

**Electrochemical-promoted annulation of aldehydes and carbazates:  
Access to 2-alkoxy/aryloxy-5-substituted 1,3,4-oxadiazole and 1,3,4-  
oxadiazol-2(3*H*)-one derivatives**

Hongjun Li,<sup>a</sup> Dong Tang,<sup>\*,b</sup> Zafar Iqbal,<sup>b</sup> Yaya Wan,<sup>b</sup> Rui Jiang,<sup>b</sup> Zhixiang Yang,<sup>\*,b</sup> and Jinhui Yang<sup>\*,a</sup>

<sup>a</sup> State Key Laboratory of High-efficiency Utilization of Coal and Green Chemical Engineering, College of Chemistry and Chemical Engineering, Ningxia University, Yinchuan, 750021, People's Republic of China.

<sup>b</sup> Ningxia Center of Agricultural Organic Synthesis, Agricultural Resource and Environment Institute of Ningxia Academy of Agriculture and Forestry Science, Yinchuan 750002, PR China.

E-mail: yang\_jh@nxu.edu.cn, tangdongabcd@126.com (D. Tang), yangzhixiang8@163.com (Z. Yang)

## Supporting Information

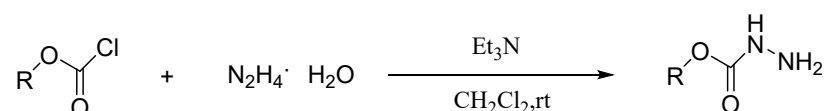
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## 1. General information

All reactions were carried out under an air atmosphere in an undivided glass beaker. Melting points were determined in open glass capillaries in an electrical melting point apparatus, and were uncorrected. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Analytical TLC was performed with silica gel GF254 plates, and the products were visualized by UV detection. Organic extracts were dried over anhydrous sodium sulphate. Solvents were removed in a rotary evaporator under reduced pressure. Column chromatography was performed on silica gel 100-200 mesh using a mixture of petroleum ether and ethyl acetate as eluent, an isolated compounds were characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, HRMS. NMR spectra for all the samples were measured in deuteriochloroform ( $\text{CDCl}_3$ ) and dimethylsulfoxide- $d_6$  ( $\text{DMSO}-d_6$ ).  $^1\text{H}$  and  $^{13}\text{C}$ -NMR spectra were recorded at ambient temperature on 400 MHz and 80 MHz spectrometer using tetramethylsilane (TMS) as internal reference. The chemical shifts are quoted in  $\delta$  units, parts per million (ppm) up field from the signal of internal TMS.  $^1\text{H}$  NMR represented as follows: Chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = R data double doublet), integration and coupling constant(s)  $J$  in Hertz (Hz). High resolution mass spectra (HRMS) were recorded on a Mass spectrometer using electrospray ionization-time of flight (ESI-TOF) reflectron experiments.

## 2. Preparation of substrates

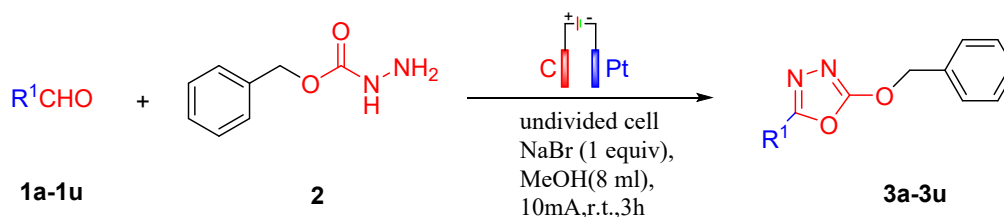
### 2.1 Procedure for the preparation of alkyl/benzyl carbazates



The alkyl/benzyl carbazates were synthesized according to the following method: the triethylamine (5 mmol, 1.0 equiv), hydrazine hydrate (0.5 g, 10 mmol, 2.0 equiv) were mixed in a flask with a magnetic stirring bar, 30 mL  $\text{CH}_2\text{Cl}_2$  was added. Then, at  $20 \pm 2^\circ\text{C}$ , slowly drip alkyl/benzyl chloroformate into the reaction solution, the dripping time is controlled at 10 min, and the reaction is kept for 2 h; After the reaction was completed as indicated by TLC, the system was quenched with water (5

mL), and extracted with ethyl acetate (10 mL × 3). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The resulting crude products were purified by silica gel chromatography (5%-20% ethyl acetate in petroleum ether) to obtain the desired alkyl/benzyl carbazates.

### 3. General procedure for synthesis of compound 3:

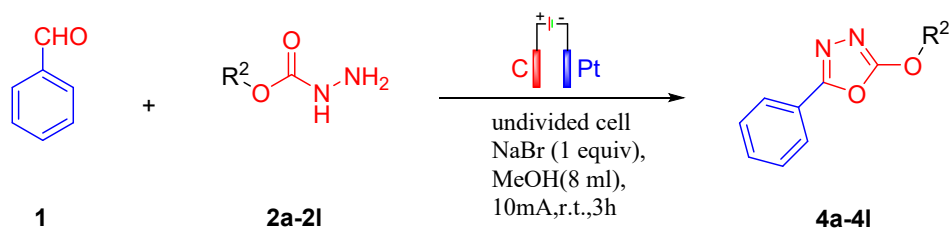


An undivided glass beaker (20 mL) was charged with aldehydes **1** (0.3 mmol), benzyl carbazate **2** (49.8 mg, 0.3 mmol), Sodium bromide (1.0 equiv., 30.6 mg) and methanol (8 mL). The beaker was equipped with platinum electrodes (1.0 cm×1.0 cm×0.1 mm) as cathode, graphite rod (Φ 6 mm, about 10 mm immersion depth in solution) as the anode (**Fig. S1**). The reaction mixture was stirred and electrolyzed for 3 h at a constant current of 10 mA at room temperature under air. After completion of the reaction, the crude mixture was concentrated under reduced pressure and then purified by silica gel chromatography (eluted with EtOAc/PE = 1:10) to afford the desired oxadiazoles **3**.



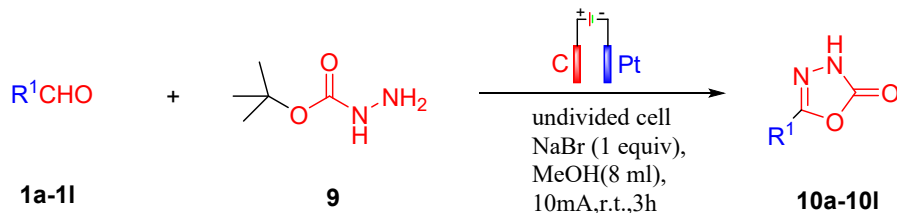
**Fig. S1** Reaction plant diagram

#### 4. General procedure for synthesis of compound 4:



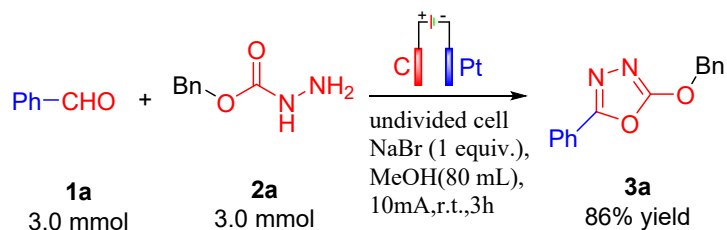
An undivided glass beaker (20 mL) was charged with benzaldehyde **1** (31.4  $\mu$ L, 0.3 mmol), carbazates **2** (0.3 mmol), Sodium bromide (1.0 equiv., 30.6 mg) and methanol (8 mL). The beaker was equipped with platinum electrodes (1.0 cm  $\times$  1.0 cm  $\times$  0.1 mm) as cathode, graphite rod ( $\Phi$  6 mm, about 10 mm immersion depth in solution) as the anode. The reaction mixture was stirred and electrolyzed for 3 h at a constant current of 10 mA at room temperature under air. After completion of the reaction, the crude mixture was concentrated under reduced pressure and then purified by silica gel chromatography (eluted with EtOAc/PE = 1:10) to afford the desired oxadiazoles **4**.

#### 5. General procedure for synthesis of compound 10:



An undivided glass beaker (20 mL) was charged with aldehydes **1** (0.3 mmol), *tert*-butyl carbazate **2** (39.6 mg, 0.3 mmol), Sodium bromide (1.0 equiv., 30.6 mg) and methanol (8 mL). The beaker was equipped with platinum electrodes (1.0 cm $\times$ 1.0 cm $\times$ 0.1 mm) as cathode, graphite rod ( $\Phi$  6 mm, about 10 mm immersion depth in solution) as the anode. The reaction mixture was stirred and electrolyzed for 3 h at a constant current of 10 mA at room temperature under air. After completion of the reaction, the crude mixture was concentrated under reduced pressure and then purified by silica gel chromatography (eluted with EtOAc/PE = 1:5) to afford the title compound **10**.

## 6. Gram-scale experiment (3.0 mmol scale)



An undivided glass beaker (100 mL) was charged with benzaldehyde **1a** (314.0  $\mu\text{L}$ , 3 mmol), benzyl carbazate **2a** (498.0 mg, 3 mmol), Sodium bromide (1.0 equiv., 300.6 mg) and methanol (80 mL). The beaker was equipped with platinum electrodes (1.0 cm $\times$ 1.0 cm $\times$ 0.1 mm) as cathode, graphite rod ( $\Phi$  6 mm, about 10 mm immersion depth in solution) as the anode (**Fig. S2**). The reaction mixture was stirred and electrolyzed for 12 h at a constant current of 10 mA at room temperature under air. After completion of the reaction, the crude mixture was concentrated under reduced pressure and then purified by silica gel chromatography (eluted with EtOAc/PE = 1:10) to afford 2-(benzyloxy)-5-phenyl-1,3,4-oxadiazole **3a** in 86% yield (650.2 mg, white solid).



**Fig. S2** Gram-scale reaction plant diagram

## 7. Optimization of the reaction conditions

**Table S1.** Optimization of the current intensity

Reaction scheme for Table S1: Benzaldehyde (1a, 0.3 mmol) reacts with benzylhydrazinecarboxylate (2a, 0.3 mmol) in an undivided cell with NaBr (1 equiv) in MeOH (8 mL) at **x mA** for 3 hours to form benzyl 1-phenyl-1H-tetrazol-5-ylidenehydrazinecarboxylate (3a).

Entry	I (mA)	Yield (%)
1	3 mA	36
2	5 mA	45
<b>3</b>	<b>10 mA</b>	<b>89</b>
4	15 mA	83
5	20 mA	81

**Table S2.** Optimization of the ratio of 1a and 2a

Reaction scheme for Table S2: Benzaldehyde (1a, 0.3 mmol) reacts with benzylhydrazinecarboxylate (2a, **x mmol**) in an undivided cell with NaBr (1 equiv) in MeOH (8 mL) at 10 mA for 3 hours to form benzyl 1-phenyl-1H-tetrazol-5-ylidenehydrazinecarboxylate (3a).

Entry	1a:2a	Yield (%)
1	1:0.5	56
<b>2</b>	<b>1:1</b>	<b>88</b>
3	1:1.2	81
4	1:1.5	79
5	1:1.8	67

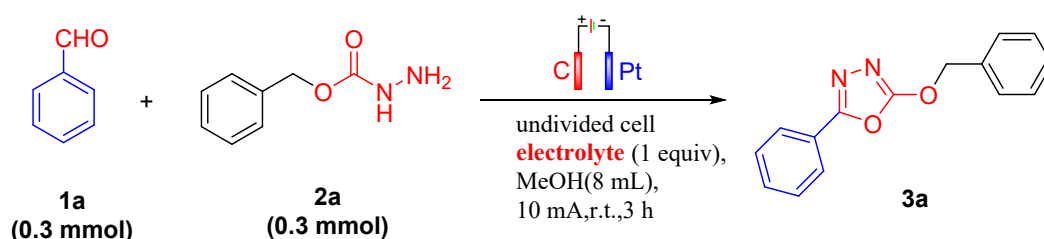
**Table S3.** Optimization of the reaction time

Reaction scheme for Table S3: Benzaldehyde (1a, 0.3 mmol) reacts with benzylhydrazinecarboxylate (2a, 0.3 mmol) in an undivided cell with NaBr (1 equiv) in MeOH (8 mL) at 10 mA for **x h** to form benzyl 1-phenyl-1H-tetrazol-5-ylidenehydrazinecarboxylate (3a).

Entry	T (h)	Yield (%)
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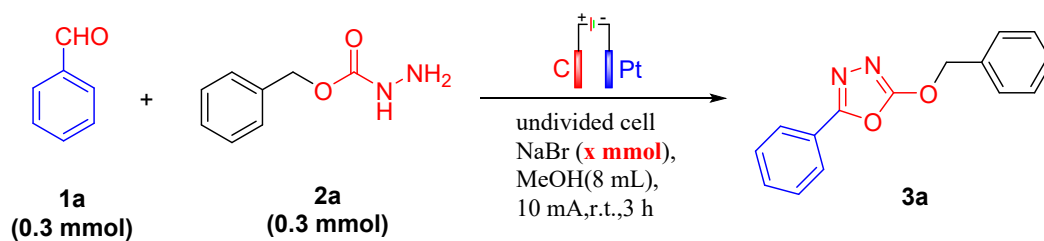
1	1	18
2	1.5	38
3	2	42
4	3	<b>90</b>
5	4	69

**Table S4.** Optimization of the electrolyte type



Entry	Electrolyte	Yield (%)
1	KI	87
2	NaI	84
3	<b>NaBr</b>	<b>91</b>
4	TBAI	85
5	LiClO <sub>4</sub>	Trace
6	NH <sub>4</sub> I	63
7	K <sub>3</sub> PO <sub>4</sub>	79

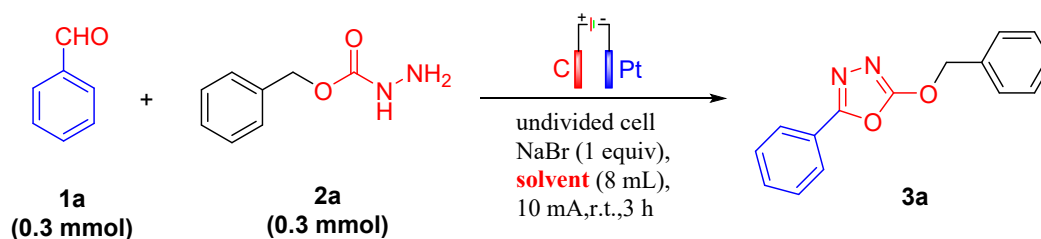
**Table S5.** Optimization of the quantity of electrolyte





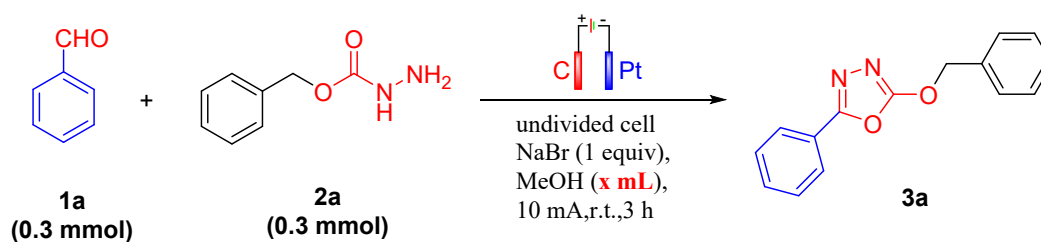
Entry	Quantity (mmol)	Yield (%)
1	0.1	63
2	0.2	78
<b>3</b>	<b>0.3</b>	<b>88</b>
4	0.6	83
5	1.0	80

**Table S6.** Optimization of the solvent conditions



Entry	Solvent	Yield (%)
1	C <sub>2</sub> H <sub>5</sub> OH	84
2	H <sub>2</sub> O	45
3	CH <sub>3</sub> CN	85
4	DMF	26
5	DMSO-d <sub>6</sub>	18
6	CH <sub>3</sub> CN+H <sub>2</sub> O (7:1)	83
7	C <sub>2</sub> H <sub>5</sub> OH+H <sub>2</sub> O (7:1)	82
<b>8</b>	<b>CH<sub>3</sub>OH</b>	<b>91</b>

**Table S7.** Optimization of the solvent volume

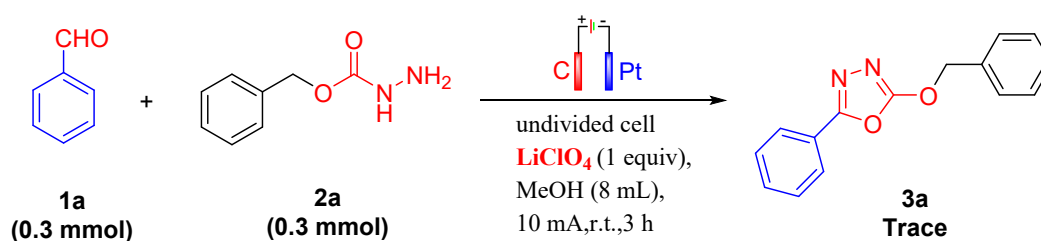


Entry	CH <sub>3</sub> OH (mL)	Yield (%)
1	4	77

2	6	81
3	8	88
4	10	83
5	15	79

## 8. Mechanistic studies

### 8.1 LiClO<sub>4</sub> experiments

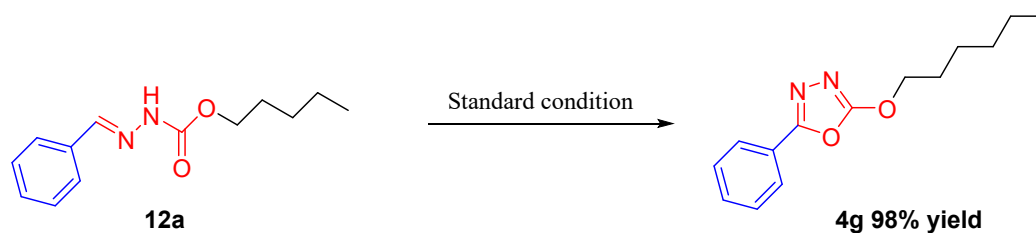


An undivided glass beaker (20 mL) was charged with benzaldehyde **1a** (31.4  $\mu$ L, 0.3 mmol), benzyl carbazate **2a** (49.8 mg, 0.3 mmol), LiClO<sub>4</sub> (1.0 equiv., 106 mg) and methanol (8 mL). The beaker was equipped with platinum electrodes (1.0 cm $\times$ 1.0 cm $\times$ 0.1 mm) as cathode, graphite rod ( $\Phi$  6 mm, about 10 mm immersion depth in solution) as the anode. The reaction mixture was stirred and electrolyzed for 3 h at a constant current of 10 mA at room temperature under air (**Fig. S3**). After completion of the reaction, only a trace amount of the desired product **3a** was observed by liquid chromatography–mass spectrometry (LCMS).



**Fig. S3** Undivided-cell reaction plant diagram

### 8.2 Intermediate 12a experiment

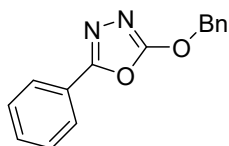


An undivided glass beaker (20 mL) was charged with **12a** (70.2  $\mu$ L, 0.3 mmol) and MeOH (8 mL)<sup>[s1]</sup>. The beaker was equipped with platinum electrodes (1.0 cm $\times$ 1.0 cm  $\times$  0.1 mm) as cathode, graphite rod ( $\Phi$  6 mm, about 10 mm immersion depth in solution) as the anode. The reaction mixture was stirred and electrolyzed for 3 h at a constant current of 10 mA at room temperature under air, the desired product **4g** could be obtained in 98% yield, indicating that **12a** may be the reaction intermediate.

## 9. References

[s1] L. Fangling, G. Fengping, L. Liangsen, Z. Kan, L. Zhen, Z. Xinwei, Y. Ying, W. Ying, Prof. Dr. G. Ziwei, Z. Heng, Prof. Dr. L. Aiwen, Electrochemical synthesis of 2, 5-disubstituted 1, 3, 4-oxadiazoles from  $\alpha$ -keto acids and acylhydrazines under mild conditions, *Eur. J. Org. Chem.*, 2020, **22**, 3257–3260.

## 10. Spectroscopic data for the products



### 2-(benzyloxy)-5-phenyl-1,3,4-oxadiazole (3a)

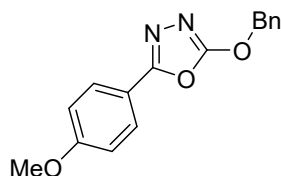
The desired product **3a** (yield 91%, white solid, 68.8 mg) was afforded by flash chromatography on silica gel (petroleum ether/EtOAc (10:1)).

**Mp:** 78–80 °C.

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*):**  $\delta$  7.85 (dd,  $J = 6.7, 1.9$  Hz, 2H), 7.50–7.29 (m, 8H), 5.47 (s, 2H);

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*)**  $\delta$  165.65, 160.75, 133.83, 131.29, 129.32, 128.98, 128.89, 128.82, 126.10, 124.04, 74.49.

**HRMS (TOF):**  $m/z$  calcd for  $C_{15}H_{13}N_2O_2^+$   $[M+H]^+$  : 253.0972, found: 253.0974.



### 2-(benzyloxy)-5-(4-methoxyphenyl)-1,3,4-oxadiazole (3b)

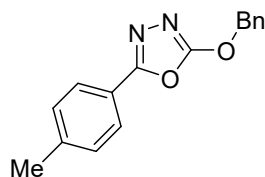
The desired product **3b** (yield 65%, white solid, 55.0 mg) was afforded by flash chromatography on silica gel (petroleum ether/EtOAc (10:1)).

