

## Electronic Supporting Information

### Ionic liquid-supported sulfonyl hydrazine: A useful reagent for traceless synthesis of pyrazoles

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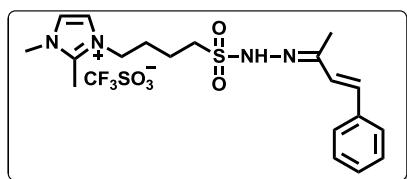
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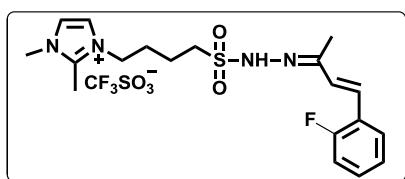
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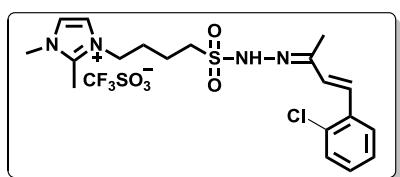
1. Physical and spectroscopic data of ionic liquid-supported sulfonyl hydrazones **9** & **10**.



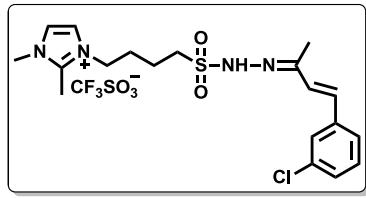
**Compound 9a:** Yield 86%; White solid; mp 150-151 °C; <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ 10.27 (s, 1H), 7.64 (d, *J* = 2.0 Hz, 1H), 7.61 (dd, *J* = 3.5, 1.7 Hz, 2H), 7.58 (s, 1H), 7.39 (t, *J* = 7.2 Hz, 2H), 7.35 – 7.30 (m, 1H), 7.10 (d, *J* = 16.6 Hz, 1H), 6.84 (d, *J* = 16.6 Hz, 1H), 4.16 (t, *J* = 7.1 Hz, 2H), 3.73 (s, 3H), 3.33 – 3.24 (m, 2H), 2.59 (s, 3H), 2.08 (s, 3H), 1.90-1.81(m, 2H), 1.78 – 1.65 (m, 2H); <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>) δ 154.5, 144.8, 136.5, 134.2, 129.3, 129.0, 128.7, 127.4, 122.8, 121.3, 121.1 (q, *J*<sub>C-F</sub> = 320.25 Hz), 49.4, 47.3, 35.1, 28.1, 20.1, 12.9, 9.6; HRMS: Calcd. for C<sub>19</sub>H<sub>27</sub>N<sub>4</sub>O<sub>2</sub>S<sup>+</sup> 375.1849, found 375.1858 [M – CF<sub>3</sub>SO<sub>3</sub>]<sup>+</sup>.



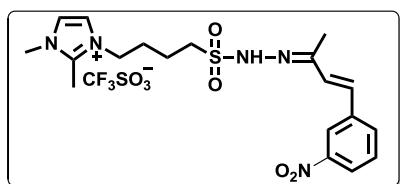
**Compound 9b:** Yield 83%; Colorless solid; mp 146-147 °C; <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ 10.39 (s, 1H), 7.75 (t, *J* = 7.7 Hz, 1H), 7.64 (d, *J* = 6.2 Hz, 2H), 7.40 – 7.33 (m, 1H), 7.29 – 7.20 (m, 2H), 7.11 (d, *J* = 16.8 Hz, 1H), 6.93 (d, *J* = 16.7 Hz, 1H), 4.18 (t, *J* = 6.9 Hz, 2H), 3.75 (s, 3H), 3.35 – 3.24 (m, 2H), 2.60 (s, 3H), 2.09 (s, 3H), 1.92 – 1.81 (m, 2H), 1.80 – 1.66 (m, 2H); <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>) δ 160.3 (d, *J*<sub>C-F</sub> = 249.0 Hz), 154.1, 144.8, 131.6 (d, *J*<sub>C-F</sub> = 5.6 Hz), 130.7 (d, *J*<sub>C-F</sub> = 8.5 Hz), 128.6 (d, *J*<sub>C-F</sub> = 3.1 Hz), 126.0 (d, *J*<sub>C-F</sub> = 2.9 Hz), 125.3 (d, *J*<sub>C-F</sub> = 3.3 Hz), 124.1 (d, *J*<sub>C-F</sub> = 11.5 Hz), 121.1 (q, *J*<sub>C-F</sub> = 320.25 Hz), 116.4 (d, *J*<sub>C-F</sub> = 22.0 Hz), 49.5, 47.3, 35.1, 28.1, 20.1, 12.8, 9.6; HRMS: Calcd. for C<sub>19</sub>H<sub>26</sub>FN<sub>4</sub>O<sub>2</sub>S<sup>+</sup> 393.1755, found 393.1736 [M – CF<sub>3</sub>SO<sub>3</sub>]<sup>+</sup>.



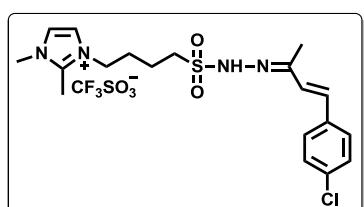
**Compound 9c:** Yield 81%; Colorless solid; mp 129-131 °C; <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ 10.44 (s, 1H), 7.86 – 7.79 (m, 1H), 7.64 (d, *J* = 3.2 Hz, 1H), 7.62 (d, *J* = 1.9 Hz, 1H), 7.53 – 7.48 (m, 1H), 7.40 – 7.33 (m, 2H), 7.26 (d, *J* = 16.4 Hz, 1H), 6.89 (d, *J* = 16.4 Hz, 1H), 4.17 (t, *J* = 7.1 Hz, 2H), 3.74 (s, 3H), 3.33 – 3.24 (m, 2H), 2.59 (s, 3H), 2.10 (s, 3H), 1.92 – 1.80 (m, 2H), 1.76-1.69 (m, 2H); <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>) δ 153.8, 144.8, 134.1, 132.9, 132.0, 130.5, 130.3, 129.0, 128.2, 127.7, 122.8, 121.3, 121.1 (q, *J*<sub>C-F</sub> = 320.25 Hz), 49.5, 47.3, 35.1, 28.1, 20.1, 13.0, 9.6; Calcd. for C<sub>19</sub>H<sub>26</sub>ClN<sub>4</sub>O<sub>2</sub>S<sup>+</sup> 409.1460, found 409.1443 [M – CF<sub>3</sub>SO<sub>3</sub>]<sup>+</sup>.



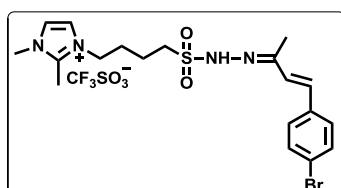
**Compound 9d:** Yield 84%; Yellow solid; mp 150-153 °C; <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ 10.31 (s, 1H), 7.67 (s, 1H), 7.63 (d, *J* = 2.0 Hz, 1H), 7.61 (d, *J* = 2.0 Hz, 1H), 7.57 (d, *J* = 7.3 Hz, 1H), 7.42 (d, *J* = 8.1 Hz, 1H), 7.40 – 7.36 (m, 1H), 7.09 (d, *J* = 16.6 Hz, 1H), 6.91 (d, *J* = 16.6 Hz, 1H), 4.16 (t, *J* = 7.1 Hz, 2H), 3.74 (s, 3H), 3.33 – 3.23 (m, 2H), 2.58 (s, 3H), 2.06 (s, 3H), 1.92 – 1.79 (m, 2H), 1.77 – 1.64 (m, 2H); <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>) δ 154.0, 144.8, 138.8, 134.1, 132.7, 131.1, 130.4, 128.6, 127.1, 125.9, 122.8, 121.3, 121.1 (q, *J*<sub>C-F</sub> = 320.25 Hz), 49.4, 47.3, 35.1, 28.1, 20.1, 12.9, 9.6; Calcd. for C<sub>19</sub>H<sub>26</sub>ClN<sub>4</sub>O<sub>2</sub>S<sup>+</sup> 409.1460, found 409.1451 [M – CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>]<sup>+</sup>.



**Compound 9e:** Yield 79%; White solid; mp 153-155 °C; <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ 10.37 (s, 1H), 8.40 (s, 1H), 8.15 (dd, *J* = 8.1, 1.7 Hz, 1H), 8.09 (d, *J* = 7.8 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 1.9 Hz, 1H), 7.61 (d, *J* = 2.0 Hz, 1H), 7.27 (d, *J* = 16.6 Hz, 1H), 7.03 (d, *J* = 16.6 Hz, 1H), 4.17 (t, *J* = 7.1 Hz, 2H), 3.74 (s, 3H), 3.35 – 3.25 (m, 2H), 2.59 (s, 3H), 2.09 (s, 3H), 1.92 – 1.80 (m, 2H), 1.78 – 1.67 (m, 2H); <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>) δ 153.7, 148.8, 144.8, 138.5, 133.2, 131.9, 131.5, 130.8, 123.3, 122.8, 122.0, 121.3, 49.5, 47.3, 35.0, 28.1, 20.1, 12.8, 9.6; Calcd. for C<sub>19</sub>H<sub>26</sub>N<sub>5</sub>O<sub>4</sub>S<sup>+</sup> 420.1700, found 420.1715 [M – CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>]<sup>+</sup>.

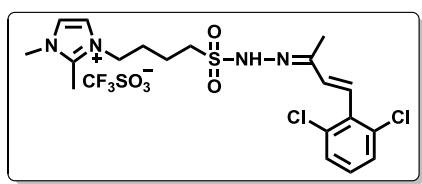


**Compound 9f:** Yield 74%; Pale yellow solid; mp 155-157 °C; <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ 10.31 (s, 1H), 7.68 – 7.58 (m, 4H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 16.6 Hz, 1H), 6.86 (d, *J* = 16.6 Hz, 1H), 4.17 (t, *J* = 7.0 Hz, 2H), 3.74 (s, 3H), 3.33 – 3.23 (m, 2H), 2.59 (s, 3H), 2.07 (s, 3H), 1.91-1.81 (m, 2H), 1.76-1.70 (m, 2H); <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>) δ 154.2, 144.8, 135.5, 133.3, 132.9, 129.6, 129.3, 129.1, 122.8, 121.3, 121.1 (q, *J*<sub>C-F</sub> = 320.25 Hz), 49.4, 47.3, 35.1, 28.1, 20.1, 12.9, 9.6; Calcd. for C<sub>19</sub>H<sub>26</sub>ClN<sub>4</sub>O<sub>2</sub>S<sup>+</sup> 409.1460, found 409.1452 [M – CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>]<sup>+</sup>.

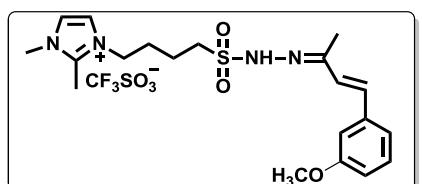


**Compound 9g:** Yield 87%; Pale yellow solid; mp 141-142 °C; <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>) δ 10.32 (s, 1H), 7.64 (d, *J* = 1.7 Hz, 2H), 7.62 (d, *J* = 1.9 Hz, 1H), 7.60 – 7.52 (m, 3H), 7.08 (d, *J* = 16.6

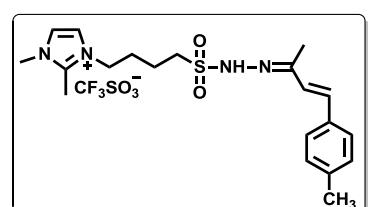
Hz, 1H), 6.87 (d,  $J$  = 16.6 Hz, 1H), 4.16 (t,  $J$  = 7.0 Hz, 2H), 3.74 (s, 3H), 3.33 – 3.23 (m, 2H), 2.59 (s, 3H), 2.07 (s, 3H), 1.90–1.81 (m, 2H), 1.76–1.68 (m, 2H);  $^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ )  $\delta$  154.2, 144.8, 135.8, 132.9, 132.2, 129.6, 129.4, 122.8, 122.0, 121.3, 121.1 (q,  $J_{C-F}$  = 320.25 Hz), 49.4, 47.3, 35.1, 28.1, 20.1, 12.9, 9.6; Calcd. for  $\text{C}_{19}\text{H}_{26}\text{BrN}_4\text{O}_2\text{S}^+$  453.0954, found 453.0927 [ $\text{M} - \text{CF}_3\text{SO}_3^-$ ] $^+$  and 455.0918 [ $\text{M} + 2 - \text{CF}_3\text{SO}_3^-$ ] $^+$



**Compound 9h:** Yield 80%; White solid; mp 155–157 °C;  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  10.46 (s, 1H), 7.62 (d,  $J$  = 2.8 Hz, 2H), 7.55 (d,  $J$  = 8.1 Hz, 2H), 7.40 – 7.32 (m, 1H), 7.01 (d,  $J$  = 16.8 Hz, 1H), 6.71 (d,  $J$  = 16.8 Hz, 1H), 4.16 (m, 2H), 3.74 (s, 3H), 3.31 – 3.24 (m, 2H), 2.58 (s, 3H), 2.10 (s, 3H), 1.91–1.81 (m, 2H), 1.76–1.67 (m, 2H);  $^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ )  $\delta$  153.3, 144.8, 137.0, 133.9, 133.6, 130.4, 129.5, 127.7, 122.8, 121.3, 121.1 (q,  $J_{C-F}$  = 320.25 Hz), 49.5, 47.3, 35.1, 28.1, 20.0, 12.6, 9.6; Calcd. for  $\text{C}_{19}\text{H}_{25}\text{Cl}_2\text{N}_4\text{O}_2\text{S}^+$  443.1070, found 443.1043 [ $\text{M} - \text{CF}_3\text{SO}_3^-$ ] $^+$ .

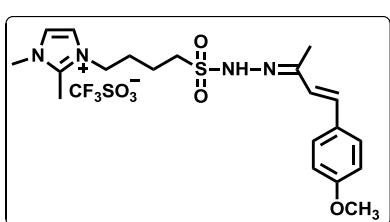


**Compound 9i:** Yield 54%; Yellow solid; mp 125–127 °C;  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  10.28 (s, 1H), 7.64 (d,  $J$  = 2.0 Hz, 1H), 7.62 (d,  $J$  = 2.0 Hz, 1H), 7.33 – 7.25 (m, 2H), 7.16 (d,  $J$  = 7.2 Hz, 2H), 7.07 (d,  $J$  = 16.6 Hz, 1H), 6.88 (dd,  $J$  = 12.7, 9.4 Hz, 2H), 4.16 (t,  $J$  = 7.1 Hz, 2H), 3.79 (s, 3H), 3.74 (s, 3H), 3.33 – 3.23 (m, 2H), 2.59 (s, 3H), 2.07 (s, 3H), 1.92 – 1.79 (m, 2H), 1.77 – 1.65 (m, 2H);  $^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ )  $\delta$  160.1, 154.5, 144.8, 138.0, 134.2, 130.3, 129.0, 122.8, 121.3, 121.1 (q,  $J_{C-F}$  = 320.25 Hz), 120.0, 115.1, 112.1, 55.6, 49.4, 47.3, 35.1, 28.1, 20.1, 12.9, 9.6; Calcd. for  $\text{C}_{19}\text{H}_{29}\text{N}_4\text{O}_3\text{S}^+$  405.1955, found 405.1972 [ $\text{M} - \text{CF}_3\text{SO}_3^-$ ] $^+$ .

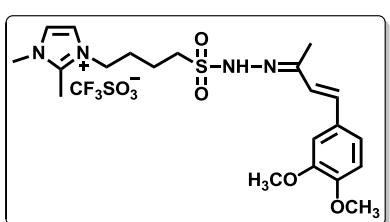


**Compound 9j:** Yield 67%; Yellow solid; mp 148–150 °C;  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  10.22 (s, 1H), 7.64 (d,  $J$  = 2.0 Hz, 1H), 7.61 (d,  $J$  = 2.0 Hz, 1H), 7.48 (d,  $J$  = 8.1 Hz, 2H), 7.19 (d,  $J$  = 8.0 Hz, 2H), 7.05 (d,  $J$  = 16.6 Hz, 1H), 6.78 (d,  $J$  = 16.6 Hz, 1H), 4.16 (t,  $J$  = 7.1 Hz, 2H), 3.74 (s, 3H), 3.32 – 3.22 (m, 2H), 2.59 (s, 3H), 2.31 (s, 3H), 2.06 (s, 3H), 1.92 – 1.78 (m, 2H), 1.76–1.68 (m, 2H);  $^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ )  $\delta$  154.7, 144.2, 138.6, 134.2, 133.7, 129.9, 127.8, 127.4, 122.8, 121.3, 121.1 (q,

$J_{C-F} = 320.25$  Hz), 49.3, 47.3, 35.1, 28.1, 21.3, 20.1, 12.9, 9.6; Calcd. for  $C_{19}H_{29}N_4O_2S^+$  389.2006, found 389.1987  $[M - CF_3SO_3^-]^+$ .

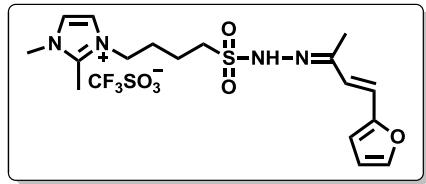


**Compound 9k:** Yield 92%; Yellow solid; mp 128-130 °C;  $^1H$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  10.17 (s, 1H), 7.64 (d,  $J = 2.0$  Hz, 1H), 7.62 (d,  $J = 2.0$  Hz, 1H), 7.53 (d,  $J = 8.8$  Hz, 2H), 7.04 (d,  $J = 16.8$  Hz, 1H), 6.96 (t,  $J = 7.0$  Hz, 2H), 6.71 (d,  $J = 16.5$  Hz, 1H), 4.16 (t,  $J = 7.1$  Hz, 2H), 3.78 (s, 3H), 3.74 (s, 3H), 3.31 – 3.23 (m, 2H), 2.59 (s, 3H), 2.05 (s, 3H), 1.92 – 1.78 (m, 2H), 1.77 – 1.64 (m, 2H);  $^{13}C$  NMR (75 MHz, DMSO- $d_6$ )  $\delta$  160.1, 154.9, 144.8, 134.0, 129.1, 128.9, 126.5, 122.8, 121.3, 121.1 (q,  $J_{C-F} = 320.25$  Hz), 114.7, 55.7, 49.3, 47.3, 35.1, 28.1, 20.1, 12.9, 9.6; Calcd. for  $C_{19}H_{29}N_4O_3S^+$  405.1955, found 405.1969  $[M - CF_3SO_3^-]^+$ .

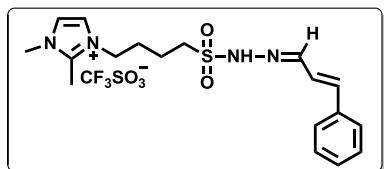


**Compound 9l:** Yield 71%; Yellow solid; mp 106-108 °C;  $^1H$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  10.19 (s, 1H), 7.65 (d,  $J = 2.0$  Hz, 1H), 7.62 (d,  $J = 2.0$  Hz, 1H), 7.21 (d,  $J = 1.6$  Hz, 1H), 7.13 – 7.04 (m, 1H), 6.97 (dd,  $J = 11.0, 5.7$  Hz, 2H), 6.76 (d,  $J = 16.5$  Hz, 1H), 4.17 (t,  $J = 7.1$  Hz, 2H), 3.81 (s, 3H), 3.77 (s, 3H), 3.74 (s, 3H), 3.31 – 3.23 (m, 2H), 2.59 (s, 3H), 2.06 (s, 3H), 1.91-1.81 (m, 2H), 1.74-1.69 (m, 2H);  $^{13}C$  NMR (75 MHz, DMSO- $d_6$ )  $\delta$  155.0, 149.9, 149.4, 144.8, 134.4, 129.4, 126.6, 122.8, 121.3, 121.3, 121.1 (q,  $J_{C-F} = 320.25$  Hz), 112.1, 109.8, 55.96, 55.95, 49.3, 47.3, 35.1, 28.1, 20.1, 12.9, 9.6; Calcd. for  $C_{19}H_{31}N_4O_4S^+$  435.2061, found 435.2096  $[M - CF_3SO_3^-]^+$ .

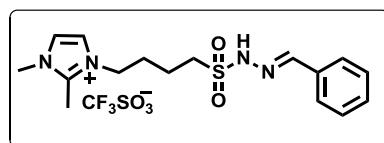
**Compound 9m:** Yield 80%; White solid; mp 138-140 °C;  $^1H$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  10.26 (s, 1H), 7.64 (d,  $J = 1.8$  Hz, 1H), 7.61 (d,  $J = 2.1$  Hz, 1H), 7.54 (d,  $J = 5.1$  Hz, 1H), 7.29 (dd,  $J = 9.8, 6.4$  Hz, 2H), 7.09 (dd,  $J = 5.1, 3.6$  Hz, 1H), 6.54 (d,  $J = 16.3$  Hz, 1H), 4.16 (t,  $J = 7.1$  Hz, 2H), 3.74 (s, 3H), 3.32 – 3.23 (m, 2H), 2.59 (s, 3H), 2.03 (s, 3H), 1.88-1.81 (m, 2H), 1.75-1.69 (m, 2H);  $^{13}C$  NMR (75 MHz, DMSO- $d_6$ )  $\delta$  157.2, 154.0, 144.8, 141.6, 128.8, 127.9, 127.5, 127.2, 122.8, 121.3, 121.1 (q,  $J_{C-F} = 320.25$  Hz), 49.3, 47.9, 35.1, 28.1, 20.1, 12.8, 9.6; Calcd. for  $C_{17}H_{25}N_4O_2S_2^+$  381.1413, found 381.1437  $[M - CF_3SO_3^-]^+$ .



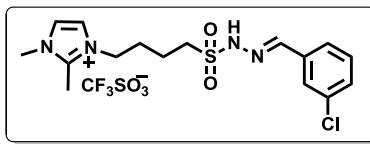
**Compound 9n:** Yield 88%; Brown solid; mp 145-146 °C;  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  10.30 (s, 1H), 7.73 (d,  $J$  = 0.9 Hz, 1H), 7.65 (d,  $J$  = 1.8 Hz, 1H), 7.63 (d,  $J$  = 1.9 Hz, 1H), 6.95 (d,  $J$  = 16.4 Hz, 1H), 6.67 (d,  $J$  = 3.3 Hz, 1H), 6.63 (s, 1H), 6.57 (d,  $J$  = 3.8 Hz, 1H), 4.17 (t,  $J$  = 6.9 Hz, 2H), 3.75 (s, 3H), 3.32 – 3.24 (m, 2H), 2.60 (s, 3H), 2.03 (s, 3H), 1.91-1.81 (m, 2H), 1.76-1.68 (m, 2H);  $^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ )  $\delta$  154.1, 152.3, 144.8, 144.4, 126.6, 122.8, 122.0, 121.3, 121.1 (q,  $J_{C-F}$  = 320.25 Hz), 112.8, 111.6, 49.4, 47.3, 35.1, 28.1, 20.0, 12.7, 9.6; Calcd. for  $\text{C}_{17}\text{H}_{25}\text{N}_4\text{O}_3\text{S}^+$  365.1642, found 365.1671 [ $\text{M} - \text{CF}_3\text{SO}_3^-$ ] $^+$ .



**Compound 9o:** Yield 59%; Light Brown solid; mp 129-131 °C;  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  11.35 (s, 1H), 7.87 (d,  $J$  = 8.7 Hz, 1H), 7.66 (d,  $J$  = 2.1 Hz, 1H), 7.63 (d,  $J$  = 2.1 Hz, 1H), 7.61 (d,  $J$  = 1.4 Hz, 1H), 7.58 (s, 1H), 7.43 – 7.31 (m, 3H), 7.02 (d,  $J$  = 16.1 Hz, 1H), 6.91 (dd,  $J$  = 16.1, 8.7 Hz, 1H), 4.16 (t,  $J$  = 7.1 Hz, 2H), 3.74 (s, 3H), 3.29 – 3.19 (m, 2H), 2.59 (s, 3H), 1.90-1.81 (m, 2H), 1.75-1.66 (m, 2H);  $^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ )  $\delta$  149.1, 144.8, 139.2, 136.2, 129.3, 127.5, 125.3, 123.3, 122.8, 121.3, 121.1 (q,  $J_{C-F}$  = 320.25 Hz), 49.9, 47.3, 35.1, 28.0, 20.1, 9.6; Calcd. for  $\text{C}_{18}\text{H}_{25}\text{N}_4\text{O}_2\text{S}^+$  361.1693, found 361.1706 [ $\text{M} - \text{CF}_3\text{SO}_3^-$ ] $^+$ .

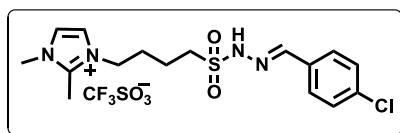


**Compound 10a:** Yield 88%; Pale yellow solid; mp 135-137 °C;  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  11.39 (s, 1H), 8.06 (s, 1H), 7.66 (d,  $J$  = 4.1 Hz, 1H), 7.65 – 7.61 (m, 2H), 7.59 (d,  $J$  = 2.0 Hz, 1H), 7.45 (d,  $J$  = 1.2 Hz, 1H), 7.43 (d,  $J$  = 2.2 Hz, 2H), 4.16 (t,  $J$  = 7.1 Hz, 2H), 3.73 (s, 3H), 3.35 – 3.25 (m, 2H), 2.57 (s, 3H), 1.91 - 1.81 (m, 2H), 1.79 – 1.66 (m, 2H);  $^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ )  $\delta$  146.90, 144.8, 134.3, 130.5, 129.3, 127.3, 122.8, 121.3, 121.1 (q,  $J_{C-F}$  = 320.25 Hz), 50.0, 47.3, 35.1, 28.0, 20.1, 9.6; Calcd for  $\text{C}_{16}\text{H}_{23}\text{N}_4\text{O}_2\text{S}^+$  335.1536, found 335.1523 [ $\text{M} - \text{CF}_3\text{SO}_3^-$ ] $^+$ .

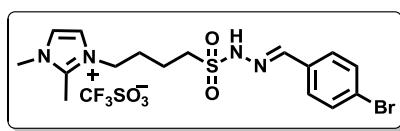


**Compound 10b:** Yield 76%; Pale yellow solid; mp 136-137 °C;  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  11.63 (s, 1H), 8.07 (s, 1H), 7.73 (s, 1H), 7.64 (d,  $J$  = 2.1 Hz, 1H), 7.60 (d,  $J$  = 1.9 Hz, 1H),

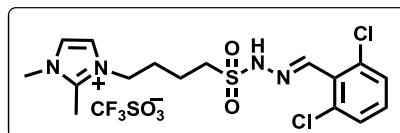
7.48 (dd,  $J = 3.7$ , 1.9 Hz, 1H), 4.17 (t,  $J = 7.1$  Hz, 1H), 3.74 (s, 1H), 3.38 – 3.28 (m, 1H), 2.59 (s, 1H), 1.93 – 1.80 (m, 2H), 1.78–1.70 (m, 2H);  $^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ )  $\delta$  145.1, 144.8, 136.5, 134.1, 131.2, 130.1, 126.4, 126.2, 122.8, 121.3, 121.1 (q,  $J_{C-F} = 320.25$  Hz), 50.1, 47.3, 35.1, 28.0, 20.1, 9.6; Calcd for  $\text{C}_{16}\text{H}_{22}\text{ClN}_4\text{O}_2\text{S}^+$  369.1147, found 369.1171 [ $\text{M} - \text{CF}_3\text{SO}_3^-$ ]<sup>+</sup>.



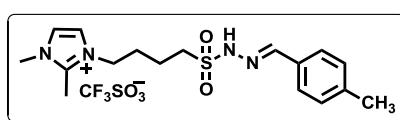
**Compound 10c:** Yield 72%; White solid; mp 154–155 °C;  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  11.52 (s, 1H), 8.06 (s, 1H), 7.69 (d,  $J = 1.7$  Hz, 1H), 7.66 (d,  $J = 3.5$  Hz, 1H), 7.64 (d,  $J = 2.1$  Hz, 1H), 7.60 (d,  $J = 2.0$  Hz, 1H), 7.52 (s, 1H), 7.49 (d,  $J = 1.6$  Hz, 1H), 4.16 (t,  $J = 7.1$  Hz, 2H), 3.74 (s, 3H), 3.36 – 3.25 (m, 2H), 2.58 (s, 3H), 1.90 – 1.79 (m, 2H), 1.78 – 1.66 (m, 2H);  $^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ )  $\delta$  145.5, 144.8, 134.9, 133.3, 129.3, 128.9, 122.8, 121.3, 121.1 (q,  $J_{C-F} = 320.25$  Hz), 50.1, 47.3, 35.1, 28.0, 20.1, 9.6; Calcd for  $\text{C}_{16}\text{H}_{22}\text{ClN}_4\text{O}_2\text{S}^+$  369.1147, found 369.1165 [ $\text{M} - \text{CF}_3\text{SO}_3^-$ ]<sup>+</sup>.



**Compound 10d:** Yield 79%; White solid; mp 132–133 °C;  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  11.55 (s, 1H), 8.05 (s, 1H), 7.66 (d,  $J = 2.3$  Hz, 1H), 7.64 (d,  $J = 2.3$  Hz, 2H), 7.62 – 7.58 (m, 3H), 4.16 (t,  $J = 7.1$  Hz, 2H), 3.74 (s, 3H), 3.34 – 3.26 (m, 2H), 2.58 (s, 3H), 1.90 – 1.79 (m, 2H), 1.78 – 1.66 (m, 2H);  $^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ )  $\delta$  145.6, 144.8, 133.6, 132.2, 129.2, 123.7, 122.8, 121.3, 121.1 (q,  $J_{C-F} = 320.25$  Hz), 50.1, 47.3, 35.1, 28.0, 20.1, 9.6; Calcd for  $\text{C}_{16}\text{H}_{22}\text{BrN}_4\text{O}_2\text{S}^+$  413.0641, found 413.0659 [ $\text{M} - \text{CF}_3\text{SO}_3^-$ ]<sup>+</sup> and 415.0643 [ $\text{M} + 2 - \text{CF}_3\text{SO}_3^-$ ]<sup>+</sup>.

