

**Supporting Information for**  
**Efficient synthesis of pyrrolo[1,2- $\alpha$ ]quinoxalines mediated by ethyl 2-**  
**(4-nitrophenyl)azocarboxylate**

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**1. General considerations**

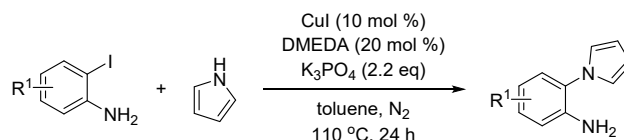
All commercially available compounds and solvents were purchased and used as received, unless otherwise noted. Analytical thin-layer chromatography (TLC) was performed on precoated silica gel 60 F254 plates. Visualization on TLC was achieved by the use of UV light (254 nm) and treatment with phosphomolybdic acid stain followed by heating. Flash chromatography was performed using silica gel (particle size 40–63  $\mu\text{m}$ , 230–400 mesh). <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on 400 MHz NMR (400 MHz for <sup>1</sup>H, 101 MHz for <sup>13</sup>C). Chemical shift values are given in parts per million relative to internal TMS (0.00 ppm for <sup>1</sup>H) or CDCl<sub>3</sub> (77.26 ppm for <sup>13</sup>C). The following abbreviations were used to describe peak splitting patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, dd = double of doublet, dt = double of triplet, td = triple of doublet. Coupling constants, *J*, were reported in hertz unit (Hz). High-resolution mass spectra were obtained from the Korea Basic Science Institute (Daegu) by using EI method and magnetic sector mass analyzer.

## 2. Preparation of oxidants and starting materials

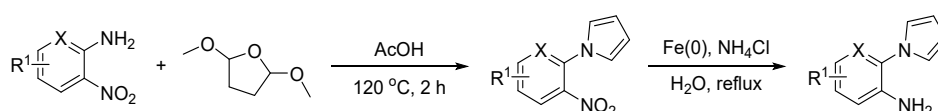
### Preparation of oxidants

All azo compounds were prepared according to the known procedure.<sup>1</sup>

### Preparation of 2-(1*H*-pyrrol-1-yl)anilines

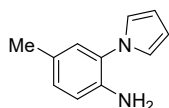


The 2-(1*H*-pyrrol-1-yl)anilines for **11**, **12**, **14**, **15**, **18**, **20**, and **21** were prepared by Cu-catalyzed C-N cross coupling reaction.<sup>2</sup>

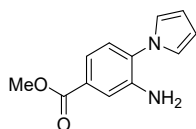


The 2-(1*H*-pyrrol-1-yl)anilines for **10**, **13**, **16**, **17**, and **19** were prepared by cyclization followed by reduction.<sup>3</sup>

The characterizations of newly synthesized 2-(1*H*-pyrrol-1-yl)anilines were provided below.



**4-methyl-2-(1*H*-pyrrol-1-yl)aniline** (for **11**); yellow solid, EtOAc/Hx=1:4, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.96 (d, *J* = 6.6 Hz, 2H), 6.81 (t, *J* = 2.1 Hz, 2H), 6.71 (d, *J* = 8.7 Hz, 1H), 6.31 (t, *J* = 2.0 Hz, 2H), 3.57 (s, 2H), 2.25 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 139.6, 129.3, 128.2, 127.8, 127.7, 121.9, 116.4, 109.5, 20.5; HRMS (EI) *m/z* calcd. For C<sub>11</sub>H<sub>12</sub>N<sub>2</sub> [M]<sup>+</sup>: 172.1000, found 172.0998.



**methyl 3-amino-4-(1*H*-pyrrol-1-yl)benzoate** (for **17**); pale solid, EtOAc/Hx=1:4, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.49 (d, *J* = 1.7 Hz, 1H), 7.45 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.19 (d, *J* = 8.1 Hz, 1H), 6.87 (t, *J* = 2.1 Hz, 2H), 6.37 (t, *J* = 2.1 Hz, 2H), 3.91 (s, 3H), 3.88 (s, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 166.8, 141.8, 131.1, 130.0, 126.8, 121.4, 119.7, 117.5, 110.2, 52.4; HRMS (EI) *m/z* calcd. For C<sub>12</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub> [M]<sup>+</sup>: 216.0899, found 216.0900.

### Preparation of 3-(4,5-diphenyloxazol-2-yl)propanal (for **53**)

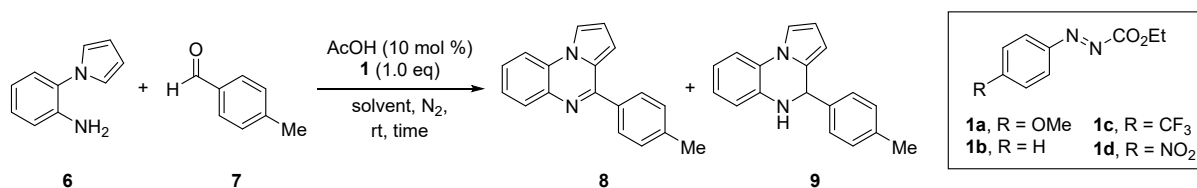
3-(4,5-diphenyloxazol-2-yl)propanal was prepared by the reduction of oxaprozin with LiAlH<sub>4</sub> followed by PCC oxidation.<sup>4</sup>

### Preparation of 2-amino-*N*-methylbenzamides

2-amino-*N*-methylbenzamides were prepared according to the known procedure.<sup>5</sup>

### 3. Optimization of azo-mediated oxidative cyclization

A 10 mL flame-dried test tube (O.D. 15 mm), which was equipped with a magnetic stir bar and charged with 2-(1*H*-pyrrol-1-yl)aniline **6** (1.0 mmol), ethyl 2-phenylazocarboxylates **1** (1.0 equiv., 1.0 mmol), was evacuated and backfilled with nitrogen (this process was repeated three times). After 1.0 mL of solvent was added, 4-methylbenzaldehyde **7** (1.2 equiv, 1.2 mmol), acetic acid (0.1 equiv, 0.1 mmol), and solvent (1.0 mL) were added in sequence. The reaction mixture was stirred at room temperature (stirring rate: 1500 rpm). The reaction mixture was concentrated on rotary evaporator. The crude mixture was dissolved in CHCl<sub>3</sub> (30 mL) and filtered through a pad of silica (to separate hydrazine byproduct). The silica pad was washed with additional CHCl<sub>3</sub> (30 mL). The reaction mixture was concentrated on rotary evaporator. The <sup>1</sup>H NMR yield of the desired product was determined by integration using an internal standard (1,1,2,2-tetrachloroethane).



entry	<b>1</b>	solvent	time (h)	yield (%) <sup>a</sup>	
				<b>8</b>	<b>9</b>
1	<b>1a</b>	MeOH	0.5	32	63
2	<b>1b</b>	MeOH	0.5	52	33
3	<b>1c</b>	MeOH	0.5	88	12
4	<b>1d</b>	MeOH	0.5	95	5
5	<b>1d</b>	toluene	0.5	55	3
6	<b>1d</b>	DMF	0.5	21	0
7	<b>1d</b>	CH <sub>3</sub> CN	0.5	12	0
8	<b>1d</b>	DMSO	0.5	0	0
9	<b>1d</b>	THF	0.5	0	0
10	<b>1d</b>	MeOH	1	99	0
11 <sup>b</sup>	<b>1d</b>	MeOH	1	99	0
12	-	MeOH	1	0	99
13 <sup>b</sup>	-	MeOH	1	0	99
14 <sup>c</sup>	<b>1d</b>	MeOH	1	0	0

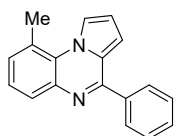
15 <sup>d</sup>	<b>1d</b>	MeOH	1	90	0
16 <sup>e</sup>	<b>1d</b>	MeOH	1	99	0
17 <sup>f</sup>	<b>1d</b>	MeOH	1	99	0

<sup>a</sup>Yield of **3a** was determined by <sup>1</sup>H NMR spectroscopy with 1,1,2,2-tetrachloroethane as internal standard. <sup>b</sup>Under air <sup>c</sup>No AcOH was used. <sup>d</sup>No light. <sup>e</sup>The use of HCl instead of AcOH. <sup>f</sup>The use of TFA instead of AcOH

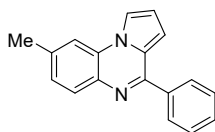
#### 4. General procedure of 1d-mediated oxidative cyclization

A 10 mL flame-dried test tube (O.D. 15 mm), which was equipped with a magnetic stir bar and charged with 2-(1*H*-pyrrol-1-yl)aniline (1.0 mmol), ethyl 2-(4-nitrophenyl)azocarboxylate **1d** (1.0 equiv., 1.0 mmol), was evacuated and backfilled with nitrogen (this process was repeated three times). After 1.0 mL of methanol was added, aldehyde (1.2 equiv, 1.2 mmol), acetic acid (0.1 equiv, 0.1 mmol), and methanol (1.0 mL) were added in sequence. The reaction mixture was stirred at room temperature for 1 h (stirring rate: 1500 rpm). The reaction mixture was concentrated on rotary evaporator. The crude mixture was dissolved in CHCl<sub>3</sub> (30 mL) and filtered through a pad of silica (to separate hydrazine byproduct). The silica pad was washed with additional CHCl<sub>3</sub> (30 mL). The reaction mixture was concentrated on rotary evaporator. The residue was purified by column chromatography (silica gel) to provide pyrrolo[1,2- $\alpha$ ]quinoxalines.

The filtered hydrazine on the pad of silica was washed with ethyl acetate several times. The filtrate was evacuated on rotovap to obtain hydrazine byproduct. The obtained hydrazine was pure enough to use recycling without further purification.

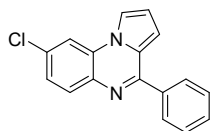


**9-methyl-4-phenylpyrrolo[1,2- $\alpha$ ]quinoxaline<sup>6</sup> (10)**; yellow solid, EtOAc/Hx=1:4, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.36 (d,  $J$  = 1.8 Hz, 1H), 7.95 (ddd,  $J$  = 20.7, 7.6, 1.8 Hz, 3H), 7.57 – 7.47 (m, 3H), 7.40 – 7.27 (m, 2H), 6.99 (d,  $J$  = 3.4 Hz, 1H), 6.89 – 6.80 (m, 1H), 2.96 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  154.3, 138.6, 138.1, 131.1, 129.8, 128.9, 128.8, 128.7, 127.6, 127.0, 125.4, 124.8, 120.4, 113.4, 108.3, 24.1.

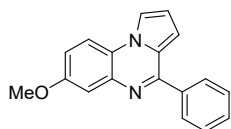


**8-methyl-4-phenylpyrrolo[1,2- $\alpha$ ]quinoxaline<sup>6</sup> (11)**; pale-yellow solid, EtOAc/Hx=1:4, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.01 (dd,  $J$  = 7.6, 1.6 Hz, 2H), 7.92 (d,  $J$  = 8.2 Hz, 1H), 7.88 (d,  $J$  = 1.5 Hz, 1H), 7.59

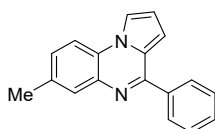
(s, 1H), 7.57 – 7.49 (m, 3H), 7.27 – 7.21 (m, 1H), 6.99 – 6.93 (m, 1H), 6.87 – 6.80 (m, 1H), 2.51 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 153.5, 138.7, 138.0, 134.4, 130.0, 129.7, 128.7, 128.7, 127.0, 126.6, 125.5, 114.3, 113.9, 113.8, 108.4, 21.9.



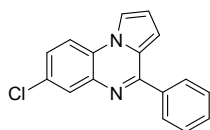
**8-chloro-4-phenylpyrrolo[1,2-*a*]quinoxaline<sup>6</sup> (12)**; pale-yellow solid, EtOAc/Hx=1:4, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.98 (d, *J* = 4.2 Hz, 1H), 7.95 (dd, *J* = 9.2, 5.3 Hz, 2H), 7.91 – 7.89 (m, 1H), 7.84 (d, *J* = 2.1 Hz, 1H), 7.56 – 7.49 (m, 3H), 7.39 (dd, *J* = 8.6, 2.1 Hz, 1H), 6.99 (dd, *J* = 4.0, 1.0 Hz, 1H), 6.92 – 6.86 (m, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 154.7, 138.4, 135.1, 133.0, 131.6, 130.2, 128.9, 128.8, 128.0, 125.9, 125.5, 115.1, 114.8, 114.0, 109.4.



**7-methoxy-4-phenylpyrrolo[1,2-*a*]quinoxaline<sup>6</sup> (13)**; yellow solid, EtOAc/Hx=1:4, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.99 (dd, *J* = 7.4, 1.8 Hz, 2H), 7.87 (d, *J* = 1.2 Hz, 1H), 7.72 (d, *J* = 9.0 Hz, 1H), 7.58 – 7.46 (m, 4H), 7.09 (dd, *J* = 9.0, 2.7 Hz, 1H), 6.95 (d, *J* = 3.3 Hz, 1H), 6.86 – 6.79 (m, 1H), 3.90 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 157.3, 154.8, 138.7, 137.5, 129.9, 128.8, 128.7, 125.2, 121.6, 116.8, 114.7, 114.4, 113.8, 111.1, 108.5, 55.9.

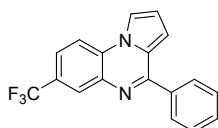


**7-methyl-4-phenylpyrrolo[1,2-*a*]quinoxaline<sup>6</sup> (14)**; yellow solid, EtOAc/Hx=1:4, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.01 (dd, *J* = 7.6, 1.9 Hz, 2H), 7.90 – 7.87 (m, 1H), 7.84 (s, 1H), 7.68 (d, *J* = 8.3 Hz, 1H), 7.58 – 7.48 (m, 3H), 7.27 (dd, *J* = 8.3, 1.4 Hz, 1H), 6.96 (dd, *J* = 4.0, 1.0 Hz, 1H), 6.83 (dd, *J* = 3.9, 2.8 Hz, 1H), 2.48 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 154.4, 138.8, 136.4, 135.1, 130.2, 129.8, 128.8, 128.7, 125.4, 125.1, 114.5, 113.8, 113.5, 108.5, 21.3.

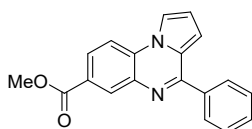


**7-chloro-4-phenylpyrrolo[1,2-*a*]quinoxaline<sup>6</sup> (15)**; yellow solid, EtOAc/Hx=1:4, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.01 (d, *J* = 2.3 Hz, 1H), 7.99 – 7.94 (m, 2H), 7.91 (dd, *J* = 2.5, 1.0 Hz, 1H), 7.75 (d, *J*

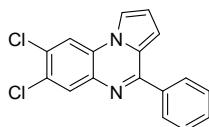
= 8.8 Hz, 1H), 7.56 – 7.50 (m, 3H), 7.42 (dd,  $J = 8.8, 2.3$  Hz, 1H), 7.00 (dd,  $J = 4.0, 1.1$  Hz, 1H), 6.88 (dd,  $J = 4.0, 2.8$  Hz, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  155.6, 138.3, 137.4, 130.6, 130.3, 129.8, 128.8, 127.6, 126.0, 125.4, 115.1, 115.0, 114.6, 109.5.



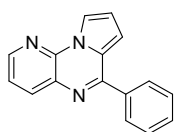
**4-phenyl-7-(trifluoromethyl)pyrrolo[1,2- $\alpha$ ]quinoxaline<sup>6</sup> (16)**; white solid, EtOAc/Hx=1:4,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.12 (d,  $J = 7.1$  Hz, 2H), 8.07 – 8.03 (m, 1H), 8.03 – 7.97 (m, 2H), 7.72 – 7.64 (m, 1H), 7.61 – 7.51 (m, 3H), 7.06 (dd,  $J = 4.0, 1.0$  Hz, 1H), 6.95 (dd,  $J = 4.0, 2.8$  Hz, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  156.5, 138.6, 138.1, 131.0, 130.5, 128.9 (q,  $J = 33.2$  Hz), 128.8, 128.7, 127.1, 125.5, 124.1 (q,  $J = 273.3$  Hz), 121.8 (q,  $J = 3.6$  Hz), 115.6, 114.9, 111.4 (q,  $J = 4.2$  Hz), 110.1;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -61.91.



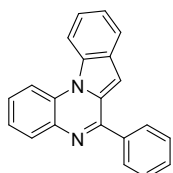
**methyl 4-phenylpyrrolo[1,2- $\alpha$ ]quinoxaline-7-carboxylate (17)**; pale-white solid, EtOAc/Hx=1:4, mp 183-185 °C,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.72 (d,  $J = 1.7$  Hz, 1H), 8.15 (dd,  $J = 8.6, 1.8$  Hz, 1H), 8.00 (dd,  $J = 6.5, 3.1$  Hz, 3H), 7.86 (d,  $J = 8.6$  Hz, 1H), 7.55 (dd,  $J = 4.9, 1.6$  Hz, 3H), 7.09 – 6.99 (m, 1H), 6.95 – 6.90 (m, 1H), 3.97 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.5, 155.2, 138.2, 135.9, 132.3, 130.2, 128.8, 128.4, 127.1, 125.6, 115.4, 115.0, 113.8, 109.7, 52.4, 29.9; HRMS (EI)  $m/z$  calcd. For  $\text{C}_{19}\text{H}_{14}\text{N}_2\text{O}_2$  [ $\text{M}$ ]<sup>+</sup>: 302.1055, found 302.1056.



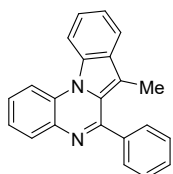
**7,8-dichloro-4-phenylpyrrolo[1,2- $\alpha$ ]quinoxaline<sup>7</sup> (18)**; yellow solid, EtOAc/Hx=1:4,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.09 (s, 1H), 7.99 – 7.94 (m, 2H), 7.93 (s, 1H), 7.89 – 7.87 (m, 1H), 7.56 – 7.50 (m, 3H), 7.02 (dd,  $J = 4.0, 0.9$  Hz, 1H), 6.90 (dd,  $J = 3.9, 2.9$  Hz, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  155.7, 138.0, 135.9, 131.3, 131.1, 130.5, 129.0, 128.9, 128.8, 126.5, 125.3, 115.4, 115.4, 115.0, 110.1.



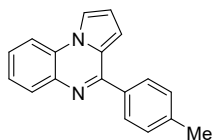
**6-phenylpyrido[3,2-e]pyrrolo[1,2- $\alpha$ ]pyrazine<sup>6</sup> (19)**; light-yellow solid, EtOAc/Hx=1:4, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.53 (dd,  $J$  = 4.6, 1.6 Hz, 1H), 8.47 (dd,  $J$  = 2.7, 1.3 Hz, 1H), 8.30 (dd,  $J$  = 8.0, 1.6 Hz, 1H), 8.00 (dd,  $J$  = 6.6, 3.0 Hz, 2H), 7.59 – 7.50 (m, 3H), 7.44 (dd,  $J$  = 8.0, 4.7 Hz, 1H), 7.06 (dd,  $J$  = 3.9, 1.3 Hz, 1H), 6.93 (dd,  $J$  = 3.8, 2.8 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  155.5, 146.8, 139.5, 138.2, 137.6, 131.4, 130.4, 128.9, 128.9, 127.0, 121.9, 116.2, 114.7, 110.6.



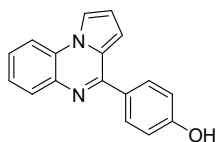
**6-phenylindolo[1,2- $\alpha$ ]quinoxaline<sup>7</sup> (20)**; yellow solid, EtOAc/Hx=1:10, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.53 (t,  $J$  = 9.3 Hz, 2H), 8.10 (d,  $J$  = 7.8 Hz, 1H), 8.06 – 7.99 (m, 2H), 7.94 (d,  $J$  = 7.6 Hz, 1H), 7.68 – 7.52 (m, 5H), 7.46 (dd,  $J$  = 8.1, 6.0 Hz, 2H), 7.26 (s, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  156.5, 138.5, 136.5, 133.3, 130.8, 130.5, 130.3, 129.5, 129.4, 128.9, 128.9, 128.6, 124.6, 124.4, 123.0, 122.9, 114.9, 114.8, 102.8.



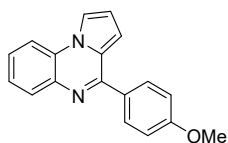
**7-methyl-6-phenylindolo[1,2- $\alpha$ ]quinoxaline<sup>8</sup> (21)**; yellow solid, EtOAc/Hx=1:4, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.46 (dd,  $J$  = 8.3, 3.9 Hz, 2H), 8.00 (dd,  $J$  = 7.9, 1.2 Hz, 1H), 7.88 (d,  $J$  = 8.1 Hz, 1H), 7.68 – 7.49 (m, 7H), 7.47 – 7.35 (m, 2H), 2.05 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  157.9, 139.9, 136.0, 132.2, 130.8, 130.5, 130.4, 129.4, 128.8, 128.7, 128.5, 126.0, 124.9, 124.0, 122.2, 121.0, 114.6, 111.1, 11.3.



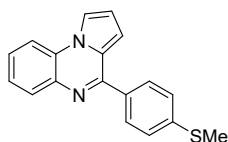
**4-(*p*-tolyl)pyrrolo[1,2- $\alpha$ ]quinoxaline<sup>6</sup> (8)**; yellow solid, EtOAc/MeOH/PE=1:5:20, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.02 (dd,  $J$  = 7.9, 1.4 Hz, 1H), 7.98 – 7.88 (m, 3H), 7.85 (dd,  $J$  = 8.0, 1.3 Hz, 1H), 7.46 (dtd,  $J$  = 15.0, 7.3, 1.5 Hz, 2H), 7.38 – 7.31 (m, 2H), 6.99 (dd,  $J$  = 4.0, 1.3 Hz, 1H), 6.87 (dd,  $J$  = 4.0, 2.7 Hz, 1H), 2.45 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  154.5, 140.0, 136.4, 135.8, 130.3, 129.4, 128.7, 127.4, 127.2, 125.5, 125.3, 114.7, 114.0, 113.7, 108.8, 21.6.



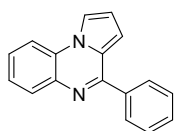
**4-(pyrrolo[1,2- $\alpha$ ]quinoxalin-4-yl)phenol<sup>9</sup> (22)**; follow the general procedure without filtering process, white solid, EtOAc/Hx=1:4, <sup>1</sup>H NMR (400 MHz, DMSO)  $\delta$  9.94 (s, 1H), 8.49 (d,  $J$  = 1.4 Hz, 1H), 8.27 (d,  $J$  = 8.2 Hz, 1H), 7.87 (d,  $J$  = 8.6 Hz, 3H), 7.50 (dt,  $J$  = 33.6, 7.6 Hz, 2H), 7.06 – 6.89 (m, 4H); <sup>13</sup>C NMR (101 MHz, DMSO)  $\delta$  159.7, 153.3, 136.1, 130.5, 129.7, 129.2, 127.8, 127.0, 125.8, 124.6, 116.7, 115.8, 115.0, 114.5, 108.8.



**4-(4-methoxyphenyl)pyrrolo[1,2- $\alpha$ ]quinoxaline<sup>6</sup> (23)**; light-yellow solid, EtOAc/Hx=1:4, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.03 (s, 1H), 8.01 – 7.94 (m, 3H), 7.86 (d,  $J$  = 7.9 Hz, 1H), 7.56 – 7.38 (m, 2H), 7.13 – 7.03 (m, 2H), 7.00 (d,  $J$  = 1.1 Hz, 1H), 6.89 (d,  $J$  = 1.3 Hz, 1H), 3.90 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  161.2, 154.1, 136.6, 131.3, 130.3, 130.3, 127.4, 127.3, 125.6, 125.4, 114.7, 114.2, 114.1, 113.8, 108.8, 55.7.

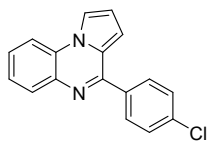


**4-(4-(methylthio)phenyl)pyrrolo[1,2- $\alpha$ ]quinoxaline (24)**; yellow solid, EtOAc/Hx=1:4, mp 90-92 °C, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.02 (dd,  $J$  = 7.9, 1.4 Hz, 1H), 7.95 (d,  $J$  = 8.5 Hz, 3H), 7.85 (dd,  $J$  = 8.0, 1.2 Hz, 1H), 7.54 – 7.43 (m, 2H), 7.41 (t,  $J$  = 5.2 Hz, 2H), 6.99 (dd,  $J$  = 4.0, 1.2 Hz, 1H), 6.88 (dd,  $J$  = 4.0, 2.8 Hz, 1H), 2.55 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  153.8, 141.1, 136.4, 135.3, 130.3, 129.2, 127.6, 127.3, 126.3, 125.5, 125.4, 114.8, 114.1, 113.8, 108.7, 15.7; HRMS (EI)  $m/z$  calcd. For C<sub>18</sub>H<sub>14</sub>N<sub>2</sub>S [M]<sup>+</sup>: 290.0878, found 290.0876.

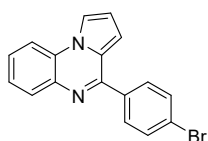


**4-phenylpyrrolo[1,2- $\alpha$ ]quinoxaline<sup>6</sup> (25)**; yellow solid, EtOAc/Hx=1:4, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.04 (dd,  $J$  = 7.9, 1.5 Hz, 1H), 8.02 – 7.96 (m, 3H), 7.85 (dd,  $J$  = 8.1, 1.2 Hz, 1H), 7.58 – 7.42 (m, 5H), 6.98 (dd,  $J$  = 4.0, 1.2 Hz, 1H), 6.88 (dd,  $J$  = 4.0, 2.8 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  154.2, 138.5, 136.2, 130.1, 129.8, 128.6, 128.5, 127.3, 127.0, 125.2, 125.1, 114.6, 113.9, 113.5, 108.6.

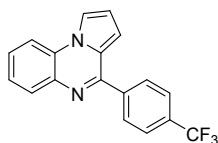




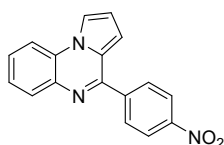
**4-(4-chlorophenyl)pyrrolo[1,2- $\alpha$ ]quinoxaline<sup>6</sup> (26)**; yellow solid, EtOAc/Hx=1:4, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.07 – 7.99 (m, 2H), 7.96 (d,  $J$  = 8.5 Hz, 2H), 7.91 – 7.86 (m, 1H), 7.58 – 7.42 (m, 4H), 6.96 (dd,  $J$  = 4.0, 1.1 Hz, 1H), 6.91 (dd,  $J$  = 3.9, 2.8 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  153.3, 137.2, 136.4, 136.1, 130.5, 130.2, 129.1, 127.9, 127.4, 125.6, 125.4, 115.0, 114.3, 113.9, 108.7.



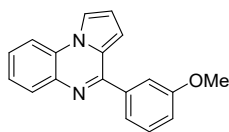
**4-(4-bromophenyl)pyrrolo[1,2- $\alpha$ ]quinoxaline<sup>6</sup> (27)**; yellow solid, EtOAc/Hx=1:4, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.03 (d,  $J$  = 8.7 Hz, 2H), 7.95 – 7.85 (m, 3H), 7.68 (d,  $J$  = 8.3 Hz, 2H), 7.53 (d,  $J$  = 7.5 Hz, 1H), 7.48 (d,  $J$  = 7.9 Hz, 1H), 6.96 (d,  $J$  = 3.5 Hz, 1H), 6.92 (d,  $J$  = 2.7 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  153.4, 137.6, 136.4, 132.0, 130.5, 130.5, 128.0, 127.4, 125.6, 125.3, 124.4, 115.1, 114.3, 113.9, 108.7.



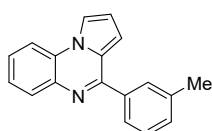
**4-(4-(trifluoromethyl)phenyl)pyrrolo[1,2- $\alpha$ ]quinoxaline<sup>6</sup> (28)**; yellow solid, EtOAc/Hx=1:4, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.11 (d,  $J$  = 8.0 Hz, 2H), 8.06 – 7.97 (m, 2H), 7.88 (dd,  $J$  = 8.2, 1.1 Hz, 1H), 7.79 (d,  $J$  = 8.1 Hz, 2H), 7.57 – 7.50 (m, 1H), 7.49 – 7.43 (m, 1H), 6.94 (dd,  $J$  = 4.0, 1.2 Hz, 1H), 6.91 (dd,  $J$  = 4.0, 2.7 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  152.8, 142.0, 136.1, 131.7 (q,  $J$  = 32.5 Hz), 130.4, 129.2, 128.0, 127.2, 125.6 (q,  $J$  = 3.7 Hz), 125.5, 125.1, 124.2 (q,  $J$  = 272.3 Hz), 115.0, 114.3, 113.8, 108.5; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -62.71.



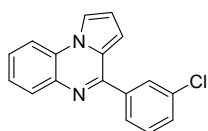
**4-(4-nitrophenyl)pyrrolo[1,2- $\alpha$ ]quinoxaline<sup>9</sup> (29)**; yellow solid, EtOAc/Hx=1:4, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.40 (d,  $J$  = 8.2 Hz, 2H), 8.19 (d,  $J$  = 8.2 Hz, 2H), 8.05 (d,  $J$  = 7.1 Hz, 2H), 7.92 (d,  $J$  = 8.0 Hz, 1H), 7.58 (t,  $J$  = 7.5 Hz, 1H), 7.50 (t,  $J$  = 7.3 Hz, 1H), 6.96 (s, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  152.1, 148.8, 144.7, 136.1, 130.7, 129.9, 128.6, 127.4, 125.9, 125.0, 124.0, 115.4, 114.7, 114.0, 108.5.



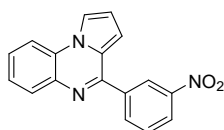
**4-(3-methoxyphenyl)pyrrolo[1,2-a]quinoxaline<sup>6</sup> (30)**; yellow solid, EtOAc/Hx=1:4, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.03 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.96 (dd, *J* = 2.6, 1.1 Hz, 1H), 7.84 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.61 – 7.39 (m, 5H), 7.10 – 7.03 (m, 1H), 7.00 (dd, *J* = 4.0, 1.1 Hz, 1H), 6.87 (dd, *J* = 3.9, 2.8 Hz, 1H), 3.89 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 160.0, 154.4, 140.0, 136.4, 130.4, 129.8, 127.7, 127.4, 125.5, 125.5, 121.3, 116.1, 114.8, 114.2, 114.0, 113.8, 108.9, 55.6.



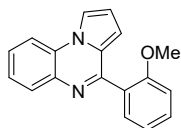
**4-(*m*-tolyl)pyrrolo[1,2-a]quinoxaline<sup>6</sup> (31)**; yellow solid, EtOAc/MeOH/PE=1:5:20, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.05 (dd, *J* = 7.9, 1.3 Hz, 1H), 8.00 (dd, *J* = 2.6, 1.2 Hz, 1H), 7.89 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.79 (d, *J* = 11.9 Hz, 2H), 7.57 – 7.39 (m, 3H), 7.34 (d, *J* = 7.6 Hz, 1H), 6.99 (dd, *J* = 4.0, 1.2 Hz, 1H), 6.90 (dd, *J* = 4.0, 2.8 Hz, 1H), 2.48 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 154.6, 138.5, 138.4, 136.3, 130.7, 130.2, 129.3, 128.5, 127.4, 127.2, 125.9, 125.5, 125.3, 114.6, 114.0, 113.7, 108.8, 21.7.



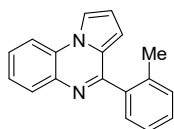
**4-(3-chlorophenyl)pyrrolo[1,2-a]quinoxaline<sup>10</sup> (32)**; pale solid, EtOAc/Hx=1:4, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.02 (d, *J* = 8.0 Hz, 1H), 7.99 (s, 2H), 7.87 (dd, *J* = 12.2, 5.0 Hz, 2H), 7.48 (td, *J* = 15.3, 6.7 Hz, 4H), 6.96 (s, 1H), 6.89 (s, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 153.0, 140.4, 136.3, 134.9, 130.5, 130.1, 129.0, 128.0, 127.4, 127.0, 125.6, 125.3, 115.1, 114.4, 113.9, 108.7.



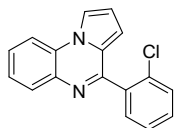
**4-(3-nitrophenyl)pyrrolo[1,2-a]quinoxaline<sup>11</sup> (33)**; yellow solid, EtOAc/Hx=1:4, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.89 (t, *J* = 1.8 Hz, 1H), 8.37 (dt, *J* = 7.7, 1.8 Hz, 2H), 8.03 (dd, *J* = 8.1, 1.4 Hz, 2H), 7.91 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.72 (t, *J* = 8.0 Hz, 1H), 7.63 – 7.53 (m, 1H), 7.53 – 7.45 (m, 1H), 6.96 (ddd, *J* = 6.8, 4.1, 2.0 Hz, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 151.8, 148.7, 140.3, 136.2, 134.8, 130.7, 129.9, 128.5, 127.4, 125.8, 125.0, 124.7, 124.0, 115.4, 114.7, 114.0, 108.4.



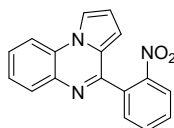
**4-(2-methoxyphenyl)pyrrolo[1,2-*a*]quinoxaline<sup>6</sup> (34)**; yellow solid, EtOAc/Hx=1:4, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.04 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.92 (dd, *J* = 2.5, 1.2 Hz, 1H), 7.84 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.57 – 7.37 (m, 4H), 7.08 (ddd, *J* = 22.1, 11.0, 4.5 Hz, 2H), 6.80 (dd, *J* = 3.9, 2.8 Hz, 1H), 6.58 (dd, *J* = 4.0, 1.2 Hz, 1H), 3.75 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 157.5, 153.7, 136.4, 130.7, 130.4, 127.7, 127.6, 126.7, 125.2, 120.9, 114.2, 113.9, 113.8, 111.7, 108.7, 55.9.



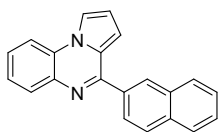
**4-(*o*-tolyl)pyrrolo[1,2-*a*]quinoxaline<sup>6</sup> (35)**; yellow solid, EtOAc/Hx=1:4, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.07 – 8.02 (m, 1H), 7.98 – 7.94 (m, 1H), 7.91 – 7.86 (m, 1H), 7.59 – 7.42 (m, 3H), 7.41 – 7.27 (m, 3H), 6.83 (dd, *J* = 3.8, 2.8 Hz, 1H), 6.57 (dd, *J* = 3.9, 1.0 Hz, 1H), 2.34 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 155.8, 137.7, 136.6, 136.2, 131.0, 130.4, 129.2, 129.1, 127.7, 127.4, 126.5, 125.8, 125.4, 114.7, 114.1, 113.9, 108.8, 19.9.



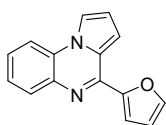
**4-(2-chlorophenyl)pyrrolo[1,2-*a*]quinoxaline<sup>10</sup> (36)**; pale solid, EtOAc/Hx=1:4, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.05 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.91 (dd, *J* = 2.6, 1.2 Hz, 1H), 7.81 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.59 – 7.45 (m, 3H), 7.45 – 7.42 (m, 1H), 7.41 – 7.35 (m, 2H), 6.81 (dd, *J* = 4.0, 2.7 Hz, 1H), 6.56 (dd, *J* = 4.0, 1.2 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 153.1, 137.0, 135.9, 133.0, 130.8, 130.4, 130.3, 130.2, 128.0, 127.4, 126.9, 125.8, 125.3, 114.7, 114.1, 113.8, 108.6.



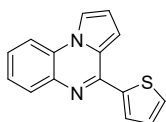
**4-(2-nitrophenyl)pyrrolo[1,2-*a*]quinoxaline (37)**; yellow solid, EtOAc/Hx=1:4, mp 169-171 °C, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.13 (dd, *J* = 8.2, 0.7 Hz, 1H), 8.00 – 7.91 (m, 2H), 7.88 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.77 (dtd, *J* = 8.8, 7.6, 1.4 Hz, 2H), 7.65 (ddd, *J* = 8.2, 7.2, 1.9 Hz, 1H), 7.60 – 7.50 (m, 1H), 7.49 – 7.41 (m, 1H), 6.83 (dd, *J* = 4.0, 2.7 Hz, 1H), 6.56 (dd, *J* = 4.0, 1.2 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 151.7, 149.1, 136.1, 133.4, 133.4, 131.4, 130.5, 130.3, 128.3, 127.5, 125.6, 125.5, 125.0, 115.2, 114.4, 114.0, 107.3; HRMS (EI) *m/z* calcd. For C<sub>17</sub>H<sub>11</sub>N<sub>3</sub>O<sub>2</sub> [M]<sup>+</sup>: 289.0851, found 289.0853.



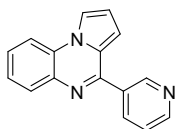
**4-(naphthalen-2-yl)pyrrolo[1,2- $\alpha$ ]quinoxaline<sup>6</sup> (38)**; yellow solid, EtOAc/MeOH/PE=1:5:20, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.51 (s, 1H), 8.10 (ddd,  $J$  = 9.1, 8.2, 1.4 Hz, 2H), 8.03 – 7.92 (m, 4H), 7.90 (d,  $J$  = 8.5 Hz, 1H), 7.58 – 7.42 (m, 4H), 7.07 (d,  $J$  = 3.1 Hz, 1H), 6.96 – 6.88 (m, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  154.5, 136.6, 136.1, 134.3, 133.4, 130.5, 129.0, 128.6, 128.5, 128.0, 127.7, 127.4, 127.1, 126.6, 126.3, 125.7, 125.5, 114.9, 114.3, 113.9, 109.0.



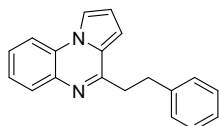
**4-(furan-2-yl)pyrrolo[1,2- $\alpha$ ]quinoxaline<sup>6</sup> (39)**; yellow solid, EtOAc/Hx=1:4, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.99 (dd,  $J$  = 7.6, 1.8 Hz, 1H), 7.93 – 7.90 (m, 1H), 7.81 – 7.76 (m, 1H), 7.70 (d,  $J$  = 0.8 Hz, 1H), 7.46 – 7.36 (m, 4H), 6.89 (dd,  $J$  = 3.9, 2.9 Hz, 1H), 6.62 (dd,  $J$  = 3.4, 1.7 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  152.3, 144.5, 143.4, 135.8, 129.9, 127.3, 127.0, 125.3, 123.1, 114.5, 114.1, 113.6, 112.8, 112.0, 108.4.



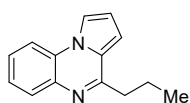
**4-(thiophen-2-yl)pyrrolo[1,2- $\alpha$ ]quinoxaline<sup>6</sup> (40)**; yellow solid, EtOAc/Hx=1:4, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.00 – 7.92 (m, 2H), 7.81 (d,  $J$  = 1.4 Hz, 1H), 7.66 (dd,  $J$  = 5.8, 3.5 Hz, 1H), 7.53 (d,  $J$  = 5.0 Hz, 1H), 7.39 – 7.32 (m, 2H), 7.22 – 7.16 (m, 2H), 6.82 – 6.78 (m, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  147.1, 142.5, 135.7, 129.7, 128.7, 128.2, 127.8, 127.2, 126.8, 125.2, 123.8, 114.6, 114.0, 113.4, 107.7.



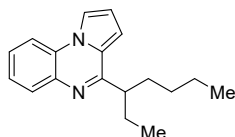
**4-(pyridin-3-yl)pyrrolo[1,2- $\alpha$ ]quinoxaline<sup>6</sup> (41)**; pale solid, EtOAc/Hx=1:4, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.27 – 9.23 (m, 1H), 8.76 (dd,  $J$  = 4.8, 1.6 Hz, 1H), 8.31 (dt,  $J$  = 7.9, 1.9 Hz, 1H), 8.05 – 8.01 (m, 2H), 7.89 (d,  $J$  = 8.2 Hz, 1H), 7.58 – 7.44 (m, 3H), 6.98 (dd,  $J$  = 4.0, 1.1 Hz, 1H), 6.92 (dd,  $J$  = 4.0, 2.8 Hz, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  151.7, 151.0, 149.8, 136.3, 136.3, 134.5, 130.6, 128.2, 127.4, 125.7, 125.3, 123.7, 115.2, 114.6, 114.0, 108.6.



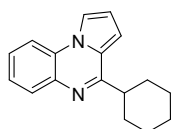
**4-phenethylpyrrolo[1,2- $\alpha$ ]quinoxaline<sup>6</sup> (42)**; yellow oil, EtOAc/Hx=1:4, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.95 (dd,  $J$  = 7.8, 1.5 Hz, 1H), 7.88 (dd,  $J$  = 2.5, 1.1 Hz, 1H), 7.80 (dd,  $J$  = 8.0, 1.2 Hz, 1H), 7.50 – 7.39 (m, 2H), 7.37 – 7.27 (m, 4H), 7.22 (dd,  $J$  = 5.2, 3.0 Hz, 1H), 6.88 (dd,  $J$  = 3.9, 1.1 Hz, 1H), 6.83 (dd,  $J$  = 3.9, 2.8 Hz, 1H), 3.36 – 3.28 (m, 2H), 3.26 – 3.20 (m, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  156.0, 141.7, 135.9, 129.4, 128.5, 127.2, 126.9, 126.8, 126.1, 125.8, 125.0, 114.1, 113.5, 113.4, 106.0, 37.4, 34.0.



**4-propylpyrrolo[1,2- $\alpha$ ]quinoxaline<sup>12</sup> (43)**; yellow solid, EtOAc/Hx=1:4, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.90 (dd,  $J$  = 7.8, 1.5 Hz, 1H), 7.86 (dd,  $J$  = 2.5, 1.1 Hz, 1H), 7.78 (dd,  $J$  = 8.0, 1.3 Hz, 1H), 7.46 – 7.36 (m, 2H), 6.88 (dd,  $J$  = 3.9, 1.1 Hz, 1H), 6.81 (dd,  $J$  = 3.9, 2.8 Hz, 1H), 2.98 (dd,  $J$  = 8.7, 6.9 Hz, 2H), 1.97 – 1.87 (m, 2H), 1.06 (t,  $J$  = 7.4 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  157.1, 135.9, 129.3, 127.1, 126.6, 125.9, 124.9, 113.9, 113.4, 113.3, 106.1, 37.7, 21.8, 14.3.

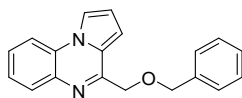


**4-(heptan-3-yl)pyrrolo[1,2- $\alpha$ ]quinoxaline<sup>13</sup> (44)**; colorless oil, EtOAc/Hx=1:20, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.96 – 7.91 (m, 1H), 7.89 (dd,  $J$  = 2.7, 1.2 Hz, 1H), 7.82 (dd,  $J$  = 7.9, 1.6 Hz, 1H), 7.47 – 7.37 (m, 2H), 6.92 (d,  $J$  = 4.0 Hz, 1H), 6.82 (dd,  $J$  = 3.9, 2.8 Hz, 1H), 3.12 – 3.01 (m, 1H), 2.01 (tt,  $J$  = 16.5, 8.3 Hz, 2H), 1.86 – 1.70 (m, 2H), 1.35 – 1.15 (m, 4H), 0.84 (dt,  $J$  = 13.9, 7.2 Hz, 6H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  161.0, 136.3, 129.8, 127.3, 127.1, 127.0, 125.2, 114.4, 113.8, 113.6, 106.5, 46.7, 34.2, 30.4, 27.7, 23.1, 14.2, 12.7.

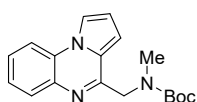


**4-cyclohexylpyrrolo[1,2- $\alpha$ ]quinoxaline<sup>6</sup> (45)**; yellow solid, EtOAc/Hx=1:4, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.93 (dd,  $J$  = 7.7, 1.5 Hz, 1H), 7.87 (d,  $J$  = 1.5 Hz, 1H), 7.81 – 7.77 (m, 1H), 7.46 – 7.36 (m, 2H), 6.94 – 6.89 (m, 1H), 6.83 – 6.80 (m, 1H), 3.12 (tt,  $J$  = 11.8, 3.2 Hz, 1H), 2.02 (d,  $J$  = 13.0 Hz, 2H), 1.97 – 1.75 (m, 5H), 1.55 – 1.32 (m, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  161.2, 136.4, 129.9, 127.4,

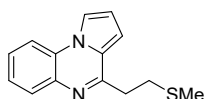
126.9, 125.8, 125.1, 114.1, 113.7, 113.4, 105.9, 43.8, 31.5, 26.8, 26.3.



