

## Base-Promoted Synthesis of Multisubstituted Benzo[b][1,4]oxazepines

Jinhai Shen,<sup>a</sup> Lulu Xue,<sup>a</sup> Xing Lin,<sup>a</sup> Guolin Cheng<sup>a</sup> and Xiuling Cui<sup>a\*</sup>

*Key Laboratory of Xiamen Marine and Gene Drugs, Institutes of Molecular Medicine and School of Biomedical Sciences, Huaqiao University & Engineering Research Center of Molecular Medicine, Ministry of Education, Xiamen 361021, China*

Corresponding Author: Xiuling Cui,

Email: [cuixl@hqu.edu.cn](mailto:cuixl@hqu.edu.cn)

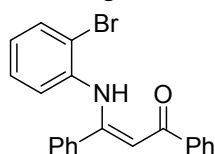
Tel & Fax: +86-592-6162996

### Context

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## 1. General information:

Unless otherwise stated, all commercial materials and solvents were used directly without further purification. Melting points were determined in open glass capillaries and were uncorrected. <sup>1</sup>H NMR spectra were recorded on 400 MHz spectrometers, and <sup>13</sup>C NMR spectra were recorded on a 100 MHz spectrometer. Chemical shifts (in ppm) were referenced to tetramethylsilane ( $\delta = 0$  ppm) in CDCl<sub>3</sub> as an internal standard at room temperature. <sup>13</sup>C NMR spectra were obtained by using the same NMR spectrometers and were calibrated with CDCl<sub>3</sub> ( $\delta = 77.00$  ppm). High-resolution mass spectra (HRMS) were equipped with an ESI source and a TOF detector. Column chromatography was performed on silica gel (70-230 mesh ASTM) using the reported eluents. Thin-layer chromatography (TLC) was carried out on 4×15 cm plates with a layer thickness of 0.2 mm (silica gel 60 F254). The *N*-(2-haloaryl) enaminones **1** were prepared according to the literatures.<sup>1-2</sup>



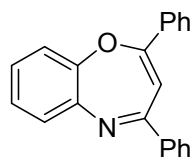
(*Z*)-3-((2-bromophenyl)amino)-1,3-diphenylprop-2-en-1-one **1a**<sup>2</sup>

Yellow solid, mp: 111–112 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  12.72 (s, 1H), 8.00 (d,  $J = 7.3$  Hz, 2H), 7.56 (d,  $J = 7.6$  Hz, 1H), 7.47 (dd,  $J = 13.0, 7.3$  Hz, 3H), 7.38 (d,  $J = 7.2$  Hz, 3H), 7.33 (d,  $J = 6.6$  Hz, 2H), 6.91 – 6.81 (m, 2H), 6.46 (d,  $J = 7.6$  Hz, 1H), 6.19 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  190.1, 160.5, 139.6, 138.5, 135.7, 132.9, 131.5, 129.8, 128.6, 128.4, 128.2, 127.5, 127.1, 125.5, 125.1, 117.3, 98.6.

## 2. General procedure for synthesis of benzo[b][1,4]oxazepines **2**:

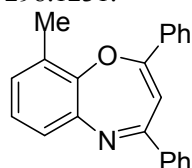
A mixture of *N*-(2-haloaryl)enaminones **1** (0.2 mmol), Cs<sub>2</sub>CO<sub>3</sub> (130 mg, 0.4mmol) in NMP (2 mL) was stirred at 120 °C under N<sub>2</sub> atmosphere for 18 h (monitored by TLC). Then H<sub>2</sub>O (20mL) was added and the resultant was extracted with EtOAc (3 x 10 mL). The combined EtOAc extracts were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. Then solvent was evaporated and the residue was purified by chromatography (silica gel, 10% EtOAc in PE) to give **2**.

## 3. Spectroscopic data for products:



2,4-Diphenylbenzo[b][1,4]oxazepine **2a**<sup>1</sup>

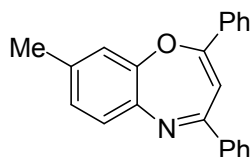
Yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.01 (dd,  $J = 6.6, 3.1$  Hz, 2H), 7.91 (dd,  $J = 6.5, 3.2$  Hz, 2H), 7.50 – 7.42 (m, 7H), 7.25 – 7.19 (m, 2H), 7.13 – 7.06 (m, 1H), 6.63 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  164.1, 163.2, 151.0, 142.1, 139.7, 133.7, 130.5, 130.3, 128.8, 128.6, 128.4, 128.1, 127.5, 126.2, 125.7, 120.8, 106.2; HRMS (ESI) *m/z* calcd for C<sub>21</sub>H<sub>16</sub>NO (MH<sup>+</sup>) 298.1232, found 298.1231.



9-Methyl-2,4-diphenylbenzo[b][1,4]oxazepine **2b**

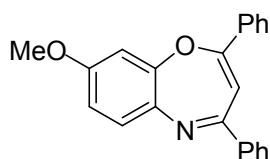
Yellow solid, mp: 114–116 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.02 – 7.93 (m, 2H), 7.92 – 7.79 (m, 2H), 7.52 – 7.36 (m, 6H), 7.28 (d,  $J = 1.4$  Hz, 1H), 7.09 (t,  $J = 7.6$  Hz, 1H), 7.06 – 6.98 (m, 1H), 6.55 (s, 1H), 2.25 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  164.1, 163.4, 150.3, 142.1, 139.8, 134.4, 130.4, 130.3,

130.1, 129.6, 128.5, 128.4, 127.5, 126.5, 126.2, 125.1, 108.0, 17.1; HRMS (ESI)  $m/z$  calcd for  $C_{22}H_{18}NO$  (MH<sup>+</sup>) 312.1388, found 312.1387.



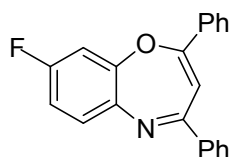
**8-Methyl-2,4-diphenylbenzo[b][1,4]oxazepine 2c**

Yellow solid, mp: 103–105 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.02 – 7.97 (m, 2H), 7.93 – 7.87 (m, 2H), 7.45 (dt,  $J$  = 7.0, 2.6 Hz, 6H), 7.34 (d,  $J$  = 8.0 Hz, 1H), 7.02 (dd,  $J$  = 8.0, 1.1 Hz, 1H), 6.90 (d,  $J$  = 1.0 Hz, 1H), 6.60 (s, 1H), 2.32 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 163.2, 162.7, 150.5, 139.8, 139.6, 138.7, 133.5, 130.3, 130.2, 128.7, 128.4, 128.6, 127.4, 126.5, 126.1, 121.2, 106.2, 20.9; HRMS (ESI)  $m/z$  calcd for  $C_{22}H_{18}NO$  (MH<sup>+</sup>) 312.1388, found 312.1386.



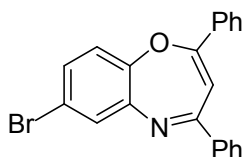
**8-Methoxy-2,4-diphenylbenzo[b][1,4]oxazepine 2d**

Yellow solid, mp: 126–128 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.02 – 7.95 (m, 2H), 7.93 – 7.82 (m, 2H), 7.45 (dt,  $J$  = 3.2, 2.7 Hz, 6H), 7.38 (d,  $J$  = 8.8 Hz, 1H), 6.79 (dd,  $J$  = 8.8, 2.7 Hz, 1H), 6.63 (d,  $J$  = 2.7 Hz, 1H), 6.60 (s, 1H), 3.80 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 161.9, 161.8, 160.1, 151.2, 139.9, 135.7, 133.5, 130.2, 130.1, 129.5, 128.8, 128.4, 127.3, 126.1, 111.2, 106.3, 106.3, 55.7; HRMS (ESI)  $m/z$  calcd for  $C_{22}H_{18}NO_2$  (MH<sup>+</sup>) 328.1338, found 328.1335.



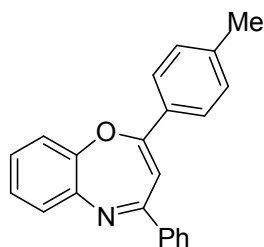
**8-Fluoro-2,4-diphenylbenzo[b][1,4]oxazepine 2e**

Yellow solid, mp: 116–118 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.03 – 7.93 (m, 2H), 7.91 – 7.80 (m, 2H), 7.43 (ddd,  $J$  = 15.1, 7.6, 4.2 Hz, 7H), 6.94 (ddd,  $J$  = 8.7, 8.0, 2.8 Hz, 1H), 6.82 (dd,  $J$  = 8.8, 2.8 Hz, 1H), 6.61 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 163.4, 163.3 (d,  $J$  = 1.7 Hz), 162.3, 160.9, 151.1 (d,  $J$  = 11.0 Hz), 139.5, 138.6 (d,  $J$  = 3.6 Hz), 133.0, 130.5 (d,  $J$  = 4.5 Hz), 129.4, 129.3, 128.8, 128.5, 127.4, 126.1, 112.7 (d,  $J$  = 22.0 Hz), 108.3 (d,  $J$  = 24.1 Hz), 106.2; HRMS (ESI)  $m/z$  calcd for  $C_{21}H_{15}FNO$  (MH<sup>+</sup>) 316.1138, found 316.1135.



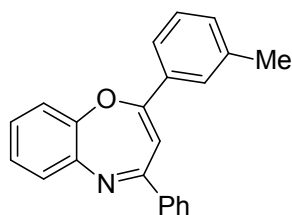
**7-Bromo-2,4-diphenylbenzo[b][1,4]oxazepine 2f**

Yellow solid, mp: 117–119 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.04 – 7.94 (m, 2H), 7.89 – 7.81 (m, 2H), 7.59 (d,  $J$  = 2.4 Hz, 1H), 7.49 – 7.42 (m, 6H), 7.28 (dd,  $J$  = 8.6, 2.5 Hz, 1H), 6.94 (d,  $J$  = 8.6 Hz, 1H), 6.62 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 165.0, 163.6, 150.2, 143.4, 139.2, 133.0, 131.1, 130.8, 130.6, 130.5, 128.8, 128.5, 127.6, 126.1, 122.2, 118.2, 106.2; HRMS (ESI)  $m/z$  calcd for  $C_{21}H_{15}BrNO$  (MH<sup>+</sup>) 376.0337, found 376.0334.



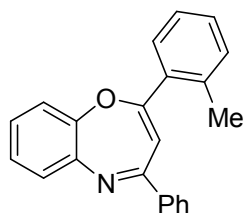
4-Phenyl-2-(*p*-tolyl)benzo[*b*][1,4]oxazepine **2g**

Yellow solid, mp: 70–72 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.04 – 7.95 (m, 2H), 7.79 (d, *J* = 8.3 Hz, 2H), 7.51 – 7.40 (m, 4H), 7.27 – 7.16 (m, 4H), 7.11 – 7.04 (m, 1H), 6.57 (s, 1H), 2.40 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 164.2, 163.4, 151.0, 142.2, 140.7, 139.8, 130.6, 130.4, 129.5, 128.5, 128.4, 128.0, 127.5, 126.2, 125.6, 120.8, 105.3, 21.4; HRMS (ESI) *m/z* calcd for C<sub>22</sub>H<sub>18</sub>NO (MH<sup>+</sup>) 312.1388, found 312.1387.



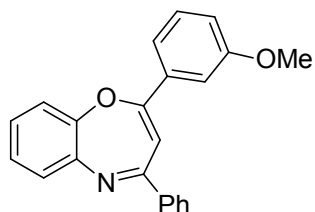
4-Phenyl-2-(*m*-tolyl)benzo[*b*][1,4]oxazepine **2h**

Yellow solid, mp: 59–61 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.01 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.50 – 7.43 (m, 4H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.23 (ddd, *J* = 9.7, 7.7, 4.9 Hz, 3H), 7.11 – 7.07 (m, 1H), 6.61 (s, 1H), 2.42 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 164.1, 163.4, 151.0, 142.1, 139.7, 138.4, 133.3, 131.2, 130.4, 128.6, 128.5, 128.4, 128.0, 127.5, 126.7, 125.7, 123.4, 120.8, 106.1, 21.5; HRMS (ESI) *m/z* calcd for C<sub>22</sub>H<sub>18</sub>NO (MH<sup>+</sup>) 312.1388, found 312.1386.



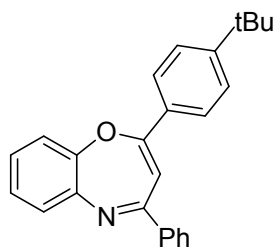
4-Phenyl-2-(*o*-tolyl)benzo[*b*][1,4]oxazepine **2i**

Yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.04 – 7.95 (m, 2H), 7.57 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.46 (td, *J* = 3.8, 1.4 Hz, 4H), 7.33 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.28 (d, *J* = 7.4 Hz, 1H), 7.22 (td, *J* = 7.6, 1.6 Hz, 2H), 7.17 (dd, *J* = 7.9, 1.8 Hz, 1H), 6.87 (dd, *J* = 7.9, 1.4 Hz, 1H), 6.22 (s, 1H), 2.54 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 165.2, 163.6, 151.2, 141.8, 139.6, 136.9, 134.6, 131.0, 130.5, 129.7, 129.2, 128.6, 128.4, 128.0, 127.5, 125.7, 125.7, 121.1, 111.0, 21.5; HRMS (ESI) *m/z* calcd for C<sub>22</sub>H<sub>18</sub>NO (MH<sup>+</sup>) 312.1388, found 312.1387.



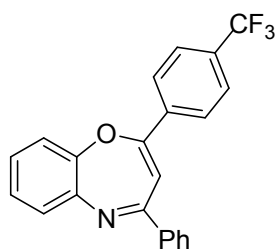
2-(3-Methoxyphenyl)-4-phenylbenzo[*b*][1,4]oxazepine **2j**

Yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.05 – 7.97 (m, 2H), 7.46 (td, *J* = 6.6, 2.4 Hz, 6H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.24 – 7.19 (m, 2H), 7.10 – 7.07 (m, 1H), 7.00 – 6.95 (m, 1H), 6.61 (s, 1H), 3.86 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 164.0, 162.8, 159.8, 150.9, 142.1, 139.7, 134.8, 130.5, 129.8, 128.5, 128.4, 128.1, 127.5, 125.7, 120.8, 118.6, 115.8, 111.8, 106.4, 55.4; HRMS (ESI) *m/z* calcd for C<sub>22</sub>H<sub>18</sub>NO<sub>2</sub> (MH<sup>+</sup>) 328.1388, found 328.1385.



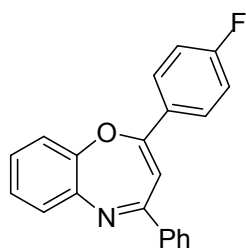
2-(4-(*tert*-Butyl)phenyl)-4-phenylbenzo[*b*][1,4]oxazepine **2k**

Yellow oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.05 – 7.97 (m, 2H), 7.88 – 7.77 (m, 2H), 7.49 – 7.43 (m, 6H), 7.23 – 7.17 (m, 2H), 7.12 – 7.05 (m, 1H), 6.59 (s, 1H), 1.35 (s, 9H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  164.2, 163.3, 153.9, 151.0, 142.2, 139.8, 130.5, 130.4, 128.5, 128.4, 128.0, 127.5, 126.0, 125.7, 125.6, 120.8, 105.5, 34.9, 31.1; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{25}\text{H}_{24}\text{NO}$  ( $\text{MH}^+$ ) 354.1858, found 354.1854.



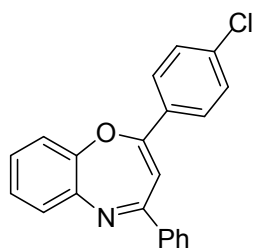
4-Phenyl-2-(4-(trifluoromethyl)phenyl)benzo[*b*][1,4]oxazepine **2l**

Yellow solid, mp: 85–87 °C.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.05 – 7.94 (m, 4H), 7.70 (d,  $J = 8.3$  Hz, 2H), 7.51 – 7.44 (m, 4H), 7.28 – 7.19 (m, 2H), 7.10 – 7.03 (m, 1H), 6.69 (s, 1H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.5, 161.3, 150.7, 141.8, 139.3, 136.7, 131.9 (d,  $J = 32.7$  Hz), 130.7, 128.8, 128.5, 128.4, 127.4, 126.4, 126.0, 125.8 (d,  $J = 3.8$  Hz), 120.6, 107.9; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{22}\text{H}_{15}\text{F}_3\text{NO}$  ( $\text{MH}^+$ ) 366.1106, found 366.1105.



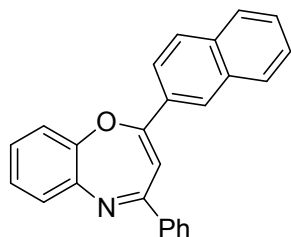
2-(4-Fluorophenyl)-4-phenylbenzo[*b*][1,4]oxazepine **2m**

Yellow oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.05 – 7.95 (m, 2H), 7.94 – 7.83 (m, 2H), 7.46 (ddd,  $J = 4.8, 3.7, 2.1$  Hz, 4H), 7.22 (ddd,  $J = 9.7, 4.4, 2.5$  Hz, 2H), 7.13 (t,  $J = 8.7$  Hz, 2H), 7.08 – 7.03 (m, 1H), 6.55 (s, 1H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  164.0 (d,  $J = 251.6$  Hz), 163.9, 162.1, 150.8, 142.0, 139.6, 130.5, 129.6 (d,  $J = 3.3$  Hz), 128.6, 128.5, 128.2 (d,  $J = 8.6$  Hz), 128.1, 127.5, 125.8, 120.6, 115.8 (d,  $J = 22.0$  Hz), 105.8 (d,  $J = 1.8$  Hz). HRMS (ESI)  $m/z$  calcd for  $\text{C}_{21}\text{H}_{15}\text{FNO}$  ( $\text{MH}^+$ ) 316.1138, found 316.1134.



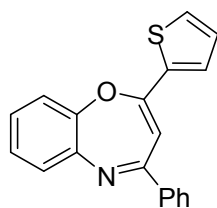
2-(4-Chlorophenyl)-4-phenylbenzo[*b*][1,4]oxazepine **2n**

Yellow solid, mp: 82–83 °C.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.03 – 7.95 (m, 2H), 7.89 – 7.78 (m, 2H), 7.49 – 7.40 (m, 6H), 7.22 (ddd,  $J = 9.7, 4.2, 2.4$  Hz, 2H), 7.08 – 7.02 (m, 1H), 6.58 (s, 1H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.8, 161.9, 150.8, 141.9, 139.5, 136.6, 131.9, 130.6, 129.0, 128.7, 128.5, 128.2, 127.5, 127.4, 125.9, 120.6, 106.4; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{21}\text{H}_{15}\text{ClNO}$  ( $\text{MH}^+$ ) 332.0842, found 332.0837.



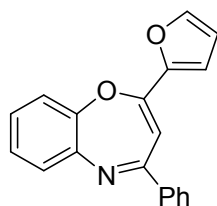
**2-(Naphthalen-2-yl)-4-phenylbenzo[b][1,4]oxazepine 2o**

Yellow solid, mp: 116–119 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.51 (s, 1H), 8.13 – 8.01 (m, 2H), 7.99 – 7.94 (m, 1H), 7.89 – 7.78 (m, 3H), 7.57 – 7.51 (m, 2H), 7.51 – 7.38 (m, 4H), 7.25 – 7.15 (m, 3H), 6.75 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 164.1, 163.0, 150.9, 142.2, 139.7, 134.1, 133.1, 130.5, 128.9, 128.6, 128.6, 128.5, 128.2, 127.7, 127.6, 127.4, 126.8, 126.5, 125.7, 122.9, 120.8, 106.6; HRMS (ESI) m/z calcd for C<sub>25</sub>H<sub>18</sub>NO (MH<sup>+</sup>) 348.1388, found 348.1386.



