

*Supporting Information*

**Solvent Controlled Rh(III)-Catalyzed Switchable [4+2] Annulation of 2-Arylindoles with Iodonium Ylides**

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## **1. General methods**

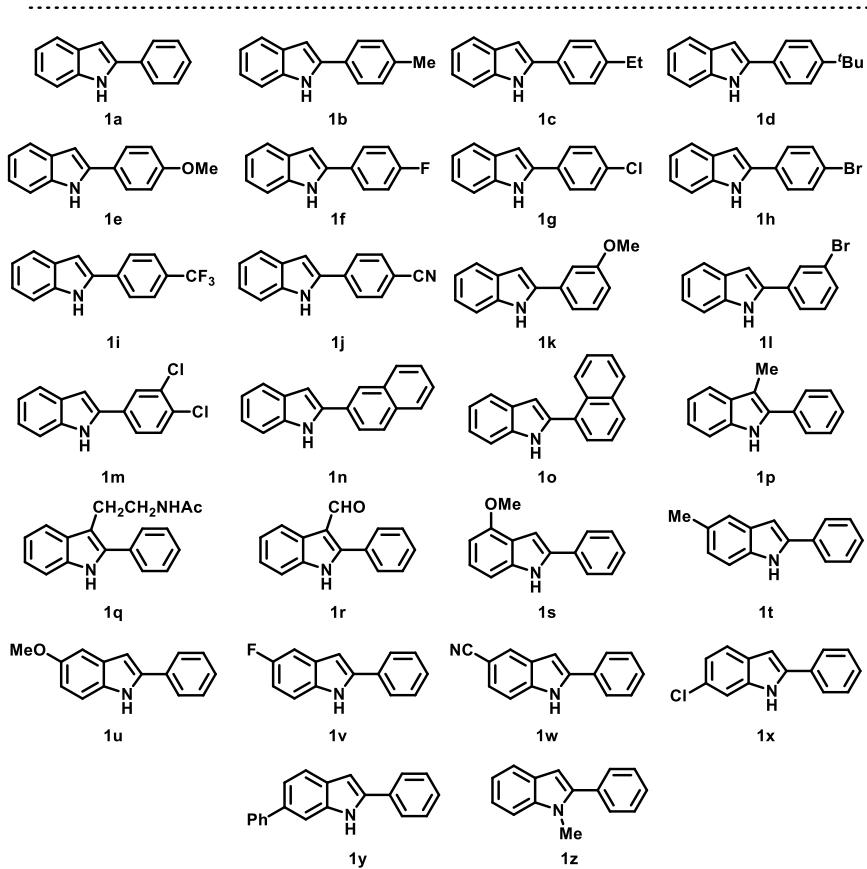
All the reactions were performed in an oven-dried glassware. Solvents were dried using standard methods. Tetrahydrofuran was dried over sodium-benzophenone ketyl. Acetonitrile and dichloromethane were distilled over calcium hydride. Unless otherwise stated, all the commercial reagents were used as received. Progress of the reaction was monitored by thin layer chromatography (Merck Silica-gel 60 F-254, 0.25 nm, pre-coated plates on alumina). Column chromatographic purifications were performed on Merck silica gel (100-200 mesh). Melting points were recorded on a digital melting point apparatus and are uncorrected.

Spectroscopic characterizations were carried at the Central Instrumentation Facility (CIF), National Institute of Pharmaceutical Education and Research (NIPER) Hyderabad.  $^1\text{H}$  NMR spectra were recorded on Bruker Avance-III FT-NMR spectrometers at 500 MHz and  $^{13}\text{C}$  NMR spectra were recorded at 125 MHz.  $^1\text{H}$  NMR chemical shifts are reported in ppm relative to the TMS ( $\delta = 0$ ) and are abbreviated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad).  $^{13}\text{C}$  NMR chemical shifts are reported in ppm relative to the residual  $\text{CDCl}_3$  signal ( $\delta = 77.16$ ) and  $\text{DMSO}-d_6$  signal ( $\delta = 39.5$ ). IR spectra was recorded on Perkin-Elmer FT-IR spectrometer. HRMS data was obtained on Agilent Q-TOF 6540 high resolution mass spectrometers.

## 2. Preparation of starting precursors:

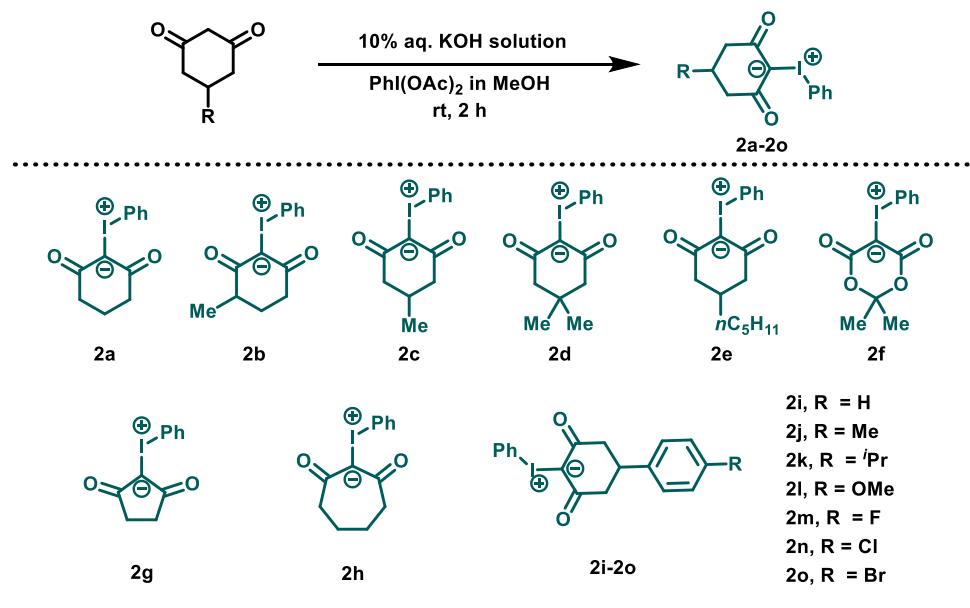
### 2.1 Synthesis of 2-Phenyl indole derivatives:

All the 2-Phenyl indole derivatives **1a-1z** were prepared according to reported literature procedure.<sup>1</sup>



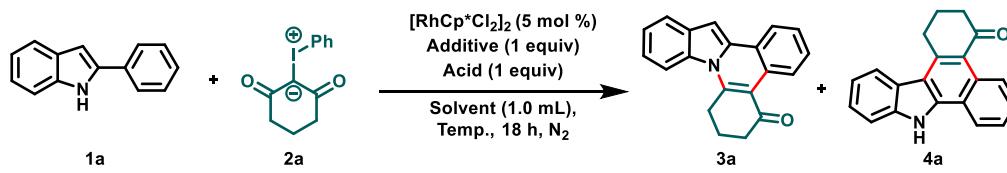
## 2.2 Synthesis of hypervalent iodonium ylides:

All the hypervalent iodonium ylides **2a-2m** were prepared by reported literature.<sup>2</sup>



## 3. Optimization studies:

### (a) Screening of Additive, Base, solvent, and temperature



Entry	Additive	Acid or base	Solvent	Temp. (°C)	<b>3a (%)<sup>b</sup></b>	<b>4a (%)<sup>b</sup></b>
1	CsOPiv	-	DCM	45	53	trace
2	AgOAc	-	DCM	45	48	trace
3	NaOAc	-	DCM	45	32	nd
4	KOAc	-	DCM	45	51	nd
5	CsOAc	-	DCM	45	58	nd
6	KPF <sub>6</sub>	-	DCM	45	nd	nd
7	AgSbF <sub>6</sub>	-	DCM	45	nd	nd
8	Cu(OAc) <sub>2</sub>	-	DCM	45	nd	nd
9	AgOTf	-	DCM	45	nd	nd
10	CsOAc	-	DCM	55	65	nd

11	CsOAc	-	DCM	65	63	nd
12 <sup>c</sup>	CsOAc	-	DCM	55	61	nd
13 <sup>d</sup>	CsOAc	-	DCM	55	51	nd
14	CsOAc	AcOH	DCM	55	35	nd
15	CsOAc	PivOH	DCM	55	31	nd
16 <sup>e</sup>	CsOAc	Ada-COOH	DCM	55	25	nd
17	CsOAc	Na <sub>2</sub> CO <sub>3</sub>	DCM	55	62	nd
<b>18</b>	<b>CsOAc</b>	<b>NaHCO<sub>3</sub></b>	DCM	<b>55</b>	<b>76</b>	<b>nd</b>
19 <sup>f</sup>	CsOAc	NaHCO <sub>3</sub>	DCM	55	72	nd
20 <sup>g</sup>	CsOAc	NaHCO <sub>3</sub>	DCM	55	65	nd
21	-	NaHCO <sub>3</sub>	DCM	55	>5	nd
22	CsOAc	K <sub>3</sub> PO <sub>4</sub>	DCM	55	59	nd
23	CsOAc	K <sub>2</sub> CO <sub>3</sub>	DCM	55	44	nd
24	CsOAc	Cs <sub>2</sub> CO <sub>3</sub>	DCM	55	51	nd
25	CsOAc	NH <sub>4</sub> CO <sub>3</sub>	DCM	55	39	nd
26 <sup>h</sup>	CsOAc	NaHCO <sub>3</sub>	DCM	55	74	nd
27 <sup>i</sup>	CsOAc	NaHCO <sub>3</sub>	DCM	55	49	nd
28	CsOAc	NaHCO <sub>3</sub>	CHCl <sub>3</sub>	55	60	nd
29	CsOAc	NaHCO <sub>3</sub>	DCE	55	53	nd
30	CsOAc	NaHCO <sub>3</sub>	DMSO	55	nd	nd
31	CsOAc	NaHCO <sub>3</sub>	DMF	55	nd	nd
32	CsOAc	NaHCO <sub>3</sub>	MeCN	55	45	nd
33	CsOAc	NaHCO <sub>3</sub>	Acetone	55	10	nd
34	CsOAc	NaHCO <sub>3</sub>	THF	55	15	nd
35	CsOAc	NaHCO <sub>3</sub>	1,4-Dioxane	55	18	nd
36	CsOAc	NaHCO <sub>3</sub>	Toluene	55	trace	nd
37	CsOAc	NaHCO <sub>3</sub>	MeOH	55	nd	nd
38	CsOAc	NaHCO <sub>3</sub>	EtOH	55	nd	nd
39	CsOAc	NaHCO <sub>3</sub>	<i>i</i> PrOH	55	nd	nd
40	CsOAc	NaHCO <sub>3</sub>	TFE	55	nd	22
41	CsOAc	NaHCO <sub>3</sub>	HFIP	55	nd	35
42	CsOAc	NaHCO <sub>3</sub>	HFIP	70	nd	44

43	CsOAc	NaHCO <sub>3</sub>	HFIP	85	nd	39
44	CsOAc	-	HFIP	70	nd	52
<b>45<sup>j</sup></b>	CsOAc	-	<b>HFIP</b>	<b>70</b>	<b>nd</b>	<b>68</b>
46 <sup>k</sup>	CsOAc	-	HFIP	70	nd	52
47 <sup>l</sup>	CsOAc	-	HFIP	70	nd	65
48 <sup>m</sup>	CsOAc	-	HFIP	70	nd	53
49	CsOAc	NaHCO <sub>3</sub>	DCM	<b>70</b>	58	nd
50	CsOAc	-	HFIP	<b>40</b>	nd	25

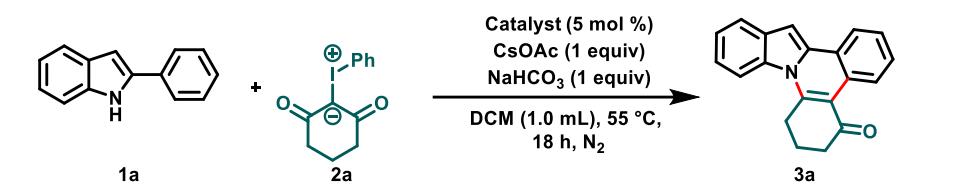
<sup>a</sup>Reaction Conditions: **1a** (0.11 mmol, 1.1 equiv), **2a** (0.10 mmol, 1.0 equiv), DCM (1 mL).

<sup>b</sup>Isolated yield. <sup>c</sup>CsOAc (2 equiv). <sup>d</sup>CsOAc (0.5 equiv). <sup>e</sup>1-Adamantane carboxylic acid.

<sup>f</sup>NaHCO<sub>3</sub> (2 equiv). <sup>g</sup>NaHCO<sub>3</sub> (0.5 equiv). <sup>h</sup>**1a** (1.5 equiv). <sup>i</sup>**1a** (0.5 equiv). <sup>j</sup>HFIP (2.0 mL).

