

## Cu(II)-Catalyzed 6 $\pi$ -Photocyclization of Non-6 $\pi$ Substrates

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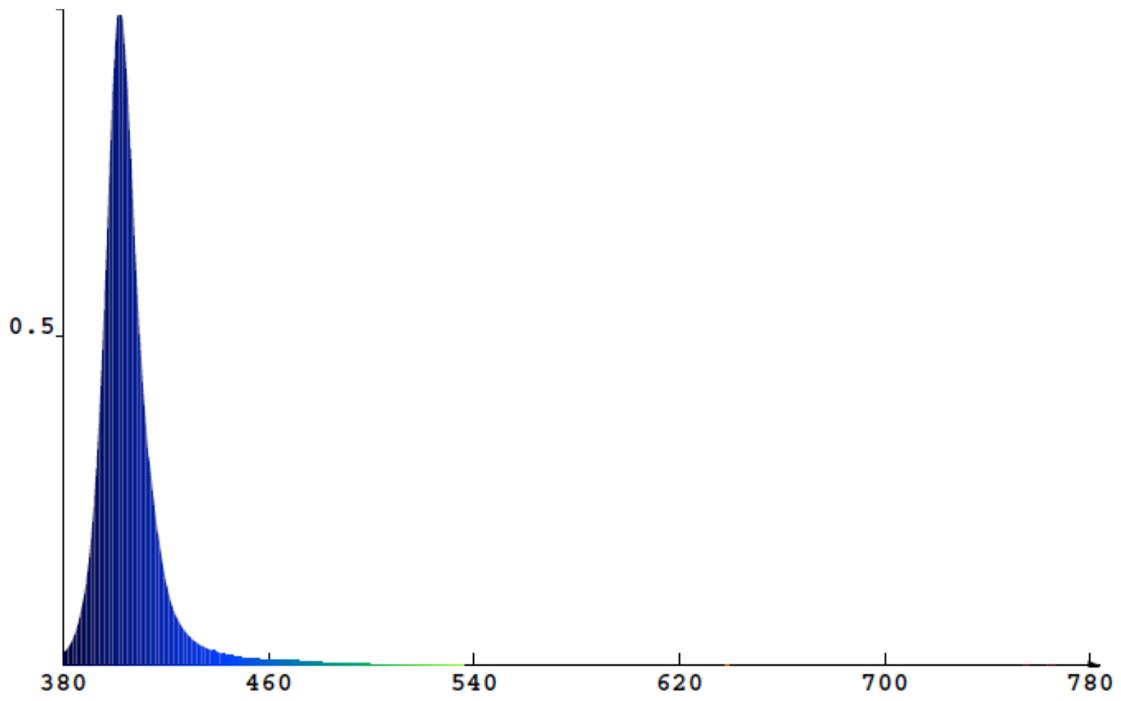
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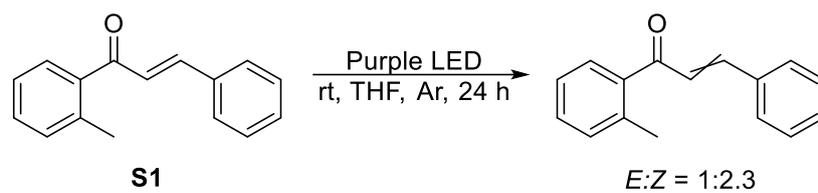
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**Figure S1. Spectral distribution of irradiance density for the purple LED strip**

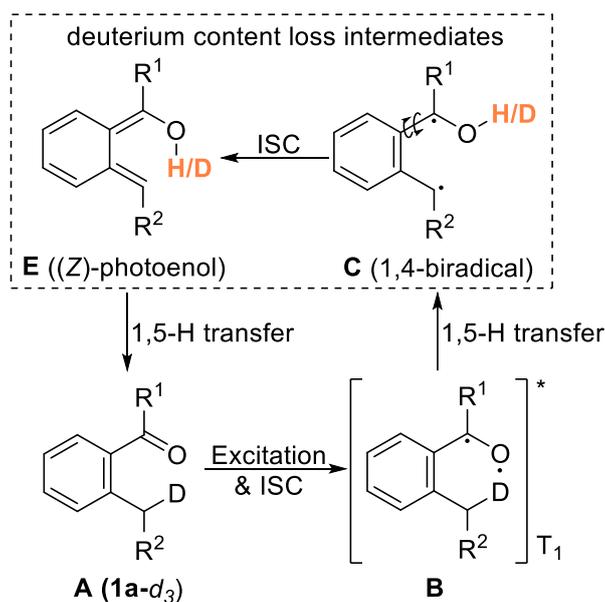


**Scheme S1. The reaction of *o*-tolyl styryl ketone**



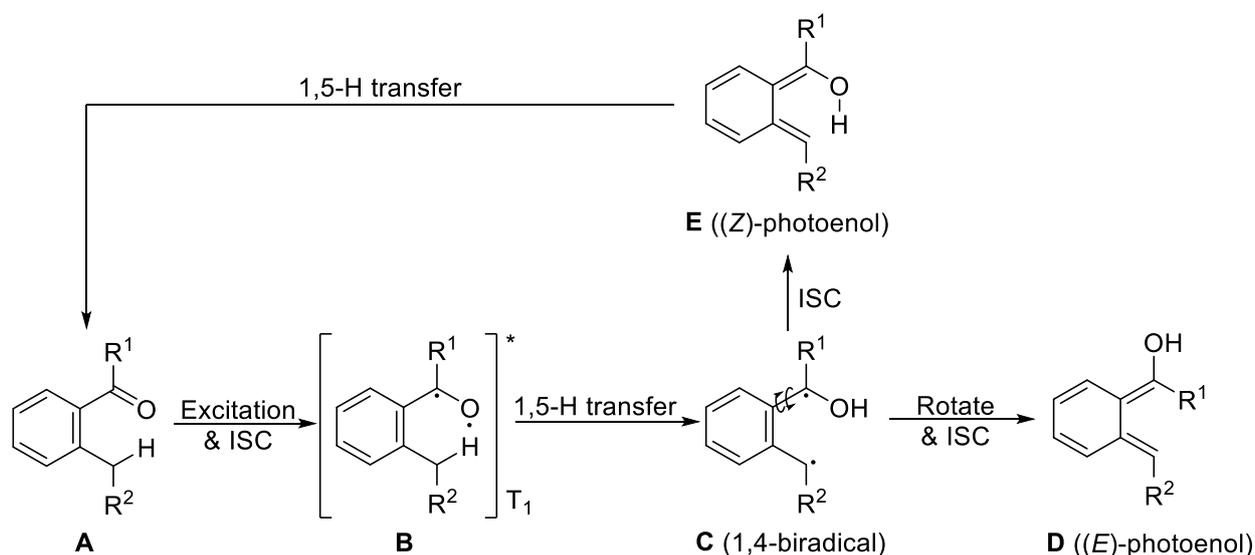
The reaction of *o*-tolyl styryl ketone only lead to the alkene isomerization. This result indicated that the excited starting material undergoes fast isomerization to de-excite, rather than 1,5-H shift and ISC to form photoenol.

### Scheme S2. The deuterium content loss process



The deuterium content loss of starting material **1a-d<sub>3</sub>** could be explained by Scheme S2. The H-D exchange of hydroxyl in **C** and **E** caused the initial deuterium content loss. The transformation of **E** to **A** eventually caused the deuterium content loss in the recovered starting material **1a-d<sub>3</sub>**.

### Scheme S3. The formation of (*E*)-photoenol



Irradiated by proper light, starting material **A** is excited to its singlet followed by ISC to triplet **B**. 1,5-H transfer of **B** gives 1,4-biradical intermediate **C**. The direct ISC of **C** forms (*Z*)-photoenol (**E**). It is a unstable intermediate, which can undergo fast 1,5-H transfer returning to starting material **A**. The ISC after a rotation of the singlet bond gives (*E*)-photoenol (**D**). It is a relatively stable intermediate, since its geometry is not suitable for further 1,5-H transfer.

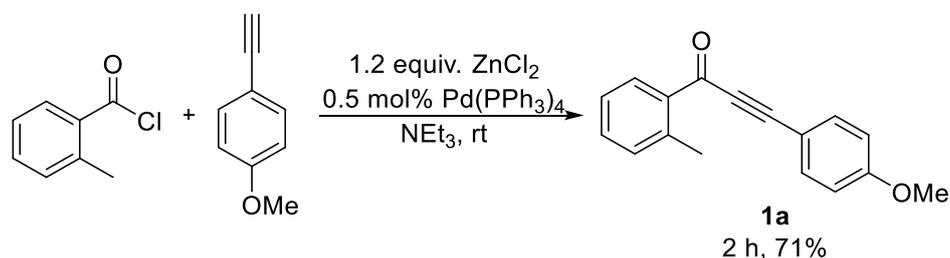
## Experimental Section

### General information

All the photo reactions were carried out using purple LED (1 m strip  $\times$  4, Greethink 5050, 12 W/m) at a distance of 8-10 cm with a cooling fan. Pyrex flasks were used for all photoreactions without any filters. Melting points were determined on a WRS-2 apparatus.  $^1\text{H}$  (400 MHz),  $^{13}\text{C}$  (100 MHz) and  $^{19}\text{F}$  (376 MHz) NMR spectra of samples in  $\text{CDCl}_3$  or  $\text{DMSO-}d_6$  were recorded on an AVANCE III 400 spectrometer. IR spectra were recorded on a Nicolet iS5 spectrometer. HRMS (EI, 70 eV) determinations were carried out on a Water GCT CA176 spectrometer. HRMS (ESI) determinations were carried out on a Bruker Daltonics APEXIII<sup>TM</sup> ESI-FTICRMS spectrometer. Anhydrous DCM was distilled with  $\text{CaH}_2$ . Anhydrous THF was distilled with Na using benzophenone as monitor. **1w**,<sup>[1]</sup> **1x**<sup>[2]</sup> and **S1**<sup>[3]</sup> were prepared according to literatures.

### Typical Procedure I for the synthesis of substrate.

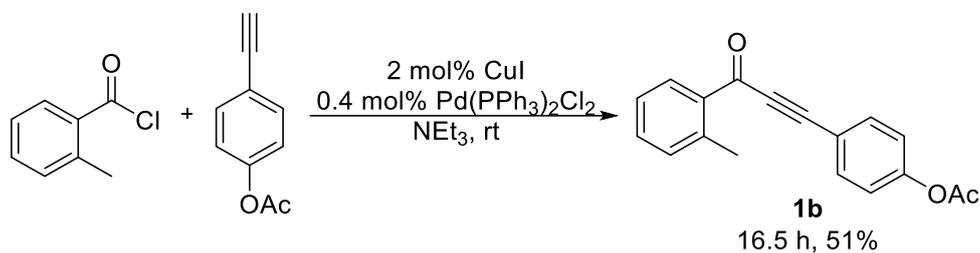
#### Synthesis of 3-(4-methoxyphenyl)-1-(*o*-tolyl)prop-2-yn-1-one (**1a**)



$\text{ZnCl}_2$  (164 mg, 1.2 mmol) and  $\text{NEt}_3$  (0.3 mL) were added subsequently into a 5 mL of centrifuge tube and stirred 10 min at rt. Then 2-methylbenzoyl chloride (154 mg, 1 mmol), 4-methoxyphenylacetylene (132 mg, 1 mmol), and  $\text{Pd}(\text{PPh}_3)_4$  (6 mg, 0.005 mmol) were added subsequently into the mixture. Then the resulting mixture was stirred at rt. The reaction was completed after 2 hours as monitored by TLC (eluent: petroleum ether/ethyl acetate = 50/1). Then the reaction was quenched with saturated  $\text{NaHCO}_3$  solution and extracted with ethyl acetate. The combined organic phases was dried over  $\text{MgSO}_4$ , filtered and concentrated in vacuum. The product was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = petroleum ether $\rightarrow$ 300/1) to afford **1a**<sup>[4]</sup> as a liquid (176 mg, 71%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.27 (d,  $J = 7.6$  Hz, 1 H), 7.61 (d,  $J = 8.8$  Hz, 2 H), 7.45 (t,  $J = 8.2$  Hz, 1 H), 7.35 (t,  $J = 7.4$  Hz, 1 H), 7.26 (d,  $J = 8.4$  Hz, 1 H), 6.92 (d,  $J = 8.8$  Hz, 2 H), 3.85 (s, 3 H), 2.67 (s, 3 H).

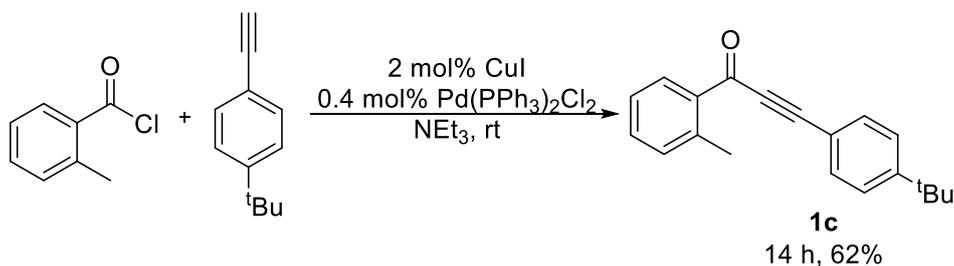
## Typical Procedure II for the synthesis of substrate.

### Synthesis of 3-(4-acetoxyphenyl)-1-(*o*-tolyl)prop-2-yn-1-one (**1b**)



4-Ethynylphenyl acetate (1.603 g, 10 mmol), CuI (38 mg, 0.2 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (28 mg, 0.04 mmol), and NEt<sub>3</sub> (20 mL) were added subsequently into a 100 mL of Schlenk flask, then 2-methylbenzoyl chloride (1.546 g, 10 mmol) was added dropwise into the mixture. The resulting mixture was stirred at rt. The reaction was completed after 16.5 hours as monitored by TLC (eluent: petroleum ether/ethyl acetate = 20/1). The product was concentrated in vacuum and purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = petroleum ether → 100/1 → 50/1) to afford **1b** as a solid (1.418 g, 51%); mp 90.4–91.3 °C (ethyl acetate/petroleum ether). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.28 (d, *J* = 5.2 Hz, 1 H), 7.67 (d, *J* = 7.2 Hz, 2 H), 7.45 (t, *J* = 8.3 Hz, 1 H), 7.36 (t, *J* = 9.4 Hz, 1 H), 7.27 (d, *J* = 7.2 Hz, 1 H), 7.16 (d, *J* = 6.3 Hz, 2 H), 2.67 (s, 3 H), 2.31 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 179.5, 168.7, 152.2, 140.4, 135.6, 134.2, 133.0, 132.9, 132.1, 125.8, 122.1, 117.8, 90.8, 88.4, 21.8, 21.0; IR (neat) 1769, 1631, 1598, 1567, 1507, 1493 cm<sup>-1</sup>; HRMS (EI, 70 eV) *m/z*: [M]<sup>+</sup> calcd for C<sub>18</sub>H<sub>14</sub>O<sub>3</sub> 278.0943, found 278.0935.

### 1) 3-(4-(*tert*-Butyl)phenyl)-1-(*o*-tolyl)prop-2-yn-1-one (**1c**)

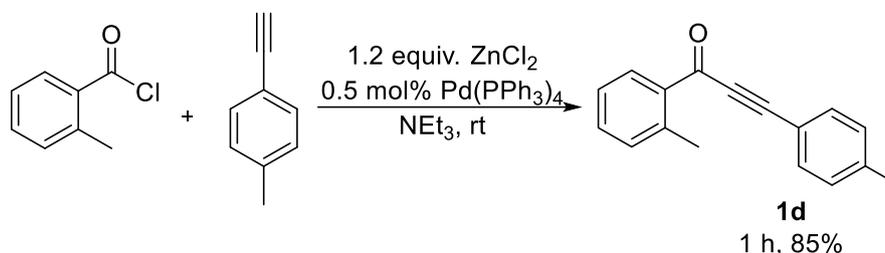


Follows Typical Procedure II.

The reaction of 2-methylbenzoyl chloride (1.547 g, 10 mmol), 1-(*tert*-butyl)-4-ethynylbenzene (1.582 g, 10 mmol), CuI (38 mg, 0.2 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (28 mg, 0.04 mmol), and NEt<sub>3</sub> (20 mL) afforded **1c** as a liquid (1.712 g, 62%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.31 (d, *J* = 8.0 Hz, 1 H), 7.66–7.55 (m, 2 H), 7.51–7.39 (m, 3 H), 7.36 (t, *J* = 7.5 Hz, 1 H), 7.28 (d, *J* = 7.5 Hz, 1 H), 2.69 (s, 3 H), 1.34 (s, 9

H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  179.9, 154.3, 140.4, 135.8, 133.1, 132.80, 132.76, 132.1, 125.8, 125.7, 117.2, 92.4, 88.2, 35.0, 31.0, 21.9; IR (neat) 1640, 1603, 1568, 1506, 1457  $\text{cm}^{-1}$ ; HRMS (EI, 70 eV)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{20}\text{H}_{20}\text{O}$  276.1514, found 276.1516.

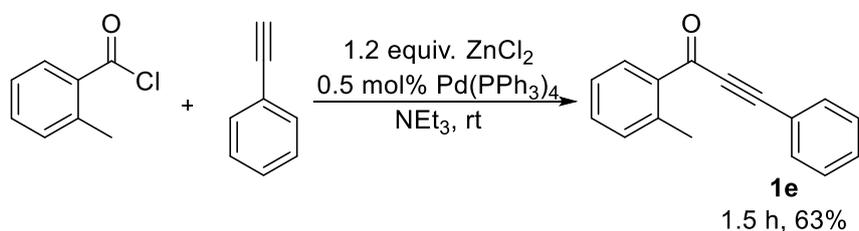
## 2) 1-(*o*-Tolyl)-3-(*p*-tolyl)prop-2-yn-1-one (**1d**)



Follows Typical Procedure I.

The reaction of 2-methylbenzoyl chloride (0.13 mL, 1 mmol), 1-ethynyl-4-methylbenzene (0.13 mL, 1 mmol),  $\text{ZnCl}_2$  (164 mg, 1.2 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (6 mg, 0.005 mmol), and  $\text{NEt}_3$  (0.3 mL) afforded **1d**<sup>[4]</sup> as a liquid (200 mg, 85%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.29 (d,  $J = 7.6$  Hz, 1 H), 7.55 (d,  $J = 8.0$  Hz, 2 H), 7.46 (t,  $J = 7.4$  Hz, 1 H), 7.36 (t,  $J = 7.3$  Hz, 1 H), 7.30-7.25 (m, 1 H), 7.21 (d,  $J = 8.0$  Hz, 2 H), 2.67 (s, 3 H), 2.40 (s, 3 H).

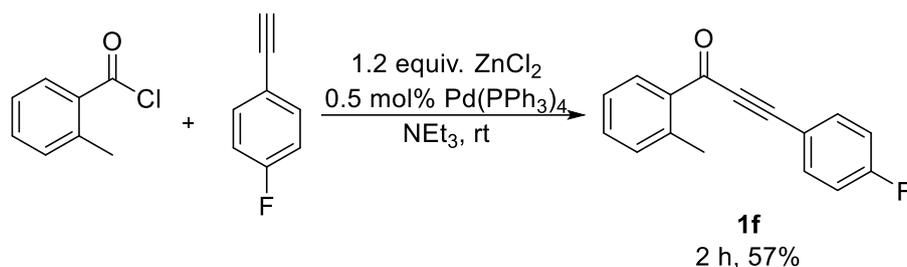
## 3) 3-Phenyl-1-(*o*-tolyl)prop-2-yn-1-one (**1e**)



Follows Typical Procedure I.

The reaction of 2-methylbenzoyl chloride (0.13 mL, 1 mmol), ethynylbenzene (102 mg, 1 mmol),  $\text{ZnCl}_2$  (164 mg, 1.2 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (6 mg, 0.005 mmol), and  $\text{NEt}_3$  (0.3 mL) afforded **1e**<sup>[4]</sup> as a liquid (138 mg, 63%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.30 (d,  $J = 7.6$  Hz, 1 H), 7.70-7.62 (m, 2 H), 7.52-7.33 (m, 5 H), 7.28 (d,  $J = 7.6$  Hz, 1H), 2.68 (s, 3 H).

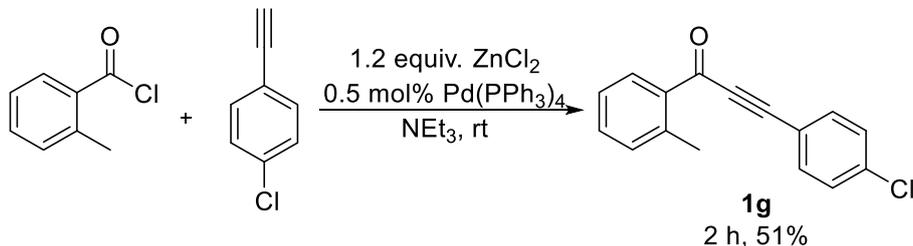
## 4) 3-(4-Fluorophenyl)-1-(*o*-tolyl)prop-2-yn-1-one (**1f**)



Follows Typical Procedure I.

The reaction of 2-methylbenzoyl chloride (154 mg, 1 mmol), 1-ethynyl-4-fluorobenzene (120 mg, 1 mmol), ZnCl<sub>2</sub> (164 mg, 1.2 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (6 mg, 0.005 mmol), and NEt<sub>3</sub> (0.3 mL) afforded **1f** as a liquid (136 mg, 57%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.27 (d, *J* = 7.6 Hz, 1 H), 7.71-7.60 (m, 2 H), 7.46 (t, *J* = 8.1 Hz, 1 H), 7.35 (t, *J* = 7.5 Hz, 1 H), 7.27 (d, *J* = 7.6 Hz, 1 H), 7.16-7.04 (m, 2 H), 2.67 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 179.6, 165.2, 162.6, 140.5, 135.6, 135.2, 135.1, 133.1, 132.9, 132.2, 125.9, 116.5, 116.3, 116.1, 90.7, 88.3, 21.9; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -106.5; IR (neat) 1638, 1598, 1573, 1510, 1485, 1459 cm<sup>-1</sup>; HRMS (EI, 70 eV) *m/z*: [M]<sup>+</sup> calcd for C<sub>16</sub>H<sub>11</sub>FO 238.0794, found 238.0788.

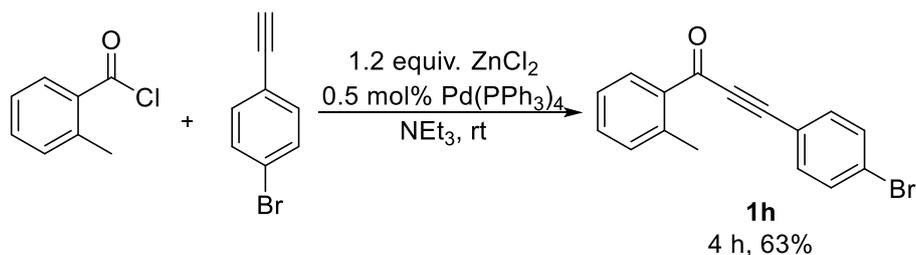
### 5) 3-(4-Chlorophenyl)-1-(*o*-tolyl)prop-2-yn-1-one (**1g**)



Follows Typical Procedure I.

The reaction of 2-methylbenzoyl chloride (154 mg, 1 mmol), 1-chloro-4-ethynylbenzene (136 mg, 1 mmol), ZnCl<sub>2</sub> (164 mg, 1.2 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (6 mg, 0.005 mmol), and NEt<sub>3</sub> (0.3 mL) afforded **1g** as a liquid (128 mg, 51%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.27 (d, *J* = 6.8 Hz, 1 H), 7.59 (d, *J* = 8.4 Hz, 2 H), 7.48 (t, *J* = 7.6 Hz, 1 H), 7.44-7.31 (m, 3 H), 7.29 (d, *J* = 7.6 Hz, 1 H), 2.67 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 179.5, 140.6, 136.9, 135.5, 134.1, 133.1, 133.0, 132.2, 129.1, 125.9, 118.8, 90.3, 89.0, 21.9; IR (neat) 1740, 1641, 1592, 1490 cm<sup>-1</sup>; HRMS (EI, 70 eV) *m/z*: [M]<sup>+</sup> calcd for C<sub>16</sub>H<sub>11</sub>ClO 254.0498, found 254.0488.

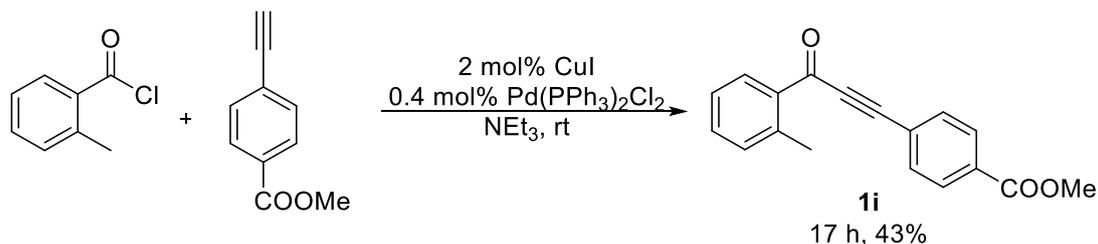
### 6) 3-(4-Bromophenyl)-1-(*o*-tolyl)prop-2-yn-1-one (**1h**)



Follows Typical Procedure I.

The reaction of 2-methylbenzoyl chloride (154 mg, 1 mmol), 1-bromo-4-ethynylbenzene (181 mg, 1 mmol), ZnCl<sub>2</sub> (164 mg, 1.2 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (6 mg, 0.005 mmol), and NEt<sub>3</sub> (0.3 mL) afforded **1h** as a solid (188 mg, 63%); mp 90.2-90.7 °C (ethyl acetate/petroleum ether). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.27 (d, *J* = 7.6 Hz, 1 H), 7.60-7.49 (m, 4 H), 7.47 (d, *J* = 7.5 Hz, 1 H), 7.37 (t, *J* = 7.3 Hz, 1 H), 7.29 (d, *J* = 7.6 Hz, 1 H), 2.67 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 179.4, 140.6, 135.4, 134.1, 133.1, 133.0, 132.2, 132.0, 125.9, 125.3, 119.2, 90.3, 89.1, 21.9; IR (neat) 1644, 1601, 1584, 1570, 1487 cm<sup>-1</sup>; HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>16</sub>H<sub>12</sub>BrO 299.0066, found 299.0060.

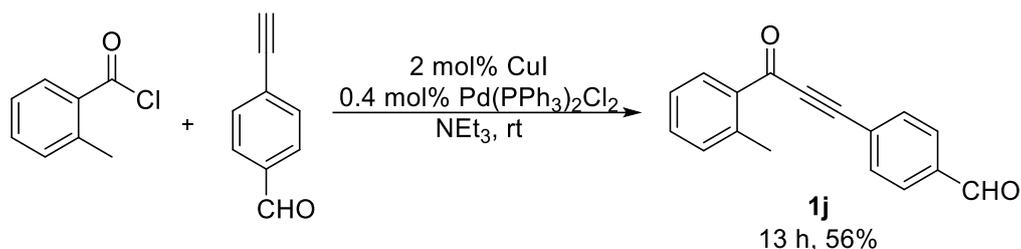
### 7) 3-(4-Methoxycarbonylphenyl)-1-(*o*-tolyl)prop-2-yn-1-one (**1i**)



Follows Typical Procedure II.

The reaction of 2-methylbenzoyl chloride (1.546 g, 10 mmol), methyl 4-ethynylbenzoate (1.602 g, 10 mmol), CuI (38 mg, 0.2 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (28 mg, 0.04 mmol), and NEt<sub>3</sub> (20 mL) afforded **1i** as a solid (1.195 g, 43%); mp 80.3-80.9 °C (ethyl acetate/petroleum ether). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.29 (d, *J* = 7.6 Hz, 1 H), 8.08 (d, *J* = 8.0 Hz, 2 H), 7.71 (d, *J* = 8.0 Hz, 2 H), 7.48 (t, *J* = 7.4 Hz, 1 H), 7.37 (t, *J* = 7.5 Hz, 1 H), 7.29 (d, *J* = 7.5 Hz, 1 H), 3.95 (s, 3 H), 2.68 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 166.2, 162.8, 142.4, 133.5, 132.1, 131.9, 131.3, 129.9, 129.3, 127.6, 126.6, 126.0, 82.6, 80.1, 52.1, 21.8; IR (neat) 1789, 1724, 1604, 1575, 1488, 1457 cm<sup>-1</sup>; HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>18</sub>H<sub>15</sub>O<sub>3</sub> 279.1016, found 279.1026.

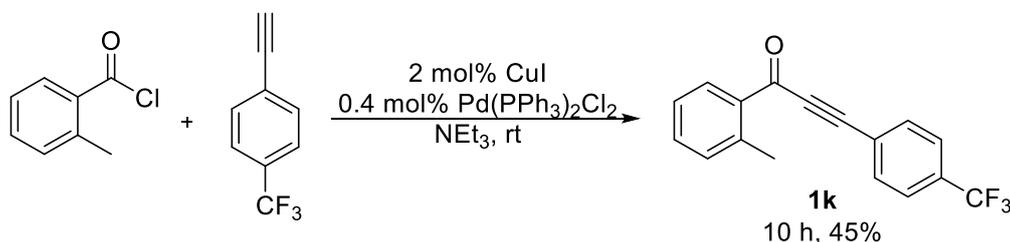
### 8) 3-(4-Formylphenyl)-1-(*o*-tolyl)prop-2-yn-1-one (**1j**)



Follows Typical Procedure II.

The reaction of 2-methylbenzoyl chloride (1.553 g, 10 mmol), 4-ethynylbenzaldehyde (1.301 g, 10 mmol), CuI (38 mg, 0.2 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (28 mg, 0.04 mmol), and NEt<sub>3</sub> (20 mL) afforded **1j** as a solid (1.389 g, 56%); mp 80.9-81.7 °C (ethyl acetate/petroleum ether). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.07 (s, 1 H), 8.29 (d, *J* = 7.6 Hz, 1 H), 7.93 (d, *J* = 8.0 Hz, 2 H), 7.81 (d, *J* = 8.2 Hz, 2 H), 7.50 (t, *J* = 7.5 Hz, 1 H), 7.38 (t, *J* = 7.6 Hz, 1 H), 7.30 (d, *J* = 7.5 Hz, 1 H), 2.68 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 191.2, 179.2, 140.8, 136.9, 135.2, 133.32, 133.28, 133.2, 132.3, 129.6, 126.3, 126.0, 90.5, 89.5, 22.0; IR (neat) 1697, 1638, 1601, 1567 cm<sup>-1</sup>; HRMS (EI, 70 eV) *m/z*: [M]<sup>+</sup> calcd for C<sub>17</sub>H<sub>12</sub>O<sub>2</sub> 248.0837, found 248.0838.

#### 9) 1-(*o*-Tolyl)-3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-one (**1k**)

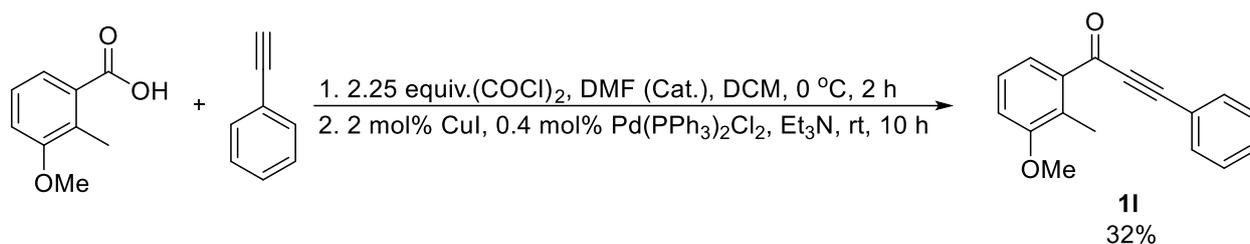


Follows Typical Procedure II.

The reaction of 2-methylbenzoyl chloride (1.546 g, 10 mmol), 1-ethynyl-4-(trifluoromethyl)benzene (1.705 g, 10 mmol), CuI (38 mg, 0.2 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (28 mg, 0.04 mmol), and NEt<sub>3</sub> (20 mL) afforded **1k**<sup>[5]</sup> as a solid (1.296 g, 45%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.29 (d, *J* = 7.8 Hz, 1 H), 7.76 (d, *J* = 8.0 Hz, 2 H), 7.68 (d, *J* = 8.0 Hz, 2 H), 7.49 (t, *J* = 7.5 Hz, 1 H), 7.38 (t, *J* = 7.5 Hz, 1 H), 7.30 (d, *J* = 7.5 Hz, 1 H), 2.68 (s, 3 H).

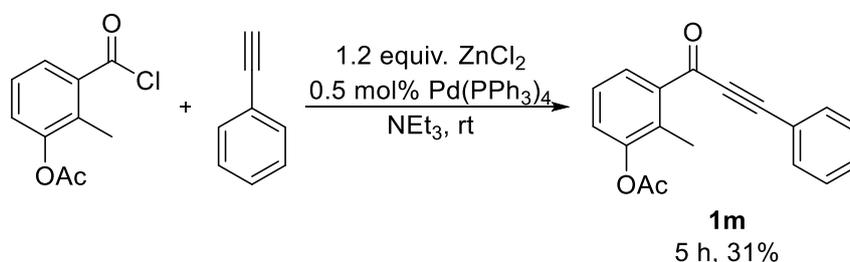
**Typical Procedure III for the synthesis of substrate.**

#### Synthesis of 1-(3-methoxy-2-methylphenyl)-3-phenylprop-2-yn-1-one (**1l**)



3-Methoxy-2-methylbenzoic acid (1.743 g, 15 mmol) was placed in a dry 100 mL of Schlenk flask under a positive pressure of argon. Then dry  $\text{CH}_2\text{Cl}_2$  (15 mL) and three drops of DMF were added and the reaction mixture was cooled to 0 °C. Oxalyl chloride (1.9 mL, 22.5 mmol) was added dropwise into the mixture and the reaction was stirred for 2 hours at 0 °C affording 3-methoxy-2-methylbenzoyl chloride as the crude product which was used without further purification. Ethynylbenzene (1.1 mL, 10 mmol), CuI (38 mg, 0.2 mmol),  $\text{Pd(PPh}_3)_2\text{Cl}_2$  (28 mg, 0.04 mmol), and  $\text{NEt}_3$  (20 mL) were added subsequently into a 100 mL of Schlenk flask. Crude 3-methoxy-2-methylbenzoyl chloride (DCM solution) was added dropwise into the mixture. The resulting mixture was stirred at rt. The reaction was completed after 10 hours as monitored by TLC (eluent: petroleum ether/ethyl acetate = 30/1). The product was concentrated in vacuum and purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 100/1) to afford **11** as a liquid (799 mg, 32%).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.81 (d,  $J = 8.0$  Hz, 1 H), 7.69-7.60 (m, 2 H), 7.50-7.39 (m, 1 H), 7.38-7.35 (m, 2 H), 7.30 (t,  $J = 8.0$  Hz, 1 H), 7.06 (d,  $J = 8.0$  Hz, 1 H), 3.87 (s, 3 H), 2.52 (s, 3 H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  180.2, 158.2, 137.6, 132.9, 130.6, 128.7, 128.6, 126.1, 124.2, 120.4, 114.5, 91.9, 88.9, 55.9, 12.5; IR (neat) 1638, 1595, 1575, 1493, 1456  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{17}\text{H}_{15}\text{O}_2$  251.1067, found 251.1065.

#### 10) 1-(3-Acetoxy-2-methylphenyl)-3-phenylprop-2-yn-1-one (**1m**)

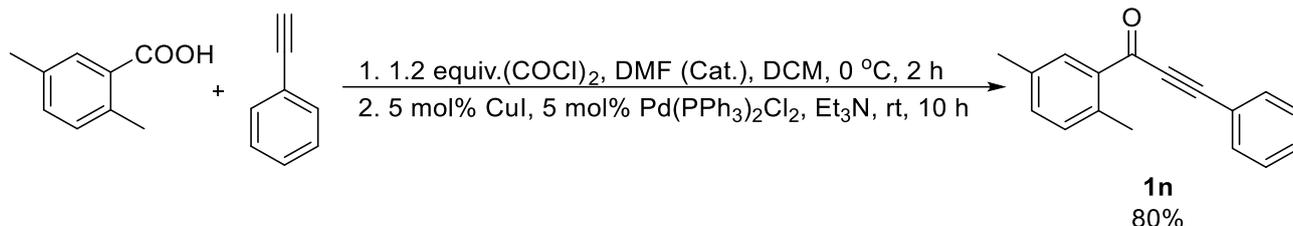


Follows Typical Procedure I.

The reaction of 3-(chlorocarbonyl)-2-methylphenyl acetate (212 mg, 1 mmol), ethynylbenzene (102 mg, 1 mmol),  $\text{ZnCl}_2$  (164 mg, 1.2 mmol),  $\text{Pd(PPh}_3)_4$  (6 mg, 0.005 mmol), and  $\text{NEt}_3$  (0.3 mL) afforded

**1m** as a solid (85 mg, 31%); mp 110.0-110.2 °C (ethyl acetate/petroleum ether). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.17 (d, *J* = 7.2 Hz, 1 H), 7.64 (d, *J* = 8.4 Hz, 2 H), 7.50-7.30 (m, 4 H), 7.25 (d, *J* = 8.4 Hz, 1 H), 2.47 (s, 3 H), 2.35 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 179.2, 169.1, 150.1, 137.8, 133.0, 132.2, 130.7, 130.5, 128.6, 126.8, 126.2, 120.1, 92.4, 88.4, 20.7, 13.2; IR (neat) 1768, 1644, 1493, 1456, 1445 cm<sup>-1</sup>; HRMS (EI, 70 eV) *m/z*: [M]<sup>+</sup> calcd for C<sub>18</sub>H<sub>14</sub>O<sub>3</sub> 278.0943, found 278.0942.

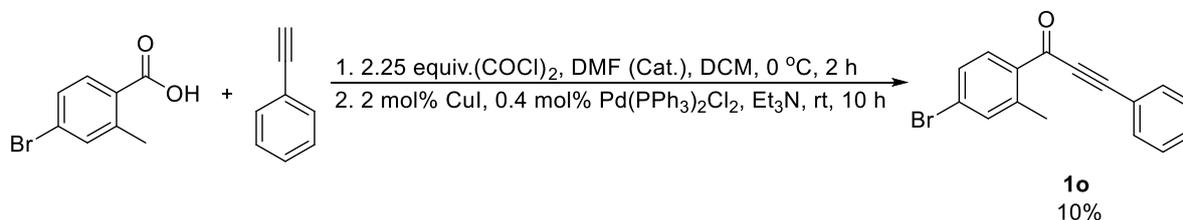
### 11) 1-(2,5-Dimethylphenyl)-3-phenylprop-2-yn-1-one (1n)



Follows Typical Procedure III.

The reaction of 2,5-dimethylbenzoic acid (2.253 mg, 15 mmol), oxalyl chloride (1.5 mL, 18 mmol), four drops of DMF, and dry CH<sub>2</sub>Cl<sub>2</sub> (20 mL) afforded 2,5-dimethylbenzoyl chloride as the crude product. The reaction of the crude 2,5-dimethylbenzoyl chloride, ethynylbenzene (2.0 mL, 18 mmol), CuI (143 mg, 0.75 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (526 mg, 0.75 mmol), and NEt<sub>3</sub> (30 mL) afforded **1n** as a liquid (2.824 mg, 80%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.07 (s, 1 H), 7.65 (d, *J* = 7.1 Hz, 2 H), 7.50-7.35 (m, 3 H), 7.26 (d, *J* = 7.8 Hz, 1 H), 7.15 (d, *J* = 7.4 Hz, 1 H), 2.62 (s, 3 H), 2.41 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 179.9, 137.3, 135.6, 135.4, 133.6, 133.5, 132.8, 132.0, 130.5, 128.6, 120.4, 91.6, 88.4, 21.4, 20.9; IR (neat) 1781, 1644, 1568, 1495, 1446 cm<sup>-1</sup>; HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>17</sub>H<sub>15</sub>O 235.1117, found 235.1129.

### 12) 1-(4-Bromo-2-methylphenyl)-3-phenylprop-2-yn-1-one (1o)

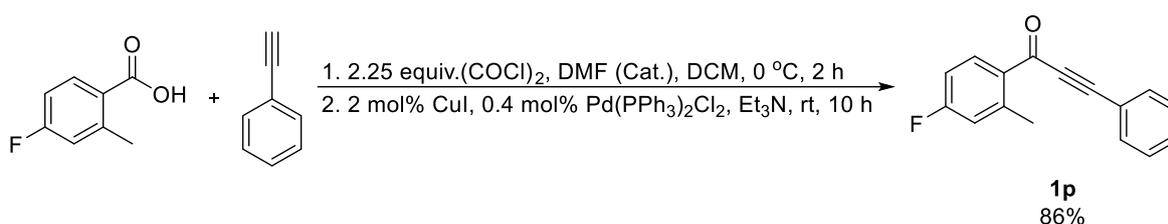


Follows Typical Procedure III.

The reaction of 4-bromo-2-methylbenzoic acid (3.225 g, 15 mmol), oxalyl chloride (1.9 mL, 22.5 mmol), a few drops of DMF, and dry CH<sub>2</sub>Cl<sub>2</sub> (15 mL) afforded 4-bromo-2-methylbenzoyl chloride as the crude product. The reaction of the crude 4-bromo-2-methylbenzoyl chloride, ethynylbenzene (1.1

mL, 10 mmol), CuI (38 mg, 0.2 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (28 mg, 0.04 mmol), and NEt<sub>3</sub> (20 mL) afforded **1o** as a solid (285 mg, 10%); mp 62.3-62.9 °C (ethyl acetate/petroleum ether). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.15 (d, *J* = 8.4 Hz, 1 H), 7.70-7.61 (m, 2 H), 7.55-7.37 (m, 5 H), 2.65 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 178.7, 142.4, 135.0, 134.6, 134.4, 132.9, 130.8, 129.1, 128.7, 127.9, 120.1, 92.3, 88.1, 21.7; IR (neat) 1641, 1590, 1550, 1493, 1448 cm<sup>-1</sup>; HRMS (EI, 70 eV) *m/z*: [M]<sup>+</sup> calcd for C<sub>16</sub>H<sub>11</sub>BrO 297.9993, found 297.9991.

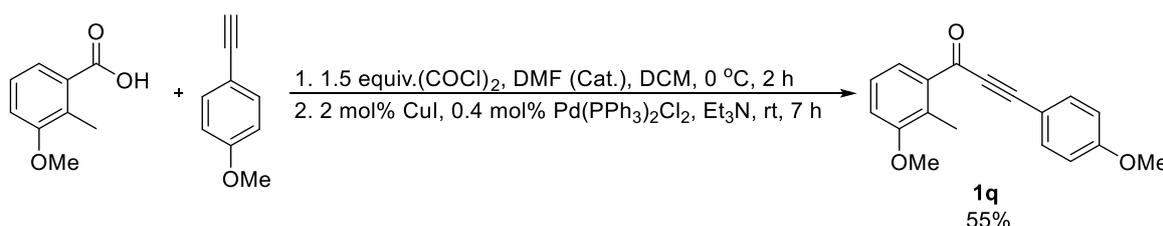
### 13) 1-(4-Fluoro-2-methylphenyl)-3-phenylprop-2-yn-1-one (1p)



Follows Typical Procedure III.

