

Supporting Information

**Copper-catalyzed in situ Oxidative-coupling for One-pot Synthesis of  
5-Aryl-1,4-disubstituted 1,2,3-Triazoles under Mild Conditions**

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## General Information and Materials.

Solvents were dried using traditional methods, and freshly distilled prior to use. All reactions were carried out in THF solvent, unless otherwise noted. Reactions were monitored by thin-layer chromatography (TLC) on silica gel GF254-precoated plates. Compounds were detected under UV light. Solvents were evaporated under reduced pressure and below 40 °C (Water bath). <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on 400 or 600 MHz using TMS as internal standard.

## Typical experimental procedures

The anhydrous solvent toluene was added into a 10 mL dry reaction bottle under the condition of ice bath, 10 mg (0.15 mmol) of azide, 41 mg (0.6 mmol) of phenylboronic acid and 8 mg (0.17 mmol) of terminal alkyne were added in turn, and then CuCl 1.3 mg (0.015 mmol) and 22 mg (0.15 mmol) of chloramine T. After the raw materials reacted completely, the reaction was extracted three times with water/dichloromethane, the organic phase was washed twice with saturated salt water, the organic phases were combined, dried with anhydrous sodium sulfate, evaporated to dryness and separated by column to obtain the product.

## Characterization of compounds 4a to 4z

**Compound 4a** The title compound was isolated as a pale-yellow solid, M.p.: 98-99 °C. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.55 (d, *J* = 7.2 Hz, 2H), 7.46 (t, *J* = 7.2 Hz, 1H), 7.42 (t, *J* = 7.0 Hz, 2H), 7.24 – 7.21 (s, 6H), 7.13 (d, *J* = 7.2 Hz, 2H), 7.02 (d, *J* = 3.0 Hz, 2H), 5.42 (s, 2H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 144.7, 135.4, 134.0, 131.2, 130.2, 129.7, 129.3, 128.9, 128.6, 128.3, 128.1, 127.8, 127.6, 126.8, 52.3. HRMS (ESI) *m/z* calculate for ([M+Na]<sup>+</sup>) C<sub>21</sub>H<sub>17</sub>N<sub>3</sub>Na<sup>+</sup>: 334.1315, Found: 334.1316.

**Compound 4b** The title compound was isolated as a pale-yellow solid, M.p.: 125-126 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.49 – 7.39 (m, 5H), 7.25 – 7.27 (m, 3H), 7.16 – 7.15 – 7.13 (m, 2H), 7.07 – 7.01 (m, 4H), 5.40 (s, 2H), 2.30 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 144.8, 137.6, 135.6, 133.7, 130.3, 129.7, 129.4, 129.2, 128.8, 128.3, 128.2, 128.0, 127.6, 126.9, 52.1, 21.3. HRMS (ESI) *m/z* calculate for ([M+Na]<sup>+</sup>) C<sub>22</sub>H<sub>19</sub>N<sub>3</sub>Na<sup>+</sup>: 348.1471, Found: 348.1473.

**Compound 4c** The title compound was isolated as a white solid, M.p.: 142-143 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.51 – 7.43 (m, 5H), 7.26 – 7.23 (m, 3H), 7.23 (d, *J* = 1.6 Hz, 1H), 7.21 (s, 1H), 7.13 – 7.10 (m, 2H), 7.03 – 7.01 (m, 2H), 5.40 (s, 2H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 143.7, 135.3, 134.1, 133.7, 130.1, 130.0, 129.5, 129.4, 128.9, 128.8, 128.4, 128.1, 127.7, 127.7, 52.3. HRMS (ESI) *m/z* calculate for ([M+Na]<sup>+</sup>) C<sub>21</sub>H<sub>16</sub>ClN<sub>3</sub>Na<sup>+</sup>: 368.0925, Found: 368.0924.

**Compound 4d** The title compound was isolated as a white solid, M.p.: 144-145 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.45 (t, *J* = 7.4 Hz, 1H), 7.40 – 7.32 (s, 6H), 7.22 – 7.20 (s, 3H), 7.08 (d, *J* = 7.2 Hz, 2H), 6.99 – 6.97 (s, 2H), 5.35 (s, 2H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 142.7, 134.3, 133.2, 130.6, 129.1, 129.0, 128.3, 127.8, 127.2, 126.6, 120.9, 51.2. HRMS (ESI) *m/z* calculate for ([M+Na]<sup>+</sup>) C<sub>21</sub>H<sub>16</sub>BrN<sub>3</sub>Na<sup>+</sup>: 412.0420, Found: 412.0421.

**Compound 4e** The title compound was isolated as a pale-yellow solid, M.p.: 98-99 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.49 – 7.30 (m, 5H), 7.19 – 7.15 (m, 3H), 7.08 – 7.02 (m, 2H), 6.95 (dd, *J* = 6.4, 2.8 Hz, 2H), 6.86 (t, *J* = 8.8 Hz, 2H), 5.34 (s, 2H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 163.3, 161.5, 143.8, 135.3, 133.7, 130.1, 129.9,

129.4, 128.8, 128.5 (d,  $J = 8.0$  Hz), 128.3, 127.7, 127.6, 127.2 (d,  $J = 3.2$  Hz), 115.6, 115.5, 52.3. HRMS (ESI)  $m/z$  calculate for ( $[M+Na]^+$ )  $C_{21}H_{16}FN_3Na^+$ : 352.1220, Found: 352.1221.

**Compound 4f** The title compound was isolated as a white solid, M.p.: 109-110 °C.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.83 – 7.78 (m, 1H), 7.76 (d,  $J = 8.6$  Hz, 1H), 7.72 – 7.66 (m, 1H), 7.57 (dd,  $J = 7.8, 1.6$  Hz, 2H), 7.51 – 7.43 (m, 3H), 7.39 (dd,  $J = 9.2, 5.8$  Hz, 3H), 7.27 – 7.20 (m, 4H), 7.17 – 7.11 (m, 2H), 5.58 (s, 2H).  $^{13}C$  NMR (151 MHz,  $CDCl_3$ )  $\delta$  144.7, 134.1, 133.2, 133.1, 132.9, 131.0, 130.3, 129.8, 129.3, 128.8, 128.6, 128.1, 128.0, 127.8, 127.8, 126.9, 126.6, 126.5, 125.2, 52.3. HRMS (ESI)  $m/z$  calculate for ( $[M+Na]^+$ )  $C_{25}H_{19}N_3Na^+$ : 384.1471, Found: 384.1471.

**Compound 4g** The title compound was isolated as a white solid, M.p.: 143-144 °C.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.82 – 7.78 (m, 1H), 7.75 (d,  $J = 8.4$  Hz, 1H), 7.71 – 7.65 (m, 1H), 7.50 – 7.42 (m, 5H), 7.40 – 7.36 (m, 3H), 7.23 – 7.20 (m, 1H), 7.16 – 7.11 (m, 2H), 7.07 (d,  $J = 8.0$  Hz, 2H), 5.56 (s, 2H), 2.30 (s, 3H).  $^{13}C$  NMR (151 MHz,  $CDCl_3$ )  $\delta$  144.8, 137.6, 133.8, 133.2, 133.0, 132.9, 130.3, 129.8, 129.3, 129.3, 128.8, 128.2, 128.1, 128.1, 127.8, 126.8, 126.8, 126.5, 126.5, 125.2, 52.3, 21.3. HRMS (ESI)  $m/z$  calculate for ( $[M+Na]^+$ )  $C_{26}H_{21}N_3Na^+$ : 398.1628, Found: 398.1627.

**Compound 4h** The title compound was isolated as a pale-yellow solid, M.p.: 123-124 °C.  $^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$  7.80 – 7.79 (m, 1H), 7.76 (d,  $J = 8.4$  Hz, 1H), 7.69 (d,  $J = 7.6$  Hz, 1H), 7.54 – 7.44 (m, 5H), 7.43 – 7.36 (m, 3H), 7.22 (t,  $J = 8.6$  Hz, 3H), 7.13 – 7.12 (m, 2H), 5.56 (s, 2H).  $^{13}C$  NMR (151 MHz,  $CDCl_3$ )  $\delta$  143.7, 134.2, 133.7, 133.2, 133.1, 132.7, 130.2, 130.1, 129.6, 129.4, 128.8, 128.1, 127.8, 127.7, 126.9, 126.6, 126.6, 125.2, 52.4. HRMS (ESI)  $m/z$  calculate for ( $[M+Na]^+$ )  $C_{25}H_{18}ClN_3Na^+$ : 418.1081, Found: 418.1080.

**Compound 4i** The title compound was isolated as a white solid, M.p.: 134-135 °C.  $^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$  7.80-7.89 (m, 1H), 7.75 (d,  $J = 8.4$  Hz, 1H), 7.70 – 7.68 (m, 1H), 7.53 – 7.46 (m, 3H), 7.41 (dt,  $J = 18.8, 7.8$  Hz, 7H), 7.22 – 7.20 (m, 1H), 7.12 (d,  $J = 7.6$  Hz, 2H), 5.56 (s, 2H).  $^{13}C$  NMR (151 MHz,  $CDCl_3$ )  $\delta$  143.7, 134.3, 133.2, 133.1, 132.7, 131.8, 130.1, 130.1, 130.0, 129.4, 128.8, 128.3,

128.0, 127.8, 127.7, 126.9, 126.6, 126.6, 125.1, 121.9, 52.4. HRMS (ESI)  $m/z$  calculate for  $([M+Na]^+)$   $C_{25}H_{18}BrN_3Na^+$ : 462.0576, Found: 462.575.

**Compound 4j** The title compound was isolated as a white solid, M.p.: 100-101 °C.  $^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$  7.80 (d,  $J = 8.2$  Hz, 1H), 7.76 – 7.75 (m, 1H), 7.70-7.68 (m, 1H), 7.51 – 7.44 (m, 5H), 7.40 – 7.37 (m, 3H), 7.22 – 7.21 (m, 1H), 7.14 (d,  $J = 7.6$  Hz, 2H), 6.80 (d,  $J = 8.4$  Hz, 2H), 5.56 (s, 2H), 3.77 (s, 3H).  $^{13}C$  NMR (151 MHz,  $CDCl_3$ )  $\delta$  159.4, 144.8, 133.3, 133.3, 133.1, 132.9, 130.3, 129.8, 129.3, 128.8, 128.2, 128.1, 127.8, 126.8, 126.6, 126.5, 125.2, 123.7, 114.0, 55.3, 52.4 . HRMS (ESI)  $m/z$  calculate for  $([M+Na]^+)$   $C_{26}H_{21}N_3NaO^+$ : 414.1577, Found: 414.1576.

**Compound 4k** The title compound was isolated as a pale-yellow solid, M.p.: 128-129 °C.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.79 (ddd,  $J = 20.4, 9.8, 6.0$  Hz, 2H), 7.73 – 7.66 (m, 1H), 7.46 (ddq,  $J = 10.6, 4.2, 2.0$  Hz, 4H), 7.42 – 7.35 (m, 3H), 7.23 – 7.19 (m, 3H), 7.01 – 6.99 (m, 2H), 5.54 (s, 2H), 2.42 (s, 3H).  $^{13}C$  NMR (151 MHz,  $CDCl_3$ )  $\delta$  143.6, 140.20, 134.4, 133.2, 133.1, 132.8, 131.7, 130.2, 130.0, 128.8, 128.3, 128.0, 127.8, 126.9, 126.6, 126.5, 125.2, 124.5, 121.8, 52.3, 21.6. HRMS (ESI)  $m/z$  calculate for  $([M+Na]^+)$   $C_{26}H_{20}BrN_3Na^+$ : 476.0733, Found: 476.0735.

**Compound 4l** The title compound was isolated as a pale-yellow solid, M.p.: 85-86 °C.  $^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$  8.06 (d,  $J = 8.6$  Hz, 2H), 7.44 (d,  $J = 7.2$  Hz, 2H), 7.42 – 7.38 (m, 1H), 7.37 – 7.35 (s, 2H), 7.22 – 7.13 (m, 5H), 6.71 (d,  $J = 8.6$  Hz, 2H), 4.37 (t,  $J = 6.6$  Hz, 2H), 3.94 (t,  $J = 5.6$  Hz, 2H), 2.29 (p,  $J = 6.0$  Hz, 2H).  $^{13}C$  NMR (151 MHz,  $CDCl_3$ )  $\delta$  163.4, 144.5, 141.8, 134.2, 130.9, 130.0, 129.9, 129.6, 128.6, 127.9, 127.9, 126.9, 126.0, 114.5, 65.1, 44.7, 29.5. HRMS (ESI)  $m/z$  calculate for  $([M+Na]^+)$   $C_{23}H_{20}N_4NaO_4^+$ : 439.1377, Found: 439.1378.

**Compound 4m** The title compound was isolated as a pale-yellow solid, M.p.: 115-116 °C.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.18 – 8.12 (m, 2H), 7.55 – 7.42 (m, 4H), 7.38 (s, 4H), 7.24 (t,  $J = 1.8$  Hz, 1H), 6.83 – 6.75 (m, 2H), 4.44 (t,  $J = 6.6$  Hz, 2H), 4.03-4.00 (m, 2H), 2.40 – 2.34 (m, 2H).  $^{13}C$  NMR (151 MHz,  $CDCl_3$ )  $\delta$  163.4, 143.5, 141.8, 134.4, 131.8, 130.2, 129.9, 129.7, 128.4, 127.9, 127.4, 126.0, 122.1, 114.5,

65.0, 44.8, 29.5. HRMS (ESI)  $m/z$  calculate for  $([M+Na]^+)$   $C_{23}H_{19}BrN_4NaO_4^+$ : 517.0482, Found: 517.0484.

**Compound 4n** The title compound was isolated as a white solid, M.p.: 95-96 °C.  $^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$  7.75 (d,  $J = 8.2$  Hz, 1H), 7.68 (dd,  $J = 11.6, 8.8$  Hz, 2H), 7.53 (d,  $J = 7.6$  Hz, 2H), 7.46 – 7.37 (m, 4H), 7.34 – 7.31 (m, 1H), 7.26 – 7.21 (m, 5H), 7.00 (s, 1H), 6.95 (d,  $J = 9.0$  Hz, 1H), 4.46 (t,  $J = 6.8$  Hz, 2H), 4.03 (t,  $J = 5.6$  Hz, 2H), 2.42 (p,  $J = 6.2$  Hz, 2H).  $^{13}C$  NMR (151 MHz,  $CDCl_3$ )  $\delta$  156.4, 144.3, 134.5, 134.3, 131.0, 130.1, 129.7, 129.4, 129.4, 129.1, 128.5, 127.9, 127.8, 127.7, 126.9, 126.8, 126.5, 123.8, 118.8, 106.7, 64.0, 45.0, 29.7. HRMS (ESI)  $m/z$  calculate for  $([M+Na]^+)$   $C_{27}H_{23}N_3NaO^+$ : 428.1733, Found: 428.1735.

**Compound 4o** The title compound was isolated as a white solid, M.p.: 148-149 °C.  $^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$  7.76 (d,  $J = 8.2$  Hz, 1H), 7.71 – 7.67 (m, 2H), 7.43 (dd,  $J = 12.2, 8.0$  Hz, 3H), 7.38 – 7.37 (m, 2H), 7.35 – 7.33 (m, 1H), 7.18 – 7.17 (m, 2H), 7.11 (d,  $J = 7.6$  Hz, 2H), 6.99 (s, 1H), 6.96 – 6.94 (m, 1H), 4.46 (t,  $J = 6.8$  Hz, 2H), 4.02 (t,  $J = 5.6$  Hz, 2H), 2.43 – 2.39 (m, 2H), 2.38 (s, 3H).  $^{13}C$  NMR (151 MHz,  $CDCl_3$ )  $\delta$  156.4, 143.3, 140.1, 134.6, 134.5, 131.7, 130.3, 130.2, 129.8, 129.4, 129.1, 128.4, 127.7, 126.9, 126.6, 124.4, 123.9, 121.8, 118.7, 106.7, 64.0, 45.0, 29.8, 21.5. HRMS (ESI)  $m/z$  calculate for  $([M+Na]^+)$   $C_{28}H_{24}BrN_3NaO^+$ : 520.0995, Found: 520.0997.

**Compound 4p** The title compound was isolated as a pale-yellow solid, M.p.: 81-82 °C.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.51 – 7.43 (m, 2H), 7.43 – 7.31 (m, 3H), 7.18 – 7.14 (m, 3H), 7.08-7.06 (m, 2H), 6.87 (d,  $J = 8.6$  Hz, 2H), 6.71 – 6.64 (m, 2H), 5.26 (s, 2H), 3.68 (s, 3H).  $^{13}C$  NMR (151 MHz,  $CDCl_3$ )  $\delta$  159.6, 144.7, 133.8, 131.1, 130.3, 129.8, 129.3, 129.2, 128.6, 128.1, 127.8, 127.5, 126.8, 114.2, 55.4, 51.7. HRMS (ESI)  $m/z$  calculate for  $([M+Na]^+)$   $C_{22}H_{19}N_3NaO^+$ : 364.1420, Found: 364.1422.

**Compound 4q** The title compound was isolated as a white solid, M.p.: 128-129 °C.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.43 – 7.40 (m, 2H), 7.38 – 7.36 (m, 2H), 7.25 (d,  $J = 8.4$  Hz, 2H), 7.03 – 6.93 (m, 4H), 6.81 – 6.76 (m, 2H), 5.32 (s, 2H), 3.77 (s, 3H), 2.44 (s, 3H).  $^{13}C$  NMR (151 MHz,  $CDCl_3$ )  $\delta$  159.6, 143.6, 140.1, 134.1, 131.7, 130.2, 130.1,

130.0, 129.2, 128.3, 127.5, 124.6, 121.8, 114.2, 55.4, 51.6, 21.6. HRMS (ESI) m/z calculate for  $([M+Na]^+)$   $C_{23}H_{20}BrN_3NaO^+$ : 456.0682, Found: 456.0680.

**Compound 4r** The title compound was isolated as a white solid, M.p.: 120-121 °C.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.50-7.46 (m, 1H), 7.44 – 7.40 (m, 2H), 7.40 – 7.35 (m, 4H), 7.22 – 7.21 (m, 3H), 6.96-6.91 (m, 4H), 4.38 (t,  $J = 7.2$  Hz, 2H), 3.16 (t,  $J = 7.4$  Hz, 2H).  $^{13}C$  NMR (151 MHz,  $CDCl_3$ )  $\delta$  143.2, 137.2, 134.5, 131.7, 130.1, 130.0, 129.9, 129.5, 128.9, 128.9, 128.3, 127.7, 127.1, 121.8, 49.6, 36.7. HRMS (ESI) m/z calculate for  $([M+Na]^+)$   $C_{22}H_{18}N_3Na^+$ : 426.0576, Found: 426.0574.

**Compound 4s** The title compound was isolated as a pale-yellow solid, M.p.: 101-102 °C.  $^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$  7.54 (d,  $J = 7.2$  Hz, 2H), 7.52 – 7.46 (m, 3H), 7.29 (t,  $J = 7.0$  Hz, 2H), 7.26 – 7.21 (m, 4H), 6.82 (t,  $J = 7.8$  Hz, 2H), 5.43 (s, 2H).  $^{13}C$  NMR (151 MHz,  $CDCl_3$ )  $\delta$  162.40 (d,  $J = 6.9$  Hz), 160.73 (d,  $J = 7.4$  Hz), 144.3, 134.1, 130.91 (dd,  $J = 22.5, 12.2$  Hz), 130.2, 129.8, 129.4, 128.5, 127.9, 127.8, 126.83, 111.55 (dd,  $J = 20.8, 4.6$  Hz), 111.04 (t,  $J = 18.4$  Hz), 40.37 (t,  $J = 3.6$  Hz). HRMS (ESI) m/z calculate for  $([M+Na]^+)$   $C_{21}H_{15}F_3N_3Na^+$ : 370.1126, Found: 370.1125.

