

## **Palladium-catalyzed Oxidative Carbonylation of the of the hydrazides : Synthesis of 1,3,4-oxadiazol-2(3H)-ones**

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### **Supporting Information**

Contents:

1. General Information
2. Synthesis and Characterization for 1,3,4-oxadiazol-2(3H)-ones

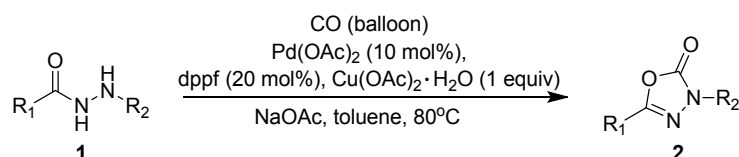
## 1. General Information

Column chromatography was carried out on silica gel.  $^1\text{H}$  NMR spectra were recorded on 400 MHz in  $\text{CDCl}_3$  or Dimethyl Sulfoxide- $\text{D}_6$  and  $^{13}\text{C}$  NMR spectra were recorded on 100 MHz in  $\text{CDCl}_3$  using TMS as internal standard. Melting points were determined on a microscopic apparatus and were uncorrected. Copies of all desired products  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra are provided. Commercially available reagents and solvents were used without further purification. Hydrazides were prepared according to following literatures:

- (1) T. Fang, Q. Tan, Z. Ding, B. Liu and B. Xu, *Org. Lett.*, 2014, 16, 2342-2345.
- (2) K. Hisler, A. G. J. Commeureuc, S.-z. Zhou and J. A. Murphy, *Tetrahedron Letters*, 2009, 50, 3290-3293.
- (3) A. A. Berezin, G. Zissimou, C. P. Constantinides, Y. Beldjoudi, J. M. Rawson and P. A. Koutentis, *J. Org. Chem.*, 2014, 79, 314-327.
- (4) X. Zhang, M. Breslav, J. Grimm, K. Guan, A. Huang, F. Liu, C. A. Maryanoff, D. Palmer, M. Patel, Y. Qian, C. Shaw, K. Sorigi, S. Stefanick and D. Xu, *J. Org. Chem.*, 2002, 67, 9471-9474.
- (5) P.-L. Wu, S.-Y. Peng, J. Magrath, *Synthesis*, 1995, (4), 435-438

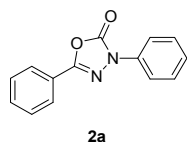
## 2. Synthesis and Characterization for 1,3,4-oxadiazol-2(3H)-ones

- 1) Typical procedure for carbonylation of hydrazides for the synthesis of 1,3,4-oxadiazol-2(3H)-ones.

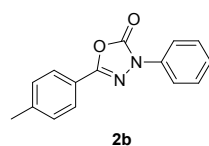


Hydrazide **1** (0.2 mmol), Pd(OAc)<sub>2</sub> (10 mol%, 4.4 mg), Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (0.2 mmol, 40 mg), dppf (20 mol%, 22.2 mg), NaOAc (0.2 mmol, 16.4 mg), and toluene (2 mL) was charged in a round bottom flask equipped with stirrer. Then, the flask was evacuated and back-filled with CO (3 times, balloon). The resulting mixture was stirred for 36h at 80°C. When the reaction was completed, the mixture was cooled to room temperature and vented to discharge the excess CO. The mixture was purified by column chromatography with petroleum ether/ethyl acetate as the eluent to give **2**.

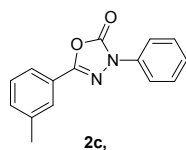
- 2) Characterization Data of 1,3,4-oxadiazol-2(3H)-ones



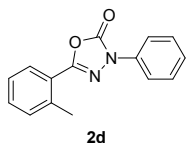
**2a**<sup>1</sup>: White solid;  $^1\text{H}$ -NMR( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = 7.94 (dd,  $J$  = 4.5, 3.7 Hz, 4H), 7.55 – 7.43 (m, 5H), 7.31 – 7.23 (m, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  = 153.4, 150.6, 135.9, 131.9, 129.1, 129.0, 126.1, 125.9, 123.3, 118.2.



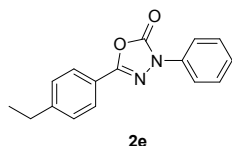
2b<sup>2</sup>: White solid; <sup>1</sup>H-NMR(CDCl<sub>3</sub>, 400 MHz): δ = 7.98 – 7.90 (m, 2H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.49 – 7.42 (m, 2H), 7.34 – 7.21 (m, 3H), 2.41 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ = 153.6, 150.6, 142.5, 136.0, 129.6, 129.1, 125.9, 125.8, 120.5, 118.1, 21.6.



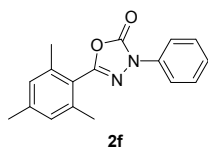
2c: White solid, m.p. 122-124°C, HRMS (ESI) calcd for C<sub>15</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub> (M + H)<sup>+</sup> 252.0972, found 252.0970; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ = 7.98 – 7.90 (m, 2H), 7.74 (dd, *J* = 10.7, 4.1 Hz, 2H), 7.49 – 7.43 (m, 2H), 7.37 (dd, *J* = 14.2, 6.6 Hz, 2H), 7.30 – 7.24 (m, 2H), 2.43 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ = 153.6, 150.6, 138.9, 135.9, 132.7, 129.1, 128.9, 126.3, 126.0, 123.2, 123.1, 118.2, 21.3.



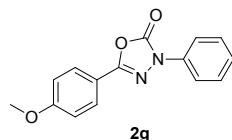
2d: White solid, m.p. 83-85°C, HRMS (ESI) calcd for C<sub>15</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub> (M + H)<sup>+</sup> 252.0972, found 252.0970; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ = 7.94 (dd, *J* = 8.7, 0.9 Hz, 2H), 7.88 – 7.83 (m, 1H), 7.49 – 7.38 (m, 3H), 7.36 – 7.24 (m, 3H), 2.69 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ = 153.7, 150.3, 138.0, 136.0, 131.7, 131.3, 129.1, 128.0, 126.1, 125.9, 121.9, 118.0, 22.2.



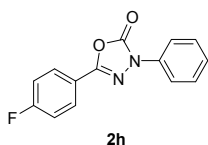
2e: White solid, m.p. 76-77°C, HRMS (ESI) calcd for C<sub>16</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub> (M + H)<sup>+</sup> 267.1128, found 267.1124; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ = 7.94 (d, *J* = 7.9 Hz, 2H), 7.84 (d, *J* = 8.2 Hz, 2H), 7.45 (t, *J* = 8.0 Hz, 2H), 7.35 – 7.23 (m, 3H), 2.71 (q, *J* = 7.6 Hz, 2H), 1.27 (t, *J* = 7.6 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ = 153.6, 150.6, 148.7, 136.0, 129.1, 128.51, 125.9, 120.7, 118.1, 28.9, 15.1.



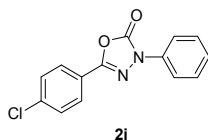
2f: White solid, m.p. 61-62°C, HRMS (ESI) calcd for C<sub>17</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub> (M + H)<sup>+</sup> 281.1285, found 281.1279; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ = 7.94 (dd, *J* = 8.8, 1.0 Hz, 1H), 7.49 – 7.42 (m, 1H), 7.29 – 7.21 (m, 0H), 6.96 (s, 1H), 2.39 (s, 6H), 2.33 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ = 153.6, 151.0, 141.3, 138.6, 136.0, 129.1, 129.0, 125.9, 120.3, 118.0, 21.2, 20.4.



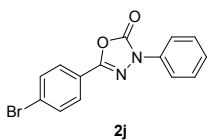
2g: White solid, m.p. 132-134°C, HRMS (ESI) calcd for C<sub>15</sub>H<sub>12</sub>N<sub>2</sub>O<sub>3</sub> (M + H)<sup>+</sup> 269.0921, found 269.0919; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ = 7.93 (d, *J* = 8.0 Hz, 2H), 7.87 (d, *J* = 8.8 Hz, 2H), 7.46 (t, *J* = 7.9 Hz, 2H), 7.29 – 7.22 (m, 2H), 6.99 (d, *J* = 8.9 Hz, 2H), 3.87 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ = 162.4, 153.5, 150.7, 136.0, 129.1, 127.7, 125.9, 118.1, 115.7, 114.4, 55.4.



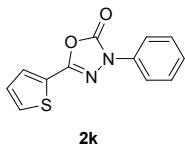
2h: White solid, m.p. 125-126°C, HRMS (ESI) calcd for C<sub>14</sub>H<sub>9</sub>N<sub>2</sub>O<sub>2</sub>F (M + H)<sup>+</sup> 257.0721, found 257.0719; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ = 7.98 – 7.88 (m, 4H), 7.49 – 7.43 (m, 2H), 7.28 (dd, *J* = 12.2, 4.5 Hz, 1H), 7.22 – 7.16 (m, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ = 166.0, 163.51, 152.6, 150.4, 135.8, 129.1, 128.2, 128.1, 126.1, 119.6, 119.6, 118.1, 116.5, 116.3.



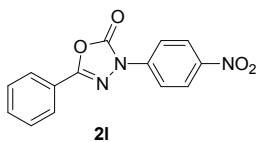
2i: White solid, m.p. 118-119°C, HRMS (ESI) calcd for C<sub>14</sub>H<sub>9</sub>N<sub>2</sub>O<sub>2</sub>Cl (M + H)<sup>+</sup> 273.0425, found 273.0422; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ = 7.94 – 7.88 (m, 2H), 7.88 – 7.83 (m, 2H), 7.46 (dq, *J* = 9.1, 1.9 Hz, 4H), 7.27 (dd, *J* = 11.2, 4.8 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ = 152.6, 150.3, 138.1, 135.8, 129.3, 129.1, 127.1, 126.1, 121.7, 118.1.



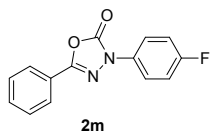
2j: White solid, m.p. 124-125°C, HRMS (ESI) calcd for C<sub>14</sub>H<sub>9</sub>N<sub>2</sub>O<sub>2</sub>Br (M + H)<sup>+</sup> 316.9919, found 316.9915; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ = 7.95 – 7.88 (m, 2H), 7.78 (dd, *J* = 8.7, 2.1 Hz, 2H), 7.63 (dd, *J* = 8.8, 2.0 Hz, 2H), 7.49 – 7.42 (m, 2H), 7.31 – 7.23 (m, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ = 152.7, 150.3, 135.7, 132.3, 129.1, 127.2, 126.6, 126.2, 122.2, 118.1.



