

Electronic Supplementary Material (ESI)

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# Supporting Information for Synthesis of pyrido[1,2-a]indol-6(7H)-ones via a visible light-photocatalyzed formal (4 + 2) cycloaddition of indole-derived bromides and alkenes or alkynes †

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## 1. General Information

$^1\text{H}/^{13}\text{C}$  NMR spectra were recorded on magnet system 400'54 ascend instrument purchased from Bruker Biospin AG. All chemical shifts are given in parts per million and are measured relative to DMSO as an internal standard. ESI/EI-MS spectra were recorded on Agilent Q-TOF 6520. Products were purified by flash chromatography on 200-300 mesh silica gel and visualized using a UV lamp (254 nm or 365 nm). All the solvents were used without further purification, unless otherwise state. the other commercial chemicals were used without further purification. All reactions were performed under an inert atmosphere of nitrogen.

General procedure for the synthesis of 3 (3a as an example):

An oven-dried 10 mL reaction syringe was charged with 2-bromo-1-(1H-indol-1-yl)-2-methylpropan-1-one (1 mmol, 1 equiv), styrene (1 mmol, 1 equiv), PC-B (1 mol %) and  $\text{Et}_3\text{N}$  (1.1 mmol, 1.1 equiv). And add 5 mL MeCN (0.2 M) solution. Reaction under blue light (10 W, 220 V, LED, wavelength 420nm-430nm) for 20 minutes. The reaction mixture was concentrated under reduced pressure and the residue was chromatographed on silica gel using hexane/ethyl acetate or dichloromethane/methanol to afford the desired product 3a (93%

yield).

## 2. Batch and Microfluidic Reactor Device

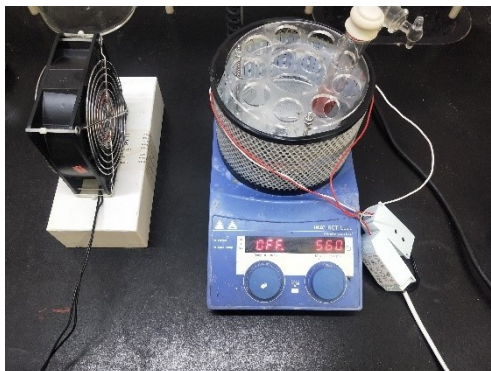


Figure 1 Batch reactor device

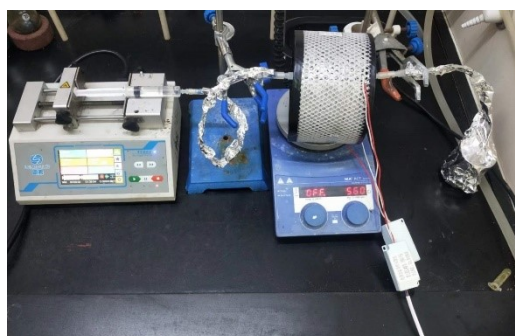


Figure 2 Microfluidic reactor device

Note: The light source is a simulated solar lamp (10W, 220V, wavelength 420nm-430nm).

## 3. Select Optimization Results

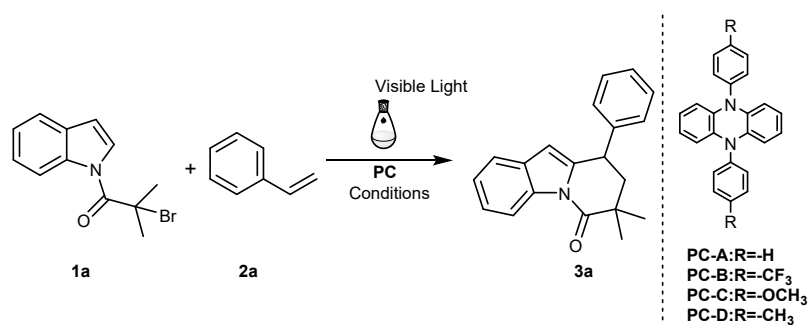
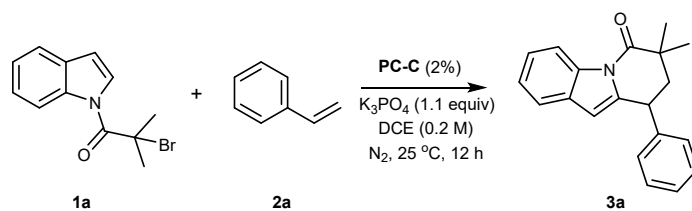


Figure 3 Optimization of reaction conditions

### 3.1 Table 1. Varying the wavelength of light.<sup>a</sup>

**Table 1** Optimizing the wavelength of light



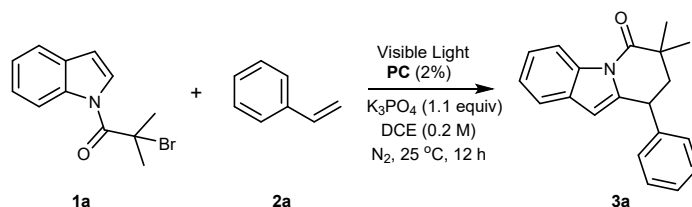
Entry	Wavelength of Light	yield 3a <sup>b</sup> (%)
1	360-370 nm	59
2	380-385 nm	53
3	390-398 nm	57
4	420-430 nm	64
5	435-445 nm	25

[a] Reaction conditions: **1a** (1 mmol, 1 equiv), **2a** (2 mmol, 2 equiv), **PC-C** (2 mmol%, 2 equiv%),  $\text{K}_3\text{PO}_4$  (1.1 mmol, 1.1 equiv), solvent: DCE (5 mL),  $\text{N}_2$ , 25°C, 12 h; The models of lamps used are 10 W、220 V、LED.

[b] Isolated yield.

### 3.2 Table 2. Varying the Catalyst.<sup>a</sup>

**Table 2** Explore the effects of different catalysts on the reaction

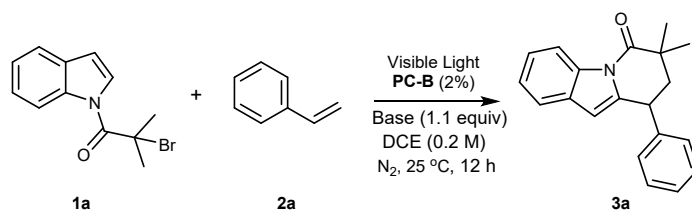


Entry	PC	yield 3a <sup>b</sup> (%)
1	<b>PC-A</b>	55
2	<b>PC-B</b>	73
3	<b>PC-C</b>	64
4	<b>PC-D</b>	41
5	None	None
6 <sup>c</sup>	<b>PC-C</b>	None

[a] Reaction conditions: **1a** (1 mmol, 1 equiv), **2a** (2 mmol, 2 equiv), **PC** (2 mmol%, 2 equiv%),  $\text{K}_3\text{PO}_4$  (1.1 mmol, 1.1 equiv), solvent: DCE (5 mL),  $\text{N}_2$ , 25°C, 12 h, bluelight (10 W、220 V、LED、wavelength 420 nm-430 nm). [b] Isolated yield. [c] no light.

### 3.3 Table 3. Varying the Base.<sup>a</sup>

**Table 3** Explore the effect of different Bases on the reaction

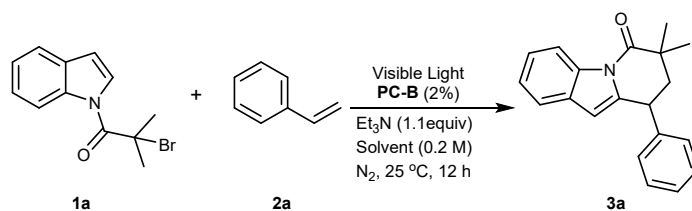


Entry	Base	yield <b>3a</b> <sup>b</sup> (%)
1	K <sub>3</sub> PO <sub>4</sub>	73
2	K <sub>2</sub> CO <sub>3</sub>	54
3	NaHCO <sub>3</sub>	57
4	LiOtBu	62
5	Et <sub>3</sub> N	81
6	DMAP	48
7	DBU	21
8	Pyridine	34
9	None	37

[a] Reaction conditions: **1a** (1 mmol, 1 equiv), **2a** (2 mmol, 2 equiv), **PC-B** (2 mmol%, 2 equiv%), Base (1.1 mmol, 1.1 equiv), solvent: DCE (5 mL), N<sub>2</sub>, 25°C, 12 h, bluelight (10 W, 220 V, LED, wavelength 420 nm-430 nm). [b] Isolated yield.

### 3.4 Table 4. Varying the Solvent.<sup>a</sup>

**Table 4** Explore the effect of different Solvents on the reaction

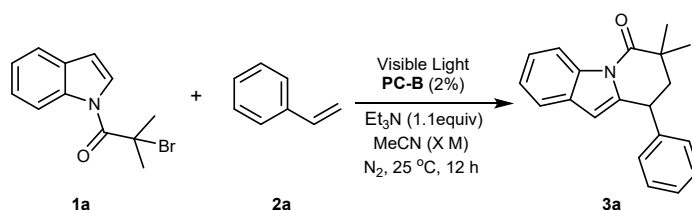


Entry	solvent	yield 3a <sup>b</sup> (%)
1	DCE	81
2	MeCN	82
3	THF	75
4	DMA	63
5	DMF	61
6	Cyclohexane	70
7	1,4-Dioxane	69

[a] Reaction conditions: **1a** (1 mmol, 1 equiv), **2a** (2 mmol, 2 equiv), **PC-B** (2 mmol%, 2 equiv%), Et<sub>3</sub>N (1.1 mmol, 1.1 equiv), solvent: (5 mL), N<sub>2</sub>, 25°C, 12 h, bluelight (10 W、220 V、LED、wavelength 420 nm-430 nm). [b] Isolated yield.

### 3.5 Table 5. Concentration.<sup>a</sup>

**Table 5** Explore the effect of substrate concentration on the reaction

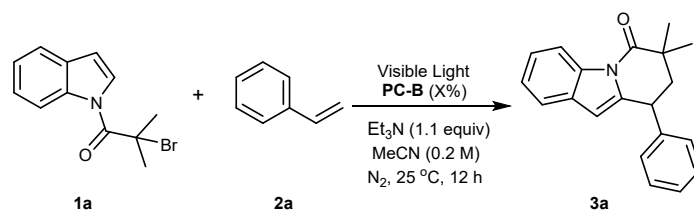


Entry	Concentration	yield 3a <sup>b</sup> (%)
1	1M	80
2	0.5M	83
3	0.2M	82
4	0.1M	64
5	0.05M	43

[a] Reaction conditions : **1a** (1 mmol, 1 equiv), **2a** (2 mmol, 2 equiv), **PC-B** (2 mmol%, 2 equiv%), Et<sub>3</sub>N (1.1 mmol, 1.1 equiv), solvent: MeCN (X mL), N<sub>2</sub>, 25°C, 12 h, bluelight (10 W、220 V、LED、wavelength 420 nm-430 nm). [b] Isolated yield.

### 3.6 Table 6. Catalyst concentration.<sup>a</sup>

**Table 6** Explore the effect of the amount of catalyst on the reaction

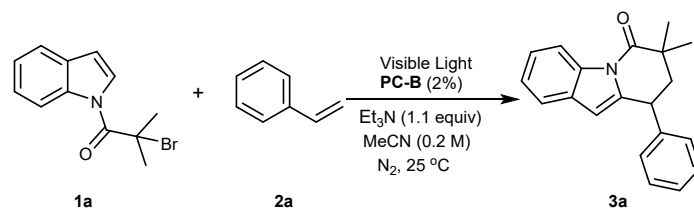


Entry	PC (X mol%)	yield <b>3a</b> <sup>b</sup> (%)
1	4	83
2	2	82
3	1	64
4	0.5	58
5	None	None

[a] Reaction conditions: **1a** (1 mmol, 1 equiv), **2a** (2 mmol, 2 equiv), **PC-B** (X% mmol, X% equiv), Et<sub>3</sub>N (1.1 mmol, 1.1 equiv), solvent: MeCN (5 mL), N<sub>2</sub>, 25°C, 12 h, bluelight (10 W、220 V、LED、wavelength 420 nm-430 nm). [b] Isolated yield.

### 3.7 Table 7. Residence time.<sup>a</sup>

**Table 7** Explore the effect of reaction time on the reaction

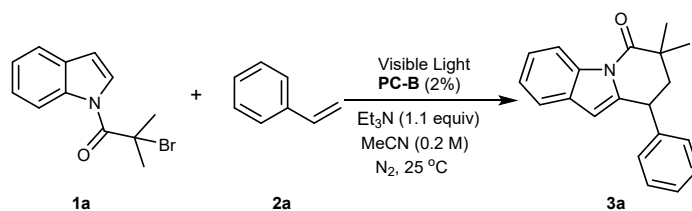


Entry	Time (h)	yield <b>3a</b> <sup>b</sup> (%)
1	1	24
2	2	31
3	3	57
4	4	78
5	6	79
6	12	82

[a] Reaction conditions: **1a** (1 mmol, 1 equiv), **2a** (2 mmol, 2 equiv), **PC-B** (2 mmol%, 2 equiv%), Et<sub>3</sub>N (1.1 mmol, 1.1 equiv), solvent: MeCN (5 mL), N<sub>2</sub>, 25°C, bluelight (10 W、220 V、LED、wavelength 420 nm-430 nm). [b] Isolated yield.

### 3.8 Table 8. Reagent Loading<sup>a</sup>

**Table 8** Explore the effect of substrate ratio on the reaction



Entry	styrene	yield 3a <sup>b</sup> (%)
1	1	43
2	2	75
3	3	80
4	4	82

[a] Reaction conditions: **1a** (1 mmol, 1 equiv), **PC-B** (2 mmol%, 2 equiv%), Et<sub>3</sub>N (1.1 mmol, 1.1 equiv), solvent: MeCN (5 mL), N<sub>2</sub>, 25°C, 4 h, bluelight (10 W, 220 V, LED, wavelength 420 nm-430 nm). [b] Isolated yield.

### 3.9 Table 9. Reagent Loadings.<sup>a</sup>

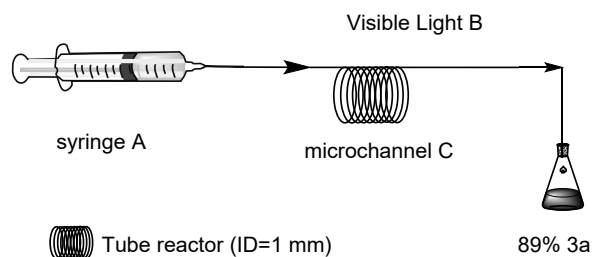
**Table 9** Optimization of microchannel reaction conditions

Entry	PC-B (equiv)	Tube diameter (mm)	Tube length (m)	Residence time (minute)	yield 3a <sup>b</sup> (%)
1	2%	1	2	30	89
2	1%	1	2	30	95
3	0.5%	1	2	30	43
4	0.1%	1	2	30	38
5	1%	1	3	30	82
6	1%	1	1	30	85
7	1%	1	0.5	30	78
8	1%	1	2	5	31
9	1%	1	2	10	56
10	1%	1	2	20	93
11	1%	1	2	40	96

[a] Reaction conditions: **1a** (1.0 mmol, 1.0 equiv), **2a** (1.0 mmol, 1.0 equiv), Et<sub>3</sub>N (1.1 mmol, 1.1 equiv), 5 mL MeCN (0.2 M) solution, N<sub>2</sub>, 25°C; bluelight (10 W, 220 V, LED, wavelength 420 nm-430 nm). [b] Isolated yield.



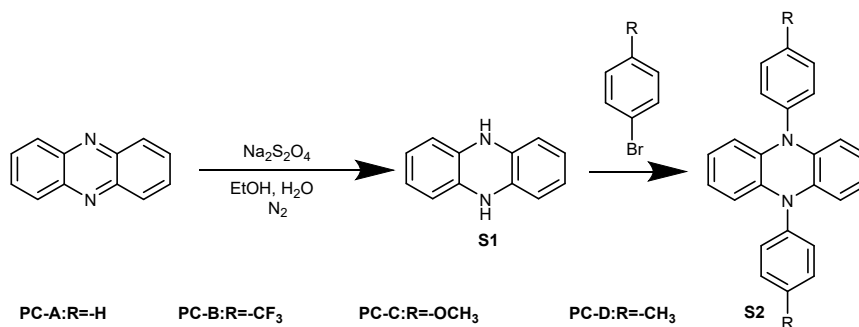
### 3.10 A Scale-up Continuous Flow Reaction.<sup>a</sup>



<sup>a</sup> Reaction conditions: **1a** (10 mmol), **2a** (1 equiv), MeCN (20 mL), Et<sub>3</sub>N (1.1 equiv), and **PC-B** (1 % equiv.) at room temperature for 20 minutes. Isolated yield.

## 4. Preparation of Substrates

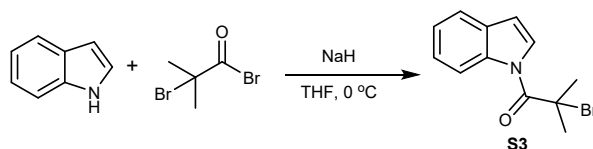
### 4.1 Method for synthesizing phenazine catalysts



**Figure 4** Synthetic method of phenazine catalyst

As shown in **Figure 4**, S1 and S2 are synthesized according to the literature<sup>1</sup>.

### 4.2 Method for synthesizing indole substrates



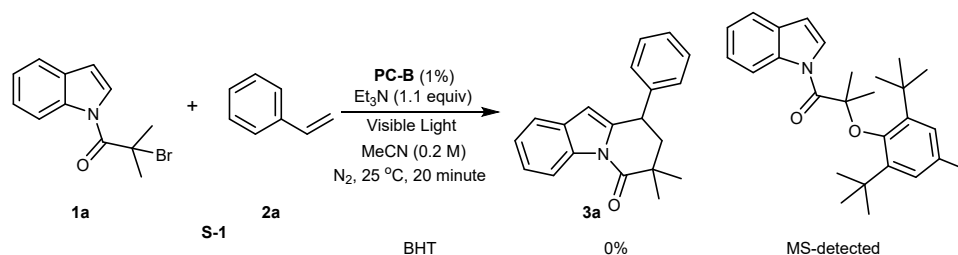
**Figure 5** Synthesis method of indole substrates

As shown in **Figure 5**: sodium hydride (15.0 mmol, 1.5 equiv) was dissolved in ultra-dry tetrahydrofuran (100 mL), and then the corresponding indole (10.0 mmol, 1.0 equiv) was slowly added under ice bath conditions for 30 minutes; Then slowly add 2-bromo-2-methylpropionyl bromide (10.0 mmol, 1.0 equiv). The reaction mixture was stirred at room temperature. After completion of the reaction the reaction mixture was quenched with water and extracted with EA.

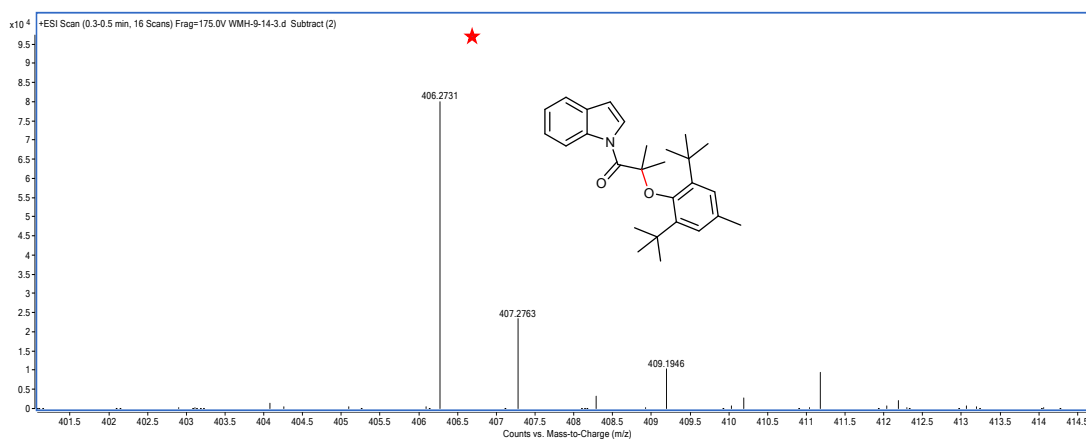
The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The residue was purified by column chromatography on silica gel or recrystallization to provide the desired product **S3**.

## 5. Experiments for Mechanistic Studies

### 5.1 Free radical capture experiment



**Figure 6** Radical trapping experiment with BHT



**Figure 7** HR-MS (EI) analysis of **S-1**

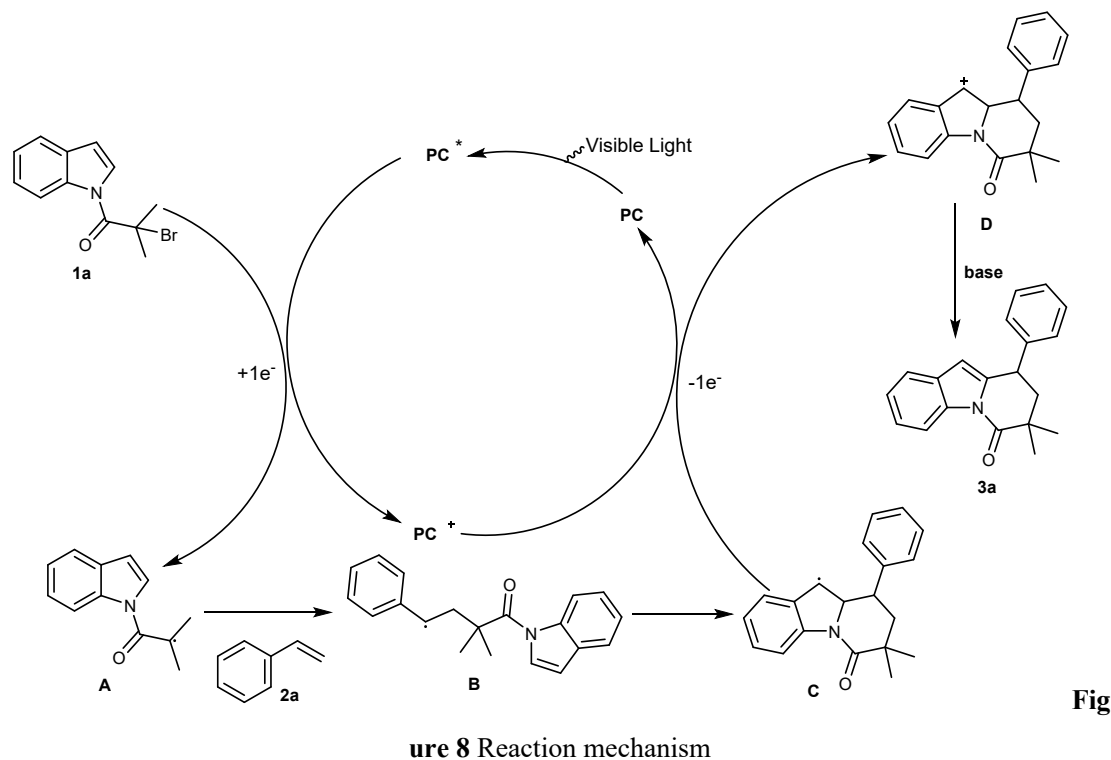
### 5.2 Variable control experiment

**Table 10** Variable Control Experiment

Entry	Changes to "standard conditions"	yield <b>3a</b> <sup>b</sup> (%)
1	No organic photocatalyst	0
2	No light	0

[a] Reaction conditions: **1a** (1 mmol, 1 equiv), **2a** (3 mmol, 3 equiv), Et<sub>3</sub>N (1.1 mmol, 1.1 equiv), solvent: MeCN (5 mL), N<sub>2</sub>, 25°C, 4 h, bluelight (10 W、220 V、LED、wavelength 420 nm-430 nm) . [b] Isolated yield.

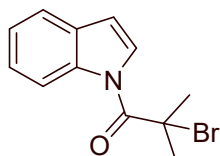
## 5.3 Discussion on theoretical reaction mechanism



Fig

## 6. Analytical data for isolated compounds

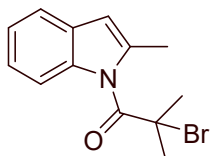
### 6.1 Characterization data for indole substrates



#### 2-bromo-1-(1H-indol-1-yl)-2-methylpropan-1-one(1a):

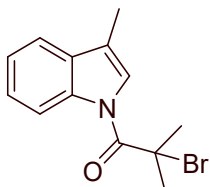
Yellow oil (2.28 g, 86% yield); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 8.36 (d, *J* = 8.2 Hz, 1H), 8.26 (d, *J* = 3.8 Hz, 1H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.39 – 7.35 (m, 1H), 7.31 (t, *J* = 7.4 Hz, 1H), 6.83 (d, *J* = 3.9 Hz, 1H), 2.16 (s, 6H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 169.51, 136.54, 130.03, 128.04, 125.64, 124.61, 121.46, 117.09, 109.27, 58.24, 32.29.

HRMS (EI) calcd for C<sub>12</sub>H<sub>12</sub>NOBr [M]: 265.0097; found: 265.0102.



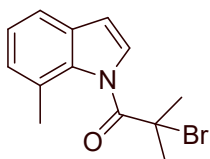
**2-bromo-2-methyl-1-(2-methyl-1H-indol-1-yl)propan-1-one(1b):**

Yellow oil (2.20 g, 79% yield);  $^1\text{H NMR}$  (400 MHz, DMSO-*d*6)  $\delta$  7.86 (d,  $J$  = 8.3 Hz, 1H), 7.51 (d,  $J$  = 7.7 Hz, 1H), 7.26 – 7.21 (m, 1H), 7.16 (td,  $J$  = 7.4, 1.0 Hz, 1H), 6.53 (s, 1H), 2.41 (s, 3H), 2.10 (s, 6H).  $^{13}\text{C NMR}$  (101 MHz, DMSO-*d*6)  $\delta$  176.36 , 138.02 , 135.86 , 129.05 , 122.90 , 122.37 , 120.55 , 114.00 , 107.00 , 60.91 , 31.45 , 14.63 . HRMS (EI) calcd for  $\text{C}_{13}\text{H}_{14}\text{NOBr}$  [M]: 279.0253; found: 279.0256.



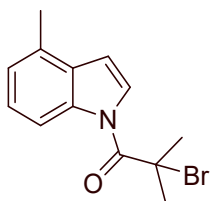
**2-bromo-2-methyl-1-(3-methyl-1H-indol-1-yl)propan-1-one(1c):**

Yellow oil (2.26 g, 81% yield);  $^1\text{H NMR}$  (400 MHz, DMSO-*d*6)  $\delta$  8.34 (d,  $J$  = 8.2 Hz, 1H), 8.06 (s, 1H), 7.58 (d,  $J$  = 7.5 Hz, 1H), 7.39 – 7.31 (m, 2H), 2.28 (s, 3H), 2.15 (s, 6H).  $^{13}\text{C NMR}$  (101 MHz, DMSO-*d*6)  $\delta$  169.04 , 136.83 , 130.98 , 125.77 , 124.65 , 124.42 , 119.48 , 117.92 , 117.14 , 58.39 , 32.31 , 9.81 . HRMS (EI) calcd for  $\text{C}_{13}\text{H}_{14}\text{NOBr}$  [M]: 279.0253; found: 279.0259.



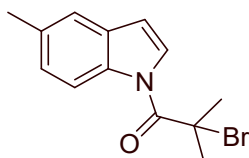
**2-bromo-2-methyl-1-(7-methyl-1H-indol-1-yl)propan-1-one(1d):**

Yellow solid (1.76 g, 63% yield);  $^1\text{H NMR}$  (400 MHz, DMSO-*d*6)  $\delta$  8.12 (d,  $J$  = 3.8 Hz, 1H), 7.49 (d,  $J$  = 7.6 Hz, 1H), 7.22 (t,  $J$  = 7.5 Hz, 1H), 7.14 (d,  $J$  = 7.3 Hz, 1H), 6.79 (d,  $J$  = 3.8 Hz, 1H), 2.29 (s, 3H), 2.20 (s, 6H).  $^{13}\text{C NMR}$  (101 MHz, DMSO-*d*6)  $\delta$  170.40 , 135.91 , 131.14 , 128.74 , 127.92 , 125.93 , 124.45 , 119.16 , 108.68 , 58.73 , 32.30 , 21.55 . HRMS (EI) calcd for  $\text{C}_{13}\text{H}_{14}\text{NOBr}$  [M]: 279.0253; found: 279.0257.



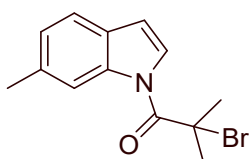
**2-bromo-2-methyl-1-(4-methyl-1H-indol-1-yl)propan-1-one(1e):**

Green oil (2.06 g, 74% yield);  $^1\text{H NMR}$  (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  8.24 (d,  $J$  = 3.9 Hz, 1H), 8.17 (d,  $J$  = 8.3 Hz, 1H), 7.25(t,  $J$  = 7.8 Hz, 1H), 7.11 (d,  $J$  = 7.3 Hz, 1H), 6.87 (d,  $J$  = 3.9 Hz, 1H), 2.49 (s, 3H), 2.15 (s, 6H).  $^{13}\text{C NMR}$  (101 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  169.50 , 136.33 , 130.49 , 129.50 , 127.46 , 125.68 , 124.99 , 114.62 , 107.76 , 58.30 , 32.30 , 18.53 . **HRMS** (EI) calcd for C<sub>13</sub>H<sub>14</sub>NOBr [M]: 279.0253; found: 279.0251.



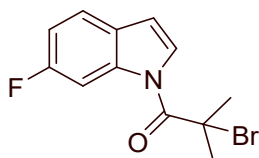
**2-bromo-2-methyl-1-(5-methyl-1H-indol-1-yl)propan-1-one(1f):**

Yellow oil (2.23 g, 80% yield);  $^1\text{H NMR}$  (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  8.24 – 8.19 (m, 2H), 7.43 (s, 1H), 7.18 (d,  $J$  = 8.5 Hz, 1H), 6.74 (d,  $J$  = 3.9 Hz, 1H), 2.40 (s, 3H), 2.14 (s, 6H).  $^{13}\text{C NMR}$  (101 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  169.29 , 134.74 , 133.70 , 130.25, 128.07 , 126.78 , 121.32 , 116.77 , 109.09 , 58.25, 32.33 , 21.35 . **HRMS** (EI) calcd for C<sub>13</sub>H<sub>14</sub>NOBr [M]: 279.0253; found: 279.0254.



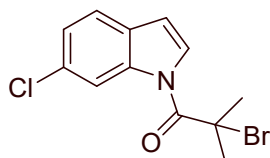
**2-bromo-2-methyl-1-(6-methyl-1H-indol-1-yl)propan-1-one(1g):**

Yellow oil (2.15 g, 77% yield);  $^1\text{H NMR}$  (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  8.24 – 8.12 (m, 2H), 7.52 (d,  $J$  = 7.9 Hz, 1H), 7.14 (dd,  $J$  = 7.9, 1.4 Hz, 1H), 6.76 (d,  $J$  = 3.8 Hz, 1H), 2.43 (s, 3H), 2.14 (s, 6H).  $^{13}\text{C NMR}$  (101 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  169.46 , 136.93 , 135.08 , 127.75 , 127.38 , 125.83 , 121.02 , 117.32 , 109.14 , 58.24 , 32.28 , 22.07 . **HRMS** (EI) calcd for C<sub>13</sub>H<sub>14</sub>NOBr [M]: 279.0253; found: 279.0249.



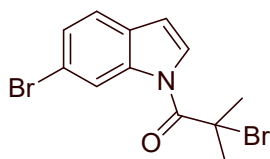
**2-bromo-1-(6-fluoro-1H-indol-1-yl)-2-methylpropan-1-one(1h):**

Yellow oil (2.12 g, 75% yield);  $^1\text{H NMR}$  (400 MHz, DMSO-*d*6)  $\delta$  8.25(d,  $J$  = 3.9 Hz, 1H), 8.09 (dd,  $J$  = 10.8, 2.5 Hz, 1H), 7.66 (dd,  $J$  = 8.6, 5.7 Hz, 1H), 7.19 (td,  $J$  = 9.0, 2.5 Hz, 1H), 6.83 (d,  $J$  = 3.9 Hz, 1H), 2.14 (s, 6H).  $^{13}\text{C NMR}$  (101 MHz, DMSO-*d*6)  $\delta$  169.66, 160.96 (d,  $J$  = 239.0 Hz), 136.60 (d,  $J$  = 13.1 Hz), 128.63 (d,  $J$  = 4.1 Hz), 126.56 (d,  $J$  = 1.2 Hz), 122.47 (d,  $J$  = 9.6 Hz), 112.53 (d,  $J$  = 23.7 Hz), 109.02, 104.24 (d,  $J$  = 28.8 Hz), 57.94, 32.13.  $^{19}\text{F NMR}$  (376 MHz, DMSO-*d*6)  $\delta$  -116.60. **HRMS** (EI) calcd for  $\text{C}_{12}\text{H}_{11}\text{NOBrF}$  [M]: 283.0003; found: 283.0004.



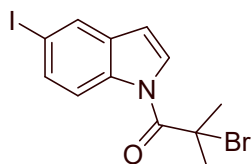
**2-bromo-1-(6-chloro-1H-indol-1-yl)-2-methylpropan-1-one(1i):**

White solid (1.98 g, 71% yield);  $^1\text{H NMR}$  (400 MHz, DMSO-*d*6)  $\delta$  8.36 (d,  $J$  = 1.9 Hz, 1H), 8.30 (d,  $J$  = 3.9 Hz, 1H), 7.68 (d,  $J$  = 8.3 Hz, 1H), 7.37 (dd,  $J$  = 8.4, 2.0 Hz, 1H), 6.85 (d,  $J$  = 3.9 Hz, 1H), 2.15 (s, 6H).  $^{13}\text{C NMR}$  (101 MHz, DMSO-*d*6)  $\delta$  169.72, 136.87, 130.14, 129.02, 128.87, 124.80, 122.76, 116.89, 109.02, 57.96, 32.09. **HRMS** (EI) calcd for  $\text{C}_{12}\text{H}_{11}\text{NOBrCl}$  [M]: 298.9707; found: 298.9711.



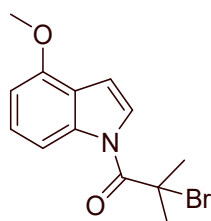
**2-bromo-1-(6-bromo-1H-indol-1-yl)-2-methylpropan-1-one(1j):**

White solid (2.29 g, 67% yield);  $^1\text{H NMR}$  (400 MHz, DMSO-*d*6)  $\delta$  8.44 (d,  $J$  = 1.7 Hz, 1H), 8.21 (d,  $J$  = 3.9 Hz, 1H), 7.56 (d,  $J$  = 8.3 Hz, 1H), 7.42 (dd,  $J$  = 8.3, 1.8 Hz, 1H), 6.77 (d,  $J$  = 3.9 Hz, 1H), 2.07 (s, 6H).  $^{13}\text{C NMR}$  (101 MHz, DMSO-*d*6)  $\delta$  169.69, 137.21, 129.15, 128.87, 127.45, 123.13, 119.72, 118.30, 109.06, 57.93, 32.09. **HRMS** (EI) calcd for  $\text{C}_{12}\text{H}_{11}\text{NOBr}_2$  [M]: 342.9202; found: 342.9208.



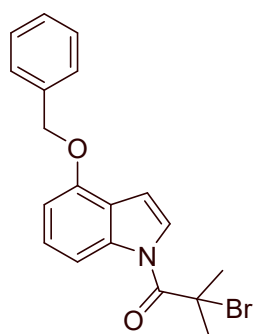
**2-bromo-1-(5-iodo-1H-indol-1-yl)-2-methylpropan-1-one(1k):**

White solid (2.35 g, 60% yield);  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  8.27 (d,  $J = 3.9$  Hz, 1H), 8.16 – 8.12 (m, 1H), 8.05 (d,  $J = 1.7$  Hz, 1H), 7.67 (dd,  $J = 8.7, 1.8$  Hz, 1H), 6.79 (dd,  $J = 3.9, 0.7$  Hz, 1H), 2.14 (s, 6H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{DMSO-}d_6$ )  $\delta$  169.55, 135.87, 133.79, 132.51, 129.96, 129.01, 119.14, 108.31, 89.20, 58.08, 32.17. HRMS (EI) calcd for  $\text{C}_{12}\text{H}_{11}\text{NOBrI}$  [M]: 390.9063; found: 390.9077.



**2-bromo-1-(4-methoxy-1H-indol-1-yl)-2-methylpropan-1-one(1l):**

Light yellow solid (2.31 g, 78% yield);  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  8.19 (d,  $J = 3.9$  Hz, 1H), 7.99 (d,  $J = 8.4$  Hz, 1H), 7.35 (t,  $J = 8.2$  Hz, 1H), 6.92 (d,  $J = 8.0$  Hz, 1H), 6.84 (d,  $J = 3.8$  Hz, 1H), 3.95 (s, 3H), 2.19 (s, 6H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{DMSO-}d_6$ )  $\delta$  169.62, 152.91, 137.70, 126.86, 126.53, 119.69, 110.04, 105.91, 105.65, 58.22, 55.88, 32.26. HRMS (EI) calcd for  $\text{C}_{13}\text{H}_{14}\text{NO}_2\text{Br}$  [M]: 295.0202; found: 295.0209.

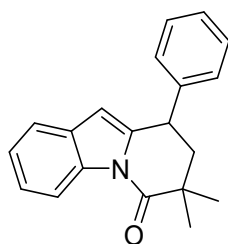


**1-(4-(benzyloxy)-1H-indol-1-yl)-2-bromo-2-methylpropan-1-one(1m):**

Light yellow solid (2.56 g, 69% yield);  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  8.16 (d,  $J = 3.9$  Hz, 1H), 7.96 – 7.91 (m, 1H), 7.53 – 7.49 (m, 2H), 7.44 – 7.39 (m, 2H), 7.36 – 7.32 (m, 1H), 7.28 (t,  $J = 8.2$  Hz, 1H), 6.96 (d,  $J = 8.0$  Hz, 1H), 6.84 (dd,  $J = 4.0, 0.7$  Hz, 1H),

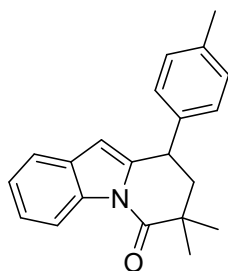
5.28 (s, 2H), 2.14 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz, DMSO-*d*6)  $\delta$  169.62 , 151.89 , 137.81 , 137.57 , 128.96 , 128.31 , 127.96 , 126.76 , 126.66 , 120.12 , 110.25, 107.19 , 106.01 , 69.85 , 58.24 , 32.26 . HRMS (EI) calcd for  $\text{C}_{19}\text{H}_{18}\text{NO}_2\text{Br}$  [M]: 371.0521; found: 371.0523.

## 6.2 Product Characterization Data



### 7,7-dimethyl-9-phenyl-8,9-dihydropyrido[1,2-a]indol-6(7H)-one(3a):

White solid (268.9 mg, 93% yield);  $^1\text{H}$  NMR (400 MHz, DMSO-*d*6)  $\delta$  8.47 (d,  $J$  = 8.1 Hz, 1H), 7.52 – 7.38 (m, 6H), 7.33 – 7.23 (m, 2H), 5.86 (s, 1H), 4.56 – 4.47 (m, 1H), 2.50 (t,  $J$  = 13.3 Hz, 1H), 1.98 (dd,  $J$  = 13.2, 4.6 Hz, 1H), 1.45 (d,  $J$  = 27.8 Hz, 6H).  $^{13}\text{C}$  NMR (101 MHz, DMSO-*d*6)  $\delta$  175.37 , 143.40 , 142.35 , 135.22 , 130.10 , 129.06 , 128.93 , 127.67 , 124.27 , 124.11 , 120.56 , 116.29 , 105.94 , 43.26 , 40.65 , 38.10 , 26.60 , 25.22 . HRMS (EI) calcd for  $\text{C}_{20}\text{H}_{19}\text{NO}$  [M]: 289.1467; found 289.1469.



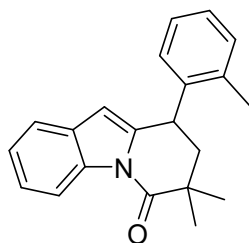
### 7,7-dimethyl-9-(p-tolyl)-8,9-dihydropyrido[1,2-a]indol-6(7H)-one(3b):

White solid (269.8mg, 89% yield);  $^1\text{H}$  NMR (400 MHz, DMSO-*d*6)  $\delta$  8.42 (d,  $J$  = 8.0 Hz, 1H), 7.49 (d,  $J$  = 7.7 Hz, 1H), 7.38 (d,  $J$  = 7.8 Hz, 2H), 7.32 – 7.28 (m, 1H), 7.28 – 7.21 (m, 3H), 5.85 (s, 1H), 4.48 (dd,  $J$  = 13.5, 4.7 Hz, 1H), 2.49 (t,  $J$  = 13.3 Hz, 1H), 2.38 (s, 3H), 1.96 (dd,  $J$  = 13.1, 4.6 Hz, 1H), 1.44 (d,  $J$  = 30.1 Hz, 6H).  $^{13}\text{C}$  NMR (101 MHz, DMSO-*d*6)  $\delta$  175.44 , 143.69 , 139.33 , 136.73 , 135.18 , 130.11 , 129.64 , 128.79 , 124.24



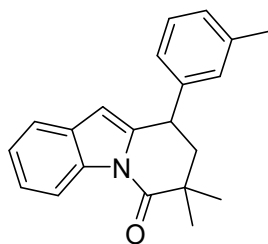
, 124.11 , 120.58 , 116.24 , 105.86 , 43.23 , 40.67 , 37.65 , 26.63 , 25.24 , 21.18 . **HRMS**

(EI) calcd for C<sub>21</sub>H<sub>21</sub>NO [M]: 303.1618; found: 303.1623.



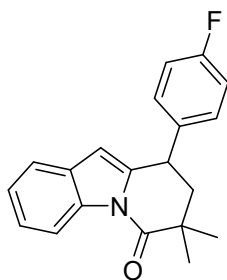
**7,7-dimethyl-9-(o-tolyl)-8,9-dihydropyrido[1,2-a]indol-6(7H)-one(3c):**

White solid (266.8 mg, 88% yield); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 8.42 (d, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 7.7 Hz, 1H), 7.38 (d, *J* = 7.8 Hz, 2H), 7.32 – 7.28 (m, 1H), 7.28 – 7.21 (m, 3H), 5.85 (s, 1H), 4.48 (dd, *J* = 13.5, 4.7 Hz, 1H), 2.49 (t, *J* = 13.3 Hz, 1H), 2.38 (s, 3H), 1.96 (dd, *J* = 13.1, 4.6 Hz, 1H), 1.44 (d, *J* = 30.1 Hz, 6H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 175.34 , 142.64 , 140.28 , 136.43 , 135.29 , 130.80 , 130.15 , 127.85 , 127.38 , 126.84 , 124.19 , 124.08 , 120.49 , 116.28 , 105.55 , 42.57 , 40.70 , 33.52 , 26.66 , 25.05 , 19.55 . **HRMS** (EI) calcd for C<sub>21</sub>H<sub>21</sub>NO [M]: 303.1618; found: 303.1628.



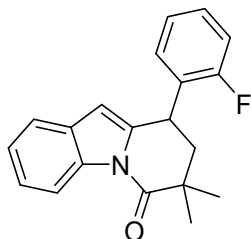
**7,7-dimethyl-9-(m-tolyl)-8,9-dihydropyrido[1,2-a]indol-6(7H)-one(3d):**

White solid (260.7 mg, 86% yield); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 8.38 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.31 – 7.26 (m, 2H), 7.26 – 7.17 (m, 3H), 7.14 (d, *J* = 7.1 Hz, 1H), 5.82 (dd, *J* = 2.0, 0.7 Hz, 1H), 4.43 (ddd, *J* = 13.5, 4.7, 2.0 Hz, 1H), 2.45 (t, *J* = 13.3 Hz, 1H), 2.32 (s, 3H), 1.92 (dd, *J* = 13.1, 4.7 Hz, 1H), 1.39 (d, *J* = 28.6 Hz, 6H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 175.42 , 143.50 , 142.30 , 138.17 , 135.18 , 130.12 , 129.52 , 128.96 , 128.31 , 126.01 , 124.25, 124.11 , 120.60 , 116.25, 105.89 , 43.25, 40.66 , 38.00 , 26.60 , 25.21 , 21.52 . **HRMS** (EI) calcd for C<sub>21</sub>H<sub>21</sub>NO [M]: 303.1618; found: 303.1629.



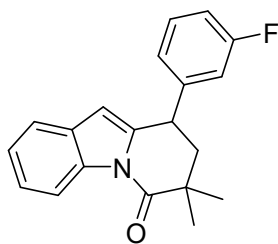
**9-(4-fluorophenyl)-7,7-dimethyl-8,9-dihydropyrido[1,2-a]indol-6(7H)-one(3e):**

White solid (236.5 mg, 77% yield);  $^1\text{H NMR}$  (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  8.38 (dd,  $J$  = 8.2, 1.1 Hz, 1H), 7.53 – 7.44 (m, 3H), 7.28 – 7.20 (m, 4H), 5.81 (d,  $J$  = 1.3 Hz, 1H), 4.51 (ddd,  $J$  = 13.4, 4.6, 1.9 Hz, 1H), 2.44 (d,  $J$  = 13.3 Hz, 1H), 1.92 (dd,  $J$  = 13.1, 4.6 Hz, 1H), 1.40 (d,  $J$  = 30.3 Hz, 6H).  $^{13}\text{C NMR}$  (101 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  175.38, 161.81 (d,  $J$  = 243.1 Hz), 143.41, 138.56 (d,  $J$  = 2.9 Hz), 135.21, 130.87 (d,  $J$  = 8.2 Hz), 130.07, 124.23 (d,  $J$  = 18.0 Hz), 120.60, 116.26, 115.91, 115.70, 105.90, 43.20, 40.67, 37.29, 26.57, 25.23.  $^{19}\text{F NMR}$  (376 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  -115.53. **HRMS** (EI) calcd for C<sub>20</sub>H<sub>18</sub>NOF [M]: 307.1372; found: 307.1376.



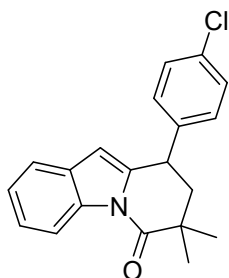
**9-(2-fluorophenyl)-7,7-dimethyl-8,9-dihydropyrido[1,2-a]indol-6(7H)-one(3f):**

White oli (239.6 mg, 78% yield);  $^1\text{H NMR}$  (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  8.42 (d,  $J$  = 8.1 Hz, 1H), 7.51 (td,  $J$  = 7.7, 1.8 Hz, 1H), 7.44 – 7.36 (m, 2H), 7.29 – 7.17 (m, 4H), 5.90 (d,  $J$  = 1.8 Hz, 1H), 4.83 – 4.63 (m, 1H), 2.47 (d,  $J$  = 13.2 Hz, 1H), 1.93 (dd,  $J$  = 13.1, 4.7 Hz, 1H), 1.39 (d,  $J$  = 23.0 Hz, 6H).  $^{13}\text{C NMR}$  (101 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  175.14, 160.89 (d,  $J$  = 244.9 Hz), 141.52, 135.21, 130.69 (d,  $J$  = 3.5 Hz), 130.04, 129.81 (d,  $J$  = 8.5 Hz), 128.75 (d,  $J$  = 13.1 Hz), 125.31 (d,  $J$  = 3.1 Hz), 124.37, 124.17, 120.62, 116.28, 116.03, 105.49, 41.57, 40.60, 31.77, 26.49, 25.01.  $^{19}\text{F NMR}$  (376 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  -114.43. **HRMS** (EI) calcd for C<sub>20</sub>H<sub>18</sub>NOF [M]: 307.1372; found: 307.1379.



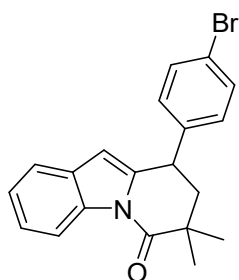
**9-(3-fluorophenyl)-7,7-dimethyl-8,9-dihydropyrido[1,2-a]indol-6(7H)-one(3g):**

White solid (224.2 mg, 73% yield); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 8.33 (d, *J* = 8.1 Hz, 1H), 7.41 – 7.29 (m, 2H), 7.21 (t, *J* = 7.2 Hz, 2H), 7.17 – 7.02 (m, 3H), 5.75 (s, 1H), 4.52 – 4.34 (m, 1H), 2.37 (t, *J* = 13.3 Hz, 1H), 1.83 (dd, *J* = 13.1, 4.7 Hz, 1H), 1.30 (d, *J* = 25.2 Hz, 6H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 175.33, 162.78 (d, *J* = 243.4 Hz), 145.30 (d, *J* = 7.3 Hz), 142.84, 135.18, 130.96 (d, *J* = 8.5 Hz), 130.06, 125.20, 124.36, 124.15, 120.65, 116.26, 115.77 (d, *J* = 21.8 Hz), 114.53 (d, *J* = 20.7 Hz), 105.93, 42.84, 40.64, 37.76, 26.53, 25.23. <sup>19</sup>F NMR (376 MHz, DMSO-*d*<sub>6</sub>) δ -113.01. HRMS (EI) calcd for C<sub>20</sub>H<sub>18</sub>NOF [M]: 307.1372; found: 307.1374.



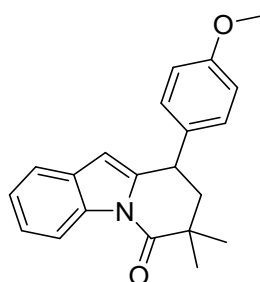
**9-(4-chlorophenyl)-7,7-dimethyl-8,9-dihydropyrido[1,2-a]indol-6(7H)-one(3h):**

White solid (226.2 mg, 70% yield); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 8.38 (d, *J* = 8.0 Hz, 1H), 7.52 – 7.42 (m, 5H), 7.23 (dt, *J* = 22.0, 7.4 Hz, 2H), 5.82 (s, 1H), 4.56 – 4.45 (m, 1H), 2.44 (d, *J* = 13.2 Hz, 1H), 1.92 (dd, *J* = 13.1, 4.5 Hz, 1H), 1.39 (d, *J* = 29.4 Hz, 6H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 175.33, 143.03, 141.45, 135.18, 132.25, 130.88, 130.06, 129.05, 124.35, 124.15, 120.62, 116.26, 105.96, 42.94, 40.66, 37.42, 26.55, 25.22. HRMS (EI) calcd for C<sub>20</sub>H<sub>18</sub>NOCl [M]: 323.1077; found: 323.1076.



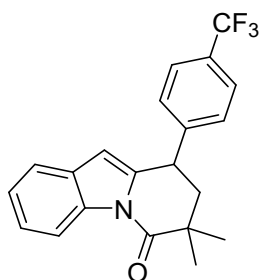
**9-(4-bromophenyl)-7,7-dimethyl-8,9-dihydropyrido[1,2-a]indol-6(7H)-one(3i):**

White solid (249.6 mg, 68% yield);  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  8.38 (d,  $J = 8.1$  Hz, 1H), 7.60 (d,  $J = 8.4$  Hz, 2H), 7.45 (t,  $J = 7.1$  Hz, 3H), 7.28 – 7.19 (m, 2H), 5.84 (d,  $J = 1.9$  Hz, 1H), 4.51 (ddd,  $J = 13.4, 4.7, 2.0$  Hz, 1H), 2.44 (d,  $J = 13.3$  Hz, 1H), 1.93 (dd,  $J = 13.1, 4.6$  Hz, 1H), 1.40 (d,  $J = 29.9$  Hz, 6H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{DMSO-}d_6$ )  $\delta$  175.33 , 142.95 , 141.89 , 135.18 , 131.98 , 131.26 , 130.06 , 124.36 , 124.16 , 120.77 , 120.64 , 116.25, 105.99 , 42.88 , 40.66 , 37.48 , 26.55 , 25.23 . **HRMS** (EI) calcd for  $\text{C}_{20}\text{H}_{18}\text{NOBr}$  [M]: 367.0572; found: 367.0573.



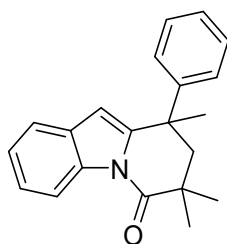
**9-(4-methoxyphenyl)-7,7-dimethyl-8,9-dihydropyrido[1,2-a]indol-6(7H)-one(3j):**

White solid (163.3 mg, 51% yield);  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  8.40 (t,  $J = 6.7$  Hz, 1H), 7.44 (d,  $J = 7.8$  Hz, 1H), 7.35 (d,  $J = 8.9$  Hz, 2H), 7.23 (dt,  $J = 21.5, 7.4$  Hz, 2H), 6.96 (d,  $J = 8.5$  Hz, 2H), 5.81 (s, 1H), 4.41 (d,  $J = 13.9$  Hz, 1H), 3.78 (s, 3H), 2.47 – 2.36 (m, 1H), 1.89 (dd,  $J = 13.4, 4.5$  Hz, 1H), 1.39 (d,  $J = 27.3$  Hz, 6H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{DMSO-}d_6$ )  $\delta$  175.44 , 158.84 , 135.24 , 134.21 , 130.13 , 129.93 , 124.21 , 124.09 , 120.54 , 119.20 , 116.28 , 114.42 , 105.87 , 55.51 , 43.45 , 40.66 , 37.26 , 26.63 , 25.23 . **HRMS** (EI) calcd for  $\text{C}_{21}\text{H}_{21}\text{NO}_2$  [M]: 320.1651; found: 320.1652.



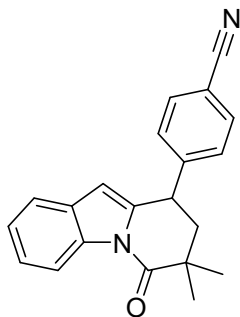
**7,7-dimethyl-9-(4-(trifluoromethyl)phenyl)-8,9-dihydropyrido[1,2-a]indol-6(7H)-one(3k):**

White solid (221.4 mg, 62% yield); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 8.41 (d, *J* = 8.0 Hz, 1H), 7.80 – 7.65 (m, 4H), 7.43 (d, *J* = 7.5 Hz, 1H), 7.29 – 7.17 (m, 2H), 5.83 (d, *J* = 1.9 Hz, 1H), 4.63 (dd, *J* = 13.4, 2.6 Hz, 1H), 2.48 (d, *J* = 13.4 Hz, 1H), 1.95 (dd, *J* = 13.1, 4.7 Hz, 1H), 1.40 (d, *J* = 30.8 Hz, 6H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 175.23 , 147.25, 142.48 , 135.17 , 130.04 , 129.90 , 128.41 (q, *J* = 31.1 Hz), 126.12 , 125.93 , 124.39 , 124.14 , 120.63 , 116.27 , 106.07 , 42.84 , 40.63 , 37.89 , 26.46 , 25.18 . <sup>19</sup>F NMR (376 MHz, DMSO-*d*<sub>6</sub>) δ -60.92 . HRMS (EI) calcd for C<sub>21</sub>H<sub>18</sub>NOF<sub>3</sub> [M]: 357.1343; found: 357.1348



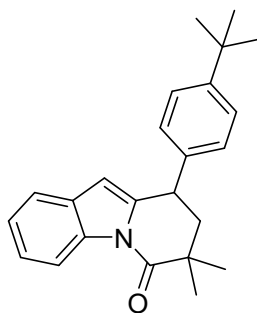
**7,7,9-trimethyl-9-phenyl-8,9-dihydropyrido[1,2-a]indol-6(7H)-one(3l):**

White solid (248.6 mg, 82% yield); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 8.48 – 8.41 (m, 1H), 7.68 – 7.64 (m, 1H), 7.36 – 7.30 (m, 2H), 7.28 – 7.23 (m, 2H), 7.21 – 7.16 (m, 1H), 7.11 – 7.04 (m, 2H), 6.75 (d, *J* = 0.7 Hz, 1H), 2.54 (d, *J* = 13.5 Hz, 1H), 2.32 (d, *J* = 14.2 Hz, 1H), 1.75 (s, 3H), 1.26 (s, 3H), 0.57 (s, 3H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 175.56 , 147.51 , 144.71 , 135.40 , 130.09 , 128.79 , 126.95 , 126.43 , 124.63 , 124.39 , 120.92 , 116.50 , 106.65 , 48.36 , 40.30 , 40.06 , 31.71 , 29.58 , 26.59 . HRMS (EI) calcd for C<sub>21</sub>H<sub>21</sub>NO [M]: 303.1618; found: 303.1623.



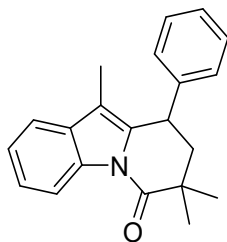
**4-(7,7-dimethyl-6-oxo-6,7,8,9-tetrahydropyrido[1,2-a]indol-9-yl)benzonitrile(3m):**

White solid (238.7 mg, 76% yield);  $^1\text{H NMR}$  (400 MHz, DMSO-*d*6)  $\delta$  8.38 (dd,  $J$  = 8.0, 1.0 Hz, 1H), 7.89 (d,  $J$  = 8.3 Hz, 2H), 7.70 (d,  $J$  = 8.4 Hz, 2H), 7.46 (d,  $J$  = 6.6 Hz, 1H), 7.30 – 7.20 (m, 2H), 5.83 (d,  $J$  = 1.2 Hz, 1H), 4.64 (ddd,  $J$  = 13.4, 4.7, 1.9 Hz, 1H), 2.49 (d,  $J$  = 5.2 Hz, 1H), 1.96 (dd,  $J$  = 13.1, 4.7 Hz, 1H), 1.40 (d,  $J$  = 31.6 Hz, 6H).  $^{13}\text{C NMR}$  (101 MHz, DMSO-*d*6)  $\delta$  175.24, 148.25, 142.28, 135.15, 133.07, 130.21, 130.01, 124.47, 124.20, 120.68, 119.30, 116.27, 110.59, 106.08, 42.55, 40.66, 38.09, 26.47, 25.22. **HRMS** (EI) calcd for  $\text{C}_{21}\text{H}_{18}\text{N}_2\text{O}$  [M]: 314.1419; found: 314.1424.