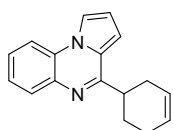
**4-((benzyloxy)methyl)pyrrolo[1,2-*a*]quinoxaline (46)**; red solid, EtOAc/Hx=1:4, mp 80-81 °C, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.98 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.92 (dd, *J* = 2.7, 1.3 Hz, 1H), 7.84 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.55 – 7.48 (m, 1H), 7.47 – 7.26 (m, 6H), 7.12 – 7.07 (m, 1H), 6.90 – 6.84 (m, 1H), 4.90 (s, 2H), 4.68 (s, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 153.2, 138.0, 135.6, 130.2, 128.6, 128.3, 128.0, 127.9, 127.8, 125.3, 125.2, 114.4, 114.1, 113.9, 107.5, 73.2, 72.7; HRMS (EI) *m/z* calcd. For C<sub>19</sub>H<sub>16</sub>N<sub>2</sub>O [M]<sup>+</sup>: 288.1263, found 288.1265.



**tert-butyl methyl(pyrrolo[1,2-*a*]quinoxalin-4-ylmethyl)carbamate (47)**; orange oil, EtOAc/Hx=1:4, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.92 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.52 – 7.45 (m, 1H), 7.42 (dd, *J* = 11.2, 4.0 Hz, 1H), 7.02 (d, *J* = 63.7 Hz, 1H), 6.84 (d, *J* = 2.7 Hz, 1H), 4.78 (d, *J* = 24.7 Hz, 2H), 2.92 (d, *J* = 34.5 Hz, 3H), 1.53 – 1.41 (m, 9H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 156.1, 152.6, 135.4, 129.9, 127.7, 125.1, 124.9, 114.5, 114.0, 113.7, 107.1, 106.0, 80.0, 52.3, 34.2, 28.6; HRMS (EI) *m/z* calcd. For C<sub>18</sub>H<sub>21</sub>N<sub>3</sub>O<sub>2</sub> [M]<sup>+</sup>: 311.1634, found 311.1635.

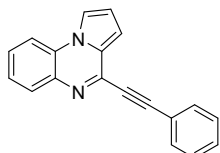


**4-(2-(methylthio)ethyl)pyrrolo[1,2-*a*]quinoxaline (48)**; yellow solid, EtOAc/Hx=1:4, mp 54-55 °C, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.91 (ddd, *J* = 4.1, 2.2, 1.3 Hz, 2H), 7.82 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.45 (dddd, *J* = 22.8, 7.8, 7.3, 1.5 Hz, 2H), 6.91 (dd, *J* = 4.0, 1.3 Hz, 1H), 6.85 (dd, *J* = 4.0, 2.7 Hz, 1H), 3.31 (ddd, *J* = 8.9, 5.8, 2.6 Hz, 2H), 3.12 – 3.03 (m, 2H), 2.20 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 155.3, 136.0, 129.7, 127.4, 127.3, 126.0, 125.3, 114.6, 113.8, 113.8, 106.3, 35.7, 32.4, 16.0; HRMS (EI) *m/z* calcd. For C<sub>14</sub>H<sub>14</sub>N<sub>2</sub>S [M]<sup>+</sup>: 242.0878, found 242.0876.

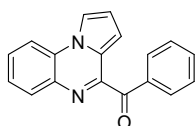


**4-(cyclohex-3-en-1-yl)pyrrolo[1,2-*a*]quinoxaline (49)**; orange solid, EtOAc/Hx=1:4, mp 82-83 °C, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.95 – 7.89 (m, 2H), 7.86 – 7.79 (m, 1H), 7.43 (dddd, *J* = 20.3, 7.7, 7.3,

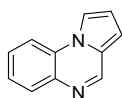
1.6 Hz, 2H), 6.92 (dd,  $J = 4.0, 1.3$  Hz, 1H), 6.83 (dd,  $J = 4.0, 2.7$  Hz, 1H), 5.89 – 5.77 (m, 2H), 3.38 (ddd,  $J = 11.0, 10.2, 4.9$  Hz, 1H), 2.78 – 2.65 (m, 1H), 2.41 – 2.23 (m, 3H), 2.13 – 2.00 (m, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  160.6, 136.3, 129.9, 127.3, 127.0, 126.8, 125.8, 125.1, 114.2, 113.7, 113.4, 105.8, 39.5, 30.0, 27.8, 26.0; HRMS (EI)  $m/z$  calcd. For  $\text{C}_{17}\text{H}_{16}\text{N}_2$   $[\text{M}]^+$ : 248.1313, found 248.1316.



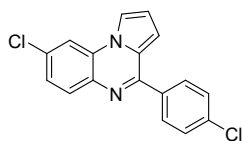
**4-(phenylethynyl)pyrrolo[1,2- $\alpha$ ]quinoxaline<sup>6</sup> (50)**; yellow solid, EtOAc/Hx=1:4,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 (dd,  $J = 7.9, 1.1$  Hz, 1H), 7.91 – 7.85 (m, 1H), 7.77 (dd,  $J = 8.0, 2.3$  Hz, 1H), 7.70 (ddd,  $J = 3.6, 3.0, 1.5$  Hz, 2H), 7.51 – 7.35 (m, 5H), 7.14 – 7.08 (m, 1H), 6.91 – 6.85 (m, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  138.7, 136.1, 132.5, 130.1, 129.7, 128.6, 128.2, 127.3, 127.1, 125.5, 121.8, 114.7, 114.2, 113.7, 107.7, 93.2, 86.0.



**phenyl(pyrrolo[1,2- $\alpha$ ]quinoxalin-4-yl)methanone<sup>14</sup> (51)**; yellow solid, EtOAc/Hx=1:10,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.17 (d,  $J = 7.8$  Hz, 2H), 8.03 (d,  $J = 7.7$  Hz, 2H), 7.94 (d,  $J = 8.3$  Hz, 1H), 7.63 (t,  $J = 7.4$  Hz, 2H), 7.50 (dd,  $J = 13.6, 7.0$  Hz, 3H), 7.22 (d,  $J = 3.9$  Hz, 1H), 6.99 – 6.95 (m, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  192.6, 150.1, 136.0, 135.0, 133.8, 131.3, 131.2, 129.6, 128.6, 128.1, 125.7, 124.6, 115.1, 115.0, 114.1, 109.1.

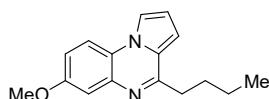


**pyrrolo[1,2- $\alpha$ ]quinoxaline<sup>15</sup> (52)**; yellow solid, EtOAc/Hx=1:4,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.82 (s, 1H), 7.97 (d,  $J = 8.4$  Hz, 1H), 7.94 (s, 1H), 7.88 (d,  $J = 8.4$  Hz, 1H), 7.54 (t,  $J = 7.1$  Hz, 1H), 7.46 (t,  $J = 7.6$  Hz, 1H), 6.93 – 6.87 (m, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  146.0, 136.1, 130.4, 128.2, 128.0, 126.7, 125.4, 114.4, 114.2, 114.0, 107.5.

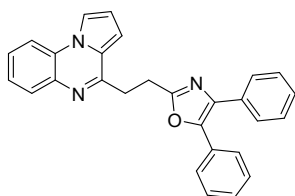


**8-chloro-4-(4-chlorophenyl)pyrrolo[1,2- $\alpha$ ]quinoxaline<sup>16</sup> (2)**; light-yellow solid, EtOAc/Hx=1:4,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 – 7.91 (m, 4H), 7.87 (d,  $J = 2.2$  Hz, 1H), 7.54 – 7.49 (m, 2H), 7.41 (dd,

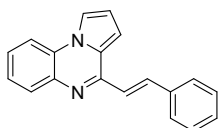
$J = 8.7, 2.2$  Hz, 1H), 6.97 (dd,  $J = 4.1, 1.3$  Hz, 1H), 6.92 (dd,  $J = 4.1, 2.8$  Hz, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  153.4, 136.8, 136.3, 134.9, 133.3, 131.6, 130.2, 129.1, 127.9, 126.1, 125.2, 115.3, 114.9, 114.1, 109.2.



**4-butyl-7-methoxy-1H-pyrrolo[1,2- $\alpha$ ]quinoxaline<sup>17</sup> (5)**; yellow oil, EtOAc/Hx=1:4,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.82 (dd,  $J = 2.7, 1.3$  Hz, 1H), 7.72 (d,  $J = 9.0$  Hz, 1H), 7.40 (d,  $J = 2.8$  Hz, 1H), 7.07 (dd,  $J = 9.0, 2.8$  Hz, 1H), 6.87 (dd,  $J = 4.0, 1.3$  Hz, 1H), 6.80 (dd,  $J = 4.0, 2.7$  Hz, 1H), 3.90 (s, 3H), 3.00 (dd,  $J = 8.8, 7.1$  Hz, 2H), 1.92 – 1.81 (m, 2H), 1.55 – 1.43 (m, 2H), 0.97 (t,  $J = 7.4$  Hz, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  157.7, 156.9, 137.0, 125.6, 121.4, 115.7, 114.3, 113.6, 112.9, 110.7, 105.8, 55.5, 35.6, 30.7, 22.9, 14.0.

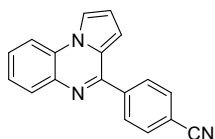


**4,5-diphenyl-2-(2-(pyrrolo[1,2- $\alpha$ ]quinoxalin-4-yl)ethyl)oxazole (53)**; pale-orange solid, EtOAc/Hx=1:4, mp 136-138 °C,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.93 (dd,  $J = 7.9, 1.2$  Hz, 1H), 7.88 (d,  $J = 1.4$  Hz, 1H), 7.82 – 7.78 (m, 1H), 7.69 – 7.63 (m, 2H), 7.58 – 7.52 (m, 2H), 7.49 – 7.29 (m, 8H), 6.98 – 6.93 (m, 1H), 6.86 – 6.80 (m, 1H), 3.63 – 3.57 (m, 2H), 3.56 – 3.49 (m, 2H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  163.0, 154.9, 145.5, 136.1, 135.4, 132.9, 129.8, 129.3, 128.8, 128.7, 128.5, 128.2, 127.5, 127.3, 126.6, 126.0, 125.3, 114.5, 113.8, 113.8, 106.3, 32.4, 26.2; HRMS (EI)  $m/z$  calcd. For  $\text{C}_{28}\text{H}_{21}\text{N}_3\text{O}$   $[\text{M}]^+$ : 415.1685, found 415.1689.

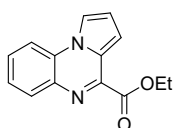


**(E)-4-styryl-1H-pyrrolo[1,2- $\alpha$ ]quinoxaline<sup>6</sup> (54)**; yellow solid, EtOAc/Hx=1:4,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.07 (d,  $J = 15.9$  Hz, 1H), 8.00 (dd,  $J = 7.6, 1.8$  Hz, 1H), 7.97 – 7.94 (m, 1H), 7.87 – 7.82 (m, 1H), 7.70 (d,  $J = 7.3$  Hz, 2H), 7.55 – 7.39 (m, 5H), 7.36 (t,  $J = 7.3$  Hz, 1H), 7.11 (dd,  $J = 4.0, 1.1$  Hz, 1H), 6.92 (dd,  $J = 3.9, 2.8$  Hz, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  150.1, 136.8, 136.6, 136.4, 130.0, 129.2, 129.0, 127.9, 127.5, 127.3, 126.3, 125.6, 123.5, 114.7, 114.0, 113.9, 106.2.





**4-(pyrrolo[1,2- $\alpha$ ]quinoxalin-4-yl)benzonitrile<sup>6</sup> (55)**; yellow solid, EtOAc/Hx=1:4, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.15 – 8.10 (m, 2H), 8.06 – 8.01 (m, 2H), 7.90 (dd,  $J$  = 8.1, 1.3 Hz, 1H), 7.86 – 7.81 (m, 2H), 7.57 (ddd,  $J$  = 8.2, 7.3, 1.5 Hz, 1H), 7.49 (ddd,  $J$  = 8.0, 7.3, 1.4 Hz, 1H), 6.97 – 6.91 (m, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  152.4, 142.9, 136.2, 132.7, 130.7, 129.6, 128.5, 127.4, 125.8, 125.0, 118.9, 115.4, 114.6, 114.0, 113.6, 108.5.

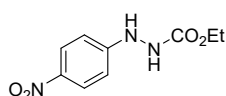


**ethyl pyrrolo[1,2- $\alpha$ ]quinoxaline-4-carboxylate<sup>18</sup> (56)**; yellow solid, EtOAc/Hx=1:4, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.17 – 8.11 (m, 1H), 8.01 (dd,  $J$  = 2.7, 1.3 Hz, 1H), 7.88 (dd,  $J$  = 8.3, 1.2 Hz, 1H), 7.64 – 7.58 (m, 1H), 7.52 (dd,  $J$  = 4.1, 1.3 Hz, 1H), 7.50 – 7.46 (m, 1H), 6.97 (dd,  $J$  = 4.1, 2.7 Hz, 1H), 4.58 (q,  $J$  = 7.1 Hz, 2H), 1.51 (t,  $J$  = 7.1 Hz, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  164.3, 143.4, 134.8, 131.7, 130.0, 128.3, 125.7, 124.7, 115.2, 115.2, 113.9, 110.2, 62.6, 14.5.

### 5. Procedure of 1d-mediated oxidative cyclization on large scale

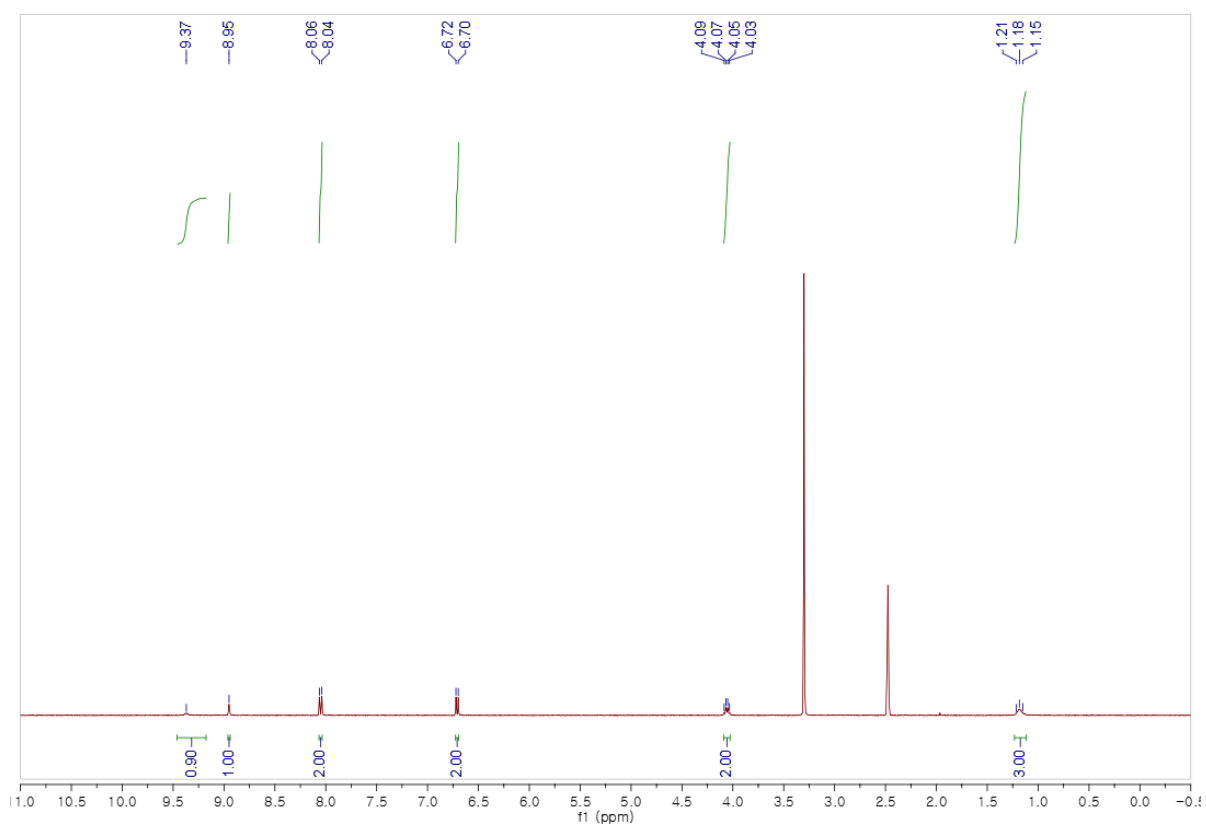
A 100 mL flame-dried round-bottom flask, which was equipped with a magnetic stir bar and charged with 2-(1*H*-pyrrol-1-yl)aniline **6** (10.0 mmol), ethyl 2-(4-nitrophenyl)azocarboxylate **1d** (1.0 equiv., 10.0 mmol), was evacuated and backfilled with nitrogen (this process was repeated three times). After 5.0 mL of methanol was added, 4-methylbenzaldehyde **7** (1.2 equiv, 12.0 mmol), acetic acid (0.1 equiv, 1.0 mmol), and methanol (5.0 mL) were added in sequence. The reaction mixture was stirred at room temperature for 1 h. The reaction mixture was concentrated on rotary evaporator. The crude mixture was dissolved in CHCl<sub>3</sub> (100 mL) and filtered through a Büchner funnel (to separate hydrazine byproduct). The Büchner funnel was washed with additional CHCl<sub>3</sub> (100 mL). The reaction mixture was concentrated on rotary evaporator. The residue was purified by column chromatography (silica gel, EtOAc/MeOH/PE=1:5:20) to provide pyrrolo[1,2- $\alpha$ ]quinoxalines.

The hydrazine was obtained in 76% yield after dry. The obtained hydrazine was pure enough to use recycling without further purification. The <sup>1</sup>H NMR of the obtained hydrazine was attached below.

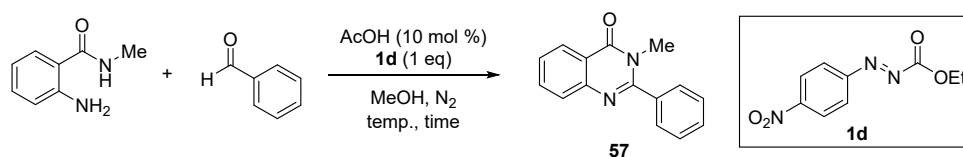


**ethyl 2-(4-nitrophenyl)hydrazinecarboxylate<sup>1</sup> (1d')**; yellow solid, <sup>1</sup>H NMR (400 MHz, DMSO)  $\delta$

9.37 (br, 1H), 8.95 (br, 1H), 8.05 (d,  $J = 9.2$  Hz, 2H), 6.71 (d,  $J = 9.2$  Hz, 2H), 4.06 (q,  $J = 6.9$  Hz, 2H), 1.18 (t,  $J = 13.1$  Hz, 3H).

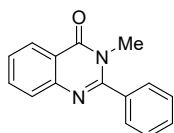


## 6. Optimization for synthesis of quinazolinones

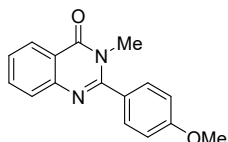


entry	temp. (°C)	time (h)	Yield (%) <sup>a</sup>
1	rt	24	44
2	rt	48	43
3	50	24	48
4	reflux	24	73
5 <sup>b</sup>	reflux	24	57

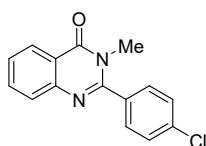
<sup>a</sup>Yield of **57** was determined by <sup>1</sup>H NMR spectroscopy with 1,1,2,2-tetrachloroethane as internal standard. <sup>b</sup>AcOH (1.2 equiv.) was used.



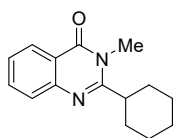
**3-methyl-2-phenylquinazolin-4(3H)-one<sup>19</sup> (57)**; white solid, EtOAc/Hx=1:1, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.28 (d, *J* = 8.0 Hz, 1H), 7.74 – 7.67 (m, 2H), 7.54 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.51 – 7.42 (m, 4H), 3.46 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 162.8, 156.2, 147.4, 135.5, 134.4, 130.2, 129.0, 128.1, 127.6, 127.1, 126.8, 120.6, 34.4.



**2-(4-methoxyphenyl)-3-methylquinazolin-4(3H)-one<sup>19</sup> (58)**; white solid, EtOAc/Hx=1:1, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.30 (d, *J* = 8.0 Hz, 1H), 7.77 – 7.69 (m, 2H), 7.56 – 7.50 (m, 2H), 7.47 (dd, *J* = 7.7, 6.2 Hz, 1H), 7.02 (d, *J* = 7.3 Hz, 2H), 3.86 (s, 3H), 3.52 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 163.1, 161.1, 156.2, 147.6, 134.4, 129.9, 127.9, 127.6, 126.9, 126.8, 120.6, 114.4, 55.7, 34.6.



**2-(4-chlorophenyl)-3-methylquinazolin-4(3H)-one<sup>19</sup> (59)**; white solid, EtOAc/Hx=1:1, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.30 (d, *J* = 8.0 Hz, 1H), 7.73 (ddd, *J* = 15.9, 11.5, 4.4 Hz, 2H), 7.55 – 7.46 (m, 5H), 3.48 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 162.7, 155.2, 147.3, 136.5, 134.5, 133.9, 129.7, 129.3, 127.6, 127.3, 126.8, 120.7, 34.4.



**2-cyclohexyl-3-methylquinazolin-4(3H)-one<sup>19</sup> (60)**; yellow solid, EtOAc/Hx=1:1, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.23 (d, *J* = 7.9 Hz, 1H), 7.72 – 7.58 (m, 2H), 7.39 (t, *J* = 7.3 Hz, 1H), 3.65 (s, 3H), 2.80 (t, *J* = 11.4 Hz, 1H), 1.82 (ddd, *J* = 31.8, 23.0, 11.7 Hz, 8H), 1.36 (dd, *J* = 22.7, 13.1 Hz, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 163.0, 160.4, 147.6, 134.1, 127.3, 126.8, 126.3, 120.4, 42.5, 31.2, 30.2, 26.4, 26.0.

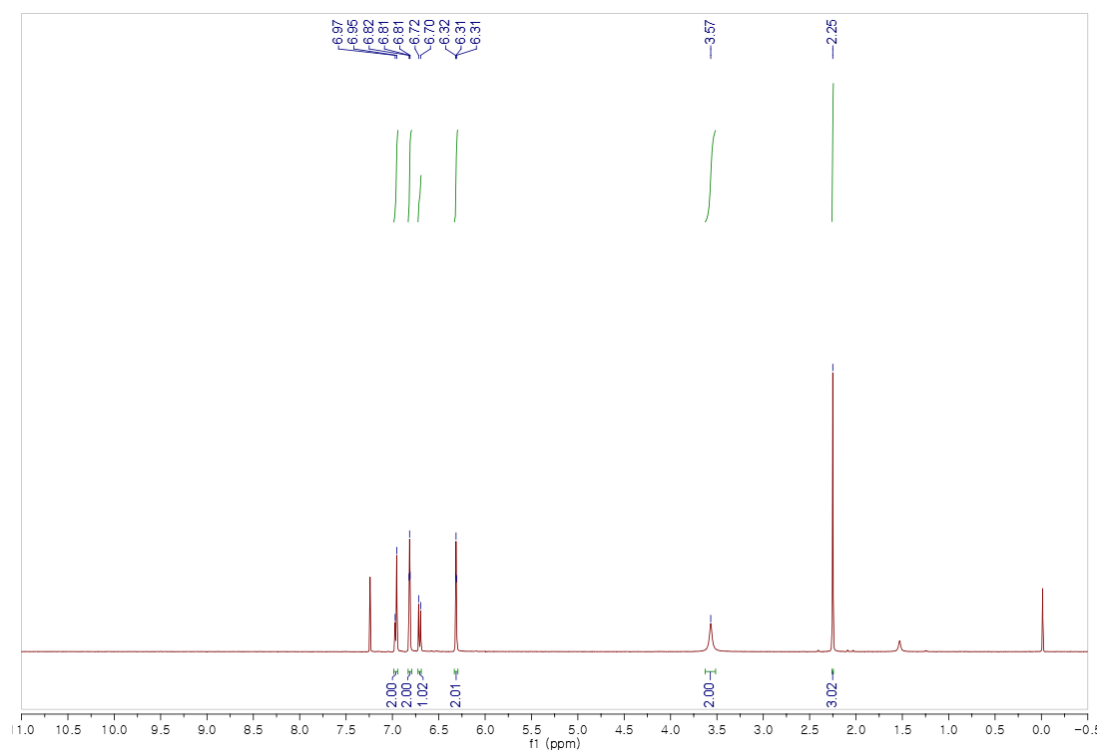
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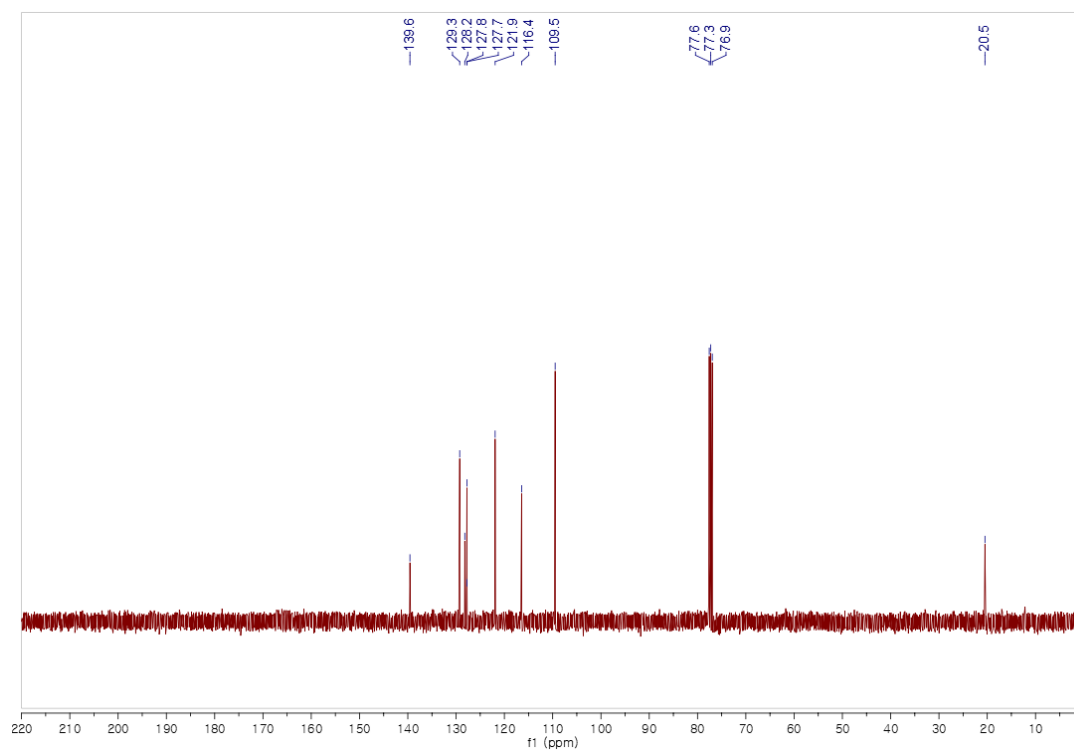
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## 8. $^1\text{H}$ , $^{13}\text{C}$ , and $^{19}\text{F}$ NMR spectra

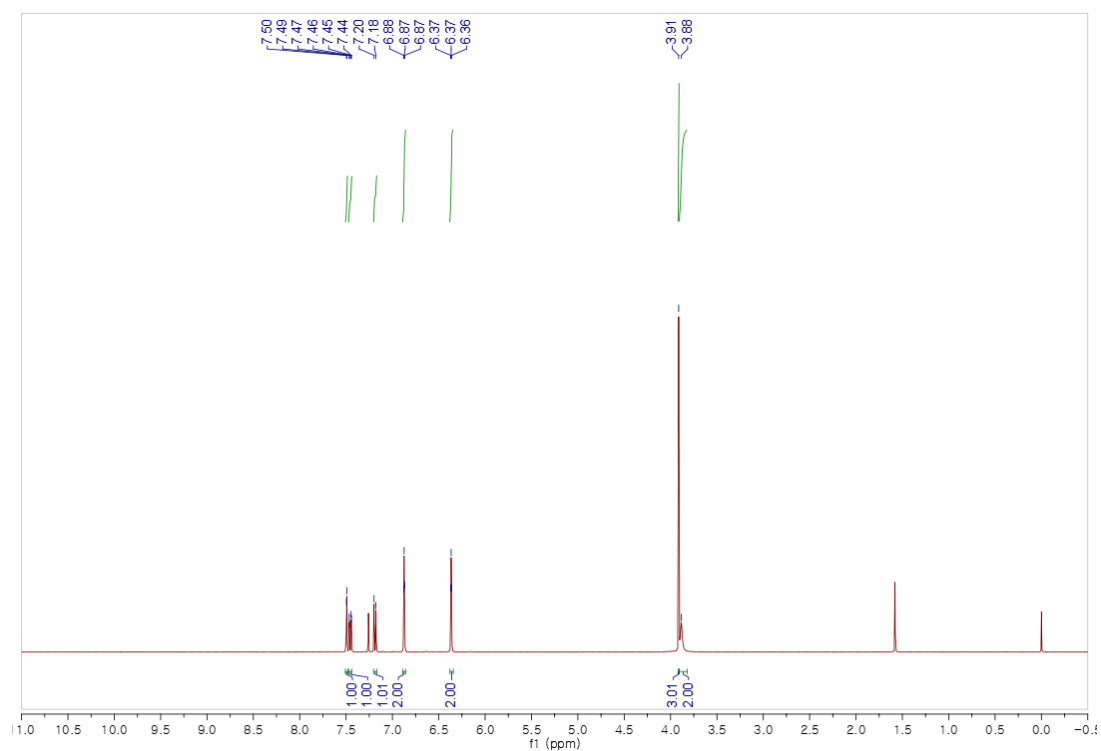
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of 4-methyl-2-(1*H*-pyrrol-1-yl)aniline (for 11)



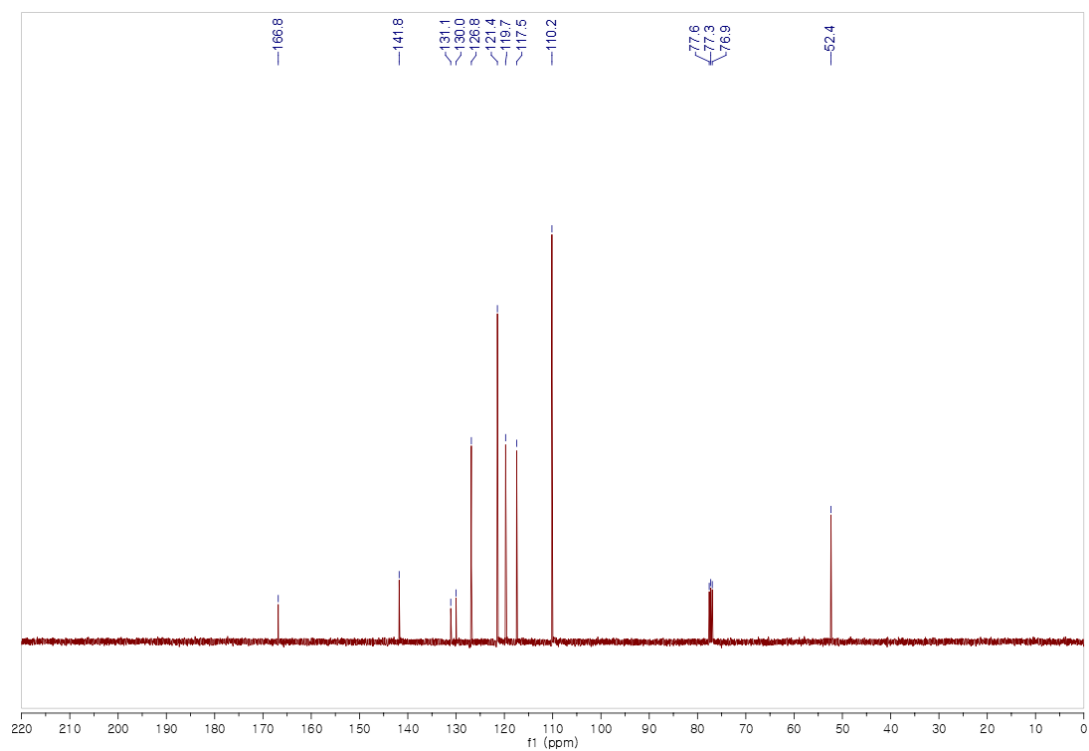
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) spectrum of 4-methyl-2-(1*H*-pyrrol-1-yl)aniline (for 11)



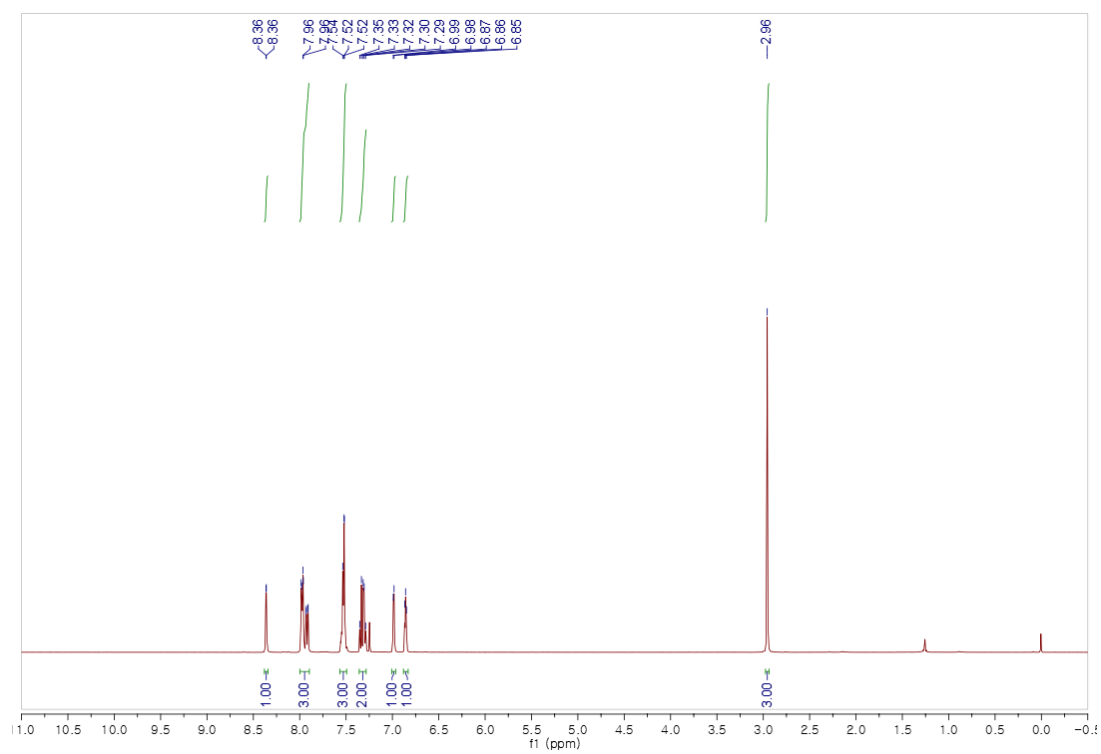
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of methyl 3-amino-4-(1*H*-pyrrol-1-yl)benzoate (for 17)**



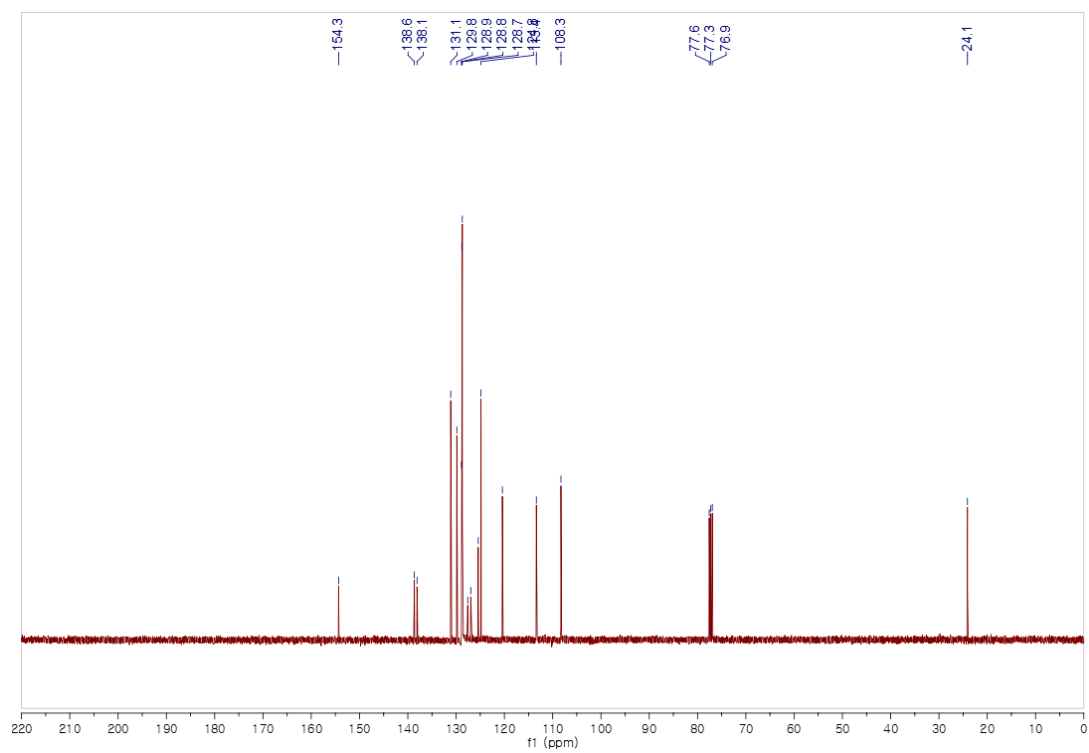
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectrum of methyl 3-amino-4-(1*H*-pyrrol-1-yl)benzoate (for 17)**



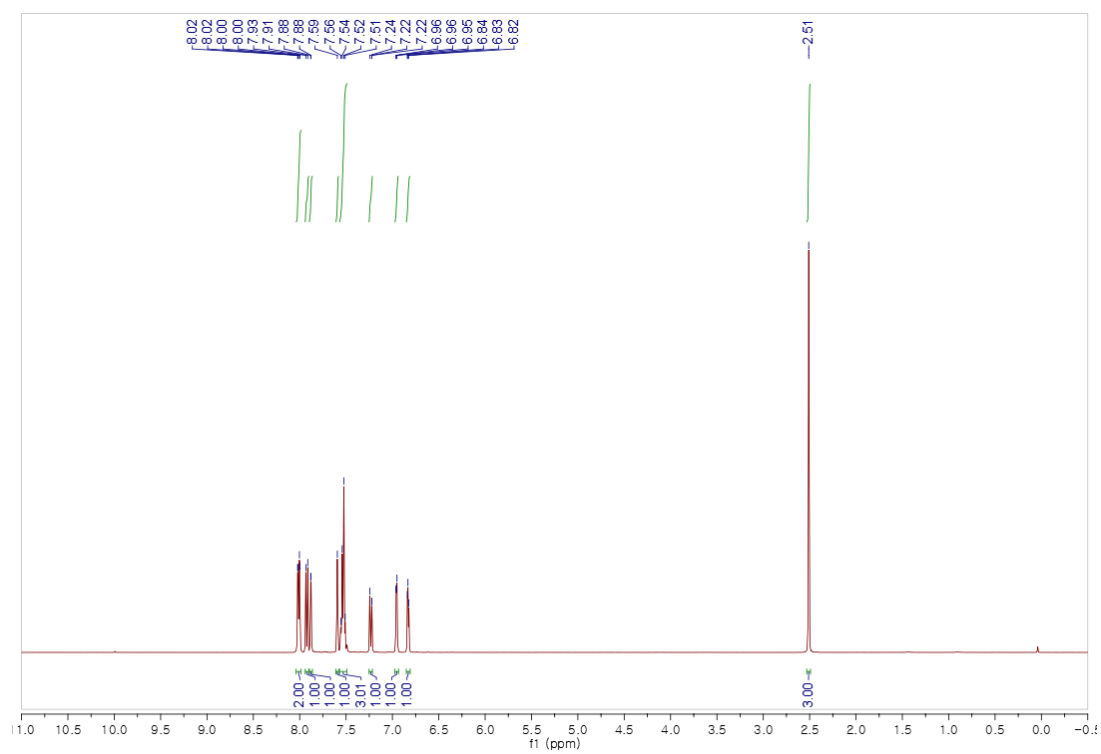
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound 10**



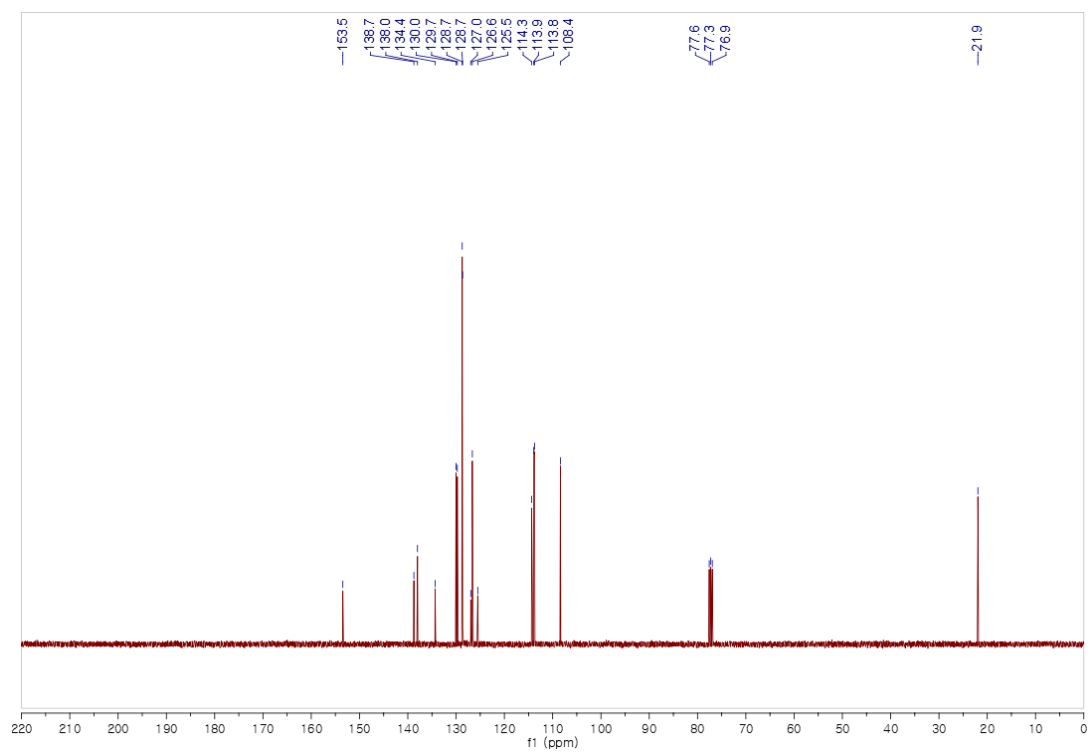
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectrum of compound 10**