**Compound 4t** The title compound was isolated as a white solid, M.p.: 139-140 °C.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.45 (d,  $J = 8.6$  Hz, 2H), 7.40 (d,  $J = 8.6$  Hz, 2H), 7.33 – 7.28 (m, 3H), 7.21 – 7.19 (m, 2H), 6.89 – 6.85 (m, 2H), 5.43 (s, 2H), 2.48 (s, 3H).  $^{13}C$  NMR (151 MHz,  $CDCl_3$ )  $\delta$  162.4, 160.7, 143.2, 140.2, 134.4, 131.7, 131.0, 130.9 (t,  $J = 10.3$  Hz), 130.2 (d,  $J = 9.3$  Hz), 130.2, 129.9, 128.3, 124.4, 121.8, 111.6 (dd,  $J = 20.9, 4.4$  Hz), 111.0, 40.2, 21.6. HRMS (ESI) m/z calculate for  $([M+Na]^+)$   $C_{21}H_{14}BrF_2N_3Na^+$ : 448.0231, Found: 448.0233

**Compound 4u** The title compound was isolated as a white solid, M.p.: 86-87 °C.  $^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$  7.44 (d,  $J = 8.0$  Hz, 2H), 7.37 (d,  $J = 7.8$  Hz, 2H), 7.26 – 7.23 (m, 4H), 7.05 (d,  $J = 1.8$  Hz, 2H), 7.02 – 7.01 (m, 2H), 5.39 (s, 2H), 2.43 (s, 3H).  $^{13}C$  NMR (151 MHz,  $CDCl_3$ )  $\delta$  163.4, 144.4, 141.8, 134.2, 130.8, 130.0, 129.9, 129.5, 128.6, 127.9, 126.9, 125.9, 114.5, 65.0, 44.7, 29.5. HRMS (ESI) m/z calculate for  $([M+Na]^+)$   $C_{22}H_{18}BrN_3Na^+$ : 426.0576, Found: 426.0575.

**Compound 4v** The title compound was isolated as a white solid, M.p.: 92-93 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.48 – 7.43 (m, 2H), 7.32 – 7.26 (m, 4H), 7.18-7.16 (m, 3H), 6.94 – 6.90 (m, 2H), 6.90 – 6.85 (m, 2H), 5.30 (s, 2H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 144.0, 135.1, 133.0, 132.8, 131.9, 131.7, 129.7, 129.0, 128.5, 128.4, 127.5, 126.6, 124.6, 122.2, 52.4. HRMS (ESI) m/z calculate for ([M+Na]<sup>+</sup>) C<sub>21</sub>H<sub>15</sub>Br<sub>2</sub>N<sub>3</sub>Na<sup>+</sup>: 491.9504, Found: 491.9503.

**Compound 4w** The title compound was isolated as a white solid, M.p.: 115-116 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.34 – 7.29 (m, 4H), 7.22 – 7.18 (m, 3H), 7.07 – 6.99 (m, 4H), 6.95-6.93 (m, 2H), 5.32 (s, 2H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 164.5, 162.8, 144.0, 135.2, 133.1, 132.1 (d, *J* = 8.6 Hz), 131.8, 129.8, 128.9, 128.5, 128.3, 127.5, 123.6, 122.1, 116.8, 116.7, 52.3. HRMS (ESI) m/z calculate for ([M+Na]<sup>+</sup>) C<sub>21</sub>H<sub>15</sub>BrFN<sub>3</sub>Na<sup>+</sup>: 430.0326, Found: 430.0325.

**Compound 4x** The title compound was isolated as a colorless liquid. <sup>1</sup>H (400 MHz, CDCl<sub>3</sub>) 7.35-7.33 (m, 3H), 7.18-7.16 (m, 3H), 7.05-7.03 (m, 2H), 6.94-6.93 (m, 2H), 5.33 (s, 2H), 2.55-2.51 (t, *J* = 8.0 Hz, 3H), 1.53 (s, 2H), 1.19-1.17 (m, 4H) 0.76-0.73(m, 3H). <sup>13</sup>C (101 MHz, CDCl<sub>3</sub>) 135.70, 129.72, 129.21, 128.83, 128.66, 127.99, 127.37, 77.34, 77.03, 76.71, 51.96, 31.48, 29.29, 25.05, 22.32, 13.96. HRMS (ESI) m/z calculate for ([M+Na]<sup>+</sup>) C<sub>20</sub>H<sub>23</sub>N<sub>3</sub>Na<sup>+</sup>: 328.19, Found: 328.45.

**Compound 4y** The title compound was isolated as a pale-yellow solid, M.p.: 98-99 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.83 (s, 1H), 7.50 – 7.39 (m, 5H), 7.26 – 7.21 (m, 3H), 7.15 – 7.11 (m, 2H), 7.02 (dd, *J* = 6.6, 2.8 Hz, 2H), 6.89 – 6.84 (m, 2H), 5.89 – 5.83 (m, 1H), 5.44 – 5.38 (m, 4H), 5.26 – 5.20 (m, 1H), 5.16 (s, 2H), 4.29 (dd, *J* = 12.6, 5.0 Hz, 1H), 4.14 (dd, *J* = 12.6, 2.0 Hz, 1H), 4.01-3.97 (m, 1H), 2.06 (d, *J* = 3.2 Hz, 6H), 2.02 (s, 3H), 1.82 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 170.6, 170.1, 169.5, 169.0, 157.9, 145.1, 144.4, 135.5, 133.4, 130.3, 129.8, 129.3, 128.8, 128.3, 128.2, 128.1, 127.6, 124.4, 121.3, 114.9, 85.9, 75.3, 72.8, 70.4, 67.8, 61.9, 61.7, 52.2, 20.8, 20.7, 20.6, 20.3. HRMS (ESI) m/z calculate for ([M+Na]<sup>+</sup>) C<sub>38</sub>H<sub>38</sub>N<sub>6</sub>NaO<sub>10</sub><sup>+</sup>: 761.2542, Found: 761.2543.

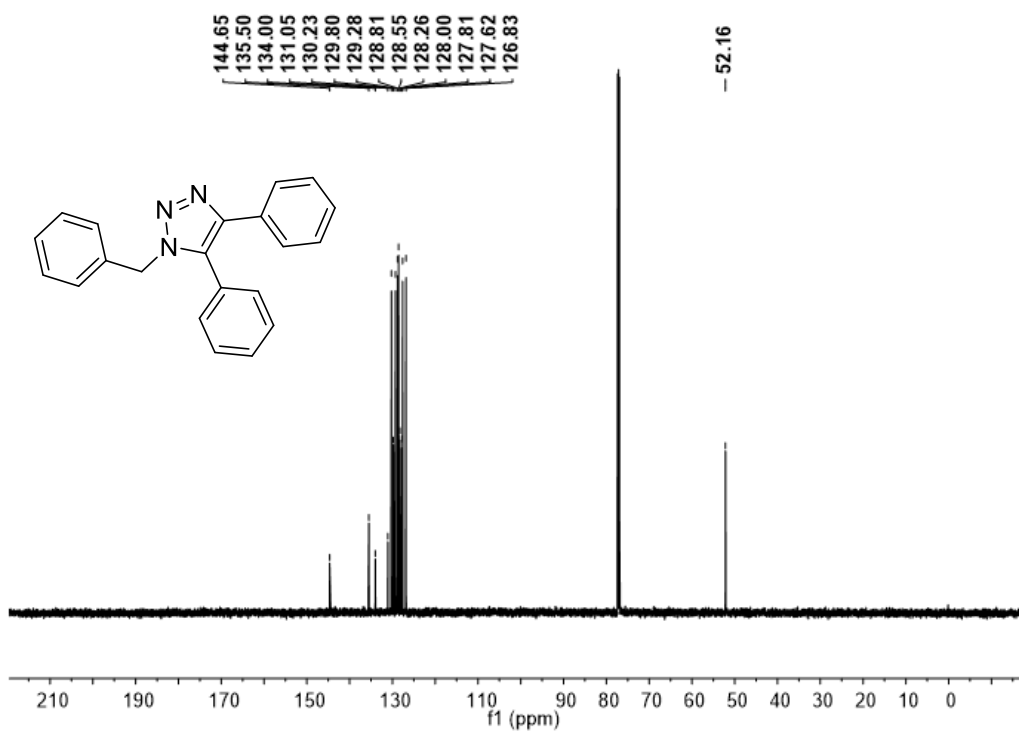
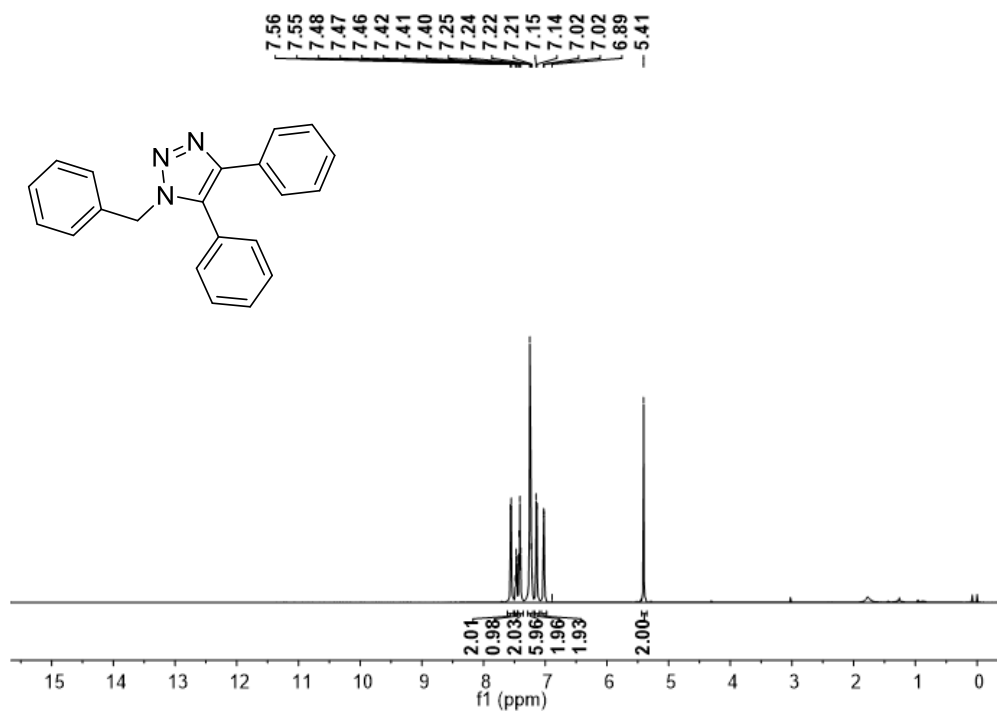
**Compound 4z** The title compound was isolated as a pale- brown liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.88 – 7.86 (m, 1H), 7.63 – 7.60 (m, 2H), 7.34 – 7.33 (m, 1H),



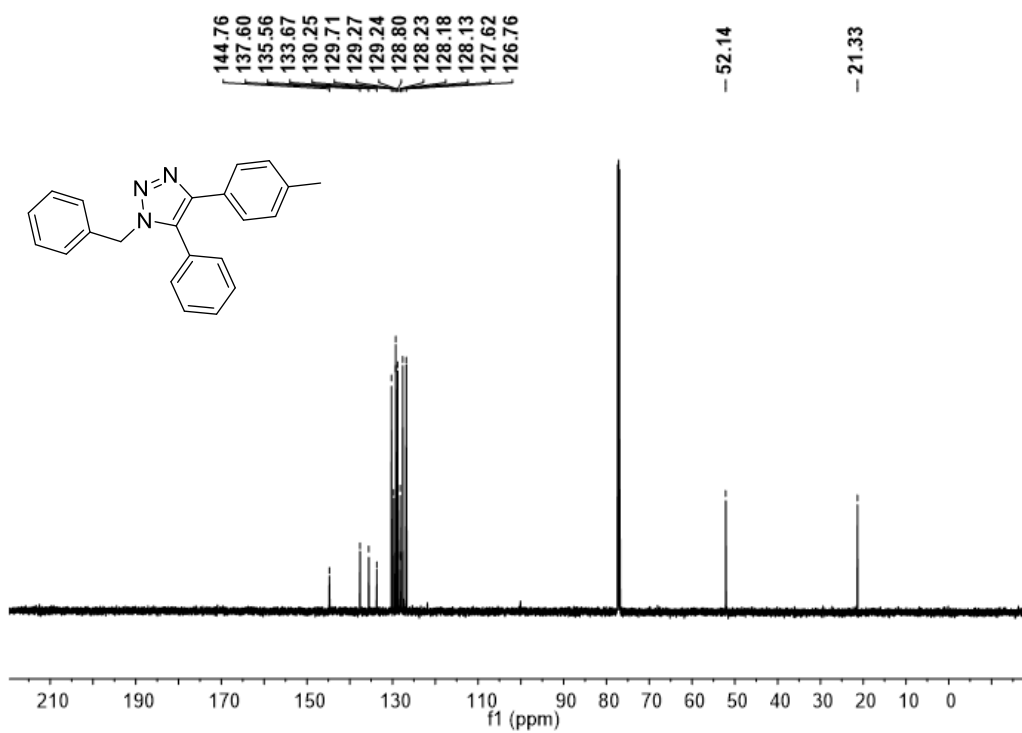
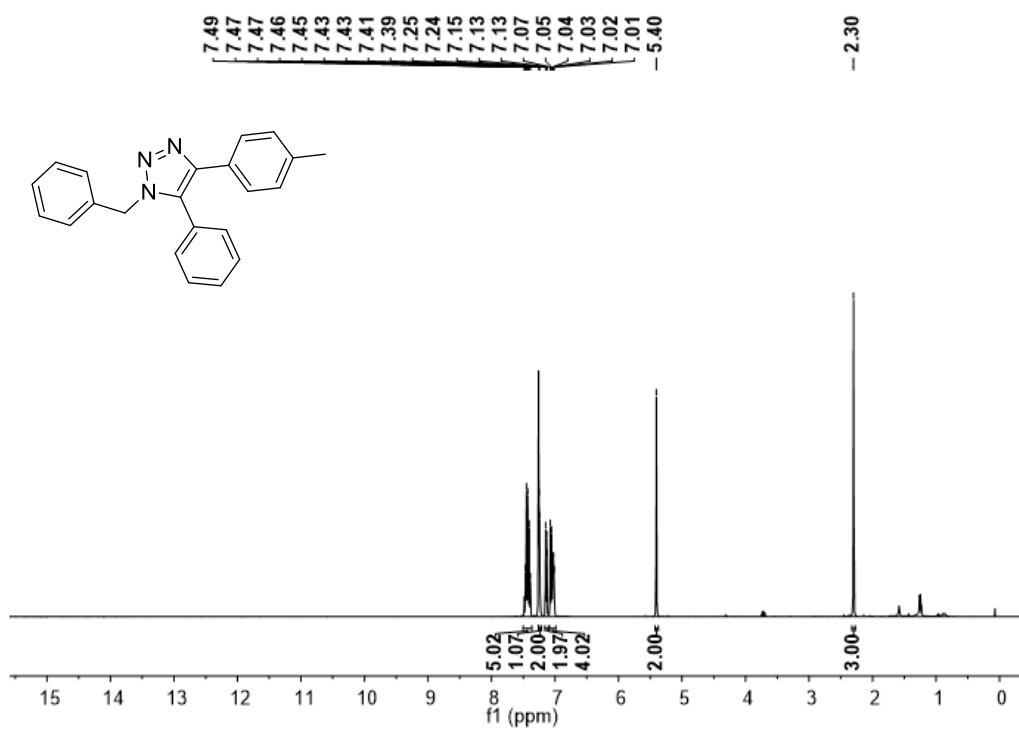
7.31 – 7.29 (m, 3H), 7.25 – 7.21 (m, 3H), 6.66 – 6.63 (m, 1H), 6.57 (d,  $J = 2.6$  Hz, 1H), 4.46 (t,  $J = 6.8$  Hz, 2H), 3.97 (t,  $J = 5.8$  Hz, 2H), 2.95 – 2.91 (m, 2H), 2.57 (dd,  $J = 18.8, 8.6$  Hz, 1H), 2.51 (s, 3H), 2.47 (s, 1H), 2.44 (t,  $J = 8.0$  Hz, 1H), 2.40 – 2.37 (m, 2H), 2.30 (t,  $J = 8.4$  Hz, 1H), 2.19 (dd,  $J = 18.6, 8.8$  Hz, 1H), 2.14 – 2.00 (m, 3H), 1.72 – 1.58 (m, 3H), 1.54 – 1.44 (m, 2H), 0.97 (s, 3H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  221.1, 156.5, 144.2, 139.8, 137.8, 134.3, 132.4, 131.2, 130.1, 129.9, 128.5, 127.7, 126.8, 126.5, 124.8, 114.4, 112.2, 64.1, 50.5, 48.1, 45.0, 44.0, 38.4, 36.0, 31.7, 29.8, 29.7, 26.6, 26.0, 21.7, 21.6, 13.9. HRMS (ESI)  $m/z$  calculate for  $([\text{M}+\text{Na}]^+)$   $\text{C}_{36}\text{H}_{39}\text{N}_3\text{NaO}_2^+$ : 568.2934, Found: 568.2935