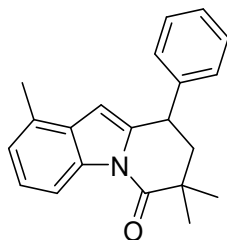
**9-(4-(tert-butyl)phenyl)-7,7-dimethyl-8,9-dihydropyrido[1,2-a]indol-6(7H)-one(3n):**

White solid (283.1 mg, 82% yield);  $^1\text{H NMR}$  (400 MHz, DMSO-*d*6)  $\delta$  8.39 (d,  $J$  = 8.1 Hz, 1H), 7.47 – 7.33 (m, 5H), 7.27 – 7.17 (m, 2H), 5.83 (d,  $J$  = 1.3 Hz, 1H), 4.43 (ddd,  $J$  = 13.4, 4.7, 2.0 Hz, 1H), 2.41 (t,  $J$  = 13.3 Hz, 1H), 1.91 (dd,  $J$  = 13.2, 4.7 Hz, 1H), 1.42 (s, 3H), 1.35 (s, 3H), 1.30 (s, 9H).  $^{13}\text{C NMR}$  (101 MHz, DMSO-*d*6)  $\delta$  175.42, 149.91, 143.50, 139.36, 135.19, 130.13, 128.56, 125.80, 124.23, 124.10, 120.60, 116.25, 105.92, 43.49, 40.65, 37.62, 34.70, 31.67, 26.60, 25.24. **HRMS** (EI) calcd for  $\text{C}_{24}\text{H}_{27}\text{NO}$  [M]: 345.2093; found: 345.2096.



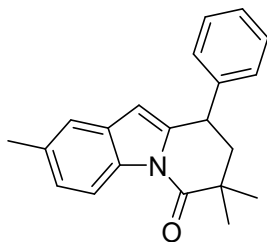
**7,7,10-trimethyl-9-phenyl-8,9-dihydropyrido[1,2-a]indol-6(7H)-one(3o):**

White oil (272.8 mg, 90% yield); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 8.41 (d, *J* = 7.4 Hz, 1H), 7.48 – 7.43 (m, 1H), 7.38 – 7.32 (m, 4H), 7.28 (ddd, *J* = 8.9, 7.3, 1.6 Hz, 3H), 4.53 (dd, *J* = 11.5, 5.2 Hz, 1H), 2.28 (t, *J* = 12.7 Hz, 1H), 2.05 (dd, *J* = 13.5, 5.5 Hz, 1H), 1.53 (d, *J* = 1.5 Hz, 3H), 1.31 (d, *J* = 27.7 Hz, 6H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 175.16 , 143.66 , 135.94 , 134.45 , 131.86 , 129.11 , 128.56 , 127.19 , 124.58 , 123.90 , 118.45 , 116.29 , 113.32 , 44.98 , 37.82 , 26.03 , 25.19 , 9.16 . HRMS (EI) calcd for C<sub>21</sub>H<sub>21</sub>NO [M]: 303.1618; found: 303.1623.



**1,7,7-trimethyl-9-phenyl-8,9-dihydropyrido[1,2-a]indol-6(7H)-one(3p):**

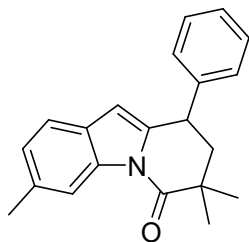
White solid (283.8 mg, 87% yield); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 8.22 (d, *J* = 8.3 Hz, 1H), 7.50 – 7.44 (m, 2H), 7.41 (t, *J* = 7.4 Hz, 2H), 7.36 – 7.32 (m, 1H), 7.16 (t, *J* = 7.8 Hz, 1H), 7.02 (d, *J* = 7.3 Hz, 1H), 5.82 (d, *J* = 1.2 Hz, 1H), 4.48 (ddd, *J* = 13.3, 4.7, 1.9 Hz, 1H), 2.45 (t, *J* = 13.2 Hz, 1H), 2.31 (s, 3H), 1.94 (dd, *J* = 13.2, 4.7 Hz, 1H), 1.40 (d, *J* = 29.5 Hz, 6H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 175.43 , 142.88 , 142.48 , 134.94 , 129.47 , 129.39 , 129.13 , 128.97 , 127.70 , 124.56 , 124.39 , 113.89 , 104.16 , 43.37 , 40.67 , 38.15 , 26.59 , 25.23 , 18.51 . HRMS (EI) calcd for C<sub>21</sub>H<sub>21</sub>NO [M]: 303.1618; found: 303.1629.



**2,7,7-trimethyl-9-phenyl-8,9-dihydropyrido[1,2-a]indol-6(7H)-one(3q):**

White oil (251.6 mg, 83% yield); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 8.25(d, *J* = 8.3 Hz, 1H), 7.42 (dt, *J* = 14.8, 7.6 Hz, 4H), 7.36 – 7.30 (m, 1H), 7.22 (s, 1H), 7.07 (d, *J* = 8.4 Hz, 1H), 5.73 (d, *J* = 1.9 Hz, 1H), 4.45 (dd, *J* = 13.0, 4.6 Hz, 1H), 2.44 (t, *J* = 13.2 Hz, 1H), 2.33 (s, 3H), 1.92 (dd, *J* = 13.1, 4.6 Hz, 1H), 1.39 (d, *J* = 29.4 Hz, 6H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 175.15 , 143.45 , 142.42 , 133.40 , 133.06 , 130.33 , 129.07 , 128.93 , 127.66 , 125.41 , 120.48 , 115.92 , 105.69 , 43.33 , 40.57 , 38.09 , 26.60 , 25.23 , 21.48 .

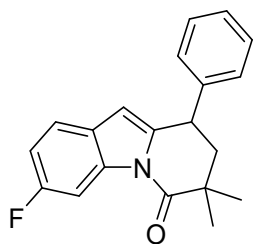
**HRMS** (EI) calcd for C<sub>21</sub>H<sub>21</sub>NO [M]: 303.1618; found: 303.1625.



**3,7,7-trimethyl-9-phenyl-8,9-dihydropyrido[1,2-a]indol-6(7H)-one(3r):**

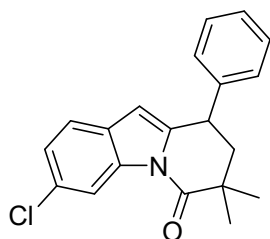
White oil (260.7 mg, 86% yield); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 8.24 (d, *J* = 0.9 Hz, 1H), 7.45 (dd, *J* = 8.3, 1.5 Hz, 2H), 7.43 – 7.37 (m, 2H), 7.37 – 7.28 (m, 2H), 7.04 (dd, *J* = 7.9, 0.9 Hz, 1H), 5.74 (d, *J* = 1.3 Hz, 1H), 4.45 (ddd, *J* = 13.4, 4.6, 1.9 Hz, 1H), 2.45 (d, *J* = 13.2 Hz, 1H), 2.41 (s, 3H), 1.93 (dd, *J* = 13.2, 4.6 Hz, 1H), 1.39 (d, *J* = 29.9 Hz, 6H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 175.37 , 142.72 , 142.42 , 135.58 , 133.59 , 129.06 , 128.92 , 127.81 , 127.65 , 125.33 , 120.19 , 116.53 , 105.78 , 43.23 , 40.64 , 38.06 , 26.63 , 25.25, 22.00 . **HRMS** (EI) calcd for C<sub>21</sub>H<sub>21</sub>NO [M]: 303.1618; found: 303.1627.





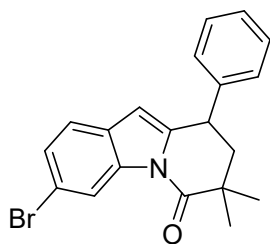
**3-fluoro-7,7-dimethyl-9-phenyl-8,9-dihydropyrido[1,2-a]indol-6(7H)-one(3s):**

White solid (248.8 mg, 81% yield); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 8.13 (dd, *J* = 10.4, 2.5 Hz, 1H), 7.50 – 7.44 (m, 3H), 7.41 (t, *J* = 7.4 Hz, 2H), 7.36 – 7.32 (m, 1H), 7.10 (ddd, *J* = 9.6, 8.6, 2.5 Hz, 1H), 5.83 (dd, *J* = 2.0, 0.7 Hz, 1H), 4.47 (ddd, *J* = 13.3, 4.7, 1.9 Hz, 1H), 2.47 (d, *J* = 13.3 Hz, 1H), 1.94 (dd, *J* = 13.1, 4.6 Hz, 1H), 1.41 (d, *J* = 32.2 Hz, 6H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 175.61, 160.11 (d, *J* = 237.2 Hz), 144.07 (d, *J* = 3.9 Hz), 142.22, 135.05 (d, *J* = 13.0 Hz), 129.01 (d, *J* = 16.0 Hz), 127.72, 126.67, 121.58 (d, *J* = 9.6 Hz), 112.05, 111.81, 105.53, 103.43, 103.14, 43.05, 40.69, 38.04, 26.45, 25.20. <sup>19</sup>F NMR (376 MHz, DMSO-*d*<sub>6</sub>) δ -118.10. HRMS (EI) calcd for C<sub>20</sub>H<sub>18</sub>NOF [M]: 307.1372; found: 307.1376.



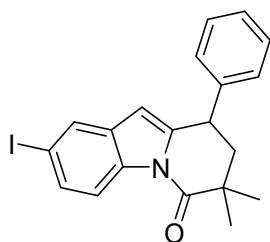
**3-chloro-7,7-dimethyl-9-phenyl-8,9-dihydropyrido[1,2-a]indol-6(7H)-one(3t):**

White solid (245.6 mg, 76% yield); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 8.41 (d, *J* = 1.9 Hz, 1H), 7.47 (t, *J* = 7.9 Hz, 3H), 7.41 (t, *J* = 7.3 Hz, 2H), 7.34 (t, *J* = 7.0 Hz, 1H), 7.27 (dd, *J* = 8.4, 2.0 Hz, 1H), 5.85 (d, *J* = 1.8 Hz, 1H), 4.48 (ddd, *J* = 13.5, 4.7, 2.0 Hz, 1H), 2.47 (d, *J* = 13.3 Hz, 1H), 1.94 (dd, *J* = 13.2, 4.6 Hz, 1H), 1.40 (d, *J* = 31.9 Hz, 6H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 175.62, 144.53, 142.11, 135.46, 129.10, 128.95, 128.68, 127.75, 124.26, 121.90, 115.98, 105.61, 42.98, 40.72, 38.04, 26.43, 25.17. HRMS (EI) calcd for C<sub>20</sub>H<sub>18</sub>NOCl [M]: 323.1077; found: 323.1071.



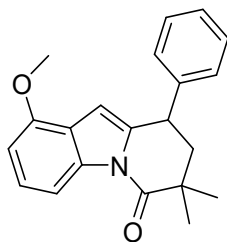
**3-bromo-7,7-dimethyl-9-phenyl-8,9-dihydropyrido[1,2-a]indol-6(7H)-one(3u):**

White solid (268.0 mg, 73% yield); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 8.56 (d, *J* = 1.9 Hz, 1H), 7.46 (d, *J* = 7.3 Hz, 2H), 7.43 – 7.36 (m, 4H), 7.34 (t, *J* = 7.2 Hz, 1H), 5.84 (d, *J* = 1.9 Hz, 1H), 4.47 (ddd, *J* = 13.6, 4.7, 2.0 Hz, 1H), 2.47 (d, *J* = 13.3 Hz, 1H), 1.94 (dd, *J* = 13.1, 4.6 Hz, 1H), 1.40 (d, *J* = 31.9 Hz, 6H). <sup>13</sup>C NMR (101 MHz, ) δ 175.62 , 144.43 , 142.09 , 135.83 , 129.11 , 128.94 , 127.75 , 126.93 , 122.32 , 118.81 , 116.75 , 105.66 , 42.97 , 40.72 , 38.02 , 26.42 , 25.17 . HRMS (EI) calcd for C<sub>20</sub>H<sub>18</sub>NOBr [M]: 367.0572; found: 367.0578.



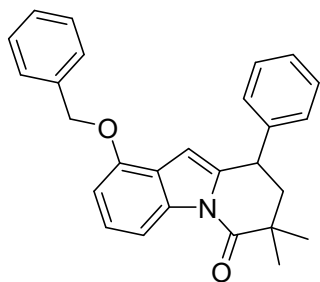
**2-iodo-7,7-dimethyl-9-phenyl-8,9-dihydropyrido[1,2-a]indol-6(7H)-one(3v):**

White solid (311.3 mg, 75% yield); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 8.18 (d, *J* = 8.6 Hz, 1H), 7.86 (d, *J* = 1.7 Hz, 1H), 7.56 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.47 – 7.44 (m, 2H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.34 (t, *J* = 7.1 Hz, 1H), 5.80 (d, *J* = 1.3 Hz, 1H), 4.49 (ddd, *J* = 13.5, 4.7, 1.9 Hz, 1H), 2.46 (s, 1H), 1.93 (dd, *J* = 13.2, 4.7 Hz, 1H), 1.39 (d, *J* = 32.6 Hz, 6H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 175.48 , 144.63 , 142.19 , 134.44 , 132.66 , 132.43 , 129.13 , 128.97 , 127.76 , 118.29 , 104.91 , 88.74 , 43.09 , 40.74 , 37.99 , 26.46 , 25.18 . HRMS (EI) calcd for C<sub>20</sub>H<sub>18</sub>NOI [M]: 415.0433; found: 415.0428.



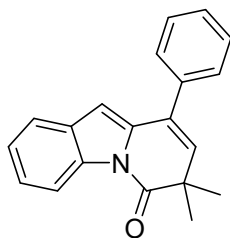
**1-methoxy-7,7-dimethyl-9-phenyl-8,9-dihydropyrido[1,2-a]indol-6(7H)-one(3w):**

White solid (217.1 mg, 68% yield); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 8.01 (d, *J* = 8.3 Hz, 1H), 7.46 – 7.37 (m, 4H), 7.36 – 7.31 (m, 1H), 7.21 (t, *J* = 8.1 Hz, 1H), 6.78 (d, *J* = 7.9 Hz, 1H), 5.76 (d, *J* = 1.9 Hz, 1H), 4.44 (ddd, *J* = 13.4, 4.6, 2.0 Hz, 1H), 3.79 (s, 3H), 2.45 (t, *J* = 13.3 Hz, 1H), 1.93 (dd, *J* = 13.2, 4.6 Hz, 1H), 1.40 (d, *J* = 26.8 Hz, 6H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 175.50, 152.25, 142.33, 141.97, 136.26, 129.04, 128.88, 127.67, 125.47, 119.72, 109.46, 105.12, 102.54, 55.63, 43.03, 40.70, 38.03, 26.57, 25.20. HRMS (EI) calcd for C<sub>21</sub>H<sub>21</sub>NO<sub>2</sub> [M]: 319.1578; found: 319.1583.



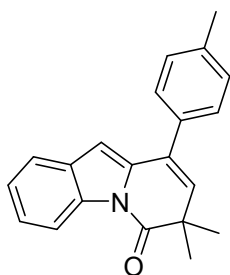
**1-(benzyloxy)-7,7-dimethyl-9-phenyl-8,9-dihydropyrido[1,2-a]indol-6(7H)-one(3x):**

White solid (264.8 mg, 67% yield); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 8.01 (d, *J* = 8.3 Hz, 1H), 7.47 – 7.42 (m, 2H), 7.42 – 7.37 (m, 4H), 7.36 – 7.33 (m, 2H), 7.32 – 7.26 (m, 2H), 7.19 (t, *J* = 8.1 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 5.78 (d, *J* = 1.9 Hz, 1H), 5.15 (d, *J* = 2.0 Hz, 2H), 4.45 (ddd, *J* = 13.4, 4.6, 2.0 Hz, 1H), 2.45 (t, *J* = 13.3 Hz, 1H), 1.93 (dd, *J* = 13.2, 4.6 Hz, 1H), 1.39 (d, *J* = 27.1 Hz, 6H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 175.52, 151.26, 142.38, 142.09, 137.50, 136.38, 129.10, 128.92, 128.89, 128.26, 127.98, 127.71, 125.40, 120.07, 109.66, 106.62, 102.47, 69.75, 43.16, 40.71, 38.06, 26.55, 25.20. HRMS (EI) calcd for C<sub>27</sub>H<sub>25</sub>NO<sub>2</sub> [M]: 395.1885; found: 395.1888.



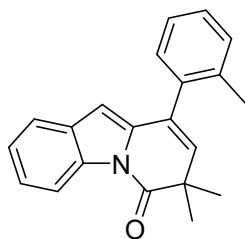
**7,7-dimethyl-9-phenylpyrido[1,2-a]indol-6(7H)-one(5a):**

Light yellow solid (269.9 mg, 94% yield);  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  8.44 (d,  $J = 8.1$  Hz, 1H), 7.62 (d,  $J = 7.6$  Hz, 1H), 7.56 (d,  $J = 7.5$  Hz, 2H), 7.53 – 7.45 (m, 3H), 7.37 (d,  $J = 8.1$  Hz, 1H), 7.30 (t,  $J = 7.5$  Hz, 1H), 6.57 (s, 1H), 6.07 (s, 1H), 1.48 (s, 6H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{DMSO-}d_6$ )  $\delta$  174.22 , 137.34 , 136.71 , 135.36 , 134.87 , 130.56 , 129.13 , 128.78 , 128.64 , 127.87 , 125.80 , 124.74 , 121.52 , 116.09 , 106.60 , 43.08 , 27.20 . **HRMS** (EI) calcd for  $\text{C}_{20}\text{H}_{17}\text{NO}$  [M]: 287.1316; found: 287.1319.



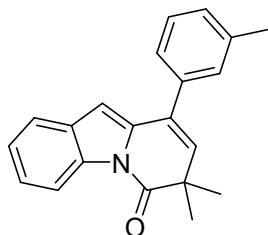
**7,7-dimethyl-9-(p-tolyl)pyrido[1,2-a]indol-6(7H)-one(5b):**

Light yellow solid (262.0 mg, 87% yield);  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  8.43 (dd,  $J = 8.1, 1.0$  Hz, 1H), 7.61 (d,  $J = 7.6$  Hz, 1H), 7.44 (d,  $J = 8.1$  Hz, 2H), 7.39 – 7.35 (m, 1H), 7.33 – 7.27 (m, 3H), 6.56 (s, 1H), 6.03 (s, 1H), 2.38 (s, 3H), 1.46 (s, 6H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{DMSO-}d_6$ )  $\delta$  174.26 , 138.10 , 136.86 , 134.92 , 134.45 , 132.76 , 130.57 , 129.65 , 128.52 , 127.72 , 125.77 , 124.72 , 121.49 , 116.09 , 106.57 , 43.06 , 27.23 , 21.28 . **HRMS** (EI) calcd for  $\text{C}_{21}\text{H}_{19}\text{NO}$  [M]: 301.1467; found: 301.1461.



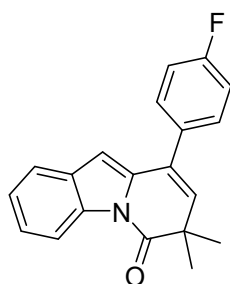
**7,7-dimethyl-9-(o-tolyl)pyrido[1,2-a]indol-6(7H)-one(5c):**

Light yellow solid (259.0 mg, 86% yield);  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  8.44 (d,  $J = 8.1$  Hz, 1H), 7.57 – 7.38 (m, 1H), 7.34 – 7.11 (m, 6H), 6.00 (s, 1H), 5.82 (s, 1H), 2.21 (s, 3H), 1.44 (s, 6H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{DMSO-}d_6$ )  $\delta$  174.17 , 137.42 , 136.59 , 136.34 , 135.62 , 134.89 , 130.64 , 130.58 , 129.91 , 128.58 , 127.04 , 126.24 , 125.59 , 124.57 , 121.27 , 116.11 , 106.26 , 43.06 , 27.08 (d,  $J = 51.2$  Hz), 19.70 . **HRMS** (EI) calcd for  $\text{C}_{21}\text{H}_{19}\text{NO}$  [M]: 301.1467; found: 301.1463.



**7,7-dimethyl-9-(m-tolyl)pyrido[1,2-a]indol-6(7H)-one(5d):**

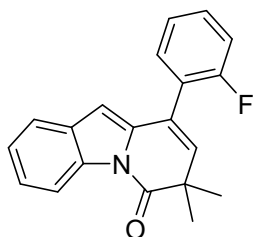
Light yellow solid (256.0 mg, 85% yield);  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  8.45 (dd,  $J = 8.1, 1.0$  Hz, 1H), 7.59 – 7.53 (m, 1H), 7.38 – 7.19 (m, 6H), 6.53 (s, 1H), 6.00 (s, 1H), 2.37 (s, 3H), 1.45 (s, 6H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{DMSO-}d_6$ )  $\delta$  174.17 , 138.33 , 137.31 , 136.76 , 135.07 , 134.91 , 130.55 , 129.33 , 129.17 , 128.90 , 127.99 , 125.71 , 124.66 , 121.43 , 116.12 , 106.61 , 43.03 , 27.18 , 21.46 . **HRMS** (EI) calcd for  $\text{C}_{21}\text{H}_{19}\text{NO}$  [M]: 301.1467; found: 301.1464.



**9-(4-fluorophenyl)-7,7-dimethylpyrido[1,2-a]indol-6(7H)-one(5e):**

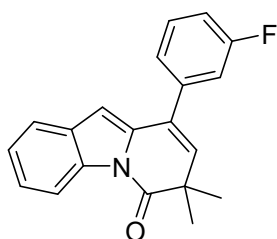
Light yellow solid (241.0 mg, 79% yield);  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  8.43 (dd,  $J = 8.1, 1.0$  Hz, 1H), 7.63 – 7.55 (m, 3H), 7.38 (td,  $J = 8.3, 7.8, 1.4$  Hz, 1H), 7.32 (t,  $J = 8.9$  Hz, 3H), 6.54 (s, 1H), 6.06 (s, 1H), 1.47 (s, 6H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{DMSO-}d_6$ )  $\delta$  174.17 , 162.49 (d,  $J = 244.9$  Hz), 136.65 , 135.53 , 134.88 , 133.69 (d,  $J = 3.3$  Hz), 130.76 (d,  $J = 8.2$  Hz), 130.52 , 126.88 , 125.86 , 124.76 , 121.52 , 116.09 , 115.87 , 106.61 , 43.10 , 27.15

.  $^{19}\text{F}$  NMR (376 MHz,  $\text{DMSO-}d_6$ )  $\delta$  -113.74 .HRMS (EI) calcd for  $\text{C}_{20}\text{H}_{16}\text{NOF}$  [M]: 305.1216; found: 305.1213.



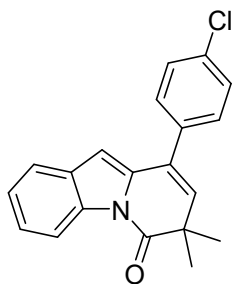
**9-(2-fluorophenyl)-7,7-dimethylpyrido[1,2-a]indol-6(7H)-one(5f):**

Light yellow solid (231.9 mg, 76% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  8.29 (d,  $J = 8.1$  Hz, 1H), 7.38 – 7.25 (m, 3H), 7.19 – 7.04 (m, 4H), 6.11 (d,  $J = 1.4$  Hz, 1H), 5.86 (s, 1H), 1.28 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{DMSO-}d_6$ )  $\delta$  173.86 , 159.85 (d,  $J = 246.4$  Hz), 137.17 , 136.27 , 134.84 , 131.75 (d,  $J = 3.3$  Hz), 130.91 (d,  $J = 8.1$  Hz), 130.46 , 125.74 , 125.06 (d,  $J = 3.5$  Hz), 124.67 , 122.28 , 121.33 , 116.45 , 116.23 , 116.15 , 106.40 , 43.17 , 26.99 .  $^{19}\text{F}$  NMR (376 MHz,  $\text{DMSO-}d_6$ )  $\delta$  -114.08 .HRMS (EI) calcd for  $\text{C}_{20}\text{H}_{16}\text{NOF}$  [M]: 305.1216; found: 305.1211.



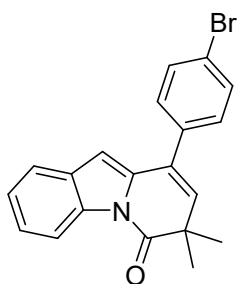
**9-(3-fluorophenyl)-7,7-dimethylpyrido[1,2-a]indol-6(7H)-one(5g):**

Light yellow solid (228.8 mg, 75% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  8.43 (d,  $J = 8.1$  Hz, 1H), 7.60 (d,  $J = 7.7$  Hz, 1H), 7.53 (td,  $J = 8.1, 6.2$  Hz, 1H), 7.42 – 7.34 (m, 3H), 7.32 – 7.25 (m, 2H), 6.59 (s, 1H), 6.12 (s, 1H), 1.46 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{DMSO-}d_6$ )  $\delta$  174.05 , 162.63 (d,  $J = 244.2$  Hz), 139.66 (d,  $J = 8.2$  Hz), 136.15 , 135.99 , 134.89 , 131.13 (d,  $J = 8.7$  Hz), 130.51 , 126.83 (d,  $J = 1.9$  Hz), 125.88 , 124.82 (d,  $J = 2.7$  Hz), 124.75 , 121.55 , 116.10 , 115.66 (d,  $J = 5.9$  Hz), 115.45 (d,  $J = 6.9$  Hz), 106.64 , 43.10 , 27.07 .  $^{19}\text{F}$  NMR (376 MHz,  $\text{DMSO-}d_6$ )  $\delta$  -112.74 .HRMS (EI) calcd for  $\text{C}_{20}\text{H}_{16}\text{NOF}$  [M]: 305.1216; found: 305.1215.



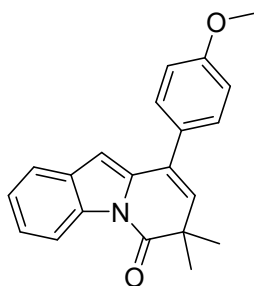
**9-(4-chlorophenyl)-7,7-dimethylpyrido[1,2-a]indol-6(7H)-one(5h):**

Light yellow solid (231.2 mg, 72% yield);  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  8.43 (d,  $J = 8.1$  Hz, 1H), 7.63 – 7.54 (m, 5H), 7.38 (ddd,  $J = 8.3, 7.3, 1.4$  Hz, 1H), 7.31 (td,  $J = 7.5, 1.1$  Hz, 1H), 6.57 (s, 1H), 6.10 (s, 1H), 1.47 (s, 6H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{DMSO-}d_6$ )  $\delta$  174.10, 136.33, 136.15, 135.76, 134.89, 133.41, 130.51, 129.15, 126.81, 125.90, 124.78, 121.53, 116.10, 106.63, 43.13, 27.11. **HRMS** (EI) calcd for  $\text{C}_{20}\text{H}_{16}\text{NOCl}$  [M]: 321.0941; found: 321.0945.



**9-(4-bromophenyl)-7,7-dimethylpyrido[1,2-a]indol-6(7H)-one(5i):**

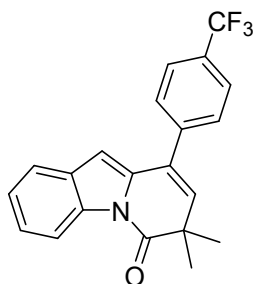
Light yellow solid (251.9 mg, 69% yield);  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  8.47 (d,  $J = 8.1$  Hz, 1H), 7.68 (d,  $J = 7.8$  Hz, 2H), 7.60 (d,  $J = 7.7$  Hz, 1H), 7.50 (d,  $J = 8.4$  Hz, 2H), 7.41 – 7.36 (m, 1H), 7.31 (t,  $J = 7.5$  Hz, 1H), 6.56 (s, 1H), 6.08 (d,  $J = 1.2$  Hz, 1H), 1.48 (s, 6H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{DMSO-}d_6$ )  $\delta$  174.03, 136.49, 136.22, 135.65, 134.91, 132.04, 130.76, 130.48, 126.91, 125.87, 124.74, 121.48, 116.12, 106.64, 43.11, 27.08. **HRMS** (EI) calcd for  $\text{C}_{20}\text{H}_{16}\text{NOBr}$  [M]: 365.0415; found: 365.0414.



**9-(4-methoxyphenyl)-7,7-dimethylpyrido[1,2-a]indol-6(7H)-one(5j):**

Light yellow solid (180.8 mg, 57% yield);  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  8.45 (d,  $J = 8.1$  Hz, 1H), 7.54 (d,  $J = 7.5$  Hz, 1H), 7.47 – 7.42 (m, 1H), 7.35 (td,  $J = 8.4, 7.9, 1.3$  Hz, 1H), 7.28 (ddd,  $J = 16.3, 7.4, 1.4$  Hz, 2H), 7.15 (dd,  $J = 8.4, 1.0$  Hz, 1H), 7.05 (td,  $J = 7.4, 1.1$  Hz, 1H), 6.17 (s, 1H), 5.94 (s, 1H), 3.76 (s, 3H), 1.47 (s, 6H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{DMSO-}d_6$ )  $\delta$  174.26 , 157.35 , 137.20 , 135.99 , 134.66 , 131.16 , 130.69 , 130.27 , 125.95 , 125.47 , 125.07 , 124.62 , 121.27 , 120.96 , 116.07 , 112.12 , 106.09 , 55.95 , 43.07 , 27.20

.**HRMS** (EI) calcd for  $\text{C}_{21}\text{H}_{19}\text{NO}_2$  [M]: 317.1416; found: 317.1413.

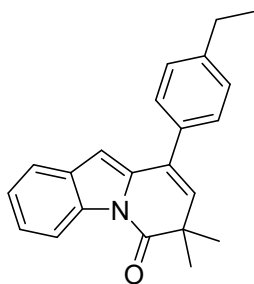


**7,7-dimethyl-9-(4-(trifluoromethyl)phenyl)pyrido[1,2-a]indol-6(7H)-one(5k):**

Light yellow solid (223.7 mg, 63% yield);  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  8.39 (d,  $J = 8.2$  Hz, 1H), 7.79 (d,  $J = 8.2$  Hz, 2H), 7.71 (d,  $J = 8.1$  Hz, 2H), 7.54 (dt,  $J = 7.5, 1.0$  Hz, 1H), 7.34 – 7.30 (m, 1H), 7.24 (td,  $J = 7.5, 1.2$  Hz, 1H), 6.52 (s, 1H), 6.10 (s, 1H), 1.42 (s, 6H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{DMSO-}d_6$ )  $\delta$  173.96 , 141.44 , 136.46 , 135.99 , 134.90 , 130.48 , 129.54 , 129.39 , 129.07 , 126.90 , 126.01 (q,  $J = 4.5$  Hz), 124.77 , 123.57 (q,  $J = 17.5$  Hz), 121.53 , 116.12 , 106.70 , 43.18 , 27.02 .  $^{19}\text{F NMR}$  (376 MHz,  $\text{DMSO-}d_6$ )  $\delta$  -61.09

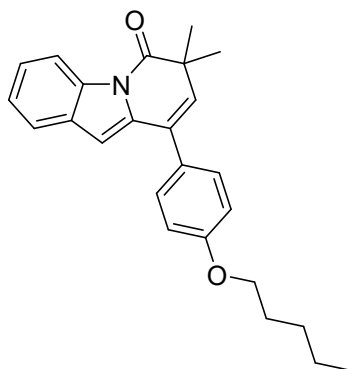
.**HRMS** (EI) calcd for  $\text{C}_{21}\text{H}_{16}\text{NOF}_3$  [M]: 355.1184; found: 355.1186.





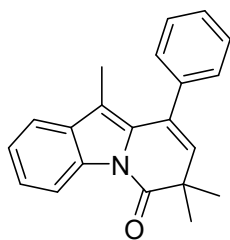
**9-(4-ethylphenyl)-7,7-dimethylpyrido[1,2-a]indol-6(7H)-one(5l):**

Light yellow solid (255.3 mg, 81% yield);  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  8.43 (d,  $J = 8.1$  Hz, 1H), 7.61 (dt,  $J = 7.6, 1.0$  Hz, 1H), 7.50 – 7.43 (m, 2H), 7.37 (ddd,  $J = 8.3, 7.2, 1.4$  Hz, 1H), 7.34 – 7.27 (m, 3H), 6.57 (s, 1H), 6.03 (s, 1H), 2.67 (q,  $J = 7.6$  Hz, 2H), 1.46 (s, 6H), 1.23 (t,  $J = 7.6$  Hz, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{DMSO-}d_6$ )  $\delta$  174.25, 144.39, 136.83, 134.95, 134.88, 134.71, 130.58, 128.57, 128.47, 127.74, 125.76, 124.71, 121.49, 116.09, 106.61, 43.05, 28.40, 27.23, 16.05. **HRMS** (EI) calcd for  $\text{C}_{22}\text{H}_{21}\text{NO}$  [M]: 315.1623; found: 315.1627.



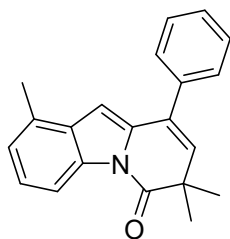
**7,7-dimethyl-9-(4-(pentyloxy)phenyl)pyrido[1,2-a]indol-6(7H)-one(5m):**

Light yellow solid (276.2 mg, 74% yield);  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  8.44 (d,  $J = 8.1$  Hz, 1H), 7.56 (d,  $J = 7.6$  Hz, 1H), 7.40 (d,  $J = 8.7$  Hz, 2H), 7.36 – 7.32 (m, 1H), 7.26 (td,  $J = 7.5, 1.1$  Hz, 1H), 6.97 (d,  $J = 8.7$  Hz, 2H), 6.52 (s, 1H), 5.93 (s, 1H), 3.94 (t,  $J = 6.5$  Hz, 2H), 1.74 – 1.66 (m, 2H), 1.43 (s, 6H), 1.40 – 1.29 (m, 4H), 0.88 (t,  $J = 7.0$  Hz, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{DMSO-}d_6$ )  $\delta$  174.20, 159.16, 137.01, 134.92, 134.38, 130.55, 129.73, 129.39, 127.46, 125.66, 124.63, 121.36, 116.10, 114.86, 106.54, 67.94, 42.98, 28.86, 28.18, 27.21, 22.38, 14.33. **HRMS** (EI) calcd for  $\text{C}_{25}\text{H}_{27}\text{NO}_2$  [M]: 373.2042; found: 373.2045.



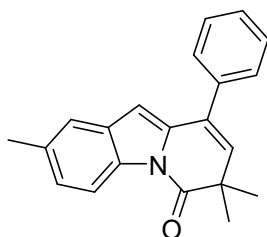
**7,7,10-trimethyl-9-phenylpyrido[1,2-a]indol-6(7H)-one(5n):**

Light yellow oily (268.0 mg, 89% yield);  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  8.44 (dt,  $J = 8.2, 0.9$  Hz, 1H), 7.49 – 7.38 (m, 4H), 7.37 – 7.29 (m, 3H), 7.25 (td,  $J = 7.5, 1.1$  Hz, 1H), 5.76 (s, 1H), 1.58 (s, 3H), 1.40 (s, 6H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{DMSO-}d_6$ )  $\delta$  173.84 , 138.42 , 135.50 , 134.04 , 132.46 , 131.10 , 129.22 , 129.10 , 128.77 , 128.38 , 126.16 , 124.35 , 119.23 , 115.95 , 114.95 , 42.49 , 27.20 , 10.17 . **HRMS** (EI) calcd for  $\text{C}_{21}\text{H}_{19}\text{NO}$  [M]: 301.1467; found: 301.1461.



**1,7,7-trimethyl-9-phenylpyrido[1,2-a]indol-6(7H)-one(5o):**

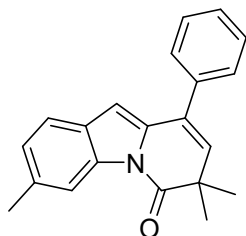
White solid (253.0 mg, 84% yield);  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  8.26 (d,  $J = 8.3$  Hz, 1H), 7.56 (dd,  $J = 8.1, 1.7$  Hz, 2H), 7.53 – 7.42 (m, 3H), 7.26 (t,  $J = 7.8$  Hz, 1H), 7.11 (d,  $J = 7.3$  Hz, 1H), 6.54 (s, 1H), 6.04 (s, 1H), 2.43 (s, 3H), 1.46 (s, 6H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{DMSO-}d_6$ )  $\delta$  174.26 , 137.42 , 136.19 , 135.23 , 134.67 , 130.59 , 129.96 , 129.18 , 128.76 , 128.66 , 127.95 , 125.93 , 125.13 , 113.68 , 104.97 , 43.08 , 27.22 , 18.57 . **HRMS** (EI) calcd for  $\text{C}_{21}\text{H}_{19}\text{NO}$  [M]: 301.1467; found: 301.1463.



**2,7,7-trimethyl-9-phenylpyrido[1,2-a]indol-6(7H)-one(5p):**

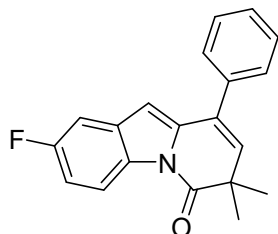
Light yellow solid (259.0 mg, 86% yield);  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  8.29 (d,  $J = 8.3$  Hz, 1H), 7.54 (dd,  $J = 8.2, 1.7$  Hz, 2H), 7.52 – 7.43 (m, 3H), 7.41 – 7.37 (m, 1H),

7.19 (dd,  $J = 8.3, 1.7$  Hz, 1H), 6.48 (s, 1H), 6.05 (s, 1H), 2.39 (s, 3H), 1.46 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz, DMSO- $d_6$ )  $\delta$  173.98, 137.38, 136.76, 135.29, 133.80, 133.08, 130.79, 129.13, 128.76, 128.63, 127.89, 126.97, 121.34, 115.77, 106.38, 42.99, 27.21, 21.51. HRMS (EI) calcd for  $\text{C}_{21}\text{H}_{19}\text{NO}$  [M]: 301.1467; found: 301.1465.



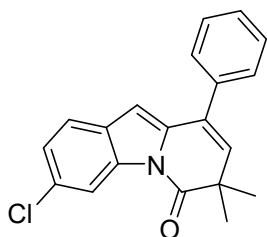
**3,7,7-trimethyl-9-phenylpyrido[1,2-a]indol-6(7H)-one(5q):**

Light yellow solid (262.0 mg, 87% yield);  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  8.29 (s, 1H), 7.54 (dd,  $J = 8.0, 1.8$  Hz, 2H), 7.48 (q,  $J = 8.9, 7.9$  Hz, 4H), 7.14 (d,  $J = 8.1$  Hz, 1H), 6.50 (s, 1H), 6.02 (s, 1H), 2.45 (s, 3H), 1.46 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz, DMSO- $d_6$ )  $\delta$  174.19, 137.41, 136.13, 135.42, 135.28, 134.73, 129.10, 128.73, 128.62, 128.27, 127.98, 125.99, 121.11, 116.34, 106.56, 43.04, 27.23, 22.11. HRMS (EI) calcd for  $\text{C}_{21}\text{H}_{19}\text{NO}$  [M]: 301.1467; found: 301.1462.



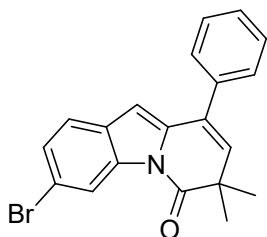
**2-fluoro-7,7-dimethyl-9-phenylpyrido[1,2-a]indol-6(7H)-one(5r):**

Light yellow solid (234.9 mg, 77% yield);  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  8.41 (dd,  $J = 9.0, 4.8$  Hz, 1H), 7.58 – 7.40 (m, 6H), 7.21 (td,  $J = 9.3, 2.7$  Hz, 1H), 6.56 (s, 1H), 6.12 (s, 1H), 1.48 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz, DMSO- $d_6$ )  $\delta$  174.10, 159.72 (d,  $J = 238.4$  Hz), 138.38, 137.12, 136.20, 132.00, 131.38, 129.16, 128.85, 128.65, 127.66, 117.33 (d,  $J = 9.3$  Hz), 113.28, 113.03, 107.25, 107.01, 106.20 (d,  $J = 3.6$  Hz), 43.07, 27.10.  $^{19}\text{F}$  NMR (376 MHz, DMSO- $d_6$ )  $\delta$  -118.23. HRMS (EI) calcd for  $\text{C}_{20}\text{H}_{16}\text{NOF}$  [M]: 305.1216; found: 305.1218.



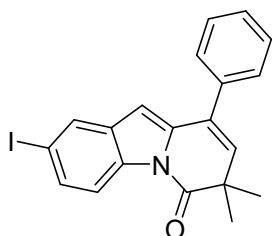
**3-chloro-7,7-dimethyl-9-phenylpyrido[1,2-a]indol-6(7H)-one(5s):**

Light yellow solid (244.0 mg, 76% yield);  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  8.44 (d,  $J = 2.0$  Hz, 1H), 7.62 (d,  $J = 8.3$  Hz, 1H), 7.56 – 7.46 (m, 5H), 7.34 (dd,  $J = 8.4, 2.0$  Hz, 1H), 6.58 (s, 1H), 6.10 (s, 1H), 1.48 (s, 6H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{DMSO-}d_6$ )  $\delta$  174.16 , 137.43 , 137.08 , 135.53 , 135.13 , 130.07 , 129.30 , 129.03 , 128.73 , 128.53 , 127.76 , 124.76 , 122.51 , 115.85 , 106.15 , 43.08 , 27.03 . **HRMS** (EI) calcd for  $\text{C}_{20}\text{H}_{16}\text{NOCl}$  [M]: 321.0941; found: 321.0943.



**3-bromo-7,7-dimethyl-9-phenylpyrido[1,2-a]indol-6(7H)-one(5t):**

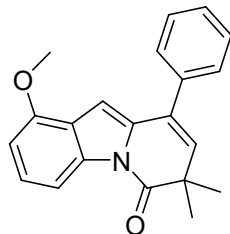
Light yellow solid (255.5 mg, 70% yield);  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  8.60 (d,  $J = 1.8$  Hz, 1H), 7.57 – 7.44 (m, 7H), 6.60 – 6.53 (m, 1H), 6.10 (s, 1H), 1.48 (s, 6H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{DMSO-}d_6$ )  $\delta$  174.28 , 137.36 , 137.08 , 135.74 , 135.47 , 129.67 , 129.10 , 128.80 , 128.58 , 127.70 , 127.53 , 123.05 , 118.66 , 118.19 , 106.23 , 43.14 , 27.05 . **HRMS** (EI) calcd for  $\text{C}_{20}\text{H}_{16}\text{NOBr}$  [M]: 365.0415; found: 365.0412.



**2-iodo-7,7-dimethyl-9-phenylpyrido[1,2-a]indol-6(7H)-one(5u):**

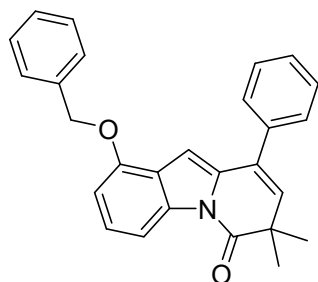
Light yellow solid (301.5 mg, 73% yield);  $^1\text{H NMR}$  (400 MHz,  $\text{DMSO-}d_6$ )  $\delta$  8.22 (d,  $J = 8.6$  Hz, 1H), 8.01 (d,  $J = 1.7$  Hz, 1H), 7.67 (dd,  $J = 8.6, 1.7$  Hz, 1H), 7.55 – 7.44 (m, 5H), 6.53 (s, 1H), 6.11 (s, 1H), 1.47 (s, 6H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{DMSO-}d_6$ )  $\delta$  174.25 ,

137.55 , 137.13 , 136.23 , 134.13 , 133.91 , 133.10 , 129.93 , 129.17 , 128.86 , 128.63 , 127.57 , 118.10 , 105.44 , 89.39 , 43.19 , 27.11 .**HRMS** (EI) calcd for C<sub>20</sub>H<sub>16</sub>NOI [M]: 413.0277; found: 413.0272.



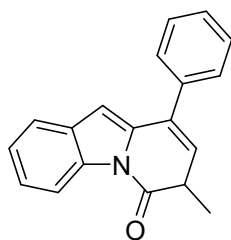
**1-methoxy-7,7-dimethyl-9-phenylpyrido[1,2-a]indol-6(7H)-one(5v):**

Light yellow solid (196.6 mg, 62% yield);<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 8.02 (d, *J* = 8.2 Hz, 1H), 7.56 – 7.44 (m, 5H), 7.33 (t, *J* = 8.1 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 6.45 (s, 1H), 6.04 (s, 1H), 3.87 (s, 3H), 1.47 (s, 6H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 174.40 , 152.84 , 137.27 , 135.88 , 135.47 , 134.80 , 129.14 , 128.79 , 128.60 , 127.82 , 127.21 , 120.21 , 109.16 , 105.75 , 103.00 , 55.86 , 43.19 , 27.22 .**HRMS** (EI) calcd for C<sub>21</sub>H<sub>19</sub>NO<sub>2</sub> [M]: 317.1416; found: 317.1412.



**1-(benzyloxy)-7,7-dimethyl-9-phenylpyrido[1,2-a]indol-6(7H)-one(5w):**

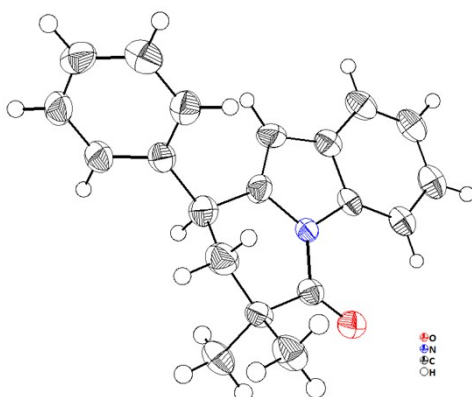
White solid (269.9 mg, 69% yield);<sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 8.02 (d, *J* = 8.2 Hz, 1H), 7.55 – 7.43 (m, 7H), 7.40 – 7.35 (m, 2H), 7.34 – 7.28 (m, 2H), 6.96 (d, *J* = 8.1 Hz, 1H), 6.44 (s, 1H), 6.04 (s, 1H), 5.24 (s, 2H), 1.47 (s, 6H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 174.40 , 151.82 , 137.42 , 137.32 , 136.01 , 135.59 , 134.99 , 129.19 , 128.95 , 128.82 , 128.61 , 128.35 , 128.09 , 127.83 , 127.11 , 120.59 , 109.35 , 107.27 , 102.94 , 69.91 , 43.19 , 27.22 .**HRMS** (EI) calcd for C<sub>27</sub>H<sub>23</sub>NO<sub>2</sub> [M]: 392.1729; found: 392.1722.



**7-methyl-9-phenylpyrido[1,2-a]indol-6(7H)-one(5x):**

Light yellow solid (237.6 mg, 87% yield); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 8.45 (d, *J* = 8.2 Hz, 1H), 7.93 (d, *J* = 3.8 Hz, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.66 – 7.60 (m, 2H), 7.43 (d, *J* = 7.1 Hz, 2H), 7.39 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.35 – 7.31 (m, 1H), 6.86 (d, *J* = 3.7 Hz, 1H), 6.74 (d, *J* = 8.6 Hz, 1H), 4.64 – 4.51 (m, 1H), 1.50 (d, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 172.49 , 138.52 , 135.70 , 131.23 , 130.76 , 129.66 , 129.05 , 127.88 , 126.83 , 126.28 , 125.33 , 124.23 , 121.45 , 116.58 , 109.52 , 43.79 , 17.42 . HRMS (EI) calcd for C<sub>19</sub>H<sub>15</sub>NO [M]: 273.1154; found: 273.1157.

## 7. Crystal Data and Structure Refinements



**Figure 9** Structure of **3a** by X-Ray crystallographic (CCDC = 2158451 )

Single crystal suitable for X-ray diffraction was obtained by slow evaporation of a saturated solution of compound **3a** (cyclohexane/CH<sub>2</sub>Cl<sub>2</sub>) in a loosely capped vial.

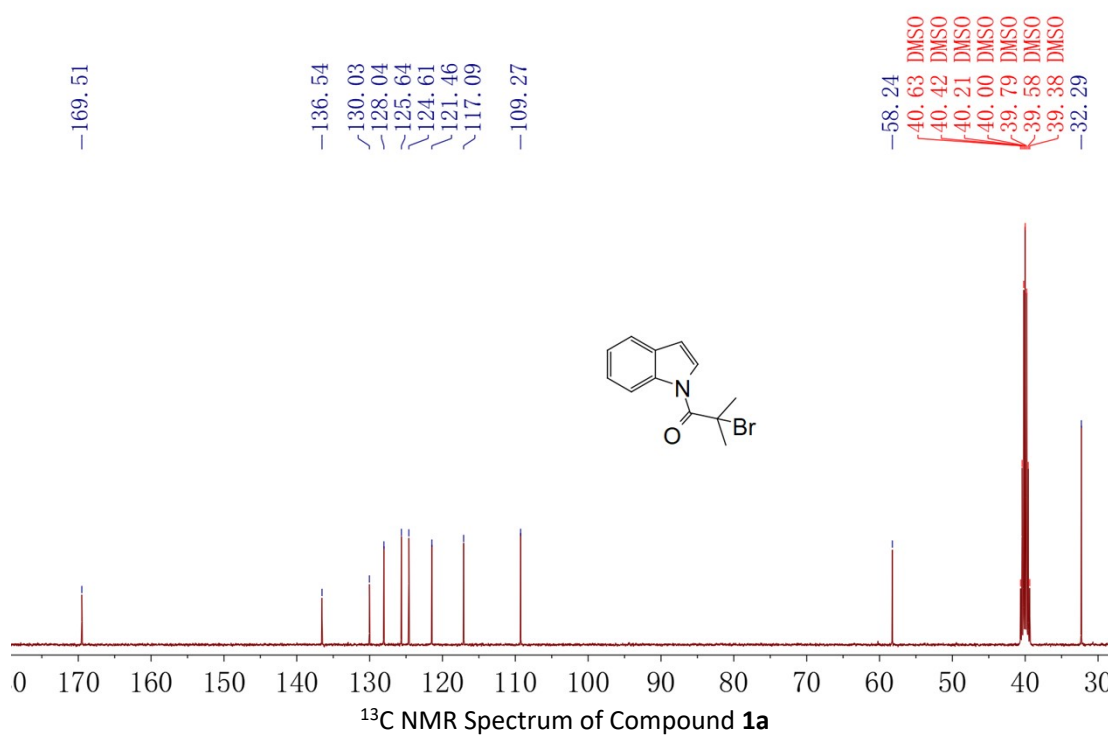
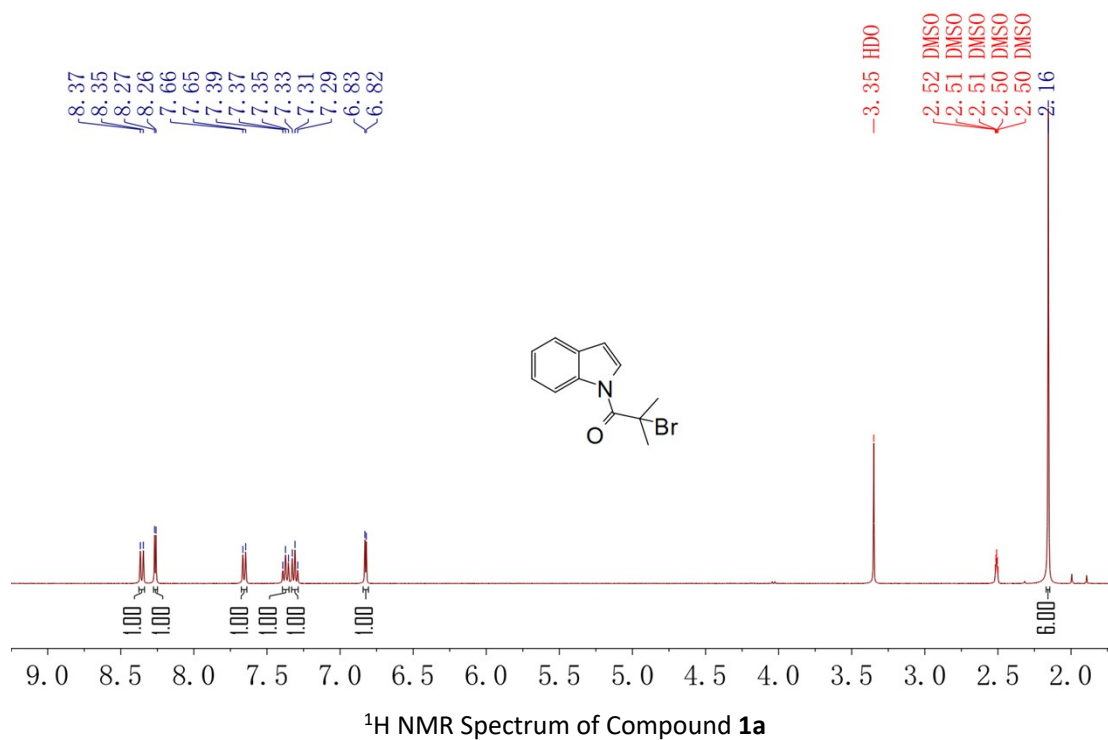
**Table 11** Crystal data and structure refinement for **3a**

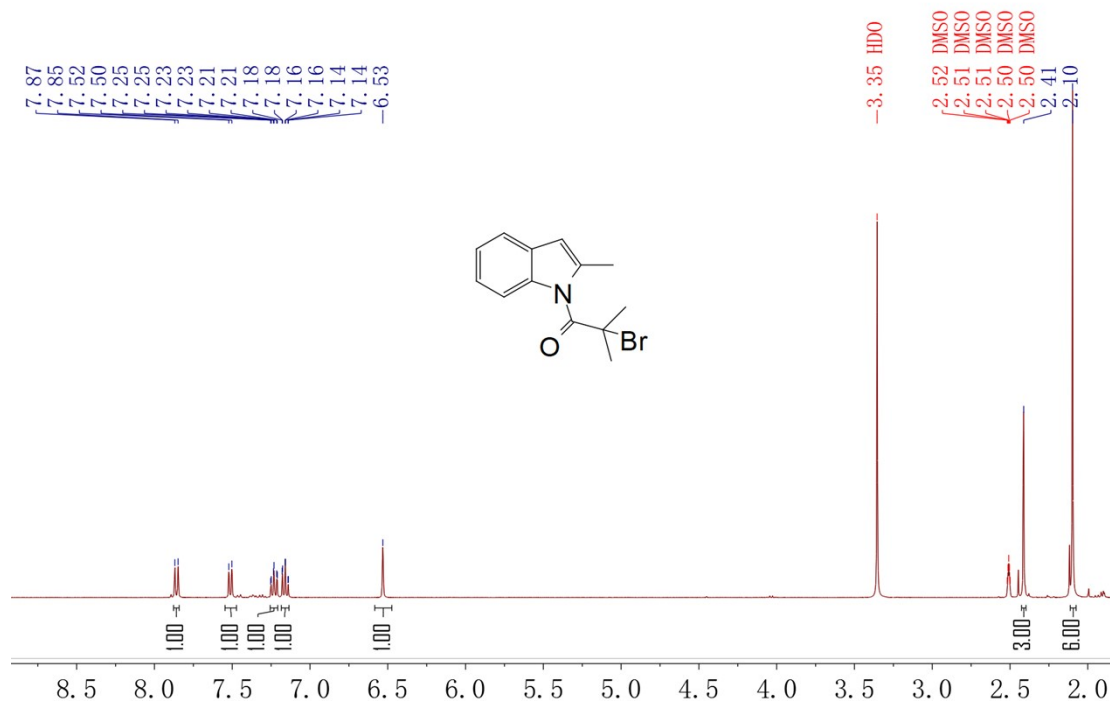
Empirical formula	C <sub>20</sub> H <sub>19</sub> NO
Formula weight	289.36
Temperature/K	193
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /c
a/Å	25.949(7)
b/Å	10.787(3)
c/Å	11.392(3)
α/°	90
β/°	101.972(8)
γ/°	90
Volume/Å <sup>3</sup>	3119.6(16)
Z	8
ρ <sub>calc</sub> /cm <sup>3</sup>	1.232
μ/mm <sup>-1</sup>	0.075

F(000)	1232.0
Crystal size/mm <sup>3</sup>	0.12 × 0.1 × 0.1
Radiation	MoK $\alpha$ ( $\lambda = 0.71073$ )
2 $\Theta$ range for data collection/ $^{\circ}$	4.286 to 55.152
Index ranges	-33 $\leq$ h $\leq$ 33, -7 $\leq$ k $\leq$ 13, -14 $\leq$ l $\leq$ 14
Reflections collected	23973
Independent reflections	7121 [R <sub>int</sub> = 0.0853, R <sub>sigma</sub> = 0.1009]
Data/restraints/parameters	7121/0/402
Largest diff. peak/hole / e $\text{\AA}^{-3}$	0.42/-0.27