<sup>k</sup>HFIP (0.5 mL). <sup>l</sup>**1a** (1.5 equiv). <sup>m</sup>**1a** (0.5 equiv). nd = not detected (reaction continued for 24 h).

### (b) Screening of Catalyst for **3a**

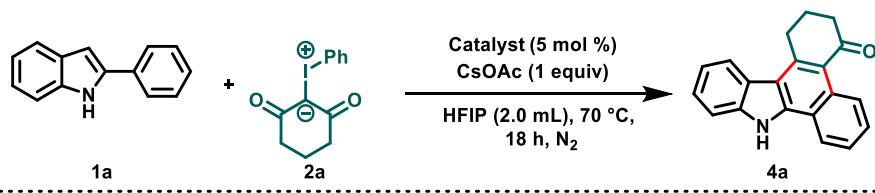


Entry	Catalyst	<b>3a (%)<sup>b</sup></b>
<b>1</b>	[Cp*RhCl <sub>2</sub> ] <sub>2</sub>	<b>76</b>
2	-	nd
3 <sup>c</sup>	[Cp*RhCl <sub>2</sub> ] <sub>2</sub>	71
4	[Cp*Rh(CH <sub>3</sub> CN) <sub>3</sub> ](SbF <sub>6</sub> ) <sub>2</sub>	62
5	[Cp*IrCl <sub>2</sub> ] <sub>2</sub>	47
6	[CoCp*(CO)I <sub>2</sub>	nd
7	[Ru( <i>p</i> -cymene)Cl <sub>2</sub> ] <sub>2</sub>	nd
8	[Rh <sub>2</sub> (OAc) <sub>4</sub> ]	nd
9	[Rh <sub>2</sub> (S-DOSP) <sub>4</sub> ]	nd

<sup>a</sup>Reaction Conditions: **1a** (0.11 mmol, 1.1 equiv.), **2a** (0.10 mmol, 1.0 equiv.), DCM (1.0 mL).

<sup>b</sup>Isolated yield. <sup>c</sup>[Cp\*RhCl<sub>2</sub>]<sub>2</sub> (3 mol %). <sup>d</sup>nd = not detected (reaction continued for 24 h).

(c) Screening of Catalyst for **4a**



Entry	Catalyst	<b>3a (%)<sup>b</sup></b>
<b>1</b>	[Cp*RhCl <sub>2</sub> ] <sub>2</sub>	<b>68</b>
2	-	nd
3 <sup>c</sup>	[Cp*RhCl <sub>2</sub> ] <sub>2</sub>	59
4	[Cp*Rh(CH <sub>3</sub> CN) <sub>3</sub> ](SbF <sub>6</sub> ) <sub>2</sub>	51
5	[Cp*IrCl <sub>2</sub> ] <sub>2</sub>	nd
6	[CoCp*(CO)I <sub>2</sub>	nd
7	[Ru( <i>p</i> -cymene)Cl <sub>2</sub> ] <sub>2</sub>	nd
8	[Rh <sub>2</sub> (OAc) <sub>4</sub> ]	nd
9	[Rh <sub>2</sub> (S-DOSP) <sub>4</sub> ]	nd

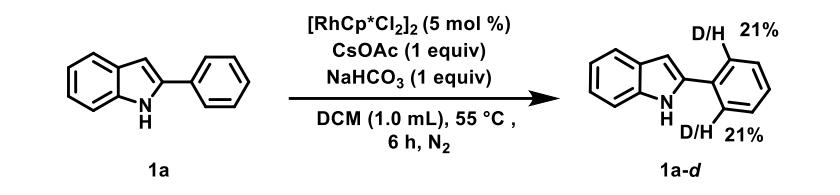
<sup>a</sup>Reaction Conditions: **1a** (0.11 mmol, 1.1 equiv.), **2a** (0.10 mmol, 1.0 equiv.), HFIP (2.0 mL).

<sup>b</sup>Isolated yield. <sup>c</sup>[Cp\*RhCl<sub>2</sub>]<sub>2</sub> (3 mol %). <sup>d</sup>nd = not detected (reaction continued for 24 h).

#### 4. Mechanistic studies:

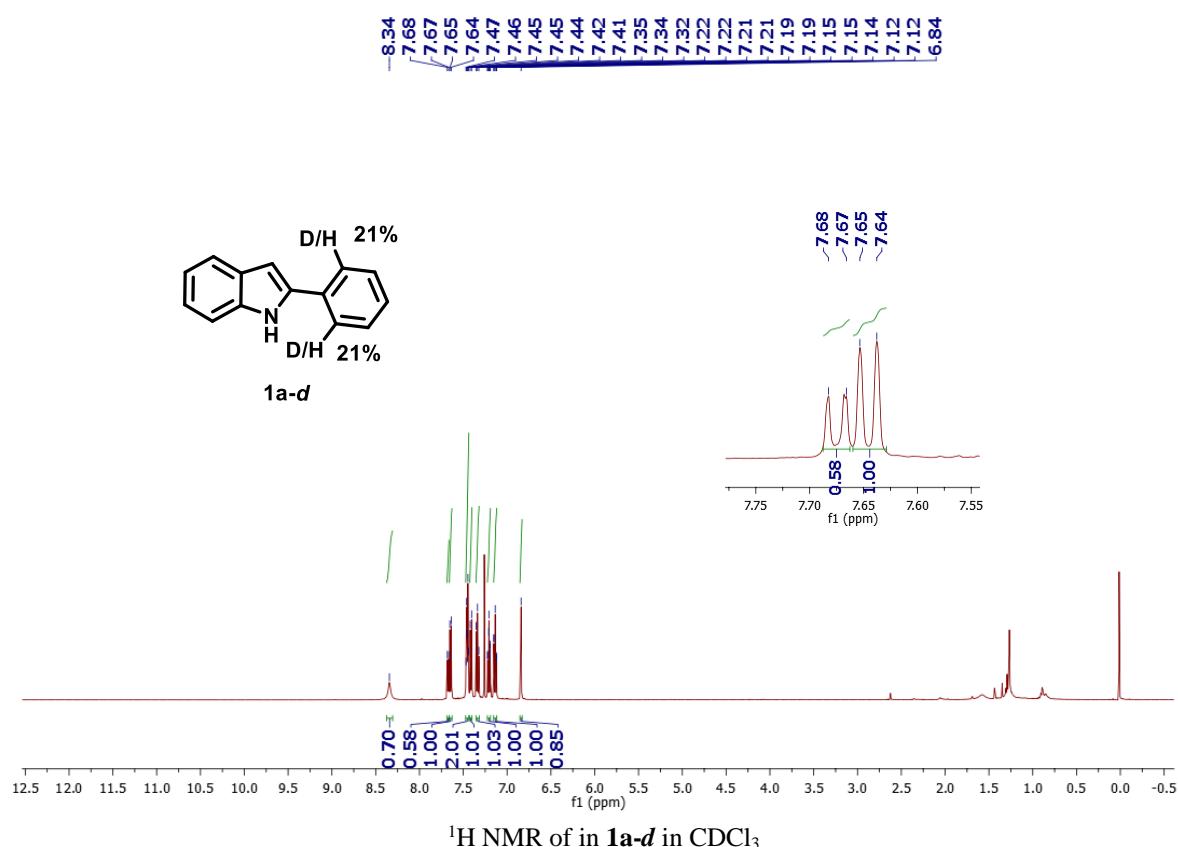
#### **4.1 Mechanistic studies for 3a product:**

(a) H/D exchange reaction for **3a** product

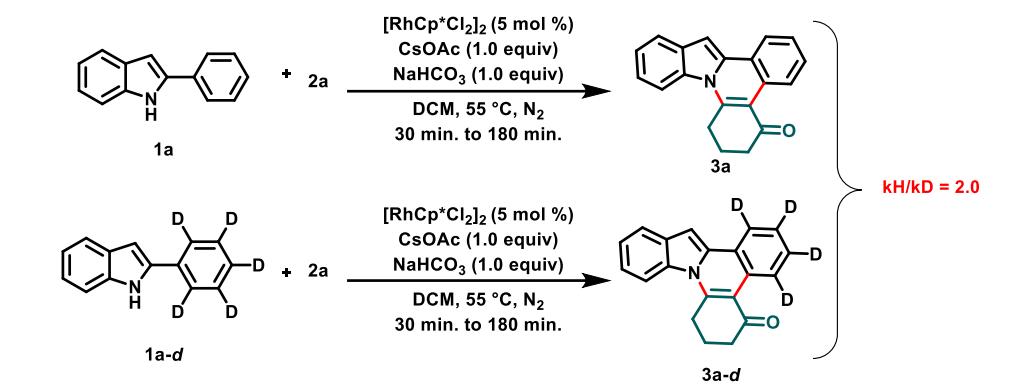


To a mixture of 2-phenyl indole **1a** (0.11 mmol, 1.1 equiv), [RhCp<sup>\*</sup>Cl<sub>2</sub>]<sub>2</sub> (5 mol %), CsOAc (1.0 equiv) and NaHCO<sub>3</sub> (1.0 equiv) in an oven dried 10 mL reaction tube was added dry DCM (1.0 mL) and CD<sub>3</sub>OD (1.29 mmol, 10 equiv) under N<sub>2</sub> atmosphere. Then the tube was capped with septa, and the resulting mixture was stirred at 55 °C on oil bath for 6 h. The residue was filtered through celite, and solvent was evaporated under reduced pressure to afford the crude **1a-d** and was used directly for the <sup>1</sup>H NMR analysis.

Found H/D exchange 21% at *ortho* position 2-phenyl indole.



(b) Parallel reactions for KIE value measurement for **3a** product



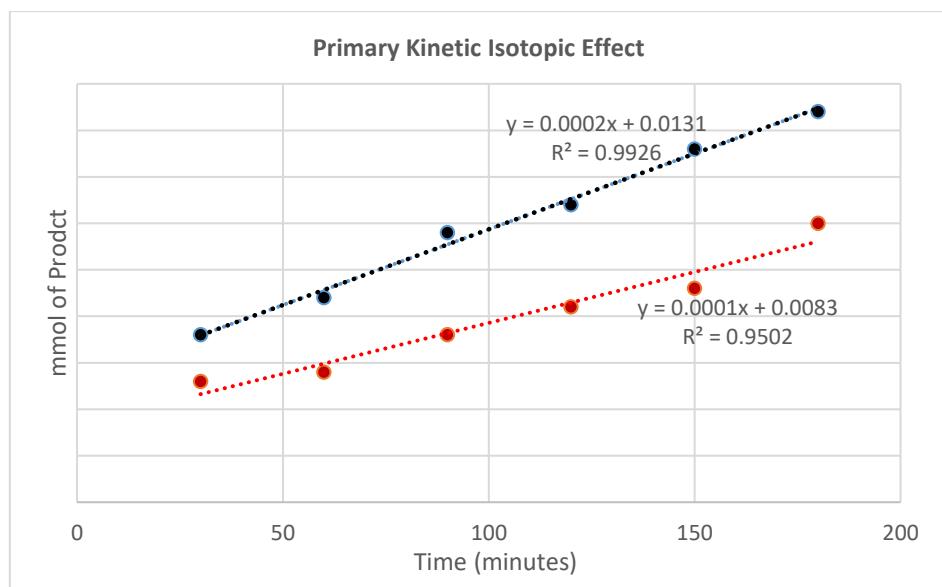
To an oven dried screw cap reaction tube equipped with a magnetic stir bar, 0.11 mmol of 2-Phenylindole H5 was subjected to standard reaction conditions. After an equal interval of 30 minutes, reaction mixture was concentrated and directly taken for NMR analysis up to 180 minutes. Identical set of experiments were performed using 2-Phenylindole-*d*<sub>5</sub> and NMR analysis was carried out.

#### Studies for 2-Phenylindole H5

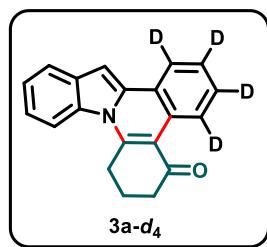
S.no	Time (minutes)	Rate conversion	Mmol of Product
1	30	0.18	0.018
2	60	0.22	0.022
3	90	0.29	0.029
4	120	0.32	0.032
5	150	0.38	0.038
6	180	0.42	0.042

#### Studies for 2-Phenylindole D5

S.no	Time (minutes)	Rate conversion	Mmol of Product
1	30	0.12	0.012
2	60	0.14	0.014
3	90	0.18	0.018
4	120	0.21	0.021
5	150	0.23	0.023
6	180	0.30	0.030



**7,8-dihydroindolo[1,2-f]phenanthridin-5(6H)-one-1,2,3,4-d<sub>4</sub> (3a- d<sub>4</sub>):**



Obtained as pale yellow solid; (19 mg, Yield = 65%), m.p. 158-159 °C,  
 $R_f$  = 0.4 (ethyl acetate/hexane: 23:77).