# Nuclear magnetic spectrum

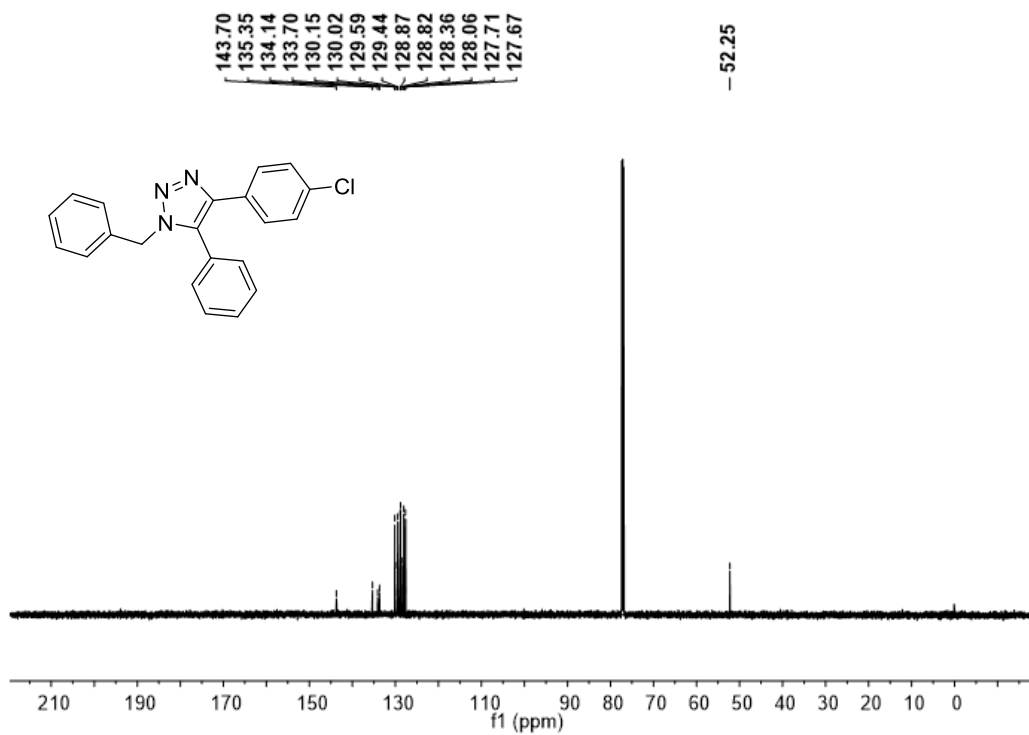
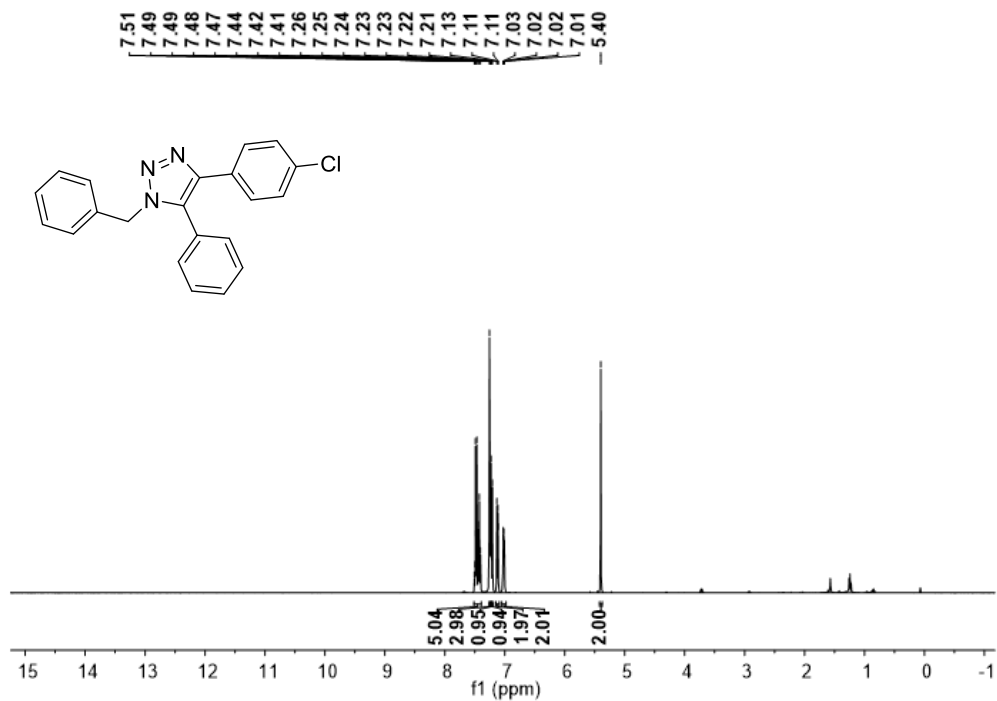
## Compound 4a of $^1\text{H}$ and $^{13}\text{C}$



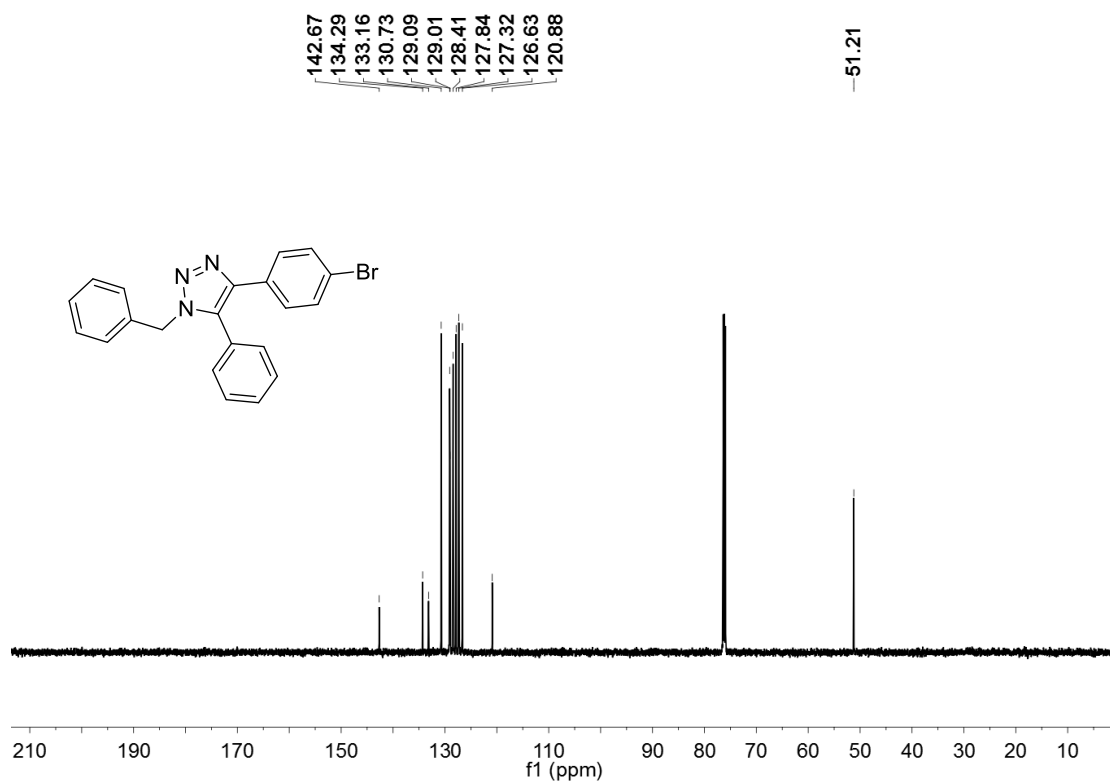
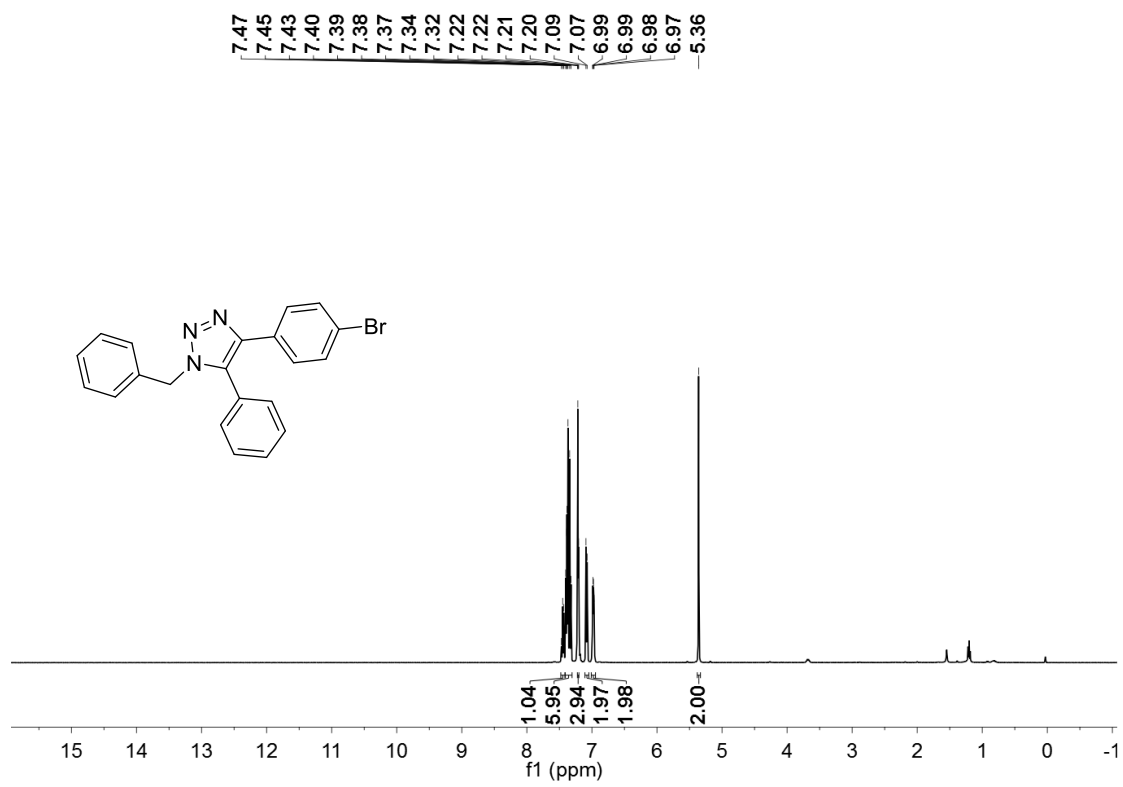
# Compound 4b of $^1\text{H}$ and $^{13}\text{C}$



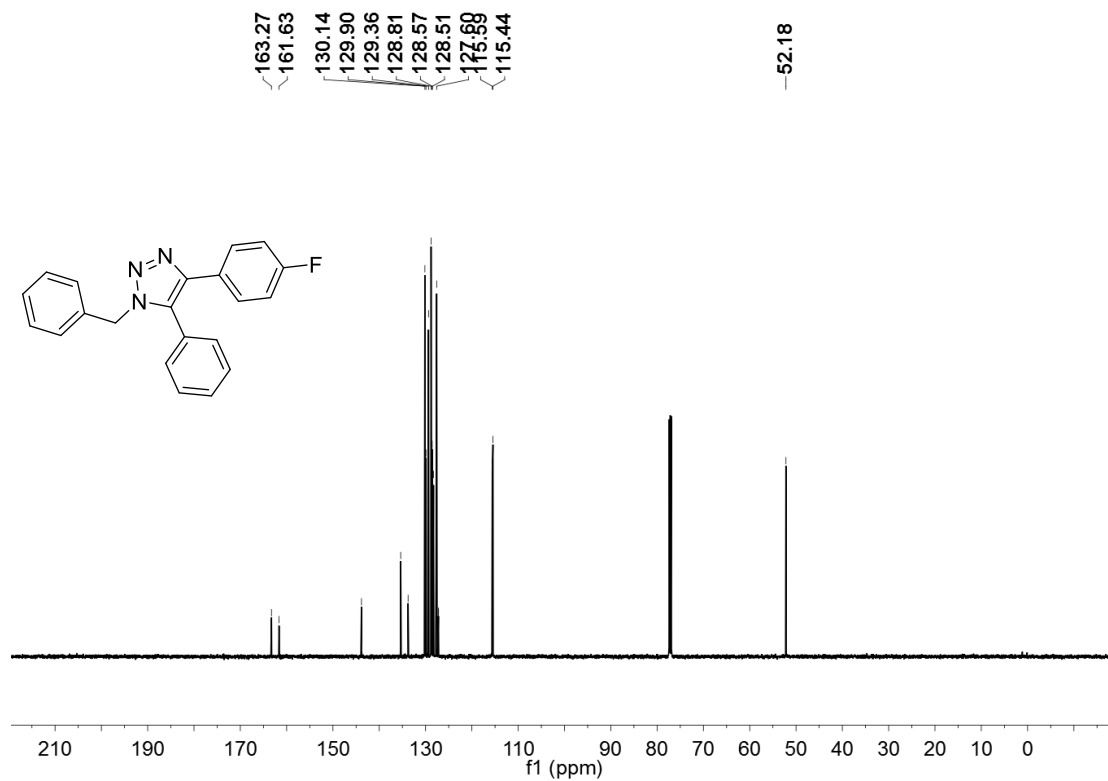
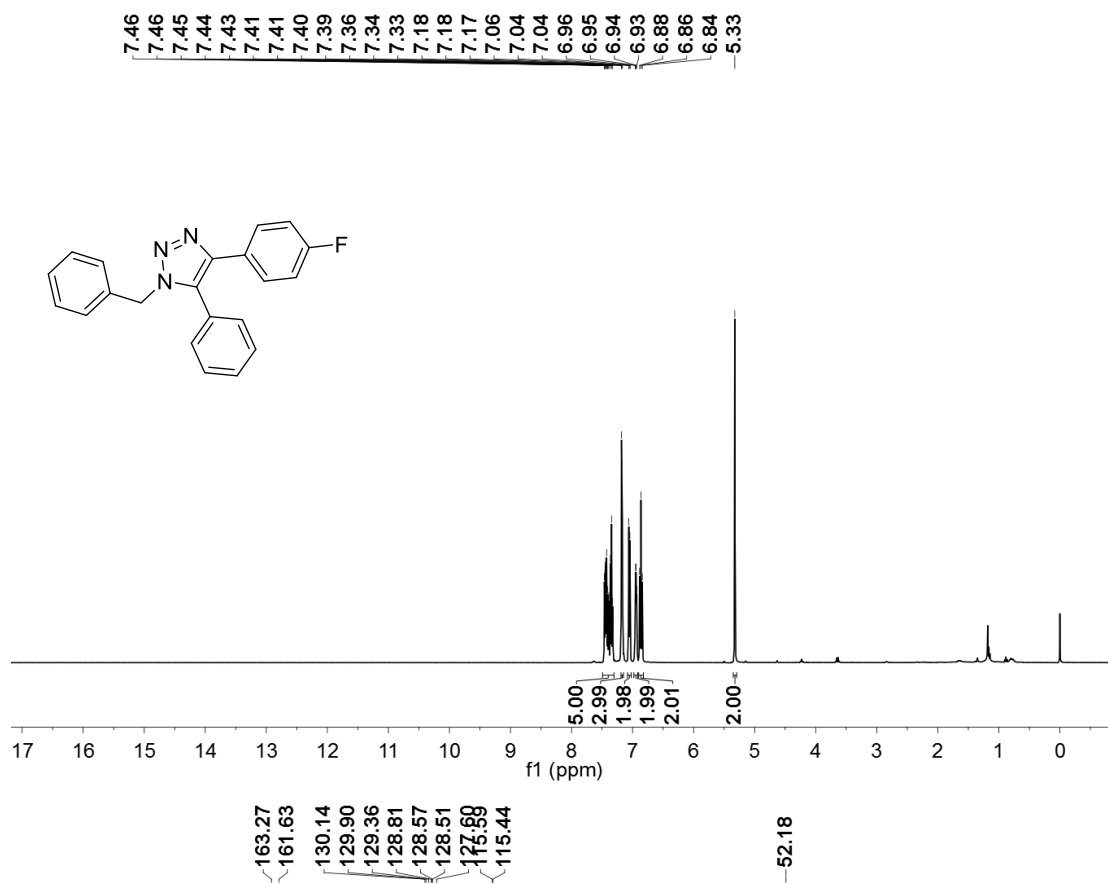
# Compound 4c of $^1\text{H}$ and $^{13}\text{C}$



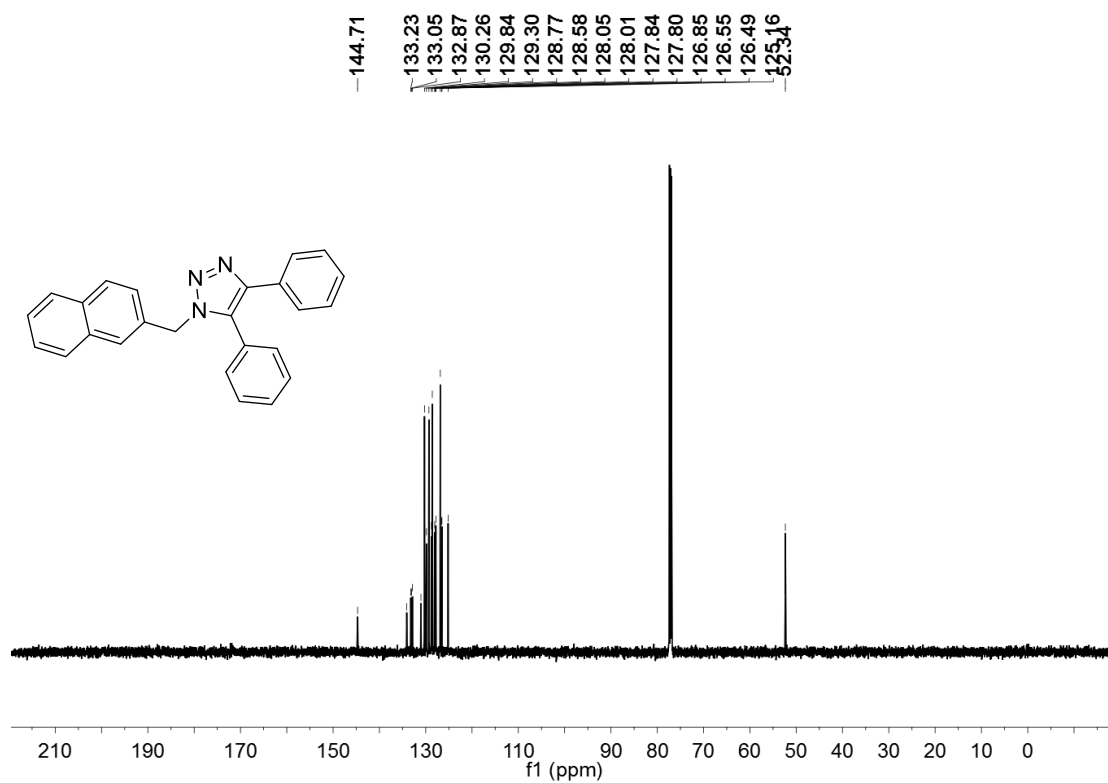
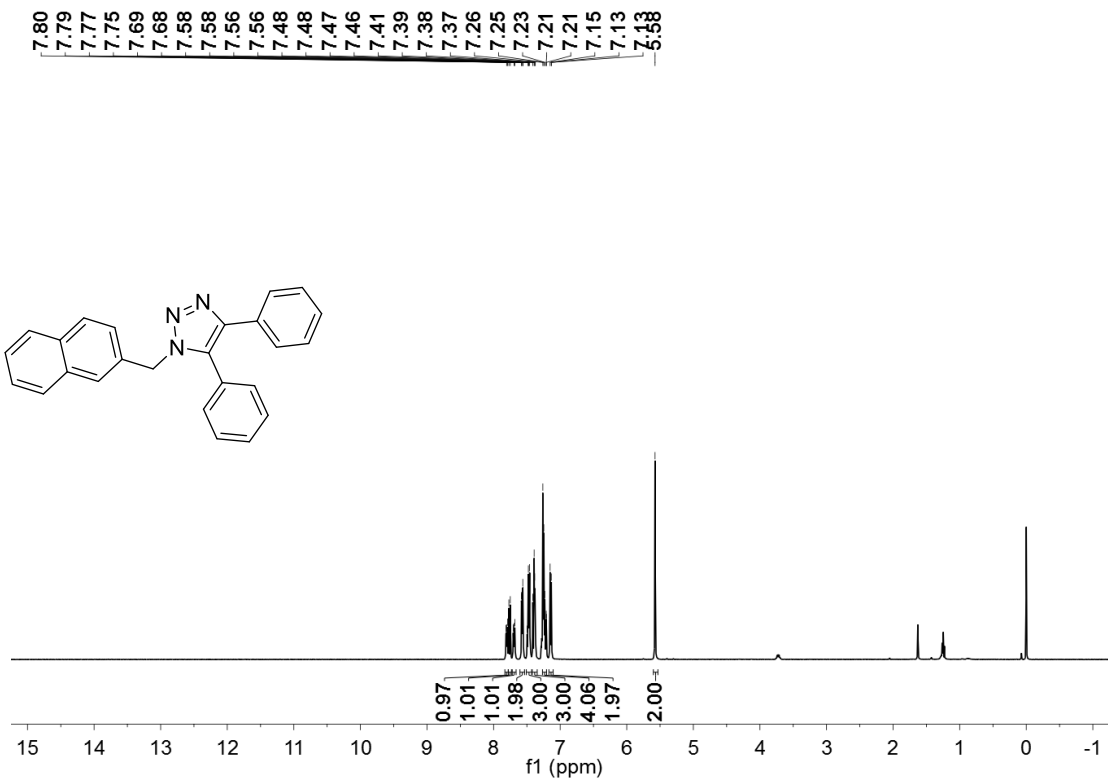
# Compound 4d of $^1\text{H}$ and $^{13}\text{C}$



