

Supporting Information for  
**Site- and Stereo-selective *trans*-Hydroboration of 1,3-Enynes Catalyzed by 1,4-Azaborine-Based Phosphine-Pd Complex**

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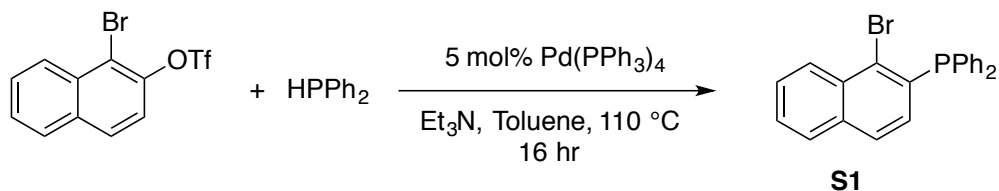
## **General**

All oxygen- and moisture-sensitive manipulations were carried out under an inert atmosphere using either standard Schlenk techniques or a glove box.

THF, Et<sub>2</sub>O, CH<sub>2</sub>Cl<sub>2</sub>, toluene, benzene, and pentane were purified by passing through a neutral alumina column under argon. All other chemicals and solvents were purchased and used as received. Enynes **4a**<sup>1</sup> [CAS: 935-01-3], **4e**<sup>2</sup> [CAS: 16124-56-4], **4g**<sup>2</sup> [CAS: 1089304-22-2], **4l**<sup>3</sup> [CAS: 3752-22-5], **4m**<sup>4</sup> [CAS: 2807-10-5], **4q**<sup>5</sup> [CAS: 73395-75-2], **6d**<sup>6</sup> [CAS: 56392-49-5], **6g**<sup>7</sup> [CAS: 1655-05-6], **6l**<sup>8</sup> [CAS: 54147-31-2], and carbamate **10**<sup>9</sup> [CAS: 145167-88-0] were synthesized according to the literature procedures and the characterization data are consistent with those reported in the literature.

<sup>11</sup>B NMR spectra were recorded on a Varian Unity/Inova 500 spectrometer at ambient temperature. <sup>11</sup>B NMR chemical shifts are externally referenced to BF<sub>3</sub>•Et<sub>2</sub>O (δ 0). <sup>1</sup>H NMR spectra were recorded on a Varian Unity/Inova 500 spectrometer. <sup>13</sup>C NMR spectra were recorded on a Varian Unity/Inova 500 or Unity/Inova 600 spectrometer. <sup>19</sup>F NMR spectra were recorded on a Varian Unity/Inova 500 spectrometer. <sup>31</sup>P NMR spectra were recorded on a Varian Unity/Inova 500 spectrometer. IR spectra were recorded on a Bruker FTIP Alpha (ATR mode) spectrometer. High-resolution mass spectroscopy data were obtained at the Mass Spectroscopy Facilities at Chemistry Department of Boston College.

### Synthesis of **S1**



The preparation of **S1** was adapted from literature procedures.<sup>10</sup> A 50-mL flask was charged with the aryl triflate (1.775 g, 5.000 mmol), which was prepared according to literature procedures.<sup>11</sup> Diphenylphosphine (931 mg, 5.00 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (251 mg, 0.220 mmol), toluene (13.0 mL), and  $\text{Et}_3\text{N}$  (0.77 mL, 5.5 mmol) were added to the reaction flask. The resulting mixture was then allowed to stir at  $110\text{ }^\circ\text{C}$  for 16 hr. At the conclusion of the reaction, the mixture was allowed to cool to the room temperature.  $\text{H}_2\text{O}$  (50 mL) was added, and the mixture was extracted with  $\text{CH}_2\text{Cl}_2$  (3 x 30 mL). The combined organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After removal of the solvent, the crude residue was purified by column chromatography on silica gel with hexanes/ $\text{EtOAc}$  (20: 1) as the eluent to afford **S1** as white solid (1.37 g, 70% yield)

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.36 (d,  $J = 8.5$  Hz, 1H), 7.79 (d,  $J = 7.5$  Hz, 1H), 7.67 (d,  $J = 8.0$  Hz, 1H), 7.60 (t,  $J = 8.0$  Hz, 1H), 7.54 (t,  $J = 8.0$  Hz, 1H), 7.30-7.37 (m, 10H), 6.86 (dd,  $J = 8.0, 2.0$  Hz, 1H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  136.9, 136.8, 136.3, 136.2, 134.4, 134.0, 133.9, 132.5, 131.3, 131.1, 129.9, 128.9, 128.7, 128.6, 128.1, 127.7, 127.6, 127.3, 127.2 (complexity due to the P-C coupling);  $^{31}\text{P}$  NMR (202 MHz,  $\text{CDCl}_3$ )  $\delta$  -3.2; IR (ATR) 3051, 1583, 1543, 1478, 1433, 1214, 1180, 1154, 998, 848, 769  $\text{cm}^{-1}$ ; HRMS (DART) calcd for  $\text{C}_{22}\text{H}_{17}^{79}\text{BrP}$  ( $[\text{M}+\text{H}]^+$ ) 391.02512, found 391.02594.

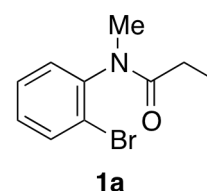
### General procedure A for the synthesis of amides

To a 500-mL flask charged with 2-bromoaniline (17.2 g, 100 mmol), pyridine (7.9 mL, 100 mmol), and  $\text{CH}_2\text{Cl}_2$  (250 mL) was added acyl chloride (100 mmol) in dropwise fashion at  $0\text{ }^\circ\text{C}$ . The resulting mixture was then allowed to stir at the same temperature for 0.5 h. Water (100 mL) was then added to quench the reaction. The biphasic mixture was then extracted with  $\text{CH}_2\text{Cl}_2$  (100 mL x 3). The combined organic phase was dried over  $\text{Na}_2\text{SO}_4$ , and volatiles were removed under reduced pressure. The residue was then dissolved in THF (250 mL), and the mixture was cooled to  $0\text{ }^\circ\text{C}$ . NaH (6.0 g, 60% in

mineral oil, 150 mmol) was then added at 0 °C in 3 portions. The resulting mixture was then allowed to stir at 0 °C for 0.5 h. Methyl iodide (9.30 mL, 150 mmol) was then added in dropwise fashion at 0 °C. The reaction mixture was then allowed to stir at room temperature for 2 h. At the conclusion of the reaction, water (100 mL) was added in a dropwise fashion to quench the reaction at 0 °C. Then the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (100 mL x 3), and the combined organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>. The resulting crude residue was purified by distillation under attenuated pressure to afford amide **1** as a yellow oil.

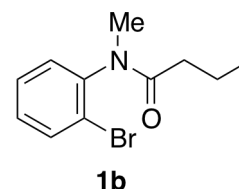
**1a** [168335-51-1]: 19.8 g, 82% yield.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.68 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.38 (td, *J* = 8.0, 1.5 Hz, 1H), 7.22-7.28 (m, 2H), 3.19 (s, 3H), 1.97 (q, *J* = 7.5 Hz, 2H), 1.06 (t, *J* = 7.5 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 173.6, 142.8, 133.8, 129.8, 129.6, 128.9, 123.5, 35.7, 27.3, 9.3; IR (ATR) 3058, 2978, 2937, 1665, 1584, 1476, 1420, 1378, 1321, 1283, 1250, 1132, 1046, 1028, 807, 766 cm<sup>-1</sup>; HRMS (DART) calcd for C<sub>10</sub>H<sub>13</sub><sup>79</sup>BrNO ([M+H]<sup>+</sup>) 242.01805, found 242.01860.



**1b**: 23.7 g, 93% yield.

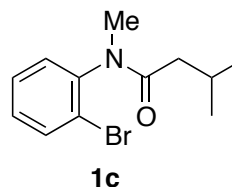
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.69 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.38 (td, *J* = 8.0, 1.0 Hz, 1H), 7.22-7.27 (m, 2H), 3.19 (s, 3H), 1.93 (t, *J* = 7.0 Hz, 2H), 1.57-1.64 (m, 2H), 0.83 (t, *J* = 7.5 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 172.8, 142.9, 133.8, 129.9, 129.6, 128.9, 123.5, 35.8, 35.6, 18.5, 13.8; IR (ATR) 2961, 2929, 2873, 1659, 1584, 1476, 1436, 1417, 1382, 1340, 1309, 1290, 1250, 1223, 1131, 1109, 1049, 894, 764 cm<sup>-1</sup>; HRMS (DART) calcd for C<sub>11</sub>H<sub>15</sub><sup>79</sup>BrNO ([M+H]<sup>+</sup>) 256.03370, found 242.03468.





**1c**: 25.3 g, 94% yield.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.69 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.38 (td, *J* = 8.0, 1.0 Hz, 1H), 7.22-7.26 (m, 2H), 3.19 (s, 3H), 2.13-2.18 (m, 1H), 1.84 (d, *J* = 7.0 Hz, 2H), 0.86 (d, *J* = 6.5 Hz, 3H), 0.83 (d, *J* = 6.5 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 172.3, 142.9,



133.8, 130.0, 129.6, 128.9, 123.5, 42.8, 35.7, 25.4, 22.6, 22.5; IR (ATR) 2956, 2929, 2870, 1662, 1584, 1476, 1419, 1376, 1337, 1305, 1262, 1140, 1116, 1053, 1031, 765 cm<sup>-1</sup>; HRMS (DART) calcd for C<sub>12</sub>H<sub>17</sub><sup>79</sup>BrNO ([M+H]<sup>+</sup>) 270.04935, found 242.05054.

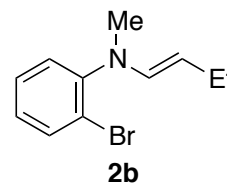
### **General procedures B for the synthesis of enamines**

To a 250-mL flask charged with **1** (20.0 mmol), PMHS (5.2 g, *M<sub>w</sub>* 1700-3200, ~80.0 mmol hydride), and toluene (30 mL) was added a toluene (2.0 mL) solution of (PPh<sub>3</sub>)<sub>2</sub>(CO)IrCl (7.8 mg, 0.01 mmol). Gelation was observed immediately and the reaction mixture was allowed to sit at room temperature for 0.5 h. Diethyl ether (100 mL) was then added, and the mixture was passed through a pad of celite. The filter cake was then washed with ether 3 times (100 mL each time). The combined organic phase was then concentrated. The residue was then purified by distillation under attenuated pressure to afford **2** as light yellow oil.

**2a** [1527467-69-1]: 2.85 g, 63% yield. The characterization data are consistent with those reported in the literature.<sup>12</sup>

**2b**: 3.41 g, 71% yield.

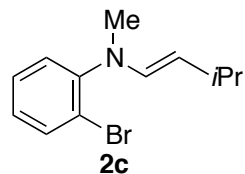
<sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 7.69 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.27 (td, *J* = 7.5, 1.5 Hz, 1H), 7.11 (d, *J* = 7.5 Hz, 1H), 6.98 (td, *J* = 8.0, 1.5 Hz, 1H), 6.18 (d, *J* = 14.0 Hz, 1H), 4.56-4.62 (m, 1H), 2.96 (s, 3H), 2.04-2.10 (m, 2H), 1.02 (t, *J* = 7.5 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ



149.0, 136.1, 134.3, 128.8, 126.9, 126.2, 120.4, 105.2, 38.8, 24.1, 16.2; IR (ATR) 3055, 2956, 2927, 2847, 2805, 1653, 1584, 1512, 1480, 1464, 1439, 1420, 1309, 1109, 969, 786 cm<sup>-1</sup>; HRMS (DART) calcd for C<sub>11</sub>H<sub>15</sub><sup>79</sup>BrN ([M+H]<sup>+</sup>) 240.03879, found 240.03281.

**2c**: 4.38 g, 86% yield.

$^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  7.58 (dd,  $J = 8.0, 1.0$  Hz, 1H), 7.29 (td,  $J = 8.0, 1.5$  Hz, 1H), 7.11 (dd,  $J = 7.5$  Hz, 1.5 Hz, 1H), 6.99 (td,  $J = 7.0, 1.5$  Hz, 1H), 6.18 (dd,  $J = 13.0$  Hz, 1.0 Hz, 1H), 4.56 (dd,  $J = 13.0, 7.0$  Hz, 1H), 2.96 (s, 3H), 2.34-2.36 (m, 1H), 1.05



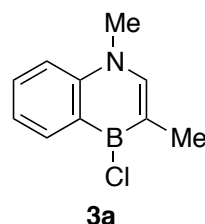
(dd,  $J = 6.0, 1.0$  Hz, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  149.1, 134.7, 134.4, 128.8, 126.9, 126.1, 120.3, 111.4, 38.8, 29.9, 24.5; IR (ATR) 2953, 2866, 2806, 1651, 1584, 1513, 1482, 1464, 1420, 1397, 1357, 1111, 986, 765  $\text{cm}^{-1}$ ; HRMS (DART) calcd for  $\text{C}_{12}\text{H}_{17}^{79}\text{BrN}$  ( $[\text{M}+\text{H}]^+$ ) 254.05444, found 254.05436.

### **General procedure C for the synthesis of C3-Substituted 1,4-azaborines**

To a 100-mL flask charged with **2** (15.0 or 20.0 mmol) was added  $n\text{BuLi}$  (6 or 8 mL, 15 or 20 mmol) at  $-78$   $^\circ\text{C}$ . The resulting mixture was allowed to stir at  $-78$   $^\circ\text{C}$  for 15 min. Diisopropylaminoboron dichloride (2.73 or 3.64 g, 15.0 or 20.0 mmol) was then added at  $-78$   $^\circ\text{C}$ . The reaction mixture was allowed to stir at  $-78$   $^\circ\text{C}$  for 1 h and then room temperature for another 1 h. At the conclusion of the reaction, solvents were removed under reduced pressure, and the resulting crude residue was purified by vacuum distillation under attenuated pressure to afford **3** as light yellow oil which slowly solidified. We were not able to obtain their HRMS data due to their extremely air and moisture sensitivity.

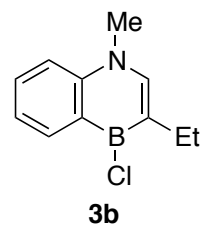
**3a**: 20.0 mmol scale, 3.0 g, 79% yield.

$^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  8.34 (d,  $J = 7.5$  Hz, 1H), 7.75 (s, 1H), 7.69 (td,  $J = 9.0, 1.5$  Hz, 1H), 7.53 (d,  $J = 9.0$  Hz, 1H), 7.34 (t,  $J = 7.5$  Hz, 1H), 3.88 (s, 3H), 2.21 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  148.6, 144.2, 133.7, 131.9, 127.6 (br), 121.9, 121.1 (br), 115.6, 42.5, 17.6;  $^{11}\text{B}$  NMR (160 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  44.6.



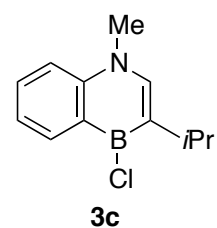
**3b**: 15.0 mmol scale, 2.14 g, 69% yield.

$^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  8.36 (dd,  $J = 8.0, 1.5$  Hz, 1H), 7.68-7.73 (m, 2H), 7.55 (d,  $J = 8.0$  Hz, 1H), 7.34 (t,  $J = 8.0$  Hz, 1H), 3.89 (s, 3H), 2.62 (q,  $J = 7.5$  Hz, 2H), 1.20 (t,  $J = 7.5$  Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  148.2, 144.2, 133.8, 131.9, 128.2 (br), 121.9, 115.6, 42.5, 25.8, 16.8 (a B-aryl carbon signal not observed);  $^{11}\text{B}$  NMR (160 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  44.2.



**3c**: 15.0 mmol scale, 3.09 g, 94% yield.

$^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  8.37 (dd,  $J = 7.5, 1.5$  Hz, 1H), 7.68-7.73 (m, 2H), 7.54 (d,  $J = 8.5$  Hz, 1H), 7.33 (td,  $J = 7.0, 1.0$  Hz, 1H), 3.91 (s, 3H), 3.17-3.21 (m, 1H), 1.26 (d,  $J = 7.5$  Hz, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  146.7, 144.0, 133.9, 132.0, 121.9, 115.6, 42.8, 30.5, 24.2 (two B-aryl carbon signals not observed);  $^{11}\text{B}$  NMR (160 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  44.1.

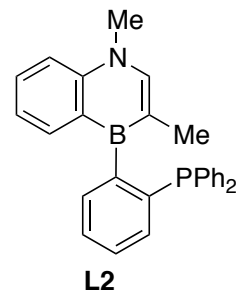


### **General procedure D for the synthesis of Senphos ligands**

To a 20-mL vial charged with *o*-bromoaryldiarylphosphine (1.0 mmol) and THF (5.0 mL) was added *n*BuLi (0.40 mL, 2.5 M in hexanes, 1.0 mmol) at  $-78$  °C. The resulting mixture was allowed to stir at  $-78$  °C for 1-2 h. 1,4-Azaborine **3** (1.0 mmol) in THF (2.0 mL) was then added. The resulting mixture was allowed to stir at  $-78$  °C for 2 h and then at room temperature for 2 h. At the conclusion of the reaction, volatiles were removed under reduced pressure. The resulting crude residue was purified by column chromatography on silica gel using pentane/ $\text{Et}_2\text{O}$  as the eluent to afford ligand **L** as a white powder.

**L2**: 240 mg, 58% yield.

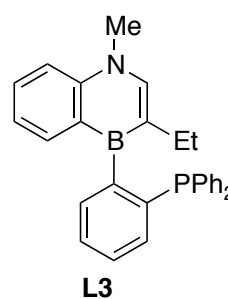
$^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  7.76 (s, 1H), 7.62-7.64 (m, 1H), 7.58-7.60 (m, 2H), 7.43-7.45 (m, 1H), 7.25-7.39 (m, 11H), 7.16-7.20 (m, 2H), 7.08 (td,  $J = 7.5, 1.5$  Hz, 1H), 3.98 (s, 3H), 1.99 (s, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  147.00, 143.48, 139.44, 139.41, 139.38,



139.30, 139.13, 139.05, 137.02, 133.95, 133.92, 133.83, 133.80, 131.89, 131.79, 130.94, 128.79, 128.74, 128.66, 128.62, 128.60, 128.53, 128.49, 127.22, 120.99, 114.98, 42.43, 19.44, 19.42 (complexity due to P-C coupling; B-aryl carbon signal not observed);  $^{11}\text{B}$  NMR (160 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  47.2;  $^{31}\text{P}$  NMR (202 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  -10.3; IR (ATR) 3051, 2923, 1604, 1585, 1540, 1491, 1477, 1454, 1432, 1269, 1171, 1101, 1046, 1026, 943, 892, 763  $\text{cm}^{-1}$ ; HRMS (DART) calcd for  $\text{C}_{28}\text{H}_{26}\text{BNP}$  ( $[\text{M}+\text{H}]^+$ ) 418.13959, found 418.18939.

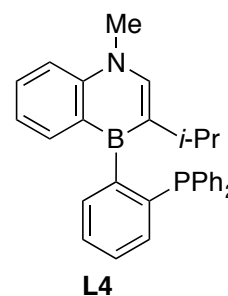
**L3:** 288 mg, 67% yield.

$^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  7.71 (s, 1H), 7.52-7.57 (m, 2H), 7.48 (d,  $J = 7.5$  Hz, 1H), 7.39 (t,  $J = 7.0$  Hz, 1H), 7.19-7.29 (m, 11H), 7.10-7.14 (m, 2H), 6.98 (td,  $J = 7.5, 1.0$  Hz, 1H), 3.94 (s, 3H), 2.38-2.41 (m, 1H), 2.29-2.32 (m, 1H), 0.94 (t,  $J = 8.0$  Hz, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  146.68, 143.36, 139.43, 139.35, 139.32, 139.28, 139.17, 139.09, 137.13, 133.98, 133.96,



133.90, 133.86, 133.78, 132.28, 132.17, 130.95, 128.77, 128.73, 128.64, 128.60, 128.53, 128.33, 127.15, 120.89, 114.94, 42.56, 26.98, 26.97, 17.01 (complexity due to P-C coupling; B-aryl carbon signal not observed);  $^{11}\text{B}$  NMR (160 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  48.5;  $^{31}\text{P}$  NMR (202 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  -10.6; IR (ATR) 3051, 2955, 2924, 2864, 1604, 1584, 1539, 1490, 1432, 1405, 1374, 1172, 1067, 763, 763  $\text{cm}^{-1}$ ; HRMS (DART) calcd for  $\text{C}_{29}\text{H}_{28}\text{BNP}$  ( $[\text{M}+\text{H}]^+$ ) 432.20524, found 432.20696.

**L4:** 360 mg, 81% yield.  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  7.73 (s, 1H), 7.52-7.57 (m, 2H), 7.46 (d,  $J = 7.0$  Hz, 1H), 7.19-7.39 (m, 12H), 7.09-7.12 (m, 2H), 6.97 (t,  $J = 7.0$  Hz, 1H), 3.96 (s, 3H), 2.72-2.77 (m, 1H), 1.03 (d,  $J = 7.0$  Hz, 3H), 0.96 (d,  $J = 6.5$  Hz, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  145.30, 143.22, 139.39, 139.36, 139.31,

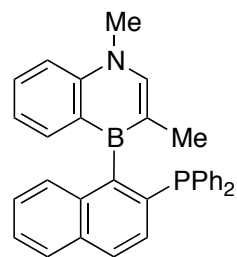


139.28, 139.22, 137.26, 134.18, 134.00, 133.92, 133.87, 133.79, 132.38, 132.28, 130.99, 128.81, 128.77, 128.68, 128.64, 128.54, 128.34, 127.14, 120.95, 114.98, 42.81, 31.02, 26.29, 23.93, (complexity due to P-C coupling; B-aryl carbon signal not observed);  $^{11}\text{B}$  NMR (160 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  46.7;  $^{31}\text{P}$  NMR (202 MHz,  $\text{CD}_2\text{Cl}_2$ )

$\delta$  -11.2; IR (ATR) 3048, 1604, 1578, 1536, 1493, 1478, 1465, 1453, 1370, 1265, 1214, 1191, 1090, 1026, 989, 814, 764  $\text{cm}^{-1}$ ; HRMS (DART) calcd for  $\text{C}_{30}\text{H}_{30}\text{BNP}$  ( $[\text{M}+\text{H}]^+$ ) 446.22292, found 446.22089.

**L5:** 320 mg, 68% yield.

$^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  7.85 (d,  $J = 8.5$  Hz, 1H), 7.78 (d,  $J = 8.0$  Hz, 1H), 7.76 (s, 1H), 7.58-7.60 (m, 2H), 7.36-7.46 (m, 4H), 7.15-7.28 (m, 11H), 6.93-6.97 (m, 1H), 4.00 (s, 3H), 1.84 (s, 3H);  $^{11}\text{B}$  NMR (160 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  47.9;  $^{31}\text{P}$  NMR (202 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  -12.2;  $^{13}\text{C}$  NMR (150 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  146.66, 143.29, 139.50, 139.40, 139.31, 139.21, 136.87, 136.09, 135.96, 133.77,

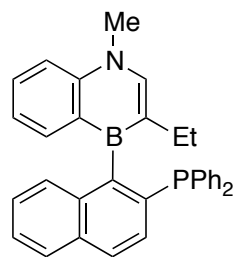


**L5**

133.73, 133.65, 133.61, 131.11, 130.43, 130.35, 128.83, 128.79, 128.70, 128.67, 128.52, 128.50, 127.53, 126.85, 125.70, 121.17, 115.21, 42.49, 19.41 (complexity due to P-C coupling; B-aryl carbon signal not observed); IR (ATR) 3048, 2923, 1604, 1585, 1540, 1490, 1456, 1432, 1401, 1371, 1280, 1212, 1169, 1103, 1047, 1025, 935, 895, 764  $\text{cm}^{-1}$ ; HRMS (DART) calcd for  $\text{C}_{32}\text{H}_{28}\text{BNP}$  ( $[\text{M}+\text{H}]^+$ ) 468.20524, found 468.20468.

**L6:** 360 mg, 75% yield.

$^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  7.85 (d,  $J = 8.5$  Hz, 1H), 7.79 (d,  $J = 6.5$  Hz, 1H), 7.77 (s, 1H), 7.53-7.61 (m, 2H), 7.39-7.45 (m, 3H), 7.33 (d,  $J = 8.0$  Hz, 1H), 7.27-7.30 (m, 6H), 7.17-7.23 (m, 4H), 7.14 (dd,  $J = 7.5, 1.0$  Hz, 1H); 6.90 (td,  $J = 6.0, 1.5$  Hz, 1H), 4.02 (s, 3H), 2.28-2.34 (m, 1H), 2.20-2.24 (m, 1H), 0.85 (t,  $J = 7.5$  Hz, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  146.23, 143.21, 139.53,



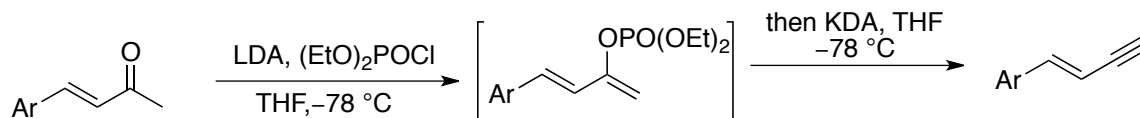
**L6**

139.45, 139.32, 139.24, 137.08, 136.49, 136.36, 135.97, 133.85, 133.75, 133.73, 133.63, 131.12, 130.84, 130.55, 128.81, 128.77, 128.68, 128.64, 128.58, 128.50, 128.48, 127.50, 126.82, 125.50, 121.07, 115.14, 42.65, 27.04, 16.28 (complexity due to P-C coupling; B-aryl carbon signal not observed);  $^{11}\text{B}$  NMR (160 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  48.0;  $^{31}\text{P}$  NMR (202 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  -10.1; IR (ATR) 3048, 2954, 2924, 2865, 1604, 1581, 1539, 1490, 1431, 1406, 1374, 1169, 1064, 864, 763  $\text{cm}^{-1}$ ; HRMS (DART) calcd for  $\text{C}_{33}\text{H}_{30}\text{BNP}$  ( $[\text{M}+\text{H}]^+$ ) 482.22089, found 482.22084.

### Gram-scale synthesis of ligand L3

To a 100-mL flask charged with *o*-bromophenyldiphenylphosphine (1.71 g, 5.00 mmol) and THF (50 mL) was added *n*BuLi (2.0 mL, 2.5 M in hexanes, 5.0 mmol) at  $-78\text{ }^{\circ}\text{C}$ . The resulting mixture was allowed to stir at  $-78\text{ }^{\circ}\text{C}$  for 2 h. 1,4-Azaborine **3b** (1.027 g, 5.000 mmol) in THF (10.0 mL) was then added. The resulting mixture was allowed to stir at  $-78\text{ }^{\circ}\text{C}$  for 2 h and then room temperature for 2 h. After removal of the solvent, the residue was passed through a pad of silica gel using  $\text{CH}_2\text{Cl}_2$  as the eluent. After removal of the solvent, the resulting crude residue was purified by column chromatography on silica gel using pentane/ $\text{Et}_2\text{O}$  (20 : 1) then  $\text{Et}_2\text{O}/\text{DCM}$  (1 : 1) as the eluent to afford ligand **L3** as a white powder (1.502 g, 71%). The characterization data are consistent with the ones obtained from the small-scale synthesis.

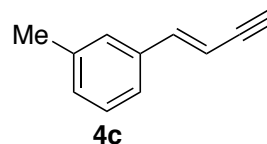
### General procedure E for the synthesis of enynes



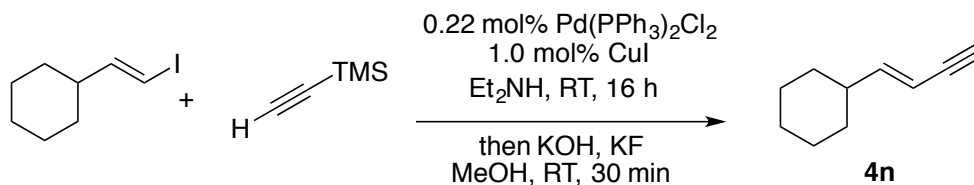
To a 250-mL flask charged with diisopropylamine (1.40 mL, 10.0 mmol) and THF (40 mL) was added *n*BuLi (4.0 mL, 2.5 M in hexanes, 10 mmol) at  $-78\text{ }^{\circ}\text{C}$ . The resulting mixture was allowed to stir at  $-78\text{ }^{\circ}\text{C}$  for 15 min. Enone (10 mmol) was then added at  $-78\text{ }^{\circ}\text{C}$  in one portion. After stirring the mixture at  $-78\text{ }^{\circ}\text{C}$  for 30 min, the diethylchlorophosphate was added, and the mixture was allowed to stir at room temperature for 1 h. Then, the reaction mixture was cooled to  $-78\text{ }^{\circ}\text{C}$ , and freshly prepared KDA (potassium diisopropyl amide)<sup>13</sup> (50 mL, 0.5 M in THF, 25.0 mmol) was added to the mixture. The mixture was allowed to stir at  $-78\text{ }^{\circ}\text{C}$  for 5-30 min. At the conclusion of the reaction, the reaction was then quenched by 1.0 M aq. HCl. The organic phase was separated, and the aqueous layer was extracted with ether ( $3 \times 50\text{ mL}$ ). The combined organic layer was then dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After removal of the solvents, the resulting crude residue was purified by column chromatography on silica gel with hexanes as the eluent to afford desired enyne.

Compounds **4b**<sup>2</sup> [CAS: 23517-04-6], **4d**<sup>2</sup> [CAS: 23517-05-7], **4f**<sup>14</sup> [CAS: 1499245-30-5], **4h**<sup>2</sup> [CAS: 141735-20-8], **4i**<sup>13</sup> [CAS: 61172-01-8], **4j**<sup>13</sup> [CAS: 72450-98-7], and **4k**<sup>13</sup> [CAS: 134987-93-2] were prepared according to this general procedure E, and the characterization data are consistent with those reported in the literature.

**4c** [CAS: 23517-06-8], 56%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.18-7.23 (m, 3H), 7.12 (d, *J* = 7.5 Hz, 1H), 7.02 (d, *J* = 16.0 Hz, 1H), 6.11 (dd, *J* = 16.0, 2.0 Hz, 1H), 3.04 (d, *J* = 2.0 Hz, 1H), 2.35 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 143.3, 138.3, 135.8, 129.7, 128.6, 127.0, 123.5, 106.7, 83.0, 79.0, 21.3; IR (ATR) 3290, 3029, 2920, 2863, 2097, 1614, 1600, 1488, 1454, 1271, 954, 776 cm<sup>-1</sup>; HRMS (DART) calcd for C<sub>11</sub>H<sub>11</sub> ([M+H]<sup>+</sup>) 143.08608, found 143.08589.



#### Synthesis of enyne **4n** [CAS: 2807-14-9]

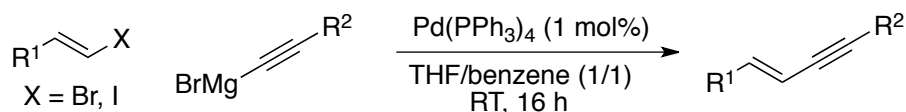


Synthesis of enyne **4n** was adapted from literature procedures<sup>15</sup>. To a 50-mL flask charged with trans-2-cyclohexylvinyl iodide<sup>16</sup> (2.36 g, 10.0 mmol), CuI (20.4 mg, 0.1 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (15.7 mg, 0.022 mmol), and Et<sub>2</sub>NH (20.0 mL) was added trimethylsilylacetylene (1.18 g, 12.0 mmol) slowly at 0 °C. The resulting mixture was allowed to stir at room temperature for 16 h. At the conclusion of the reaction, the reaction was quenched with H<sub>2</sub>O (20 mL) followed by addition of hexanes (30 mL). The organic layer was separated, and the aqueous layer was extracted with hexanes (3 × 20 mL). The combined organic layer was then concentrated and the residue was dissolved in MeOH (30 mL). To the resulting methanolic solution was added KF (4.6 g, 79 mmol) and KOH (200 mg, 3.60 mmol) in one portion. The resulting mixture was allowed to stir at room temperature for 0.5 h. The reaction mixture was then diluted by H<sub>2</sub>O (100 mL) followed by extraction with hexanes (3 × 30 mL). The combined organic layer was then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent, the residue was purified by

column chromatography on silica gel with hexanes as the eluent to afford **4n** as a colorless liquid (2.14 g, 80%).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.24 (dd,  $J = 16.0, 7.0$  Hz, 1H), 5.44 (dt,  $J = 16.0, 1.5$  Hz, 1H), 2.80 (d,  $J = 2.0$  Hz, 1H), 2.03-2.09 (m, 1H), 1.66-1.78 (m, 6H), 1.09-1.29 (m, 4H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  152.2, 106.1, 82.8, 75.7, 41.2, 32.1, 26.0, 25.8; IR (ATR) 3311, 2923, 2851, 2012, 1448, 957, 842  $\text{cm}^{-1}$ ; HRMS (DART) calcd for  $\text{C}_{10}\text{H}_{15}$  ( $[\text{M}+\text{H}]^+$ ) 135.11738, found 135.11741.

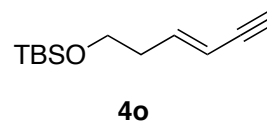
### General procedure F for the synthesis of enynes



To a 100-mL flask charged with *trans*-alkenyl bromide or iodide<sup>12,17,18</sup> (5.0 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (6.0 mg, 0.050 mmol), and benzene (12 mL) was added alkynylmagnesium bromide (12.0 mL, 0.5 M in THF, 6.0 mmol) slowly at 0 °C. The resulting mixture was allowed to stir at room temperature for 16 h. The reaction was then quenched by 1.0 M aq. HCl (20 mL), and the organic layer was separated. The aqueous layer was then extracted with diethyl ether ( $3 \times 30$  mL). The combined organic layer was then dried over  $\text{Na}_2\text{SO}_4$ . After removal of the solvent, the resulting crude residue was purified by column chromatography on silica gel with hexanes as the eluent to afford desired enynes.

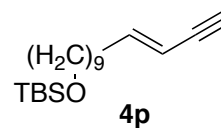
Compound **6e** was prepared according to this general procedure F, and the characterization data are consistent with those reported in the literature.<sup>19</sup>

**4o** [CAS: 408305-79-3]: 65%.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.24 (dt,  $J = 16.0, 7.0$  Hz, 1H), 5.50-5.54 (m, 1H), 3.66 (t,  $J = 6.5$  Hz, 2H), 2.79 (d,  $J = 2.0$  Hz, 1H), 2.30-2.35 (m, 2H), 0.89 (s, 9H), 0.05 (s, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  143.2, 110.3, 82.4, 75.9, 62.0, 36.6, 25.9, 18.3, -5.3; IR (ATR) 3314, 2954, 2929, 2895, 2857, 2739, 2106, 1631, 1471, 1361, 1094, 957, 933, 774  $\text{cm}^{-1}$ ; HRMS (DART) calcd for  $\text{C}_{12}\text{H}_{23}\text{OSi}$  ( $[\text{M}+\text{H}]^+$ ) 211.15182, found 211.15118.

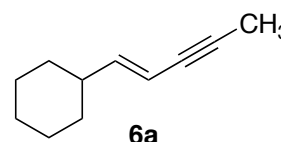




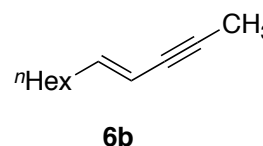
**4p**, [CAS: 129077-84-5], 62%.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.25 (dt,  $J = 16.0, 7.5$  Hz, 1H), 5.45 (dd,  $J = 16.5, 2.0$  Hz, 1H), 3.60 (t,  $J = 7.0$  Hz, 2H), 2.77 (d,  $J = 2.0$  Hz, 1H), 2.08-2.13 (m, 2H), 1.49 (m, 2H), 1.37-1.40 (m, 2H), 2.27 (br, 10H), 0.90 (s, 9H), 0.05 (s, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  147.0, 108.4, 82.6, 75.5, 63.3, 33.0, 32.9, 29.5, 29.4, 29.3, 29.1, 28.3, 26.0, 25.8, 18.4, -5.2; IR (ATR) 3314, 2926, 2854, 1462, 1360, 1095, 1005, 956, 833, 774  $\text{cm}^{-1}$ ; HRMS (DART) calcd for  $\text{C}_{19}\text{H}_{37}\text{OSi}$  ( $[\text{M}+\text{H}]^+$ ) 309.26137, found 309.26197.



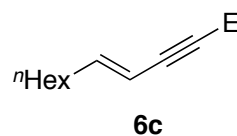
**6a**, [CAS: 2807-15-0], 87%.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.01 (dd,  $J = 16.0, 7.0$  Hz, 1H), 5.38 (m, 1H), 1.98-2.00 (m, 1H), 1.92 (d,  $J = 2.0$  Hz, 3H), 1.62-1.73 (m, 5H), 1.05-1.33 (m, 5H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  148.9, 107.4, 84.2, 78.5, 41.1, 32.4, 26.0, 25.8, 4.2; IR (ATR) 3017, 2922, 2850, 2222, 1447, 955  $\text{cm}^{-1}$ ; HRMS (DART) calcd for  $\text{C}_{11}\text{H}_{17}$  ( $[\text{M}+\text{H}]^+$ ) 149.13303, found 149.13343.



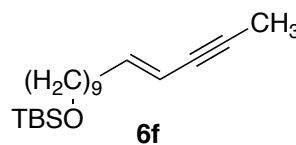
**6b**, [CAS: 66717-35-9], 89%.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.04 (dt,  $J = 16.5, 7.0$  Hz, 1H), 5.40-5.44 (m, 1H), 2.05 (t,  $J = 7.0$  Hz, 2H), 1.92 (d,  $J = 2.0$  Hz, 3H), 1.24-1.38 (m, 8H), 0.88 (t,  $J = 7.0$  Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  143.5, 109.7, 83.9, 78.4, 32.9, 31.6, 28.8, 28.7, 22.6, 14.1, 4.2; IR (ATR) 3020, 2956, 2925, 2855, 1458, 953  $\text{cm}^{-1}$ ; HRMS (DART) calcd for  $\text{C}_{11}\text{H}_{17}$  ( $[\text{M}+\text{H}]^+$ ) 151.14856, found 151.14868.



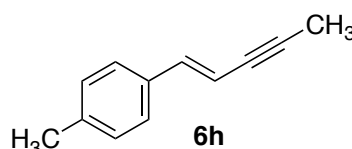
**6c**, [CAS: 110795-71-6], 71%.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.05 (dt,  $J = 16.0, 7.0$  Hz, 1H), 5.42-5.46 (m, 1H), 2.27-2.32 (m, 2H), 2.07 (q,  $J = 7.0$  Hz, 2H), 1.23-1.38 (m, 8H), 1.15 (t,  $J = 7.5$  Hz, 3H), 0.88 (t,  $J = 7.0$  Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  143.4, 109.7, 89.9, 78.5, 32.9, 31.7, 28.8, 28.7, 22.6, 14.1, 13.9, 13.0; IR (ATR) 3019, 2957, 2873, 2855, 1457, 1377, 1318, 952  $\text{cm}^{-1}$ ; HRMS (DART) calcd for  $\text{C}_{12}\text{H}_{21}$  ( $[\text{M}+\text{H}]^+$ ) 165.16433, found 165.16474.



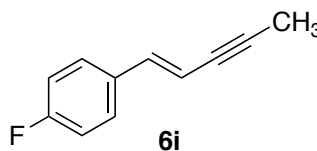
**6f**, 85%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 6.50 (dt, *J* = 14.0, 3.0 Hz, 1H), 5.96 (d, *J* = 14.0 Hz, 1H), 3.60 (t, *J* = 7.0 Hz, 2H), 2.05 (t, *J* = 7.0 Hz, 2H), 1.49-1.52 (m, 2H), 1.36-1.38 (m, 2H), 1.27 (br, 13H), 0.90 (s, 9H), 0.05 (s, 6H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 143.5, 109.7, 83.9, 78.4, 63.3, 32.9, 32.8, 29.5, 29.4, 29.3, 29.1, 28.8, 26.0, 25.8, 18.4, 4.1, -5.2; IR (FT-ATR) 2925, 2854, 1462, 1253, 1096, 953, 833, 773 cm<sup>-1</sup>; HRMS (DART) calcd. for C<sub>13</sub>H<sub>25</sub>OSi ([M+H]<sup>+</sup>) 323.27702, found 323.27662.



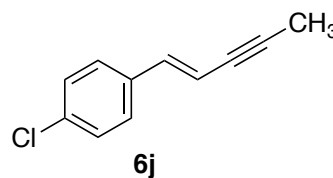
**6h**, 97%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.25 (d, *J* = 6.0 Hz, 2H), 7.12 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 16.5 Hz, 1H), 6.08 (dq, *J* = 16.0, 2.0 Hz, 1H), 2.34 (s, 3H), 2.01 (d, *J* = 2.5 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 140.0, 138.2, 133.8, 129.3, 125.9, 107.7, 87.8, 79.0, 21.2, 4.6; IR (FT-ATR) 3025, 2914, 2850, 2217, 1609, 1513, 1440, 1376, 955, 798, cm<sup>-1</sup>; HRMS (DART) calcd. for C<sub>12</sub>H<sub>13</sub> ([M+H]<sup>+</sup>) 157.10173, found 157.10240.



**6i** 93%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.31 (dd, *J* = 8.0, 5.0 Hz, 2H), 7.00 (t, *J* = 8.5 Hz, 2H), 6.82 (d, *J* = 16.5 Hz, 1H), 6.04 (dq, *J* = 16.5, 1.5 Hz, 1H), 2.09 (d, *J* = 2.0 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 162.7 (d, *J* = 246.8 Hz), 138.8, 132.7 (d, *J* = 2.9 Hz), 127.6 (d, *J* = 8.5 Hz), 115.8 (d, *J* = 21.9 Hz), 108.6 (d, *J* = 2.9 Hz), 88.3, 78.7, 4.4; <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) δ -113.2; IR (FT-ATR) 3037, 2915, 2850, 2219, 1599, 1506, 1227, 1156, 952, 868, 851 cm<sup>-1</sup>; HRMS (DART) calcd. for C<sub>11</sub>H<sub>10</sub>F ([M+H]<sup>+</sup>) 161.07665, found 161.07606.

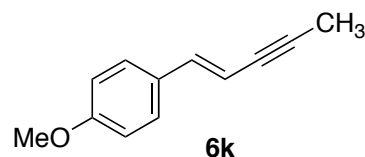


**6j**, 75%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.28 (s, 4H), 6.82 (d, *J* = 16.0 Hz, 1H), 6.10 (dq, *J* = 16.5, 2.0 Hz, 1H), 2.01 (d, *J* = 2.5 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 138.7, 135.0, 133.9, 128.8, 127.2, 109.5, 88.9, 78.7, 4.5; IR (FT-

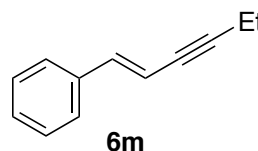


ATR) 3032, 2914, 2848, 2215, 1615, 1592, 1490, 1089, 1011, 954, 806  $\text{cm}^{-1}$ ; HRMS (DART) calcd. for  $\text{C}_{11}\text{H}_{10}^{35}\text{Cl}$  ( $[\text{M}+\text{H}]^+$ ) 177.04710, found 177.04736.

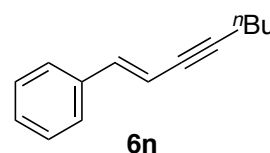
**6k**, 60%.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.01 (d,  $J = 8.0$  Hz, 2H), 6.84 (d,  $J = 9.0$  Hz, 2H), 6.82 (d,  $J = 17.0$  Hz, 1H), 5.98 (dq,  $J = 16.5, 2.5$  Hz, 1H), 3.81 (s, 3H), 2.01 (d,  $J = 2.0$  Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  159.7, 139.6, 129.3, 127.3, 114.0, 106.4, 87.3, 79.1, 59.2, 4.5; IR (FT-ATR) 3030, 3001, 2955, 2934, 2912, 2835, 2217, 1604, 1509, 1440, 1275, 1173, 1030, 952, 847  $\text{cm}^{-1}$ ; HRMS (DART) calcd. for  $\text{C}_{12}\text{H}_{13}\text{O}$  ( $[\text{M}+\text{H}]^+$ ) 173.09664, found 173.09594.



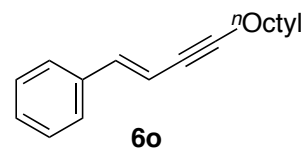
**6m**, 73%.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.26-7.36 (m, 5H), 6.90 (d,  $J = 16.0$  Hz, 1H), 6.18 (dt,  $J = 16.0, 2.5$  Hz, 1H), 2.39-2.44 (m, 2H), 1.21-1.25 (m, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  140.0, 136.6, 128.6, 128.2, 126.0, 108.8, 94.2, 79.1, 13.9, 13.3; IR (FT-ATR) 3059, 3027, 2975, 2936, 2842, 2211, 1594, 1491, 1448, 1375, 1316, 952, 746, 690  $\text{cm}^{-1}$ ; HRMS (DART) calcd. for  $\text{C}_{14}\text{H}_{17}$  ( $[\text{M}+\text{H}]^+$ ) 157.10173, found 157.10136.



**6n**, 80%.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36 (d,  $J = 7.0$  Hz, 2H), 7.31 (t,  $J = 7.0$  Hz, 2H), 7.25 (t,  $J = 7.0$  Hz, 1H), 6.87 (d,  $J = 16.5$  Hz, 1H), 6.15 (dt,  $J = 16.0, 7.5$  Hz, 1H), 2.38 (td,  $J = 7.0, 2.5$  Hz, 2H), 1.53-1.57 (m, 2H), 1.43-1.48 (m, 2H), 0.94 (t,  $J = 7.0$  Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  139.9, 136.6, 128.6, 128.2, 126.0, 108.9, 93.0, 79.7, 30.8, 22.0, 19.3, 13.6; IR (FT-ATR) 3060, 3027, 2956, 2871, 2212, 1614, 1595, 1464, 1027, 745, 689  $\text{cm}^{-1}$ ; HRMS (DART) calcd. for  $\text{C}_{14}\text{H}_{17}$  ( $[\text{M}+\text{H}]^+$ ) 185.13033, found 185.13310.

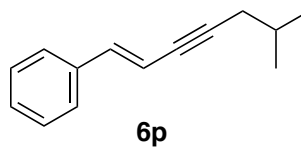


**6o**, 44%.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36 (d,  $J = 7.5$  Hz, 2H), 7.31 (d,  $J = 7.5$  Hz, 2H), 7.25 (t,  $J = 7.5$  Hz, 1H), 6.87 (d,  $J = 16.0$  Hz, 1H), 6.15 (dt,  $J = 16.5, 2.5$  Hz, 1H), 2.36 (td,  $J = 7.5, 2.5$  Hz, 2H), 1.53-1.58 (m, 2H), 1.40-1.44 (m, 2H), 1.30 (br, 8H), 0.89 (t,  $J = 7.5$  Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  139.9, 136.6, 128.6, 128.2, 126.0, 108.9, 93.1, 79.7,



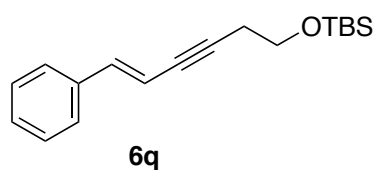
31.8, 29.2, 29.1, 29.0, 28.8, 22.7, 19.6, 14.1; IR (FT-ATR) 3060, 3027, 2953, 2924, 2854, 2210, 1596, 1490, 1465, 1429, 950, 745, 689  $\text{cm}^{-1}$ ; HRMS (DART) calcd. for  $\text{C}_{18}\text{H}_{25}$  ( $[\text{M}+\text{H}]^+$ ) 241.19563, found 241.19513.

**6p**, 43%.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36 (d,  $J = 7.5$  Hz, 2H), 7.31 (t,  $J = 7.5$  Hz, 2H), 7.25 (t,  $J = 7.5$  Hz, 1H), 6.88 (d,  $J = 16.0$  Hz, 1H), 6.18 (dt,  $J = 17.0, 2.5$  Hz, 1H), 2.27 (dd,



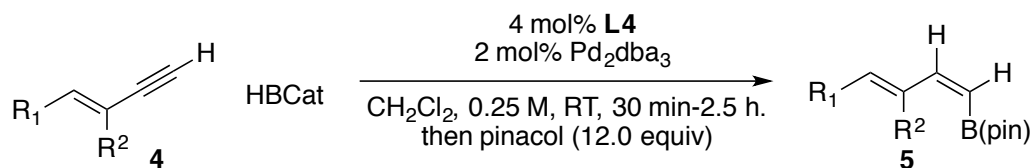
$J = 6.0, 1.0$  Hz, 2H), 1.84-1.90 (m, 1H), 1.02 (d,  $J = 7.0$  Hz, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  139.9, 136.6, 128.6, 128.2, 126.0, 108.9, 91.9, 80.6, 28.8, 28.2, 22.0; IR (FT-ATR) 3060, 3027, 2957, 2828, 2211, 1615, 1463, 1343, 1027, 745, 689  $\text{cm}^{-1}$ ; HRMS (DART) calcd. for  $\text{C}_{14}\text{H}_{17}$  ( $[\text{M}+\text{H}]^+$ ) 185.13303, found 185.13370.

**6q**, 86%.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36 (d,  $J = 7.5$  Hz, 2H), 7.31 (t,  $J = 7.5$  Hz, 2H), 7.26 (t,  $J = 6.5$  Hz, 1H), 6.88 (d,  $J = 16.0$  Hz, 1H), 6.13 (dt,  $J = 16.5, 2.5$  Hz, 1H), 3.78 (t,  $J = 7.5$  Hz, 2H), 2.59 (td,  $J = 7.0, 2.0$



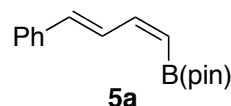
Hz, 2H), 0.90 (s, 9H), 0.10 (s, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  140.4, 136.5, 128.6, 128.3, 126.1, 108.6, 89.1, 80.8, 62.0, 25.9, 24.0, 18.4, -5.2; IR (FT-ATR) 3028, 2953, 2882, 2855, 2219, 1491, 1253, 1098, 951, 876, 775, 745, 689  $\text{cm}^{-1}$ ; HRMS (DART) calcd. for  $\text{C}_{18}\text{H}_{27}\text{OSi}$  ( $[\text{M}+\text{H}]^+$ ) 287.18312, found 287.18437.

### General procedure G for catalytic hydroboration of terminal 1,3-enynes



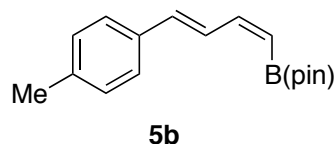
To a 5-mL vial charged with 1,3-enyne **4** (0.25 mmol), the catalyst (Pd<sub>2</sub>dba<sub>3</sub>/L4) solution (0.05 M in CH<sub>2</sub>Cl<sub>2</sub>, 0.20 mL, 0.01 mmol), and CH<sub>2</sub>Cl<sub>2</sub> (0.80 mL) was added HBCat (39 μL, 0.375 mmol). The resulting mixture was allowed to stir at room temperature until completion as monitored by TLC. At the conclusion of the reaction, the crude <sup>1</sup>H NMR was taken to determine ratio of the *trans/cis* hydroboration adducts (using <sup>3</sup>J<sub>H,H</sub> of CH next to boron as the diagnostic tool to assign the *trans/cis* hydroboration adducts). Then, pinacol (354 mg, 3.0 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (3.0 mL) was introduced, and the resulting mixture was allowed to stir at room temperature for 1 hr. After removal of the solvent, the crude residue was purified by column chromatography on silica gel with (Hex/EtOAc = 100: 1) as the eluent to afford dienyl boronates **5**. The ratio of *trans/cis* hydroboration adducts for the Bpin products may slightly differ from the ratio originally observed for the Bcat intermediates (this latter ratio is shown in Table 2). The spectra (including the integration of both diastereomers in the inset) for the Bpin products are provided in the NMR collection.

**5a**: 30 min, *EE/EZ* >98 : 2, 85% yield. Crystals of **5a** suitable for single crystal X-ray diffraction analysis were grown from slow



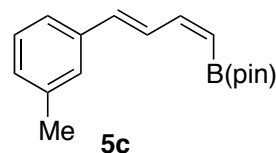
evaporation of a pentane solution at -30 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.66 (dd, *J* = 15.5, 11.0 Hz, 1H), 7.45 (d, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.25 (t, *J* = 7.5 Hz, 1H), 7.02 (t, *J* = 12.0 Hz, 1H), 6.65 (d, *J* = 15.5 Hz, 1H), 5.47 (d, *J* = 13.0 Hz, 1H), 1.33 (s, 12H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 150.3, 137.2, 136.3, 129.4, 128.6, 127.9, 126.9, 119.5 (br), 83.1, 24.9; <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) δ 29.6; IR (ATR) 2978, 2930, 1624, 1587, 1571, 1451, 1423, 1379, 1330, 1279, 1258, 1215, 1113, 1007, 964, 782 cm<sup>-1</sup>; HRMS (DART) calcd for C<sub>16</sub>H<sub>22</sub>BO<sub>2</sub> ([M+H]<sup>+</sup>) 257.17128, found 257.17055.

**5b**: 30 min, *EZ/EE* >98 : 2, 86% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.62 (ddd, *J* = 16.0, 11.0, 1.0 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.01 (t, *J* = 12.0



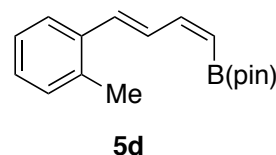
Hz, 1H), 6.63 (d, *J* = 11.0 Hz, 1H), 5.42 (d, *J* = 13.0 Hz, 1H), 2.35 (s, 3H), 1.32 (s, 12H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 150.6, 137.8, 136.4, 134.4, 129.3, 128.5, 126.8, 119.3 (br), 83.1, 24.9, 21.3; <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) δ 29.3; IR (ATR) 2978, 2926, 1624, 1586, 1297, 1279, 1113, 1106, 965, 878, 846 cm<sup>-1</sup>; HRMS (DART) calcd for C<sub>17</sub>H<sub>24</sub>BO<sub>2</sub> ([M+H]<sup>+</sup>) 271.18693, found 271.18643.

**5c**: 30 min, *EZ/EE* = 98 : 2, 82% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.65 (dd, *J* = 16.0, 11.5 Hz, 1H), 7.22-7.29 (m, 3H), 7.07 (d, *J* = 7.5 Hz, 1H), 7.02 (t, *J* = 13.0 Hz, 1H), 6.63 (d, *J* =



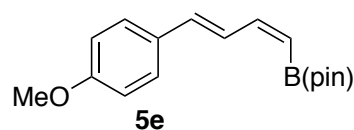
11.0 Hz, 1H), 5.46 (d, *J* = 13.0 Hz, 1H), 2.36 (s, 3H), 1.33 (s, 12H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 150.4, 138.4, 137.1, 136.5, 129.2, 128.7, 128.4, 127.8, 123.8, 119.4 (br), 83.1, 24.9; <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) δ 29.3; IR (ATR) 2980, 2931, 1620, 1597, 1587, 1421, 1402, 1372, 1316, 1279, 1138, 975, 868, 845 cm<sup>-1</sup>; HRMS (DART) calcd for C<sub>17</sub>H<sub>24</sub>BO<sub>2</sub> ([M+H]<sup>+</sup>) 271.18693, found 271.18597.

**5d**: 30 min, *EZ/EE* = 98 : 2, 80% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.58 (dd, *J* = 15.5, 11.0 Hz, 1H), 7.54 (d, *J* = 7.5 Hz, 1H), 7.15-7.21 (m, 3H), 7.08 (d, *J* = 11.5 Hz, 1H), 6.86 (d, *J* = 15.5 Hz, 1H), 5.47 (d, *J* = 13.0 Hz, 1H), 2.38 (s, 3H), 1.31 (s,



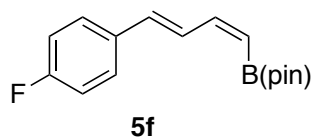
12H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 150.7, 136.0, 135.9, 134.0, 130.6, 130.4, 127.7, 126.1, 125.8, 119.7 (br), 83.1, 24.9; <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) δ 29.3; IR (ATR) 2979, 2931, 1624, 1594, 1579, 1507, 1431, 1406, 1390, 1371, 1279, 1231, 1113, 1006, 965, 875, 860 cm<sup>-1</sup>; HRMS (DART) calcd for C<sub>17</sub>H<sub>24</sub>BO<sub>2</sub> ([M+H]<sup>+</sup>) 271.18693, found 271.18753.

**5e**: 30 min, *EZ/EE* >98 : 2, 76% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.54 (ddd, *J* = 16.0, 11.5, 1.0 Hz, 1H), 7.40 (dd, *J* = 8.5, 3.0 Hz, 2H), 7.00 (t, *J* = 12.5 Hz, 1H),

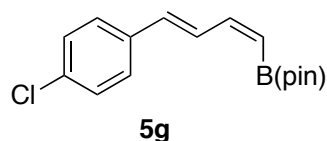


6.89 (dd,  $J = 8.5, 3.0$  Hz, 2H), 6.60 (d,  $J = 15.5$  Hz, 1H), 5.41 (d,  $J = 13.0$  Hz, 1H), 3.82 (s, 3H), 1.32 (s, 12H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  159.5, 150.7, 136.0, 130.0, 128.1, 127.5, 118.4 (br), 114.1, 83.0, 55.3, 24.9;  $^{11}\text{B}$  NMR (160 MHz,  $\text{CDCl}_3$ )  $\delta$  29.4; IR (FT-ATR) 2994, 2976, 2935, 2837, 1624, 1605, 1584, 1570, 1510, 1463, 1414, 1389, 1371, 1329, 1297, 1245, 1174, 1141, 1111, 1030, 1107, 964, 877, 846  $\text{cm}^{-1}$ ; HRMS (DART) calcd. for  $\text{C}_{17}\text{H}_{24}\text{BO}_3$  ( $[\text{M}+\text{H}]^+$ ) 287.18185, found 287.28239.

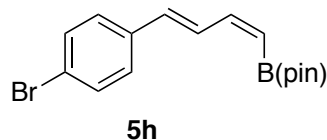
**5f**: 30 min,  $EZ/EE >98 : 2$ , 88% yield.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57 (dd,  $J = 15.5, 11.0$  Hz, 1H), 7.39-7.42 (m, 2H), 6.97-7.05 (m, 3H), 6.62 (d,  $J = 15.5$  Hz, 1H), 5.46 (d,  $J = 13.0$  Hz, 1H), 1.33 (s, 12H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  162.5 (d,  $J = 246.6$  Hz), 150.1, 135.0, 133.4 (d,  $J = 3.7$  Hz), 129.1 (d,  $J = 1.0$  Hz), 128.3 (d,  $J = 11.0$  Hz), 119.7 (br), 115.6 (d,  $J = 21.7$  Hz), 83.1, 24.9;  $^{11}\text{B}$  NMR (160 MHz,  $\text{CDCl}_3$ )  $\delta$  29.6;  $^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )  $\delta$  -113.7; IR (ATR) 2979, 2932, 1619, 1587, 1566, 1422, 1371, 1258, 1141, 1113, 965, 880, 848  $\text{cm}^{-1}$ ; HRMS (DART) calcd for  $\text{C}_{16}\text{H}_{21}\text{BFO}_2$  ( $[\text{M}+\text{H}]^+$ ) 274.15404, found 274.15335.



**5g**: 2.5 hr,  $EZ/EE = 98 : 2$ , 82% yield.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62 (ddd,  $J = 15.5, 11.0, 1.0$  Hz, 1H), 7.35 (dt,  $J = 8.5, 2.0$  Hz, 2H), 7.31 (dt,  $J = 8.0, 2.5$  Hz, 2H), 7.00 (t,  $J = 12.0$  Hz, 1H), 6.60 (d,  $J = 14.5$  Hz, 1H), 5.49 (d,  $J = 13.5$  Hz, 1H), 1.33 (s, 12H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  149.9, 135.7, 134.8, 133.5, 129.9, 128.8, 128.0, 120.7 (br), 83.2, 24.9;  $^{11}\text{B}$  NMR (160 MHz,  $\text{CDCl}_3$ )  $\delta$  29.2; IR (ATR) 2978, 2928, 1623, 1584, 1490, 1430, 1371, 1297, 1216, 1192, 1165, 1143, 1113, 1091, 1011, 965, 876, 846  $\text{cm}^{-1}$ ; HRMS (DART) calcd for  $\text{C}_{16}\text{H}_{21}\text{B}^{35}\text{ClO}_2$  ( $[\text{M}+\text{H}]^+$ ) 291.13231, found 291.13168.

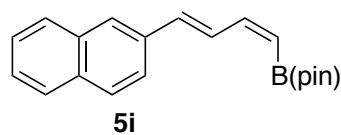


**5h**: 2.5 hr,  $EZ/EE = 98 : 2$ , 76% yield.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64 (ddd,  $J = 15.5, 10.5, 1.0$  Hz, 1H), 7.46 (dt,  $J = 9.5, 2.5$  Hz, 2H), 7.30 (dt,  $J = 9.5, 2.5$  Hz, 2H), 6.99 (d,  $J = 12.0$  Hz, 1H), 6.57 (d,  $J = 15.0$  Hz, 1H), 5.50 (d,  $J = 13.5$  Hz, 1H), 1.32 (s, 12H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  149.9, 136.2, 134.9, 131.7, 130.0, 128.3, 121.7, 120.5 (br),



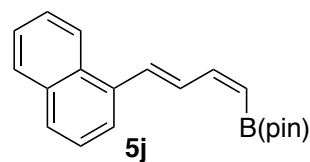
81.2, 24.9;  $^{11}\text{B}$  NMR (160 MHz,  $\text{CDCl}_3$ )  $\delta$  29.3; IR (ATR) 2977, 2930, 1621, 1591, 1428, 1280, 1164, 1131, 1112, 1007, 964, 876, 864  $\text{cm}^{-1}$ ; HRMS (DART) calcd for  $\text{C}_{17}\text{H}_{24}\text{B}^{79}\text{BrO}_2$  ( $[\text{M}+\text{H}]^+$ ) 335.08180, found 335.08263.

**5i**: 45 min, *EZ/EE* > 98 : 2, 80% yield.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.76-7.81 (m, 5H), 7.68 (dd,  $J = 8.0, 1.0$  Hz, 1H), 7.42-7.48 (m, 2H), 7.08 (t,  $J = 12.5$  Hz, 1H), 6.82 (d,  $J =$



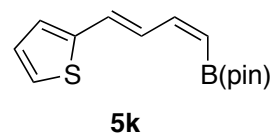
15.5 Hz, 1H), 5.51 (d,  $J = 12.0$  Hz, 1H), 1.35 (s, 12H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  150.4, 136.4, 134.8, 133.6, 133.2, 129.7, 128.2, 128.1, 127.6, 127.3, 126.2, 126.0, 123.6, 119.6 (br), 83.1, 24.9;  $^{11}\text{B}$  NMR (160 MHz,  $\text{CDCl}_3$ )  $\delta$  29.4; IR (FT-ATR) 3057, 2977, 2931, 1614, 1600, 1583, 1506, 1444, 1370, 1329, 1261, 1142, 1016, 838  $\text{cm}^{-1}$ ; HRMS (DART) calcd. for  $\text{C}_{20}\text{H}_{24}\text{BO}_2$  ( $[\text{M}+\text{H}]^+$ ) 307.18693, found 307.18708.

**5j**: 45 min, *EZ/EE* > 98 : 2, 81% yield.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.18 (d,  $J = 8.0$  Hz, 1H), 7.86 (dd,  $J = 8.0, 1.5$  Hz, 1H), 7.72-7.81 (m, 3H), 7.48-7.55 (m, 3H), 7.44 (d,  $J = 15.5$  Hz, 1H), 7.18 (t,  $J = 12.0$  Hz, 1H), 5.55 (d,  $J = 14.0$  Hz, 1H),



1.33 (s, 12H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  150.5, 134.4, 133.7, 133.0, 132.0, 131.2, 128.6, 128.3, 126.1, 125.8, 125.6, 123.9, 123.6, 120.1 (br), 83.2, 24.9;  $^{11}\text{B}$  NMR (160 MHz,  $\text{CDCl}_3$ )  $\delta$  29.3; IR (FT-ATR) 3054, 2977, 2928, 1612, 1582, 1509, 1424, 1390, 1370, 1332, 1298, 1279, 1165, 1112, 965, 879  $\text{cm}^{-1}$ ; HRMS (DART) calcd. for  $\text{C}_{20}\text{H}_{24}\text{BO}_2$  ( $[\text{M}+\text{H}]^+$ ) 307.18693, found 307.18717

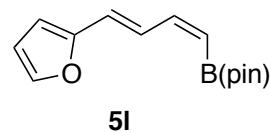
**5k**: 30 min, *EZ/EE* = 97 : 3, 81% yield.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50 (dd,  $J = 16.5, 11.5$  Hz, 1H), 7.21 (d,  $J = 5.5$  Hz, 1H), 7.03 (d,  $J = 3.5$  Hz, 1H), 6.98 (t,  $J = 5.0$  Hz, 1H), 6.95 (t,  $J$



= 12.0 Hz, 1H), 6.76 (d,  $J = 16.0$  Hz, 1H), 5.44 (d,  $J = 13.5$  Hz, 1H), 1.32 (s, 12H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  149.6, 142.7, 129.3, 128.8, 127.6, 126.5, 125.1, 119.3 (br), 83.1, 24.9;  $^{11}\text{B}$  NMR (160 MHz,  $\text{CDCl}_3$ )  $\delta$  29.2; IR (ATR) 2977, 2928, 1612, 1584, 1514, 1434, 1417, 1351, 1329, 1297, 1257, 1214, 1193, 1164, 1112, 1004, 966, 954, 880, 866  $\text{cm}^{-1}$ ; HRMS (DART) calcd for  $\text{C}_{14}\text{H}_{20}\text{BO}_2\text{S}$  ( $[\text{M}+\text{H}]^+$ ) 263.12771, found 263.12744.

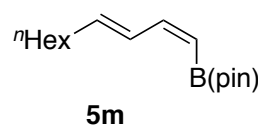


**5l**: 45 min, *EZ/EE* = 97 : 3, 84% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.51 (dd, *J* = 11.5, 1.5 Hz, 1H), 7.41 (d, *J* = 1.5 Hz, 1H), 6.94 (t, *J* = 12.0 Hz, 1H), 6.44 (d, *J* = 11.0 Hz, 1H), 6.39-



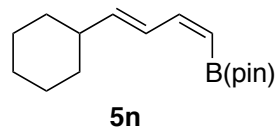
6.41 (m, 1H), 6.35 (d, *J* = 3.0 Hz, 1H), 5.44 (d, *J* = 13.5 Hz, 1H), 1.32 (s, 12H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 153.1, 149.8, 142.6, 127.8, 123.7, 119.8 (br), 111.7, 109.5, 83.1, 24.8; <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) δ 29.3; IR (ATR) 2978, 2929, 1599, 1546, 1481, 1389, 1259, 1185, 1112, 1013, 965, 882, 846 cm<sup>-1</sup>; HRMS (DART) calcd for C<sub>14</sub>H<sub>20</sub>BO<sub>2</sub> ([M+H]<sup>+</sup>) 247.15055, found 247.15100.

**5m**: 30 min, *EZ/EE* = 94 : 6, 82%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 6.80-6.88 (m, 2H), 5.81-5.87 (m, 1H), 5.24 (d, *J* = 11.0 Hz, 1H), 2.15 (q, *J* = 7.0 Hz, 2H), 1.36-1.43 (m, 2H), 1.27-1.34 (m, 18H),



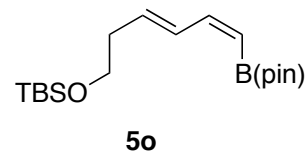
0.89 (t, *J* = 6.5 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 151.0, 140.1, 130.7, 118.5 (br), 82.9, 32.7, 31.7, 29.0, 28.9, 24.8, 22.6, 14.1; <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) δ 29.3; IR (FT-ATR) 2977, 2954, 2929, 2857, 1597, 1471, 1462, 1452, 1420, 1389, 1371, 1289, 1254, 1212, 1143, 1089, 1005, 976, 965, 935, 863, 744 cm<sup>-1</sup>; HRMS (DART) calcd. for C<sub>16</sub>H<sub>30</sub>BO<sub>2</sub> ([M+H]<sup>+</sup>) 265.23388, found 265.23352.

**5n**: 30 min, *EZ/EE* = 97 : 3, 87% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 6.79-6.85 (m, 2H), 5.75-5.79 (m, 1H), 5.25 (d, *J* = 12.0 Hz, 1H), 2.06-2.10 (m, 1H), 1.64-1.76 (m, 5H), 1.07-1.29 (m,



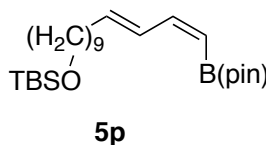
17H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 151.3, 145.6, 128.3, 116.5 (br), 82.9, 40.8, 32.5, 26.1, 25.9, 24.9; <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) δ 29.3; IR (FT-ATR) 2978, 2924, 2851, 1639, 1590, 1445, 1427, 1389, 1297, 1145, 1007, 966, 768 cm<sup>-1</sup>; HRMS (DART) calcd. for C<sub>16</sub>H<sub>28</sub>BO<sub>2</sub> ([M+H]<sup>+</sup>) 263.21823, found 263.21808.