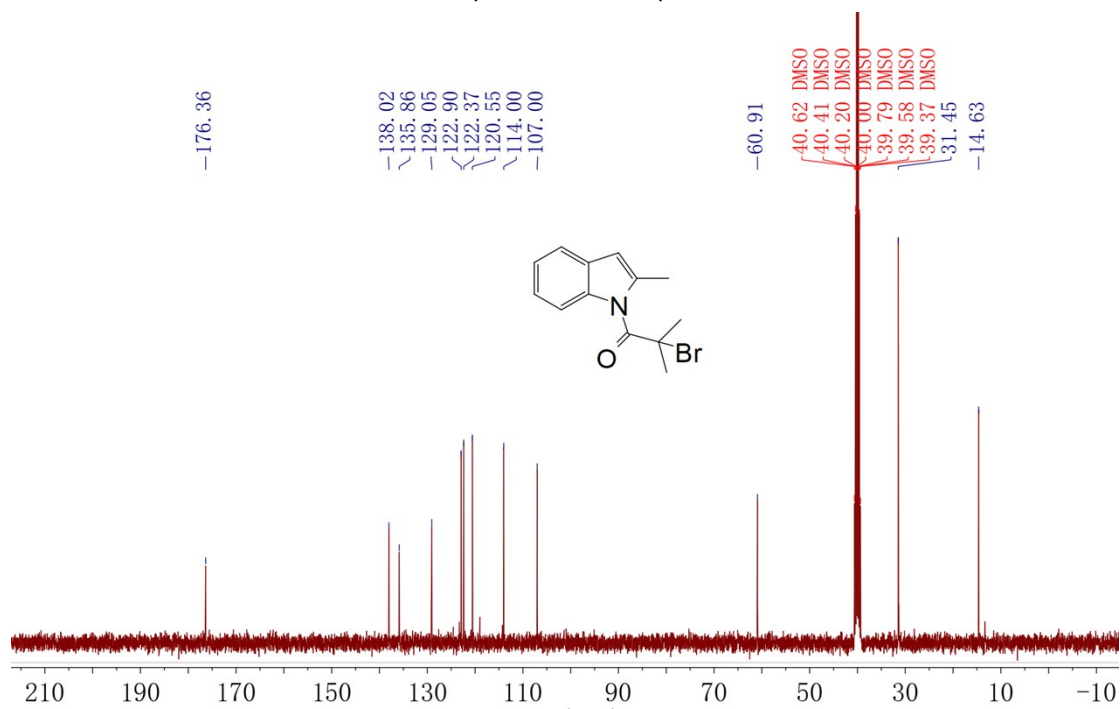


## 8. $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra

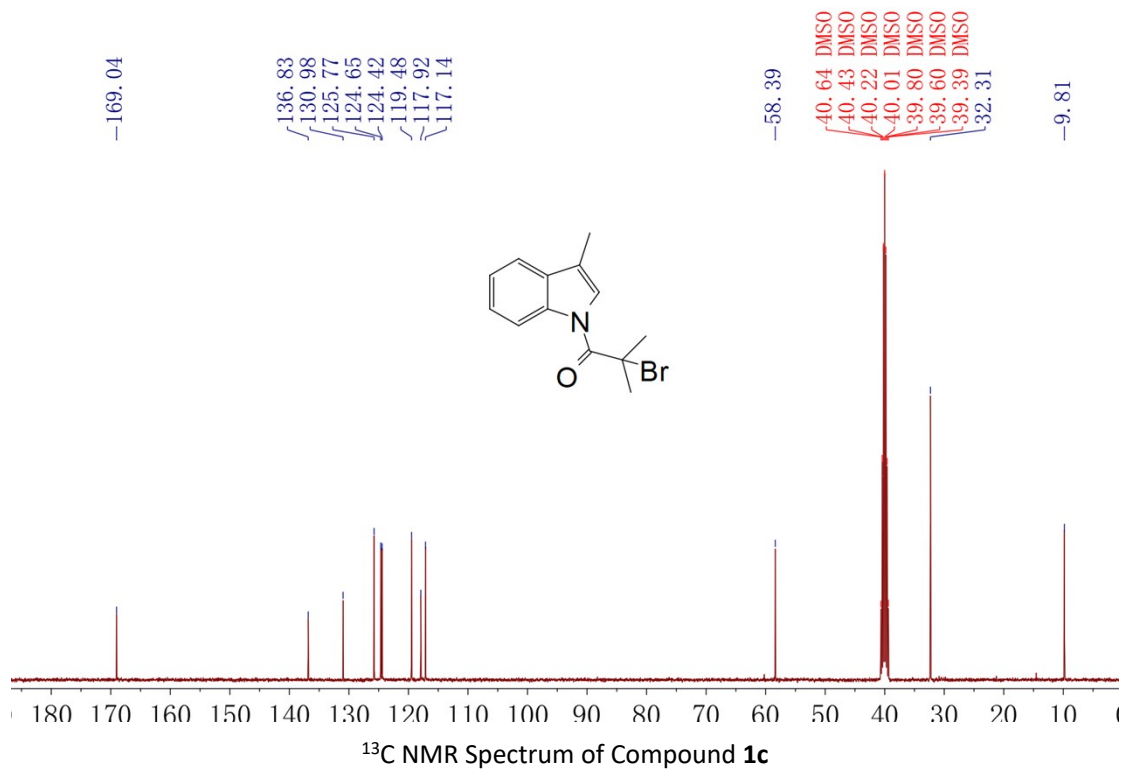
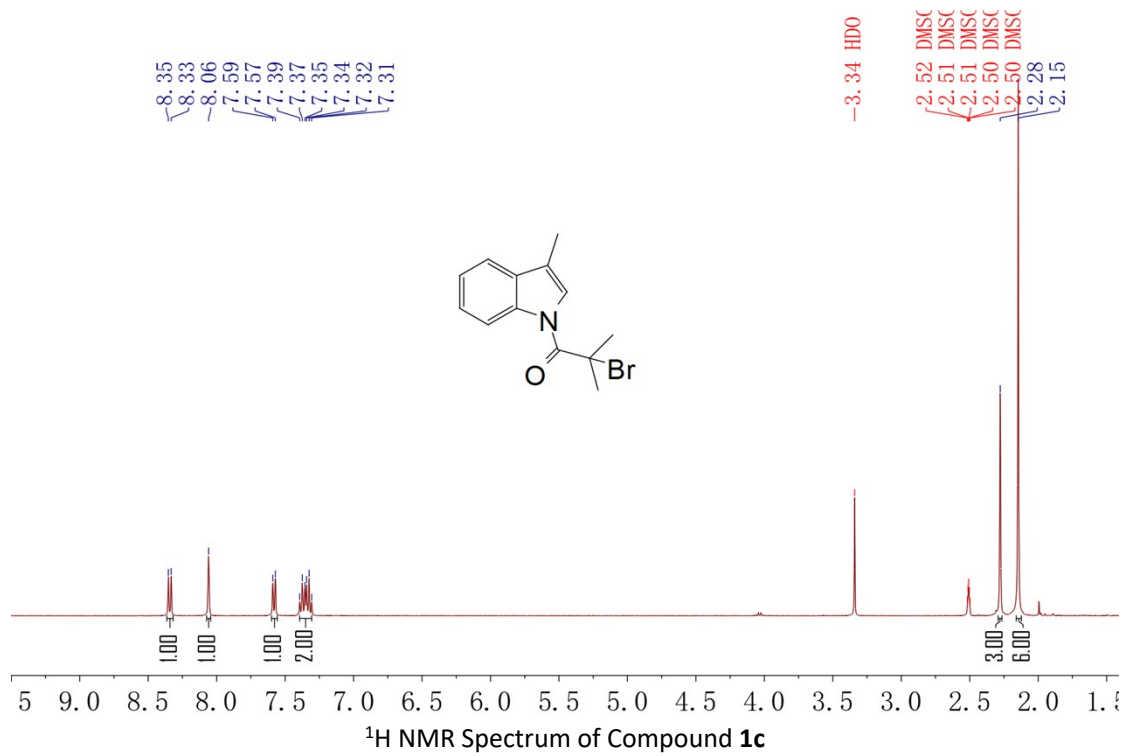


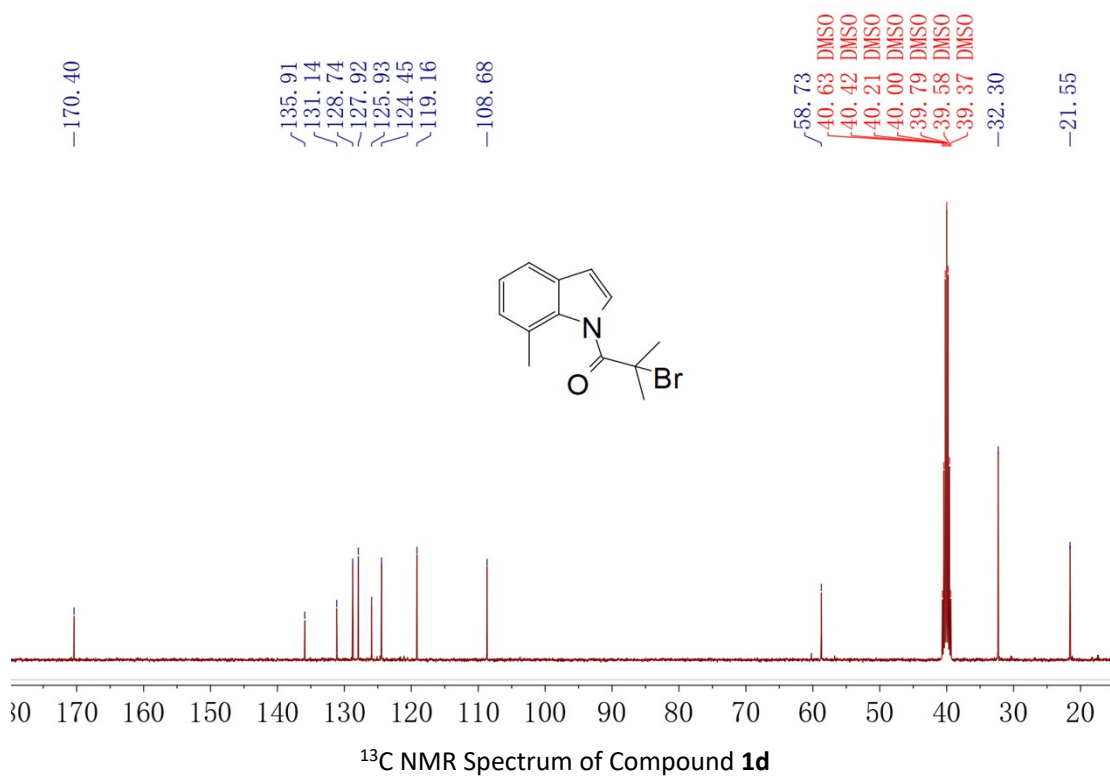
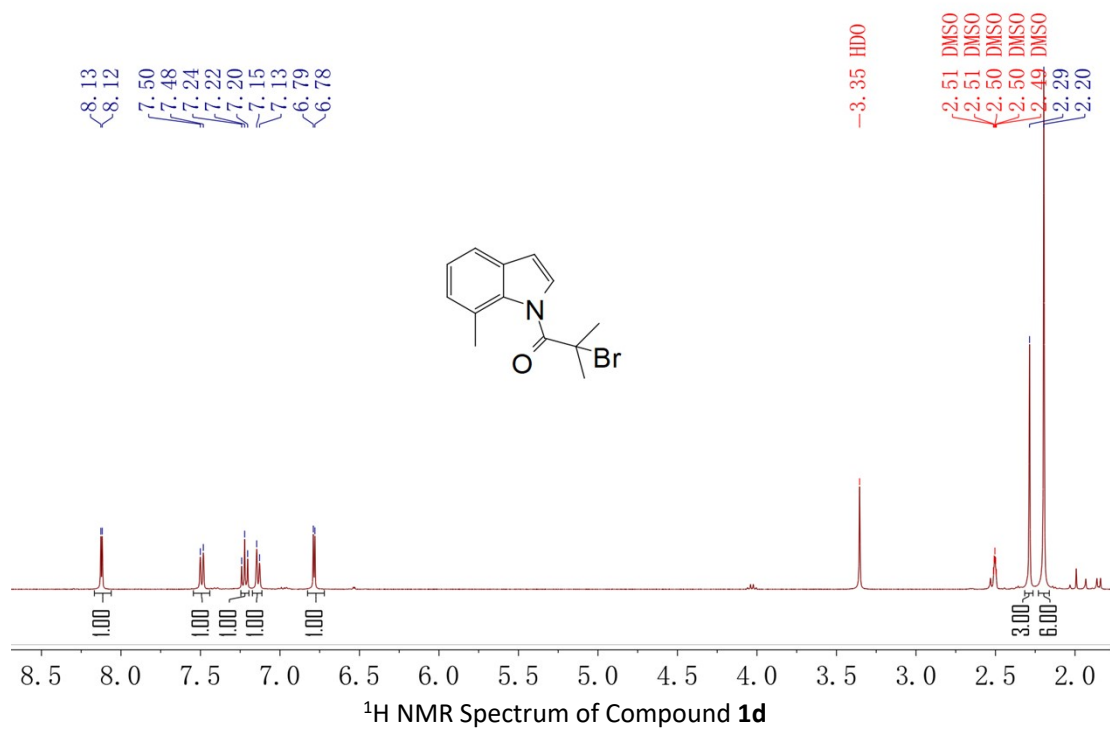


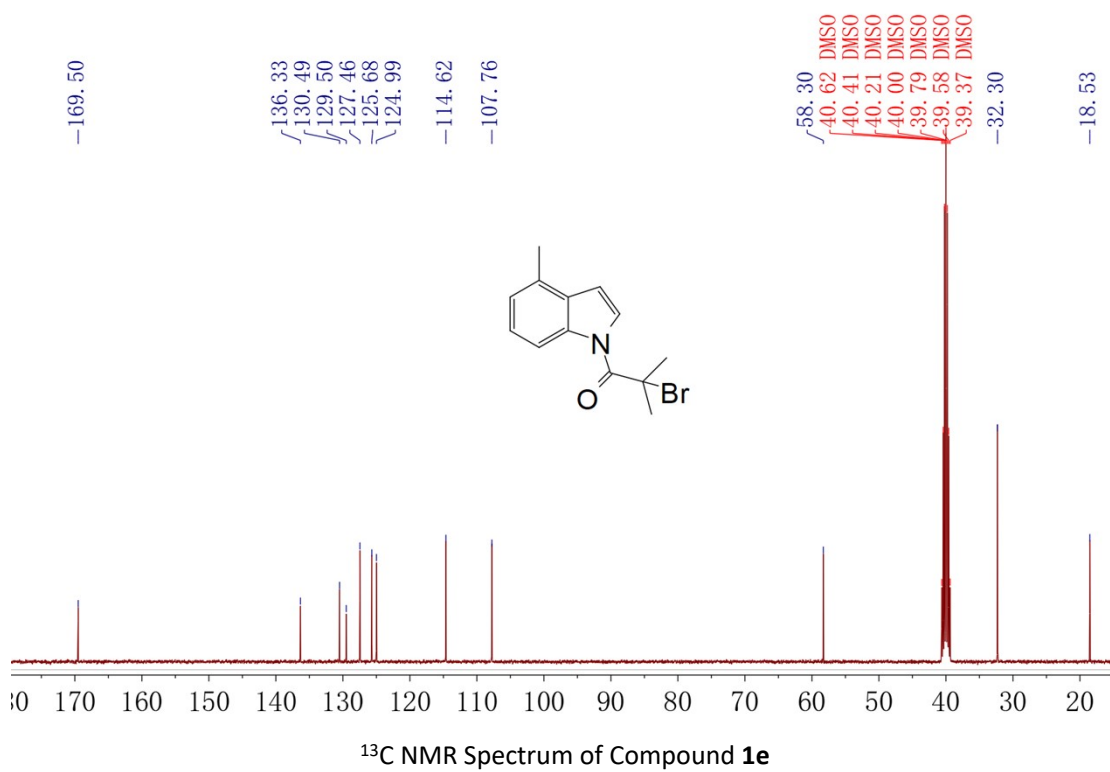
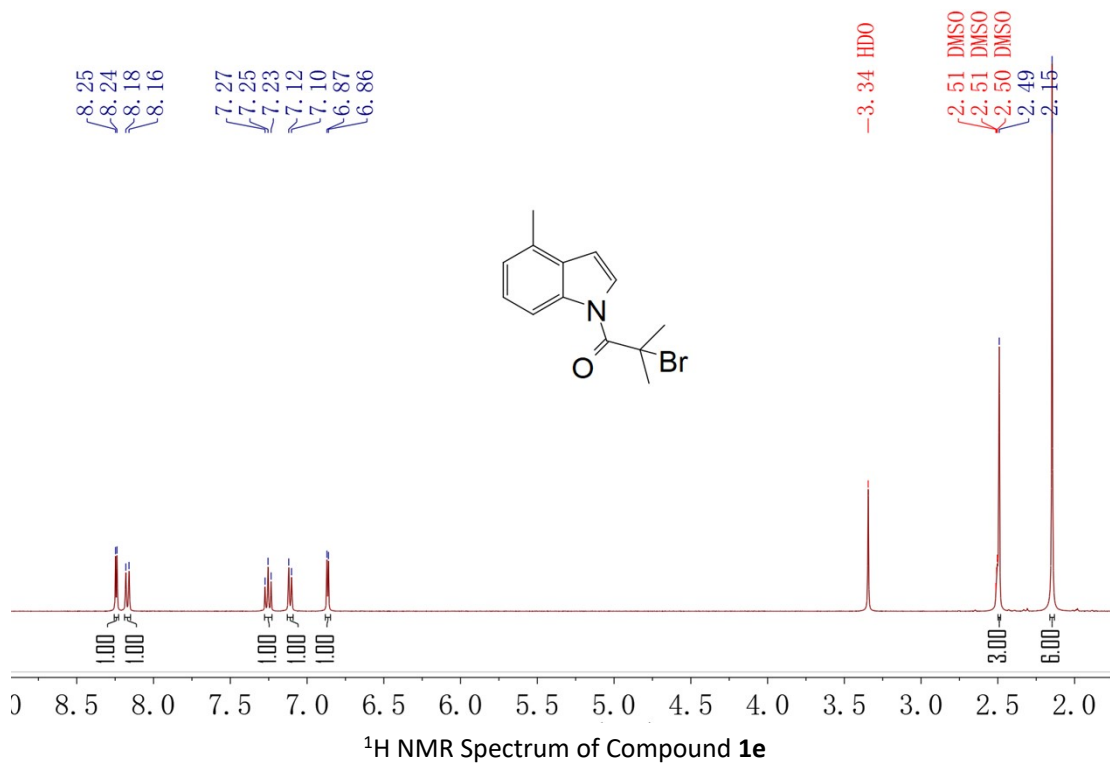
**<sup>1</sup>H NMR Spectrum of Compound **1b****

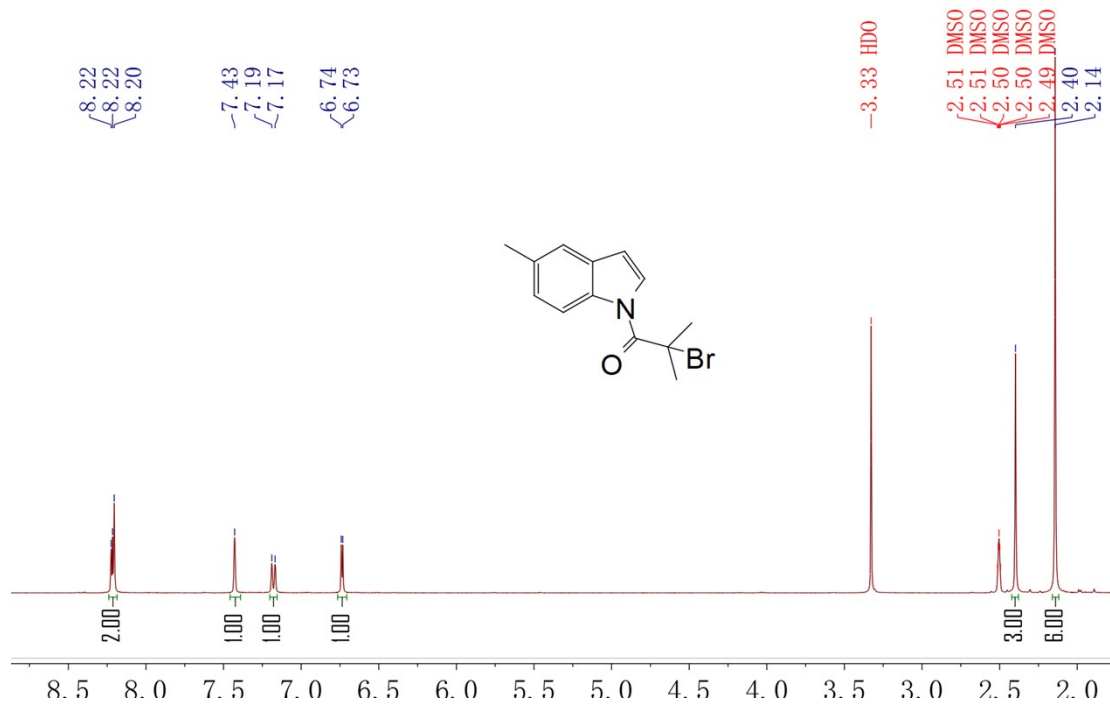


**<sup>13</sup>C NMR Spectrum of Compound **1b****

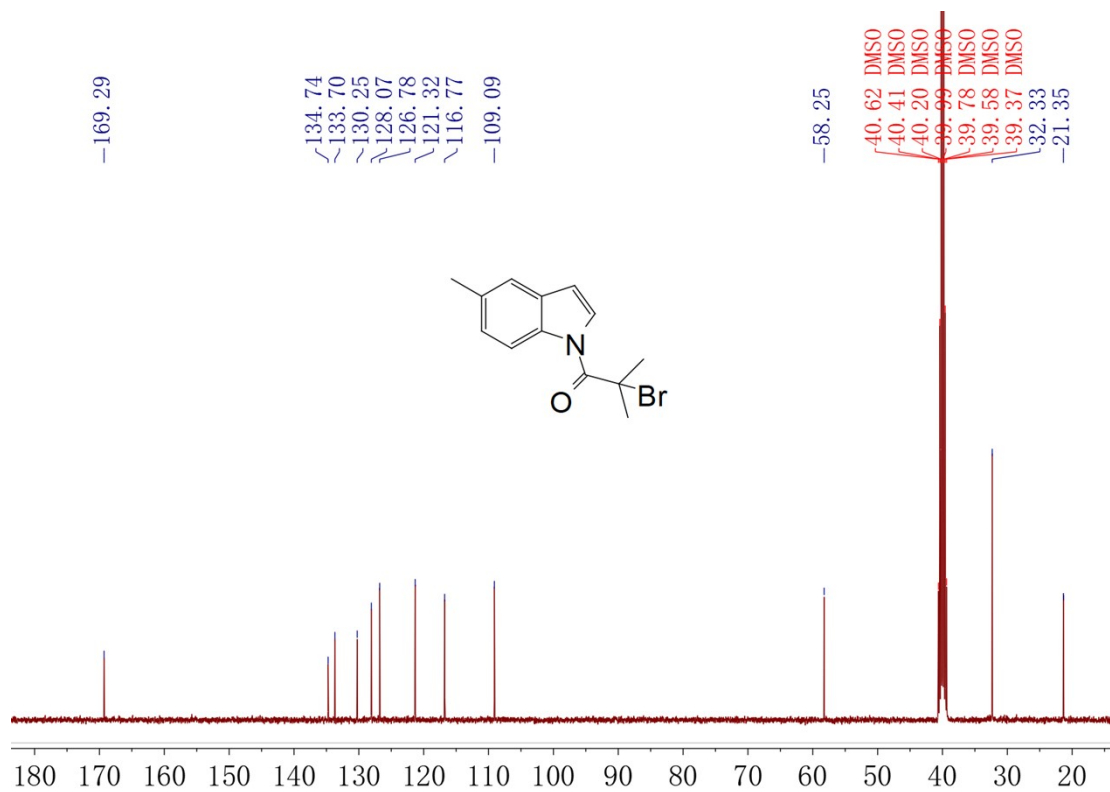




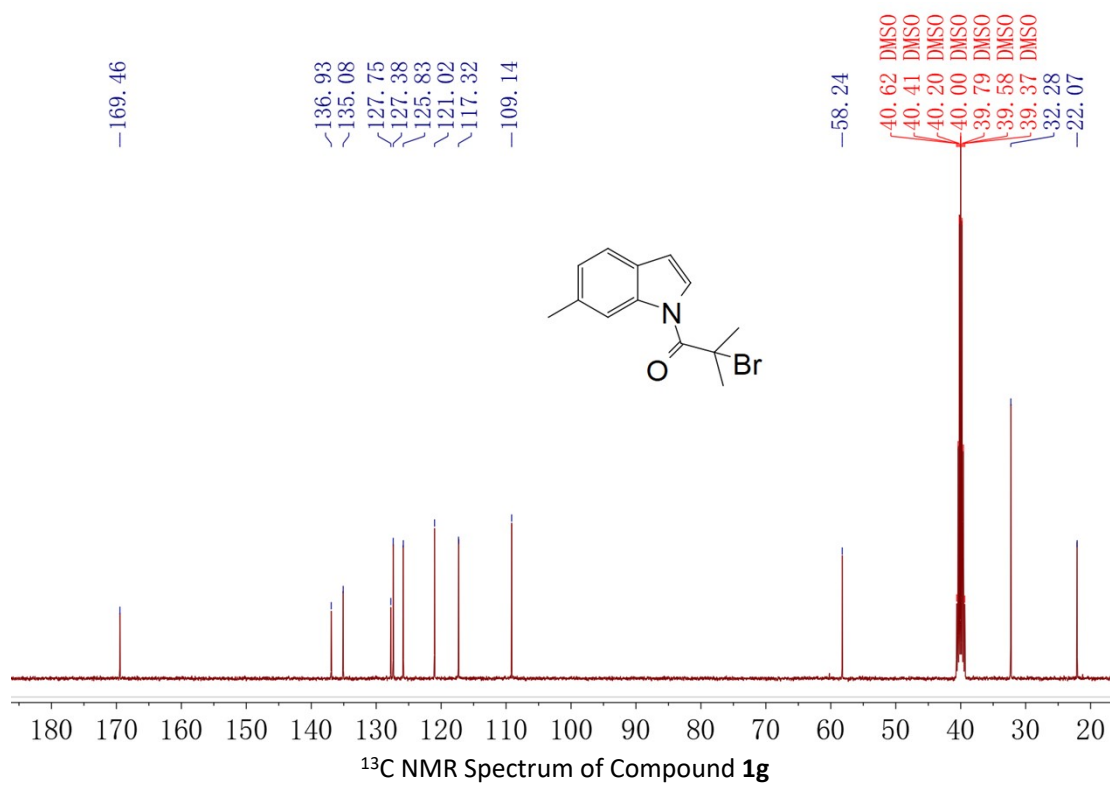
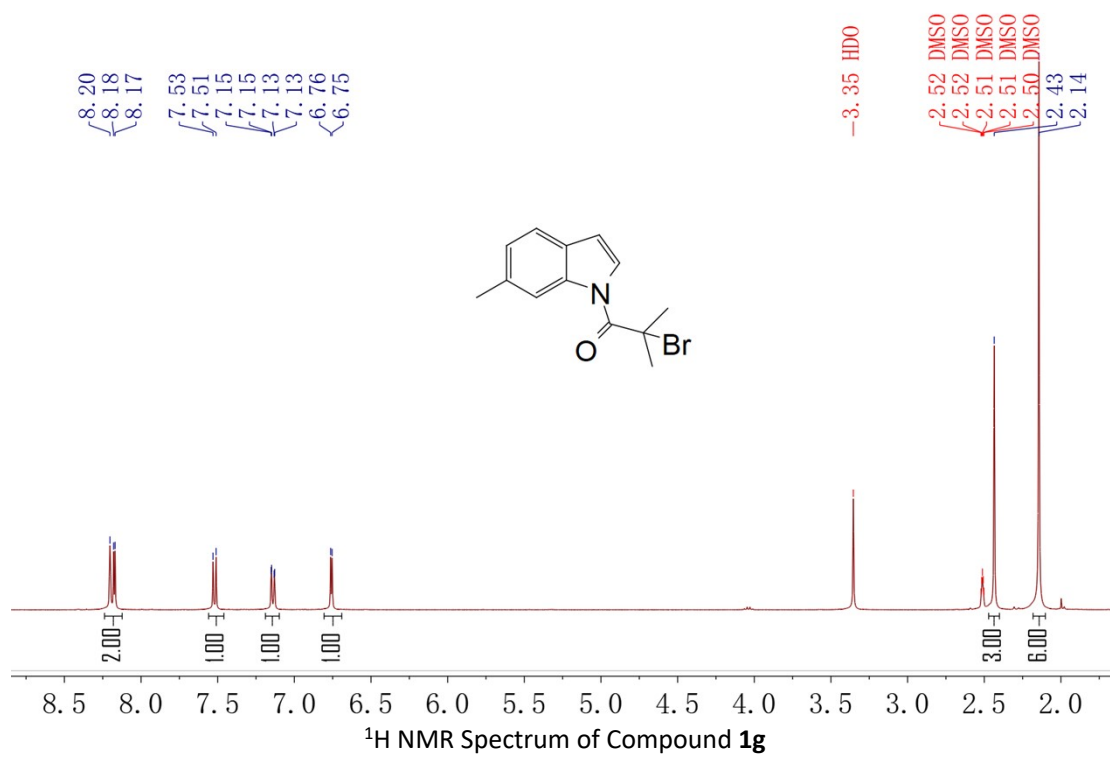


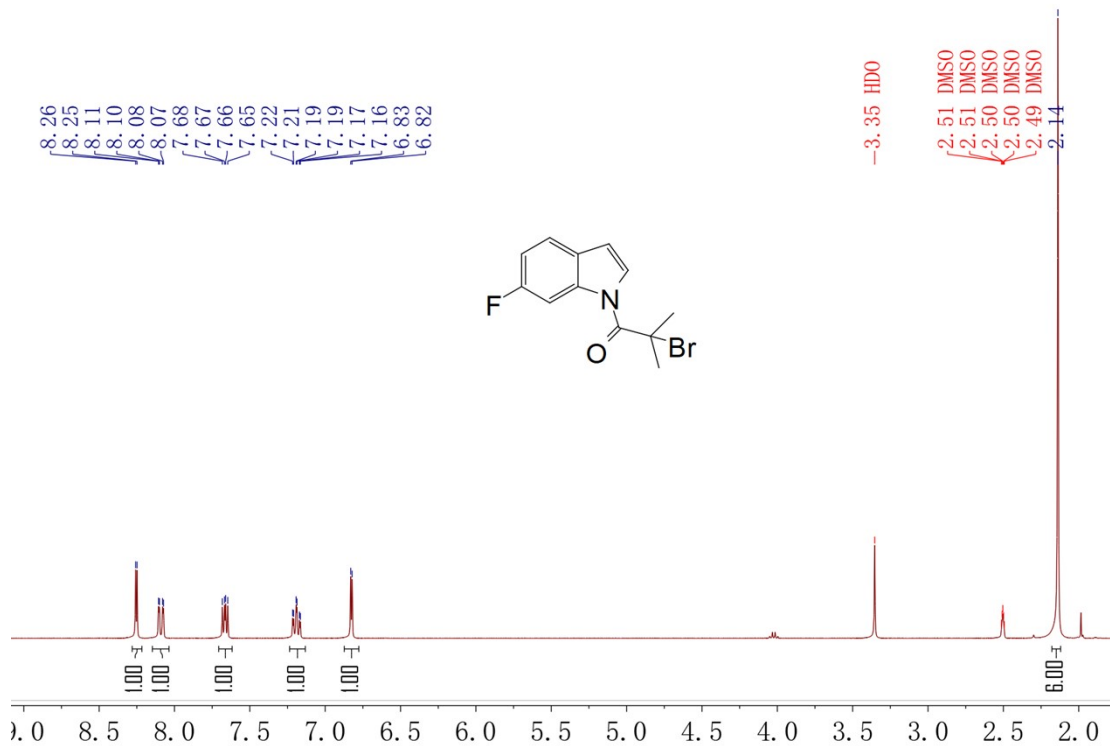


<sup>1</sup>H NMR Spectrum of Compound 1f

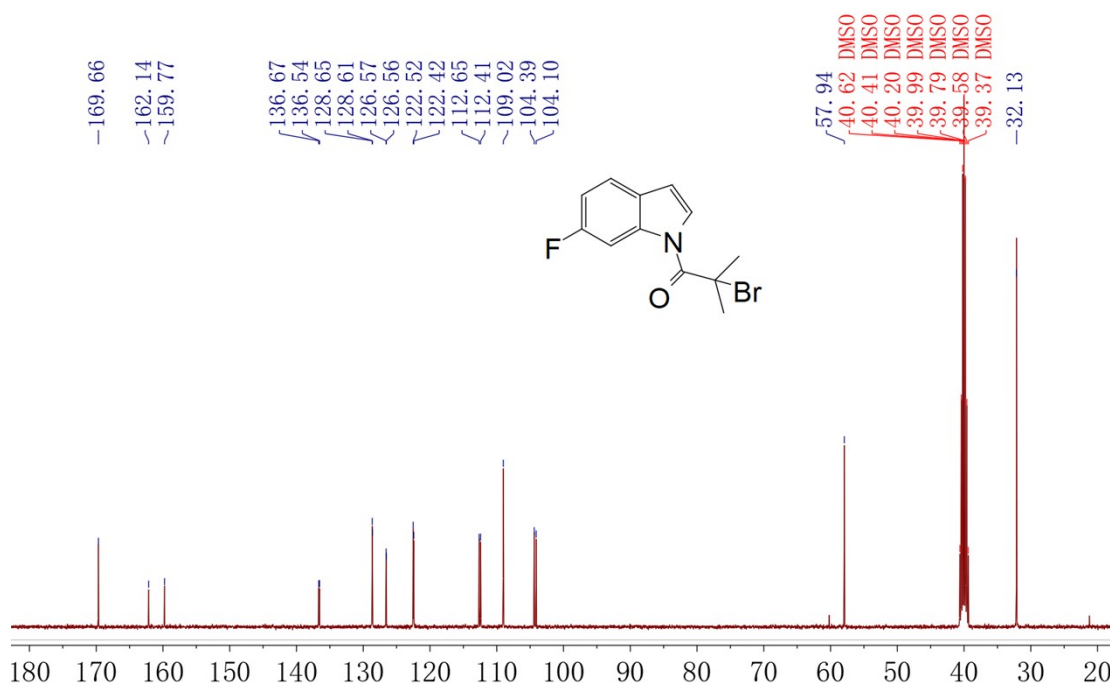


<sup>13</sup>C NMR Spectrum of Compound 1f



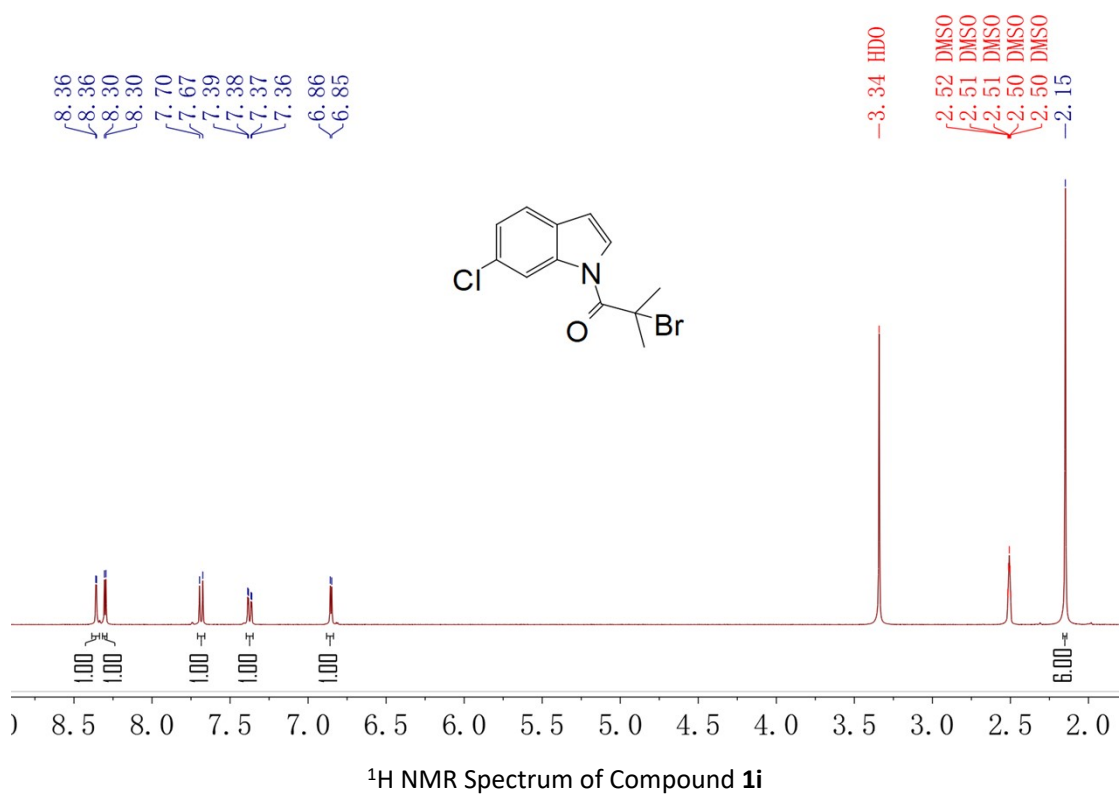
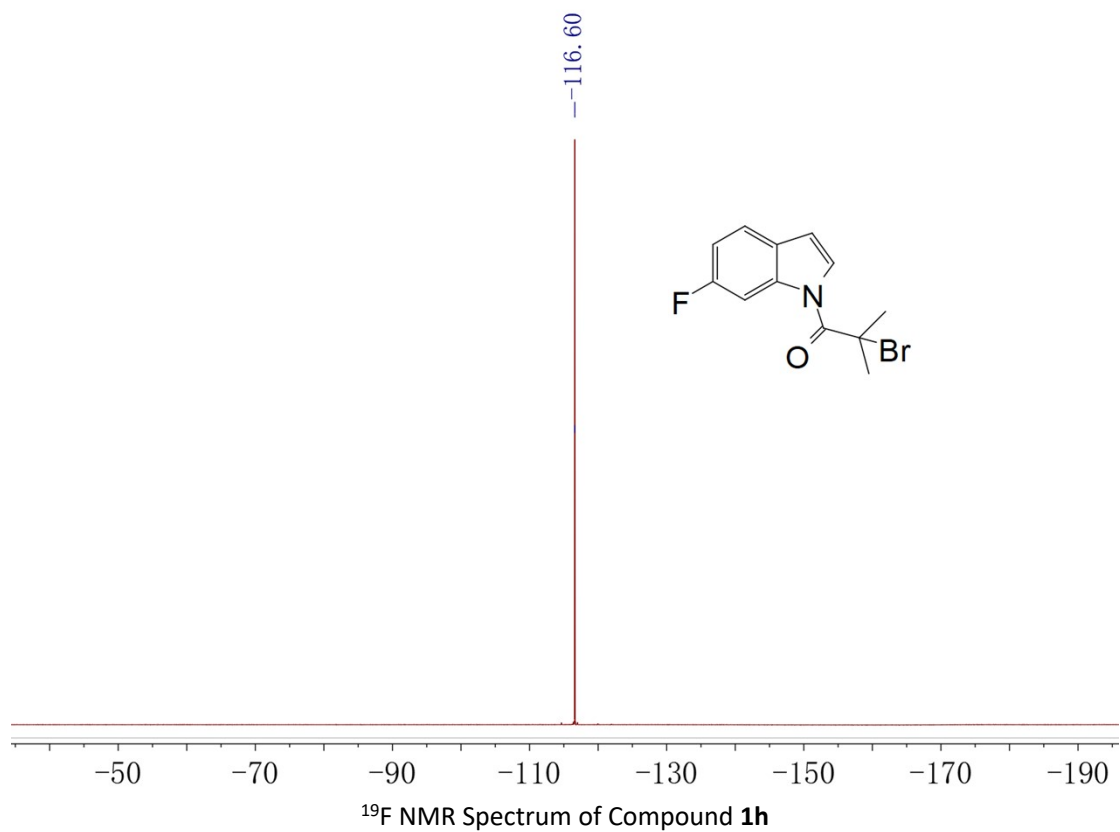


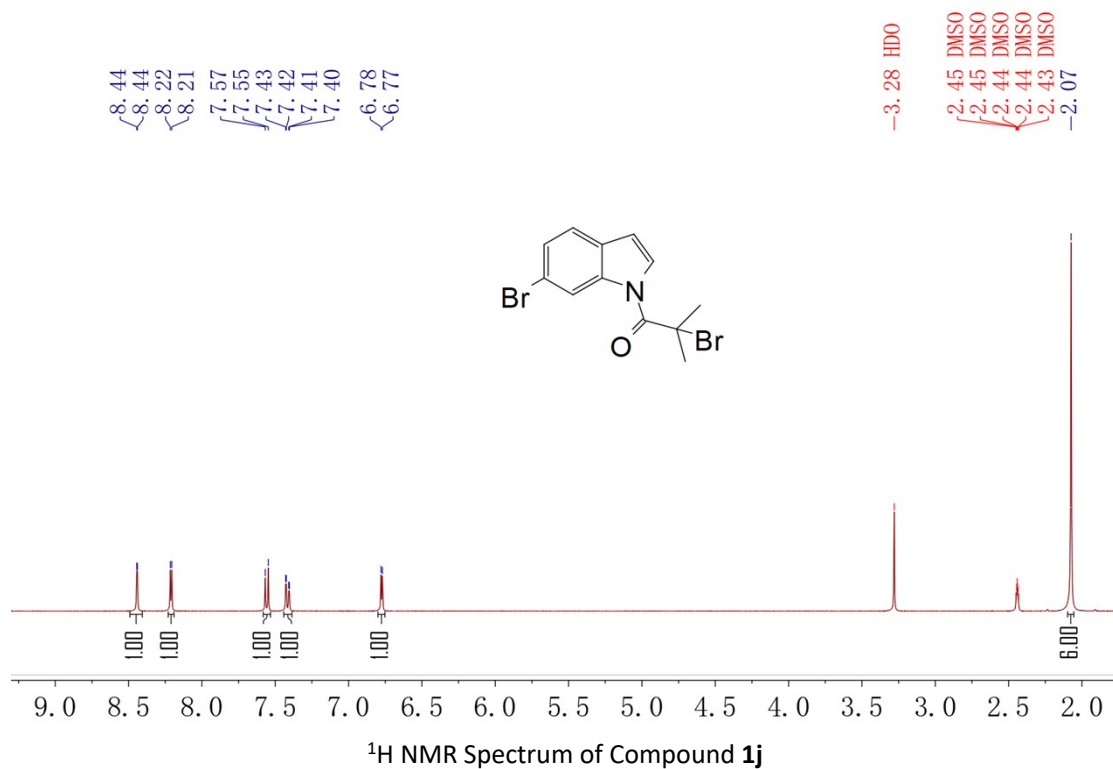
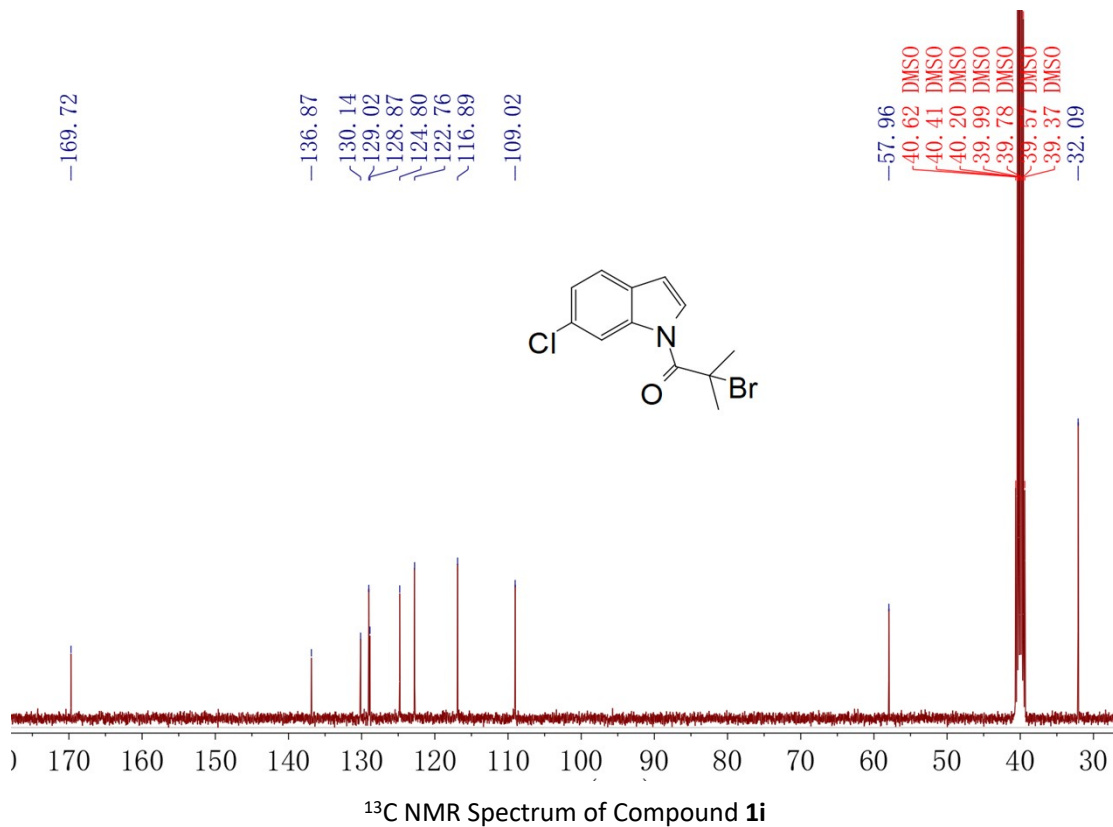
<sup>1</sup>H NMR Spectrum of Compound 1h

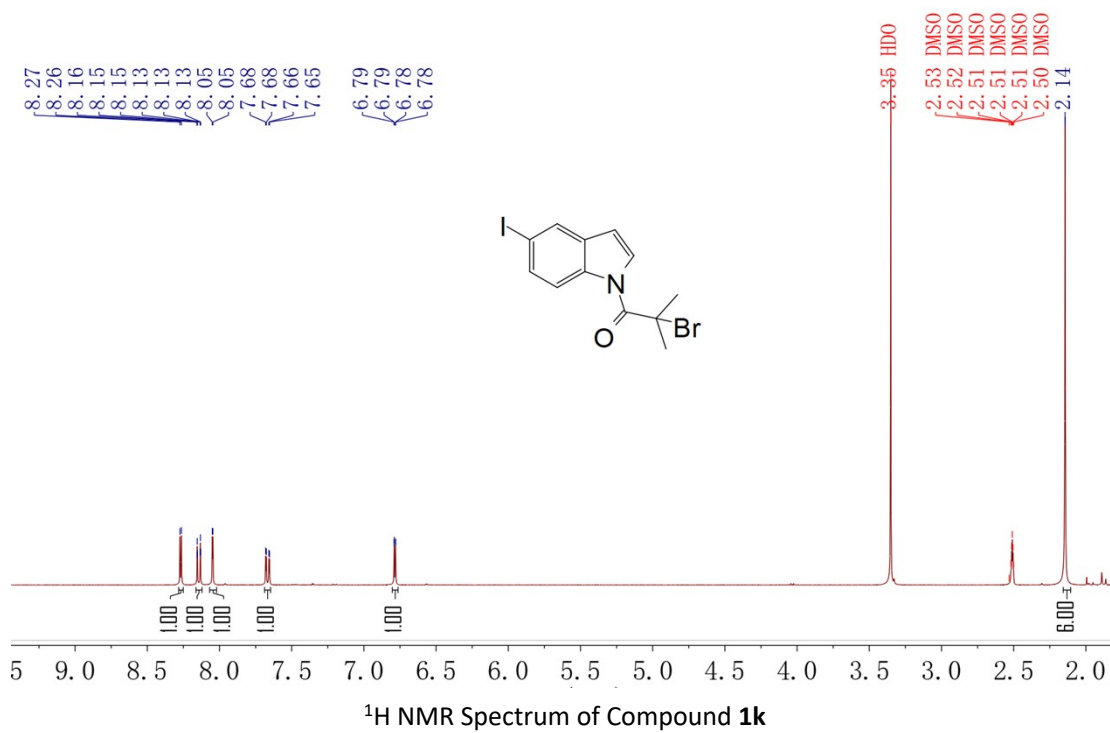
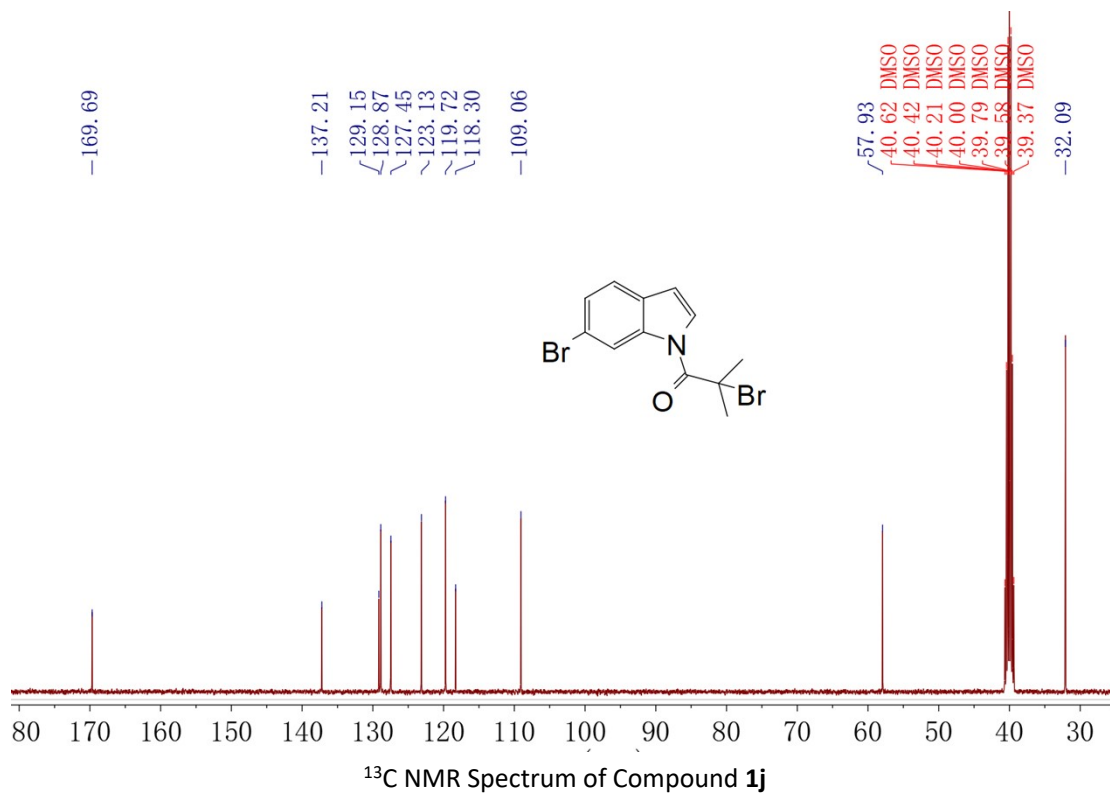


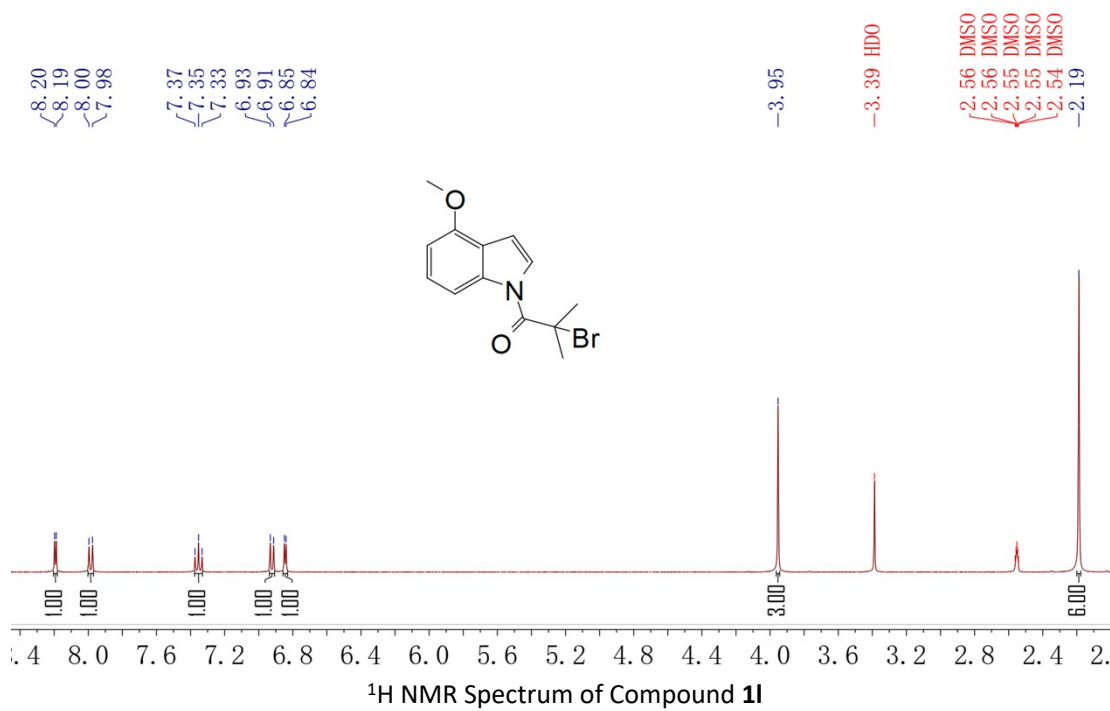
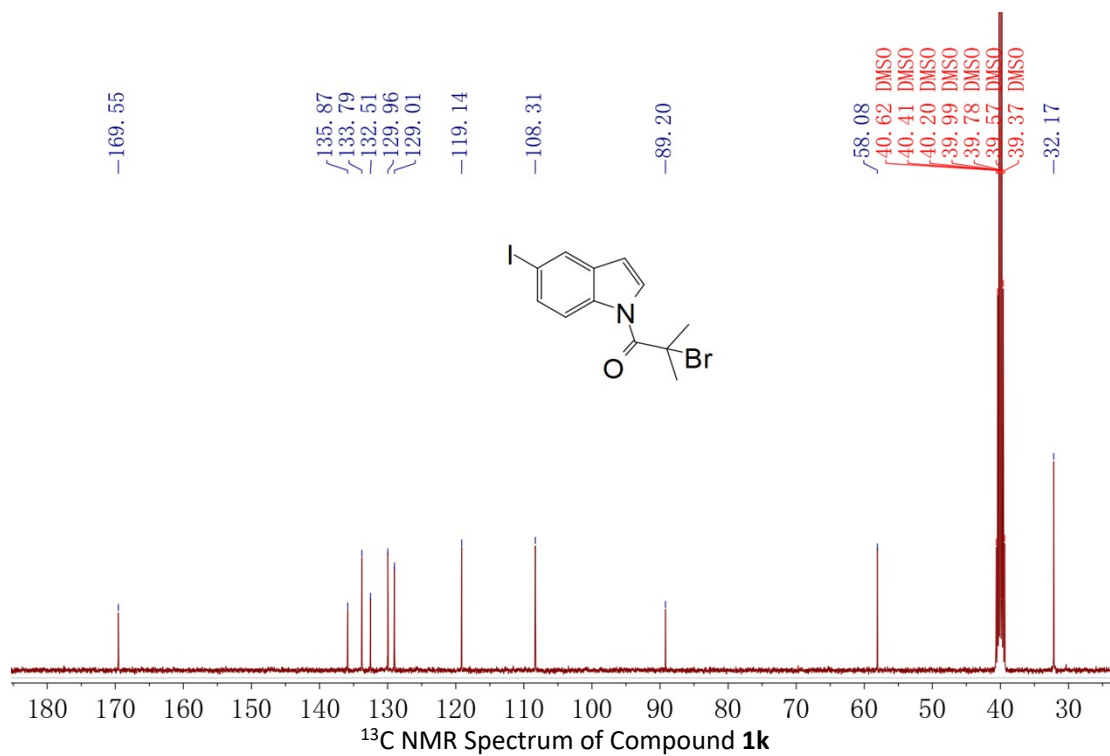
<sup>13</sup>C NMR Spectrum of Compound 1h

