.8, 58.8;  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  -1.9 (2B), -4.1 [2B, B(3, 6)-Ph], -11.1 (2B), -12.9 (4B); HRMS: calculated for  $\text{C}_{14}\text{H}_{18}\text{B}_{10}\text{Br}_2^-$  (M-H)<sup>-</sup> 453.0685, found 453.0693.



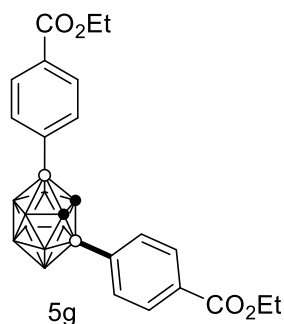
**5e:** 28.9mg. Yield 76%. White solid (Melting point: 173.8°C). Purified by column chromatography with *n*-hexane as eluent.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.55-7.53 (m, 4H), 7.36-7.34 (m, 4H), 3.80 (s, 2H, Cage C-H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  136.4, 134.4, 128.6, 58.9;  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  -2.0 (2B), -4.2 [2B, B(3, 6)-Ph], -11.2 (2B), -13.0 (4B); HRMS: calculated for  $\text{C}_{14}\text{H}_{18}\text{B}_{10}\text{Cl}_2^-$  (M-H) $^-$  365.1686, found 365.1683.



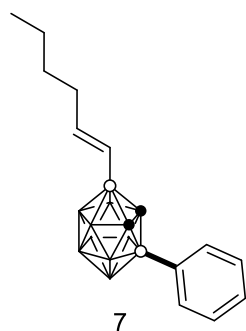
**5f:** 23.5mg. Yield 71%. White solid (Melting point: 112.9°C). Purified by column chromatography with *n*-hexane as eluent.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.38-7.30 (m, 6H), 7.13-7.10 (m, 2H), 3.83 (s, 2H, Cage C-H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  162.6 ( $J = 200\text{Hz}$ ), 130.1 ( $J = 12.5\text{Hz}$ ), 128.6 ( $J = 12.5\text{Hz}$ ), 119.9 ( $J = 25\text{Hz}$ ), 116.9 ( $J = 25\text{Hz}$ ), 58.9;  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  -2.0 (2B), -4.5 [2B, B(3, 6)-Ph], -11.0 (2B), -12.9 (4B); HRMS: calculated for  $\text{C}_{14}\text{H}_{18}\text{B}_{10}\text{F}_2^-$  (M-H) $^-$  333.2234, found 333.2252.



**5g:** 34.7 mg. Yield 83%. White solid (Melting point: 107.6°C). Purified by column chromatography with *n*-hexane/EtOAc=8:1 as eluent.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  8.02-8.01 (m, 4H), 7.70-7.69 (m, 4H), 4.40-4.36 (m, 4H,  $-\text{CH}_2-$ ), 3.91 (s, 2H, Cage C-H), 1.41-1.37 (m, 6H,  $-\text{CH}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  166.2, 133.1, 131.7, 129.1, 115.1, 61.2, 58.7, 14.3;  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  -1.8 (2B), -4.2 [2B, B(3, 6)-Ph], -10.9 (2B), -12.7 (4B); HRMS: calculated for  $\text{C}_{20}\text{H}_{28}\text{B}_{10}\text{O}_4^-$  (M-H) $^-$  441.2845, found 441.2849.



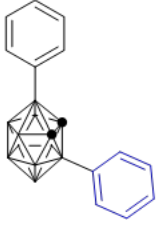
**7:** 20.8 mg. Yield 71%. Colorless liquid. Purified by column chromatography with *n*-hexane as eluent.

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.62-7.60 (m, 2H), 7.42-7.35 (m, 3H), 6.31-6.23 (m, 1H), 5.63-5.58 (d, 1H,  $J = 18\text{Hz}$ ), 3.62 (s, 2H, Cage C-H), 2.15-2.10 (m, 2H), 1.42-1.26 (m, 4H), 0.92-0.88 (t, 3H,  $J = 10\text{Hz}$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  149.4, 133.2, 129.7, 128.3, 59.0, 35.2, 30.6, 22.3, 14.0;  $^{11}\text{B}\{^1\text{H}\}$  NMR (160 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  -2.7 (2B), -4.7 [2B, B(6)-Ph & B(3)-Alkenyl], -11.9 (2B), -13.2 (4B); HRMS: calculated for  $\text{C}_{14}\text{H}_{26}\text{B}_{10}^-$  (M-H) $^-$  303.2892, found 303.2891.

YHB-16-H

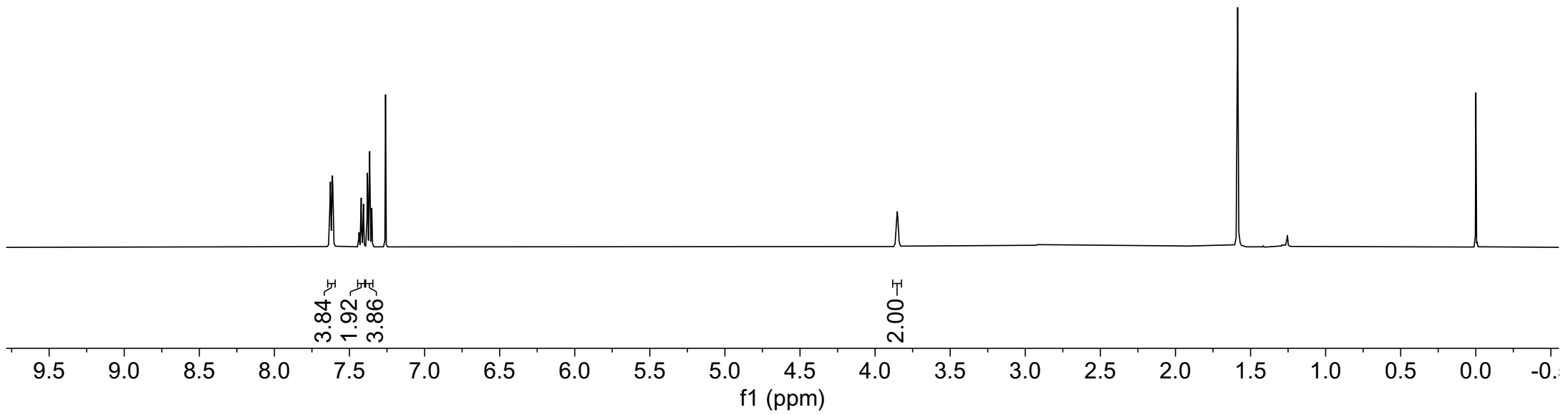
7.63  
7.61  
7.61  
7.44  
7.44  
7.43  
7.43  
7.42  
7.42  
7.41  
7.41  
7.40  
7.38  
7.38  
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7.37  
7.37  
7.36  
7.35  
7.35  
7.35  
7.26

3.85

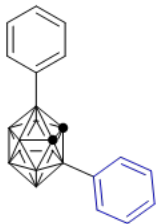


3a

<sup>1</sup>HNMR, CDCl<sub>3</sub>, 500MHz, 298K



YHB-16-C



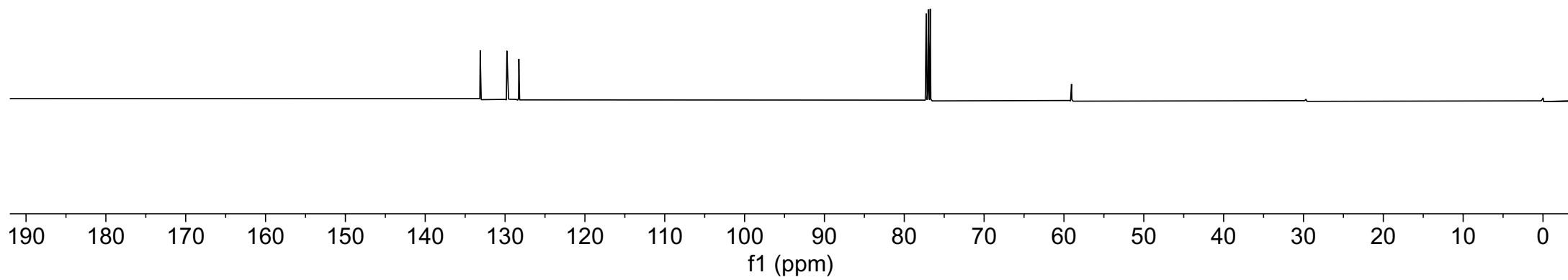
3a

<sup>13</sup>CNMR, CDCl<sub>3</sub>, 125MHz, 298K

~133.1  
~129.8  
~128.3

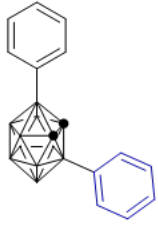
77.3  
77.0  
76.7

—59.1





YHB-16-B

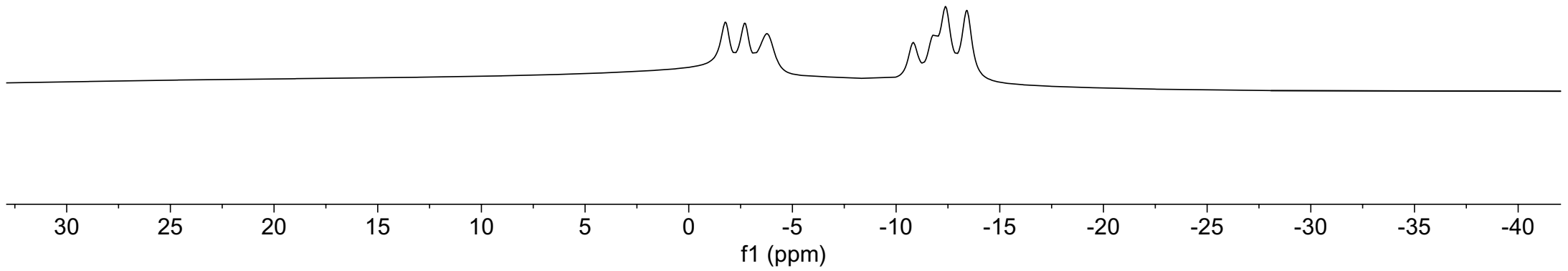


3a

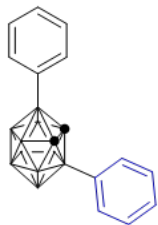
$^{11}\text{B}$ NMR,  $\text{CDCl}_3$ , 160MHz, 298K

~ -1.8  
~ -2.7  
~ -3.8

~ -10.8  
~ -11.8  
~ -12.4  
~ -13.4



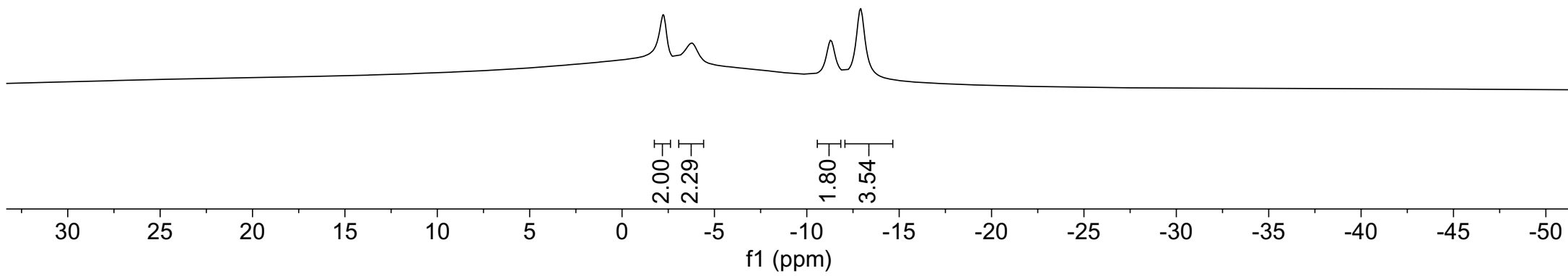
YHB-16-B{H}



3a

$^{11}\text{B}\{^1\text{H}\}$ NMR,  $\text{CDCl}_3$ , 160MHz, 298K

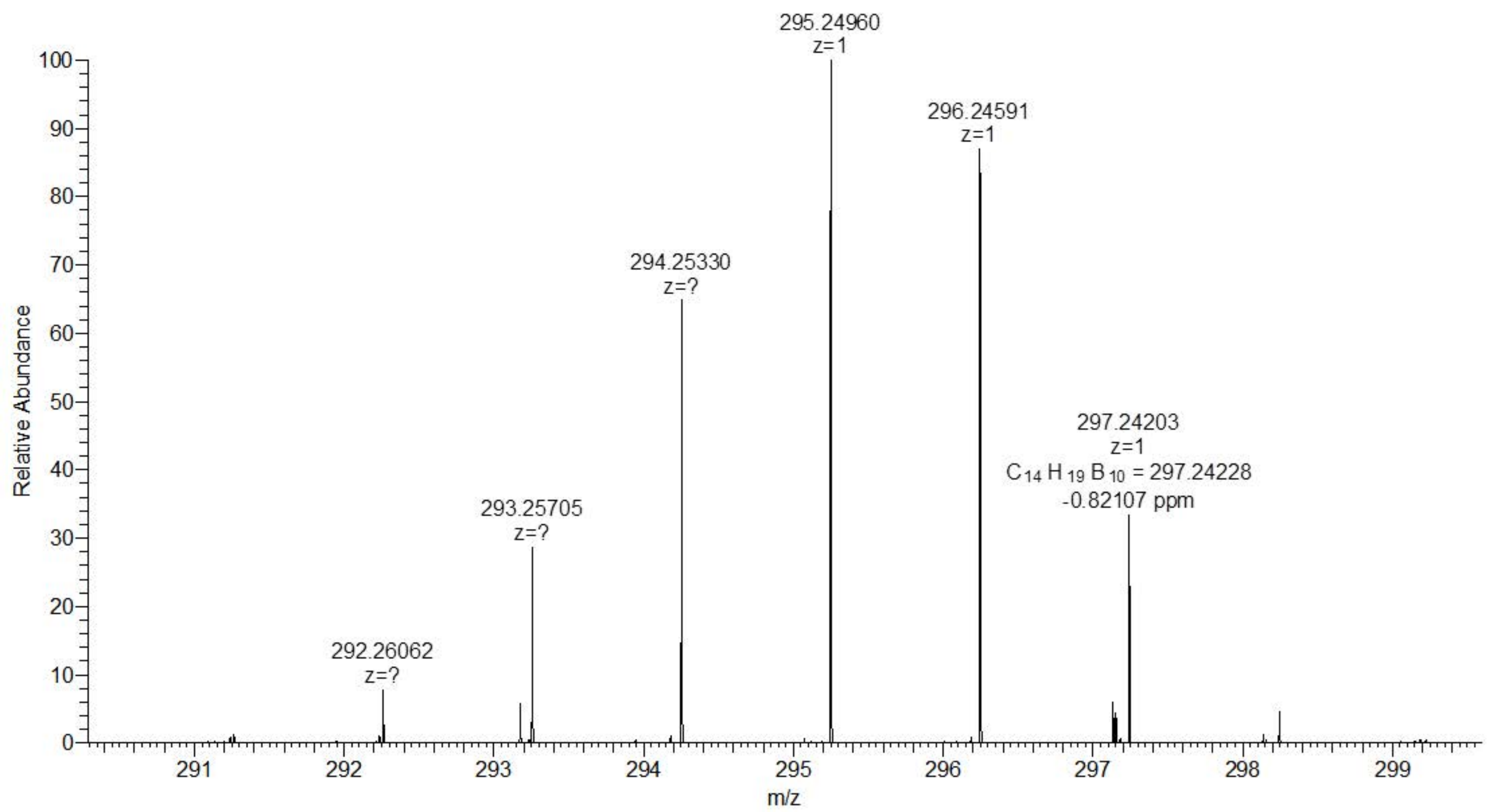
--2.2  
--3.8  
  
--11.3  
--12.9



YHB-16

HRMS (ESI)  $m/z$  calcd for  $C_{14}H_{19}B_{10} \cdot (M-H)^-$  297.2422, found 297.2420.

YHB-16 #12 RT: 0.11 AV: 1 NL: 1.56E8  
T: FTMS - p ESI Full ms [100.0000-800.0000]

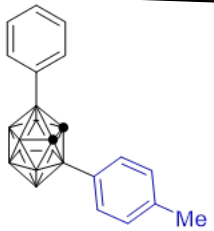


YHB-20-H

7.62  
7.61  
7.51  
7.50  
7.43  
7.43  
7.42  
7.42  
7.42  
7.41  
7.41  
7.40  
7.38  
7.38  
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7.36  
7.36  
7.35  
7.35  
7.35  
7.19  
7.18

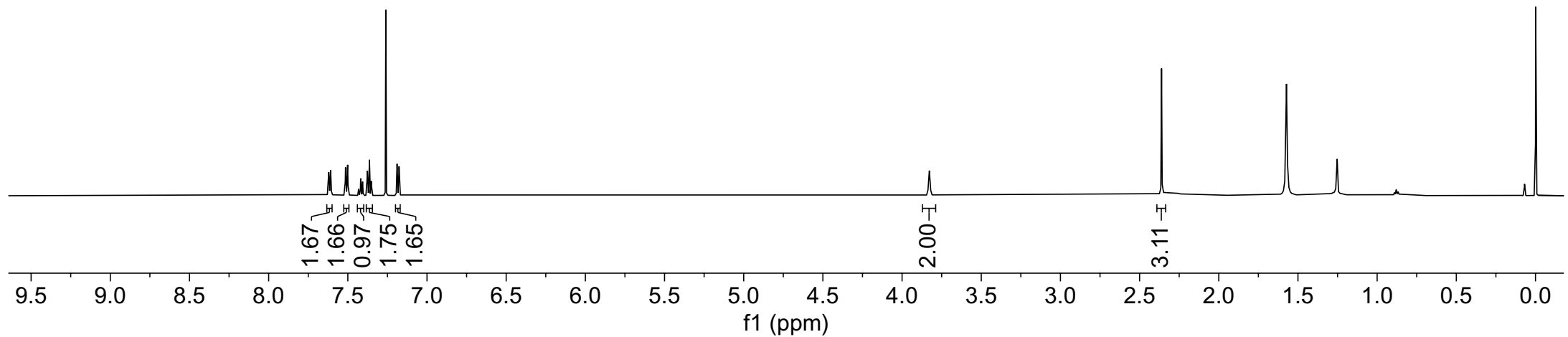
3.83

2.36

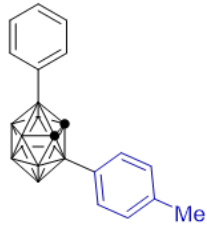


3b

<sup>1</sup>H NMR, CDCl<sub>3</sub>, 500 MHz, 298 K

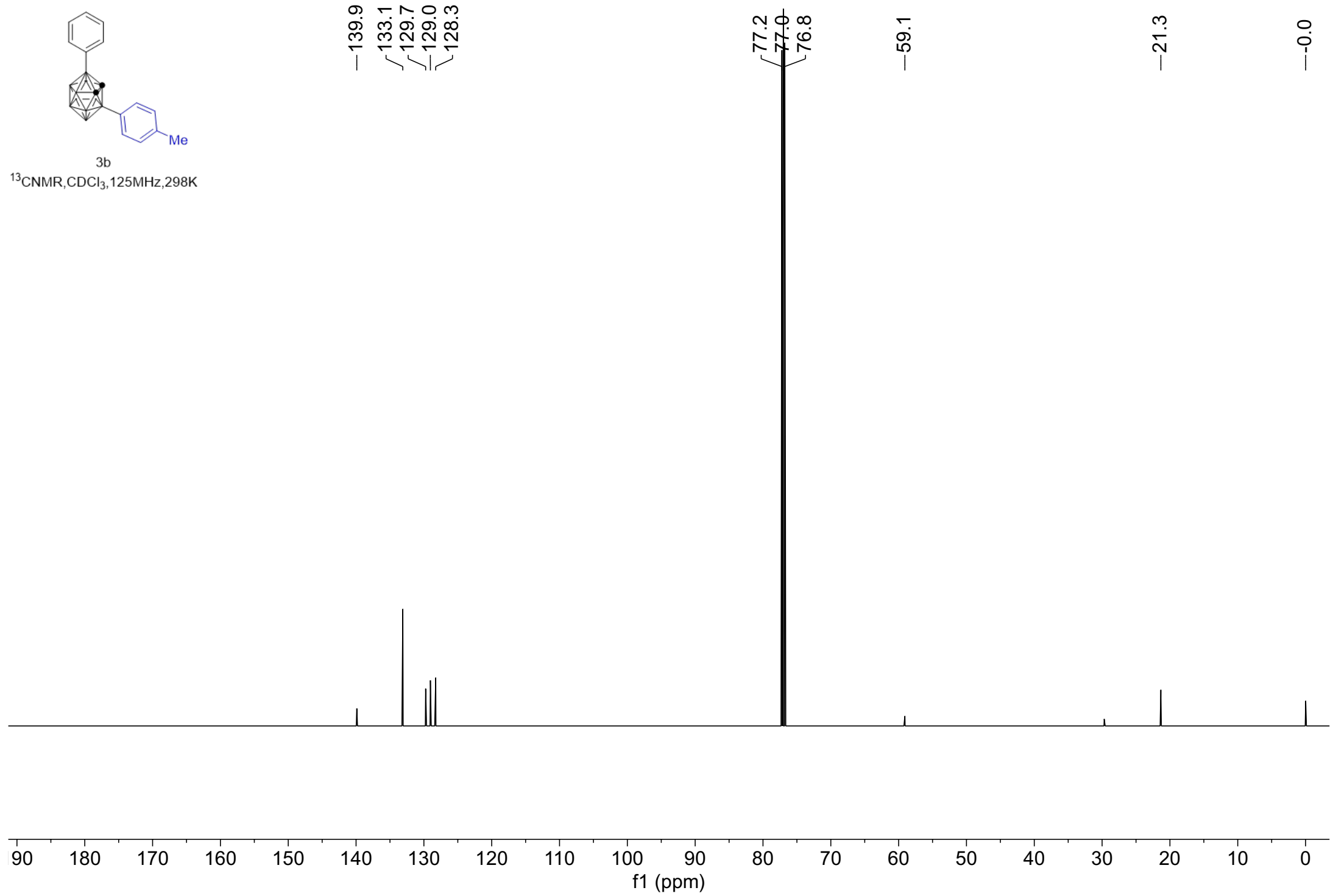


YHB-20-C

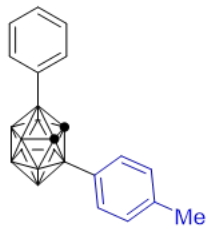


3b

$^{13}\text{C}$ NMR,  $\text{CDCl}_3$ , 125MHz, 298K



YHB-20-B

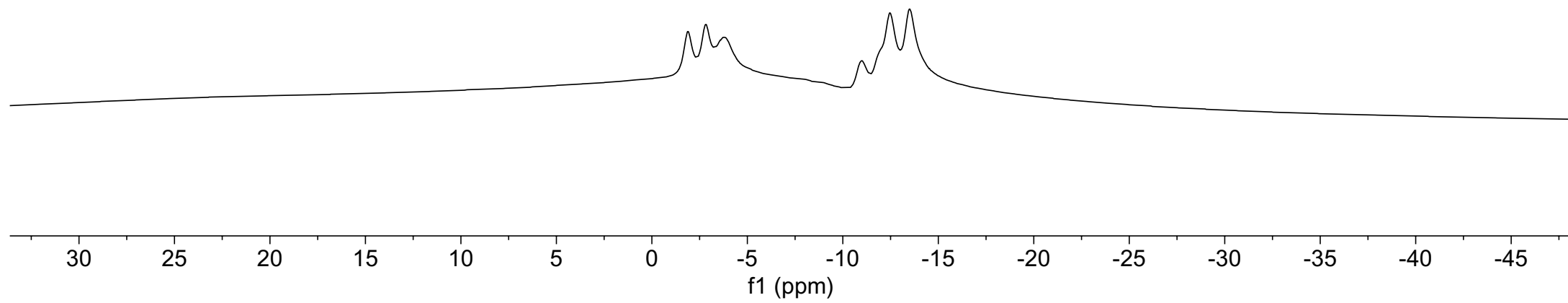


3b

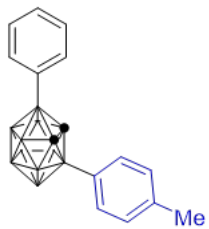
$^{11}\text{B}$ NMR,  $\text{CDCl}_3$ , 160MHz, 298K

~1.9  
~2.8  
~3.8

~11.0  
~12.5  
~13.5



YHB-20-B{H}

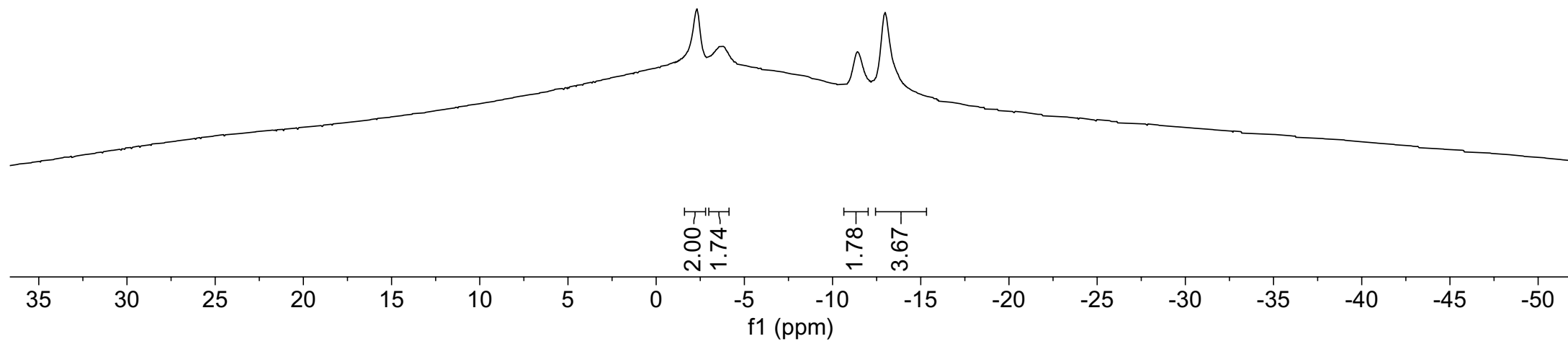


3b

$^{11}\text{B}\{^1\text{H}\}$ NMR,  $\text{CDCl}_3$ , 160MHz, 298K

--2.3  
--3.7

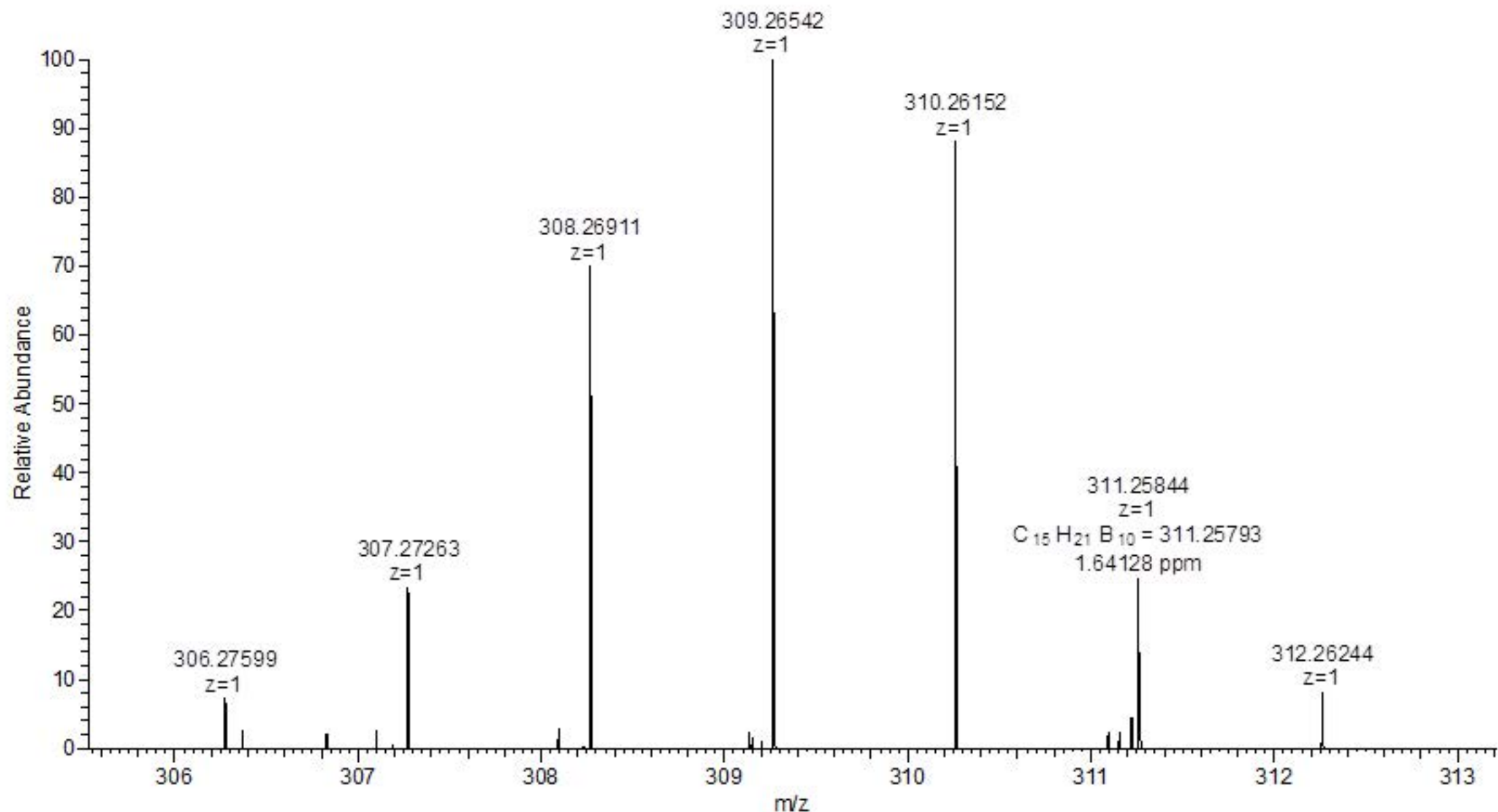
--11.4  
--13.0



Y20

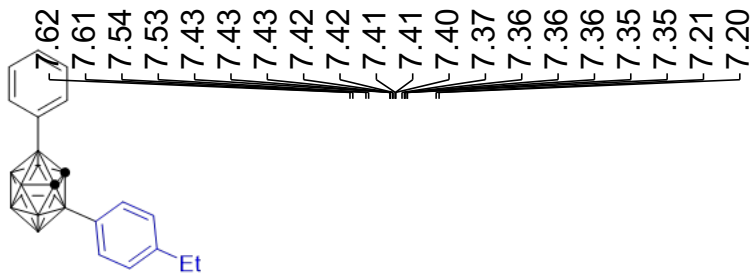
HRMS (ESI)  $m/z$  calcd for  $C_{15}H_{22}B_{10} \cdot (M-H)^-$  311.2579, found 311.2584.

Y20 #10 RT: 0.09 AV: 1 SB: 3 0.03-0.08 NL: 2.36E5  
T: FTMS - p ESI Full ms [100.0000-800.0000]



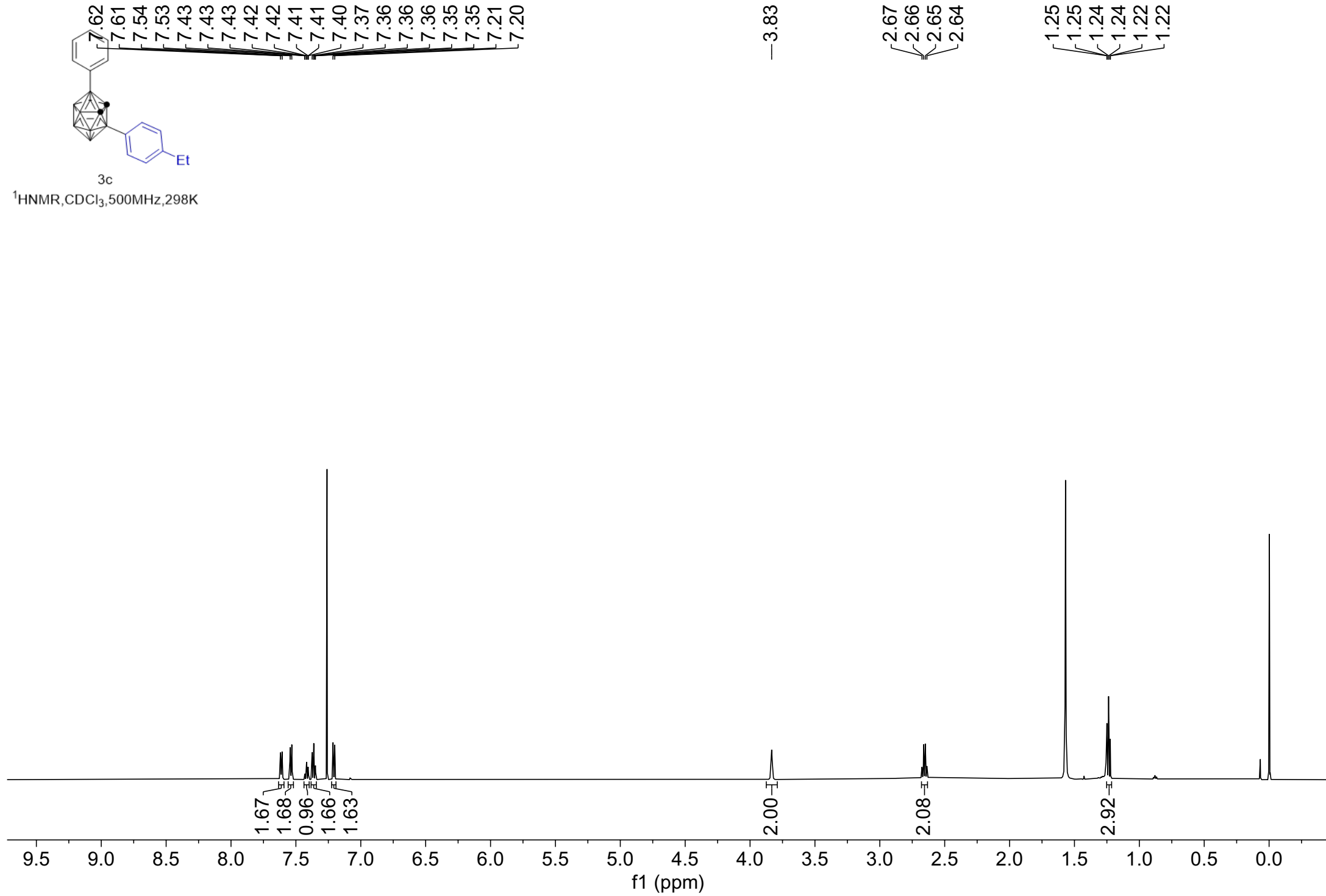


YHB-21-H

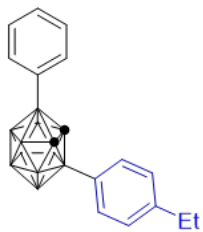


3c

<sup>1</sup>HNMR, CDCl<sub>3</sub>, 500MHz, 298K

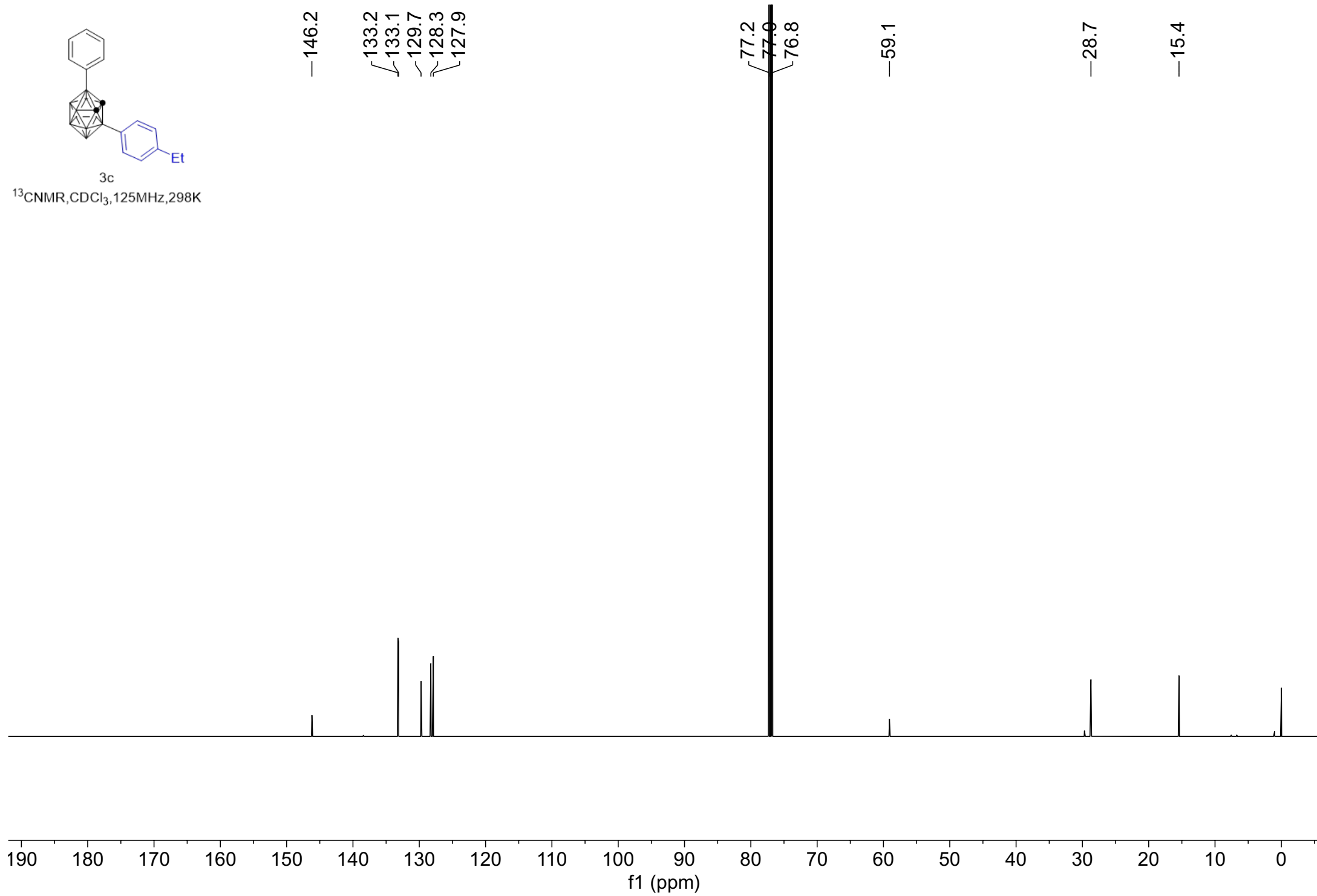


YHB-21-C

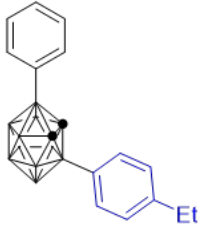


3c

$^{13}\text{C}$ NMR,  $\text{CDCl}_3$ , 125MHz, 298K



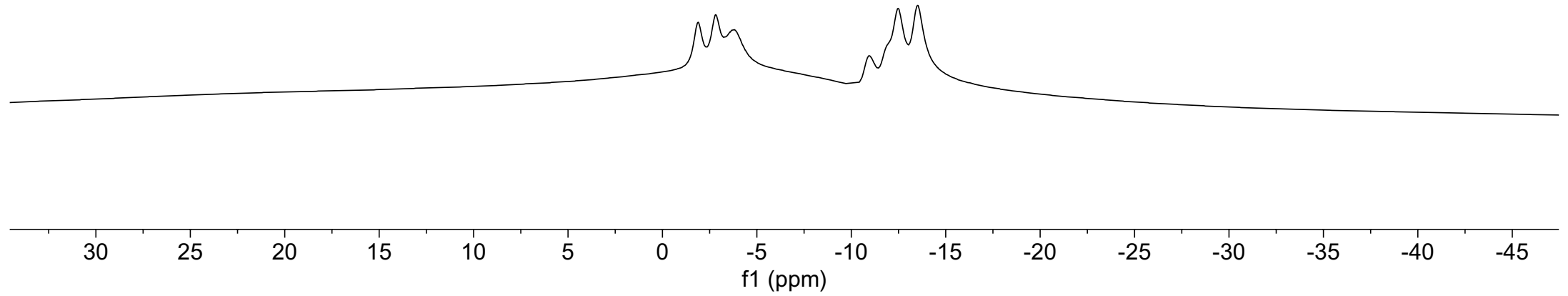
YHB-21-B



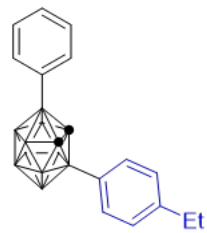
$^{11}\text{B}$ NMR,  $\text{CDCl}_3$ , 160MHz, 298K

