

# Supporting Information

## Nickel- and Copper-Catalyzed Direct Alkynylation of Azoles and Polyfluoroarenes with Terminal Alkynes under O<sub>2</sub> or Atmospheric Conditions

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### Instrumentation and Chemicals

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at 400 MHz and 100 MHz, respectively, for CDCl<sub>3</sub> solutions. <sup>19</sup>F NMR was measured at 373 MHz for CDCl<sub>3</sub> solutions with hexafluorobenzene as an external standard. MS data were obtained by EI. GC analysis was carried out using a silicon OV-17 column (i. d. 2.6 mm x 1.5 m) or a CBP-1 capillary column (i. d. 0.5 mm x 25 m).

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Toluene was stored over slices of sodium. DMSO was freshly distilled from CaH<sub>2</sub> prior to use. Terminal alkynes **2a-c**, **2e-2j**, **2m-o** were synthesized via the Sonogashira coupling of aryl halides with trimethylsilylacetylene<sup>1,2</sup> and subsequent desilylation with K<sub>2</sub>CO<sub>3</sub>/MeOH. Benzoxazoles **1b-1d** were obtained through the condensation of 2-aminophenol derivatives with triethyl orthoformate.<sup>3</sup> 5-Aryloxazoles **1e-1k** were prepared by the van Leusen reaction with TosMIC and the corresponding aldehydes.<sup>4</sup>

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<sup>1</sup> Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 16, 4467.

<sup>2</sup> Hundertmark, T.; Littke, A. F.; Buchwald, S. L.; Fu, G. C. *Org. Lett.* **2000**, 2, 1729.

<sup>3</sup> Cho, S. H.; Kim, J. Y.; Lee, S. Y.; Chang, S. *Angew. Chem., Int. Ed.* **2009**, 48, 9127.

<sup>4</sup> van Leusen, A. M.; Hoogenboom, B. E.; Sinderius, H. *Tetrahedron Lett.* **1972**, 13, 2369.

## Experimental Procedure

**Synthesis of 3ad (Table 1, entry 4):** NiBr<sub>2</sub> · diglyme (8.7 mg, 0.025 mmol), 4,4'-di(*tert*-butyl)-2,2'-bipyridine (dtbpy, 6.9 mg, 0.025 mmol), LiO-*t*-Bu (120 mg, 1.5 mmol), and biphenyl (ca. 50 mg, internal standard) were placed in a 20 mL two-necked reaction flask equipped with a reflux condenser, which was then filled with O<sub>2</sub> by using the standard Schlenk technique. A solution of benzoxazole (**1a**, 60 mg, 0.50 mmol) and phenylacetylene (**2d**, 102 mg, 1.0 mmol) in toluene (2.5 mL) was added dropwise. After the reaction mixture was stirred at 100 °C for 1 h, the consumption of **1a** was checked by GC analysis. The resulting mixture was then poured into water. The mixture was extracted with diethyl ether, and the combined organic layer was dried over sodium sulfate. Concentration in vacuo followed by silica gel column purification with hexane/ethyl acetate (98/2, v/v) gave 2-(phenylethynyl)benzoxazole (**3ad**, 53 mg, 0.24 mmol) in 48% yield.

**Synthesis of 3al (Table 1, entry 12):** To a mixture of NiBr<sub>2</sub> · diglyme (8.7 mg, 0.025 mmol), 4,4'-di(*tert*-butyl)-2,2'-bipyridine (dtbpy, 6.9 mg, 0.025 mmol), LiO-*t*-Bu (120 mg, 1.5 mmol), (triisopropylsilyl)acetylene (**2l**, 182 mg, 1.0 mmol), and biphenyl (ca. 50 mg, internal standard) in toluene (2.5 mL) placed in a 20 mL two-necked reaction flask equipped with a reflux condenser was added a solution of benzoxazole (**1a**, 60 mg, 0.50 mmol) in toluene (1.0 mL) over 30 min at 80 °C under O<sub>2</sub> (1atm, balloon). After the completion of the addition, the reaction mixture was heated for additional 1.5 h at the same temperature. The consumption of **1a** was checked by GC analysis, and the resulting mixture was poured into water. The mixture was extracted with diethyl ether, and the combined organic layer was dried over sodium sulfate. Concentration in vacuo followed by silica gel column purification with hexane/ethyl acetate (99/1, v/v) gave 2-[(triisopropylsilyl)ethynyl]benzoxazole (**3al**, 84 mg, 0.28 mmol) in 56% yield.

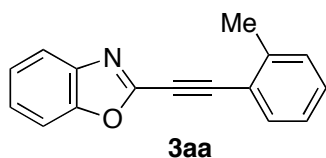
**Synthesis of 3el (Table 2):** To a mixture of NiBr<sub>2</sub> · diglyme (26 mg, 0.075 mmol), 4,4'-di(*tert*-butyl)-2,2'-bipyridine (dtbpy, 20 mg, 0.075 mmol), LiO-*t*-Bu (120 mg, 1.5 mmol), 5-phenyloxazole (**1e**, 73 mg, 0.50 mmol), and biphenyl (ca. 50 mg, internal standard) in toluene (2.5 mL) placed in a 20 mL two-necked reaction flask equipped with a reflux condenser was added a solution of (triisopropylsilyl)acetylene (**2l**, 273 mg, 1.5 mmol) in toluene (1.0 mL) over 30 min at 120 °C under O<sub>2</sub> (1atm, balloon). After the completion of the addition, the reaction mixture was heated for additional 1.5 h at the same temperature. The consumption of **1e** was checked by GC analysis, and the resulting mixture was poured into water. The mixture was extracted with diethyl

ether, and the combined organic layer was dried over sodium sulfate. Concentration in vacuo followed by silica gel column purification with hexane/ethyl acetate (98/2, v/v) gave 5-phenyl-2-[(triisopropylsilyl)ethynyl]oxazole (**3el**, 65 mg, 0.20 mmol) in 40% yield.

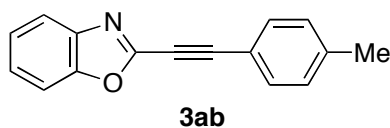
**Synthesis of 11ad (Table 3):** Cu(OTf)<sub>2</sub> (36 mg, 0.10 mmol), LiO-*t*-Bu (40 mg, 0.50 mmol), 1,10-phenanthroline·OH<sub>2</sub> (40 mg, 0.20 mmol), 1-methylnaphthalene (ca. 50 mg, internal standard), and DMSO (0.50 mL) were placed in a 20 mL two-necked reaction flask equipped with a drying tube lined with calcium chloride. The mixture was stirred for 5 min at room temperature. A solution of **10a** (252 mg, 1.5 mmol) in DMSO (0.50 mL) and that of **2d** (51 mg, 0.50 mmol) in DMSO (0.50 mL) were added in sequence, and the solution was stirred for room temperature under atmospheric conditions. The consumption of **2d** was confirmed by GC analysis, and the resulting mixture was then quenched with water. The mixture was extracted with ethyl acetate and the organic layer was dried over sodium sulfate. Concentration in vacuo followed by silica gel column purification with hexane and GPC separation gave **11ad** (80 mg, 0.30 mmol) in 60 % yield.

## Characterization Data for Compounds

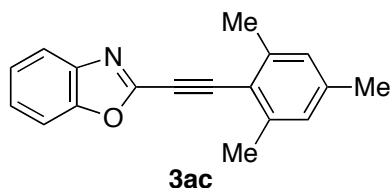
$^1\text{H}$  and  $^{13}\text{C}$  spectra for all products were attached to the last part. Compounds **3ab**,<sup>5</sup> **3ad**,<sup>5</sup> **3ah**,<sup>5</sup> **3ai**,<sup>5</sup> **3ak**,<sup>5</sup> **3al**,<sup>5</sup> **3el**,<sup>5</sup> **11ab**,<sup>6</sup> **11ad**,<sup>6</sup> **11ae**,<sup>6</sup> **11am**,<sup>6</sup> and **11an**<sup>6</sup> are found in the literature.



**2-[(2-Methylphenyl)ethynyl]benzoxazole (3aa):** mp 61 °C (from hexane);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.58 (s, 3H), 7.21 (t,  $J = 7.6$  Hz, 1H), 7.28 (d,  $J = 7.6$  Hz, 1H), 7.32-7.45 (m, 3H), 7.52-7.58 (m, 1H), 7.63 (d,  $J = 7.6$  Hz, 1H), 7.74-7.80 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  20.6, 81.1, 92.5, 110.6, 120.1, 120.4, 125.0, 125.8, 126.2, 129.8, 130.4, 132.9, 141.1, 141.7, 147.9, 150.3; MS  $m/z$  233 ( $\text{M}^+$ ); Elemental analysis calcd for,  $\text{C}_{16}\text{H}_{11}\text{NO}$ : C 82.38, H 4.75, N 6.00; found: C 82.17, H 4.80, N 5.96.

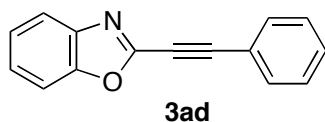


**2-[(4-Methylphenyl)ethynyl]benzoxazole (3ab):**<sup>5</sup>  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.38 (s, 3H), 7.20 (d,  $J = 8.0$  Hz, 2H), 7.34-7.43 (m, 2H), 7.49-7.54 (m, 1H), 7.55 (d,  $J = 8.0$  Hz, 2H), 7.71-7.78 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  21.6, 93.8, 110.5, 117.1, 120.3, 124.9, 126.1, 129.3, 132.3, 140.8, 141.1, 147.9, 150.3 (One signal was overlapped by other signal).

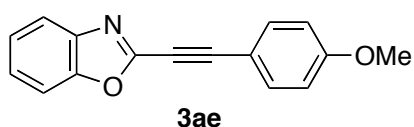


**2-[(2,4,6-Trimethylphenyl)ethynyl]benzoxazole (3ac):** mp 117-119 °C (from hexane);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.31 (s, 3H), 2.53 (s, 6H), 6.91 (s, 2H), 7.34-7.42 (m, 2H), 7.50-7.56 (m, 1H), 7.73-7.79 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  20.8, 21.4, 84.7, 92.0, 110.4, 117.1, 120.2, 124.9, 126.0, 127.9, 140.3, 141.2, 141.8, 148.2, 150.3; MS  $m/z$  261 ( $\text{M}^+$ ); Elemental analysis calcd for,  $\text{C}_{18}\text{H}_{15}\text{NO}$ : C 82.73, H 5.79, N 5.36; found: C 82.56, H 5.79, N 5.30.

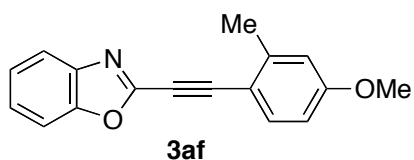
<sup>5</sup> Matsuyama, N.; Hirano, K.; Satoh, T.; Miura, M. *Org. Lett.* **2009**, *11*, 4156.



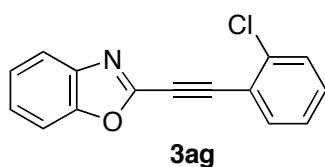
**2-(Phenylethynyl)benzoxazole (3ad)**<sup>5</sup>: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.35-7.49 (m, 5H), 7.54 (d, *J* = 7.3 Hz, 1H), 7.64-7.69 (m, 2H), 7.77 (d, *J* = 7.3 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 77.5, 93.4, 110.6, 120.2, 120.4, 125.0, 126.3, 128.6, 130.3, 132.5, 141.1, 147.7, 150.3.



**2-[(4-Methoxyphenyl)ethynyl]benzoxazole (3ae)**: mp 111 °C (from toluene); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 3.84 (s, 3H), 6.91 (d, *J* = 8.9 Hz, 2H), 7.33-7.42 (m, 2H), 7.49-7.55 (m, 1H), 7.60 (d, *J* = 8.9 Hz, 2H), 7.70-7.77 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 55.4, 76.6, 94.0, 110.5, 112.1, 114.3, 120.2, 124.9, 126.0, 134.2, 141.1, 148.1, 150.3, 161.2; MS *m/z* 249 (M<sup>+</sup>); Elemental analysis calcd for, C<sub>16</sub>H<sub>11</sub>NO<sub>2</sub>: C 77.10, H 4.45, N 5.62; found: C 76.87, H 4.44, N 5.63.

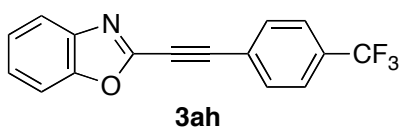


**2-[(4-Methoxy-2-methylphenyl)ethynyl]benzoxazole (3af)**: mp 95 °C (from hexane); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 2.55 (s, 3H), 3.82 (s, 3H), 6.75 (dd, *J* = 2.5, 8.5 Hz, 1H), 6.79 (d, *J* = 2.2 Hz, 1H), 7.33-7.42 (m, 2H), 7.50-7.54 (m, 1H), 7.56 (d, *J* = 8.5 Hz, 1H), 7.71-7.77 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 20.9, 55.3, 80.2, 93.2, 110.4, 111.7, 112.1, 115.4, 120.2, 124.9, 126.0, 134.5, 141.2, 143.8, 148.2, 150.3, 161.2; MS *m/z* 263 (M<sup>+</sup>); Elemental analysis calcd for, C<sub>17</sub>H<sub>13</sub>NO<sub>2</sub>: C 77.55, H 4.98, N 5.32; found: C 77.52, H 4.70, N 5.29.

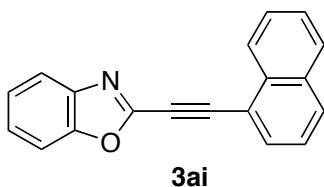


<sup>6</sup> Wei, Y.; Zhao, H.; Kan, J.; Su, W.; Hong, M. *J. Am. Chem. Soc.* **2010**, *132*, 2522.

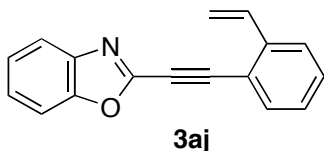
**2-[(2-Chlorophenyl)ethynyl]benzoxazole (3ag):** mp 112 °C (from hexane);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30 (m, 1H), 7.35-7.44 (m, 3H), 7.46 (m, 1H), 7.56 (d,  $J = 7.3$  Hz, 1H), 7.68 (dd,  $J = 1.8, 7.6$  Hz, 1H), 7.78 (d,  $J = 7.3$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  81.9, 89.7, 110.7, 120.5, 125.1, 126.5, 126.7, 129.6, 131.3, 134.2, 137.0, 141.0, 147.4, 150.4 (One signal was overlapped by other signal); MS  $m/z$  253 ( $\text{M}^+$ ); Elemental analysis calcd for,  $\text{C}_{15}\text{H}_8\text{ClNO}$ : C 71.02, H 3.18, Cl 13.98, N 5.52; found: C 70.89, H 3.25, Cl 13.76, N 5.50.



**2-[(4-Trifluoromethylphenyl)ethynyl]benzoxazole (3ah):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36-7.47 (m, 2H), 7.55 (d,  $J = 8.3$  Hz, 1H), 7.67 (d,  $J = 8.0$  Hz, 2H), 7.73-7.80 (m, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  79.35, 91.32, 110.68, 120.60, 123.56 (q,  $J = 272.5$  Hz), 124.01, 125.21, 125.58 (q,  $J = 3.8$  Hz), 126.67, 131.91 (q,  $J = 33.3$  Hz), 132.69, 140.94, 147.09, 150.36.

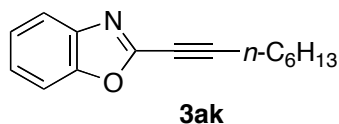


**2-(1-Naphthylethynyl)benzoxazole (3ai):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38-7.47 (m, 2H), 7.50 (t,  $J = 7.8$  Hz, 1H), 7.55-7.62 (m, 2H), 7.64-7.68 (m, 1H), 7.81 (d,  $J = 8.0$  Hz, 1H), 7.88-7.99 (m, 3H), 8.47 (d,  $J = 8.3$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  82.1, 91.6, 110.6, 117.8, 120.4, 125.1, 125.2, 125.9, 126.4, 127.0, 127.6, 128.5, 131.0, 132.3, 133.0, 133.3, 141.2, 147.9, 150.4.

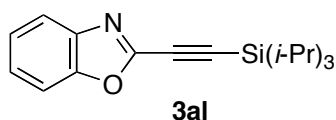


**2-[(2-Vinylphenyl)ethynyl]benzoxazole (3aj):** mp 104 °C (from hexane);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.46 (dd,  $J = 0.7, 11.2$  Hz, 1H), 5.91 (dd,  $J = 0.7, 16.7$  Hz, 1H), 7.26-7.36 (m, 2H), 7.36-7.46 (m, 3H), 7.55 (d,  $J = 7.3$  Hz, 1H), 7.66 (d,  $J = 8.0$  Hz, 2H), 7.73-7.81 (d,  $J = 7.3$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  81.7, 91.9, 110.6, 117.1, 118.8, 120.4, 124.9, 125.0, 126.3, 127.7, 130.5, 133.4, 134.1, 140.5, 141.1, 147.7, 150.3; MS  $m/z$  245 ( $\text{M}^+$ ); Elemental analysis calcd for,

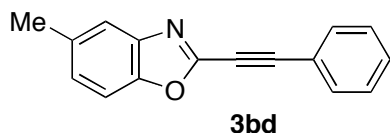
C<sub>17</sub>H<sub>11</sub>NO: C 83.25, H 4.52, N 5.71; found: C 83.17, H 4.67, N 5.63.



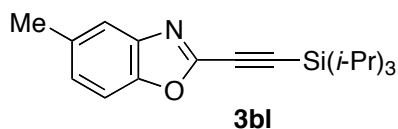
**2-(1-Octynyl)benzoxazole (3ak)**<sup>5</sup>: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.90 (t, *J* = 6.9 Hz, 3H), 1.24-1.42 (m, 4H), 1.42-1.52 (m, 2H), 1.63-1.72 (m, 2H), 2.50 (t, *J* = 6.9 Hz, 2H), 7.30-7.41 (m, 2H), 7.45-7.52 (m, 1H), 7.66-7.73 (m, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 14.0, 19.3, 22.5, 27.7, 28.5, 31.2, 69.4, 96.4, 110.4, 120.2, 124.8, 125.9, 140.9, 147.8, 150.1.



**2-[(Triisopropylsilyl)ethynyl]benzoxazole (3al)**<sup>5</sup>: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.16-1.20 (m, 21H), 7.32-7.42 (m, 2H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.72 (t, *J* = 7.6 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 11.0, 18.5, 93.4, 98.9, 110.6, 120.4, 125.0, 126.4, 140.7, 147.0, 150.1.

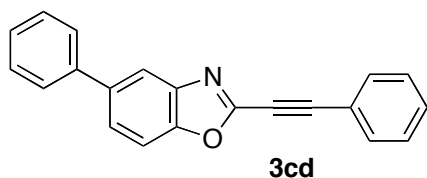


**5-Methyl-2-(phenylethynyl)benzoxazole (3bd)**: mp 58 °C (from hexane); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 2.50 (s, 3H), 7.21 (d, *J* = 8.3 Hz, 1H), 7.36-7.48 (m, 4H), 7.54 (s, 1H), 7.65 (d, *J* = 8.3 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 21.4, 77.6, 93.1, 109.9, 120.2, 120.3, 127.5, 128.6, 130.3, 132.4, 134.9, 141.3, 147.8, 148.6; MS *m/z* 233 (M<sup>+</sup>); Elemental analysis calcd for, C<sub>16</sub>H<sub>11</sub>NO: C 82.38, H 4.75, N 6.00; found: C 82.31, H 4.71, N 5.99.

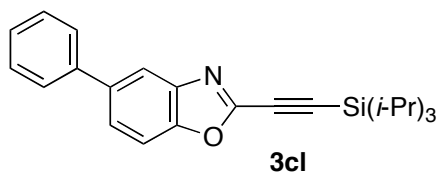


**5-Methyl-2-[(triisopropylsilyl)ethynyl]benzoxazole (3bl)**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.11-1.23 (m, 21H), 2.45 (s, 3H), 7.19 (d, *J* = 8.3 Hz, 1H), 7.36 (d, *J* = 8.3 Hz, 1H), 7.49 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 11.1, 18.5, 21.4, 93.6, 98.5, 109.9, 120.2, 127.6, 134.9, 140.9, 147.1, 148.3; HRMS *m/z*

(M<sup>+</sup>) calcd for C<sub>19</sub>H<sub>27</sub>NOSi, 313.1862. Found 313.1865.

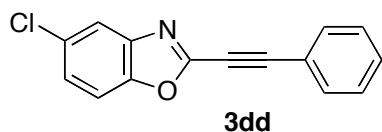


**5-Phenyl-2-(phenylethynyl)benzoxazole (3cd):** mp 127 °C (from hexane); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.35-7.44 (m, 6H), 7.45-7.73 (m, 6H), 7.95 (d, *J* = 1.8 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 77.5, 93.6, 110.5, 118.7, 120.2, 125.9, 127.4, 127.4, 128.6, 128.9, 130.3, 132.4, 138.9, 140.6, 141.7, 148.2, 149.8; MS *m/z* 295 (M<sup>+</sup>); Elemental analysis calcd for, C<sub>21</sub>H<sub>13</sub>NO: C 85.40, H 4.44, N 4.74; found: C 85.38, H 4.45, N 4.69.

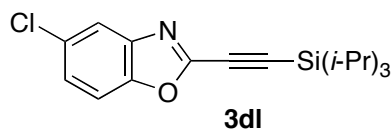


**5-Phenyl-2-[(triisopropylsilyl)ethynyl]benzoxazole (3cl):** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.15-1.26 (m, 21H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.3 Hz, 2H), 7.54-7.65 (m, 4H), 7.92 (d, *J* = 1.8 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 11.1, 18.5, 93.4, 99.2, 110.6, 118.7, 126.1, 127.4, 127.4, 128.9, 139.0, 140.6, 141.4, 147.5, 149.6; HRMS *m/z* (M<sup>+</sup>) calcd for C<sub>24</sub>H<sub>29</sub>NOSi, 375.2018. Found 375.2015.

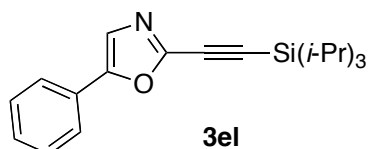




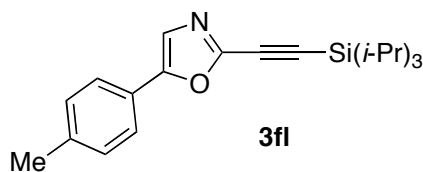
**5-Chloro-2-(phenylethynyl)benzoxazole (3dd):** mp 126 °C (from hexane);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32-7.51 (m, 5H), 7.66 (d,  $J$  = 8.3 Hz, 2H), 7.74 (d,  $J$  = 2.2 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  77.1, 94.2, 111.3, 120.0, 120.3, 126.6, 128.7, 130.6, 130.6, 132.5, 142.2, 148.9, 149.0; MS  $m/z$  253 ( $\text{M}^+$ ); Elemental analysis calcd for,  $\text{C}_{15}\text{H}_8\text{ClNO}$ : C 71.02, H 3.18, Cl 13.98, N 5.52; found: C 71.09, H 3.18, Cl 13.83, N 5.53.



**5-Chloro-2-[(triisopropylsilyl)ethynyl]benzoxazole (3dl):** mp 59 °C (from hexane);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.13-1.21 (m, 21H), 7.37 (dd,  $J$  = 2.2 Hz, 8.7 Hz, 1H), 7.44 (d,  $J$  = 8.7 Hz, 1H), 7.71 (d,  $J$  = 2.2 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  11.0, 18.5, 92.9, 100.1, 111.3, 120.3, 126.8, 130.6, 141.9, 148.1, 148.6; HRMS  $m/z$  ( $\text{M}^+$ ) calcd for  $\text{C}_{18}\text{H}_{24}\text{ClNOSi}$ , 333.1316 Found 333.1318; Elemental analysis calcd for,  $\text{C}_{18}\text{H}_{24}\text{ClNOSi}$ : C 64.74, H 7.24, Cl 10.62, N 4.19; found: C 64.46, H 7.06, Cl 10.38, N 4.26.

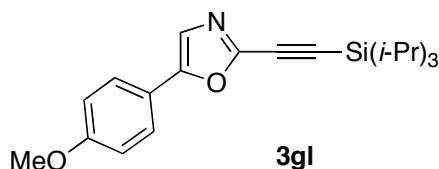


**5-Phenyl-2-[(triisopropylsilyl)ethynyl]oxazole (3el):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.13-1.22 (m, 21H), 7.34 (s, 1H), 7.35 (t,  $J$  = 7.3 Hz, 1H), 7.42 (t,  $J$  = 7.3 Hz, 2H), 7.67 (d,  $J$  = 7.3 Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  11.1, 18.5, 93.4, 96.7, 122.9, 124.6, 127.4, 128.9, 145.7, 151.8 (One signal was overlapped by other signal).

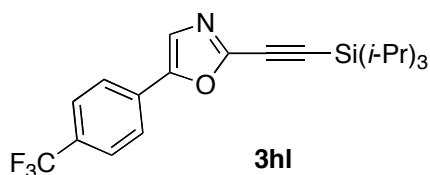


**5-(4-Methylphenyl)-2-[(triisopropylsilyl)ethynyl]oxazole (3fl):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$

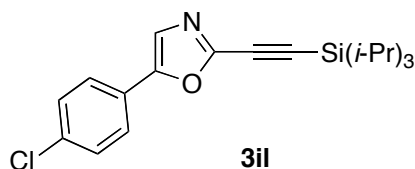
1.13-1.22 (m, 21H), 2.38 (s, 3H), 7.22 (d,  $J = 8.0$  Hz, 2H), 7.28 (s, 1H), 7.56 (d,  $J = 8.0$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  11.1, 18.5, 21.4, 93.5, 96.4, 122.2, 124.5, 124.6, 129.6, 139.1, 145.4, 152.0; HRMS  $m/z$  ( $\text{M}^+$ ) calcd for  $\text{C}_{21}\text{H}_{29}\text{NOSi}$ , 339.2018. Found 339.2025.