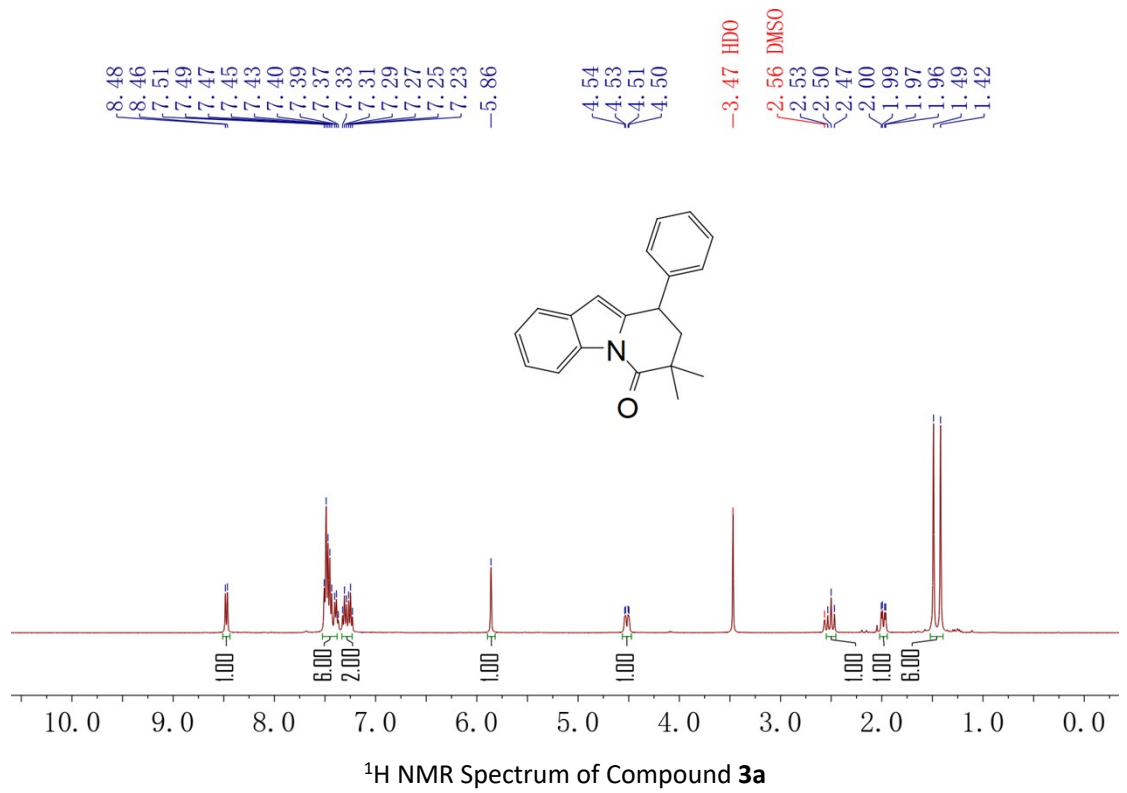
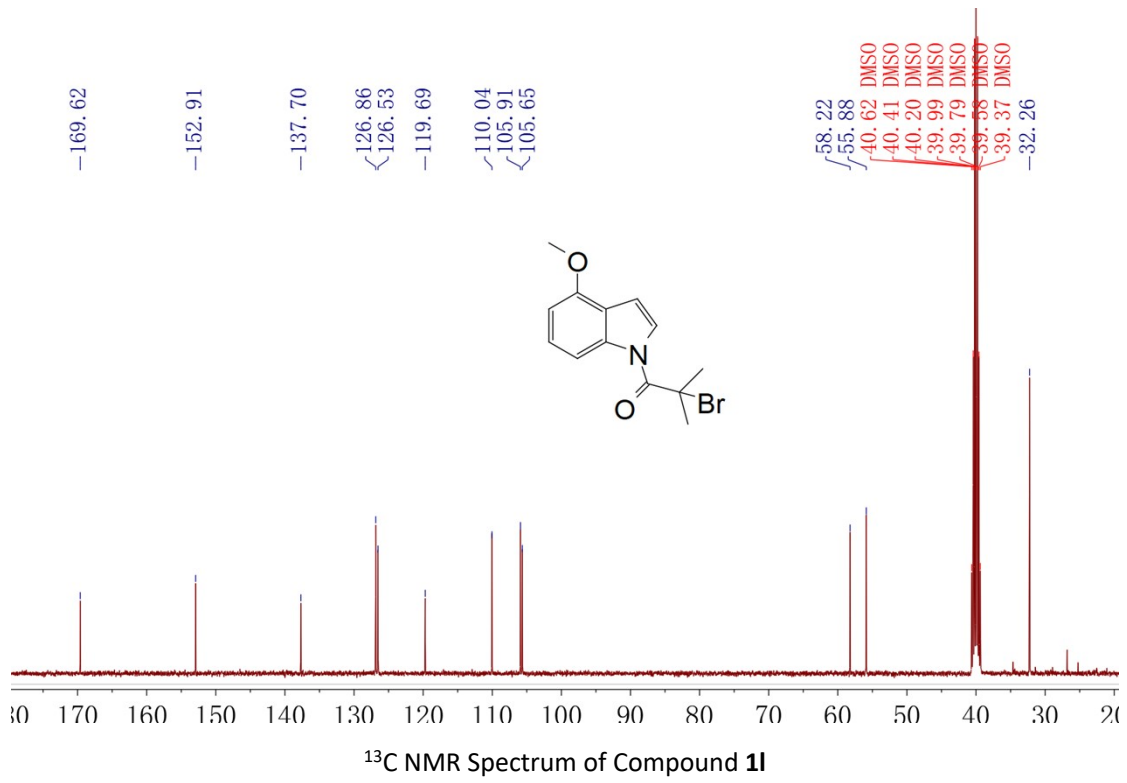


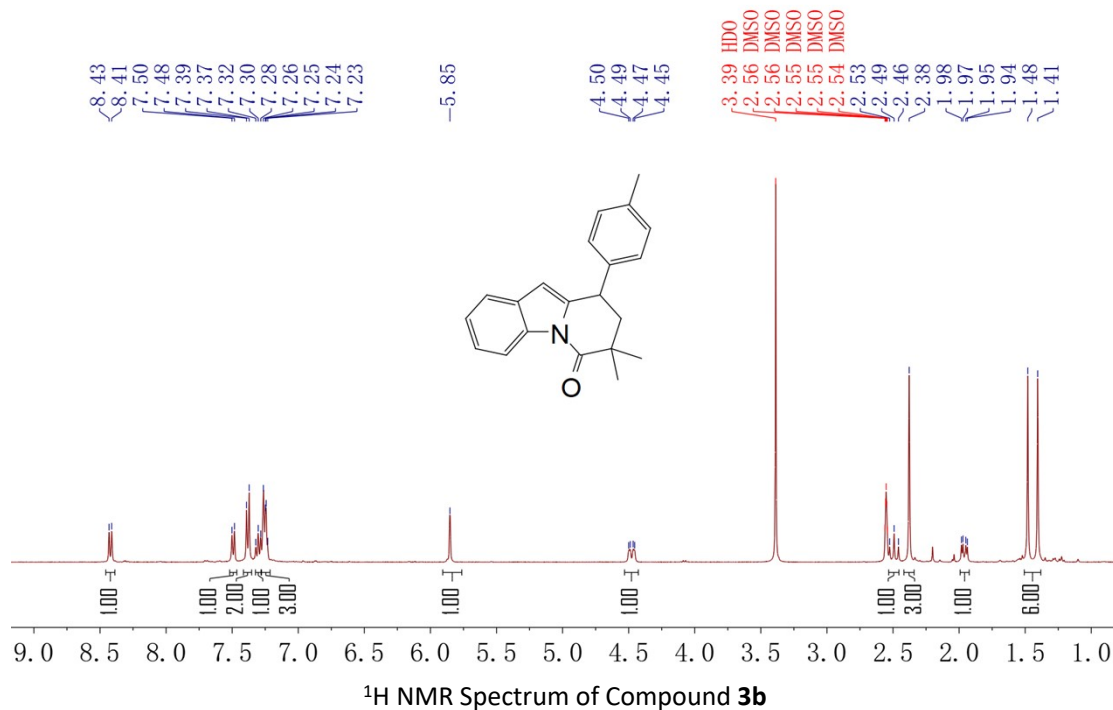
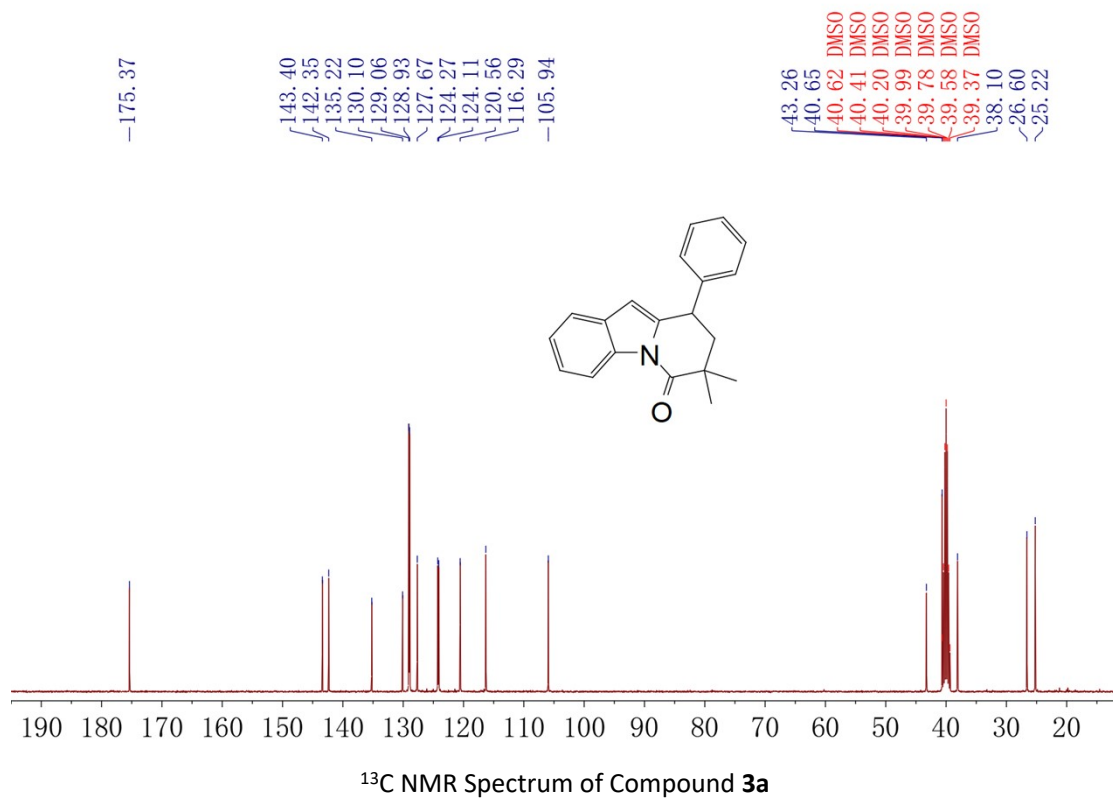


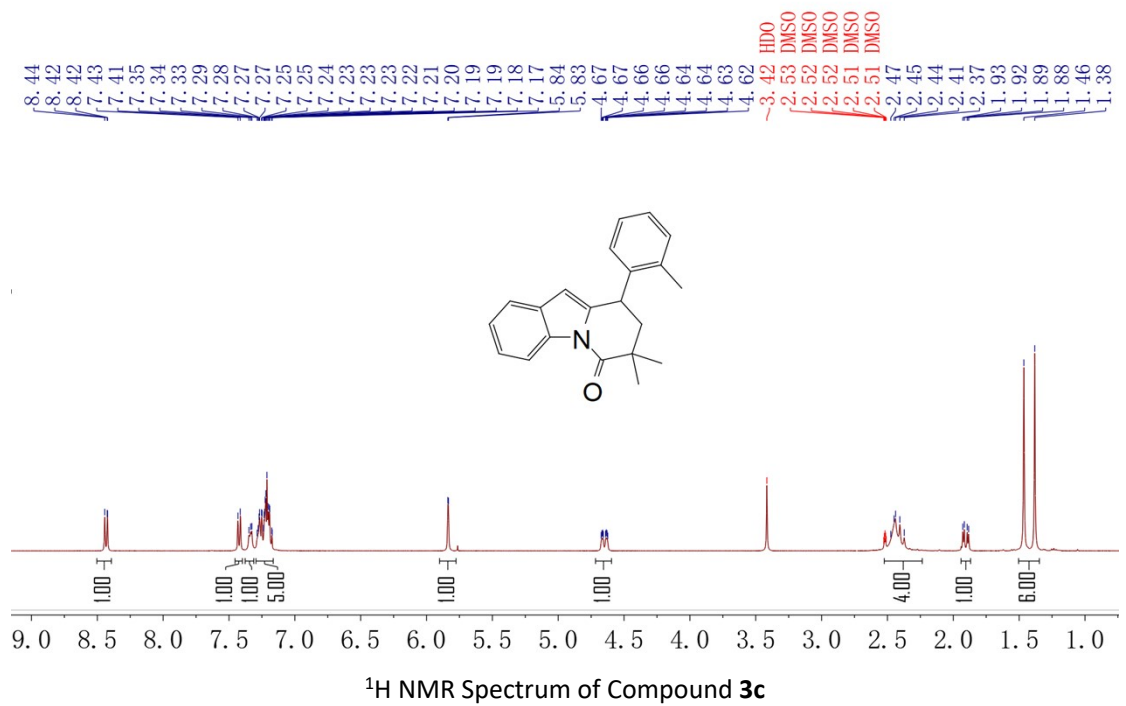
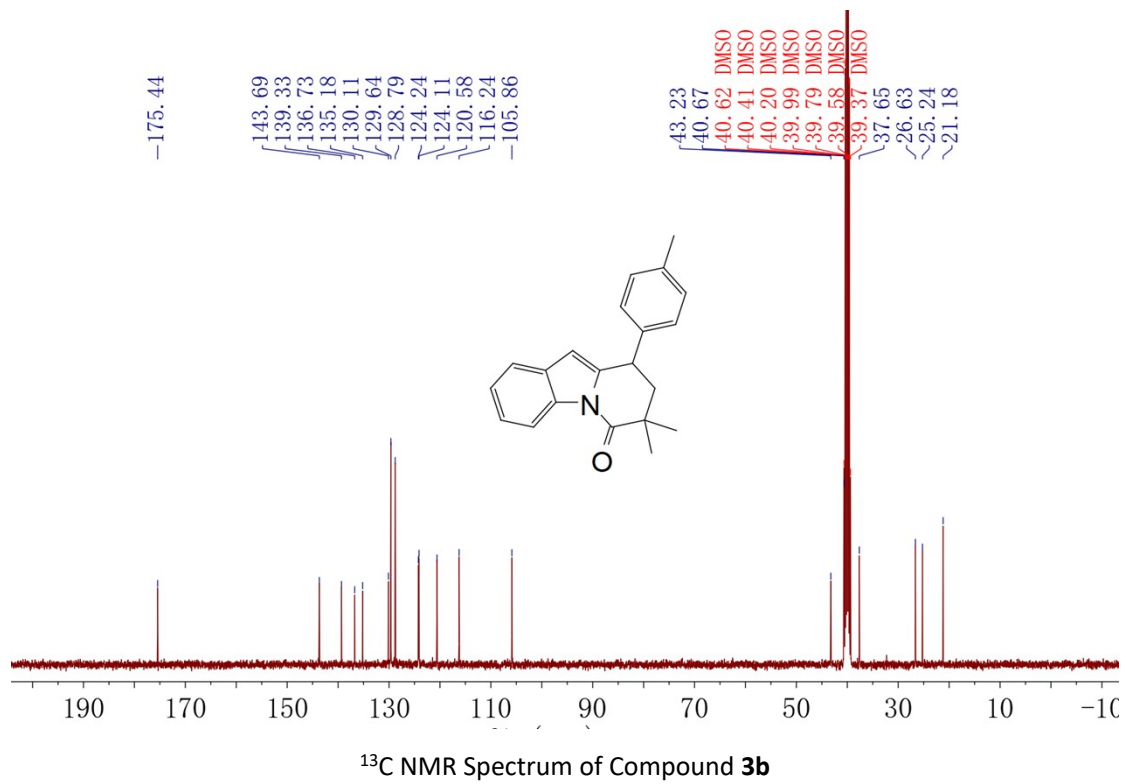


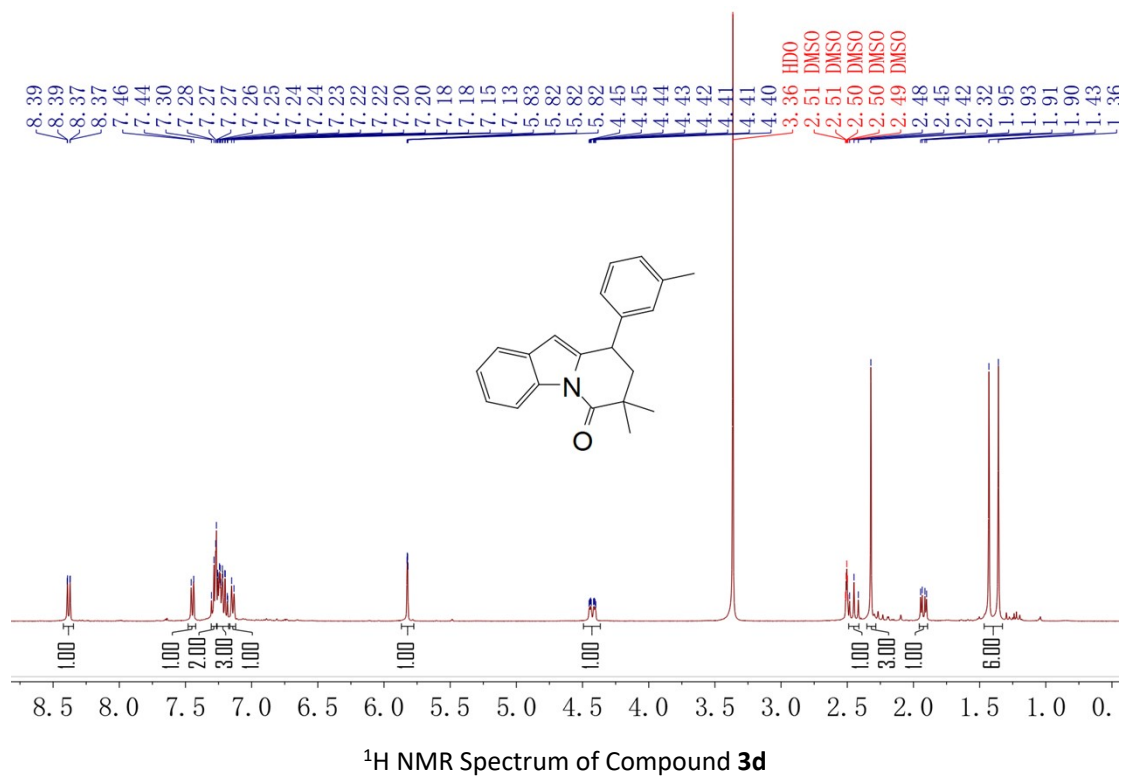
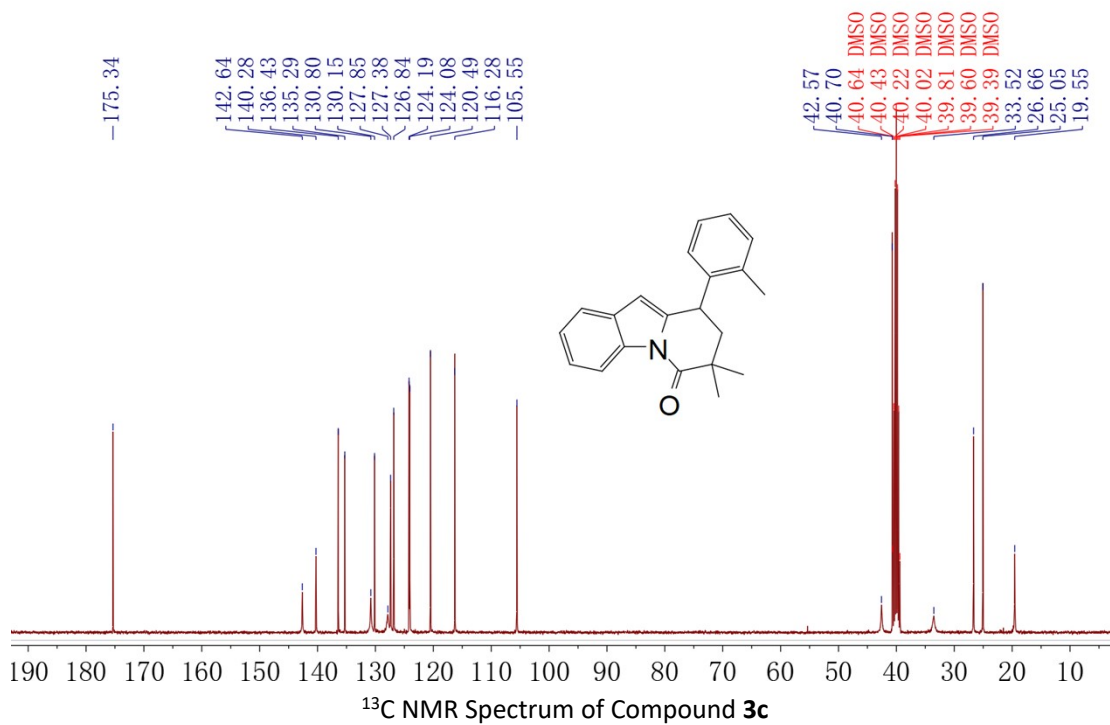




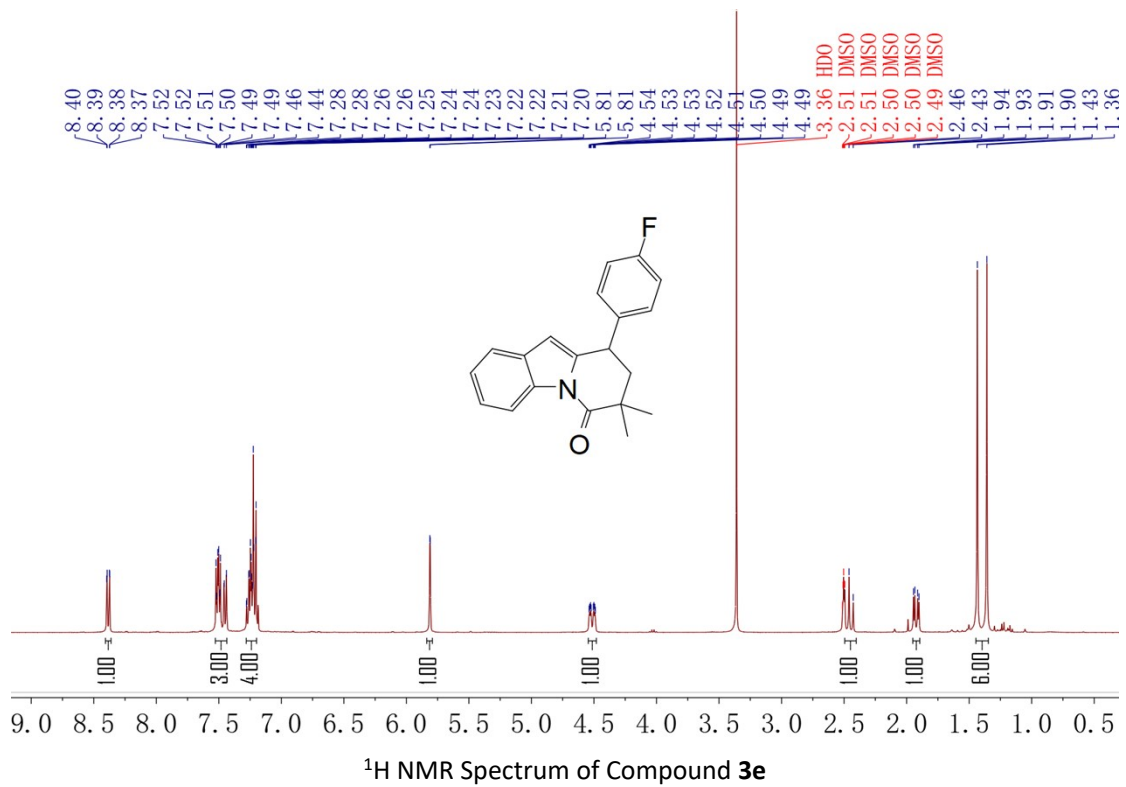
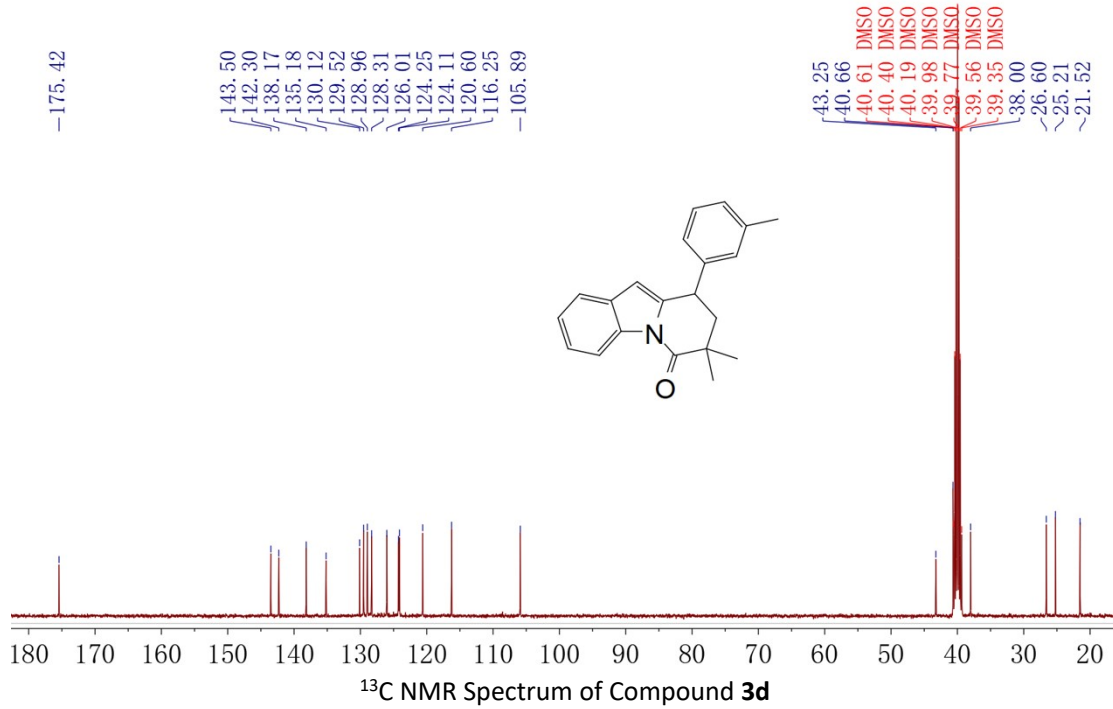


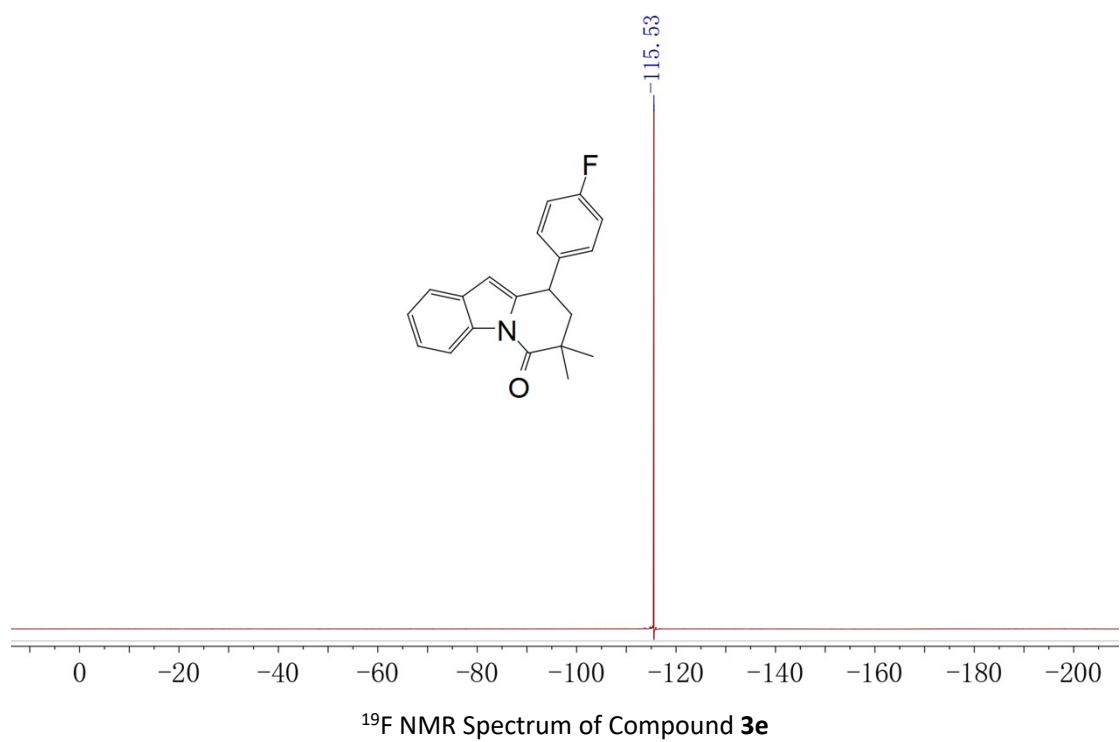
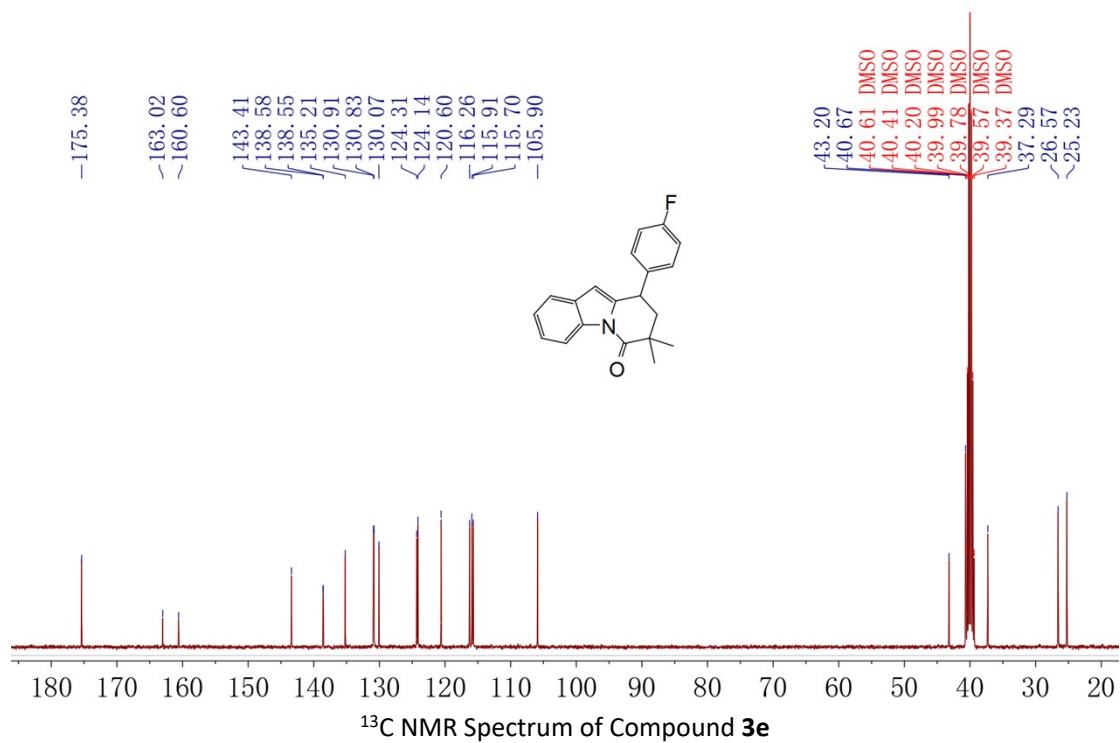


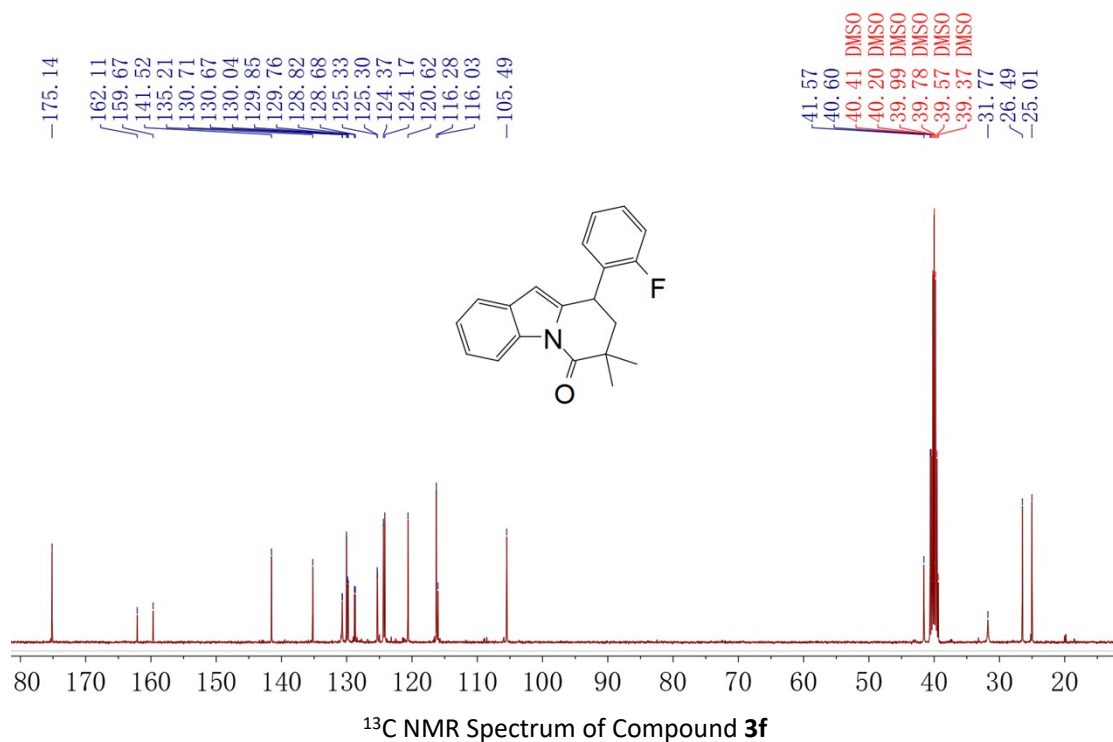
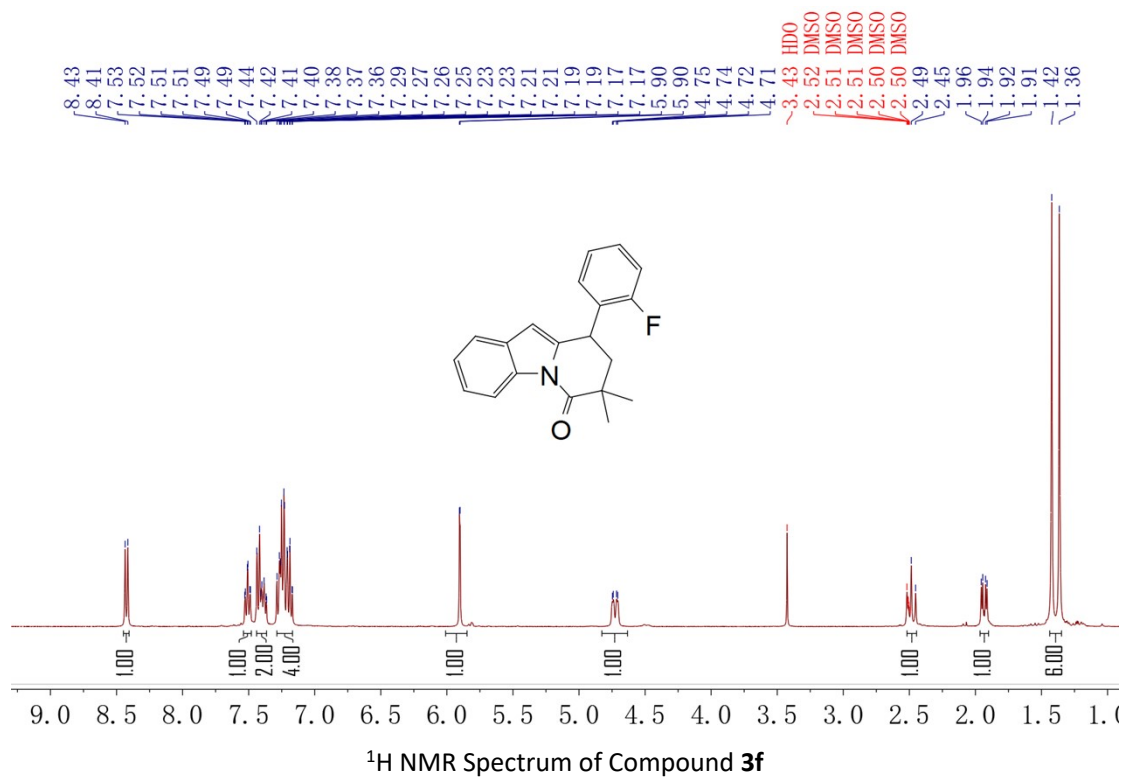


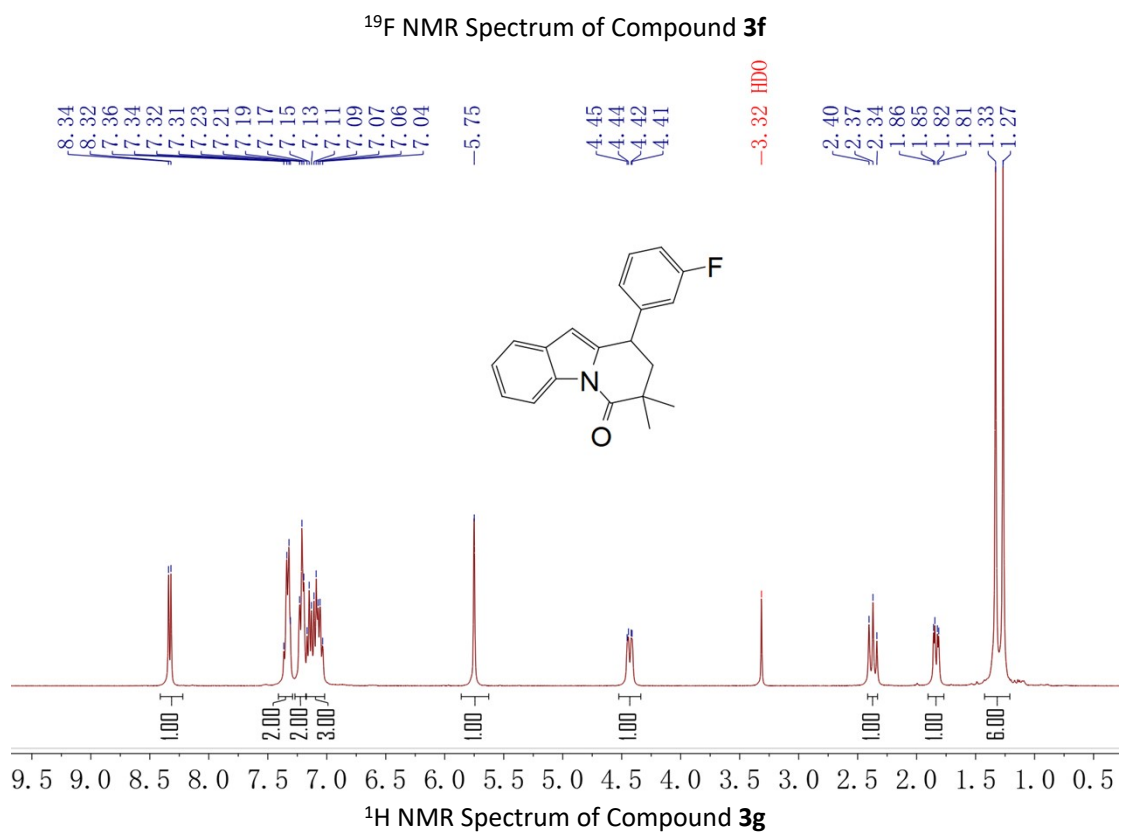
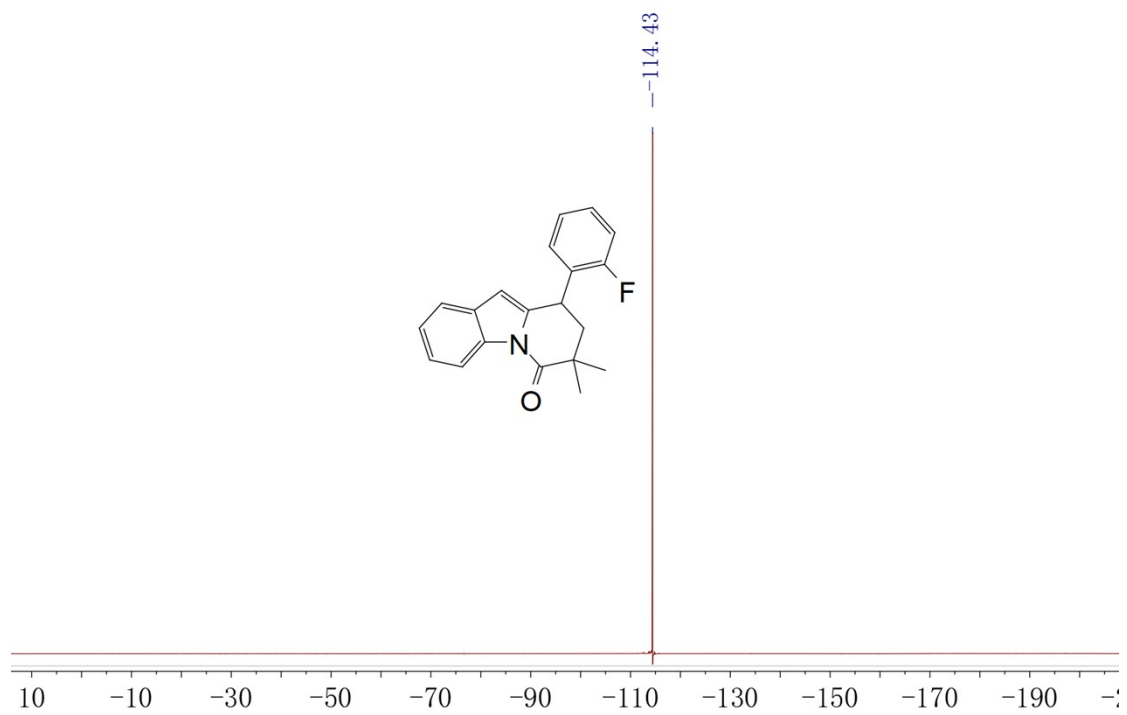


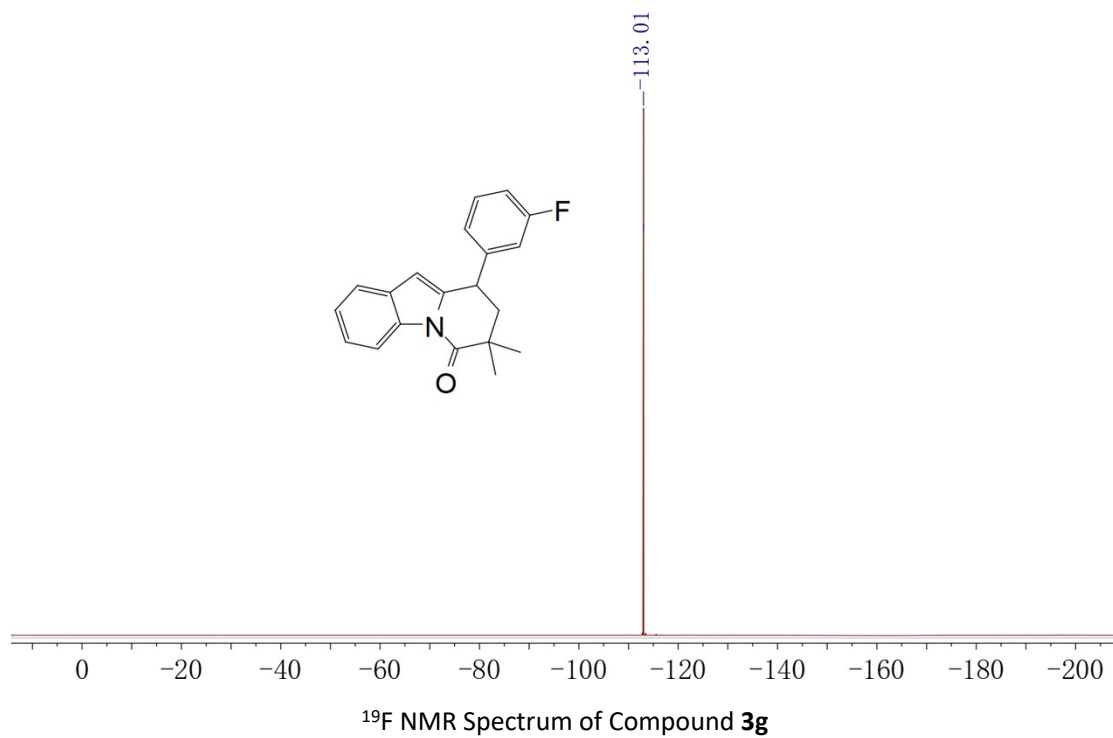
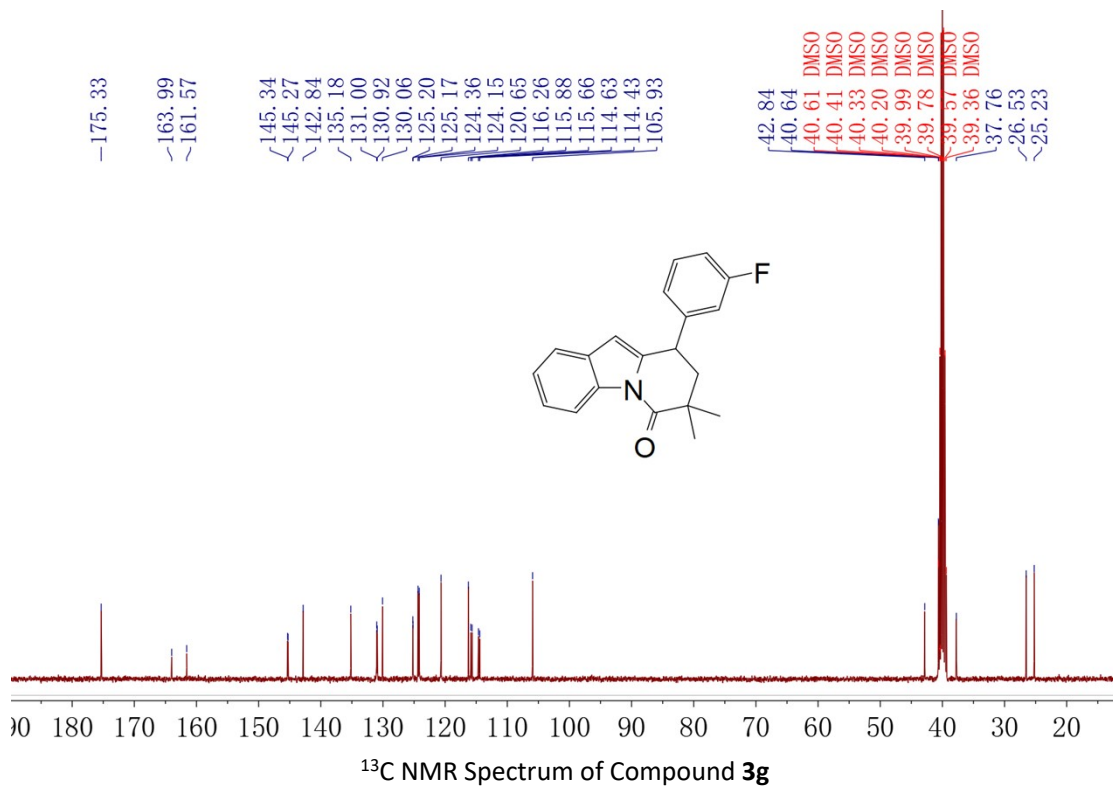


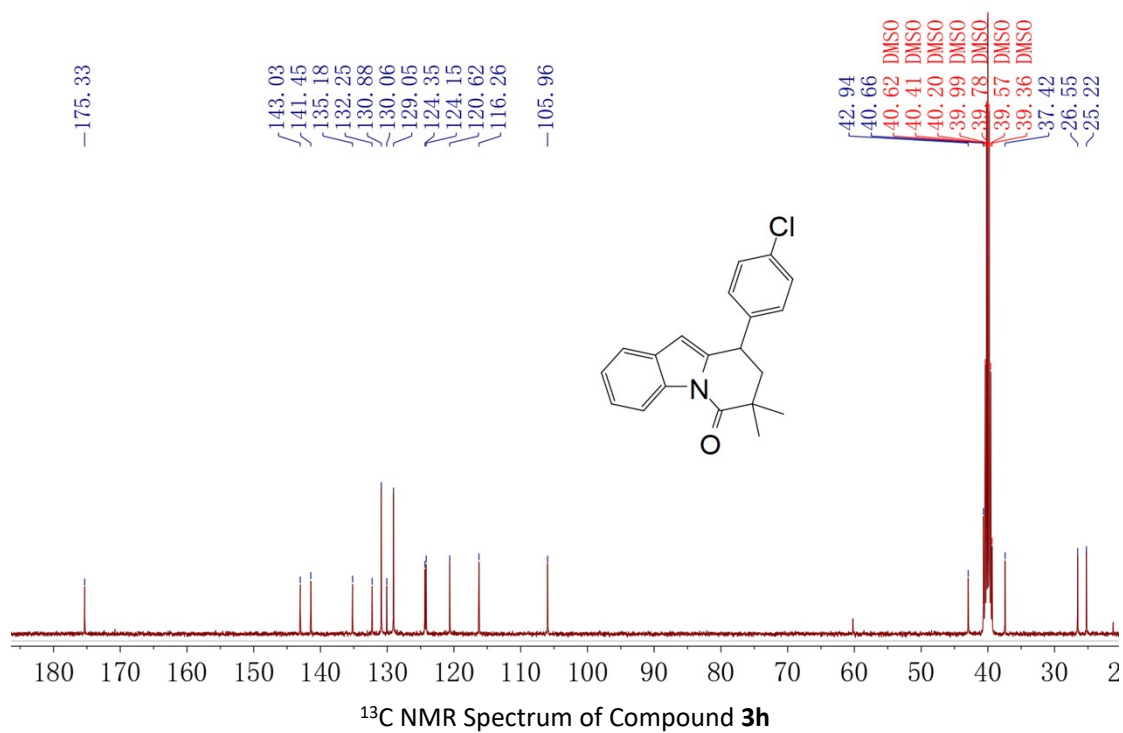
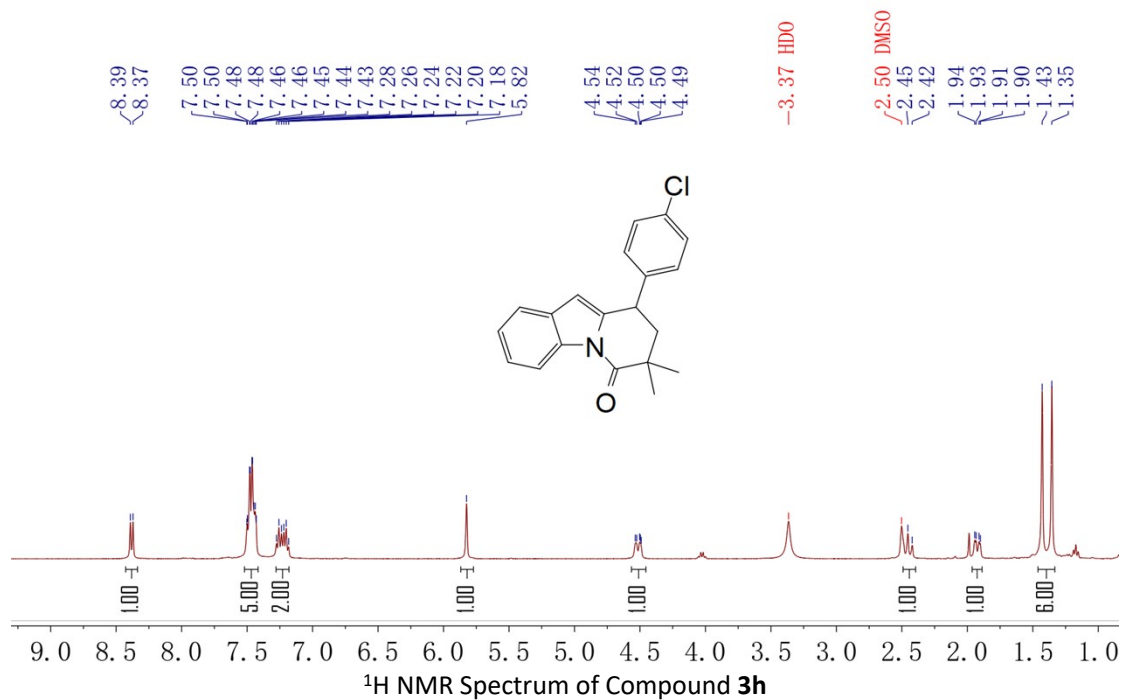


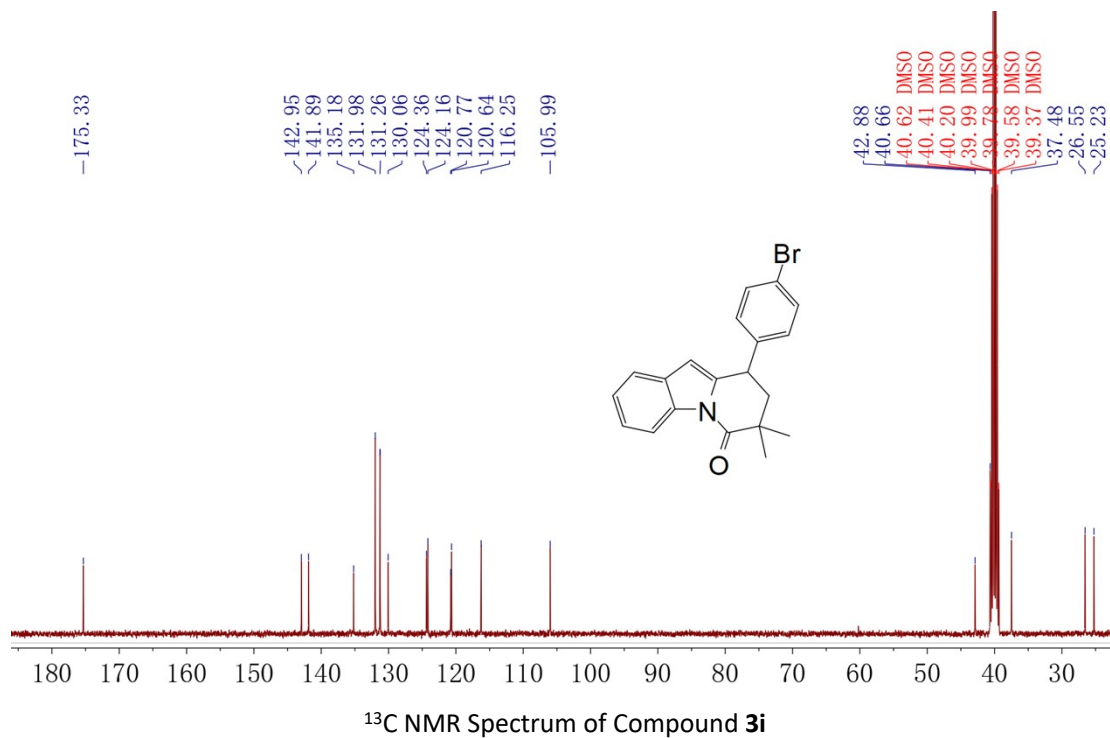
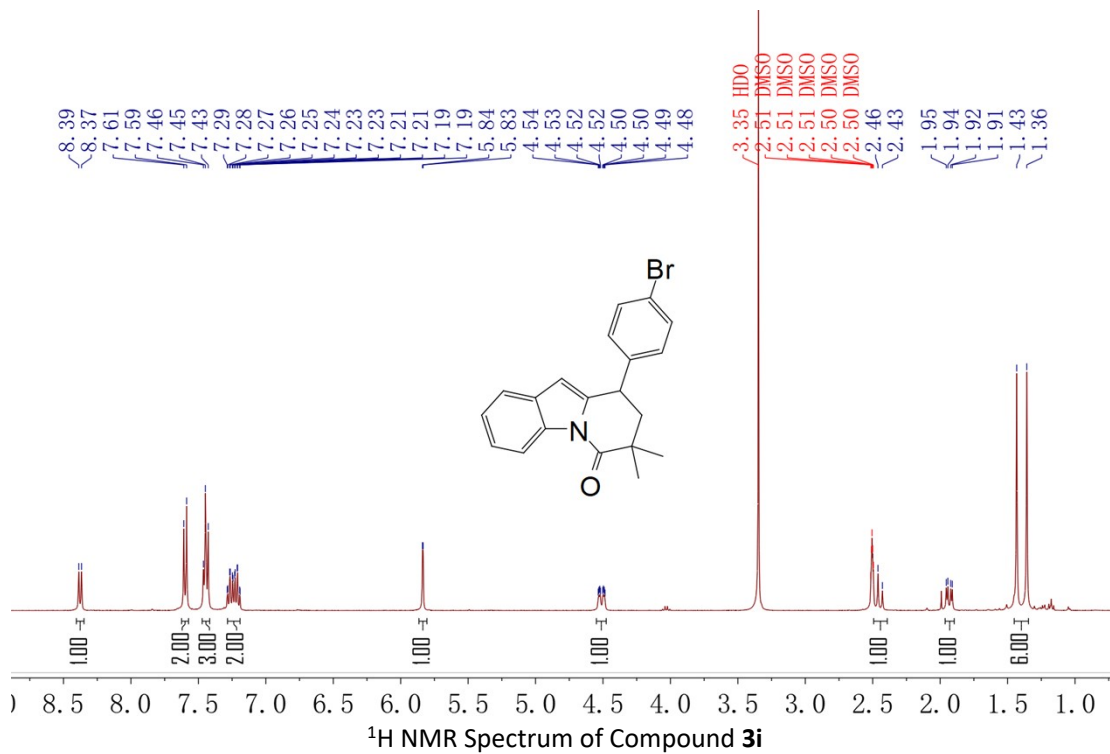