~ -1.9  
~ -2.8  
~ -3.8

~ -10.9  
~ -12.5  
~ -13.5



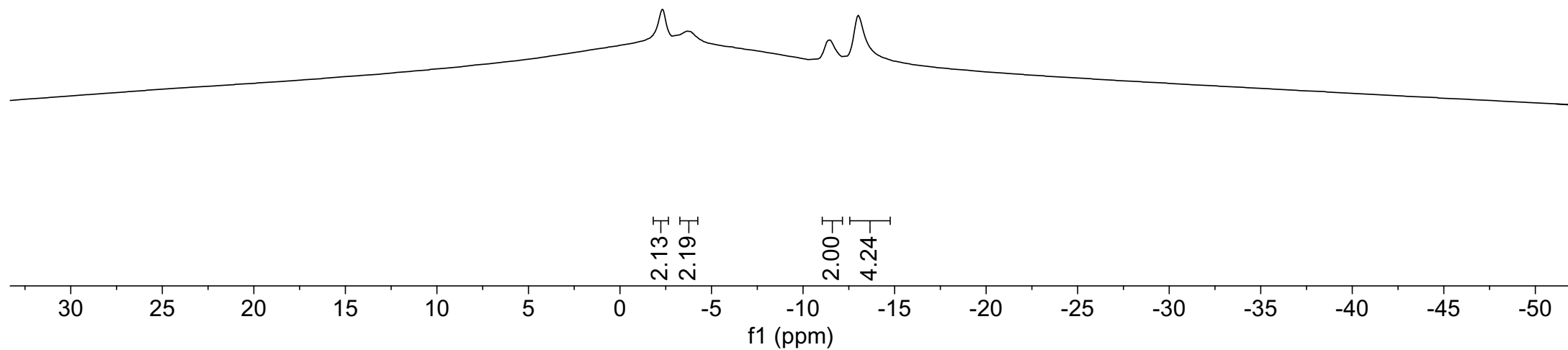
YHB-21-B{H}



3c

$^{11}\text{B}\{^1\text{H}\}$ NMR,  $\text{CDCl}_3$ , 160MHz, 298K

--2.3  
--3.7  
--11.4  
--13.0

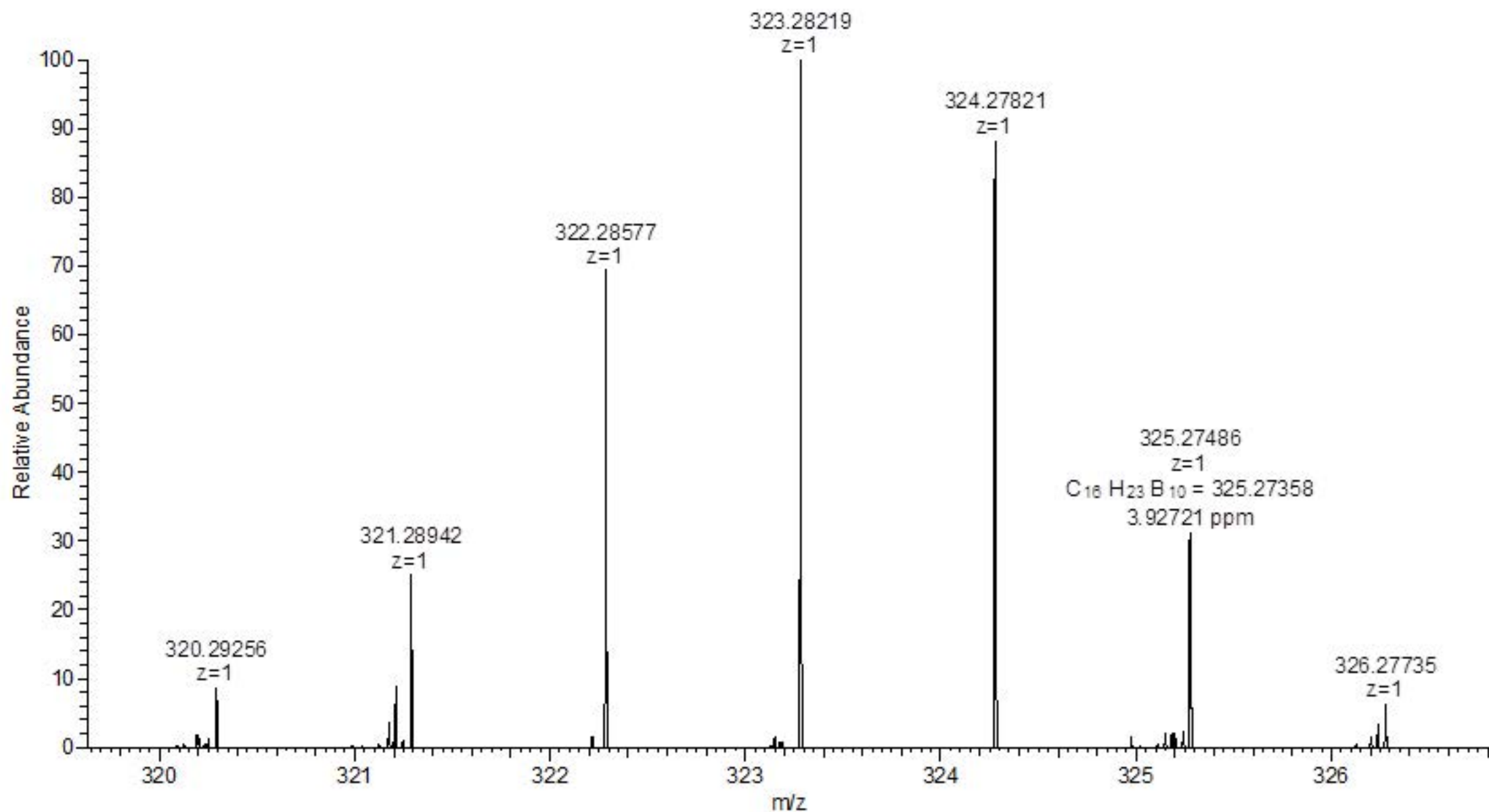


Y21

HRMS (ESI)  $m/z$  calcd for  $C_{16}H_{24}B_{10} (M-H)^-$  325.2735, found 311.2748.

Y21 #10 RT: 0.10 AV: 1 SB: 3 0.02-0.05 NL: 4.52E5

T: FTMS - p ESI Full ms [100.0000-800.0000]

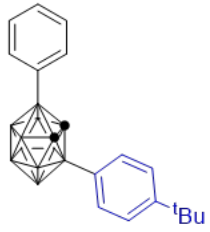


YHB-22-H

7.61  
7.60  
7.60  
7.57  
7.57  
7.56  
7.55  
7.43  
7.43  
7.43  
7.42  
7.42  
7.41  
7.41  
7.40  
7.40  
7.39  
7.39  
7.39  
7.39  
7.38  
7.37  
7.37  
7.37  
7.36  
7.36  
7.36  
7.35  
7.35  
7.35

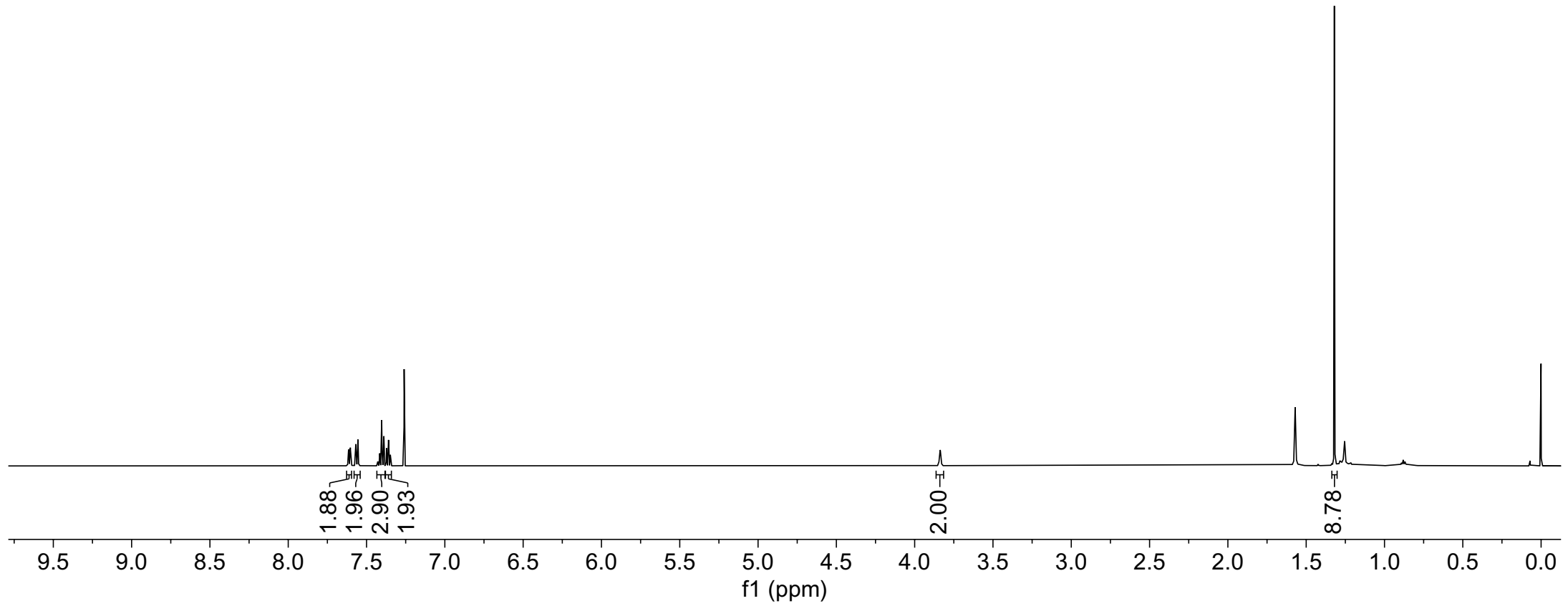
—3.84

—1.32

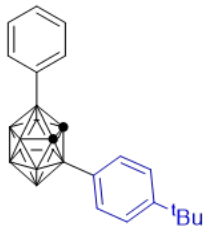


3d

<sup>1</sup>HNMR, CDCl<sub>3</sub>, 500MHz, 298K



YHB-22-C



3d

$^{13}\text{C}$ NMR,  $\text{CDCl}_3$ , 125MHz, 298K

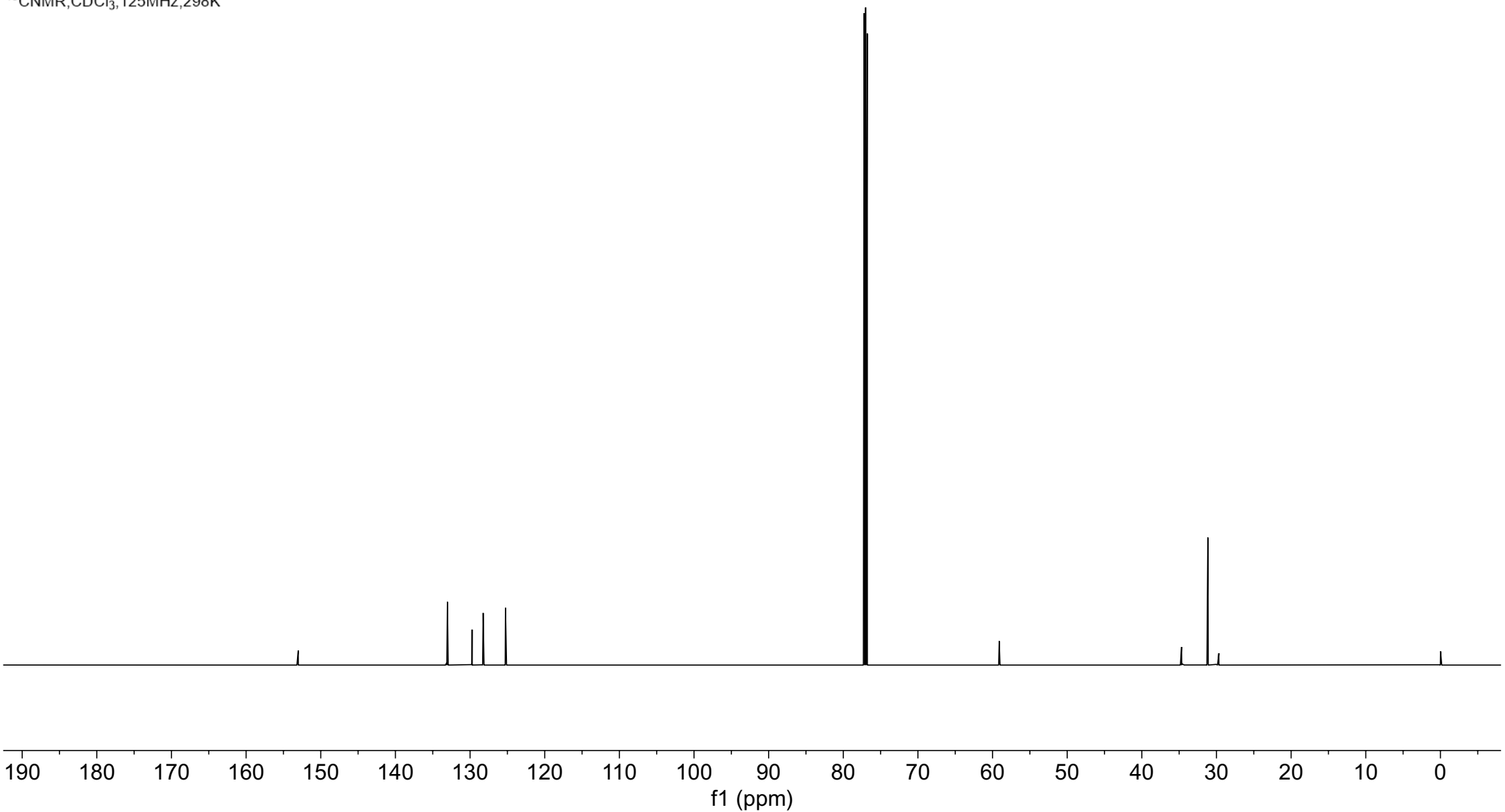
—153.0

133.1  
133.0  
129.7  
128.2  
125.3

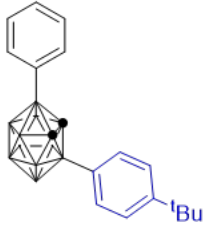
77.2  
77.0  
76.8

—59.1

—34.7  
—31.2



YHB-22-B

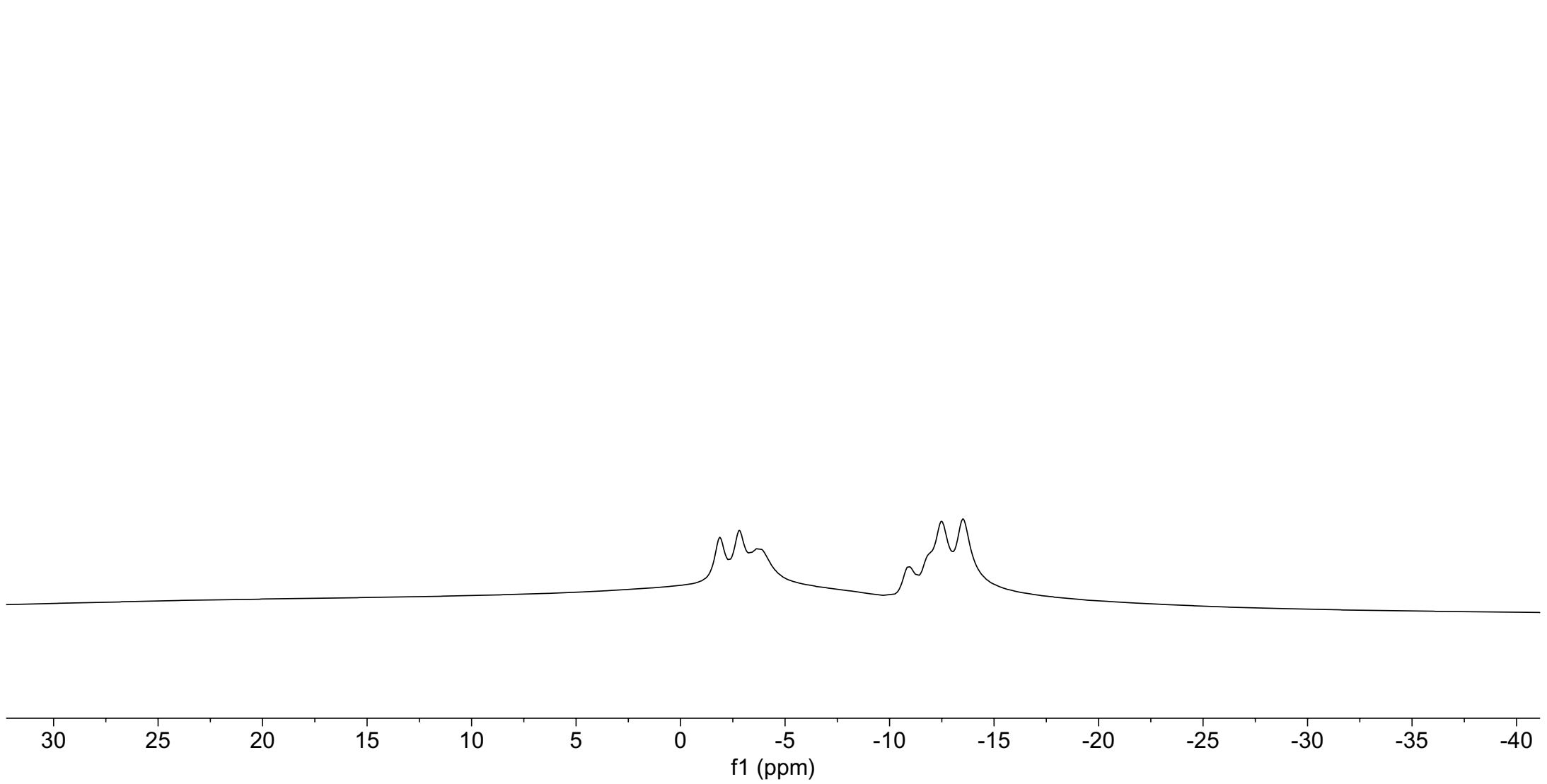


3d

$^{11}\text{B}$ NMR,  $\text{CDCl}_3$ , 160MHz, 298K

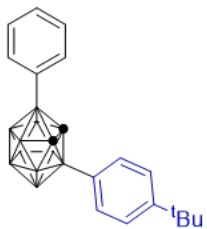
~1.9  
--2.8  
~3.8

~10.9  
~12.5  
~13.5





YHB-22-B{H}



3d

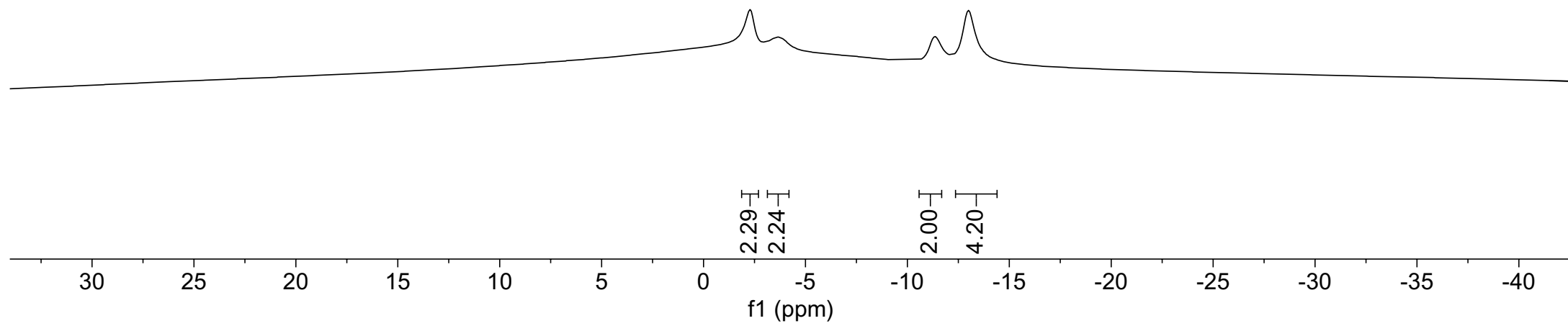
$^{11}\text{B}\{^1\text{H}\}$ NMR,  $\text{CDCl}_3$ , 160MHz, 298K

--2.3

--3.7

--11.4

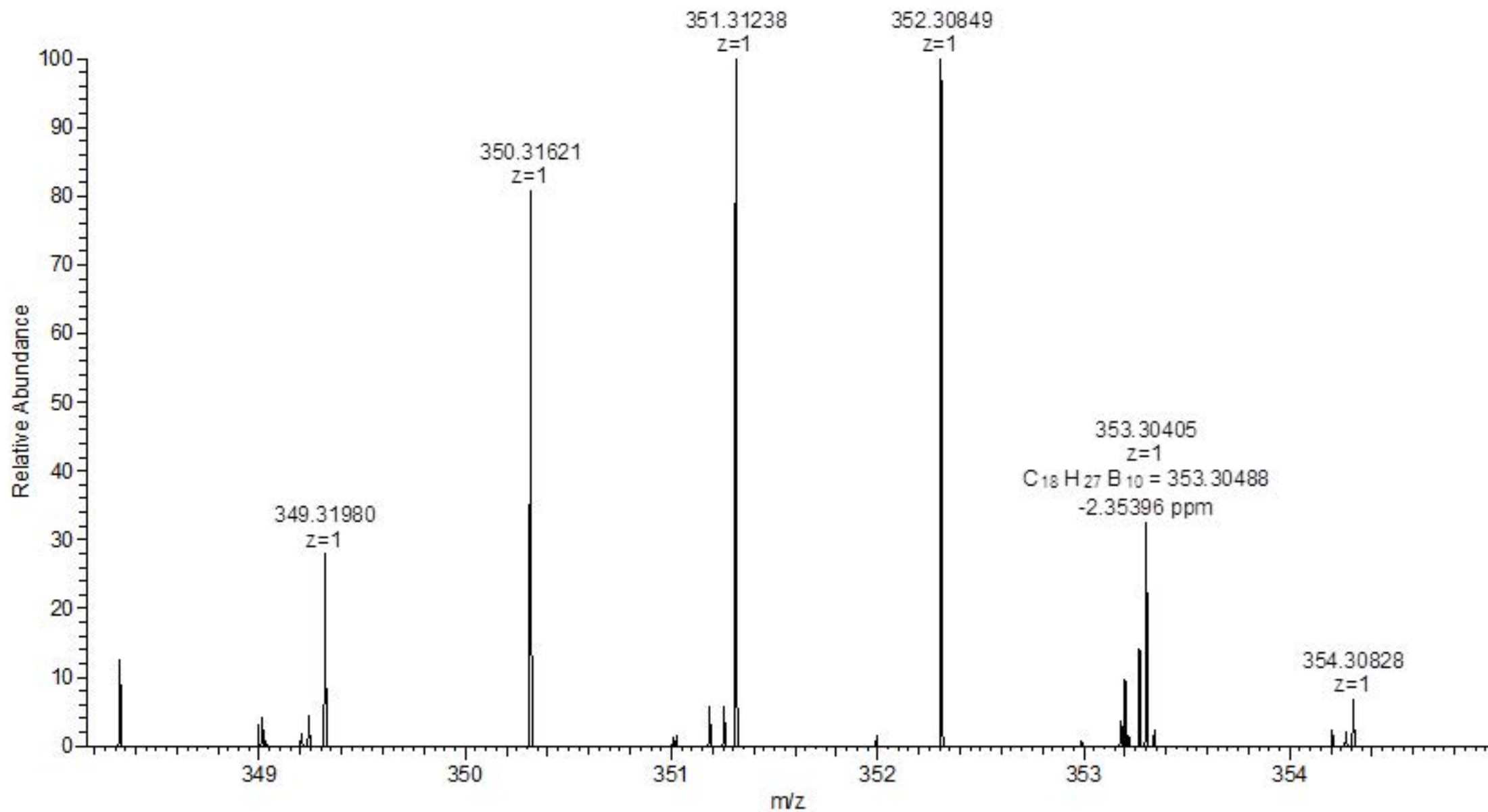
--13.0



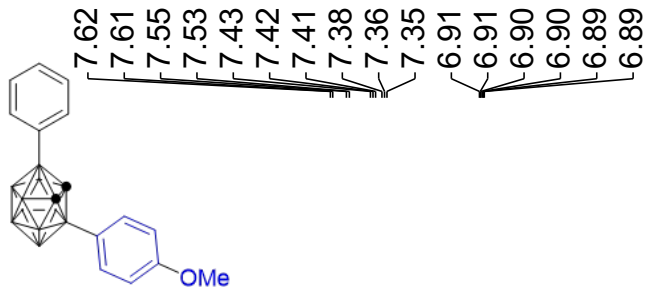
HRMS (ESI)  $m/z$  calcd for  $C_{18}H_{28}B_{10} \cdot (M-H)^-$  353.3048, found 353.3040.

Y22 #36 RT: 0.35 AV: 1 SB: 3 0.01-0.06 NL: 1.65E6

T: FTMS - p ESI Full ms [100.0000-800.0000]

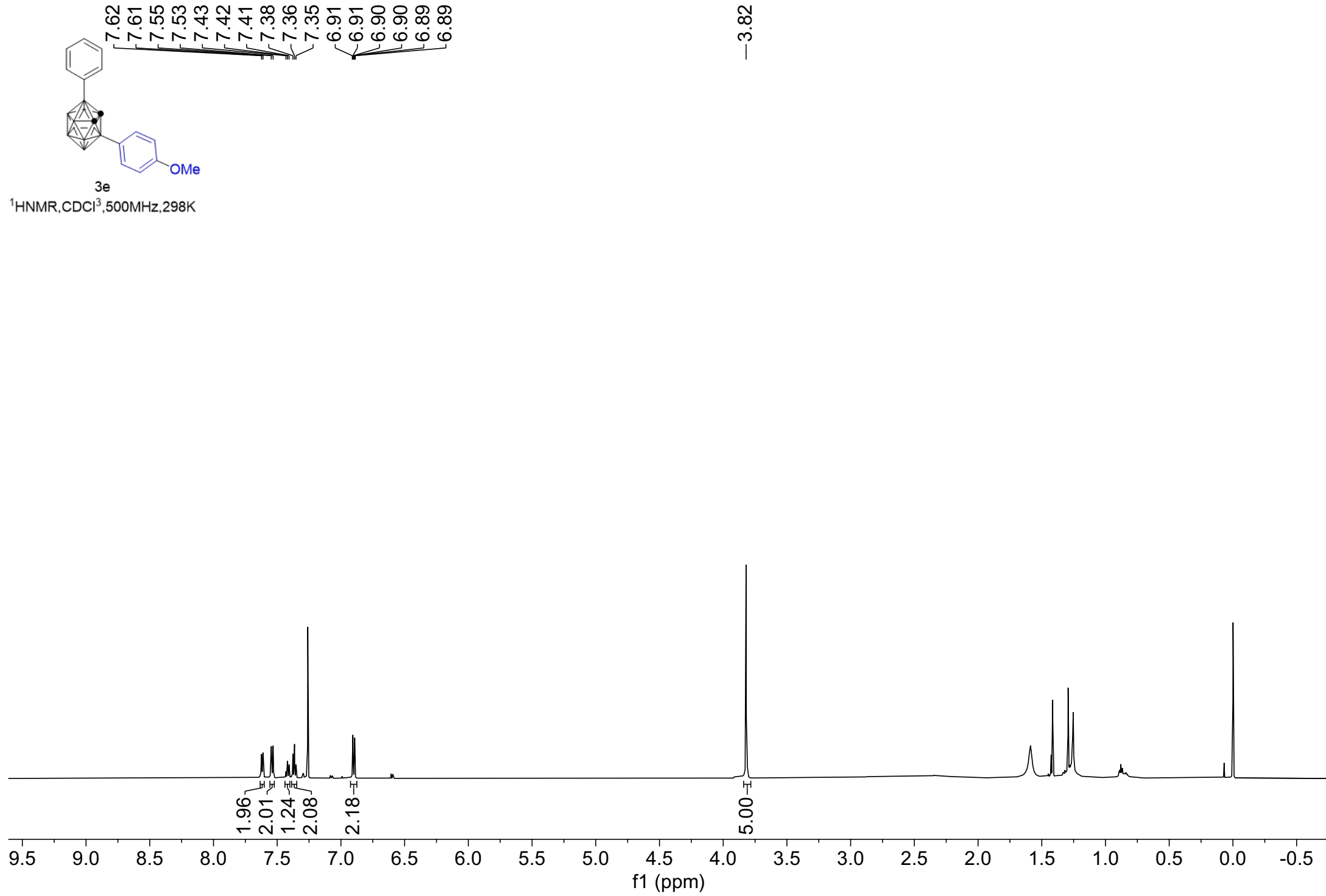


YHB-26-H

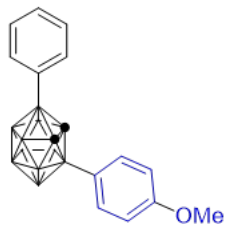


3e

<sup>1</sup>H NMR, CDCl<sub>3</sub>, 500 MHz, 298 K



YHB-26-C



3e

<sup>13</sup>CNMR, CDCl<sub>3</sub>, 125MHz, 298K

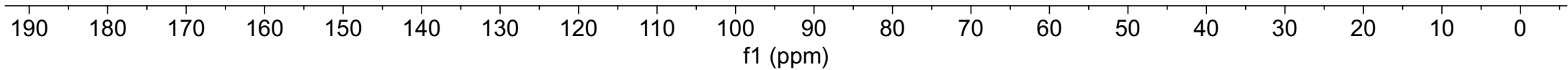
— 161.0

134.6  
— 133.1  
— 129.7  
128.3

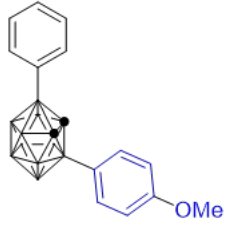
— 113.9

77.2  
— 77.0  
76.8

— 59.1  
— 55.2



YHB-26-B

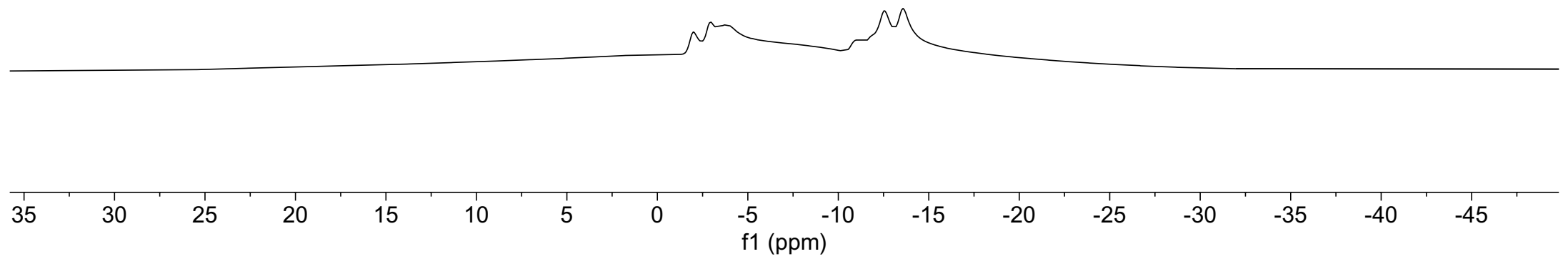


3e

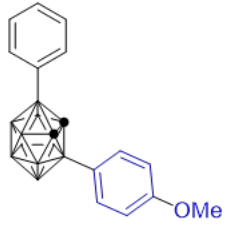
$^{11}\text{BNMR}$ ,  $\text{CDCl}_3$ , 160MHz, 298K

-2.1  
-3.0  
-4.1

-12.7  
-13.7  
-13.9



YHB-26-BH



3e

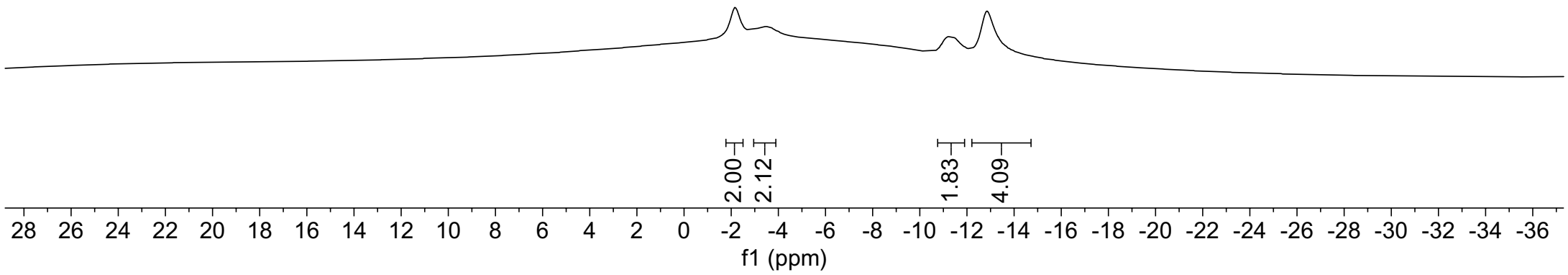
$^{11}\text{B}\{^1\text{H}\}$ NMR,  $\text{CDCl}_3$ , 160MHz, 298K

--2.2

--3.5

--11.3

--12.9

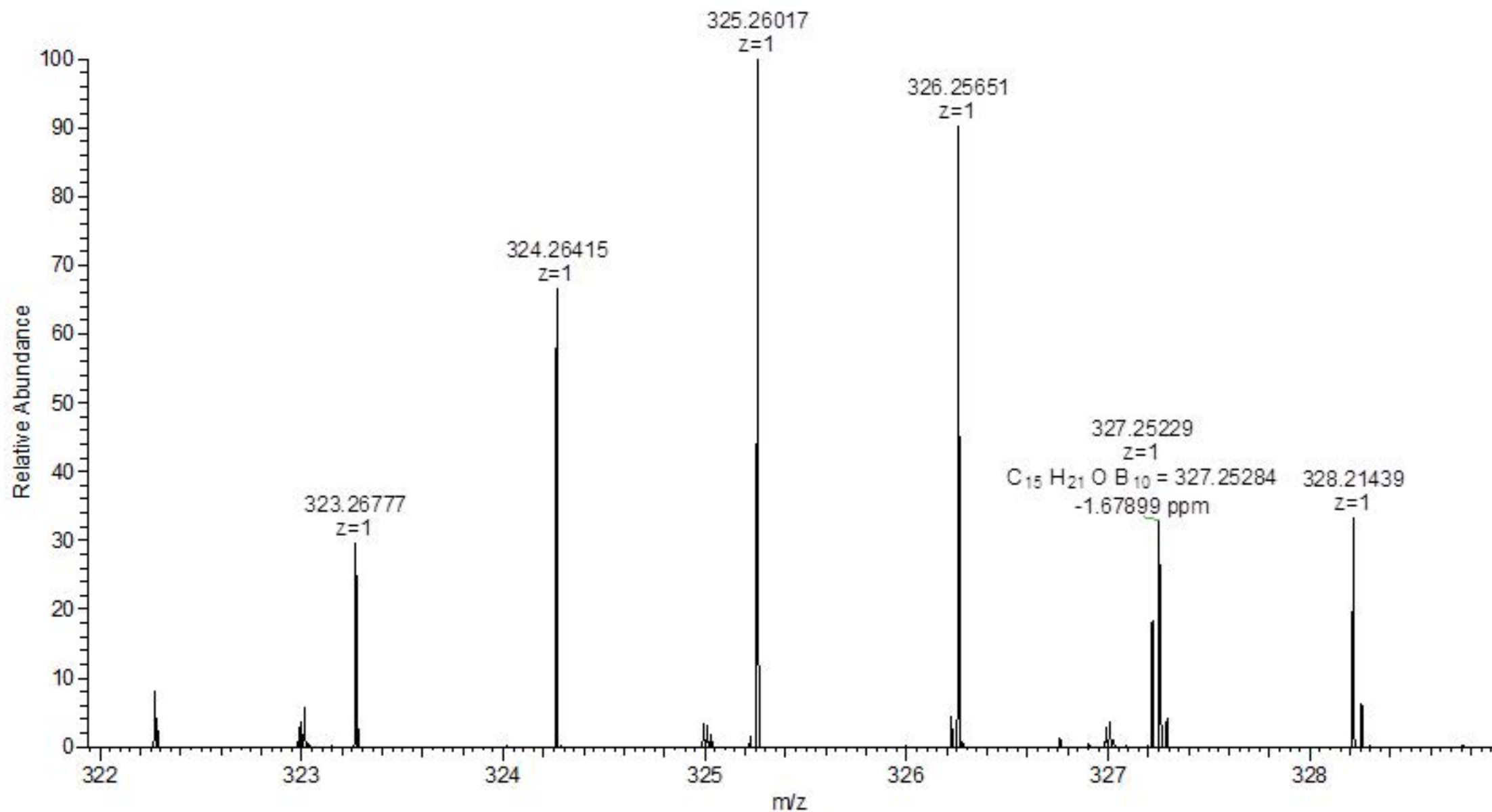


Y26

HRMS (ESI)  $m/z$  calcd for  $C_{15}H_{22}B_{10}O$  (M-H)  $327.2528$ , found  $327.2522$ .