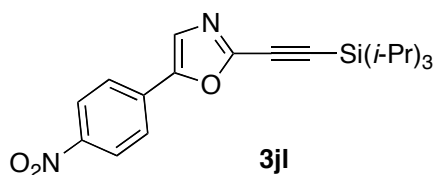
**5-(4-Methoxyphenyl)-2-[(triisopropylsilyl)ethynyl]oxazole (3gl):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.10-1.22 (m, 21H), 3.84 (s, 3H), 6.94 (d,  $J = 9.1$  Hz, 2H), 7.21 (s, 1H), 7.60 (d,  $J = 9.1$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  11.1, 18.5, 55.3, 93.5, 96.2, 114.4, 120.2, 121.4, 126.1, 145.1, 151.9, 160.2; HRMS  $m/z$  ( $\text{M}^+$ ) calcd for  $\text{C}_{21}\text{H}_{29}\text{NO}_2\text{Si}$ , 355.1968. Found 355.1968.



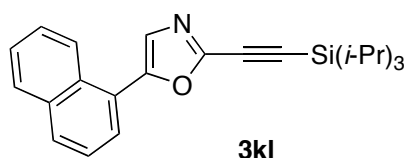
**5-(4-Trifluoromethylphenyl)-2-[(triisopropylsilyl)ethynyl]oxazole (3hl):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.11-1.23 (m, 21H), 7.45 (s, 1H), 7.67 (d,  $J = 8.0$  Hz, 2H), 7.78 (d,  $J = 8.0$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  11.1, 18.5, 93.0, 97.7, 123.8 (q,  $J_F = 272.2$  Hz), 124.6, 124.6, 126.0 (q,  $J_F = 3.8$  Hz), 130.5 (q,  $J_F = 1.5$  Hz), 130.6 (q,  $J_F = 32.7$  Hz), 146.4, 150.3; HRMS  $m/z$  ( $\text{M}^+$ ) calcd for  $\text{C}_{21}\text{H}_{26}\text{F}_3\text{NOSi}$ , 393.1736. Found 393.1739.



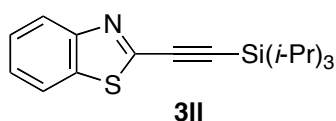
**5-(4-Chlorophenyl)-2-[(triisopropylsilyl)ethynyl]oxazole (3il):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.12-1.21 (m, 21H), 7.38 (s, 1H), 7.39 (d,  $J = 8.7$  Hz, 2H), 7.60 (d,  $J = 8.7$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  11.1, 18.5, 93.2, 97.1, 123.2, 125.8, 125.8, 129.2, 134.8, 145.8, 150.8; HRMS  $m/z$  ( $\text{M}^+$ ) calcd for  $\text{C}_{20}\text{H}_{26}\text{ClNOSi}$ , 359.1472. Found 359.1472.



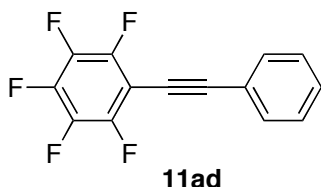
**5-(4-Nitrophenyl)-2-[(triisopropylsilyl)ethynyl]oxazole (3jl):** mp 62 °C (from hexane);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.13-1.22 (m, 21H), 7.55 (s, 1H), 7.83 (d,  $J = 8.7$  Hz, 2H), 8.29 (d,  $J = 8.7$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  11.1, 18.5, 92.7, 98.6, 124.5, 124.9, 126.1, 132.9, 147.0, 147.4, 149.5; MS  $m/z$  370 ( $\text{M}^+$ ); Elemental analysis calcd for,  $\text{C}_{20}\text{H}_{26}\text{N}_2\text{O}_3\text{Si}$ : C 64.83, H 7.07, N 7.56; found: C 64.72, H 6.79, N 7.34.



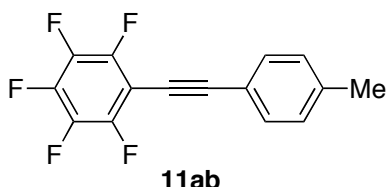
**5-(1-Naphthyl)-2-[(triisopropylsilyl)ethynyl]oxazole (3kl):** mp 85 °C (from hexane);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.14-1.24 (m, 21H), 7.46 (s, 1H), 7.51-7.62 (m, 3H), 7.79 (dd,  $J = 1.1, 7.7$  Hz, 1H), 7.91 (m, 2H), 8.27 (d,  $J = 8.3$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  11.1, 18.5, 93.4, 96.9, 124.6, 124.7, 125.2, 126.28, 126.31, 126.9, 127.2, 128.8, 129.97, 130.01, 133.8, 146.1, 151.0; MS  $m/z$  375 ( $\text{M}^+$ ); Elemental analysis calcd for,  $\text{C}_{24}\text{H}_{29}\text{NOSi}$ : C 76.75, H 7.78, N 3.73; found: C 76.75, H 7.59, N 3.66.



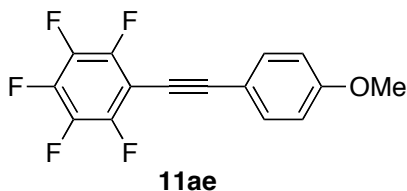
**2-[(Triisopropylsilyl)ethynyl]benzothiazole (3ll):**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.12-1.27 (m, 21H), 7.40-7.47 (m, 1H), 7.47-7.55 (m, 1H), 7.83 (d,  $J = 7.6$  Hz, 1H), 8.06 (d,  $J = 8.0$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  11.2, 18.6, 98.8, 100.8, 121.2, 123.7, 126.3, 126.7, 135.3, 148.4, 152.8; HRMS  $m/z$  ( $\text{M}^+$ ) calcd for  $\text{C}_{18}\text{H}_{25}\text{NSSi}$ , 335.1477. Found 335.1476.



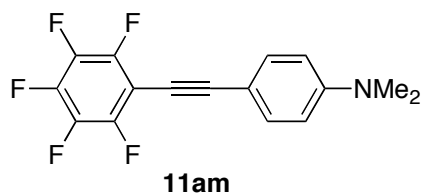
**1,2,3,4,5-Pentafluoro-6-(phenylethynyl)benzene (11ad):** m.p. 106-108 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37 -7.44 (m, 3H), 7.57-7.60 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  73.1-73.2 (m), 100.3-100.7 (m), 101.6-101.7 (m), 121.7, 128.7, 129.8, 132.1, 137.8 (dm,  $J_F = 251.1$  Hz), 141.5 (dm,  $J_F = 236.9$  Hz), 147.3 (dm,  $J_F = 253.1$  Hz);  $^{19}\text{F}$  NMR (373 MHz,  $\text{CDCl}_3$ )  $\delta$  0.8 (dt,  $J = 6.8, 20.5$  Hz), 9.8 (t,  $J = 20.5$  Hz), 26.6 (dd,  $J = 6.8, 20.5$  Hz); HRMS  $m/z$  ( $\text{M}^+$ ) calcd for  $\text{C}_{14}\text{H}_5\text{F}_5$ : 268.0311, found: 268.0310.



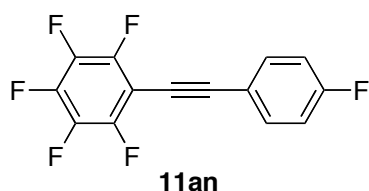
**1,2,3,4,5-Pentafluoro-6-[(4-methylphenyl)ethynyl]benzene (11ab):** m.p. 101-103 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.40 (s, 3H), 7.19 (d,  $J = 8.3$  Hz, 2H), 7.47 (d,  $J = 8.3$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  21.7, 72.6-72.7 (m), 100.5-100.9 (m), 102.0-102.1 (m), 118.6, 129.4, 131.9, 137.8 (dm,  $J_F = 251.1$  Hz), 141.4 (dm,  $J_F = 255.9$  Hz), 147.2 (dm,  $J_F = 253.1$  Hz), 160.8;  $^{19}\text{F}$  NMR (373 MHz,  $\text{CDCl}_3$ )  $\delta$  0.4 (dt,  $J = 6.8, 20.5$  Hz), 9.2 (t,  $J = 20.5$  Hz), 26.2 (dd,  $J = 6.8, 20.5$  Hz); HRMS  $m/z$  ( $\text{M}^+$ ) calcd for  $\text{C}_{15}\text{H}_7\text{F}_5$ : 282.0468, found: 282.0468.



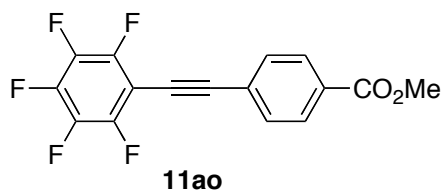
**1,2,3,4,5-Pentafluoro-6-[(4-methoxyphenyl)ethynyl]benzene (11ae):** m.p. 93-95 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.85 (s, 3H), 6.90 (d,  $J = 9.1$  Hz, 2H), 7.52 (d,  $J = 9.1$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  55.5, 72.0-72.1 (m), 100.6-101.0 (m), 102.0-102.1 (m), 113.7, 114.3, 133.7, 137.8 (dm,  $J_F = 250.1$  Hz), 141.2 (dm,  $J_F = 255.9$  Hz), 147.1 (dm,  $J_F = 252.1$  Hz), 160.8;  $^{19}\text{F}$  NMR (373 MHz,  $\text{CDCl}_3$ )  $\delta$  0.4 (dt,  $J = 6.9, 20.5$  Hz), 8.9 (t,  $J = 20.5$  Hz), 26.1 (dd,  $J = 6.9, 20.5$  Hz); HRMS  $m/z$  ( $\text{M}^+$ ) calcd for  $\text{C}_{15}\text{H}_7\text{F}_5\text{O}$ : 298.0417, found: 298.0419.



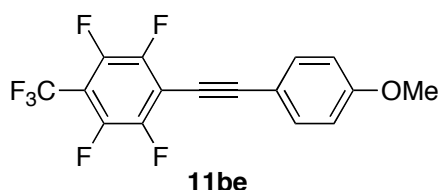
***N,N*-Dimethyl-4-[(pentafluorophenyl)ethynyl]aniline (11am):** m.p. 155-158 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.02 (s, 6H), 6.65 (d,  $J = 9.1$  Hz, 2H), 7.44 (d,  $J = 9.1$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  40.2, 71.4-71.5 (m), 101.2-101.6 (m), 103.7-103.8 (m), 108.2, 111.7, 133.3, 137.8 (dm,  $J_F = 250.1$  Hz), 140.7 (dm,  $J_F = 255.0$  Hz), 146.9 (dm,  $J_F = 252.1$  Hz), 151.0;  $^{19}\text{F}$  NMR (373 MHz,  $\text{CDCl}_3$ )  $\delta$  0.0 (dt,  $J = 6.8, 22.8$  Hz), 7.6 (t,  $J = 22.8$  Hz), 25.5 (dd,  $J = 6.8, 22.8$  Hz); HRMS  $m/z$  ( $\text{M}^+$ ) calcd for  $\text{C}_{16}\text{H}_{10}\text{F}_5\text{N}$ : 311.0733, found: 311.0731.



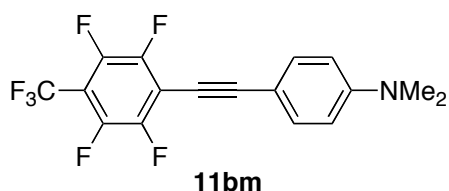
**1,2,3,4,5-Pentafluoro-6-[(4-fluorophenyl)ethynyl]benzene (11an):** m.p. 93-95 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.07-7.12 (m, 2H), 7.55-7.59 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  73.0-73.1 (m), 100.1-100.5 (m), 100.5-100.6 (m), 116.1 (d,  $J_F = 22.1$  Hz), 117.8 (d,  $J_F = 3.8$  Hz), 134.1 (d,  $J_F = 8.6$  Hz), 137.8 (dm,  $J_F = 252.0$  Hz), 141.6 (dm,  $J_F = 256.9$  Hz), 147.3 (dm,  $J_F = 253.1$  Hz), 163.5 (d,  $J_F = 251.1$  Hz);  $^{19}\text{F}$  NMR (373 MHz,  $\text{CDCl}_3$ )  $\delta$  0.8 (dt,  $J = 6.8, 20.5$  Hz), 10.0 (t,  $J = 20.5$  Hz), 26.5 (dd,  $J = 6.8, 20.5$  Hz), 54.2-54.3 (m); HRMS  $m/z$  ( $\text{M}^+$ ) calcd for  $\text{C}_{14}\text{H}_4\text{F}_6$ : 286.0217, found: 286.0220.



**Methyl 4-[(perfluorophenyl)ethynyl]benzoate (11ao):** m.p. 112-114 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.94 (s, 3H), 7.63 (d,  $J = 8.3$  Hz, 2H), 8.05 (d,  $J = 8.3$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  52.5, 75.7-75.8 (m), 99.8-100.1 (m), 100.5-100.6 (m), 126.1, 129.8, 130.9, 132.0, 137.8 (dm,  $J_F = 252.1$  Hz), 141.9 (dm,  $J_F = 257.9$  Hz), 147.3 (dm,  $J_F = 254.0$  Hz), 166.4;  $^{19}\text{F}$  NMR (373 MHz,  $\text{CDCl}_3$ )  $\delta$  1.3 (dt,  $J = 6.8, 20.5$  Hz), 11.1 (t,  $J = 20.5$  Hz), 27.2 (dd,  $J = 6.8, 20.5$  Hz); HRMS  $m/z$  ( $\text{M}^+$ ) calcd for  $\text{C}_{16}\text{H}_7\text{F}_5\text{O}_2$ : 326.0366, found: 326.0360.

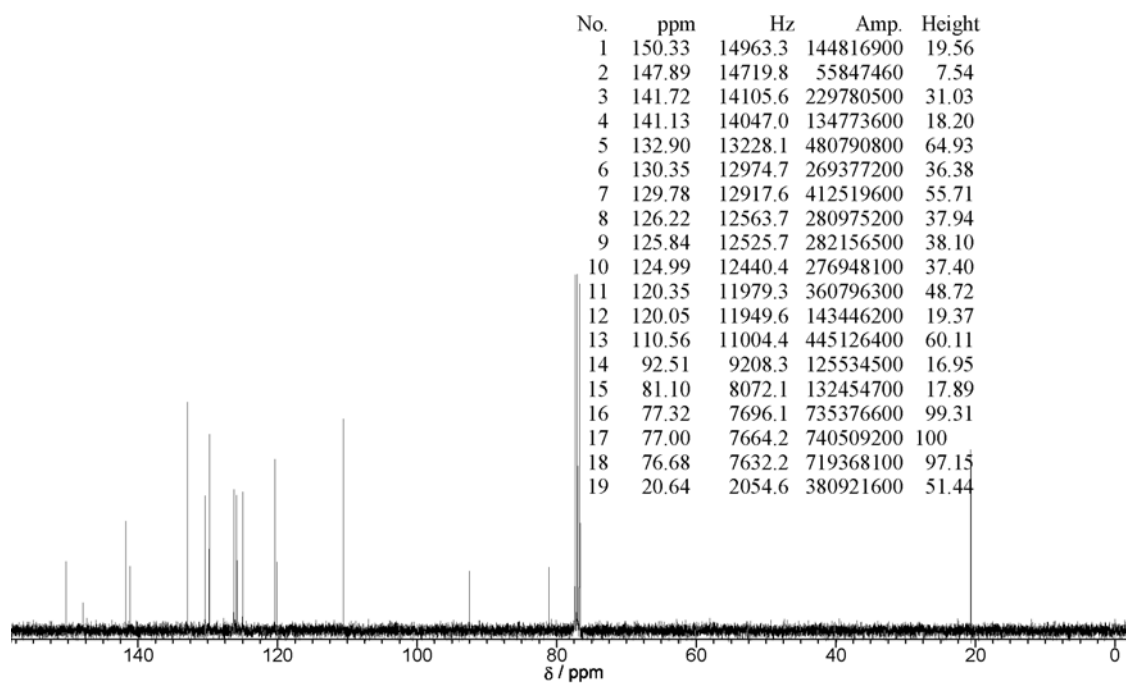
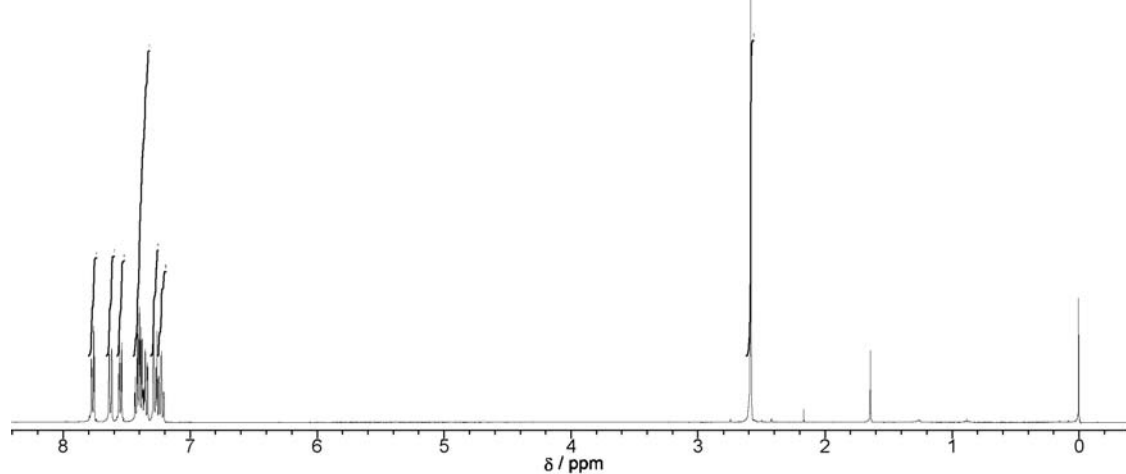
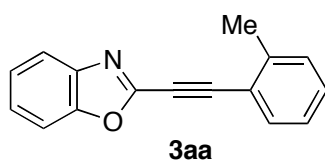


**1,2,4,5-Tetrafluoro-3-[(4-methoxyphenyl)ethynyl]-6-(trifluoromethyl)benzene (11be):** m.p. 79-81 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.86 (s, 3H), 6.92 (d,  $J = 9.1$  Hz, 2H), 7.55 (d,  $J = 9.1$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  55.6, 72.6-72.7 (m), 105.6-105.7 (m), 108.3-109.3 (m), 109.4-109.8 (m), 113.1, 114.4, 121.0 (qm,  $J_F = 273.2$  Hz), 134.0, 144.2 (dm,  $J_F = 256.9$  Hz), 146.8 (dm,  $J_F = 256.8$  Hz), 161.3;  $^{19}\text{F}$  NMR (373 MHz,  $\text{CDCl}_3$ )  $\delta$  21.1-21.4 (m), 27.2-27.4 (m), 106.4 (t,  $J = 21.7$  Hz); HRMS  $m/z$  ( $\text{M}^+$ ) calcd for  $\text{C}_{16}\text{H}_7\text{F}_7\text{O}$ : 348.0385, found: 348.0385.

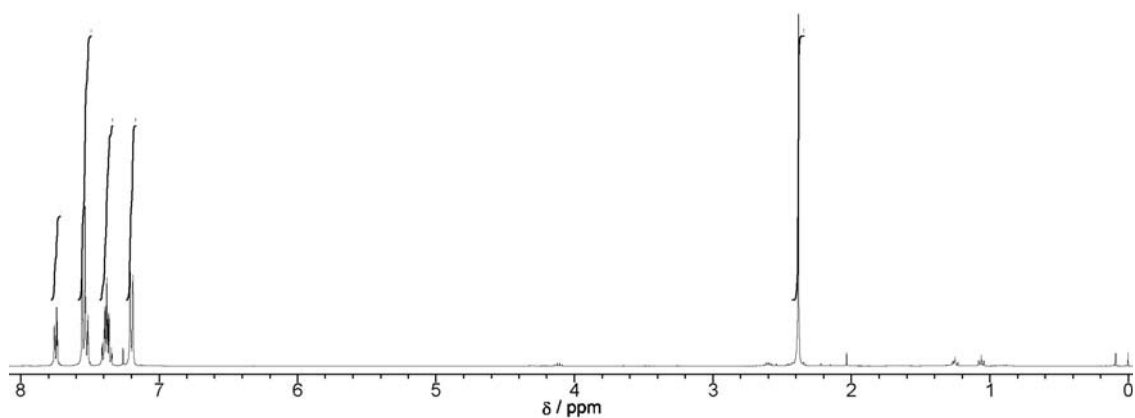
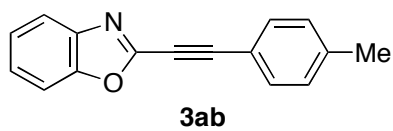


***N,N*-Dimethyl-4-[(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)ethynyl]aniline (11bm):** m.p. 143-145 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  3.03 (s, 6H), 6.66 (d,  $J = 9.1$  Hz, 2H), 7.46 (d,  $J = 9.1$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  40.1, 72.4-72.5 (m), 107.1-108.4 (m), 107.3, 107.7-107.8 (m), 110.1-110.5 (m), 111.7, 121.1 (qm,  $J_F = 275.1$  Hz), 133.7, 144.2 (dm,  $J_F = 258.8$  Hz), 146.6 (dm,  $J_F = 251.1$  Hz), 151.4;  $^{19}\text{F}$  NMR (373 MHz,  $\text{CDCl}_3$ )  $\delta$  20.8-21.1 (m), 26.7-26.8 (m), 106.8 (t,  $J = 22.8$  Hz); HRMS  $m/z$  ( $\text{M}^+$ ) calcd for  $\text{C}_{17}\text{H}_{10}\text{F}_7\text{N}$ : 361.0701, found: 361.0699.

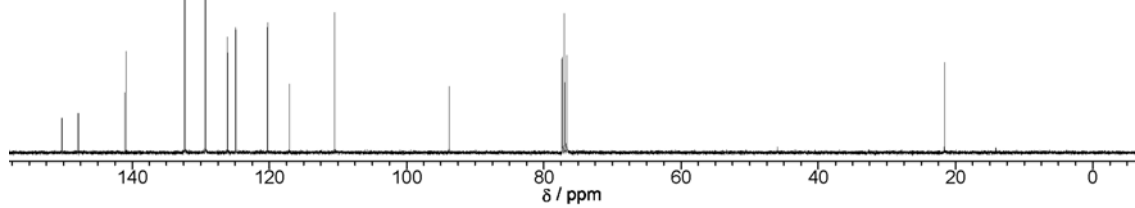
[<sup>1</sup>H and <sup>13</sup>C NMR Spectra of **3aa**]



[<sup>1</sup>H and <sup>13</sup>C NMR Spectra of **3ab**]

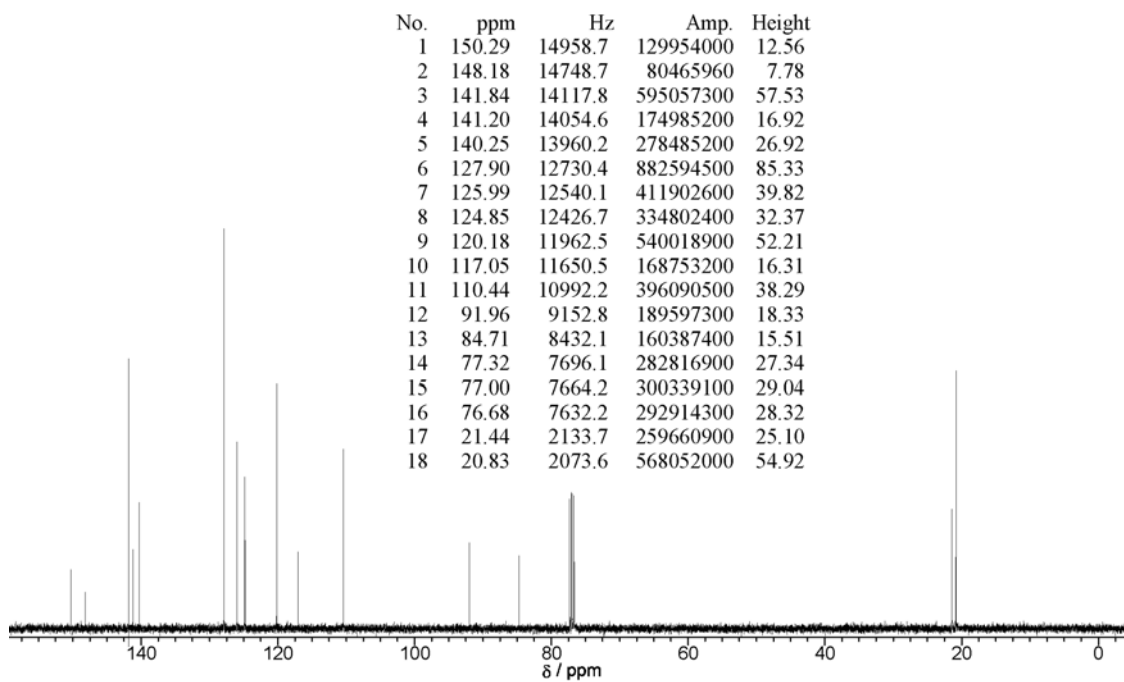
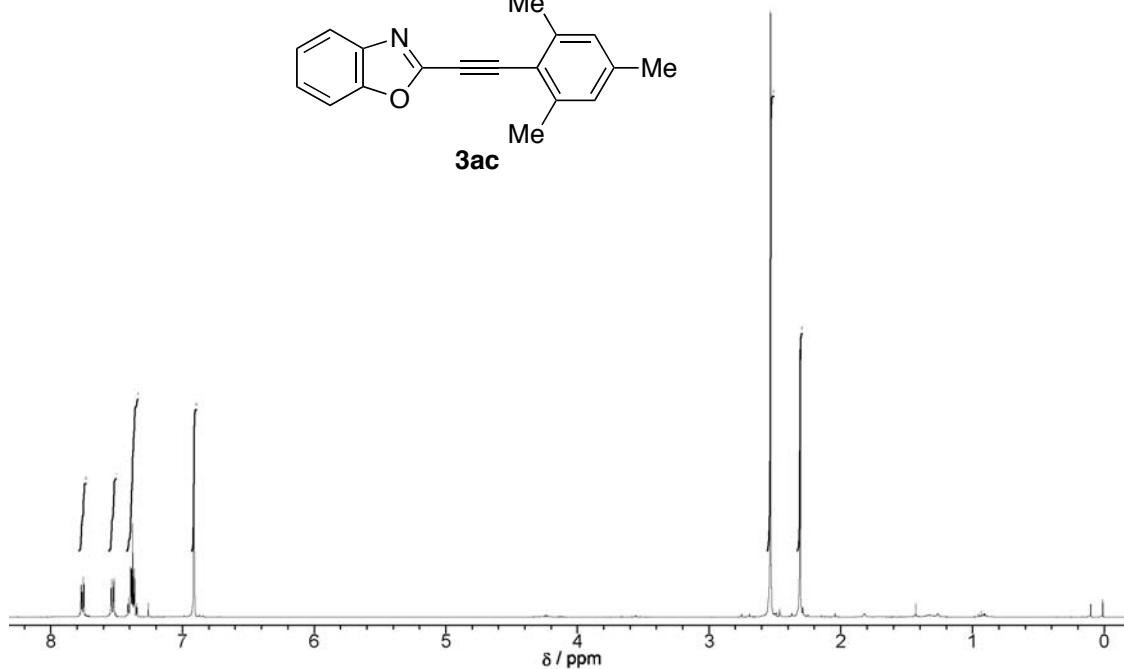
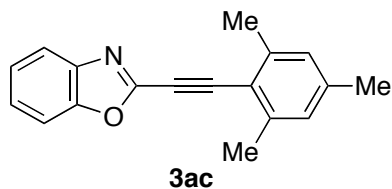