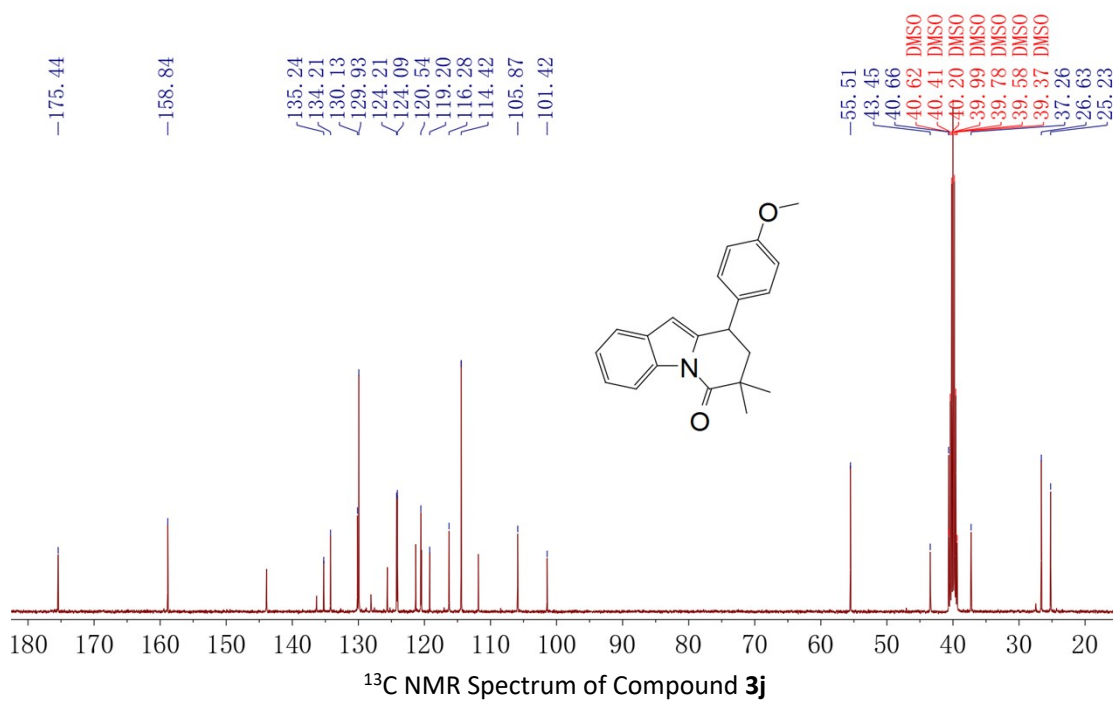
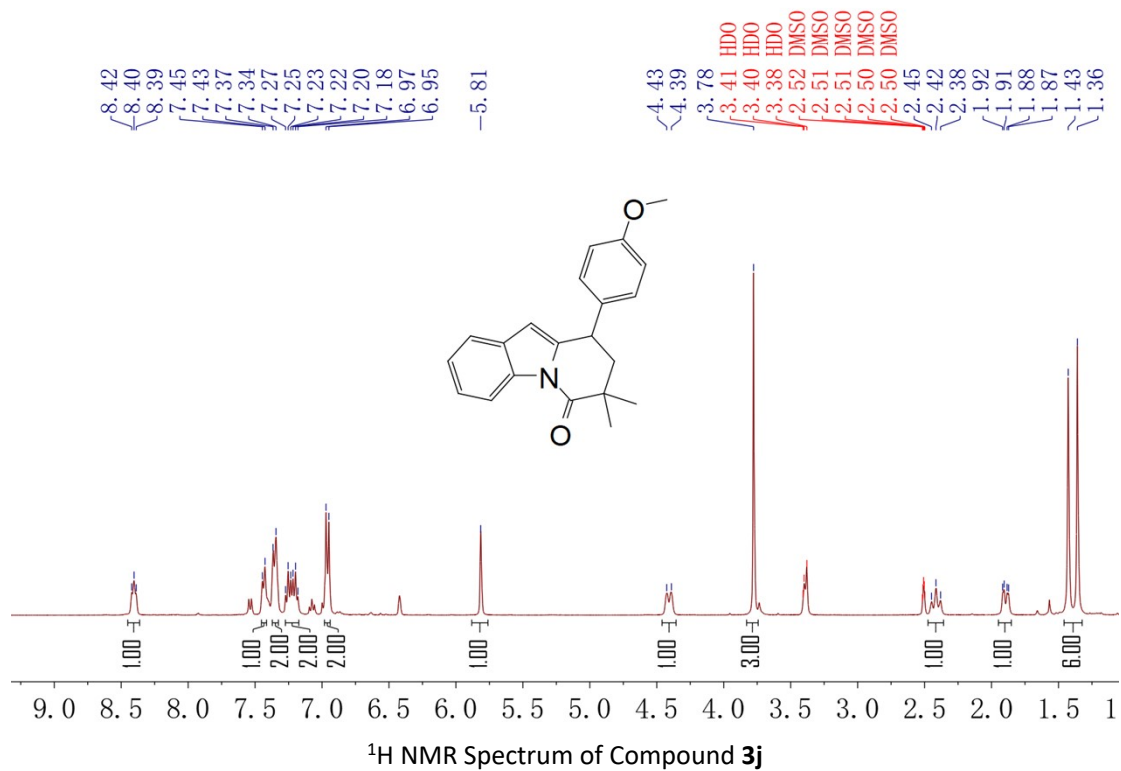




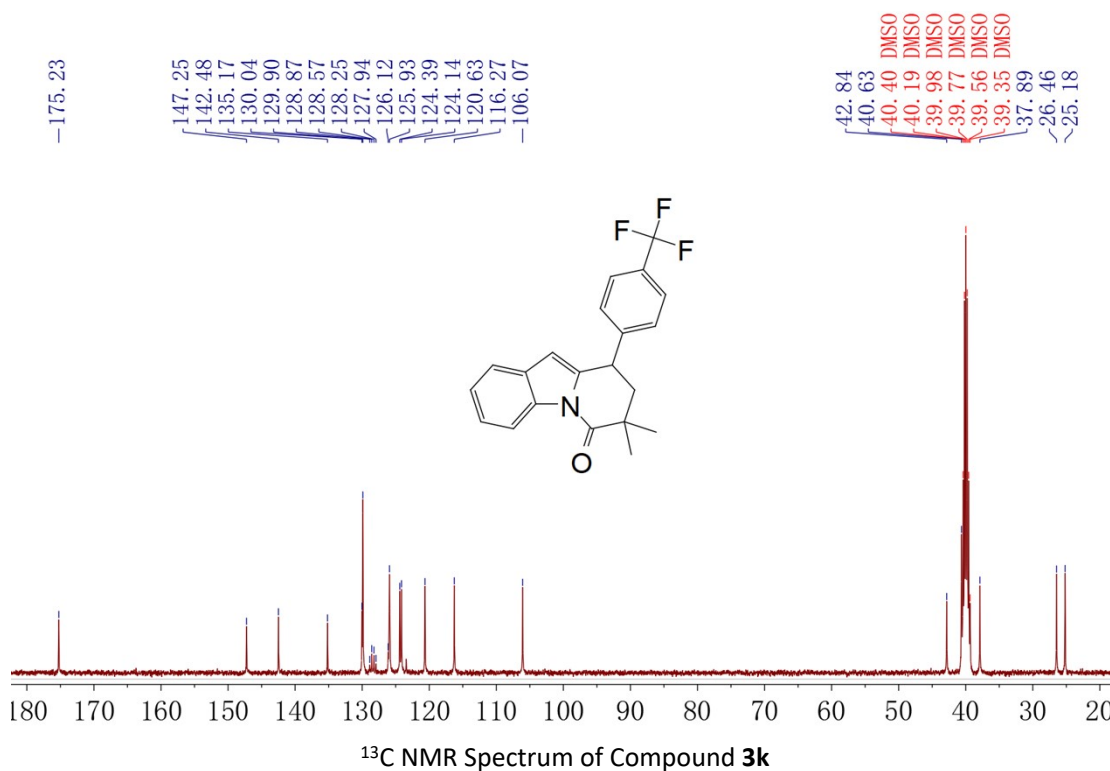
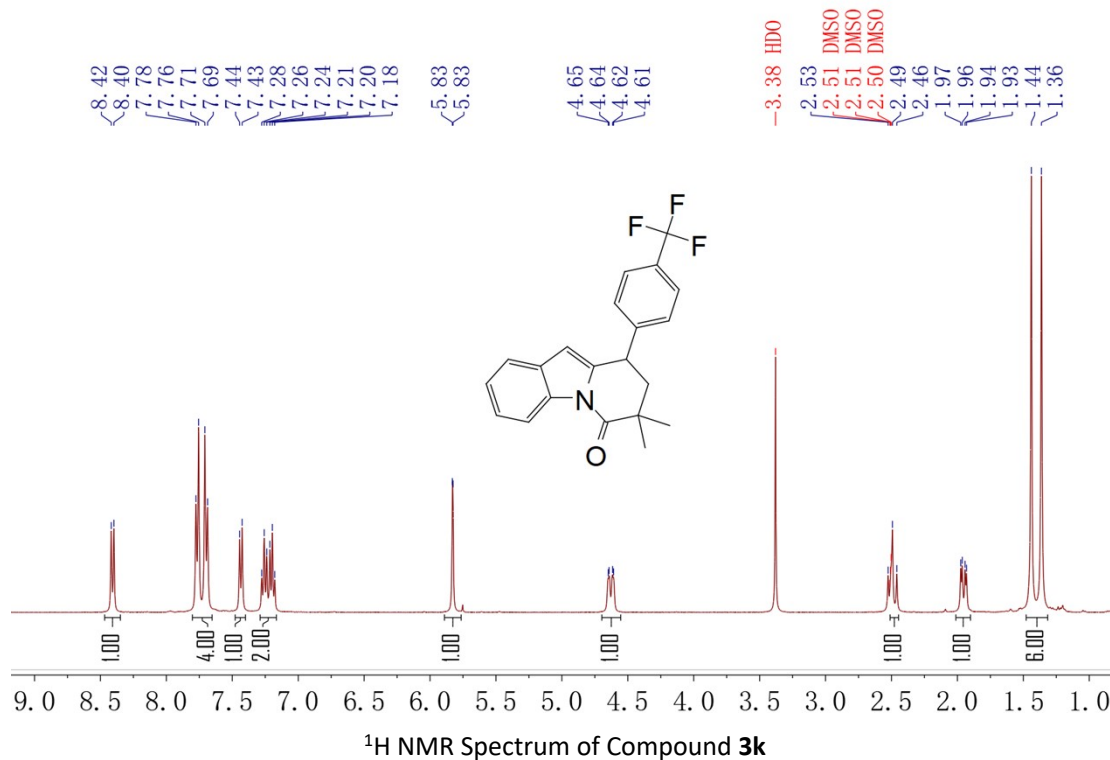


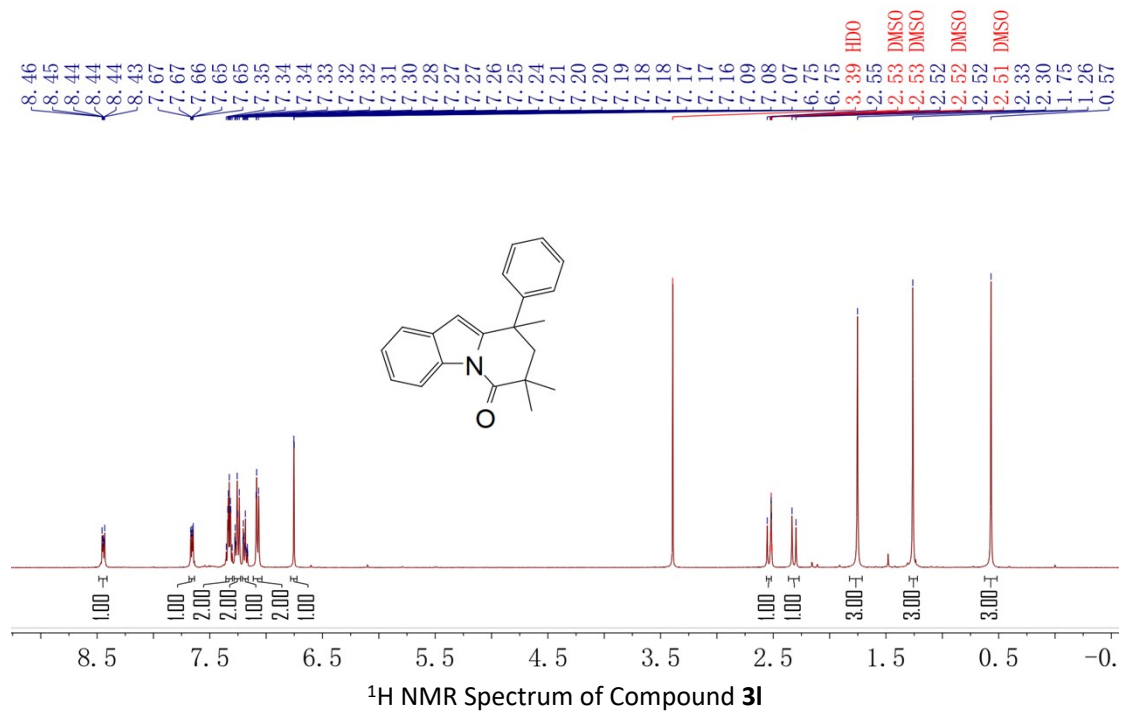
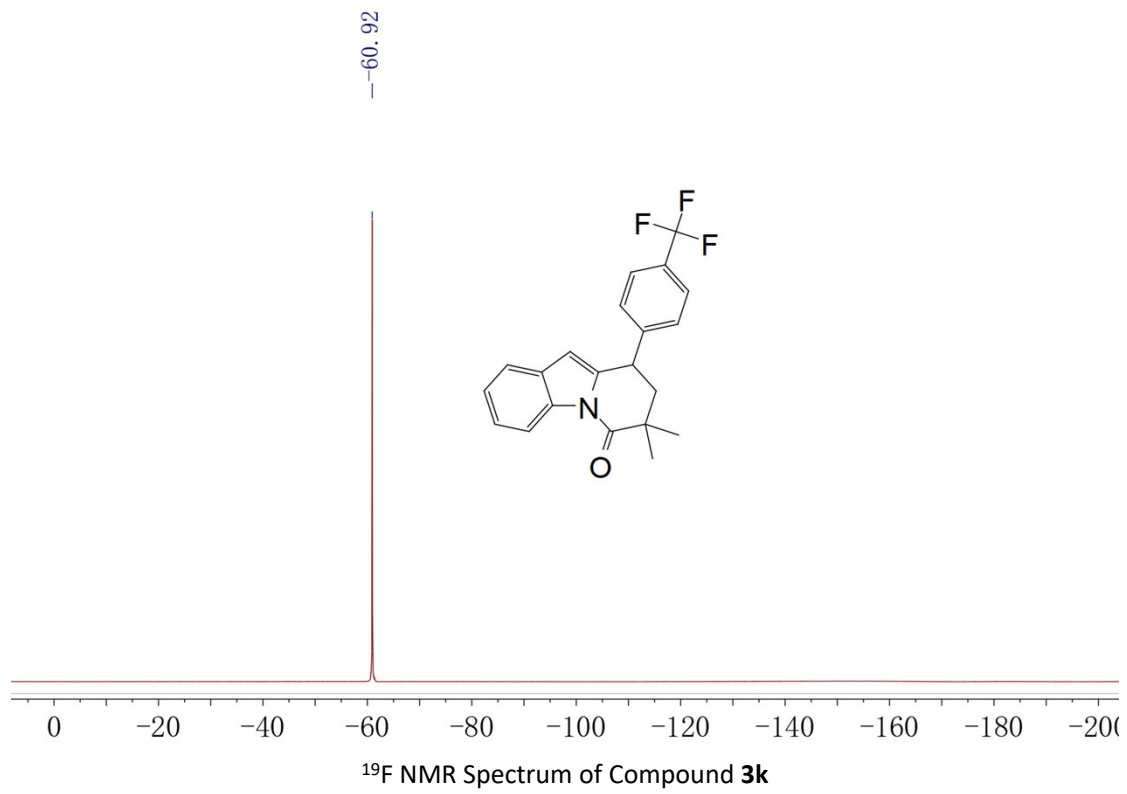


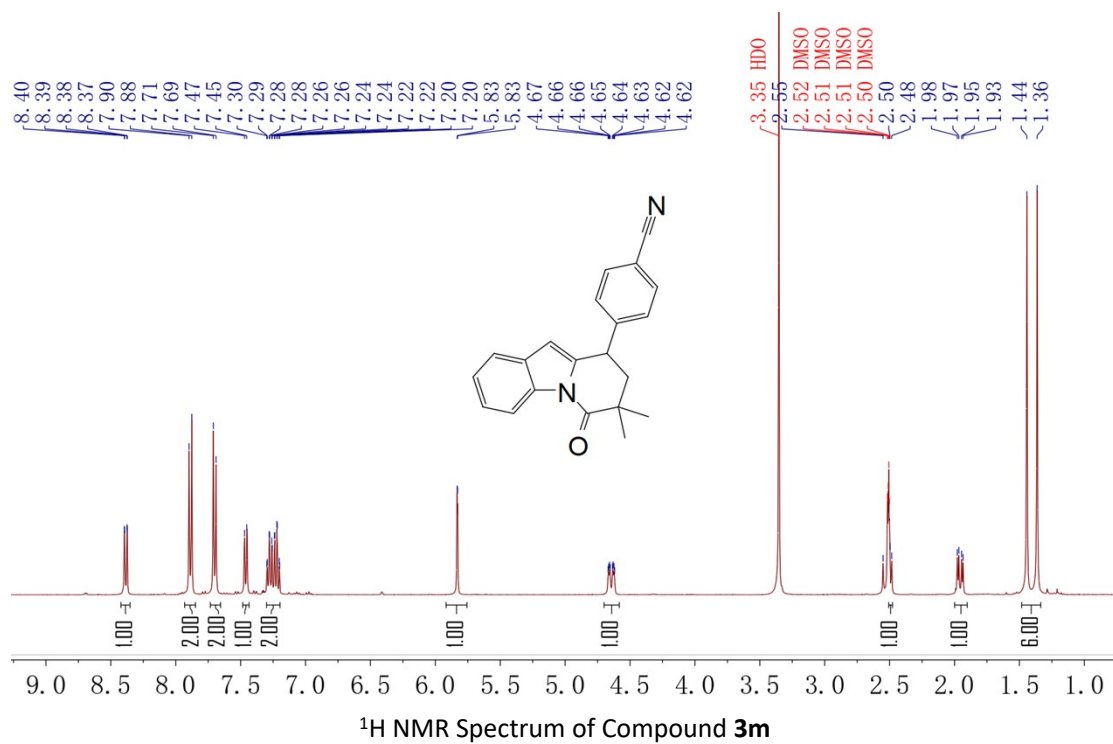
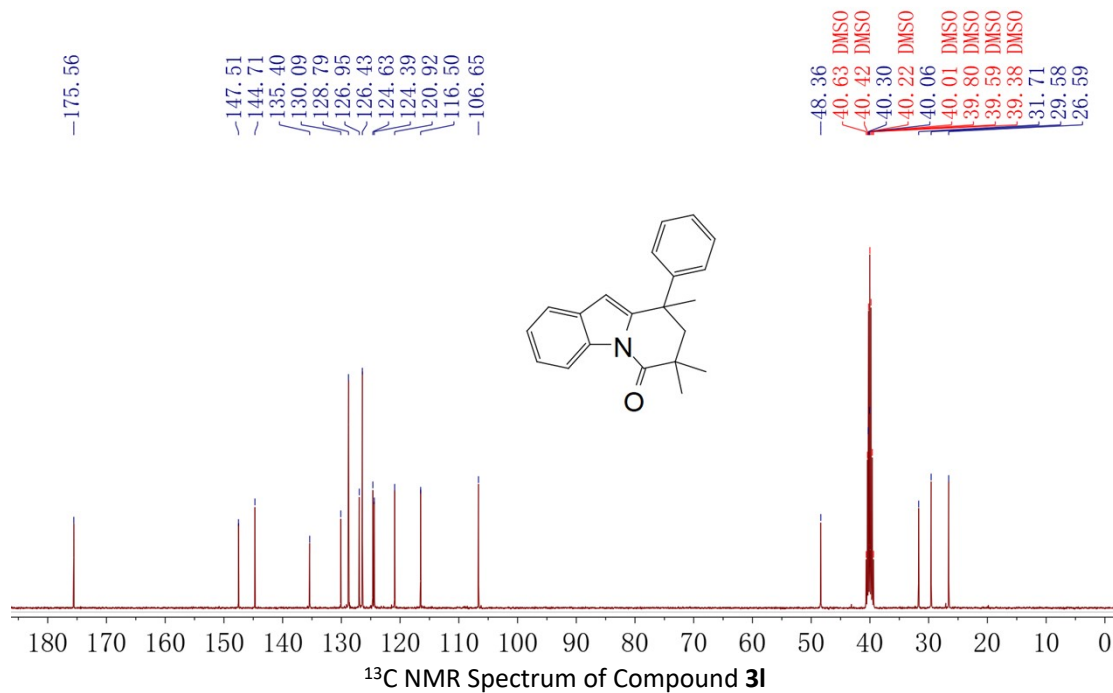


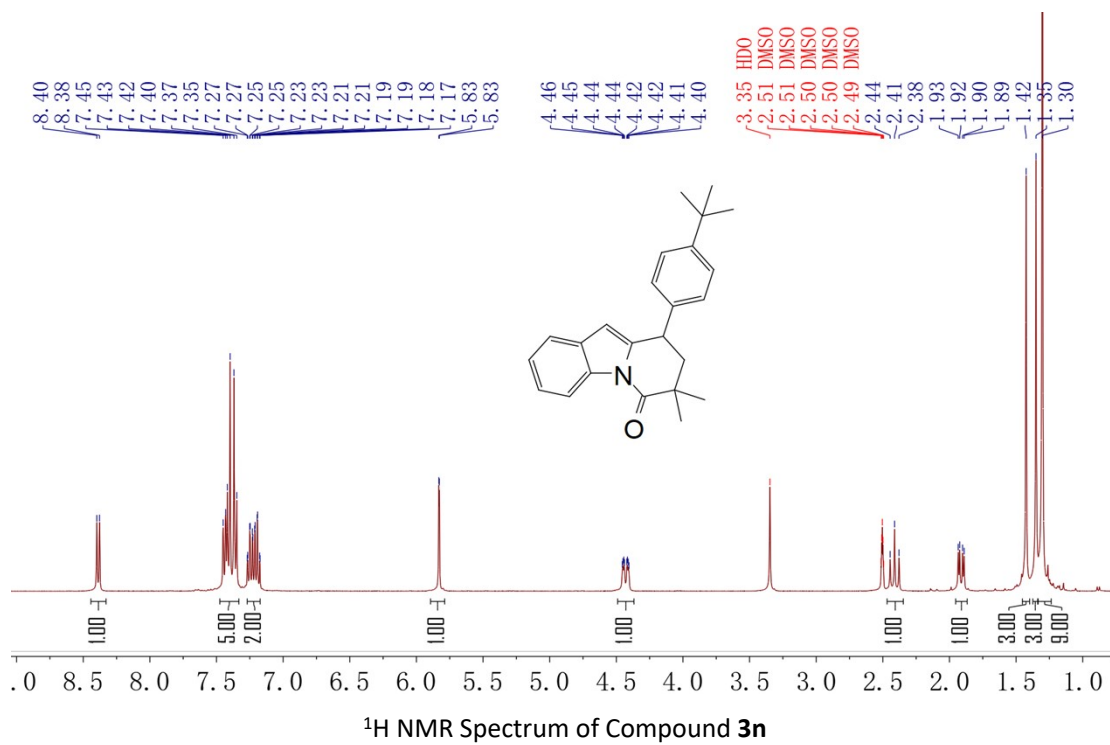
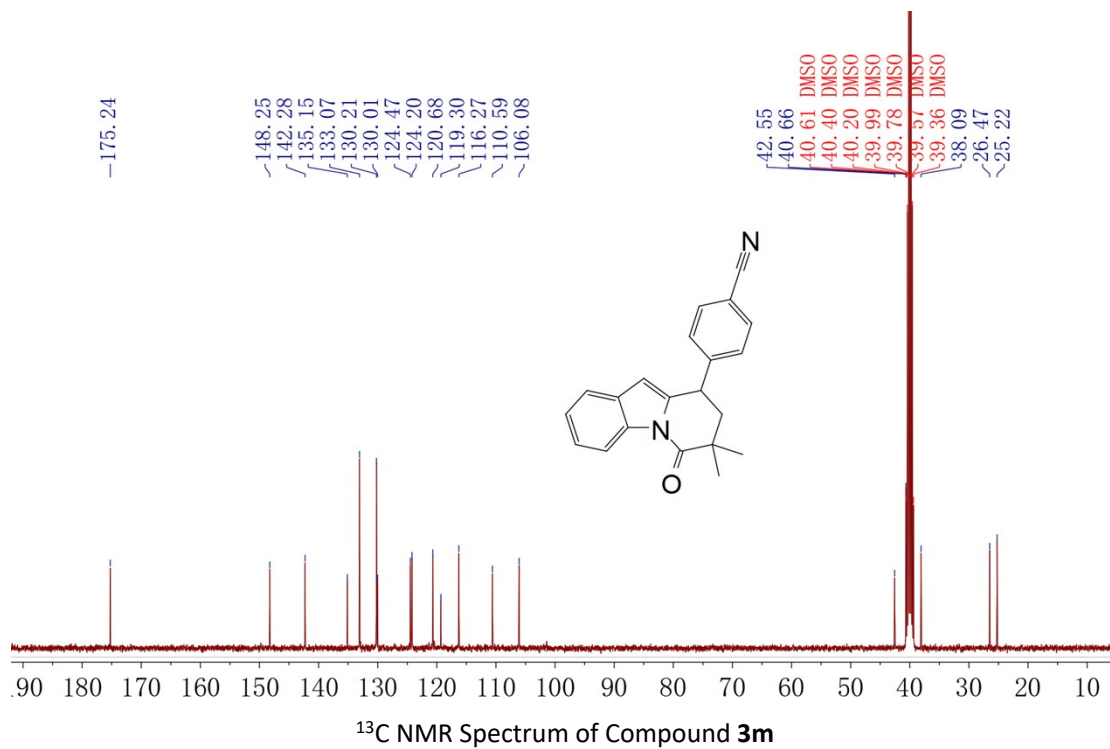


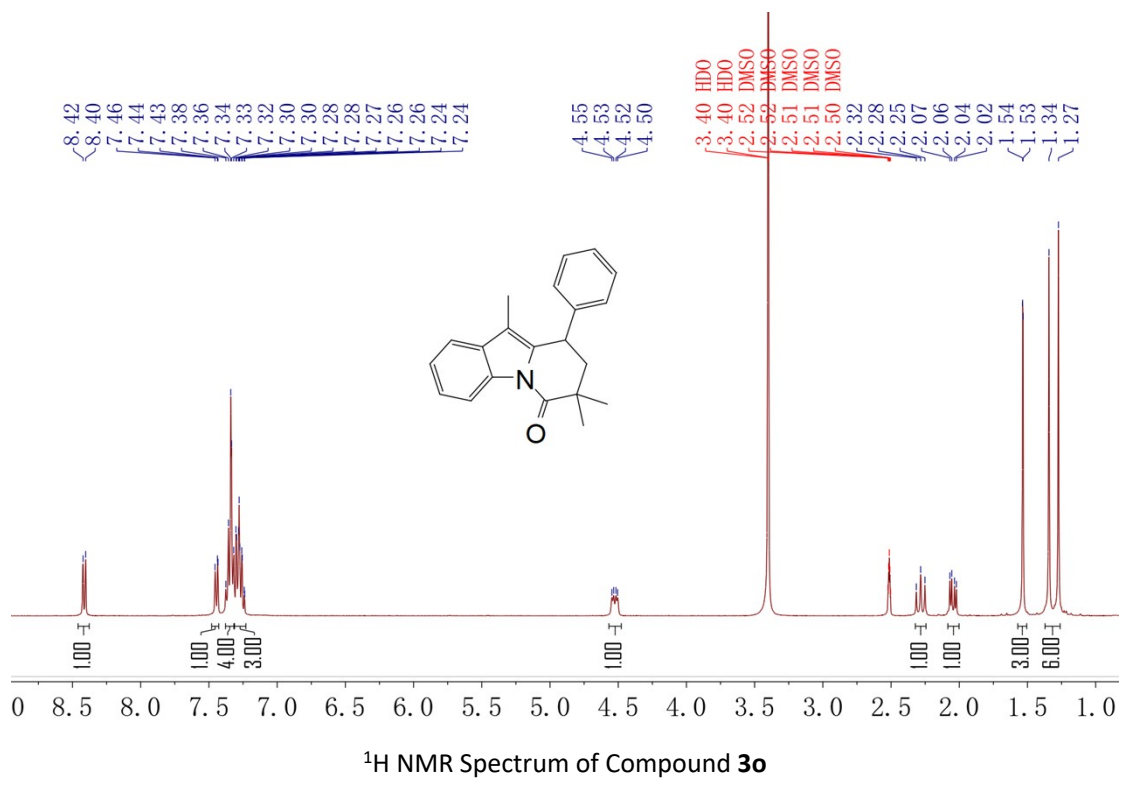
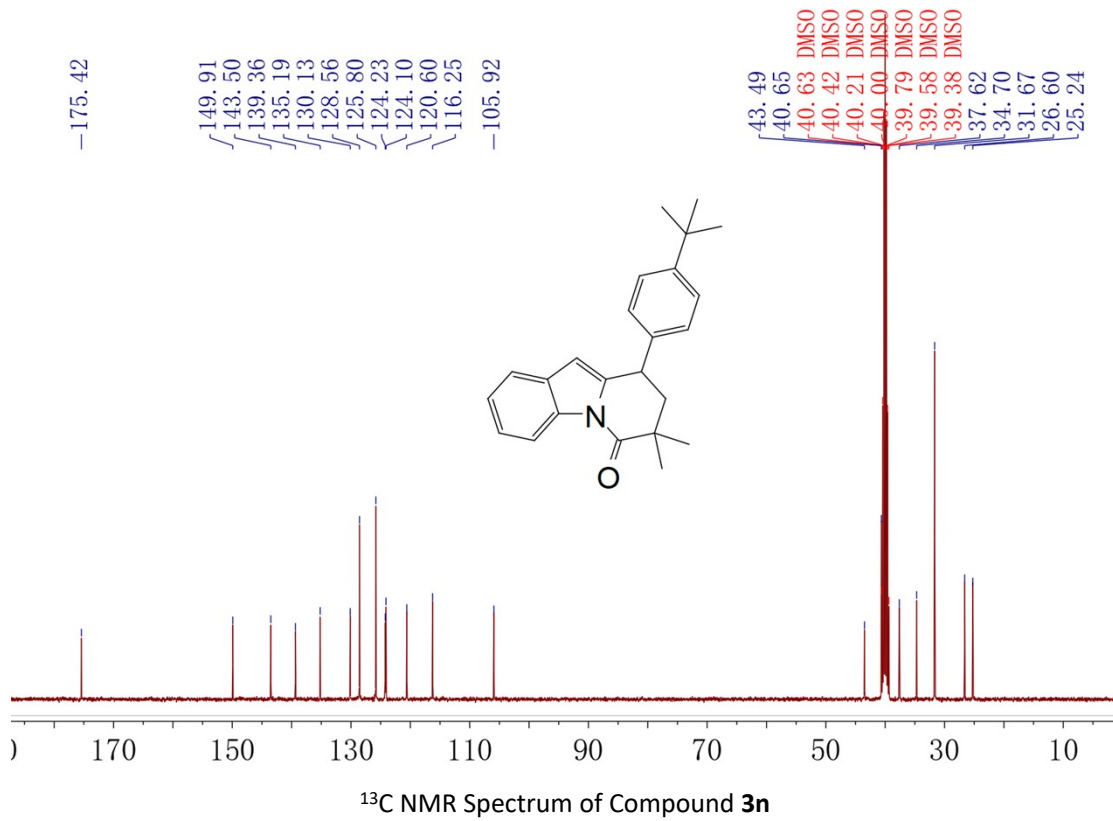


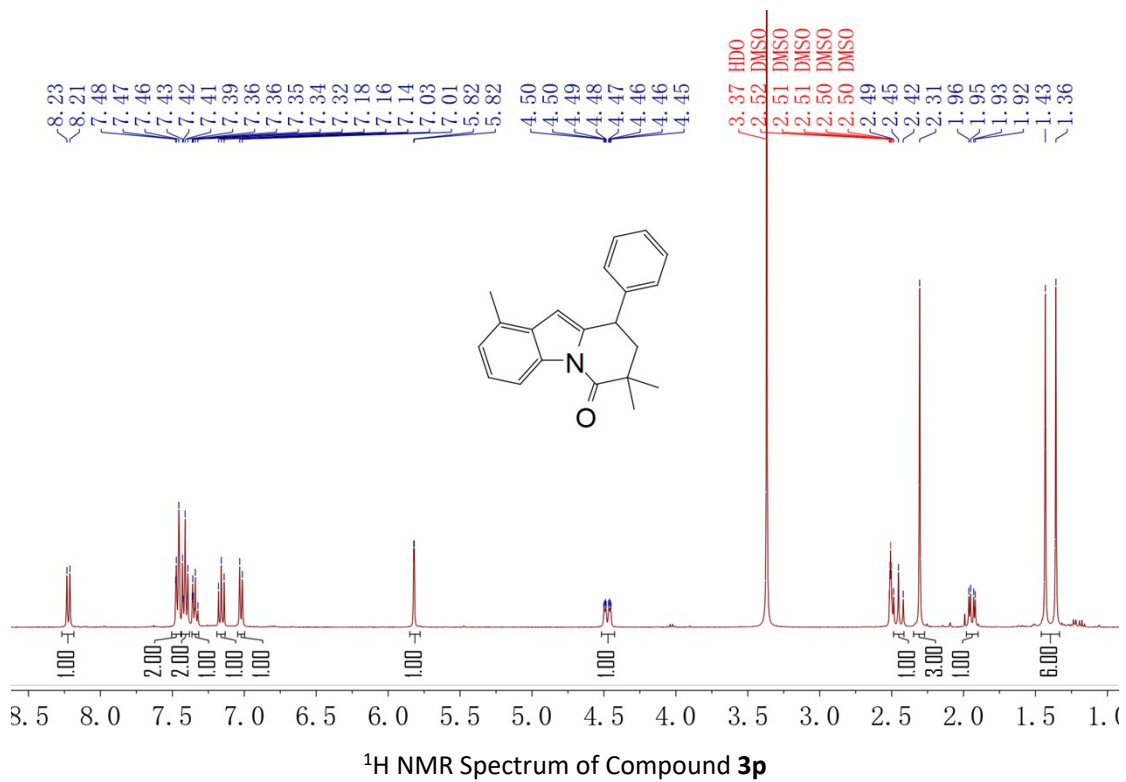
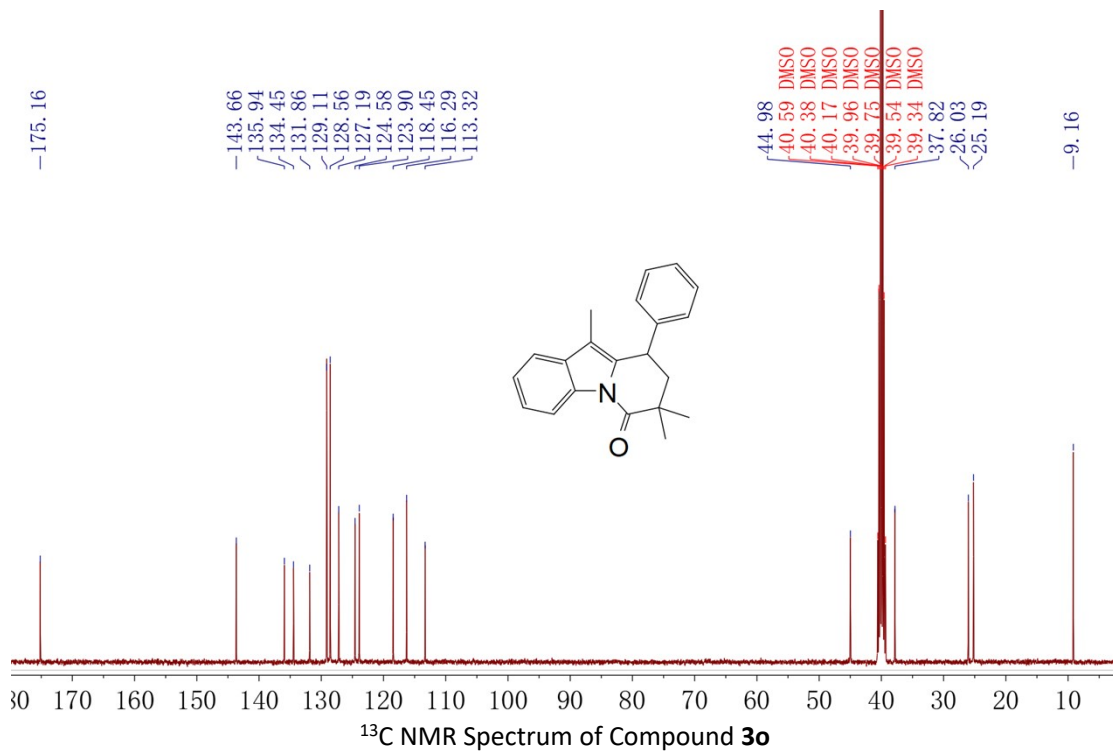


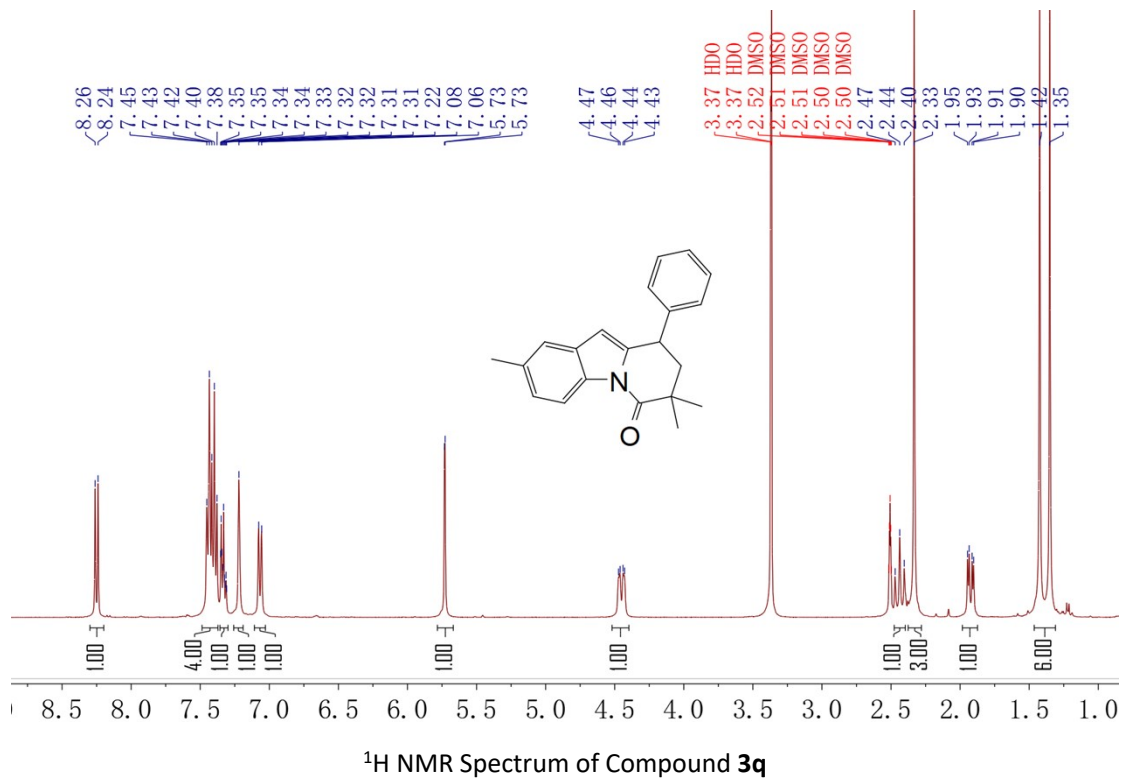
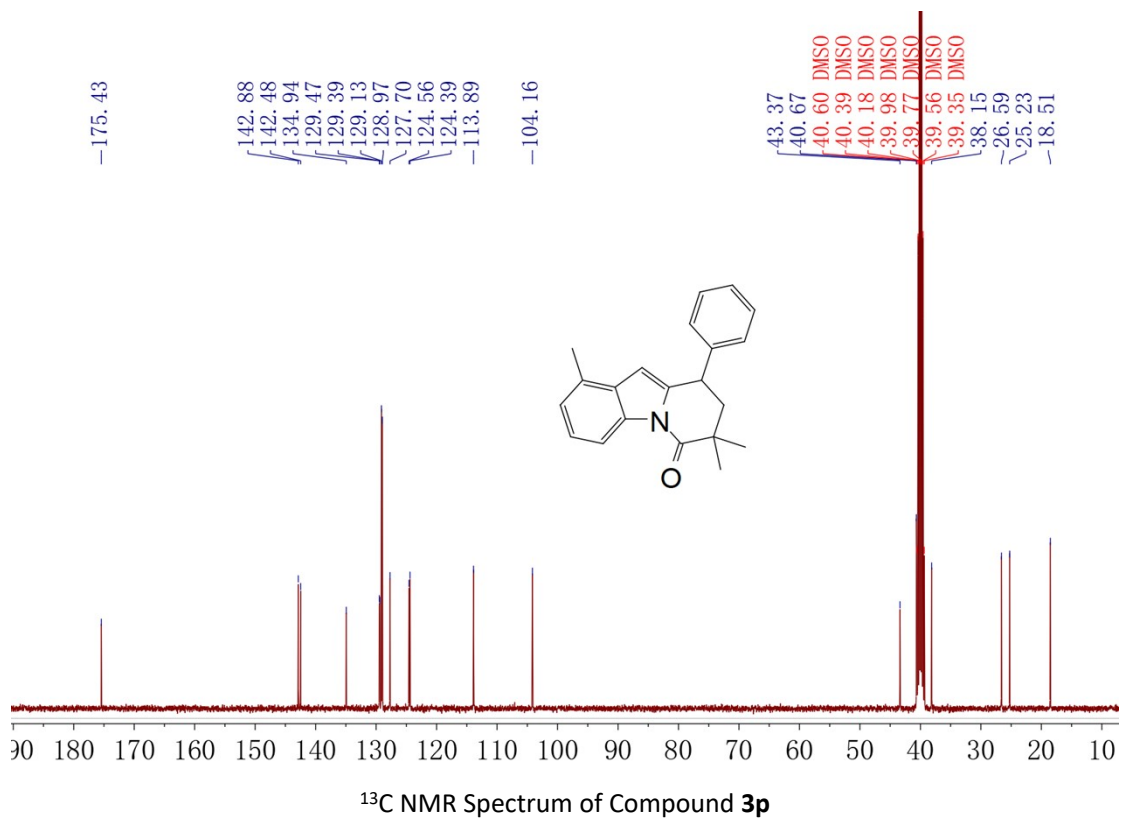


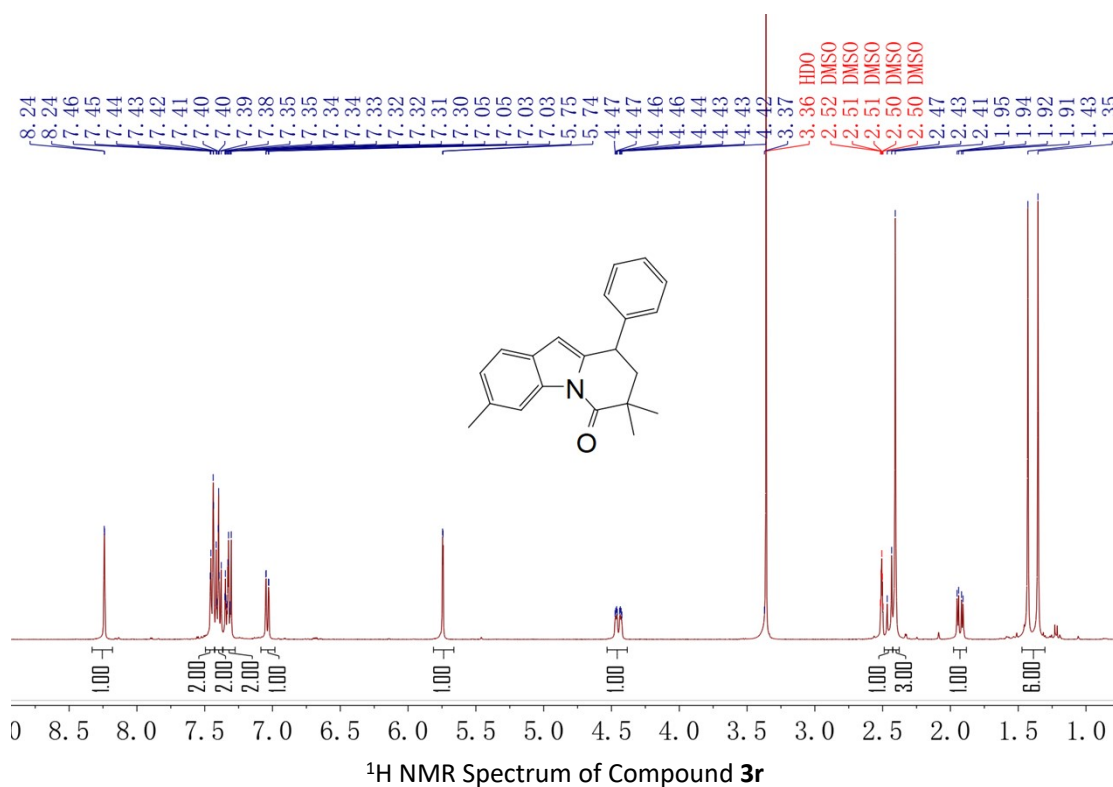
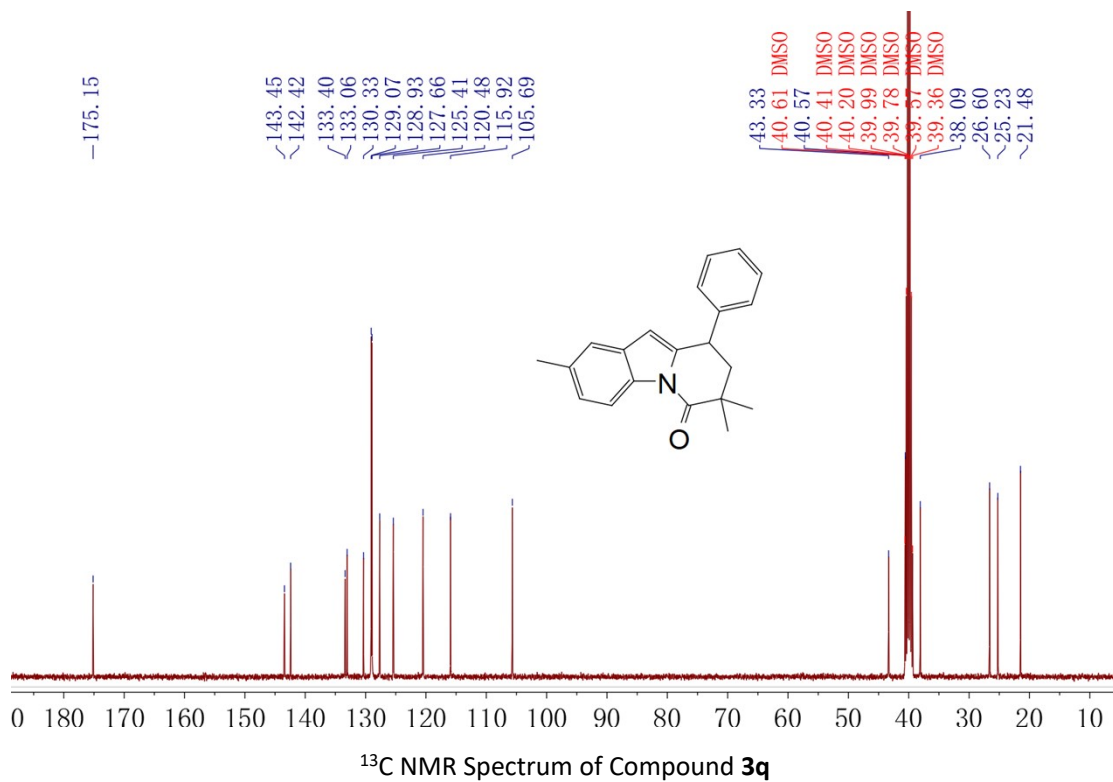




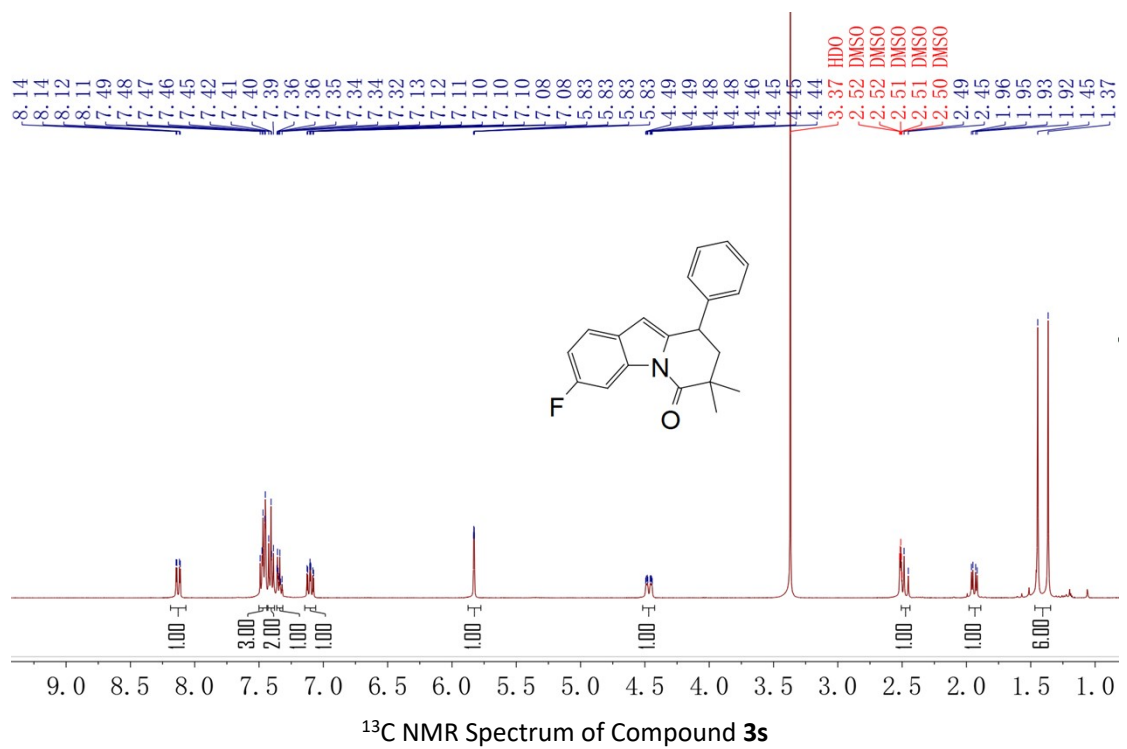
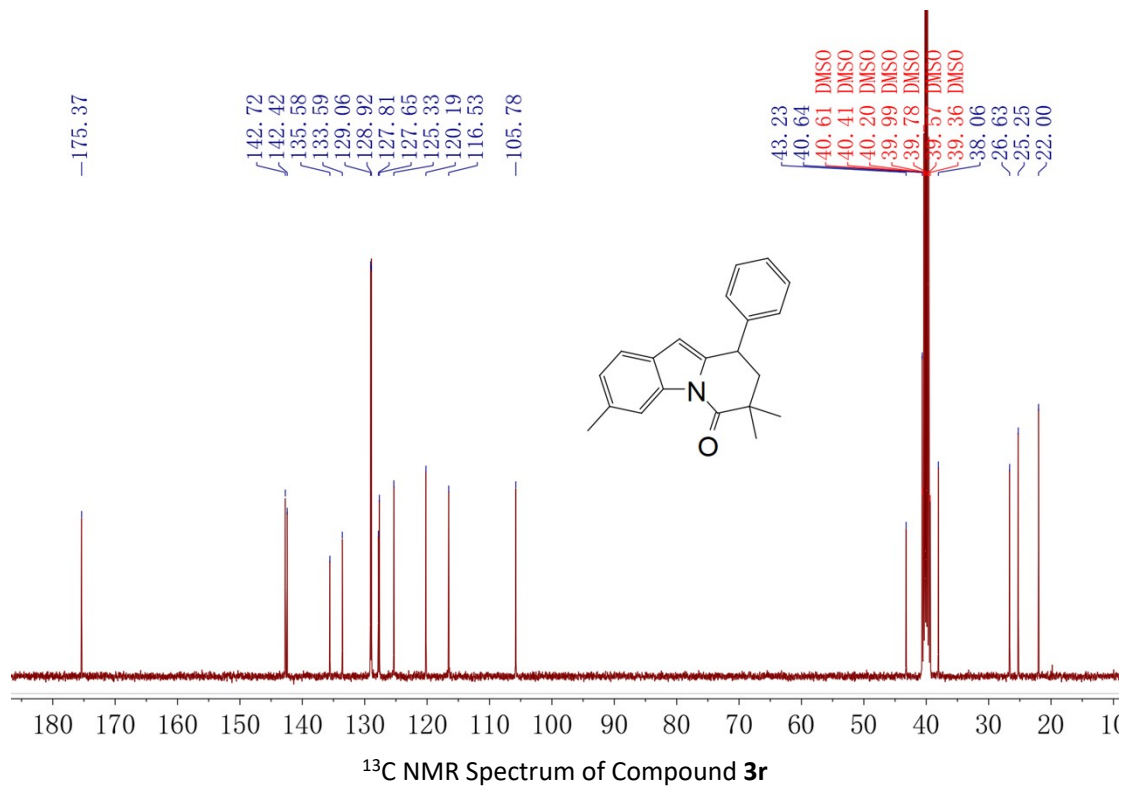


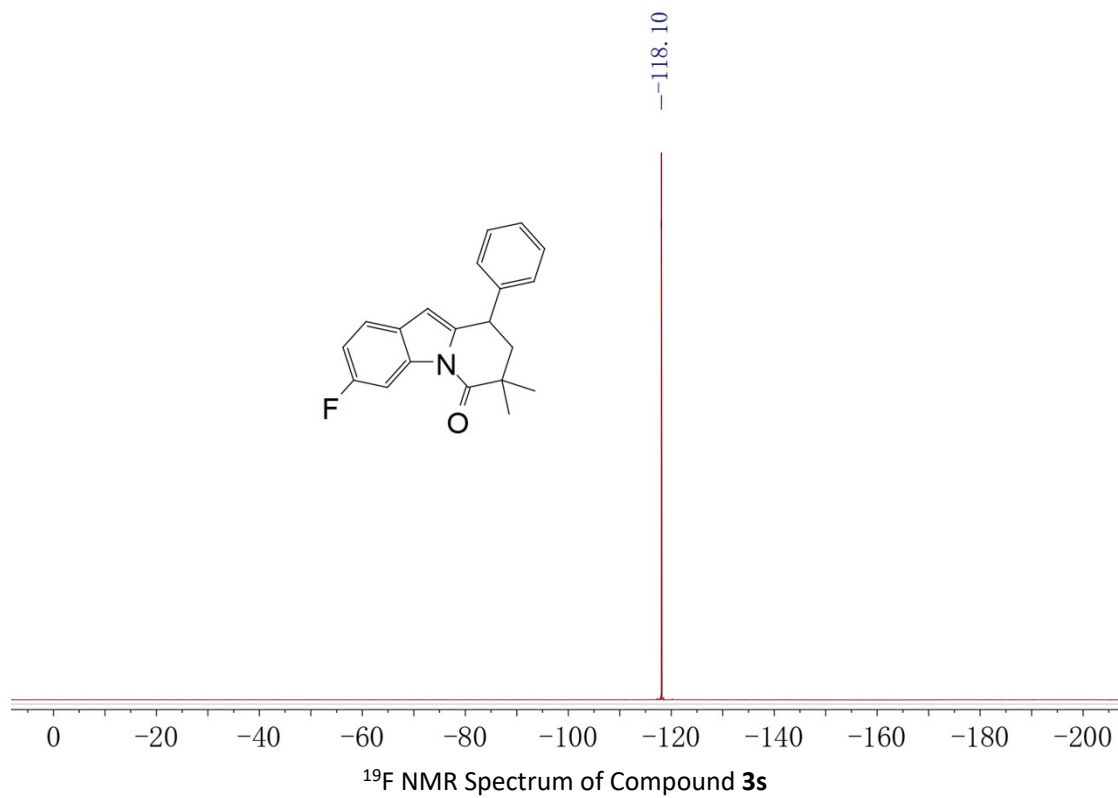
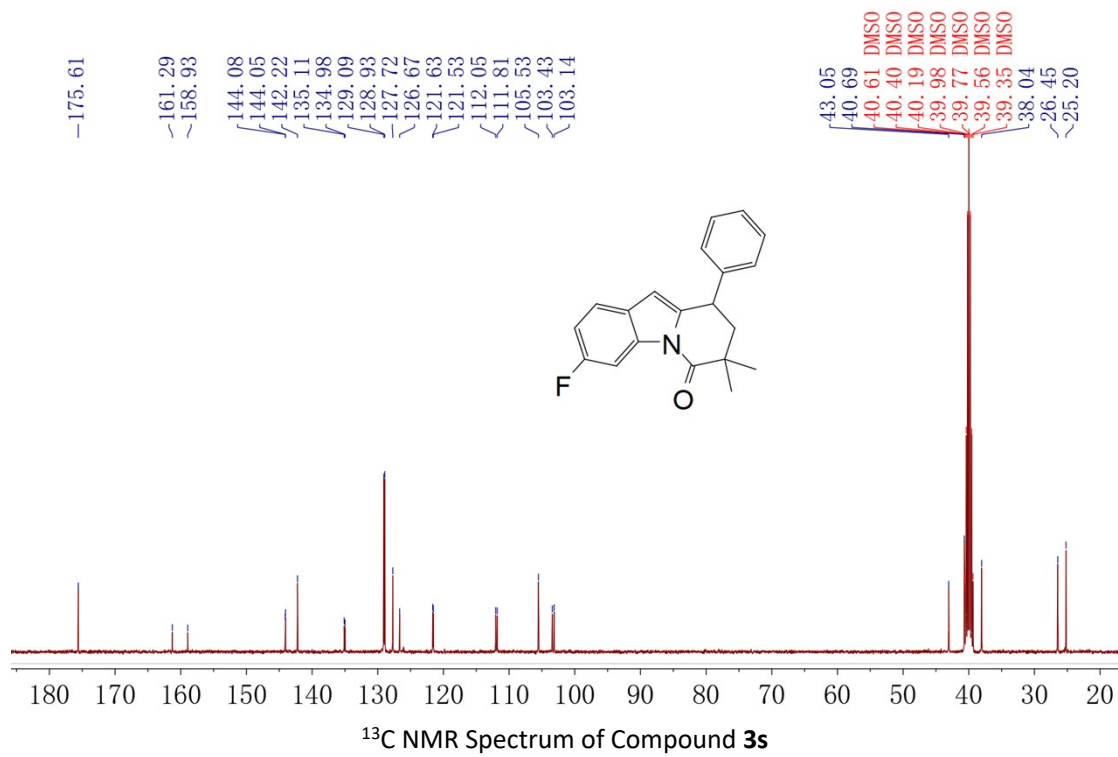