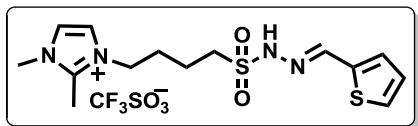


**Compound 10e:** Yield 77%; White solid; mp 152–154 °C;  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  11.75 (s, 1H), 8.16 (s, 1H), 7.63 (d,  $J = 2.0$  Hz, 1H), 7.61 (d,  $J = 2.0$  Hz, 1H), 7.58 (d,  $J = 1.2$  Hz, 1H), 7.55 (s, 1H), 7.45 (dd,  $J = 9.0$ , 7.0 Hz, 1H), 4.16 (t,  $J = 7.1$  Hz, 2H), 3.75 (s, 3H), 3.36 – 3.27 (m, 2H), 2.59 (s, 3H), 1.91–1.82 (m, 2H), 1.80 – 1.67 (m, 2H);  $^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ )  $\delta$  144.8, 141.6, 134.3, 131.8, 130.4, 129.6, 122.8, 121.3, 121.1 (q,  $J_{C-F} = 320.25$  Hz), 50.4, 47.3, 35.1, 28.0, 20.2, 9.6; Calcd for  $\text{C}_{16}\text{H}_{21}\text{Cl}_2\text{N}_4\text{O}_2\text{S}^+$  403.0757, found 403.0728 [ $\text{M} - \text{CF}_3\text{SO}_3^-$ ]<sup>+</sup>.



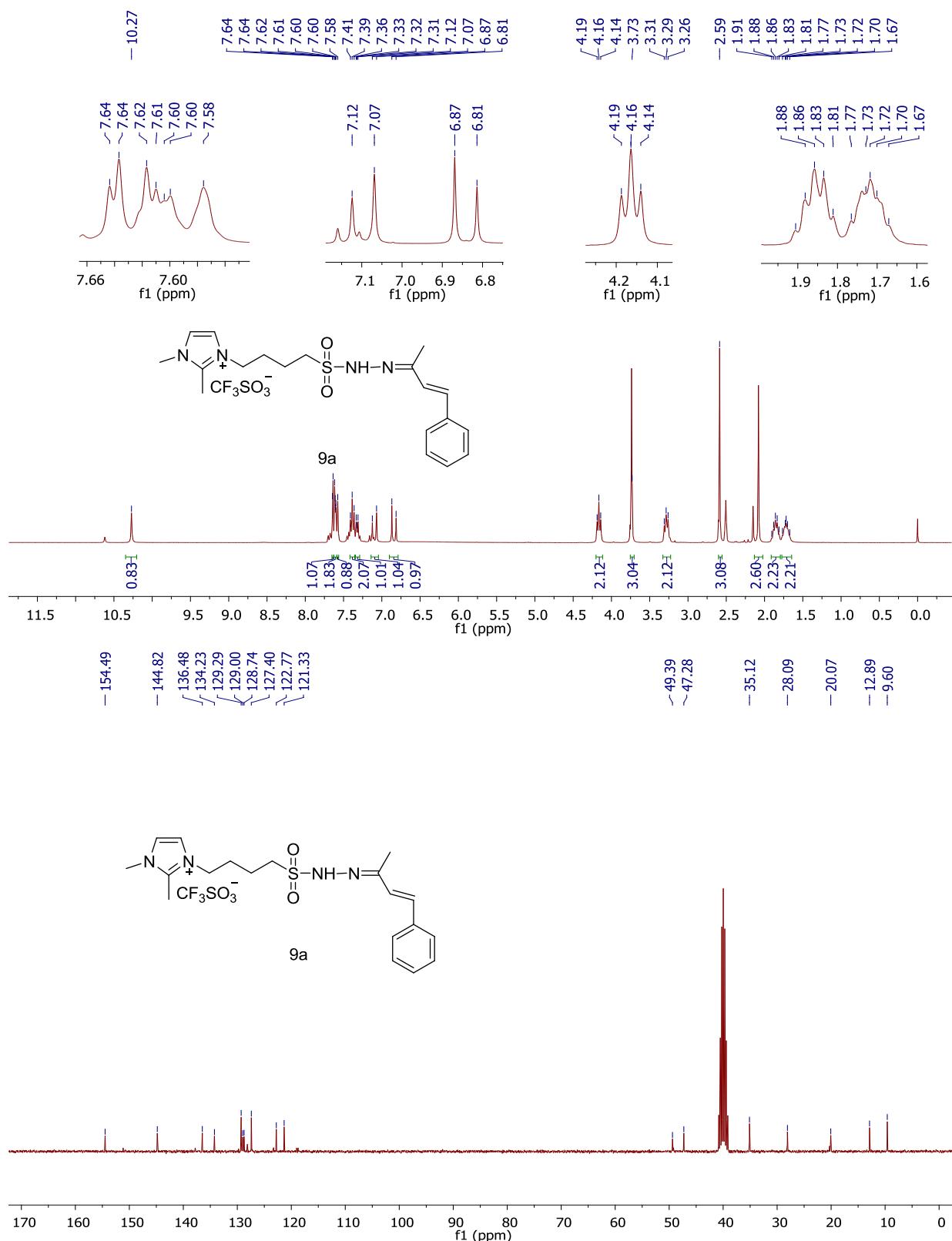
**Compound 10f:** Yield 89%; White solid; mp 131–132 °C;  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  8.02 (s, 1H), 7.63 (d,  $J = 2.1$

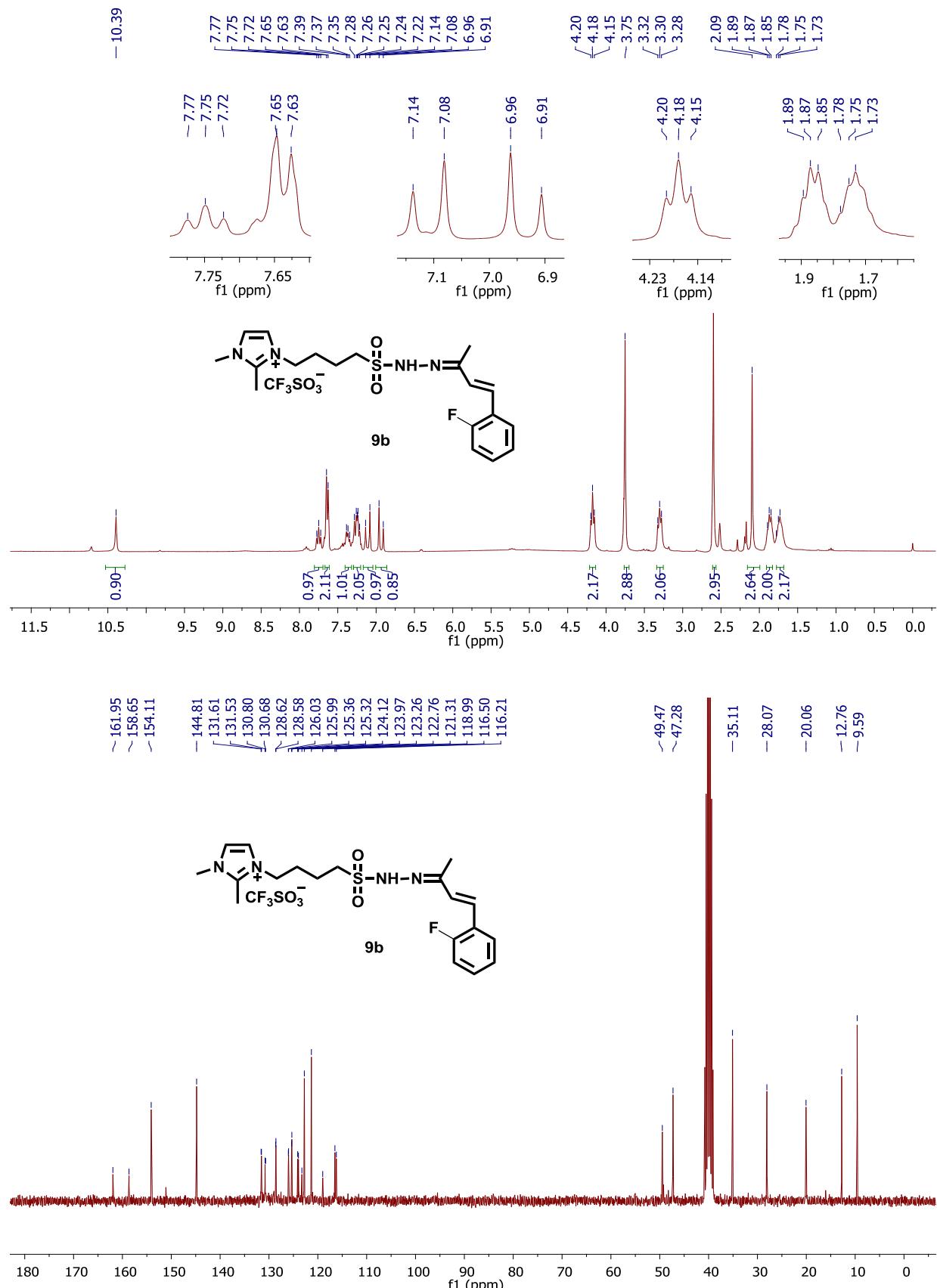
Hz, 1H), 7.59 (d,  $J$  = 2.0 Hz, 1H), 7.54 (d,  $J$  = 8.1 Hz, 2H), 7.25 (d,  $J$  = 8.0 Hz, 2H), 4.16 (t,  $J$  = 7.1 Hz, 2H), 3.73 (s, 3H), 3.34 – 3.24 (m, 2H), 2.58 (s, 3H), 2.33 (s, 3H), 1.89 – 1.79 (m, 2H), 1.78 – 1.65 (m, 2H);  $^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ )  $\delta$  147.1, 144.8, 140.3, 131.6, 129.8, 127.3, 122.8, 121.3, 121.1 (q,  $J_{C-F}$  = 320.25 Hz), 49.9, 47.3, 35.1, 28.0, 21.4, 20.1, 9.6; Calcd for  $\text{C}_{17}\text{H}_{25}\text{N}_4\text{O}_2\text{S}^+$  349.1693, found 349.1682 [M – CF<sub>3</sub>SO<sub>3</sub>]<sup>+</sup>.

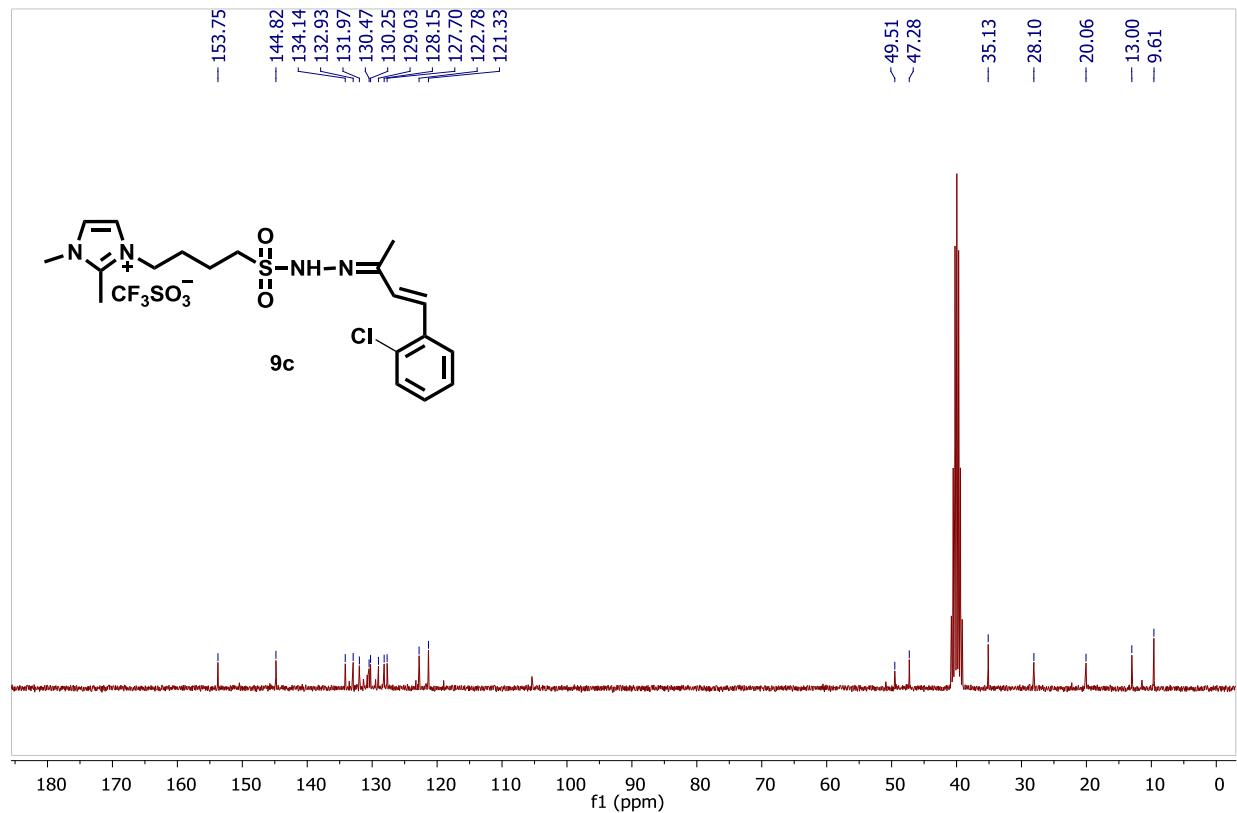
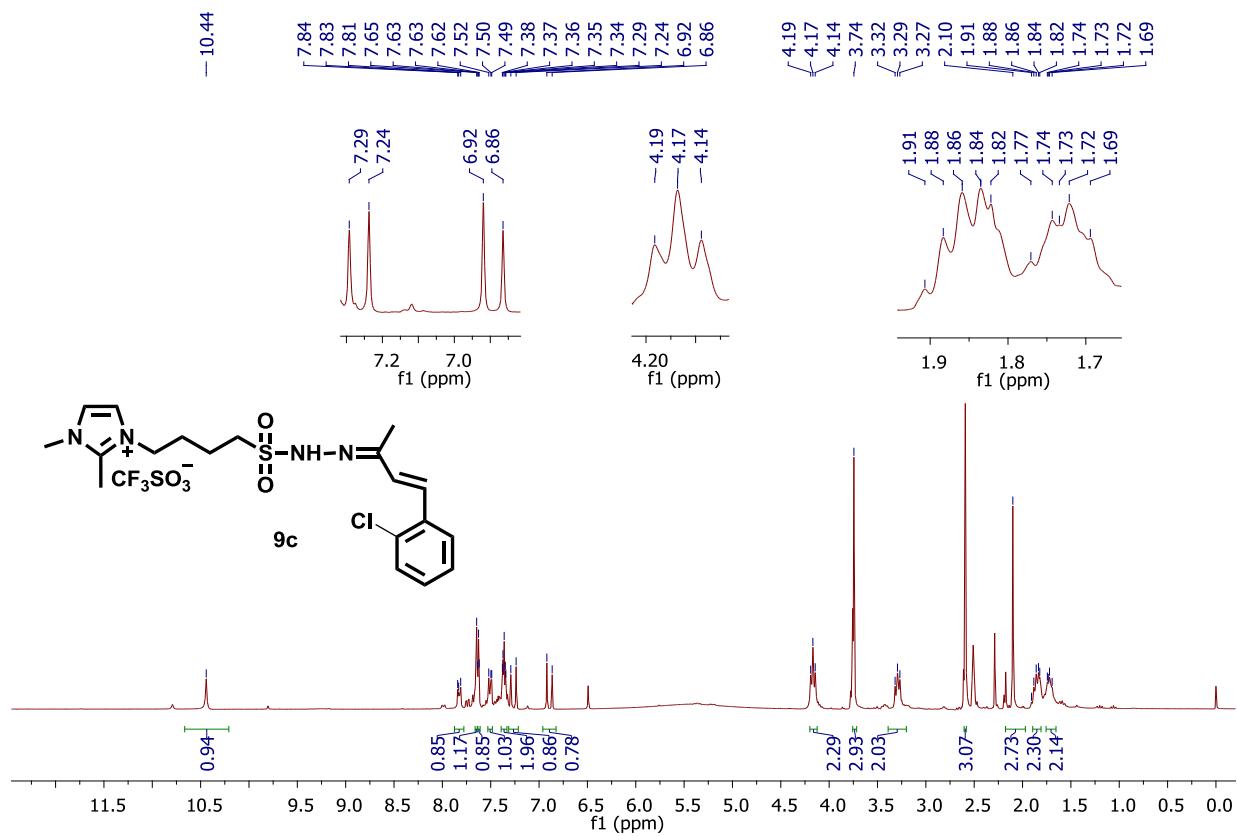


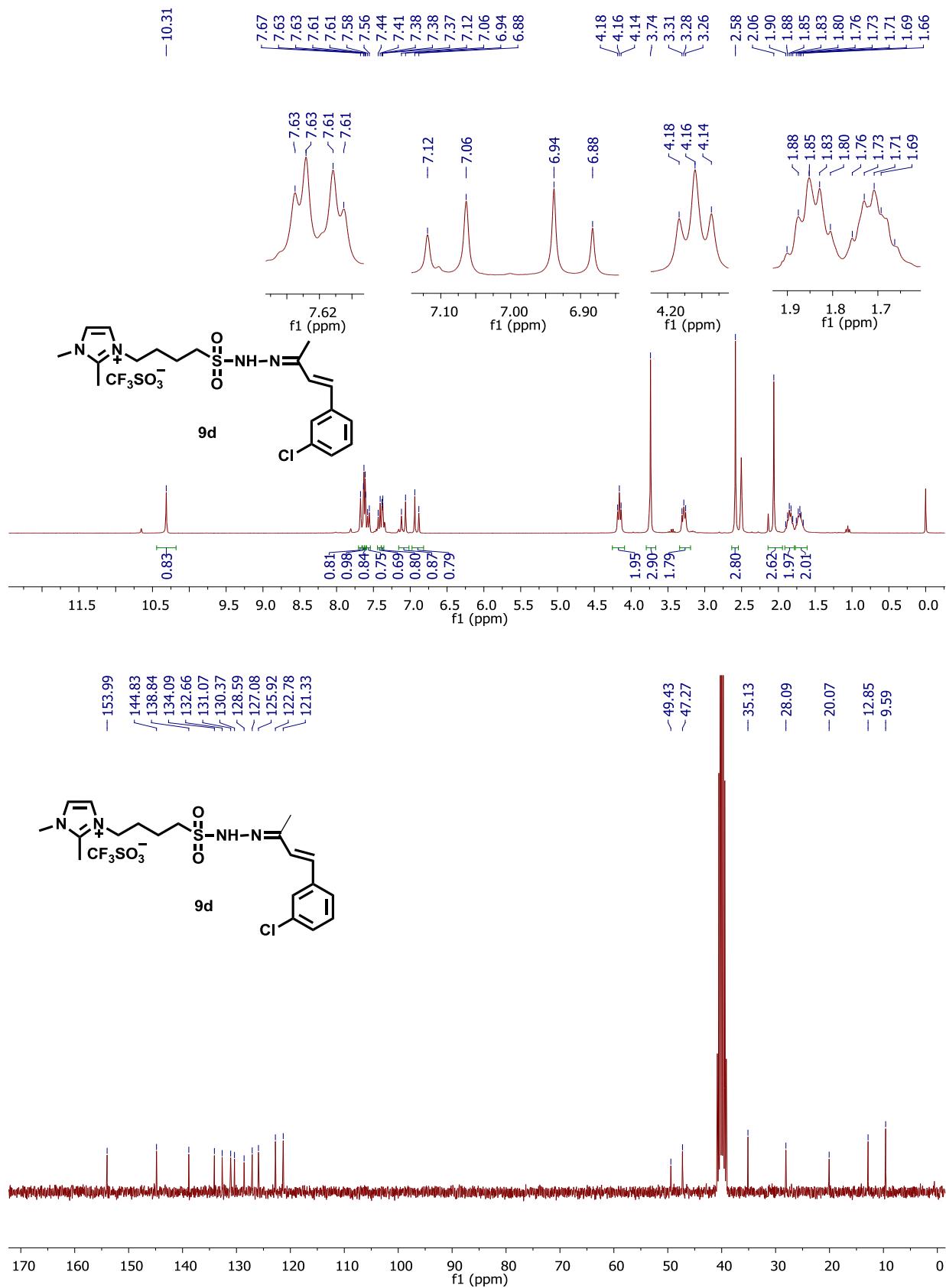
**Compound 10g:** Yield 88%; Pale yellow solid; mp 126–127 °C;  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  11.37 (s, 1H), 8.25 (s, 1H), 7.66 – 7.62 (m, 2H), 7.60 (d,  $J$  = 2.1 Hz, 1H), 7.42 (dd,  $J$  = 3.6, 0.9 Hz, 1H), 7.12 (dd,  $J$  = 5.0, 3.6 Hz, 1H), 4.16 (t,  $J$  = 7.1 Hz, 2H), 3.74 (s, 3H), 3.28 – 3.17 (m, 2H), 2.58 (s, 3H), 1.89 – 1.79 (m, 2H), 1.76 – 1.67 (m, 2H);  $^{13}\text{C}$  NMR (75 MHz, DMSO- $d_6$ )  $\delta$  144.8, 142.2, 138.8, 131.1, 129.1, 128.3, 122.8, 121.3, 121.1 (q,  $J_{C-F}$  = 320.25 Hz), 50.1, 47.3, 35.1, 28.0, 20.1, 9.6; Calcd for  $\text{C}_{14}\text{H}_{21}\text{N}_4\text{O}_2\text{S}_2^+$  341.1100, found 341.1092 [M – CF<sub>3</sub>SO<sub>3</sub>]<sup>+</sup>.

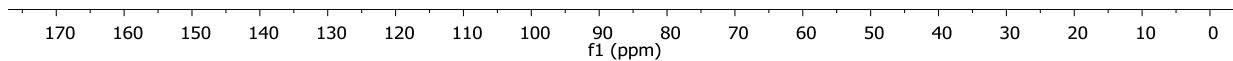
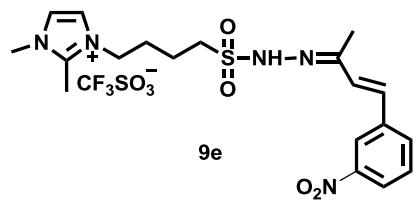
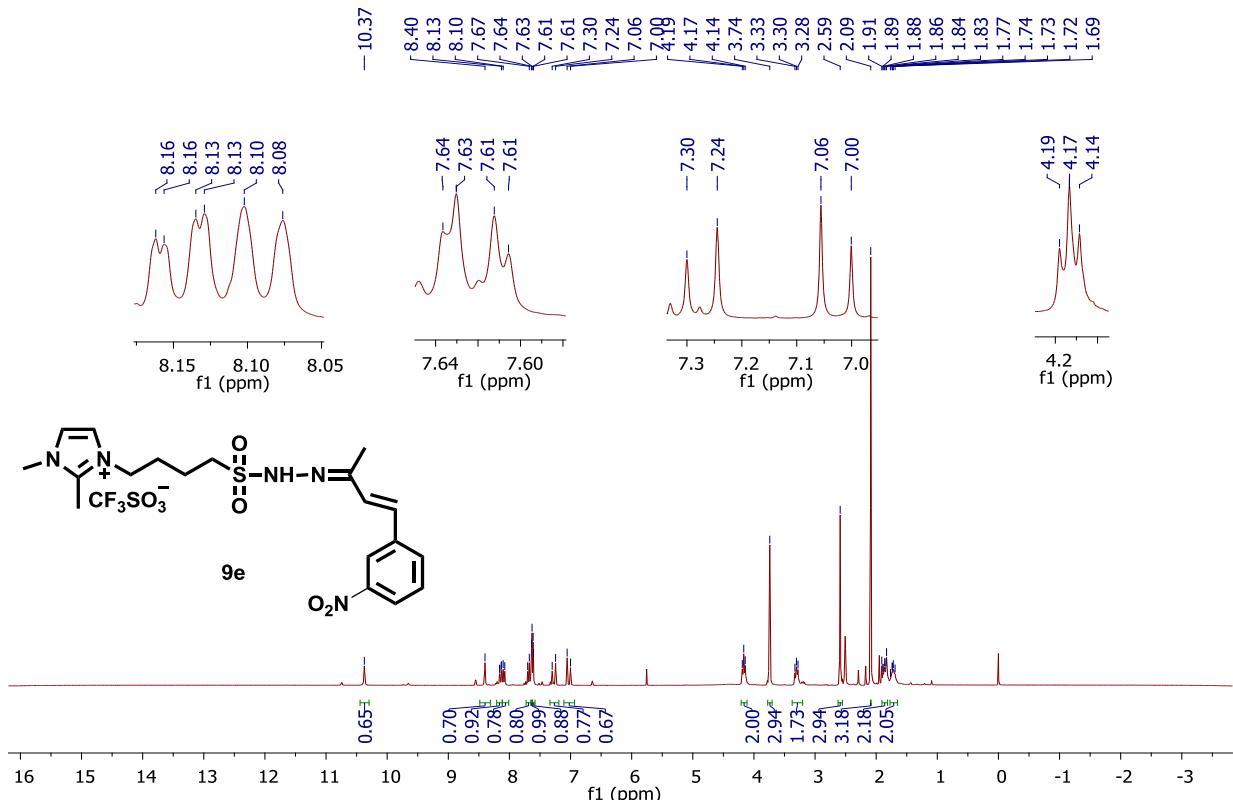
2. Copies of  $^1\text{H}$  and  $^{13}\text{C}$  NMR of ionic liquid-supported sulfonyl hydrazones **9** & **10**.