**5o**: 30 min, *EZ/EE* >98 : 2, 86% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 6.88-6.93 (m, 1H), 6.82 (t, *J* = 12.0 Hz, 1H), 5.80-5.86 (m, 1H), 5.28 (d, *J* = 13.5 Hz, 1H), 3.69 (t, *J* = 7.0 Hz, 2H), 2.14 (q, *J* = 7.0 Hz, 2H), 1.28 (s, 12H), 0.88 (s, 9H), 0.05 (s, 6H); <sup>13</sup>C NMR (125 MHz,

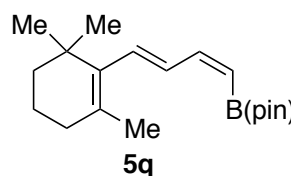


CDCl<sub>3</sub>) δ 150.7, 135.7, 132.5, 117.3 (br), 82.9, 62.7, 36.4, 25.9, 24.8, 18.3, -5.3; <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) δ 29.2; IR (ATR) 2979, 2954, 2929, 1643, 1590, 1471, 1424, 1300, 1257, 1215, 1145, 1097, 1006, 966, 937, 876, 835 cm<sup>-1</sup>; HRMS (DART) calcd for C<sub>18</sub>H<sub>36</sub>BO<sub>3</sub>Si ([M+H]<sup>+</sup>) 339.25268, found 339.25257.

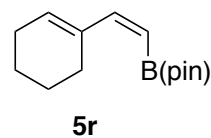
**5p**: 30 min, *EZ/EE* = 96 : 4, 91% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 6.82-6.86 (m, 2H), 5.81-5.87 (m, 1H), 5.24 (d, *J* = 12.0, 1H), 3.60 (t, *J* = 6.5 Hz, 2H), 2.14 (q, *J* = 7.0 Hz, 2H), 1.47-1.54 (m, 2H), 1.38-1.43 (m, 2H), 1.28 (m, 22H), 0.89 (s, 9H), 0.05 (s, 6H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 151.0, 140.1, 130.7, 116.8 (br), 82.9, 63.3, 32.9, 32.7, 29.6, 29.5, 29.4, 29.2, 29.0, 26.0, 25.8, 24.8, 18.3, -5.3; <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) δ 29.2; IR (ATR) 2978, 2926, 2854, 1641, 1589, 1463, 1424, 1388, 1378, 1329, 1299, 1255, 1215, 1144, 1096, 1006, 965, 879, 773 cm<sup>-1</sup>; HRMS (DART) calcd for C<sub>25</sub>H<sub>50</sub>BO<sub>3</sub>Si ([M+H]<sup>+</sup>) 437.36223, found 437.36140.



**5q**: 30 min, *EZ/EE* = 95 : 5, 93% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.06 (dd, *J* = 16.0, 11.5 Hz, 1H), 6.90 (t, *J* = 12.0 Hz, 1H), 6.30 (d, *J* = 11.0 Hz, 1H), 5.31 (d, *J* = 13.5 Hz, 1H), 2.06 (t, *J* = 6.5 Hz, 2H), 1.77 (d, *J* = 1.0 Hz, 3H), 1.59-1.64 (m, 2H), 1.46-1.48 (m, 2H), 1.30 (s, 12H), 1.08 (s, 6H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 151.8, 137.0, 135.2, 132.9, 132.0, 116.5 (br), 82.8, 40.2, 34.0, 33.7, 28.9, 24.8, 24.5, 21.7, 19.2; <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) δ 29.3; IR (FT-ATR) 2976, 2928, 2865, 2824, 1607, 1580, 1424, 1389, 1370, 1327, 1297, 1257, 1212, 1164, 1143, 1113, 1009, 967, 846, 771 cm<sup>-1</sup>; HRMS (DART) calcd. for C<sub>19</sub>H<sub>32</sub>BO<sub>2</sub> ([M+H]<sup>+</sup>) 303.24953, found 235.25009.

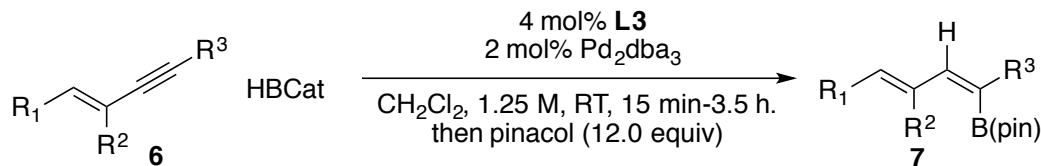


**5r**<sup>20</sup> [CAS: 1192488-91-7]: 30 min, *EZ/EE* = 97 : 3, 70% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 6.65 (d, *J* = 14.5 Hz, 1H), 5.83 (t, *J* = 5.0 Hz, 1H), 5.18 (d, *J* = 15.0 Hz, 1H), 2.24-2.27 (m, 2H), 2.11-2.15 (m, 2H), 1.54-1.66 (m, 4H), 1.30 (s, 12H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 149.7, 137.9, 132.0, 114.1 (br), 83.3, 26.3, 26.0, 24.8, 22.4, 22.1; <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) δ 30.5; IR (FT-ATR) 2977, 2927, 2858, 2831, 1628, 1598, 1434, 1389, 1370, 1298, 1228, 1141,



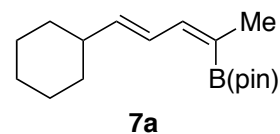
1107, 1004, 966, 918, 845, 801, 775  $\text{cm}^{-1}$ ; HRMS (DART) calcd. for  $\text{C}_{14}\text{H}_{24}\text{BO}_2$  ( $[\text{M}+\text{H}]^+$ ) 235.18693, found 235.18714.

**General procedure H for catalytic hydroboration of internal 1,3-enynes**



To a 5-mL vial charged with 1,3-enyne **6** (0.25 mmol) and the catalyst ( $\text{Pd}_2\text{dba}_3/\text{L3}$ ) solution (0.05 M in  $\text{CH}_2\text{Cl}_2$ , 0.20 mL, 0.01 mmol) was added HBCat (39  $\mu\text{L}$ , 0.375 mmol). The resulting mixture was allowed to stir at room temperature until completion as monitored by TLC. At the conclusion of the reaction, the crude  $^1\text{H}$  NMR was taken to determine ratio of the *trans/cis* hydroboration adducts (using chemical shift of *CH* next to  $\text{R}^1$  (**7a-7l**), or  $\text{CH}_2$  next to *CB* (**7m-7q**) as the diagnostic tool to assign the *trans/cis* hydroboration adducts). Then, pinacol (354 mg, 3.0 mmol) in  $\text{CH}_2\text{Cl}_2$  (3.0 mL) was introduced, and the resulting mixture was allowed to stir at room temperature 1 hr. After removal of the solvent, the residue was purified by column chromatography on silica gel with (Hex/EtOAc = 100: 1) as the eluent to afford dienyl boronates **7**. The ratio of *trans/cis* hydroboration adducts for the Bpin products may slightly differ from the ratio originally observed for the Bcat intermediates (this latter ratio is shown in Table 3). The spectra (including the integration of both diastereomers in the inset) for the Bpin products are provided in the NMR collection. 1D-NOE experiments were performed for **7a**, **7g**, *cis*-**7g** (independently synthesized)<sup>21</sup>, **7l**, and **7q** as representative compounds. The 1D-NOE spectra for **7a**, **7g**, **7l**, and **7q** are consistent with *trans*-hydroboration.

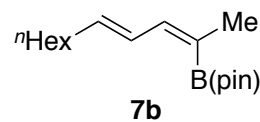
**7a**: 1.5 hr, *EE/EZ* = 96: 4, 92% yield. Crystals of **7a** suitable for single crystal X-ray diffraction analysis were grown from slow



evaporation of a pentane solution at  $-30\text{ }^\circ\text{C}$ .  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.79 (ddd,  $J = 15.5, 11.0, 1.0$  Hz, 1H), 6.56 (d,  $J = 10.5$  Hz, 1H), 5.63 (dd  $J = 15.5, 7.0$  Hz, 2H), 1.98-2.10 (m, 1H), 1.82 (s, 3H), 1.70-1.75 (m, 4H), 1.63-1.66 (m, 1H), 1.08-1.29 (m, 17H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  146.1, 142.4, 127.6, 82.9, 40.7, 32.7, 26.2, 25.9, 24.9, 22.3 (B-alkenyl carbon signal not observed);  $^{11}\text{B}$  NMR (160 MHz,

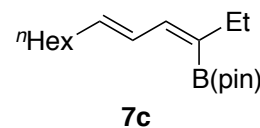
CDCl<sub>3</sub>)  $\delta$  29.7; IR (ATR) 2977, 2923, 2850, 1634, 1593, 1449, 1421, 1400, 1371, 1343, 1290, 1212, 1085, 975, 865, 672 cm<sup>-1</sup>; HRMS (DART) calcd for C<sub>17</sub>H<sub>30</sub>BO<sub>2</sub> ([M+H]<sup>+</sup>) 277.23388, found 277.23525.

**7b**: 30 min, *EE/EZ* = 93 : 7, 80% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  6.82 (dd, *J* = 15.0, 10.5 Hz, 1H), 6.56 (d, *J* = 10.5 Hz, 1H), 5.69 (dt, *J* = 15.0, 7.0 Hz, 1H), 2.11 (q, *J* = 7.0 Hz, 2H), 1.82



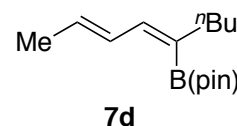
(s, 3H), 1.36-1.42 (m, 2H), 1.23-1.32 (m, 18H), 0.89 (t, *J* = 7.0 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  145.8, 136.8, 130.0, 82.9, 32.7, 31.8, 29.2, 28.9, 24.9, 22.6, 22.4, 14.1 (B-alkenyl carbon signal not observed); <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>)  $\delta$  29.7; IR (ATR) 2977, 2956, 2925, 2854, 1640, 1596, 1453, 1421, 1389, 1371, 1267, 1254, 1214, 1143, 1110, 1093, 975, 965, 836, 686 cm<sup>-1</sup>; HRMS (DART) calcd. for C<sub>17</sub>H<sub>32</sub>BO<sub>2</sub> ([M+H]<sup>+</sup>) 279.24953, found 279.25033.

**7c**: 2 hr, *EE/EZ* = 82 : 18, 93% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  6.80 (dd, *J* = 15.5, 11.5 Hz, 1H), 6.53 (d, *J* = 11.5 Hz, 1H), 5.71 (dt, *J* = 15.0, 8.0 Hz, 1H), 2.08-2.17 (m, 4H), 1.37-1.43 (m, 2H),



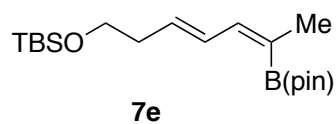
1.26-1.32 (m, 18H), 1.00 (t, *J* = 7.0 Hz, 3H), 0.88 (t, *J* = 7.0 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  143.9, 136.9, 130.1, 82.9, 32.8, 31.8, 29.8, 29.1, 28.9, 24.8, 22.6, 14.8, 14.1; <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>)  $\delta$  30.0; IR (ATR) 2958, 2925, 2855, 1639, 1591, 1458, 1425, 1405, 1388, 1378, 1290, 1214, 1143, 1109, 967, 833, 673 cm<sup>-1</sup>; HRMS (DART) calcd for C<sub>18</sub>H<sub>34</sub>BO<sub>2</sub> ([M+H]<sup>+</sup>) 293.26594, found 293.26518.

**7d**: 2 hr, *EE/EZ* = 81 : 19, 77% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  6.72-6.82 (m, 1H), 6.51 (d, *J* = 11.5 Hz, 1H), 5.69-5.73 (m, 1H), 2.13 (t, *J* = 7.5 Hz, 2H), 1.78 (d, *J* = 7.0 Hz, 3H), 1.25-1.38 (m,

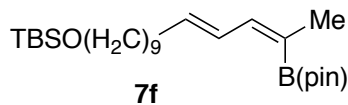


16H), 0.88 (t, *J* = 7.5 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  144.5, 131.5, 131.2, 82.9, 34.5, 32.6, 24.8, 22.3, 18.3, 14.0 (B-alkenyl carbon signal not observed); <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>)  $\delta$  29.9; IR (ATR) 2977, 2956, 2929, 2871, 2858, 1642, 1591, 1466, 1424, 1405, 1378, 1301, 1285, 1245, 1213, 1144, 1111, 978, 966, 864, 703 cm<sup>-1</sup>; HRMS (DART) calcd for C<sub>15</sub>H<sub>28</sub>BO<sub>2</sub> ([M+H]<sup>+</sup>) 251.21823, found 251.21859.

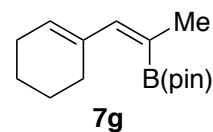
**7e**: 30 min, *EE/EZ* = 92 : 8, 84% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 6.87 (dd, *J* = 15.0, 10.5 Hz, 1H), 6.56 (d, *J* = 11.0 Hz, 1H), 5.67 (dt, *J* = 15.5, 7.0 Hz, 1H), 3.66 (t, *J* = 7.0 Hz, 2H), 2.35 (q, *J* = 7.0 Hz, 2H), 1.83 (s, 3H), 1.28 (s, 12H), 0.89 (s, 9H), 0.06 (s, 6H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 145.5, 132.2, 131.9, 83.0, 63.0, 36.4, 26.9, 24.8, 22.4, 18.3, -5.3 (B-alkenyl carbon signal not observed); <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) δ 29.7; IR (ATR) 2978, 2957, 2925, 2855, 1641, 1589, 1466, 1424, 1389, 1279, 1007, 965, 879, 847 cm<sup>-1</sup>; HRMS (DART) calcd for C<sub>19</sub>H<sub>38</sub>BO<sub>3</sub>Si ([M+H]<sup>+</sup>) 353.26833, found 353.26890.



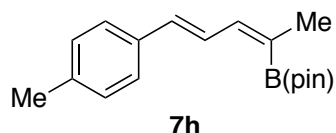
**7f**: 30 min, *EE/EZ* = 94 : 6, 89% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 6.81 (dd, *J* = 15.0, 10.5 Hz, 1H), 6.56 (d, *J* = 10.0 Hz, 1H), 5.69 (dt, *J* = 15.0, 7.0 Hz, 1H), 3.59 (t, *J* = 7.0 Hz, 2H), 2.11 (q, *J* = 7.5 Hz, 2H), 1.82 (s, 3H), 1.49-1.55 (m, 2H), 1.36-1.39 (m, 2H), 1.23-1.29 (m, 22H), 0.89 (s, 9H), 0.05 (s, 6H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 145.9, 136.8, 130.0, 82.9, 63.3, 32.9, 32.7, 29.6, 29.5, 29.4, 29.2, 25.7, 25.8, 24.9, 22.4, 18.3, -5.3 (B-alkenyl carbon signal not observed); <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) δ 30.0; IR (ATR) 2978, 2926, 2854, 1640, 1596, 1462, 1421, 1400, 1389, 1253, 1214, 1144, 1094, 1034, 1005, 975, 835, 812 cm<sup>-1</sup>; HRMS (DART) calcd for C<sub>26</sub>H<sub>52</sub>BO<sub>3</sub>Si ([M+H]<sup>+</sup>) 451.37788, found 451.37929.



**7g**: 30 min, *EE/EZ* = 97 : 3, 79% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 6.31 (s, 1H), 5.65 (s, 1H), 2.15 (br, 2H), 2.08 (br, 2H), 1.83 (s, 3H), 1.54-1.63 (m, 4H), 1.28 (s, 12H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 143.1, 137.2, 127.7, 83.3, 27.1, 25.7, 24.7, 23.1, 22.6, 22.2 (B-alkenyl carbon signal not observed); <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) δ 31.0; IR (ATR) 2977, 2927, 2857, 2832, 1608, 1446, 1398, 1389, 1221, 1213, 1189, 1143, 1107, 963, 920, 670 cm<sup>-1</sup>; HRMS (DART) calcd for C<sub>15</sub>H<sub>26</sub>BO<sub>2</sub> ([M+H]<sup>+</sup>) 249.20258, found 249.20367.

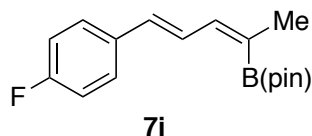


**7h**: 15 min, *EE/EZ* >98 : 2, 87% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.63 (dd, *J* = 15.5, 11.0 Hz, 1H), 7.32 (d, *J* = 7.5 Hz, 2H), 7.14 (d, *J* = 7.5 Hz, 2H), 6.77 (d, *J* = 11.0 Hz, 1H), 6.51 (d, *J* = 15.5 Hz, 1H), 2.35 (s, 3H), 1.93 (s, 3H),



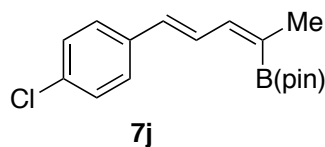
1.34 (s, 12H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 145.6, 137.1, 135.1, 133.4, 129.2, 128.3, 126.4, 83.1, 24.9, 22.6, 21.2 (B-alkenyl carbon signal not observed); <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) δ 29.7; IR (FT-ATR) 2976, 2883, 1620, 1587, 1508, 1450, 1397, 1289, 1136, 1034, 1014, 964, 805 cm<sup>-1</sup>; HRMS (DART) calcd for C<sub>18</sub>H<sub>26</sub>BO<sub>2</sub> ([M+H]<sup>+</sup>) 285.20258, found 285.20216.

**7i**: 15 min, *EE/EZ* >98 : 2, 87% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.58 (dd, *J* = 15.5, 10.5 Hz, 1H), 7.35-7.38 (m, 2H), 7.01 (t, *J* = 8.5 Hz, 2H), 6.74 (d, *J* = 11.0 Hz, 1H), 6.48



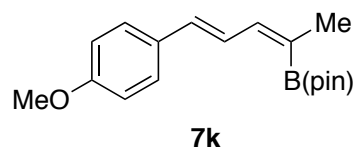
(d, *J* = 15.5 Hz, 1H), 1.92 (s, 3H), 1.33 (s, 12H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 161.2 (d, *J* = 245.8 Hz), 145.2, 134.0 (d, *J* = 3.8 Hz), 132.0, 128.9, 127.9 (d, *J* = 8.5 Hz, 1H), 115.5 (d, *J* = 20.9 Hz), 83.2, 24.9, 22.7 (B-alkenyl carbon signal not observed); <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) δ 29.7; <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>) δ -114.6; IR (ATR) 2978, 2933, 1621, 1596, 1581, 1506, 1451, 1396, 1318, 1245, 1229, 1140, 1110, 1090, 966, 857, 817, 774, 685 cm<sup>-1</sup>; HRMS (DART) calcd for C<sub>17</sub>H<sub>23</sub>BFO<sub>2</sub> ([M+H]<sup>+</sup>) 289.17751, found 289.17695.

**7j**: 15 min, *EE/EZ* >98 : 2, 85% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.63 (dd, *J* = 15.5, 11.0 Hz, 1H), 7.26-7.33 (m, 4H), 6.74 (d, *J* = 10.5 Hz, 1H), 6.45 (d, *J* = 15.5 Hz, 1H),



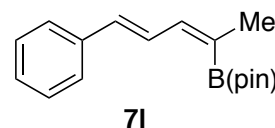
1.93 (s, 3H), 1.33 (s, 12H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 145.0, 136.4, 132.8, 131.9, 129.7, 128.7, 127.6, 83.2, 24.9, 22.7 (B-alkenyl carbon signal not observed); <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) δ 29.7; IR (ATR) 3046, 3001, 2885, 1619, 1595, 1584, 1448, 1406, 1390, 1371, 1284, 1246, 1165, 1136, 1109, 1088, 1008, 964, 864, 683 cm<sup>-1</sup>; HRMS (DART) calcd for C<sub>17</sub>H<sub>23</sub>B<sup>35</sup>ClO<sub>2</sub> ([M+H]<sup>+</sup>) 305.14796, found 305.14837.

**7k**: 15 min, *EE/EZ* >98 : 2, 90% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.55 (dd, *J* = 15.5, 10.5 Hz, 1H), 7.36 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 2H), 6.75 (d, *J* = 11.0 Hz, 1H), 6.48 (d, *J* = 15.5 Hz, 1H), 3.82 (s, 3H), 1.92 (s, 3H), 1.34 (s,



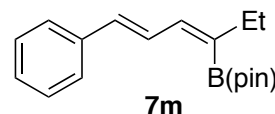
12H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 159.1, 141.8, 133.0, 130.7, 127.7, 127.2, 114.0, 83.1, 55.2, 24.9, 22.6 (B-alkenyl carbon signal not observed); <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) δ 29.8; IR (ATR) 2974, 2928, 2885, 2836, 1620, 1605, 1588, 1447, 1371, 1297, 1267, 1252, 1211, 1166, 1136, 1109, 1091, 1047, 977, 684 cm<sup>-1</sup>; HRMS (DART) calcd for C<sub>18</sub>H<sub>26</sub>BO<sub>3</sub> ([M+H]<sup>+</sup>) 301.19750, found 301.19769.

**7l**: 15 min, *EE/EZ* >98 : 2, 88% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.66 (dd, *J* = 16.0, 11.5 Hz, 1H), 7.41 (d, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.21 (t, *J* = 7.5 Hz, 1H), 6.76 (d, *J* =



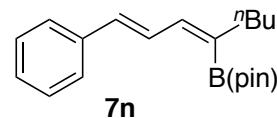
11.0 Hz, 1H), 6.52 (d, *J* = 15.5 Hz, 1H), 1.92 (s, 3H), 1.33 (s, 12H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 145.4, 137.8, 133.4, 129.2, 128.5, 127.3, 126.5, 83.2, 24.9, 22.7 (B-alkenyl carbon signal not observed); <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) δ 29.7; IR (FT-ATR) 2982, 2942, 2886, 1618, 1597, 1586, 1452, 1422, 1403, 1391, 1372, 1353, 1316, 1290, 1277, 1246, 1206, 1167, 1136, 1112, 1088, 1073, 976, 965, 869, 755, 682 cm<sup>-1</sup>; HRMS (DART) calcd. for C<sub>17</sub>H<sub>24</sub>BO<sub>2</sub> ([M+H]<sup>+</sup>) 271.18693, found 271.18705.

**7m**: 3.5 hr, *EE/EZ* = 95 : 5, 96% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.64 (dd, *J* = 15.5, 11.0 Hz, 1H), 7.40 (d, *J* = 7.0 Hz, 2H), 7.31 (t, *J* = 7.0 Hz, 2H), 7.21 (t, *J* = 7.5 Hz, 1H), 6.73 (d, *J* =

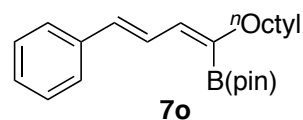


11.0 Hz, 1H), 6.54 (d, *J* = 16.0 Hz, 1H), 2.25 (q, *J* = 7.0 Hz, 2H), 1.34 (s, 12H), 1.05 (t, *J* = 7.5 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 143.5, 137.9, 133.5, 129.3, 128.5, 127.3, 126.5, 83.1, 30.0, 24.9, 14.7 (B-alkenyl carbon signal not observed); <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) δ 30.0; IR (ATR) 2975, 2930, 2870, 1622, 1598, 1448, 1404, 1370, 1349, 1282, 1269, 1213, 1140, 1109, 1043, 968, 866, 705 cm<sup>-1</sup>; HRMS (DART) calcd for C<sub>18</sub>H<sub>26</sub>BO<sub>2</sub> ([M+H]<sup>+</sup>) 282.20258, found 282.20342.

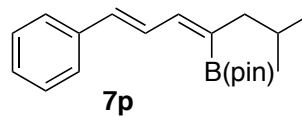
**7n**: 3.5 hr, *EE/EZ* = 93 : 7, 88% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.62 (dd, *J* = 15.5, 11.0 Hz, 1H), 7.40 (d, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.21 (t, *J* = 7.5 Hz, 1H), 6.71 (d, *J* = 11.5 Hz, 1H), 6.52 (d, *J* = 16.5 Hz, 1H), 2.23 (t, *J* = 7.5 Hz, 2H), 1.38-1.43 (m, 2H), 1.27-1.35 (m, 14H), 0.91 (t, *J* = 7.0 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 144.2, 137.9, 133.4, 129.2, 128.5, 127.2, 126.5, 83.1, 36.7, 32.5, 24.9, 24.7, 14.0 (B-alkenyl carbon signal not observed); <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) δ 30.0; IR (ATR) 2976, 2957, 2929, 2871, 1714, 1680, 1597, 1449, 1404, 1390, 1371, 1326, 1245, 1214, 1140, 1008, 973, 748, 690 cm<sup>-1</sup>; HRMS (DART) calcd for C<sub>20</sub>H<sub>30</sub>BO<sub>2</sub> ([M+H]<sup>+</sup>) 313.23388, found 313.23470.



**7o**: 3.5 hr, *EE/EZ* = 93 : 7, 90% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.60 (dd, *J* = 15.5, 10.5 Hz, 1H), 7.38 (dd, *J* = 7.0, 1.0 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.19 (t, *J* = 6.5 Hz, 1H), 6.69 (d, *J* = 11.0 Hz, 1H), 6.51 (d, *J* = 15.5 Hz, 1H), 2.21 (t, *J* = 7.5 Hz, 2H), 1.39-1.42 (m, 2H), 1.32 (m, 12H), 1.26 (br, 10H), 0.87 (t, *J* = 6.5 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 144.2, 137.9, 133.4, 129.2, 128.5, 127.3, 126.5, 83.1, 37.1, 31.9, 30.3, 29.5, 29.4, 29.3, 24.9, 22.7, 14.1 (B-alkenyl carbon signal not observed); <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) δ 29.9; IR (ATR) 2976, 2955, 2924, 2853, 1587, 1449, 1423, 1404, 1389, 1371, 1350, 1292, 1270, 1142, 1109, 868, 690 cm<sup>-1</sup>; HRMS (DART) calcd for C<sub>24</sub>H<sub>38</sub>BO<sub>2</sub> ([M+H]<sup>+</sup>) 369.29648, found 369.29744.



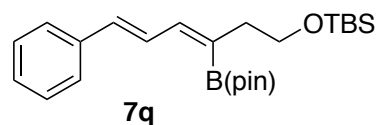
**7p**: 3.5 hr, *EE/EZ* = 86 : 14, 86% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.63 (dd, *J* = 15.0, 10.5 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.21 (t, *J* = 7.5 Hz, 1H), 6.68 (d, *J* = 11.0 Hz, 1H), 6.54 (d, *J* = 16.0 Hz, 1H), 2.12 (d, *J* = 6.5 Hz, 2H), 1.71-1.77 (m, 1H), 1.33 (s, 12H), 0.89 (d, *J* = 7.0 Hz, 6H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 145.4, 137.9, 133.5, 129.1, 128.5, 127.3, 126.5, 83.1, 46.4, 29.1, 24.9, 22.5 (B-alkenyl carbon signal not observed); <sup>11</sup>B NMR (160 MHz, CDCl<sub>3</sub>) δ 30.0; IR (ATR) 2976, 2953, 2929, 2867, 1621, 1597, 1586, 1464, 1449, 1424, 1404, 1389, 1371, 1292, 1281, 1212, 1165,





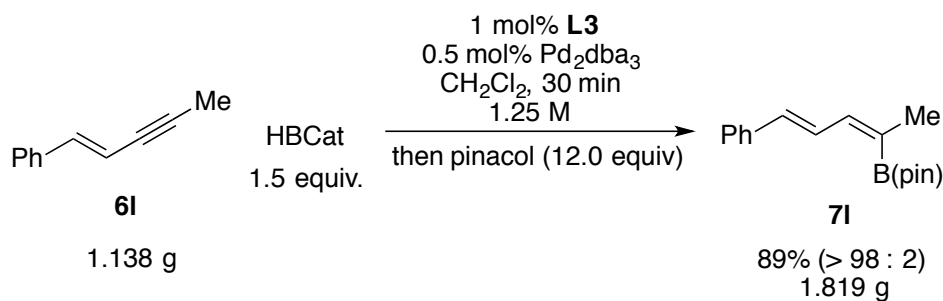
1141, 1108, 1029, 966, 865, 749, 691  $\text{cm}^{-1}$ ; HRMS (DART) calcd for  $\text{C}_{20}\text{H}_{30}\text{BO}_2$  ( $[\text{M}+\text{H}]^+$ ) 313.23388, found 313.23389.

**7q**: 3.5 hr, *EE/EZ* = 93 : 7, 86% yield.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.66 (dd,  $J$  = 16.0, 11.5 Hz, 1H), 7.41 (d,  $J$  = 8.0 Hz, 2H), 7.32 (t,  $J$  = 8.0 Hz, 2H), 7.22 (t,  $J$  = 7.5 Hz, 1H), 6.77 (d,  $J$  = 11.0 Hz, 1H), 6.55 (d,  $J$  = 15.5 Hz,



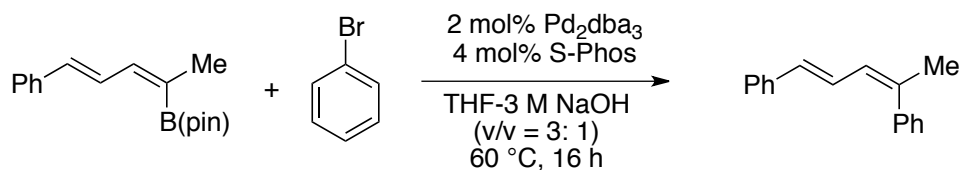
1H), 3.66 (t,  $J$  = 7.0 Hz, 2H), 2.45 (t,  $J$  = 7.0 Hz, 2H), 1.32 (s, 12H), 0.90 (s, 9H), 0.06 (s, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  147.2, 137.7, 134.3, 129.1, 128.5, 127.4, 126.6, 83.1, 63.7, 40.6, 26.0, 24.9, 18.4, -5.2 (B-alkenyl carbon signal not observed);  $^{11}\text{B}$  NMR (160 MHz,  $\text{CDCl}_3$ )  $\delta$  29.7; IR (ATR) 2976, 2953, 2928, 2885, 2856, 1623, 1588, 1471, 1449, 1426, 1293, 1269, 1248, 1213, 1163, 1141, 1082, 1026, 1006, 967, 949, 832, 774, 748, 671  $\text{cm}^{-1}$ ; HRMS (DART) calcd for  $\text{C}_{24}\text{H}_{38}^{11}\text{BO}_3\text{Si}$  ( $[\text{M}+\text{H}]^+$ ) 413.26833, found 413.26786.

### Gram-scale trans-hydroboration of **7l**



To a 20-mL vial charged with ligand **L3** (34.5 mg, 0.0800 mmol) and Pd<sub>2</sub>dba<sub>3</sub> (36.6 mg, 0.0400 mmol) was added CH<sub>2</sub>Cl<sub>2</sub> (1.4 mL). The resulting mixture was allowed to stir at room temperature for 16 hr to generate the Pd/L complex. Then, 1,3-enyne **6l** (1.138 g, 8.000 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5.0 mL) was added to the catalyst solution, followed by slow addition (ca. 5 min) of HBCat (1.25 mL, 12.0 mmol) via syringe. The resulting mixture was allowed to stir at room temperature for 0.5 hr. At the conclusion of the reaction, the crude NMR was then taken to determine the stereoselectivity. The crude mixture was then poured into a 500-mL flask charged with a pinacol solution (11.3 g, 96.0 mmol) in 50 mL CH<sub>2</sub>Cl<sub>2</sub>. The resulting mixture was then allowed to stir at room temperature for 1 hr. The mixture was then diluted with water (200 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 50 mL). The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent, the residue was purified by column chromatography on silica gel with hexanes/EtOAc (100: 1) as the eluent to afford **7l** as a white solid (1.819 g, 84%, *EE/EZ* > 98: 2). The characterization data are consistent with those described using the general procedure H.

### Suzuki-Miyaura coupling of **7l** with bromobenzene (eq 2)

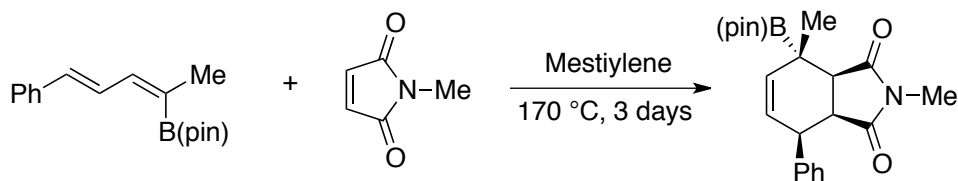


The protocol for the Suzuki-Miyaura coupling was adapted from literature procedures.<sup>22</sup> To a 20-mL reaction flask charged with S-Phos (3.2 mg, 0.0080 mmol), Pd<sub>2</sub>dba<sub>3</sub> (3.6 mg, 0.0040 mmol), dienyl boronate **7l** (51.2 mg, 0.190 mmol), and bromobenzene (47.0 mg, 0.300 mmol) was added THF (1.8 mL) followed by 3.0 M aq. NaOH (0.60 mL, 1.80

mmol). After degasing the reaction mixture via freeze-pump-thaw cycles (3 times), the reaction mixture was allowed to stir at 60 °C for 16 hr. At the conclusion of the reaction, the reaction mixture was allowed to cool to the room temperature. Water (2.0 mL) and ether (2.0 mL) were then added to quench the reaction. The organic layer was separated, and the aqueous layer was extracted 3 times with ether. The combined organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent, the crude residue was purified by column chromatography on silica gel using hexanes as the eluent to afford **8** as colorless oil (36.4 mg, 87%).

*EZ/EE* > 98: 2. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.38-7.42 (m, 2H), 7.24-7.33 (m, 7H), 7.17-7.19 (m, 1H), 6.88 (dd, *J* = 15.5, 11.5 Hz, 1H), 6.55 (d, *J* = 15.5 Hz, 1H), 6.33 (d, *J* = 10.5 Hz, 1H), 2.21 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 141.5, 139.5, 137.8, 131.3, 128.5, 128.4, 128.2, 127.6, 127.1, 126.7, 126.2, 25.6; IR (ATR) 3077, 3027, 2929, 1594, 1572, 1492, 1442, 1433, 1371, 1073, 1026, 1000, 963, 765, 747, 700, 691 cm<sup>-1</sup>; HRMS (DART) calcd for C<sub>17</sub>H<sub>17</sub> ([M+H]<sup>+</sup>) 221.13303, found 221.13331.

### *Diels-Alder Reaction of 7l with N-methyl maleimide (eq 3)*

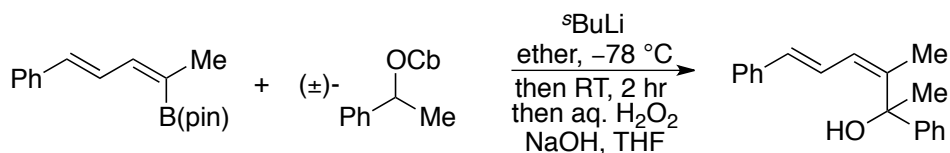


The Diels-Alder reaction was adapted from literature procedures.<sup>23</sup> To a J-Y tube charged with dienyl boronate **7l** (51.2 mg, 0.190 mmol) and *N*-Me maleimide (22.2 mg, 0.200 mmol) was added mesitylene (1.0 mL). The resulting mixture was heated at 170 °C for 3 days. At the conclusion of the reaction, the mixture was allowed to cool to room temperature. The mixture was then directly subjected to the column chromatography on silica gel with hexanes/EtOAc (7: 1) as the eluent to afford **9** as white solid (49.2 mg, 67%). Crystals of **9** suitable for single crystal X-ray diffraction analysis were grown from slow evaporation of a pentane solution at -30 °C.

*endo/exo* >98: 2. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.33 (t, *J* = 7.5 Hz, 2H), 7.21-7.28 (m, 3H), 6.08 (dd, *J* = 10.0, 4.0 Hz, 1H), 5.92 (dd, *J* = 14.5, 3.0 Hz, 1H), 3.58-3.61 (m, 1H), 3.44 (t, *J* = 7.5 Hz, 1H), 3.29 (d, *J* = 8.0 Hz, 1H), 2.75 (s, 3H), 1.54 (s, 3H), 1.29 (s, 6H),

1.25 (s, 6H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  178.1, 176.9, 141.0, 138.1, 129.4, 128.6, 128.2, 127.2, 84.8, 48.7, 46.7, 41.9, 25.2, 24.8, 24.6, 20.6 (B-allyl carbon signal not observed);  $^{11}\text{B}$  NMR (160 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  32.6; IR (ATR) 3030, 2976, 2930, 2873, 1772, 1696, 1453, 1431, 1372, 1318, 1285, 1213, 1166, 1105, 966, 914, 732  $\text{cm}^{-1}$ ; HRMS (DART) calcd for  $\text{C}_{22}\text{H}_{29}\text{BNO}_4$  ( $[\text{M}+\text{H}]^+$ ) 382.21896, found 382.22021.

#### Homologation of **7l** (eq 4)



The homologation reaction was adapted from literature procedures.<sup>24</sup> To a 20-mL vial charged with racemic carbamate (125 mg, 0.500 mmol) and anhydrous  $\text{Et}_2\text{O}$  (2.0 mL) was slowly added  $^s\text{BuLi}$  (0.38 mL, 1.4 M in cyclohexane, 0.53 mmol) in a dropwise fashion within 2 min at  $-78\text{ }^\circ\text{C}$ . The resulting mixture was allowed to stir at  $-78\text{ }^\circ\text{C}$  for 30 min, and then dienyl boronate ester **7l** (140 mg, 0.518 mmol) in  $\text{Et}_2\text{O}$  (1.0 mL) was added dropwise within 2 min by vigorous stirring at  $-78\text{ }^\circ\text{C}$ . The reaction mixture was allowed to stir at  $-78\text{ }^\circ\text{C}$  for 30 min, and then at room temperature for 2 hr. At the conclusion of the reaction, the reaction mixture was quenched with  $\text{H}_2\text{O}$  (0.10 mL). After removal of the solvent, the mixture was passed through a pad of silica gel with hexanes/ $\text{EtOAc}$  (7: 1) as the eluent to afford the crude homologated product. This crude material was then dissolved in anhydrous THF (2.0 mL) containing BHT (2.5 mg), and the mixture was cooled to  $0\text{ }^\circ\text{C}$ . Then, an ice-cold mixture of 3.0 M NaOH (1.4 mL) and 30% aq.  $\text{H}_2\text{O}_2$  (0.7 mL) was added all at once at  $0\text{ }^\circ\text{C}$ . The resulting mixture was then allowed to stir at room temperature for 0.5 hr. Then the mixture was diluted with  $\text{H}_2\text{O}$  (10 mL) and extracted with  $\text{Et}_2\text{O}$  (3 X 10 mL). The combined organic layer was then dried over  $\text{Na}_2\text{SO}_4$ . After removal of the solvent, the residue was purified by column chromatography on silica gel with hexanes/ $\text{EtOAc}$  (15: 1) as the eluent to afford **11** as a colorless oil (82.0 mg, 62%).

$^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  7.52-7.54 (m, 2H), 7.35-7.38 (m, 2H), 7.22-7.28 (m, 3H), 7.13-7.19 (m, 4H), 6.29 (d,  $J = 15.0\text{ Hz}$ , 1H), 6.09 (d,  $J = 11.5\text{ Hz}$ , 1H), 2.10 (s, 1H), 1.93 (s, 3H), 1.77 (s, 3H);  $^{13}\text{C}$  NMR (160 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  148.8, 144.4, 138.4 132.1, 129.0,

128.8, 128.4, 127.7, 127.6, 127.3, 126.8, 126.0, 78.0, 30.0, 23.8; IR (ATR) 3559 3447, 3057, 3022, 2972, 2936, 1595, 1491, 1446, 1369, 1308, 1268, 1066, 999, 907, 748, 692  $\text{cm}^{-1}$ ; HRMS calcd for  $\text{C}_{19}\text{H}_{19}$  ( $[\text{M}+\text{H}-\text{H}_2\text{O}]^+$ ) 247.14868, found 247.14847.

#### ***Preparation of complex 12 and its use in trans-hydroboration***

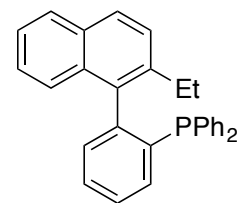
To a 5-ml vial charged 1,4-azaborine **L4** (21 mg, 0.047 mmol) and  $\text{Pd}_2\text{dba}_3$  (21 mg, 0.023 mmol) was added  $\text{CH}_2\text{Cl}_2$  (0.90 ml). The mixture was stirred at room temperature for 4 hours. Then,  $\text{CH}_2\text{Cl}_2$  was removed under vacuum. The resulting mixture was recrystallized from benzene/pentane to afford complex **12** as reddish crystal suitable for single crystal X-ray diffraction analysis (27 mg, 73% yield). Due to conformational dynamics the  $^1\text{H}$  and  $^{13}\text{C}$  NMR signals are broad.  $^{11}\text{B}$  NMR (160 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  32.4 (br);  $^{31}\text{P}$  NMR (202 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  29.2 (br); IR (ATR) 3051, 2949, 2919, 2859, 1638, 1620, 1572, 1447, 1434, 1366, 1331, 1181, 1094, 1076, 953, 758, 744, 694, 640  $\text{cm}^{-1}$ .

#### ***Hydroboration of 4a with complex 12***

A 5-mL vial was charged with complex **12** (7.9 mg, 0.01 mmol) and  $\text{CH}_2\text{Cl}_2$  (1.0 ml), and the mixture was stirred for 10 min to produce a homogeneous solution. Then, HBCat (45 mg, 0.375 mmol) and 1,3-enyne **4a** (32 mg, 0.25 mmol) were added. The resulting mixture was allowed to stir at room temperature for 30 min. Then, pinacol (354 mg, 3.0 mmol) in  $\text{CH}_2\text{Cl}_2$  (3.0 mL) was introduced, and the mixture was allowed to stir at room temperature for 1 hr. After removal of the solvent, the crude residue was purified by column chromatography on silica gel with (Hex/EtOAc = 100: 1) as the eluent to afford **5a** as light yellow oil (52 mg, 81%, >98:2 *trans*-hydroboration selectivity). The characterization data is identical to those reported under general procedure G (Table 2).

### ***Synthesis of CC-L3 and its performance in hydroboration reactions***

To a 20-mL round bottom flask containing 1-bromo-2-ethylnaphthalene<sup>25</sup> (94 mg, 0.40 mmol) and magnesium (23 mg, 0.96 mmol) were added THF (5.0 mL). The reaction mixture was then heated to 65 °C in an oil bath and 1,2-dibromoethane (2.0 μL) was added dropwise via syringe to initiate the reaction. After heating the mixture at 65 °C for 60 min, 1-bromo-2-chloro-benzene (84 mg,



**CC-L3**

0.44 mmol) was added at the same temperature slowly over one hour. After an additional 1 hour of stirring at 65 °C, the reaction mixture was allowed to cool to room temperature, and the reaction vessel was moved into the glove box. Anhydrous copper(I) chloride (8.0 mg, 0.08 mmol) was added into the mixture. Then, ClPPh<sub>2</sub> (88 mg, 0.40 mmol) was added via syringe. The resulting mixture was stirred at room temperature for 12 hours. The reaction was quenched with H<sub>2</sub>O (10 mL), and the resulting mixture was extracted with Et<sub>2</sub>O (2 times, 10 mL each). The combined organic layers were dried over MgSO<sub>4</sub>, concentrated and purified by column chromatography on silica gel with hexanes/EtOAc (100/1) as the eluent to afford a white solid (50 mg, 30% yield).

<sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 7.84 (d, *J* = 8.5 Hz, 1H, ArH), 7.81 (dt, *J* = 8.2, 0.9 Hz, 1H, ArH), 7.49 (td, *J* = 7.4, 1.4 Hz, 1H, ArH), 7.45 – 7.38 (m, 2H, ArH), 7.37 – 7.13 (m, 12H, ArH), 7.09 – 7.01 (m, 3H, ArH), 2.31 – 2.11 (m, 2H, CH<sub>2</sub>CH<sub>3</sub>), 0.99 (t, *J* = 7.6 Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>); <sup>13</sup>C NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 146.14 (d, *J* = 33.5 Hz), 140.37 (d, *J* = 1.9 Hz), 138.63 (d, *J* = 11.8 Hz), 137.95 (d, *J* = 12.9 Hz), 137.48 (d, *J* = 12.9 Hz), 137.17 (d, *J* = 7.3 Hz), 134.87 (d, *J* = 1.9 Hz), 134.20 (d, *J* = 20.5 Hz), 133.81 (d, *J* = 20.0 Hz), 133.46 (d, *J* = 2.1 Hz), 132.07, 131.34 (d, *J* = 6.2 Hz), 129.46, 128.83, 128.74, 128.68, 128.60, 128.57, 128.22, 127.99 (d, *J* = 12.4 Hz), 126.94, 126.88, 125.90, 125.03, 27.16 (d, *J* = 1.7 Hz), 15.30; <sup>31</sup>P NMR (202 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ -15.39; IR (ATR) 3050, 2964, 1476, 1457, 1432, 1374, 1088, 1067, 1025, 951, 817, 763, 741, 711, 695, 678, 621, 504, 429, 417; HRMS (DART) calcd for C<sub>30</sub>H<sub>26</sub>P ([M+H]<sup>+</sup>) 417.17721, found 417.17894.

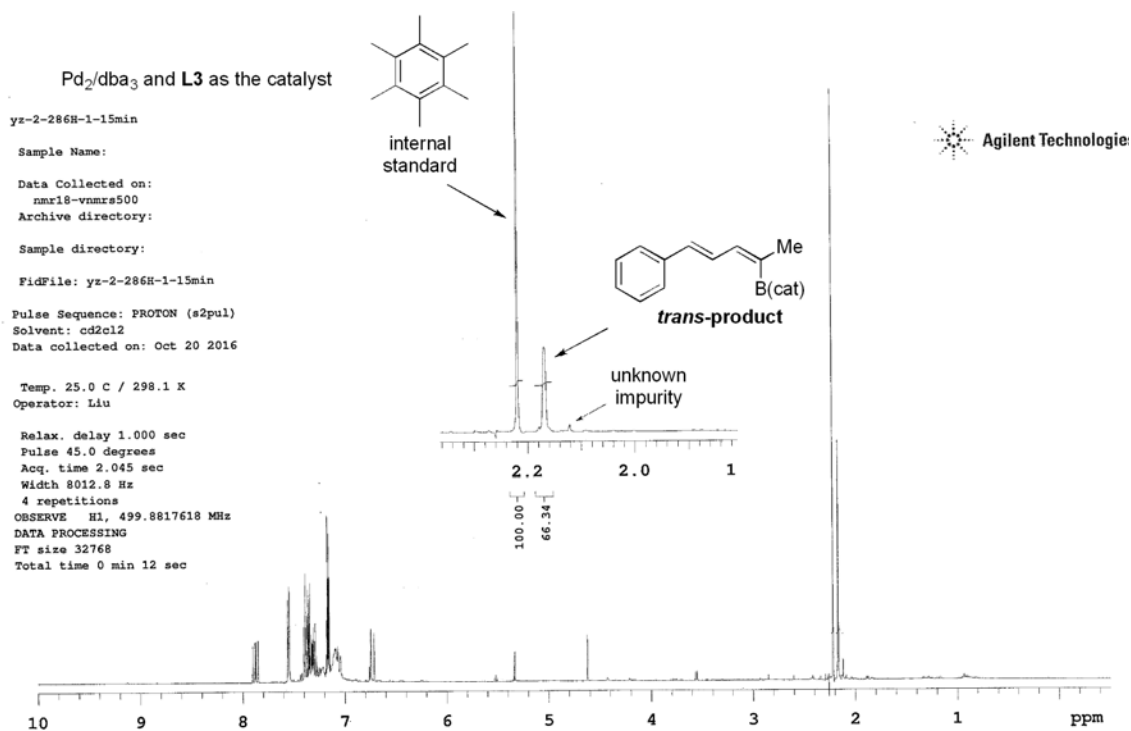
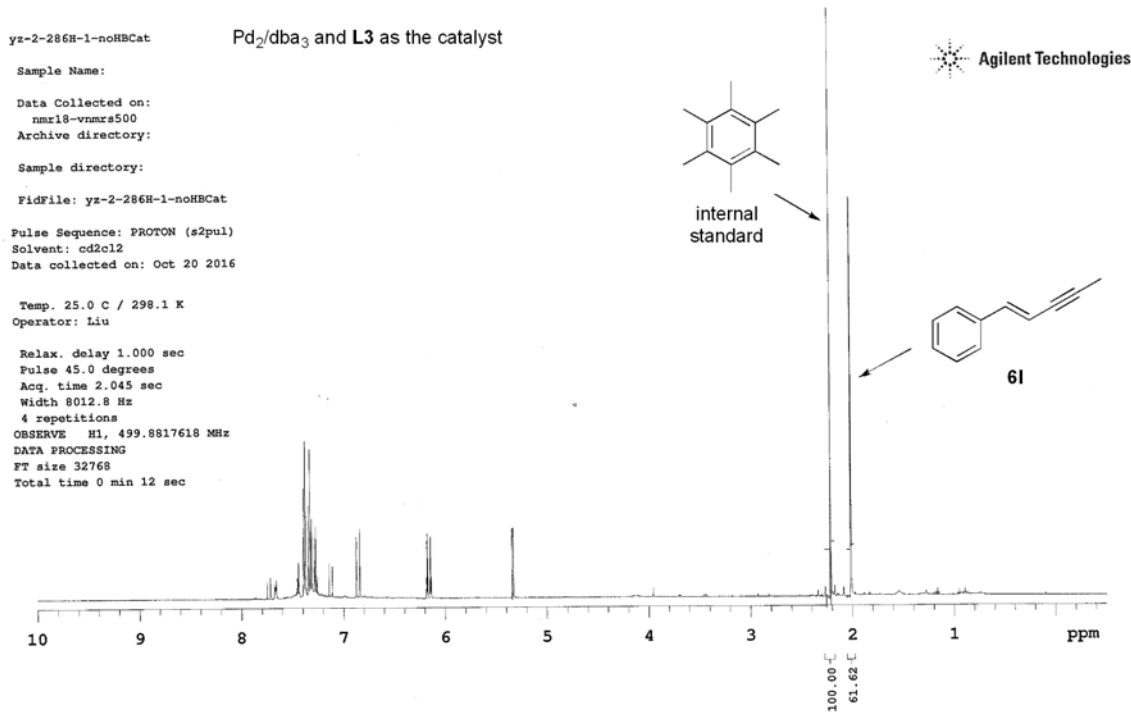
### ***Comparative Trans-Hydroboration Catalysis Pd/L3 vs. Pd/CC-L3***

To a 4-mL vial charged with ligand **L3** (21.6 mg, 0.050 mmol) or **CC-L3** (20.8 mg, 0.050 mmol) and Pd<sub>2</sub>dba<sub>3</sub> (22.9 mg, 0.025 mmol) was added CH<sub>2</sub>Cl<sub>2</sub> (1.0 mL). The resulting mixture was allowed to stir at room temperature for 16 hours to generate the Pd/L complexes. The resulting two stock solutions (0.05 M in CH<sub>2</sub>Cl<sub>2</sub>) were used for the catalytic reactions.

To a 4-mL vial charged with stock solution of catalyst (200 μL, 0.05 M in CH<sub>2</sub>Cl<sub>2</sub>, 0.01 mmol), internal standard hexamethylbenzene, **6I** (35.5mg, 0.25 mmol), was added catecholborane (45.0 mg, 0.375 mmol). The resulting mixture was allowed to stir at room temperature for 15 min. After removal of the solvent, the conversion, the percentage of *trans*-, *cis*-hydroboration and allene products were determined by <sup>1</sup>H NMR.

catalyst	conversion (%)	<i>trans</i> -hydroboration (%)	<i>cis</i> -hydroboration (%)	allene (%)
Pd/L3	100	>98	0	0
Pd/CC-L3	71	52	9	6

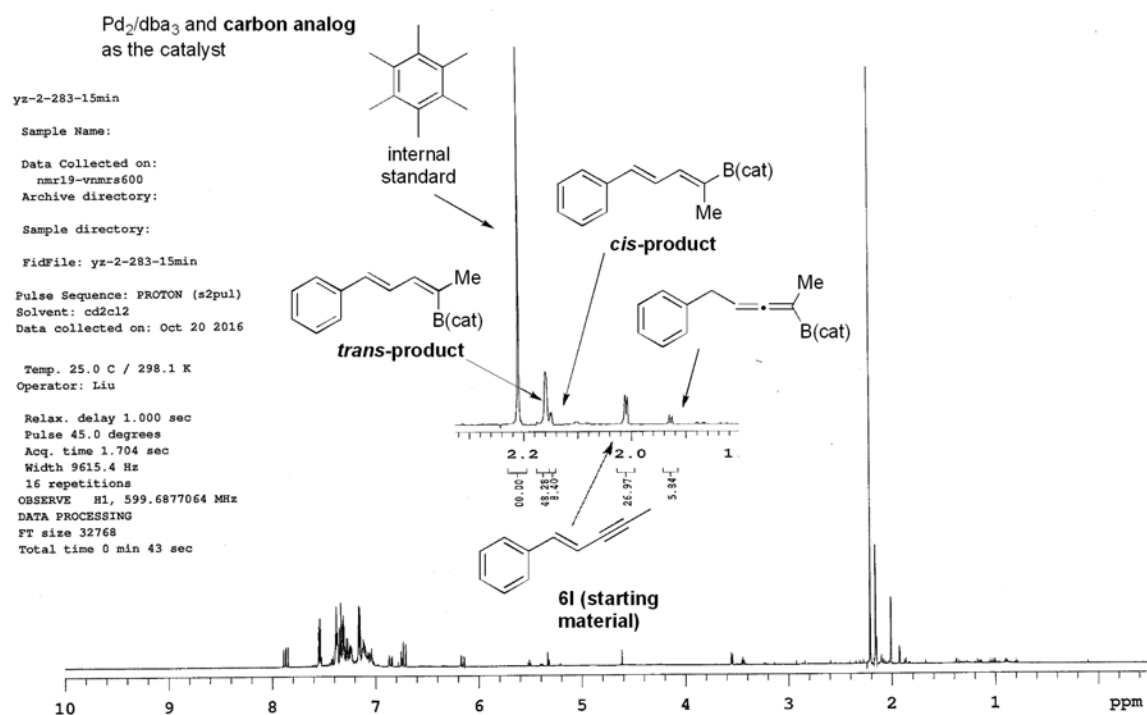
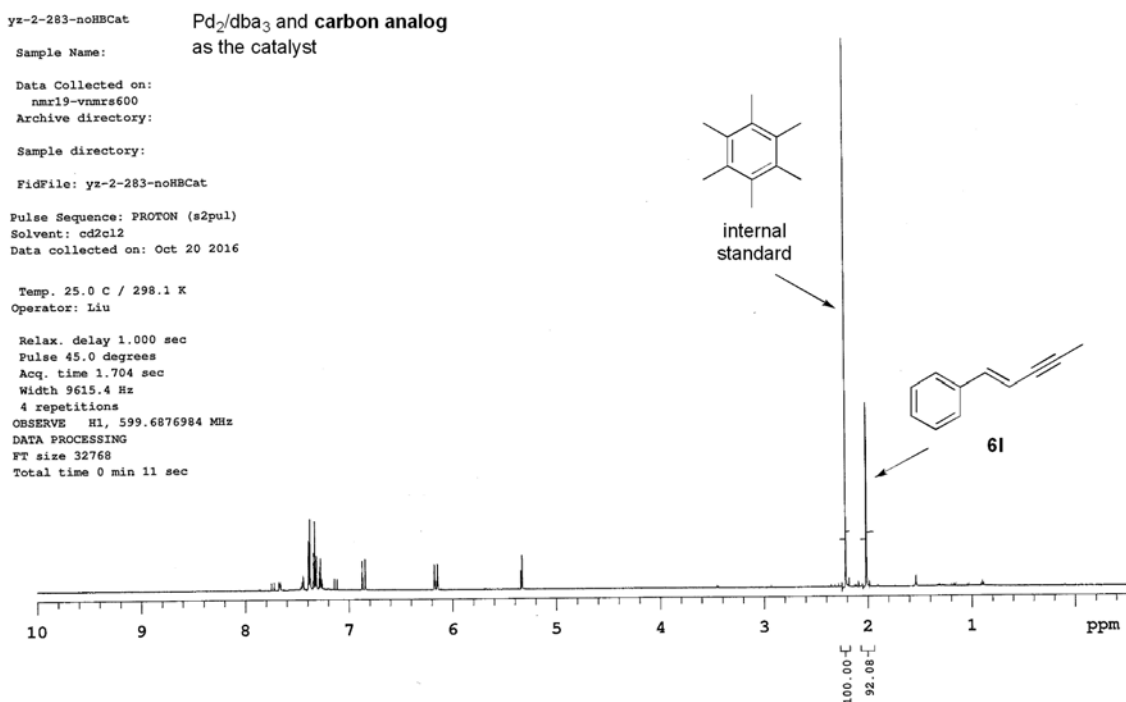
$^1\text{H}$  NMR before addition of H-BCat for Pd/L3 system.



$^1\text{H}$  NMR at the conclusion of the reaction.



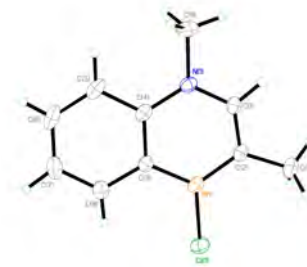
$^1\text{H}$  NMR before addition of H-BCat for Pd/CC-L3 system.



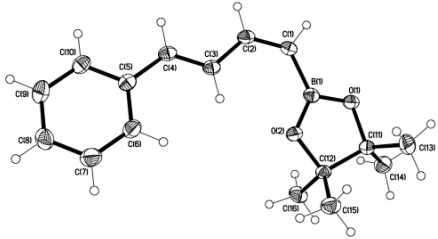
$^1\text{H}$  NMR at the conclusion of the reaction.

### Crystallographic data for 3a (Liu160)

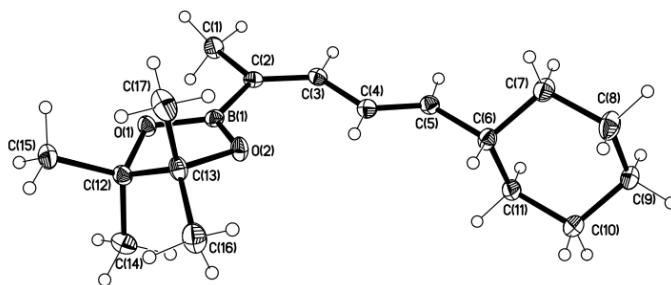
Identification code	liu160	
Empirical formula	C <sub>10</sub> H <sub>11</sub> B Cl N	
Formula weight	191.46	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.6350(13) Å	$\alpha = 89.640(3)^\circ$
	b = 9.2691(16) Å	$\beta = 79.774(3)^\circ$
	c = 14.887(3) Å	$\gamma = 70.461(3)^\circ$
Volume	975.5(3) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.304 Mg/m <sup>3</sup>	
Absorption coefficient	0.339 mm <sup>-1</sup>	
F(000)	400	
Crystal size	0.27 x 0.19 x 0.12 mm <sup>3</sup>	
Theta range for data collection	2.34 to 25.00°	
Index ranges	-9<=h<=9, -11<=k<=11, -17<=l<=17	
Reflections collected	9361	
Independent reflections	3416 [R(int) = 0.0550]	
Completeness to theta = 25.00°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9605 and 0.9141	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	3416 / 0 / 323	
Goodness-of-fit on F <sup>2</sup>	0.980	
Final R indices [I>2sigma(I)]	R1 = 0.0488, wR2 = 0.1344	
R indices (all data)	R1 = 0.0548, wR2 = 0.1426	
Largest diff. peak and hole	0.405 and -0.257 e.Å <sup>-3</sup>	



### Crystallographic data for 5a

Empirical formula	C <sub>16</sub> H <sub>21</sub> BO <sub>2</sub>	
Formula weight	256.14	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C c	
Unit cell dimensions	a = 8.2753(8) Å	$\alpha = 90^\circ$ .
	b = 23.637(3) Å	$\beta = 91.4540(18)^\circ$ .
	c = 15.5395(16) Å	$\gamma = 90^\circ$ .
Volume	3038.5(5) Å <sup>3</sup>	
Z	8	
Density (calculated)	1.120 Mg/m <sup>3</sup>	
Absorption coefficient	0.071 mm <sup>-1</sup>	
F(000)	1104	
Crystal size	0.600 x 0.450 x 0.380 mm <sup>3</sup>	
Theta range for data collection	1.723 to 28.360°.	
Index ranges	-10 ≤ h ≤ 11, -31 ≤ k ≤ 31, -20 ≤ l ≤ 20	
Reflections collected	21673	
Independent reflections	7208 [R(int) = 0.0213]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7457 and 0.7003	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	7208 / 2 / 351	
Goodness-of-fit on F <sup>2</sup>	1.033	
Final R indices [I > 2σ(I)]	R1 = 0.0352, wR2 = 0.0890	
R indices (all data)	R1 = 0.0378, wR2 = 0.0907	
Absolute structure parameter	0.1(2)	
Extinction coefficient	na	
Largest diff. peak and hole	0.274 and -0.164 e. Å <sup>-3</sup>	

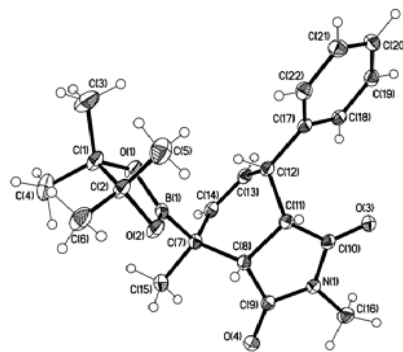
*Crystallographic data for 7a*



Empirical formula	C <sub>17</sub> H <sub>29</sub> B O <sub>2</sub>
Formula weight	276.21
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2 <sub>1</sub> /c
Unit cell dimensions	a = 11.7894(15) Å      α = 90° b = 6.7732(9) Å      β = 96.611(2)° c = 21.252(3) Å      γ = 90°
Volume	1685.7(4) Å <sup>3</sup>
Z	4
Density (calculated)	1.088 Mg/m <sup>3</sup>
Absorption coefficient	0.068 mm <sup>-1</sup>
F(000)	608
Crystal size	0.350 x 0.160 x 0.120 mm <sup>3</sup>
Theta range for data collection	1.739 to 28.268°
Index ranges	-15 ≤ h ≤ 15, -9 ≤ k ≤ 8, -28 ≤ l ≤ 28
Reflections collected	31882
Independent reflections	4162 [R(int) = 0.0457]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.7082
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	4162 / 0 / 186
Goodness-of-fit on F <sup>2</sup>	1.027
Final R indices [I > 2σ(I)]	R1 = 0.0420, wR2 = 0.0965
R indices (all data)	R1 = 0.0584, wR2 = 0.1055
Extinction coefficient	na
Largest diff. peak and hole	0.341 and -0.229 e.Å <sup>-3</sup>

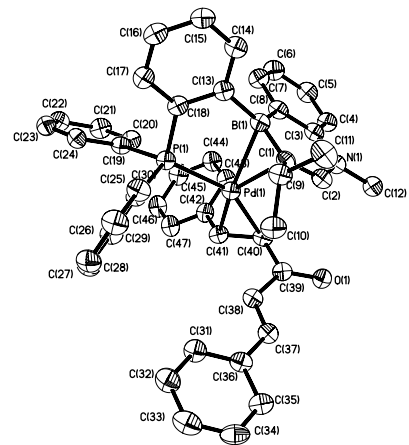
### Crystallographic data for 9

Identification code	C22H28BNO4
Empirical formula	C22H28BNO4
Formula weight	381.26
Temperature	100(2) K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	P2 <sub>1</sub> /c
Unit cell dimensions	a = 7.1599(3) Å      α = 90° b = 17.6140(8) Å     β = 90.955(2)° c = 33.0261(15) Å    γ = 90°
Volume	4164.5(3) Å <sup>3</sup>
Z	8
Density (calculated)	1.216 Mg/m <sup>3</sup>
Absorption coefficient	0.658 mm <sup>-1</sup>
F(000)	1632
Crystal size	0.300 x 0.060 x 0.050 mm <sup>3</sup>
Theta range for data collection	2.676 to 66.712°
Index ranges	-8 ≤ h ≤ 8, -20 ≤ k ≤ 20, -39 ≤ l ≤ 39
Reflections collected	45317
Independent reflections	7370 [R(int) = 0.0244]
Completeness to theta = 66.750°	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7528 and 0.6635
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	7370 / 0 / 517
Goodness-of-fit on F <sup>2</sup>	1.008
Final R indices [I > 2σ(I)]	R1 = 0.0344, wR2 = 0.0863
R indices (all data)	R1 = 0.0360, wR2 = 0.0878
Extinction coefficient	na
Largest diff. peak and hole	0.319 and -0.198 e. Å <sup>-3</sup>



### Crystallographic data for 12

Empirical formula	C <sub>54</sub> H <sub>51</sub> BNO Pd
Formula weight	878.14
Temperature	100(2) K
Wavelength	1.54178 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 12.0431(9) Å b = 15.5970(12) Å c = 23.7704(17) Å $\alpha = 85.720(3)^\circ$ $\beta = 89.462(3)^\circ$ $\gamma = 87.941(4)^\circ$
Volume	4449.5(6) Å <sup>3</sup>
Z	4
Density (calculated)	1.311 Mg/m <sup>3</sup>
Absorption coefficient	3.999 mm <sup>-1</sup>
F(000)	1824
Crystal size	0.220 x 0.130 x 0.050 mm <sup>3</sup>
Theta range for data collection	2.843 to 66.771°
Index ranges	-14 ≤ h ≤ 14, -18 ≤ k ≤ 18, 0 ≤ l ≤ 28
Reflections collected	15665
Independent reflections	15665 [R(int) = ?]
Completeness to theta = 67.679°	97.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7528 and 0.4399
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	15665 / 45 / 1137
Goodness-of-fit on F <sup>2</sup>	1.060
Final R indices [I > 2σ(I)]	R1 = 0.0617, wR2 = 0.1714
R indices (all data)	R1 = 0.0697, wR2 = 0.1838
Extinction coefficient	na
Largest diff. peak and hole	2.032 and -1.121 e.Å <sup>-3</sup>

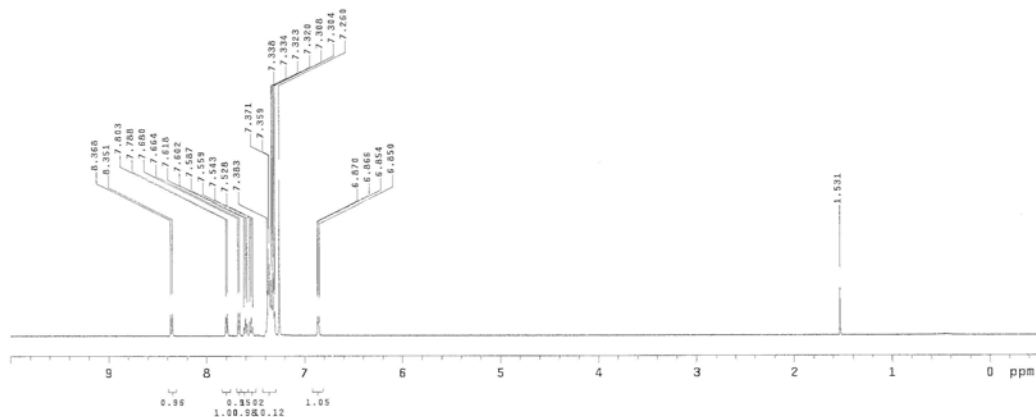
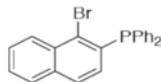


## References

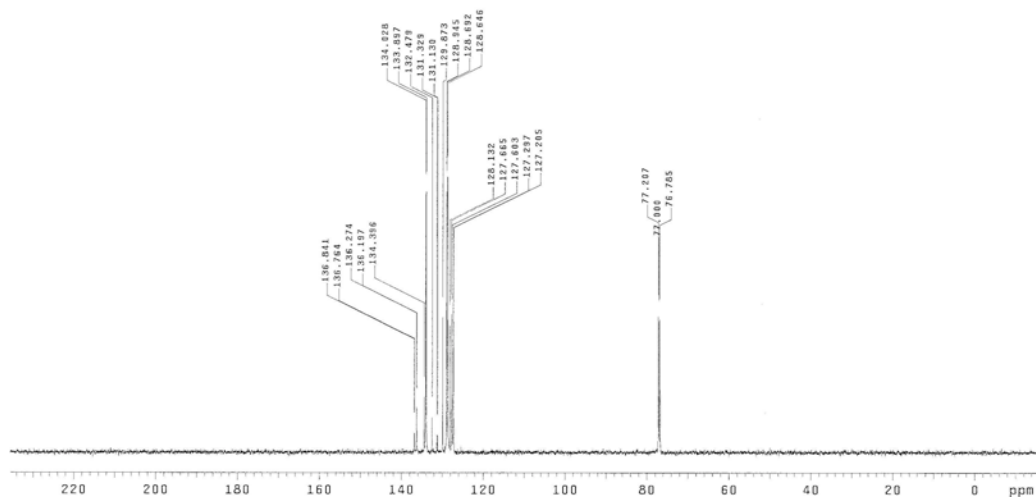
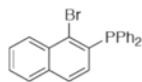
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**NMR spectra of all compounds**  
**Compound S1**

