

## One-pot synthesis of 5-phenylsulfonyl-3-arylisoxazolines and 3-arylisoxazoles from alkynes and (phenylsulfonyl)ethene

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### General Experimental

Unless otherwise noted, all chemicals were purchased from commercial suppliers (Aladdin) and used without further purification. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded at ambient temperature on a Bruker DPX-300 (<sup>1</sup>H: 300 MHz; <sup>13</sup>C: 75 MHz) or a Bruker AVANCE III 500 spectrometer (<sup>1</sup>H: 500 MHz; <sup>13</sup>C: 125 MHz). Chemical shifts are reported in  $\delta$  units, parts per million (ppm), and were referenced to CDCl<sub>3</sub> (7.26 or 77.0 ppm) as the internal standard. The coupling constants *J* are given in Hz. Column chromatography was performed using EM Silica gel 60 (300-400 mesh). The GC-MS analyses were performed on a Thermo Scientific™ equipment (TSQ 8000 Evo). Melting points (m.p.) are determined with an Optimelt MPA 100 apparatus and are not corrected. High-resolution mass spectrometry (HRMS) was performed on an Agilent Q-TOF 6540 MS instrument with an ESI source.

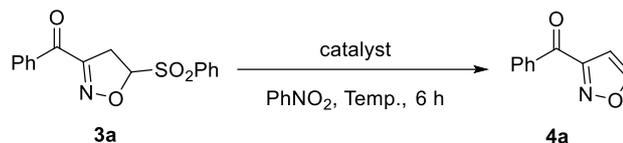
### Experimental Procedures, Spectral and Analytical data

#### General procedure for the synthesis of **3** and **4**

A sealed tube equipped with a magnetic stirrer bar was charged with alkyne **1a-m** (0.3 mmol), sulfonylethene **2** (0.6 mmol, 2.0 equiv), Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (0.6 mmol, 2.0 equiv), KI (0.3 mmol, 1.0 equiv) and PhNO<sub>2</sub> (2 ml) under N<sub>2</sub>. The mixture was then heated to 100 °C and stirred for 12 h. Upon the reaction completion, the resulting solution was quenched with saturated aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. The collected organic extracts were dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent to afford products **3a-m**.

When the 1,3-dipolar cycloaddition was complete, K<sub>2</sub>CO<sub>3</sub> (0.03 mmol, 0.1 equiv) was added, and the mixture was stirred at 100 °C for more 6 h. The mixture was cooled and extracted with EtOAc (3×10 ml). The collected organic extracts were dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography using petroleum ether/ethyl acetate as eluent to afford products **4**.

### Optimization of the reaction conditions for the synthesis of 4a



**Table S1.** Optimization of the aromization reaction.<sup>a</sup>

Entry	Catalyst	Temp. (°C)	Yield (%) <sup>b</sup>
1	HCl	100	28
2	H <sub>2</sub> SO <sub>4</sub>	100	46
3	TfOH	100	33
4	TsOH	100	37
5	FeCl <sub>3</sub>	100	25
6	Na <sub>2</sub> CO <sub>3</sub>	100	63
7	K <sub>2</sub> CO <sub>3</sub>	100	91
8	K <sub>3</sub> PO <sub>4</sub>	100	72
9	KOH	100	14
10	Et <sub>3</sub> N	100	24
11	DMAP	100	28
12	DIPEA	100	64
13	DBU	100	70
14	DABCO	100	66
15	K <sub>2</sub> CO <sub>3</sub>	80	81
16	K <sub>2</sub> CO <sub>3</sub>	60	39

<sup>a</sup>Reagents and conditions: **3a** (0.2 mmol, 1 equiv.), catalyst (10 mol%), PhNO<sub>2</sub> (2 ml), 6 h.

<sup>b</sup>Isolated yield.

### Characterization of products 3 and 4

*Phenyl(5-phenylsulfonyl-4,5-dihydroisoxazol-3-yl)methanone (3a)*. Light yellow solid (80 mg, 85%). M.p. 115~117 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.03 (dd, *J* = 11.9, 7.7 Hz, 4H), 7.71 (t, *J* = 7.3 Hz, 1H), 7.64 – 7.58 (m, 3H), 7.45 (t, *J* = 7.7 Hz, 2H), 5.57 (dd, *J* = 11.2, 4.8 Hz, 1H), 4.04 (dd, *J* = 19.3, 4.7 Hz, 1H), 3.83 (dd, *J* = 19.3, 11.2 Hz, 1H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 184.5, 157.2, 134.8 (two carbon), 134.2, 130.3, 129.8, 129.4, 128.5, 93.3, 36.7. HRMS *m/z* (ESI) calcd for C<sub>16</sub>H<sub>14</sub>NO<sub>4</sub>S (M+H)<sup>+</sup> 316.0638, found 316.0645.

*(5-Phenylsulfonyl-4,5-dihydroisoxazol-3-yl)(p-tolyl)methanone (3b)*. Light yellow solid (80 mg, 81%). M.p. 149~152 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.05 – 7.99 (m, 2H), 7.95 (d, *J* = 8.3 Hz, 2H), 7.74 – 7.67 (m, 1H), 7.61 (ddd, *J* = 8.5, 6.5, 1.7 Hz, 2H), 7.29 – 7.17 (m, 2H), 5.56 (dd, *J* = 11.1, 4.9 Hz, 1H), 4.03 (dd, *J* = 19.4, 4.9 Hz, 1H), 3.83 (dd, *J* = 19.4, 11.1 Hz, 1H), 2.41 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 184.0, 157.3, 145.5, 138.4, 134.8, 132.4, 130.4, 129.8, 129.4, 129.3, 93.3, 37.0, 21.8. HRMS *m/z* (ESI) calcd for C<sub>17</sub>H<sub>16</sub>NO<sub>4</sub>S (M+H)<sup>+</sup> 330.0795, found 330.0803.

(4-Nitrophenyl)(5-phenylsulfonyl-4,5-dihydroisoxazol-3-yl)methanone (**3c**). Light yellow solid (59 mg, 55%). M.p. 182~185 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.35 – 8.22 (m, 4H), 8.02 (dd, *J* = 5.3, 3.3 Hz, 2H), 7.75 (ddd, *J* = 6.6, 3.9, 1.3 Hz, 1H), 7.69 – 7.59 (m, 2H), 5.60 (dd, *J* = 11.2, 4.9 Hz, 1H), 4.10 (dd, *J* = 19.4, 4.9 Hz, 1H), 3.83 (dd, *J* = 19.4, 11.2 Hz, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 183.1, 157.4, 150.8, 139.4, 135.0, 134.8, 131.4, 129.8, 129.5, 123.6, 93.6, 36.0. HRMS *m/z* (ESI) calcd for C<sub>16</sub>H<sub>13</sub>N<sub>2</sub>O<sub>6</sub>S (M+H)<sup>+</sup> 361.0489, found 361.0496.

(4-Chlorophenyl)(5-phenylsulfonyl-4,5-dihydroisoxazol-3-yl)methanone (**3d**). Light yellow solid (73 mg, 70%). M.p. 161~163 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.07 – 7.98 (m, 4H), 7.72 (ddd, *J* = 6.6, 3.9, 1.3 Hz, 1H), 7.65 – 7.56 (m, 2H), 7.47 – 7.38 (m, 2H), 5.57 (dd, *J* = 11.2, 4.9 Hz, 1H), 4.04 (dd, *J* = 19.4, 4.9 Hz, 1H), 3.82 (dd, *J* = 19.4, 11.2 Hz, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 183.2, 157.2, 141.0, 134.8, 133.1, 131.7, 129.8, 129.4, 129.3, 128.9, 93.3, 36.6. HRMS *m/z* (ESI) calcd for C<sub>16</sub>H<sub>13</sub>ClNO<sub>4</sub>S (M+H)<sup>+</sup> 350.0248, found 350.0259.

(4-Fluorophenyl)(5-phenylsulfonyl-4,5-dihydroisoxazol-3-yl)methanone (**3e**). Light yellow solid (59 mg, 59%). M.p. 143~146 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.18 – 8.08 (m, 2H), 8.06 – 7.99 (m, 2H), 7.76 – 7.68 (m, 1H), 7.65 – 7.57 (m, 2H), 7.19 – 7.08 (m, 2H), 5.57 (dd, *J* = 11.1, 4.8 Hz, 1H), 4.05 (dd, *J* = 19.4, 4.8 Hz, 1H), 3.83 (dd, *J* = 19.4, 11.1 Hz, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 182.8, 166.5 (d, *J* = 257.4 Hz), 157.3, 134.9, 133.2, 133.1, 131.2 (d, *J* = 2.9 Hz), 129.8, 129.4, 115.8 (d, *J* = 22.0 Hz), 93.3, 36.7. HRMS *m/z* (ESI) calcd for C<sub>16</sub>H<sub>13</sub>FNO<sub>4</sub>S (M+H)<sup>+</sup> 334.0544, found 334.0552.

4-(5-Phenylsulfonyl-4,5-dihydroisoxazole-3-carbonyl)benzotrile (**3f**). Light yellow solid (63 mg, 62%). M.p. 156~159 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.21 – 8.16 (m, 2H), 8.04 – 7.99 (m, 2H), 7.78 – 7.72 (m, 3H), 7.62 (dd, *J* = 10.8, 4.9 Hz, 2H), 5.59 (dd, *J* = 11.2, 4.8 Hz, 1H), 4.07 (dd, *J* = 19.3, 4.8 Hz, 1H), 3.82 (dd, *J* = 19.3, 11.2 Hz, 1H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 183.3, 157.3, 137.9, 135.0, 134.8, 132.2, 130.6, 129.7, 129.5, 117.7, 117.2, 93.5, 36.0. HRMS *m/z* (ESI) calcd for C<sub>17</sub>H<sub>13</sub>N<sub>2</sub>O<sub>4</sub>S (M+H)<sup>+</sup> 341.0591, found 341.0598.

(4-Methoxyphenyl)(5-phenylsulfonyl-4,5-dihydroisoxazol-3-yl)methanone (**3g**). Light yellow solid (77 mg, 75%). M.p. 180~183 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.11 – 8.05 (m, 2H), 8.05 – 7.99 (m, 2H), 7.74 – 7.67 (m, 1H), 7.65 – 7.57 (m, 2H), 6.97 – 6.90 (m, 2H), 5.55 (dd, *J* = 11.1, 4.8 Hz, 1H), 4.03 (dd, *J* = 19.4, 4.9 Hz, 1H), 3.88 (s, 3H), 3.83 (dd, *J* = 19.4, 11.1 Hz, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 182.6, 164.7, 157.3, 135.0, 134.8, 132.9, 129.8, 129.4, 127.8, 113.8, 93.2, 55.6, 37.2. HRMS *m/z* (ESI) calcd for C<sub>17</sub>H<sub>16</sub>NO<sub>5</sub>S (M+H)<sup>+</sup> 346.0744, found 346.0750.

(2-Methoxyphenyl)(5-phenylsulfonyl-4,5-dihydroisoxazol-3-yl)methanone (**3h**). Light yellow solid (73 mg, 71%). M.p. 140~143 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.99 (d, *J* = 7.4 Hz, 2H), 7.71 (t, *J* = 7.3 Hz, 1H), 7.59 (t, *J* = 7.7 Hz, 2H), 7.54 – 7.39 (m, 2H), 7.02 – 6.94 (m, 2H), 5.56 (dd, *J* = 11.2, 5.1 Hz, 1H), 4.03 (dd, *J* = 19.2, 5.1 Hz, 1H), 3.85 (s, 3H), 3.78 (dd, *J* = 19.2, 11.2 Hz, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 186.5, 158.6, 158.1, 135.1, 134.7, 134.2, 130.4, 129.7, 129.3, 126.4, 120.3, 111.8, 93.9, 55.8, 35.8. HRMS *m/z* (ESI) calcd for C<sub>17</sub>H<sub>16</sub>NO<sub>5</sub>S (M+H)<sup>+</sup> 346.0744, found 346.0757.