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound 11**



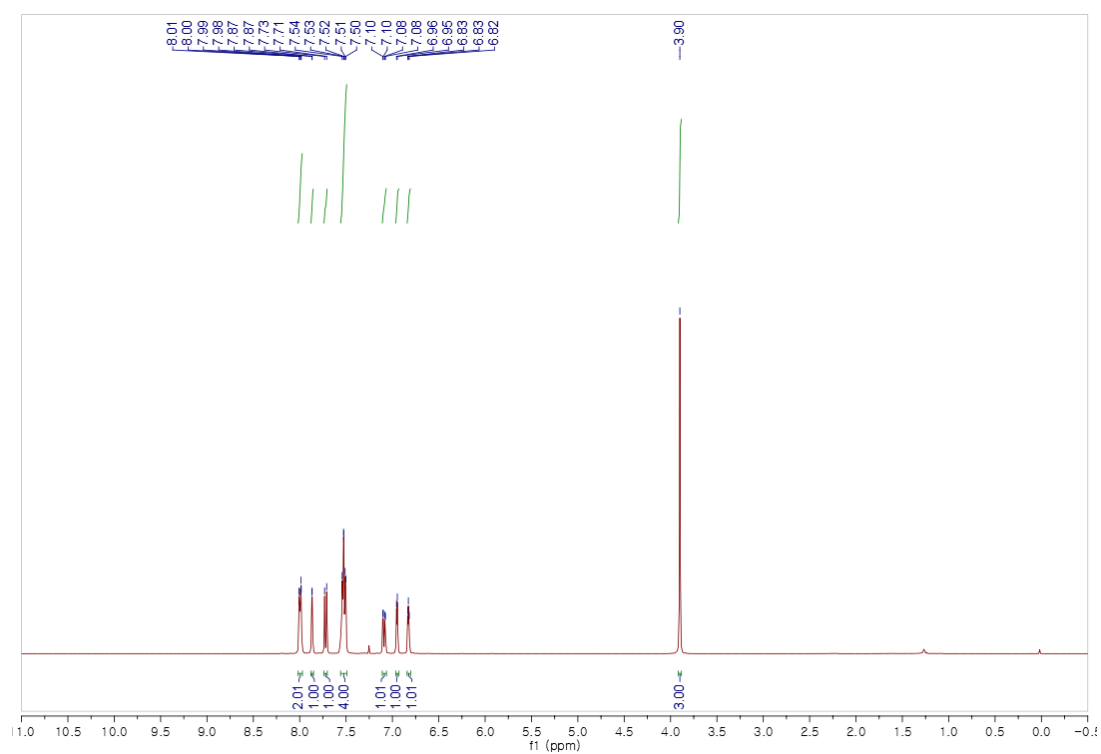
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectrum of compound 11**



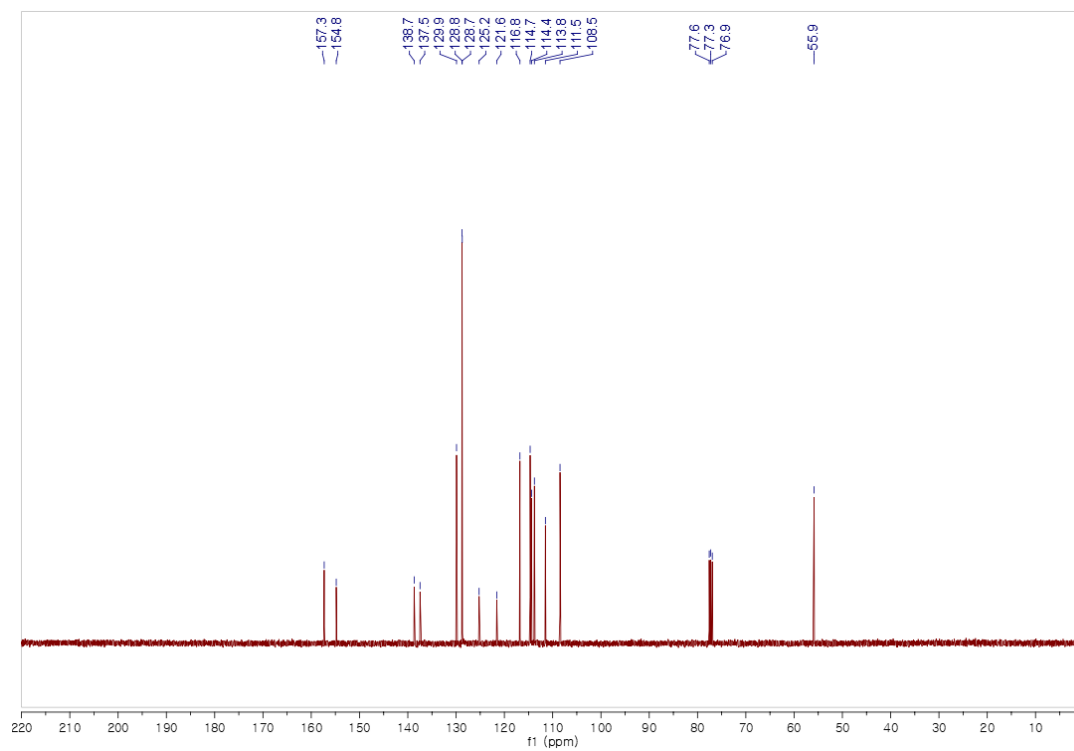




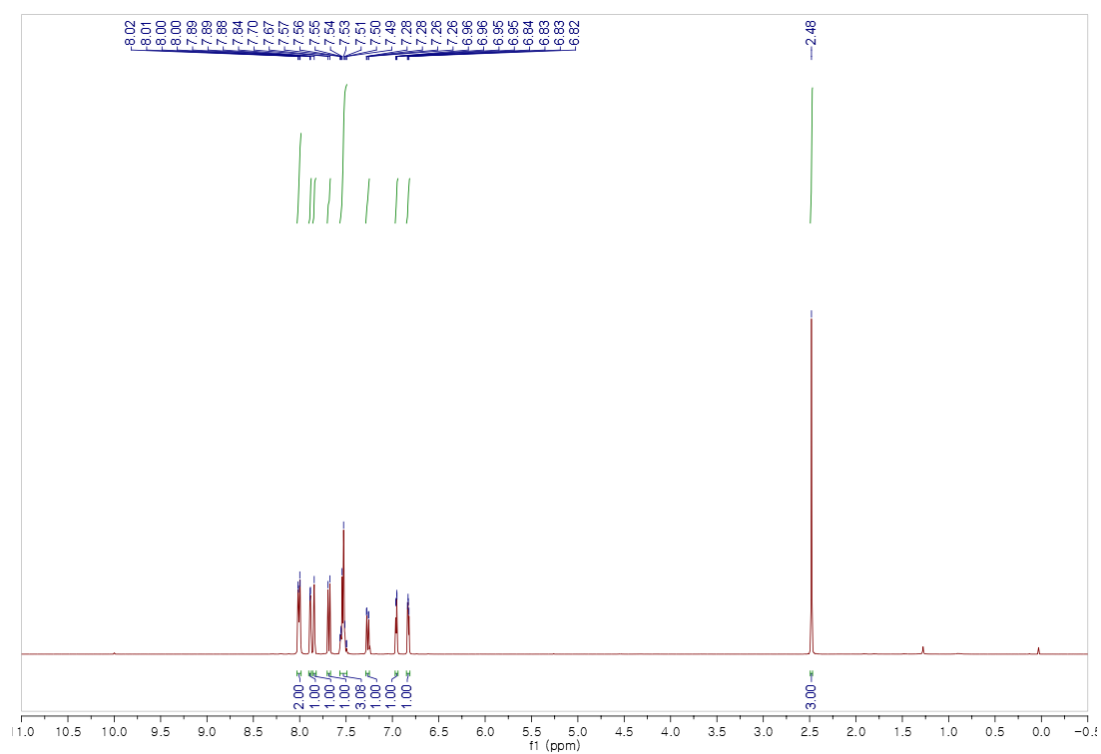
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound 13**



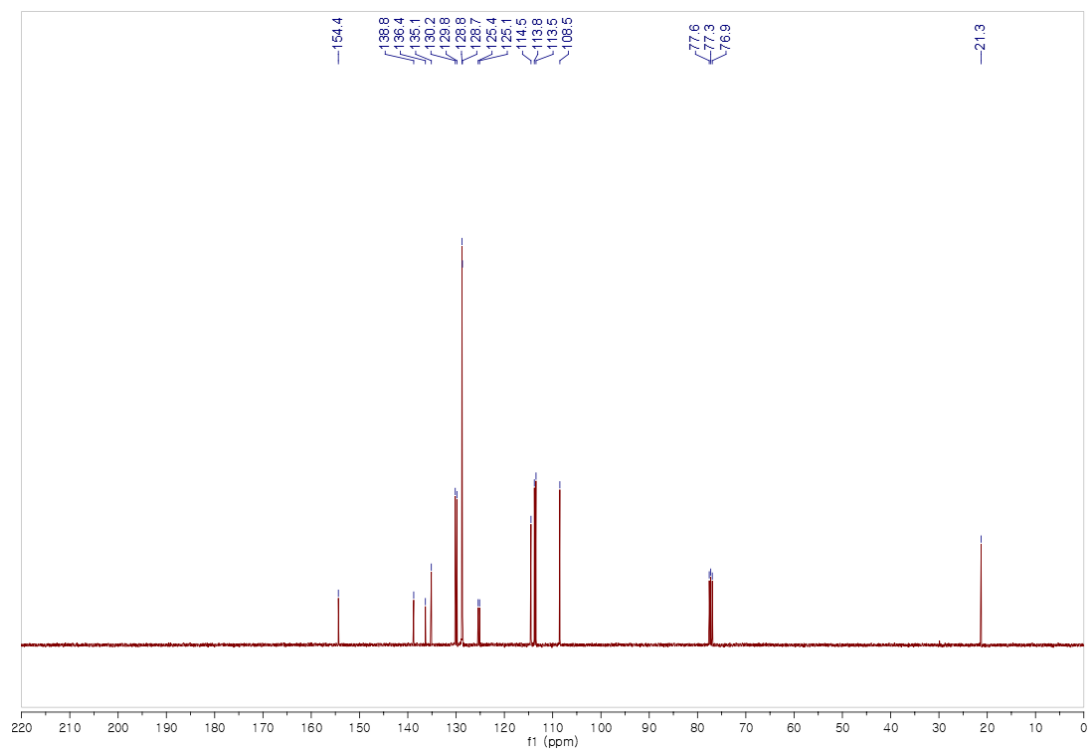
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectrum of compound 13**



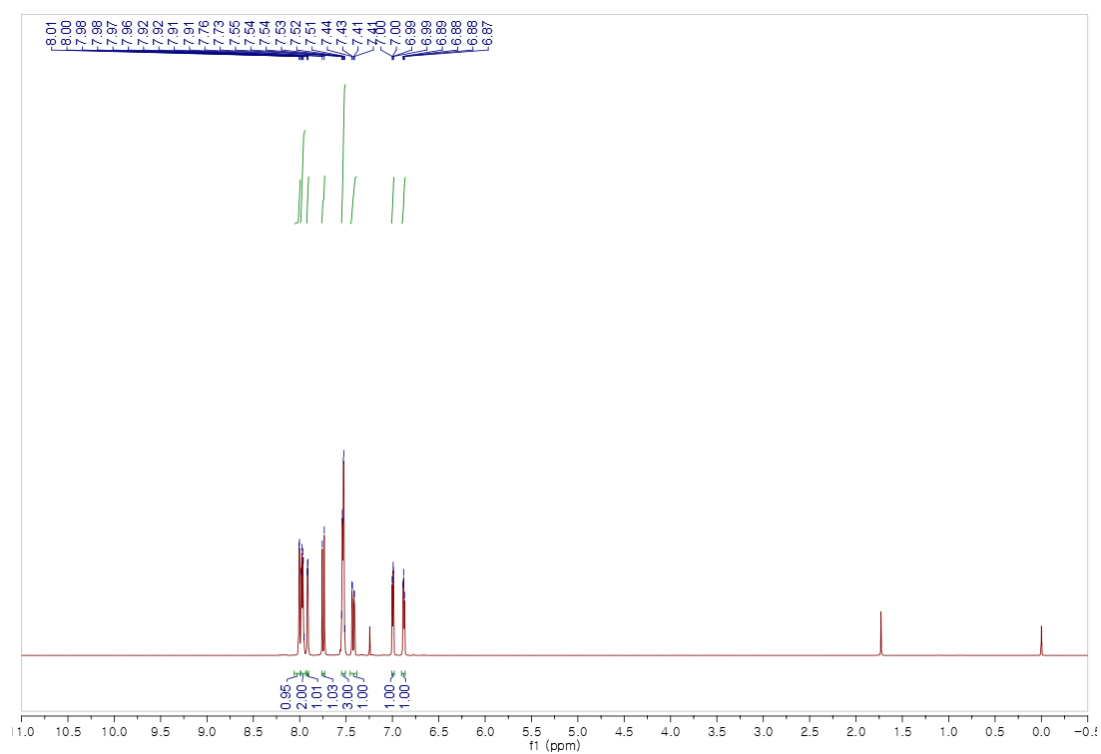
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of compound 14**



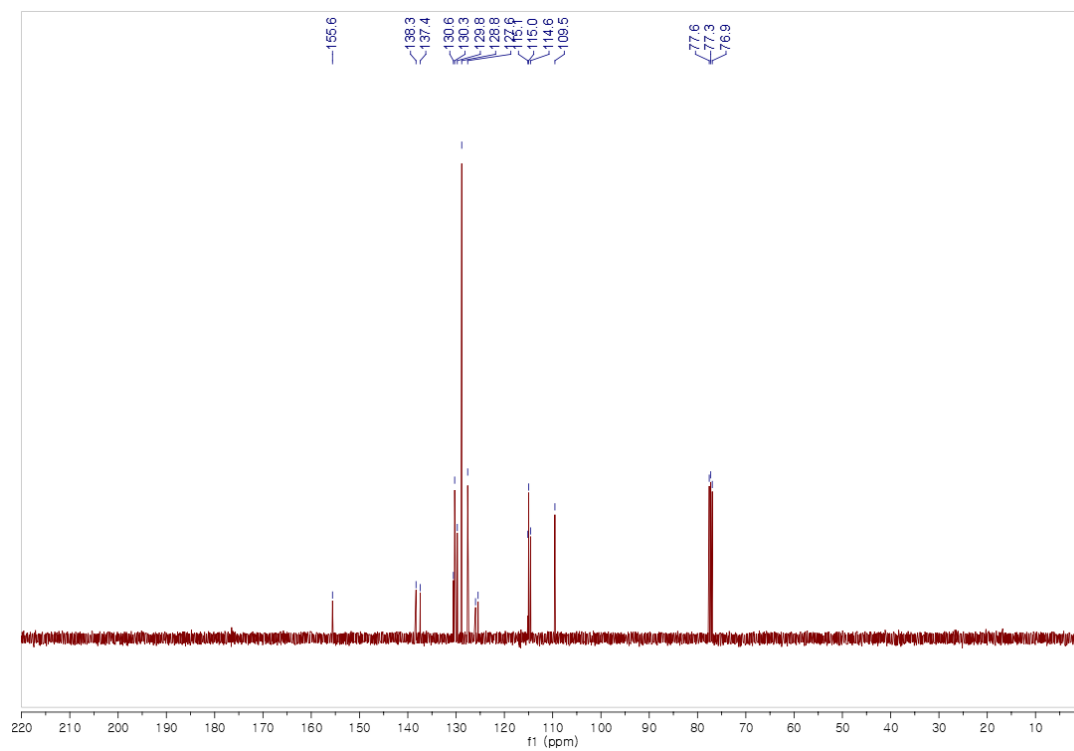
**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) spectrum of compound 14**



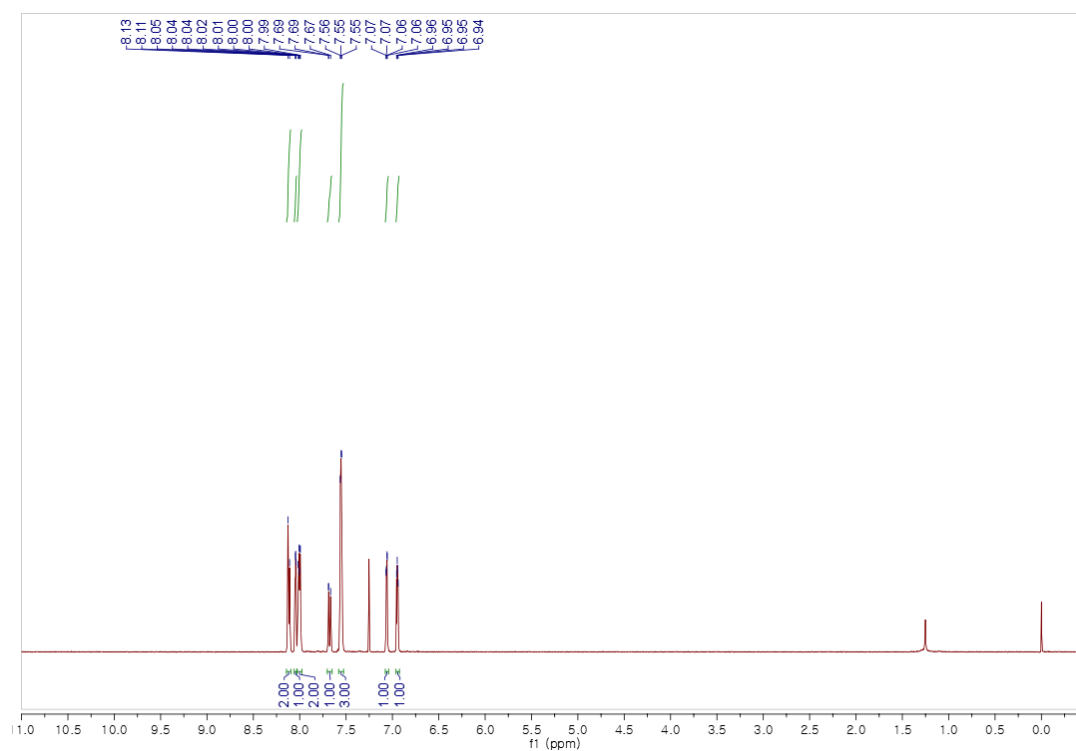
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of compound 15**



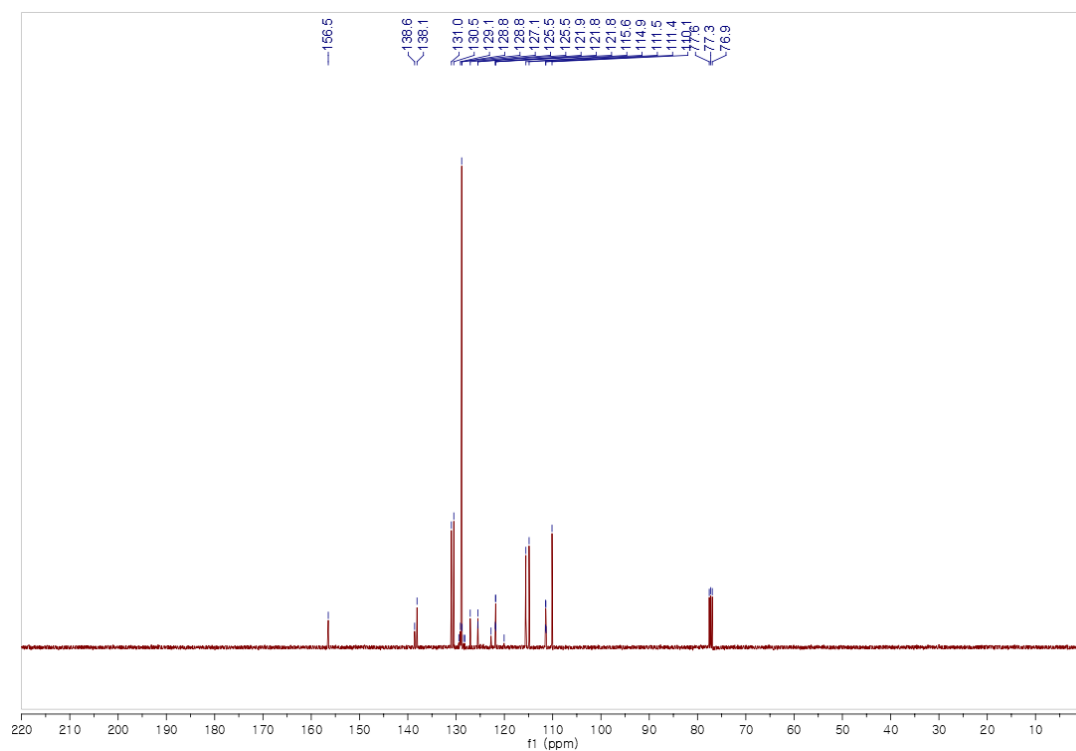
**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) spectrum of compound 15**

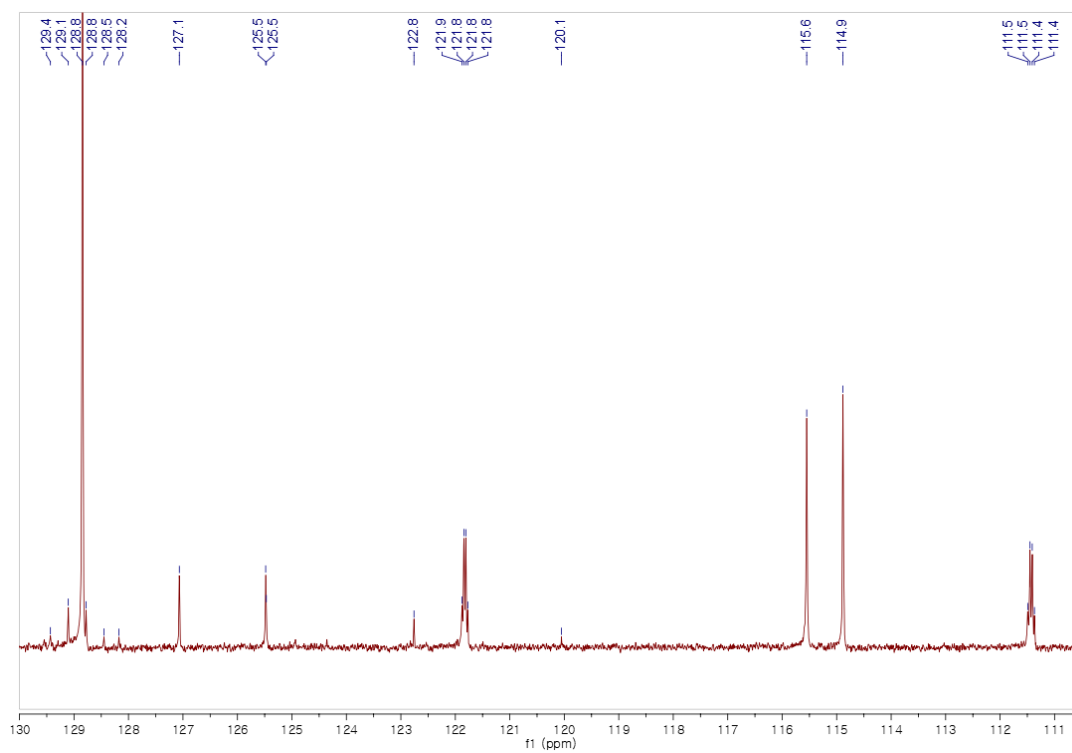


**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound 16**

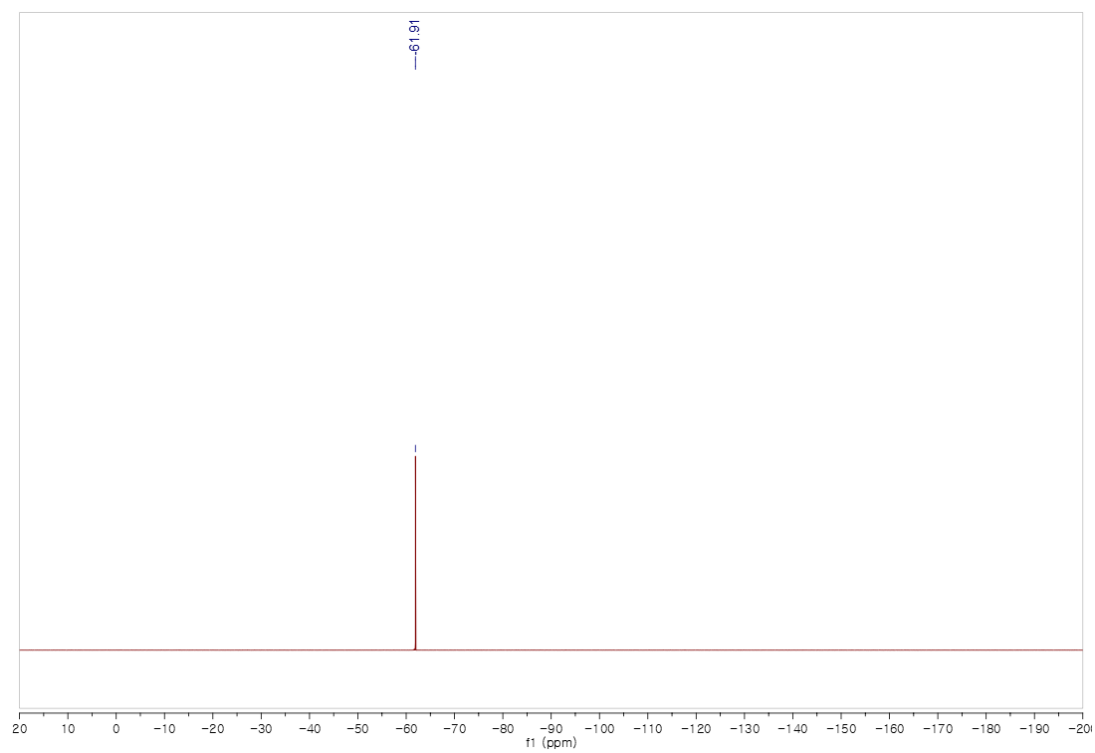


**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectrum of compound 16**

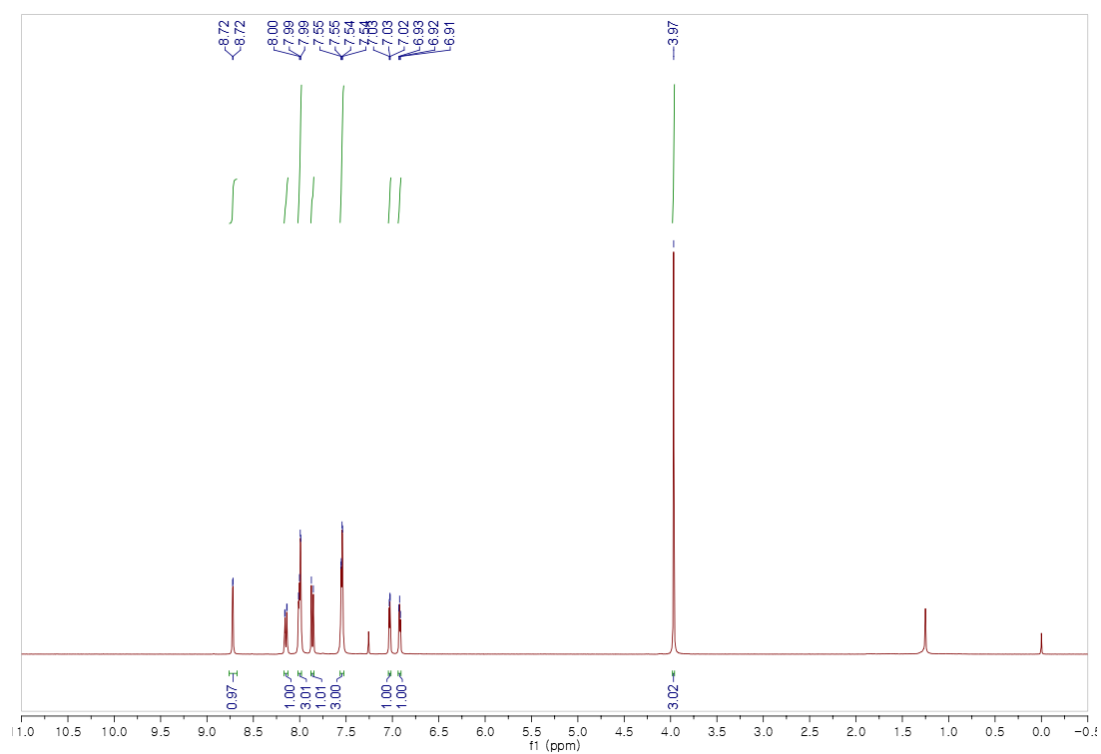




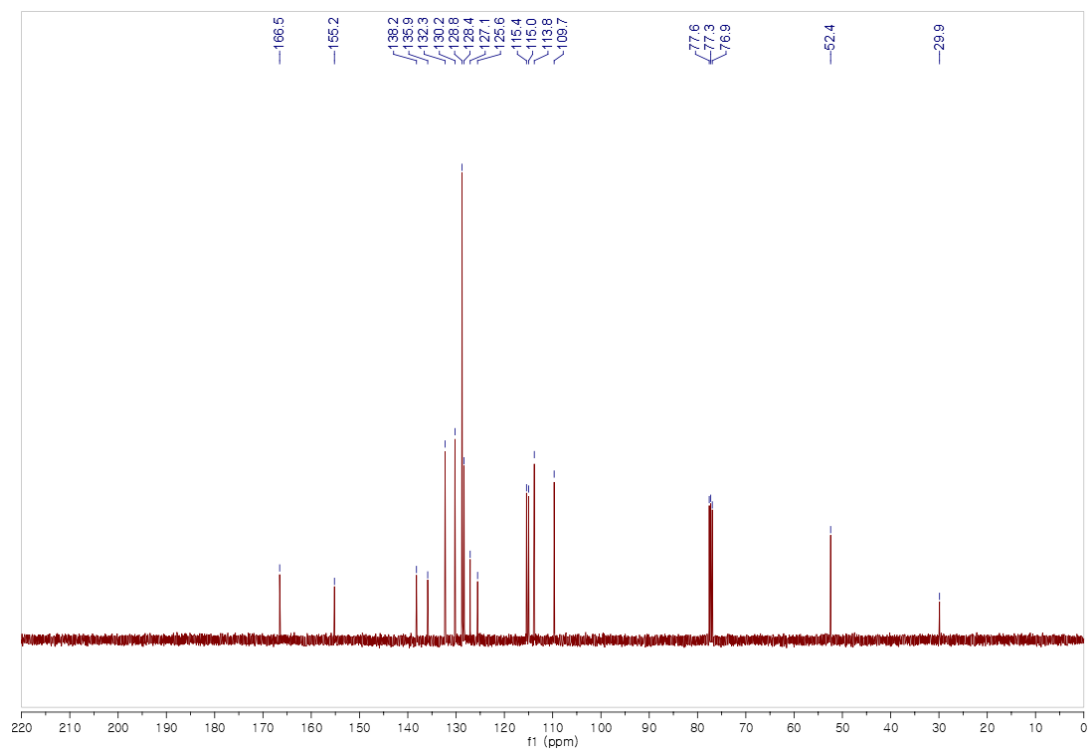
**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) spectrum of compound 16**



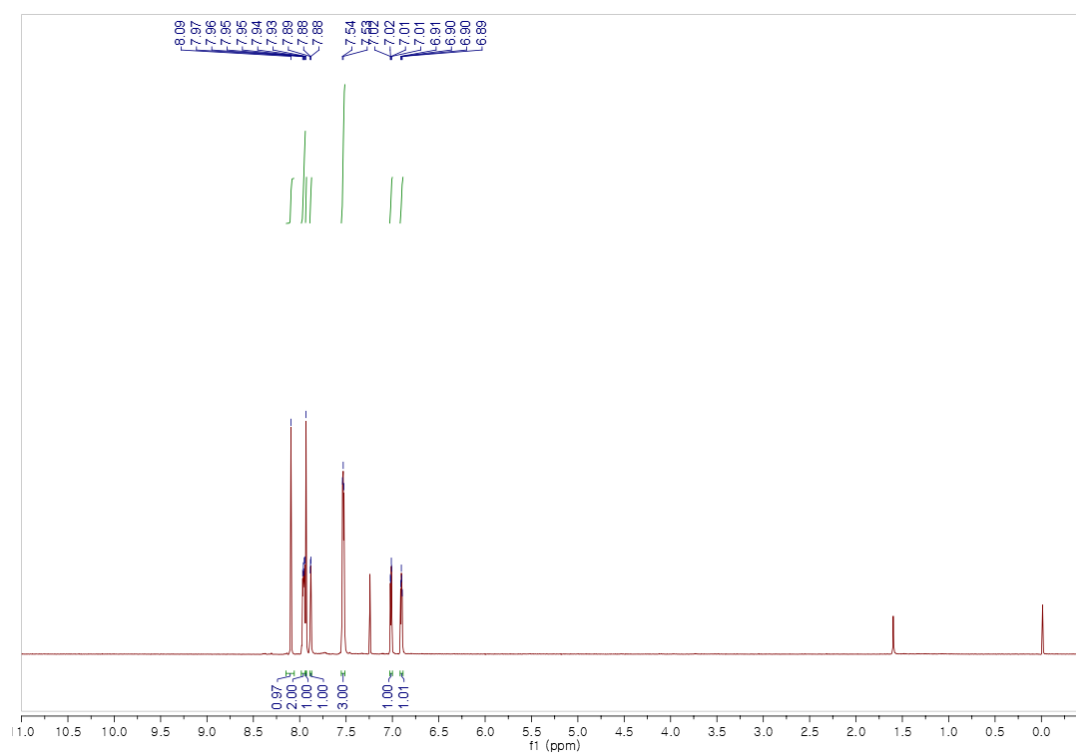
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound 17**



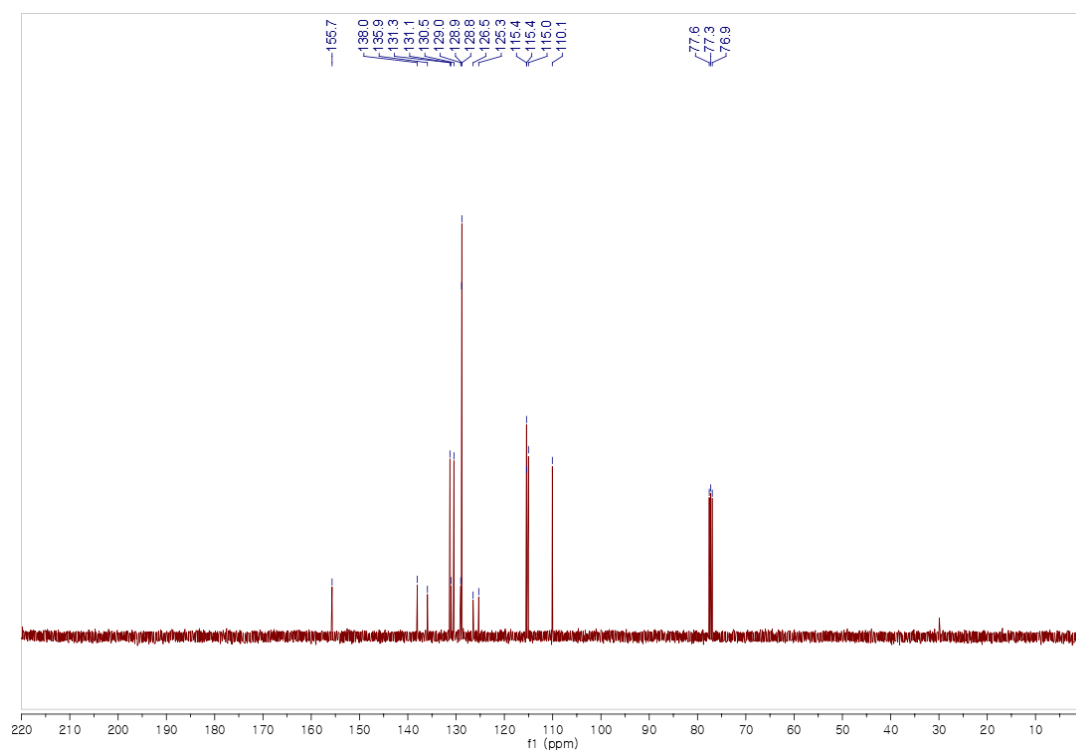
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectrum of compound 17**



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound 18**

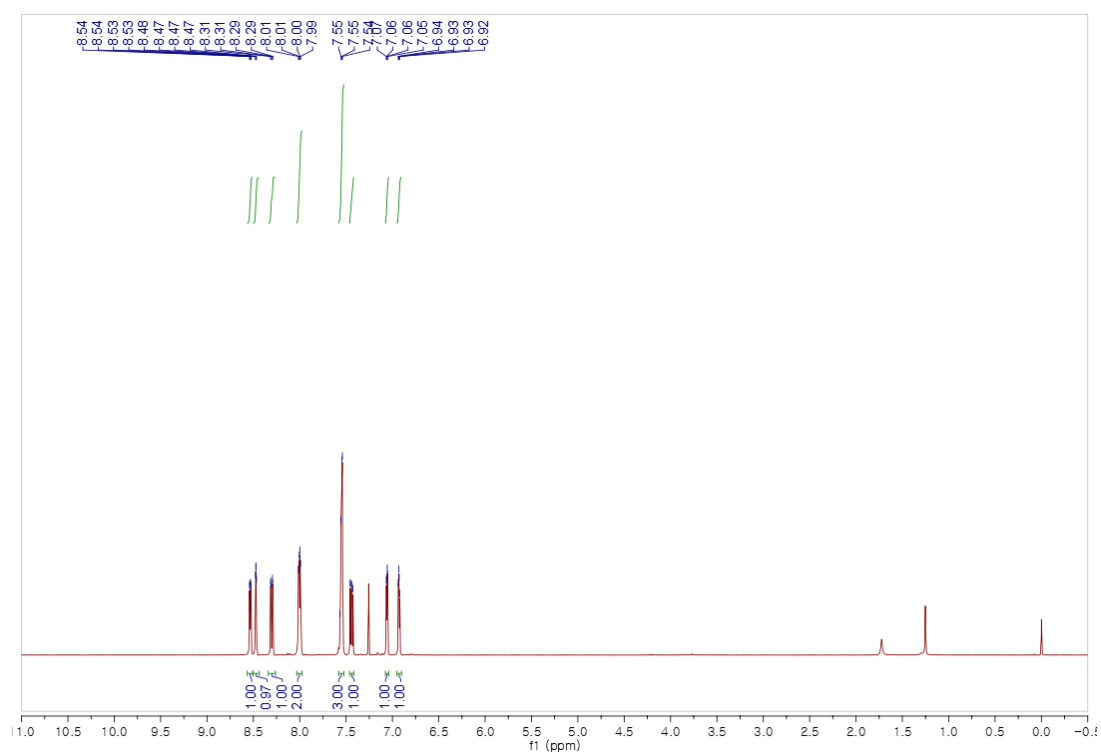


**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectrum of compound 18**

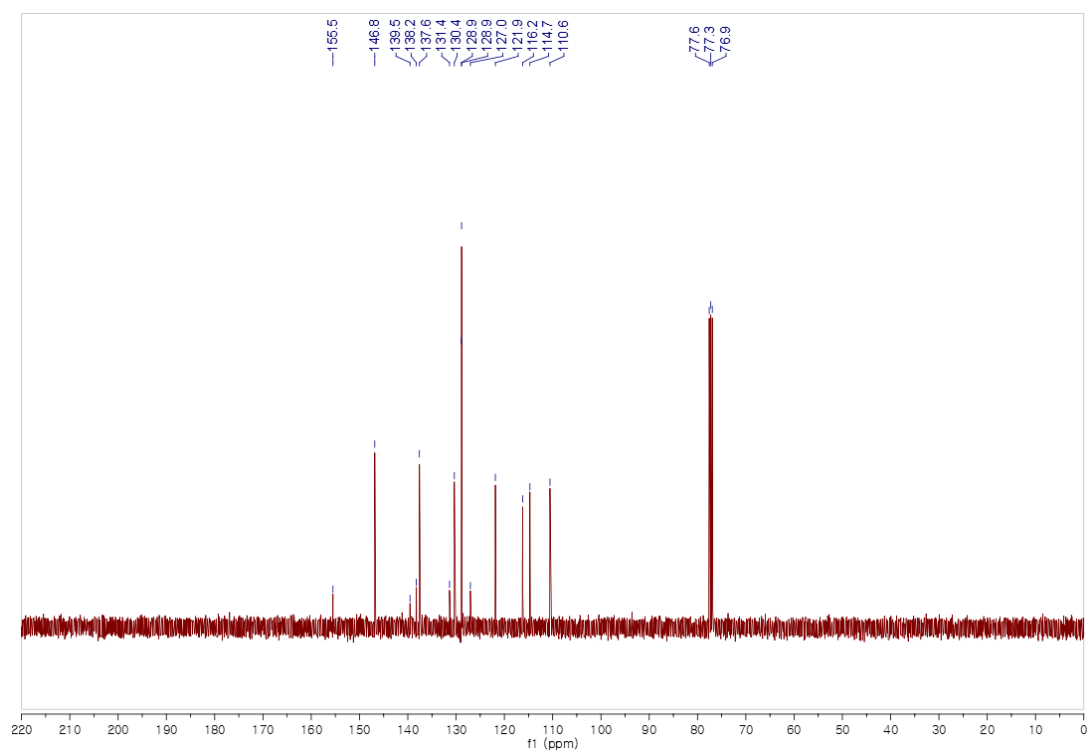




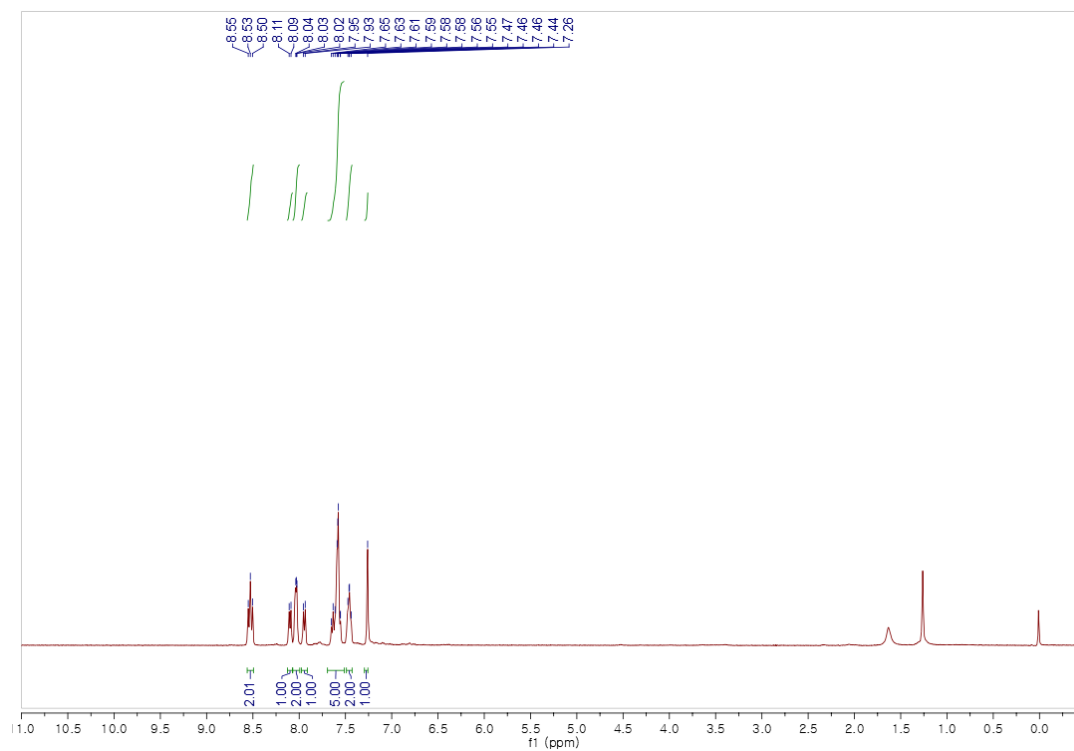
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of compound 19**