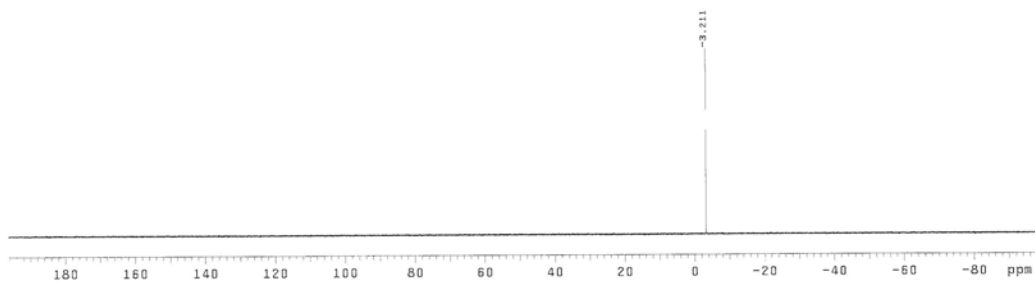
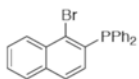


<b>PULSE SEQUENCE</b> Relax. delay 5.000 sec Pulse 45.0 degrees Acq. time 2.176 sec Width 15096.2 Hz 15 repetitions	<b>OBSERVE</b> H1, 499.8000021	<b>DATA PROCESSING</b> FT size 65536 Total time 1 minutes	skx-12-159-H1 Solvent: cdc13 Temp. 25.0 C / 298.1 K Operator: Liu VNMR5-600 "nmr18"
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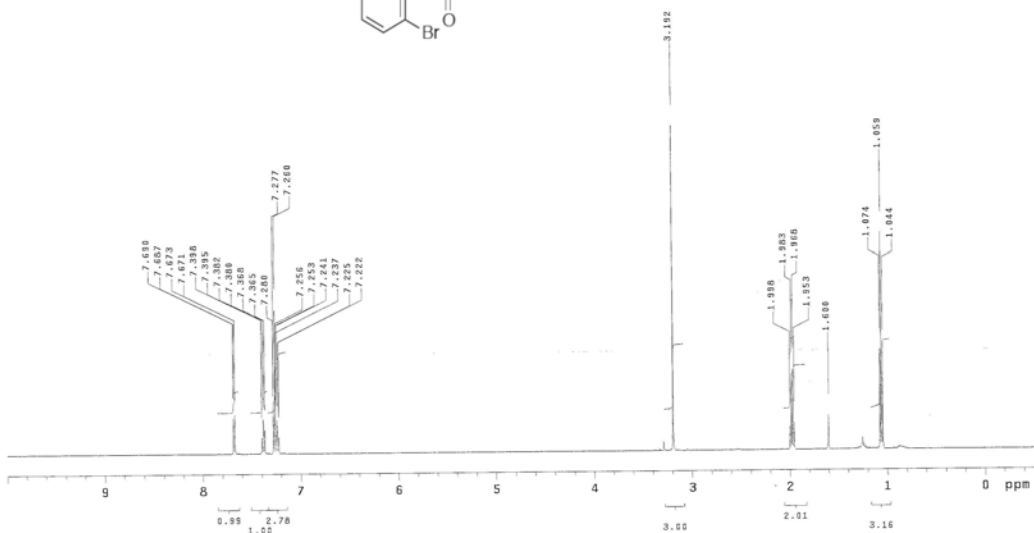
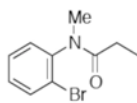
<b>PULSE SEQUENCE</b> Relax. delay 1.800 sec Pulse 45.0 degrees Acq. time 0.865 sec Width 37876.8 Hz 160 repetitions	<b>OBSERVE</b> C13, 152.7813202 <b>DECOUPLE</b> H1, 999.6005456 Power 45 dB Continuously on WALTZ-16 modulated	<b>DATA PROCESSING</b> Line broadening 3.0 Hz FT size 65536 Total time 4 minutes	skx-12-159-C13 Solvent: cdc13 Temp. 25.0 C / 298.1 K Operator: Liu VNMR5-600 "nmr18"
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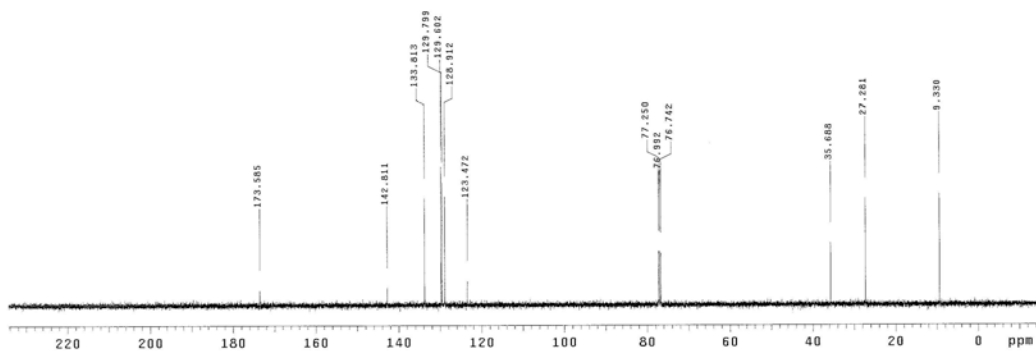
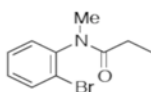


<b>PULSE SEQUENCE</b> Relax. delay 1.000 sec Pulse 45.0 degree Acq. time 2.351 sec Width 59523.8 Hz 58 repetitions	<b>OBSERVE</b> P31, 202.3554578 <b>DECOUPLE</b> H1, 499.8833015 Power 40 dB on during acquisition off during delay WALTZ-16 modulated	<b>DATA PROCESSING</b> Line broadening 0.5 Hz FT size 85536 Total time 1 minute	sxu-12-159-P31 Solvent: cdcl3 Temp: 25.0 C / 298.1 K Operator: Liu VNMRS-500 "nar18"
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### Compound 1a

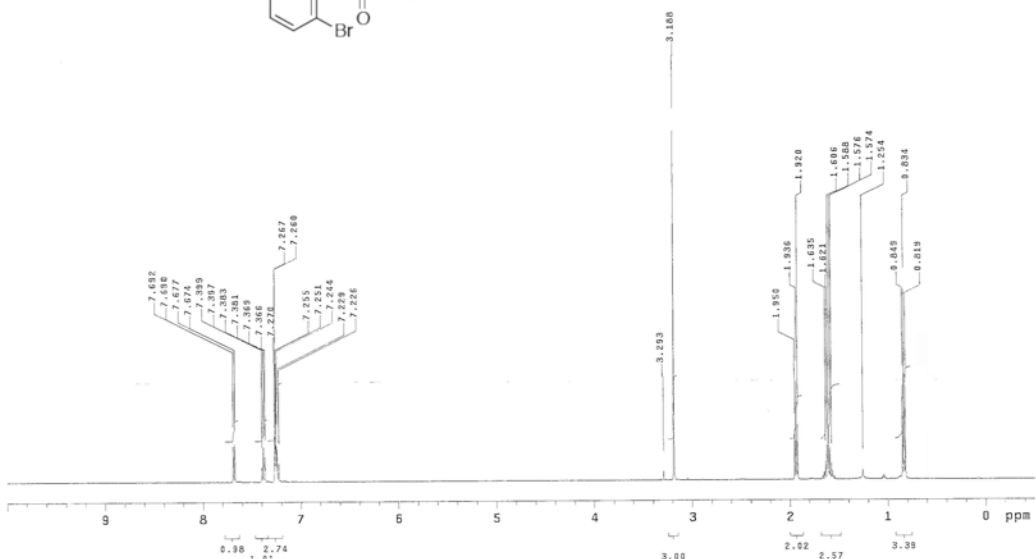
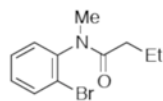


<b>PULSE SEQUENCE</b> Relax. delay 5.000 sec Pulse 45.0 degree Acq. time 2.045 sec Width 6021.6 Hz 8 repetitions	<b>OBSERVE</b> H1, 499.8800016	<b>DATA PROCESSING</b> FT size 32768 Total time 1 minute	sxu-12-235-2-H1 Solvent: cdcl3 Temp: 25.0 C / 298.1 K Operator: Liu VNMRS-500 "nar18"
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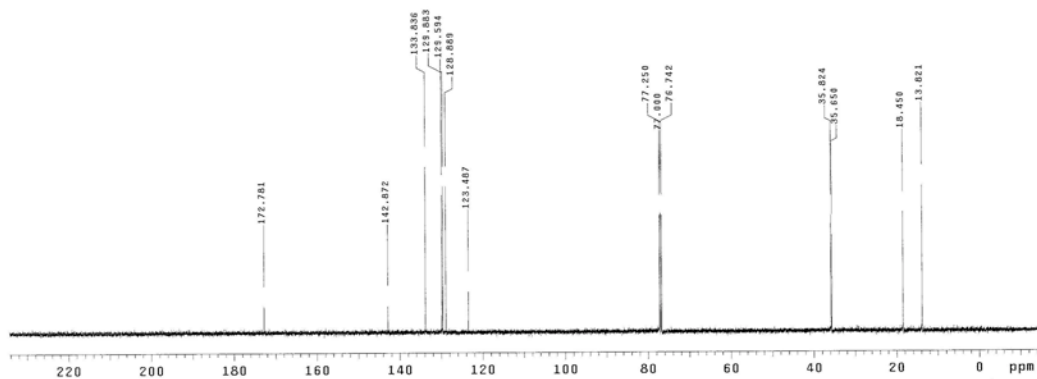
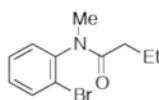


<b>PULSE SEQUENCE</b> Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 1.048 sec Width 31250.0 Hz 76 repetitions	<b>OBSERVE</b> C13, 125.6951388 DECOUPLE H1, 499.8038915 Power 40 dB Continuously on WALTZ-16 modulated	<b>DATA PROCESSING</b> Line broadening 0.5 Hz FT size 65536 Total time 2 minutes	sku-12-235-2-C13 Solvent: cdcl3 Temp: 25.0 C / 298.1 K Operator: Liu VNMRS-500 "nar18"
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### Compound 1b

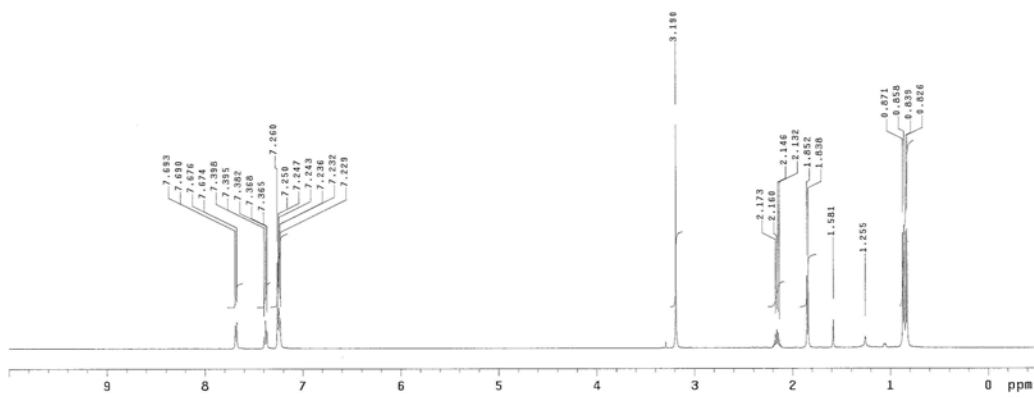
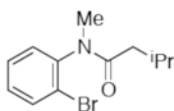


<b>PULSE SEQUENCE</b> Relax. delay 5.000 sec Pulse 45.0 degrees Acq. time 2.045 sec Width 8012.8 Hz 8 repetitions	<b>OBSERVE</b> H1, 499.8808016	<b>DATA PROCESSING</b> FT size 32768 Total time 1 minute	sku-12-235-1-H1 Solvent: cdcl3 Temp: 25.0 C / 298.1 K Operator: Liu VNMRS-500 "nar18"
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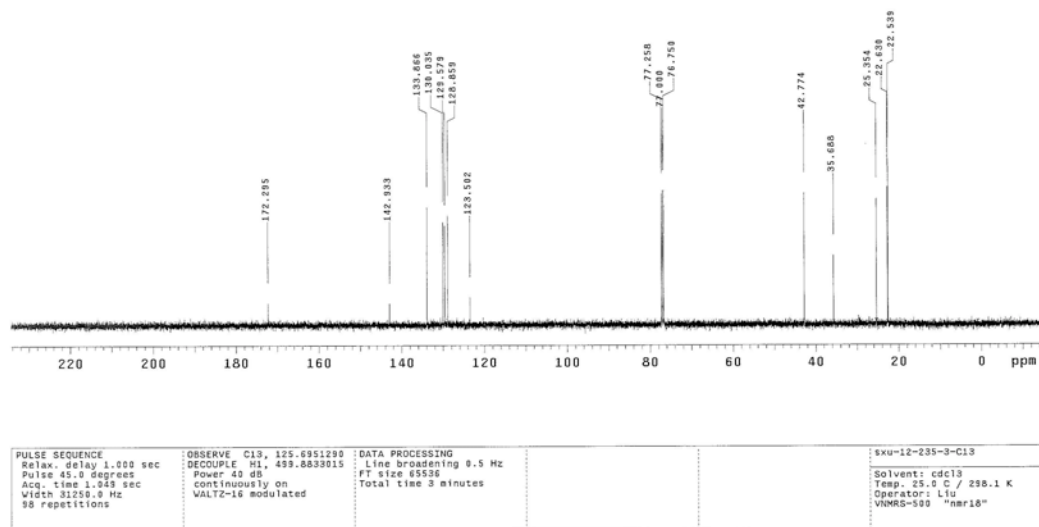
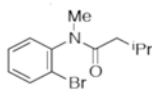


<b>PULSE SEQUENCE</b> Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 1.049 sec Width 31250.0 Hz 166 repetitions	<b>OBSERVE</b> C13, 125.6951319 <b>DECOUPLE</b> H1, 499.8033015 Power 40 dB continuously on WALTZ-16 modulated	<b>DATA PROCESSING</b> Line Broadening 0.5 Hz FT size 65536 Total time 3 minutes	sku-12-235-1-C13 Solvent: cdCl3 Temp. 25.0 C / 298.1 K Operator: Liu VNMR5-500 "nvr18"
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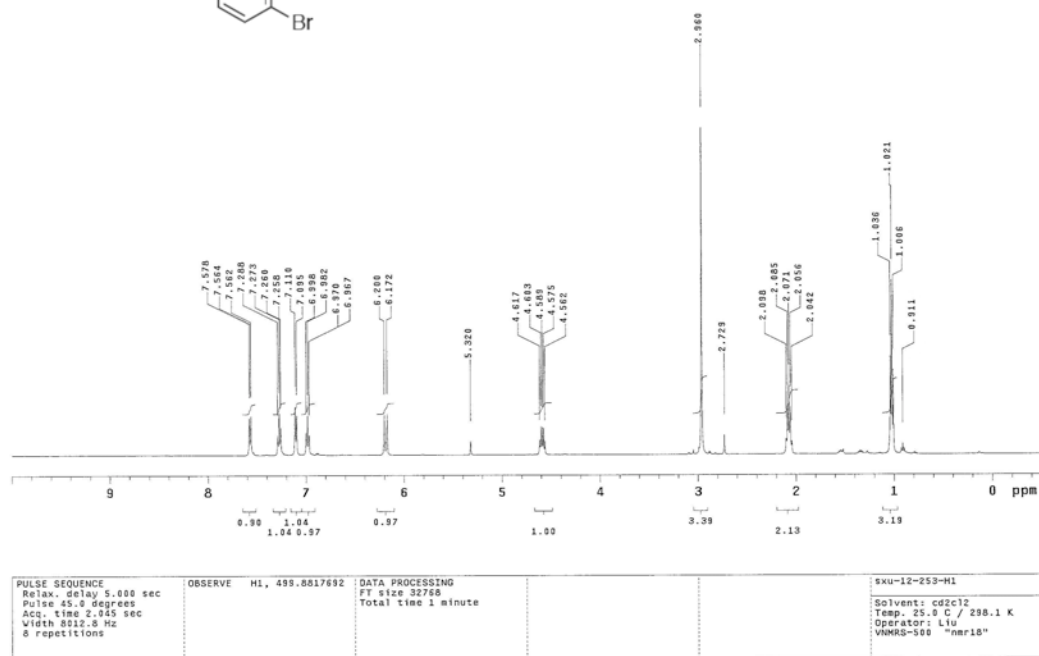
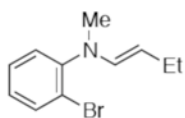
**Compound 1c**

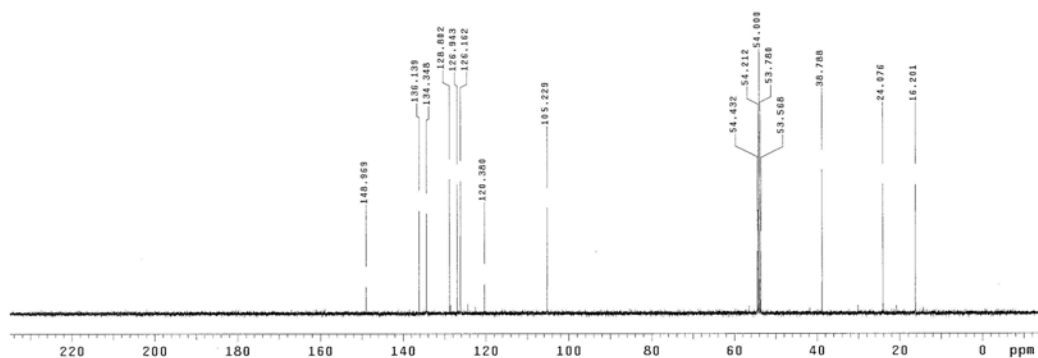
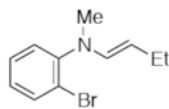


<b>PULSE SEQUENCE</b> Relax. delay 5.000 sec Pulse 45.0 degrees Acq. time 2.945 sec Width 8012.8 Hz 16 repetitions	<b>OBSERVE</b> H1, 499.8000016	<b>DATA PROCESSING</b> FT size 32768 Total time 1 minutes	sku-12-235-3-H1 Solvent: cdCl3 Temp. 25.0 C / 298.1 K Operator: Liu VNMR5-500 "nvr18"
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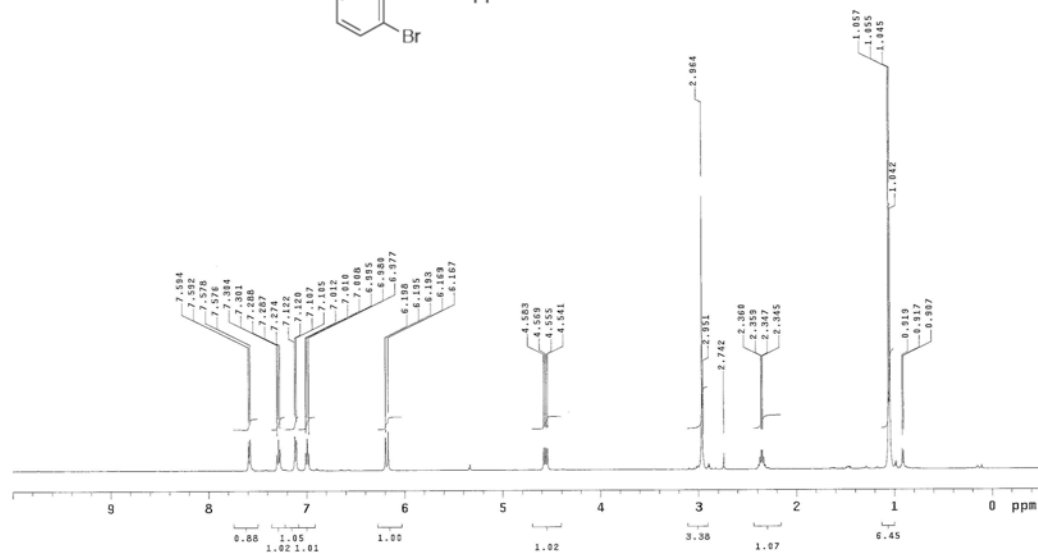
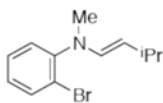
Compound 2b



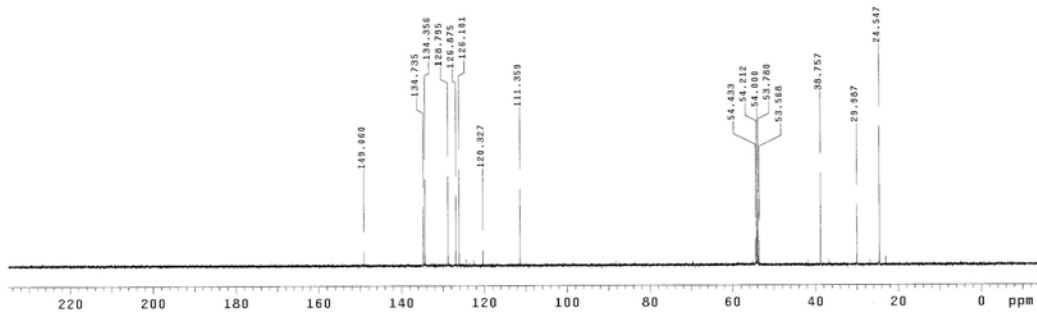
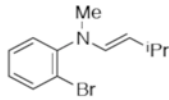


<b>PULSE SEQUENCE</b> Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 1.049 sec Width 31236.0 Hz 148 repetitions	<b>OBSERVE</b> C13, 125.6952907 DECOUPLE H1, 499.0842612 Power 49 dB Continuously on VMLT2-16 modulated	<b>DATA PROCESSING</b> Line broadening 0.5 Hz FT size 65536 Total time 5 minutes	sxu-12-253-C13 Solvent: cd2c12 Temp: 25.0 C / 298.1 K Operator: Liu VNMR5-500 "nar18"
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## Compound 2c

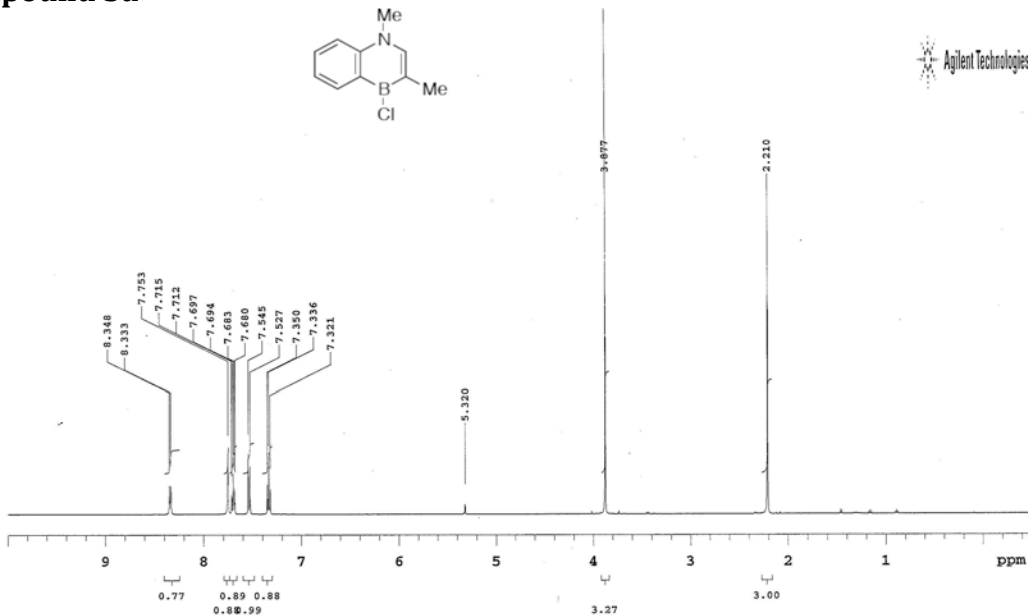
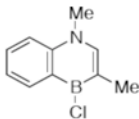


<b>PULSE SEQUENCE</b> Relax. delay 5.000 sec Pulse 45.0 degrees Acq. time 2.945 sec Width 8012.0 Hz 4 repetitions	<b>OBSERVE</b> H1, 499.8617618	<b>DATA PROCESSING</b> FT size 32768 Total time 1 minute	sxu-12-261-H1 Solvent: cd2c12 Temp: 25.0 C / 298.1 K Operator: Liu VNMR5-500 "nar18"
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<b>PULSE SEQUENCE</b> Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 1.548 sec Width 31250.0 Hz 170 repetitions	<b>OBSERVE</b> C13, 125.6952907 <b>DECOUPLE</b> H1, 499.6042612 Power 40 dB continuously on WALTZ-16 modulated	<b>DATA PROCESSING</b> Line broadening 0.5 Hz FT size 65536 Total time 5 minutes	sxu-12-261-C13 Solvent: cd2cl2 Temp: 25.0 C / 298.1 K Operator: Liu VNMRS-500 "ner18"
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### Compound 3a

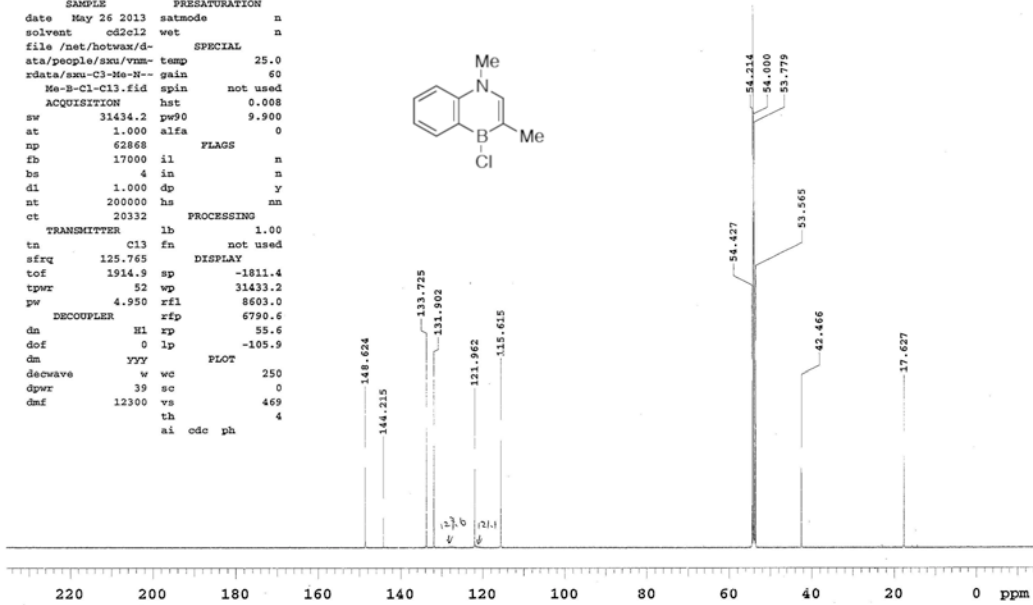
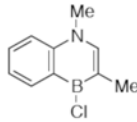


<b>PULSE SEQUENCE</b> Relax. delay 5.000 sec Pulse 45.0 degrees Acq. time 2.048 sec Width 8001.6 Hz 8 repetitions	<b>OBSERVE</b> H1, 500.1052267	<b>DATA PROCESSING</b> FT size 32768 Total time 1 minute	UO Inova-500 standard 1H Solvent: cd2cl2 Temp: 25.0 C / 298.1 K Operator: sxu INOVA-500 "nmr500.uoregon.edu"
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UO Inova-500 Carbon-13