(2-Chlorophenyl)(5-phenylsulfonyl-4,5-dihydroisoxazol-3-yl)methanone (**3i**). Light yellow solid (69 mg, 66%). M.p. 146~149 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.99 (dd, *J* = 5.2, 3.4 Hz, 2H), 7.77 – 7.69 (m, 1H), 7.60 (dd, *J* = 10.5, 4.7 Hz, 2H), 7.47 – 7.38 (m, 3H), 7.37 – 7.30 (m, 1H), 5.62 (dd, *J* = 11.3, 5.1 Hz, 1H), 4.02 (dd, *J* = 19.4, 5.1 Hz, 1H), 3.78 (dd, *J* = 19.4, 11.3 Hz, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 185.9, 157.8, 135.8, 134.9, 134.6, 132.7, 132.1, 130.4, 130.3, 129.9, 129.4, 126.5, 94.4, 35.1. HRMS *m/z* (ESI) calcd for C<sub>16</sub>H<sub>13</sub>ClNO<sub>4</sub>S (M+H)<sup>+</sup> 350.0248, found 350.0255.

(2-Bromophenyl)(5-phenylsulfonyl-4,5-dihydroisoxazol-3-yl)methanone (**3j**). Light yellow solid (73 mg, 62%). M.p. 155~159 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.99 (dd, *J* = 5.2, 3.3 Hz, 2H), 7.77 – 7.68 (m, 1H), 7.64 – 7.53 (m, 3H), 7.43 – 7.31 (m, 3H), 5.63 (dd, *J* = 11.3, 5.1 Hz, 1H), 4.03 (dd, *J* = 19.3, 5.1 Hz, 1H), 3.78 (dd, *J*

= 19.3, 11.3 Hz, 1H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  186.6, 157.7, 137.8, 134.9, 134.6, 133.6, 132.7, 130.2, 129.9, 129.4, 127.1, 120.1, 94.5, 35.1. HRMS  $m/z$  (ESI) calcd for  $\text{C}_{16}\text{H}_{13}\text{BrNO}_4\text{S}$  ( $\text{M}+\text{H}$ ) $^+$  393.9743, found 393.9753.

*(3-Methoxyphenyl)(5-(phenylsulfonyl)-4,5-dihydroisoxazol-3-yl)methanone (3k)*. Light yellow solid (74 mg, 72%). M.p. 142~145 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00 (dd,  $J = 5.2, 3.3$  Hz, 2H), 7.72 (ddd,  $J = 6.7, 3.9, 1.3$  Hz, 1H), 7.65 – 7.56 (m, 2H), 7.52 (d,  $J = 8.0$  Hz, 1H), 7.45 – 7.38 (m, 1H), 7.24 (dd,  $J = 10.6, 4.8$  Hz, 2H), 5.58 (dd,  $J = 11.1, 4.7$  Hz, 1H), 4.02 (dd,  $J = 19.4, 4.7$  Hz, 1H), 3.81 (dd,  $J = 19.4, 11.1$  Hz, 1H), 2.41 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  187.6, 158.2, 138.8, 135.1, 134.80 (two carbons), 132.4, 131.5, 131.0, 129.9, 129.4, 125.4, 93.9, 36.1 20.6. HRMS  $m/z$  (ESI) calcd for  $\text{C}_{17}\text{H}_{16}\text{NO}_5\text{S}$  ( $\text{M}+\text{H}$ ) $^+$  346.0744, found 346.0756.

*Naphthalen-1-yl(5-phenylsulfonyl-4,5-dihydroisoxazol-3-yl)methanone (3l)*. Light yellow solid (81 mg, 74%). M.p. 172~175 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.45 (d,  $J = 8.6$  Hz, 1H), 8.08 – 8.01 (m, 3H), 7.92 – 7.84 (m, 2H), 7.75 – 7.69 (m, 1H), 7.61 (ddd,  $J = 8.3, 7.2, 1.5$  Hz, 3H), 7.58 – 7.53 (m, 1H), 7.49 (dd,  $J = 8.1, 7.4$  Hz, 1H), 5.63 (dd,  $J = 11.2, 4.5$  Hz, 1H), 4.12 (dd,  $J = 19.3, 4.6$  Hz, 1H), 3.92 (dd,  $J = 19.3, 11.2$  Hz, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  186.9, 158.7, 134.7 (two carbons), 134.2, 133.6, 132.2, 132.0, 130.4, 129.9, 129.4, 128.6, 128.4, 126.7, 125.0, 124.1, 93.9, 36.4. HRMS  $m/z$  (ESI) calcd for  $\text{C}_{20}\text{H}_{16}\text{NO}_4\text{S}$  ( $\text{M}+\text{H}$ ) $^+$  366.0795, found 366.0806.

*(5-Phenylsulfonyl-4,5-dihydroisoxazol-3-yl)(thiophen-2-yl)methanone (3m)*. Light yellow solid (51 mg, 53%). M.p. 126~129 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.14 (dd,  $J = 3.9, 1.1$  Hz, 1H), 8.04 – 7.99 (m, 2H), 7.77 (dd,  $J = 4.9, 1.1$  Hz, 1H), 7.73 – 7.69 (m, 1H), 7.63 – 7.59 (m, 2H), 7.15 (dd,  $J = 4.9, 4.0$  Hz, 1H), 5.57 (dd,  $J = 11.3, 4.9$  Hz, 1H), 4.03 (dd,  $J = 19.3, 4.9$  Hz, 1H), 3.79 (dd,  $J = 19.3, 11.3$  Hz, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  175.8, 157.1, 140.4, 136.6, 136.5, 134.9, 134.8, 129.8, 129.4, 128.6, 93.5, 36.3. HRMS  $m/z$  (ESI) calcd for  $\text{C}_{14}\text{H}_{12}\text{NO}_4\text{S}_2$  ( $\text{M}+\text{H}$ ) $^+$  322.0202, found 322.0217.

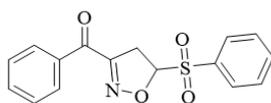
*Isoxazol-3-yl(phenyl)methanone (4a)*. Yellow oil (40 mg, 77% for two steps).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.54 (d,  $J = 1.5$  Hz, 1H), 8.30 (d,  $J = 7.6$  Hz, 2H), 7.64 (t,  $J = 7.4$  Hz, 1H), 7.52 (t,  $J = 7.8$  Hz, 2H), 6.90 (d,  $J = 1.5$  Hz, 1H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  185.4, 160.8, 159.0, 135.6, 134.0, 130.6, 128.5, 105.5. HRMS  $m/z$  (ESI) calcd for  $\text{C}_{10}\text{H}_8\text{NO}_2$  ( $\text{M}+\text{H}$ ) $^+$  174.0550, found 174.0554.

*Isoxazol-3-yl(p-tolyl)methanone (4b)*. Yellow oil (39 mg, 70% for two steps).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.53 (d,  $J = 1.6$  Hz, 1H), 8.25 – 8.20 (m, 2H), 7.32 (d,  $J = 8.0$  Hz, 2H), 6.90 (d,  $J = 1.7$  Hz, 1H), 2.45 (s, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  185.0, 161.0, 158.9, 145.2, 133.2, 130.8, 129.3, 105.5, 21.8. HRMS  $m/z$  (ESI) calcd for  $\text{C}_{11}\text{H}_{10}\text{NO}_2$  ( $\text{M}+\text{H}$ ) $^+$  188.0706, found 188.0715.

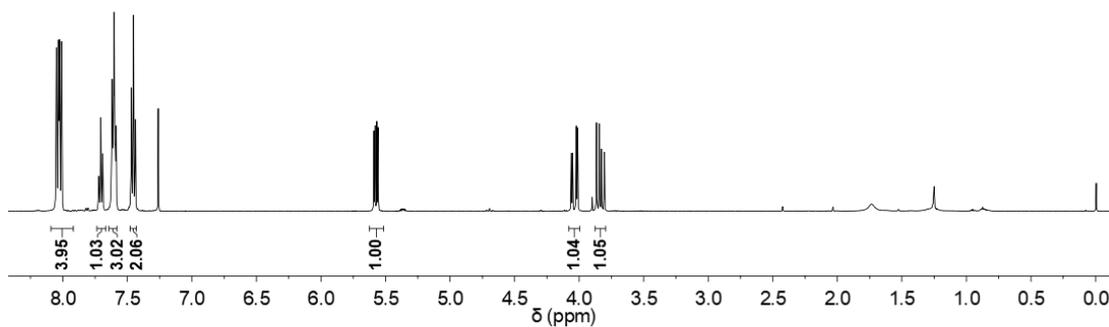
*Isoxazol-3-yl(4-nitrophenyl)methanone (4c)*. Yellow oil (27 mg, 41% for two steps).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.60 (d,  $J = 1.7$  Hz, 1H), 8.53 – 8.49 (m, 2H), 8.38 – 8.34 (m, 2H), 6.98 (d,  $J = 1.7$  Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  183.8, 160.5, 159.6, 150.7, 140.1, 131.7, 123.6, 105.5. HRMS  $m/z$  (ESI) calcd for  $\text{C}_{10}\text{H}_7\text{N}_2\text{O}_4$  ( $\text{M}+\text{H}$ ) $^+$  219.0400, found 219.0409.