The reaction of 4-fluoro-2-methylbenzoic acid (2.314 g, 15 mmol), oxalyl chloride (1.9 mL, 22.5 mmol), a few drops of DMF, and dry CH<sub>2</sub>Cl<sub>2</sub> (15 mL) afforded 4-fluoro-2-methylbenzoyl chloride as the crude product. The reaction of the crude 4-fluoro-2-methylbenzoyl chloride, ethynylbenzene (1.1 mL, 10 mmol), CuI (38 mg, 0.2 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (28 mg, 0.04 mmol), and NEt<sub>3</sub> (20 mL) afforded **1p**<sup>[6]</sup> as a solid (3.070g, 86%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.32 (t, *J* = 7.3 Hz, 1 H), 7.63 (d, *J* = 7.2 Hz, 2 H), 7.50-7.34 (m, 3 H), 7.02 (t, *J* = 8.2 Hz, 1 H), 6.94 (d, *J* = 9.8 Hz, 1 H), 2.67 (s, 3 H).

### 14) 1-(3-Methoxy-2-methylphenyl)-3-(4-methoxyphenyl)prop-2-yn-1-one (1q)

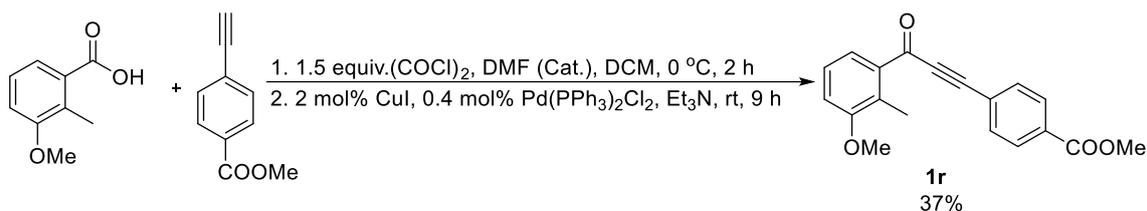


Follows Typical Procedure III.

The reaction of 3-methoxy-2-methylbenzoic acid (1.663 g, 10 mmol), oxalyl chloride (1.5 mL, 18 mmol), three drops of DMF, and dry CH<sub>2</sub>Cl<sub>2</sub> (10 mL) afforded 3-methoxy-2-methylbenzoyl chloride as the crude product. The reaction of the crude 3-methoxy-2-methylbenzoyl chloride, 1-ethynyl-4-methoxybenzene (1.323 g, 10 mmol), CuI (38 mg, 0.2 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (28 mg, 0.04 mmol), and NEt<sub>3</sub> (20 mL) afforded **1q** as a solid (1.531 g, 55%); mp 78.9-79.7 °C (ethyl acetate/petroleum ether).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.80 (d,  $J = 8.0$  Hz, 1 H), 7.68-7.53 (m, 2 H), 7.32 (t,  $J = 8.0$  Hz, 1 H), 7.07 (d,  $J = 8.0$  Hz, 1 H), 6.98-6.87 (m, 2 H), 3.89 (s, 3 H), 3.87 (s, 3 H), 2.54 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  180.4, 161.6, 158.2, 138.0, 135.0, 128.4, 126.0, 124.0, 114.35, 114.26, 112.1, 93.1, 88.9, 55.9, 55.4, 12.5; IR (neat) 1635, 1605, 1574, 1512, 1460  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{18}\text{H}_{17}\text{O}_3$  281.1172, found 281.1178.

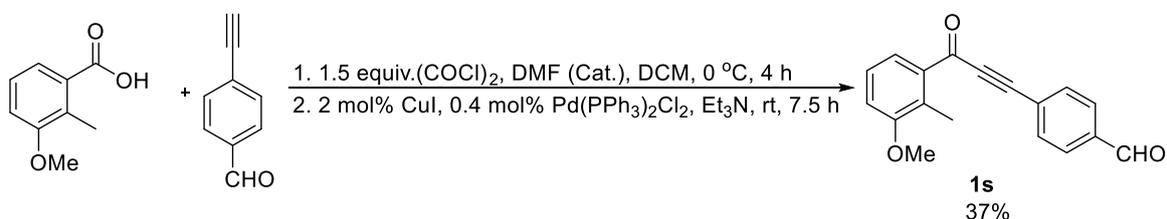
### 15) 1-(3-Methoxy-2-methylphenyl)-3-(4-methoxycarbonylphenyl)prop-2-yn-1-one (1r)



Follows Typical Procedure III.

The reaction of 3-methoxy-2-methylbenzoic acid (1.662 g, 10 mmol), oxalyl chloride (1.5 mL, 18 mmol), three drops of DMF, and dry  $\text{CH}_2\text{Cl}_2$  (10 mL) afforded 3-methoxy-2-methylbenzoyl chloride as the crude product. The reaction of the crude 3-methoxy-2-methylbenzoyl chloride, methyl 4-ethynylbenzoate (1.602 g, 10 mmol), CuI (38 mg, 0.2 mmol),  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (29 mg, 0.04 mmol), and  $\text{NEt}_3$  (20 mL) afforded **1r** as a solid (1.135 g, 37%); mp 119.3-119.8  $^\circ\text{C}$  (ethyl acetate/petroleum ether).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.06 (d,  $J = 7.6$  Hz, 2 H), 7.81 (d,  $J = 8.0$  Hz, 1 H), 7.69 (d,  $J = 8.0$  Hz, 2 H), 7.31 (t,  $J = 8.0$  Hz, 1 H), 7.08 (d,  $J = 8.0$  Hz, 1 H), 3.94 (s, 3 H), 3.87 (s, 3 H), 2.51 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  179.8, 166.1, 158.2, 137.1, 132.7, 131.5, 129.6, 128.9, 126.1, 124.8, 124.4, 114.7, 90.5, 90.0, 55.9, 52.4, 12.5; IR (neat) 1716, 1642, 1580, 1456, 1429, 1402  $\text{cm}^{-1}$ ; HRMS (EI, 70 eV)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{19}\text{H}_{16}\text{O}_4$  308.1049, found 308.1053.

### 16) 1-(3-Methoxy-2-methylphenyl)-3-(4-formylphenyl)prop-2-yn-1-one (1s)

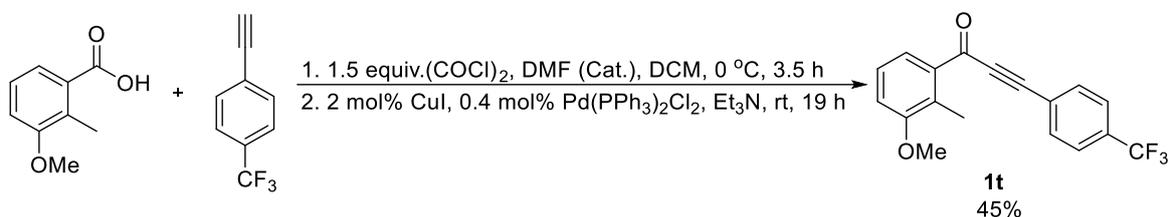


Follows Typical Procedure III.

The reaction of 3-methoxy-2-methylbenzoic acid (1.664 g, 10 mmol), oxalyl chloride (1.3 mL, 15 mmol), three drops of DMF, and dry  $\text{CH}_2\text{Cl}_2$  (10 mL) afforded 3-methoxy-2-methylbenzoyl chloride

as the crude product. The reaction of the crude 3-methoxy-2-methylbenzoyl chloride, 4-ethynylbenzaldehyde (1.310 g, 10 mmol), CuI (38 mg, 0.2 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (30 mg, 0.04 mmol), and NEt<sub>3</sub> (20 mL) afforded **1s** as a solid (1.038 g, 37%); mp 124.1-124.8 °C (ethyl acetate/petroleum ether). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.05 (s, 1 H), 7.91 (d, *J* = 7.6 Hz, 2 H), 7.83-7.74 (m, 3 H), 7.32 (t, *J* = 8.0 Hz, 1 H), 7.09 (d, *J* = 8.0 Hz, 1 H), 3.88 (s, 3 H), 2.52 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 191.1, 179.5, 158.2, 137.0, 133.2, 129.5, 128.9, 126.2, 124.4, 114.9, 91.0, 89.6, 55.9, 12.5; IR (neat) 1706, 1638, 1605, 1576, 1564, 1472 cm<sup>-1</sup>; HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>18</sub>H<sub>15</sub>O<sub>3</sub> 279.1016, found 279.1023.

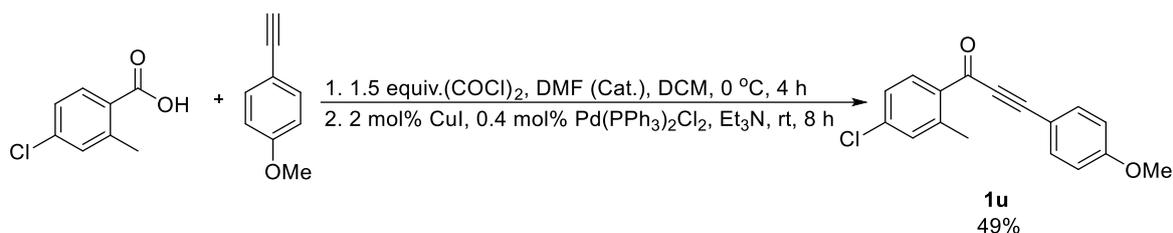
**17) 1-(3-Methoxy-2-methylphenyl)-3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-one (1t)**



Follows Typical Procedure III.

The reaction of 3-methoxy-2-methylbenzoic acid (1.665 g, 10 mmol), oxalyl chloride (1.3 mL, 15 mmol), three drops of DMF, and dry CH<sub>2</sub>Cl<sub>2</sub> (10 mL) afforded 3-methoxy-2-methylbenzoyl chloride as the crude product. The reaction of the crude 3-methoxy-2-methylbenzoyl chloride, 1-ethynyl-4-(trifluoromethyl)benzene (1.701 g, 10 mmol), CuI (39 mg, 0.2 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (30 mg, 0.04 mmol), and NEt<sub>3</sub> (20 mL) afforded **1t** as a solid (1.431 g, 45%); mp 95.6-96.1 °C (ethyl acetate/petroleum ether). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.81 (d, *J* = 8.0 Hz, 1 H), 7.75 (d, *J* = 8.0 Hz, 2 H), 7.67 (d, *J* = 8.0 Hz, 2 H), 7.32 (t, *J* = 8.0 Hz, 1 H), 7.09 (d, *J* = 8.0 Hz, 1 H), 3.88 (s, 3 H), 2.52 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 179.4, 158.1, 136.7, 132.8, 131.7 (q, *J* = 32.86 Hz), 128.7, 126.1, 125.3 (q, *J* = 3.79 Hz), 124.3, 124.0 (d, *J* = 1.61 Hz), 123.5 (q, *J* = 272.57 Hz), 114.7, 89.9, 89.0, 55.6, 12.3; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -63.1; IR (neat) 1651, 1635, 1610, 1575, 1461, 1440 cm<sup>-1</sup>; HRMS (EI, 70 eV) *m/z*: [M]<sup>+</sup> calcd for C<sub>18</sub>H<sub>13</sub>F<sub>3</sub>O<sub>2</sub> 318.0868, found 318.0869.

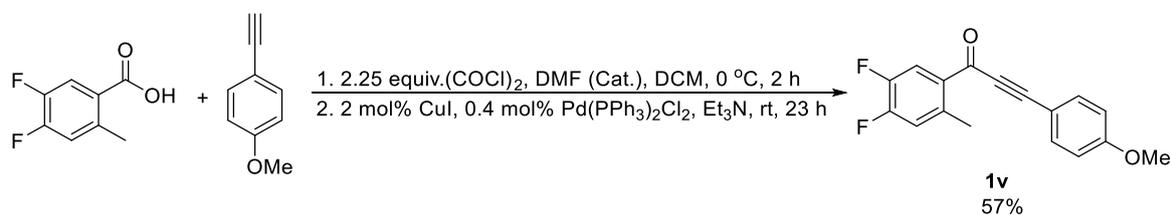
**18) 1-(4-Chloro-2-methylphenyl)-3-(4-methoxyphenyl)prop-2-yn-1-one (1u)**



Follows Typical Procedure III.

The reaction of 4-chloro-2-methylbenzoic acid (1.712 g, 10 mmol), oxalyl chloride (1.3 mL, 15 mmol), three drops of DMF, and dry CH<sub>2</sub>Cl<sub>2</sub> (10 mL) afforded 4-chloro-2-methylbenzoyl chloride as the crude product. The reaction of the crude 4-chloro-2-methylbenzoyl chloride, 1-ethynyl-4-methoxybenzene (1.331 g, 10 mmol), CuI (39 mg, 0.2 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (30 mg, 0.04 mmol), and NEt<sub>3</sub> (20 mL) afforded **1u** as a solid (1.395 g, 49%); mp 126.8-128.1 °C (ethyl acetate/petroleum ether). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.20 (d, *J* = 8.4 Hz, 1 H), 7.60 (d, *J* = 8.0 Hz, 2 H), 7.32 (d, *J* = 8.4 Hz, 1 H), 7.26 (s, 1 H), 6.92 (d, *J* = 8.0 Hz, 2 H), 3.85 (s, 3 H), 2.64 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 178.6, 161.7, 142.2, 138.8, 135.0, 134.34, 134.26, 132.0, 126.0, 114.4, 111.8, 93.4, 88.1, 55.4, 21.7; IR (neat) 1638, 1609, 1558, 1513, 1445 cm<sup>-1</sup>; HRMS (EI, 70 eV) *m/z*: [M]<sup>+</sup> calcd for C<sub>17</sub>H<sub>13</sub>ClO<sub>2</sub> 284.0604, found 284.0605.

### 19) 1-(4,5-Difluoro-2-methylphenyl)-3-(4-methoxyphenyl)prop-2-yn-1-one (**1v**)

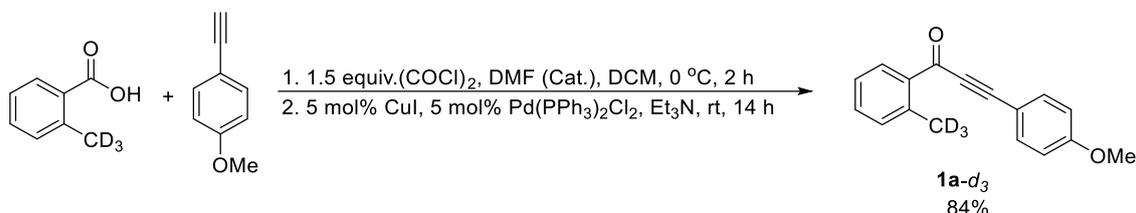


Follows Typical Procedure III.

The reaction of 4,5-difluoro-2-methylbenzoic acid (2.535 g, 15 mmol), oxalyl chloride (2.0 mL, 22.5 mmol), a few drops of DMF, and dry CH<sub>2</sub>Cl<sub>2</sub> (15 mL) afforded 4,5-difluoro-2-methylbenzoyl chloride as the crude product. The reaction of the crude 4,5-difluoro-2-methylbenzoyl chloride, 1-ethynyl-4-methoxybenzene (1.323g, 10 mmol), CuI (38 mg, 0.2 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (28 mg, 0.04 mmol), and NEt<sub>3</sub> (20 mL) afforded **1v** as a solid (1.635 g, 57%); mp 128.2-129.0 °C (ethyl acetate/petroleum ether). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.11 (t, *J* = 8.6 Hz, 1 H), 7.68-7.57 (m, 2 H), 7.08 (t, *J* = 8.2 Hz, 1 H), 6.98-6.91 (m, 2 H), 3.88 (s, 3 H), 2.64 (s, 3 H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 177.2, 161.9, 153.8, 153.7, 151.3, 151.1, 149.1, 149.0, 146.6, 146.5, 138.3, 138.25, 138.21, 138.18, 135.1, 132.30, 132.27,

132.23, 121.88, 121.86, 121.70, 121.68, 120.8, 120.6, 114.5, 111.6, 93.9, 87.8, 55.4, 21.3.;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -130.64 (ddd,  $J = 21.8, 10.9, 8.2$  Hz), -140.54 (ddd,  $J = 21.8, 10.9, 8.2$  Hz); IR (neat) 1638, 1604, 1592, 1513, 1448  $\text{cm}^{-1}$ ; HRMS (EI, 70 eV)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{17}\text{H}_{13}\text{F}_2\text{O}_2$  287.0878, found 287.0875.

## 20) 3-(4-Methoxyphenyl)-1-(2-(methyl- $d_3$ )phenyl)prop-2-yn-1-one (**1a-d<sub>3</sub>**)

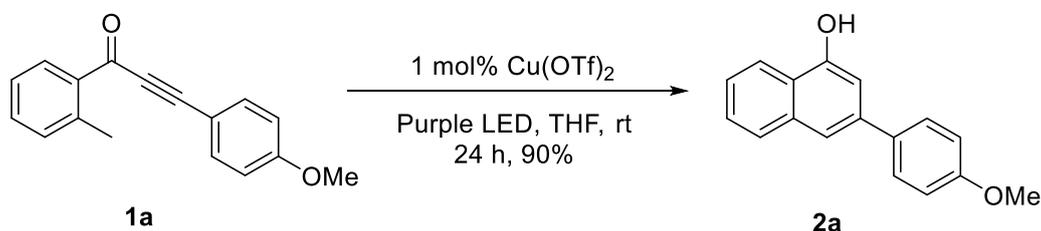


Follows Typical Procedure III.

2-(methyl- $d_3$ )benzoic acid was synthesized according to literature procedure.<sup>[7]</sup> The reaction of 2-(methyl- $d_3$ )benzoic acid (1.043 g, 7.5 mmol), oxalyl chloride (1.0 mL, 11.3 mmol), three drops of DMF, and dry  $\text{CH}_2\text{Cl}_2$  (7.5 mL) afforded 2-(methyl- $d_3$ )benzoyl chloride as the crude product. The reaction of the crude 2-(methyl- $d_3$ )benzoyl chloride, 1-ethynyl-4-methoxybenzene (0.993 g, 7.5 mmol), CuI (72 mg, 0.375 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (263 mg, 0.375 mmol), and NEt<sub>3</sub> (15 mL) afforded **1a-d<sub>3</sub>** as a solid (1.594 g, 84%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.28 (d,  $J = 7.6$  Hz, 1 H), 7.61 (d,  $J = 7.6$  Hz, 2 H), 7.46 (t,  $J = 7.3$  Hz, 1 H), 7.36 (t,  $J = 8.0$  Hz, 1 H), 7.28 (s, 1 H), 6.92 (d,  $J = 7.4$  Hz, 2 H), 3.86 (s, 3 H).

## Typical Procedure IV for the Cu(OTf)<sub>2</sub>-catalyzed 6 $\pi$ -photocyclization.

### Synthesis of 3-(4-methoxyphenyl)naphthalen-1-ol (**2a**)

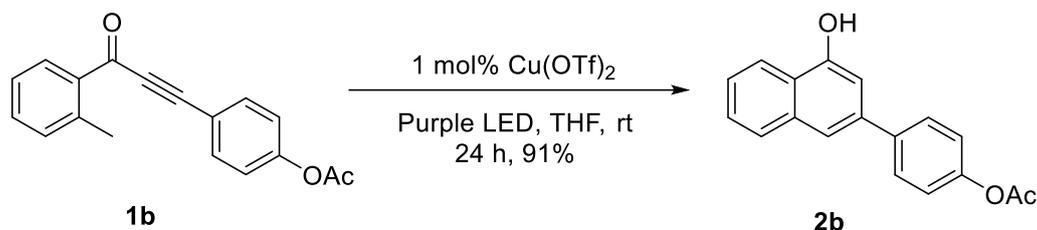


**1a** (50 mg, 0.2 mmol), Cu(OTf)<sub>2</sub> (1 mg, 0.002 mmol), and dry THF (10 mL) were added subsequently to a dry 25 mL of Schlenk tube. The mixture was irradiated by purple LED at rt under argon. The photoreaction was completed after 24 h as monitored by TLC (eluent: petroleum ether/ethyl acetate = 20/1). The solvent was removed and the residue was purified by flash column chromatography on

silica gel (eluent: petroleum ether/ethyl acetate = 50/1→20/1) to afforded **2a**<sup>[8]</sup> as a solid (45 mg, 90%).  
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.18 (d, *J* = 8.0 Hz, 1 H), 7.84 (d, *J* = 8.0 Hz, 1 H), 7.63-7.57 (m, 3 H), 7.52-7.42 (m, 2 H), 7.07 (s, 1 H), 6.99 (d, *J* = 8.0 Hz, 2 H), 3.86 (s, 3 H).

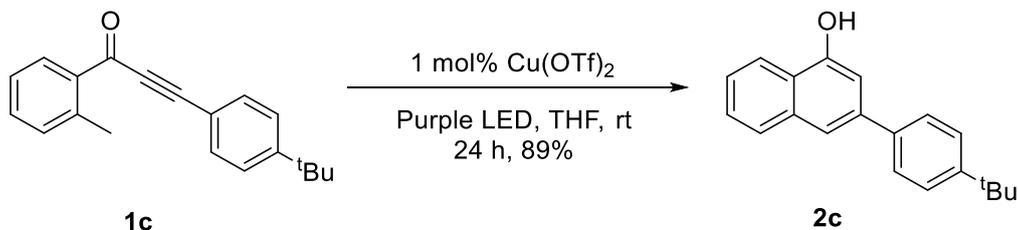
The following compounds were prepared according to Typical Procedure IV.

### 1) 3-(4-Acetoxyphenyl)naphthalen-1-ol (**2b**)



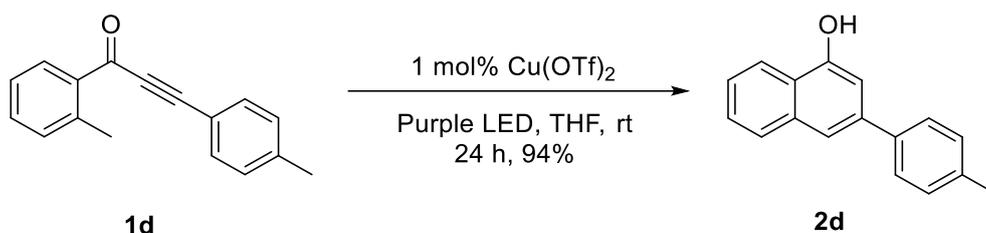
The reaction of **1b** (56 mg, 0.2 mmol), Cu(OTf)<sub>2</sub> (1 mg, 0.002 mmol), and dry THF (10 mL) afforded **2b** as a solid (51 mg, 91%); mp 179.3-179.8 °C (ethyl acetate/petroleum ether). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 10.36 (s, 1 H), 8.17 (d, *J* = 8.0 Hz, 1 H), 7.93 (d, *J* = 8.0 Hz, 1 H), 7.78 (d, *J* = 8.4 Hz, 2 H), 7.68 (s, 1 H), 7.59-7.42 (m, 2 H), 7.30 (d, *J* = 8.4 Hz, 2 H), 7.19 (s, 1 H), 2.35 (s, 3 H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ 169.7, 154.2, 150.5, 138.5, 137.8, 135.1, 128.35, 128.28, 127.1, 125.3, 124.3, 122.8, 122.4, 116.7, 107.5, 21.4; IR (neat) 3358, 1760, 1737, 1589, 1503, 1401 cm<sup>-1</sup>; HRMS (EI, 70 eV) *m/z*: [M]<sup>+</sup> calcd for C<sub>18</sub>H<sub>14</sub>O<sub>3</sub> 278.0943, found 278.0938.

### 3) 3-(4-(*tert*-Butyl)phenyl)naphthalen-1-ol (**2c**)



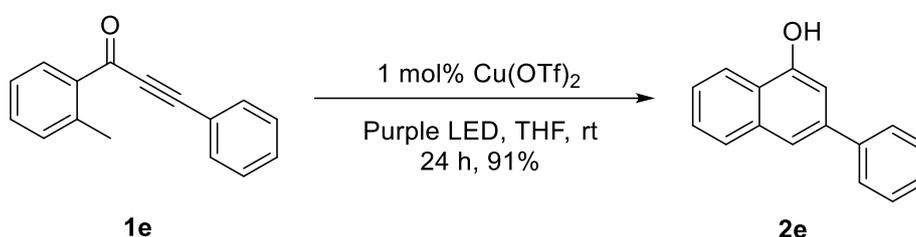
The reaction of **1c** (55 mg, 0.2 mmol), Cu(OTf)<sub>2</sub> (1 mg, 0.002 mmol), and dry THF (10 mL) afforded **2c** as a liquid (49 mg, 89%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 10.30 (s, 1 H), 8.15 (d, *J* = 8.0 Hz, 1 H), 7.91 (d, *J* = 8.4 Hz, 1 H), 7.72-7.60 (m, 3 H), 7.57-7.39 (m, 4 H), 7.19 (s, 1 H), 1.36 (s, 9 H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ 154.1, 150.4, 138.5, 138.0, 135.1, 128.3, 127.0, 126.9, 126.2, 125.1, 124.3, 122.3, 116.3, 107.5, 34.7, 31.6; IR (neat) 3404, 1714, 1663, 1635, 1598, 1580, 1513, 1404 cm<sup>-1</sup>; HRMS (EI, 70 eV) *m/z*: [M]<sup>+</sup> calcd for C<sub>20</sub>H<sub>20</sub>O 276.1514, found 276.1520.

### 2) 3-(4-Methylphenyl)naphthalen-1-ol (**2d**)



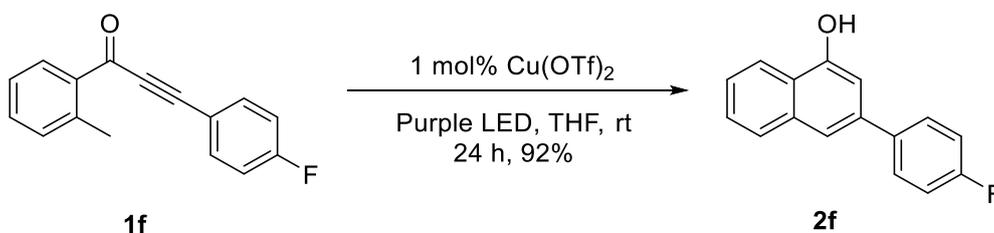
The reaction of **1d** (47 mg, 0.2 mmol), Cu(OTf)<sub>2</sub> (1 mg, 0.002 mmol), and dry THF (10 mL) afforded **2d**<sup>[9]</sup> as a solid (44 mg, 94%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.15 (d, *J* = 8.0 Hz, 1 H), 7.84 (d, *J* = 8.0 Hz, 1 H), 7.63 (s, 1 H), 7.57 (d, *J* = 8.0 Hz, 2 H), 7.54-7.40 (m, 2 H), 7.32-7.20 (m, 2 H), 7.06 (s, 1 H), 5.32 (s, 1 H), 2.41 (s, 3 H).

#### 4) 3-Phenylnaphthalen-1-ol (**2e**)



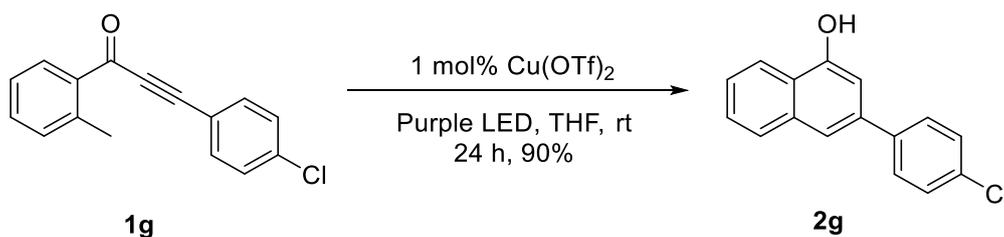
The reaction of **1e** (44 mg, 0.2 mmol), Cu(OTf)<sub>2</sub> (0.7 mg, 0.002 mmol), and dry THF (10 mL) afforded **2e**<sup>[10]</sup> as a solid (40 mg, 91%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.20 (d, *J* = 7.6 Hz, 1 H), 7.88 (d, *J* = 8.0 Hz, 1 H), 7.71-7.65 (m, 3 H), 7.59-7.44 (m, 4 H), 7.43-7.33 (m, 1 H), 7.09 (s, 1 H), 5.42 (s, 1 H).

#### 7) 3-(4-Fluorophenyl)naphthalen-1-ol (**2f**)



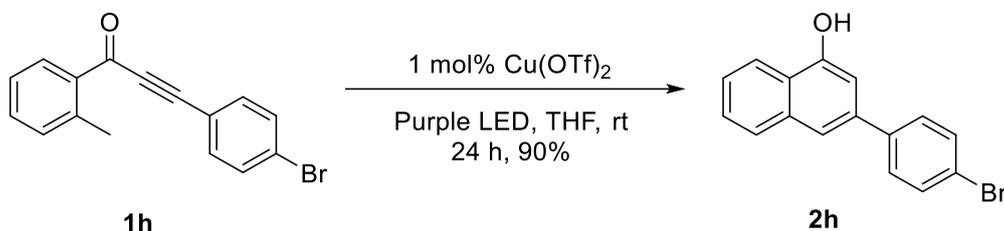
The reaction of **1f** (48 mg, 0.2 mmol), Cu(OTf)<sub>2</sub> (1 mg, 0.002 mmol), and dry THF (10 mL) afforded **2f**<sup>[8]</sup> as a solid (44 mg, 92%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.17 (d, *J* = 8.0 Hz, 1 H), 7.85 (d, *J* = 7.2 Hz, 1 H), 7.64-7.56 (m, 3 H), 7.55-7.47 (m, 2 H), 7.44 (d, *J* = 8.4 Hz, 2 H), 7.04 (s, 1 H), 5.39 (s, 1 H).

#### 6) 3-(4-Chlorophenyl)naphthalen-1-ol (**2g**)



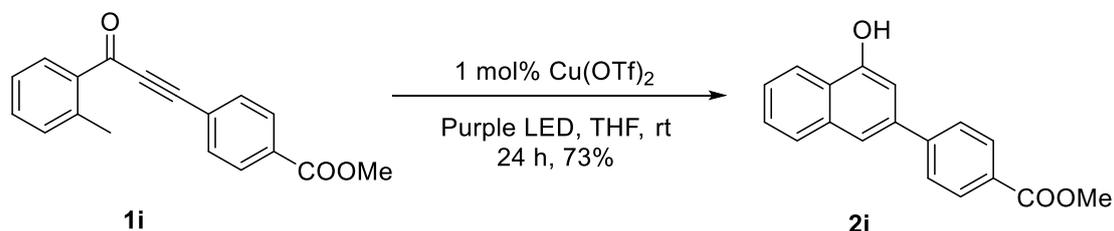
The reaction of **1g** (51 mg, 0.2 mmol), Cu(OTf)<sub>2</sub> (1 mg, 0.002 mmol), and dry THF (10 mL) afforded **2g**<sup>[8]</sup> as a solid (46 mg, 90%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.17 (d, *J* = 7.8 Hz, 1 H), 7.85 (d, *J* = 7.2 Hz, 1 H), 7.64-7.59 (m, 3 H), 7.56-7.48 (m, 2 H), 7.46-7.40 (m, 2 H), 7.05 (s, 1 H), 5.39 (s, 1 H).

### 5) 3-(4-Bromophenyl)naphthalen-1-ol (**2h**)



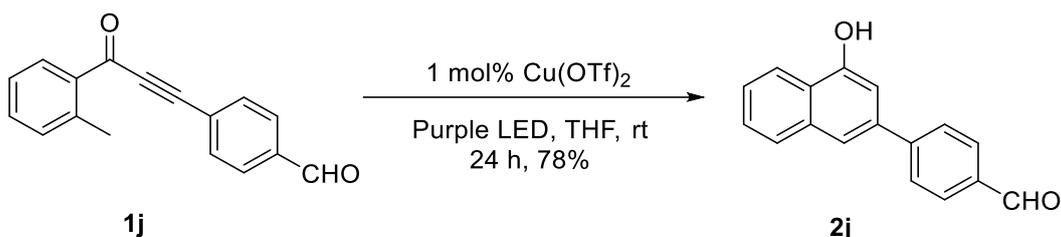
The reaction of **1f** (60 mg, 0.2 mmol), Cu(OTf)<sub>2</sub> (1 mg, 0.002 mmol), and dry THF (10 mL) afforded **2f** as a solid (54 mg, 90%); mp 161.3-161.8 °C (ethyl acetate/petroleum ether). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.21-8.11 (m, 1 H), 7.89-7.81 (m, 1 H), 7.65-7.44 (m, 7 H), 7.06-6.99 (m, 1 H), 5.38 (s, 1 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 152.0, 139.8, 137.6, 134.9, 131.9, 128.8, 128.0, 127.1, 125.5, 123.7, 121.7, 121.5, 118.6, 107.9; IR (neat) 3390, 1635, 1598, 1578, 1496, 1397 cm<sup>-1</sup>; HRMS (EI, 70 eV) *m/z*: [M]<sup>+</sup> calcd for C<sub>16</sub>H<sub>11</sub>BrO 297.9993, found 298.0000.

### 8) 3-(4-Methoxycarbonylphenyl)naphthalen-1-ol (**2i**)



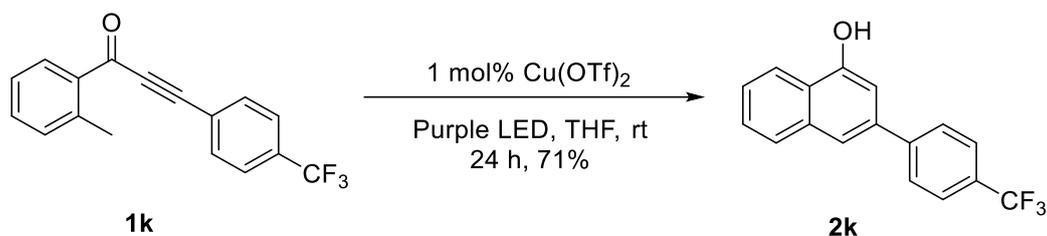
The reaction of **1i** (56 mg, 0.2 mmol), Cu(OTf)<sub>2</sub> (0.7 mg, 0.002 mmol), and dry THF (10 mL) afforded **2i** as a solid (41 mg, 73%); mp 195.6-195.9 °C (ethyl acetate/petroleum ether). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 10.49 (s, 1 H), 8.20 (d, *J* = 8.0 Hz, 1 H), 8.11 (d, *J* = 8.0 Hz, 2 H), 7.95 (d, *J* = 8.0 Hz, 1 H), 7.90 (d, *J* = 7.6 Hz, 2 H), 7.78 (s, 1 H), 7.61-7.47 (m, 2 H), 7.26 (s, 1 H), 3.92 (s, 3 H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ 166.6, 154.5, 145.5, 137.3, 135.1, 130.4, 128.9, 128.7, 127.6, 127.4, 125.9, 124.9, 122.5, 117.5, 107.3, 52.7; IR (neat) 3351, 1683, 1597, 1577, 1409 cm<sup>-1</sup>; HRMS (EI, 70 eV) *m/z*: [M]<sup>+</sup> calcd for C<sub>18</sub>H<sub>14</sub>O<sub>3</sub> 278.0943, found 278.0936.

### 9) 3-(4-Formylphenyl)naphthalen-1-ol (**2j**)



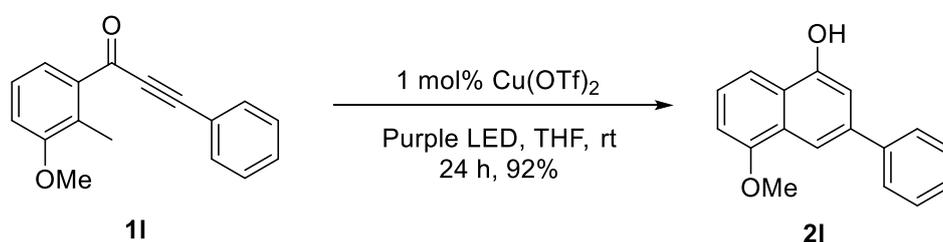
The reaction of **1j** (50 mg, 0.2 mmol), Cu(OTf)<sub>2</sub> (1 mg, 0.002 mmol), and dry THF (10 mL) afforded **2j** as a liquid (39 mg, 78%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 10.47 (s, 1 H), 10.11 (s, 1 H), 8.20 (d, *J* = 8.0 Hz, 1 H), 8.08 (d, *J* = 8.4 Hz, 2 H), 8.04-7.92 (m, 3 H), 7.82 (s, 1 H), 7.63-7.48 (m, 2 H), 7.27 (s, 1 H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ 193.2, 154.4, 146.7, 137.2, 135.6, 135.0, 130.7, 128.7, 127.9, 127.4, 125.9, 124.9, 122.4, 117.8, 107.3; IR (neat) 3276, 1695, 1603, 1580, 1406 cm<sup>-1</sup>; HRMS (EI, 70 eV) *m/z*: [M]<sup>+</sup> calcd for C<sub>17</sub>H<sub>12</sub>O<sub>2</sub> 248.0837, found 248.0838.

### 10) 3-(4-(Trifluoromethyl)phenyl)naphthalen-1-ol (**2k**)



The reaction of **1k** (58 mg, 0.2 mmol), Cu(OTf)<sub>2</sub> (1 mg, 0.002 mmol), and dry THF (10 mL) afforded **2k**<sup>[8]</sup> as a solid (41 mg, 71%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.20 (d, *J* = 7.6 Hz, 1 H), 7.88 (d, *J* = 8.0 Hz, 1 H), 7.77 (d, *J* = 8.1 Hz, 2 H), 7.72 (d, *J* = 8.1 Hz, 2 H), 7.67 (s, 1 H), 7.60-7.48 (m, 2 H), 7.07 (s, 1 H), 5.53 (s, 1 H).

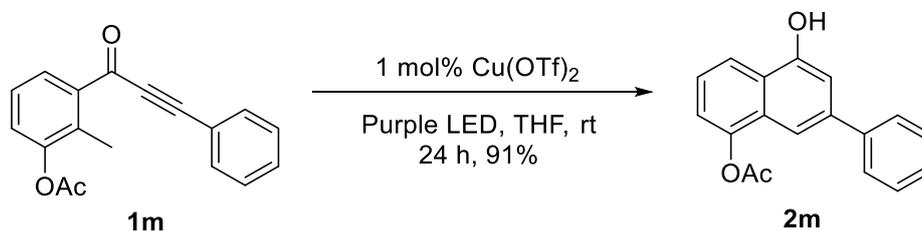
### 11) 5-Methoxy-3-phenylnaphthalen-1-ol (**2l**)



The reaction of **1l** (50 mg, 0.2 mmol), Cu(OTf)<sub>2</sub> (1 mg, 0.002 mmol), and dry THF (10 mL) afforded **2l** as a solid (46 mg, 92%); mp 167.2-167.9 °C (ethyl acetate/petroleum ether). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.11 (s, 1 H), 7.75 (d, *J* = 8.5 Hz, 1 H), 7.72-7.68 (m, 2 H), 7.50-7.43 (m, 2 H), 7.42-7.33 (m, 2 H), 7.12 (d, *J* = 1.67, 1 H), 6.88 (d, *J* = 7.6 Hz, 1 H), 5.47 (s, 1 H), 4.02 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 155.6, 151.4, 141.1, 138.0, 128.6, 127.22, 127.18, 127.0, 125.2, 124.4, 113.4, 112.8,

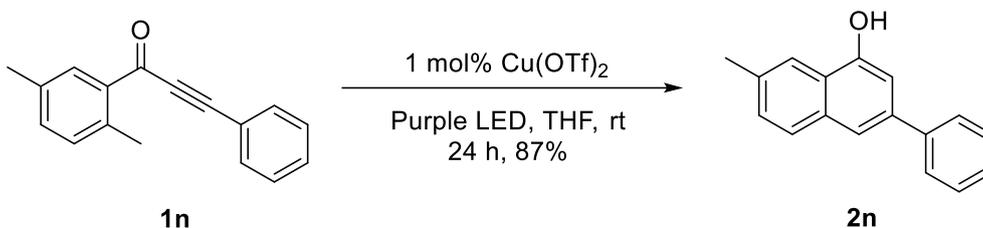
108.9, 104.7, 55.5; IR (neat) 3379, 1601, 1499, 1465, 1402  $\text{cm}^{-1}$ ; HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{17}\text{H}_{15}\text{O}_2$  251.1067, found 251.1071.

### 12) 5-Acetoxy-3-phenylnaphthalen-1-ol (2m)



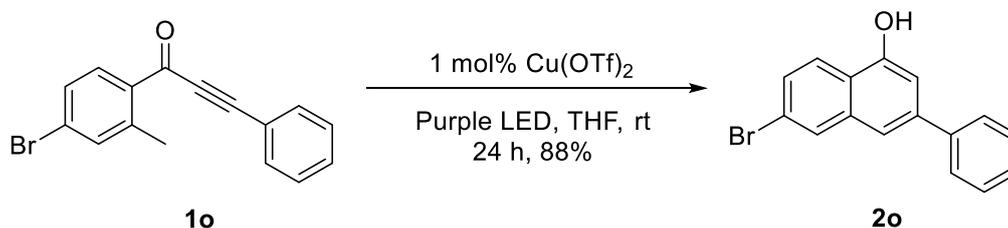
The reaction of **1m** (56 mg, 0.2 mmol),  $\text{Cu}(\text{OTf})_2$  (1 mg, 0.002 mmol), and dry THF (10 mL) afforded **2m**<sup>[11]</sup> as a liquid (51 mg, 91%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.99 (d,  $J = 8.4$  Hz, 1 H), 7.62-7.51 (m, 3 H), 7.50-7.33 (m, 4 H), 7.31-7.24 (m, 1 H), 6.94 (s, 1 H), 5.87 (s, 1 H), 2.51 (s, 3 H).

### 13) 7-Methyl-3-phenylnaphthalen-1-ol (2n)



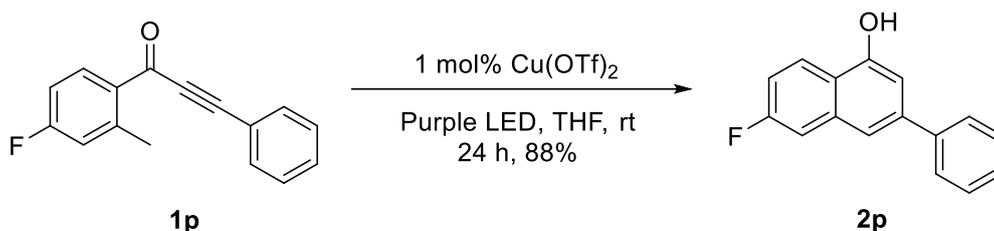
The reaction of **1n** (47 mg, 0.2 mmol),  $\text{Cu}(\text{OTf})_2$  (1 mg, 0.002 mmol), and dry THF (10 mL) afforded **2n**<sup>[12]</sup> as a solid (41 mg, 87%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94 (s, 1 H), 7.76 (d,  $J = 8.3$  Hz, 1 H), 7.67 (d,  $J = 7.7$  Hz, 2 H), 7.61 (s, 1 H), 7.46 (t,  $J = 7.6$  Hz, 2 H), 7.40-7.32 (m, 2 H), 7.07 (s, 1 H), 5.35 (s, 1 H), 2.55 (s, 3 H).