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1	150.25	14954.9	341416800	9.80
2	147.86	14717.5	388818000	11.16
3	141.07	14040.9	592722400	17.02
4	140.87	14021.1	1002897000	28.79
5	132.33	13171.8	2646459000	75.97
6	129.34	12873.5	2849392000	81.80
7	126.11	12552.3	1140303000	32.74
8	124.89	12431.3	1239372000	35.58
9	120.26	11970.1	1286617000	36.94
10	117.08	11653.5	680035500	19.52
11	110.47	10996.0	1386591000	39.81
12	93.81	9337.7	651703500	18.71
13	77.31	7695.4	929706600	26.69
14	77.00	7664.2	1374322000	39.45
15	76.67	7631.5	944326000	27.11
16	21.62	2152.0	860939100	24.72

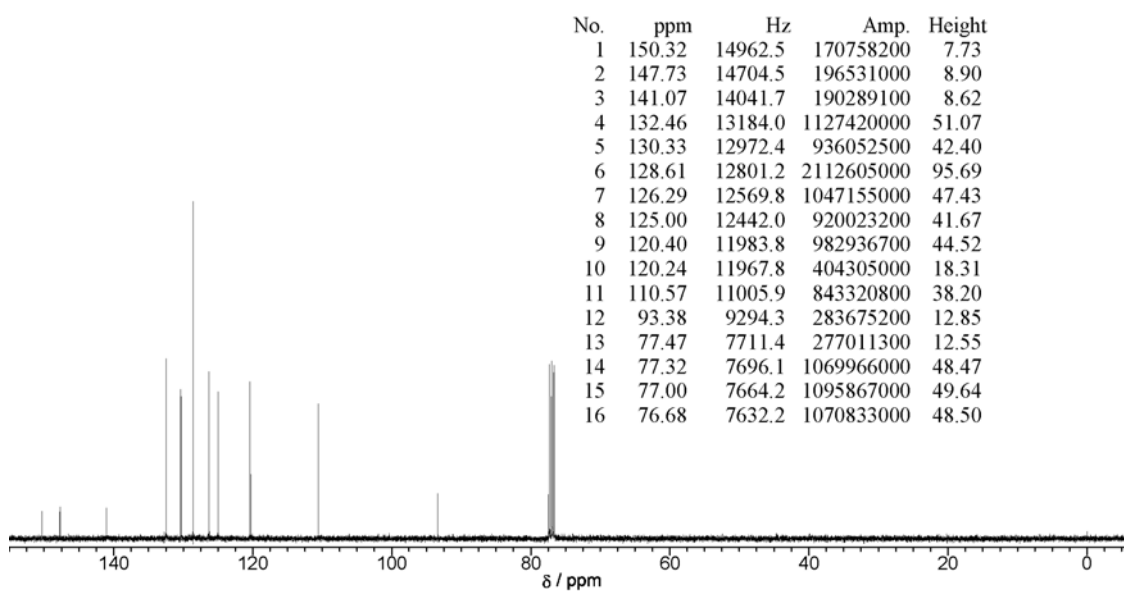
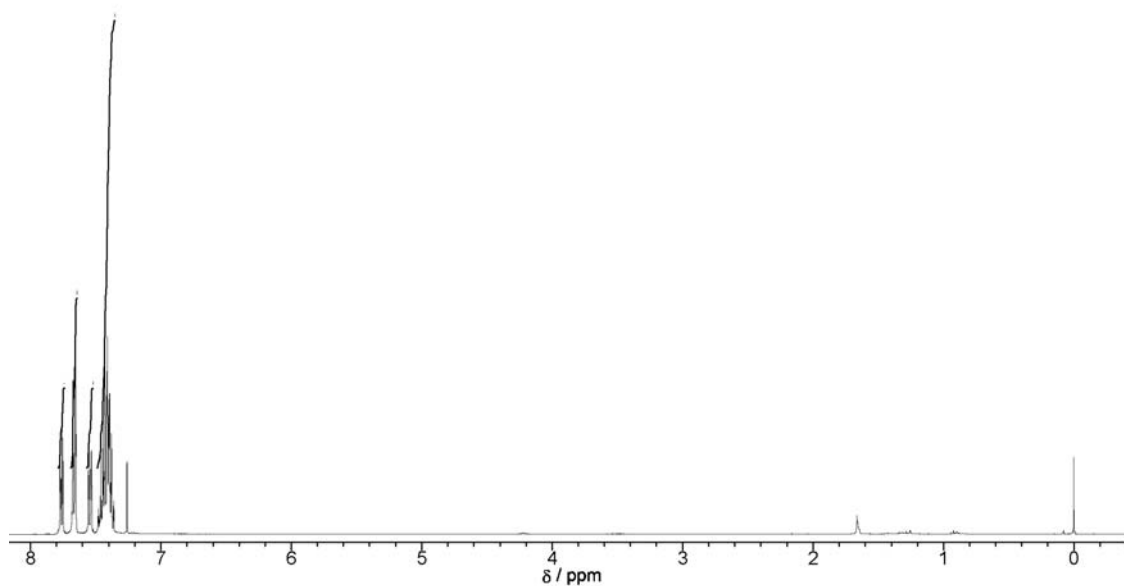
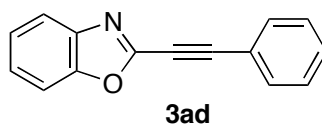




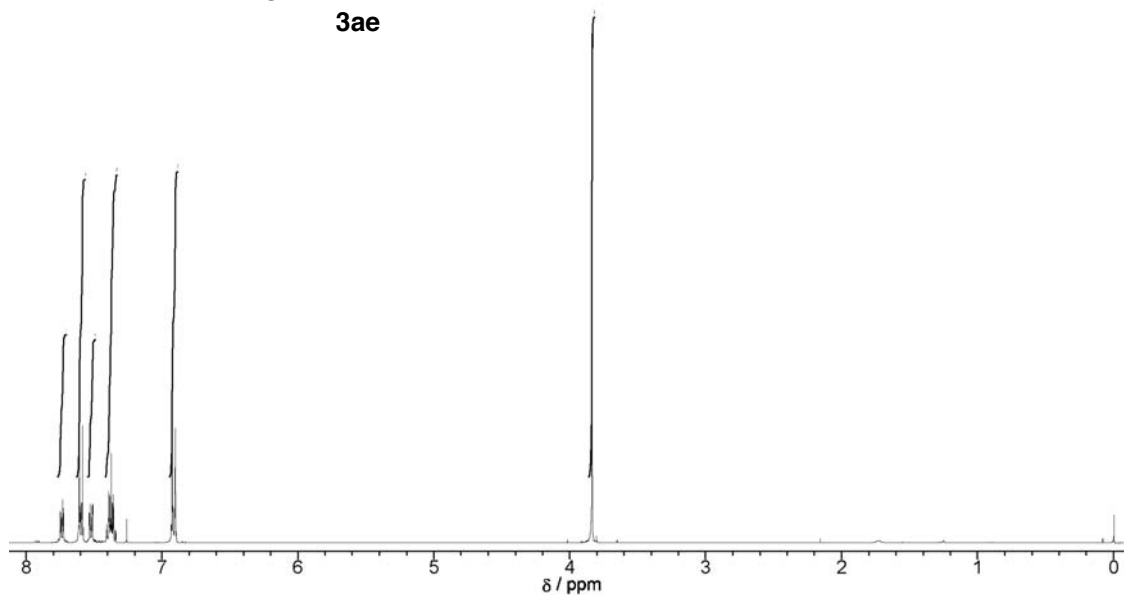
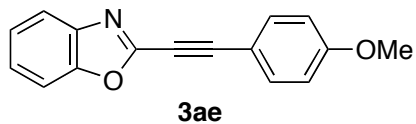
[<sup>1</sup>H and <sup>13</sup>C NMR Spectra of **3ac**]



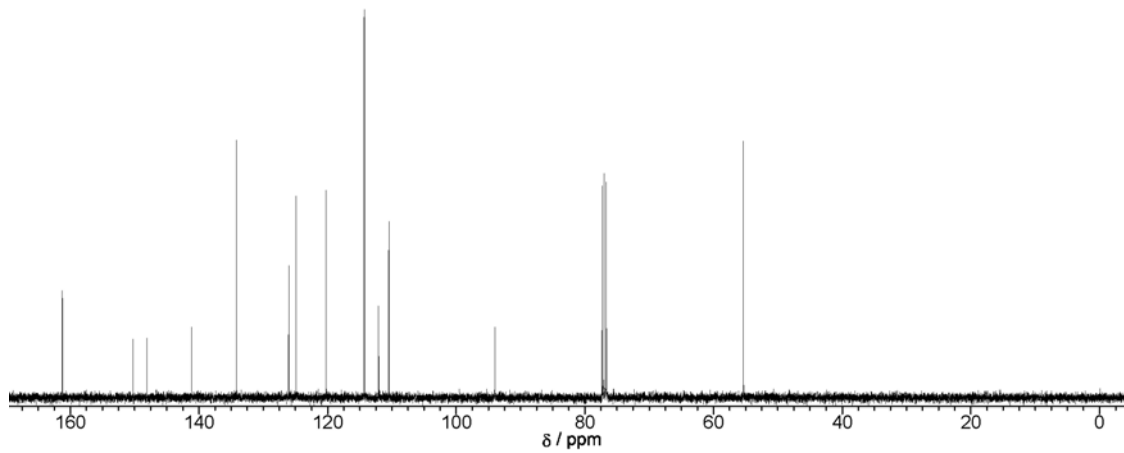
[<sup>1</sup>H and <sup>13</sup>C NMR Spectra of **3ad**]



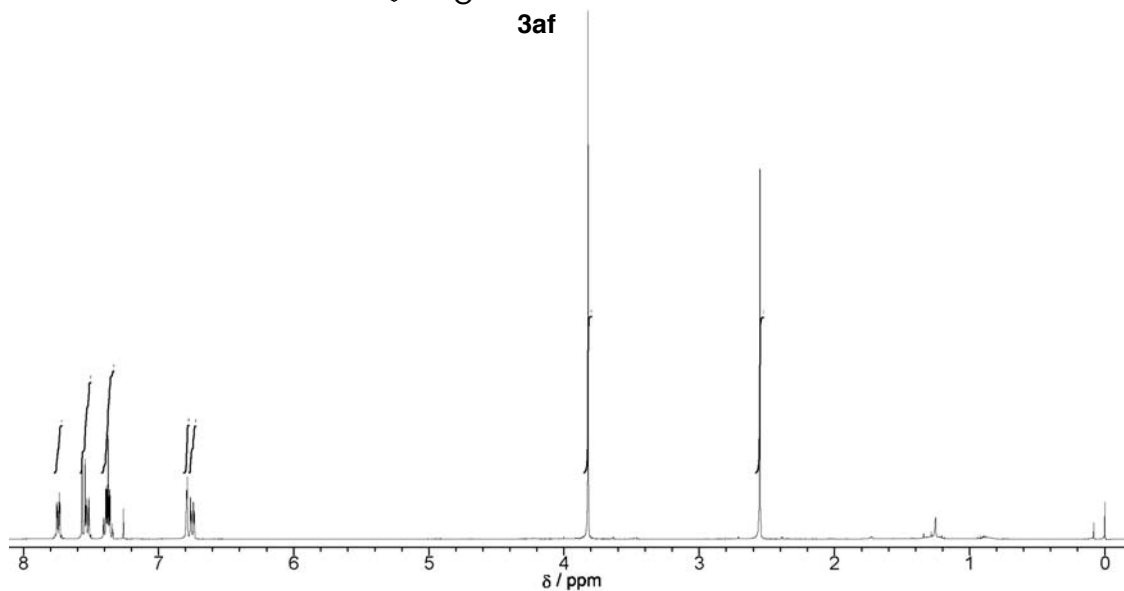
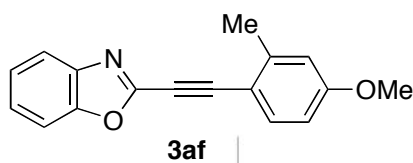
[<sup>1</sup>H and <sup>13</sup>C NMR Spectra of **3ae**]



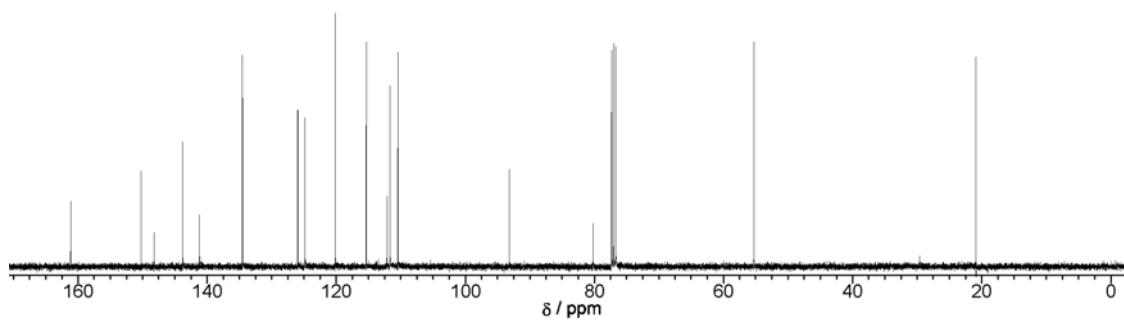
No.	ppm	Hz	Amp.	Height	No.	ppm	Hz	Amp.	Height
1	161.22	16047.0	274387100	22.75	10	112.07	11155.1	234918600	19.48
2	150.25	14954.9	149779200	12.42	11	110.47	10995.2	452846300	37.54
3	148.05	14736.5	153311500	12.71	12	93.97	9353.7	181034500	15.01
4	141.13	14047.0	181202800	15.02	13	77.32	7696.1	544949700	45.18
5	134.17	13354.5	628910500	52.14	14	77.00	7664.2	576439000	47.79
6	126.03	12544.7	319676900	26.50	15	76.68	7632.2	554425400	45.97
7	124.88	12429.8	518968300	43.03	16	76.64	7628.4	205401900	17.03
8	120.21	11965.6	533724500	44.25	17	55.35	5508.9	659003000	54.64
9	114.31	11378.0	998060200	82.75					



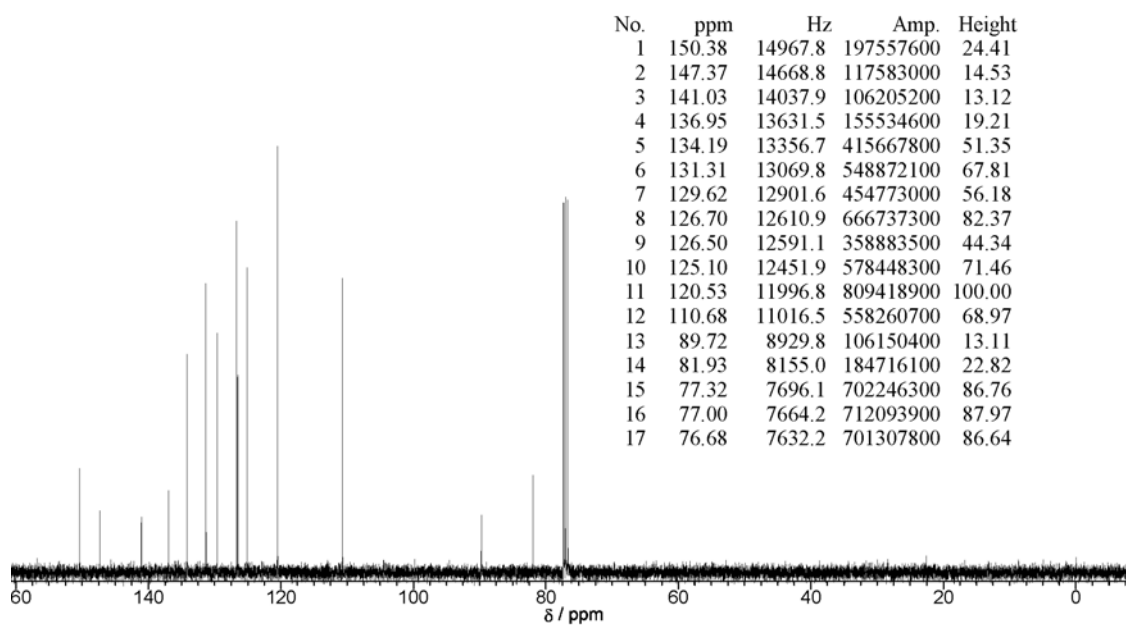
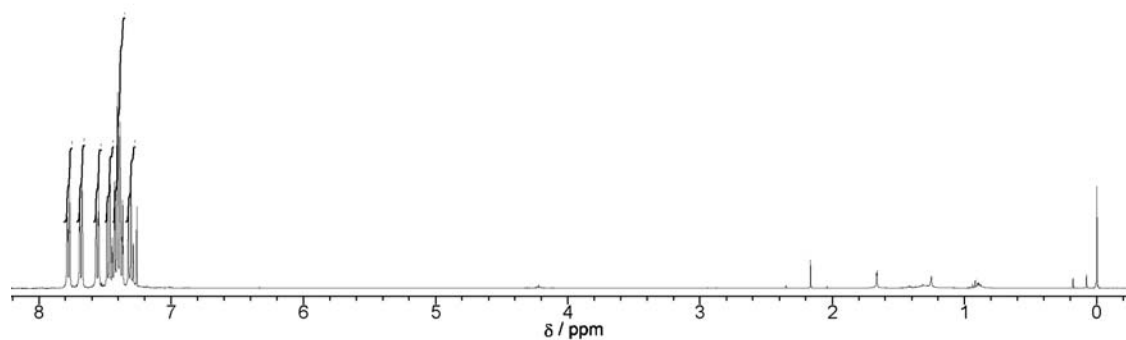
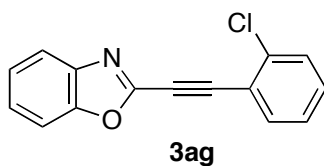
[<sup>1</sup>H and <sup>13</sup>C NMR Spectra of **3af**]



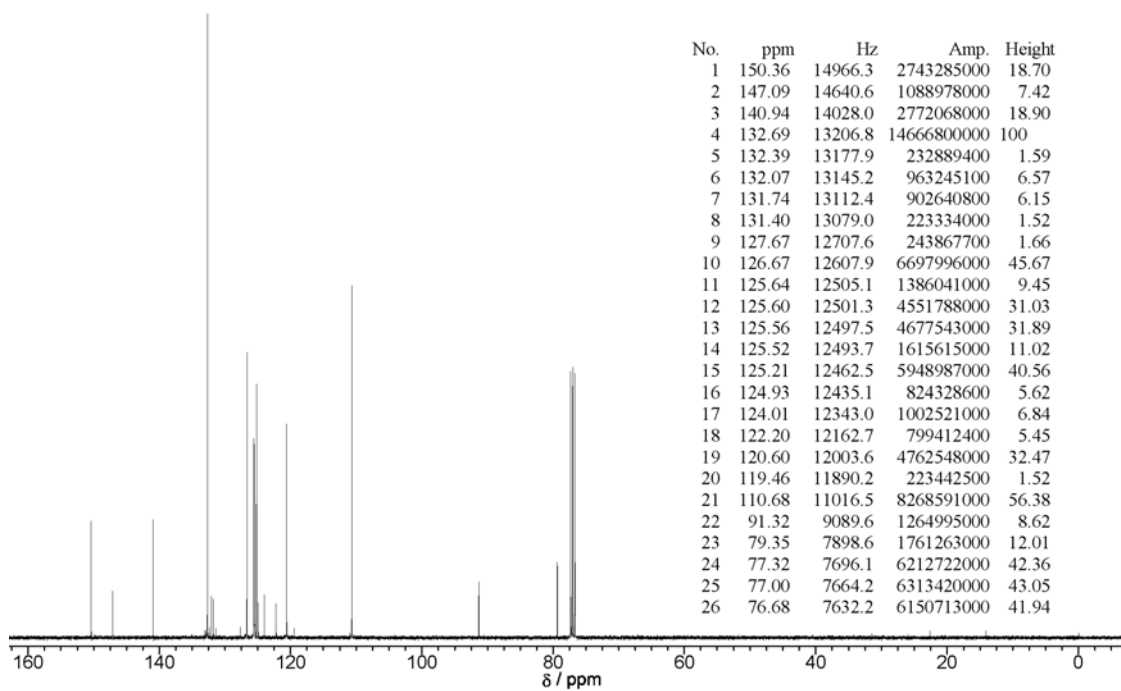
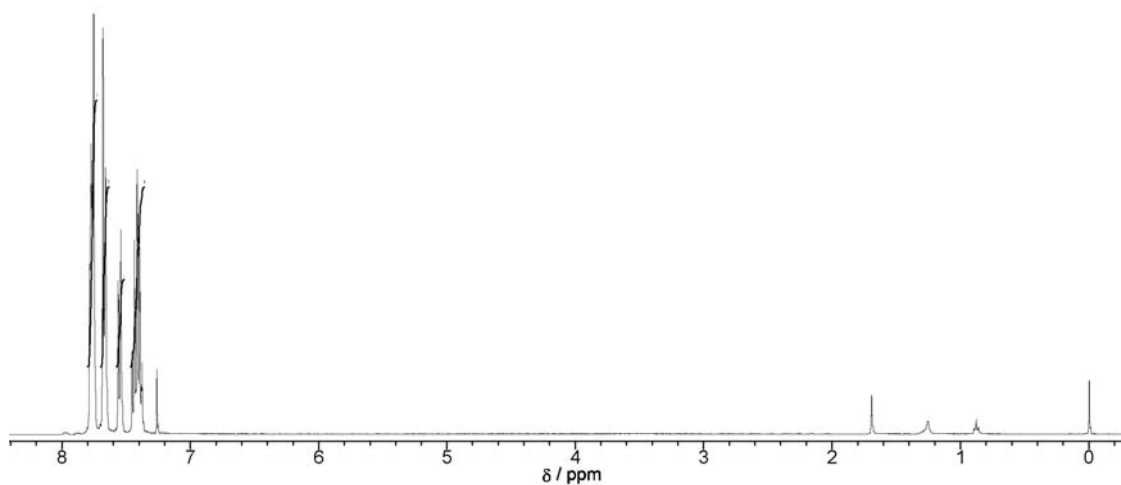
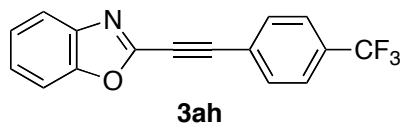
No.	ppm	Hz	Amp.	Height	No.	ppm	Hz	Amp.	Height
1	161.16	16040.9	358661400	24.30	11	112.13	11160.4	392471400	26.59
2	150.26	14956.4	530823500	35.96	12	111.67	11114.7	1008361000	68.31
3	148.21	14752.5	189934600	12.87	13	110.44	10993.0	1196248000	81.04
4	143.78	14311.1	696000100	47.15	14	93.16	9272.2	542532600	36.75
5	141.20	14053.8	289956600	19.64	15	80.19	7981.5	233058200	15.79
6	134.52	13389.5	1180539000	79.97	16	77.32	7696.1	1208357000	81.86
7	125.96	12537.9	868767000	58.85	17	77.00	7664.2	1243966000	84.27
8	124.85	12426.7	801464700	54.29	18	76.68	7632.2	1226558000	83.09
9	120.17	11961.0	1412470000	95.68	19	55.28	5502.1	1253291000	84.90
10	115.37	11483.1	1253034000	84.88	20	20.89	2079.7	1172241000	79.41



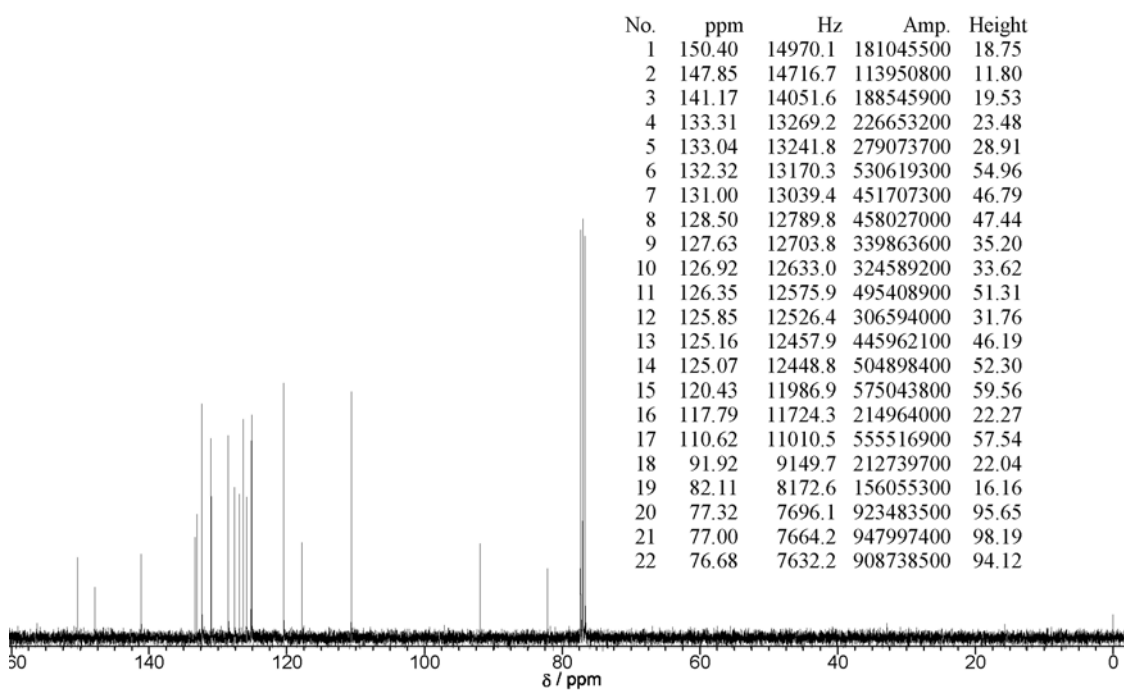
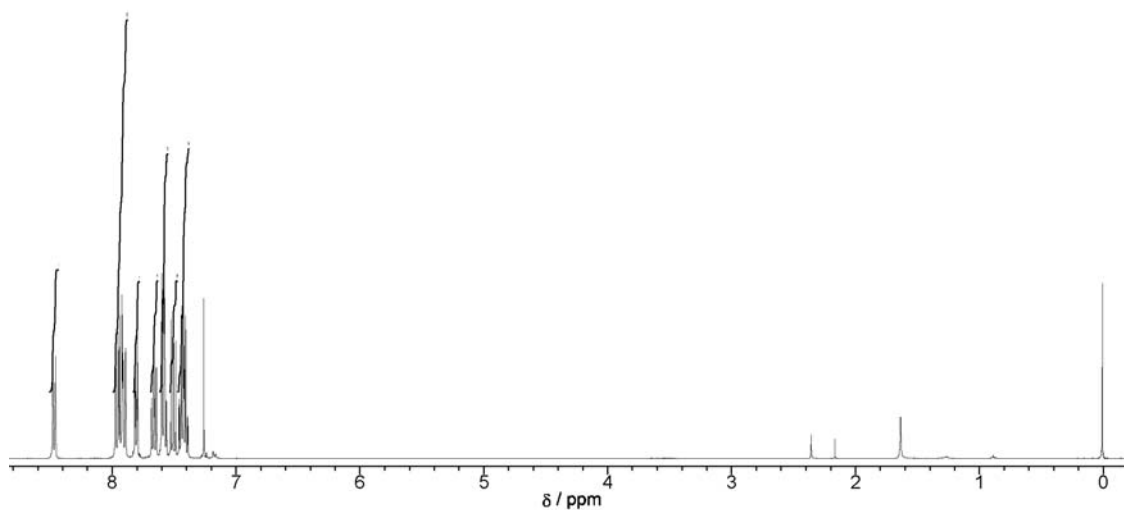
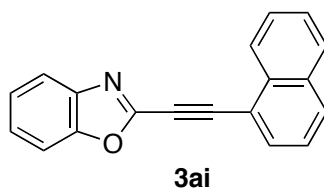
[<sup>1</sup>H and <sup>13</sup>C NMR Spectra of **3ag**]