**Mp:** 95–97 °C.

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*):**  $\delta$  7.79 (d,  $J = 8.9$  Hz, 2H), 7.44 (dd,  $J = 7.7, 1.9$  Hz, 2H), 7.38–7.30 (m, 3H), 6.89 (d,  $J = 8.9$  Hz, 2H), 5.45 (s, 2H), 3.78 (s, 3H);

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*):**  $\delta$  165.38, 161.96, 160.73, 133.96, 129.24, 128.82, 128.78, 127.85, 116.62, 114.40, 74.35, 55.43.

**HRMS (TOF):**  $m/z$  calcd for  $C_{16}H_{15}N_2O_3^+$   $[M+H]^+$  : 283.1077, found: 283.1072.



### 2-(benzyloxy)-5-(p-tolyl)-1,3,4-oxadiazole (3c)

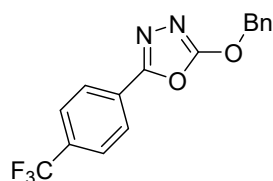
The desired product **3c** (yield 85%, white solid, 67.8 mg) was afforded by flash chromatography on silica gel (petroleum ether/EtOAc (10:1)).

**Mp:** 72–74 °C.

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*):**  $\delta$  7.90–7.78 (m, 2H), 7.54 (dd,  $J = 7.4, 2.2$  Hz, 2H), 7.49–7.39 (m, 3H), 7.32–7.26 (m, 2H), 5.56 (s, 2H), 2.42 (s, 3H);

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*):**  $\delta$  165.52, 160.92, 141.71, 133.94, 129.66, 129.25, 128.83, 128.79, 126.07, 121.32, 74.40, 21.60.

**HRMS (TOF):**  $m/z$  calcd for  $C_{15}H_{12}ClN_2O_2^+$   $[M+H]^+$ : 287.0582, found: 287.0585.



### 2-(benzyloxy)-5-(4-(trifluoromethyl)phenyl)-1,3,4-oxadiazole (**3d**)

The desired product **3d** (yield 88%, white solid, 84.5 mg) was afforded by flash chromatography on silica gel (petroleum ether/EtOAc (10:1)).

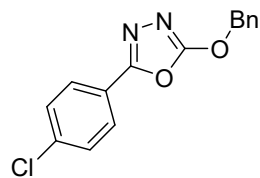
**Mp:** 83–85 °C.

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*):**  $\delta$  7.97 (d,  $J = 8.2$  Hz, 2H), 7.65 (d,  $J = 8.3$  Hz, 2H), 7.48–7.42 (m, 2H), 7.40–7.30 (m, 3H), 5.49 (s, 2H);

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*):**  $\delta$  165.94, 159.56, 133.61, 129.43, 128.93, 128.85, 127.26, 126.37, 126.11, 126.07, 126.03, 125.99, 74.81;

**<sup>19</sup>F NMR (376 MHz, Chloroform-*d*):**  $\delta$  -63.09.

**HRMS (TOF):**  $m/z$  calcd for  $C_{16}H_{12}F_3N_2O_2^+$   $[M+H]^+$ : 321.0845, found: 321.0841.



### 2-(benzyloxy)-5-(4-chlorophenyl)-1,3,4-oxadiazole (**3e**)

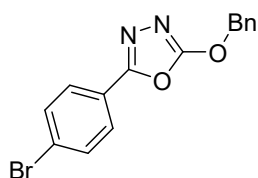
The desired product **3e** (yield 97%, white solid, 83.2 mg) was afforded by flash chromatography on silica gel (petroleum ether/EtOAc (10:1)).

**Mp:** 91–92 °C.

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*):**  $\delta$  7.88 (d,  $J$  = 8.3 Hz, 2H), 7.61–7.36 (m, 7H), 5.56 (s, 2H);

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*):**  $\delta$  165.69, 159.92, 137.46, 133.74, 129.36, 128.88, 128.82, 127.35, 122.53, 74.63.

**HRMS (TOF):**  $m/z$  calcd for C<sub>15</sub>H<sub>12</sub>ClN<sub>2</sub>O<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup> : 287.0582, found: 287.0585.



### 2-(benzyloxy)-5-(4-bromophenyl)-1,3,4-oxadiazole (**3f**)

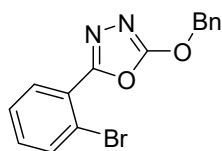
The desired product **3f** (yield 88%, white solid, 87.1 mg) was afforded by flash chromatography on silica gel (petroleum ether/EtOAc (10:1)).

**Mp:** 122–124 °C.

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*):**  $\delta$  7.71 (d,  $J$  = 8.6 Hz, 2H), 7.56–7.49 (m, 2H), 7.47–7.40 (m, 2H), 7.33 (dq,  $J$  = 4.8, 2.9, 2.5 Hz, 3H), 5.46 (s, 2H);

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*):**  $\delta$  165.70, 160.01, 133.73, 132.31, 129.35, 128.88, 128.82, 127.50, 125.85, 122.97, 74.65.

**HRMS (TOF):**  $m/z$  calcd for C<sub>15</sub>H<sub>12</sub>BrN<sub>2</sub>O<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup> : 331.0077, found: 331.0071.



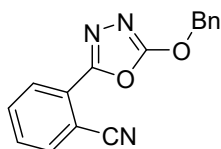
### 2-(benzyloxy)-5-(2-bromophenyl)-1,3,4-oxadiazole (**3g**)

The desired product **3g** (yield 79%, yellow oil, 78.2 mg) was afforded by flash chromatography on silica gel (petroleum ether/EtOAc (10:1)).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*):**  $\delta$  7.74 (dd,  $J$  = 7.7, 1.8 Hz, 1H), 7.62 (dd,  $J$  = 8.0, 1.3 Hz, 1H), 7.44 (dd,  $J$  = 7.3, 2.2 Hz, 2H), 7.33 (dt,  $J$  = 8.2, 5.1, 2.8 Hz, 4H), 7.25 (td,  $J$  = 7.7, 1.8 Hz, 1H), 5.47 (s, 2H);

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*):**  $\delta$  165.93, 159.50, 134.51, 133.76, 132.16, 131.13, 129.34, 128.95, 128.81, 127.53, 125.35, 121.24, 74.65.

**HRMS (TOF):**  $m/z$  calcd for C<sub>15</sub>H<sub>12</sub>BrN<sub>2</sub>O<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup> : 331.0077, found: 331.0071.



### 2-(5-(benzyloxy)-1,3,4-oxadiazol-2-yl)benzonitrile (3h)

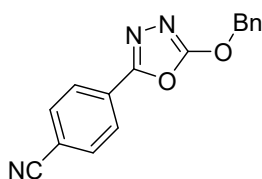
The desired product **3h** (yield 62%, white solid, 51.5 mg) was afforded by flash chromatography on silica gel (petroleum ether/EtOAc (10:1)).

**Mp:** 79–80 °C.

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*):**  $\delta$  8.02 (dd,  $J = 8.0, 1.2$  Hz, 1H), 7.75 (dd,  $J = 7.9, 1.3$  Hz, 1H), 7.64 (td,  $J = 7.7, 1.4$  Hz, 1H), 7.53 (td,  $J = 7.7, 1.3$  Hz, 1H), 7.49–7.42 (m, 2H), 7.35 (dd,  $J = 5.1, 2.1$  Hz, 3H), 5.51 (s, 2H);

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*):**  $\delta$  166.01, 158.02, 134.86, 133.49, 133.04, 131.19, 129.44, 129.06, 128.82, 128.45, 126.12, 116.93, 109.85, 75.02.

**HRMS (TOF):**  $m/z$  calcd for  $C_{16}H_{12}N_3O_2^+$  [M+H]<sup>+</sup> : 278.0924, found: 278.0927.



### 4-(5-(benzyloxy)-1,3,4-oxadiazol-2-yl)benzonitrile (3i)

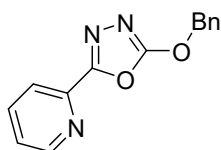
The desired product **3i** (yield 90%, white solid, 74.8 mg) was afforded by flash chromatography on silica gel (petroleum ether/EtOAc (10:1)).

**Mp:** 123–124 °C.

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*):**  $\delta$  7.95 (d,  $J = 8.5$  Hz, 2H), 7.68 (d,  $J = 8.5$  Hz, 2H), 7.48–7.41 (m, 2H), 7.34 (dd,  $J = 5.1, 2.1$  Hz, 3H), 5.49 (s, 2H);

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*):**  $\delta$  166.03, 159.16, 133.49, 132.82, 129.49, 128.96, 128.87, 127.88, 126.47, 117.97, 114.68, 74.97.

**HRMS (TOF):**  $m/z$  calcd for  $C_{16}H_{12}N_3O_2^+$  [M+H]<sup>+</sup> : 278.0924, found: 278.0928.



### 2-(benzyloxy)-5-(pyridin-2-yl)-1,3,4-oxadiazole (3k)

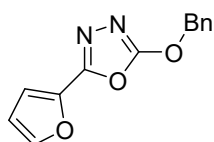
The desired product **3k** (yield 91%, light yellow powder, 69.1 mg) was afforded by flash chromatography on silica gel (petroleum ether/EtOAc (10:1)).

**Mp:** 98–100 °C.

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*):**  $\delta$  8.63 (ddd,  $J = 4.8, 2.9, 1.6$  Hz, 1H), 8.04–7.97 (m, 1H), 7.74 (ddd,  $J = 9.5, 6.2, 1.7$  Hz, 1H), 7.42 (dt,  $J = 7.1, 2.1$  Hz, 2H), 7.37–7.26 (m, 4H), 5.49 (s, 2H);

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*):**  $\delta$  166.22, 159.92, 150.15, 143.51, 137.10, 133.77, 129.20, 128.75, 128.59, 125.44, 122.05, 74.58.

**HRMS (TOF):**  $m/z$  calcd for C<sub>14</sub>H<sub>12</sub>N<sub>3</sub>O<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup> : 254.0924, found: 254.0927.



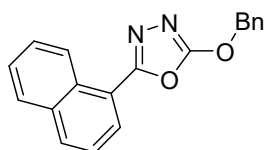
#### 2-(benzyloxy)-5-(furan-2-yl)-1,3,4-oxadiazole (**3l**)

The desired product **3l** (yield 74%, yellow oil, 90.5 mg) was afforded by flash chromatography on silica gel (petroleum ether/EtOAc (10:1)).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*):**  $\delta$  7.52 (dd,  $J = 1.8, 0.8$  Hz, 1H), 7.46–7.40 (m, 2H), 7.34 (dd,  $J = 5.0, 2.1$  Hz, 3H), 6.94 (dd,  $J = 3.6, 0.8$  Hz, 1H), 6.48 (dd,  $J = 3.5, 1.8$  Hz, 1H), 5.47 (s, 2H);

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*):**  $\delta$  165.11, 153.77, 145.30, 139.24, 133.68, 129.34, 128.81, 112.94, 111.91, 77.24, 74.78.

**HRMS (TOF):**  $m/z$  calcd for C<sub>13</sub>H<sub>11</sub>N<sub>2</sub>O<sub>3</sub><sup>+</sup> [M+H]<sup>+</sup> : 243.0764, found: 243.0761.



#### 2-(benzyloxy)-5-(naphthalen-1-yl)-1,3,4-oxadiazole (**3m**)

The desired product **3m** (yield 81%, white solid, 73.4 mg) was afforded by flash chromatography on silica gel (petroleum ether/EtOAc (10:1)).

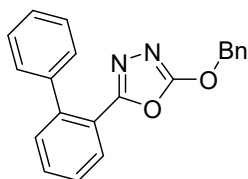
**Mp:** 101–102 °C.



**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*):**  $\delta$  9.12 (d,  $J$  = 8.6 Hz, 1H), 7.95 (d,  $J$  = 7.3 Hz, 1H), 7.89 (d,  $J$  = 8.3 Hz, 1H), 7.81 (d,  $J$  = 8.2 Hz, 1H), 7.57 (ddd,  $J$  = 8.4, 6.7, 1.4 Hz, 1H), 7.52–7.40 (m, 4H), 7.40–7.29 (m, 3H), 5.51 (s, 2H);

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*):**  $\delta$  165.49, 160.89, 133.91, 133.81, 132.14, 129.85, 129.32, 128.94, 128.83, 128.62, 128.03, 127.65, 126.66, 126.25, 124.84, 120.50, 74.54.

**HRMS (TOF):**  $m/z$  calcd for C<sub>19</sub>H<sub>15</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup> : 303.1128, found: 303.1124.



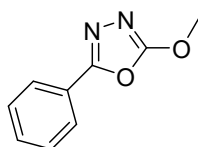
### 2-((1,1'-biphenyl)-2-yl)-5-(benzyloxy)-1,3,4-oxadiazole (3n)

The desired product **3n** (yield 92%, yellow oil, 90.5 mg) was afforded by flash chromatography on silica gel (petroleum ether/EtOAc (10:1)).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*):**  $\delta$  7.79 (dd,  $J$  = 7.8, 1.4 Hz, 1H), 7.45 (td,  $J$  = 7.5, 1.5 Hz, 1H), 7.39–7.23 (m, 10H), 7.18 (dd,  $J$  = 7.2, 2.5 Hz, 2H), 5.27 (s, 2H);

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*):**  $\delta$  165.76, 161.15, 141.86, 140.25, 133.89, 131.15, 130.99, 130.08, 129.16, 128.72, 128.70, 128.67, 128.30, 127.66, 127.62, 123.00, 74.20.

**HRMS (TOF):**  $m/z$  calcd for C<sub>21</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup> : 329.1285, found: 329.1281.



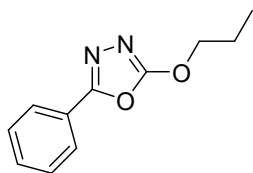
### 2-methoxy-5-phenyl-1,3,4-oxadiazole (4a)

The desired product **4a** (yield 91%, yellow oil, 48.0 mg) was afforded by flash chromatography on silica gel (petroleum ether/EtOAc (10:1)).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*):**  $\delta$  7.83 (dd,  $J$  = 7.7, 2.0 Hz, 2H), 7.43–7.32 (m, 3H), 4.13 (s, 3H);

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*):**  $\delta$  166.34, 160.75, 131.21, 128.92, 126.04, 124.04, 59.38.

**HRMS (TOF):**  $m/z$  calcd for C<sub>9</sub>H<sub>9</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup> : 177.0659, found: 177.0653.



### 2-phenyl-5-propoxy-1,3,4-oxadiazole (**4b**)

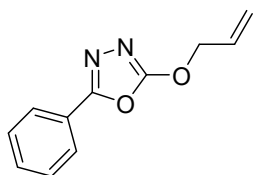
The desired product **4b** (yield 86%, white solid, 52.6 mg) was afforded by flash chromatography on silica gel (petroleum ether/EtOAc (10:1)).

**Mp:** 39–40 °C.

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*):**  $\delta$  7.87–7.76 (m, 2H), 7.35 (d,  $J = 5.7$  Hz, 3H), 4.39 (td,  $J = 6.7, 1.6$  Hz, 2H), 1.79 (q,  $J = 7.1$  Hz, 2H), 0.95 (td,  $J = 7.4, 2.5$  Hz, 3H);

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*):**  $\delta$  165.81, 160.36, 131.08, 128.86, 125.96, 124.13, 74.62, 22.01, 9.98.

**HRMS (TOF):**  $m/z$  calcd for  $C_{11}H_{13}N_2O_2^+$  [ $M+H$ ]<sup>+</sup> : 205.0972, found: 205.0973.



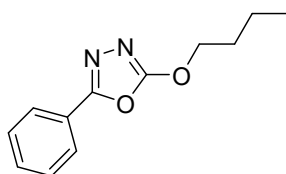
### 2-(allyloxy)-5-phenyl-1,3,4-oxadiazole (**4c**)

The desired product **4c** (yield 65%, yellow oil, 39.4 mg) was afforded by flash chromatography on silica gel (petroleum ether/EtOAc (10:1)).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*):**  $\delta$  7.78 (dd,  $J = 8.2, 1.6$  Hz, 2H), 7.47–7.37 (m, 3H), 5.89 (ddt,  $J = 17.2, 10.2, 5.9$  Hz, 1H), 5.35–5.23 (m, 3H), 4.35 (dt,  $J = 5.9, 1.5$  Hz, 2H);

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*):**  $\delta$  162.46, 153.46, 131.60, 130.75, 128.97, 125.70, 123.83, 119.44, 71.62.

**HRMS (TOF):**  $m/z$  calcd for  $C_{11}H_{11}N_2O_2^+$  [ $M+H$ ]<sup>+</sup> : 203.0815, found: 203.0812.



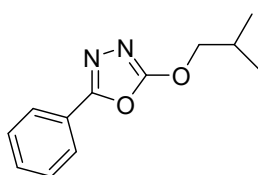
### 2-butoxy-5-phenyl-1,3,4-oxadiazole (**4d**)

The desired product **4d** (yield 87%, yellow oil, 56.9 mg) was afforded by flash chromatography on silica gel (petroleum ether/EtOAc (10:1)).

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*):**  $\delta$  7.86–7.76 (m, 2H), 7.34 (dd,  $J = 5.0, 2.7$  Hz, 3H), 4.43 (t,  $J = 6.6$  Hz, 2H), 1.79–1.69 (m, 2H), 1.39 (qd,  $J = 7.5, 1.9$  Hz, 2H), 0.88 (dd,  $J = 8.3, 6.4$  Hz, 3H);

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*):**  $\delta$  165.80, 160.35, 131.07, 128.86, 125.95, 124.13, 72.97, 30.56, 18.72, 13.54.

**HRMS (TOF):**  $m/z$  calcd for  $C_{12}H_{15}N_2O_2^+$   $[M+H]^+$  : 219.1128, found: 219.1122.



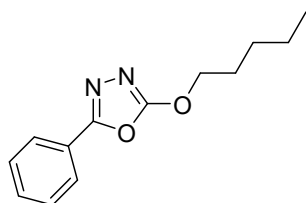
#### 2-isobutoxy-5-phenyl-1,3,4-oxadiazole (**4e**)

The desired product **4e** (yield 85%, yellow oil, 55.6 mg) was afforded by flash chromatography on silica gel (petroleum ether/EtOAc (10:1));

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*):**  $\delta$  7.83 (dd,  $J = 7.3, 2.5$  Hz, 2H), 7.42–7.28 (m, 3H), 4.21 (d,  $J = 6.6$  Hz, 2H), 2.10 (dt,  $J = 13.4, 6.7$  Hz, 1H), 1.02–0.87 (m, 6H);

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*):**  $\delta$  165.91, 160.37, 131.09, 128.87, 125.98, 124.14, 78.93, 27.87, 18.65.

**HRMS (TOF):**  $m/z$  calcd for  $C_{12}H_{15}N_2O_2^+$   $[M+H]^+$  : 219.1128, found: 219.1123.



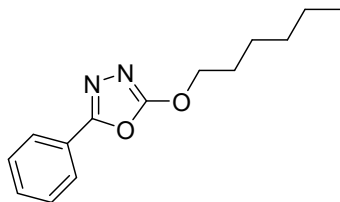
#### 2-(pentyloxy)-5-phenyl-1,3,4-oxadiazole (**4f**)

The desired product **4f** (yield 86%, yellow oil, 59.9 mg) was afforded by flash chromatography on silica gel (petroleum ether/EtOAc (10:1));

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*):**  $\delta$  7.82 (dd,  $J = 7.5, 2.4$  Hz, 2H), 7.42–7.29 (m, 3H), 4.42 (t,  $J = 6.6$  Hz, 2H), 1.76 (dd,  $J = 8.0, 6.4$  Hz, 2H), 1.41–1.24 (m, 4H), 0.83 (t,  $J = 7.0$  Hz, 3H);

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*):**  $\delta$  165.80, 160.35, 131.07, 128.86, 125.96, 124.14, 73.26, 28.28, 27.58, 22.19, 13.85;

**HRMS (TOF):**  $m/z$  calcd for C<sub>13</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup> : 233.1285, found: 233.1288.



#### **2-(hexyloxy)-5-phenyl-1,3,4-oxadiazole (4g)**

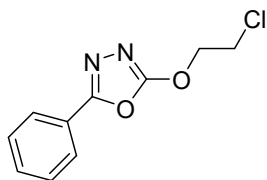
The desired product **4g** (yield 89%, white solid, 65.7 mg) was afforded by flash chromatography on silica gel (petroleum ether/EtOAc (10:1)).

**Mp:** 45–47 °C.

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*):**  $\delta$  7.90–7.77 (m, 2H), 7.39–7.29 (m, 3H), 4.43 (t,  $J$  = 6.6 Hz, 2H), 1.82–1.70 (m, 2H), 1.43–1.30 (m, 2H), 1.24 (dp,  $J$  = 7.2, 3.2 Hz, 4H), 0.85–0.75 (m, 3H);

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*):**  $\delta$  165.81, 160.36, 131.07, 128.86, 125.97, 124.16, 73.28, 31.27, 28.55, 25.15, 22.46, 13.92;

**HRMS (TOF):**  $m/z$  calcd for C<sub>14</sub>H<sub>19</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup> : 247.1441, found: 247.1443.



