

## Supporting Information

### Electrochemical synthesis of 1,2,4-oxadiazoles from amidoximes through dehydrogenative cyclization

Chan Jiang,<sup>a</sup> Mingfang Li,<sup>a</sup> Leitao Xu,<sup>a</sup> Yangjie Yi,<sup>a</sup> Jiao Ye,<sup>a\*</sup> Aixi Hu<sup>a\*</sup>

<sup>a</sup> College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, China.  
E-mail addresses: [yejiao@hnu.edu.cn](mailto:yejiao@hnu.edu.cn) (Jiao Ye), [axhu@hnu.edu.cn](mailto:axhu@hnu.edu.cn) (Aixi Hu).

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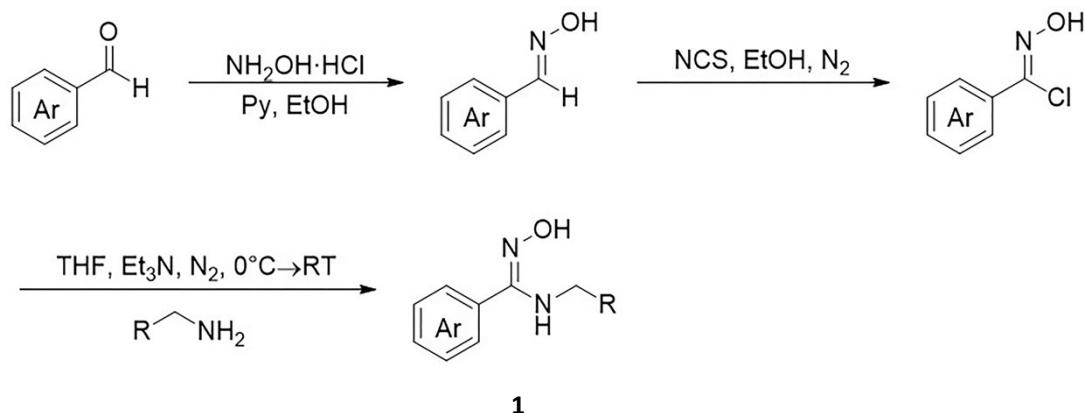
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## 1. General materials and methods

Unless otherwise noted, all commercial reagents and solvents were obtained from the commercial provider and used without further purification. Column chromatography was performed using silica gel (200–300 mesh). Cyclic voltammograms were recorded on a CHI 600E potentiostat. The instrument for measuring the melting point is the RY-1G melting point instrument (Tianjin Tianguang Optical Instrument Co., Ltd.). NMR spectra were recorded on a Varianinova-400 (1 H: 400 MHz, 13 C: 101 MHz) spectrometer using TMS as internal reference. Chemical shifts ( $\delta$ ) and coupling constants (J) are expressed in ppm and Hz, respectively. The instrument for electrolysis is DC regulated power supply (IT6722, made in China). The anode electrode and cathode electrode are Pt ( $1.0 \times 1.0$  cm $^2$ ) and Pt ( $1.5 \times 1.5$  cm $^2$ ) (Wuhan Gao Shi Rui Lian Technology Co., Ltd.), respectively. Thin layer chromatography (TLC) employed the glass silica gel plates ( $0.20 \pm 0.03$  mm).

## 2. Experimental Section

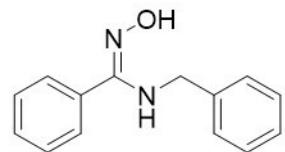
### 2.1. General procedure for synthesis of *N*-benzyl amideoxime 1<sup>[1]</sup>



A mixture of aldehyde (5.0 mmol), hydroxylamine hydrochloride (5.5 mmol), pyridine (7.5 mmol) in EtOH (20 mL) was stirred at refluxing for 2 h. The reaction was detected by TLC. After reaction, HCl aqueous was added into the reaction mixture to remove unreacted pyridine and extracted with dichloromethane (20 mL × 3). The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and then concentrated in vacuo to give the oxime. The obtained oxime was directly reacted in the next step.

In a round bottom flask equipped with a stir bar, the obtained oxime and EtOH (10 mL) were added, followed by the addition of *N*-chlorosuccinimide (7.5 mmol) in five portions, and the mixture was stirred for 4 h under a nitrogen atmosphere. The chlorooxime generated was used in situ. To the solution of benzylamine (5.0 mmol) and trimethylamine (7.5 mmol) in THF (10 mL) at 0°C was added the chlorooxime dropwisely under a nitrogen atmosphere. The reaction mixture was stirred at 0°C for 2 h and room temperature for 4 h. It was then evaporated and the residue was diluted with water. The aqueous layer was extracted with dichloromethane (20 mL × 3). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated. The crude material was purified by column chromatography over silica gel (Petroleum ether : ethyl acetate = 2 : 1) to afford the desired product.

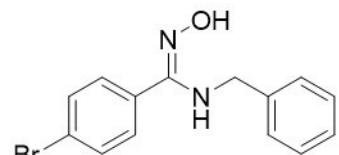
**(Z)-*N*-Benzyl-*N'*-hydroxybenzimidamide (1a):**



white solid (0.882 g, 78.0% yield), m.p. 114-115°C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ: 9.85 (d, *J* = 2.4 Hz, 1H), 7.40-7.32 (m, 5H), 7.26 (t, *J* = 7.2 Hz, 2H), 7.19 (d, *J* = 6.8 Hz, 1H), 7.11 (d, *J* = 7.6 Hz, 2H), 6.30 (t, *J* = 7.2 Hz, 1H), 4.15 (d, *J* = 6.8 Hz, 2H); <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ: 155.31, 141.41, 132.90, 129.41, 128.66, 128.64, 128.55, 127.06, 127.01, 46.89; HRMS (ESI): *m/z* [M+H]<sup>+</sup> calc. for C<sub>14</sub>H<sub>15</sub>N<sub>2</sub>O 227.1179, found 227.1185.

Characterization data match those of previously reported literature.<sup>[2]</sup>

**(Z)-*N*-Benzyl-4-bromo-*N'*-hydroxybenzimidamide (1b):**

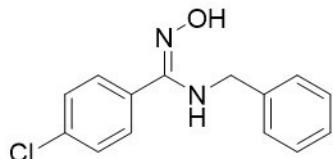


white solid (1.155 g, 76.0% yield), m.p. 138-140°C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ: 9.99 (s, 1H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.27 (dd, *J* = 12.0, 7.9 Hz, 4H), 7.18 (t, *J* = 8.0 Hz, 1H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.36 (t, *J* = 8.0 Hz, 1H), 4.15 (d, *J* = 8.0 Hz,

2H);  $^{13}\text{C}$  NMR (101 MHz, DMSO- $d_6$ )  $\delta$ : 154.40, 141.25, 132.19, 131.67, 130.53, 128.69, 127.10, 127.00, 122.73, 46.88; HRMS (ESI):  $m/z$  [M+H] $^+$  calc. for C<sub>14</sub>H<sub>14</sub>BrN<sub>2</sub>O 305.0284, found 305.0289.

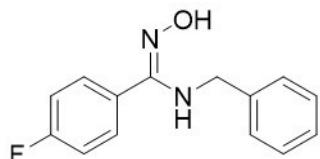
Characterization data match those of previously reported literature. [2]

**(Z)-N-Benzyl-4-chloro-N'-hydroxybenzimidamide (1c):**



white solid (1.001 g, 77.0% yield), m.p. 117-119°C;  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$ : 9.98 (s, 1H), 7.42 (d,  $J$  = 8.4 Hz, 2H), 7.35 (d,  $J$  = 8.4 Hz, 2H), 7.26 (t,  $J$  = 7.2 Hz, 2H), 7.19 (d,  $J$  = 7.2 Hz, 1H), 7.11 (d,  $J$  = 7.2 Hz, 2H), 6.37 (t,  $J$  = 7.2 Hz, 1H), 4.15 (d,  $J$  = 7.2 Hz, 2H);  $^{13}\text{C}$  NMR (101 MHz, DMSO- $d_6$ )  $\delta$ : 154.33, 141.26, 134.06, 131.82, 130.26, 128.75, 128.69, 127.10, 127.01, 46.88; HRMS (ESI):  $m/z$  [M+H] $^+$  calc. for C<sub>14</sub>H<sub>14</sub>ClN<sub>2</sub>O 261.0789, found 261.0793.

**(Z)-N-Benzyl-4-fluorine-N'-hydroxybenzimidamide (1d):**



white solid (0.915 g, 75.0% yield), m.p. 90-92°C;  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$ : 9.90 (s, 1H), 7.41-7.34 (m, 2H), 7.26 (t,  $J$  = 6.8 Hz, 2H), 7.19 (dd,  $J$  = 8.8, 4.4 Hz, 3H), 7.11 (d,  $J$  = 7.2 Hz, 2H), 6.35 (t,  $J$  = 6.8 Hz, 1H), 4.15 (d,  $J$  = 7.2 Hz, 2H);  $^{13}\text{C}$  NMR (101 MHz, DMSO- $d_6$ )  $\delta$ : 162.84 (d,  $J_{C-F}$  = 247.0 Hz), 154.44, 141.31, 130.71, 130.63, 129.35 (d,  $J_{C-F}$  = 3.1 Hz), 128.67, 127.08, 127.01, 115.71, 115.49, 46.87;  $^{19}\text{F}$  NMR (376 MHz, DMSO- $d_6$ )  $\delta$ : -112.38- -112.53; HRMS (ESI):  $m/z$  [M+H] $^+$  calc. for C<sub>14</sub>H<sub>14</sub>FN<sub>2</sub>O 245.1085, found 245.1089.

**(Z)-N-Benzyl-2-bromo-N'-hydroxybenzimidamide (1e):**

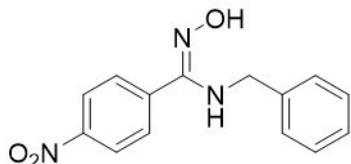


white solid (1.247 g, 82.0% yield), m.p. 124-125°C;  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$ : 9.66 (s, 1H), 7.68-7.62 (m, 1H), 7.35-7.28 (m, 2H), 7.24 (t,  $J$  = 7.2 Hz, 2H), 7.20-

7.10 (m, 2H), 7.07 (d,  $J$  = 7.2 Hz, 2H), 6.53 (t,  $J$  = 6.8 Hz, 1H), 3.95 (d,  $J$  = 6.0 Hz, 2H);  $^{13}\text{C}$  NMR (101 MHz, DMSO- $d_6$ )  $\delta$ : 153.52, 141.04, 133.81, 132.90, 132.35, 131.28, 128.56, 127.78, 127.15, 123.48, 46.31; HRMS (ESI):  $m/z$  [M+H] $^+$  calc. for C<sub>14</sub>H<sub>14</sub>BrN<sub>2</sub>O 305.0284, found 305.0290.

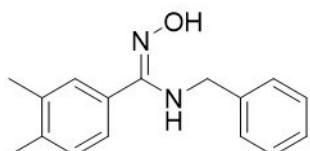
Characterization data match those of previously reported literature.<sup>[2]</sup>

**(Z)-N-Benzyl-N'-hydroxy-4-nitrobenzimidamide (1f):**



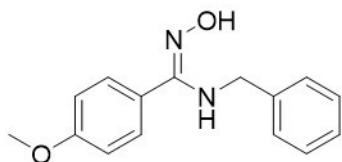
light yellow solid (1.152 g, 85.0% yield), m.p. 84-87°C;  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$ : 10.32 (s, 1H), 8.20 (d,  $J$  = 8.1 Hz, 2H), 7.61 (d,  $J$  = 8.1 Hz, 2H), 7.25 (t,  $J$  = 7.2 Hz, 2H), 7.17 (t,  $J$  = 7.0 Hz, 1H), 7.10 (d,  $J$  = 7.5 Hz, 2H), 6.50 (t,  $J$  = 6.9 Hz, 1H), 4.19 (d,  $J$  = 7.0 Hz, 2H);  $^{13}\text{C}$  NMR (101 MHz, DMSO- $d_6$ )  $\delta$ : 179.83, 154.00, 148.16, 140.82, 139.07, 129.70, 128.72, 127.16, 123.89, 47.01, 45.85, 29.98, 8.88; HRMS (ESI):  $m/z$  [M+H] $^+$  calc. for C<sub>14</sub>H<sub>14</sub>N<sub>3</sub>O<sub>3</sub> 272.1030, found 272.1038.

**(Z)-N-Benzyl-N'-hydroxy-3,4-dimethylbenzimidamide (1g):**



white solid (0.813 g, 64.0% yield), m.p. 116-118°C;  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$ : 9.76 (s, 1H), 7.27 (t,  $J$  = 7.2 Hz, 2H), 7.19 (d,  $J$  = 7.2 Hz, 1H), 7.12 (t,  $J$  = 8.8 Hz, 4H), 7.07 (d,  $J$  = 7.6 Hz, 1H), 6.20 (t,  $J$  = 6.8 Hz, 1H), 4.15 (d,  $J$  = 6.8 Hz, 2H), 2.20 (s, 3H), 2.18 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz, DMSO- $d_6$ )  $\delta$ : 155.40, 141.54, 137.56, 136.42, 130.35, 129.63, 128.65, 127.02, 125.96, 46.97, 19.71; HRMS (ESI):  $m/z$  [M+H] $^+$  calc. for C<sub>16</sub>H<sub>19</sub>N<sub>2</sub>O 255.1492, found 255.1498.

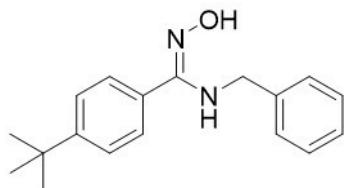
**(Z)-N-Benzyl-N'-hydroxy-4-methoxybenzimidamide (1h):**



white solid (1.064 g, 83.0% yield), m.p. 139-140°C;  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$ : 9.73 (s, 1H), 7.26 (t,  $J$  = 7.6 Hz, 4H), 7.19 (d,  $J$  = 7.1 Hz, 1H), 7.13 (d,  $J$  = 7.4 Hz, 2H), 6.91 (d,  $J$  = 8.6 Hz, 2H), 6.22 (t,  $J$  = 6.4 Hz, 1H), 4.15 (d,  $J$  = 6.9 Hz, 2H), 3.75 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz, DMSO- $d_6$ )  $\delta$ : 160.26, 155.26, 141.36, 129.88, 128.68, 127.03, 114.09, 55.61, 46.94, 45.86; HRMS (ESI):  $m/z$  [M+H] $^+$  calc. for C<sub>15</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub> 257.1285, found 257.1291.

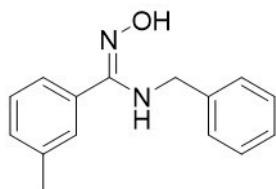
Characterization data match those of previously reported literature.<sup>[2]</sup>

**(Z)-N-Benzyl-4-(tert-butyl)-N'-hydroxybenzimidamide (1i):**



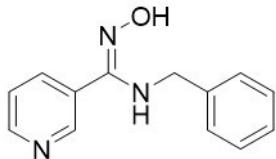
white solid (0.960 g, 68.0% yield), m.p. 143-146°C;  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$ : 9.82 (s, 1H), 7.39 (d,  $J$  = 8.4 Hz, 2H), 7.28 (dd,  $J$  = 15.8, 8.4 Hz, 4H), 7.17 (dd,  $J$  = 21.6, 7.2 Hz, 3H), 6.20 (t,  $J$  = 7.2 Hz, 1H), 4.17 (d,  $J$  = 7.2 Hz, 2H), 1.27 (s, 9H);  $^{13}\text{C}$  NMR (101 MHz, DMSO- $d_6$ )  $\delta$ : 155.24, 151.92, 141.47, 130.03, 128.68, 128.25, 127.01, 125.42, 46.94, 34.86, 31.49; HRMS (ESI):  $m/z$  [M+H] $^+$  calc. for C<sub>18</sub>H<sub>23</sub>N<sub>2</sub>O 283.1805, found 283.1810.

**(Z)-N-Benzyl-N'-hydroxy-3-methylbenzimidamide (1j):**



white solid (0.937 g, 78.0% yield), m.p. 107-109°C;  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$ : 9.81 (s, 1H), 7.25 (dd,  $J$  = 15.2, 7.6 Hz, 3H), 7.16-7.21 (m, 2H), 7.13 (d,  $J$  = 10.8 Hz, 4H), 6.25 (t,  $J$  = 6.8 Hz, 1H), 4.14 (d,  $J$  = 7.2 Hz, 2H), 2.27 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz, DMSO- $d_6$ )  $\delta$ : 155.41, 141.47, 137.78, 132.82, 130.02, 129.16, 128.57, 127.05, 125.69, 46.96, 21.38; HRMS (ESI):  $m/z$  [M+H] $^+$  calc. for C<sub>15</sub>H<sub>17</sub>N<sub>2</sub>O 241.1335, found 241.1339.

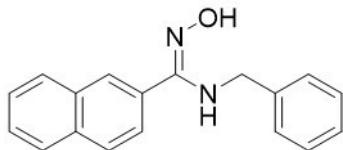
**(Z)-N-Benzyl-N'-hydroxynicotinimidamide (1k):**



Light yellow solid (0.852 g, 75.0% yield), m.p. 129-131°C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ: 10.08 (s, 1H,), 8.57 (d, *J* = 3.9 Hz, 1H), 8.49 (s, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.38 (dd, *J* = 7.5, 5.0 Hz, 1H), 7.26 (t, *J* = 7.3 Hz, 2H), 7.18 (t, *J* = 7.1 Hz, 1H), 7.10 (d, *J* = 7.4 Hz, 2H), 6.51 (t, *J* = 6.9 Hz, 1H), 4.17 (d, *J* = 7.0 Hz, 2H); <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ: 152.89, 150.33, 149.00, 141.15, 136.02, 128.79, 127.07, 123.72, 46.86; HRMS (ESI): *m/z* [M+H]<sup>+</sup> calc. for C<sub>13</sub>H<sub>14</sub>N<sub>3</sub>O 228.1131, found 228.1136.

Characterization data match those of previously reported literature.<sup>[3]</sup>

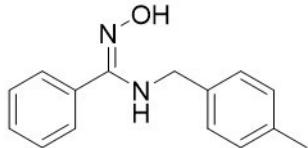
**(Z)-N-Benzyl-N'-hydroxy-2-naphthimidamide (1l):**



white solid (1.216 g, 88.0% yield), m.p. 100-103°C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ: 10.74 (s, 1H), 8.02 (dd, *J* = 22.8, 13.6 Hz, 4H), 7.62 (t, *J* = 6.2 Hz, 2H), 7.52 (d, *J* = 8.3 Hz, 1H), 7.32-7.19 (m, 3H), 7.14 (d, *J* = 7.2 Hz, 2H), 4.35 (d, *J* = 5.8 Hz, 2H); <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ: 158.09, 139.55, 134.06, 132.63, 128.89, 128.18, 127.52, 127.25, 125.38, 47.20; HRMS (ESI): *m/z* [M+H]<sup>+</sup> calc. for C<sub>18</sub>H<sub>17</sub>N<sub>2</sub>O 277.1335, found 277.1339.

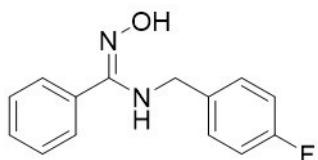
Characterization data match those of previously reported literature.<sup>[2]</sup>

**(Z)-N'-Hydroxy-N-(4-methylbenzyl)benzimidamide (1m):**



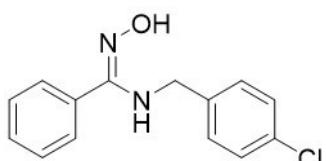
white solid (0.937 g, 78.0% yield), m.p. 101-103°C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ: 9.84 (s, 1H), 7.36 (s, 5H), 7.06 (d, *J* = 8.0 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.21 (t, *J* = 6.8 Hz, 1H), 4.10 (d, *J* = 6.8 Hz, 2H), 2.24 (s, 3H); <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ: 155.34, 138.31, 136.08, 132.95, 129.31, 128.58, 127.01, 46.70, 21.10; HRMS (ESI): *m/z* [M+H]<sup>+</sup> calc. for C<sub>15</sub>H<sub>17</sub>N<sub>2</sub>O 241.1335, found 241.1341.

**(Z)-N-(4-Fluorobenzyl)-N'-hydroxybenzimidamide (1n):**



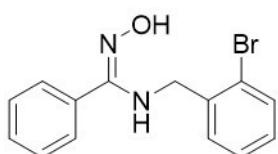
white solid (0.976 g, 80.0% yield), m.p. 90-93°C;  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$ : 9.86 (d,  $J = 2.8$  Hz, 1H), 7.35 (dd,  $J = 6.4, 5.6$  Hz, 5H), 7.10 (dt,  $J = 19.2, 8.0$  Hz, 4H), 6.34 (t,  $J = 6.7$  Hz, 1H), 4.12 (d,  $J = 6.9$  Hz, 2H);  $^{13}\text{C}$  NMR (101 MHz, DMSO- $d_6$ )  $\delta$ : 161.48 (d,  $J_{C-F} = 242.8$  Hz), 155.15, 137.57 (d,  $J_{C-F} = 2.9$  Hz), 132.90, 129.41, 129.00, 128.92, 128.64, 128.52, 115.45, 115.24, 46.21;  $^{19}\text{F}$  NMR (376 MHz, DMSO- $d_6$ )  $\delta$ : -116.48; HRMS (ESI):  $m/z$  [M+H] $^+$  calc. for  $\text{C}_{14}\text{H}_{14}\text{FN}_2\text{O}$  245.1085, found 245.1090.

**(Z)-N-(4-Chlorobenzyl)-N'-hydroxybenzimidamide (1o):**



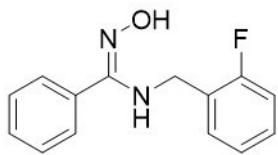
white solid (1.066 g, 82.0% yield), m.p. 110-112°C;  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$ : 9.87 (s, 1H), 7.36 (d,  $J = 6.8$  Hz, 3H), 7.31 (d,  $J = 8.0$  Hz, 4H), 7.12 (d,  $J = 8.4$  Hz, 2H), 6.40 (t,  $J = 6.8$  Hz, 1H), 4.14 (d,  $J = 7.2$  Hz, 2H);  $^{13}\text{C}$  NMR (101 MHz, DMSO- $d_6$ )  $\delta$ : 179.83, 155.07, 140.54, 132.83, 131.54, 129.44, 128.87, 128.75- 128.40, 46.22, 29.99; HRMS (ESI):  $m/z$  [M+H] $^+$  calc. for  $\text{C}_{14}\text{H}_{14}\text{ClN}_2\text{O}$  261.0789, found 261.0791.

**(Z)-N-(2-Bromobenzyl)-N'-hydroxybenzimidamide (1p):**



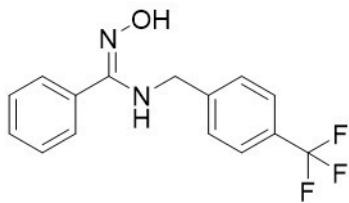
white solid (1.140 g, 75.0% yield), m.p. 110-112°C;  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$ : 9.84 (d,  $J = 2.4$  Hz, 1H), 7.42 (d,  $J = 8.4$  Hz, 2H), 7.27-7.37 (m, 5H), 7.04 (d,  $J = 8.0$  Hz, 2H), 6.38 (t,  $J = 6.8$  Hz, 1H), 4.09 (d,  $J = 7.2$  Hz, 2H);  $^{13}\text{C}$  NMR (101 MHz, DMSO- $d_6$ )  $\delta$ : 155.05, 140.98, 132.82, 131.49, 129.35, 128.58, 120.03, 46.27; HRMS (ESI):  $m/z$  [M+H] $^+$  calc. for  $\text{C}_{14}\text{H}_{14}\text{BrN}_2\text{O}$  305.0284, found 305.0289.

**(Z)-N-(2-Fluorobenzyl)-N'-hydroxybenzimidamide (1q):**



white solid (1.013 g, 83.0% yield), m.p. 100-103°C;  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$ : 9.99-9.90 (m, 1H), 7.41-7.28 (m, 6H), 7.28-7.21 (m, 1H), 7.15 (t,  $J$  = 7.6 Hz, 1H), 7.05 (t,  $J$  = 9.4 Hz, 1H), 6.28 (d,  $J$  = 6.0 Hz, 1H), 4.21 (d,  $J$  = 4.4 Hz, 2H);  $^{13}\text{C}$  NMR (101 MHz, DMSO- $d_6$ )  $\delta$ : 160.01 (d,  $J_{\text{C}-\text{F}}$  = 244.7 Hz), 155.12, 132.66, 129.49, 129.24 (d,  $J_{\text{C}-\text{F}}$  = 4.6 Hz), 129.10 (d,  $J_{\text{C}-\text{F}}$  = 8.1 Hz), 128.66, 128.46, 128.07 (d,  $J_{\text{C}-\text{F}}$  = 14.7 Hz), 124.76 (d,  $J_{\text{C}-\text{F}}$  = 3.4 Hz), 115.29 (d,  $J_{\text{C}-\text{F}}$  = 21.2 Hz), 40.76 (d,  $J_{\text{C}-\text{F}}$  = 4.3 Hz);  $^{19}\text{F}$  NMR (376 MHz, DMSO- $d_6$ )  $\delta$ : -119.64- -119.80; HRMS (ESI):  $m/z$  [M+H] $^+$  calc. for C<sub>14</sub>H<sub>14</sub>FN<sub>2</sub>O 245.1085, found 245.1093.

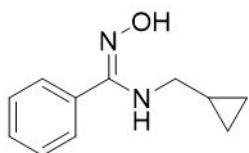
**(Z)-N'-Hydroxy-N-(4-(trifluoromethyl)benzyl)benzimidamide (1r):**



white solid (1.073 g, 73.0% yield), m.p. 122-123°C;  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$ : 9.92 (s, 1H), 7.62 (d,  $J$  = 8.0 Hz, 2H), 7.35 (dd,  $J$  = 9.0, 3.4 Hz, 7H), 6.52 (t,  $J$  = 6.8 Hz, 1H), 4.25 (d,  $J$  = 6.8 Hz, 2H);  $^{13}\text{C}$  NMR (101 MHz, DMSO- $d_6$ )  $\delta$ : 154.98, 146.45, 132.78, 129.46, 128.67, 128.49, 127.67, 125.55, 125.52, 125.48, 125.44, 46.54;  $^{19}\text{F}$  NMR (376 MHz, DMSO- $d_6$ )  $\delta$ : -60.82; HRMS (ESI):  $m/z$  [M+H] $^+$  calc. for C<sub>15</sub>H<sub>14</sub>F<sub>3</sub>N<sub>2</sub>O 295.1053, found 295.1060.

Characterization data match those of previously reported literature.<sup>[4]</sup>

**(Z)-N-(Cyclopropylmethyl)-N'-hydroxybenzimidamide (1s):**

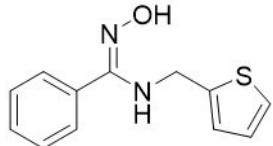


white solid (0.752 g, 79.0% yield), m.p. 49-52°C;  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$ : 9.74 (s, 1H), 7.40 (s, 5H), 5.72 (t,  $J$  = 6.4 Hz, 1H), 2.78 (t,  $J$  = 6.8 Hz, 2H), 0.80 (ddd,  $J$  = 12.6, 7.2, 5.2 Hz, 1H), 0.32 (dt,  $J$  = 8.0, 5.6 Hz, 2H), 0.00 (q,  $J$  = 5.2 Hz, 2H);  $^{13}\text{C}$

NMR (101 MHz, DMSO-*d*<sub>6</sub>)  $\delta$ : 155.28, 133.23, 129.31, 128.63, 47.99, 12.88, 3.34; HRMS (ESI): *m/z* [M+H]<sup>+</sup> calc. for C<sub>11</sub>H<sub>15</sub>N<sub>2</sub>O 191.1179, found 191.1182.

Characterization data match those of previously reported literature.<sup>[4]</sup>

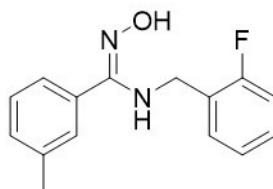
**(Z)-N'-Hydroxy-N-(thiophen-2-ylmethyl)benzimidamide (1t):**



white solid (0.967 g, 83.3% yield), m.p. 130-132°C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$ : 9.89 (s, 1H), 7.40 (s, 5H), 7.33 (d, *J* = 4.8 Hz, 1H), 6.91-6.88 (m, 1H), 6.75 (s, 1H), 6.31 (t, *J* = 6.8 Hz, 1H), 4.31 (d, *J* = 6.8 Hz, 2H); <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>)  $\delta$ : 154.70, 144.81, 132.75, 129.50, 128.63, 127.20, 125.05, 124.75, 42.28; HRMS (ESI): *m/z* [M+H]<sup>+</sup> calc. for C<sub>12</sub>H<sub>13</sub>N<sub>2</sub>OS 233.0743, found 233.0753.

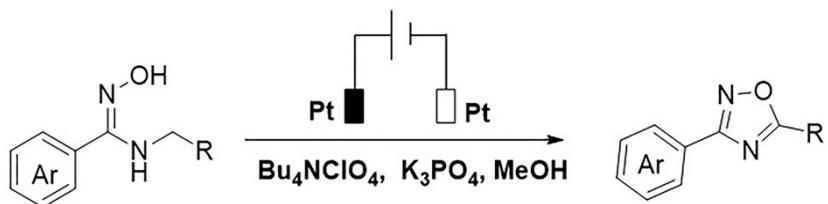
Characterization data match those of previously reported literature.<sup>[4]</sup>

**(Z)-N-(2-Fluorobenzyl)-N'-hydroxy-3-methylbenzimidamide (1u):**



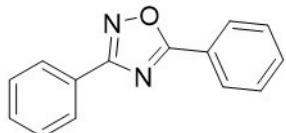
white solid (0.942 g, 73.0% yield), m.p. 102-103°C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$ : 9.88 (d, *J* = 4.4 Hz, 1H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.21-7.27 (m, 2H), 7.15-7.21 (m, 2H), 7.12 (d, *J* = 7.2 Hz, 2H), 7.02-7.09 (m, 1H), 6.25 (t, *J* = 6.0 Hz, 1H), 4.20 (d, *J* = 6.4 Hz, 2H), 2.27 (s, 3H); <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>)  $\delta$ : 160.02 (d, *J*<sub>C-F</sub> = 244.7 Hz), 155.20, 137.83, 132.58, 130.10, 129.28 (d, *J*<sub>C-F</sub> = 4.6 Hz), 129.08 (d, *J*<sub>C-F</sub> = 8.4 Hz), 128.53, 128.16 (d, *J*<sub>C-F</sub> = 16.6 Hz), 125.58, 124.76 (d, *J*<sub>C-F</sub> = 3.4 Hz), 115.28 (d, *J*<sub>C-F</sub> = 21.3 Hz), 40.78 (d, *J*<sub>C-F</sub> = 4.3 Hz), 21.36; <sup>19</sup>F NMR (376 MHz, DMSO-*d*<sub>6</sub>)  $\delta$ : -119.65- -119.77; HRMS (ESI): *m/z* [M+H]<sup>+</sup> calc. for C<sub>15</sub>H<sub>16</sub>FN<sub>2</sub>O 259.1241, found 259.1249.

## 2.2. General procedure for synthesis of 1,2,4-oxadiazole 2



In an undivided cell equipped with two platinum electrodes, amidoxime **1** (0.5 mmol),  $K_3PO_4$  (1.5 mmol, 0.318 g),  $Bu_4NClO_4$  (1 mmol, 0.342 g) were added to the MeOH (10 mL). The reaction mixture was stirred and electrolyzed at a constant voltage of 3 V for 2 h at 30°C. After the reaction was completed, the reaction mixture was evaporated and then diluted with  $H_2O$  and extracted with dichloromethane (20 mL  $\times$  3). The combined organic layer was dried over anhydrous  $Na_2SO_4$ . Subsequently, the solvent was removed under reduced pressure and the remaining crude product was purified by column chromatography over silica gel ( $V_{PE} : V_{EtOAc} = 16:1$ ) to afford the corresponding products.

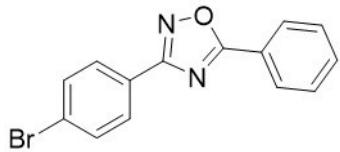
### **3,5-Diphenyl-1,2,4-oxadiazole (2a):**



white solid (0.092 g, 82.7% yield), m.p. 109-111°C;  $^1H$  NMR (400 MHz,  $DMSO-d_6$ )  $\delta$ : 8.20 (d,  $J = 7.2$  Hz, 2H), 8.14 ~8.09 (m 2H), 7.75 (t,  $J = 7.2$  Hz, 1H), 7.68 (t,  $J = 7.6$  Hz, 2H), 7.62 (d,  $J = 6.8$  Hz, 3H);  $^{13}C$  NMR (101 MHz,  $DMSO-d_6$ )  $\delta$ : 175.89, 168.73, 133.83, 132.13, 130.03, 129.74, 128.38, 127.57, 126.61, 123.83; HRMS (ESI):  $m/z$  [M+H] $^+$  calc. for  $C_{14}H_{11}N_2O$  223.0866, found 223.0869.

Characterization data match those of previously reported literature.<sup>[2]</sup>

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

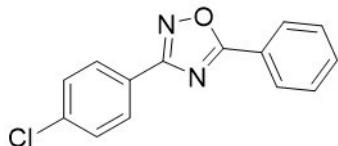


white solid (0.105 g, 70.0% yield), m.p. 110-112°C;  $^1H$  NMR (400 MHz,  $DMSO-d_6$ )  $\delta$ : 8.19 (d,  $J = 8.0$  Hz, 2H), 8.03 (d,  $J = 8.0$  Hz, 2H), 7.82 (d,  $J = 8.0$  Hz, 2H), 7.75 (t,  $J = 8.0$  Hz, 1H), 7.68 (t,  $J = 8.0$  Hz, 2H);  $^{13}C$  NMR (101 MHz,  $DMSO-d_6$ )  $\delta$ : 176.11,

168.07, 133.93, 132.85, 130.05, 129.53, 128.42, 125.78, 123.71; HRMS (ESI): *m/z* [M+H]<sup>+</sup> calc. for C<sub>14</sub>H<sub>10</sub>BrN<sub>2</sub>O 300.9971, found 300.9979.

Characterization data match those of previously reported literature.<sup>[2]</sup>

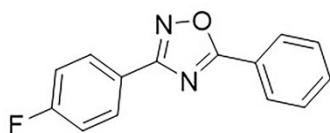
**3-(4-Chlorophenyl)-5-phenyl-1,2,4-oxadiazole (2c):**



white solid (0.095 g, 74.2% yield), m.p. 104-106°C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ: 8.19 (d, *J* = 7.2 Hz, 2H), 8.11 (d, *J* = 8.4 Hz, 2H), 7.76 (d, *J* = 7.2 Hz, 1H), 7.68 (dd, *J* = 7.7, 6.8 Hz, 4H); <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ: 176.09, 167.95, 136.87, 133.95, 130.07, 129.94, 129.38, 128.42, 125.47, 123.71; HRMS (ESI): *m/z* [M+H]<sup>+</sup> calc. for C<sub>14</sub>H<sub>10</sub>ClN<sub>2</sub>O 257.0476, found 257.0479.

Characterization data match those of previously reported literature.<sup>[5]</sup>

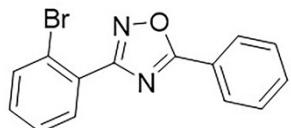
**3-(4-Fluorophenyl)-5-phenyl-1,2,4-oxadiazole (2d):**



white solid (0.085 g, 70.8% yield), m.p. 111-114°C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ: 8.22-8.12 (m, 4H), 7.75 (t, *J* = 7.2 Hz, 1H), 7.67 (t, *J* = 7.6 Hz, 2H), 7.44 (t, *J* = 8.8 Hz, 2H); <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ: 175.94, 167.91, 164.47 (d, *J*<sub>C-F</sub> = 250.3 Hz), 133.86, 130.15, 130.06, 130.02, 128.38, 123.74, 123.18 (d, *J*<sub>C-F</sub> = 3.1 Hz), 117.01, 116.79; <sup>19</sup>F NMR (376 MHz, DMSO-*d*<sub>6</sub>) δ: -108.42; HRMS (ESI): *m/z* [M+H]<sup>+</sup> calc. for C<sub>14</sub>H<sub>10</sub>FN<sub>2</sub>O 241.0772, found 241.0779.

Characterization data match those of previously reported literature.<sup>[5]</sup>

**3-(2-Bromophenyl)-5-phenyl-1,2,4-oxadiazole (2e):**

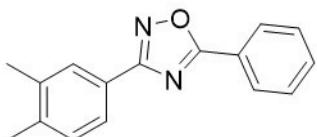


white solid (0.090 g, 60.0% yield), m.p. 77-79°C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ: 8.15 (d, *J* = 7.2 Hz, 2H), 7.82-7.90 (m, 2H), 7.71 (t, *J* = 7.6 Hz, 1H), 7.63 (t, *J* = 7.6 Hz, 2H), 7.49-7.60 (m, 2H); <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ: 175.39, 168.51,

134.40, 133.87, 133.11, 132.41, 130.01, 128.43, 128.10, 123.61, 121.84; HRMS (ESI):  $m/z$  [M+H]<sup>+</sup> calc. for C<sub>14</sub>H<sub>10</sub>BrN<sub>2</sub>O 300.9971, found 300.9979.

Characterization data match those of previously reported literature.<sup>[6]</sup>

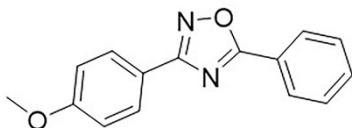
**3-(3,4-Dimethylphenyl)-5-phenyl-1,2,4-oxadiazole (2g):**



white solid (0.095 g, 76.0% yield), m.p. 112-114°C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$ : 8.18 (d, *J* = 7.2 Hz, 2H), 7.87 (s, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.74 (t, *J* = 7.6 Hz, 1H), 7.67 (t, *J* = 7.6 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 1H), 2.33 (s, 3H), 2.31 (s, 3H); <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>)  $\delta$ : 175.67, 168.78, 140.89, 137.81, 133.75, 130.74, 130.02, 128.35, 125.08, 124.12, 123.91, 19.86; HRMS (ESI):  $m/z$  [M+H]<sup>+</sup> calc. for C<sub>16</sub>H<sub>15</sub>N<sub>2</sub>O 251.1179, found 251.1182.

Characterization data match those of previously reported literature.<sup>[5]</sup>

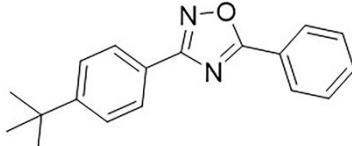
**3-(4-Methoxyphenyl)-5-phenyl-1,2,4-oxadiazole (2h):**



white solid (0.065 g, 51.6% yield), m.p. 98-99°C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$ : 8.19-8.11 (m, 2H), 8.07-7.97 (m, 2H), 7.75-7.68 (m, 1H), 7.65 (t, *J* = 7.6 Hz, 2H), 7.17-7.09 (m, 2H), 3.84 (d, *J* = 2.8 Hz, 3H); <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>)  $\delta$ : 175.56, 168.43, 162.26, 133.70, 129.98, 129.26, 128.32, 123.91, 118.88, 115.12, 55.87; HRMS (ESI):  $m/z$  [M+H]<sup>+</sup> calc. for C<sub>15</sub>H<sub>13</sub>N<sub>2</sub>O<sub>2</sub> 253.0972, found 253.0975.

Characterization data match those of previously reported literature.<sup>[5]</sup>

**3-(4-(tert-Butyl)phenyl)-5-phenyl-1,2,4-oxadiazole (2i):**

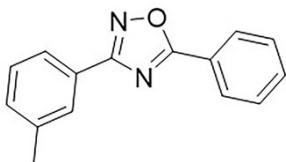


white solid (0.085 g, 61.1% yield), m.p. 135-137°C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$ : 8.16 (d, *J* = 7.2 Hz, 2H), 8.00 (d, *J* = 8.0 Hz, 2H), 7.71 (t, *J* = 6.8 Hz, 1H), 7.63 (t, *J* = 7.6 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 1.29 (s, 9H); <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>)

$\delta$ : 175.65, 168.60, 154.80, 133.64, 129.90, 128.28, 127.36, 126.37, 123.88, 35.11, 31.26; HRMS (ESI):  $m/z$  [M+H]<sup>+</sup> calc. for C<sub>18</sub>H<sub>19</sub>N<sub>2</sub>O 279.1492, found 279.1498.