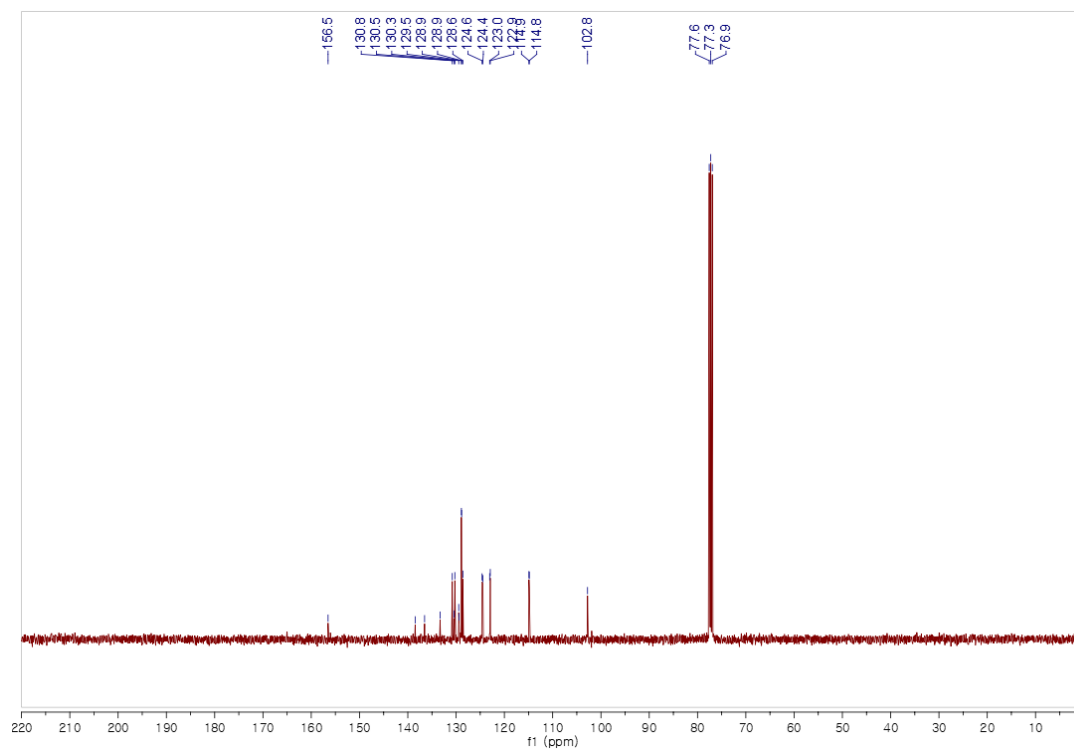
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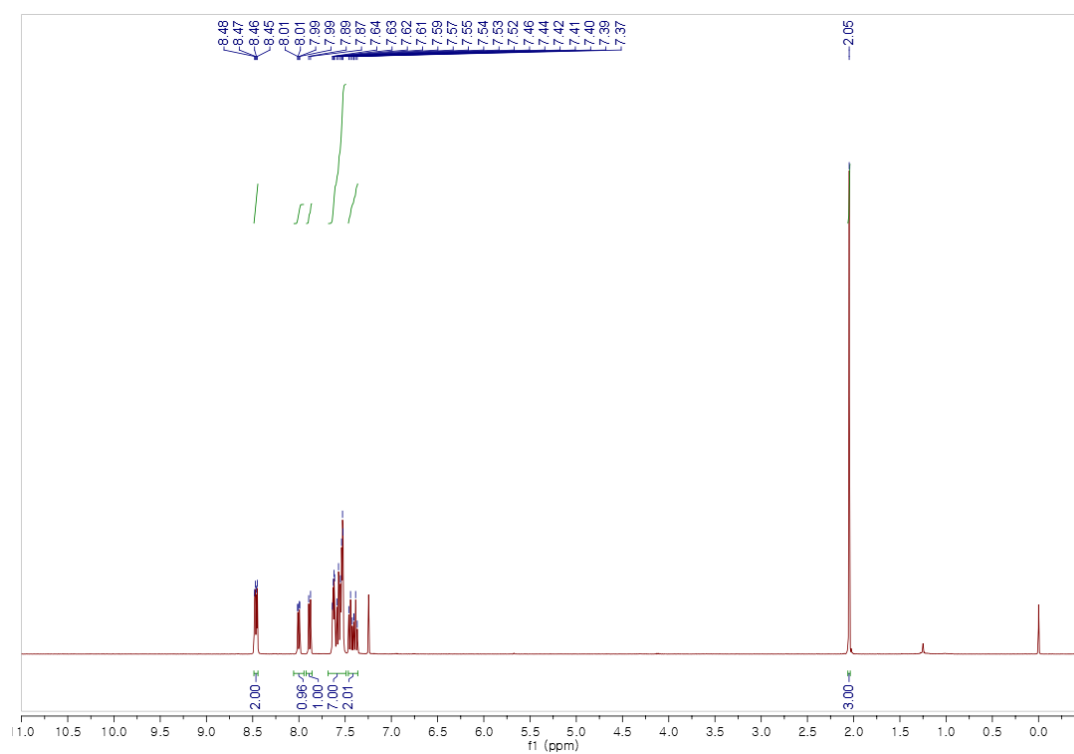
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound 20**



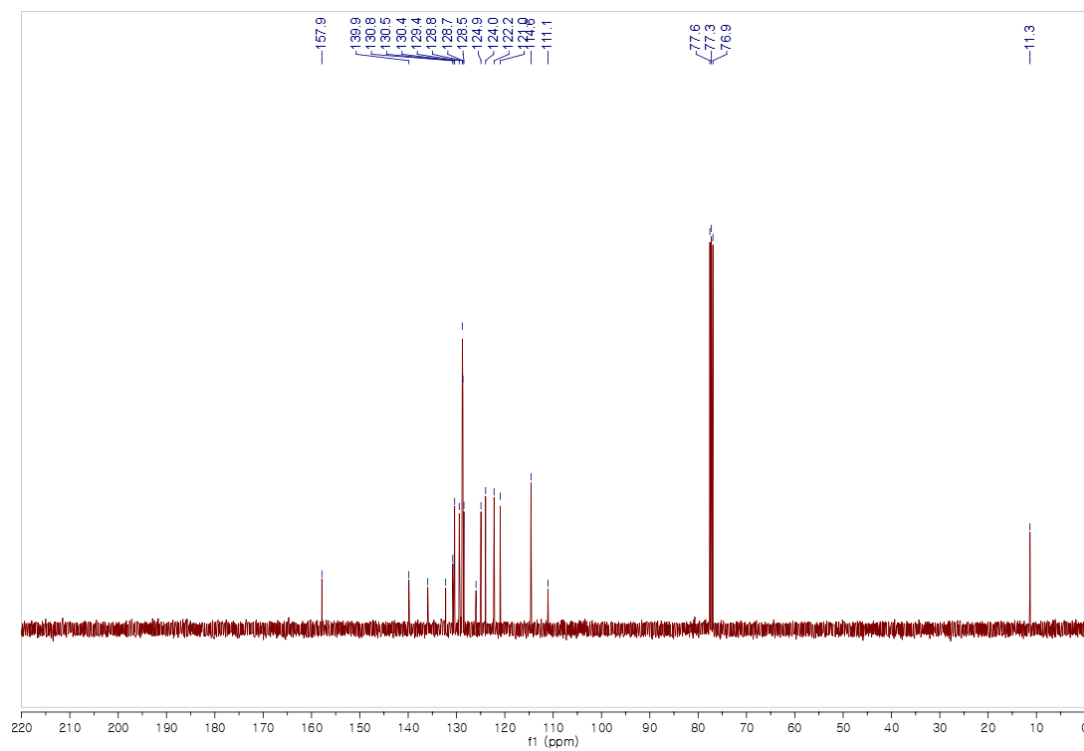
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectrum of compound 20**



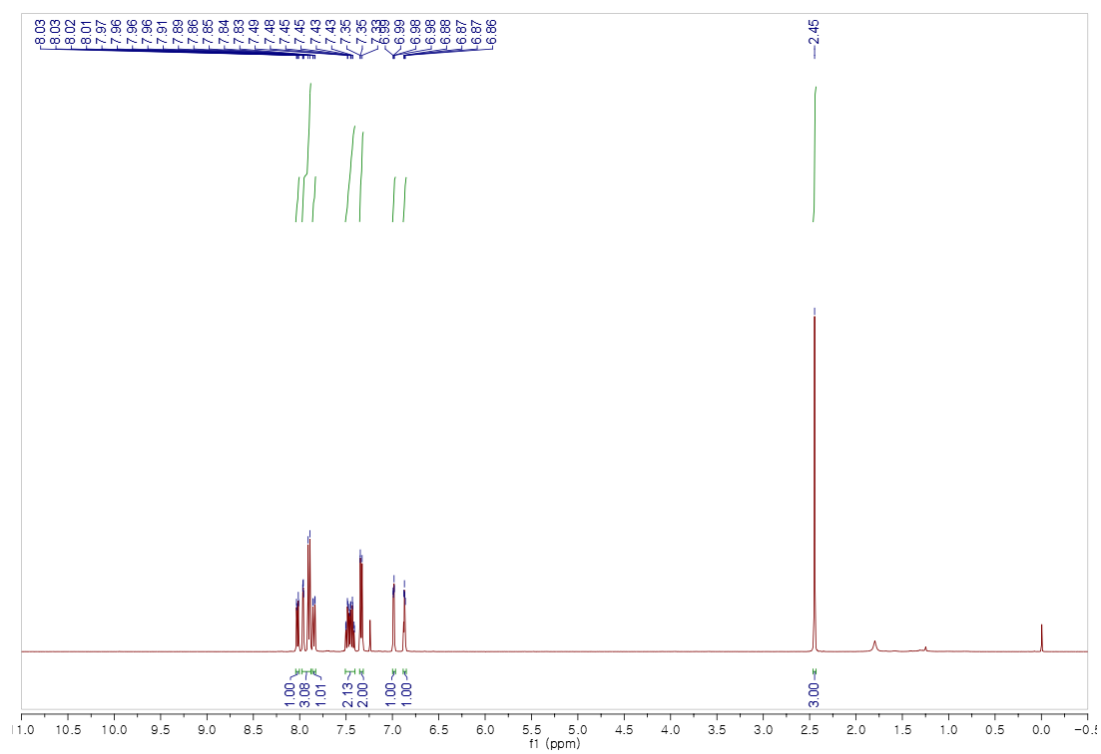
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound 21**



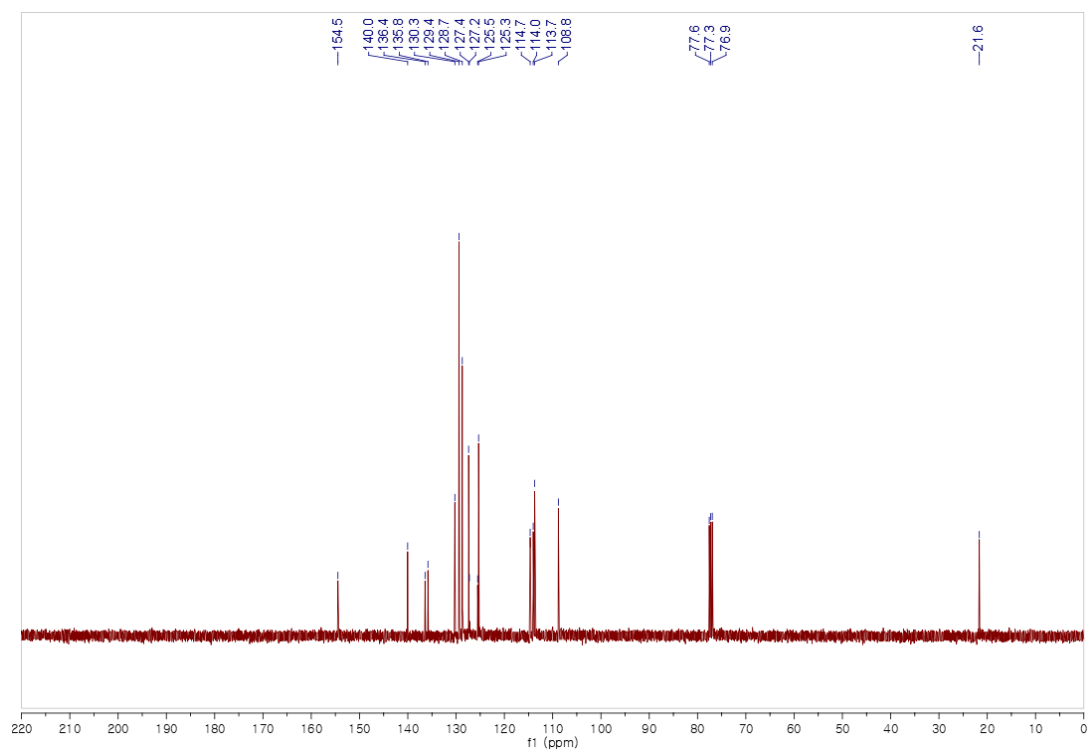
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectrum of compound 21**



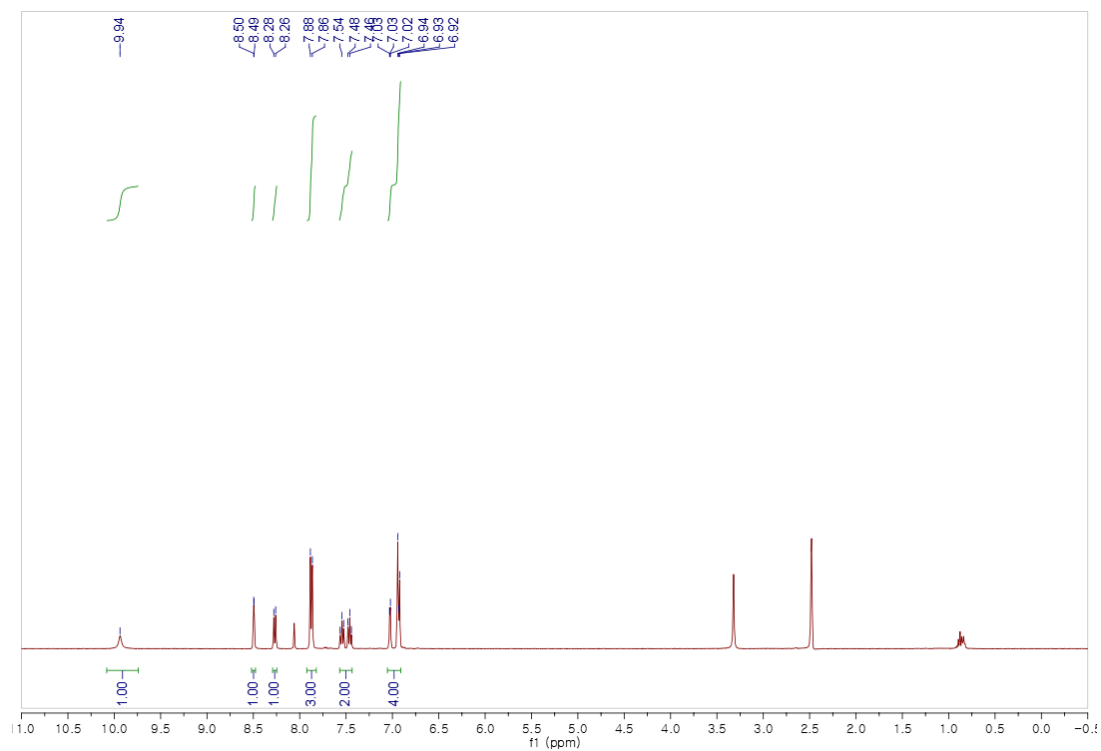
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound 8**



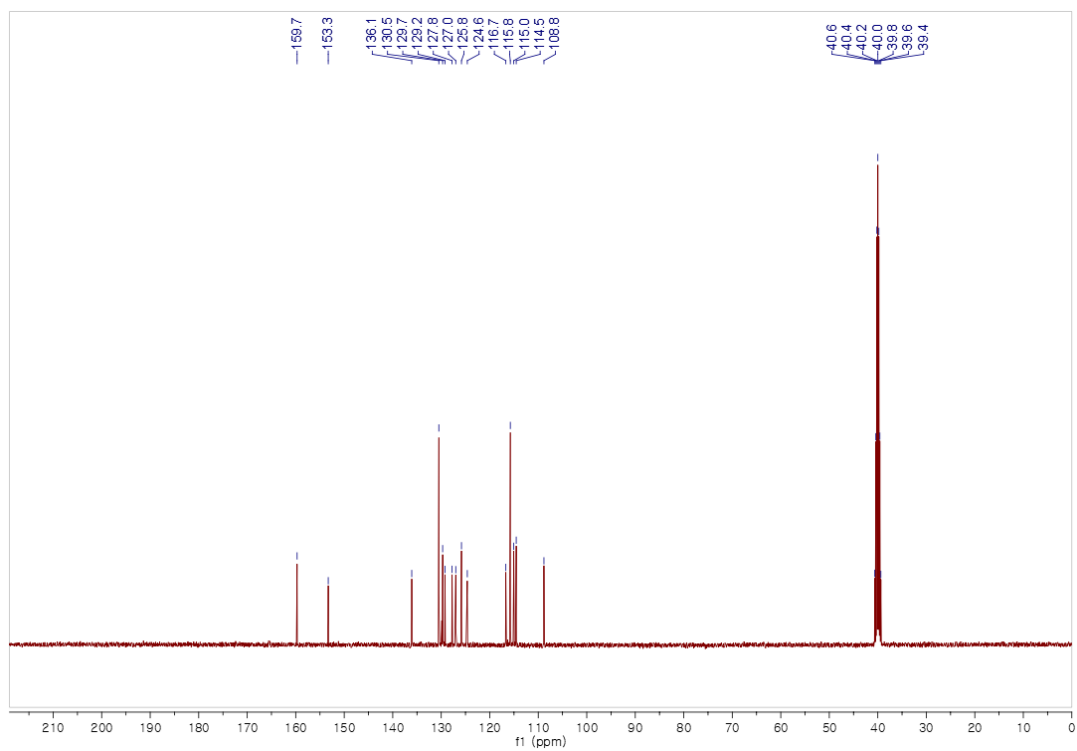
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectrum of compound 8**



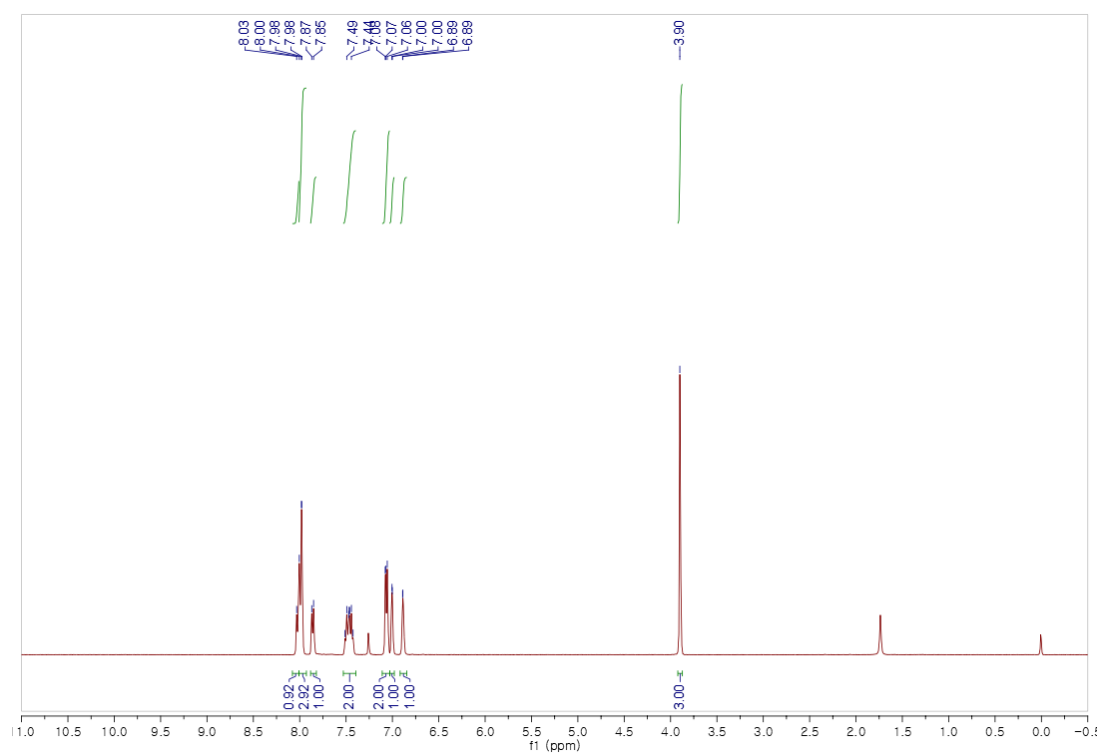
**<sup>1</sup>H NMR (400 MHz, DMSO) spectrum of compound 22**



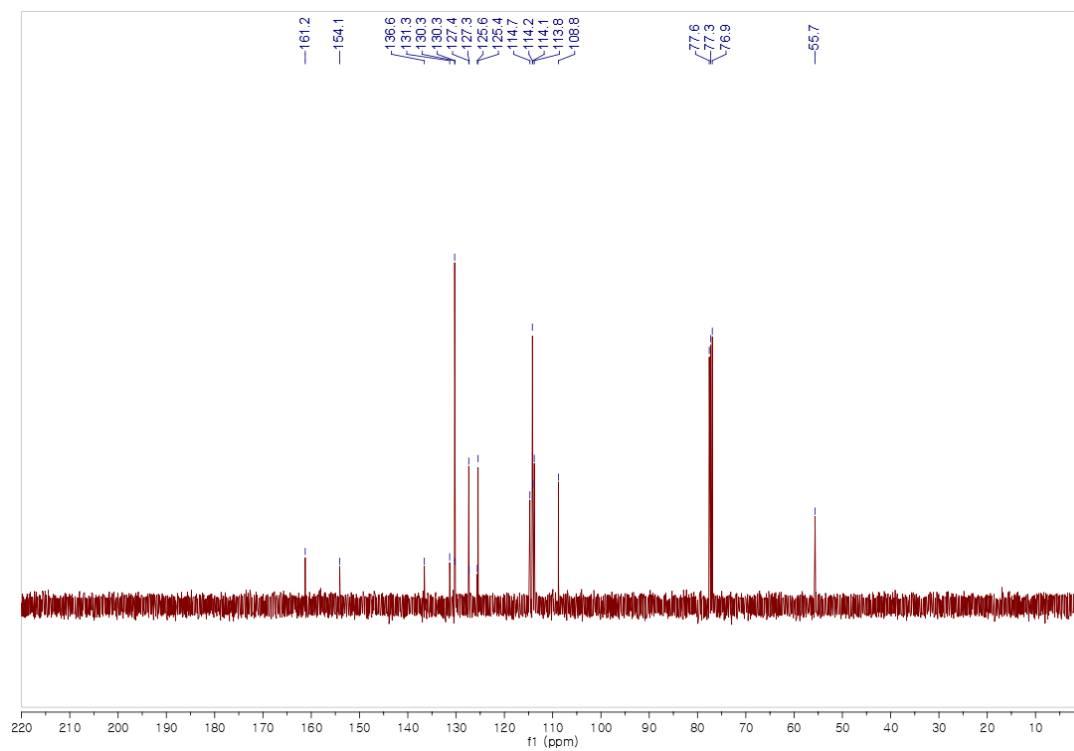
**<sup>13</sup>C NMR (101 MHz, DMSO) spectrum of compound 22**



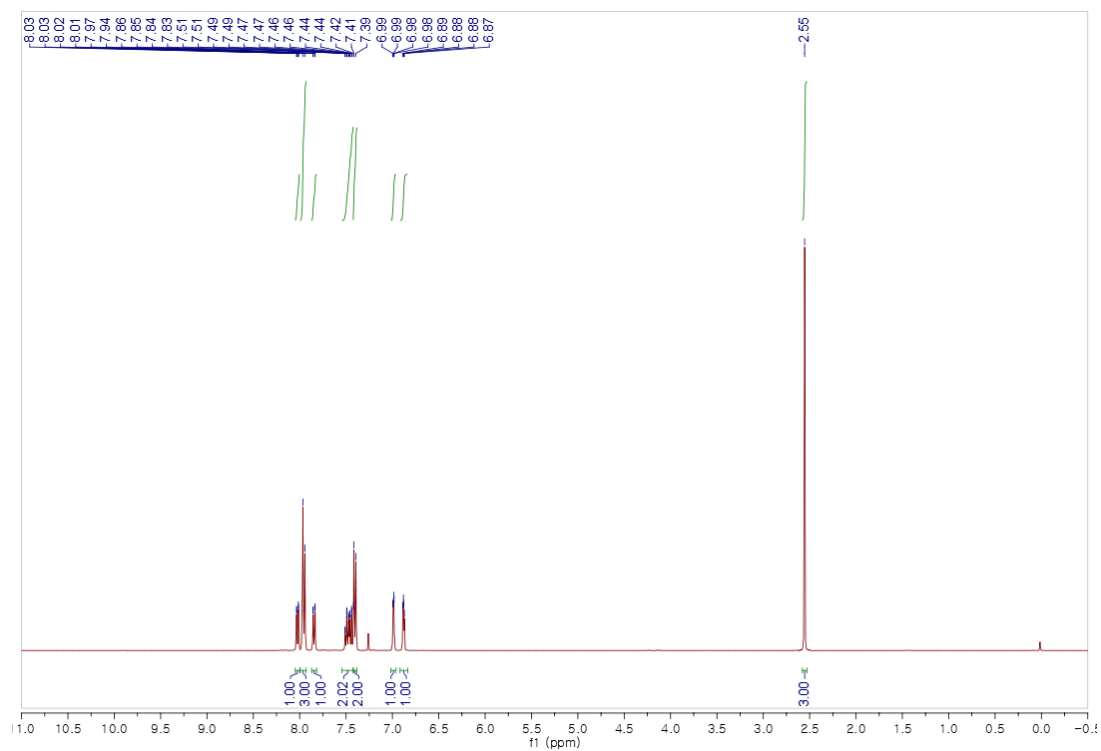
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound 23**



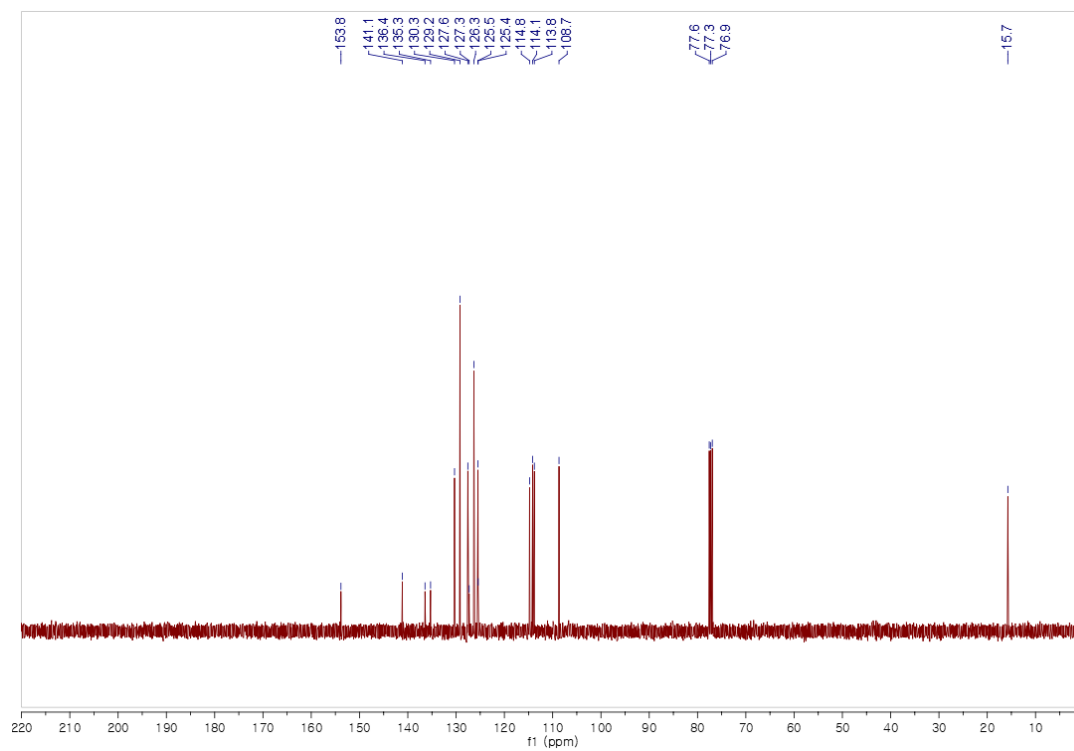
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectrum of compound 23**



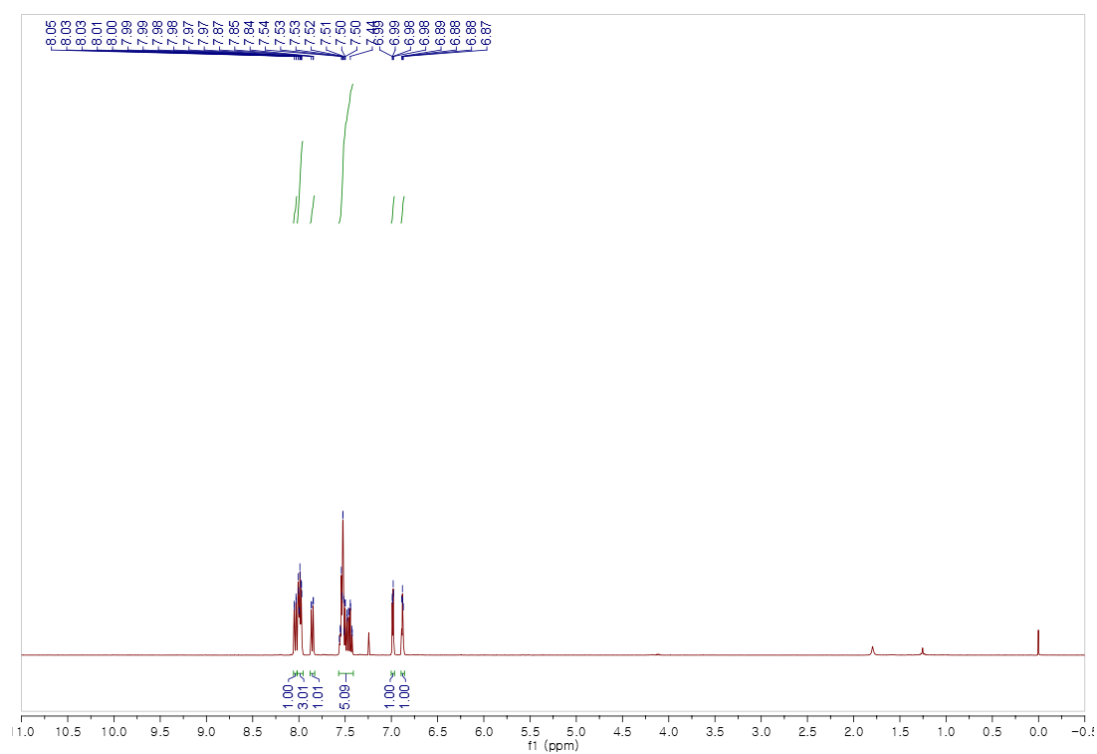
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound 24**



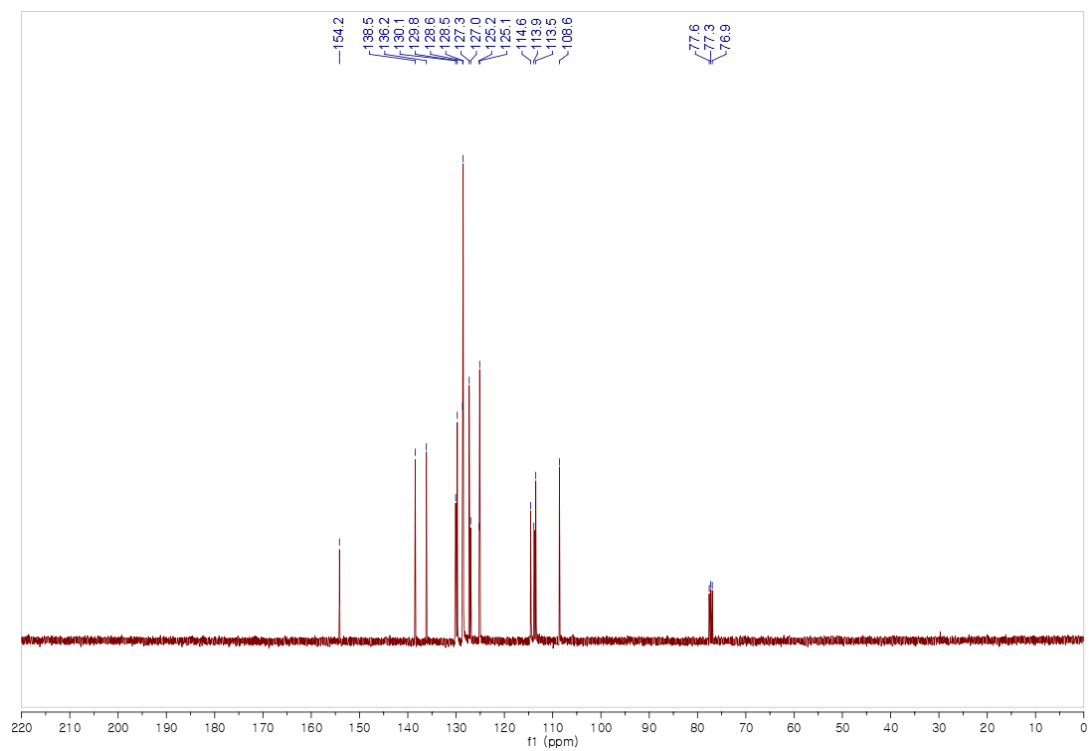
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectrum of compound 24**



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound 25**

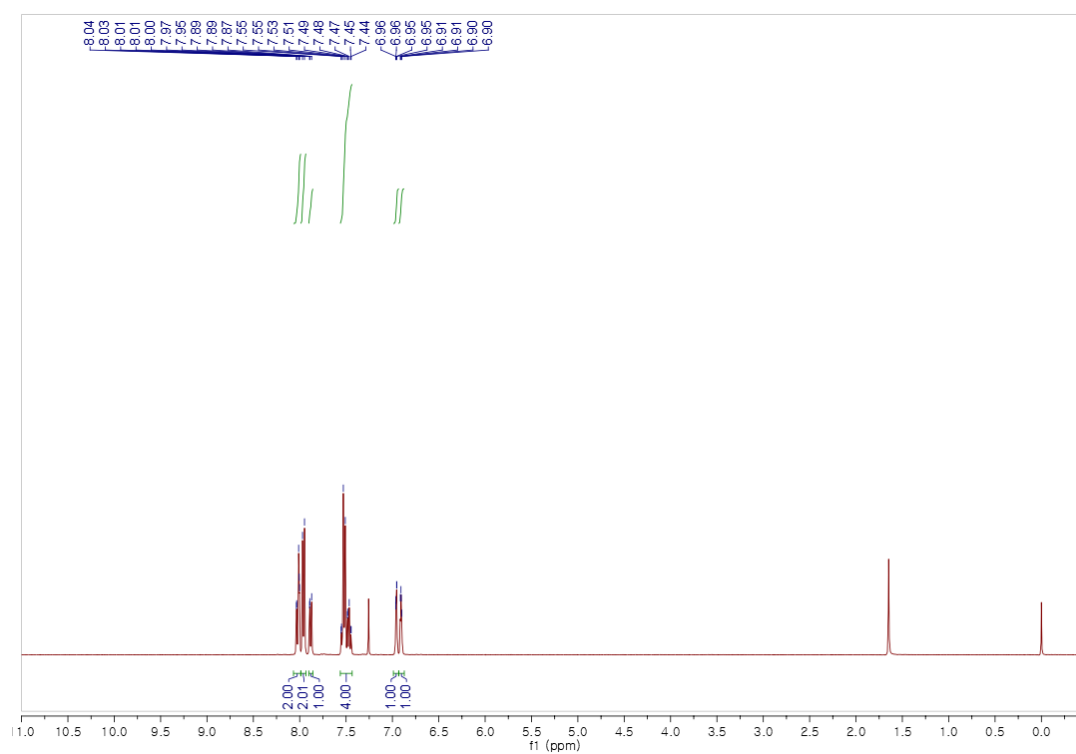


**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectrum of compound 25**

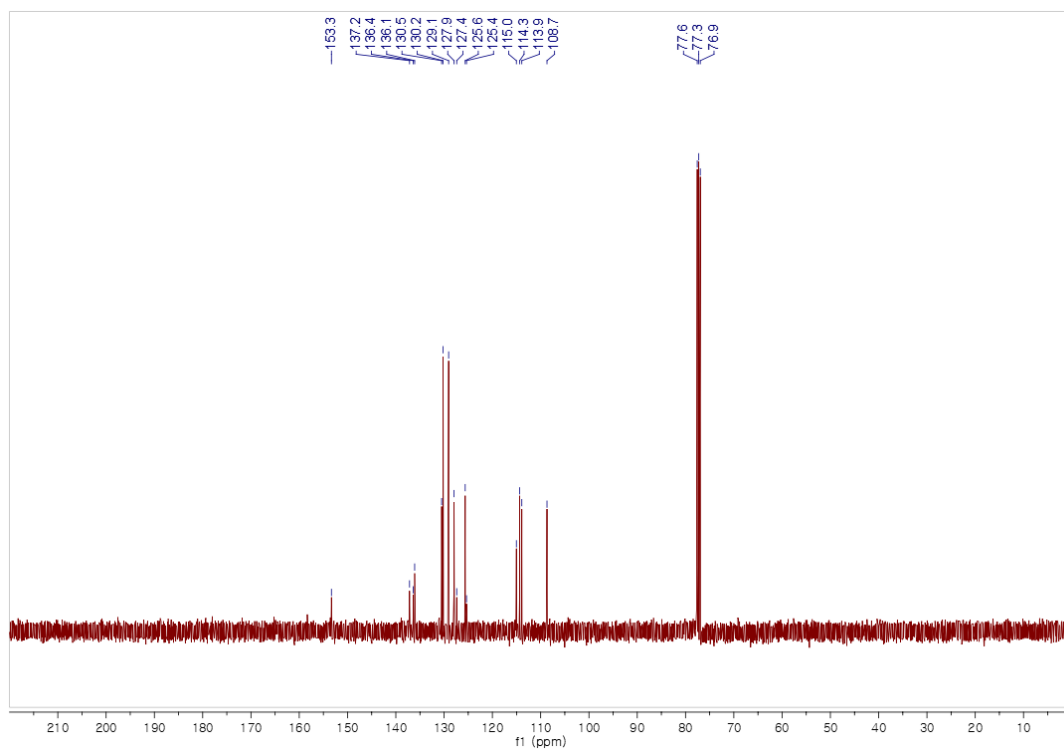




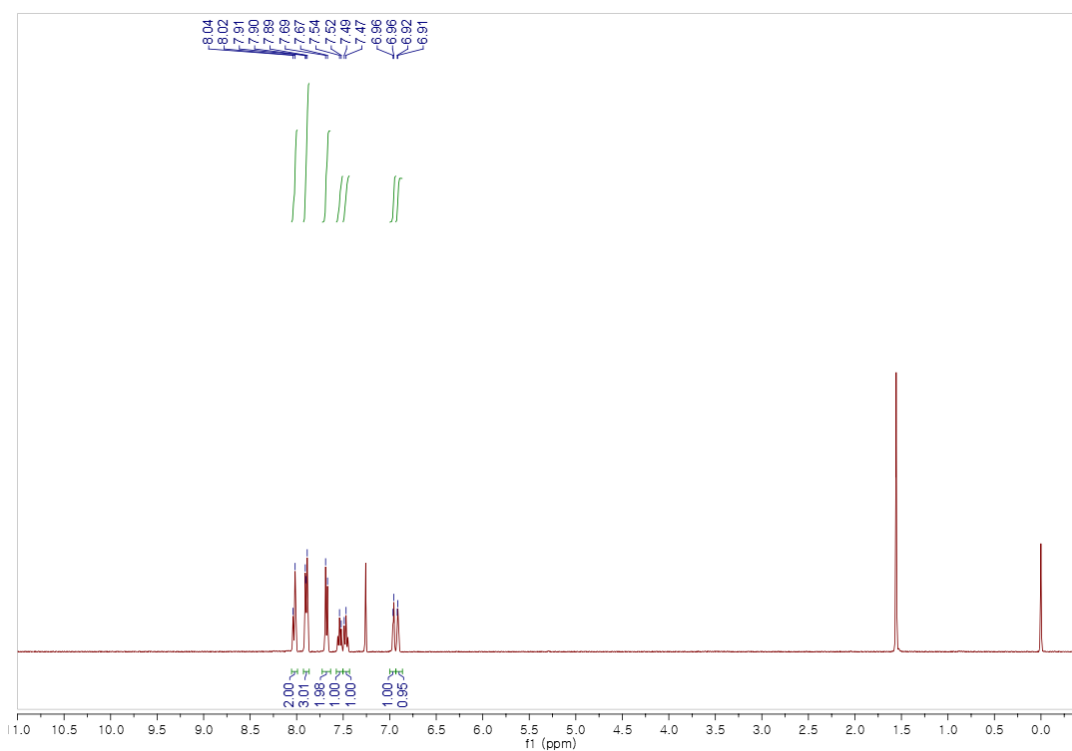
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound 26**



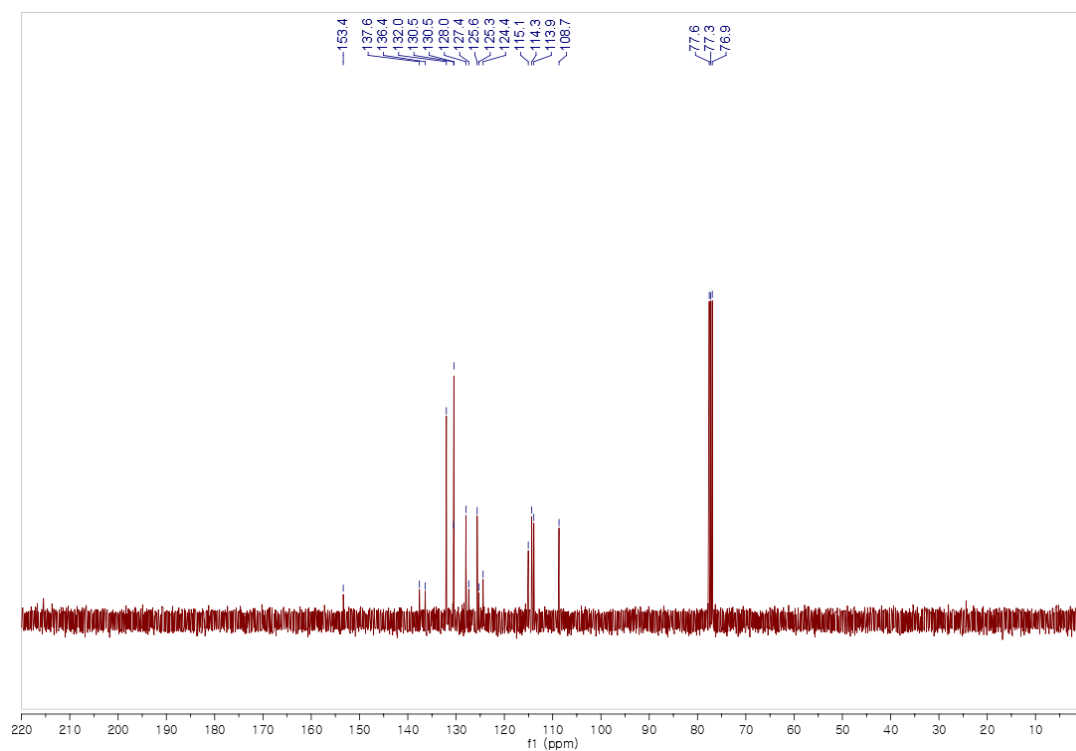
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectrum of compound 26**



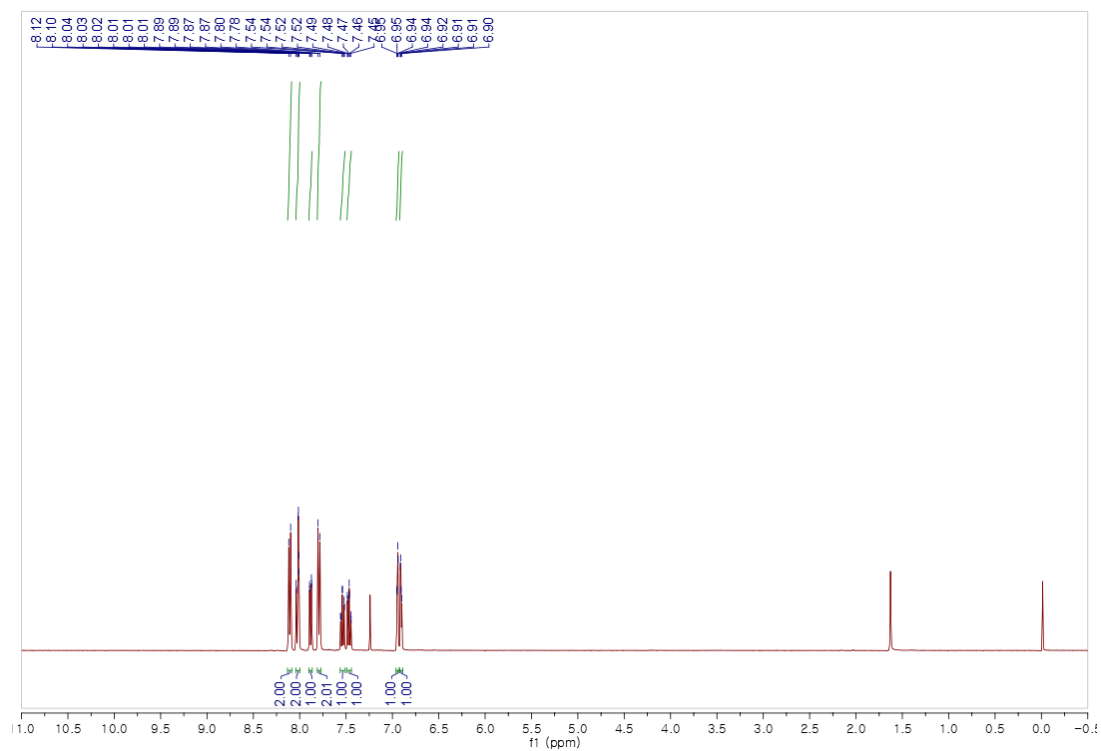
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound 27**