#### **2-(2-chloroethoxy)-5-phenyl-1,3,4-oxadiazole (4h)**

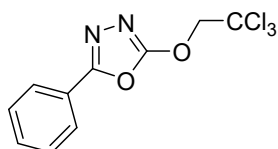
The desired product **4h** (yield 90%, white solid, 60.5 mg) was afforded by flash chromatography on silica gel (petroleum ether/EtOAc (10:1));

**Mp:** 86–88 °C;

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*):**  $\delta$  7.86 (dd,  $J$  = 7.7, 1.8 Hz, 2H), 7.48–7.35 (m, 3H), 4.76–4.66 (m, 2H), 3.91–3.80 (m, 2H);

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*):**  $\delta$  165.27, 160.99, 131.41, 128.99, 126.14, 123.86, 72.00, 40.77;

**HRMS (TOF):**  $m/z$  calcd for C<sub>10</sub>H<sub>10</sub>ClN<sub>2</sub>O<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup> : 225.0425, found: 225.0428.



#### 2-phenyl-5-(2, 2, 2-trichloroethoxy)-1,3,4-oxadiazole (4i)

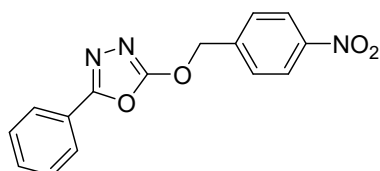
The desired product **4i** (yield 51%, white solid, 44.5 mg) was afforded by flash chromatography on silica gel (petroleum ether/EtOAc (10:1));

**Mp:** 112–114 °C.

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*):**  $\delta$  7.91 (dd,  $J = 8.0, 1.7$  Hz, 2H), 7.50–7.39 (m, 3H), 5.06 (s, 2H);

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*):**  $\delta$  164.73, 161.53, 131.70, 129.08, 126.28, 123.58, 93.15, 80.67;

**HRMS (TOF):**  $m/z$  calcd for  $C_{10}H_8Cl_3N_2O_2^+$   $[M+H]^+$  : 292.9646, found: 292.9649.



#### 2-((4-nitrobenzyl)oxy)-5-phenyl-1,3,4-oxadiazole (4j)

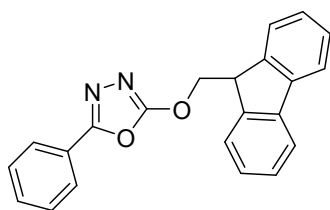
The desired product **4j** (yield 59%, white solid, 52.6 mg) was afforded by flash chromatography on silica gel (petroleum ether/EtOAc (10:1)).

**Mp:** 158–160 °C.

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*):**  $\delta$  8.21 (d,  $J = 8.7$  Hz, 2H), 7.86 (dd,  $J = 7.9, 1.7$  Hz, 2H), 7.62 (d,  $J = 8.7$  Hz, 2H), 7.47–7.37 (m, 3H), 5.57 (s, 2H);

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*):**  $\delta$  165.33, 161.14, 148.31, 140.80, 131.51, 129.03, 128.92, 126.15, 124.00, 123.80, 72.55.

**HRMS (TOF):**  $m/z$  calcd for  $C_{15}H_{12}N_3O_4^+$   $[M+H]^+$  : 298.0822, found: 298.0825.



#### 2-((9H-fluoren-9-yl)methoxy)-5-phenyl-1,3,4-oxadiazole (4k)

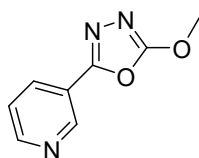
The desired product **4k** (yield 74%, white solid, 75.5 mg) was afforded by flash chromatography on silica gel (petroleum ether/EtOAc (10:1)).

**Mp:** 146–148 °C.

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*):**  $\delta$  7.94–7.83 (m, 2H), 7.72 (d, *J* = 7.5 Hz, 2H), 7.64–7.57 (m, 2H), 7.45–7.33 (m, 5H), 7.27 (td, *J* = 7.5, 1.2 Hz, 2H), 4.74 (d, *J* = 7.1 Hz, 2H), 4.41 (t, *J* = 7.1 Hz, 1H);

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*):**  $\delta$  165.70, 160.81, 142.70, 141.43, 131.34, 128.99, 128.18, 127.35, 126.16, 125.18, 124.02, 120.25, 74.60, 46.67.

**HRMS (TOF):** *m/z* calcd for C<sub>22</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup> : 341.1285, found: 341.1281.



#### **2-methoxy-5-(pyridin-3-yl)-1,3,4-oxadiazole (7a)**

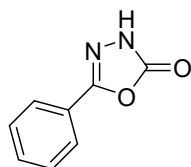
The desired product **7a** (yield 62%, light yellow powder, 32.9 mg) was afforded by flash chromatography on silica gel (petroleum ether/EtOAc (10:1)).

**Mp:** 74–76 °C.

**<sup>1</sup>H NMR (400 MHz, Chloroform-*d*):**  $\delta$  9.09 (dd, *J* = 2.3, 0.9 Hz, 1H), 8.67 (dd, *J* = 4.9, 1.7 Hz, 1H), 8.17 (ddd, *J* = 8.0, 2.3, 1.7 Hz, 1H), 7.36 (ddd, *J* = 8.0, 4.9, 0.9 Hz, 1H), 4.20 (s, 3H);

**<sup>13</sup>C NMR (101 MHz, Chloroform-*d*):**  $\delta$  166.65, 158.66, 152.01, 147.16, 133.30, 123.71, 120.54, 59.69.

**HRMS (TOF):** *m/z* calcd for C<sub>8</sub>H<sub>8</sub>N<sub>3</sub>O<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup> : 178.0611, found: 178.0614.



#### **5-phenyl-1,3,4-oxadiazol-2(3H)-one (10a)**

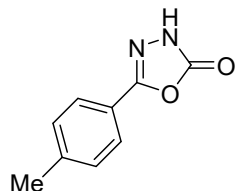
The desired product **10a** (yield 71%, white solid, 34.5 mg) was afforded by flash chromatography on silica gel (petroleum ether/EtOAc (5:1)).

**Mp:** 134–136 °C.

**<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>-*d*<sub>6</sub>):**  $\delta$  12.60 (s, 1H), 7.79 (dd,  $J = 7.8, 1.8$  Hz, 2H), 7.63–7.48 (m, 3H);

**<sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>-*d*<sub>6</sub>):**  $\delta$  154.94, 154.25, 131.89, 129.68, 125.68, 124.43.

**HRMS (TOF):**  $m/z$  calcd for C<sub>8</sub>H<sub>7</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup> : 163.0502, found: 163.0504.



**5-(*p*-tolyl)-1,3,4-oxadiazol-2(3*H*)-one (10b)**

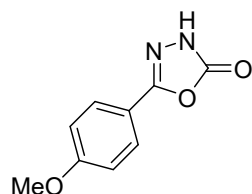
The desired product **10b** (yield 85%, white solid, 44.9 mg) was afforded by flash chromatography on silica gel (petroleum ether/EtOAc (5:1)).

**Mp:** 156–158 °C.

**<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>-*d*<sub>6</sub>):**  $\delta$  12.54 (s, 1H), 7.68 (d,  $J = 8.3$  Hz, 2H), 7.35 (d,  $J = 8.1$  Hz, 2H), 2.38 (s, 3H);

**<sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>-*d*<sub>6</sub>):**  $\delta$  154.94, 154.37, 141.94, 130.19, 125.64, 121.69, 21.52.

**HRMS (TOF):**  $m/z$  calcd for C<sub>9</sub>H<sub>9</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup> : 177.0659, found: 177.0653.



**5-(4-methoxyphenyl)-1,3,4-oxadiazol-2(3*H*)-one (10c)**

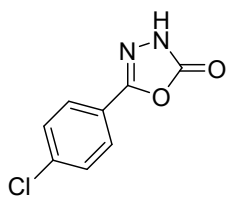
The desired product **10c** (yield 70%, white solid, 40.3 mg) was afforded by flash chromatography on silica gel (petroleum ether/EtOAc (5:1)).

**Mp:** 180–182 °C.

**<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>-*d*<sub>6</sub>):**  $\delta$  12.40 (s, 1H), 7.73 (d,  $J = 8.9$  Hz, 2H), 7.09 (d,  $J = 8.9$  Hz, 2H), 3.83 (s, 3H);

**<sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>-*d*<sub>6</sub>):**  $\delta$  162.08, 155.02, 154.33, 127.55, 116.78, 115.17, 55.93.

**HRMS (TOF):**  $m/z$  calcd for C<sub>9</sub>H<sub>9</sub>N<sub>2</sub>O<sub>3</sub><sup>+</sup> [M+H]<sup>+</sup> : 193.0608, found: 193.0603.



**5-(4-chlorophenyl)-1,3,4-oxadiazol-2(3H)-one (10d)**

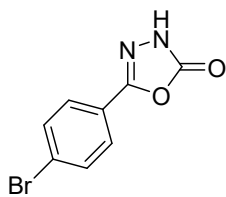
The desired product **10d** (yield 77%, white solid, 45.3 mg) was afforded by flash chromatography on silica gel (petroleum ether/EtOAc (5:1)).

**Mp:** 225–226 °C.

**<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>-*d*<sub>6</sub>):**  $\delta$  12.68 (s, 1H), 7.80 (d, *J* = 8.6 Hz, 2H), 7.62 (d, *J* = 8.7 Hz, 2H);

**<sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>-*d*<sub>6</sub>):**  $\delta$  154.81, 153.47, 136.54, 129.86, 127.50, 123.33.

**HRMS (TOF):** *m/z* calcd for C<sub>8</sub>H<sub>6</sub>ClN<sub>2</sub>O<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup> : 197.0112, found: 197.0115.



**5-(4-bromophenyl)-1,3,4-oxadiazol-2(3H)-one (10e)**

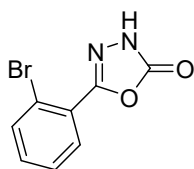
The desired product **10e** (yield 80%, white solid, 57.4 mg) was afforded by flash chromatography on silica gel (petroleum ether/EtOAc (5:1)).

**Mp:** 233–234 °C.

**<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>-*d*<sub>6</sub>):**  $\delta$  12.68 (s, 1H), 7.79–7.70 (m, 4H);

**<sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>-*d*<sub>6</sub>):**  $\delta$  154.80, 153.58, 132.78, 127.64, 125.37, 123.67.

**HRMS (TOF):** *m/z* calcd for C<sub>8</sub>H<sub>6</sub>BrN<sub>2</sub>O<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup> : 240.9607, found: 240.9609.



**5-(2-bromophenyl)-1,3,4-oxadiazol-2(3H)-one (10f)**

The desired product **10f** (yield 79%, white solid, 56.6 mg) was afforded by flash chromatography on silica gel (petroleum ether/EtOAc (5:1)).

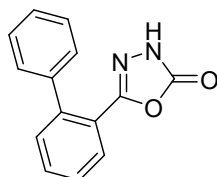


**Mp:** 147–148 °C.

**<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>-*d*<sub>6</sub>):**  $\delta$  12.81 (s, 1H), 7.83 (ddd,  $J = 11.8, 7.8, 1.6$  Hz, 2H), 7.58 (td,  $J = 7.6, 1.4$  Hz, 1H), 7.52 (td,  $J = 7.7, 1.9$  Hz, 1H);

**<sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>-*d*<sub>6</sub>):**  $\delta$  154.75, 153.07, 134.80, 133.28, 131.35, 128.60, 125.28, 120.54.

**HRMS (TOF):**  $m/z$  calcd for C<sub>8</sub>H<sub>6</sub>BrN<sub>2</sub>O<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup> : 240.9607, found: 240.9608.



### 5-([1,1'-biphenyl]-2-yl)-1,3,4-oxadiazol-2(3H)-one (10g)

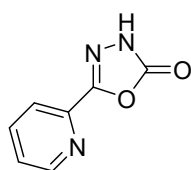
The desired product **10g** (yield 81%, white solid, 57.8 mg) was afforded by flash chromatography on silica gel (petroleum ether/EtOAc (5:1)).

**Mp:** 168–170 °C.

**<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>-*d*<sub>6</sub>):**  $\delta$  12.41 (s, 1H), 7.78 (dd,  $J = 7.7, 1.4$  Hz, 1H), 7.66 (td,  $J = 7.6, 1.4$  Hz, 1H), 7.56 (td,  $J = 7.6, 1.3$  Hz, 1H), 7.50–7.37 (m, 4H), 7.34–7.27 (m, 2H);

**<sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>-*d*<sub>6</sub>):**  $\delta$  154.88, 154.74, 141.54, 140.24, 131.95, 131.49, 129.94, 128.93, 128.81, 128.37, 128.08, 123.17.

**HRMS (TOF):**  $m/z$  calcd for C<sub>14</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup> : 239.0815, found: 239.0817.



### 5-(pyridin-2-yl)-1,3,4-oxadiazol-2(3H)-one (10h)

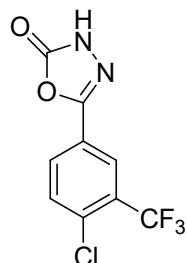
The desired product **10h** (yield 82%, light yellow powder, 40.1 mg) was afforded by flash chromatography on silica gel (petroleum ether/EtOAc (5:1)).

**Mp:** 168–170 °C.

**<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>-*d*<sub>6</sub>):**  $\delta$  12.77 (s, 1H), 8.77–8.66 (m, 1H), 7.98 (tt,  $J = 7.7, 1.8$  Hz, 1H), 7.94–7.88 (m, 1H), 7.57 (ddd,  $J = 7.5, 4.8, 1.3$  Hz, 1H);

**<sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>):**  $\delta$  154.96, 153.69, 150.52, 143.49, 138.09, 126.35, 121.89.

**HRMS (TOF):** *m/z* calcd for C<sub>7</sub>H<sub>6</sub>N<sub>3</sub>O<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup> : 164.0455, found: 164.0457.



**5-(4-chloro-3-(trifluoromethyl)phenyl)-1,3,4-oxadiazol-2(3*H*)-one (10i)**

The desired product **10i** (yield 78%, white solid, 61.8 mg) was afforded by flash chromatography on silica gel (petroleum ether/EtOAc (5:1)).

**Mp:** 159–160 °C. (literature : 158–159 °C)

**<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):**  $\delta$  12.84 (s, 1H), 8.05 (dq, *J* = 4.2, 2.2 Hz, 2H), 7.90 (d, *J* = 8.9 Hz, 1H).

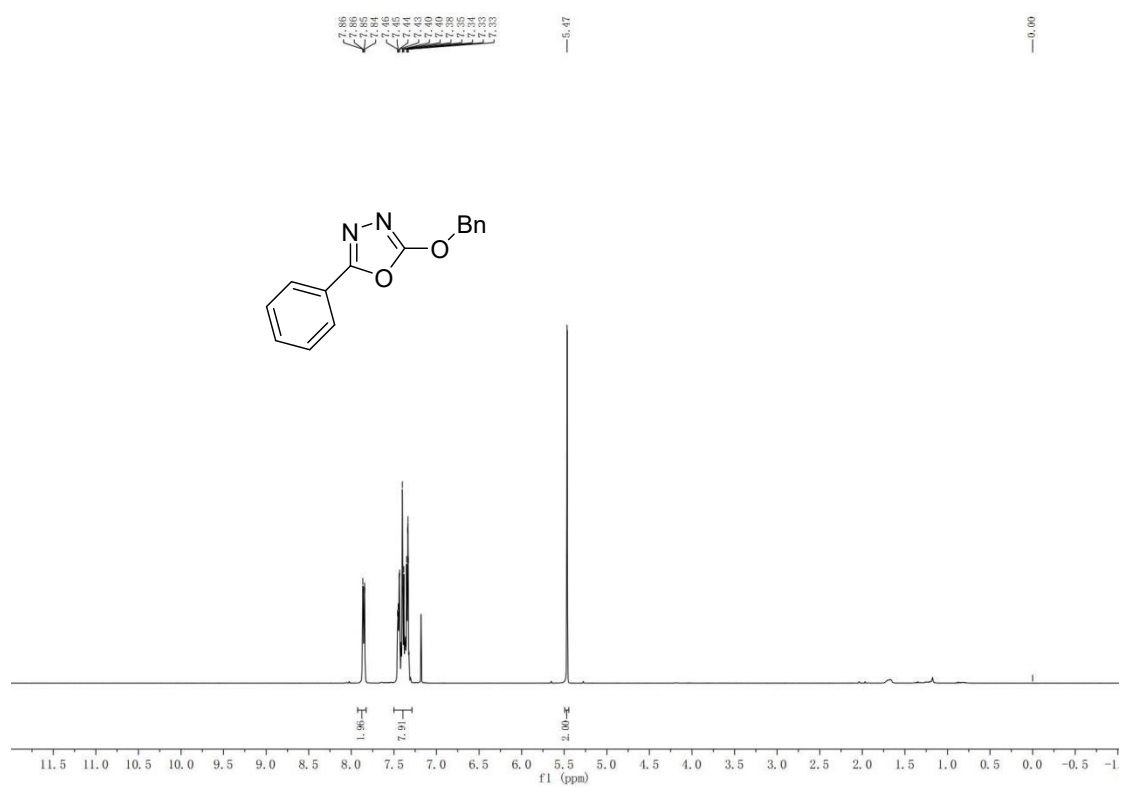
**<sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>):**  $\delta$  154.59, 152.39, 133.88, 133.86, 133.28, 130.95, 128.26, 128.15, 127.84, 125.52, 124.60, 124.54, 124.49, 124.07, 124.03, 121.35.

**<sup>19</sup>F NMR (376 MHz, DMSO-*d*<sub>6</sub>):**  $\delta$  -61.95.

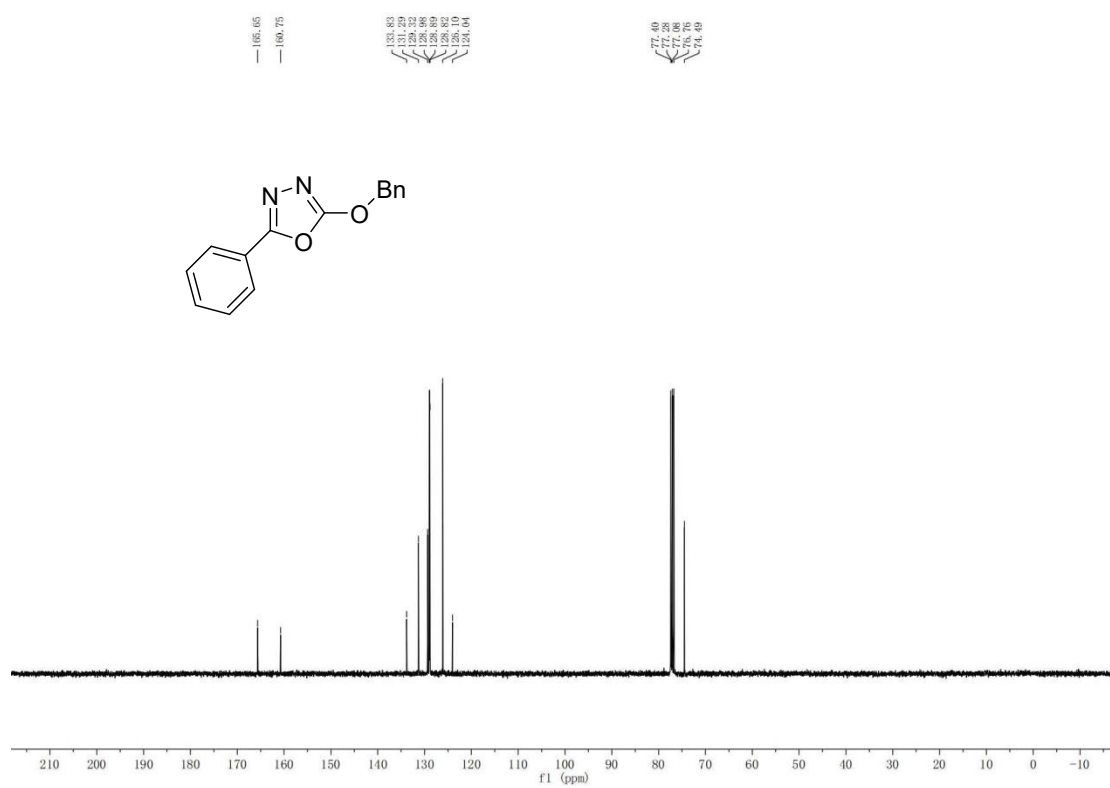
**HRMS (TOF):** *m/z* calcd for C<sub>9</sub>H<sub>4</sub>ClF<sub>3</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup> : 263.9913, found:263.9915.