Characterization data match those of previously reported literature.<sup>[5]</sup>

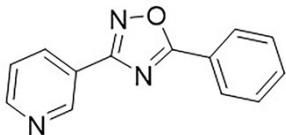
**5-Phenyl-3-(m-tolyl)-1,2,4-oxadiazole (2j):**



white solid (0.076 g, 64.7% yield), m.p. 87-89°C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$ : 8.19 (d, *J* = 8.0 Hz, 2H), 7.90 (d, *J* = 8.0 Hz, 2H), 7.75 (t, *J* = 6.0 Hz, 1H), 7.67 (t, *J* = 8.0 Hz, 2H), 7.41-7.52 (m, 2H), 2.42 (s, 3H); <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>)  $\delta$ : 175.77, 168.78, 139.09, 133.74, 132.70, 129.98, 129.57, 128.34, 127.95, 126.56, 124.72, 123.87, 21.35; HRMS (ESI):  $m/z$  [M+H]<sup>+</sup> calc. for C<sub>15</sub>H<sub>13</sub>N<sub>2</sub>O 237.1022, found 237.1025.

Characterization data match those of previously reported literature.<sup>[5]</sup>

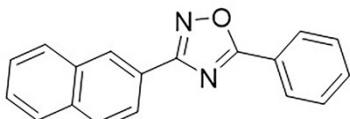
**5-Phenyl-3-(pyridin-3-yl)-1,2,4-oxadiazole (2k):**



white solid (0.075 g, 67.0% yield), m.p. 168-170°C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$ : 9.26 (s, 1H), 8.82 (d, *J* = 3.6 Hz, 1H), 8.45 (d, *J* = 8.0 Hz, 1H), 8.21 (d, *J* = 7.6 Hz, 2H), 7.77 (t, *J* = 7.6 Hz, 1H), 7.62-7.72 (m, 3H); <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>)  $\delta$ : 176.24, 167.04, 152.89, 148.27, 135.18, 134.03, 130.09, 128.48, 124.82, 123.62, 122.93; HRMS (ESI):  $m/z$  [M+H]<sup>+</sup> calc. for C<sub>13</sub>H<sub>10</sub>N<sub>3</sub>O 224.0818, found 224.0822.

Characterization data match those of previously reported literature.<sup>[6]</sup>

**3-(Naphthalen-2-yl)-5-phenyl-1,2,4-oxadiazole (2l):**

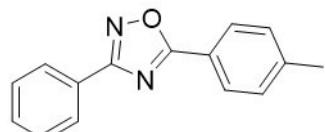


white solid (0.085 g, 62.5% yield), m.p. 121-123°C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$ : 8.62 (s, 1H), 8.13 (d, *J* = 7.6 Hz, 2H), 8.04 (dd, *J* = 8, 0.4 Hz, 3H) 7.94 (d, *J* = 6.8

Hz, 1H), 7.66 (d,  $J$  = 6.8 Hz, 1H), 7.63-7.54 (m, 4H);  $^{13}\text{C}$  NMR (101 MHz, DMSO- $d_6$ )  $\delta$ : 175.87, 168.78, 134.69, 133.76, 133.06, 129.97, 129.35, 128.51 – 128.12, 128.01, 127.50, 123.92; HRMS (ESI):  $m/z$  [M+H] $^+$  calc. for  $\text{C}_{18}\text{H}_{13}\text{N}_2\text{O}$  273.1022, found 273.1028.

Characterization data match those of previously reported literature.<sup>[6]</sup>

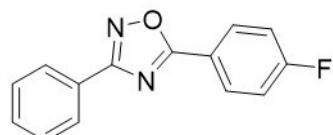
**3-Phenyl-5-(p-tolyl)-1,2,4-oxadiazole (2m):**



white solid (0.076 g, 64.7% yield), m.p. 113-115°C;  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$ : 8.09 (dd,  $J$  = 7.6, 3.2 Hz, 4H), 7.61 (d,  $J$  = 7.2 Hz, 3H), 7.48 (d,  $J$  = 8.0 Hz, 2H), 2.44 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz, DMSO- $d_6$ )  $\delta$ : 175.98, 168.67, 144.28, 132.08, 130.59, 129.72, 128.36, 127.56, 126.71, 121.14, 21.73; HRMS (ESI):  $m/z$  [M+H] $^+$  calc. for  $\text{C}_{15}\text{H}_{13}\text{N}_2\text{O}$  237.1022, found 237.1025.

Characterization data match those of previously reported literature.<sup>[5]</sup>

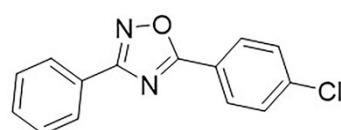
**5-(4-Fluorophenyl)-3-phenyl-1,2,4-oxadiazole (2n):**



white solid (0.085 g, 70.8% yield), m.p. 108-110°C;  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$ : 8.28-8.21 (m, 2H), 8.08 (d,  $J$  = 6.4 Hz, 2H), 7.60 (d,  $J$  = 6.8 Hz, 3H), 7.50 (t,  $J$  = 8.0 Hz, 2H);  $^{13}\text{C}$  NMR (101 MHz, DMSO- $d_6$ )  $\delta$ : 175.05, 168.74, 166.42 (d,  $J_{C-F}$  = 253.2 Hz), 132.15, 131.34, 131.24, 129.73, 127.57, 126.55, 120.58 (d,  $J_{C-F}$  = 3.0 Hz), 117.43, 117.21;  $^{19}\text{F}$  NMR (376 MHz, DMSO- $d_6$ )  $\delta$ : -105.26; HRMS (ESI):  $m/z$  [M+H] $^+$  calc. for  $\text{C}_{14}\text{H}_{10}\text{FN}_2\text{O}$  241.0772, found 241.0779.

Characterization data match those of previously reported literature.<sup>[5]</sup>

**5-(4-Chlorophenyl)-3-phenyl-1,2,4-oxadiazole (2o):**



white solid (0.100 g, 78.1% yield), m.p. 125-127°C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ: 8.18 (d, *J* = 8.4 Hz, 2H), 8.08 (d, *J* = 6.0 Hz, 2H), 7.72 (d, *J* = 8.8 Hz, 2H), 7.61 (t, *J* = 5.6 Hz, 3H); <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ: 175.05, 168.79, 138.68, 132.18, 130.20, 129.74, 127.57, 126.48, 122.70; HRMS (ESI): *m/z* [M+H]<sup>+</sup> calc. for C<sub>14</sub>H<sub>10</sub>ClN<sub>2</sub>O 257.0476, found 257.0479.

Characterization data match those of previously reported literature.<sup>[7]</sup>

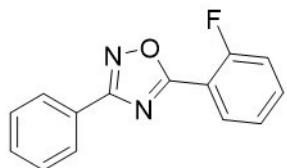
**5-(2-Bromophenyl)-3-phenyl-1,2,4-oxadiazole (2p):**



white solid (0.105 g, 70.0% yield), m.p. 60-62°C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ: 8.08 (t, *J* = 8.4 Hz, 4H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.60 (q, *J* = 6.0 Hz, 3H); <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ: 175.18, 168.80, 133.14, 132.19, 130.27, 129.74, 127.65, 126.48, 123.03; HRMS (ESI): *m/z* [M+H]<sup>+</sup> calc. for C<sub>14</sub>H<sub>10</sub>BrN<sub>2</sub>O 300.9971, found 300.9975.

Characterization data match those of previously reported literature.<sup>[7]</sup>

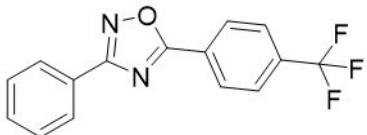
**5-(2-Fluorophenyl)-3-phenyl-1,2,4-oxadiazole (2q):**



white solid (0.090 g, 75.0% yield), m.p. 100-102°C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ: 8.21 (s, 1H), 8.06-8.12 (m, 2H), 7.78 (d, *J* = 3.6 Hz, 1H), 7.45-7.64 (m, 5H); <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ: 172.90, 168.46, 160.43 (d, *J*<sub>C-F</sub> = 258.8 Hz), 136.11 (d, *J*<sub>C-F</sub> = 8.9 Hz), 132.17, 131.32, 129.74, 127.59, 126.44, 125.92 (d, *J*<sub>C-F</sub> = 3.6 Hz), 117.75 (d, *J*<sub>C-F</sub> = 20.7 Hz), 112.27 (d, *J*<sub>C-F</sub> = 11.3 Hz); <sup>19</sup>F NMR (376 MHz, DMSO-*d*<sub>6</sub>) δ: -109.52; HRMS (ESI): *m/z* [M+H]<sup>+</sup> calc. for C<sub>14</sub>H<sub>10</sub>FN<sub>2</sub>O 241.0772, found 241.0774.

Characterization data match those of previously reported literature.<sup>[7]</sup>

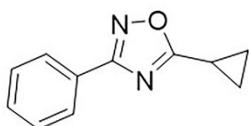
**3-Phenyl-5-(4-(trifluoromethyl)phenyl)-1,2,4-oxadiazole (2r):**



white solid (0.140 g, 96.5% yield), m.p. 101-102°C;  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$ : 8.35 (d,  $J$  = 8.0 Hz, 2H), 8.06-8.09 (m, 2H), 8.00 (d,  $J$  = 8.0 Hz, 2H), 7.56-7.63 (m, 3H);  $^{13}\text{C}$  NMR (101 MHz, DMSO- $d_6$ )  $\delta$ : 174.66, 168.90, 133.13 (d,  $J_{C-F}$  = 32.4 Hz), 132.25, 129.73, 129.27, 127.56, 126.95, 126.91, 126.87, 126.84, 126.30;  $^{19}\text{F}$  NMR (376 MHz, DMSO- $d_6$ )  $\delta$ : -61.91; HRMS (ESI):  $m/z$  [M+H] $^+$  calc. for C<sub>15</sub>H<sub>10</sub>F<sub>3</sub>N<sub>2</sub>O 291.0740, found 291.0746.

Characterization data match those of previously reported literature.<sup>[4]</sup>

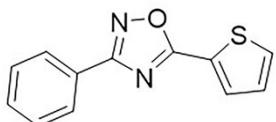
**5-Cyclopropyl-3-phenyl-1,2,4-oxadiazole (2s):**



colorless oil (0.038 g, 40.9% yield);  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$ : 7.96 (d,  $J$  = 7.6 Hz, 2H), 7.49-7.61 (m, 3H), 2.36-2.44 (m, 1H), 1.28 (dd,  $J$  = 4.9, 3.6 Hz, 2H), 1.19 (d,  $J$  = 2.8 Hz, 2H);  $^{13}\text{C}$  NMR (101 MHz, DMSO- $d_6$ )  $\delta$ : 182.26, 167.95, 131.86, 129.61, 127.41, 126.77, 10.46, 7.70; HRMS (ESI):  $m/z$  [M+H] $^+$  calc. for C<sub>11</sub>H<sub>11</sub>N<sub>2</sub>O 187.0866, found 187.0869.

Characterization data match those of previously reported literature.<sup>[4]</sup>

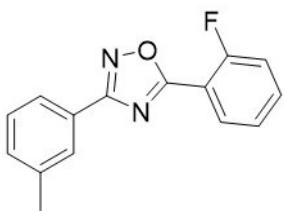
**3-Phenyl-5-(thiophen-2-yl)-1,2,4-oxadiazole (2t):**



white solid (0.092 g, 80.7% yield), m.p. 108-109°C;  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$ : 8.06 (d,  $J$  = 4.8 Hz, 1H), 8.02 (d,  $J$  = 4.8 Hz, 3H), 7.58-7.51 (m, 3H), 7.32 (t,  $J$  = 4.4 Hz, 1H);  $^{13}\text{C}$  NMR (101 MHz, DMSO- $d_6$ )  $\delta$ : 171.53, 168.56, 134.38, 133.15, 132.07, 129.62, 127.55, 126.38, 124.99; HRMS (ESI):  $m/z$  [M+H] $^+$  calc. for C<sub>12</sub>H<sub>9</sub>N<sub>2</sub>OS 229.0430, found 229.0436.

Characterization data match those of previously reported literature.<sup>[4]</sup>

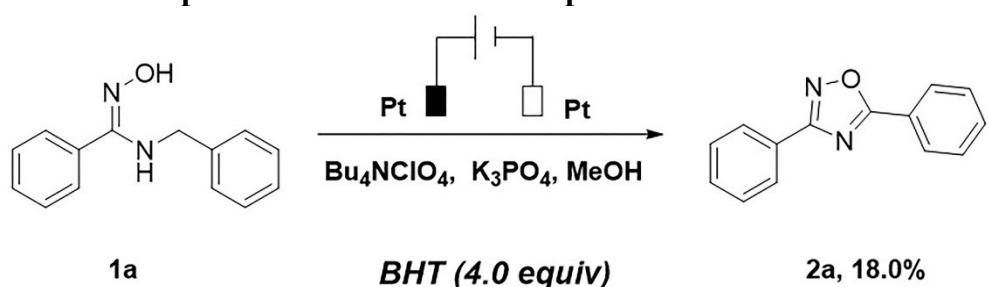
### 5-(2-Fluorophenyl)-3-(*m*-tolyl)-1,2,4-oxadiazole (2u):



white solid (0.096 g, 75.6% yield), m.p. 99-102°C;  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$ : 8.17 (dd,  $J$  = 13.6, 7.2 Hz, 1H), 7.85 (d,  $J$  = 8.8 Hz, 2H), 7.76 (dd,  $J$  = 13.6, 7.2 Hz, 1H), 7.49-7.53 (m, 1H), 7.42-7.49 (m, 2H), 7.40 (d,  $J$  = 7.2 Hz, 1H), 2.39 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz, DMSO- $d_6$ )  $\delta$ : 172.80 (d,  $J_{C-F}$  = 4.2 Hz), 168.48, 160.41 (d,  $J_{C-F}$  = 258.9 Hz), 139.10, 136.04 (d,  $J_{C-F}$  = 9.0 Hz), 132.75, 131.27, 129.58, 127.93, 126.35, 125.87 (d,  $J_{C-F}$  = 3.4 Hz), 124.73, 117.70 (d,  $J_{C-F}$  = 20.7 Hz), 112.25 (d,  $J_{C-F}$  = 11.4 Hz), 21.32;  $^{19}\text{F}$  NMR (376 MHz, DMSO- $d_6$ )  $\delta$ : -109.45- -109.56; HRMS (ESI):  $m/z$  [M+H] $^+$  calc. for  $\text{C}_{15}\text{H}_{12}\text{FN}_2\text{O}$  255.0928, found 255.0929.

Characterization data match those of previously reported literature.<sup>[6]</sup>

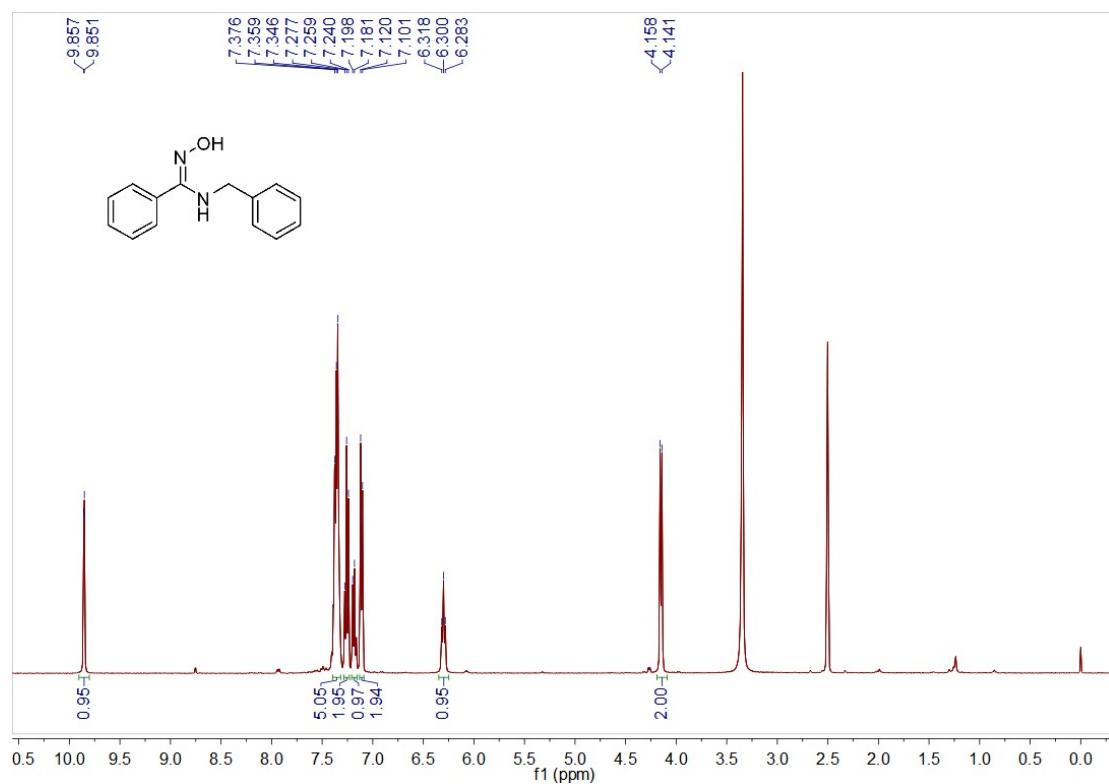
### **2.3. General procedure for the control experiment**



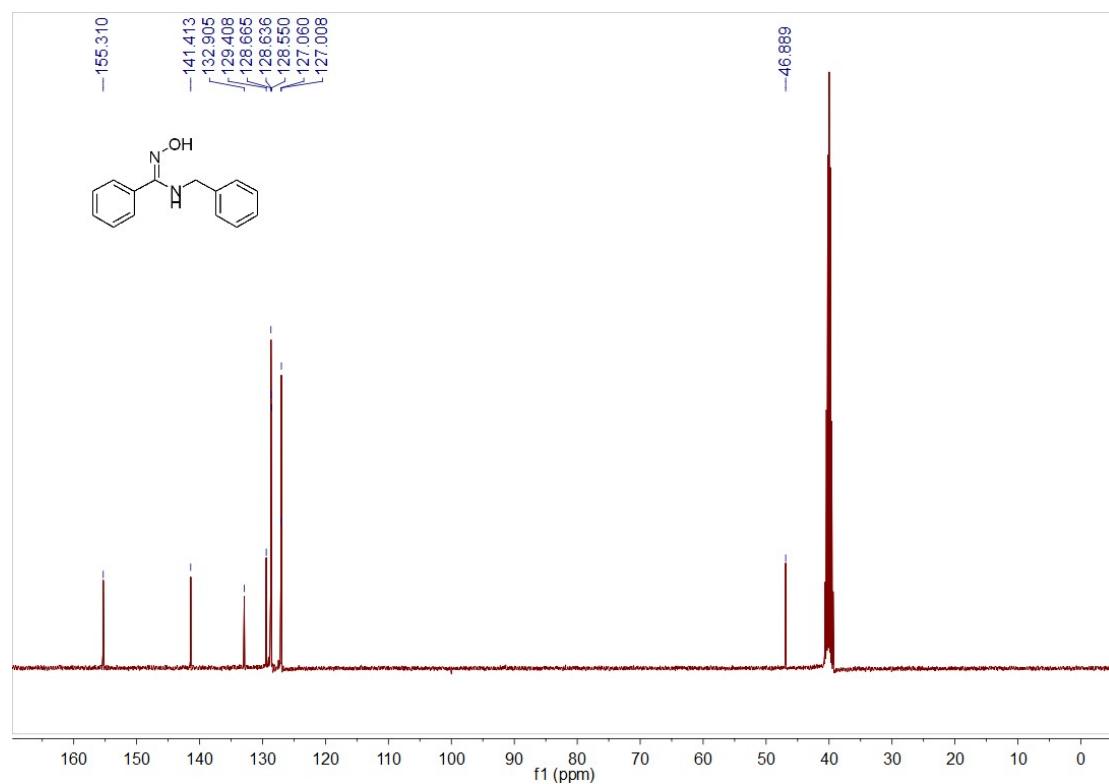
In an undivided cell equipped with two platinum electrodes, amidoxime **1a** (0.5 mmol, 0.113 g), BHT (2.0 mmol, 0.441 g), K<sub>3</sub>PO<sub>4</sub> (1.5 mmol, 0.318 g), Bu<sub>4</sub>NClO<sub>4</sub> (1 mmol, 0.342 g) were added to the MeOH (10 mL). The reaction mixture was stirred and electrolyzed at a constant voltage of 3 V for 2 h at 30°C. After the reaction was completed, the reaction mixture was evaporated and then diluted with H<sub>2</sub>O and extracted with dichloromethane (20 mL × 3). The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Subsequently, the solvent was removed under reduced pressure and the remaining crude product was purified by column chromatography over silica gel ( $V_{\text{PE}} : V_{\text{EtOAc}} = 16:1$ ) to afford 0.020 g of **2a**, yield 18.0%.

### 3. $^1\text{H}$ and $^{13}\text{C}$ NMR spectra for new compounds

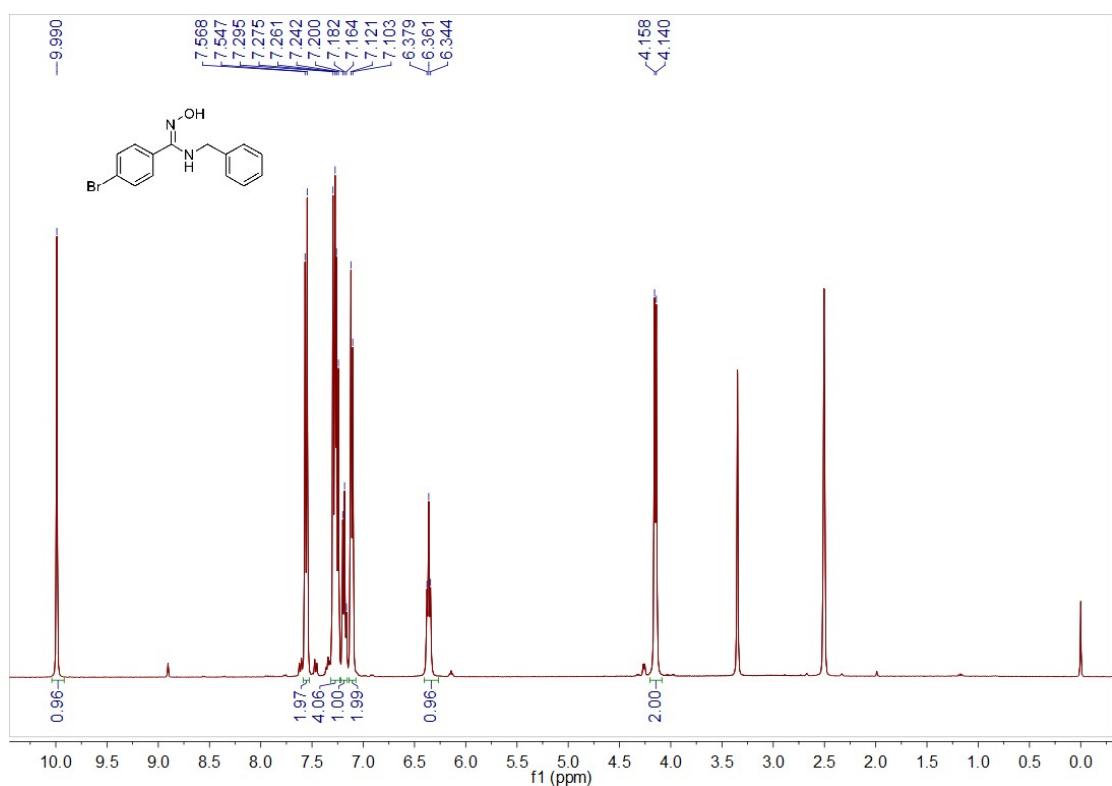
$^1\text{H}$  NMR spectrum of 1a (DMSO, 400 MHz):



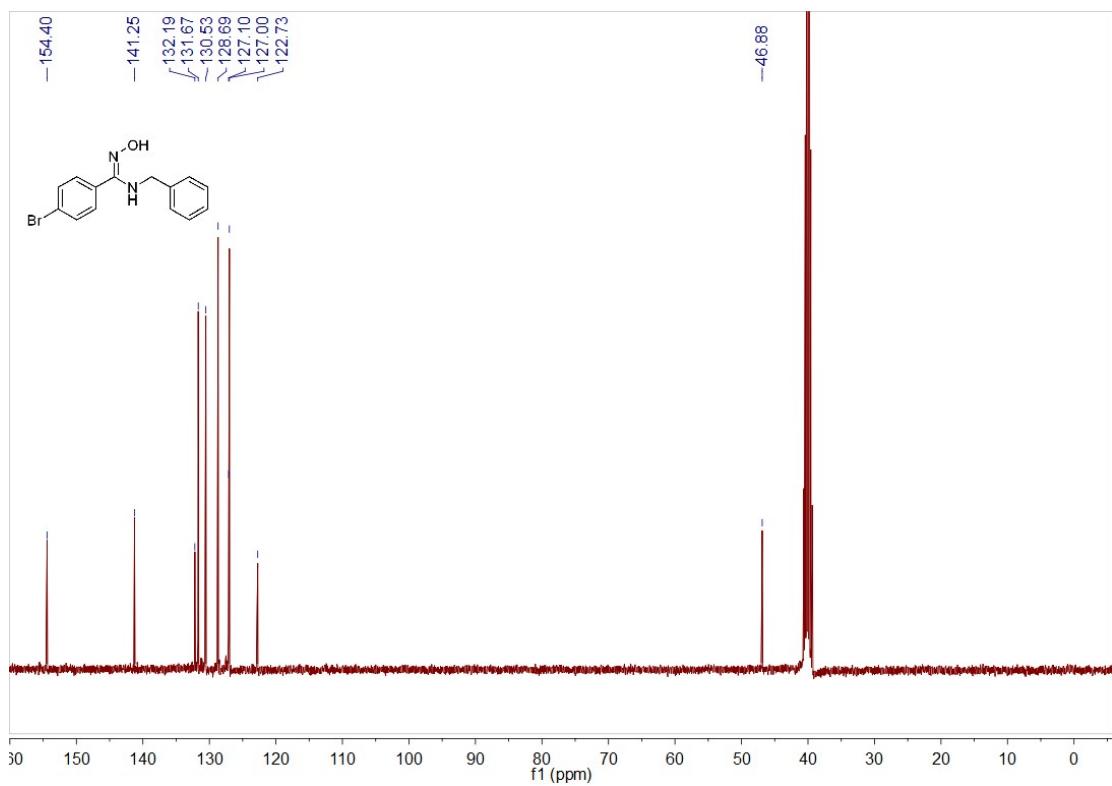
$^{13}\text{C}$  NMR spectrum of 1a (DMSO, 101 MHz):



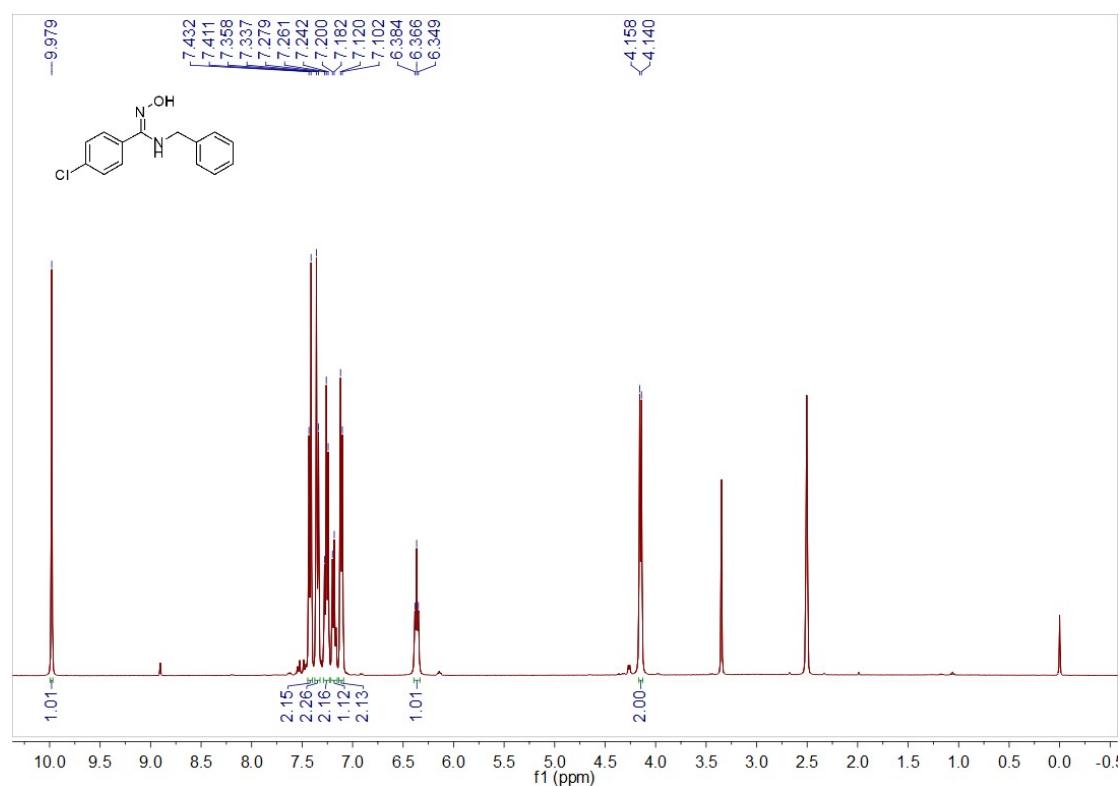
**<sup>1</sup>H NMR spectrum of 1b (DMSO, 400 MHz):**



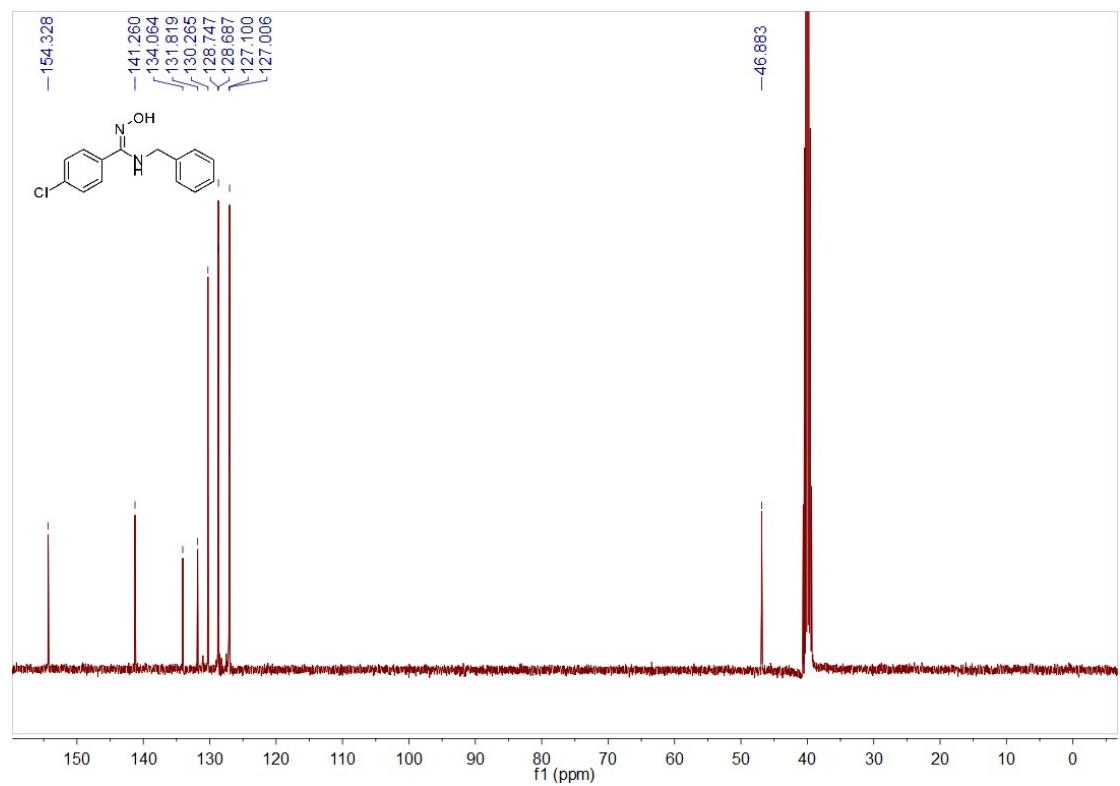
**<sup>13</sup>C NMR spectrum of 1b (DMSO-d<sub>6</sub>, 101 MHz):**



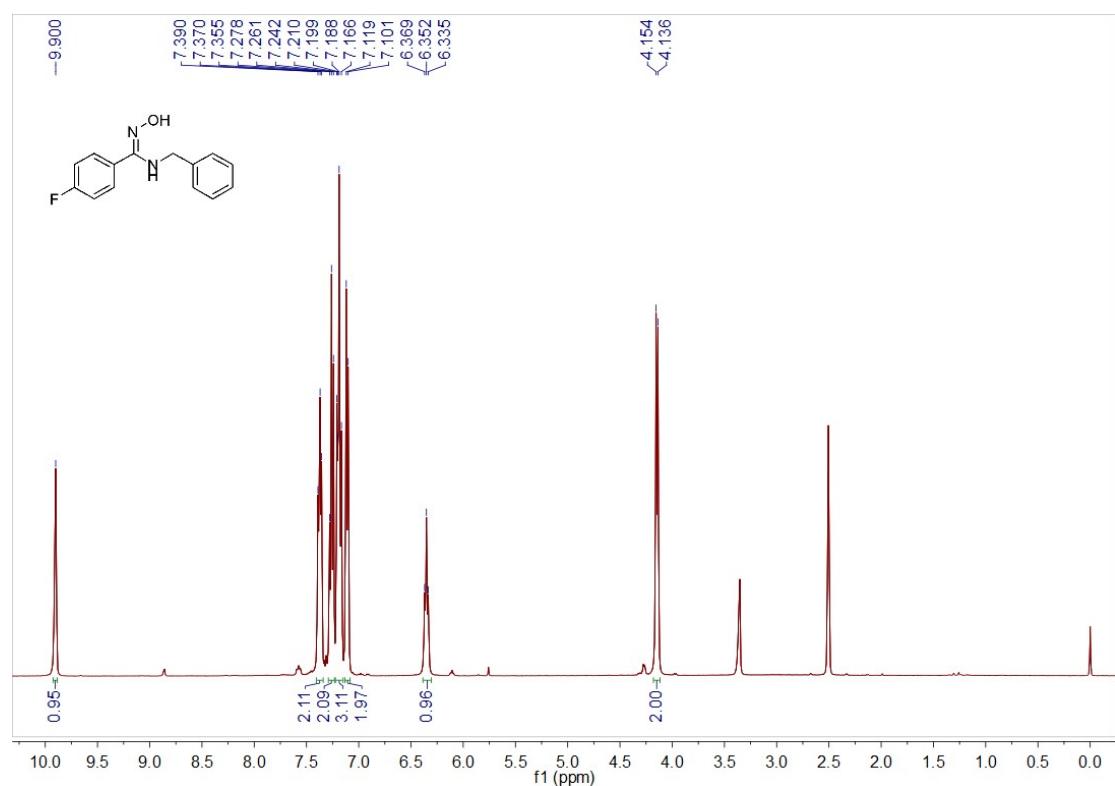
**<sup>1</sup>H NMR spectrum of 1c (DMSO-d<sub>6</sub>, 400 MHz):**



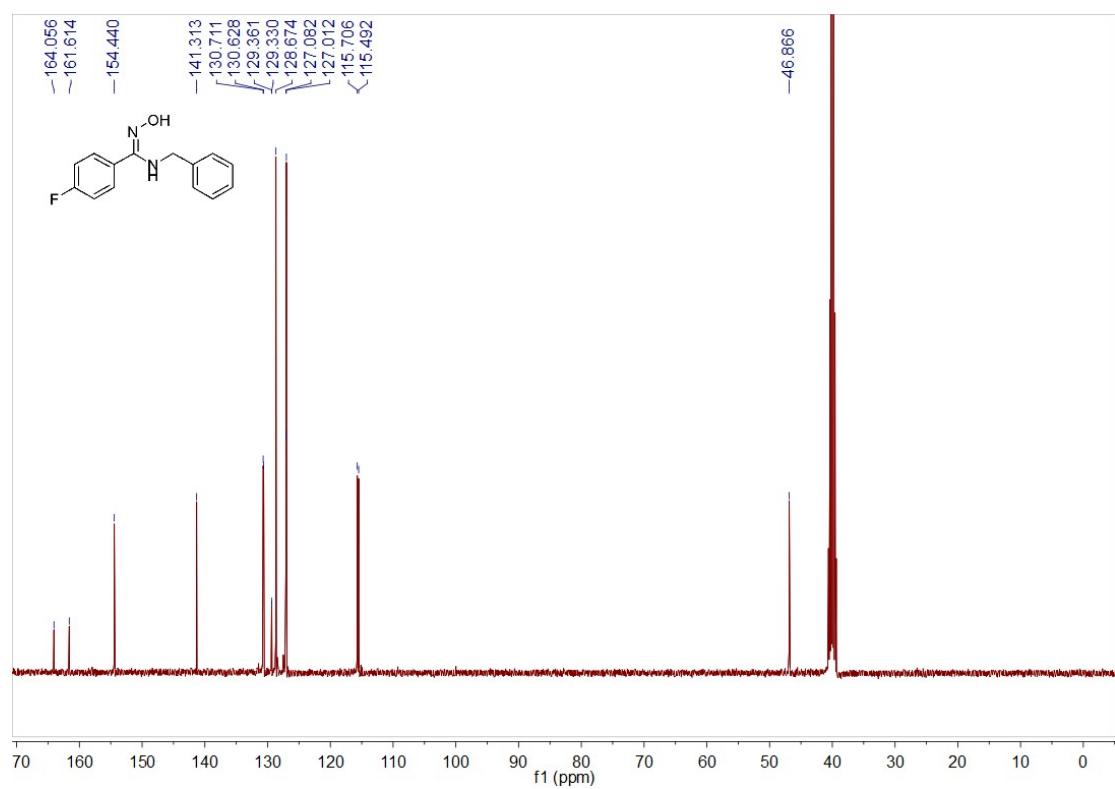
**<sup>13</sup>C NMR spectrum of 1c (DMSO-d<sub>6</sub>, 101 MHz):**



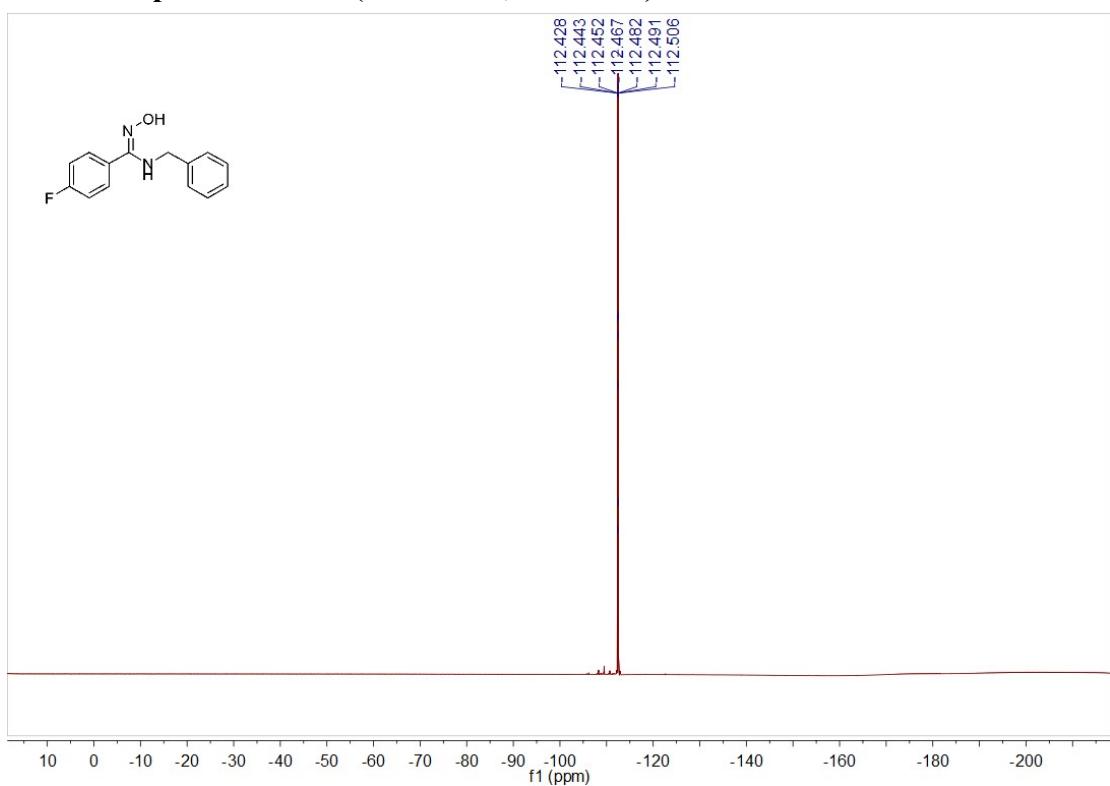
**<sup>1</sup>H NMR spectrum of 1d (DMSO-d<sub>6</sub>, 400 MHz):**