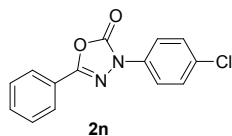
2k: Yellow solid, m.p. 120-122°C, HRMS (ESI) calcd for C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>O<sub>2</sub>S (M + H)<sup>+</sup> 245.0379, found 245.0377; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ = 7.91 (d, *J* = 7.9 Hz, 2H), 7.68 (dd, *J* = 3.6, 0.7 Hz, 1H), 7.55 (d, *J* = 4.9 Hz, 1H), 7.46 (dd, *J* = 10.8, 5.1 Hz, 2H), 7.29 – 7.24 (m, 2H), 7.16 (dd, *J* = 4.8, 3.9 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ = 150.2, 150.0, 135.8, 130.21, 129.8, 129.1, 128.0, 126.1, 124.8, 118.2.



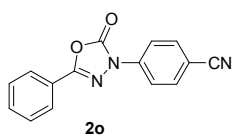
2l: Yellow solid; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ = 8.34 (d, *J* = 9.1 Hz, 2H), 8.18 (d, *J* = 9.0 Hz, 2H), 7.95 (d, *J* = 7.3 Hz, 2H), 7.57 (dt, *J* = 25.2, 7.3 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ = 154.3, 150.0, 144.8, 140.8, 132.6, 129.1, 126.1, 125.0, 122.6, 117.8.



2n: White solid, m.p. 142-144°C, HRMS (ESI) calcd for  $C_{14}H_9N_2O_2F$  ( $M + H$ )<sup>+</sup> 257.0721, found 257.0719; <sup>1</sup>H NMR ( $CDCl_3$ , 400 MHz):  $\delta$  = 8.01 – 7.86 (m, 4H), 7.59 – 7.48 (m, 3H), 7.21 – 7.12 (m, 2H). <sup>13</sup>C NMR ( $CDCl_3$ , 100 MHz)  $\delta$  = 161.7, 159.2, 153.5, 150.6, 132.0, 129.0, 125.9, 123.2, 120.1, 120.0, 116.1, 115.9.



2o<sup>4</sup>: White solid; <sup>1</sup>H NMR ( $CDCl_3$ , 400 MHz):  $\delta$  = 7.96 – 7.84 (m, 4H), 7.57 – 7.46 (m, 3H), 7.44 – 7.37 (m, 2H). <sup>13</sup>C NMR ( $CDCl_3$ , 100 MHz)  $\delta$  = 153.5, 150.3, 134.5, 132.0, 131.4, 129.2, 129.0, 125.9, 123.0, 119.2.

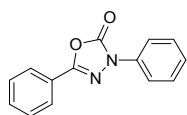


2p: White solid, m.p. 180-182°C, HRMS (ESI) calcd for  $C_{15}H_9N_3O_2$  ( $M + H$ )<sup>+</sup> 263.0768, found 264.0764; <sup>1</sup>H NMR ( $CDCl_3$ , 400 MHz):  $\delta$  = 8.11 (d,  $J$  = 8.7 Hz, 2H), 7.98 – 7.89 (m, 2H), 7.75 (d,  $J$  = 8.6 Hz, 2H), 7.61 – 7.48 (m, 3H). <sup>13</sup>C NMR ( $CDCl_3$ , 100 MHz)  $\delta$  = 174.2, 154.1, 149.9, 139.2, 133.3, 132.4, 129.1, 126.0, 122.6, 118.2, 117.9, 109.2.

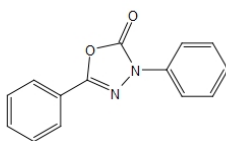
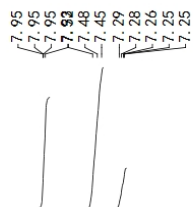
Citation for the known compounds:

1. M. Marky, H. Meier, A. Wunderli, H. Heimgartner and H. Schmid, *Helv. Chim. Acta*, 1978, 61, 1477-1510.
2. P. Guenter, S. Erich, S. Norbert, M. Thomas, R. Guenter, *Ger. Offen.*, 1980, DE 2833470 A1 19800207.
3. G. Scherowsky and B. Kundu, *Liebigs Ann. Chem.*, 1977, 1235-1247.
4. C. Grunwald, C. Rundfeldt, H. J. Lankau, T. Arnold, N. Hofgen, R. Dost, U. Egerland, H. J. Hofmann and K. Unverferth, *J. Med. Chem.*, 2006, 49, 1855-1866.

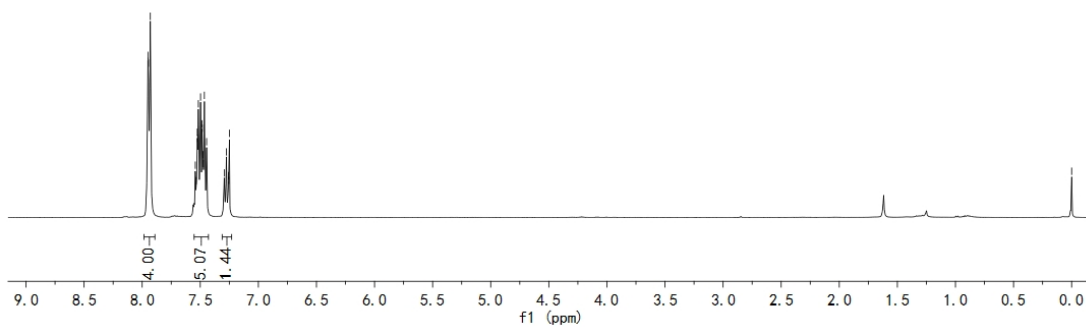
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**2a**



**2a**



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150.64

135.97

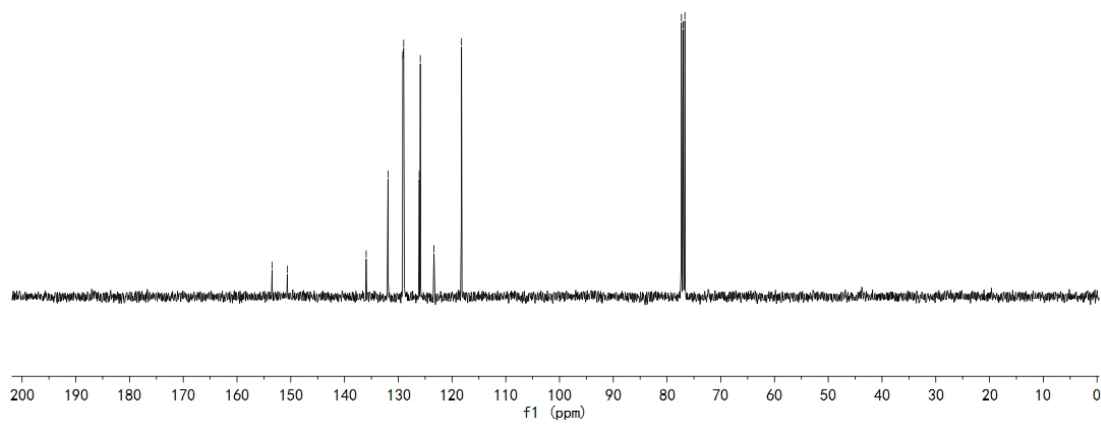
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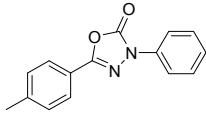
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123.36