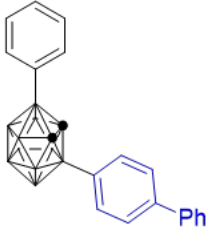
Y26 #53-74 RT: 0.52-0.71 AV: 11 SB: 5 0.02-0.09 NL: 1.62E6

T: FTMS - p ESI Full ms [100.0000-800.0000]



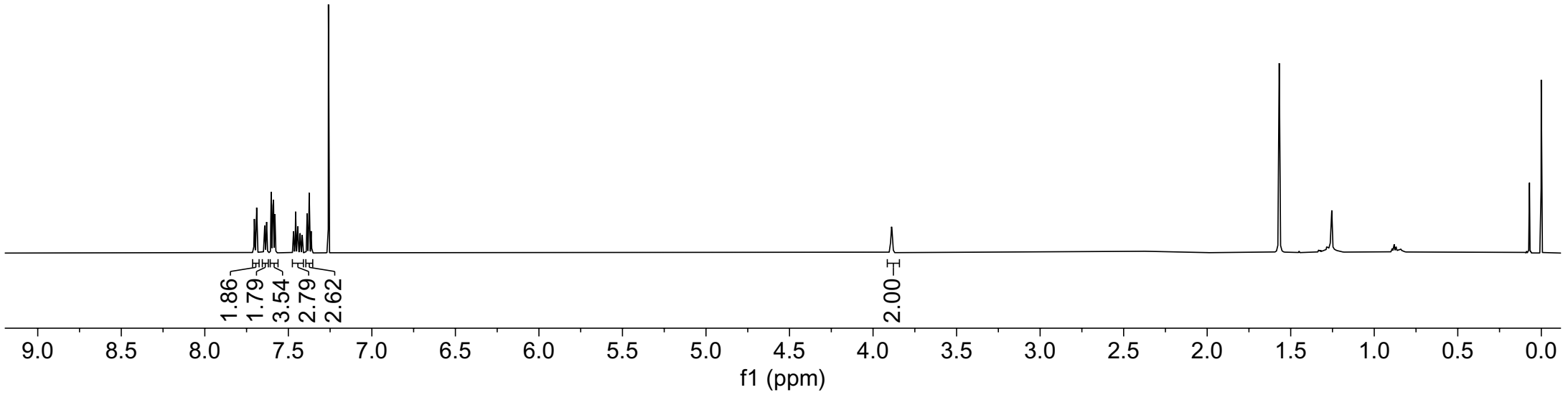
YHB-23-H

7.70  
7.70  
7.69  
7.69  
7.64  
7.64  
7.63  
7.63  
7.61  
7.60  
7.60  
7.59  
7.59  
7.59  
7.58  
7.58  
7.58  
7.47  
7.47  
7.47  
7.47  
7.46  
7.45  
7.44  
7.44  
7.43  
7.43  
7.43  
7.43  
7.42  
7.42  
7.42  
7.41  
7.39  
7.39  
7.39  
7.38  
7.38  
7.37  
7.37  
7.36  
3.89



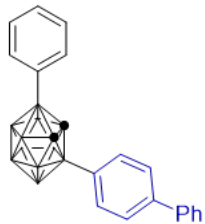
3f

$^1\text{H NMR, CDCl}_3, 500\text{ MHz, 298 K}$





YHB-23-C



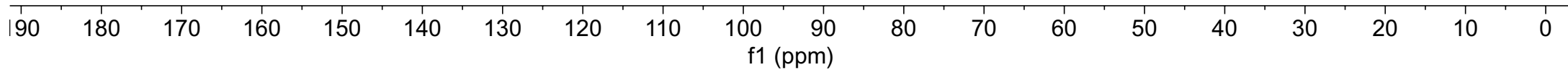
3f

$^{13}\text{C}$ NMR,  $\text{CDCl}_3$ , 125MHz, 298K

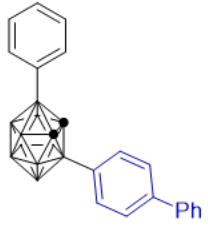
~142.7  
~140.4  
133.6  
133.1  
~129.8  
128.9  
128.3  
127.7  
127.1  
127.0

77.2  
77.0  
76.8

—59.1



YHB-23-B

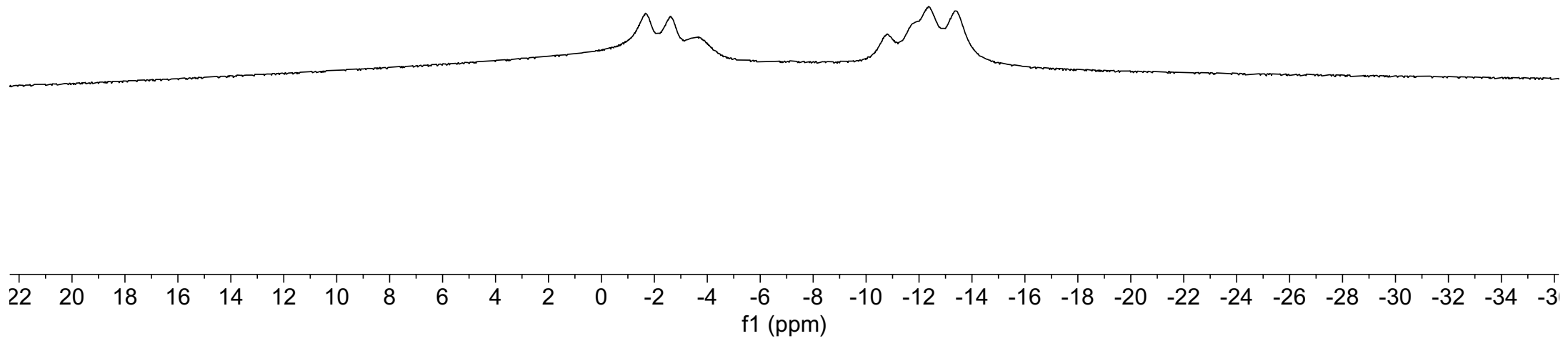


3f

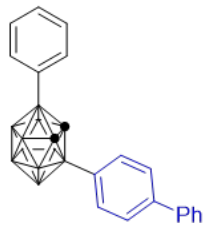
$^{11}\text{BNMR}$ ,  $\text{CDCl}_3$ , 160MHz, 298K

--1.7  
--2.6  
--3.7

~-10.7  
~-12.3  
~-13.4



YHB-23-B{H}

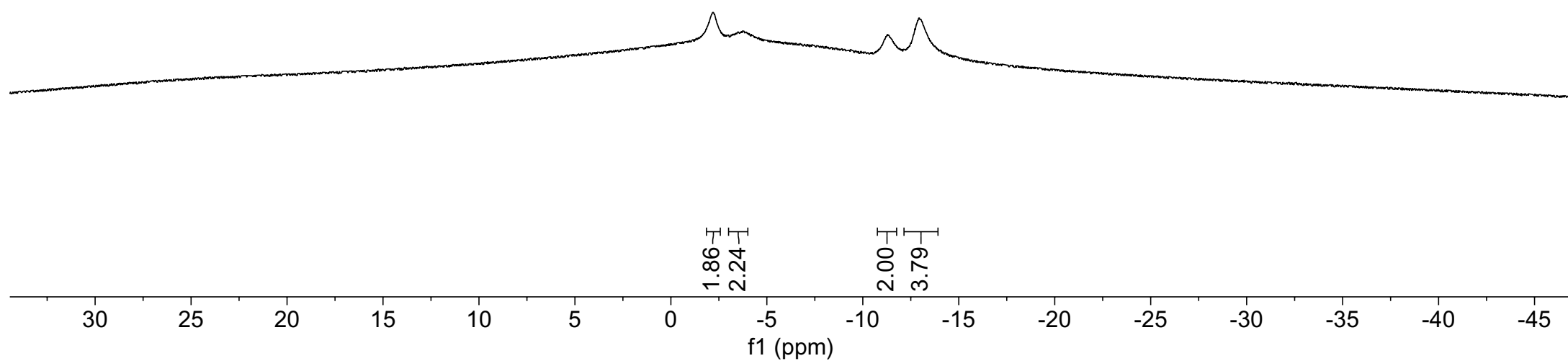


3f

$^{11}\text{B}\{^1\text{H}\}$ NMR,  $\text{CDCl}_3$ , 160MHz, 298K

--2.2  
--3.7

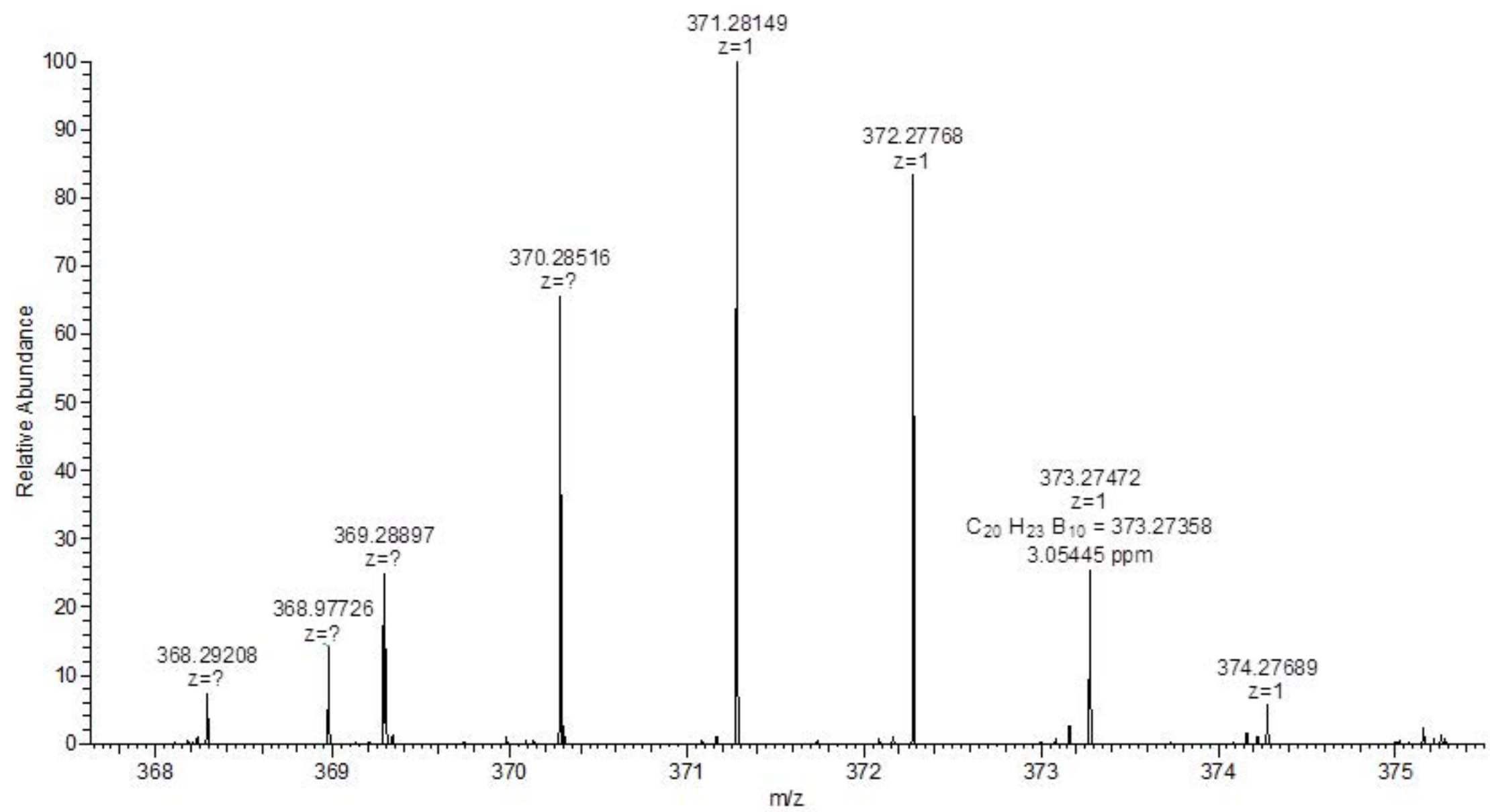
--11.3  
--12.9



Y23

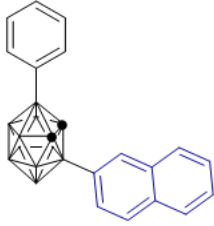
HRMS (ESI)  $m/z$  calcd for  $C_{20}H_{24}B_{10} \cdot (M-H)^-$  373.2735, found 373.2747.

Y23 #16 RT: 0.15 AV: 1 NL: 1.95E7  
T: FTMS - p ESI Full ms [100.0000-800.0000]



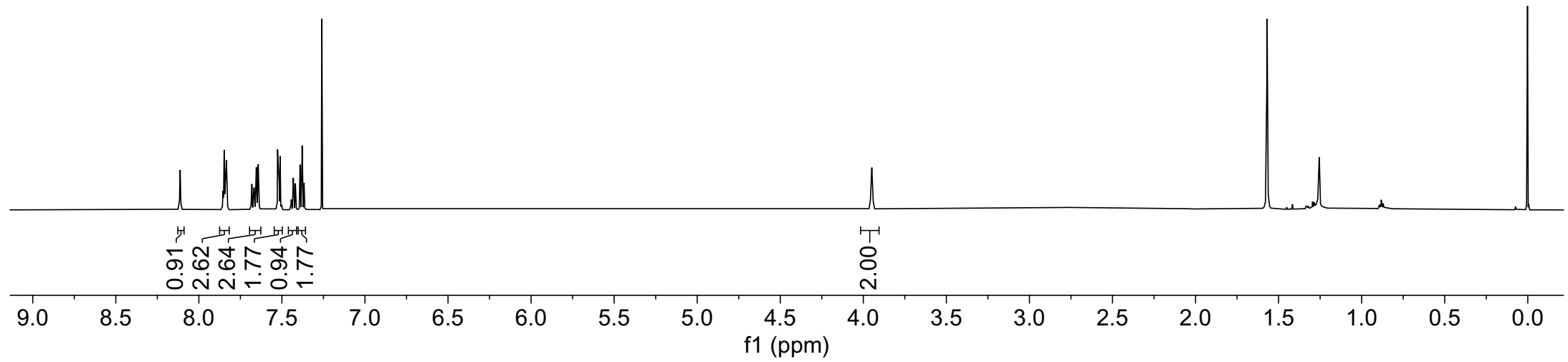
YHB-92-H

8.11  
7.85  
7.85  
7.84  
7.83  
7.68  
7.68  
7.67  
7.67  
7.65  
7.64  
7.64  
7.53  
7.53  
7.53  
7.52  
7.52  
7.51  
7.51  
7.51  
7.50  
7.45  
7.44  
7.44  
7.44  
7.43  
7.43  
7.42  
7.42  
7.42  
7.39  
7.39  
7.38  
7.38  
7.38  
7.37  
7.37  
7.36  
3.95

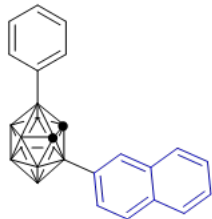


3g

$^1\text{H NMR}$ ,  $\text{CDCl}_3$ , 500MHz, 298K



YHB-92-C



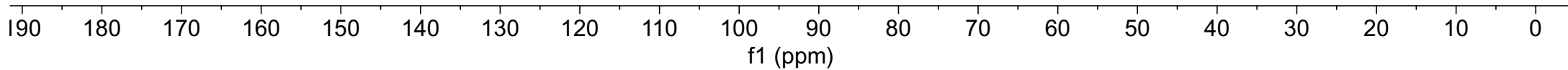
3g

$^{13}\text{C}$ NMR,  $\text{CDCl}_3$ , 125MHz, 298K

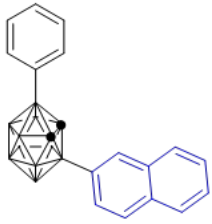
133.8  
133.8  
133.2  
132.8  
129.8  
129.3  
128.3  
128.0  
127.8  
127.7  
127.0  
126.6

77.2  
77.0  
76.8

59.2



YHB-92-B

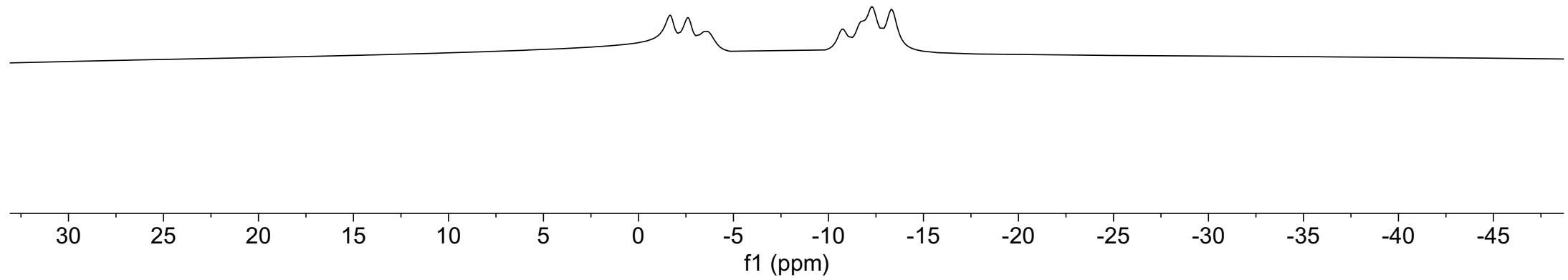


3g

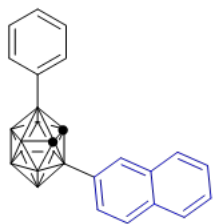
$^{11}\text{B}$ NMR,  $\text{CDCl}_3$ , 160MHz, 298K

~1.7  
~2.6  
~3.6

~10.7  
~12.3  
~13.4



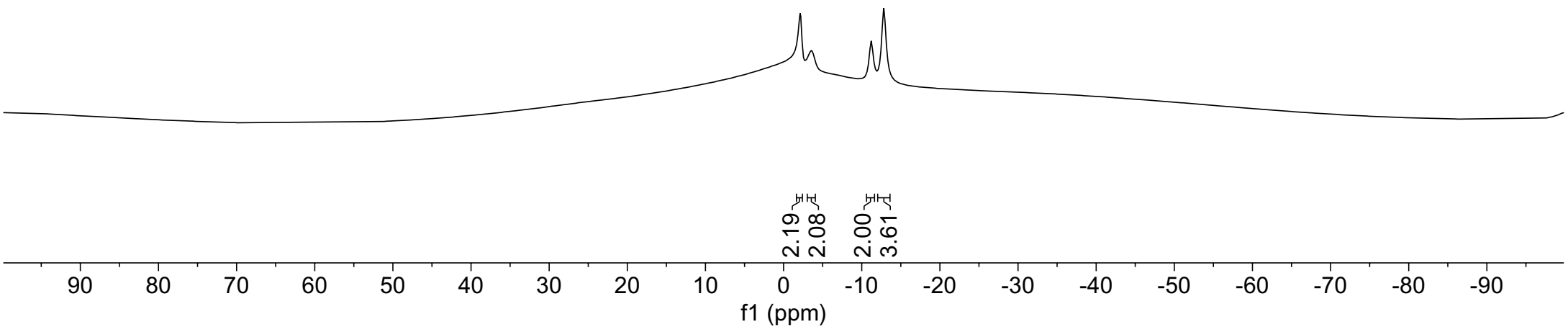
YHB-92-B{H}



3g

$^{11}\text{B}\{^1\text{H}\}$ NMR,  $\text{CDCl}_3$ , 160MHz, 298K

~2.1  
~3.6  
~-11.2  
~-12.8

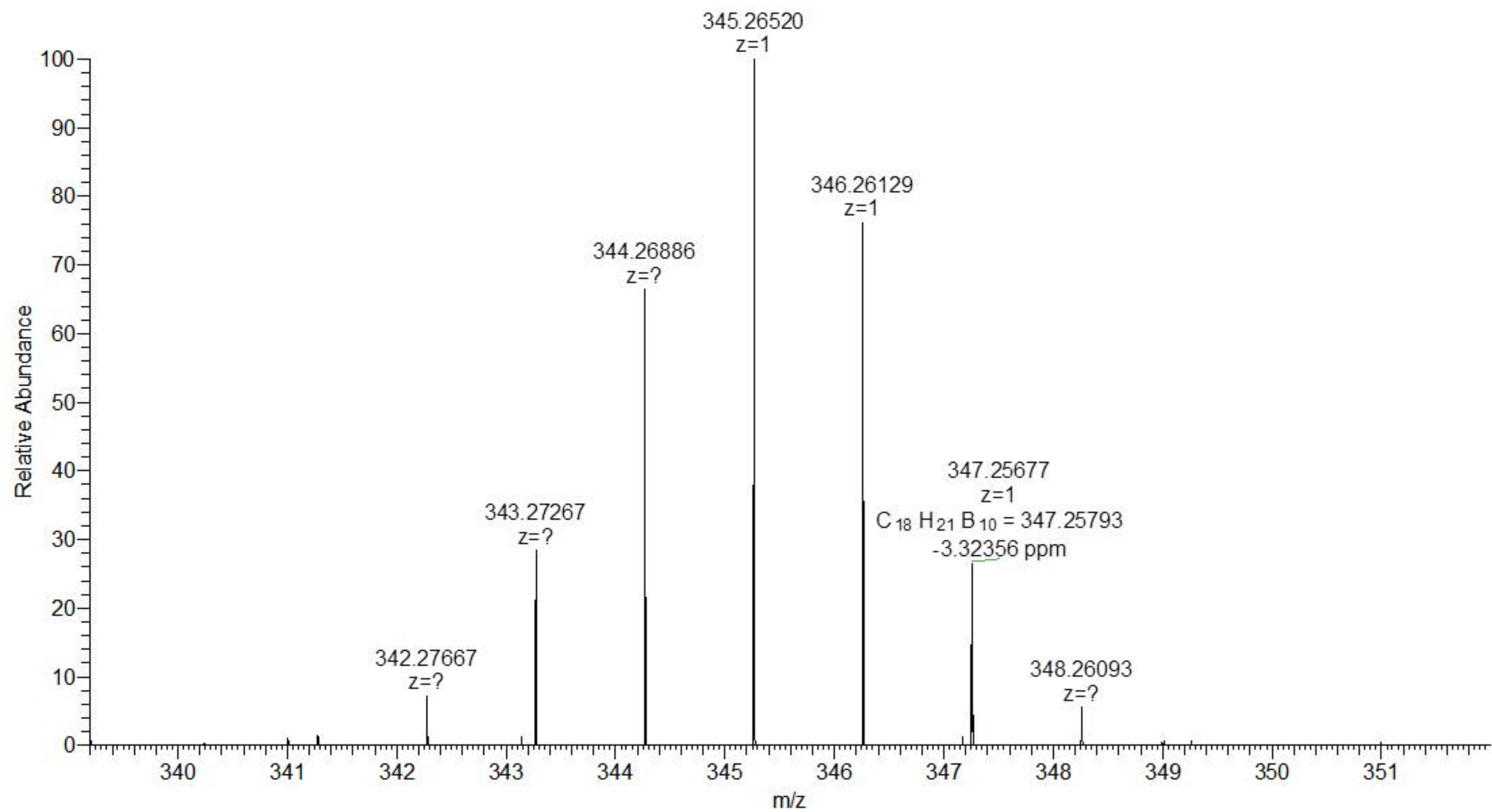




Y-92

HRMS (ESI)  $m/z$  calcd for  $C_{18}H_{22}B_{10} (M-H)^-$  347.2579, found 347.2567

Y92 #8 RT: 0.07 AV: 1 NL: 3.95E7  
T: FTMS - p ESI Full ms [100.0000-600.0000]

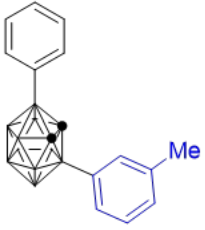


YHB-32-H

7.63  
7.62  
7.44  
7.43  
7.43  
7.42  
7.42  
7.42  
7.41  
7.41  
7.41  
7.38  
7.38  
7.38  
7.37  
7.37  
7.36  
7.36  
7.36  
7.35  
7.25  
7.25  
7.24  
7.24  
7.23  
7.22

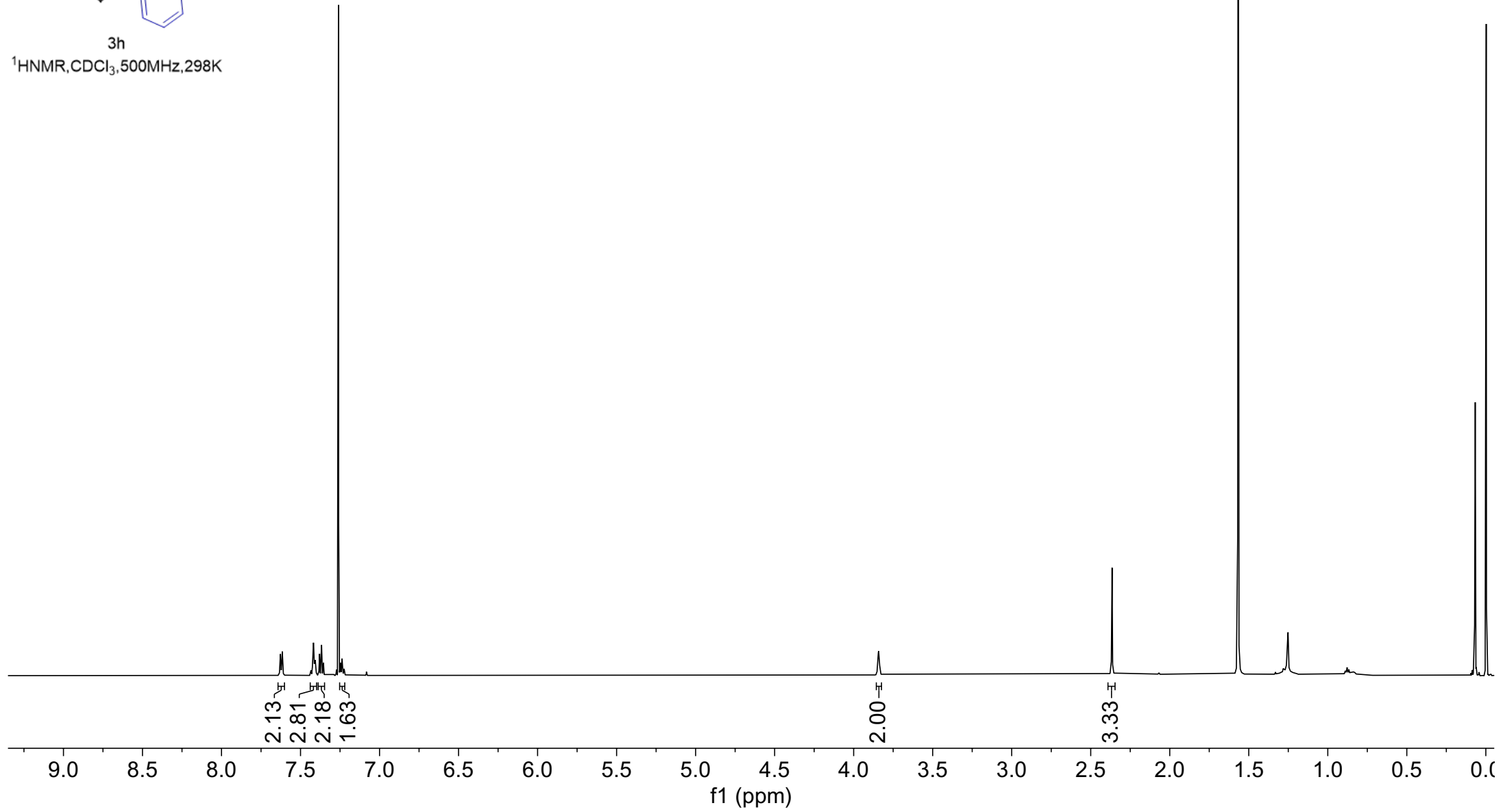
—3.84

—2.37

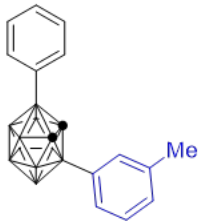


3h

<sup>1</sup>HNMR, CDCl<sub>3</sub>, 500MHz, 298K

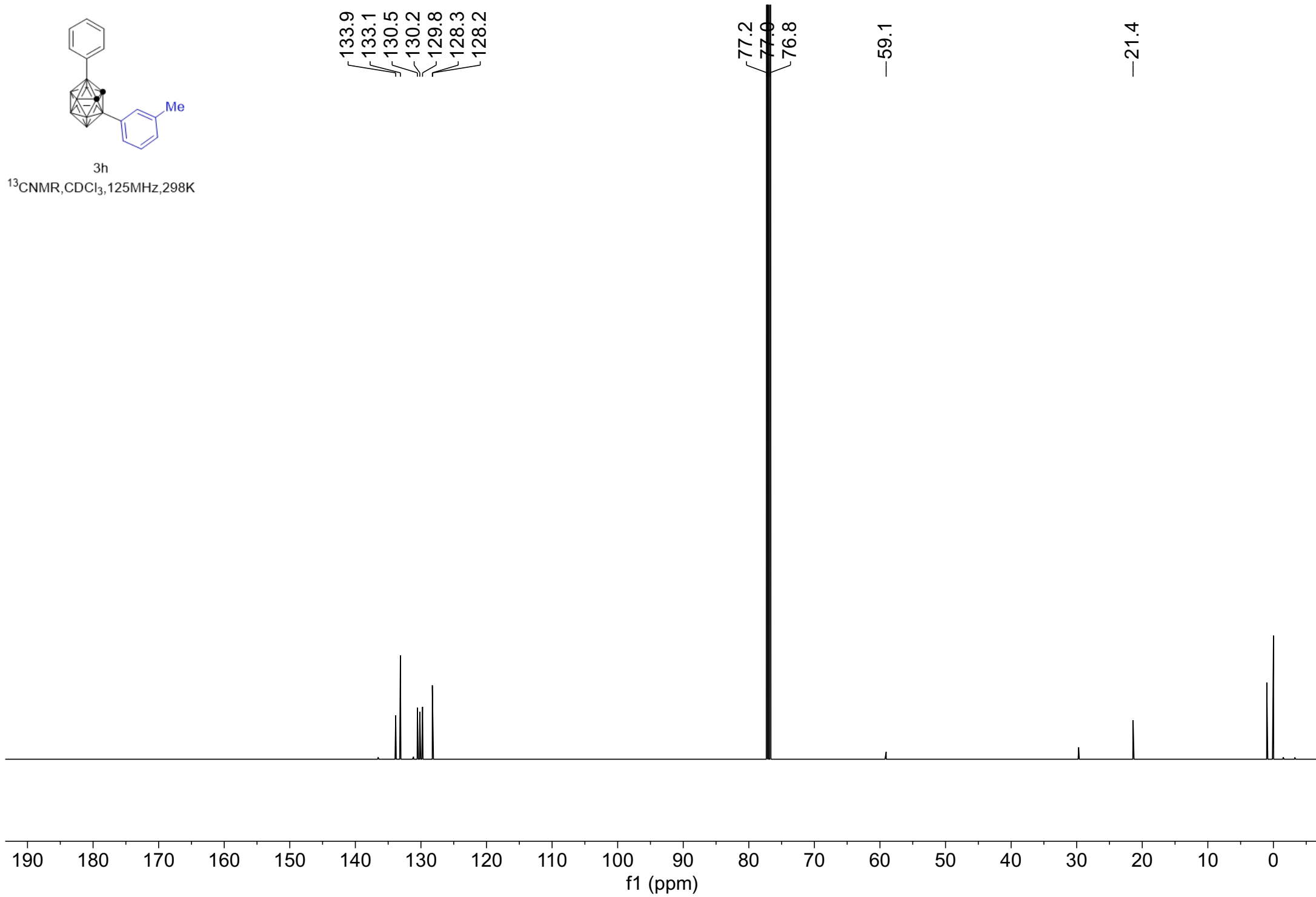


YHB-32-C

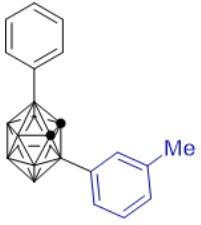


3h

$^{13}\text{C}$ NMR,  $\text{CDCl}_3$ , 125MHz, 298K



YHB-32-B

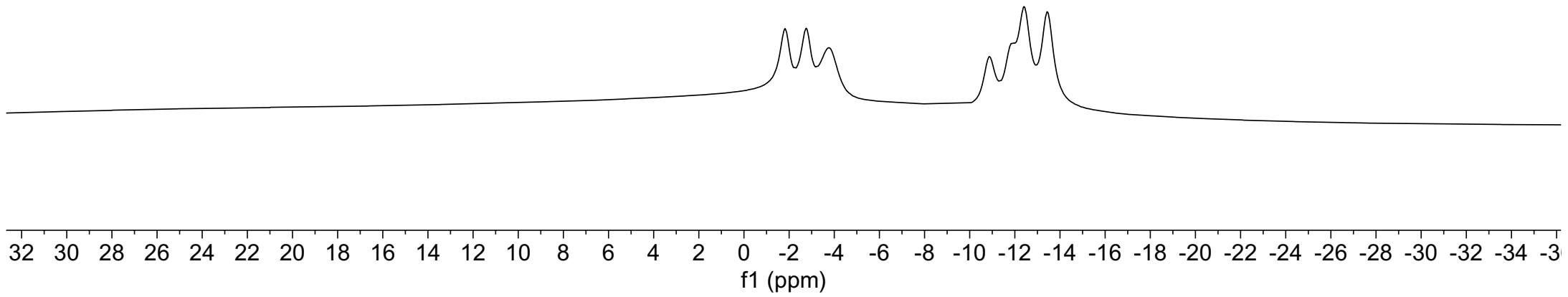


3h

$^{11}\text{B}$ NMR,  $\text{CDCl}_3$ , 160MHz, 298K

~1.8  
~2.8  
~3.8

~10.9  
~11.8  
~12.4  
~13.4



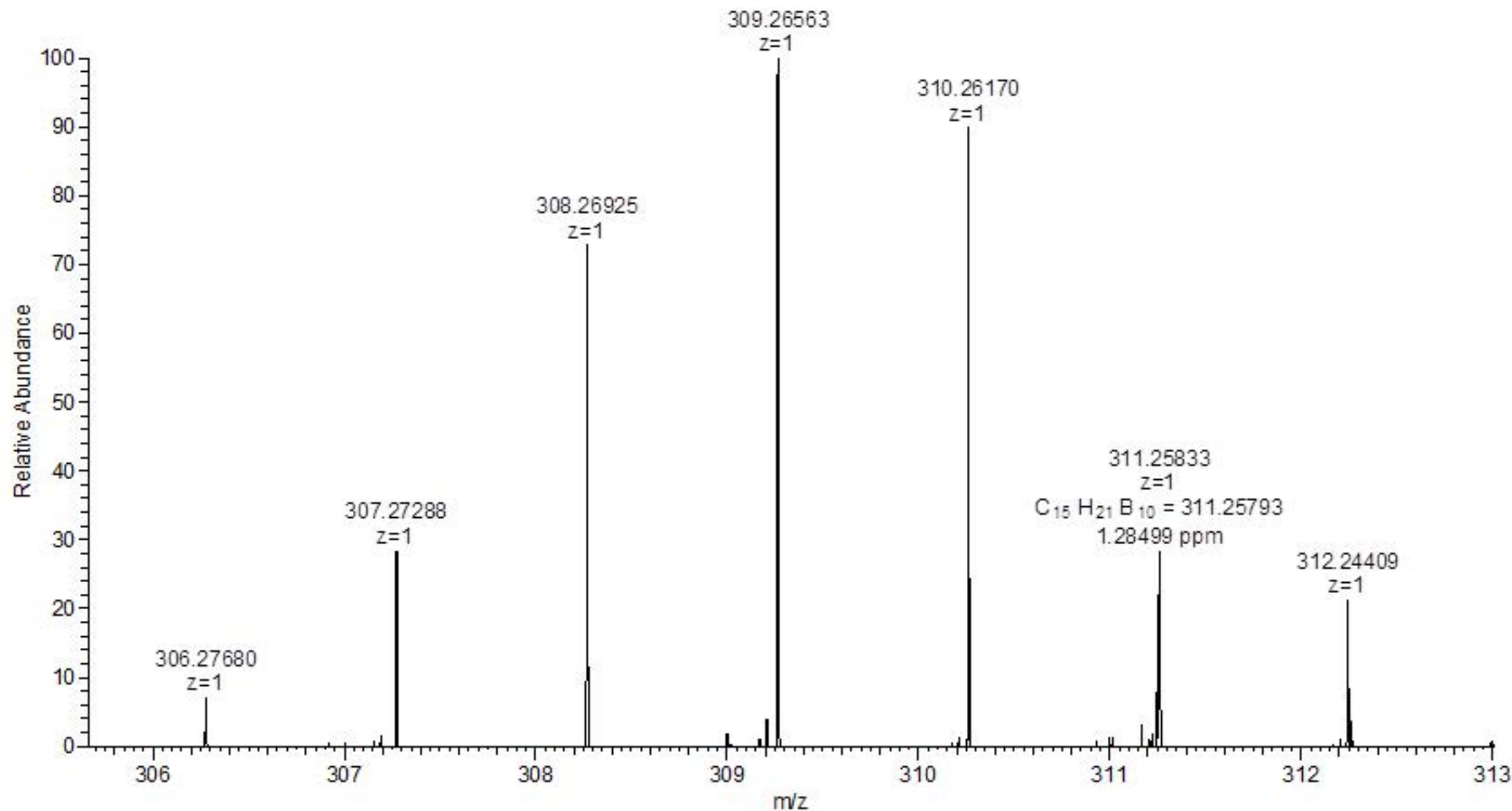


Y32←

HRMS (ESI)  $m/z$  calcd for  $C_{15}H_{22}B_{10} \cdot (M-H)^-$  311.2579, found 311.2583.