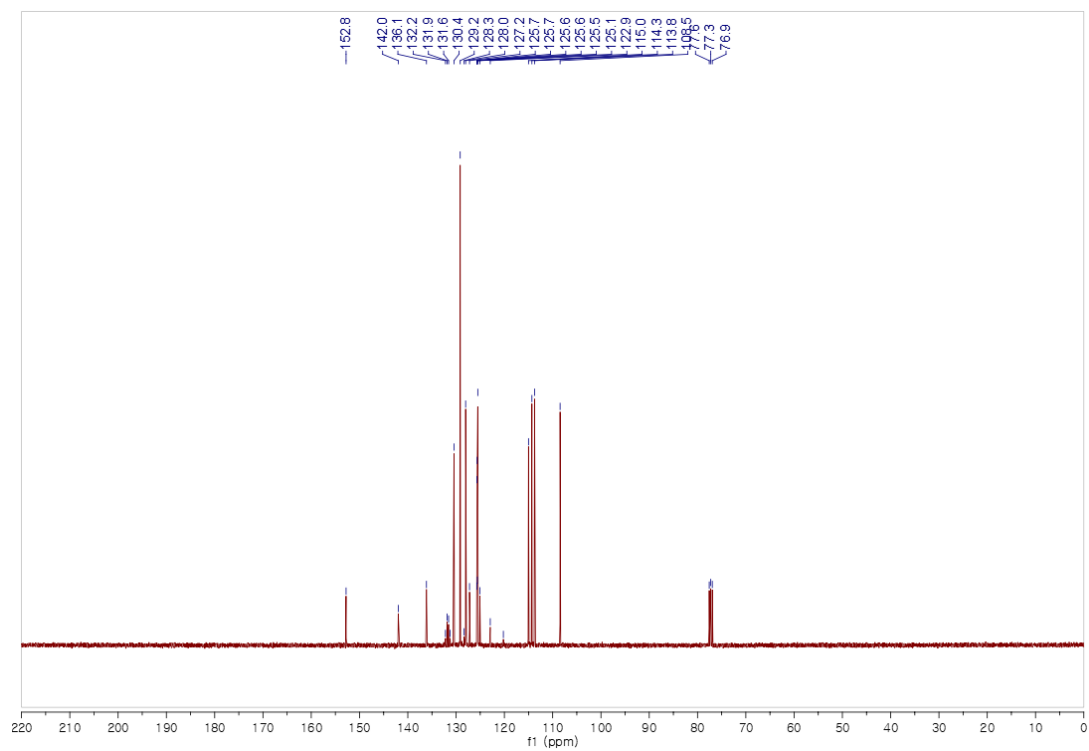
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectrum of compound 27**

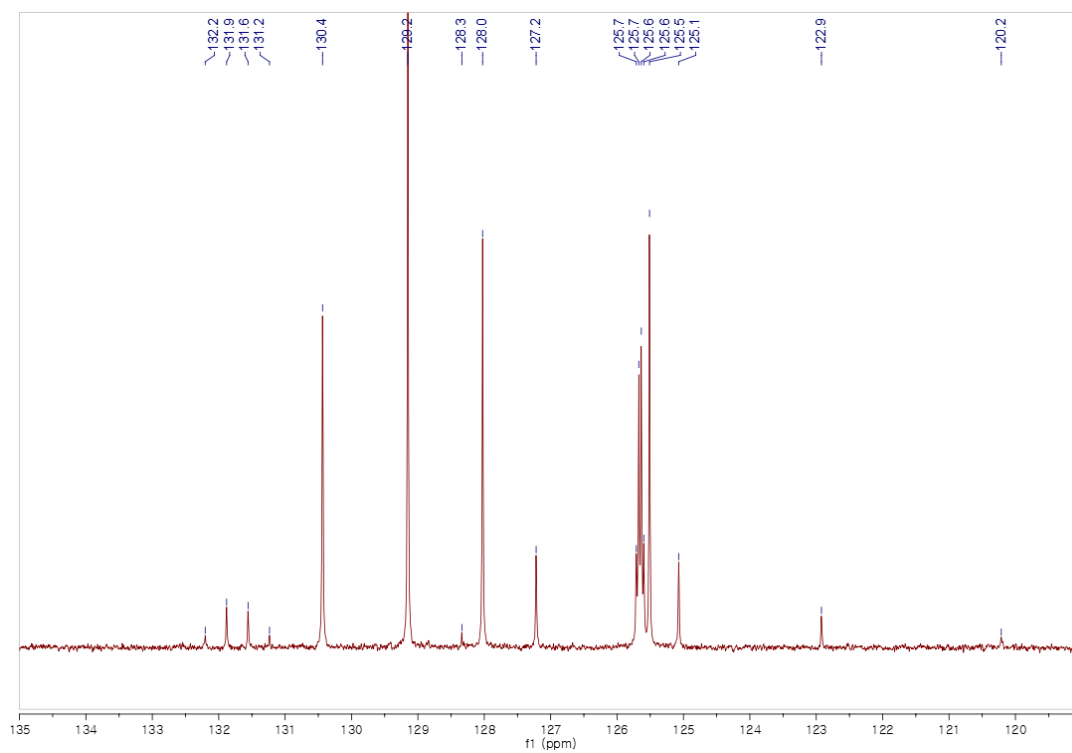


**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound 28**

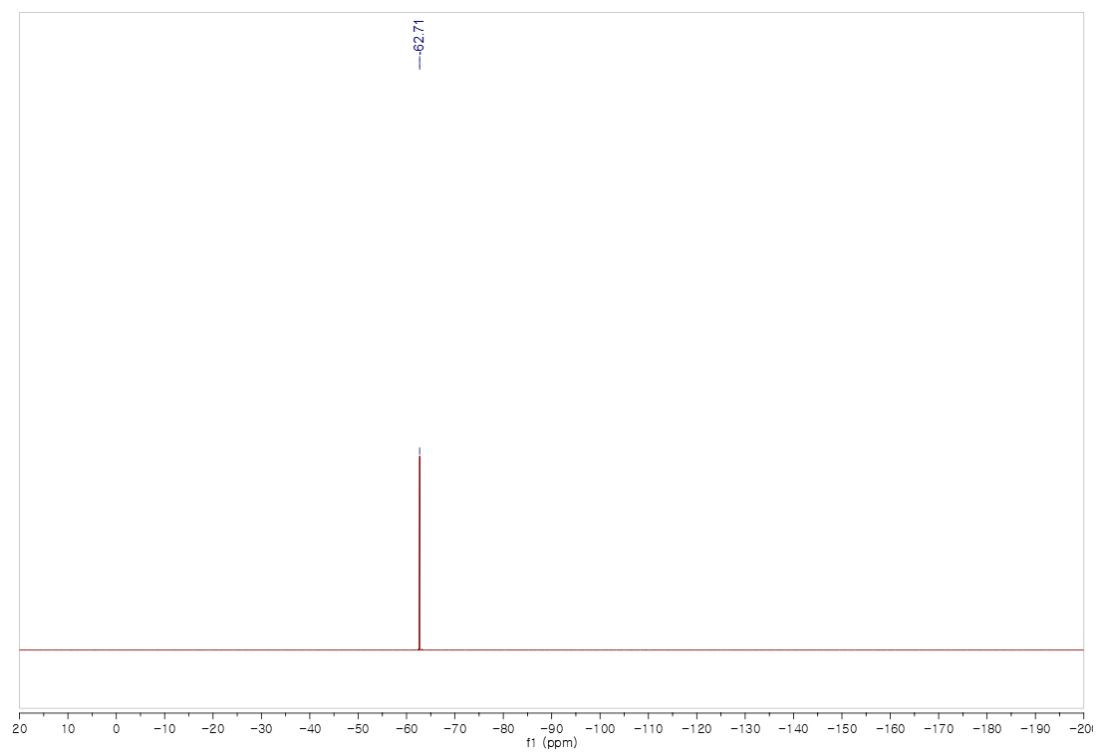


**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectrum of compound 28**

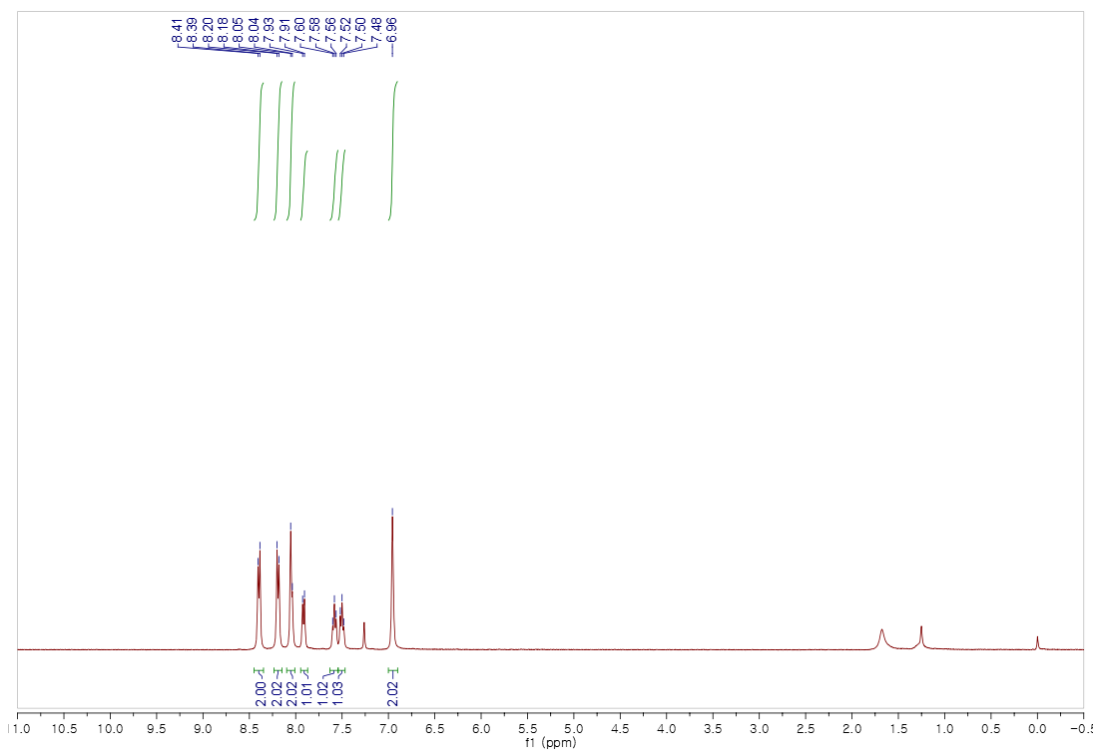




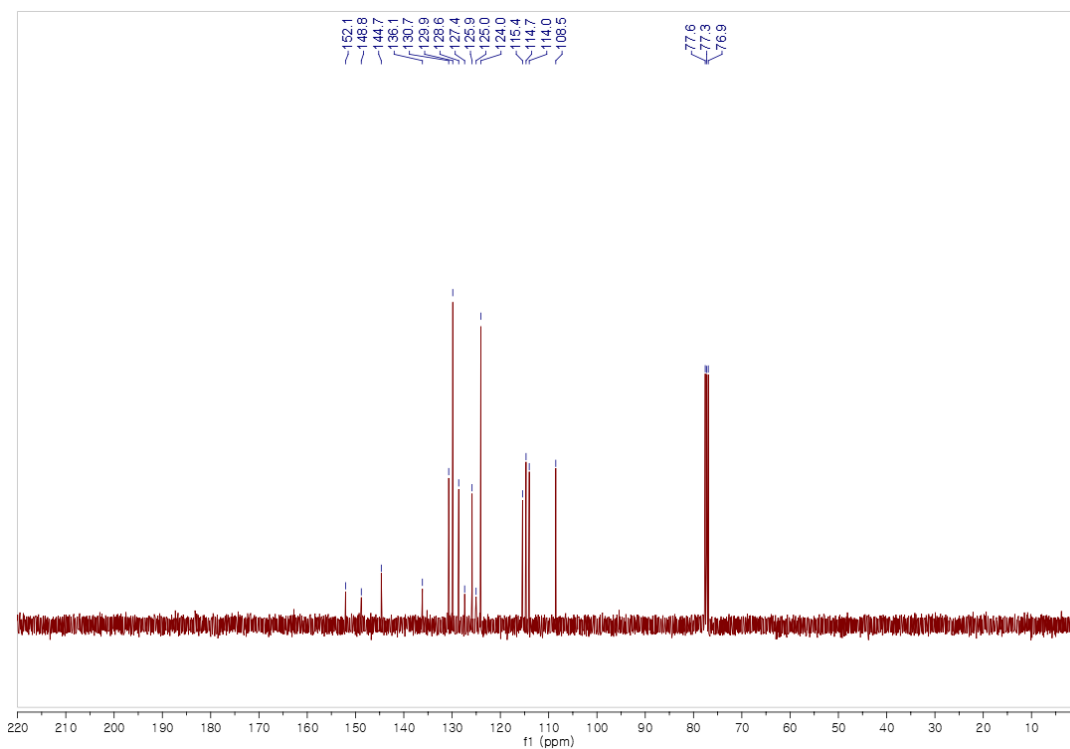
**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) spectrum of compound 28**



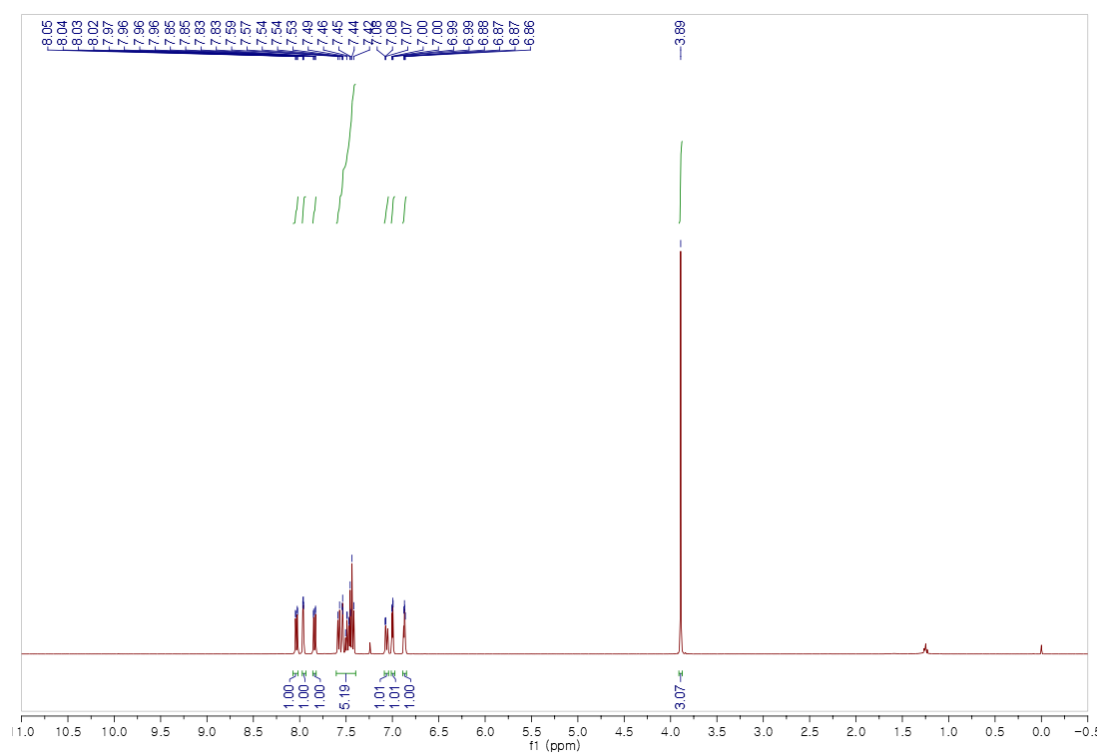
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound 29**



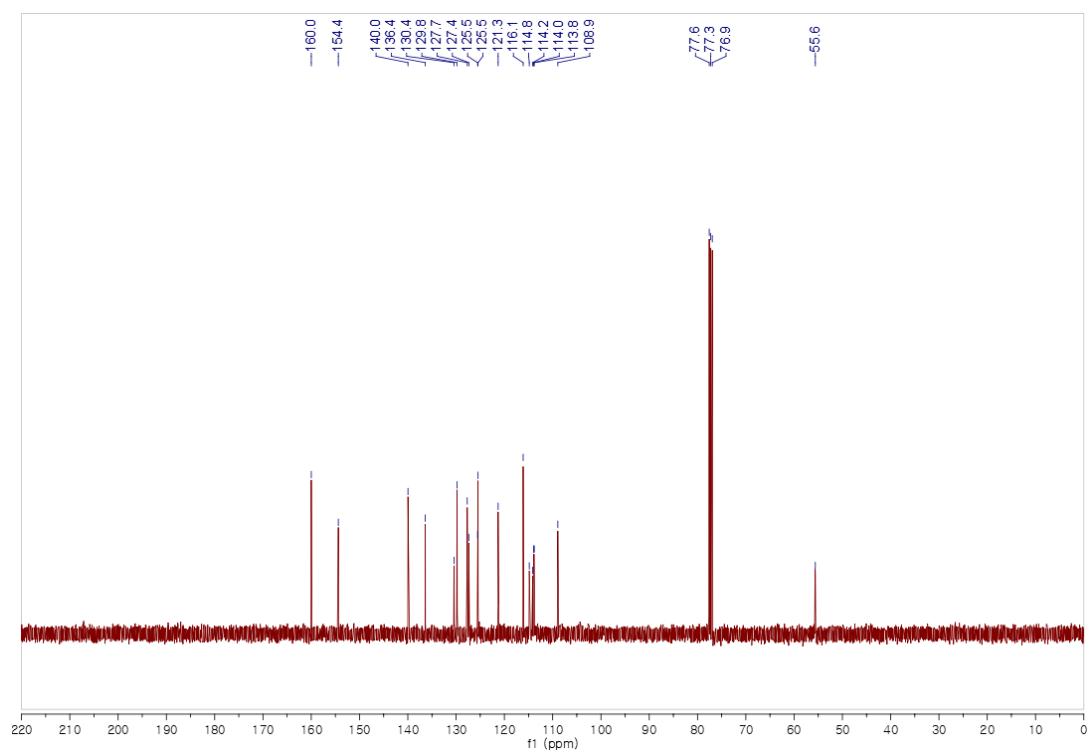
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectrum of compound 29**



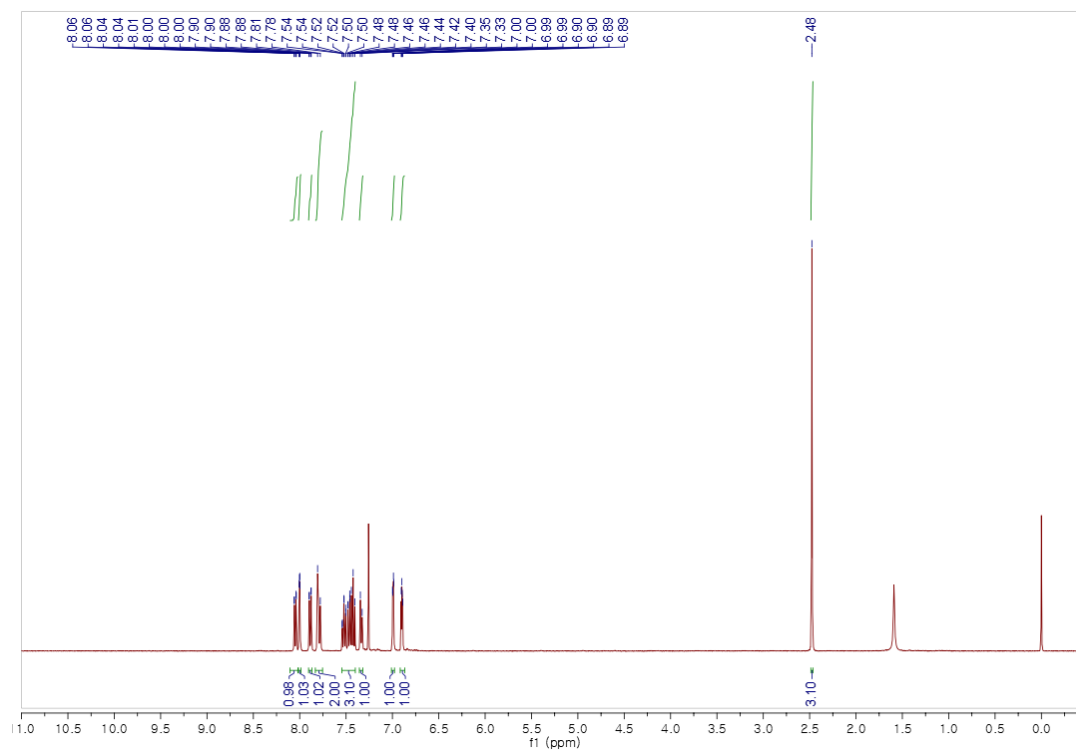
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound 30**



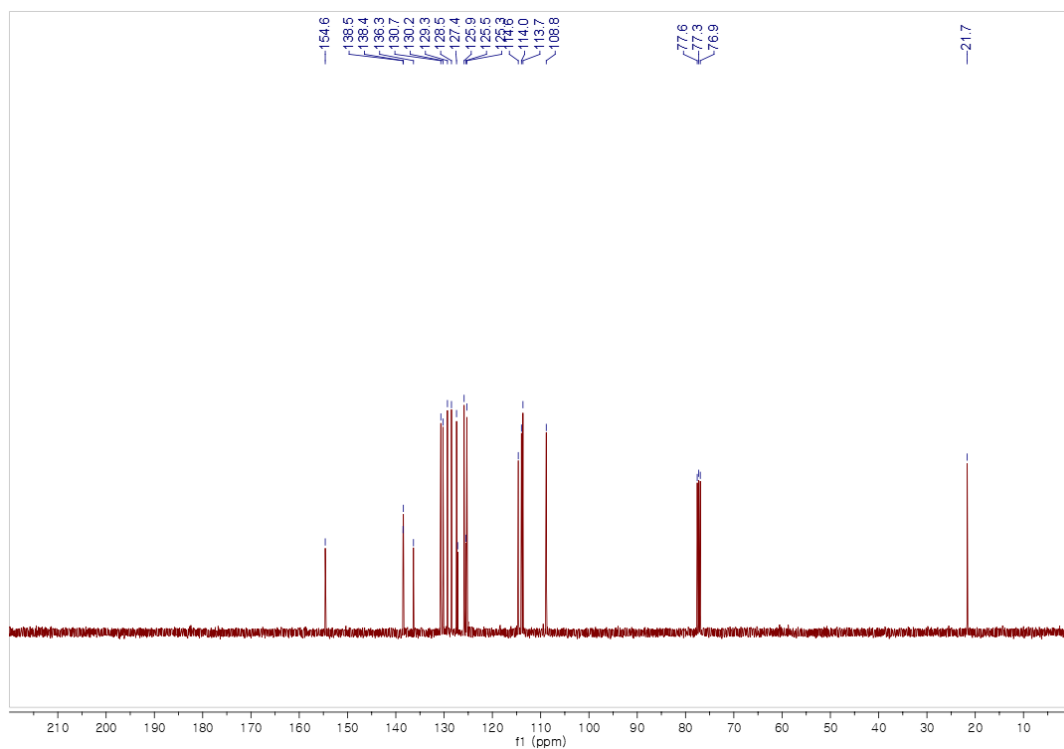
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectrum of compound 30**



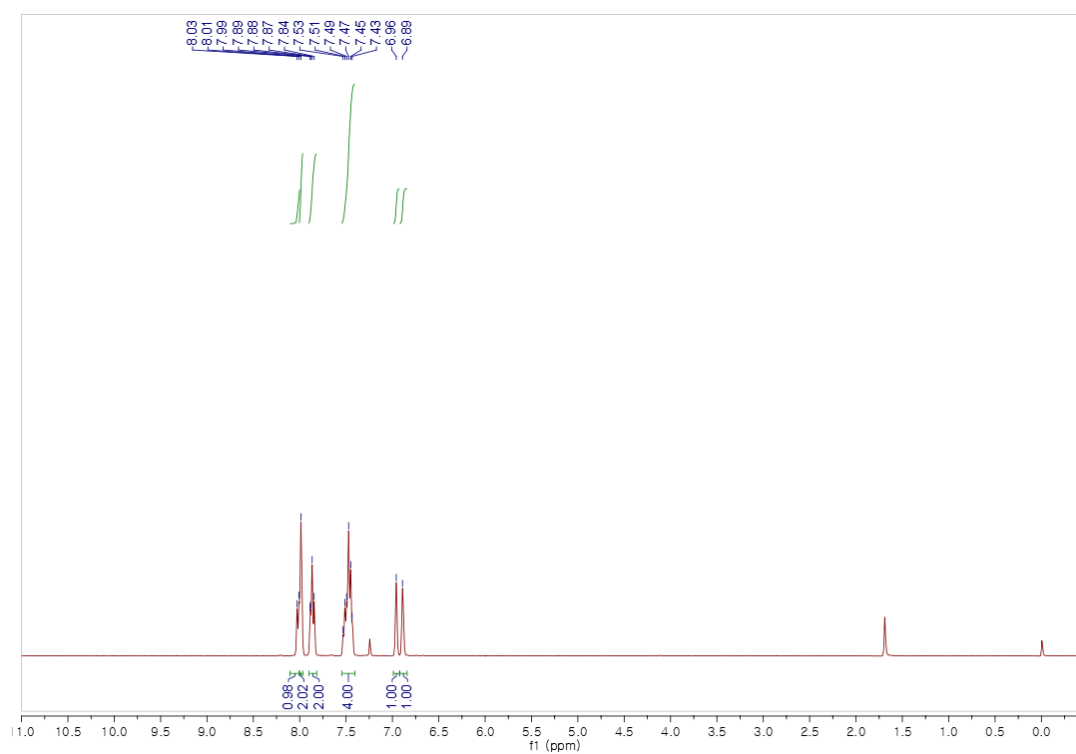
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound 31**



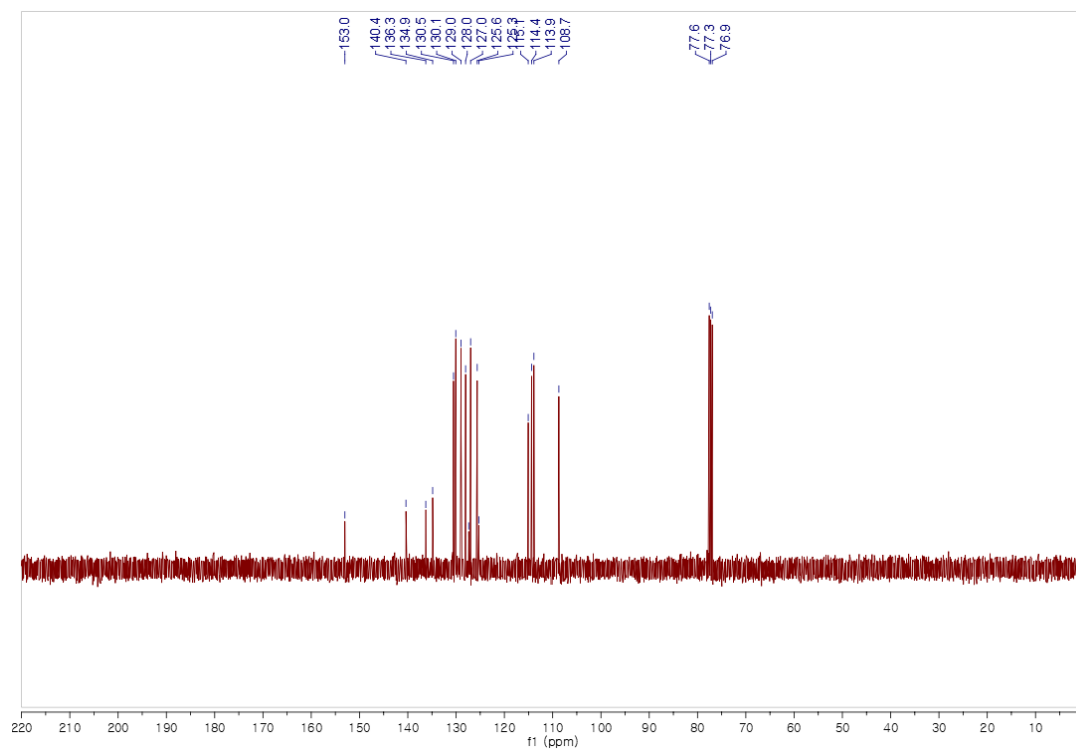
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectrum of compound 31**



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound 32**

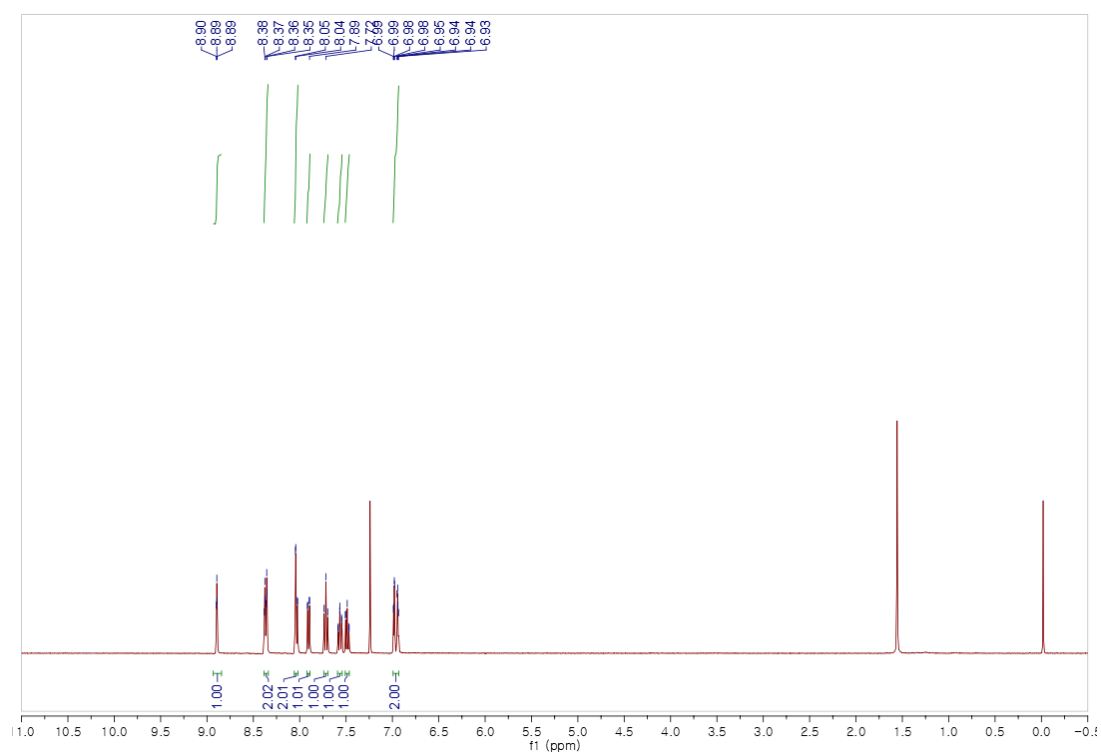


**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectrum of compound 32**

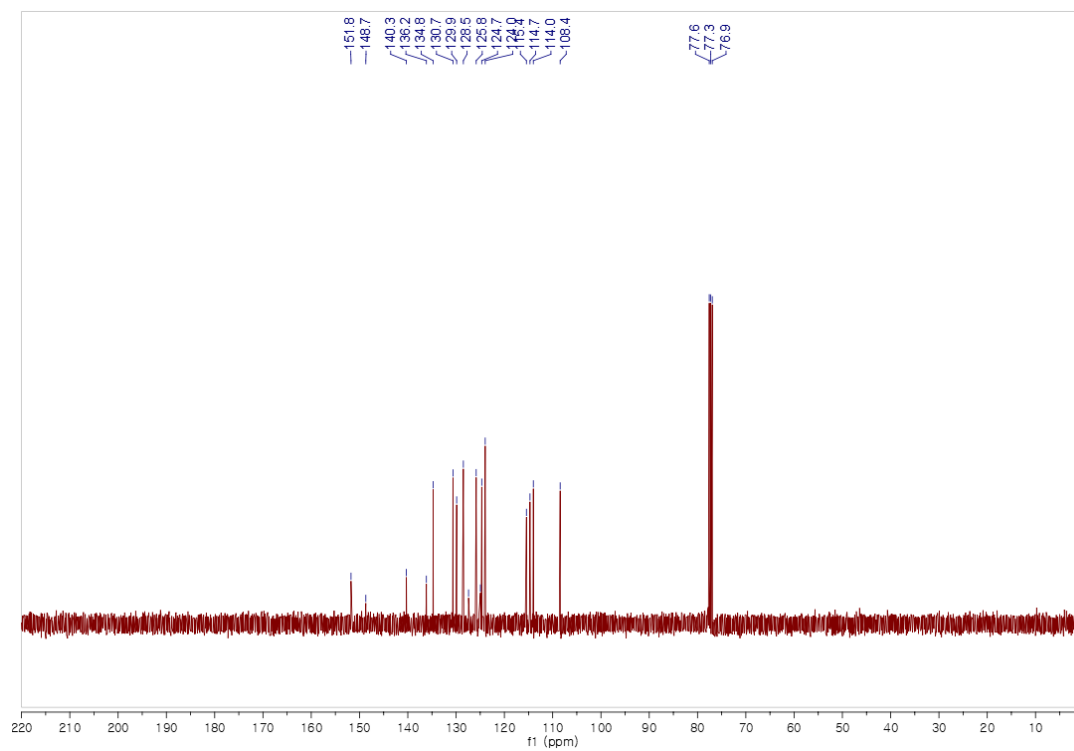




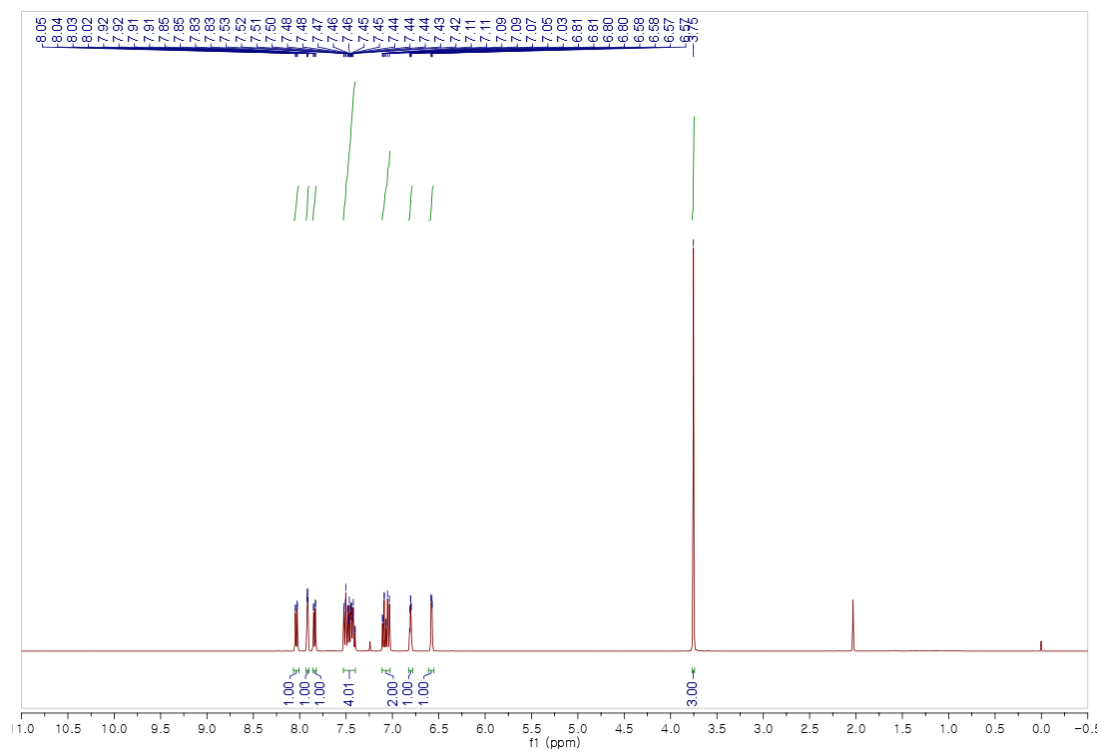
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound 33**



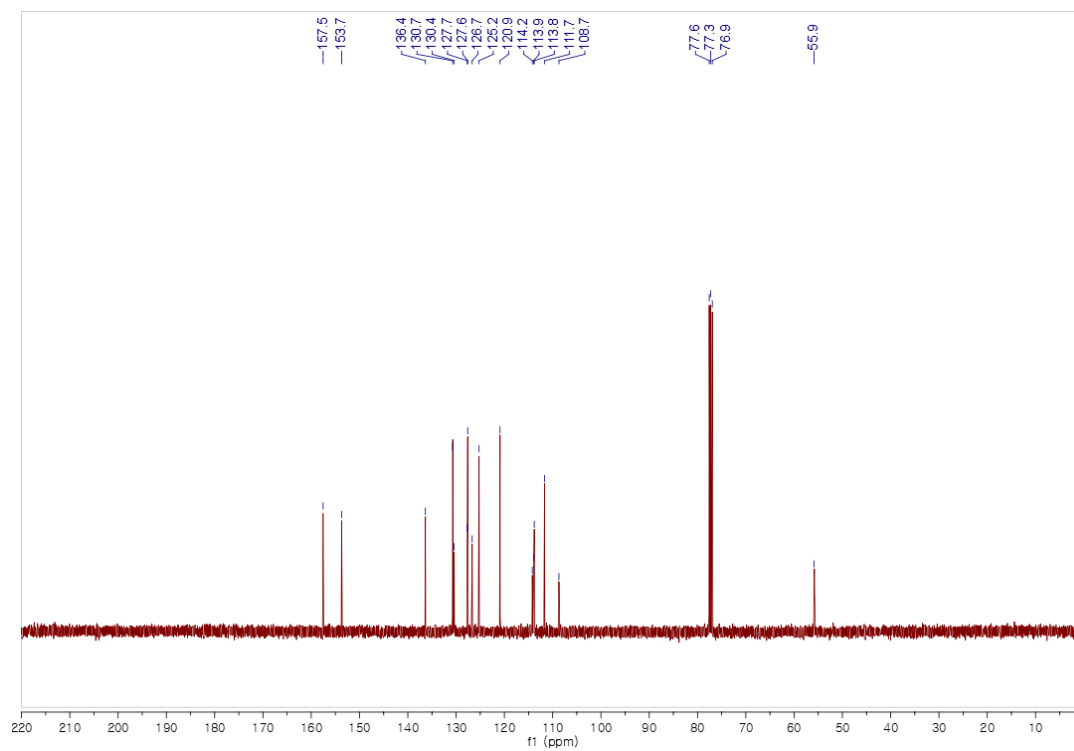
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectrum of compound 33**



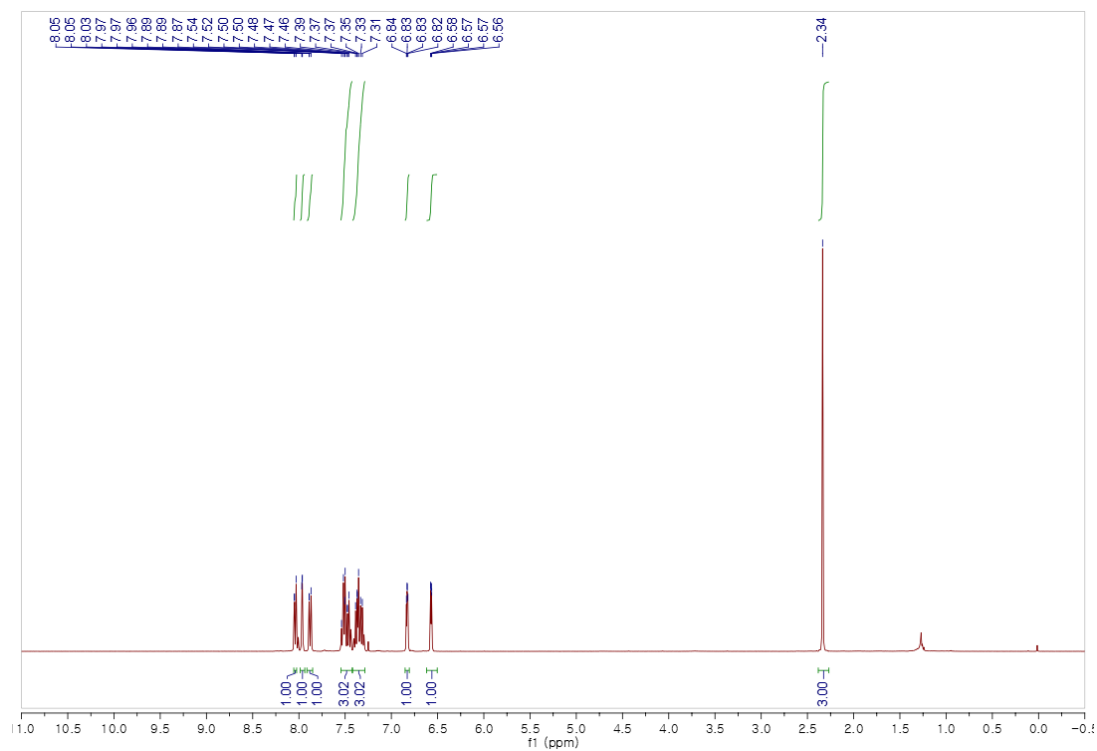
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound 34**



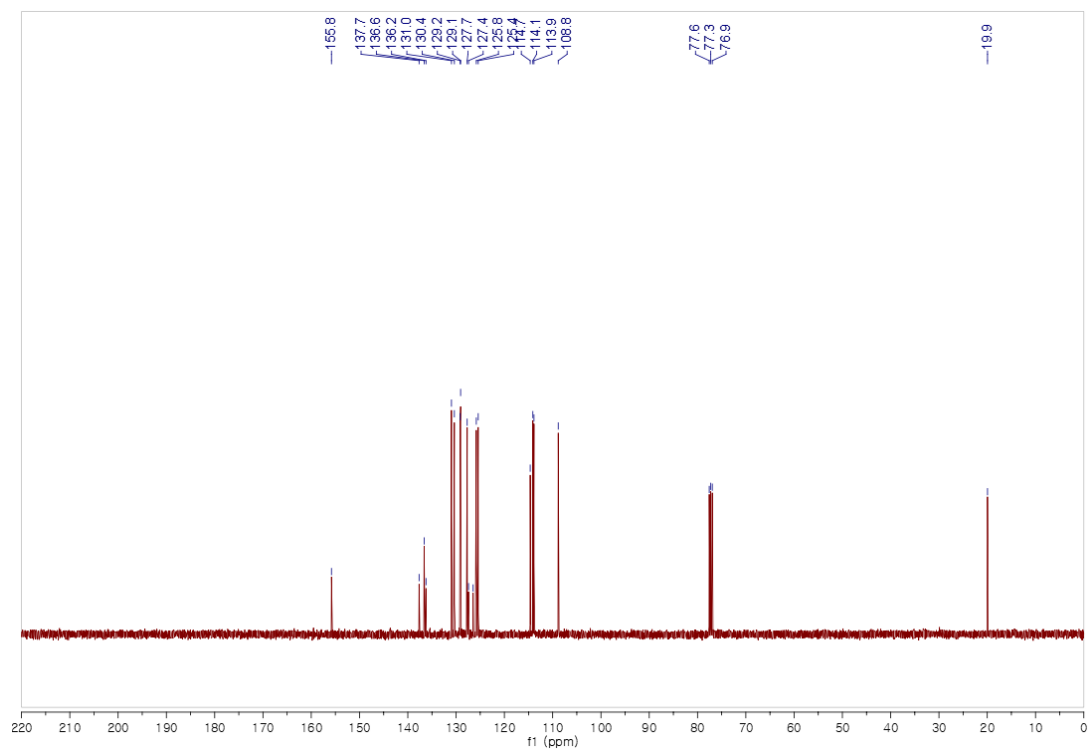
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectrum of compound 34**