# Copies of <sup>1</sup>H and <sup>13</sup>C NMR Spectra

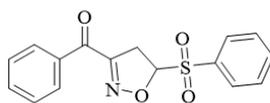
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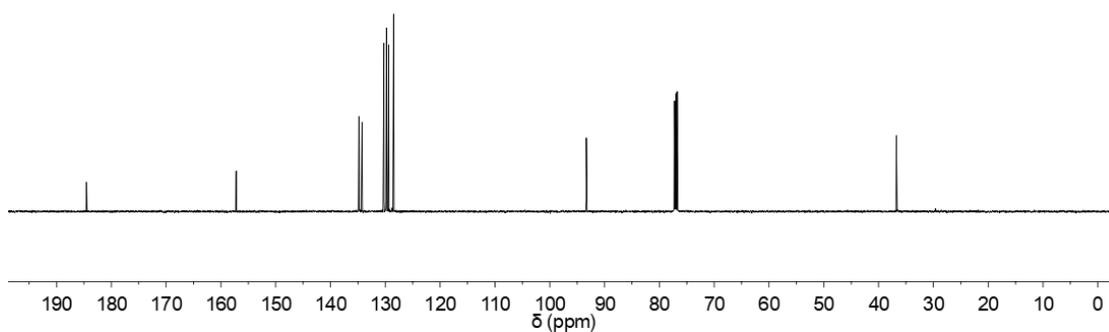
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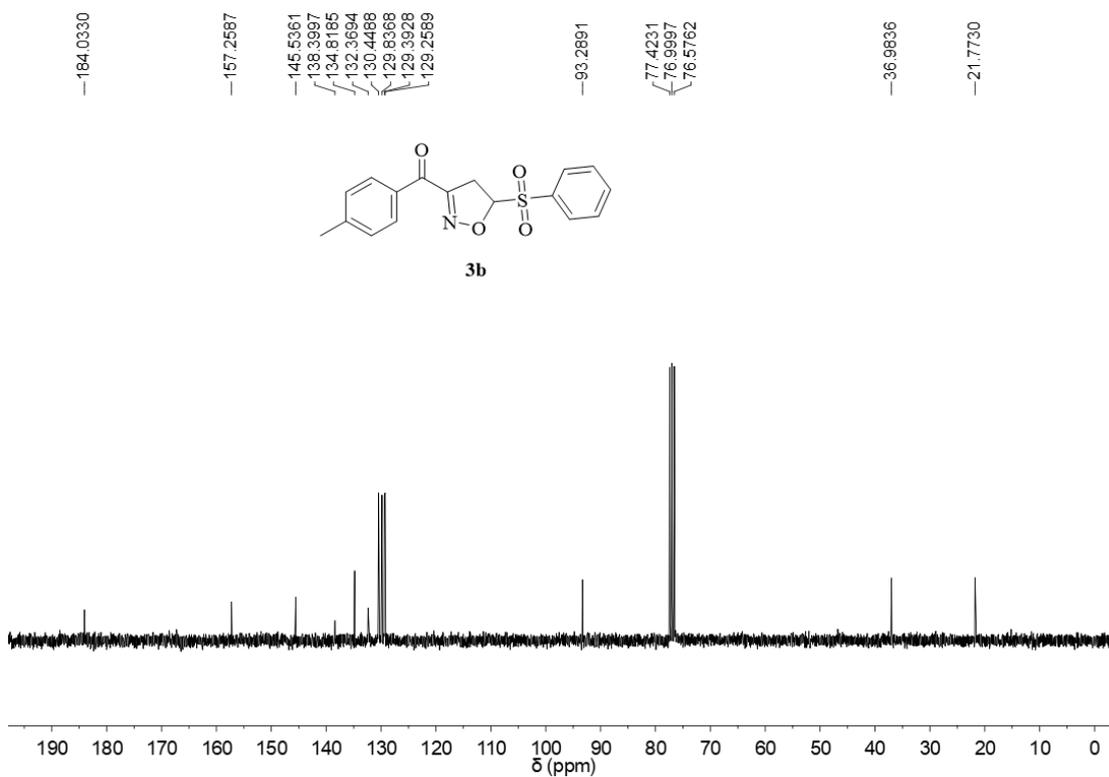
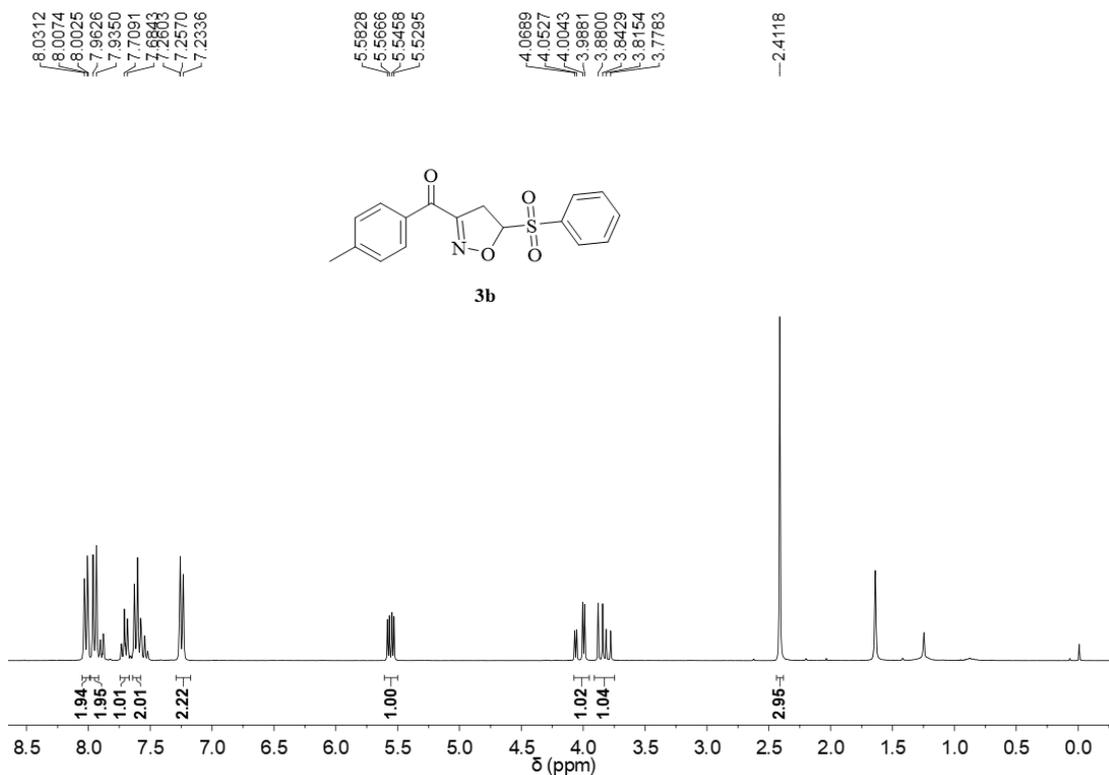


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**3a**

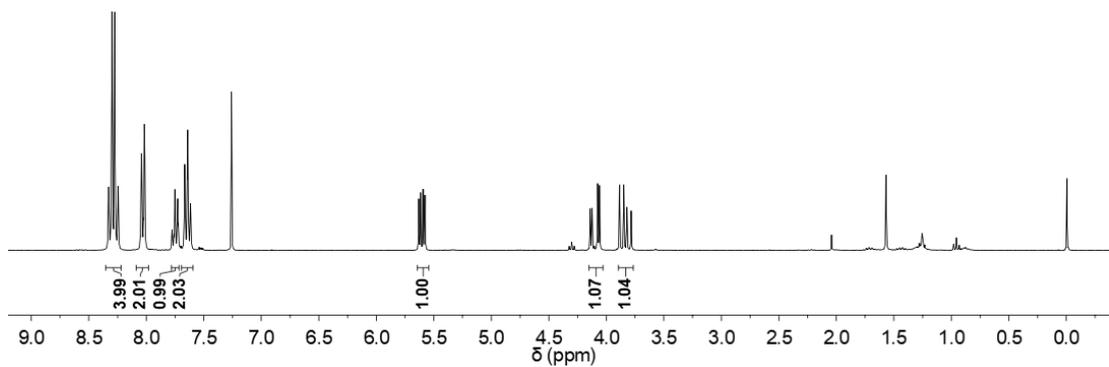
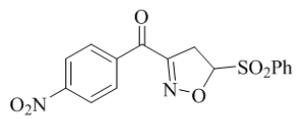




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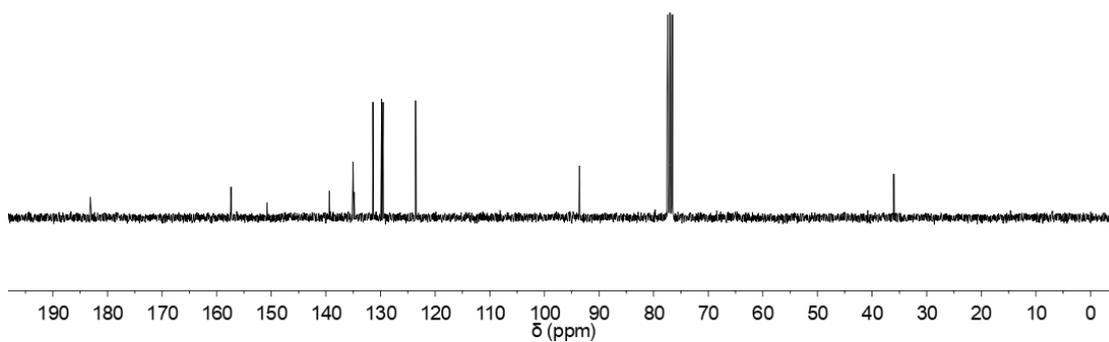
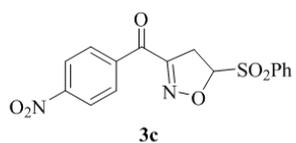
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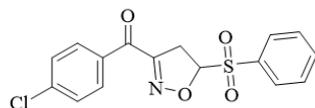
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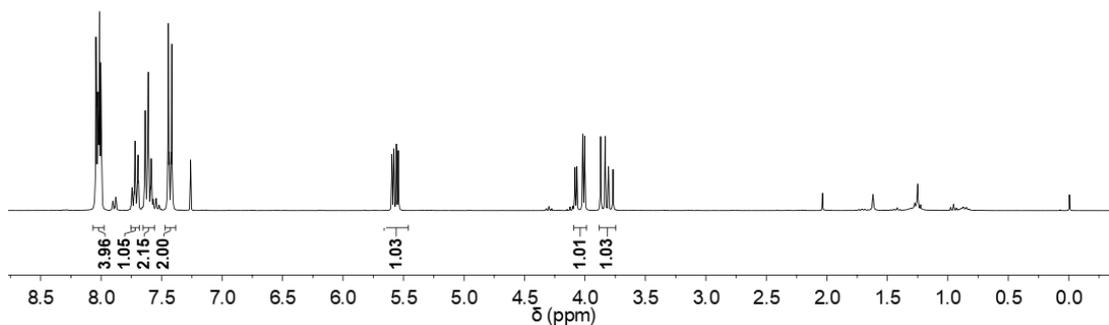
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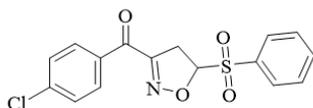
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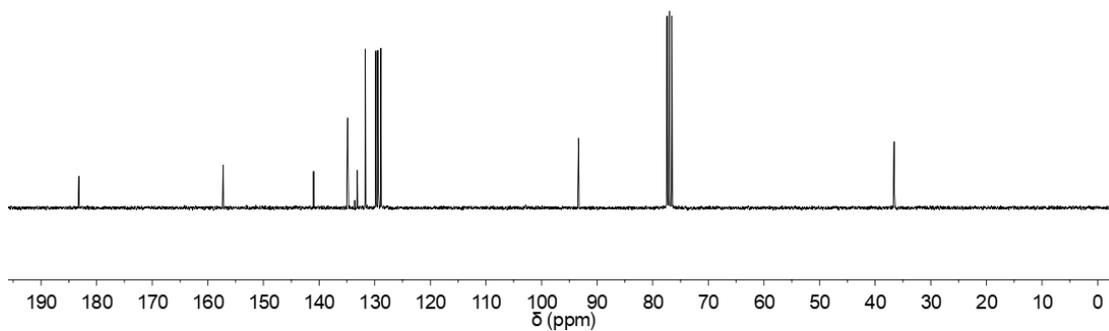
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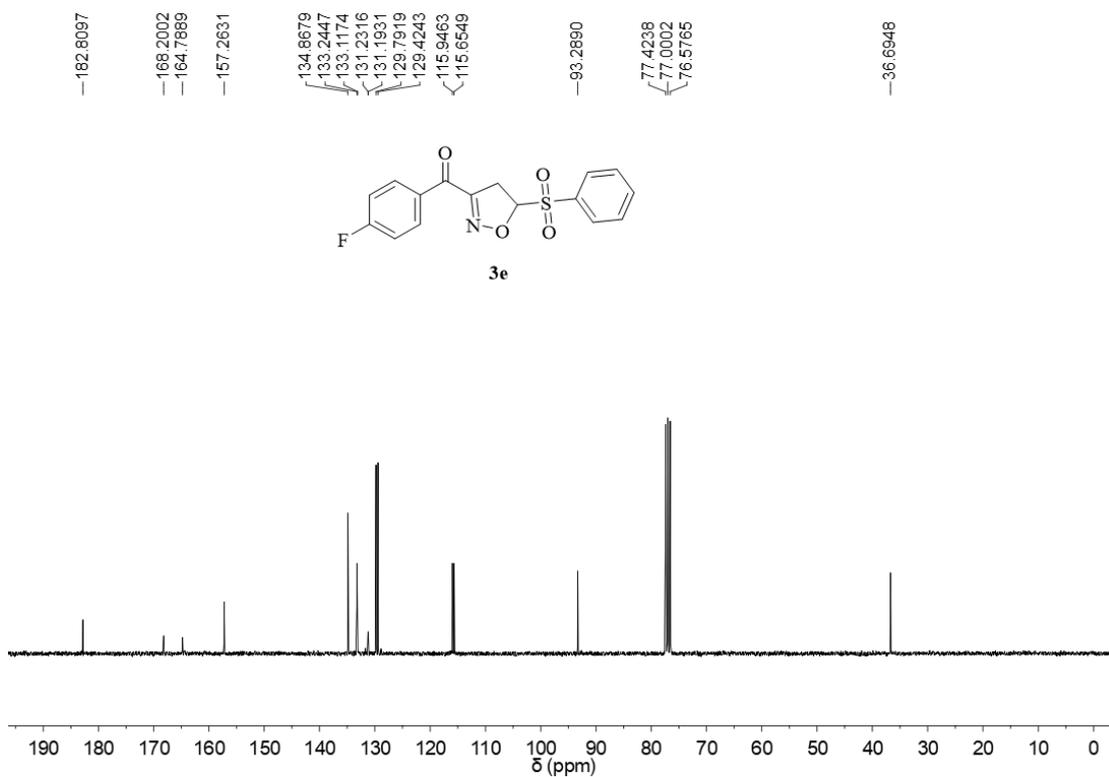
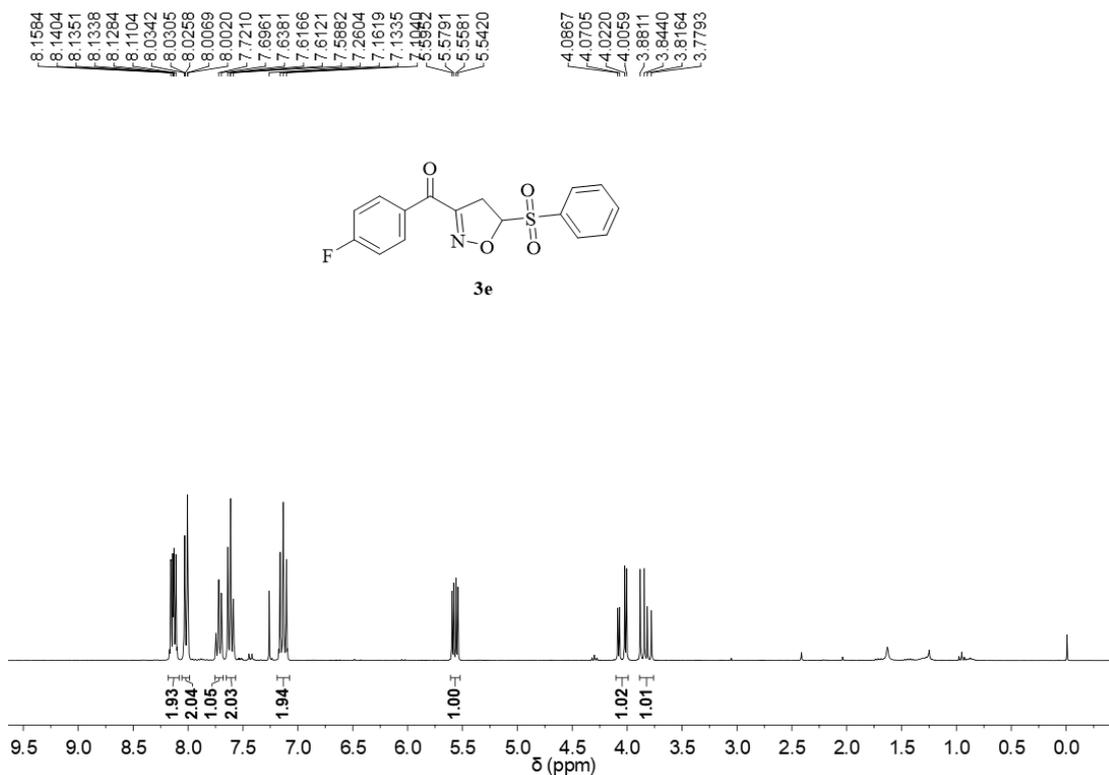