### 13) 6-Bromo-3-phenylnaphthalen-1-ol (2o)



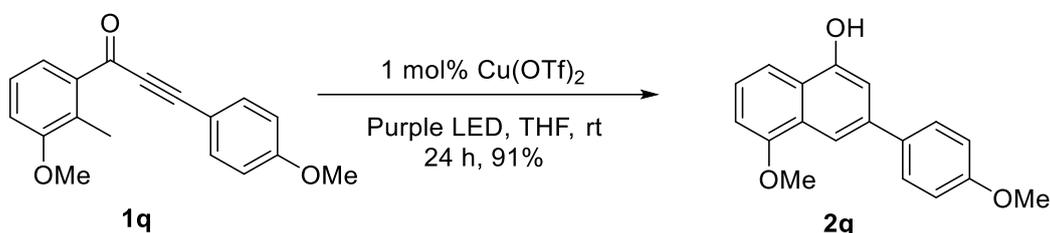
The reaction of **1o** (60 mg, 0.2 mmol),  $\text{Cu}(\text{OTf})_2$  (1 mg, 0.002 mmol), and dry THF (10 mL) afforded **2o**<sup>[12]</sup> as a solid (53 mg, 88%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.06 (d,  $J = 8.8$  Hz, 1 H), 8.01 (s, 1 H), 7.65 (d,  $J = 7.2$  Hz, 2 H), 7.58-7.34 (m, 5 H), 7.08 (s, 1 H), 5.30 (s, 1 H).

### 13) 6-Fluoro-3-phenylnaphthalen-1-ol (2p)



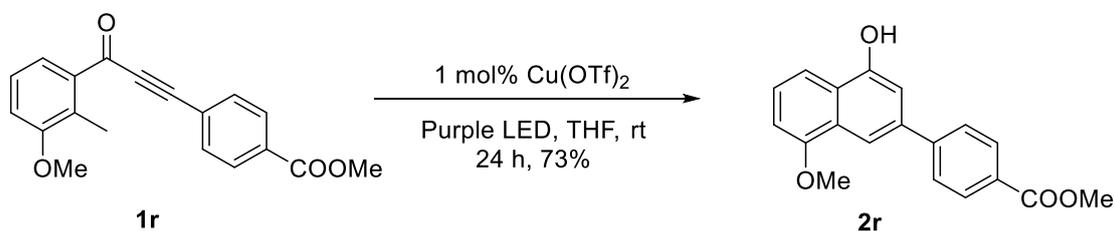
The reaction of **1p** (60 mg, 0.2 mmol),  $\text{Cu(OTf)}_2$  (1 mg, 0.002 mmol), and dry THF (10 mL) afforded **2p**<sup>[13]</sup> as a solid (53 mg, 88%).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.19 (t,  $J = 7.2$  Hz, 1 H), 7.65 (d,  $J = 7.6$  Hz, 2 H), 7.56 (s, 1 H), 7.53-7.42 (m, 3 H), 7.41-7.34 (m, 1 H), 7.30-7.19 (m, 1 H), 7.01 (s, 1 H), 5.46 (s, 1 H).

#### 14) 5-Methoxy-3-(4-methoxyphenyl)naphthalen-1-ol (**2q**)



The reaction of **1q** (56 mg, 0.2 mmol),  $\text{Cu(OTf)}_2$  (1 mg, 0.002 mmol), and dry THF (10 mL) afforded **2q** as a solid (51 mg, 91%); mp 172.3-172.9 °C (ethyl acetate/petroleum ether).  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  10.24 (s, 1 H), 7.80 (s, 1 H), 7.72 (d,  $J = 8.4$  Hz, 1 H), 7.65 (d,  $J = 8.8$  Hz, 2 H), 7.36 (t,  $J = 8.2$  Hz, 1 H), 7.18 (s, 1 H), 7.09 (d,  $J = 8.8$  Hz, 2 H), 6.99 (d,  $J = 7.6$  Hz, 1 H), 4.00 (s, 3 H), 3.84 (s, 3 H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{DMSO-}d_6$ )  $\delta$  159.4, 155.3, 154.1, 137.7, 133.6, 128.3, 127.0, 125.02, 124.95, 114.9, 114.6, 109.6, 108.1, 105.5, 56.0, 55.7; IR (neat) 3293, 1605, 1507, 1467, 1398  $\text{cm}^{-1}$ ; HRMS (EI, 70 eV)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{18}\text{H}_{16}\text{O}_3$  280.1099, found 280.1091.

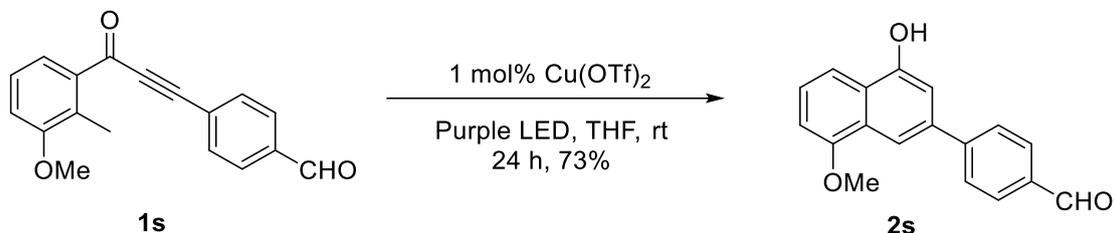
#### 15) 5-Methoxy-3-(4-methoxycarbonylphenyl)naphthalen-1-ol (**2r**)



The reaction of **1r** (62 mg, 0.2 mmol),  $\text{Cu(OTf)}_2$  (1 mg, 0.002 mmol), and dry THF (10 mL) afforded **2r** as a solid (45 mg, 73%); mp 175.1- 176.8 °C (ethyl acetate/petroleum ether).  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  10.45 (s, 1 H), 8.11 (d,  $J = 7.6$  Hz, 2 H), 7.95 (s, 1 H), 7.87 (d,  $J = 7.6$  Hz, 2 H), 7.76 (d,  $J = 8.4$  Hz, 1 H), 7.43 (t,  $J = 7.6$  Hz, 1 H), 7.26 (s, 1 H), 7.03 (d,  $J = 7.6$  Hz, 1 H), 4.01 (s, 3 H), 3.92

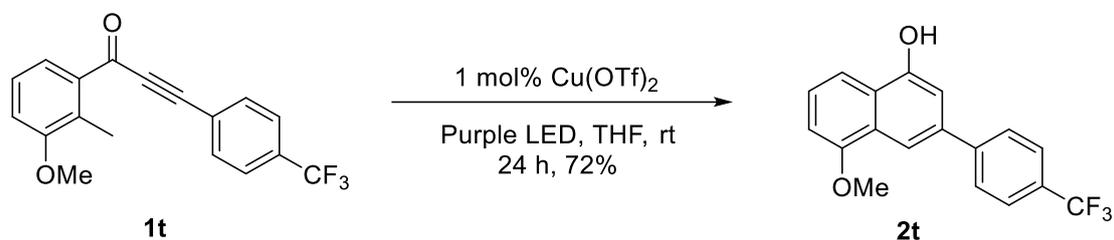
(s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-}d_6$ )  $\delta$  167.1, 156.1, 154.9, 146.2, 137.1, 130.9, 129.3, 128.0, 127.3, 126.5, 126.3, 115.1, 111.5, 108.4, 106.3, 56.6, 53.1; IR (neat) 3424, 1725, 1609, 1508, 1462, 1443, 1400  $\text{cm}^{-1}$ ; HRMS (EI, 70 eV)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{19}\text{H}_{16}\text{O}_4$  308.1049, found 308.1046.

#### 16) 5-Methoxy-3-(4-formylphenyl)naphthalen-1-ol (2s)



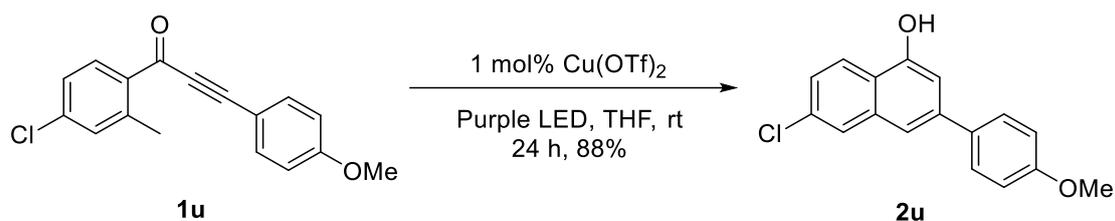
The reaction of **1s** (56 mg, 0.2 mmol),  $\text{Cu(OTf)}_2$  (1 mg, 0.002 mmol), and dry THF (10 mL) afforded **2s** as a liquid (41 mg, 73%).  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  10.43 (s, 1 H), 10.10 (s, 1 H), 8.06 (d,  $J = 8.0$  Hz, 2 H), 8.00-7.92 (m, 3 H), 7.77 (d,  $J = 8.4$  Hz, 1 H), 7.45 (t,  $J = 8.2$  Hz, 1 H), 7.28 (s, 1 H), 7.05 (d,  $J = 7.2$  Hz, 1 H), 4.02 (s, 3 H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-}d_6$ )  $\delta$  193.2, 155.6, 154.4, 146.9, 136.6, 135.5, 130.8, 127.9, 126.8, 126.2, 125.9, 114.6, 111.3, 107.9, 105.9, 56.1; IR (neat) 3306, 1695, 1602, 1565, 1509, 1462, 1404  $\text{cm}^{-1}$ ; HRMS (EI, 70 eV)  $m/z$ :  $[\text{M}]^+$  calcd for  $\text{C}_{18}\text{H}_{14}\text{O}_3$  278.0943, found 278.0937.

#### 17) 5-Methoxy-3-(4-(trifluoromethyl)phenyl)naphthalen-1-ol (2t)



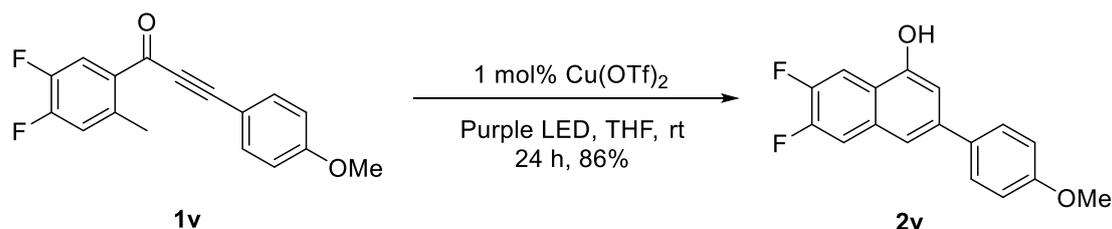
The reaction of **1t** (64 mg, 0.2 mmol),  $\text{Cu(OTf)}_2$  (1 mg, 0.002 mmol), and dry THF (10 mL) afforded **2t** as a solid (46 mg, 72%); mp 157.3-158.2  $^\circ\text{C}$  (ethyl acetate/petroleum ether).  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  10.44 (s, 1 H), 7.97-7.93 (m, 3 H), 7.89 (d,  $J = 8.4$  Hz, 2 H), 7.77 (d,  $J = 8.4$  Hz, 1 H), 7.45 (t,  $J = 8.0$  Hz, 1 H), 7.25 (s, 1 H), 7.05 (d,  $J = 7.6$  Hz, 1 H), 4.03 (s, 3 H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{DMSO}$ )  $\delta$  155.6, 154.5, 145.2, 136.3, 128.3, 128.0, 126.8, 126.40, 126.36, 126.1, 125.8, 123.6, 114.6, 111.1, 107.9, 105.9, 56.1;  $^{19}\text{F}$  NMR (376 MHz,  $\text{DMSO-}d_6$ )  $\delta$  -60.8. IR (neat) 3340, 1619, 1600, 1513, 1462, 1402  $\text{cm}^{-1}$ ; HRMS (ESI, negative mode)  $m/z$ :  $[\text{M-H}]^-$  calcd for  $\text{C}_{18}\text{H}_{12}\text{F}_3\text{O}_2$  317.0784, found 317.0793.

#### 18) 6-Chloro-3-(4-methoxyphenyl)naphthalen-1-ol (2u)



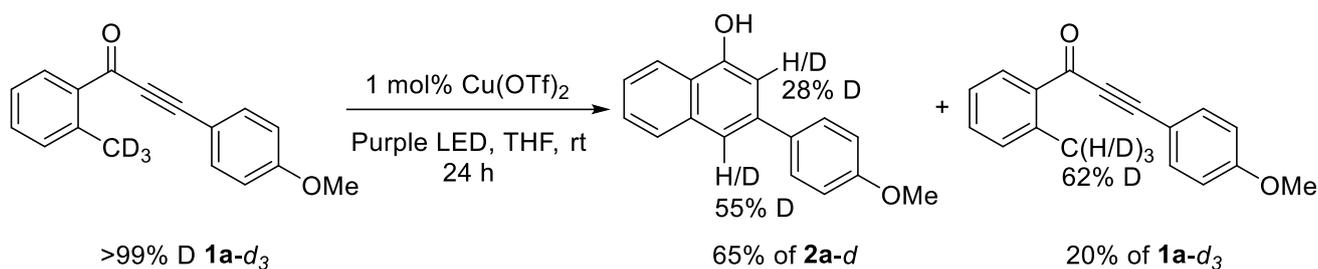
The reaction of **1u** (57mg, 0.2 mmol), Cu(OTf)<sub>2</sub> (1 mg, 0.002 mmol), and dry THF (10 mL) afforded **2u** as a solid (50 mg, 88%), mp 163.8-164.4 °C (ethyl acetate/petroleum ether). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 10.49 (s, 1 H), 8.14 (d, *J* = 8.9 Hz, 1 H), 8.00 (s, 1 H), 7.68 (d, *J* = 8.7 Hz, 2 H), 7.62 (s, 1 H), 7.43 (d, *J* = 8.9 Hz, 1 H), 7.18 (s, 1 H), 7.11 (d, *J* = 8.7 Hz, 2 H), 3.85 (s, 3 H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ 159.6, 154.2, 139.9, 136.0, 132.8, 131.7, 128.4, 126.6, 125.2, 124.8, 122.3, 115.1, 114.9, 107.9, 55.7; IR (neat) 3351, 1630, 1610, 1592, 1577, 1504 cm<sup>-1</sup>; HRMS (EI, 70 eV) *m/z*: [M]<sup>+</sup> calcd for C<sub>17</sub>H<sub>13</sub>ClO<sub>2</sub> 284.0604, found 284.0609.

#### 19) 6,7-Difluoro-3-(4-methoxyphenyl)naphthalen-1-ol (2v)



The reaction of **1v** (57 mg, 0.2 mmol), Cu(OTf)<sub>2</sub> (1 mg, 0.002 mmol), and dry THF (10 mL) afforded **2v** as a solid (49 mg, 86%); mp 158.1-159.0 °C (ethyl acetate/petroleum ether). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 10.59 (s, 1 H), 7.99-7.85 (m, 2 H), 7.71-7.58 (m, 3 H), 7.19 (s, 1 H), 7.09 (d, *J* = 8.8 Hz, 2 H), 3.84 (s, 3 H); <sup>13</sup>C NMR (100 MHz, DMSO) δ 159.5, 153.6, 151.1, 151.0, 149.7, 149.5, 148.7, 148.5, 147.2, 147.1, 139.2, 132.6, 132.3, 132.2, 128.2, 120.52, 120.46, 115.2, 114.8, 114.2, 114.0, 108.9, 108.7, 107.7, 55.5; <sup>19</sup>F NMR (376 MHz, DMSO) δ -138.1 (ddd, *J* = 21.0, 11.6, 8.7 Hz), -139.3 (ddd, *J* = 20.9, 11.8, 8.3 Hz); IR (neat) 3360, 2838, 1613, 1587, 1513, 1493, 1402 cm<sup>-1</sup>; HRMS (EI, 70 eV) *m/z*: [M]<sup>+</sup> calcd for C<sub>17</sub>H<sub>12</sub>F<sub>2</sub>O<sub>2</sub> 286.0805, found 286.0807.

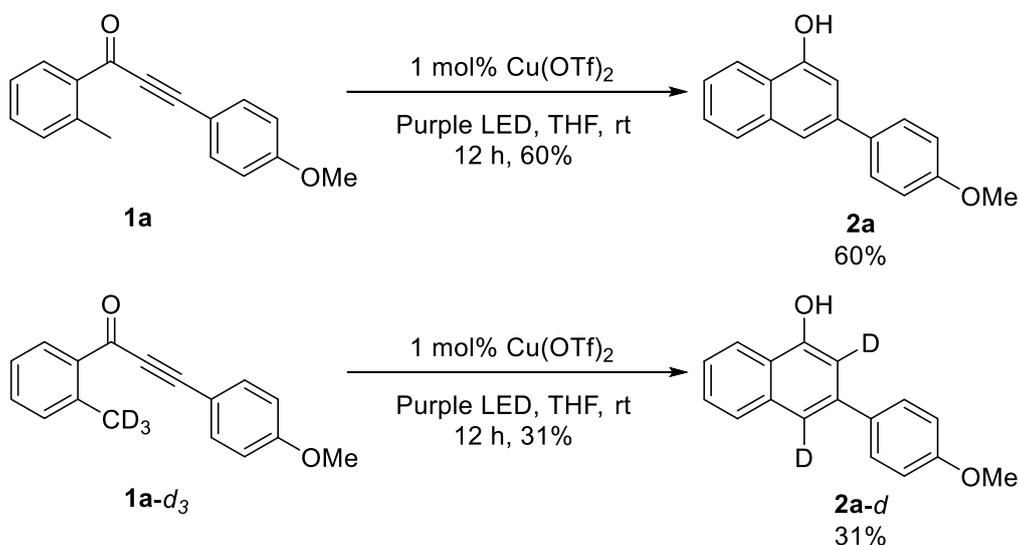
## Procedure of the deuterium labeling experiments



**1a-d<sub>3</sub>** (51 mg, 0.2 mmol), Cu(OTf)<sub>2</sub> (1 mg, 0.002 mmol), and dry THF (10 mL) were added subsequently to a dry 25 mL of Schlenk tube. The mixture was irradiated by purple LED at rt under argon for 24 h. The solvent was removed and the residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 50/1→20/1) to afford **1a-d<sub>3</sub>** as a solid (10 mg, 20%) and **2a-d** as a solid (33 mg, 65%).

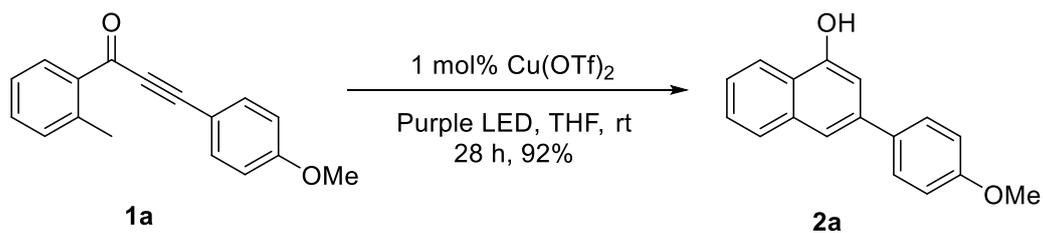
## Procedure of the KIE experiments

The KIE was determined by parallel reactions of **1a** and **1a-d<sub>3</sub>**.



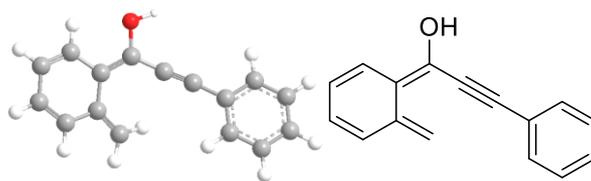
**1a** (50 mg, 0.2 mmol), Cu(OTf)<sub>2</sub> (0.9 mg, 0.002 mmol), and dry THF (10 mL) were added subsequently to a dry 25 mL of Schlenk tube. **1a-d<sub>3</sub>** (50 mg, 0.2 mmol), Cu(OTf)<sub>2</sub> (0.8 mg, 0.002 mmol), and dry THF (10 mL) were added subsequently to a dry 25 mL of Schlenk tube. The two reactions were irradiated by purple LED at rt under argon for 12 h. The crude reaction mixture was plugged through a short silica gel column and then evaporated. The yields were determined by crude <sup>1</sup>H NMR analysis using 1,3,5-trimethoxybenzene (16.8 mg, 0.1 mmol) as internal standard.

### Gram scale synthesis of 3-(4-methoxyphenyl)naphthalen-1-ol (**2a**)

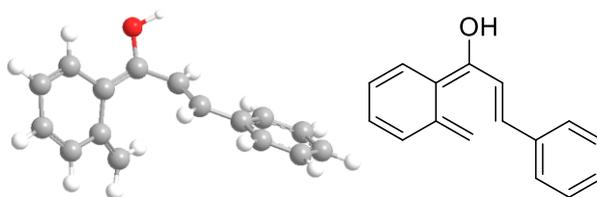


**1a** (1.001 g, 4 mmol), Cu(OTf)<sub>2</sub> (14 mg, 0.04 mmol), and dry THF (200 mL) were added subsequently to a dry 500 mL of Schlenk tube. The mixture was irradiated by purple LED at rt under argon. The photoreaction was completed after 28 h as monitored by TLC (eluent: petroleum ether/ethyl acetate = 10/1). The solvent was removed and the residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 20/1→10/1) to afford **2a**<sup>[8]</sup> as a solid (920 mg, 92%).

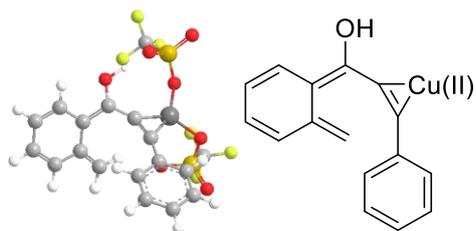
**DFT calculated atom coordinates.**



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Atom	X	Y	Z
C(1)	-0.097	0.876	0.048
C(2)	-1.281	0.614	-0.014
C(3)	1.251	1.261	0.068
O(4)	1.486	2.616	-0.015
H(5)	0.639	3.058	-0.133
C(6)	-2.636	0.207	-0.056
C(7)	-2.951	-1.147	-0.279
C(8)	-3.681	1.13	0.132
C(9)	-4.275	-1.561	-0.305
H(10)	-2.146	-1.855	-0.435
C(11)	-5.002	0.705	0.1
H(12)	-3.442	2.172	0.305
C(13)	-5.305	-0.639	-0.117
H(14)	-4.507	-2.605	-0.477
H(15)	-5.8	1.423	0.247
H(16)	-6.337	-0.966	-0.141
C(17)	2.341	0.418	0.115
C(18)	3.654	1	-0.057
C(19)	2.253	-1.052	0.264
C(20)	4.75	0.233	-0.266
H(21)	3.73	2.078	-0.062
C(22)	3.456	-1.803	-0.077
C(23)	4.641	-1.203	-0.316
H(24)	5.717	0.698	-0.422
H(25)	3.376	-2.885	-0.076
H(26)	5.522	-1.796	-0.53
C(27)	1.186	-1.735	0.747
H(28)	0.296	-1.256	1.122
H(29)	1.225	-2.817	0.801



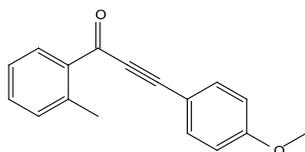
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Atom	X	Y	Z
C(1)	-0.925	0.226	-0.35
H(2)	-0.386	-0.484	-0.971
C(3)	-0.211	1.198	0.242
H(4)	-0.712	1.966	0.828
C(5)	-2.361	-0.002	-0.233
C(6)	-2.966	-0.954	-1.07
C(7)	-3.176	0.685	0.684
C(8)	-4.332	-1.2	-1.008
H(9)	-2.349	-1.5	-1.776
C(10)	-4.54	0.44	0.745
H(11)	-2.735	1.405	1.363
C(12)	-5.126	-0.502	-0.102
H(13)	-4.777	-1.938	-1.664
H(14)	-5.15	0.978	1.461
H(15)	-6.191	-0.694	-0.048
C(16)	1.225	1.394	0.05
O(17)	1.57	2.69	-0.264
H(18)	0.796	3.131	-0.631
C(19)	2.233	0.47	0.113
C(20)	3.524	0.8	-0.465
C(21)	2.1	-0.877	0.727
C(22)	4.444	-0.157	-0.722
H(23)	3.695	1.825	-0.761
C(24)	3.055	-1.883	0.268
C(25)	4.175	-1.541	-0.402
H(26)	5.377	0.102	-1.208
H(27)	2.873	-2.913	0.557
H(28)	4.895	-2.299	-0.687
C(29)	1.261	-1.176	1.741
H(30)	1.223	-2.183	2.141
H(31)	0.606	-0.442	2.188



III			
Atom	X	Y	Z
Cu(1)	-0.44	-0.427	-0.771
O(2)	-2.311	0.048	-0.601
O(3)	0.601	-1.847	1.465
S(4)	0.056	-2.935	0.634
C(5)	-1.443	-3.559	1.559
S(6)	-3.038	1.187	-1.26
C(7)	-3.85	1.997	0.213
O(8)	-2.074	2.224	-1.743
O(9)	-4.081	0.818	-2.189
O(10)	-0.594	-2.362	-0.623
O(11)	0.893	-4.095	0.369
F(12)	-1.061	-4.087	2.725
F(13)	-2.071	-4.491	0.846
F(14)	-2.28	-2.547	1.795
F(15)	-4.665	1.146	0.824
F(16)	-4.539	3.066	-0.181
F(17)	-2.897	2.389	1.072
C(18)	0.8	1.038	-0.622
C(19)	1.421	-0.011	-0.968
C(20)	0.777	2.358	-0.138
O(21)	-0.203	3.161	-0.394
H(22)	-0.954	2.747	-0.973
C(23)	2.545	-0.802	-1.321
C(24)	3.834	-0.256	-1.142
C(25)	2.401	-2.111	-1.814
C(26)	4.951	-1.013	-1.452
H(27)	3.936	0.753	-0.766
C(28)	3.528	-2.861	-2.11
H(29)	1.414	-2.533	-1.93
C(30)	4.799	-2.317	-1.931
H(31)	5.941	-0.596	-1.317
H(32)	3.414	-3.877	-2.466
H(33)	5.676	-2.91	-2.16
C(34)	1.878	2.896	0.632

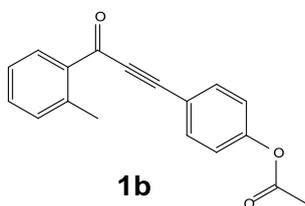
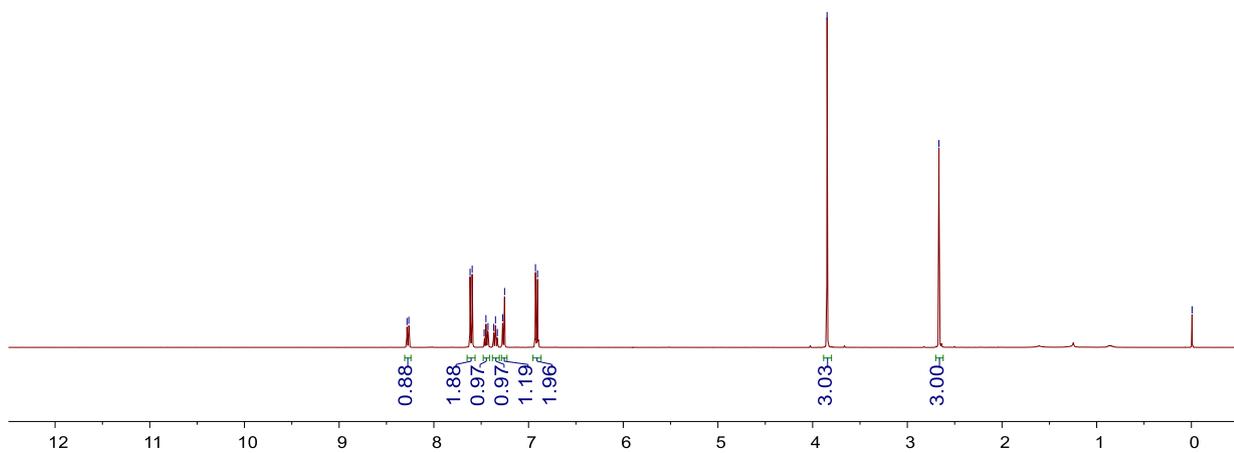
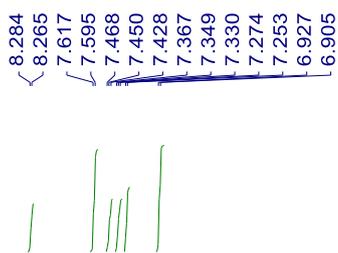
C(35)	2.086	4.284	0.535
C(36)	2.769	2.098	1.453
C(37)	3.183	4.893	1.116
H(38)	1.387	4.866	-0.05
C(39)	3.909	2.771	2
C(40)	4.112	4.12	1.837
H(41)	3.334	5.959	0.999
H(42)	4.601	2.185	2.591
H(43)	4.981	4.592	2.278
C(44)	2.554	0.778	1.838

# NMR Spectra



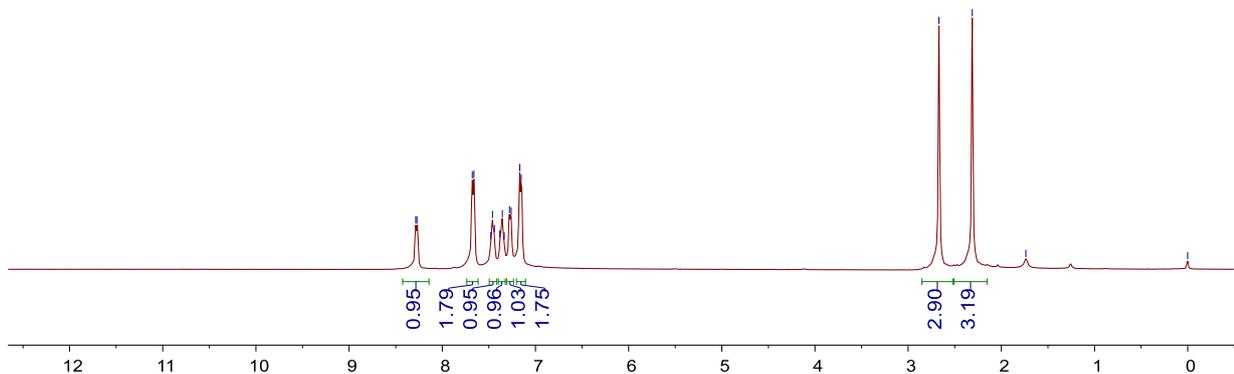
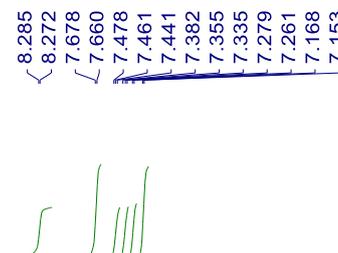
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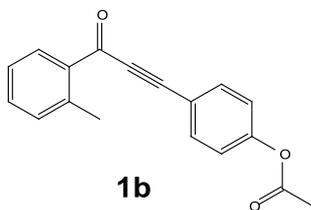
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**1b**

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134.183

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132.116

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~ 90.839

~ 88.380

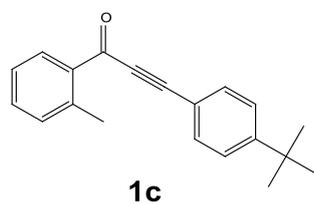
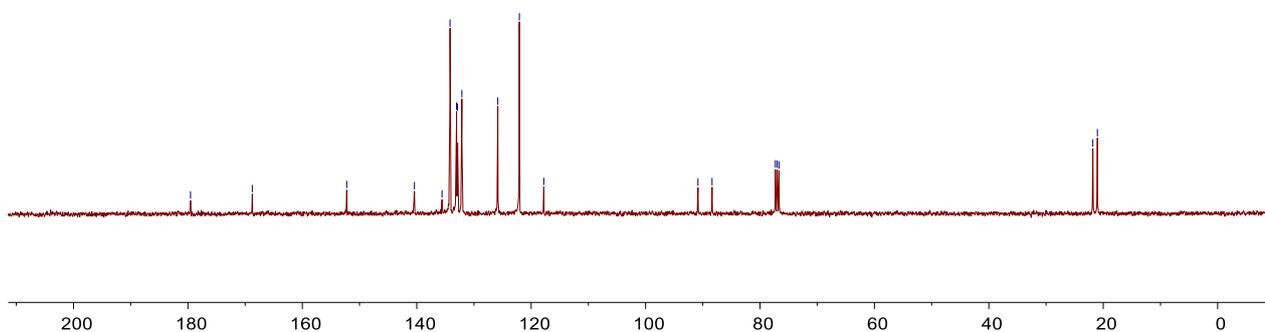
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77.000

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7.343

7.286

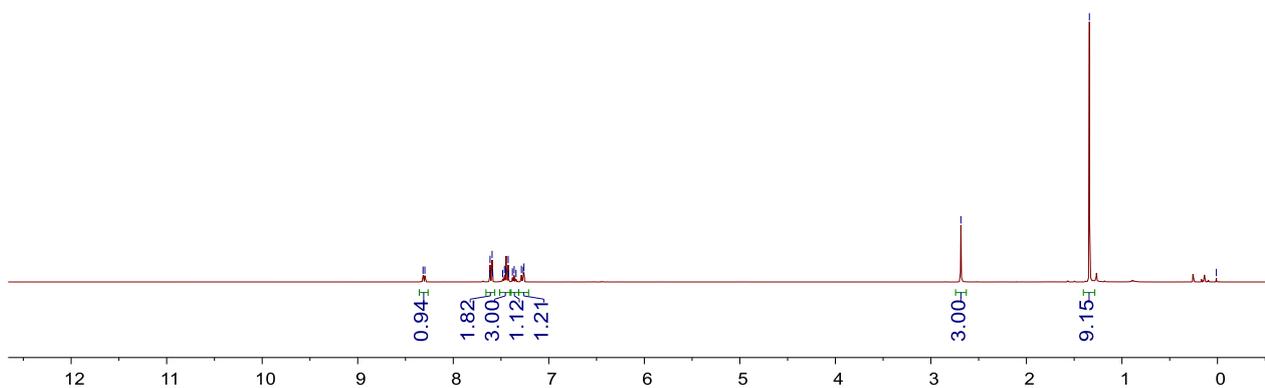
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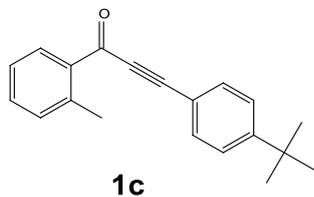
7.260

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— 1.341

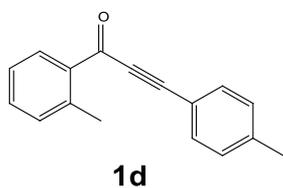
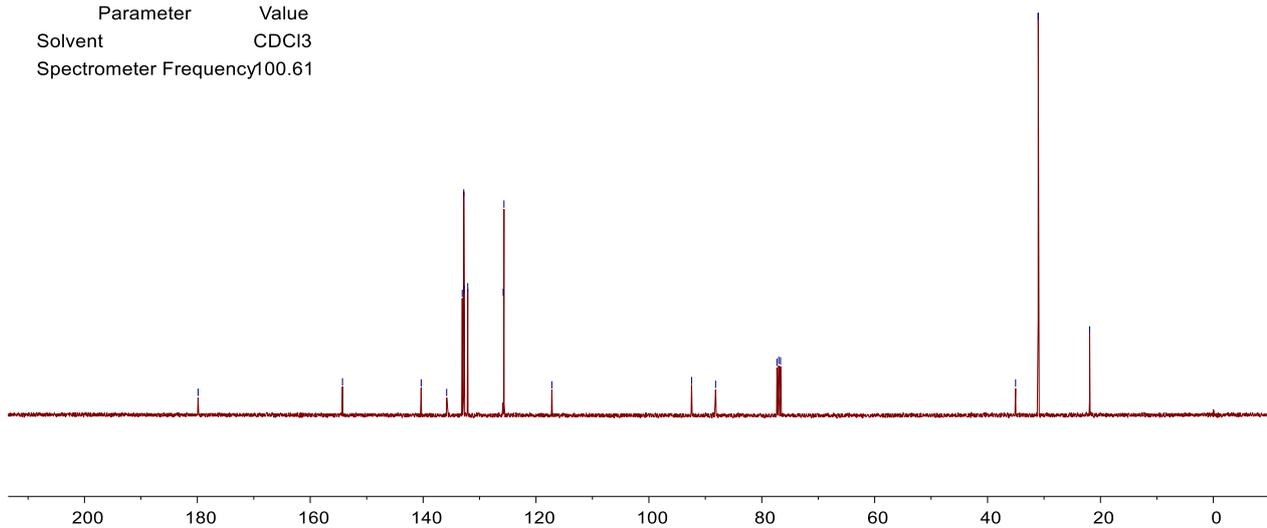
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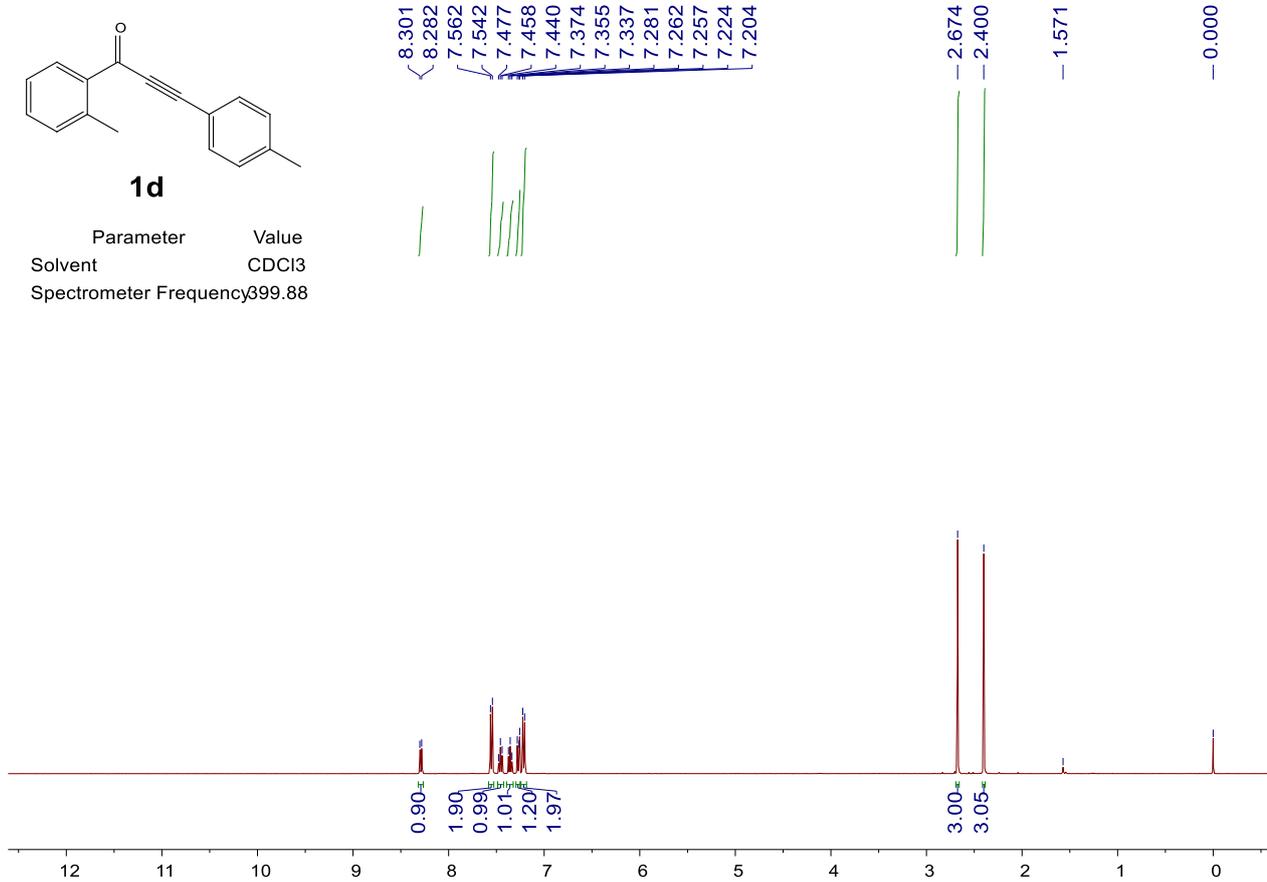
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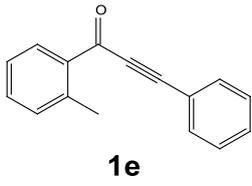
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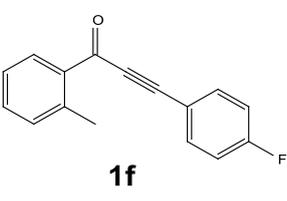
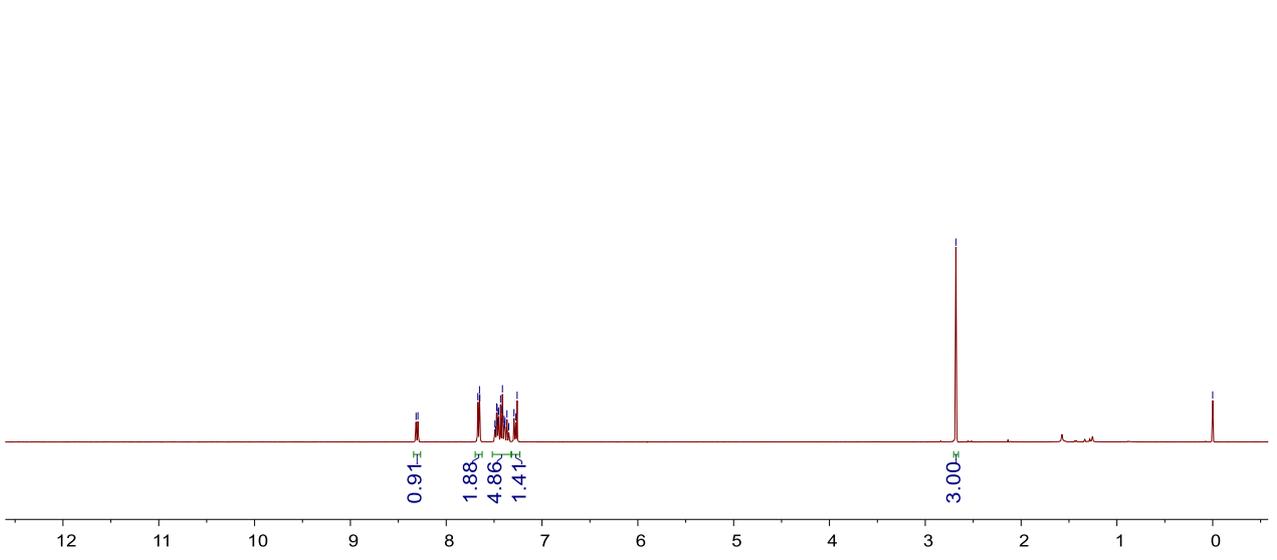
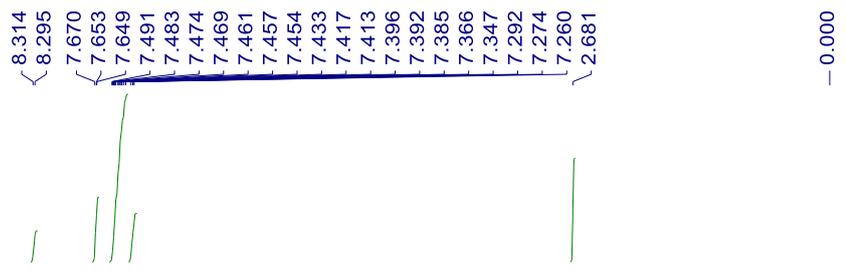
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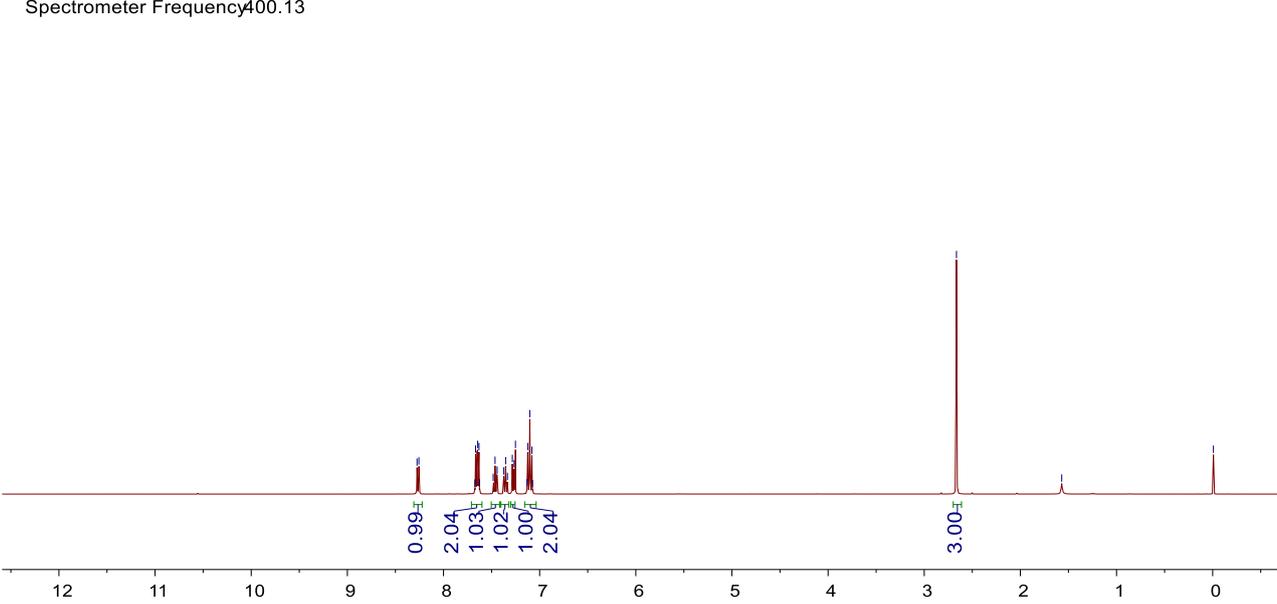
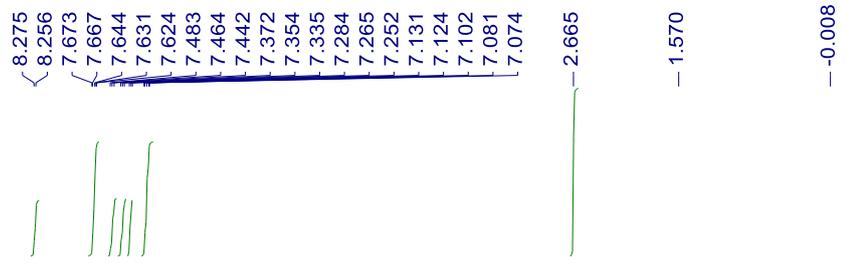