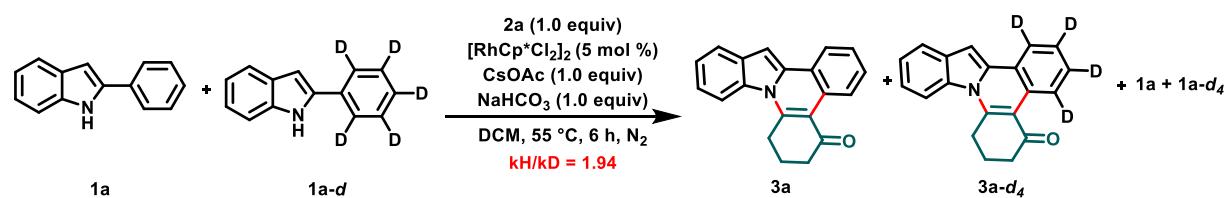
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 8.10 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 7.8 Hz, 1H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.32 (t, *J* = 7.8 Hz, 1H), 7.25 (s, 1H), 3.66 (t, *J* = 6.1 Hz, 2H), 2.76 (t, *J* = 6.5 Hz, 2H), 2.30 (p, *J* = 12.6, 6.5 Hz, 2H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 197.7, 151.0, 136.4, 133.7, 131.6, 124.7, 123.5, 121.8, 121.2, 116.3, 113.7, 111.7, 97.1, 39.0, 30.8, 21.5.

**IR (Neat, v/cm<sup>-1</sup>)** 3266, 3043, 2958, 2870, 1636, 1564, 1418, 1329, 1244, 1135, 1034.

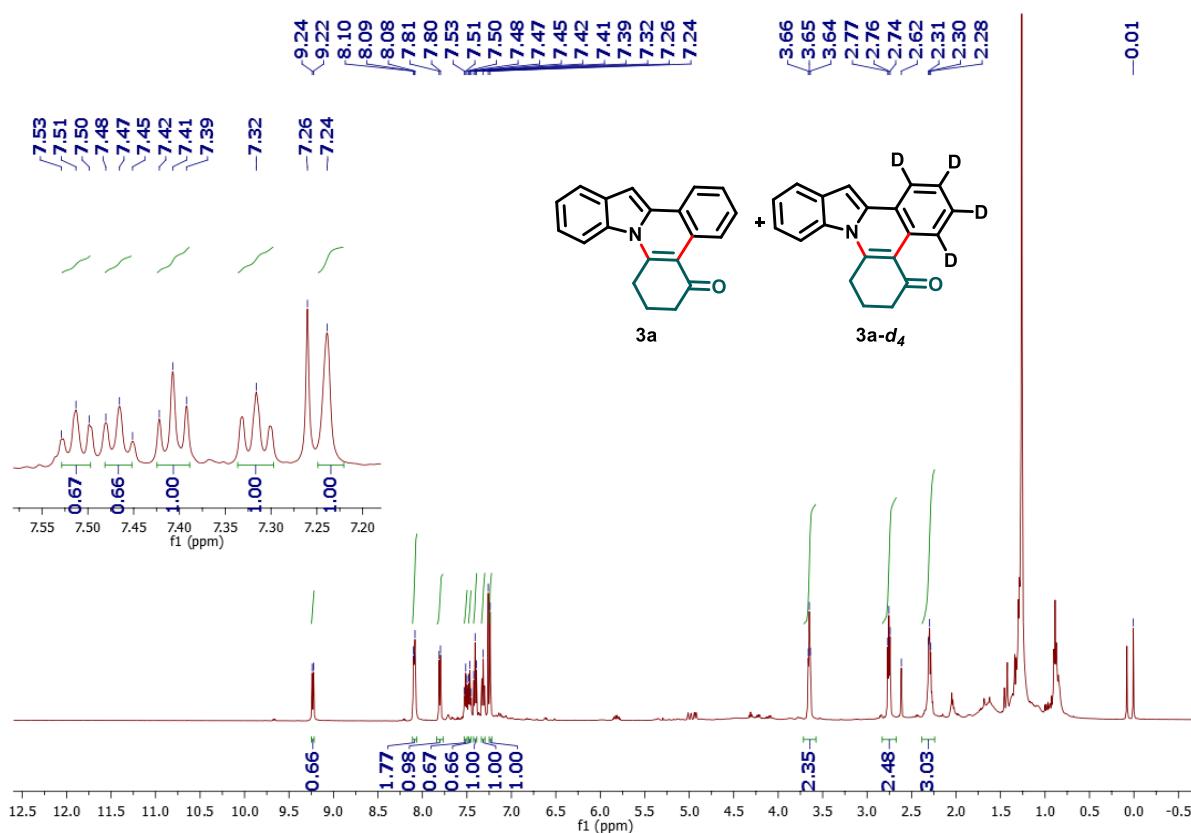
**HRMS (ESI) *m/z*:** [M+H]<sup>+</sup> calcd for C<sub>20</sub>H<sub>12</sub>D<sub>4</sub>NO 290.1478; Found 290.1477.

(c) Competitive reactions for KIE value measurement for **3a** product



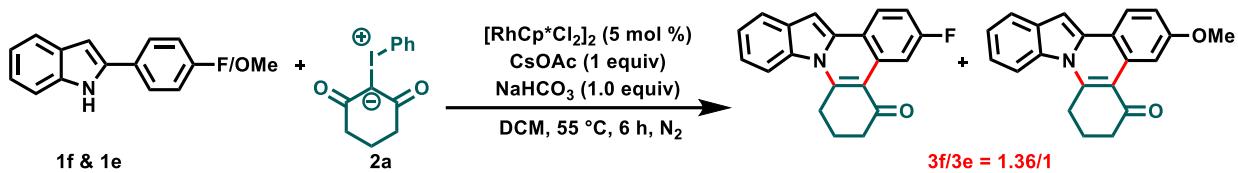
To a mixture of **1a** (0.11 mmol, 1.1 equiv), **1a-d** (0.11 mmol, 1.1 equiv), **2a** (0.10 mmol, 1.0 equiv),  $[\text{RhCp}^*\text{Cl}_2]_2$  (5 mol %), CsOAc (1.0 equiv) and NaHCO<sub>3</sub> (1.0 equiv) in an oven dried 10 mL reaction tube was added dry DCM (1.0 mL) under N<sub>2</sub> atmosphere. Then the tube was capped with septa, and the resulting mixture was stirred at 55 °C on oil bath for 6 h. The reaction mixture was filtered by silica pad, solvent was evaporated under reduced pressure to give mixture of the product mixture of products **3a** and **3a-d<sub>4</sub>** and **1a** and **1a-d<sub>5</sub>**. The KIE was determined by the <sup>1</sup>H NMR integration.

A kinetic isotopic effect of these two reactions was determined to be  $kH/kD = 1.94$  (0.66/0.34)

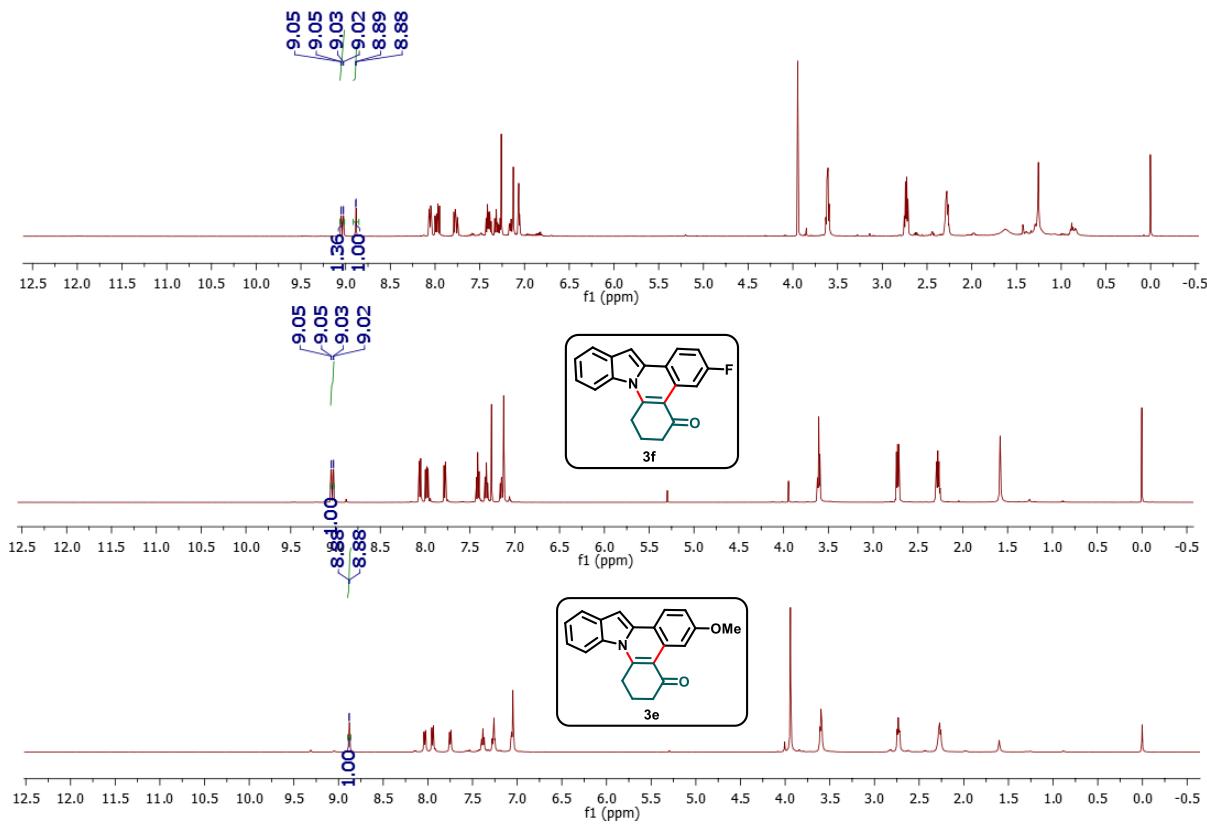


<sup>1</sup>H NMR spectrum of mixture **3a** and **3a-d<sub>4</sub>** (CDCl<sub>3</sub>, 500 MHz)

(d) Competitive reaction between 2-phenyl indoles:

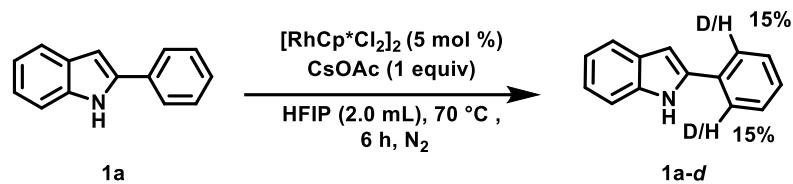


To a mixture of **1f** (0.11 mmol, 1.1 equiv), **1e** (0.11 mmol, 1.1 equiv), **2a** (0.10 mmol, 1.0 equiv), [RhCp\*Cl<sub>2</sub>]<sub>2</sub> (5 mol %) and CsOAc (1.0 equiv) in an oven dried 10 mL reaction tube was added DCM (1.0 mL) under N<sub>2</sub> atmosphere. Then the tube was capped with septa, and the resulting mixture was stirred at 55 °C on oil bath for 6 h. The reaction mixture was filtered by celite pad, solvent was evaporated under reduced pressure to give mixture of the product **3f** and **3e** which was submitted for NMR. The ratio of **3f/3e** of purified product was determined to be **1.36/1.0** by <sup>1</sup>H NMR integration (see below). Resulting, the reaction **3f** is proceeding **1.36** times faster than **3e**.