Y32 #30 RT: 0.29 AV: 1 SB: 4 0.04-0.11 NL: 4.34E6

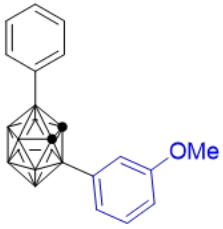
T: FTMS - p ESI Full ms [100.0000-800.0000]



YHB-33-H

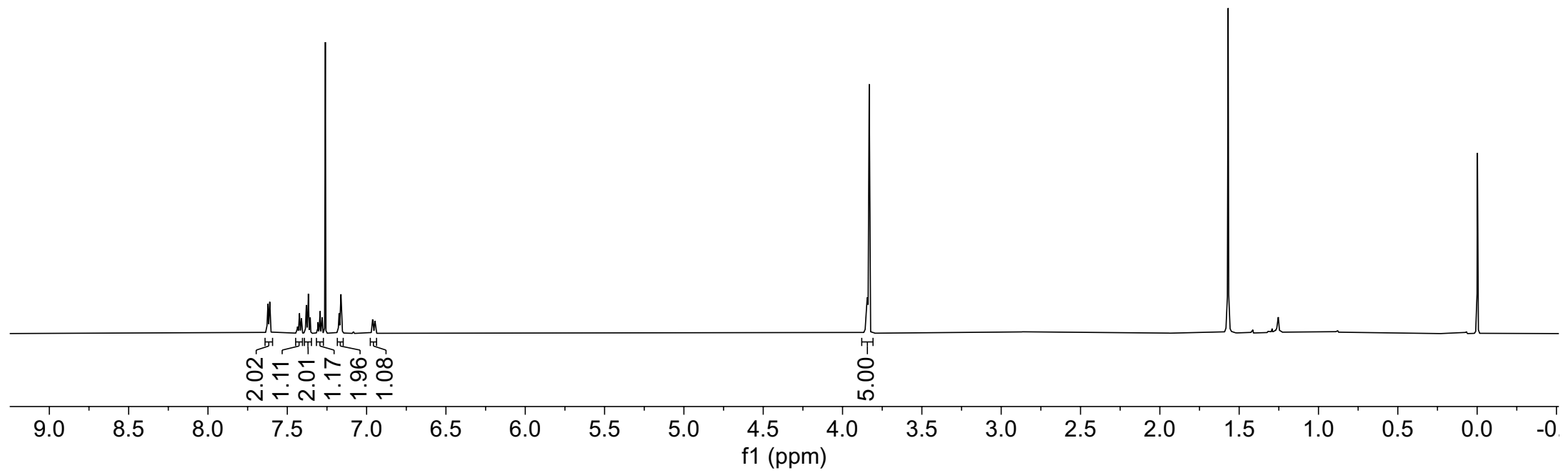
7.62  
7.61  
7.44  
7.43  
7.42  
7.42  
7.41  
7.41  
7.41  
7.38  
7.37  
7.36  
7.31  
7.29  
7.28  
7.17  
7.16  
6.96  
6.96  
6.96  
6.96  
6.95  
6.95  
6.94  
6.94

3.84  
3.83

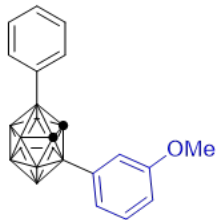


3i

<sup>1</sup>HNMR, CDCl<sub>3</sub>, 500MHz, 298K



YHB-33-C



3i

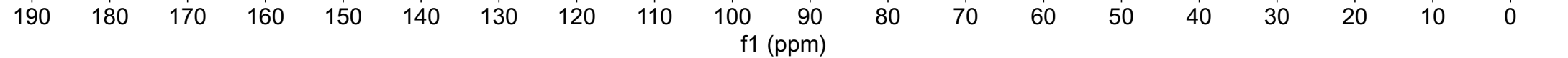
$^{13}\text{C}$ NMR,  $\text{CDCl}_3$ , 125MHz, 298K

—159.3

133.1  
129.8  
129.5  
128.3  
125.2  
119.2  
114.8

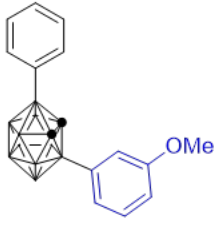
77.2  
77.0  
76.8

—59.1  
—55.3





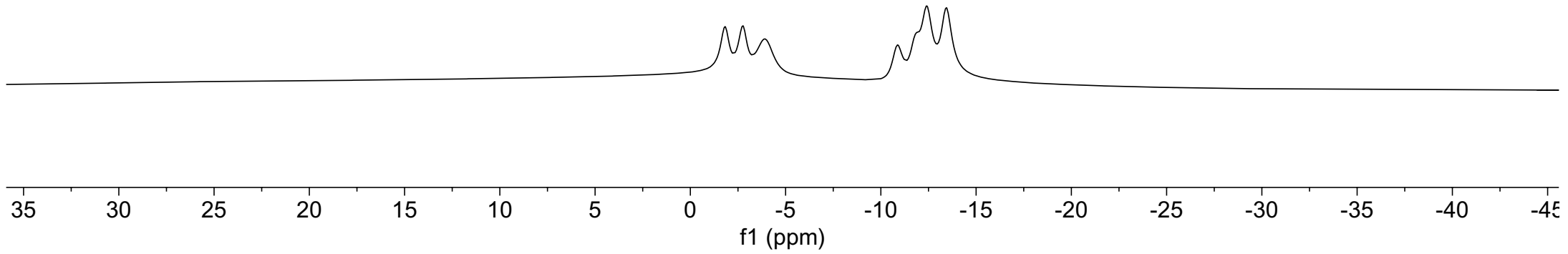
YHB-33-B



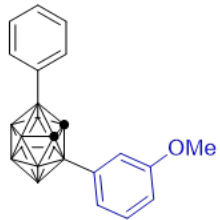
3i

$^{11}\text{B}$ NMR,  $\text{CDCl}_3$ , 160MHz, 298K

~1.8  
~2.7  
~3.9  
  
~-10.9  
~-12.4  
~-13.5



YHB-33-B{H}



3i

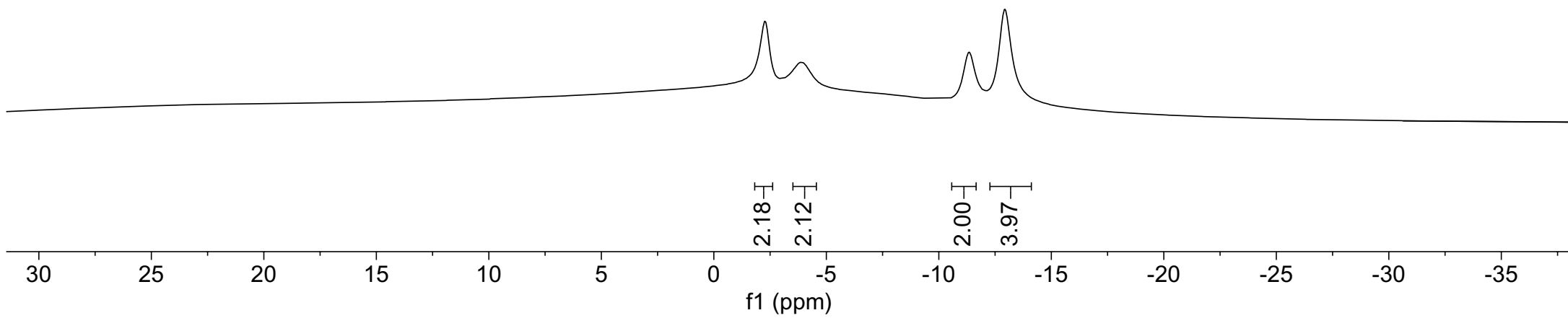
<sup>11</sup>B{<sup>1</sup>H}NMR, CDCl<sub>3</sub>, 160MHz, 298K

--2.3

--3.9

--11.3

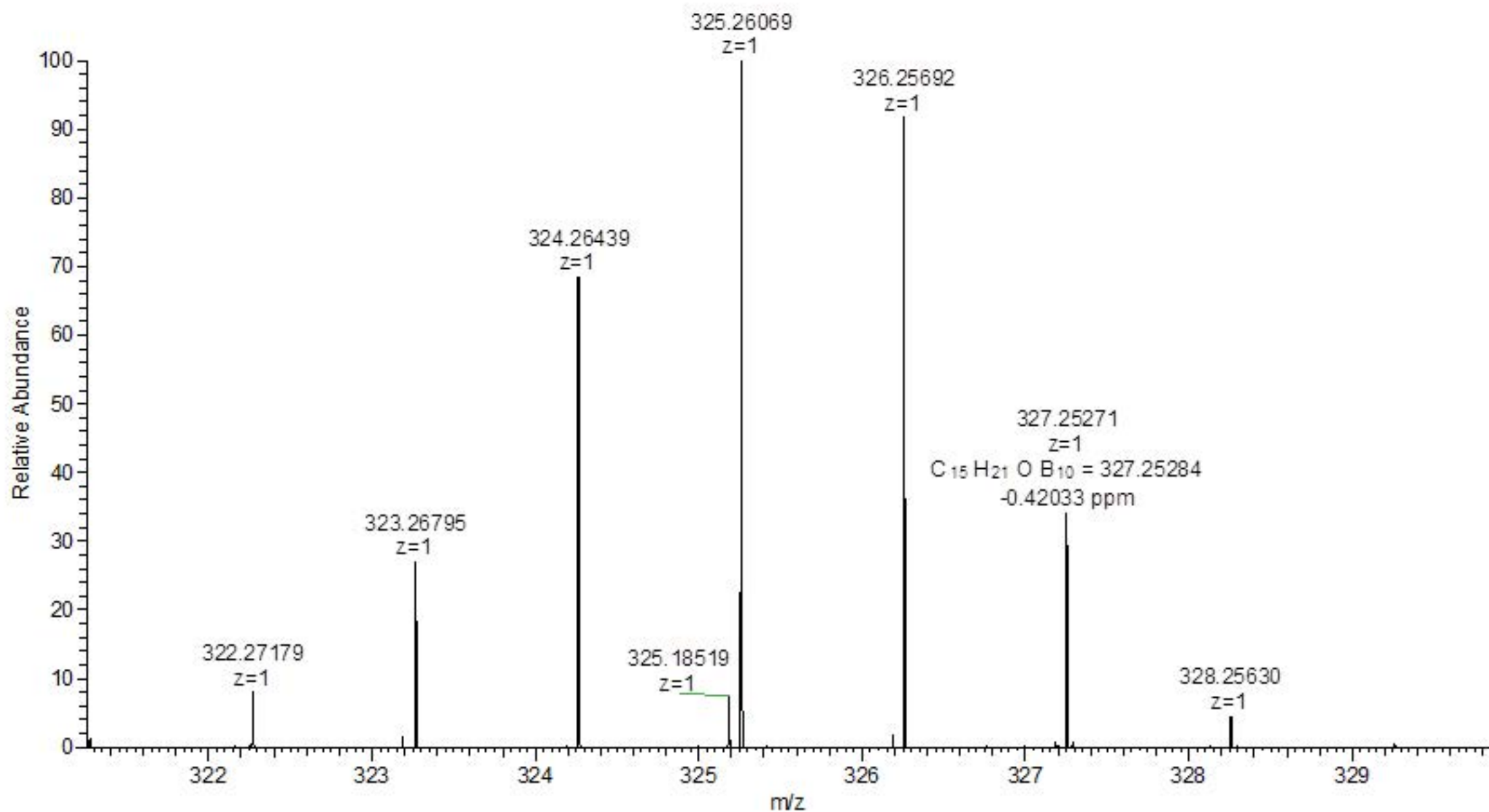
--12.9



Y33

HRMS (ESI)  $m/z$  calcd for  $C_{15}H_{22}B_{10}O$  (M-H) 327.2528, found 327.2527.

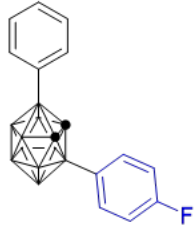
Y33 #26 RT: 0.25 AV: 1 SB: 3 0.02-0.06 NL: 2.99E7  
T: FTMS - p ESI Full ms [100.0000-800.0000]



YHB-31-H

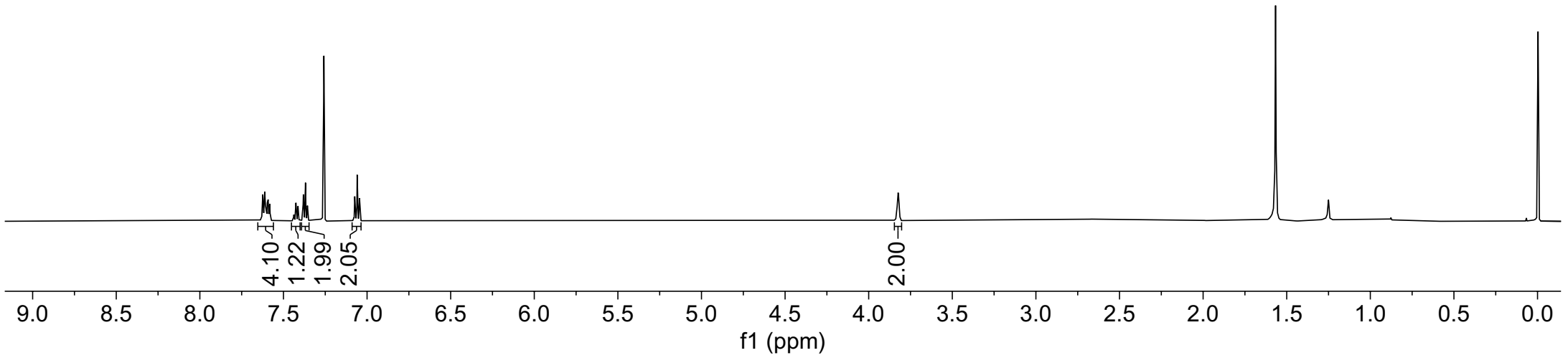
7.62  
7.61  
7.61  
7.61  
7.60  
7.59  
7.58  
7.44  
7.44  
7.44  
7.43  
7.43  
7.42  
7.42  
7.41  
7.41  
7.38  
7.37  
7.36  
7.08  
7.07  
7.07  
7.06  
7.06  
7.06  
7.05  
7.04  
7.04

3.82

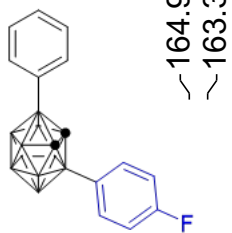


3k

$^1\text{H NMR, CDCl}_3, 500\text{ MHz, 298 K}$

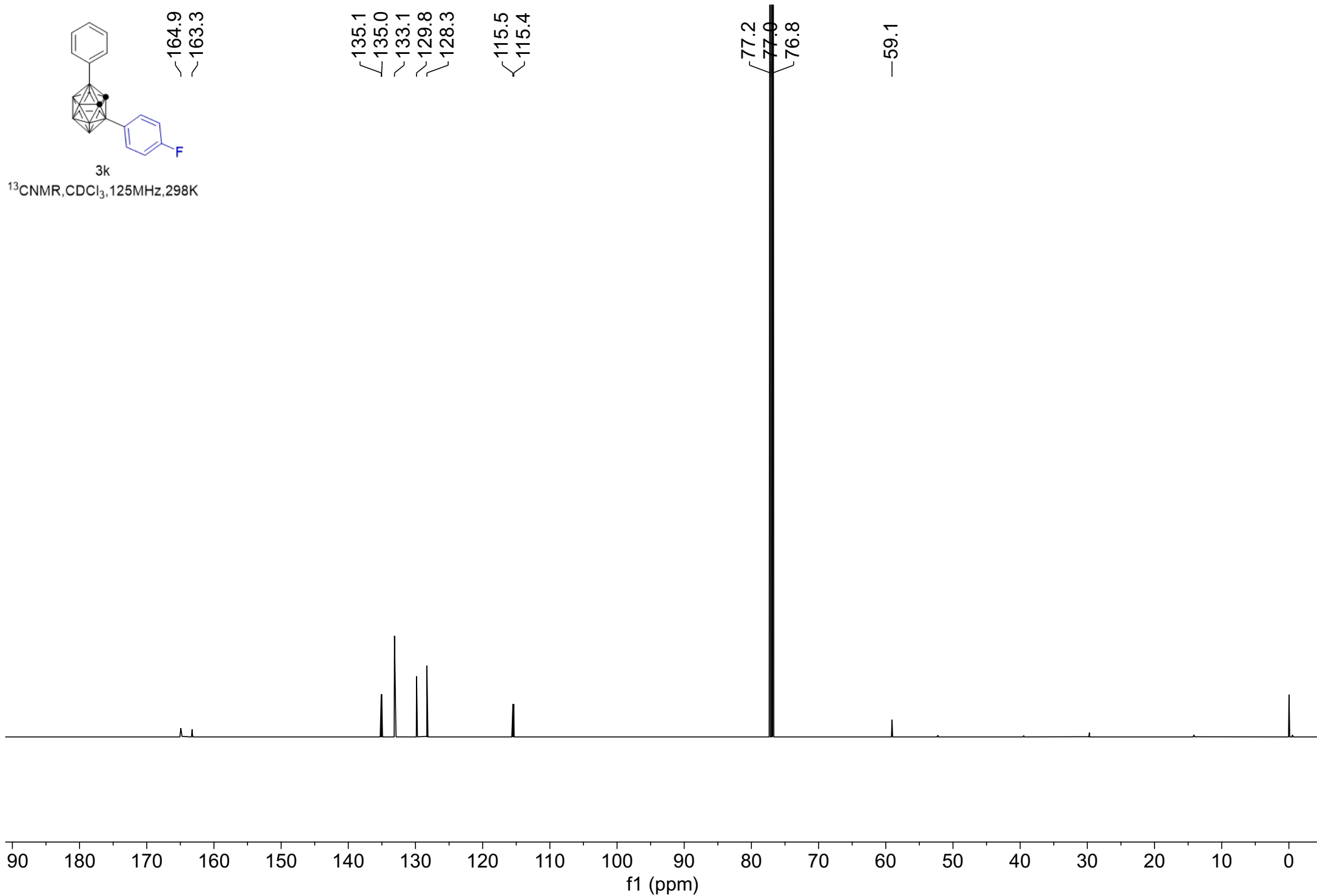


YHB-31-C

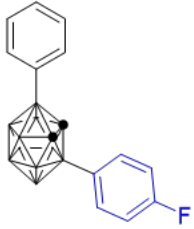


3k

$^{13}\text{C}$ NMR,  $\text{CDCl}_3$ , 125MHz, 298K



YHB-31-B

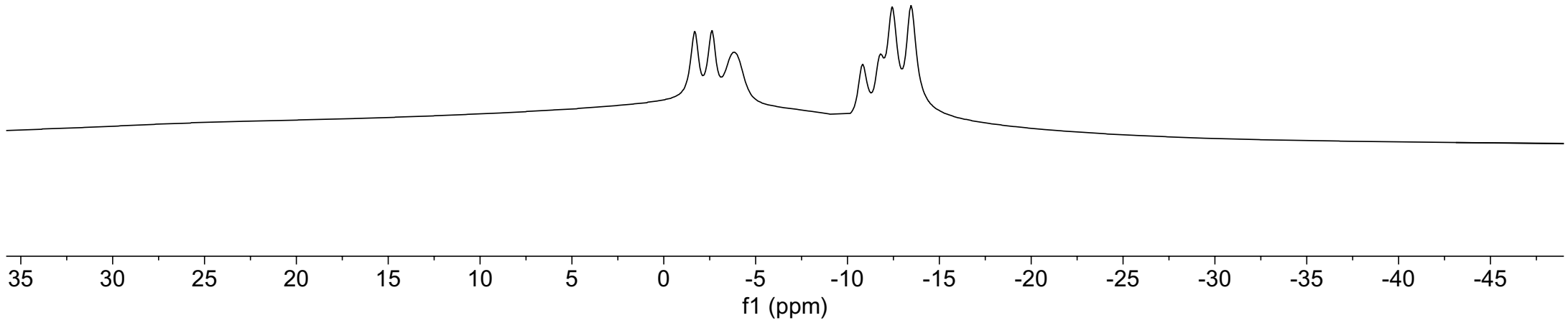


3k

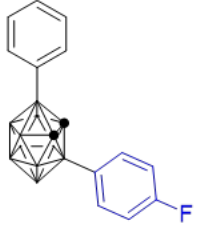
$^{11}\text{B}$ NMR,  $\text{CDCl}_3$ , 160MHz, 298K

~1.7  
~2.6  
~3.8

~10.8  
~11.8  
~12.4  
~13.5



YHB-31-B{H}



3k

$^{11}\text{B}\{^1\text{H}\}$ NMR,  $\text{CDCl}_3$ , 160MHz, 298K

--2.1

--3.9

--11.3

--13.0



2.19

2.10

2.00

3.56

30

25

20

15

10

5

0

-5

-10

-15

-20

-25

-30

-35

-40

-45

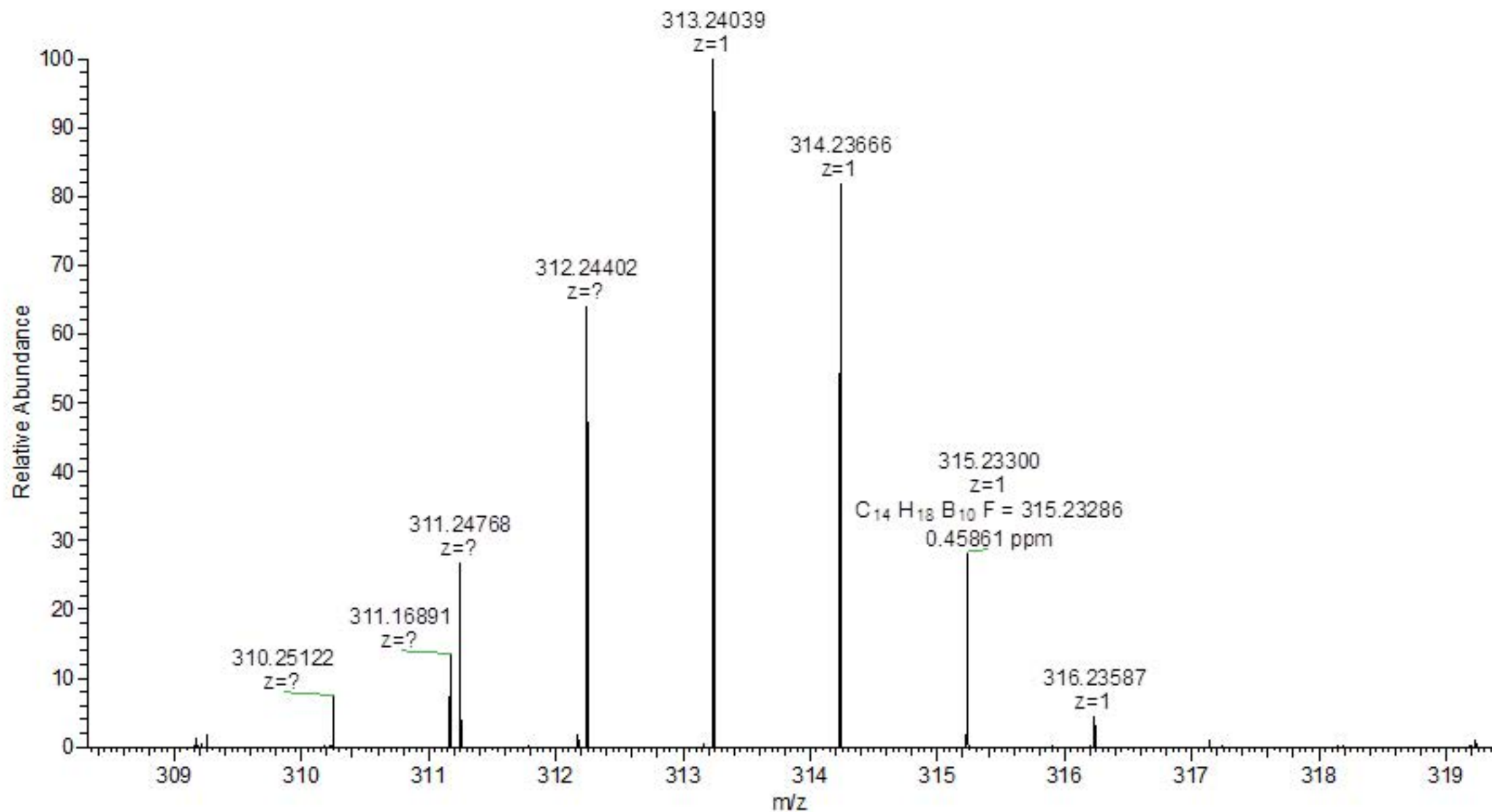
f1 (ppm)

Y31←

HRMS (ESI)  $m/z$  calcd for  $C_{14}H_{19}B_{10}F$  (M-H)  $315.2328$ , found  $315.2330$ .

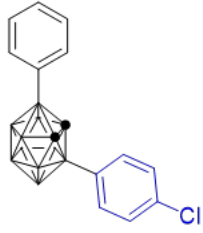
Y31 #12 RT: 0.11 AV: 1 NL: 7.48E7

T: FTMS - p ESI Full ms [100.0000-800.0000]





YHB-30-H

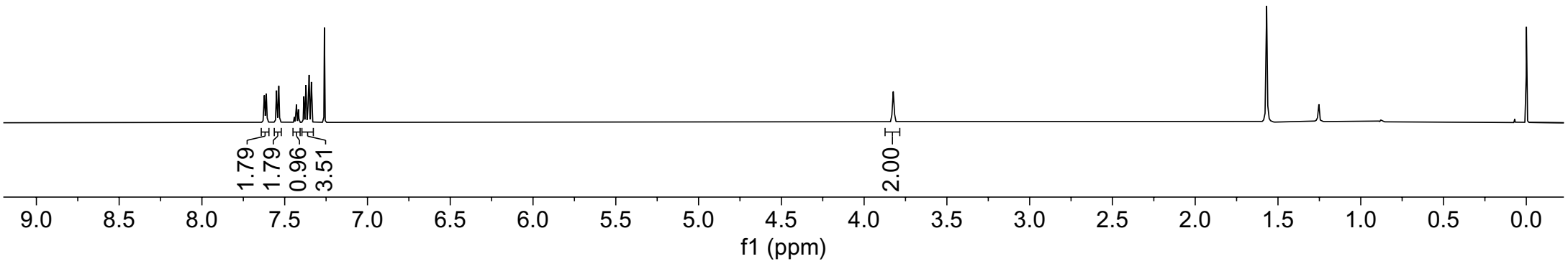


3I

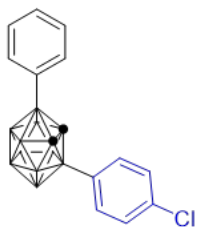
$^1\text{H NMR}$ ,  $\text{CDCl}_3$ , 500MHz, 298K

7.62  
7.61  
7.55  
7.54  
7.44  
7.43  
7.42  
7.38  
7.37  
7.36  
7.36  
7.35  
7.34  
7.34

—3.82



YHB-30-C



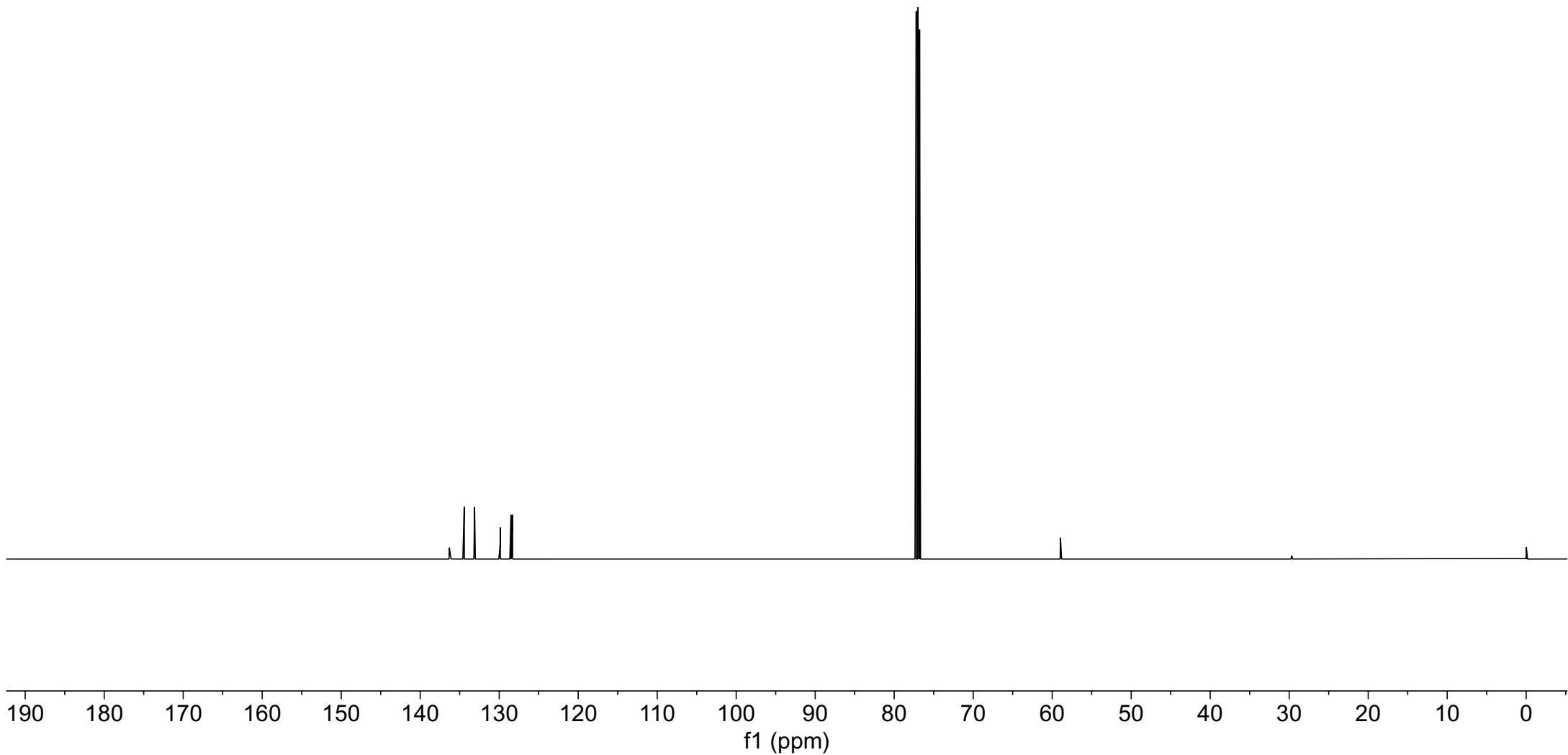
3I

<sup>13</sup>CNMR, CDCl<sub>3</sub>, 125MHz, 298K

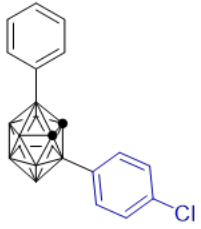
136.3  
134.4  
133.1  
129.9  
128.5  
128.3

77.2  
77.0  
76.8

59.0



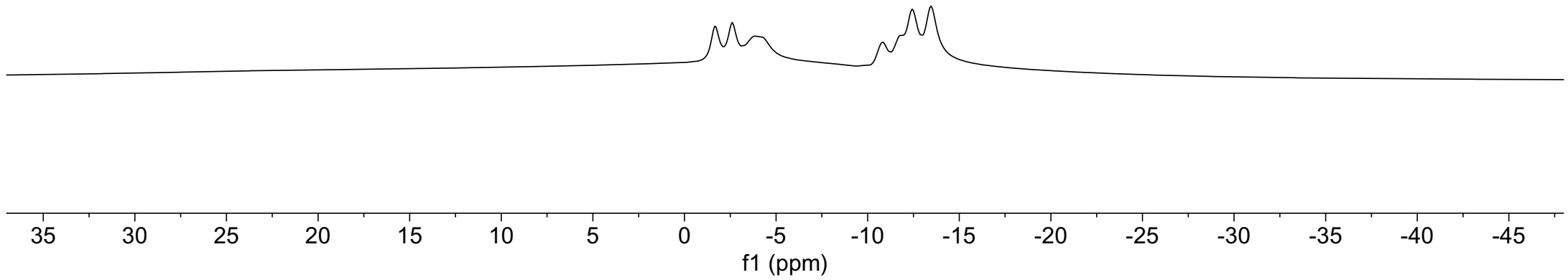
YHB-30-B



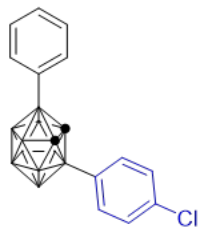
3I

$^{11}\text{B}$ NMR,  $\text{CDCl}_3$ , 160MHz, 298K

~1.7  
~2.6  
~4.1  
~-10.8  
~-11.7  
~-12.4  
~-13.5



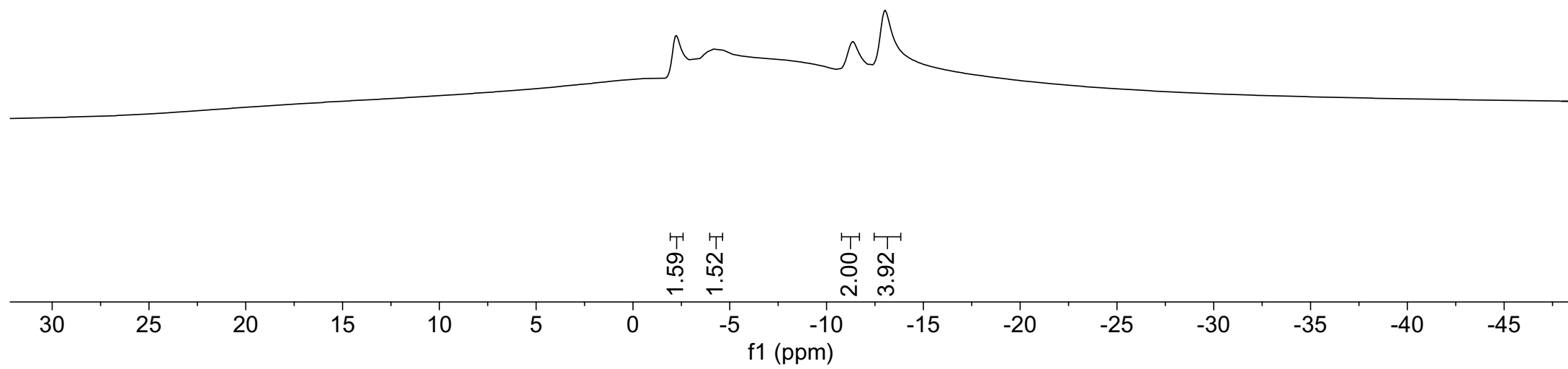
YHB-30-B{H}



3I

$^{11}\text{B}\{^1\text{H}\}$ NMR,  $\text{CDCl}_3$ , 160MHz, 298K

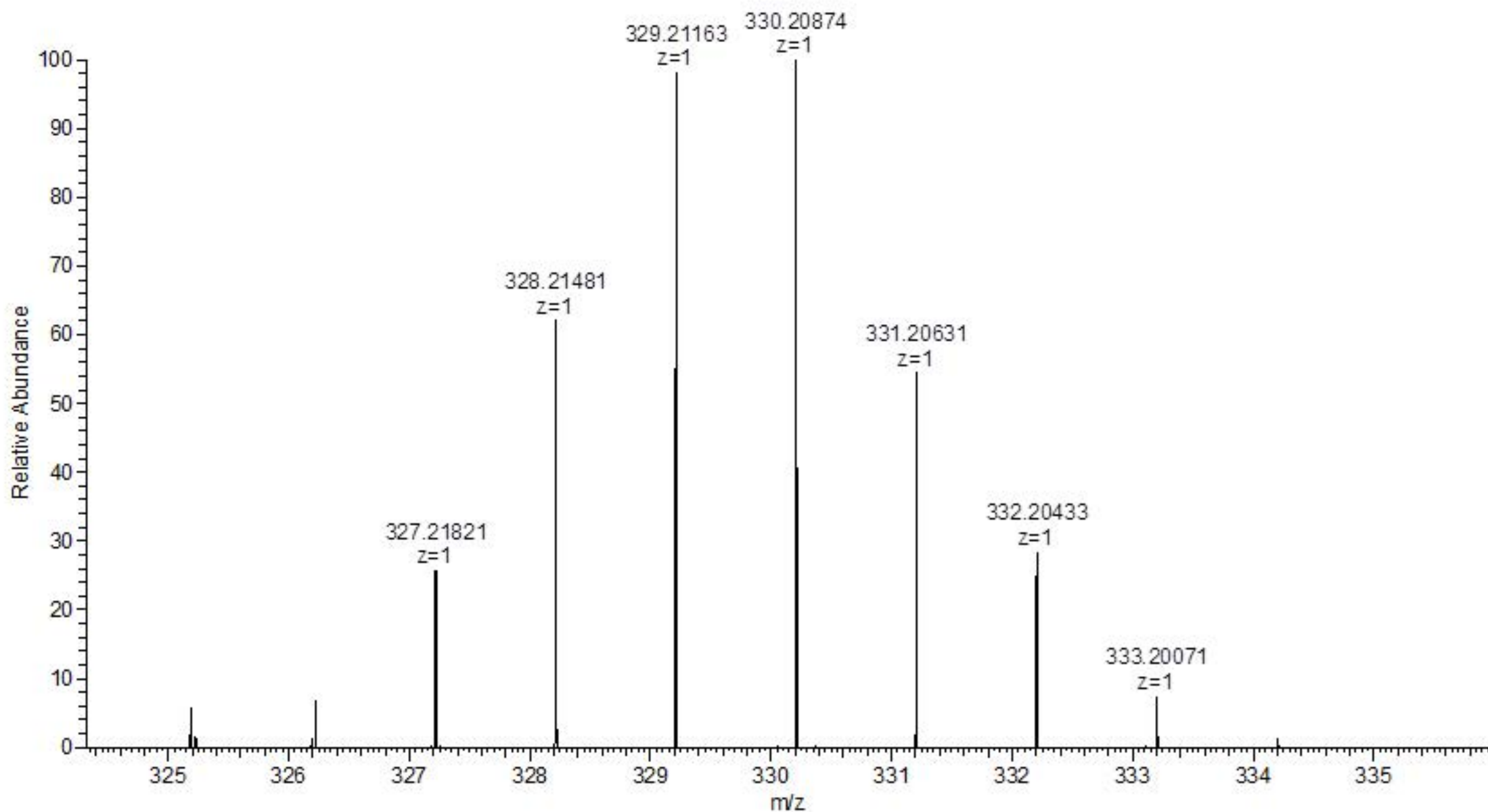
--2.2  
--4.4  
--11.4  
--13.0



Y30

HRMS (ESI)  $m/z$  calcd for  $C_{14}H_{19}B_{10}Cl$  (M-H) 331.2076, found 331.2063.

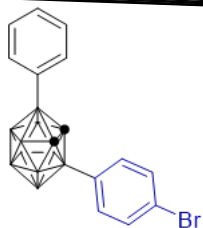
y30 #16 RT: 0.15 AV: 1 SB: 3 0.01-0.06 NL: 1.58E8  
T: FTMS - p ESI Full ms [100.0000-800.0000]



YHB-35-H

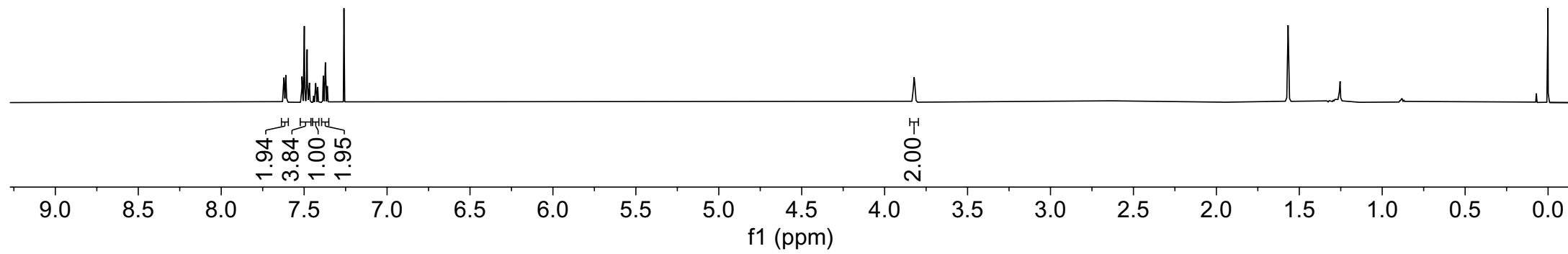
7.62  
7.61  
7.61  
7.51  
7.51  
7.50  
7.50  
7.50  
7.48  
7.48  
7.47  
7.47  
7.45  
7.44  
7.44  
7.43  
7.43  
7.43  
7.42  
7.42  
7.42  
7.39  
7.38  
7.37  
7.36  
7.36  
7.36

—3.82

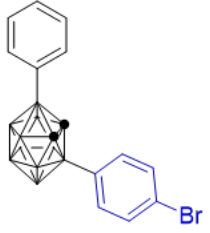


3m

<sup>1</sup>H NMR, CDCl<sub>3</sub>, 500 MHz, 298 K



YHB-35-C



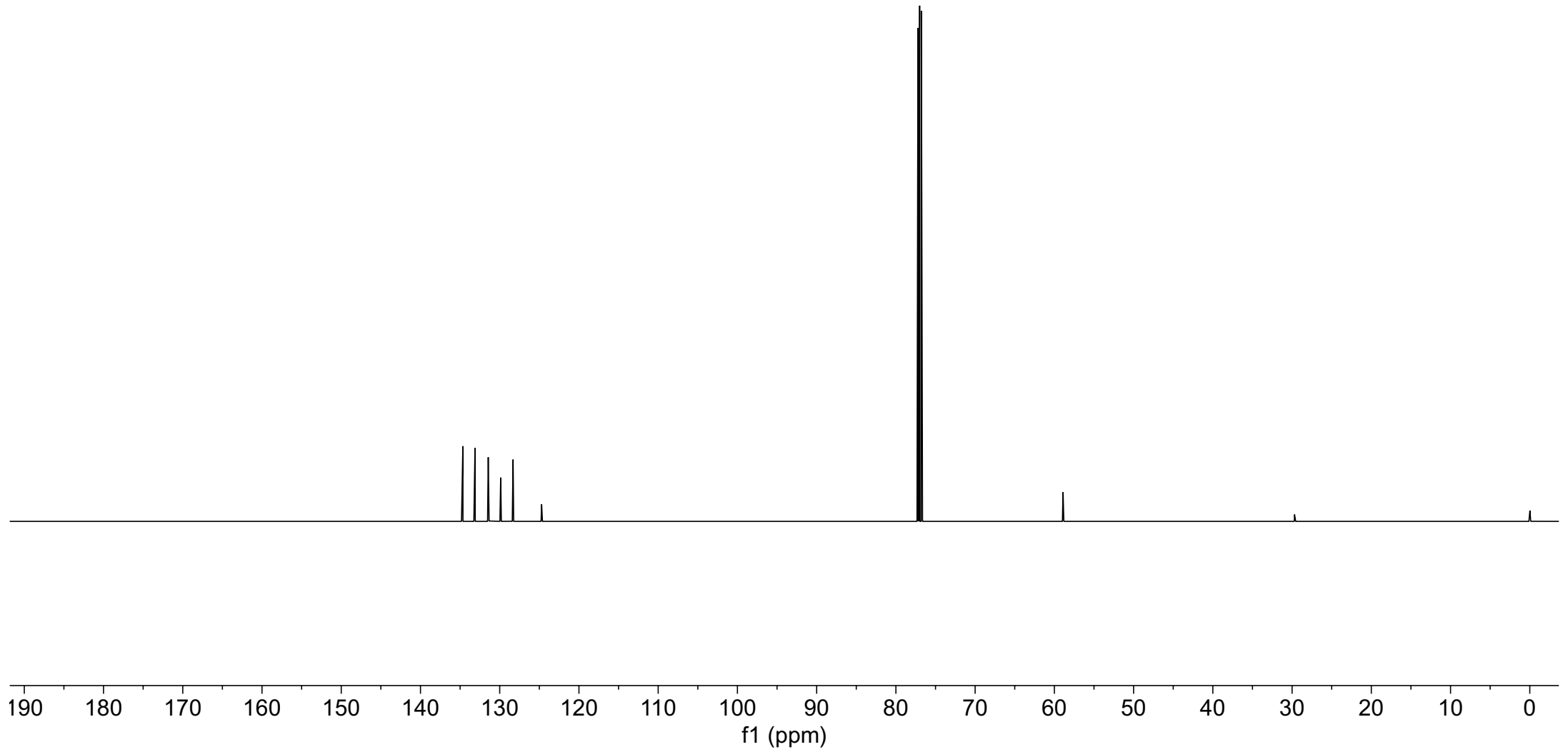
3m

$^{13}\text{C}$ NMR,  $\text{CDCl}_3$ , 125MHz, 298K

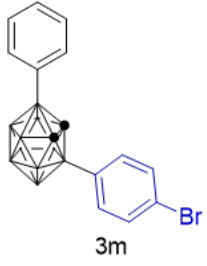
134.6  
133.1  
131.5  
129.9  
128.3

77.2  
77.0  
76.8

58.9

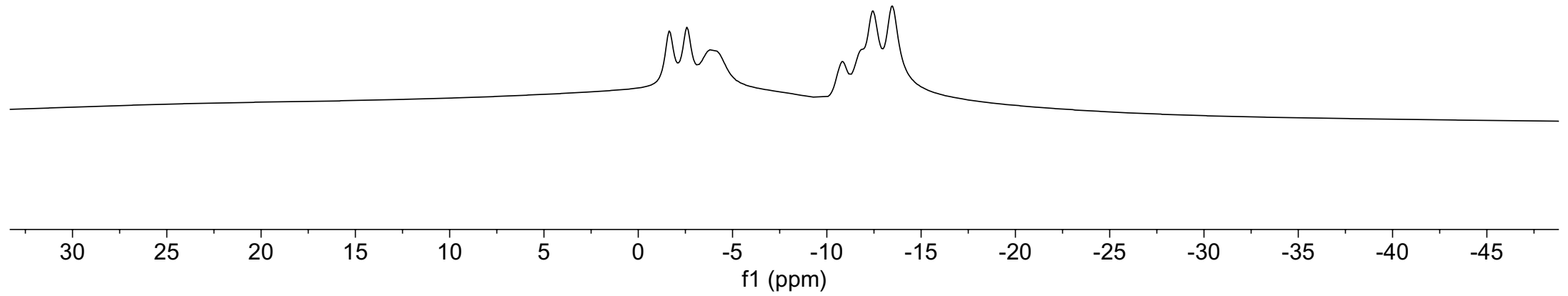


YHB-35-B



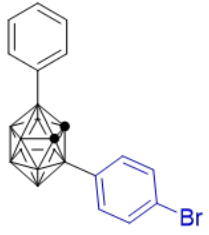
$^{11}\text{B}$ NMR,  $\text{CDCl}_3$ , 160MHz, 298K