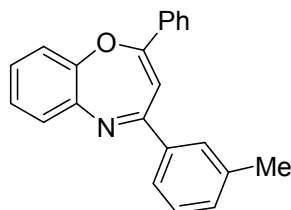
**4-Phenyl-2-(thiophen-2-yl)benzo[b][1,4]oxazepine 2p**

Yellow solid, mp: 88–90 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.02 – 7.96 (m, 2H), 7.61 (dd, *J* = 3.7, 1.0 Hz, 1H), 7.50 – 7.40 (m, 5H), 7.25 – 7.21 (m, 2H), 7.15 – 7.09 (m, 2H), 6.47 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 163.7, 158.2, 150.8, 141.9, 139.7, 138.1, 130.5, 128.7, 128.5, 128.4, 128.3, 128.2, 127.5, 127.3, 125.9, 120.8, 104.5; HRMS (ESI) m/z calcd for C<sub>19</sub>H<sub>14</sub>NOS (MH<sup>+</sup>) 304.0796, found 304.07962.



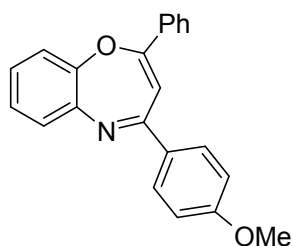
**2-(Furan-2-yl)-4-phenylbenzo[b][1,4]oxazepine 2q**

Yellow solid, mp: 95–97 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.06 – 7.99 (m, 2H), 7.45 (ddd, *J* = 7.0, 4.1, 2.2 Hz, 5H), 7.22 (dt, *J* = 5.9, 2.3 Hz, 2H), 7.01 (dd, *J* = 14.4, 6.4 Hz, 2H), 6.52 (dd, *J* = 4.1, 2.4 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 163.8, 154.2, 151.0, 148.5, 144.6, 141.9, 139.5, 130.5, 128.8, 128.4, 128.1, 127.5, 125.9, 120.5, 112.1, 112.0, 104.1; HRMS (ESI) m/z calcd for C<sub>19</sub>H<sub>14</sub>NO<sub>2</sub> (MH<sup>+</sup>) 288.1025, found 288.1020.



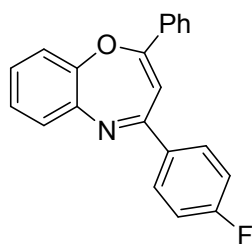
**2-Phenyl-4-(*m*-tolyl)benzo[b][1,4]oxazepine 2r**

Yellow solid, mp: 105–108 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.00 – 7.88 (m, 2H), 7.84 (s, 1H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.52 – 7.39 (m, 4H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 7.4 Hz, 1H), 7.25 – 7.16 (m, 2H), 7.12 – 7.04 (m, 1H), 6.62 (s, 1H), 2.44 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 164.3, 163.0, 151.1, 142.1, 139.7, 138.2, 133.4, 131.3, 130.3, 128.7, 128.6, 128.3, 128.0, 128.0, 126.2, 125.7, 124.7, 120.8, 106.3, 21.5; HRMS (ESI) m/z calcd for C<sub>22</sub>H<sub>18</sub>NO (MH<sup>+</sup>) 312.1388, found 312.1384.



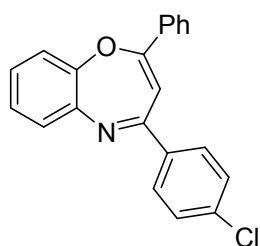
**4-(4-Methoxyphenyl)-2-phenylbenzo[b][1,4]oxazepine 2s**

Yellow solid, mp: 106–108 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.00 – 7.96 (m, 2H), 7.94 – 7.87 (m, 2H), 7.48 – 7.41 (m, 4H), 7.23 – 7.15 (m, 2H), 7.11 – 7.06 (m, 1H), 6.99 – 6.94 (m, 2H), 6.62 (s, 1H), 3.86 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 163.2, 162.8, 161.6, 151.0, 142.2, 133.5, 132.4, 130.2, 129.1, 128.7, 128.4, 127.6, 126.1, 125.7, 120.7, 113.7, 106.0, 55.4; HRMS (ESI) m/z calcd for C<sub>22</sub>H<sub>18</sub>NO<sub>2</sub> (MH<sup>+</sup>) 328.1338, found 328.1333.



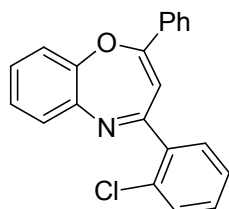
**4-(4-Fluorophenyl)-2-phenylbenzo[b][1,4]oxazepine 2t**

Yellow solid, mp: 105–107 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.04 – 7.99 (m, 2H), 7.95 – 7.86 (m, 2H), 7.44 (ddd, *J* = 9.3, 3.9, 2.1 Hz, 4H), 7.24 – 7.19 (m, 2H), 7.16 – 7.08 (m, 3H), 6.58 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 164.4 (d, *J* = 250.7 Hz), 163.3, 162.8, 150.9, 142.0, 135.9 (d, *J* = 3.0 Hz), 133.3, 130.5, 129.7, 129.6, 128.8, 128.8 (d, *J* = 34.5 Hz), 126.2, 125.8, 120.9, 115.4 (d, *J* = 21.7 Hz), 105.8; HRMS (ESI) m/z calcd for C<sub>21</sub>H<sub>15</sub>FNO (MH<sup>+</sup>) 316.1138, found 316.1136.



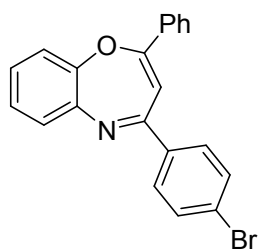
**4-(4-Chlorophenyl)-2-phenylbenzo[b][1,4]oxazepine 2u**

Yellow solid, mp: 82–84 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.02 – 7.85 (m, 4H), 7.48 – 7.39 (m, 6H), 7.22 (ddd, *J* = 5.3, 3.7, 2.7 Hz, 2H), 7.08 (d, *J* = 9.4 Hz, 1H), 6.56 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 163.4, 162.7, 150.8, 141.9, 138.1, 136.6, 133.2, 130.5, 128.8, 128.8, 128.6, 128.5, 128.3, 126.2, 125.8, 120.8, 105.6; HRMS (ESI) m/z calcd for C<sub>21</sub>H<sub>15</sub>ClNO (MH<sup>+</sup>) 332.0842, found 332.0840.



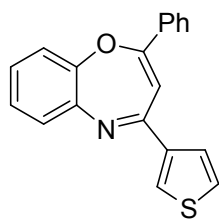
**4-(2-Chlorophenyl)-2-phenylbenzo[b][1,4]oxazepine 2v**

Yellow solid, mp: 135–137 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.47 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.75 – 7.70 (m, 2H), 7.65 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.58 (ddd, *J* = 8.6, 7.2, 1.7 Hz, 1H), 7.44 – 7.35 (m, 5H), 7.31 (td, *J* = 7.6, 1.3 Hz, 1H), 7.00 – 6.93 (m, 2H), 6.36 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 158.3, 153.9, 152.7, 149.8, 133.2, 132.5, 132.1, 130.7, 128.7, 128.1, 126.0, 125.3, 125.1, 124.2, 122.1, 121.8, 117.6, 116.0, 98.4; HRMS (ESI) m/z calcd for C<sub>21</sub>H<sub>15</sub>ClNO (MH<sup>+</sup>) 332.0842, found 332.0839.



4-(4-Bromophenyl)-2-phenylbenzo[b][1,4]oxazepine **2w**

Yellow solid, mp: 104–106 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.95 – 7.83 (m, 4H), 7.59 – 7.55 (m, 2H), 7.43 (ddd, *J* = 8.0, 4.9, 3.1 Hz, 4H), 7.23 – 7.18 (m, 2H), 7.08 (dd, *J* = 6.0, 3.5 Hz, 1H), 6.55 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 163.4, 162.8, 150.8, 141.9, 138.5, 133.2, 131.6, 130.5, 129.1, 128.8, 128.5, 128.4, 126.2, 125.8, 125.1, 120.8, 105.6; HRMS (ESI) *m/z* calcd for C<sub>21</sub>H<sub>15</sub>BrNO (MH<sup>+</sup>) 376.0337, found 376.0331.



2-Phenyl-4-(thiophen-3-yl)benzo[b][1,4]oxazepine **2x**

Yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.93 – 7.85 (m, 2H), 7.82 (dd, *J* = 2.9, 1.2 Hz, 1H), 7.76 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.41 (dddd, *J* = 18.4, 8.0, 4.3, 2.2 Hz, 5H), 7.23 – 7.15 (m, 2H), 7.09 – 7.05 (m, 1H), 6.61 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 163.1, 159.4, 150.9, 143.5, 142.1, 133.3, 130.3, 128.7, 128.6, 127.9, 126.8, 126.6, 126.1, 126.0, 125.7, 120.8, 105.9; HRMS (ESI) *m/z* calcd for C<sub>19</sub>H<sub>14</sub>NOS (MH<sup>+</sup>) 304.0796, found 304.0796.

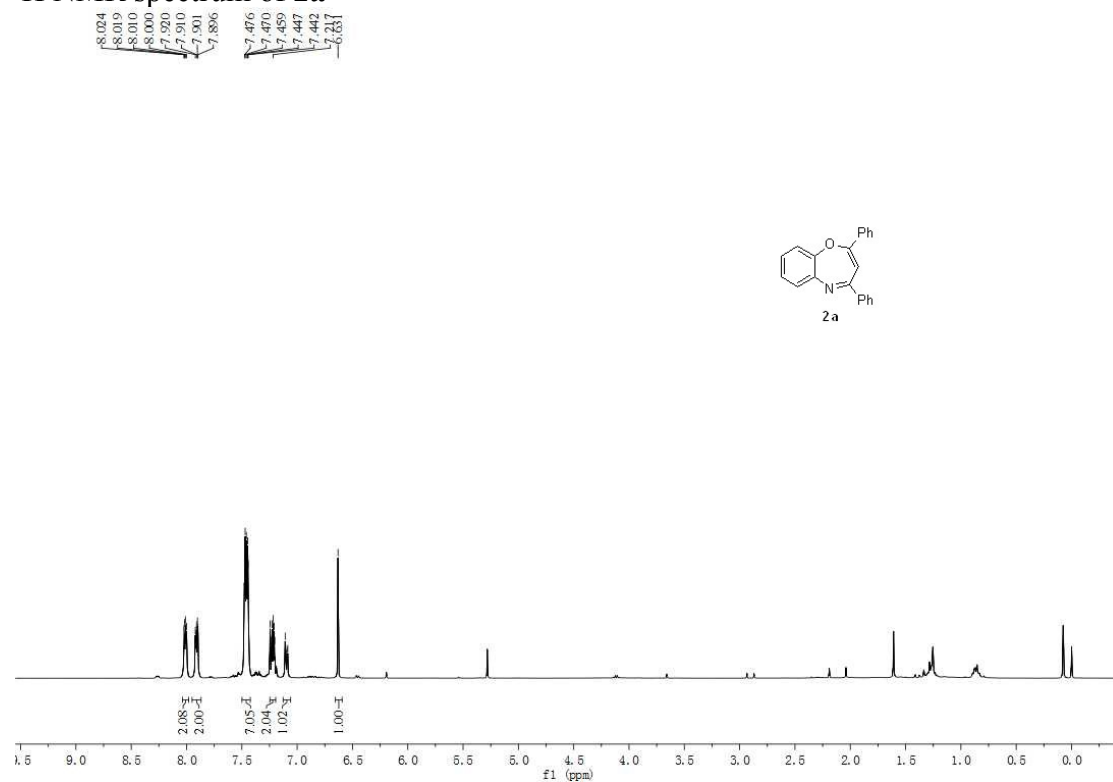
**Reference:**

1. R. Bernini, S. Cacchi, G. Fabrizi, E. Filisti and A. Sferrazza, *Synlett.*, 2009, **9**, 1480 - 1484.
2. R. Bernini, G. Fabrizi, A. Sferrazza and S. Cacchi, *Angew. Chem., Int. Ed.*, 2009, **48**, 8078–8081.

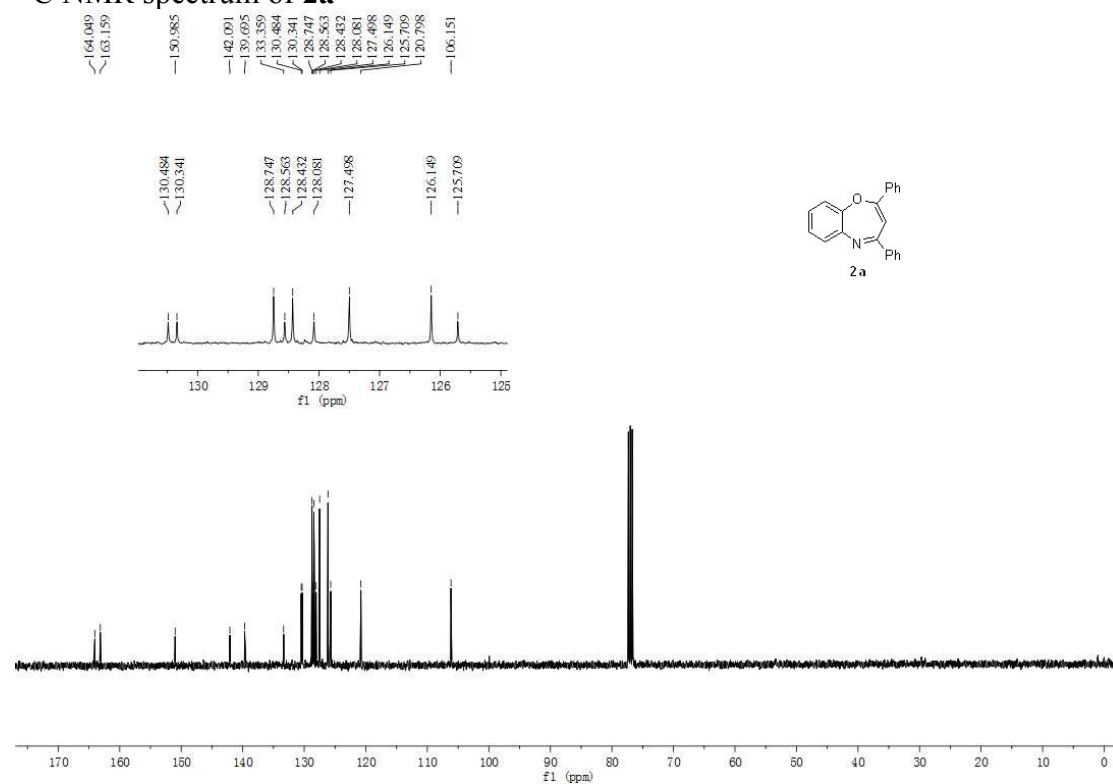


## 4. $^1\text{H}$ NMR, $^{13}\text{C}$ NMR spectra of products

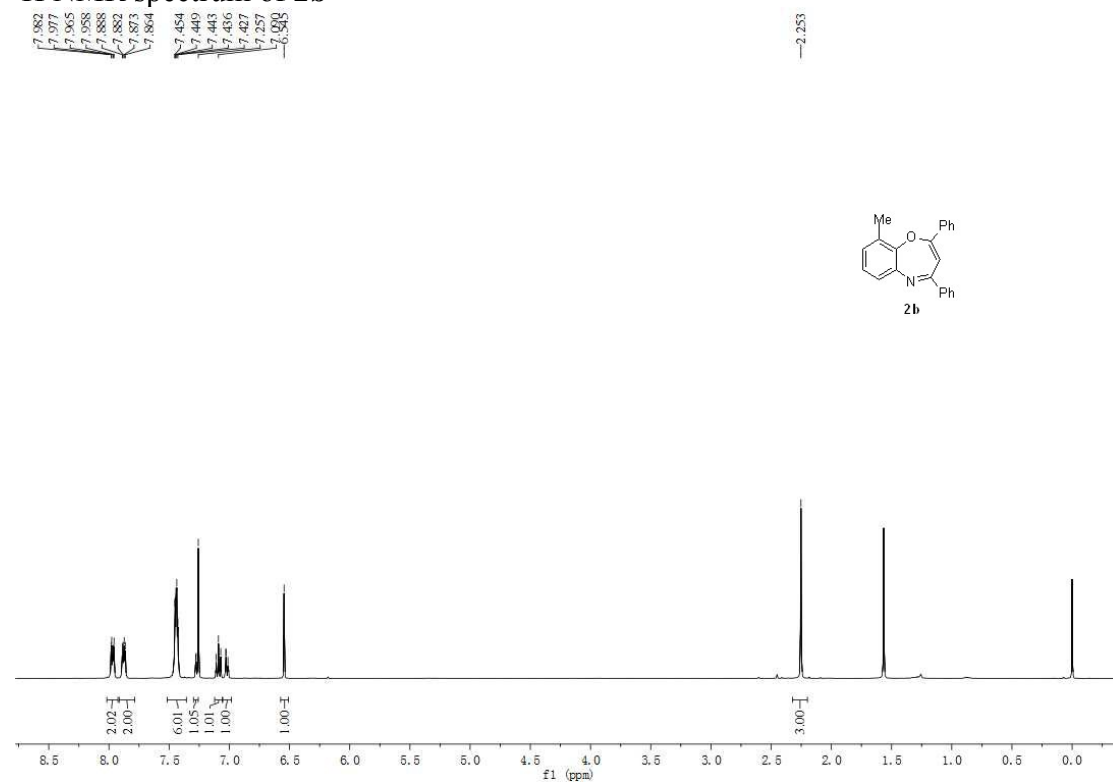
### $^1\text{H}$ NMR spectrum of **2a**



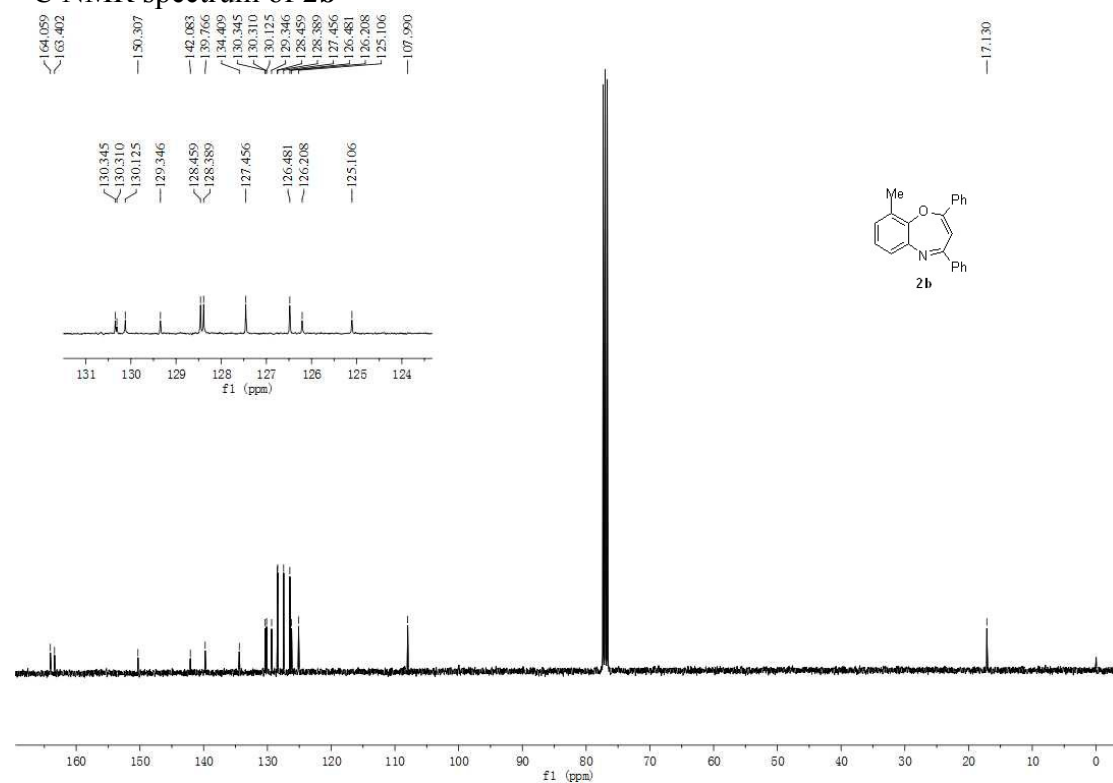
### $^{13}\text{C}$ NMR spectrum of **2a**