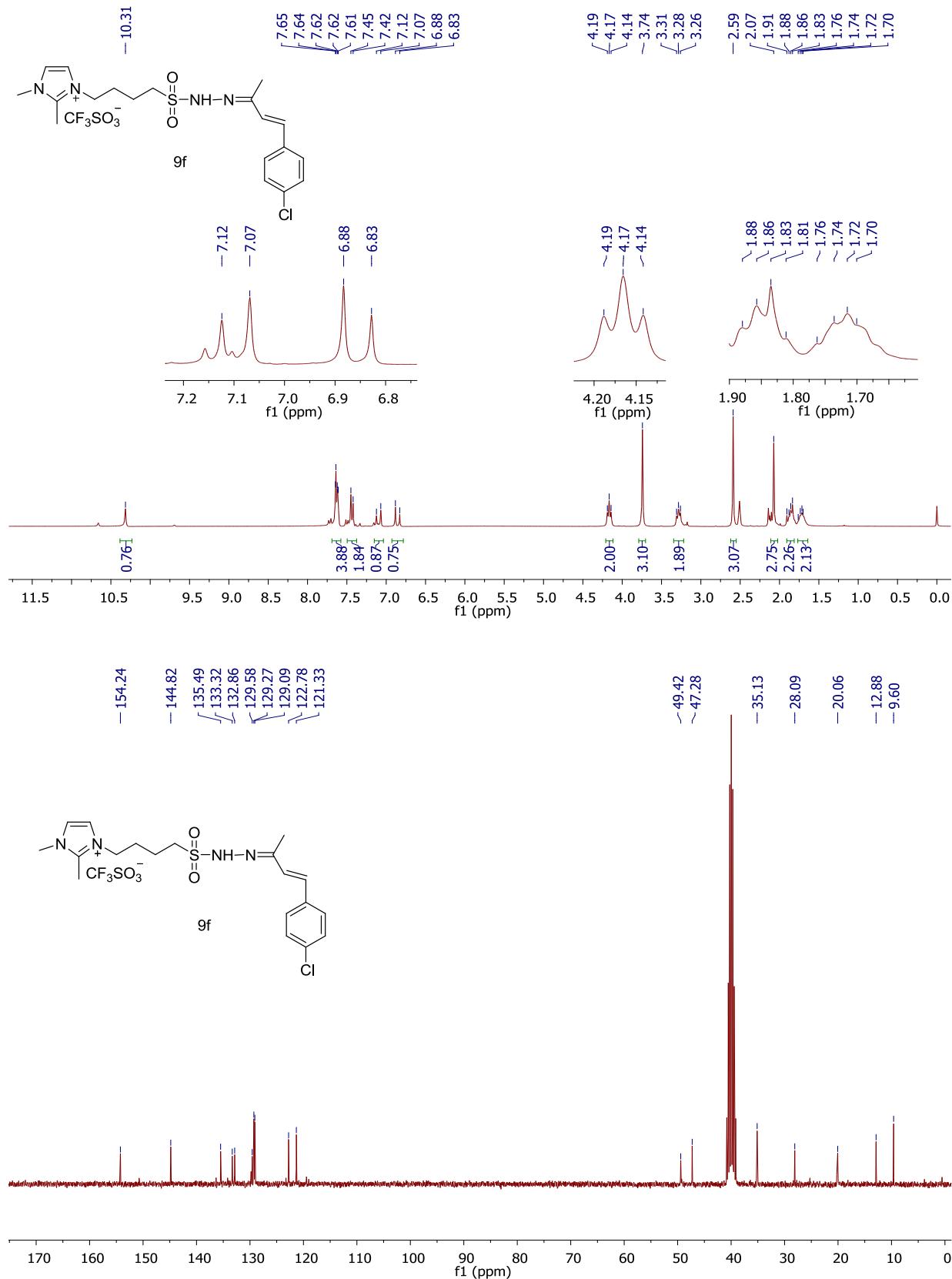


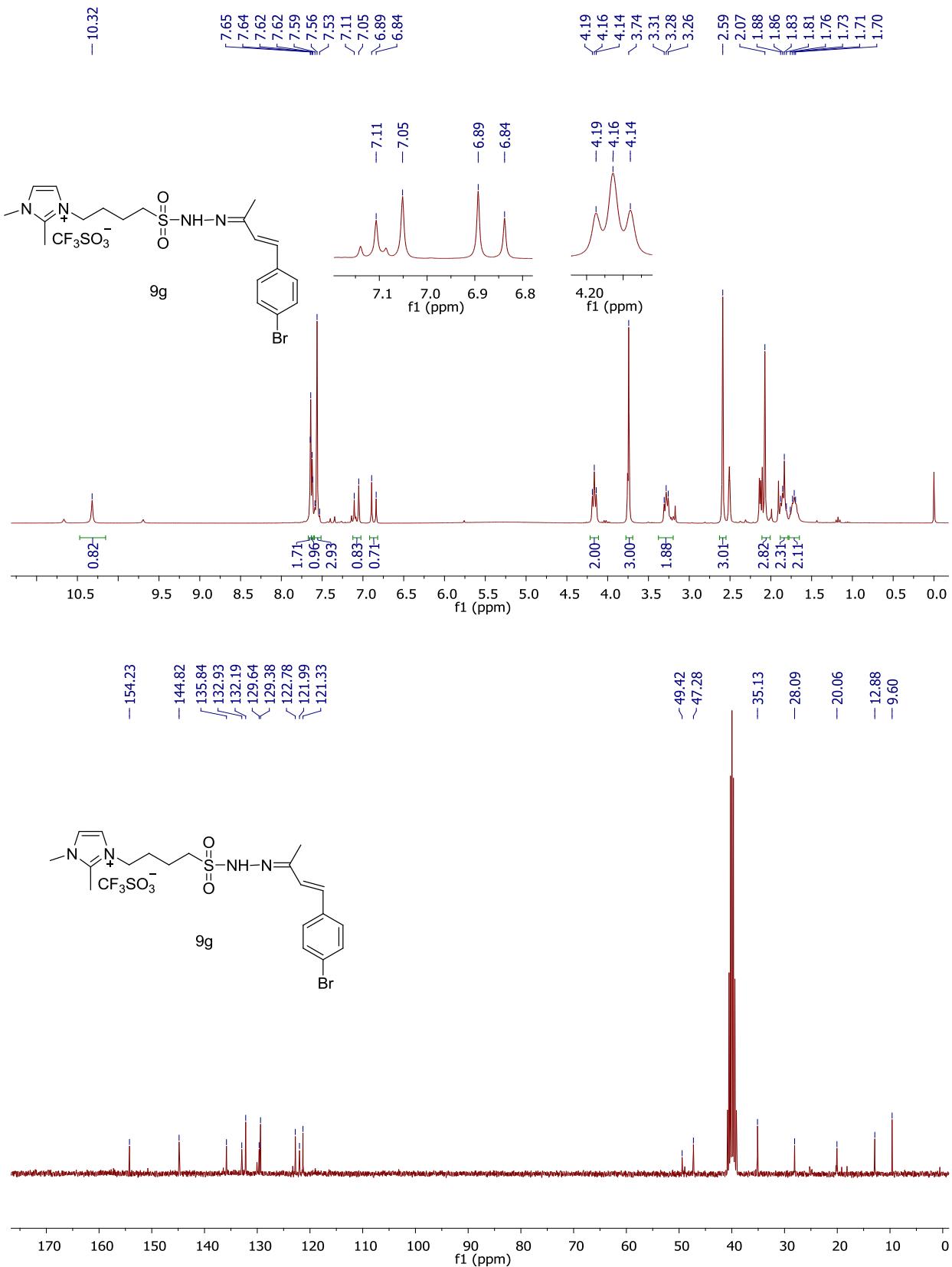


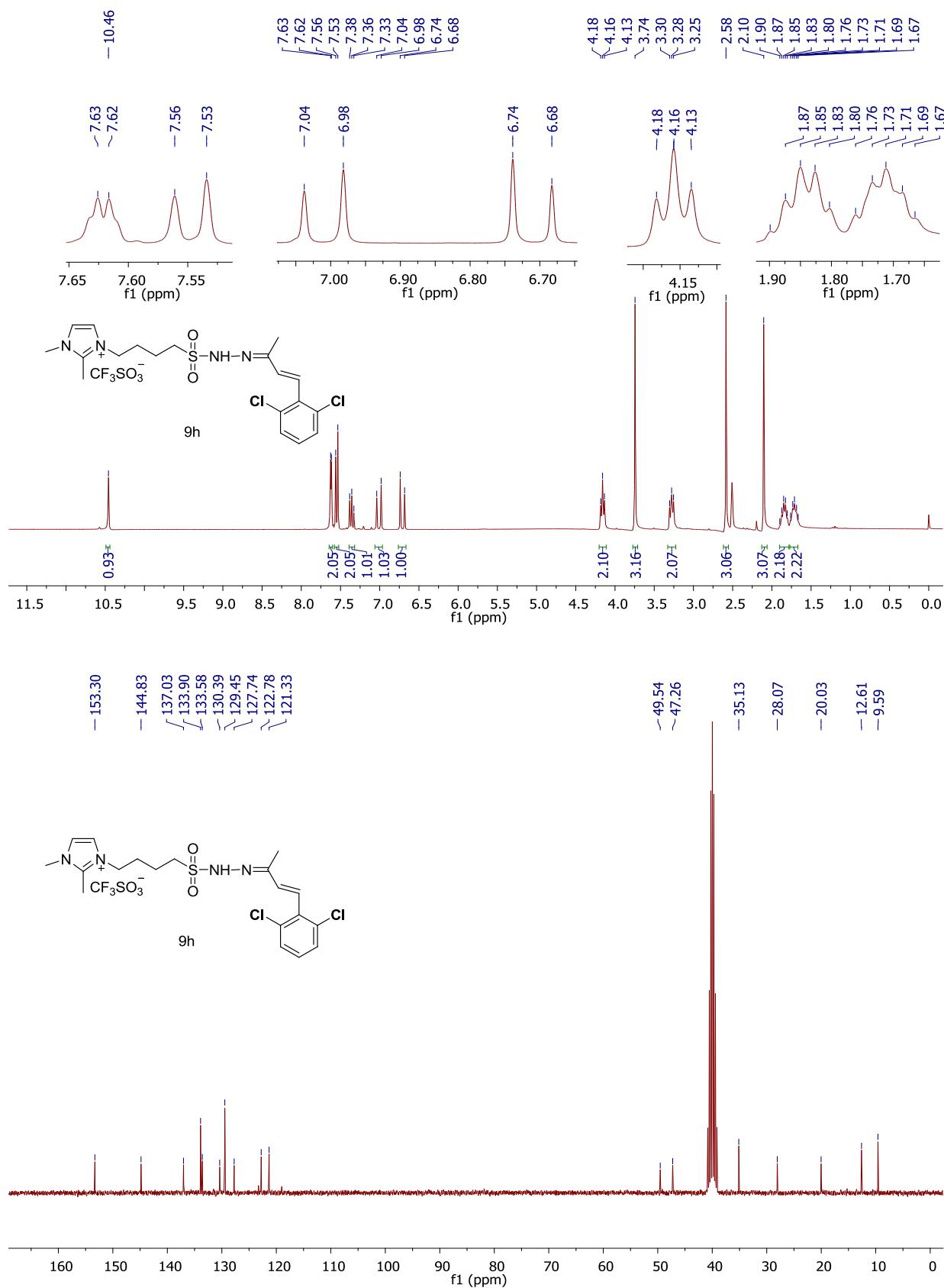


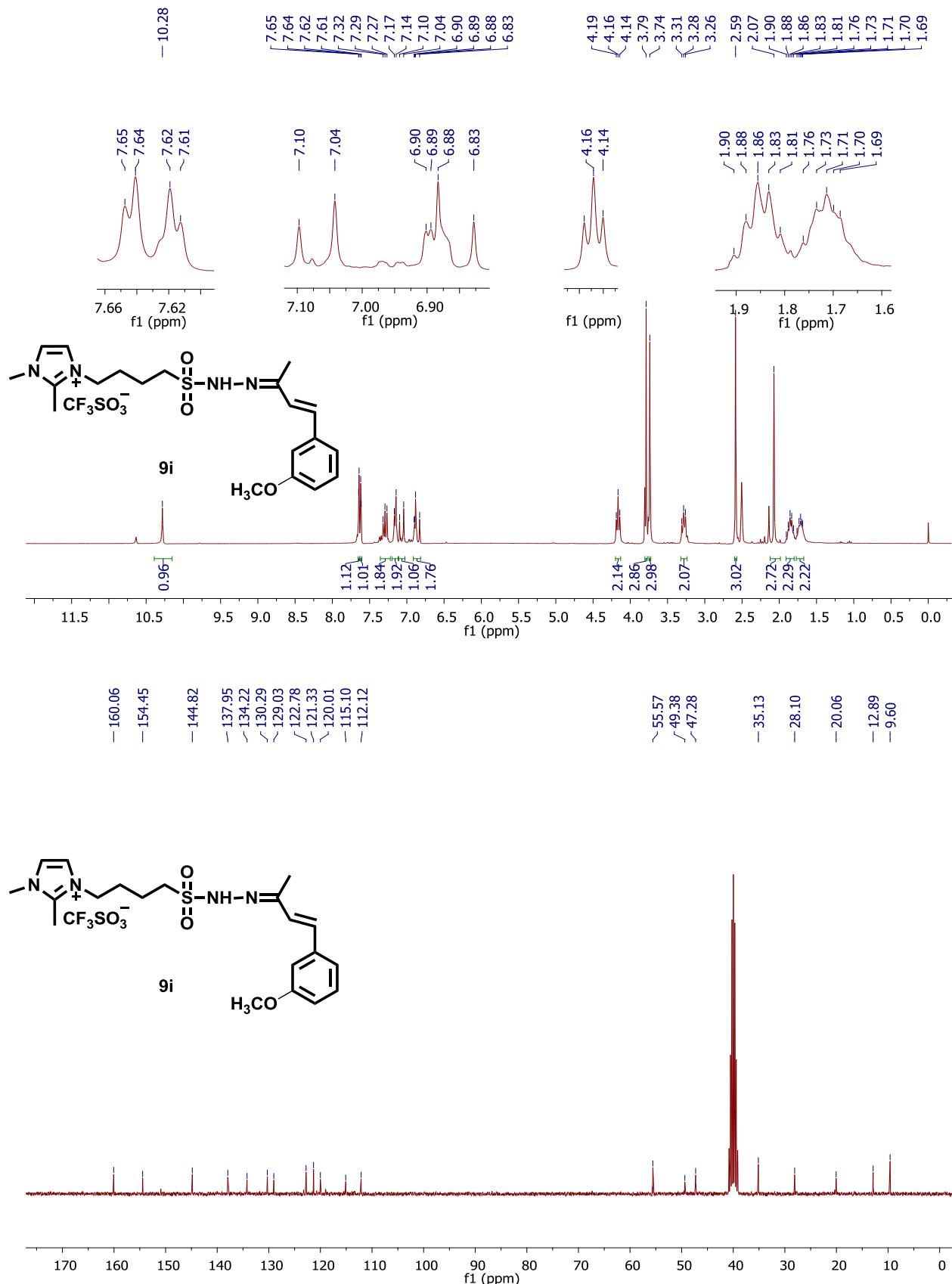


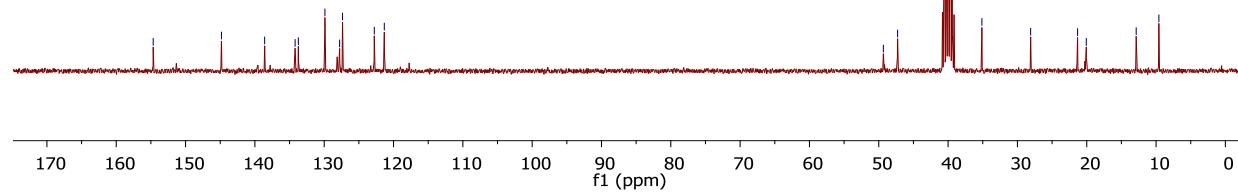
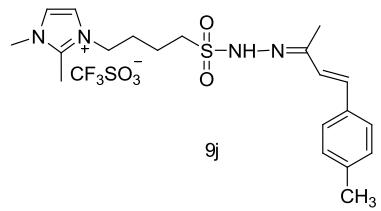
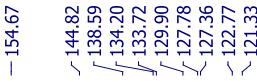
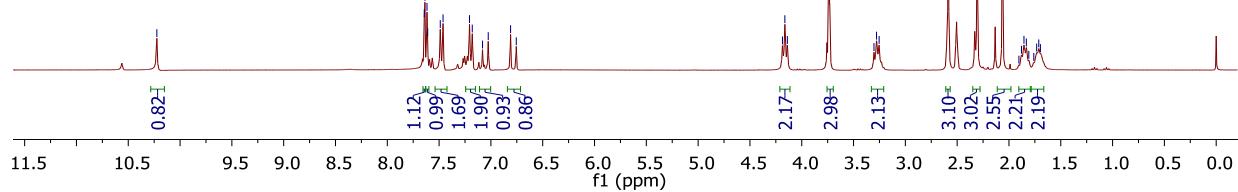
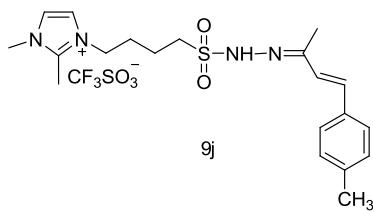
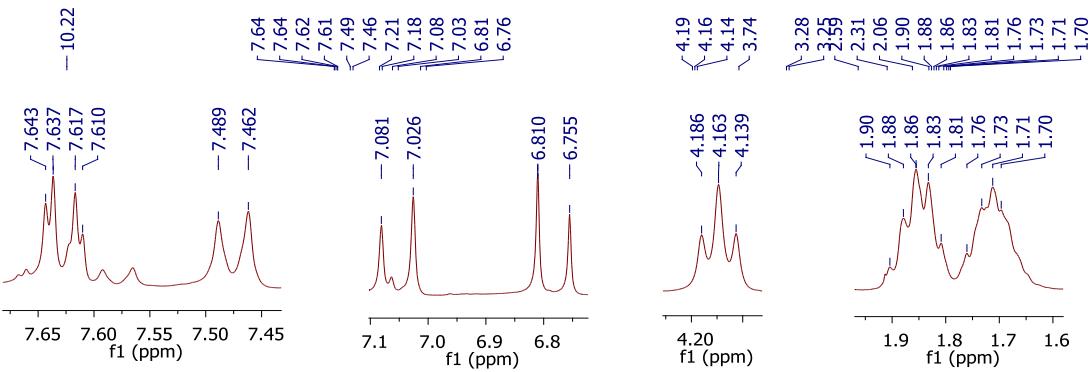


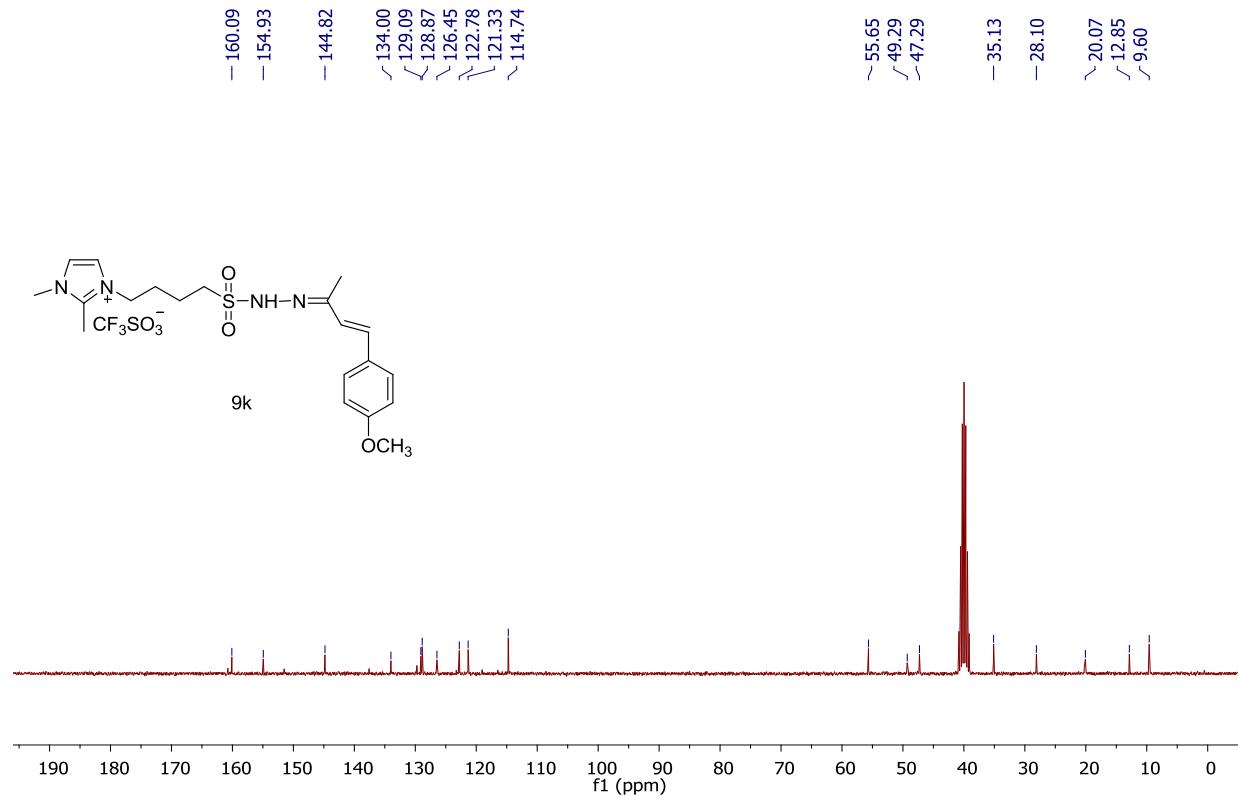
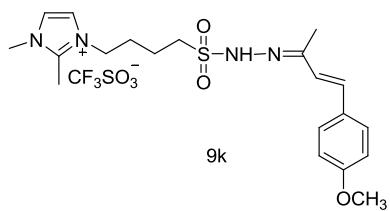
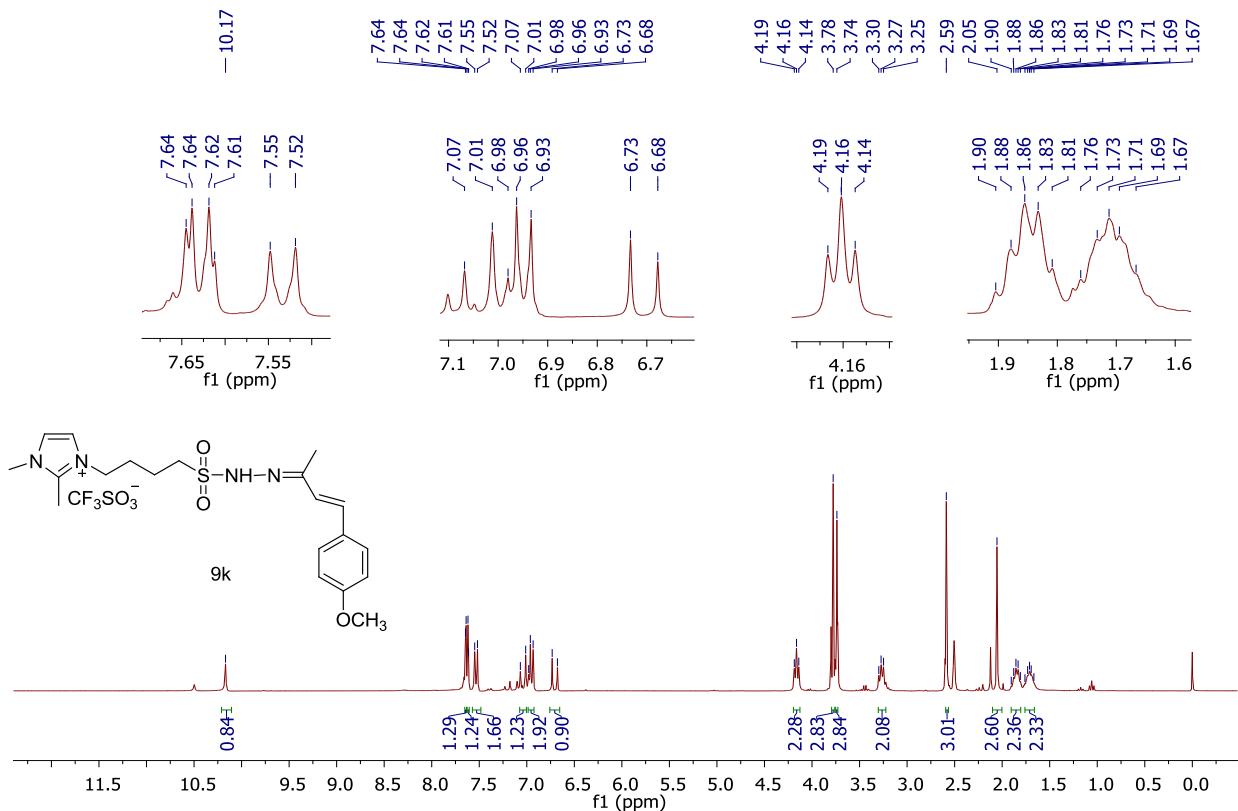


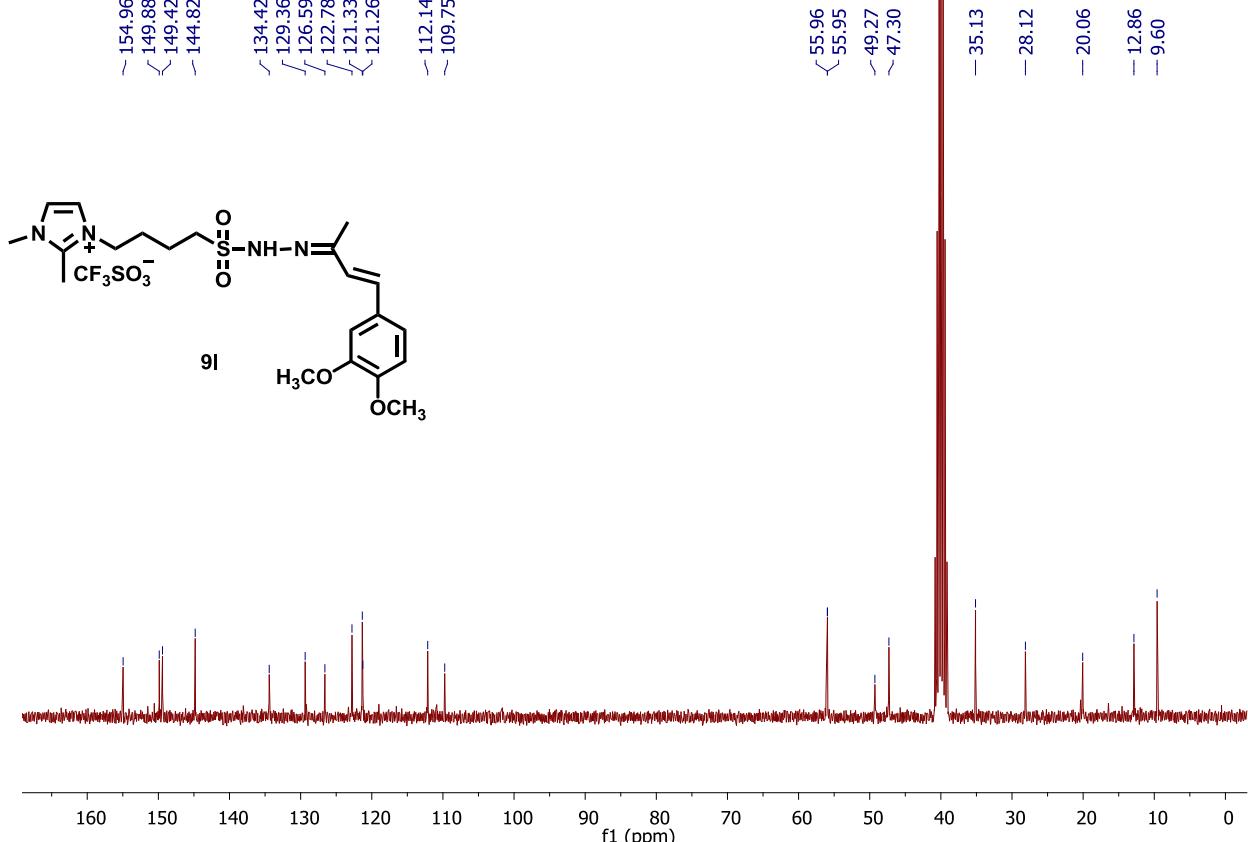
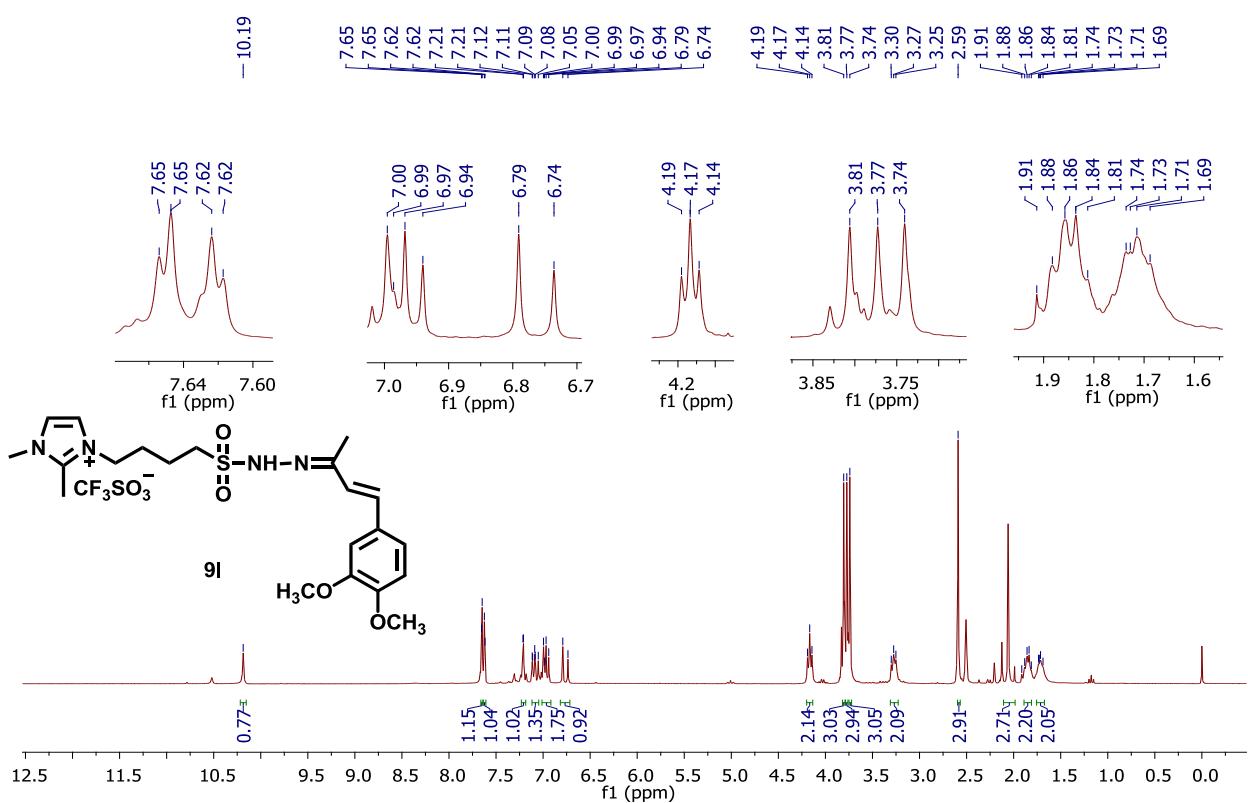