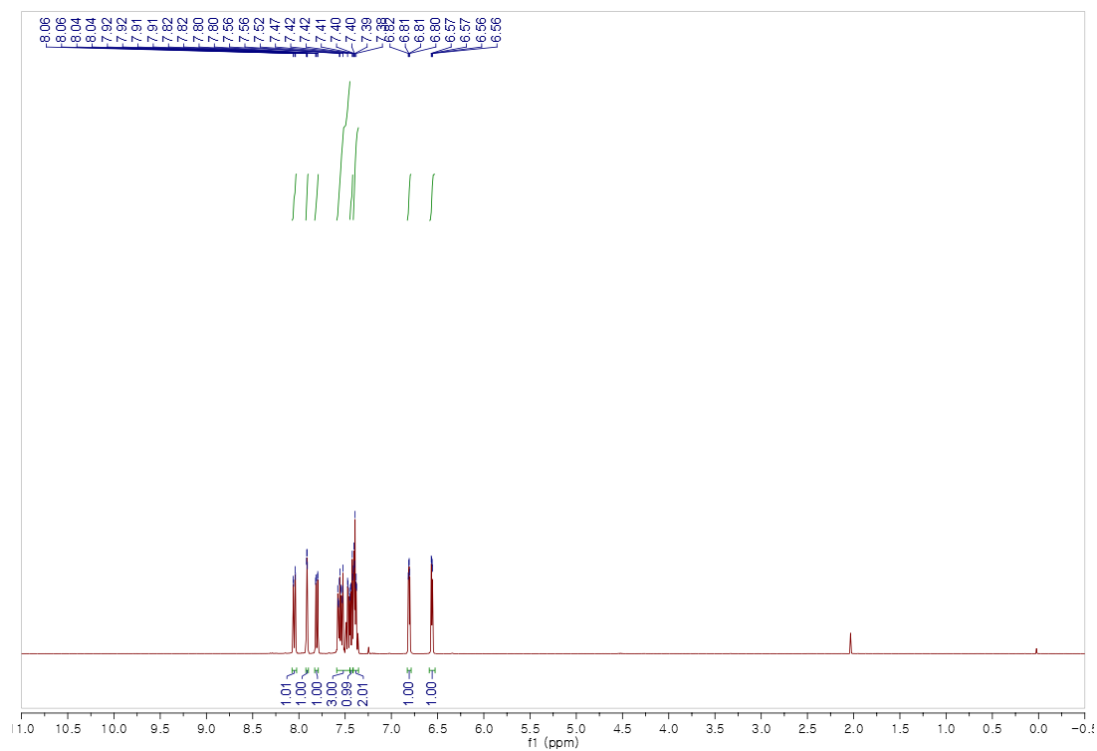
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound 35**



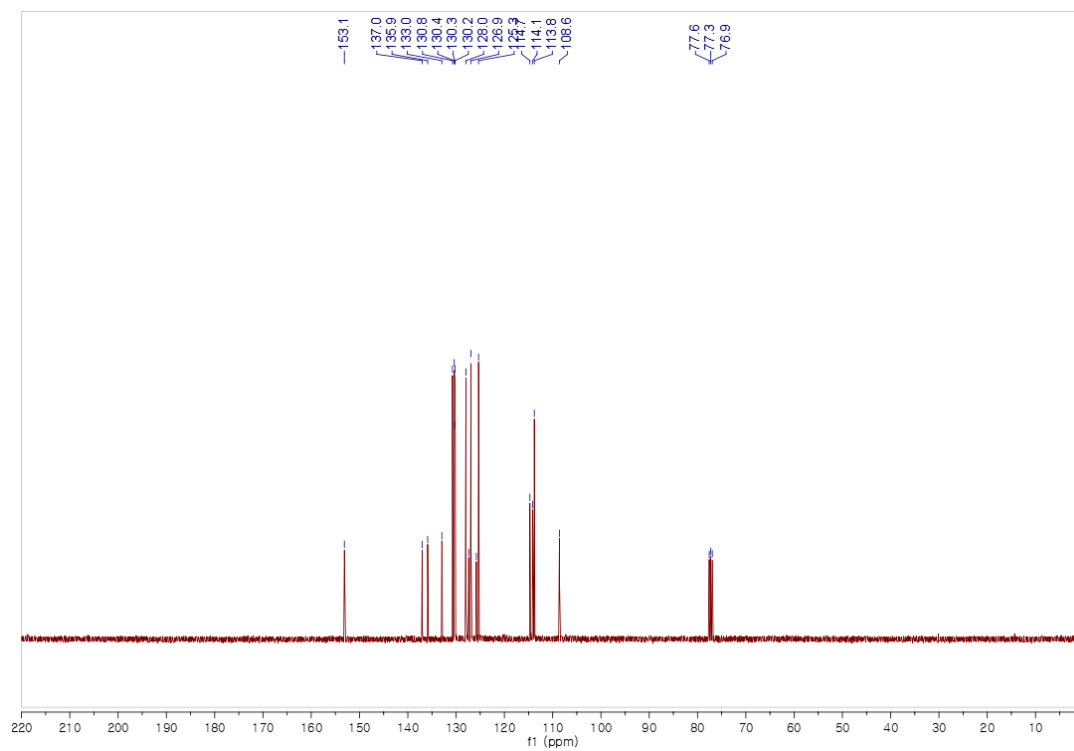
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectrum of compound 35**



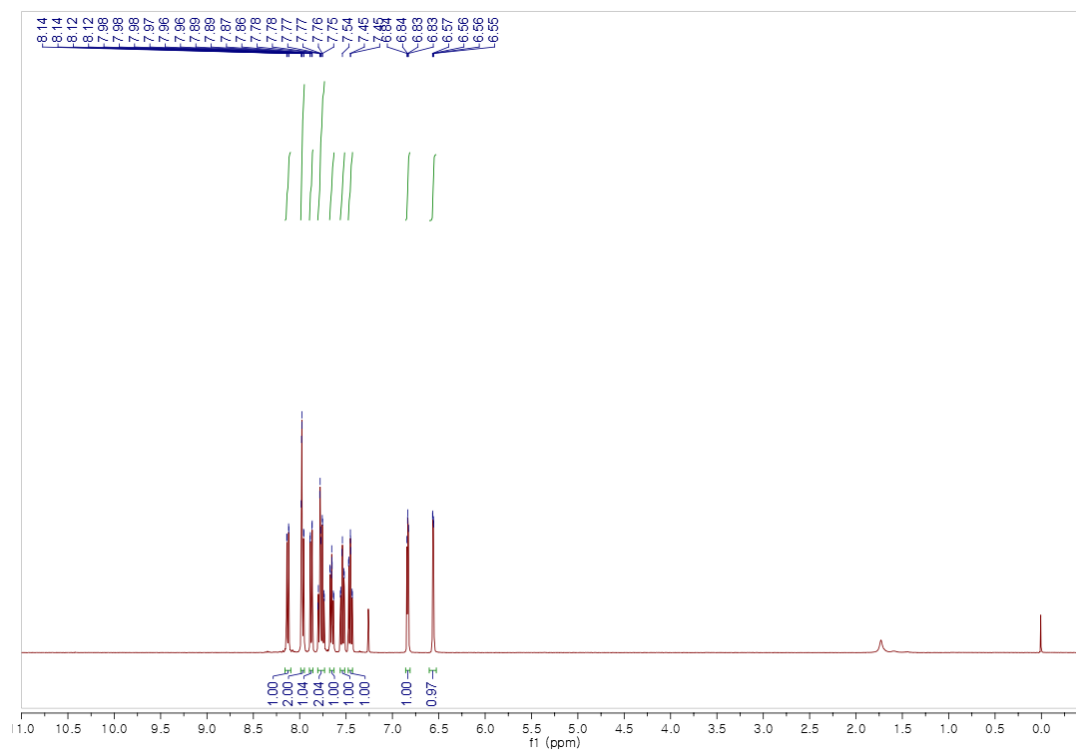
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound 36**



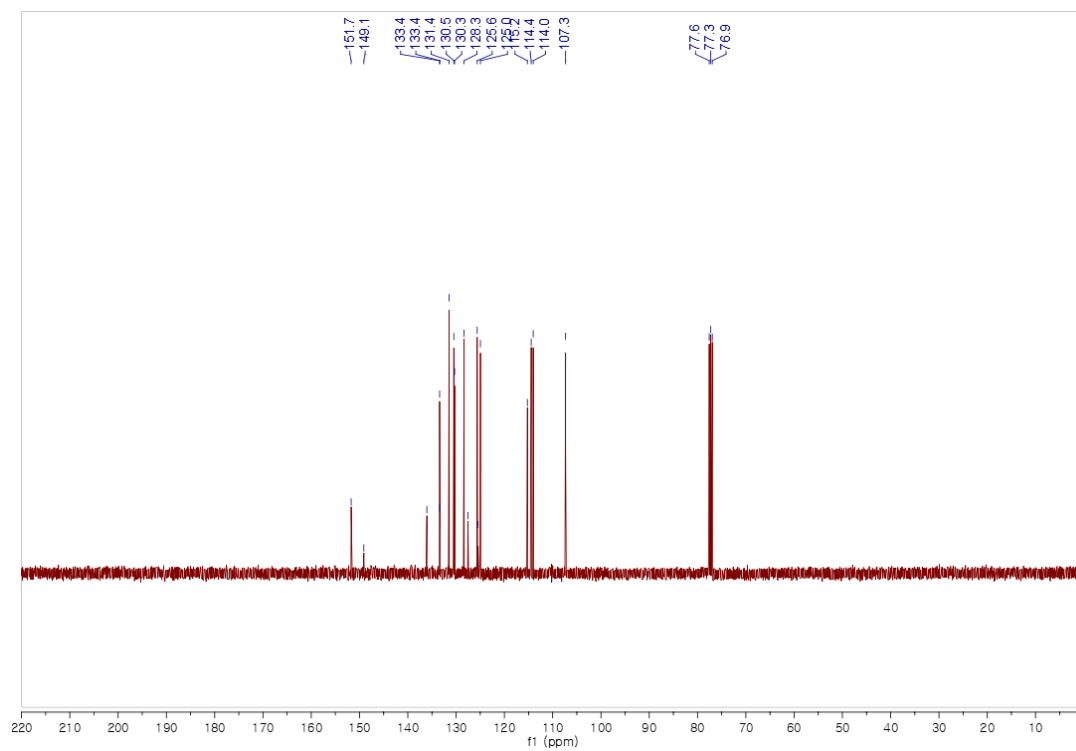
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectrum of compound 36**



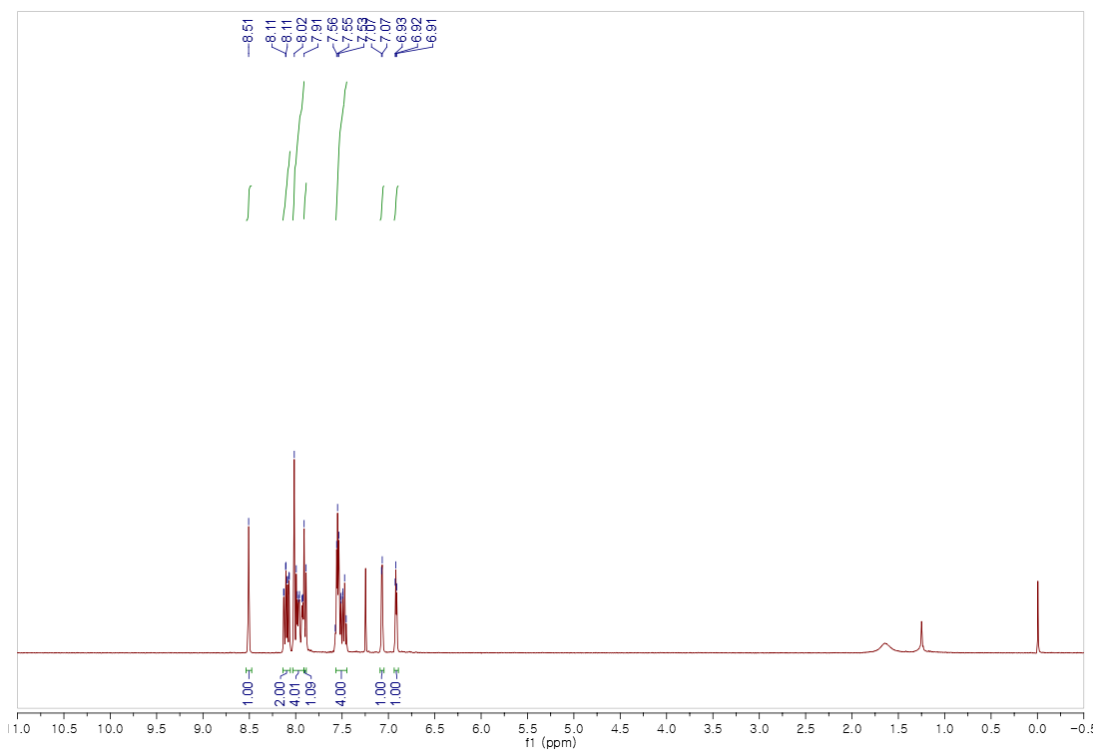
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of compound 37**



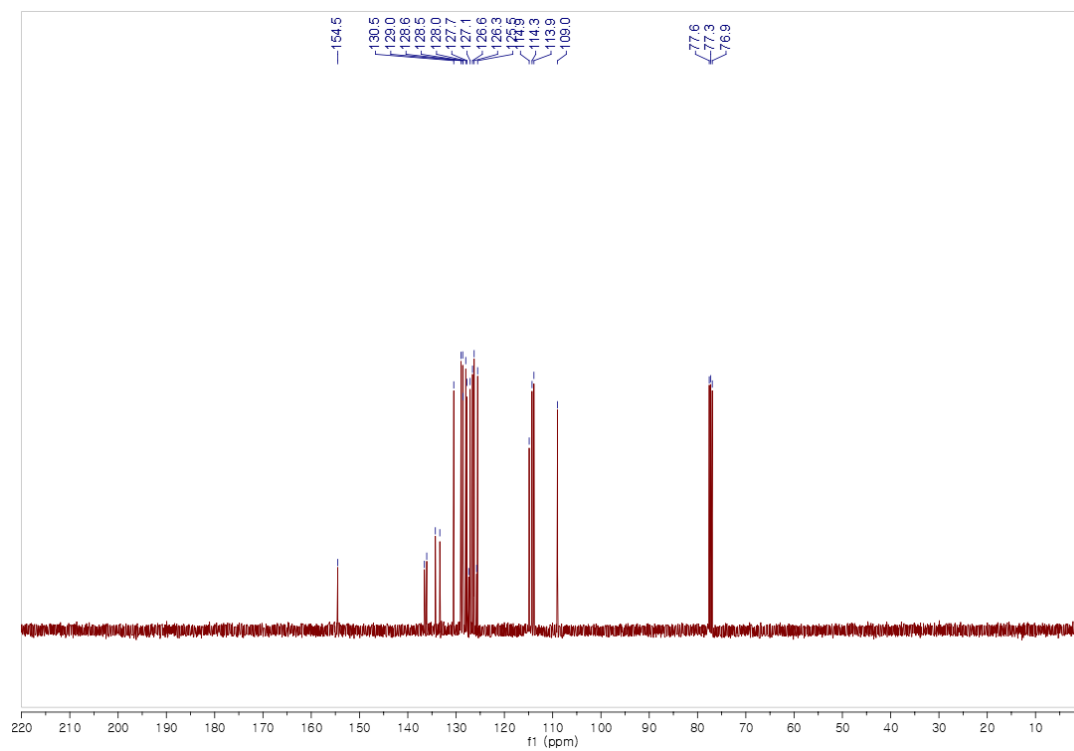
**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) spectrum of compound 37**



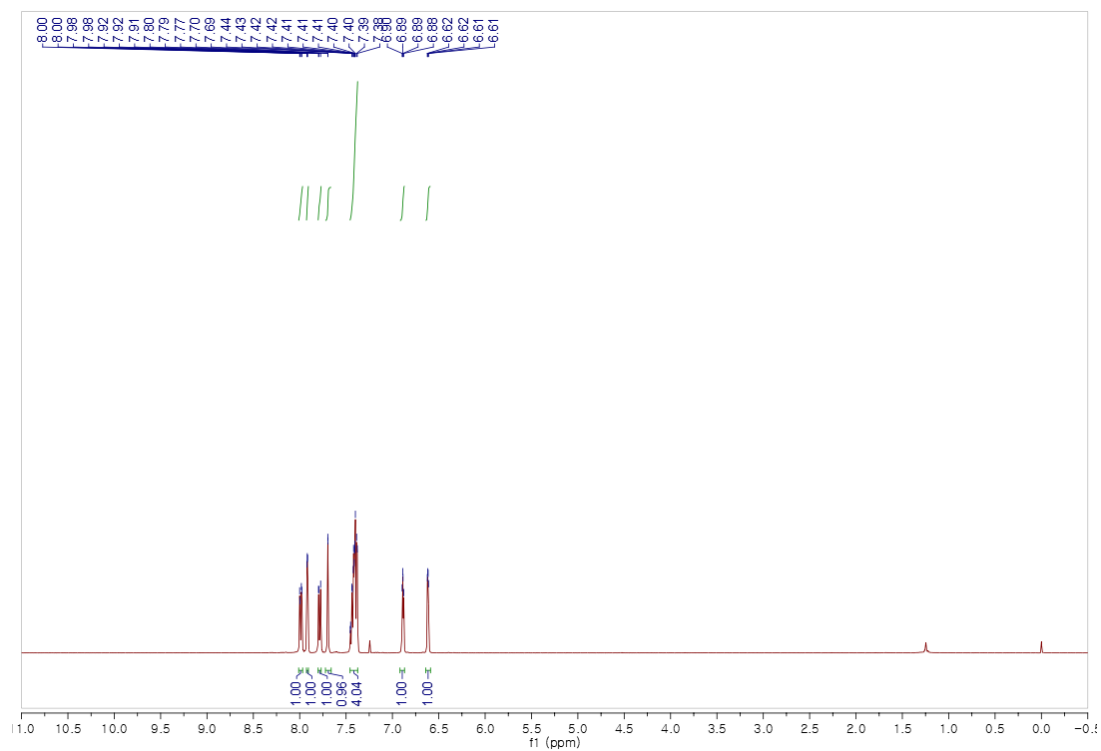
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound 38**



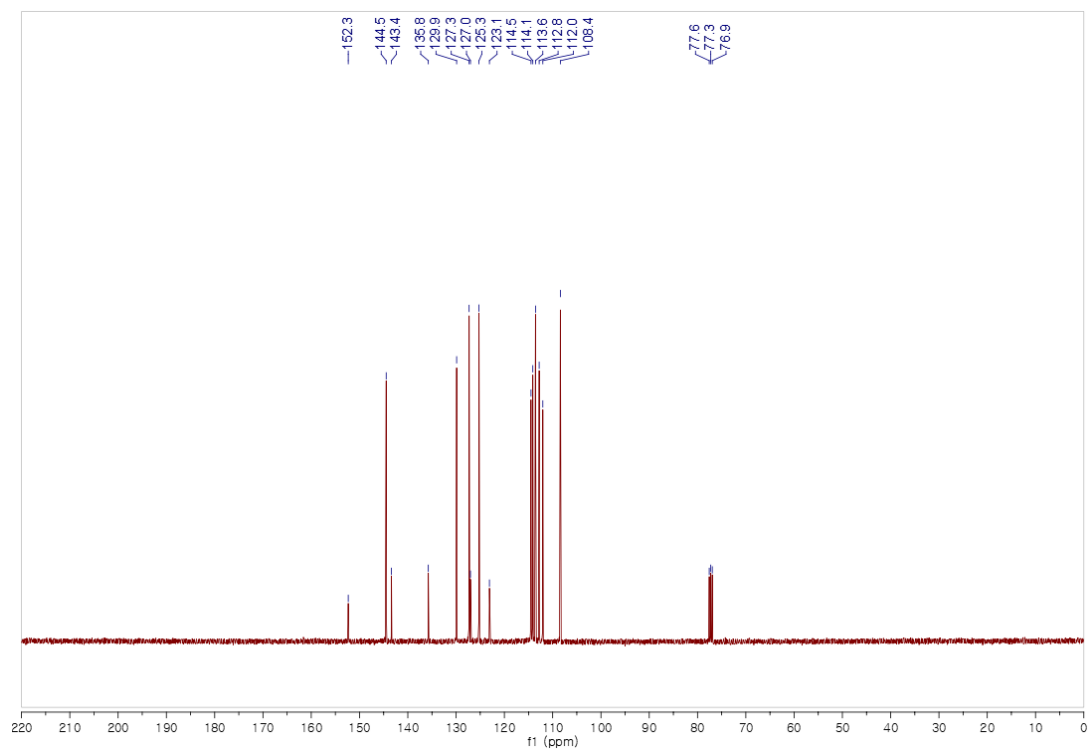
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectrum of compound 38**



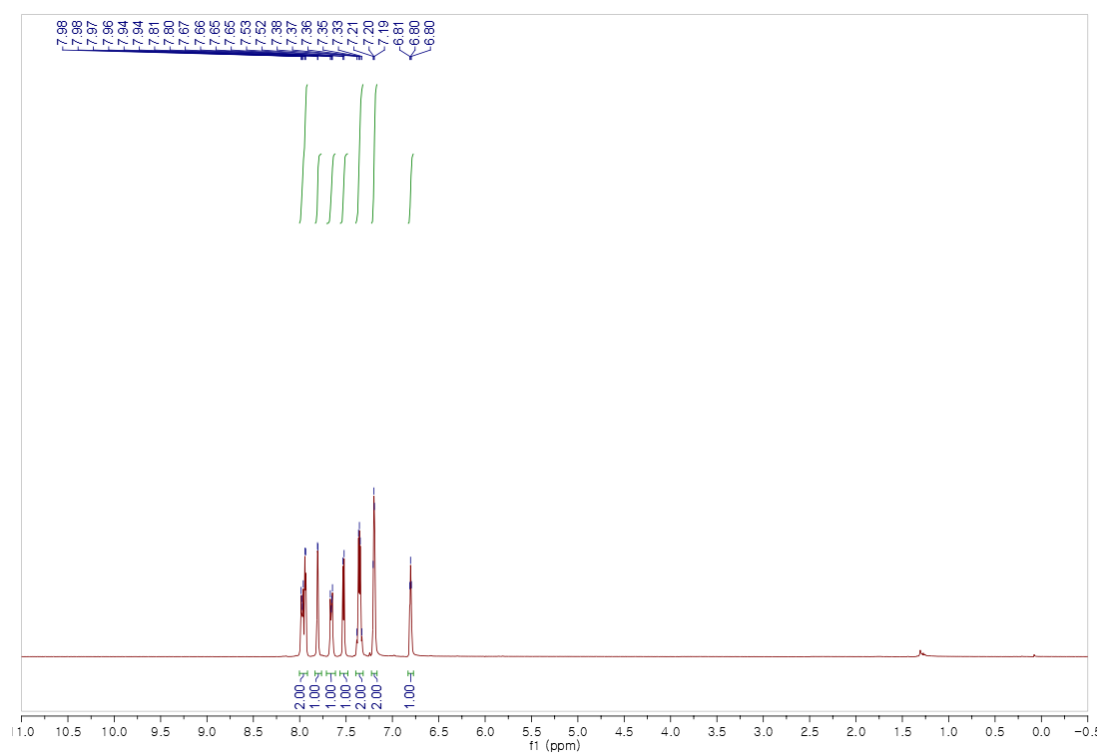
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound 39**



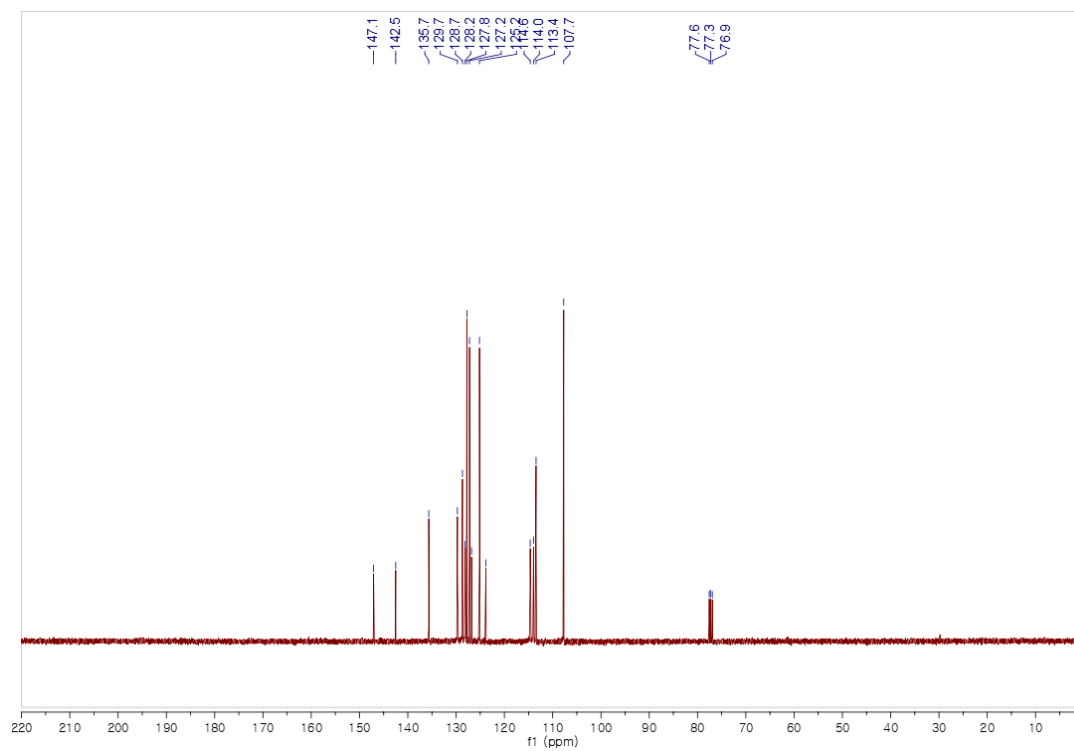
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectrum of compound 39**



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound 40**

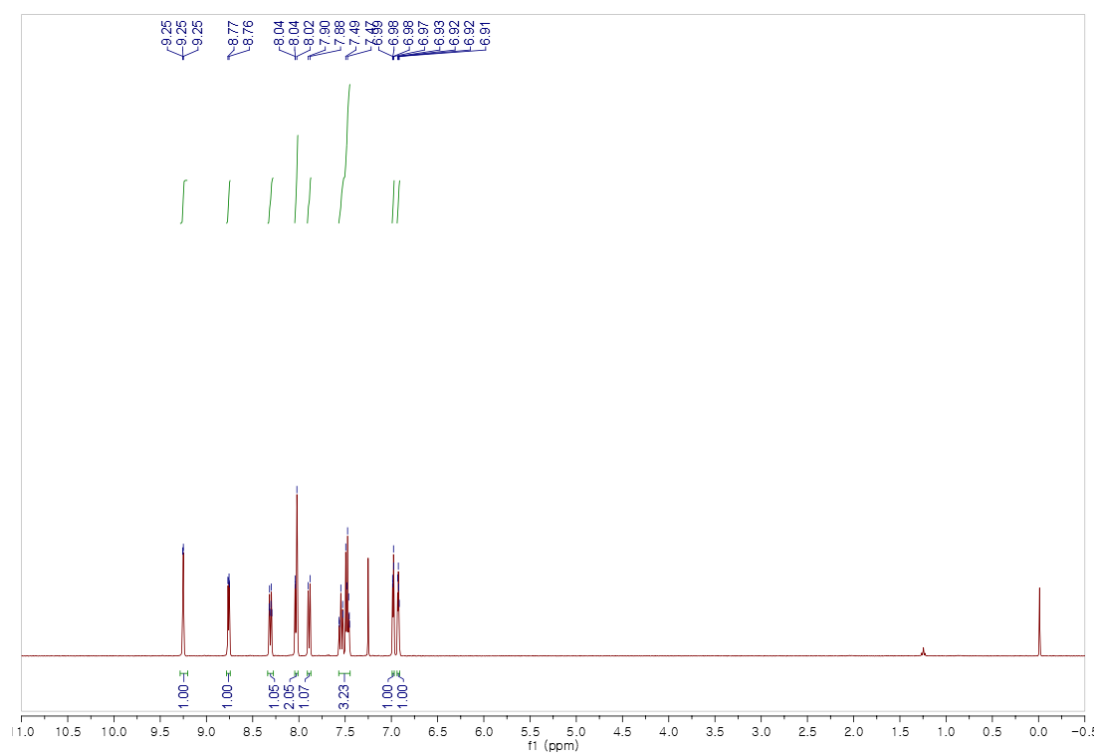


**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectrum of compound 40**

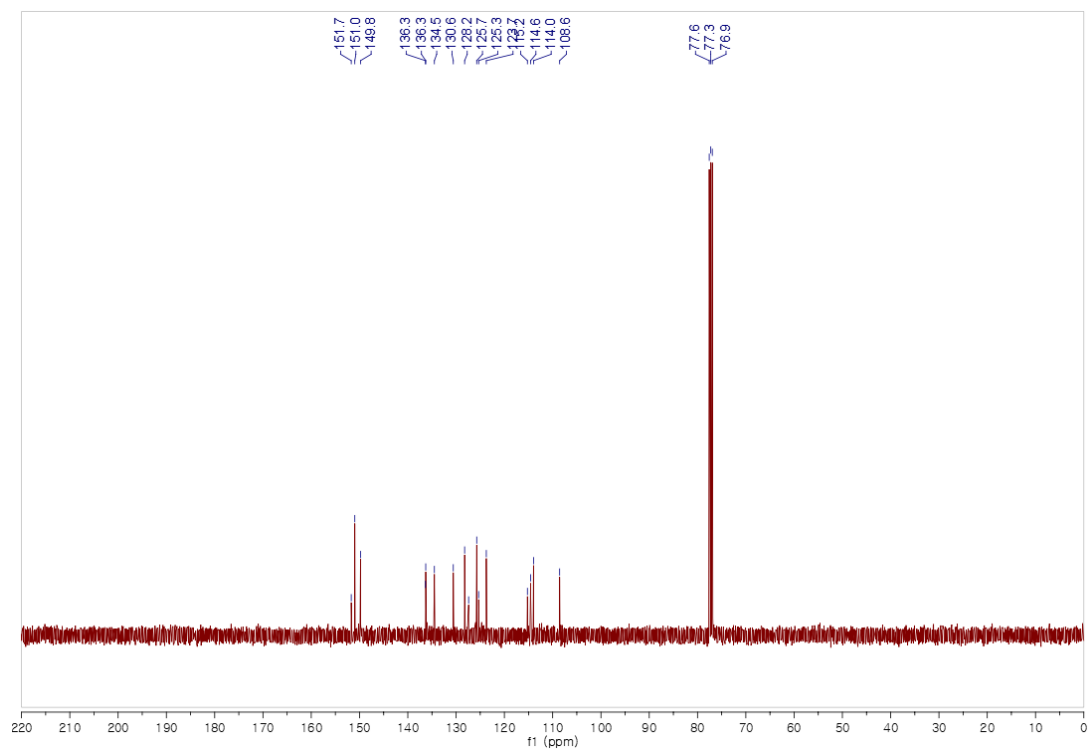




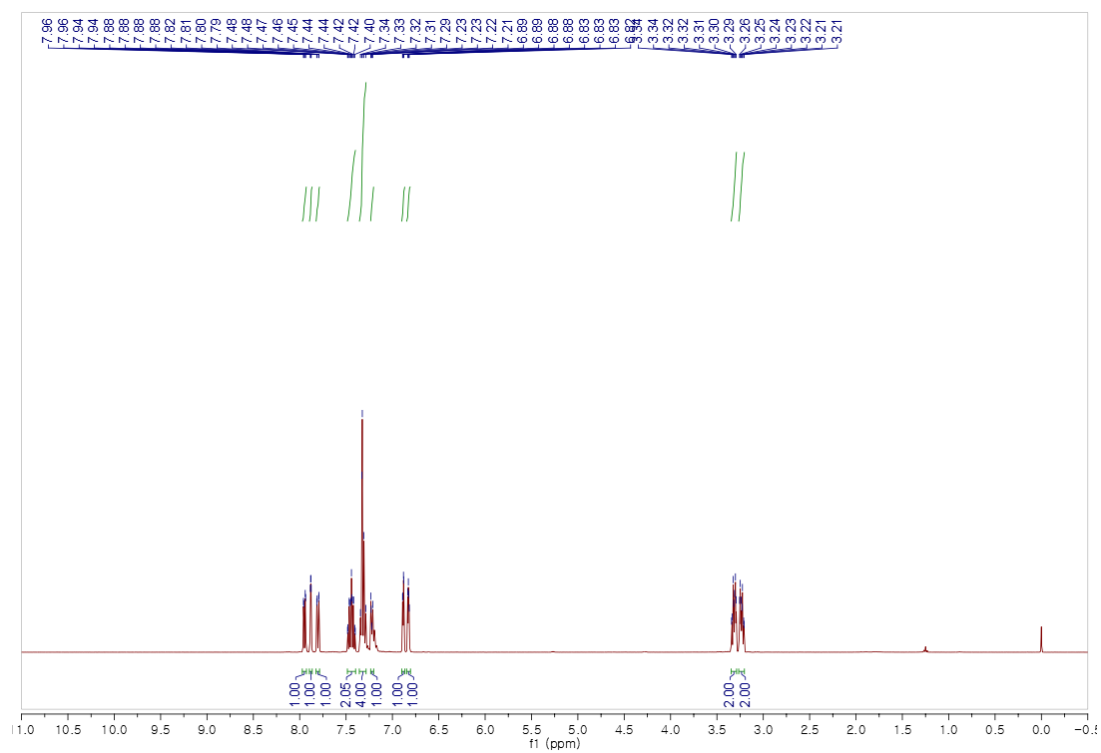
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound 41**



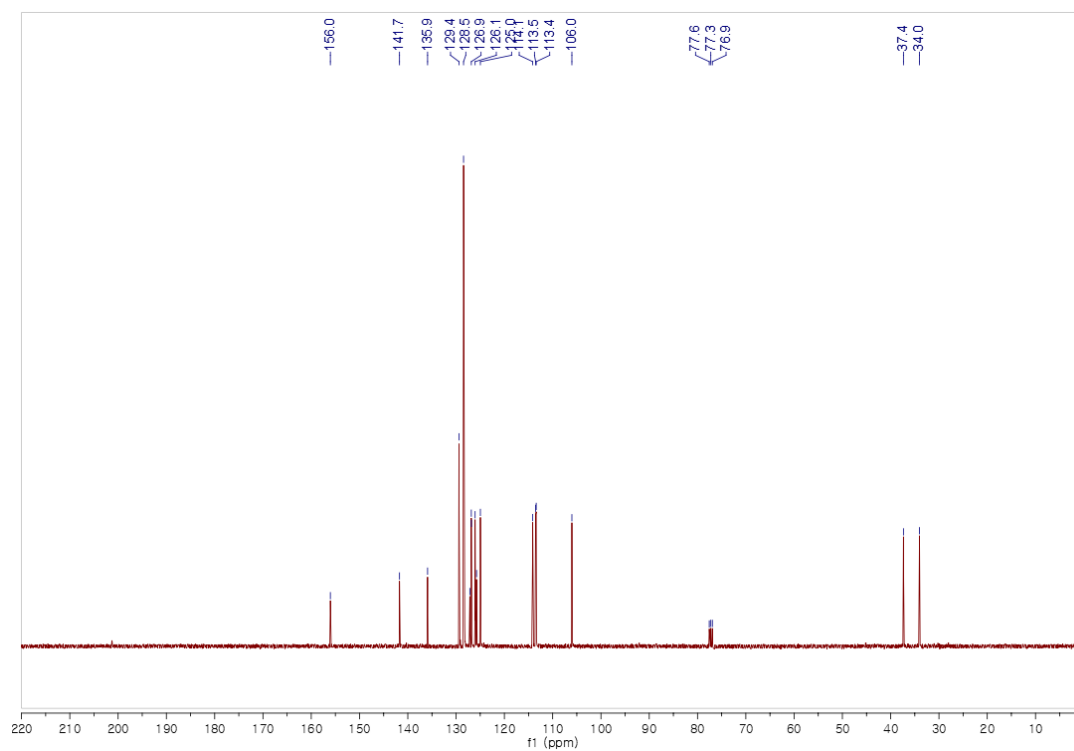
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectrum of compound 41**



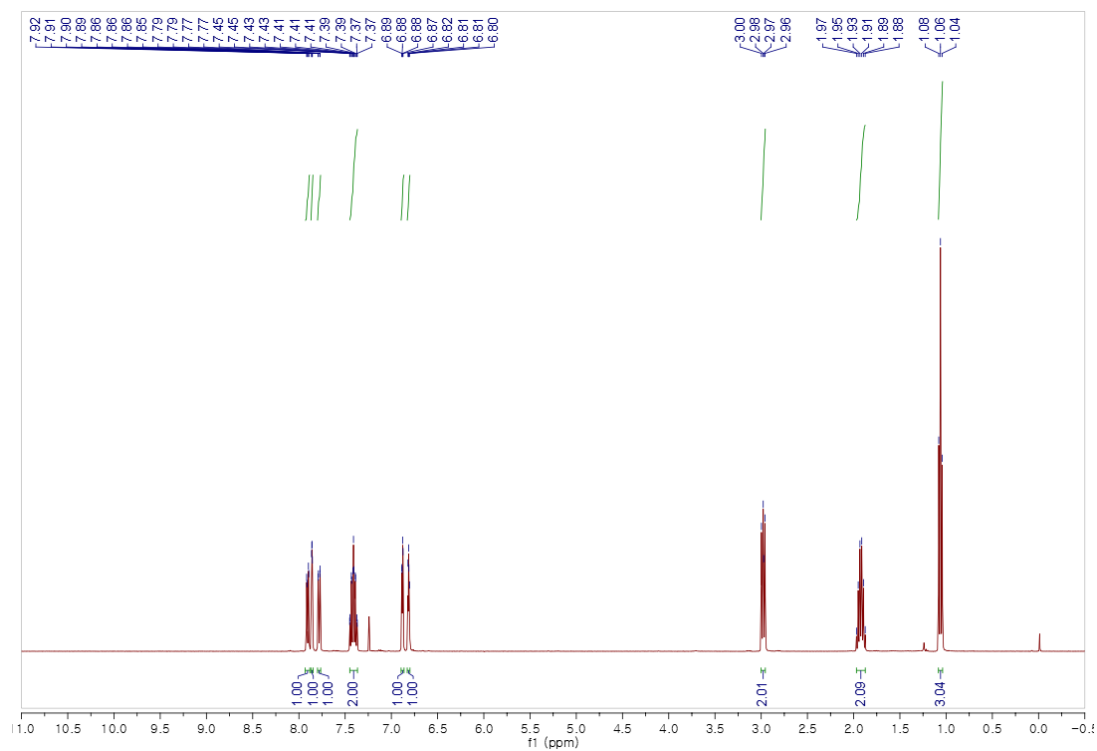
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound 42**



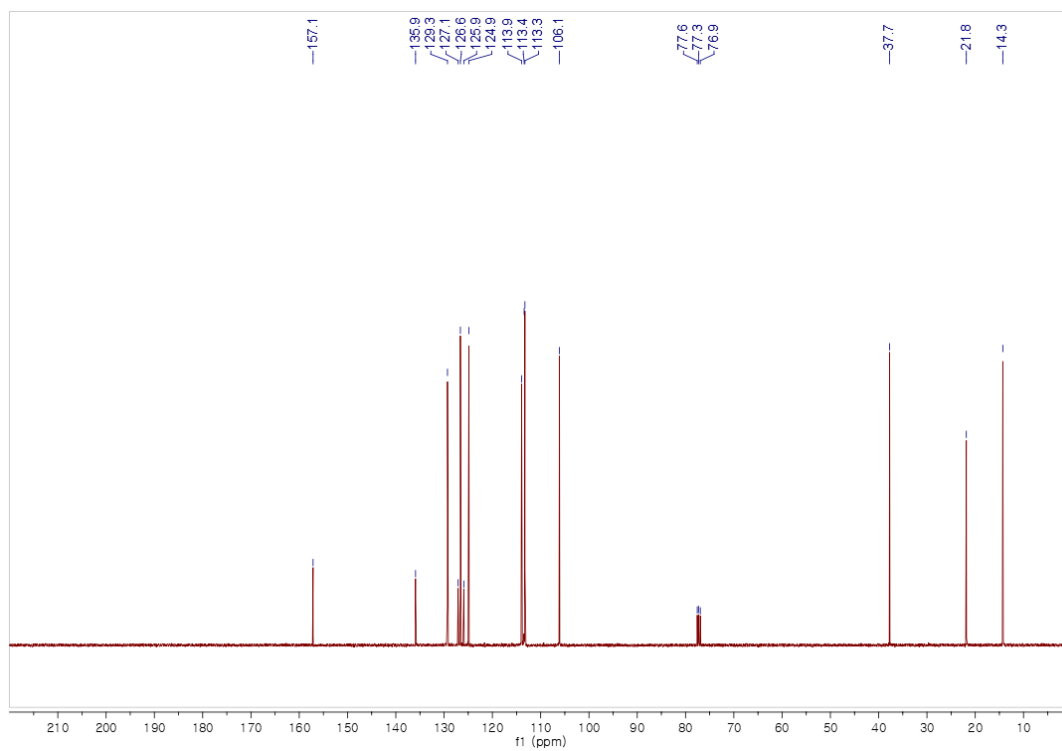
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectrum of compound 42**



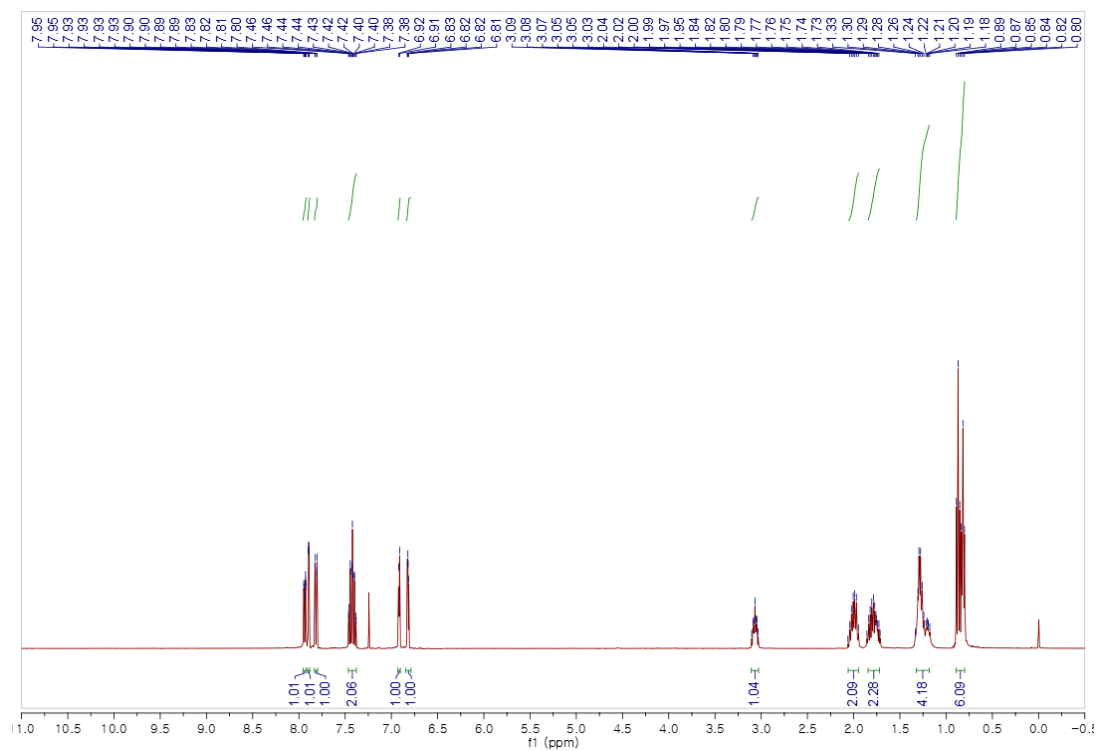
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound 43**