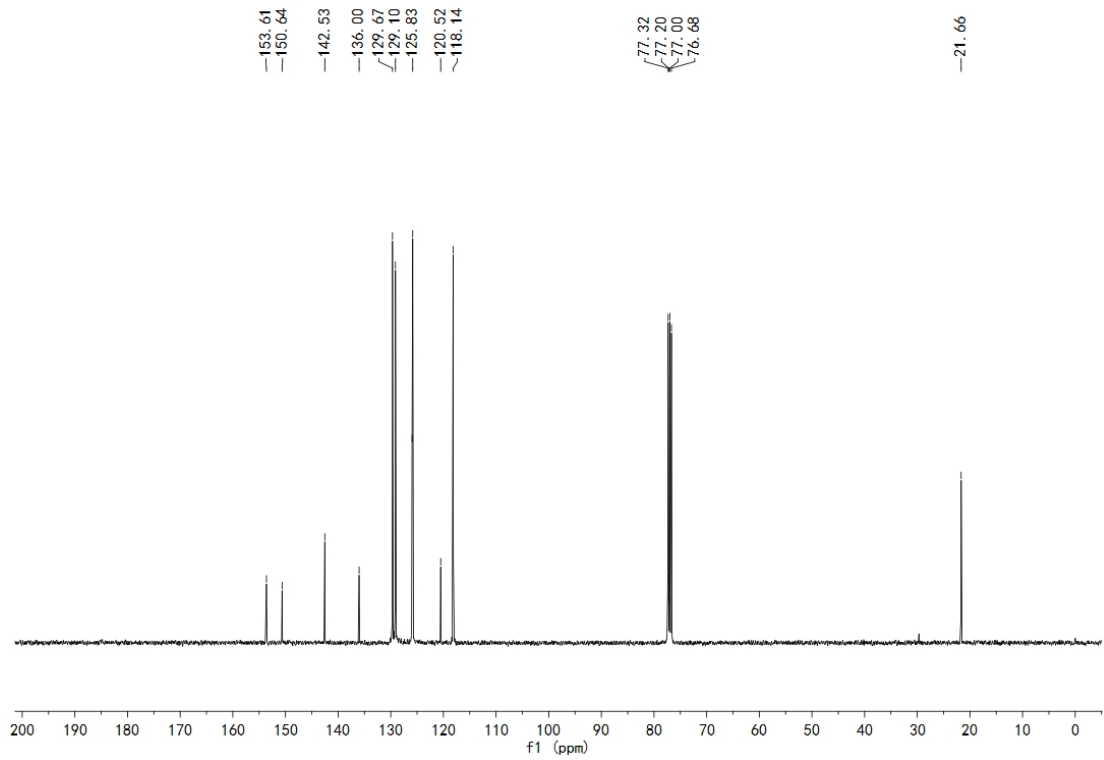
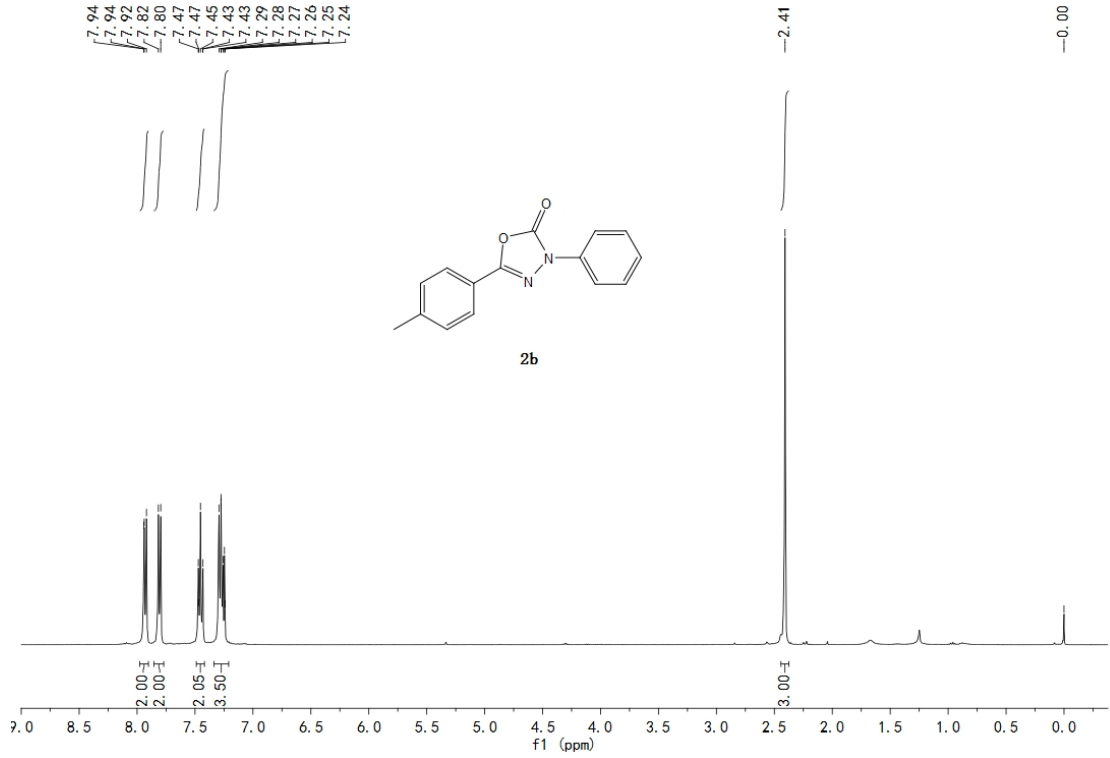
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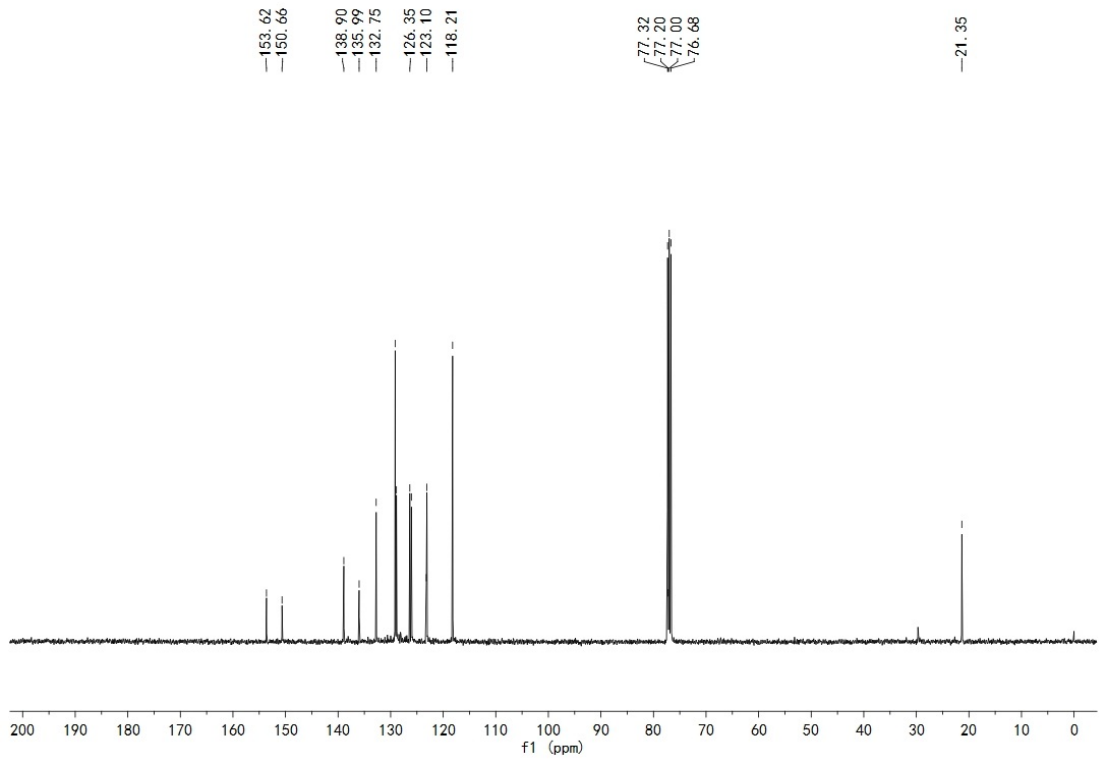
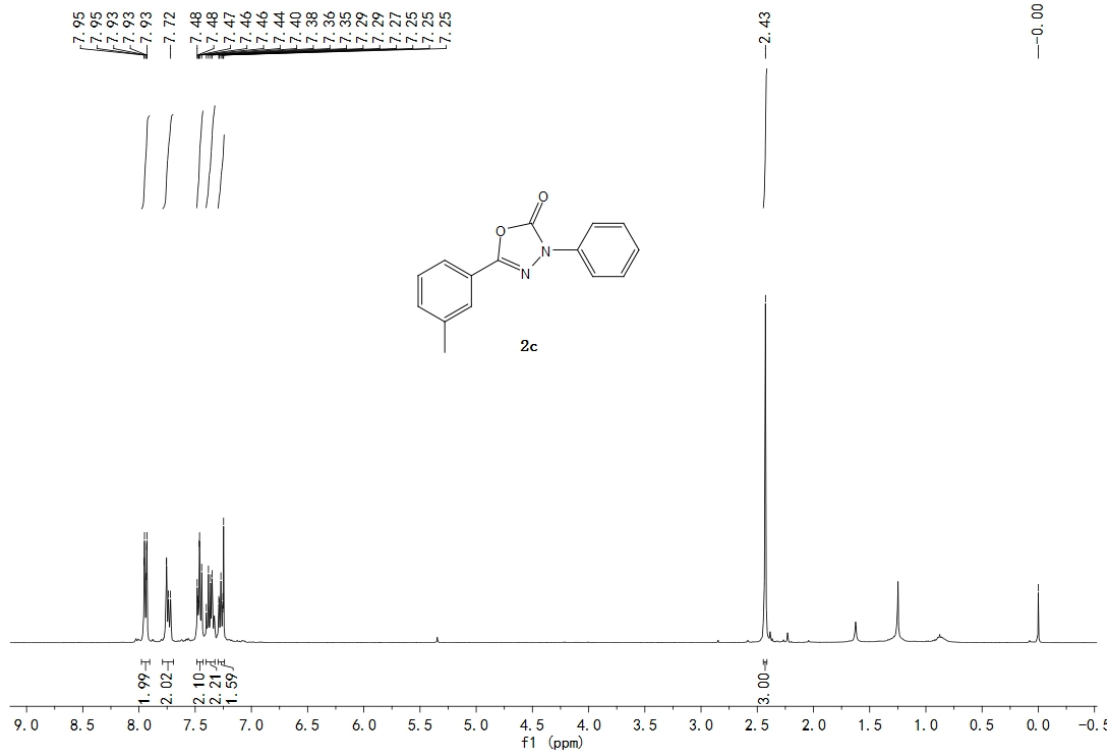
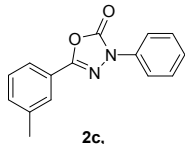
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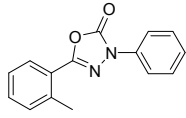