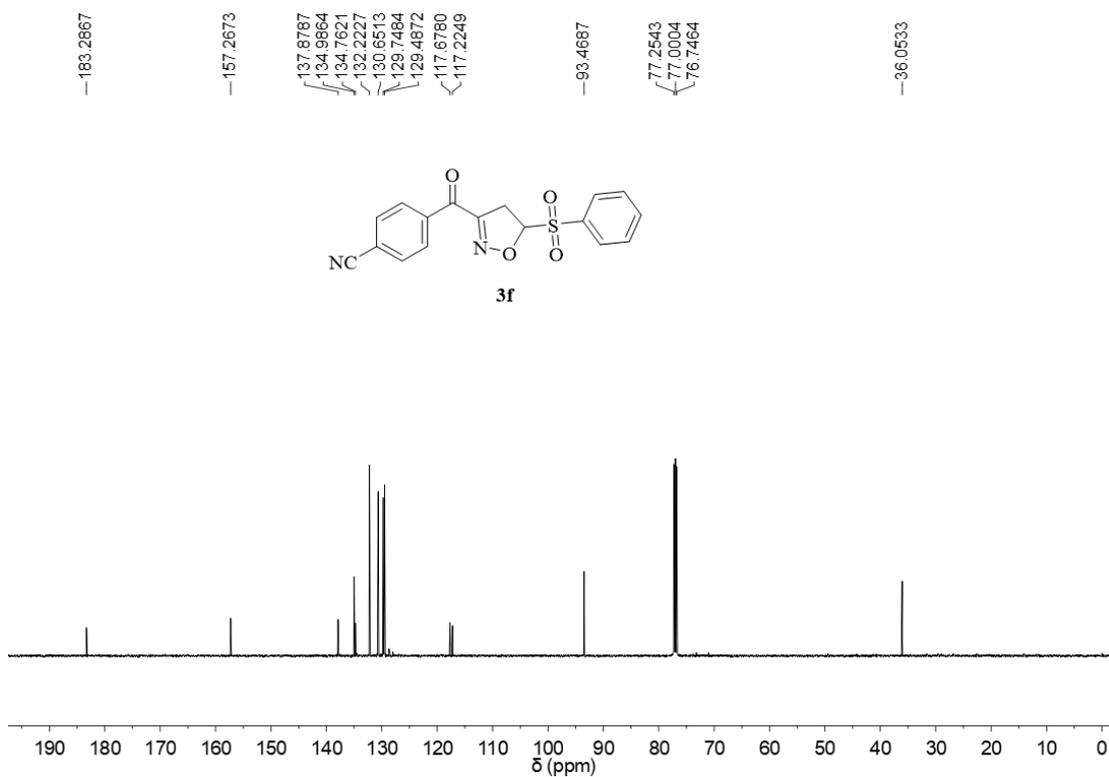
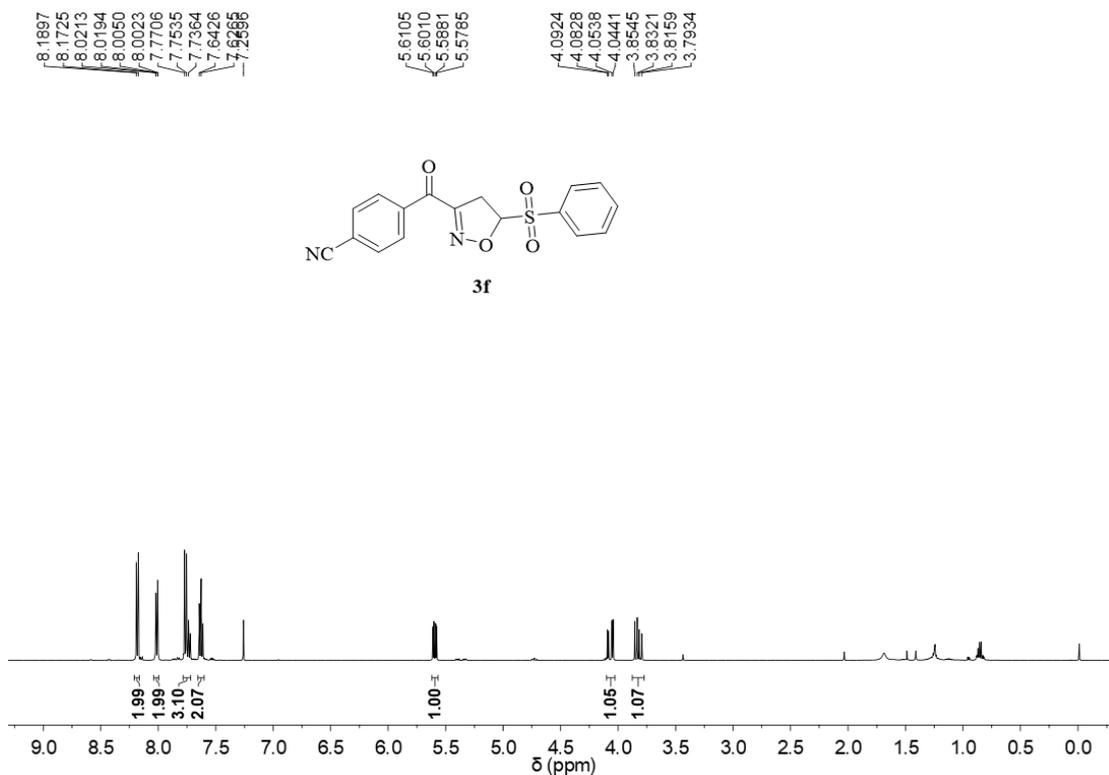
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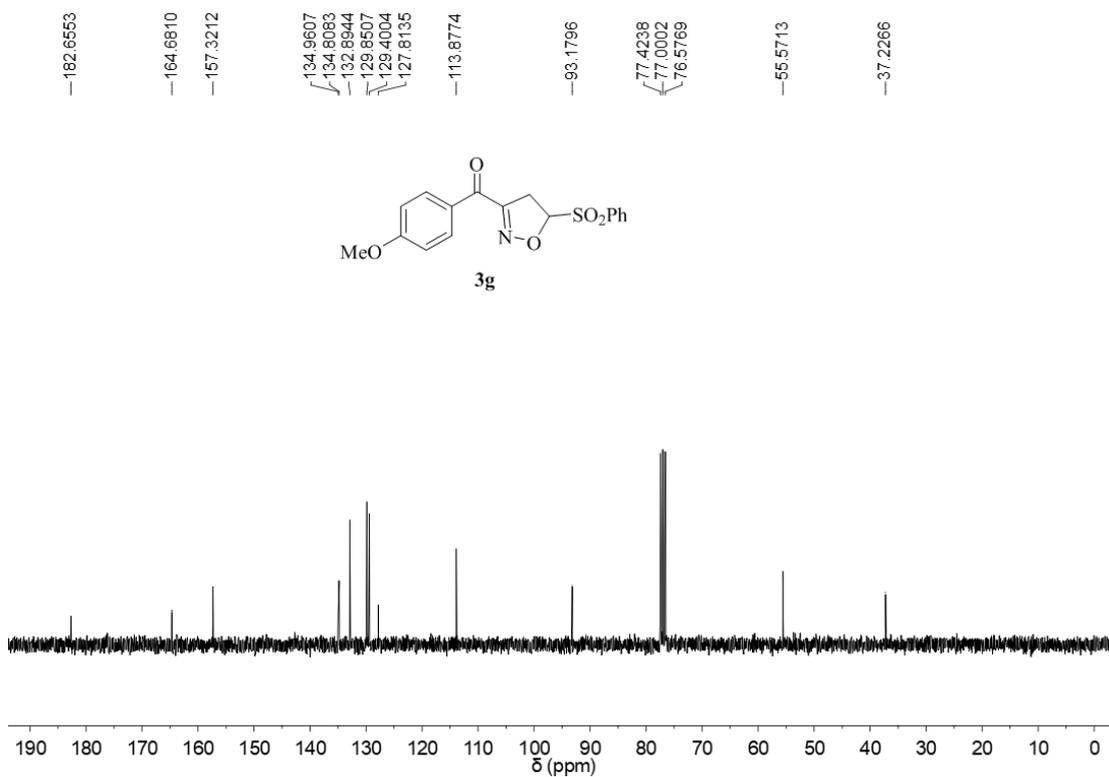
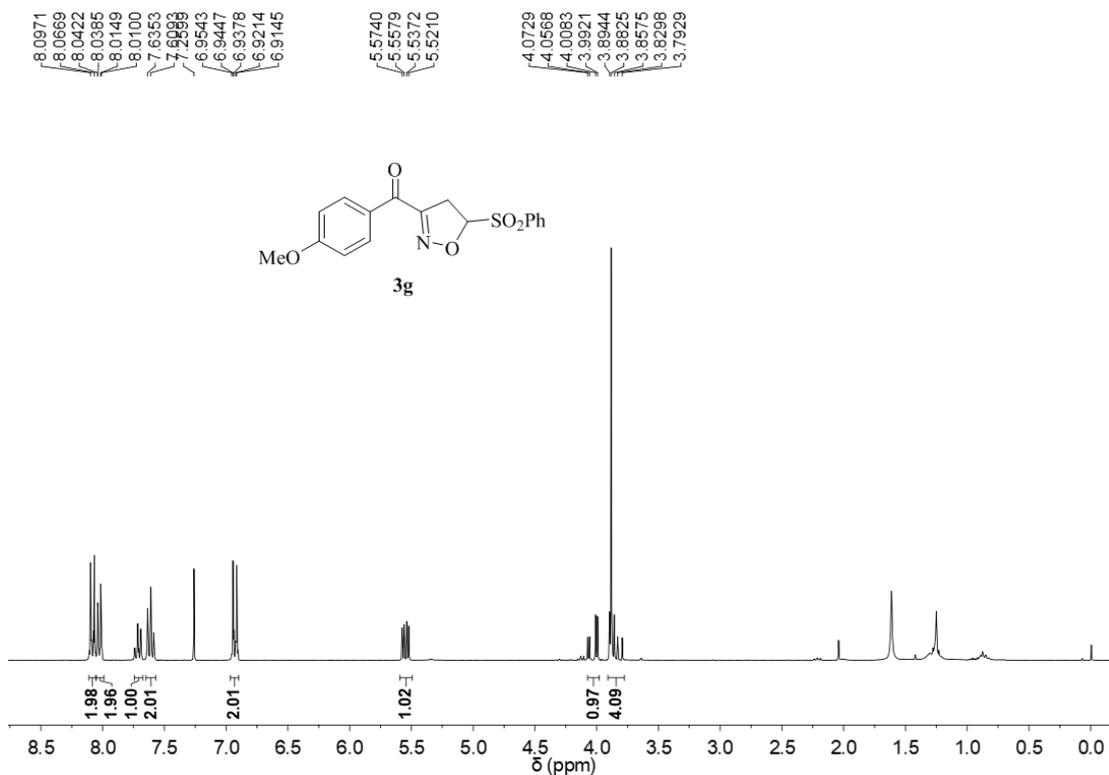