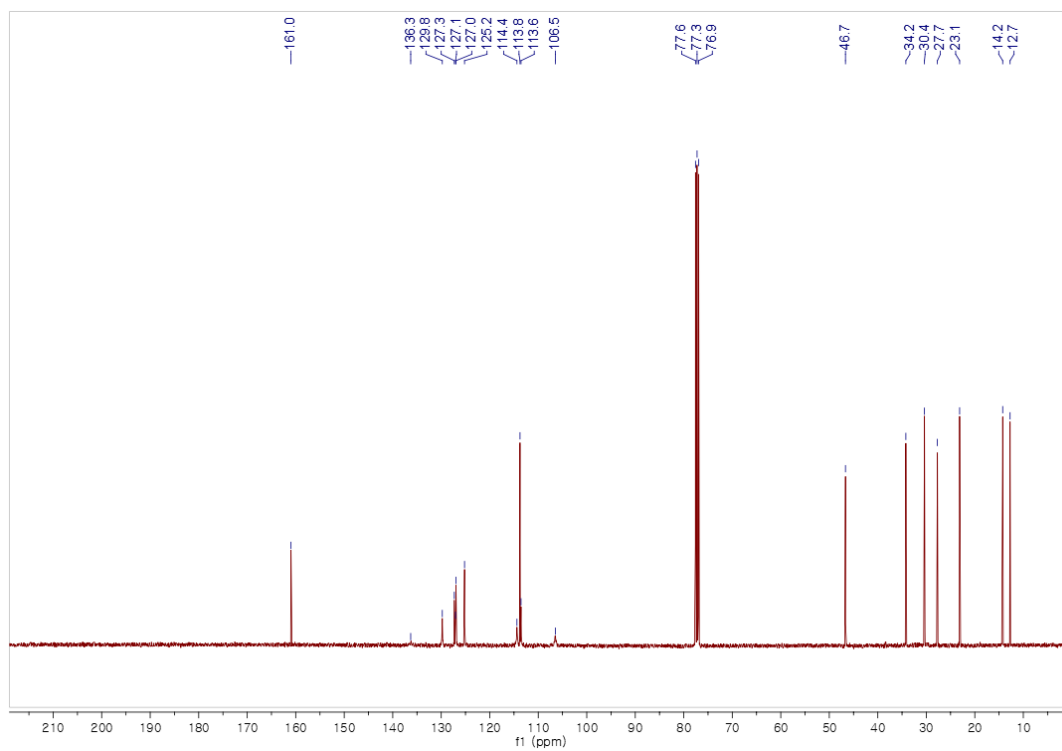
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectrum of compound 43**



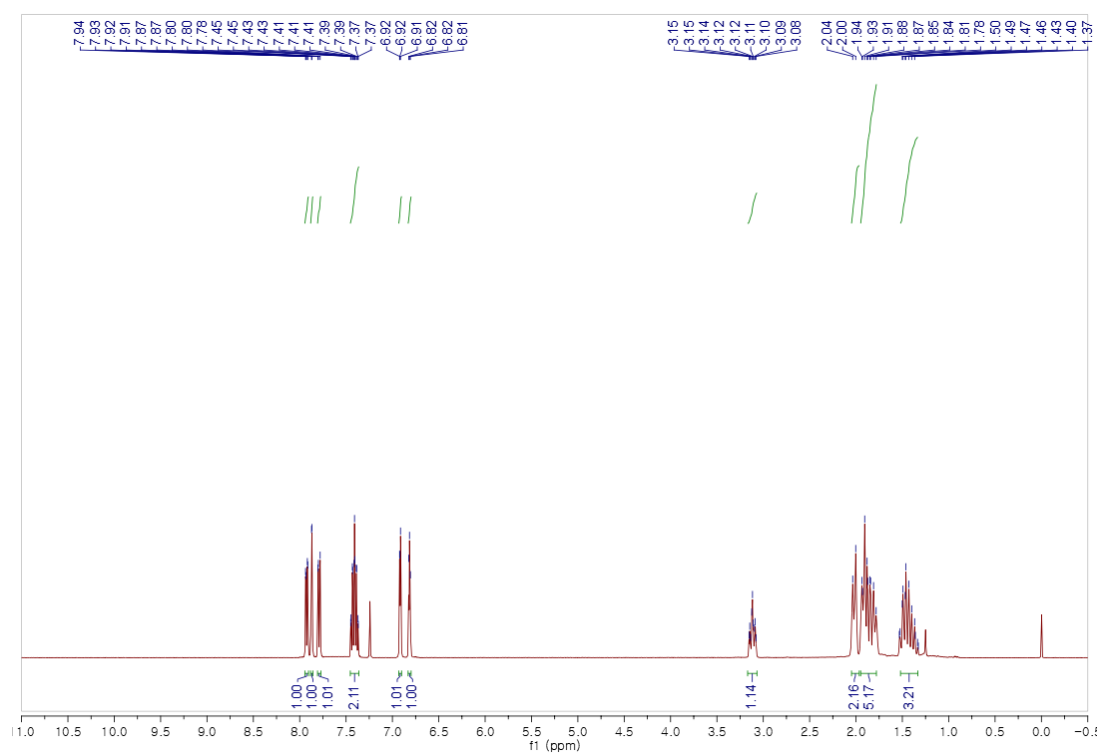
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound 44**



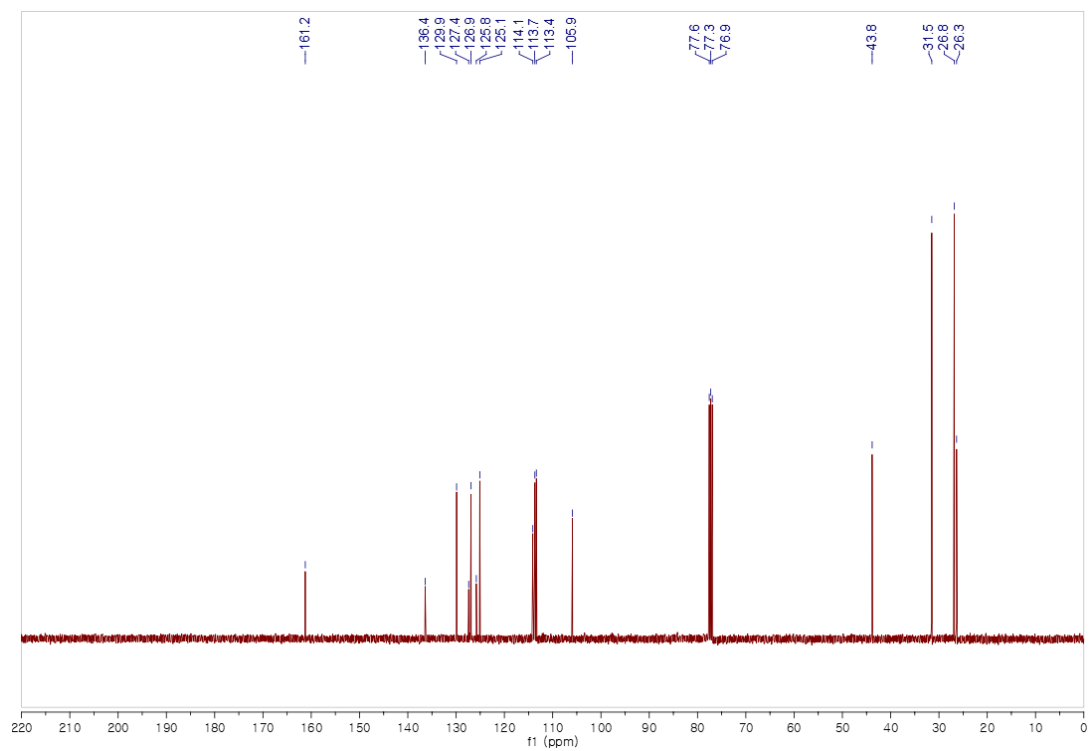
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectrum of compound 44**



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound 45**

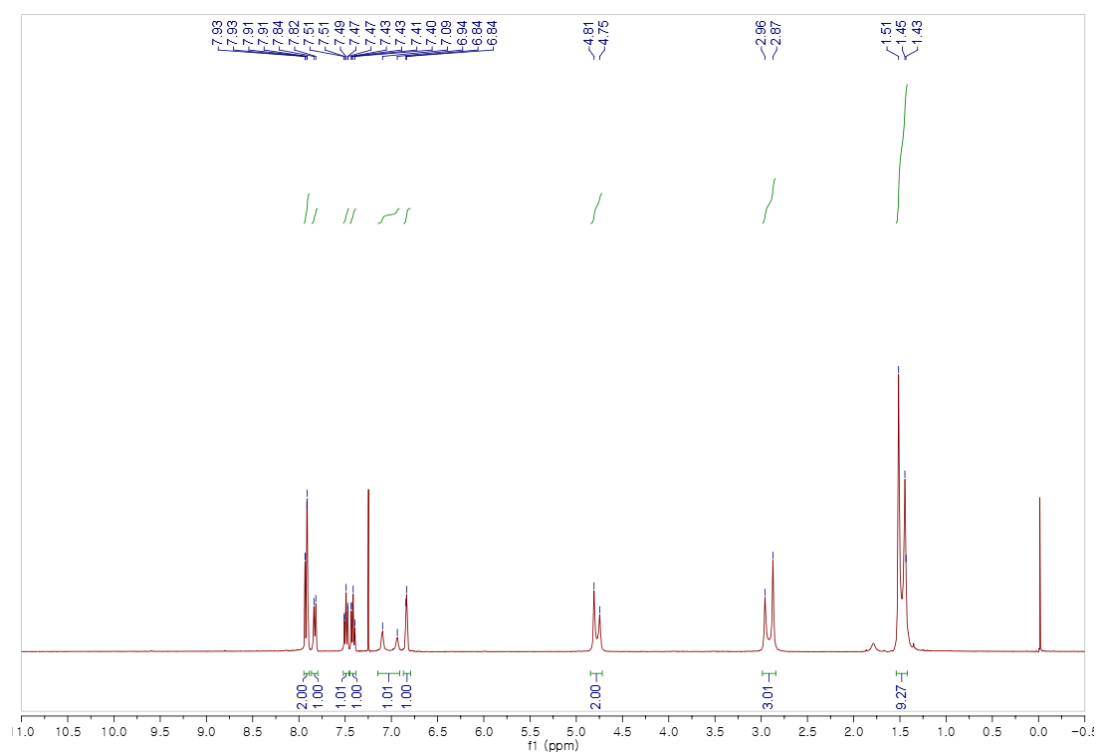


**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectrum of compound 45**

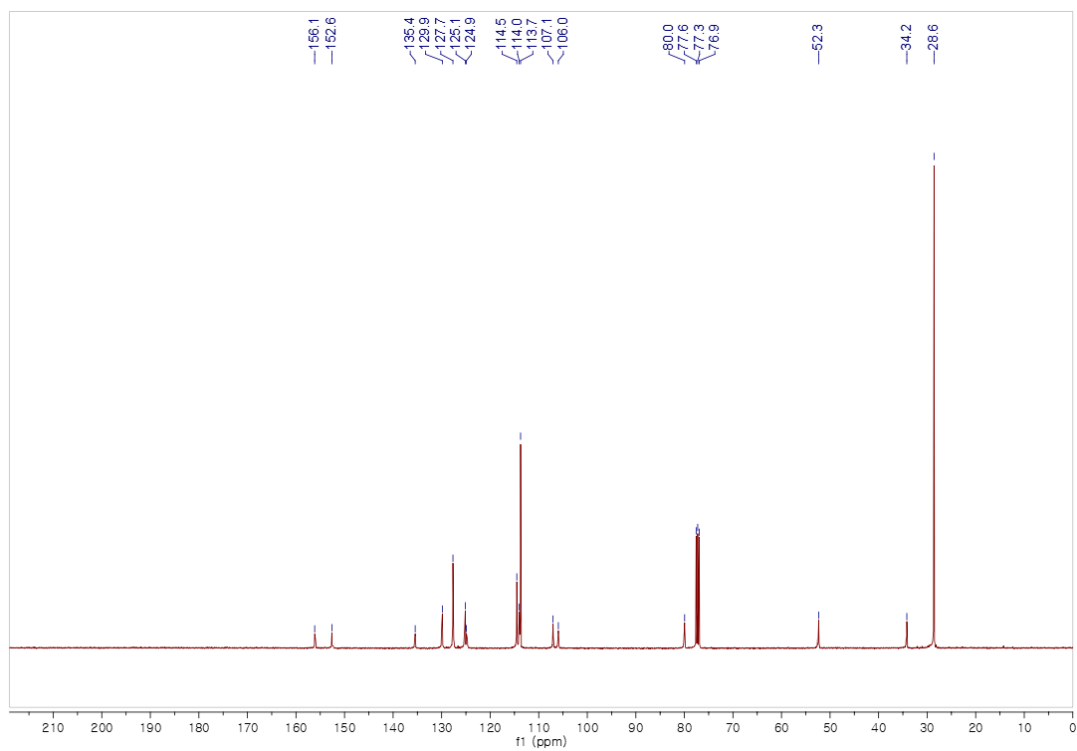




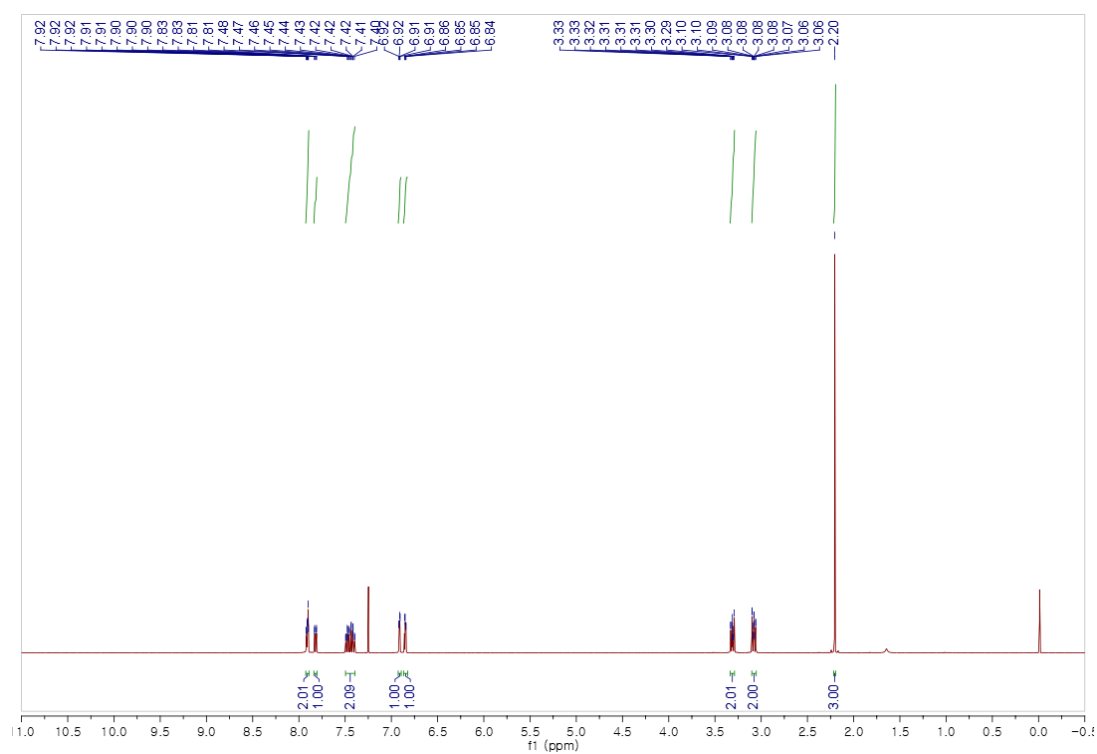
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound 47**



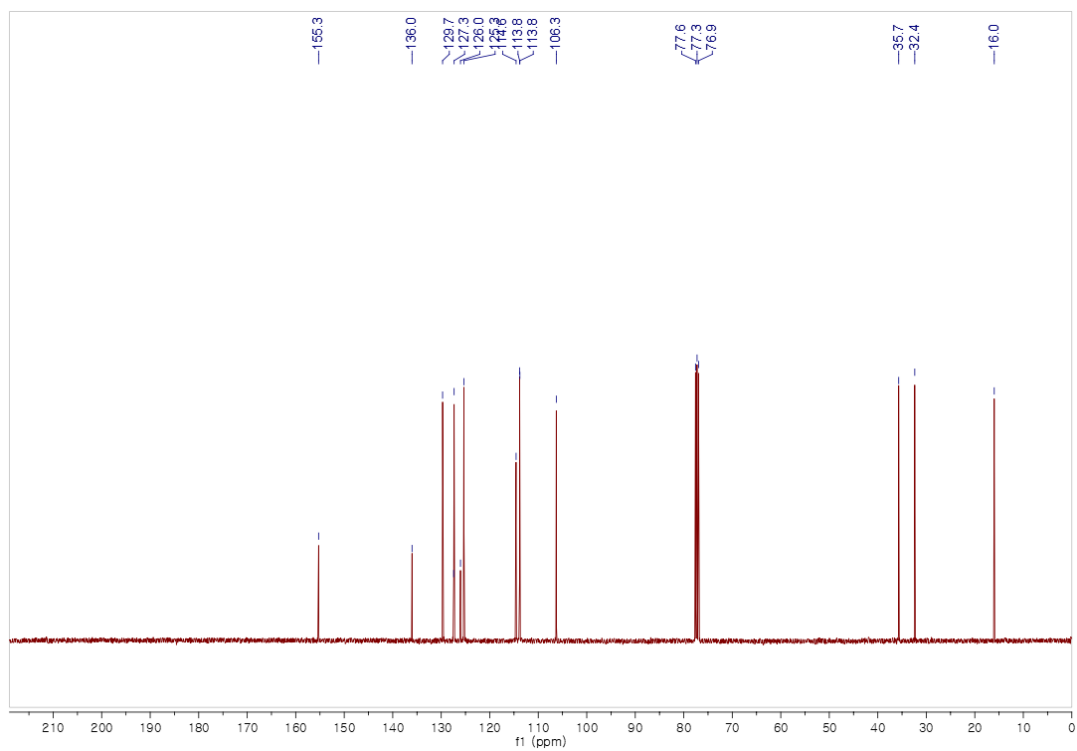
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectrum of compound 47**



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound 48**

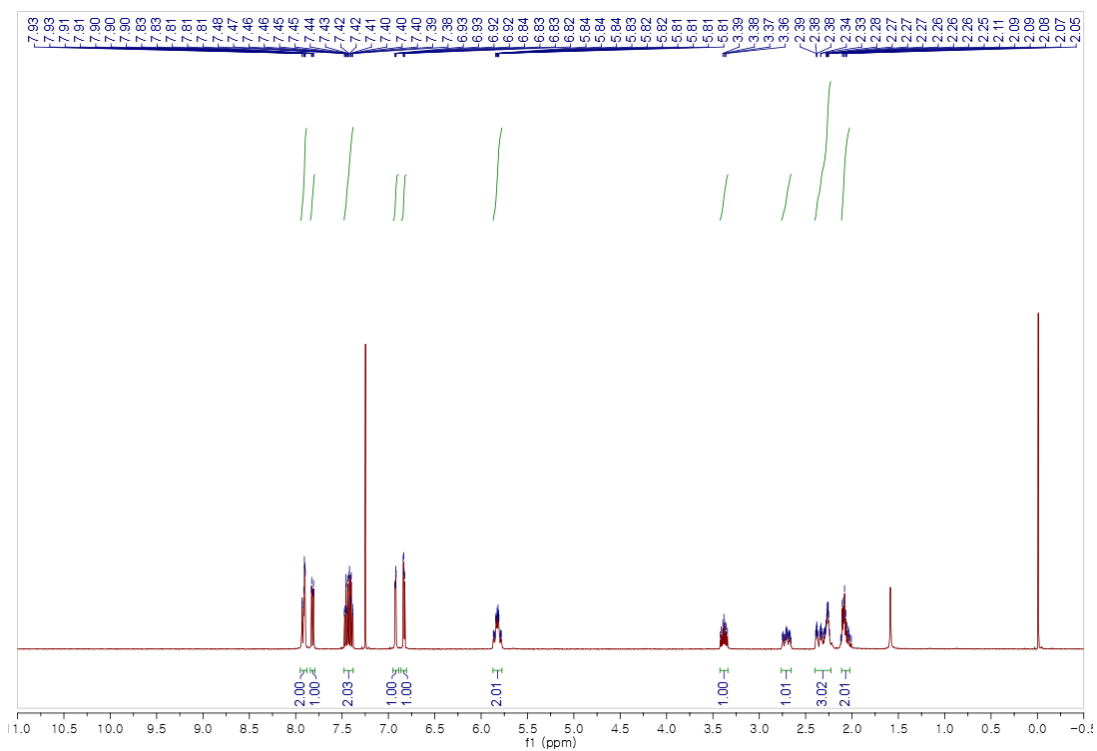


**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectrum of compound 48**

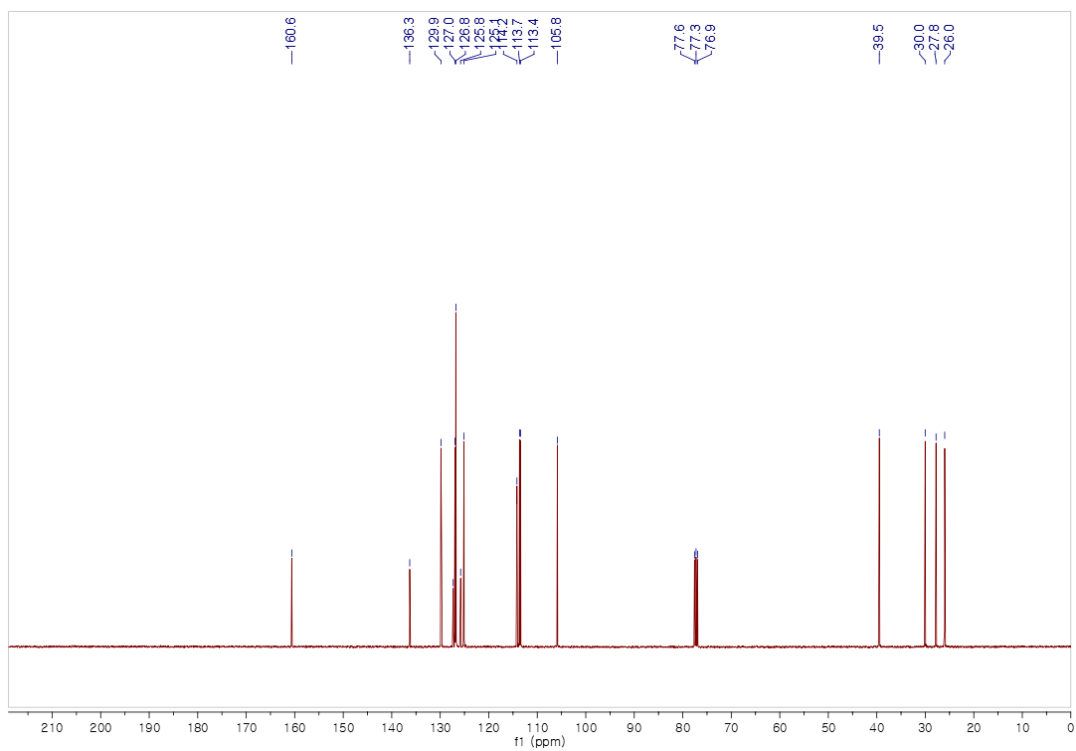




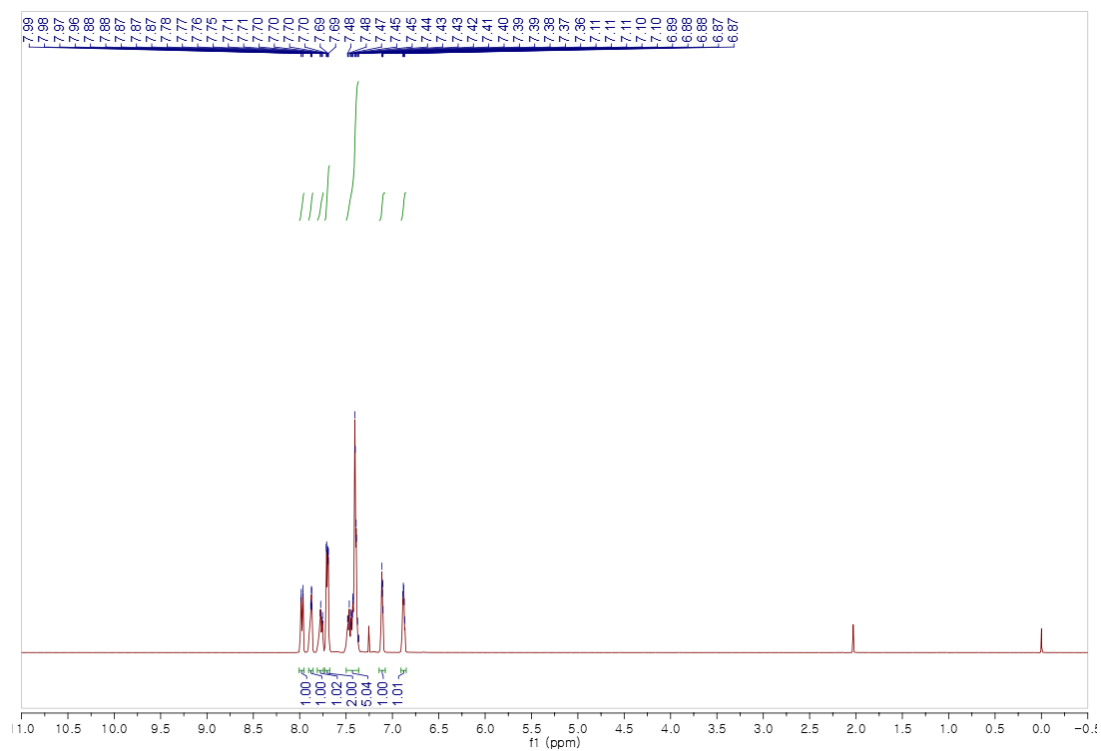
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound 49**



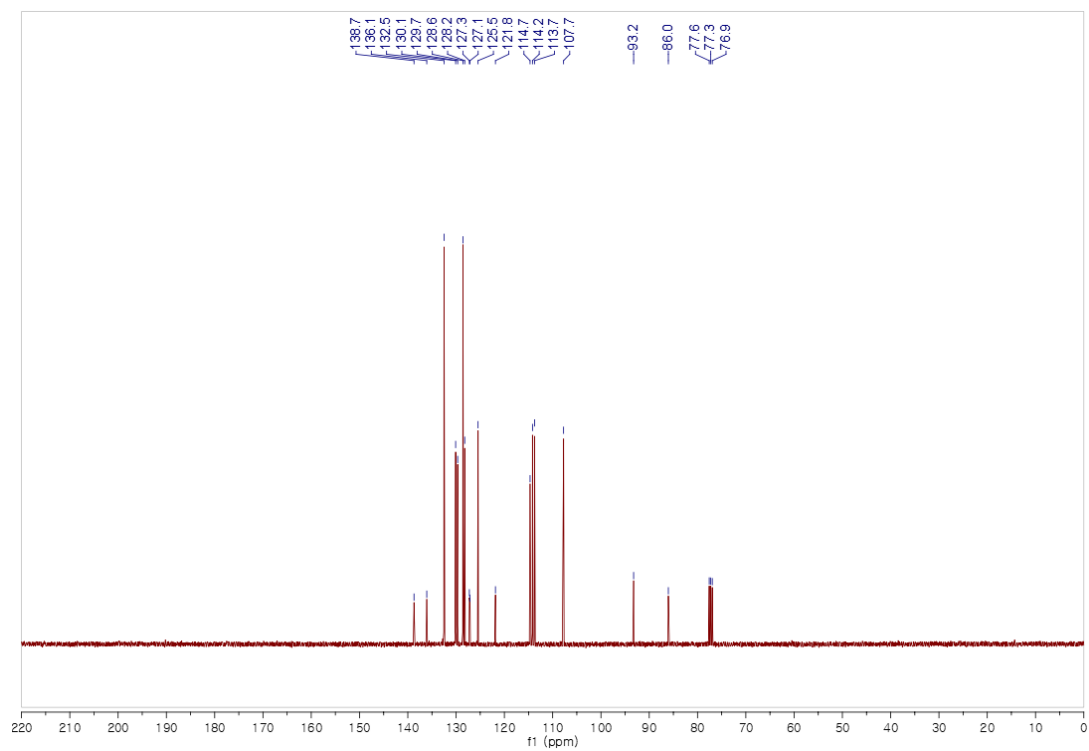
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectrum of compound 49**



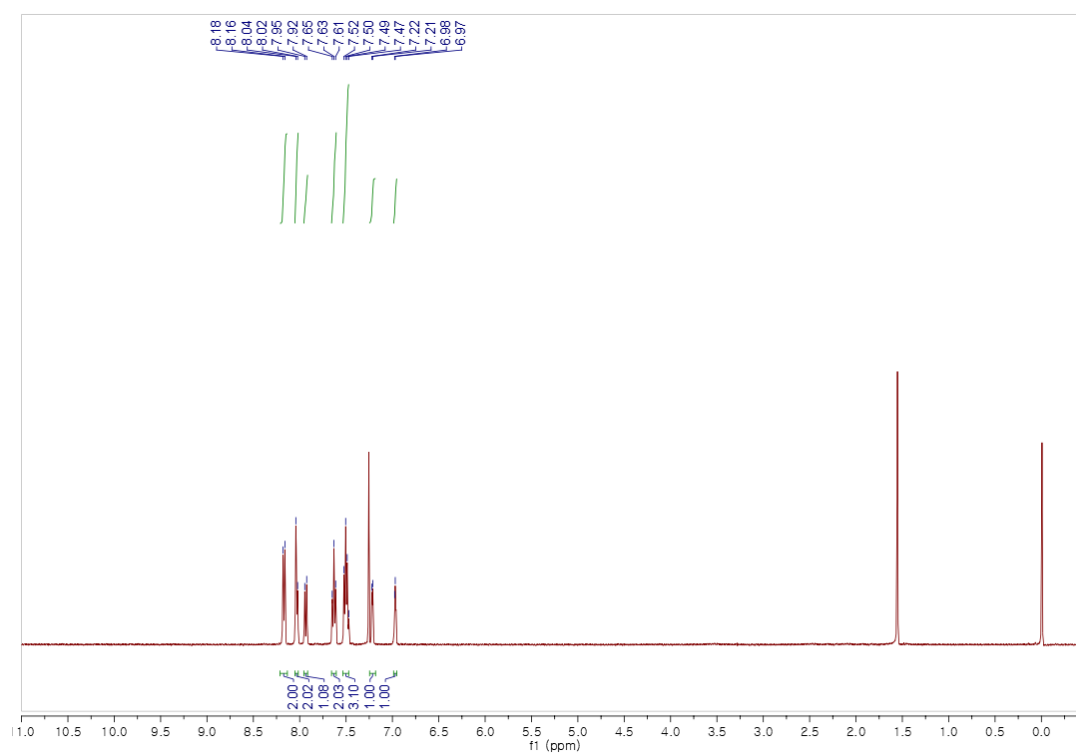
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound 50**



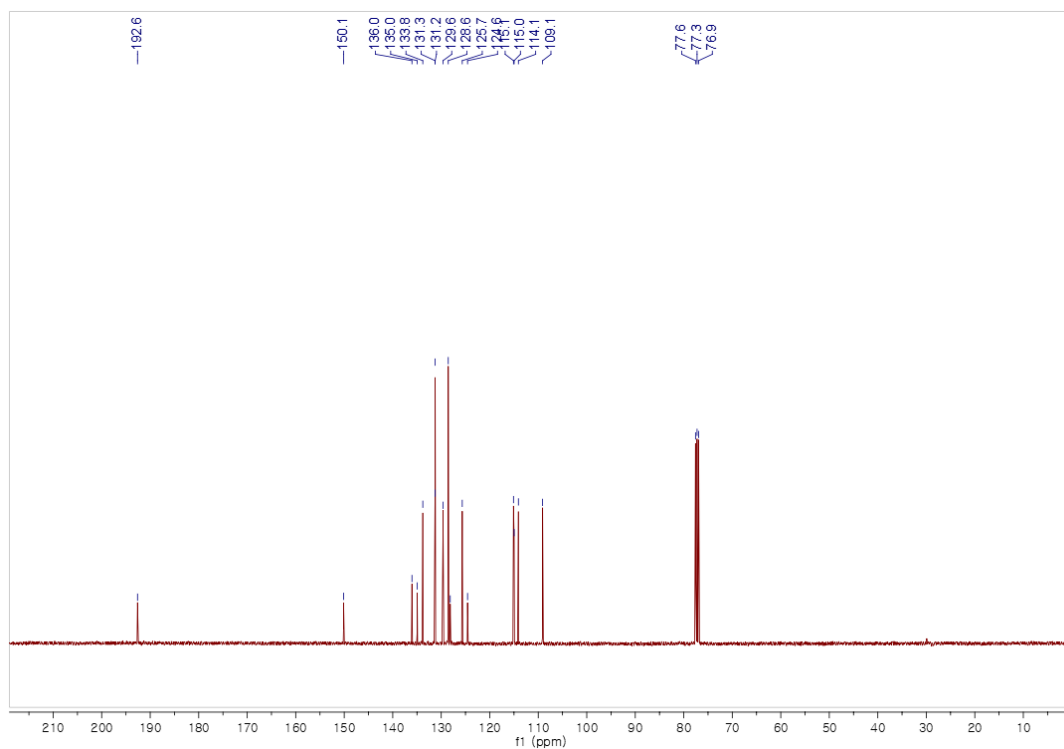
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectrum of compound 50**



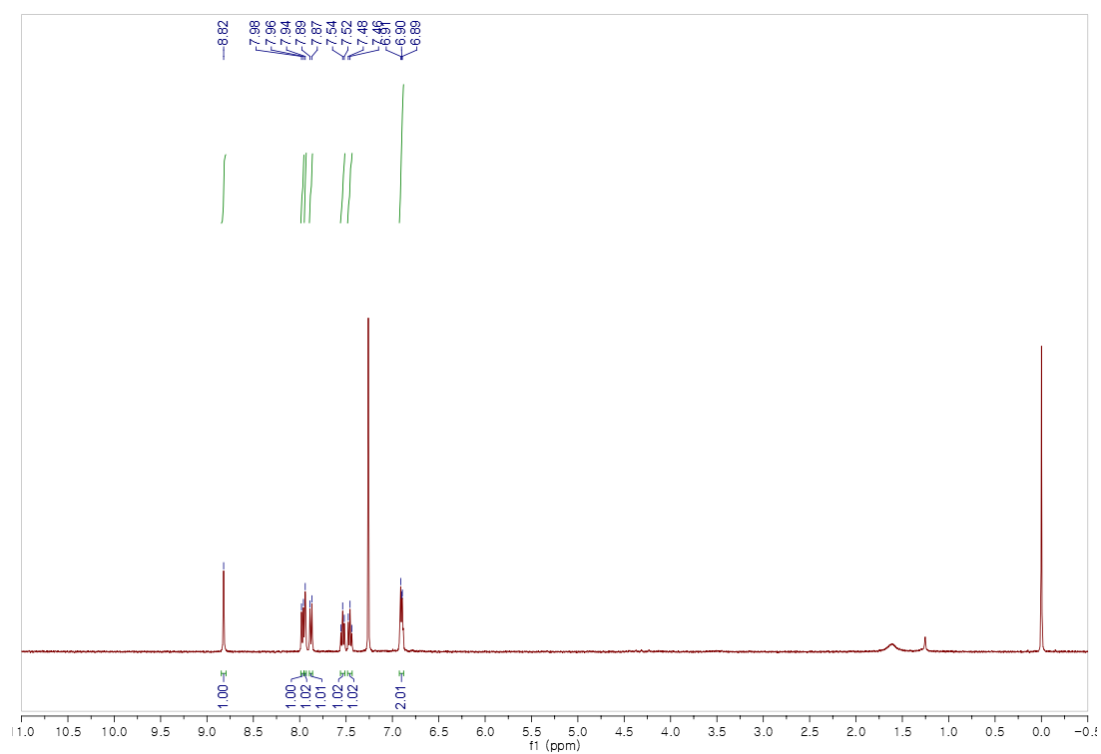
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound 51**



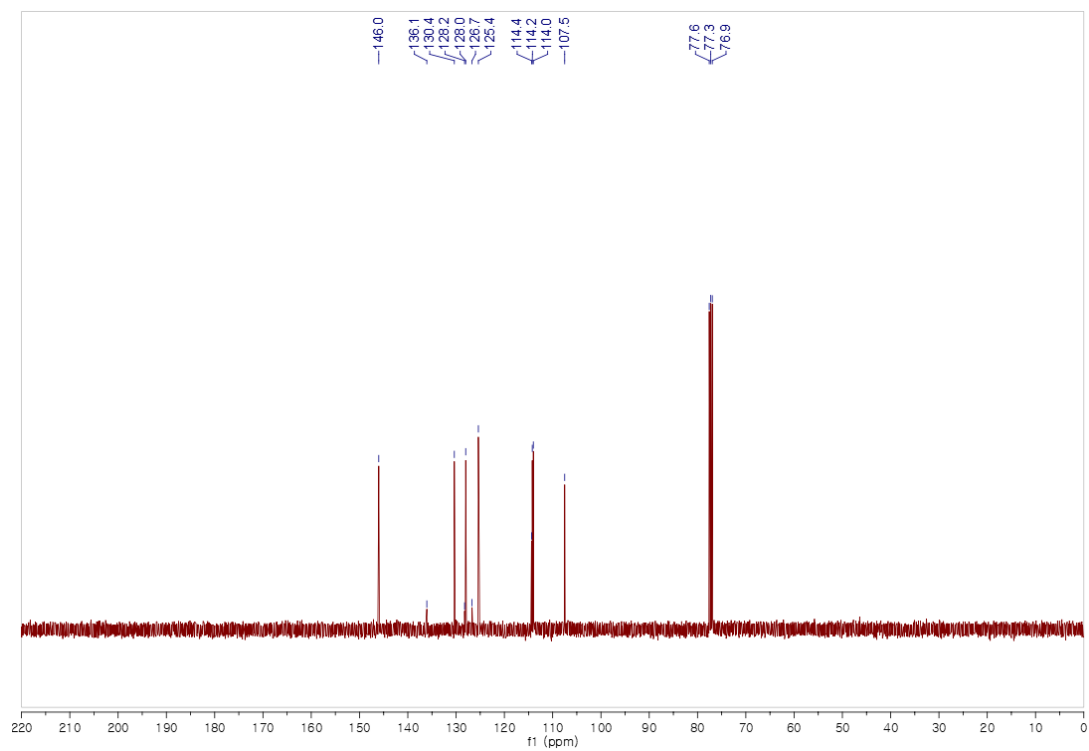
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectrum of compound 51**



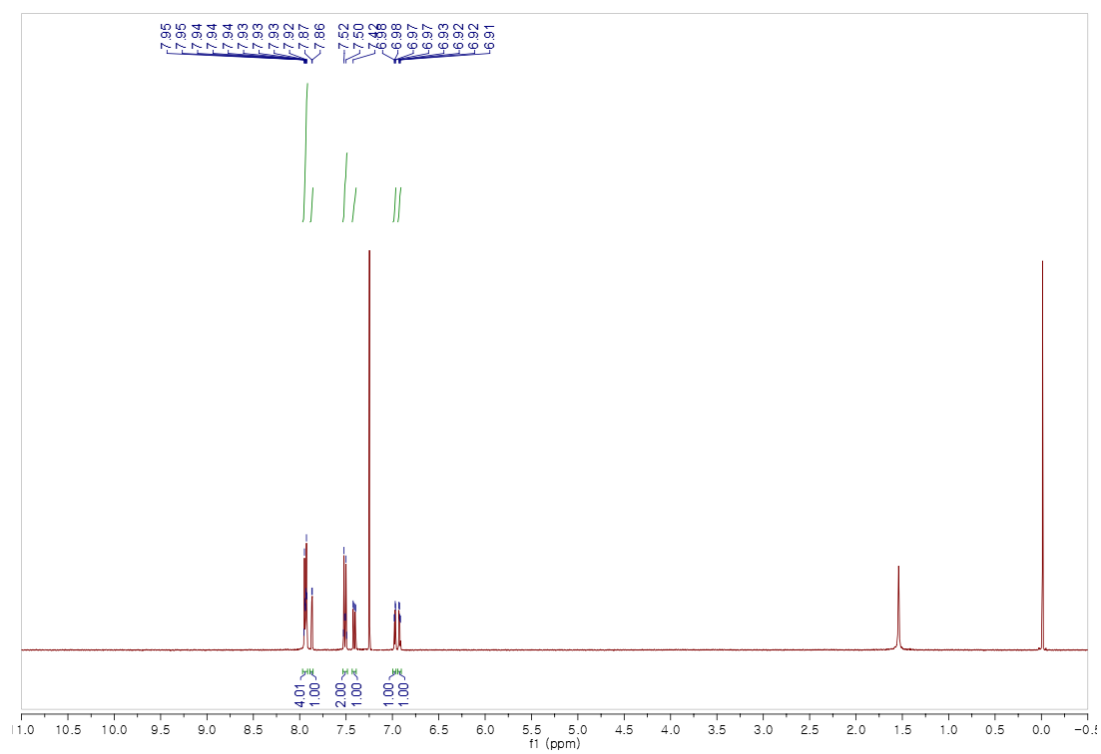
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound 52**



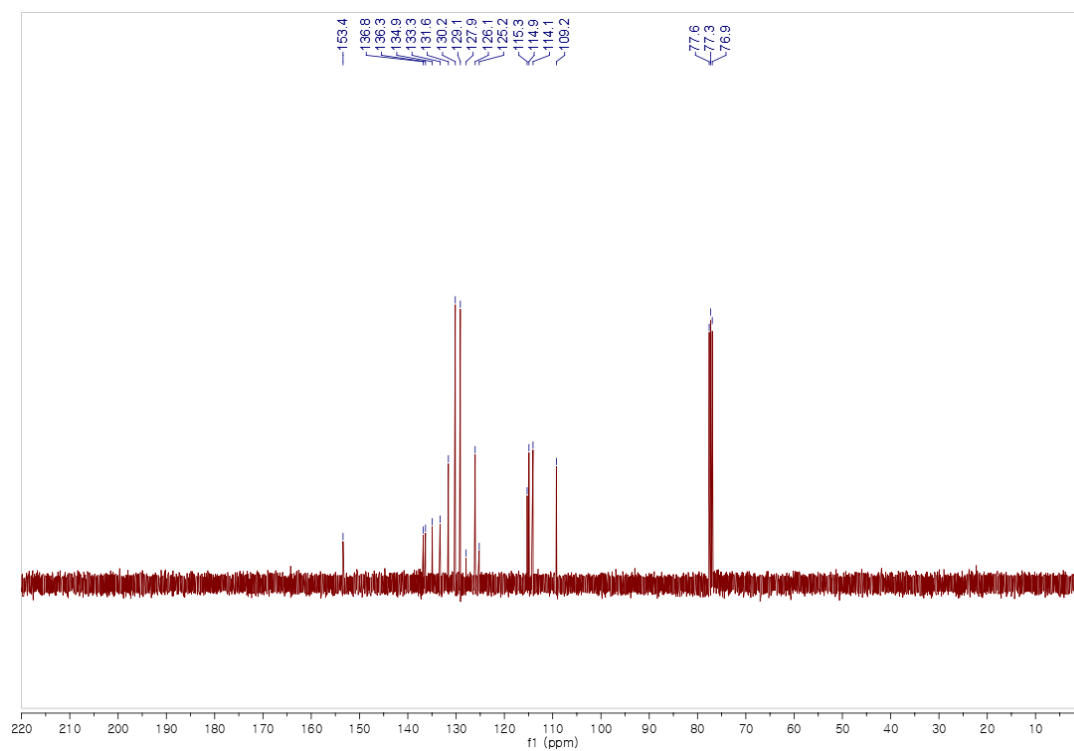
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectrum of compound 52**