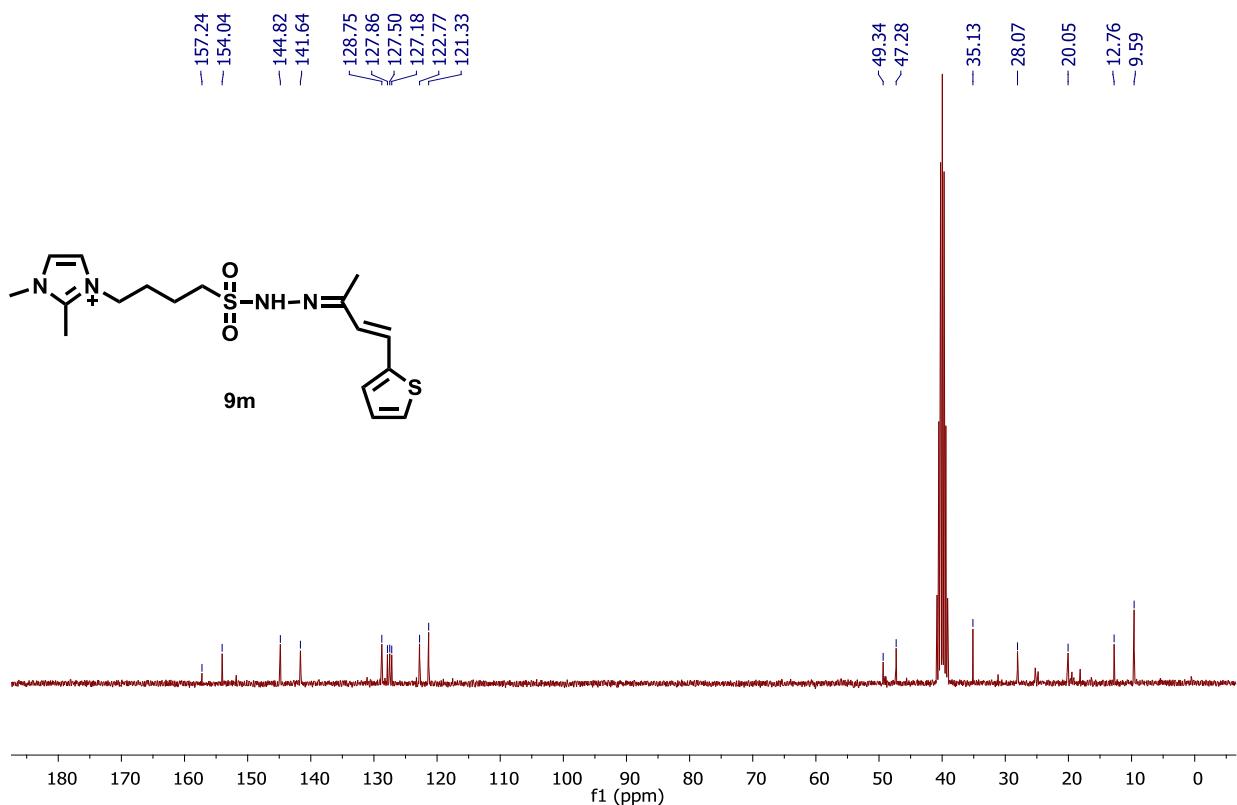
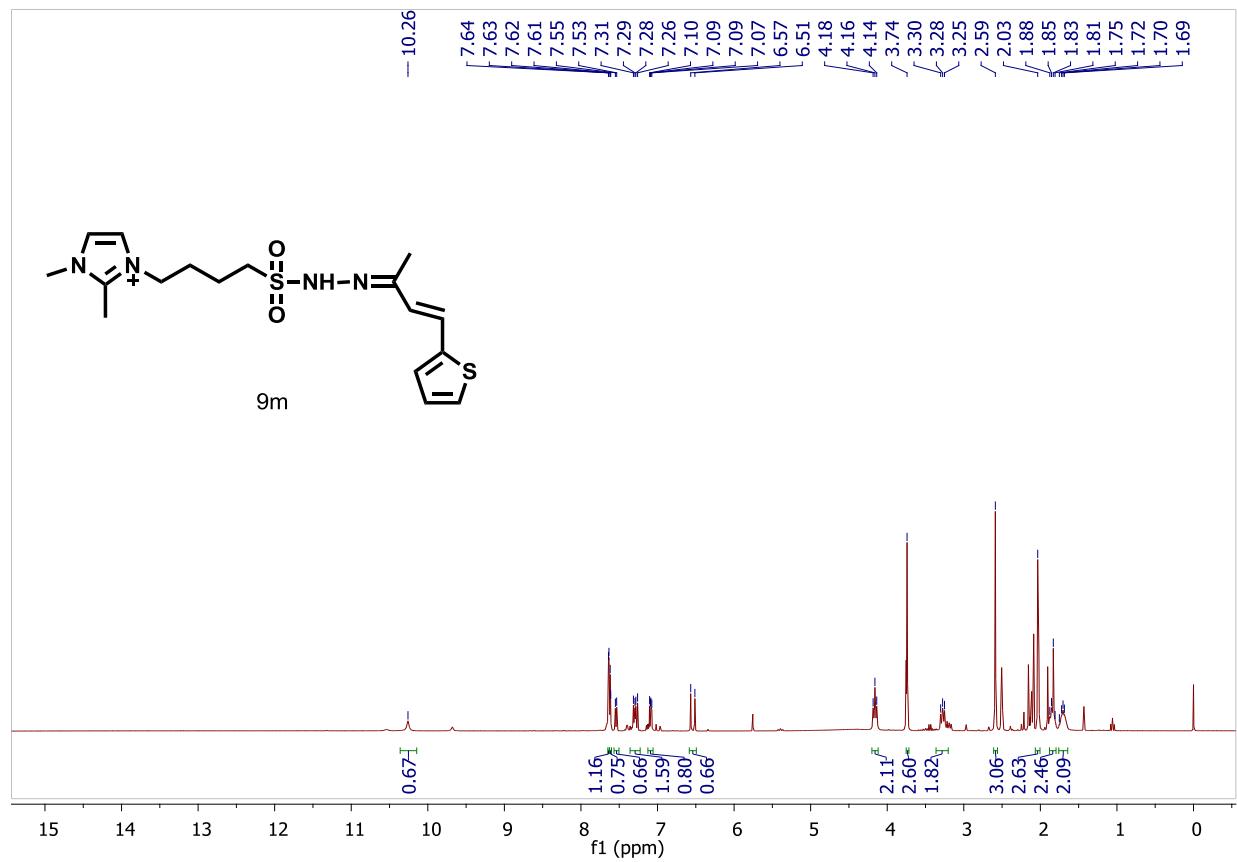