~1.6  
~2.6  
~4.0  
-10.8  
-12.4  
-13.5





YHB-35-B{H}



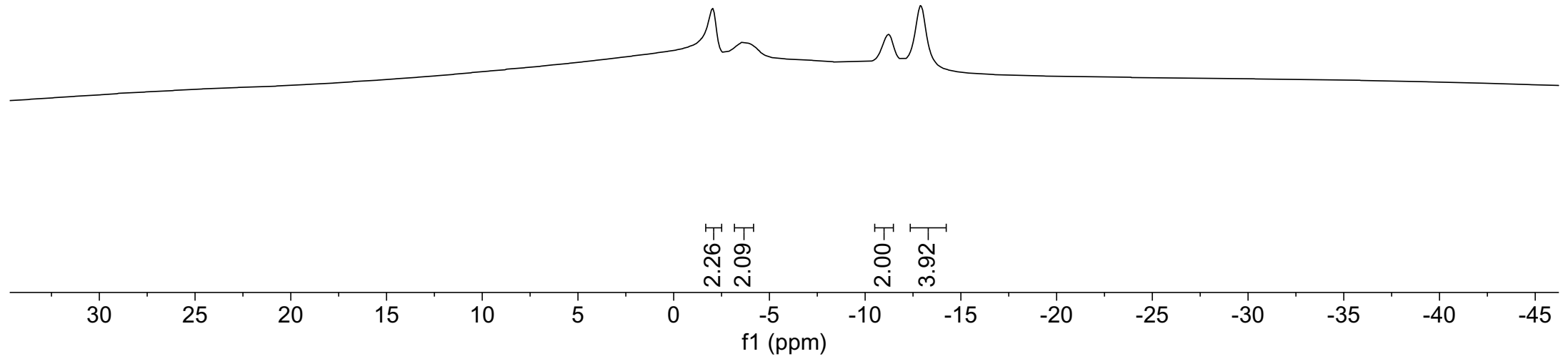
$^{11}\text{B}\{^1\text{H}\}$ NMR,  $\text{CDCl}_3$ , 160MHz, 298K

--2.0

--3.7

--11.2

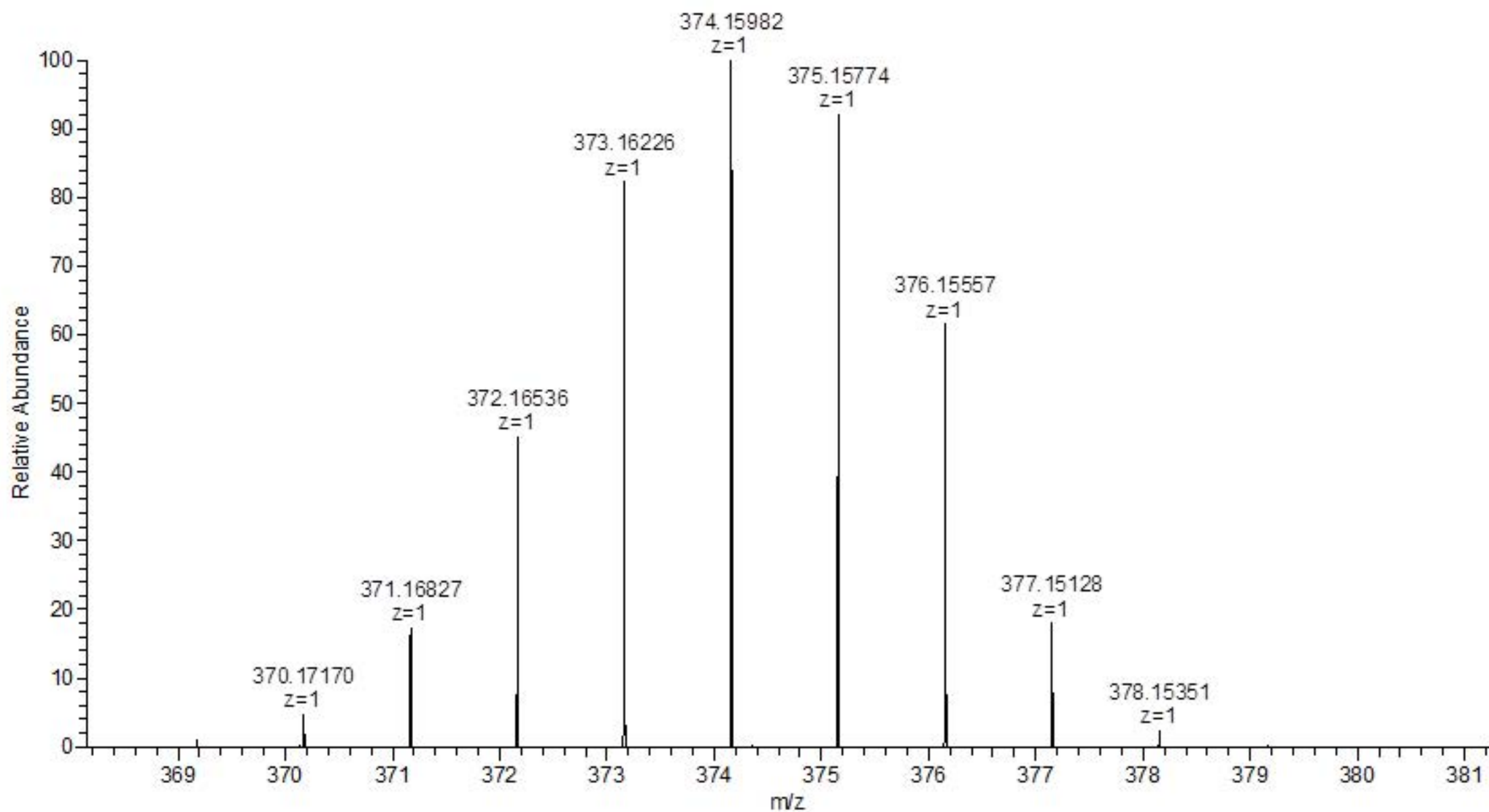
--12.9



Y35

HRMS (ESI)  $m/z$  calcd for  $C_{14}H_{19}Br$  (M-H) $^-$  375.1580, found 375.1577.

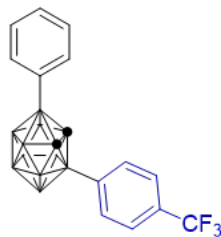
y35 #63-71 RT: 0.62-0.68 AV: 4 NL: 1.46E8  
T: FTMS - p ESI Full ms [100.0000-800.0000]



YHB-24-H

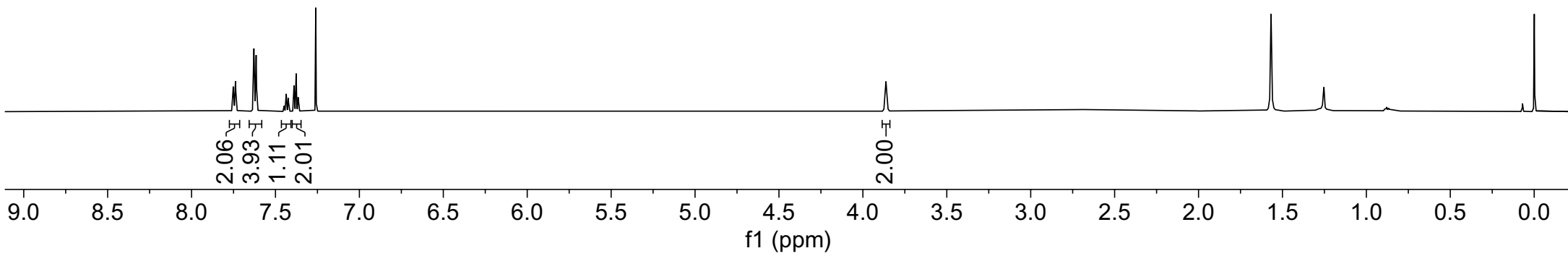
7.75  
7.74  
7.63  
7.62  
7.45  
7.45  
7.45  
7.44  
7.44  
7.43  
7.43  
7.42  
7.42  
7.39  
7.38  
7.37  
7.37

3.86

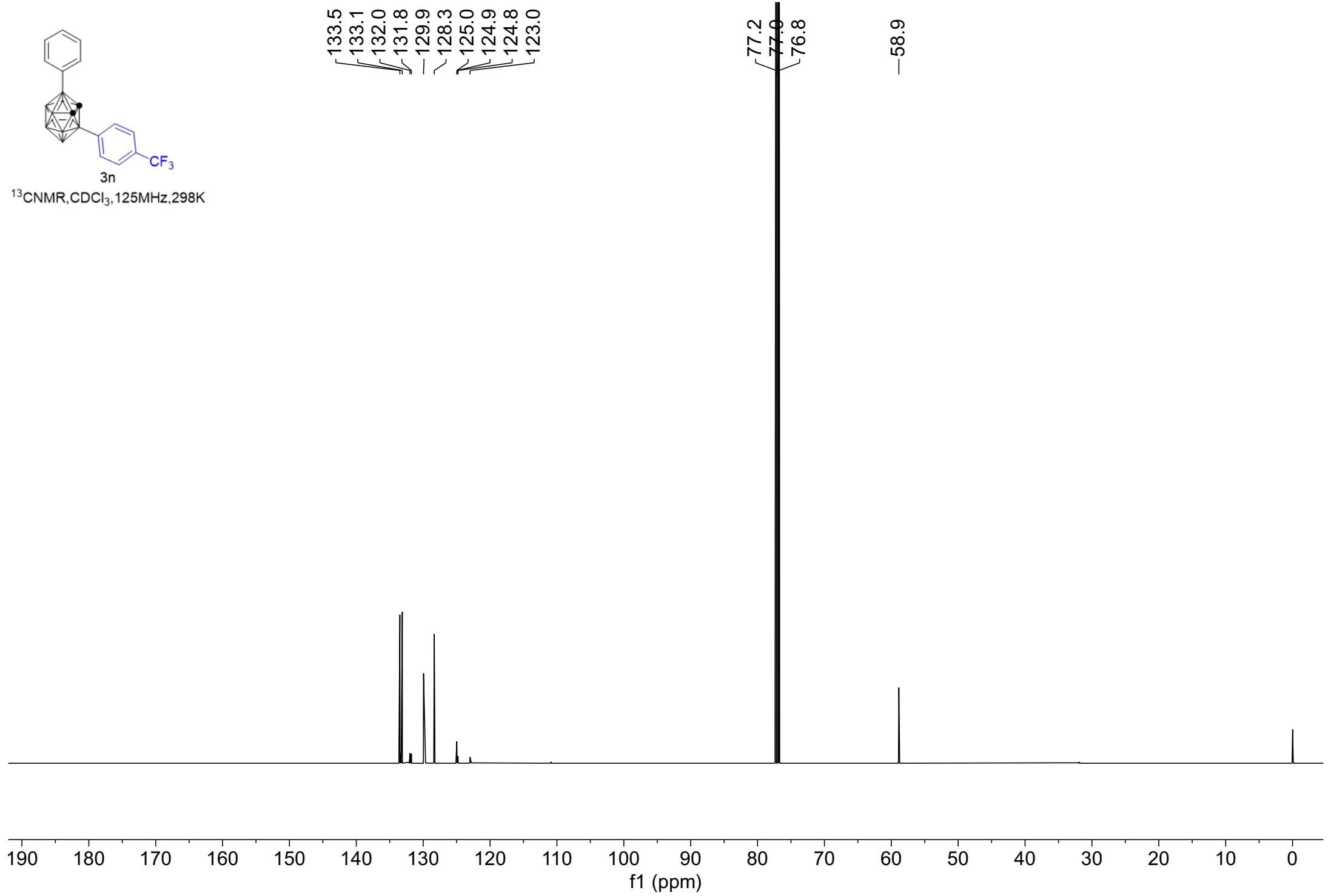
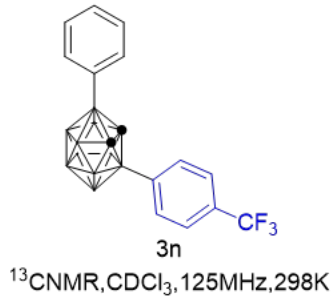


3n

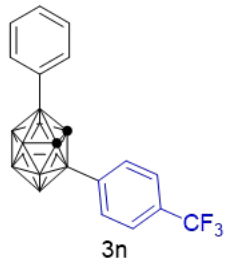
<sup>1</sup>HNMR, CDCl<sub>3</sub>, 500MHz, 298K



YHB-24-C



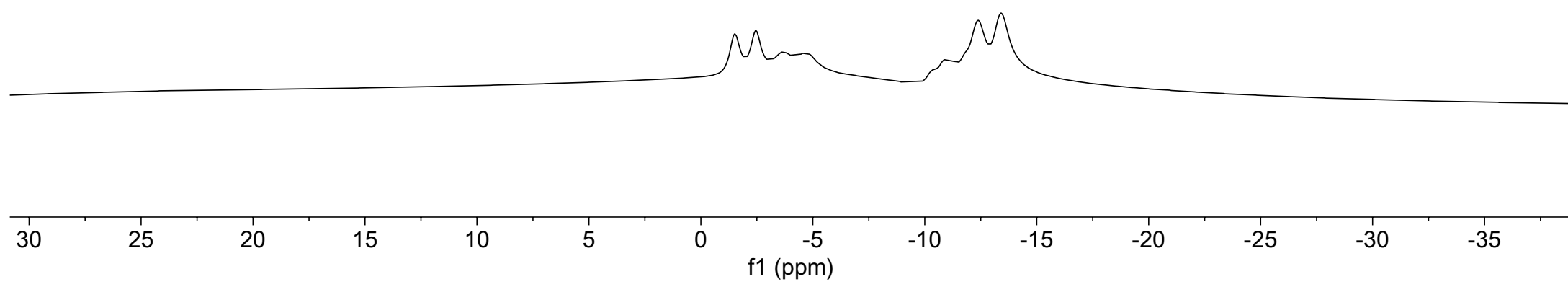
YHB-24-B



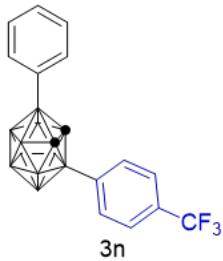
$^{11}\text{B}$ NMR,  $\text{CDCl}_3$ , 160MHz, 298K

--1.5  
--2.5  
--3.7  
--4.7

--10.9  
--12.4  
--13.4

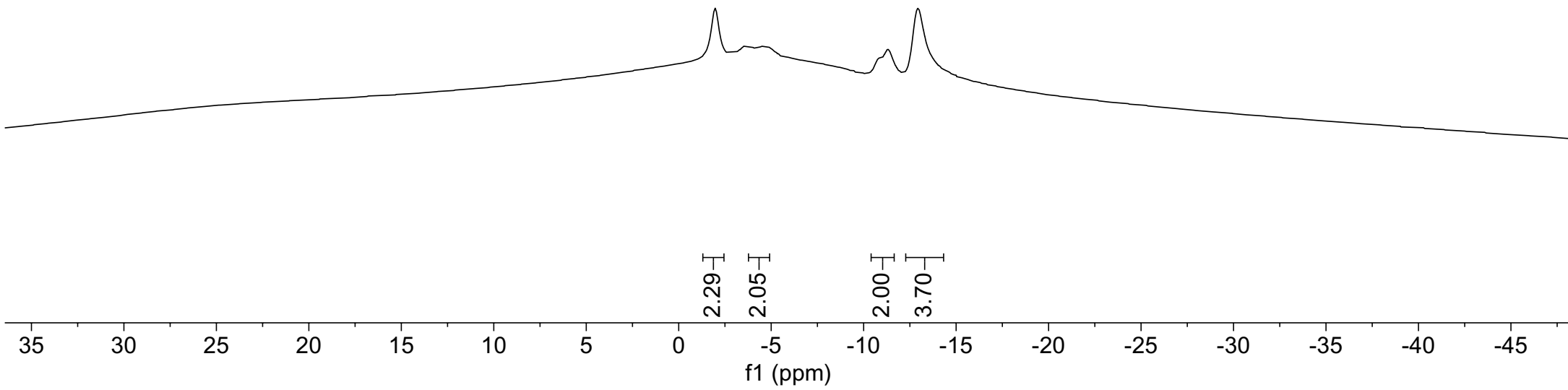


YHB-24-B{H}



$^{11}\text{B}\{^1\text{H}\}$ NMR,  $\text{CDCl}_3$ , 160MHz, 298K

--2.0  
--4.7  
--11.3  
--12.9

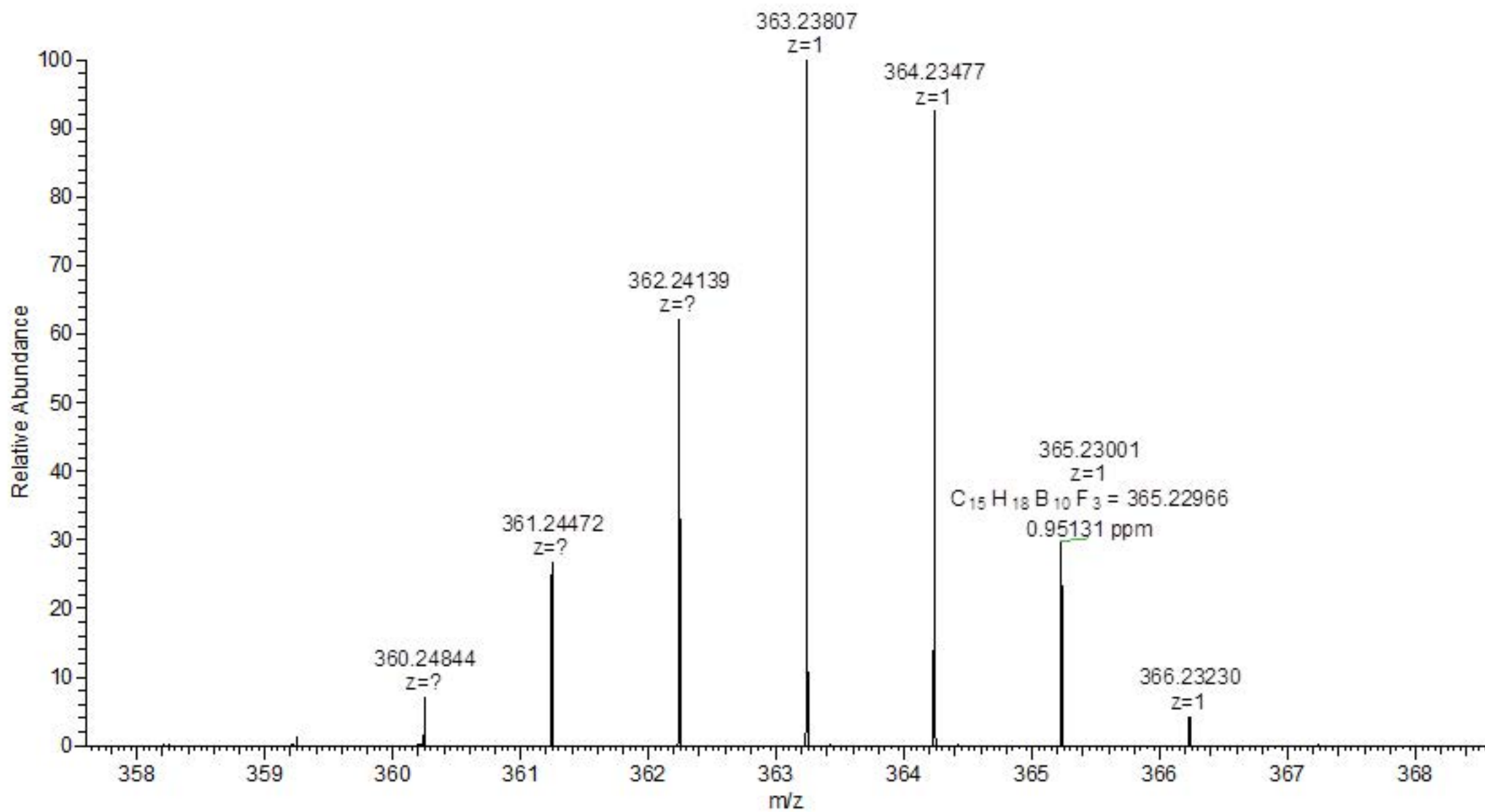


Y24

HRMS (ESI)  $m/z$  calcd for  $C_{15}H_{19}B_{10}F_3 \cdot (M-H)^-$  365.2296, found 365.2300.

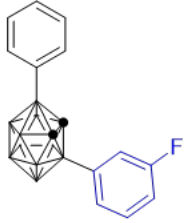
Y24 #18 RT: 0.17 AV: 1 NL: 4.85E8

T: FTMS - p ESI Full ms [100.0000-800.0000]



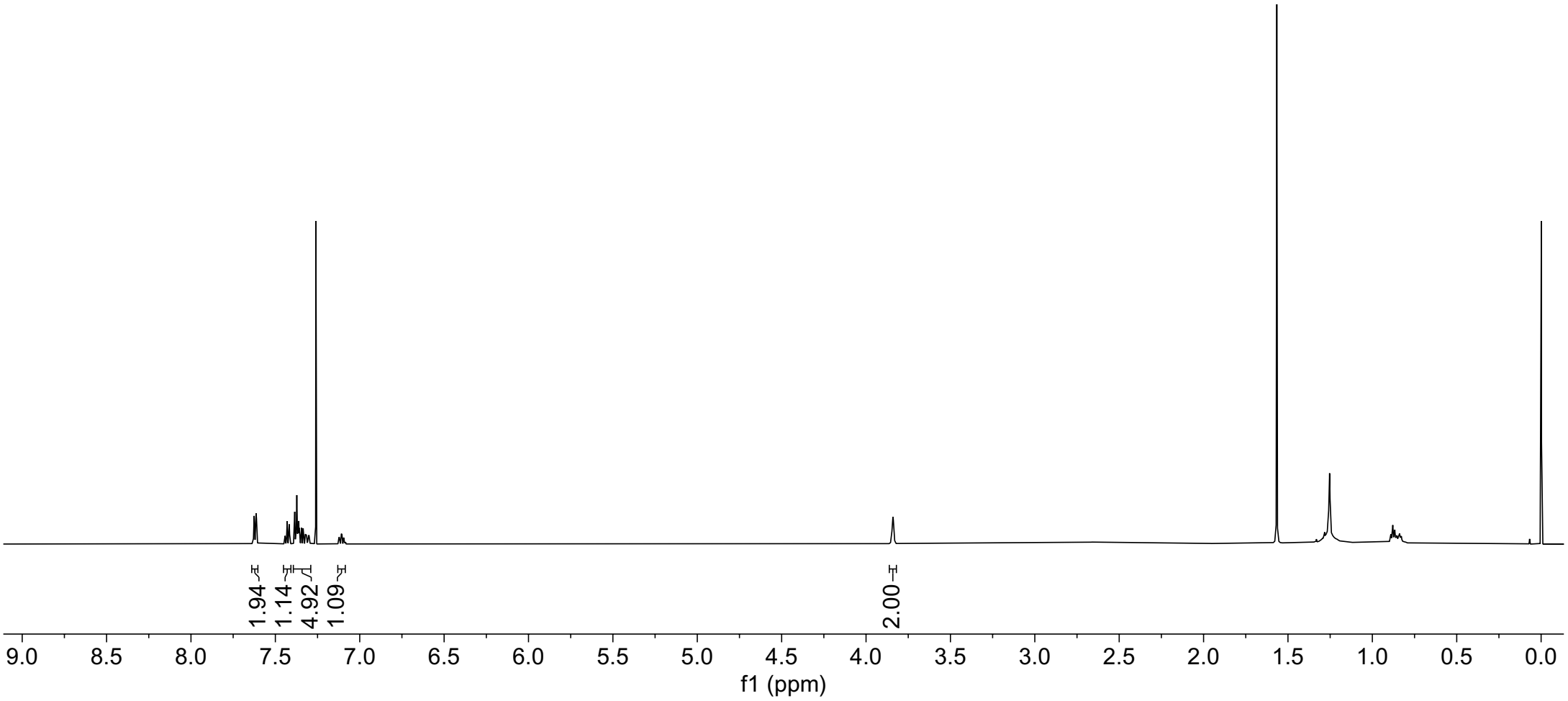
YHB-34-H

7.63  
7.61  
7.61  
7.44  
7.44  
7.44  
7.43  
7.43  
7.43  
7.42  
7.42  
7.42  
7.39  
7.39  
7.37  
7.36  
7.36  
7.36  
7.35  
7.34  
7.34  
7.33  
7.32  
7.32  
7.30  
7.30  
7.13  
7.12  
7.12  
7.12  
7.11  
7.11  
7.11  
7.10  
7.10  
7.09  
7.09  
3.84



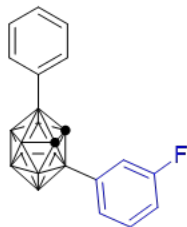
3o

<sup>1</sup>H NMR, CDCl<sub>3</sub>, 500 MHz, 298 K



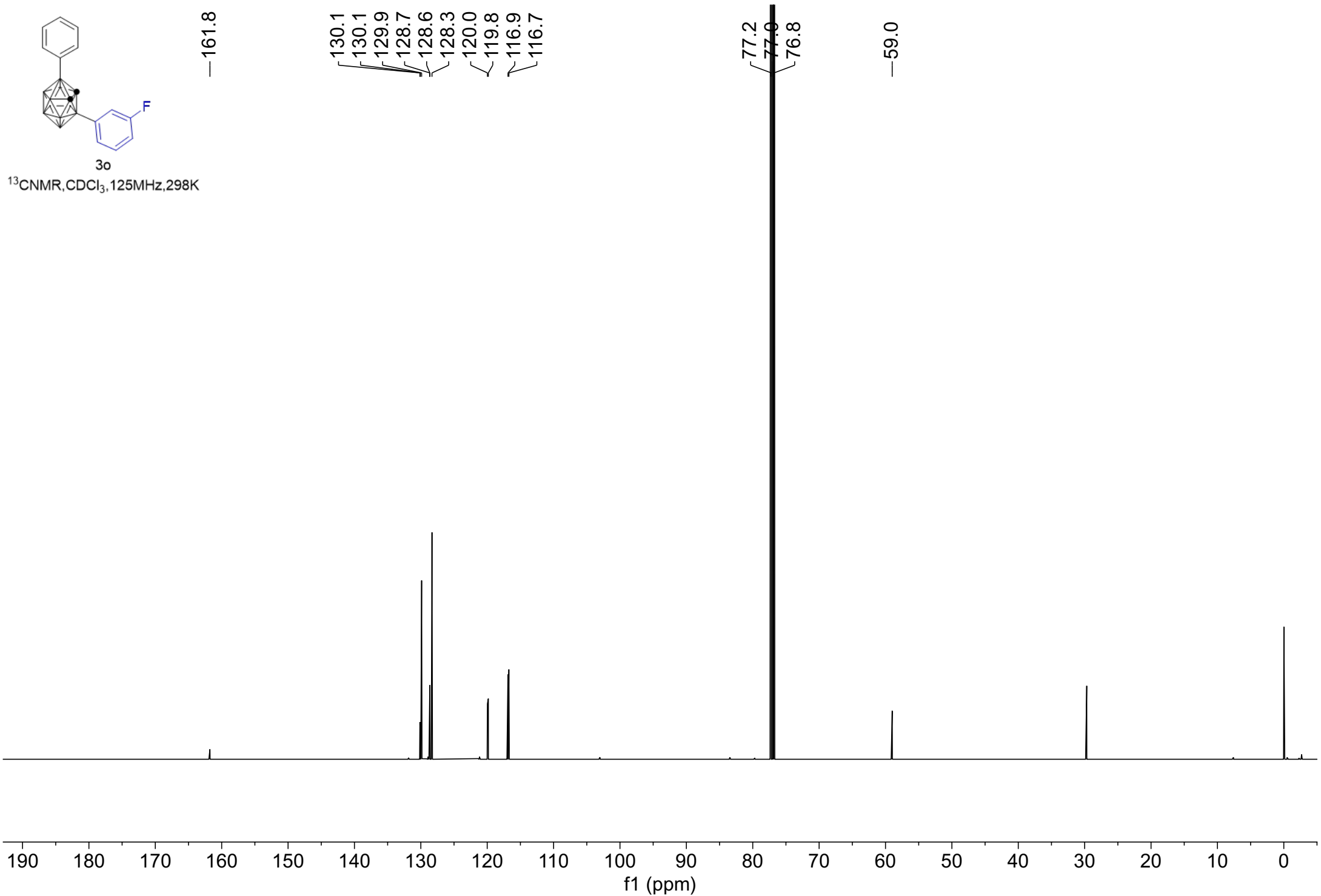


YHB-34-C

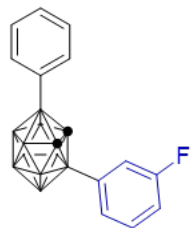


3o

$^{13}\text{C}$ NMR,  $\text{CDCl}_3$ , 125MHz, 298K



YHB-34-B

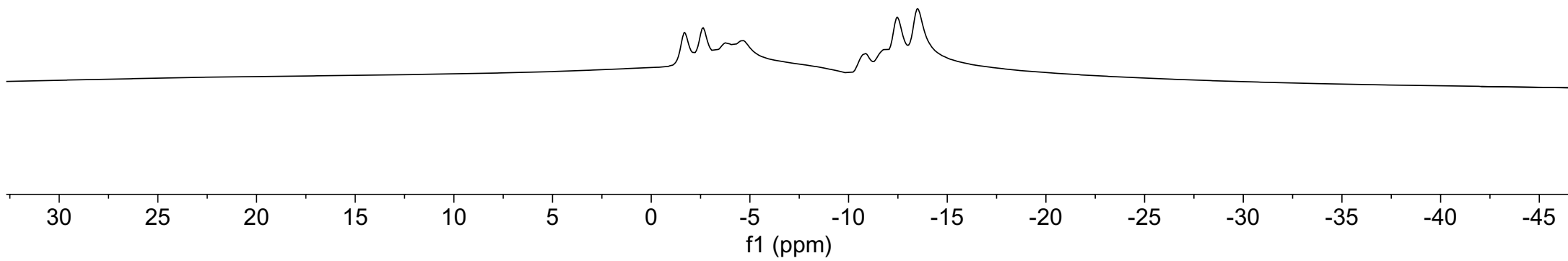


3o

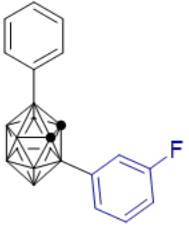
$^{11}\text{B}$ NMR,  $\text{CDCl}_3$ , 160MHz, 298K

1.7  
2.6  
3.8  
4.7

10.8  
11.7  
12.5  
13.5



YHB-34-B{H}

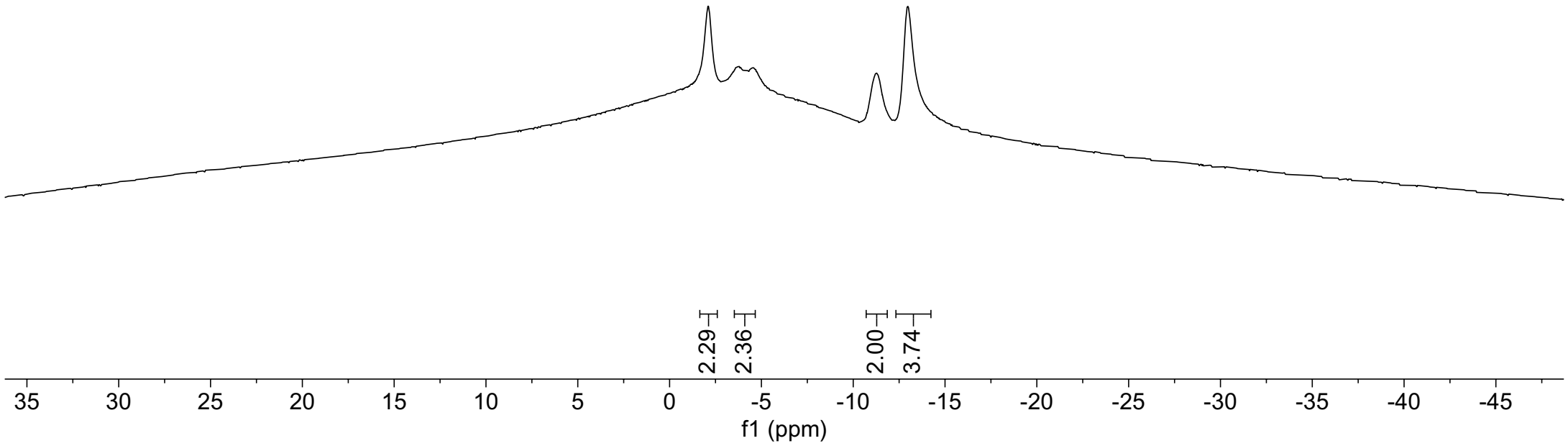


3o

$^{11}\text{B}\{^1\text{H}\}$ NMR,  $\text{CDCl}_3$ , 160MHz, 298K

-2.1  
-3.7  
-4.6

-11.3  
-13.0

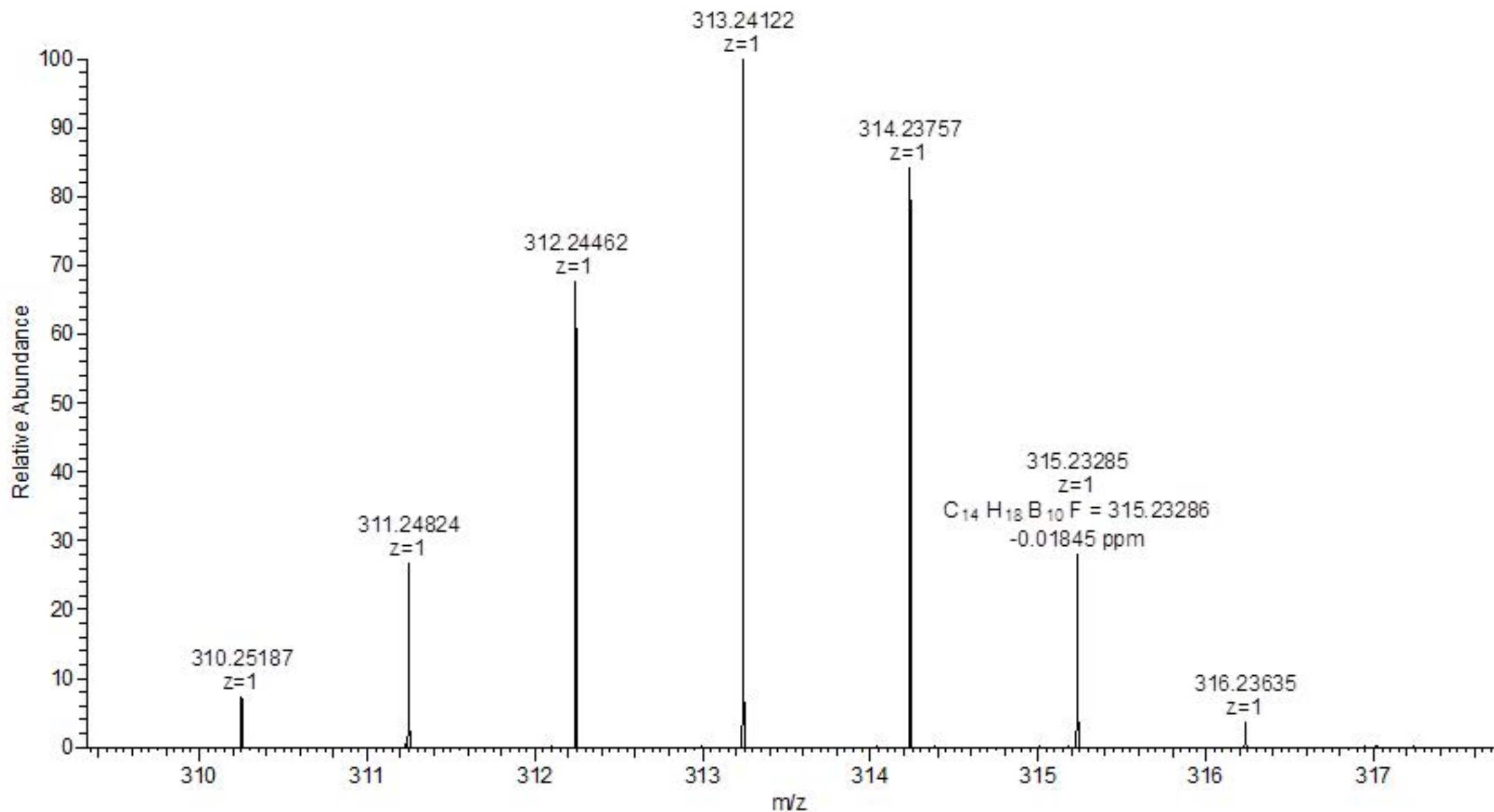


Y34

HRMS (ESI)  $m/z$  calcd for  $C_{14}H_{19}B_{10}F$  (M-H) 315.2328, found 315.2328.