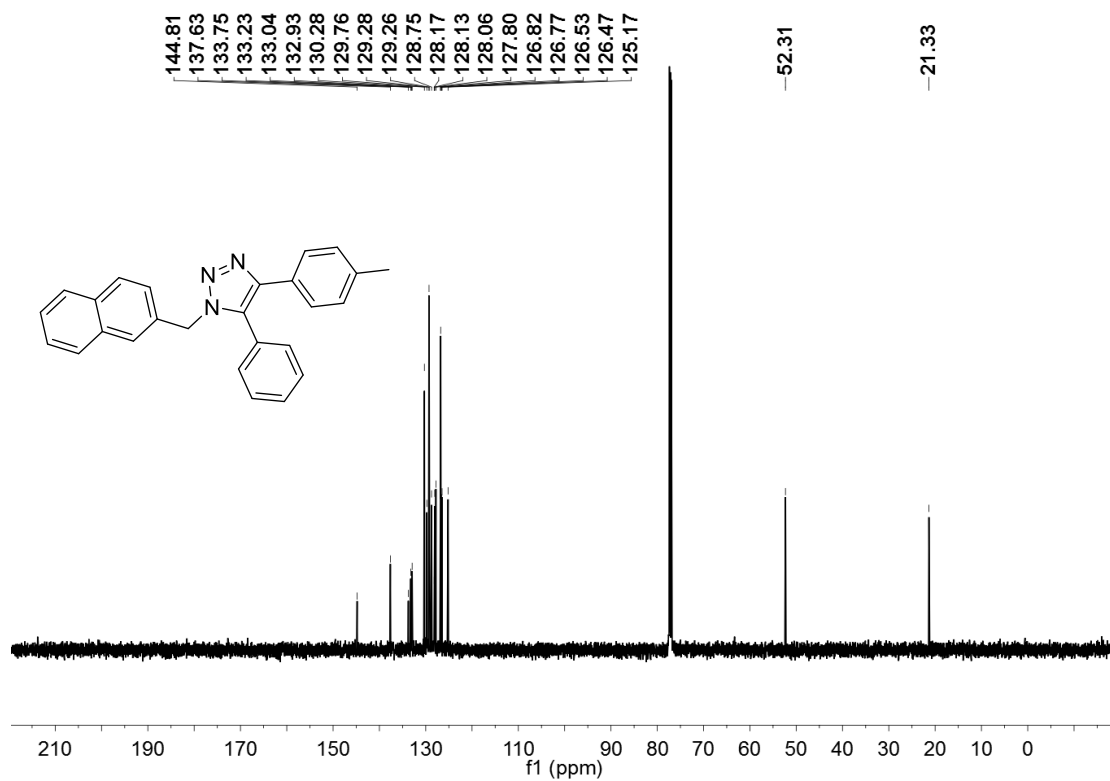
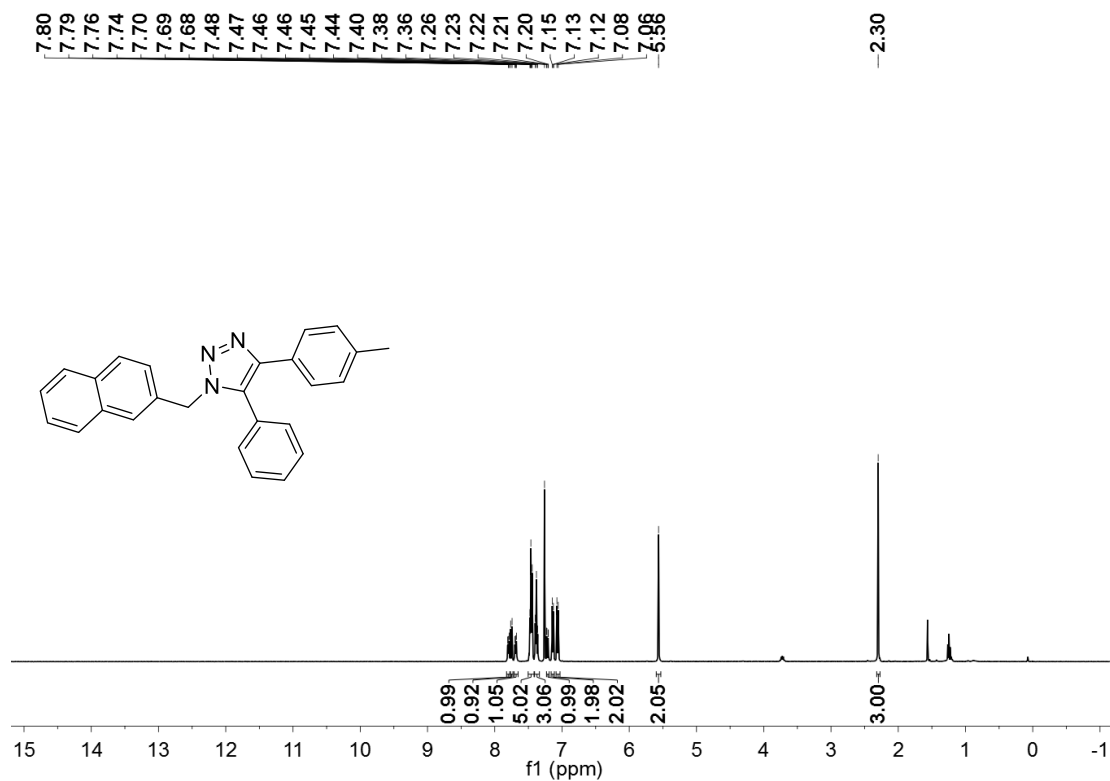
# Compound 4e of $^1\text{H}$ and $^{13}\text{C}$



# Compound 4f of $^1\text{H}$ and $^{13}\text{C}$

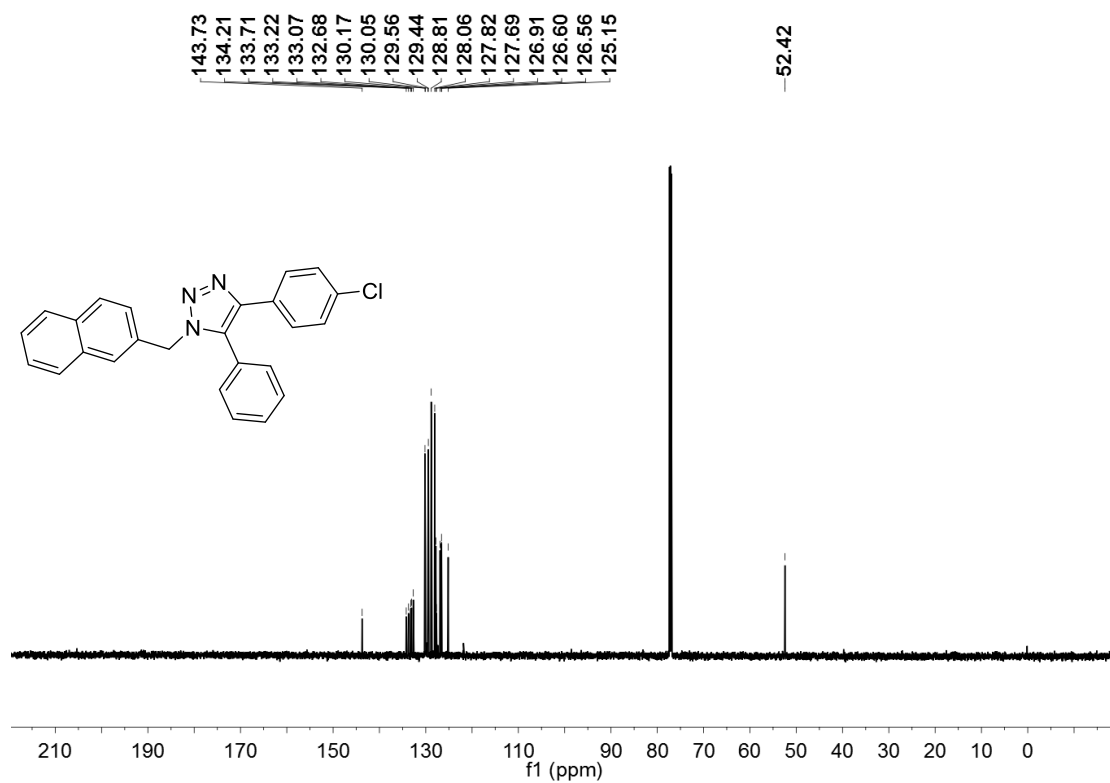
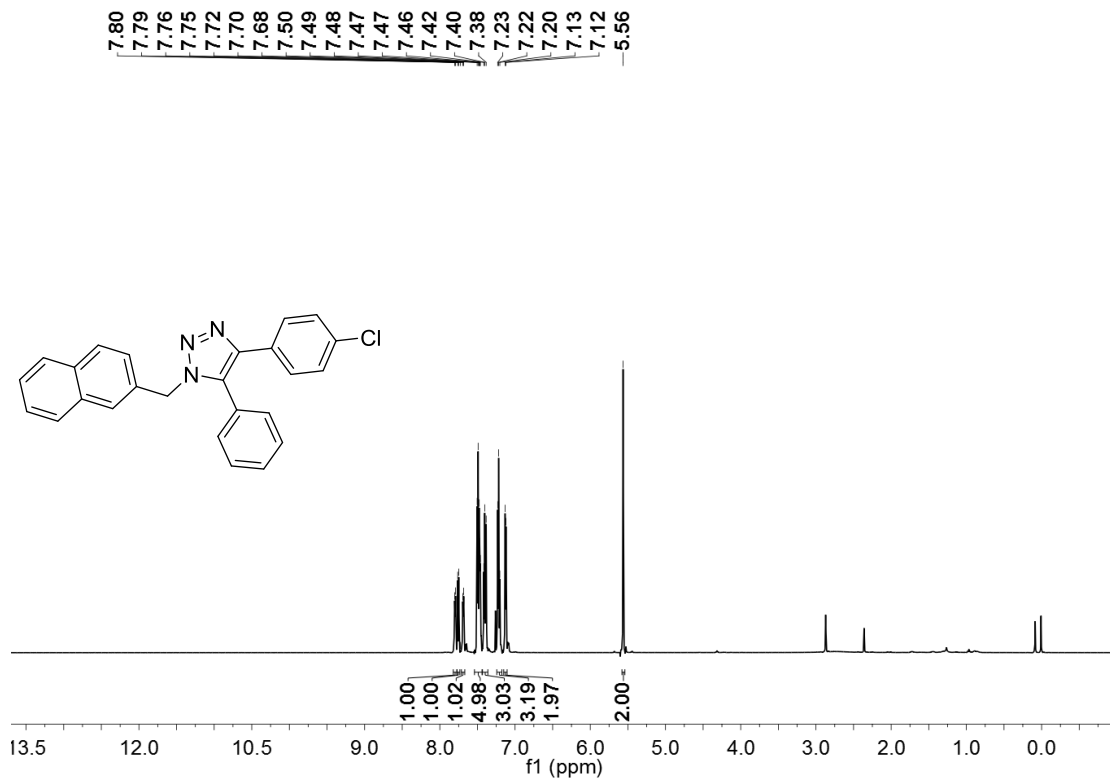


# Compound 4g of $^1\text{H}$ and $^{13}\text{C}$

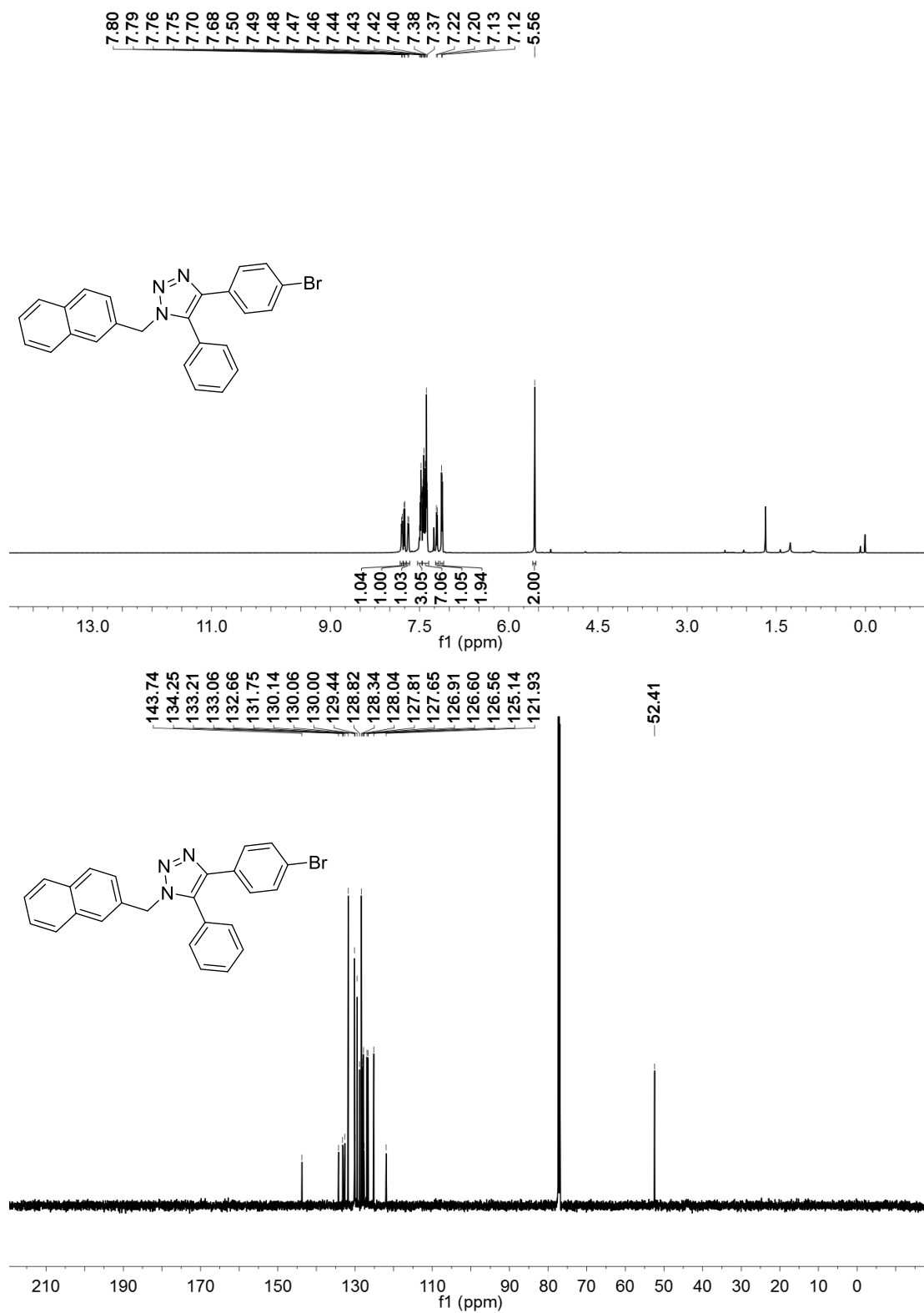




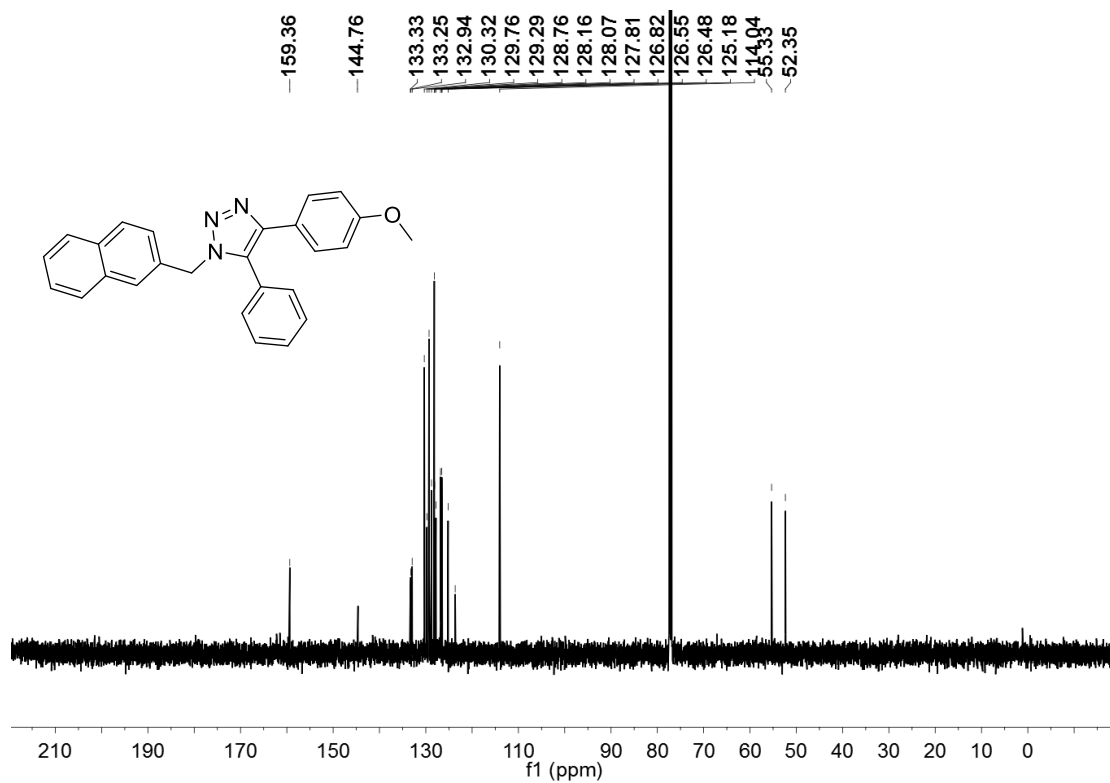
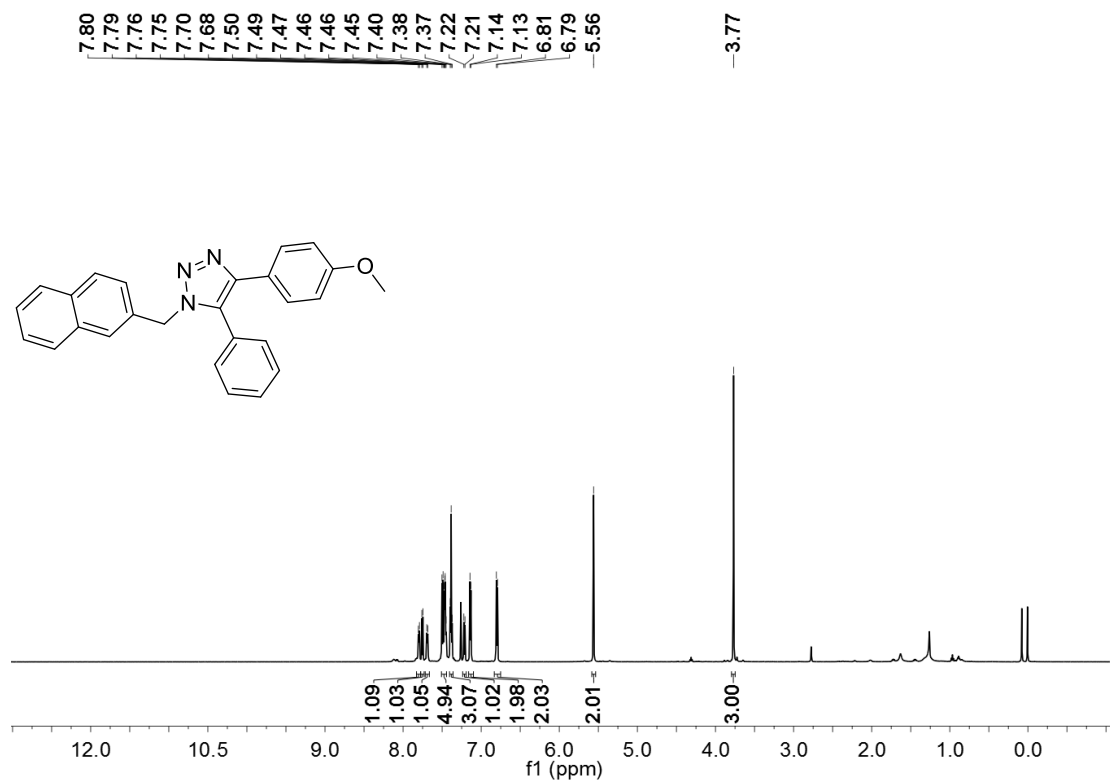
# Compound 4h of $^1\text{H}$ and $^{13}\text{C}$