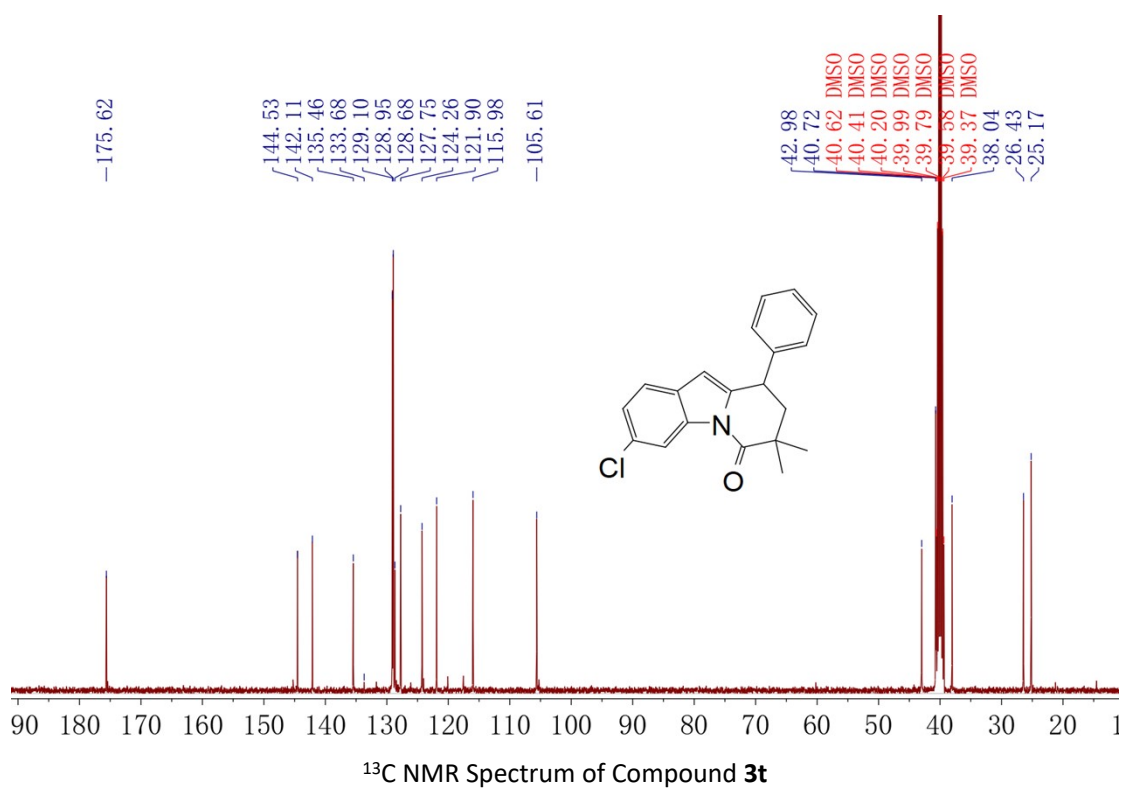
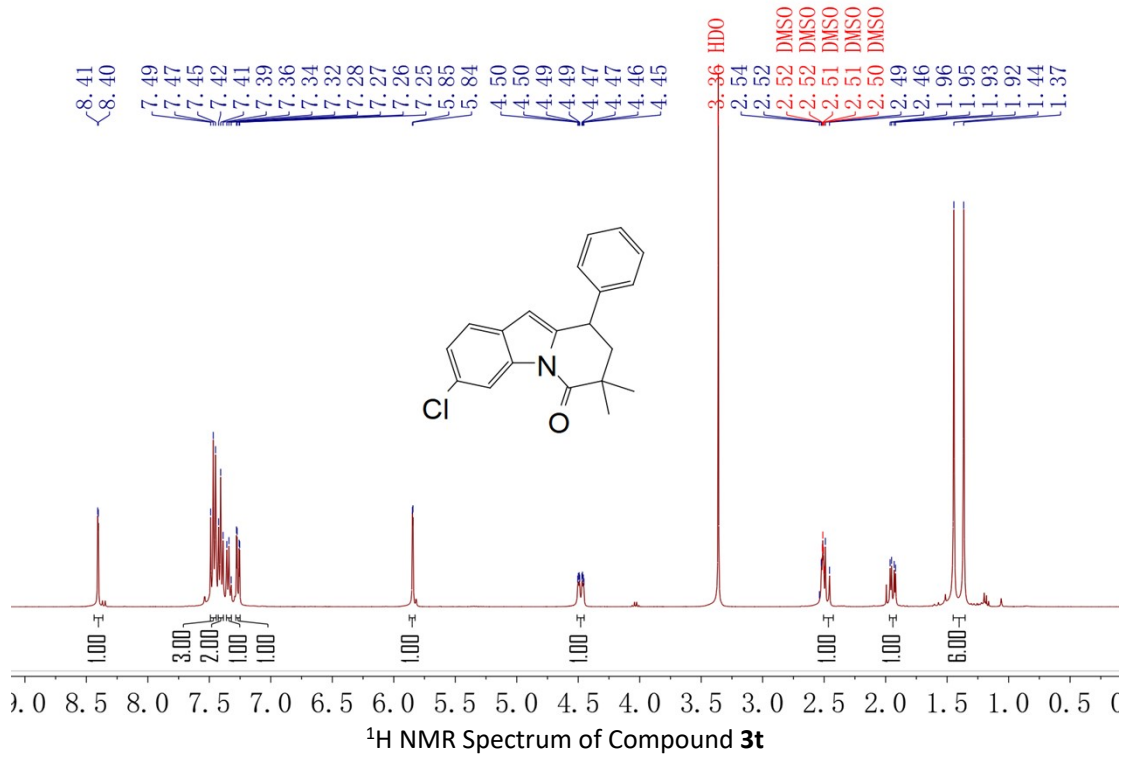


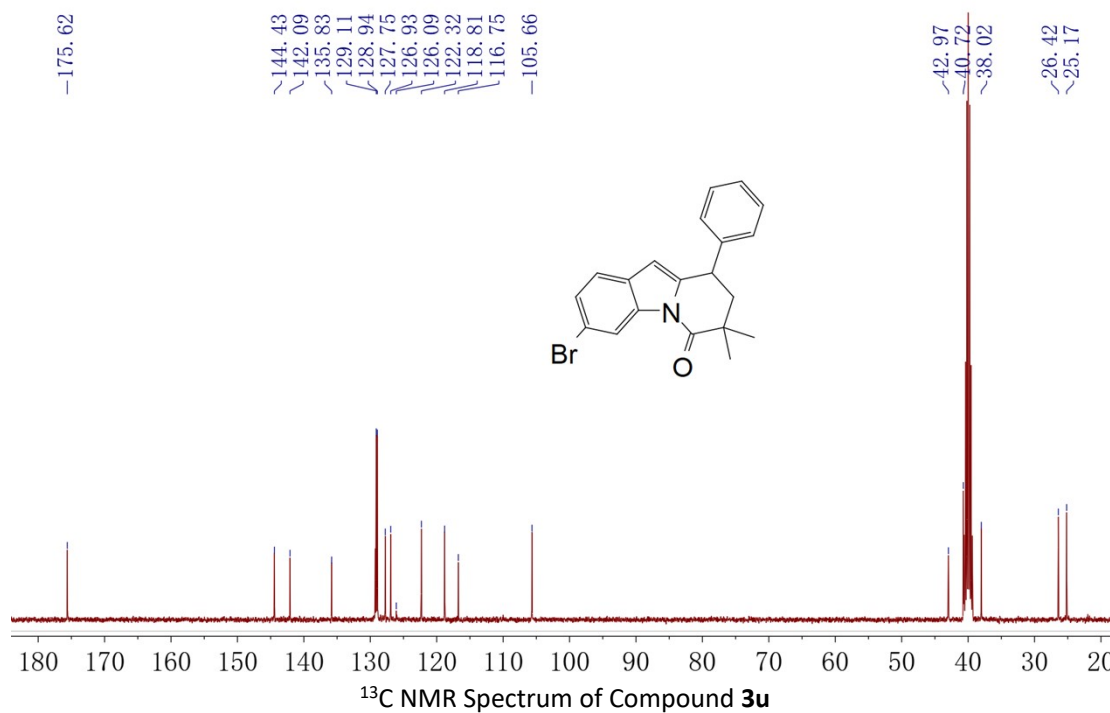
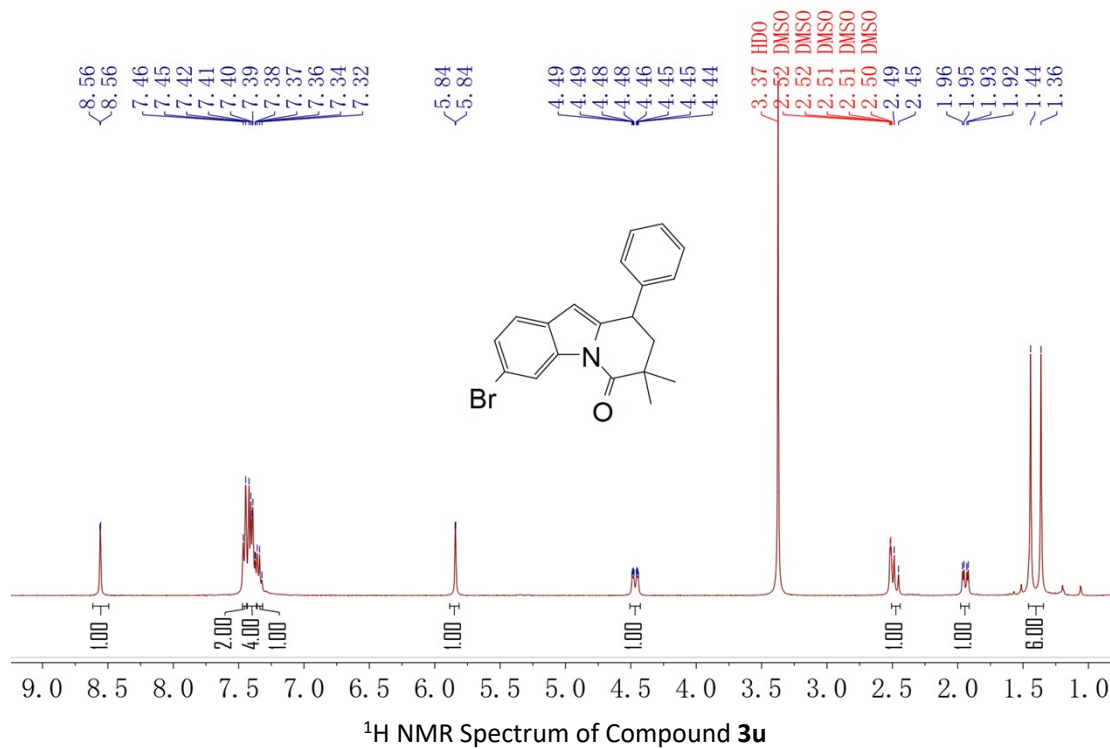


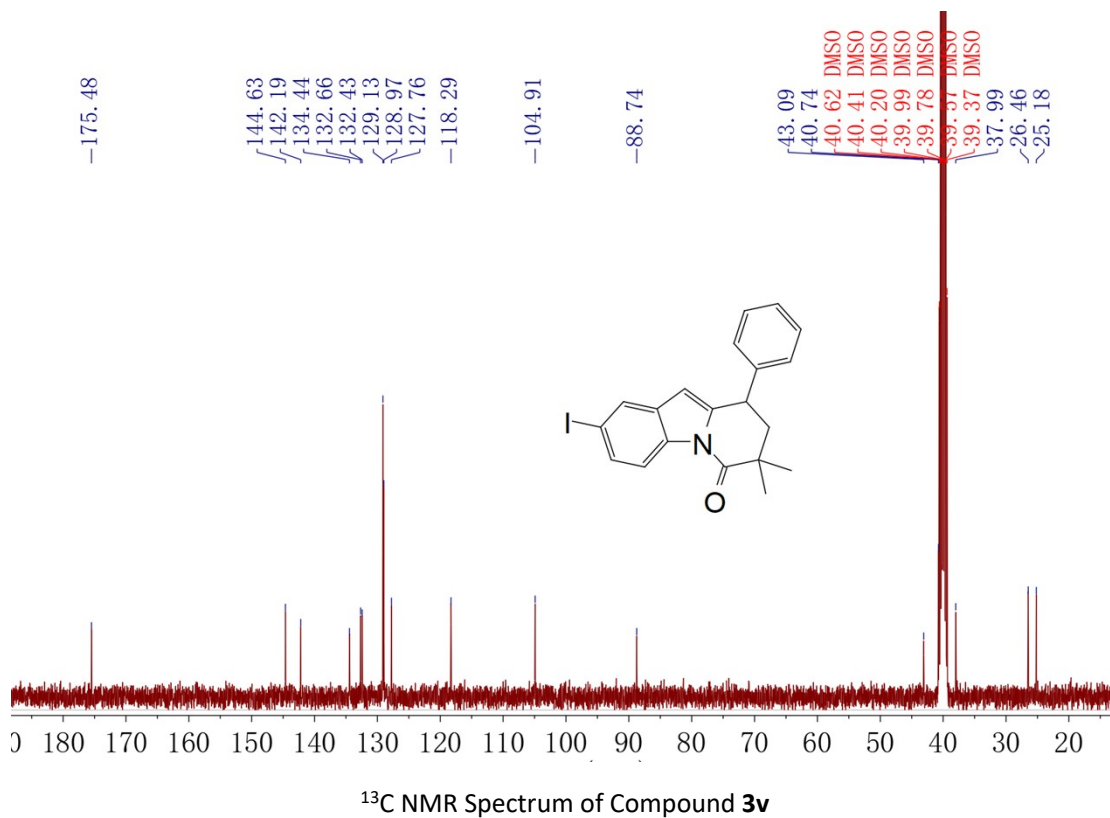
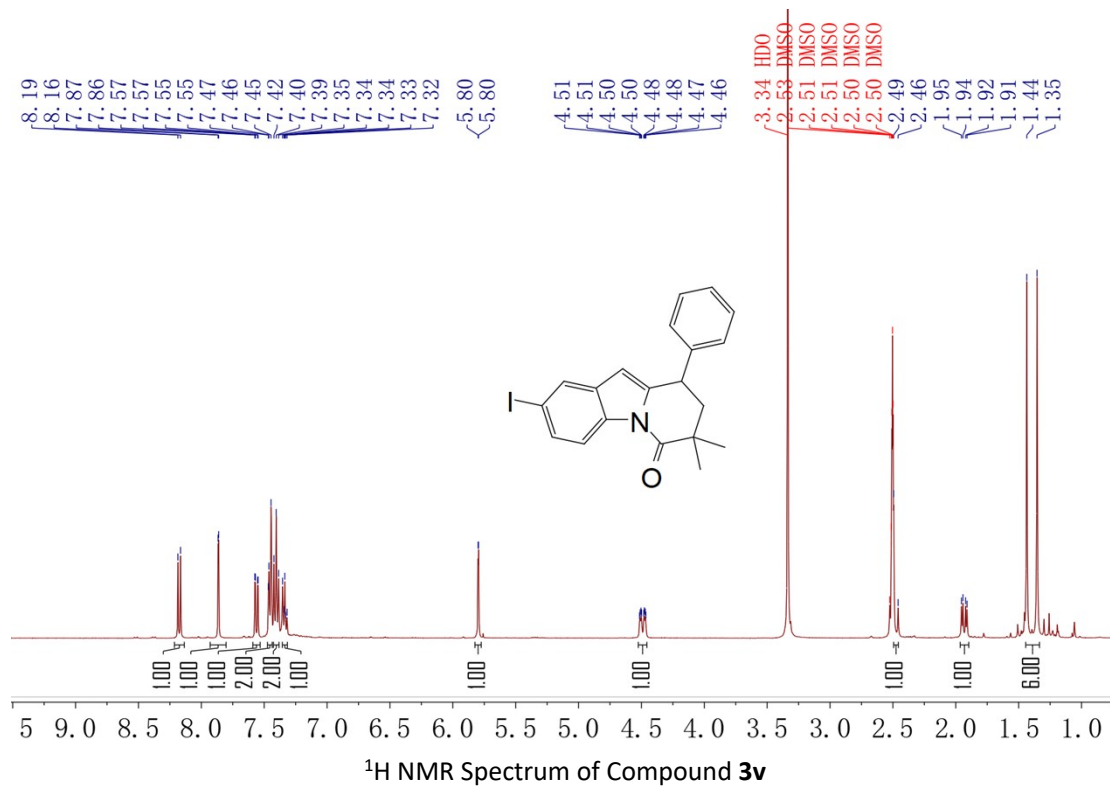


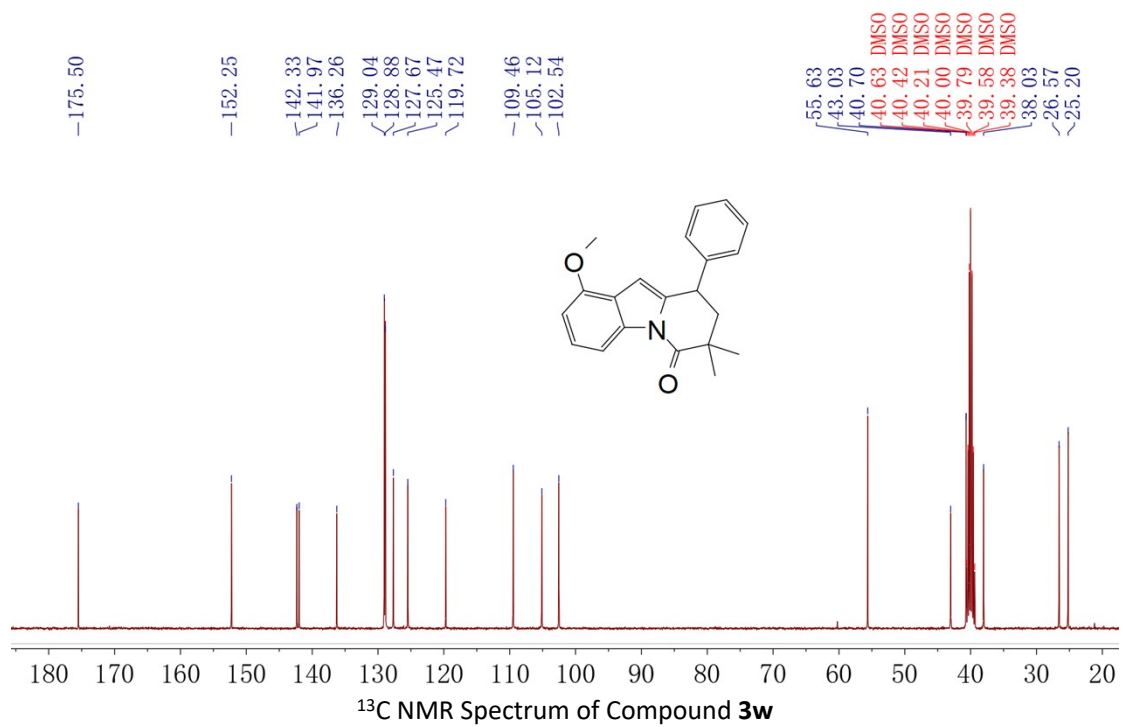
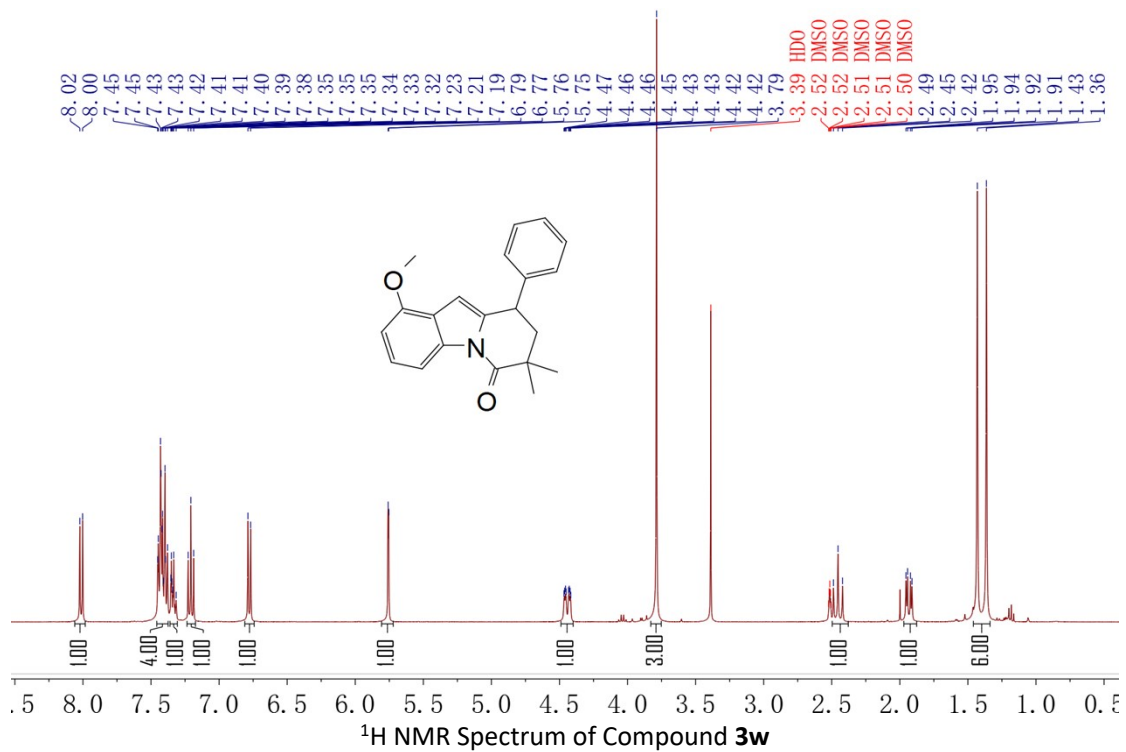


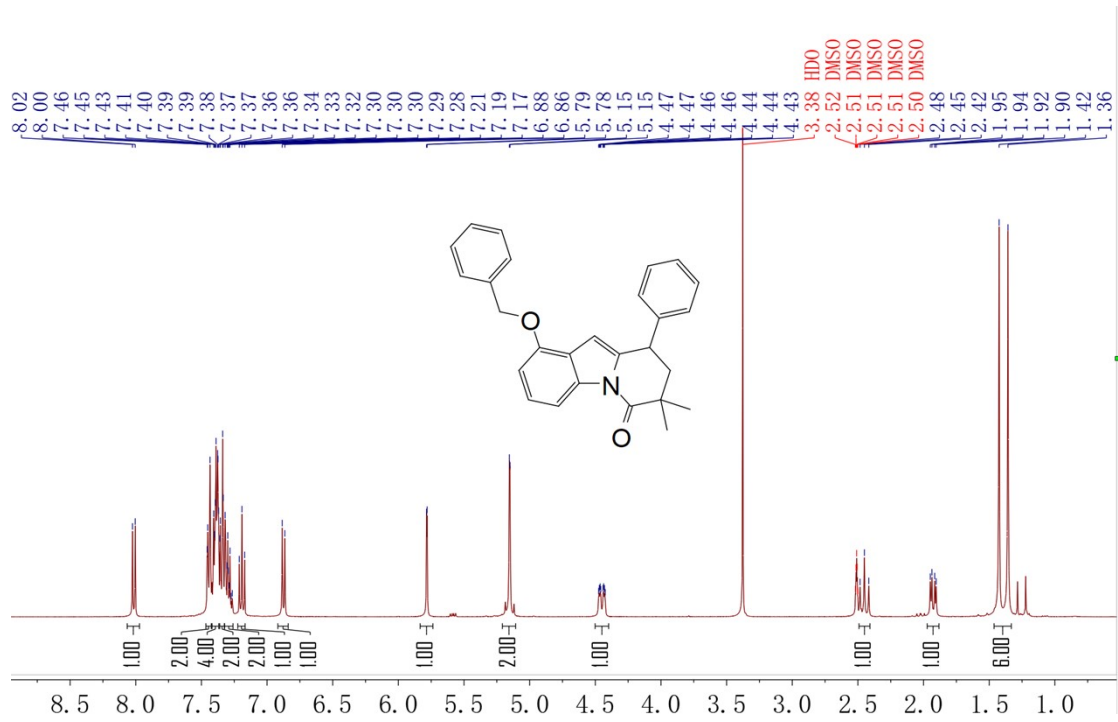




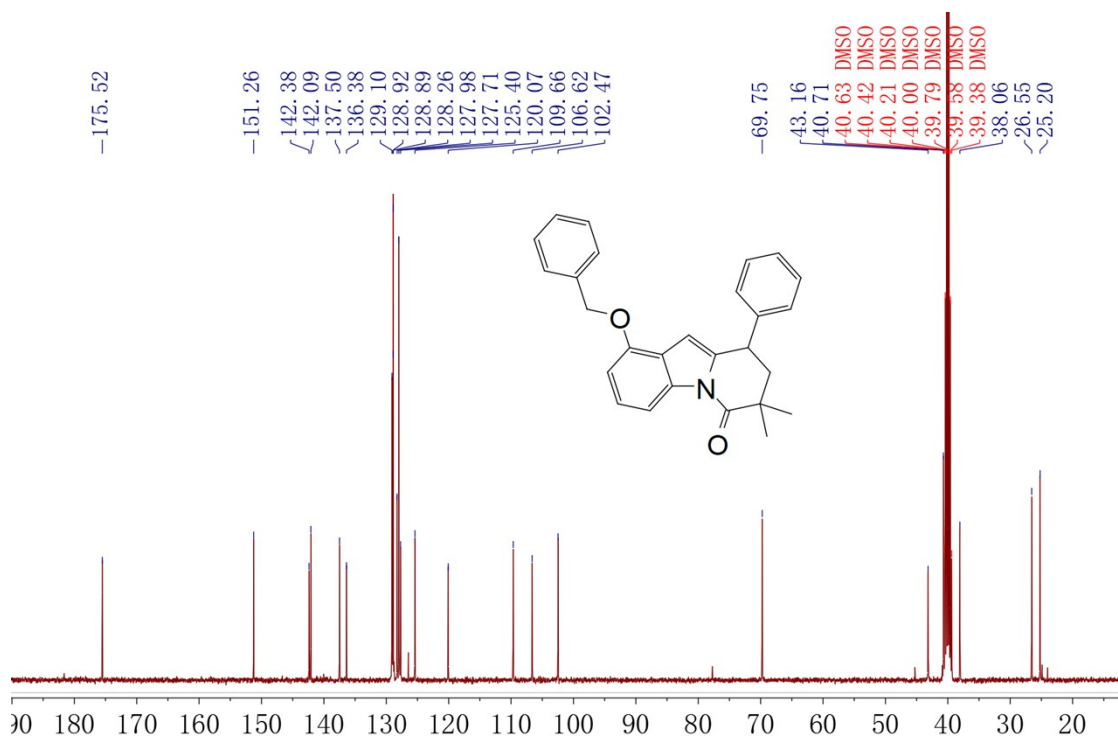




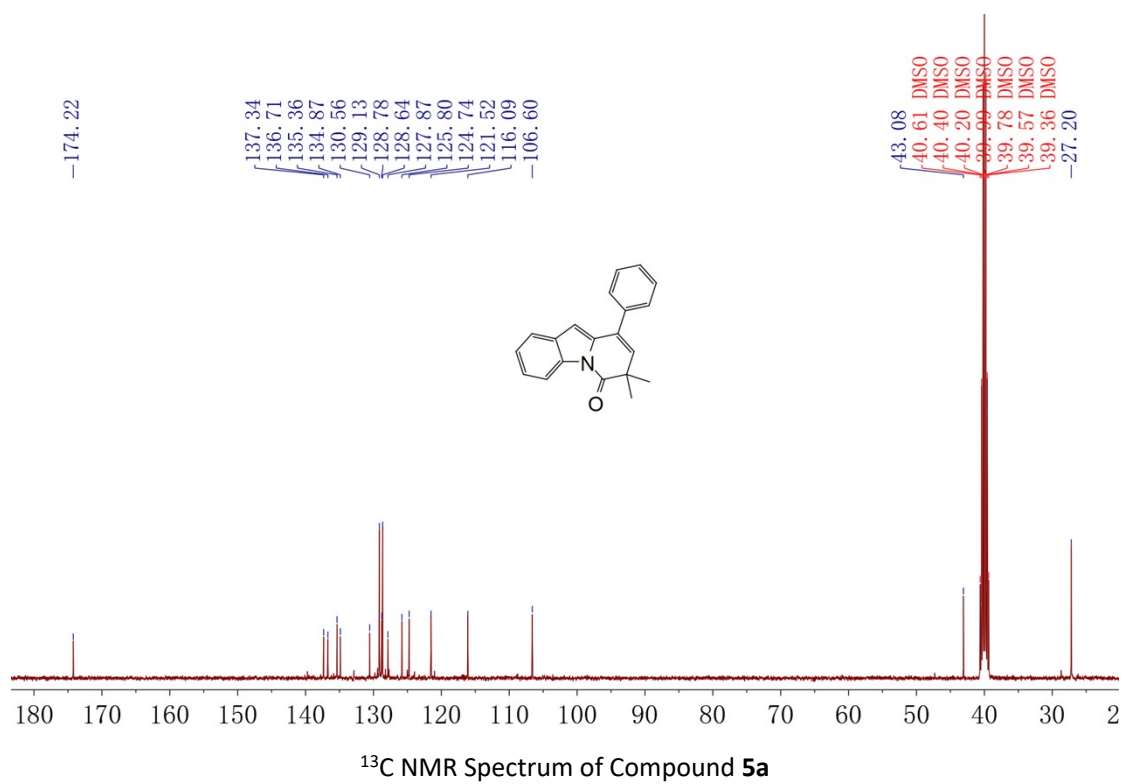
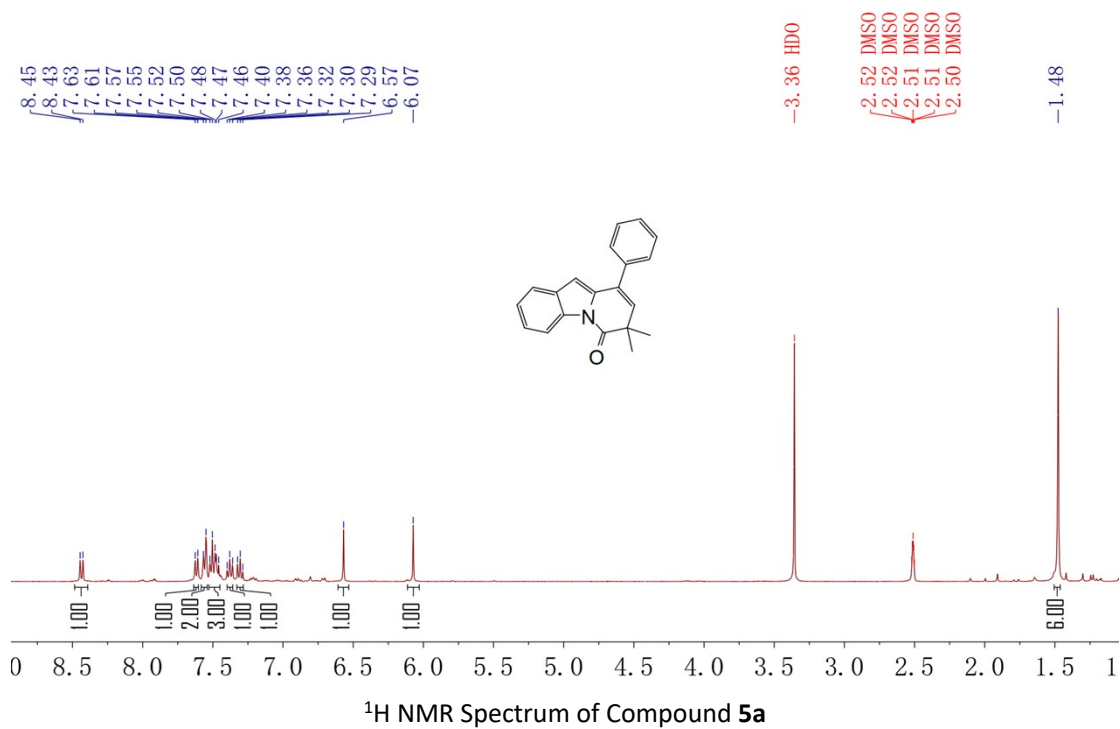




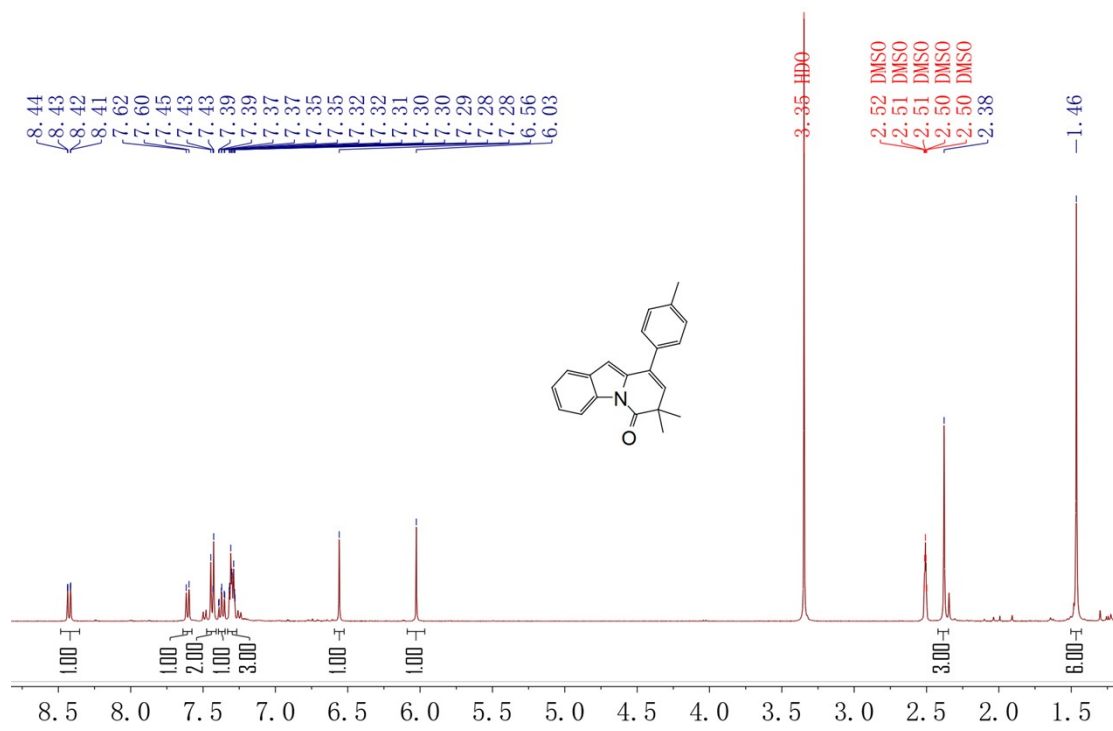
**<sup>1</sup>H NMR Spectrum of Compound 3x**



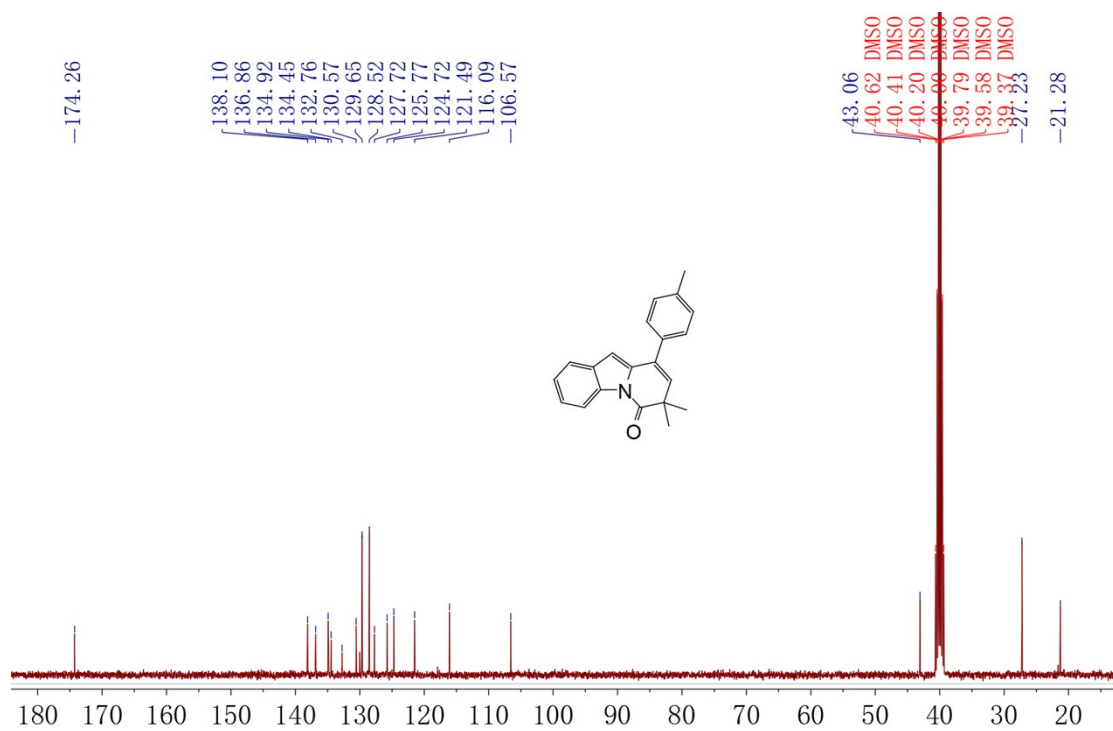
**<sup>13</sup>C NMR Spectrum of Compound 3x**



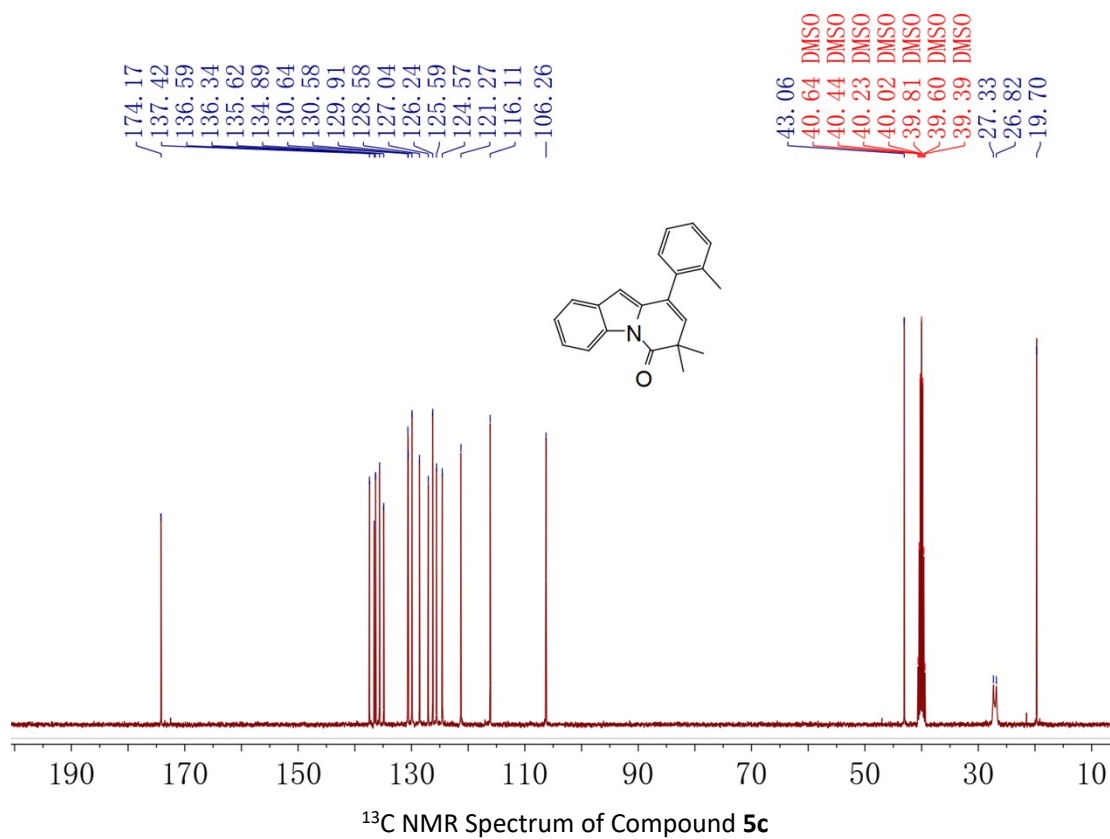
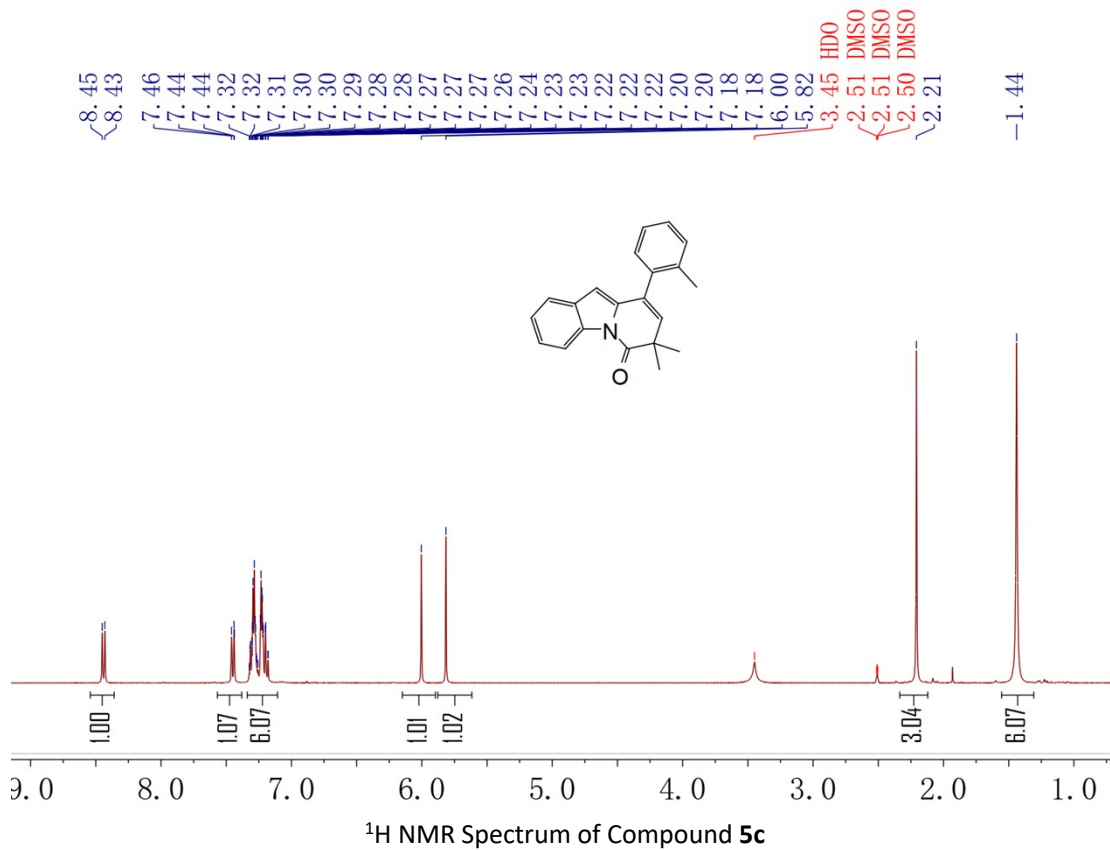


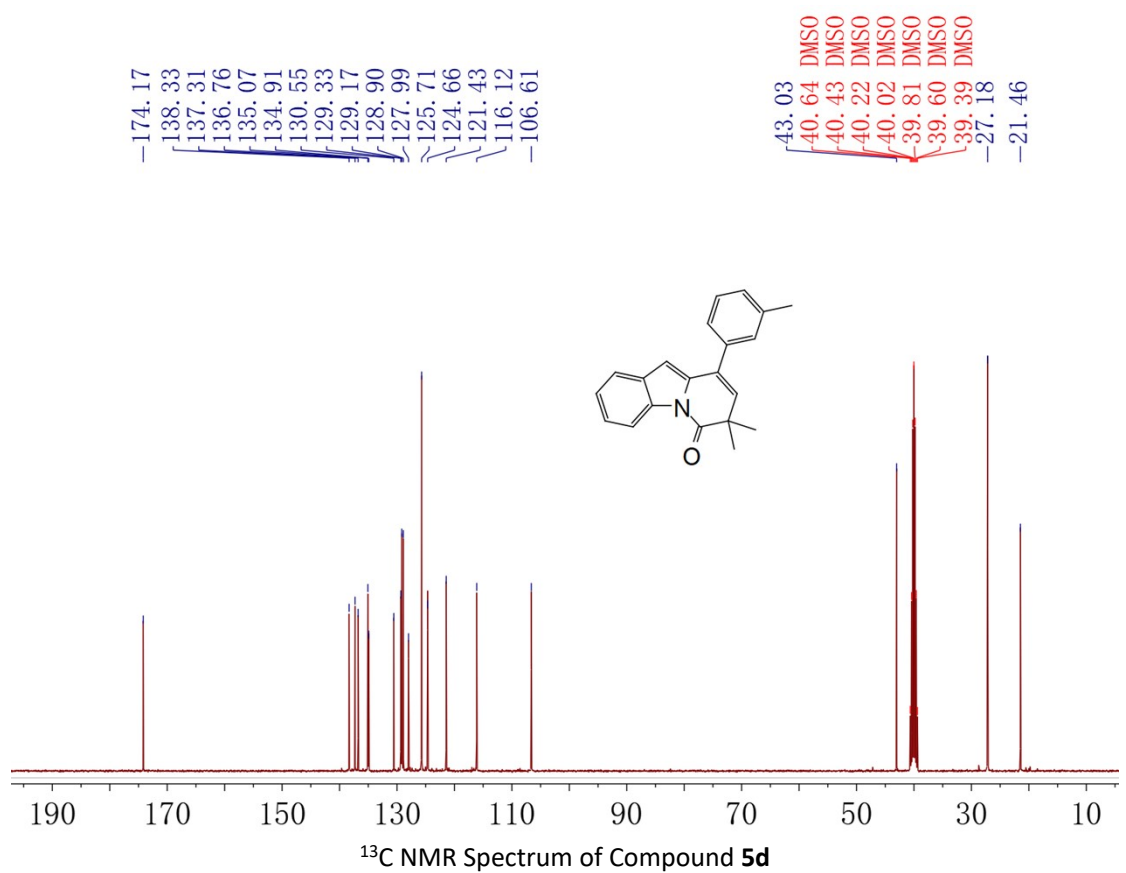
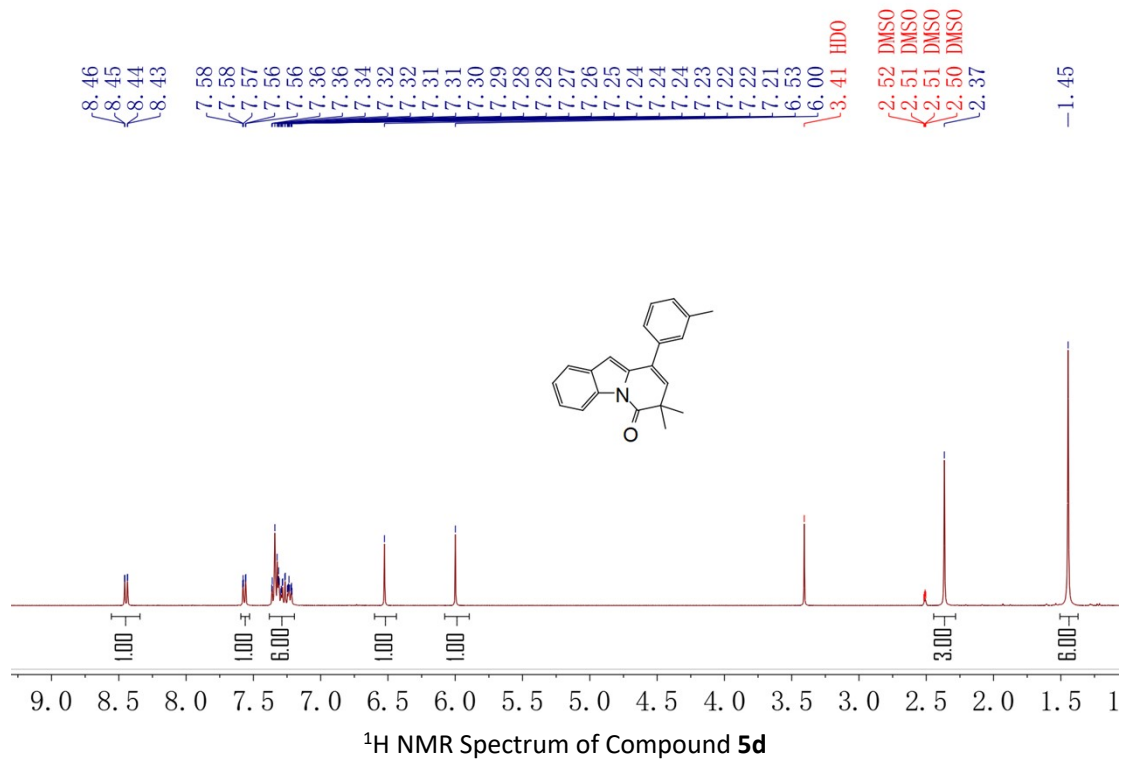


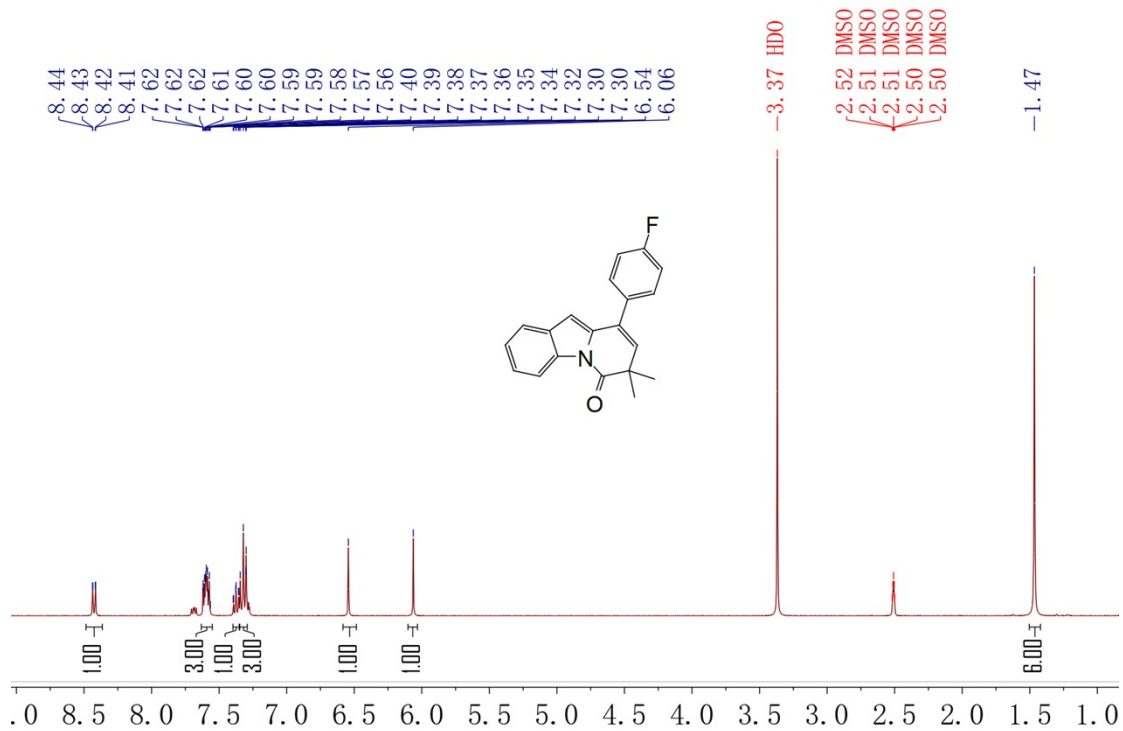
<sup>1</sup>H NMR Spectrum of Compound 5b



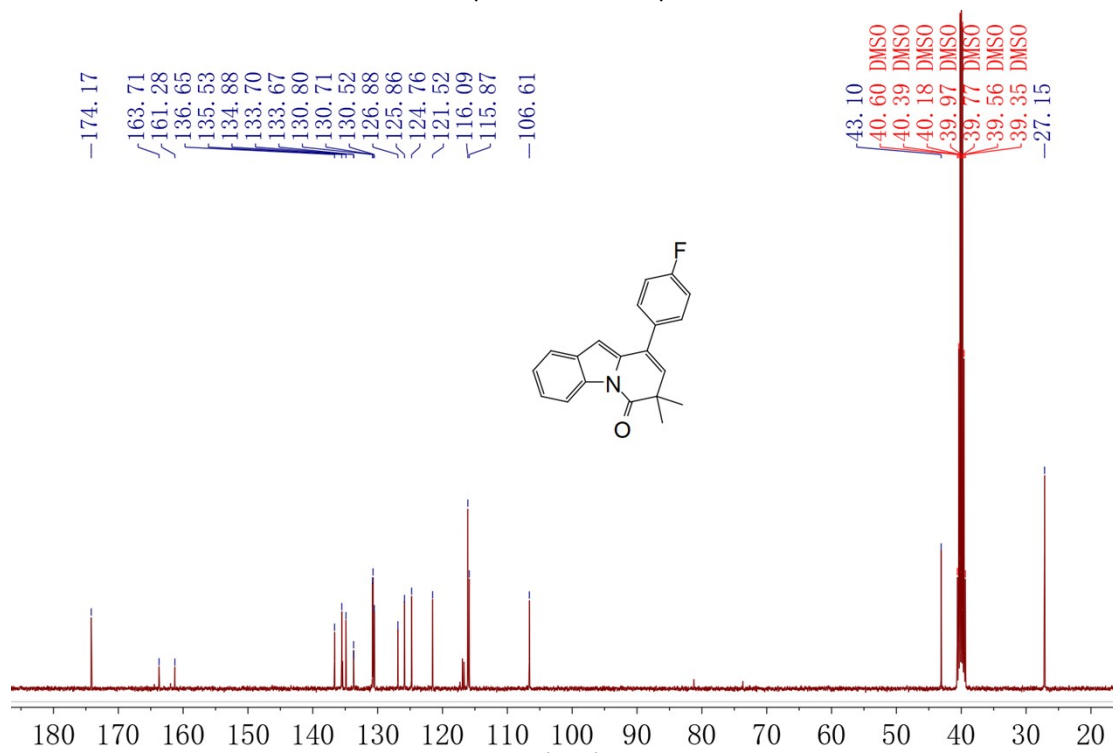
<sup>13</sup>C NMR Spectrum of Compound 5b