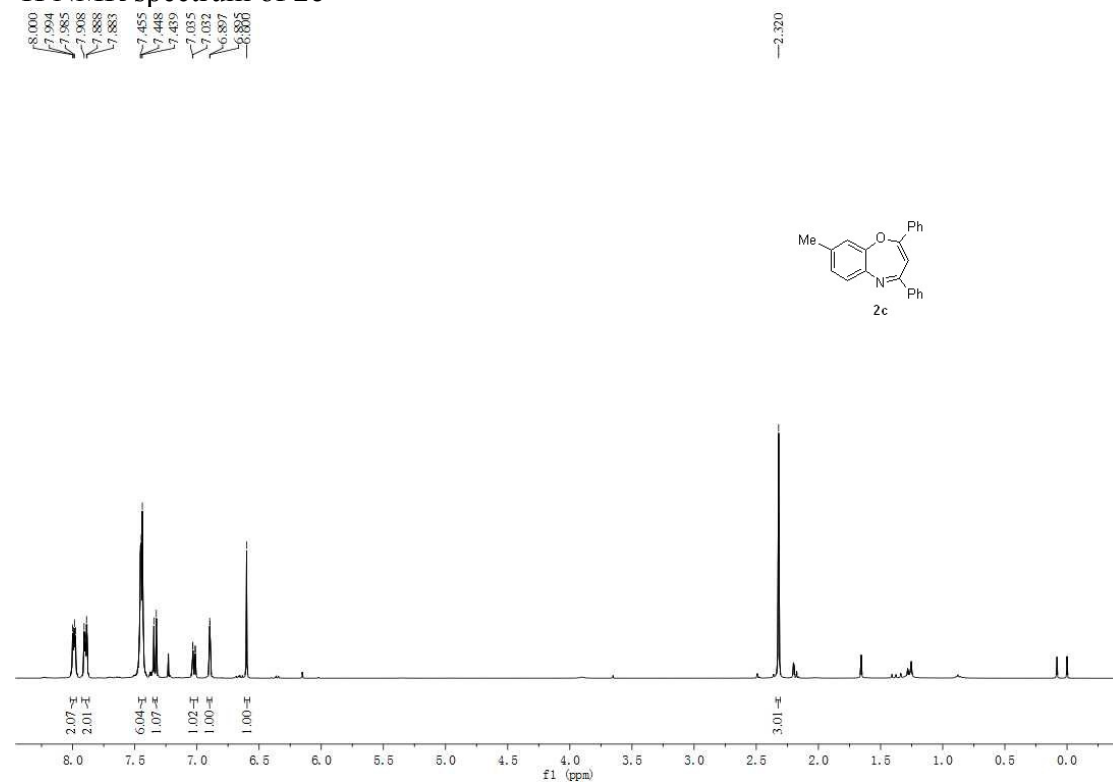
### <sup>1</sup>H NMR spectrum of **2b**



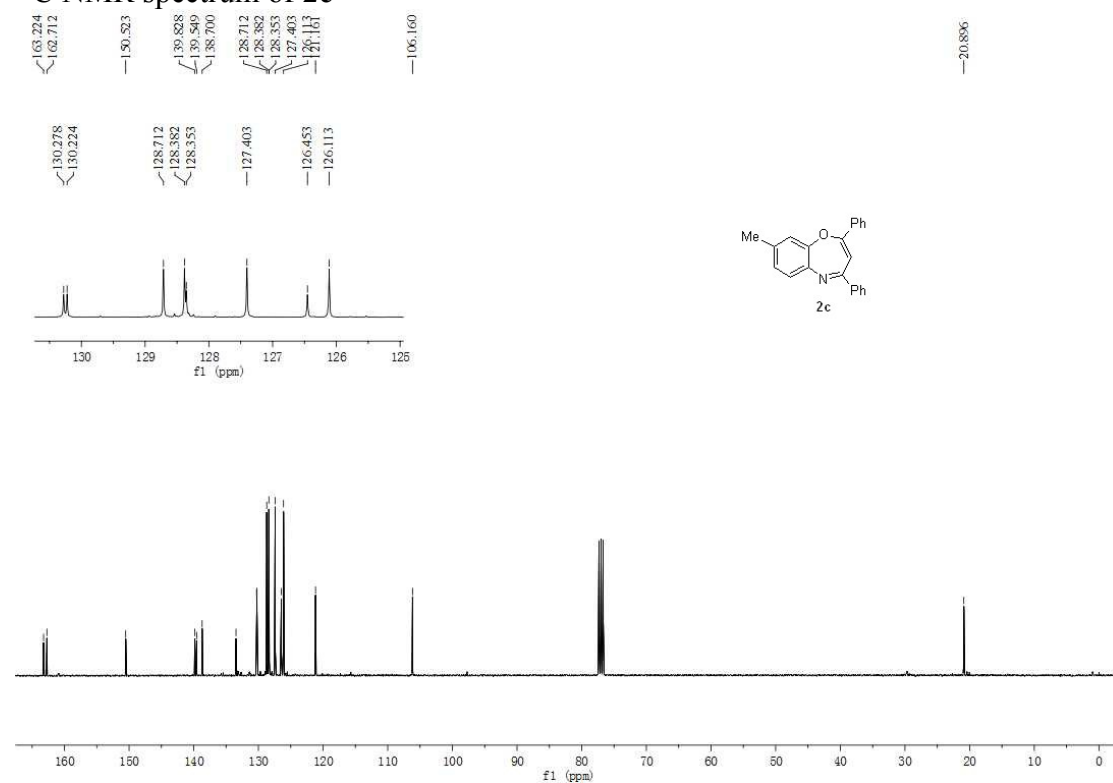
### <sup>13</sup>C NMR spectrum of **2b**