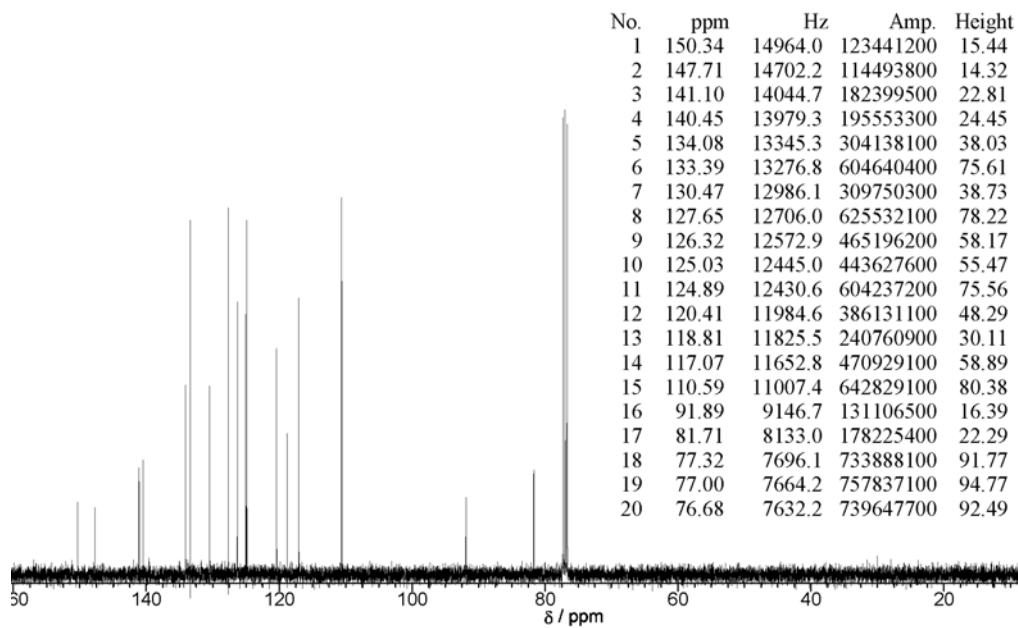
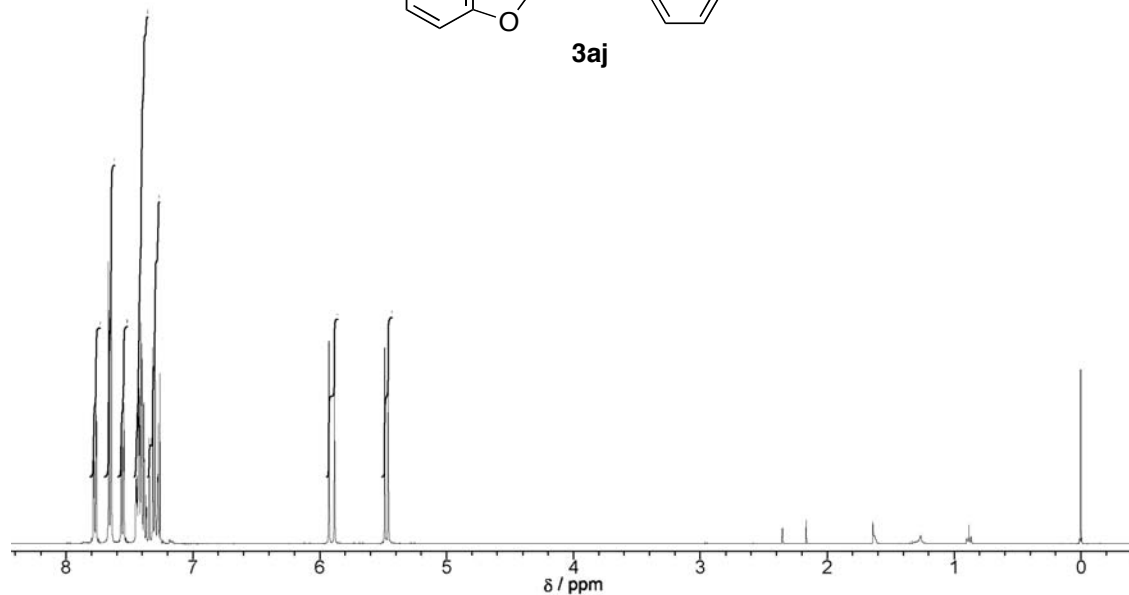
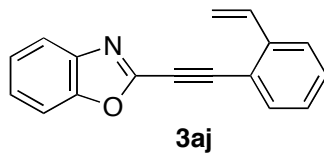
[<sup>1</sup>H and <sup>13</sup>C NMR Spectra of **3ah**]



[<sup>1</sup>H and <sup>13</sup>C NMR Spectra of **3ai**]

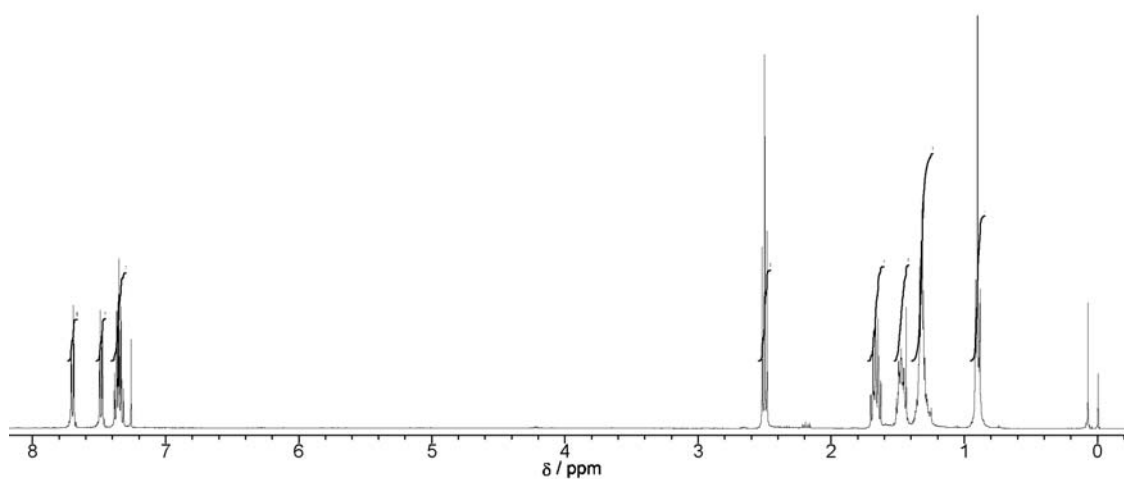
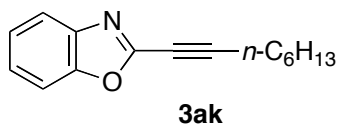


[<sup>1</sup>H and <sup>13</sup>C NMR Spectra of **3aj**]

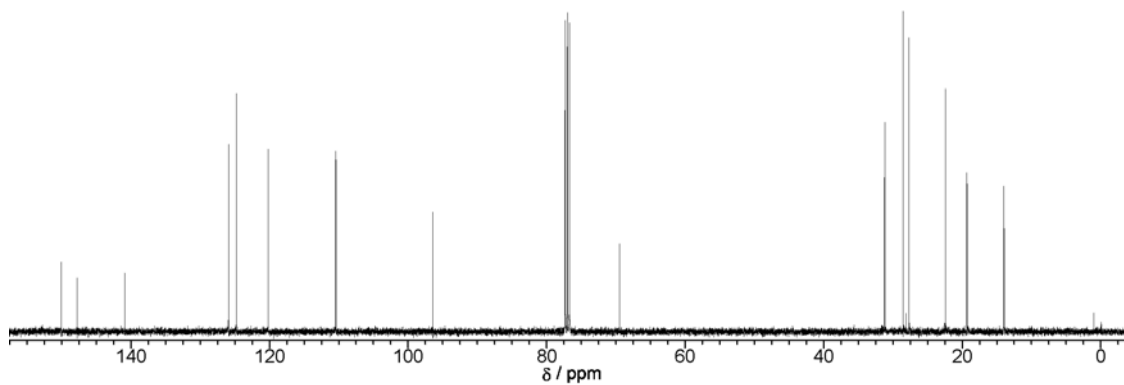




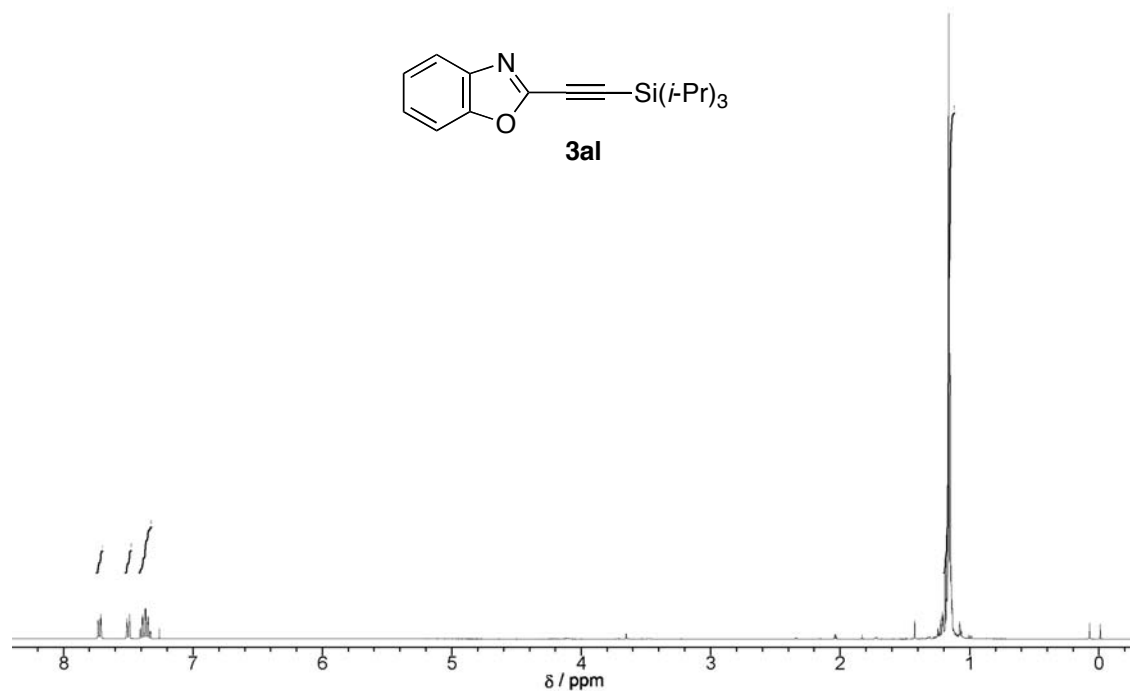
[<sup>1</sup>H and <sup>13</sup>C NMR Spectra of **3ak**]



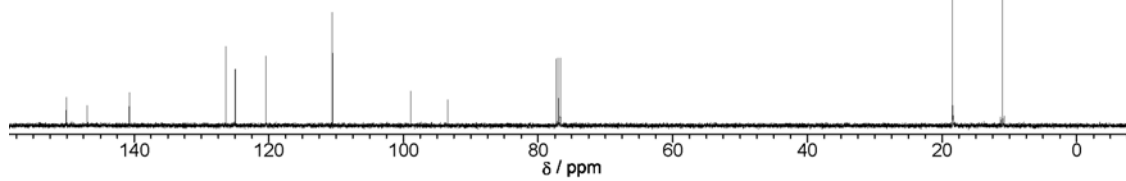
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2	147.78	14709.1	352488600	16.68	11	76.68	7632.2	2035829000	96.36
3	140.90	14024.2	385466500	18.24	12	69.44	6911.5	579797200	27.44
4	125.91	12532.5	1235339000	58.47	13	31.22	3107.1	1381091000	65.37
5	124.77	12419.1	1571213000	74.37	14	28.52	2838.4	2112478000	99.99
6	120.19	11963.3	1203691000	56.97	15	27.67	2754.0	1938683000	91.76
7	110.41	10989.9	1191945000	56.42	16	22.45	2234.2	1601797000	75.82
8	96.44	9599.5	787732900	37.28	17	19.31	1922.2	1042307000	49.33
9	77.32	7696.1	2049546000	97.01	18	13.99	1392.5	915253200	43.32



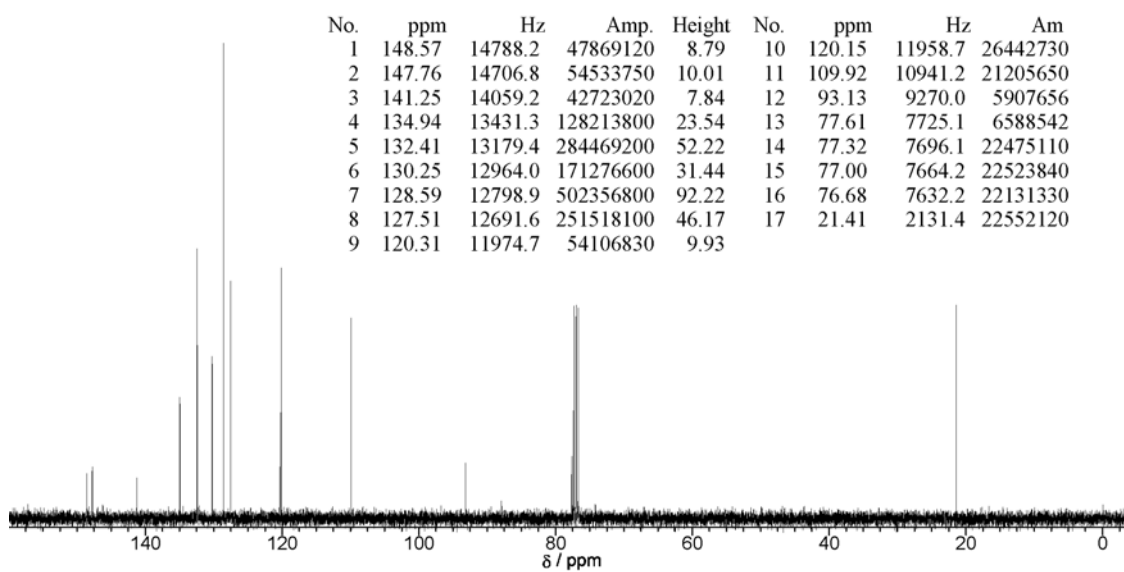
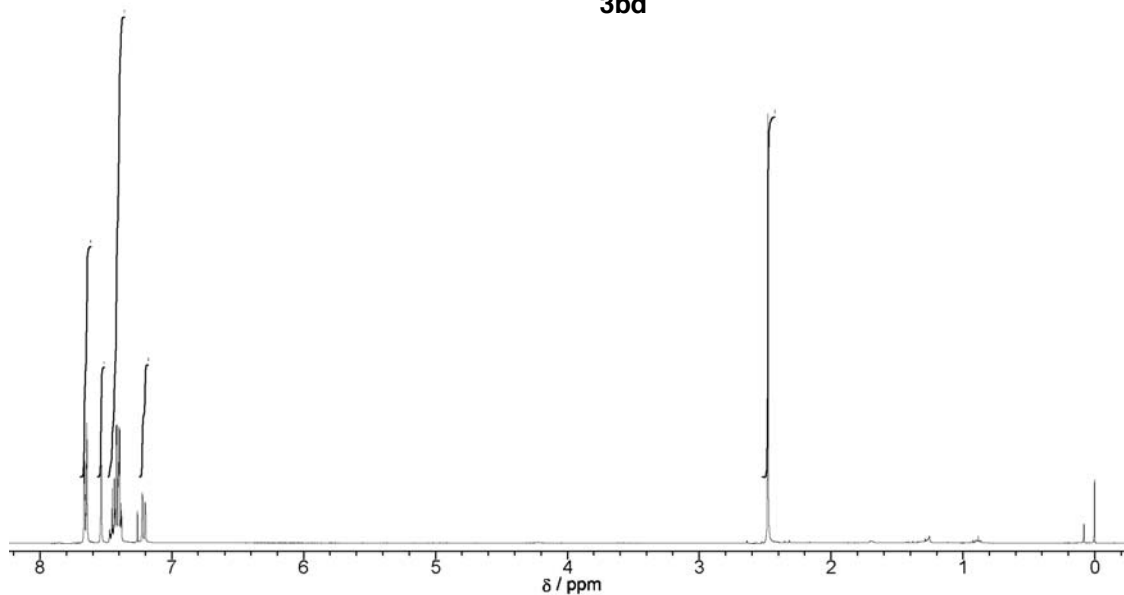
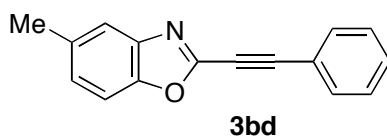
[<sup>1</sup>H and <sup>13</sup>C NMR Spectra of **3al**]



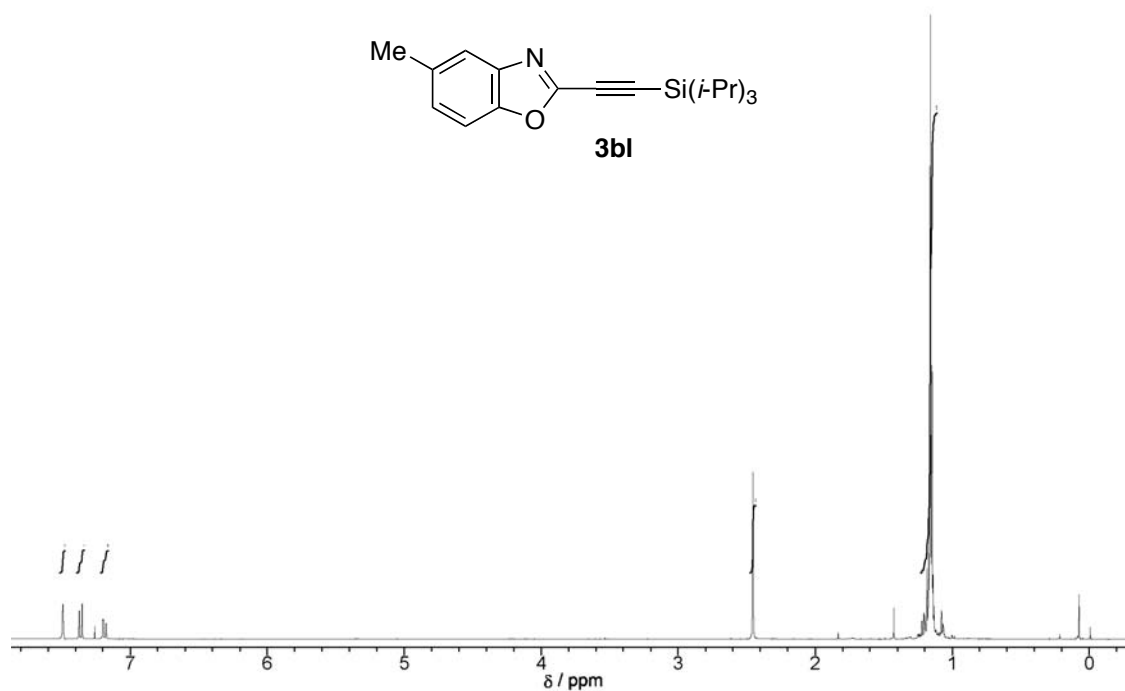
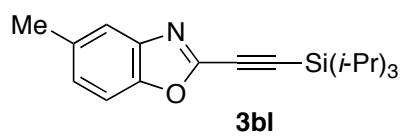
No.	ppm	Hz	Amp.	Height
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3	140.72	14006.7	127919400	5.30
4	126.38	12579.0	306320800	12.69
5	124.99	12441.2	211746000	8.77
6	120.43	11986.9	268880900	11.14
7	110.55	11003.6	437308800	18.12
8	98.90	9843.8	132726800	5.50
9	93.42	9298.1	100858500	4.18
10	77.32	7696.1	258513700	10.71
11	77.00	7664.2	262025400	10.85
12	76.68	7632.2	261459500	10.83
13	18.48	1839.2	1808975000	74.94
14	11.04	1098.7	817674400	33.87



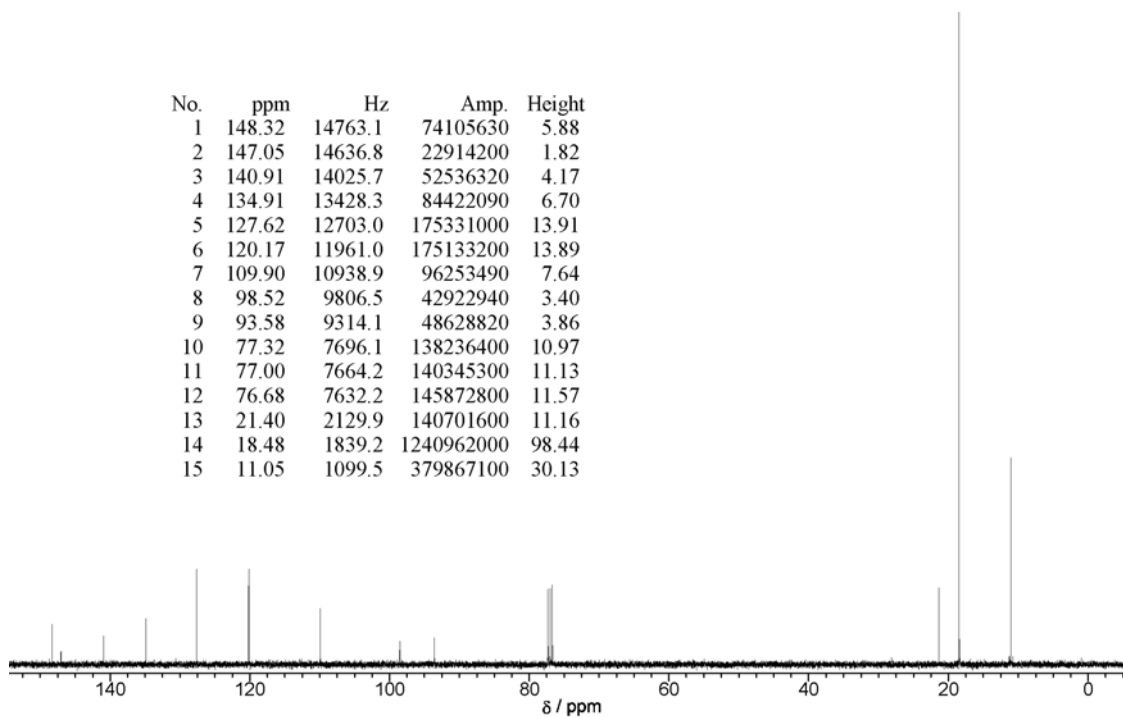
[<sup>1</sup>H and <sup>13</sup>C NMR Spectra of **3bd**]