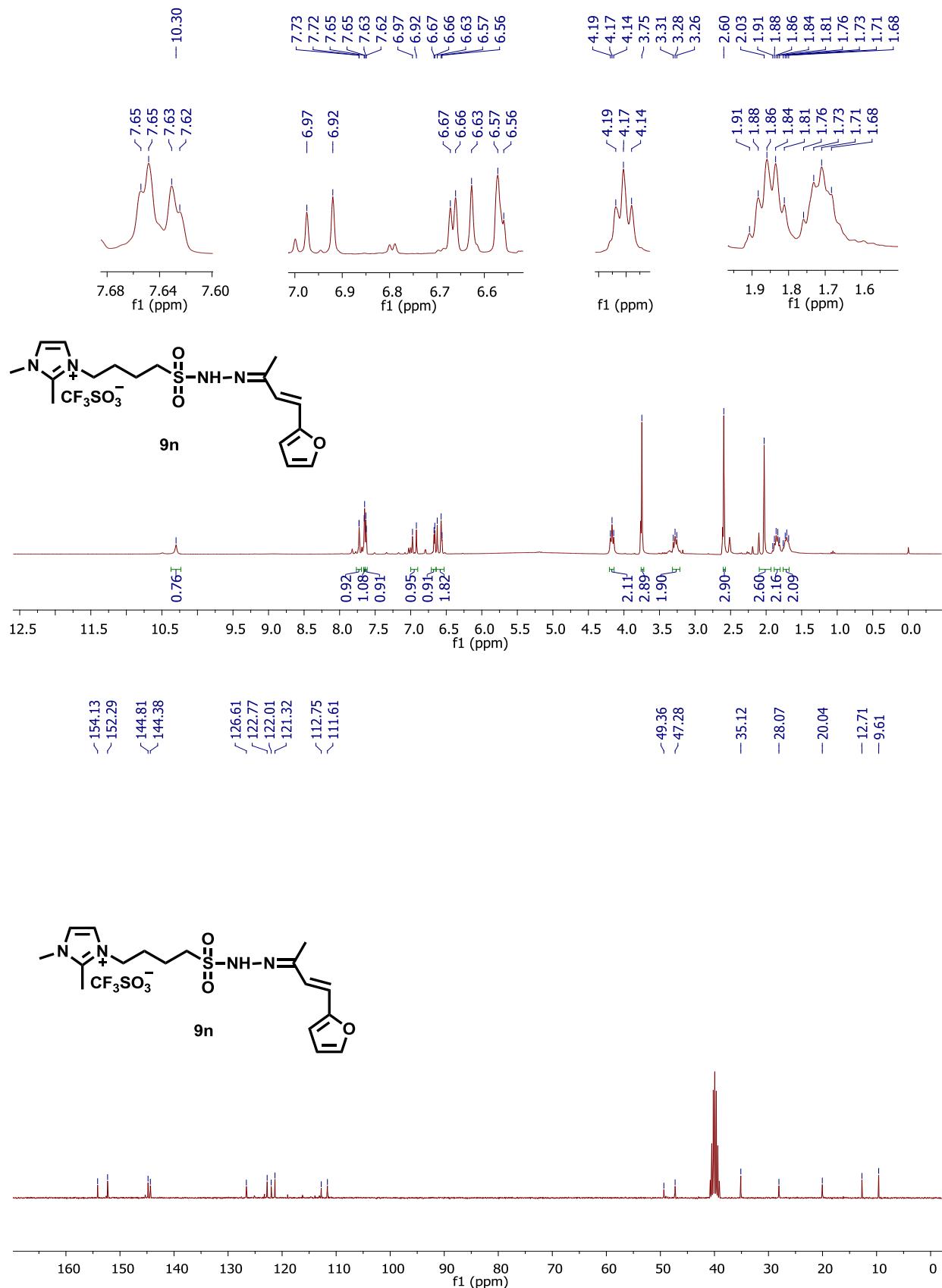


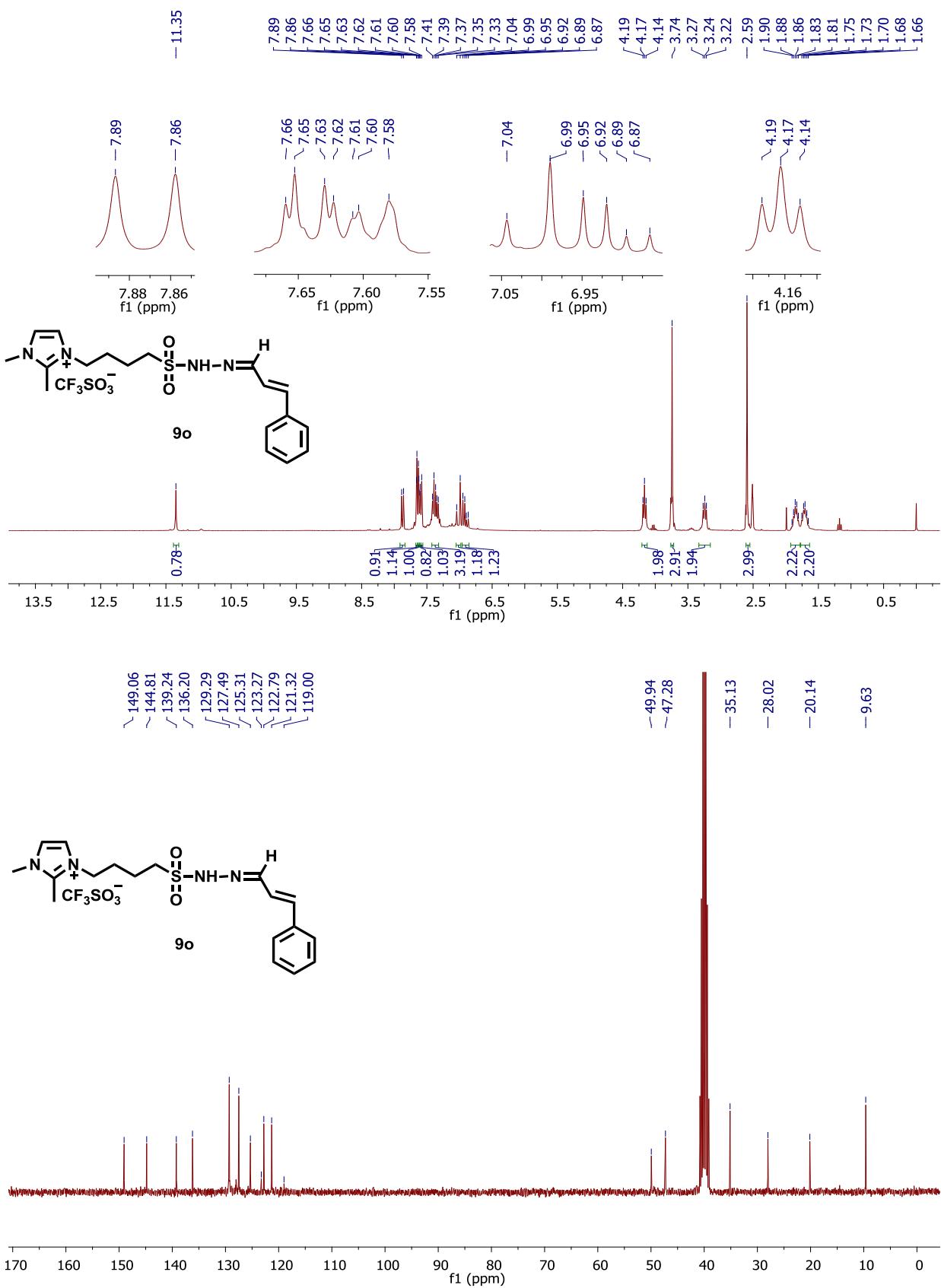


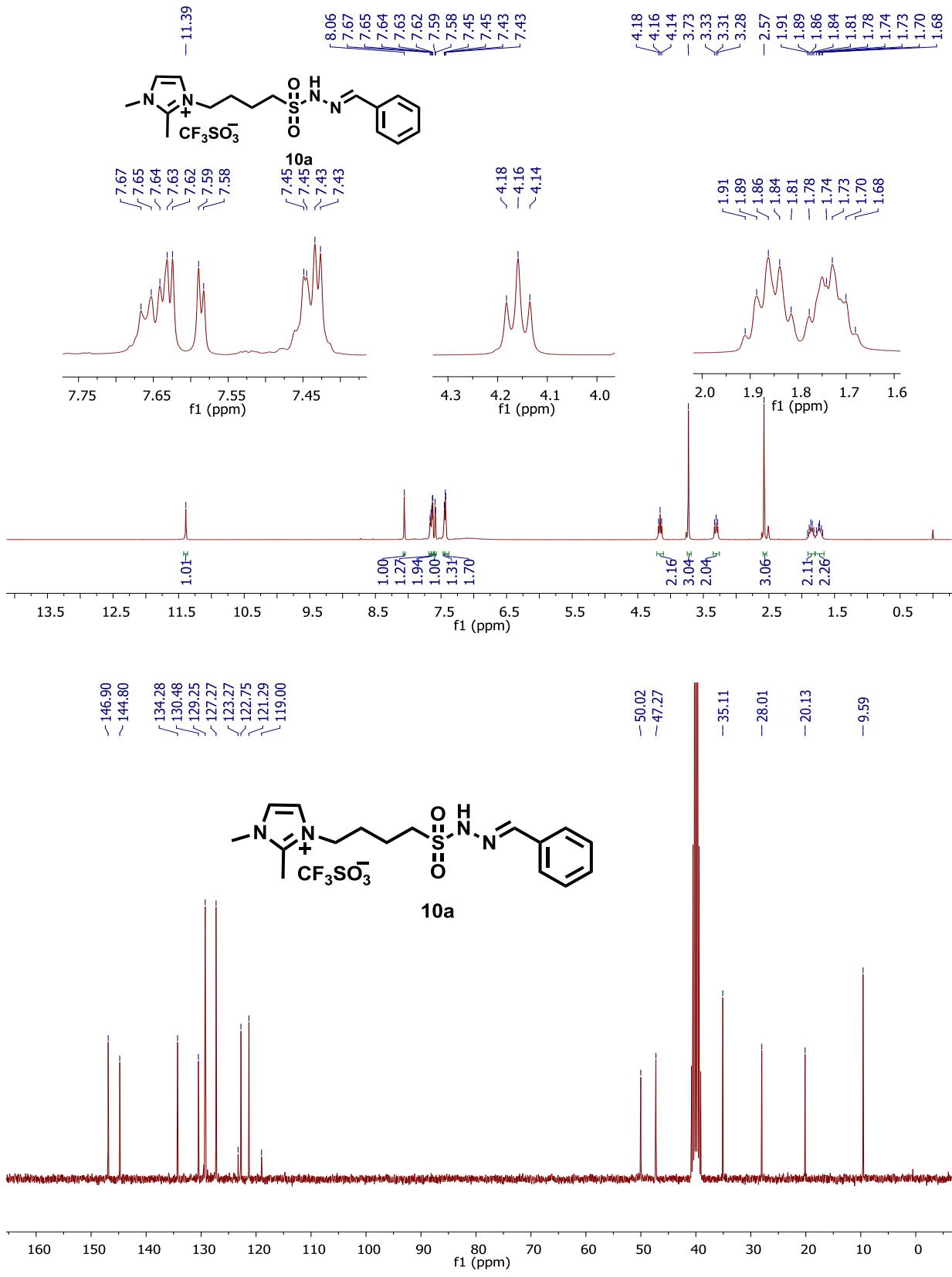


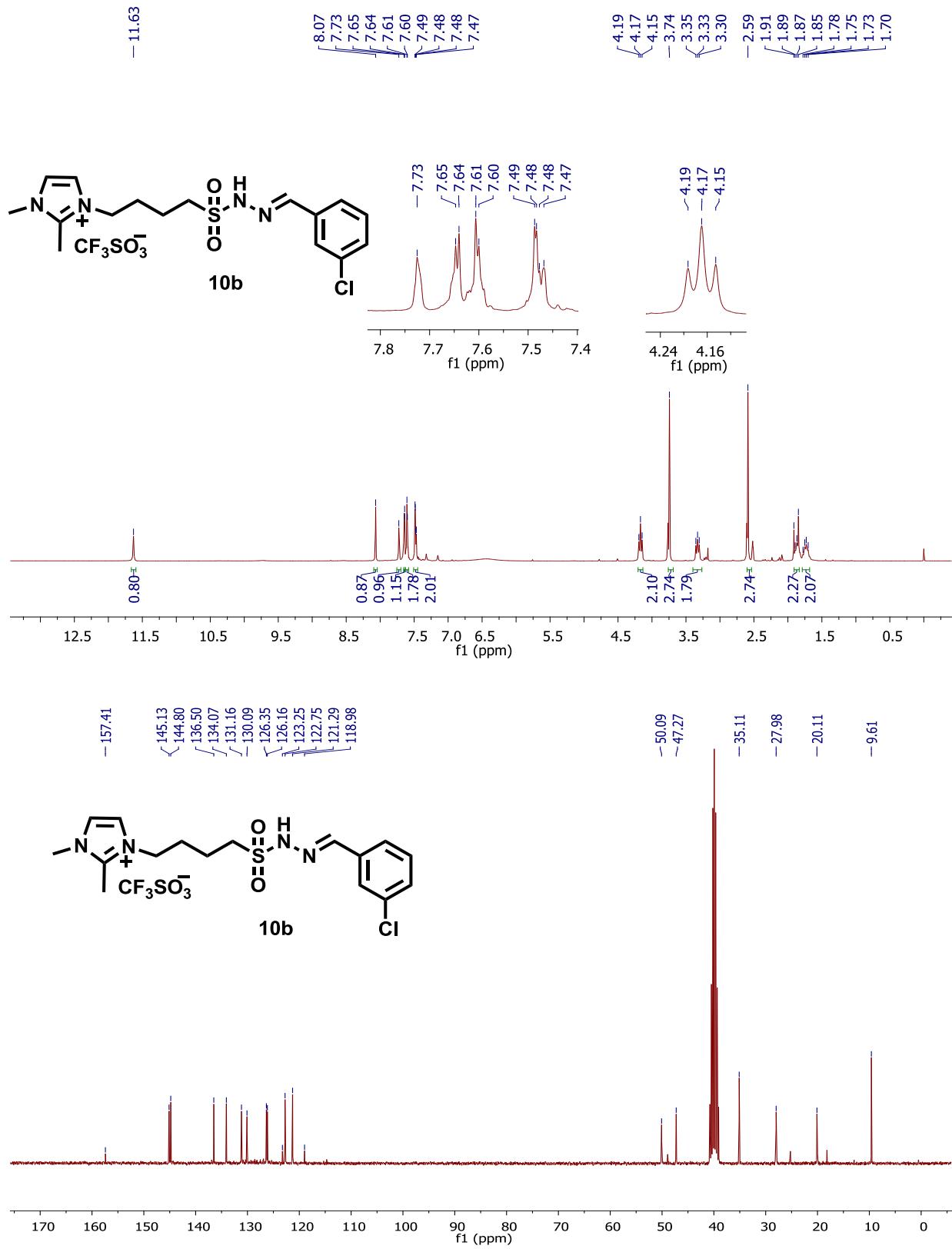


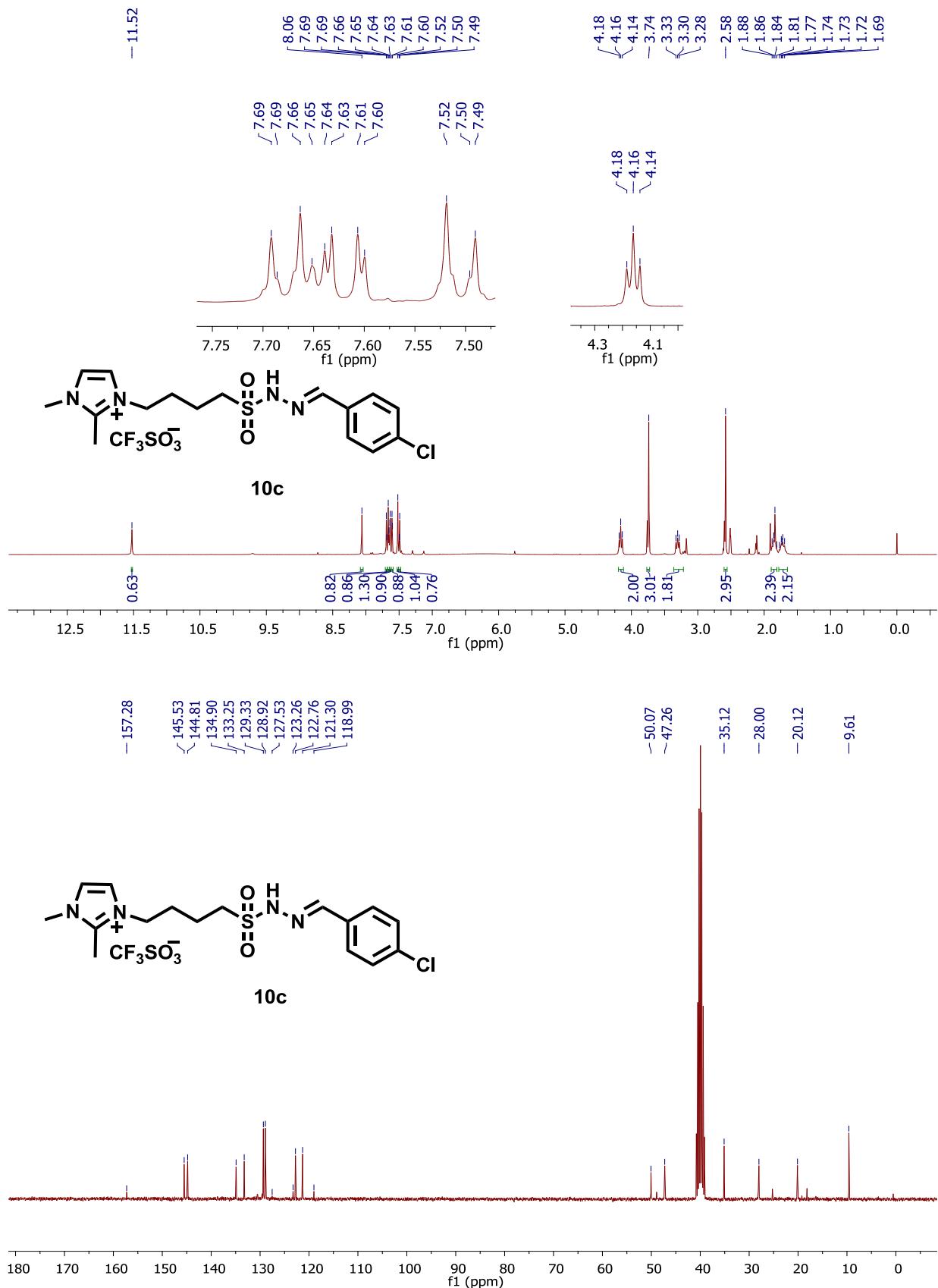


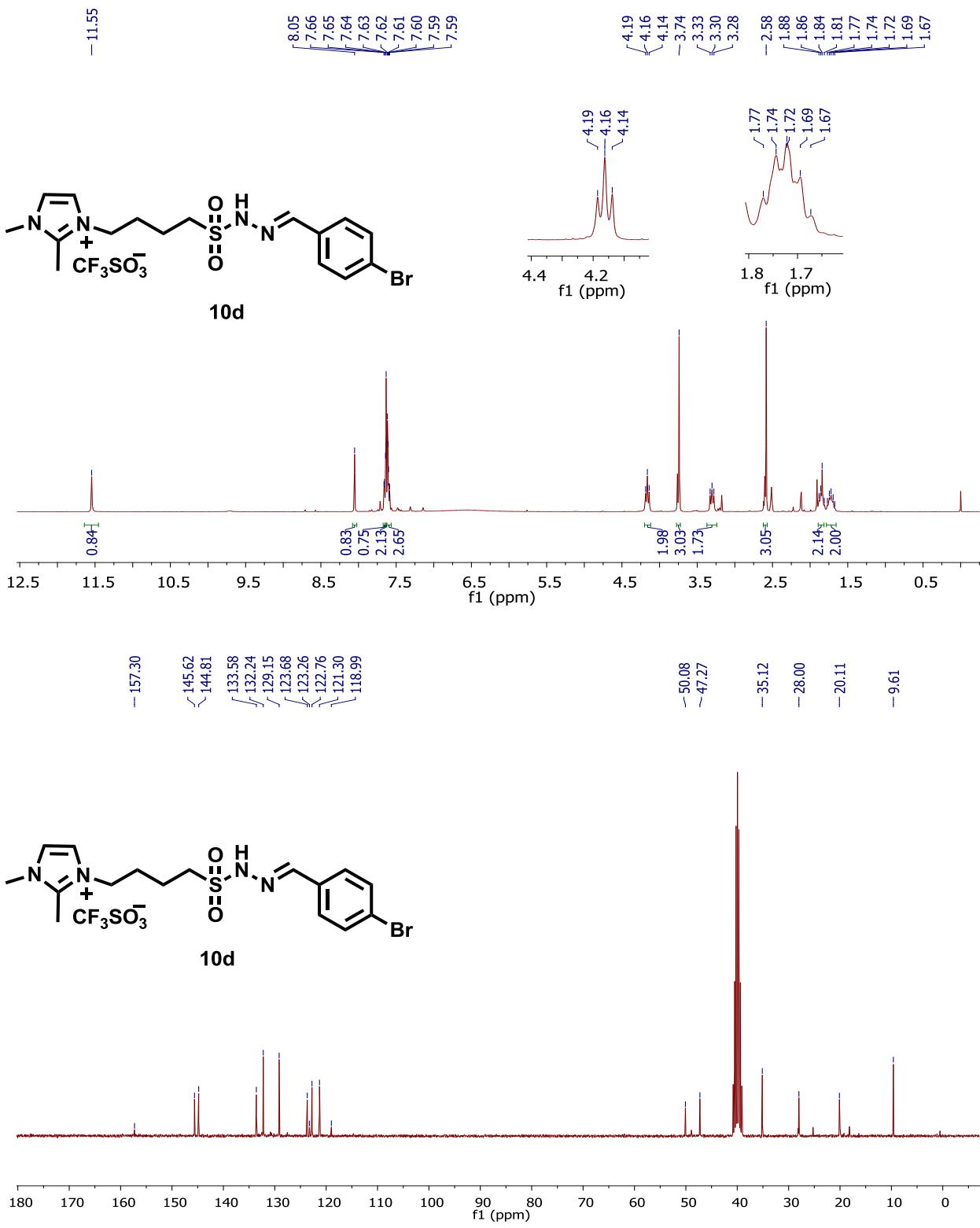


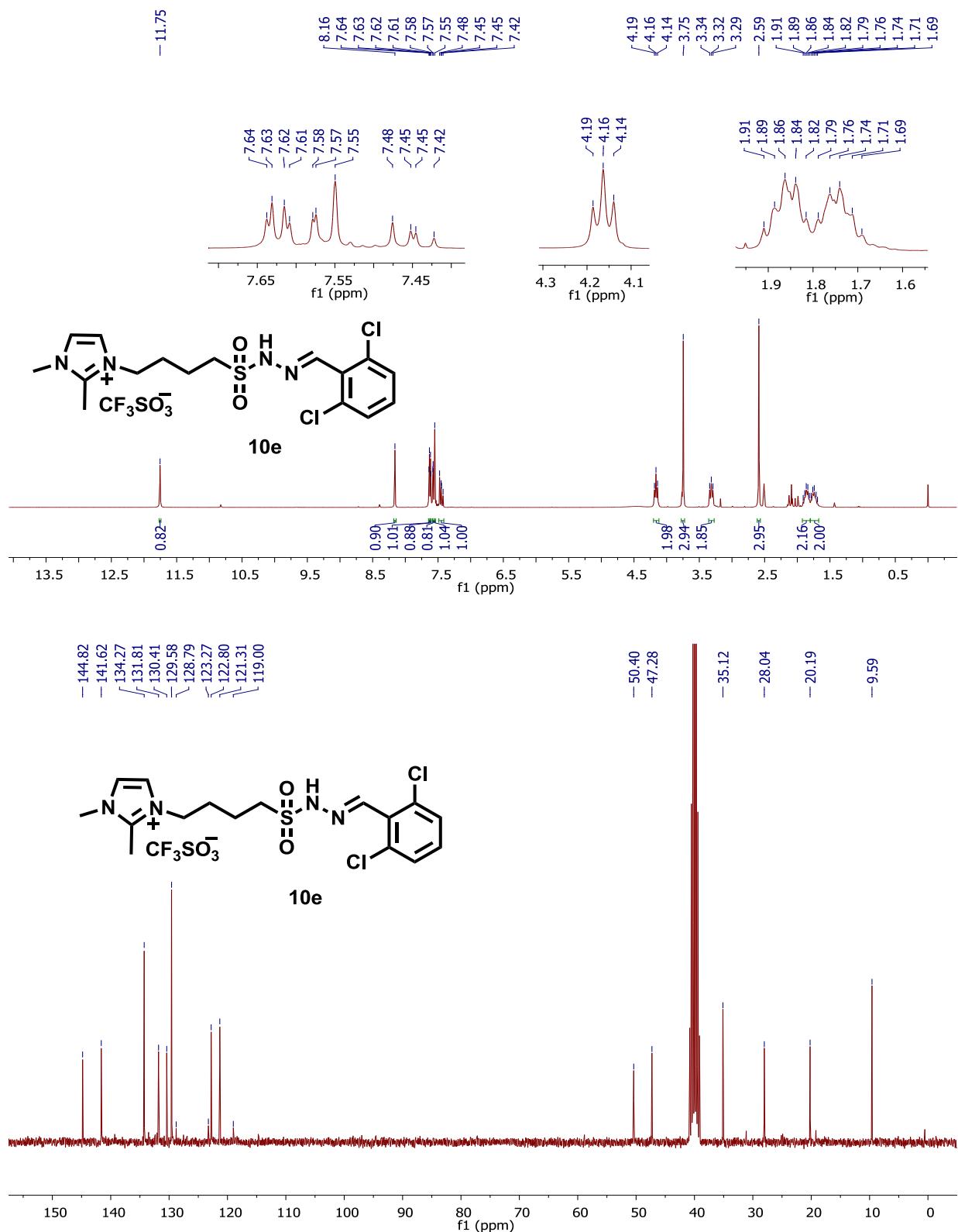


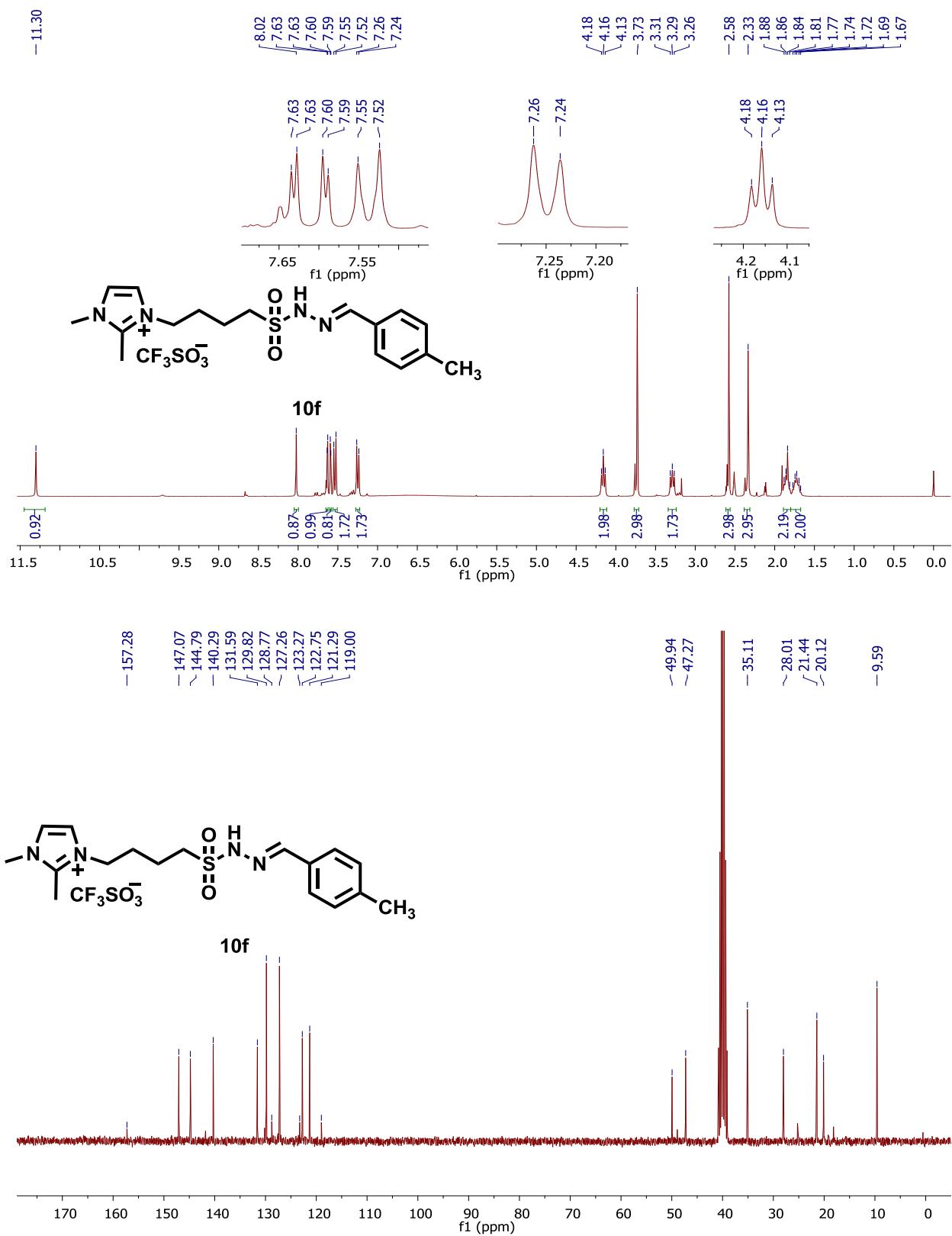


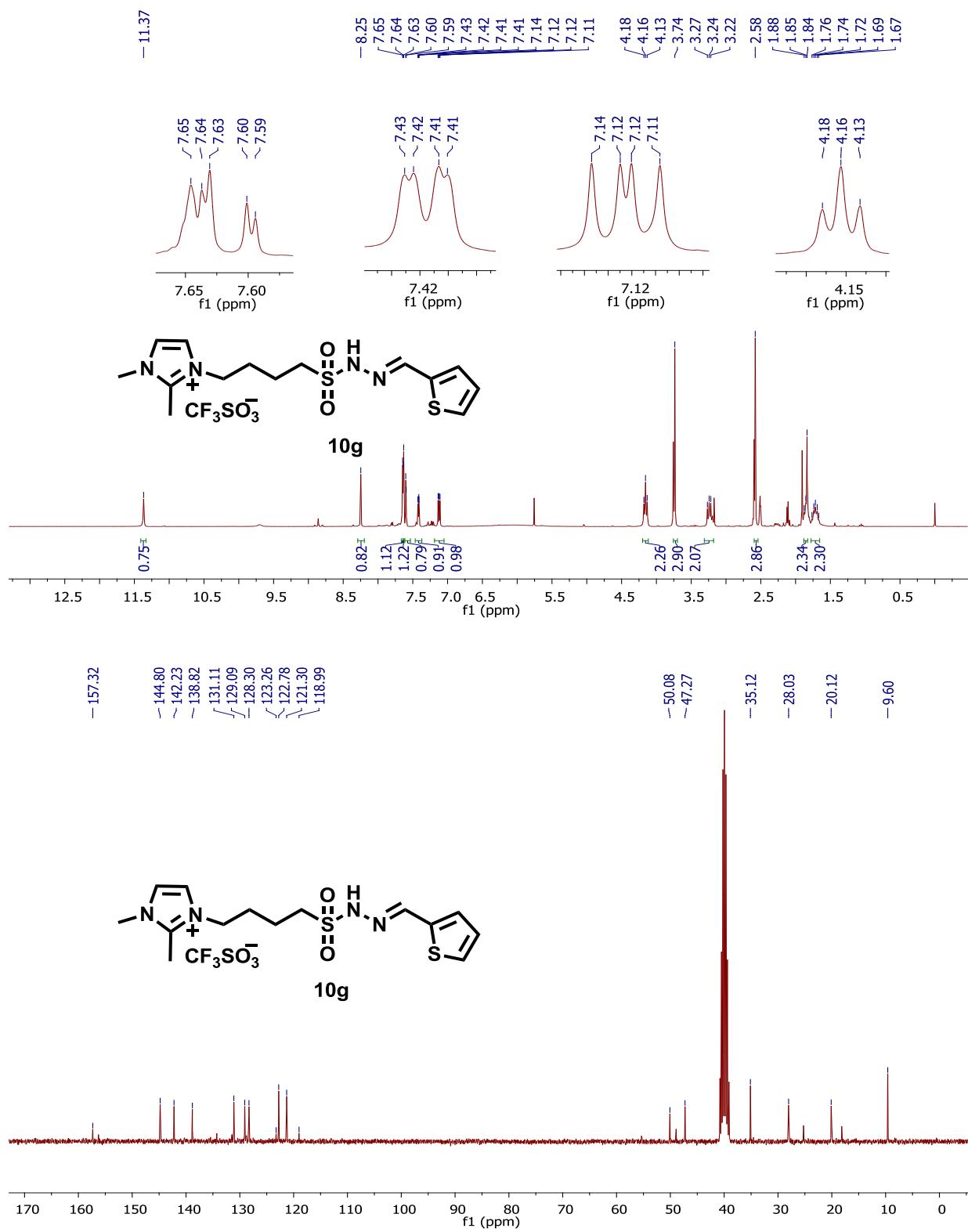




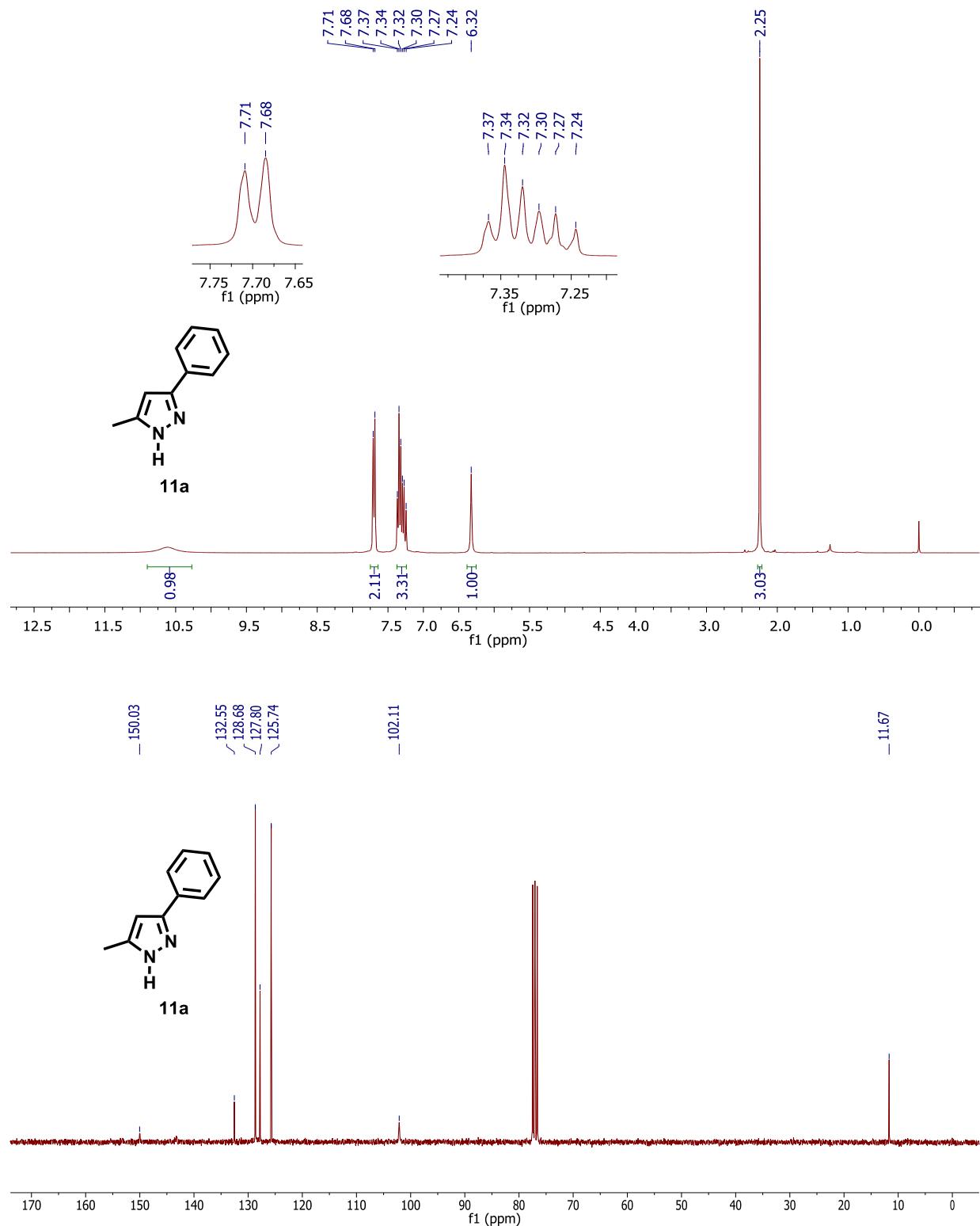








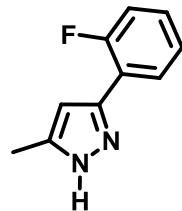
3. Copies of  $^1\text{H}$  and  $^{13}\text{C}$  NMR of pyrazoles **11** & **13**.



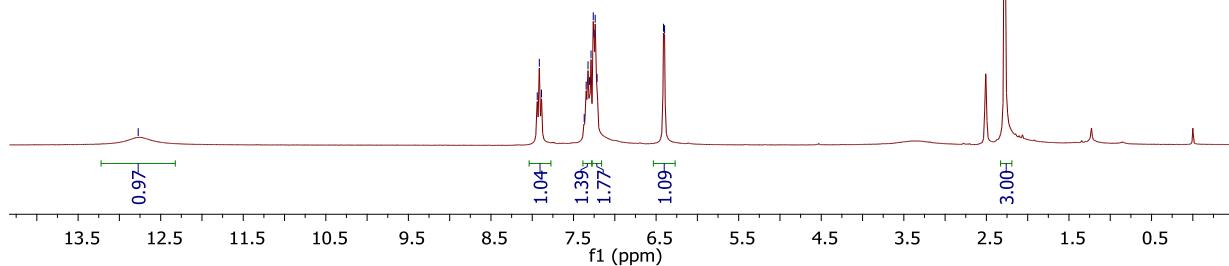
- 12.77

7.94  
7.91  
7.89  
7.37  
7.35  
7.32  
7.31  
7.29  
7.26  
7.24  
7.21  
6.41  
6.40

2.28



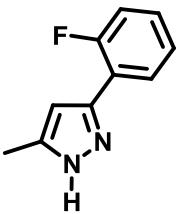
**11b**



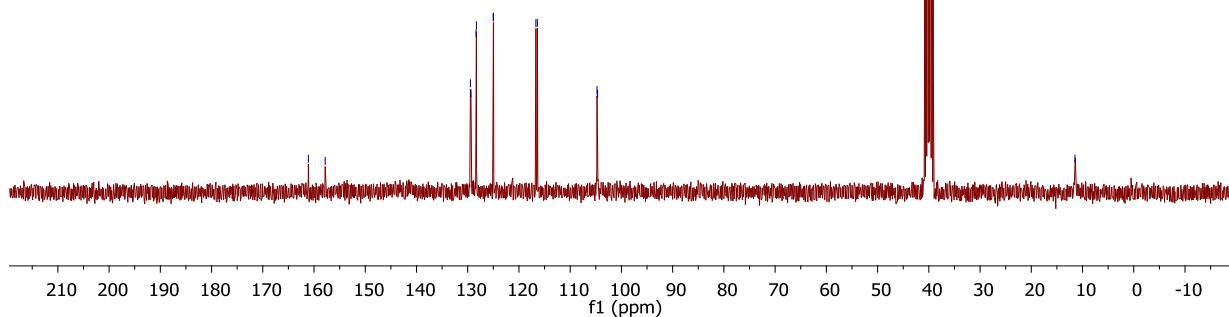
- 161.10  
- 157.83

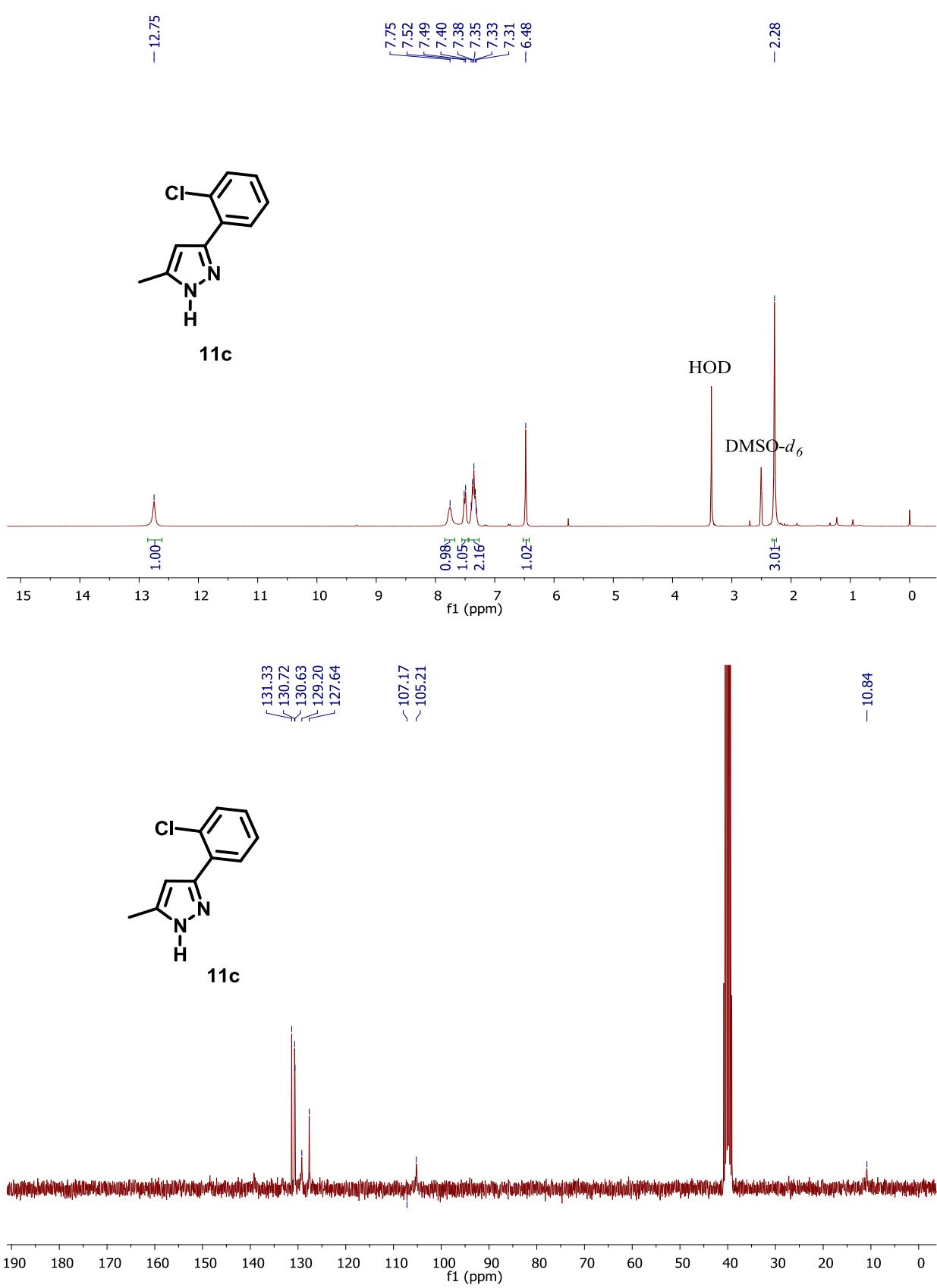
129.48  
129.37  
128.35  
128.30  
125.02  
124.98  
116.70  
116.41  
104.77  
104.65

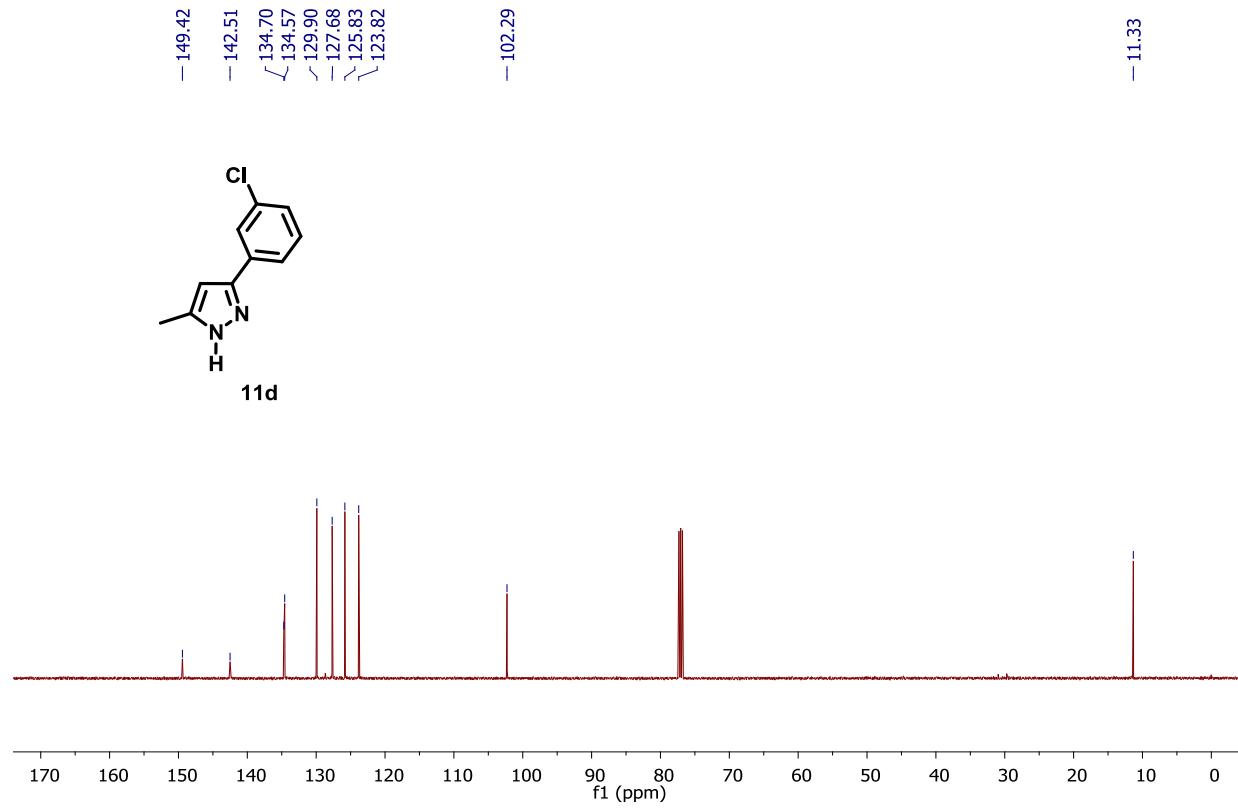
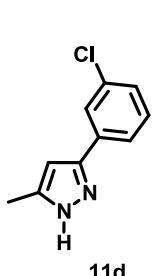
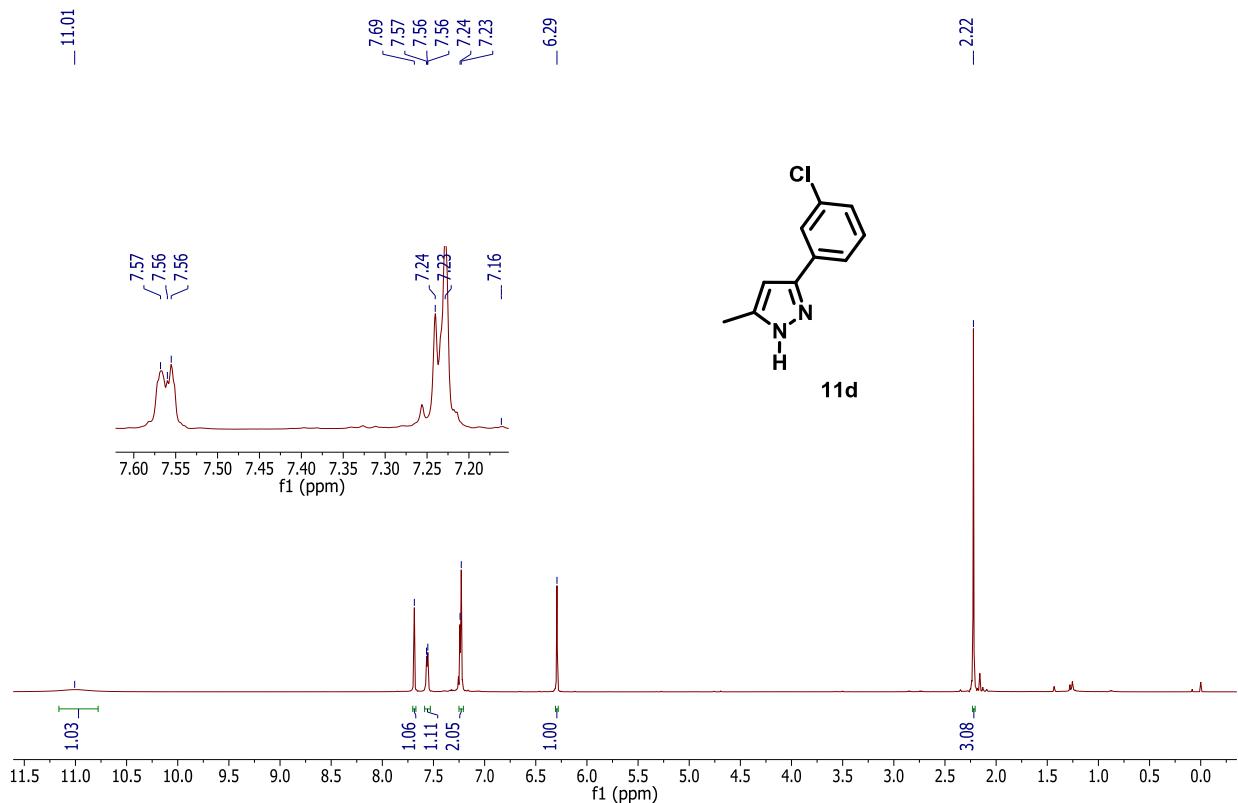
- 11.48