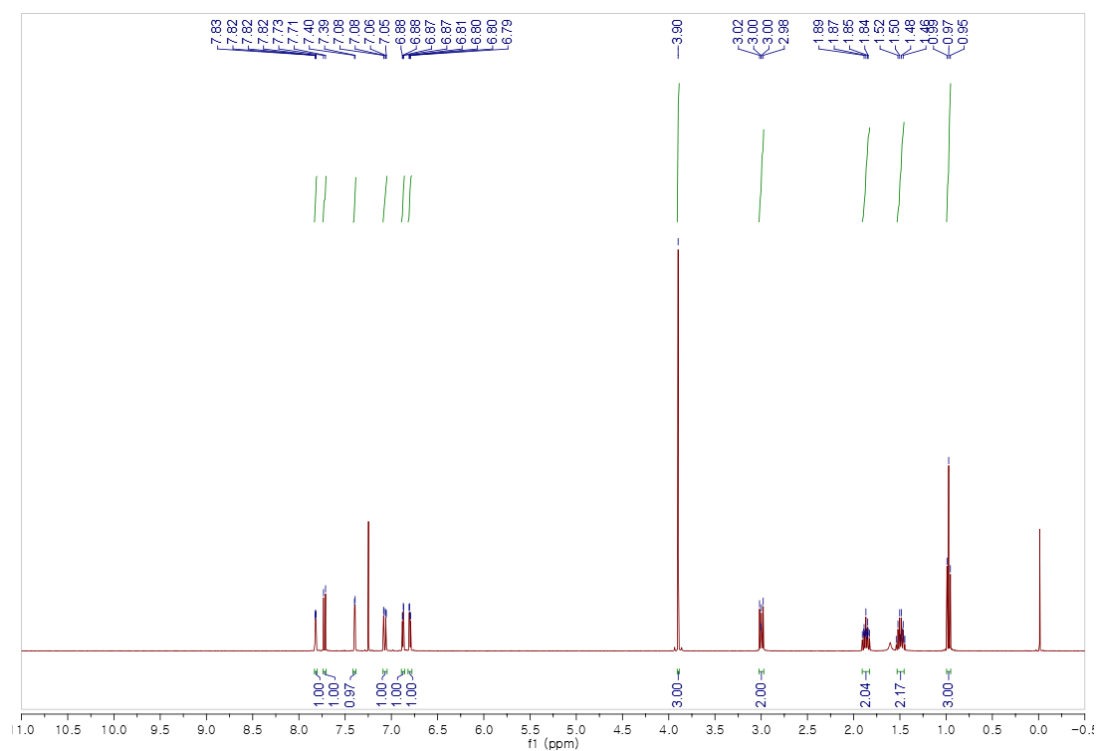
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound 2**



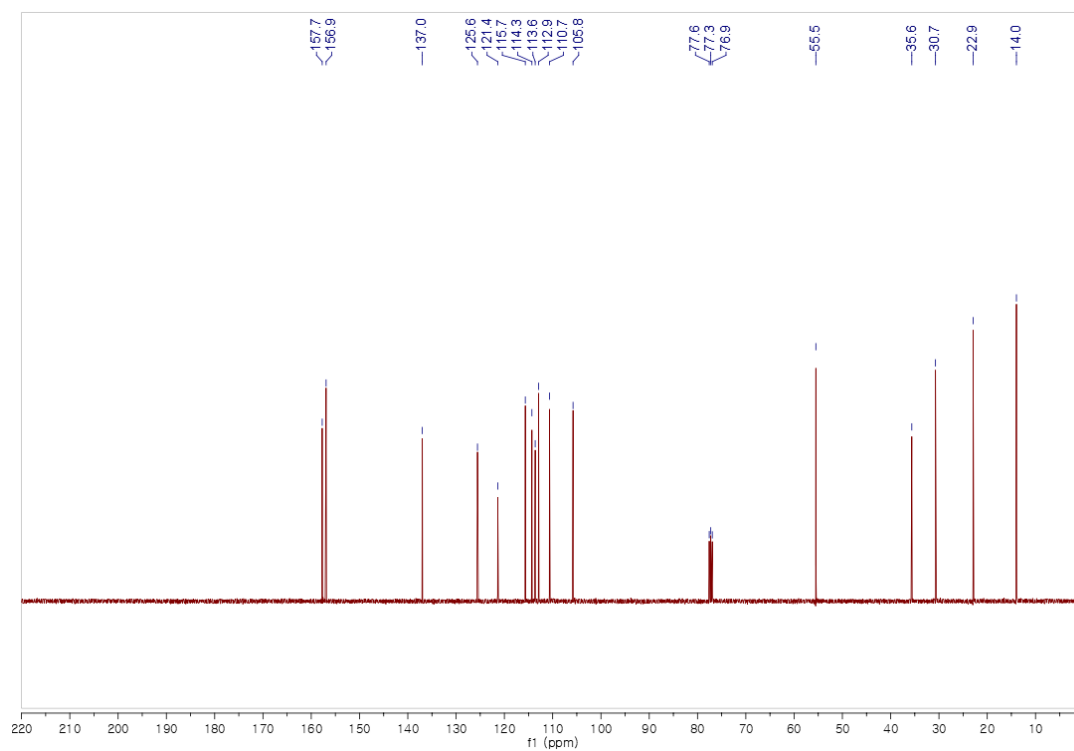
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectrum of compound 2**



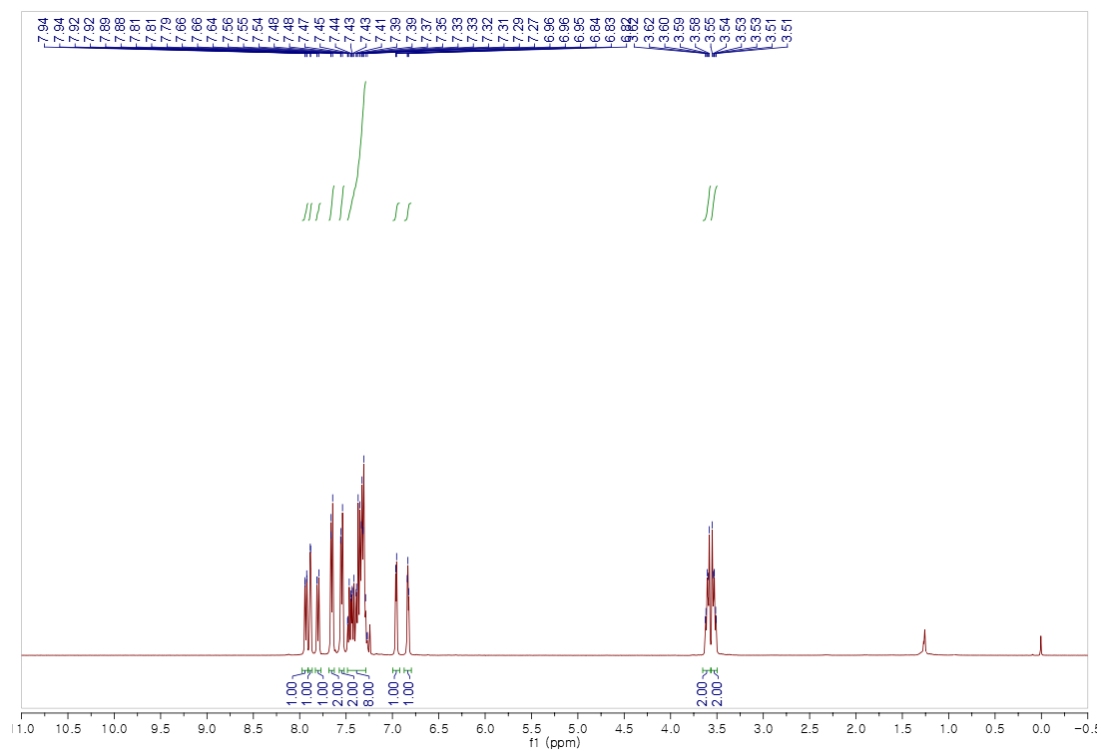
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound 5**



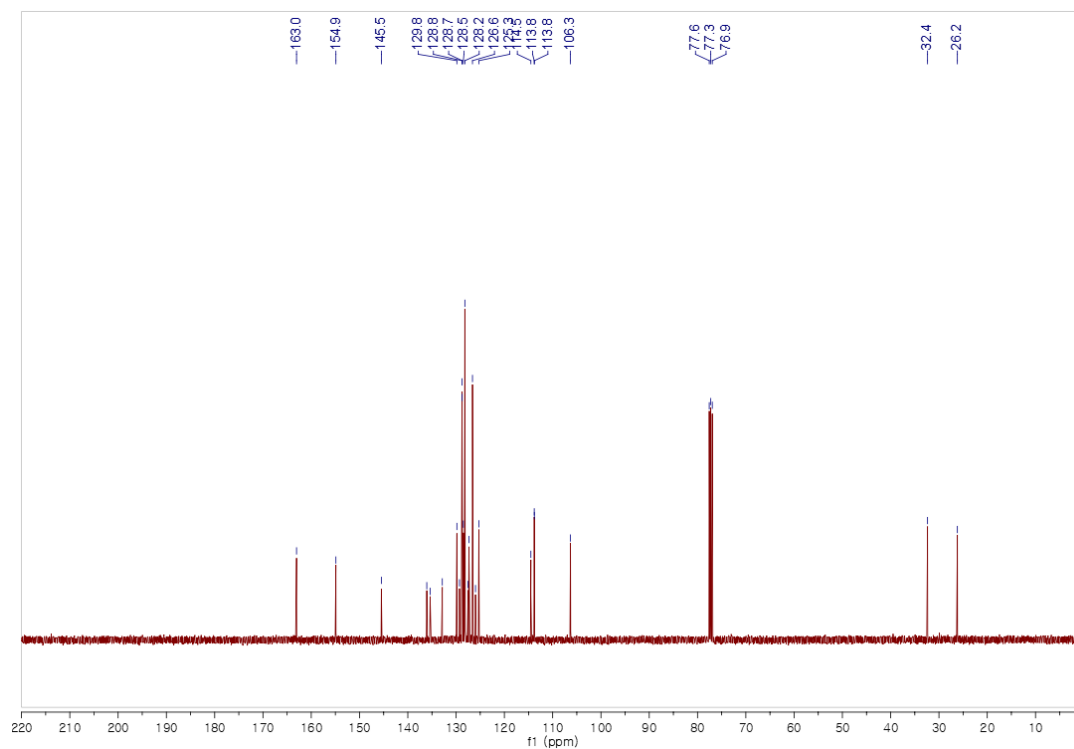
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectrum of compound 5**



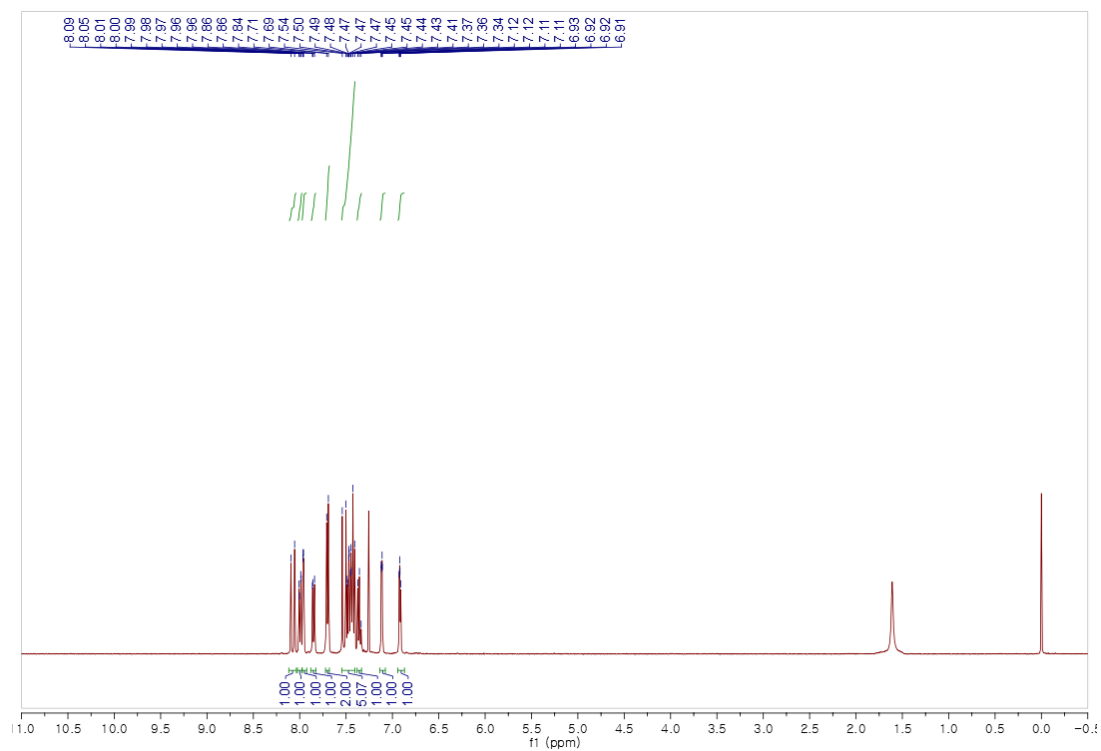
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of compound 53**



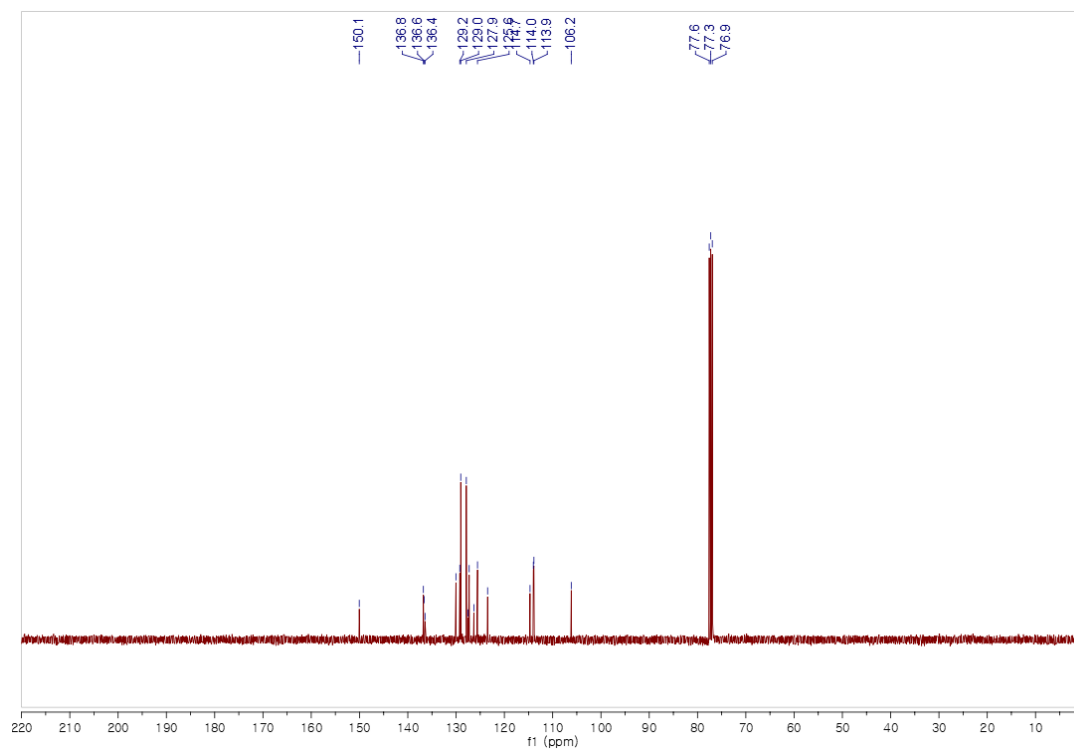
**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) spectrum of compound 53**



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound 54**

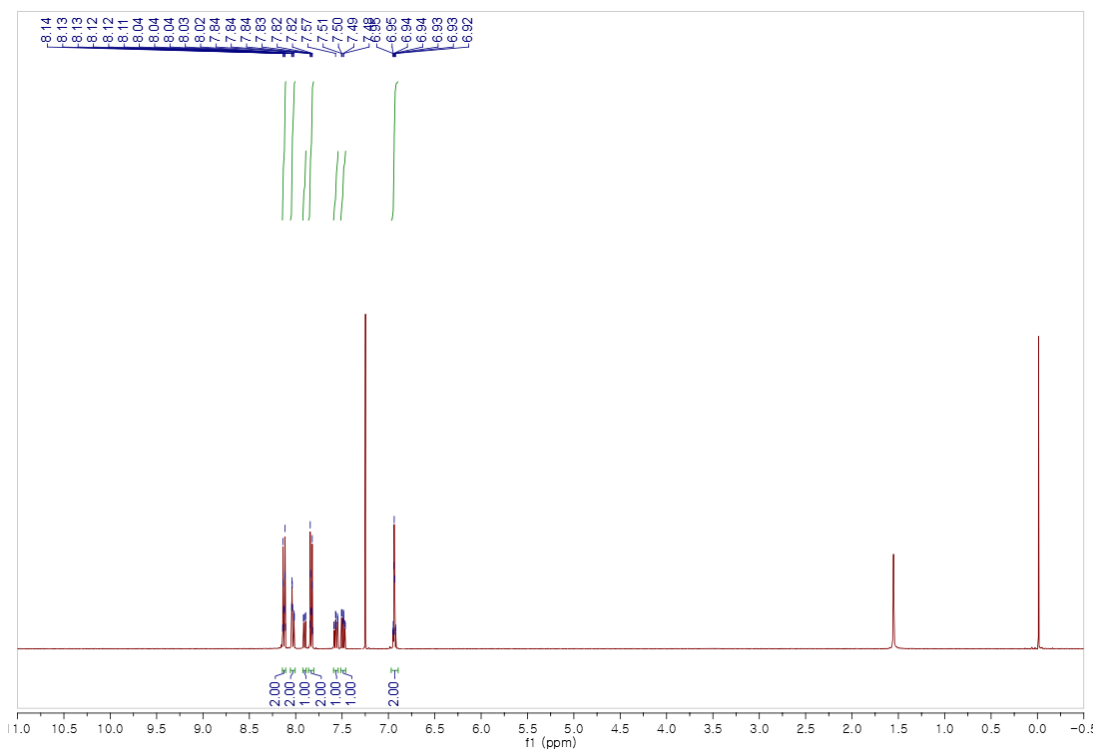


**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectrum of compound 54**

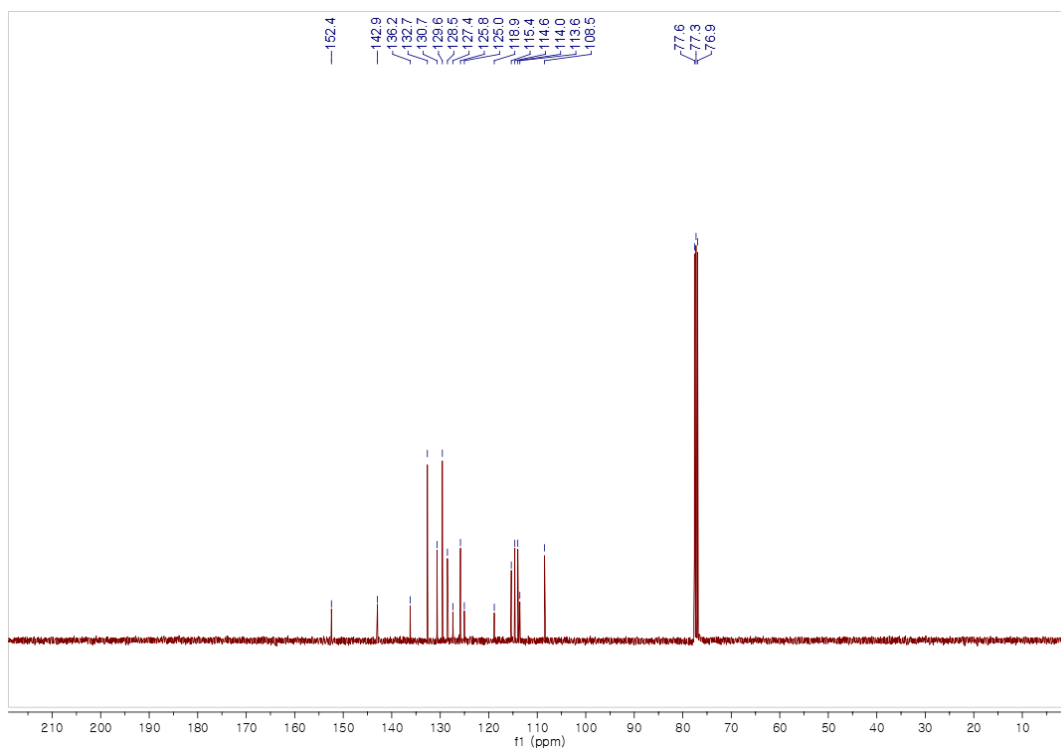




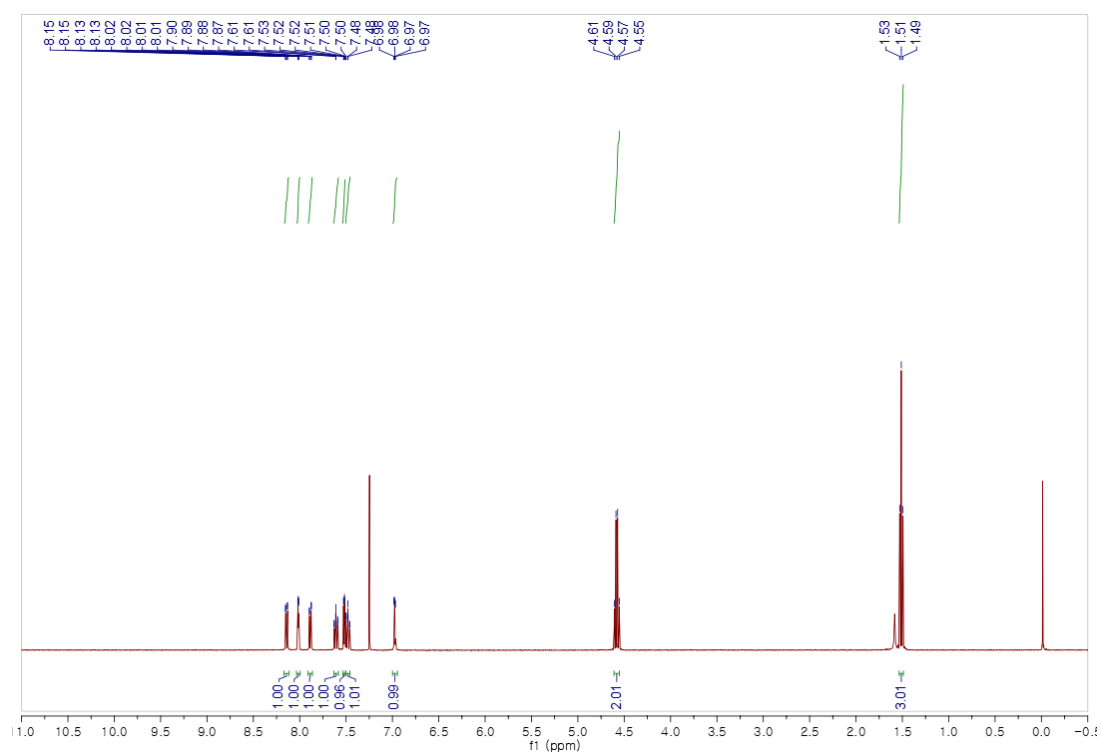
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound 55**



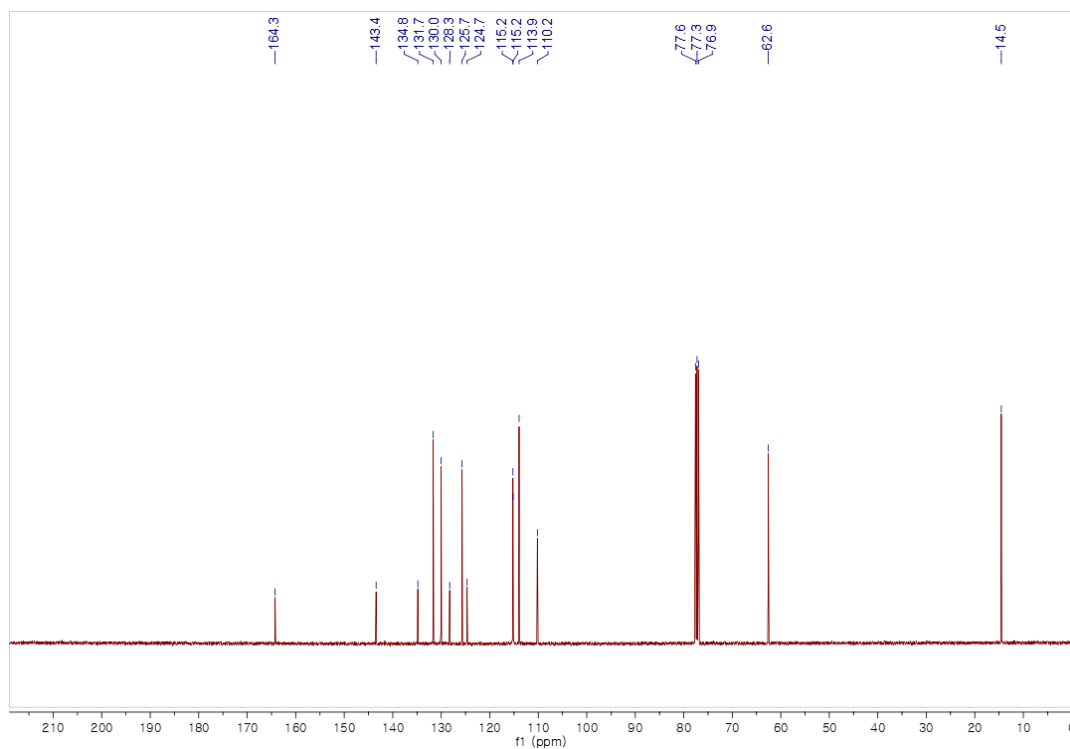
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectrum of compound 55**



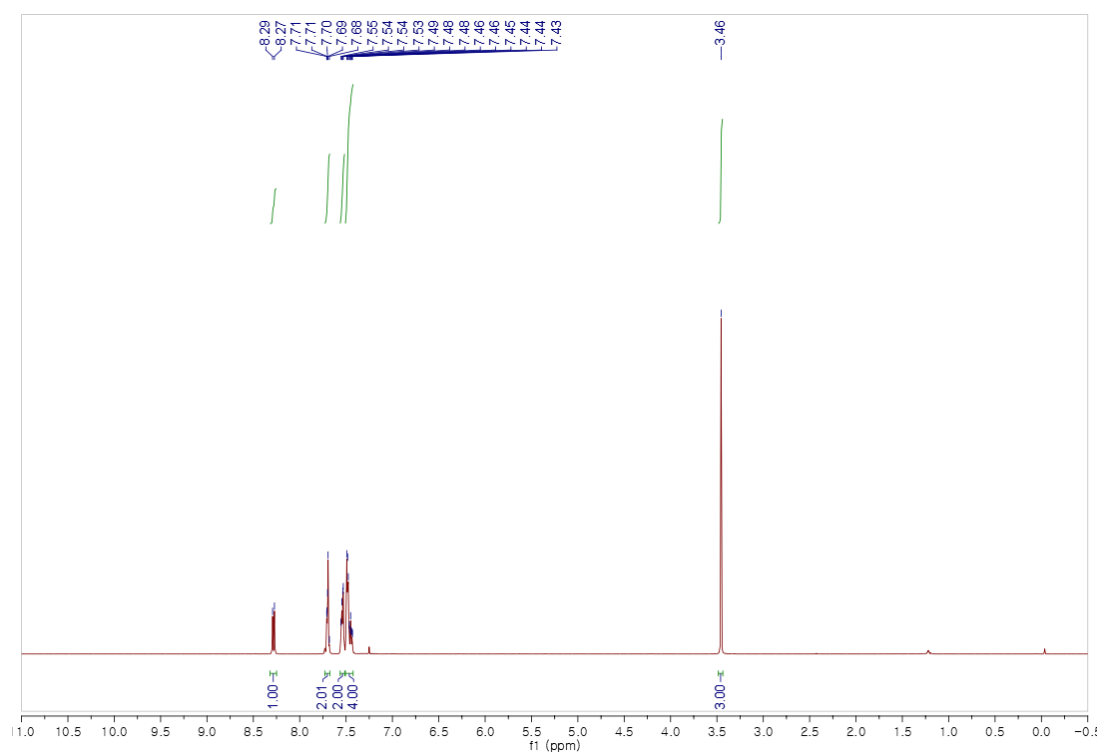
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectrum of compound 56**



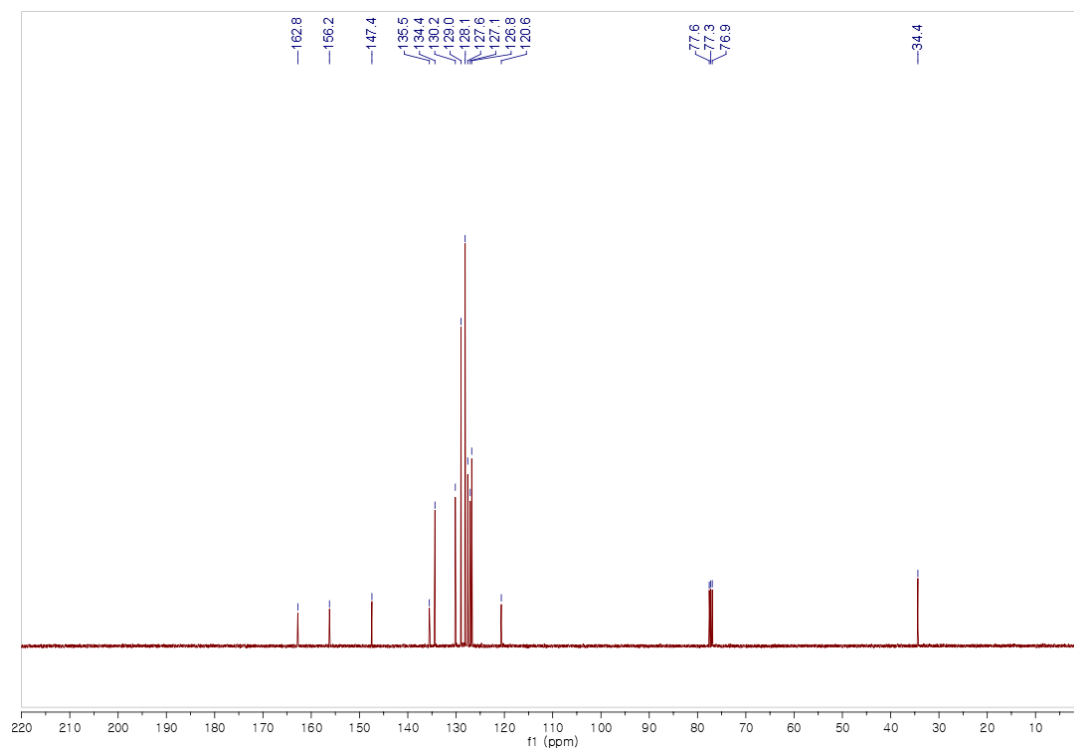
**$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) spectrum of compound 56**



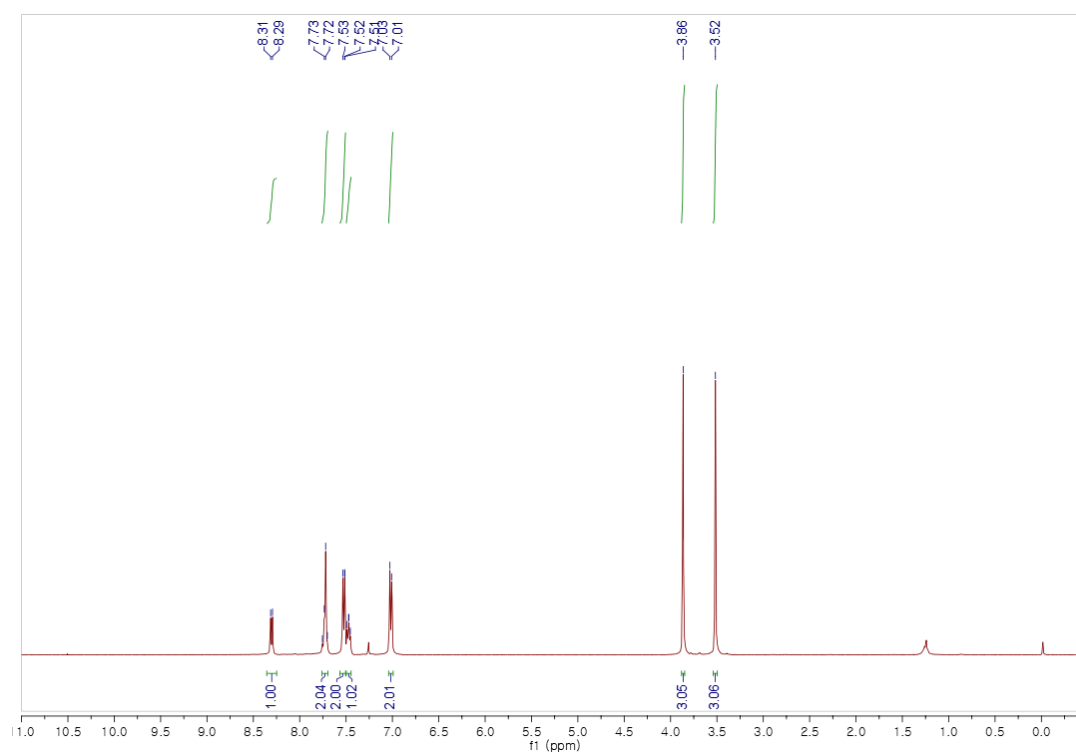
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound 57**



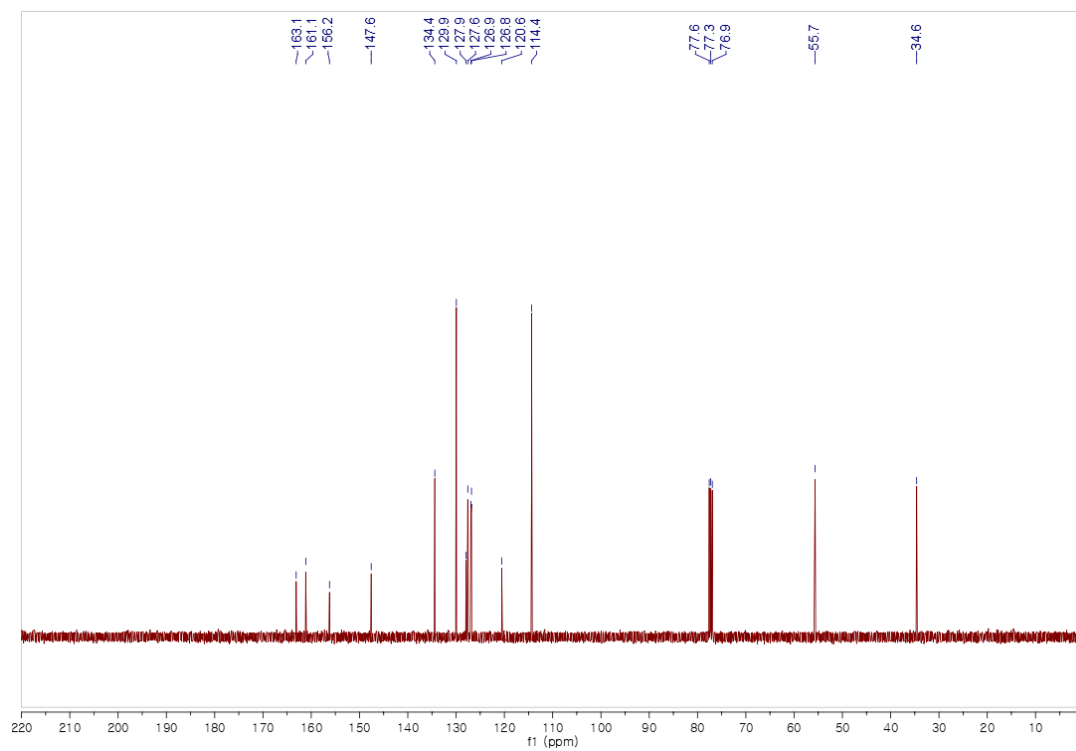
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectrum of compound 57**



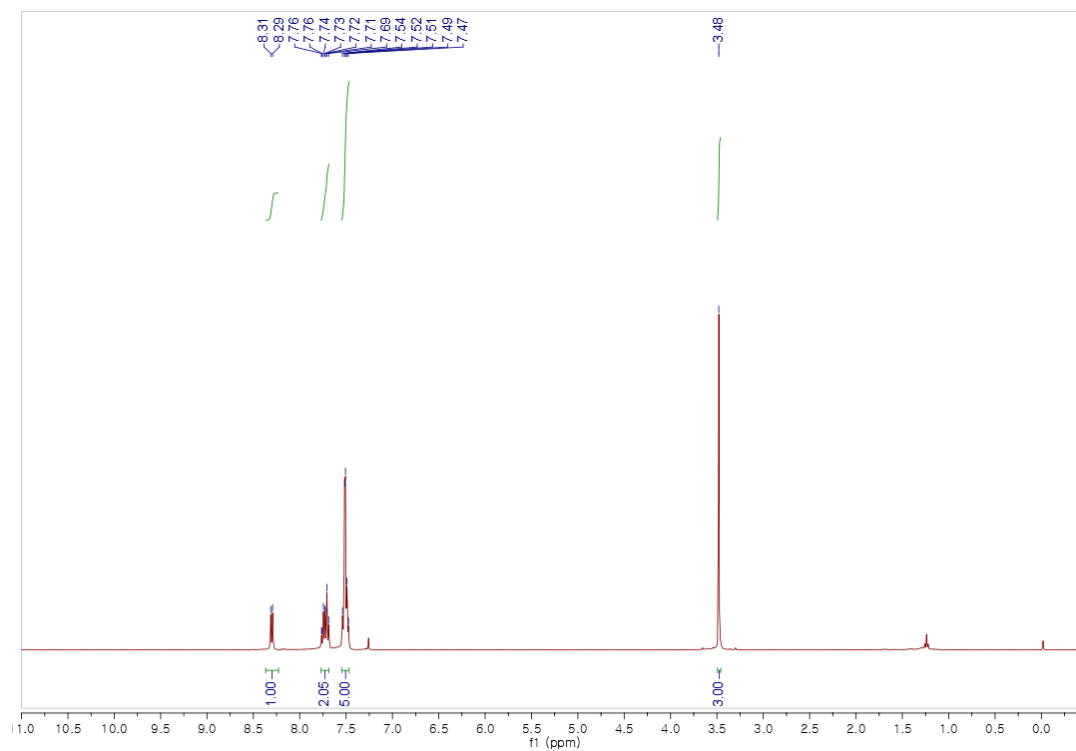
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound 58**



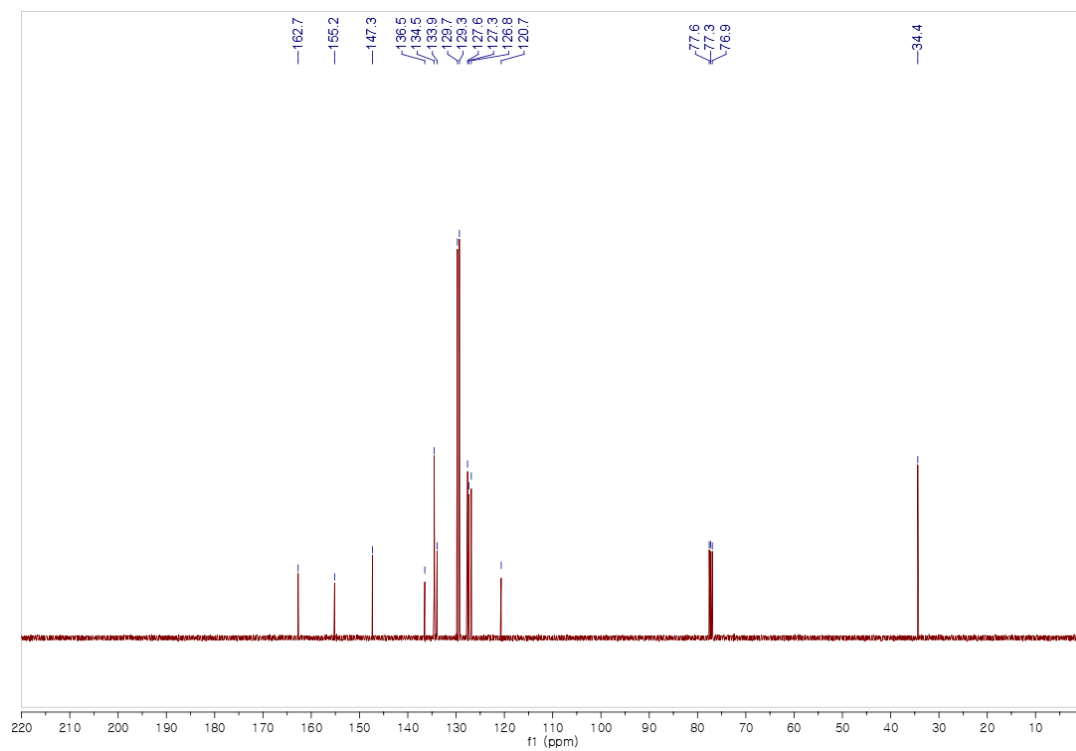
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectrum of compound 58**



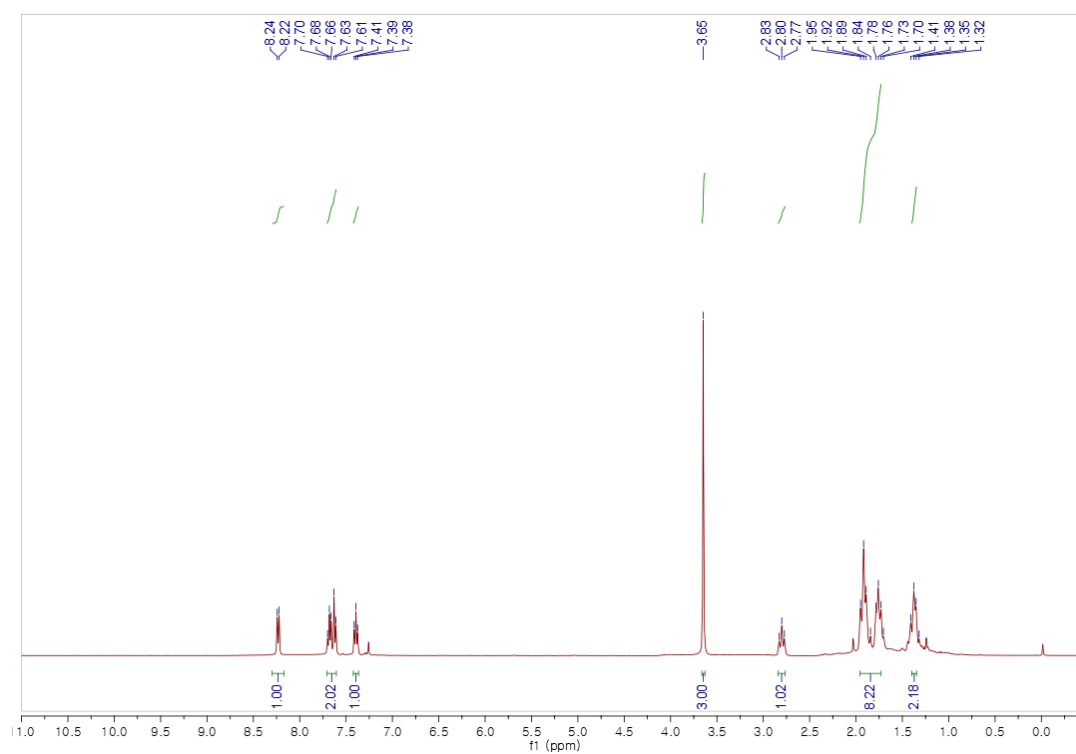
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound 59**



**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectrum of compound 59**



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectrum of compound 60**



**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) spectrum of compound 60**