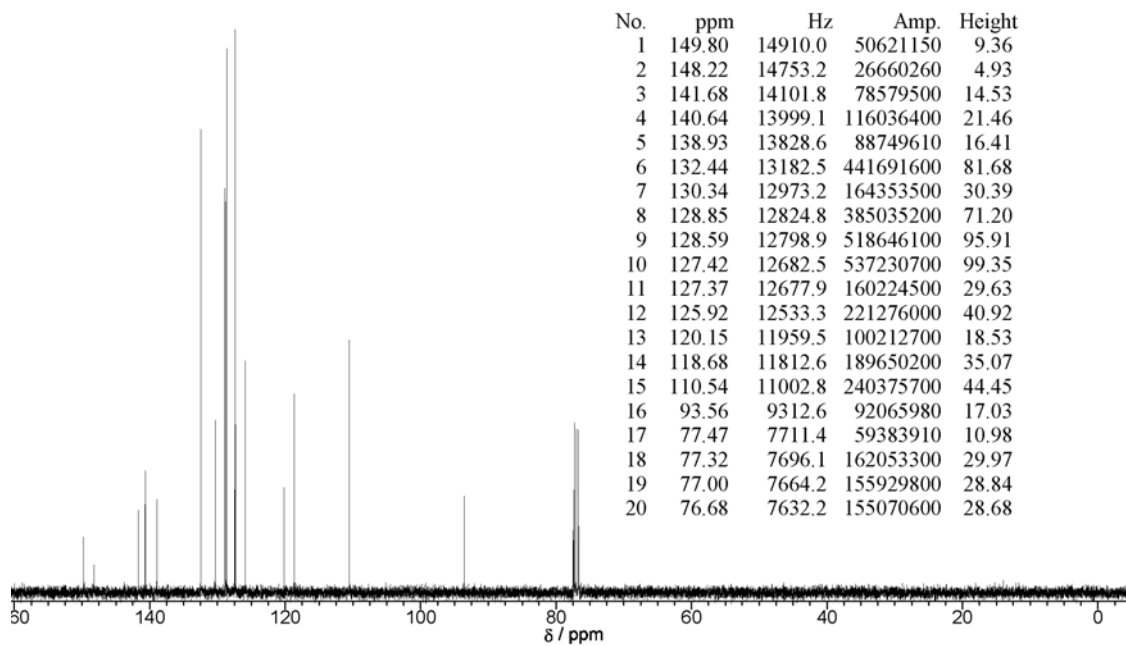
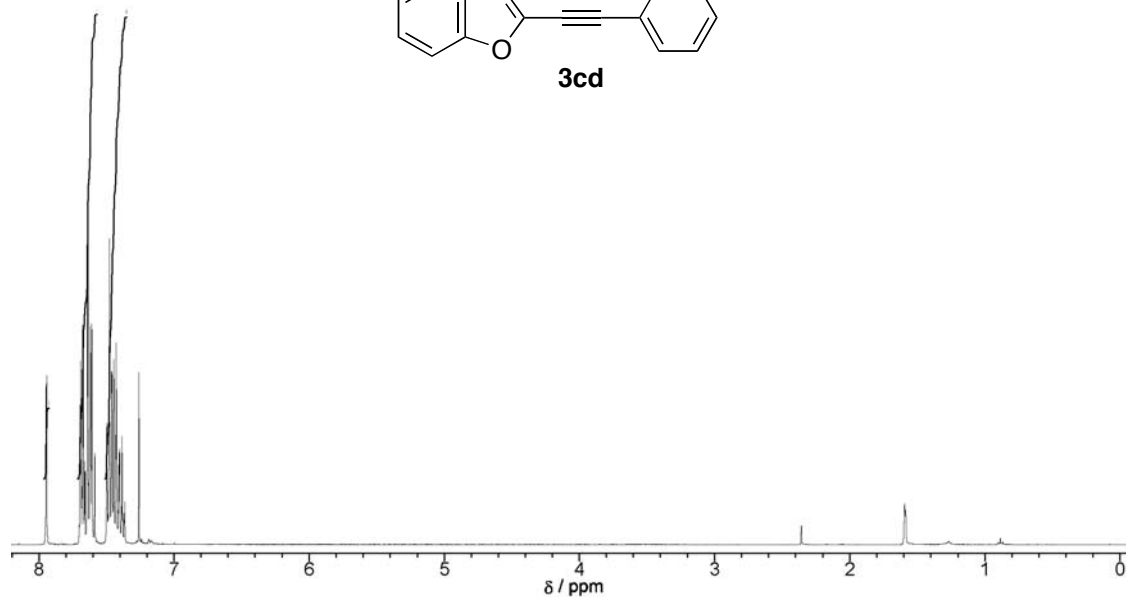
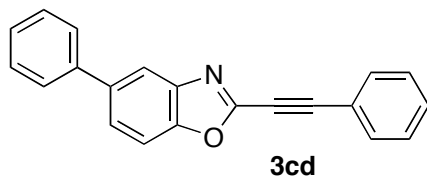
[<sup>1</sup>H and <sup>13</sup>C NMR Spectra of **3bl**]



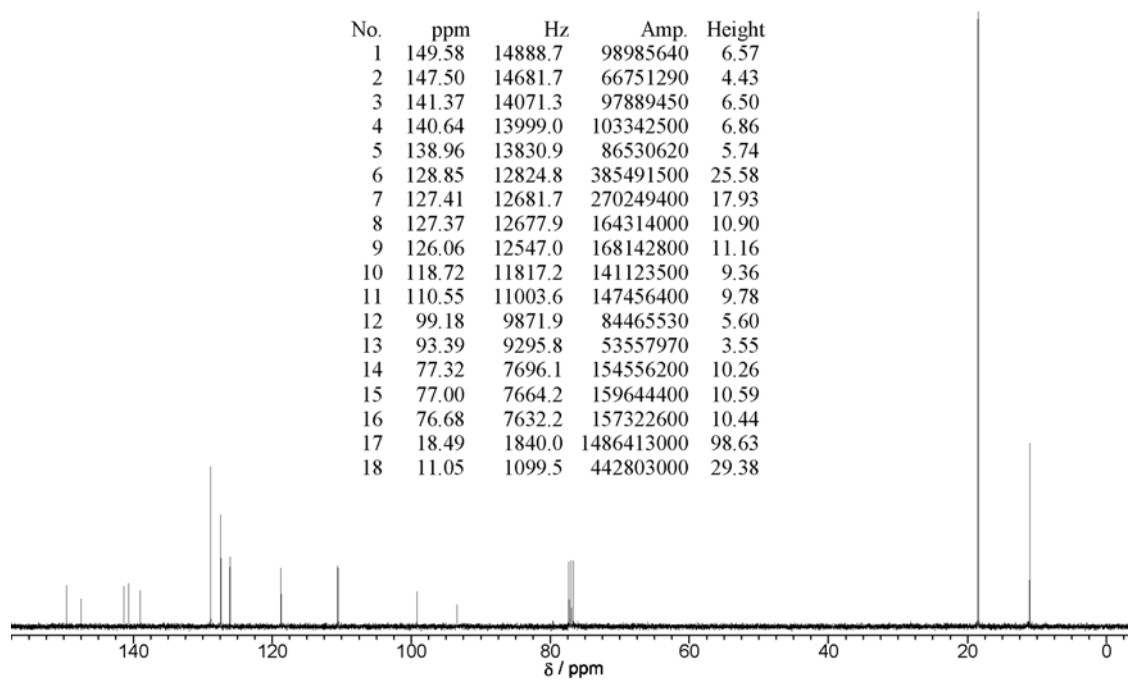
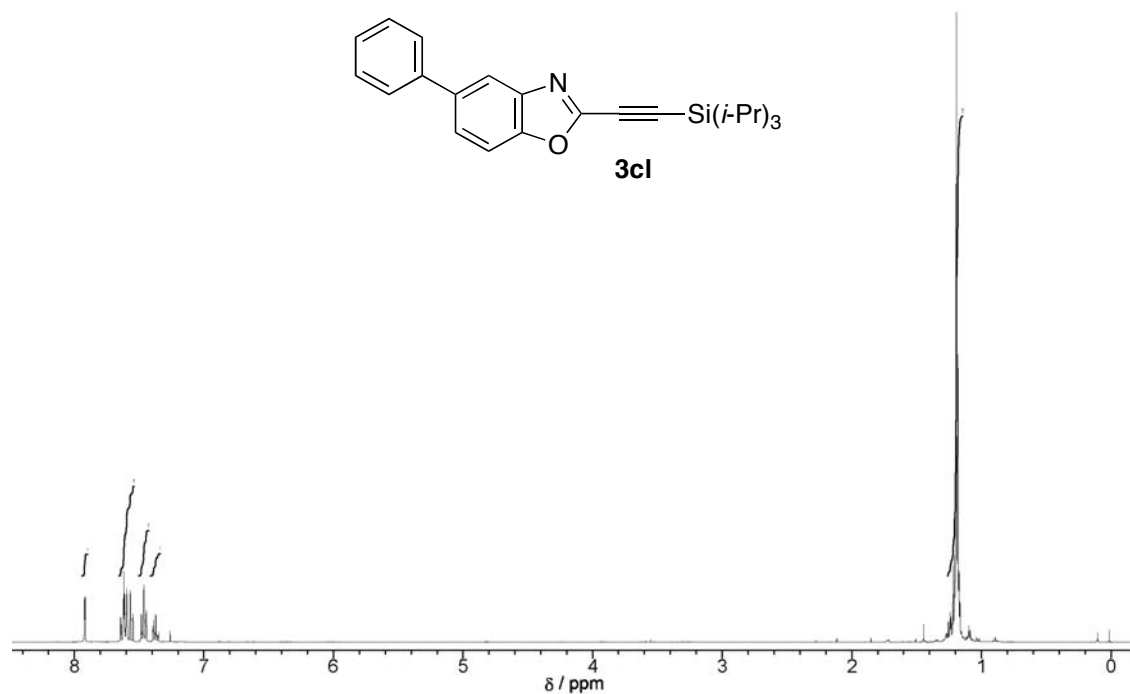
No.	ppm	Hz	Amp.	Height
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3	140.91	14025.7	52536320	4.17
4	134.91	13428.3	84422090	6.70
5	127.62	12703.0	175331000	13.91
6	120.17	11961.0	175133200	13.89
7	109.90	10938.9	96253490	7.64
8	98.52	9806.5	42922940	3.40
9	93.58	9314.1	48628820	3.86
10	77.32	7696.1	138236400	10.97
11	77.00	7664.2	140345300	11.13
12	76.68	7632.2	145872800	11.57
13	21.40	2129.9	140701600	11.16
14	18.48	1839.2	1240962000	98.44
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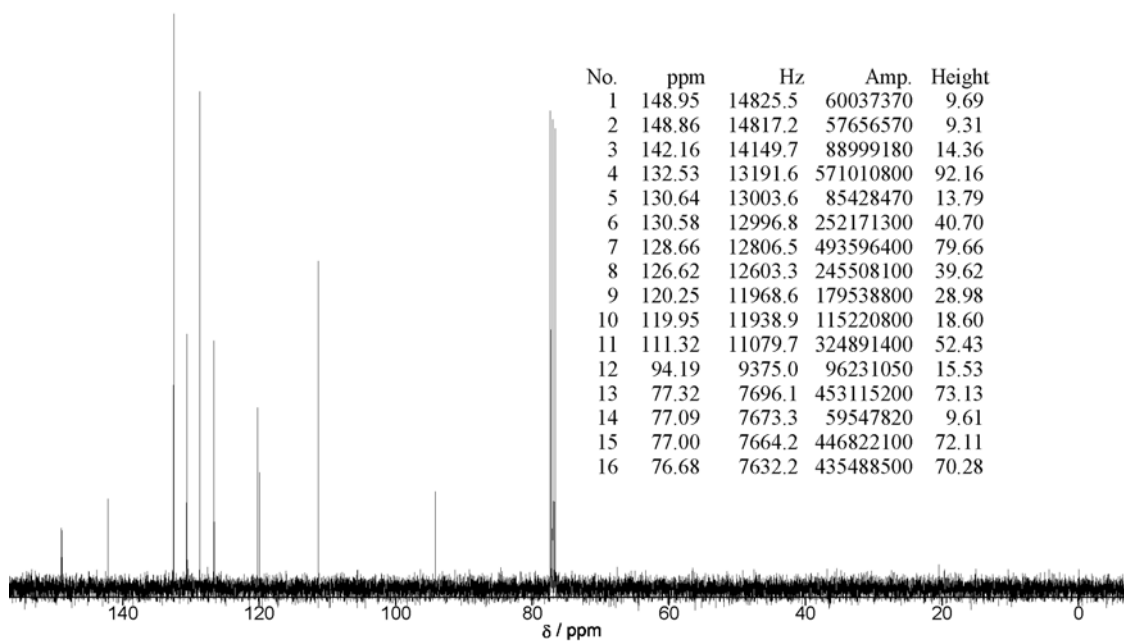
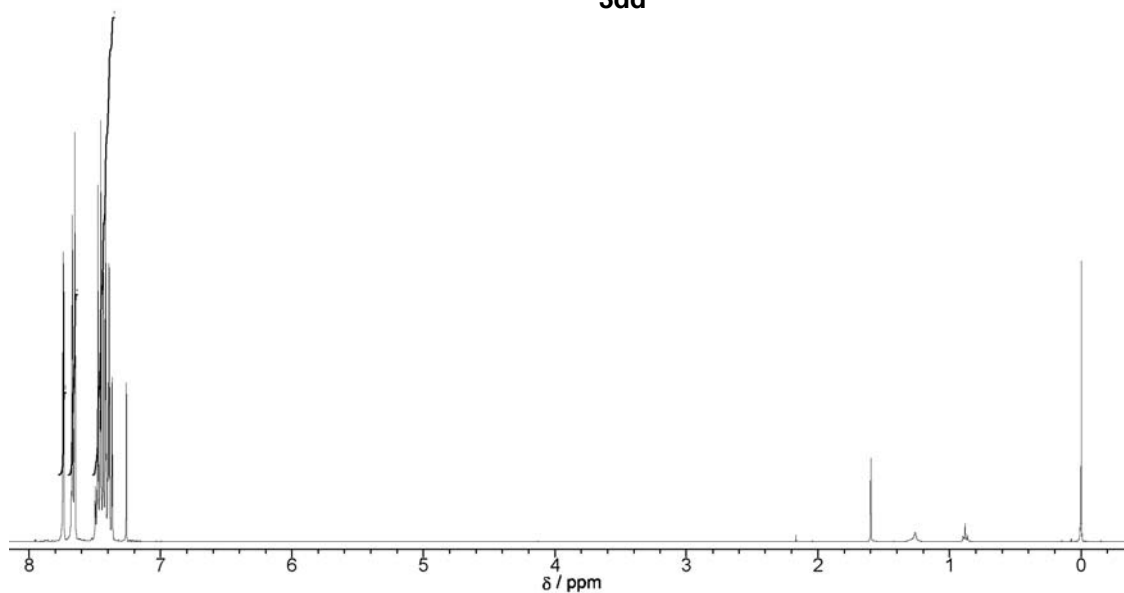
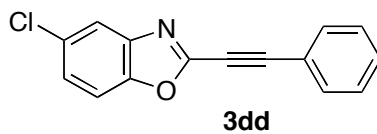
[<sup>1</sup>H and <sup>13</sup>C NMR Spectra of **3cd**]



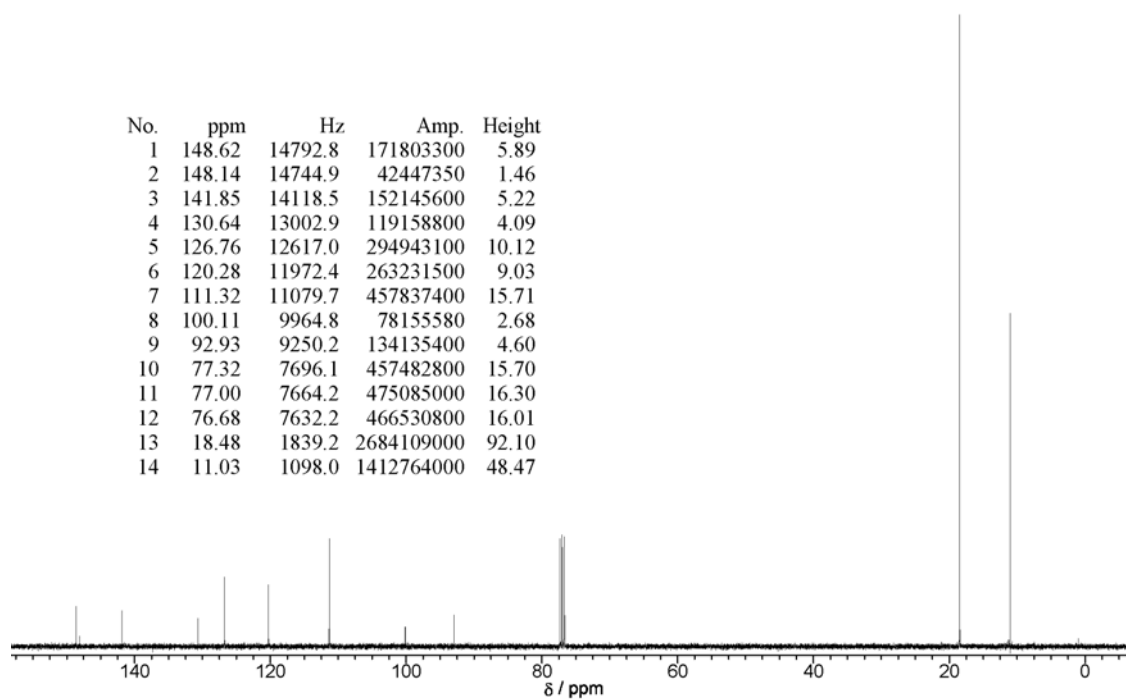
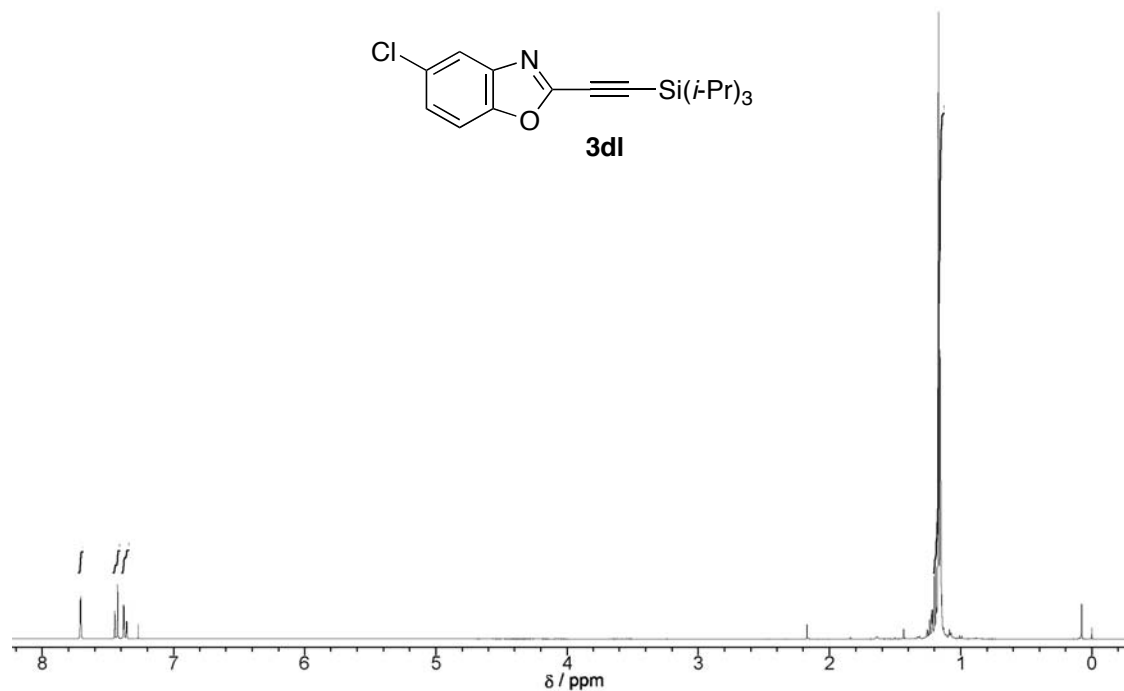
[<sup>1</sup>H and <sup>13</sup>C NMR Spectra of **3cl**]



[<sup>1</sup>H and <sup>13</sup>C NMR Spectra of **3dd**]

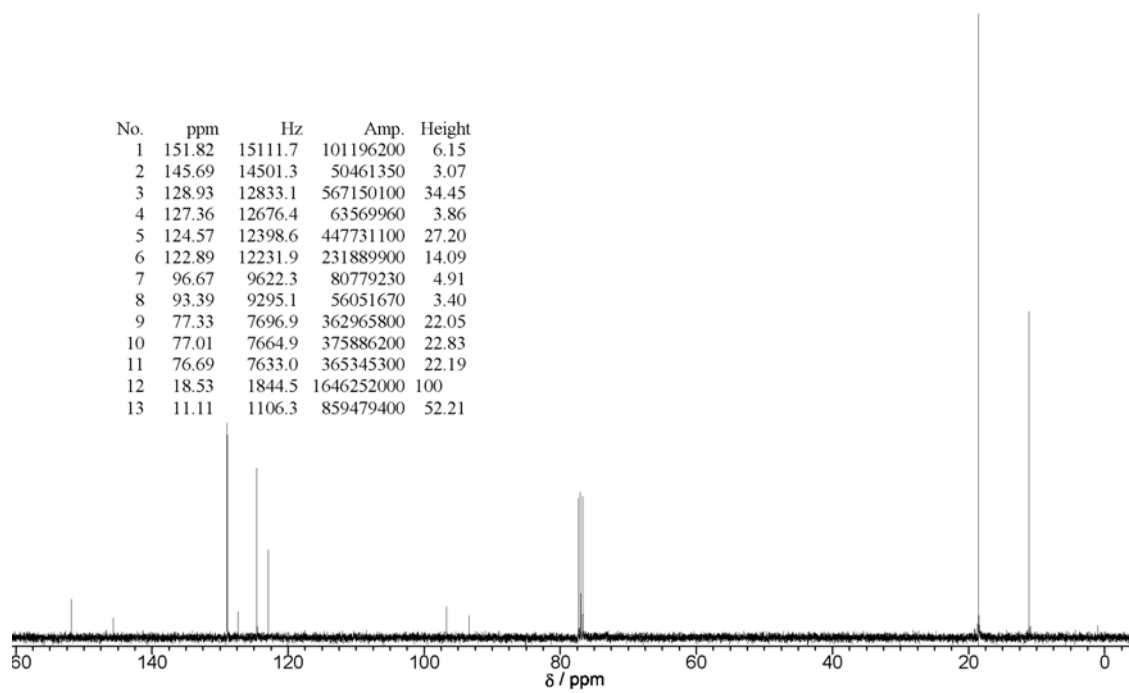
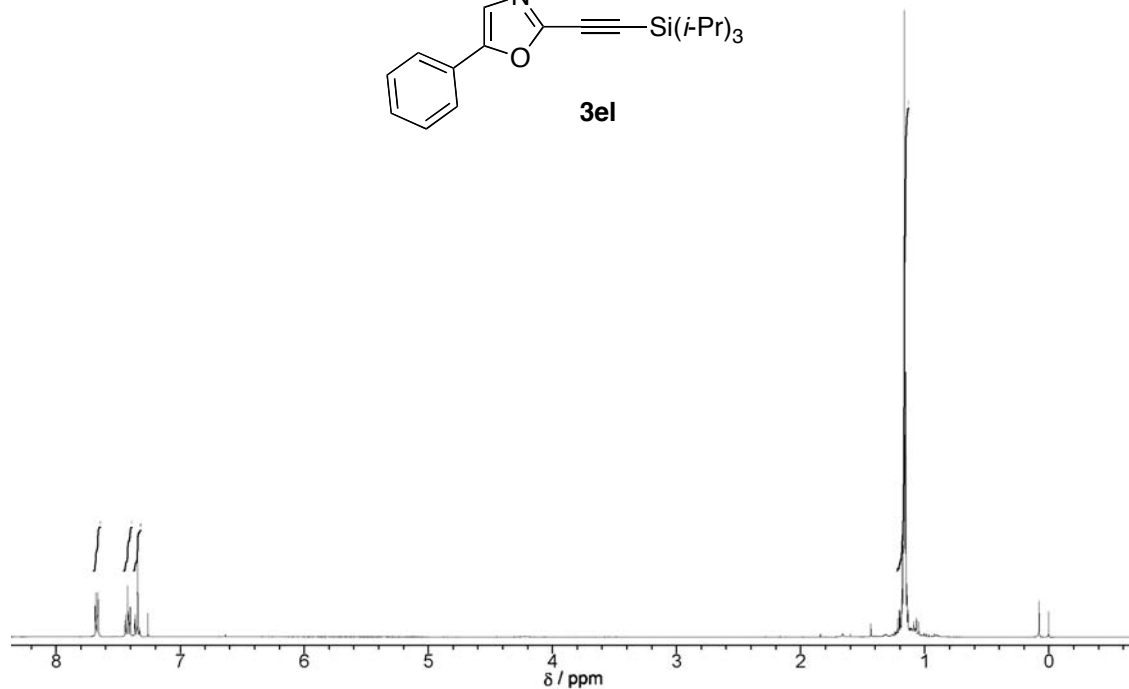
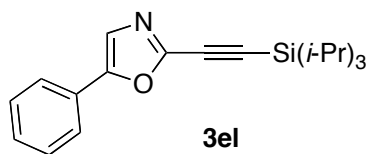