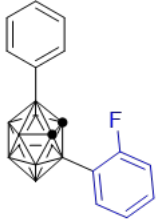
y34 #26 RT: 0.25 AV: 1 SB: 3 0.04-0.08 NL: 5.19E7

T: FTMS - p ESI Full ms [100.0000-800.0000]



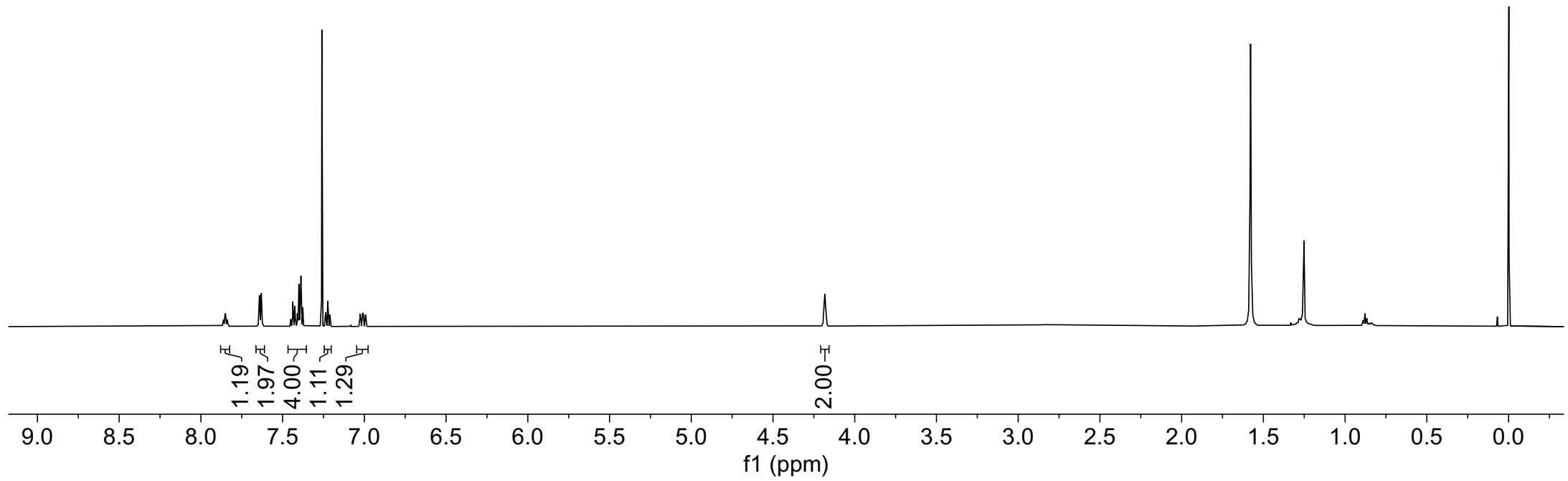
YHB-72-H

7.86  
7.86  
7.85  
7.85  
7.84  
7.84  
7.64  
7.63  
7.63  
7.45  
7.45  
7.45  
7.44  
7.44  
7.44  
7.43  
7.43  
7.43  
7.42  
7.42  
7.41  
7.41  
7.40  
7.39  
7.39  
7.38  
7.38  
7.37  
7.24  
7.22  
7.21  
7.03  
7.02  
7.01  
7.01  
7.01  
7.01  
6.99  
6.99  
4.18

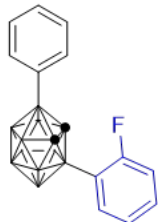


3p

<sup>1</sup>HNMR, CDCl<sub>3</sub>, 500MHz, 298K



YHB-72-C



3p

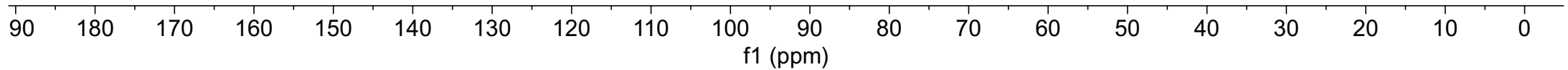
$^{13}\text{C}$ NMR,  $\text{CDCl}_3$ , 125MHz, 298K

~165.7  
~164.1

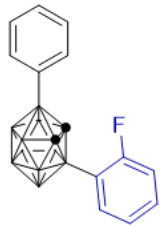
138.0  
137.9  
133.0  
131.8  
131.8  
129.7  
128.3  
124.7  
124.7  
115.2  
115.1

77.2  
77.0  
76.8

58.3



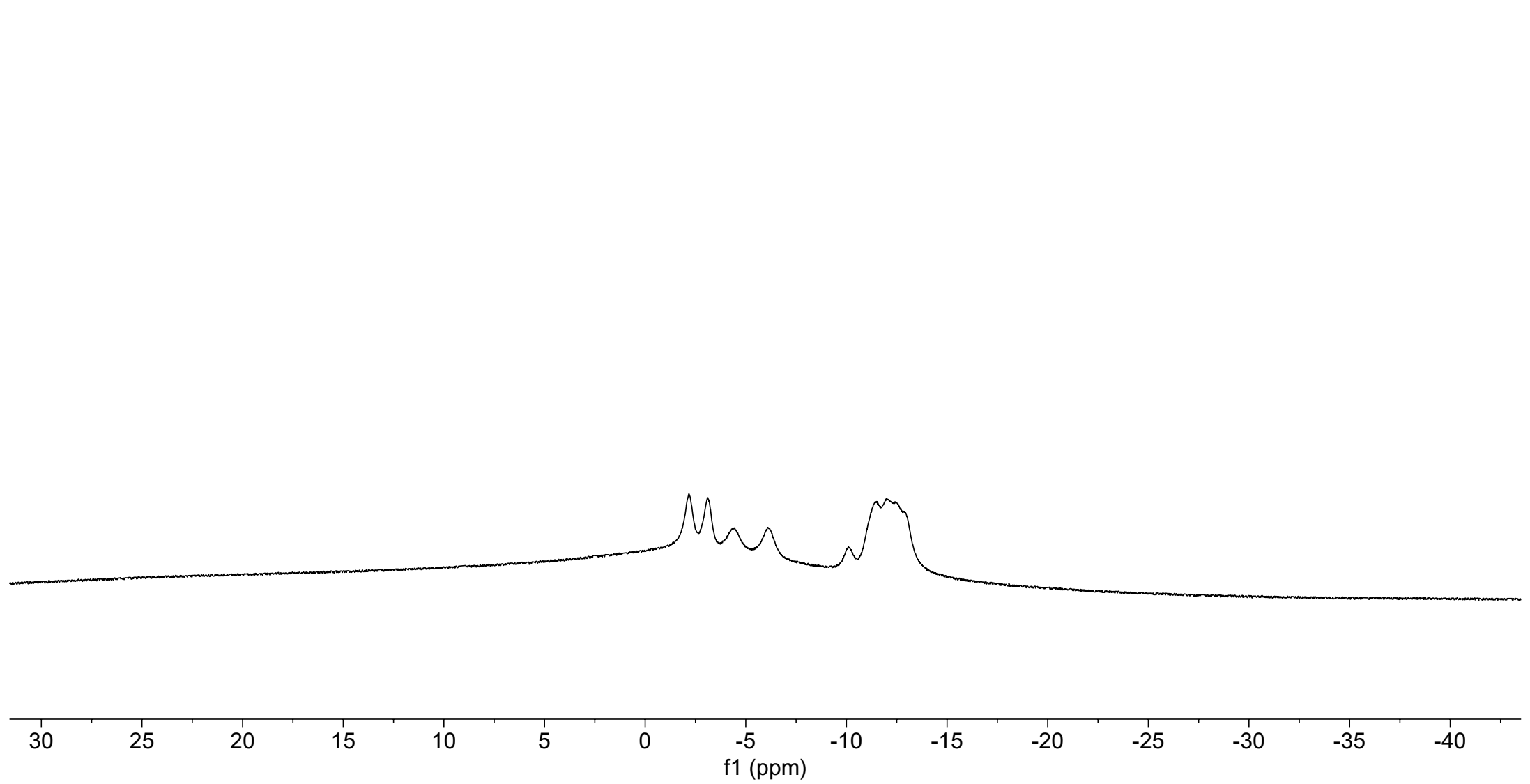
YHB-72-B



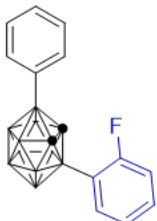
3p

$^{11}\text{B}$ NMR,  $\text{CDCl}_3$ , 160MHz, 298K

~ -2.2  
~ -3.1  
~ -4.4  
~ -6.1  
  
~ -10.1  
~ -11.3  
~ -12.1



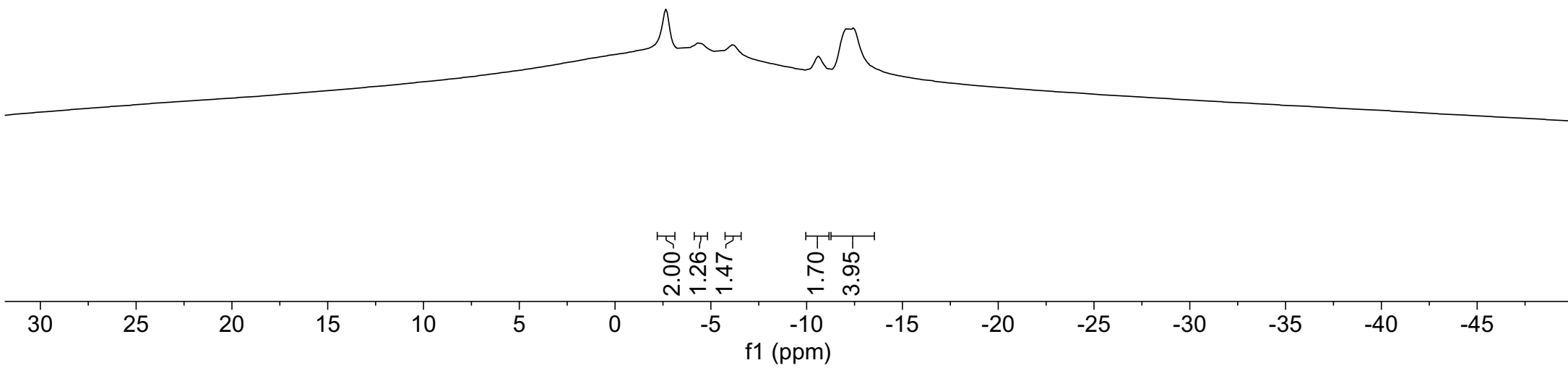
YHB-72-B{H}



3p

$^{11}\text{B}\{^1\text{H}\}$  NMR,  $\text{CDCl}_3$ , 160 MHz, 298 K

~ -2.6  
- - -4.4  
~ -6.1  
- - -10.6  
- - -12.1



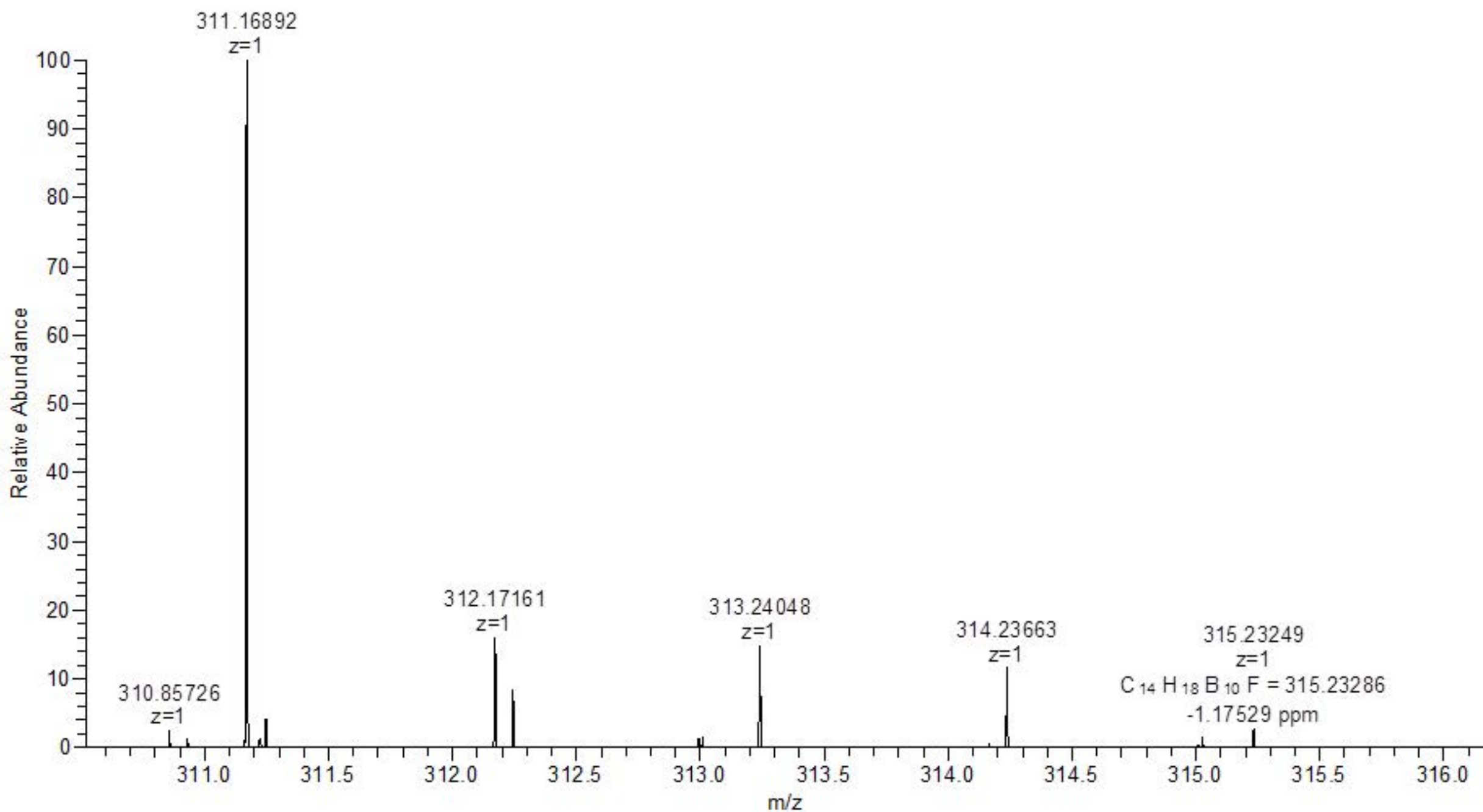


Y-72

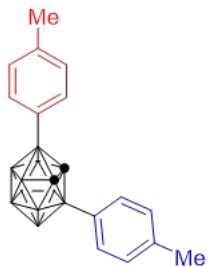
HRMS (ESI)  $m/z$  calcd for  $C_{14}H_{19}B_{10}F$  (M-H) 315.2328, found 315.2324

Y72 #8-15 RT: 0.07-0.13 AV: 4 SB: 4 0.02-0.06, 0.08-0.09 NL: 3.51E6

T: FTMS - p ESI Full ms [100.0000-600.0000]



YHB-57-H



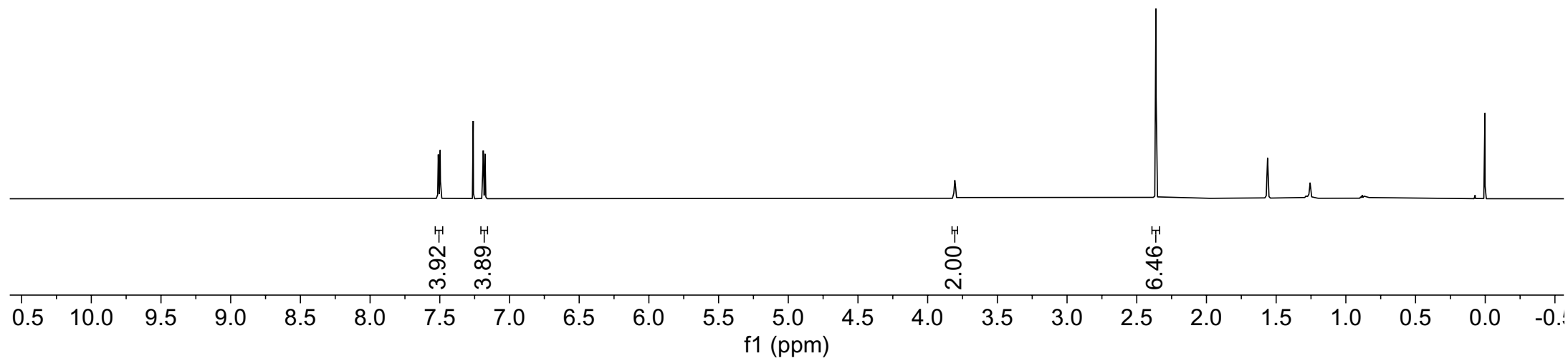
5a

$^1\text{H NMR, CDCl}_3, 500\text{MHz, 298K}$

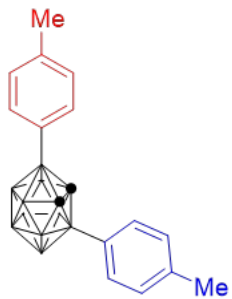
7.51  
7.50  
7.19  
7.18

3.81

2.36



YHB-57-C



5a

$^{13}\text{C}$ NMR,  $\text{CDCl}_3$ , 125MHz, 298K

—139.8

—133.1

—129.0

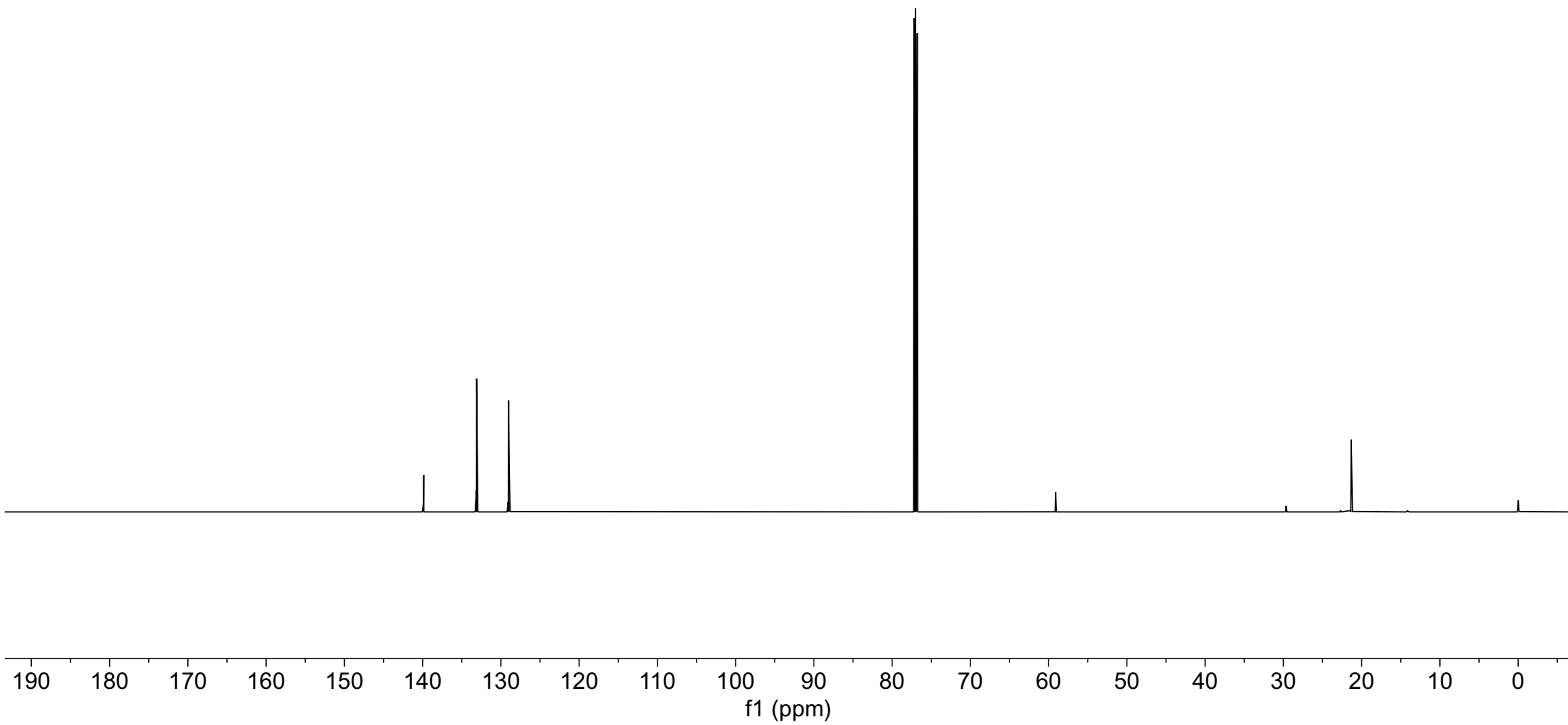
77.2

77.0

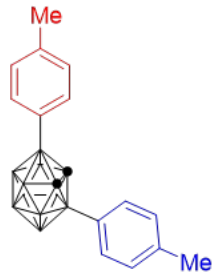
76.8

—59.1

—21.3



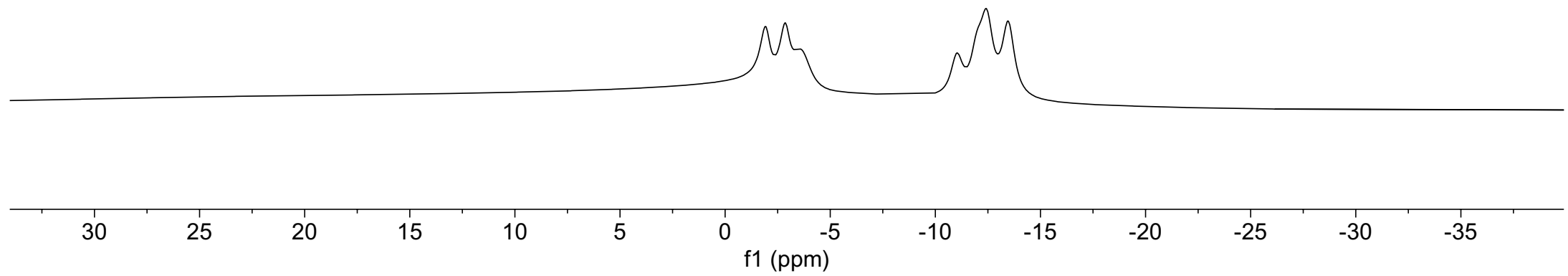
YHB-57-B



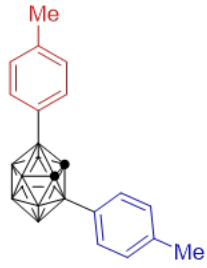
5a

$^{11}\text{B}$ NMR,  $\text{CDCl}_3$ , 160MHz, 298K

~1.9  
~2.8  
~3.6  
--11.0  
~12.3  
--13.5



YHB-57-B{H}

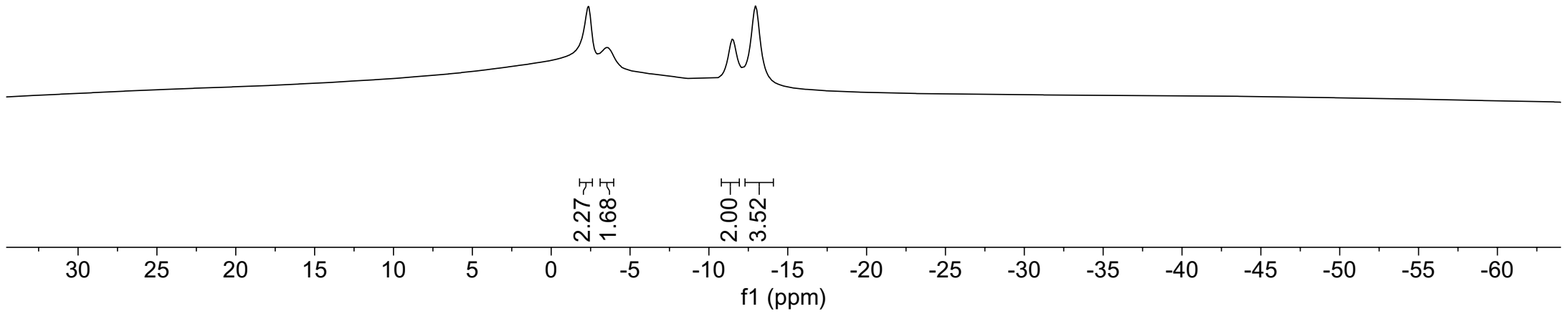


5a

$^{11}\text{B}\{^1\text{H}\}$  NMR,  $\text{CDCl}_3$ , 160 MHz, 298 K

~2.3  
~3.5

~-11.5  
~-13.0

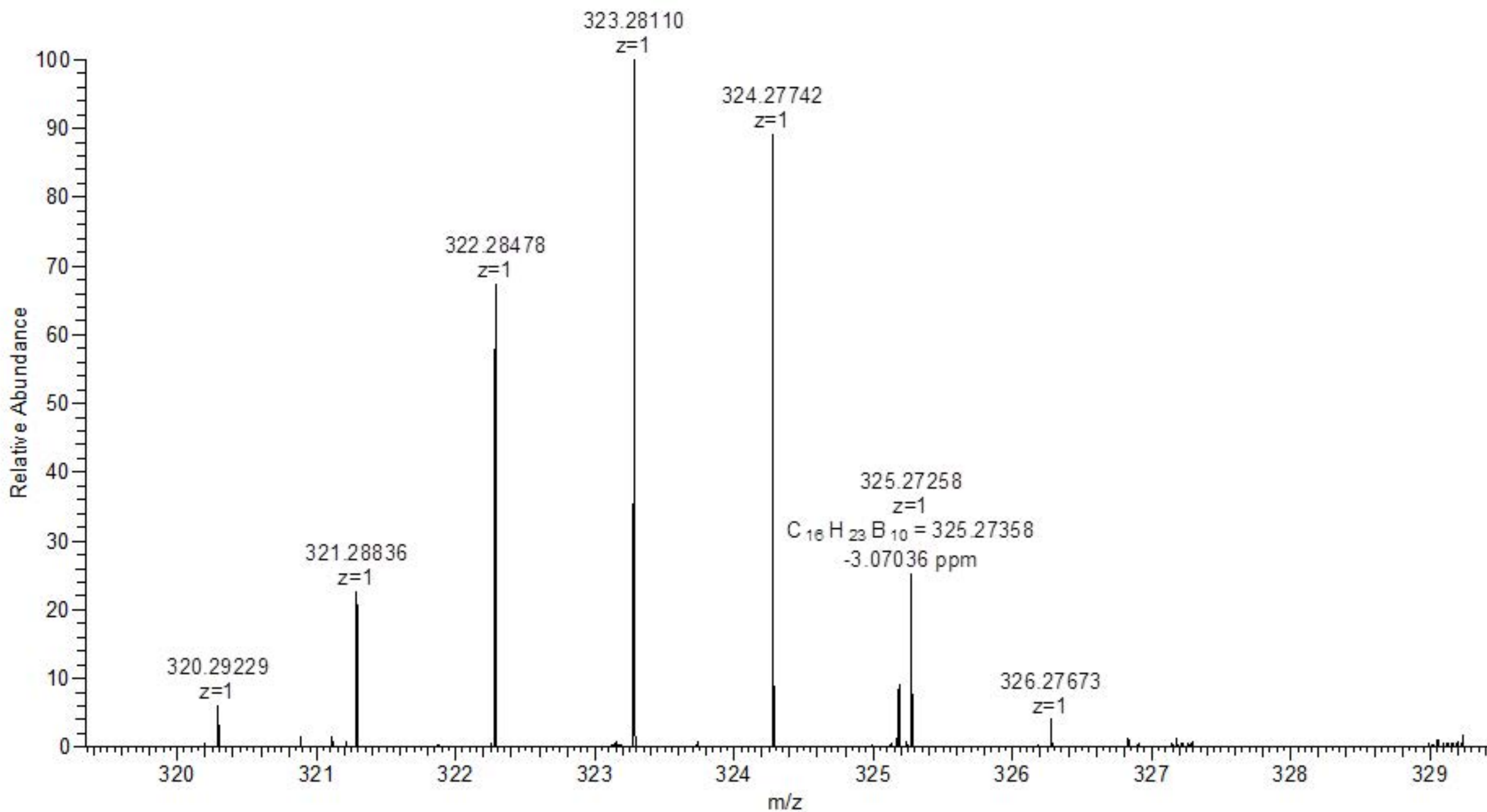


Y-57

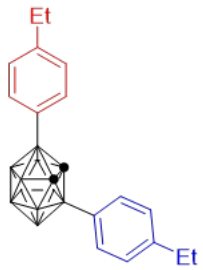
HRMS (ESI)  $m/z$  calcd for  $C_{16}H_{23}B_{10} (M-H)^-$  325.2735, found 352.2725

Y57 #14 RT: 0.13 AV: 1 SB: 4 0.13-0.20 NL: 4.82E6

T: FTMS - p ESI Full ms [100.0000-600.0000]



YHB-56-H



5b

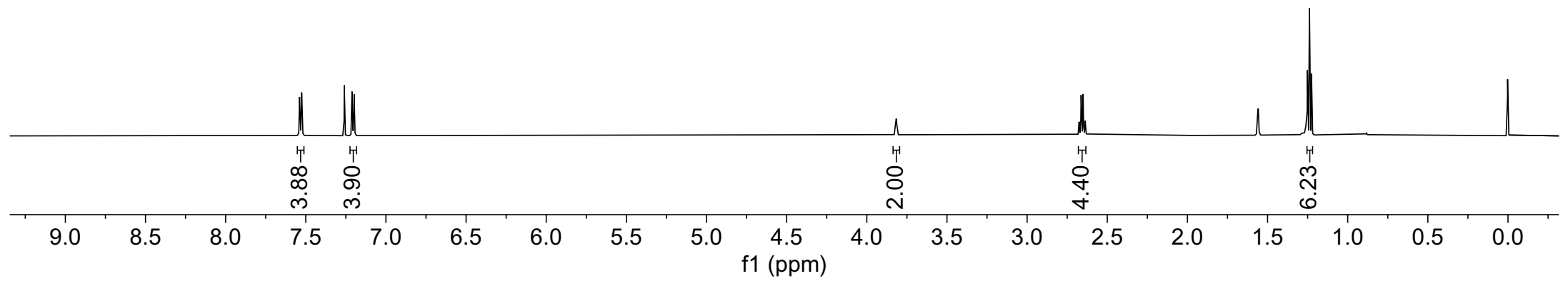
<sup>1</sup>HNMR, CDCl<sub>3</sub>, 500MHz, 298K

7.54  
7.53  
7.21  
7.20

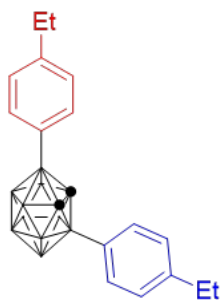
3.82

2.68  
2.66  
2.65  
2.64

1.25  
1.24  
1.23



YHB-56-C



5b

$^{13}\text{C}$ NMR,  $\text{CDCl}_3$ , 125MHz, 298K

—146.1

—133.2

—127.9

77.2

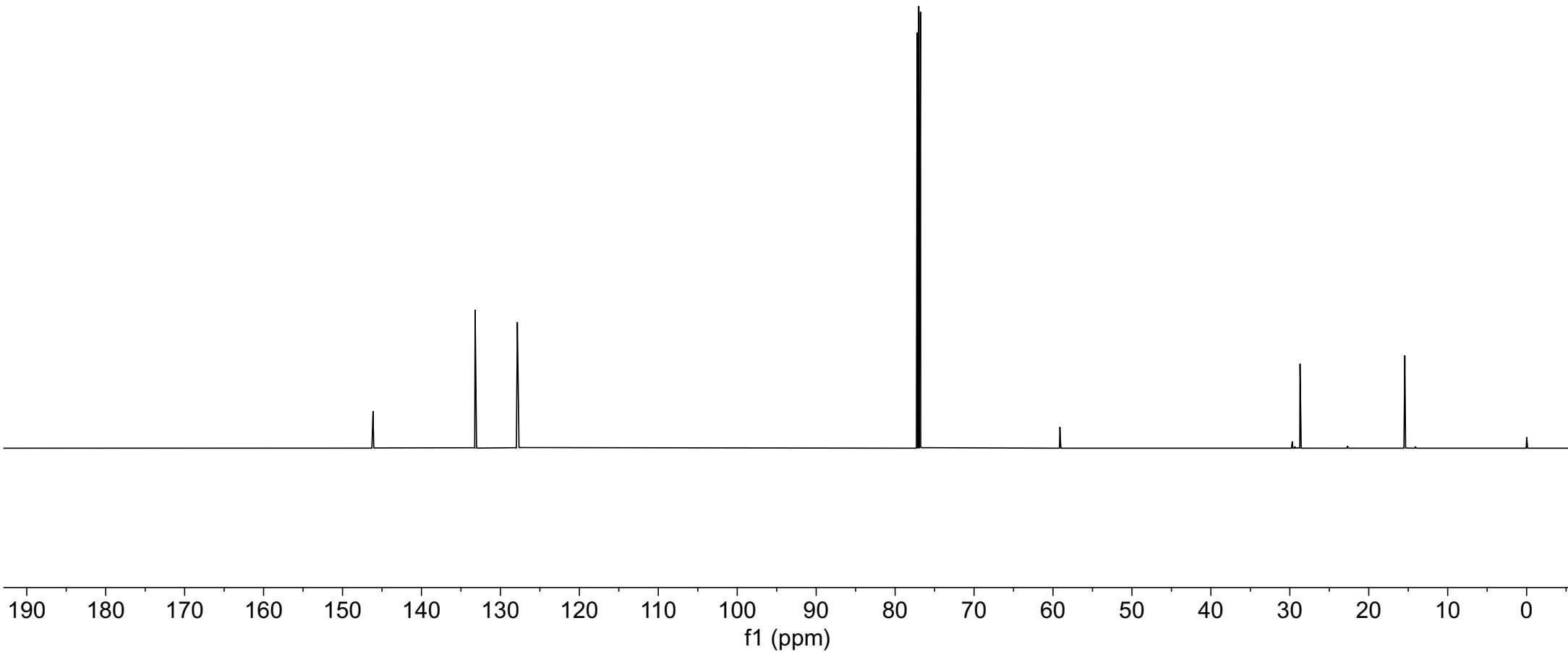
77.0

76.8

—59.1

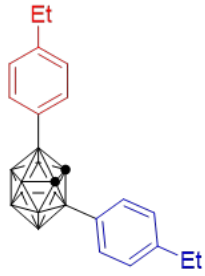
—28.7

—15.4





YHB-56-B

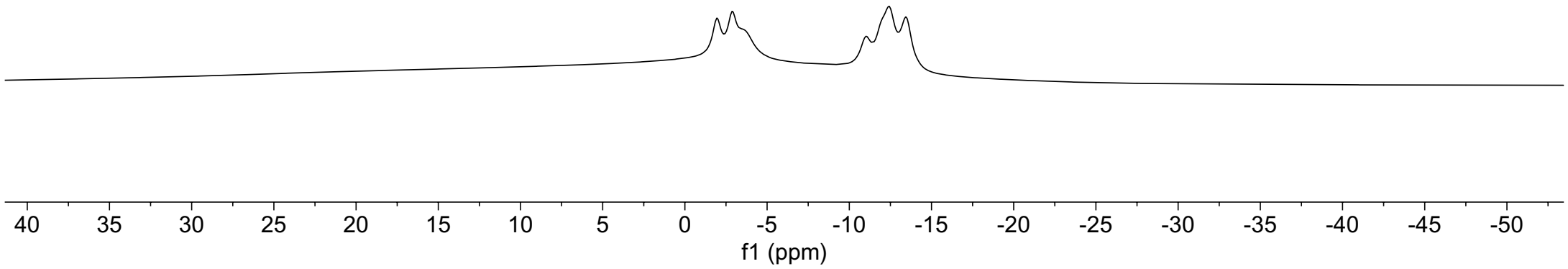


5b

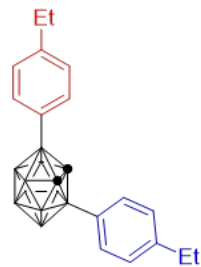
$^{11}\text{B}$ NMR,  $\text{CDCl}_3$ , 160MHz, 298K

~ -1.9  
~ -2.9

~ -11.0  
~ -12.4  
~ -13.5



YHB-56-B{H}

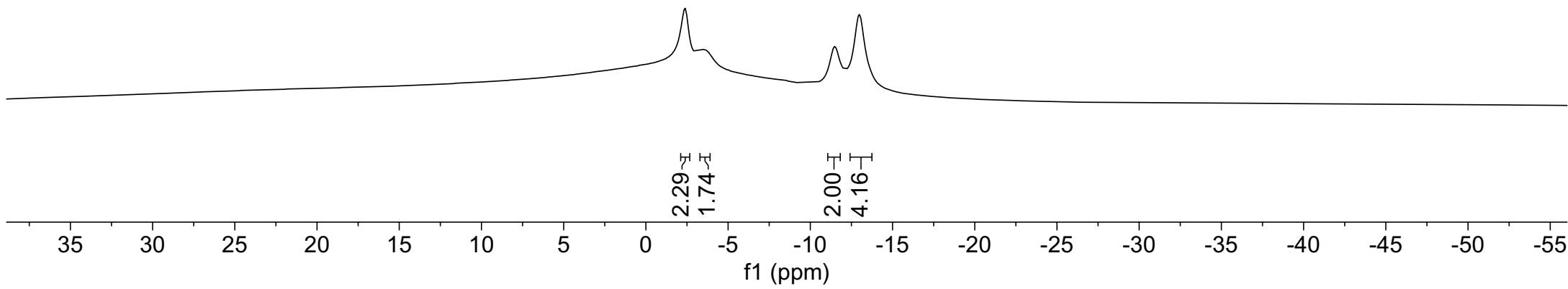


5b

$^{11}\text{B}\{^1\text{H}\}$ NMR,  $\text{CDCl}_3$ , 160MHz, 298K

~ -2.4  
~ -3.5

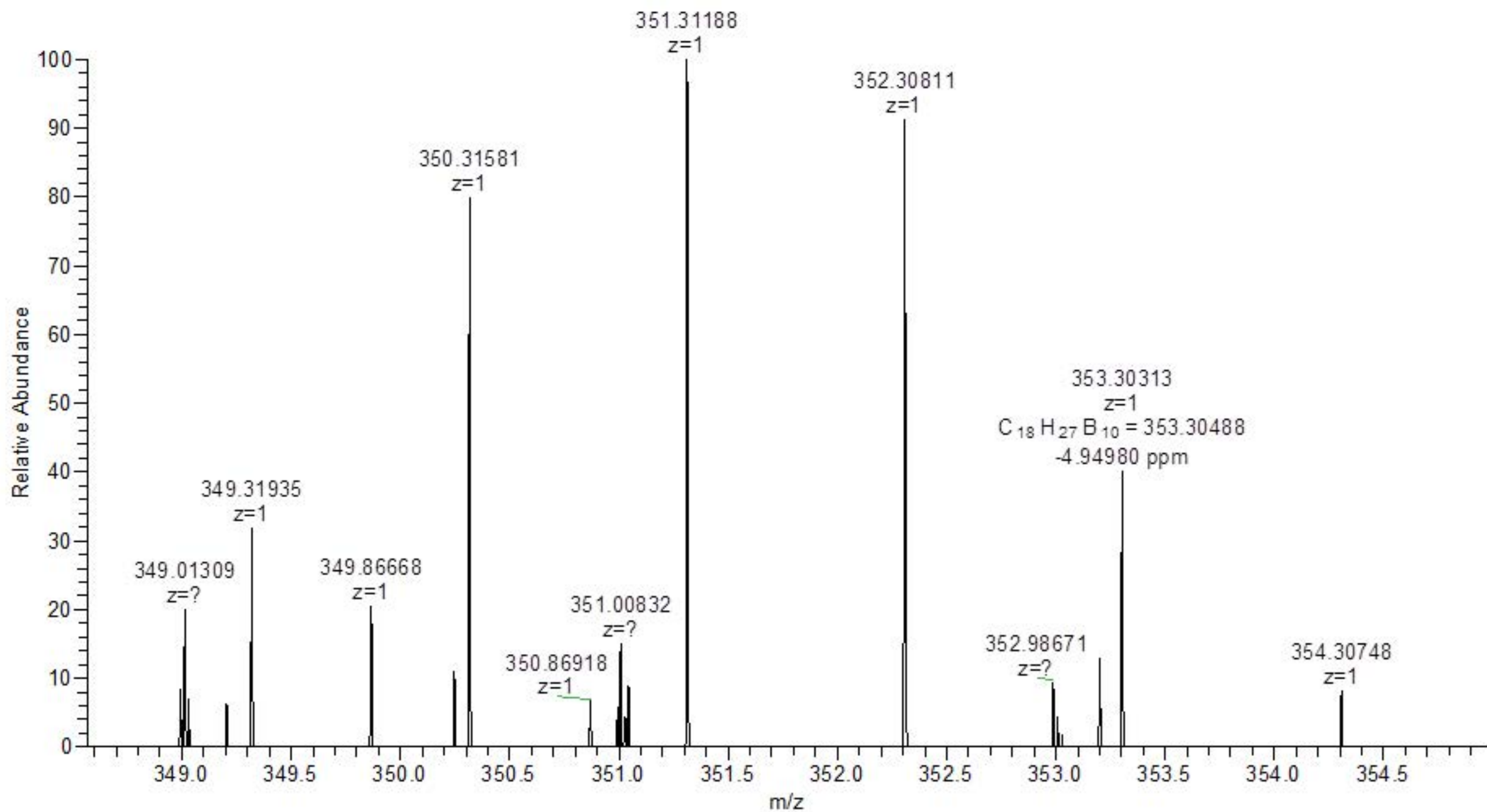
~ -11.5  
~ -13.0



Y-56

HRMS (ESI)  $m/z$  calcd for  $C_{18}H_{28}B_{10} (M-H)^-$  353.3048, found 353.3031

Y56 #12 RT: 0.12 AV: 1 SB: 20 0.28-0.65 , 0.02-0.05 NL: 4.04E5  
T: FTMS - p ESI Full ms [100.0000-600.0000]