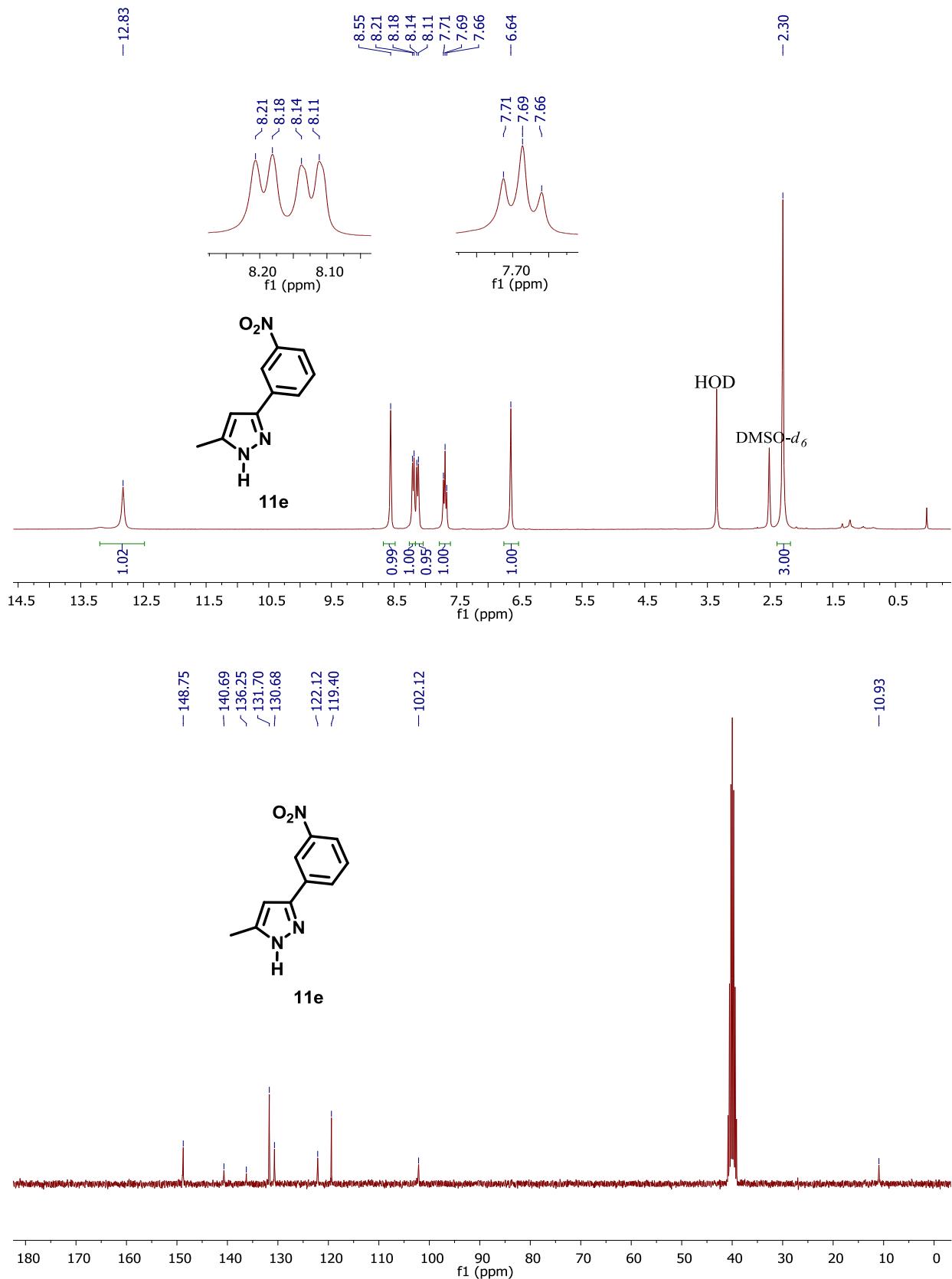


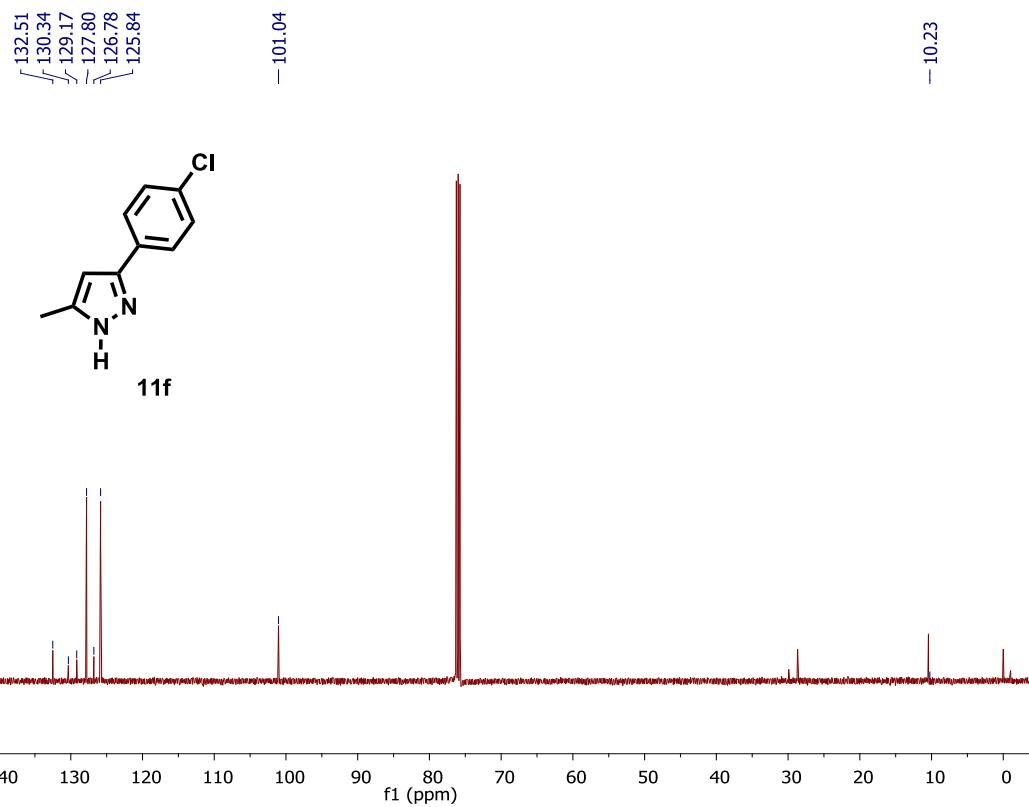
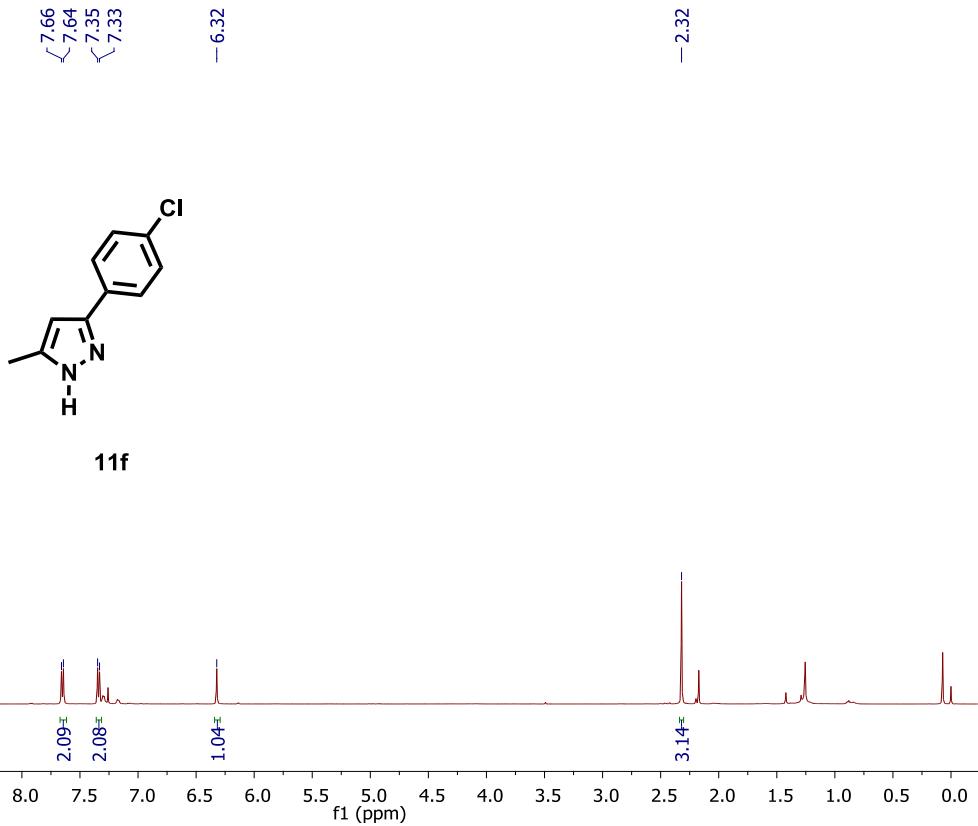
**11b**

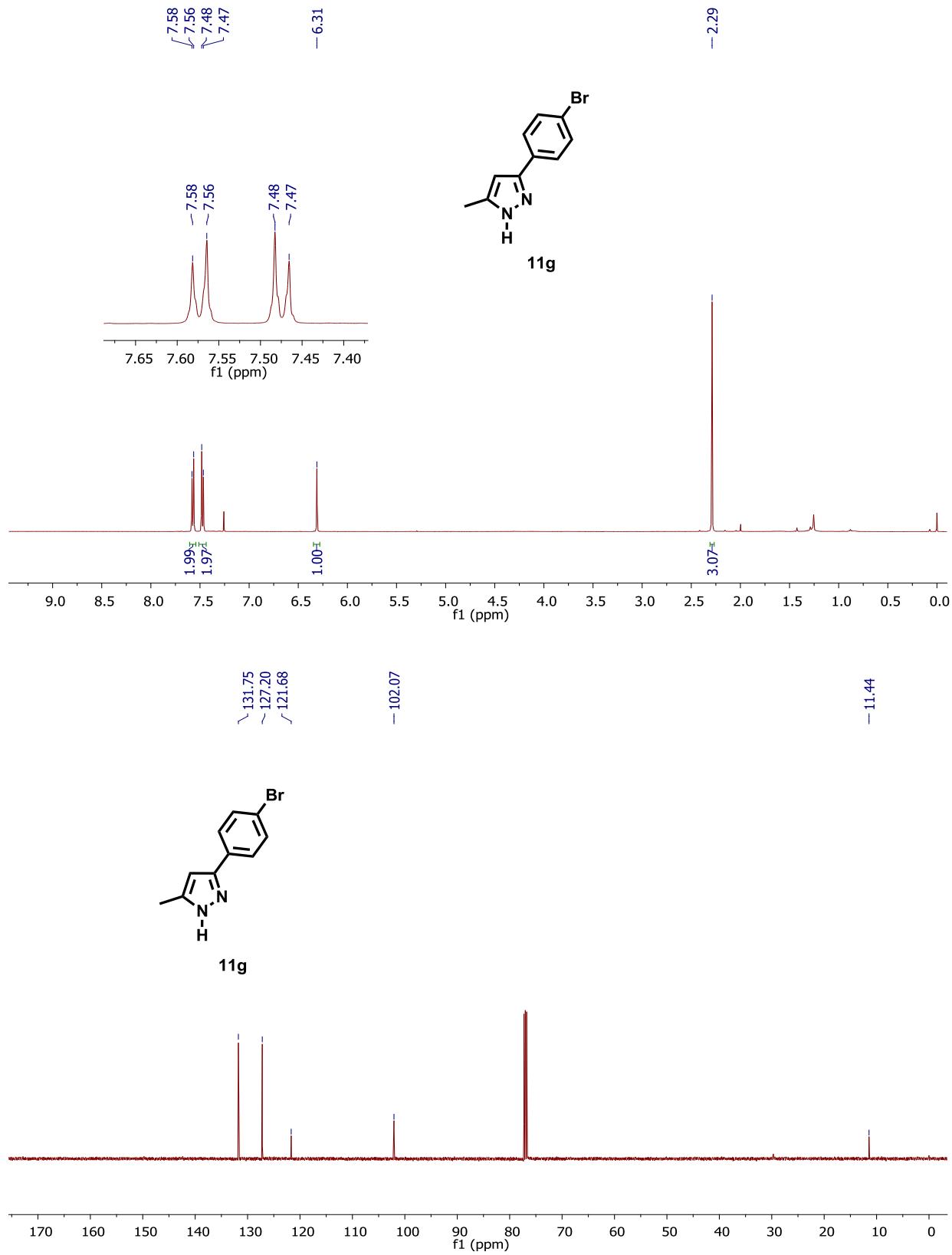


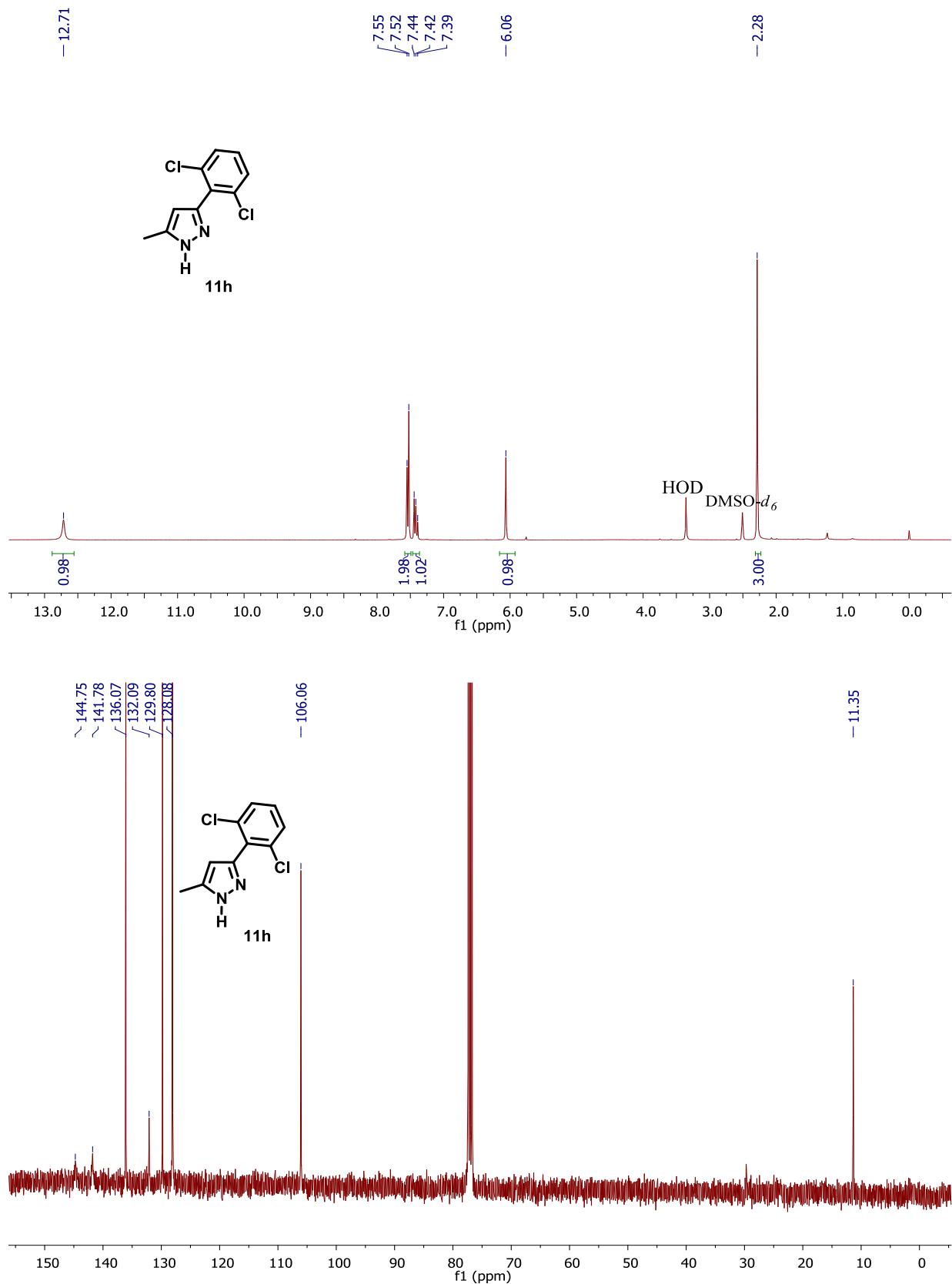


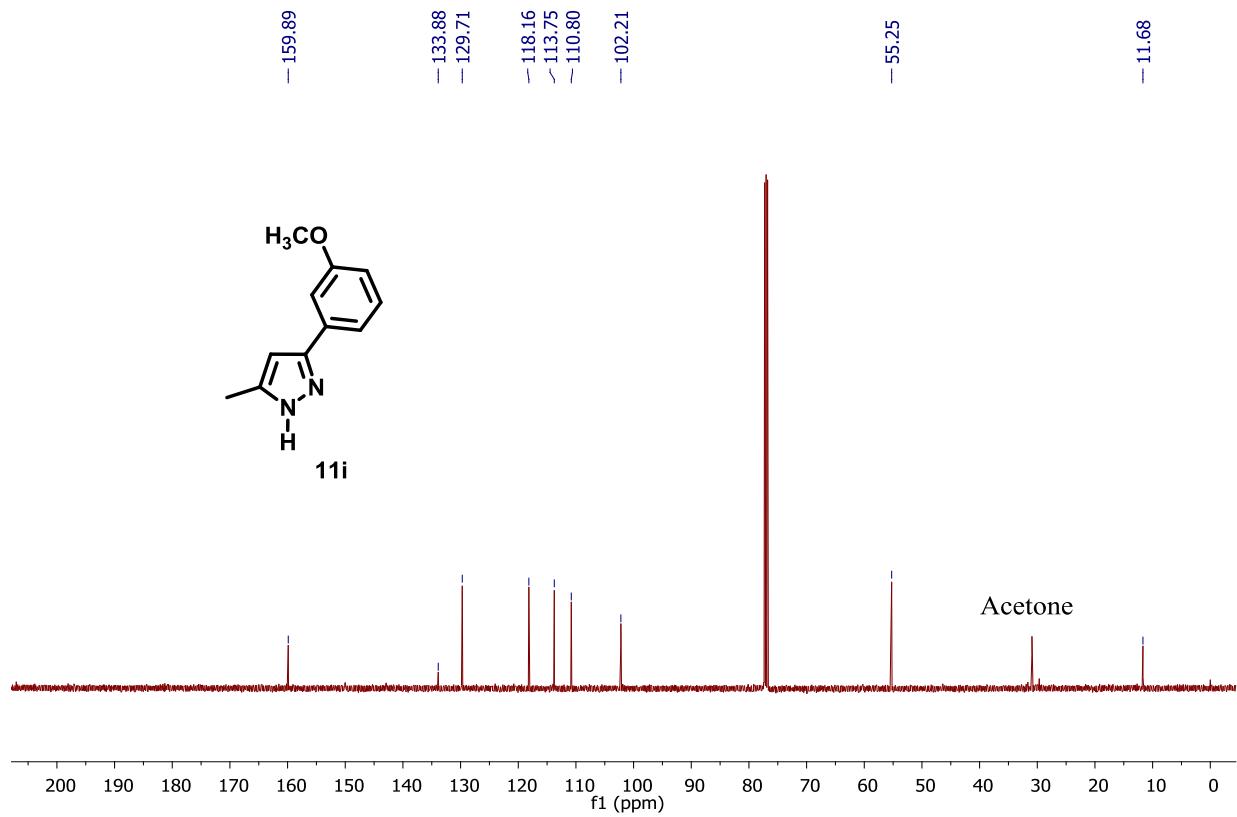
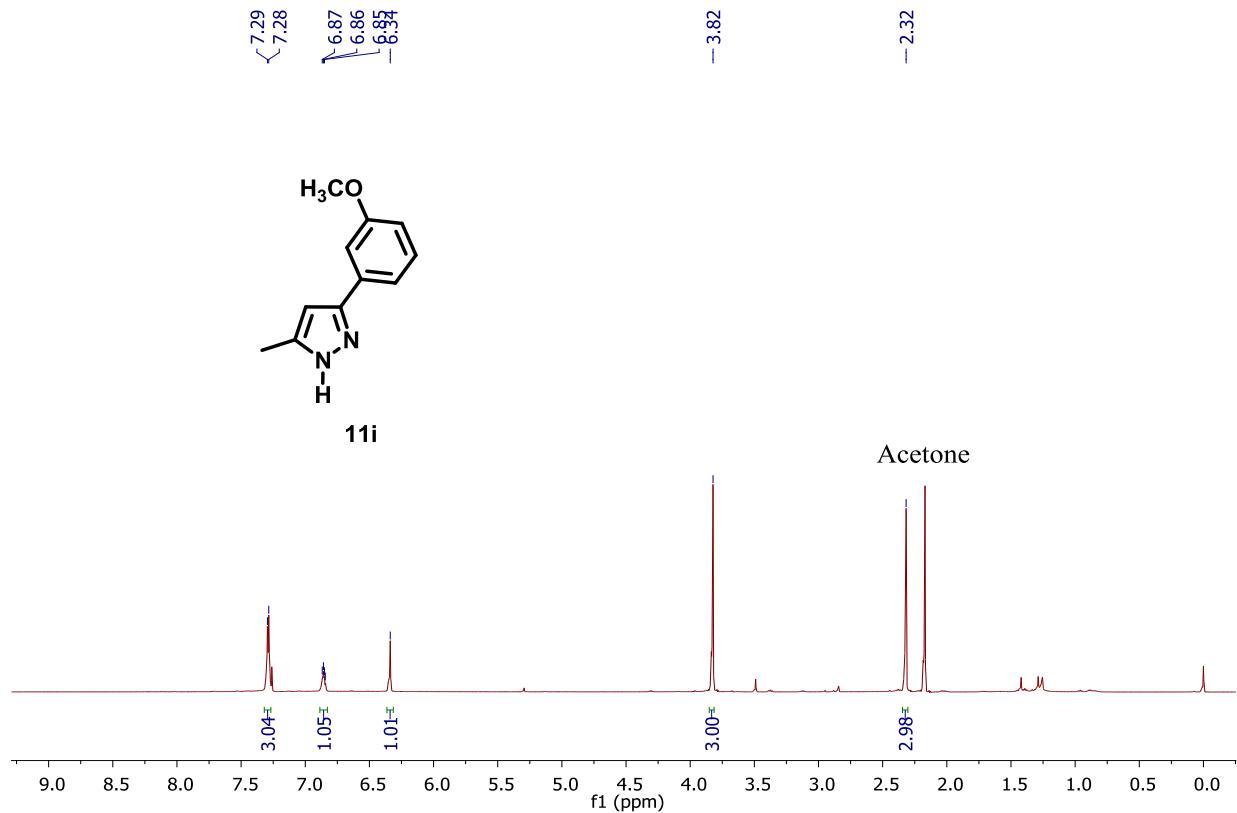