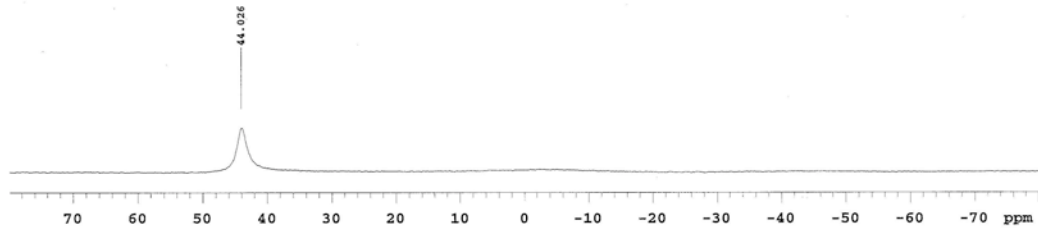
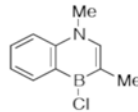
expl CARBON

```
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solvent cd2cl2 wet n
file /net/hotwax/d- SPECIAL
sta/people/sxu/vmm- temp 25.0
rdata/sxu-C3-Me-N-- gain 50
Me-B-Cl-C13.fid spin not used
ACQUISITION hst 0.008
sw 31434.2 pw90 9.900
at 1.000 alfa 0
np 62868 FLAGS
fb 17000 il n
bs 4 in n
dl 1.000 dp y
nt 200000 hs mn
ct 20332 PROCESSING
TRANSMITTER lh 1.00
tn C13 fn not used
sfrq 125.765 DISPLAY
tof 1914.9 sp -1811.4
tpwr 52 wp 31433.2
pw 4.950 rfl 8603.0
DECOUPLER rfp 6790.6
dn H1 rp 55.6
dof 0 lp -105.9
dm 777 PLOT
decwave w wd 250
dpwr 39 sc 0
dmf 12300 vs 469
ai cdc ph 4
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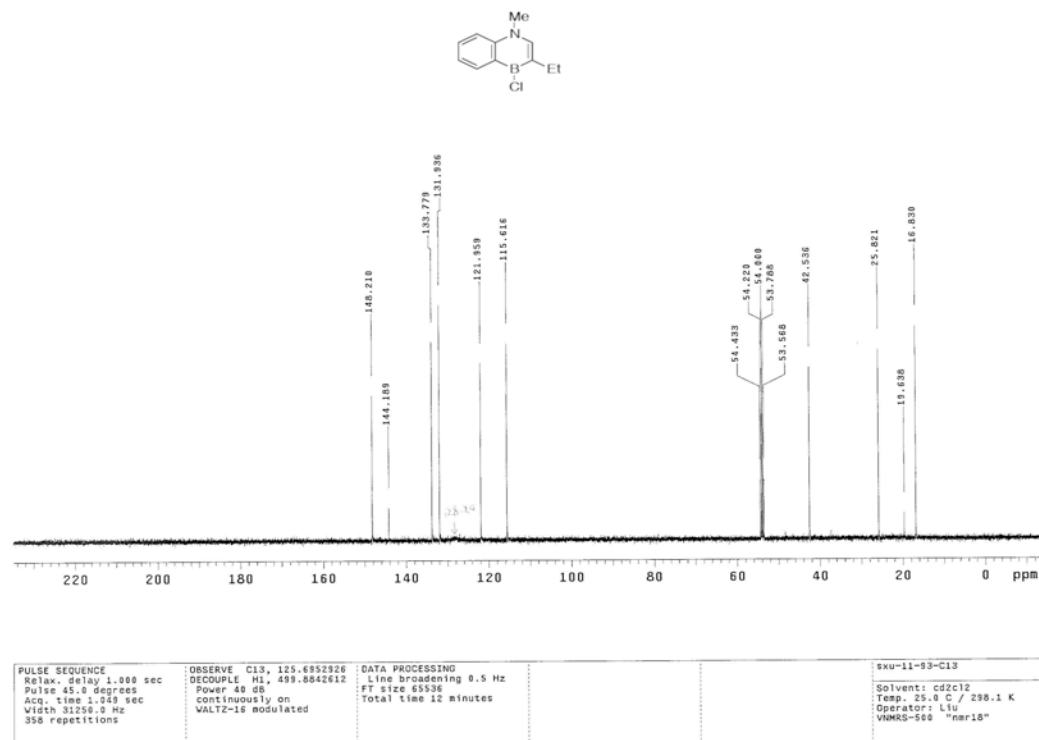
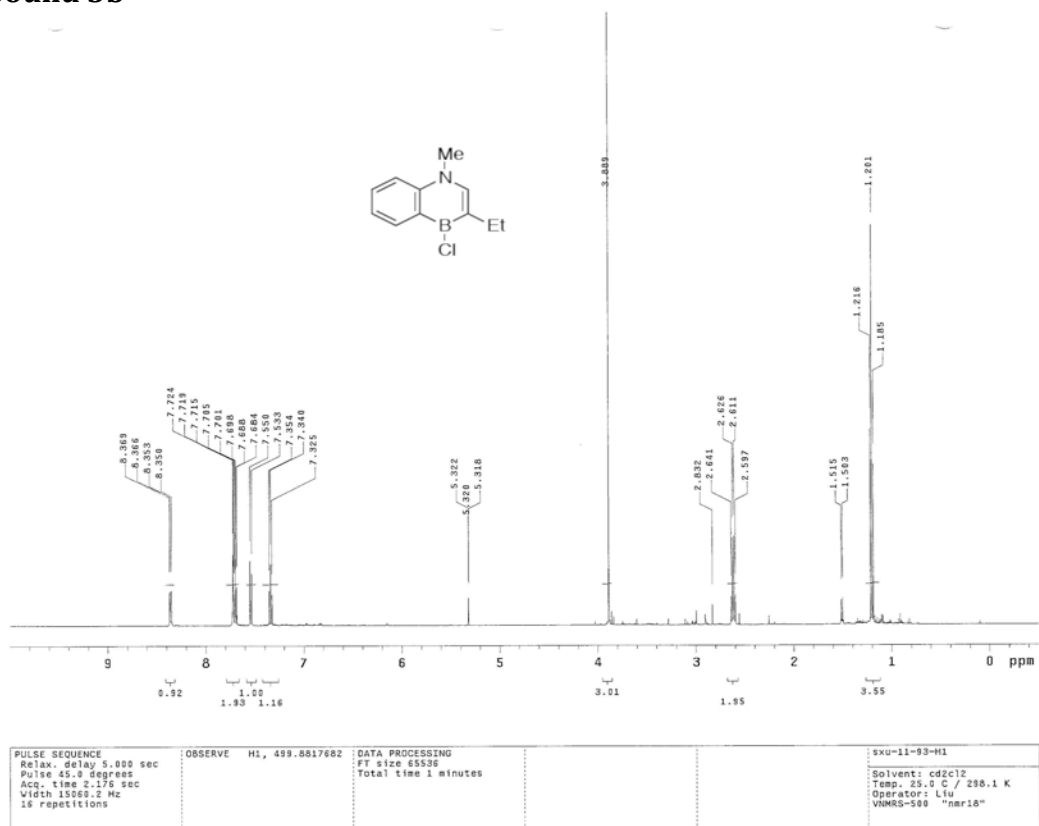


expl Boron-11

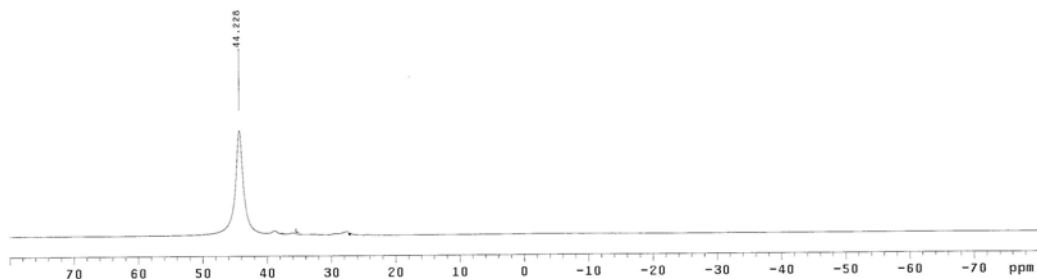
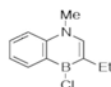
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solvent cd2cl2 wet n
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at 0.200 spin not used
np 16000 hst 0.008
fb 22000 pw90 10.000
bs 8 alfa 0
dl 0.200 FLAGS
nt 2000 il n
et 80 in n
TRANSMITTER dp y
tn B11 hs mn
sfrq 96.268 PROCESSING
tof 2891.6 lb 10.00
tpwr 58 fa not used
pw 8.000 DISPLAY
DECOUPLER sp -7705.1
dn H1 wp 15400.4
dof 0 rfl 20063.5
dm nnn rfp 0
decwave w rp -33.2
dpwr 36 lp -28.8
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wc 250
sc 0
vs 11070
th 10
ai cdc ph
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# Compound 3b

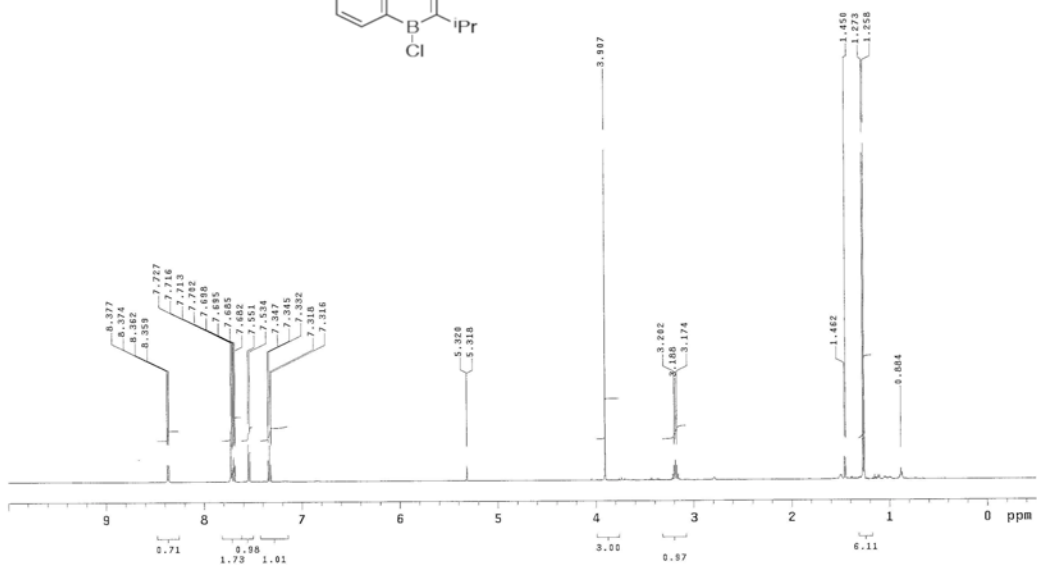
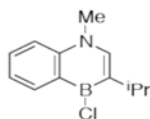




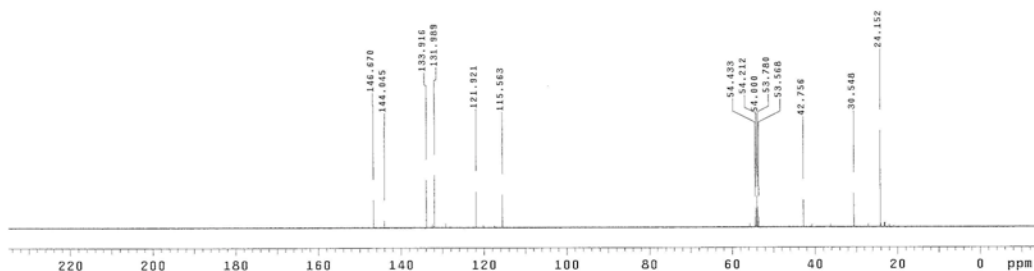
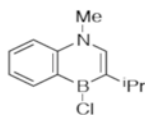


PULSE SEQUENCE Relax, delay 5.010 sec Pulse 90.0 degrees Acq. time 0.028 sec Width 32051.3 Hz 1000 repetitions	OBSERVE B11, 160.3919248	DATA PROCESSING Line broadening 10.0 Hz FT size 32768 Total time 1 minute	solu-11-93-B11 Solvent: cd2c12 Temp. 25.0 C / 298.1 K Operator: Liu VNMR5-500 "nmr18"
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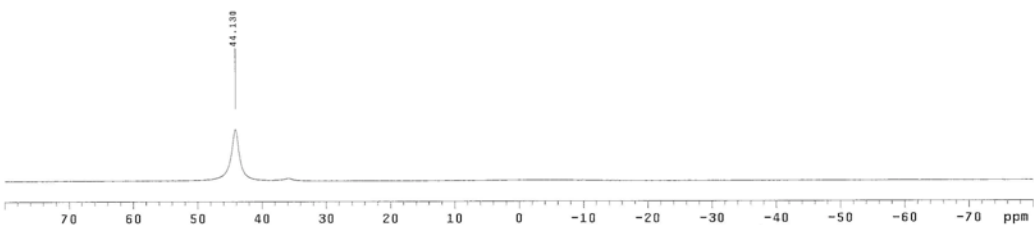
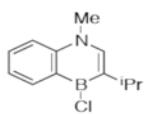
### Compound 3c



PULSE SEQUENCE Relax, delay 5.000 sec Pulse 45.0 degrees Acq. time 2.045 sec Width 8012.8 Hz 16 repetitions	OBSERVE H1, 499.8015100	DATA PROCESSING FT size 32768 Total time 1 minutes	solu-11-167-H1 Solvent: cd2c12 Temp. 25.0 C / 298.1 K Operator: Liu VNMR5-500 "nmr18"
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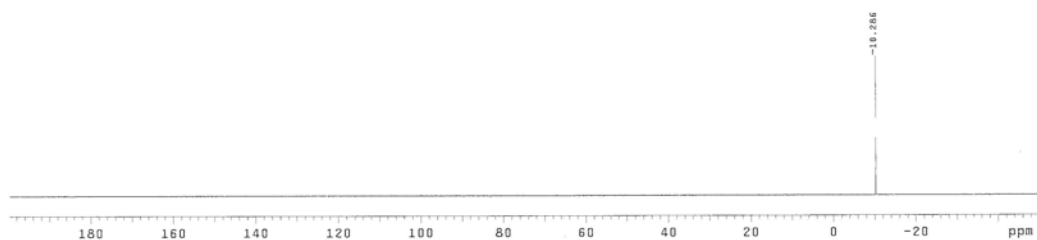
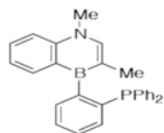


<b>PULSE SEQUENCE</b> Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 1.088 sec Width 31250.0 Hz 268 repetitions	<b>OBSERVE</b> C13, 125.8952826 <b>DECOUPLE</b> H1, 439.8642612 Power 40 dB continuously on WALTZ-16 modulated	<b>DATA PROCESSING</b> Line broadening 0.5 Hz FT size 65536 Total time 9 minutes	8xu-11-167-C13 Solvent: cd2Cl2 Temp: 25.0 C / 298.1 K Operator: Liu VNMRS-500 "nar18"
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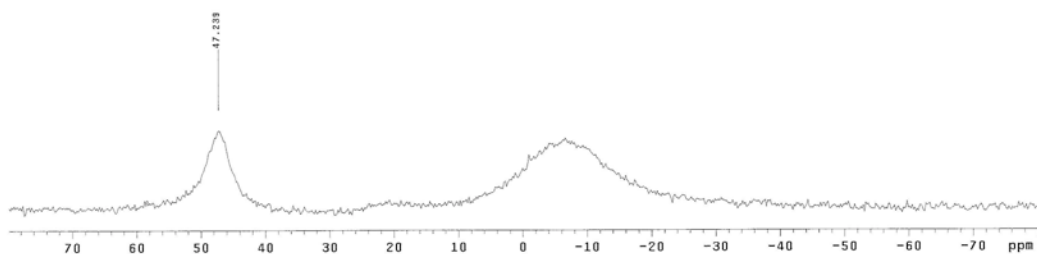
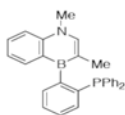


<b>PULSE SEQUENCE</b> Relax. delay 0.010 sec Pulse 90.0 degrees Acq. time 0.020 sec Width 32051.3 Hz 1000 repetitions	<b>OBSERVE</b> B11, 160.3819092	<b>DATA PROCESSING</b> Line broadening 10.0 Hz FT size 32768 Total time 1 minute	8xu-11-167-B11 Solvent: cd2Cl2 Temp: 25.0 C / 298.1 K Operator: Liu VNMRS-500 "nar18"
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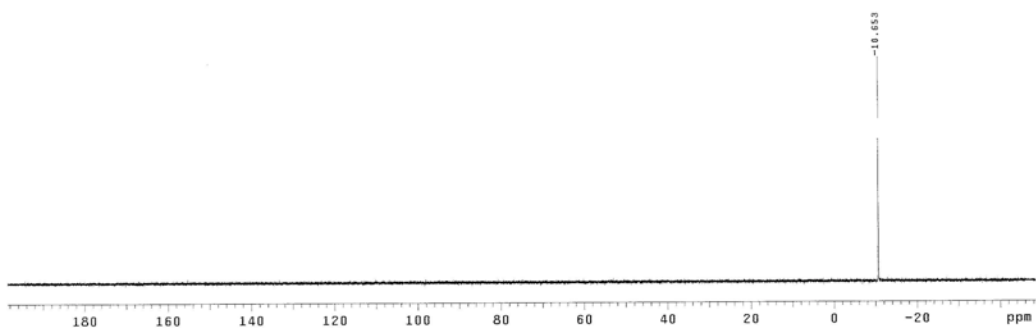
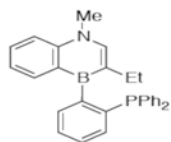


PULSE SEQUENCE	OBSERVE P31, 161.826658	DATA PROCESSING	solu-11-297-P31
Relax. delay 1.000 sec	DECOUPLE H1, 399.7699432	Line broadening 0.5 Hz	Solvent: cd2cl2
Pulse 45.0 degrees	Power 41 dB	FT size 85326	Temp. 25.0 C / 298.1 K
Acq. time 0.613 sec	on during acquisition	Total time 1 minutes	Operator: Liu
Width 40322.5 Hz	off during delay		VNMR-400 "nhr14"
56 repetitions	VALTZ-16 modulated		

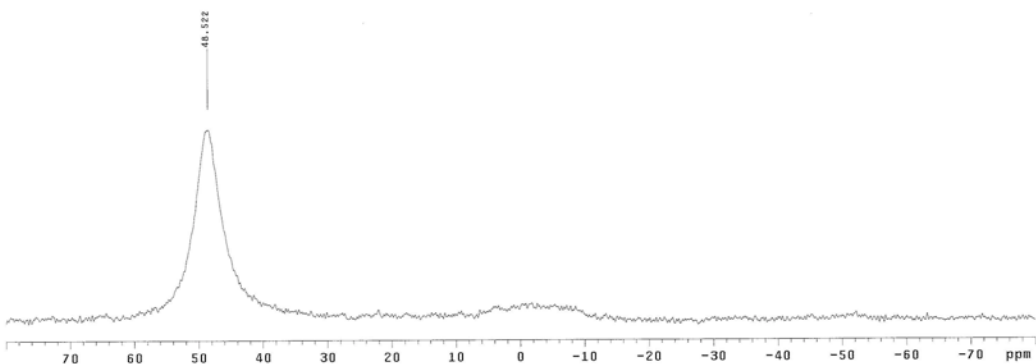
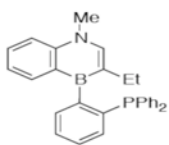


PULSE SEQUENCE	OBSERVE B11, 160.3471556	DATA PROCESSING	solu-10-297-B11
Relax. delay 0.010 sec		Line broadening 15.0 Hz	Solvent: cd2cl2
Pulse 80.0 degrees		FT size 2648	Temp. 25.0 C / 298.1 K
Acq. time 0.020 sec		Total time 1 minute	Operator: Liu
Width 32051.3 Hz			INVA-600 "nhr11"
1800 repetitions			



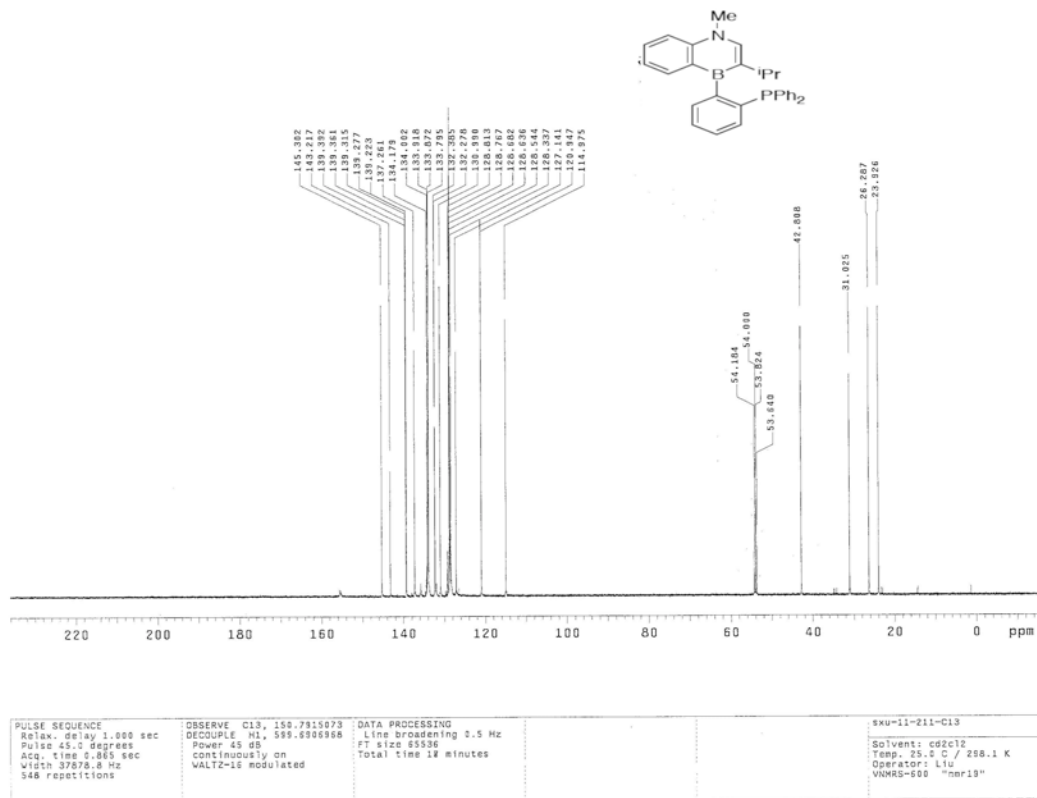
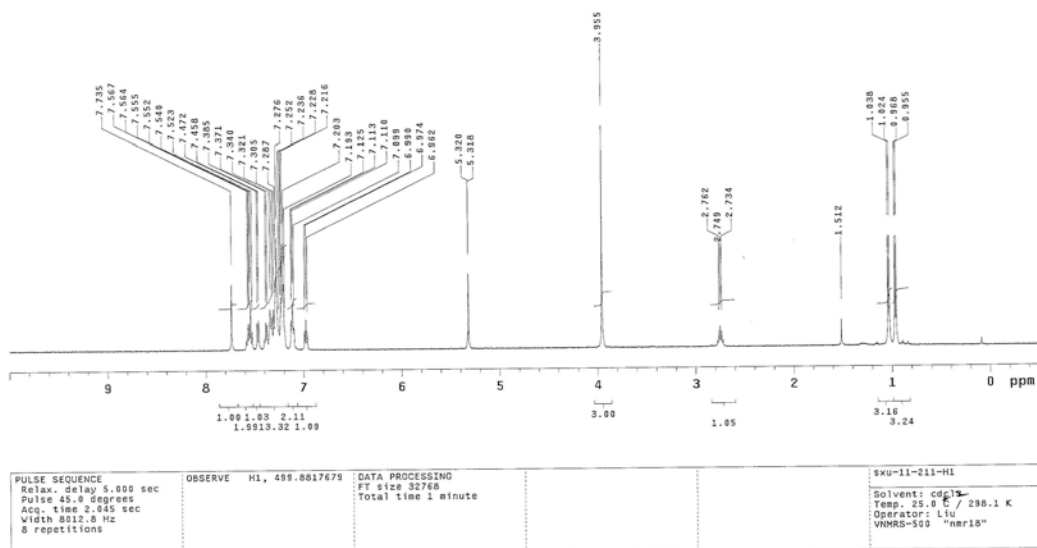
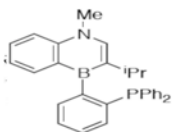


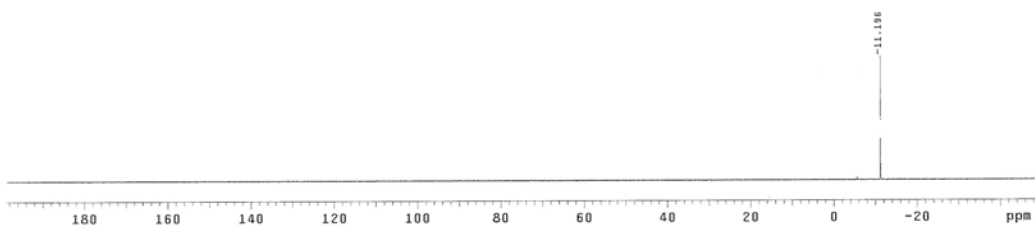
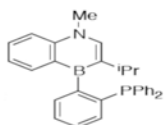
<b>PULSE SEQUENCE</b> Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 0.655 sec Width 50000.0 Hz 220 repetitions	<b>OBSERVE</b> P31, 202.3550463 <b>DECOUPLE</b> H1, 499.8842612 Power 40 dB on during acquisition off during delay WALTZ-16 modulated	<b>DATA PROCESSING</b> Line broadening 0.5 Hz FT size 6536 Total time 5 minutes	sxu-12-259-P31 Solvent: cdcl2 Temp. 25.0 C / 298.1 K Operator: Liu VNMRS-500 "nmr18"
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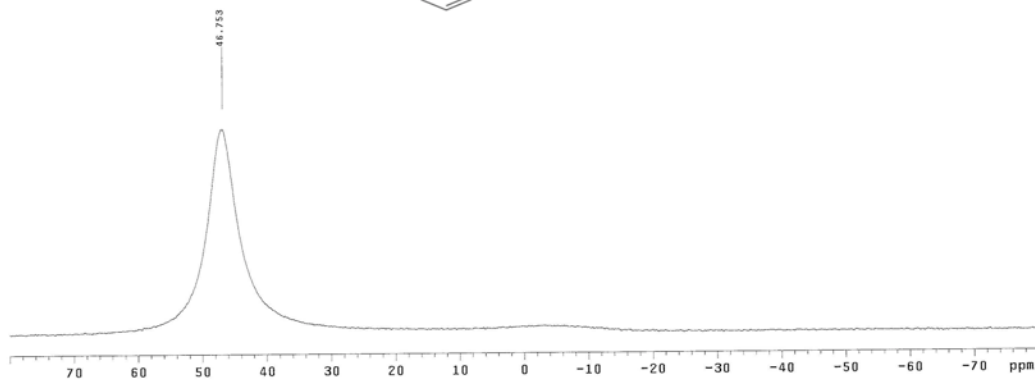
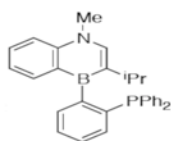
<b>PULSE SEQUENCE</b> Relax. delay 0.010 sec Pulse 90.0 degrees Acq. time 0.020 sec Width 32051.3 Hz 1000 repetitions	<b>OBSERVE</b> B11, 160.3817077 <b>DECOUPLE</b> H1, 499.8842612 Power 40 dB on during acquisition off during delay WALTZ-16 modulated	<b>DATA PROCESSING</b> Line broadening 10.0 Hz FT size 32760 Total time 1 minute	sxu-12-259-B11 Solvent: cdcl2 Temp. 25.0 C / 298.1 K Operator: Liu VNMRS-500 "nmr18"
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# Compound L4





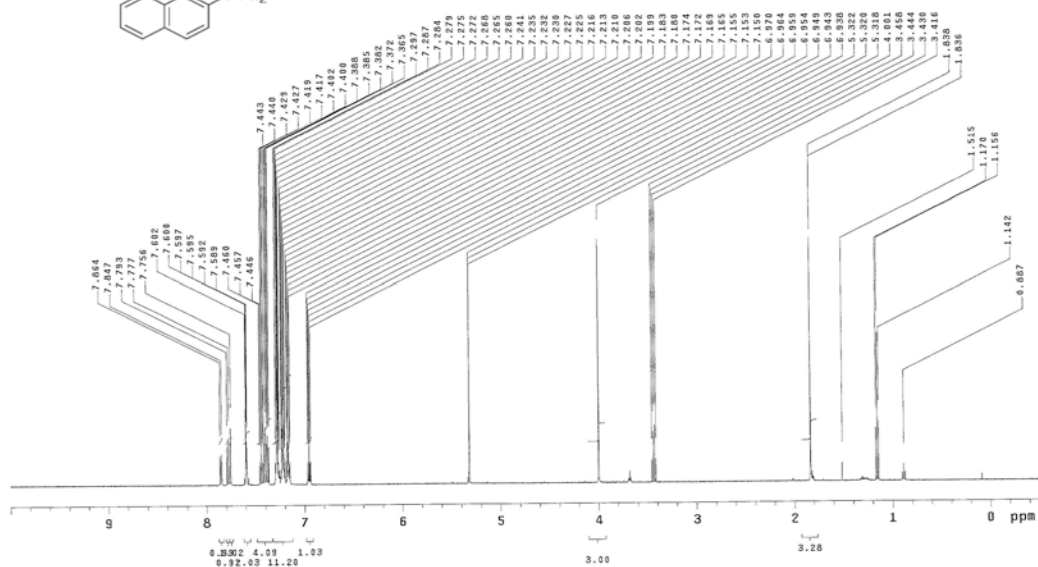
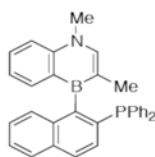
<b>PULSE SEQUENCE</b> Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 0.655 sec Width 50000.0 Hz 30 repetitions	<b>OBSERVE</b> P31, 202.3558463 <b>DECOUPLE</b> H1, 499.8842612 Power 40 dB on during acquisition off during delay WALTZ-16 modulated	<b>DATA PROCESSING</b> Line broadening 0.5 Hz FT size 65536 Total time 1 minute	skx-11-211-P31 Solvent: cd2cl2 Temp. 25.0 C / 298.1 K Operator: Liu VNMRS-500 "nmr18"
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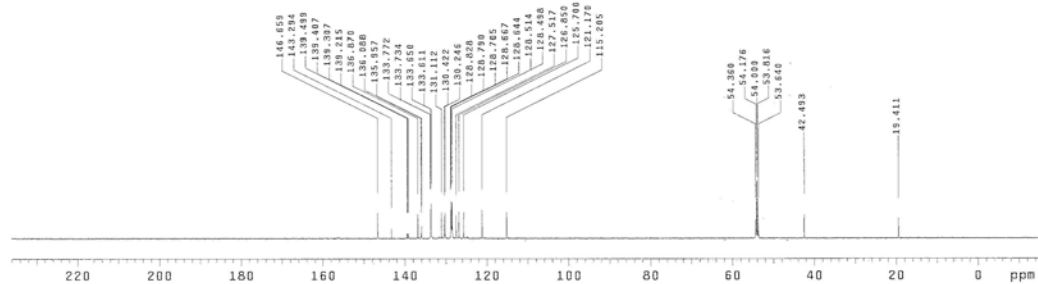
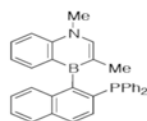
<b>PULSE SEQUENCE</b> Relax. delay 0.010 sec Pulse 90.0 degrees Acq. time 0.020 sec Width 32351.3 Hz 1000 repetitions	<b>OBSERVE</b> B11, 160.3819874 <b>DECOUPLE</b> H1, 499.8842612 Power 40 dB on during acquisition off during delay WALTZ-16 modulated	<b>DATA PROCESSING</b> Line broadening 10.0 Hz FT size 32768 Total time 1 minute	skx-11-211-611 Solvent: cd2cl2 Temp. 25.0 C / 298.1 K Operator: Liu VNMRS-500 "nmr18"
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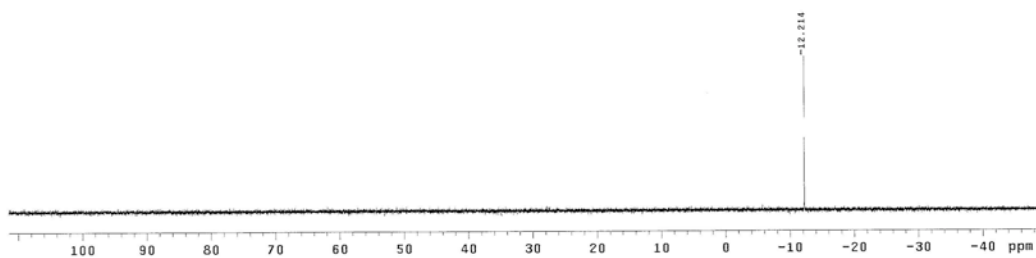
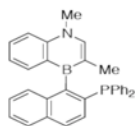
# Compound L5



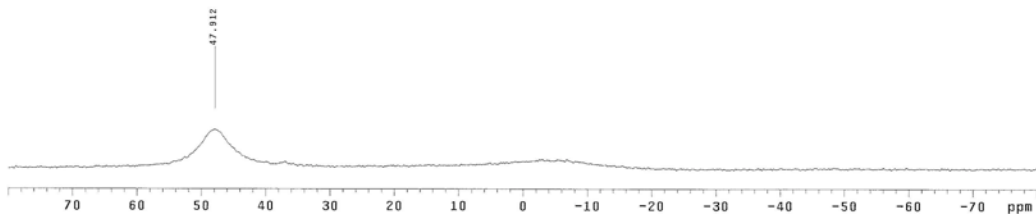
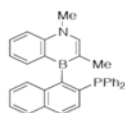
<b>PULSE SEQUENCE</b> Relax. delay 5.000 sec Pulse 45.0 degrees Acq. time 2.045 sec Width 8012.0 Hz 16 repetitions	<b>OBSERVE</b> H1, 499.6817682	<b>DATA PROCESSING</b> FT size 32768 Total time 1 minutes	sxu-10-33-H1 Solvent: cdCl3 Temp: 25.0 C / 298.1 K Operator: Liu VNMRS-500 "nar10"
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<b>PULSE SEQUENCE</b> Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 0.455 sec Width 37878.0 Hz 712 repetitions	<b>OBSERVE</b> C13, 159.7915015 <b>DECDUPLE</b> H1, 599.5909958 Power 45 dB continuously on WALTZ-16 modulated	<b>DATA PROCESSING</b> Line broadening 3.0 Hz FT size 65536 Total time 22 minutes	sxu-10-33-C13 Solvent: cdCl3 Temp: 25.0 C / 298.1 K Operator: Liu VNMRS-500 "nar10"
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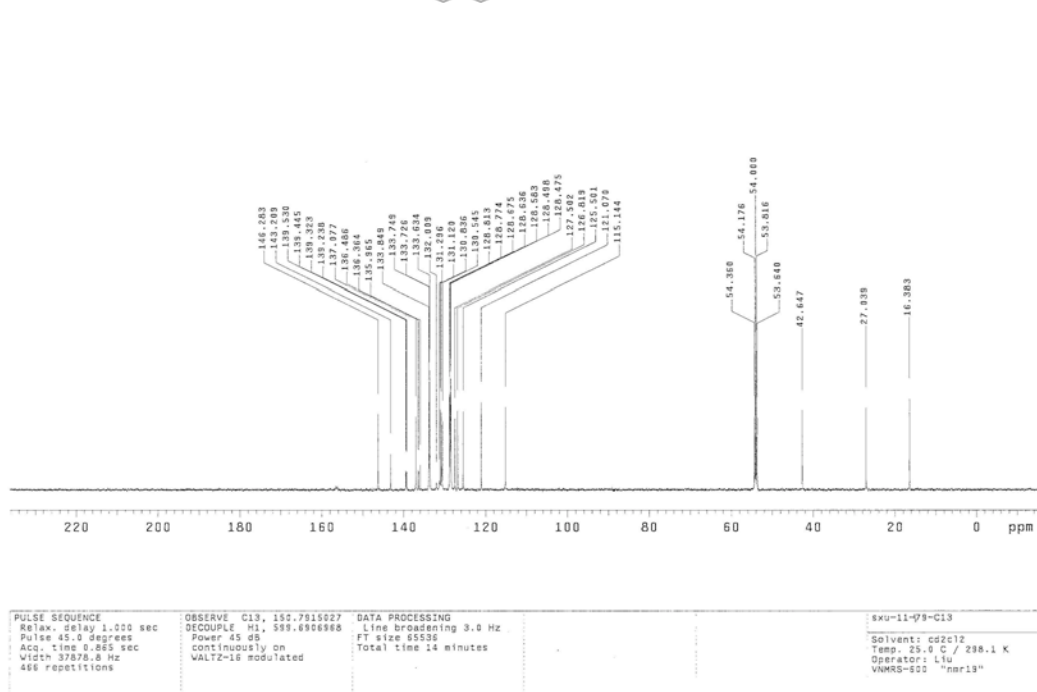
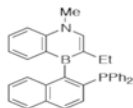
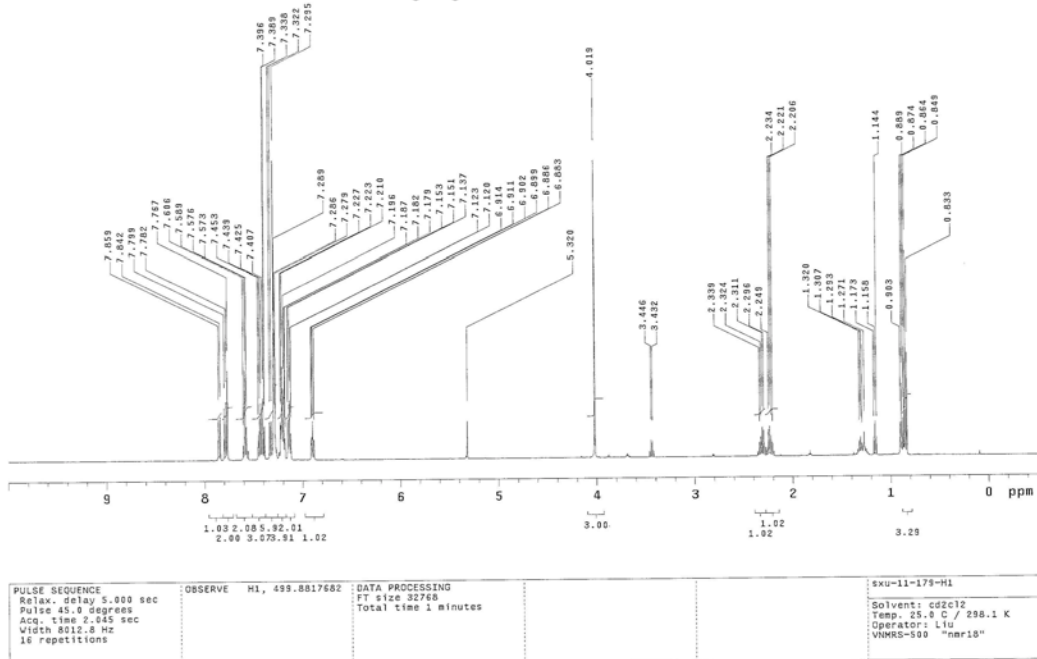
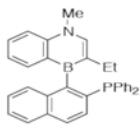


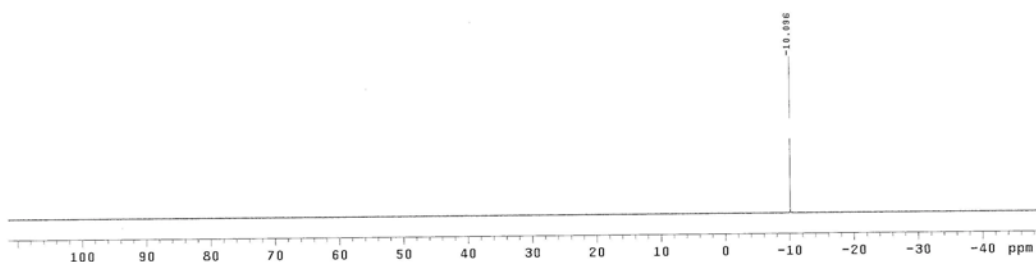
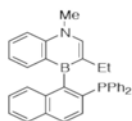
<b>PULSE SEQUENCE</b> Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 0.035 sec Width 50000.0 Hz 24 repetitions	<b>OBSERVE</b> F31, 200.3558463 <b>DECOUPLE</b> M1, 499.0042612 Power 49 dB on during acquisition off during delay WALTZ-16 modulated	<b>DATA PROCESSING</b> Line broadening 0.5 Hz FT size 65536 Total time 1 minute	sxu-11-33-p31 Solvent: cd2cl2 Temp: 25.0 C / 298.1 K Operator: Liu VNMRS-500 "nar18"
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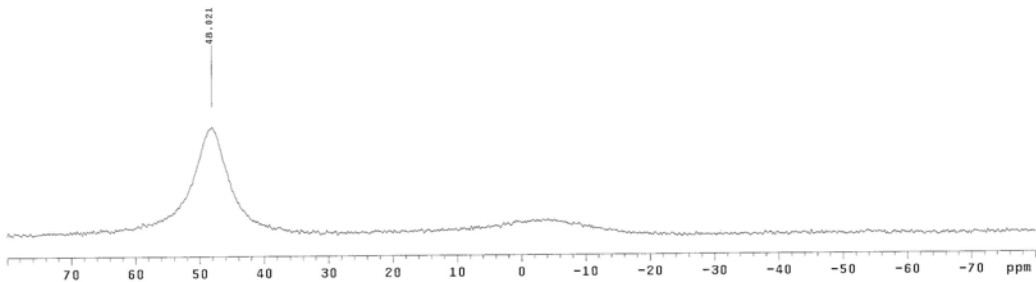
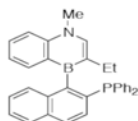
<b>PULSE SEQUENCE</b> Relax. delay 0.010 sec Pulse 90.0 degrees Acq. time 0.020 sec Width 32051.3 Hz 1000 repetitions	<b>OBSERVE</b> 011, 100.3619305	<b>DATA PROCESSING</b> Line broadening 10.0 Hz FT size 32768 Total time 1 minute	sxu-11-33-011 Solvent: cd2cl2 Temp: 25.0 C / 298.1 K Operator: Liu VNMRS-500 "nar18"
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# Compound L6



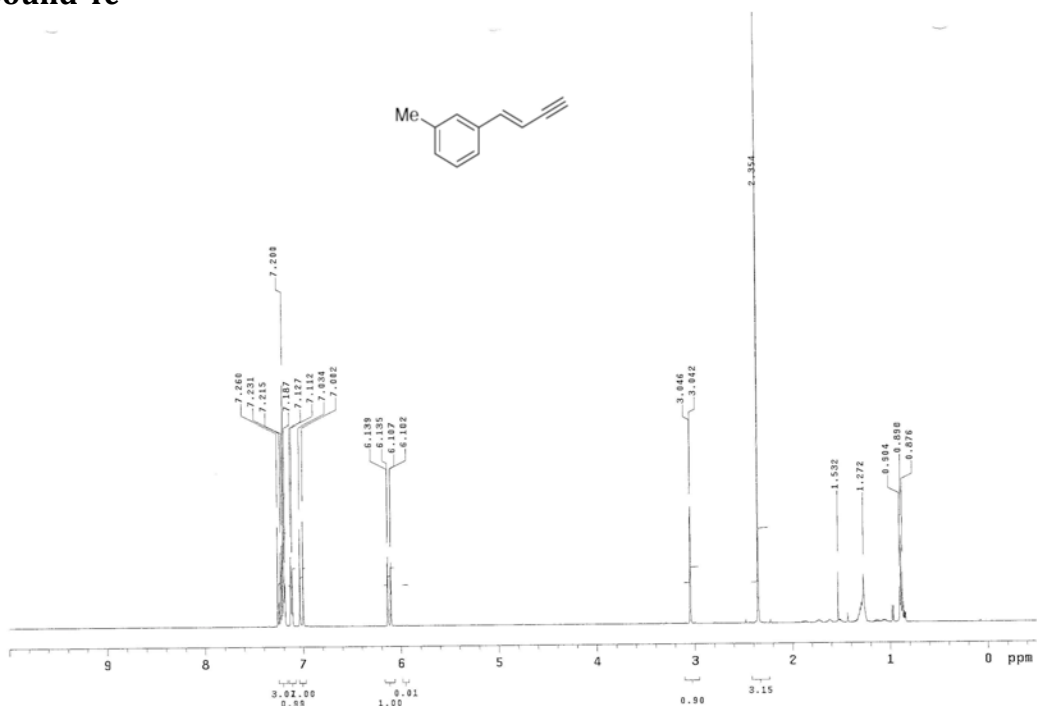
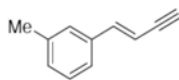


PULSE SEQUENCE Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 0.655 sec Width 50000.0 Hz 82 repetitions	OBSERVE F31, 202.3554578 DECOUPLE H1, 499.8833013 Power 40 dB on during acquisition off during delay WALTZ-16 modulated	DATA PROCESSING Line broadening 0.5 Hz FT size 85338 Total time 2 minutes	skx-11-179-P31
			Solvent: cdCl3 Temp: 25.0 C / 298.1 K Operator: Liu VNMRS-500 "nar18"

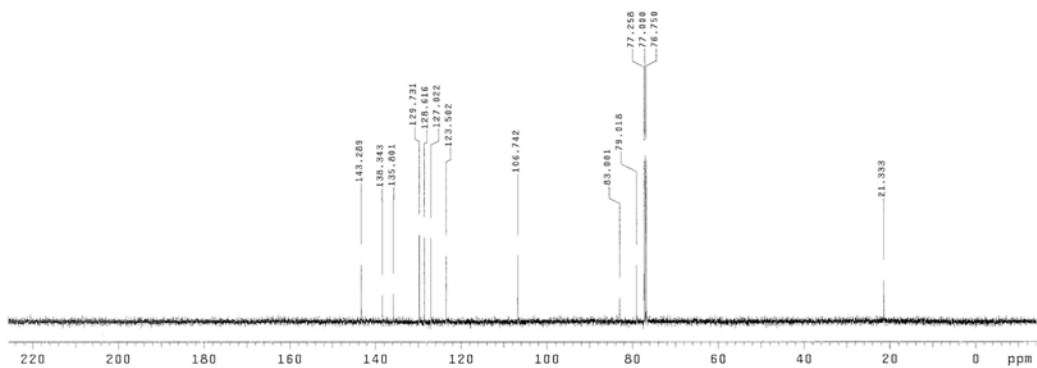
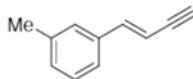


PULSE SEQUENCE Relax. delay 0.010 sec Pulse 30.0 degrees Acq. time 0.020 sec Width 32051.0 Hz 1000 repetitions	OBSERVE B11, 180.3819933 DECOUPLE H1, 499.8842612 Power 40 dB on during acquisition off during delay WALTZ-16 modulated	DATA PROCESSING Line broadening 10.0 Hz FT size 32768 Total time 1 minute	skx-11-179-B11
			Solvent: cdCl2 Temp: 25.0 C / 298.1 K Operator: Liu VNMRS-500 "nar18"

# Compound 4c

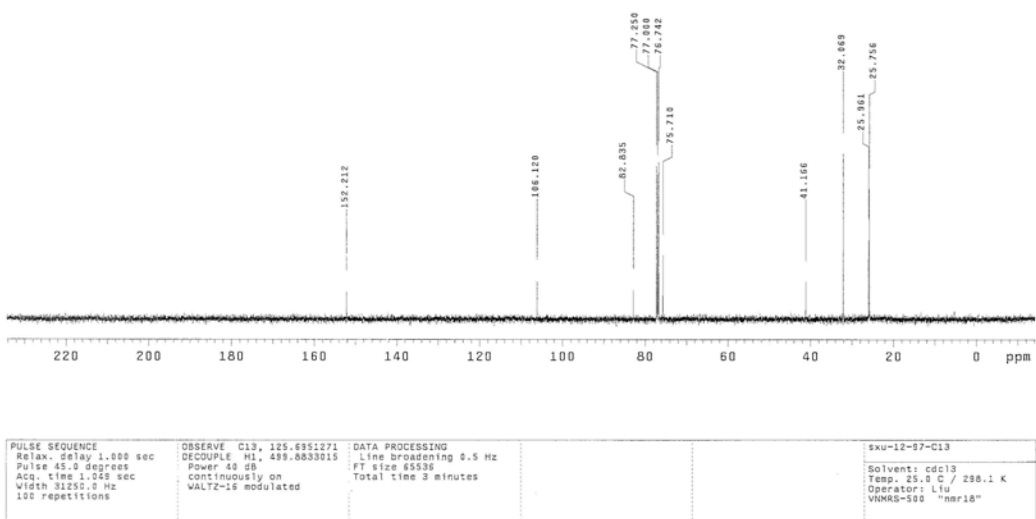
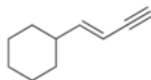
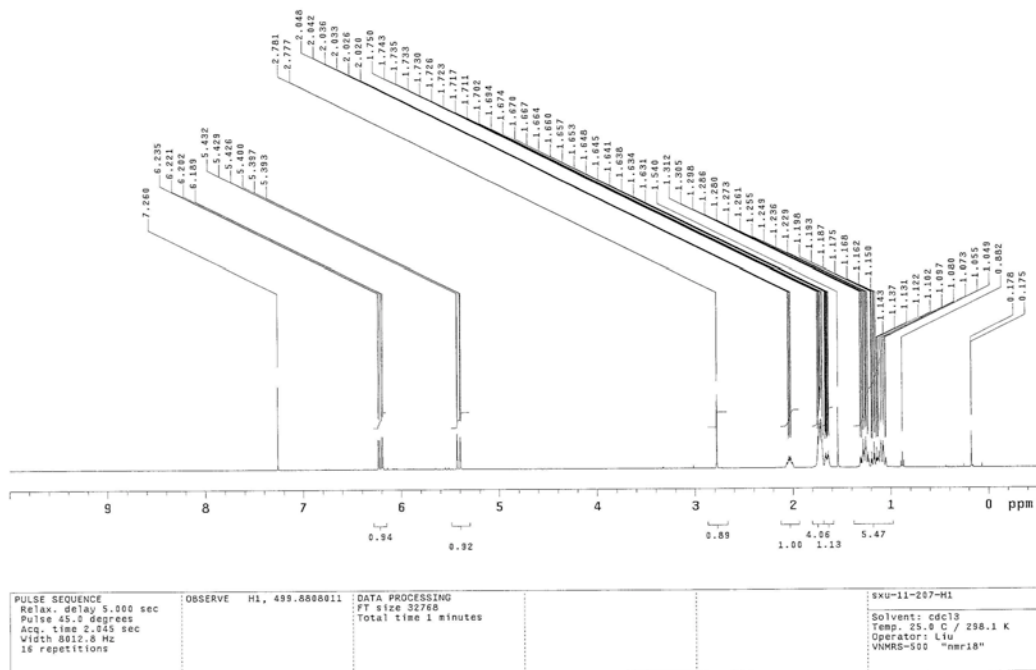
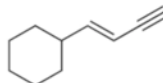


<b>PULSE SEQUENCE</b> Relax. delay 5.000 sec Pulse 45.0 degrees Acq. time 2.245 sec Width 8012.8 Hz 16 repetitions	OBSERVE H1, 499.0088017	<b>DATA PROCESSING</b> FT size 32768 Total time 1 minutes	sxu-12-33-H1 Solvent: cdcl3 Temp. 25.0 C / 298.1 K Operator: Liu VIEWS-500 "nmr16"
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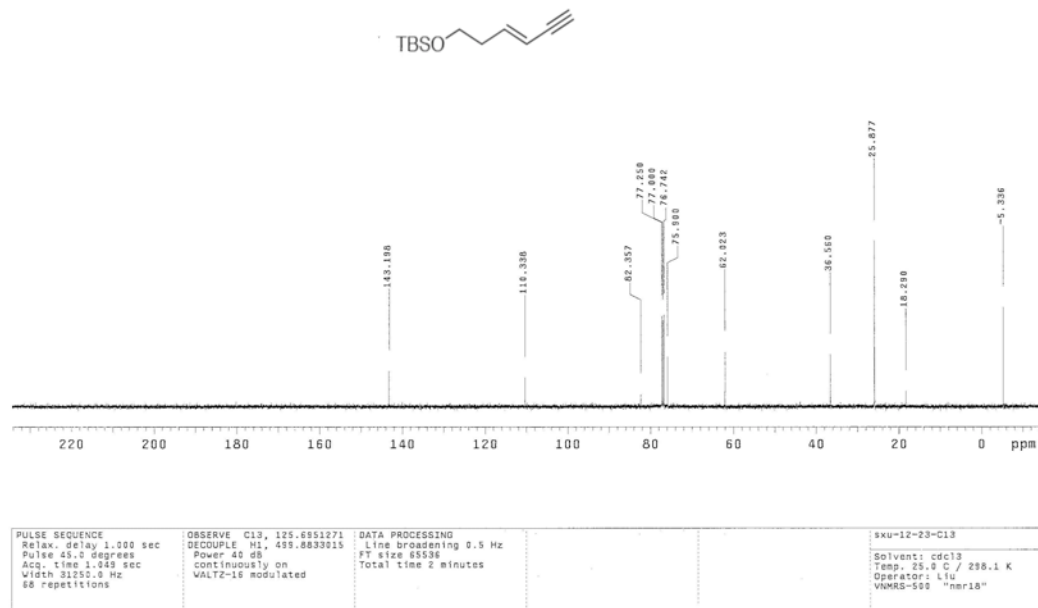
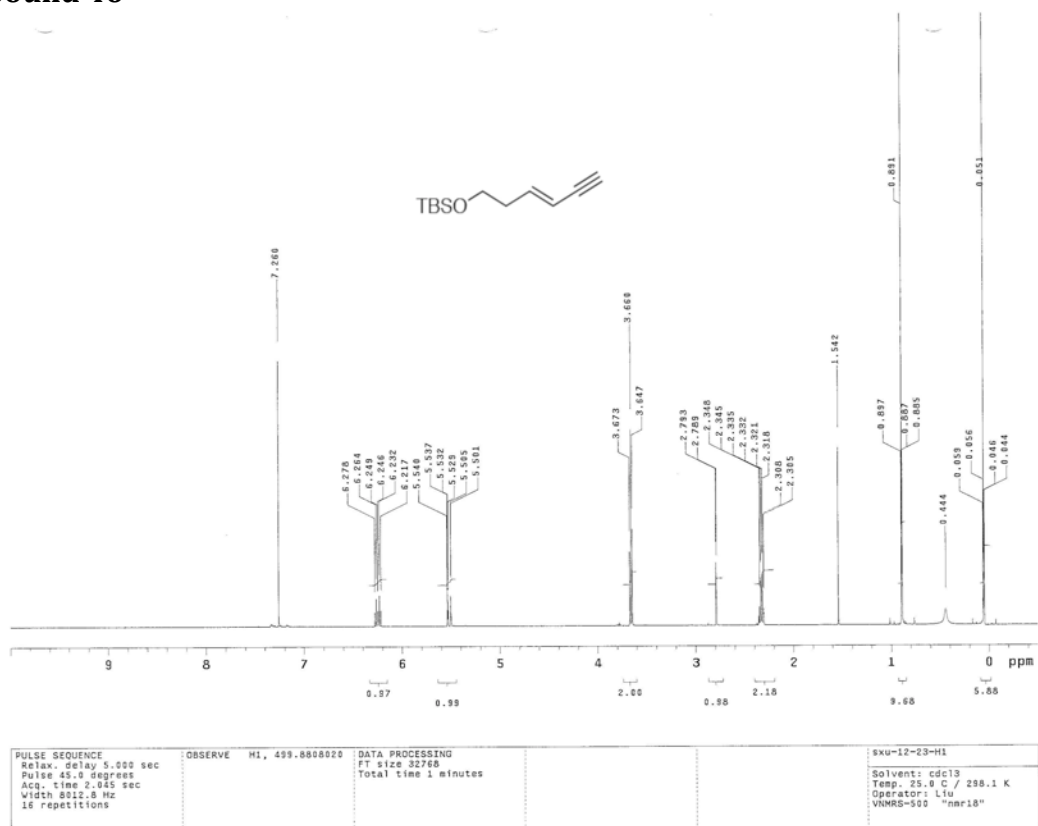


<b>PULSE SEQUENCE</b> Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 1.049 sec Width 31250.0 Hz 72 repetitions	OBSERVE C13, 125.6951280 DECOUPLE H1, 499.8693015 Power 48 db continuously on VALTZ-16 modulated	<b>DATA PROCESSING</b> Line broadening 0.5 Hz FT size 65536 Total time 2 minutes	sxu-12-33-C13 Solvent: cdcl3 Temp. 25.0 C / 298.1 K Operator: Liu VIEWS-500 "nmr16"