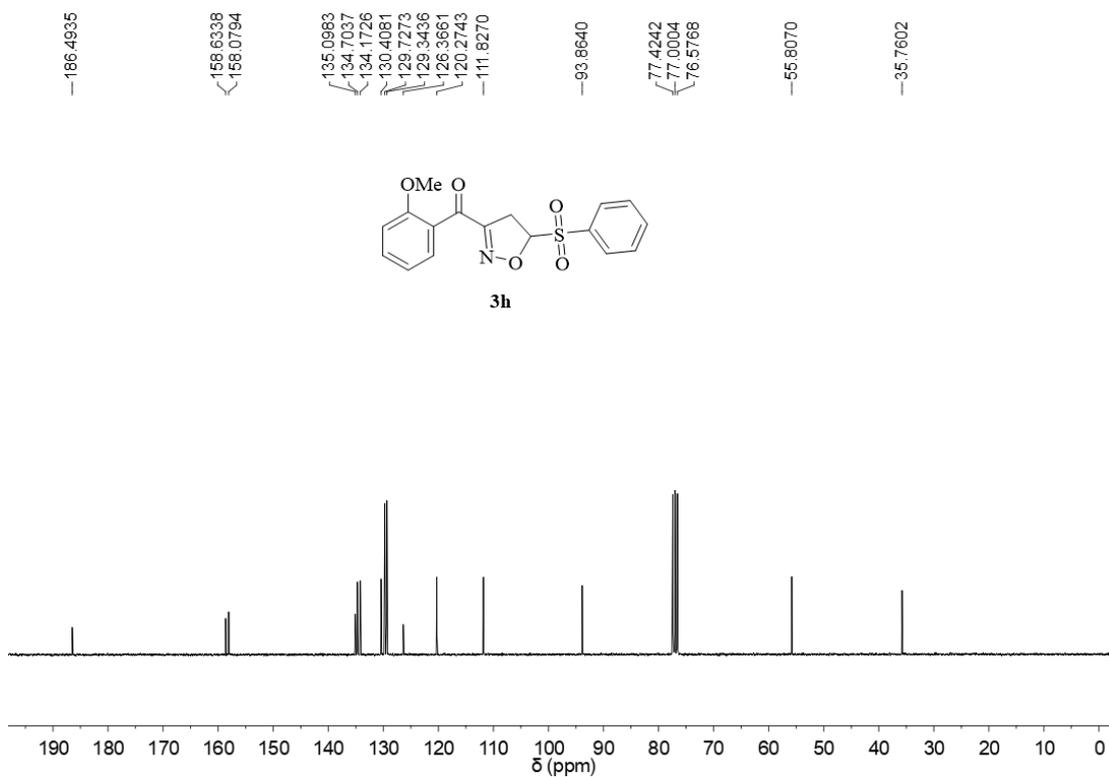
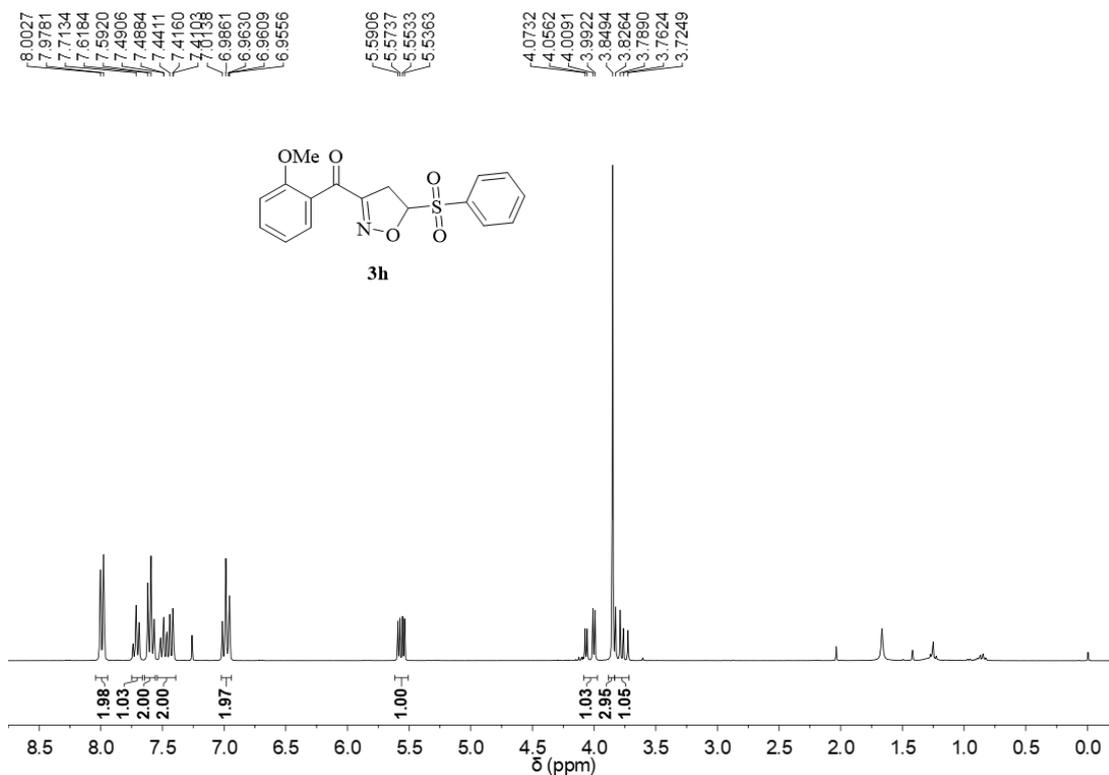
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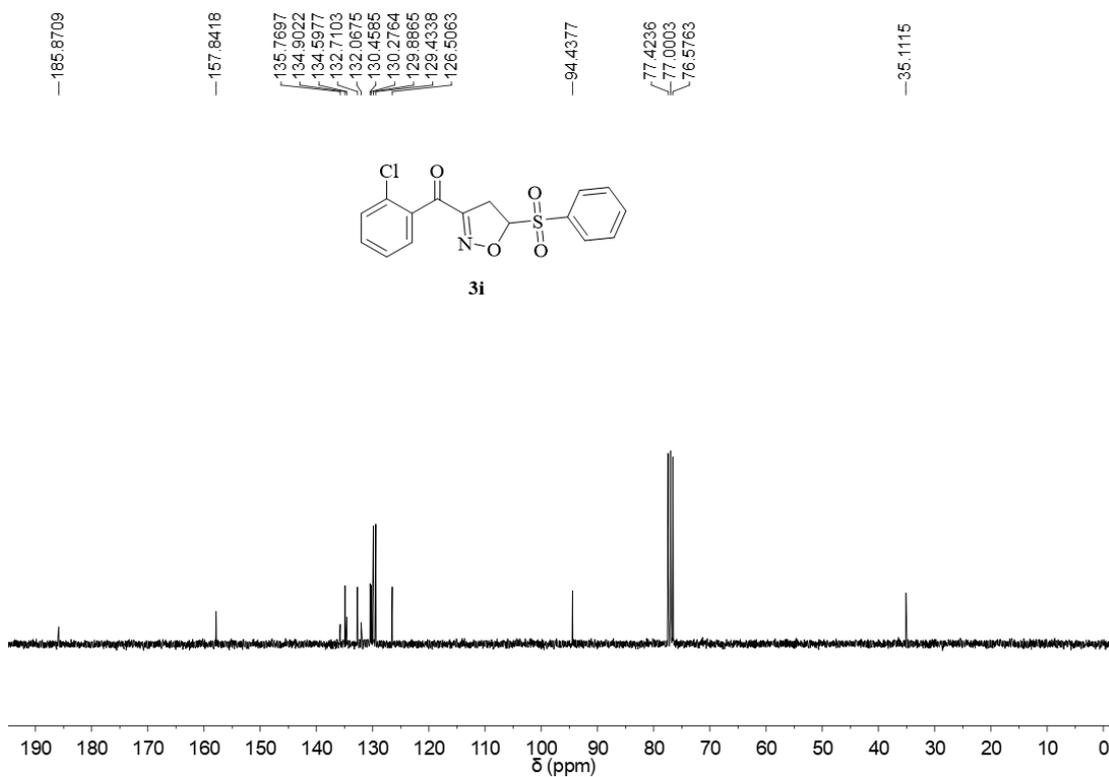
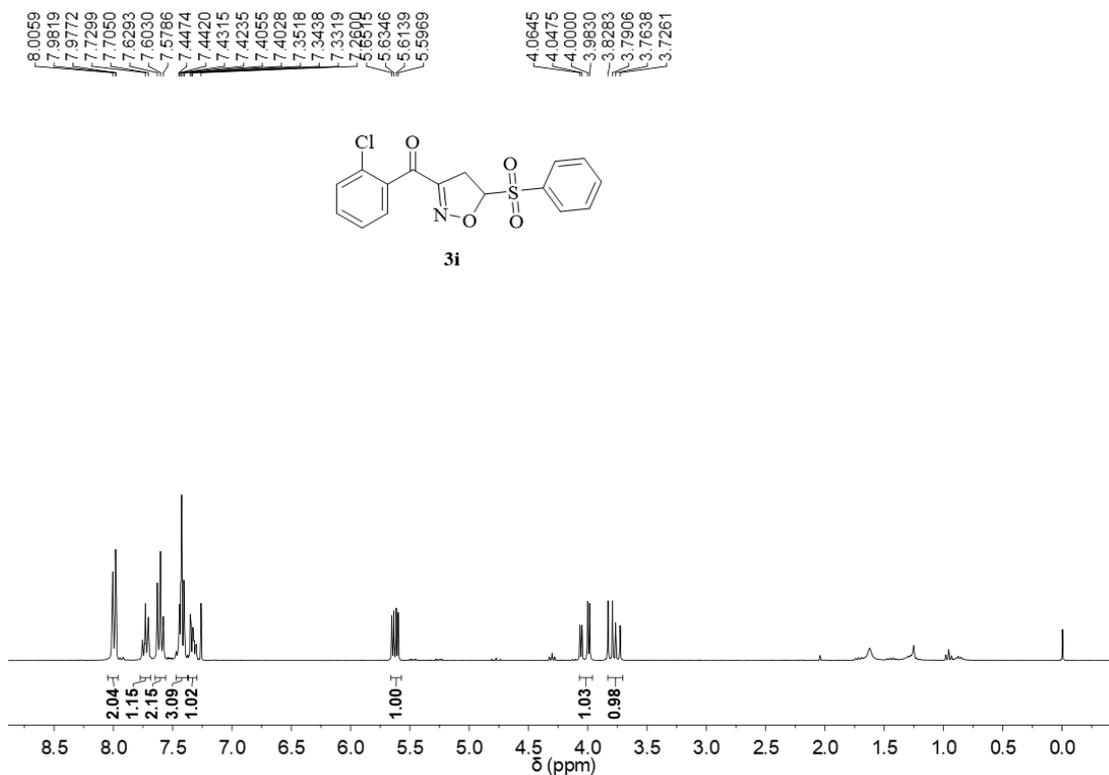