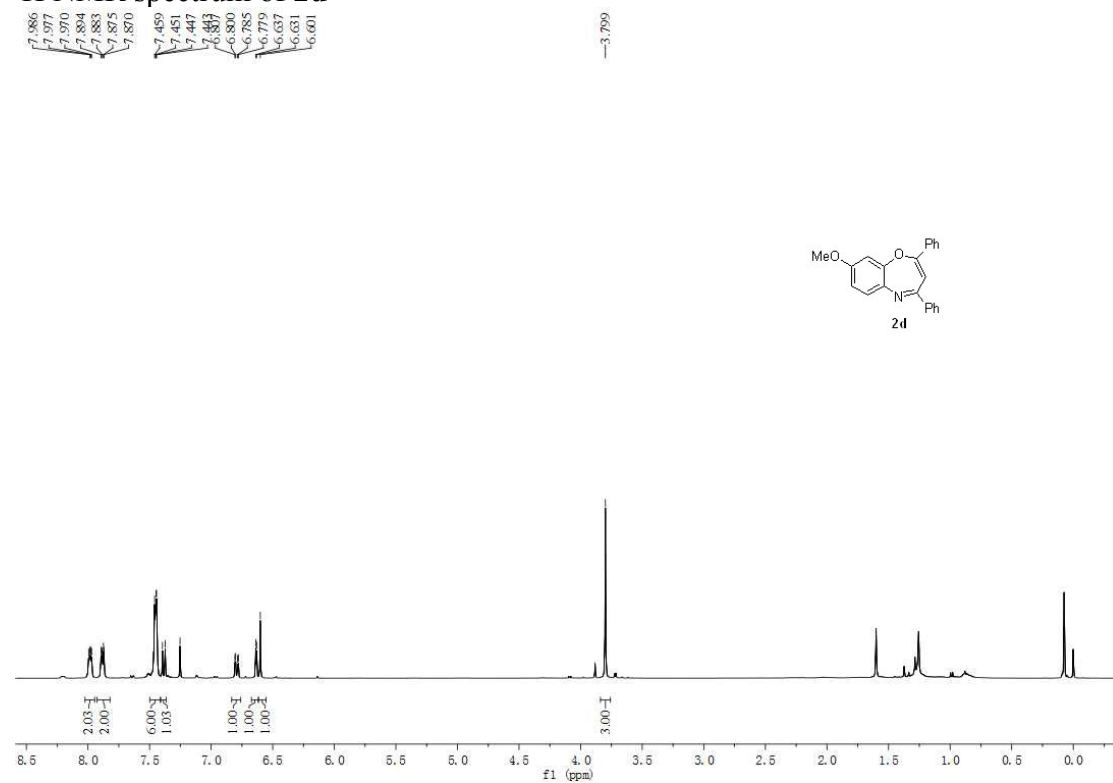
<sup>1</sup>H NMR spectrum of **2c**



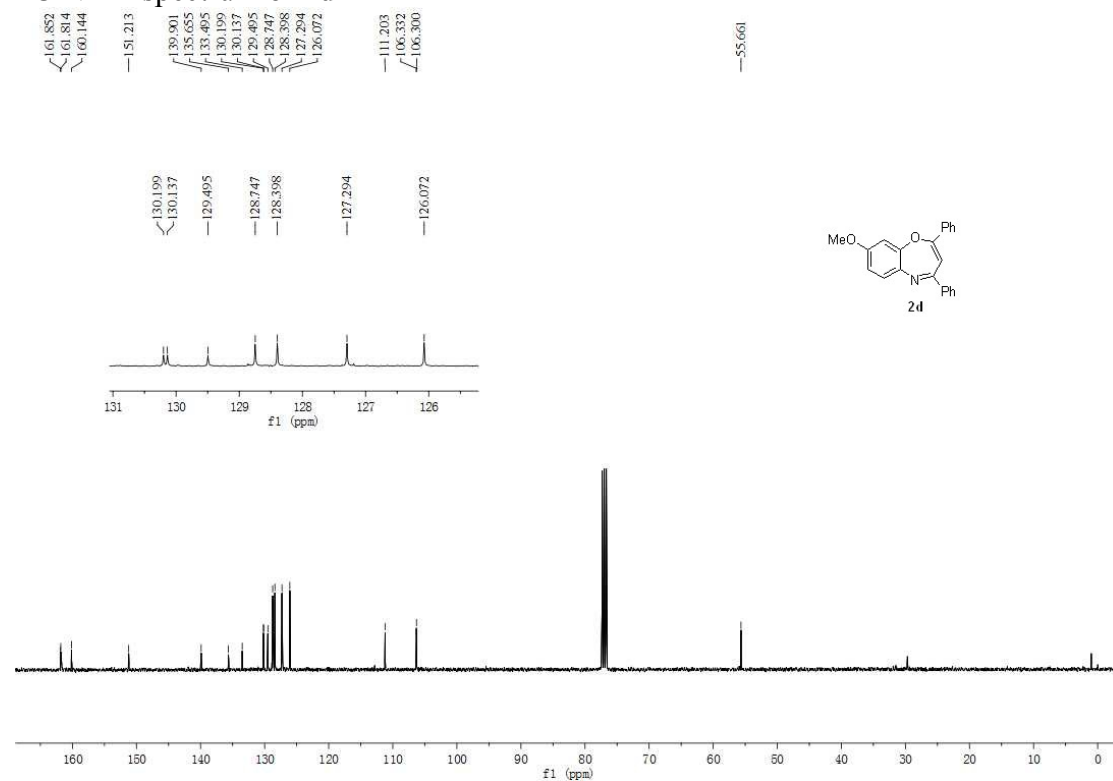
<sup>13</sup>C NMR spectrum of **2c**



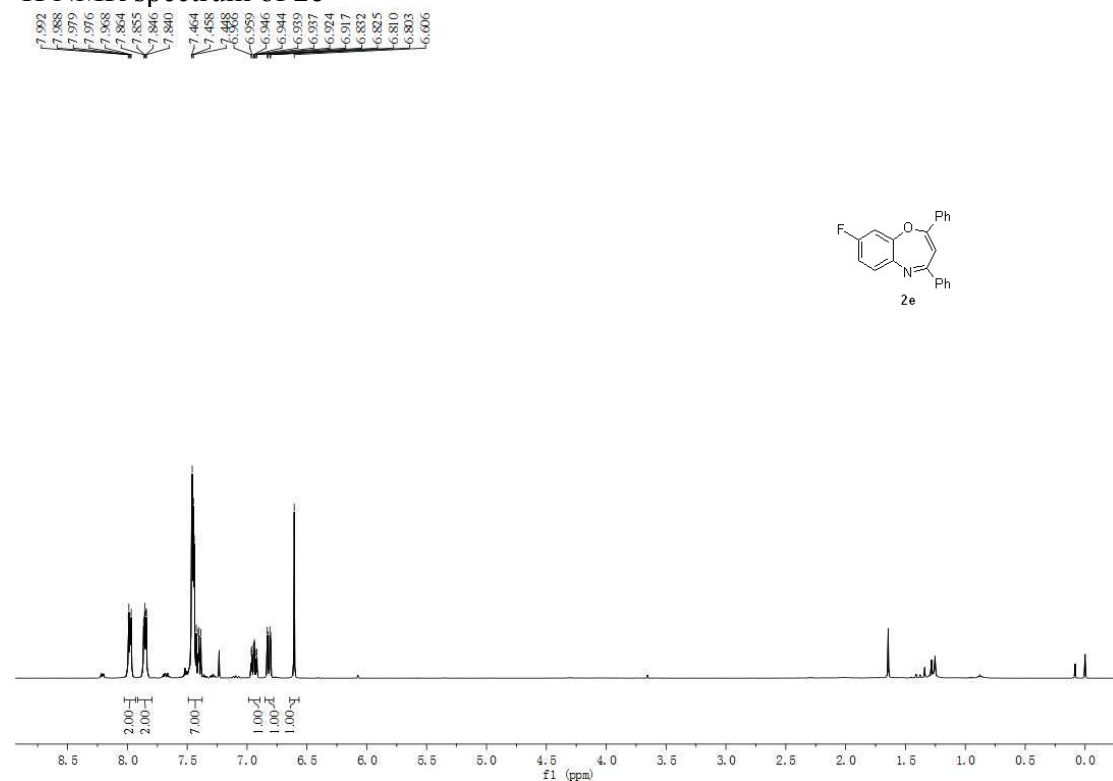
### <sup>1</sup>H NMR spectrum of 2d



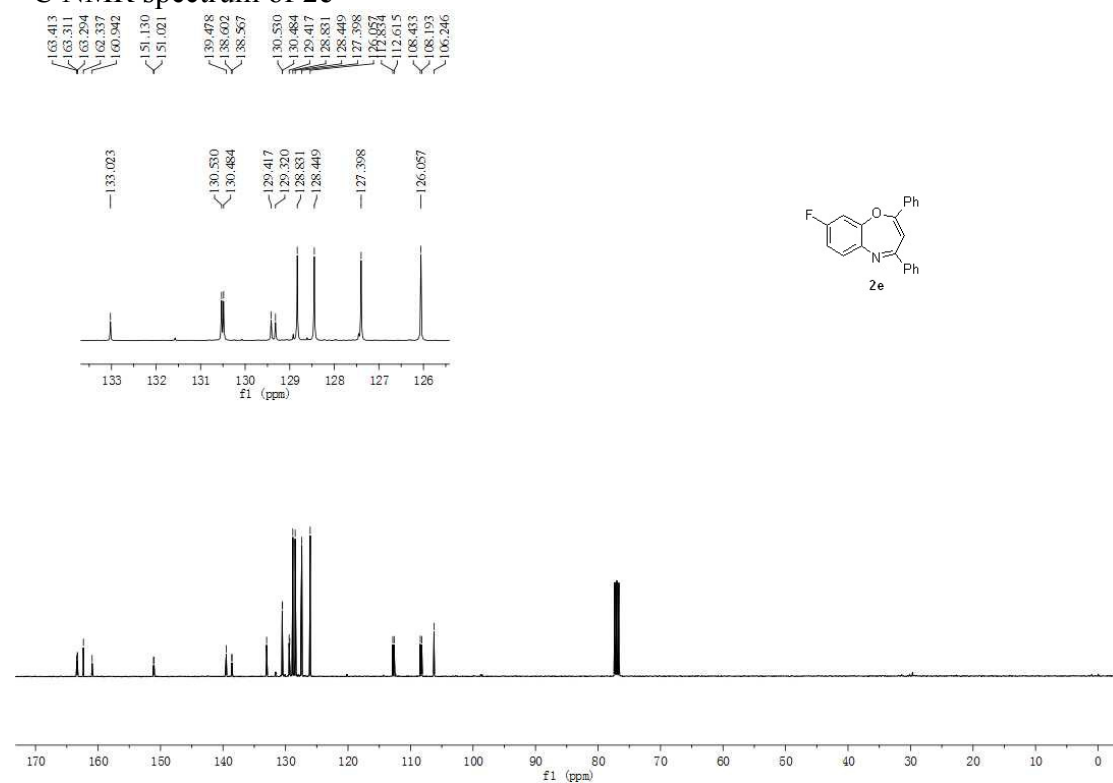
### <sup>13</sup>C NMR spectrum of 2d



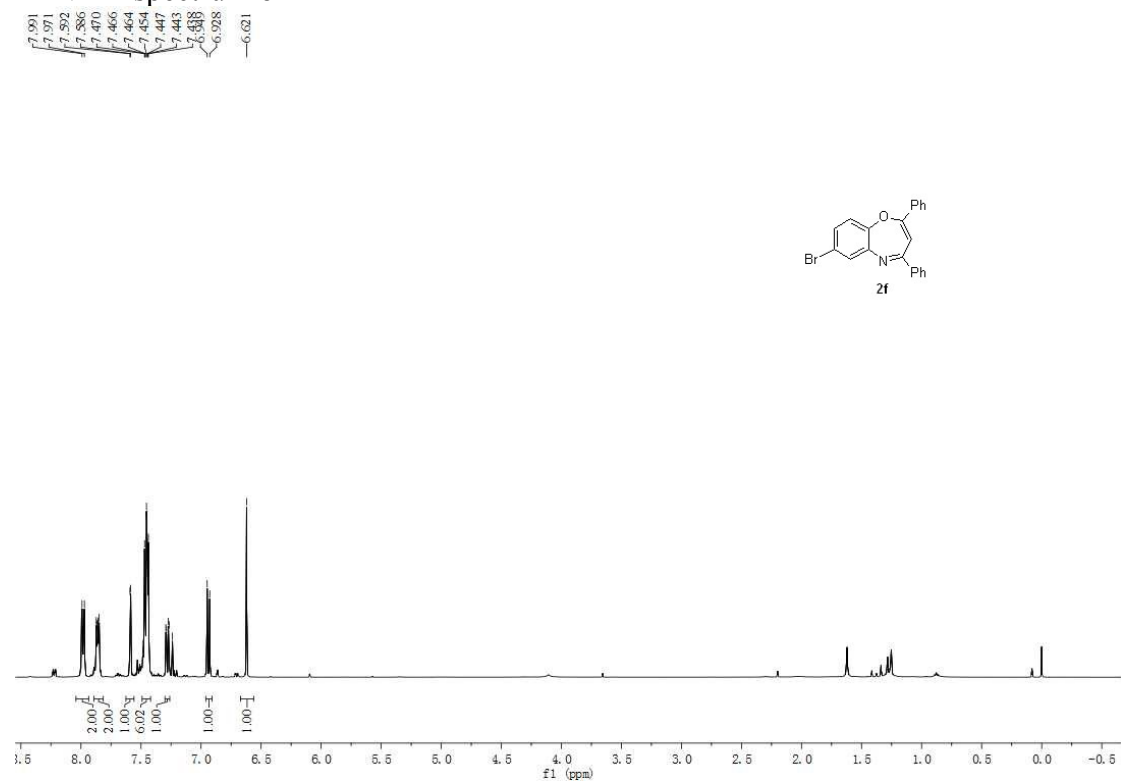
### <sup>1</sup>H NMR spectrum of 2e



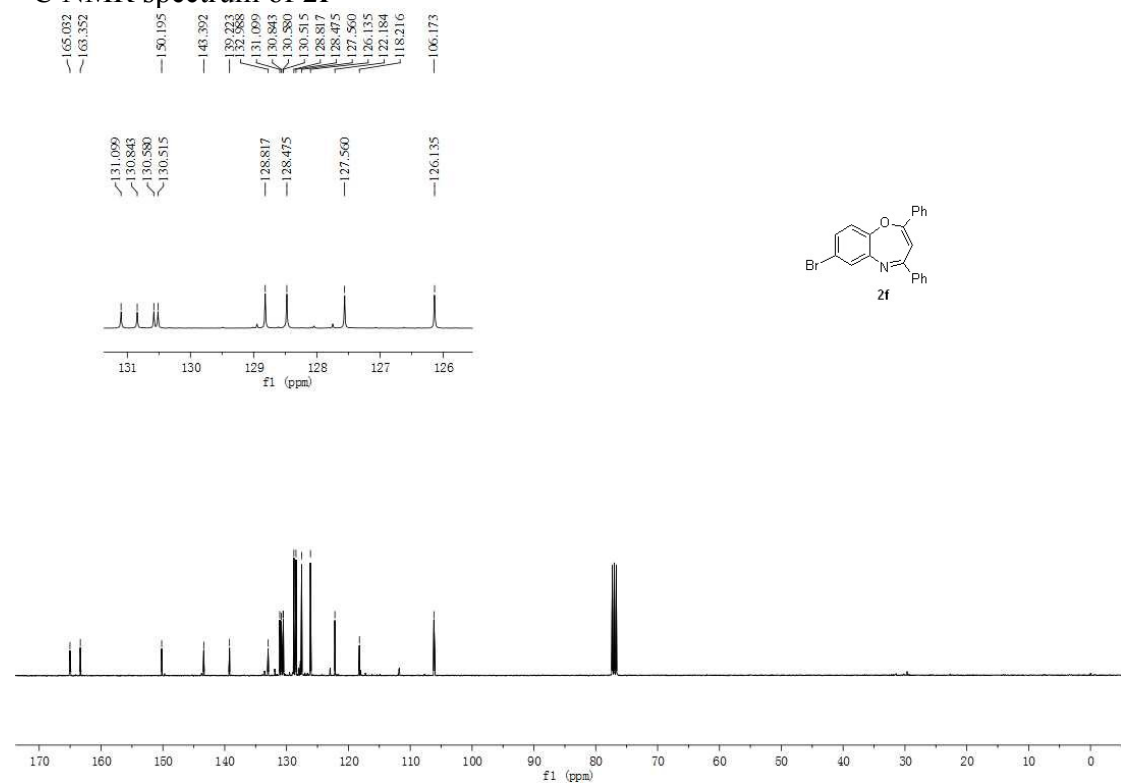
### <sup>13</sup>C NMR spectrum of 2e



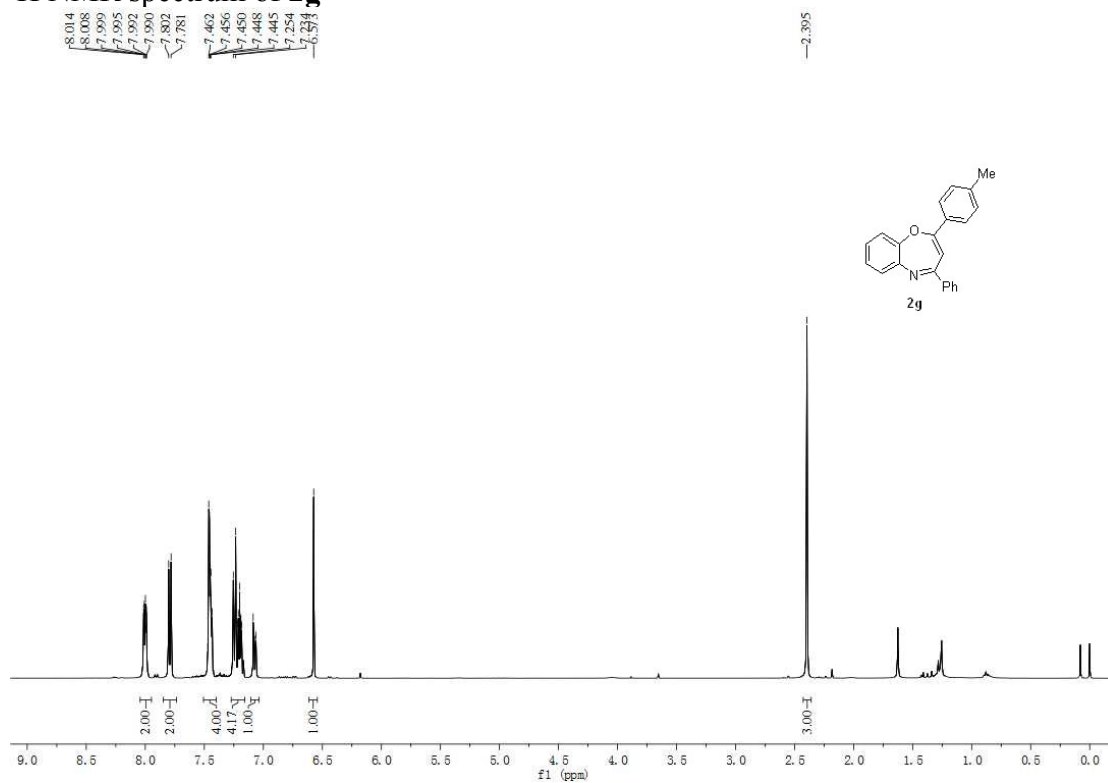
### $^1\text{H}$ NMR spectrum of **2f**



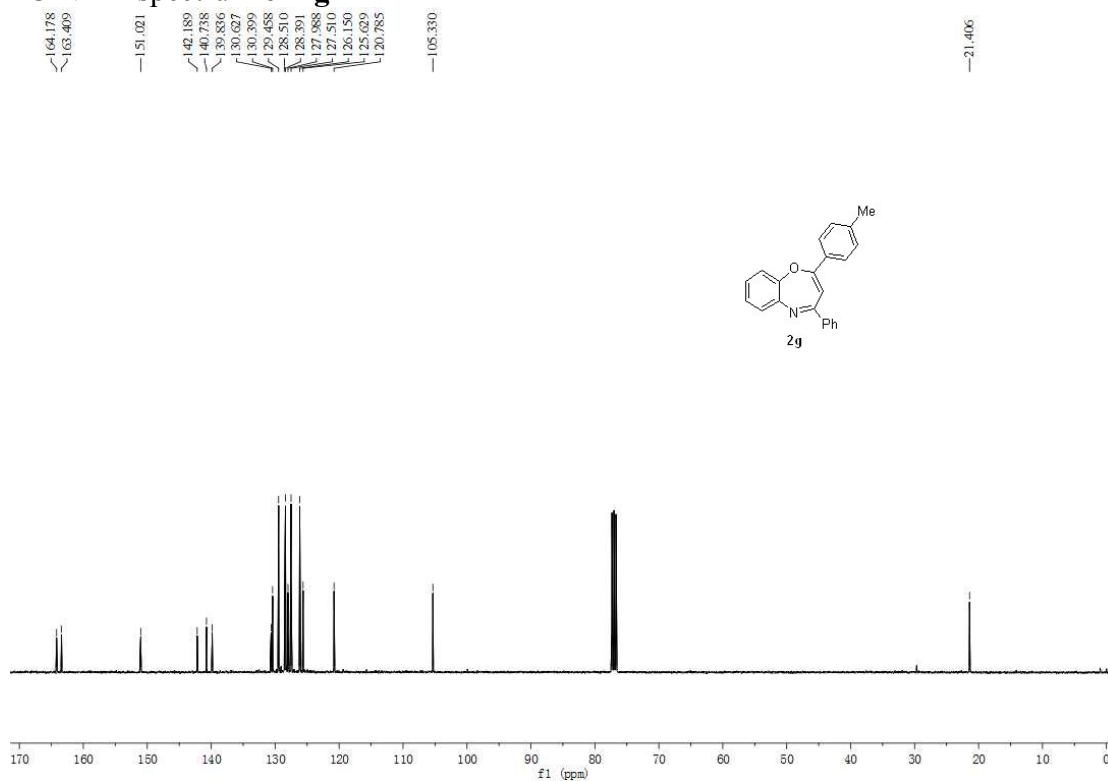
### $^{13}\text{C}$ NMR spectrum of **2f**



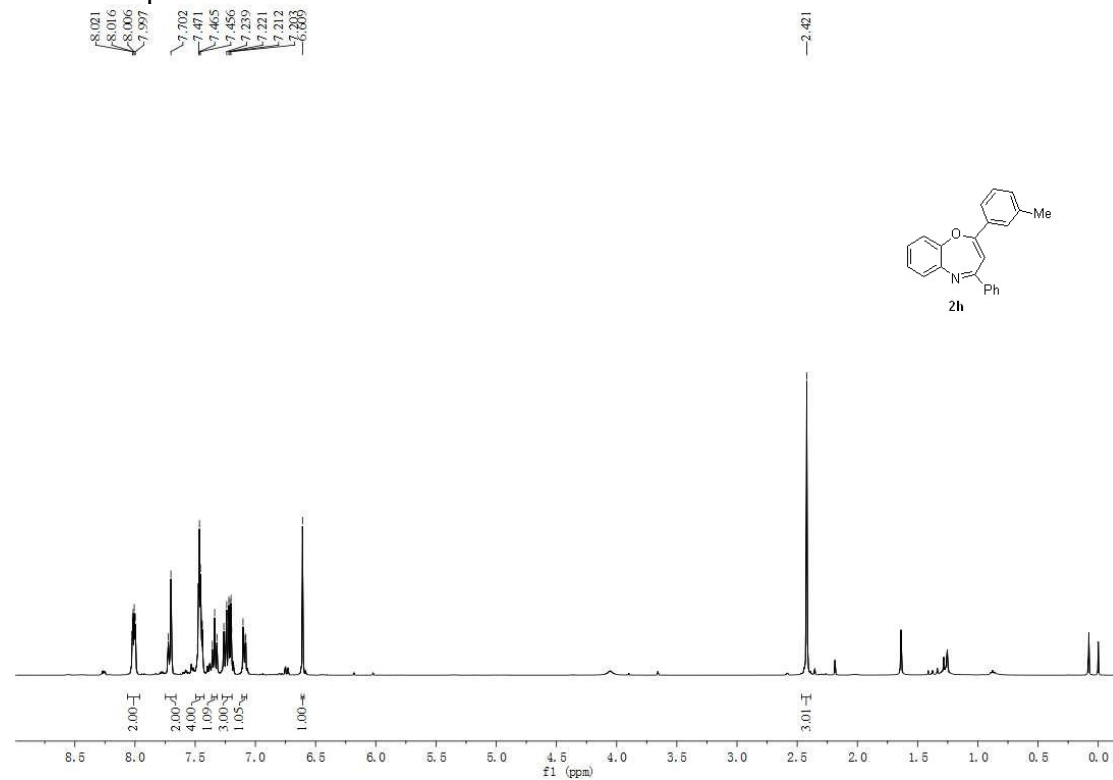
### <sup>1</sup>H NMR spectrum of **2g**



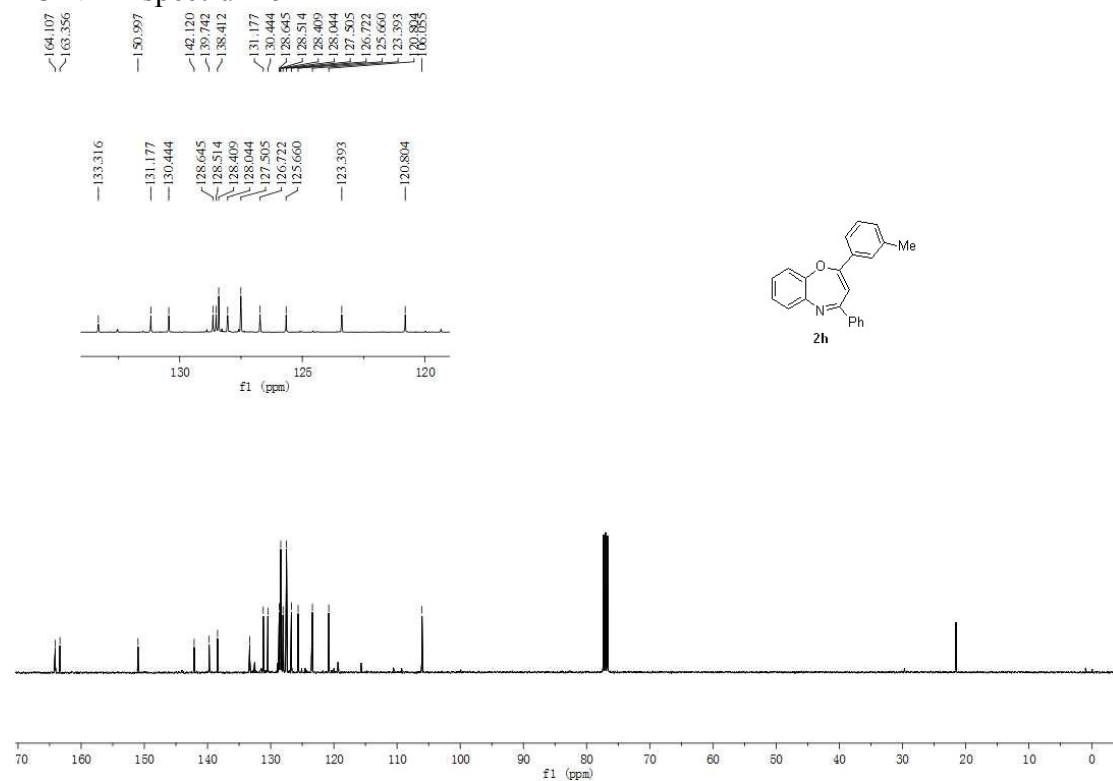
### <sup>13</sup>C NMR spectrum of **2g**