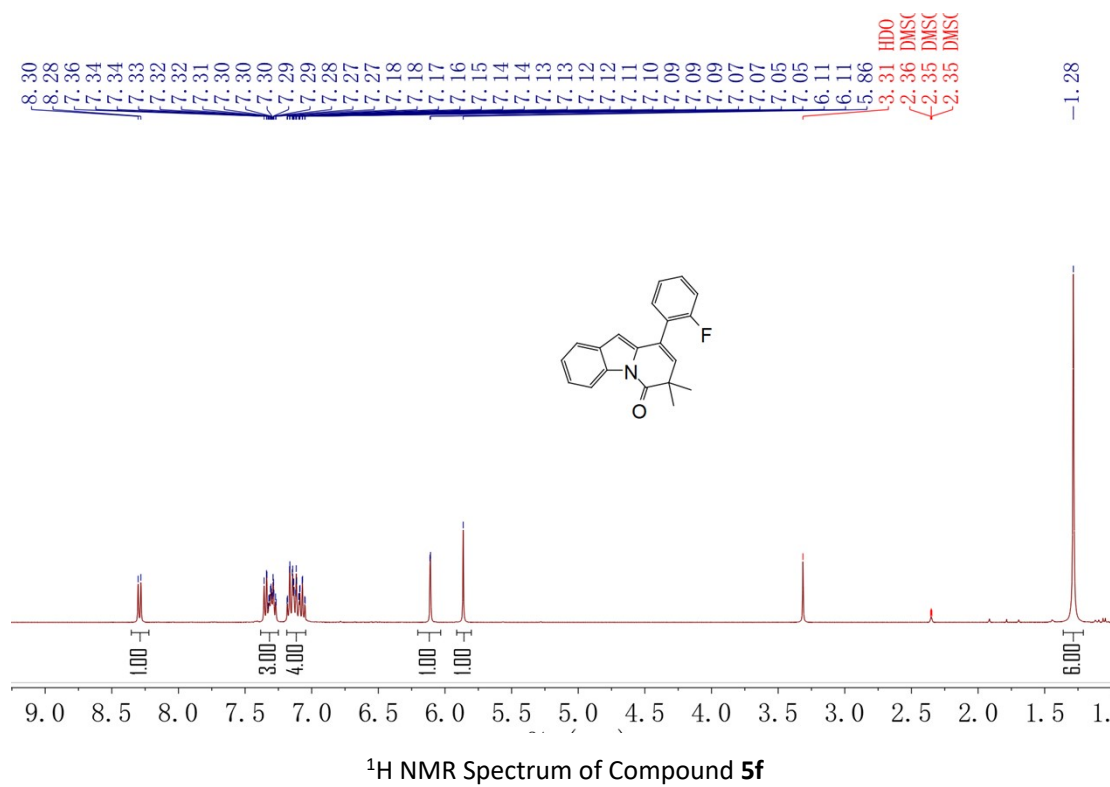
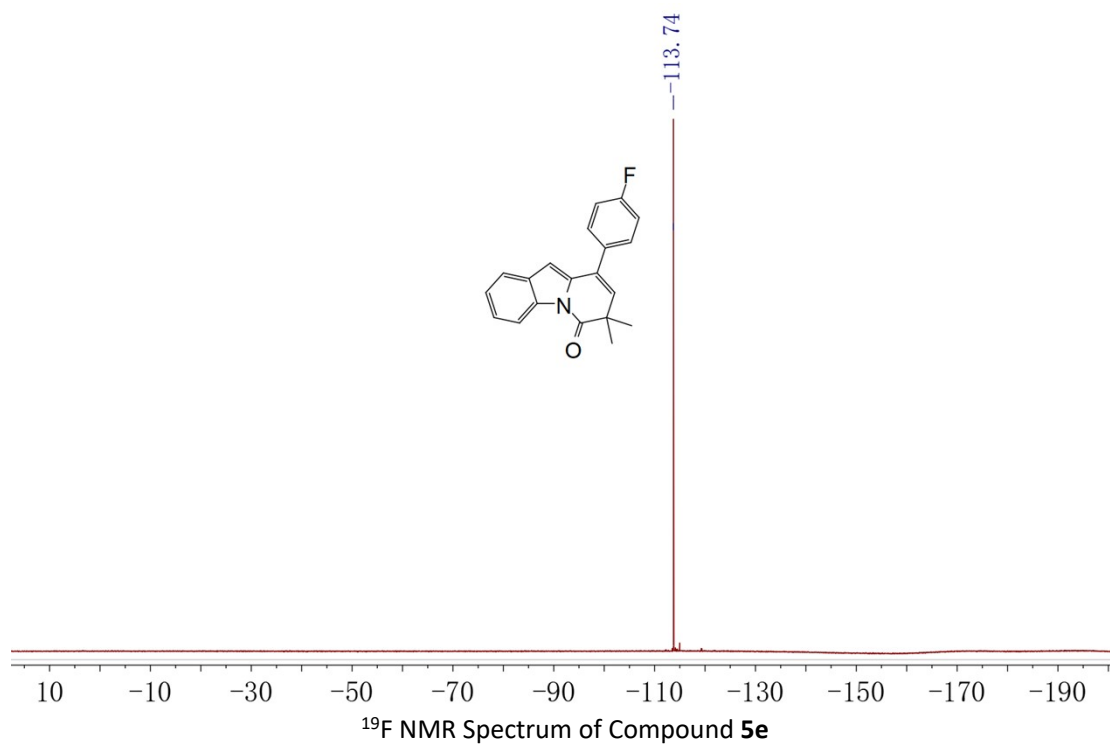


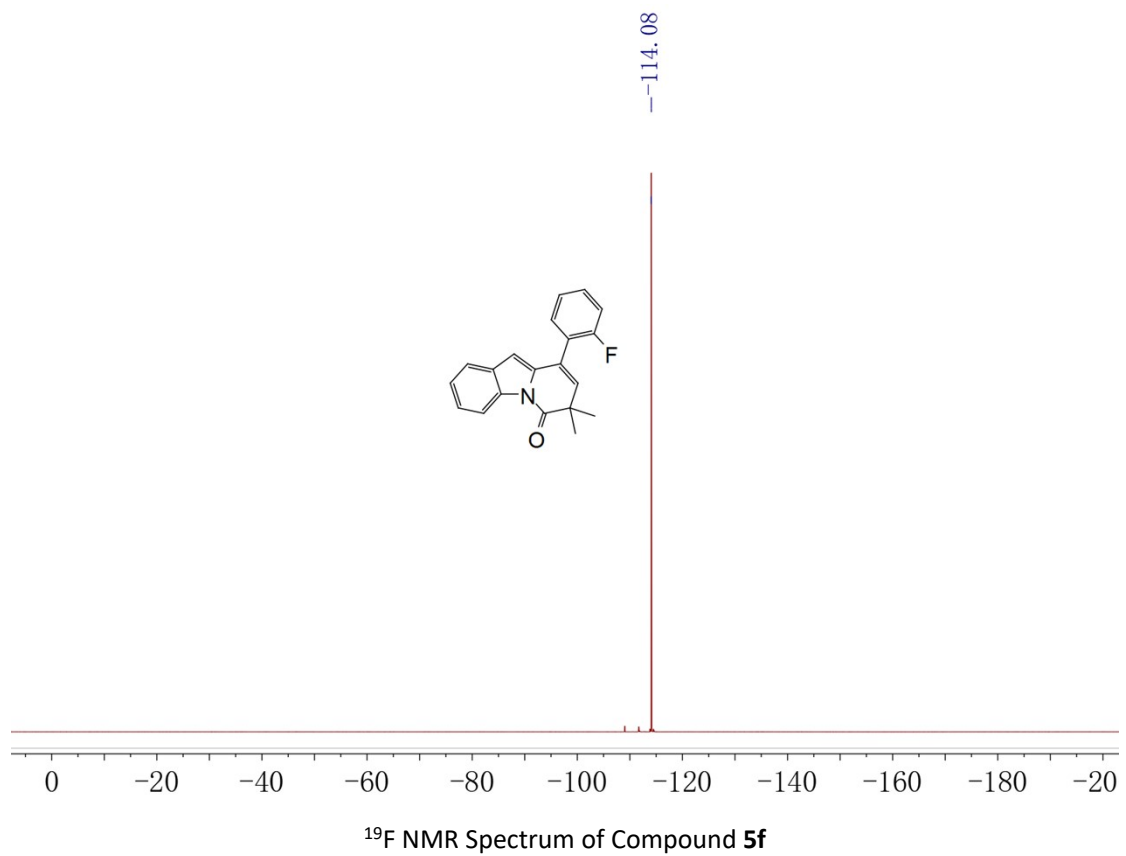
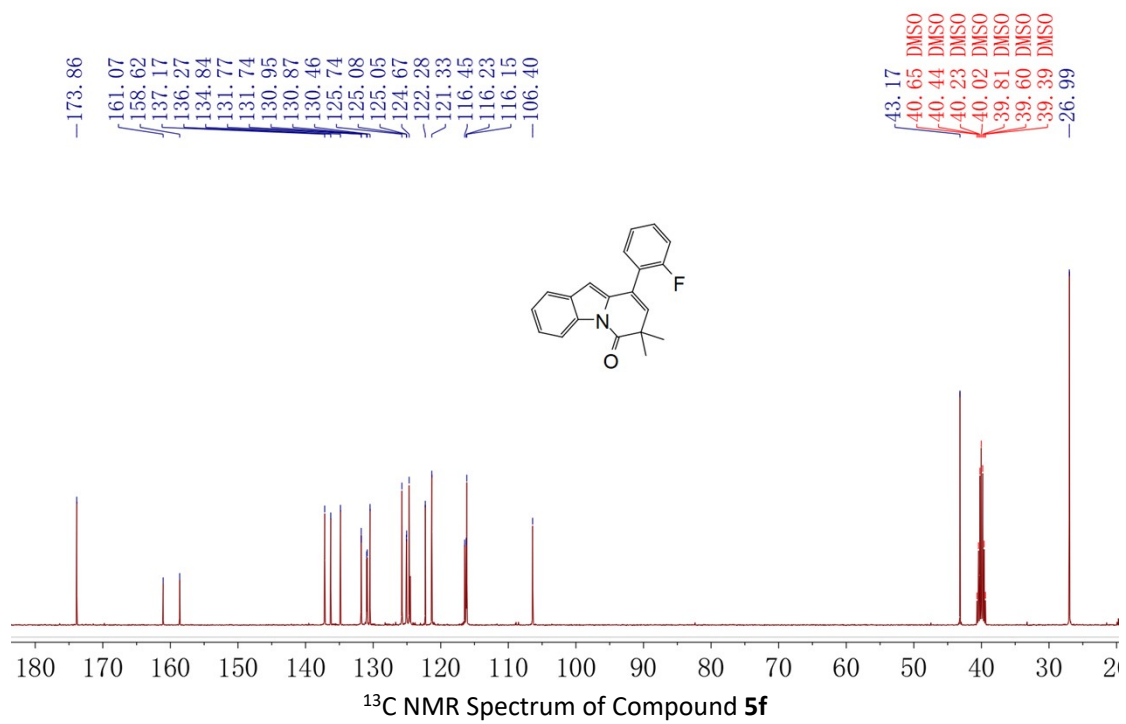


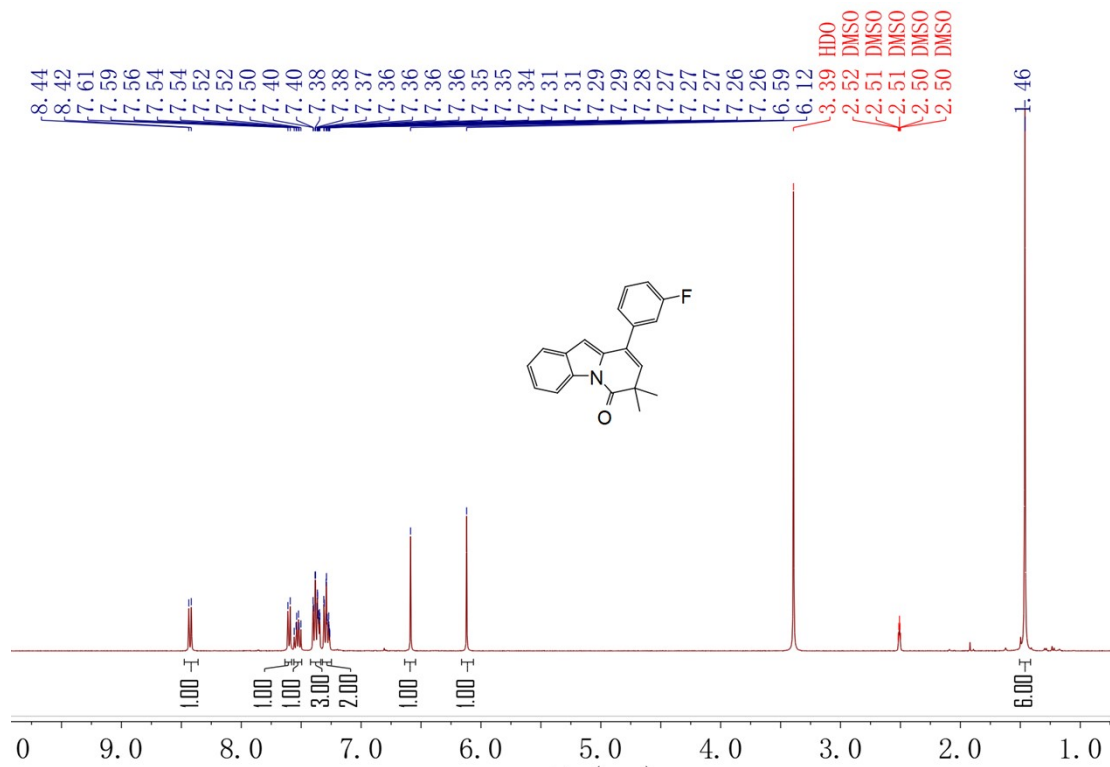
<sup>1</sup>H NMR Spectrum of Compound 5e



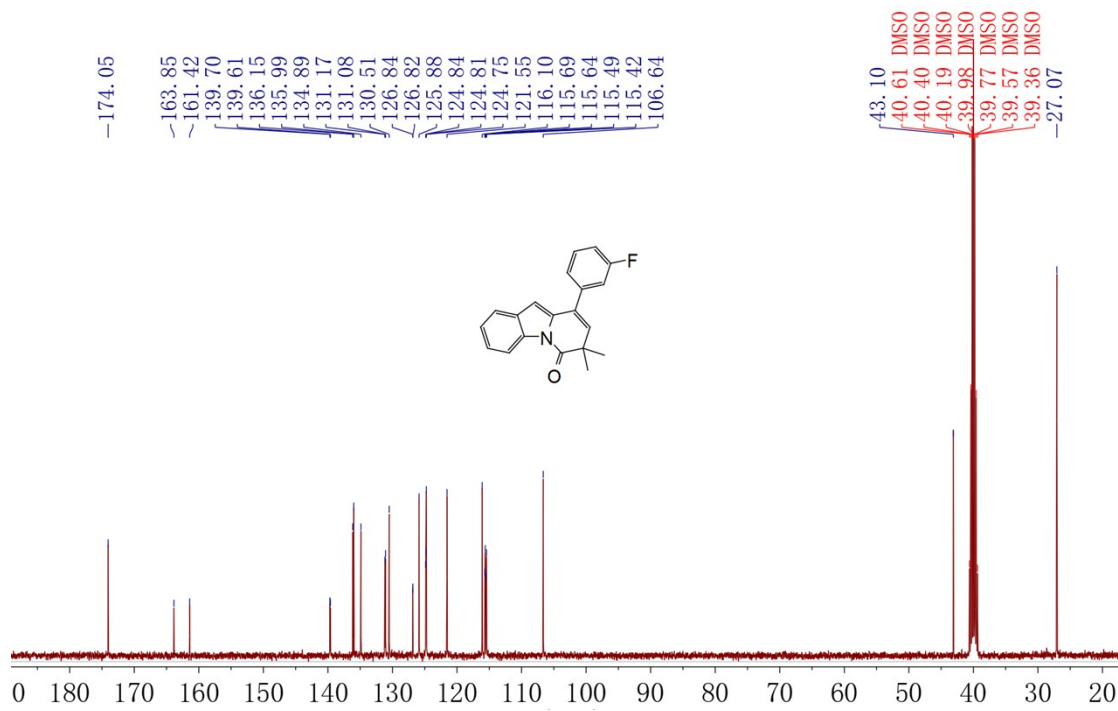
<sup>13</sup>C NMR Spectrum of Compound 5e



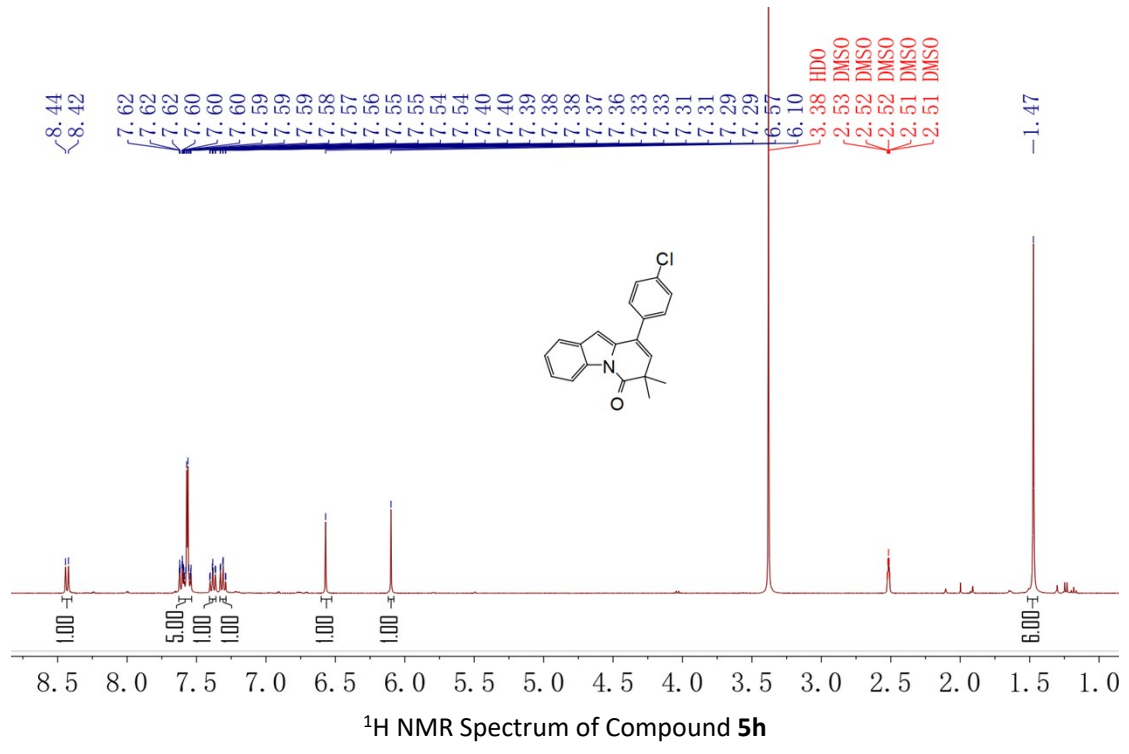
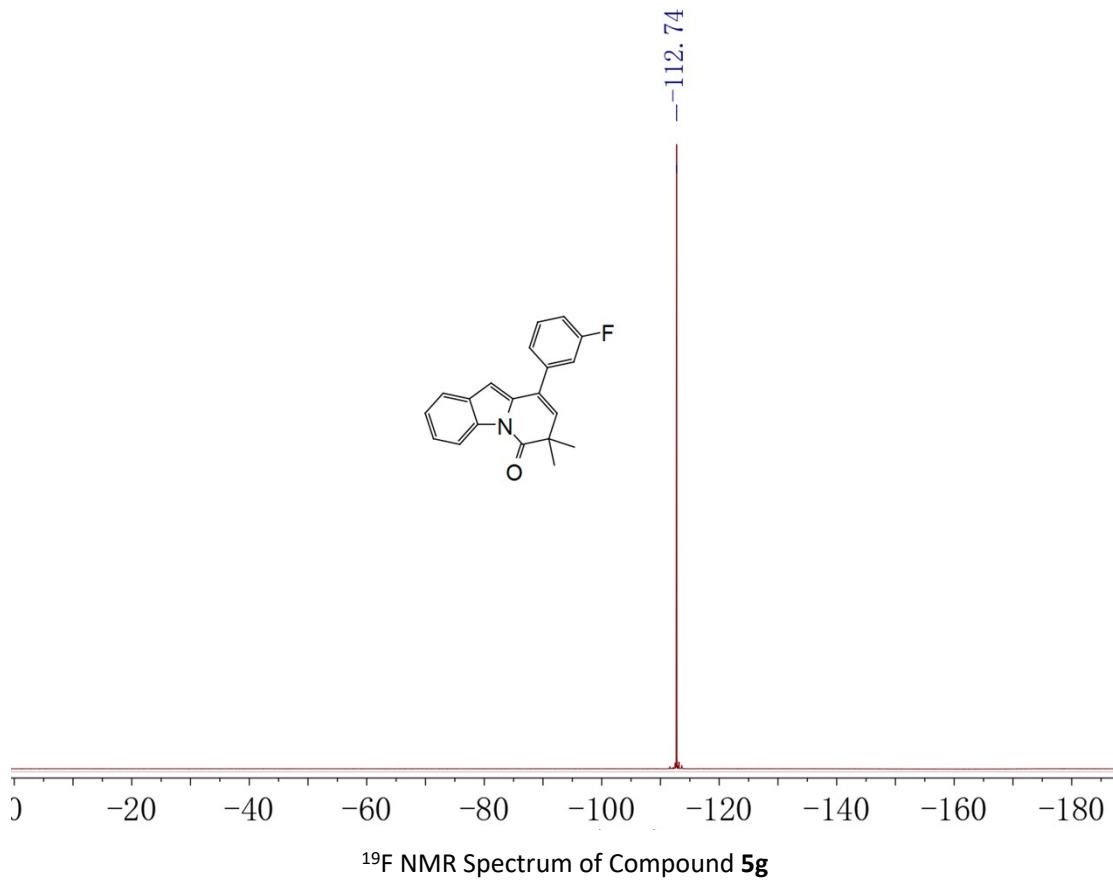




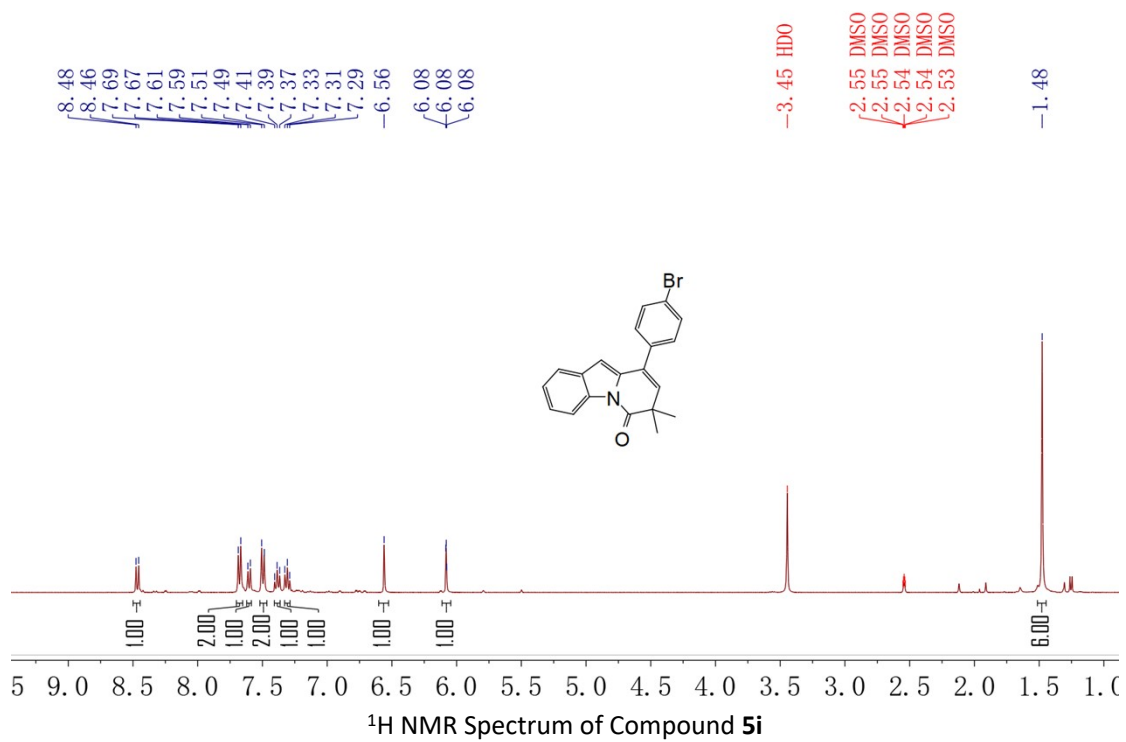
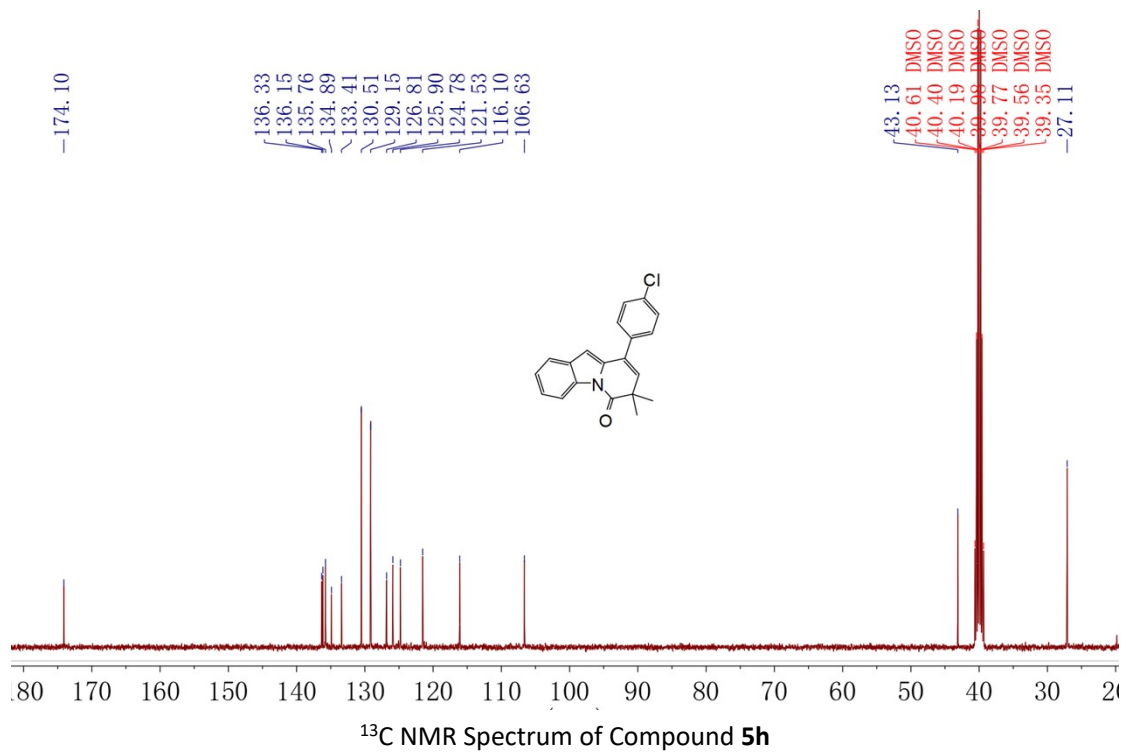
<sup>1</sup>H NMR Spectrum of Compound 5g

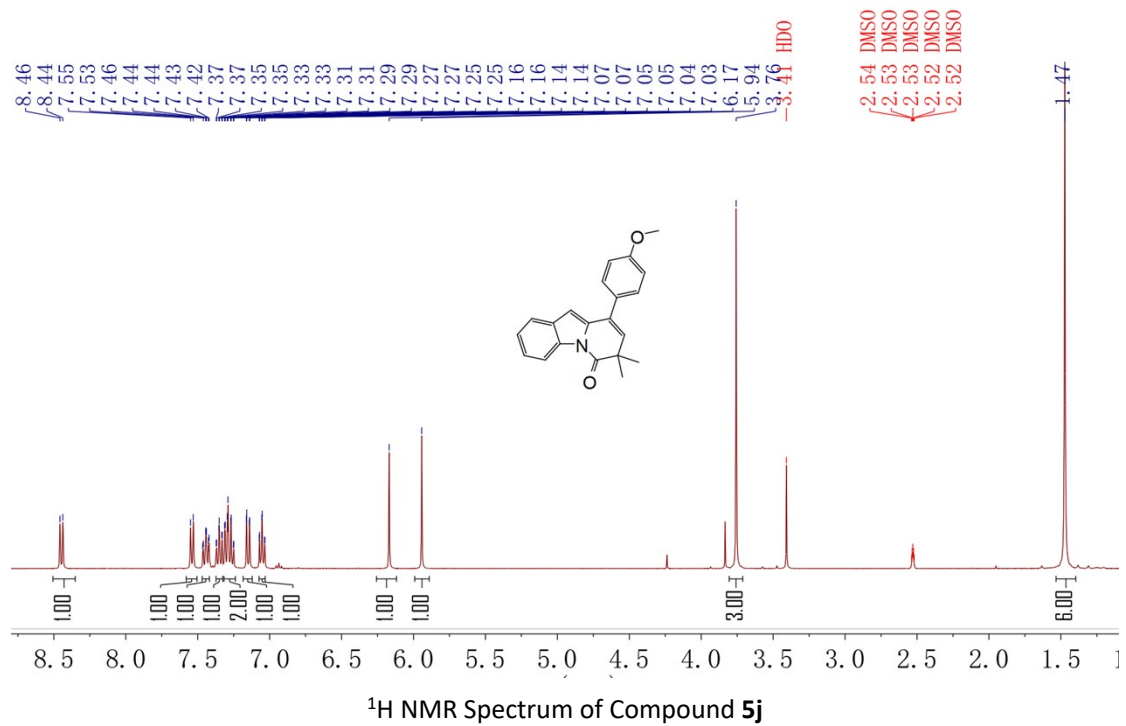
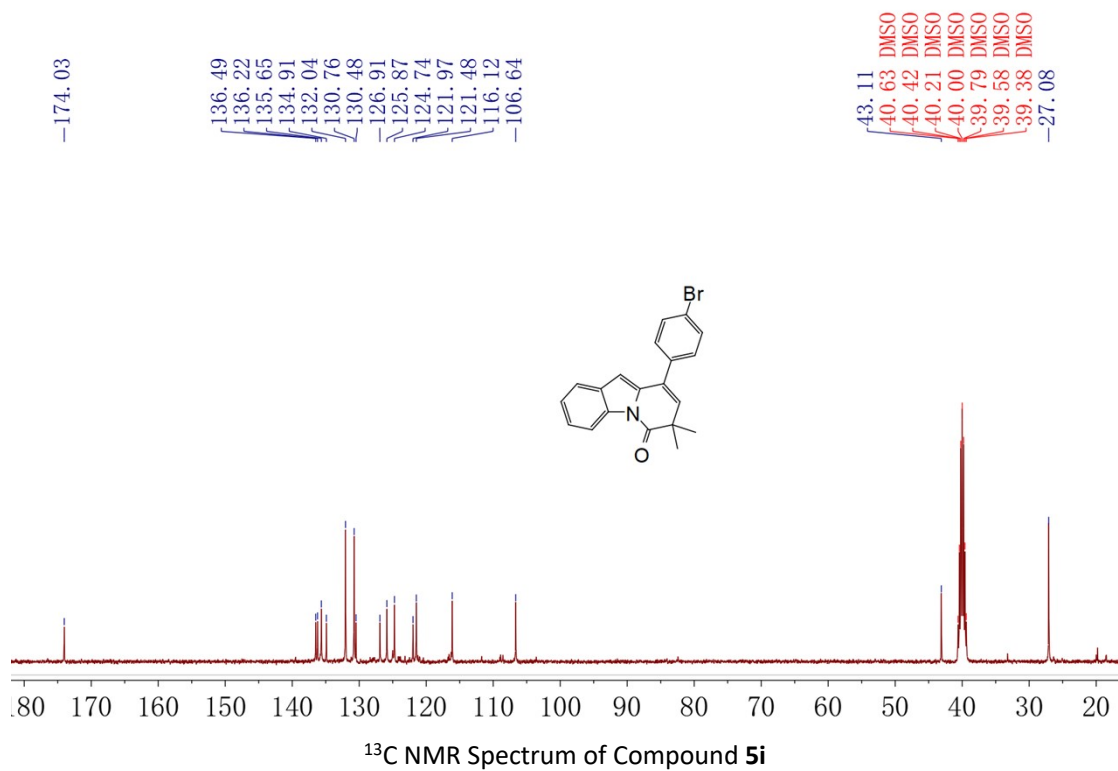


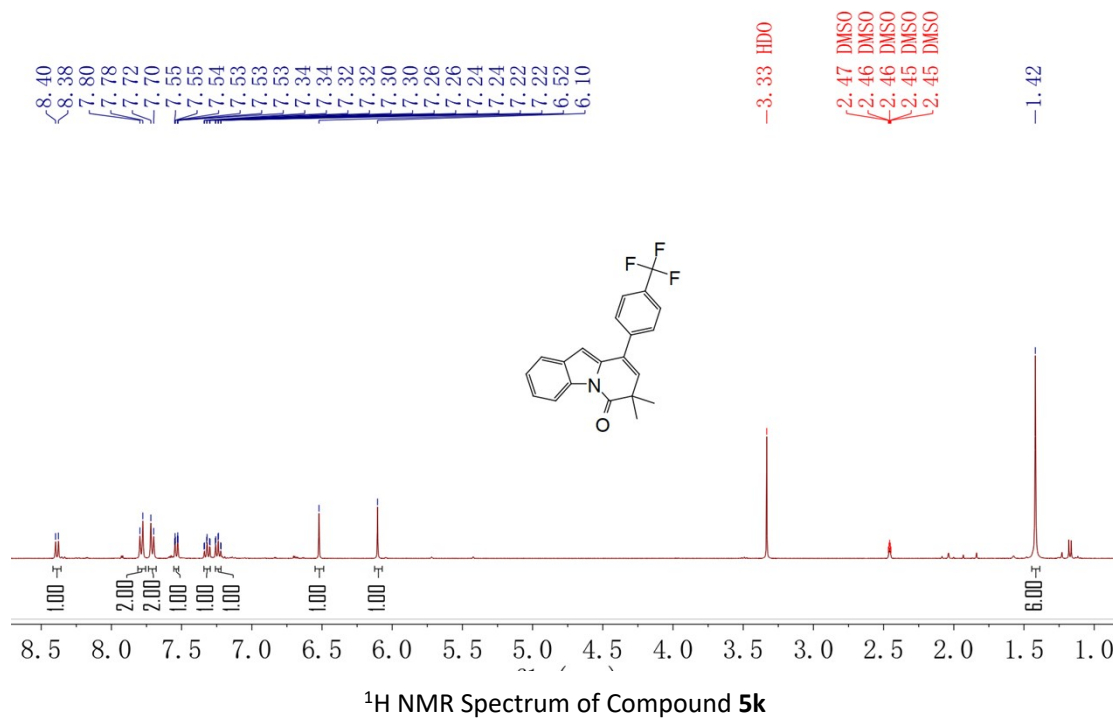
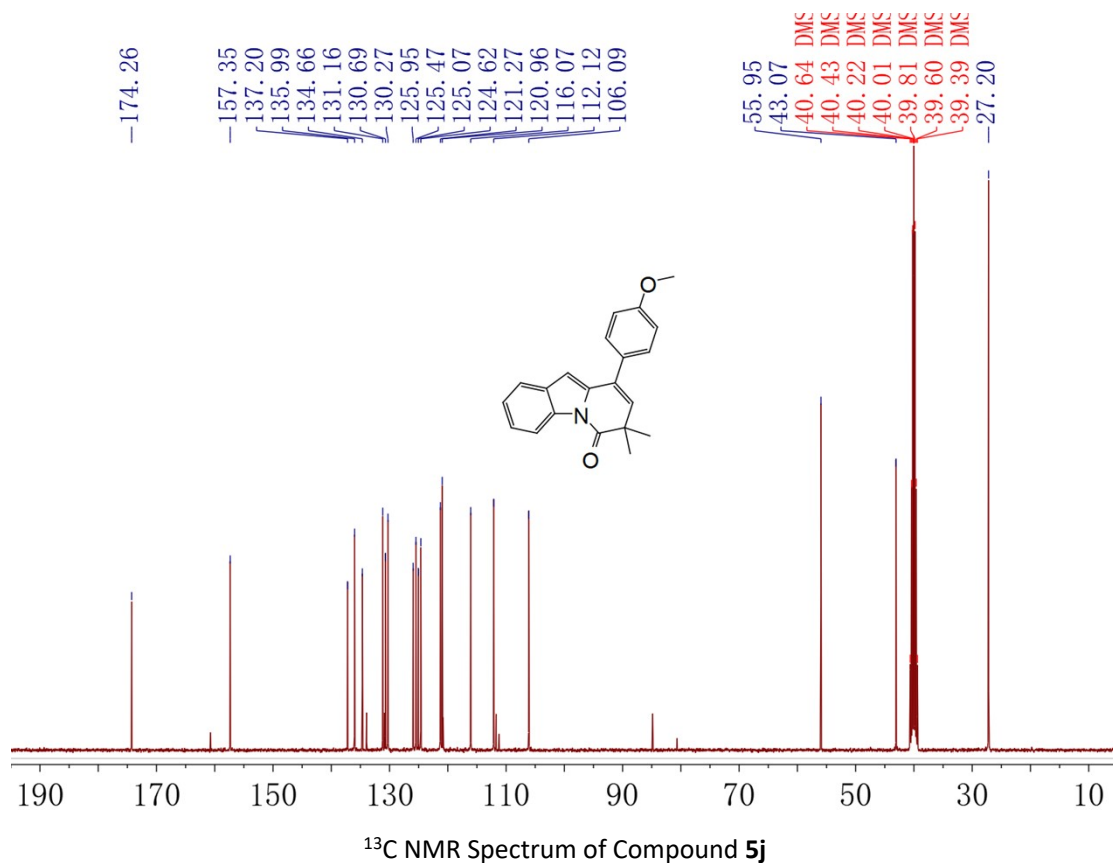
<sup>13</sup>C NMR Spectrum of Compound 5g

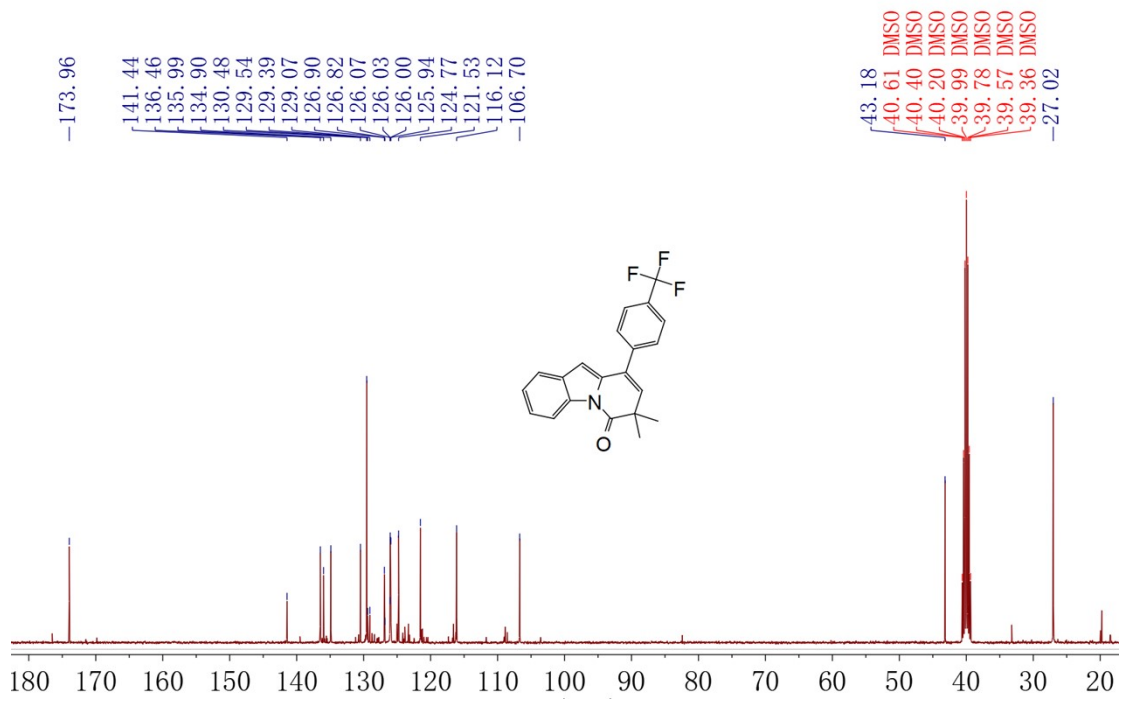




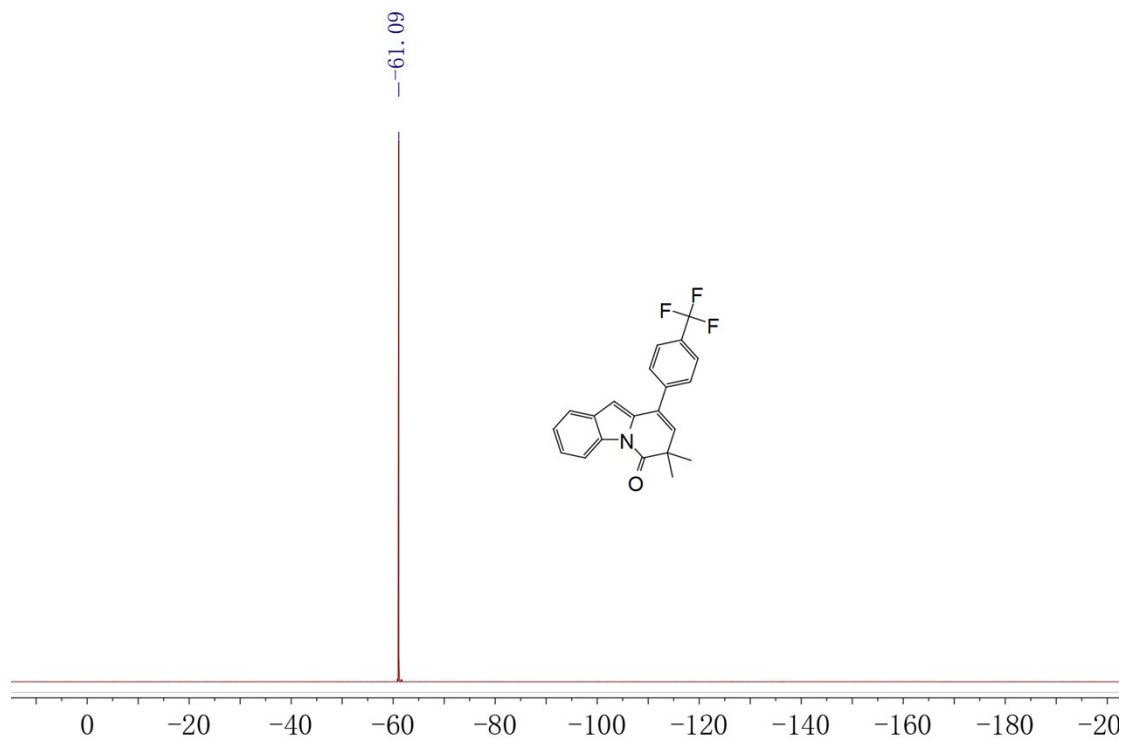




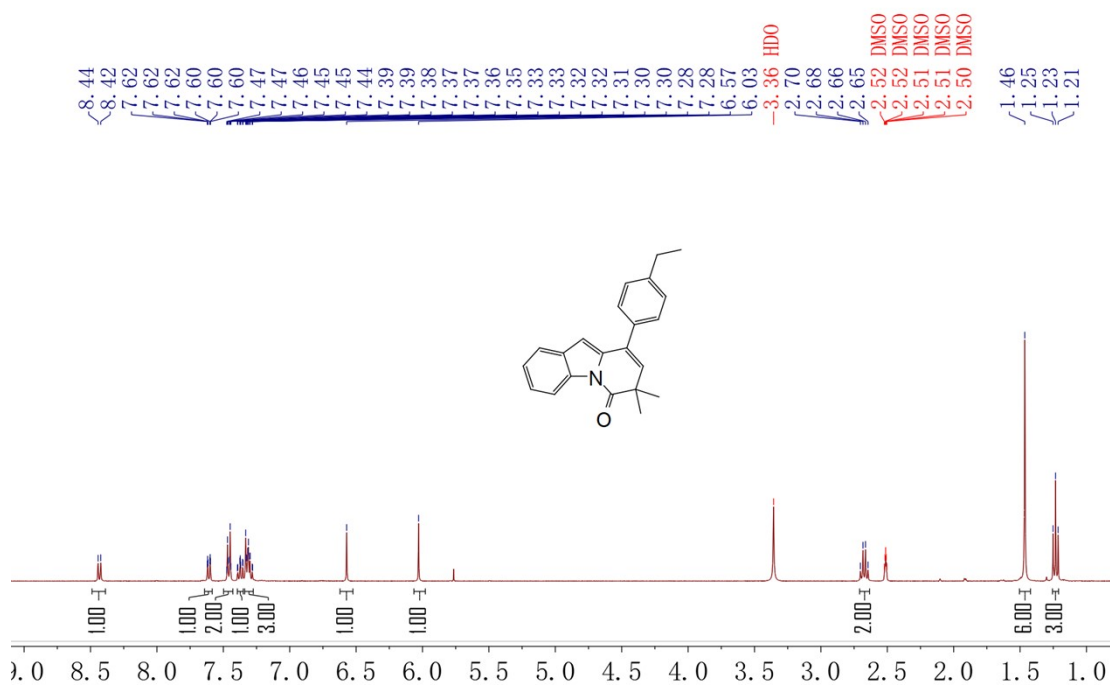




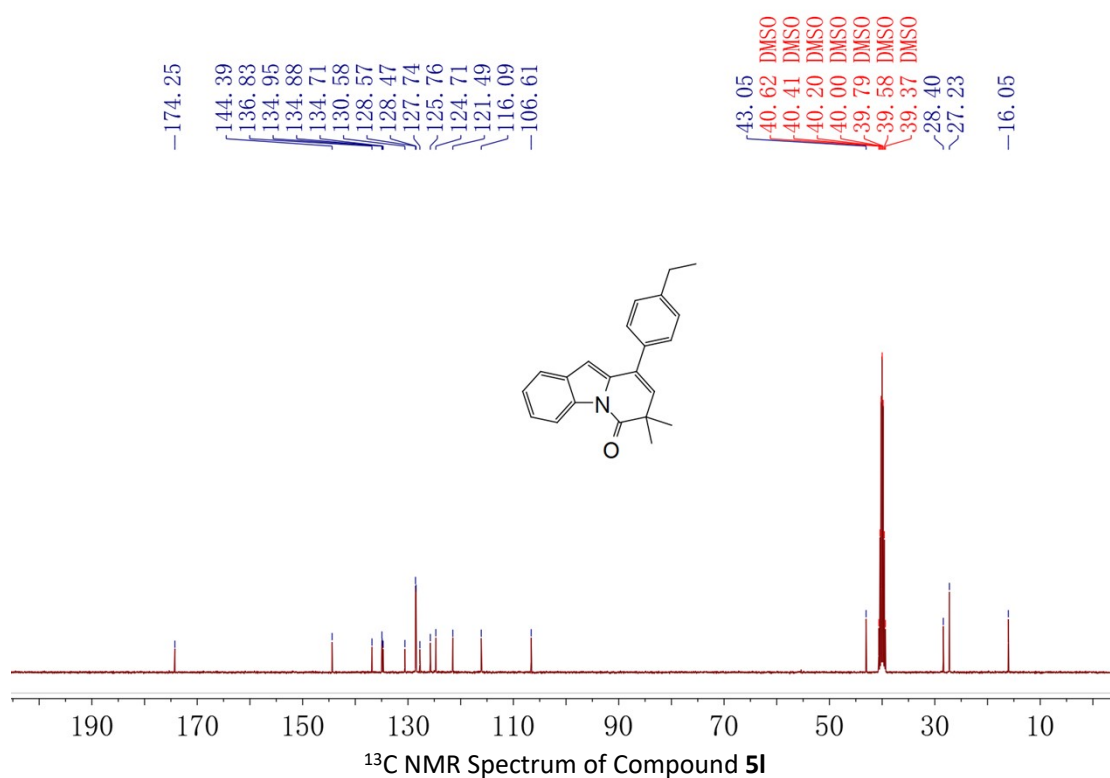
<sup>13</sup>C NMR Spectrum of Compound 5k



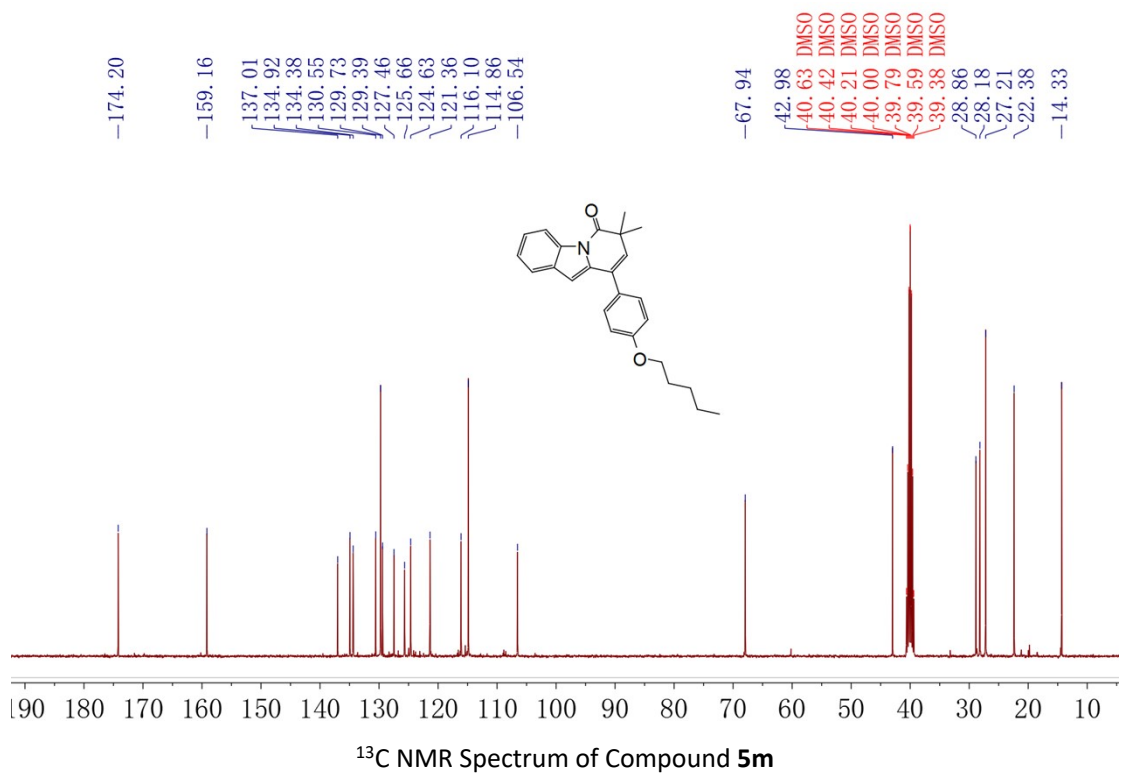
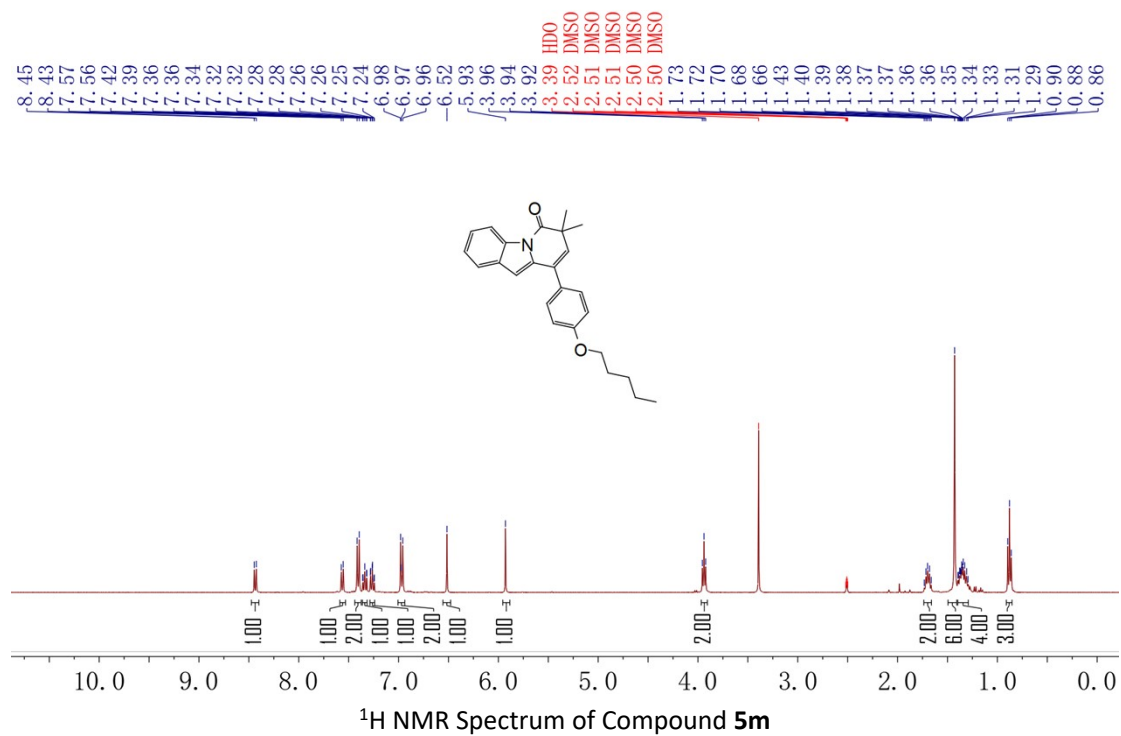
<sup>19</sup>F NMR Spectrum of Compound 5k

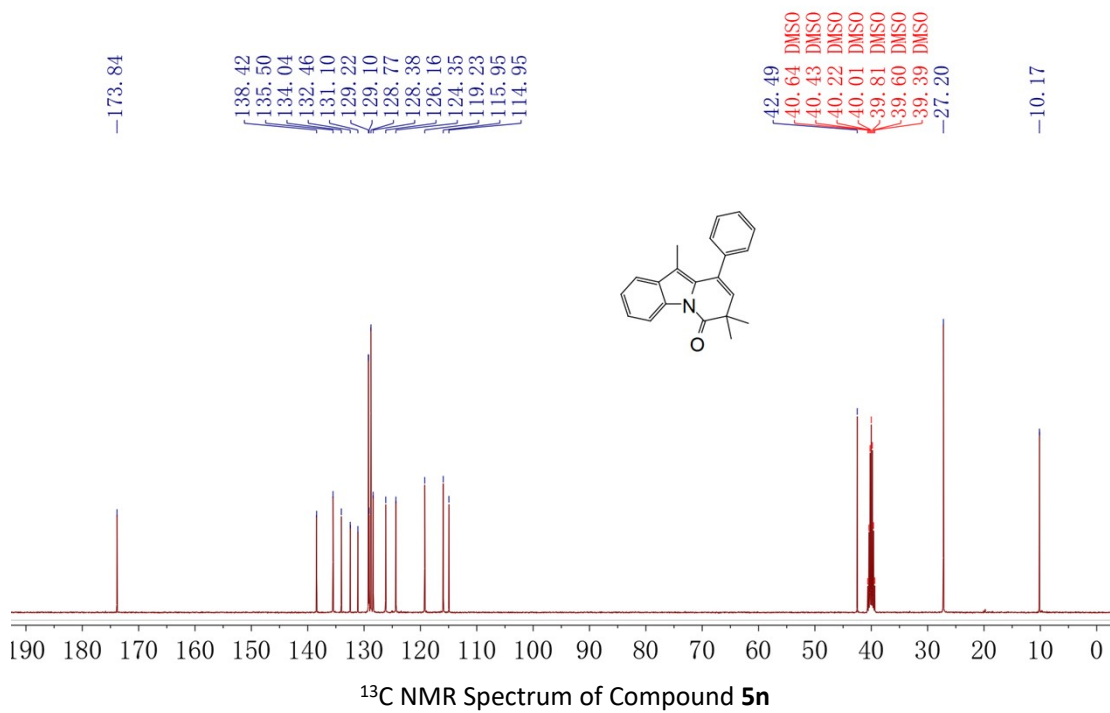
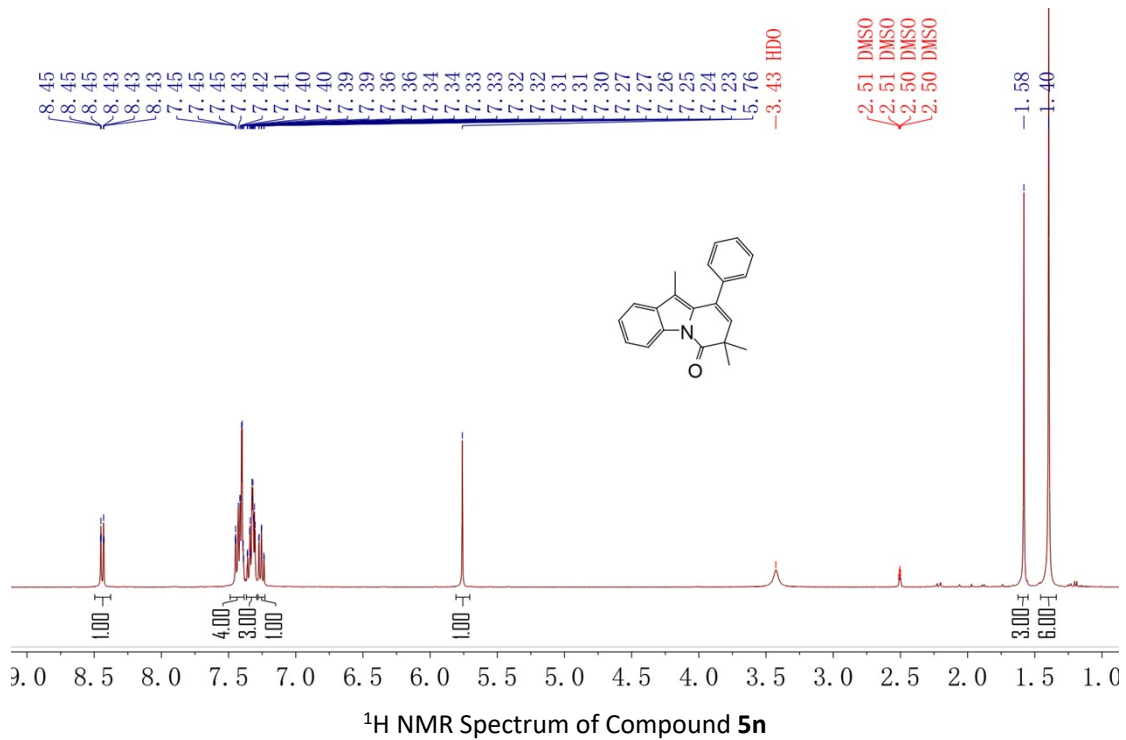