2b

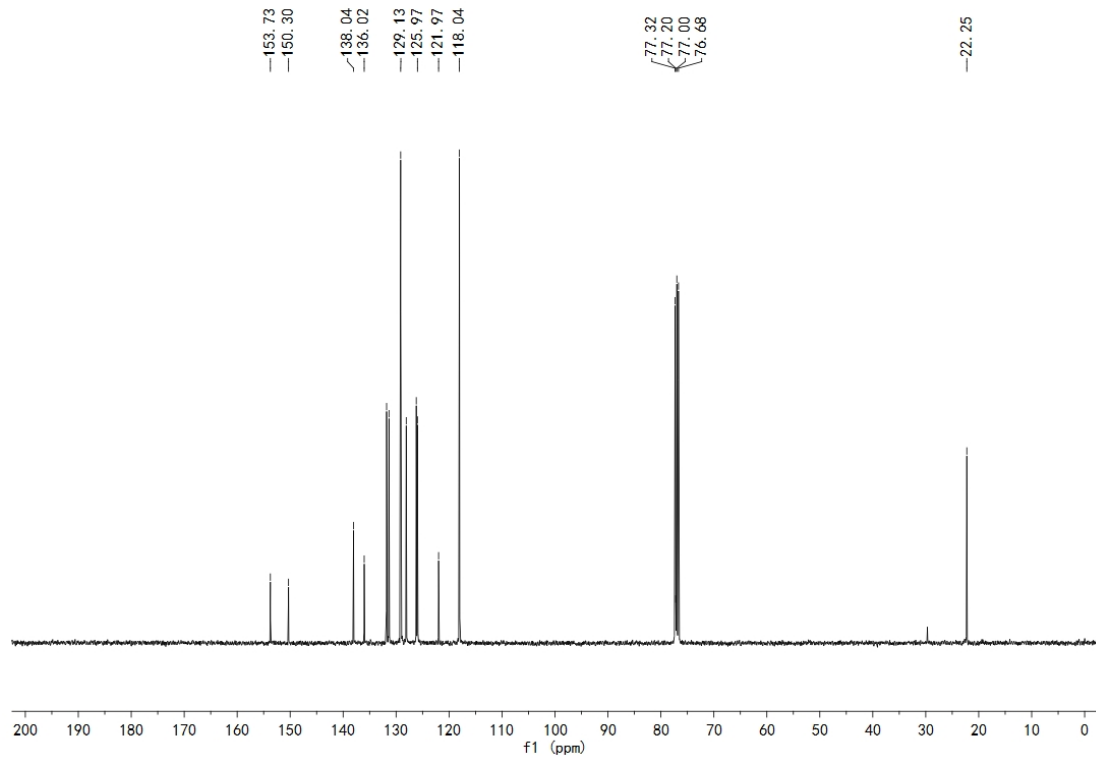
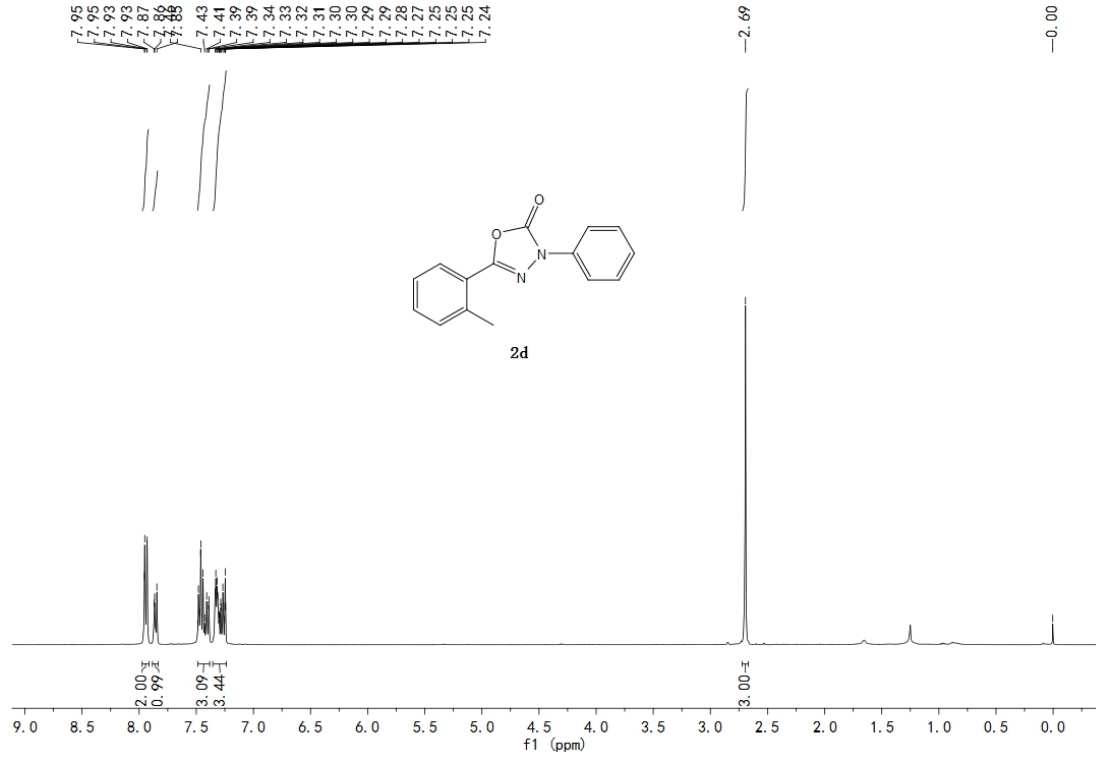


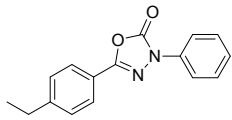




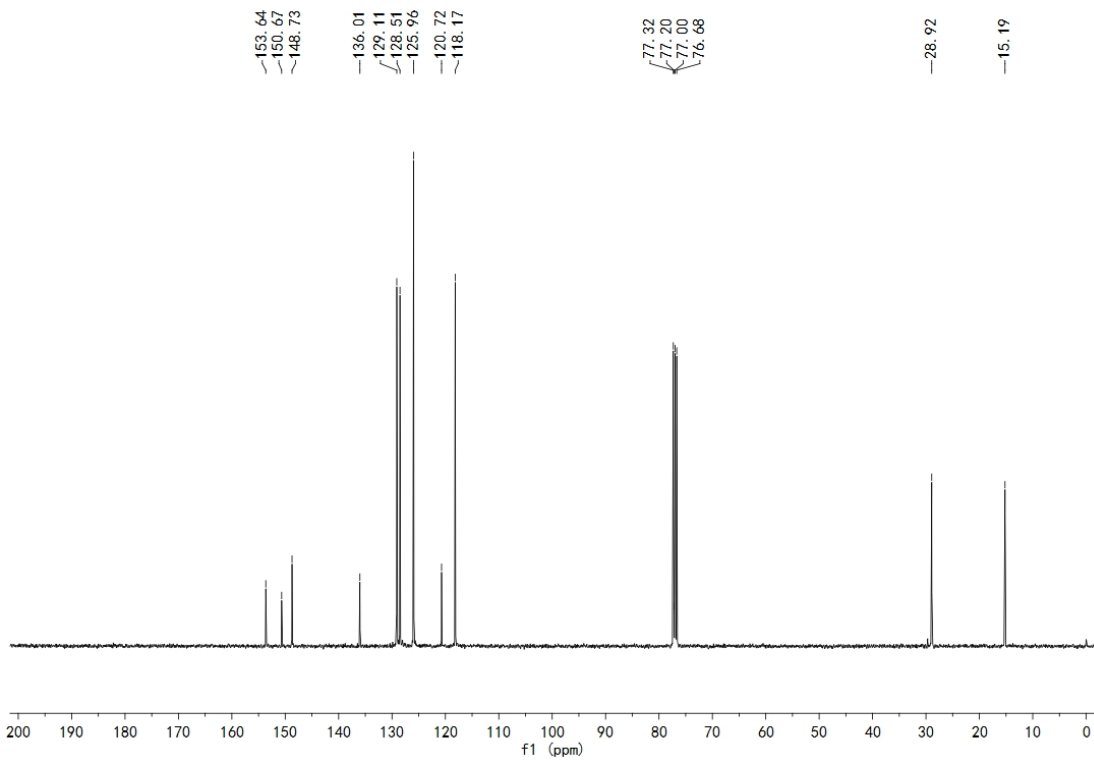
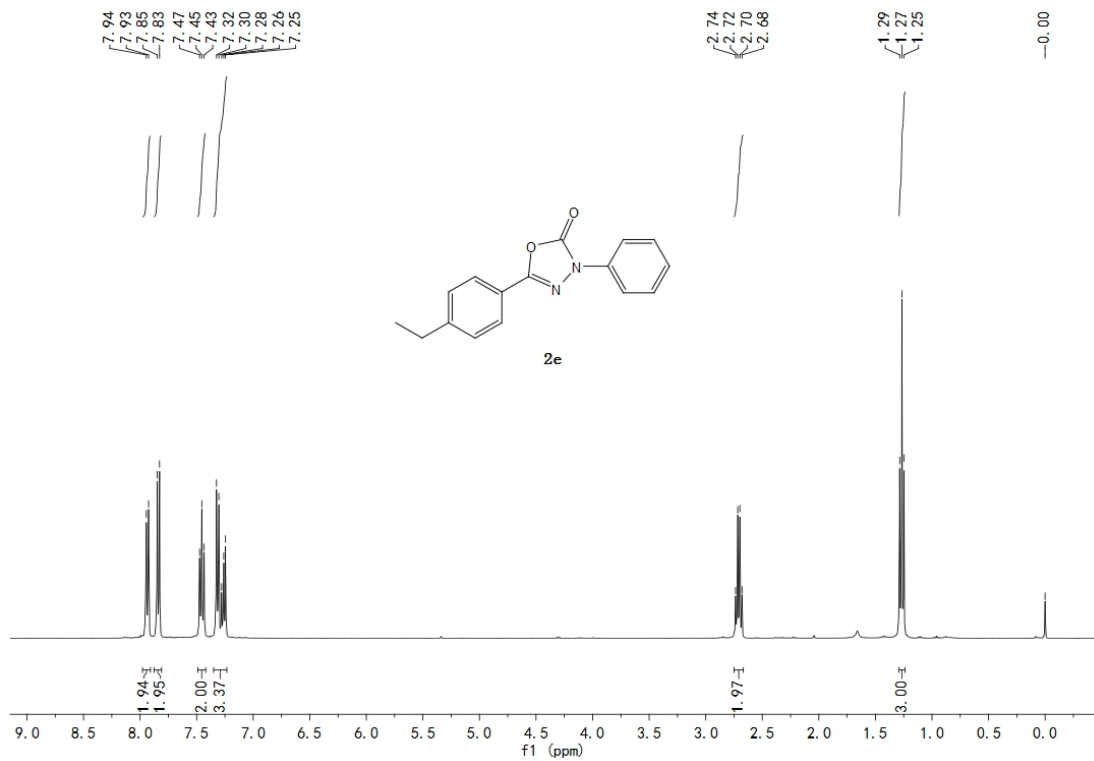