### [<sup>1</sup>H and <sup>13</sup>C NMR Spectra of **3dl**]

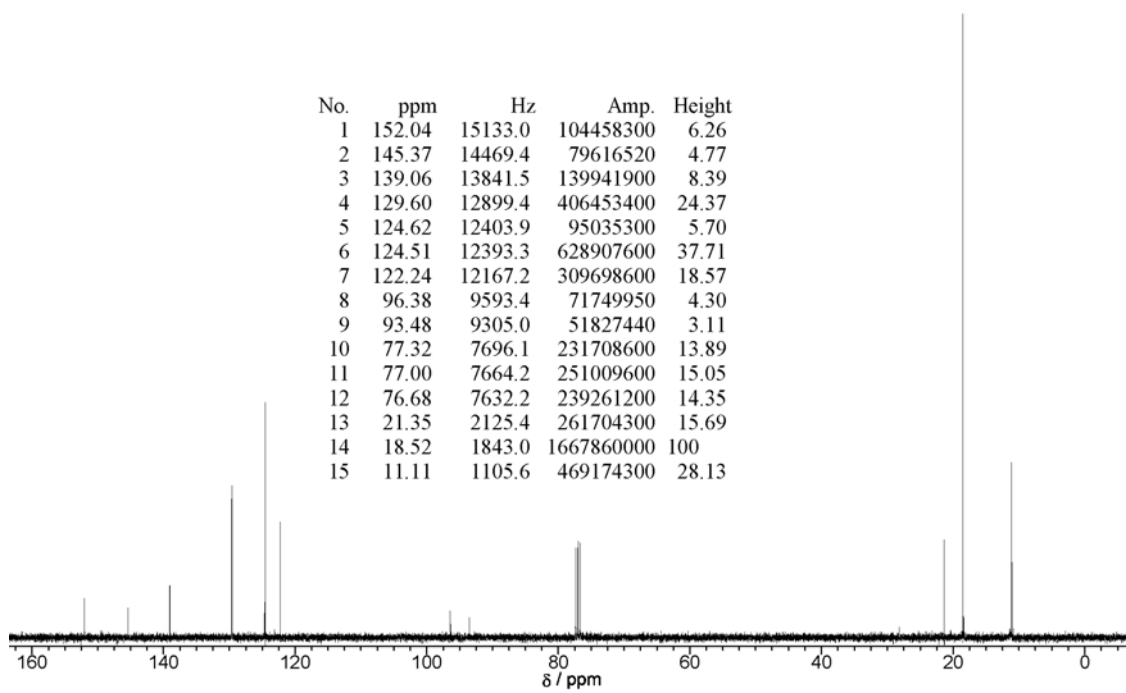
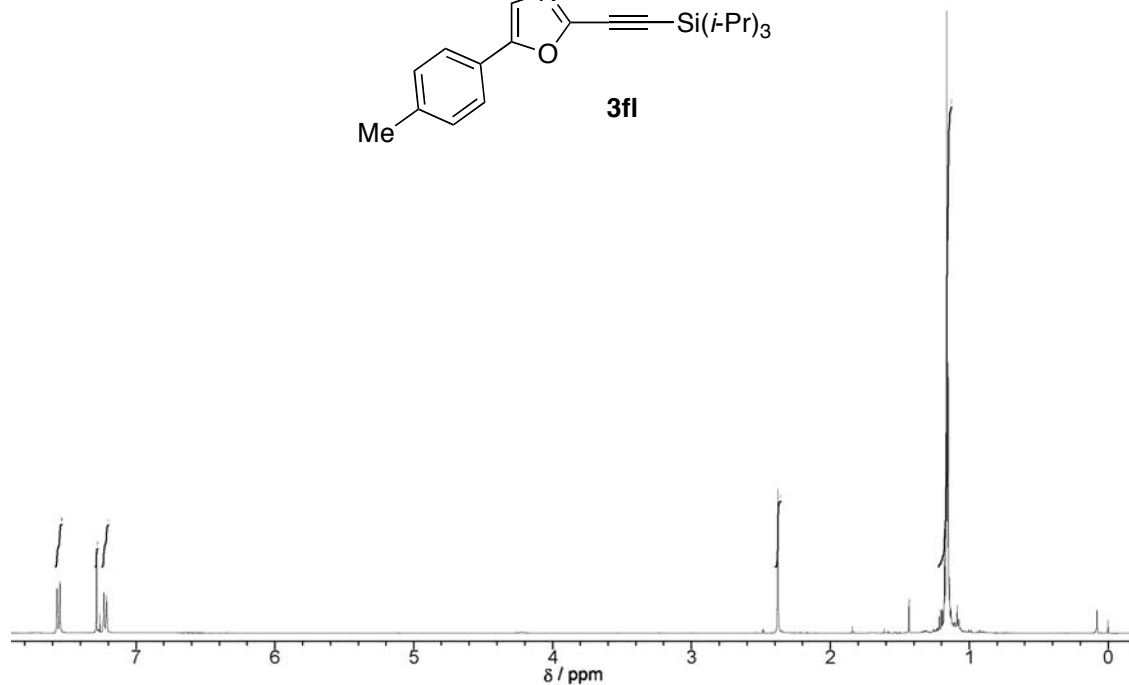
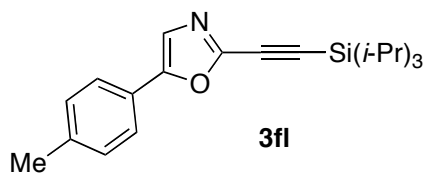




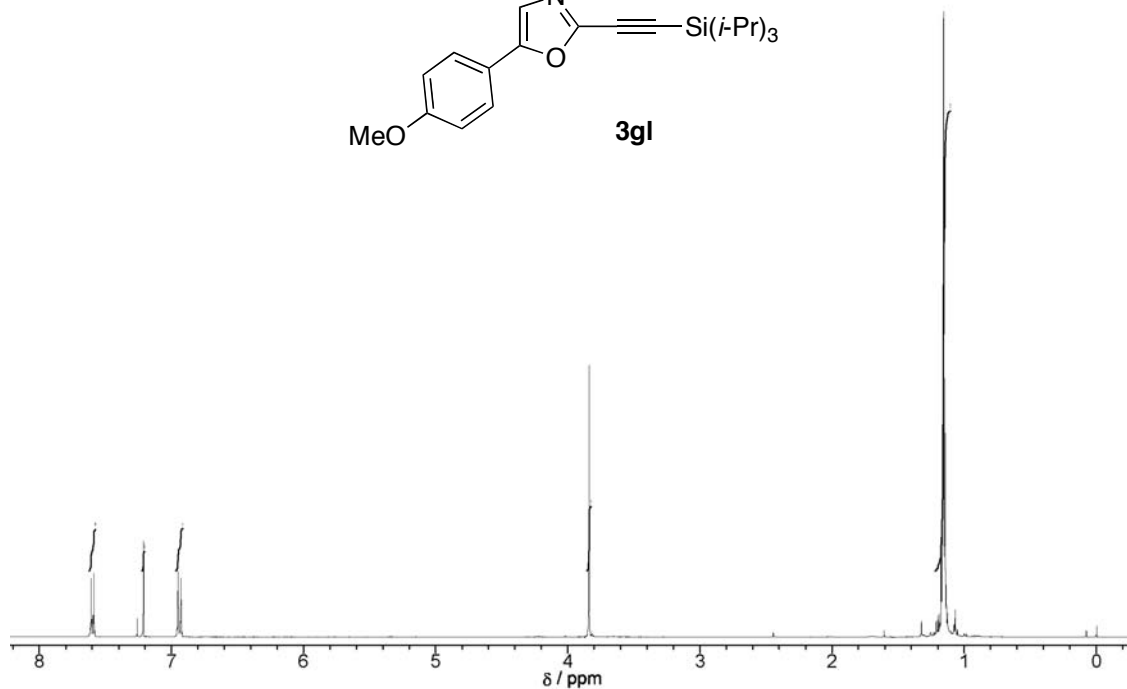
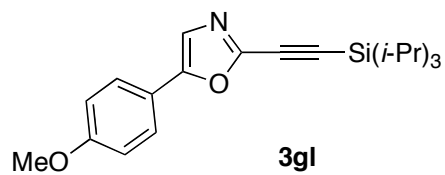
[<sup>1</sup>H and <sup>13</sup>C NMR Spectra of **3el**]



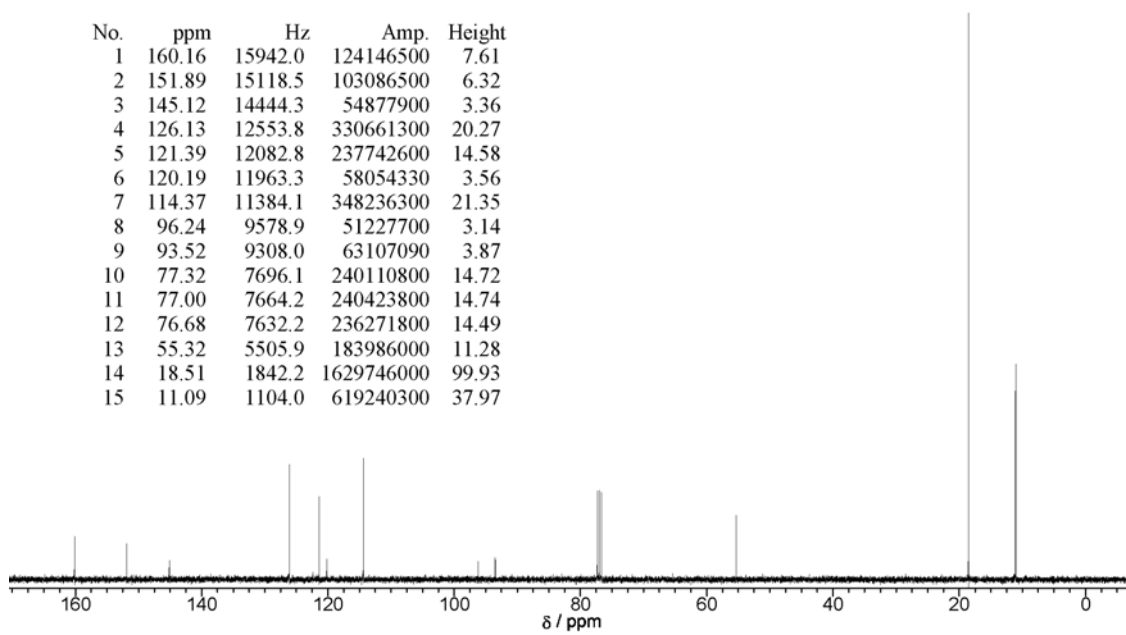
[<sup>1</sup>H and <sup>13</sup>C NMR Spectra of **3fl**]



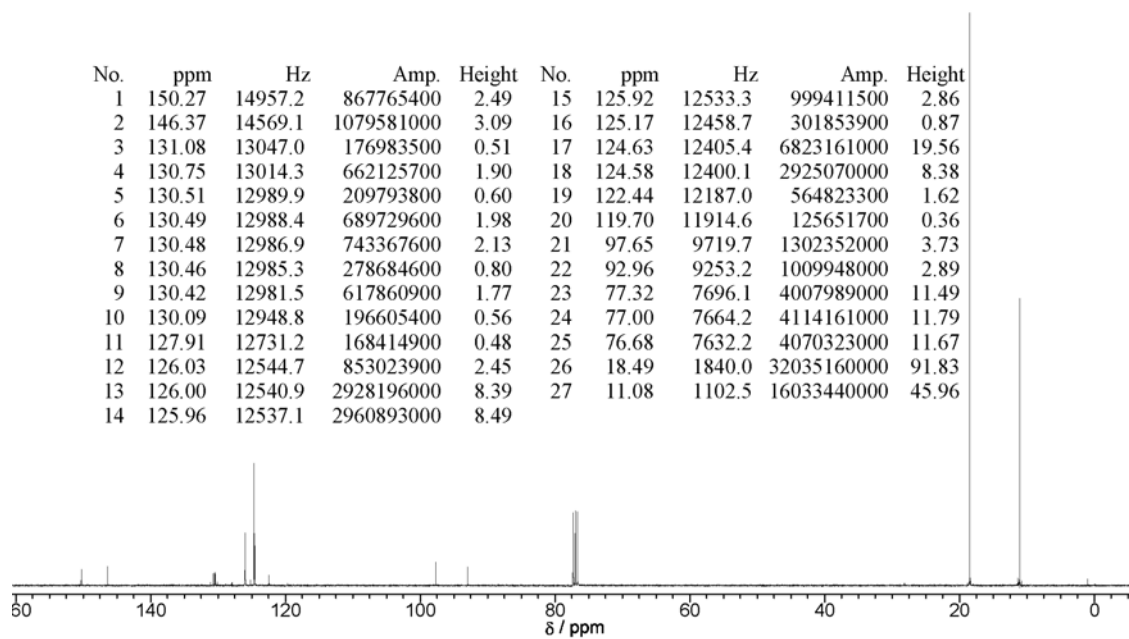
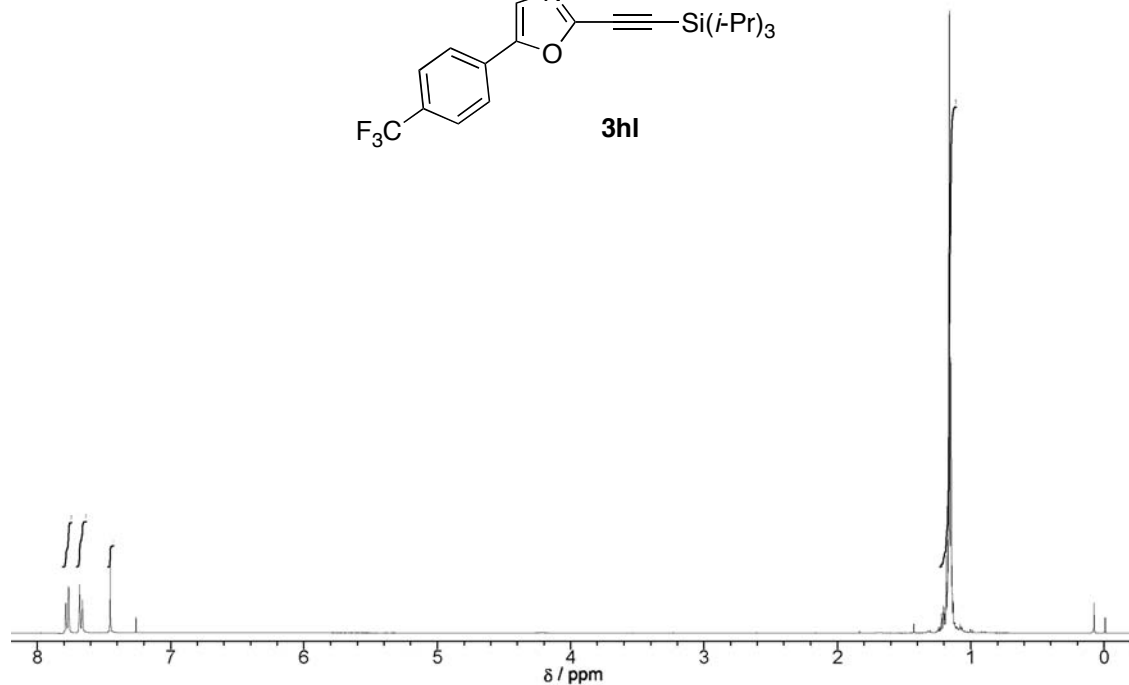
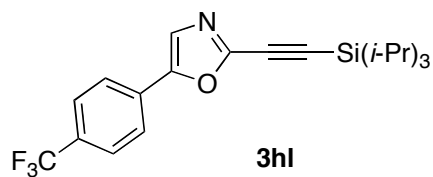
[<sup>1</sup>H and <sup>13</sup>C NMR Spectra of **3gl**]



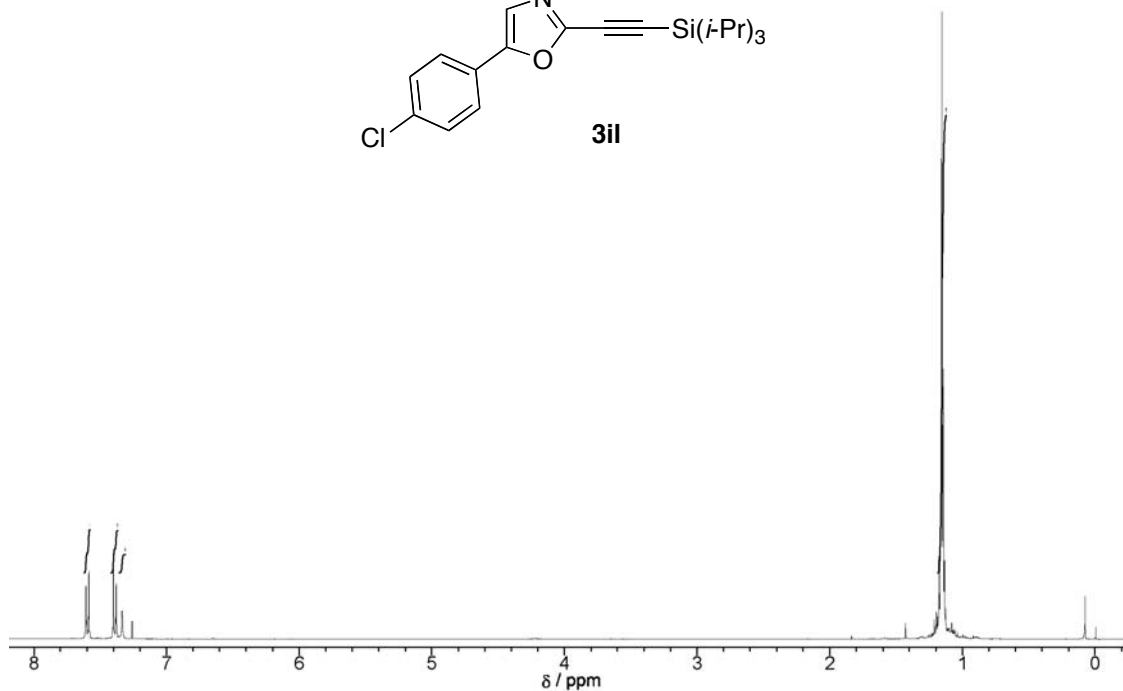
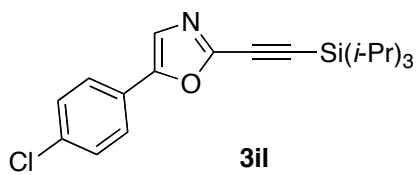
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2	151.89	15118.5	103086500	6.32
3	145.12	14444.3	54877900	3.36
4	126.13	12553.8	330661300	20.27
5	121.39	12082.8	237742600	14.58
6	120.19	11963.3	58054330	3.56
7	114.37	11384.1	348236300	21.35
8	96.24	9578.9	51227700	3.14
9	93.52	9308.0	63107090	3.87
10	77.32	7696.1	240110800	14.72
11	77.00	7664.2	240423800	14.74
12	76.68	7632.2	236271800	14.49
13	55.32	5505.9	183986000	11.28
14	18.51	1842.2	1629746000	99.93
15	11.09	1104.0	619240300	37.97



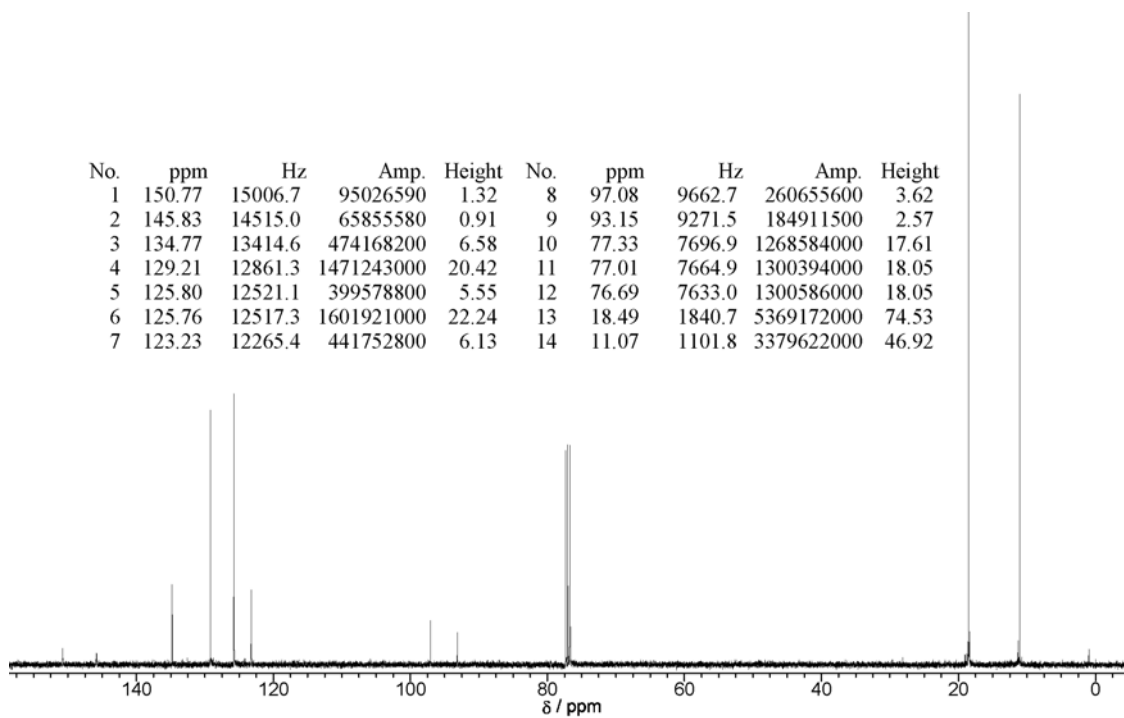
[<sup>1</sup>H and <sup>13</sup>C NMR Spectra of **3hl**]



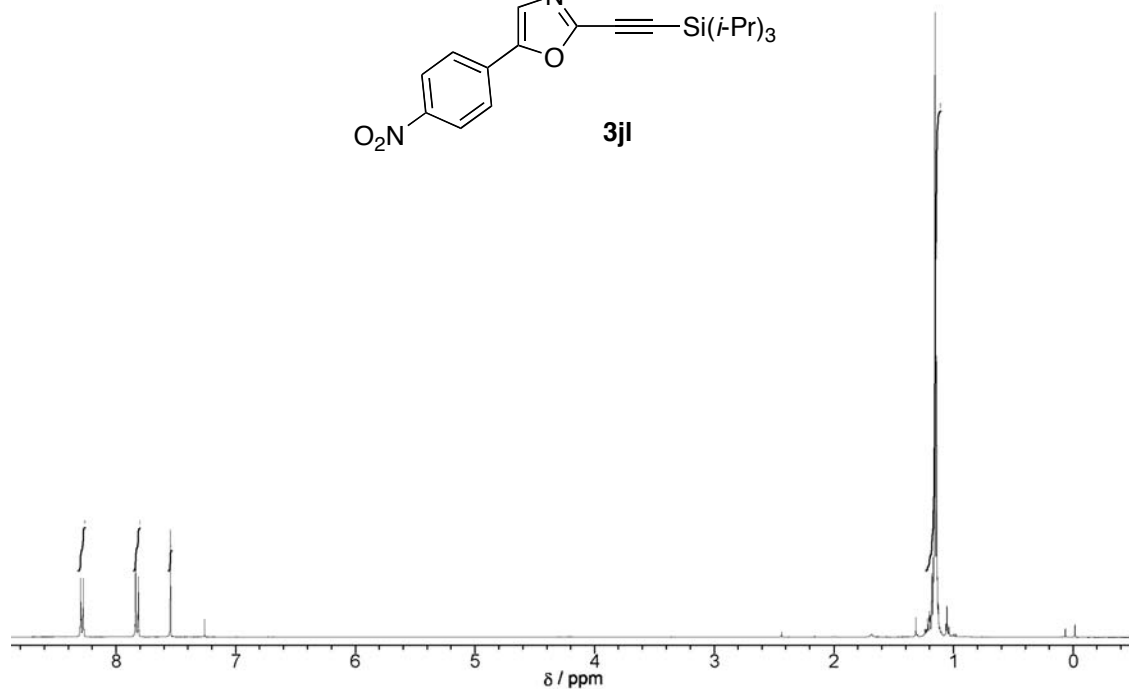
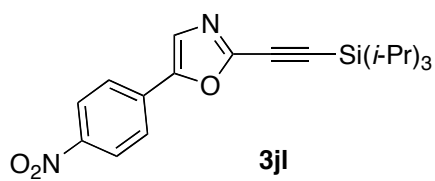
[<sup>1</sup>H and <sup>13</sup>C NMR Spectra of **3il**]



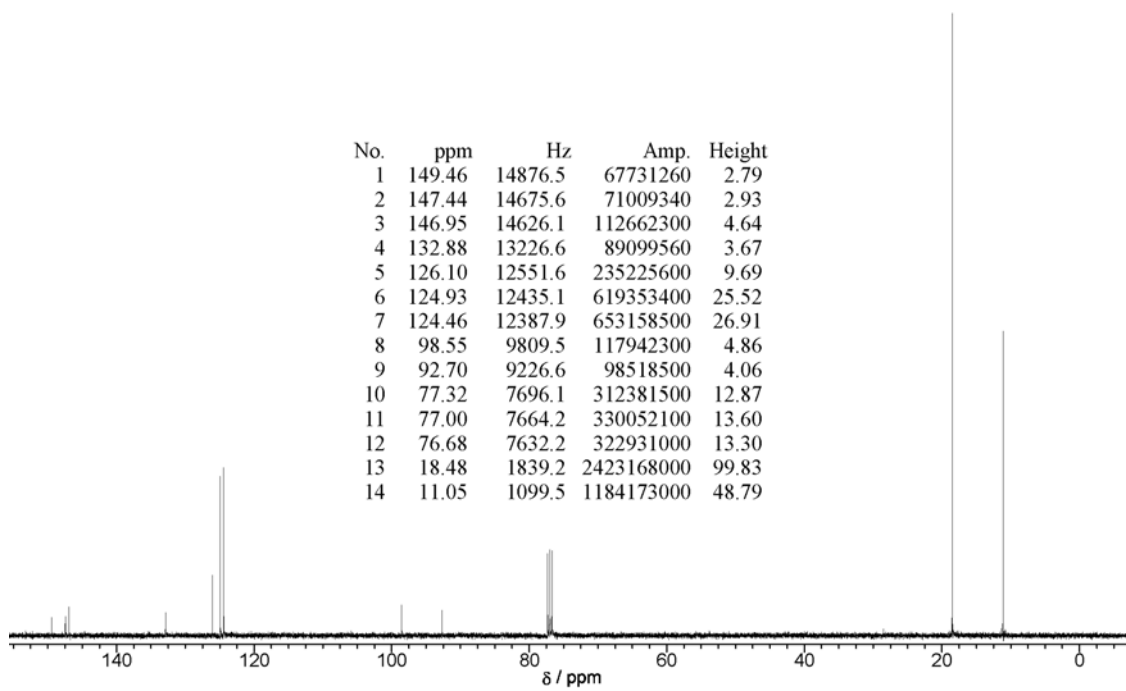
No.	ppm	Hz	Amp.	Height	No.	ppm	Hz	Amp.	Height
1	150.77	15006.7	95026590	1.32	8	97.08	9662.7	260655600	3.62
2	145.83	14515.0	65855580	0.91	9	93.15	9271.5	184911500	2.57
3	134.77	13414.6	474168200	6.58	10	77.33	7696.9	1268584000	17.61
4	129.21	12861.3	1471243000	20.42	11	77.01	7664.9	1300394000	18.05
5	125.80	12521.1	399578800	5.55	12	76.69	7633.0	1300586000	18.05
6	125.76	12517.3	1601921000	22.24	13	18.49	1840.7	5369172000	74.53
7	123.23	12265.4	441752800	6.13	14	11.07	1101.8	3379622000	46.92