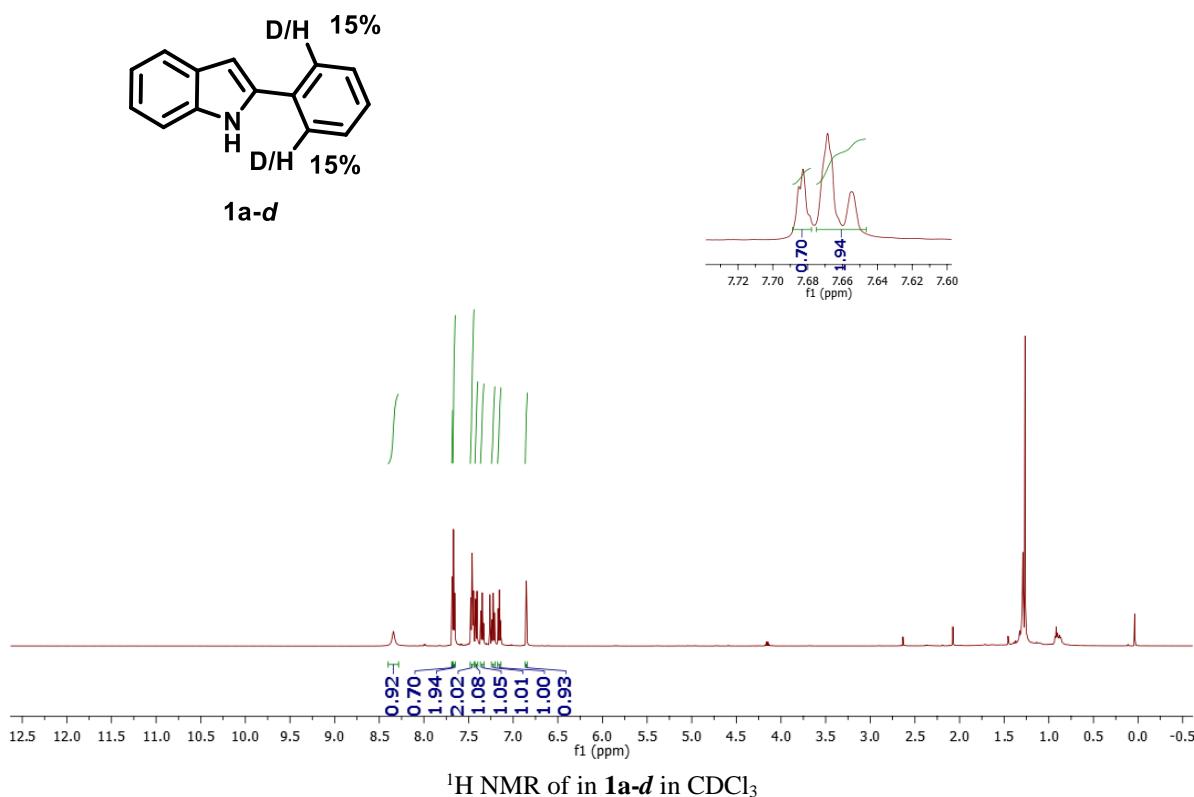
#### **4.2 Mechanistic studies for 4a product:**

(a) H/D exchange reaction for **4a** product

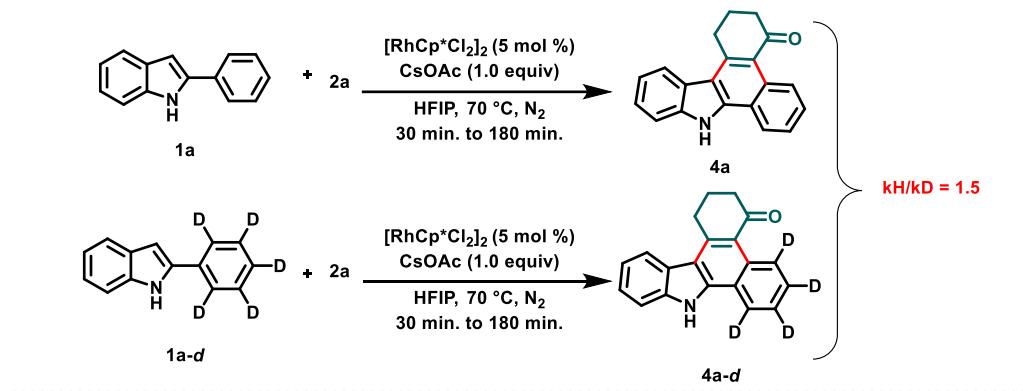


To a mixture of 2-phenyl indole **1a** (0.11 mmol, 1.1 equiv), [RhCp\*Cl<sub>2</sub>]<sub>2</sub> (5 mol %) and CsOAc (1.0 equiv) in an oven dried 10 mL reaction tube was added HFIP (2.0 mL) and CD<sub>3</sub>OD (1.29 mmol, 10 equiv) under N<sub>2</sub> atmosphere. Then the tube was capped with septa, and the resulting mixture was stirred at 70 °C on oil bath for 6 h. The residue was filtered through celite and solvent as evaporated under reduced pressure to afford the crude **1a-d** and was directly used for proton <sup>1</sup>H analysis.

Found H/D exchange 15% at *ortho* position 2-phenyl indole.



(b) Parallel reactions for KIE value measurement for **4a** product



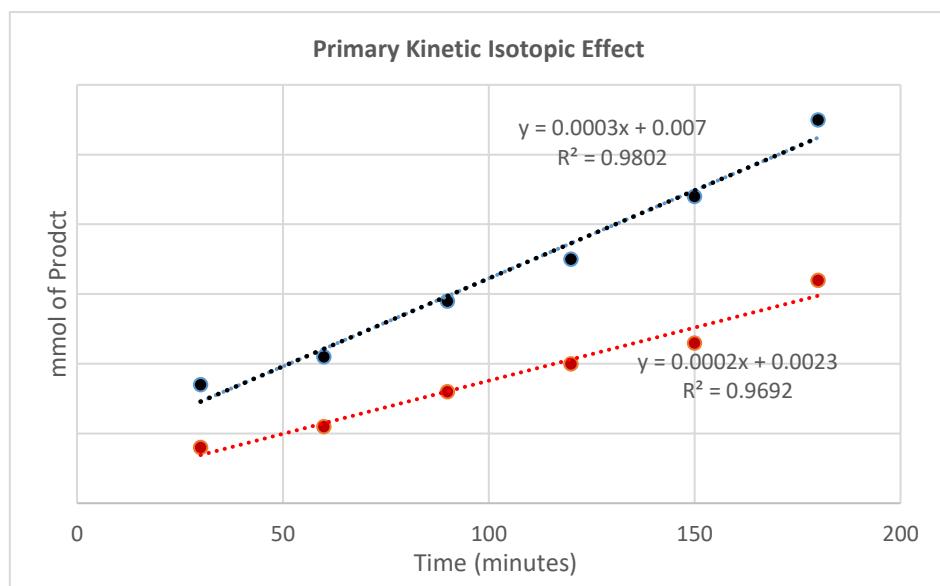
To an oven dried screw cap reaction tube equipped with a magnetic stir bar, 0.11 mmol of 2-Phenylindole H5 was subjected to standard reaction conditions. After an equal interval of 30 minutes, reaction mixture was concentrated and directly taken for NMR analysis up to 180 minutes. Identical set of experiments were performed using D5-2-Phenylindole and NMR analysis was carried out.

#### Studies for 2-Phenylindole H5

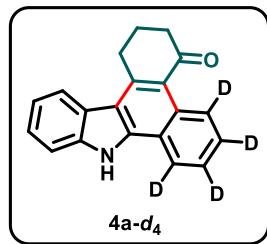
S.no	Time (minutes)	Rate conversion	Mmol of Product
1	30	0.17	0.017
2	60	0.21	0.021
3	90	0.29	0.029
4	120	0.33	0.033
5	150	0.44	0.044
6	180	0.55	0.05

#### Studies for 2-Phenylindole D5

S.no	Time (minutes)	Rate conversion	Mmol of Product
1	30	0.08	0.008
2	60	0.11	0.011
3	90	0.16	0.016
4	120	0.20	0.020
5	150	0.23	0.023
6	180	0.32	0.032



**1,2,3,9-tetrahydro-4*H*-dibenzo[*a,c*]carbazol-4-one-5,6,7,8-*d*<sub>4</sub> (4a- d<sub>4</sub>):**



Obtained as pale yellow solid; (17 mg, Yield = 59%), m.p. 158-159 °C,  
 $R_f$  = 0.4 (ethyl acetate/hexane: 30:70).

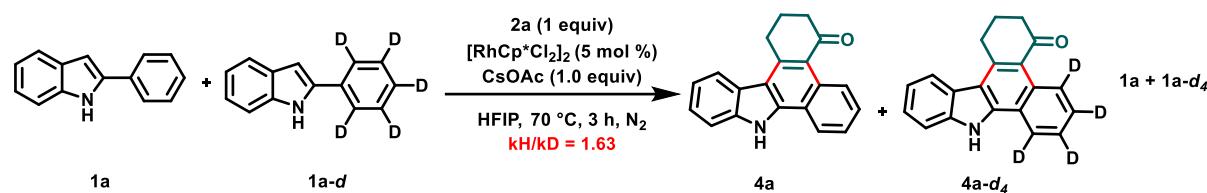
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 9.09 (s, 1H), 8.26 (d, *J* = 7.9 Hz, 1H), 7.64 (d, *J* = 8.1 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 3.73 (t, *J* = 6.2 Hz, 2H), 2.88 (t, *J* = 6.4 Hz, 2H), 2.37 (t, *J* = 6.9, 12.9 Hz, 2H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 200.0, 145.4, 139.0, 138.3, 128.5, 125.3, 124.9, 122.7, 121.2, 120.2, 116.1, 111.6, 40.9, 29.6, 22.7.

**IR (Neat, v/cm<sup>-1</sup>)** 3262, 3205, 3043, 2938, 2870, 1628, 1547, 1454, 1248, 1187, 1123.

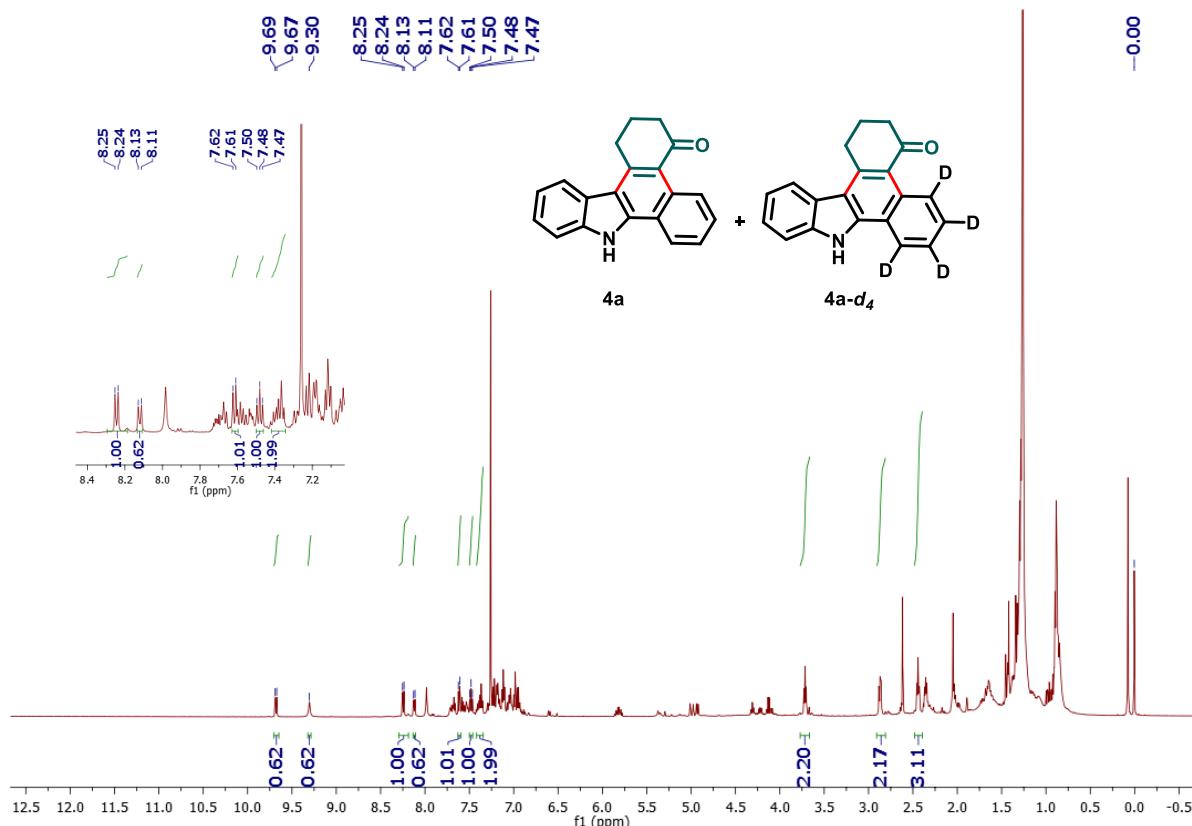
**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calcd for C<sub>20</sub>H<sub>12</sub>D<sub>4</sub>NO 290.1478; Found 290.1474.