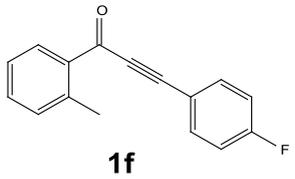
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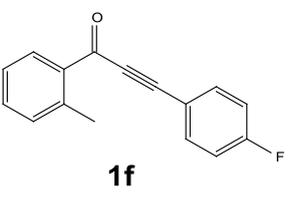
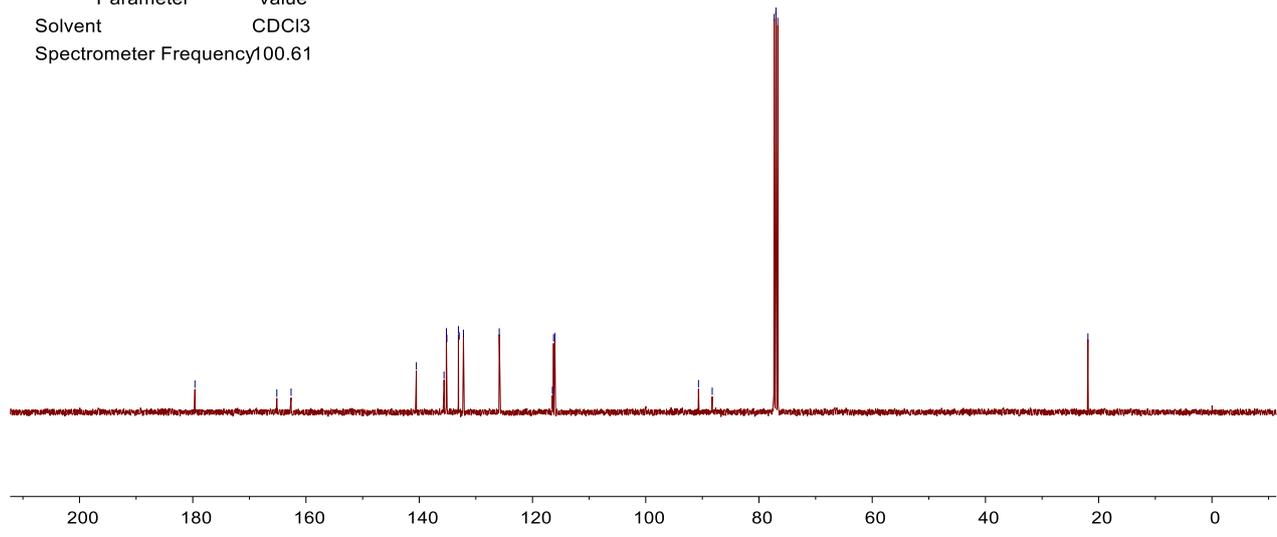
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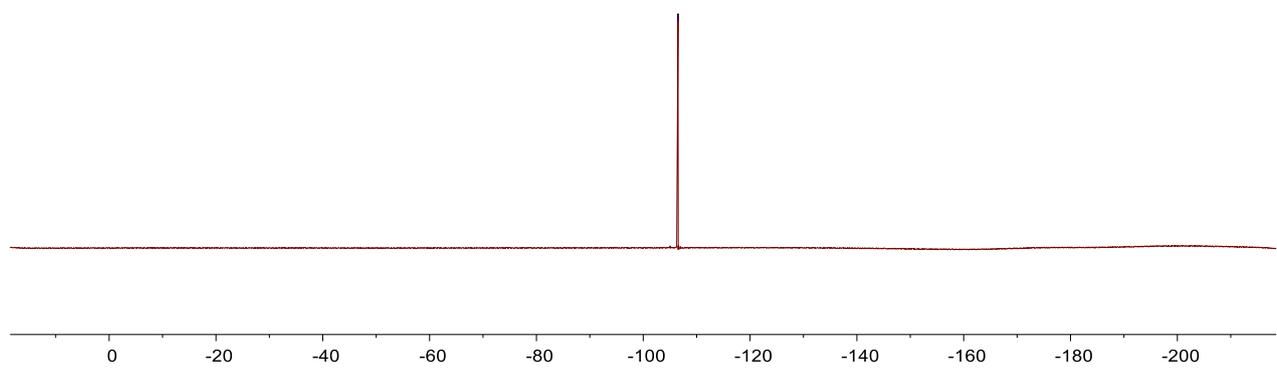


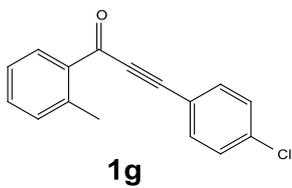
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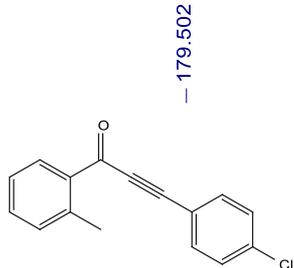
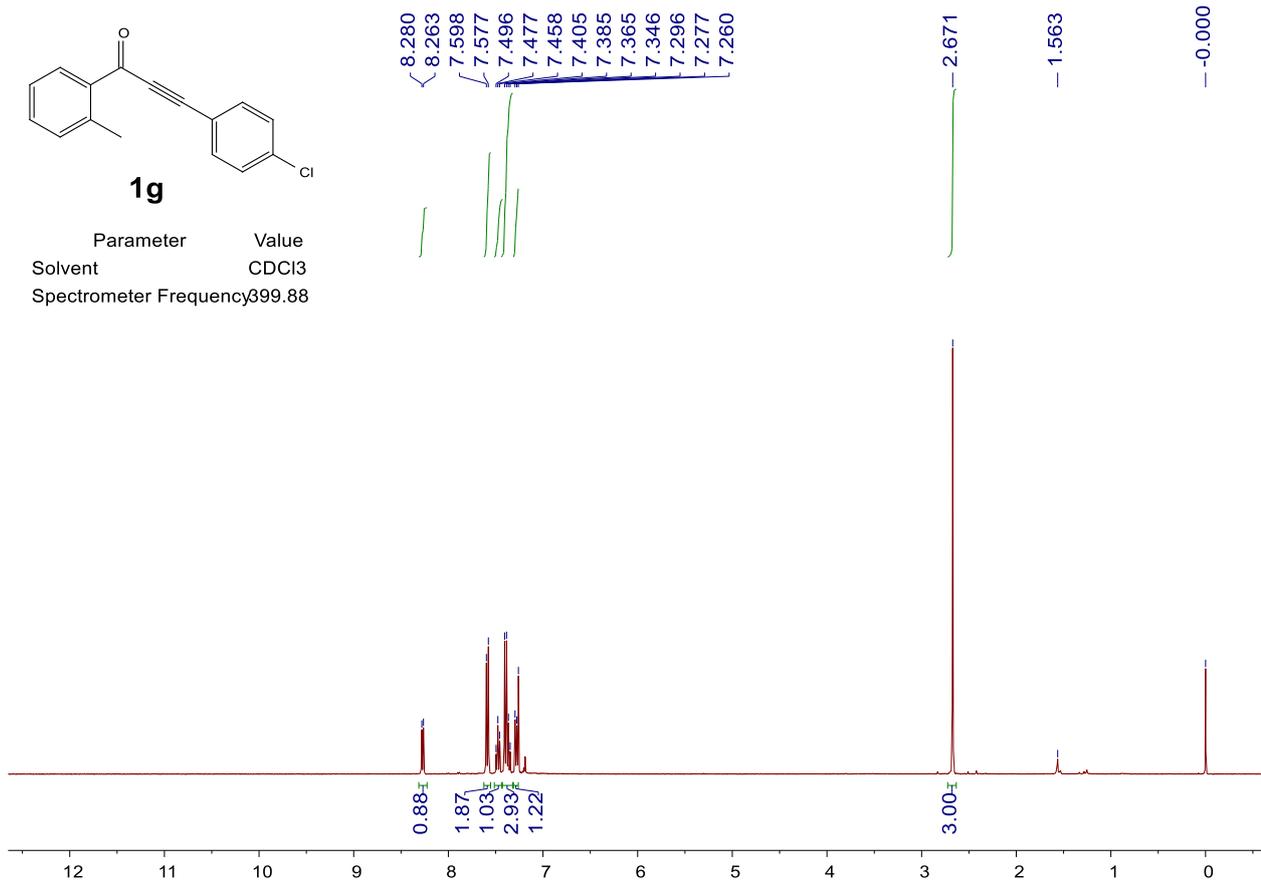
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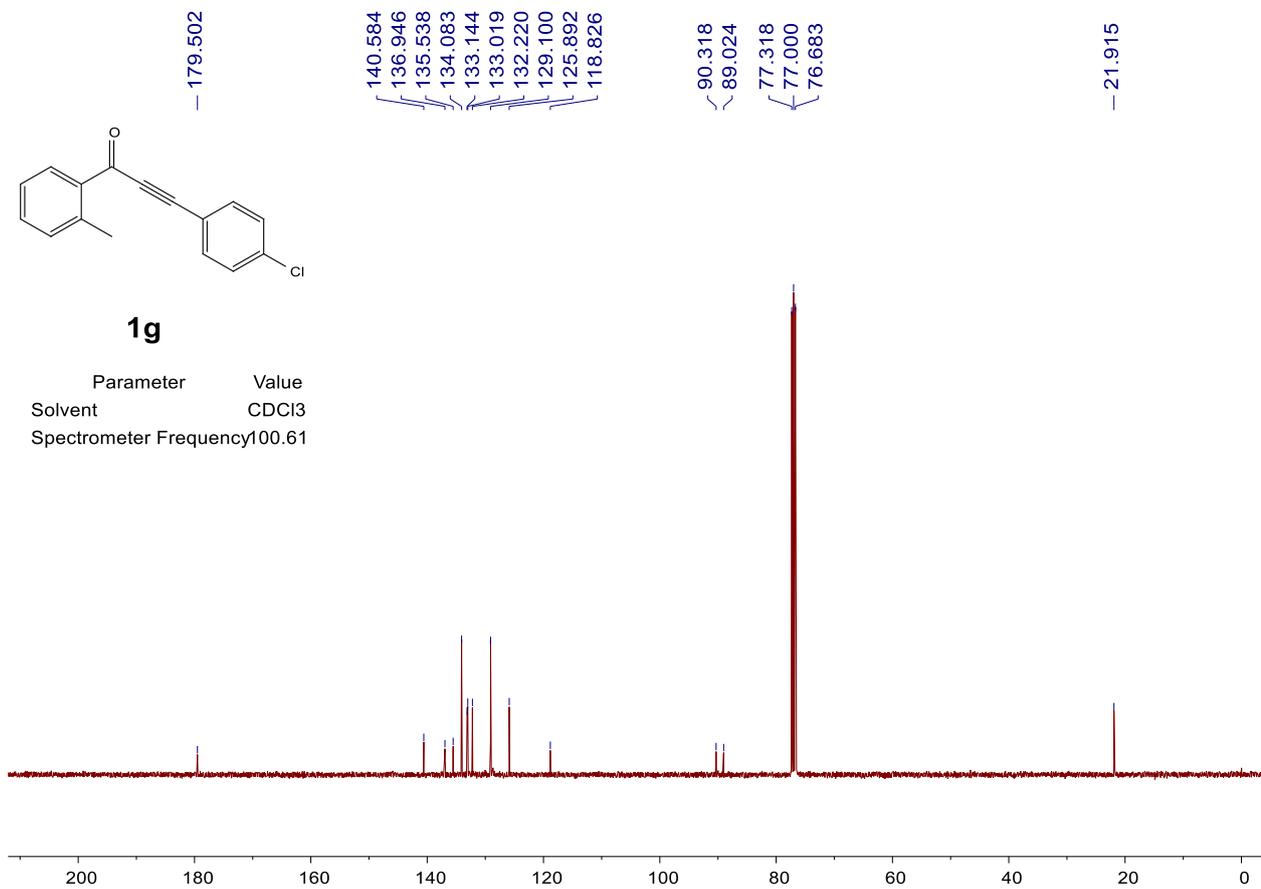


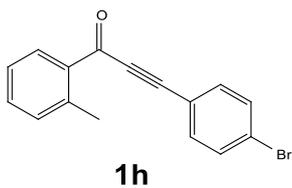


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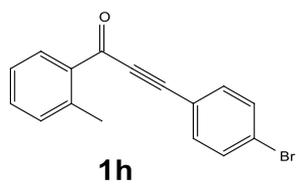
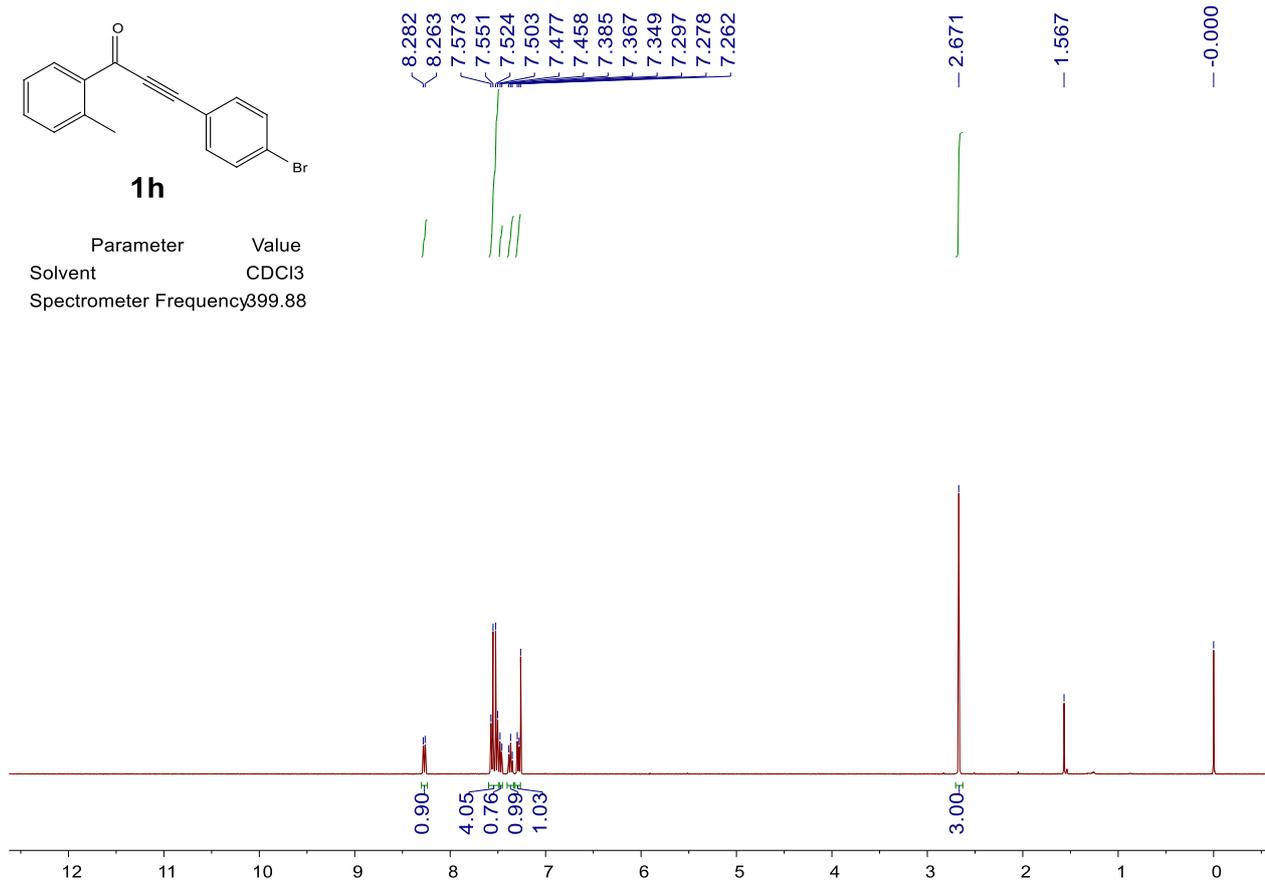


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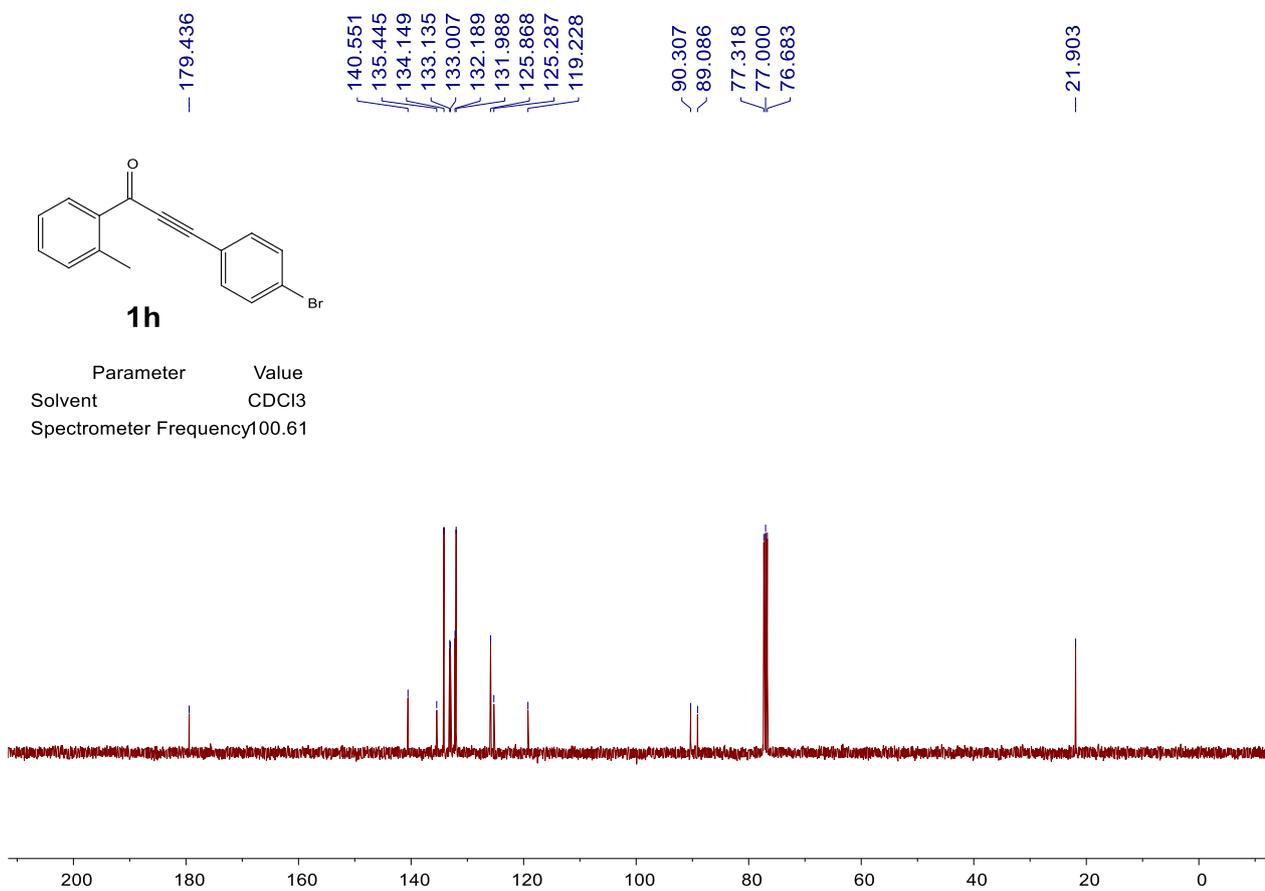


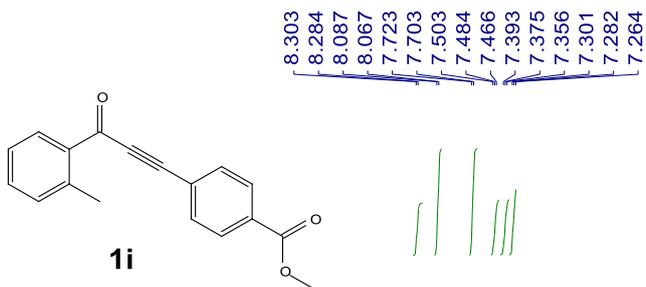


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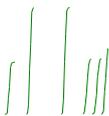


Parameter Value  
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 Spectrometer Frequency 100.61



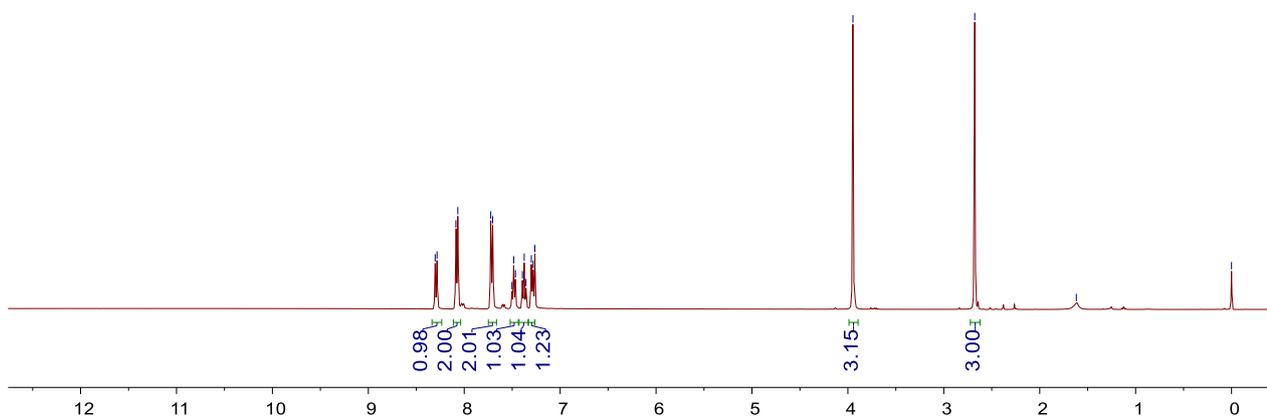


8.303  
8.284  
8.087  
8.067  
7.723  
7.703  
7.503  
7.484  
7.466  
7.393  
7.375  
7.356  
7.301  
7.282  
7.264



3.948  
2.677  
1.618  
-0.000

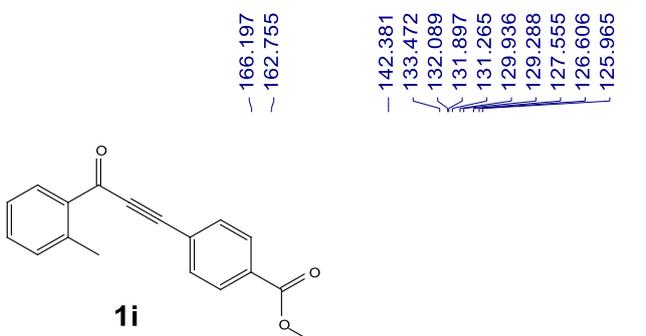
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Spectrometer Frequency 400.17



0.98  
2.00  
2.01  
1.03  
1.04  
1.23

3.15  
3.00

12 11 10 9 8 7 6 5 4 3 2 1 0

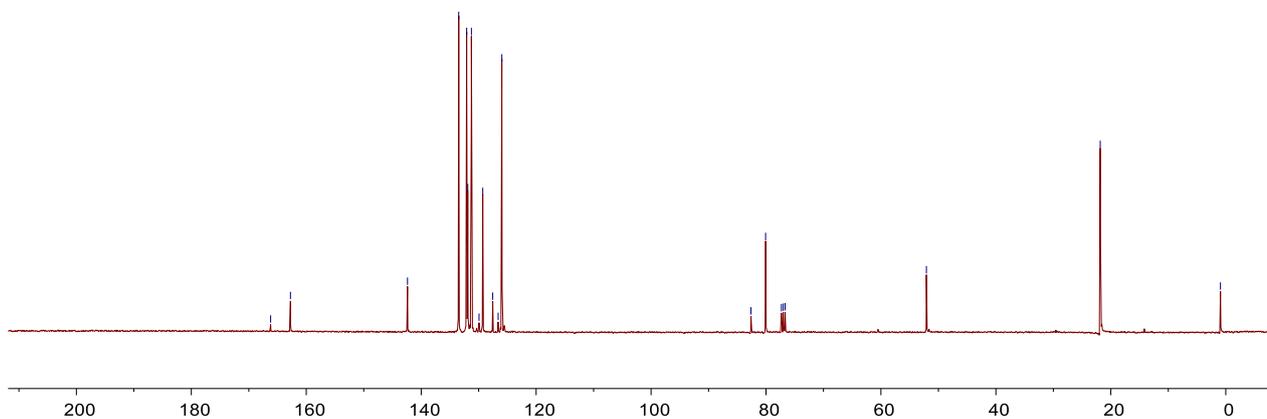


166.197  
162.755  
142.381  
133.472  
132.089  
131.897  
131.265  
129.936  
129.288  
127.555  
126.606  
125.965

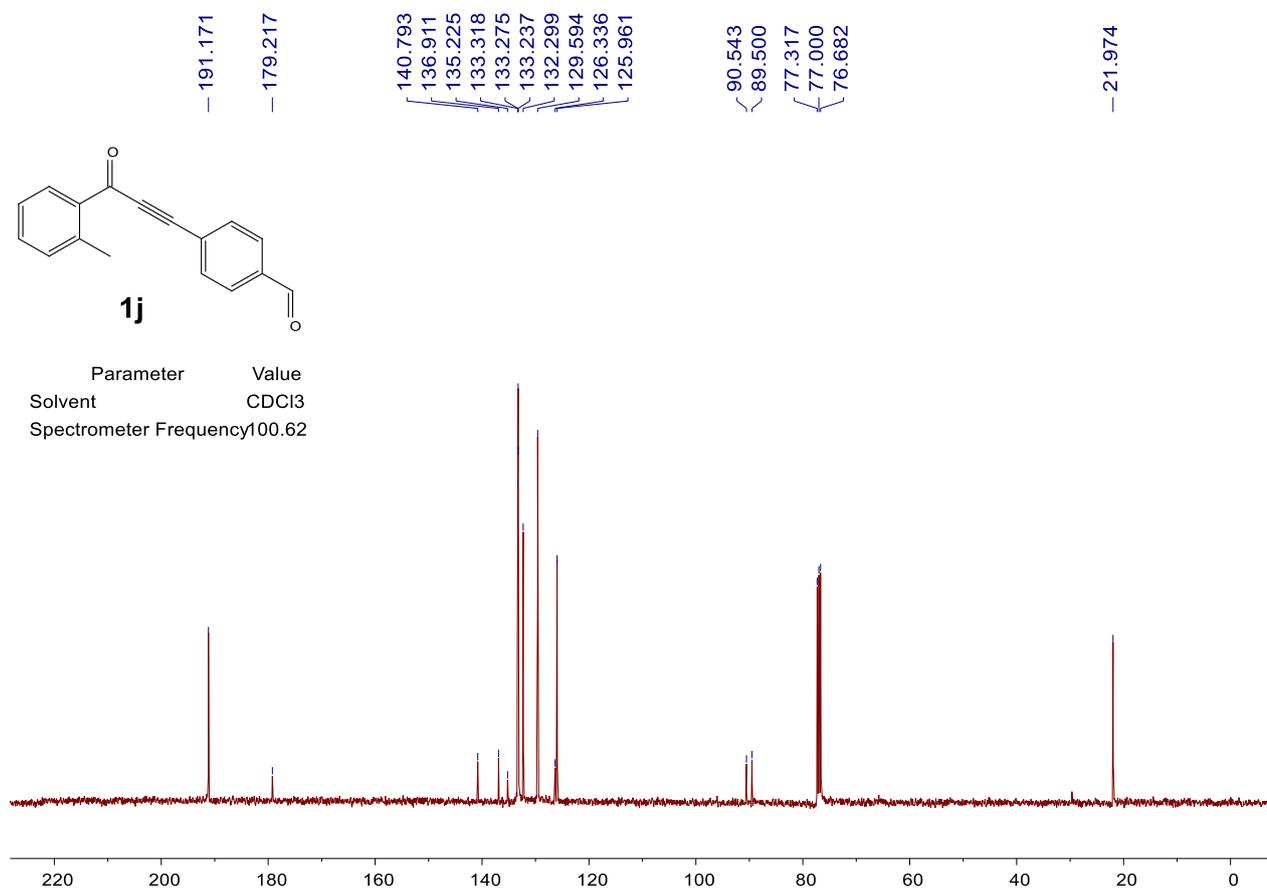
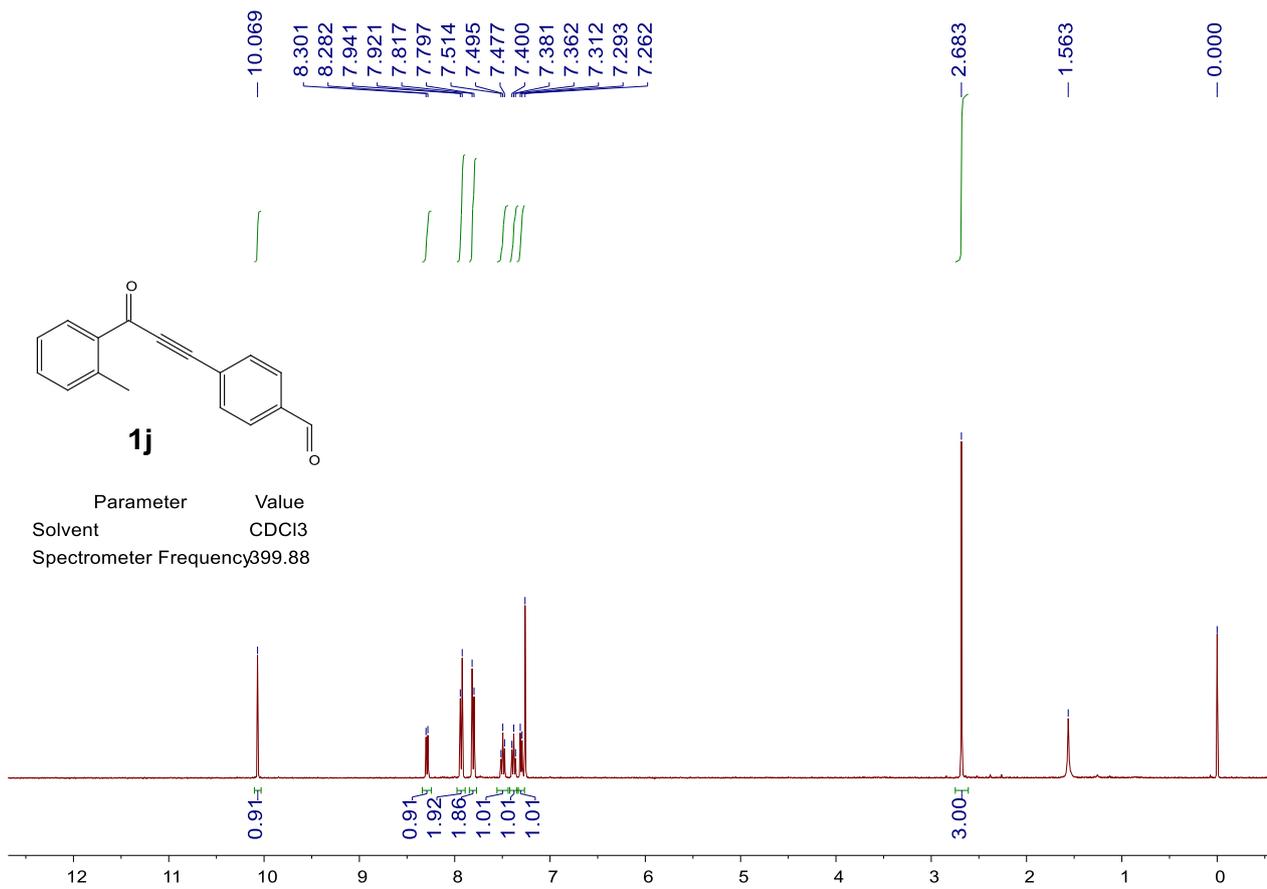
82.620  
80.073  
77.319  
77.000  
76.682

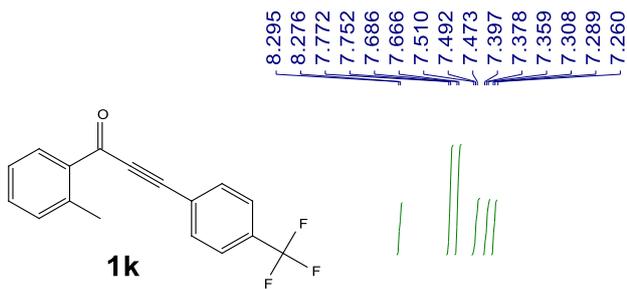
52.093  
21.840  
0.920

Parameter Value  
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Spectrometer Frequency 100.62



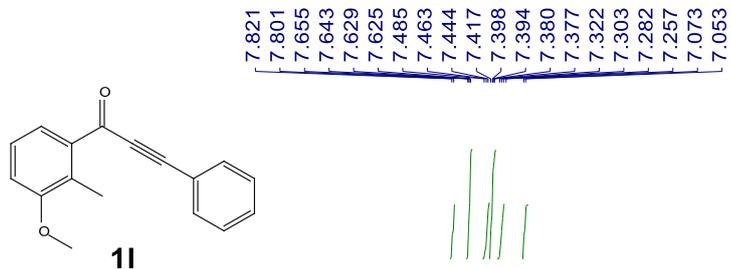
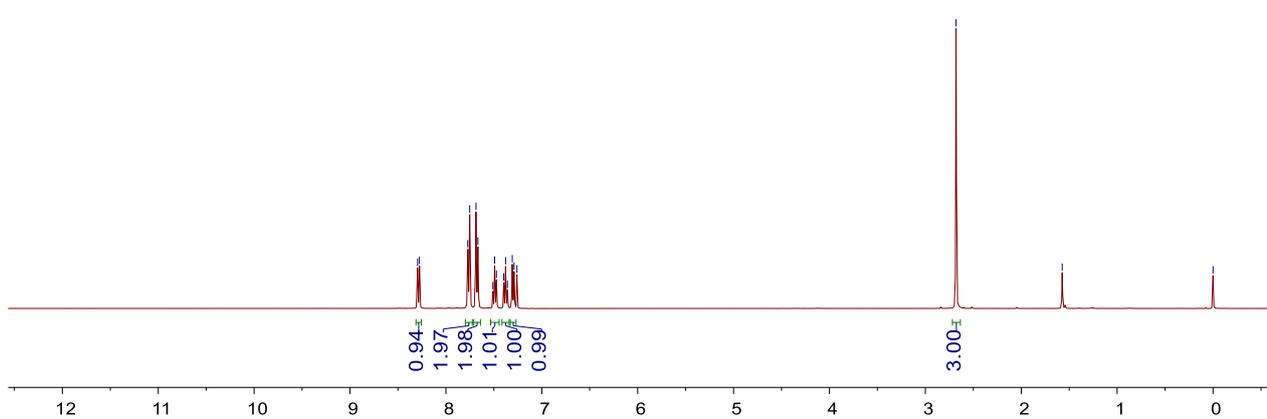
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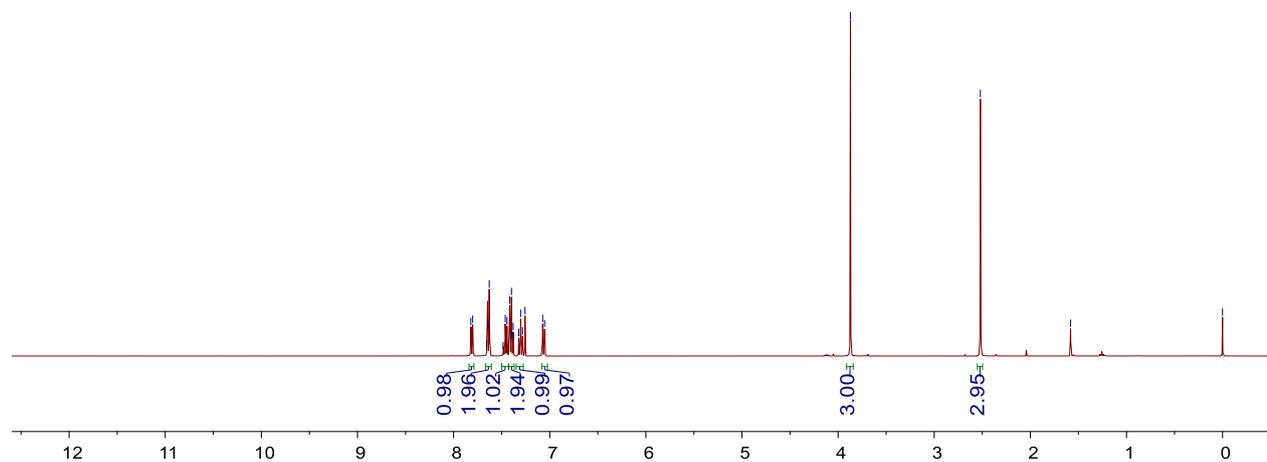
8.295  
8.276  
7.772  
7.752  
7.686  
7.666  
7.510  
7.492  
7.473  
7.397  
7.378  
7.359  
7.308  
7.289  
7.260

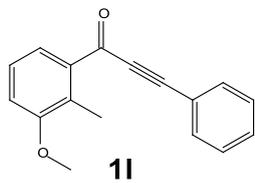
Parameter Value  
Solvent CDCl<sub>3</sub>  
Spectrometer Frequency 399.78