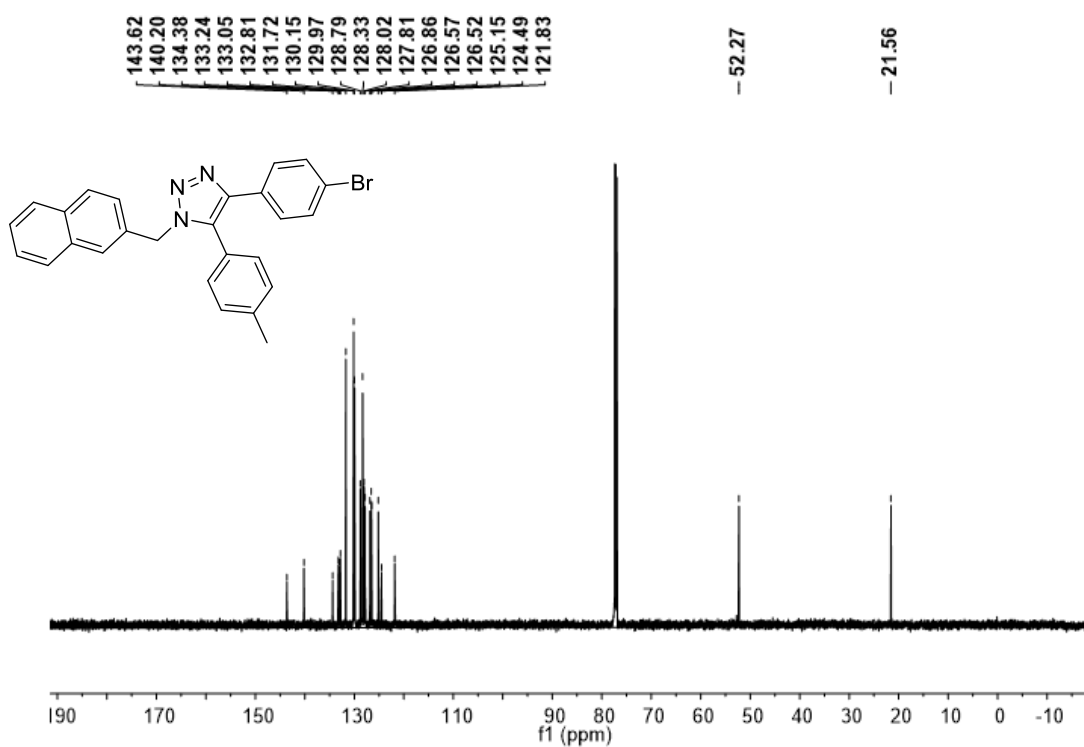
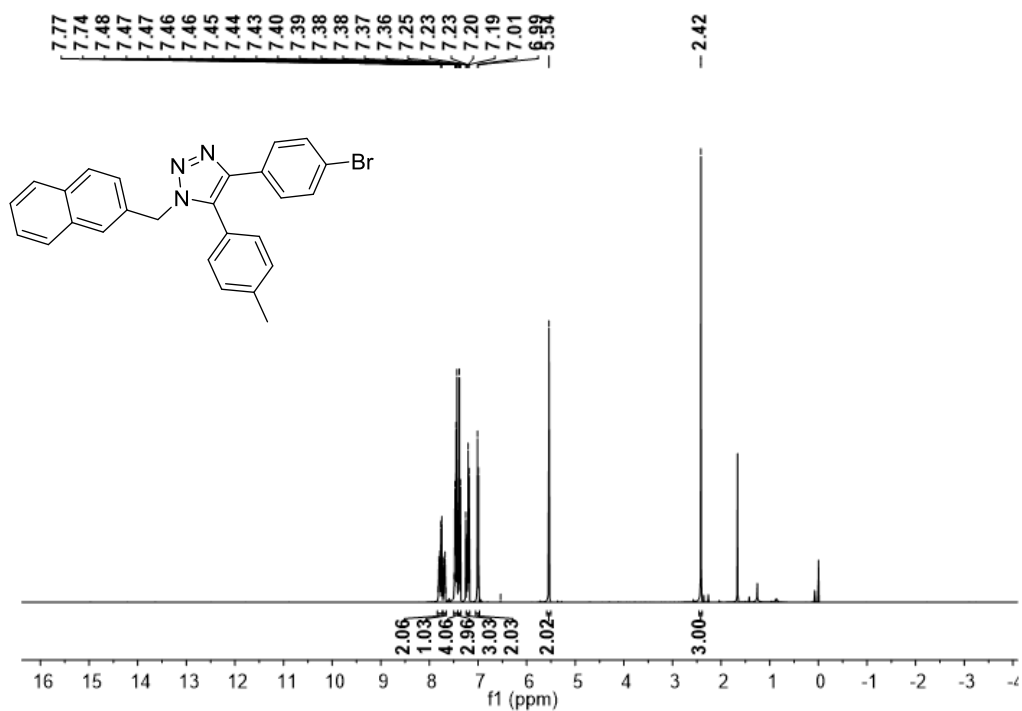
# Compound 4i of $^1\text{H}$ and $^{13}\text{C}$



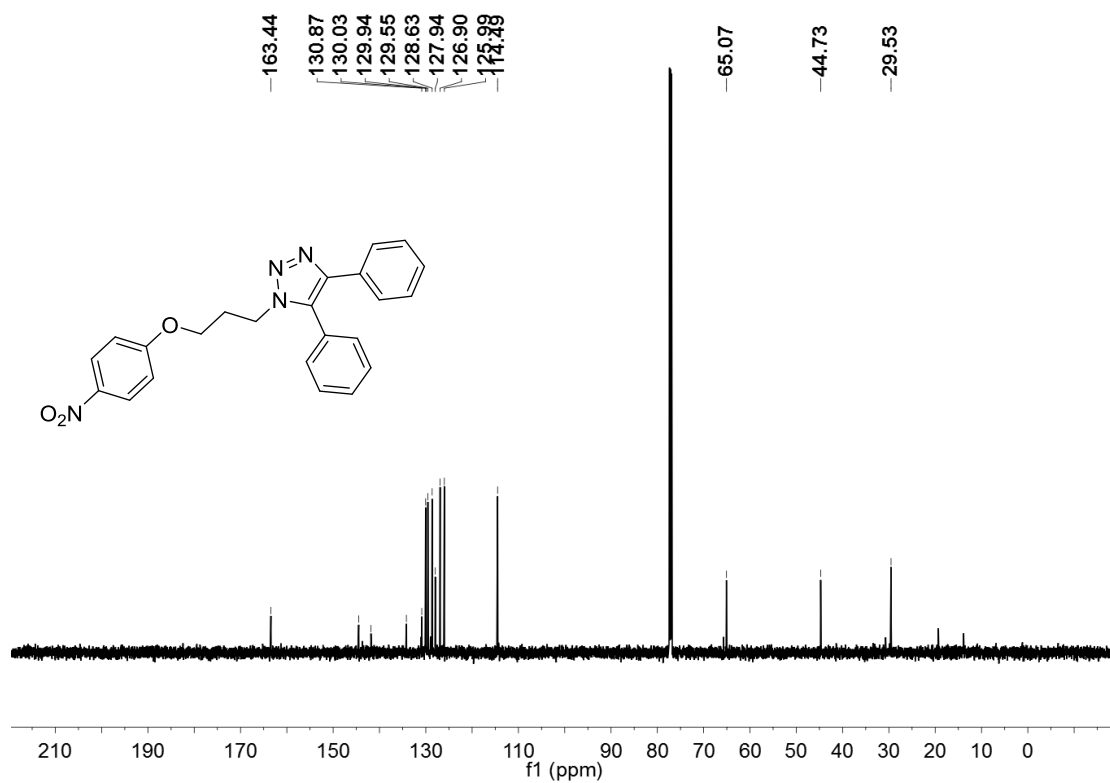
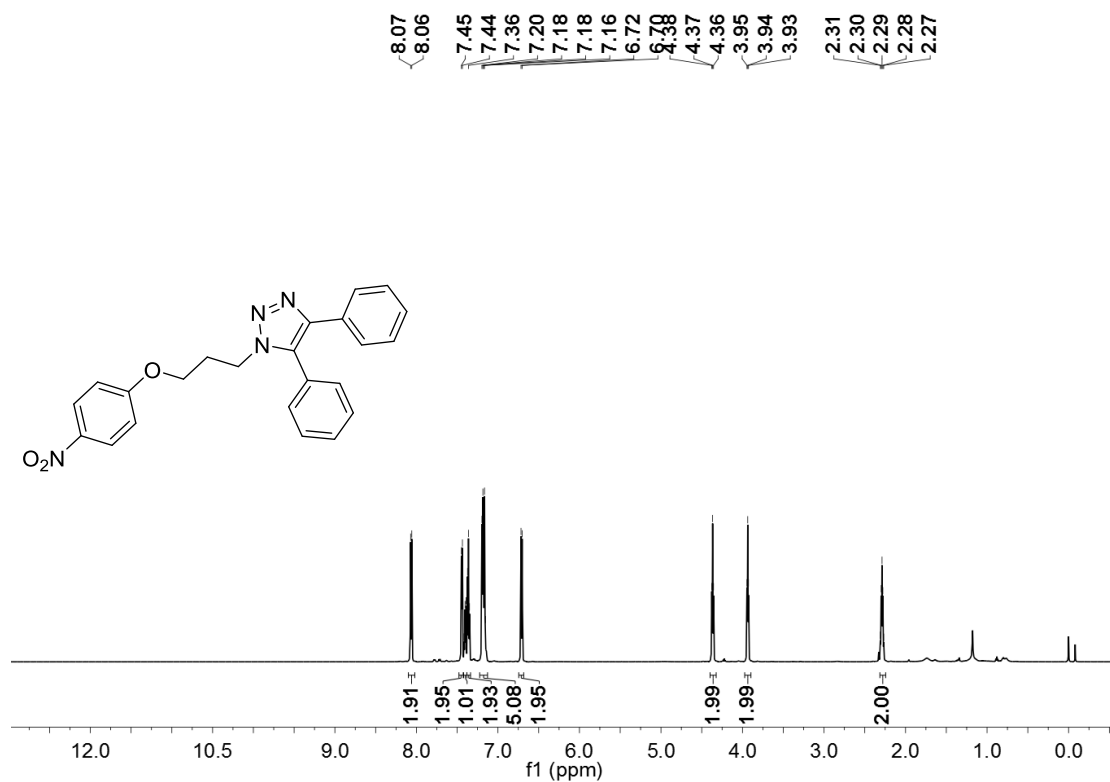
# Compound 4j of $^1\text{H}$ and $^{13}\text{C}$



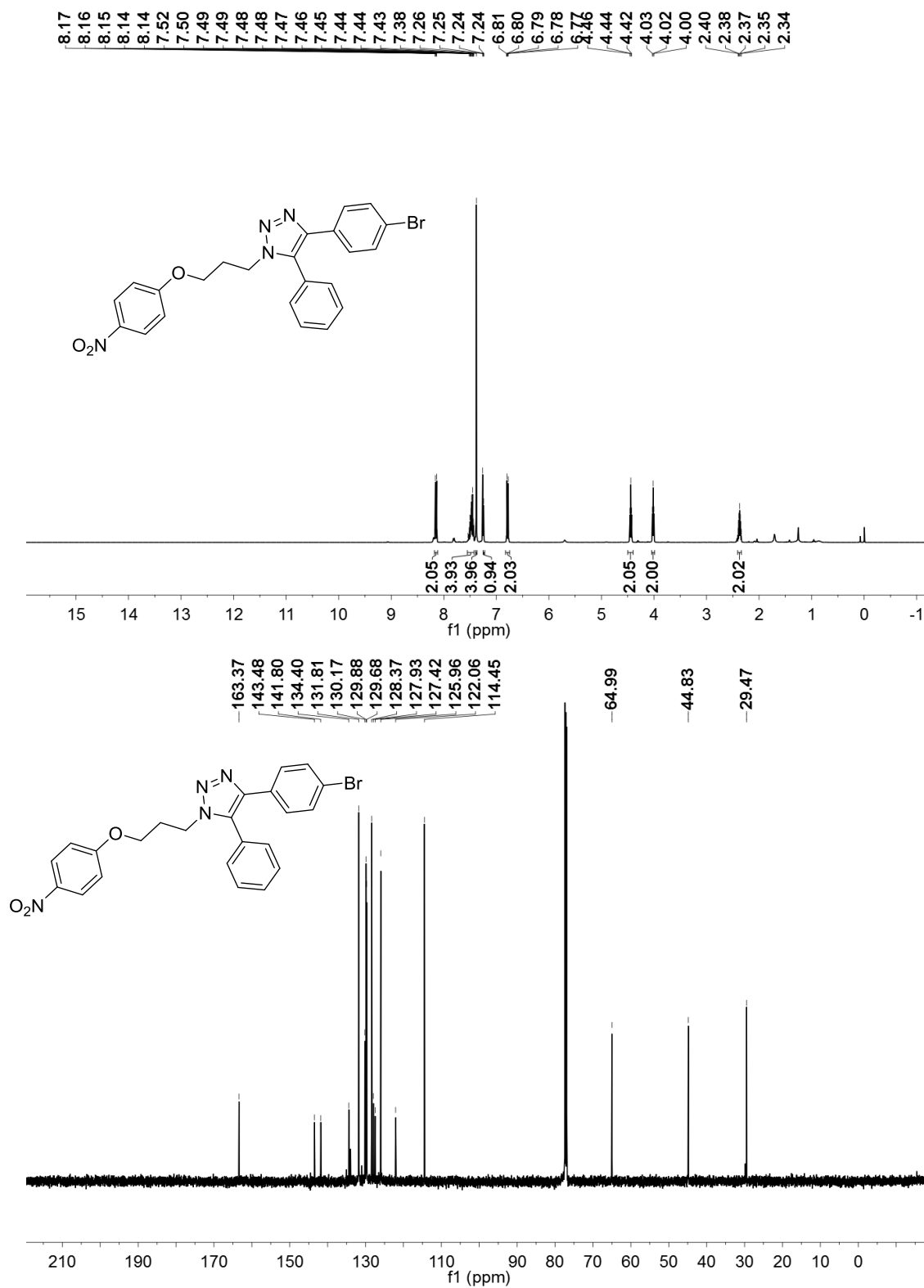
Compound 4k of  $^1\text{H}$  and  $^{13}\text{C}$



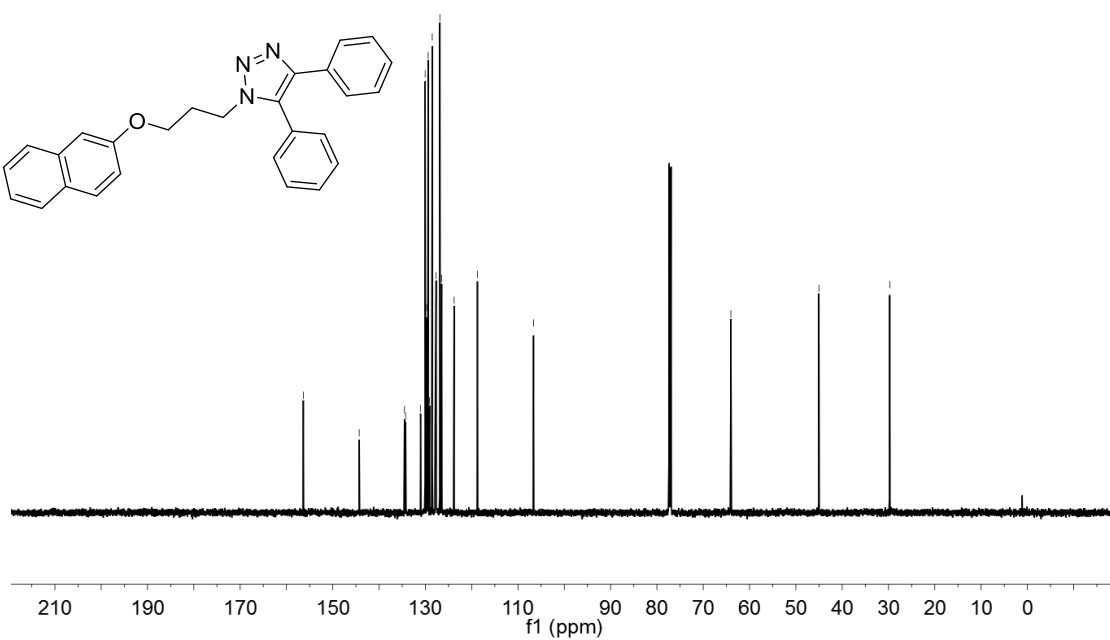
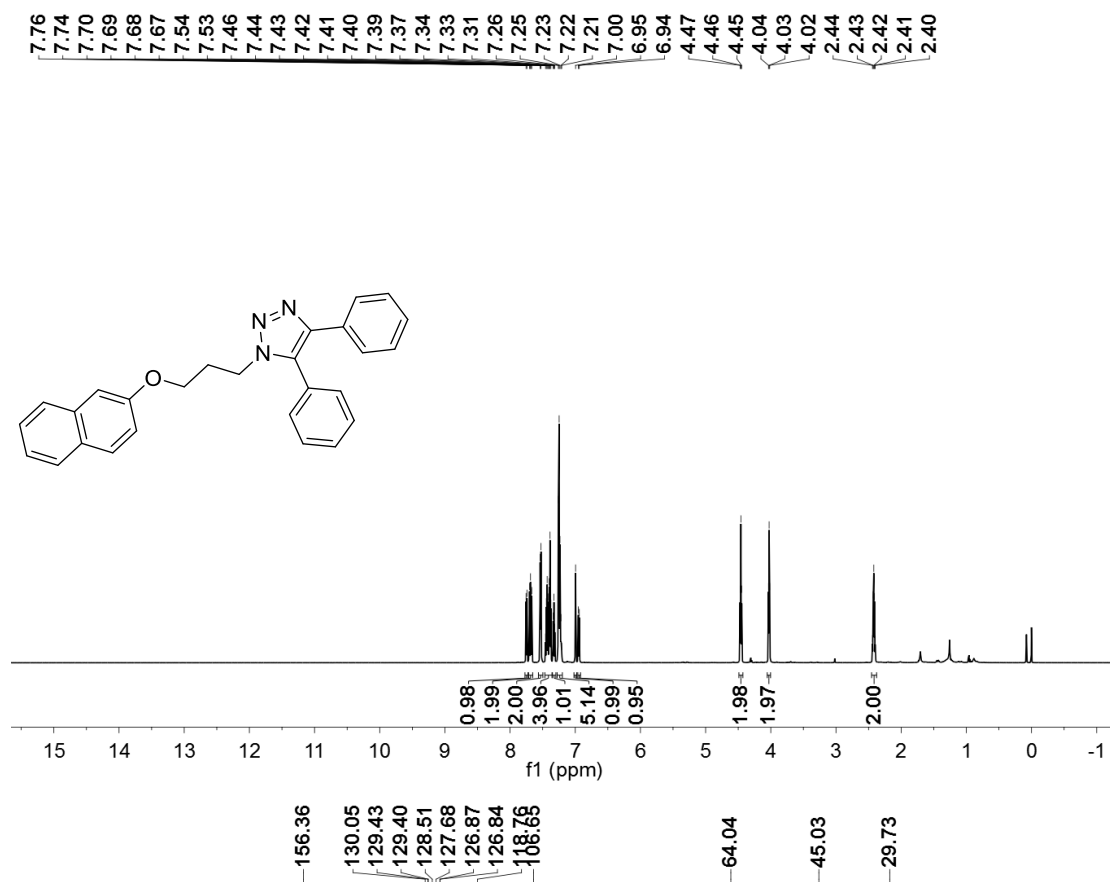
Compound 4l of  $^1\text{H}$  and  $^{13}\text{C}$