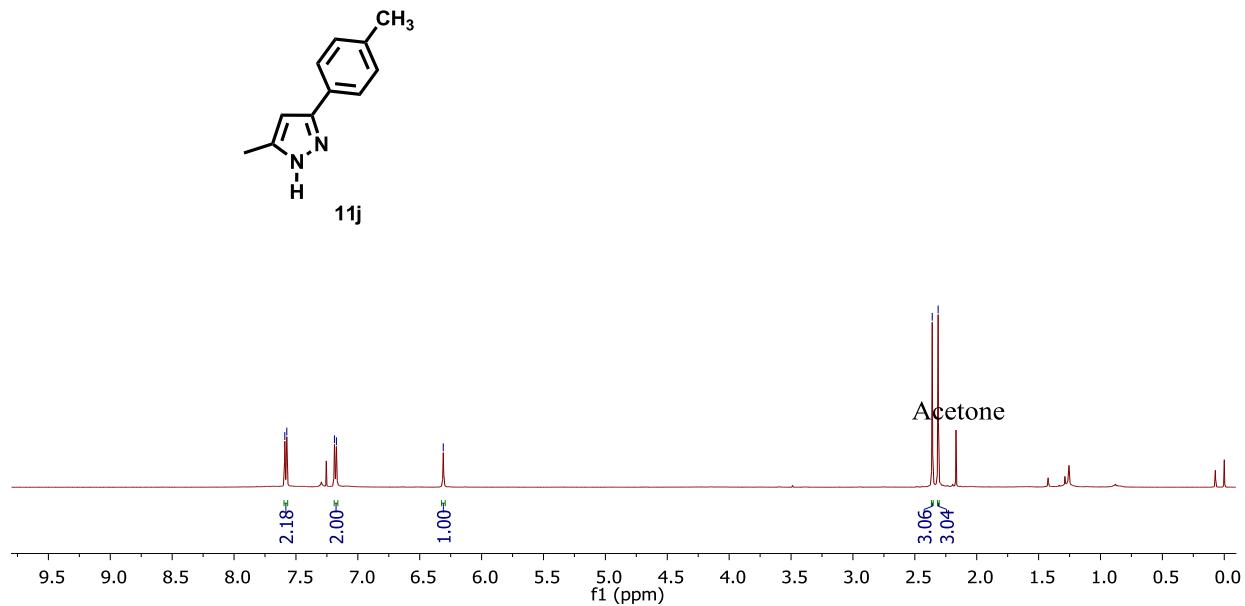


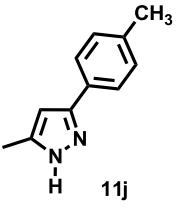


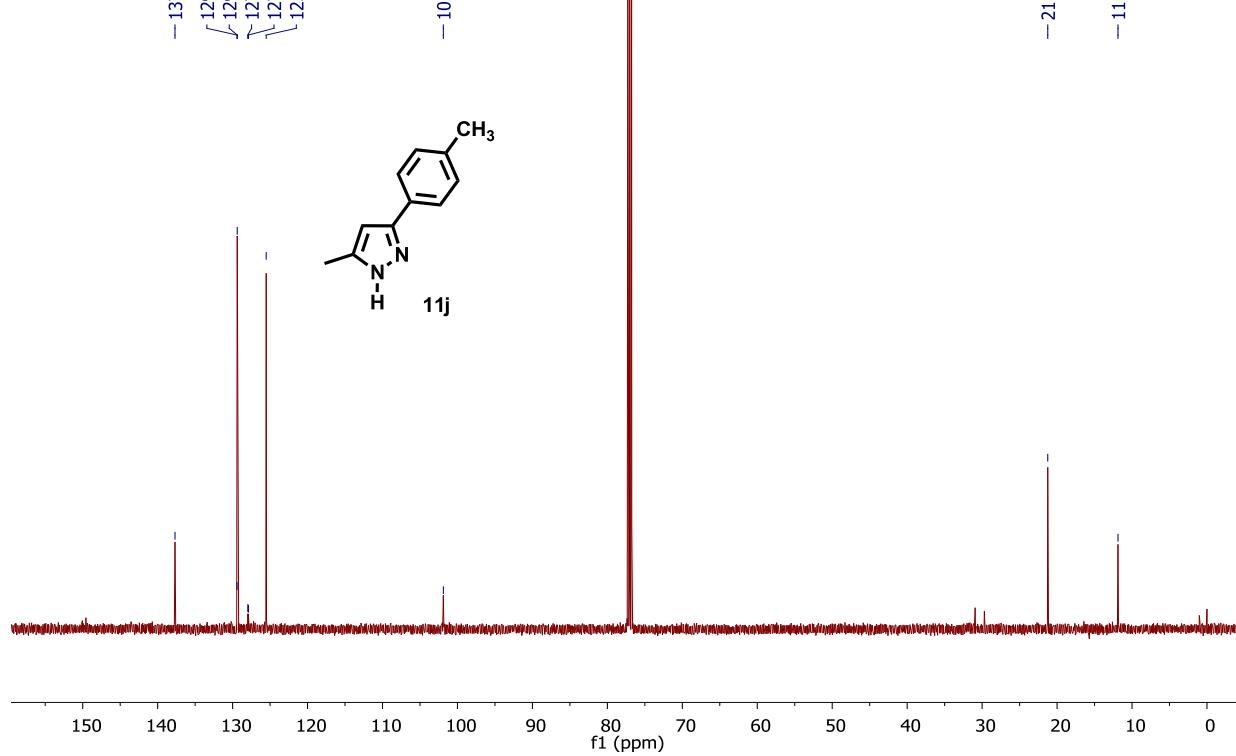


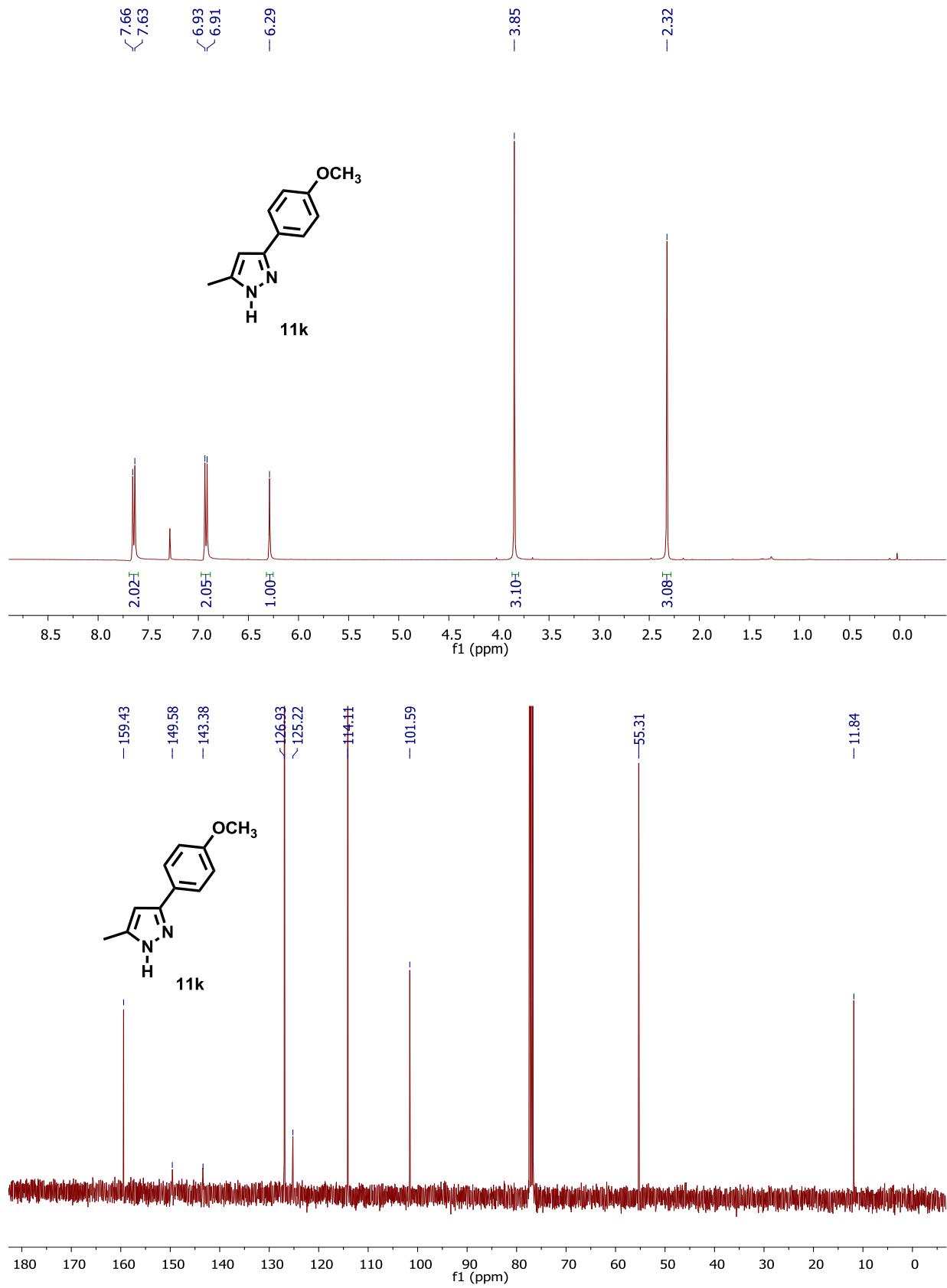


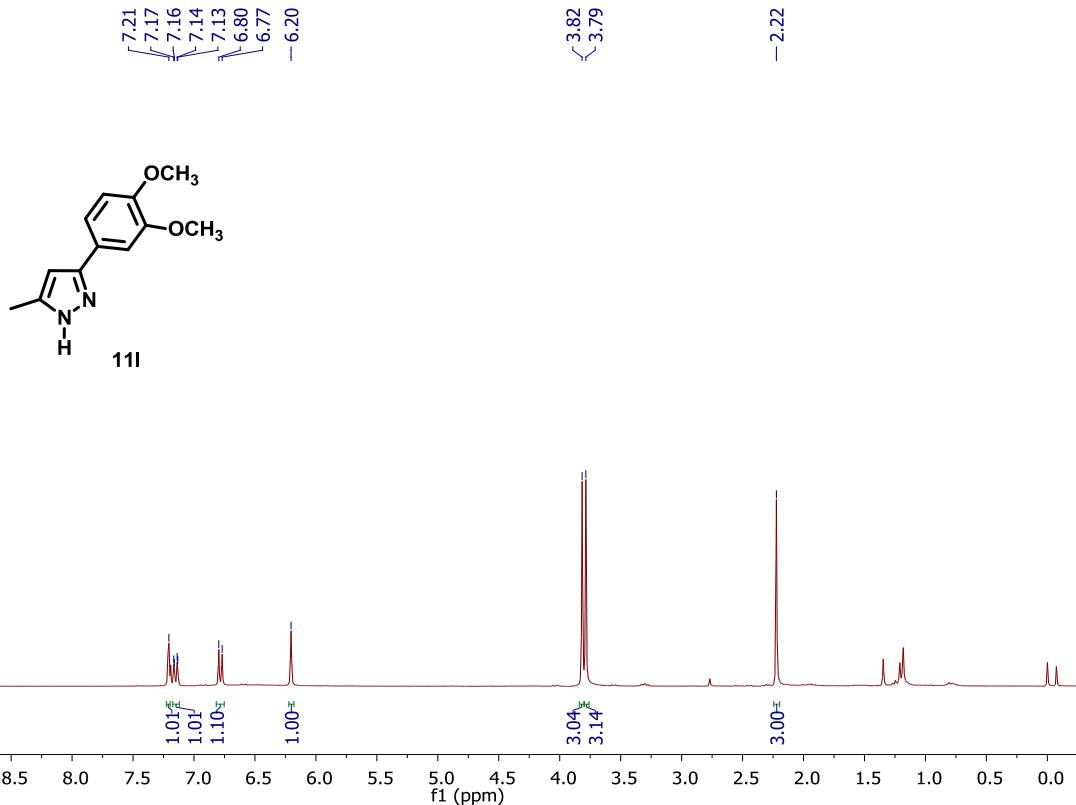




$\text{CH}_3$   
  
**11j**

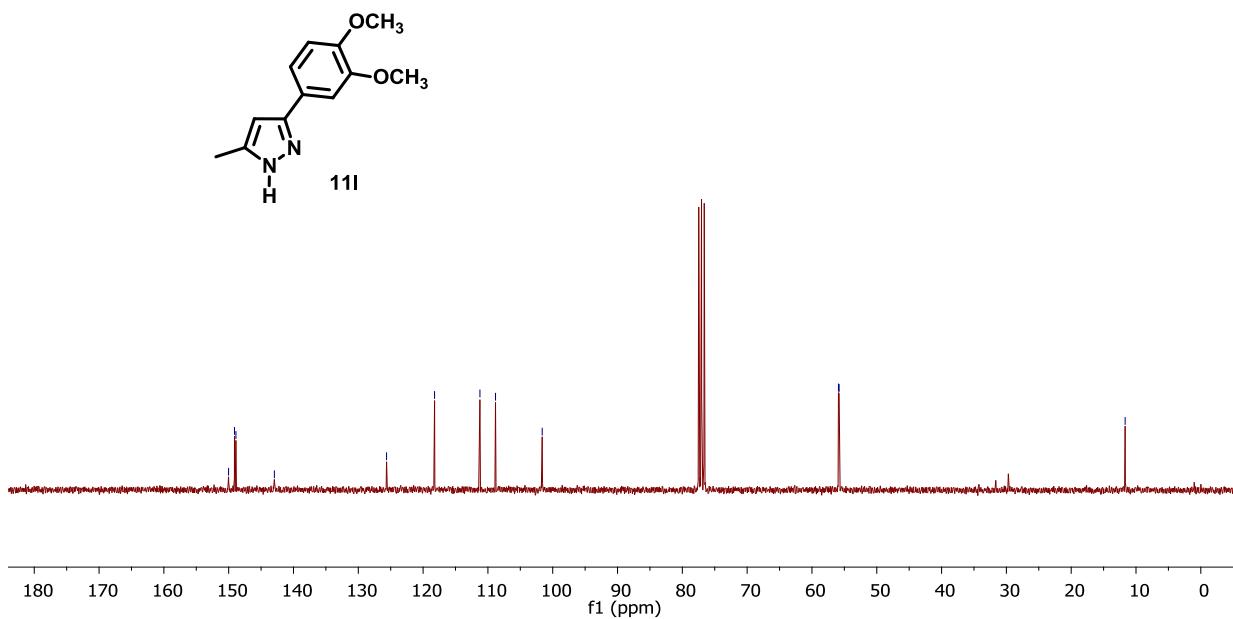


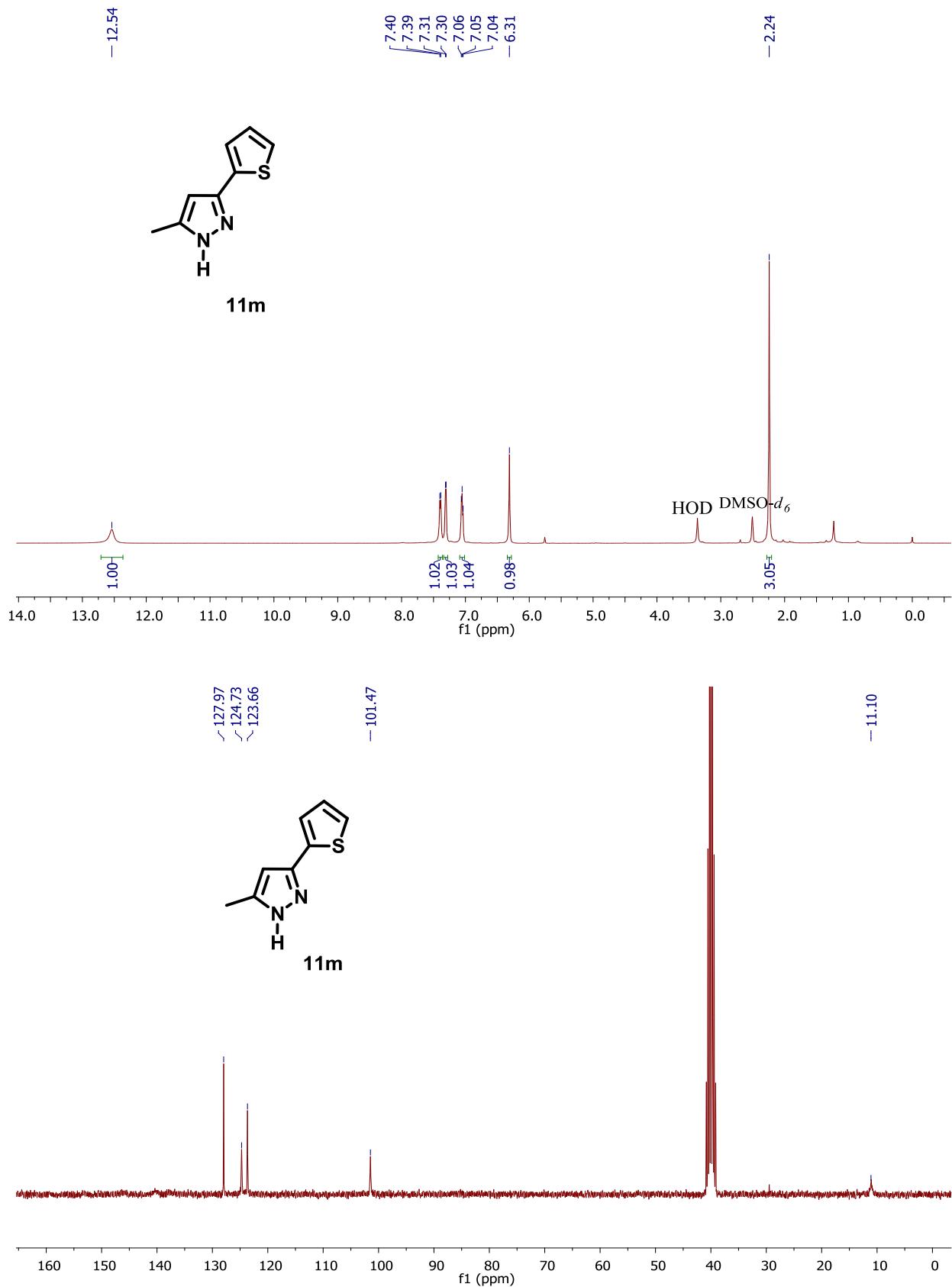


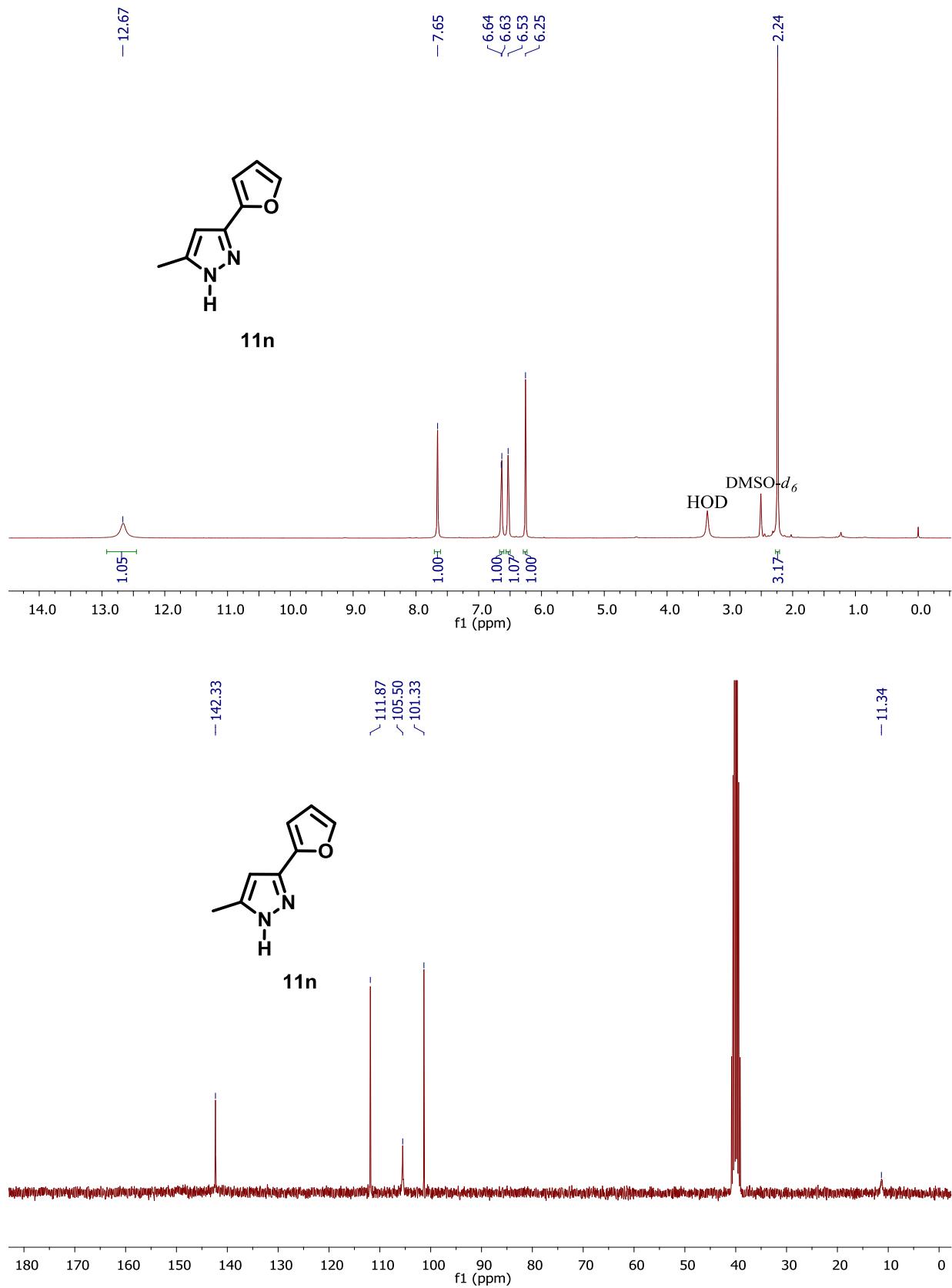


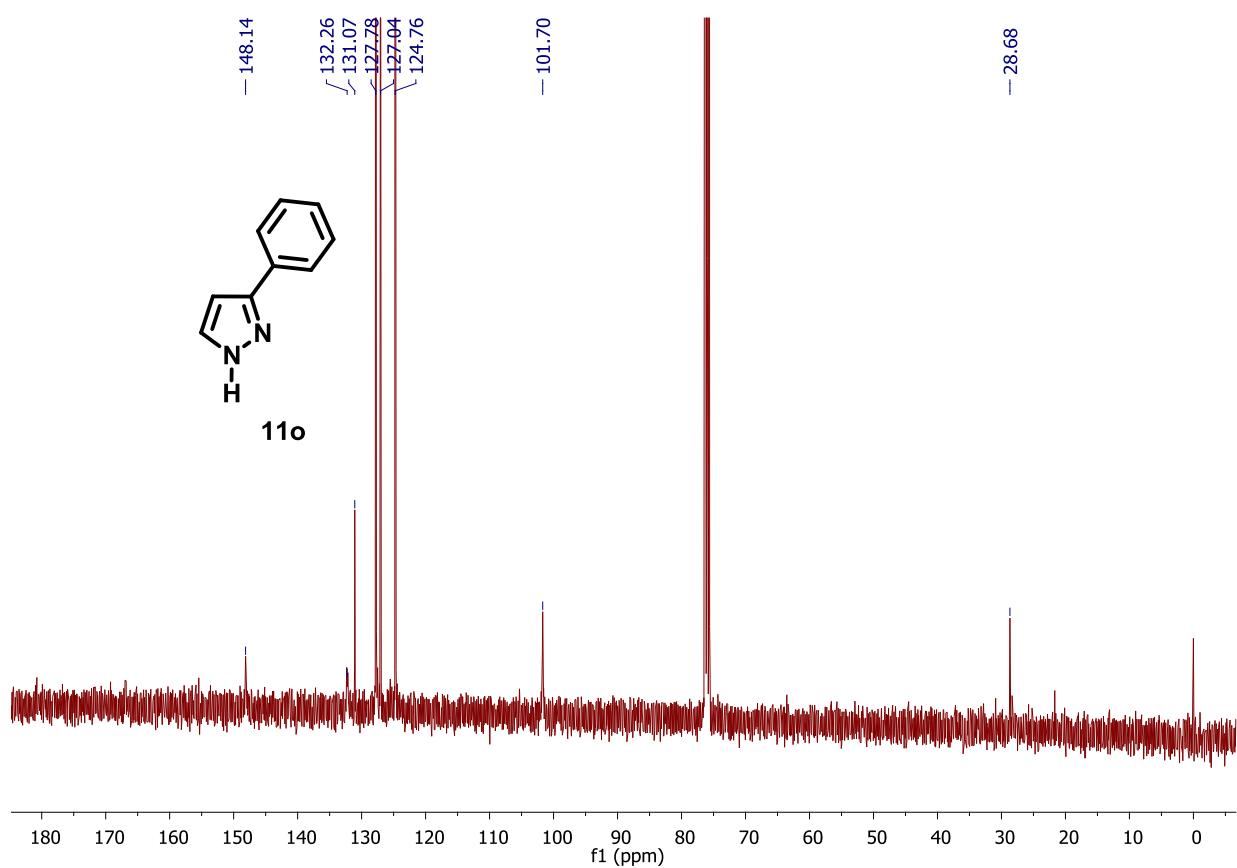
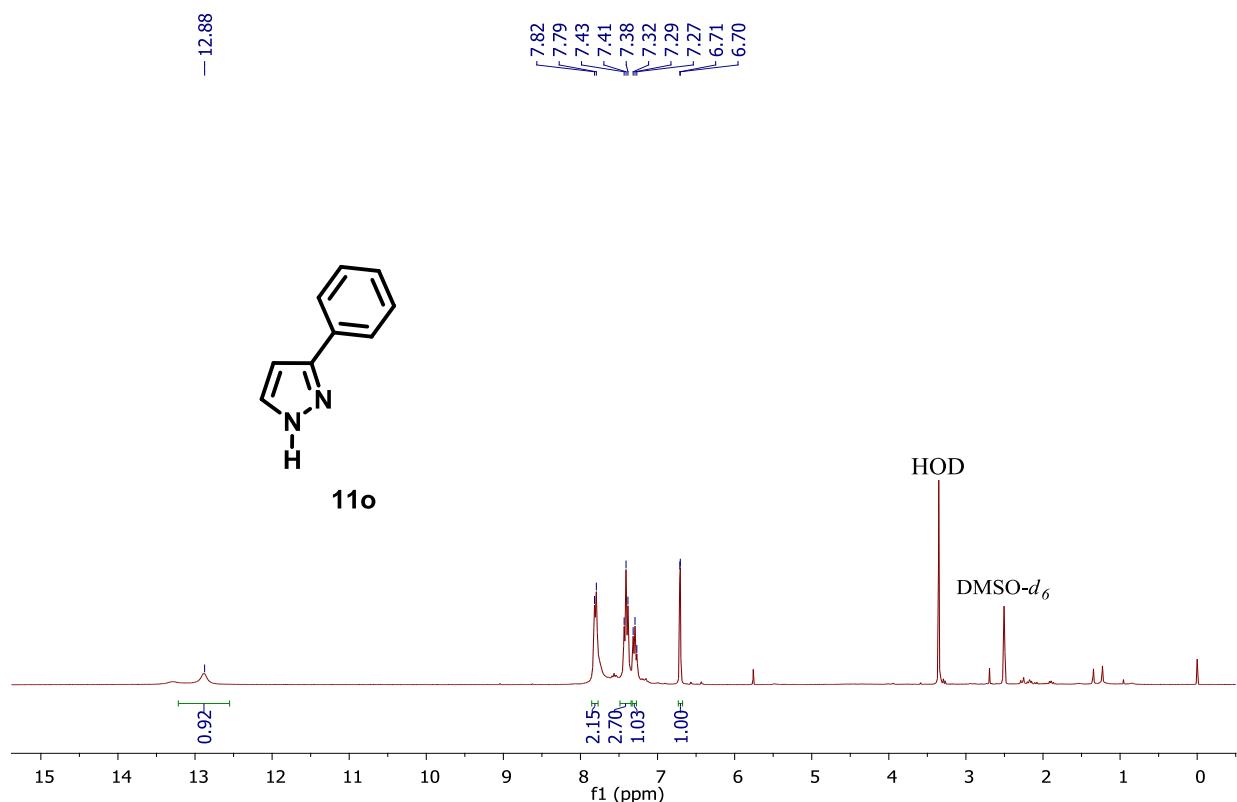
**Chemical Shifts (δ ppm):**

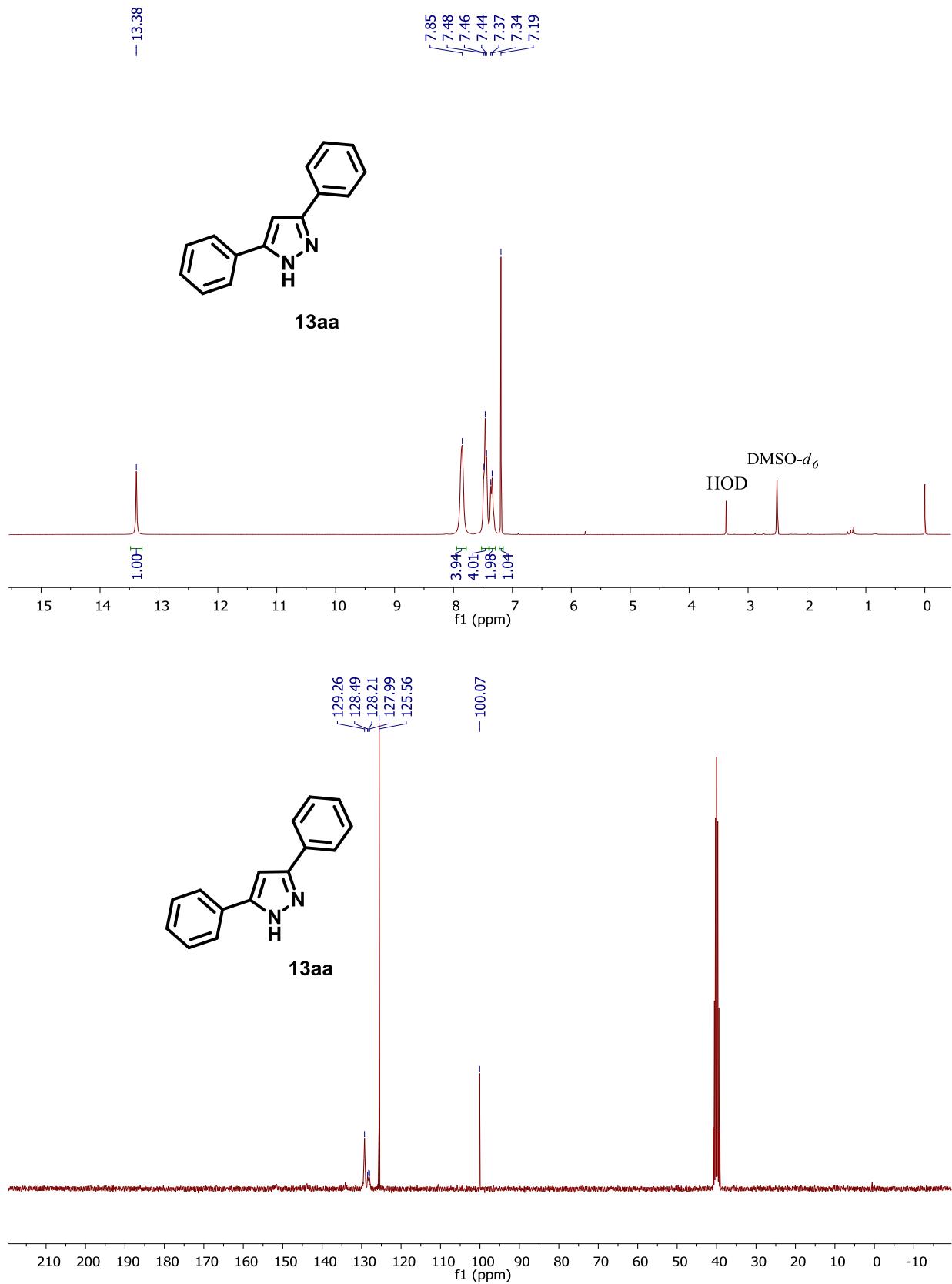
- 150.02
- 149.10
- 148.88
- 142.95
- 125.64
- 118.23
- 111.23
- 108.83
- 101.62
- 55.91
- 55.81
- 11.67