(c) Competitive reactions for KIE value measurement for **4a** product

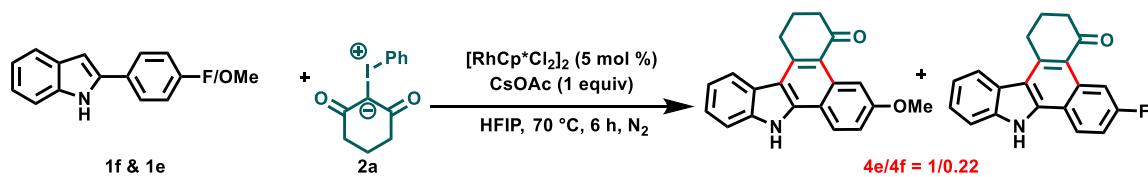


To a mixture of **1a** (0.11 mmol, 1.1 equiv), **1a-d** (0.11 mmol, 1.1 equiv), **2a** (0.10 mmol, 1.0 equiv),  $[\text{RhCp}^*\text{Cl}_2]_2$  (5 mol %) and  $\text{CsOAc}$  (1.0 equiv) in an oven dried 10 mL reaction tube was added HFIP (2.0 mL) under  $\text{N}_2$  atmosphere. Then the tube was capped with septa, and the resulting mixture was stirred at  $70^\circ\text{C}$  on oil bath for 3 h. The reaction mixture was filtered by celite pad, solvent was evaporated under reduced pressure to give mixture of the product mixture of products **4a** and **4a-d<sub>4</sub>** and **1a** and **1a-d<sub>4</sub>**. The KIE was determined by the  $^1\text{H}$  NMR integration.

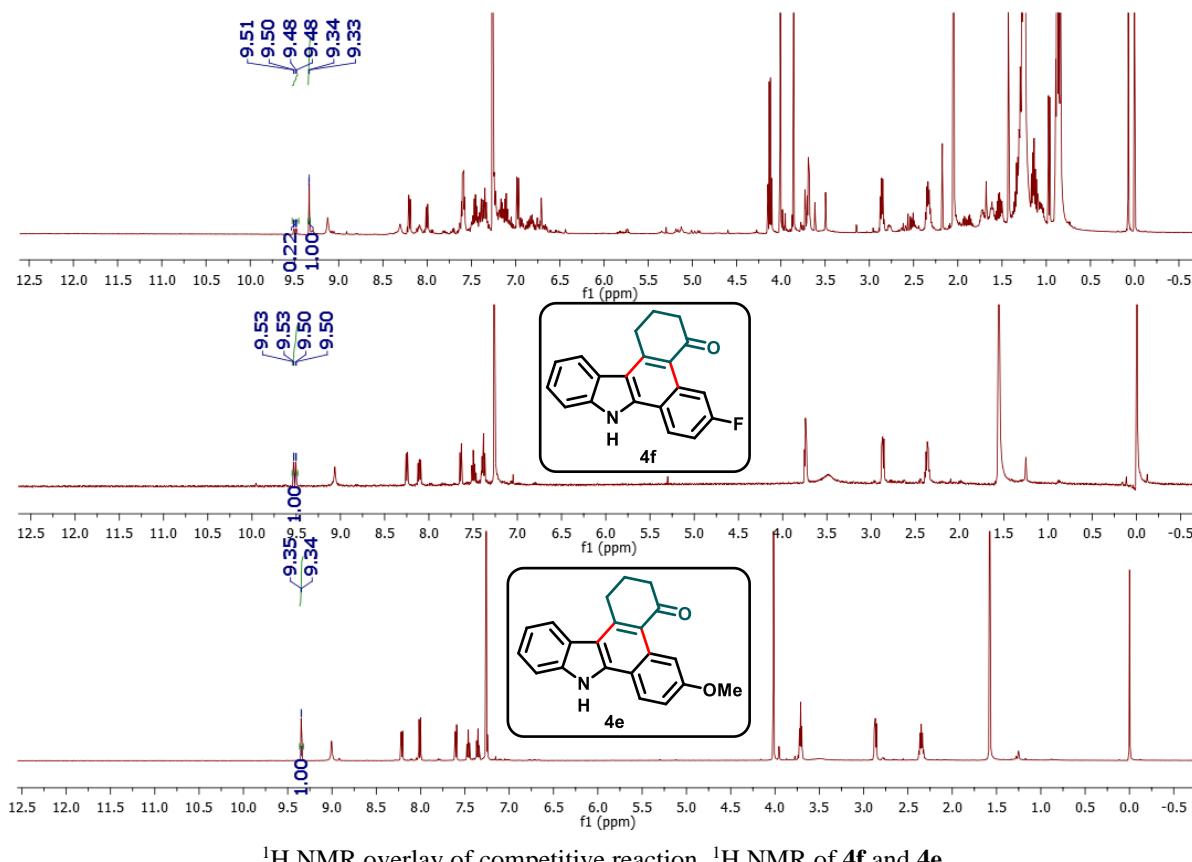
A kinetic isotopic effect of these two reactions was determined to be  $k\text{H}/k\text{D} = 1.63$  (0.62/0.38).



(d) Competitive reaction between 2-phenyl indoles:



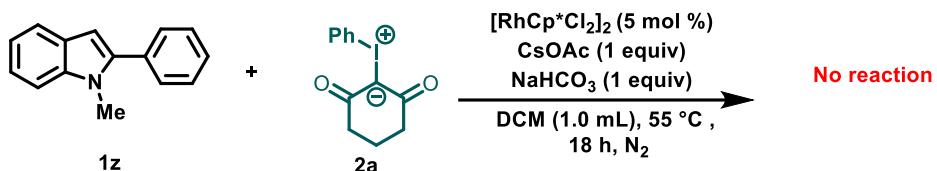
To a mixture of **1f** (0.11 mmol, 1.1 equiv), **1e** (0.11 mmol, 1.1 equiv), **2a** (0.10 mmol, 1.0 equiv), [RhCp\*Cl<sub>2</sub>]₂ (5 mol %) and CsOAc (1.0 equiv) in an oven dried 10 mL reaction tube was added HFIP (2.0 mL) under N<sub>2</sub> atmosphere. Then the tube was capped with septa, and the resulting mixture was stirred at 70 °C on oil bath for 6 h. The reaction mixture was filtered by celite pad, solvent was evaporated under reduced pressure to give mixture of the product **4e** and **4f** which was submitted for NMR. The ratio of **4e**/**4f** of purified product was determined to be **1.0/0.22** by <sup>1</sup>H NMR integration (see below). Resulting, the reaction **4e** is proceeding **4.5** times faster than **4f**.



<sup>1</sup>H NMR overlay of competitive reaction, <sup>1</sup>H NMR of **4f** and **4e**

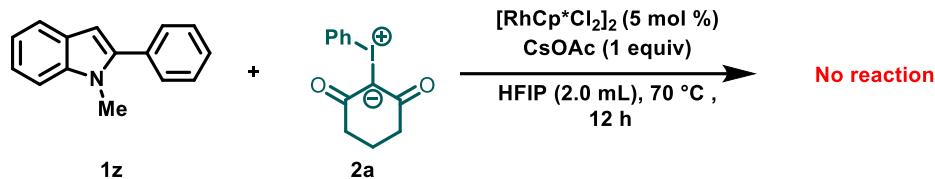
#### 4.3 Studies on Directing groups:

a) Reaction of **1z** with iodonium ylide for **3a** product:



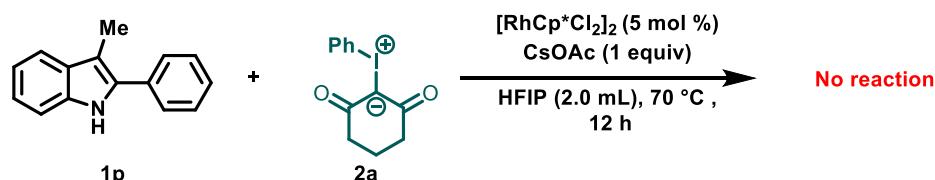
To an oven dried 10 mL reaction tube with a magnetic stir bar was charged with **1z** (0.11 mmol, 1.1 equiv), **2a** (0.10 mmol, 1.0 equiv),  $[\text{RhCp}^*\text{Cl}_2]_2$  (5.0 mol %), CsOAc (0.10 mmol, 1.0 equiv),  $\text{NaHCO}_3$  (0.10 mmol, 1.0 equiv) and dry DCM (1.0 mL) was added under  $\text{N}_2$  atmosphere. Then, the tube was capped with septa, and the resulting mixture was stirred at 55  $^\circ\text{C}$  for the period of 18 h. Further, the reaction was monitored by TLC to confirm the product formations and it was observed that starting material **1z** was intact and the desired product was not formed.

b) Reaction of **1z** with iodonium ylide for **4a** product:



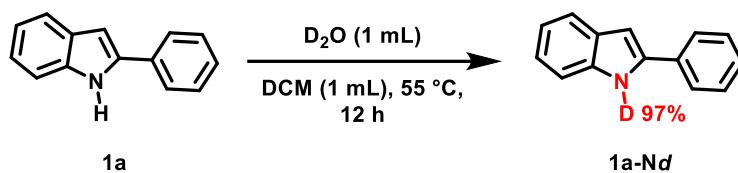
To an oven dried 10 mL reaction tube with a magnetic stir bar was charged with **1z** (0.11 mmol, 1.1 equiv), **2a** (0.10 mmol, 1.0 equiv),  $[\text{RhCp}^*\text{Cl}_2]_2$  (5.0 mol %), CsOAc (0.10 mmol, 1.0 equiv), and HFIP (2.0 mL) was added under  $\text{N}_2$  atmosphere. Then, the tube was capped with septa, and the resulting mixture was stirred at 70  $^\circ\text{C}$  for the period of 12 h. Further, the reaction was monitored by TLC to confirm the product formations and it was observed that starting material **1y** was intact and the desired product was not formed.

c) Reaction of **1p** with iodonium ylide for **4a** product:



To an oven dried 10 mL reaction tube with a magnetic stir bar was charged with **1k** (0.11 mmol, 1.1 equiv), **2a** (0.10 mmol, 1.0 equiv),  $[\text{RhCp}^*\text{Cl}_2]_2$  (5.0 mol %), CsOAc (0.10 mmol, 1.0 equiv), and HFIP (2.0 mL) was added under  $\text{N}_2$  atmosphere. Then, the tube was capped with septa, and the resulting mixture was stirred at 70 °C for the period of 12 h. Further, the reaction was monitored by TLC to confirm the product formations and it was observed that starting material **1p** was intact and the desired product was not formed.

d) Preparation of 2-phenyl-1*d*-indole:



To a solution of **1a** (0.051 mmol, 1.0 equiv), in 1 mL DCM was added deuterium oxide ( $\text{D}_2\text{O}$ ) 1mL. Then the contents were stirred at 55 °C on an oil bath for 12 h. Then solvent was evaporated under reduced pressure and the residue was subjected for  $^1\text{H}$  NMR.