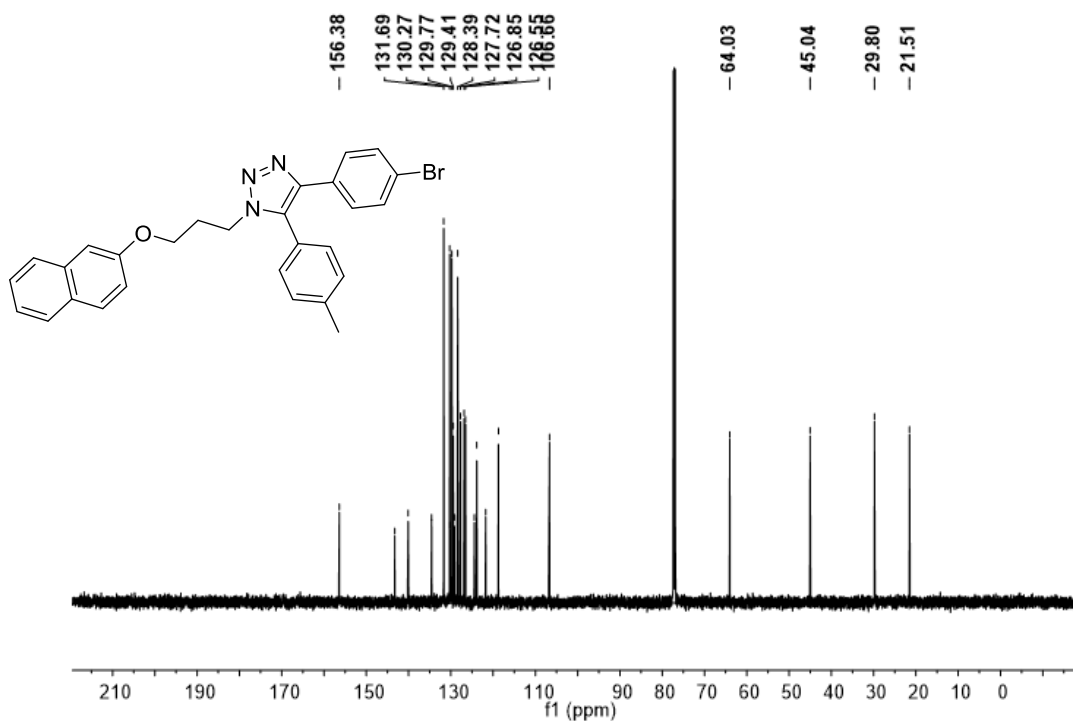
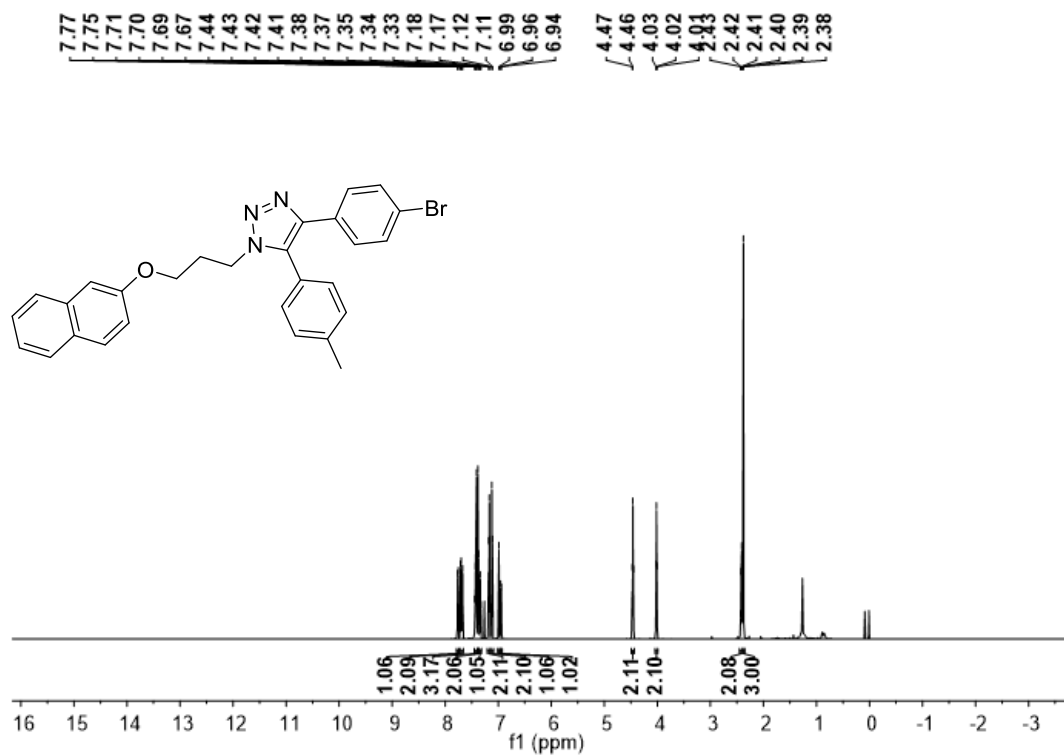
# Compound 4m of $^1\text{H}$ and $^{13}\text{C}$



# Compound 4n of $^1\text{H}$ and $^{13}\text{C}$

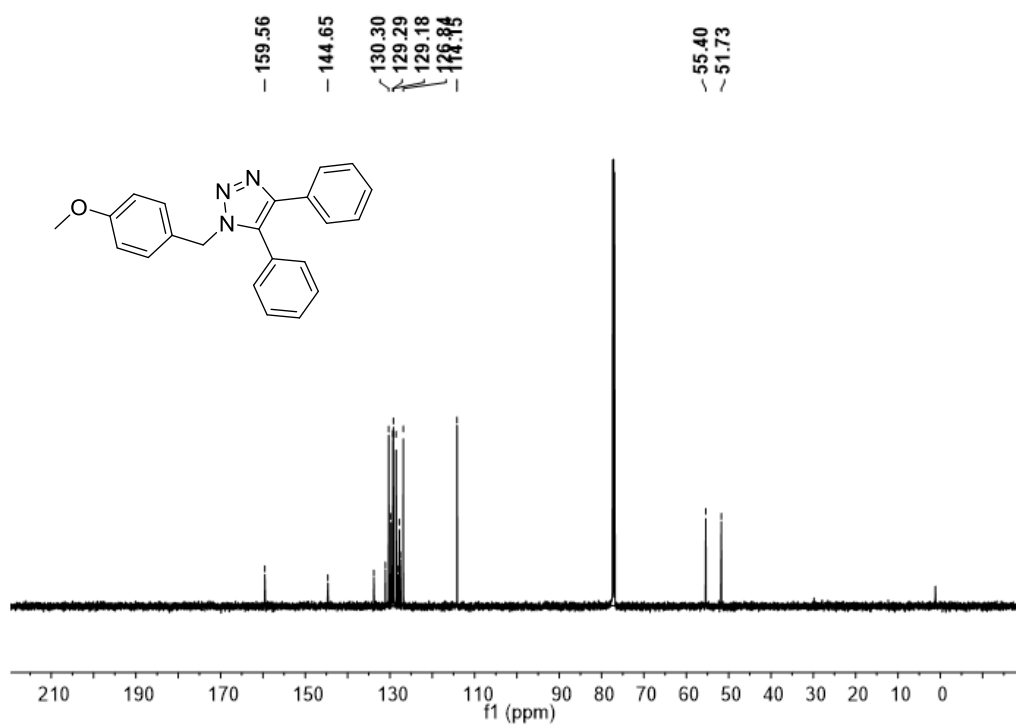
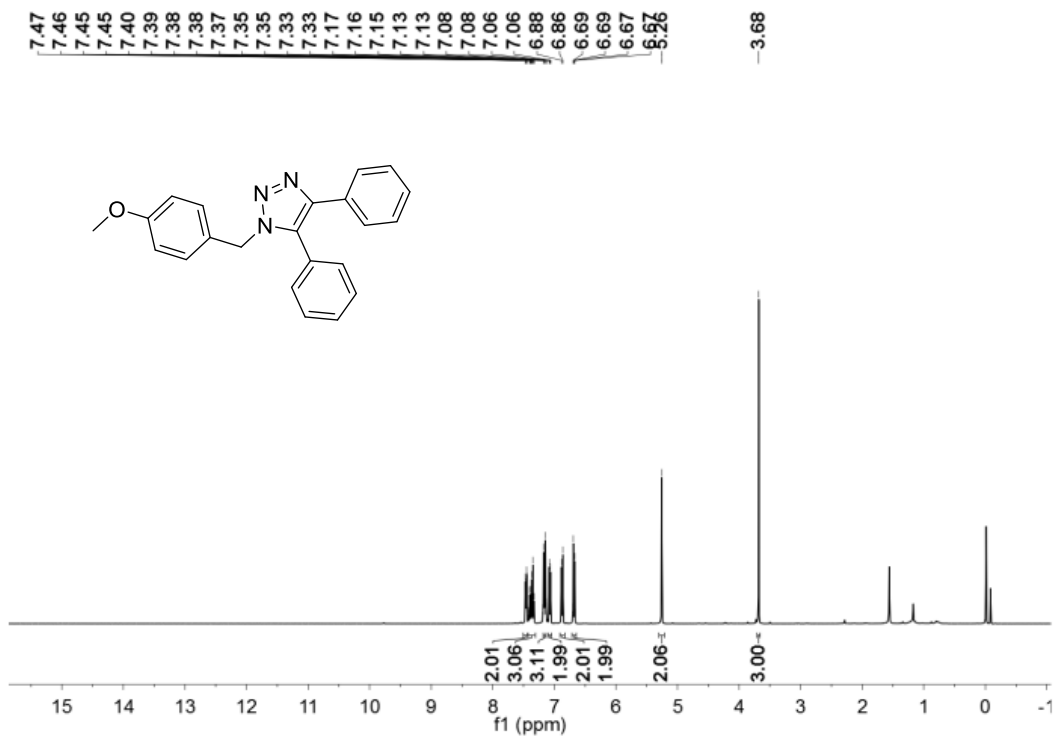


# Compound 4o of $^1\text{H}$ and $^{13}\text{C}$

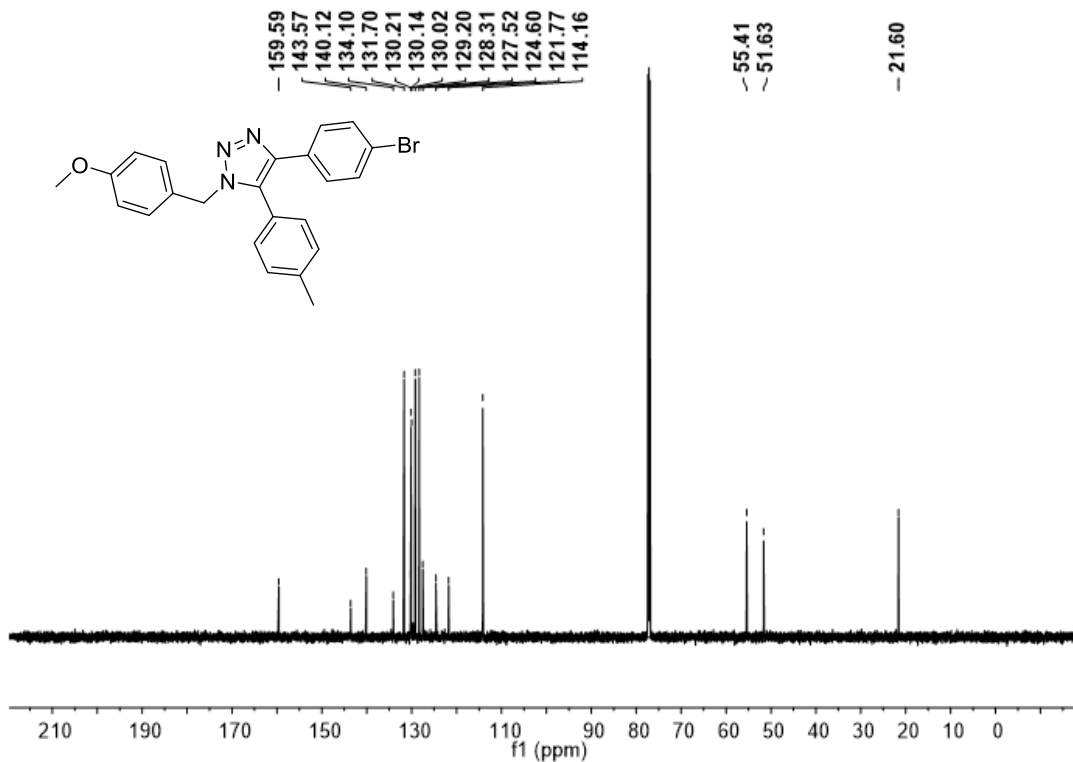
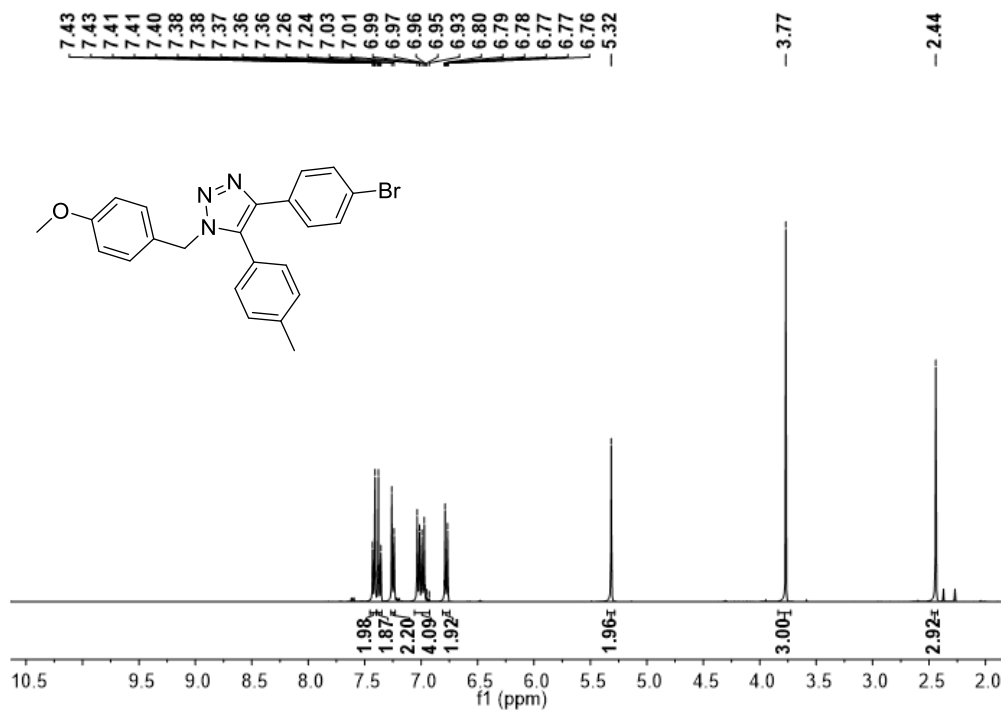