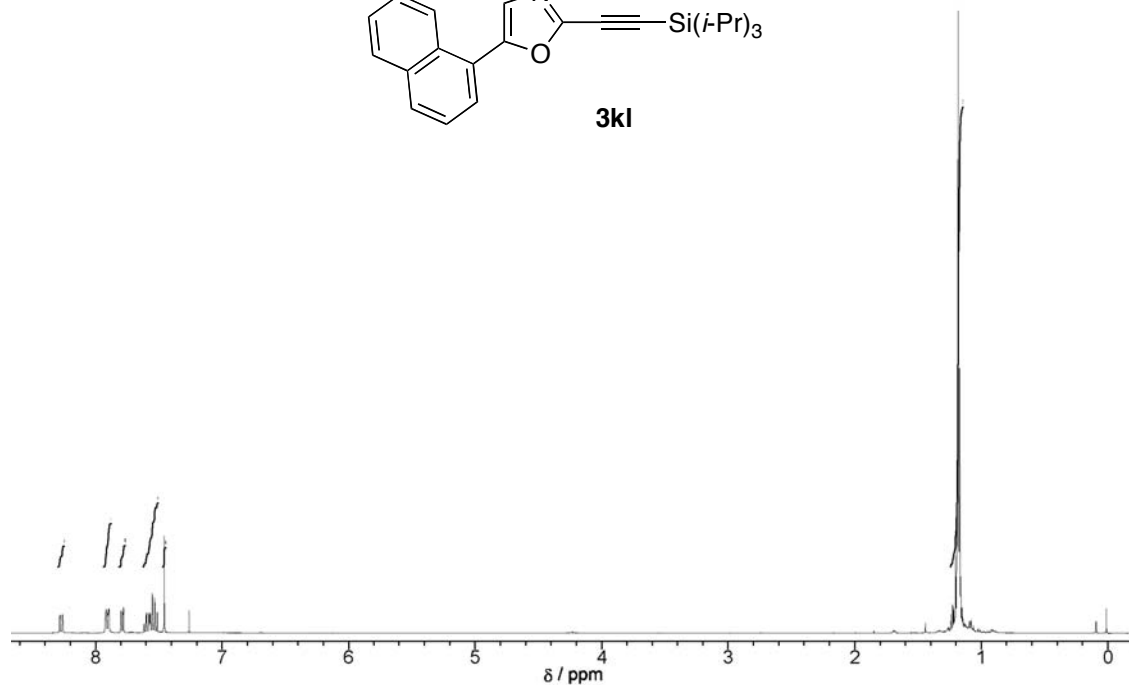
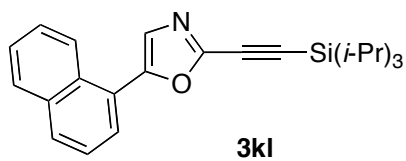
[<sup>1</sup>H and <sup>13</sup>C NMR Spectra of **3jl**]



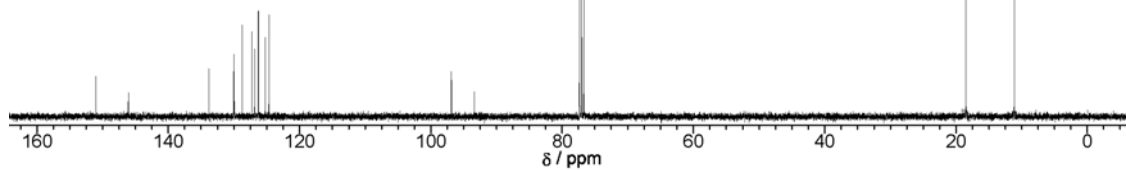
No.	ppm	Hz	Amp.	Height
1	149.46	14876.5	67731260	2.79
2	147.44	14675.6	71009340	2.93
3	146.95	14626.1	112662300	4.64
4	132.88	13226.6	89099560	3.67
5	126.10	12551.6	235225600	9.69
6	124.93	12435.1	619353400	25.52
7	124.46	12387.9	653158500	26.91
8	98.55	9809.5	117942300	4.86
9	92.70	9226.6	98518500	4.06
10	77.32	7696.1	312381500	12.87
11	77.00	7664.2	330052100	13.60
12	76.68	7632.2	322931000	13.30
13	18.48	1839.2	2423168000	99.83
14	11.05	1099.5	1184173000	48.79



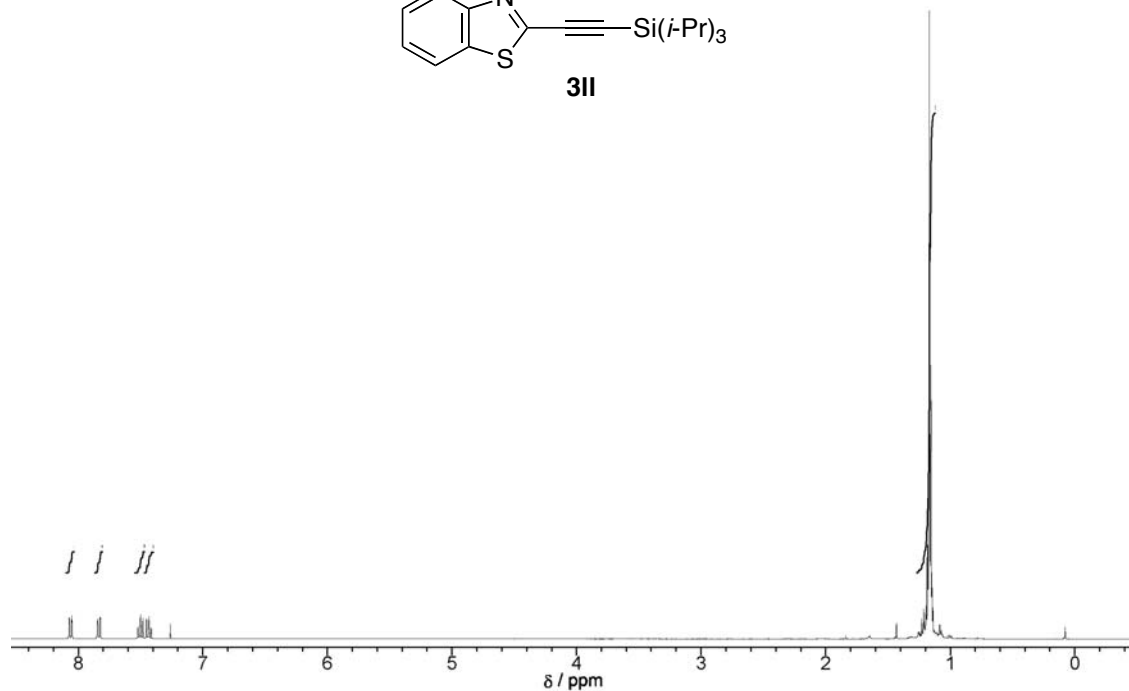
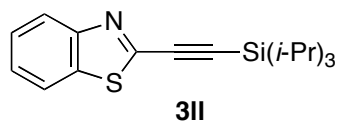
[<sup>1</sup>H and <sup>13</sup>C NMR Spectra of **3kl**]



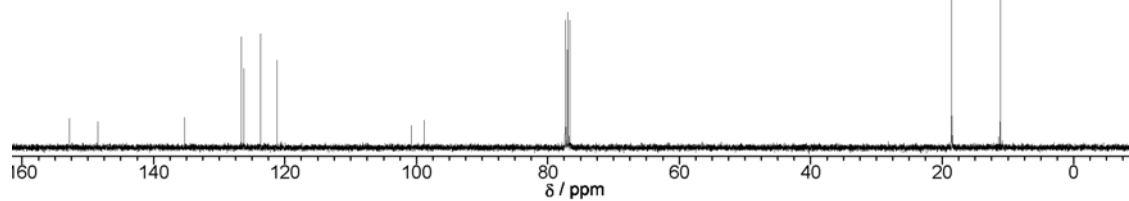
No.	ppm	Hz	Amp.	Height
1	151.04	15034.1	121222800	6.42
2	146.09	14540.9	72786680	3.86
3	133.81	13318.7	145131000	7.69
4	130.01	12940.4	136555800	7.23
5	129.97	12936.6	185991700	9.85
6	128.76	12816.4	277060300	14.68
7	127.24	12665.0	257272300	13.63
8	126.86	12626.9	204997300	10.86
9	126.31	12572.1	317430600	16.82
10	126.28	12569.1	320284200	16.97
11	125.23	12464.8	238094600	12.61
12	124.66	12408.5	307240100	16.28
13	124.63	12404.7	86940780	4.61
14	96.86	9640.6	135590600	7.18
15	93.35	9292.0	75523220	4.00
16	77.33	7696.9	380035600	20.13
17	77.01	7664.9	378950000	20.07
18	76.69	7633.0	361832900	19.17
19	18.53	1844.5	1508786000	79.93
20	11.11	1105.6	633289300	33.55



[<sup>1</sup>H and <sup>13</sup>C NMR Spectra of **3II**]

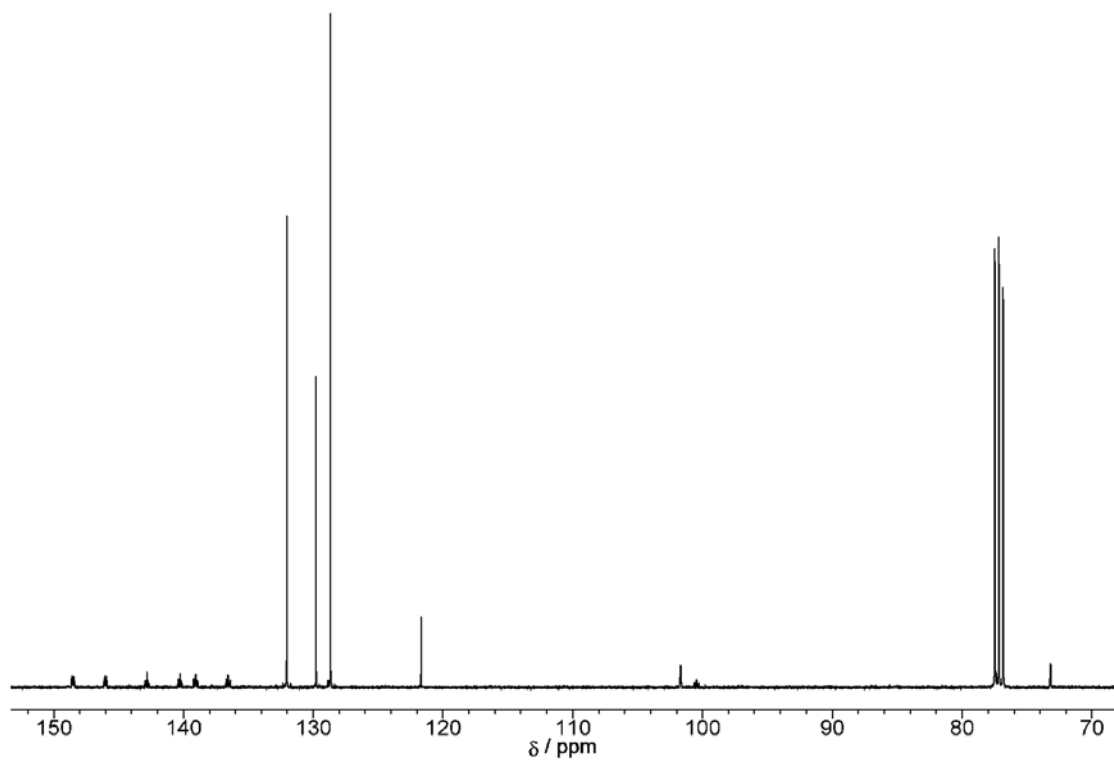
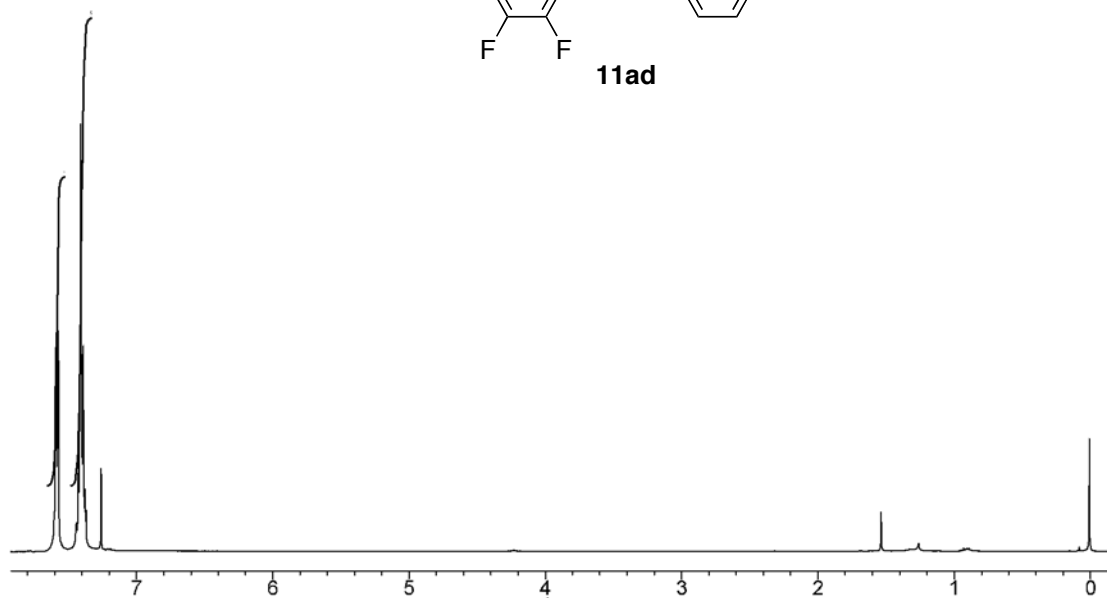
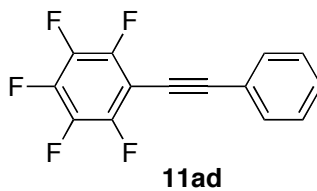


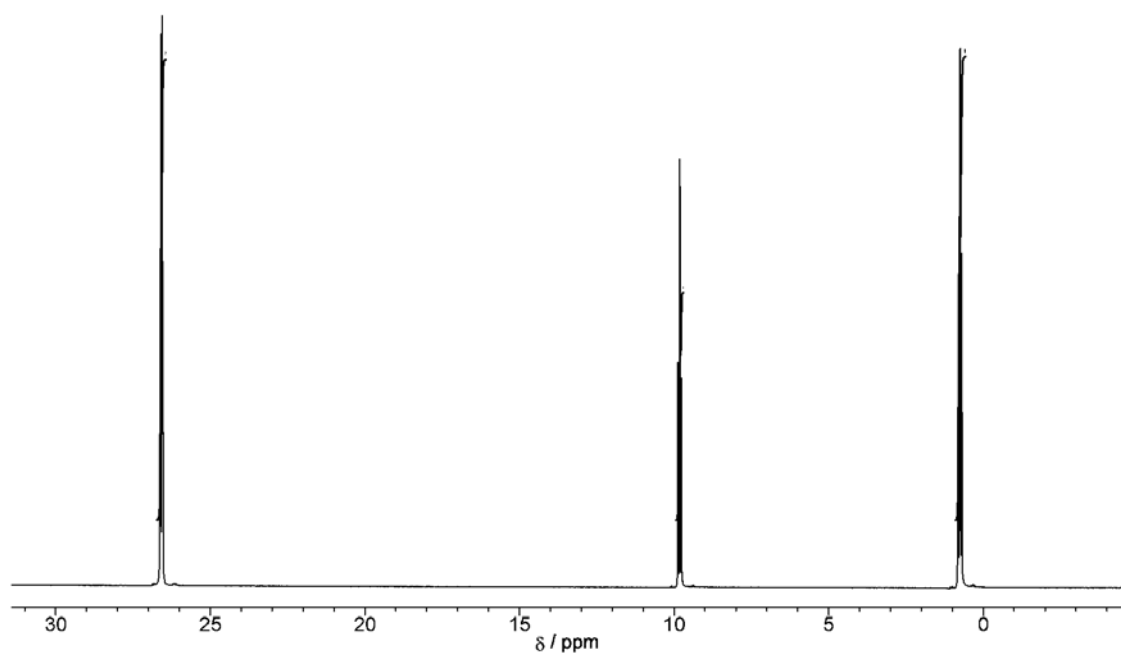
No.	ppm	Hz	Amp.	Height
1	152.79	15208.3	118132600	4.66
2	148.43	14773.8	105437300	4.16
3	135.26	13463.3	122565000	4.83
4	126.65	12605.6	450515900	17.76
5	126.26	12567.5	319913800	12.61
6	123.73	12315.6	462484800	18.23
7	121.22	12065.3	354907400	13.99
8	100.77	10030.2	89856510	3.54
9	98.80	9833.9	111082700	4.38
10	77.32	7696.1	515960800	20.34
11	77.00	7664.2	550109200	21.69
12	76.68	7632.2	516715800	20.37
13	18.57	1848.3	1816032000	71.60
14	11.16	1110.9	1387833000	54.72



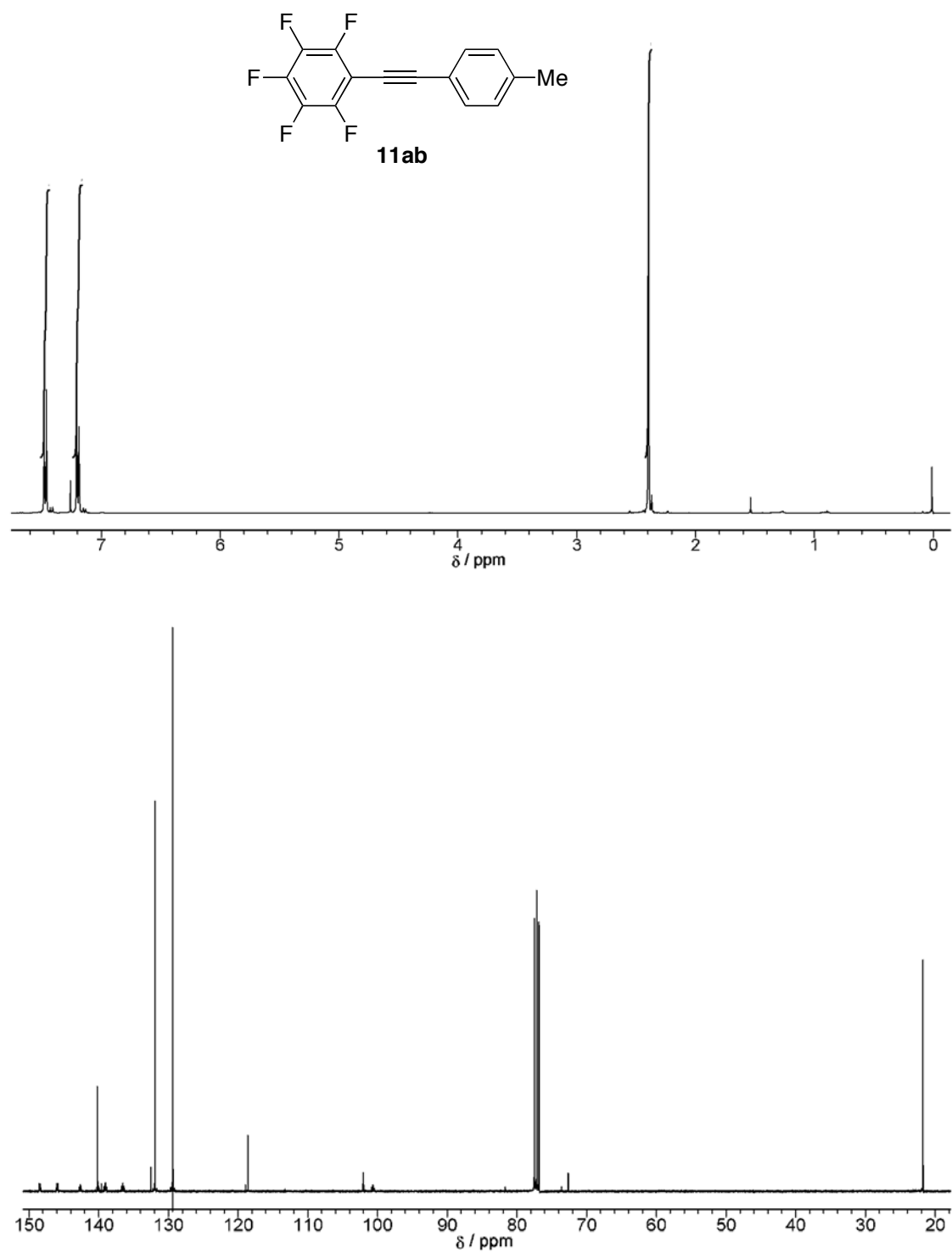


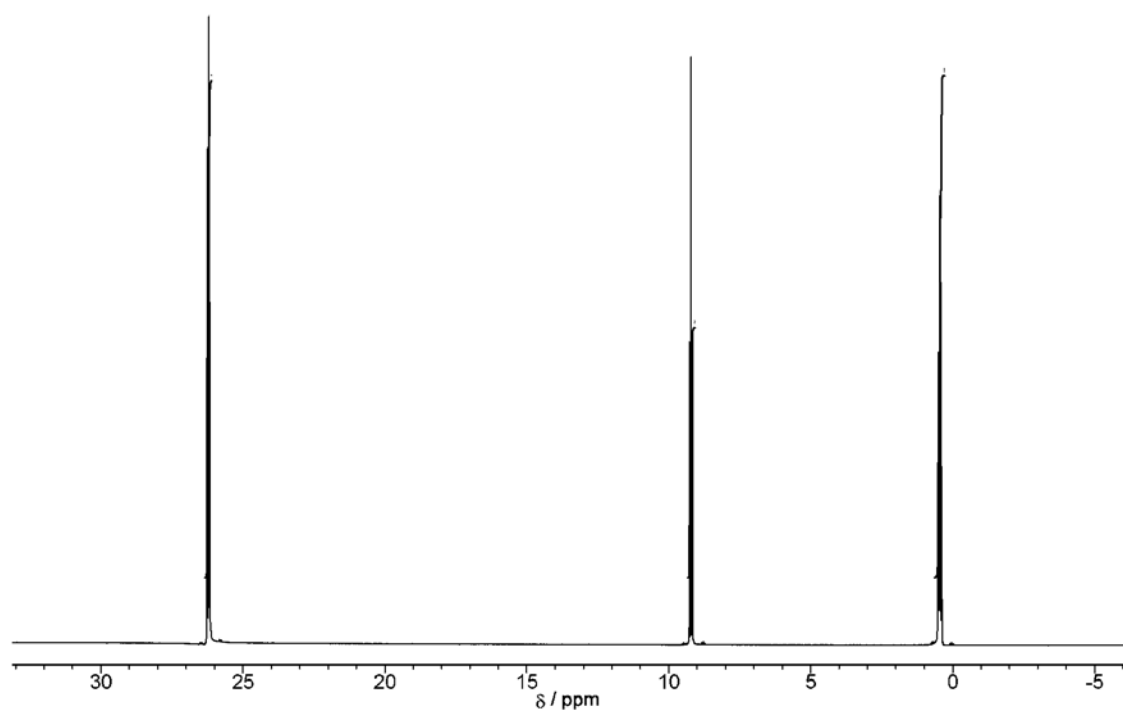
[ $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{19}\text{F}$  NMR Spectra of **11ad**]



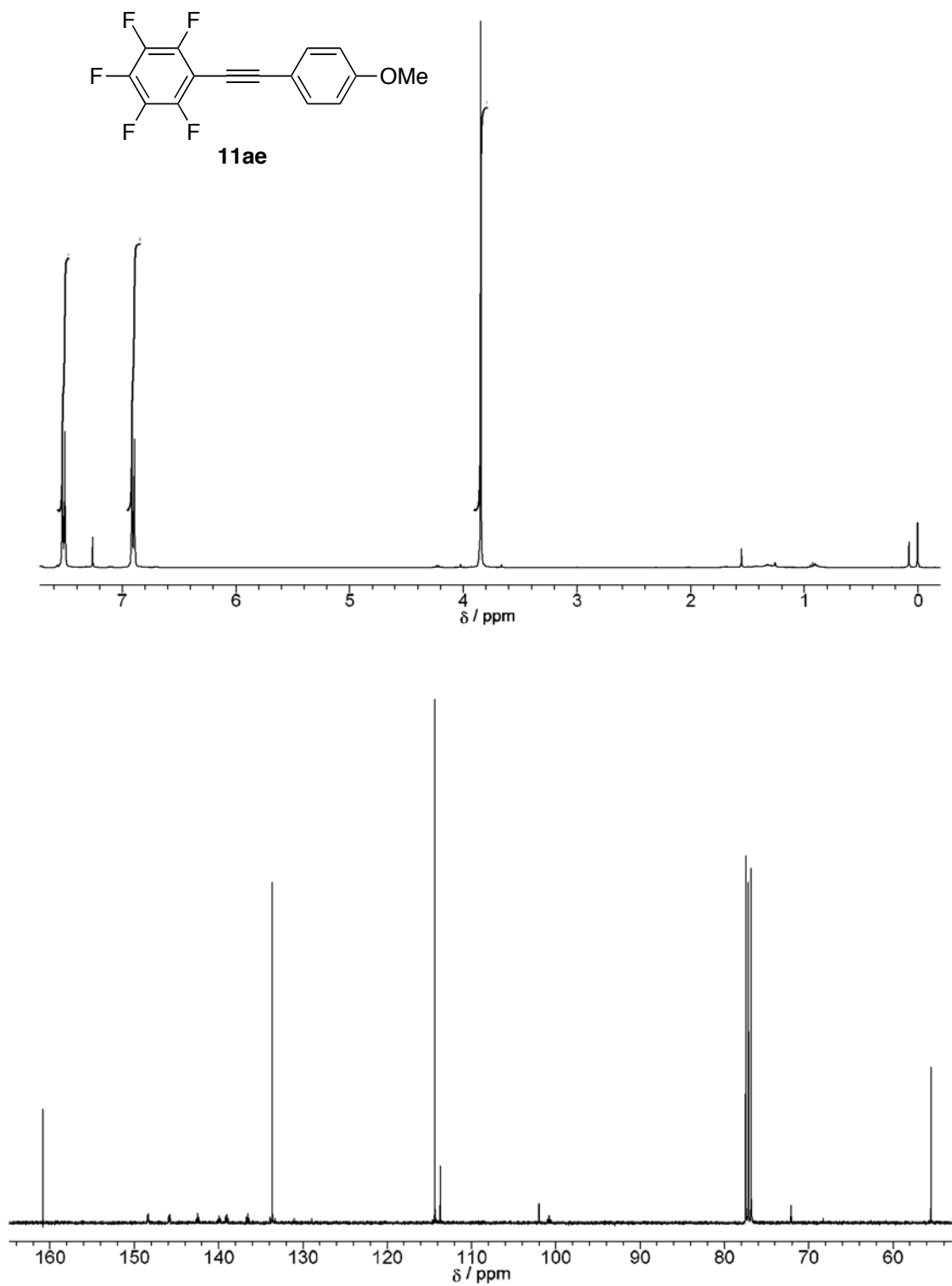


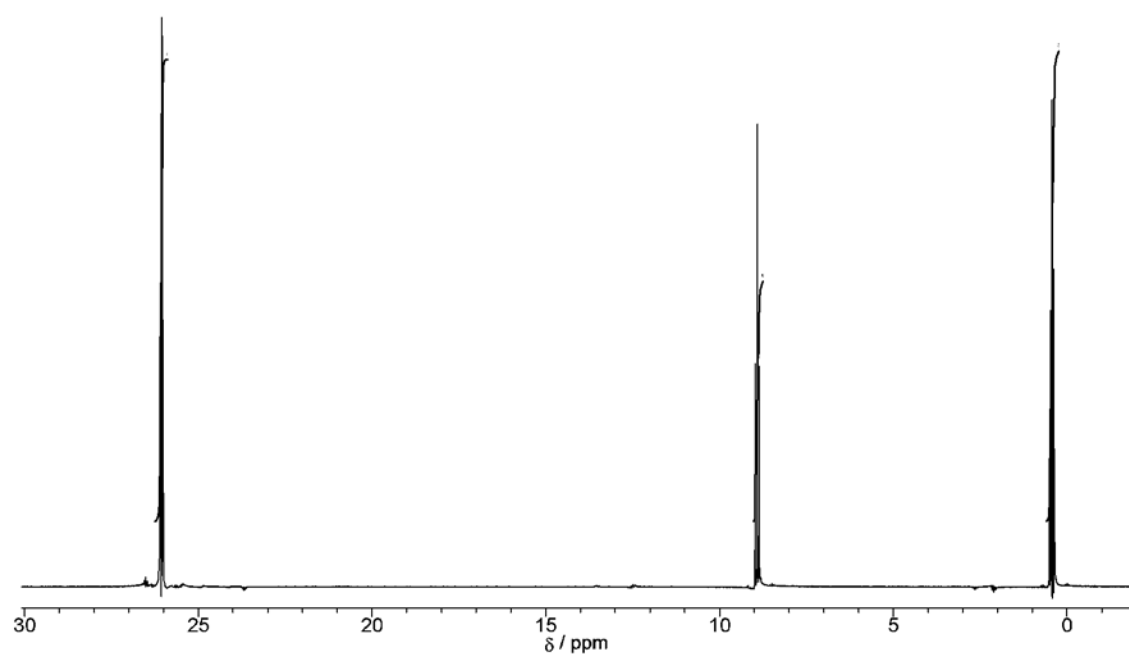
[ $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{19}\text{F}$  NMR Spectra of **11ab**]