*Found H/D exchange 97% at NH of 2-phenyl indole.*

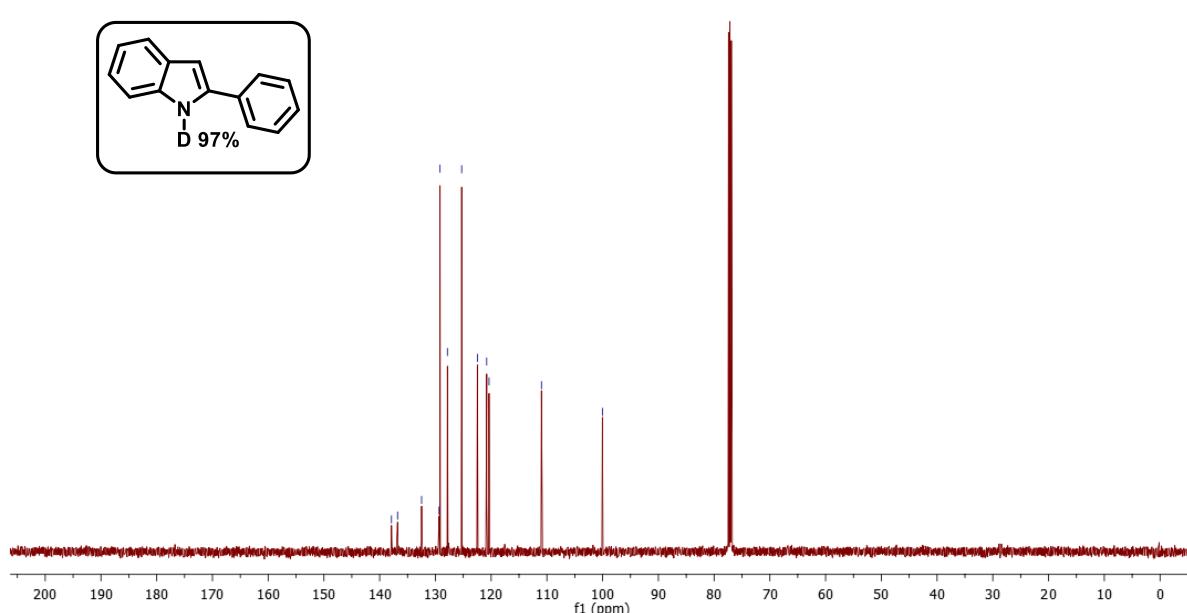
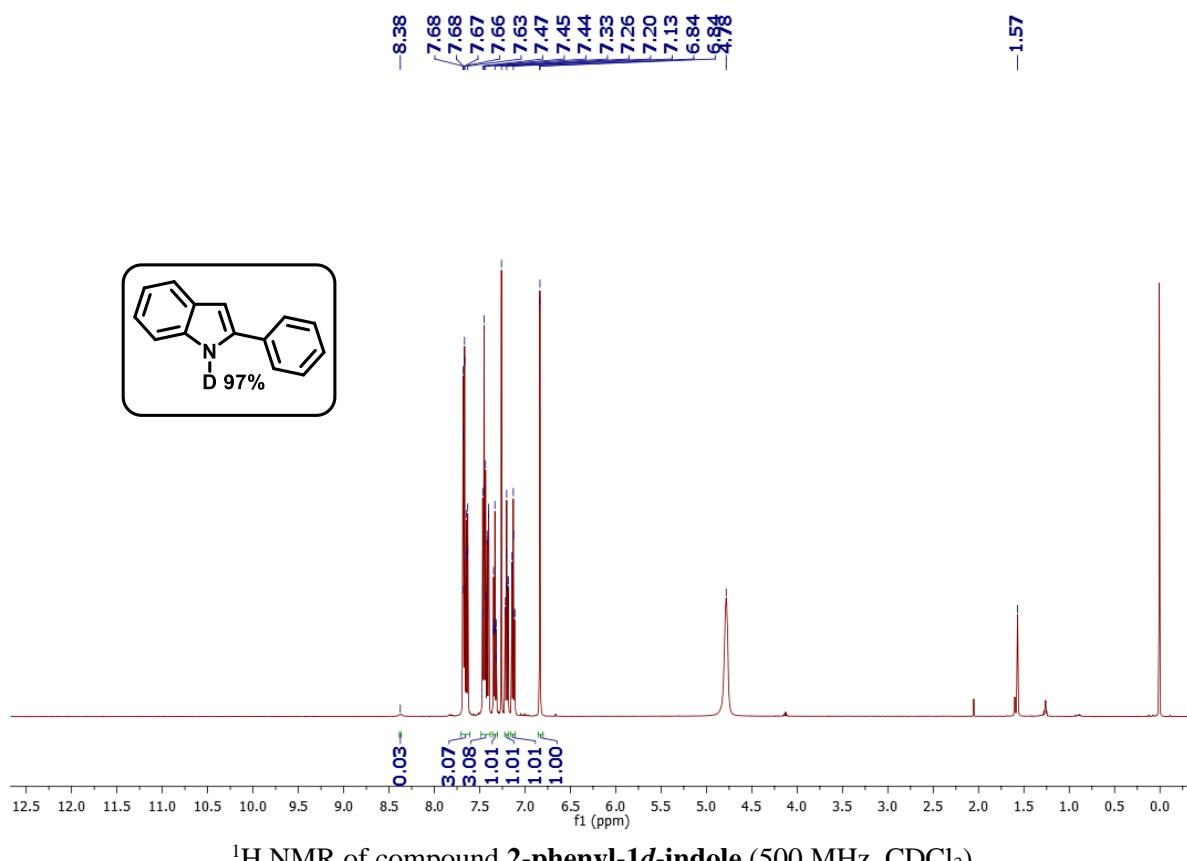
### 2-phenyl-1*d*-indole

**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )** δ 7.71 – 7.61 (m, 3H), 7.49 – 7.38 (m, 3H), 7.36 – 7.30 (m, 1H), 7.20 (ddd,  $J = 8.1, 7.1, 1.2$  Hz, 1H), 7.16 – 7.11 (m, 1H), 6.84 (d,  $J = 0.8$  Hz, 1H).

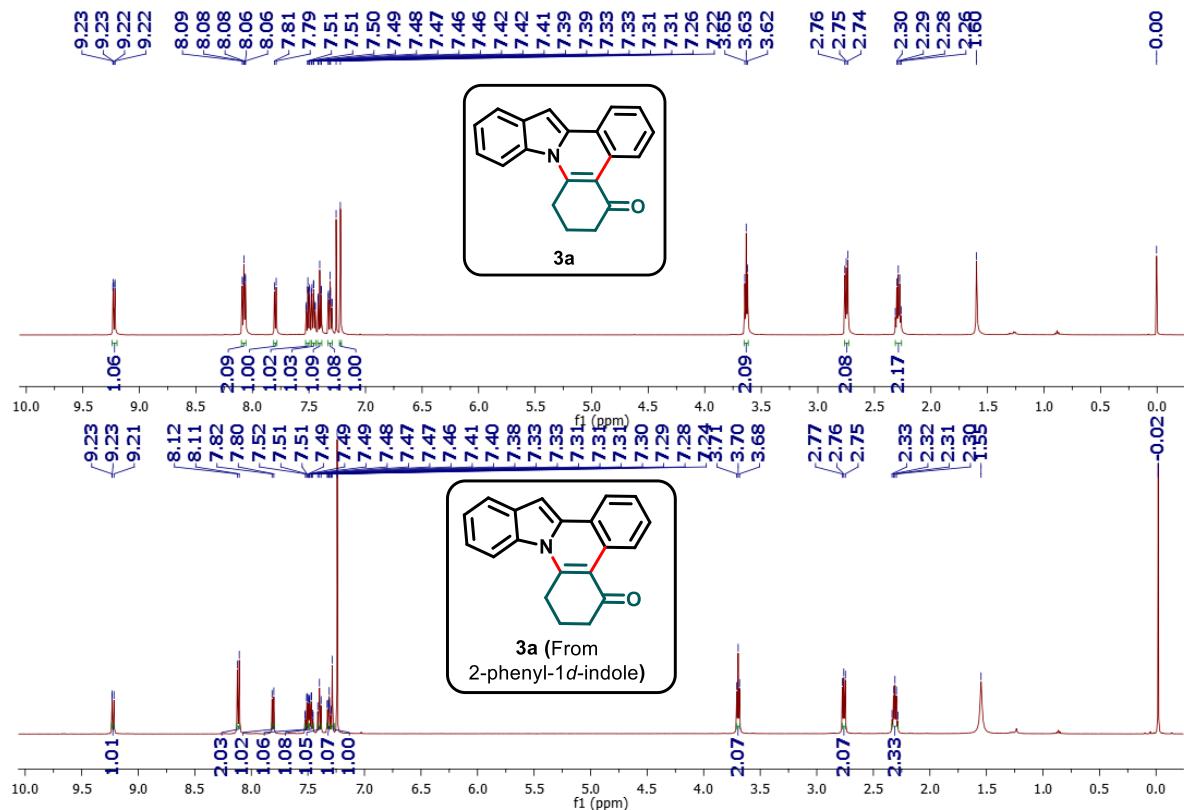
**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )** δ 137.9, 136.8, 132.5, 129.3, 129.2, 127.8, 125.3, 122.5, 120.8, 120.4, 110.0, 100.0.

**HRMS (ESI)**  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{14}\text{H}_{11}\text{DN}$  195.1028; Found 195.1023.

**2-Phenyl-1d-indole:**

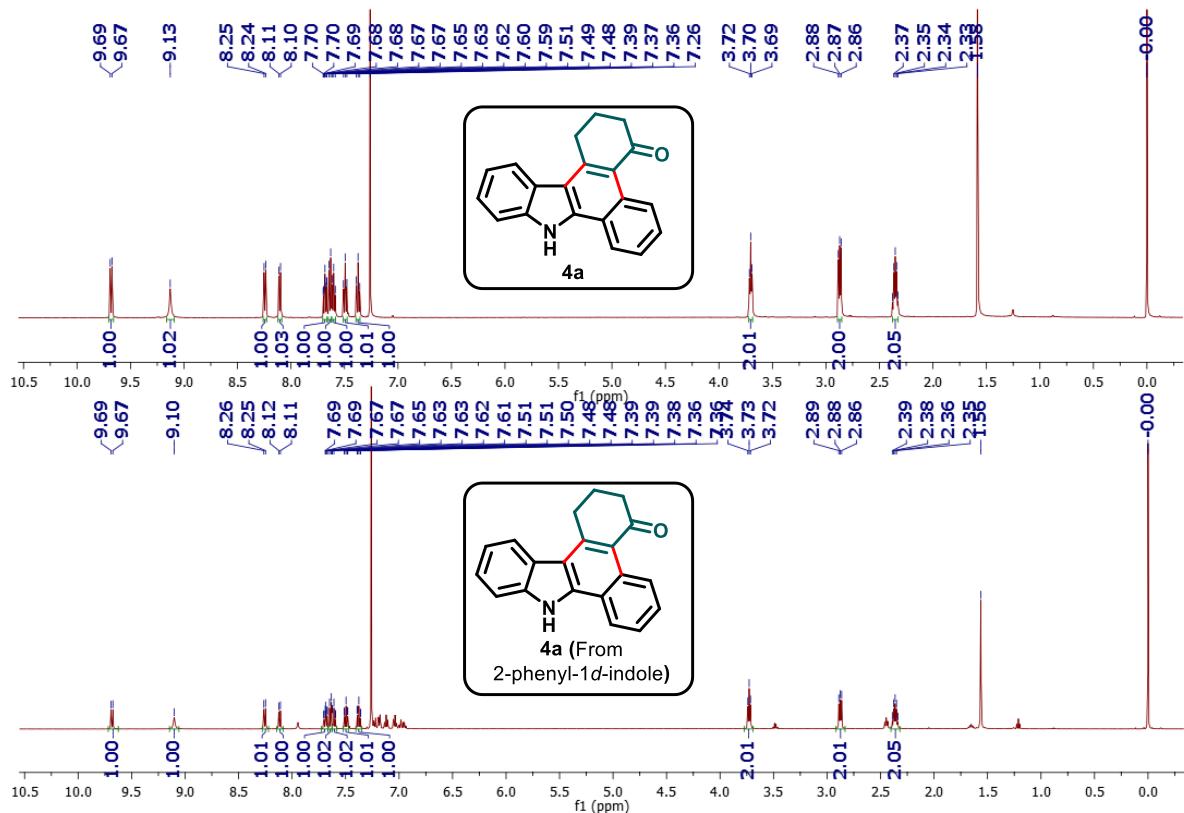


### **7,8-dihydroindolo[1,2-f]phenanthridin-5(6*H*)-one:**



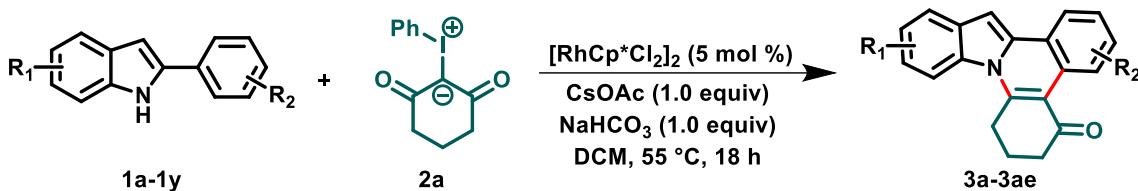
<sup>1</sup>H NMR of compound **3a** and **3a** from 2-phenyl-1*d*-indole (500 MHz, CDCl<sub>3</sub>)

### **1,2,3,9-tetrahydro-4*H*-dibenzo[*a,c*]carbazol-4-one (4a):**



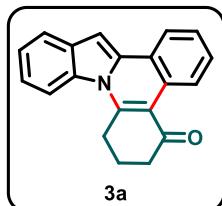
<sup>1</sup>H NMR of compound **4a** and **4a** from 2-phenyl-1*d*-indole (500 MHz, CDCl<sub>3</sub>)

## 5. General procedure for product 3:



**General procedure A:** In a 10 mL oven dried reaction tube with a magnetic stir bar was charged with 2-phenylindole derivatives **1** (0.11 mmol, 1.1 equiv), Iodonium ylide **2a** (0.10 mmol, 1.0 equiv), [RhCp\*Cl<sub>2</sub>]<sub>2</sub> (5 mol %), CsOAc (1.0 equiv) and NaHCO<sub>3</sub> (1.0 equiv) in 1 mL of dry DCM under N<sub>2</sub> atmosphere. Then the tube was capped with septa and the resulting mixture was stirred at 55 °C on oil bath for 18 h. The reaction completion was monitored by TLC. Upon completion of reaction, the solvent was evaporated under reduced pressure and the crude product was directly purified by a silica gel column chromatography by using ethyl acetate/hexane as the eluent to afford the corresponding product **3**.