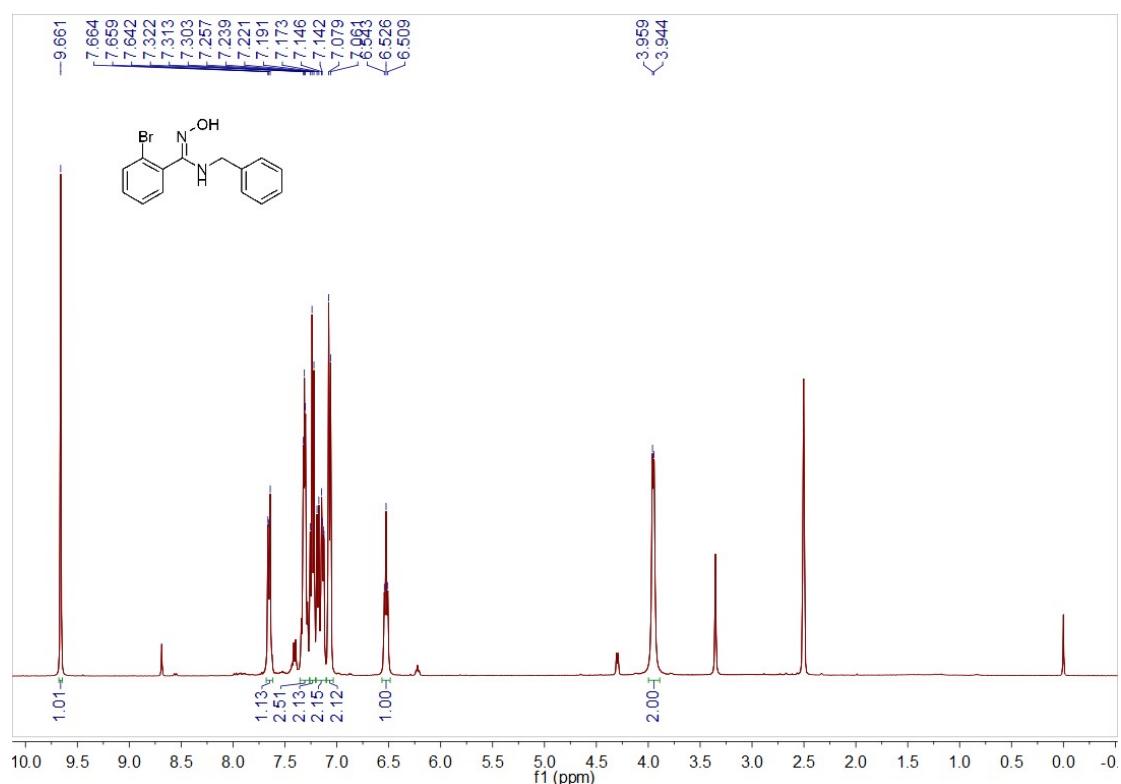
**<sup>13</sup>C NMR spectrum of 1d (DMSO-d<sub>6</sub>, 101 MHz):**



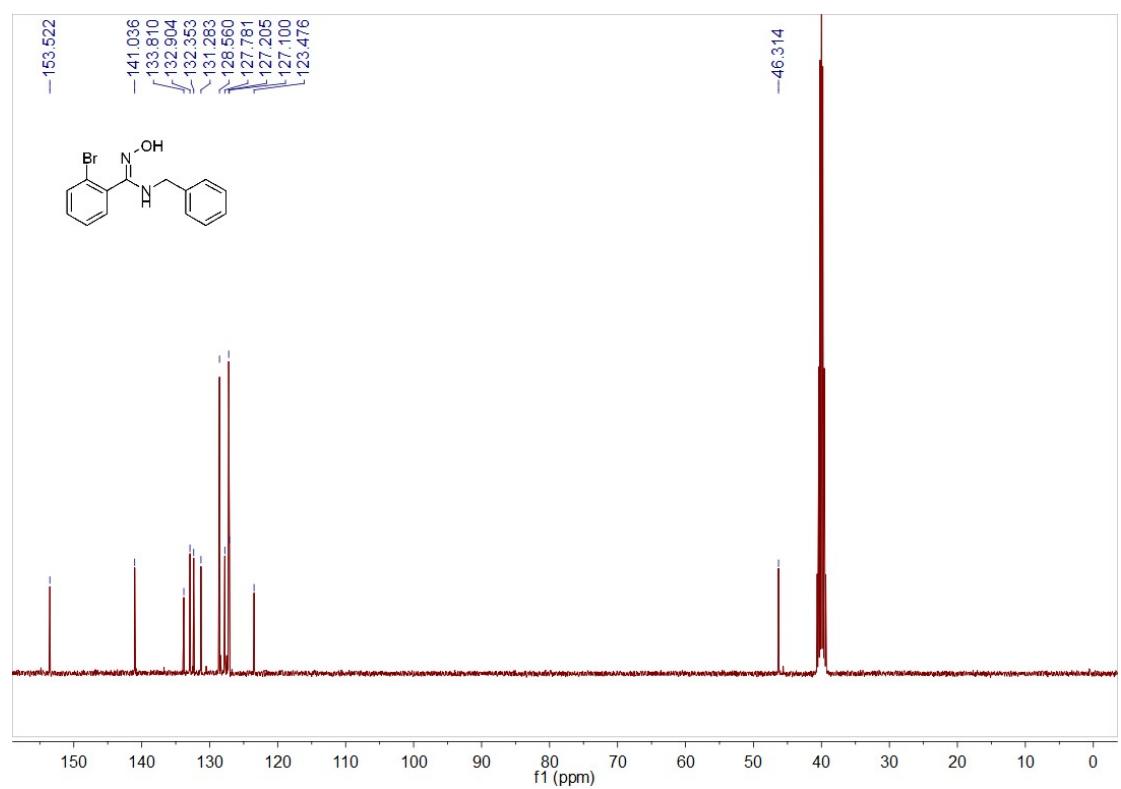
**<sup>19</sup>F NMR spectrum of 1d (DMSO-d6, 376 MHz):**



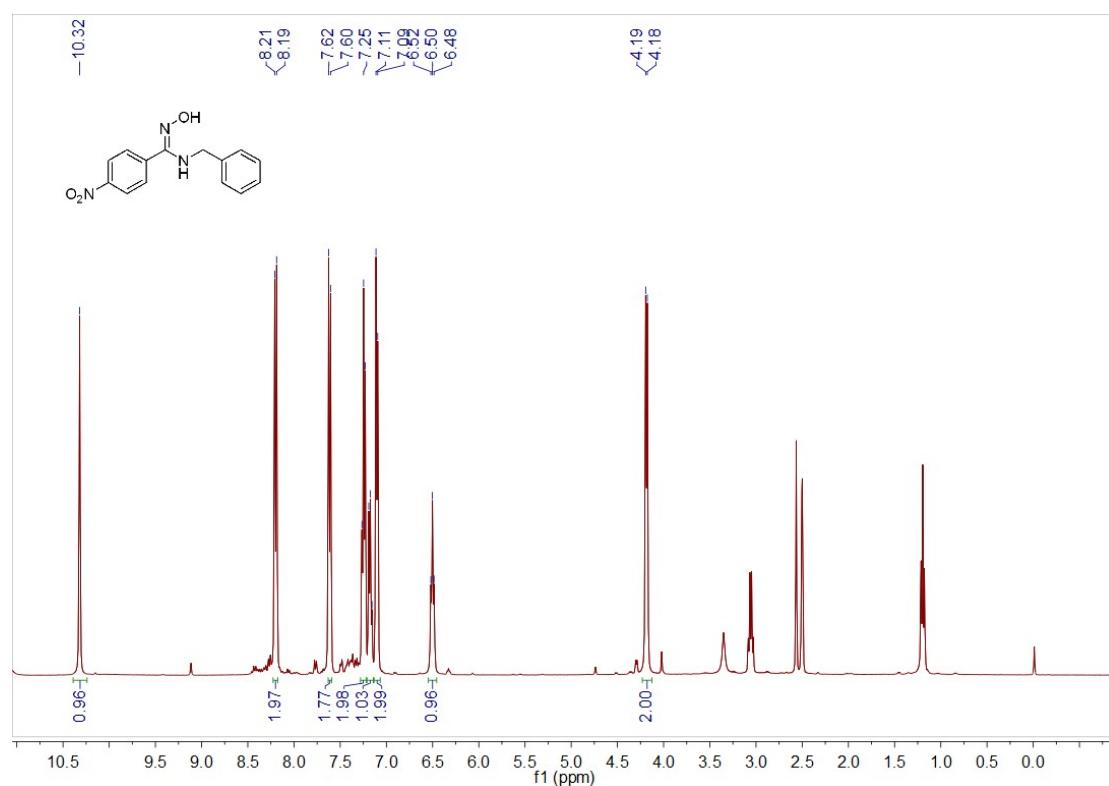
**<sup>1</sup>H NMR spectrum of 1e (DMSO-d<sub>6</sub>, 400 MHz):**



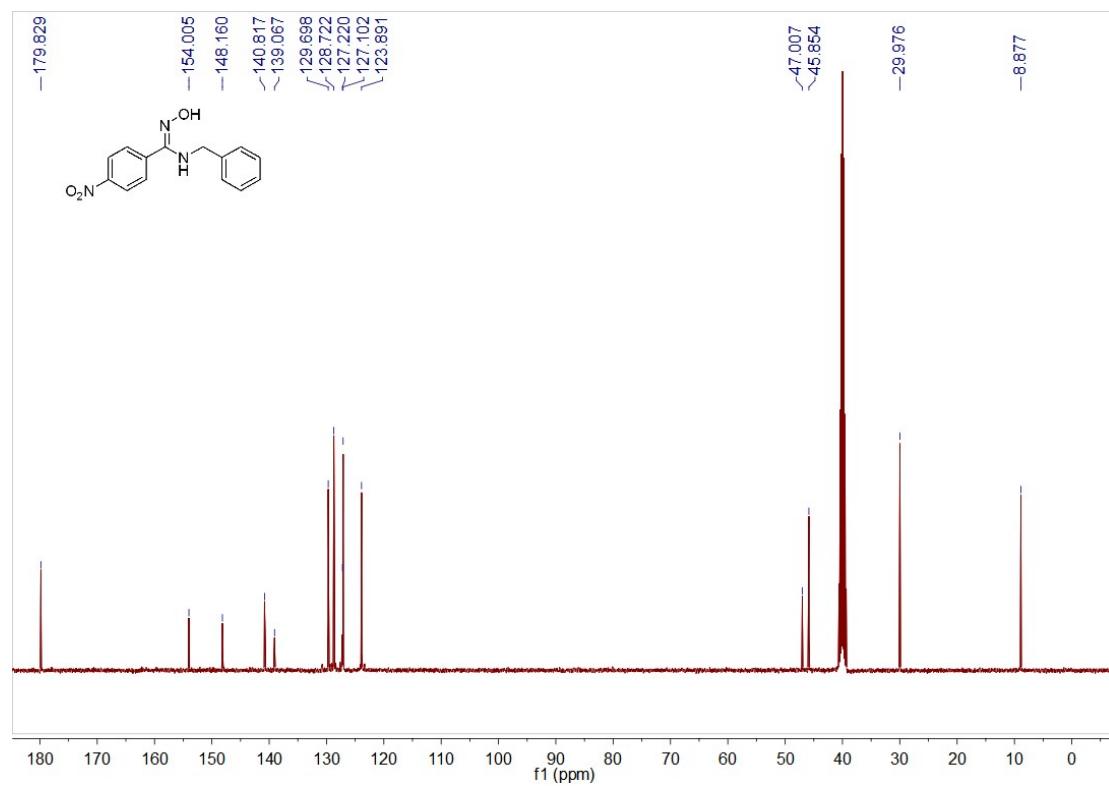
**<sup>13</sup>C NMR spectrum of 1e (DMSO-d<sub>6</sub>, 101 MHz):**



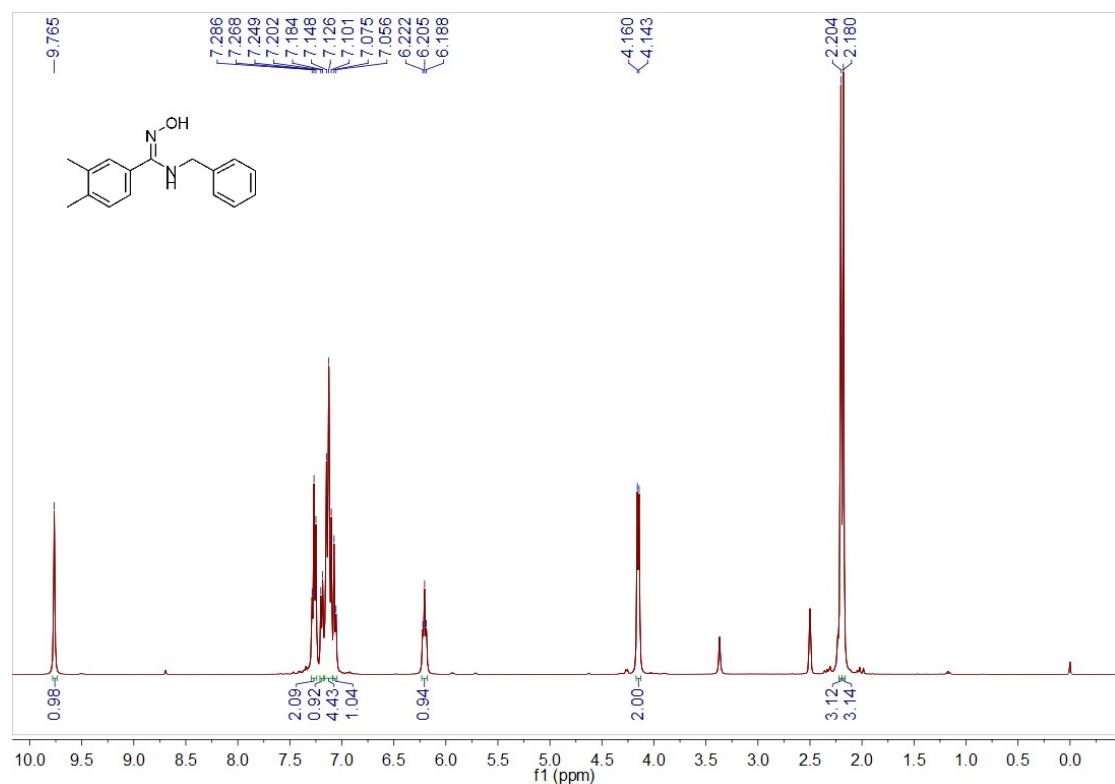
**<sup>1</sup>H NMR spectrum of 1f (DMSO-d<sub>6</sub>, 400 MHz):**



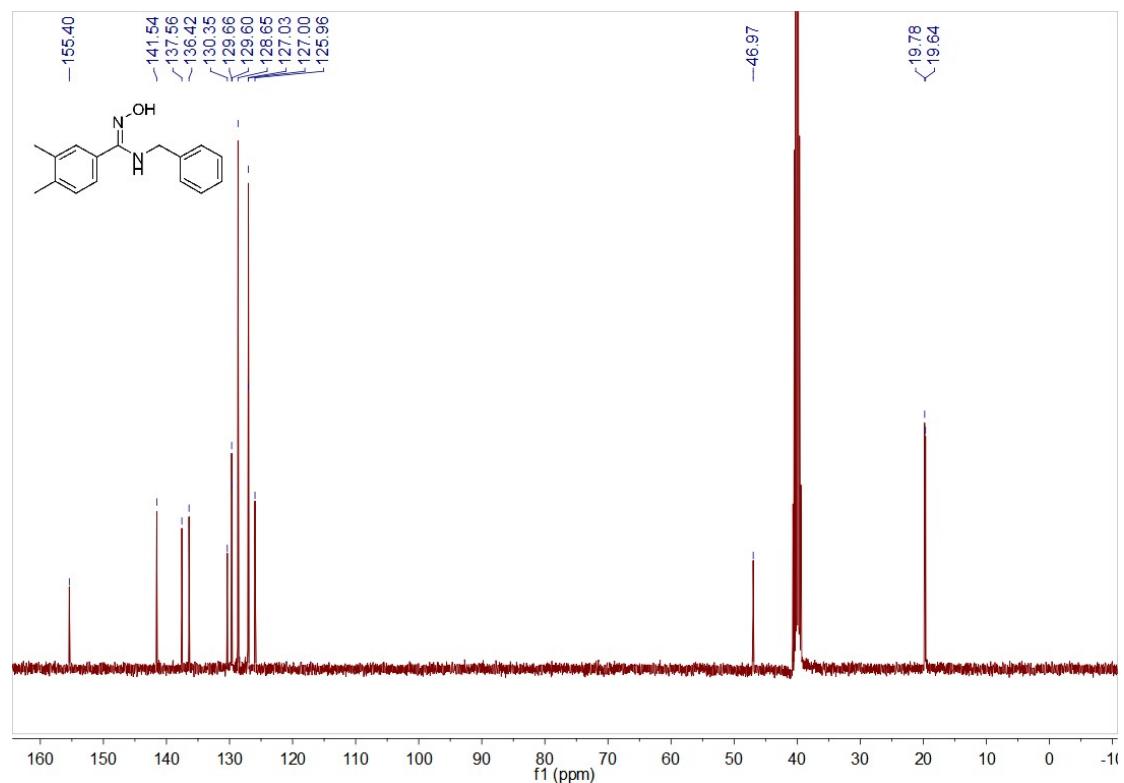
**<sup>13</sup>C NMR spectrum of 1f (DMSO-d<sub>6</sub>, 101 MHz):**



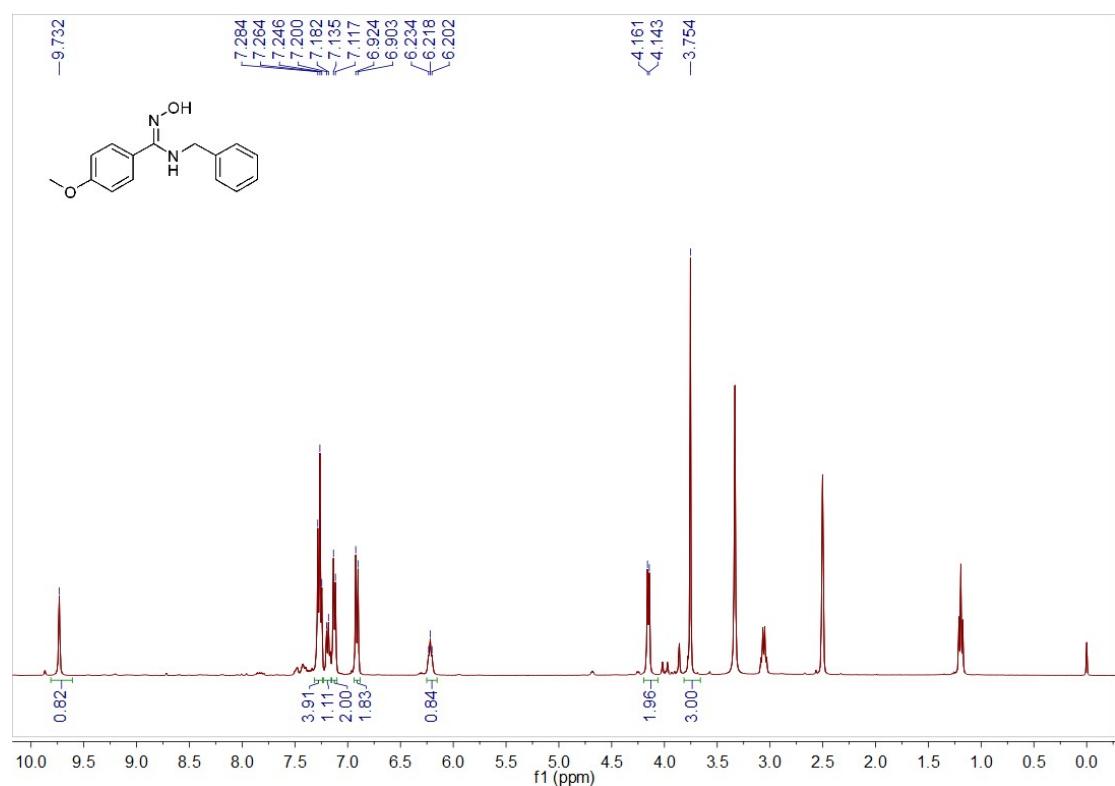
**<sup>1</sup>H NMR spectrum of 1g (DMSO-d<sub>6</sub>, 400 MHz):**



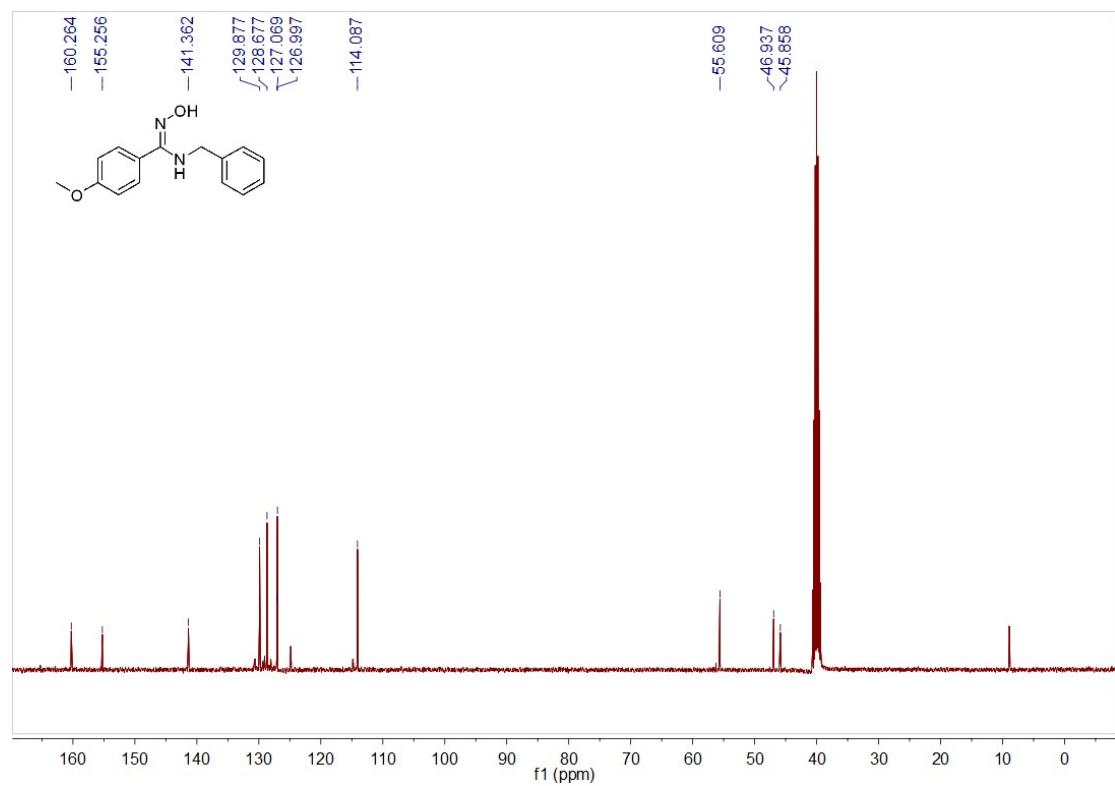
**<sup>13</sup>C NMR spectrum of 1g (DMSO-d<sub>6</sub>, 101 MHz):**



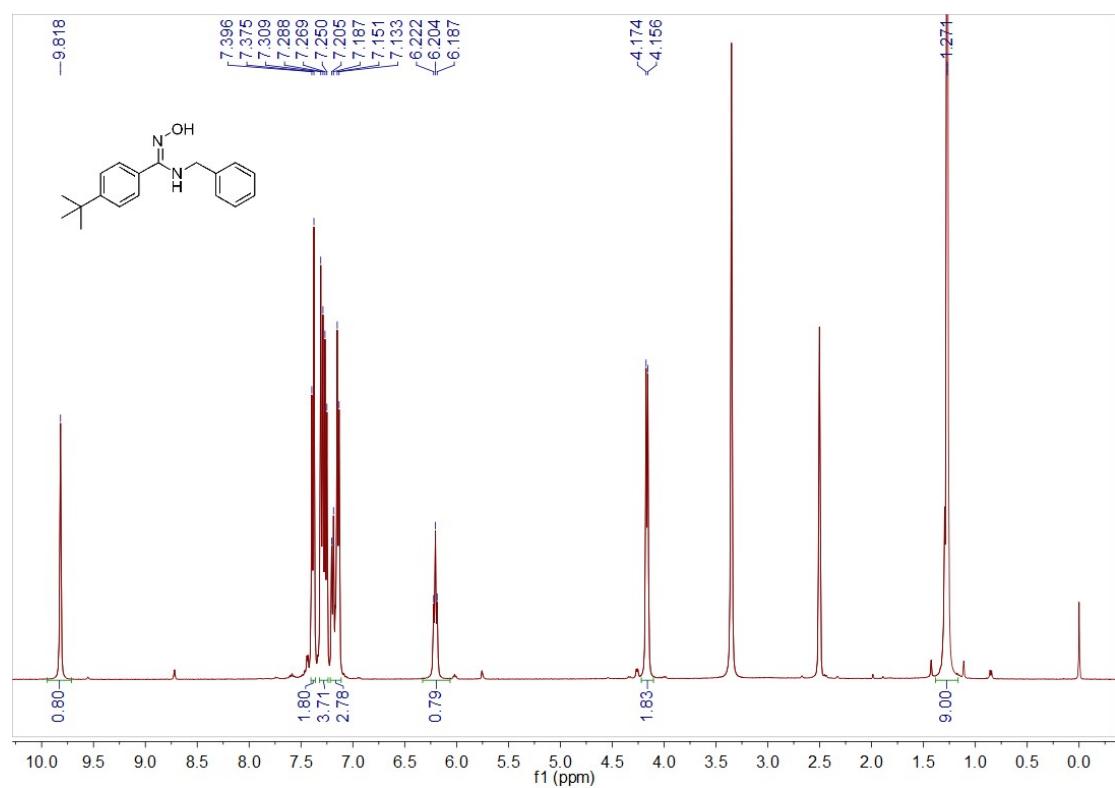
**<sup>1</sup>H NMR spectrum of 1h (DMSO-d<sub>6</sub>, 400 MHz):**



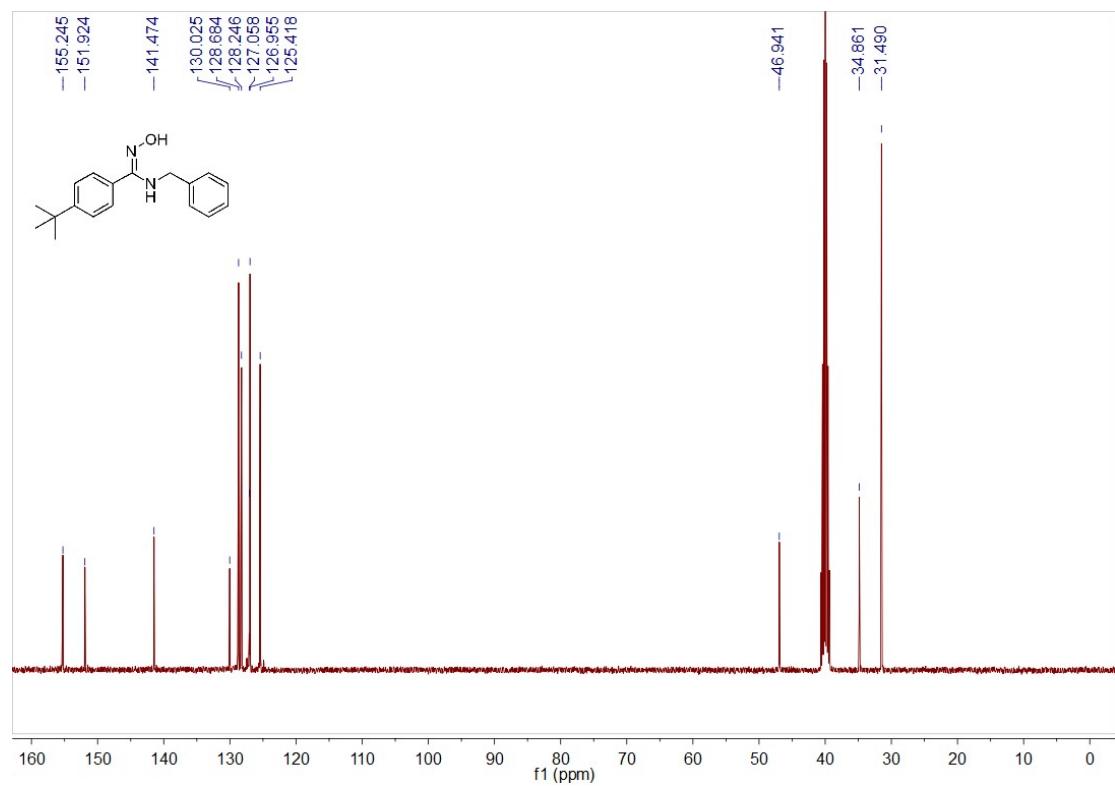
**<sup>13</sup>C NMR spectrum of 1h (DMSO-d<sub>6</sub>, 101 MHz):**



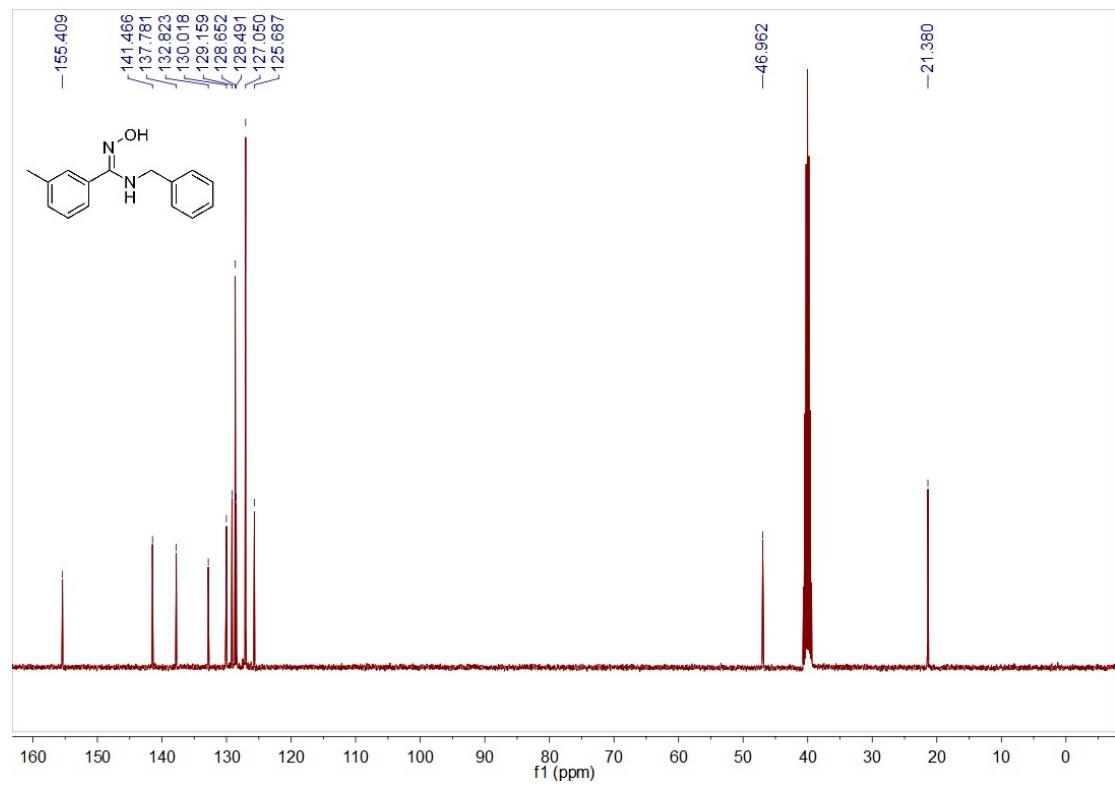
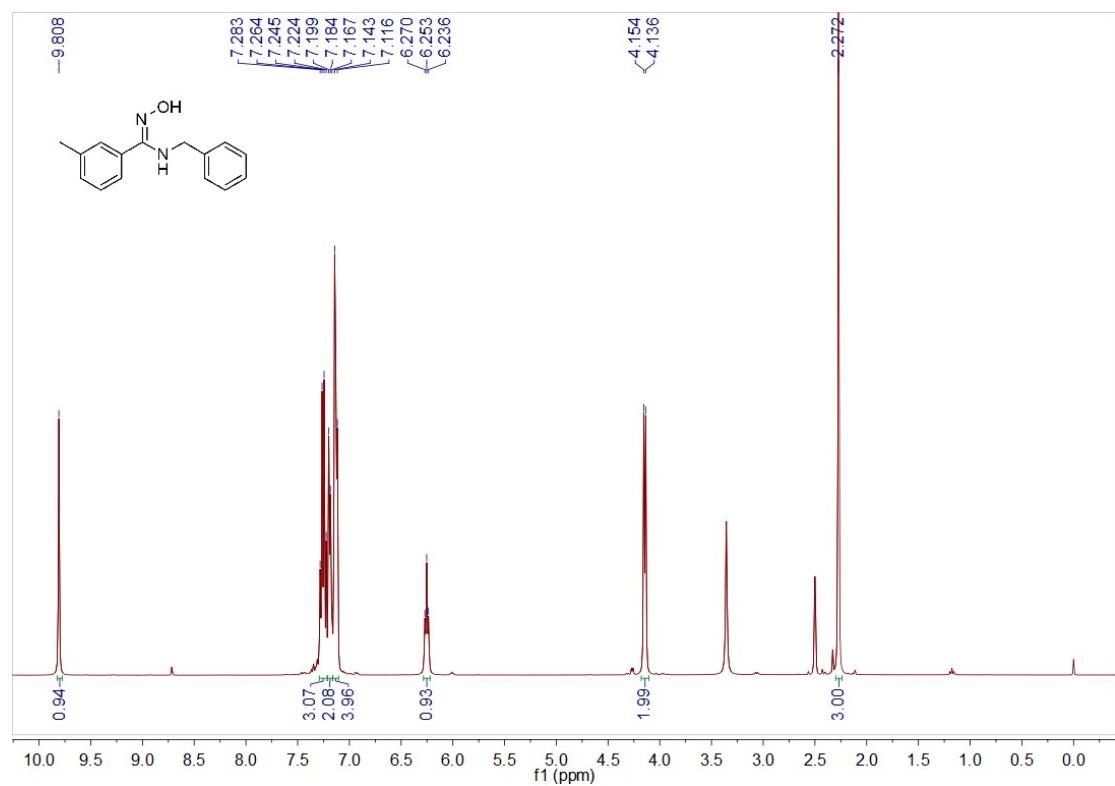
**<sup>1</sup>H NMR spectrum of 1i (DMSO-d<sub>6</sub>, 400 MHz):**



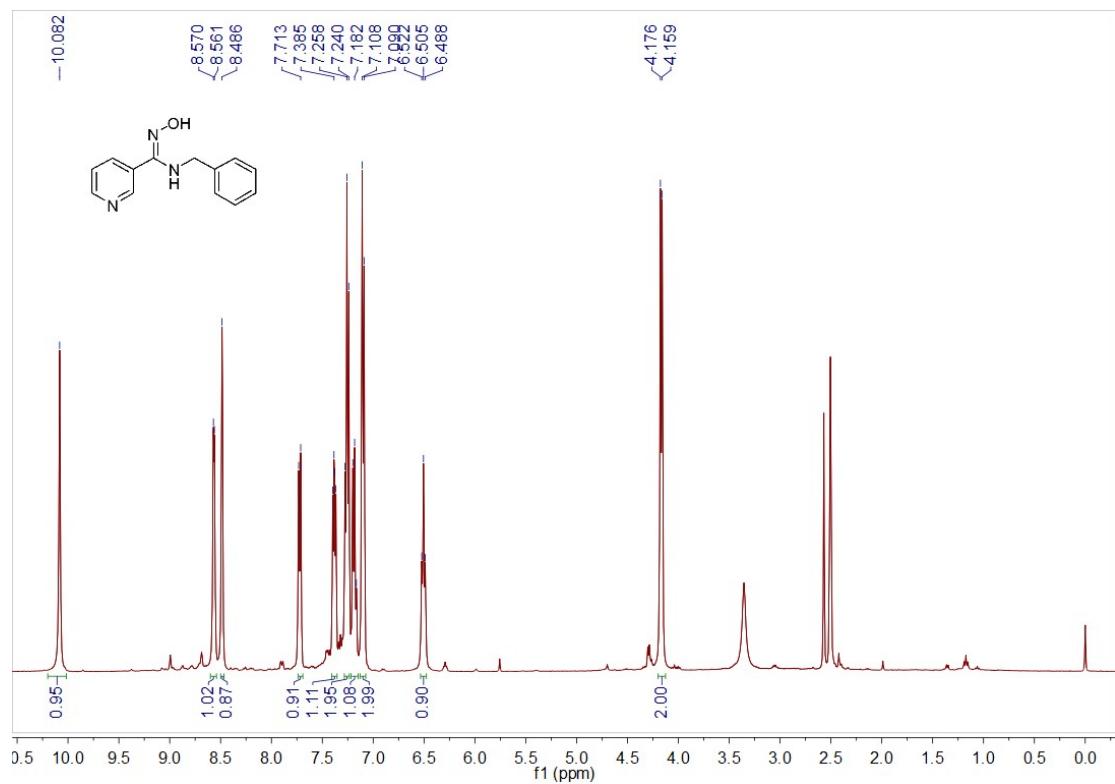
**<sup>13</sup>C NMR spectrum of 1i (DMSO-d<sub>6</sub>, 101 MHz):**



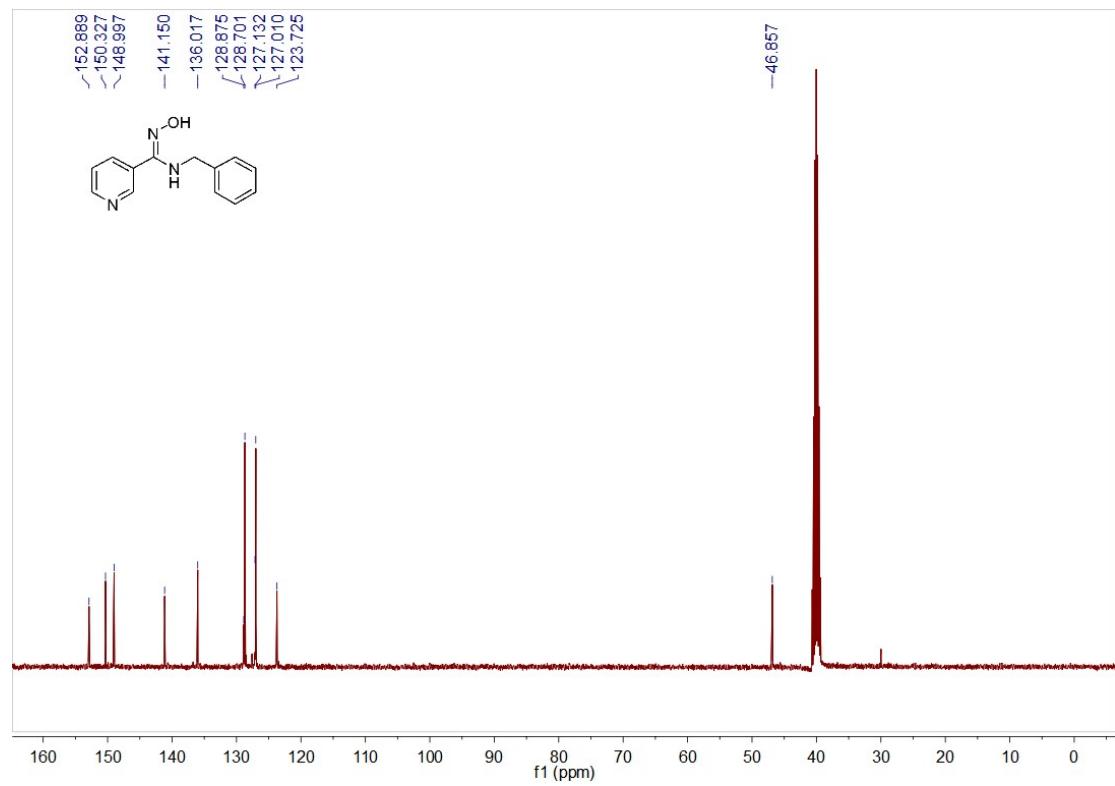
**<sup>1</sup>H NMR spectrum of 1j (DMSO-d<sub>6</sub>, 400 MHz):**