## 11. Copies of NMR spectra

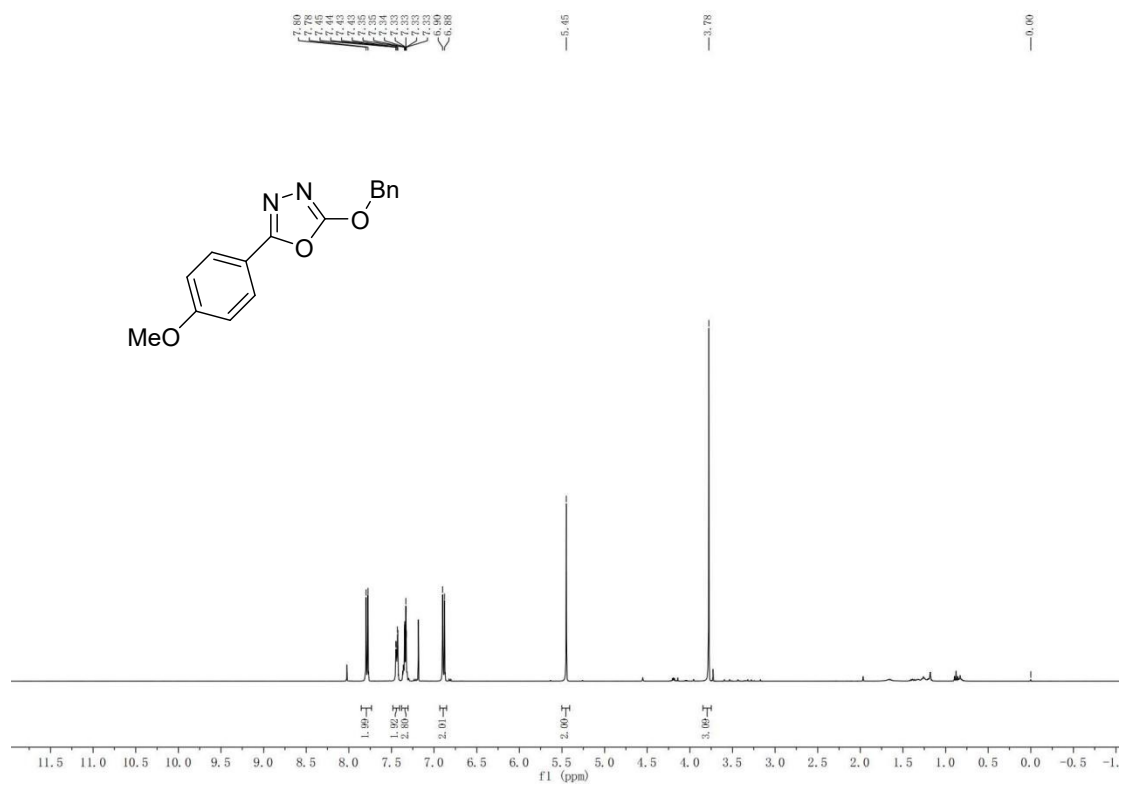
**3a** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



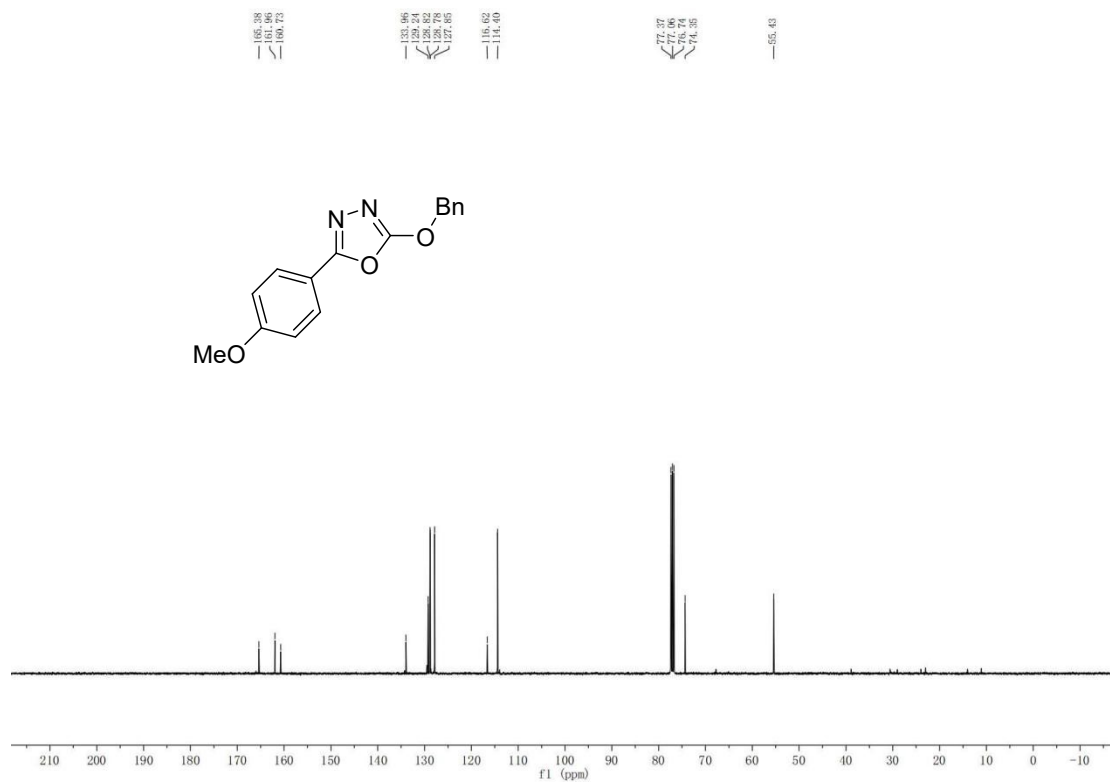
**3a** <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)



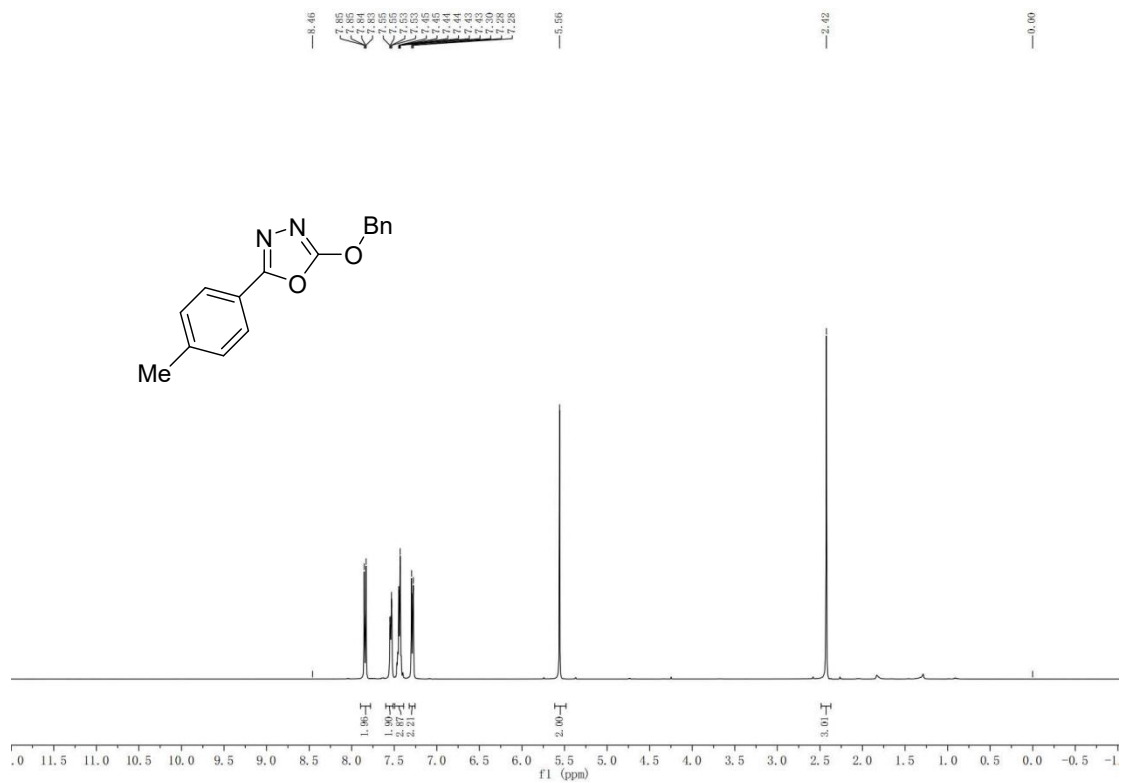
**3b** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



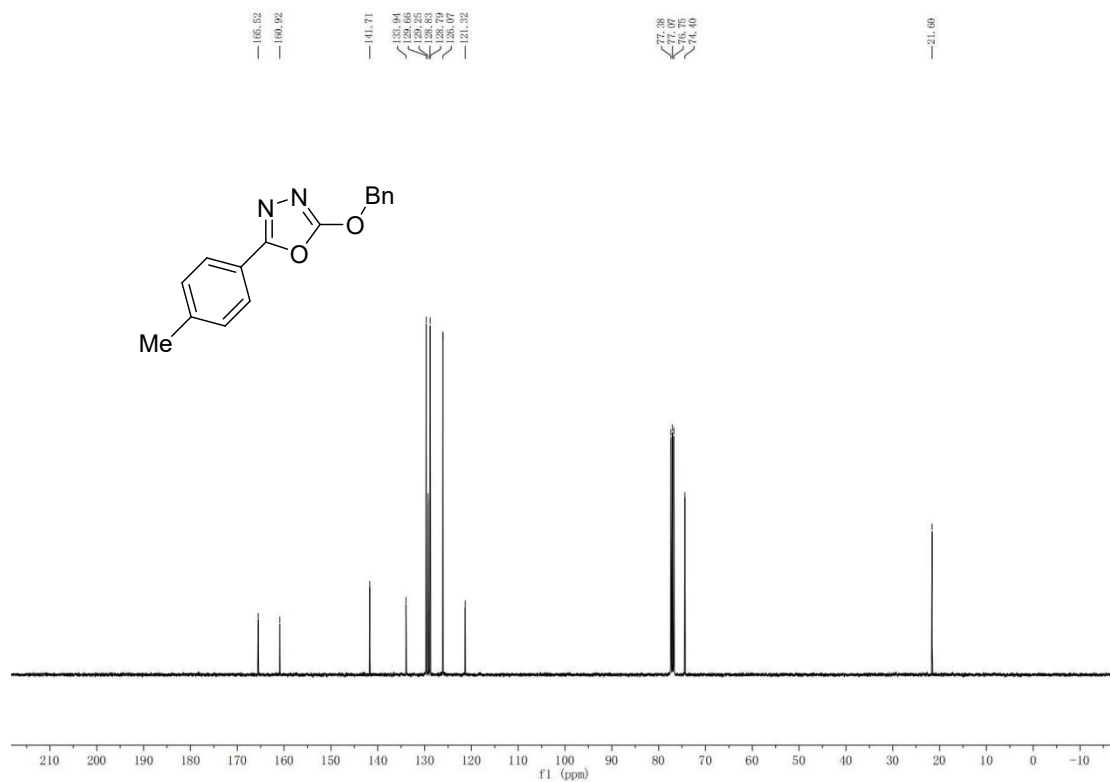
**3b** <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)



**3c** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

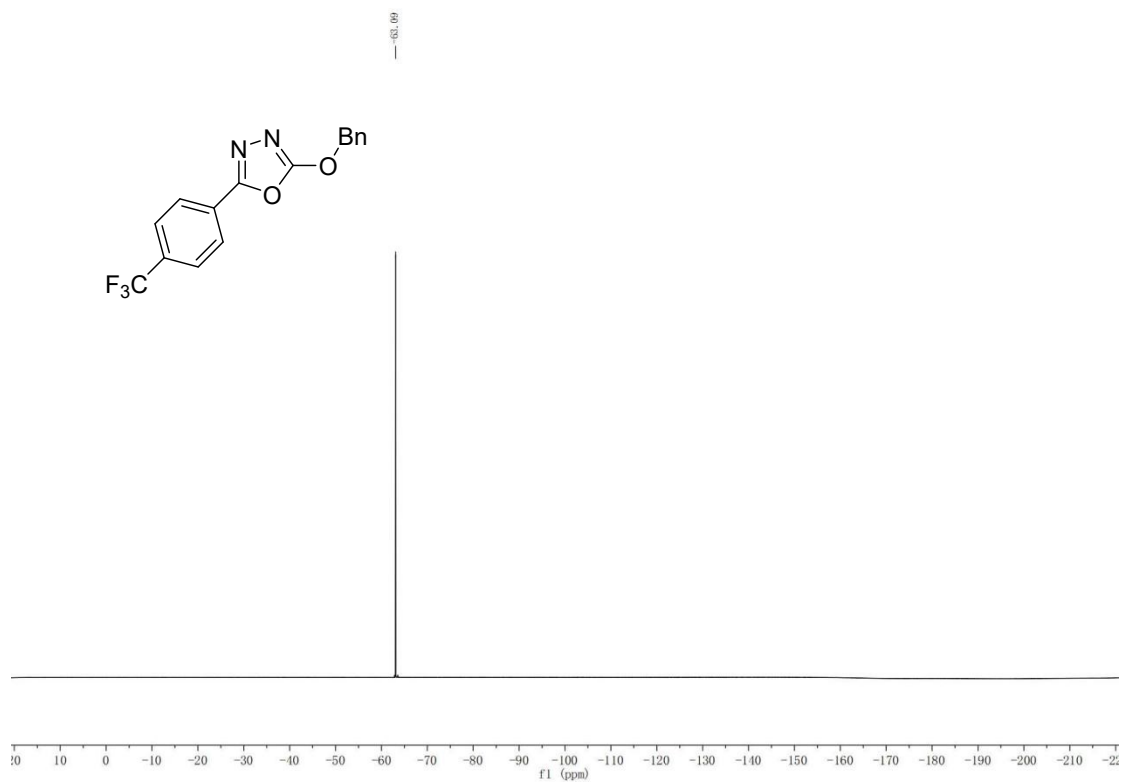


**3c**  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

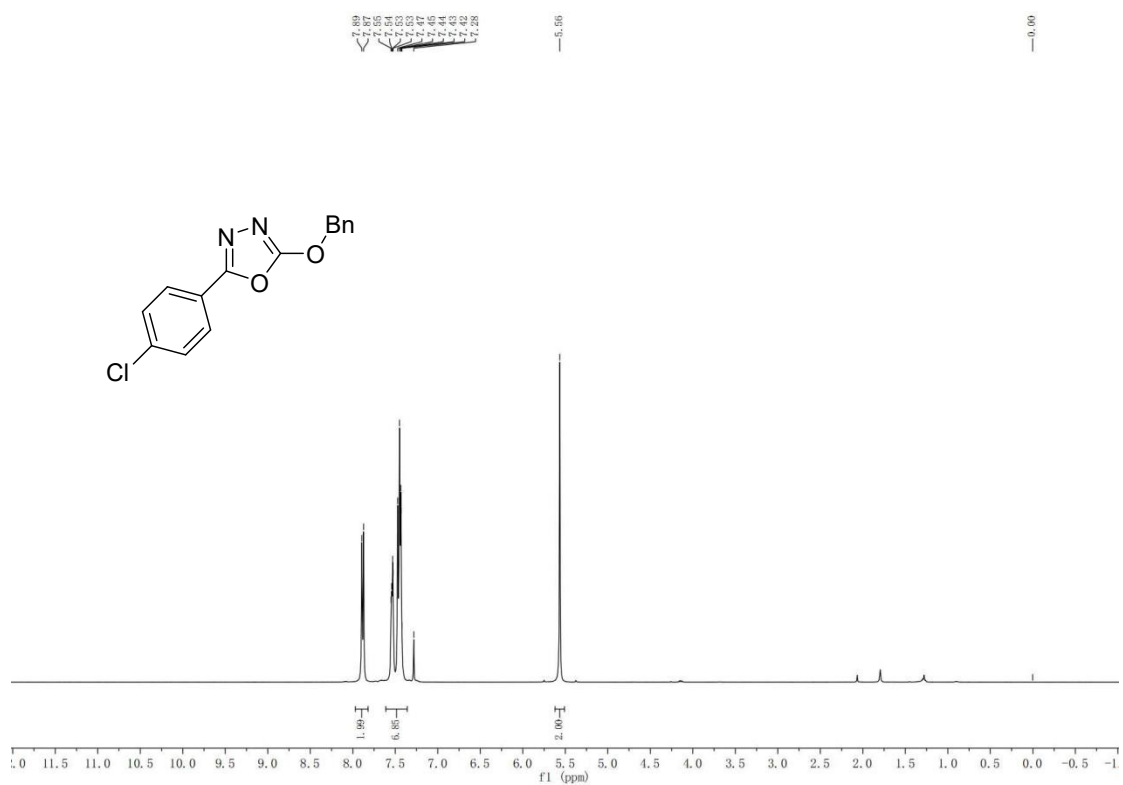


**3d**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )





**3e** <sup>1</sup>H NMR (400 MHz, )





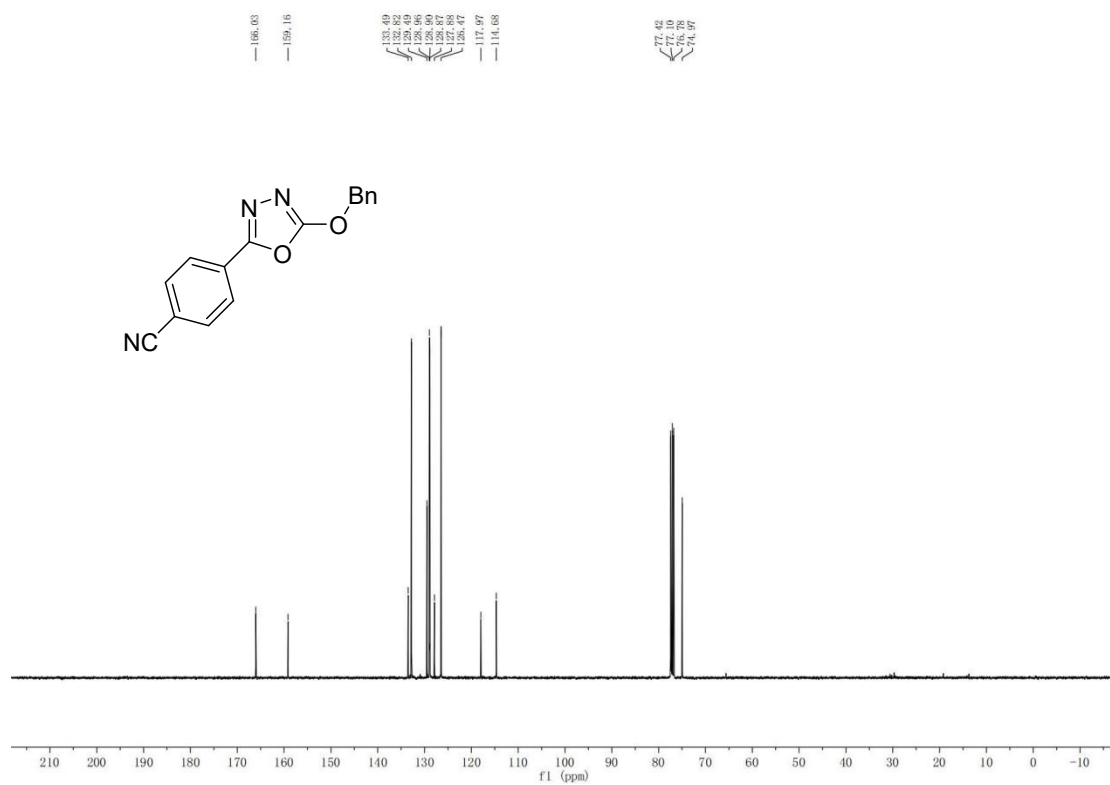




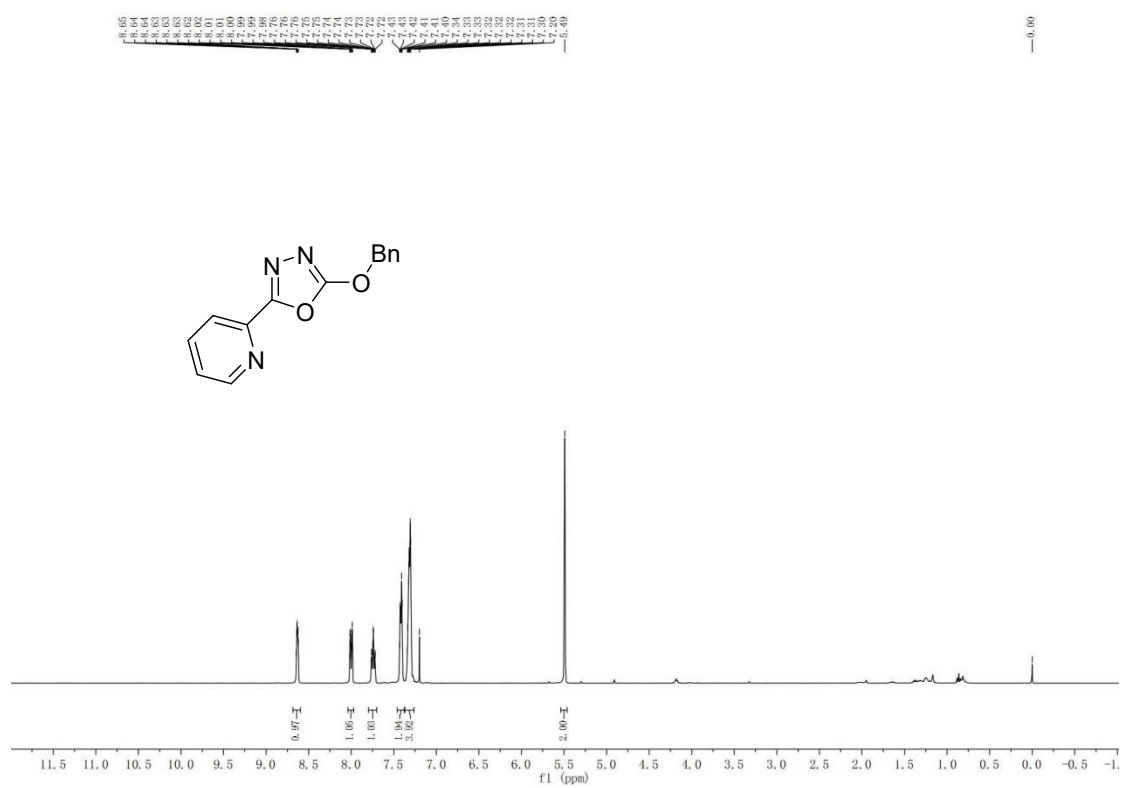




**3i**  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )



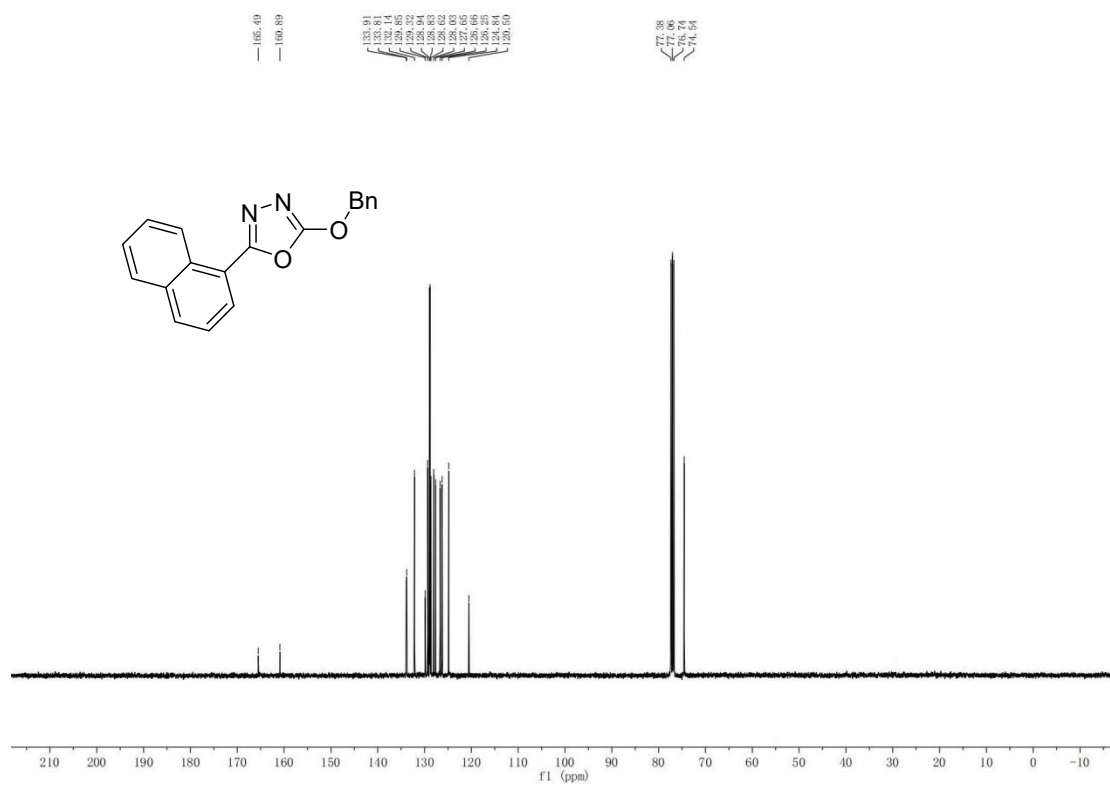
**3k**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