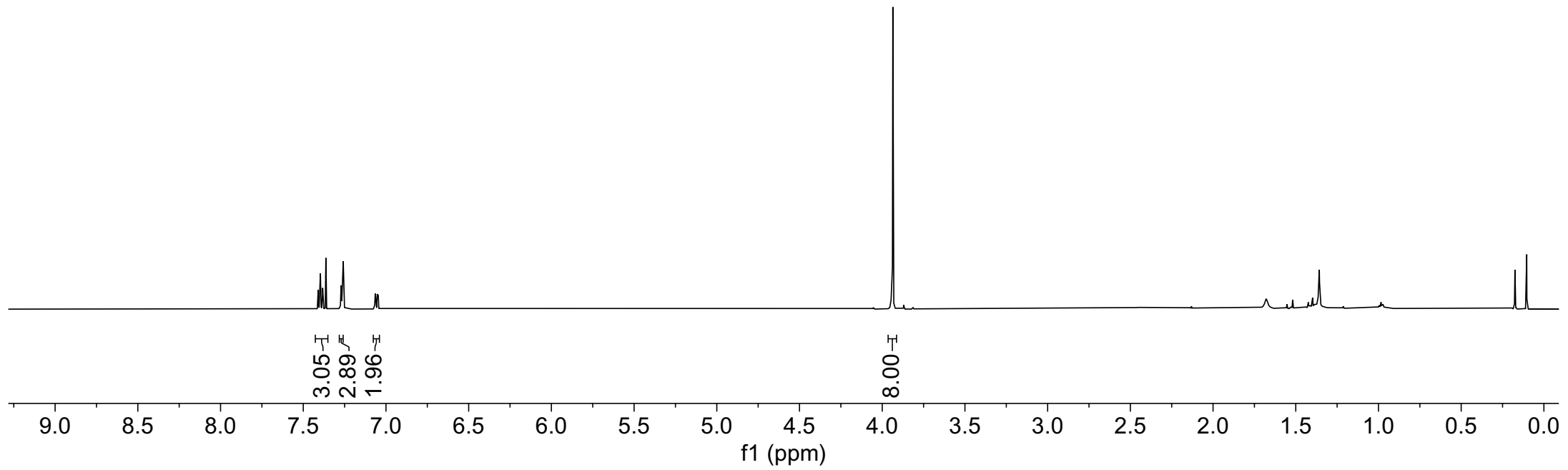


YHB-60-H

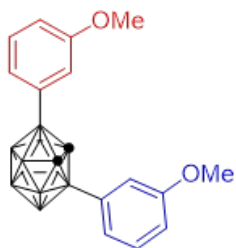


5c

$^1\text{H NMR}$ ,  $\text{CDCl}_3$ , 500MHz, 298K



YHB-60-C



5c

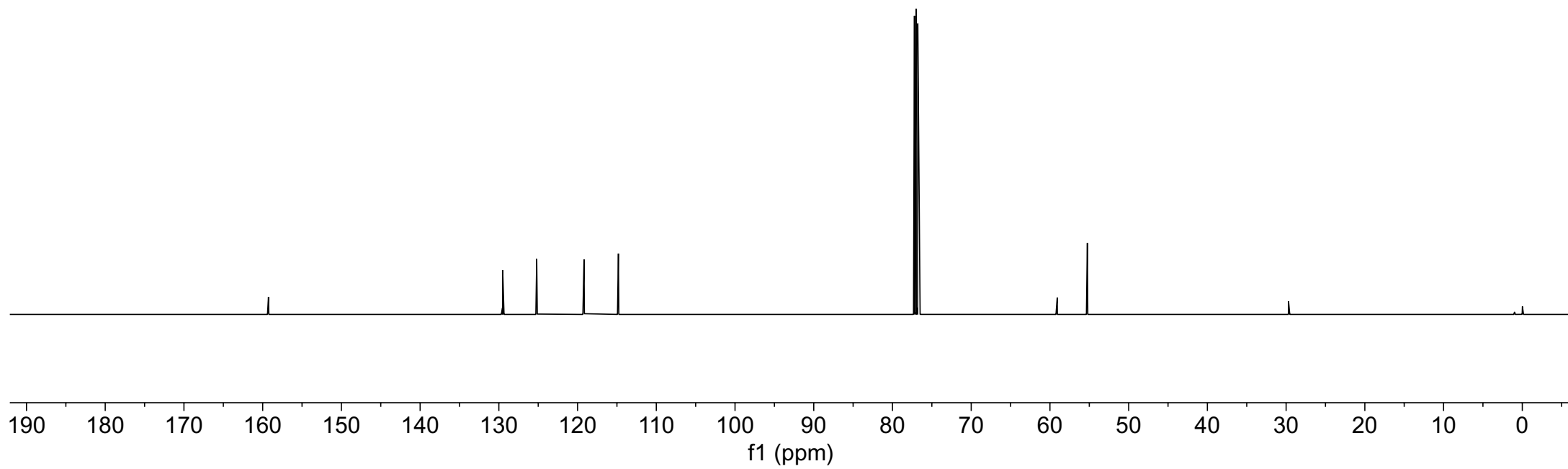
$^{13}\text{C}$ NMR,  $\text{CDCl}_3$ , 125MHz, 298K

—159.3

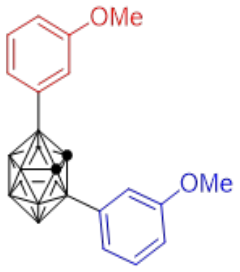
129.5  
125.2  
119.2  
114.8

77.2  
77.0  
76.8

—59.1  
—55.2



YHB-60-B

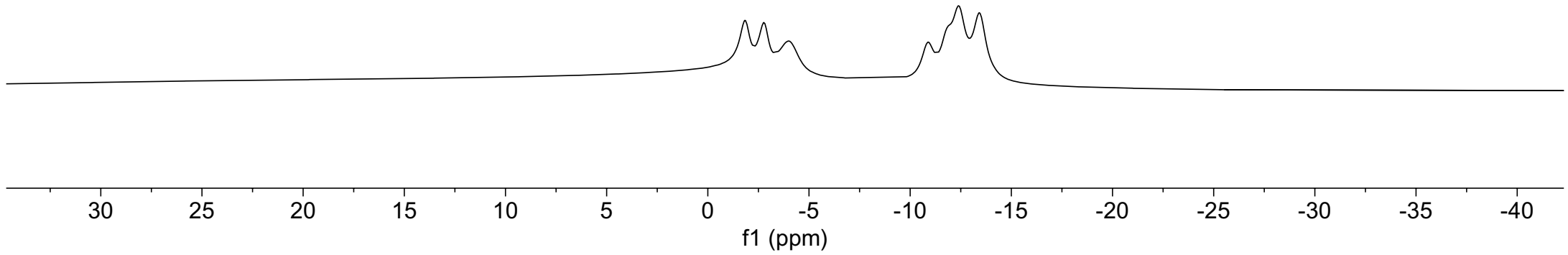


5c

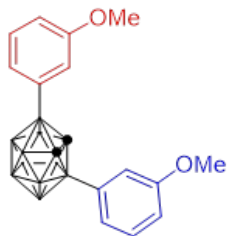
$^{11}\text{B}$ NMR,  $\text{CDCl}_3$ , 160MHz, 298K

~1.8  
~2.8  
~4.0

--10.9  
~12.4  
--13.5



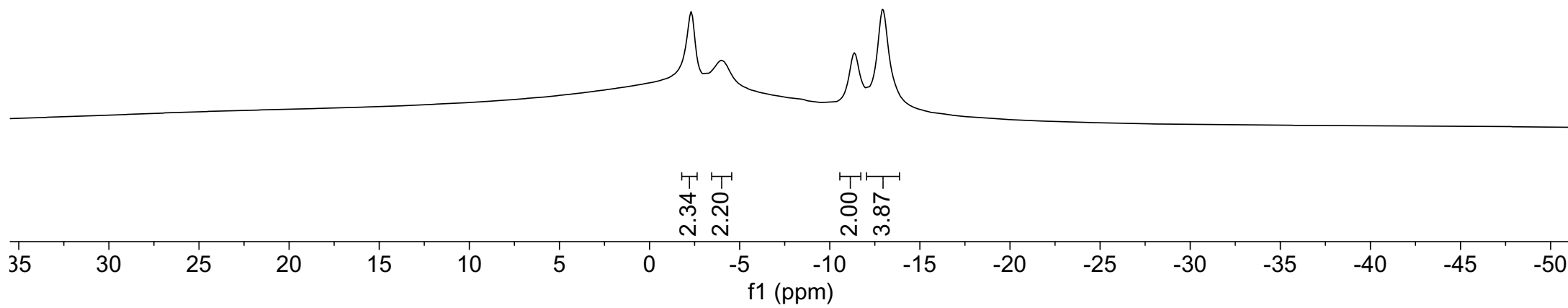
YHB-60-B{H}



5c

$^{11}\text{B}\{^1\text{H}\}$ NMR,  $\text{CDCl}_3$ , 160MHz, 298K

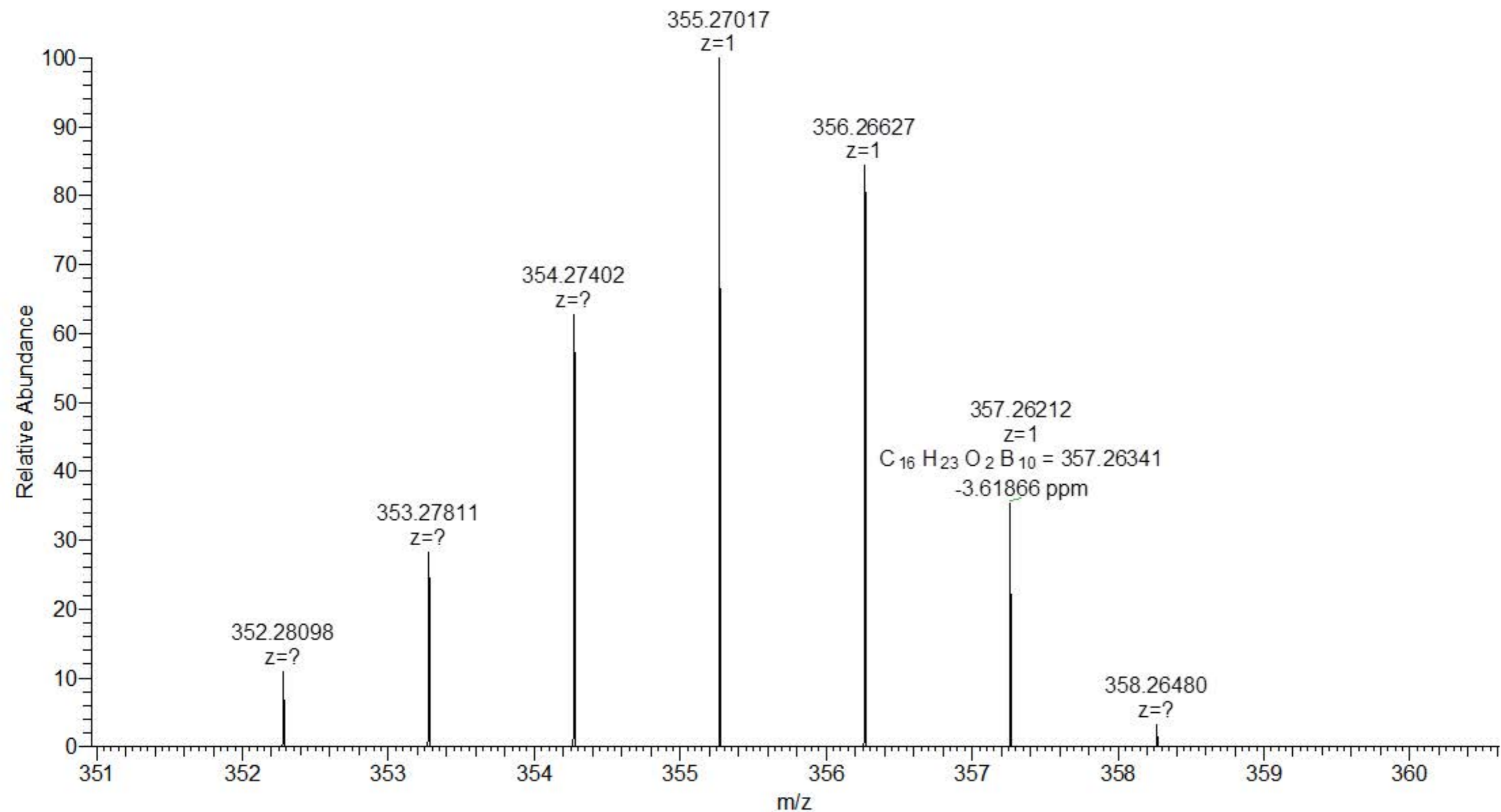
--2.3  
--4.0  
--11.4  
--12.9



Y-60

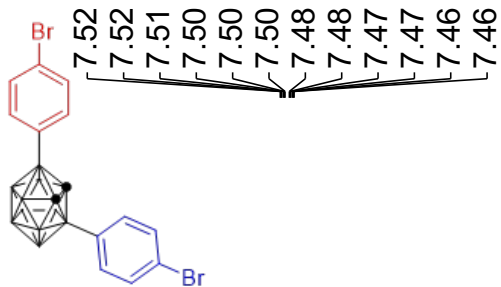
HRMS (ESI)  $m/z$  calcd for  $C_{16}H_{24}B_{10}O_2 \cdot (M-H)^-$  357.2634, found 357.2621

Y60 #12 RT: 0.11 AV: 1 NL: 1.60E7  
T: FTMS - p ESI Full ms [100.0000-600.0000]



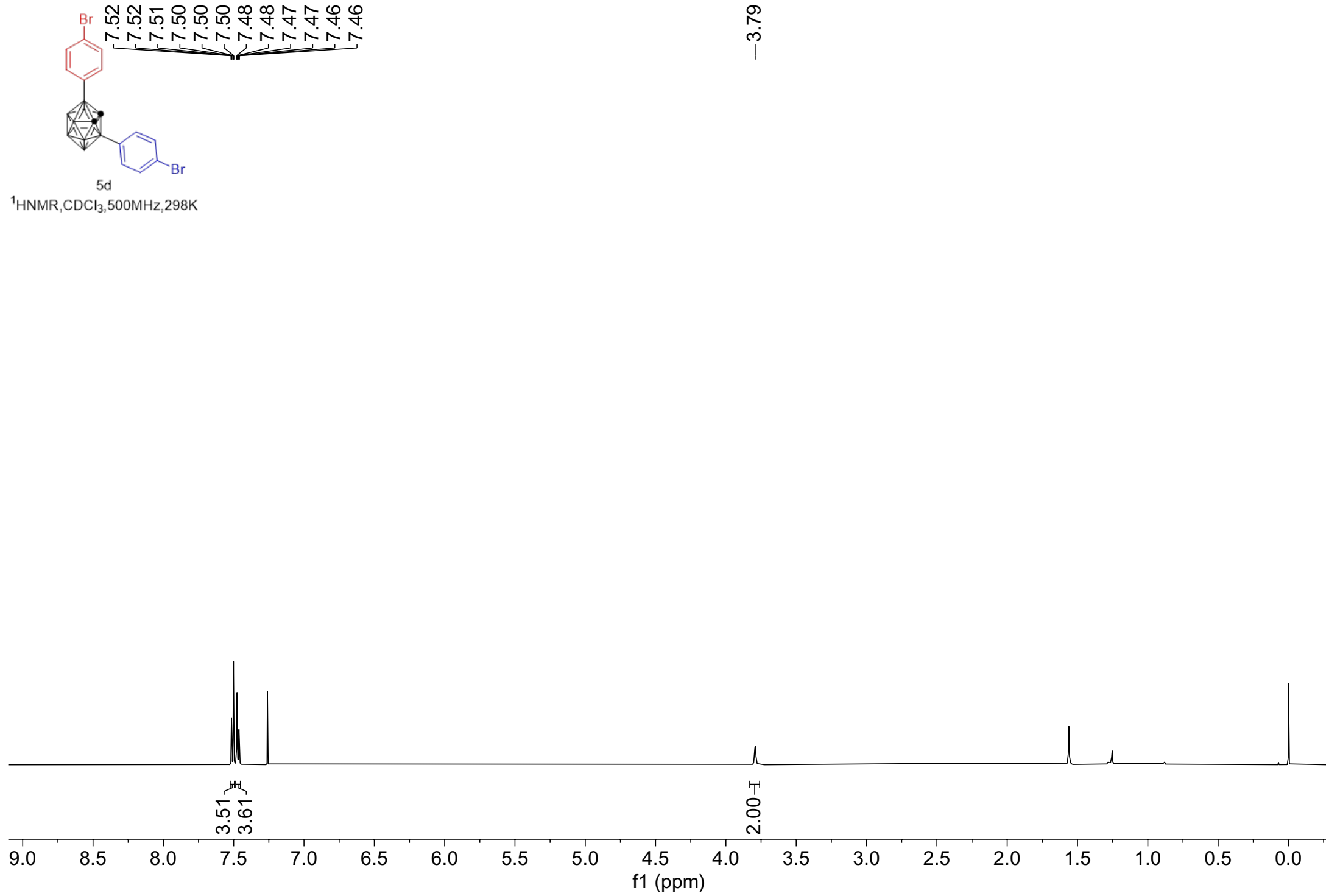


YHB-89-H

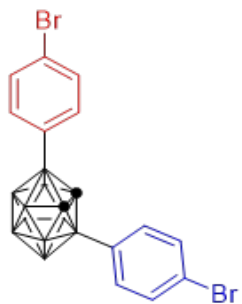


5d

$^1\text{H NMR}$ ,  $\text{CDCl}_3$ , 500 MHz, 298 K



YHB-89-C



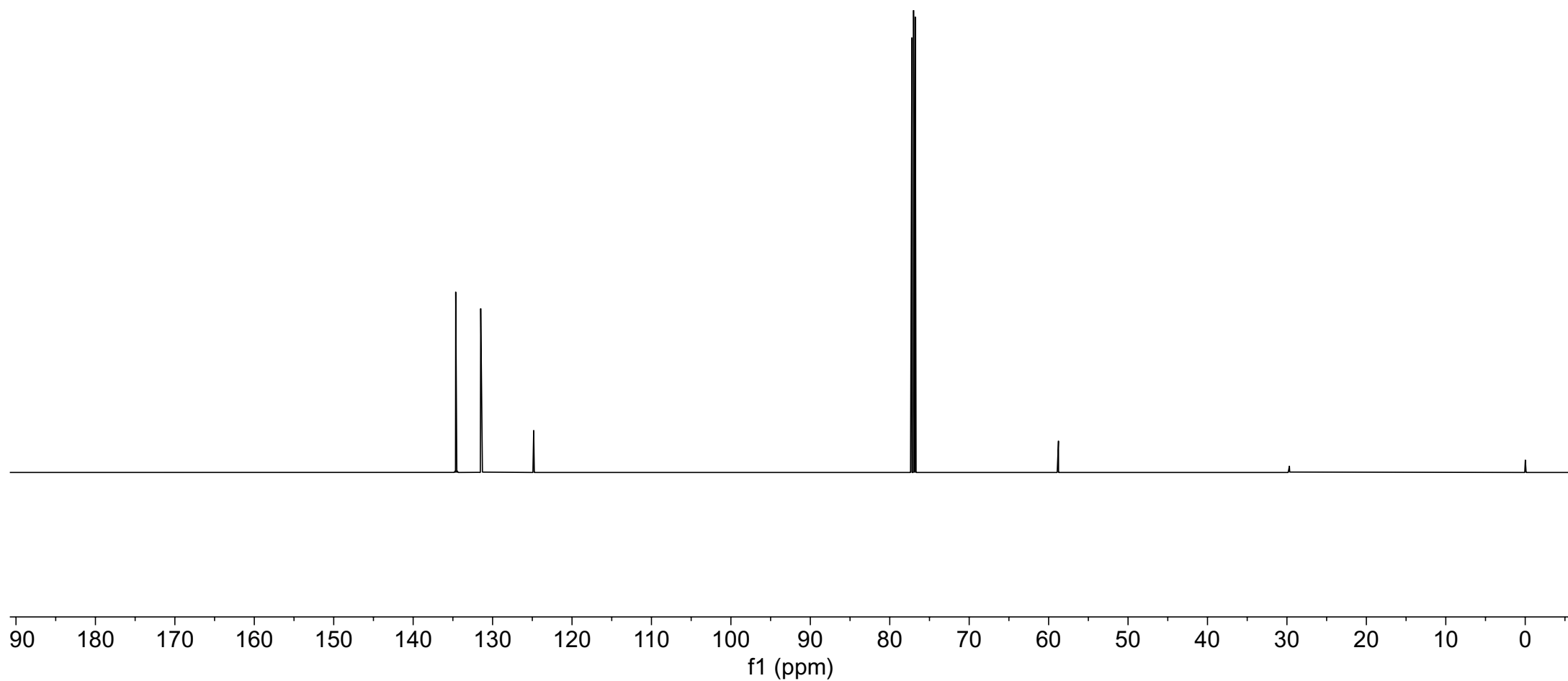
5d

$^{13}\text{C}$ NMR,  $\text{CDCl}_3$ , 125MHz, 298K

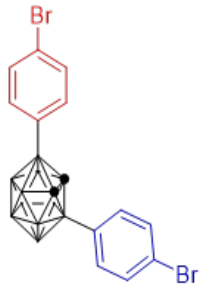
—134.6  
—131.5  
—124.8

{77.2  
77.0  
76.8

—58.8



YHB-89-B

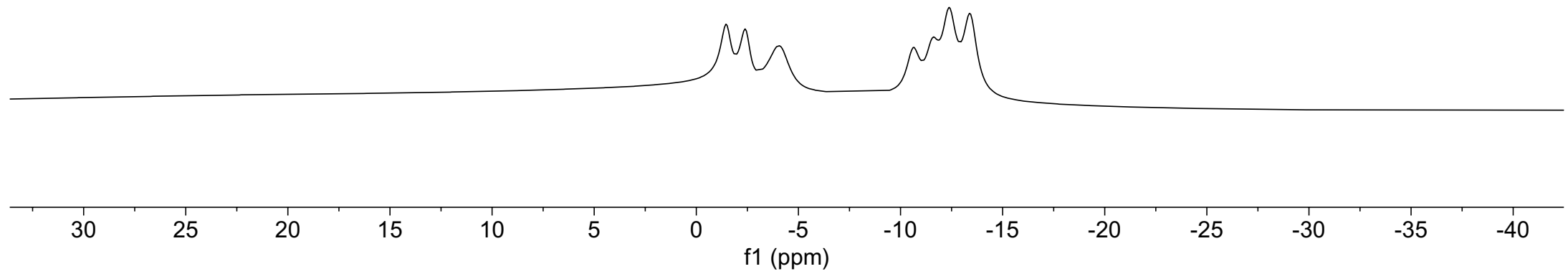


5d

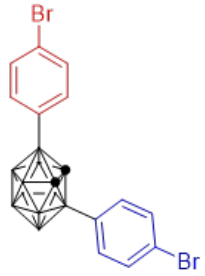
$^{11}\text{B}$ NMR,  $\text{CDCl}_3$ , 160MHz, 298K

1.5  
2.4  
4.0

10.6  
11.6  
12.4  
13.4



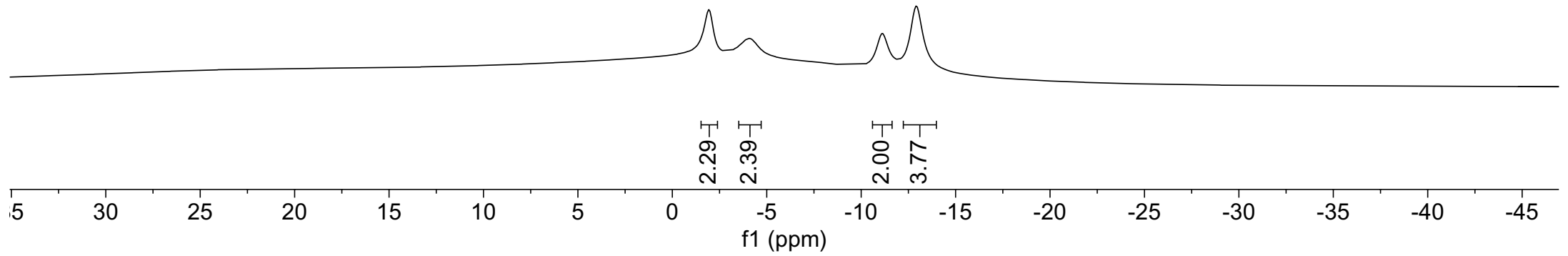
YHB-89-B{H}



5d

$^{11}\text{B}\{^1\text{H}\}$ NMR,  $\text{CDCl}_3$ , 160MHz, 298K

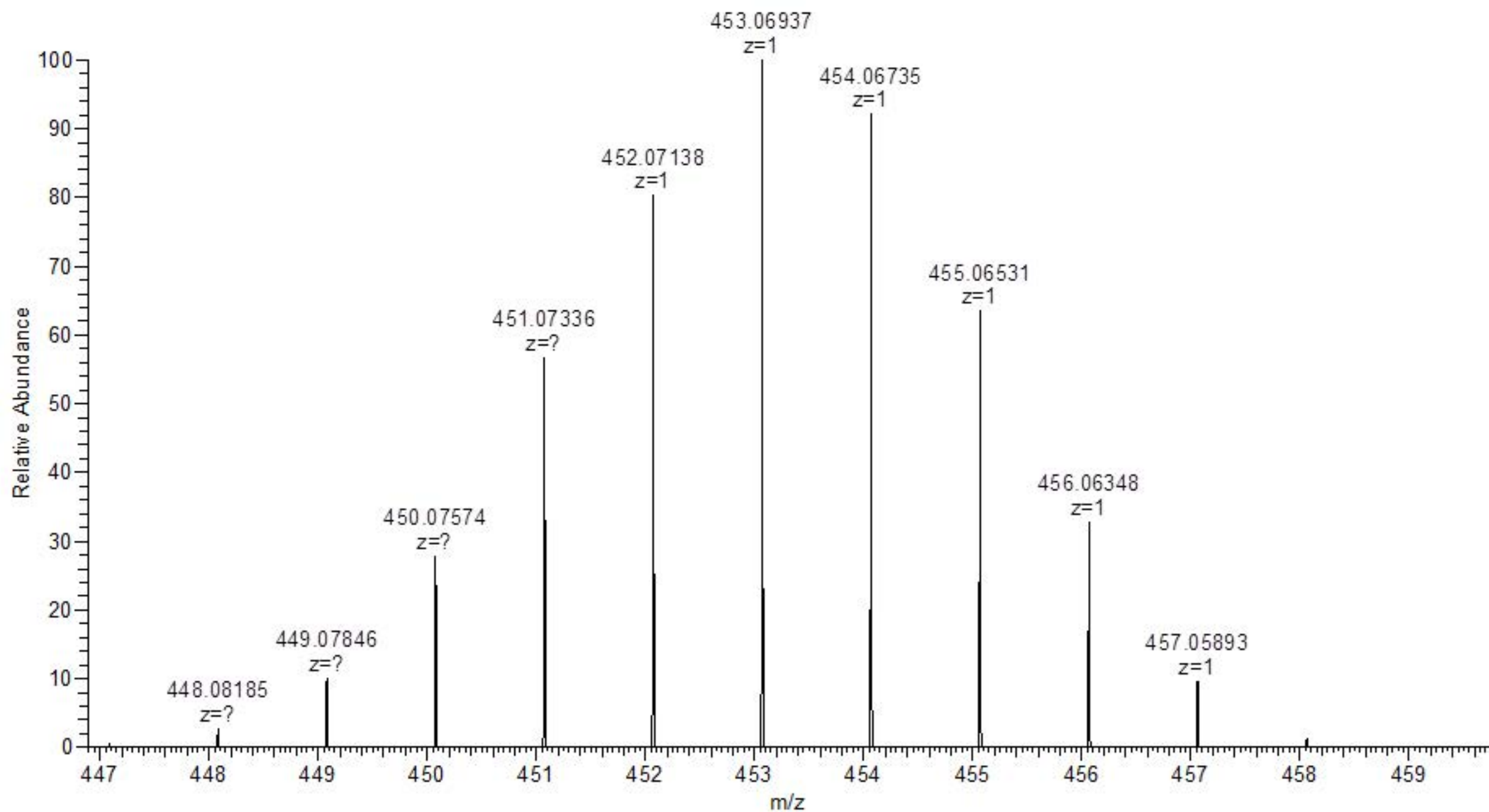
--1.9  
--4.1  
--11.1  
--12.9



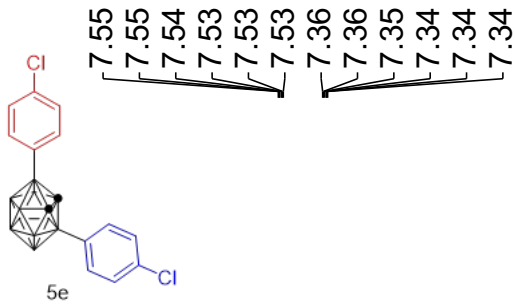
Y-89

HRMS (ESI)  $m/z$  calcd for  $C_{14}H_{18}B_{10}Br_2 \cdot (M-H)^-$  453.0685, found 453.0693

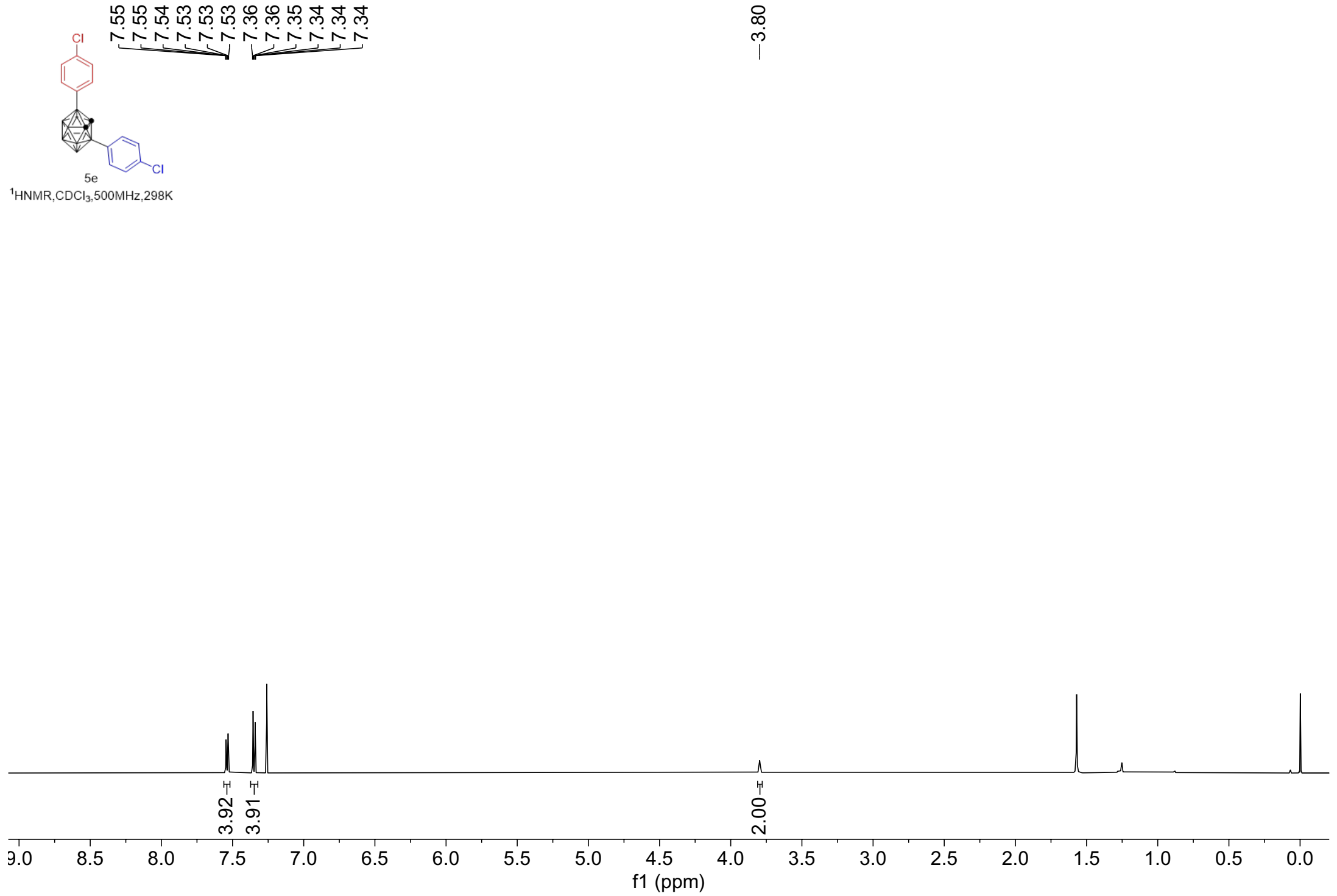
Y89 #16 RT: 0.15 AV: 1 NL: 9.09E8  
T: FTMS - p ESI Full ms [100.0000-600.0000]



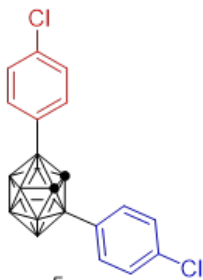
YHB-88-H



$^1\text{H NMR, CDCl}_3, 500\text{MHz, 298K}$



YHB-88-C

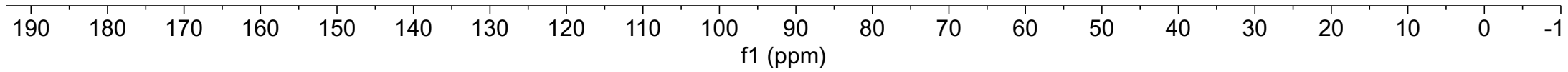


$^{13}\text{C}$ NMR,  $\text{CDCl}_3$ , 125MHz, 298K

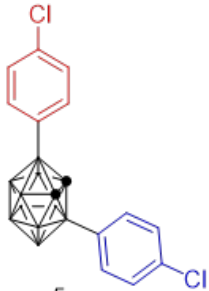
~136.4  
~134.4  
~128.6

77.2  
77.0  
76.8

—58.9

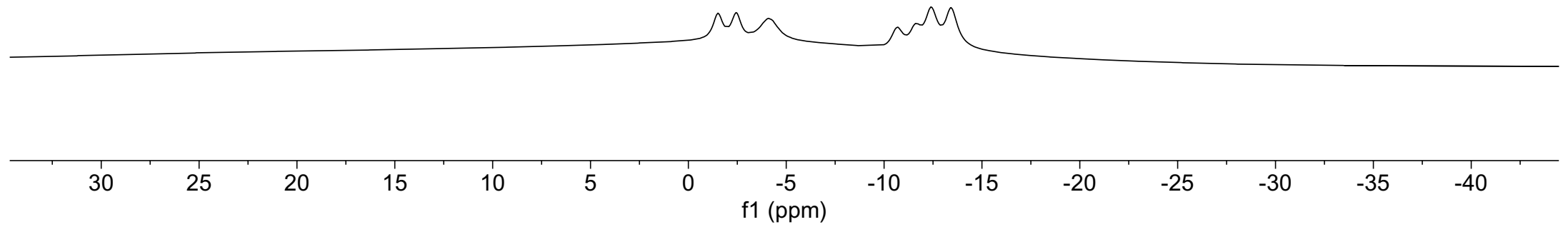


YHB-88-B



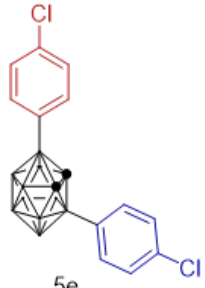
$^{11}\text{B}$ NMR,  $\text{CDCl}_3$ , 160MHz, 298K

--1.5  
~2.5  
--4.1  
  
~-10.7  
~-11.6  
~-12.4  
~-13.4



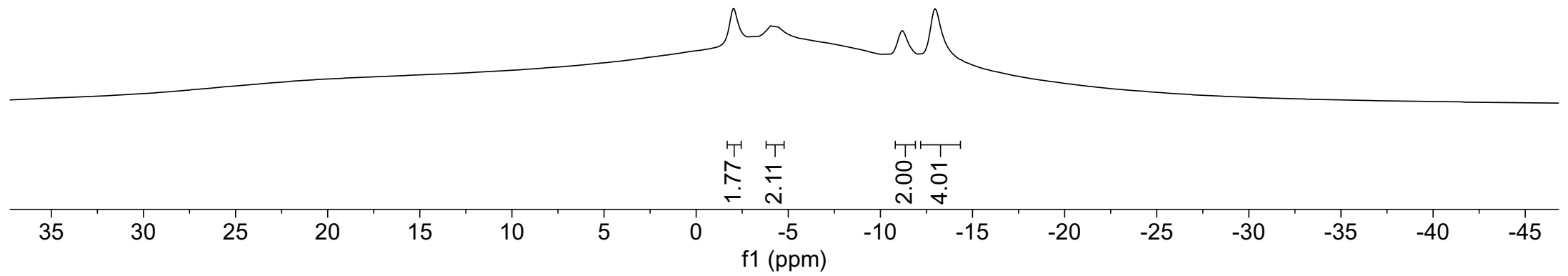


YHB-88-B{H}



$^{11}\text{B}\{^1\text{H}\}$ NMR,  $\text{CDCl}_3$ , 160MHz, 298K

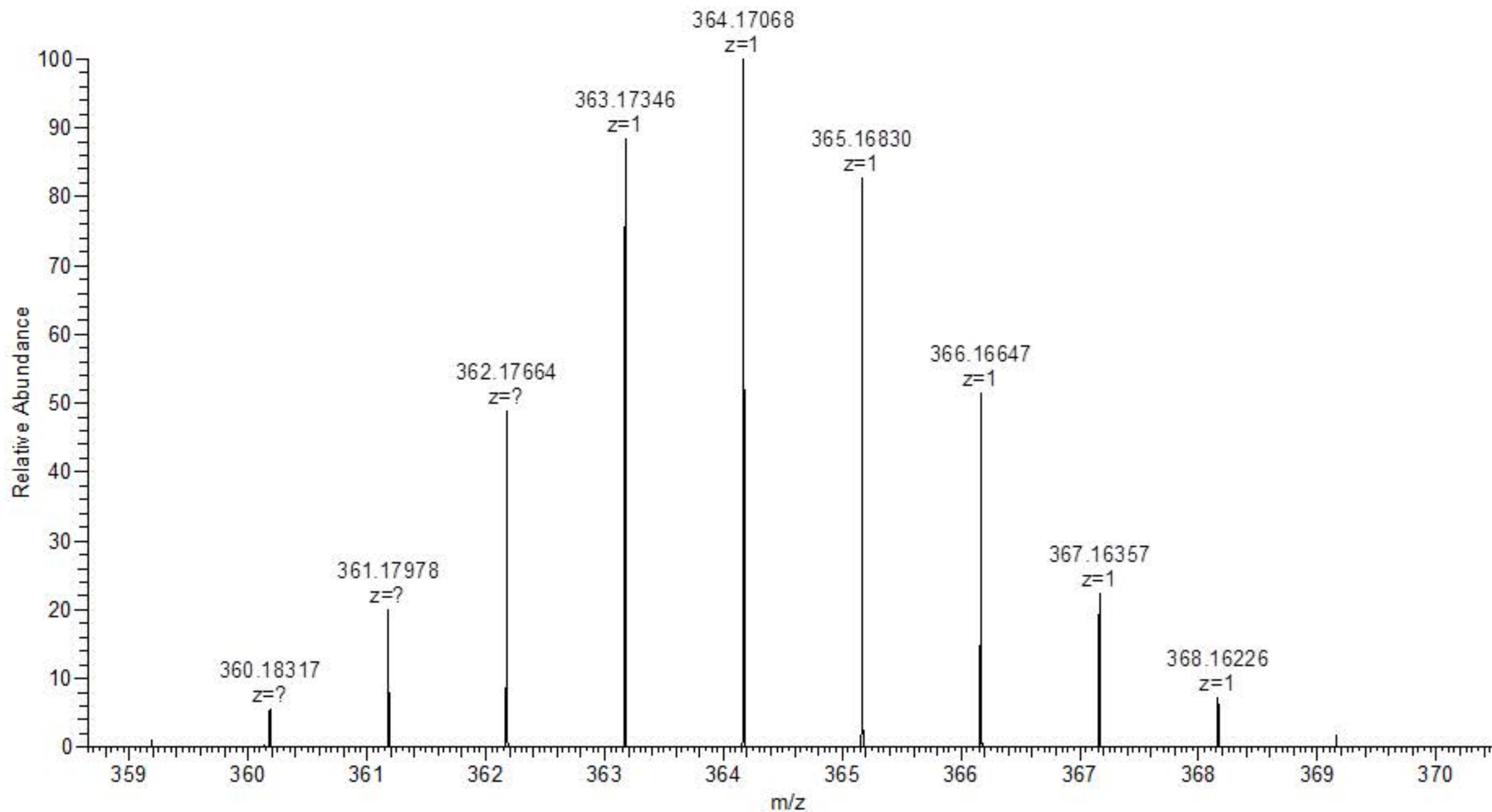
--2.0  
--4.2  
--11.2  
--13.0



HRMS (ESI)  $m/z$  calcd for  $C_{14}H_{18}B_{10}Cl_2 \cdot (M-H)$  365.1686, found 365.1683.