### 7,8-dihydroindolo[1,2-f]phenanthridin-5(6H)-one (3a):



Prepared by following procedure A, obtained as pale yellow solid; (22 mg, Yield = 76%), m.p. 164–165 °C, R<sub>f</sub> = 0.5 (ethyl acetate/hexane: 25:75).

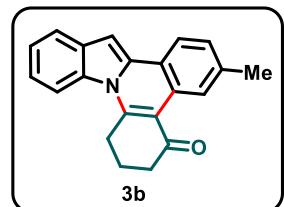
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 9.22 (dd, *J* = 8.3, 0.9 Hz, 1H), 8.09 – 8.06 (m, 2H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.51 (ddd, *J* = 8.4, 7.1, 1.5 Hz, 1H), 7.46 (td, *J* = 7.5, 1.3 Hz, 1H), 7.42 – 7.39 (m, 1H), 7.31 (ddd, *J* = 8.5, 7.1, 1.3 Hz, 1H), 7.22 (s, 1H), 3.63 (t, *J* = 6.1 Hz, 2H), 2.75 (t, *J* = 6.8 Hz, 2H), 2.29 (p, *J* = 6.3, z12.7 Hz, 2H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 197.7, 151.0, 136.3, 133.6, 131.6, 128.4, 127.3, 127.0, 126.1, 124.6, 123.5, 123.1, 121.8, 121.2, 116.3, 113.6, 97.1, 38.9, 30.7, 21.5.

**IR (Neat, v/cm<sup>-1</sup>)** 3116, 3002, 2920, 2864, 1628, 1559, 1457, 1378, 1281, 1182, 1050, 941, 850, 761.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calcd for C<sub>20</sub>H<sub>16</sub>NO 286.1227; Found 286.1226.

### 3-methyl-7,8-dihydroindolo[1,2-f]phenanthridin-5(6H)-one: (3b):



Prepared by following procedure A, obtained as pale yellow solid; (22 mg, Yield = 73%), m.p. 204–205 °C, R<sub>f</sub> = 0.5 (ethyl acetate/hexane: 25:75).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 8.90 (d, *J* = 2.5 Hz, 1H), 8.07 (d, *J* = 8.6 Hz, 1H), 7.99 (d, *J* = 8.7 Hz, 1H), 7.77 (d, *J* = 7.8 Hz, 1H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.29

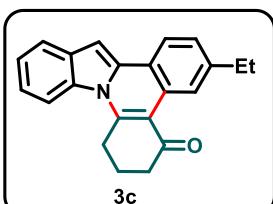
(d,  $J = 8.3$  Hz, 1H), 7.10 (s, 1H), 7.08 (dd,  $J = 8.8, 2.5$  Hz, 1H), 3.95 (s, 3H), 3.66 (t,  $J = 5.9$  Hz, 2H), 2.76 (t,  $J = 6.2$  Hz, 2H), 2.30 (p,  $J = 6.1, 12.5$  Hz, 2H).

**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  197.9, 159.9, 151.8, 136.6, 133.4, 132.0, 127.7, 124.6, 123.6, 121.2, 120.8, 118.2, 116.6, 116.3, 113.2, 108.9, 95.4, 55.6, 39.0, 30.8, 21.5.

**IR (Neat, v/cm<sup>-1</sup>)** 3030, 2951, 2923, 2853, 1738, 1637, 1608, 1593, 1568, 1485, 1455, 1409, 1392, 1353, 1316, 1292, 1250, 1226, 1184, 1160, 1084, 1054, 1021, 1002, 931, 876.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calcd for  $\text{C}_{21}\text{H}_{18}\text{NO}$  300.1383; Found 300.1376.

### 3-ethyl-7,8-dihydroindolo[1,2-f]phenanthridin-5(6H)-one (3c):



Prepared by following procedure A, obtained as pale yellow solid; (24 mg, Yield = 78%), m.p. 180–181 °C,  $R_f = 0.5$  (ethyl acetate/hexane: 25:75).

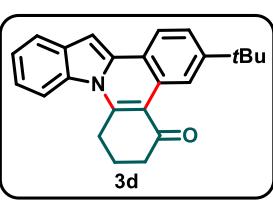
**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  9.09 (s, 1H), 8.09 – 8.05 (m, 1H), 8.01 (t,  $J = 7.0$  Hz, 1H), 7.78 (d,  $J = 7.8$  Hz, 1H), 7.39 (t,  $J = 7.5$  Hz, 1H), 7.33 (d,  $J = 8.1$  Hz, 1H), 7.31 – 7.27 (m, 1H), 7.18 (d,  $J = 7.2$  Hz, 1H), 3.67 – 3.60 (m, 2H), 2.81 (q,  $J = 7.6$  Hz, 2H), 2.77 – 2.72 (m, 2H), 2.31 – 2.25 (m, 2H), 1.33 (t,  $J = 7.6$  Hz, 3H).

**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  197.8, 151.1, 144.9, 136.6, 133.6, 131.8, 127.5, 126.2, 125.9, 123.4, 123.2, 122.5, 121.5, 121.0, 116.3, 113.7, 96.4, 39.0, 30.8, 29.6, 21.5, 15.9.

**IR (Neat, v/cm<sup>-1</sup>)** 2961, 2944, 2865, 1635, 1592, 1569, 1483, 1417, 1393, 1352, 1332, 1282, 1250, 1158, 1126, 1083, 1009, 929, 884.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calcd for  $\text{C}_{22}\text{H}_{20}\text{NO}$  314.1540; Found 314.1532.

### 3-(tert-butyl)-7,8-dihydroindolo[1,2-f]phenanthridin-5(6H)-one (3d):



Prepared by following procedure A, obtained as pale yellow solid; (24 mg, Yield = 70%), m.p. 174–175 °C,  $R_f = 0.5$  (ethyl acetate/hexane: 25:75).

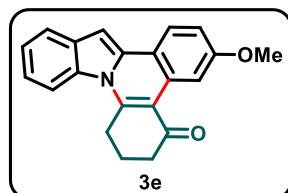
**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  9.36 (d,  $J = 1.9$  Hz, 1H), 8.13 (d,  $J = 8.6$  Hz, 1H), 8.08 (d,  $J = 8.4$  Hz, 1H), 7.81 (d,  $J = 7.4$  Hz, 1H), 7.57 (dd,  $J = 8.4, 2.0$  Hz, 1H), 7.40 (t,  $J = 7.4$  Hz, 1H), 7.31 (ddd,  $J = 8.4, 7.1, 1.3$  Hz, 1H), 7.26 (s, 1H), 3.71 (t,  $J = 6.1$  Hz, 2H), 2.78 (t,  $J = 6.4$  Hz, 2H), 2.32 (p,  $J = 12.8, 6.3$  Hz, 2H), 1.44 (s, 9H).

**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  197.8, 151.5, 151.0, 136.4, 133.5, 131.7, 128.8, 127.2, 125.9, 125.0, 123.4, 123.3, 122.8, 122.2, 121.4, 121.0, 116.2, 113.7, 96.3, 39.0, 31.4, 30.7, 29.7, 21.5.

**IR (Neat, v/cm<sup>-1</sup>)** 3052, 2946, 2924, 2854, 1738, 1650, 1593, 1567, 1486, 1455, 1435, 1392, 1359, 1331, 1283, 1258, 1183, 1108, 1060, 1009, 926, 906, 888.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calcd for C<sub>24</sub>H<sub>24</sub>NO 342.1853; Found 342.1847.

**3-methoxy-7,8-dihydroindolo[1,2-f]phenanthridin-5(6H)-one (3e):**



Prepared by following procedure A, obtained as pale yellow solid; (22 mg, Yield = 71%), m.p. 145-146 °C, R<sub>f</sub> = 0.5 (ethyl acetate/hexane: 25:75).

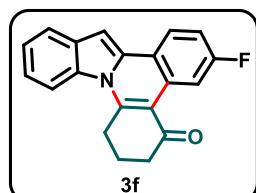
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 8.88 (d, J = 2.1 Hz, 1H), 8.03 (d, J = 8.5 Hz, 1H), 7.95 (d, J = 8.8 Hz, 1H), 7.75 (d, J = 7.8 Hz, 1H), 7.38 (t, J = 7.4 Hz, 1H), 7.27 (d, J = 10.0 Hz, 1H), 7.07 – 7.03 (m, 2H), 3.94 (s, 3H), 3.60 (t, J = 5.9 Hz, 2H), 2.73 (t, J = 6.8 Hz, 2H), 2.27 (p, J = 6.3, 12.2 Hz, 2H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 197.9, 159.9, 151.7, 136.5, 133.4, 132.0, 127.7, 124.6, 123.5, 121.1, 120.8, 118.2, 116.5, 116.3, 113.1, 108.9, 95.3, 55.5, 39.0, 30.7, 21.4.

**IR (Neat, v/cm<sup>-1</sup>)** 3001, 2970, 2931, 2839, 1738, 1640, 1610, 1593, 1569, 1485, 1443, 1421, 1390, 1331, 1296, 1258, 1229, 1165, 1037, 1012, 998, 907, 888.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calcd for C<sub>21</sub>H<sub>18</sub>NO<sub>2</sub> 316.1333; Found 316.1337.

**3-fluoro-7,8-dihydroindolo[1,2-f]phenanthridin-5(6H)-one (3f):**



Prepared by following procedure A, obtained as pale yellow solid; (18 mg, Yield = 59%), m.p. 170-171 °C, R<sub>f</sub> = 0.5 (ethyl acetate/hexane: 25:75).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 9.04 (dd, J = 12.6, 2.6 Hz, 1H), 8.06 (d, J = 8.6 Hz, 1H), 7.98 (dd, J = 8.8, 5.9 Hz, 1H), 7.78 (d, J = 7.8 Hz, 1H), 7.41 (t, J = 7.4 Hz, 1H), 7.32 (ddd, J = 8.4, 7.1, 1.2 Hz, 1H), 7.17 – 7.13 (m, 1H), 7.12 (s, 1H), 3.61 (t, J = 7.2 Hz, 2H), 2.73 (t, J = 6.1 Hz, 2H), 2.28 (t, J = 6.3, 12.7 Hz, 2H).

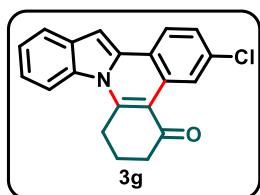
**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 197.3, 162.8 (d, J = 245.0 Hz), 152.0, 135.8, 133.6, 131.7, 127.9 (d, J = 10.3 Hz), 125.0 (d, J = 9.0 Hz), 123.8, 121.9, 121.1 (2C), 116.4, 115.5 (d, J = 23.9 Hz), 113.1 (d, J = 25.9 Hz), 112.7 (d, J = 3.4 Hz), 96.8, 38.8, 30.7, 21.4.

**<sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>)** δ -106.92

**IR (Neat, v/cm<sup>-1</sup>)** 3131, 3069, 2961, 1640, 1607, 1595, 1573, 1455, 1418, 1393, 1360, 1332, 1290, 1267, 1182, 1152, 1105, 1084, 1030, 933, 914, 888.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calcd for C<sub>20</sub>H<sub>15</sub>FNO 304.1133; Found 304.1133.

**3-chloro-7,8-dihydroindolo[1,2-f]phenanthridin-5(6H)-one (3g):**



Prepared by following procedure A, obtained as pale yellow solid; (22 mg, Yield = 69%), m.p. 228-229 °C,  $R_f$  = 0.5 (ethyl acetate/hexane: 25:75).

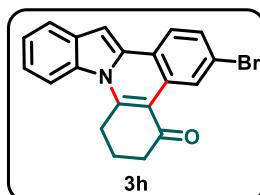
**$^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  9.24 (d,  $J$  = 2.1 Hz, 1H), 7.99 (d,  $J$  = 8.6 Hz, 1H), 7.74 (d,  $J$  = 8.6 Hz, 2H), 7.41 (t,  $J$  = 7.4 Hz, 1H), 7.31 (t,  $J$  = 7.8 Hz, 1H), 7.25 (dd,  $J$  = 8.6, 2.2 Hz, 1H), 7.02 (s, 1H), 3.47 (t,  $J$  = 6.1 Hz, 2H), 2.67 (t,  $J$  = 7.1 Hz, 2H), 2.22 (P,  $J$  = 6.3, 12.9 Hz, 2H).

**$^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  197.2, 151.8, 135.3, 134.3, 133.6, 131.5, 127.4, 127.2, 126.5, 124.2, 123.7, 122.8, 122.1, 121.2, 116.4, 112.4, 97.3, 38.7, 30.6, 21.3.