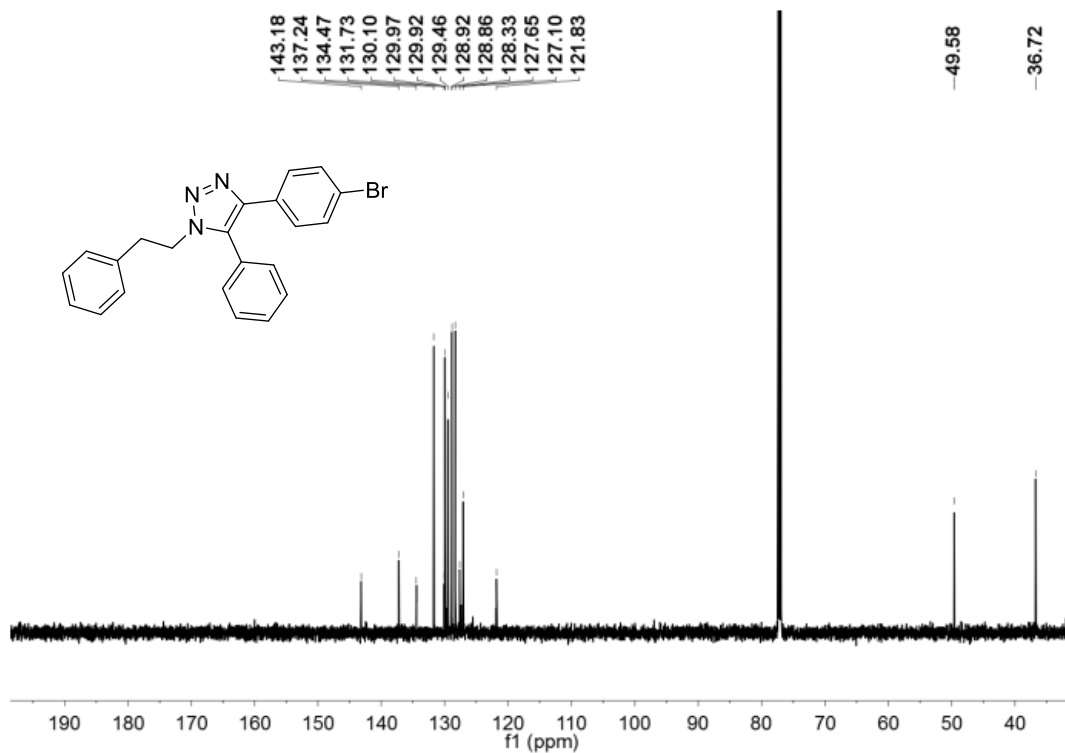
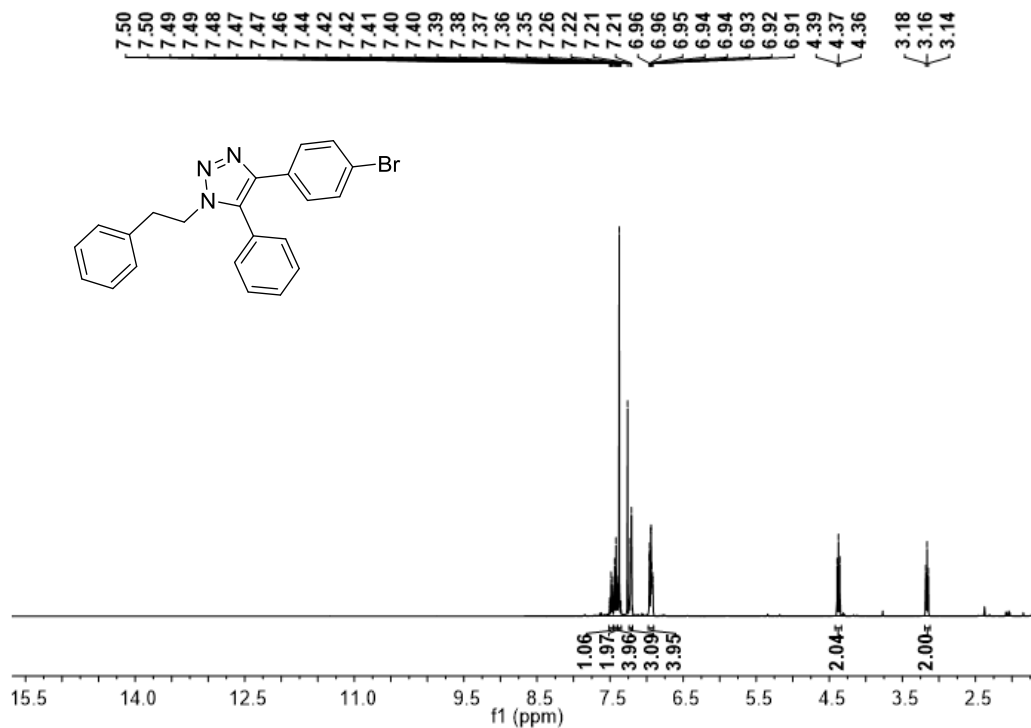
Compound 4p of  $^1\text{H}$  and  $^{13}\text{C}$



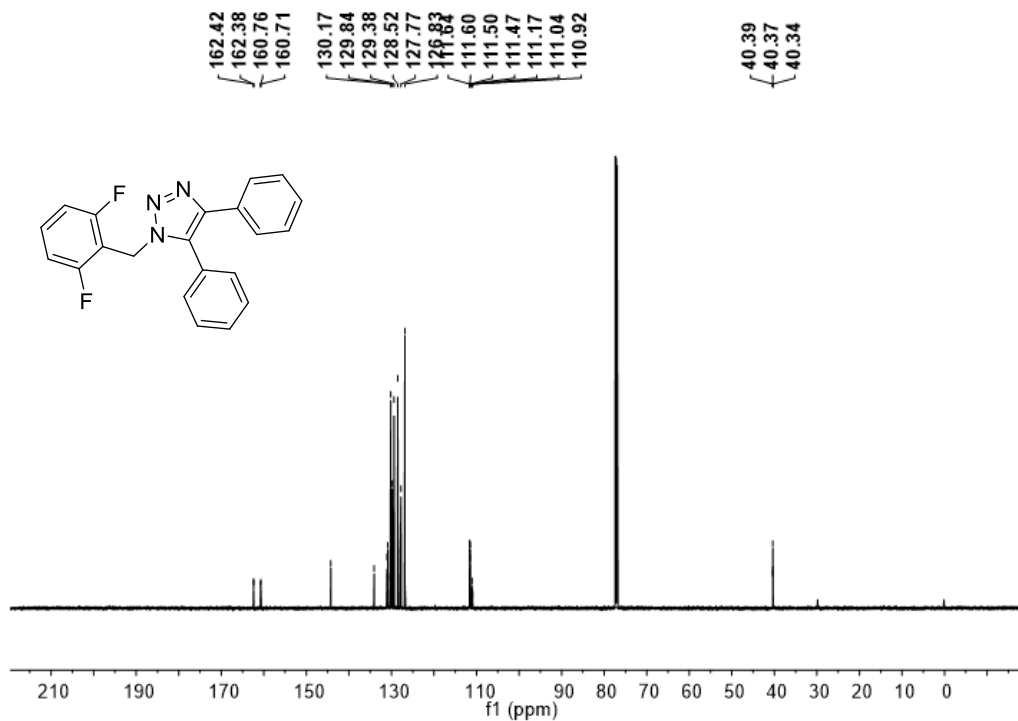
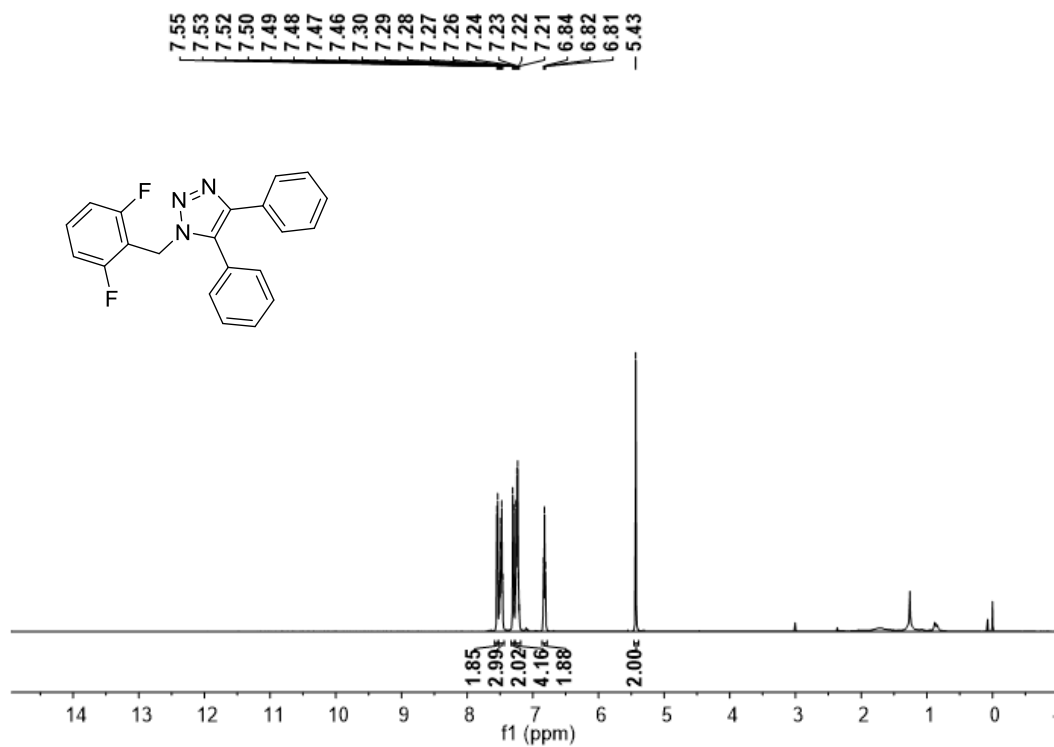
# Compound 4q of $^1\text{H}$ and $^{13}\text{C}$



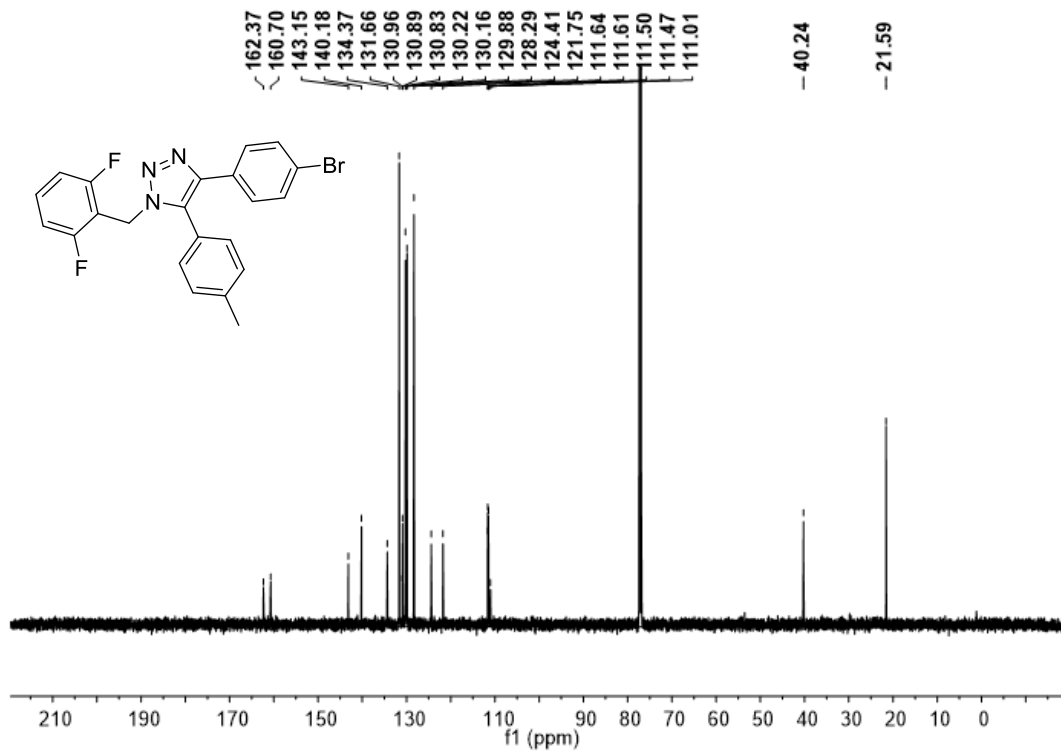
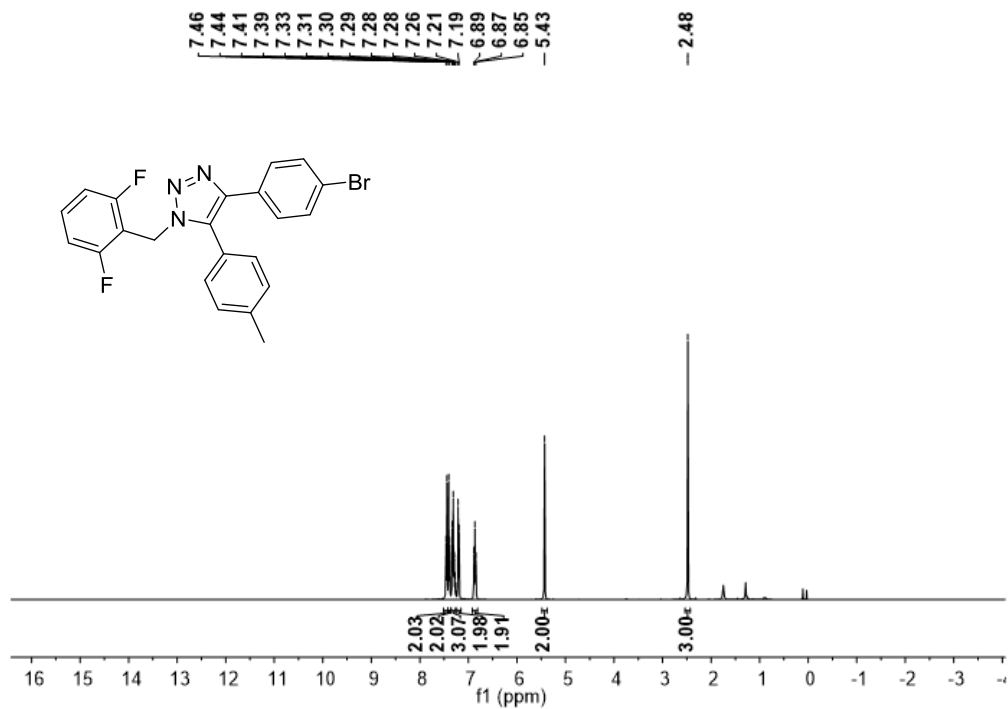
# Compound 4r of $^1\text{H}$ and $^{13}\text{C}$



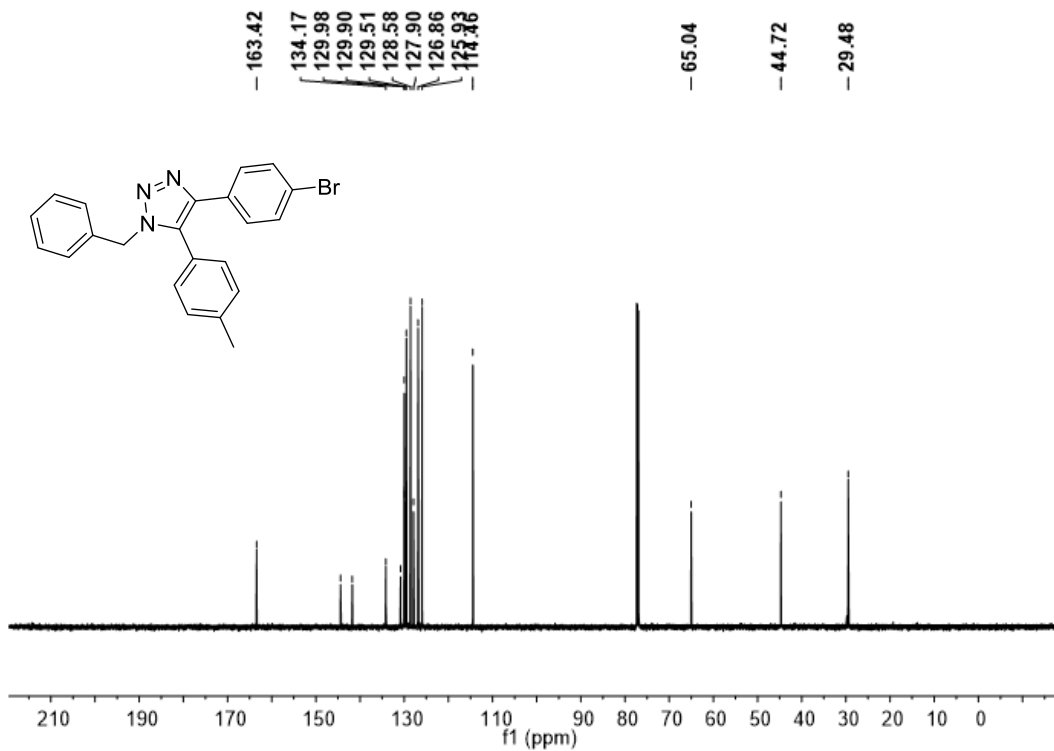
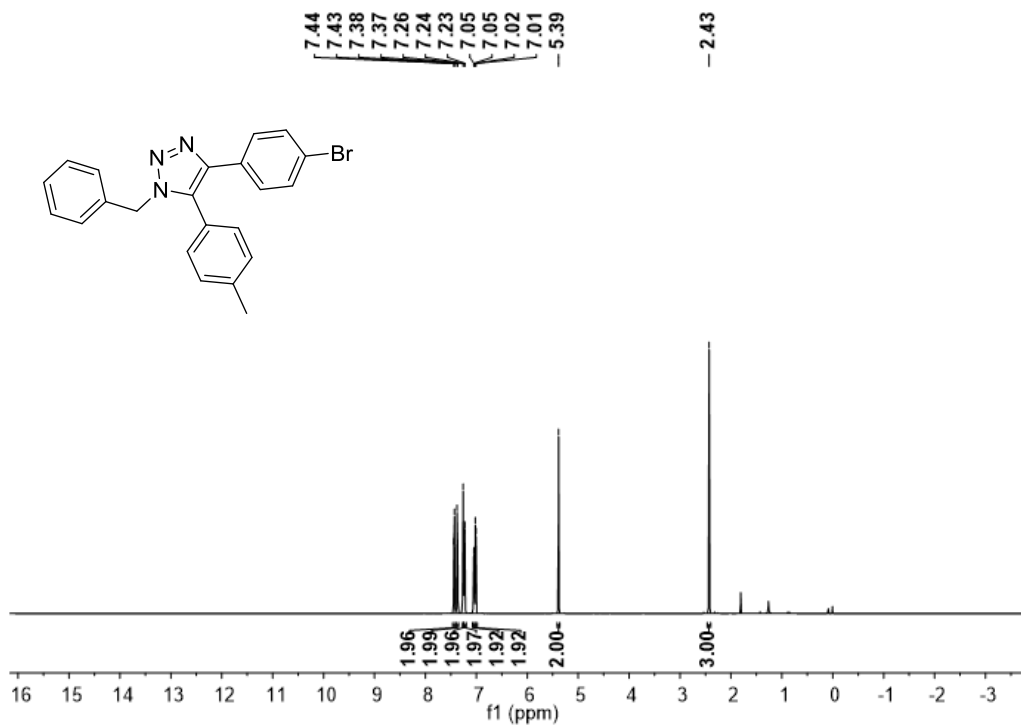
# Compound 4s of $^1\text{H}$ and $^{13}\text{C}$