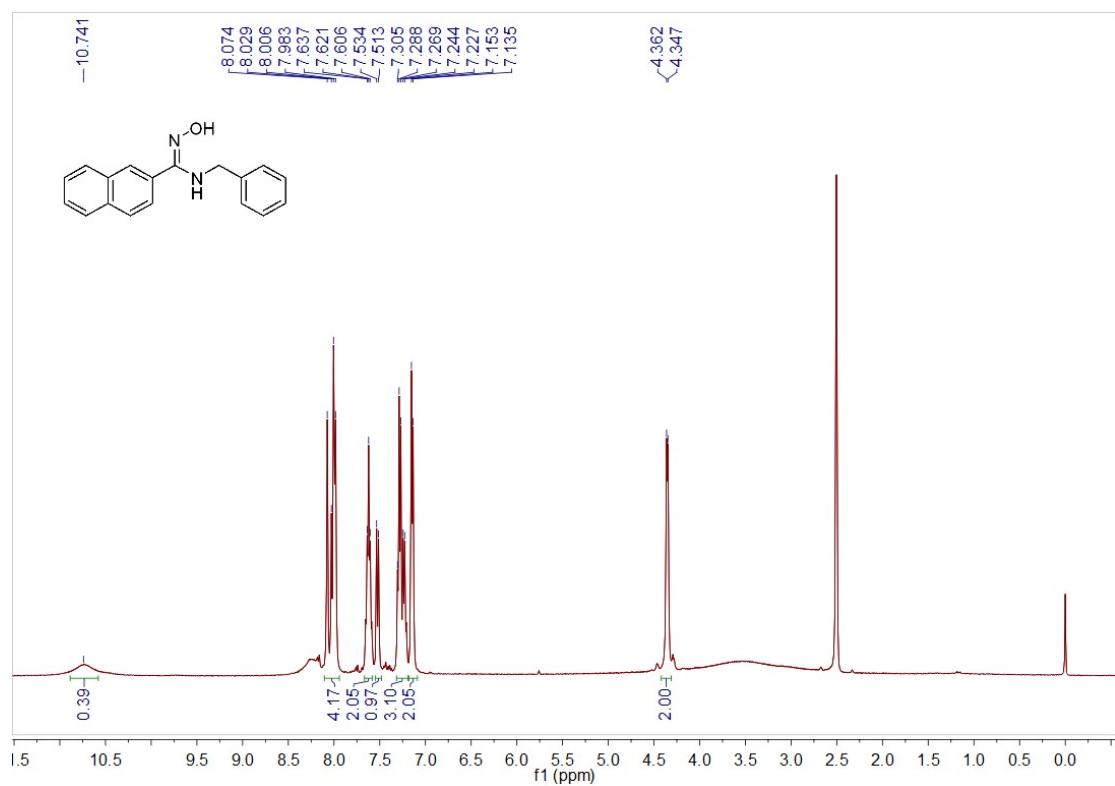
**<sup>1</sup>H NMR spectrum of 1k (DMSO-d<sub>6</sub>, 400 MHz):**



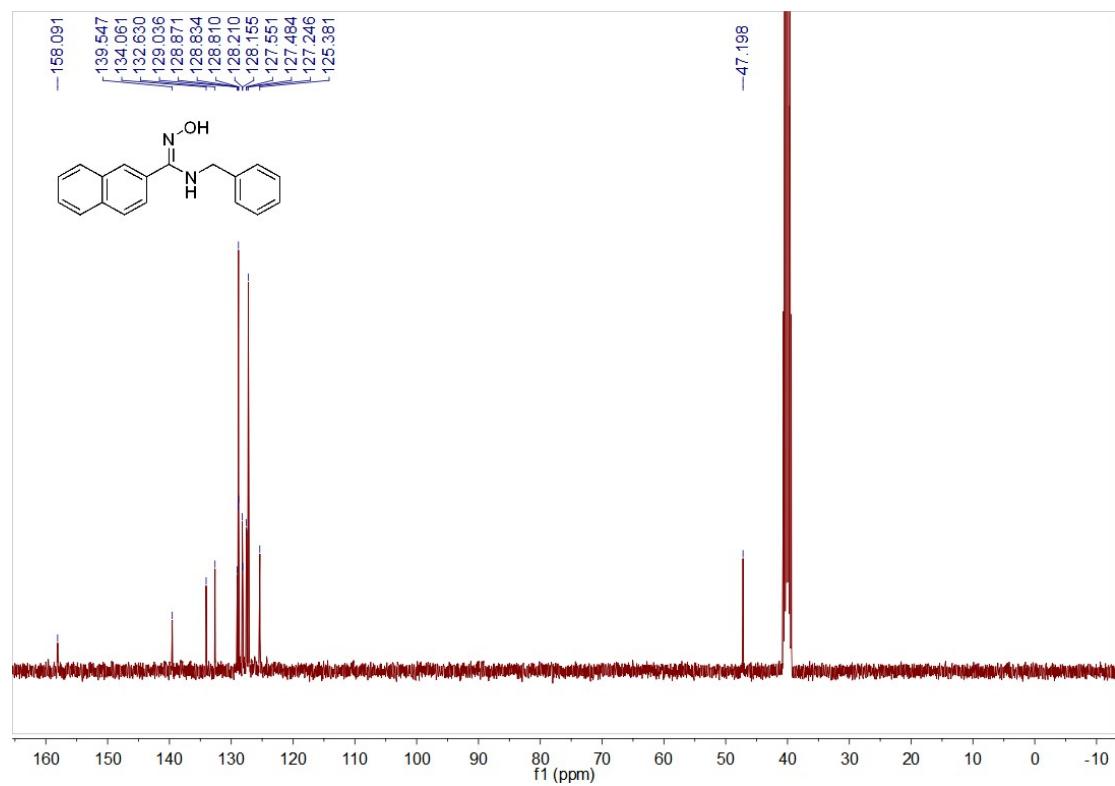
**<sup>13</sup>C NMR spectrum of 1j (DMSO-d<sub>6</sub>, 101 MHz):**



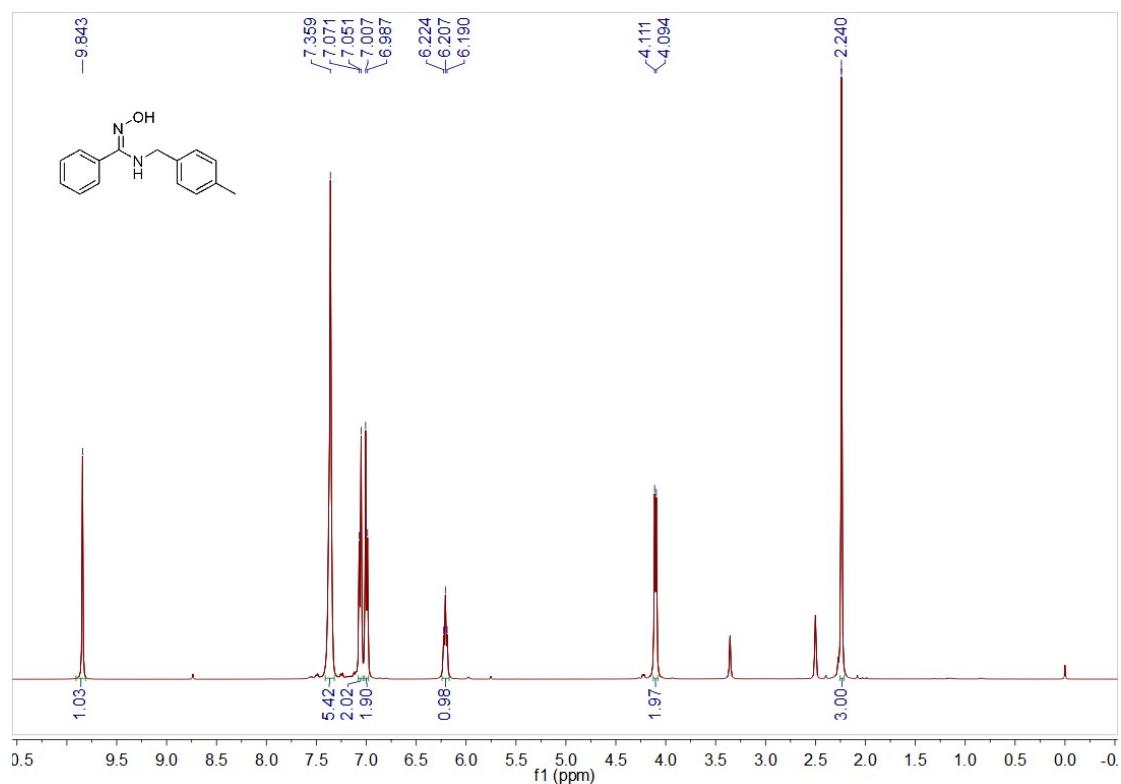
**<sup>1</sup>H NMR spectrum of 11 (DMSO-d<sub>6</sub>, 400 MHz):**



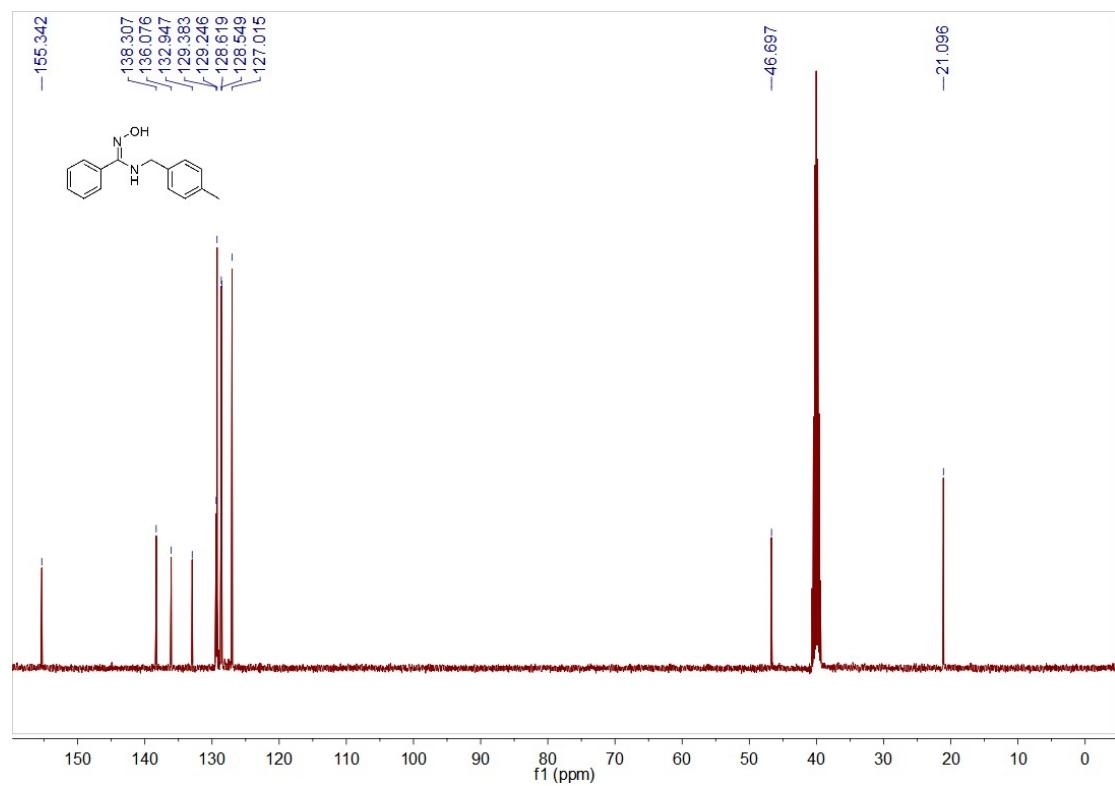
**<sup>13</sup>C NMR spectrum of 11 (DMSO-d<sub>6</sub>, 101 MHz):**



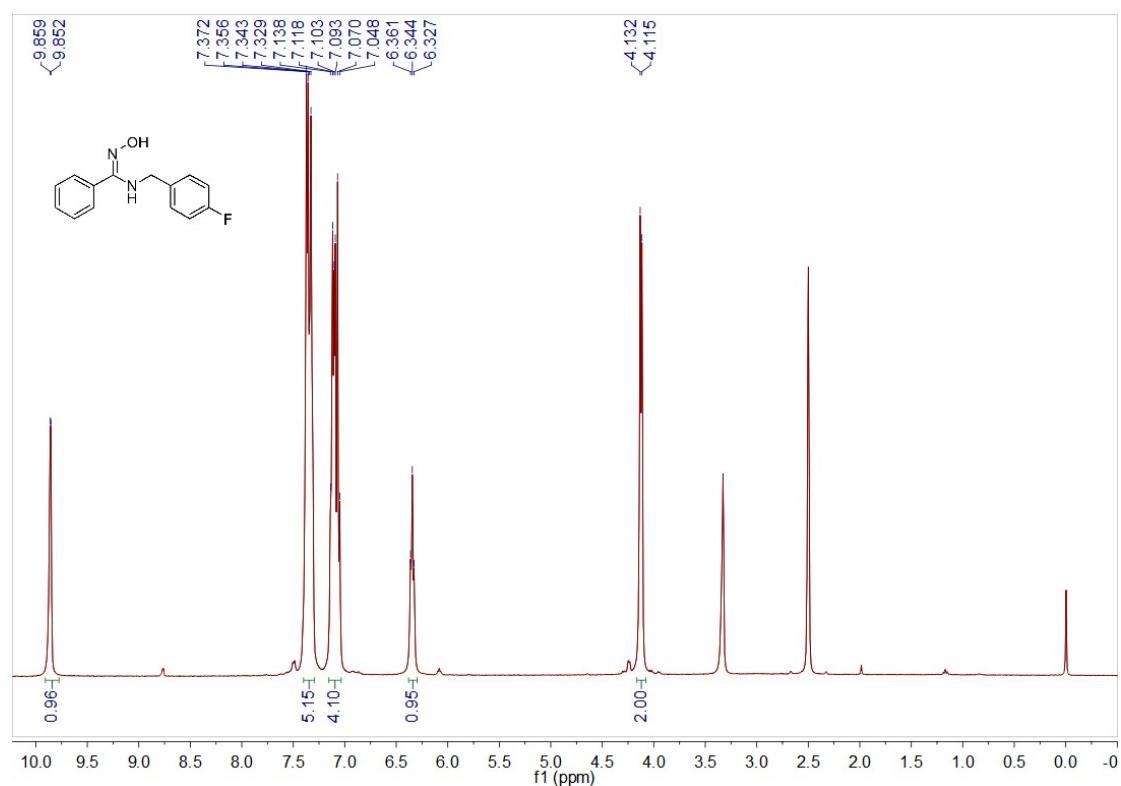
**<sup>1</sup>H NMR spectrum of 1m (DMSO-d6, 400 MHz):**



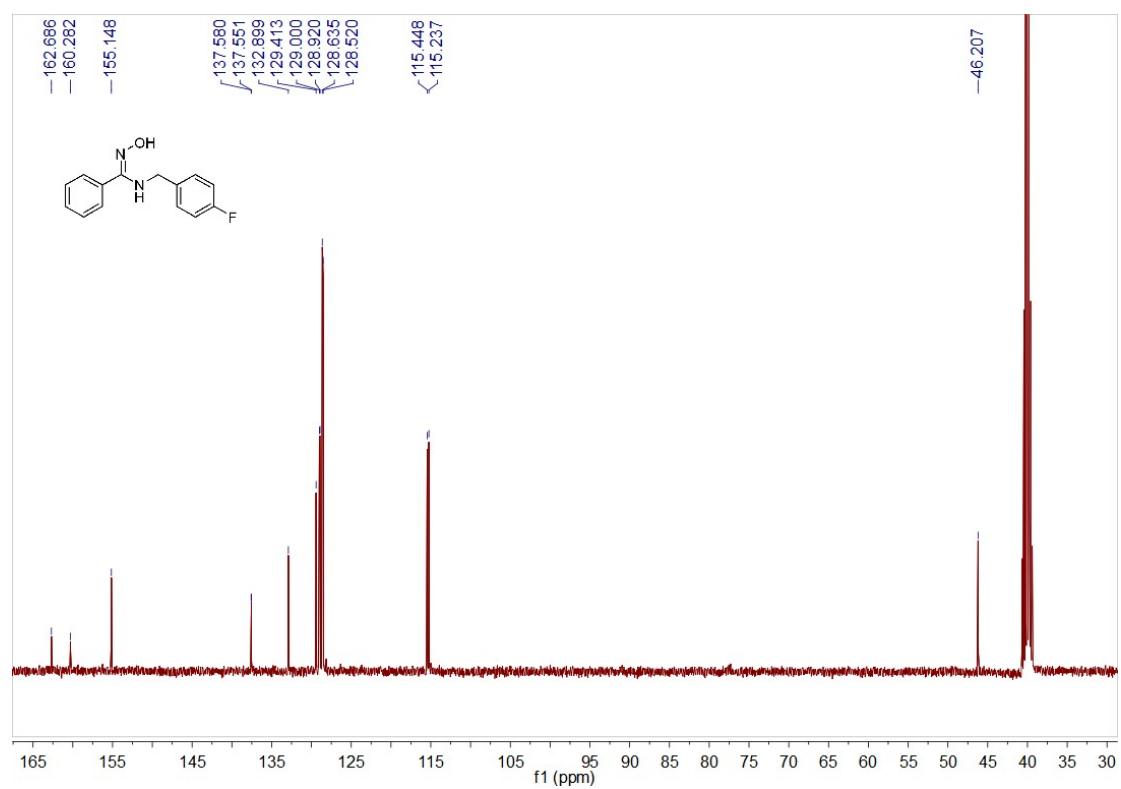
**<sup>13</sup>C NMR spectrum of 1m (DMSO-d6, 101 MHz):**



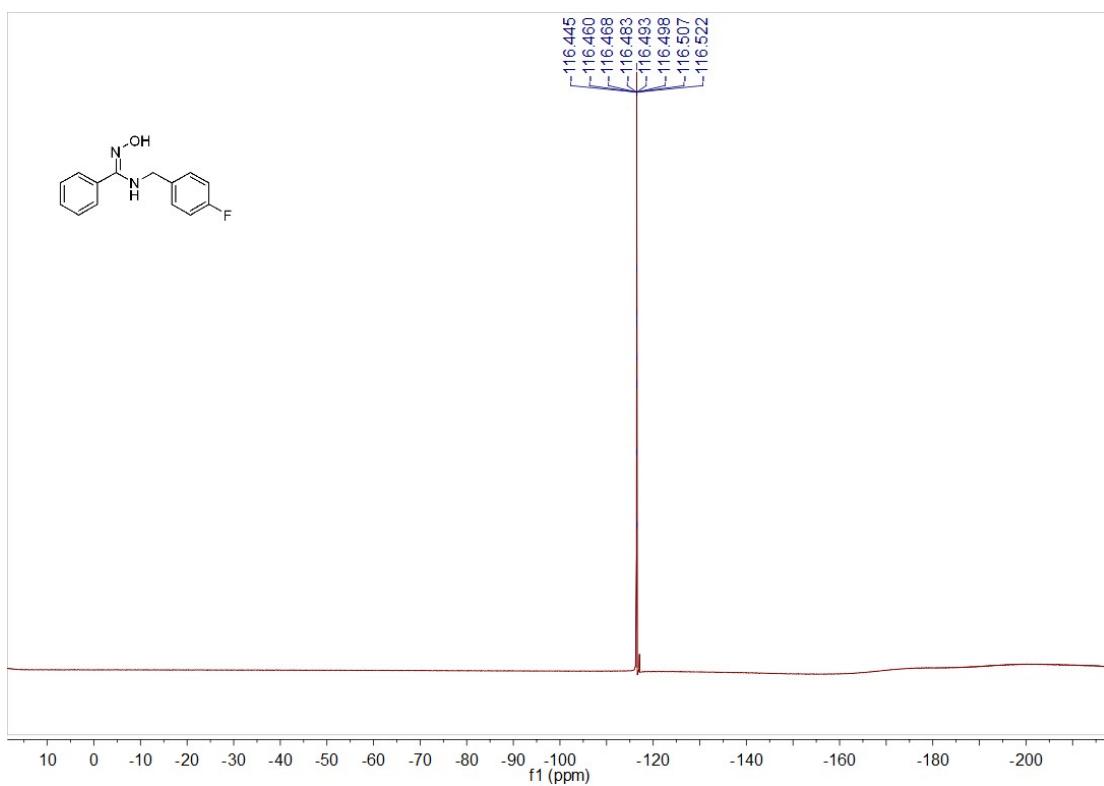
**<sup>1</sup>H NMR spectrum of 1n (DMSO-d<sub>6</sub>, 400 MHz):**



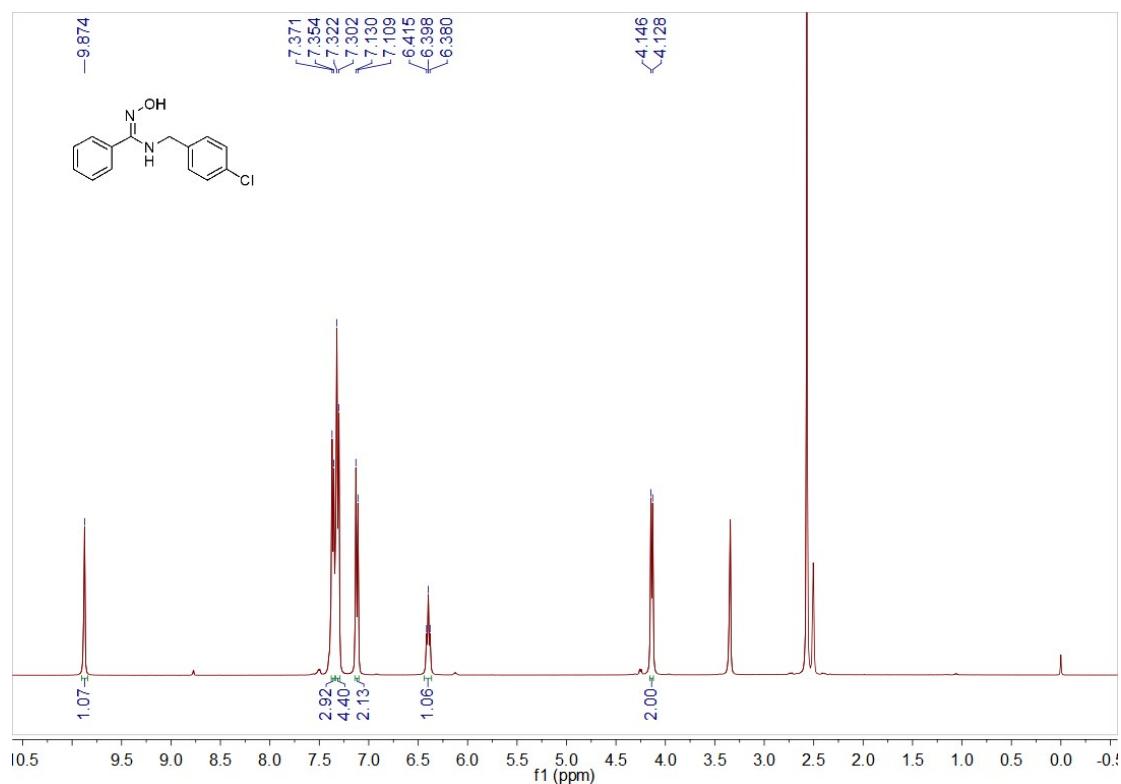
**<sup>13</sup>C NMR spectrum of 1n (DMSO-d<sub>6</sub>, 101 MHz):**



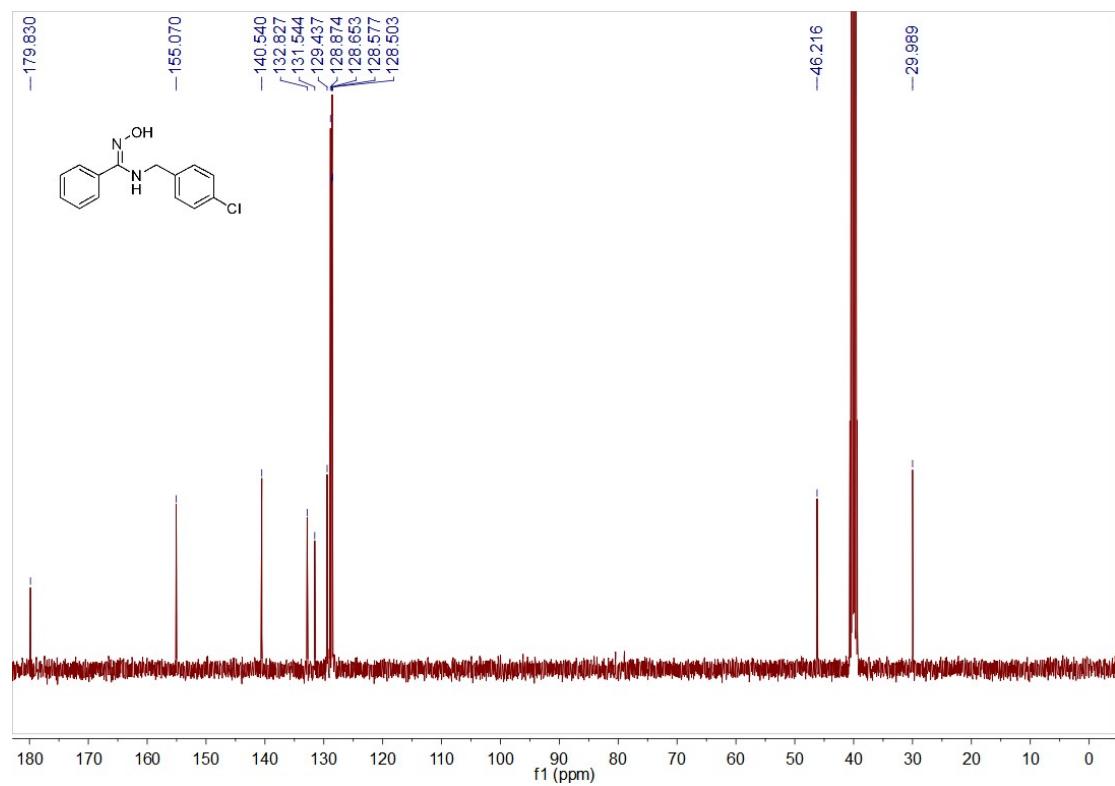
**<sup>19</sup>F NMR spectrum of 1n (DMSO-d<sub>6</sub>, 376 MHz):**



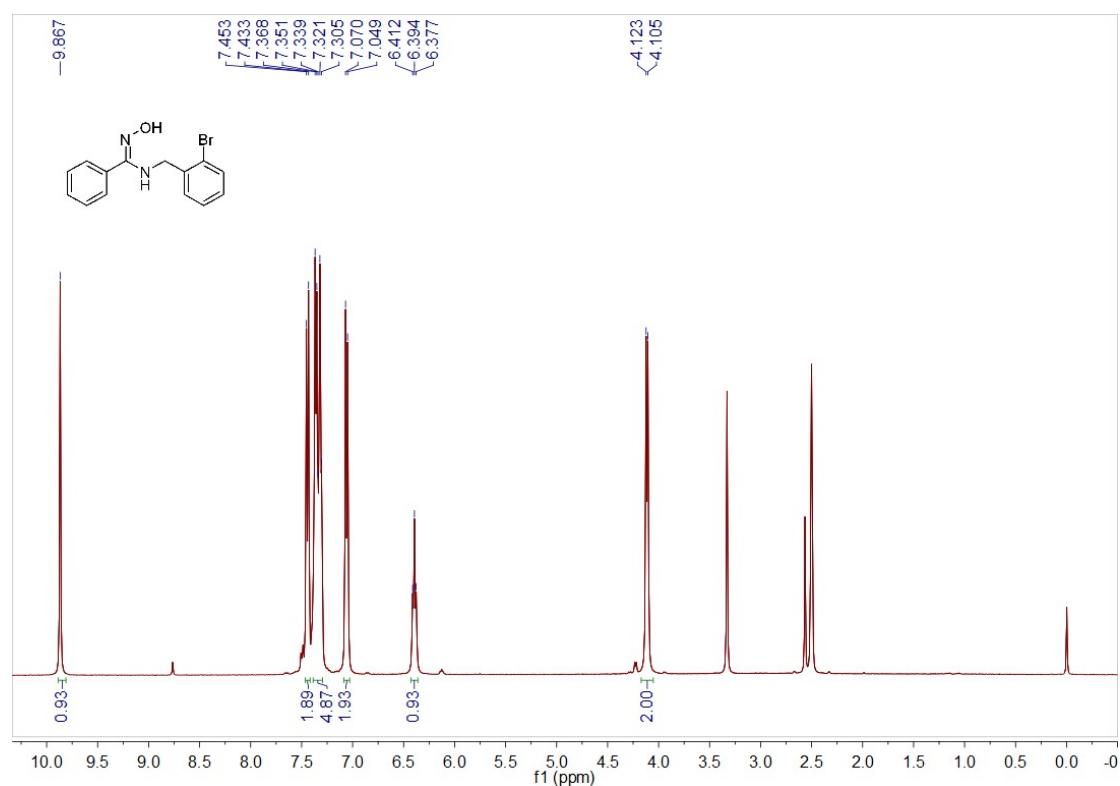
**<sup>1</sup>H NMR spectrum of 1o (DMSO-d<sub>6</sub>, 400 MHz):**



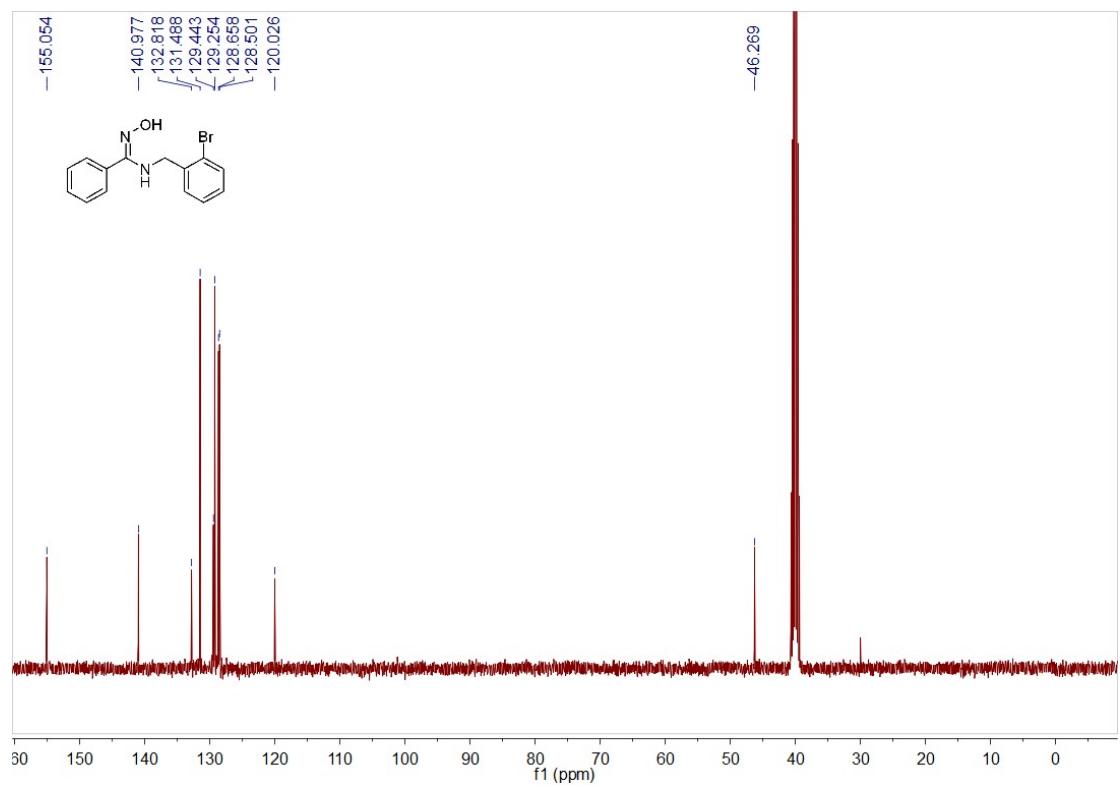
**<sup>13</sup>C NMR spectrum of 1o (DMSO-d<sub>6</sub>, 101 MHz):**



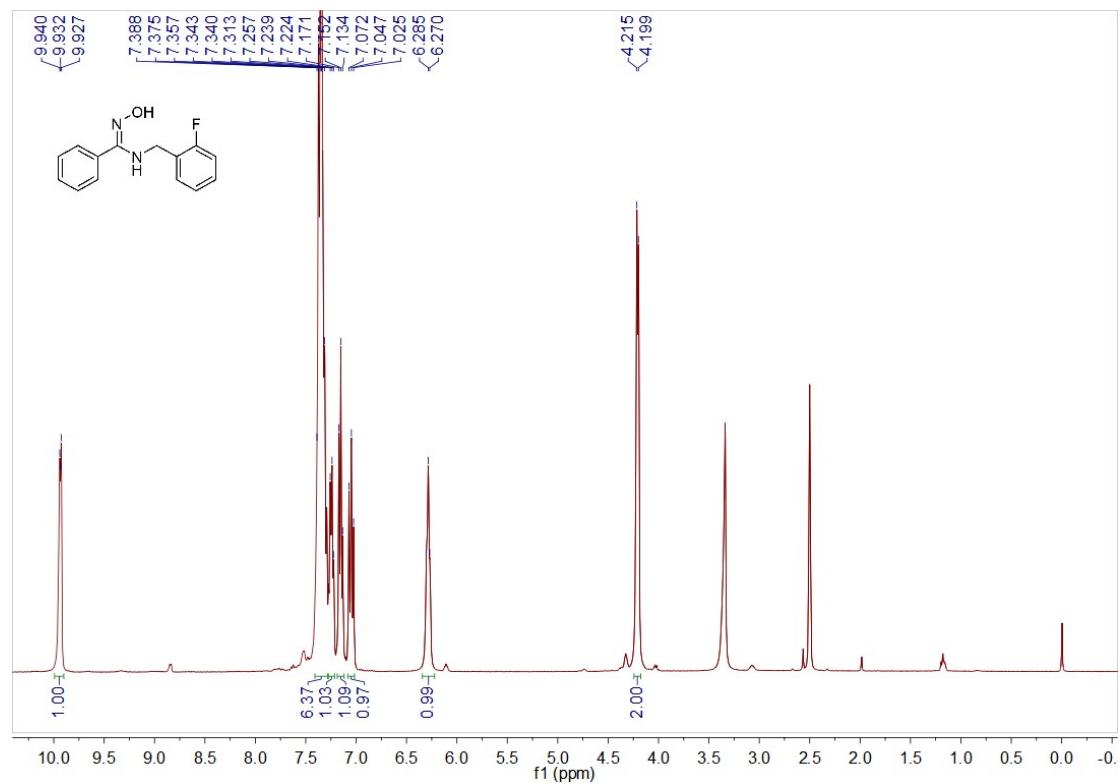
**<sup>1</sup>H NMR spectrum of 1p (DMSO-d<sub>6</sub>, 400 MHz):**



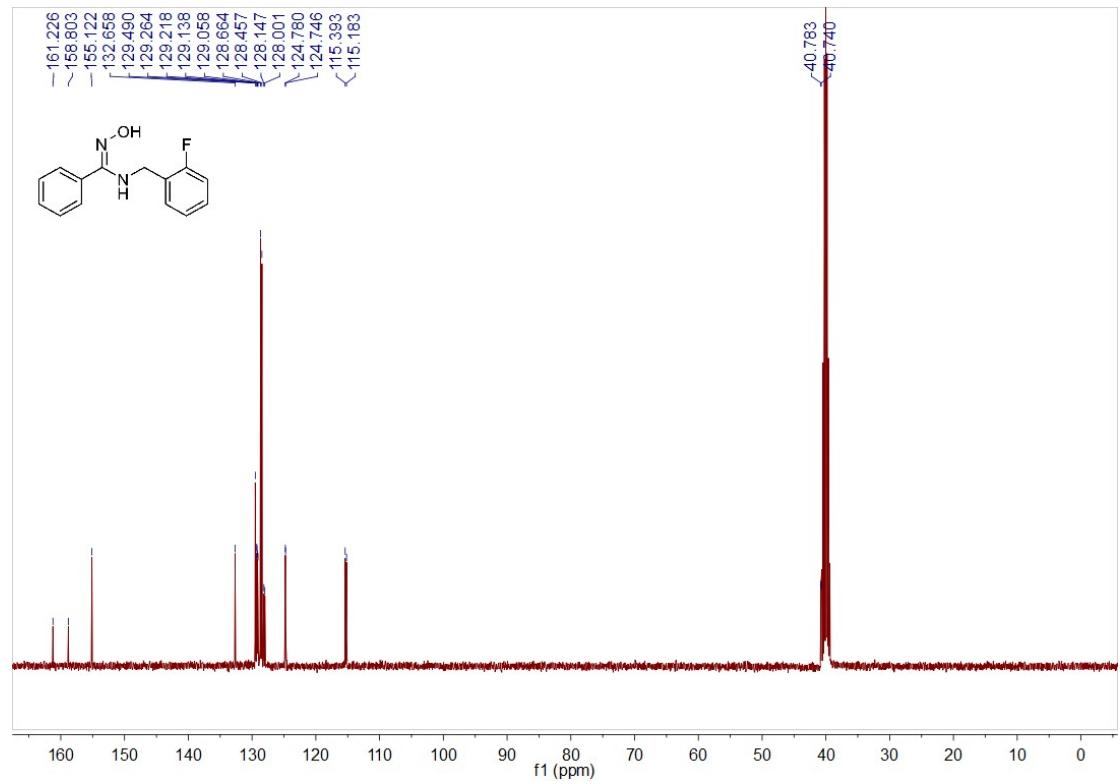
**<sup>13</sup>C NMR spectrum of 1p (DMSO-d<sub>6</sub>, 101 MHz):**



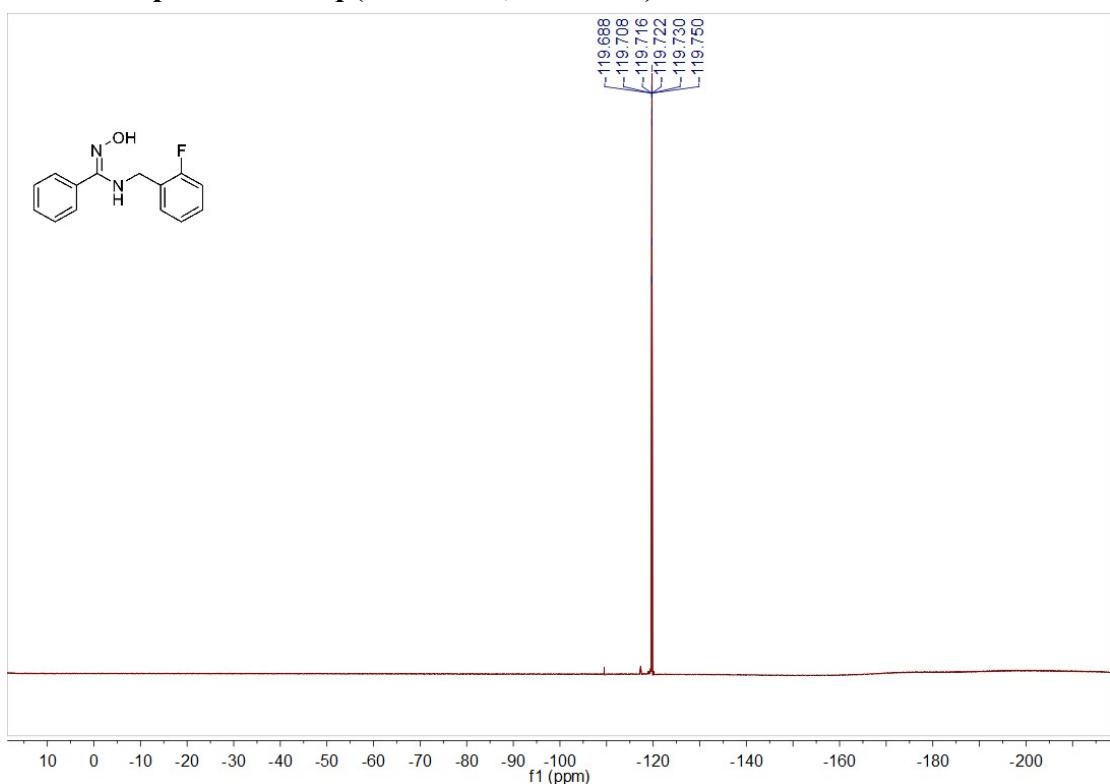
**<sup>1</sup>H NMR spectrum of 1q (DMSO-d<sub>6</sub>, 400 MHz):**