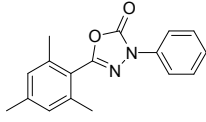
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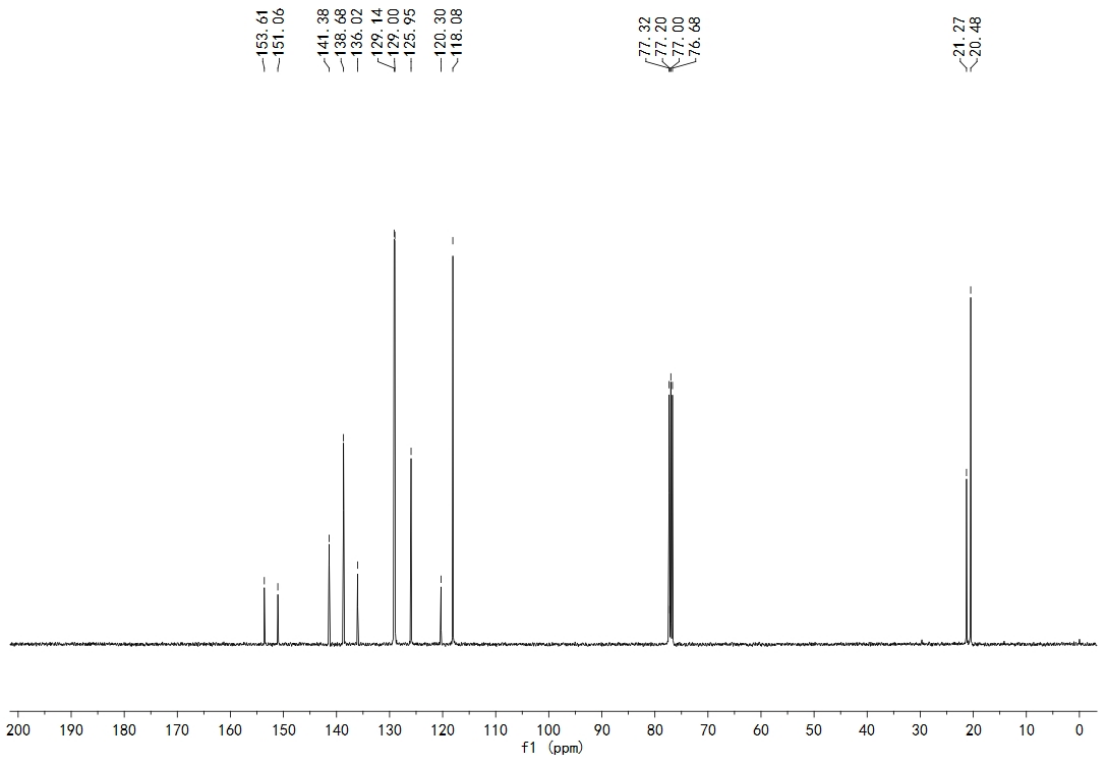
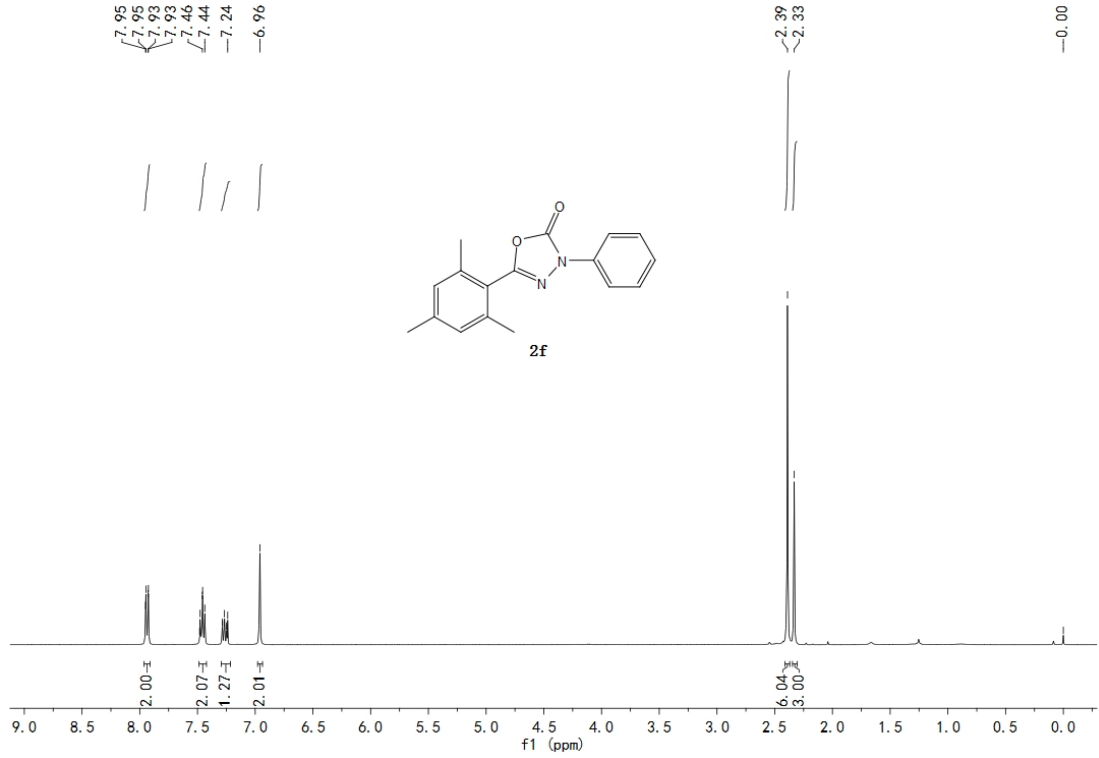


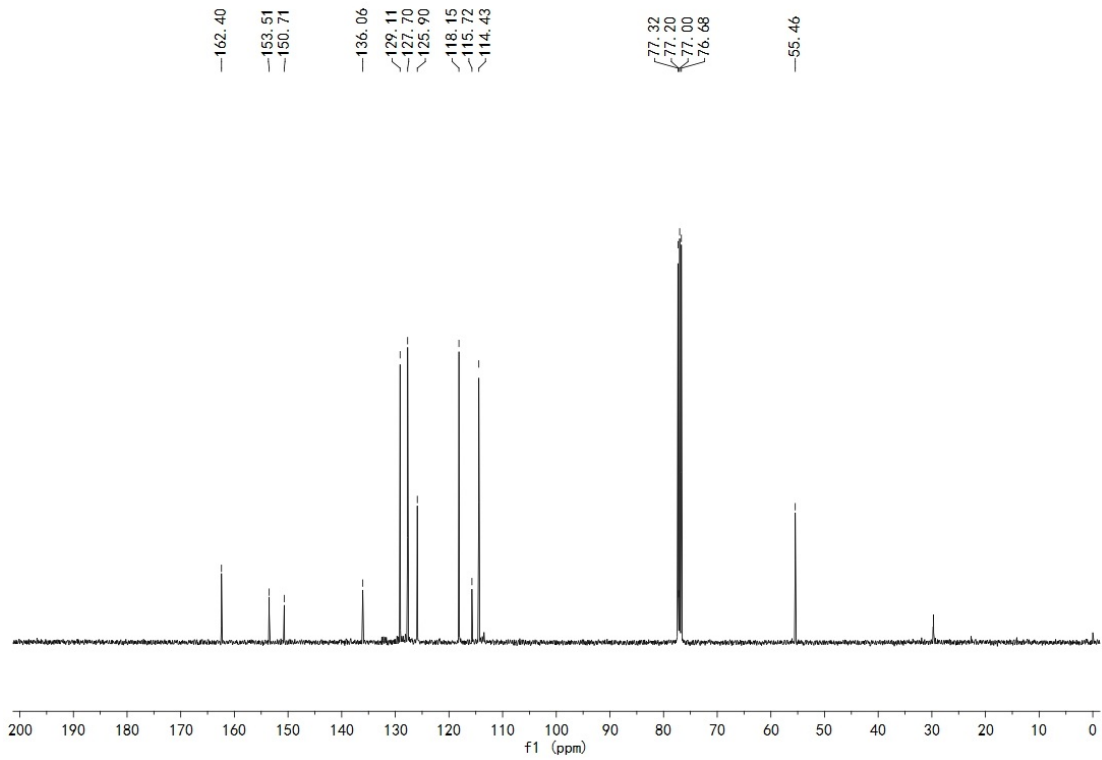
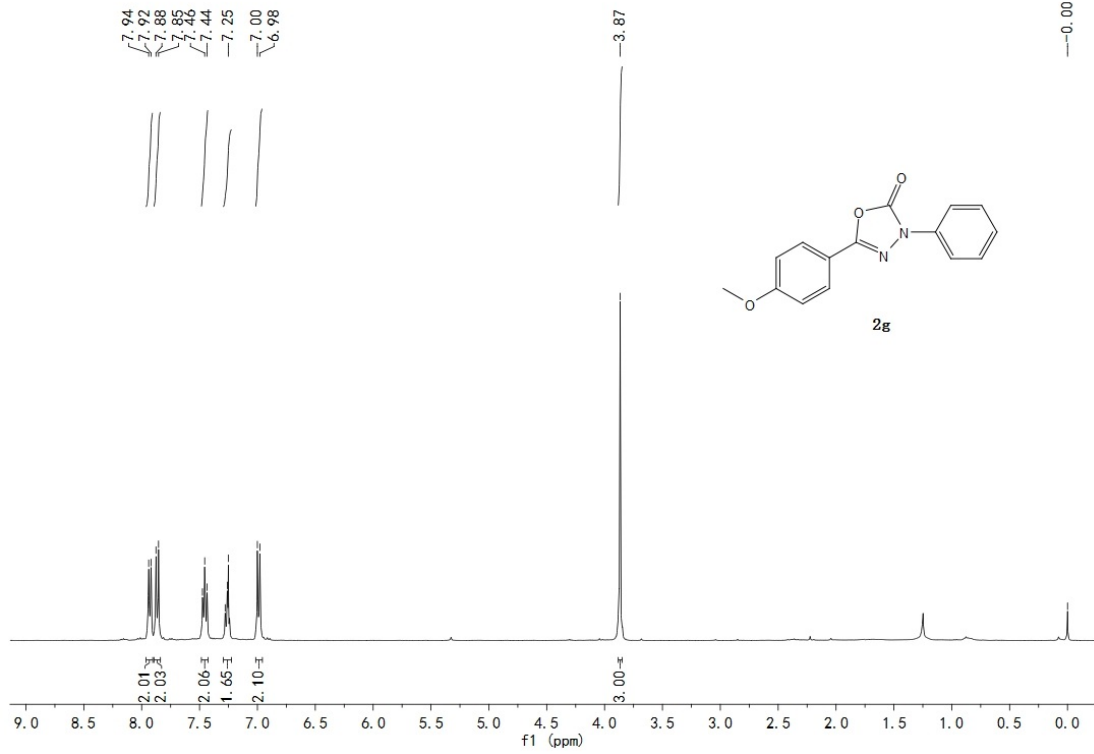
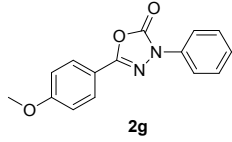
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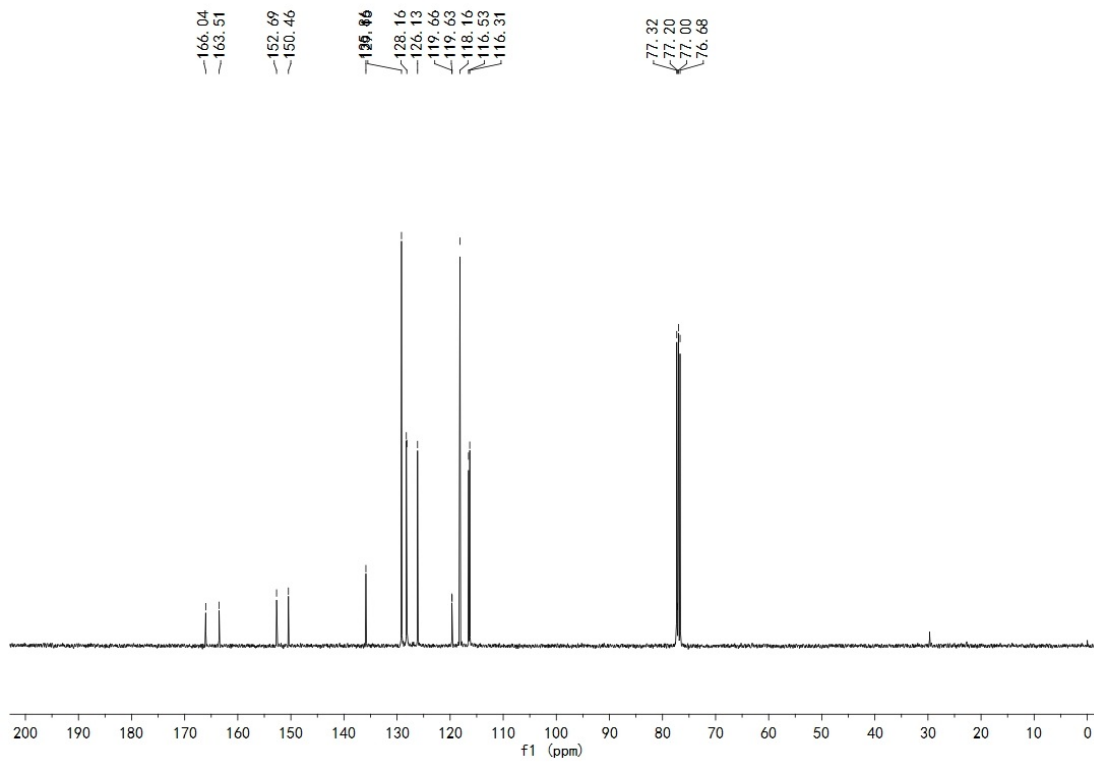
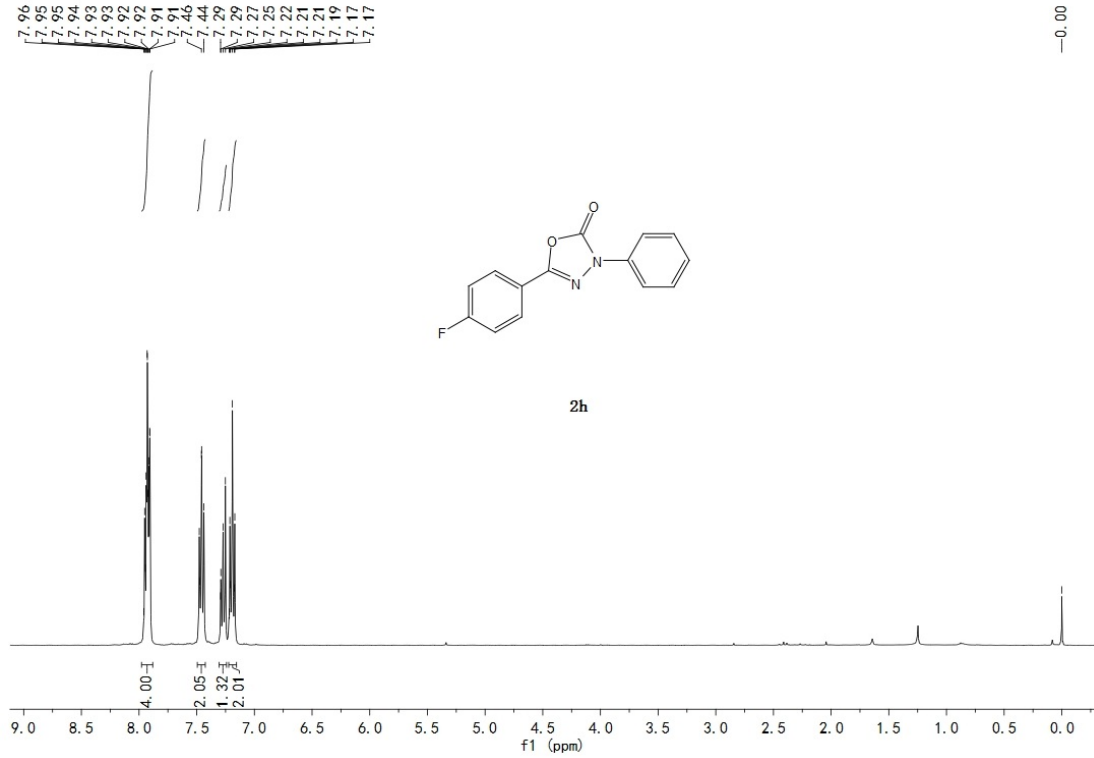
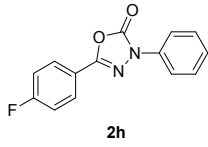