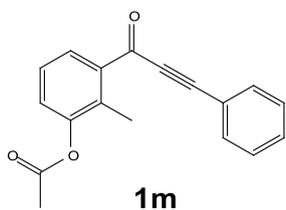
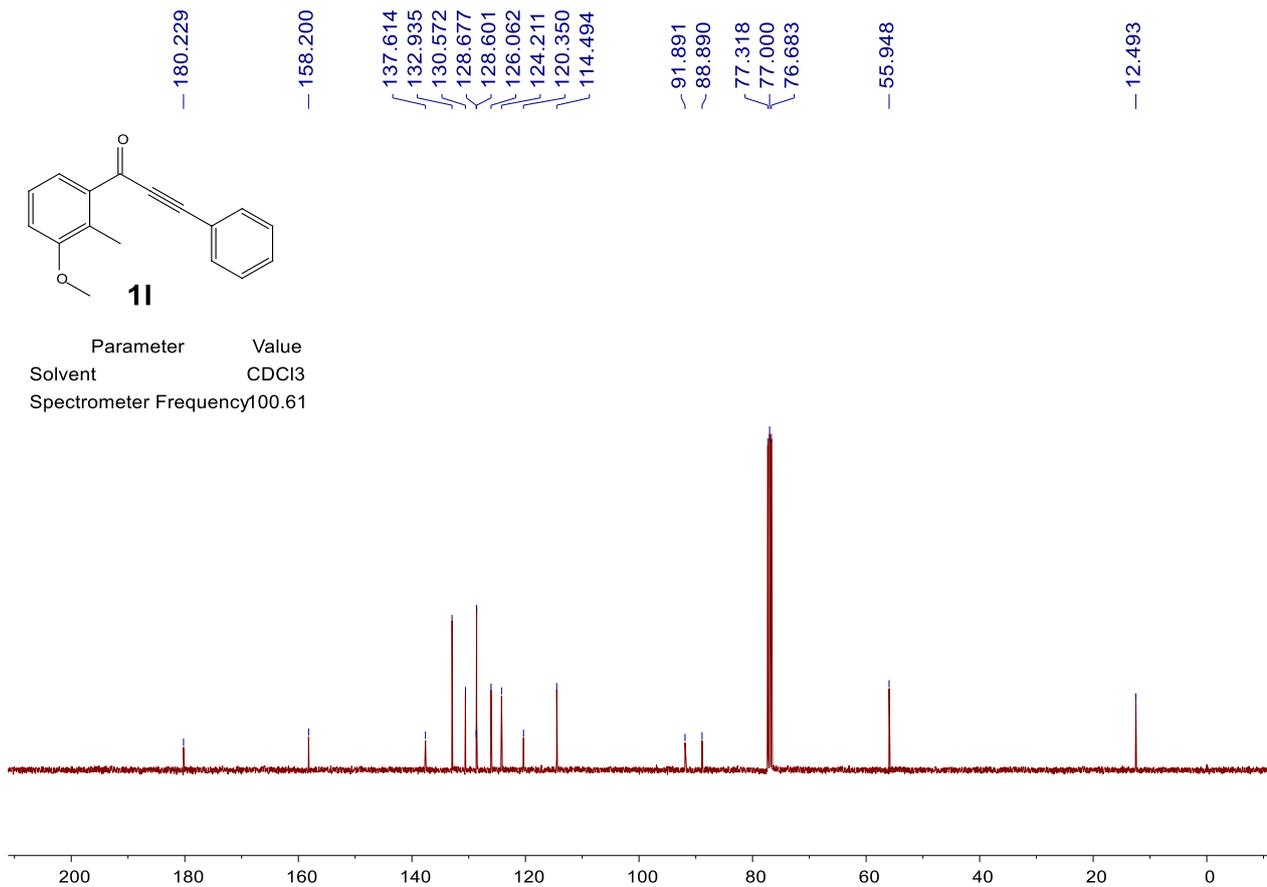
7.821  
7.801  
7.655  
7.643  
7.629  
7.625  
7.485  
7.463  
7.444  
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7.398  
7.394  
7.380  
7.377  
7.322  
7.303  
7.282  
7.257  
7.073  
7.053

Parameter Value  
Solvent CDCl<sub>3</sub>  
Spectrometer Frequency 400.13

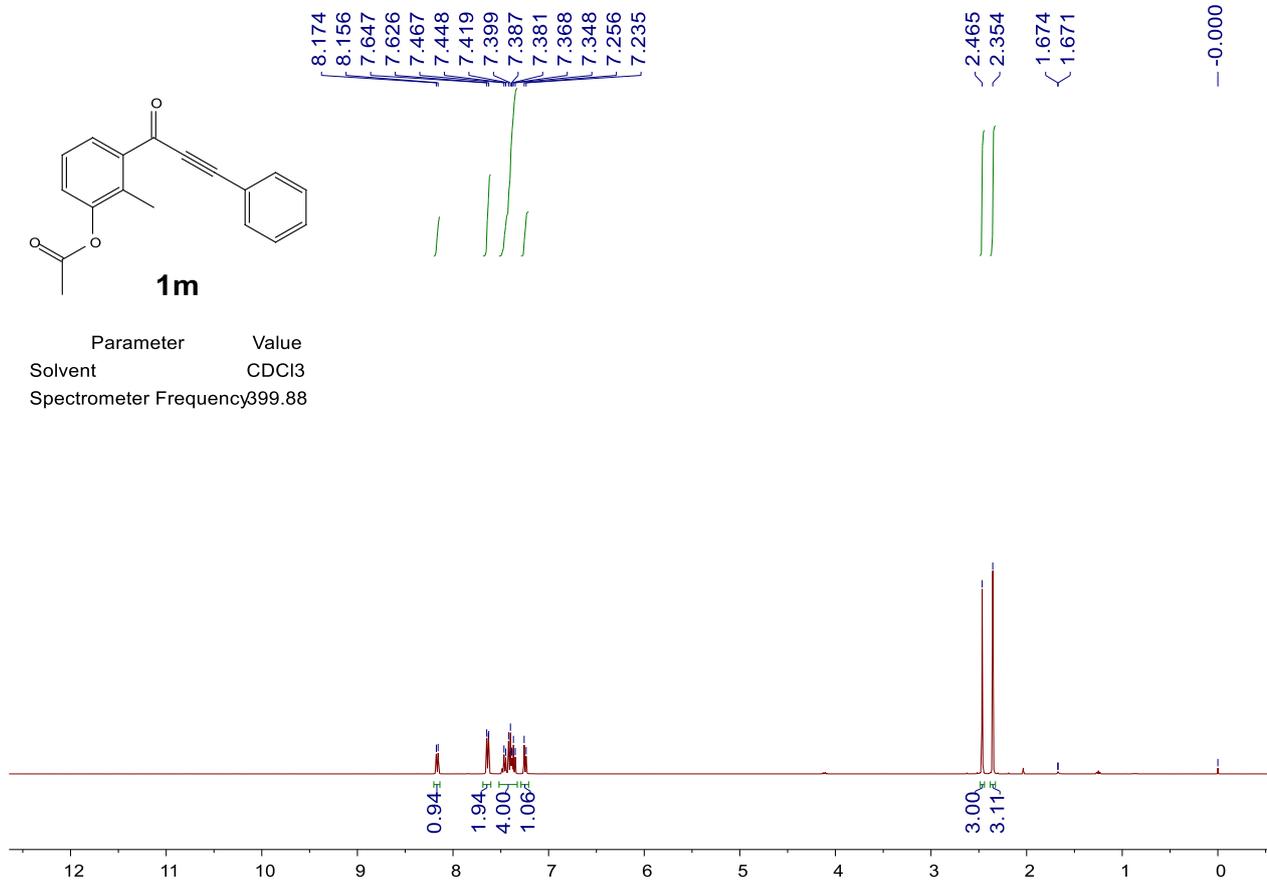


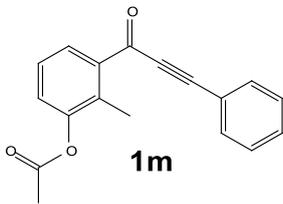


Parameter Value  
 Solvent CDCl<sub>3</sub>  
 Spectrometer Frequency 100.61



Parameter Value  
 Solvent CDCl<sub>3</sub>  
 Spectrometer Frequency 399.88





— 179.185

— 169.112

— 150.064  
 — 137.766  
 — 132.967  
 — 132.236  
 — 130.738  
 — 130.502  
 — 128.649  
 — 126.808  
 — 126.235  
 — 120.107

— 92.391

— 88.438

— 77.317

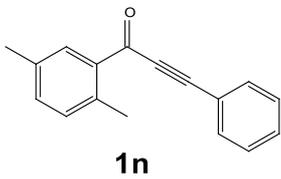
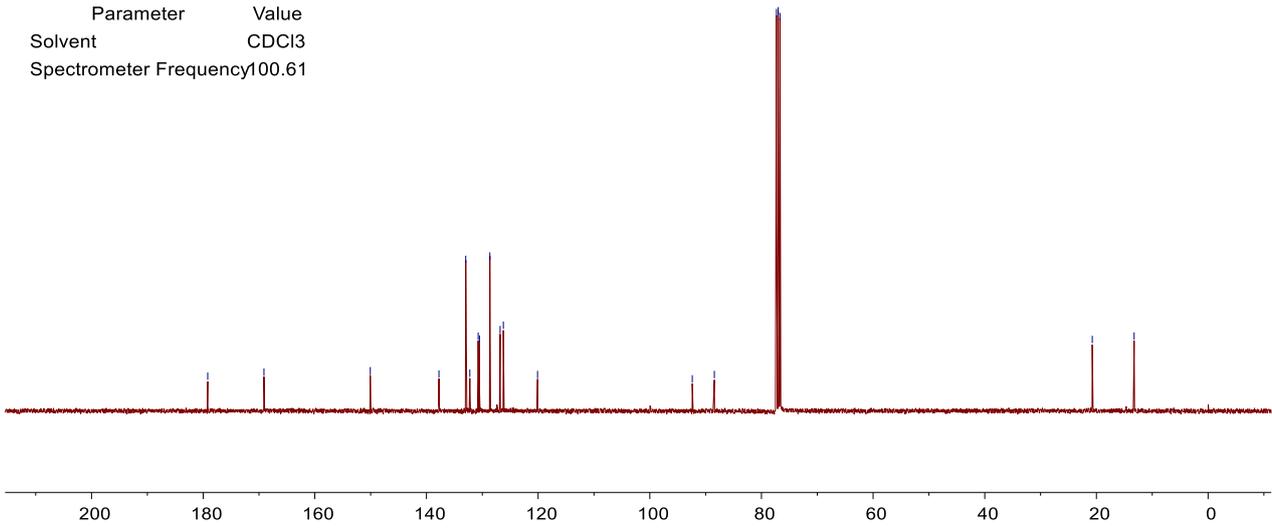
— 77.000

— 76.682

— 20.745

— 13.243

Parameter Value  
 Solvent CDCl<sub>3</sub>  
 Spectrometer Frequency 100.61



8.068  
 7.654  
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 7.458  
 7.441  
 7.419  
 7.402  
 7.385  
 7.272  
 7.252  
 7.160  
 7.141

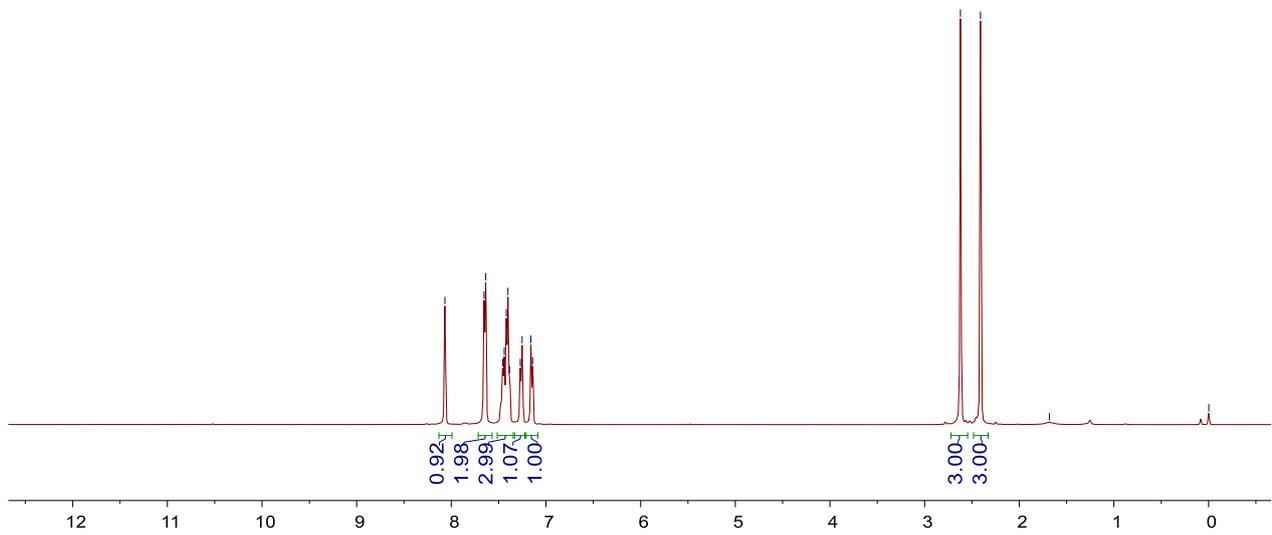
— 2.622

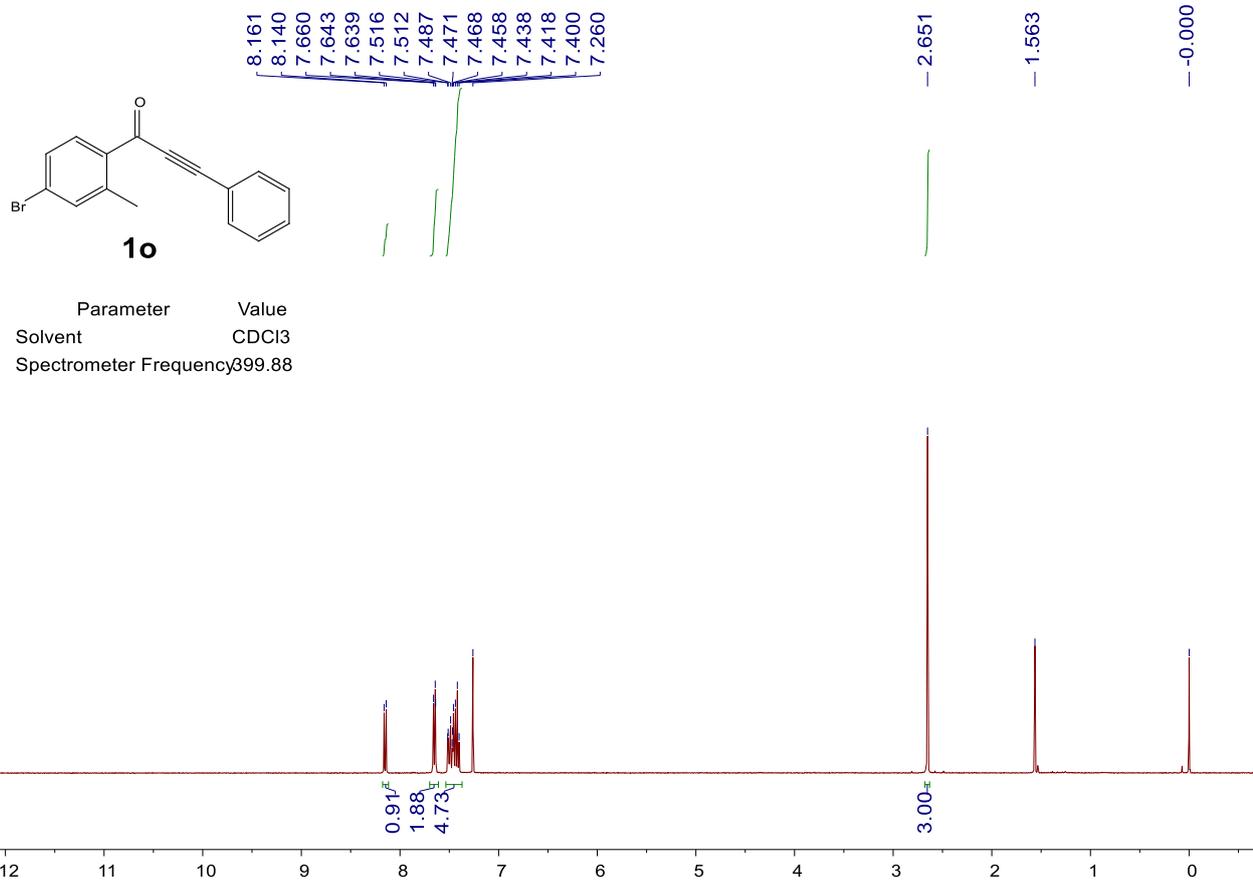
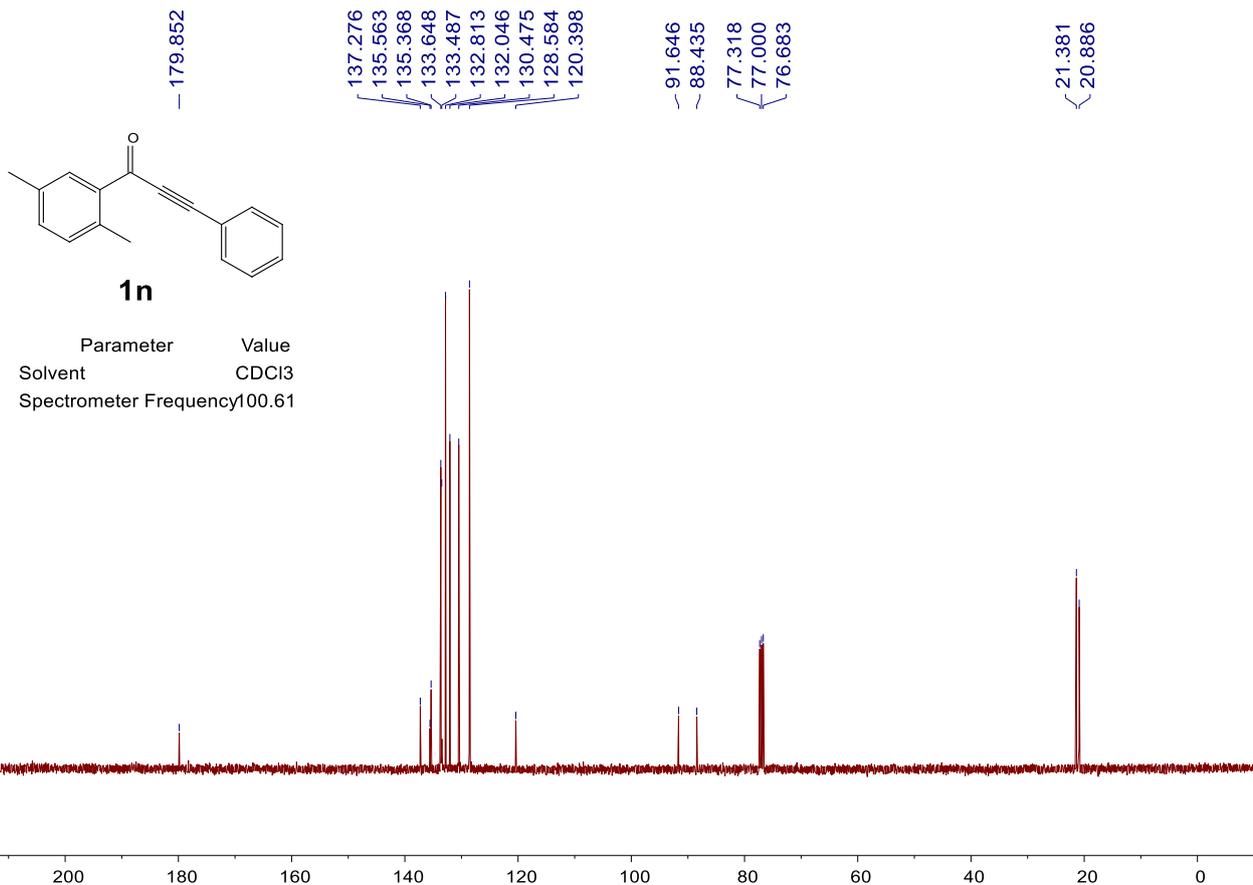
— 2.410

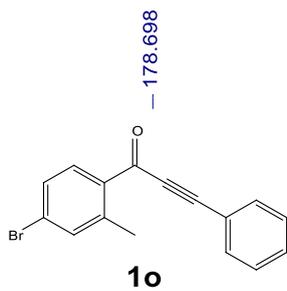
— 1.682

— -0.002

Parameter Value  
 Solvent CDCl<sub>3</sub>  
 Spectrometer Frequency 400.13

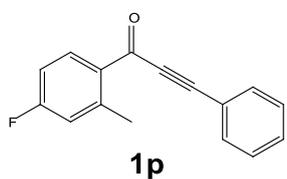
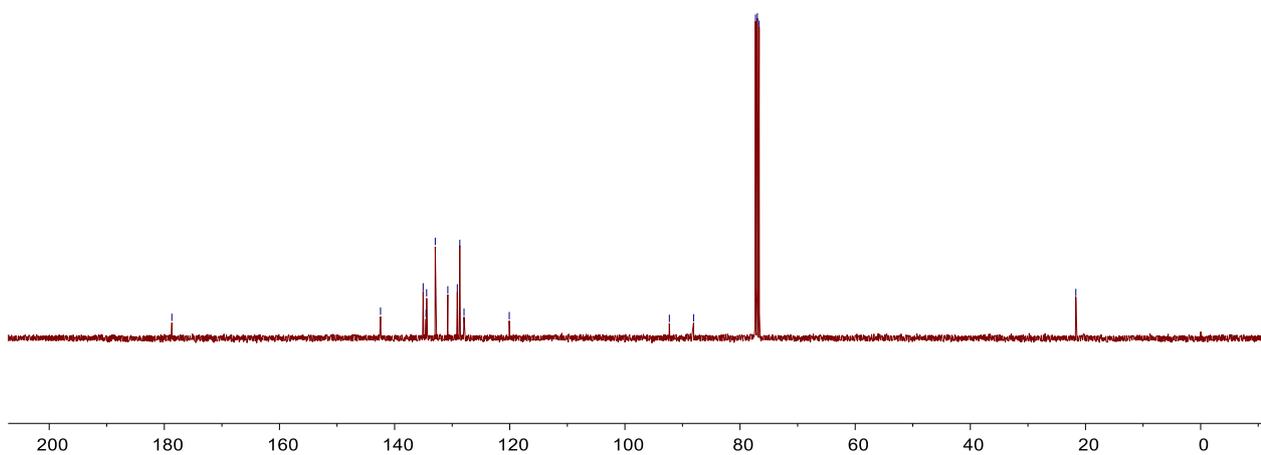






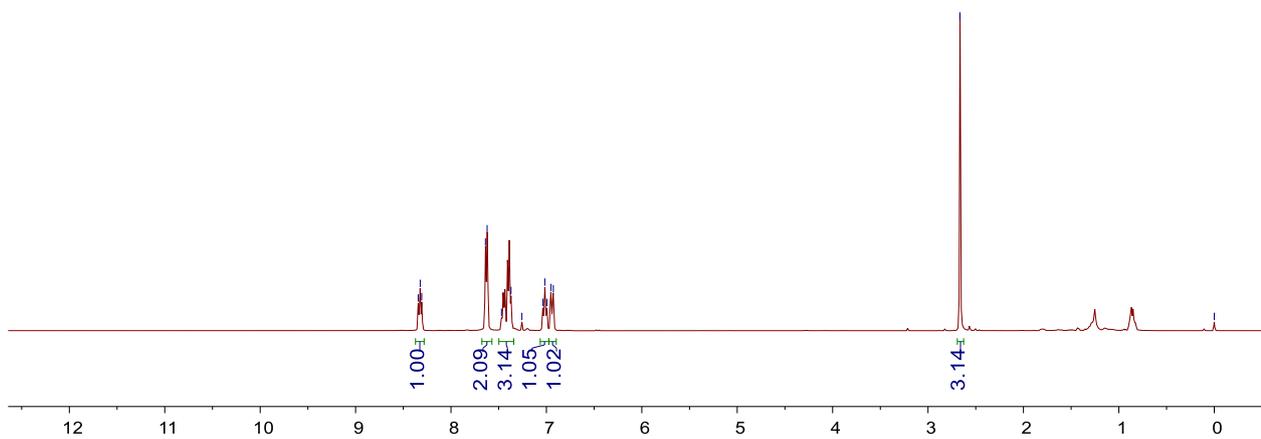
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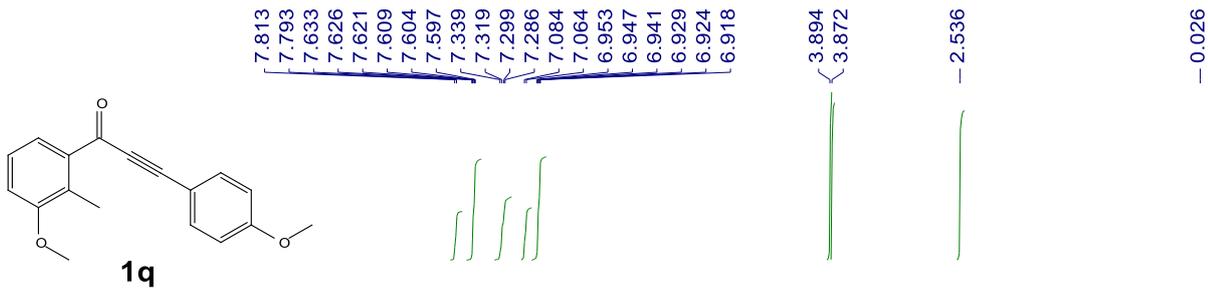
178.698  
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 135.047  
 134.552  
 134.439  
 132.943  
 130.762  
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 128.682  
 127.948  
 120.090  
 92.283  
 88.074  
 77.318  
 77.000  
 76.682  
 21.682



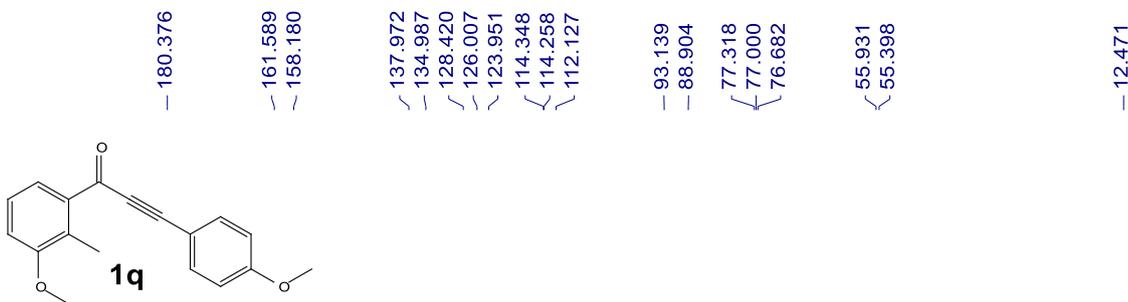
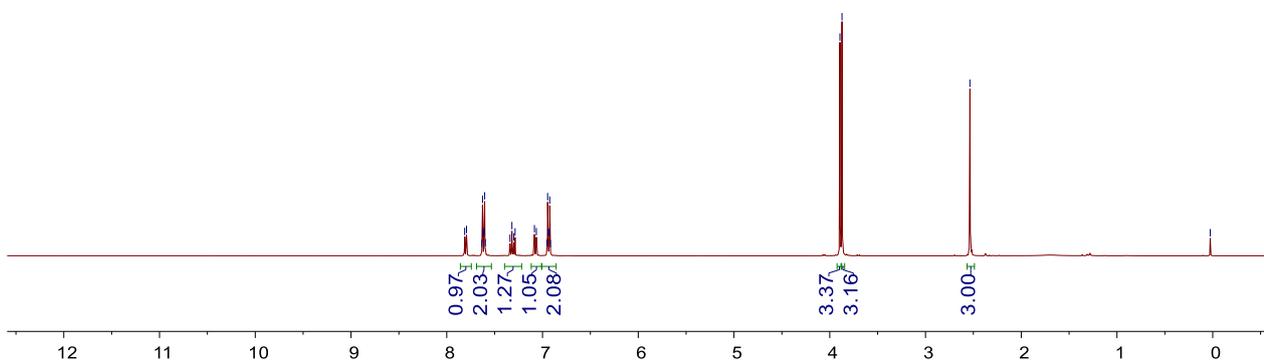
Parameter Value  
 Solvent CDCl<sub>3</sub>  
 Spectrometer Frequency 399.78

8.344  
 8.323  
 8.307  
 7.639  
 7.621  
 7.471  
 7.371  
 7.257  
 7.036  
 7.016  
 6.995  
 6.952  
 6.927  
 2.666  
 0.000

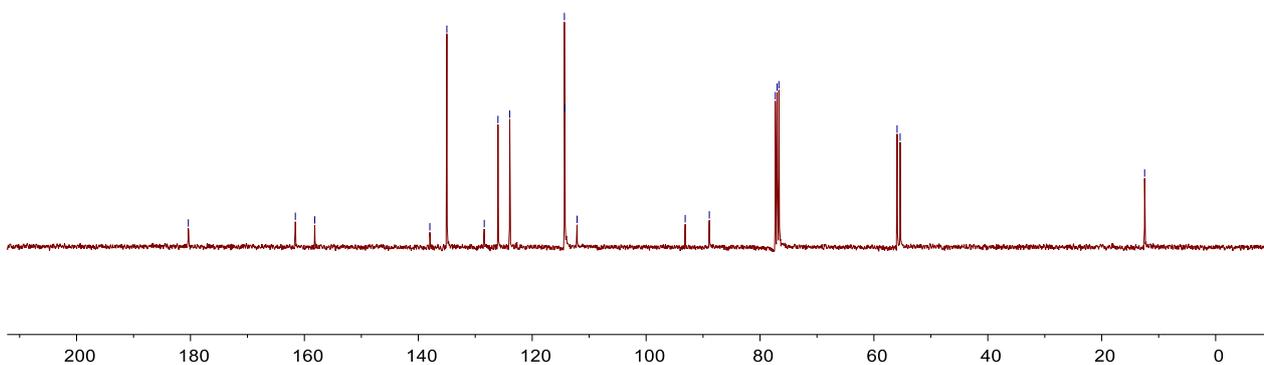


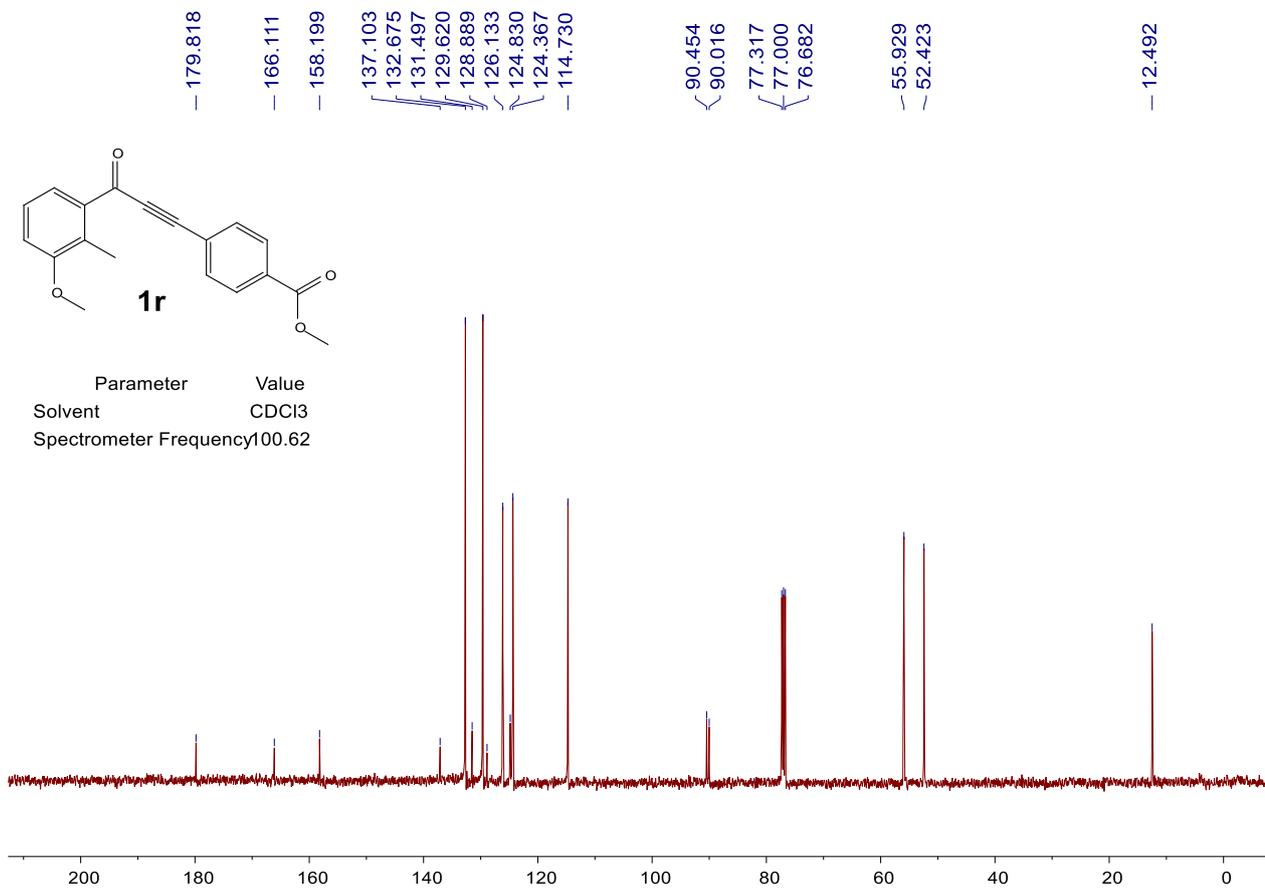
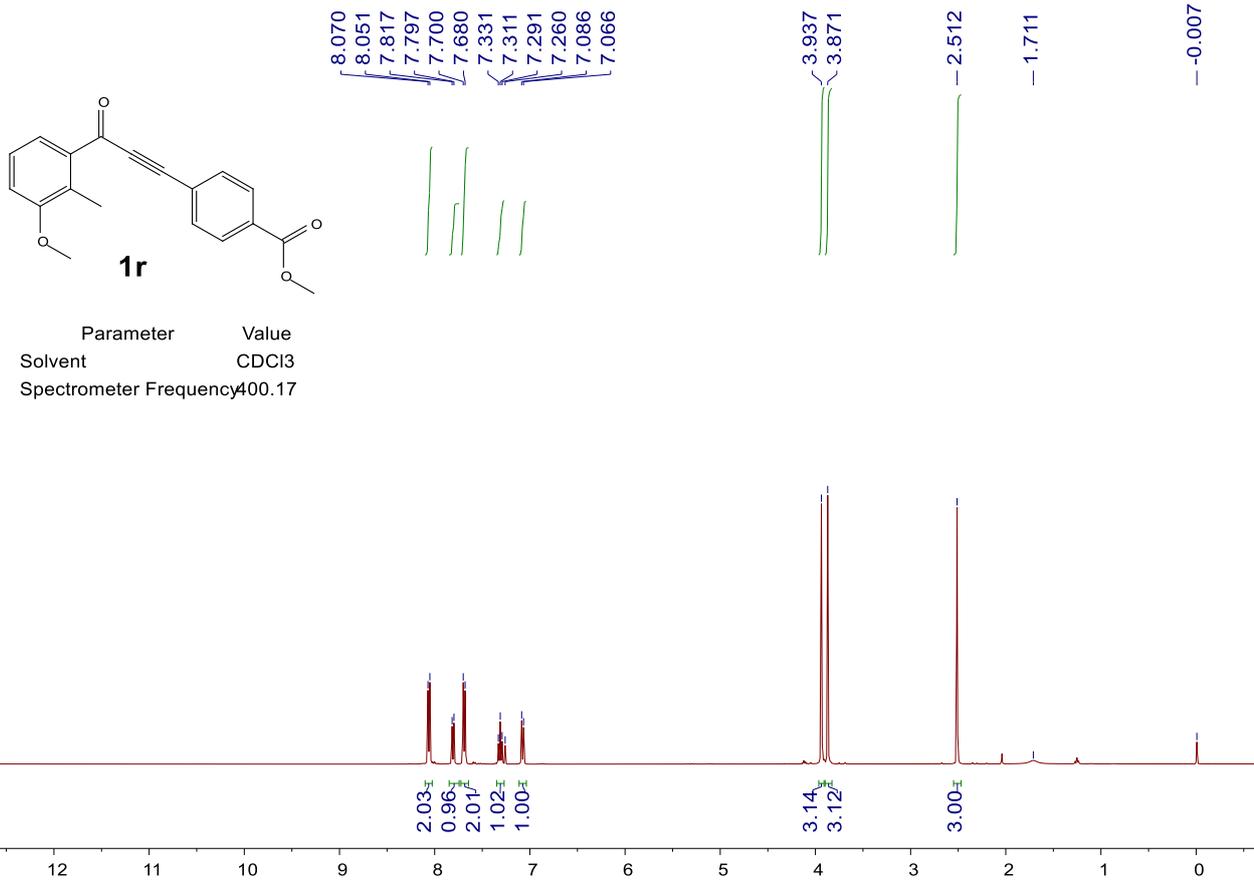


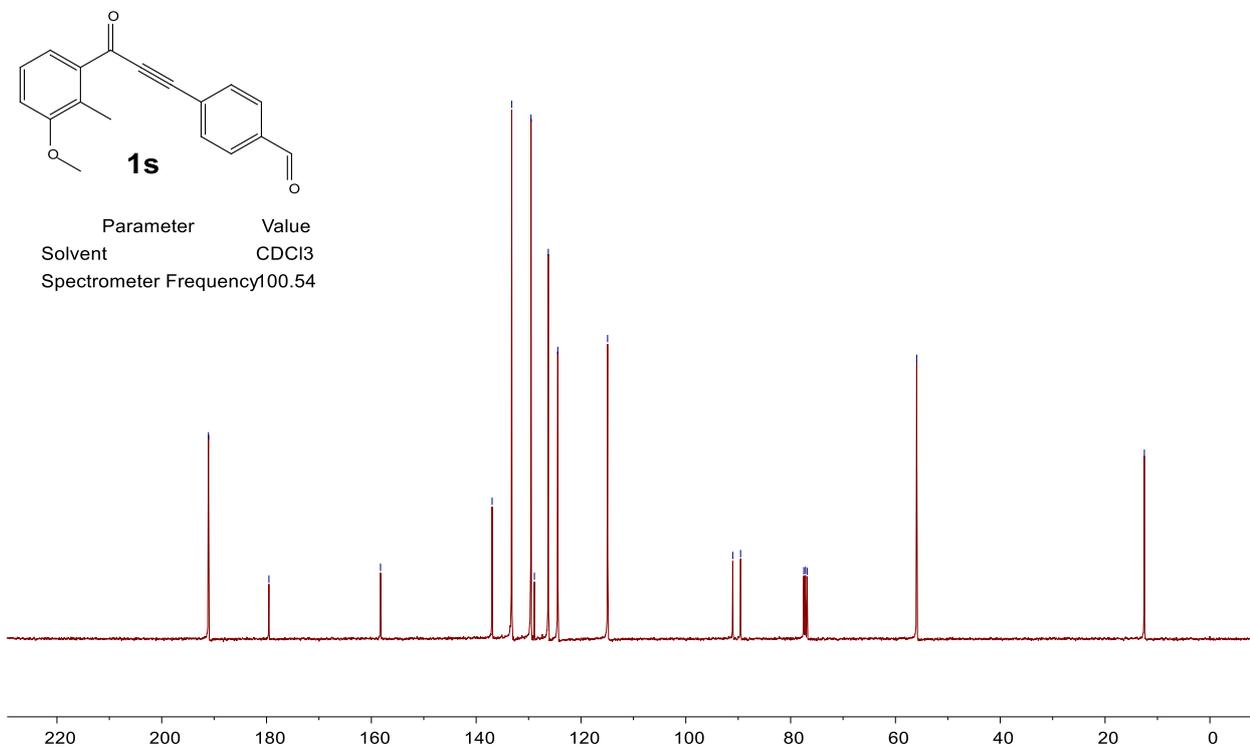
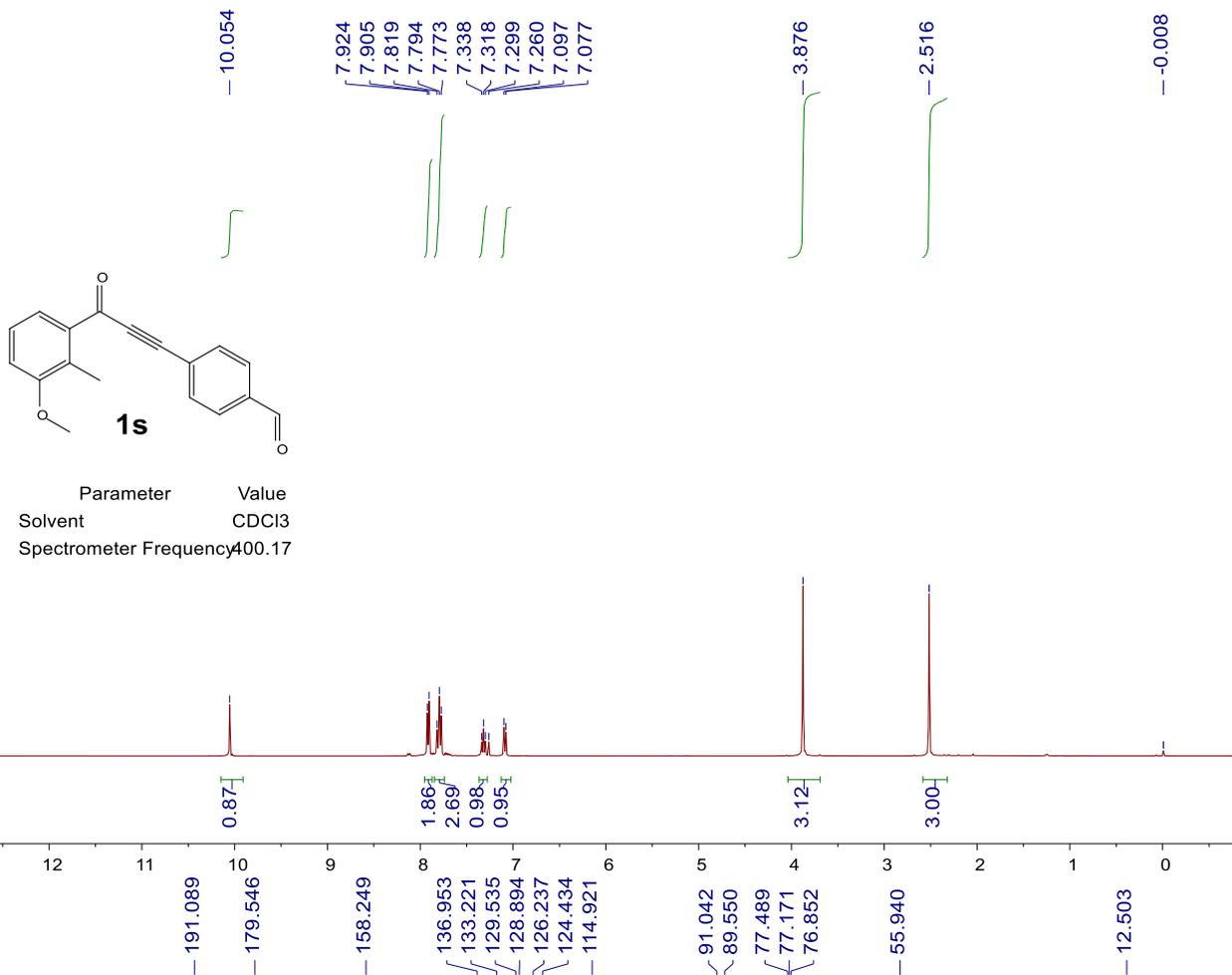
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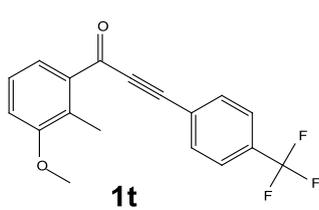