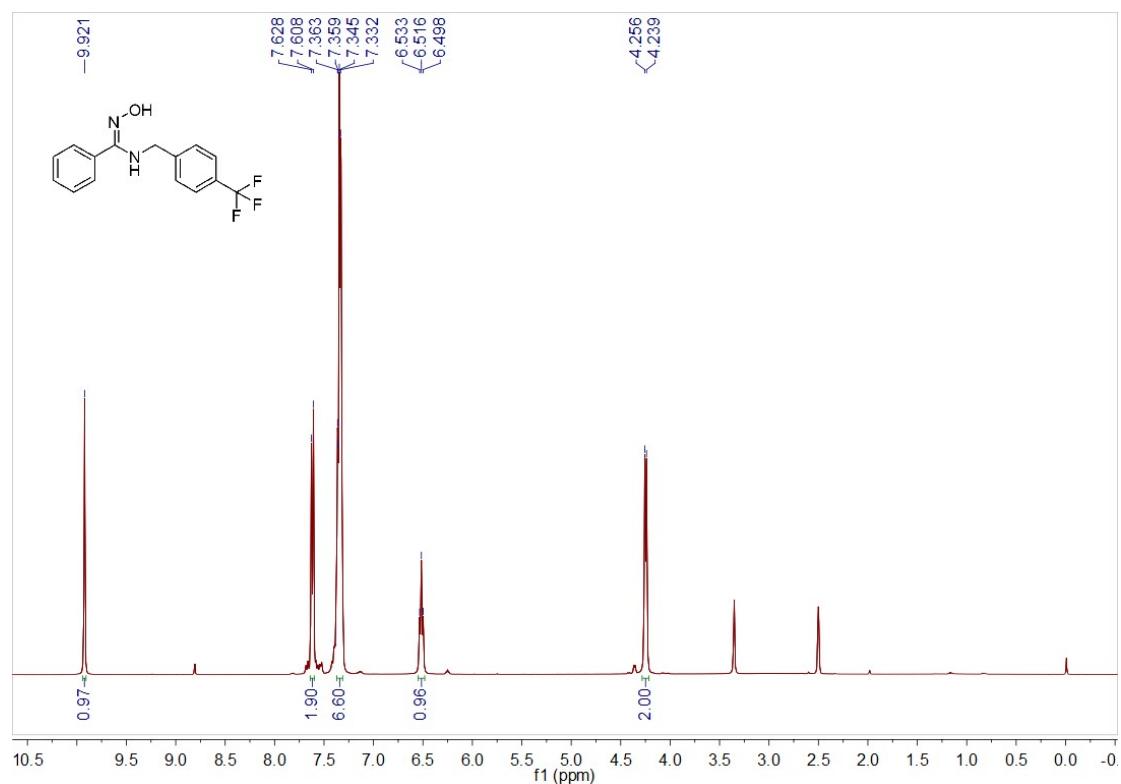
**<sup>13</sup>C NMR spectrum of 1q (DMSO-d<sub>6</sub>, 101 MHz):**



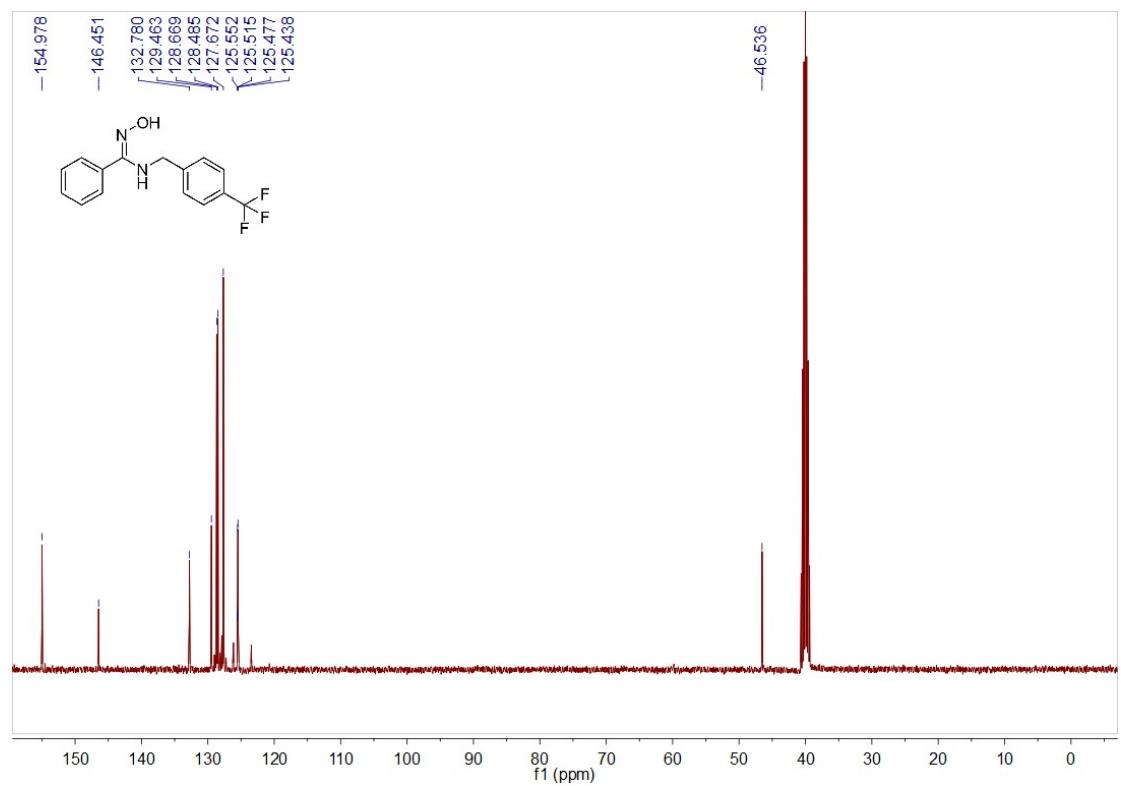
**<sup>19</sup>F NMR spectrum of 1q (DMSO-d6, 376 MHz):**



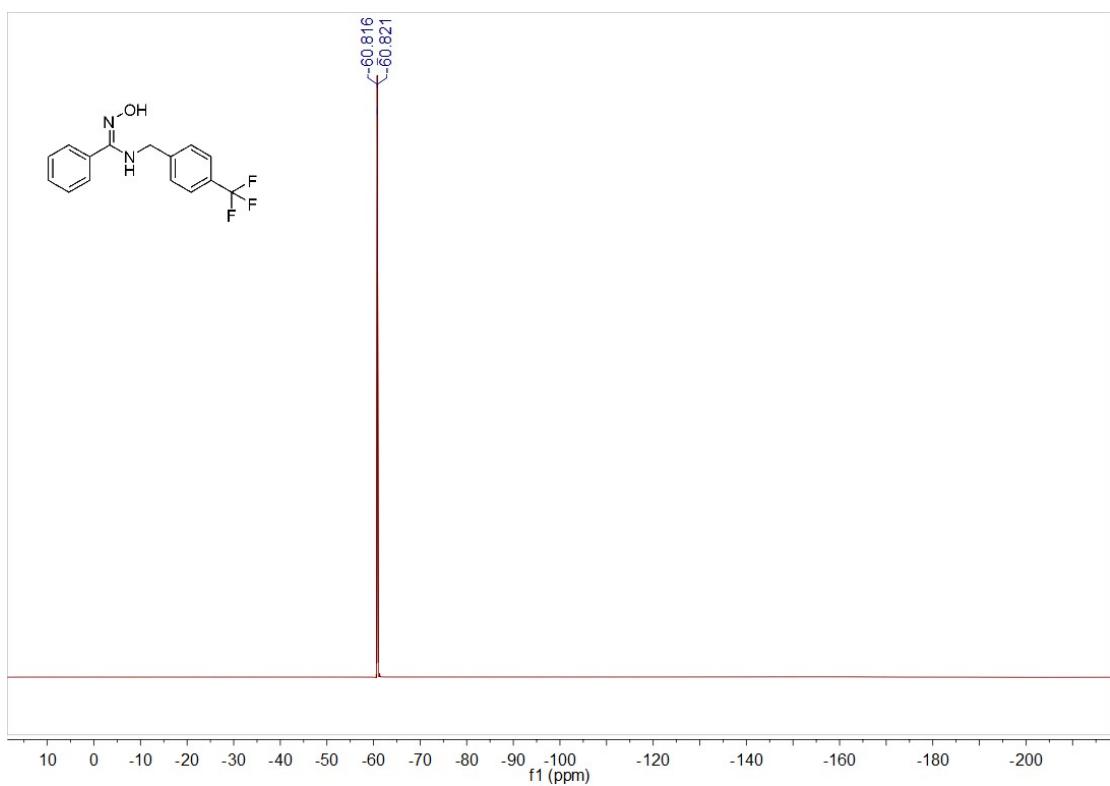
**<sup>1</sup>H NMR spectrum of 1r (DMSO-d<sub>6</sub>, 400 MHz):**



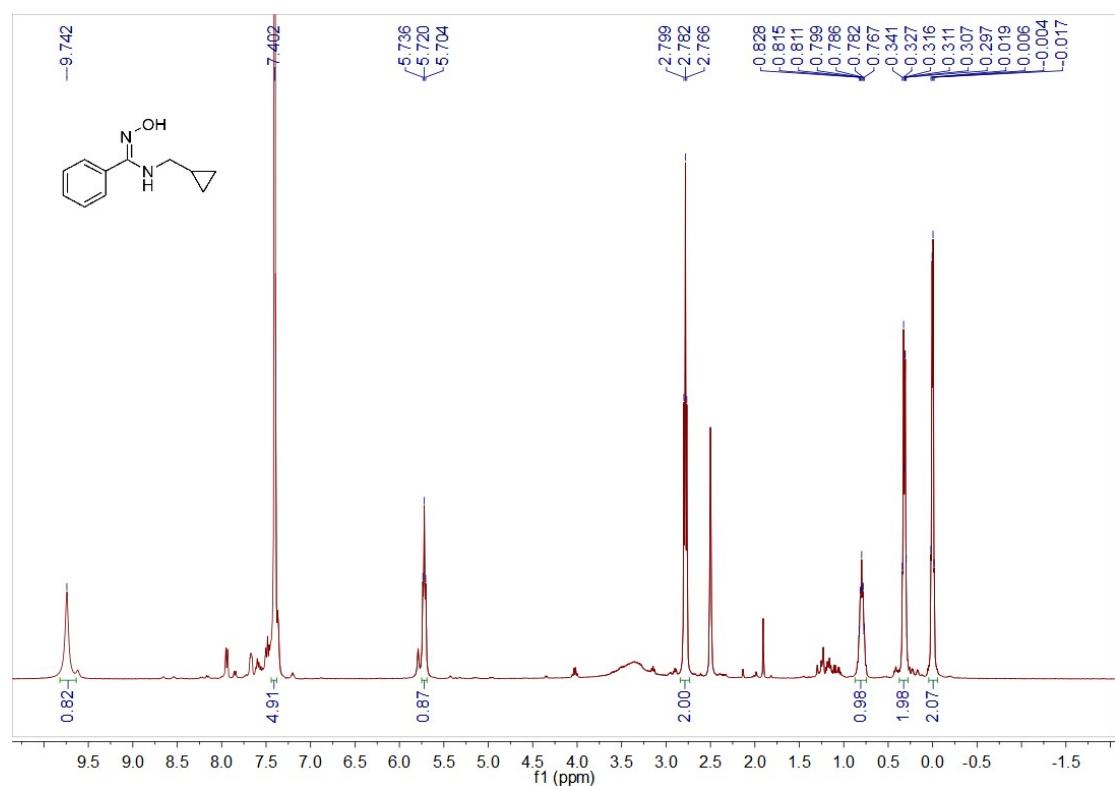
**<sup>13</sup>C NMR spectrum of 1r (DMSO-d<sub>6</sub>, 101 MHz):**



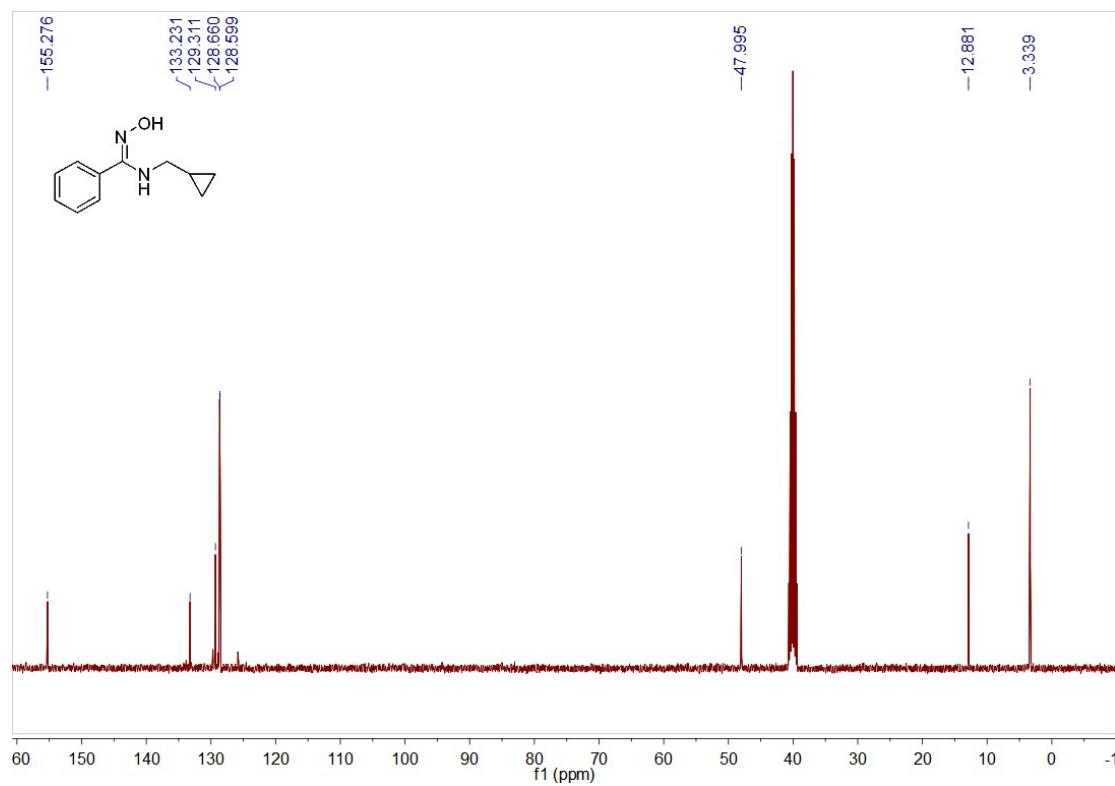
**<sup>19</sup>F NMR spectrum of 1r (DMSO-d<sub>6</sub>, 376 MHz):**



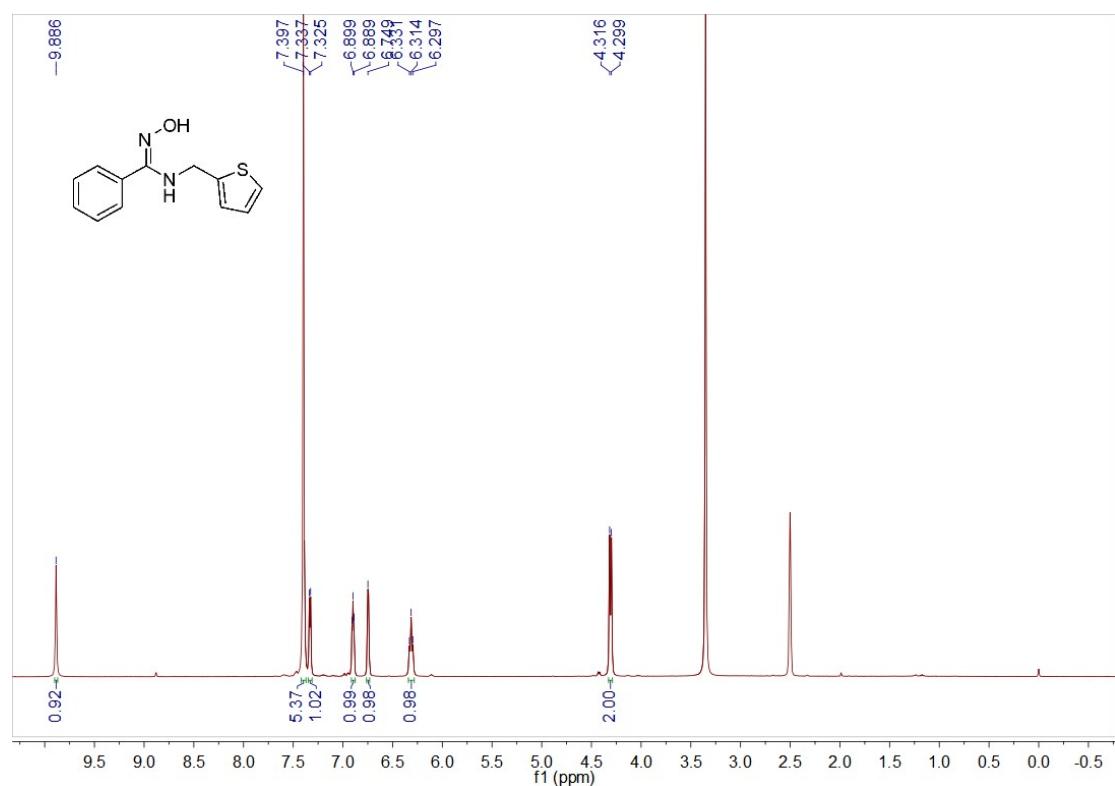
**<sup>1</sup>H NMR spectrum of 1s (DMSO-d<sub>6</sub>, 400 MHz):**



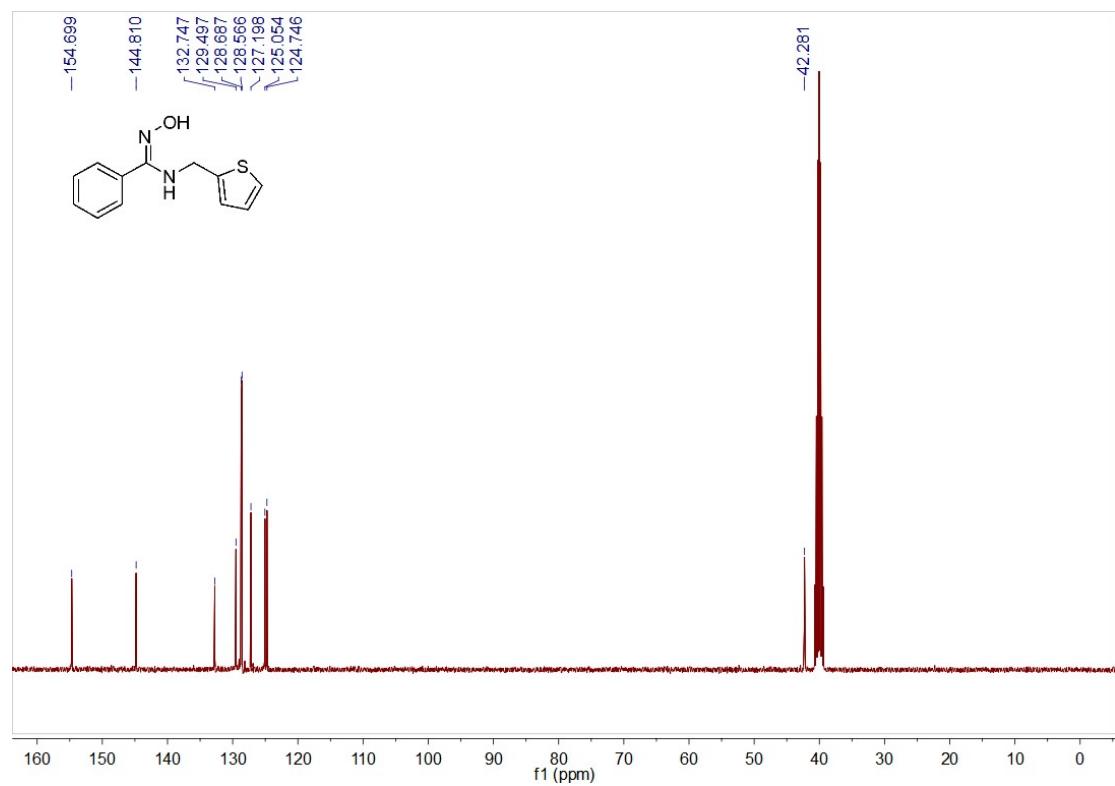
**<sup>13</sup>C NMR spectrum of 1s (DMSO-d<sub>6</sub>, 101 MHz):**



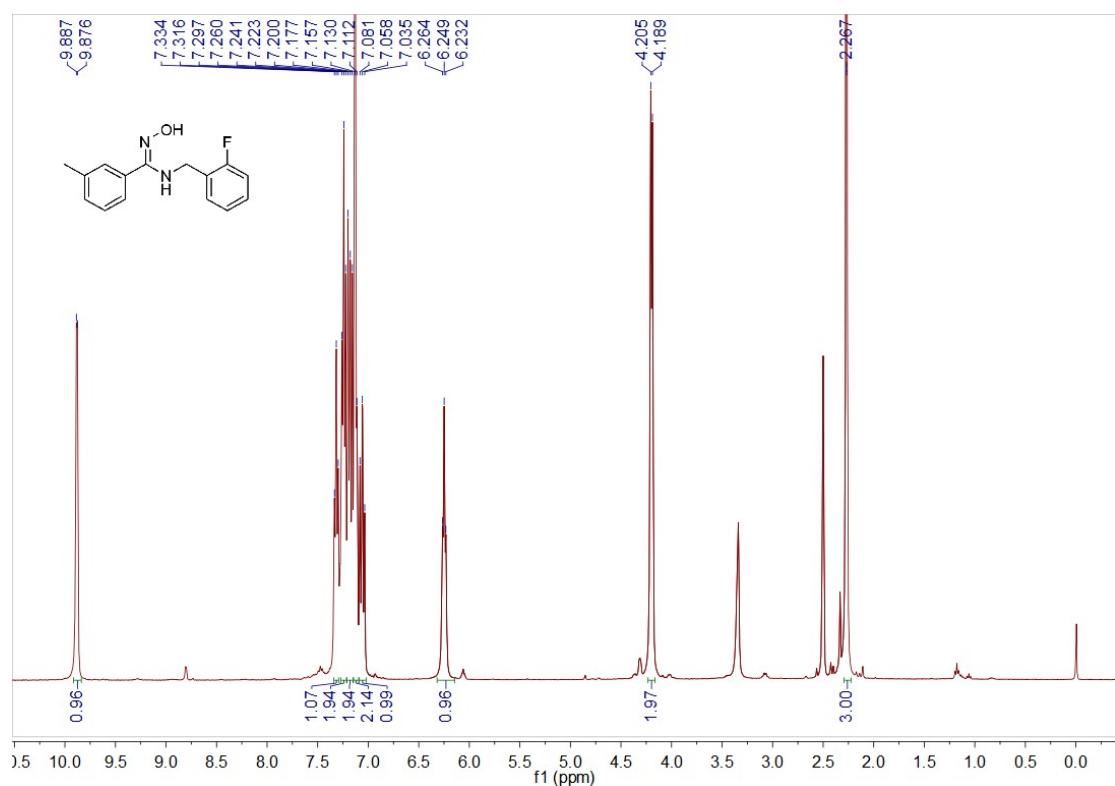
**<sup>1</sup>H NMR spectrum of 1t (DMSO-d<sub>6</sub>, 400 MHz):**



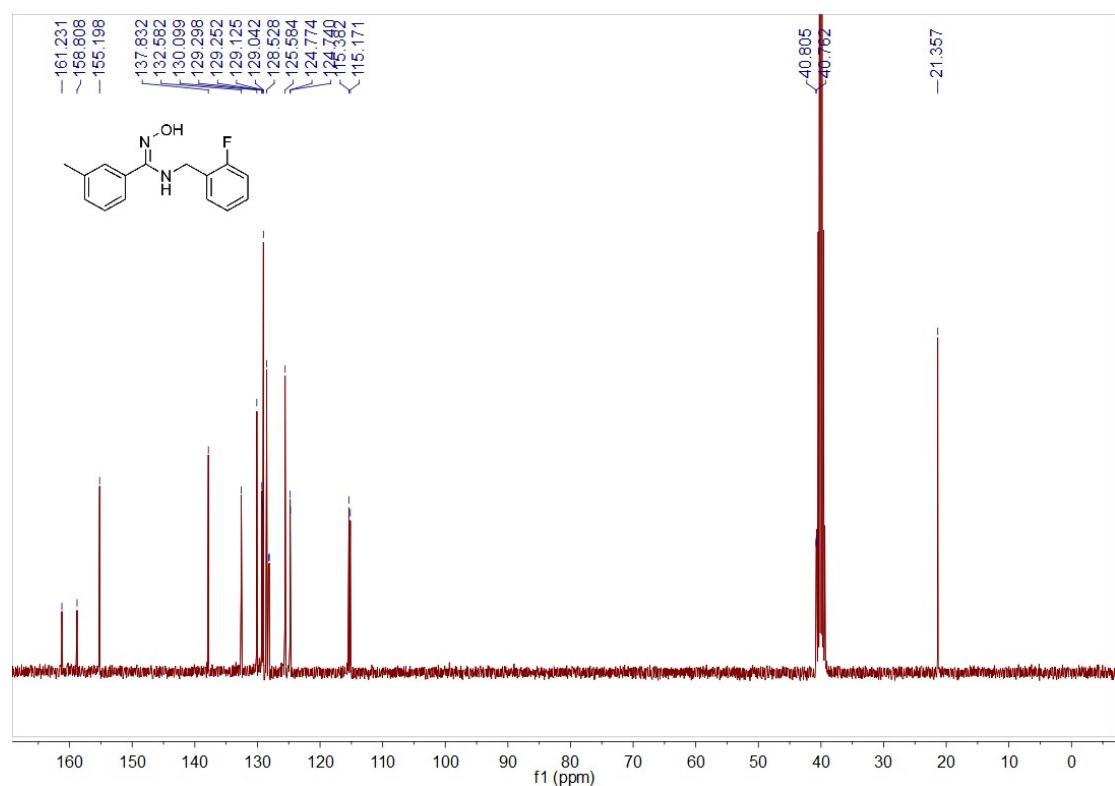
**<sup>13</sup>C NMR spectrum of 1t (DMSO-d<sub>6</sub>, 101 MHz):**



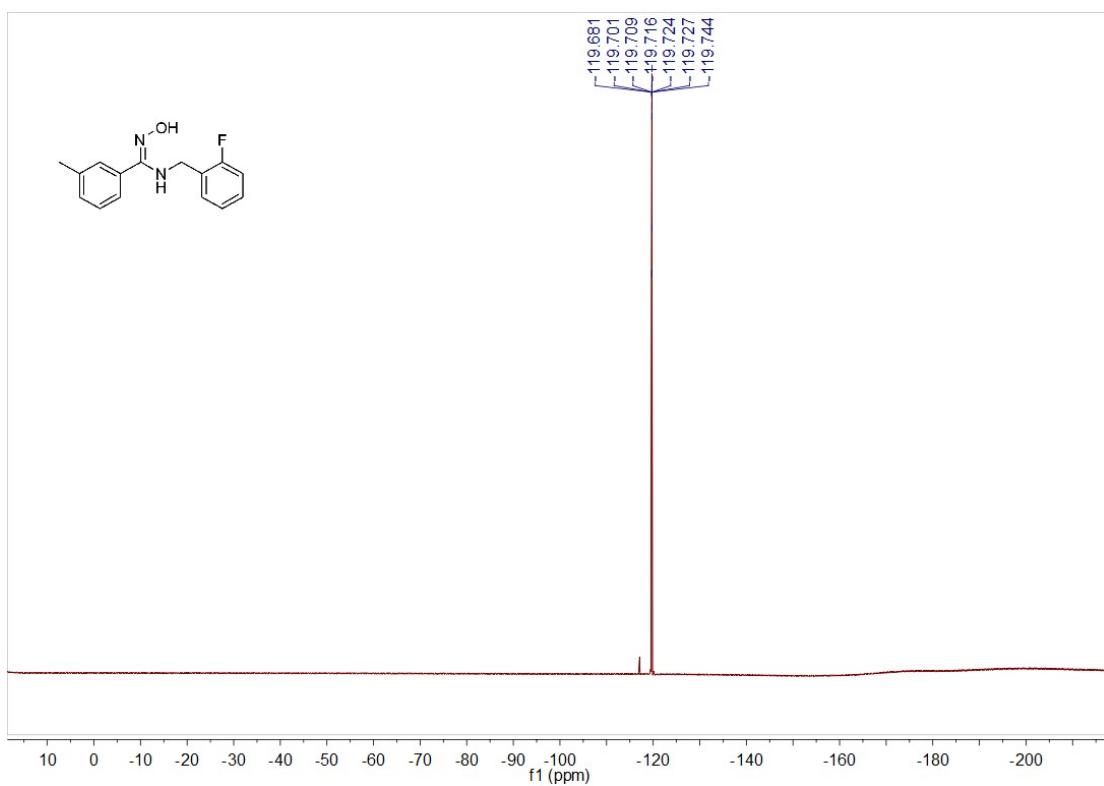
**<sup>1</sup>H NMR spectrum of 1u (DMSO-d<sub>6</sub>, 400 MHz):**



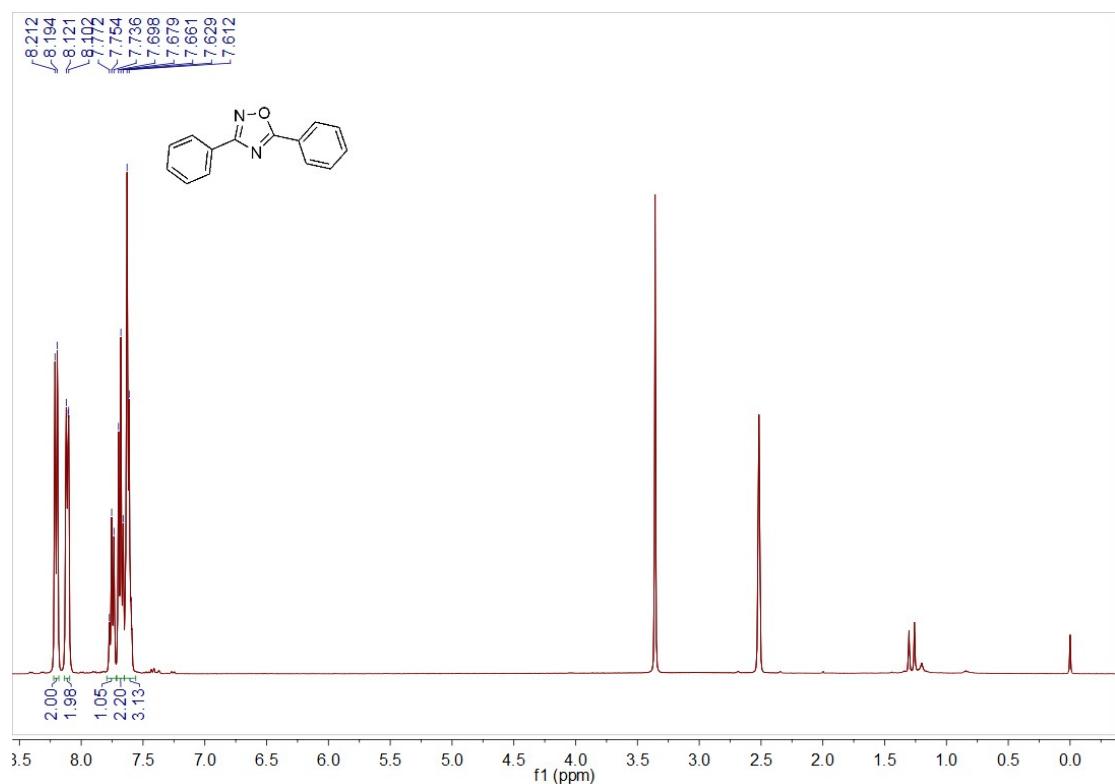
**<sup>13</sup>C NMR spectrum of 1u (DMSO-d<sub>6</sub>, 101 MHz):**



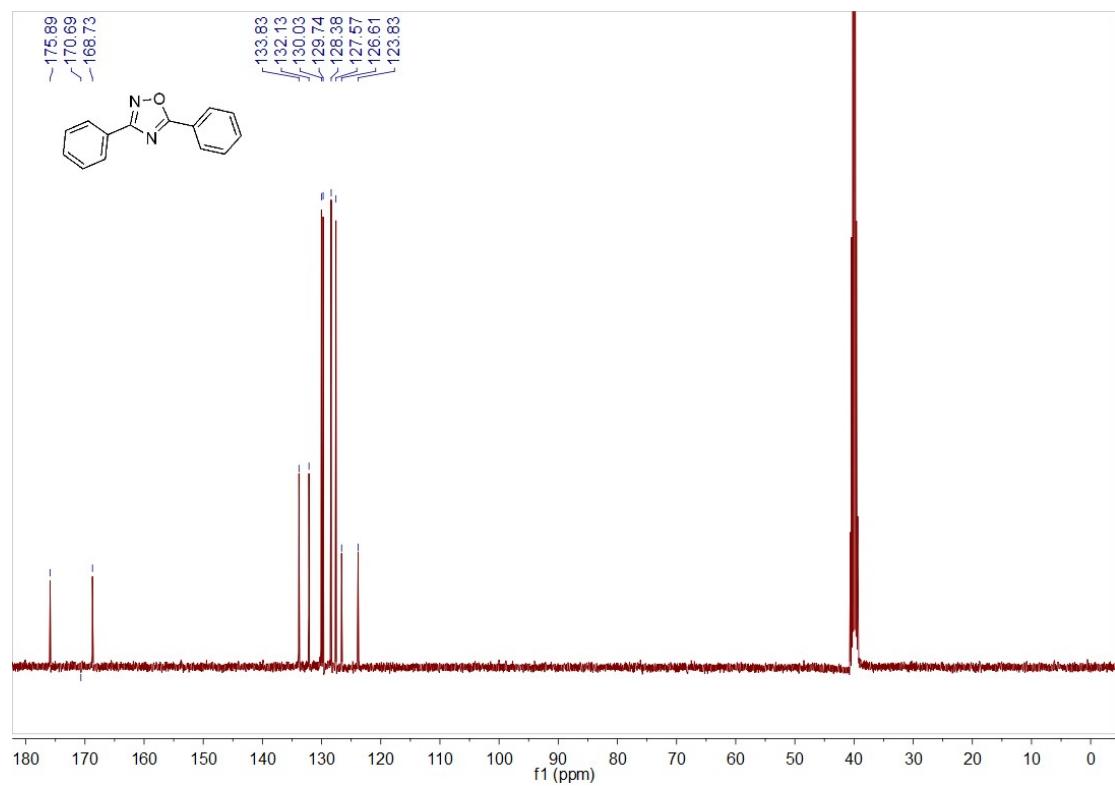
**<sup>19</sup>F NMR spectrum of 1n (DMSO-d<sub>6</sub>, 376 MHz):**



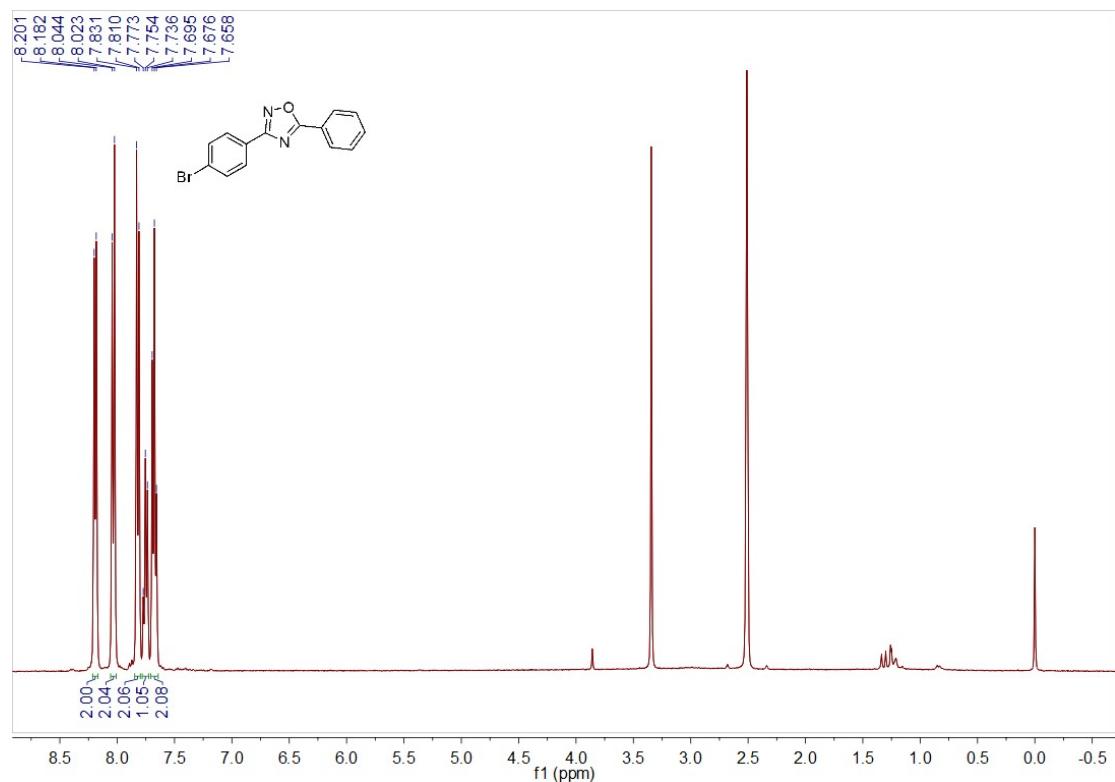
**<sup>1</sup>H NMR spectrum of 2a (DMSO-d<sub>6</sub>, 400 MHz):**