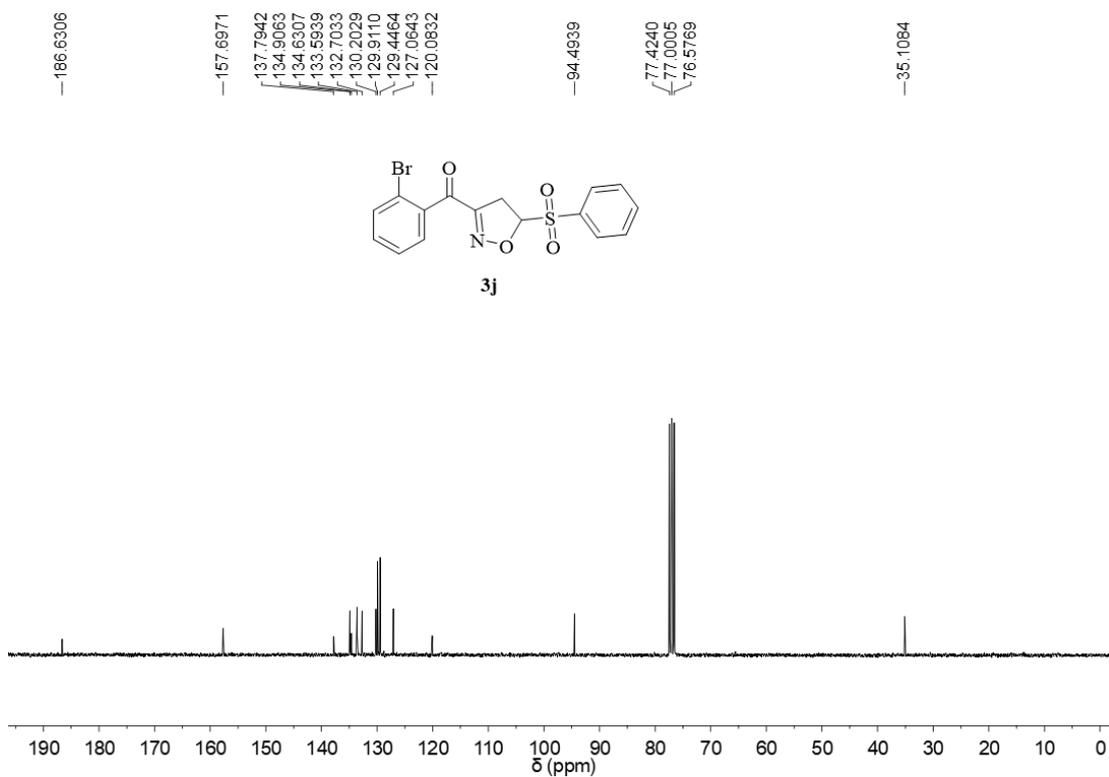
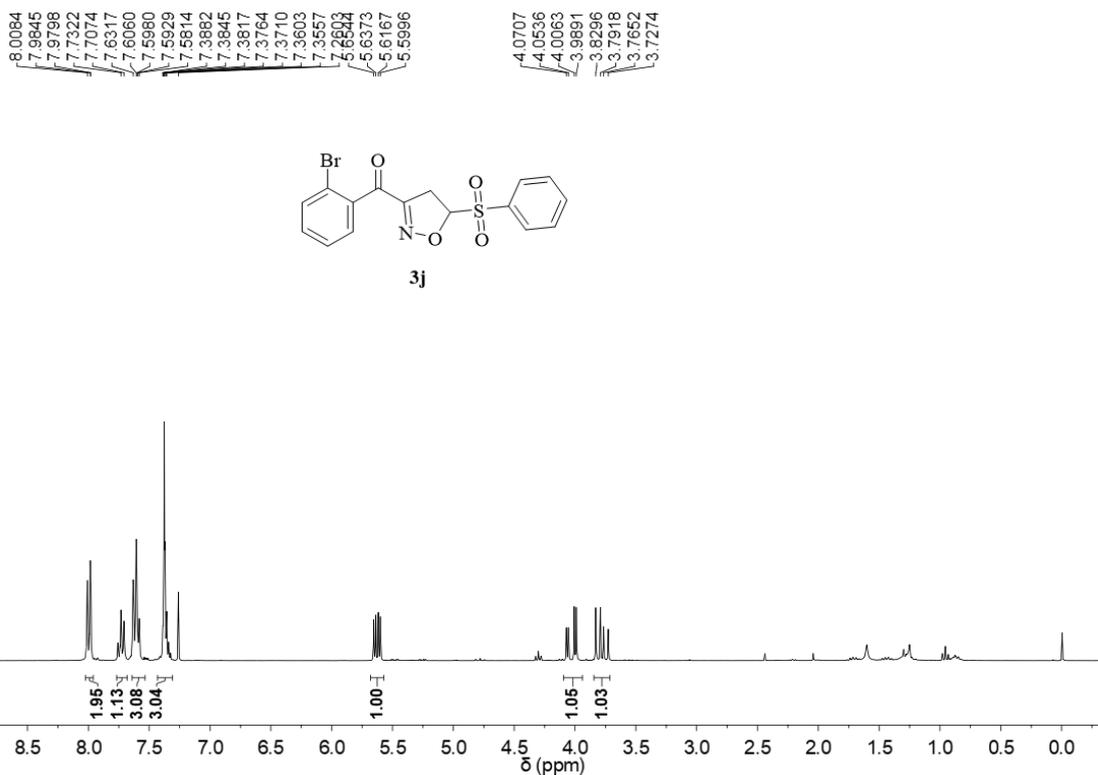


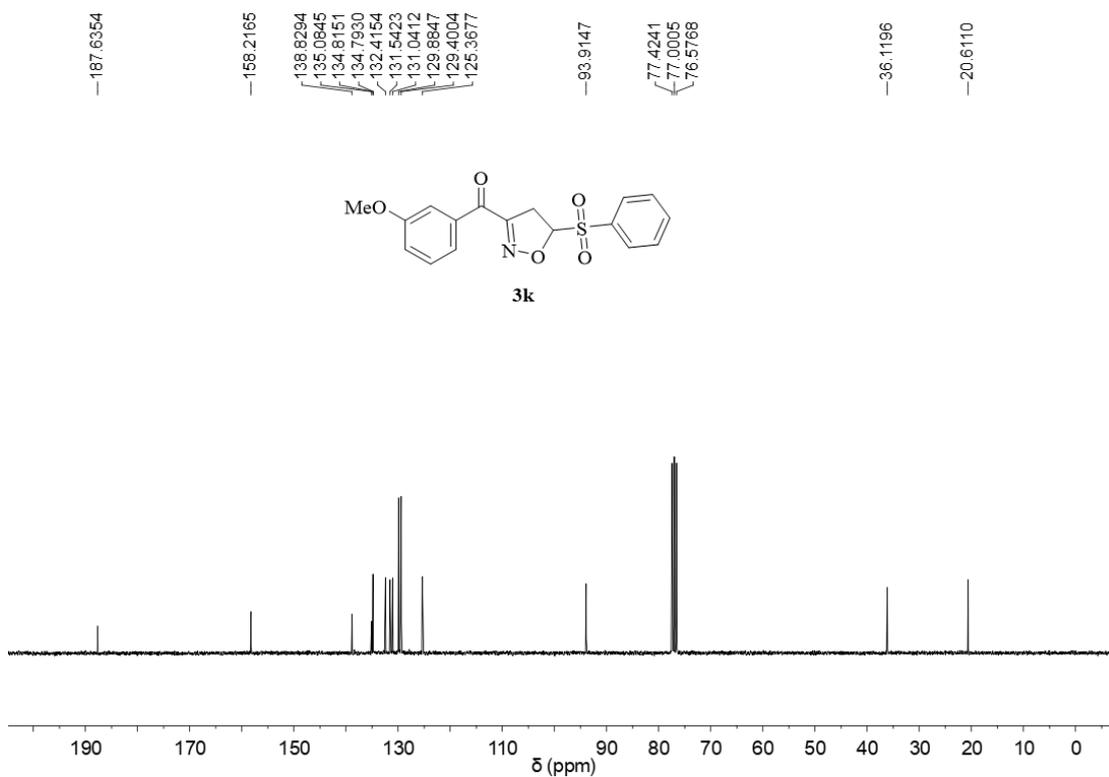
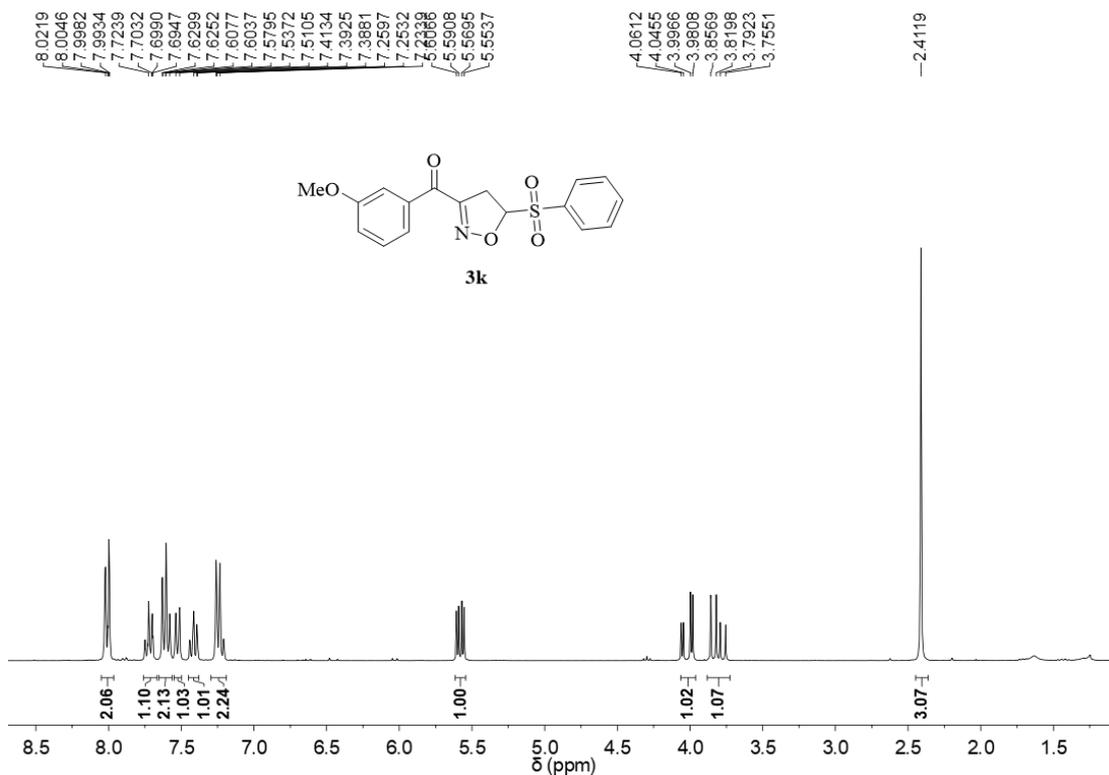