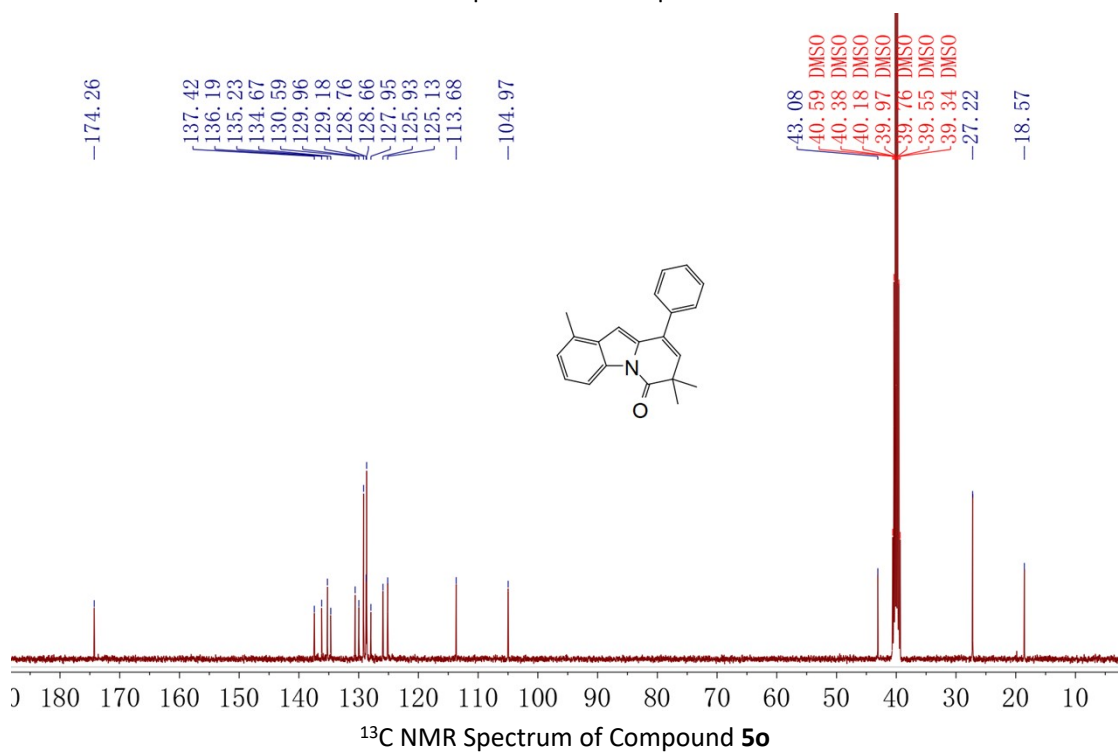
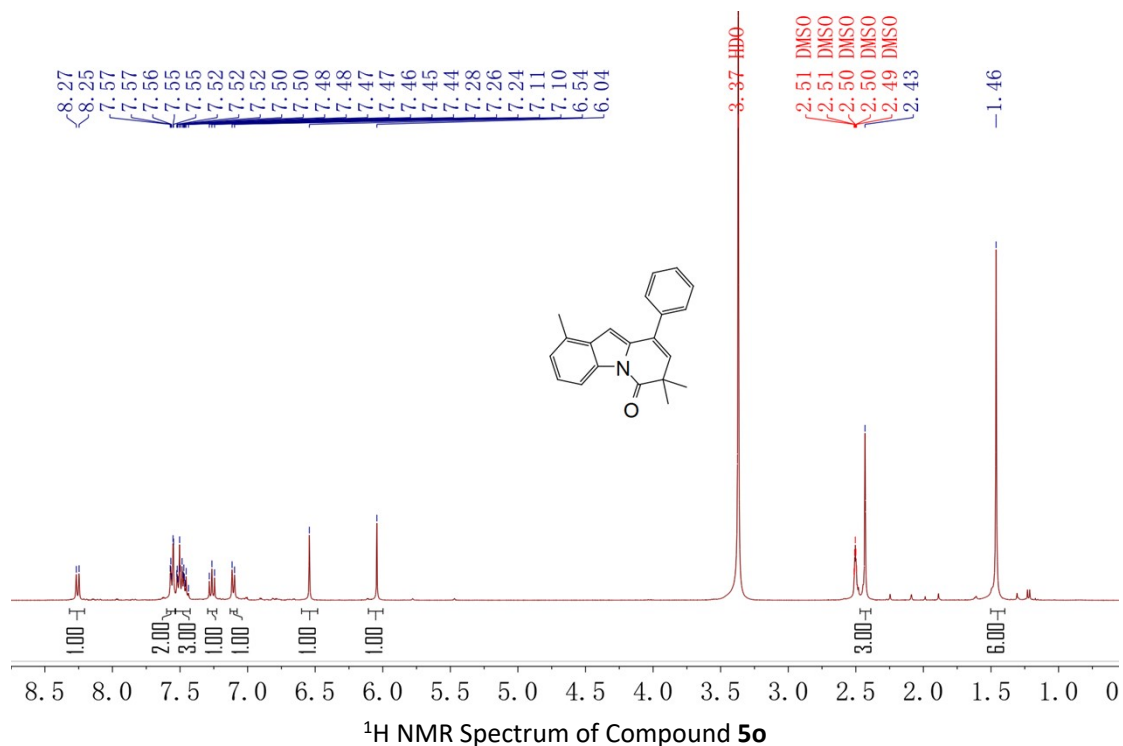
<sup>1</sup>H NMR Spectrum of Compound 5I



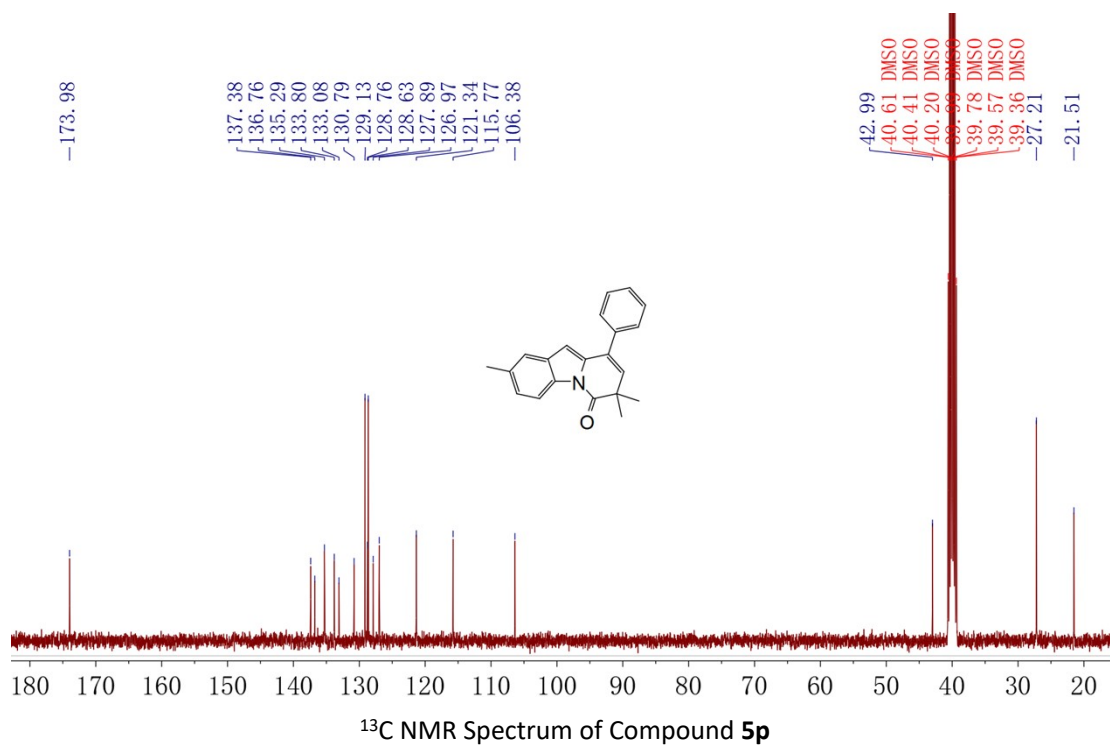
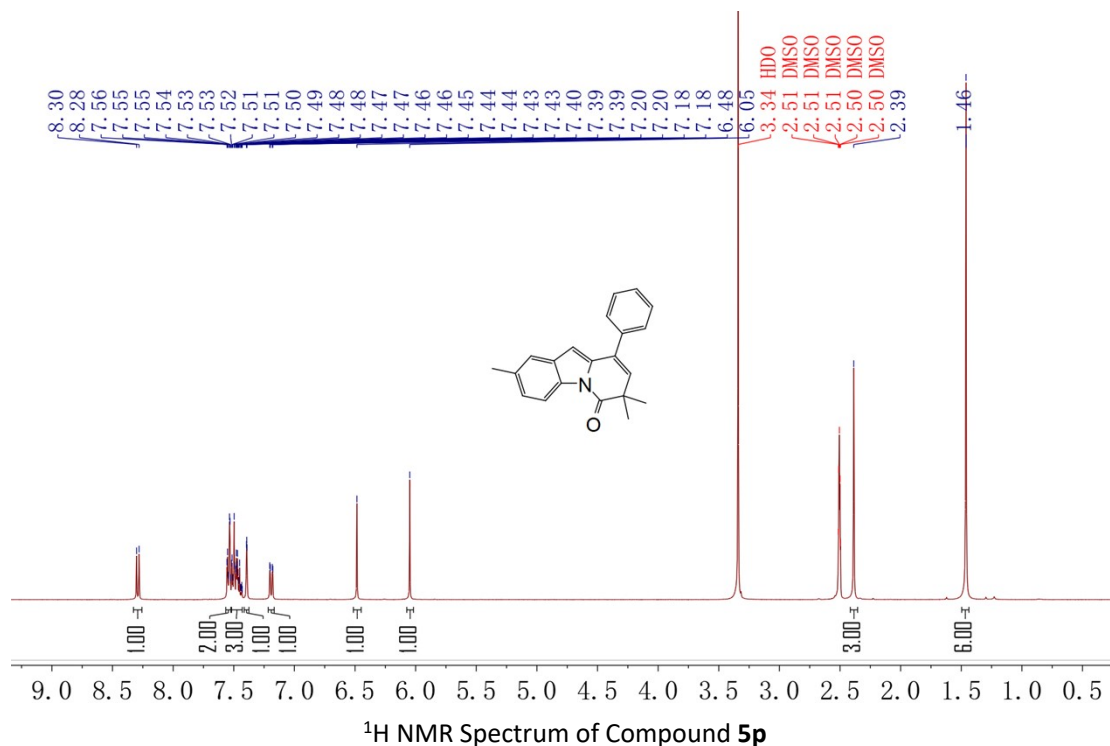
<sup>13</sup>C NMR Spectrum of Compound 5I

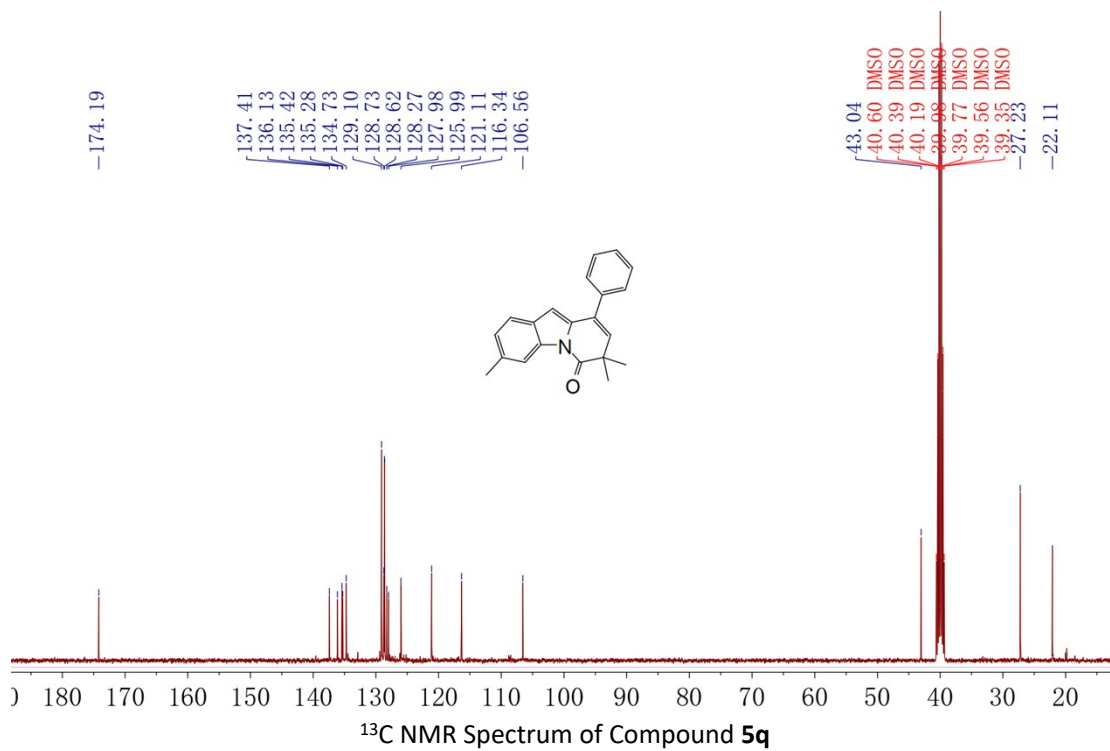
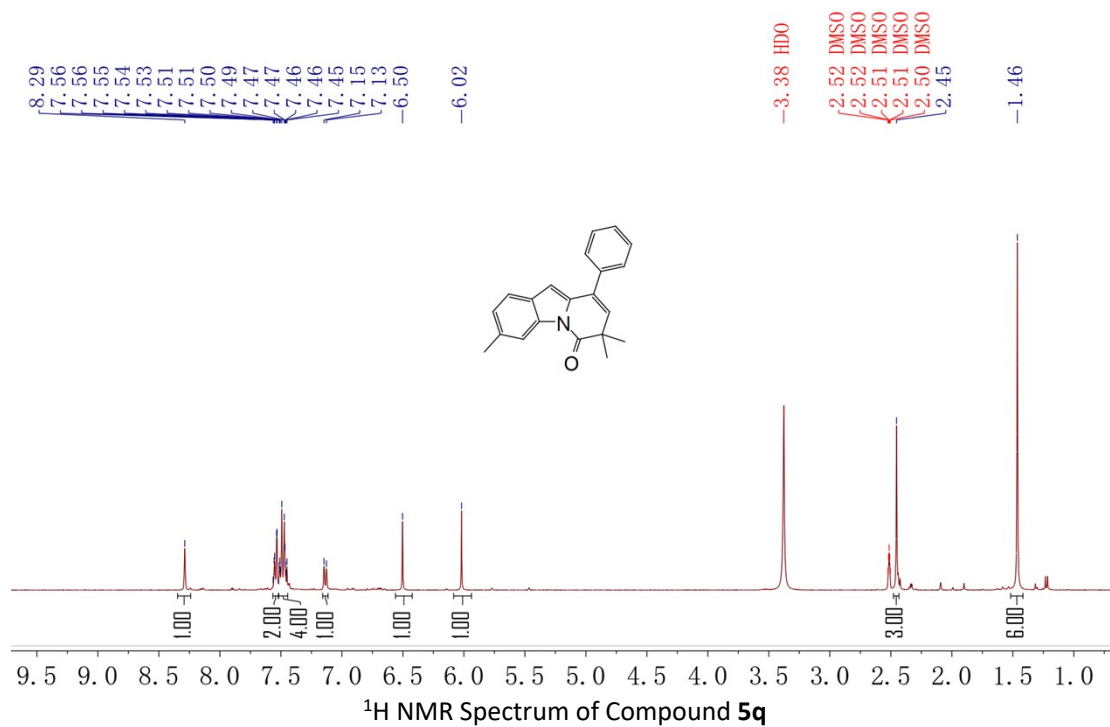


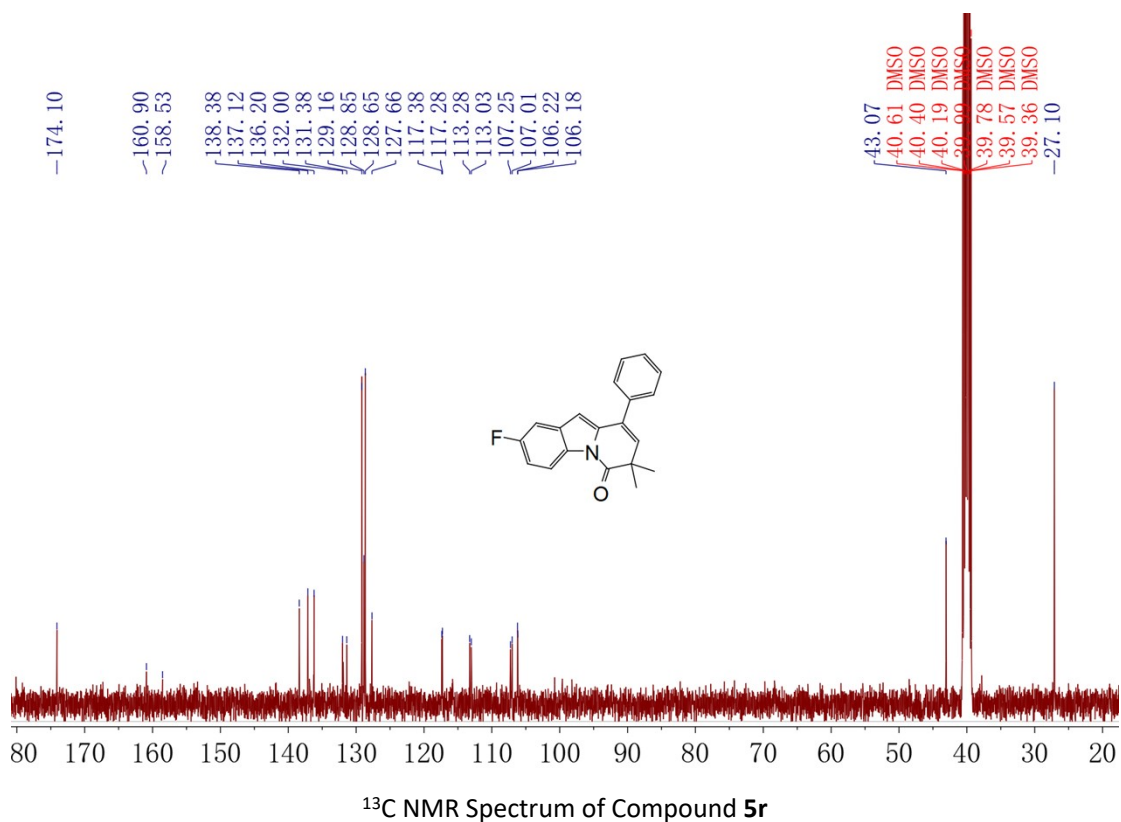
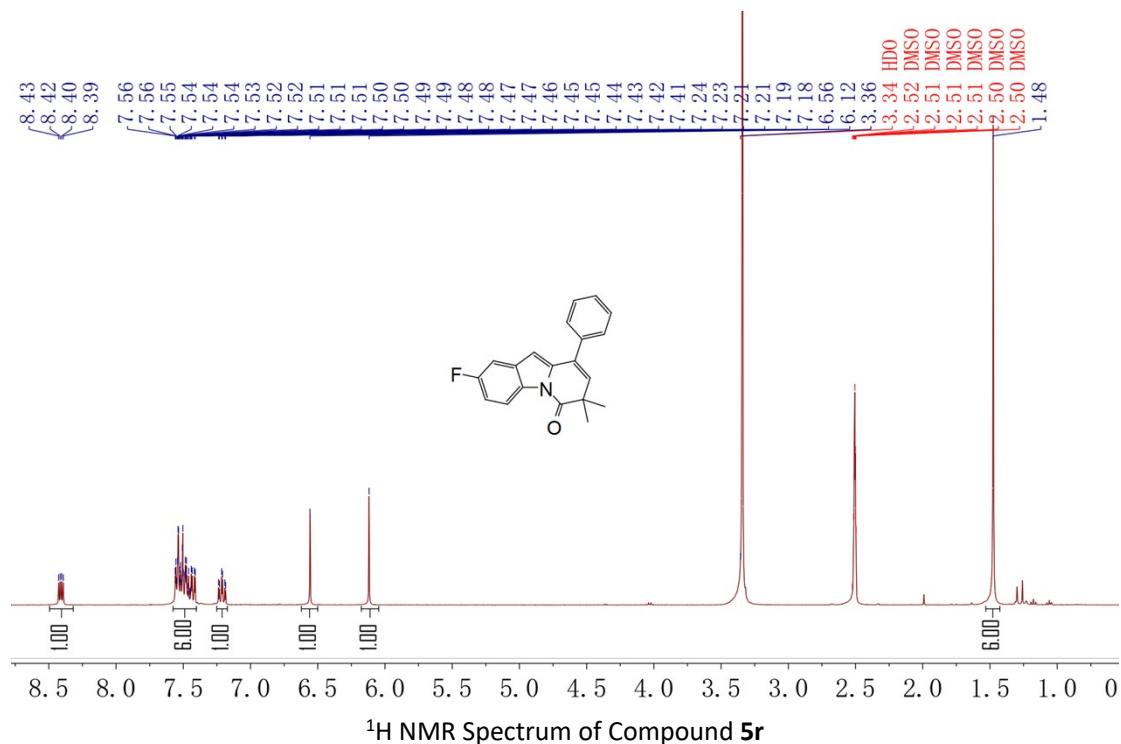


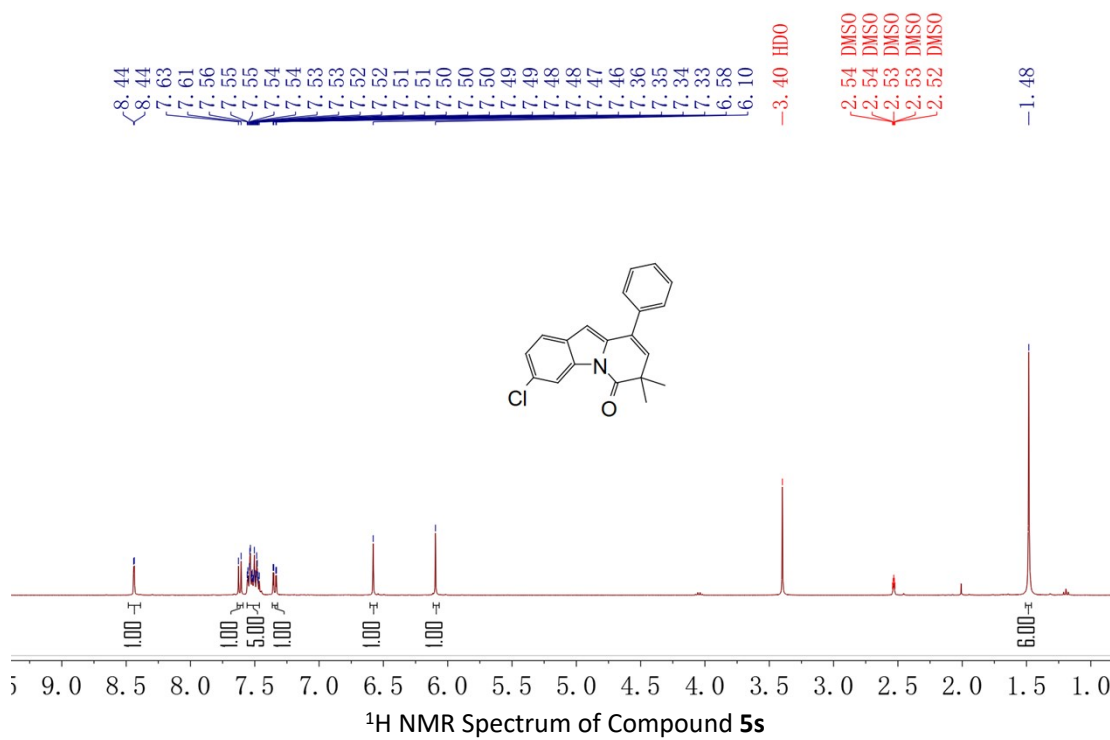
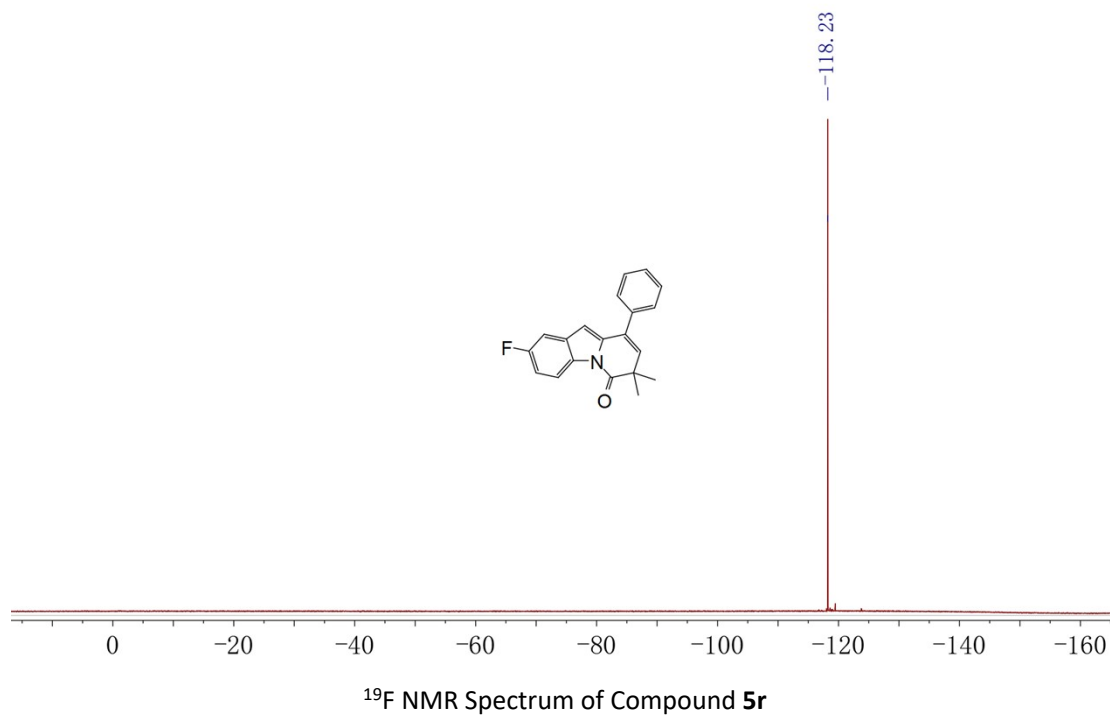


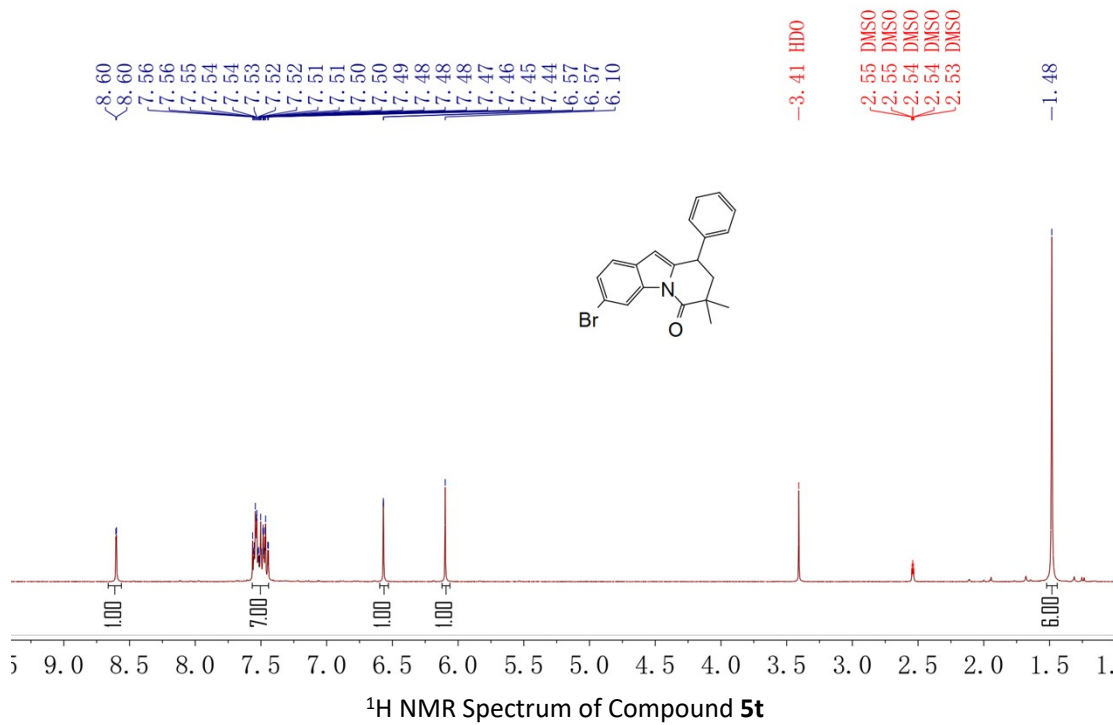
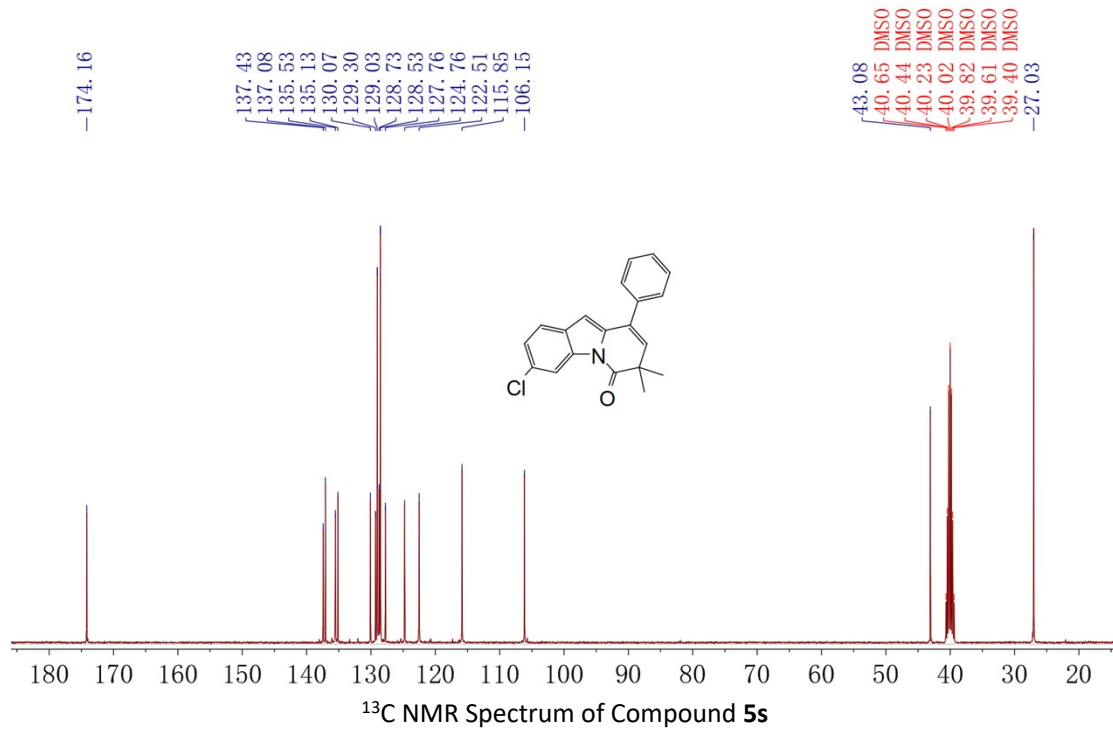


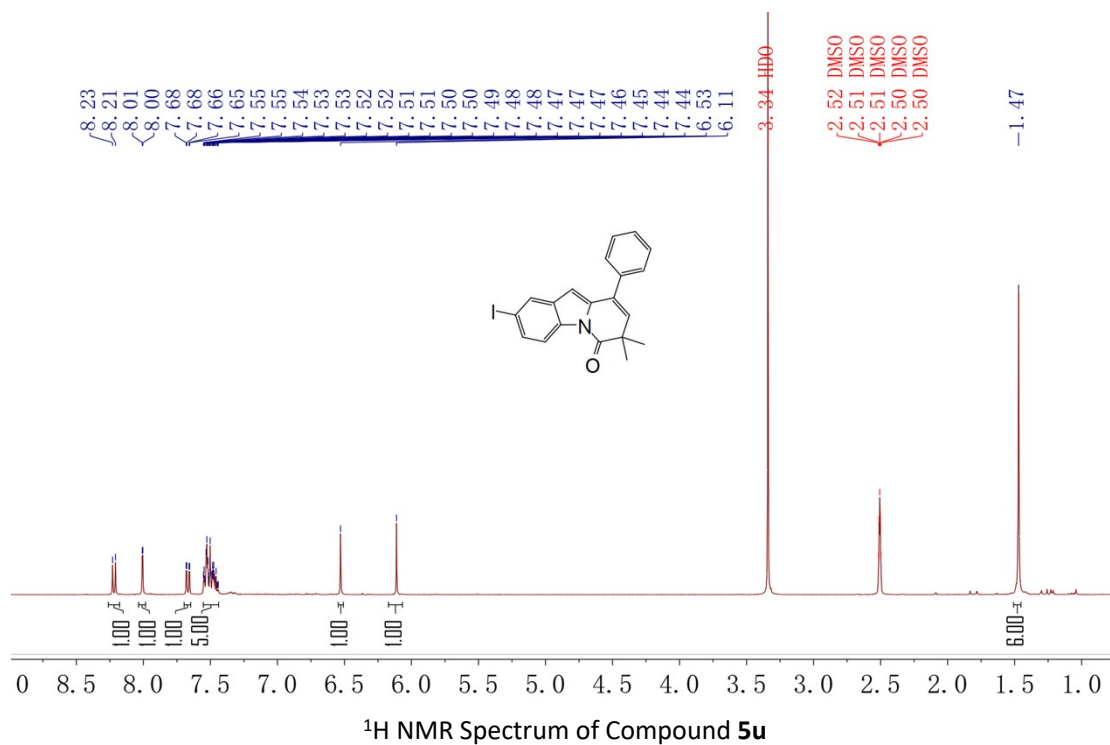
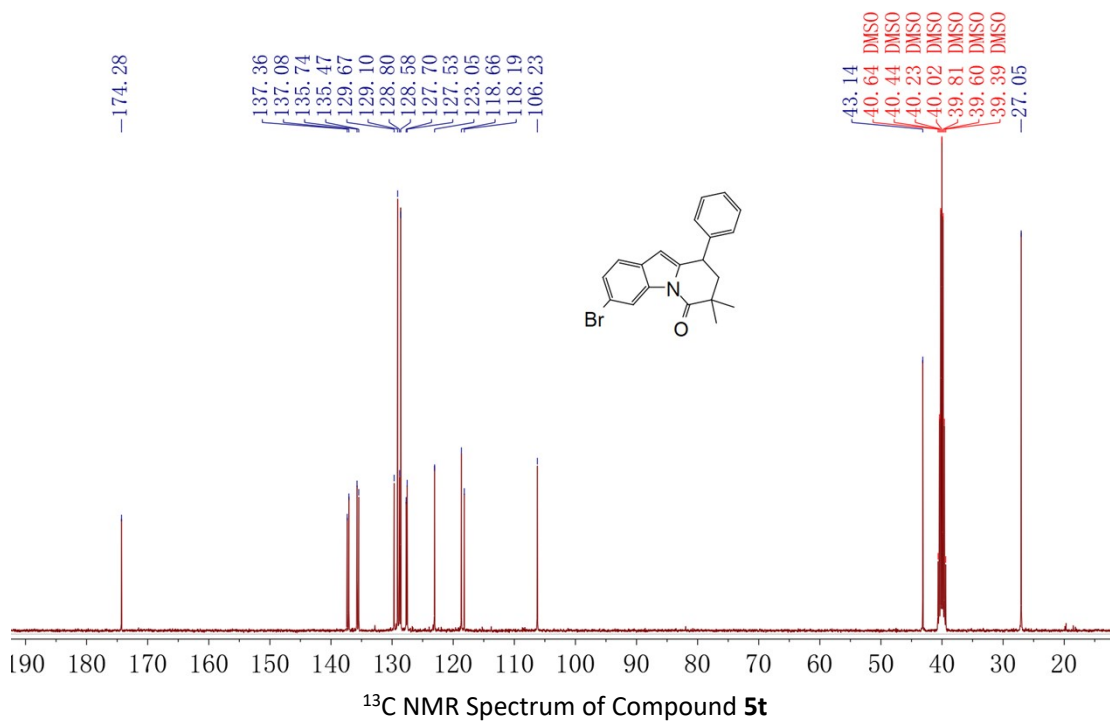


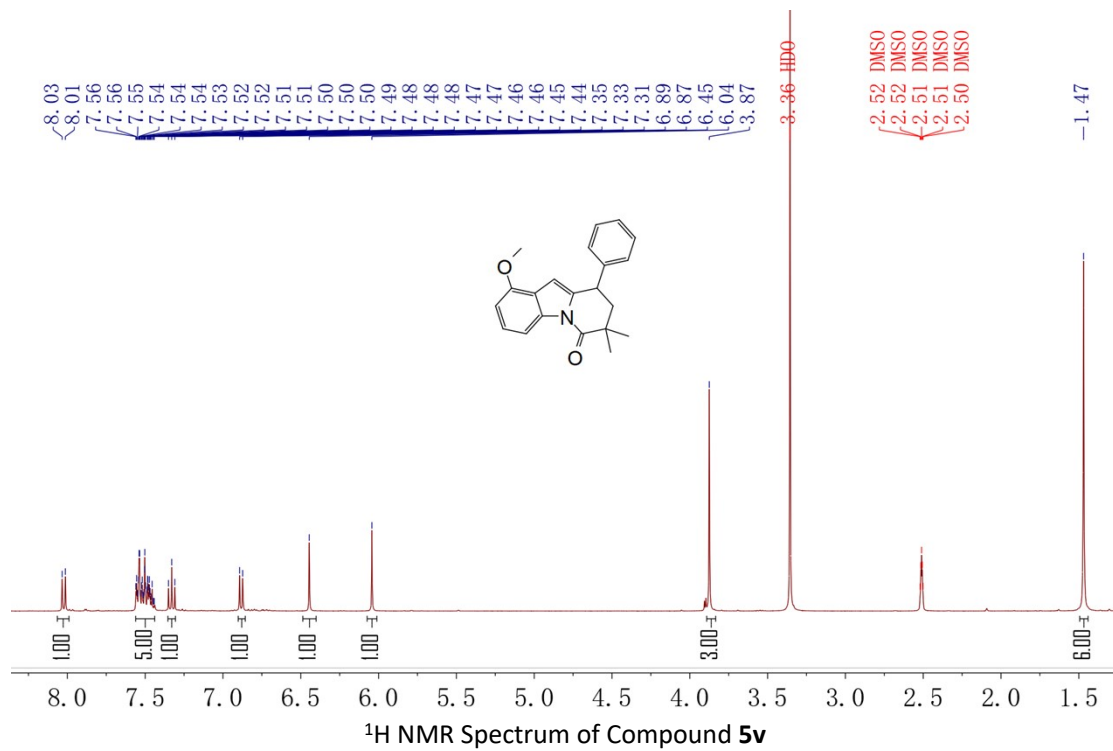
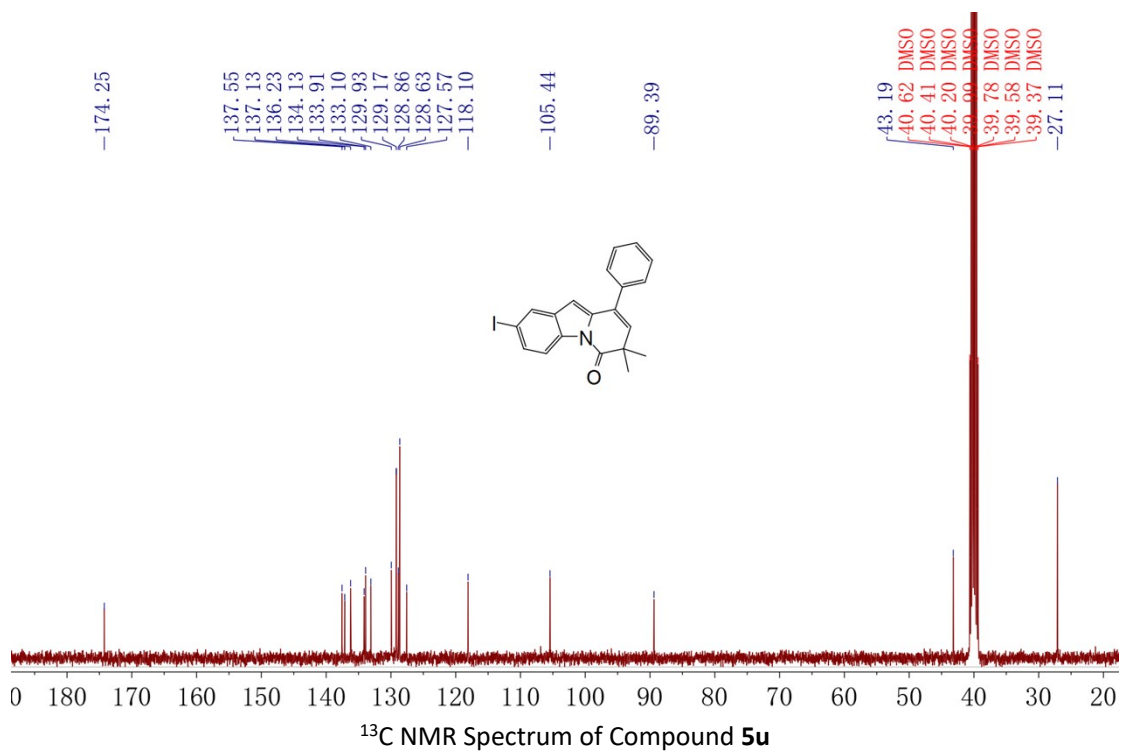


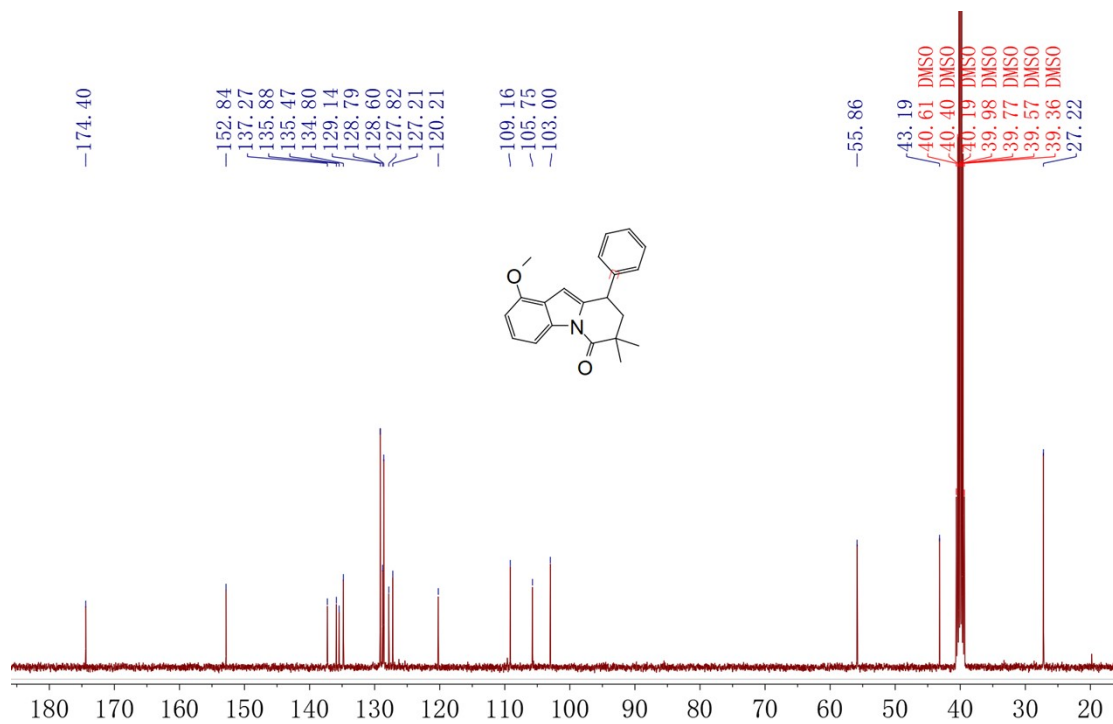




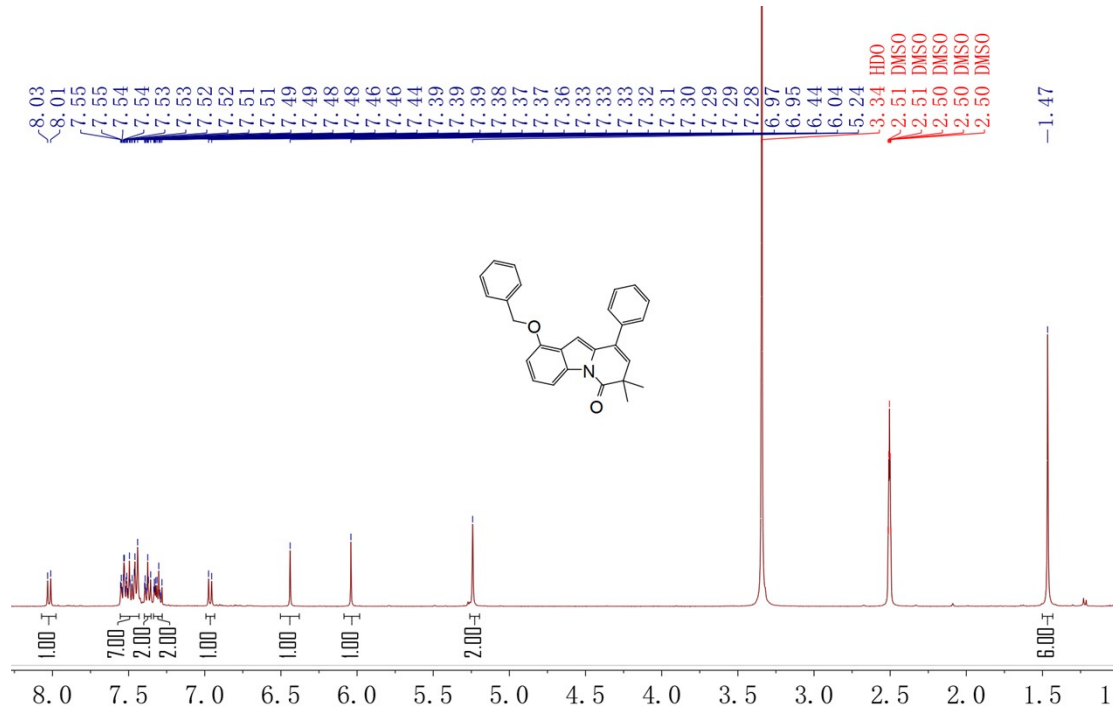






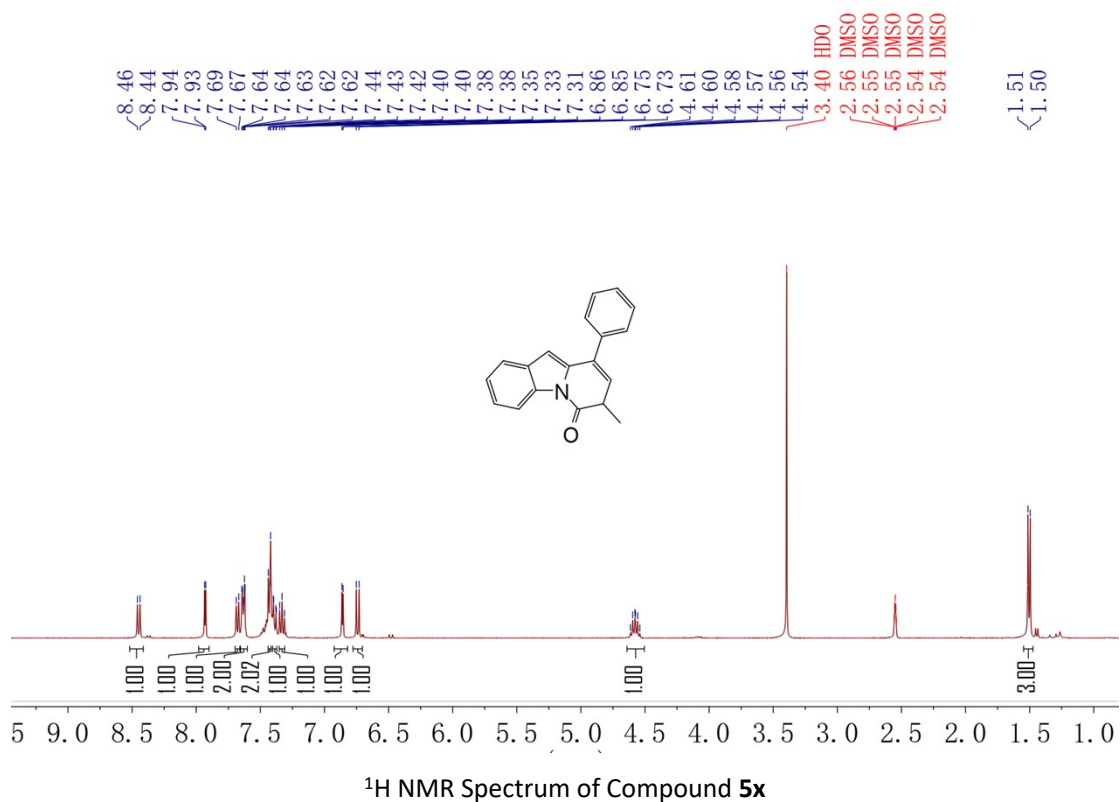
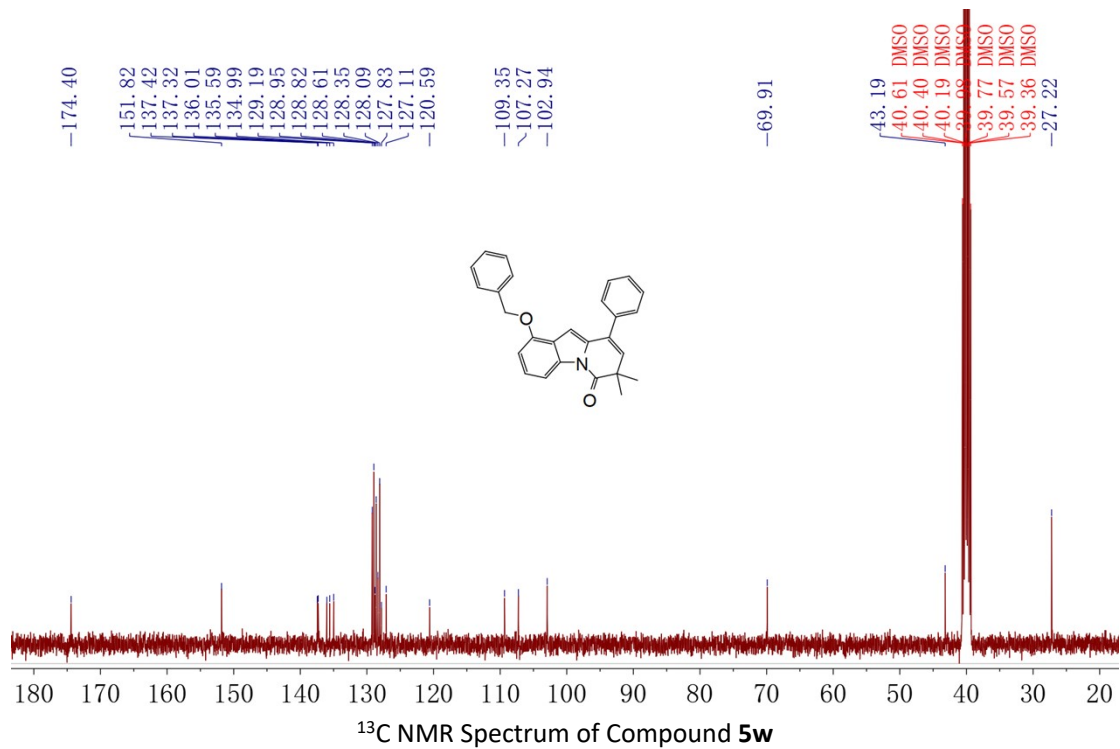


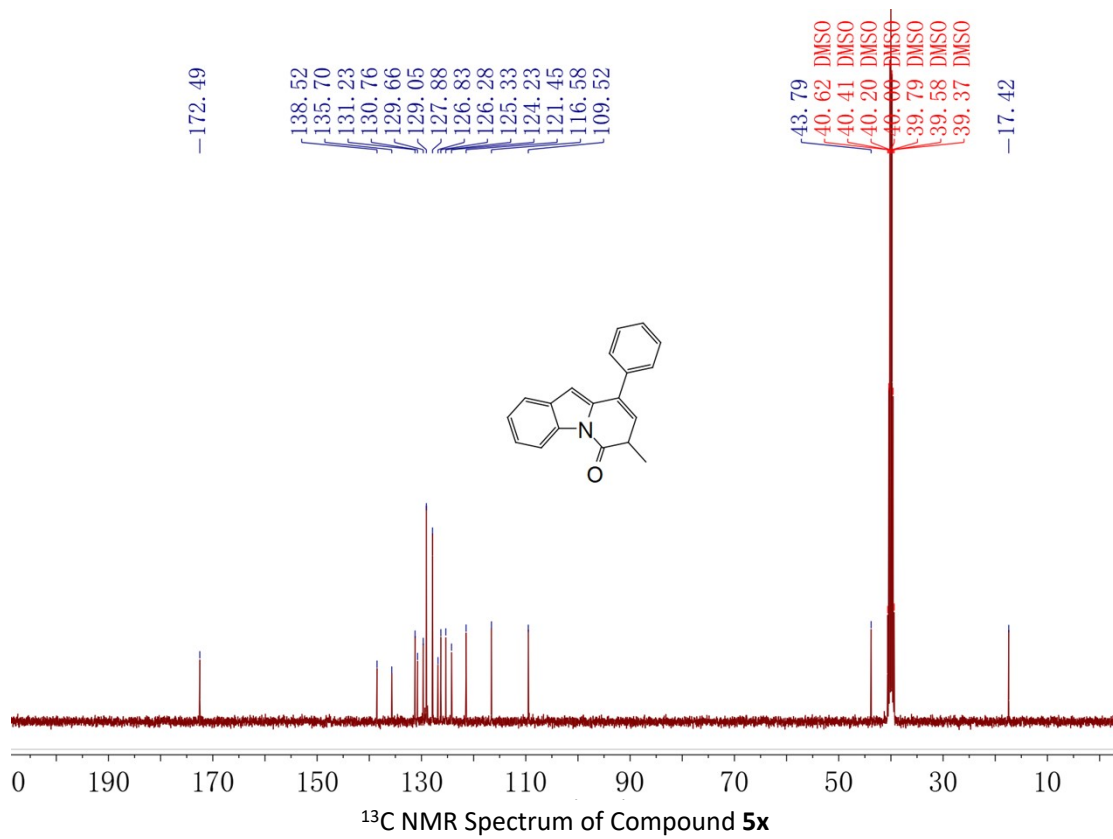
**<sup>13</sup>C NMR Spectrum of Compound 5v**



**<sup>1</sup>H NMR Spectrum of Compound 5w**







## 9. References

1. J. C. Theriot, C. H. Lim, H. Yang, M. D. Ryan, C. B. Musgrave and G. M. Miyake, *Science*, 2016, **352**, 1082-1086.