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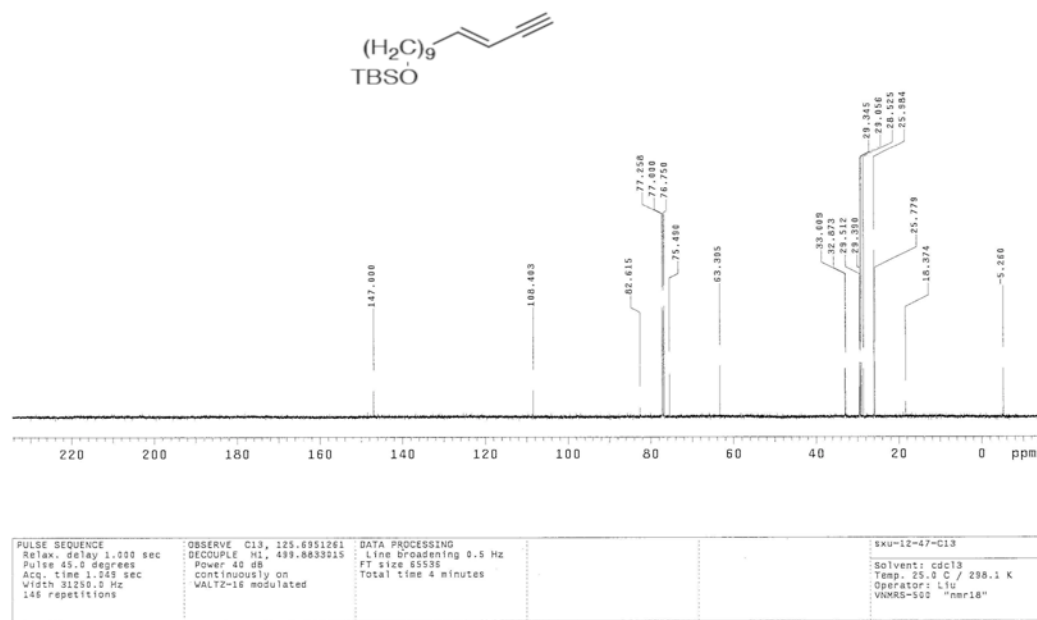
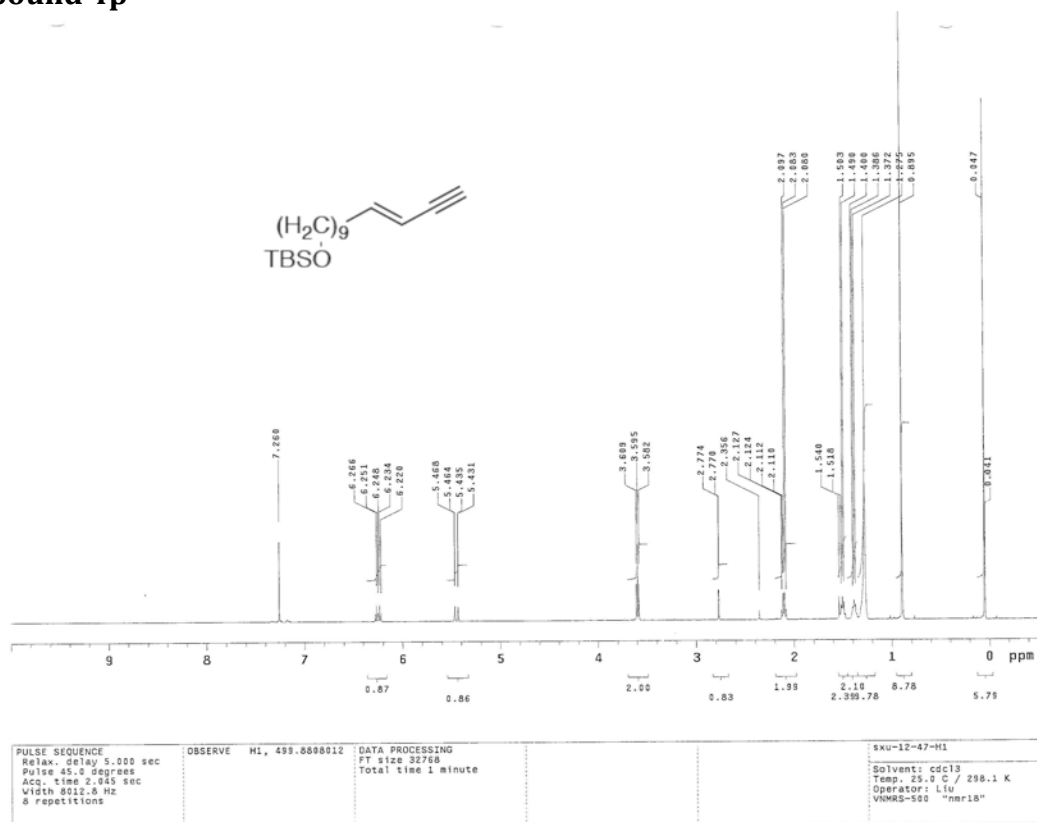
# Compound 4n



# Compound 4o

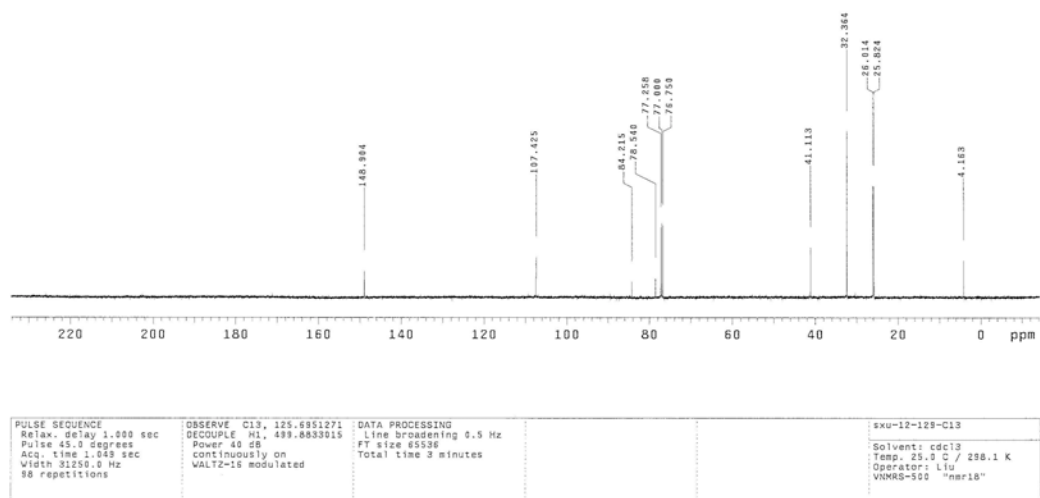
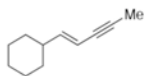
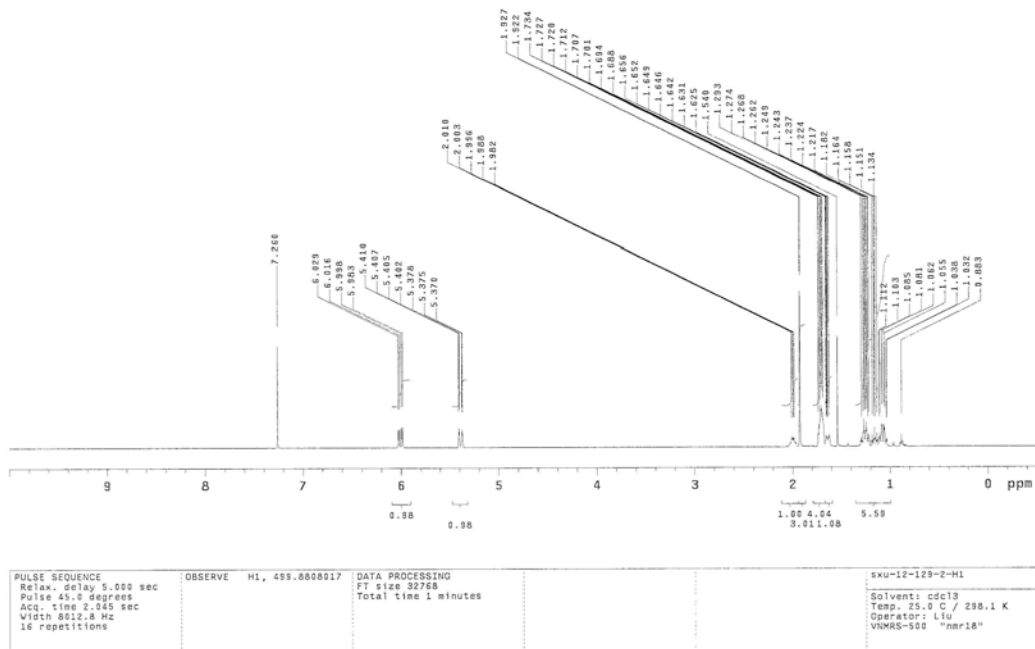
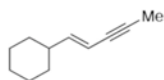


# Compound 4p

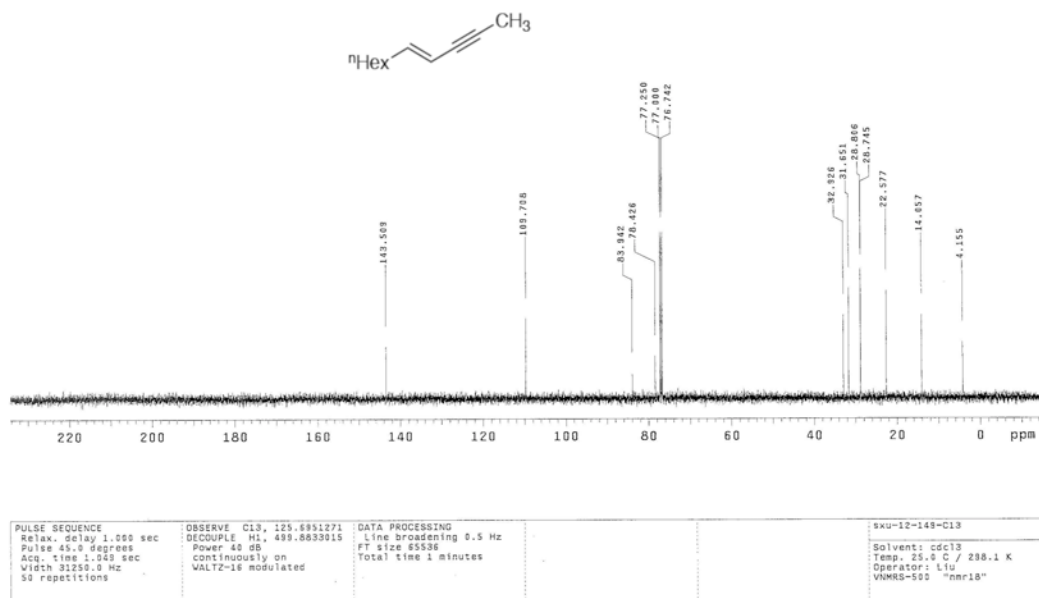
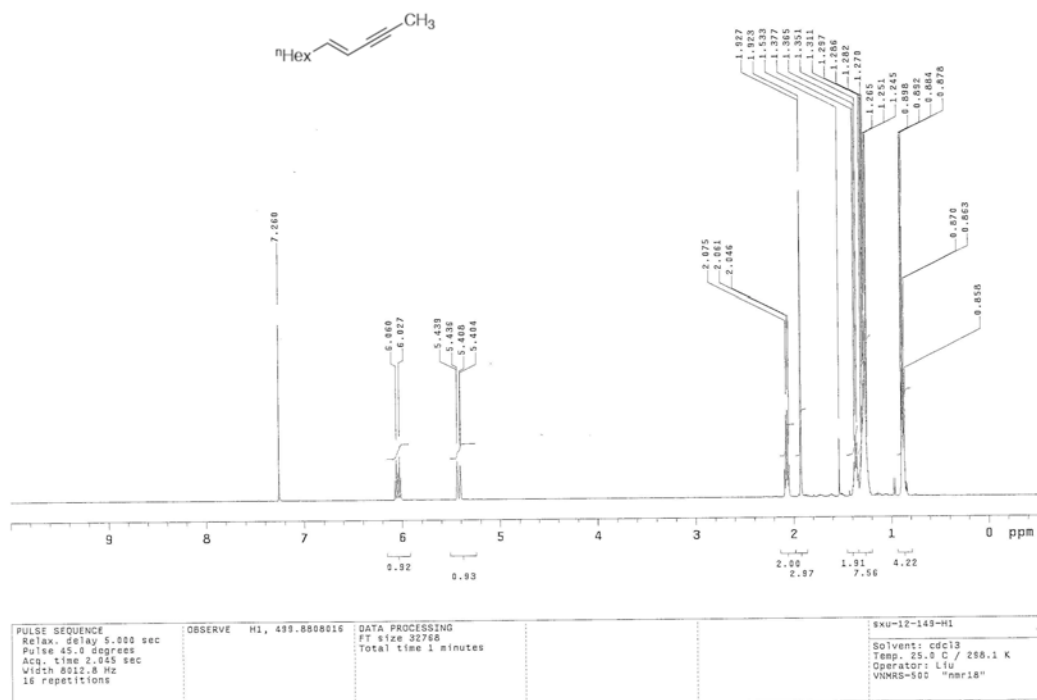




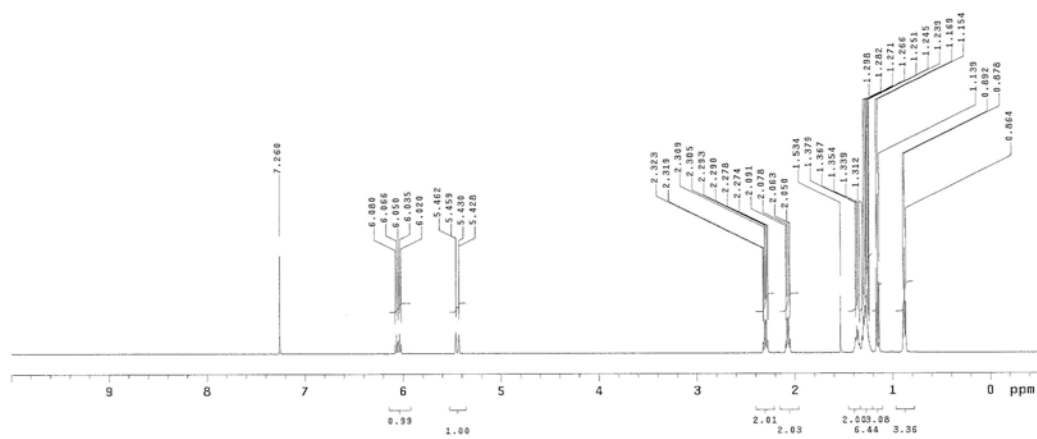
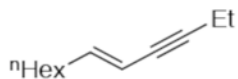
# Compound 6a



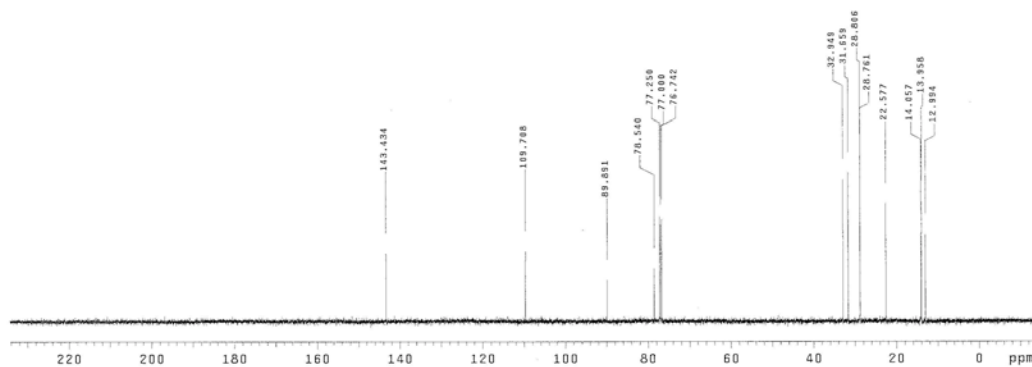
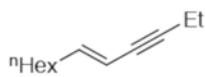
# Compound 6b



# Compound 6c

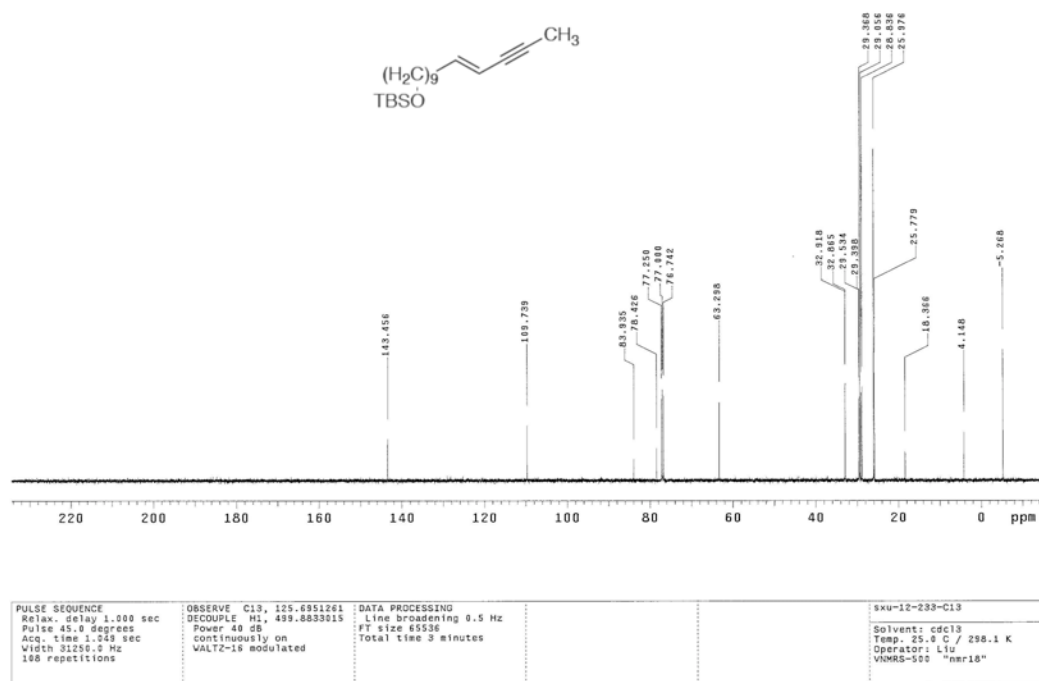
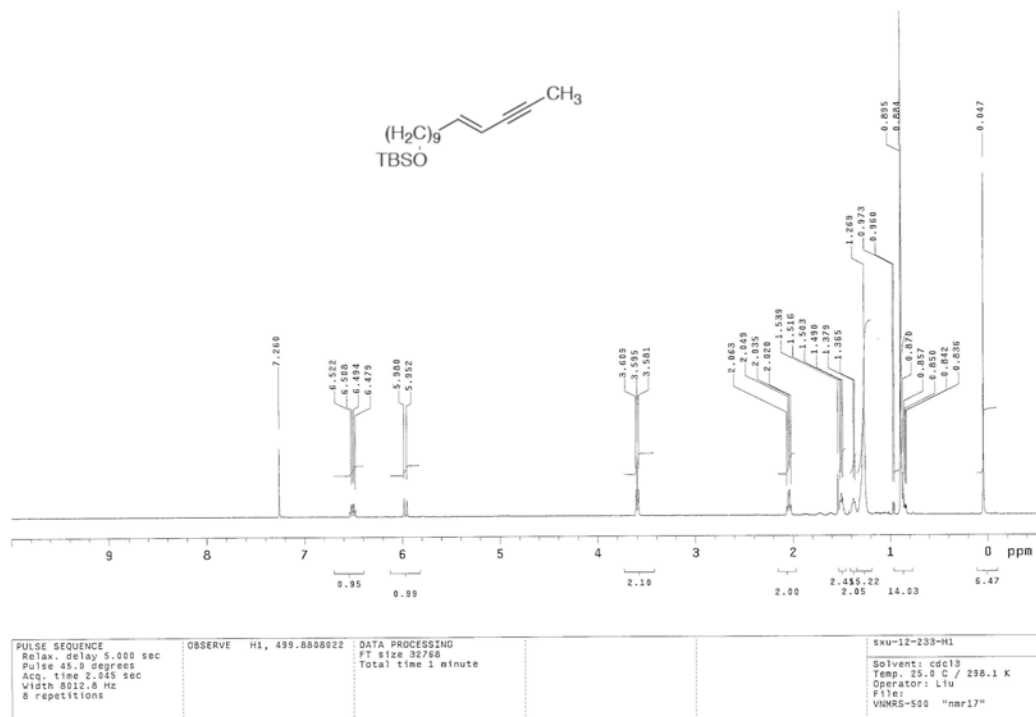


PULSE SEQUENCE Relax. delay 5.000 sec Pulse 45.0 degrees Acq. time 2.945 sec Width 8012.8 Hz 16 repetitions	OBSERVE H1, 499.8608016	DATA PROCESSING FT size 32768 Total time 1 minutes	sxu-12-227-H1 Solvent: cdcl3 Temp: 25.8 C / 298.1 K Operator: Liu VNMR5-500 "nmr16"
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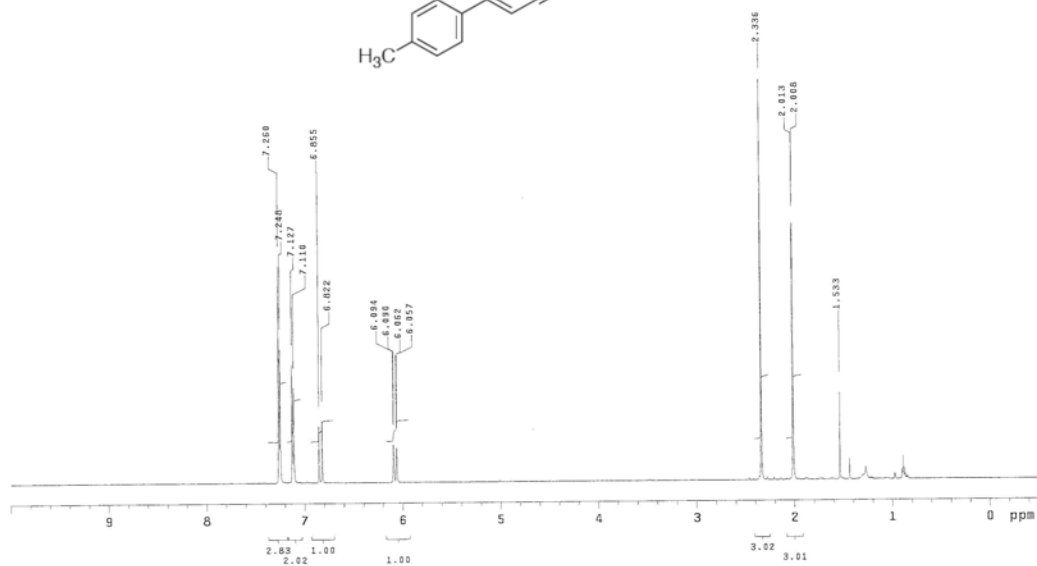
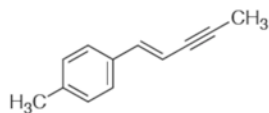


PULSE SEQUENCE Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 1.249 sec Width 31250.0 Hz 60 repetitions	OBSERVE C13, 125.6951271 DECOUPLE H1, 499.8608016 Power 40 dB continuously on WALTZ-16 modulated	DATA PROCESSING Line broadening 0.5 Hz FT size 55536 Total time 2 minutes	sxu-12-227-C13 Solvent: cdcl3 Temp: 25.8 C / 298.1 K Operator: Liu VNMR5-500 "nmr16"
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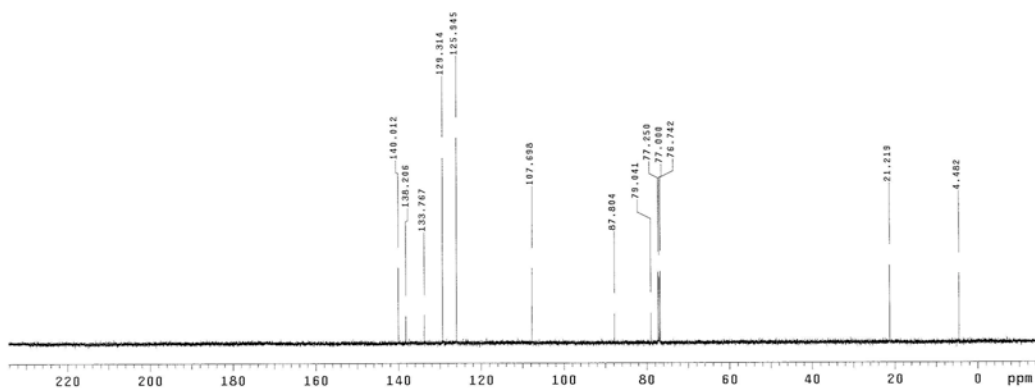
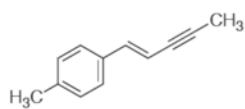
# Compound 6f



# Compound 6h

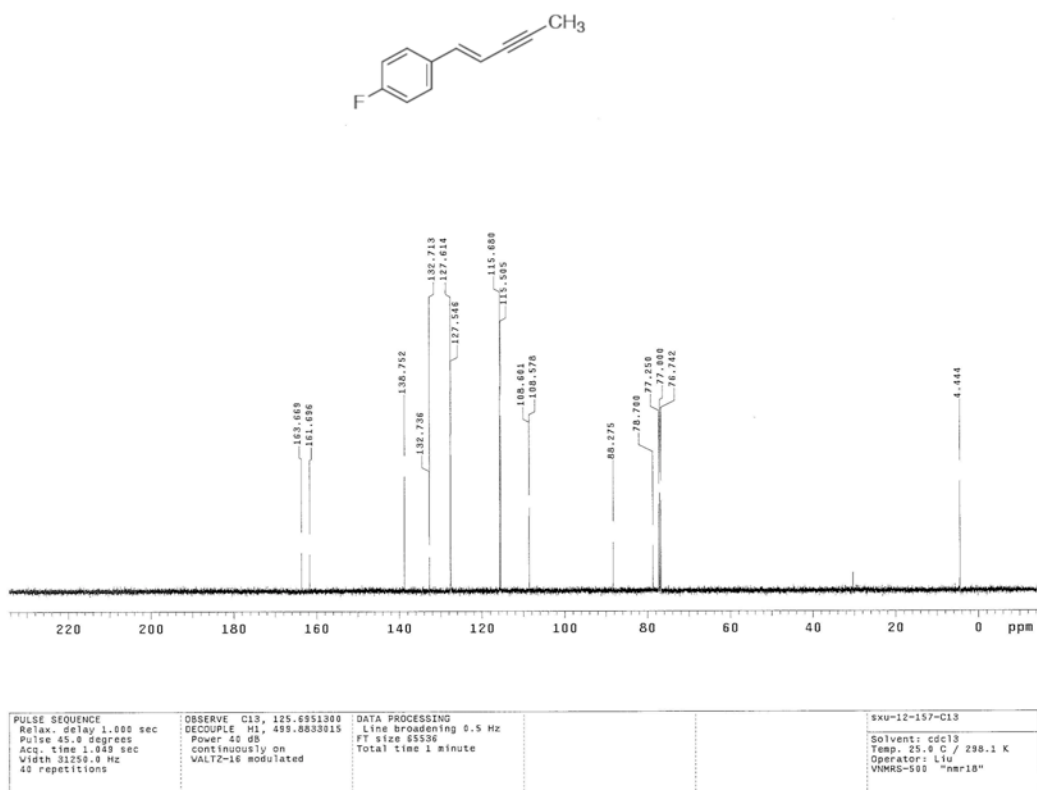
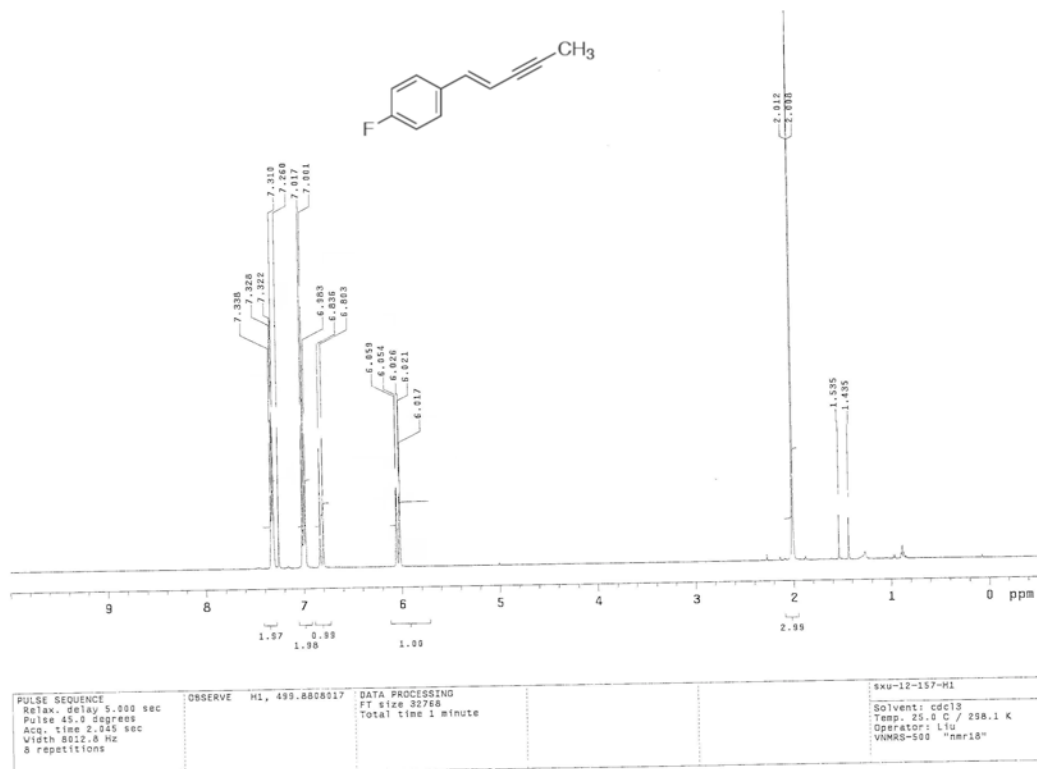


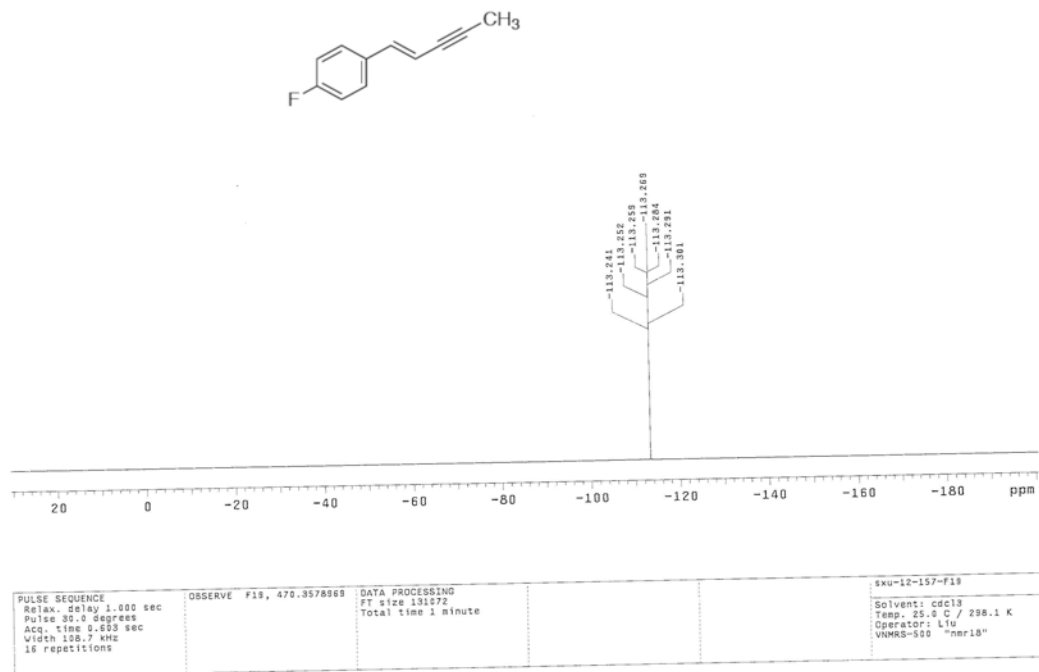
<b>PULSE SEQUENCE</b> Relax. delay 5.000 sec Pulse 45.0 degrees Acq. time 2.176 sec Width 15060.2 Hz 8 repetitions	<b>OBSERVE</b> M1, 499.8098016	<b>DATA PROCESSING</b> FT size 65536 Total time 1 minute	sxu-12-171-1-H1 Solvent: cdcl3 Temp. 25.0 C / 298.1 K Operator: Liu VNMRS-500 "nmr10"
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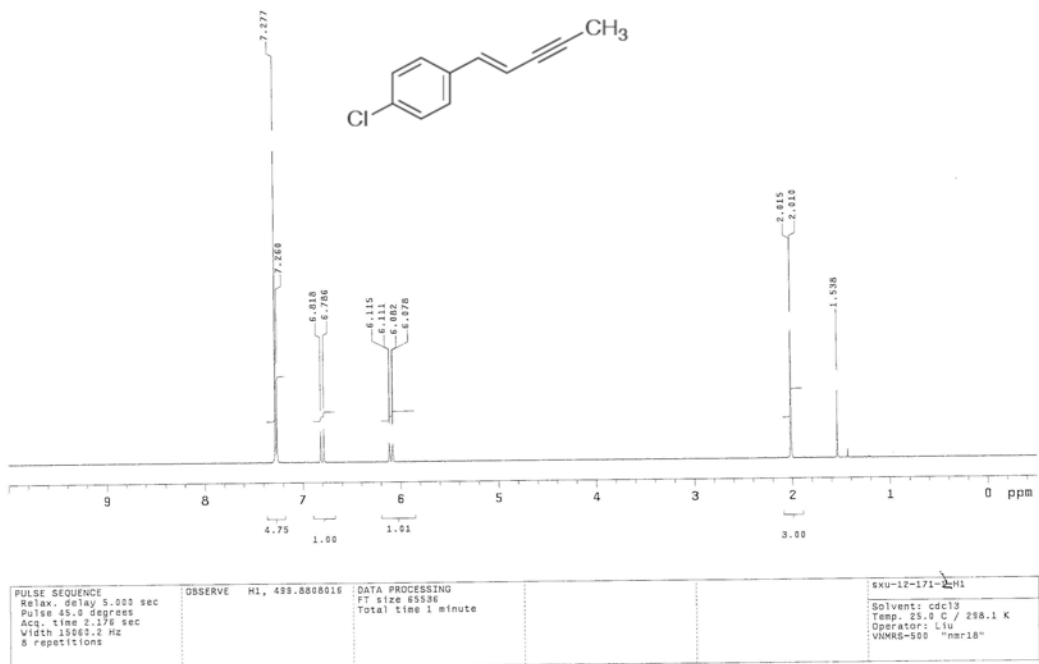
<b>PULSE SEQUENCE</b> Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 1.849 sec Width 31250.0 Hz 36 repetitions	<b>OBSERVE</b> C13, 125.6851300 <b>DECUPLE</b> M1, 499.8039115 Power 40 dB continuously on VALTZ-16 modulated	<b>DATA PROCESSING</b> Line broadening 0.5 Hz FT size 65536 Total time 1 minute	sxu-12-171-1-C13 Solvent: cdcl3 Temp. 25.0 C / 298.1 K Operator: Liu VNMRS-500 "nmr10"
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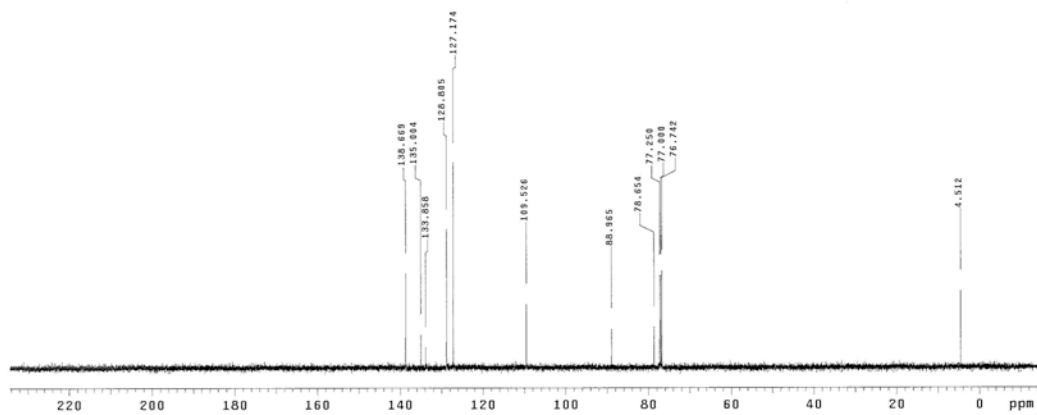
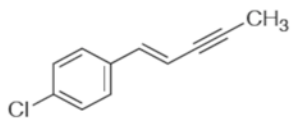
# Compound 6i





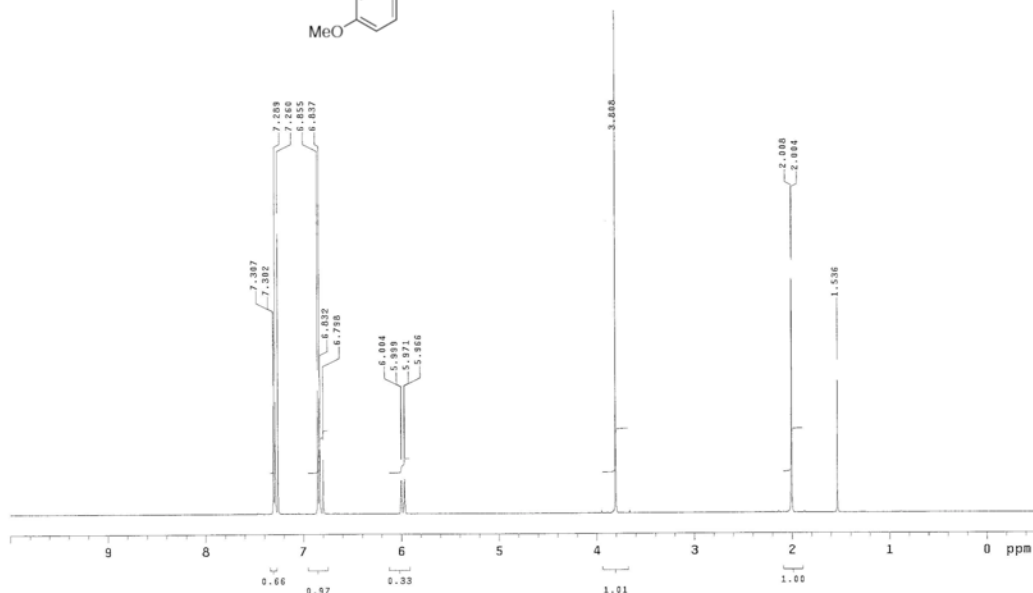
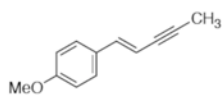
### Compound 6j





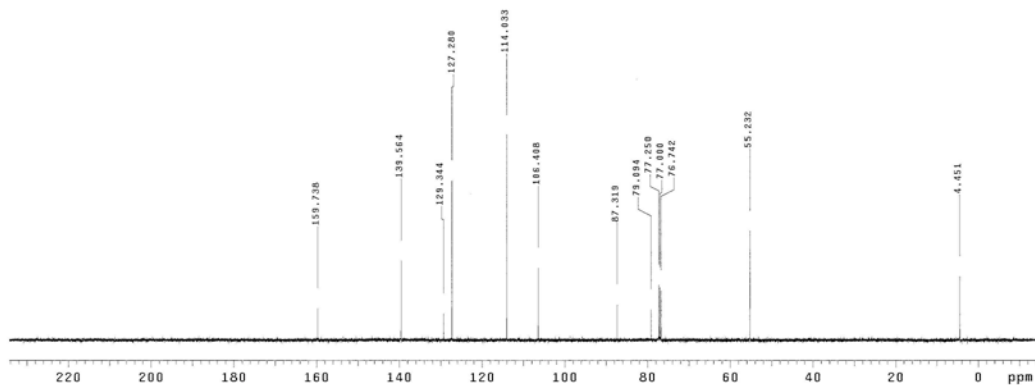
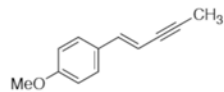
<b>PULSE SEQUENCE</b> Relax. delay 1.000 sec Pulse 45.0 degree Acq. time 1.948 sec Width 31250.0 Hz 28 repetitions	<b>OBSERVE</b> C13, 125.6951290 <b>DECOUPLE</b> H1, 499.6033015 Power 4b db continuously on VALTZ-16 modulated	<b>DATA PROCESSING</b> Line broadening 0.5 Hz FT size 65536 Total time 1 minute	sxu-12-171-2-C13 Solvent: cdcl3 Temp. 25.0 C / 298.1 K Operator: Liu VNMRS-500 "nar18"
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Compound 6k



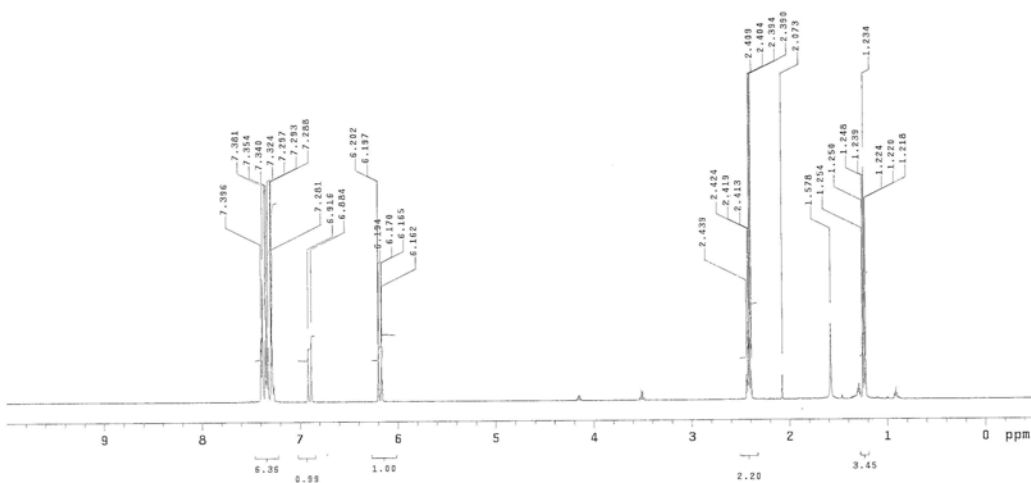
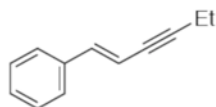
<b>PULSE SEQUENCE</b> Relax. delay 5.000 sec Pulse 45.0 degree Acq. time 2.176 sec Width 15000.2 Hz 16 repetitions	<b>OBSERVE</b> H1, 499.8600016	<b>DATA PROCESSING</b> FT size 85536 Total time 2 minutes	sxu-12-175-H1 Solvent: cdcl3 Temp. 25.0 C / 298.1 K Operator: Liu File: VNMRS-500 "nar17"
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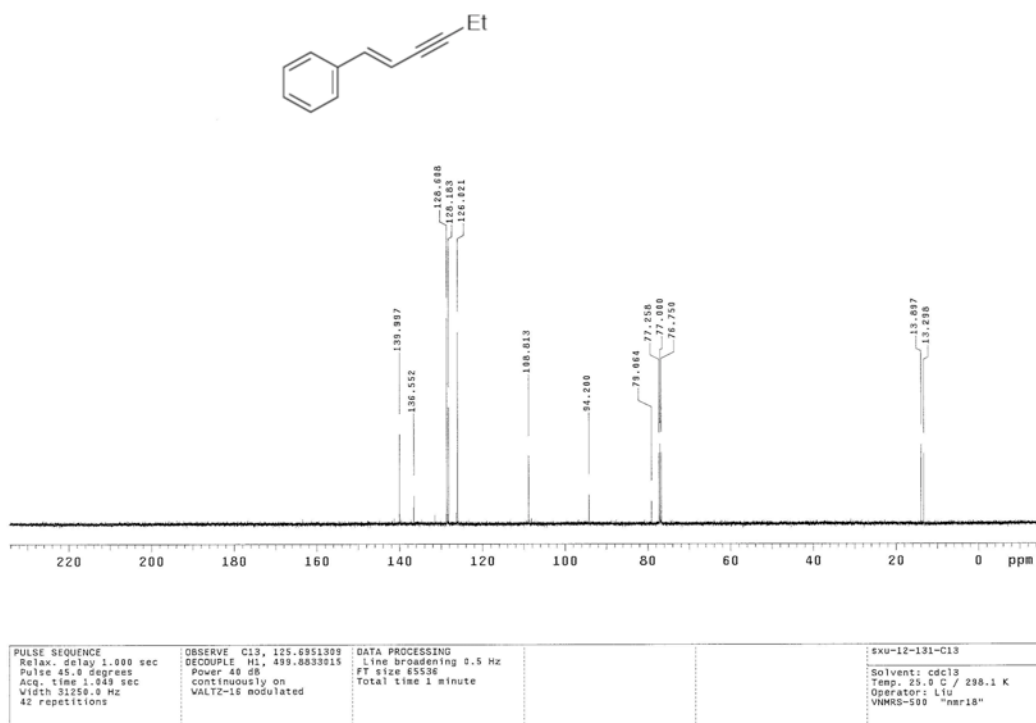


<b>PULSE SEQUENCE</b> Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 1.049 sec Width 31250.0 Hz 22 repetitions	<b>OBSERVE</b> C13, 125.6951326 DECOUPLE H1, 499.0835915 Power 40 dB Continuously on WALTZ-16 modulated	<b>DATA PROCESSING</b> Line broadening 0.5 Hz FT size 65536 Total time 1 minute	sku-12-175-C13 Solvent: cdcl3 Temp. 25.0 C / 298.1 K Operator: Liu VNMRS-500 "nmr18"
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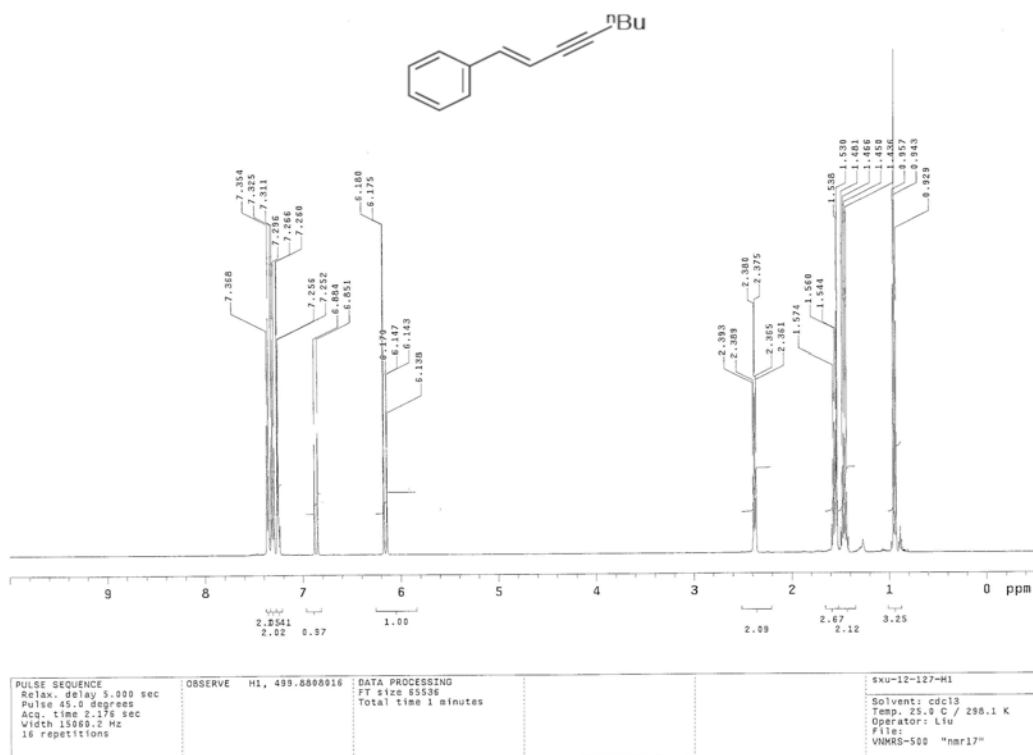
**Compound 6m**

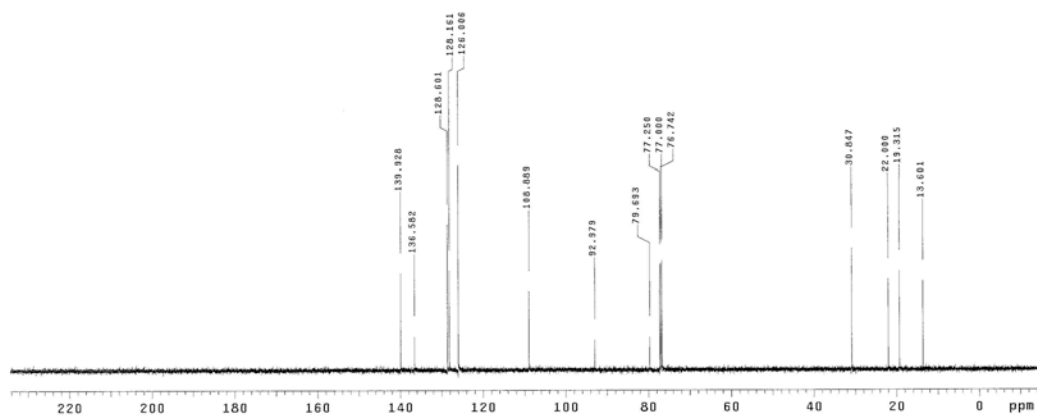
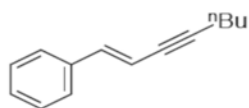


<b>PULSE SEQUENCE</b> Relax. delay 5.000 sec Pulse 45.0 degrees Acq. time 2.049 sec Width 7396.0 Hz 16 repetitions	<b>OBSERVE</b> H1, 499.7720124	<b>DATA PROCESSING</b> FT size 32768 Total time 1 minutes	sku-12-191-H1 Solvent: cdcl3 Temp. 25.0 C / 298.1 K Operator: Liu INOVA-500 "nmr11"
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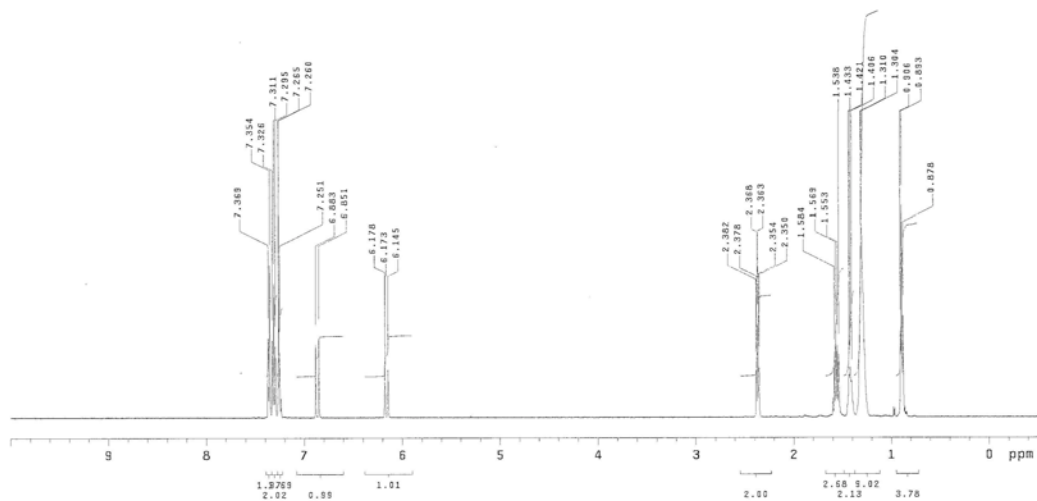
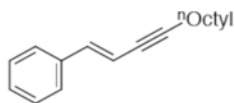
### Compound 6n



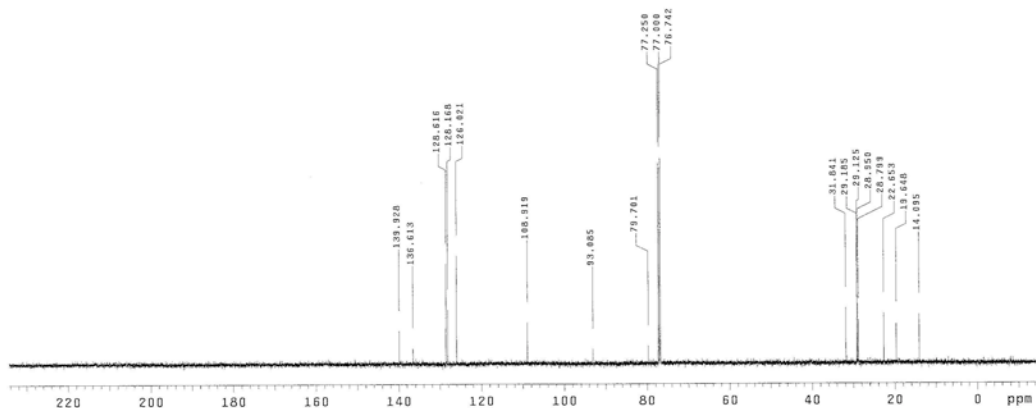
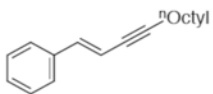


PULSE SEQUENCE Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 1.049 sec Width 31250.0 Hz 38 repetitions	OBSERVE C13, 125.8951300 DECOUPLE H1, 499.8683015 Power 48 db continuously on WALTZ-16 modulated	DATA PROCESSING Line broadening 0.5 Hz FT size 65536 Total time 1 minute	skx-12-127-C13 Solvent: cdc13 Temp. 25.0 C / 298.1 K Operator: Liu VNMR5-500 "nmr18"
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## Compound 60

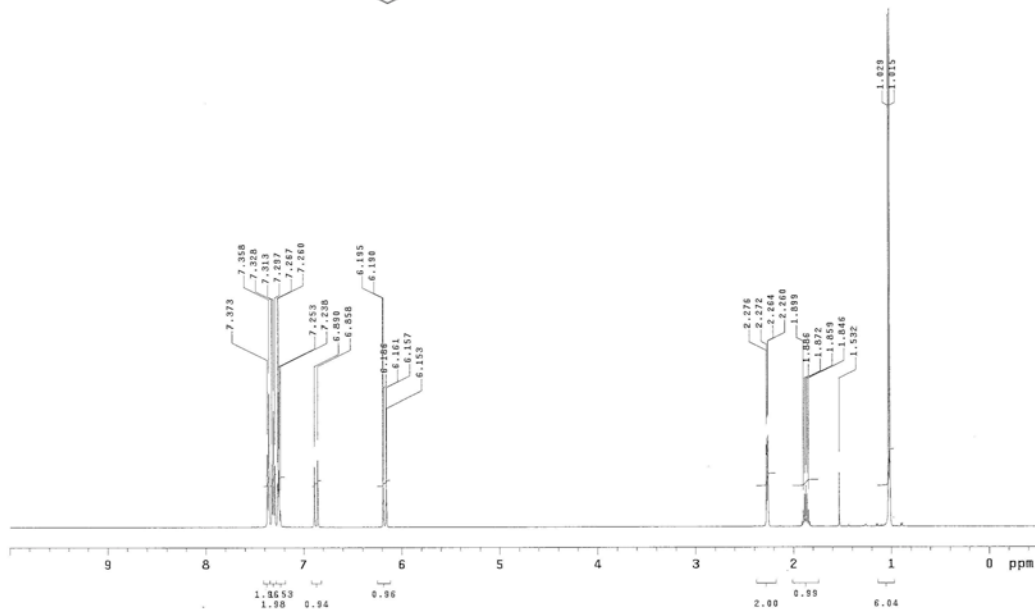
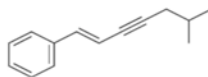


PULSE SEQUENCE Relax. delay 5.000 sec Pulse 45.0 degrees Acq. time 2.045 sec Width 8032.0 Hz 8 repetitions	OBSERVE H1, 499.8686017	DATA PROCESSING FT size 32768 Total time 1 minute	skx-12-169-1-H1 Solvent: cdc13 Temp. 25.0 C / 298.1 K Operator: Liu VNMR5-500 "nmr18"
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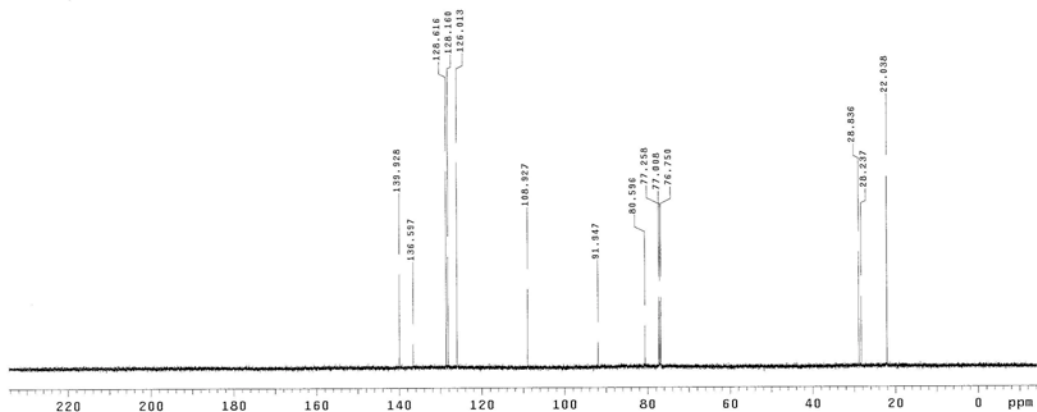
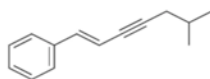


<b>PULSE SEQUENCE</b> Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 1.258 sec Width 31250.0 Hz 208 repetitions	<b>OBSERVE</b> C13, 125.6951071 <b>DECOUPLE</b> H1, 499.8633015 Power 40 dB continuously on WALTZ-16 modulated	<b>DATA PROCESSING</b> Line broadening 0.5 Hz FT size 65536 Total time 8 minutes	sku-12-169-1-C13 Solvent: cdcl3 Temp. 25.0 C / 298.1 K Operator: Liu VNMRS-500 "nmr18"
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### Compound 6p

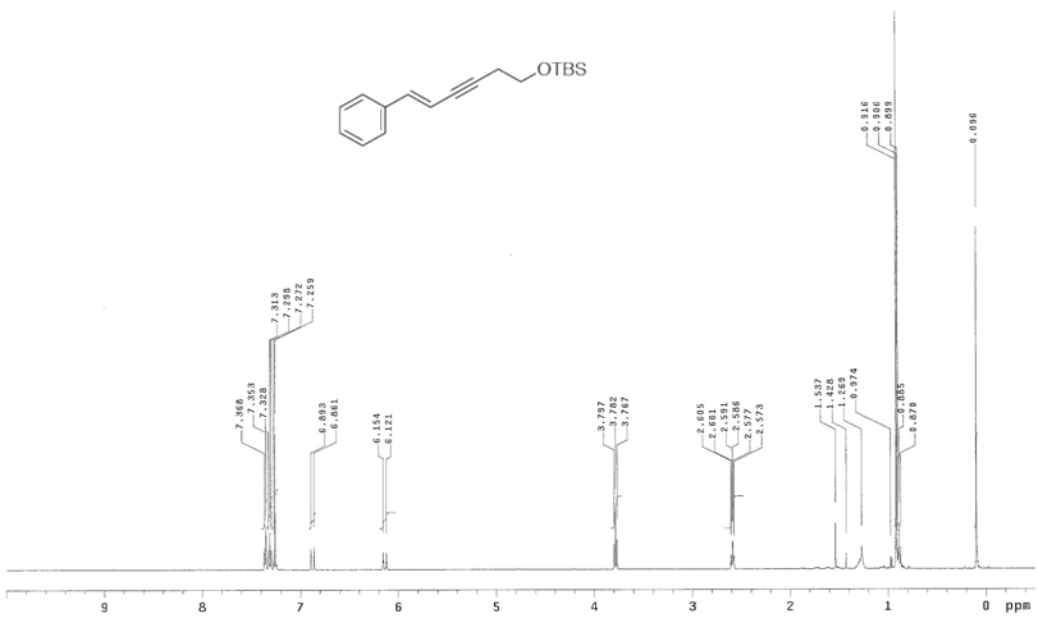
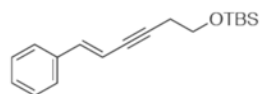


<b>PULSE SEQUENCE</b> Relax. delay 5.000 sec Pulse 45.0 degrees Acq. time 2.045 sec Width 8022.8 Hz 16 repetitions	<b>OBSERVE</b> H1, 499.8608017	<b>DATA PROCESSING</b> FT size 32768 Total time 1 minutes	sku-12-201-2-H1 Solvent: cdcl3 Temp. 25.0 C / 298.1 K Operator: Liu VNMRS-500 "nmr18"
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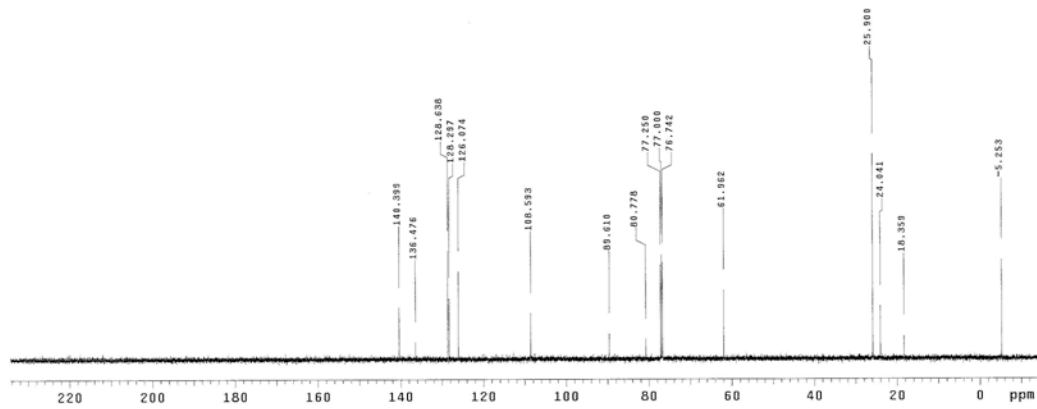
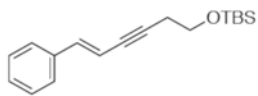


<b>PULSE SEQUENCE</b> Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 1.043 sec Width 31250.0 Hz 42 repetitions	<b>OBSERVE</b> C13, 125.6951290 <b>DECOUPLE</b> H1, 499.8853015 Power 40 dB Continuously on VALTZ-16 modulated	<b>DATA PROCESSING</b> Line broadening 0.5 Hz FT size 65536 Total time 1 minute	sxu-12-261-2-C13 Solvent: cdcl3 Temp. 25.0 C / 298.1 K Operator: Liu VNMRS-500 "nmr18"
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Compound 6q

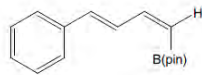
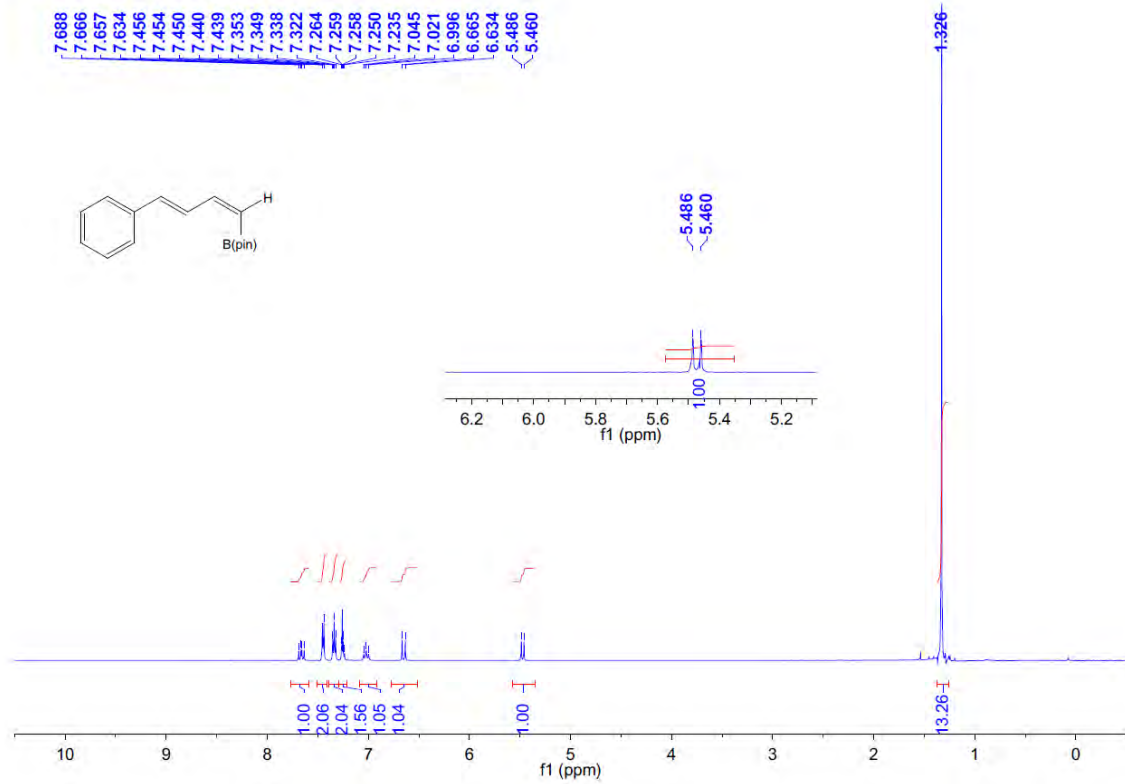


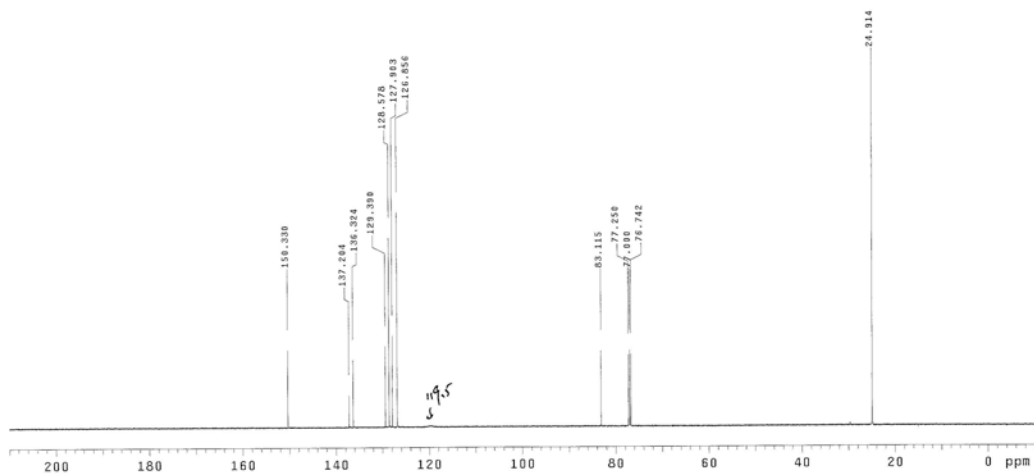
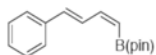
<b>PULSE SEQUENCE</b> Relax. delay 5.000 sec Pulse 45.0 degrees Acq. time 2.045 sec Width 6012.0 Hz 16 repetitions	<b>OBSERVE</b> H1, 499.8808020	<b>DATA PROCESSING</b> FT size 32768 Total time 1 minutes	sxu-12-213-1-H1 Solvent: cdcl3 Temp. 25.0 C / 298.1 K Operator: Liu VNMRS-500 "nmr18"
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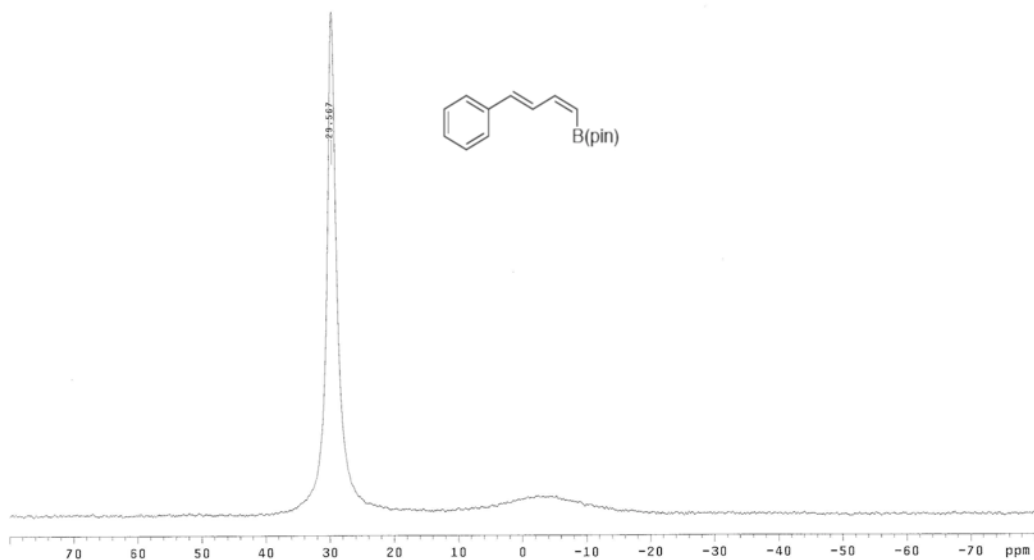
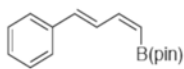
<b>PULSE SEQUENCE</b> Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 1.049 sec Width 31250.0 Hz 64 repetitions	<b>OBSERVE</b> C13, 125.6951271 <b>DECOUPLE</b> H1, 499.8833015 Power 48 dB continuously on WALTZ-16 modulated	<b>DATA PROCESSING</b> Line broadening 0.5 Hz FT size 65536 Total time 2 minutes	sku-12-213-1-C13 Solvent: cdcl3 Temp: 25.0 C / 298.1 K Operator: Liu VMMS-500 "mar10"
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### Compound 5a



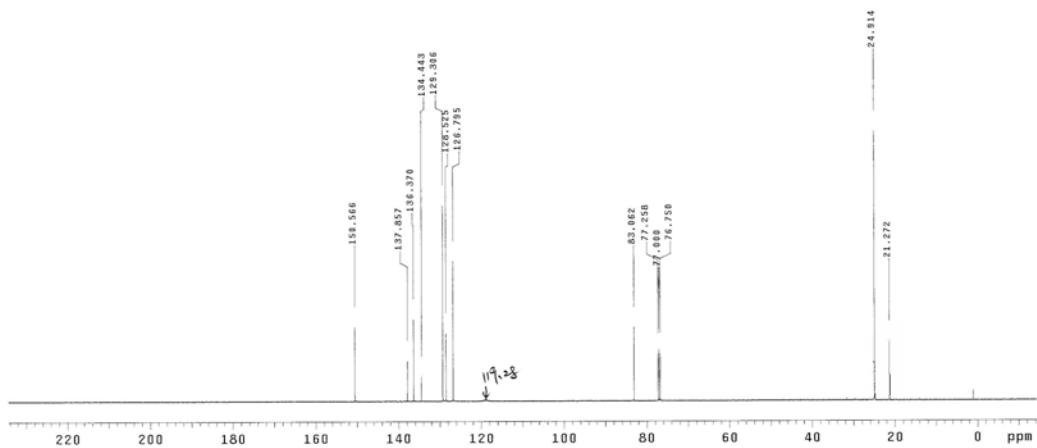
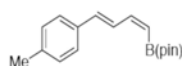
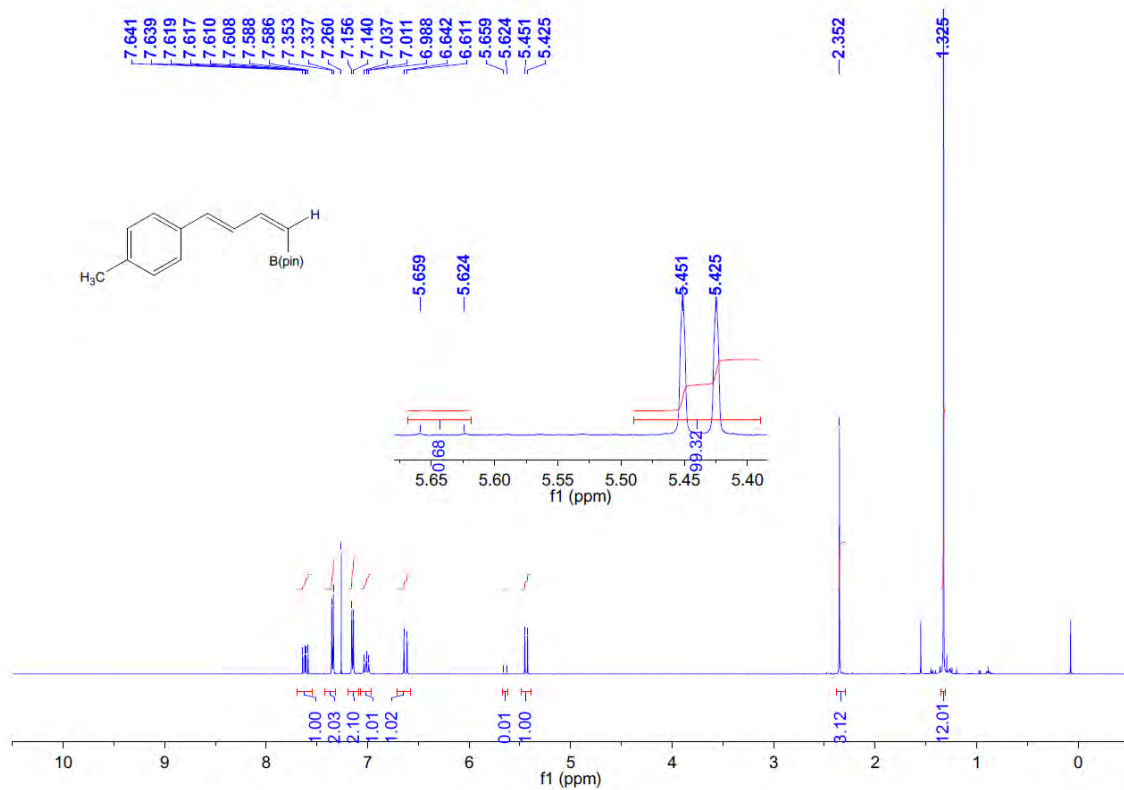


<b>PULSE SEQUENCE</b> Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 1.049 sec Width 31350.0 Hz 412 repetitions	<b>OBSERVE</b> C13, 125.6951300 <b>DECOUPLE</b> H1, 499.0833015 Power 40 dB Continuously on WALTZ-16 modulated	<b>DATA PROCESSING</b> Line broadening 0.5 Hz FT size 65536 Total time 14 minutes	sxu-11-241-C13 Solvent: cdc13 Temp. 25.0 C / 298.1 K Operator: Liu File: VNMRS-500 "nmr17"
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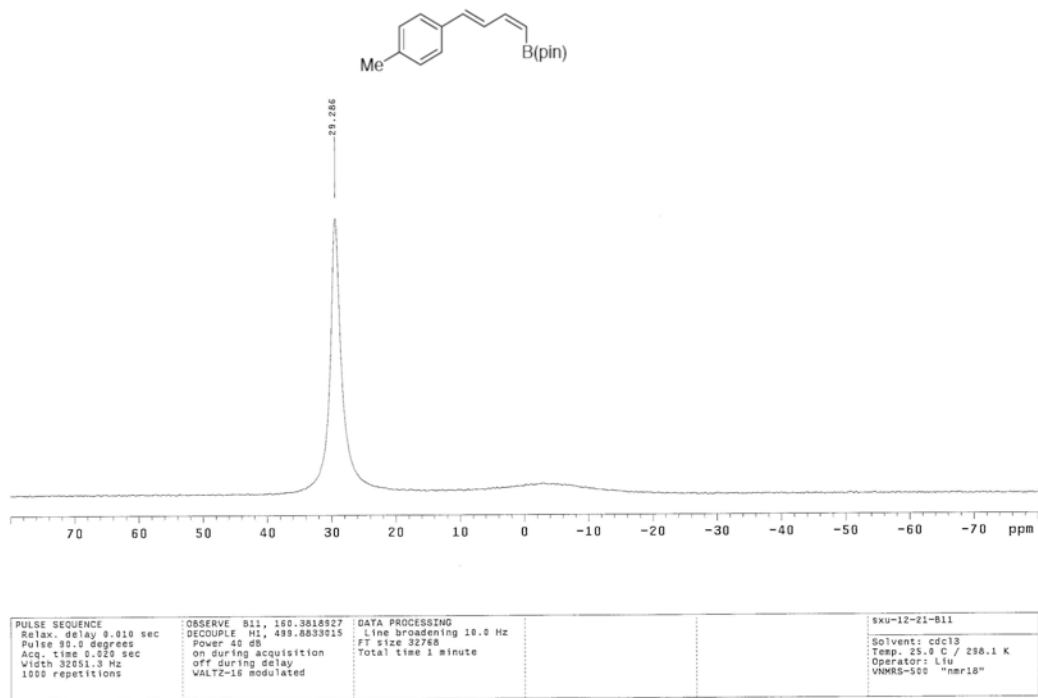
<b>PULSE SEQUENCE</b> Relax. delay 0.310 sec Pulse 80.0 degrees Acq. time 0.020 sec Width 32051.3 Hz 1024 repetitions	<b>OBSERVE</b> H1, 160.3810266 <b>DECOUPLE</b> H1, 499.0833015 Power 40 dB On during acquisition Off during delay WALTZ-16 modulated	<b>DATA PROCESSING</b> Line broadening 10.0 Hz FT size 32768 Total time 1 minute	sxu-11-241-H1 Solvent: cdc13 Temp. 25.0 C / 298.1 K Operator: Liu File: VNMRS-500 "nmr17"
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# Compound 5b

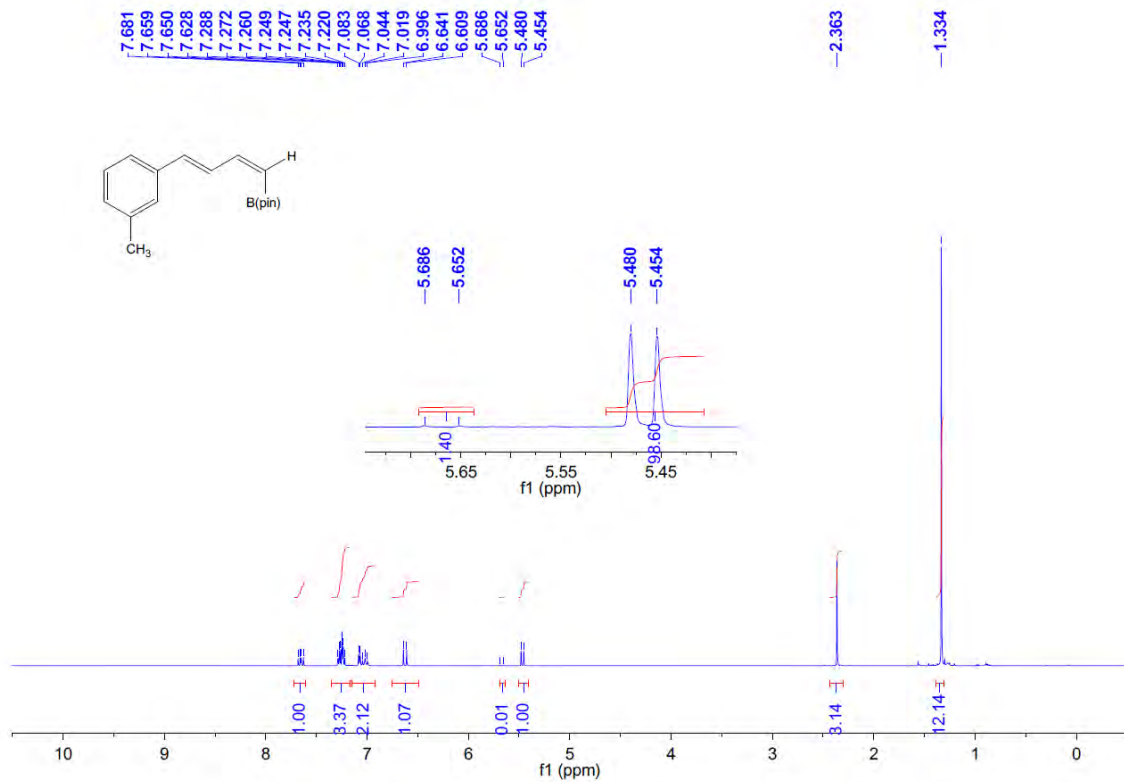


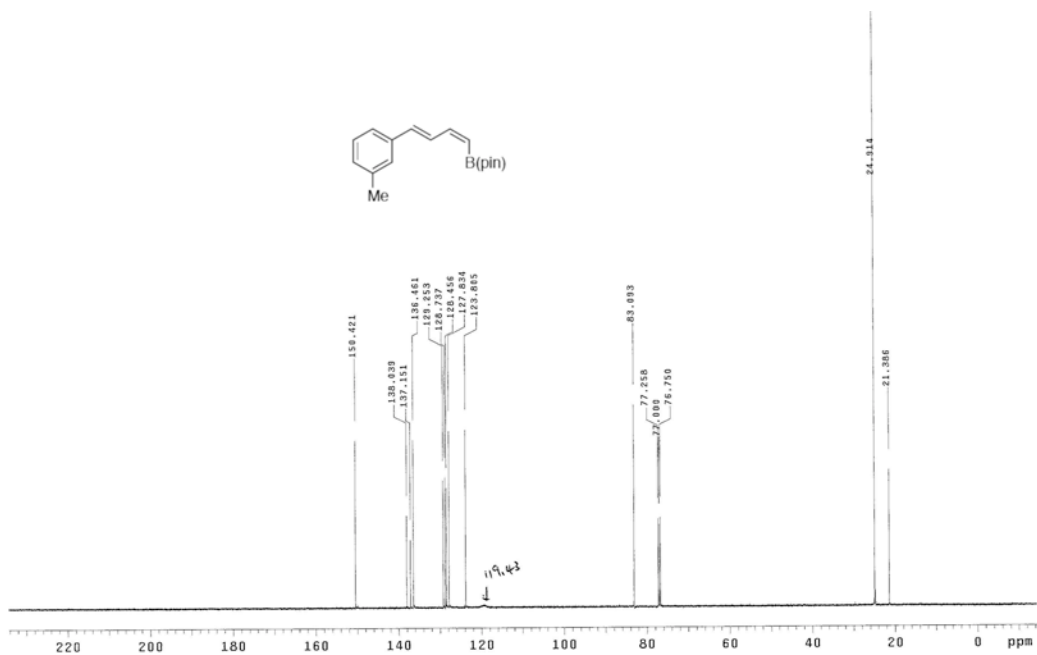
<b>PULSE SEQUENCE</b> Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 1.048 sec Width 31250.0 Hz 622 repetitions	<b>OBSERVE</b> C13, 125.6951389 DECOUPLE H1, 499.8033015 Power 40 dB continuously on WALTZ-16 modulated	<b>DATA PROCESSING</b> Line Broadening 0.5 Hz FT size 65536 Total time 21 minutes	sxu-12-21-C13 Solvent: cdcl3 Temp. 25.0 C / 298.1 K Operator: Liu VNMR5-500 "mr18"
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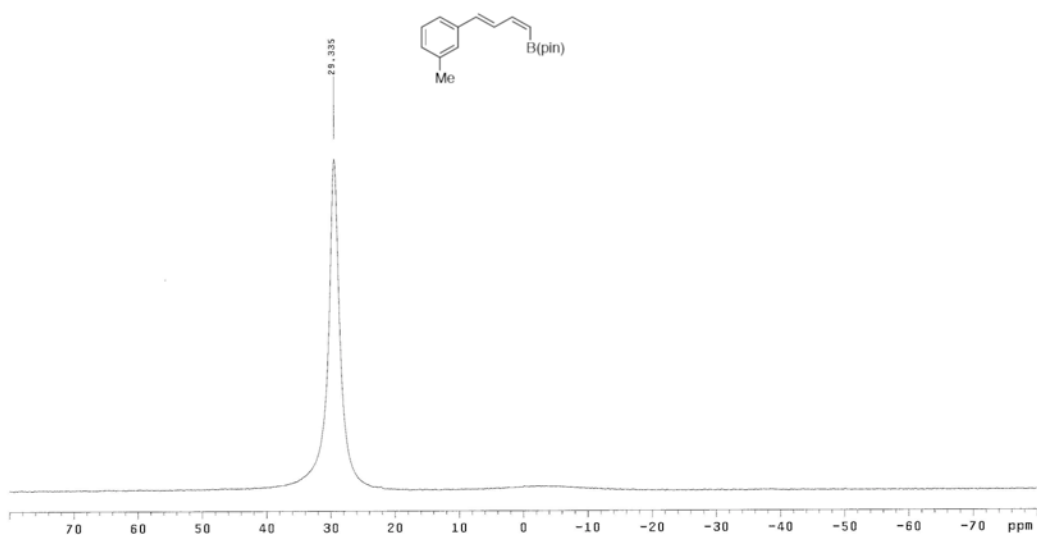


### Compound 5c



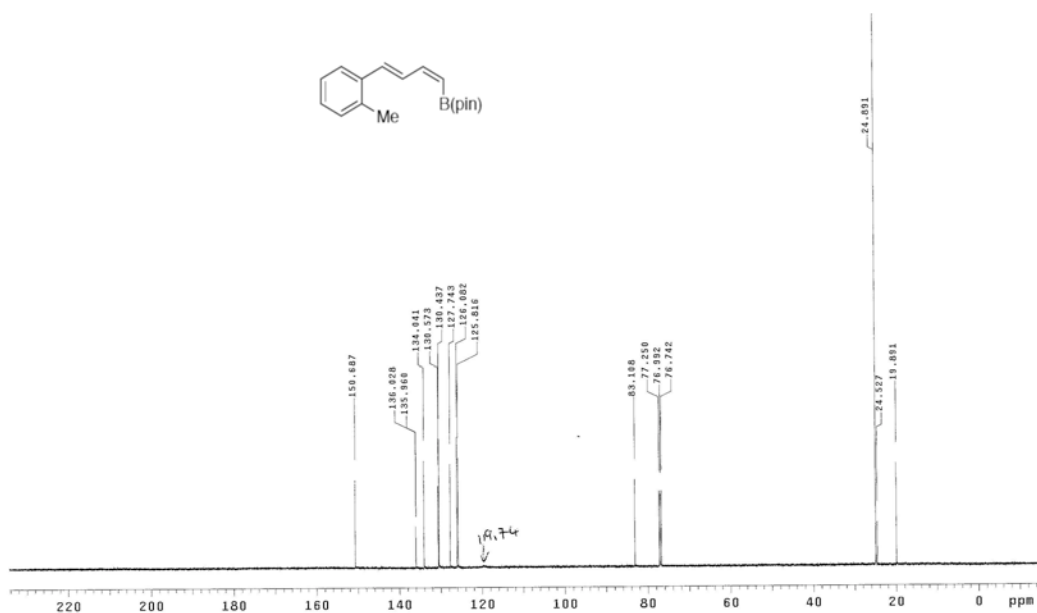
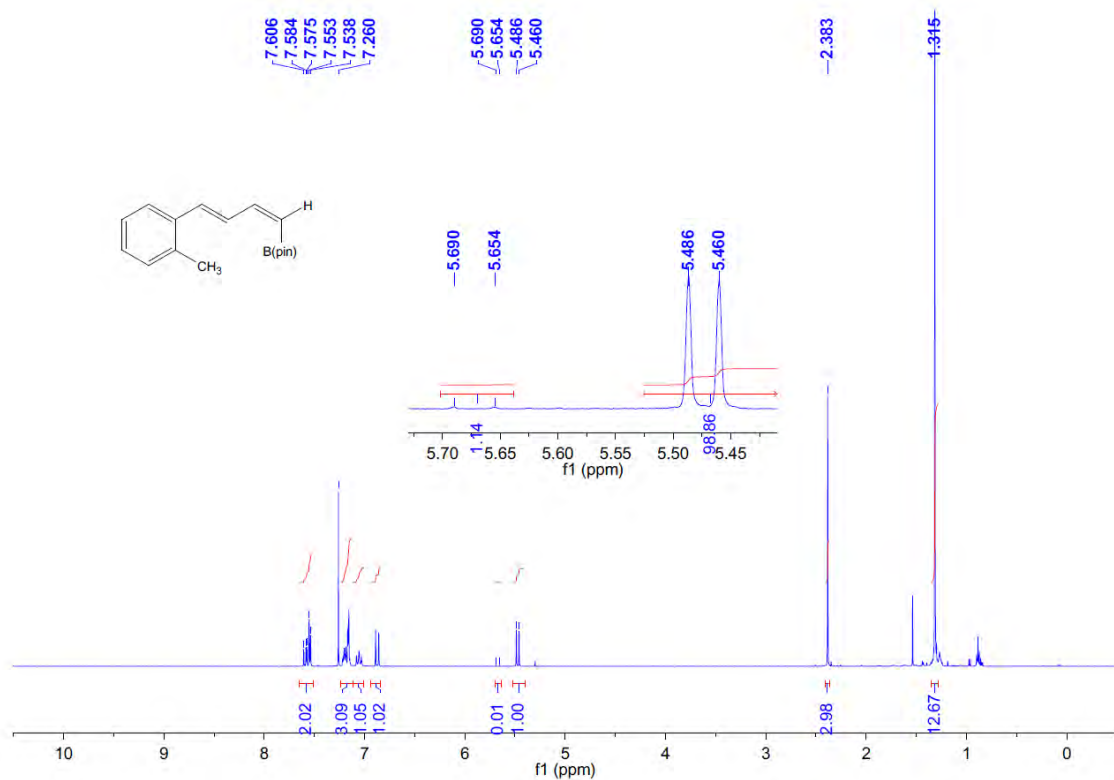


<b>PULSE SEQUENCE</b> Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 1.049 sec Width 33290.0 Hz 436 repetitions	<b>OBSERVE</b> C13, 125.6951309 <b>DECUPLE</b> W1, 499.8833915 Power 40 dB continuously on WALTZ-16 modulated	<b>DATA PROCESSING</b> Line broadening 0.5 Hz FT size 65536 Total time 14 minutes	sxu-12-51-C13 Solvent: cdCl3 Temp. 25.0 C / 298.1 K Operator: Liu VNMRS-500 "nmr18"
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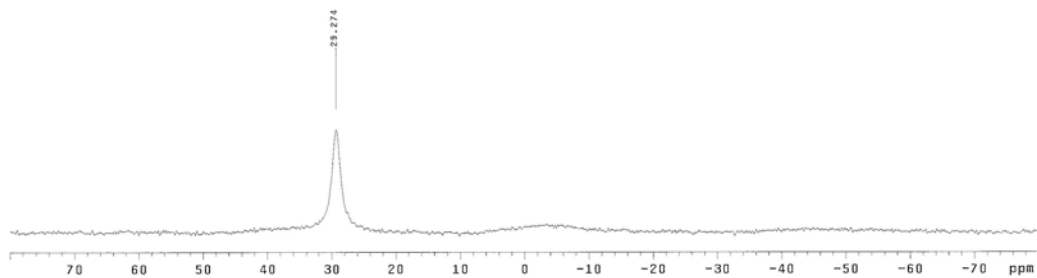