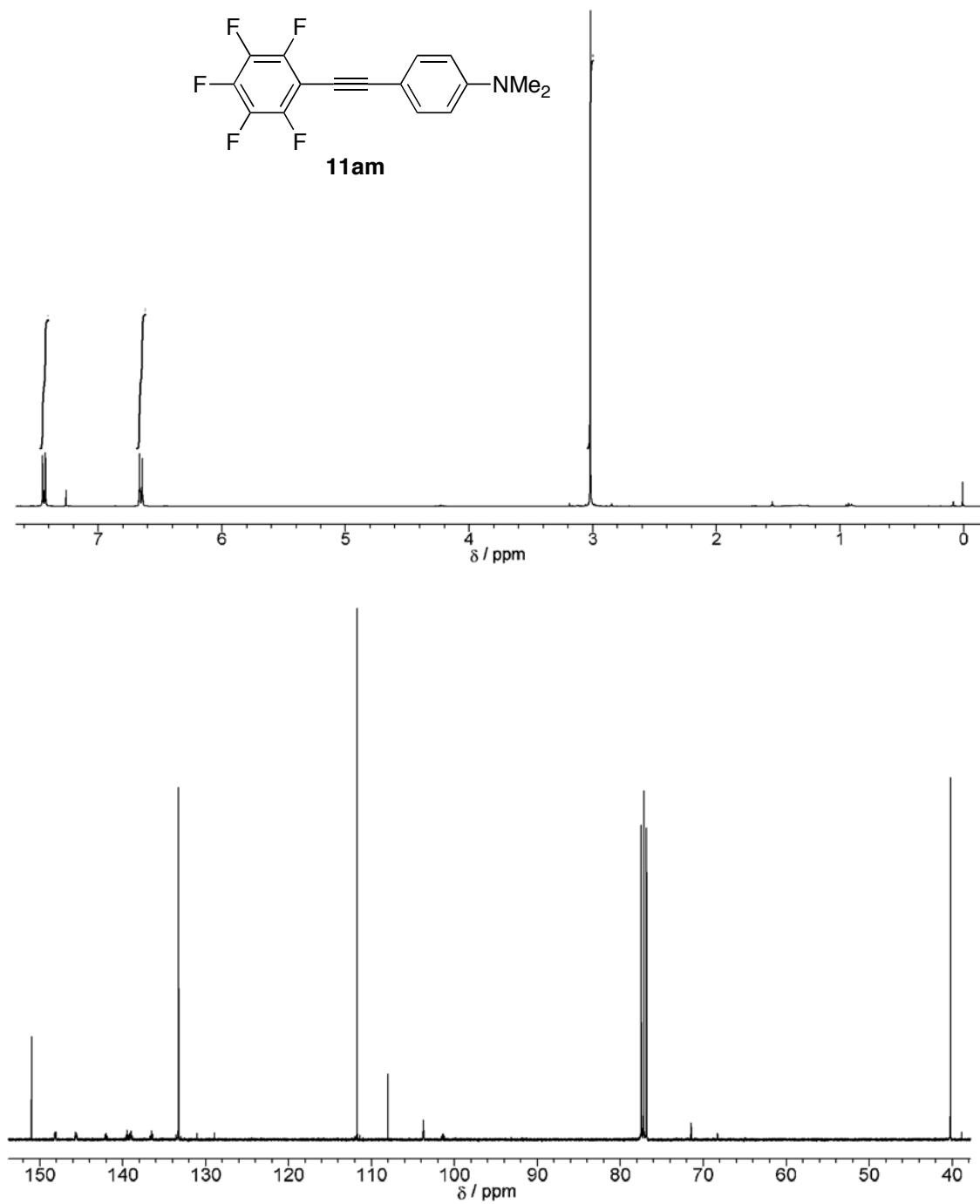


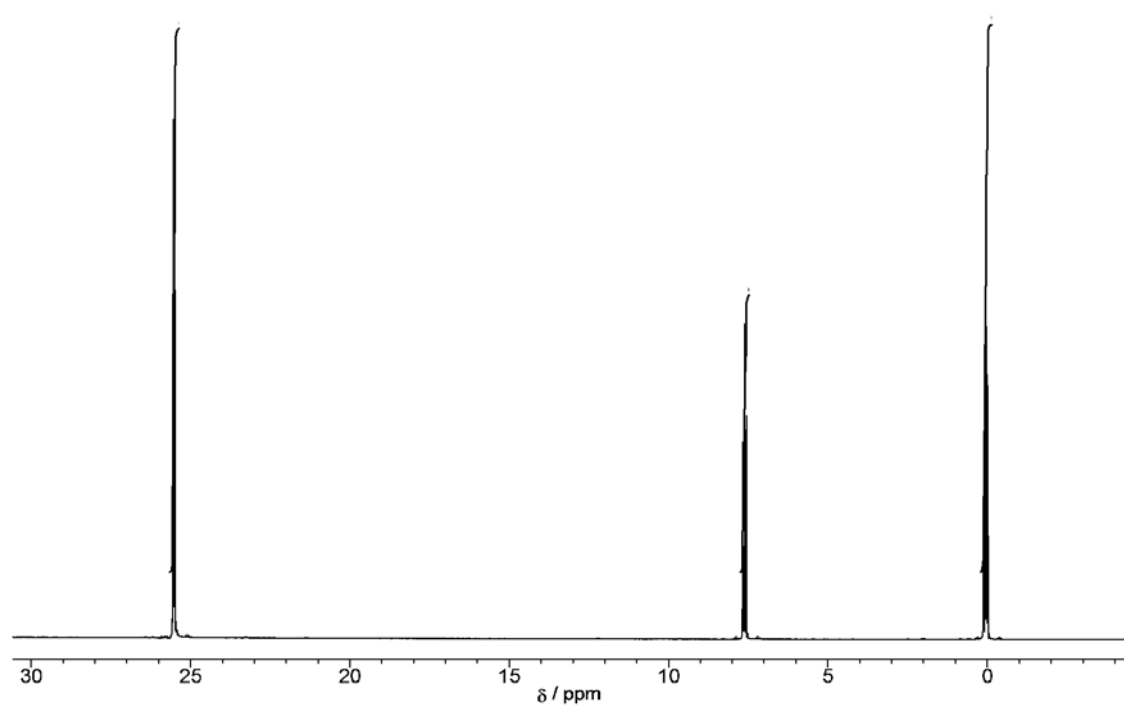
[ $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{19}\text{F}$  NMR Spectra of **11ae**]





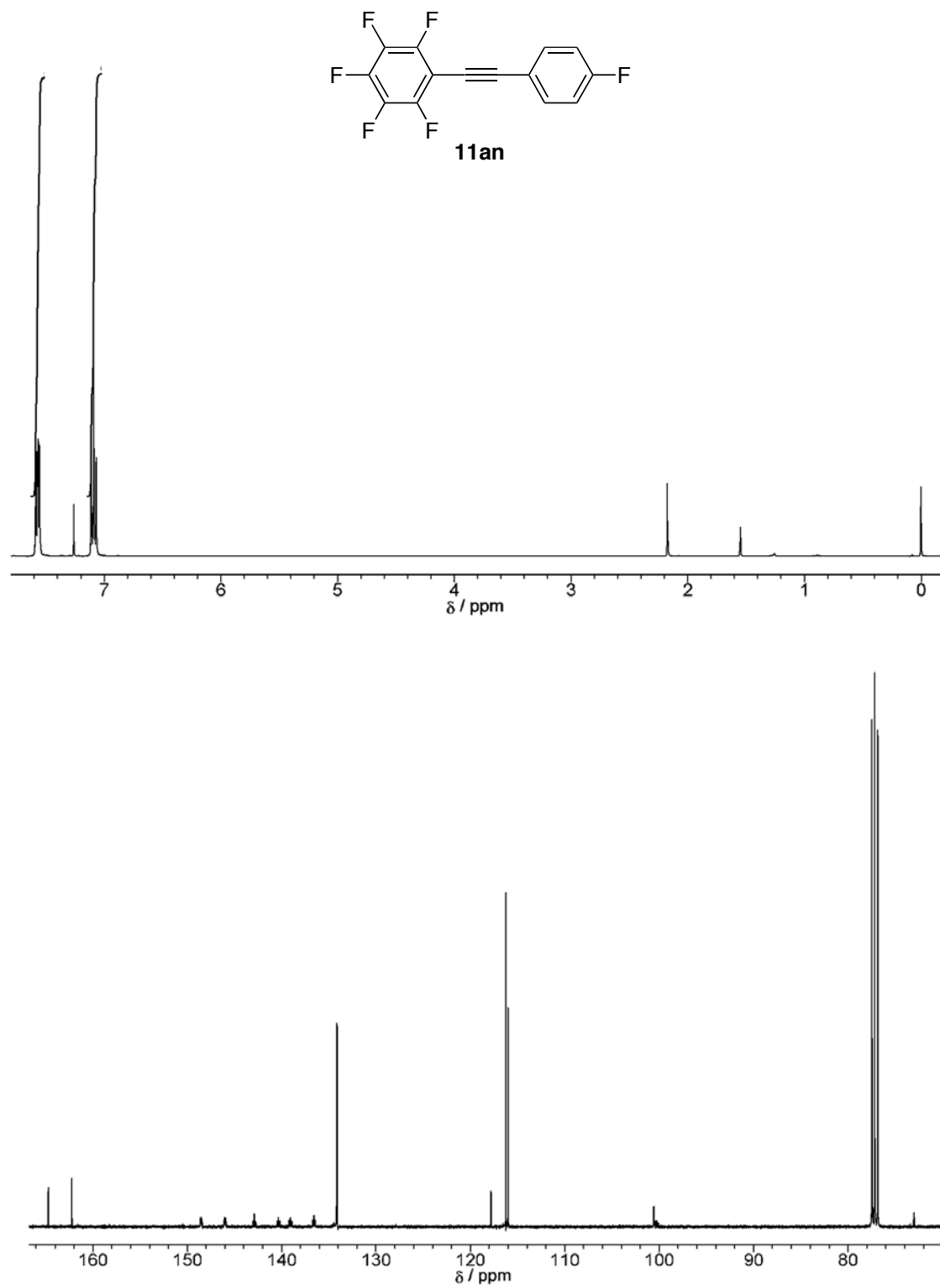
[ $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{19}\text{F}$  NMR Spectra of **11am**]

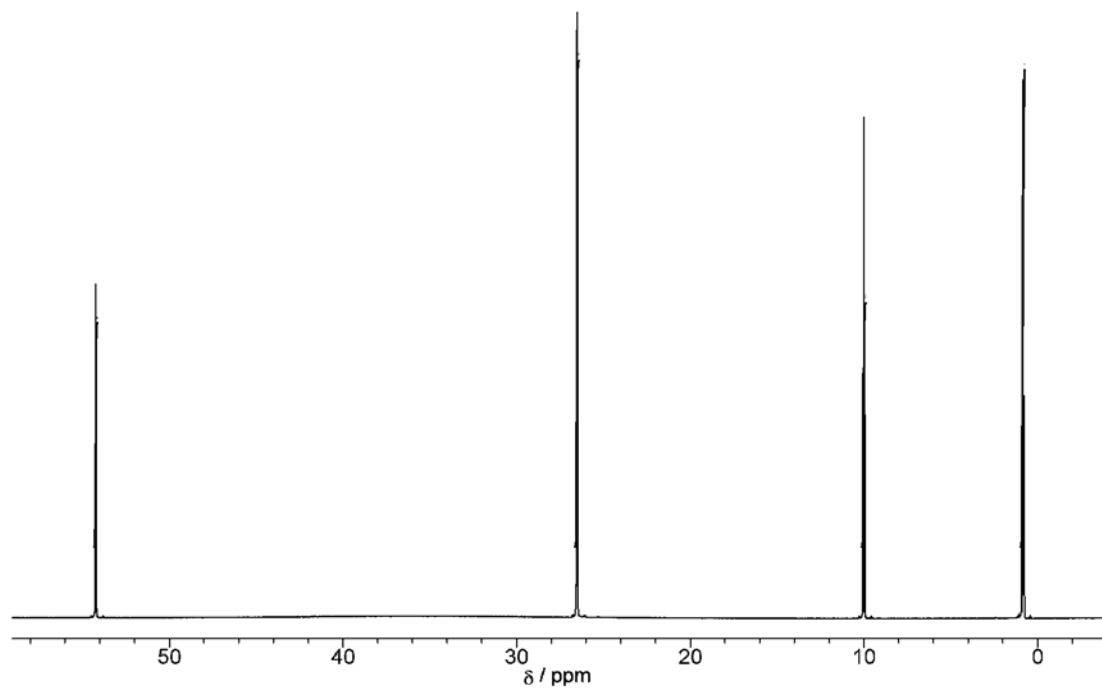




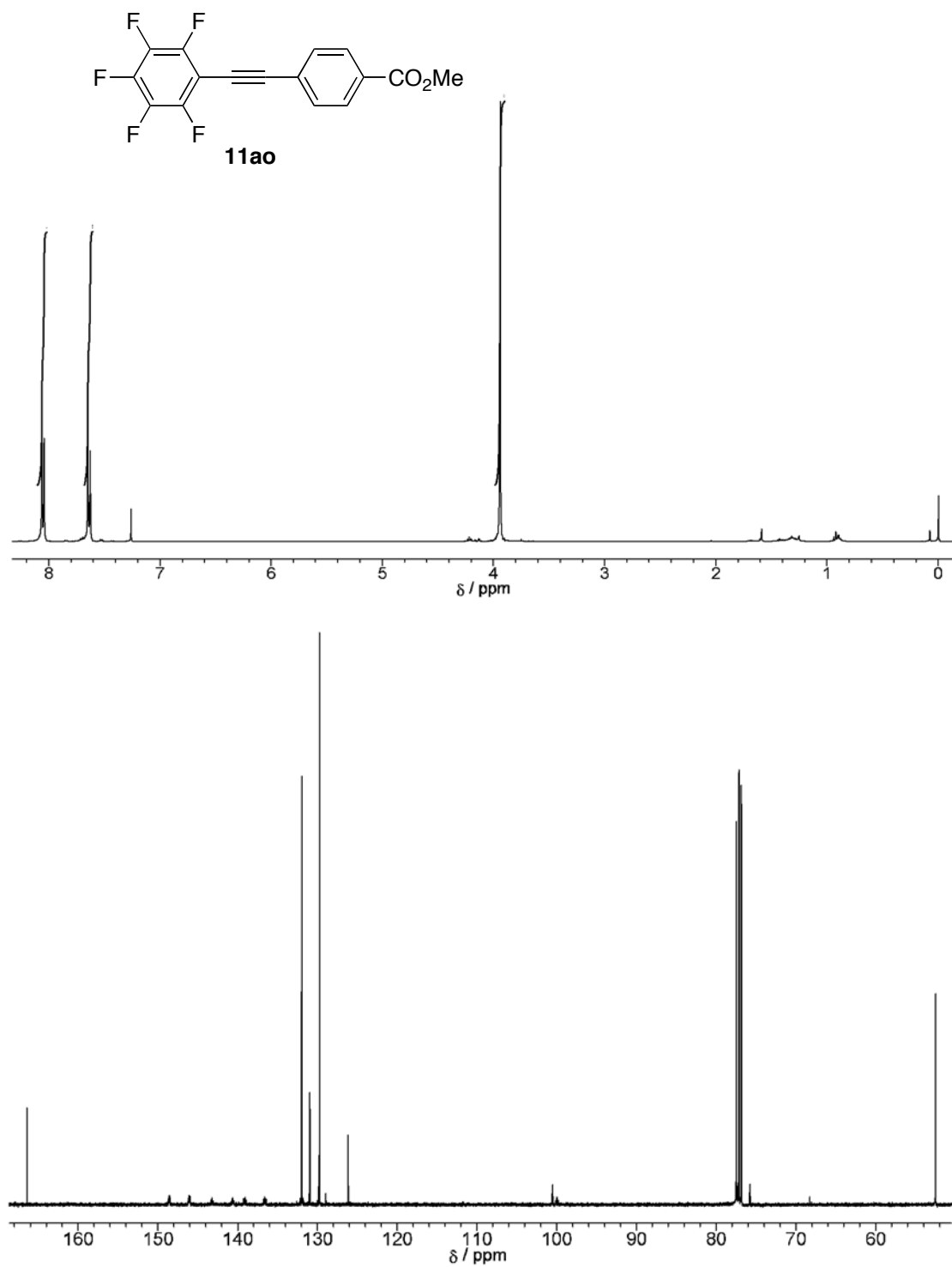


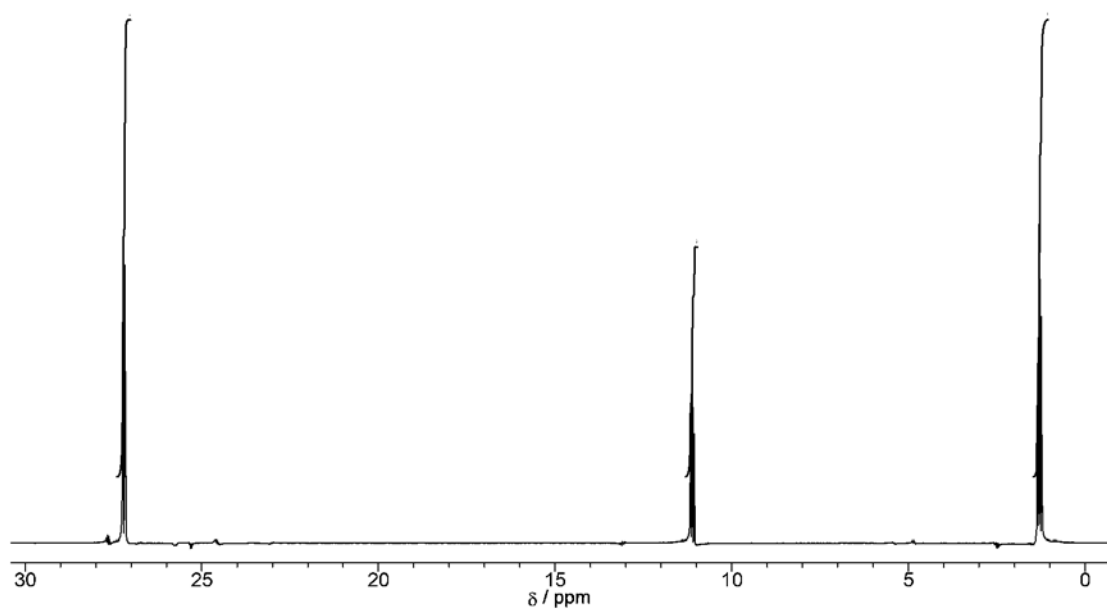
[ $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{19}\text{F}$  NMR Spectra of **11an**]



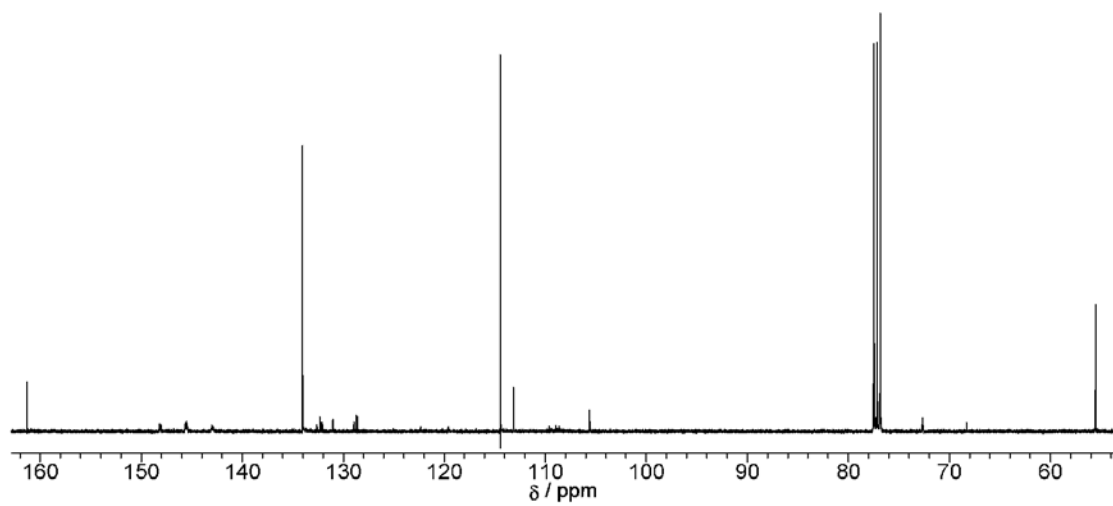
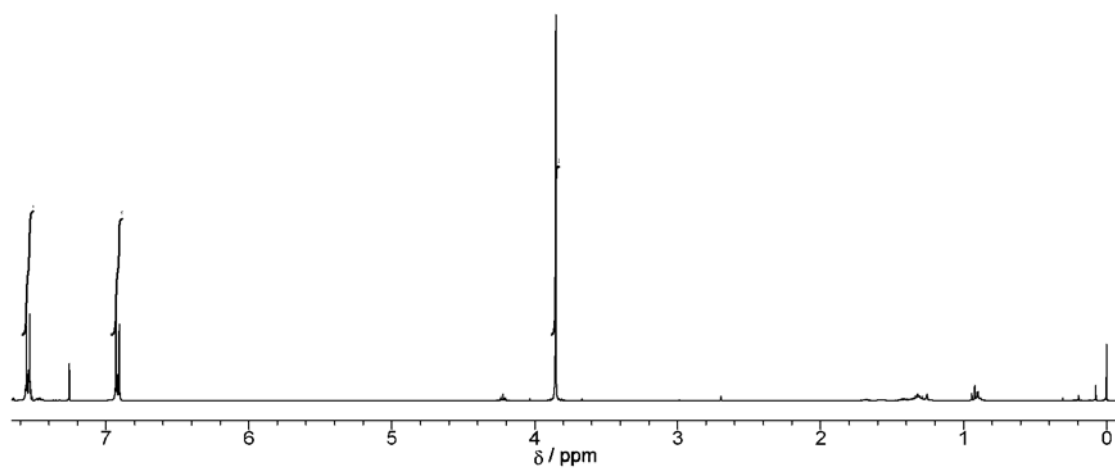
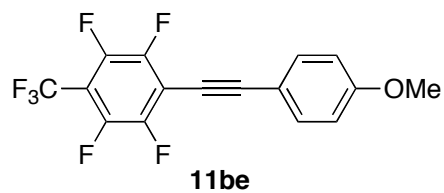


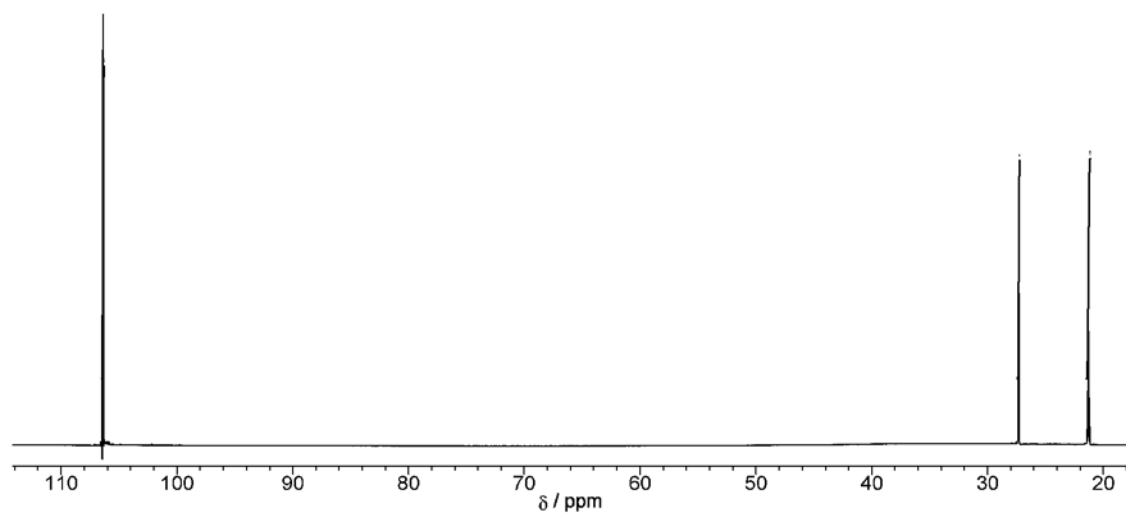
[ $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{19}\text{F}$  NMR Spectra of **11ao**]





[ $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{19}\text{F}$  NMR Spectra of **11be**]





[ $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{19}\text{F}$  NMR Spectra of **11bm**]