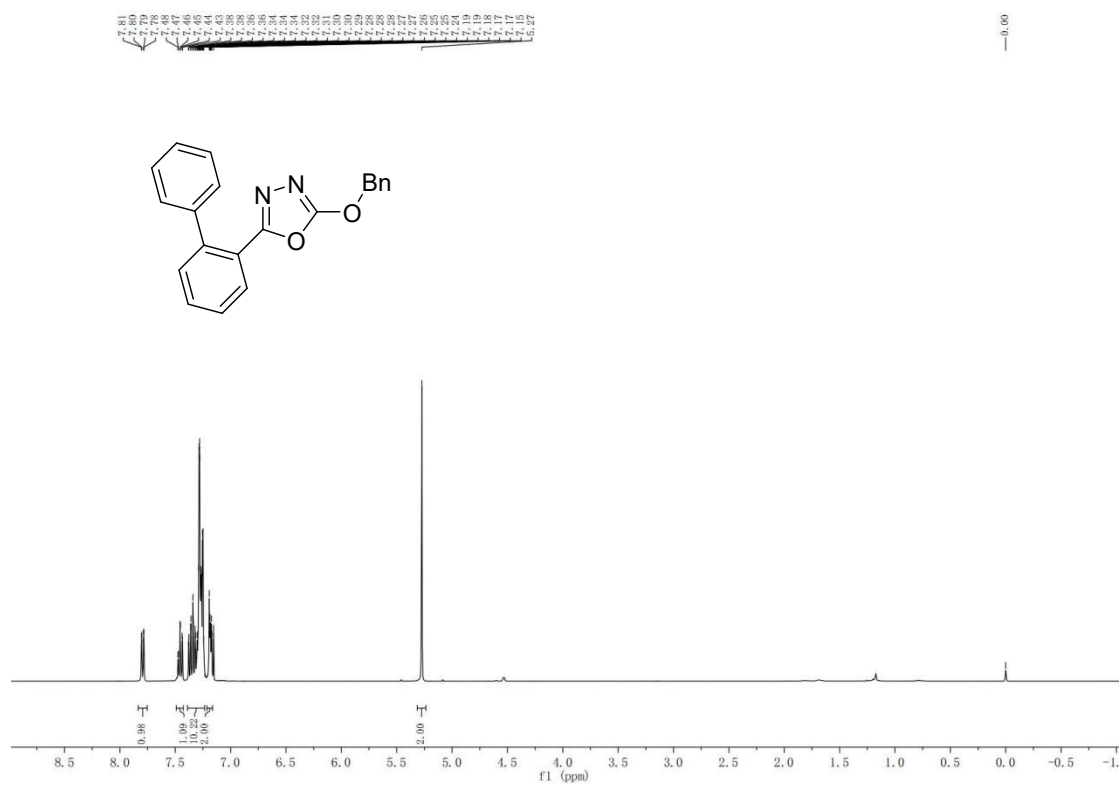




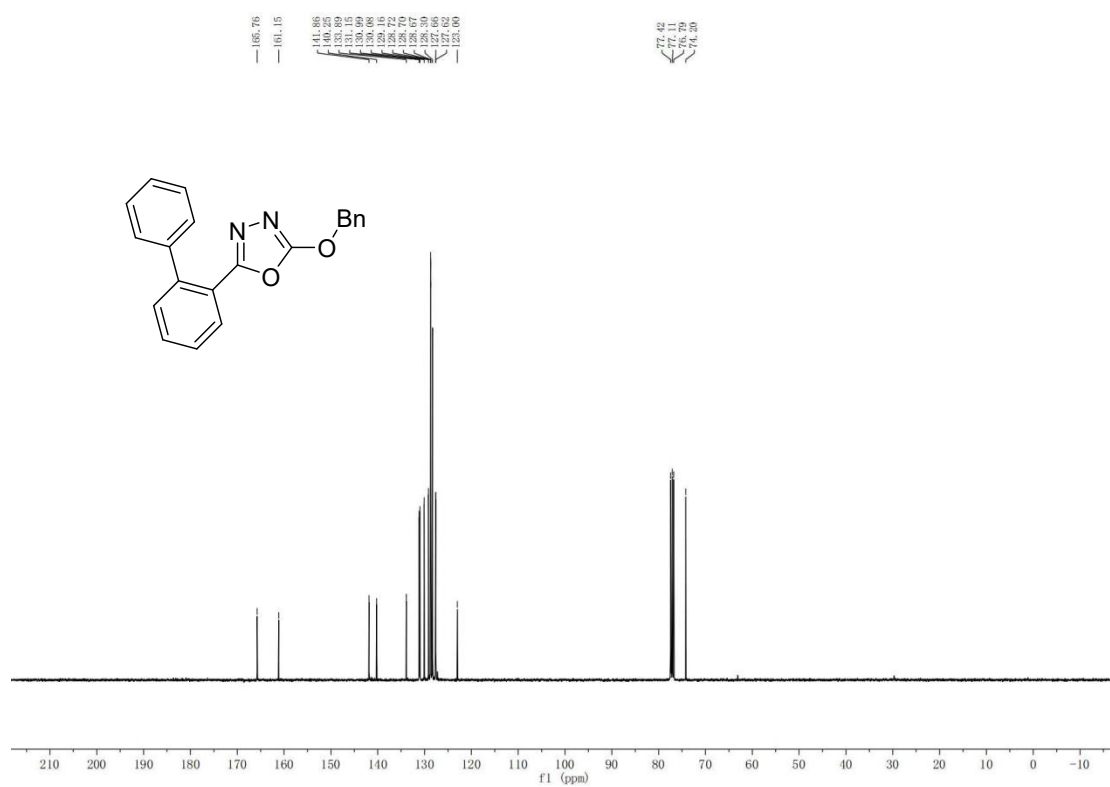
**3m**  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )



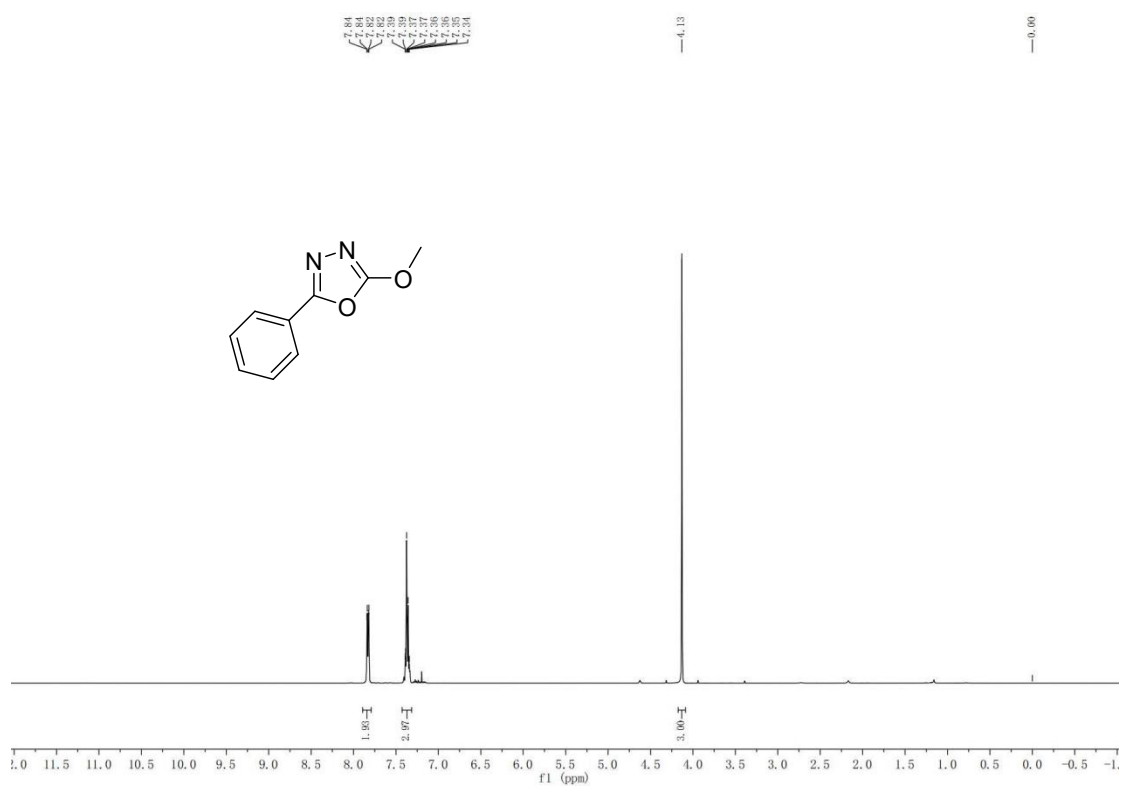
**3n**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



**3n** <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)

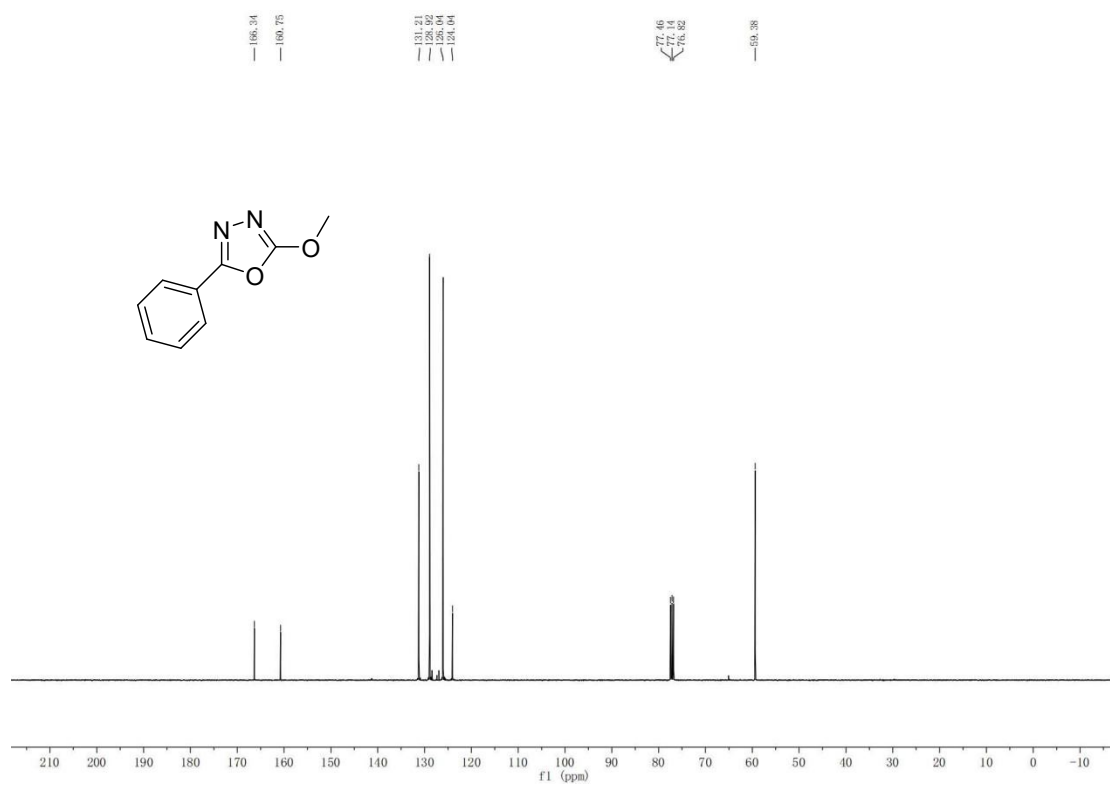


**4a** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

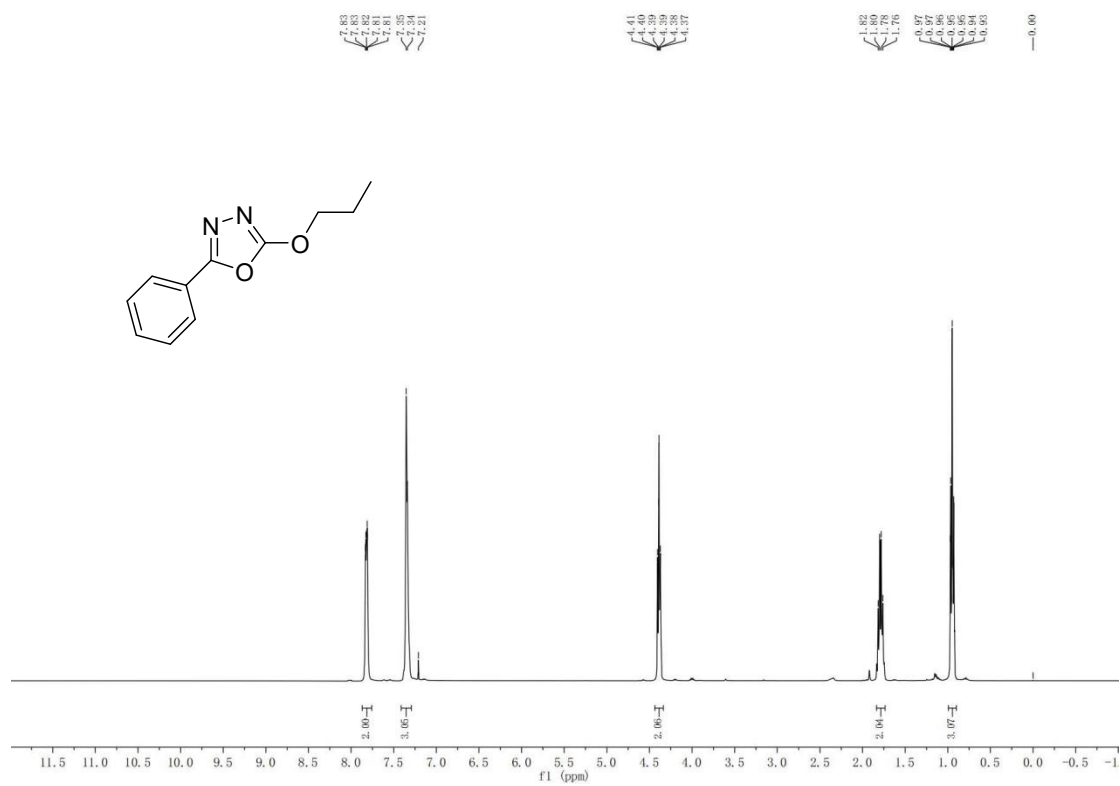




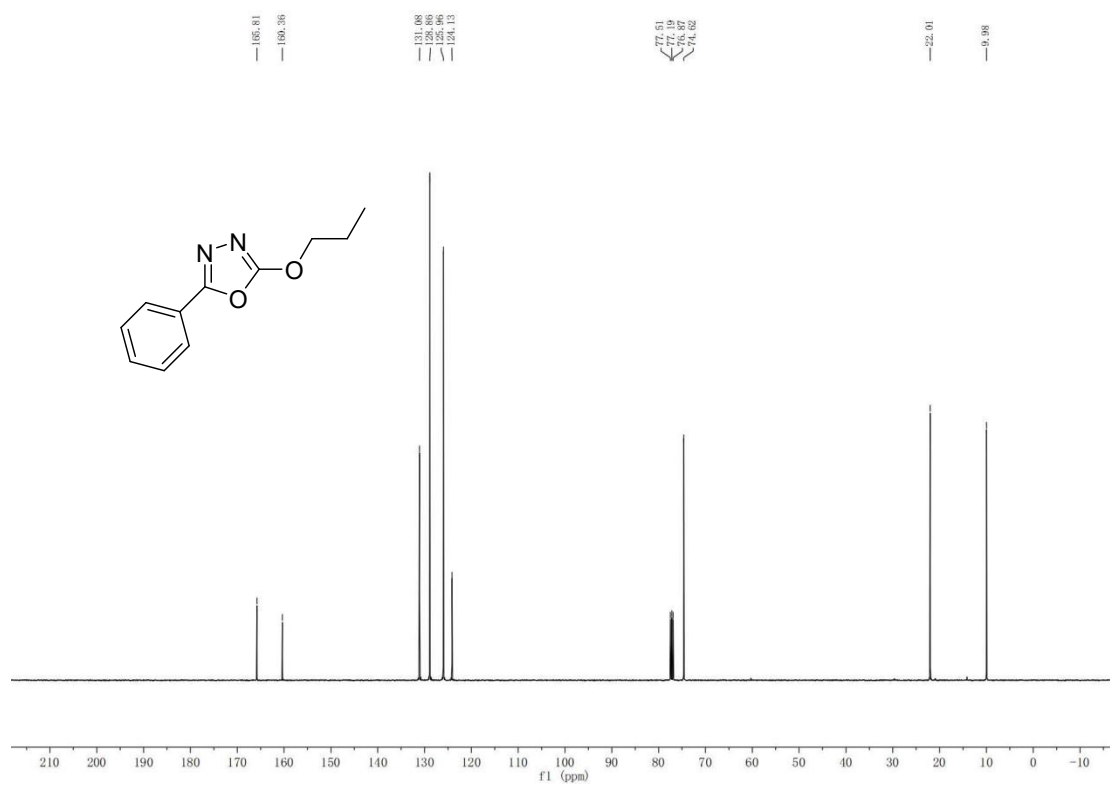
**4a**  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )



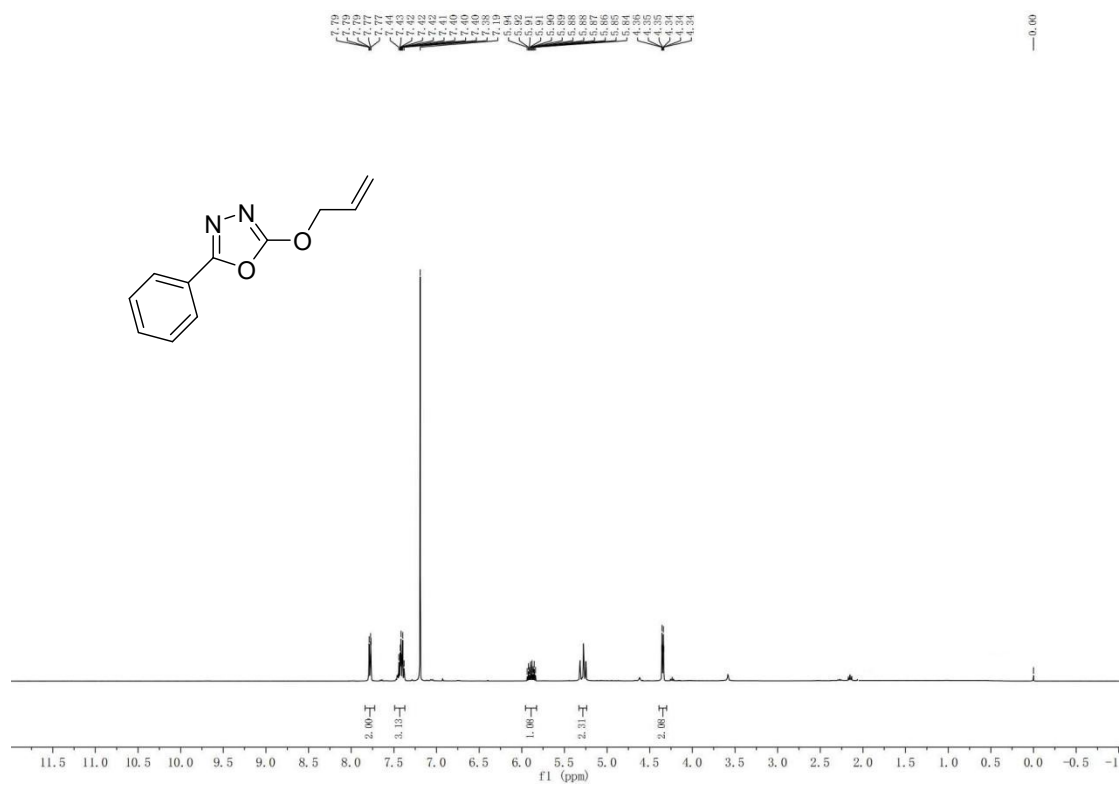
**4b**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