Y88 #18 RT: 0.17 AV: 1 NL: 4.14E9

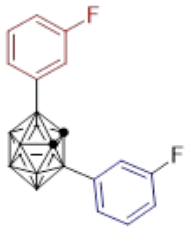
T: FTMS - p ESI Full ms [100.0000-600.0000]



YHB-58-H

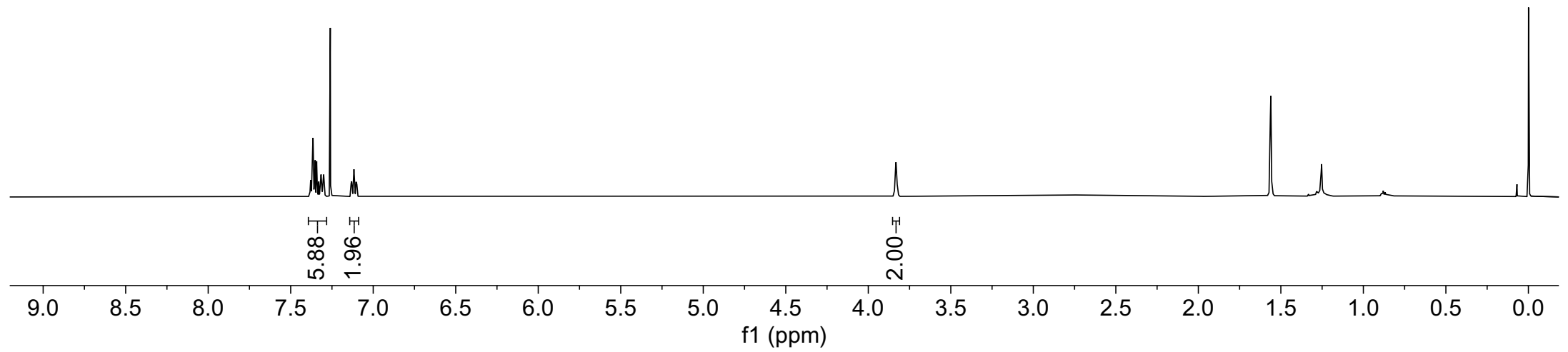
7.38  
7.36  
7.36  
7.35  
7.34  
7.34  
7.33  
7.32  
7.32  
7.30  
7.30  
7.13  
7.13  
7.13  
7.12  
7.12  
7.12  
7.12  
7.11  
7.11  
7.11  
7.11  
7.10  
7.10  
7.10

3.83

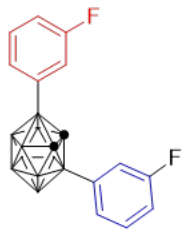


5f

<sup>1</sup>HNMR, CDCl<sub>3</sub>, 500MHz, 298K



YHB-58-C



5f

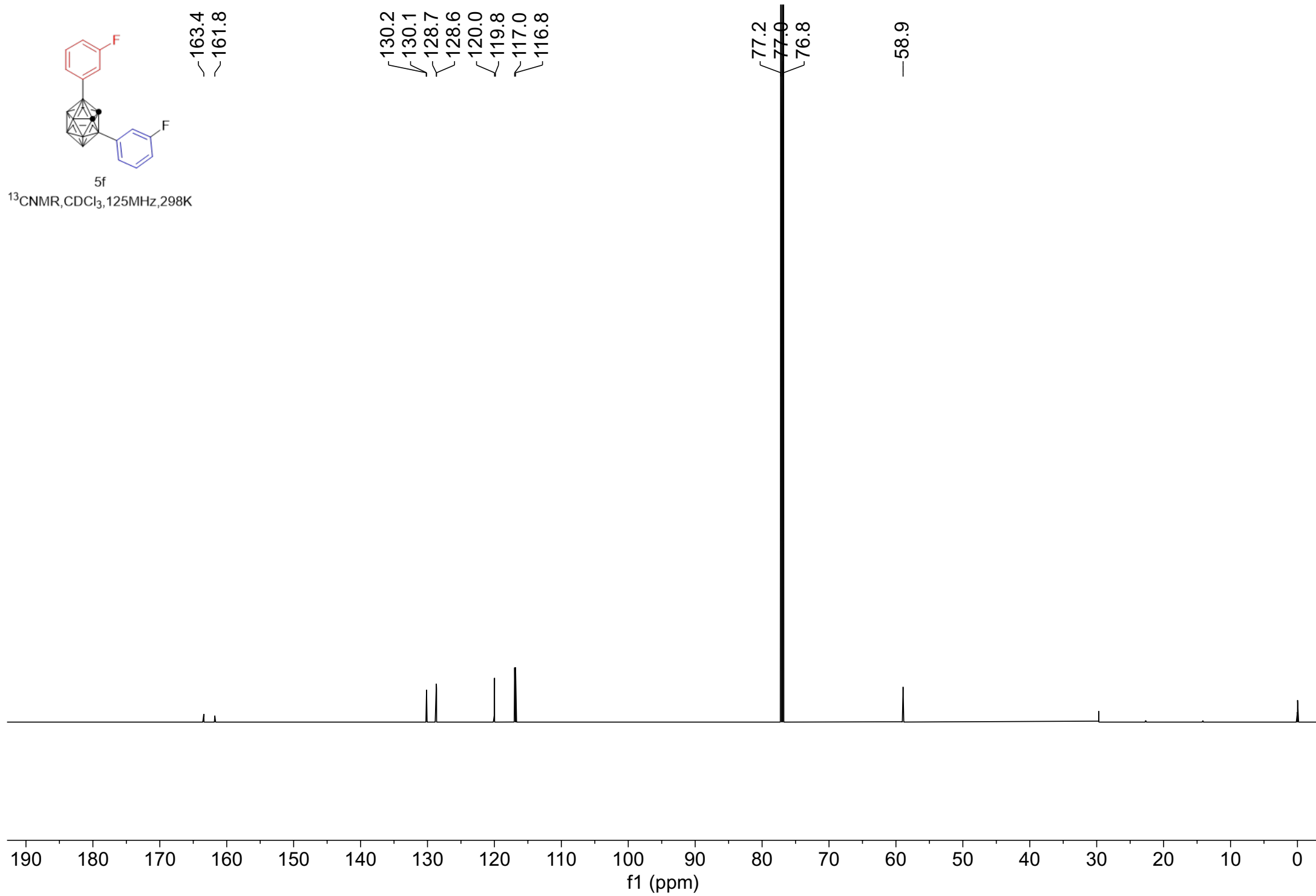
$^{13}\text{C}$ NMR,  $\text{CDCl}_3$ , 125MHz, 298K

~163.4  
~161.8

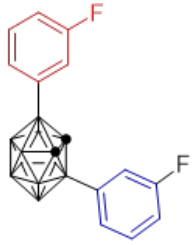
130.2  
130.1  
128.7  
128.6  
120.0  
119.8  
117.0  
116.8

77.2  
77.0  
76.8

—58.9



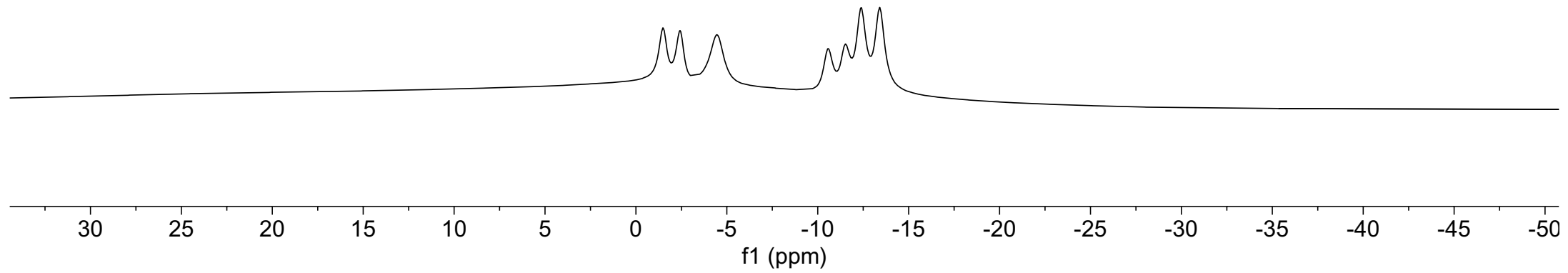
YHB-58-B



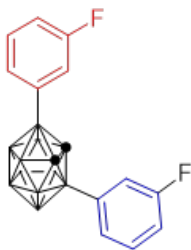
5f

$^{11}\text{B}$ NMR,  $\text{CDCl}_3$ , 160MHz, 298K

--1.5  
~2.4  
--4.5  
  
~10.6  
~11.5  
~12.4  
~13.4



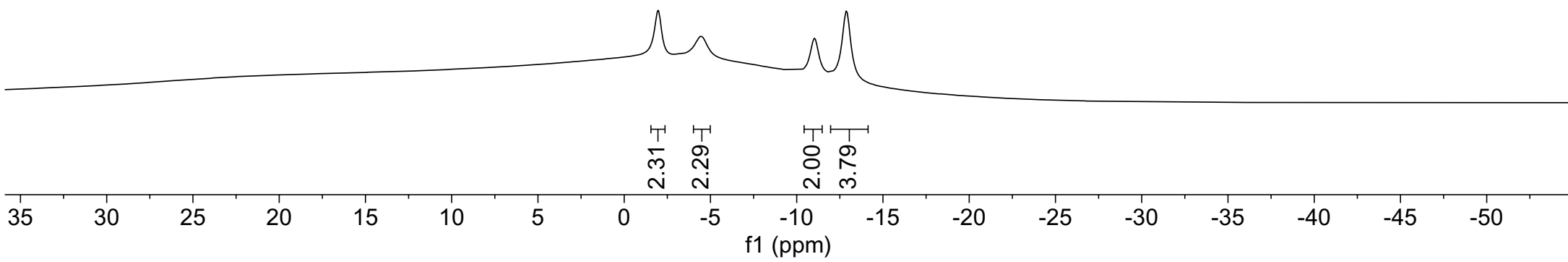
YHB-58-B{H}



5f

$^{11}\text{B}\{^1\text{H}\}$ NMR,  $\text{CDCl}_3$ , 160MHz, 298K

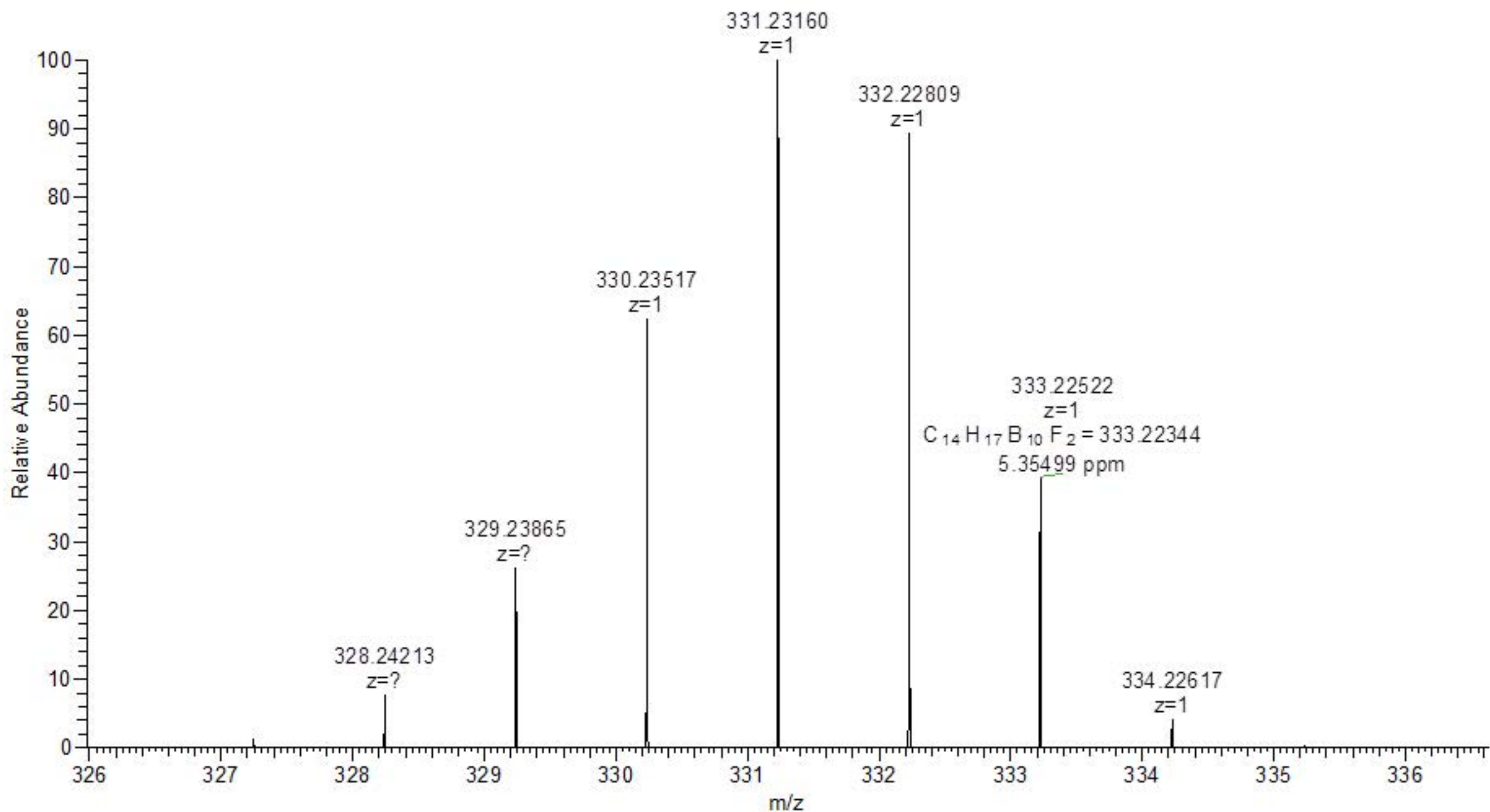
--2.0  
--4.5  
--11.0  
--12.9



Y-58

HRMS (ESI)  $m/z$  calcd for  $C_{14}H_{18}B_{10}F_2$  (M-H)<sup>-</sup> 333.2234, found 333.2252

Y58 #44 RT: 0.42 AV: 1 NL: 4.20E9  
T: FTMS - p ESI Full ms [100.0000-600.0000]

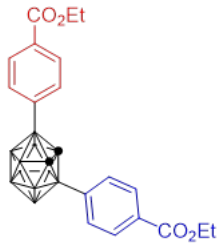


YHB-68-H

8.02  
8.02  
8.02  
8.01  
8.01  
8.01  
7.70  
7.70  
7.69  
7.69

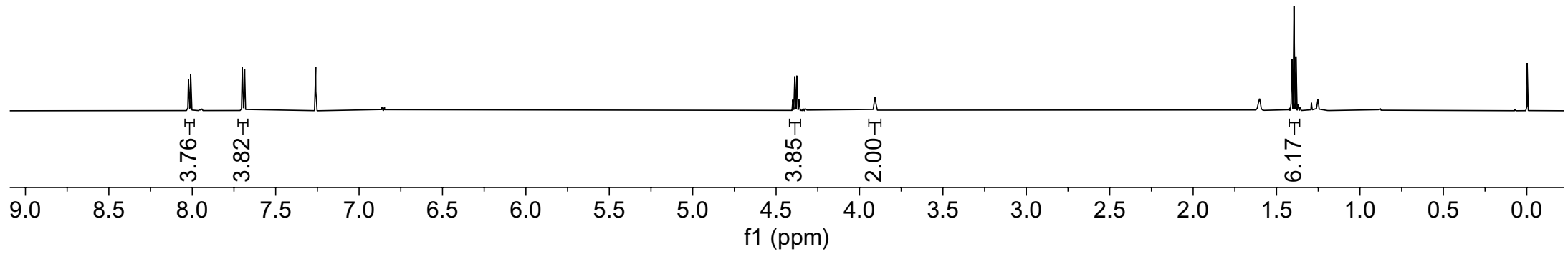
4.40  
4.40  
4.39  
4.39  
4.38  
4.37  
4.36  
—3.91

1.41  
1.41  
1.40  
1.38  
1.37



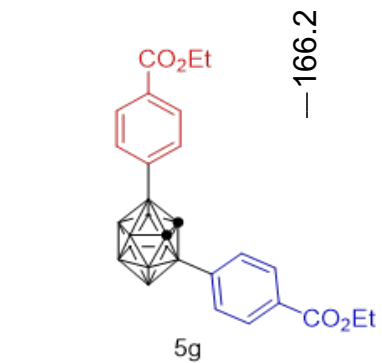
5g

<sup>1</sup>HNMR, CDCl<sub>3</sub>, 500MHz, 298K

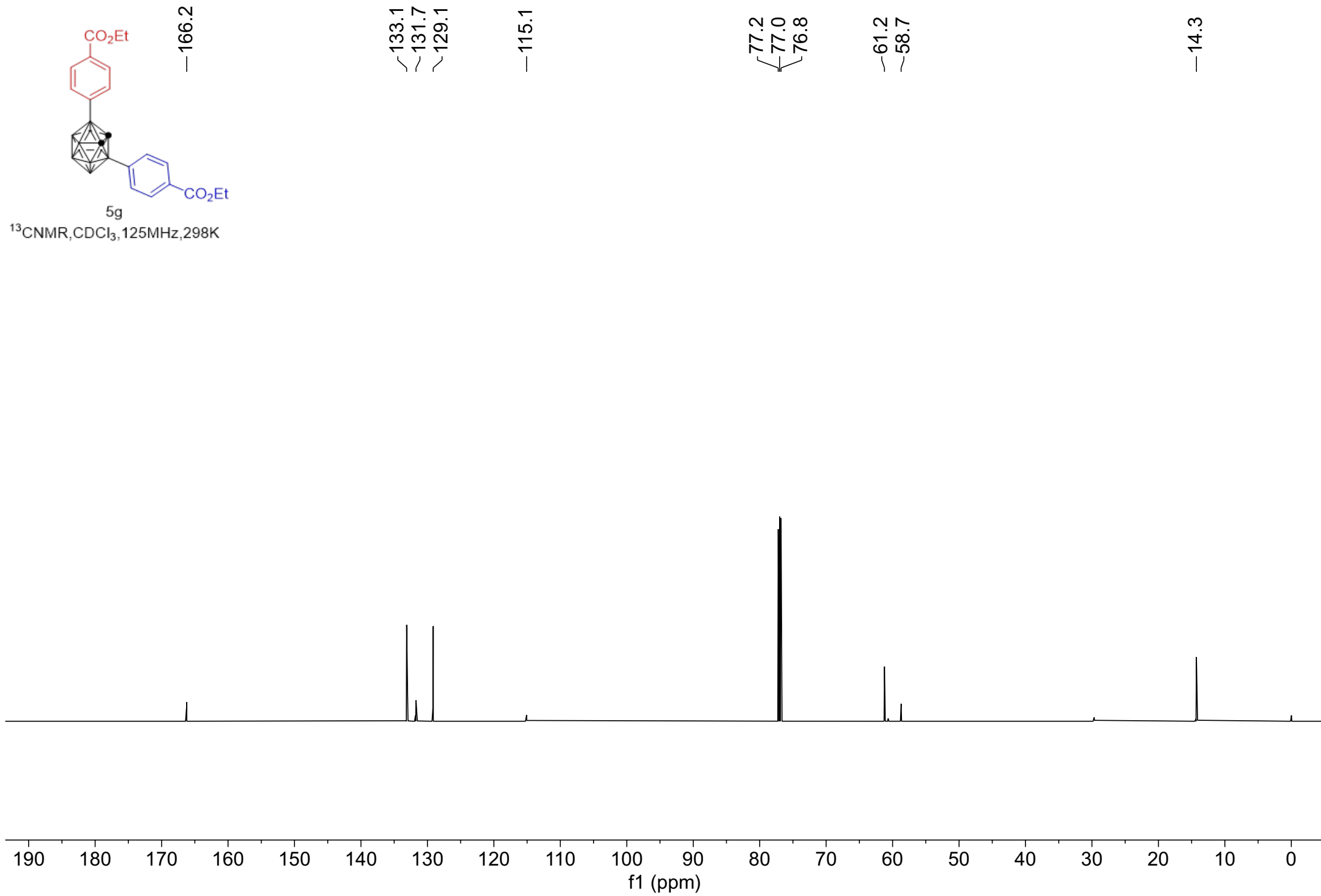




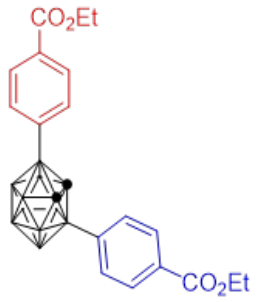
YHB-68-C



$^{13}\text{C}$ NMR,  $\text{CDCl}_3$ , 125MHz, 298K



YHB-68-B

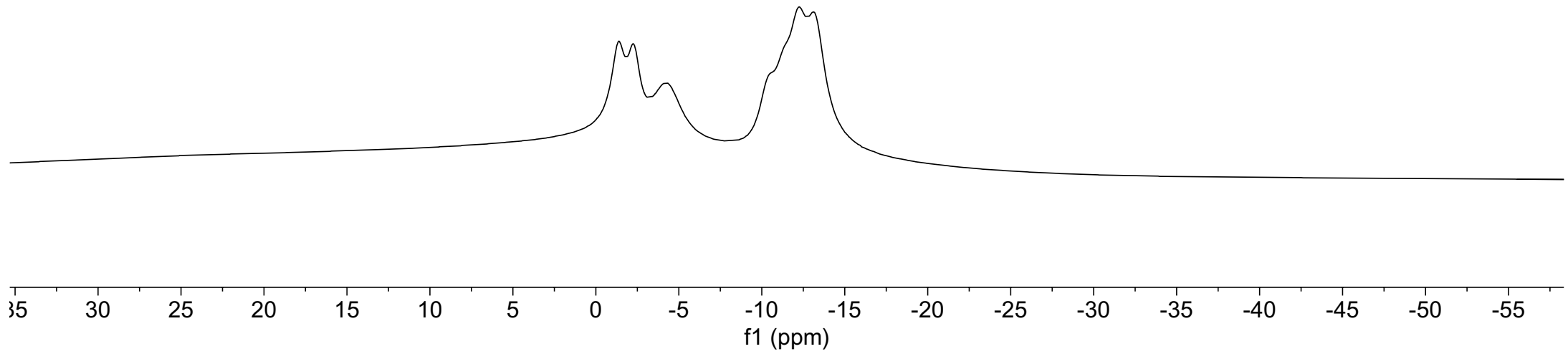


5g

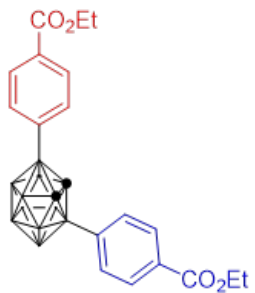
<sup>11</sup>B NMR, CDCl<sub>3</sub>, 160 MHz, 298 K

~1.4  
~2.3  
~4.3

~12.2  
~13.2



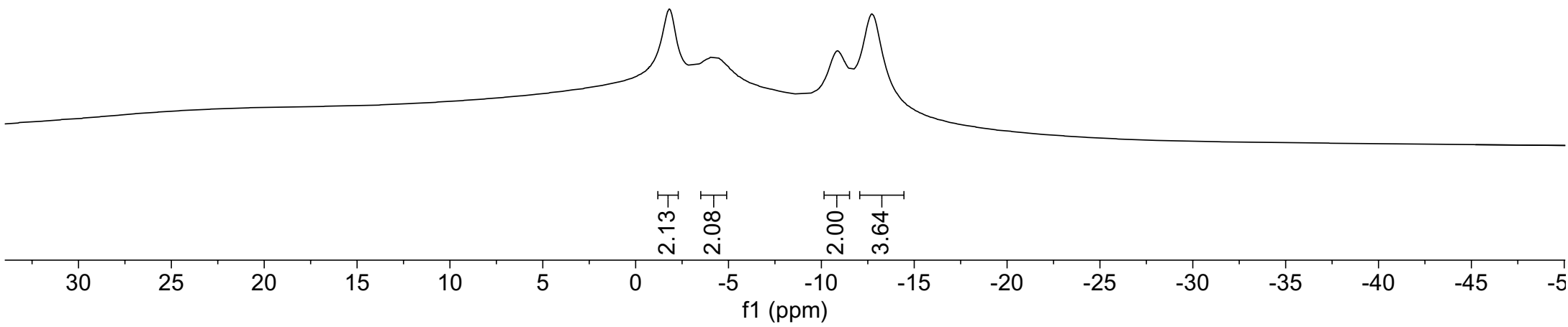
YHB-68-B{H}



5g

$^{11}\text{B}\{^1\text{H}\}$ NMR,  $\text{CDCl}_3$ , 160MHz, 298K

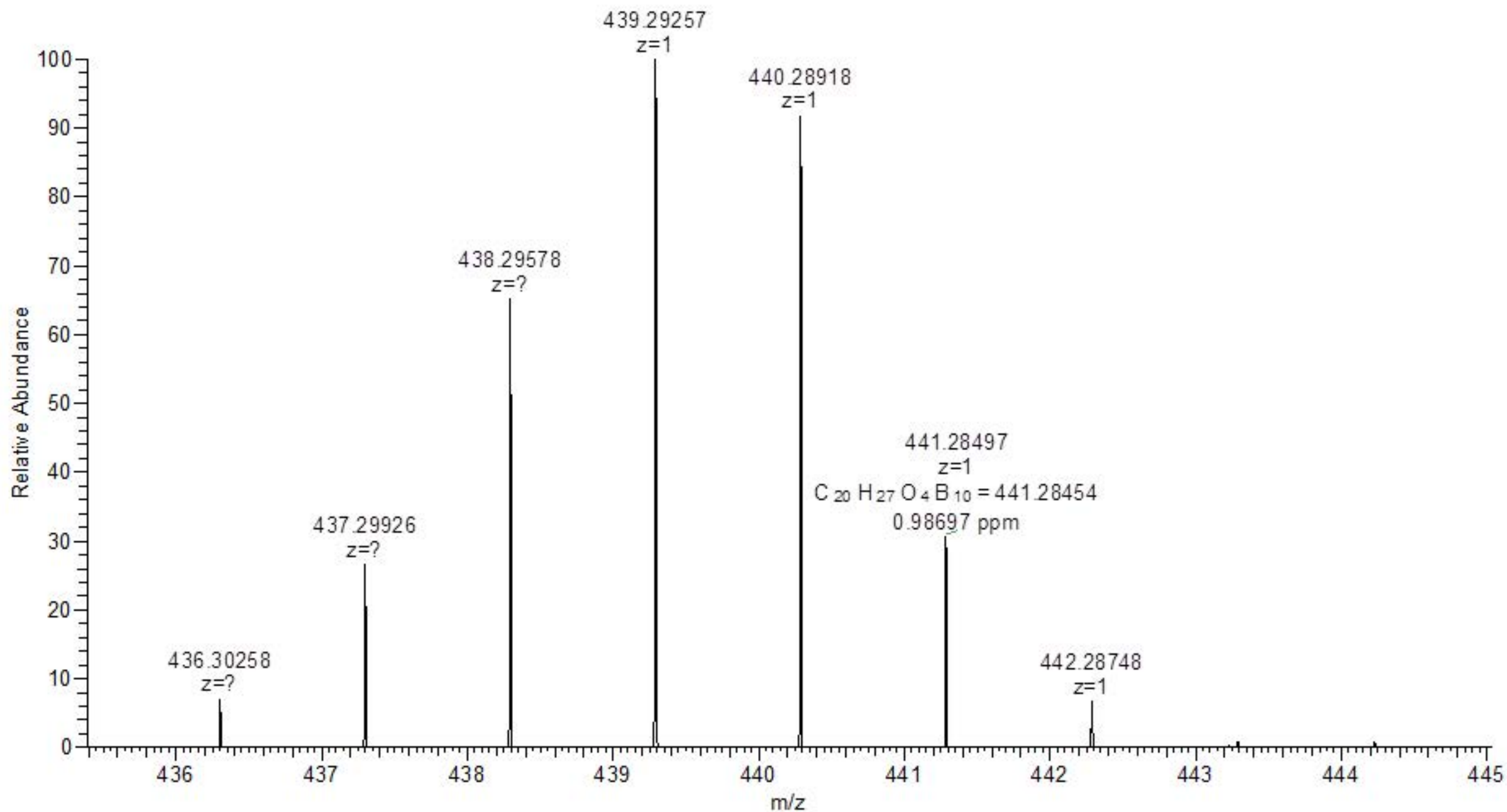
--1.8  
--4.2  
--10.9  
--12.7



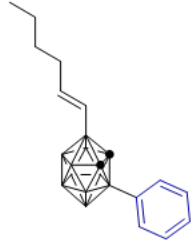
Y-68

HRMS (ESI)  $m/z$  calcd for  $C_{20}H_{28}B_{10}O_4$  (M-H) 441.2845, found 441.2849

Y68 #12 RT: 0.11 AV: 1 NL: 3.93E8  
T: FTMS - p ESI Full ms [100.0000-600.0000]



YHB-33-H



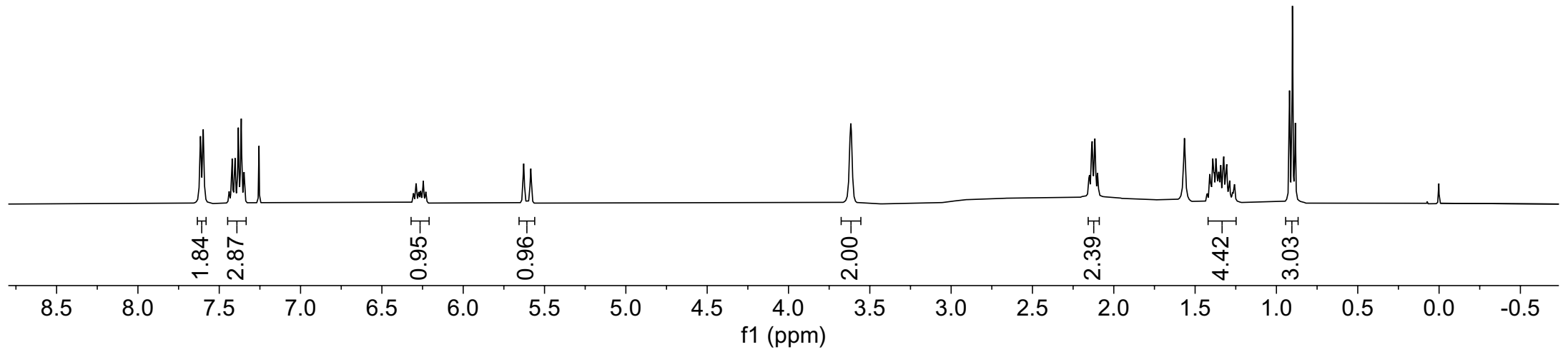
7

$^1\text{H NMR}$ ,  $\text{CDCl}_3$ , 500MHz, 298K

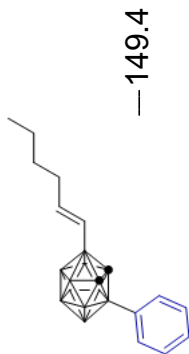
7.62  
7.60  
7.42  
7.40  
7.38  
7.36  
7.35  
7.26  
6.31  
6.29  
6.27  
6.26  
6.25  
6.23  
5.63  
5.58

3.62

2.15  
2.13  
2.12  
2.10  
1.57  
1.42  
1.41  
1.40  
1.39  
1.37  
1.35  
1.34  
1.32  
1.31  
1.29  
1.27  
1.26  
0.92  
0.90  
0.88

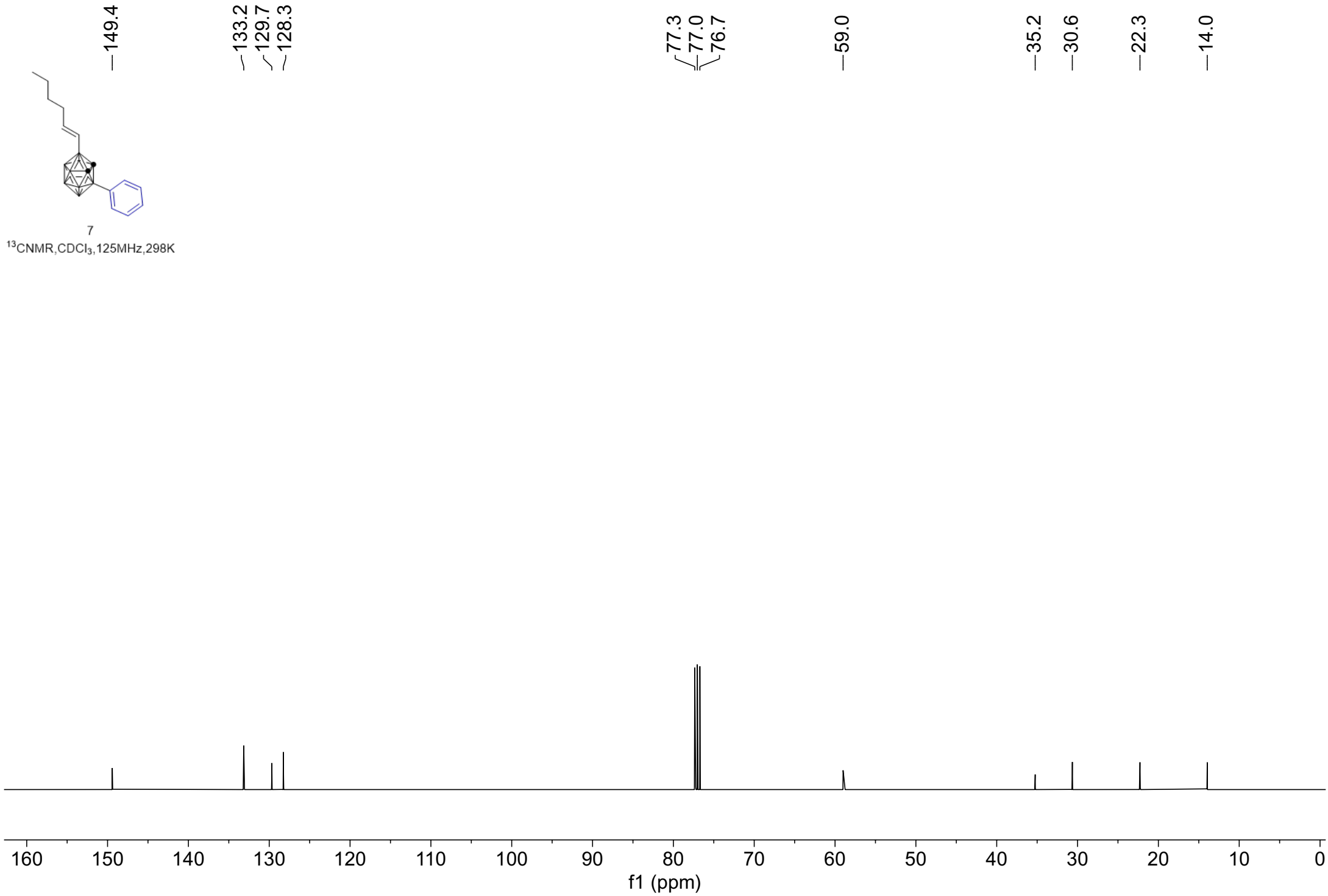


YHB-33-C

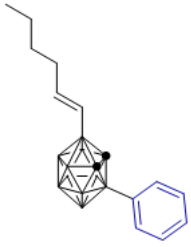


7

<sup>13</sup>CNMR, CDCl<sub>3</sub>, 125MHz, 298K



YHB-33-B

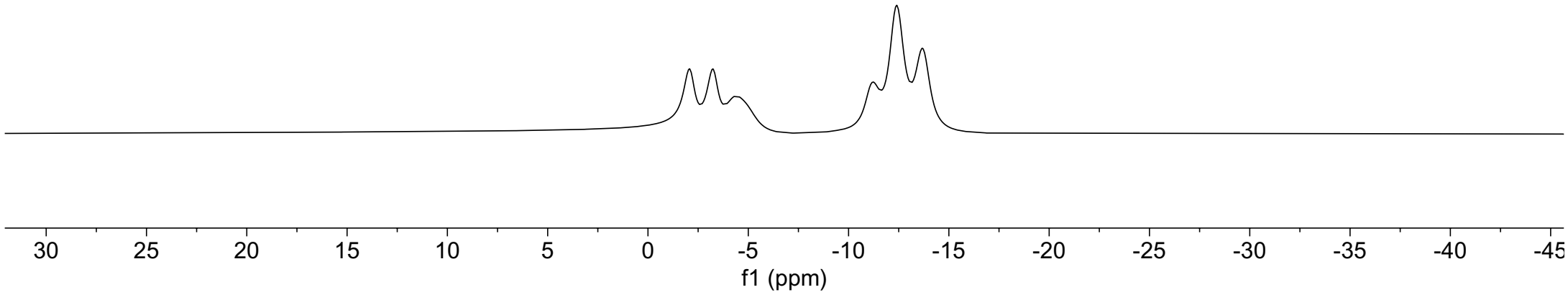


7

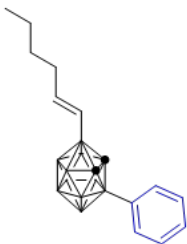
$^{11}\text{B}$ NMR,  $\text{CDCl}_3$ , 160MHz, 298K

-2.1  
-3.2  
-4.4

-11.2  
-12.4  
-13.7



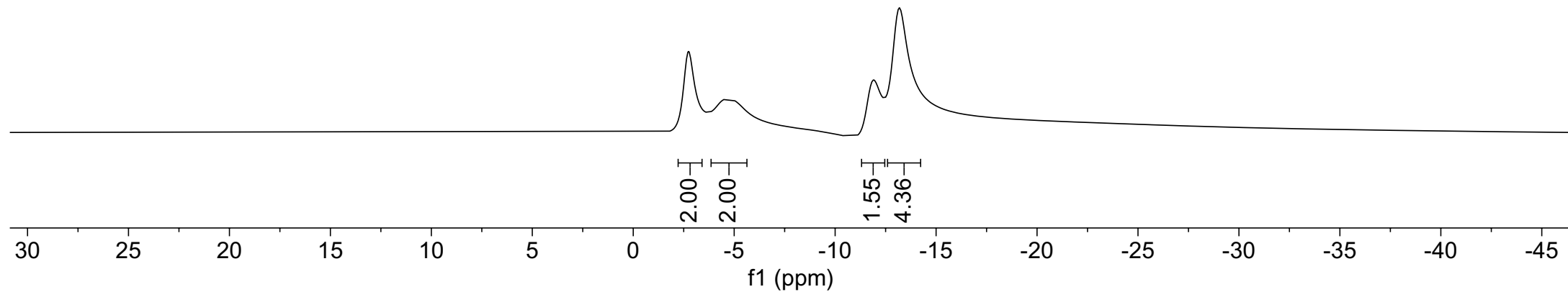
YHB-33-B{H}



7

$^{11}\text{B}\{^1\text{H}\}$ NMR,  $\text{CDCl}_3$ , 160MHz, 298K

--2.7  
--4.7  
--11.9  
--13.2





Y-33

HRMS m/z calcd for C<sub>14</sub>H<sub>26</sub>B<sub>10</sub> ([M-H]<sup>-</sup>) 303.2892, found 303.2891

y33 #11 RT: 0.11 AV: 1 NL: 1.78E8

T: FTMS - p ESI Full ms [100.0000-1500.0000]