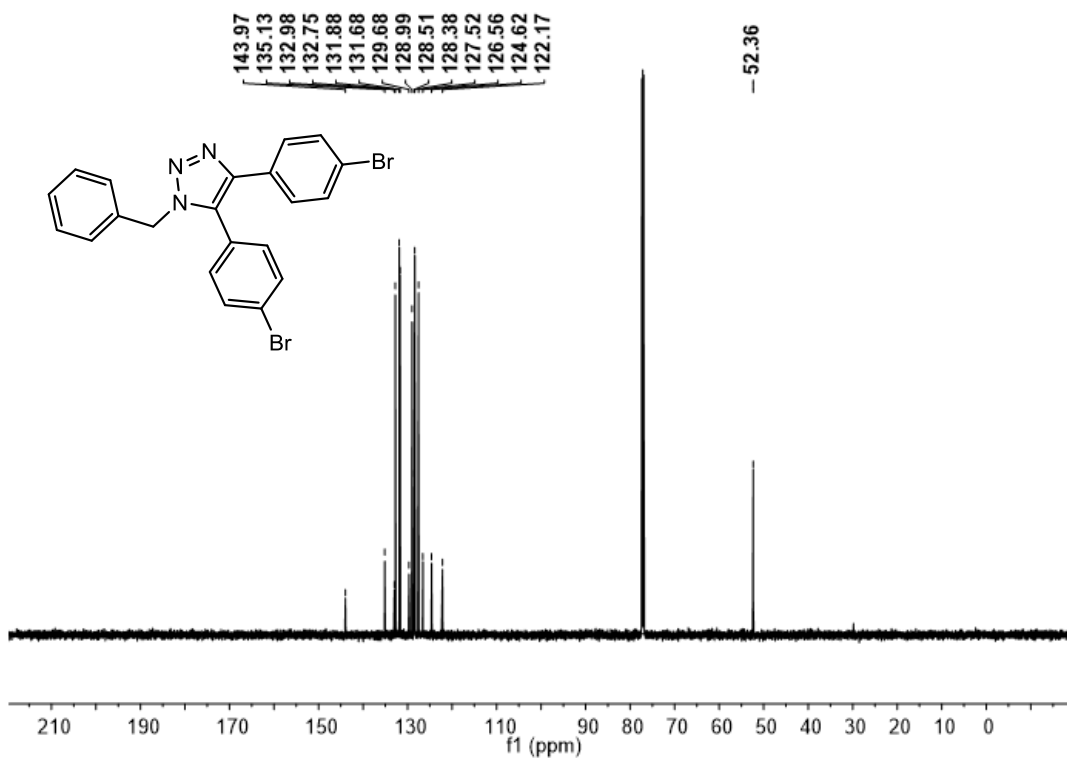
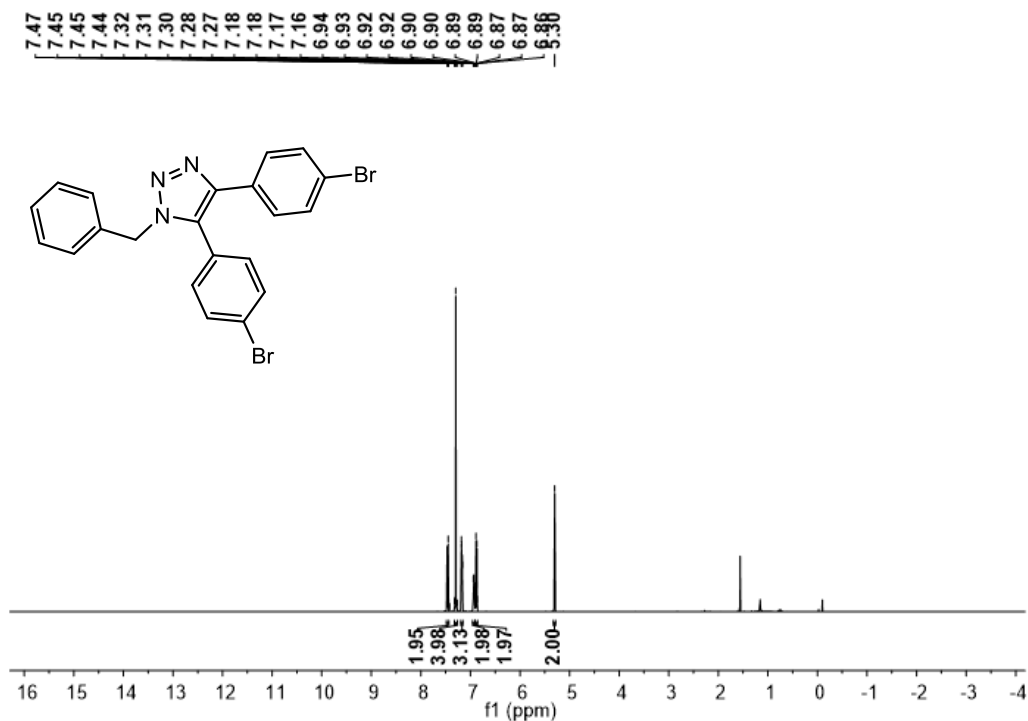
Compound 4t of  $^1\text{H}$  and  $^{13}\text{C}$



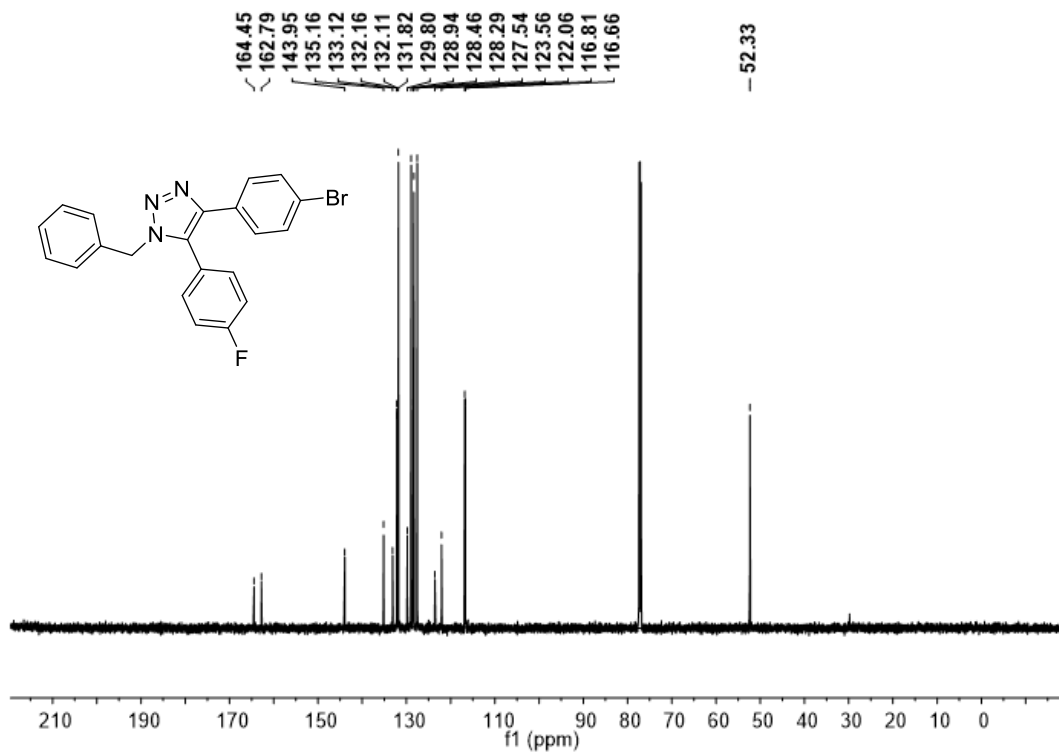
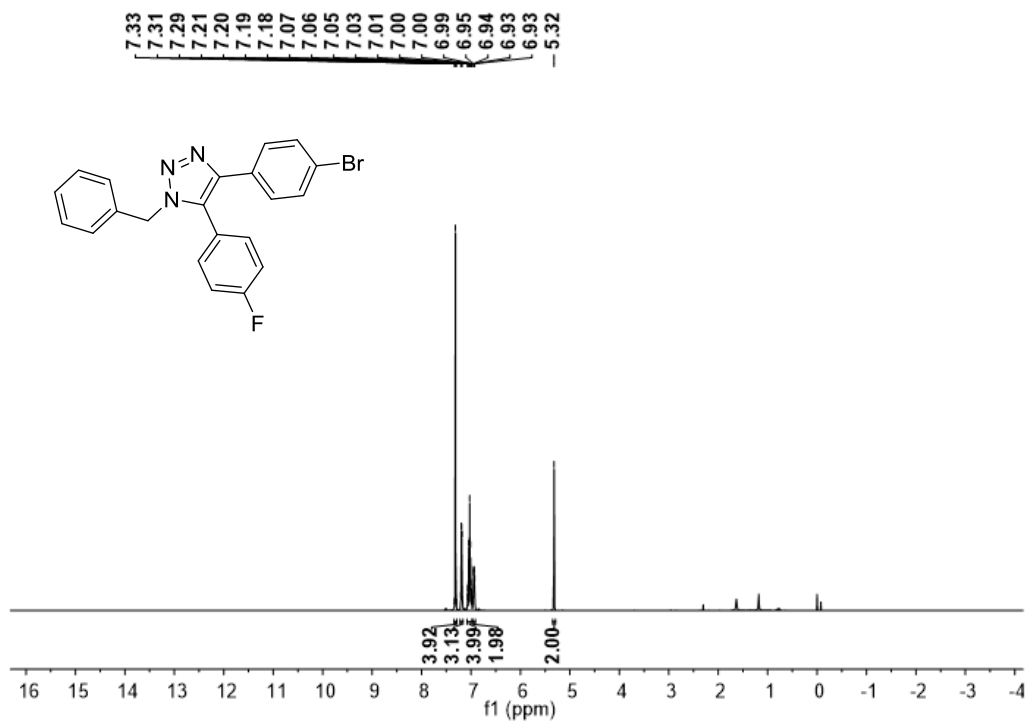
# Compound 4u of $^1\text{H}$ and $^{13}\text{C}$



# Compound 4v of $^1\text{H}$ and $^{13}\text{C}$

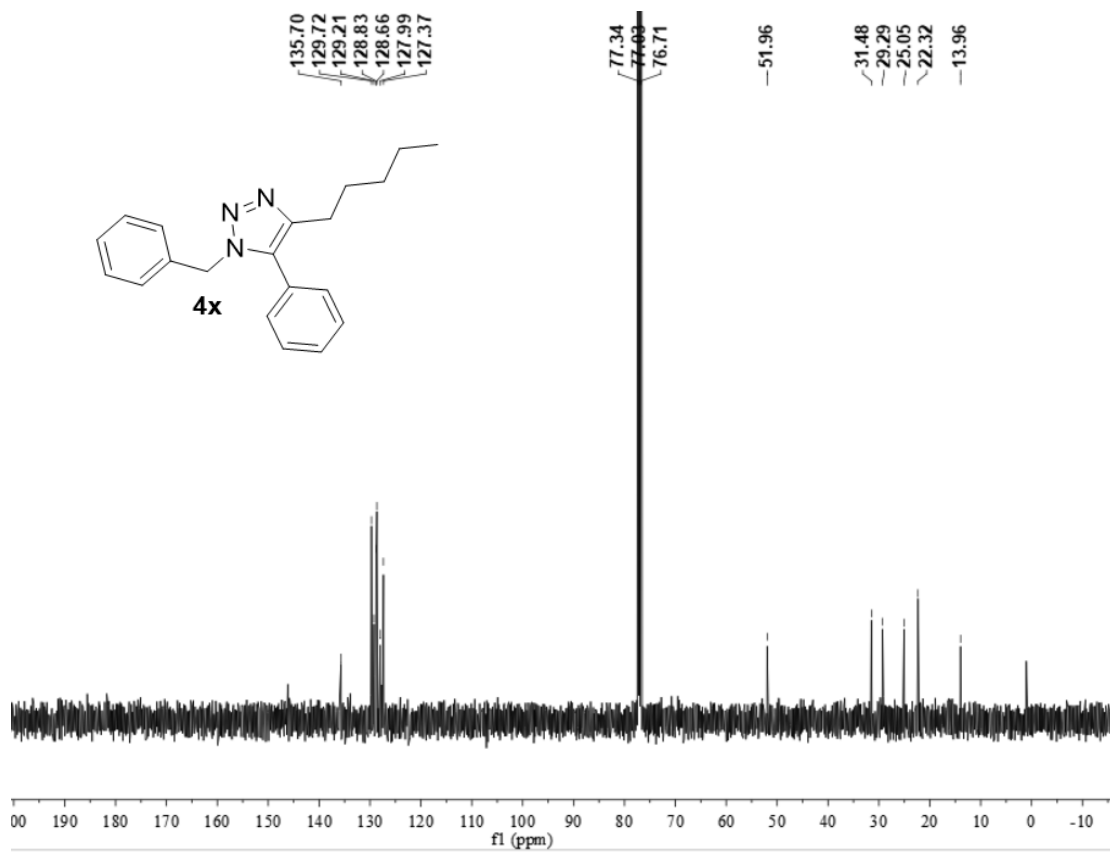
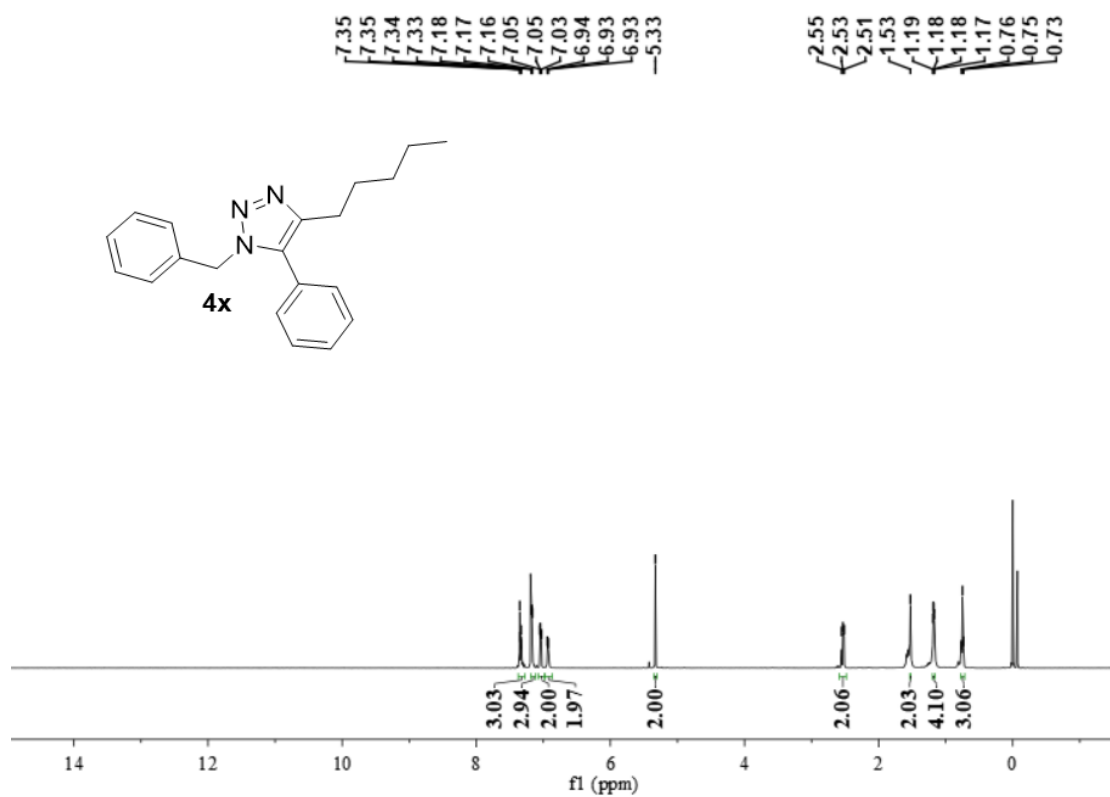


# Compound 4w of $^1\text{H}$ and $^{13}\text{C}$

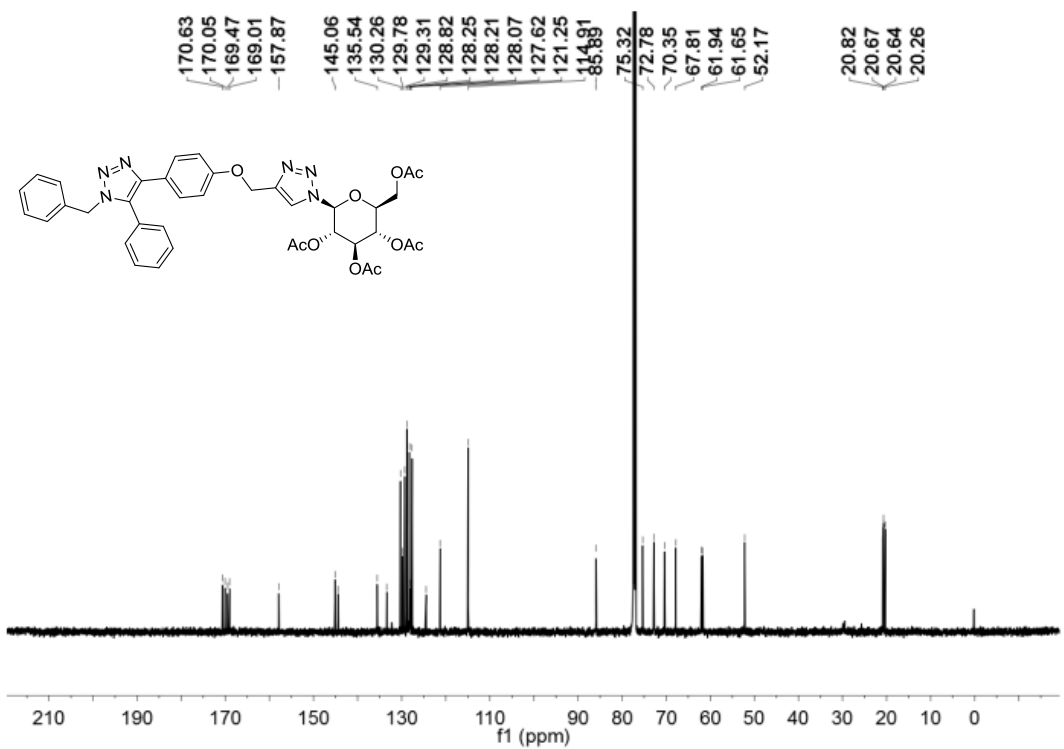
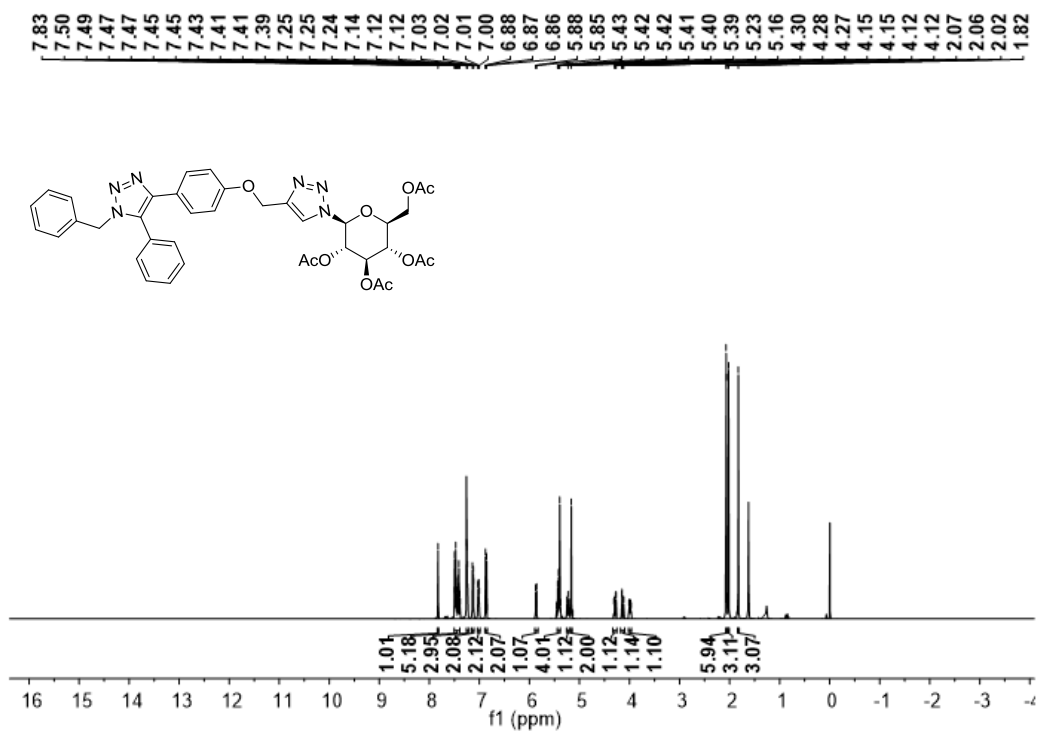




Compound 4x of  $^1\text{H}$  and  $^{13}\text{C}$



# Compound 4y <sup>1</sup>H and <sup>13</sup>C



# Compound 4z of $^1\text{H}$ and $^{13}\text{C}$