Parameter Value  
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 Spectrometer Frequency 100.52

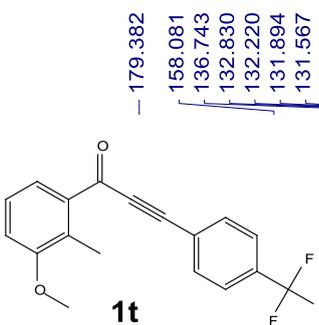
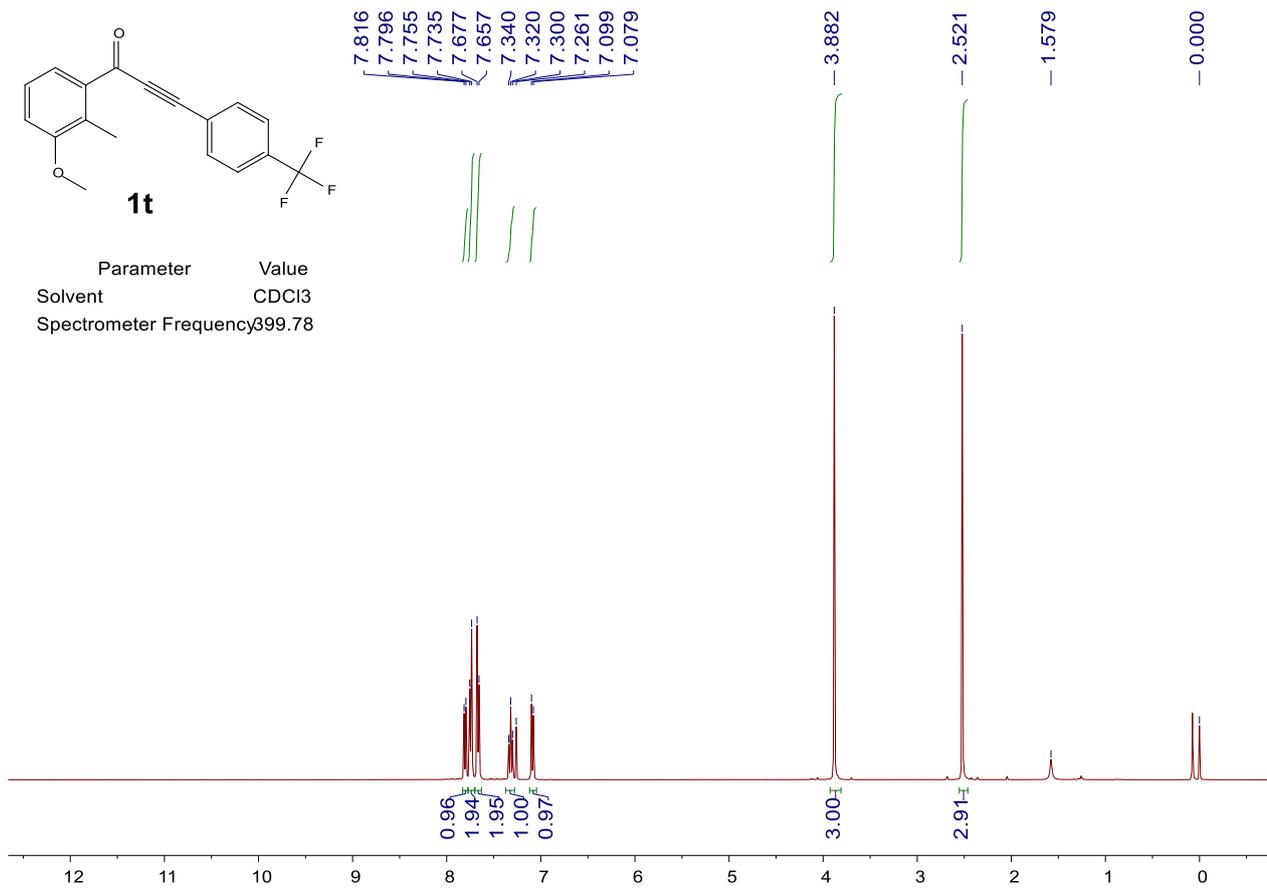




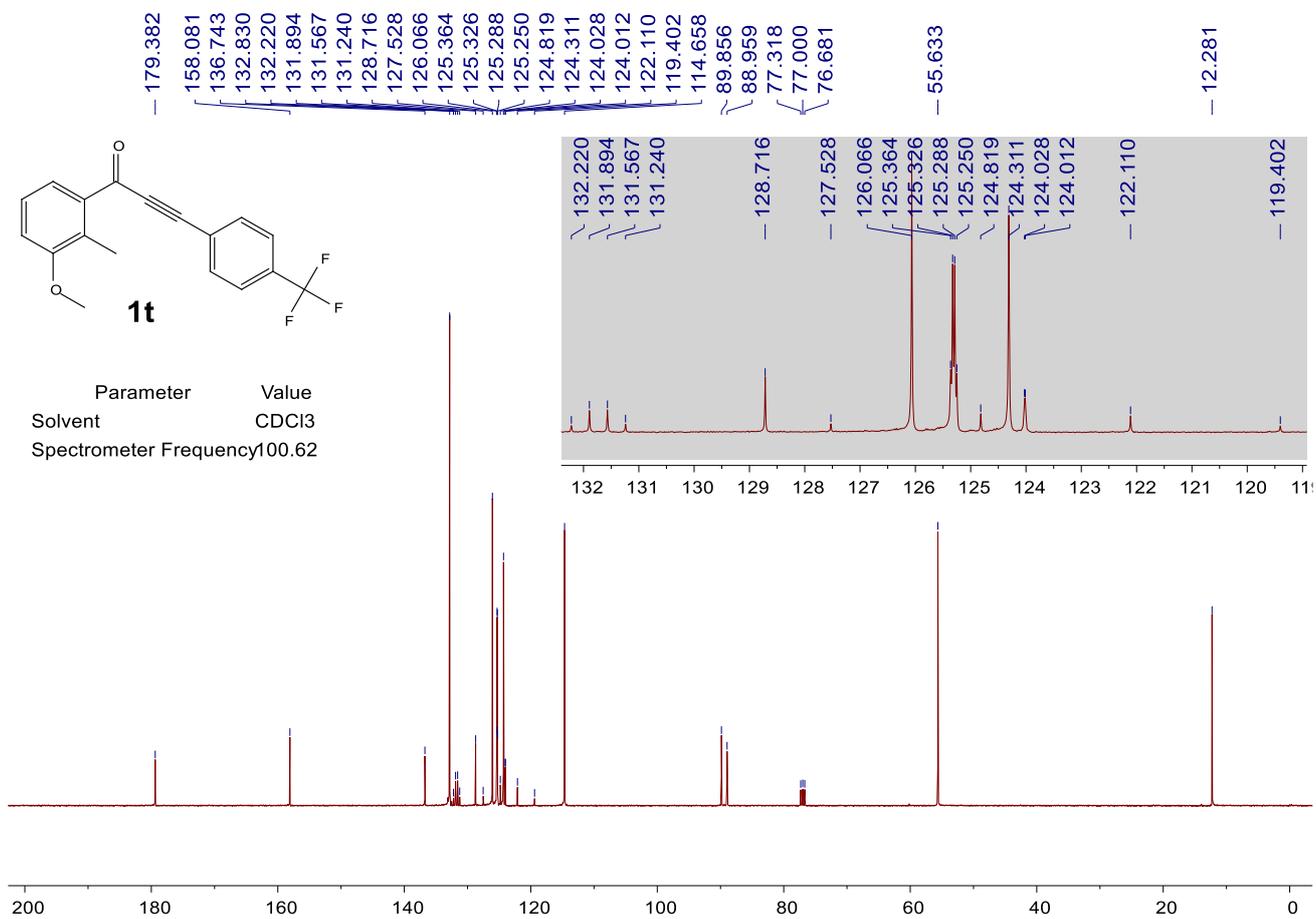


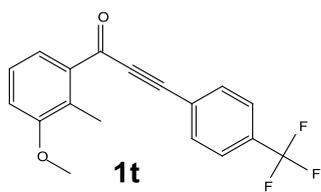


Parameter Value  
 Solvent CDCl<sub>3</sub>  
 Spectrometer Frequency 399.78



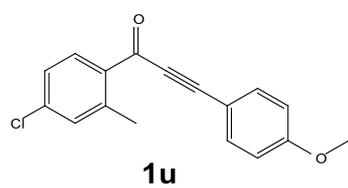
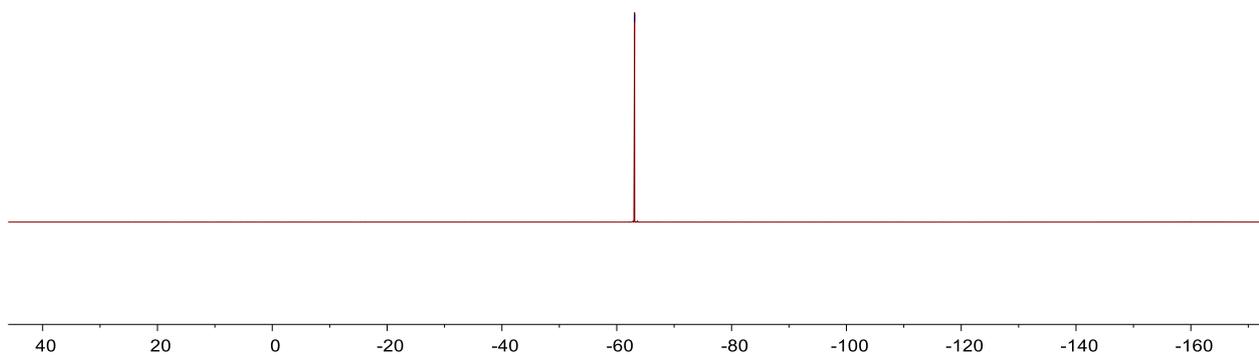
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 Spectrometer Frequency 100.62



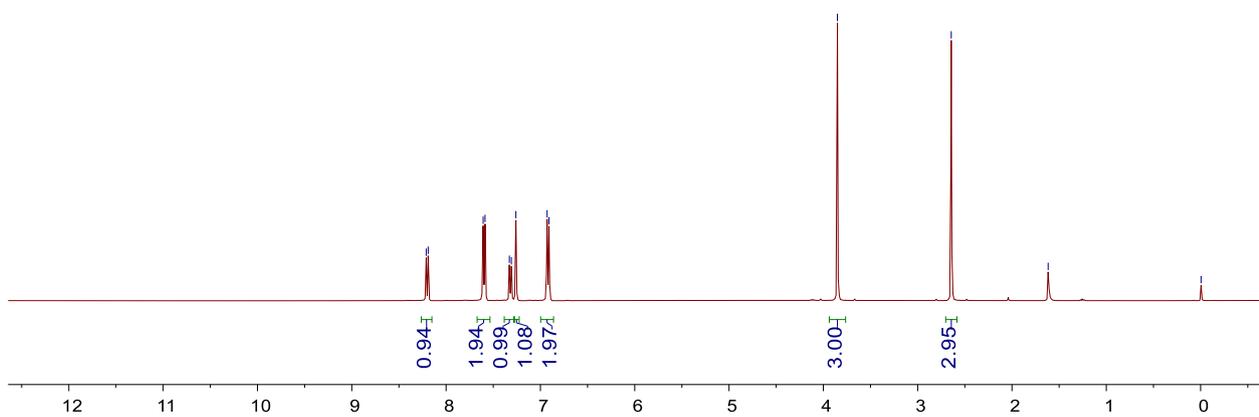
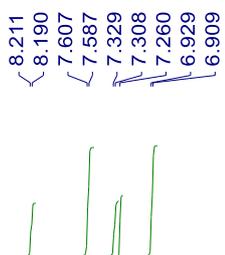


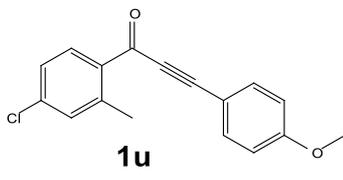
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 Spectrometer Frequency 376.54

— -63.106



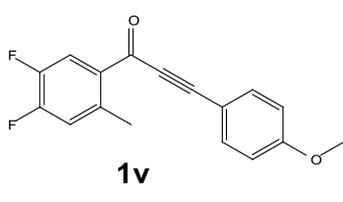
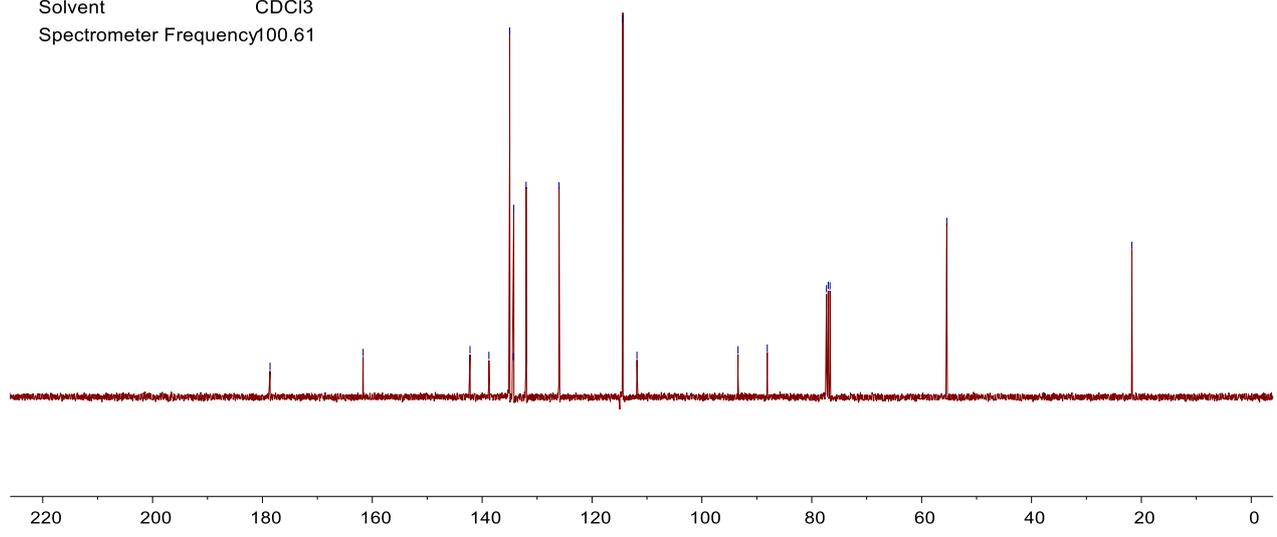
Parameter Value  
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 Spectrometer Frequency 400.17





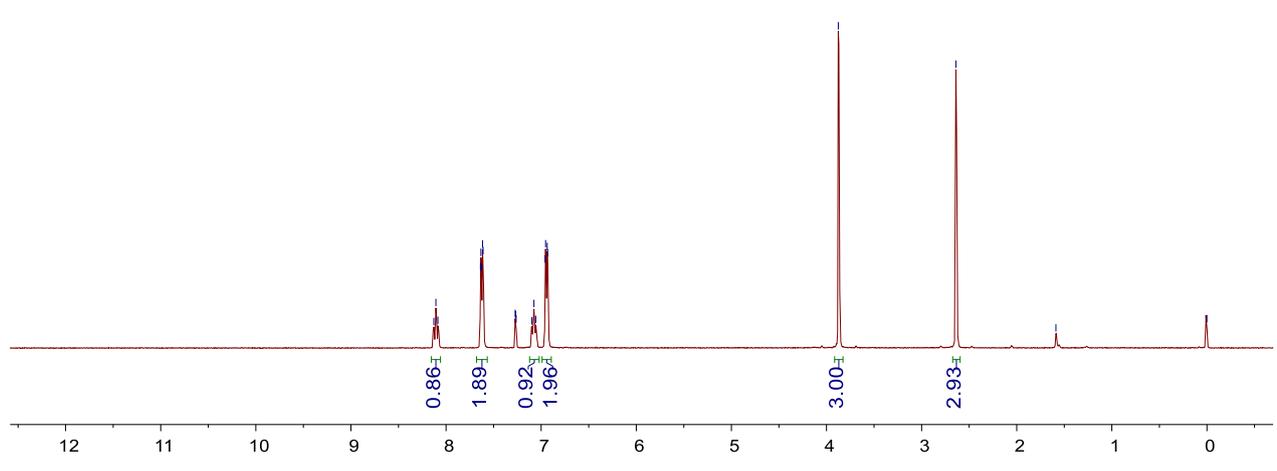
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- 161.681
- 142.210
- 138.769
- 134.994
- 134.336
- 134.262
- 131.996
- 126.007
- 114.396
- 111.824
- 93.422
- 88.099
- 77.317
- 77.000
- 76.682
- 55.418
- 21.723

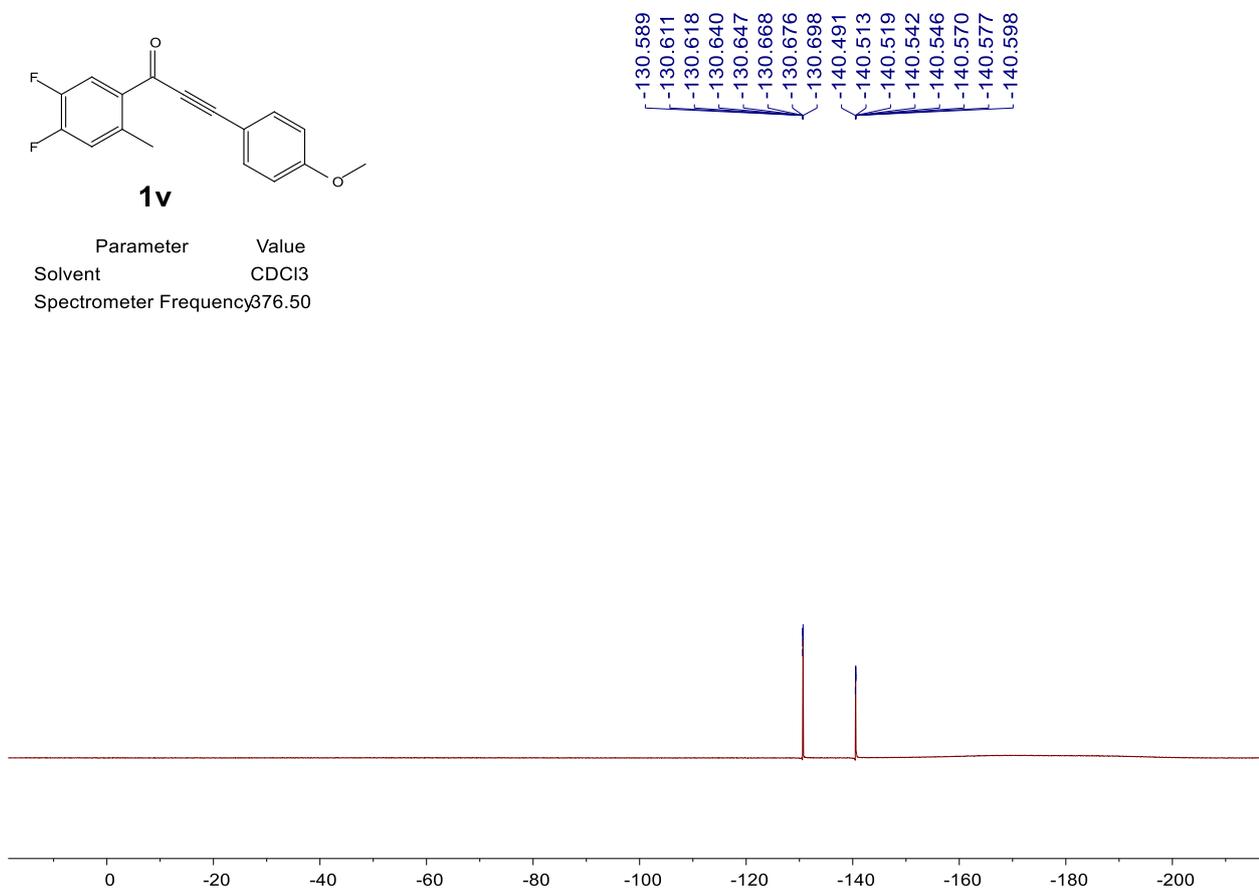
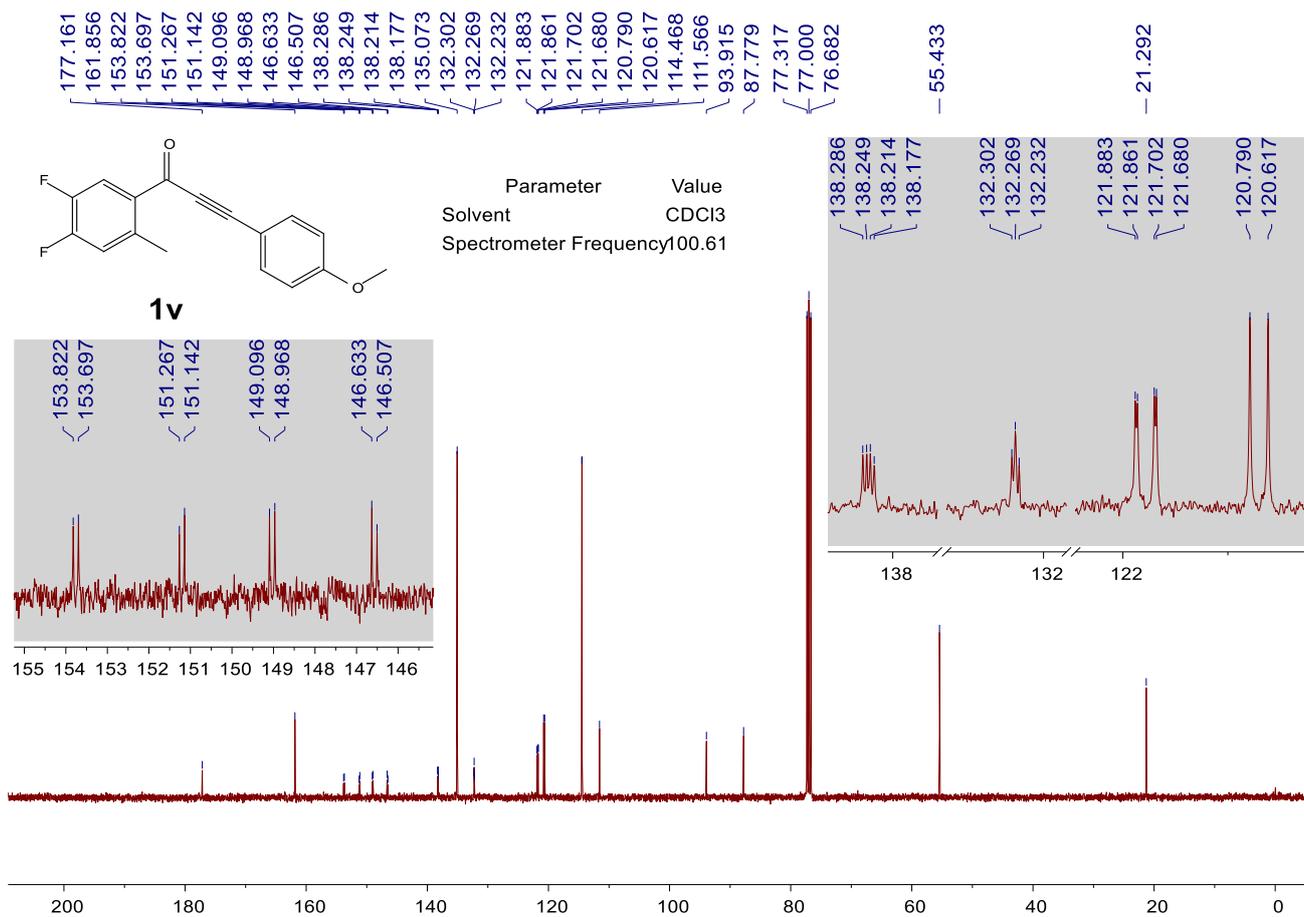
Parameter Value  
 Solvent CDCl3  
 Spectrometer Frequency 100.61

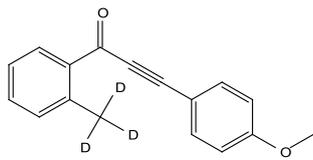


- 8.129
- 8.107
- 8.086
- 7.638
- 7.633
- 7.628
- 7.616
- 7.611
- 7.273
- 7.268
- 7.263
- 7.098
- 7.076
- 7.057
- 6.959
- 6.953
- 6.937
- 6.931
- 3.876
- 2.639
- 1.588
- 0.000

Parameter Value  
 Solvent CDCl3  
 Spectrometer Frequency 399.88







**1a-d<sub>3</sub>**

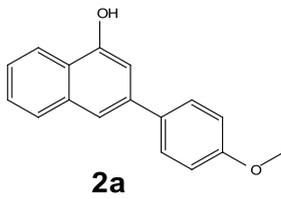
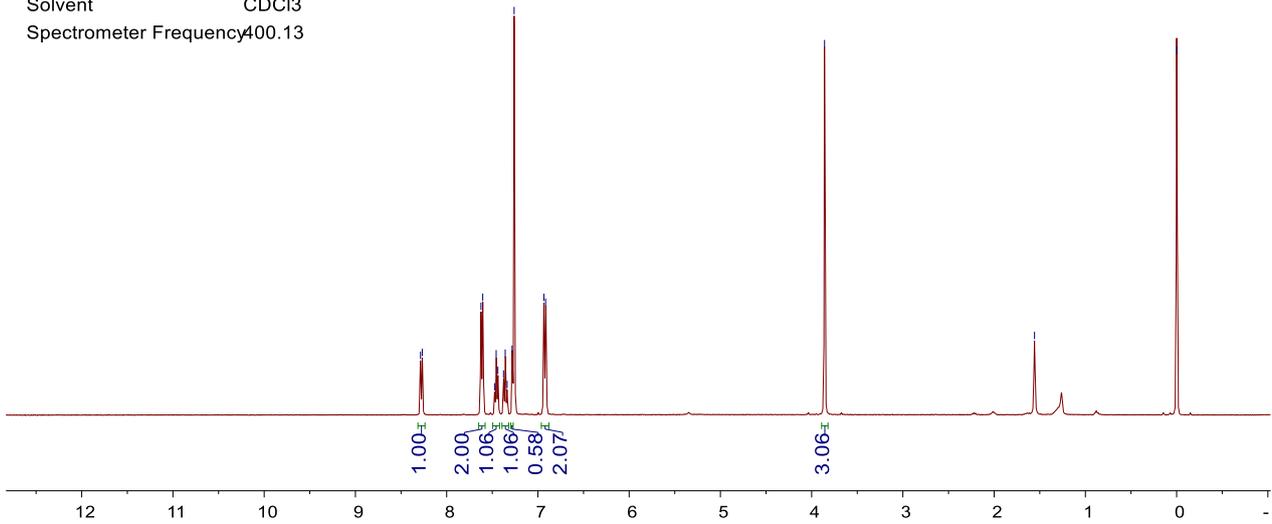
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7.358  
7.337  
7.283  
7.261  
6.934  
6.915

3.858

1.557

-0.003

Parameter Value  
Solvent CDCl<sub>3</sub>  
Spectrometer Frequency 400.13



**2a**

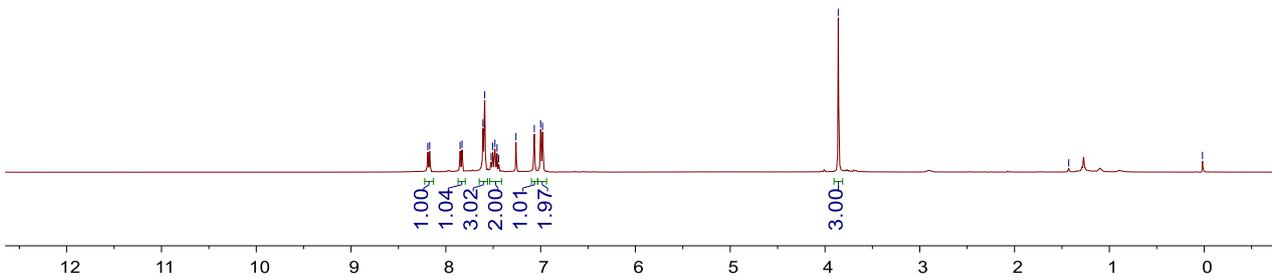
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8.171  
7.849  
7.829  
7.609  
7.590  
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7.505  
7.482  
7.460  
7.442  
7.260  
7.067  
7.000  
6.980

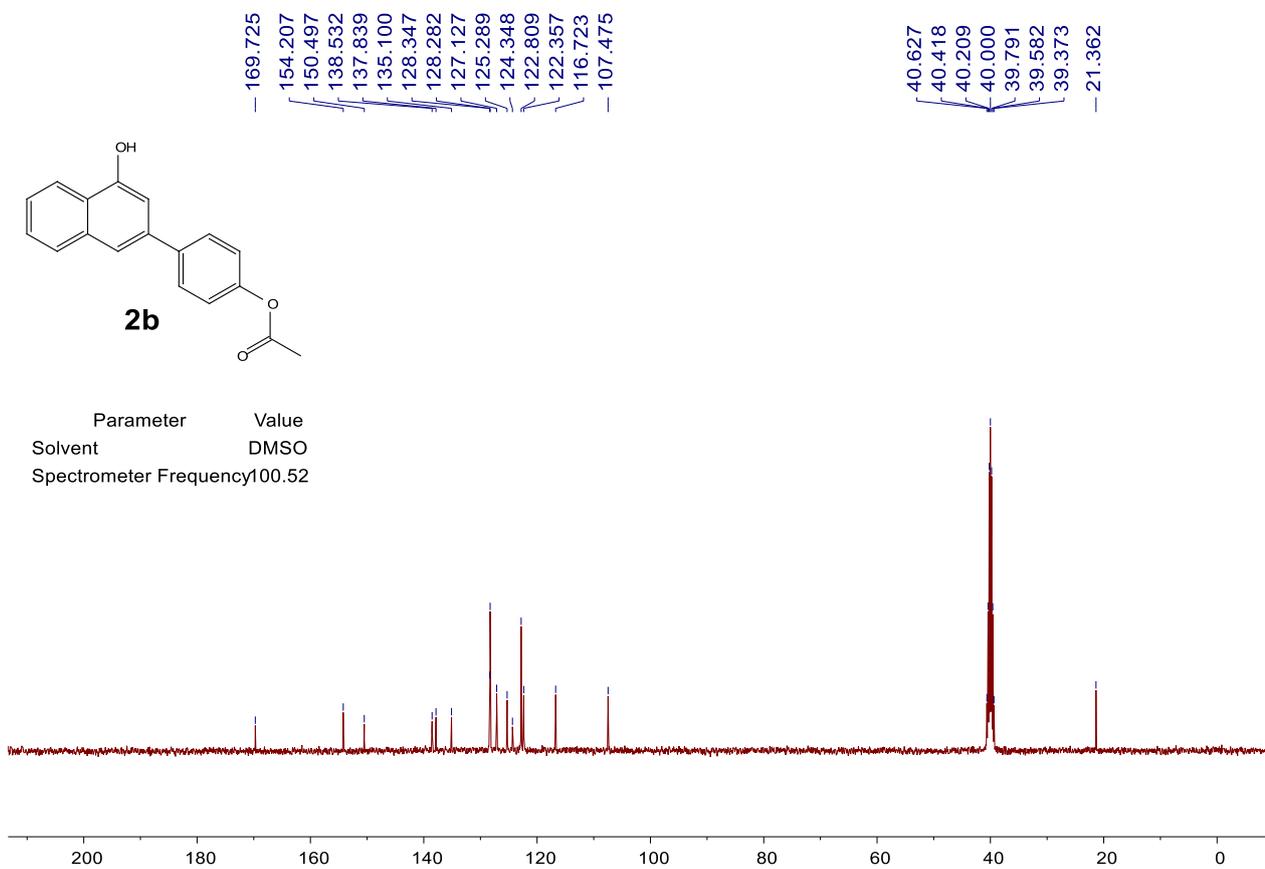
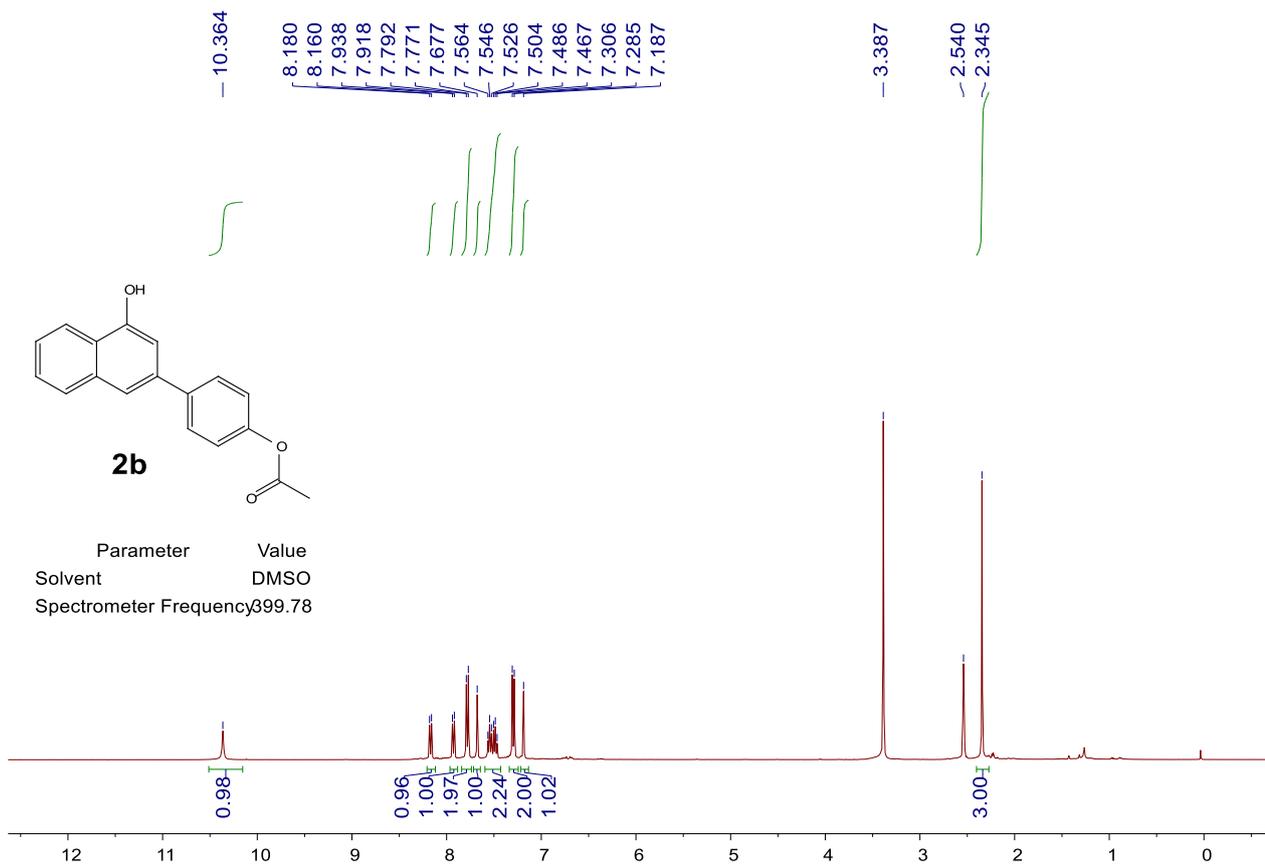
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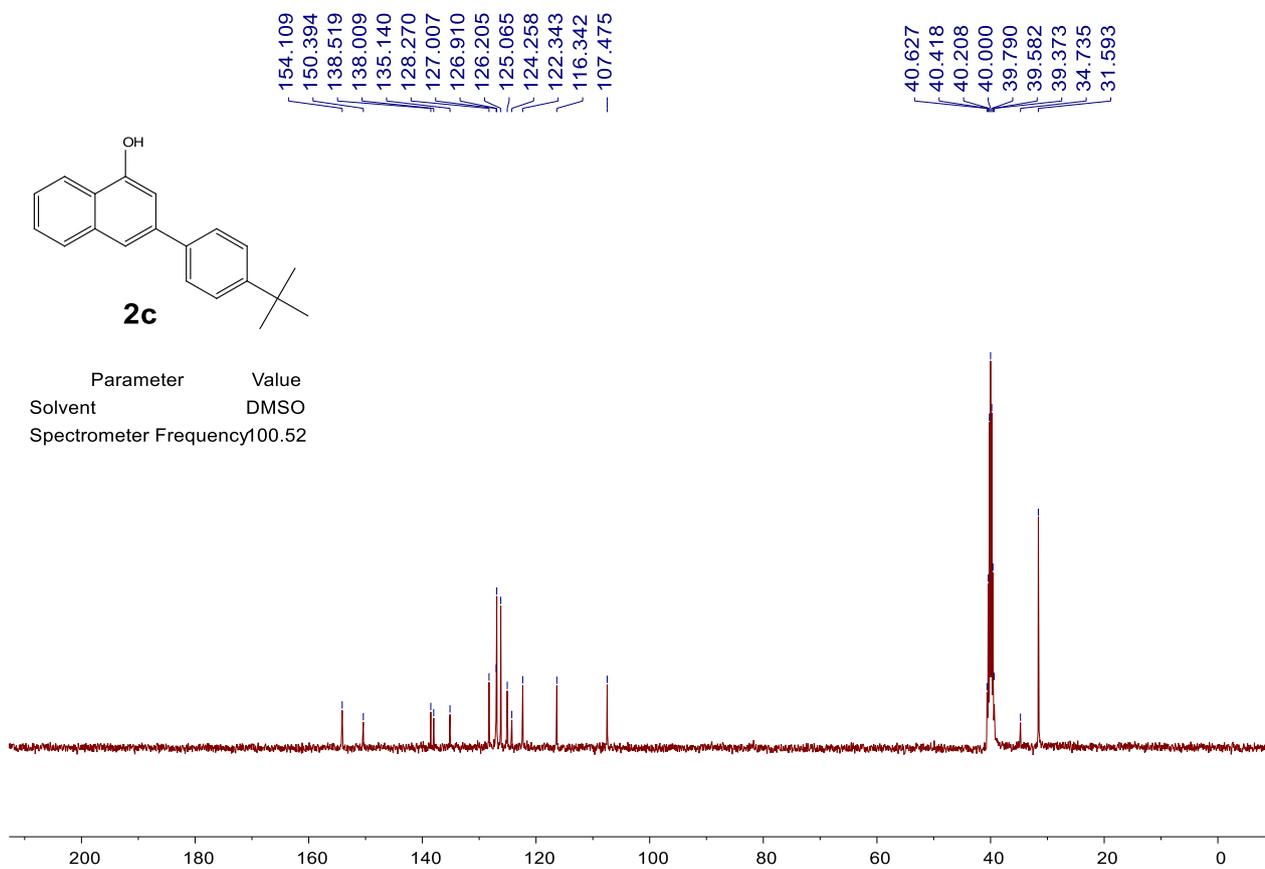
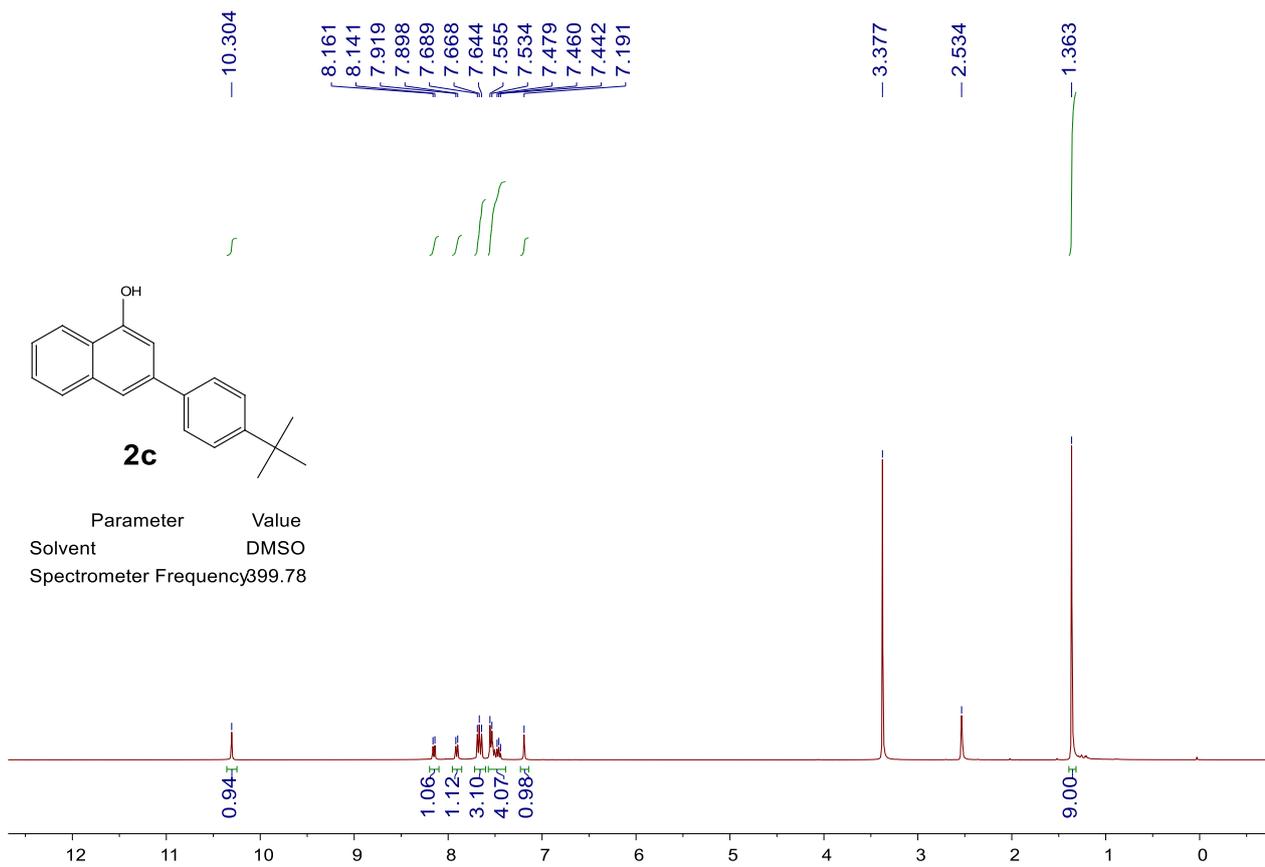
1.429

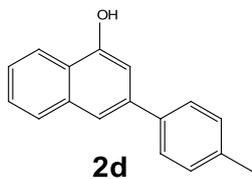
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Parameter Value  
Solvent CDCl<sub>3</sub>  
Spectrometer Frequency 400.13