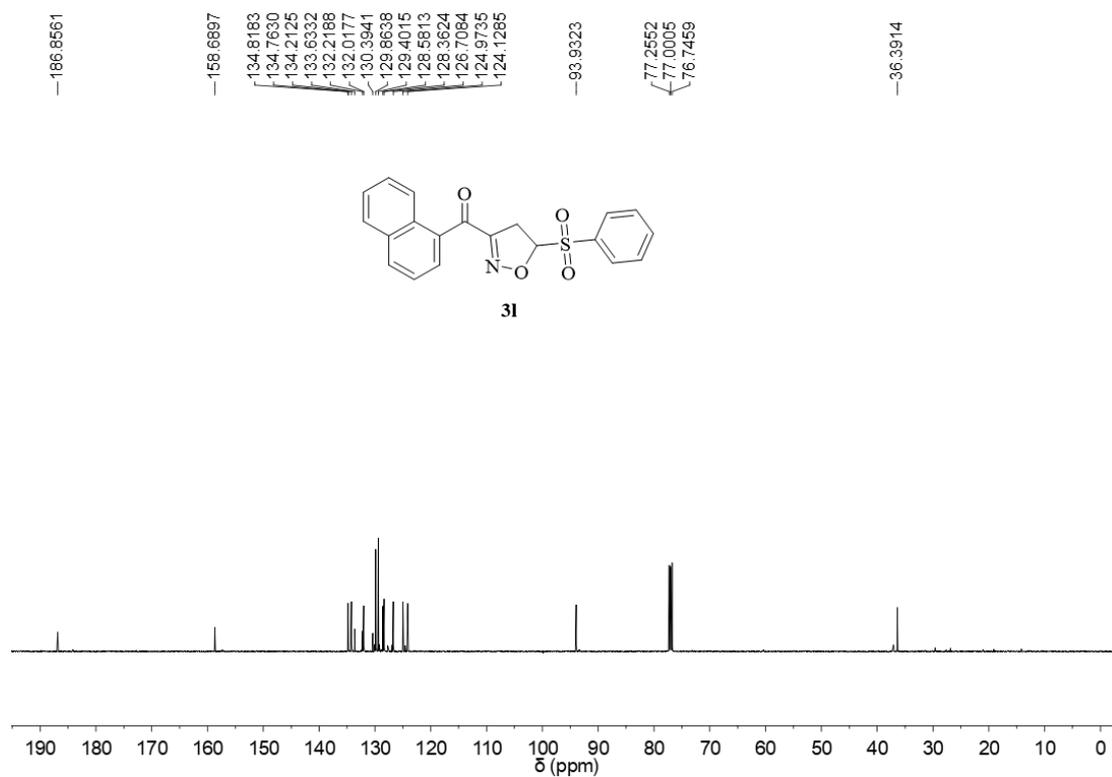
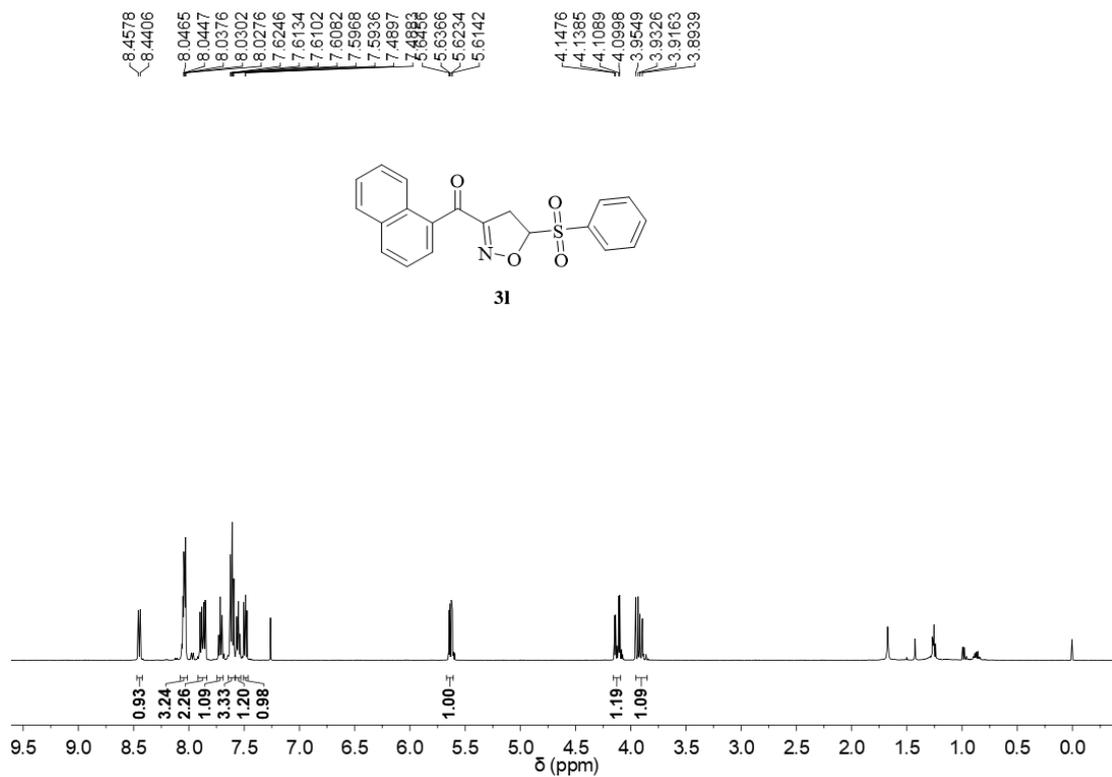








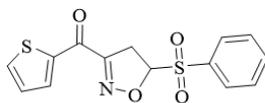




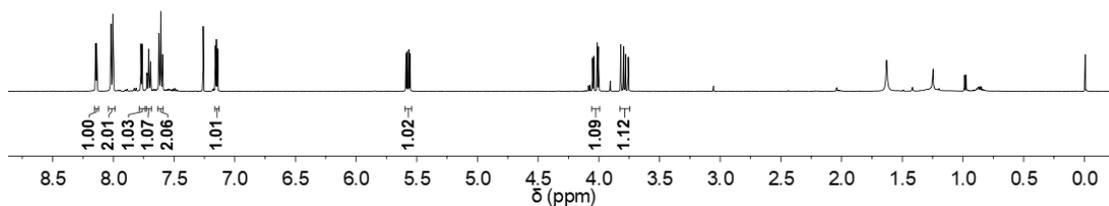
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**3m**