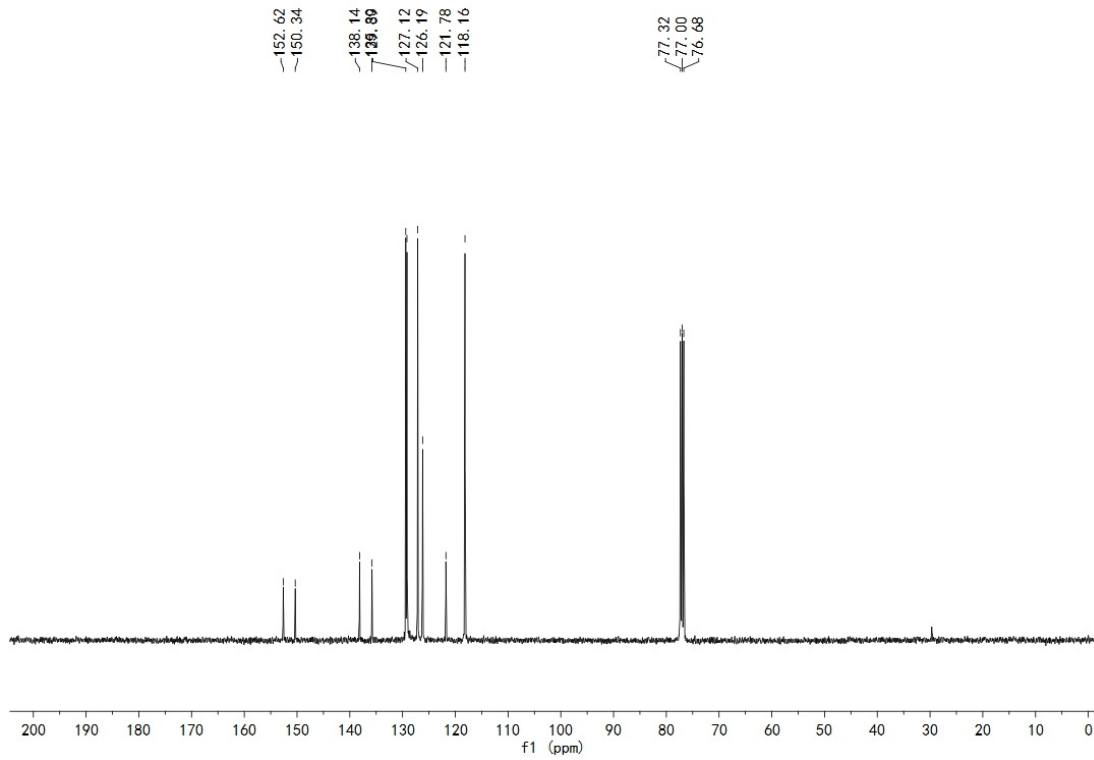
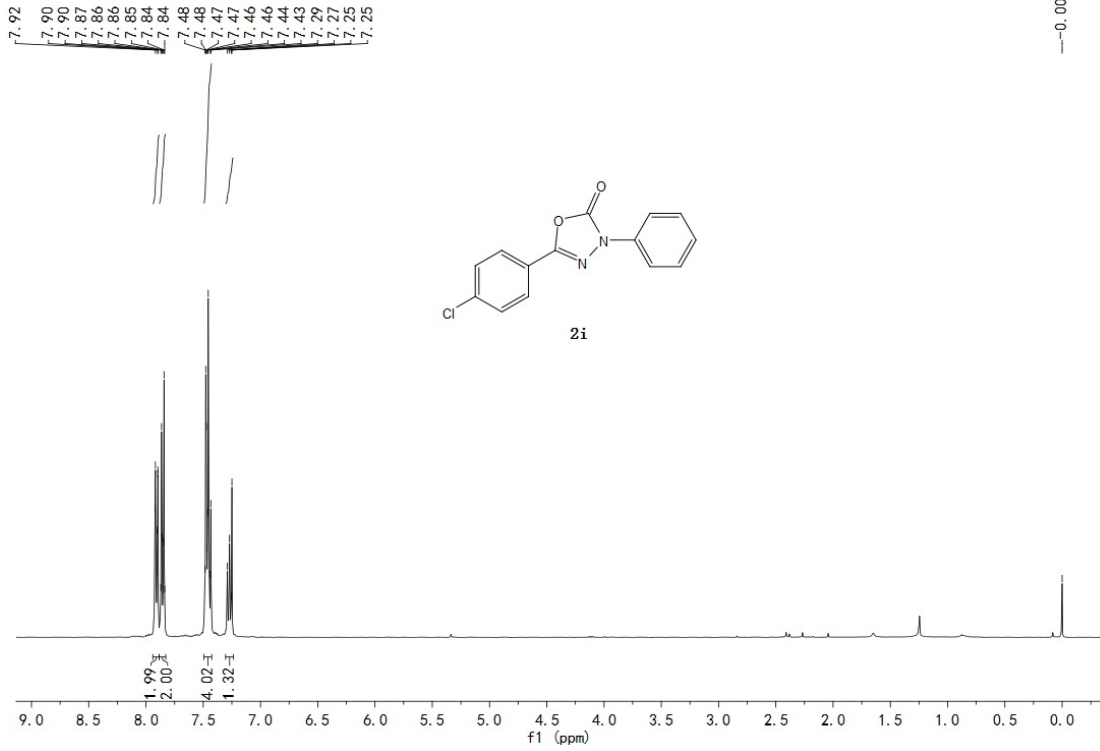
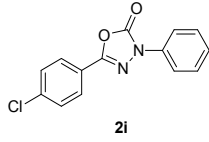