### <sup>1</sup>H NMR spectrum of **2h**

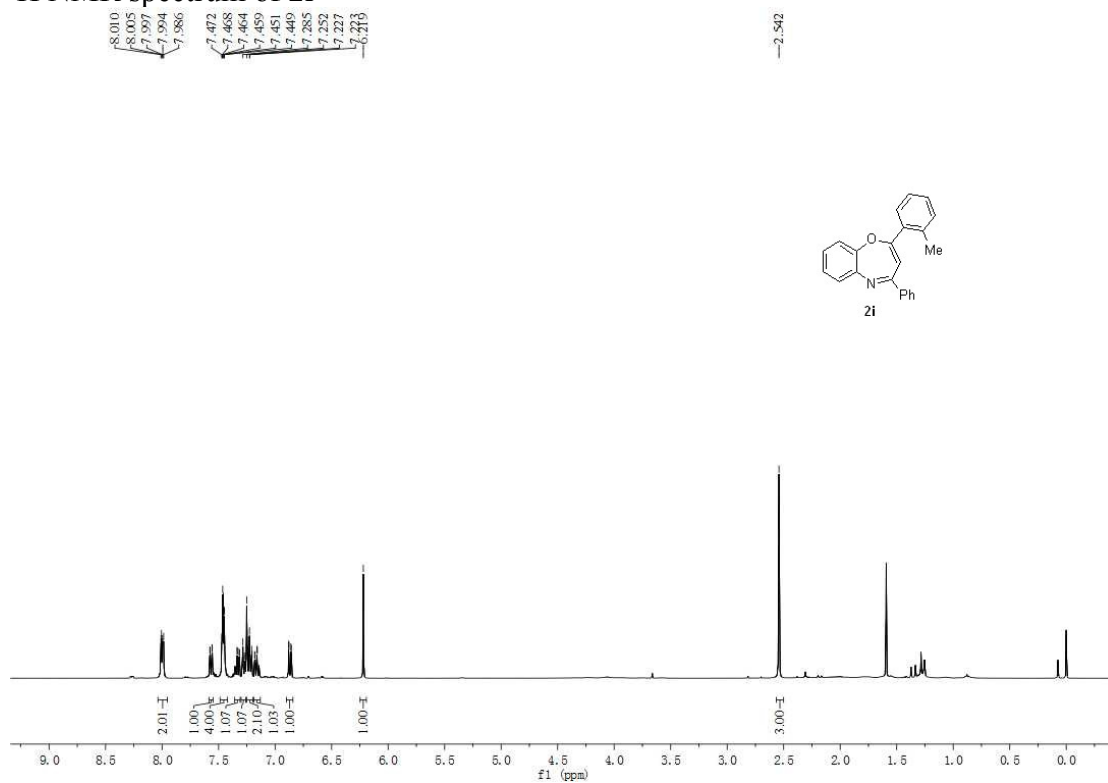


### <sup>13</sup>C NMR spectrum of **2h**

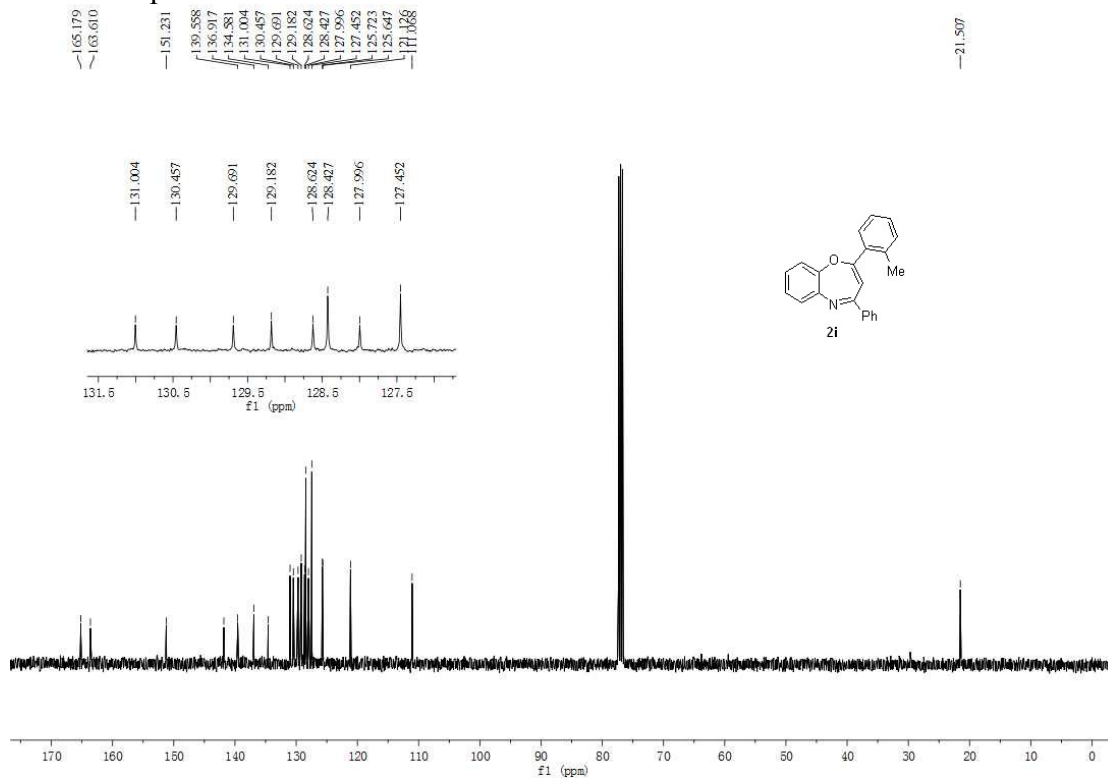




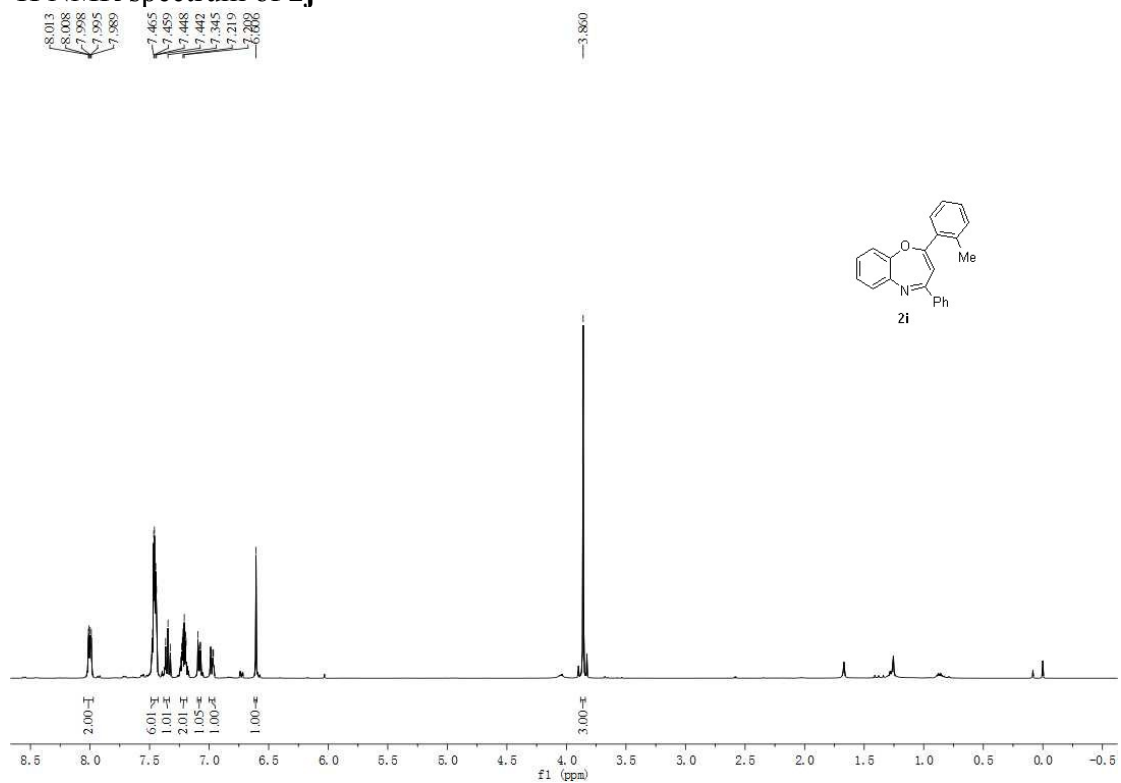
### <sup>1</sup>H NMR spectrum of **2i**



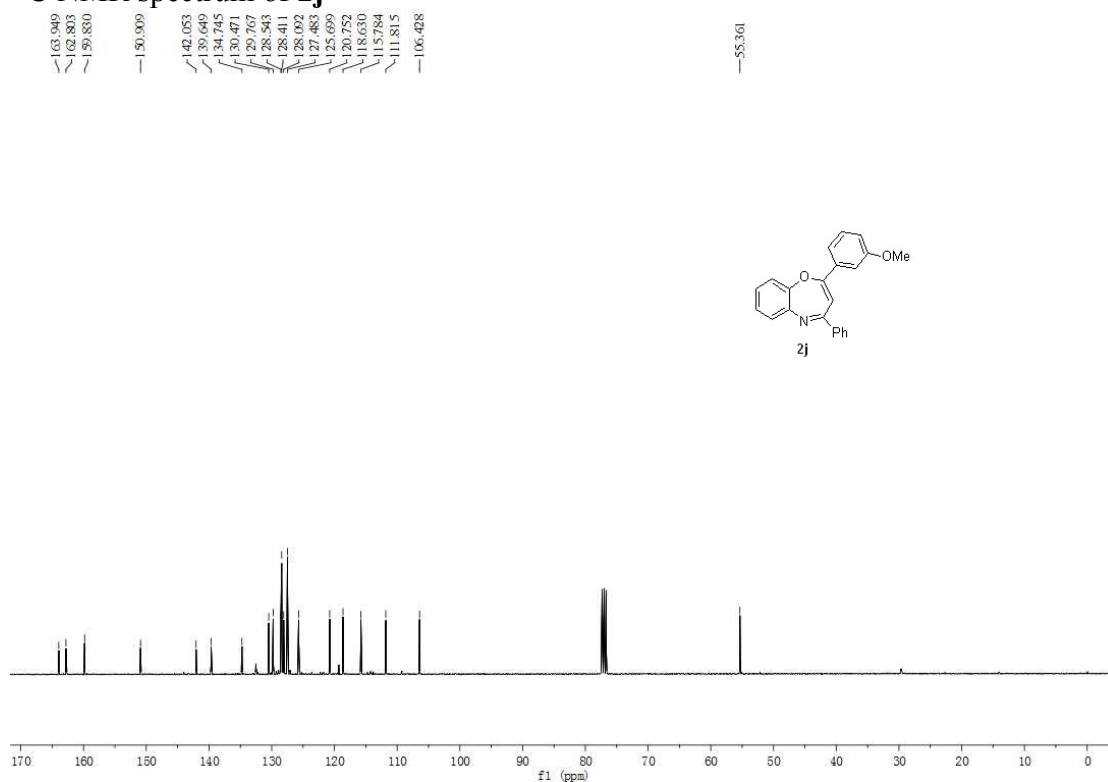
### <sup>13</sup>C NMR spectrum of **2i**