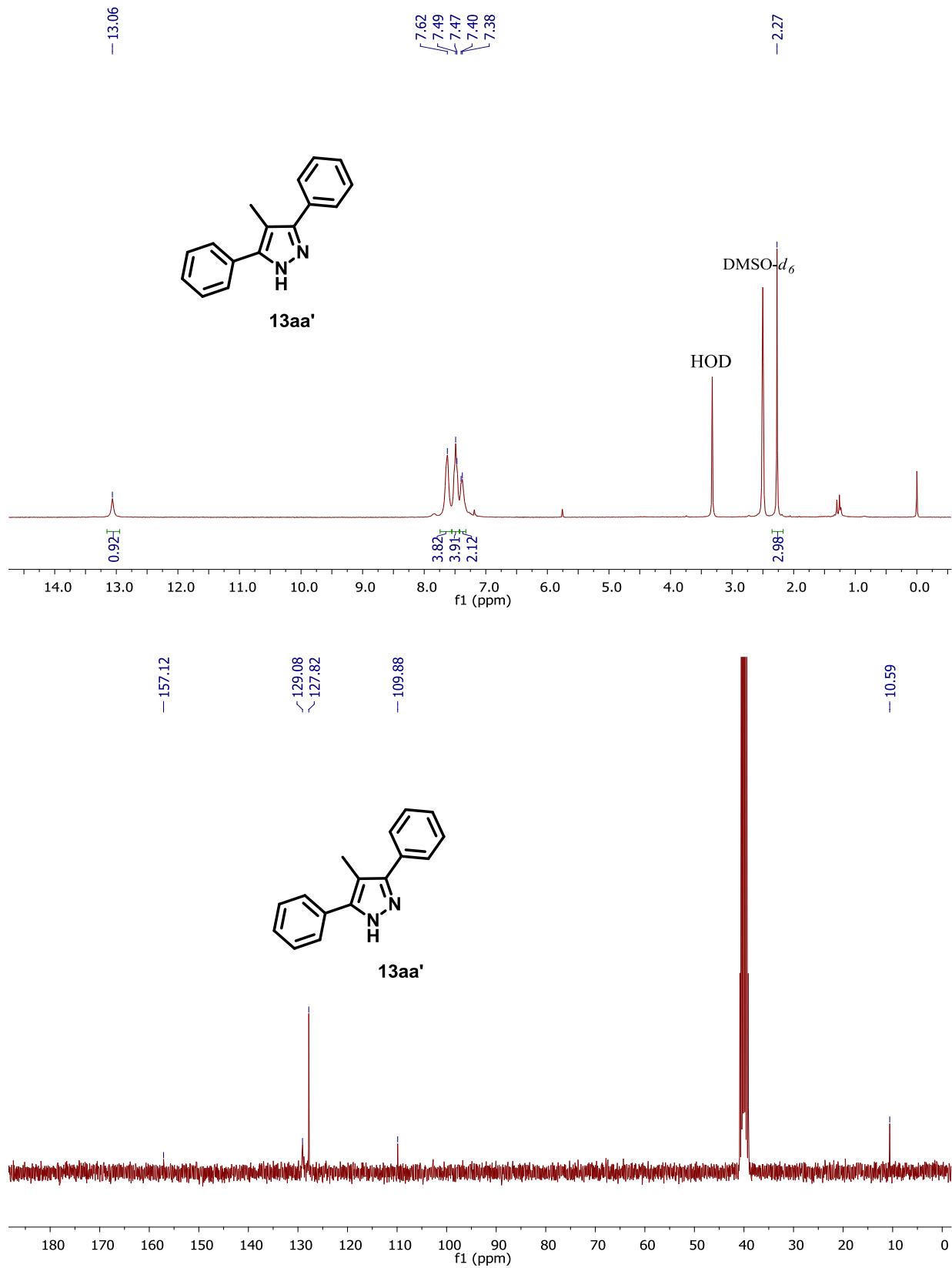


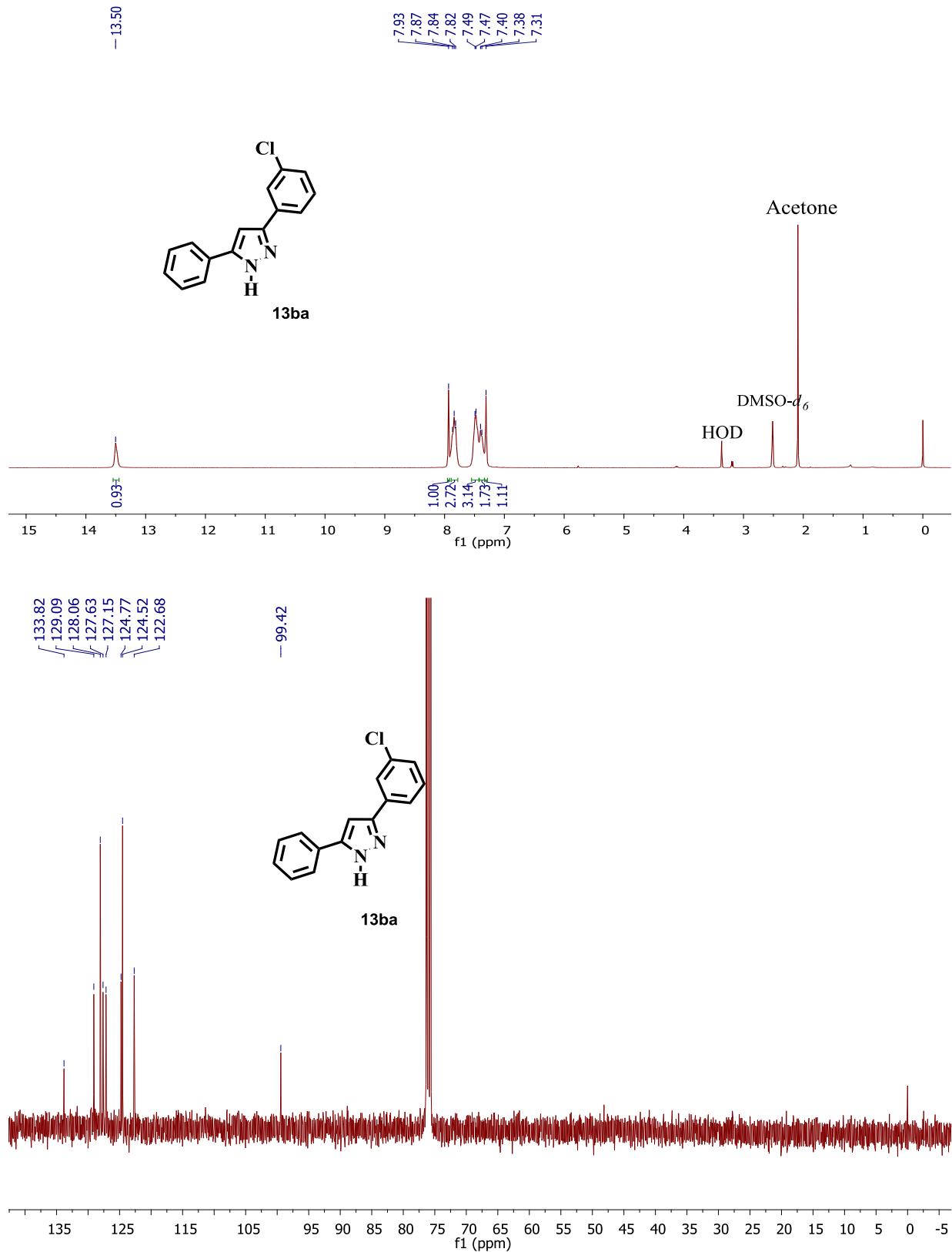


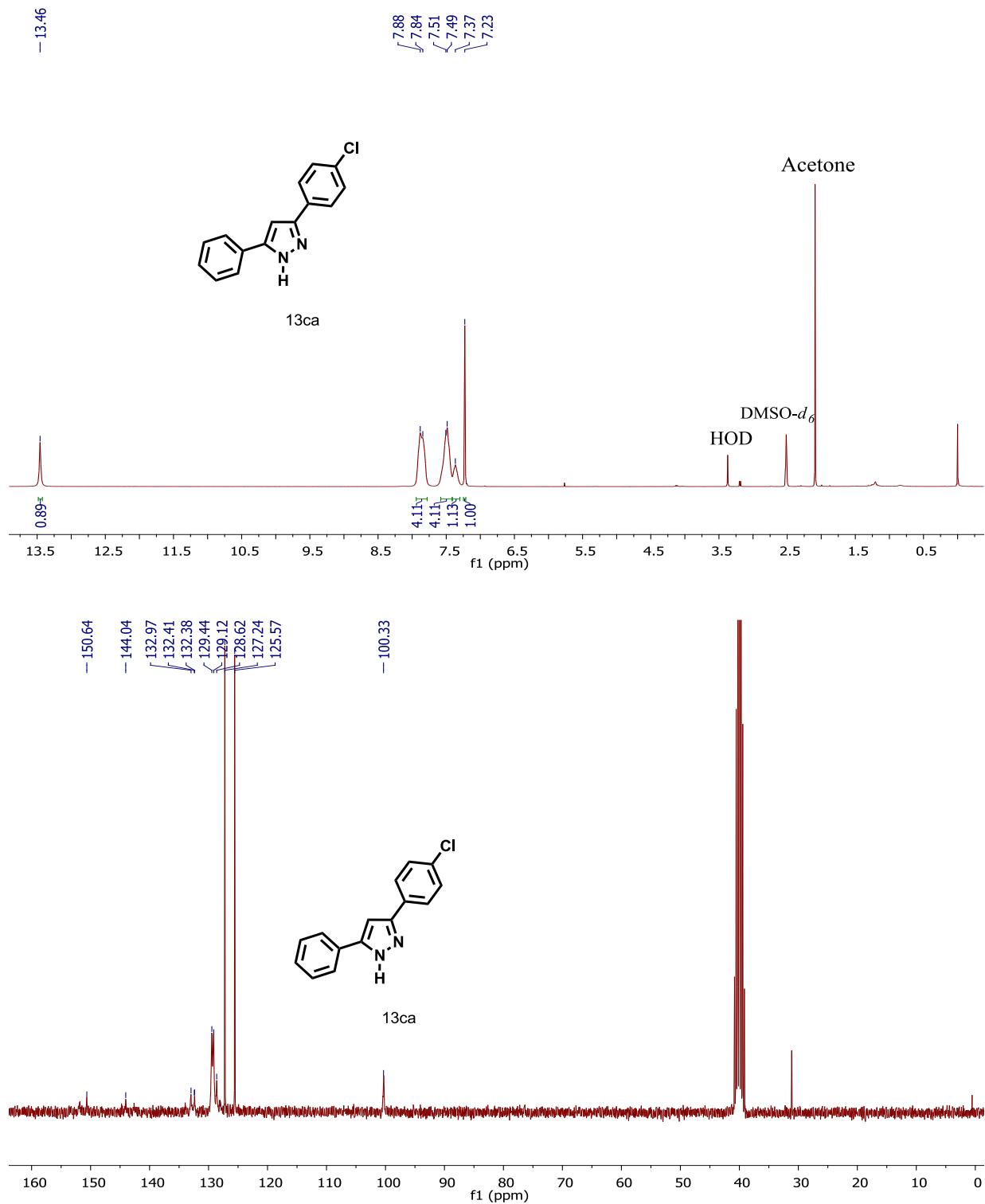


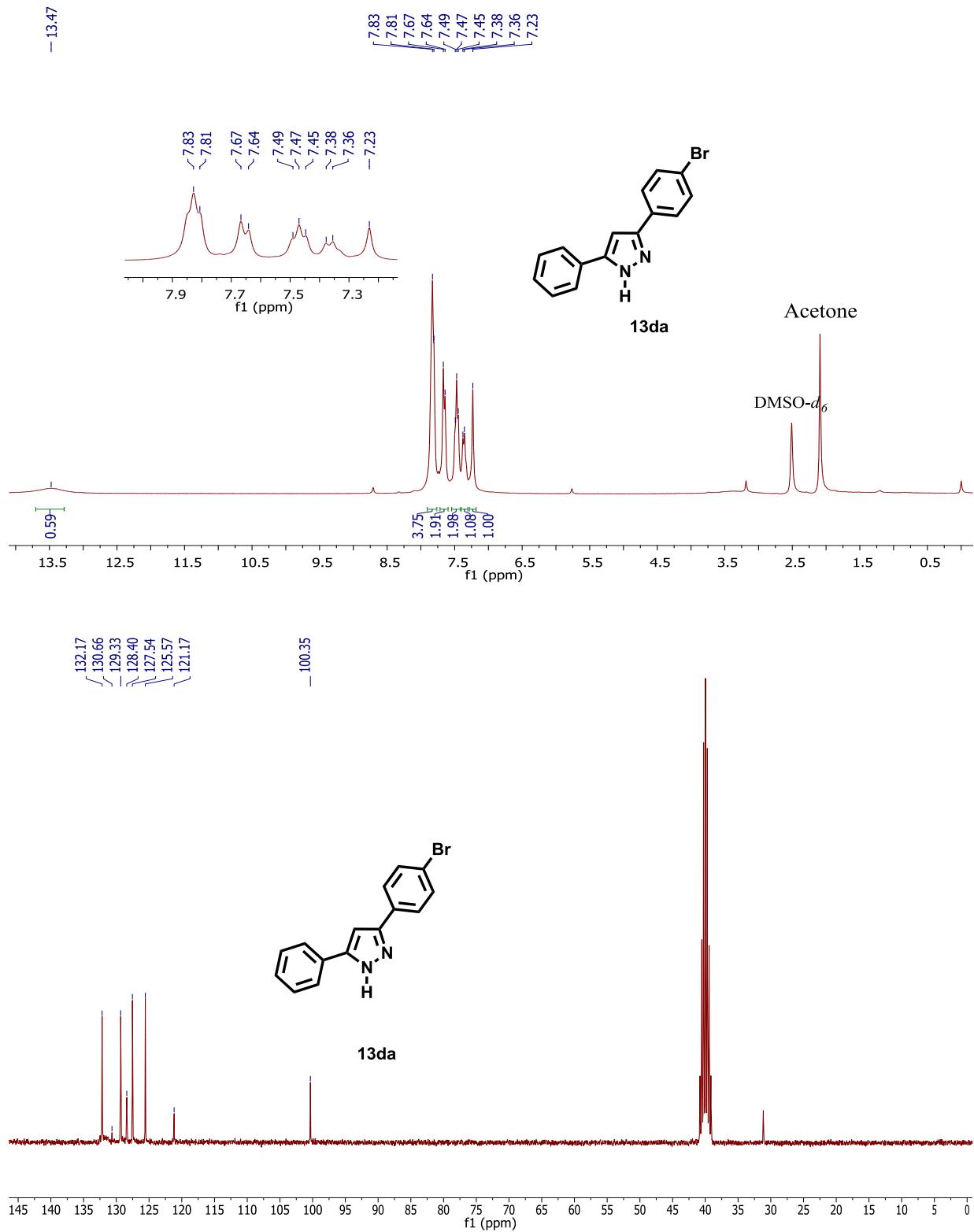


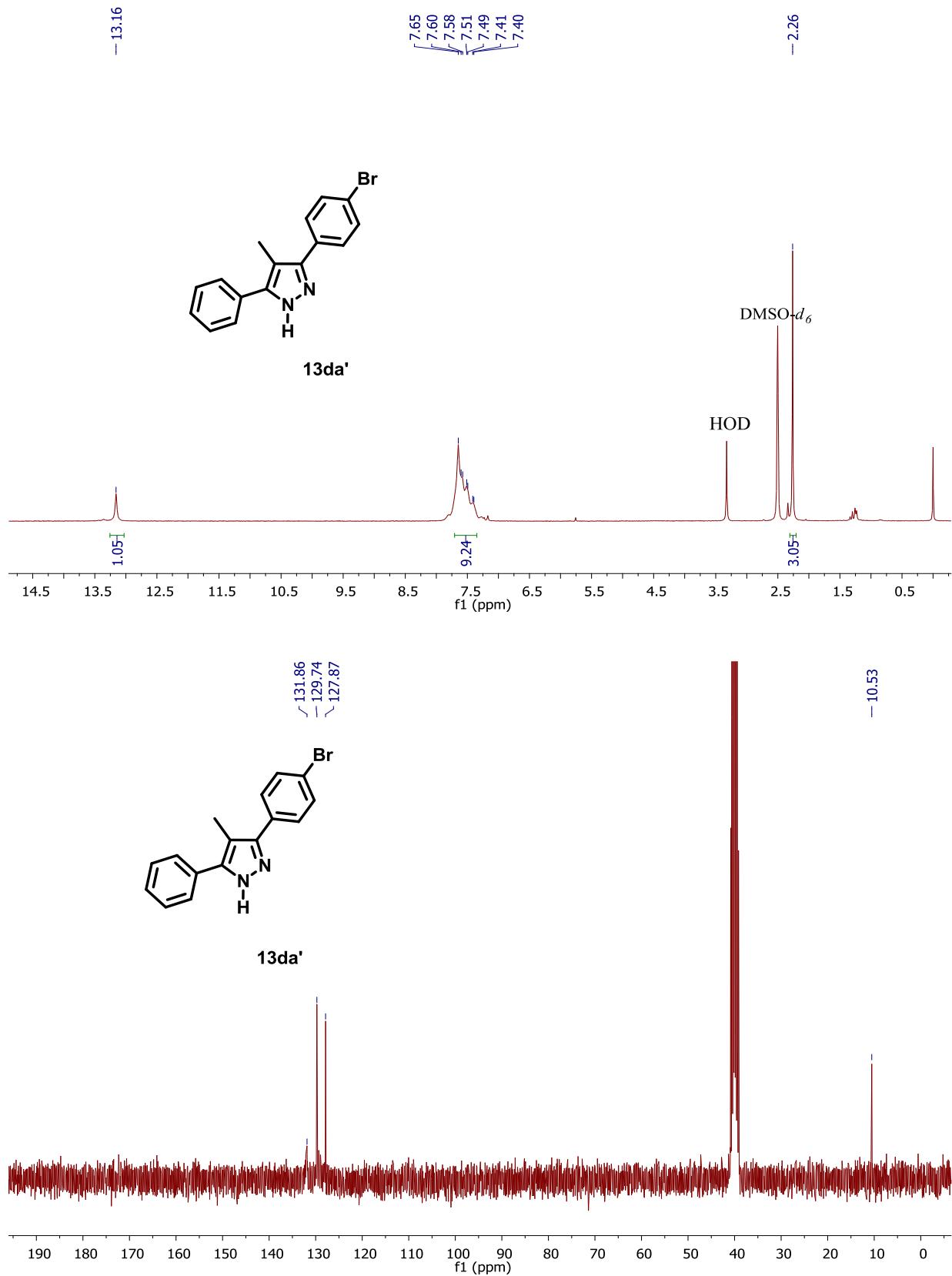


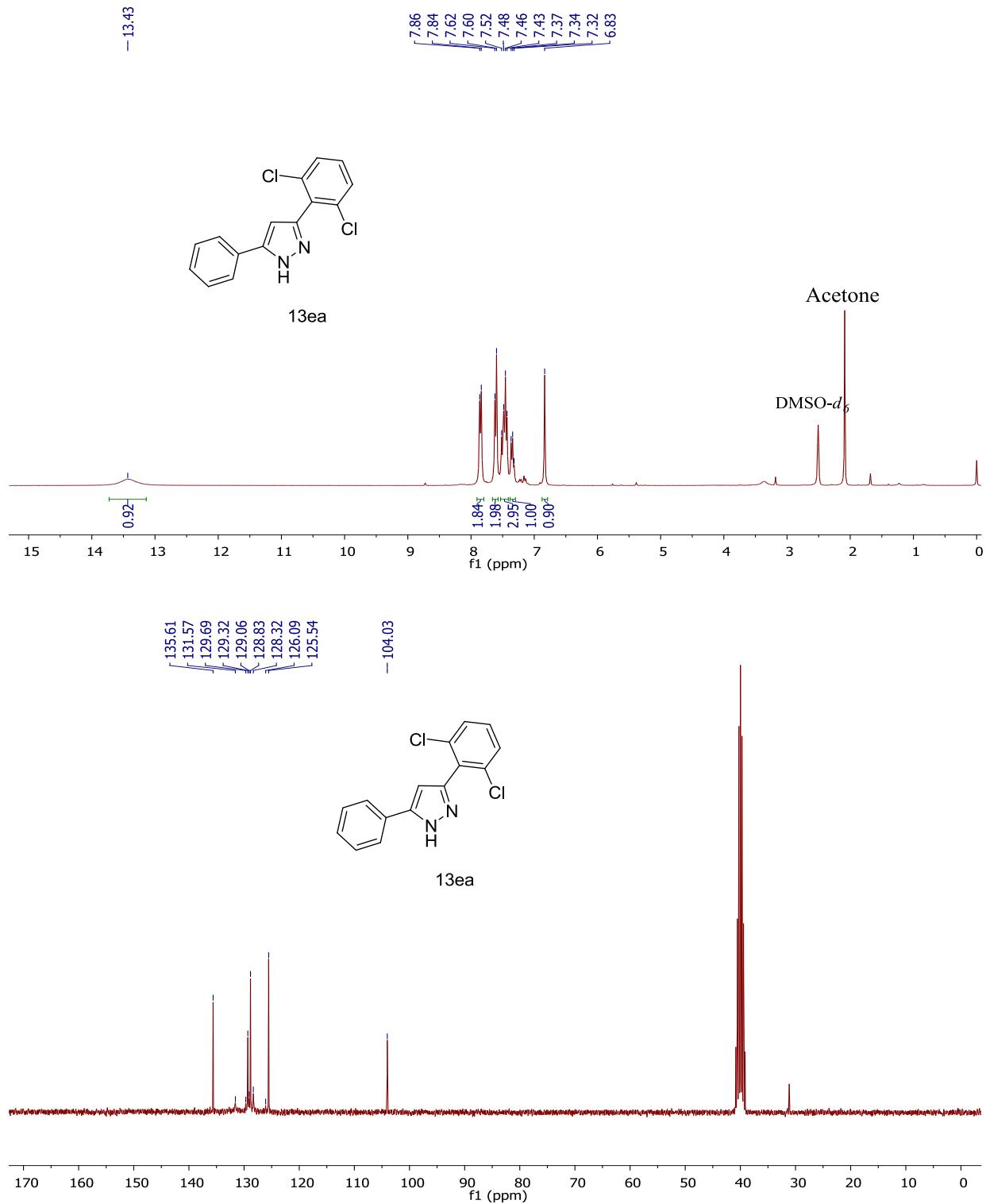


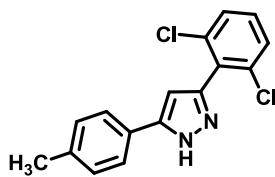
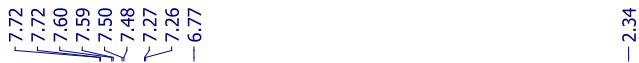




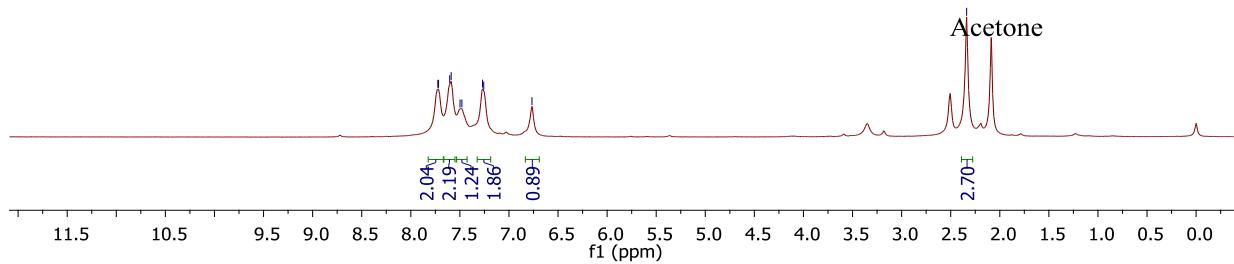






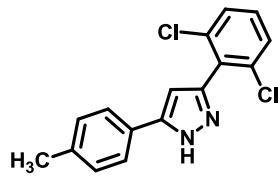


**13eb**

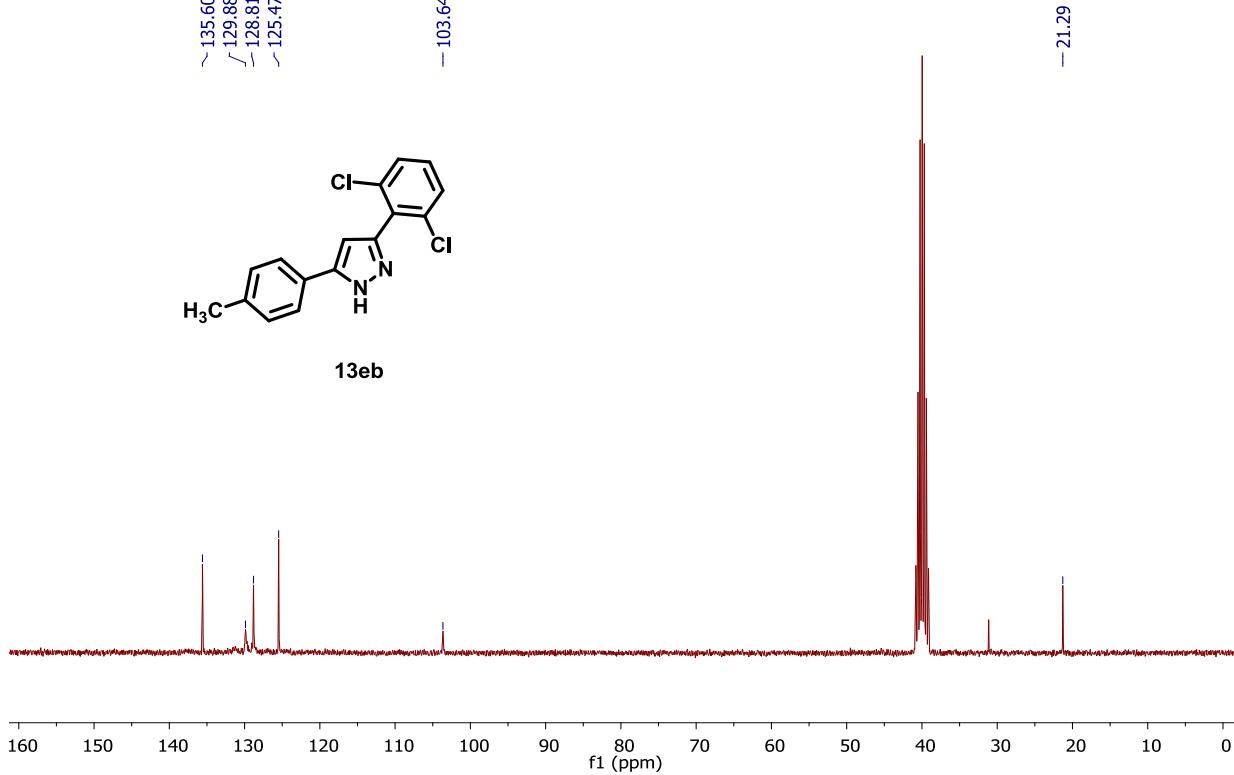


-103.64

-21.29



**13eb**

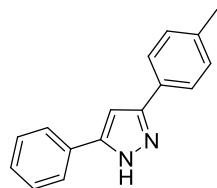


-13.30

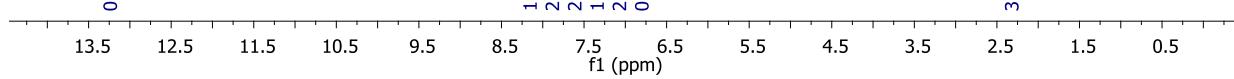
7.85  
7.83  
7.74  
7.72  
7.47  
7.45  
7.42  
7.35  
7.33  
7.31  
7.28  
7.25  
7.13

-2.34

Acetone



13fa

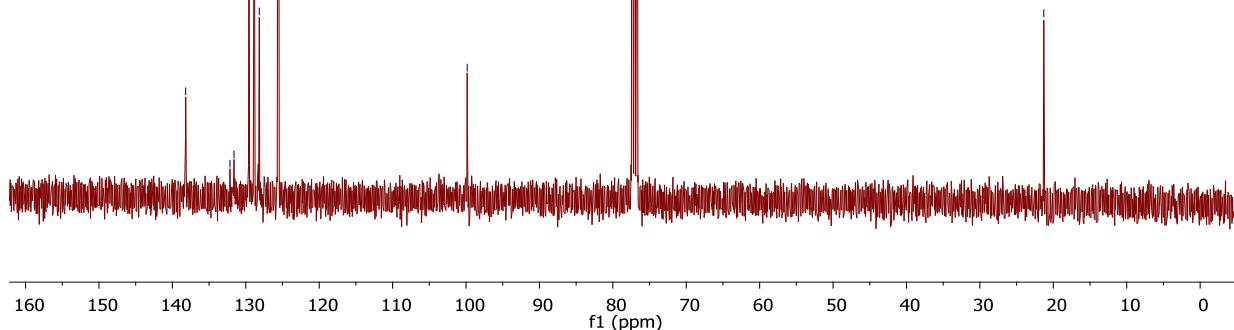


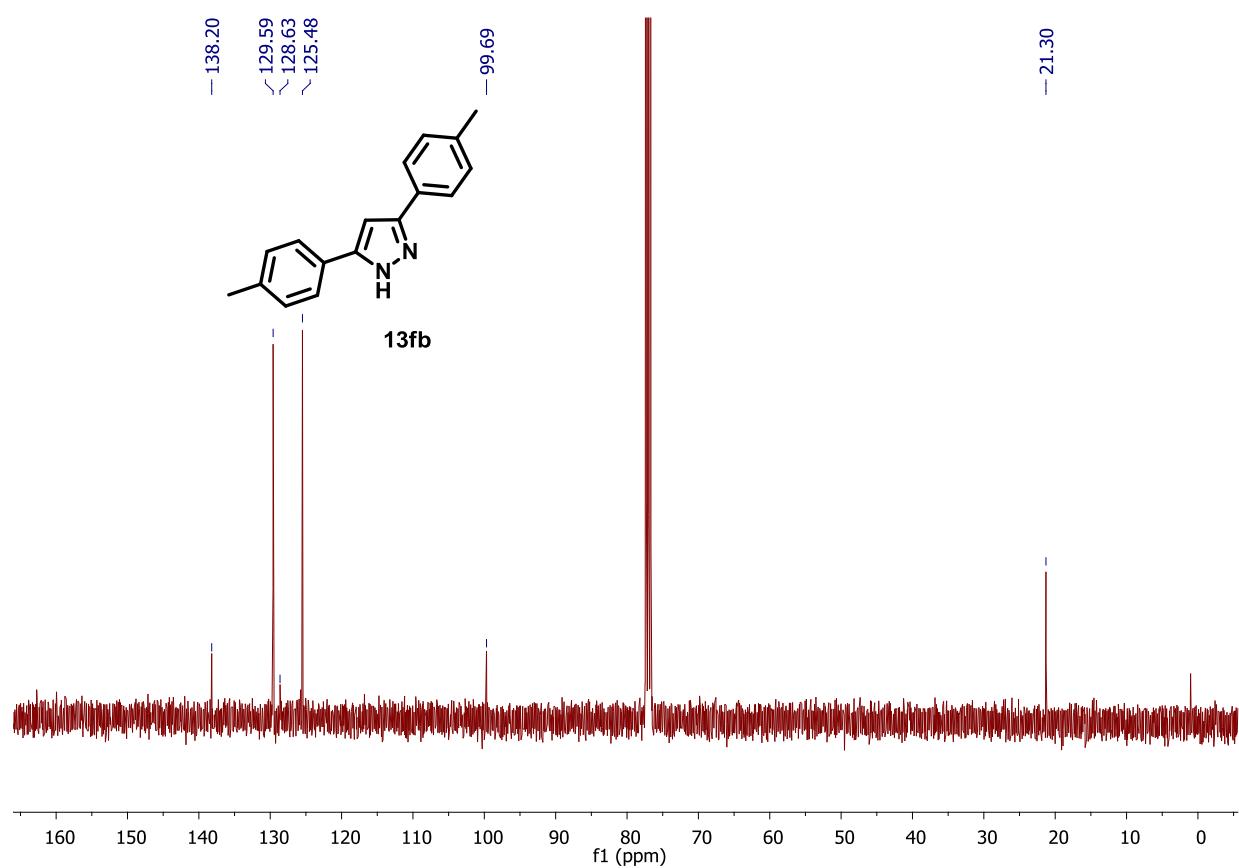
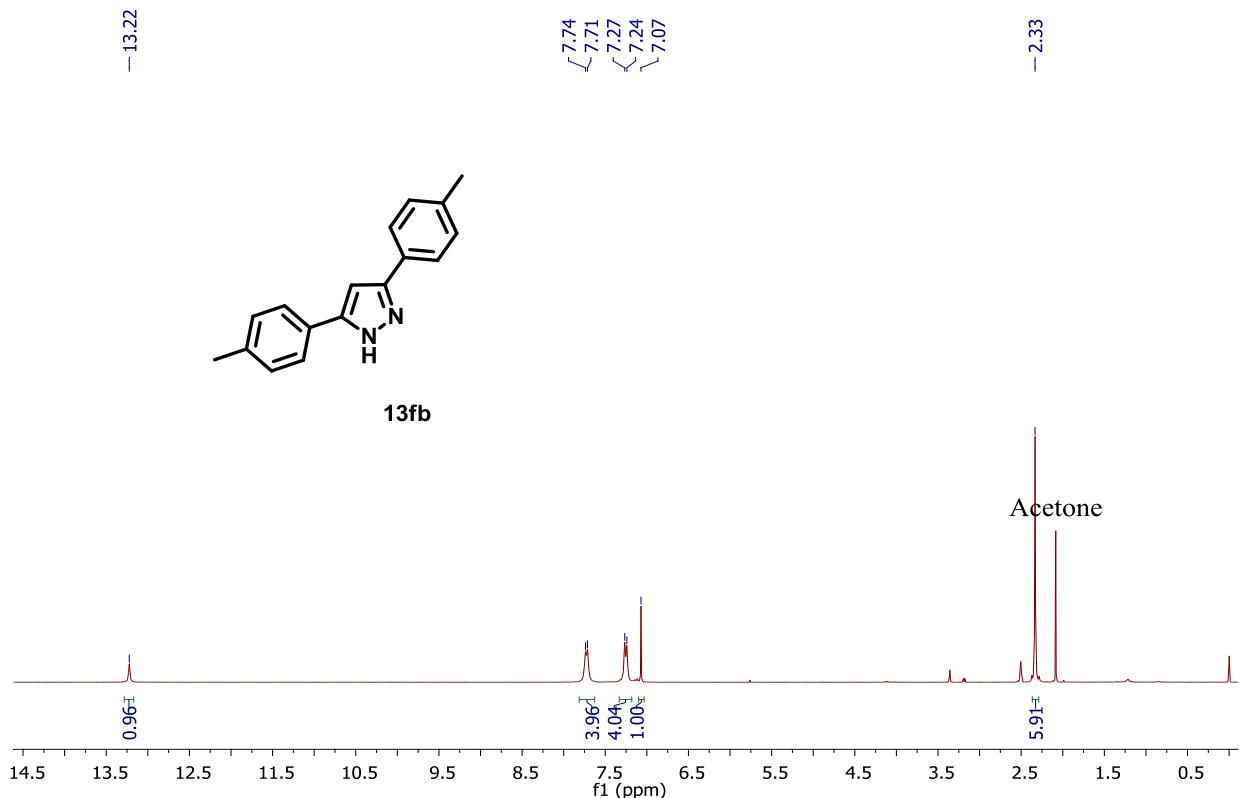
138.19  
132.15  
131.60  
129.58  
128.84  
128.16  
125.63  
125.1

-99.84

-21.29

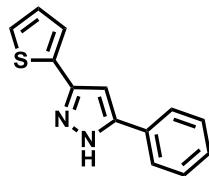
13fa



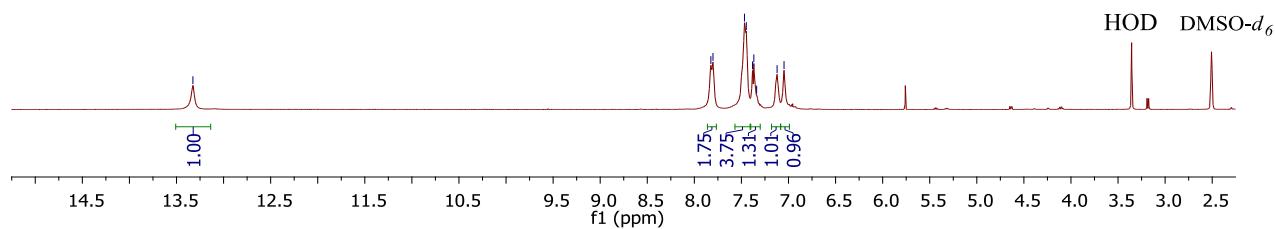


-13.33

7.82  
7.80  
7.47  
7.45  
7.38  
7.37  
7.34  
7.12  
7.05

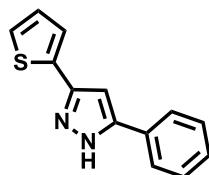


13ga



130.20  
128.97  
128.50  
127.60  
125.58  
124.91  
124.12

-100.20



13ga