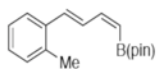


<b>PULSE SEQUENCE</b> Relax. delay 0.010 sec Pulse 90.0 degrees Acq. time 0.320 sec Width 32091.3 Hz 1000 repetitions	<b>OBSERVE</b> B11, 160.3816716	<b>DATA PROCESSING</b> Line broadening 10.0 Hz FT size 32768 Total time 1 minute	sxu-12-95-1-011 Solvent: cdCl3 Temp. 25.0 C / 298.1 K Operator: Liu VNMRS-500 "nmr18"
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# Compound 5d

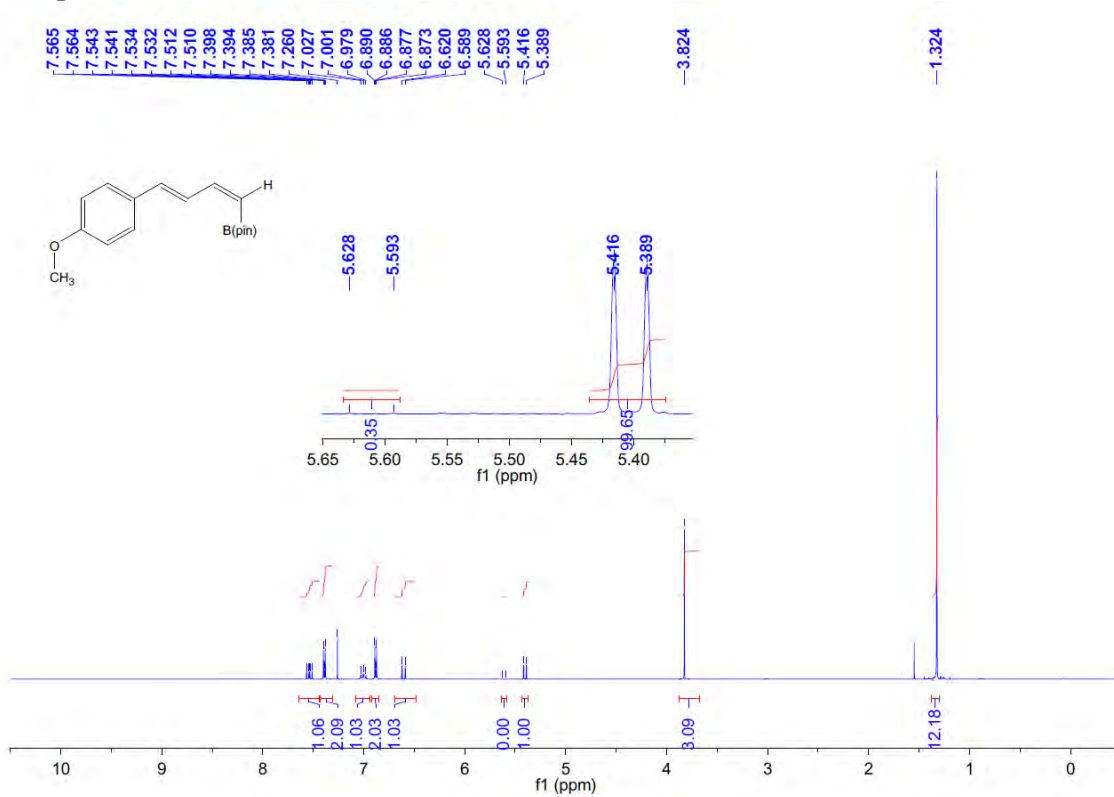


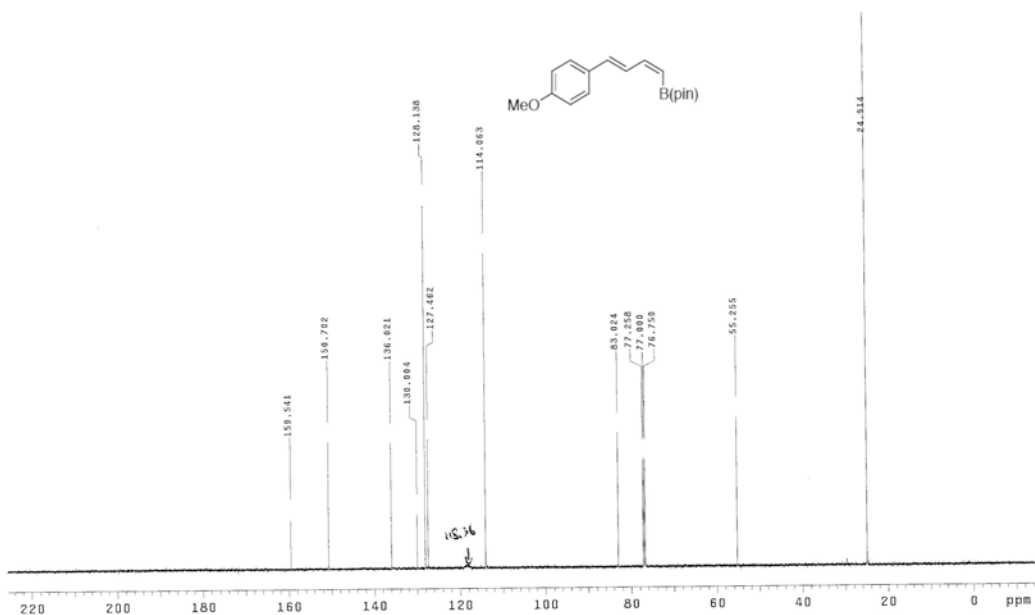
<b>PULSE SEQUENCE</b> Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 1.049 sec Width 31250.0 Hz 250 repetitions	<b>OBSERVE</b> C13, 125.6951309 <b>DECOUPLE</b> H1, 499.8633915 Power 49.98 continuously on VALTZ-16 modulated	<b>DATA PROCESSING</b> Line broadening 0.5 Hz FT size 65536 Total time 7 minutes	Sxu-12-81-1-C13 Solvent: cdcl3 Temp. 25.0 C / 298.1 K Operator: Liu VNMRS-500 "nmr18"
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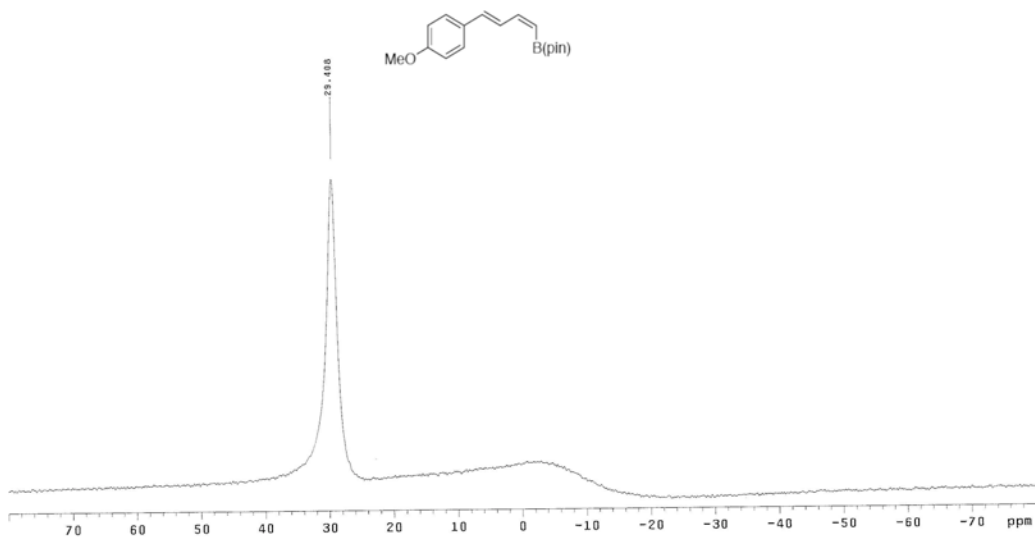
<b>PULSE SEQUENCE</b>	<b>OBSERVE</b> 811, 160, 2816736	<b>DATA PROCESSING</b>	sku-12-01-1-011
Relax. delay 0.010 sec	DECOUPLE M1, 499, 6833015	Line broadening 10.0 Hz	Solvent: cdcl3
Pulse 90.0 degrees	Power 40 dB	FT size 32768	Temp: 25.0 C / 298.1 K
Acq. time 0.220 sec	on during acquisition	Total time 1 minute	Operator: Liu
Width 32051.3 Hz	off during delay		VNMR5-500 "ner18"
100 repetitions	WALTZ-16 modulated		

### Compound 5e



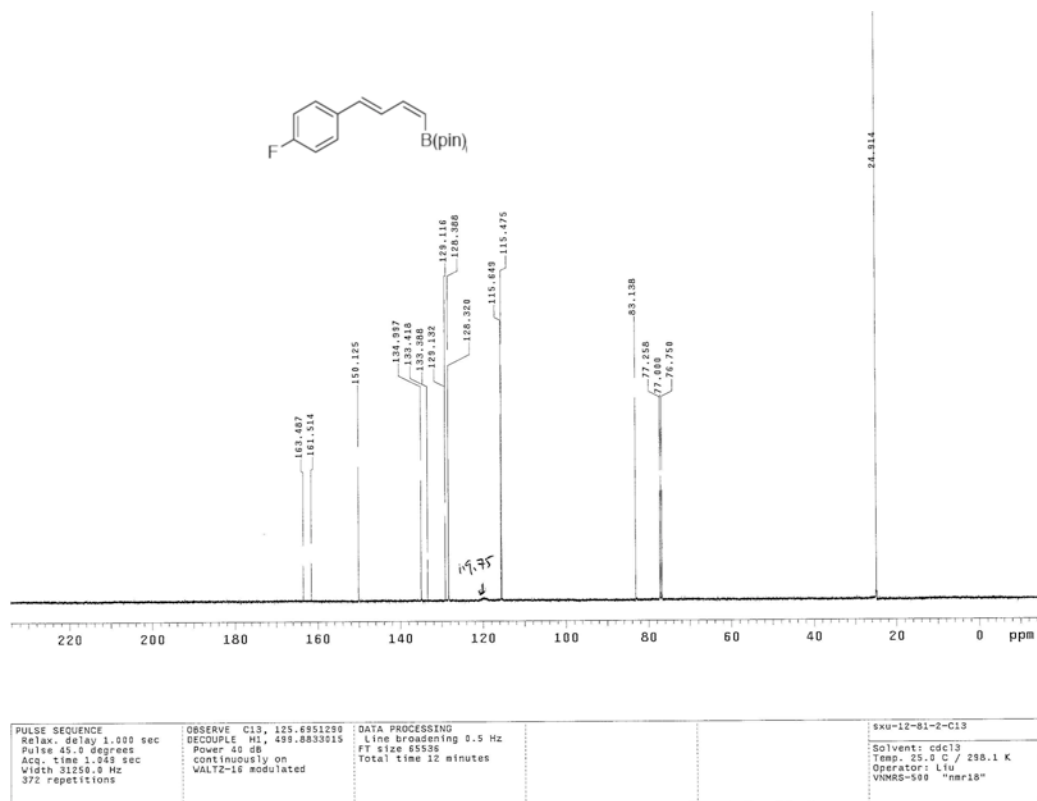
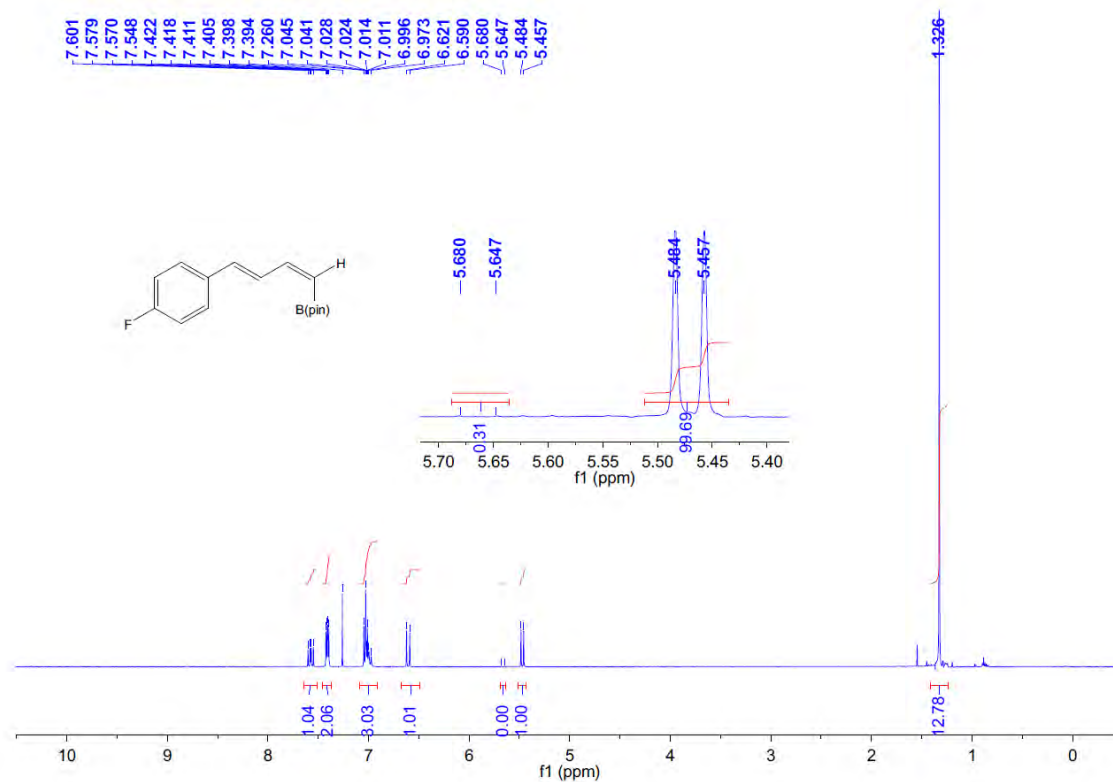


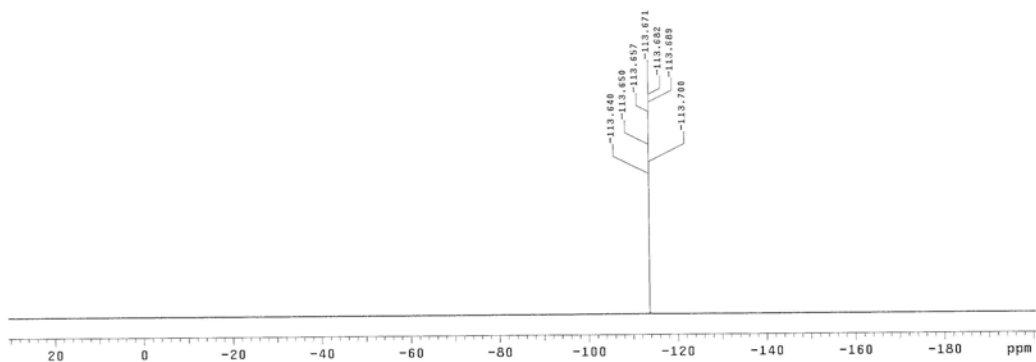
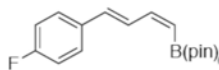
<b>PULSE SEQUENCE</b> Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 1.049 sec Width 32500.0 Hz 210 repetitions	<b>OBSERVE</b> C13, 125.6851308 DECUPLE H1, 499.8683315 Power 40 dB continuously on VALTZ-16 modulated	<b>DATA PROCESSING</b> Line broadening 0.5 Hz FT size 65535 Total time 7 minutes	sku-11-271-C13 Solvent: cdcl3 Temp. 25.0 C / 298.1 K Operator: Liu VNMRS-500 "mr18"
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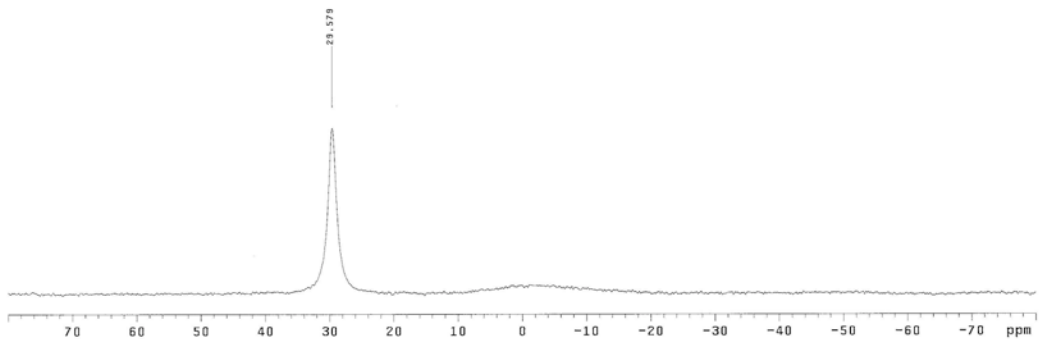
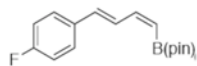
<b>PULSE SEQUENCE</b> Relax. delay 0.010 sec Pulse 68.5 degrees Acq. time 0.020 sec Width 32051.0 Hz 1000 repetitions	<b>OBSERVE</b> 611, 160.3819005	<b>DATA PROCESSING</b> Line broadening 10.0 Hz FT size 32768 Total time 1 minute	sku-11-271-1-B11 Solvent: cdcl3 Temp. 25.0 C / 298.1 K Operator: Liu VNMRS-500 "mr18"
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# Compound 5f



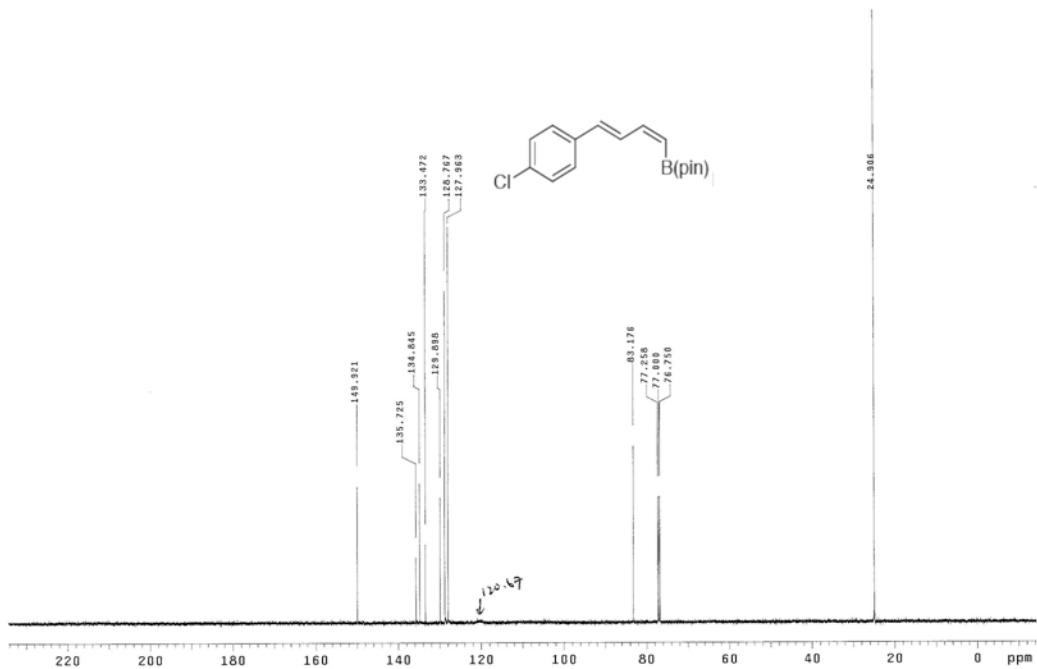
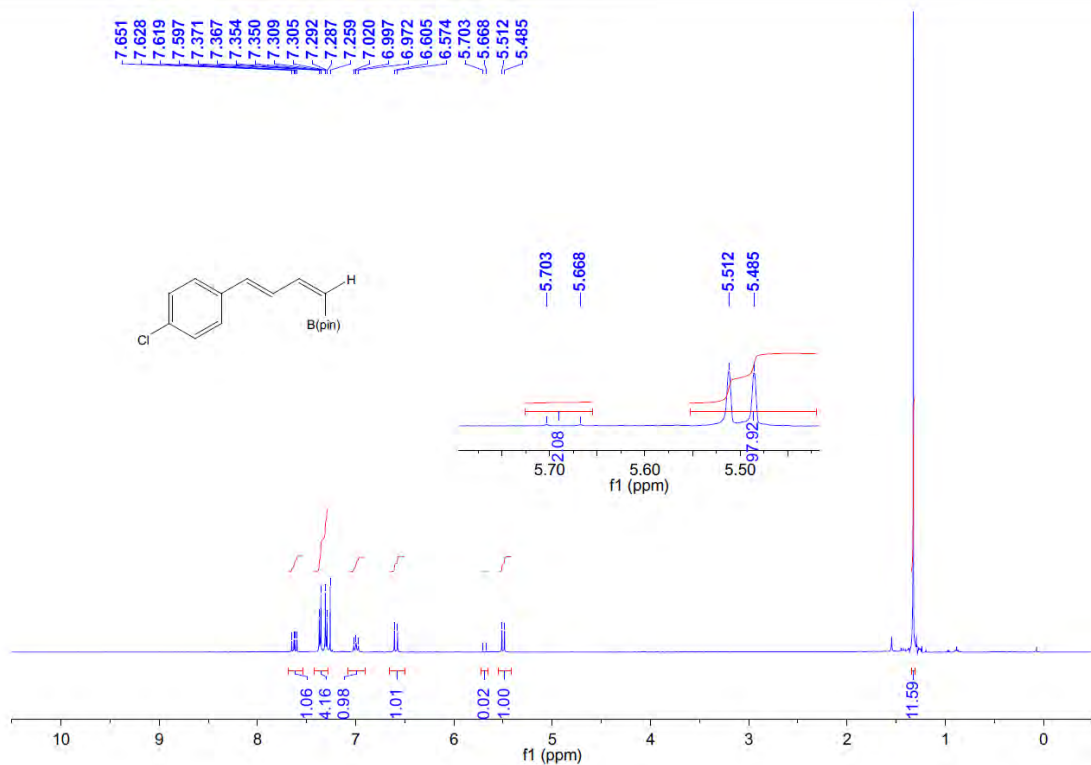


PULSE SEQUENCE Relax. delay 1.000 sec Pulse 30.0 degrees Acq. time 0.863 sec Width 138.7 kHz 14 repetitions	OBSERVE F19, 470.3578969	DATA PROCESSING FT size 131072 Total time 1 minute	skx-12-81-2-F19 Solvent: cdcl3 Temp. 25.0 C / 298.1 K Operator: Liu VNMRS-500 "nmr18"
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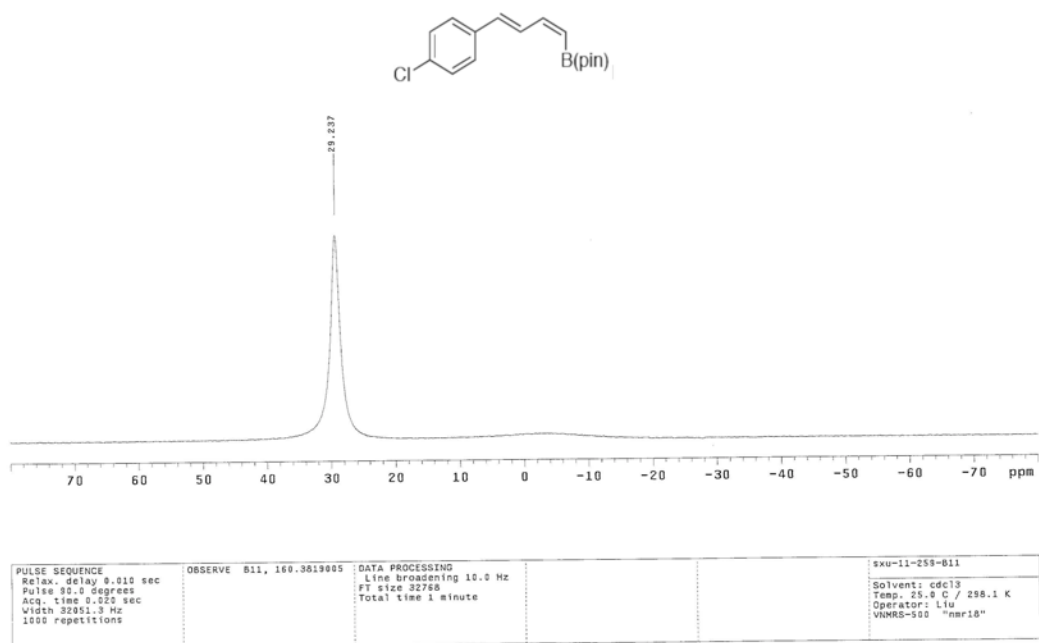
PULSE SEQUENCE Relax. delay 0.010 sec Pulse 90.0 degrees Acq. time 0.120 sec Width 32051.3 Hz 100 repetitions	OBSERVE B11, 160.3816266 DECOUPLE H1, 499.8033015 Power 48 db on during acquisition off during delay WALTZ-16 modulated	DATA PROCESSING Line broadening 10.0 Hz FT size 32768 Total time 1 minute	skx-12-81-2-B11 Solvent: cdcl3 Temp. 25.0 C / 298.1 K Operator: Liu VNMRS-500 "nmr18"
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# Compound 5g

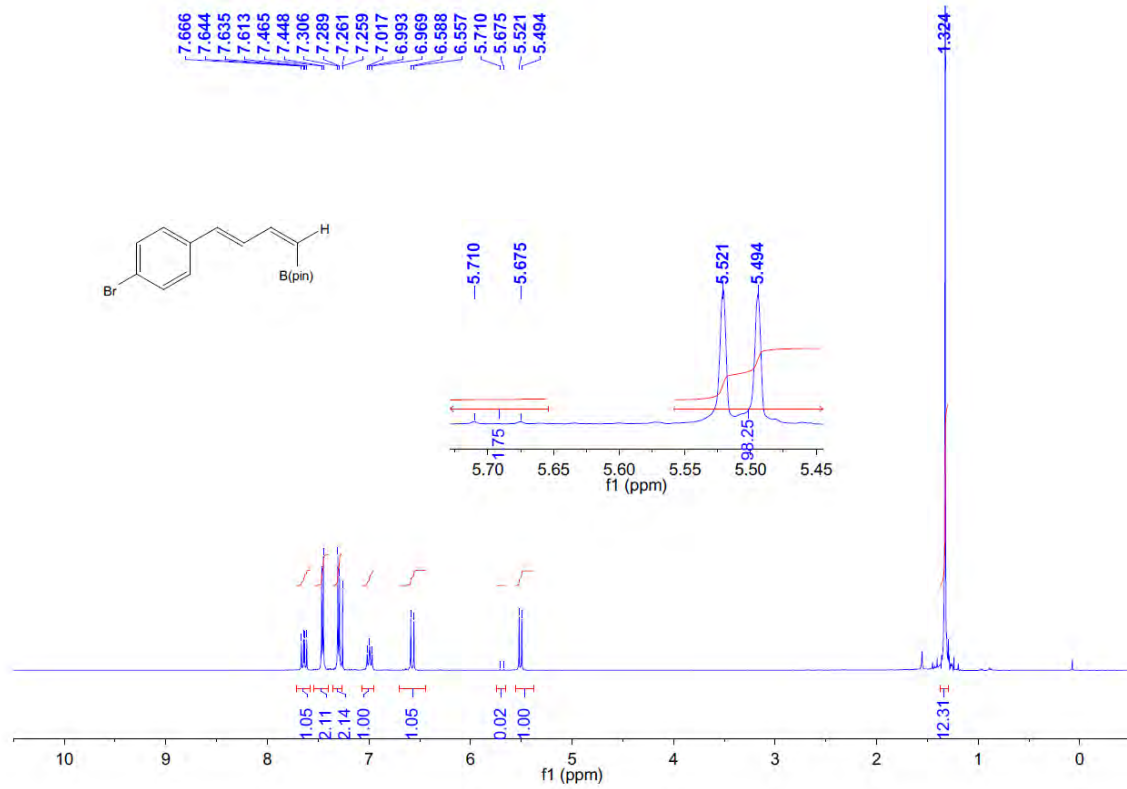


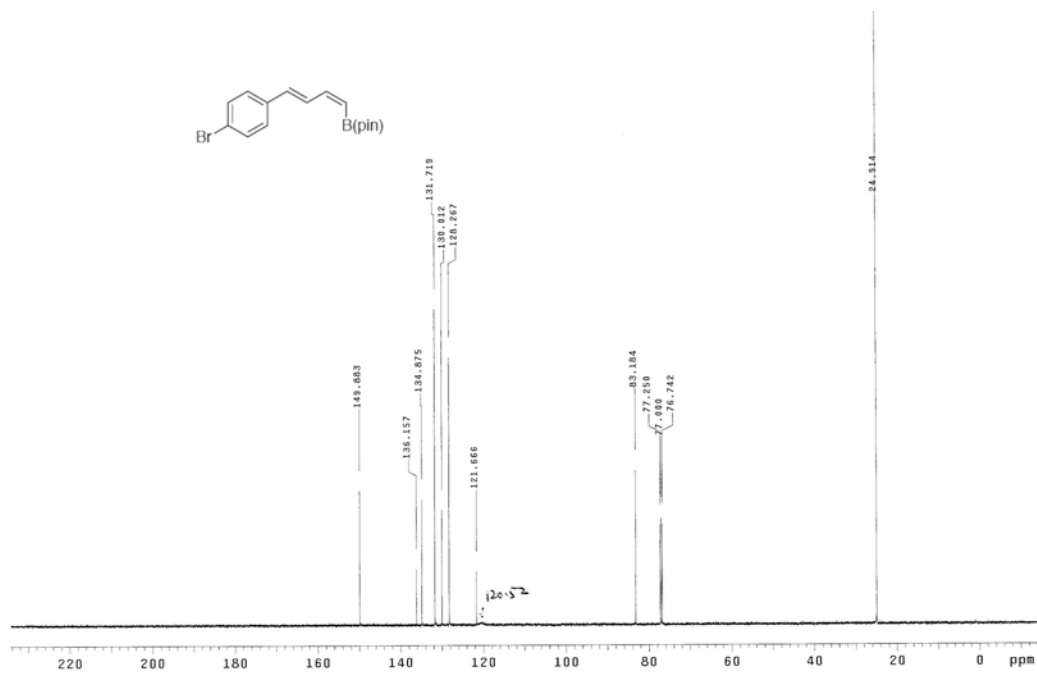
<p>PULSE SEQUENCE Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 1.048 sec Width 31250.0 Hz 178 repetitions</p>	<p>OBSERVE C13, 125.6951300 DECOUPLE H1, 499.8633015 Power 40 dB continuously on WALTZ-16 modulated</p>	<p>DATA PROCESSING Line broadening 0.5 Hz FT size 65536 Total time 9 minutes</p>	<p>sku=11-259-Cl3 Solvent: cdcl3 Temp: 25.0 C / 298.1 K Operator: Liu VNMRS-500 "nmr18"</p>
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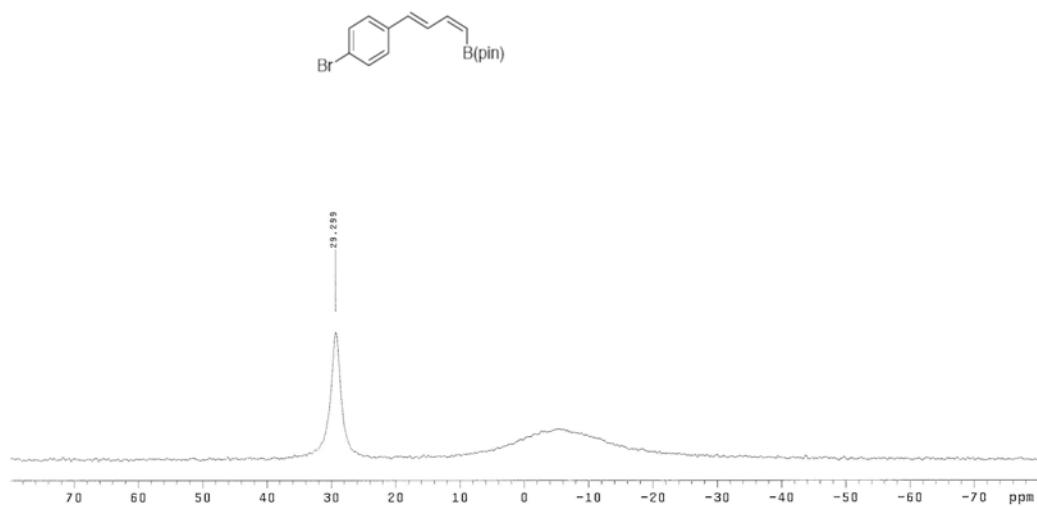


### Compound 5h



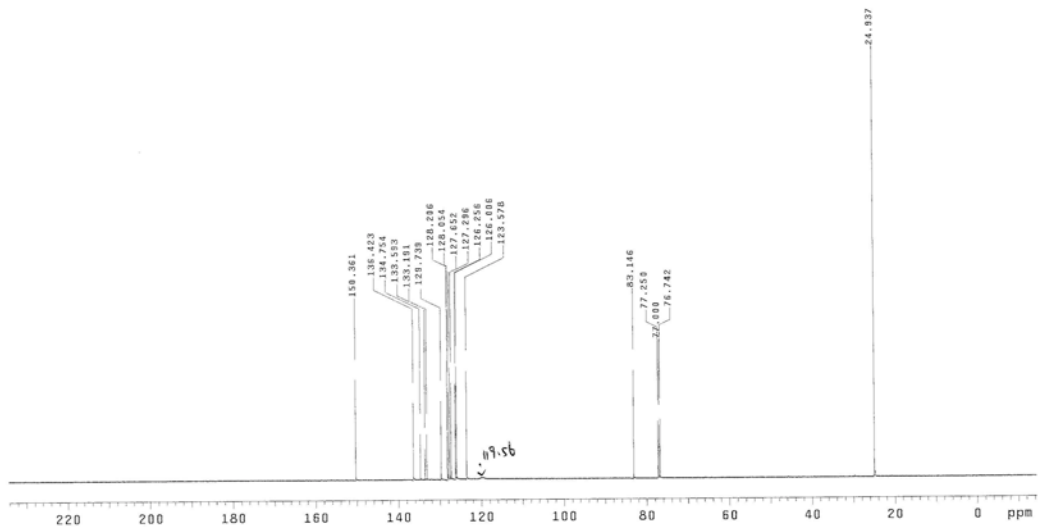
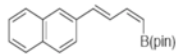
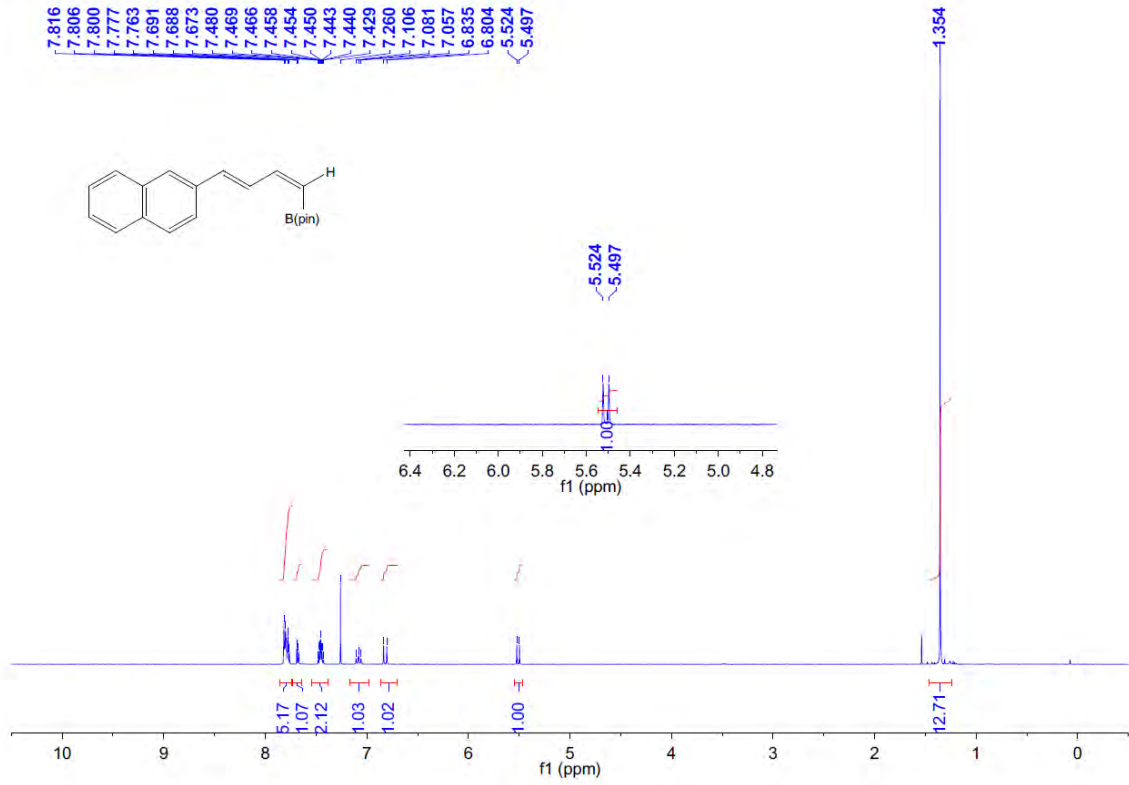


<b>PULSE SEQUENCE</b> Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 1.049 sec Width 31250.0 Hz 270 repetitions	<b>OBSERVE</b> C13, 125.6951300 DECOUPLE H1, 499.8633915 Power 40 dB continuously on WALTZ-16 modulated	<b>DATA PROCESSING</b> Line broadening 0.5 Hz FT size 65536 Total time 9 minutes	sxu-12-87-C13 Solvent: cdcl3 Temp. 25.0 C / 298.1 K Operator: Liu VNMR5-500 "nmr16"
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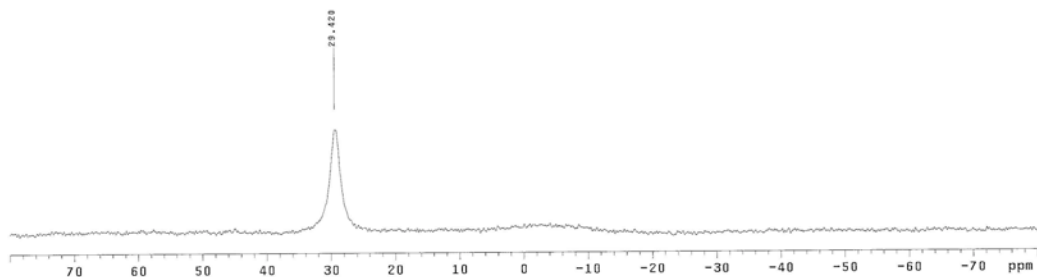
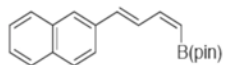


<b>PULSE SEQUENCE</b> Relax. delay 0.010 sec Pulse 80.6 degrees Acq. time 0.026 sec Width 32251.0 Hz 792 repetitions	<b>OBSERVE</b> B11, 160.3471265	<b>DATA PROCESSING</b> Line broadening 15.0 Hz FT size 2048 Total time 1 minute	sxu-12-87-B11 Solvent: cdcl3 Temp. 25.0 C / 298.1 K Operator: Liu INOVA-500 "nmr11"
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# Compound 5i

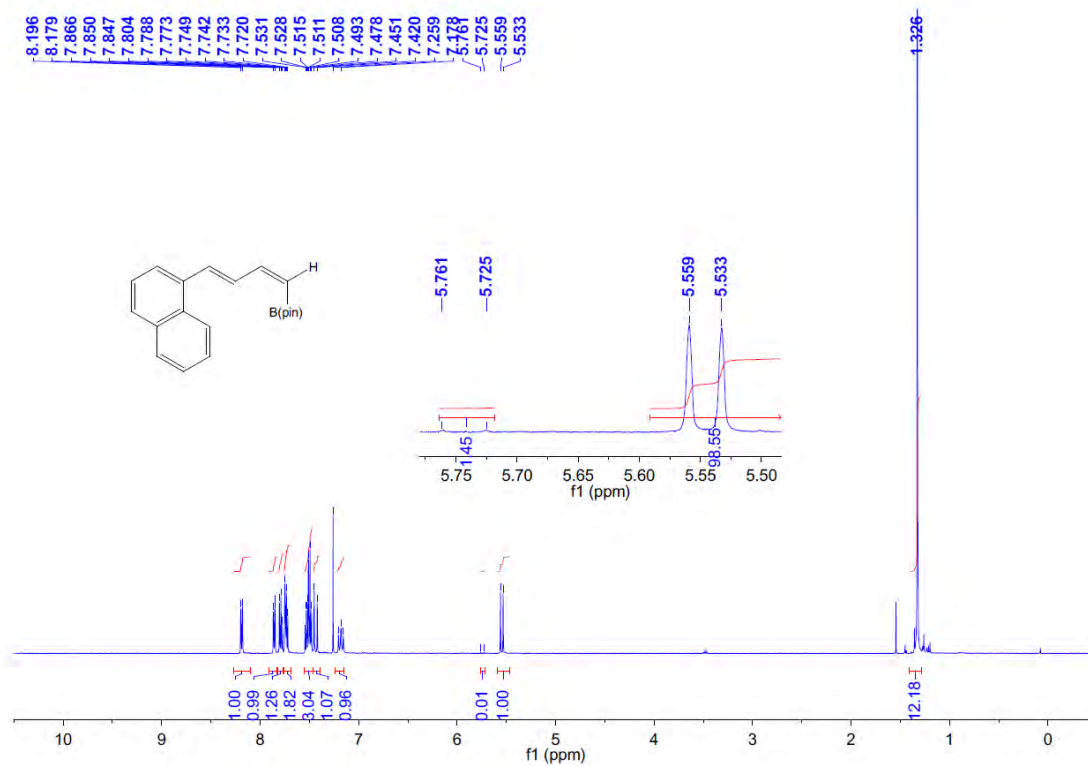


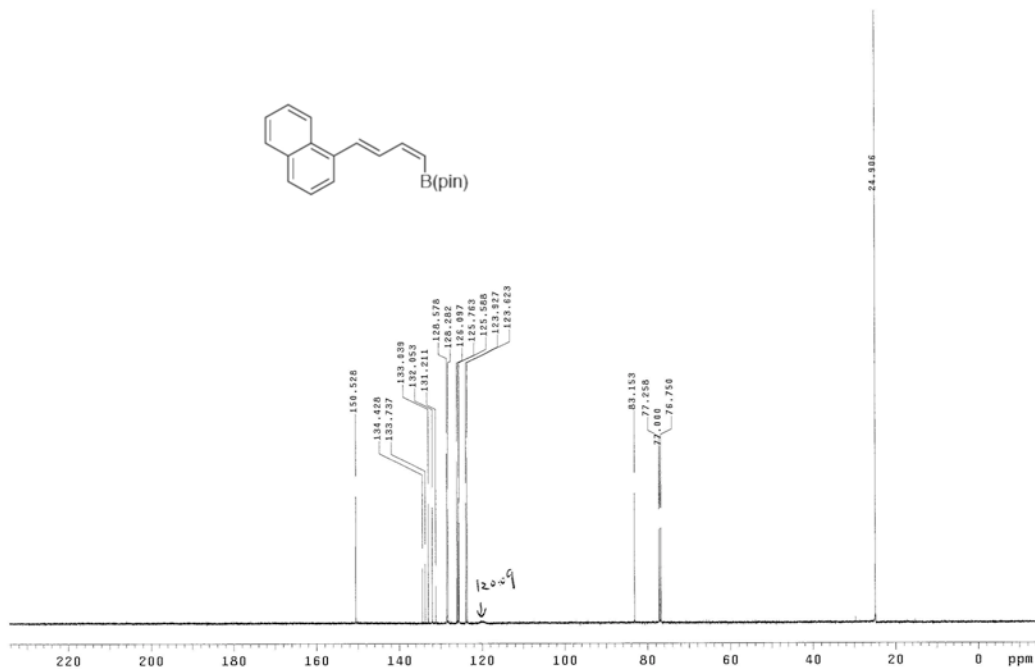
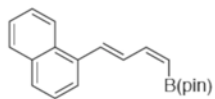
<p>PULSE SEQUENCE Relax, delay 1.000 sec Pulse 45.0 degrees Acq. time 1.049 sec Width 31250.0 Hz 76 repetitions</p>	<p>OBSERVE C13, 125.6951338 DECOUPLE H1, 499.8693015 Power 40 db continuously on WALTZ-16 modulated</p>	<p>DATA PROCESSING Line broadening 0.5 Hz FT size 65335 Total time 24 minutes</p>	<p>solu-12-79-2-C13 Solvent: cdc13 Temp: 25.0 C / 298.1 K Operator: Liu VNMR5-500 "nmr16"</p>
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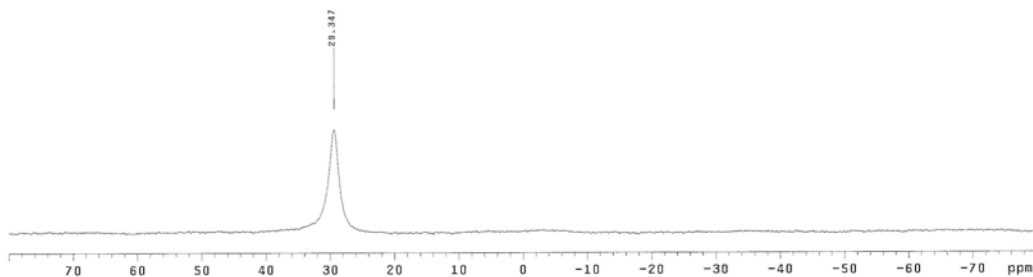
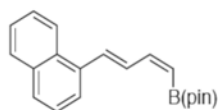
PULSE SEQUENCE	OBSERVE B11, 160.3616736	DATA PROCESSING	skx-12-79-2-B11
Relax. delay 0.010 sec	DECOUPLE H1, 499.8833015	Line broadening 10.0 Hz	Solvent: cdCl3
Pulse 90.0 degree	Power 40 dB	FT size 32768	Temp. 25.0 C / 298.1 K
Acq. time 0.025 sec	on during acquisition	Total time 1 minute	Operator: Liu
Width 32051.3 Hz	off during delay		WMS-500 "mar18"
100 repetitions	WALTZ-16 modulated		

### Compound 5j



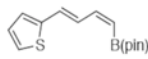
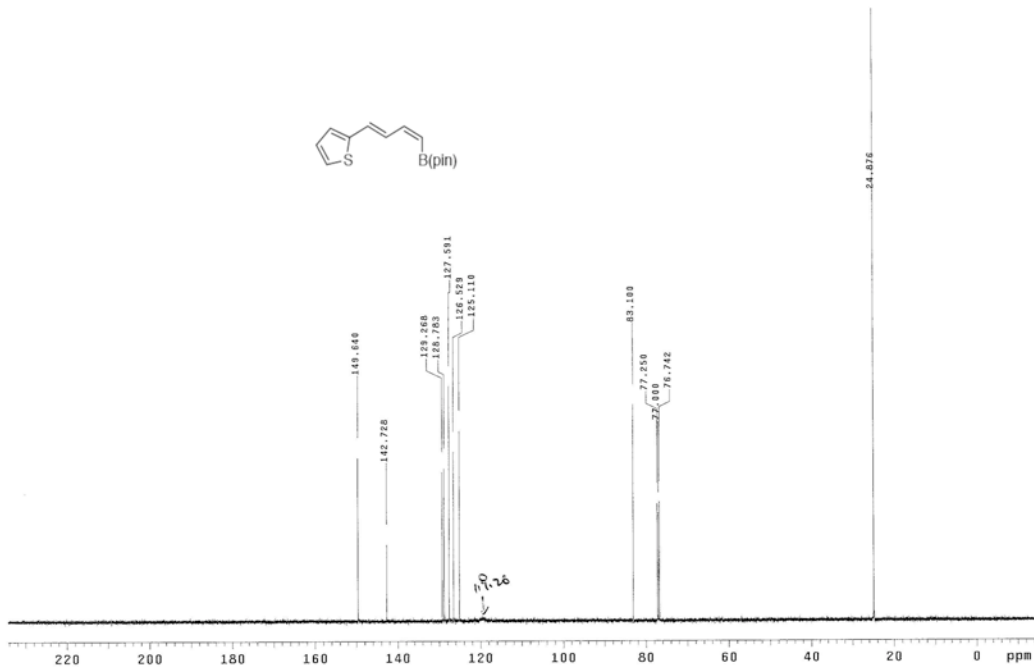
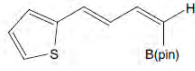
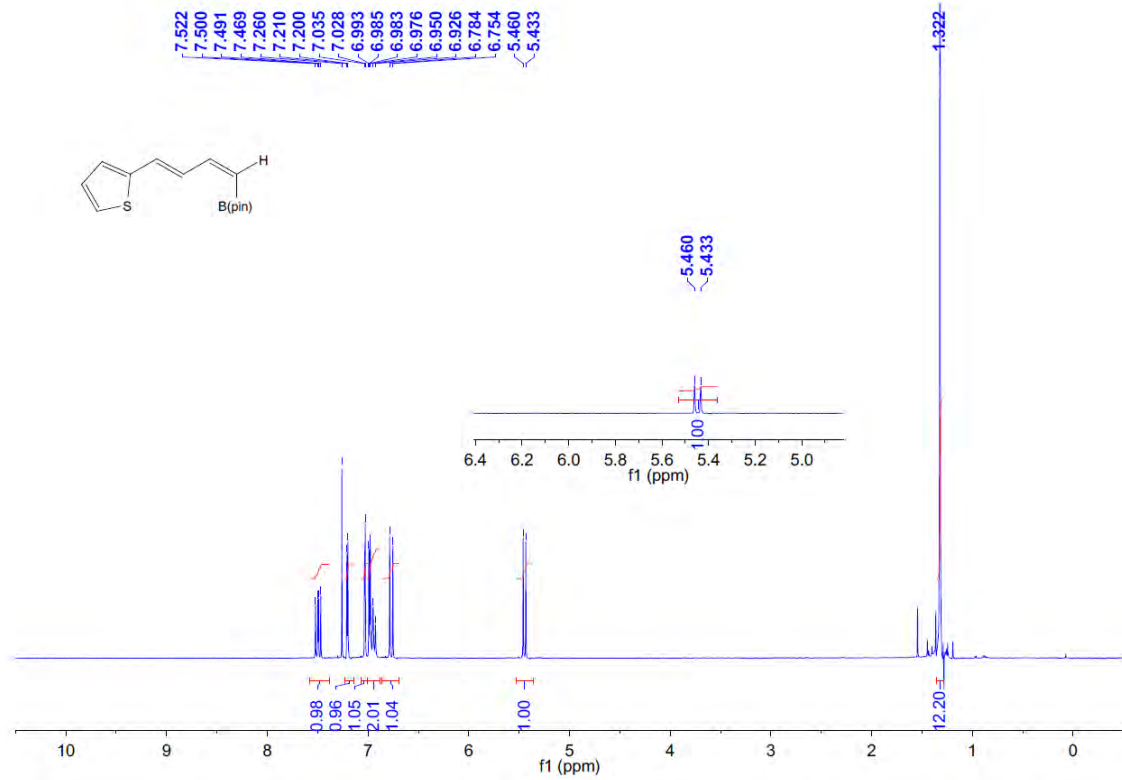


<b>PULSE SEQUENCE</b> Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 1.848 sec Width 31250.0 Hz 300 repetitions	<b>OBSERVE</b> C13, 125.6951319 <b>DECOUPLE</b> H1, 499.8033015 Power 48 dB continuously on WALTZ-16 modulated	<b>DATA PROCESSING</b> Line broadening 0.5 Hz FT size 65536 Total time 10 minutes	sxu-12-79-3-C13 Solvent: cdc13 Temp. 25.0 C / 298.1 K Operator: Liu VNMRS-500 "nar18"
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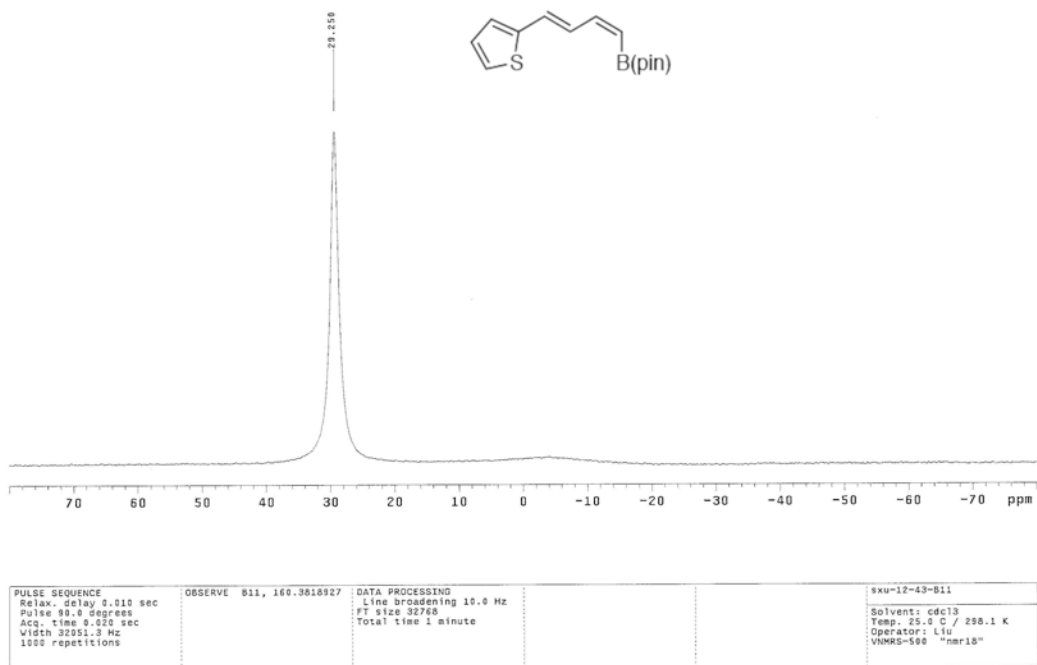


<b>PULSE SEQUENCE</b> Relax. delay 0.010 sec Pulse 90.0 degrees Acq. time 0.020 sec Width 32051.3 Hz 100 repetitions	<b>OBSERVE</b> H1, 160.3816736 <b>DECOUPLE</b> H1, 499.8033015 Power 40 dB on during acquisition off during delay WALTZ-16 modulated	<b>DATA PROCESSING</b> Line broadening 10.0 Hz FT size 32768 Total time 1 minute	sxu-12-79-3-B11 Solvent: cdc13 Temp. 25.0 C / 298.1 K Operator: Liu VNMRS-500 "nar18"
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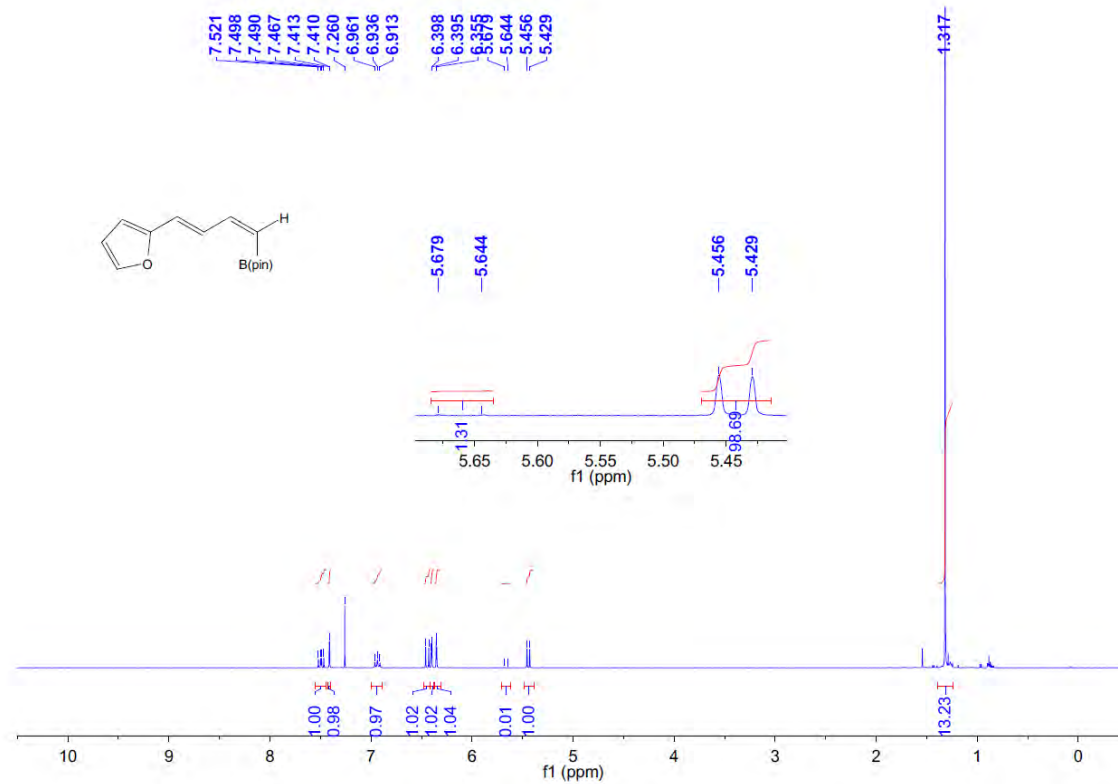
# Compound 5k

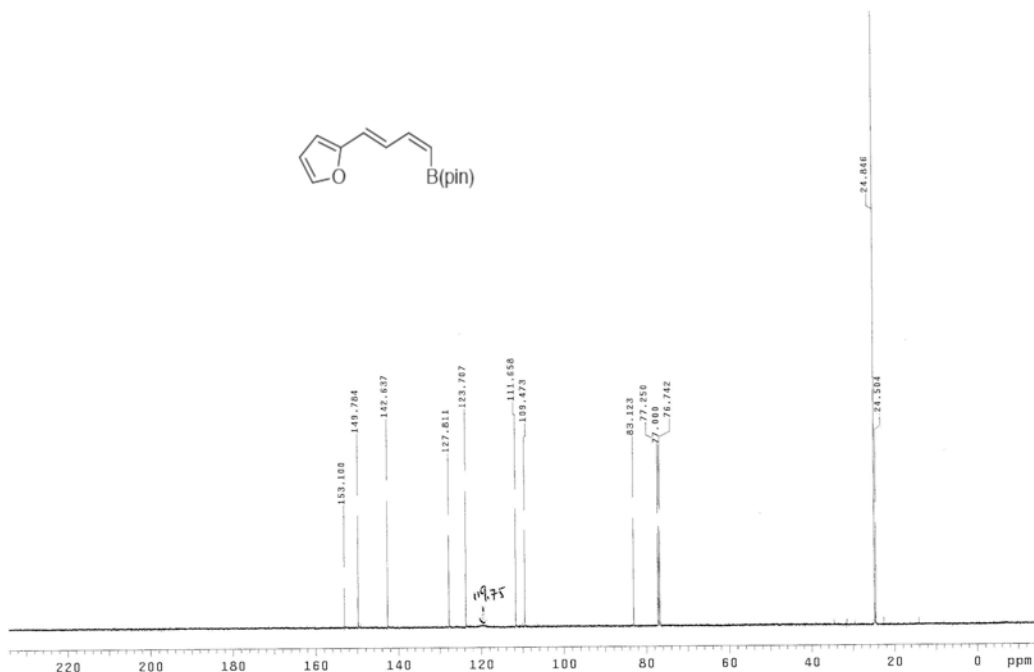
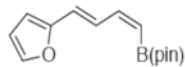


<p>PULSE SEQUENCE</p> <p>Relax. delay 1.000 sec</p> <p>Pulse 45.0 degrees</p> <p>Acq. time 1.043 sec</p> <p>Width 31250.0 Hz</p> <p>152 repetitions</p>	<p>OBSERVE C13, 125.6951328</p> <p>DECOUPLE H1, 489.9833015</p> <p>Power 40 dB</p> <p>Continuously on</p> <p>WALTZ-16 modulated</p>	<p>DATA PROCESSING</p> <p>Line broadening 0.5 Hz</p> <p>FT size 65536</p> <p>Total time 5 minutes</p>	<p>SKU-12-51-2-C13</p> <p>Solvent: cdcl3</p> <p>Temp. 25.0 C / 298.1 K</p> <p>Operator: Liu</p> <p>VMRS-500 "narr18"</p>
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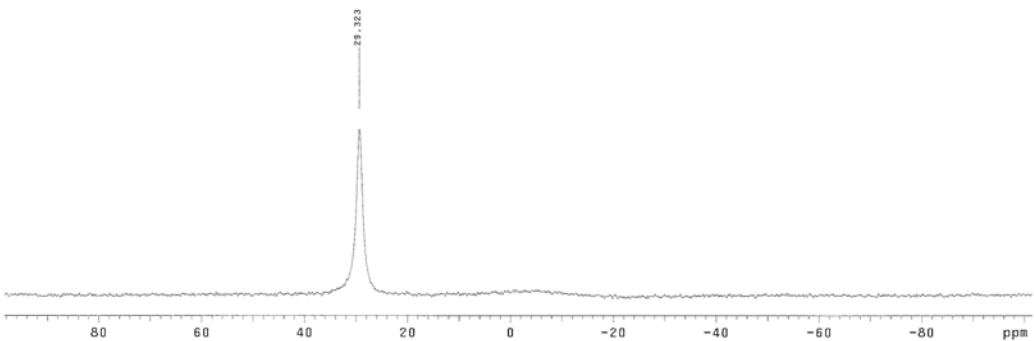
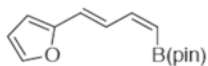


### Compound 51





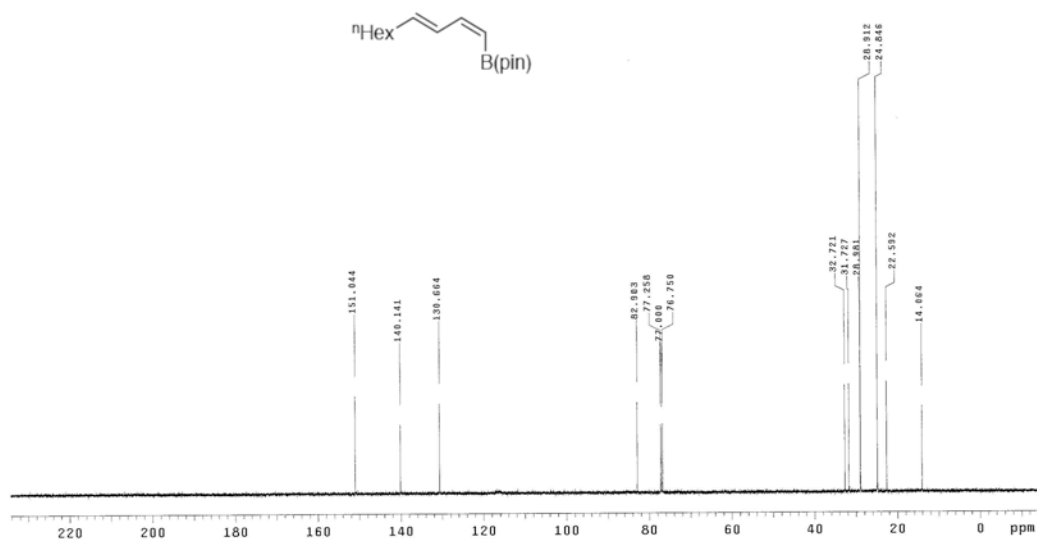
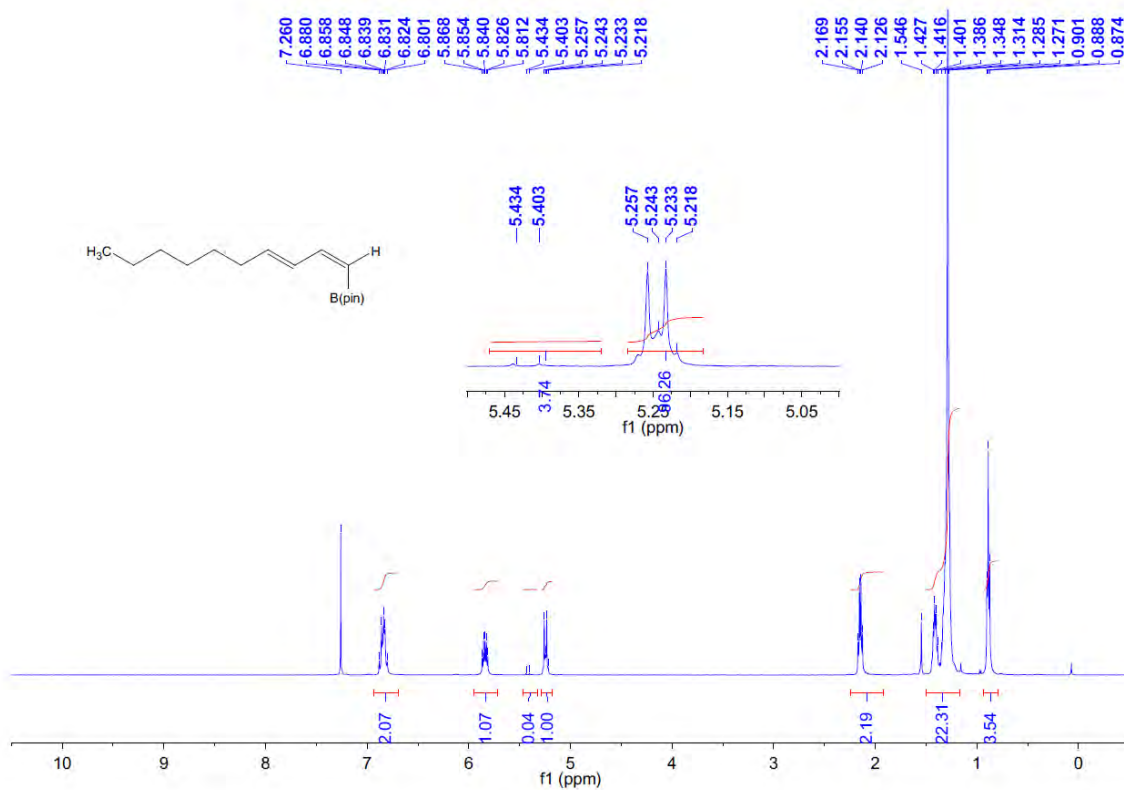
<b>PULSE SEQUENCE</b> Relax. delay 1.200 sec Pulse 45.0 degrees Acq. time 1.048 sec Width 31250.0 Hz 332 repetitions	<b>OBSERVE</b> C13, 125.8951308 <b>DECOUPLE</b> H1, 499.8833015 Power 40 dB continuously on WALTZ-16 modulated	<b>DATA PROCESSING</b> Line broadening 0.5 Hz FT size 65526 Total time 11 minutes	skx-12-79-1-C13 Solvent: cdcl3 Temp. 25.0 C / 298.1 K Operator: Liu VNMR5-500 "nmr18"
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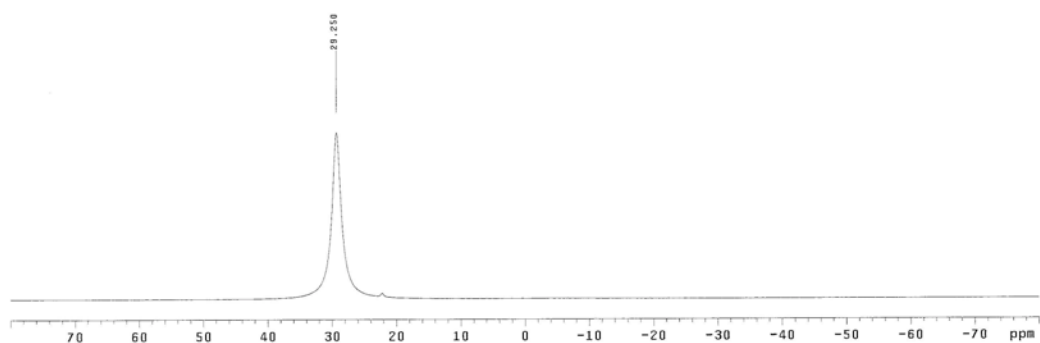
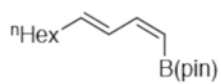
<b>PULSE SEQUENCE</b> Relax. delay 0.010 sec Pulse 90.0 degrees Acq. time 0.020 sec Width 32051.3 Hz 100 repetitions	<b>OBSERVE</b> H1, 160.3618887 <b>DECOUPLE</b> H1, 499.8833815 Power 40 dB on during acquisition off during delay WALTZ-16 modulated	<b>DATA PROCESSING</b> Line broadening 10.0 Hz FT size 32768 Total time 1 minute	skx-12-79-1-B11 Solvent: cdcl3 Temp. 25.0 C / 298.1 K Operator: Liu VNMR5-500 "nmr18"
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# Compound 5m

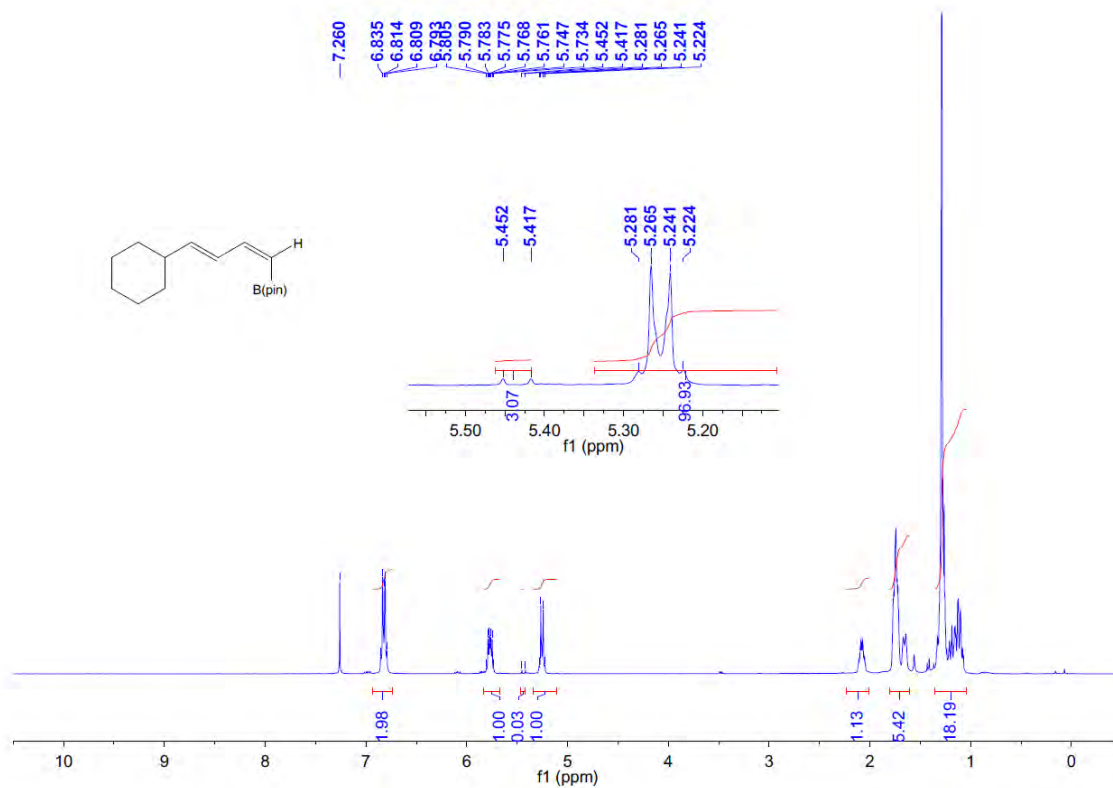
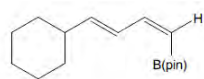


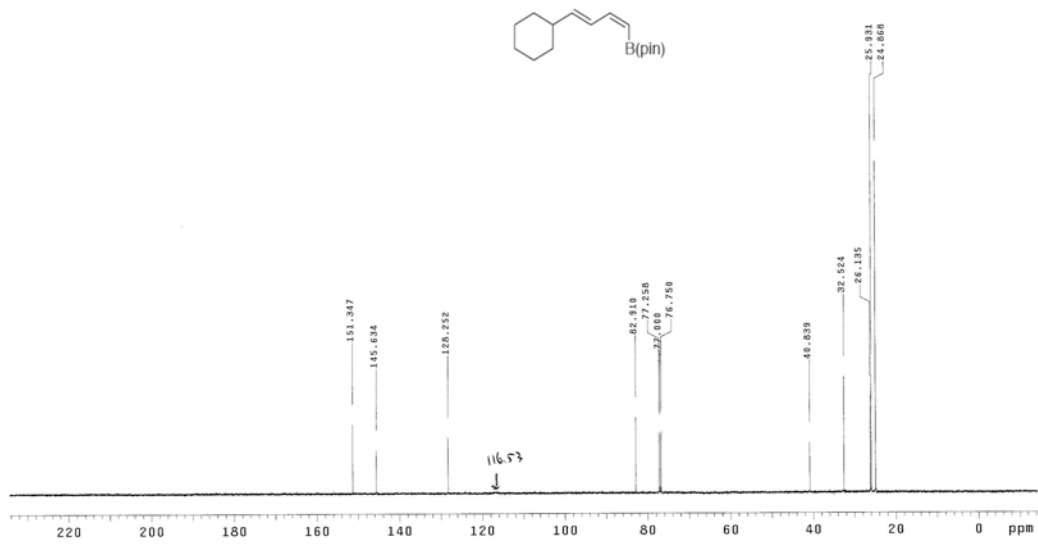
<b>PULSE SEQUENCE</b> Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 1.849 sec Width 31250.0 Hz 42 repetitions	<b>OBSERVE</b> C13, 125.6951280 <b>DECOUPLE</b> H1, 499.8633015 Power 48 continuously on VALTZ-16 modulated	<b>DATA PROCESSING</b> Line broadening 0.5 Hz FT size 85536 Total time 1 minute	sxu-12-245-1-C13 Solvent: cdcl3 Temp: 25.0 C / 298.1 K Operator: Liu VNMRS-500 "nmr18"
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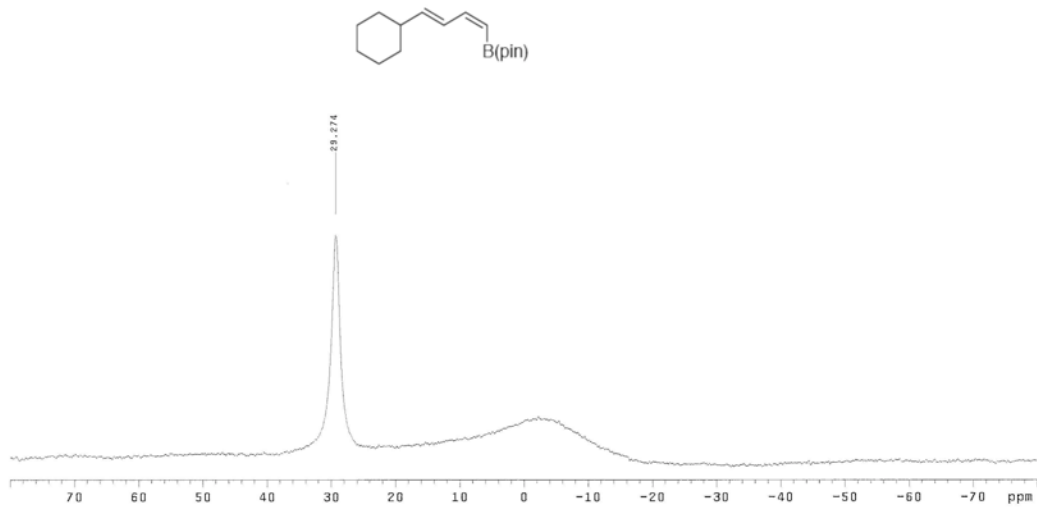
PULSE SEQUENCE	OBSERVE 611, 160.3818755	DATA PROCESSING	skw-12-245-1-b11
Relax. delay 0.010 sec	DECOUPLE M1, 489.8833015	Line Broadening 10.0 Hz	Solvent: cdcl3
Pulse 90.0 degrees	Power 40 dB	FT size 32768	Temp. 25.0 C / 298.1 K
Acq. time 0.020 sec	on during acquisition	Total time 1 minute	Operator: Liu
Width 32051.3 Hz	off during delay		VNMR5-500 "nmr18"
500 repetitions	VALTZ-16 modulated		

### Compound 5n



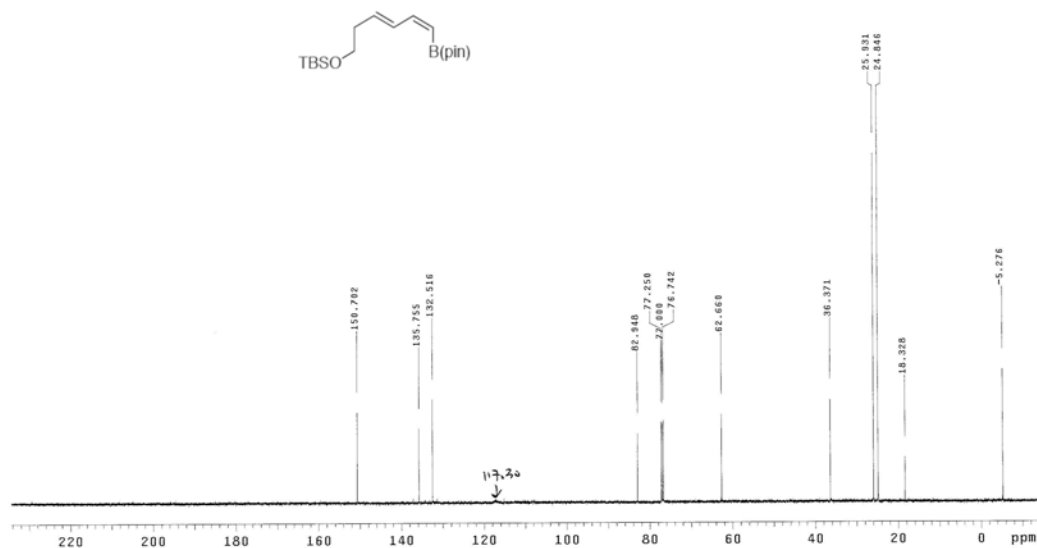
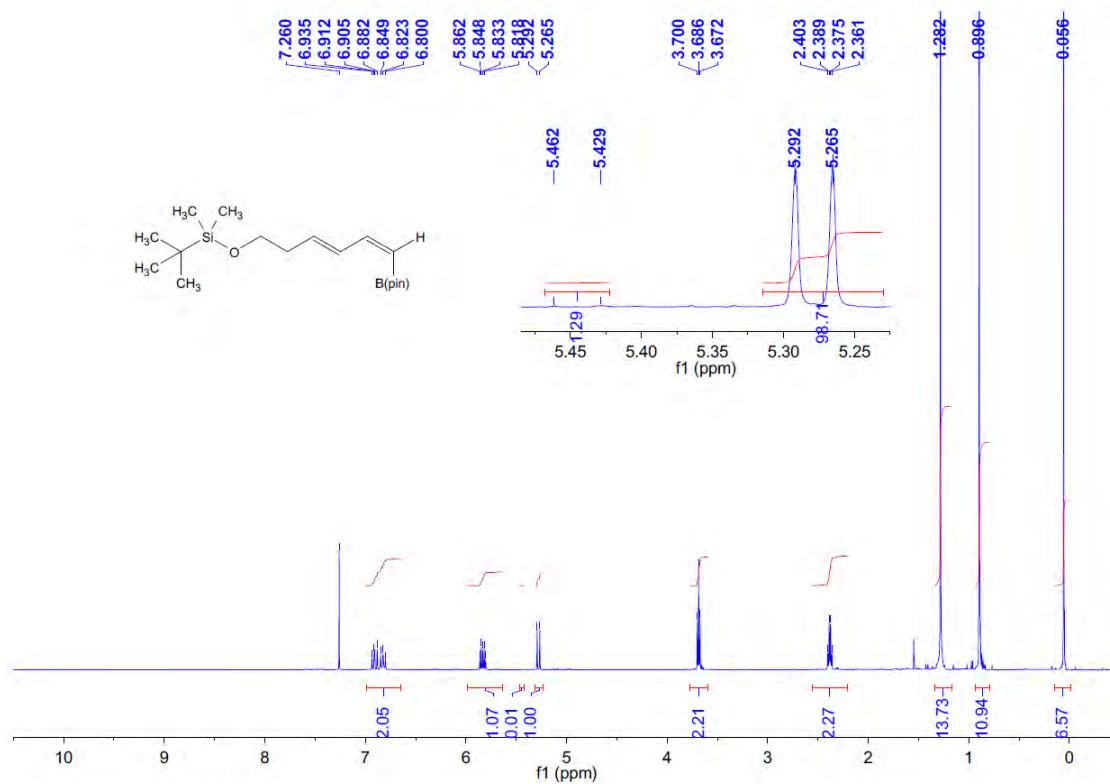


<b>PULSE SEQUENCE</b> Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 1.049 sec Width 32550.0 Hz 108 repetitions	<b>OBSERVE</b> C13, 125.6991280 DECOUPLE H1, 499.6833015 Power 40 dB continuously on WALTZ-16 modulated	<b>DATA PROCESSING</b> Line broadening 0.5 Hz FT size 65536 Total time 3 minutes	sxu-11-277-C13 Solvent: cdCl3 Temp. 25.0 C / 298.1 K Operator: Liu VNMRS-500 "nmr18"
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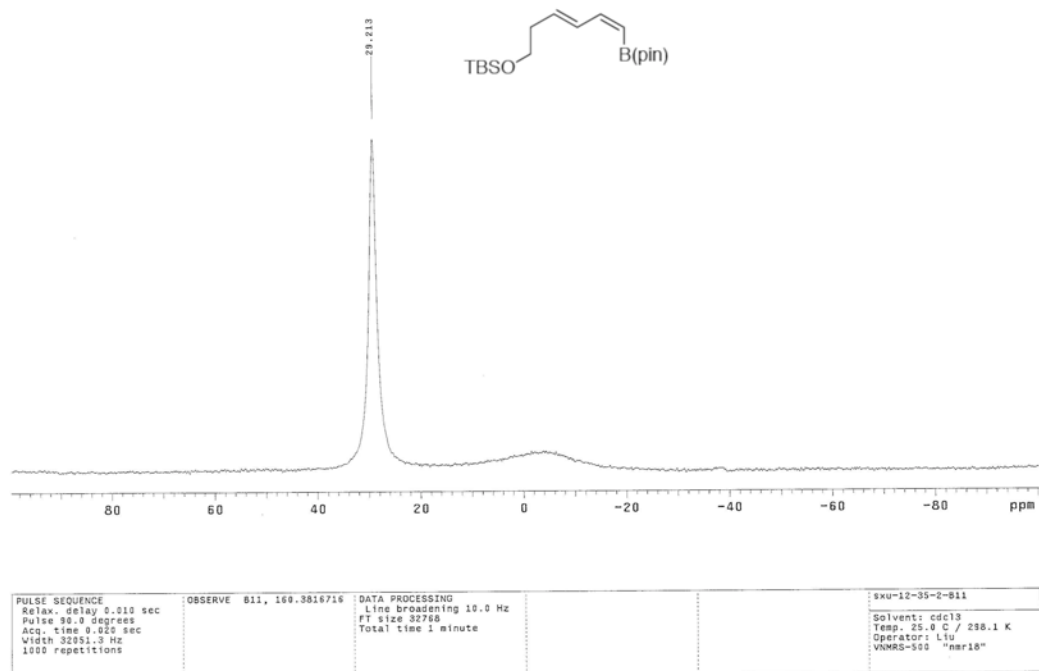