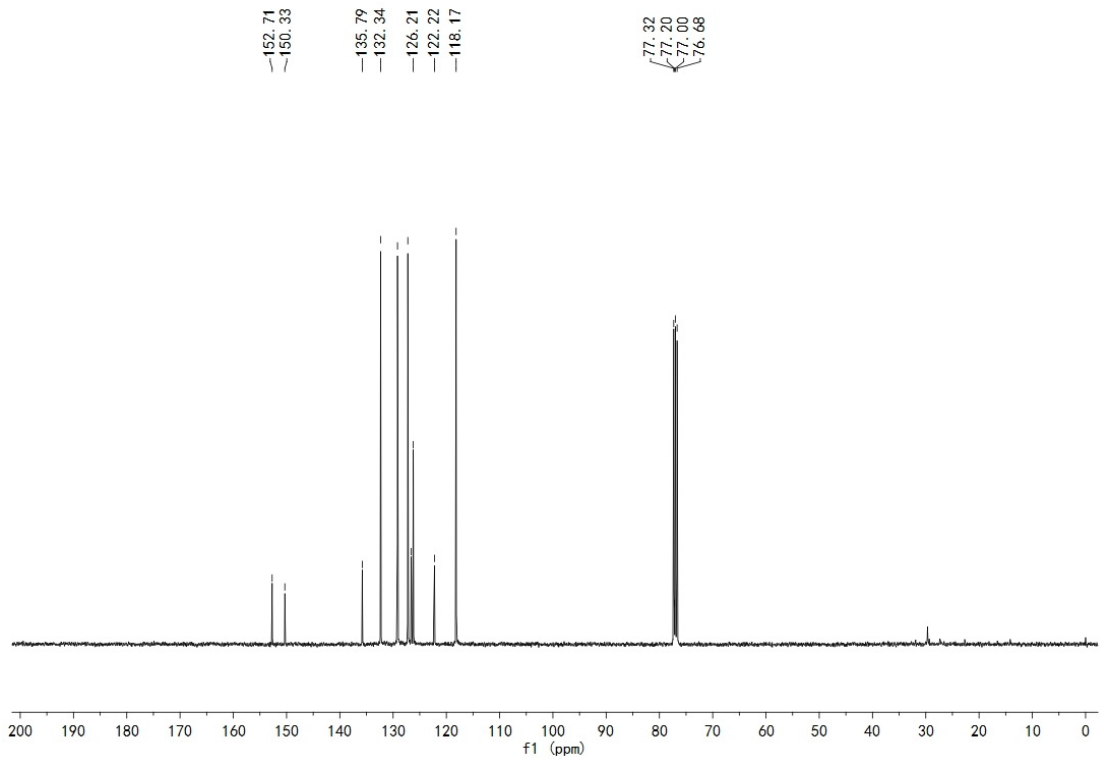
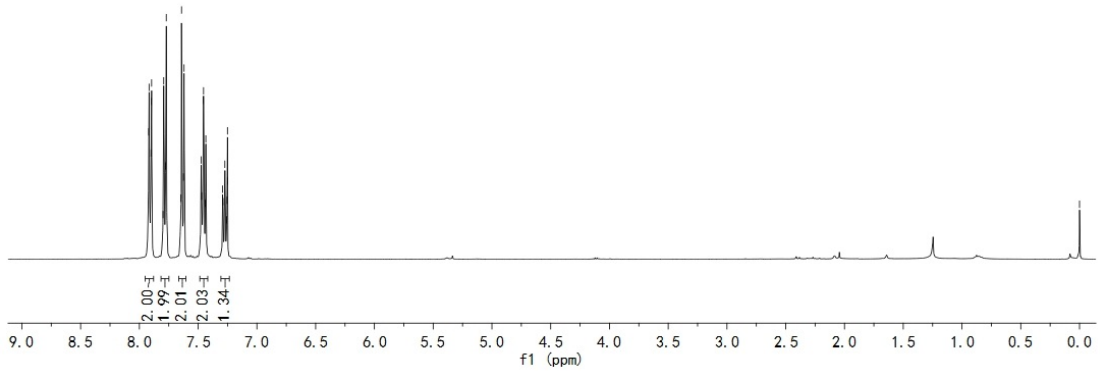
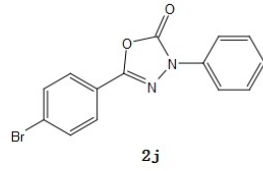
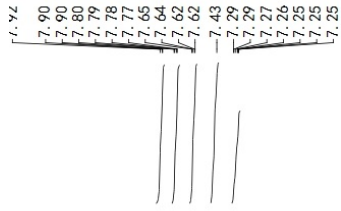
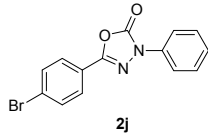
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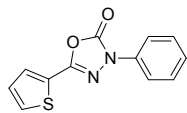




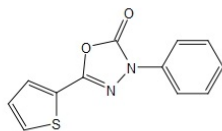
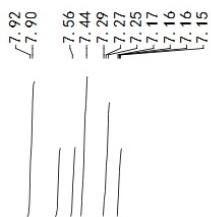




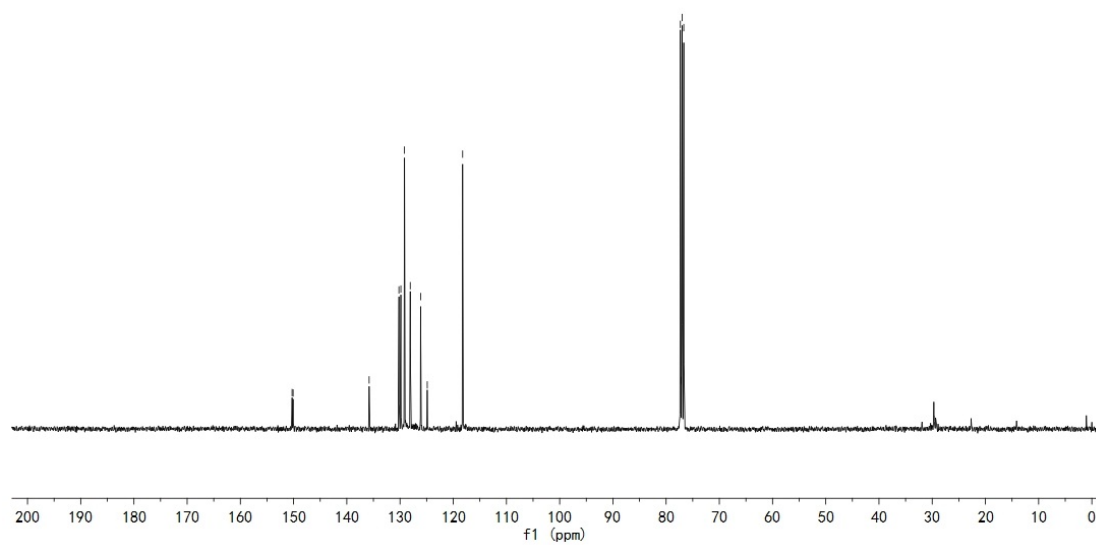
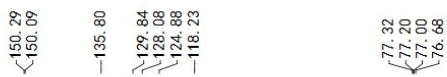
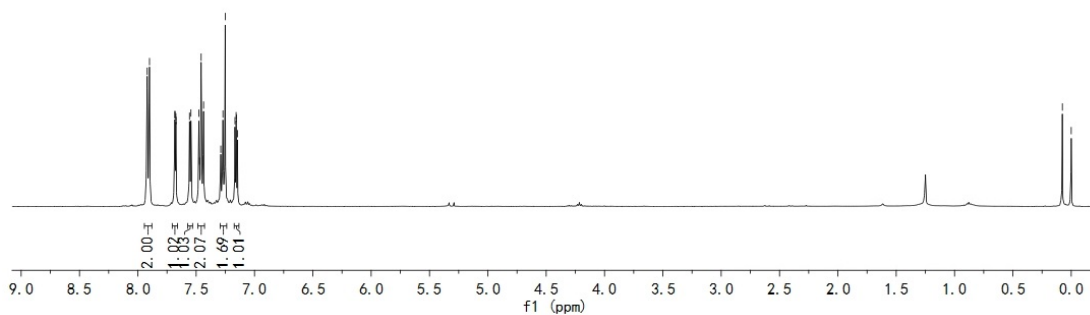