**4b**  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

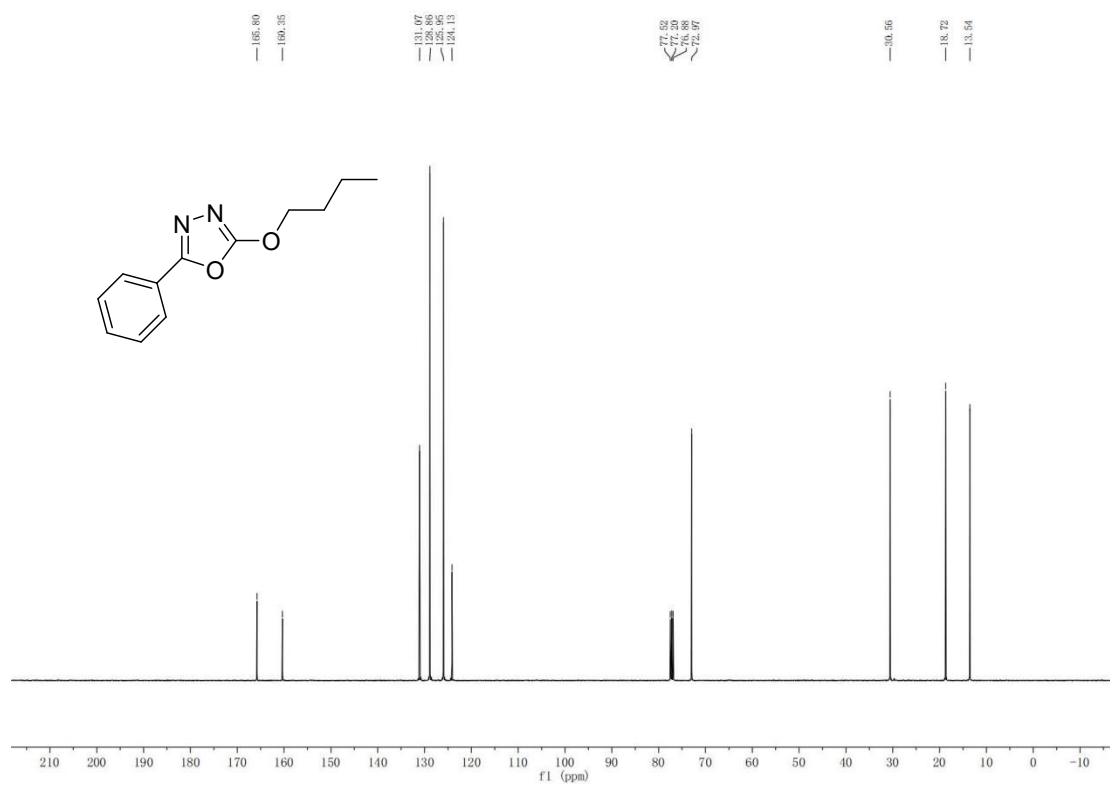


**4c**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

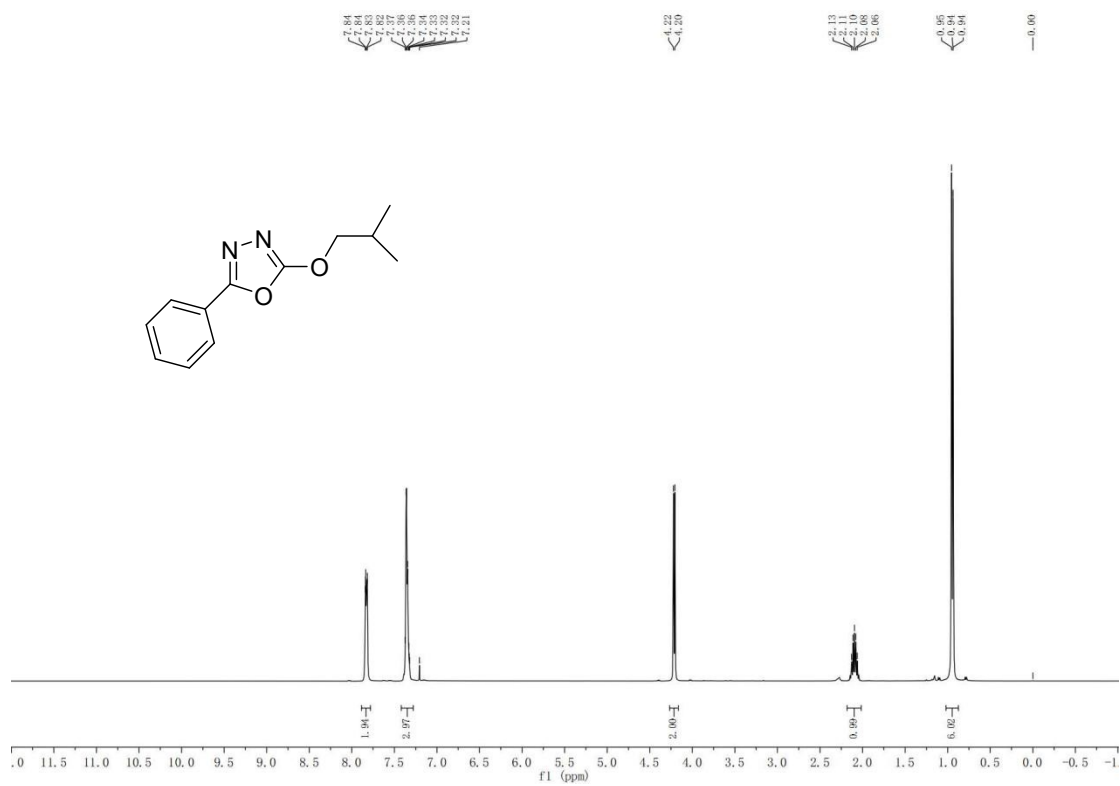




**4d**  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )



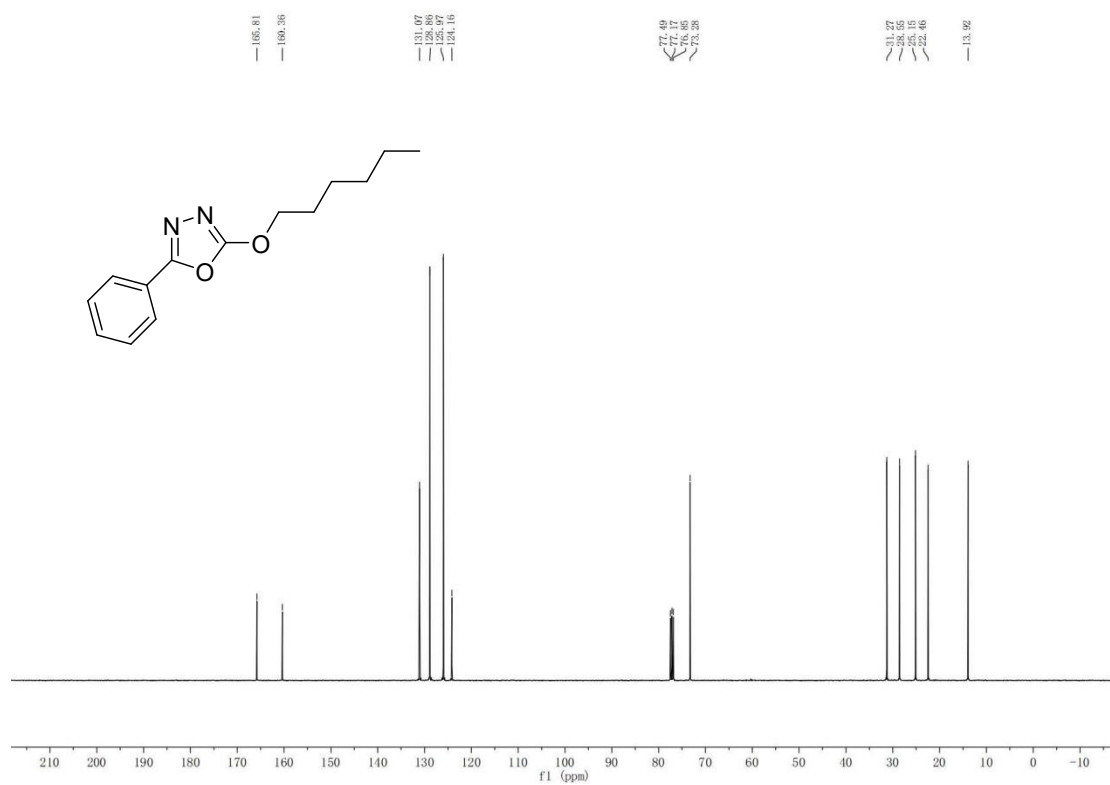
**4e**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



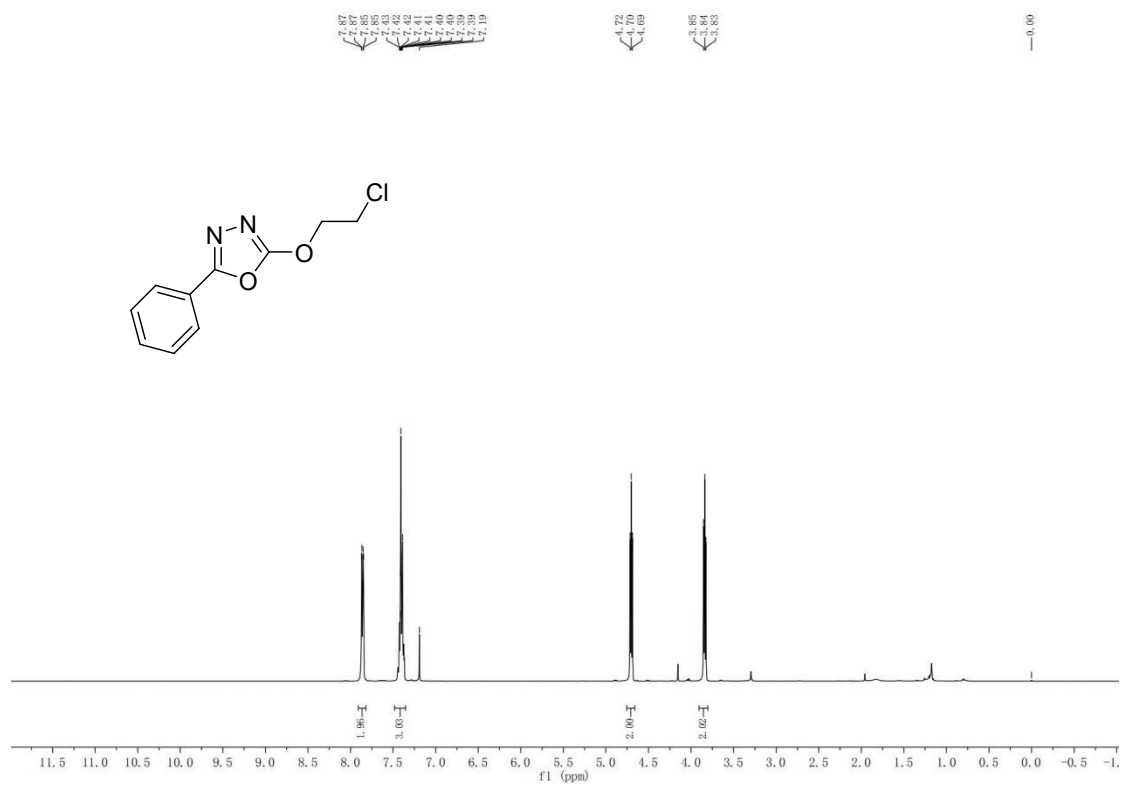




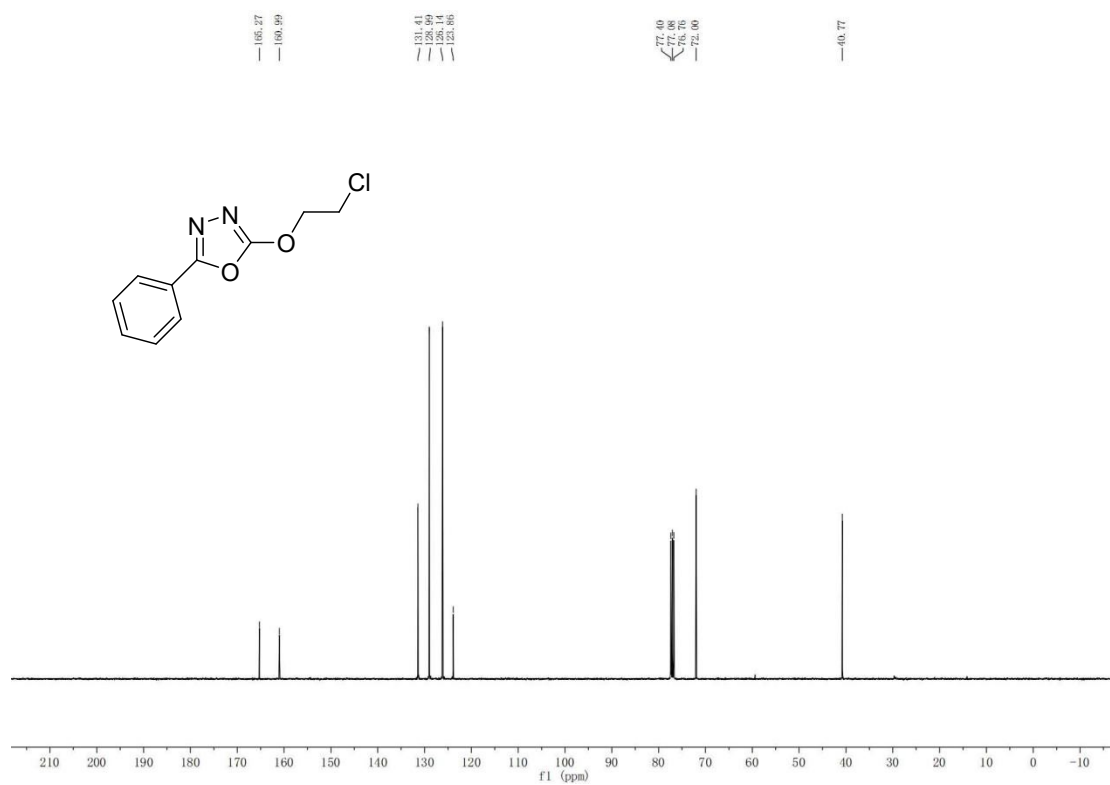
**4g**  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )



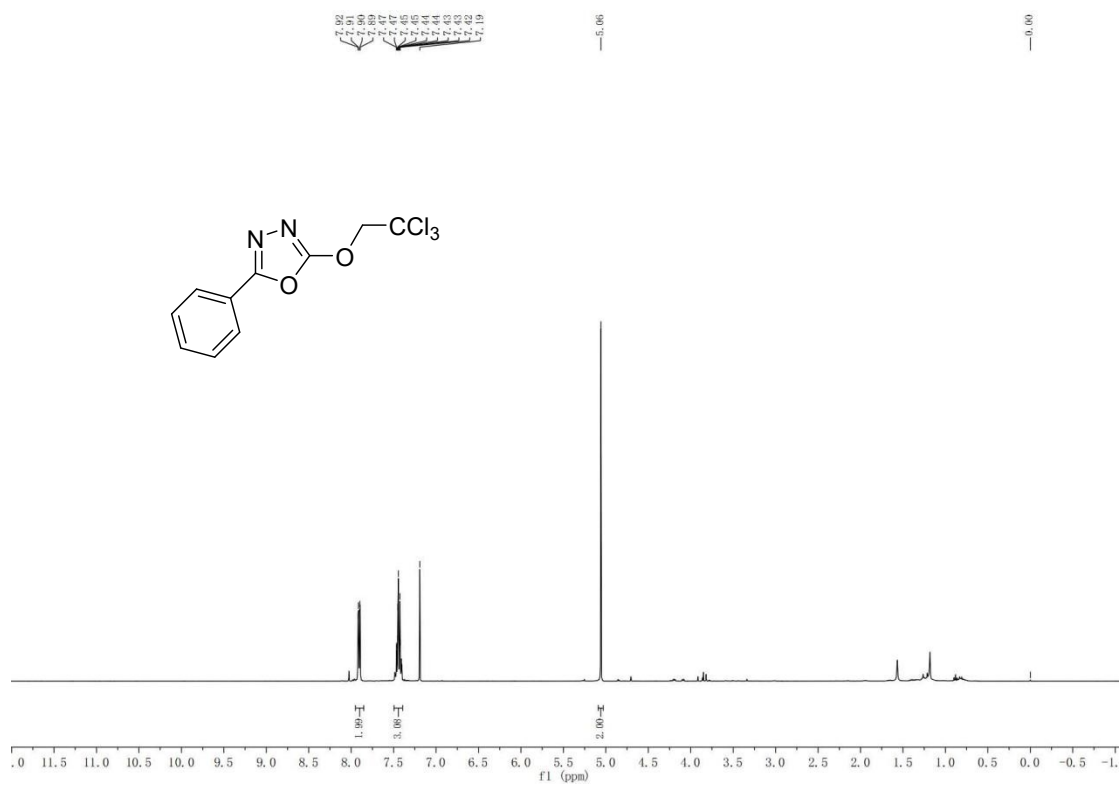
**4h**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



**4h**  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )



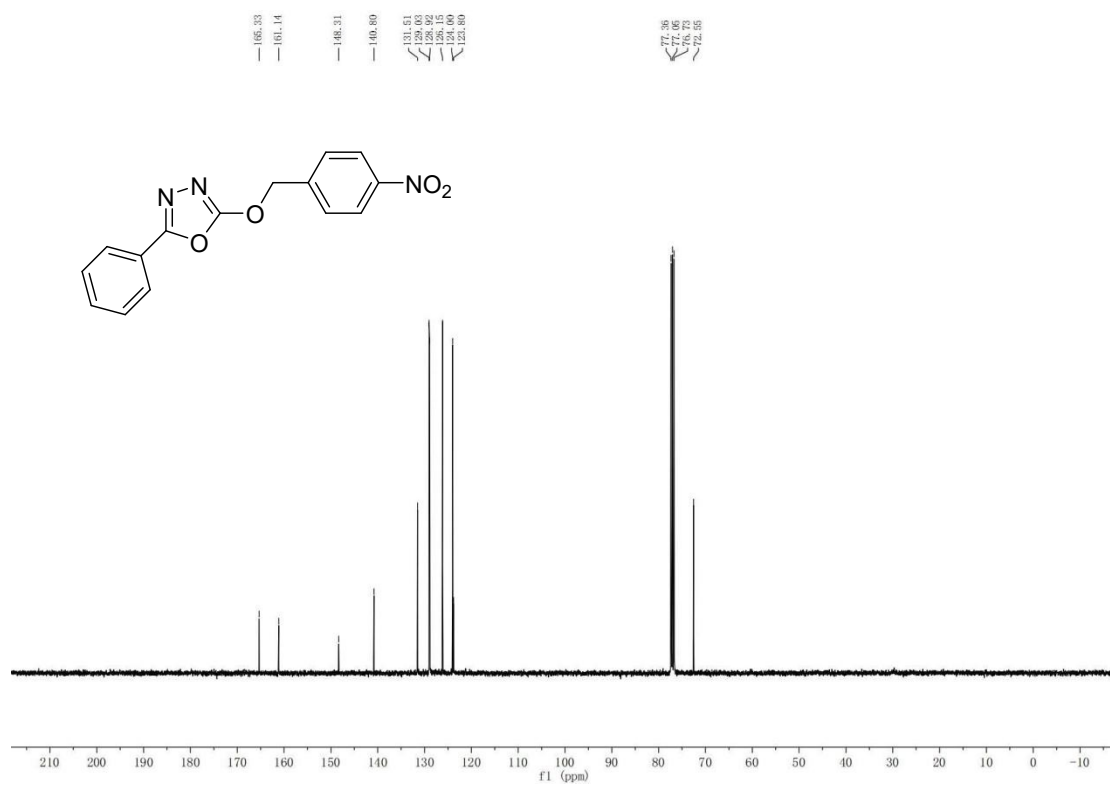
**4i**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