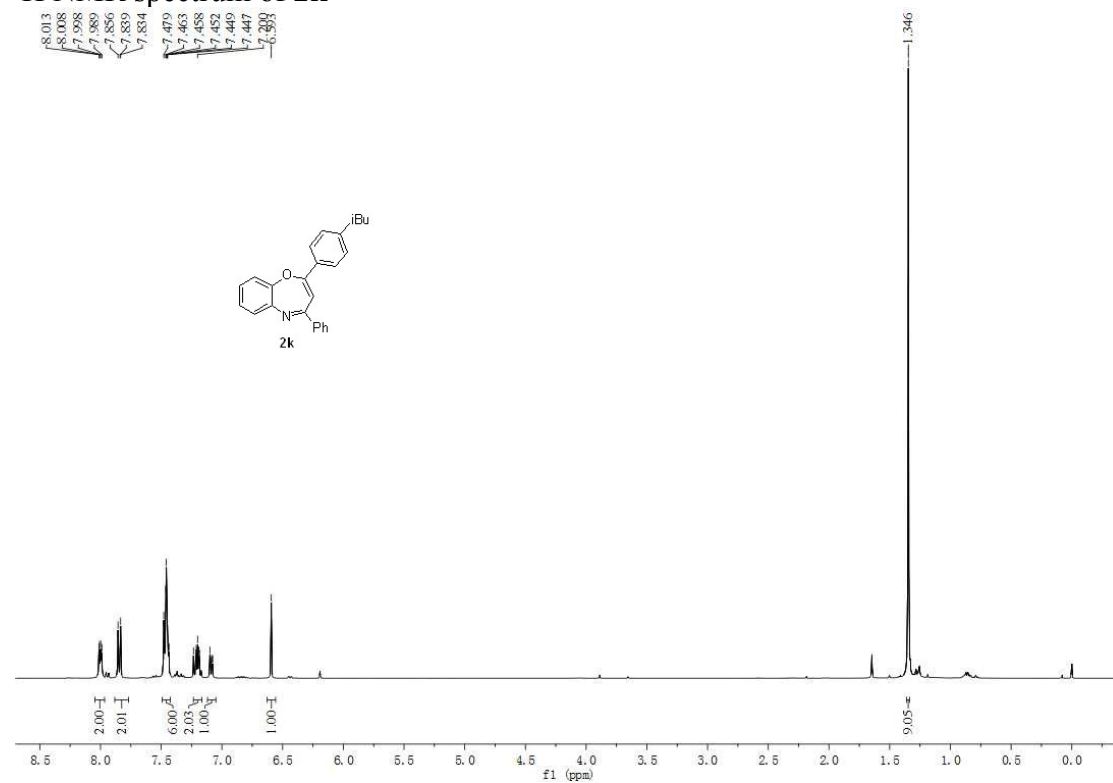
<sup>1</sup>H NMR spectrum of **2j**



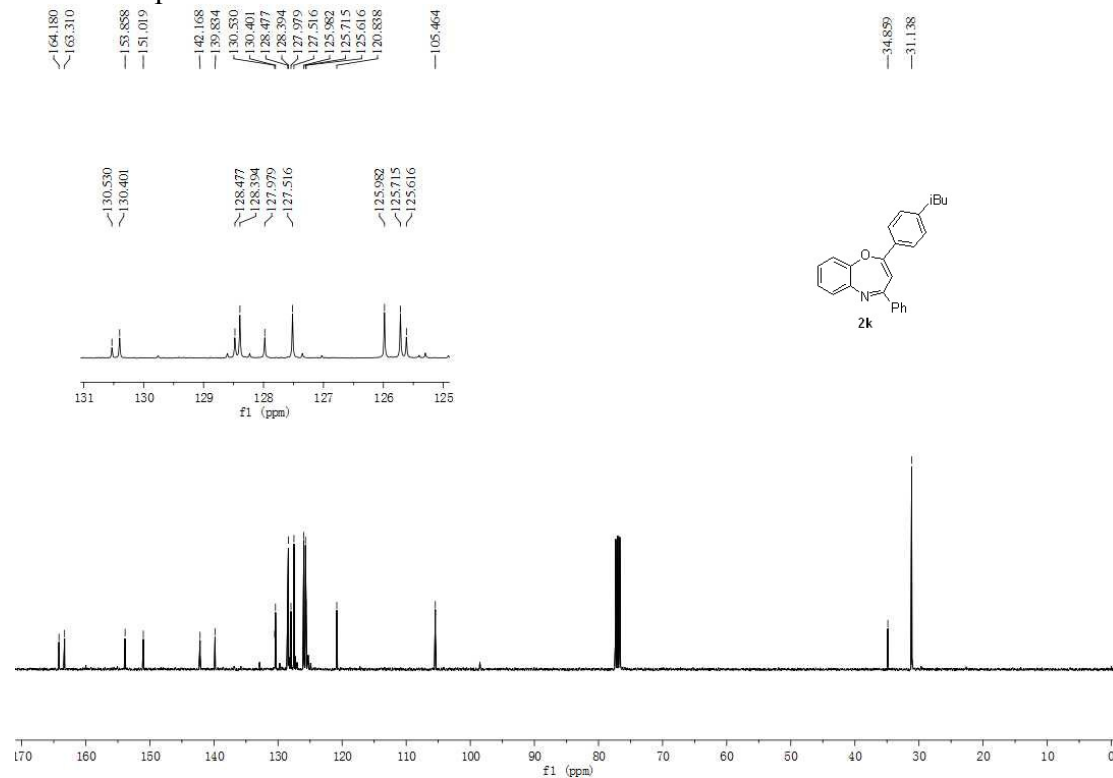
<sup>13</sup>C NMR spectrum of **2j**



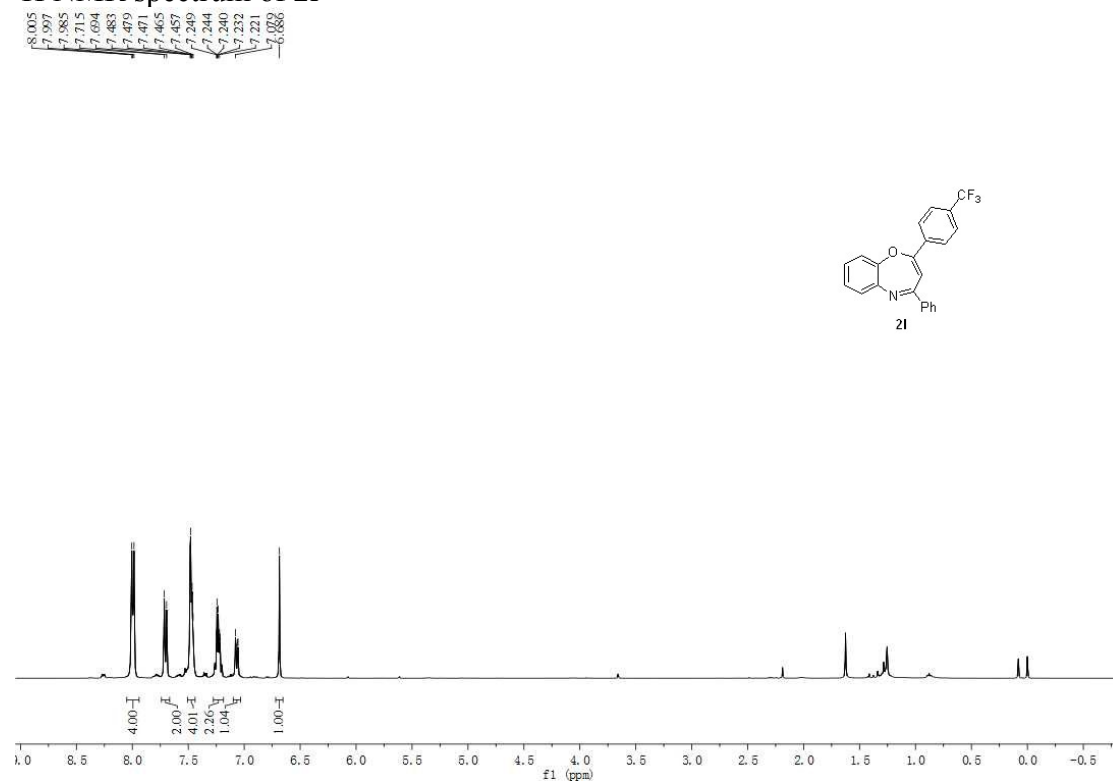
<sup>1</sup>H NMR spectrum of **2k**



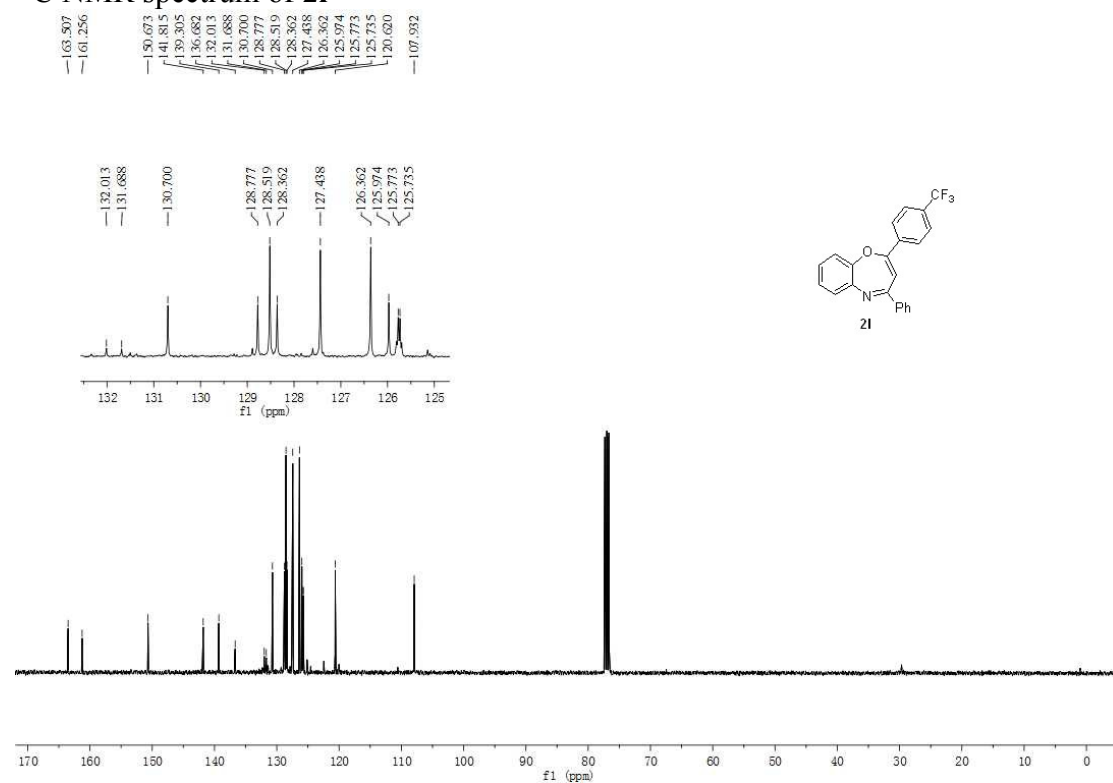
<sup>13</sup>C NMR spectrum of **2k**



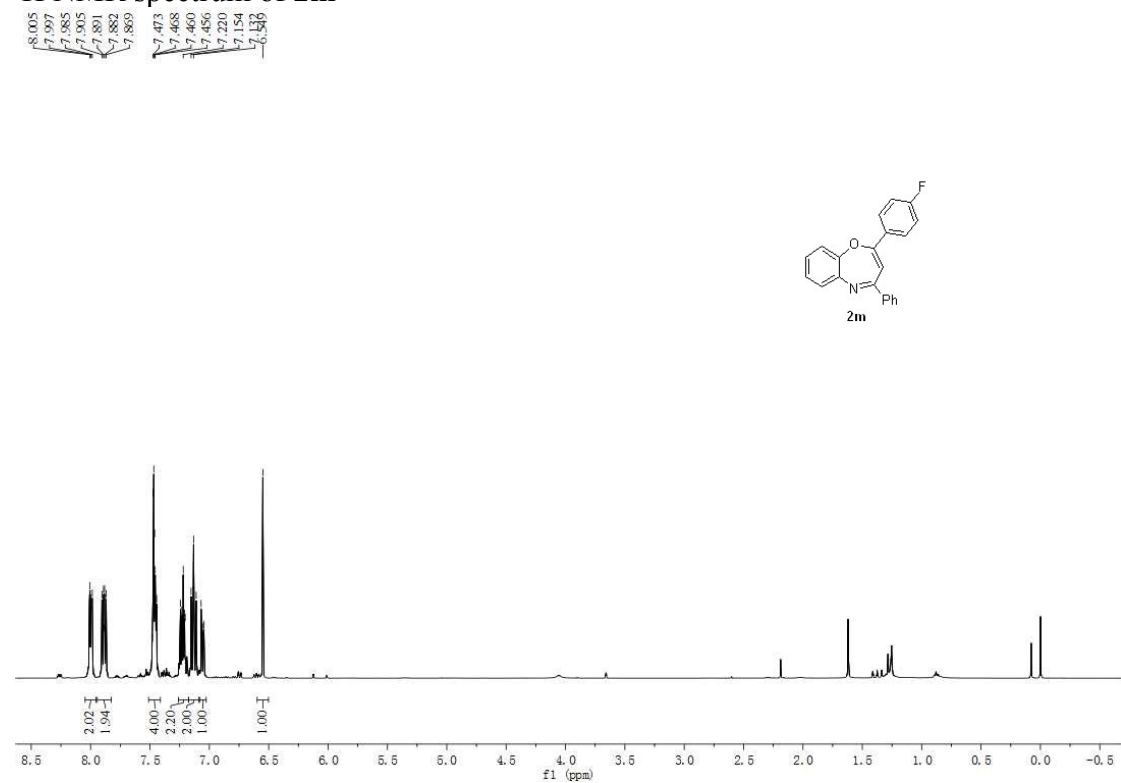
### <sup>1</sup>H NMR spectrum of 21



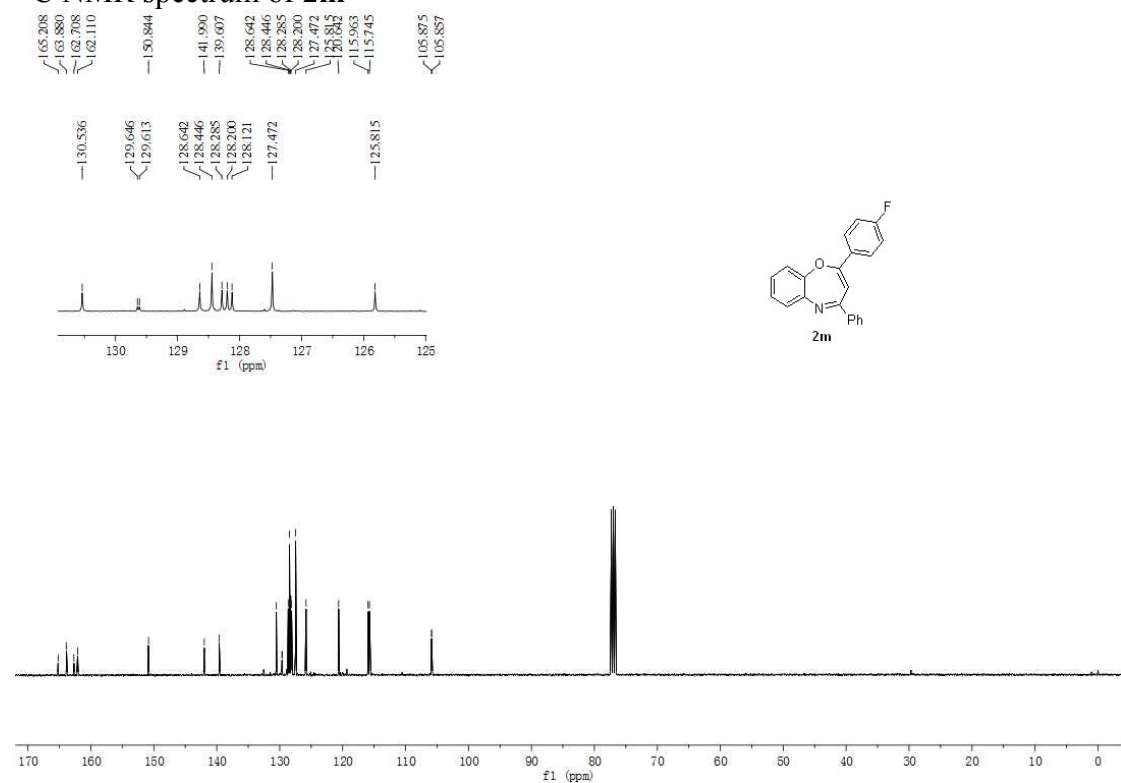
### <sup>13</sup>C NMR spectrum of 21



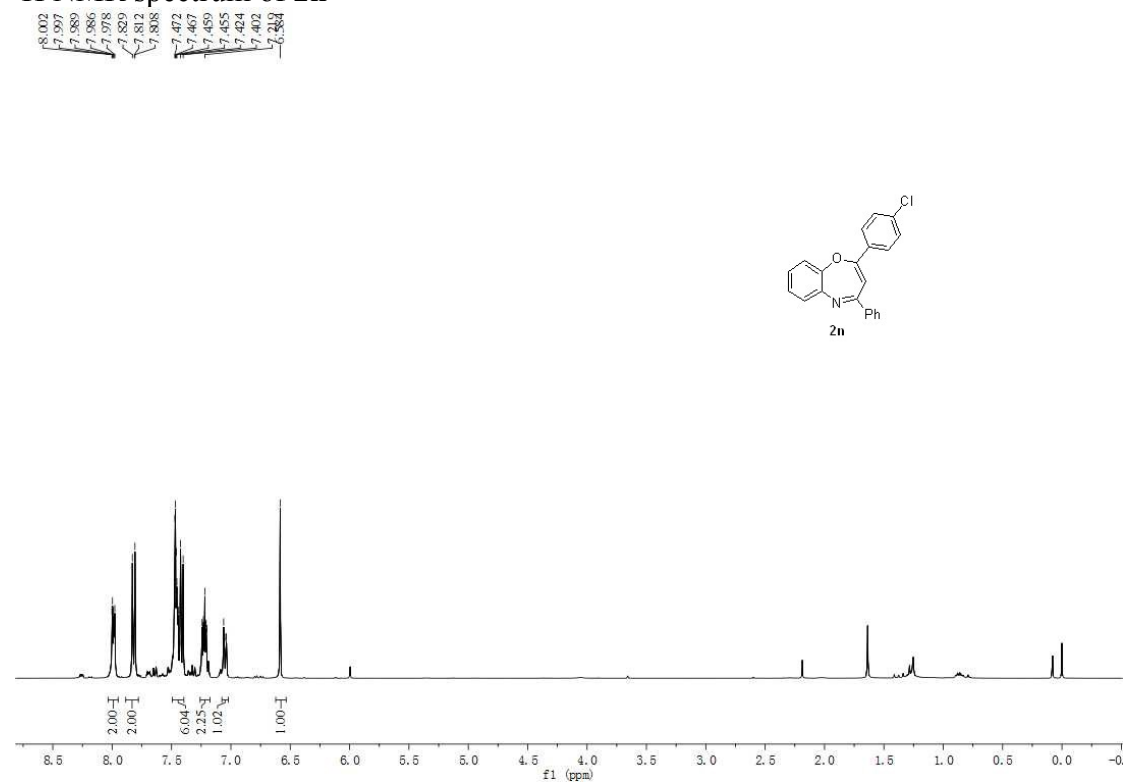
### $^1\text{H}$ NMR spectrum of **2m**



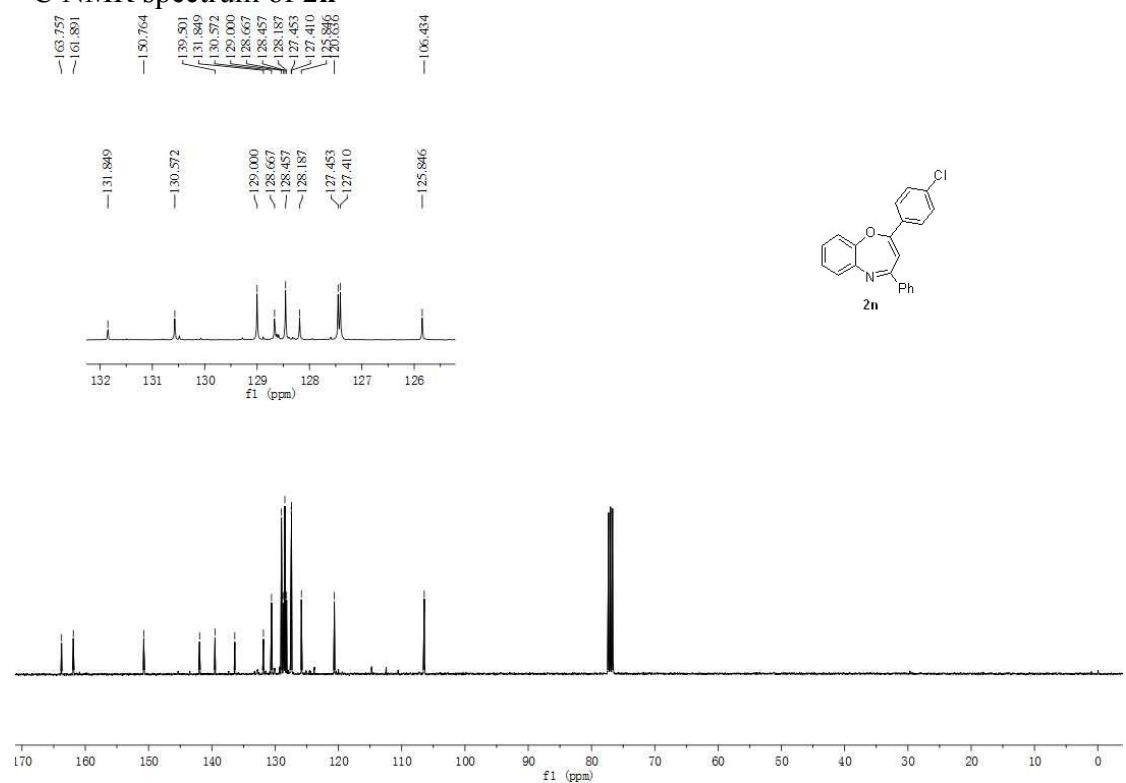
### $^{13}\text{C}$ NMR spectrum of **2m**



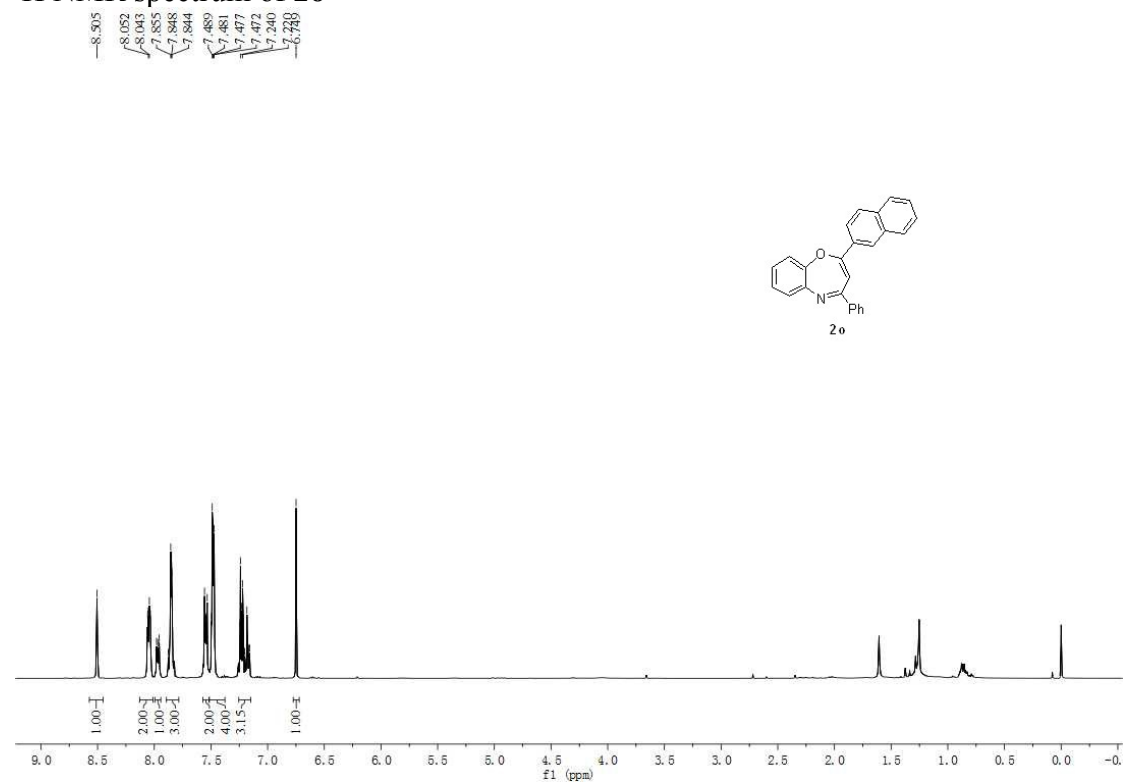
### <sup>1</sup>H NMR spectrum of 2n



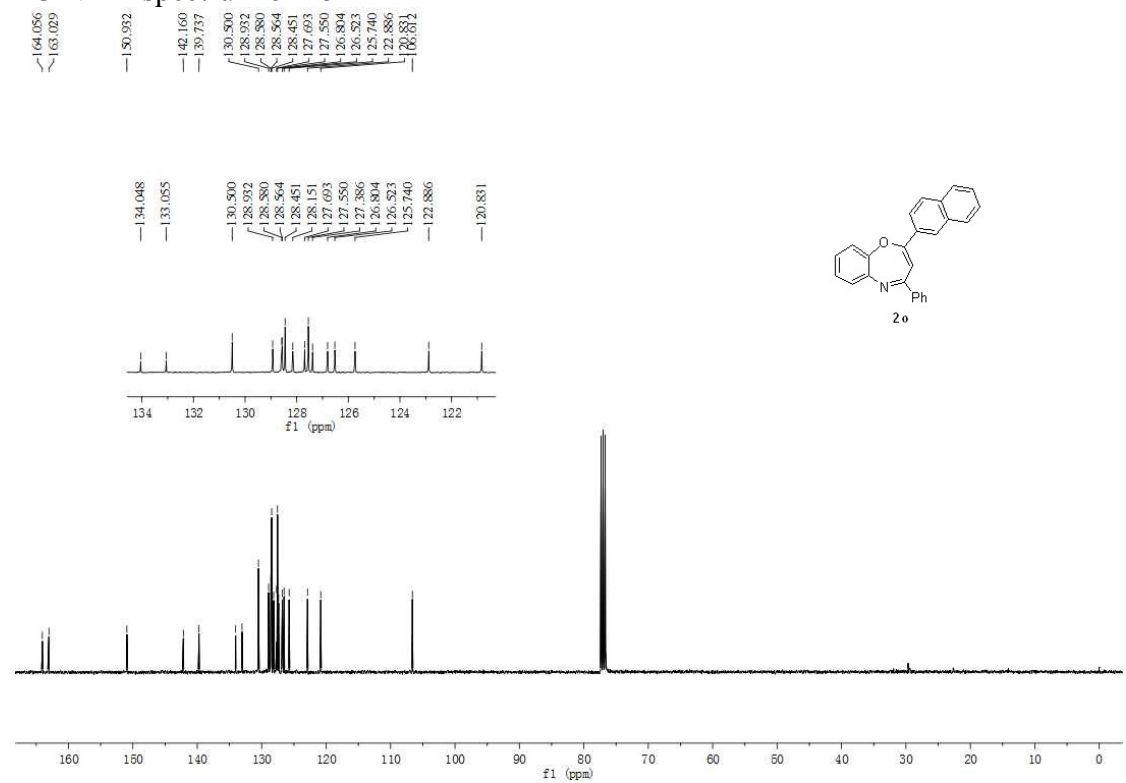
### <sup>13</sup>C NMR spectrum of 2n



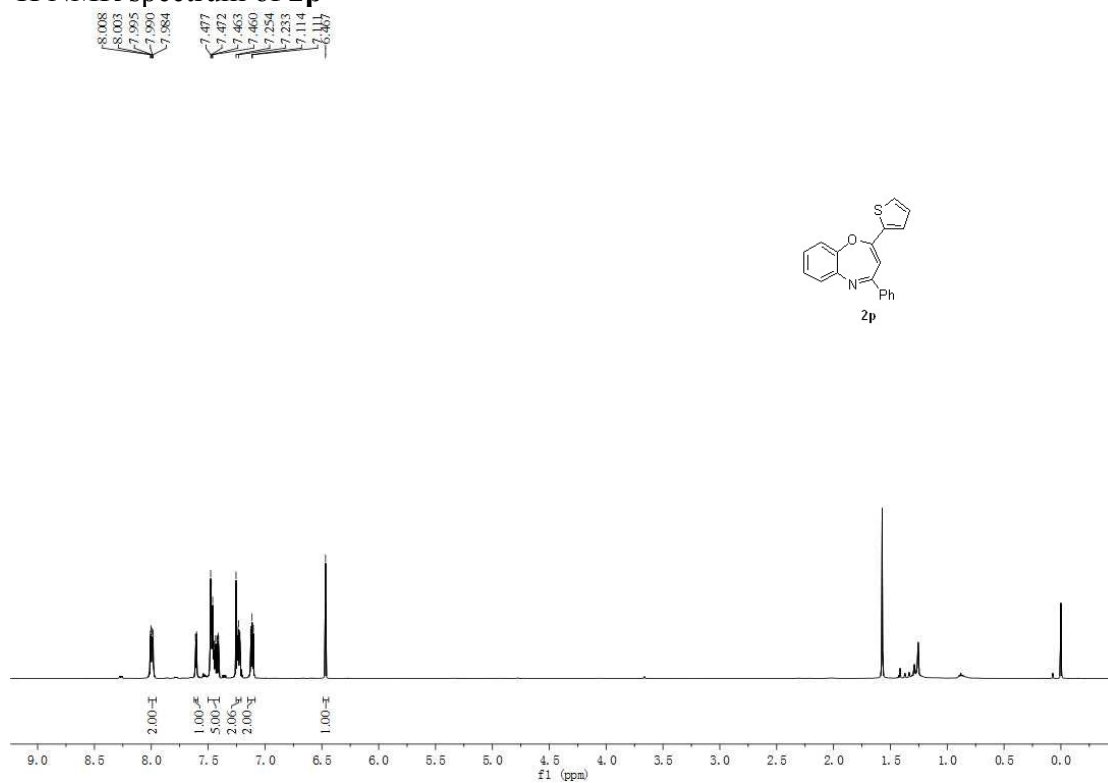
### <sup>1</sup>H NMR spectrum of **2o**