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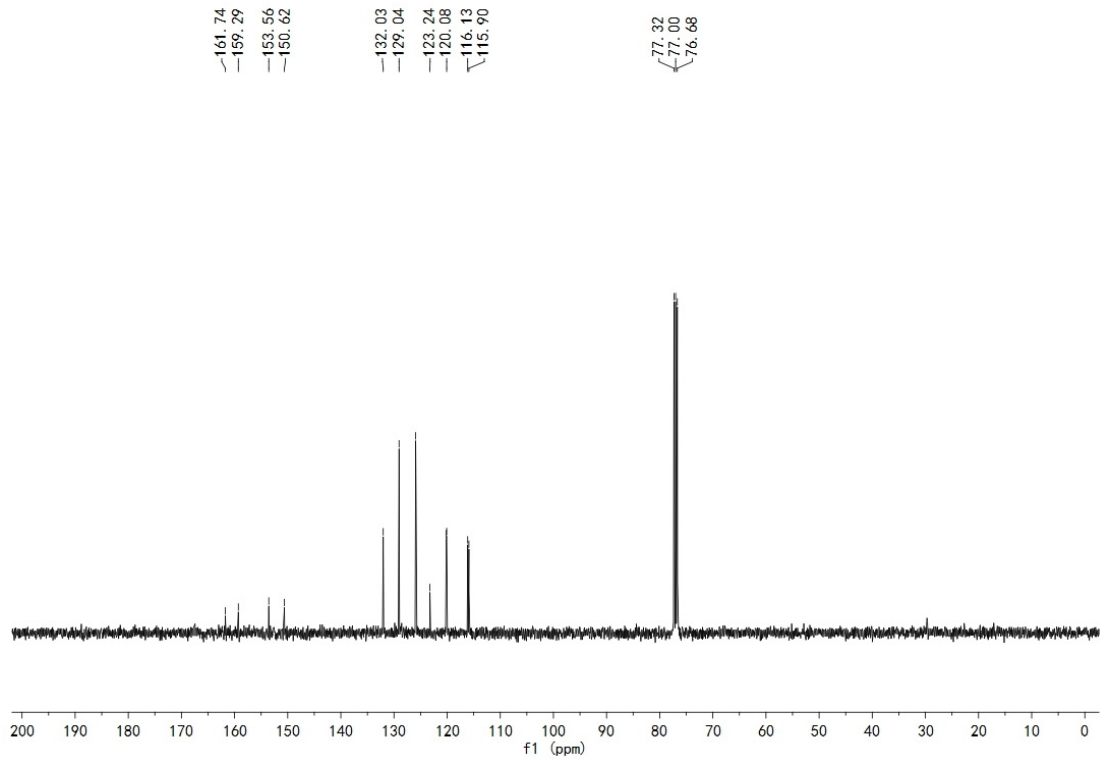
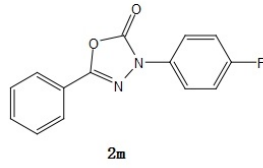
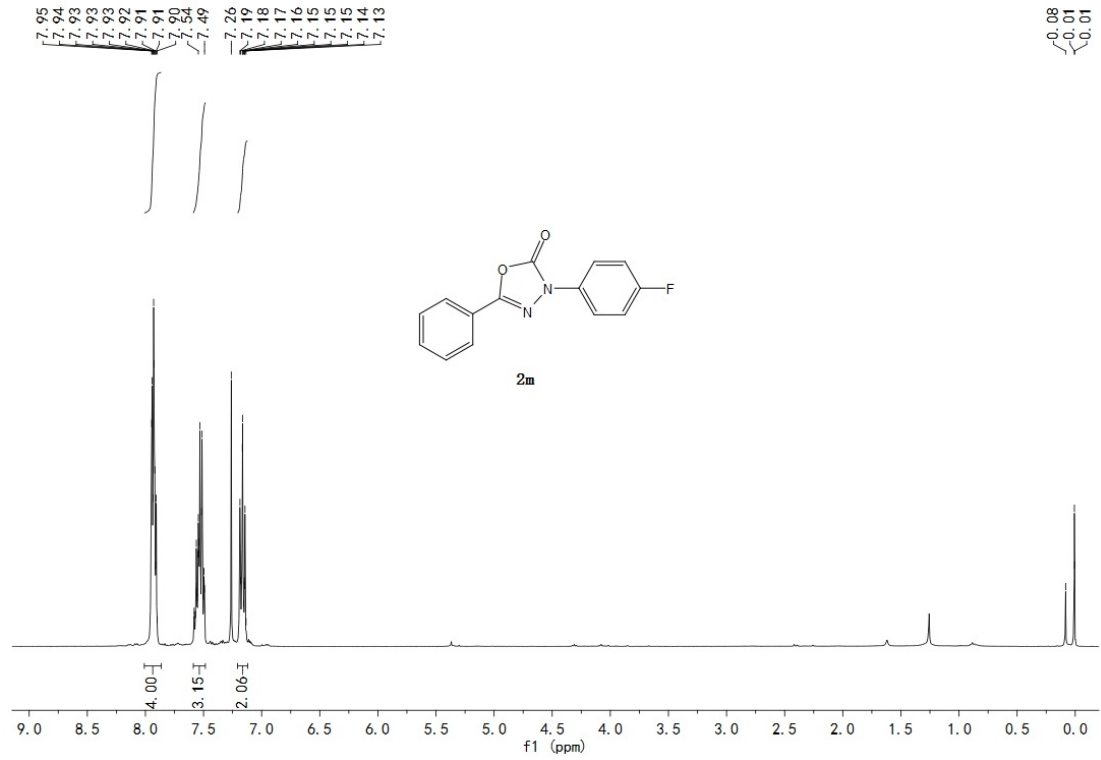
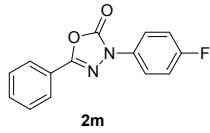


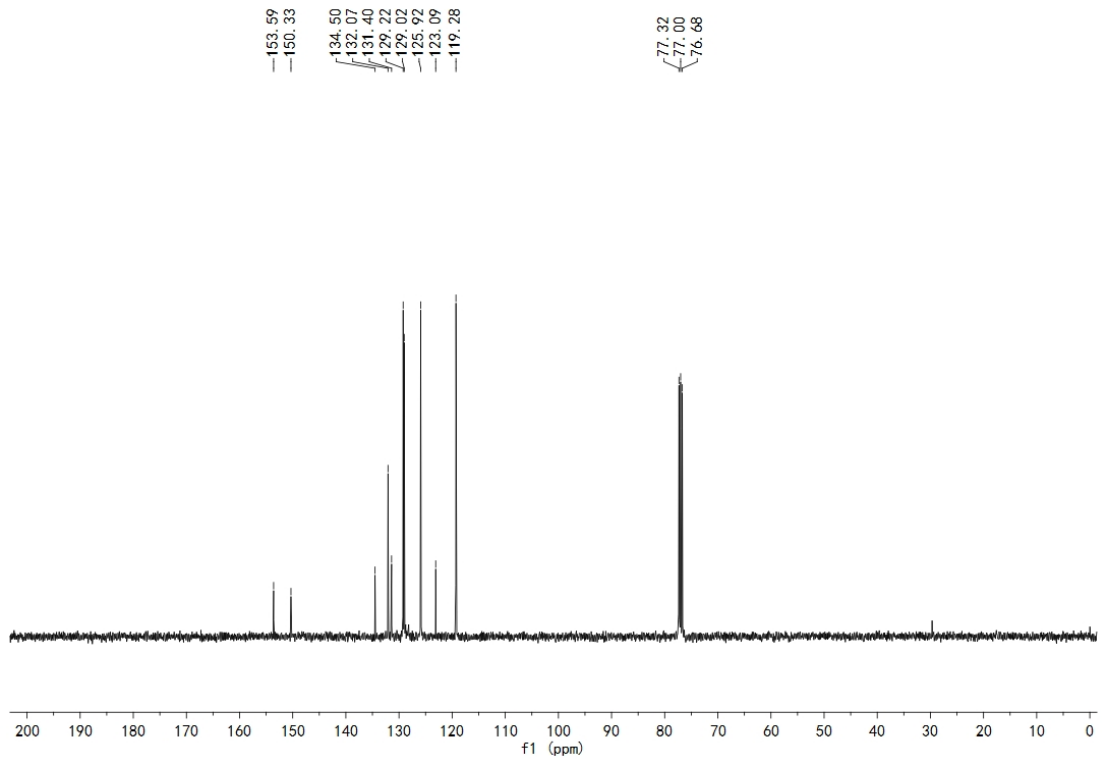
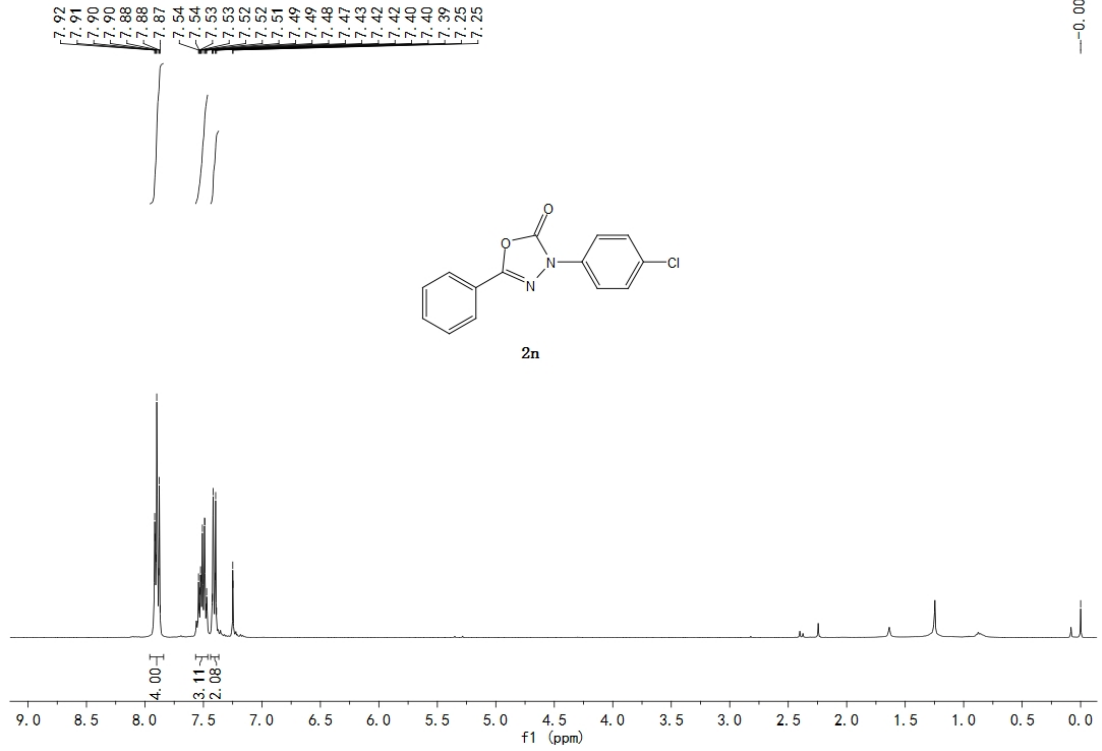
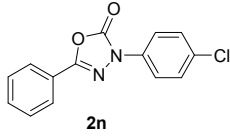
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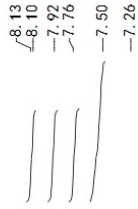
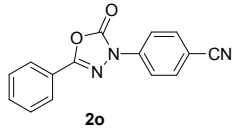




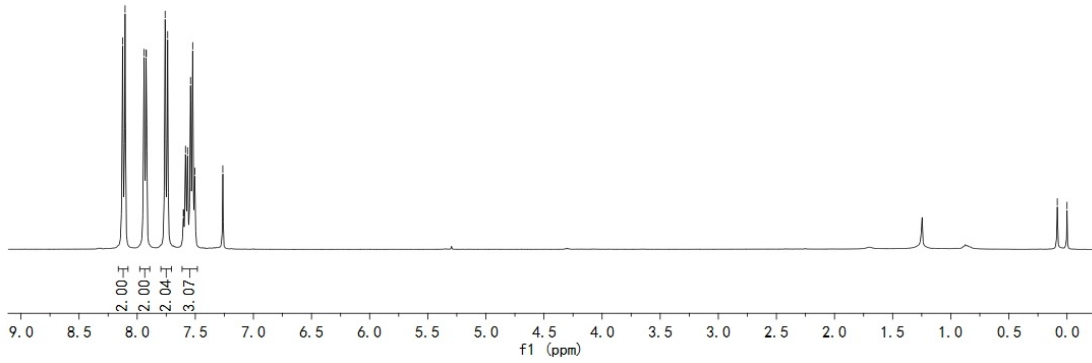
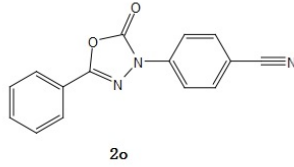








0.08  
0.00



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122.66  
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109.20  
77.32  
77.00  
76.68