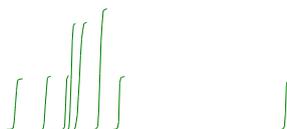






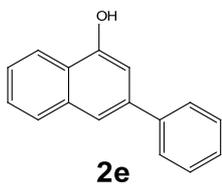
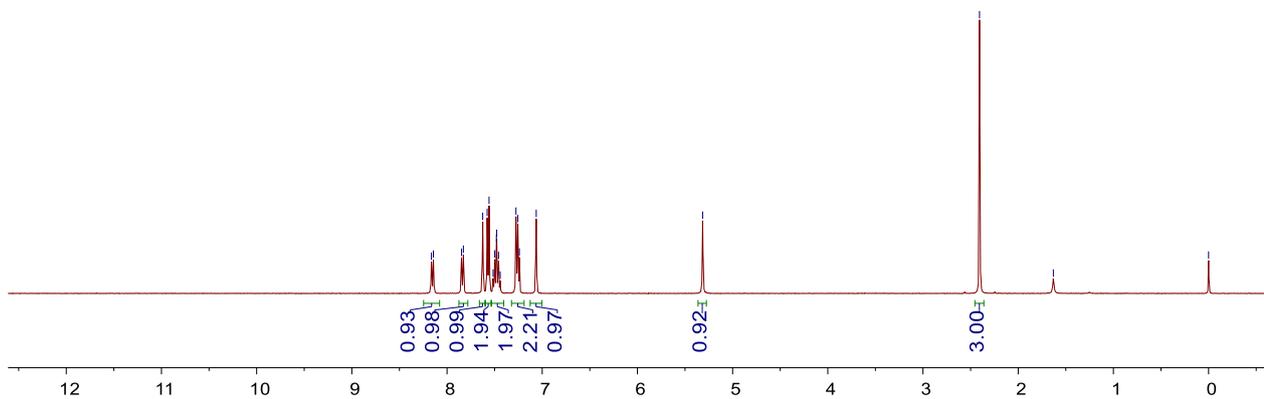


8.164  
8.144  
7.848  
7.828  
7.625  
7.578  
7.558  
7.516  
7.499  
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7.459  
7.442  
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7.256  
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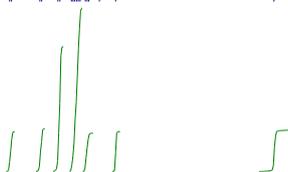


2.406  
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Parameter Value  
Solvent CDCl<sub>3</sub>  
Spectrometer Frequency 399.88

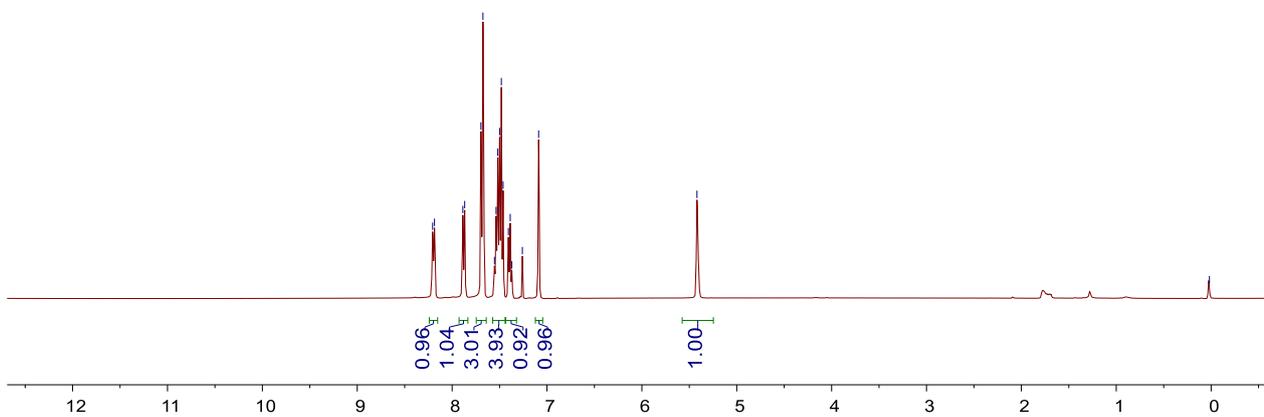


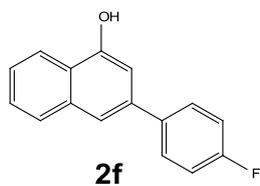
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7.537  
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-5.419



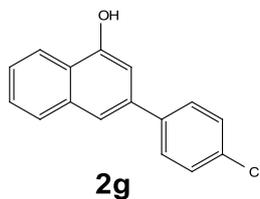
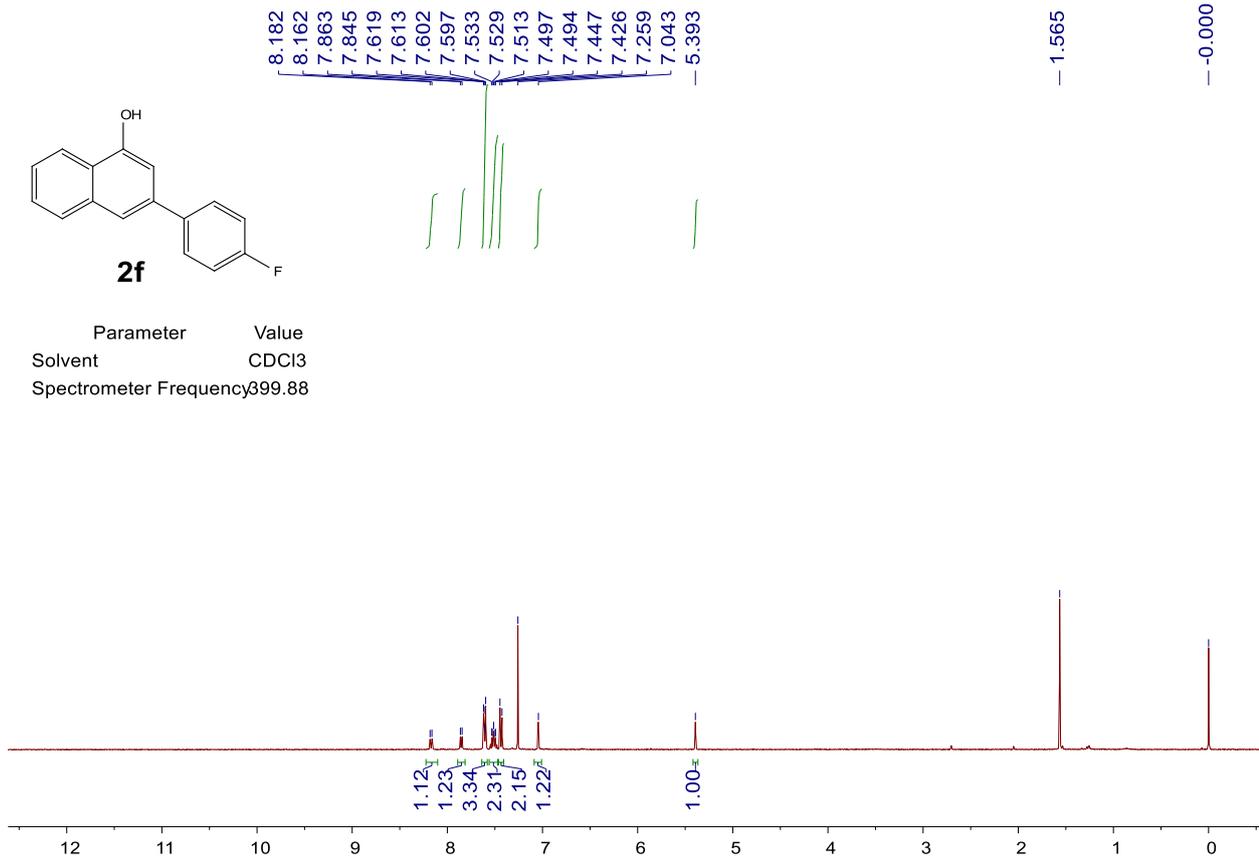
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Parameter Value  
Solvent CDCl<sub>3</sub>  
Spectrometer Frequency 400.17

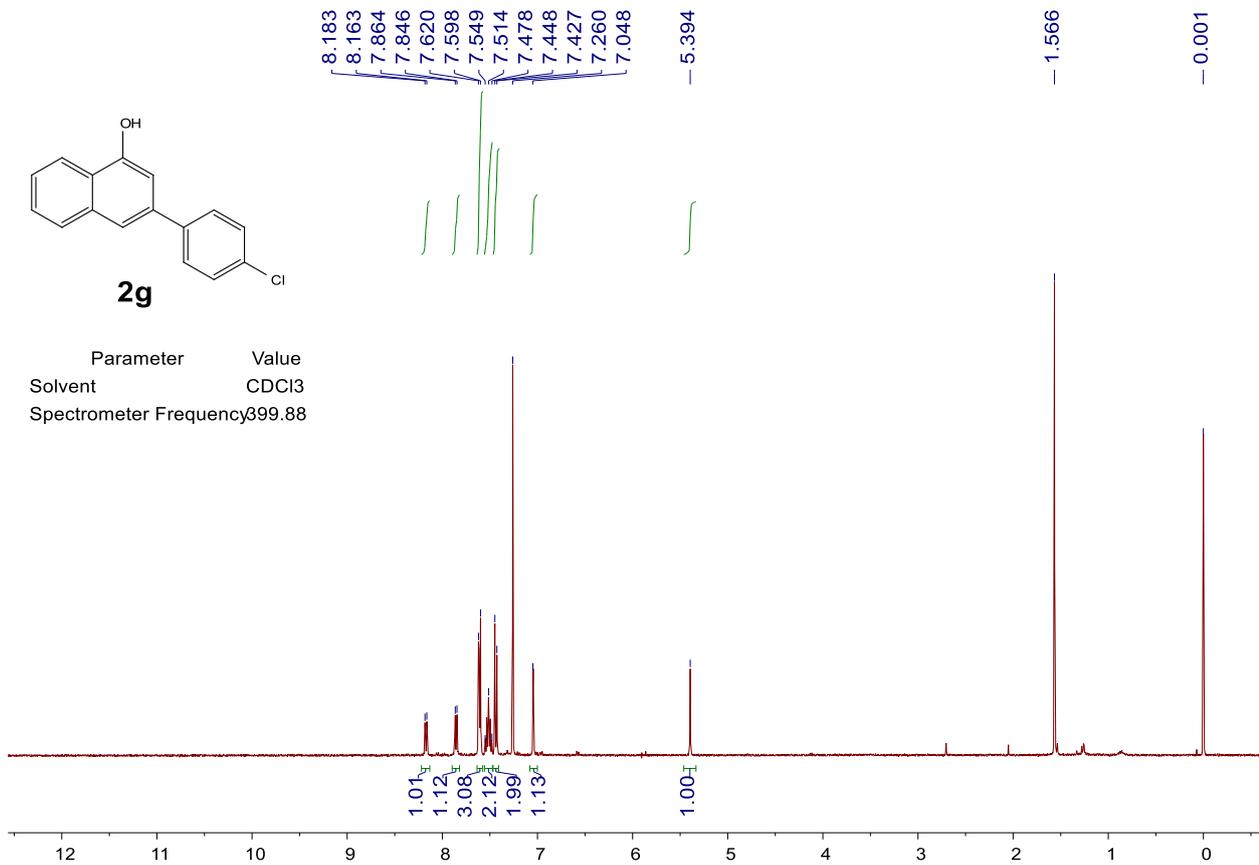


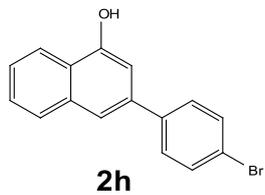


Parameter Value  
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 Spectrometer Frequency 399.88



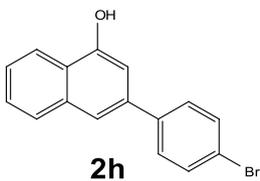
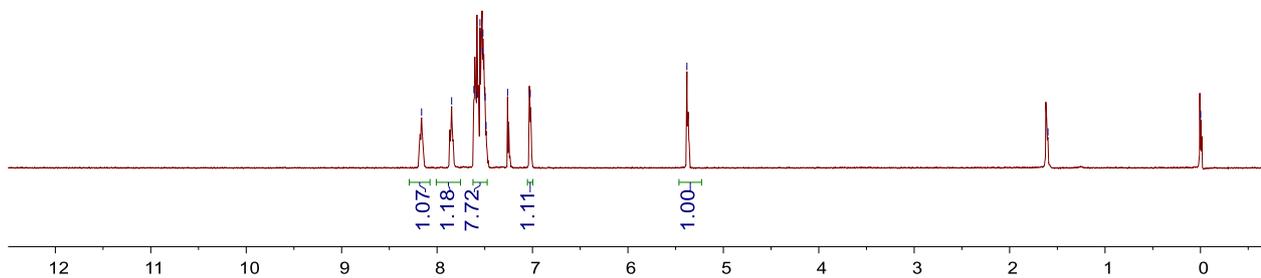
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 Spectrometer Frequency 399.88





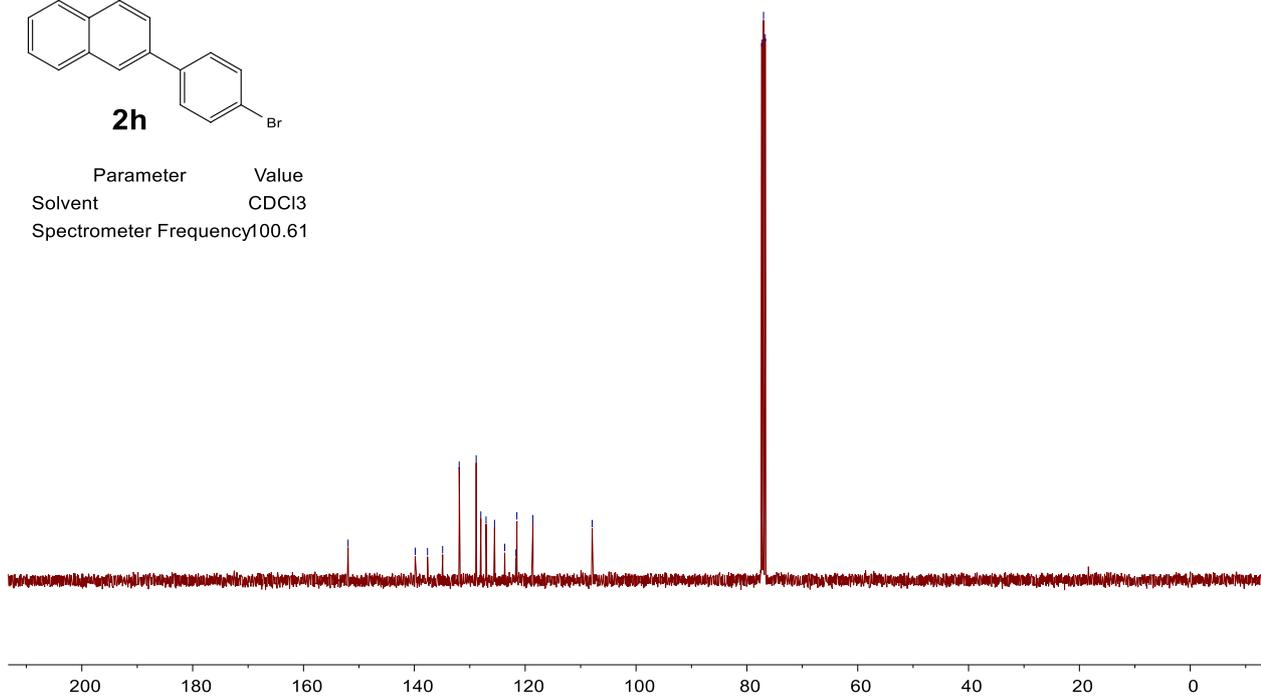
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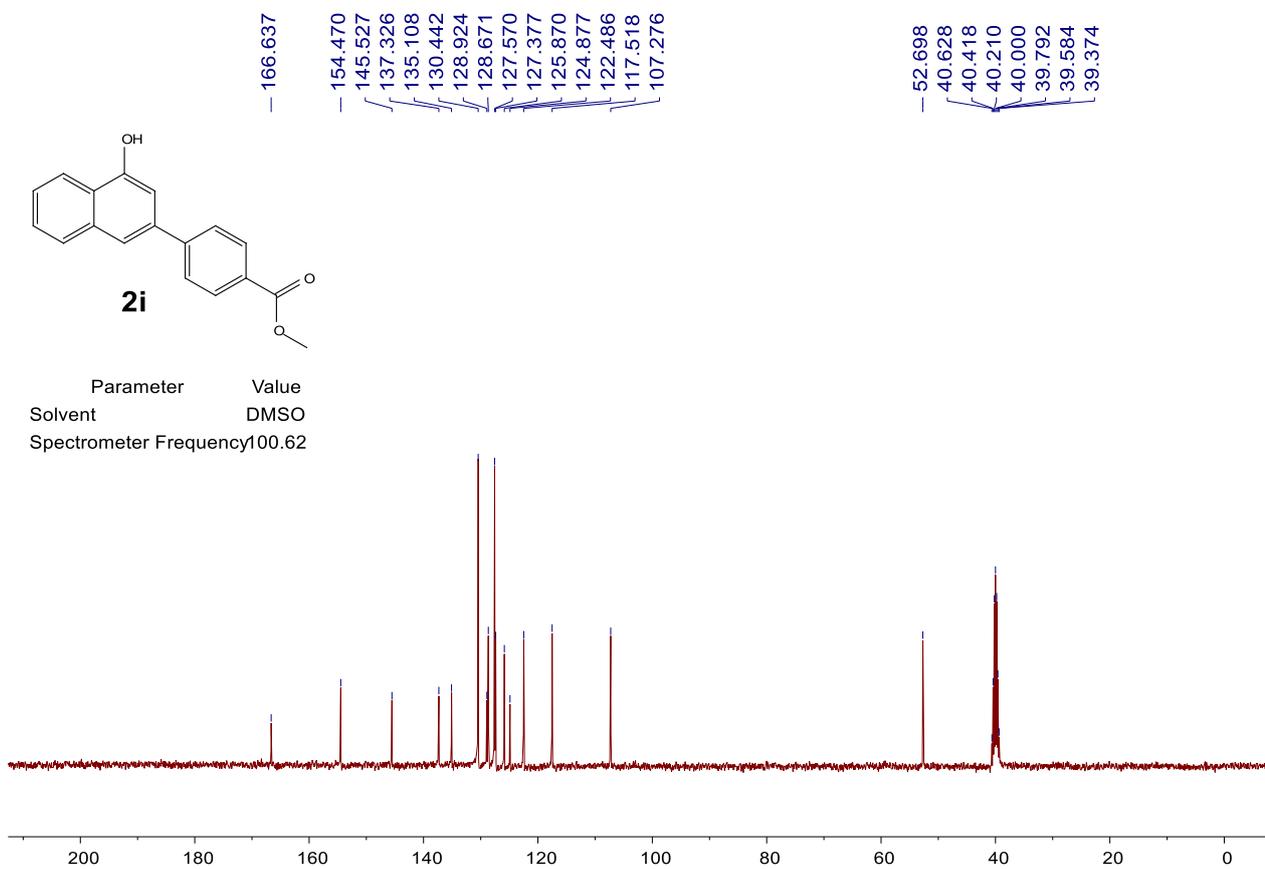
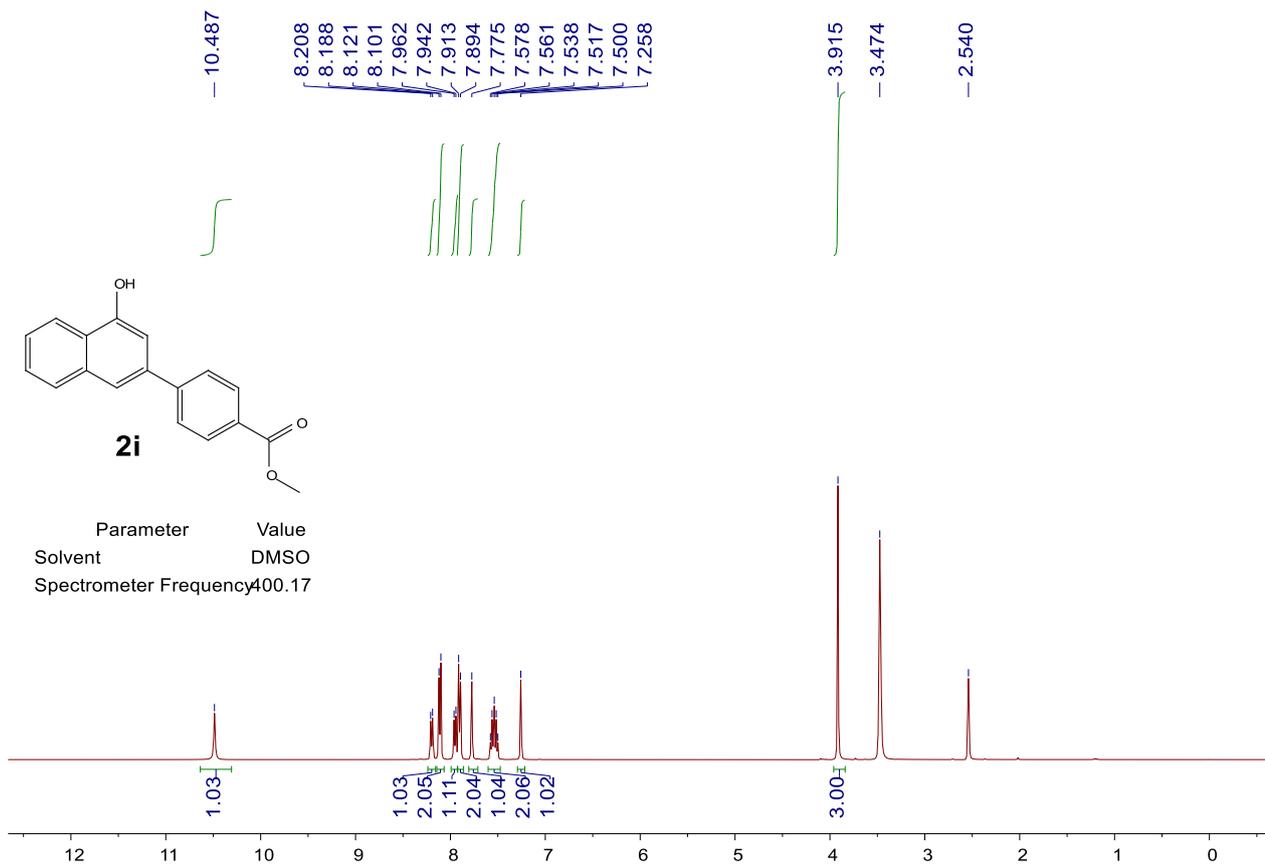
8.163  
 7.848  
 7.614  
 7.588  
 7.550  
 7.524  
 7.520  
 7.497  
 7.487  
 7.261  
 7.024  
 - 5.382  
 - 1.599  
 - -0.002

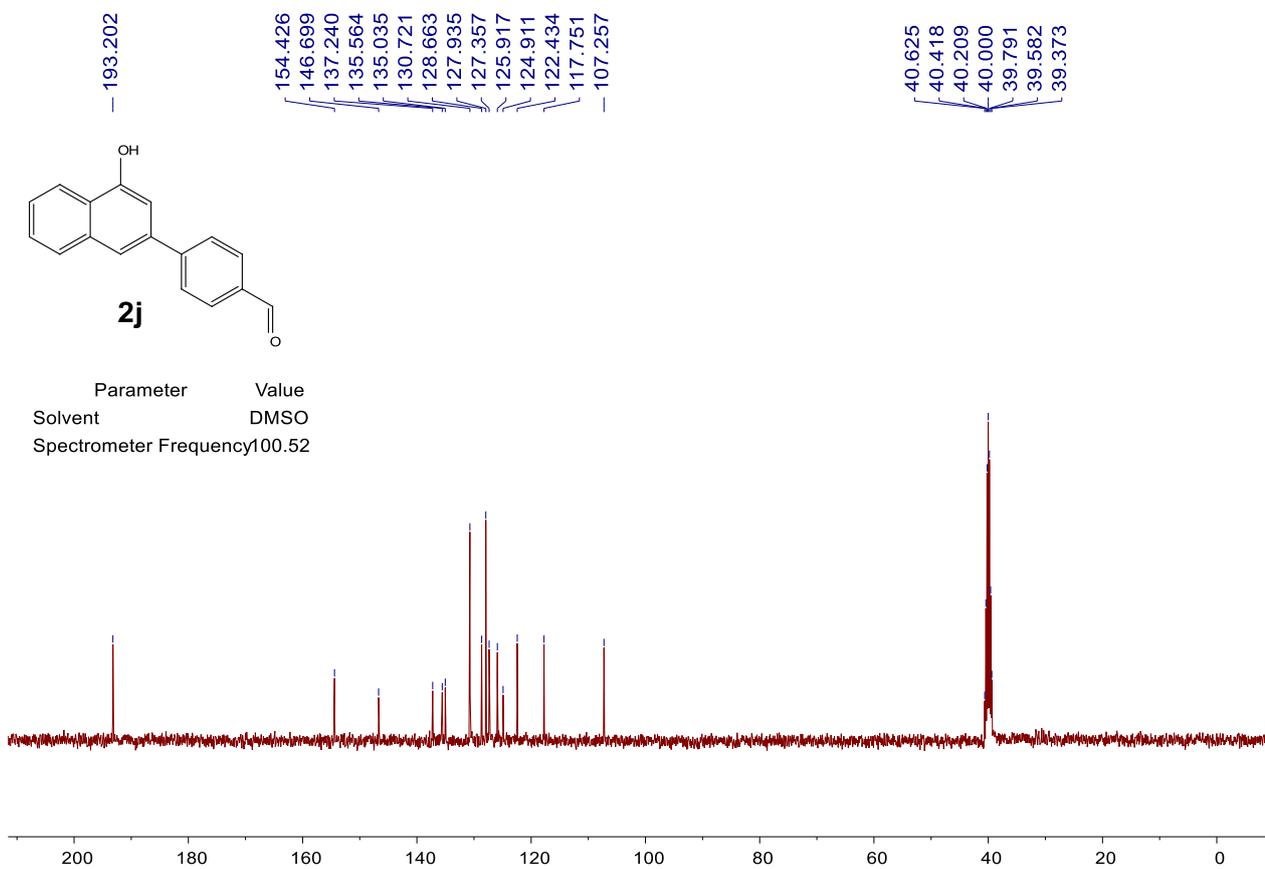
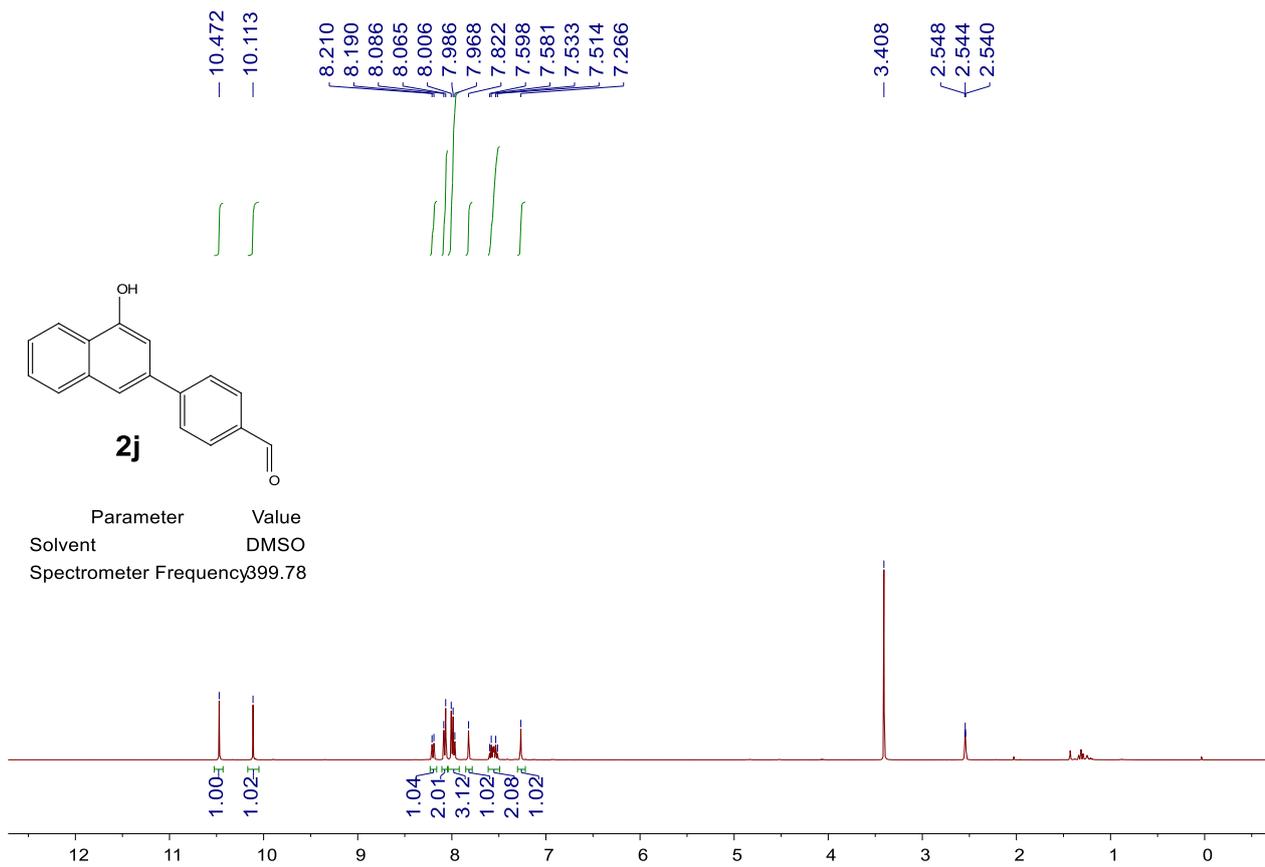


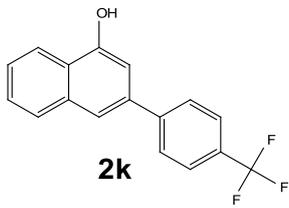
Parameter Value  
 Solvent CDCl3  
 Spectrometer Frequency 100.61

151.959  
 139.845  
 137.623  
 134.895  
 131.904  
 128.844  
 128.005  
 127.061  
 125.536  
 123.693  
 121.672  
 121.500  
 118.608  
 - 107.911  
 77.317  
 77.000  
 76.682







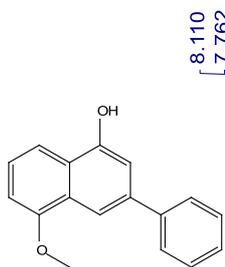
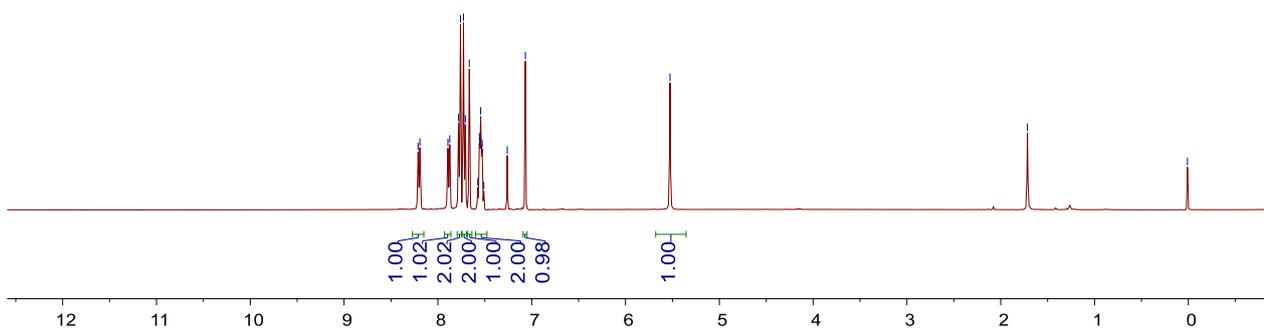


Parameter Value  
 Solvent CDCl<sub>3</sub>  
 Spectrometer Frequency 400.17

8.211  
 8.192  
 7.893  
 7.873  
 7.780  
 7.760  
 7.727  
 7.707  
 7.665  
 7.574  
 7.557  
 7.553  
 7.544  
 7.533  
 7.528  
 7.511  
 7.260  
 7.067  
 5.525

-1.715

-0.010

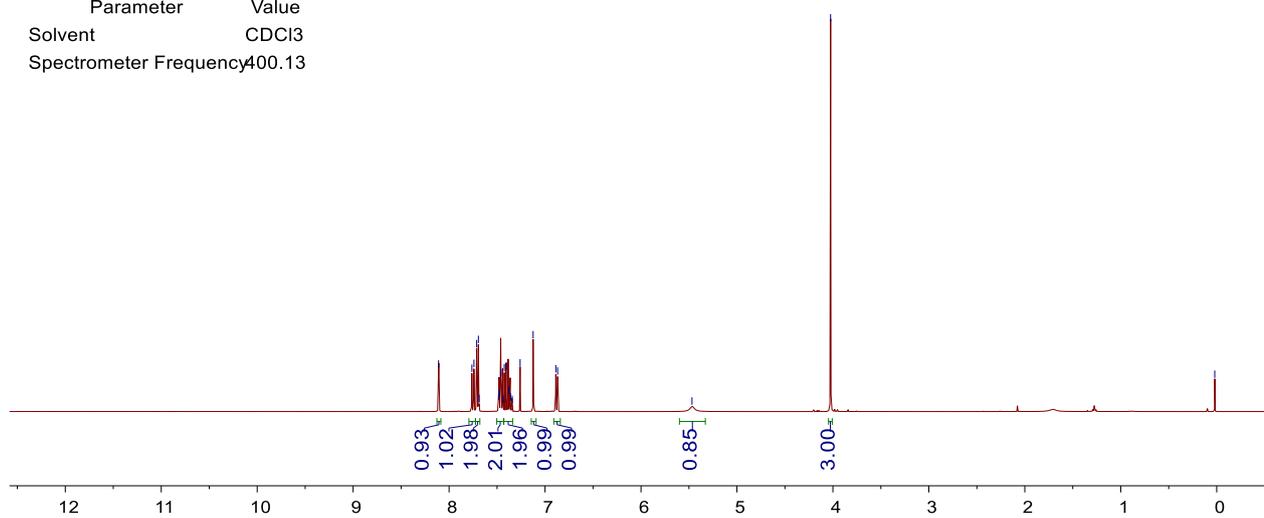


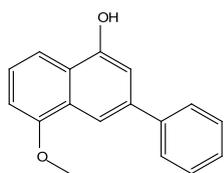
Parameter Value  
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 Spectrometer Frequency 400.13

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 7.741  
 7.712  
 7.695  
 7.687  
 7.484  
 7.476  
 7.459  
 7.437  
 7.425  
 7.404  
 7.378  
 7.358  
 7.342  
 7.260  
 7.124  
 6.888  
 6.869  
 5.468

4.024

-0.020

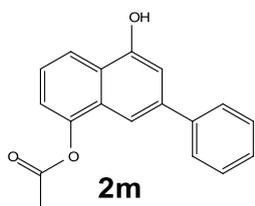
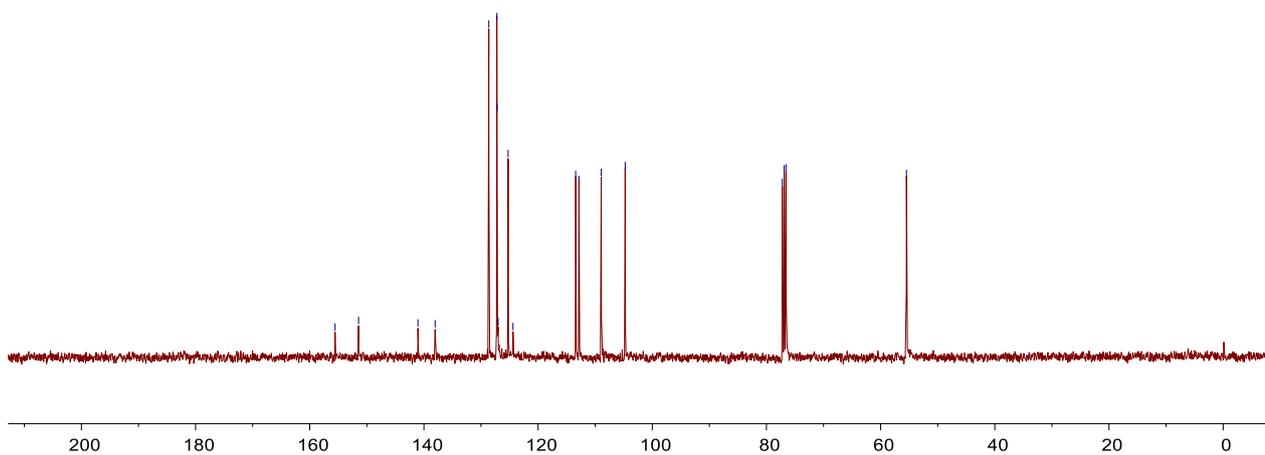




**2l**

155.562  
151.449  
141.050  
138.042  
128.633  
127.223  
127.180  
126.994  
125.246  
124.392  
113.420  
112.842  
108.941  
104.744  
77.220  
76.902  
76.585  
55.478

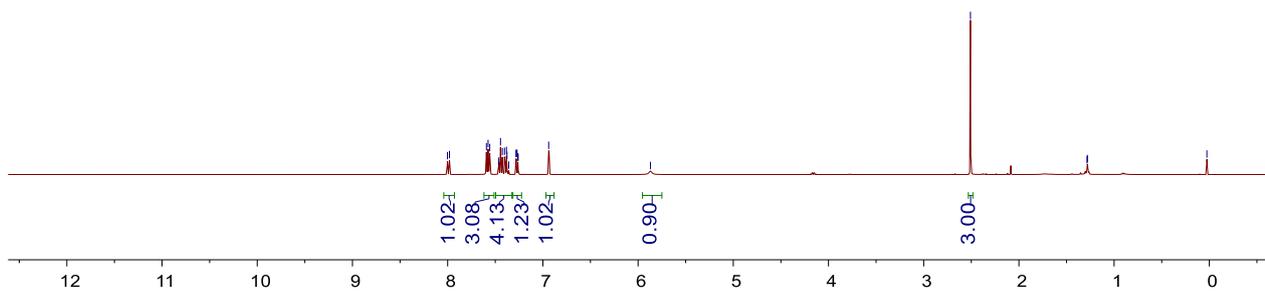
Parameter Value  
Solvent CDCl3  
Spectrometer Frequency 100.62

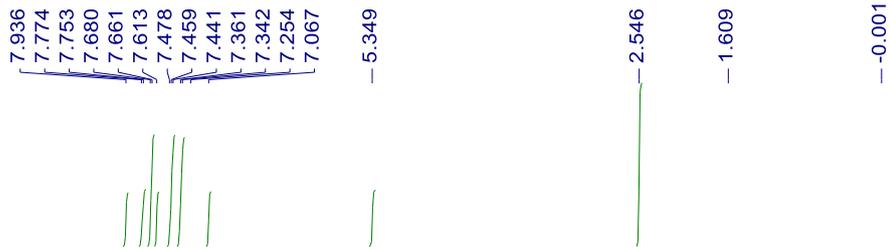
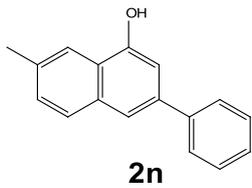


**2m**

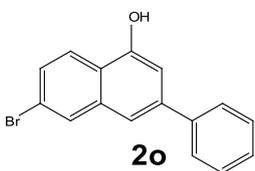
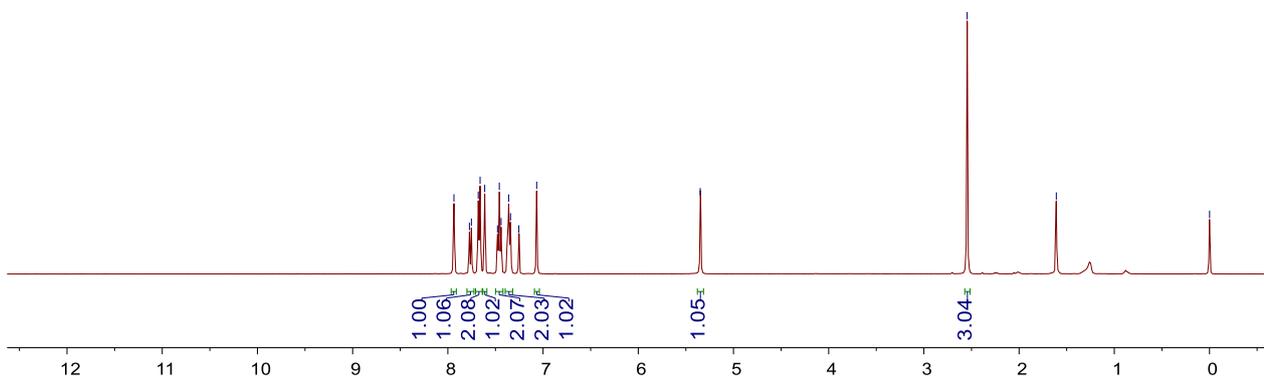
8.002  
7.981  
7.593  
7.575  
7.558  
7.465  
7.445  
7.426  
7.403  
7.382  
7.377  
7.359  
7.281  
7.279  
7.271  
7.262  
7.260  
6.939  
5.870  
2.509  
1.284  
1.280  
0.026