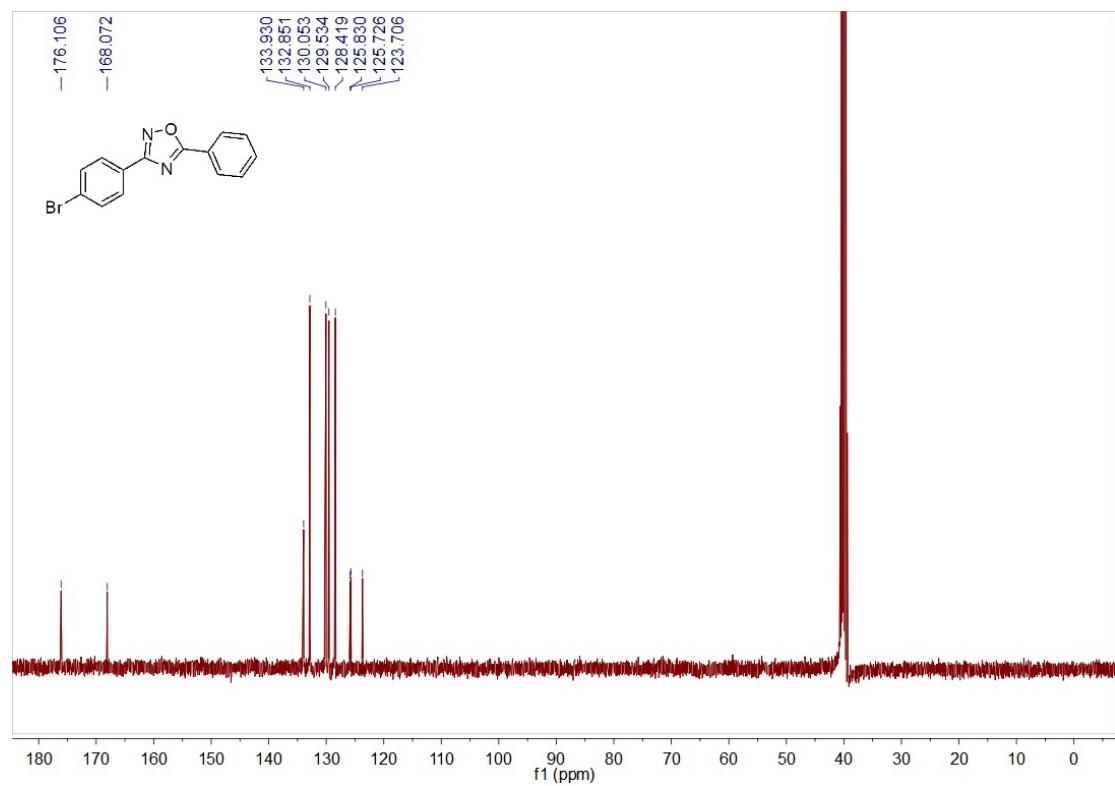
**<sup>13</sup>C NMR spectrum of 2a (DMSO-d<sub>6</sub>, 101 MHz):**



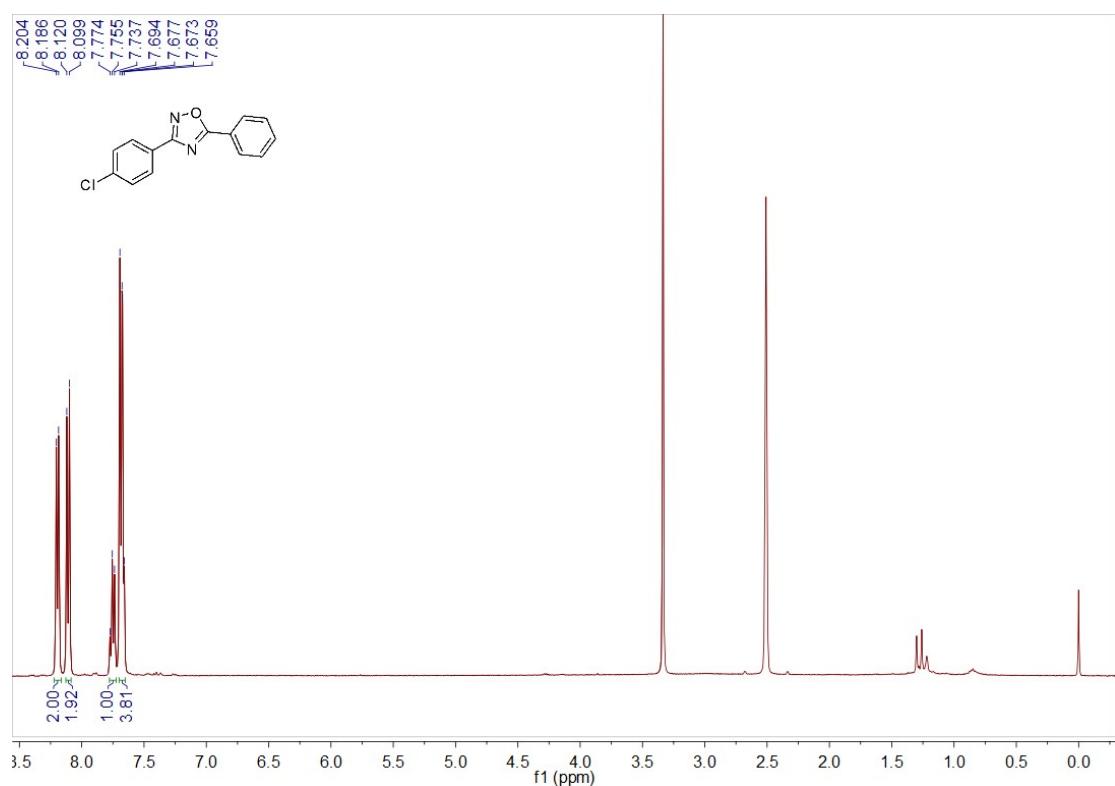
**<sup>1</sup>H NMR spectrum of 2b (DMSO-d<sub>6</sub>, 400 MHz):**



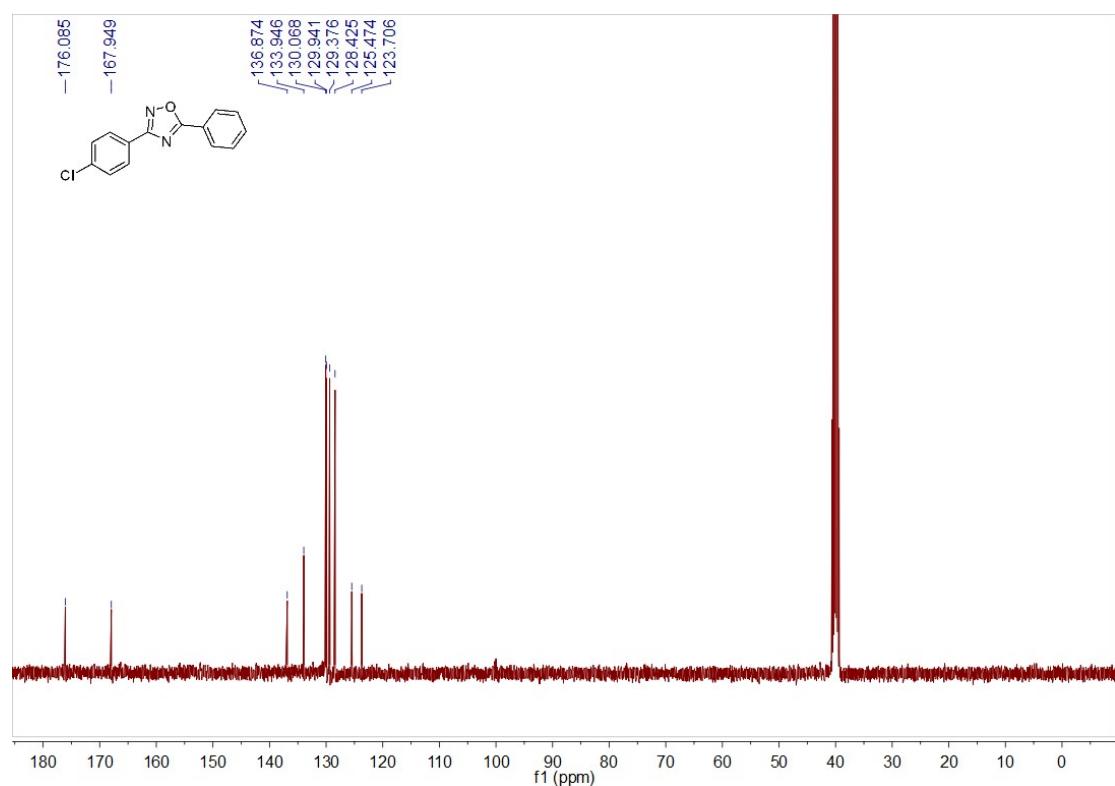
**<sup>13</sup>C NMR spectrum of 2b (DMSO-d<sub>6</sub>, 101 MHz):**



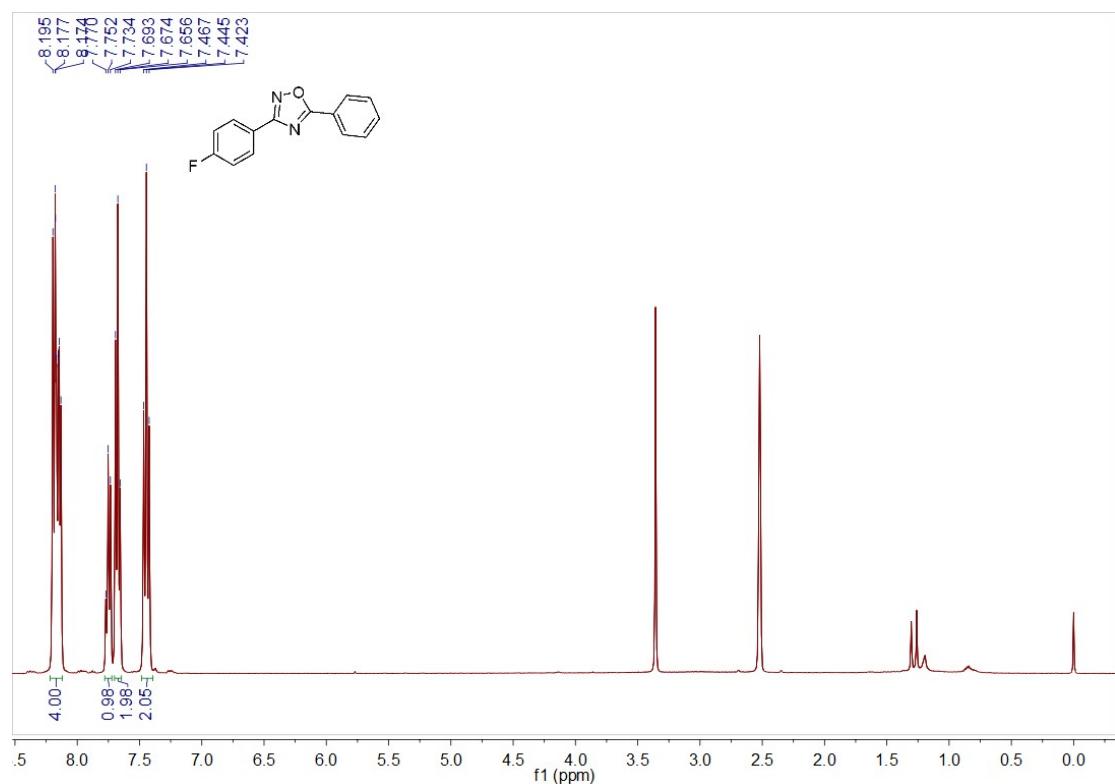
**<sup>1</sup>H NMR spectrum of 2c (DMSO-d<sub>6</sub>, 400 MHz):**



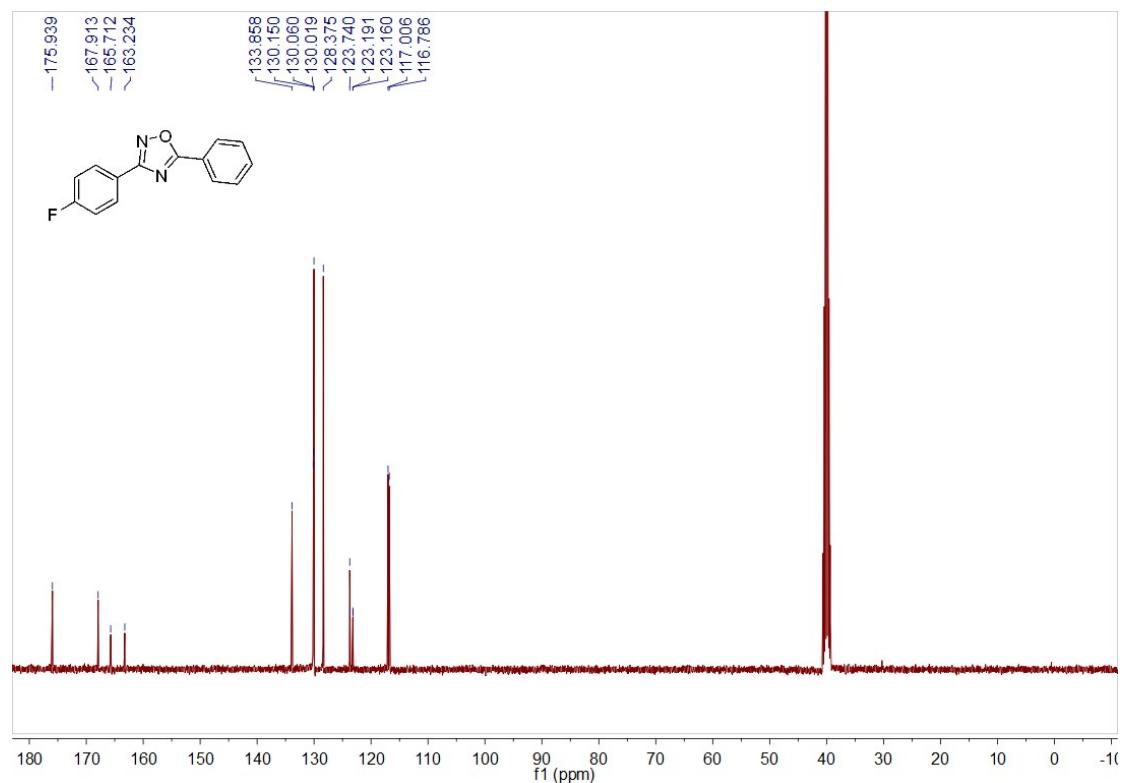
**<sup>13</sup>C NMR spectrum of 2c (DMSO-d<sub>6</sub>, 101 MHz):**



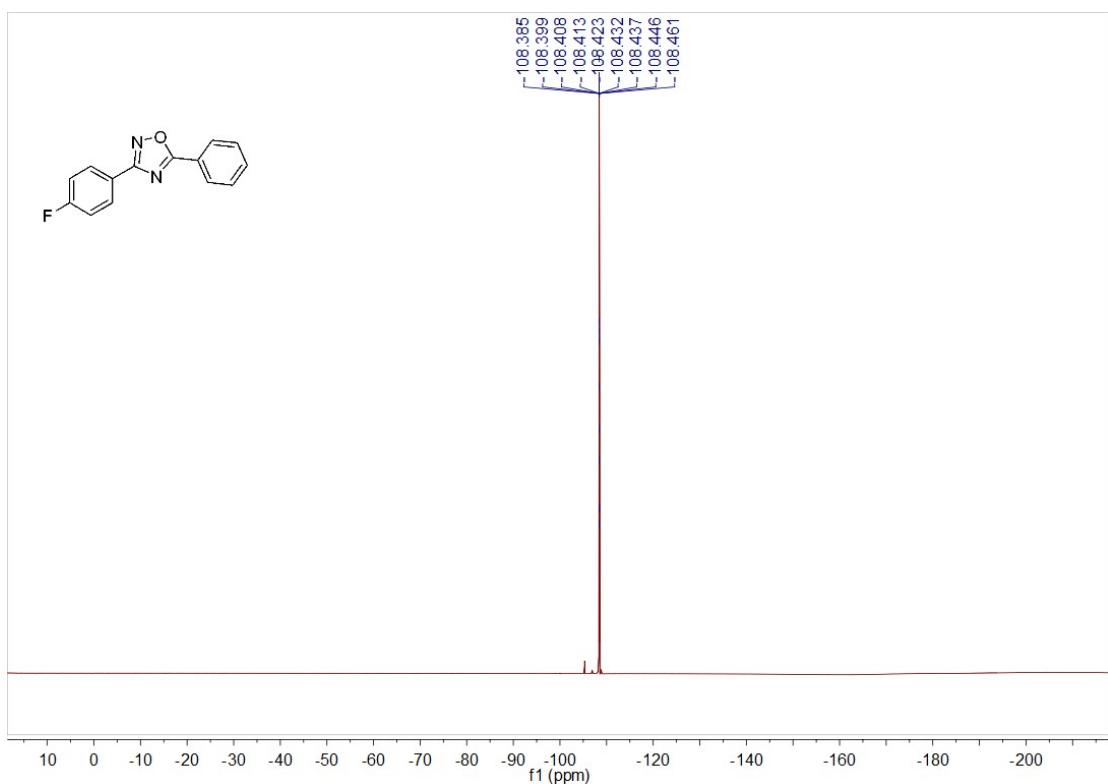
**<sup>1</sup>H NMR spectrum of 2d (DMSO-d<sub>6</sub>, 400 MHz):**



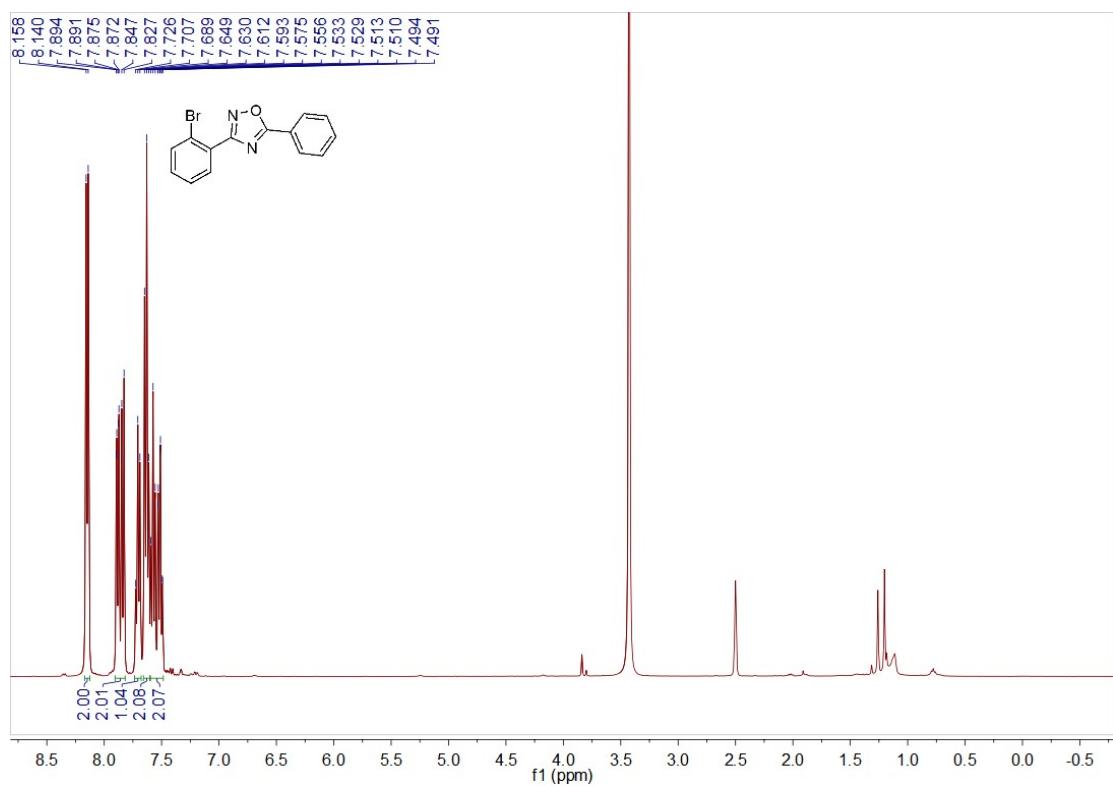
**<sup>13</sup>C NMR spectrum of 2d (DMSO-d<sub>6</sub>, 101 MHz):**



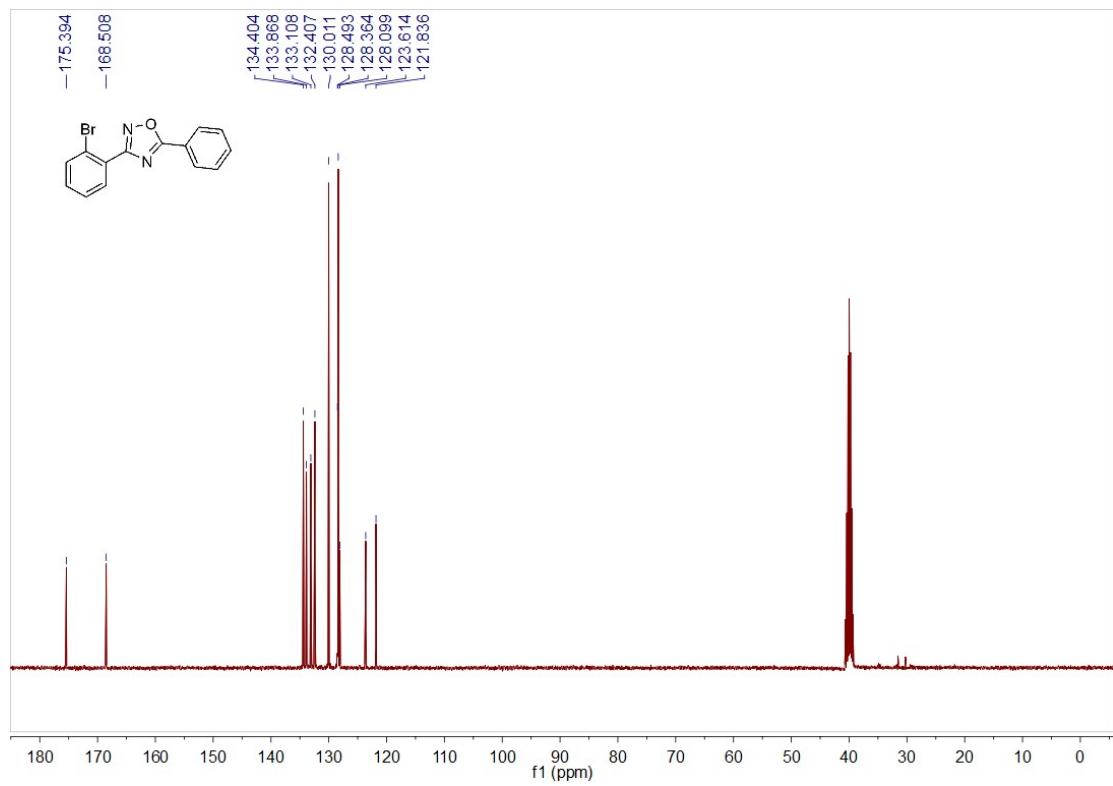
**<sup>19</sup>F NMR spectrum of 2d (DMSO-d6, 376 MHz):**



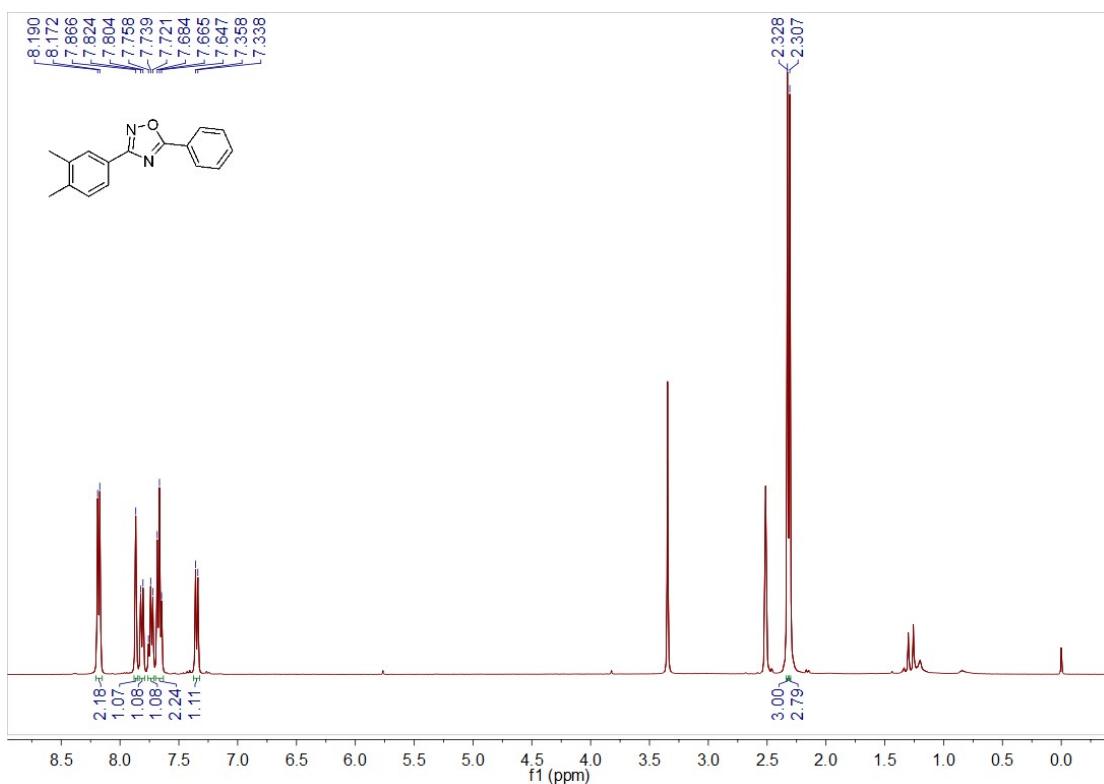
**<sup>1</sup>H NMR spectrum of 2e (DMSO-d<sub>6</sub>, 400 MHz):**



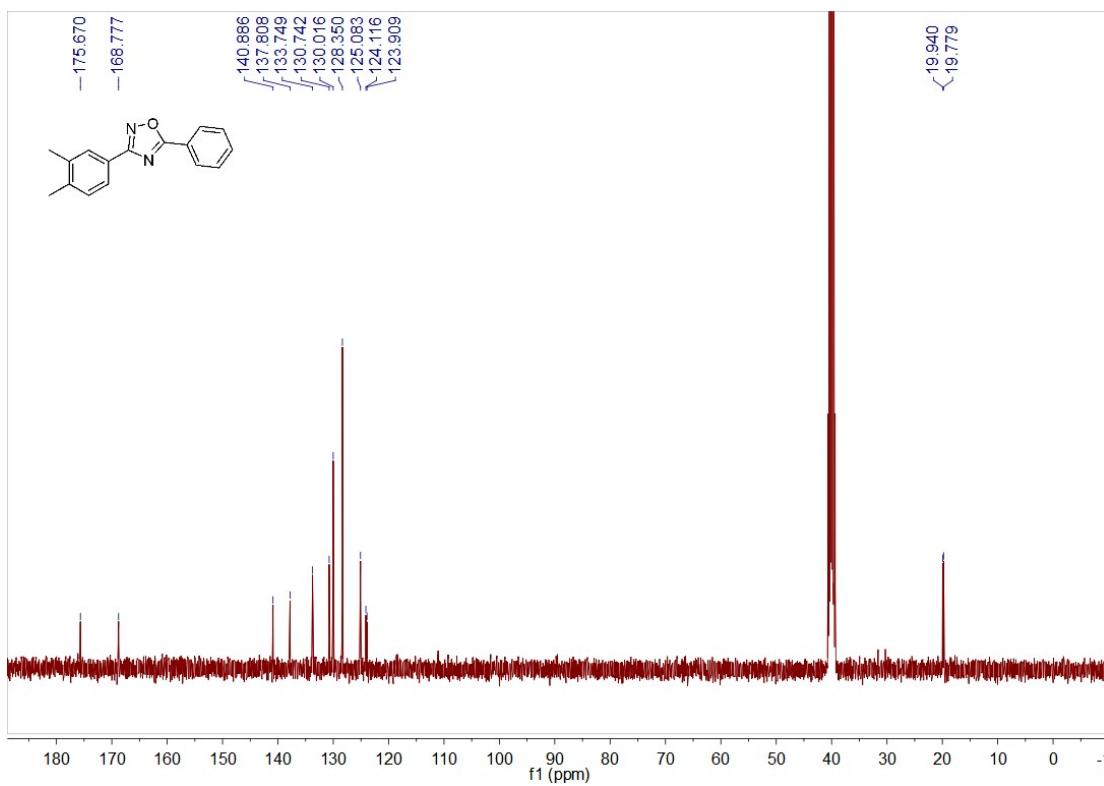
**<sup>13</sup>C NMR spectrum of 2e (DMSO-d<sub>6</sub>, 101 MHz):**



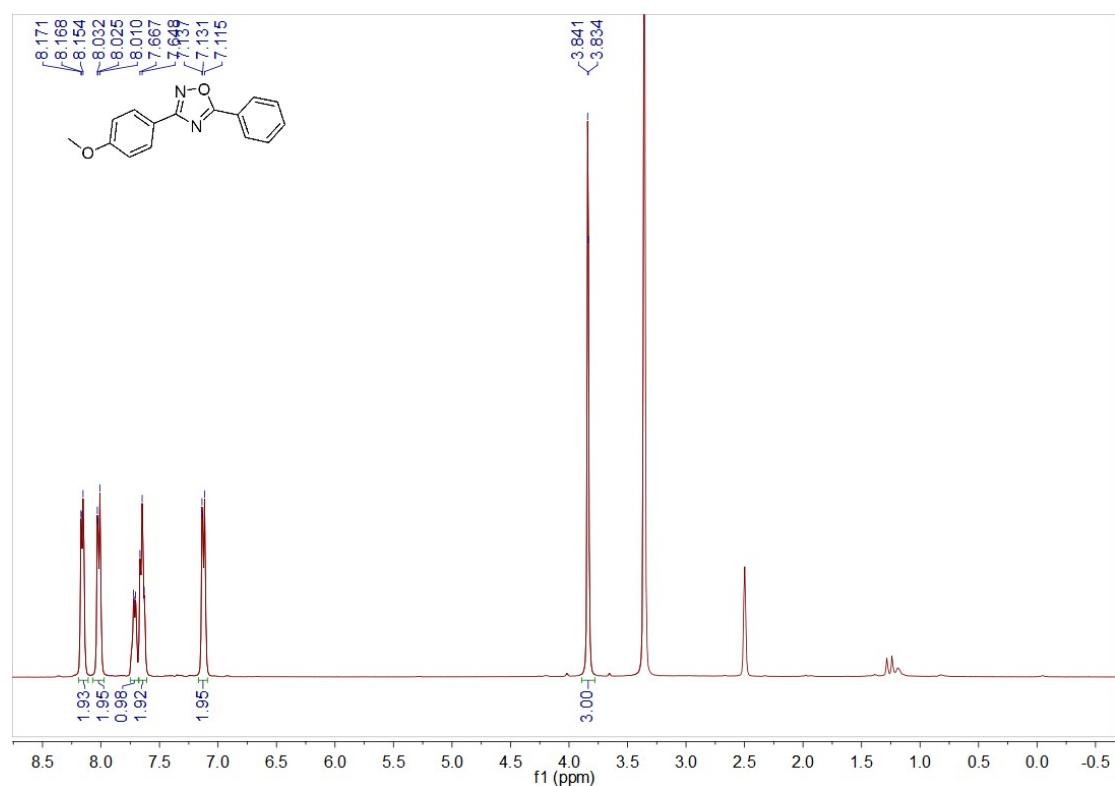
**<sup>1</sup>H NMR spectrum of 2g (DMSO-d<sub>6</sub>, 400 MHz):**



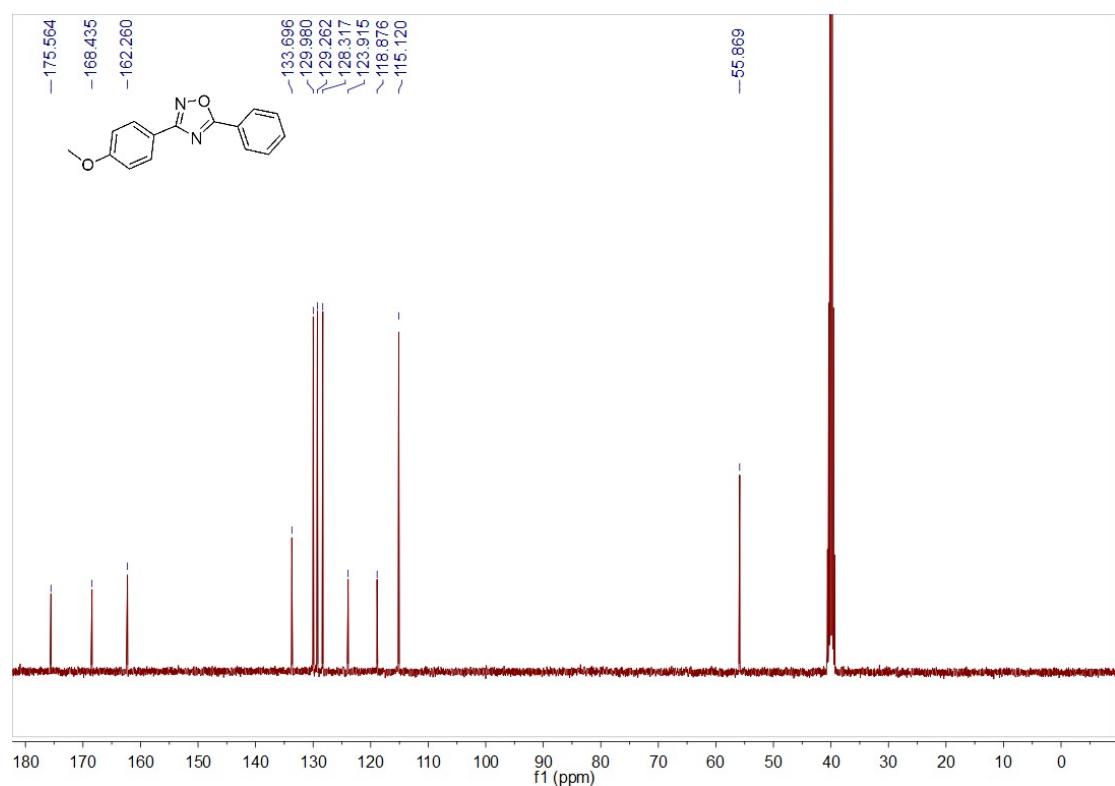
**<sup>13</sup>C NMR spectrum of 2g (DMSO-d<sub>6</sub>, 101 MHz):**



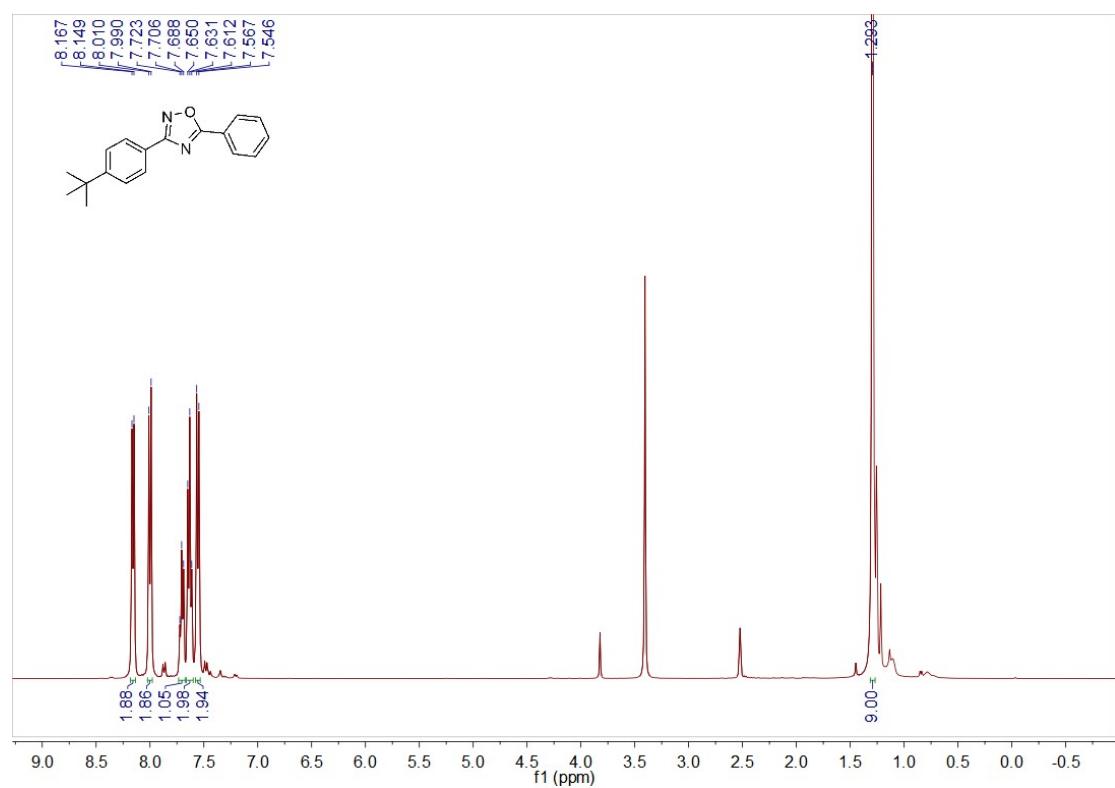
**<sup>1</sup>H NMR spectrum of 2h (DMSO-d<sub>6</sub>, 400 MHz):**



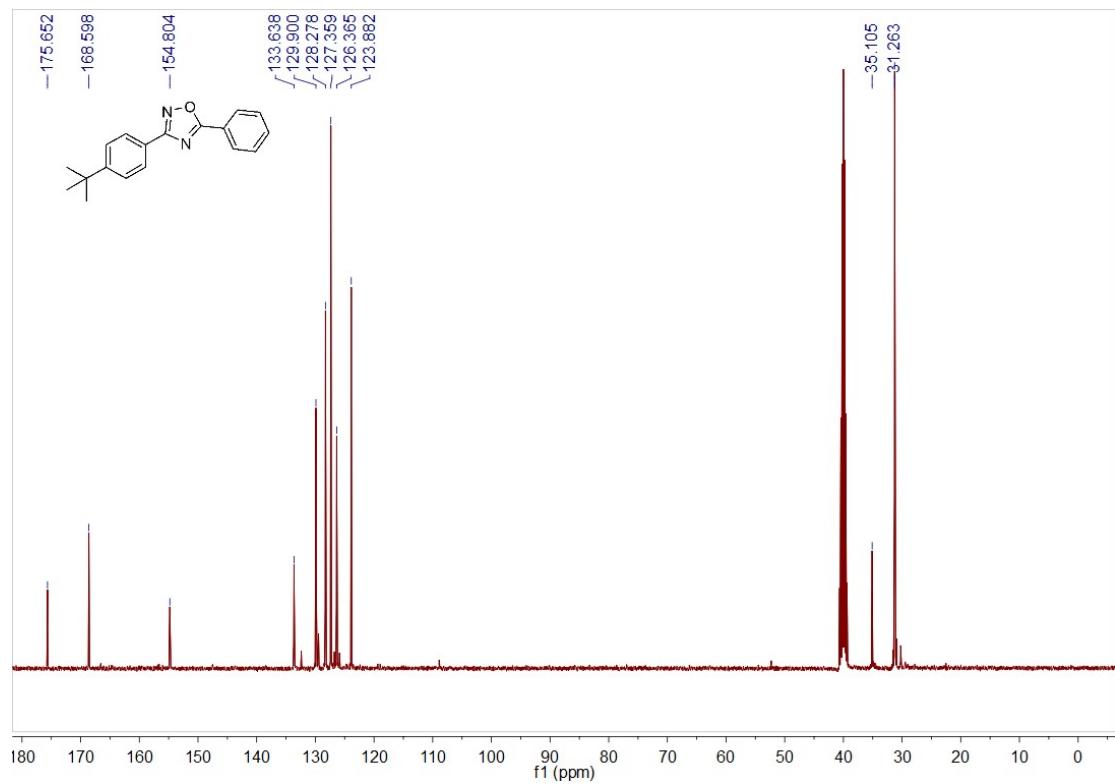
**<sup>13</sup>C NMR spectrum of 2h (DMSO-d<sub>6</sub>, 101 MHz):**