<b>PULSE SEQUENCE</b> Relax. delay 0.010 sec Pulse 60.5 degrees Acq. time 0.520 sec Width 32051.3 Hz 1024 repetitions	<b>OBSERVE</b> B11, 160.9818966	<b>DATA PROCESSING</b> Line broadening 10.0 Hz FT size 32768 Total time 1 minute	sxu-11-277-B11 Solvent: cdCl3 Temp. 25.0 C / 298.1 K Operator: Liu VNMRS-500 "nmr18"
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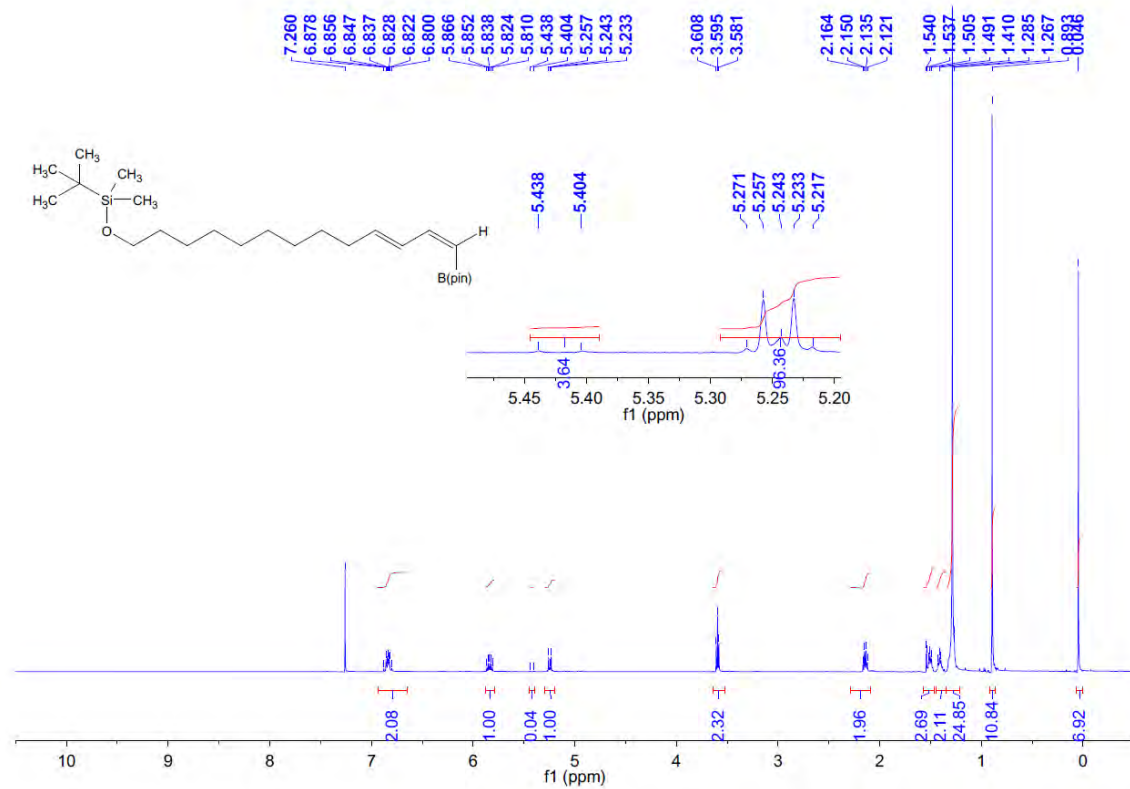
# Compound 5o



<b>PULSE SEQUENCE</b> Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 1.049 sec Width 31250.0 Hz 100 repetitions	<b>OBSERVE</b> C13, 125.6951280 DECOUPLE H3, 499.6033915 Power 46 dB continuously on MALTZ-1E modulated	<b>DATA PROCESSING</b> Line broadening 0.5 Hz FT size 65536 Total time 3 minutes	sxu-12-35-2-C13 Solvent: cdc13 Temp. 25.0 C / 298.1 K Operator: Liu VNMRS-500 "nmr18"
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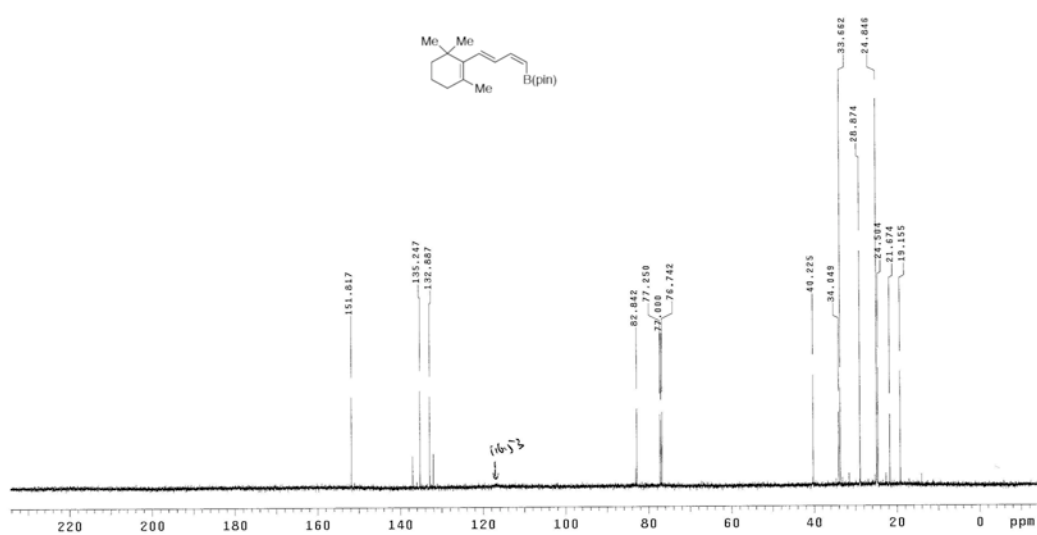
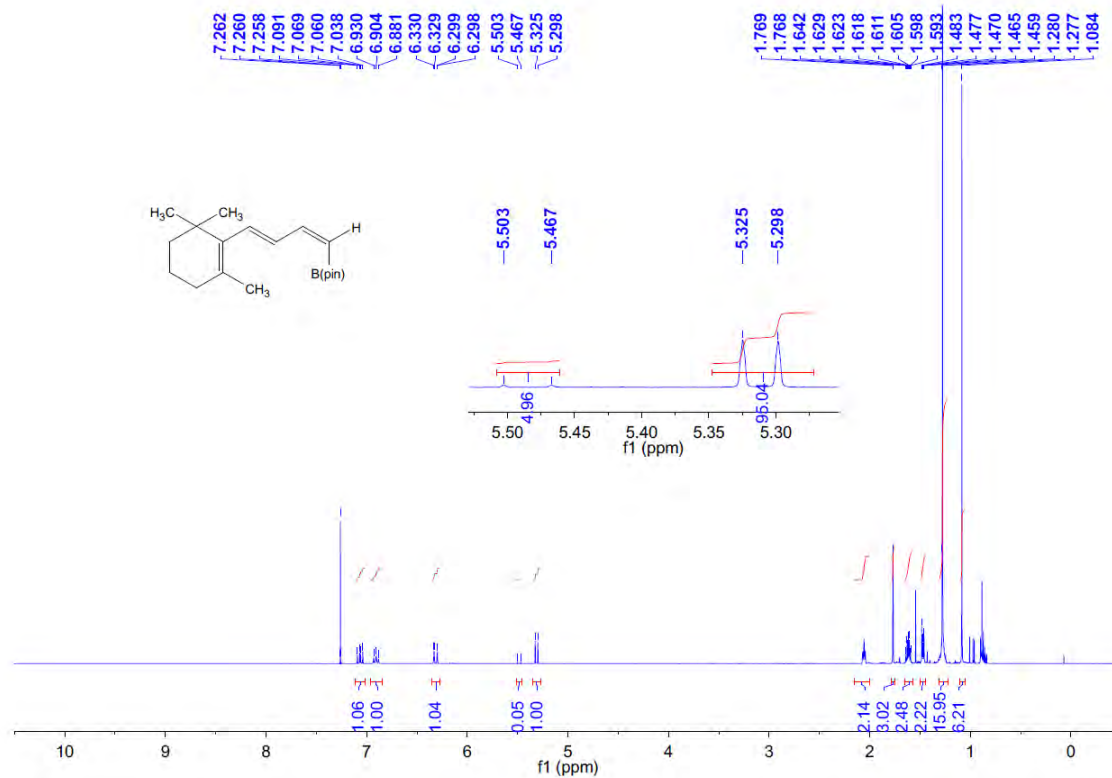


### Compound 5p

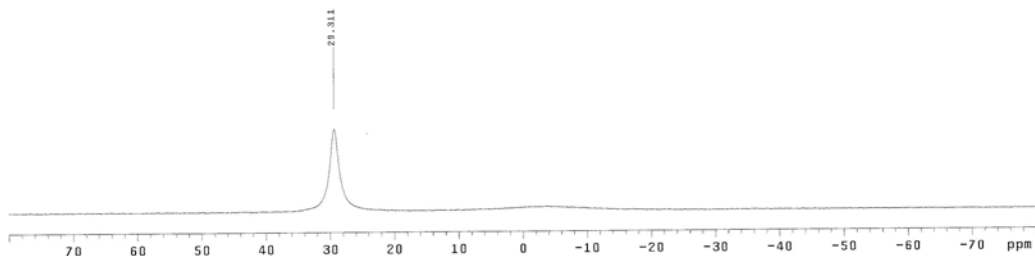
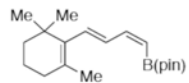




# Compound 5q

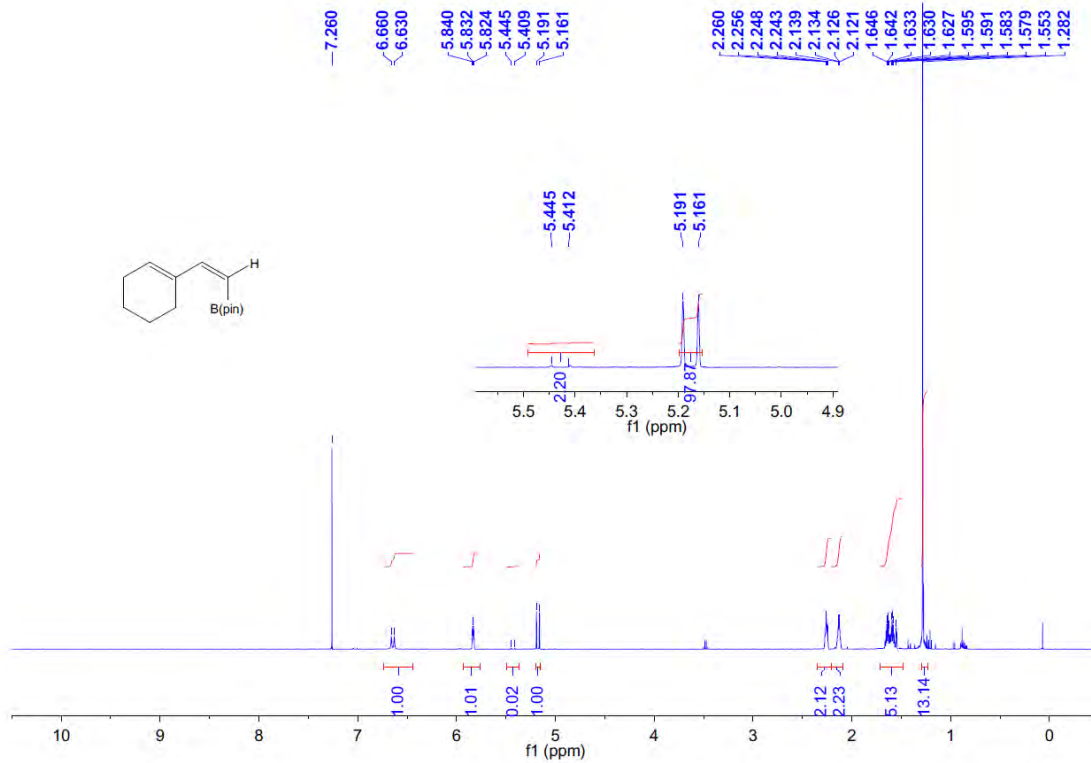
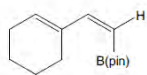


<b>PULSE SEQUENCE</b> Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 1.049 sec Width 32150.0 Hz 112 repetitions	<b>OBSERVE</b> C13, 125.6951280 <b>DECUPLE</b> H1, 498.8833015 Power 48 dB continuously on WALTZ-16 modulated	<b>DATA PROCESSING</b> Line broadening 0.5 Hz FT size 65536 Total time 3 minutes	<b>EXU-11-269-C13</b> Solvent: cdc13 Temp. 25.0 C / 298.1 K Operator: Liu VNMRS-500 "nmr18"
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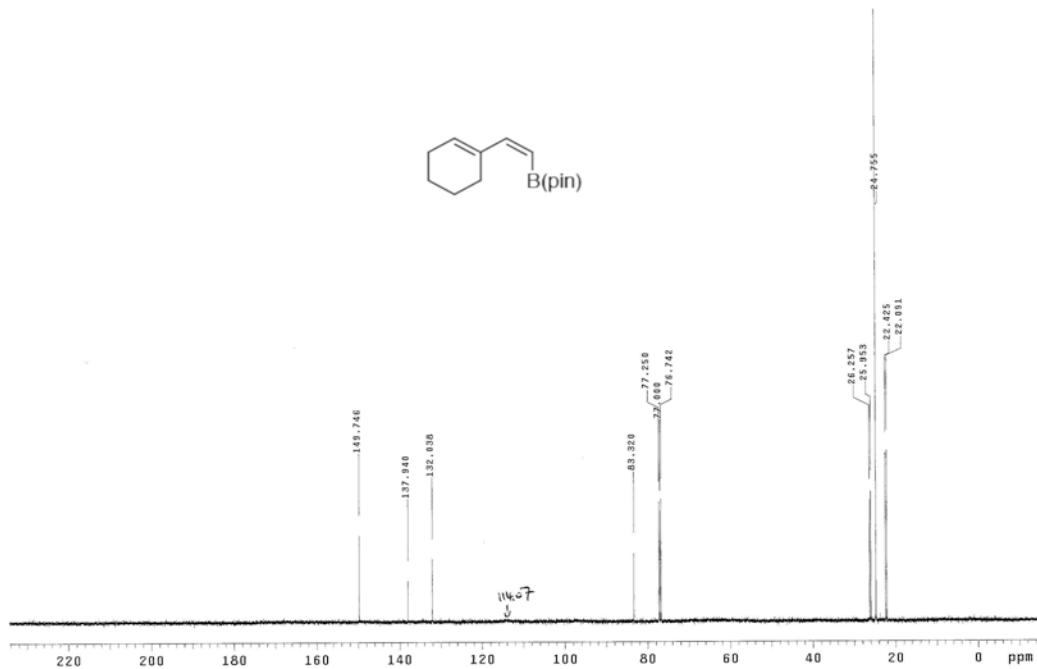
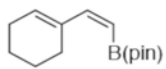


PULSE SEQUENCE	OBSERVE 611, 160.3618966	DATA PROCESSING	5xu-11-269-811
Relax. delay 0.010 sec		Line broadening 10.0 Hz	Solvent: cdcl3
Pulse 90.0 degrees		FT size 32768	Temp. 25.0 C / 298.1 K
Acq. time 0.820 sec		Total time 1 minute	Operator: Liu
Width 32051.3 Hz			VNMRS-500 "nmr18"
1224 repetitions			

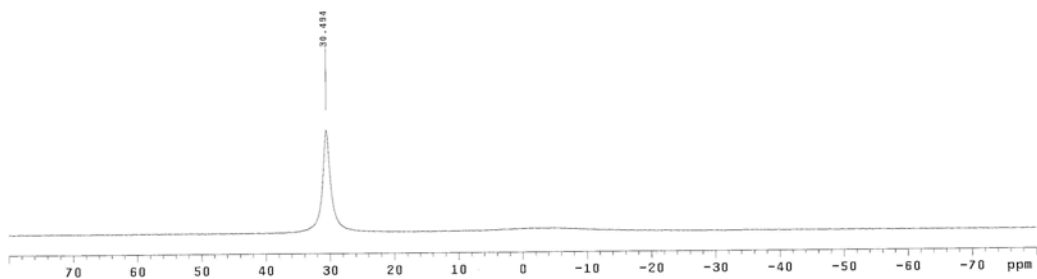
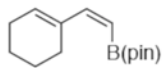
### Compound 5r





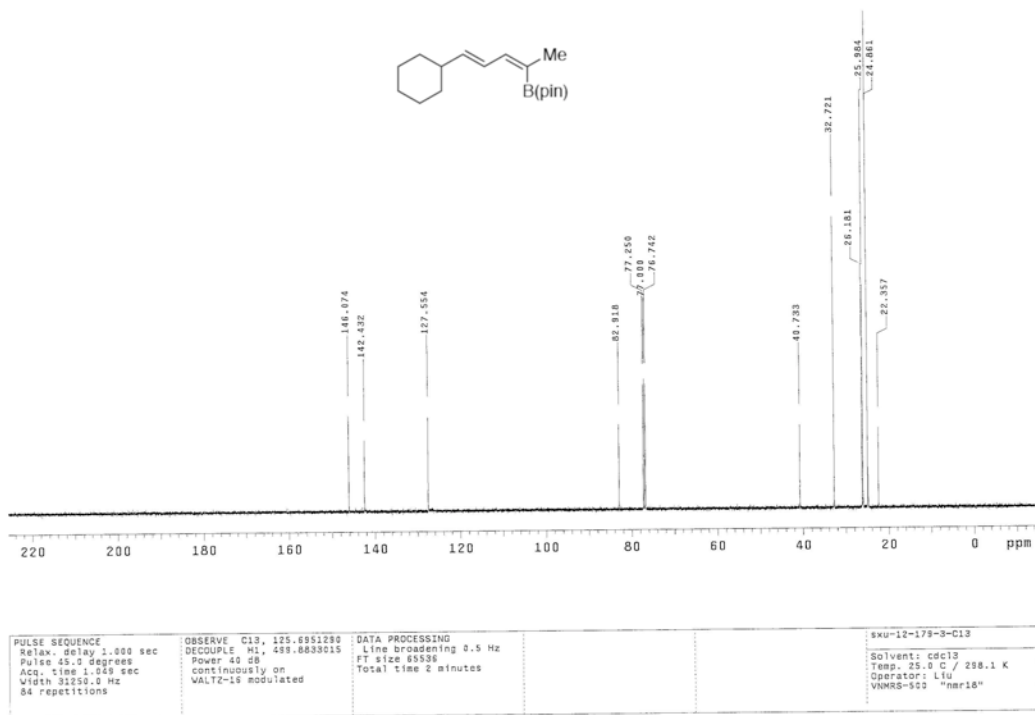
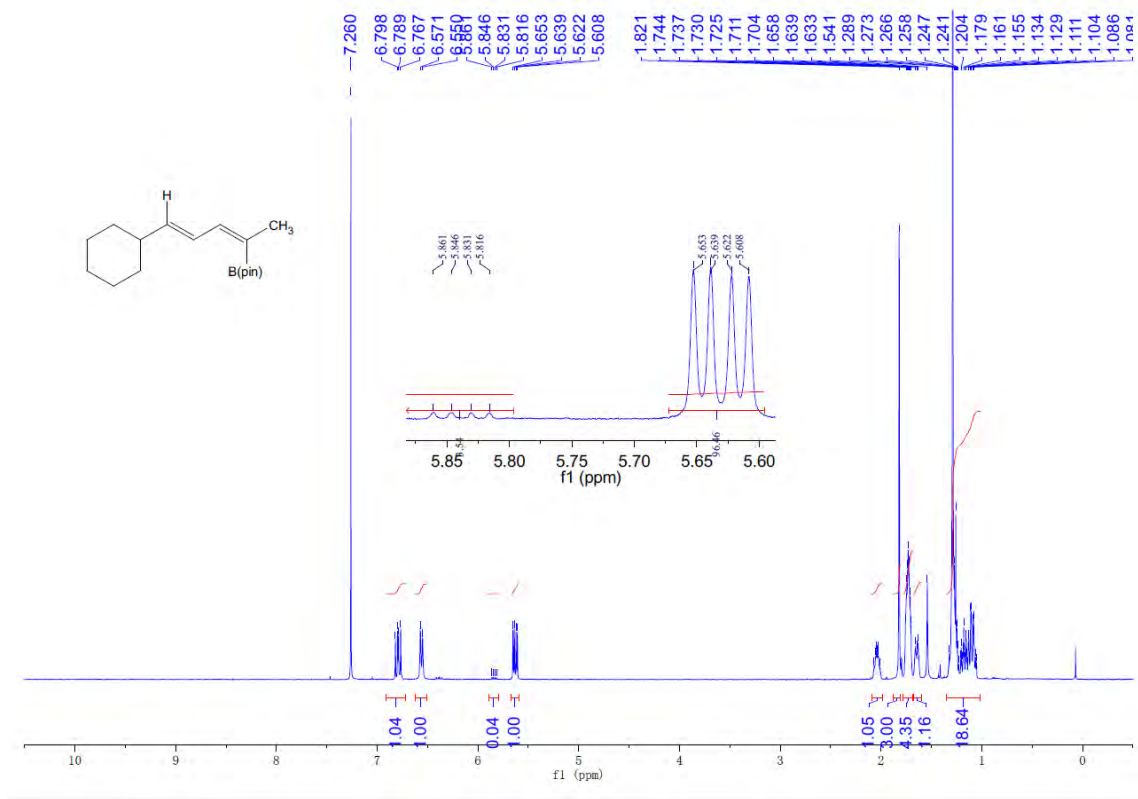


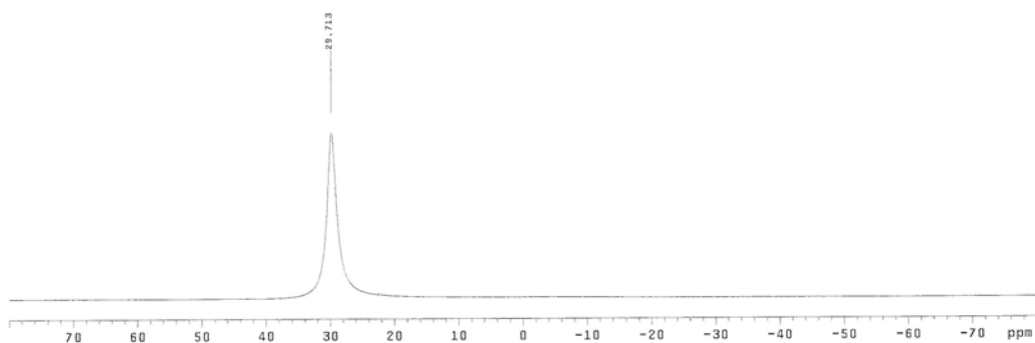
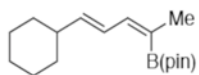
<b>PULSE SEQUENCE</b> Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 1.049 sec Width 31250.0 Hz 160 repetitions	<b>OBSERVE</b> C13, 125.6951290 <b>DECOUPLE</b> H1, 499.8633015 Power 40 dB continuously on WALTZ-16 modulated	<b>DATA PROCESSING</b> Line broadening 0.5 Hz FT size 65536 Total time 5 minutes	sxu-11-257-C13 Solvent: cdcl3 Temp. 25.0 C / 298.1 K Operator: Liu VNMR5-560 "nmr18"
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<b>PULSE SEQUENCE</b> Relax. delay 0.010 sec Pulse 30.0 degrees Acq. time 0.320 sec Width 32051.3 Hz 1224 repetitions	<b>OBSERVE</b> B11, 160.3616266 <b>DECOUPLE</b> H1, 499.8633015 Power 40 dB on during acquisition off during delay WALTZ-16 modulated	<b>DATA PROCESSING</b> Line broadening 10.0 Hz FT size 32768 Total time 1 minute	sxu-11-257-B11 Solvent: cdcl3 Temp. 25.0 C / 298.1 K Operator: Liu VNMR5-560 "nmr18"
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# Compound 7a





PULSE SEQUENCE Relax. delay 0.010 sec Pulse 90.0 degrees Acc. time 0.020 sec Width 32051.3 Hz 1000 repetitions	OBSERVE B11, 160.3816755 DECOUPLE H1, 499.6833015 Power 40 dB on during acquisition off during delay VOLTAGE-16 modulated	DATA PROCESSING Line broadening 10.0 Hz FT size 32768 Total time 1 minute	skx-12-179-3-811 Solvent: cdcl3 Temp: 23.0 C / 298.1 K Operator: Liu VNMRS-900 "ner18"
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yz-2-283H-1  
Selective band center: 1.82 (ppm); width: 8.8 (Hz)

Sample Name:

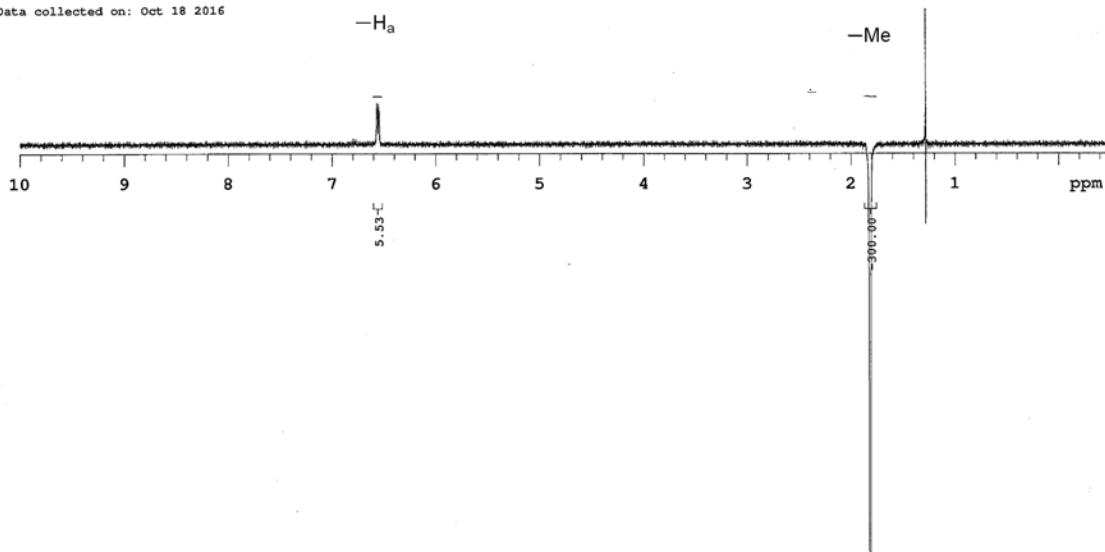
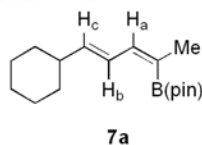
Data Collected on:  
nmr19-vnmrs600

Archive directory:

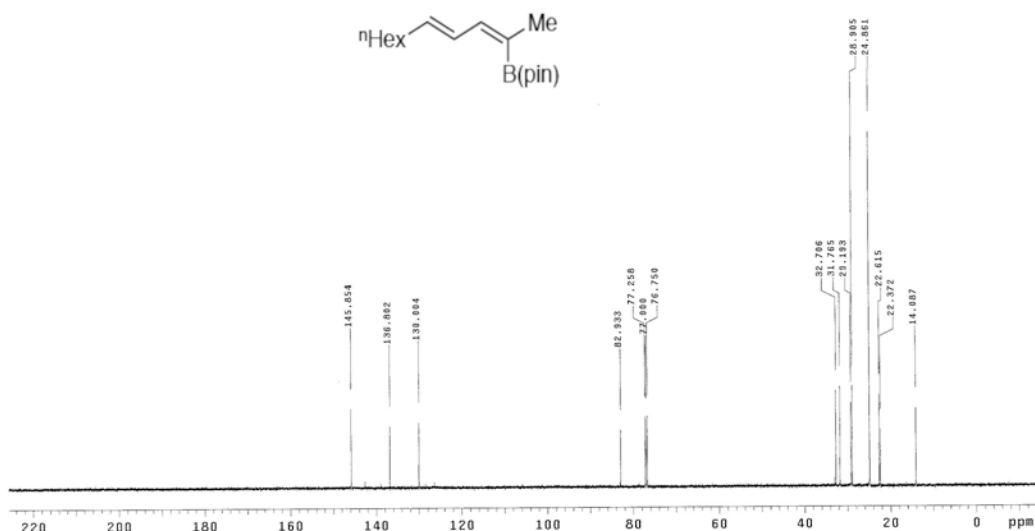
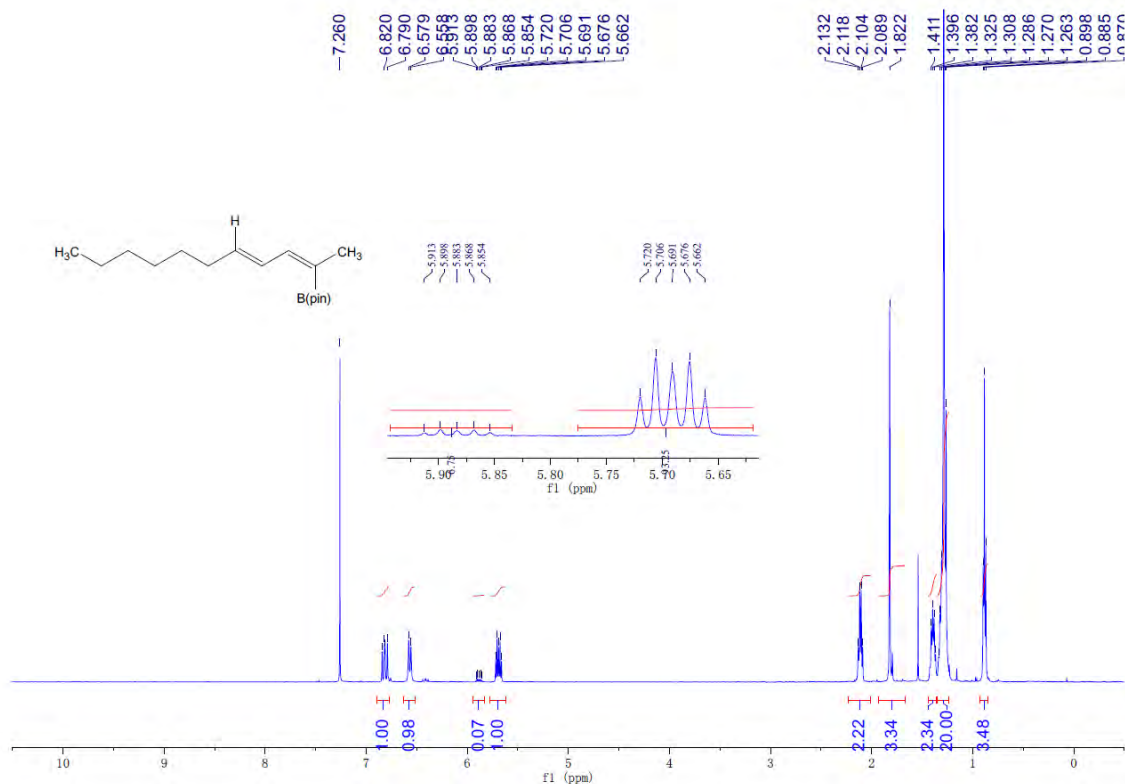
Sample directory:

FidFile: yz-2-283H-1-noesy1

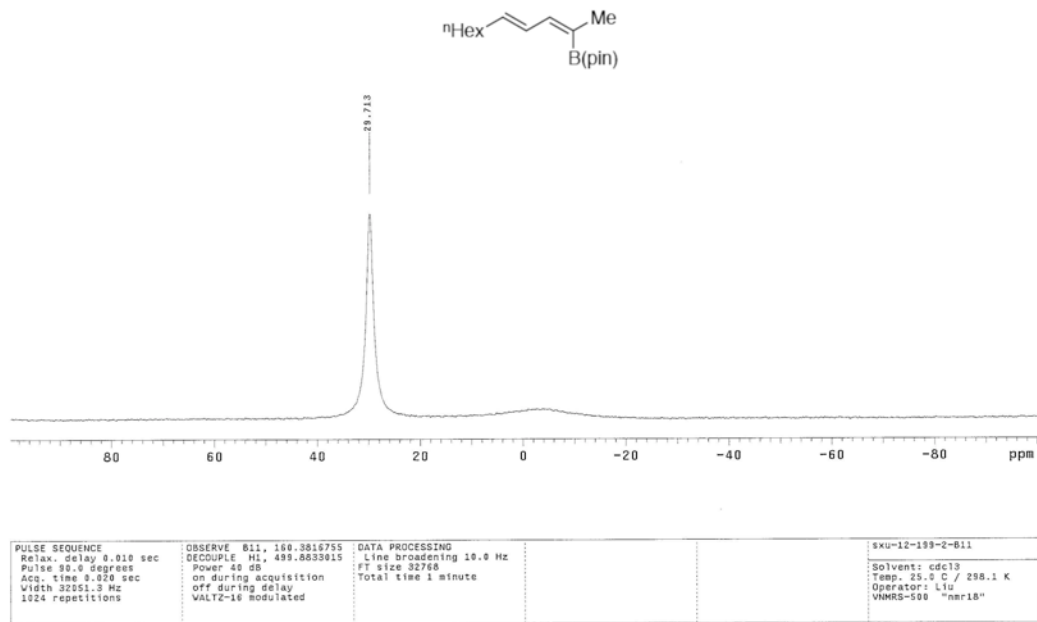
Pulse Sequence: NOESY1D  
Solvent: cdcl3  
Data collected on: Oct 18 2016



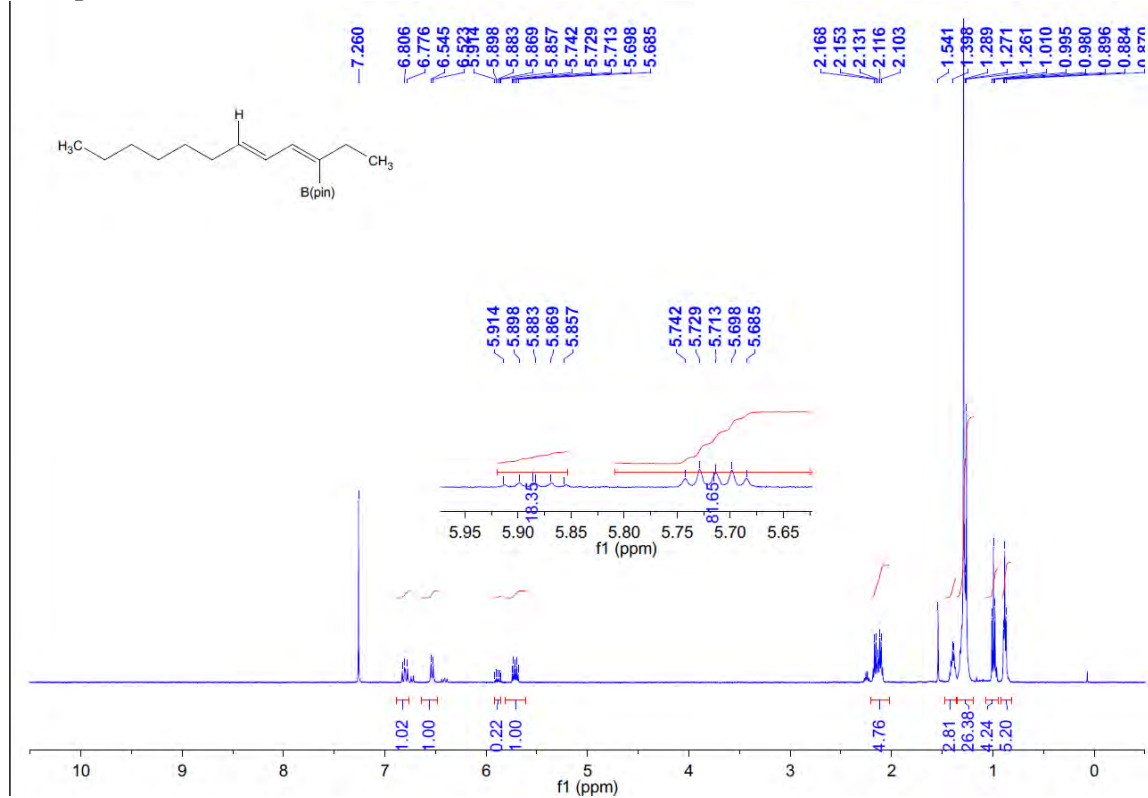
# Compound 7b

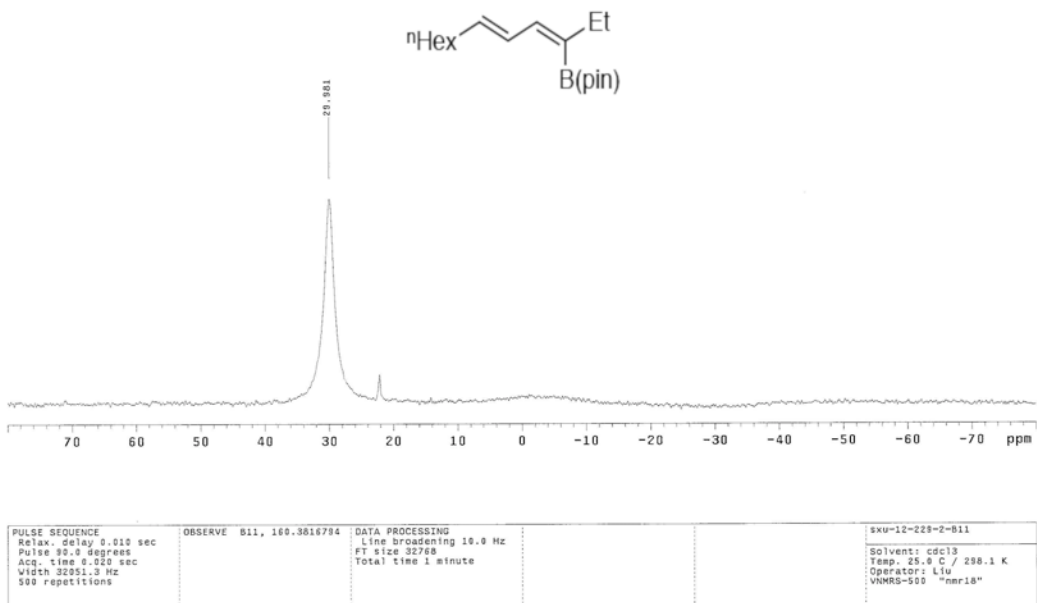
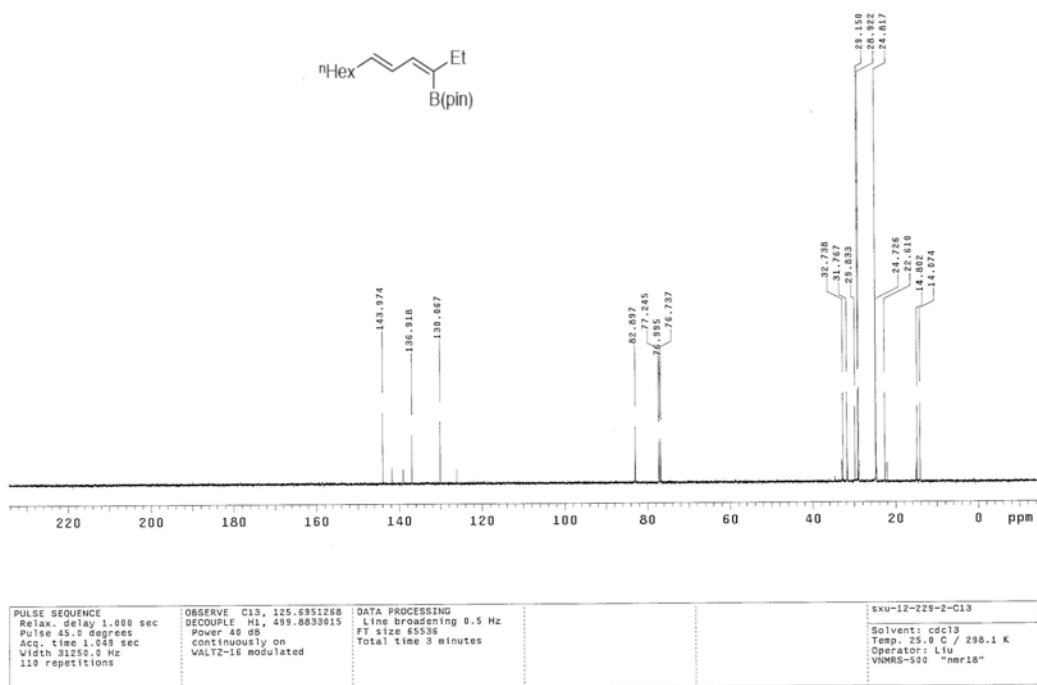


<b>PULSE SEQUENCE</b> Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 1.348 sec Width 31250.0 Hz 94 repetitions	<b>OBSERVE</b> C13, 125.6951271 <b>DECOUPLE</b> H1, 499.6033015 Power 48 dB continuously on VALTZ-16 modulated	<b>DATA PROCESSING</b> Line broadening 0.5 Hz FT size 65536 Total time 3 minutes	sxu-12-199-2-C13 Solvent: cdcl3 Temp: 25.0 C / 298.1 K Operator: Liu VNMRS-500 "mar18"
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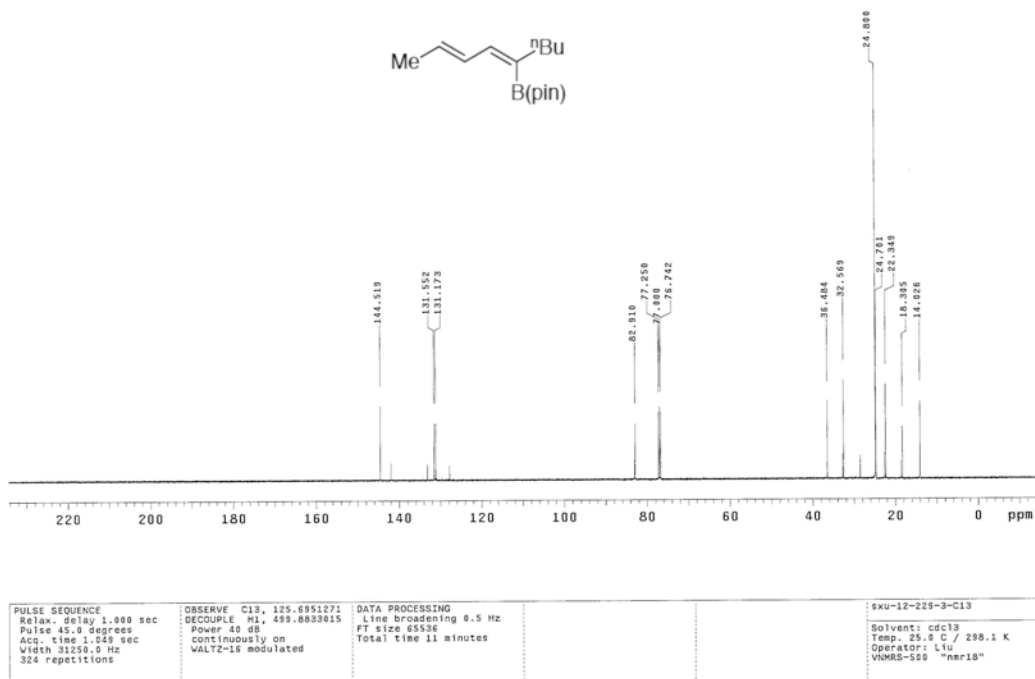
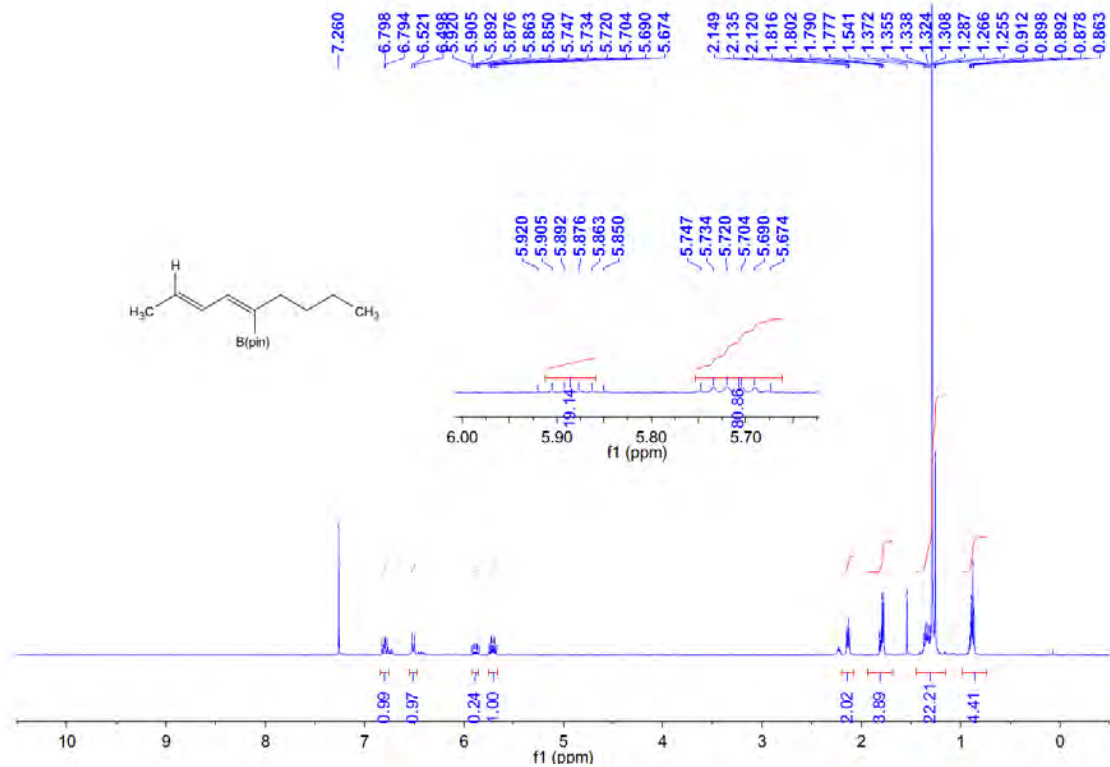


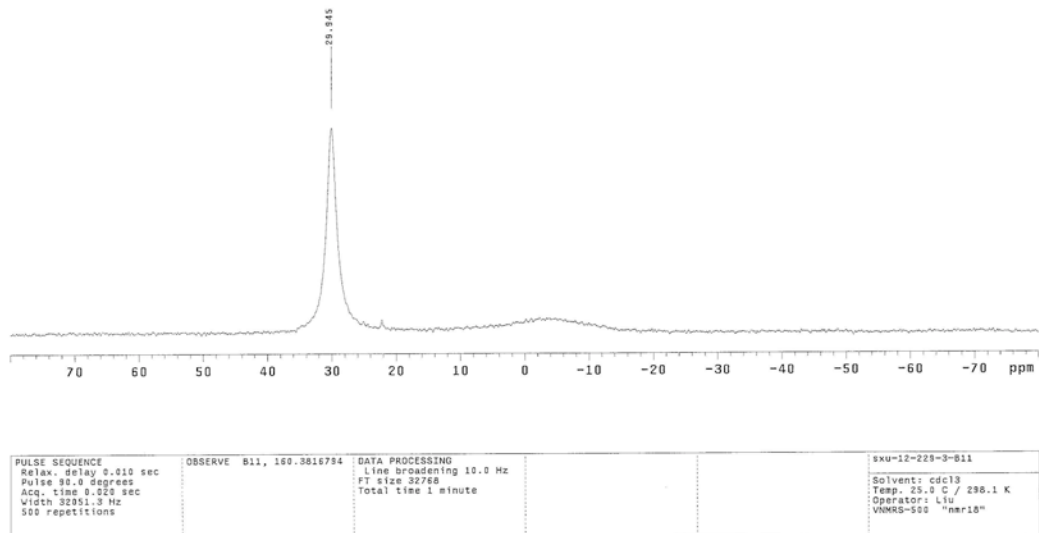
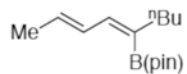
### Compound 7c



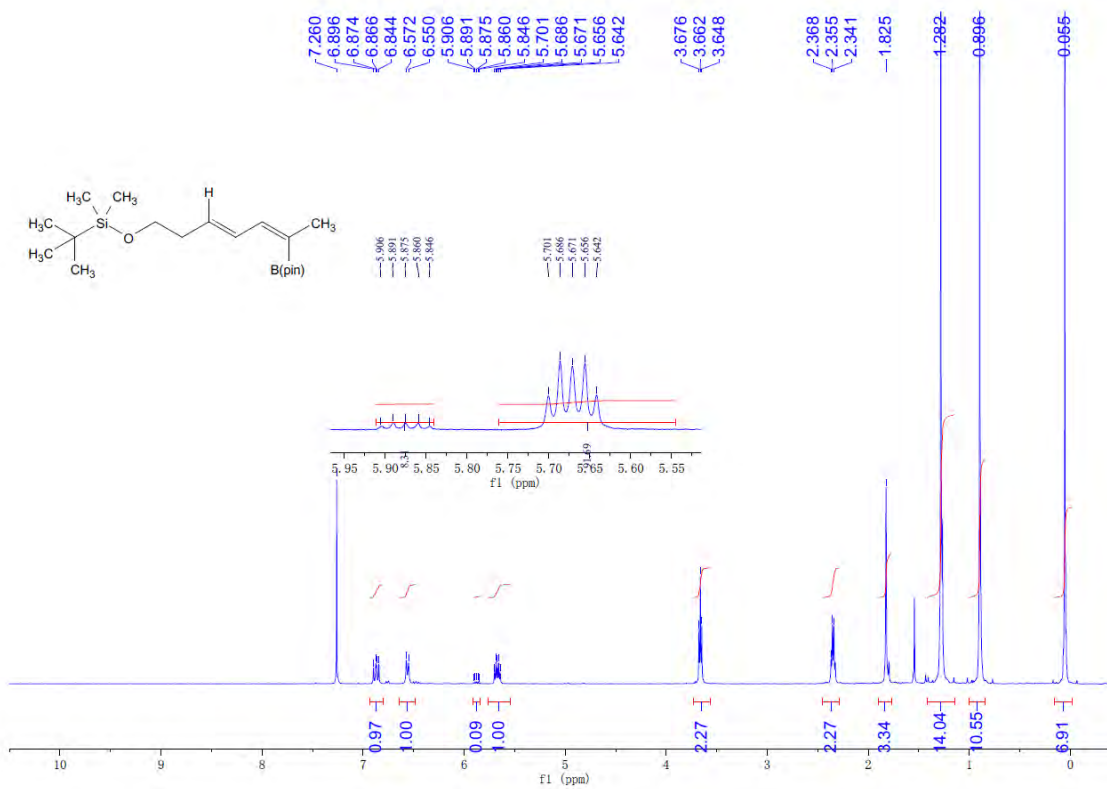


# Compound 7d

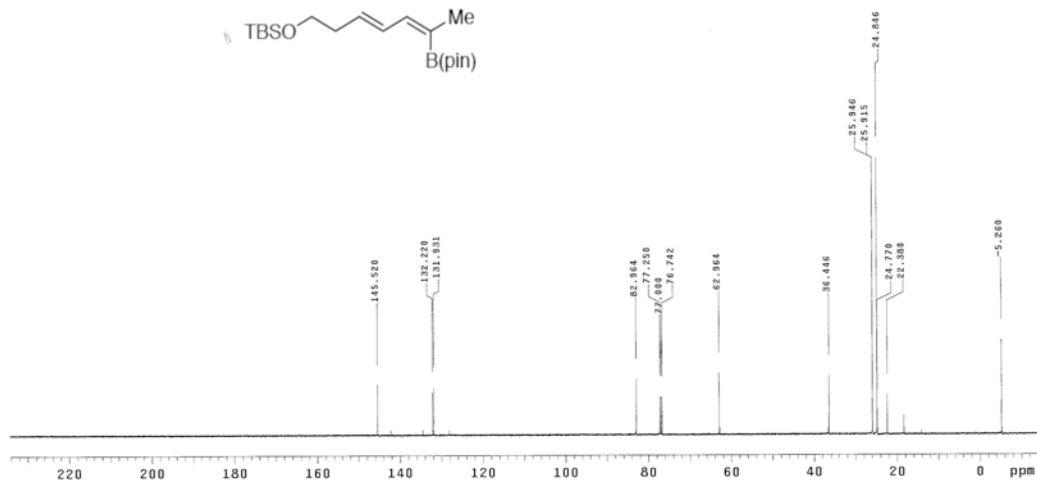
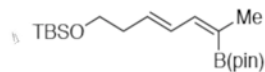




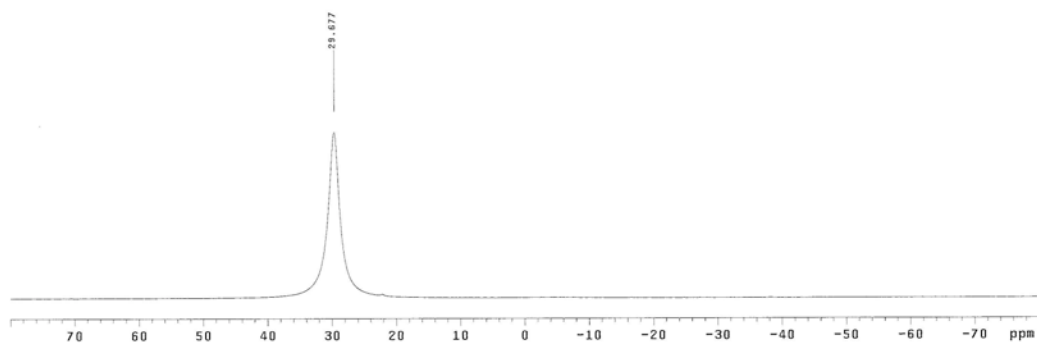
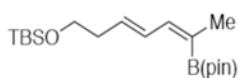
### Compound 7e





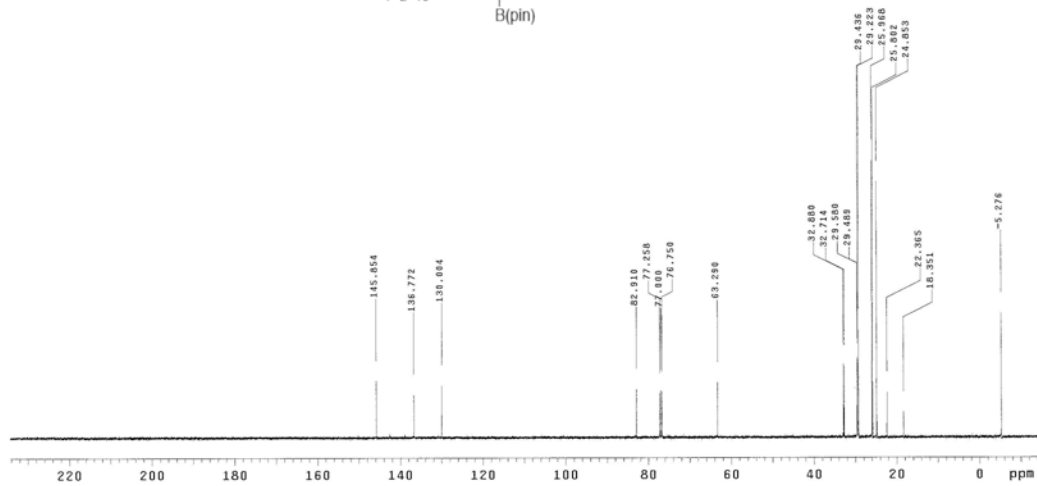
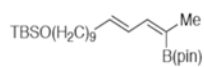
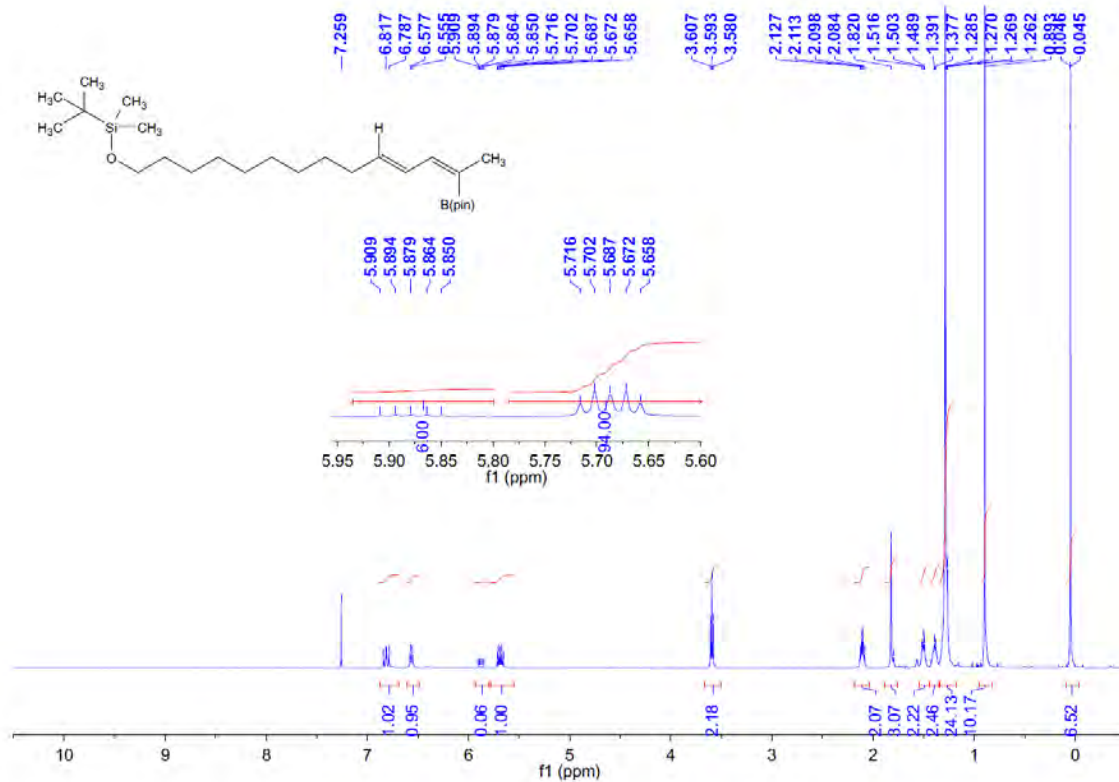


<b>PULSE SEQUENCE</b> Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 1.249 sec Width 31250.0 Hz 84 repetitions	<b>OBSERVE</b> C13, 125.6951280 <b>DECOUPLE</b> H1, 499.8833015 Power 40 dB continuously on VALTZ-16 modulated	<b>DATA PROCESSING</b> Line broadening 0.5 Hz FT size 65536 Total time 2 minutes	sxu-12-245-2-C13 Solvent: cdCl3 Temp. 25.0 C / 298.1 K Operator: Liu VNMR5-500 "nmr16"
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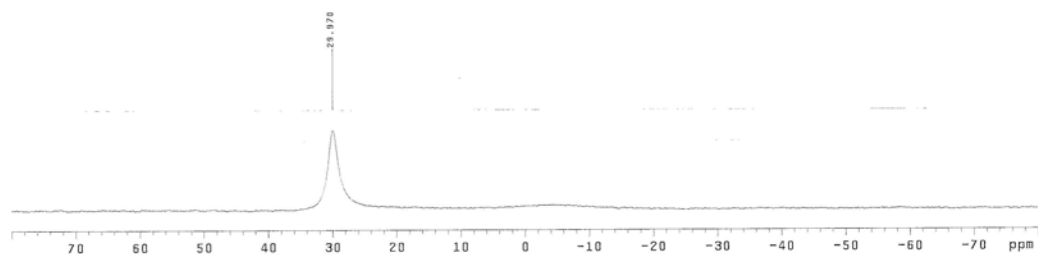
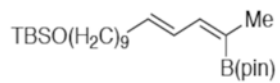


<b>PULSE SEQUENCE</b> Relax. delay 2.010 sec Pulse 90.0 degrees Acq. time 0.020 sec Width 32051.3 Hz 500 repetitions	<b>OBSERVE</b> B11, 150.3816755 <b>DECOUPLE</b> H1, 499.8833015 Power 40 dB on during acquisition off during delay VALTZ-16 modulated	<b>DATA PROCESSING</b> Line broadening 10.0 Hz FT size 32768 Total time 1 minute	sxu-12-245-2-B11 Solvent: cdCl3 Temp. 25.0 C / 298.1 K Operator: Liu VNMR5-500 "nmr16"
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# Compound 7f

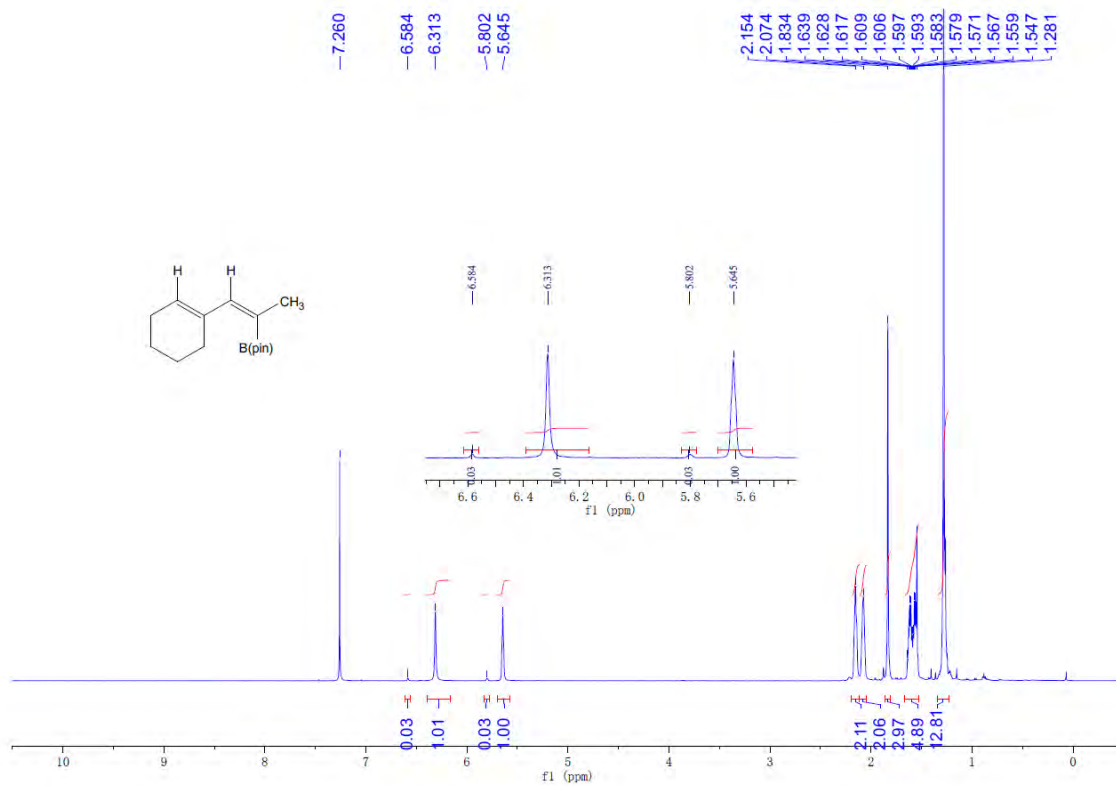


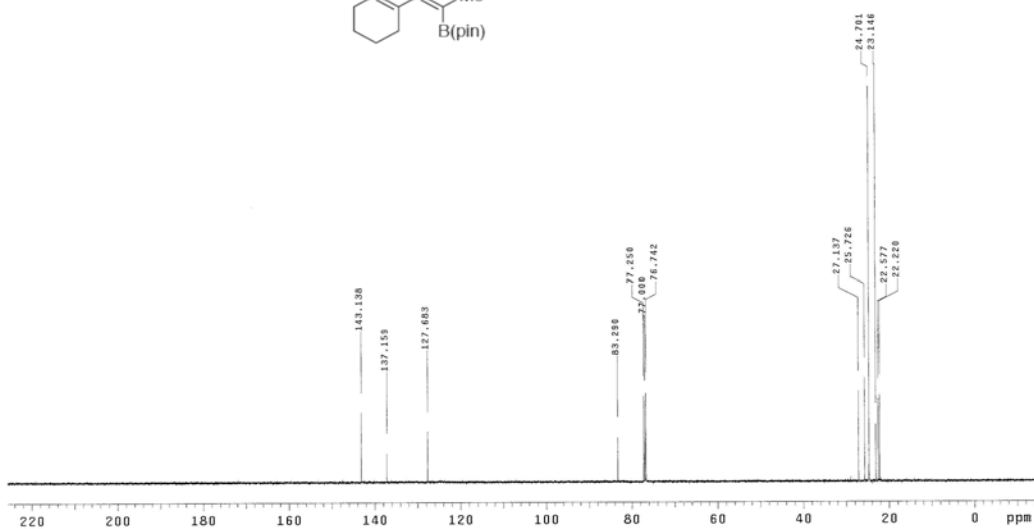
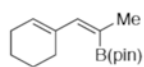
<b>PULSE SEQUENCE</b> Relax. delay 1.000 sec Pulse 45.0 degree Acq. time 1.049 sec Width 31250.0 Hz 46 repetitions	<b>OBSERVE C13, 125.6951280</b> DECOUPLE H1, 499.8833015 Power 4a continuously on WALTZ-16 modulated	<b>DATA PROCESSING</b> Line broadening 0.5 Hz FT size 6538 Total time 1 minutes	sxu-12-237-2-C13 Solvent: cdcl3 Temp. 25.0 C / 298.1 K Operator: Liu VNMRS-506 "nmr18"
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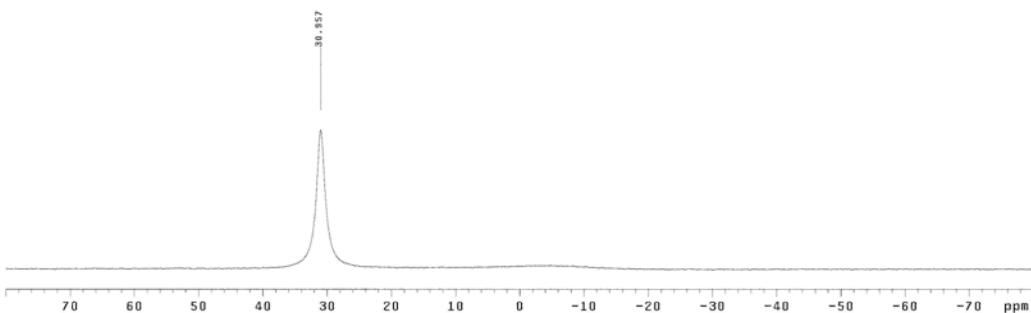
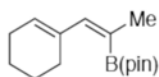
<b>PULSE SEQUENCE</b>	<b>OBSERVE</b> 811.160.8616266	<b>DATA PROCESSING</b>	exu-12-237-2-B11
Relax. delay 0.010 sec	DECOUPLE M1, 499.8633015	Line broadening 10.0 Hz	Solvent: cdcl3
Pulse 90.0 degrees	Power 40 dB	FT size 32768	Temp. 25.0 C / 298.1 K
Acq. time 0.320 sec	on during acquisition	Total time 1 minute	Operator: Liu
Width 32051.3 Hz	off during delay		VNMR-500 "nar16"
1024 repetitions	WALTZ-16 modulated		

### Compound 7g





<b>PULSE SEQUENCE</b> Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 1.049 sec Width 31250.0 Hz 210 repetitions	<b>OBSERVE</b> C13, 125.6951280 <b>DECOUPLE</b> H1, 499.6833015 Power 40 dB continuously on WALTZ-16 modulated	<b>DATA PROCESSING</b> Line broadening 0.5 Hz FT size 65536 Total time 7 minutes	skx-12-241-C13 Solvent: cdcl3 Temp. 25.0 C / 298.1 K Operator: Liu VNMRS-500 "nvr18"
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<b>PULSE SEQUENCE</b> Relax. delay 0.010 sec Pulse 90.0 degrees Acq. time 0.020 sec Width 32051.3 Hz 1000 repetitions	<b>OBSERVE</b> 011, 169.3816775 <b>DECOUPLE</b> H1, 499.6833015 Power 40 dB on during acquisition off during delay WALTZ-16 modulated	<b>DATA PROCESSING</b> Line broadening 10.0 Hz FT size 32768 Total time 1 minute	txxu-12-297-1-811 Solvent: cdcl3 Temp. 25.0 C / 298.1 K Operator: Liu VNMRS-500 "nvr18"
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yz-2-287-H  
Selective band center: 1.83 (ppm); width: 11.1 (Hz)

Sample Name:

Data Collected on:  
nmr19-vnmrs600  
Archive directory:

Sample directory:

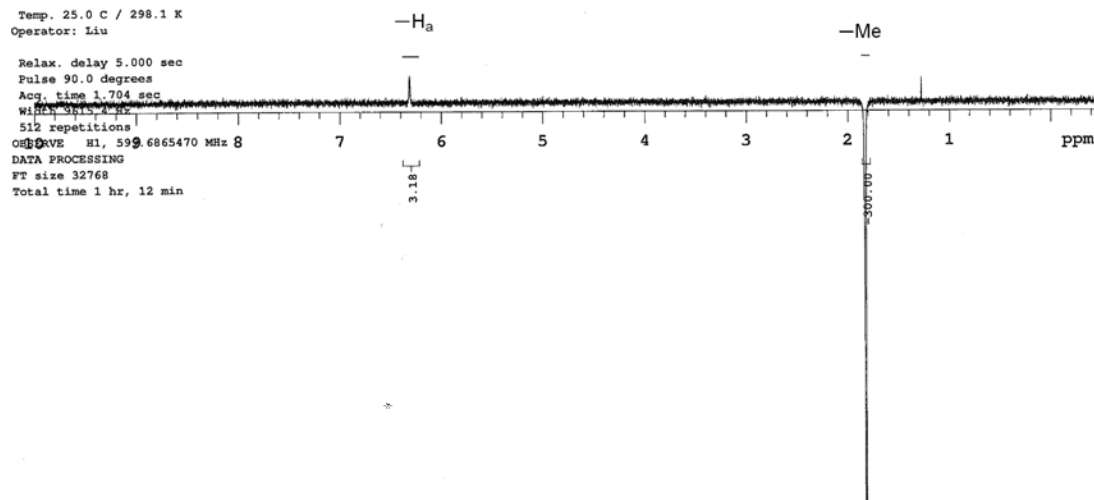
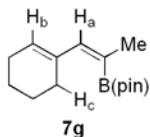
FidFile: NOESY1D

Pulse Sequence: NOESY1D  
Solvent: cdcl3  
Data collected on: Oct 21 2016

Temp. 25.0 C / 298.1 K  
Operator: Liu

Relax. delay 5.000 sec  
Pulse 90.0 degrees  
Acq. time 1.704 sec  
Width 315.1 Hz

512 repetitions  
OBSERVE H1, 599.6865470 MHz 8  
DATA PROCESSING  
FT size 32768  
Total time 1 hr, 12 min



## Compound *cis*-7g

yz-2-284-2H-*cis* product

Sample Name:

Data Collected on:  
nmr19-vnmrs600  
Archive directory:

Sample directory:

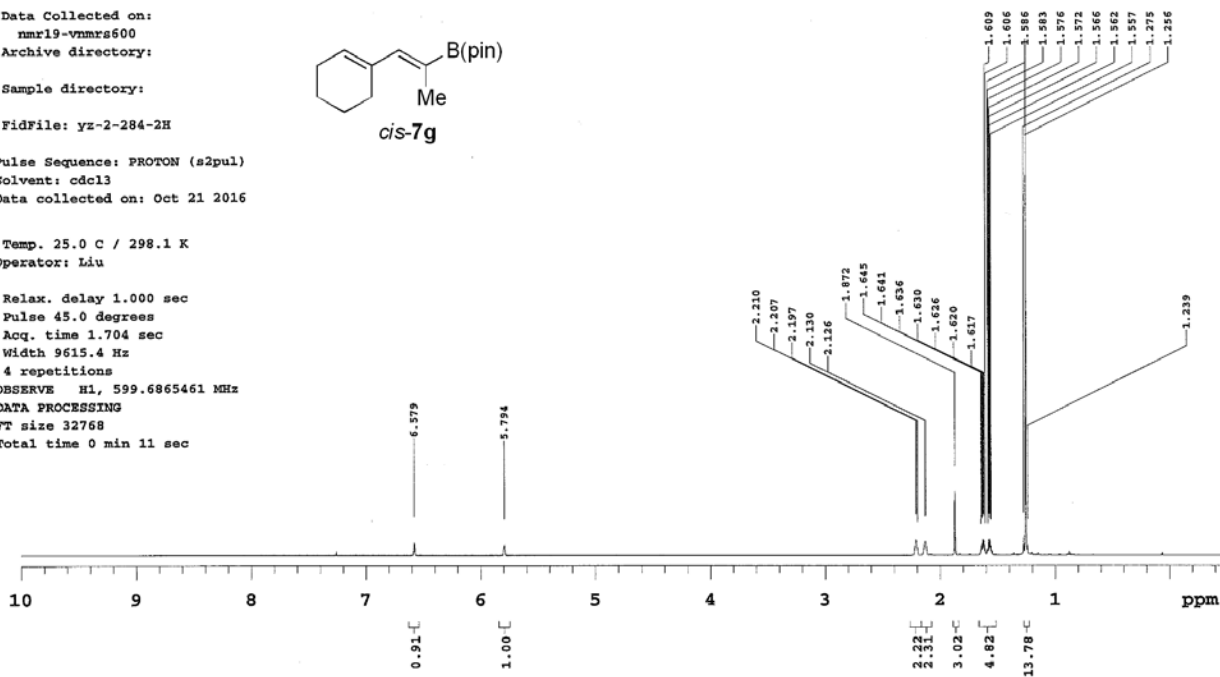
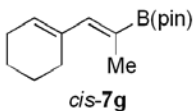
FidFile: yz-2-284-2H

Pulse Sequence: PROTON (s2pul)  
Solvent: cdcl3  
Data collected on: Oct 21 2016

Temp. 25.0 C / 298.1 K  
Operator: Liu

Relax. delay 1.000 sec  
Pulse 45.0 degrees  
Acq. time 1.704 sec  
Width 9615.4 Hz  
4 repetitions

OBSERVE H1, 599.6865461 MHz  
DATA PROCESSING  
FT size 32768  
Total time 0 min 11 sec



yz-2-284-2H-noesy  
 Selective band center: 1.87 (ppm); width: 8.5 (Hz)

Sample Name:

Data Collected on:

nmr19-vmrs600

Archive directory:

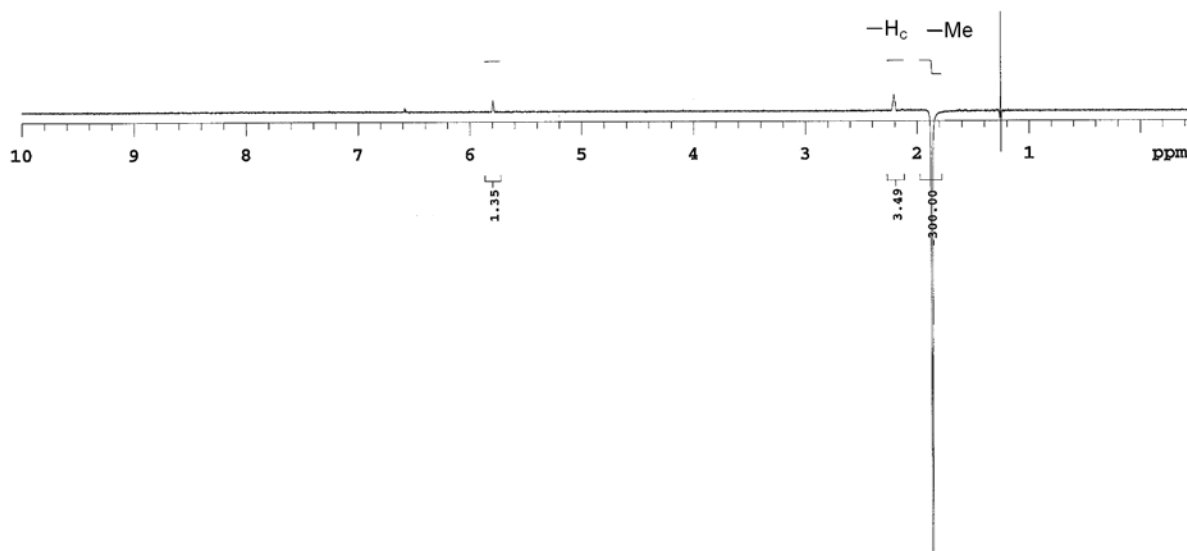
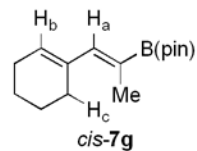
Sample directory:

FidFile: yz-2-284-2H-noesy1

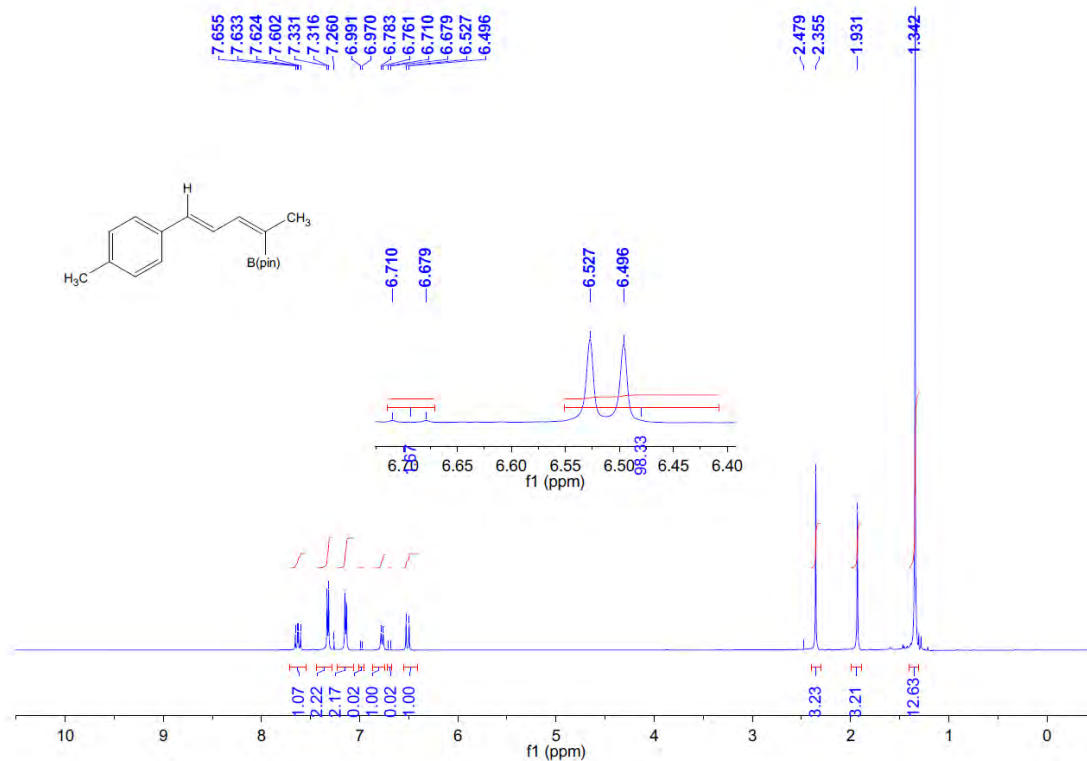
Pulse Sequence: NOESY1D

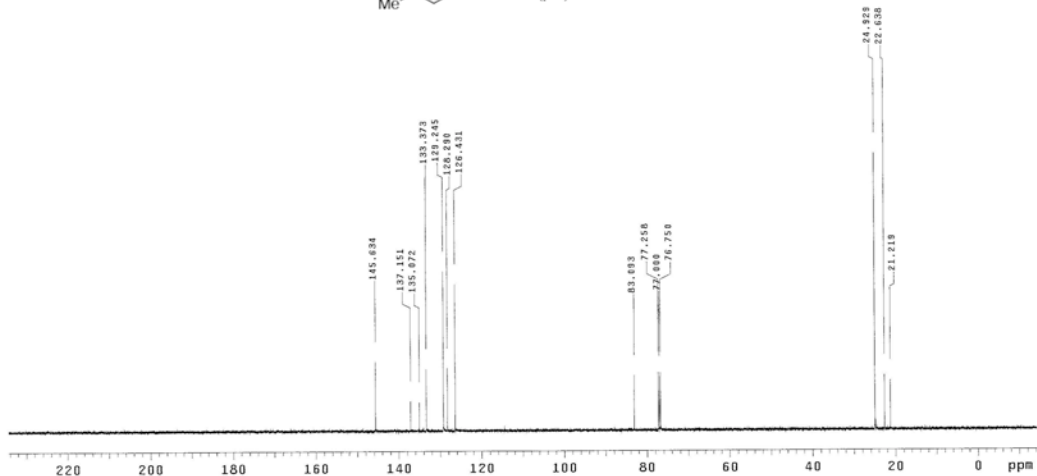
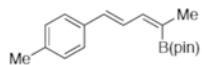
Solvent: cdcl3

Data collected on: Oct 21 2016

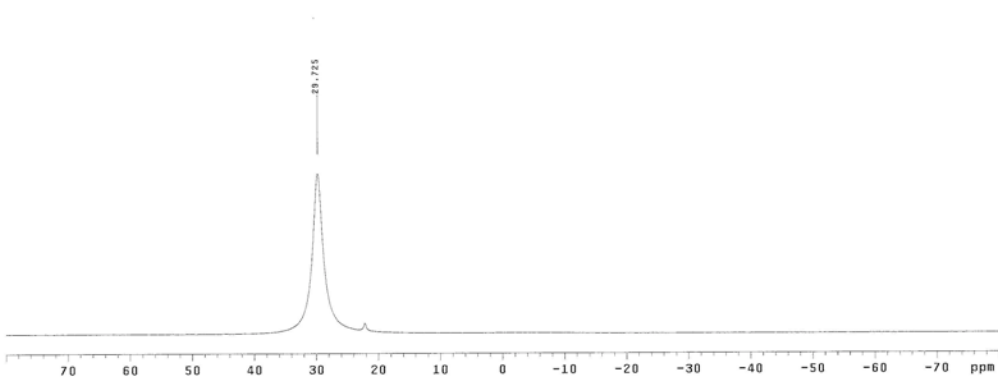
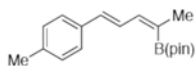


## Compound 7h





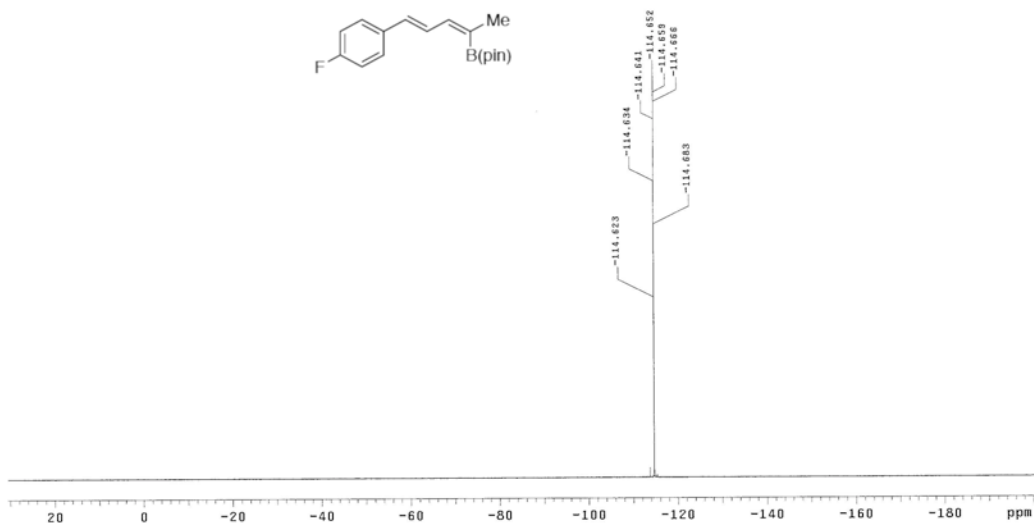
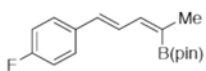
<b>PULSE SEQUENCE</b> Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 1.043 sec Width 31250.0 Hz 88 repetitions	<b>OBSERVE</b> C13, 125.6951309 <b>DECOUPLE</b> H1, 499.8633015 Power 48 db continuously on WALTZ-16 modulated	<b>DATA PROCESSING</b> Line broadening 0.5 Hz FT size 65336 Total time 2 minutes	sxu-12-209-1-C13 Solvent: cdcl3 Temp. 25.0 C / 298.1 K Operator: Liu VNMR5-500 "nmr16"
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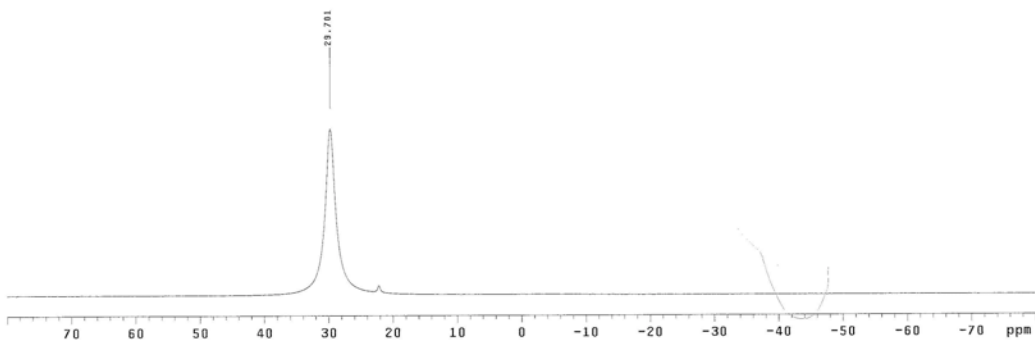
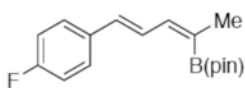