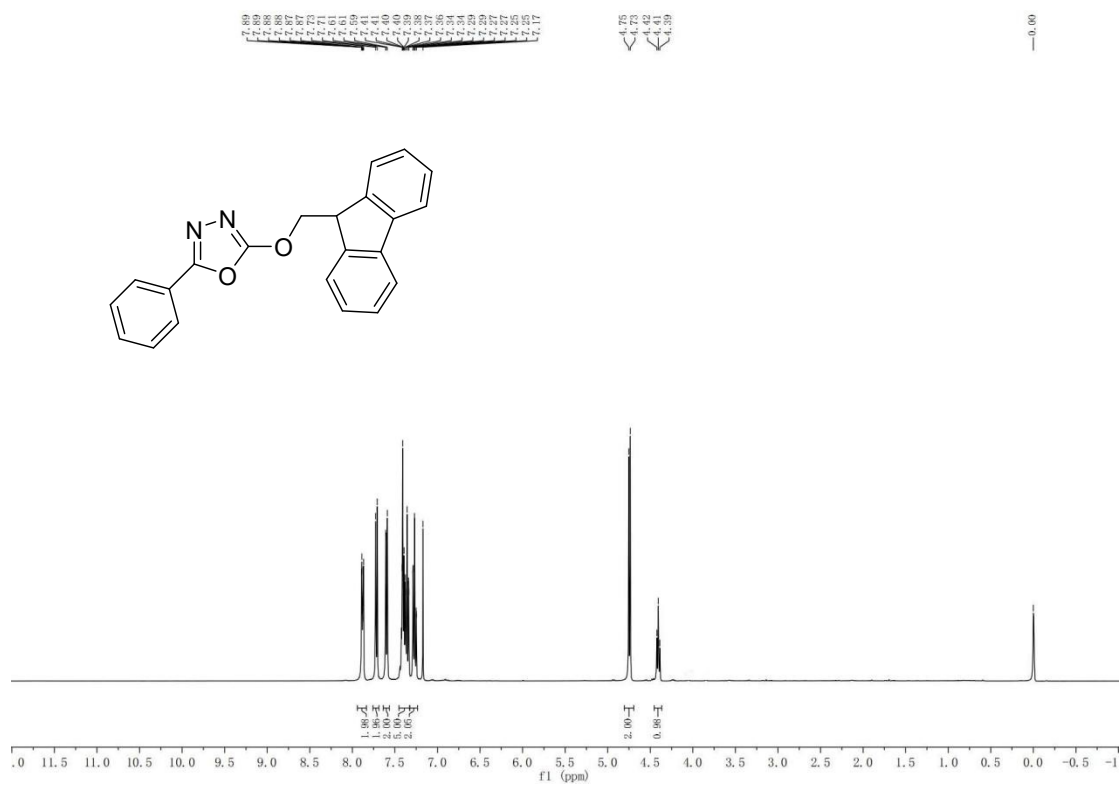




**4j**  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )

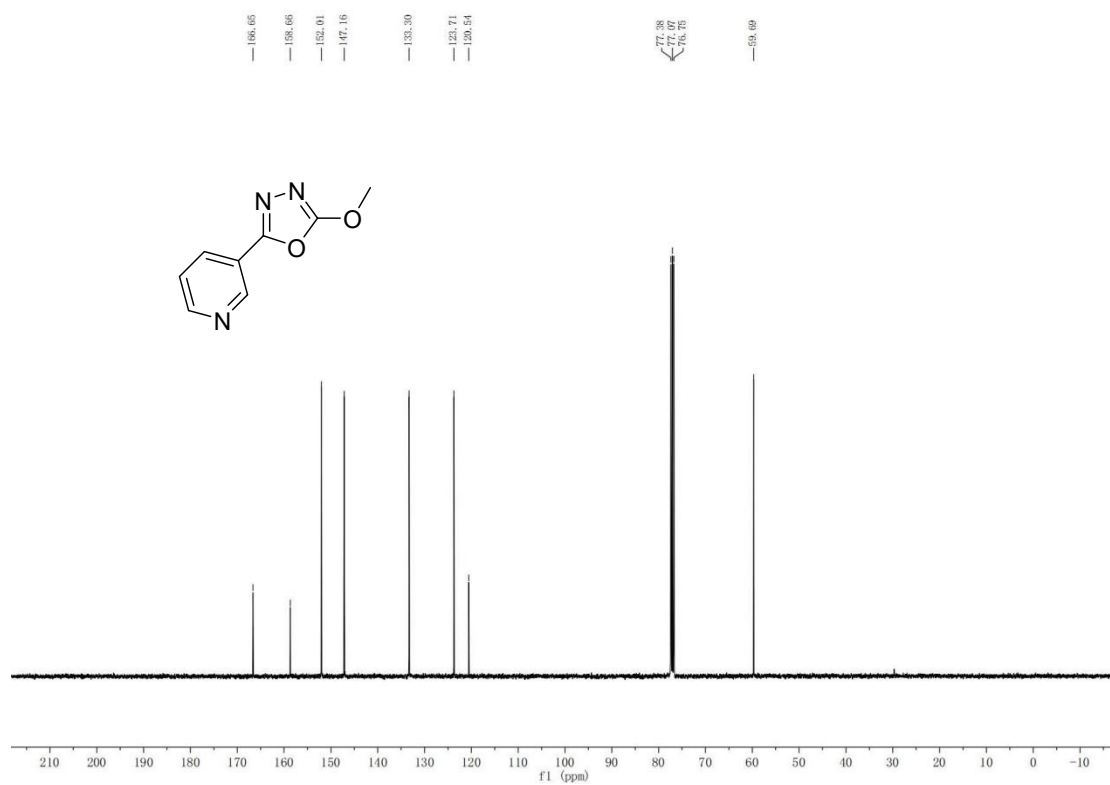


**4k**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )

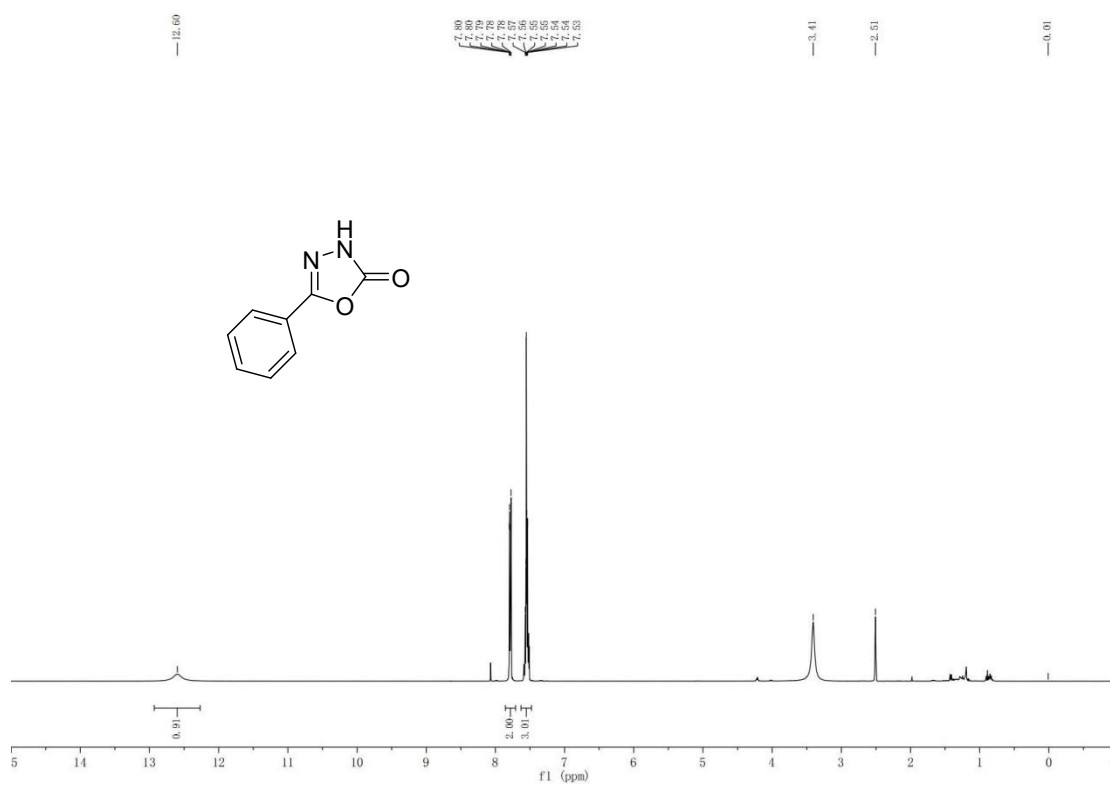




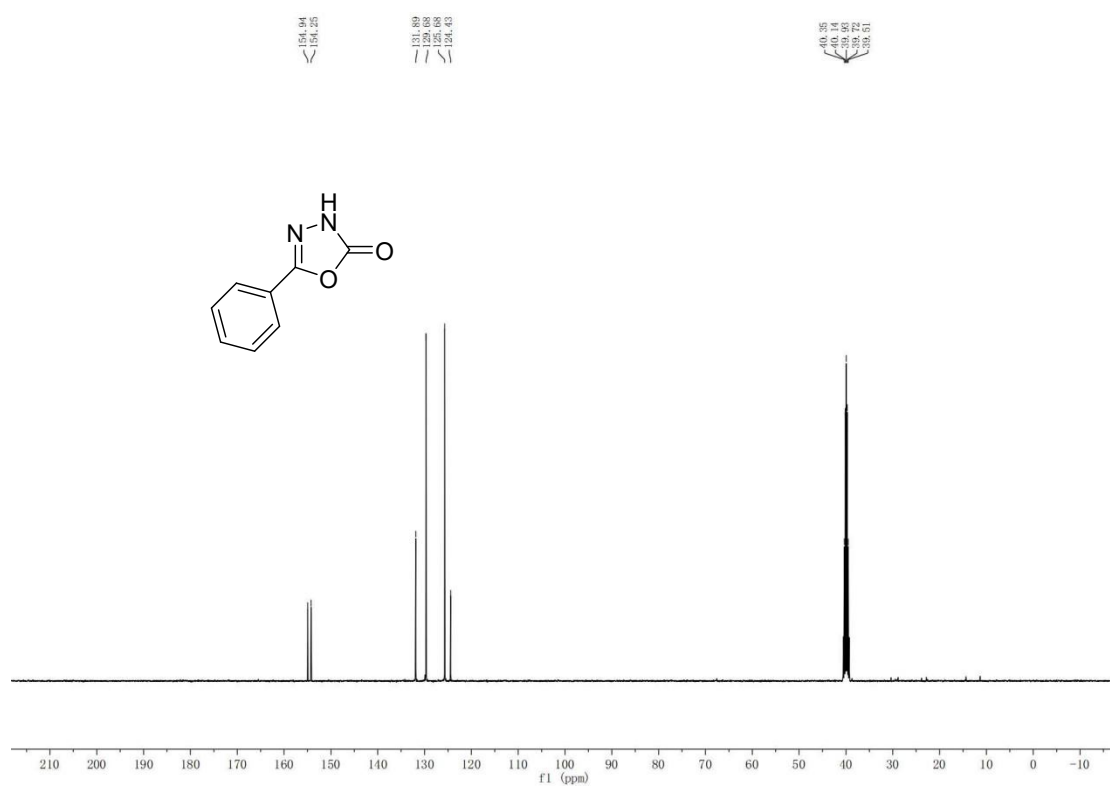
**7a**  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )



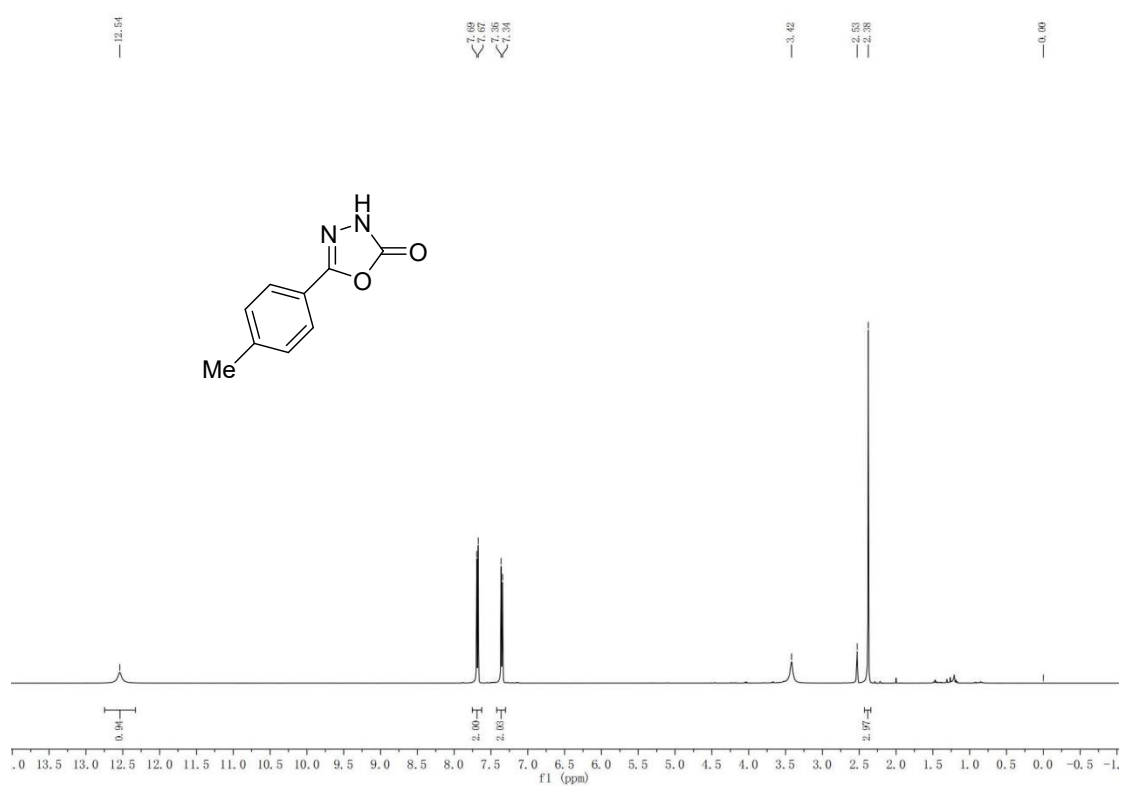
**10a**  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ )



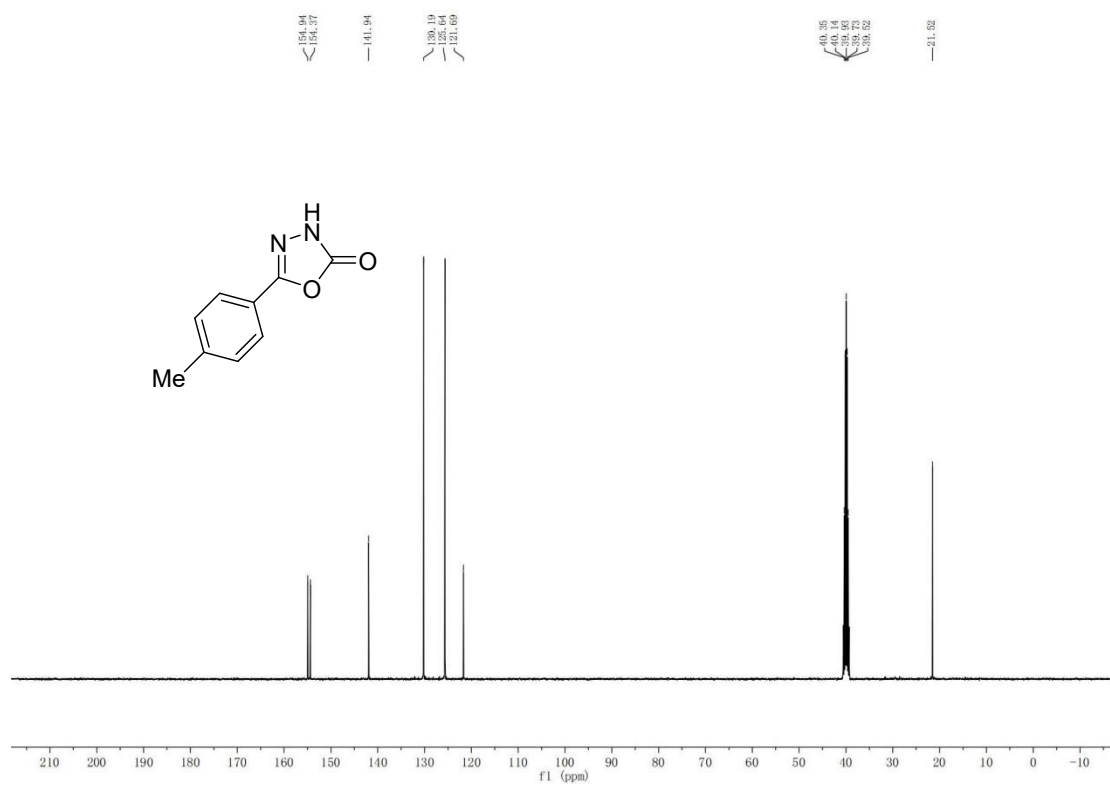
**10a**  $^{13}\text{C}$  NMR (101 MHz, DMSO-d6)



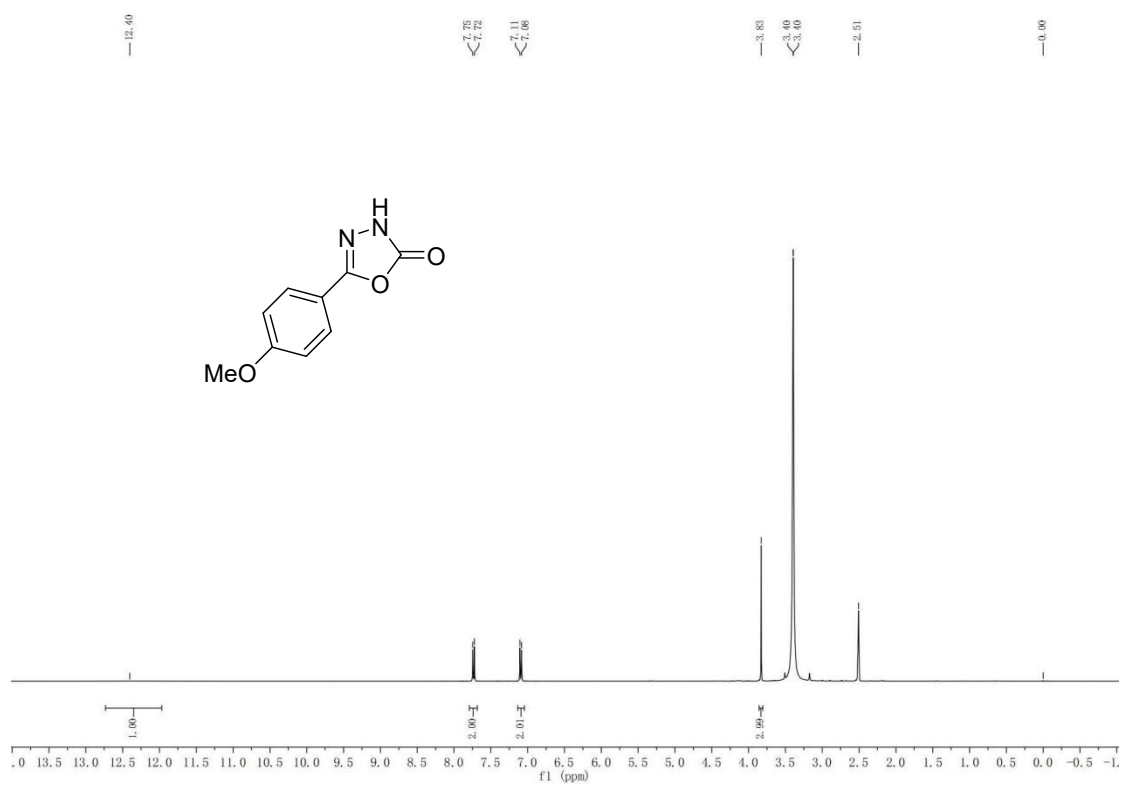
**10b**  $^1\text{H}$  NMR (400 MHz, DMSO-d6)



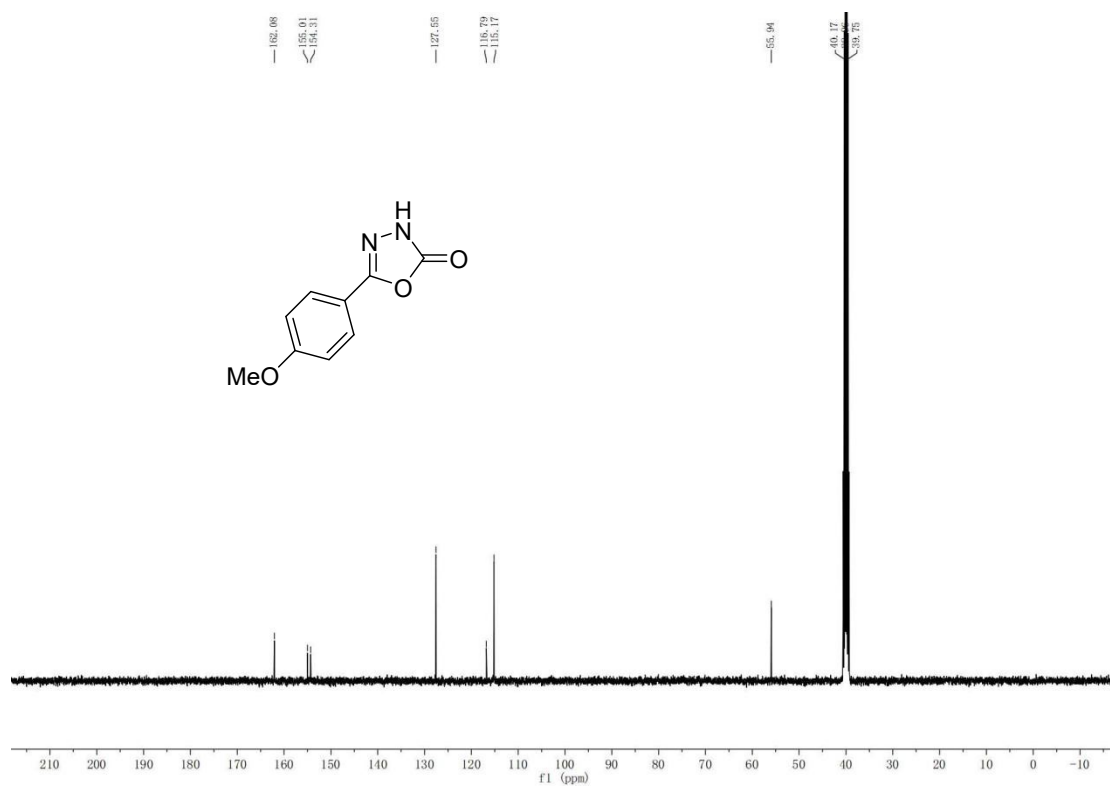
**10b**  $^{13}\text{C}$  NMR (101 MHz, DMSO-d<sub>6</sub>)