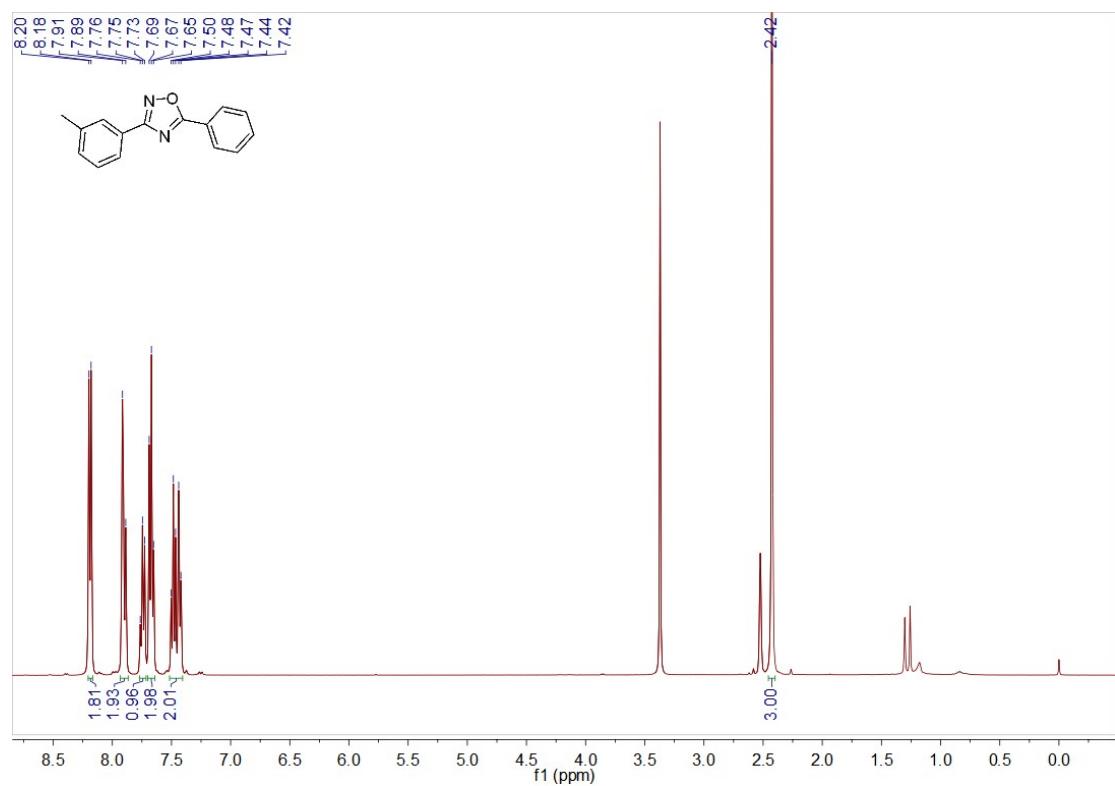
**<sup>1</sup>H NMR spectrum of 2i (DMSO-d<sub>6</sub>, 400 MHz):**



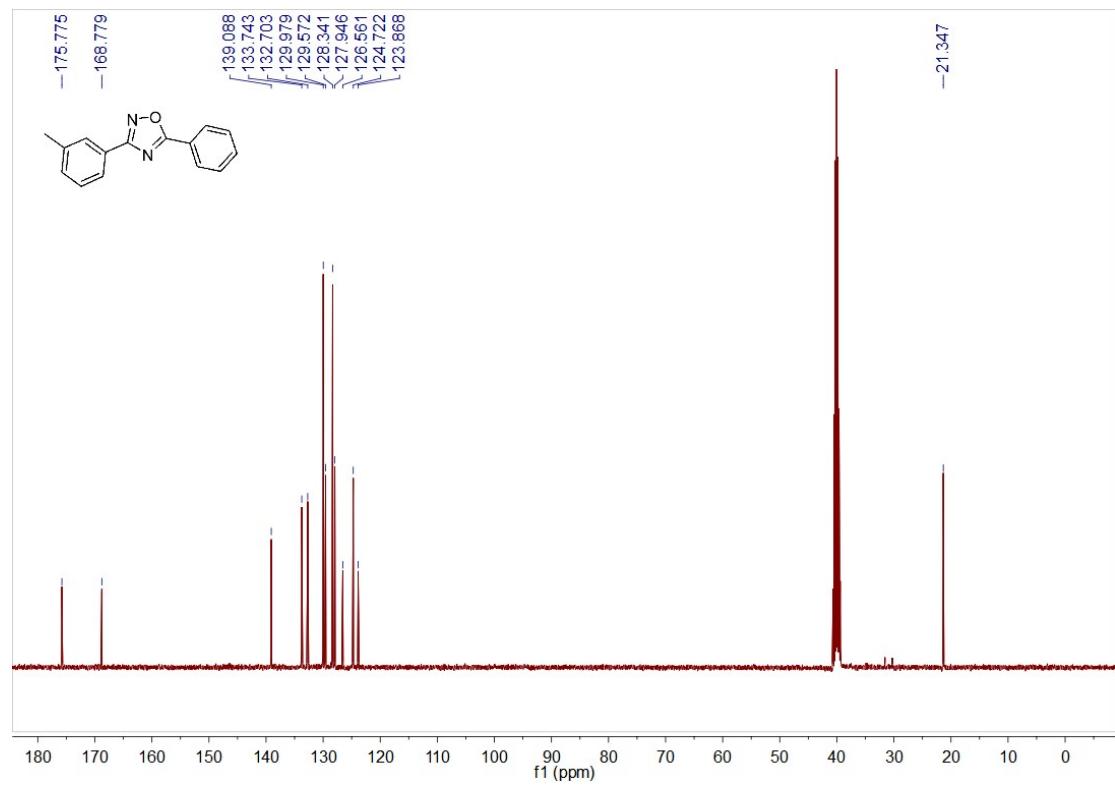
**<sup>13</sup>C NMR spectrum of 2i (DMSO-d<sub>6</sub>, 101 MHz):**



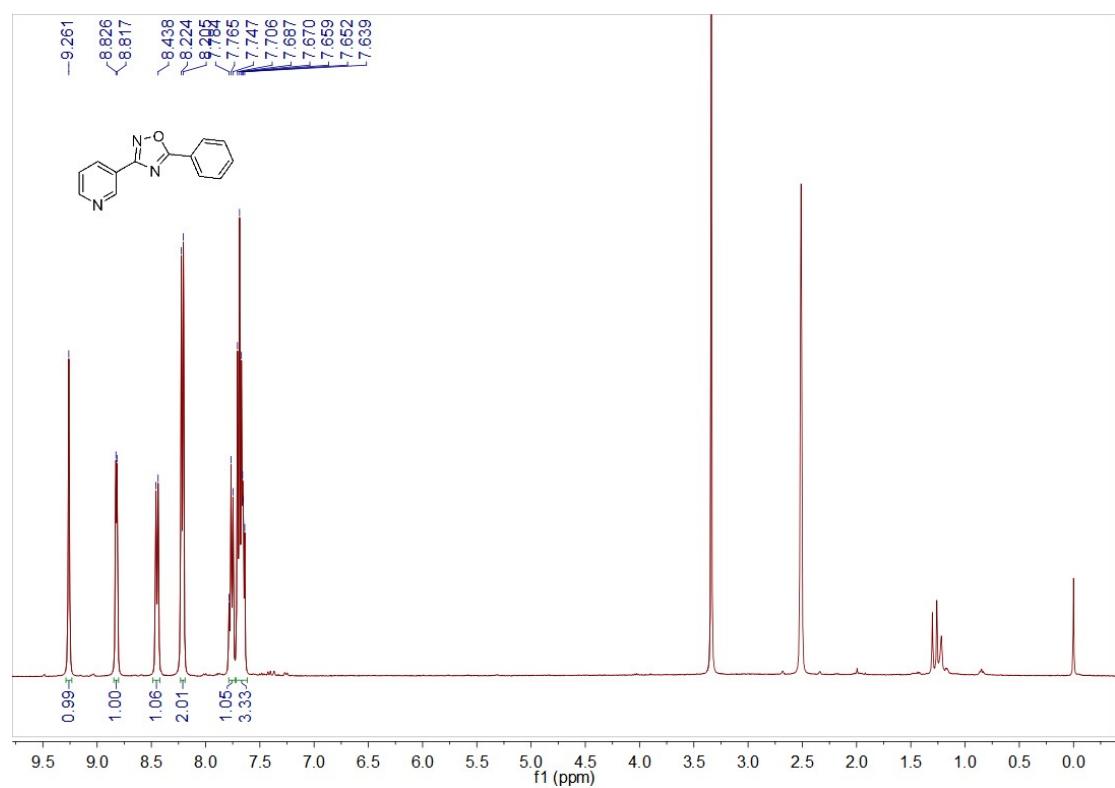
**<sup>1</sup>H NMR spectrum of 2j (DMSO-d<sub>6</sub>, 400 MHz):**



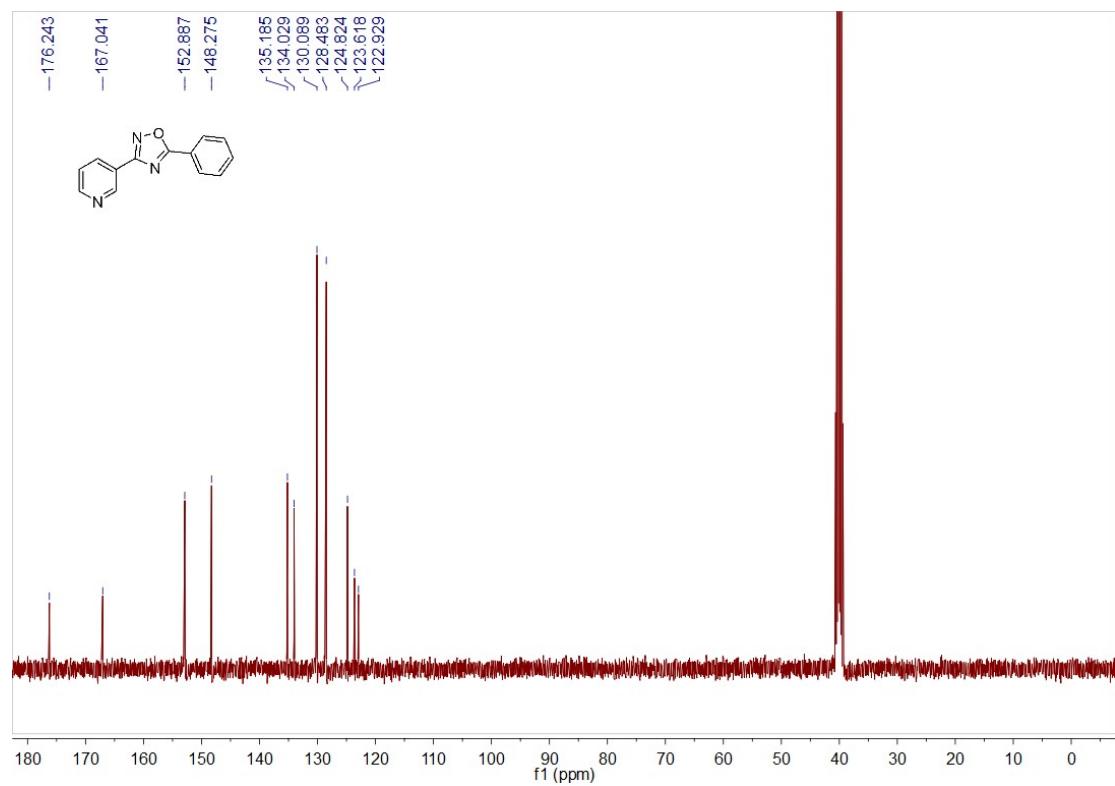
**<sup>13</sup>C NMR spectrum of 2j (DMSO-d<sub>6</sub>, 101 MHz):**



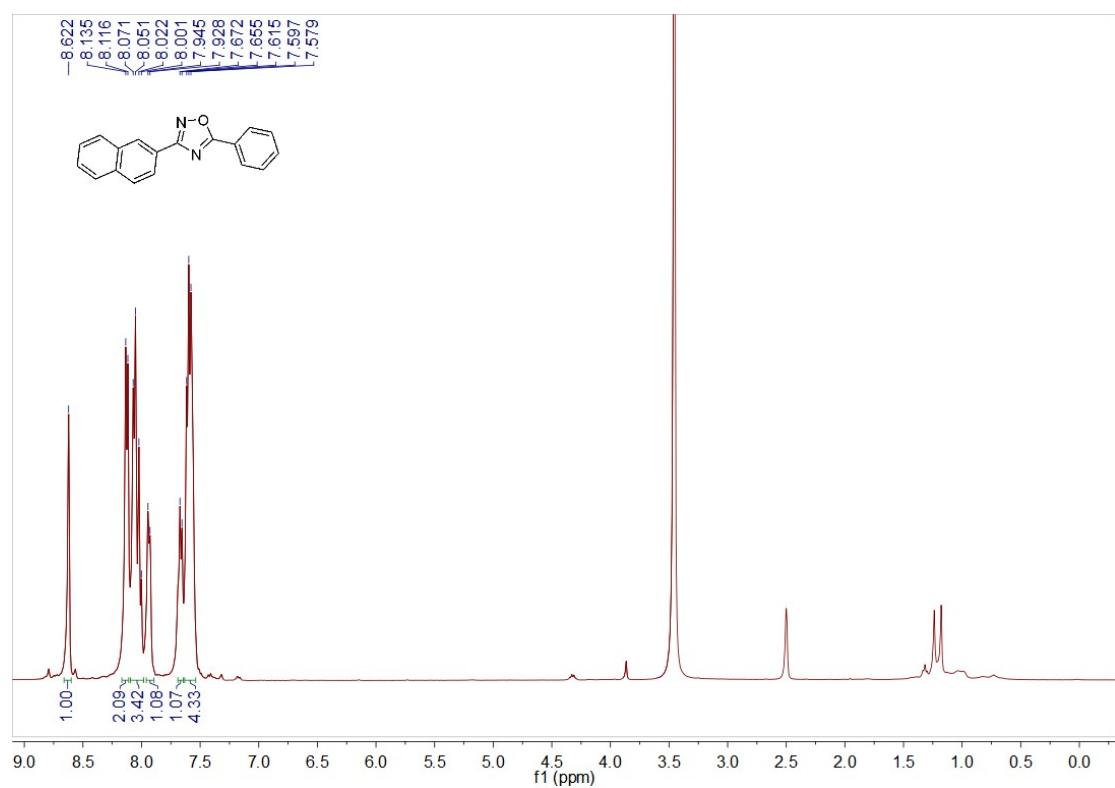
**<sup>1</sup>H NMR spectrum of 2k (DMSO-d<sub>6</sub>, 400 MHz):**



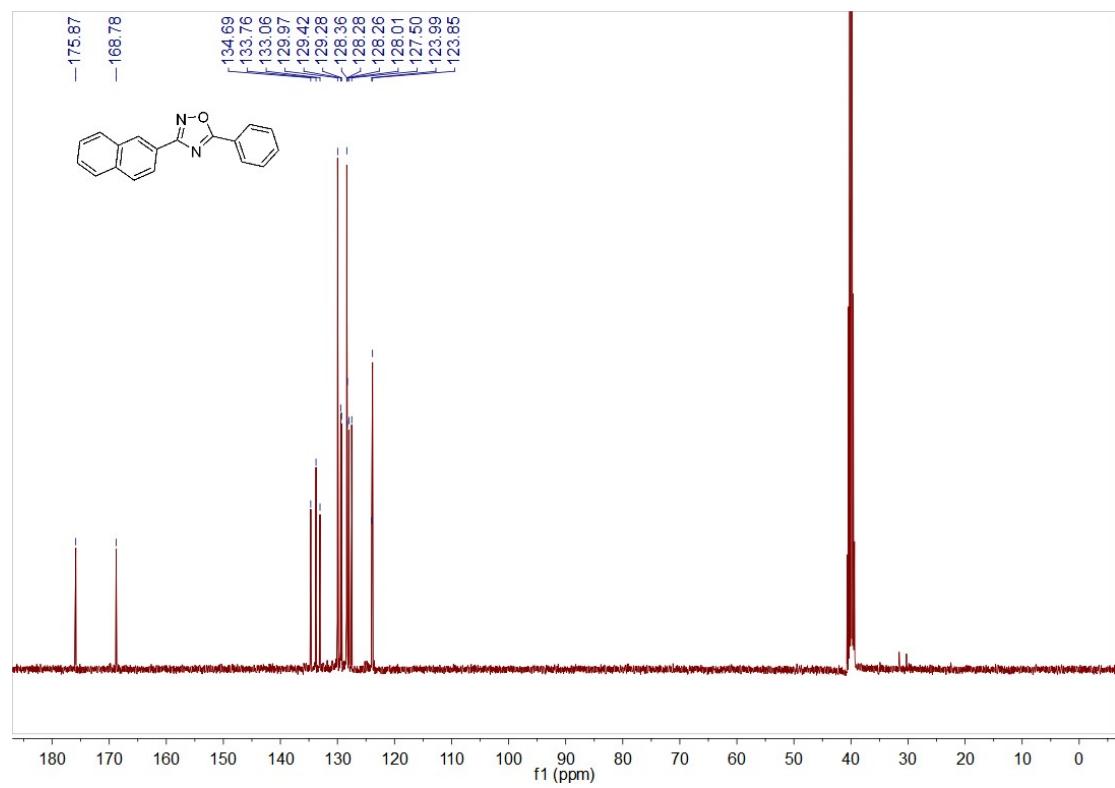
**<sup>13</sup>C NMR spectrum of 2k (DMSO-d<sub>6</sub>, 101 MHz):**



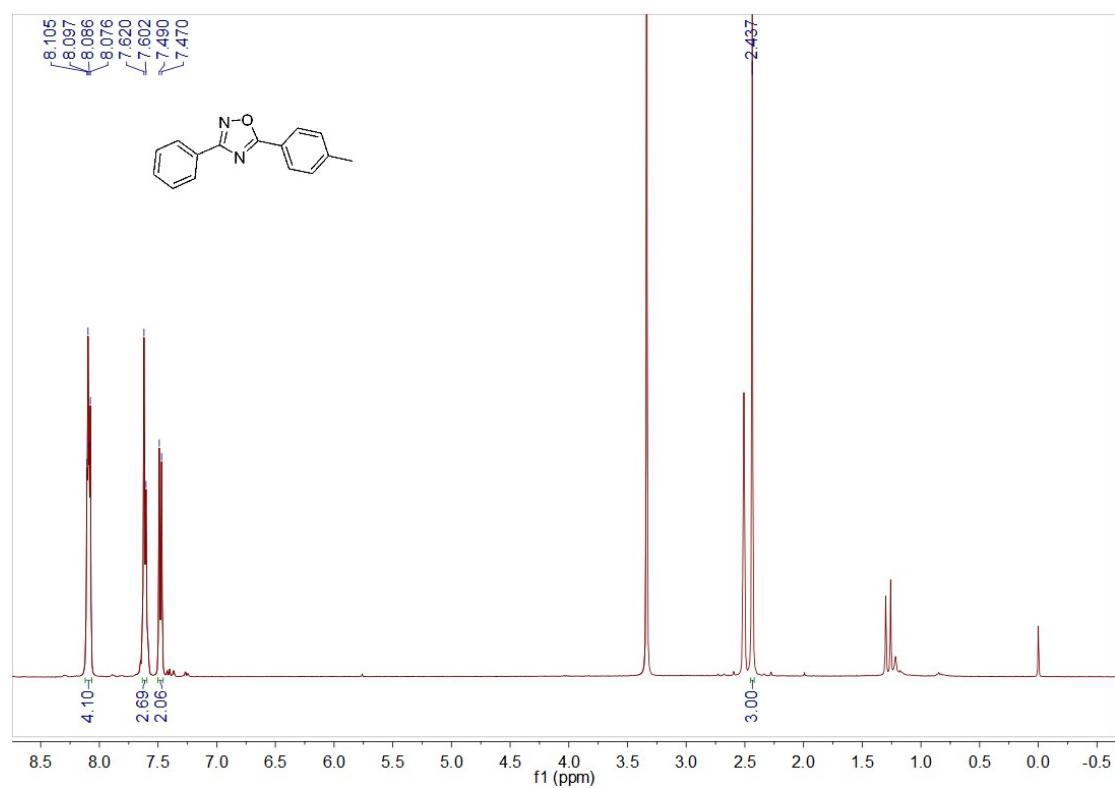
**<sup>1</sup>H NMR spectrum of 2l (DMSO-d<sub>6</sub>, 400 MHz):**



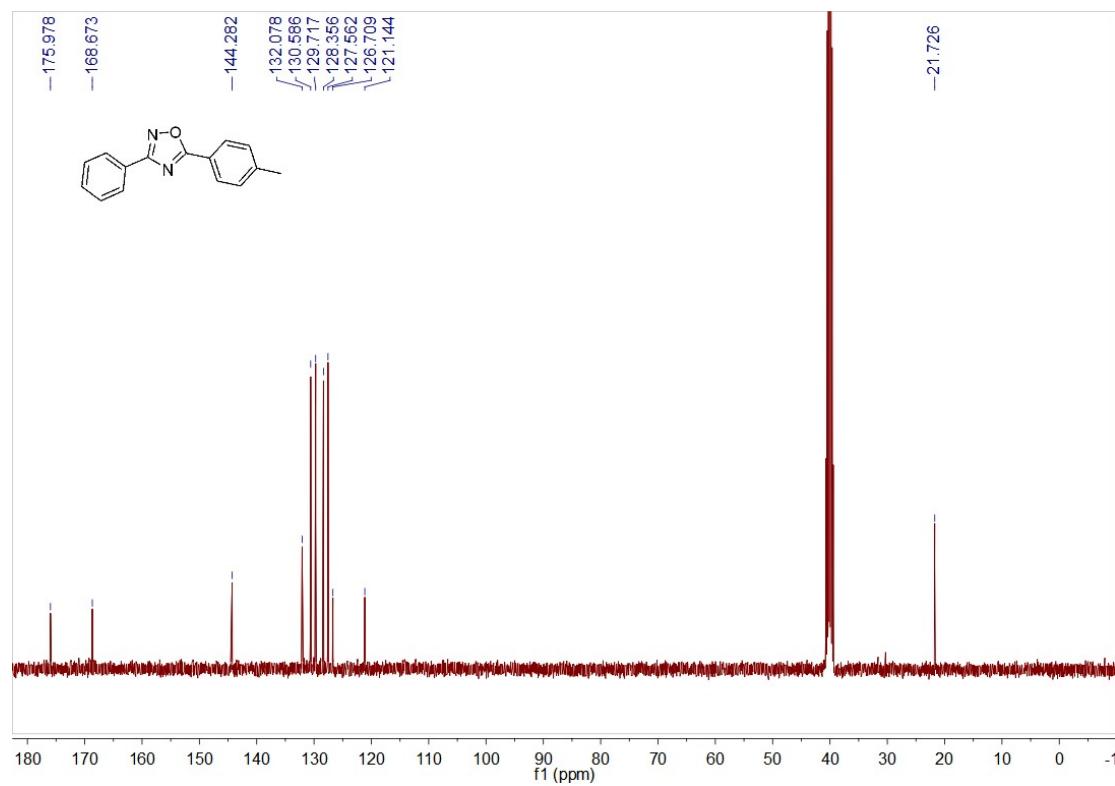
**<sup>13</sup>C NMR spectrum of 2l (DMSO-d<sub>6</sub>, 101 MHz):**



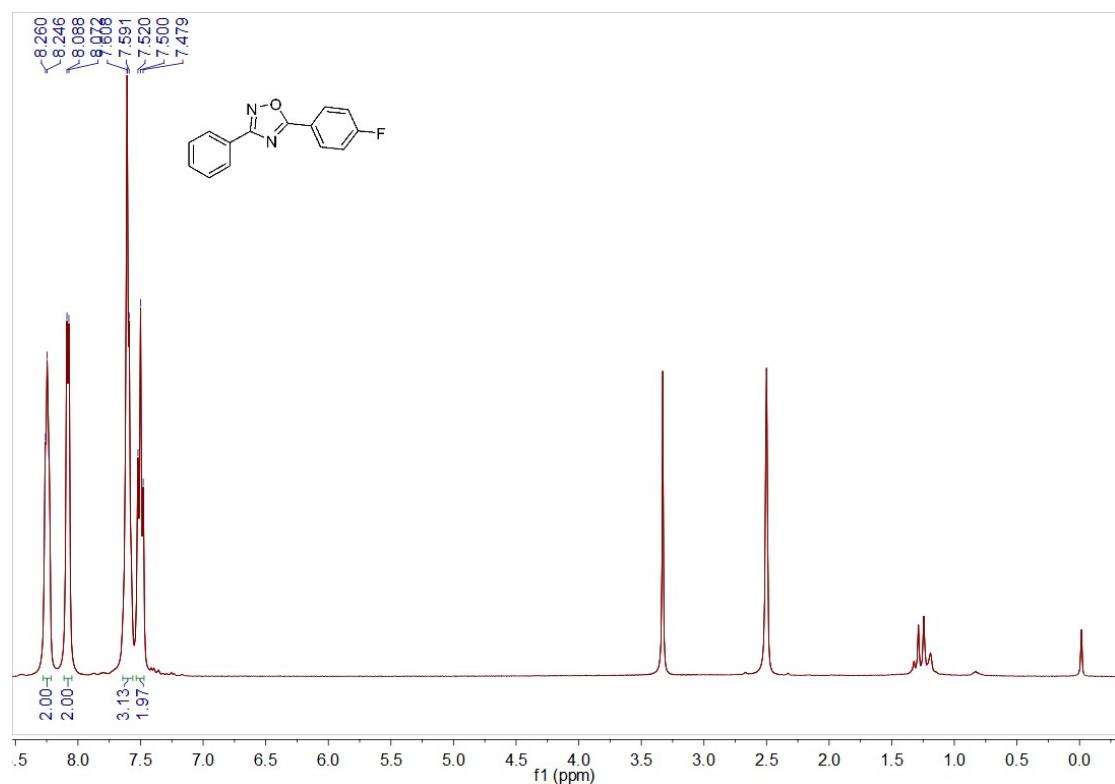
**<sup>1</sup>H NMR spectrum of 2m (DMSO-d<sub>6</sub>, 400 MHz):**



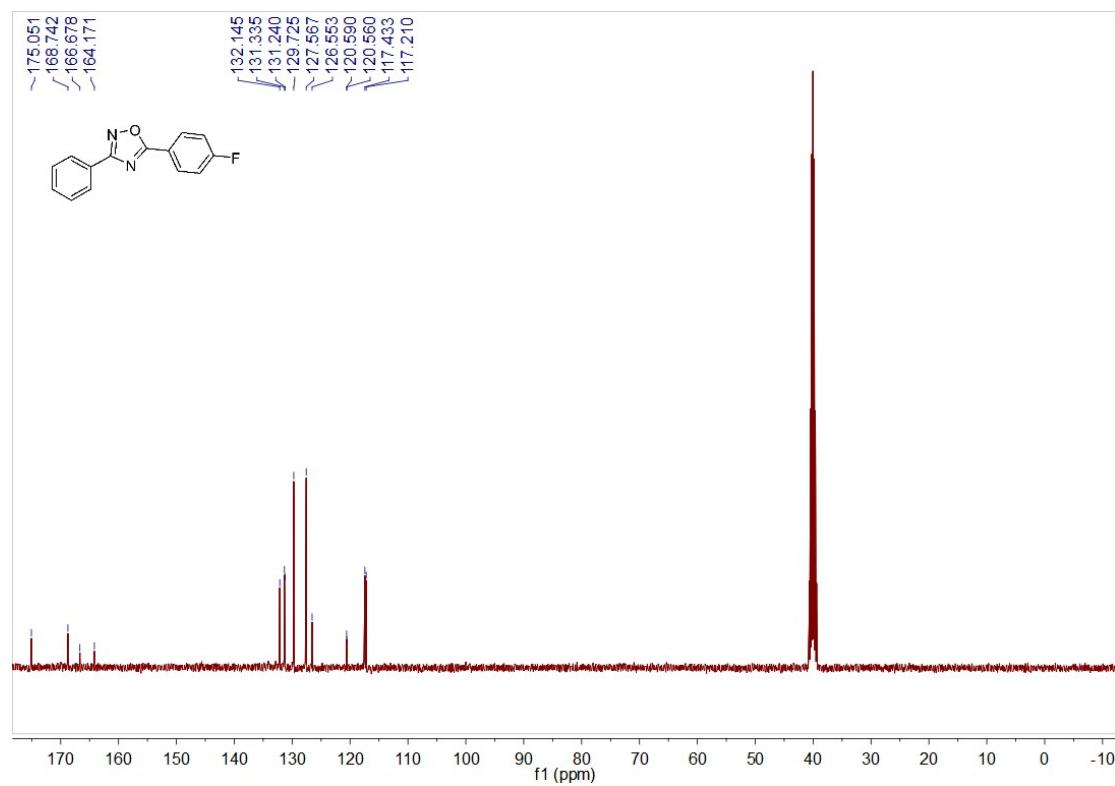
**<sup>13</sup>C NMR spectrum of 2m (DMSO-d<sub>6</sub>, 101 MHz):**



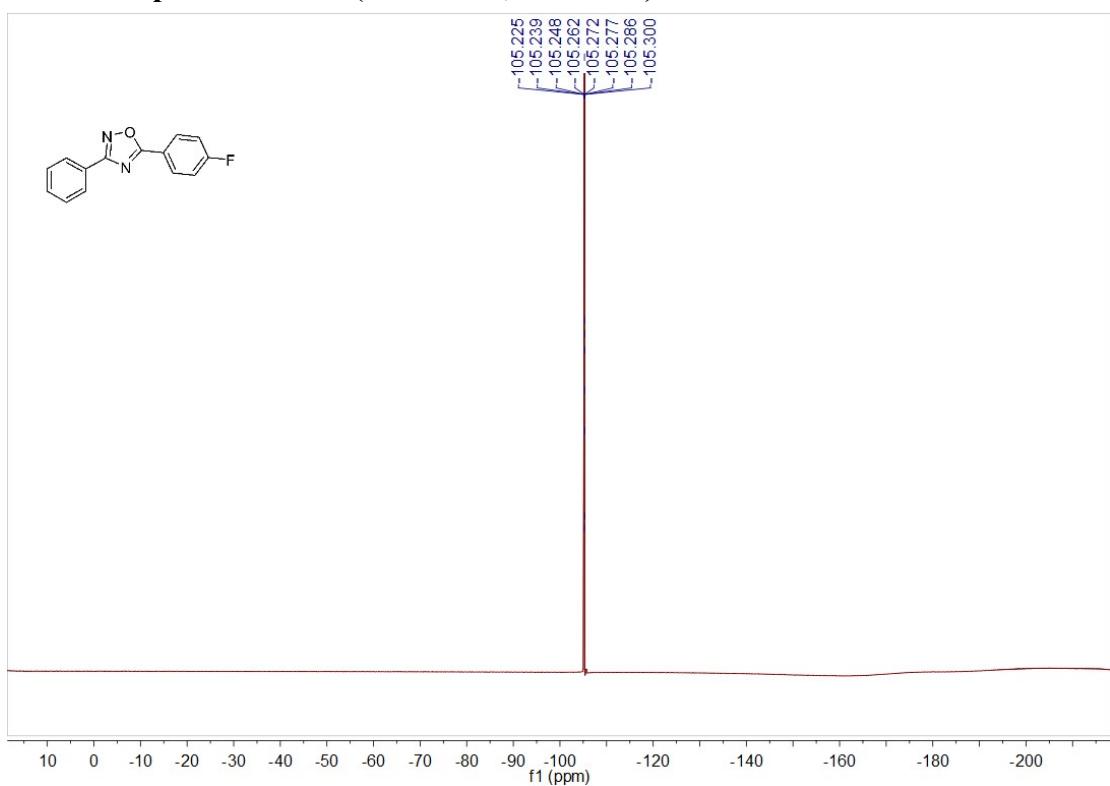
**<sup>1</sup>H NMR spectrum of 2n (DMSO-d<sub>6</sub>, 400 MHz):**



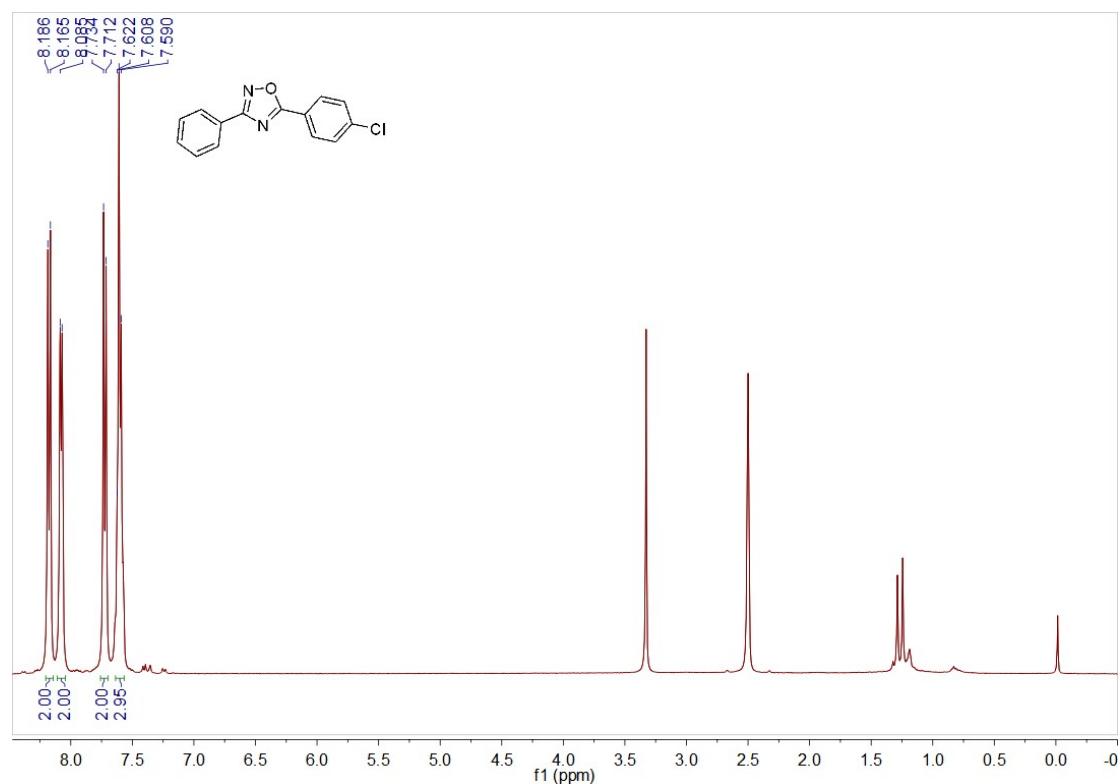
**<sup>13</sup>C NMR spectrum of 2n (DMSO-d<sub>6</sub>, 101 MHz):**



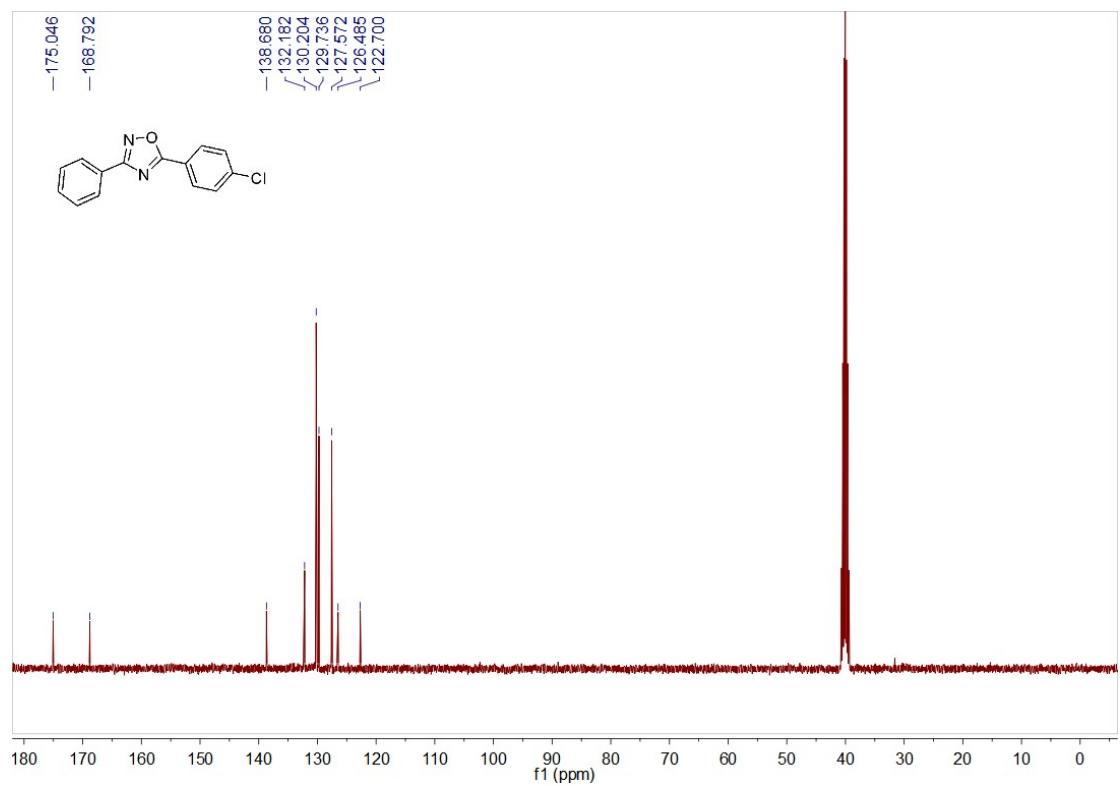
**<sup>19</sup>F NMR spectrum of 2n (DMSO-d6, 376 MHz):**



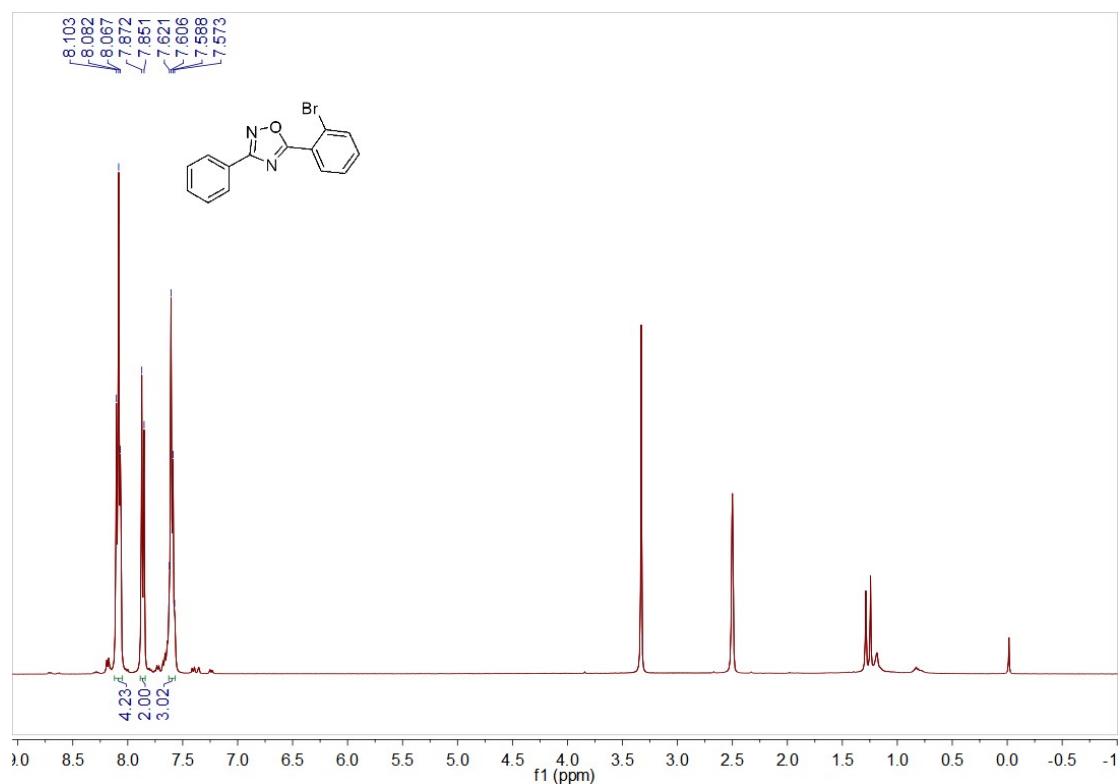
**<sup>1</sup>H NMR spectrum of 2o (DMSO-d<sub>6</sub>, 400 MHz):**