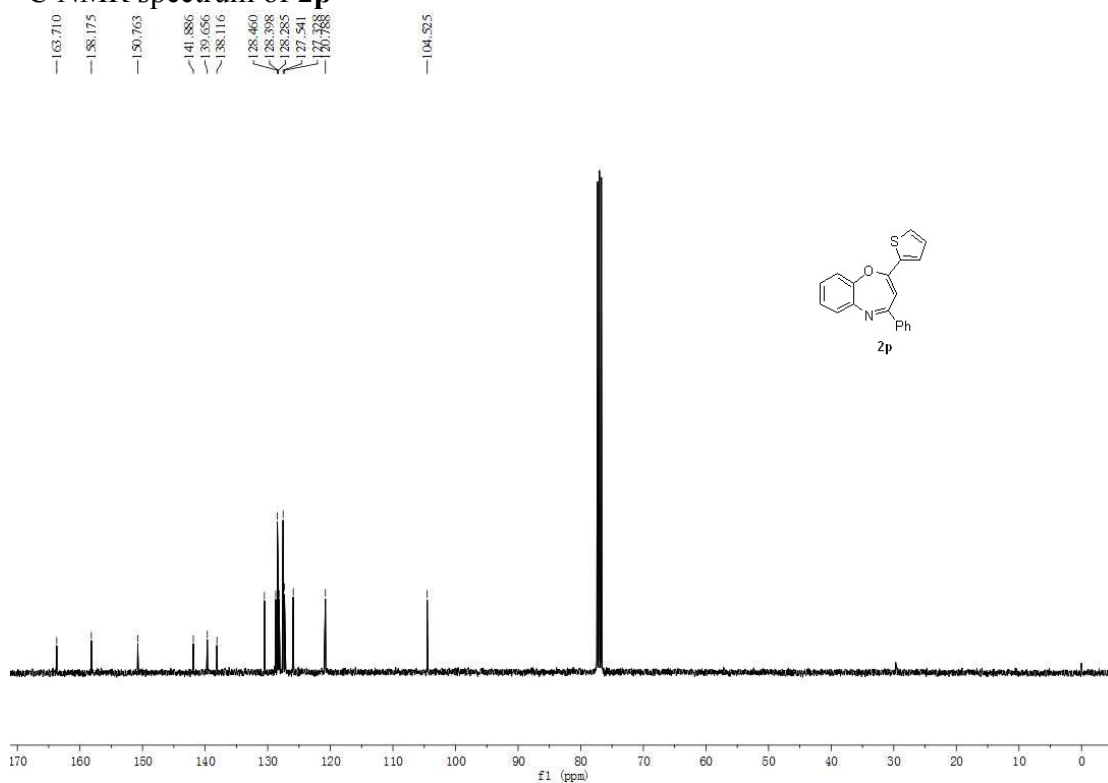
### <sup>13</sup>C NMR spectrum of **2o**



### <sup>1</sup>H NMR spectrum of 2p

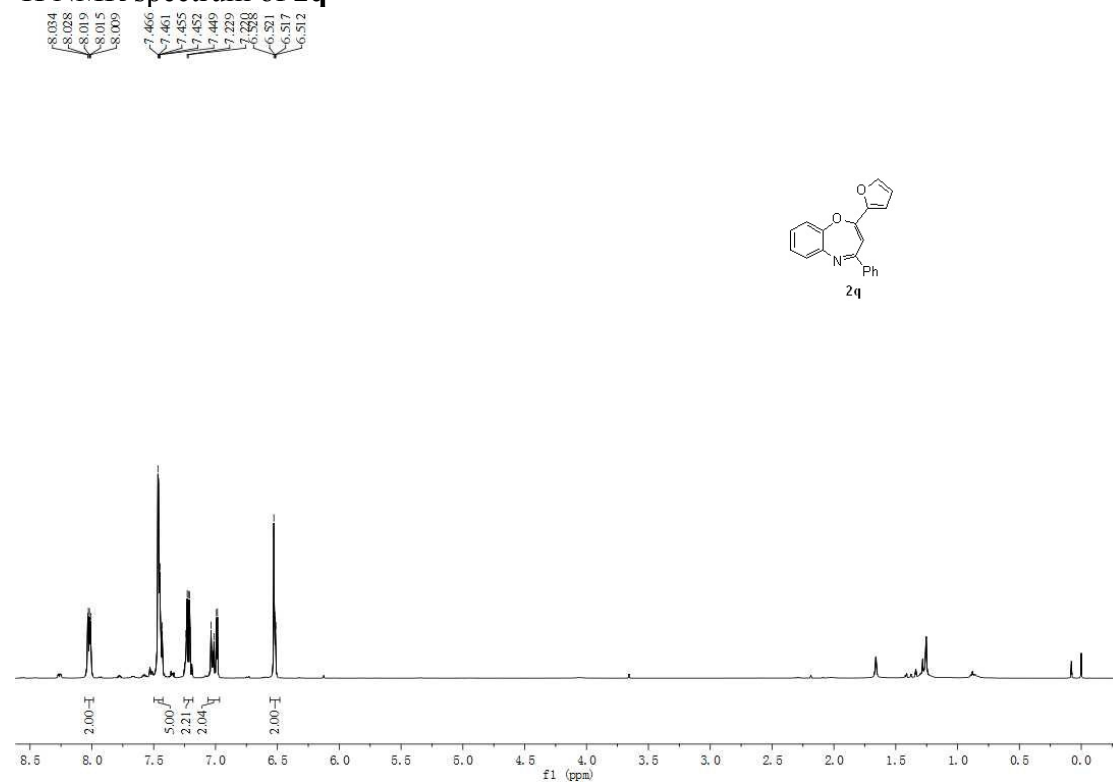


### <sup>13</sup>C NMR spectrum of 2p

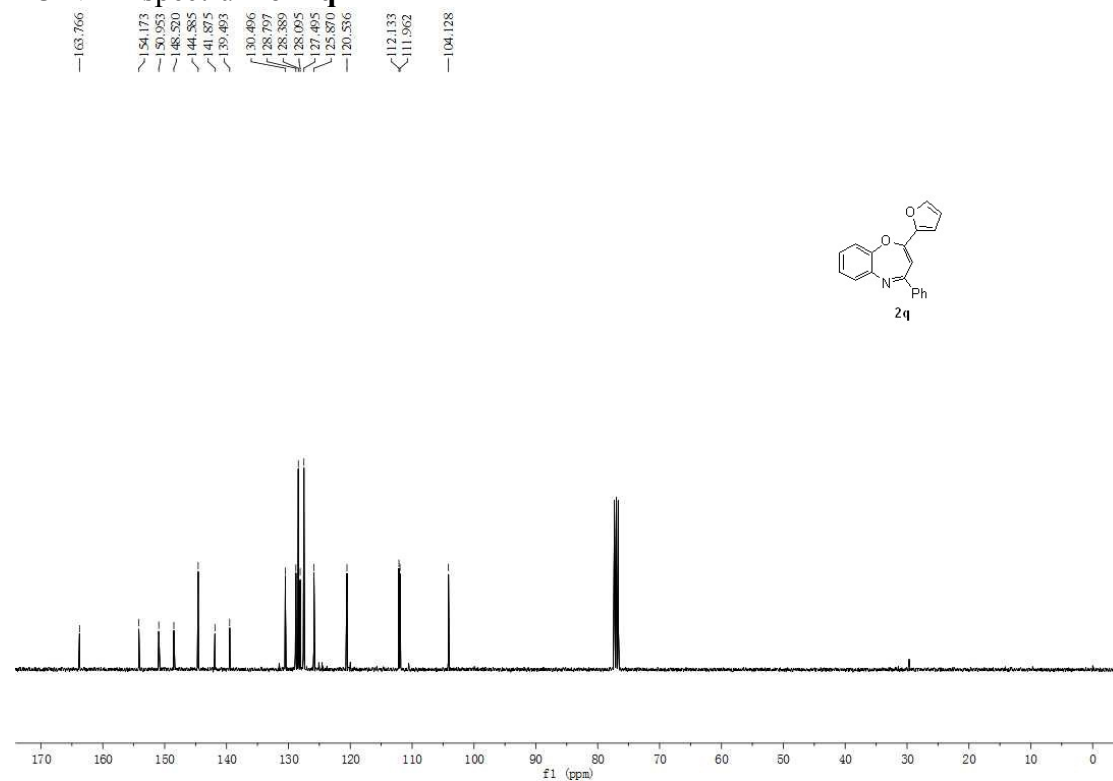




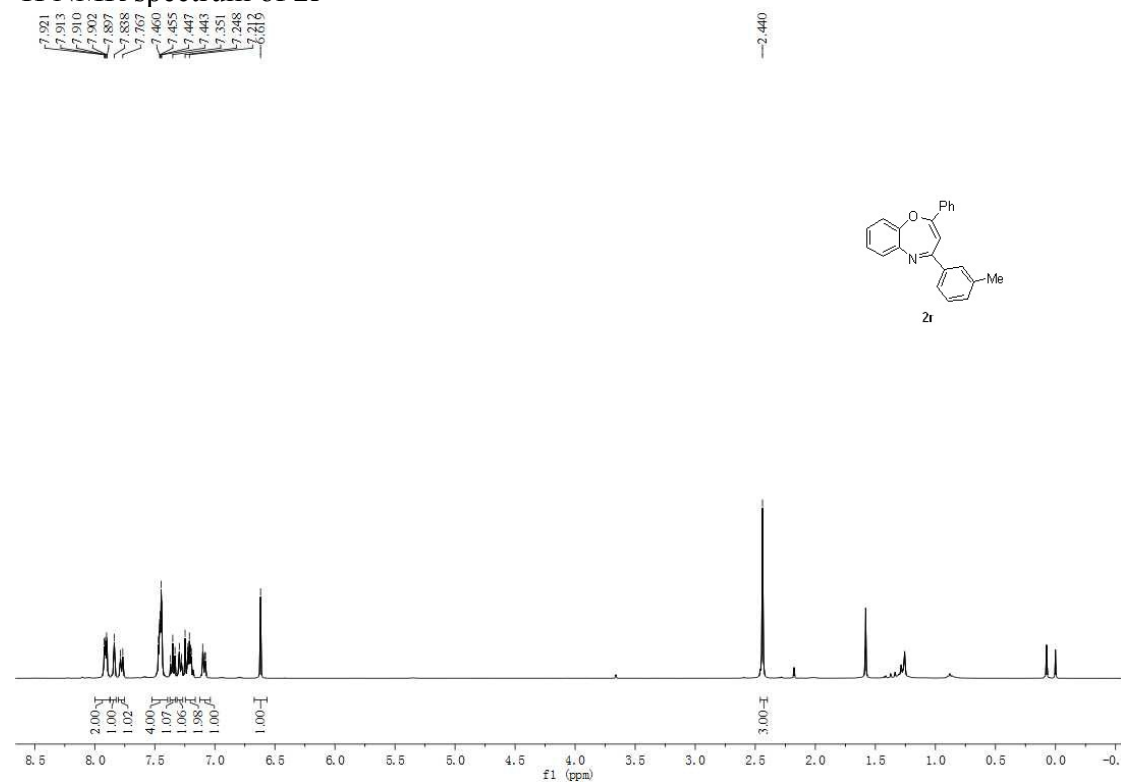
### $^1\text{H}$ NMR spectrum of **2q**



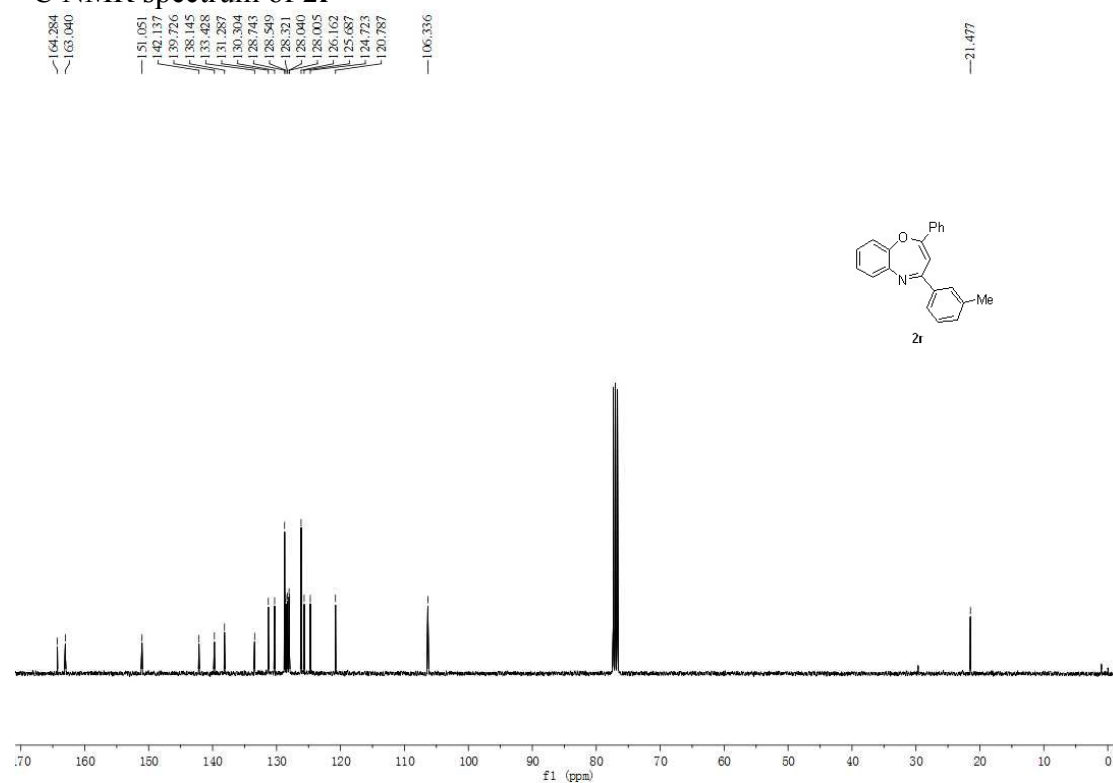
### $^{13}\text{C}$ NMR spectrum of **2q**