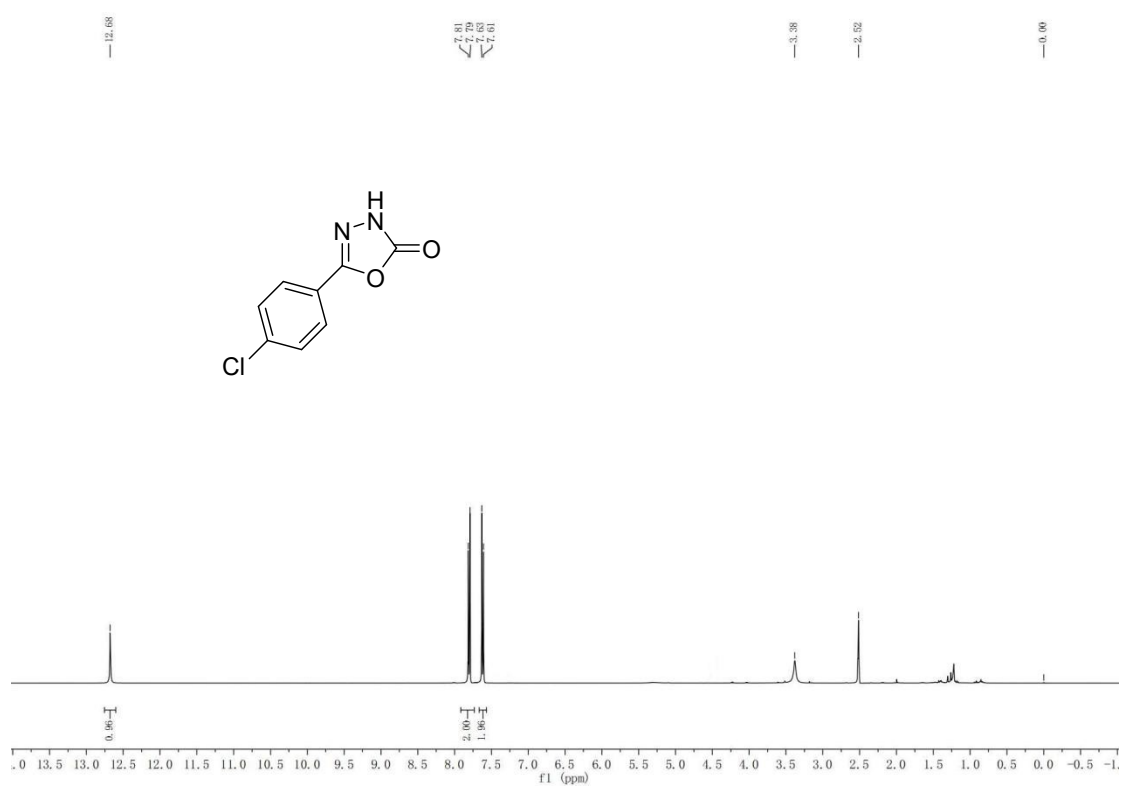
**10c**  $^1\text{H}$  NMR (400 MHz, DMSO-d<sub>6</sub>)



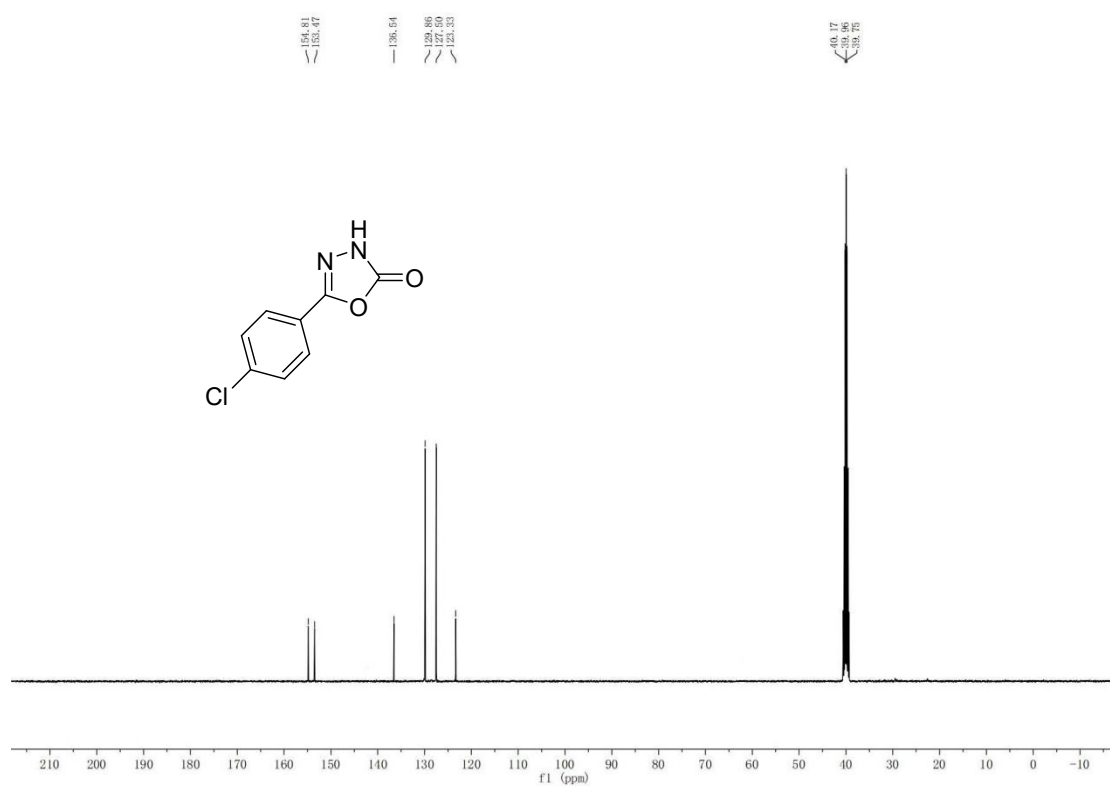
**10c**  $^{13}\text{C}$  NMR (101 MHz, DMSO-d6)



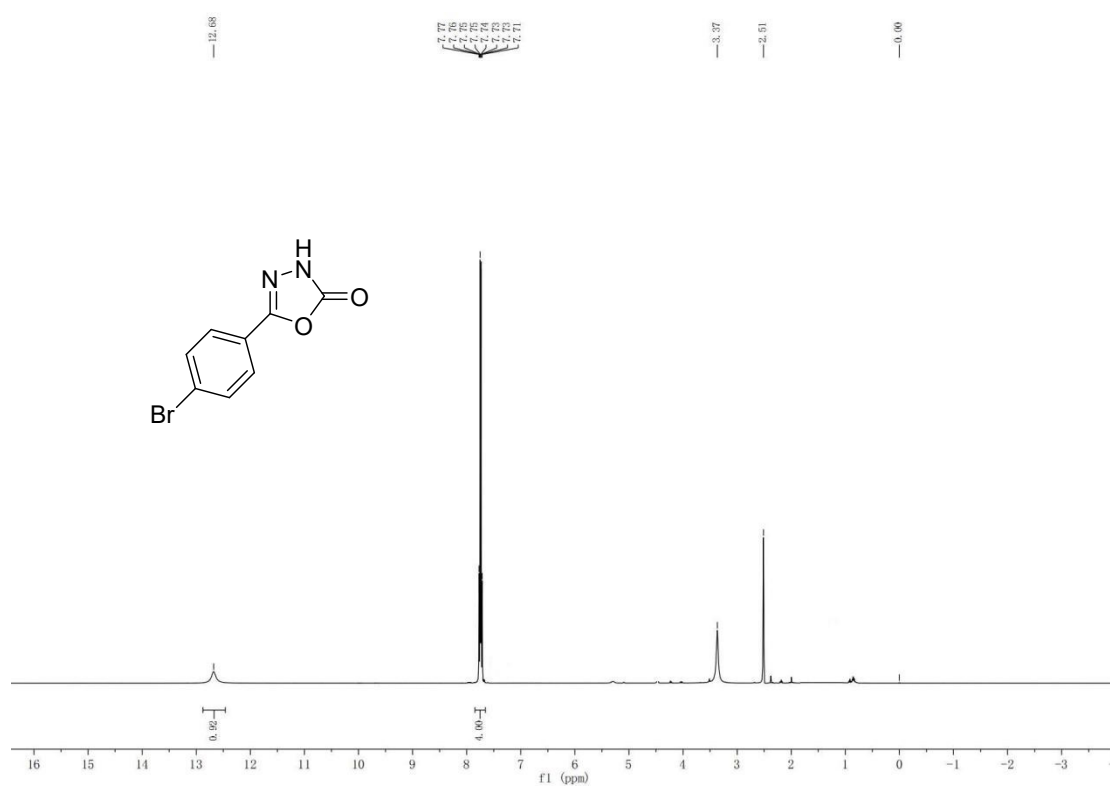
**10d**  $^1\text{H}$  NMR (400 MHz, DMSO-d6)



**10d**  $^{13}\text{C}$  NMR (101 MHz, DMSO-d6)

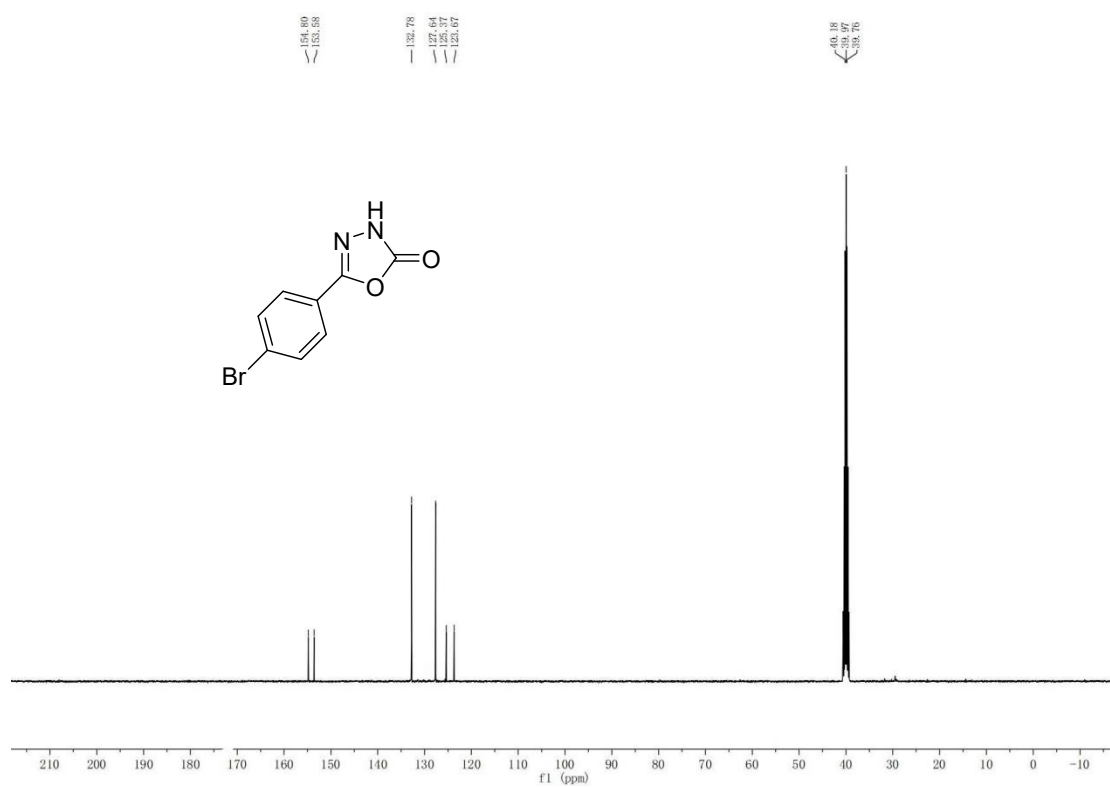


**10e**  $^1\text{H}$  NMR (400 MHz, DMSO-d6)

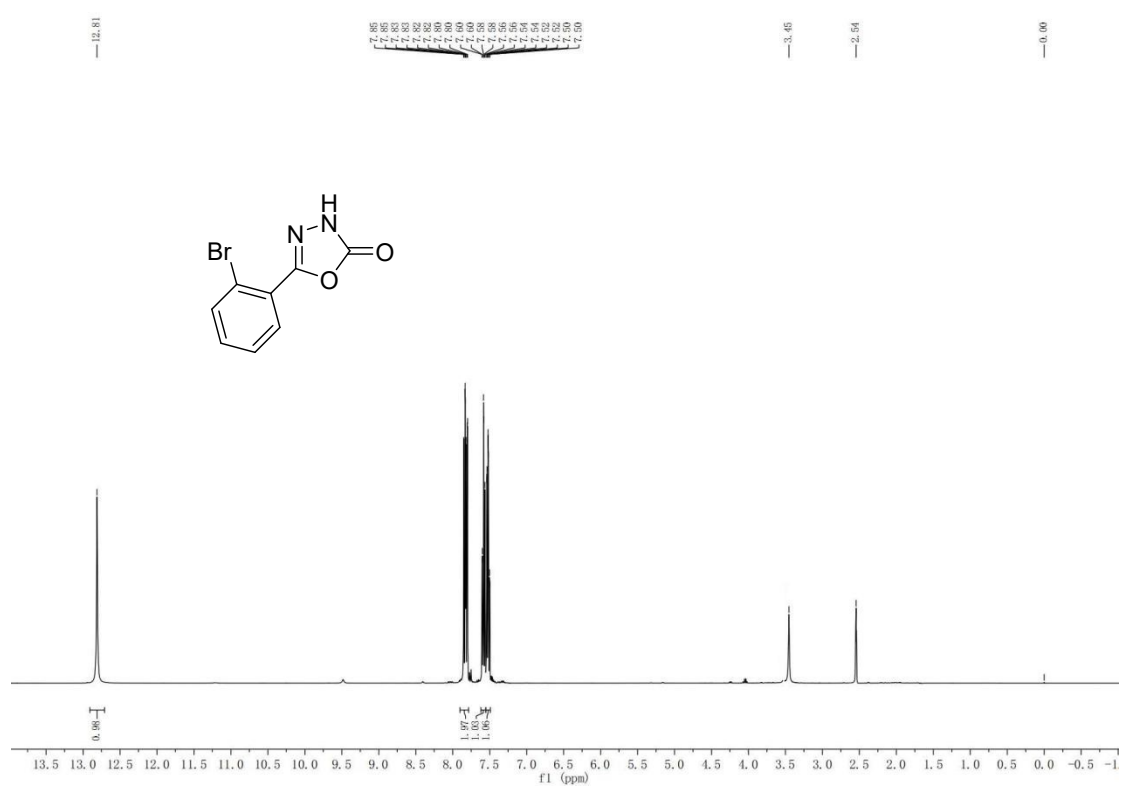




**10e**  $^{13}\text{C}$  NMR (101 MHz, DMSO-d6)



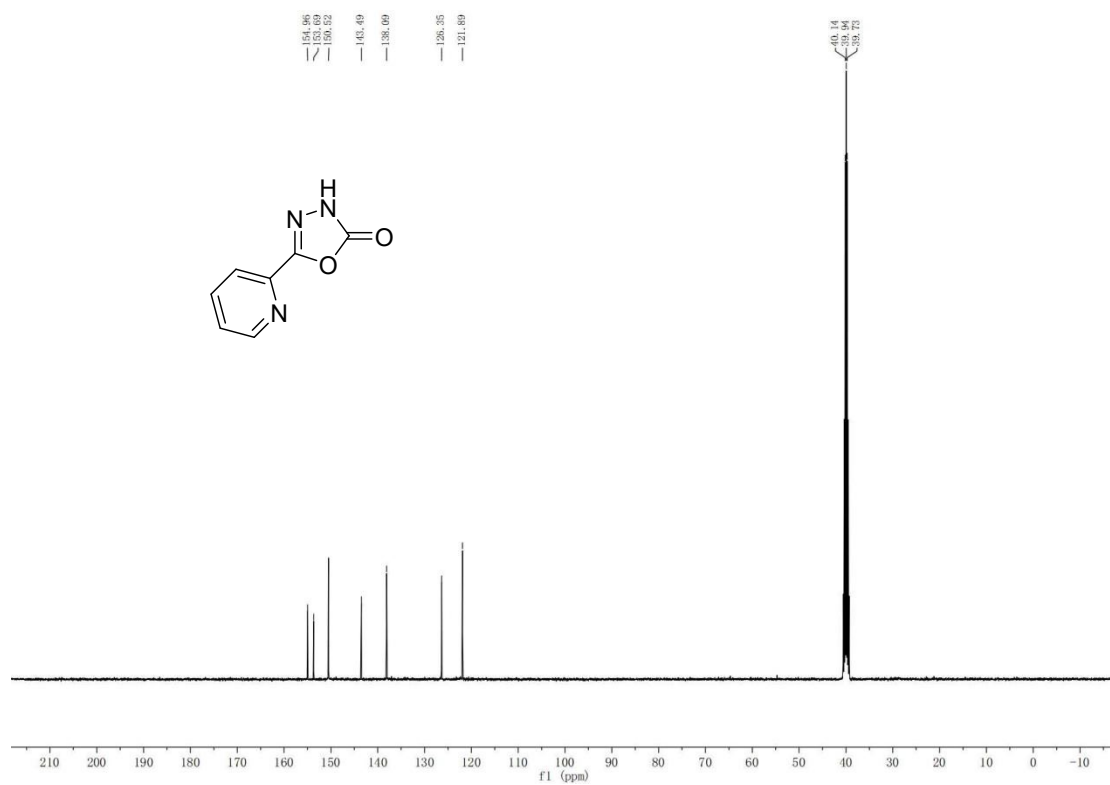
**10f**  $^1\text{H}$  NMR (400 MHz, DMSO-d6)



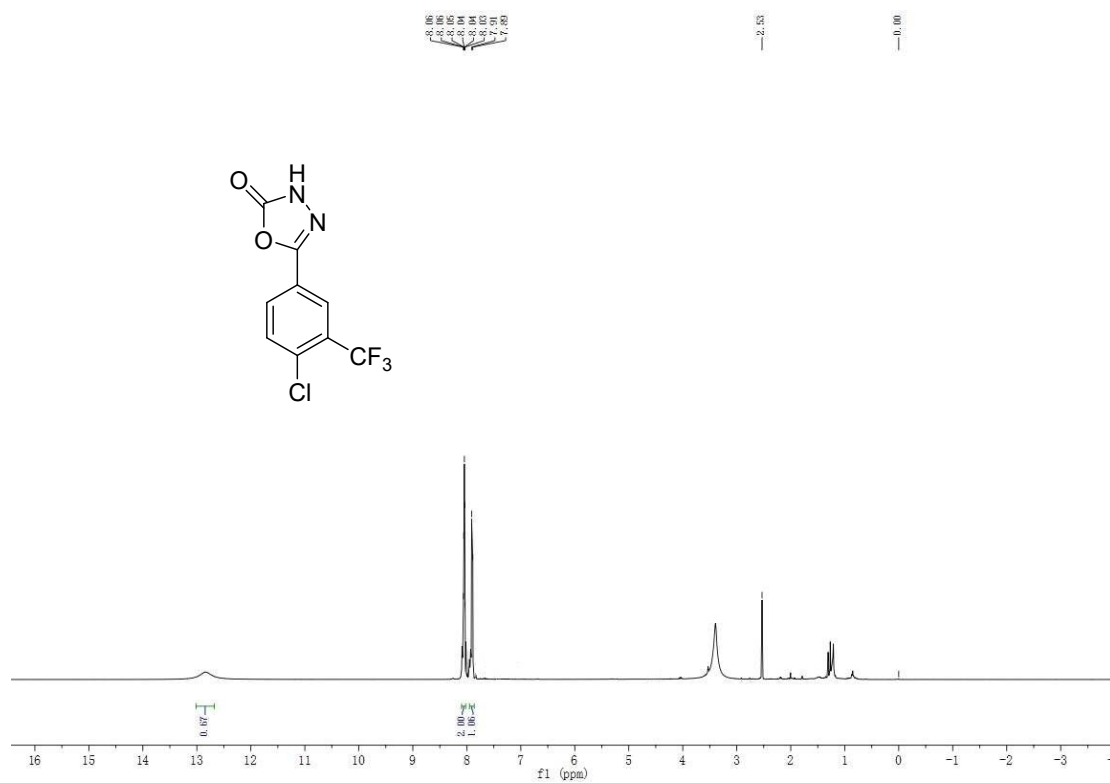




**10h**  $^{13}\text{C}$  NMR (101 MHz, DMSO-d<sub>6</sub>)



**10i**  $^1\text{H}$  NMR (400 MHz, DMSO-d<sub>6</sub>)



**10ih**  $^{13}\text{C}$  NMR (101 MHz, DMSO-d<sub>6</sub>)