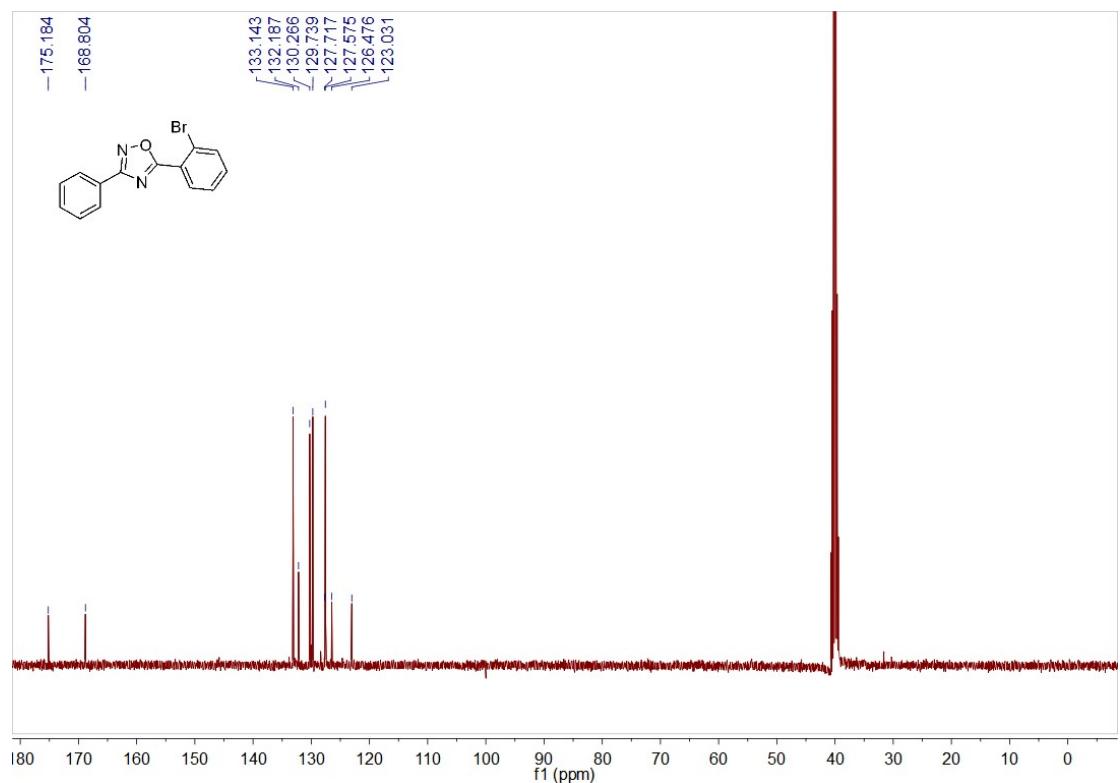
**<sup>13</sup>C NMR spectrum of 2o (DMSO-d<sub>6</sub>, 101 MHz):**



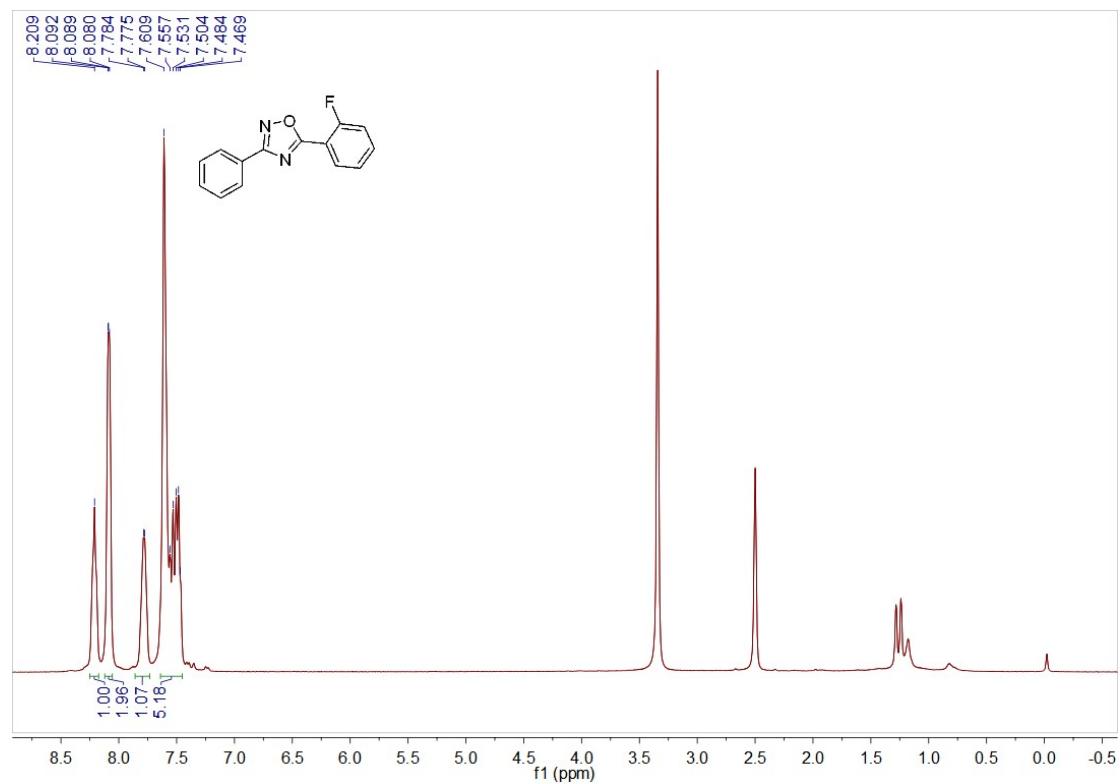
**<sup>1</sup>H NMR spectrum of 2p (DMSO-d<sub>6</sub>, 400 MHz):**



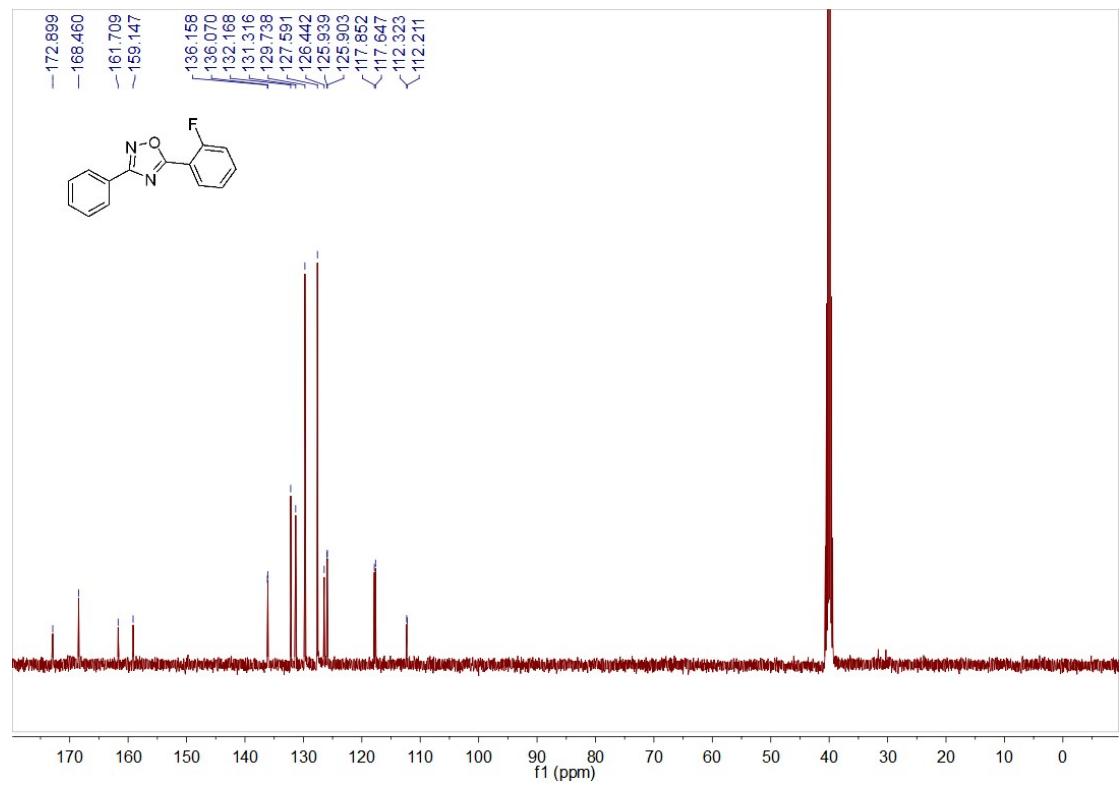
**<sup>13</sup>C NMR spectrum of 2p (DMSO-d<sub>6</sub>, 101 MHz):**



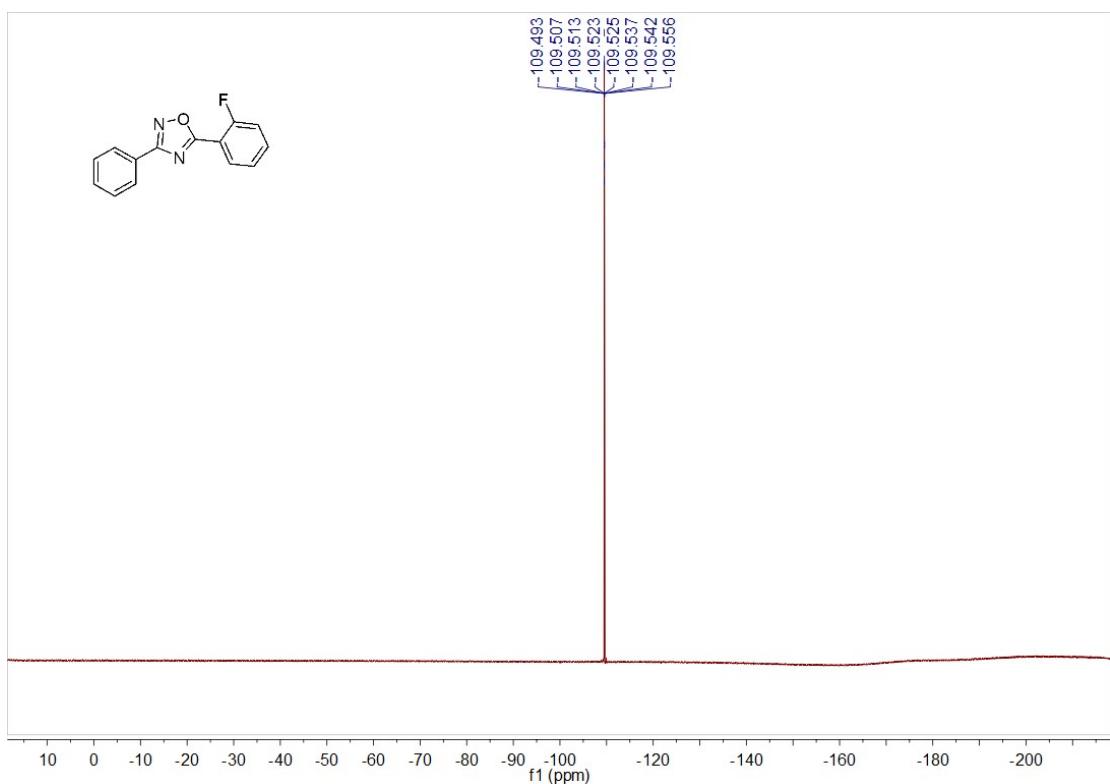
**<sup>1</sup>H NMR spectrum of 2q (DMSO-d<sub>6</sub>, 400 MHz):**



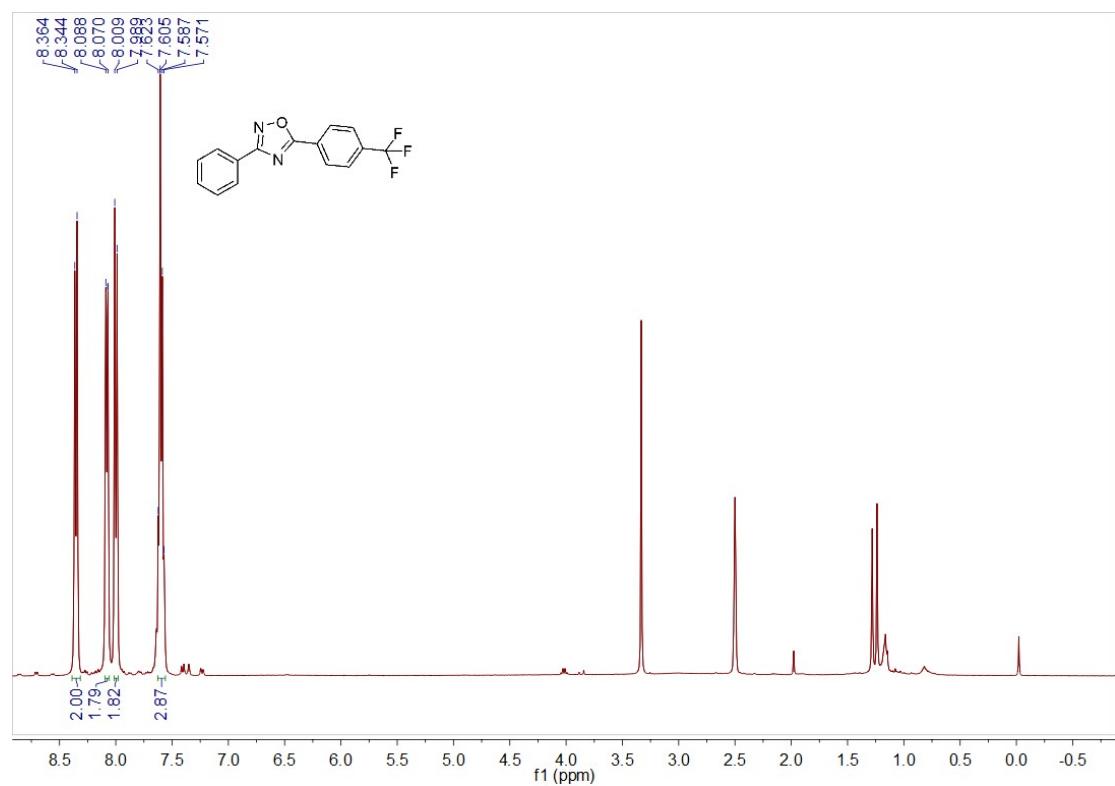
**<sup>13</sup>C NMR spectrum of 2q (DMSO-d<sub>6</sub>, 101 MHz):**



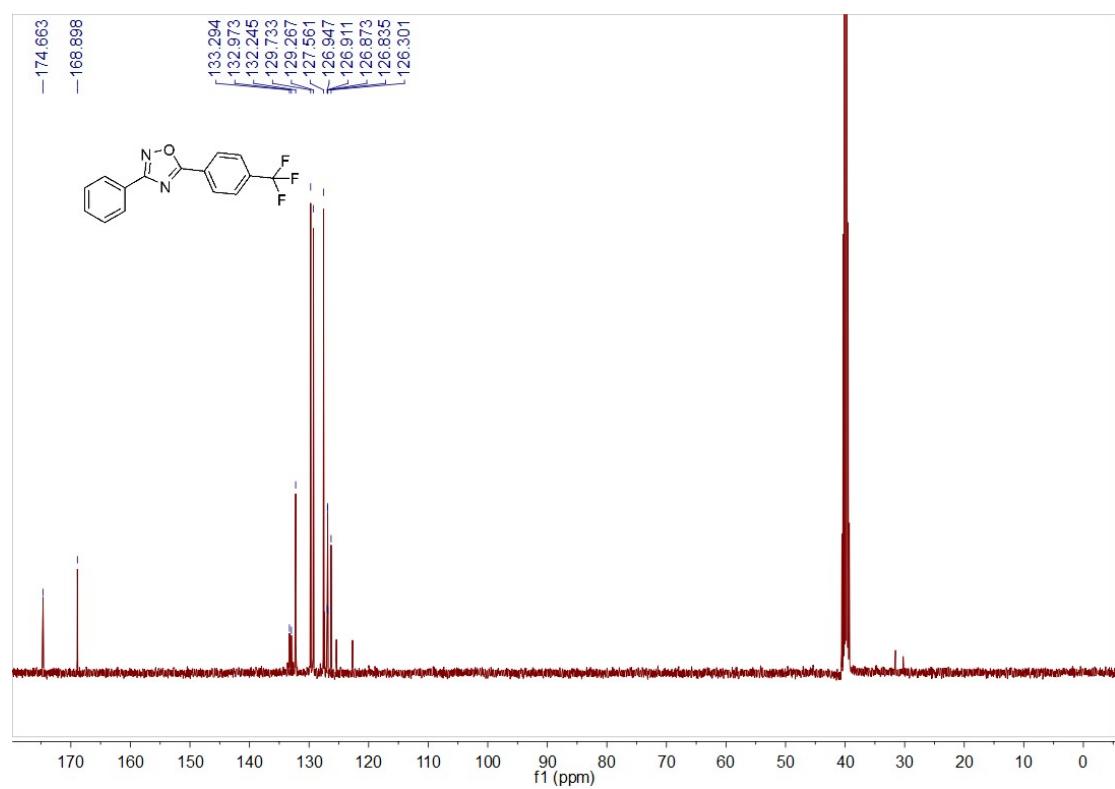
**<sup>19</sup>F NMR spectrum of 2q (DMSO-d6, 376 MHz):**



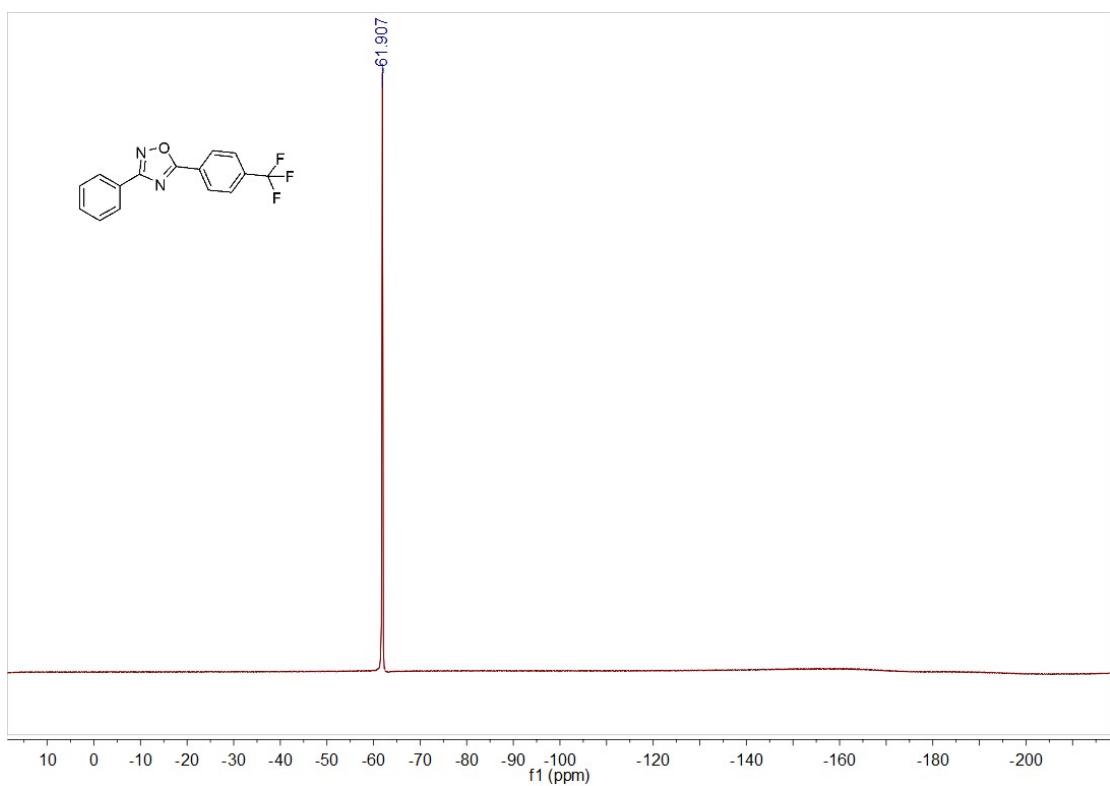
**<sup>1</sup>H NMR spectrum of 2r (DMSO-d<sub>6</sub>, 400 MHz):**



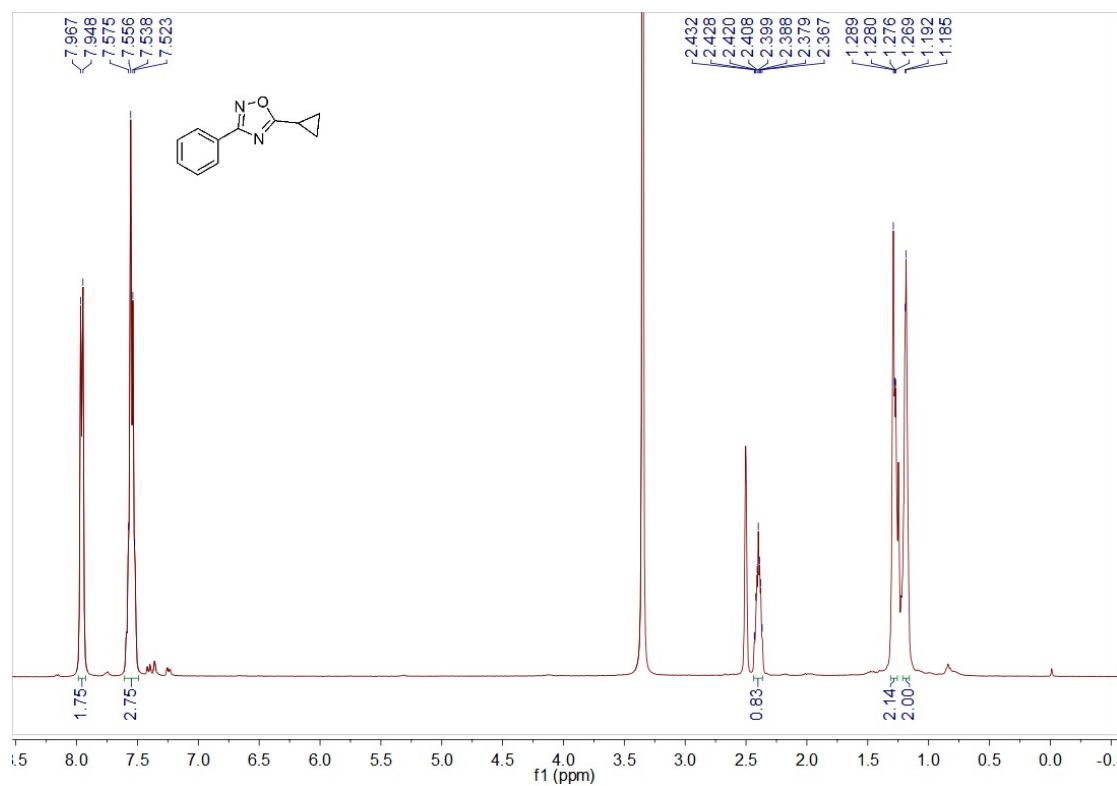
**<sup>13</sup>C NMR spectrum of 2r (DMSO-d<sub>6</sub>, 101 MHz):**



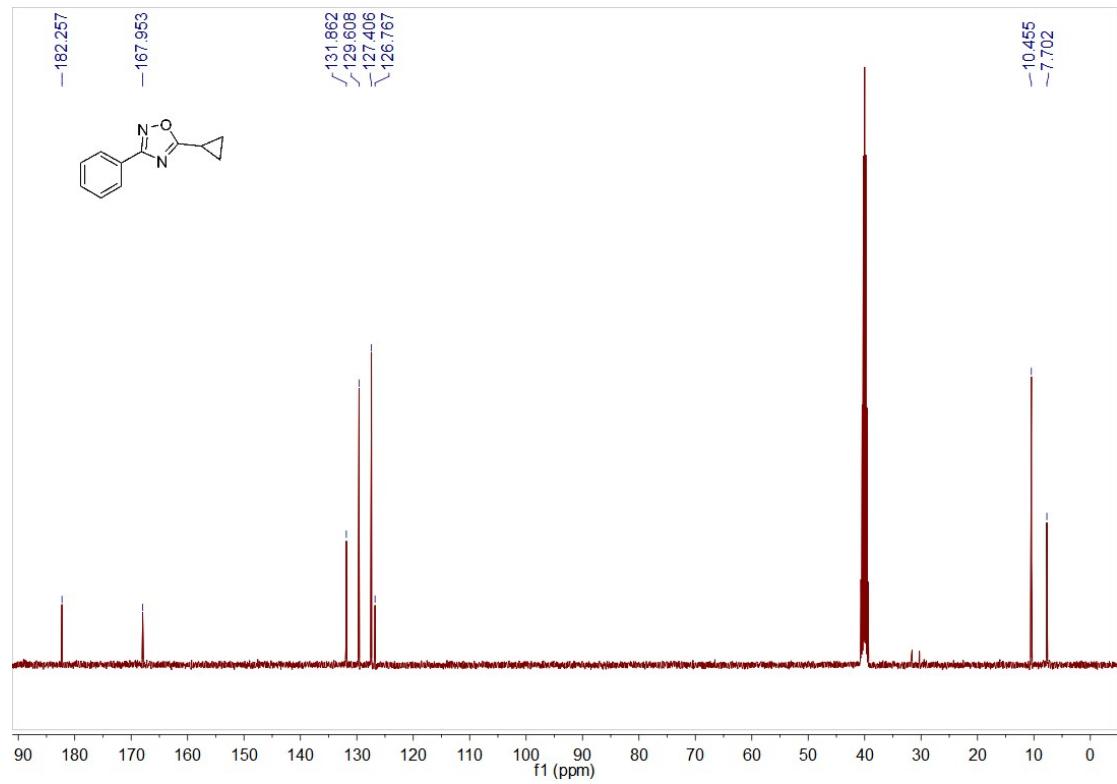
**<sup>19</sup>F NMR spectrum of 2r (DMSO-d<sub>6</sub>, 376 MHz):**



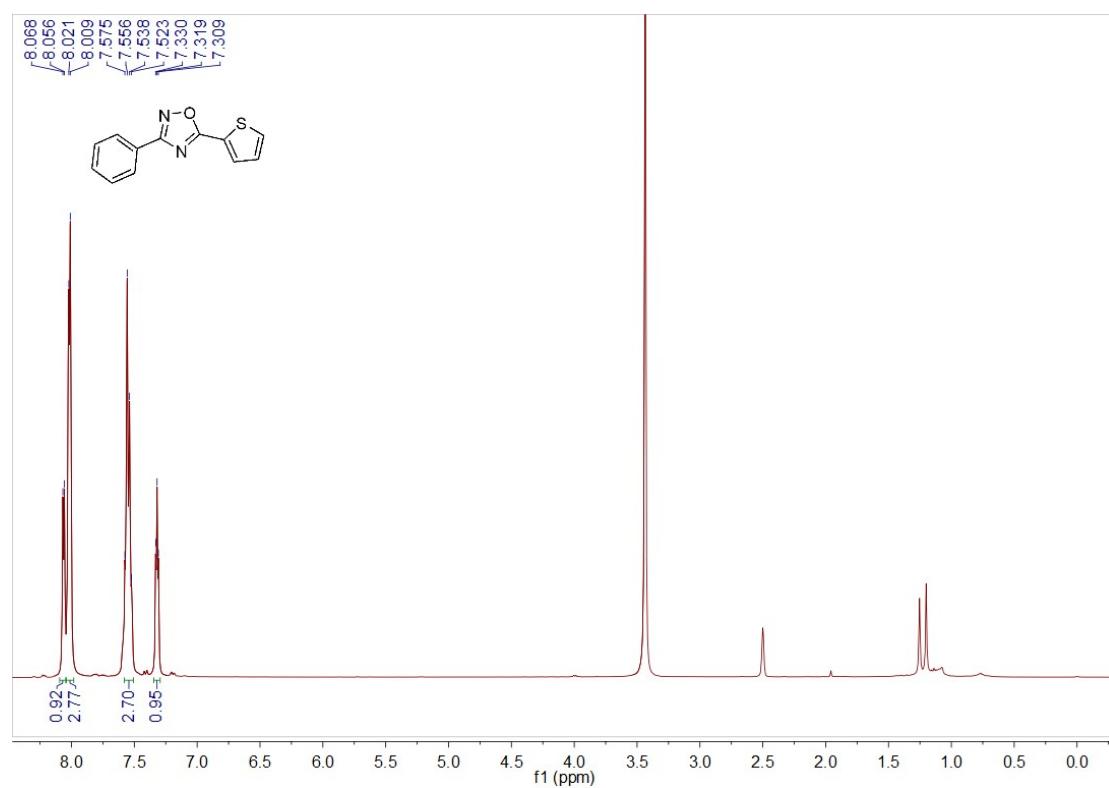
**<sup>1</sup>H NMR spectrum of 2s (DMSO-d<sub>6</sub>, 400 MHz):**



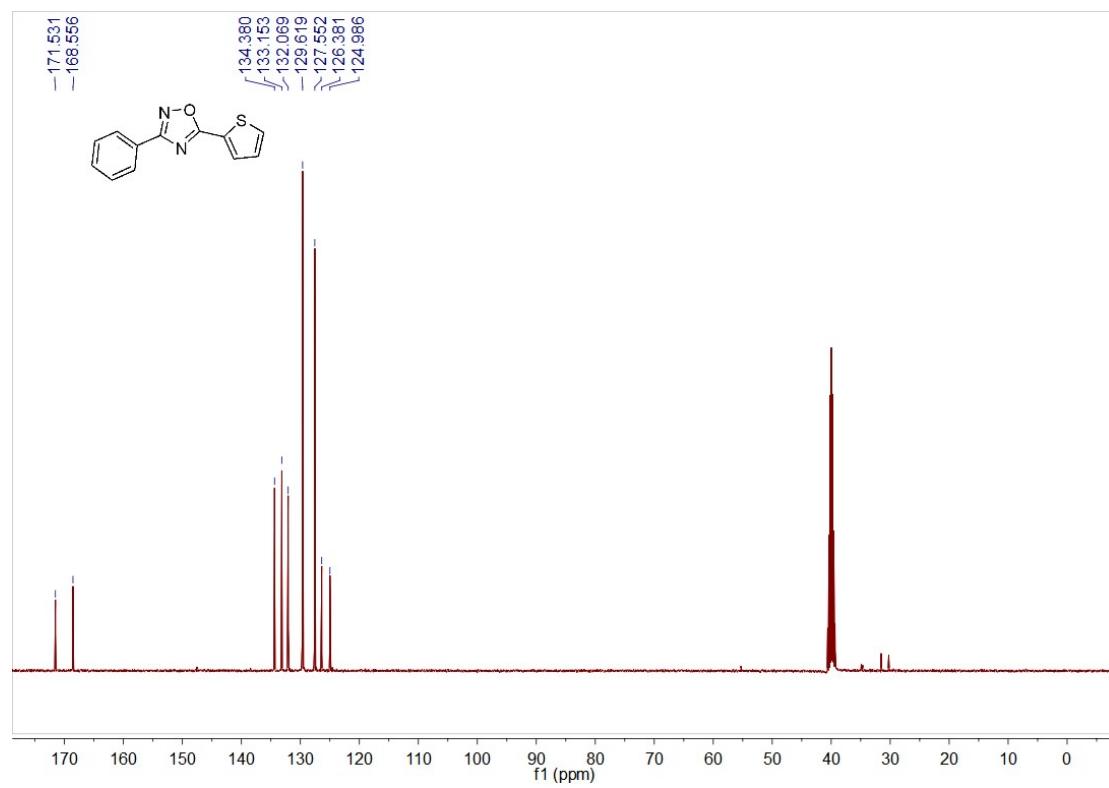
**<sup>13</sup>C NMR spectrum of 2s (DMSO-d<sub>6</sub>, 101 MHz):**



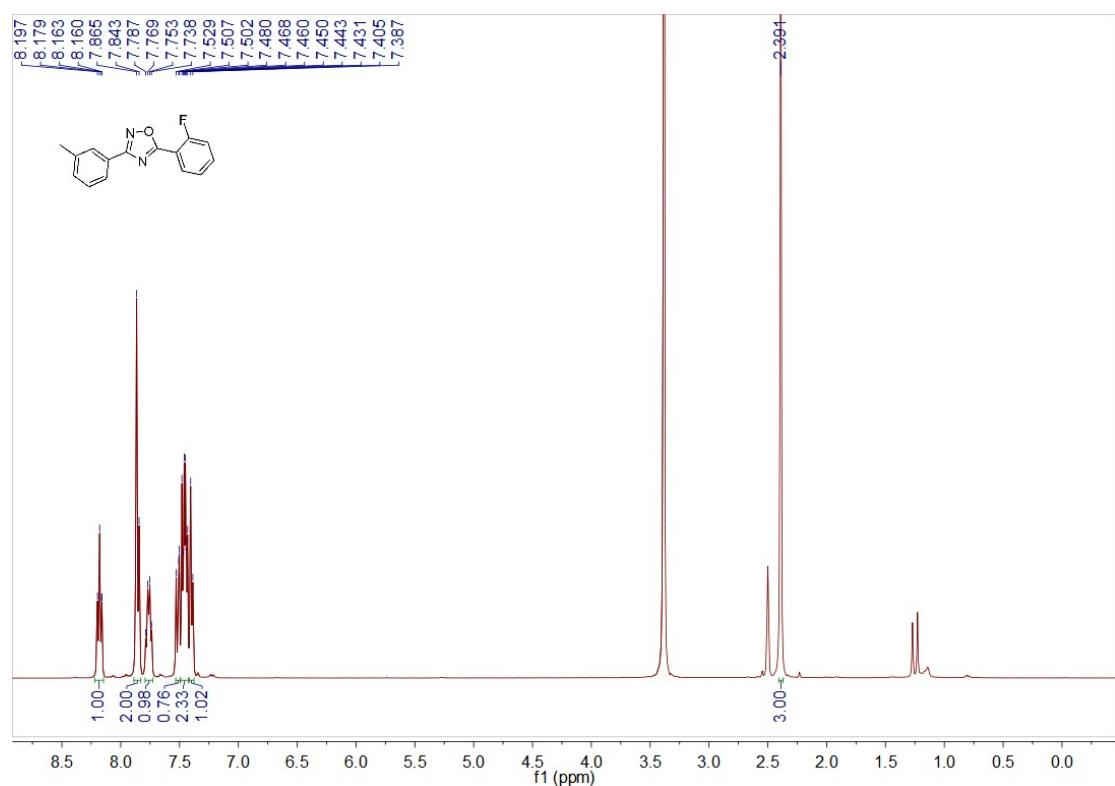
**<sup>1</sup>H NMR spectrum of 2t (DMSO-d<sub>6</sub>, 400 MHz):**



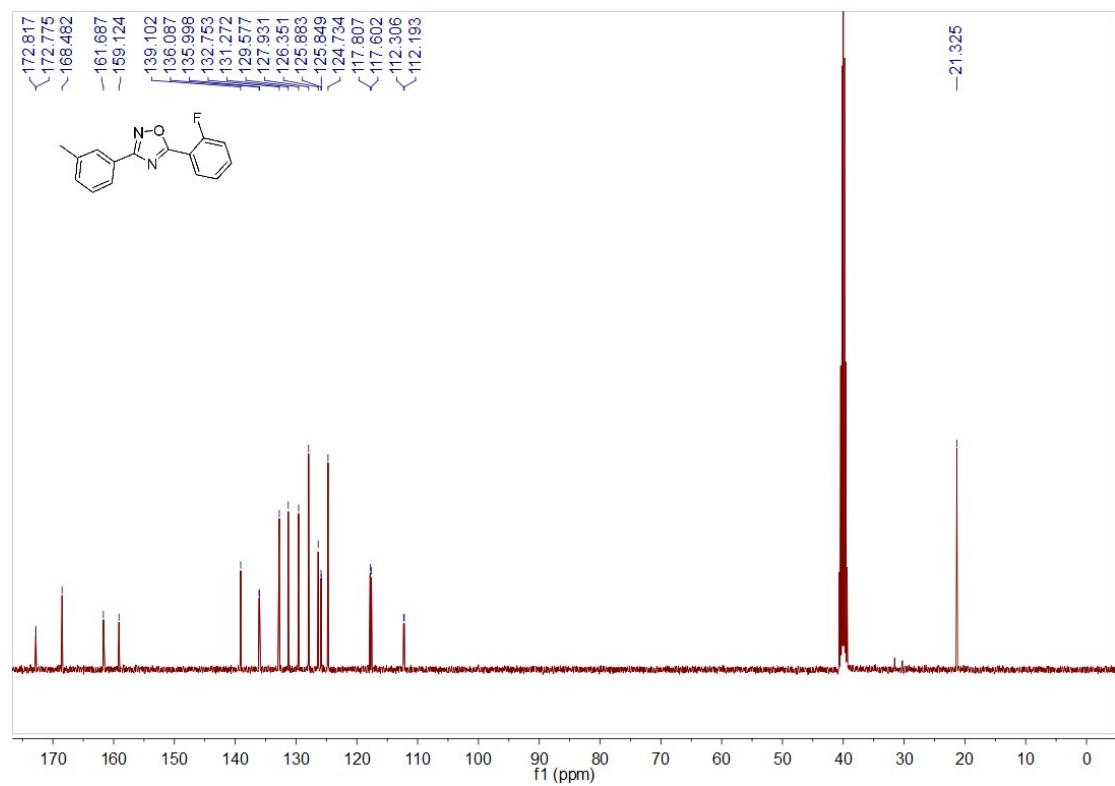
**<sup>13</sup>C NMR spectrum of 2t (DMSO-d<sub>6</sub>, 101 MHz):**



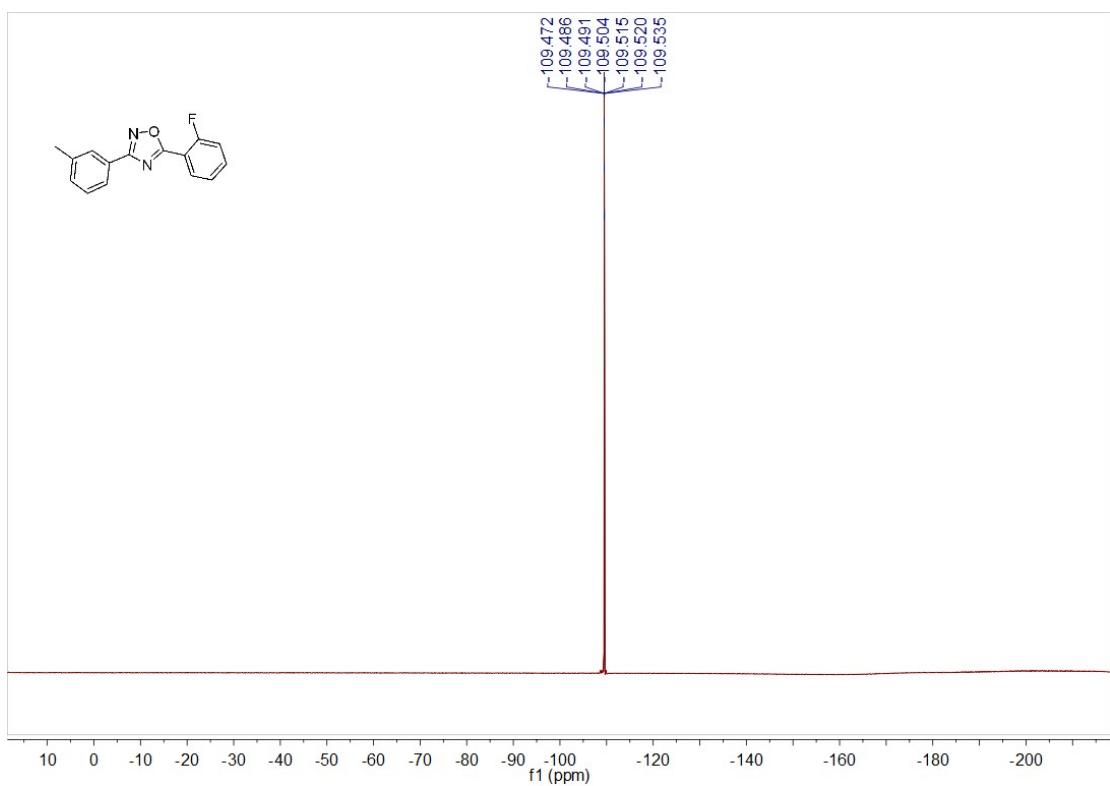
**<sup>1</sup>H NMR spectrum of 2u (DMSO-d<sub>6</sub>, 400 MHz):**



**<sup>13</sup>C NMR spectrum of 2u (DMSO-d<sub>6</sub>, 101 MHz):**



**<sup>19</sup>F NMR spectrum of 2u (DMSO-d6, 376 MHz):**



#### **4. References**

1. Gerfaud T, Wei H L, Neuville L, Zhu J P, *Organic letters*, **2011**, 13, 6172-6175.
2. Zhang F L, Wang Y F, Chiba S, *Organic & biomolecular chemistry*, **2013**, 11, 6003-6007.
3. Dürüst Y, *Magnetic resonance in chemistry*, **1998**, 36, 878-880.
4. Parker P D, Pierce J G, *Synthesis*, **2016**, 48, 1902-1909.
5. Wang C, Rui X Y, Si D J, Dai R P, Zhu Y Y, Wen H M, Li W, Liu J, *Advanced Synthesis & Catalysis*, **2021**, 363, 2825-2833.
6. Kuram M R, Kim W G, Myung K, Hong S Y, *European Journal of Organic Chemistry*, **2016**, 438-442.
7. Li E, Wang M, Wang Z, Yu W Q, Chang J B, *Tetrahedron*, **2018**, 74, 4613-4618.