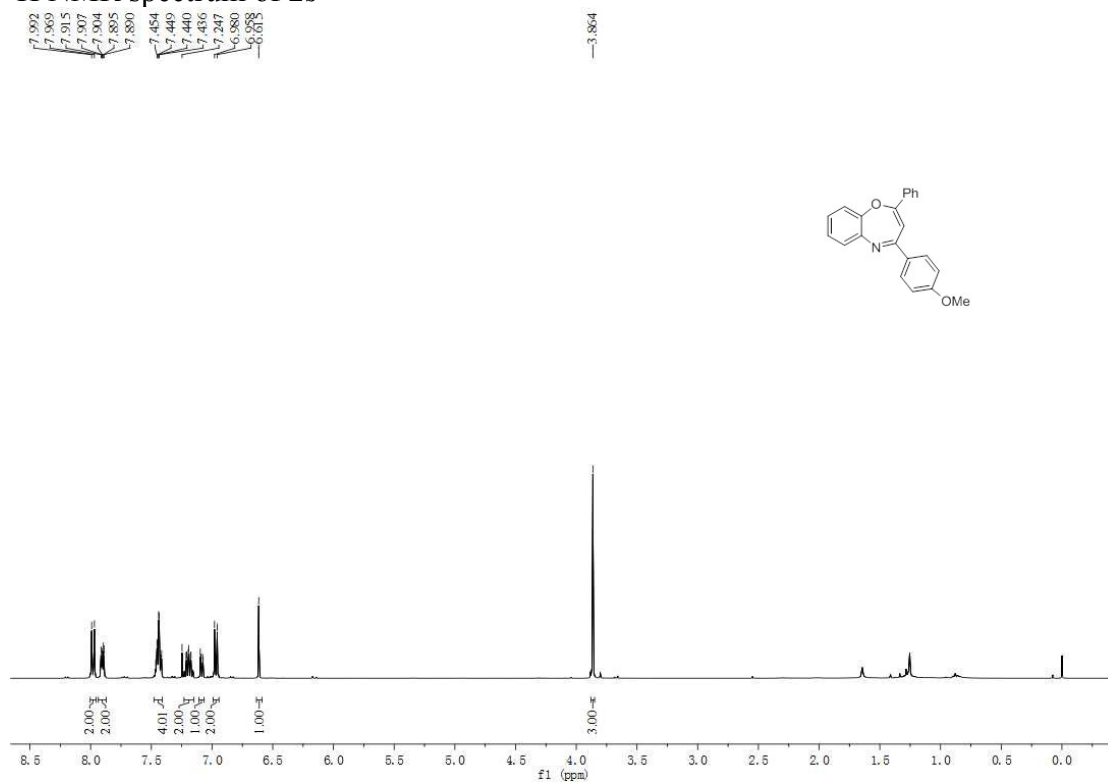
### <sup>1</sup>H NMR spectrum of 2r



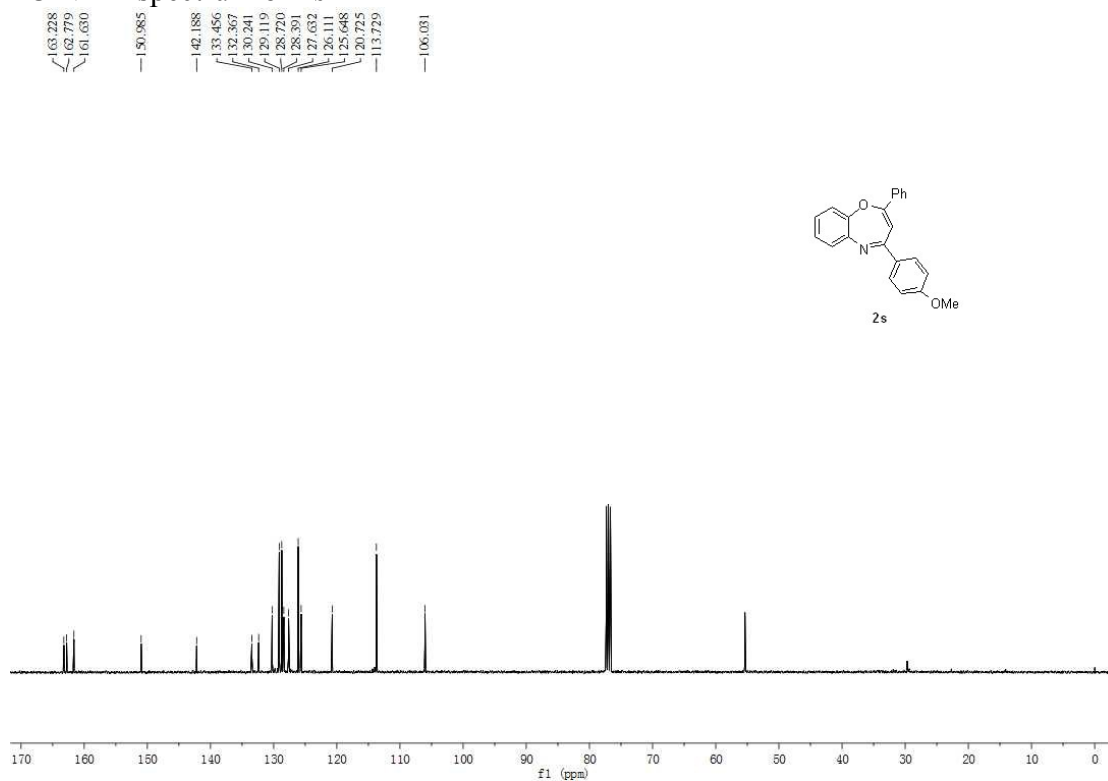
### <sup>13</sup>C NMR spectrum of 2r



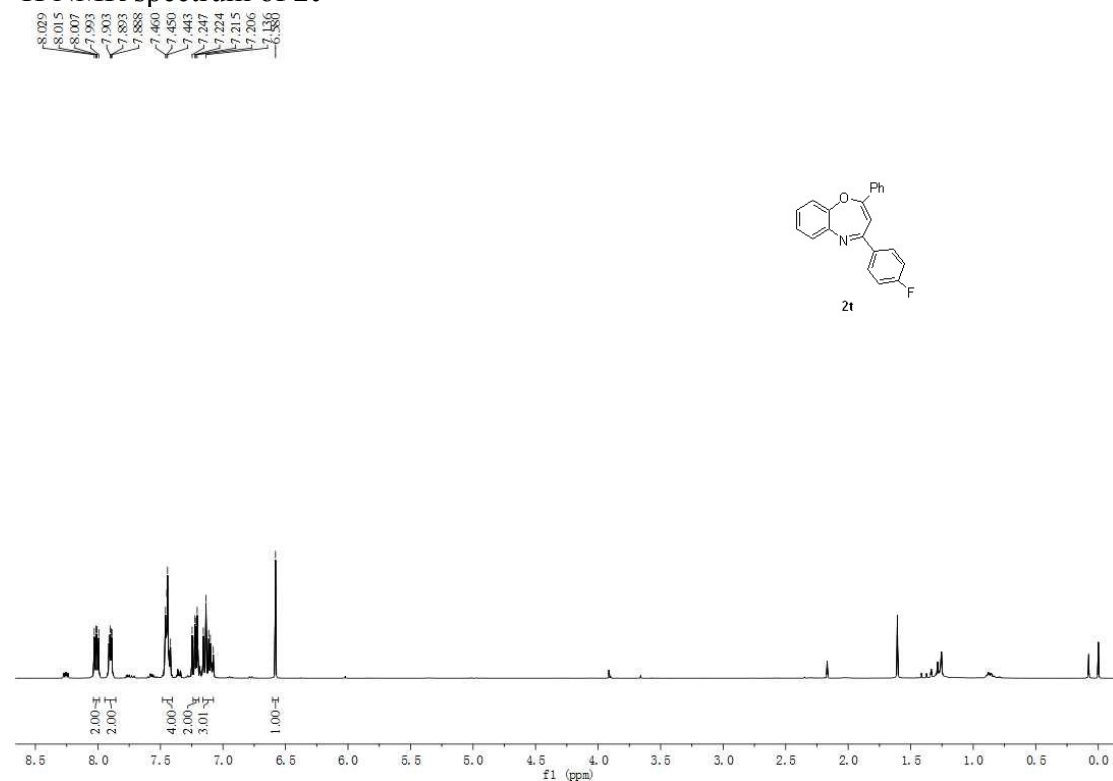
### $^1\text{H}$ NMR spectrum of **2s**



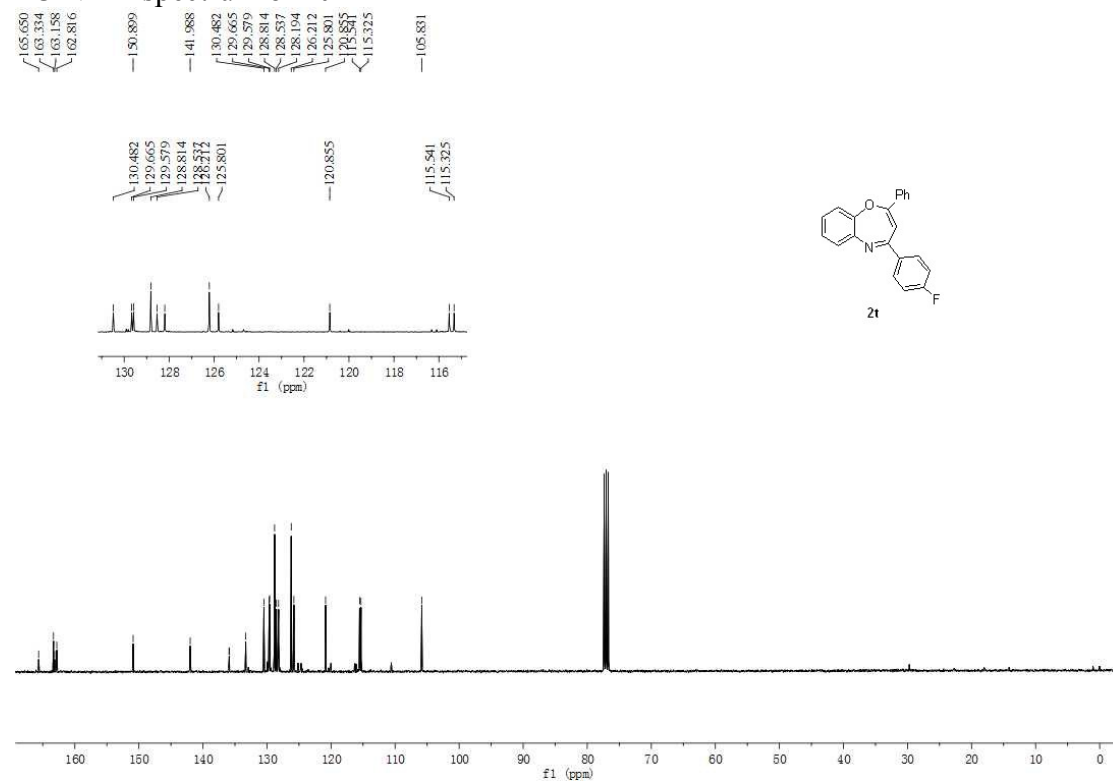
### $^{13}\text{C}$ NMR spectrum of **2s**



### <sup>1</sup>H NMR spectrum of 2t

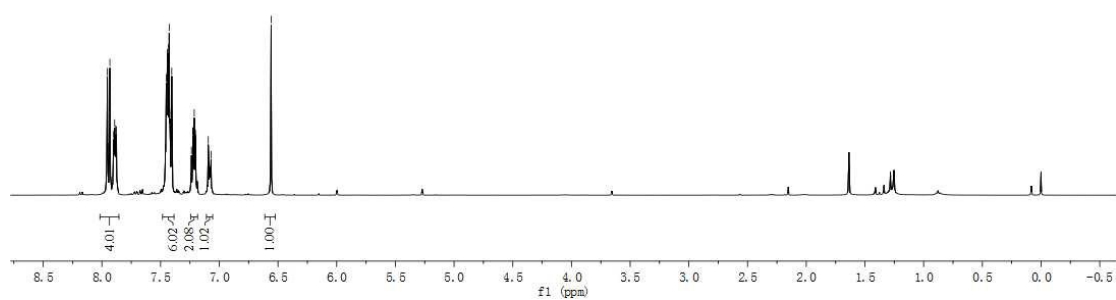
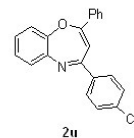


### <sup>13</sup>C NMR spectrum of 2t



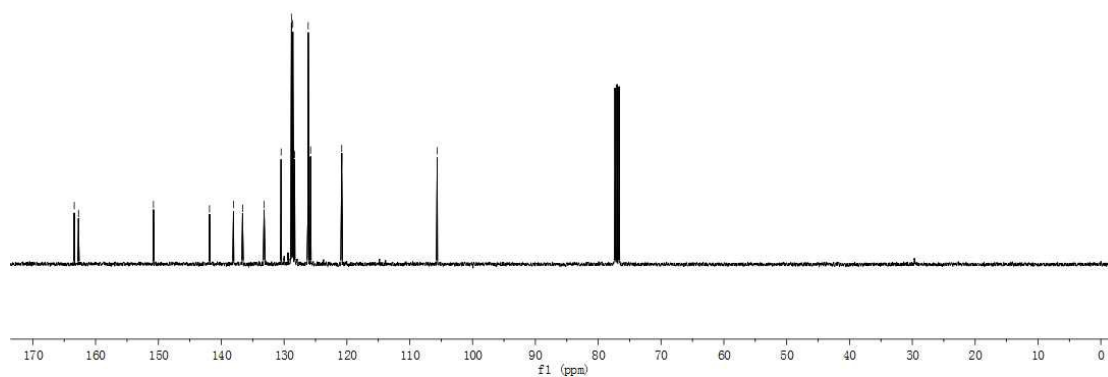
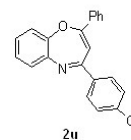
### <sup>1</sup>H NMR spectrum of **2u**

7.953  
7.937  
7.932  
7.900  
7.891  
7.887  
7.882  
7.876  
7.452  
7.443  
7.435  
7.427  
7.422  
7.405  
6.553

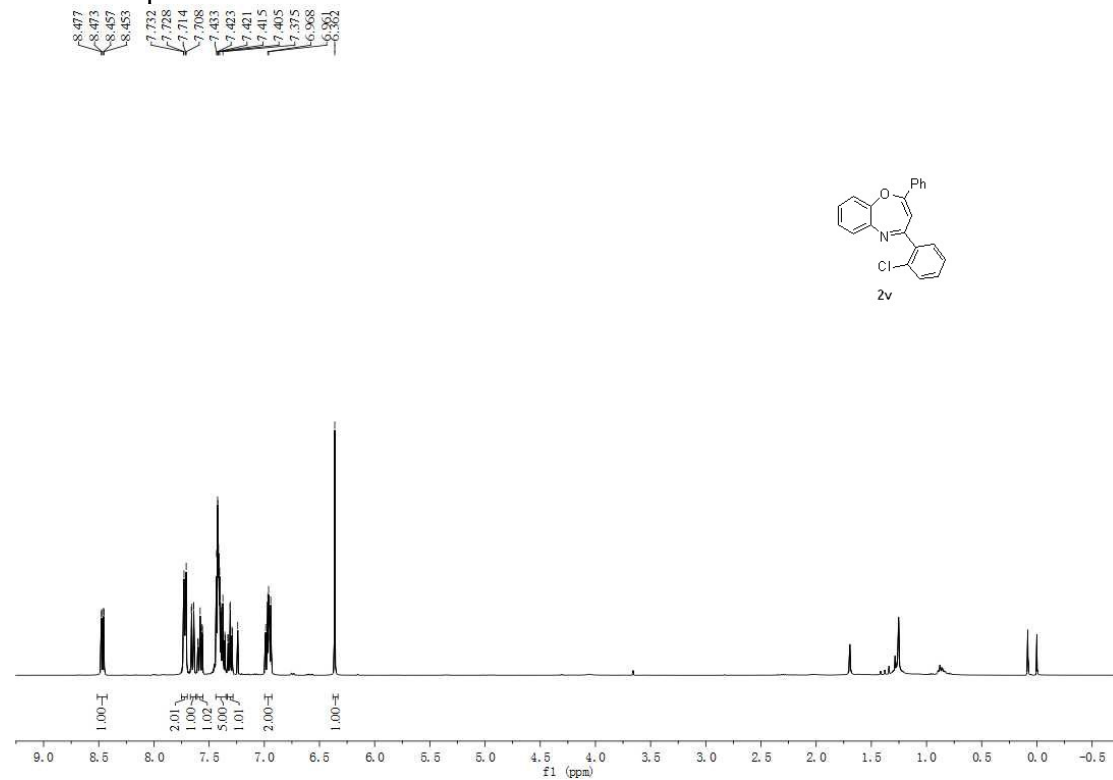


### <sup>13</sup>C NMR spectrum of **2u**

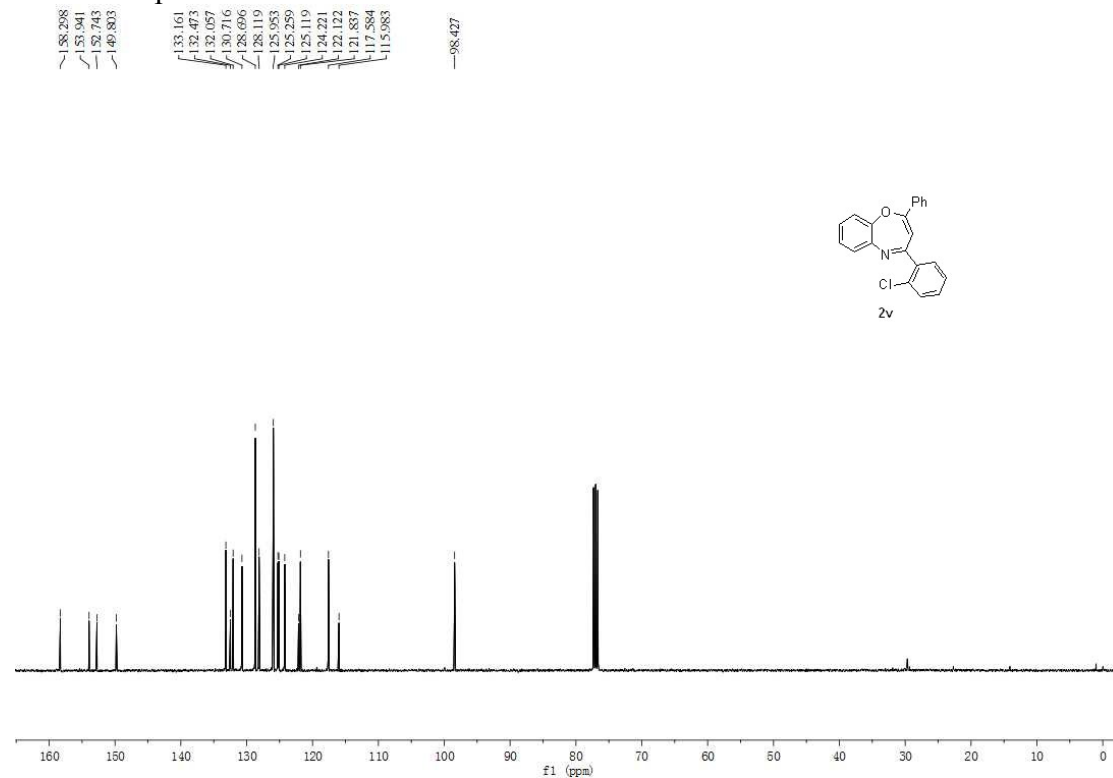
163.400  
162.720  
150.788  
141.874  
138.065  
136.697  
135.179  
130.472  
128.827  
128.705  
128.607  
128.330  
128.320  
126.102  
125.774  
120.824  
105.024



### <sup>1</sup>H NMR spectrum of 2v

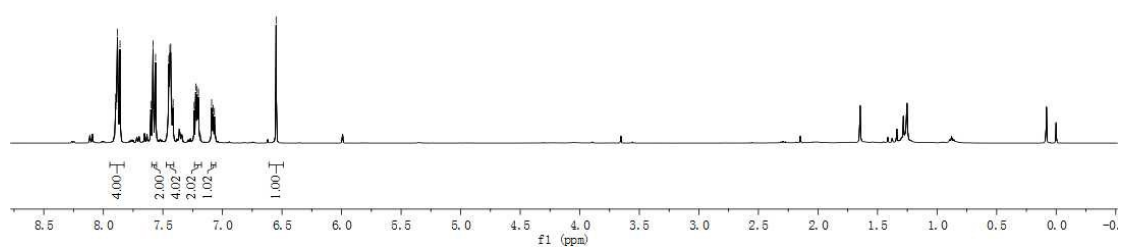
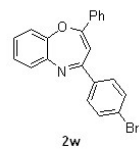


### <sup>13</sup>C NMR spectrum of 2v



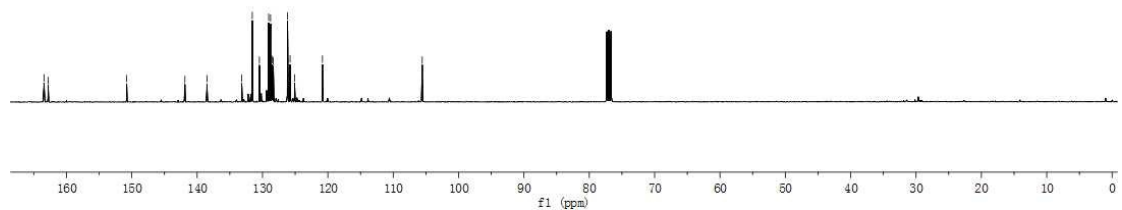
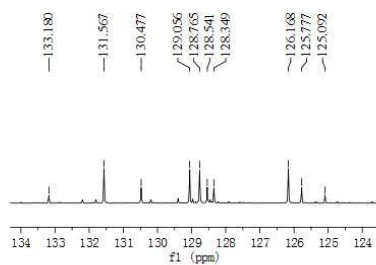
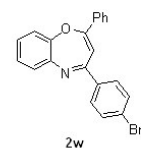
### $^1\text{H}$ NMR spectrum of **2w**

7.897  
7.888  
7.882  
7.873  
7.865  
7.860  
7.853  
7.562  
7.450  
7.441  
7.438  
7.434  
7.427  
7.225  
7.213  
6.306

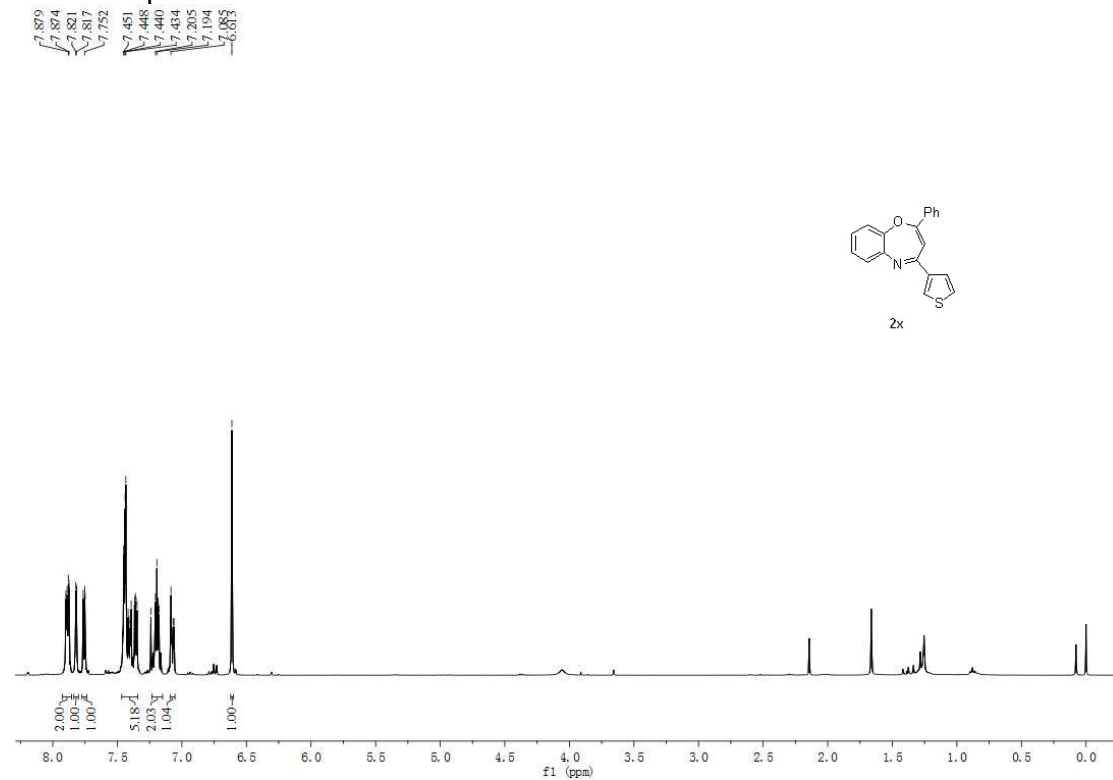


### $^{13}\text{C}$ NMR spectrum of **2w**

163.488  
162.833  
150.784  
141.887  
38.504  
33.180  
31.567  
30.477  
29.056  
28.765  
28.541  
28.349  
26.168  
25.777  
25.092  
20.828  
105.559



### <sup>1</sup>H NMR spectrum of **2x**



### <sup>13</sup>C NMR spectrum of **2x**