<b>PULSE SEQUENCE</b> Relax. delay 0.610 sec Pulse 90.0 degrees Acq. time 0.220 sec Width 32851.3 Hz 500 repetitions	<b>OBSERVE</b> 811, 160.3816755 <b>DECOUPLE</b> H1, 499.8633015 Power 40 db on during acquisition off during delay WALTZ-16 modulated	<b>DATA PROCESSING</b> Line broadening 10.0 Hz FT size 32768 Total time 1 minute	sxu-12-209-1-811 Solvent: cdcl3 Temp. 25.0 C / 298.1 K Operator: Liu VNMR5-500 "nmr16"
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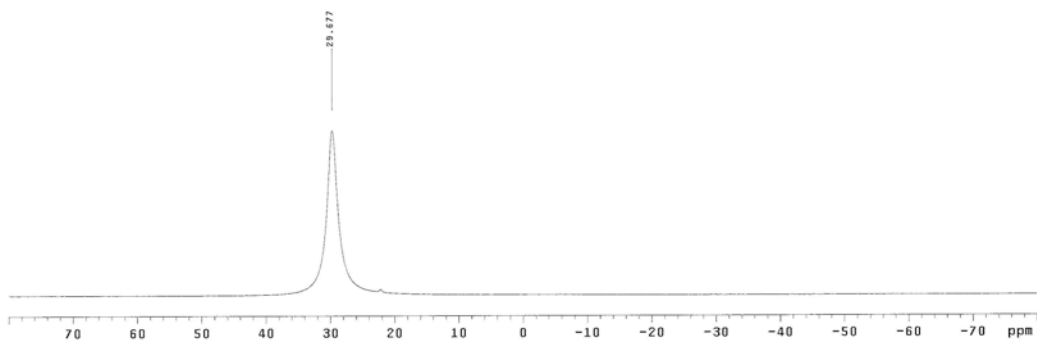
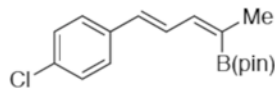


PULSE SEQUENCE Relax. delay 1.000 sec Pulse 30.0 degrees Acq. time 0.063 sec Width 126.7 kHz 22 repetitions	OBSERVE F19, 476.3578969	DATA PROCESSING FT size 131372 Total time 1 minute	skx-12-209-3-F19 Solvent: cdc13 Temp. 25.0 C / 298.1 K Operator: Liu VNMR5-500 "nmr18"
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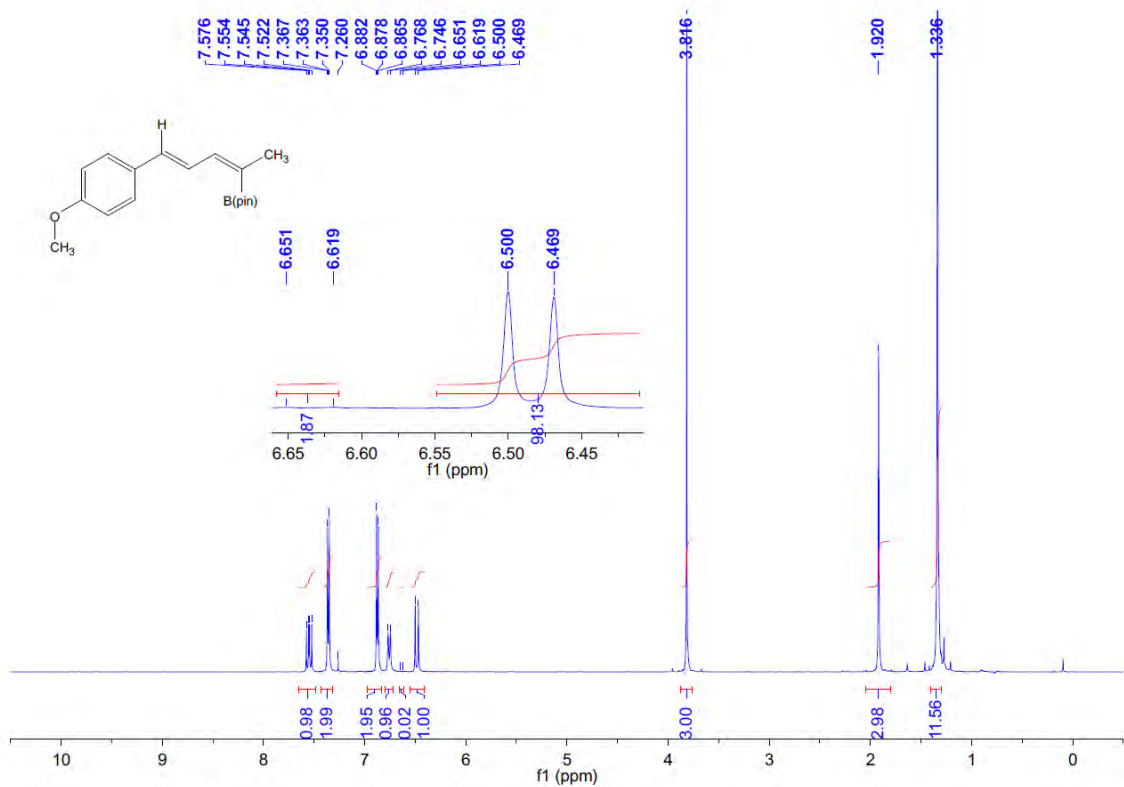
PULSE SEQUENCE Relax. delay 9.010 sec Pulse 50.0 degrees Acq. time 5.020 sec Width 32051.3 Hz 560 repetitions	OBSERVE B11, 160.3816755 DECOUPLE H1, 499.8833015 Power 48 dB on during acquisition off during delay WALTZ-16 modulated	DATA PROCESSING Line broadening 10.0 Hz FT size 32758 Total time 1 minute	skx-12-209-3-B11 Solvent: cdc13 Temp. 25.0 C / 298.1 K Operator: Liu VNMR5-500 "nmr18"
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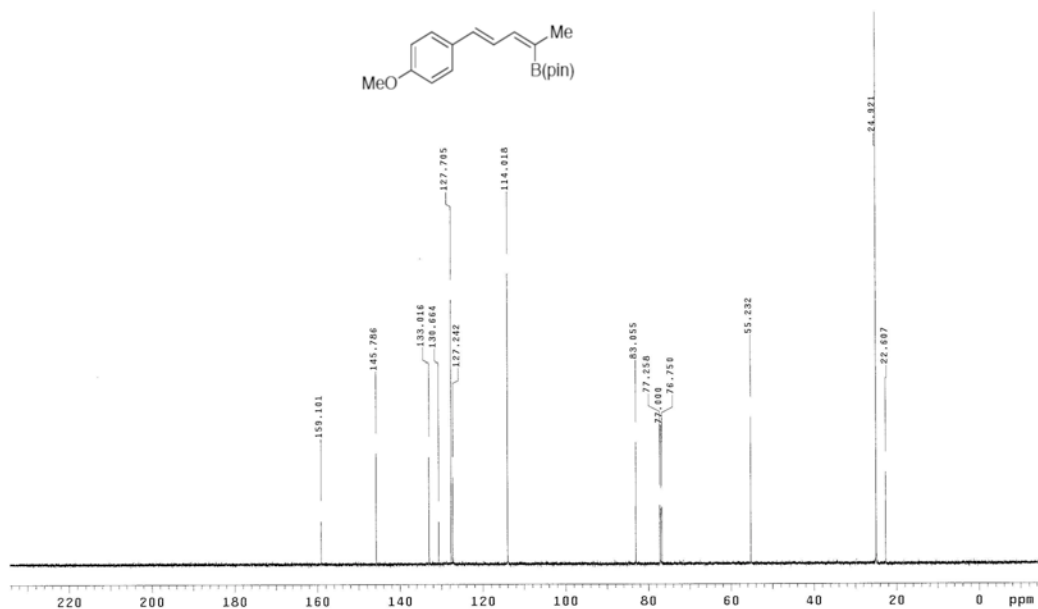
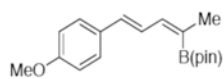




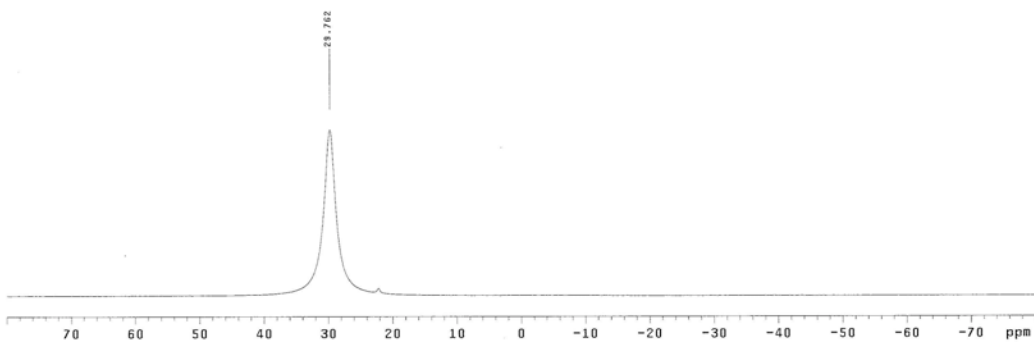
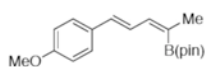
PULSE SEQUENCE	OBSERVE B11, 160.3816755	DATA PROCESSING	sxu-12-229-4-B11
Relax. delay 0.010 sec	DECOUPLE H1, 499.8833015	Line broadening 10.0 Hz	Solvent: cdcl3
Pulse 90.0 degrees	Power 48 dB	FT size 32768	Temp. 25.0 C / 298.1 K
Acq. time 0.223 sec	on during acquisition	Total time 1 minute	Operator: Liu
Width 32051.3 Hz	off during delay		VNMRS-500 "mar18"
500 repetitions	WALTZ-16 modulated		

**Compound 7k**



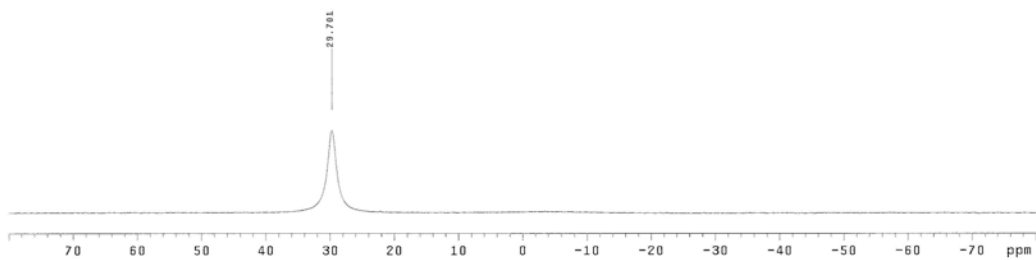
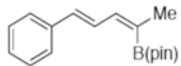


<b>PULSE SEQUENCE</b> Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 1.049 sec Width 31250.0 Hz 88 repetitions	<b>OBSERVE</b> C13, 125.6951309 <b>DECOUPLE</b> H1, 499.8833015 Power 40 db continuously on WALTZ-16 modulated	<b>DATA PROCESSING</b> Line broadening 0.5 Hz FT size 6538 Total time 3 minutes	sxu-12-209-2-C13 Solvent: cdcl3 Temp. 25.0 C / 298.1 K Operator: Liu VNMRS-500 "nmr18"
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<b>PULSE SEQUENCE</b> Relax. delay 9.010 sec Pulse 90.0 degrees Acq. time 0.920 sec Width 32051.3 Hz 500 repetitions	<b>OBSERVE</b> B11, 160.3816753 <b>DECOUPLE</b> H1, 499.8833015 Power 40 db on during acquisition off during delay WALTZ-16 modulated	<b>DATA PROCESSING</b> Line broadening 10.0 Hz FT size 32768 Total time 1 minute	sxu-12-209-2-B11 Solvent: cdcl3 Temp. 25.0 C / 298.1 K Operator: Liu VNMRS-500 "nmr18"
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PULSE SEQUENCE Relax. delay 0.010 sec Pulse 90.0 degrees Acc. time 0.020 sec Width 32051.3 Hz 1000 repetitions	OBSERVE 811, 160.3816784	DATA PROCESSING Line broadening 10.0 Hz FT size 32768 Total time 1 minute	skx-12-135-2-B11 Solvent: cdcl3 Temp: 25.0 C / 298.1 K Operator: Liu VNMRS-500 "narr18"
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yz-2-278H-1  
Selective band center: 1.90 (ppm); width: 83.8 (Hz)

Sample Name:

Data Collected on:

nmr19-vnmrs600

Archive directory:

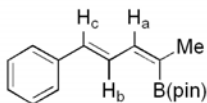
Sample directory:

FidFile: yz-2-278H-1-noesy1

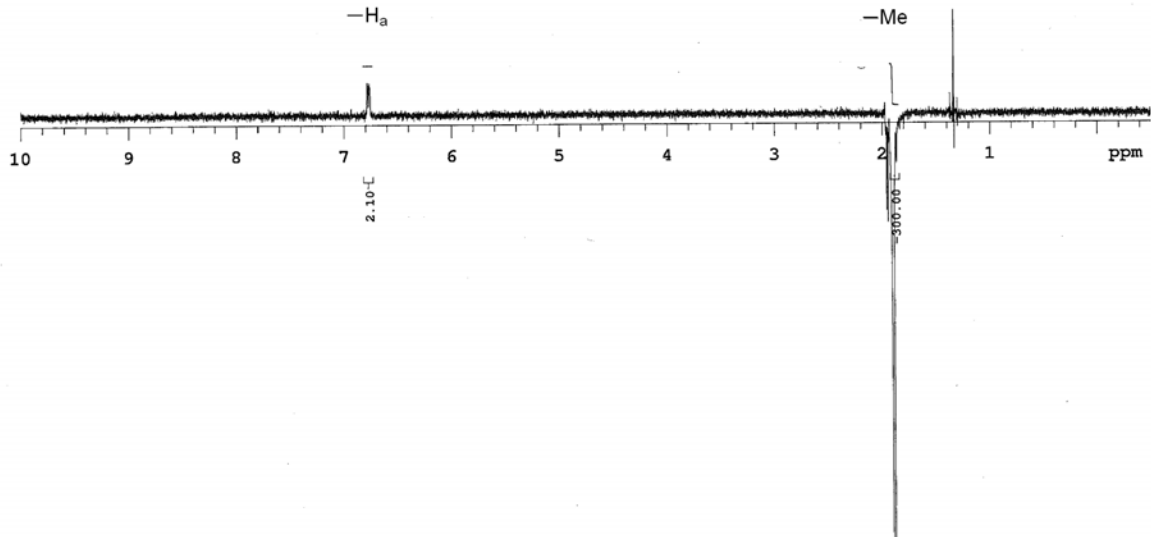
Pulse Sequence: NOESY1D

Solvent: cd2cl2

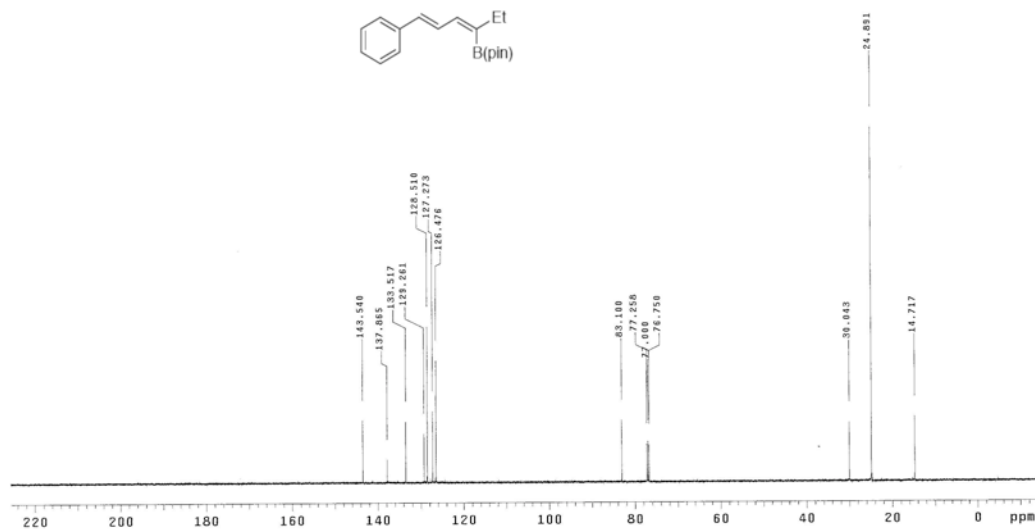
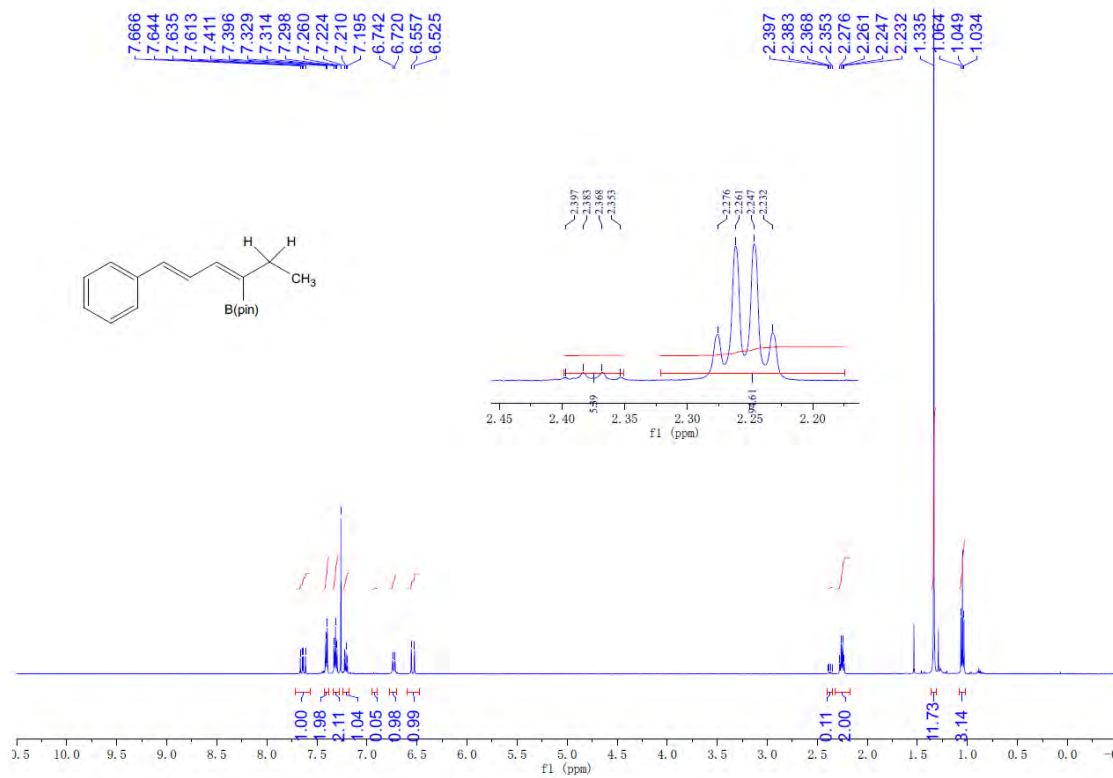
Data collected on: Oct 14 2016



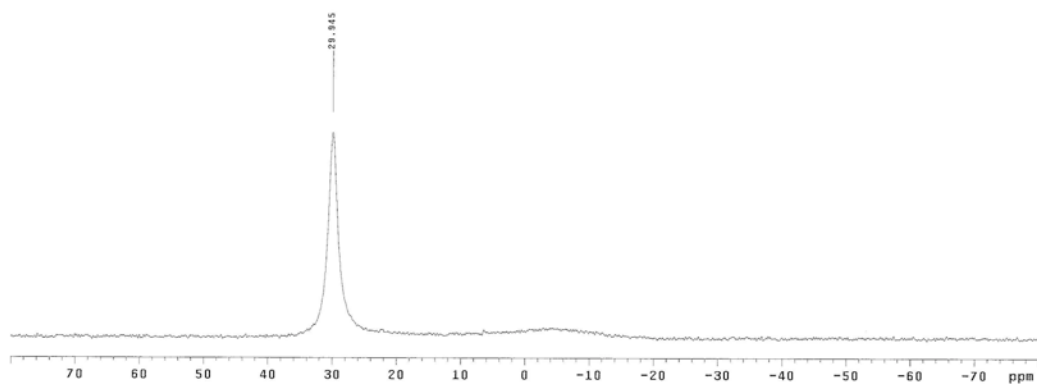
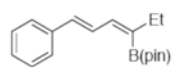
71



# Compound 7m

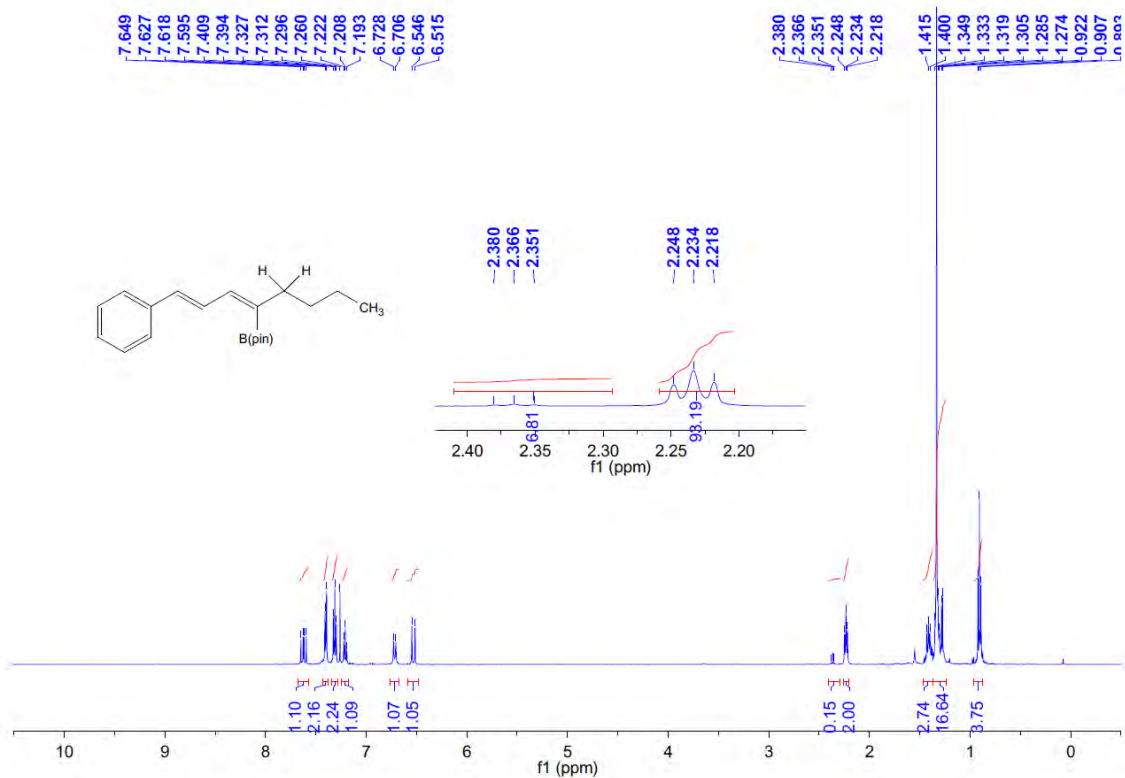


<b>PULSE SEQUENCE</b> Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 1.845 sec Width 31250.0 Hz 60 repetitions	<b>OBSERVE</b> C13, 125.6951319 <b>DECOUPLE</b> H1, 499.8839315 Power 48 dB continuously on WALTZ-16 modulated	<b>DATA PROCESSING</b> Line broadening 0.5 Hz FT size 65536 Total time 2 minutes	sxu-12-159-1-C13 Solvent: cdCl3 Temp. 25.0 C / 296.1 K Operator: Liu VIEWS-500 "mer16"
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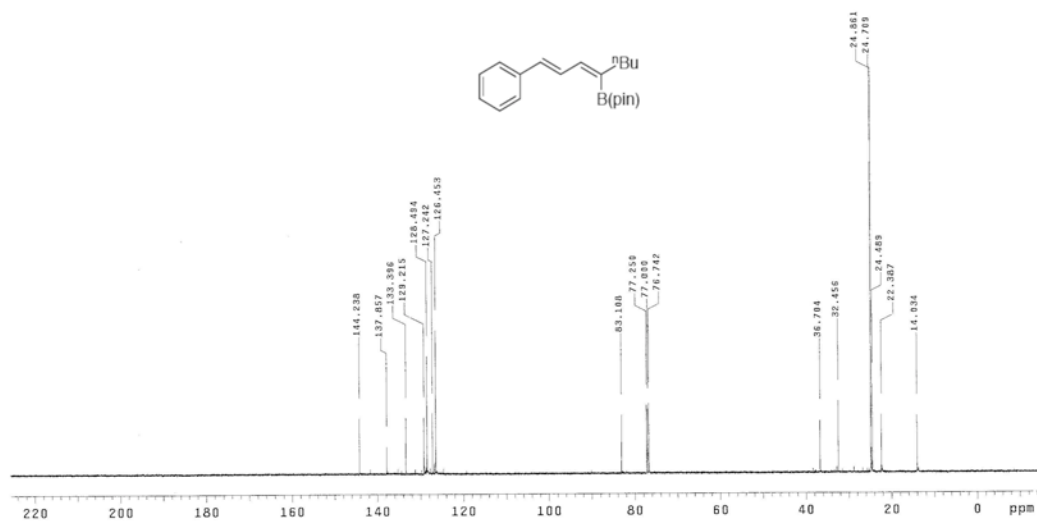


<b>PULSE SEQUENCE</b>	<b>OBSERVE</b> B11, 160.3816755	<b>DATA PROCESSING</b>	skx-12-199-1-B11
Relax. delay 0.919 sec	DECOUPLE M1, 499.8833015	Line broadening 10.0 Hz	Solvent: cdcl3
Pulse 90.0 degrees	Power 40 dB	FT size 32768	Temp. 25.0 C / 298.1 K
Acq. time 0.020 sec	on during acquisition	Total time 1 minute	Operator: Liu
Width 32051.3 Hz	off during delay		VMRS-500 "nar18"
1024 repetitions	WALTZ-16 modulated		

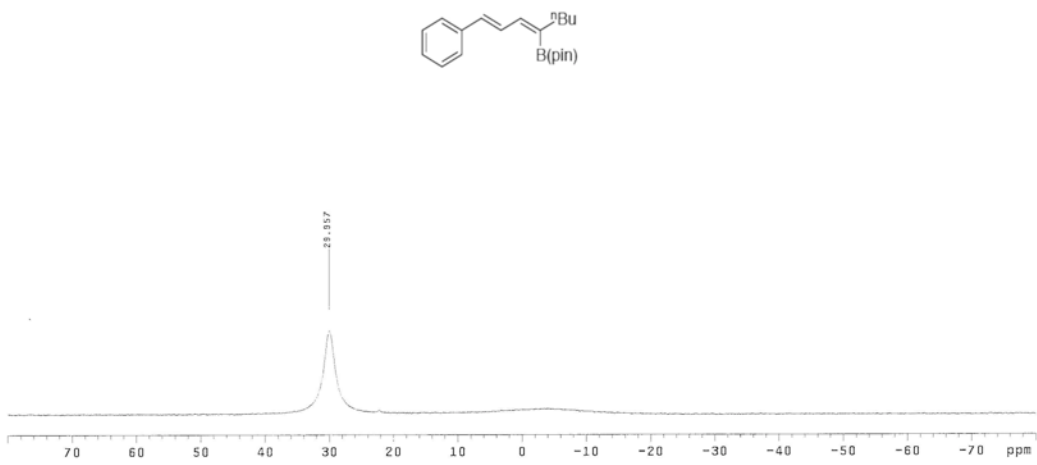
### Compound 7n





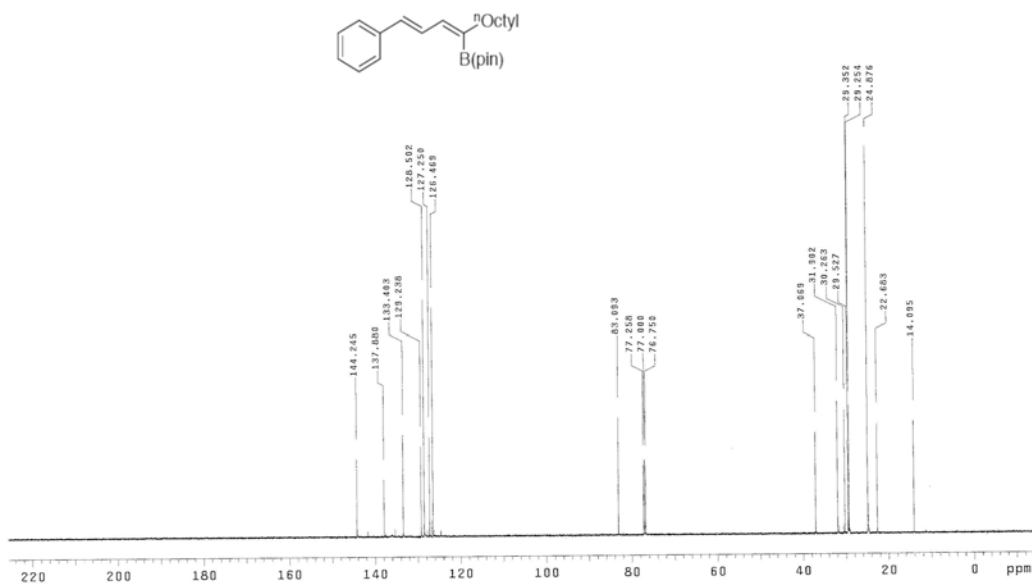
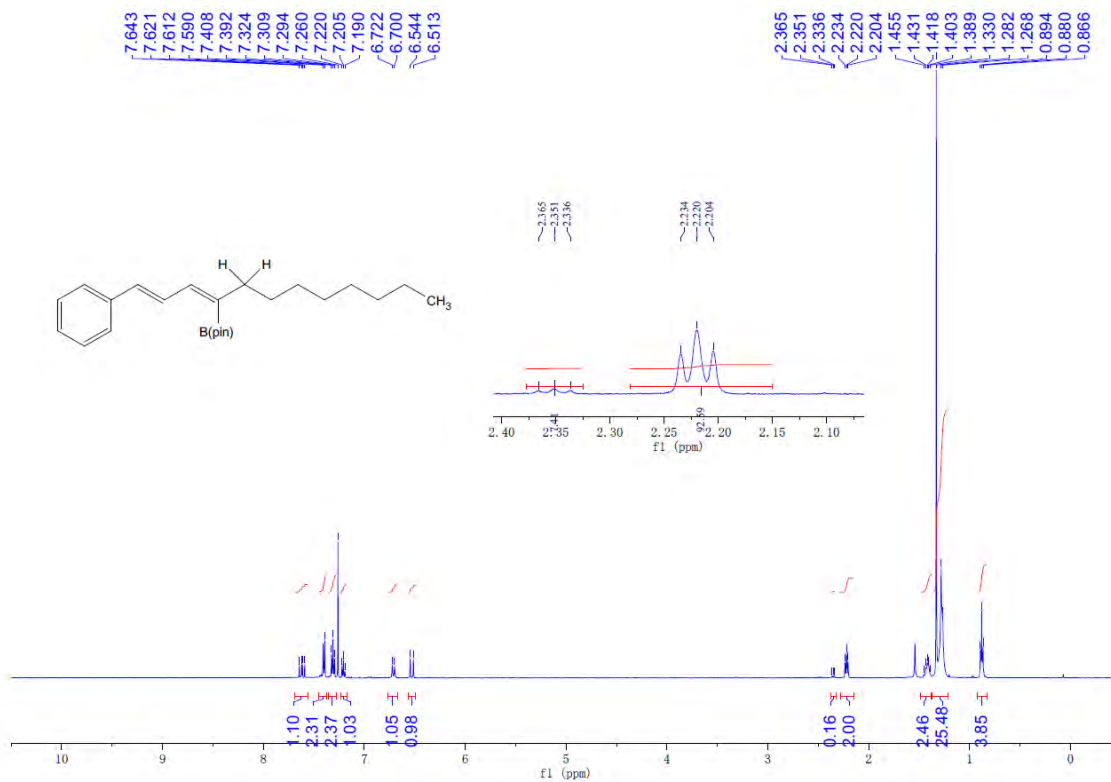


<b>PULSE SEQUENCE</b> Relax. delay 1.000 sec Pulse 45.0 degree Acq. time 1.048 sec Width 31250.0 Hz 200 repetitions	<b>OBSERVE</b> C13, 125.6951309 DECOUPLE H1, 499.8633015 Power 40 dB continuously on WALTZ-16 modulated	<b>DATA PROCESSING</b> Line broadening 0.5 Hz FT size 65536 Total time 6 minutes	sxu-12-185-C13 Solvent: cdcl3 Temp. 25.0 C / 298.1 K Operator: Liu VNMRS-500 "nar18"
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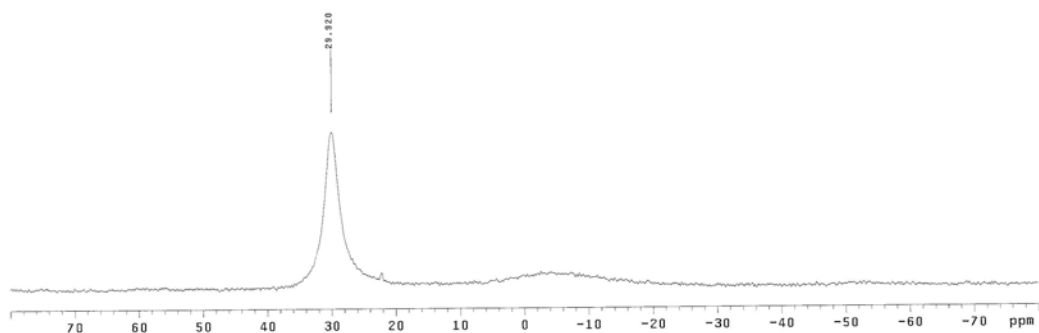
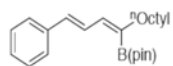


<b>PULSE SEQUENCE</b> Relax. delay 0.010 sec Pulse 95.0 degree Acq. time 1.020 sec Width 32051.3 Hz 1000 repetitions	<b>OBSERVE</b> 811, 160.3618848	<b>DATA PROCESSING</b> Line broadening 10.0 Hz FT size 32768 Total time 1 minute	sxu-12-185-811 Solvent: cdcl3 Temp. 25.0 C / 298.1 K Operator: Liu VNMRS-500 "nar18"
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# Compound 7o

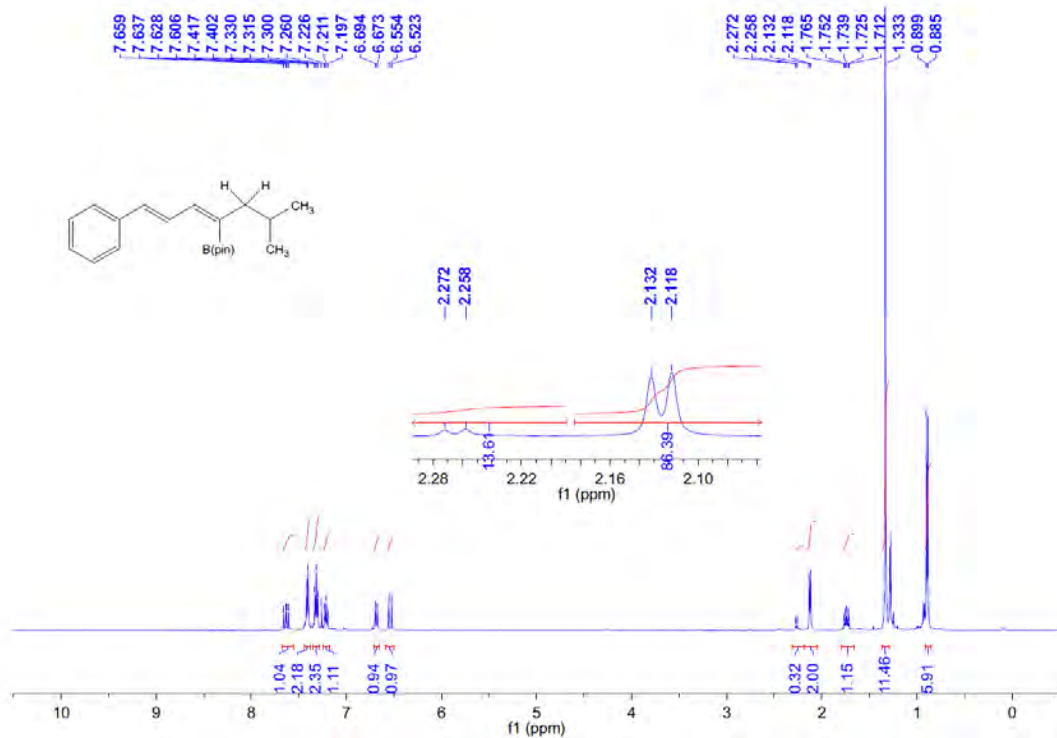


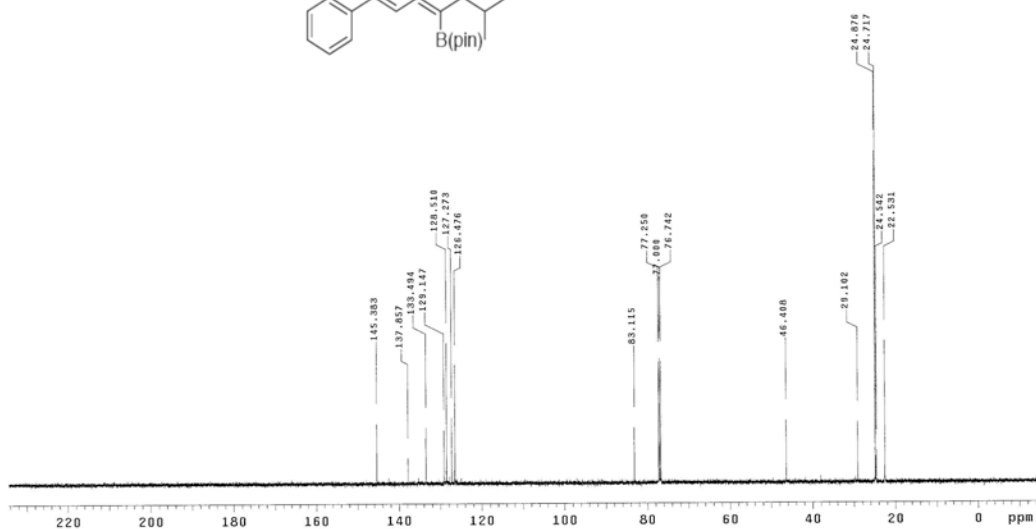
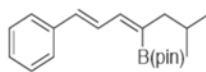
<b>PULSE SEQUENCE</b> Relax_delay 1.000 sec Pulse 45.0 degrees Acq. time 1.249 sec Width 31250.0 Hz 174 repetitions	<b>OBSERVE</b> C13, 125.6551309 <b>DECOUPLE</b> H1, 499.8653015 Power 40 dB Continuously on WALTZ-16 modulated	<b>DATA PROCESSING</b> Line broadening 0.5 Hz FT size 65536 Total time 5 minutes	sxu-12-193-C13 Solvent: cdCl3 Temp. 25.0 C / 298.1 K Operator: Liu VNMRS-500 "mr18"
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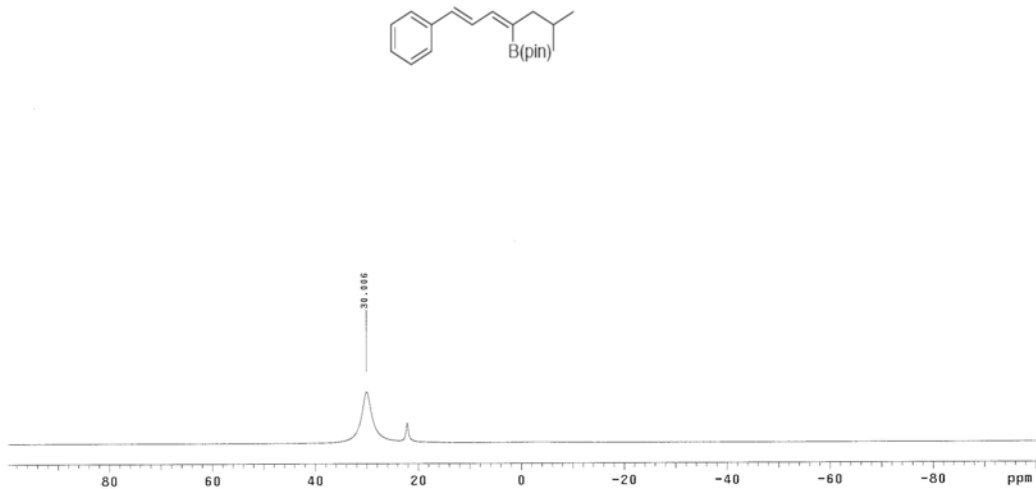
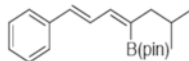
<b>PULSE SEQUENCE</b> Relax. delay 0.010 sec Pulse 90.0 degrees Acq. time 8.520 sec Width 32051.3 Hz 1000 repetitions	<b>OBSERVE</b> 811.169.9816775 <b>DECUPLE</b> H1.499.8833915 Power 40 dB on during acquisition off during delay VALTZ-16 modulated	<b>DATA PROCESSING</b> Line broadening 10.0 Hz FT size 32768 Total time 1 minute	skx-12-193-811 Solvent: cdcl3 Temp: 25.0 C / 298.1 K Operator: Liu VMRS-500 "nmr16"
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### Compound 7p



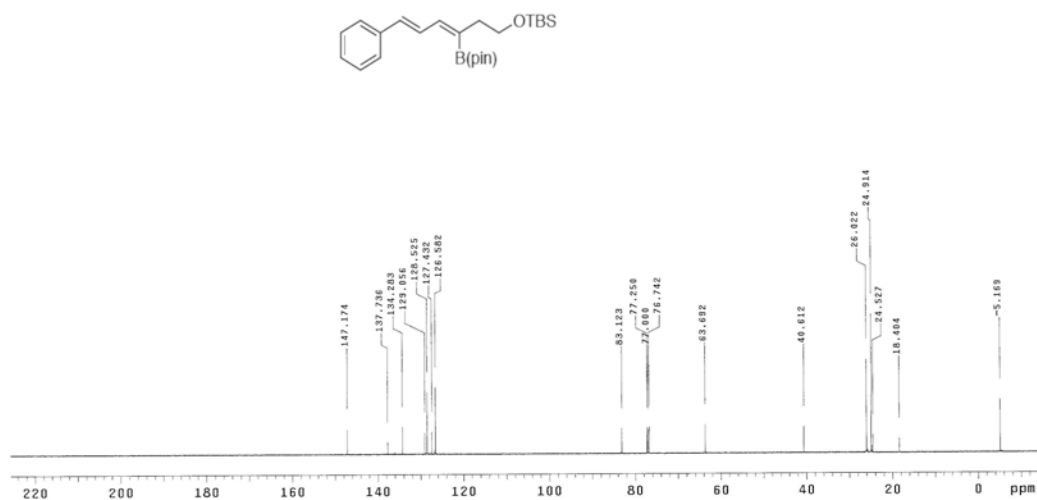
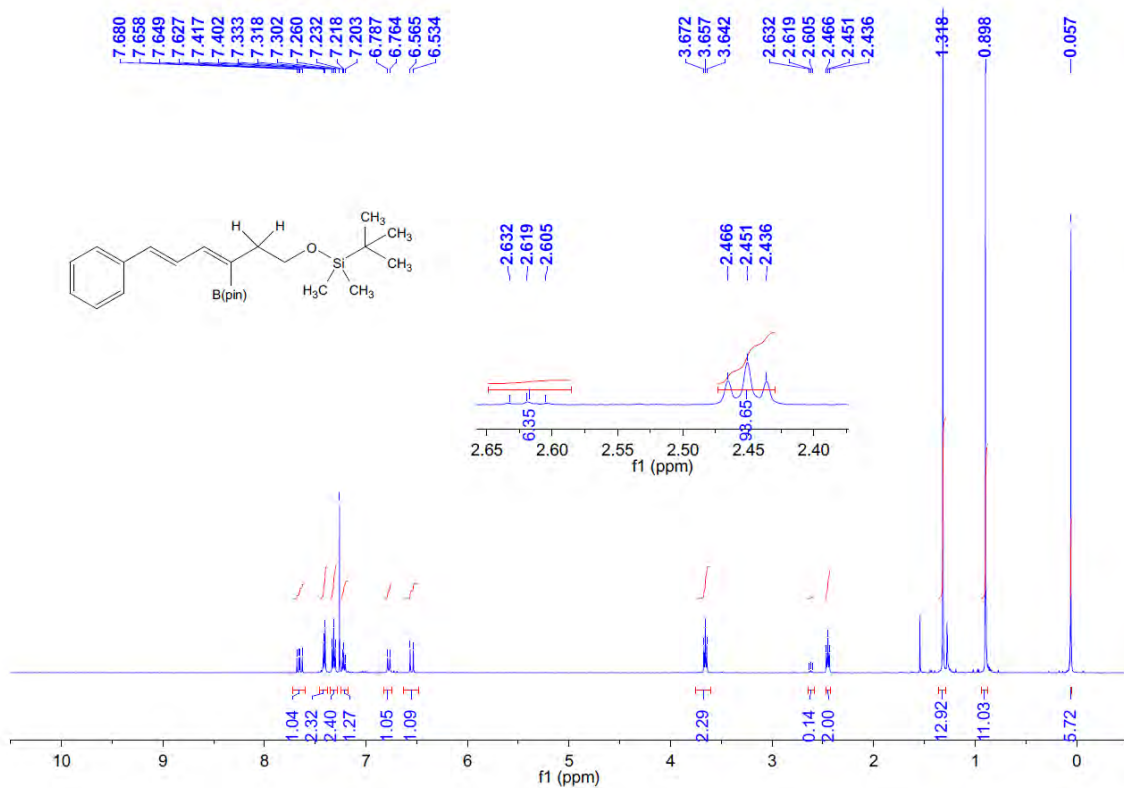


<b>PULSE SEQUENCE</b> Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 1.049 sec Width 32250.0 Hz 100 repetitions	<b>OBSERVE</b> C13, 125.6951290 <b>DECOUPLE</b> H1, 499.8833015 Power 40 dB continuously on WALTZ-16 modulated	<b>DATA PROCESSING</b> Line broadening 0.5 Hz FT size 65536 Total time 3 minutes	sxu-12-211-C13 Solvent: cdcl3 Temp. 25.0 C / 298.1 K Operator: Liu VNMRS-500 "nmr18"
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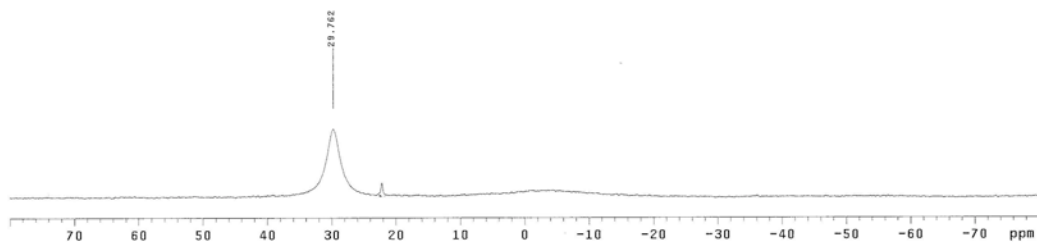
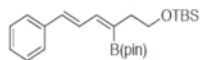


<b>PULSE SEQUENCE</b> Relax. delay 9.010 sec Pulse 90.0 degrees Acq. time 0.829 sec Width 32051.3 Hz 1000 repetitions	<b>OBSERVE</b> H1, 160.3816716 <b>DECOUPLE</b> H1, 499.8833015 Power 40 dB on during acquisition off during delay WALTZ-16 modulated	<b>DATA PROCESSING</b> Line broadening 10.0 Hz FT size 32768 Total time 1 minute	sxu-12-211-H1 Solvent: cdcl3 Temp. 25.0 C / 298.1 K Operator: Liu VNMRS-500 "nmr18"
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# Compound 7q



<b>PULSE SEQUENCE</b> Relax. delay 1.000 sec Pulse 45.0 degrees Acq. time 1.045 sec Width 31250.0 Hz 216 repetitions	<b>OBSERVE</b> C13, 125.6951300 <b>DECOUPLE</b> H1, 499.8033015 Power 48 dB continuously on WALTZ-16 modulated	<b>DATA PROCESSING</b> Line broadening 0.5 Hz FT size 65536 Total time 7 minutes	sku-12-215-C13 Solvent: cdc13 Temp: 25.0 C / 298.1 K Operator: Liu VNMDS-1D "nmr18"
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PULSE SEQUENCE	OBSERVE B11, 160.3818731	DATA PROCESSING	skx-12-215-B11
Relax. delay 0.010 sec	DECOUPLE M1, 499.6639015	Line broadening 10.0 Hz	Solvent: cdcl3
Pulse 95.0 degrees	Power 40 dB	FT size 32768	Temp. 25.0 C / 298.1 K
Acq. time 0.020 sec	on during acquisition	Total time 1 minute	Operator: Liu
Width 32251.3 Hz	off during delay		VNMRS-500 "nmr18"
1000 repetitions	WALTZ-16 modulated		

yz-2-283H-2  
 Selective band center: 2.46 (ppm); width: 28.2 (Hz)

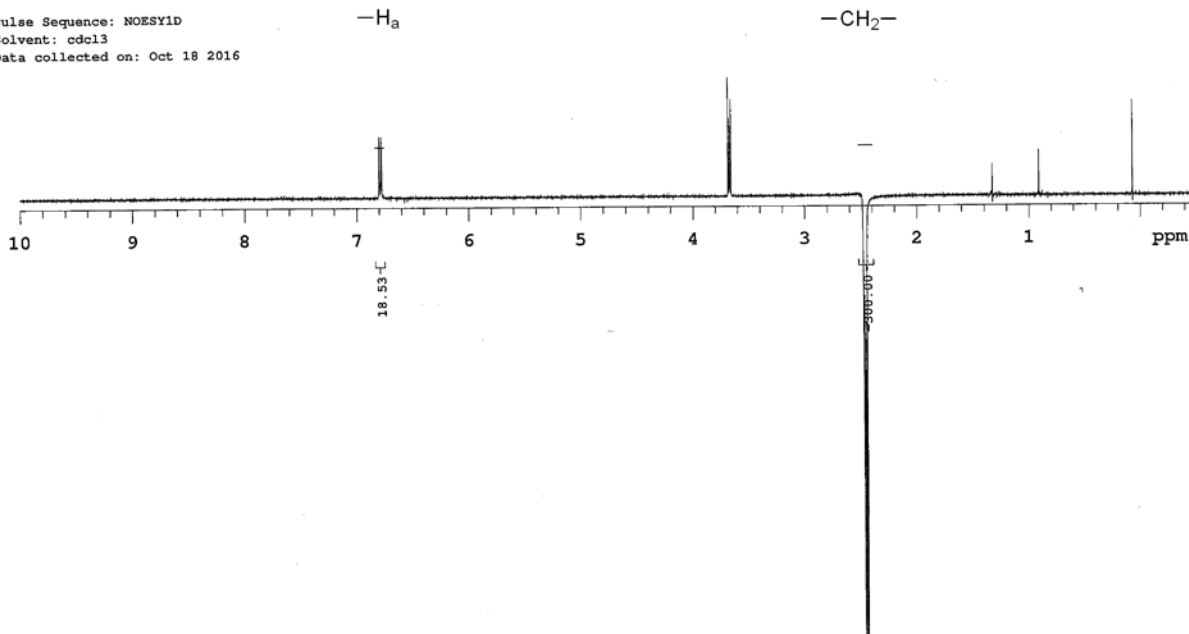
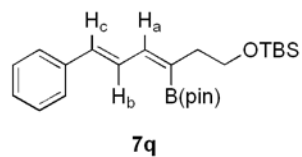
Sample Name:

Data Collected on:  
 nmrl9-vnmrs600  
 Archive directory:

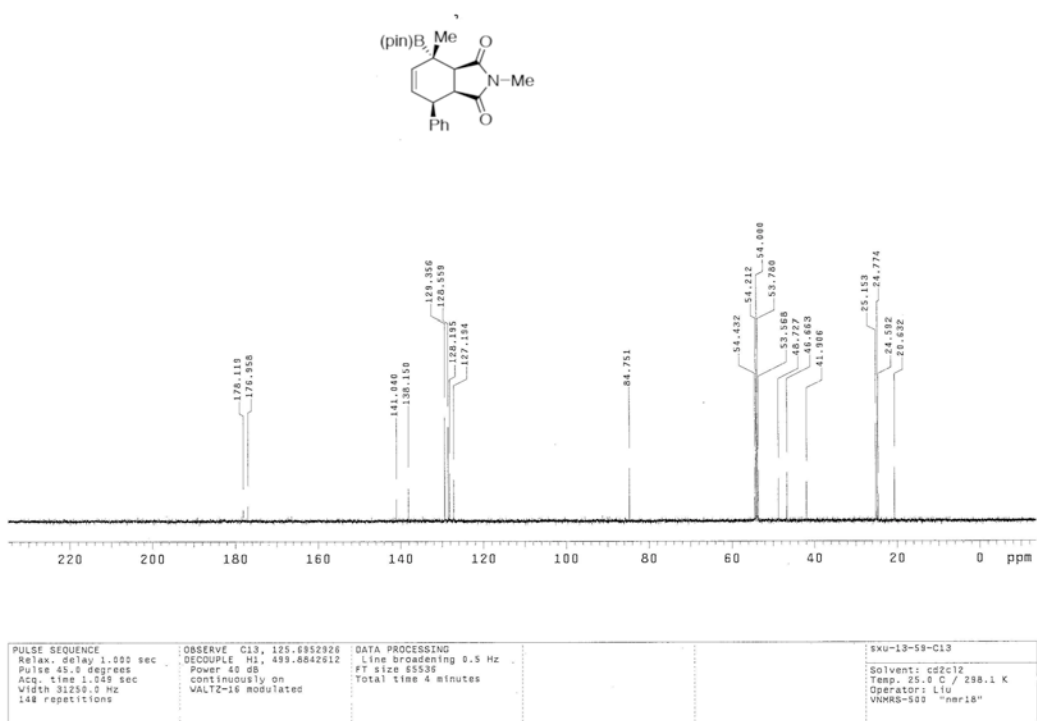
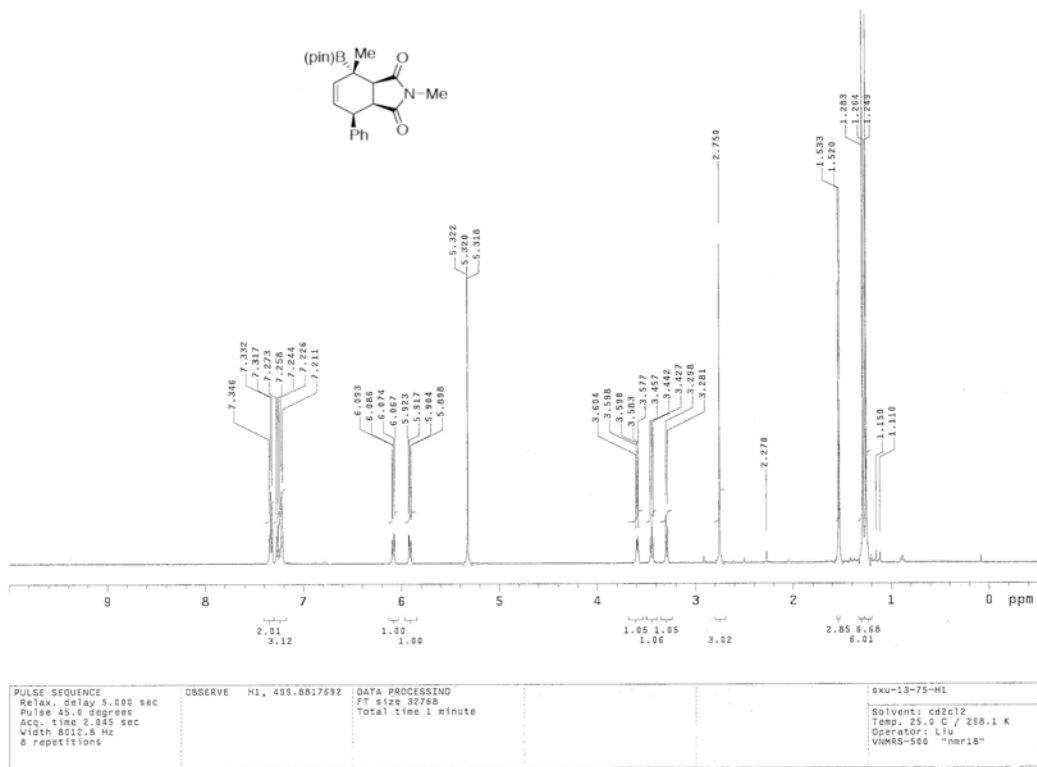
Sample directory:

FidFile: yz-2-283H-2-noesy1

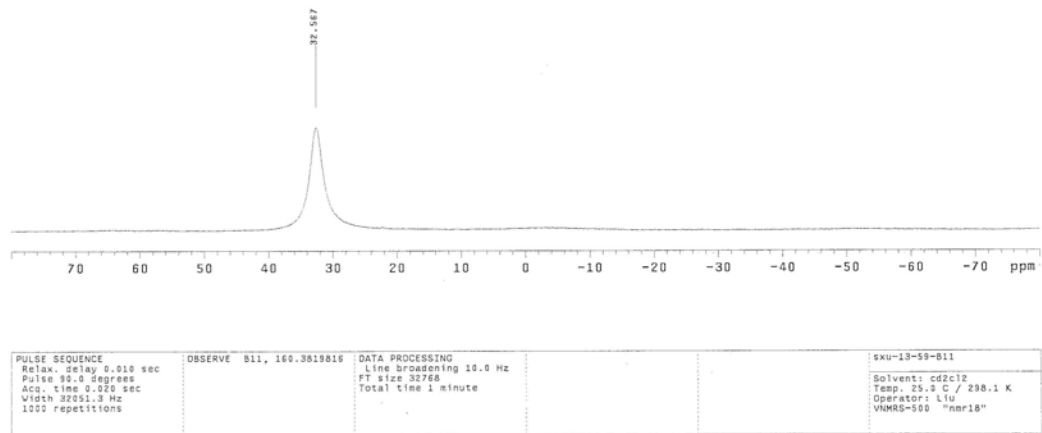
Pulse Sequence: NOESY1D  
 Solvent: cdcl3  
 Data collected on: Oct 18 2016



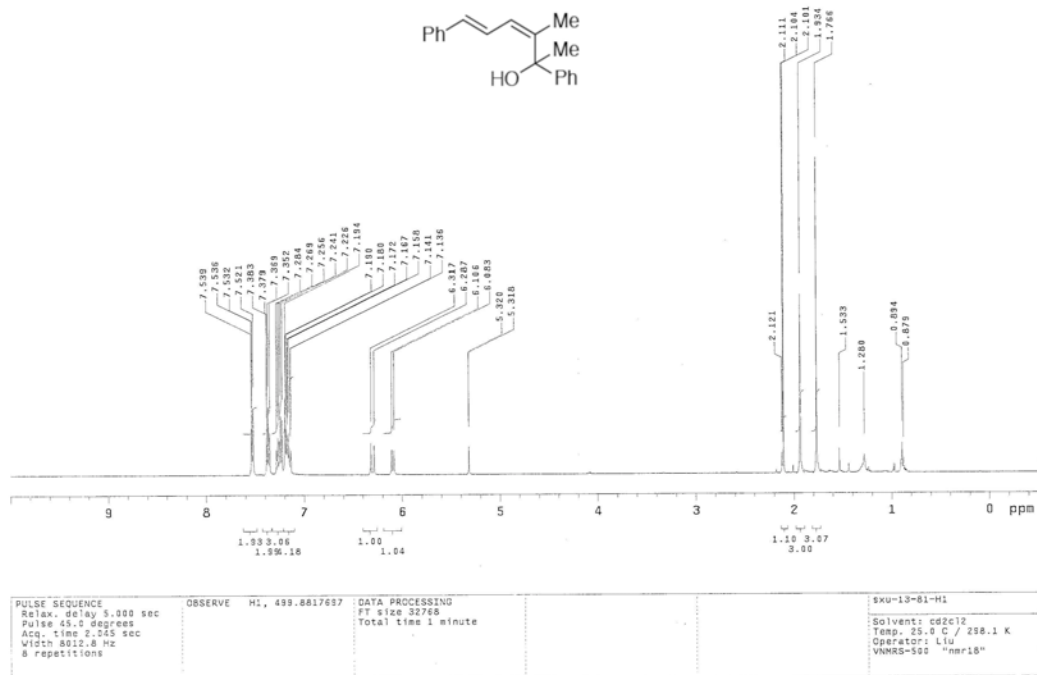


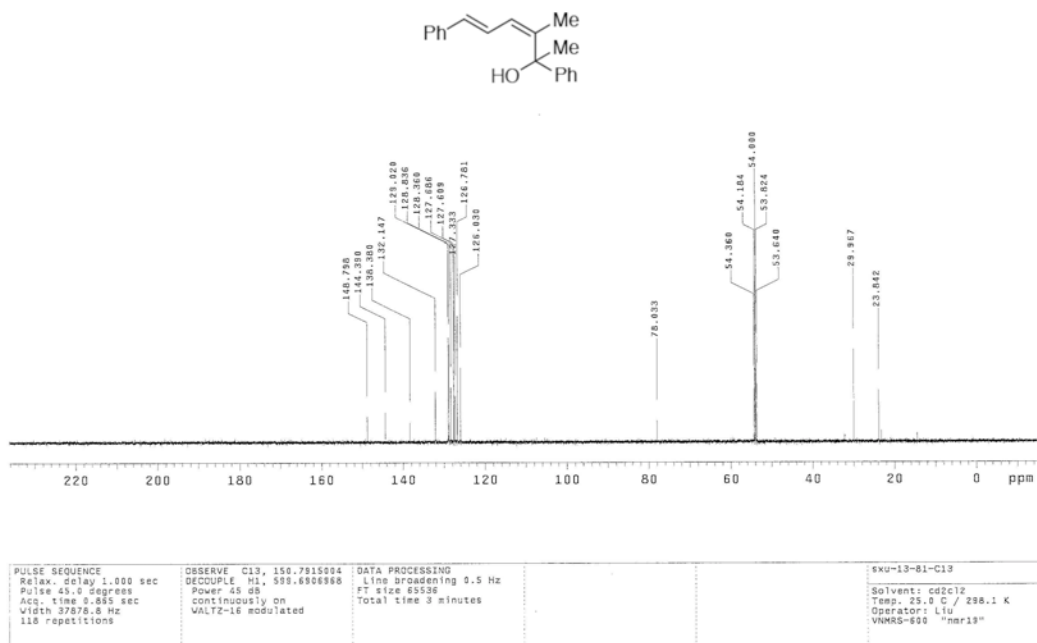




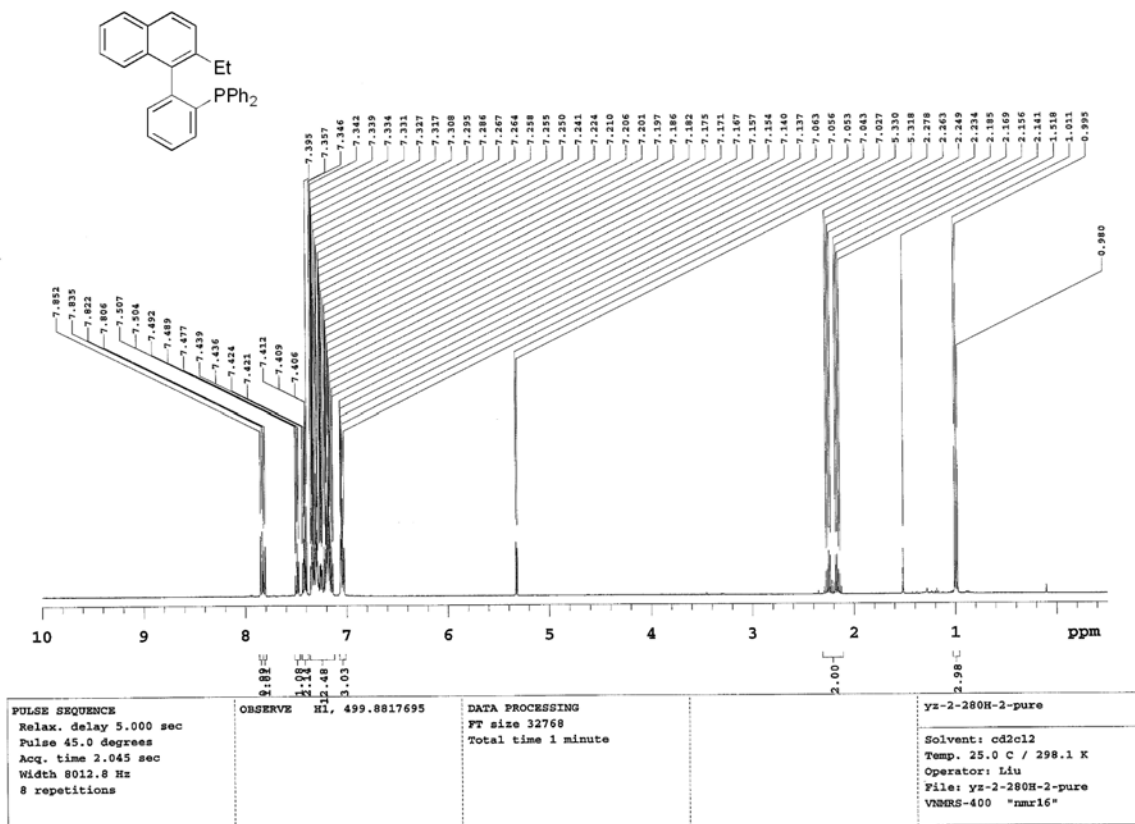


**Compound 11**





### Ligand CC-L3



yz-2-280C-2-pure

Sample Name:

Data Collected on:  
nmr18-vnmrs500  
Archive directory:

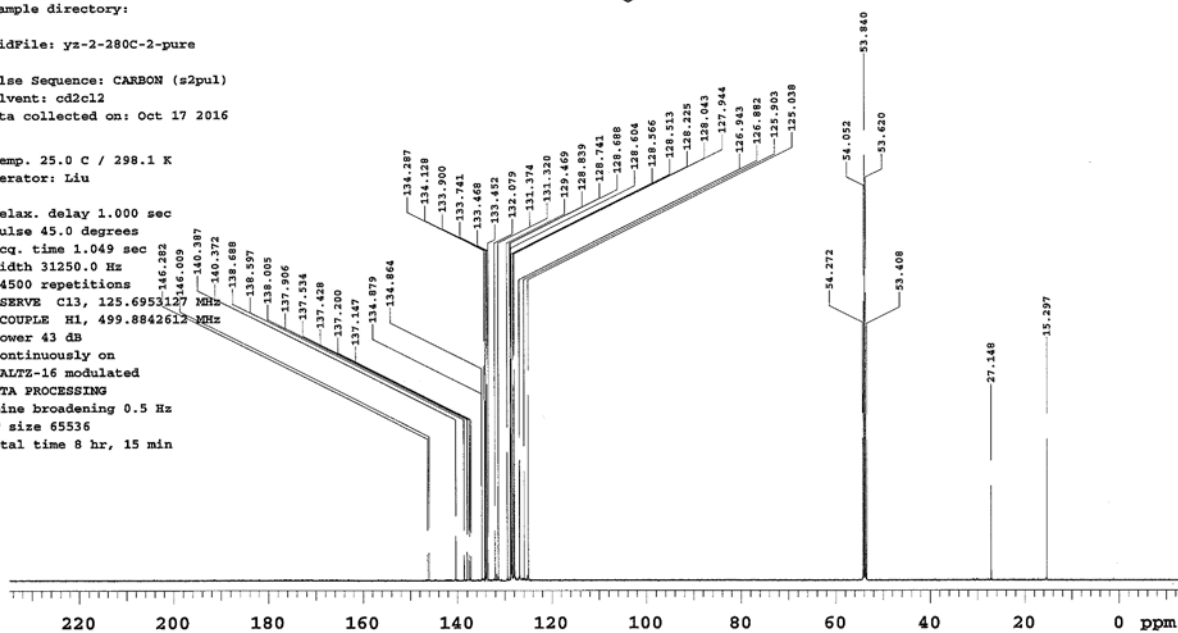
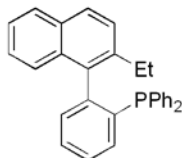
Sample directory:

FidFile: yz-2-280C-2-pure

Pulse Sequence: CARBON (s2pul)  
Solvent: cd2cl2  
Data collected on: Oct 17 2016

Temp. 25.0 C / 298.1 K  
Operator: Liu

Relax. delay 1.000 sec  
Pulse 45.0 degrees  
Acq. time 1.049 sec  
Width 31250.0 Hz  
14500 repetitions  
OBSERVE C13, 125.6953127 MHz  
DECOUPLE H1, 499.8842612 MHz  
Power 43 dB  
continuously on  
WALTZ-16 modulated  
DATA PROCESSING  
Line broadening 0.5 Hz  
FT size 65536  
Total time 8 hr, 15 min



yz-2-280P-2-pure

Sample Name:

Data Collected on:  
nmr18-vnmrs500  
Archive directory:

Sample directory:

FidFile: yz-2-280P-2-pure

Pulse Sequence: PHOSPHORUS (s2pul)  
Solvent: cd2cl2  
Data collected on: Oct 17 2016

Temp. 25.0 C / 298.1 K  
Operator: Liu

Relax. delay 1.000 sec  
Pulse 45.0 degrees  
Acq. time 0.655 sec  
Width 50000.0 Hz  
64 repetitions  
OBSERVE P31, 202.3557276 MHz  
DECOUPLE H1, 499.8842612 MHz  
Power 43 dB  
on during acquisition  
off during delay  
WALTZ-16 modulated  
DATA PROCESSING  
Line broadening 0.5 Hz  
FT size 65536  
Total time 1 min 46 sec