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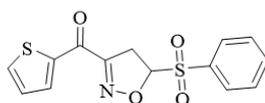
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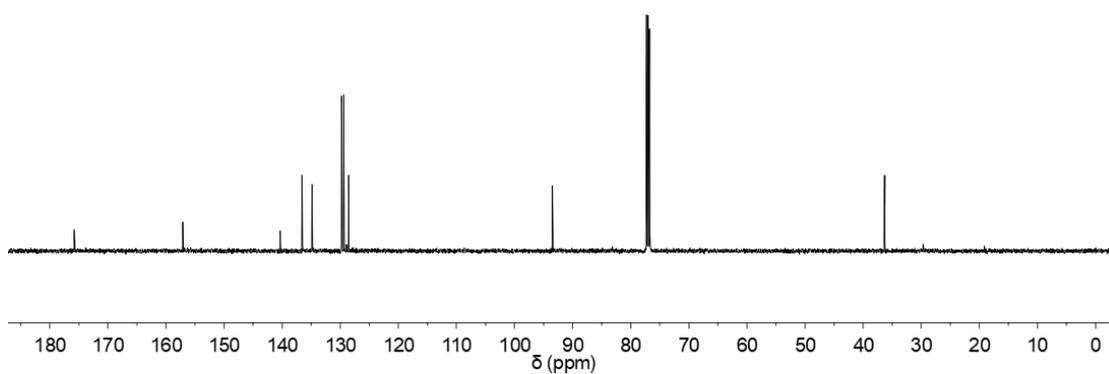
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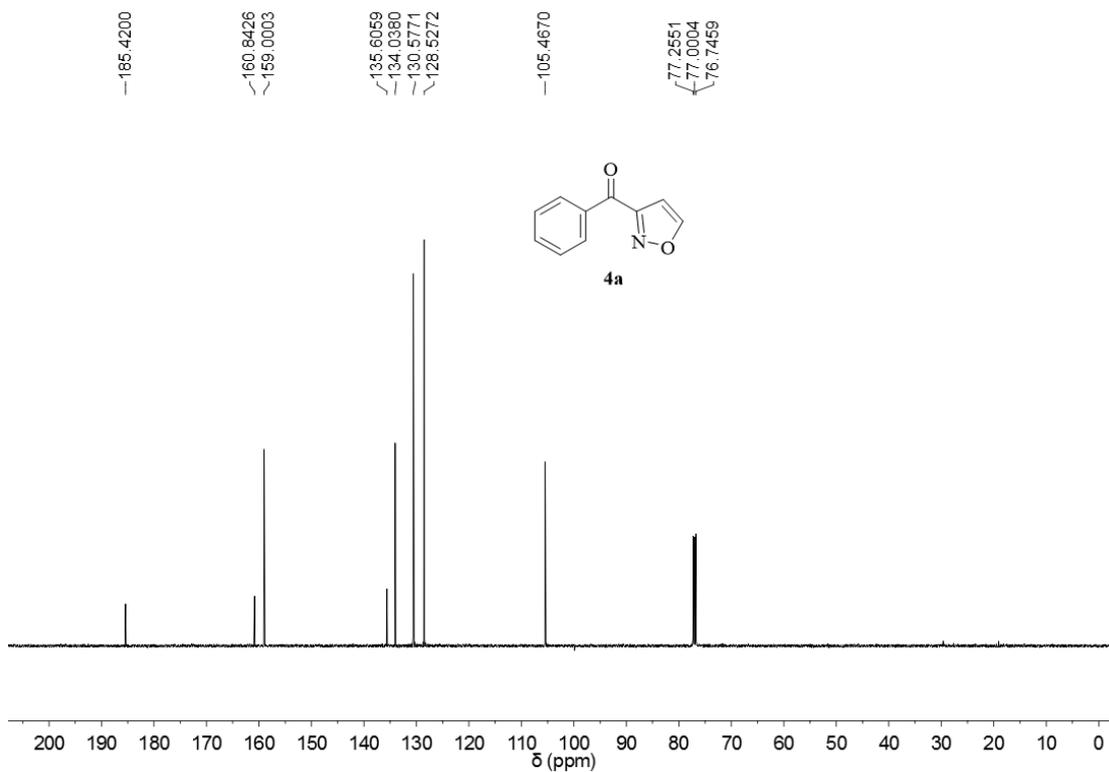
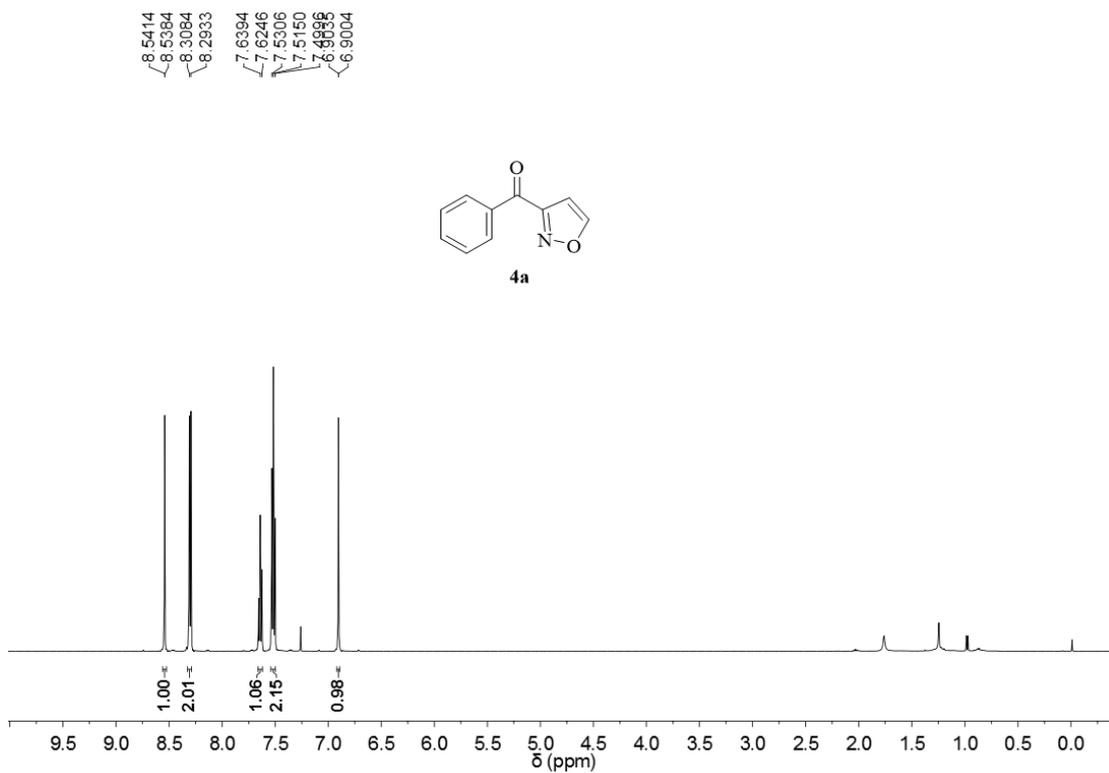
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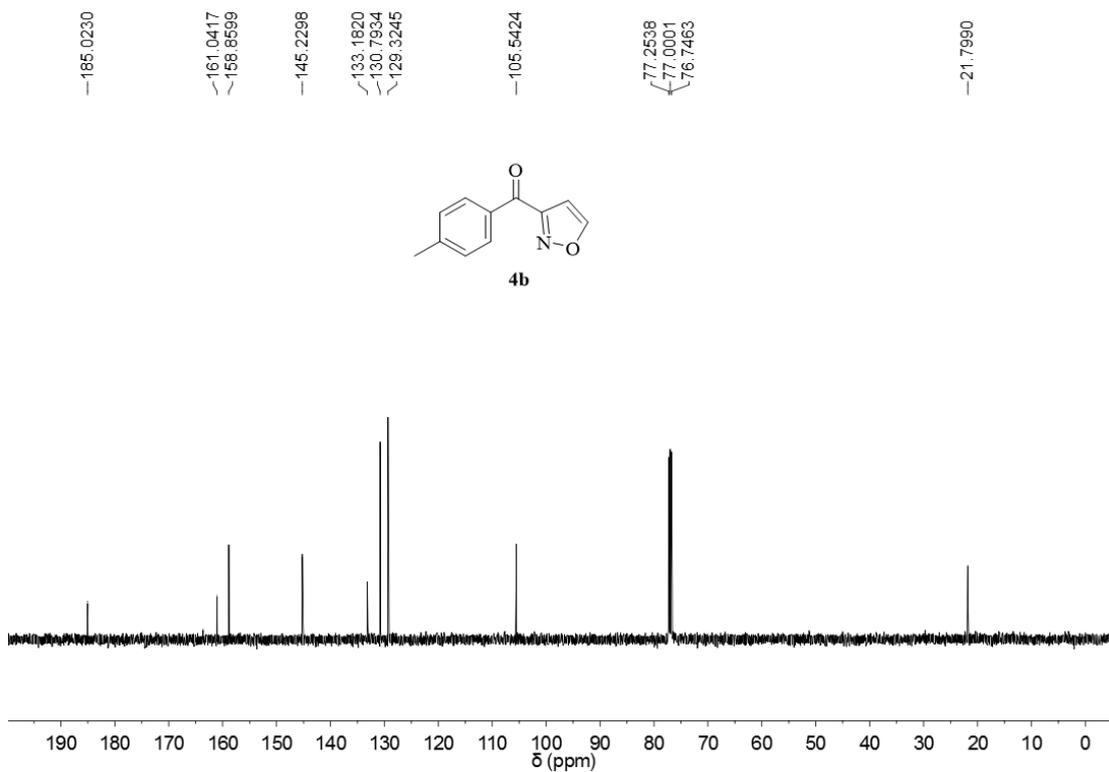
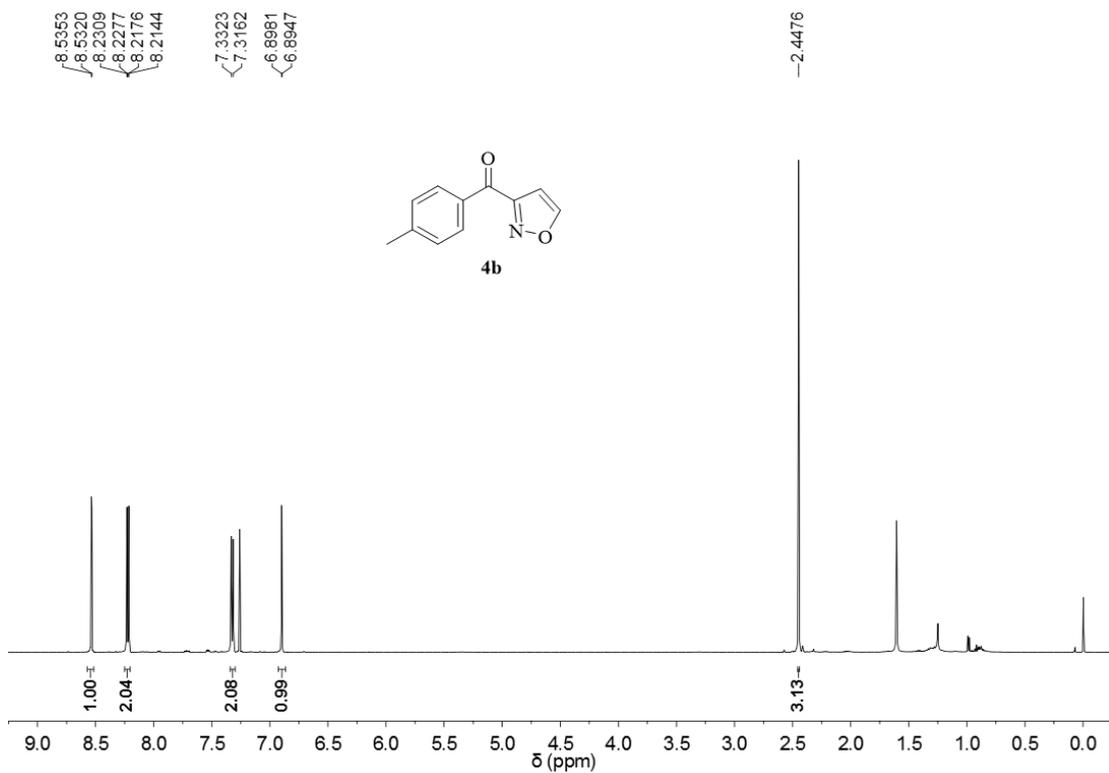
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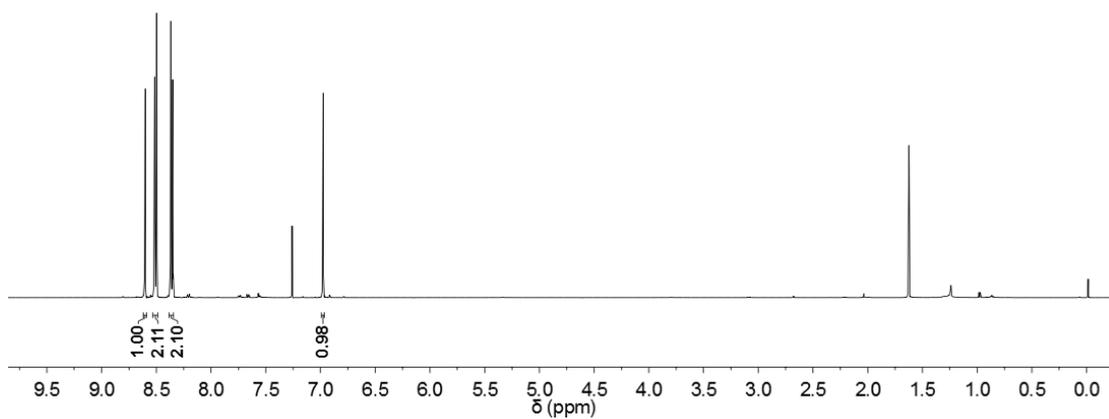
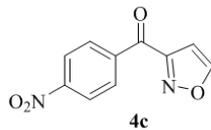
**3m**







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