Parameter Value  
Solvent CDCl3  
Spectrometer Frequency 400.13

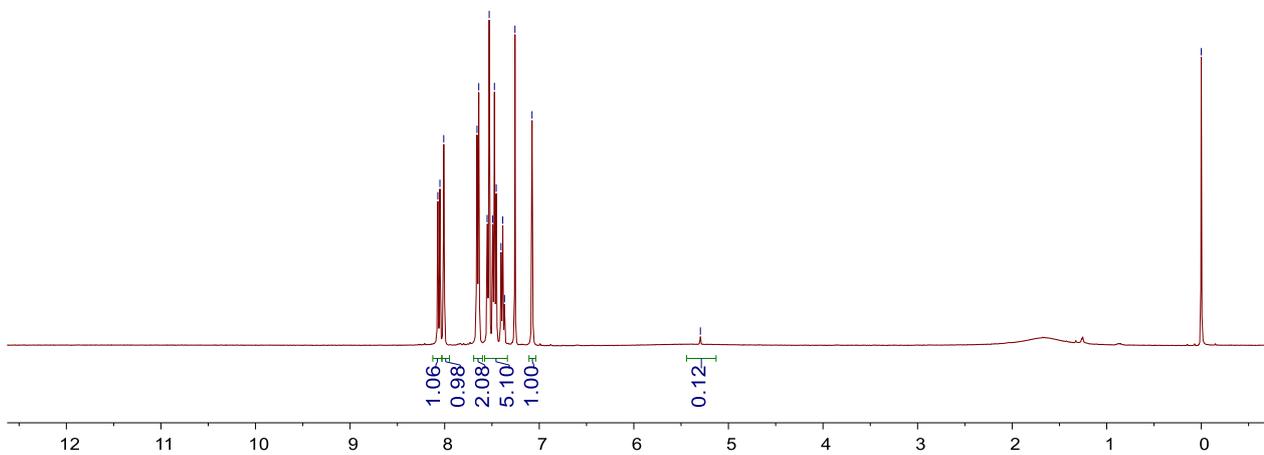


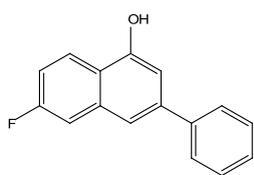


Parameter Value  
Solvent CDCl3  
Spectrometer Frequency 400.13



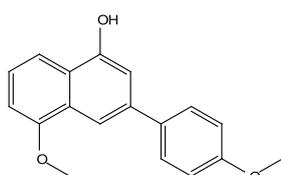
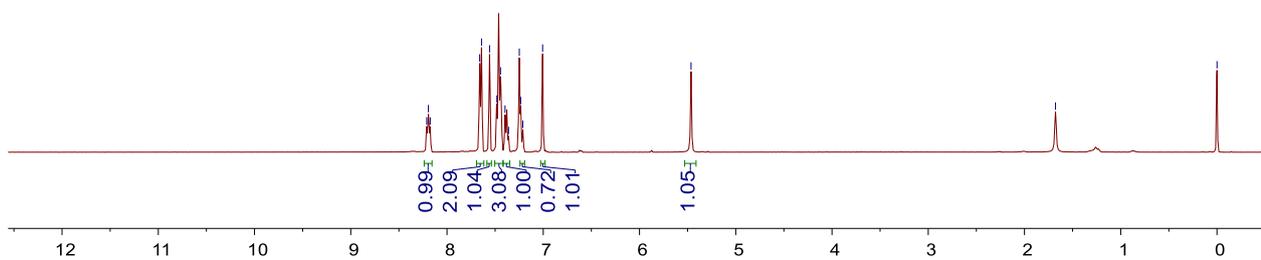
Parameter Value  
Solvent CDCl3  
Spectrometer Frequency 400.13





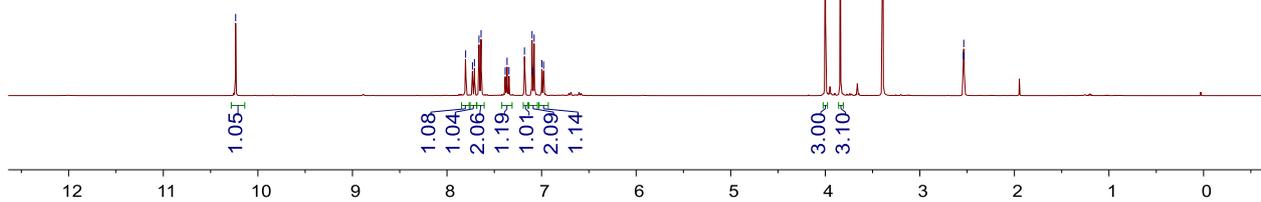
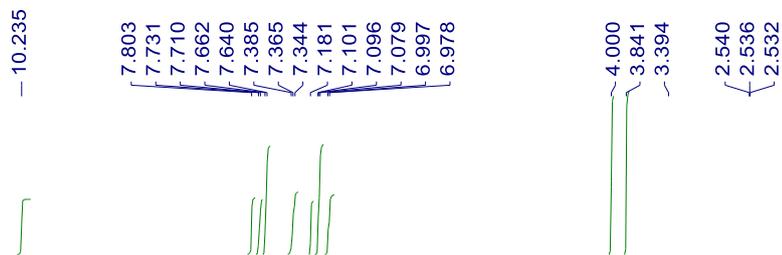
**2p**

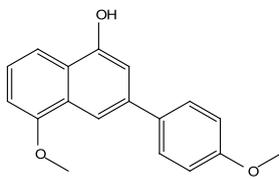
Parameter Value  
 Solvent CDCl<sub>3</sub>  
 Spectrometer Frequency 399.78



**2q**

Parameter Value  
 Solvent DMSO  
 Spectrometer Frequency 399.78



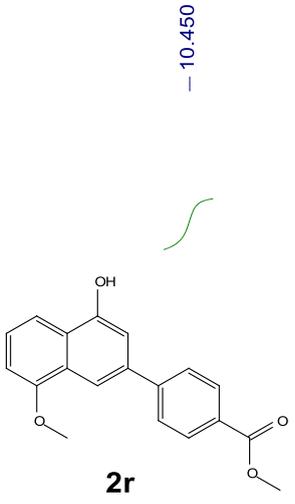
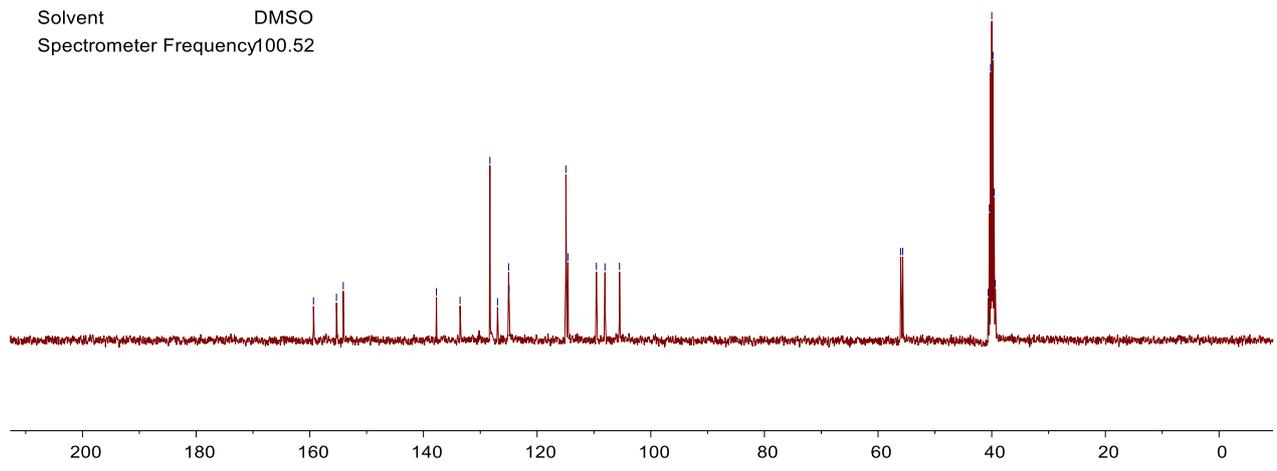


**2q**

Parameter Value  
 Solvent DMSO  
 Spectrometer Frequency 100.52

- 159.356
- 155.313
- 154.113
- 137.715
- 133.561
- 128.306
- 126.970
- 125.020
- 124.950
- 114.935
- 114.577
- 109.565
- 108.058
- 105.497

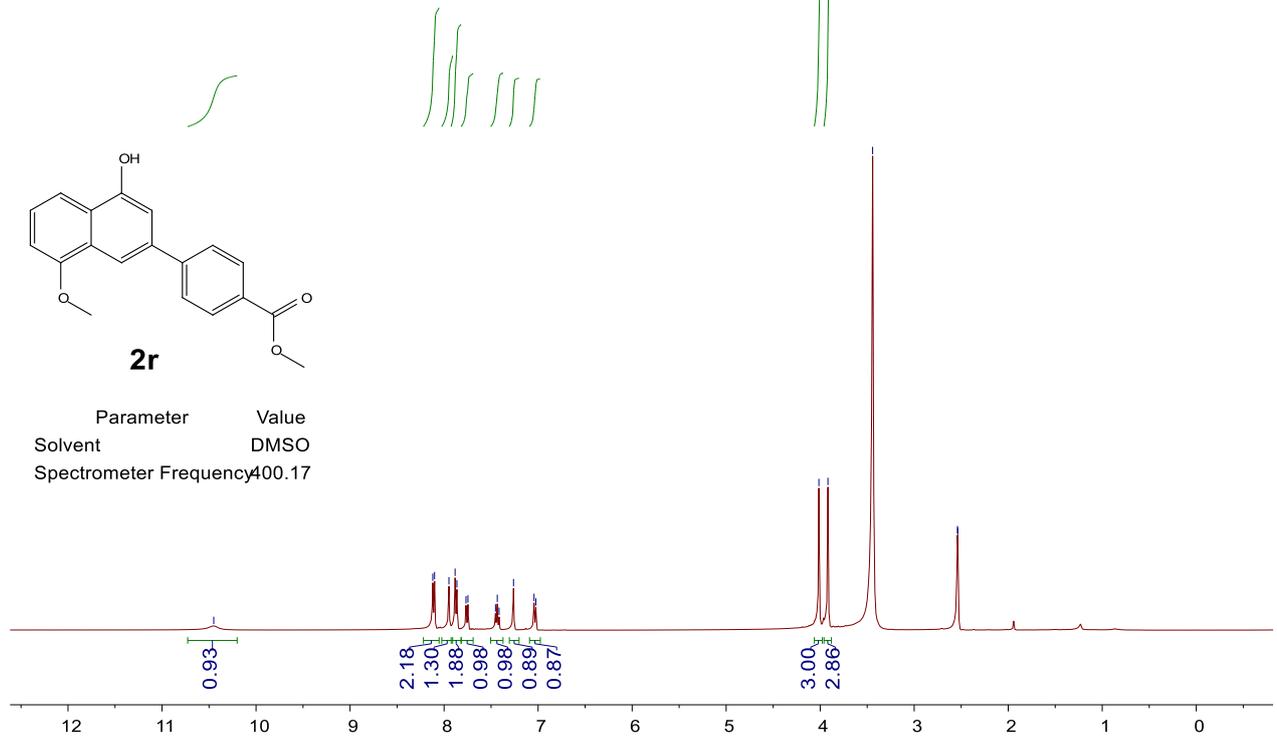
- 56.009
- 55.660
- 40.625
- 40.417
- 40.208
- 40.000
- 39.790
- 39.581
- 39.371

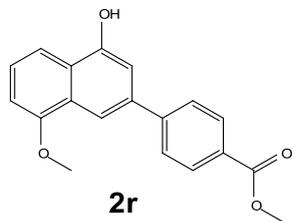


**2r**

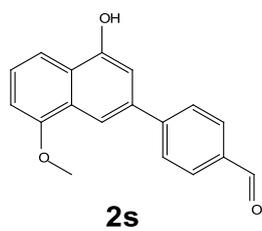
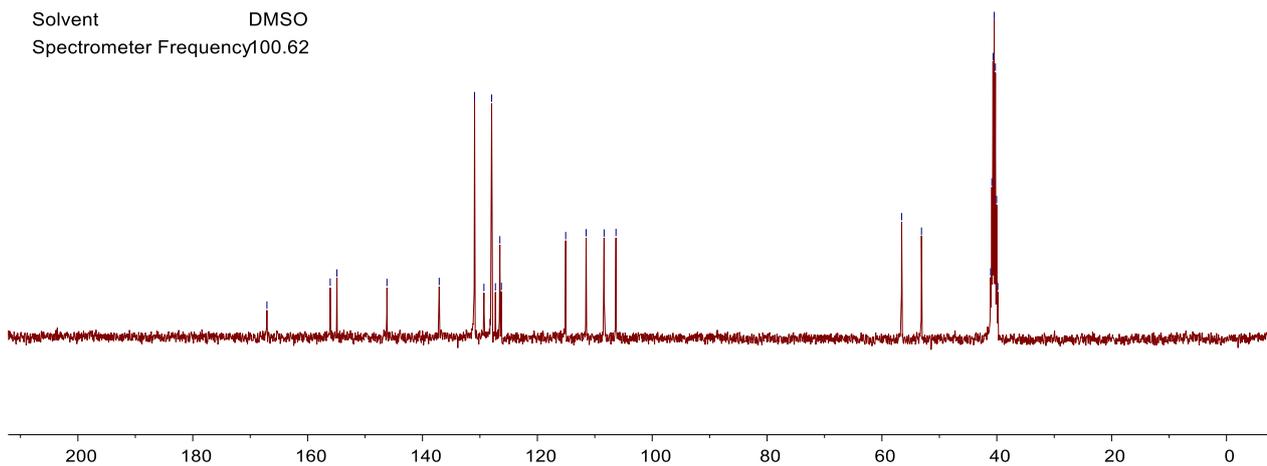
Parameter Value  
 Solvent DMSO  
 Spectrometer Frequency 400.17

- 10.450
- 8.120
- 8.101
- 7.948
- 7.883
- 7.864
- 7.767
- 7.746
- 7.453
- 7.434
- 7.415
- 7.262
- 7.043
- 7.024
- 4.014
- 3.917
- 3.442
- 2.540
- 2.537

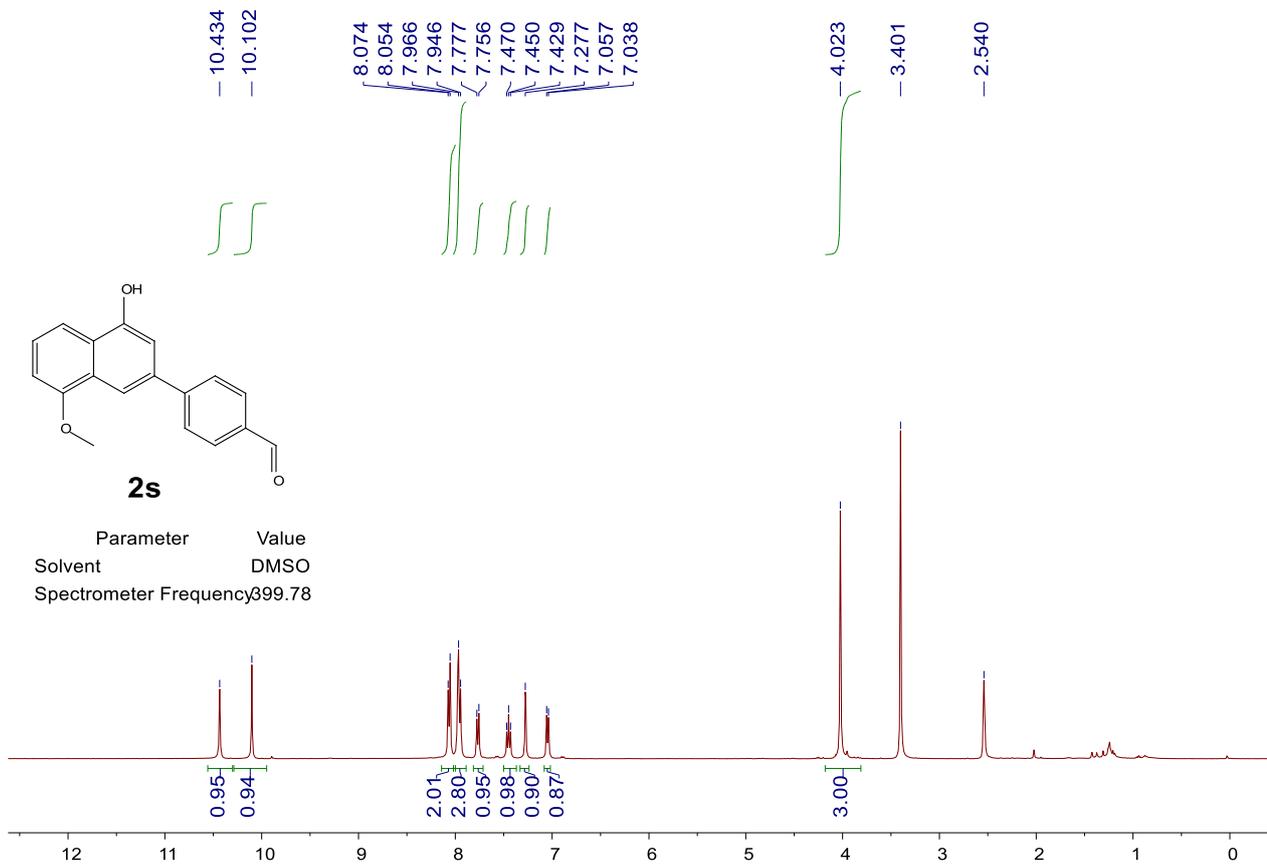


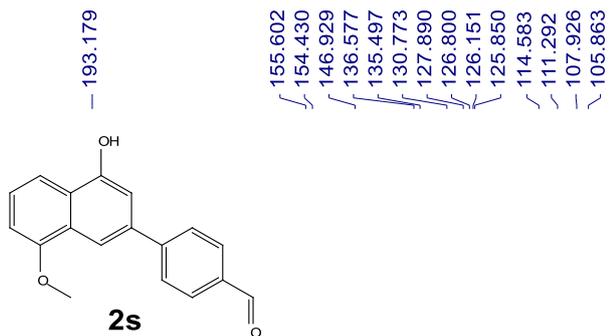


Parameter Value  
 Solvent DMSO  
 Spectrometer Frequency 100.62

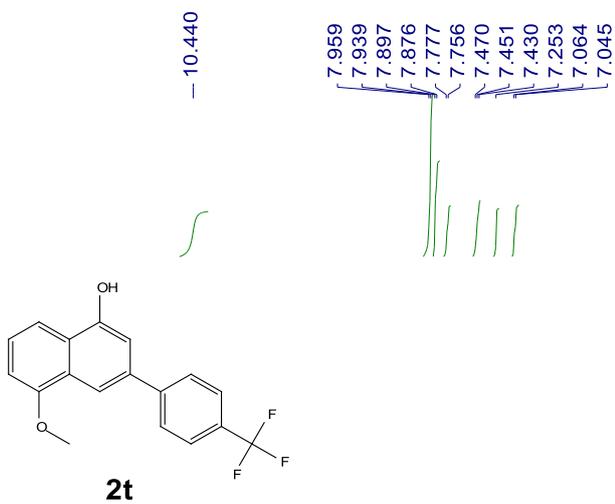
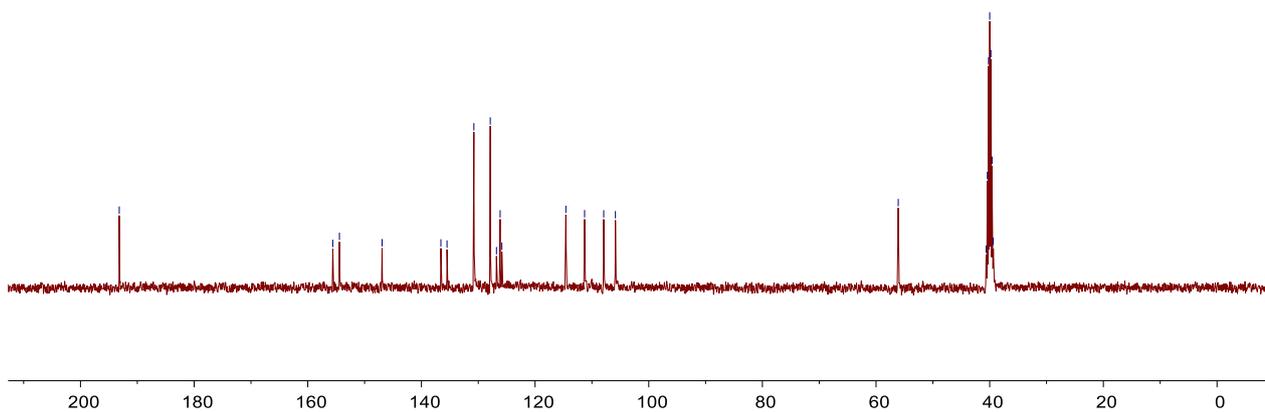


Parameter Value  
 Solvent DMSO  
 Spectrometer Frequency 399.78

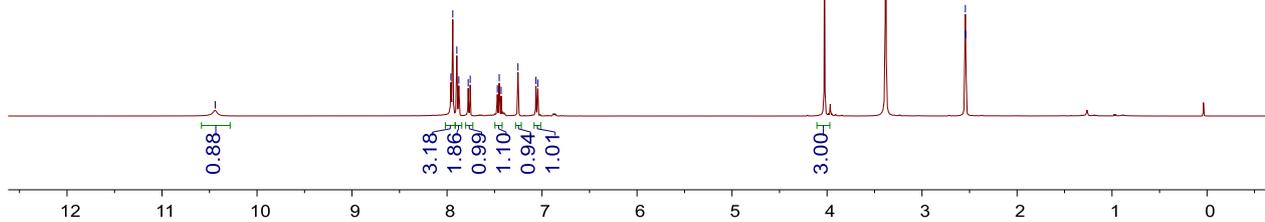


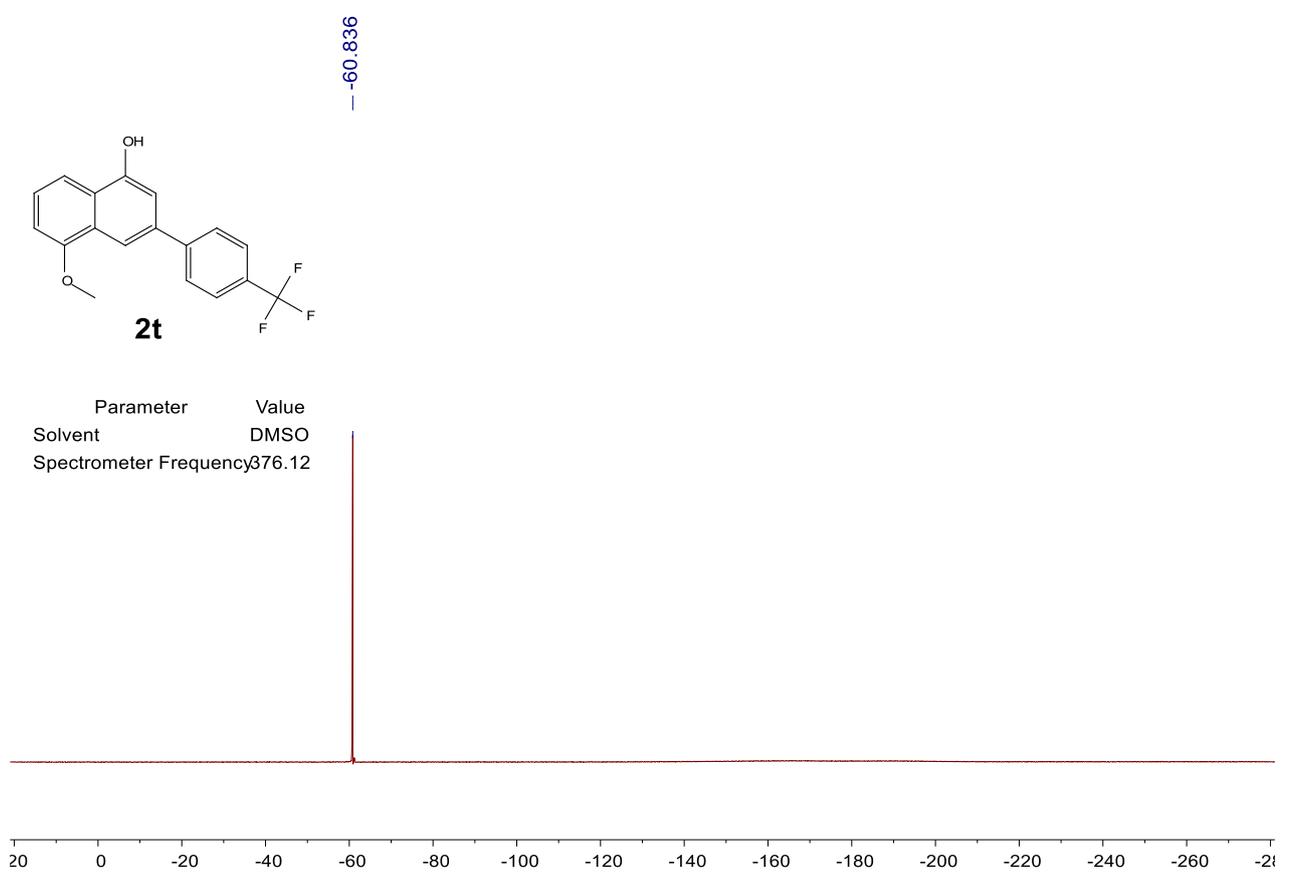
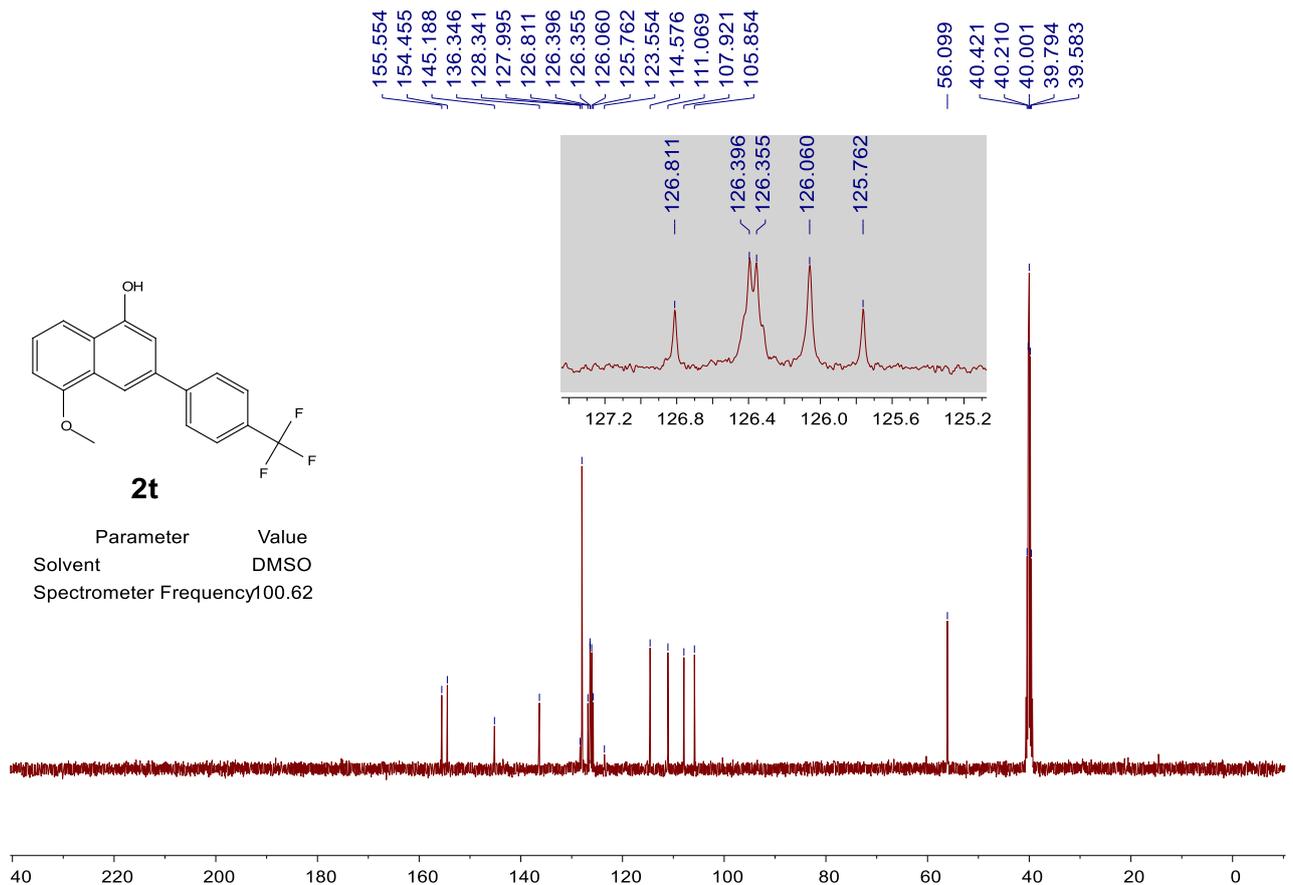


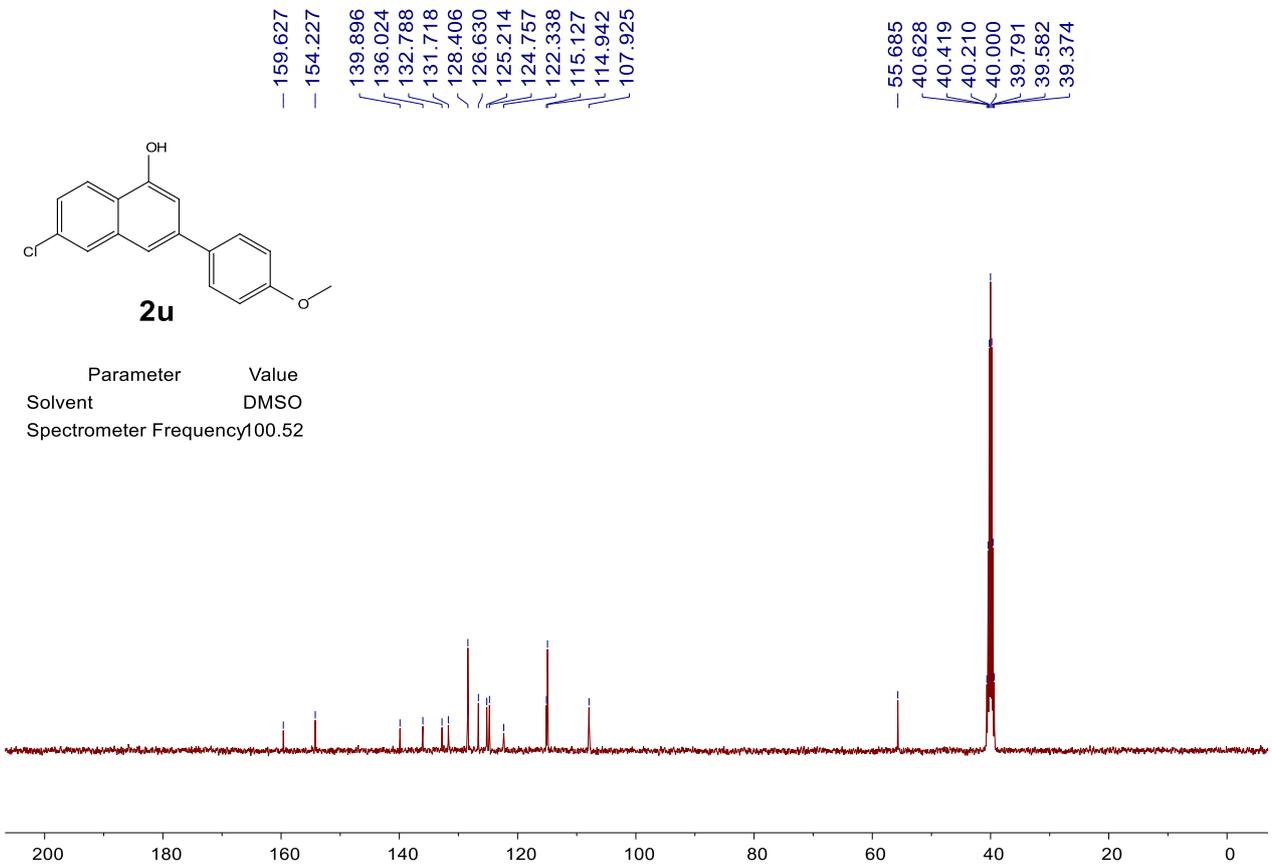
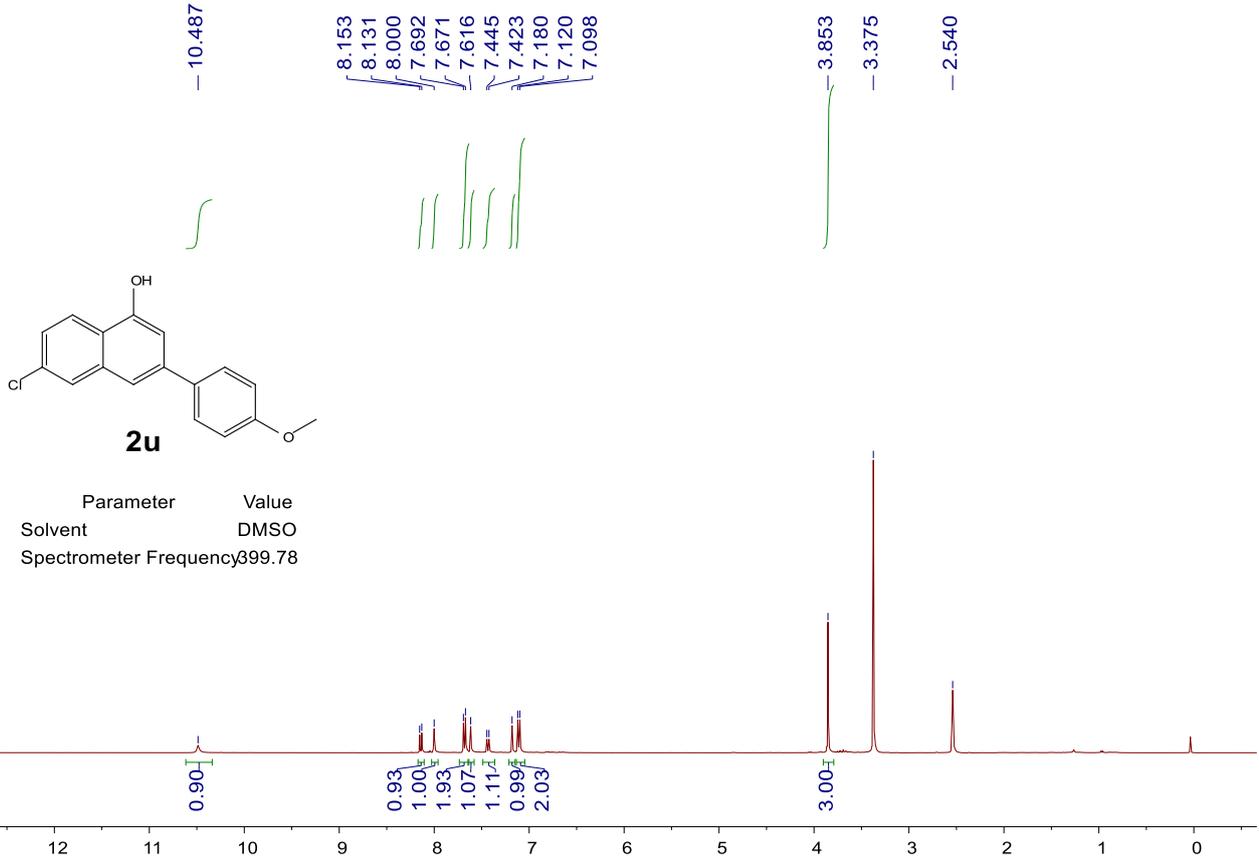
Parameter Value  
 Solvent DMSO  
 Spectrometer Frequency 100.52

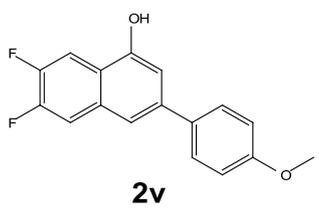
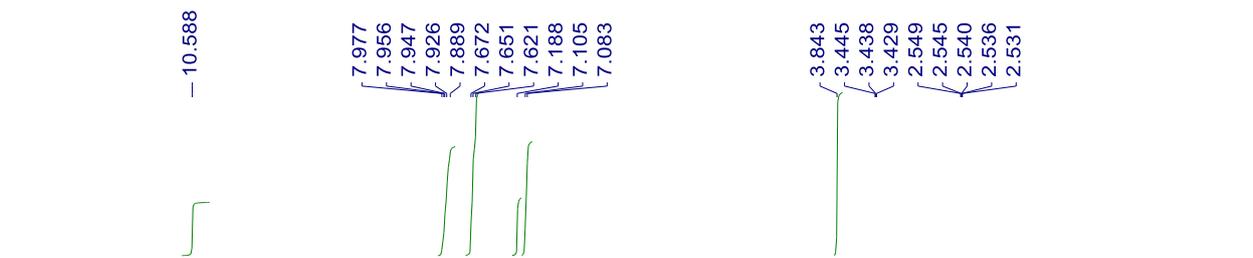


Parameter Value  
 Solvent DMSO  
 Spectrometer Frequency 399.78

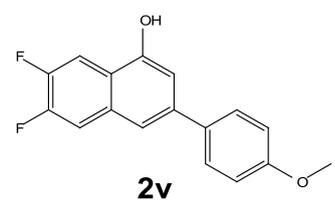
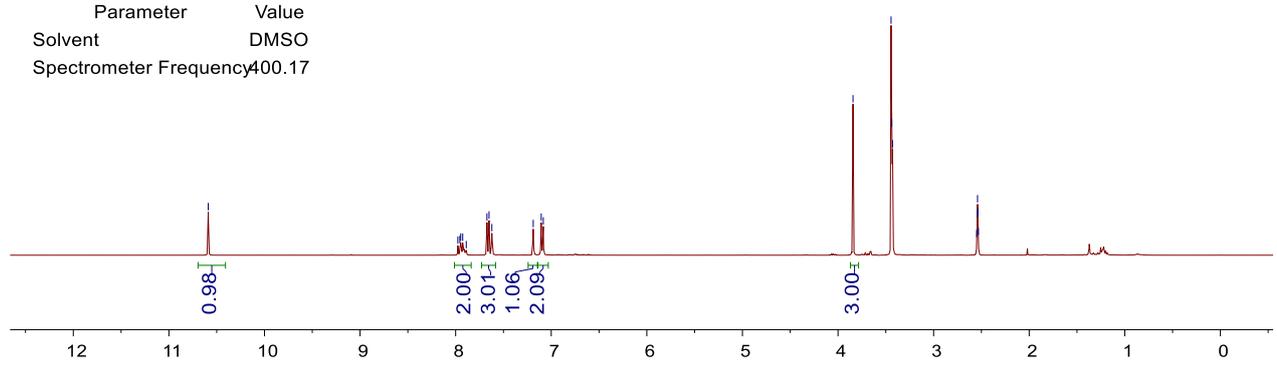




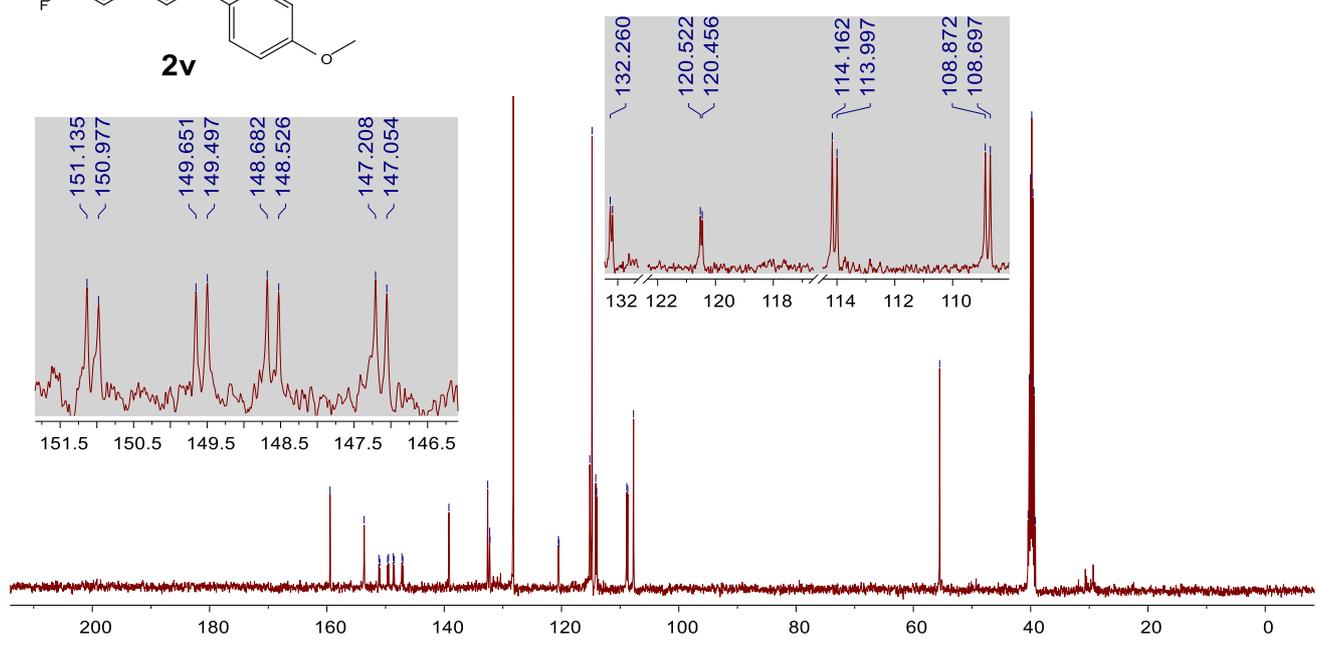


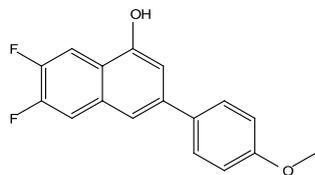


Parameter Value  
 Solvent DMSO  
 Spectrometer Frequency 400.17



Parameter Value  
 Solvent DMSO  
 Spectrometer Frequency 100.62

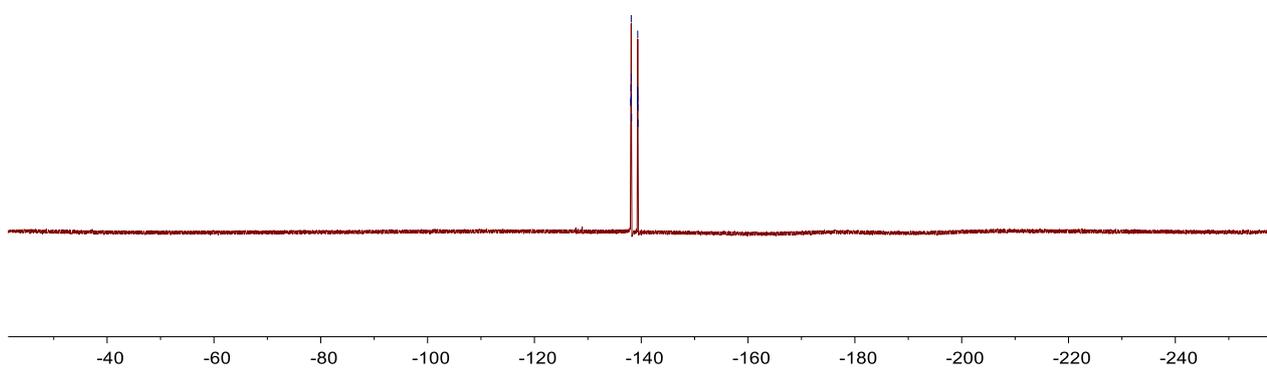




**2v**

Parameter Value  
Solvent DMSO  
Spectrometer Frequency 376.50

-138.062  
-138.085  
-138.092  
-138.118  
-138.143  
-138.151  
-138.174  
-139.283  
-139.305  
-139.314  
-139.339  
-139.363  
-139.372  
-139.395



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