**IR (Neat, v/cm<sup>-1</sup>)** 3112, 3053, 2934, 2850, 1653, 1609, 1596, 1566, 1533, 1467, 1432, 1409, 1388, 1352, 1290, 1264, 1204, 1180, 1134, 1108, 1054, 1027, 961, 925, 891.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calcd for  $\text{C}_{20}\text{H}_{15}\text{ClNO}$  320.0837; Found 320.0834.

**3-bromo-7,8-dihydroindolo[1,2-f]phenanthridin-5(6H)-one (3h):**



Prepared by following procedure A, obtained as pale yellow solid; (24 mg, Yield = 65%), m.p. 234-235 °C,  $R_f$  = 0.5 (ethyl acetate/hexane: 25:75).

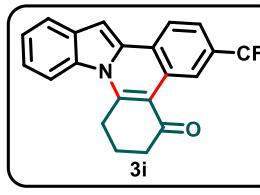
**$^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  9.42 (d,  $J$  = 1.8 Hz, 1H), 8.02 (d,  $J$  = 8.5 Hz, 1H), 7.77 (d,  $J$  = 7.8 Hz, 1H), 7.73 (d,  $J$  = 8.5 Hz, 1H), 7.42 (dd,  $J$  = 5.0, 12.5 Hz, 2H), 7.33 (ddd,  $J$  = 8.4, 7.2, 1.2 Hz, 1H), 7.09 (s, 1H), 3.53 (t,  $J$  = 5.8 Hz, 2H), 2.69 (t,  $J$  = 7.11 Hz, 2H), 2.24 (p,  $J$  = 6.2, 12.5 Hz, 2H).

**$^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  197.2, 151.9, 135.4, 133.6, 131.5, 130.3, 129.6, 127.5, 124.4, 123.8, 123.2, 122.7, 122.2, 121.3, 116.4, 112.4, 97.5, 38.7, 30.6, 21.3.

**IR (Neat, v/cm<sup>-1</sup>)** 3110, 3048, 2959, 2929, 2857, 1654, 1604, 1595, 1565, 1478, 1455, 1430, 1388, 1352, 1289, 1263, 1203, 1180, 1134, 1080, 1053, 1028, 1007, 932, 858.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calcd for  $\text{C}_{20}\text{H}_{15}\text{BrNO}$  364.0332; Found 364.0333.

**3-(trifluoromethyl)-7,8-dihydroindolo[1,2-f]phenanthridin-5(6H)-one (3i):**



Prepared by following procedure A, obtained as pale yellow solid; (24 mg, Yield = 68%), m.p. 230-231 °C,  $R_f$  = 0.5 (ethyl acetate/hexane: 25:75).

**$^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  9.59 (s, 1H), 8.06 (d,  $J$  = 8.6 Hz, 1H), 8.01 (d,  $J$  = 8.3 Hz, 1H), 7.82 (d,  $J$  = 7.8 Hz, 1H), 7.59 (d,  $J$  = 8.3 Hz, 1H), 7.44 (t,  $J$  = 7.4 Hz,

1H), 7.37 (t,  $J$  = 7.8 Hz, 1H), 7.24 (s, 1H), 3.55 (t,  $J$  = 6.0 Hz, 2H), 2.71 (t,  $J$  = 6.4 Hz, 2H), 2.26 (t,  $J$  = 6.2, 12.6 Hz, 2H).

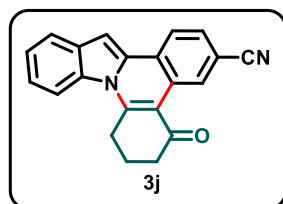
**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  197.3, 152.0, 134.9, 133.8, 131.3, 129.9, 127.0, 126.0, 124.5 (q,  $J$  = 4.2 Hz), 124.4 (q,  $J$  = 272.4), 123.9, 123.6, 123.5, (d,  $J$  = 3.5 Hz), 122.6 (q,  $J$  = 245.9 Hz), 121.6, 116.4, 112.7, 98.9, 38.7, 30.6, 21.3.

**$^{19}\text{F}$  NMR (470 MHz,  $\text{CDCl}_3$ )**  $\delta$  -62.22.

**IR (Neat, v/cm<sup>-1</sup>)** 3112, 3062, 2954, 1652, 1608, 1595, 1562, 1488, 1473, 1422, 1394, 1364, 1346, 1296, 1265, 1183, 1157, 1079, 1028, 915, 870.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calcd for  $\text{C}_{21}\text{H}_{15}\text{F}_3\text{NO}$  354.1101; Found 354.1102.

### 5-oxo-5,6,7,8-tetrahydroindolo[1,2-f]phenanthridine-3-carbonitrile (3j):



Prepared by following procedure A, obtained as pale yellow solid; (18 mg, Yield = 57%), m.p. 265–267 °C,  $R_f$  = 0.5 (ethyl acetate/hexane: 32:68).

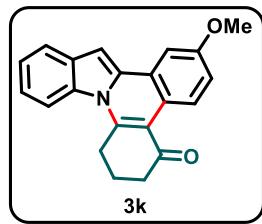
**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  9.66 (d,  $J$  = 1.3 Hz, 1H), 8.13 (d,  $J$  = 8.4 Hz, 1H), 8.09 (d,  $J$  = 8.3 Hz, 1H), 7.86 (d,  $J$  = 7.5 Hz, 1H), 7.61 (dd,  $J$  = 8.3, 1.5 Hz, 1H), 7.47 (t,  $J$  = 7.2 Hz, 1H), 7.44 – 7.40 (m, 1H), 7.38 (s, 1H), 3.67 (t,  $J$  = 6.1 Hz, 2H), 2.76 (t,  $J$  = 6.2 Hz, 2H), 2.32 (p,  $J$  = 12.7, 6.2 Hz, 2H).

**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  197.2, 152.5, 134.5, 134.04, 131.9, 131.3, 131.3, 129.6, 128.0, 127.8, 126.2, 124.2, 123.7, 123.3, 121.9, 119.5, 116.5, 100.1, 38.7, 30.8, 21.3.

**IR (Neat, v/cm<sup>-1</sup>)** 3129, 3104, 3055, 2951, 2219, 1639, 1594, 1567, 1527, 1483, 1455, 1333, 1293, 1277, 1255, 1187, 1142, 1027, 1014, 913, 888, 849.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calcd for  $\text{C}_{21}\text{H}_{15}\text{N}_2\text{O}$  311.1179; Found 311.1178.

### 2-methoxy-7,8-dihydroindolo[1,2-f]phenanthridin-5(6*H*)-one (3k):



Prepared by following procedure A, obtained as pale yellow solid; (21 mg, Yield = 67%), m.p. 170–171 °C,  $R_f$  = 0.5 (ethyl acetate/hexane: 28:72).

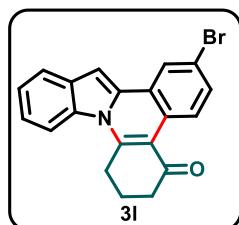
**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  9.20 (d,  $J$  = 9.2 Hz, 1H), 8.10 (d,  $J$  = 8.6 Hz, 1H), 7.81 (d,  $J$  = 7.8 Hz, 1H), 7.49 (d,  $J$  = 2.7 Hz, 1H), 7.40 (t,  $J$  = 7.4 Hz, 1H), 7.34 – 7.29 (m, 1H), 7.21 (s, 1H), 7.11 (dd,  $J$  = 9.2, 2.8 Hz, 1H), 3.95 (s, 3H), 3.65 (t,  $J$  = 6.1 Hz, 2H), 2.74 (t,  $J$  = 7.1 Hz, 2H), 2.29 (p,  $J$  = 6.5, 13.1 Hz, 2H).

**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  197.8, 158.6, 149.1, 136.2, 133.8, 131.5, 129.0, 126.2, 123.4, 121.8, 121.2, 119.9, 116.5, 116.3, 113.7, 105.7, 97.1, 55.5, 38.9, 30.6, 21.6.

**IR (Neat, v/cm<sup>-1</sup>)** 3065, 3023, 2970, 1945, 2846, 1738, 1633, 1593, 1554, 1494, 1455, 1422, 1378, 1365, 1314, 1294, 1285, 1216, 1135, 1086, 1040, 1008, 950, 877.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calcd for C<sub>21</sub>H<sub>18</sub>NO<sub>2</sub> 316.1333; Found 316.1326.

**2-bromo-7,8-dihydroindolo[1,2-f]phenanthridin-5(6H)-one (3l):**



Prepared by following procedure A, obtained as pale yellow solid; (22 mg, Yield = 61%), m.p. 201-202 °C, R<sub>f</sub> = 0.5 (ethyl acetate/hexane: 25:75).

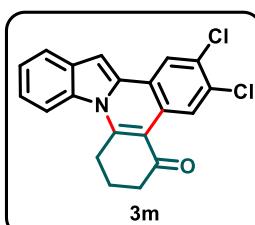
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 9.13 (d, J = 9.0 Hz, 1H), 8.15 (d, J = 2.1 Hz, 1H), 8.08 (d, J = 8.5 Hz, 1H), 7.81 (d, J = 7.5 Hz, 1H), 7.56 (dd, J = 9.0, 2.2 Hz, 1H), 7.43 (t, J = 7.7 Hz, 1H), 7.35 (ddd, J = 8.5, 7.1, 1.3 Hz, 1H), 7.19 (s, 1H), 3.61 (t, J = 6.1 Hz, 2H), 2.73 (t, J = 6.5 Hz, 2H), 2.29 (p, J = 6.1, 12.6 Hz, 2H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 197.4, 151.2, 134.6, 133.7, 131.3, 131.2, 128.9, 126.3, 125.5, 124.8, 123.7, 122.3, 121.4, 121.2, 116.3, 112.9, 97.9, 38.8, 30.6, 21.3.

**IR (Neat, v/cm<sup>-1</sup>)** 3136, 3044, 2961, 2892, 1737, 1637, 1587, 1564, 1478, 1466, 1410, 1390, 1353, 1313, 1284, 1246, 1179, 1133, 1081, 1051, 1007, 982, 944, 907.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calcd for C<sub>20</sub>H<sub>15</sub>BrNO 364.0332; Found 364.0333.

**2,3-dichloro-7,8-dihydroindolo[1,2-f]phenanthridin-5(6H)-one (3m):**



Prepared by following procedure A, obtained as pale yellow solid; (17.6 mg, Yield = 50%), m.p. 170-171 °C, R<sub>f</sub> = 0.5 (ethyl acetate/hexane: 25:75).

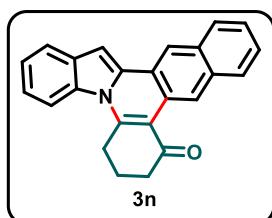
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 9.46 (s, 1H), 8.09 (d, J = 9.3 Hz, 2H), 7.82 (d, J = 7.5 Hz, 1H), 7.44 (t, J = 7.2 Hz, 1H), 7.37 (ddd, J = 8.4, 7.1, 1.3 Hz, 1H), 7.22 (s, 1H), 3.65 (t, J = 6.1 Hz, 2H), 2.74 (t, J = 6.5 Hz, 2H), 2.30 (p, J = 6.5, 12.9 Hz, 2H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 197.0, 152.0, 134.1, 133.7, 132.3, 131.3, 131.2, 128.7, 125.5, 124.3, 124.1, 124.0, 122.7, 121.5, 116.4, 111.9, 98.3, 38.6, 30.6, 21.2.

**IR (Neat, v/cm<sup>-1</sup>)** 3118, 3034, 2942, 2867, 1738, 1653, 1634, 1596, 1567, 1537, 1478, 1453, 1433, 1355, 1331, 1314, 1277, 1244, 1207, 1171, 1130, 1055, 1010, 952, 904, 867.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calcd for C<sub>20</sub>H<sub>14</sub>Cl<sub>2</sub>NO 354.0447; Found 354.0450.

**7,8-dihydrobenzo[*j*]indolo[1,2-*f*]phenanthridin-9(6*H*)-one (3n):**



Prepared by following procedure A, obtained as yellow solid; (22 mg, Yield = 65%), m.p. 195–196 °C,  $R_f$  = 0.5 (ethyl acetate/hexane: 25:75).

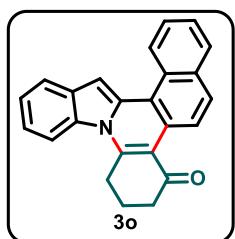
**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  9.71 (s, 1H), 8.33 (s, 1H), 7.98 – 7.95 (m, 1H), 7.94 (d,  $J$  = 8.5 Hz, 1H), 7.81 – 7.78 (m, 1H), 7.75 (d,  $J$  = 7.6 Hz, 1H), 7.47 (dd,  $J$  = 6.3, 3.1 Hz, 2H), 7.38 (t,  $J$  = 7.3 Hz, 1H), 7.31 – 7.27 (m, 1H), 7.24 (s, 1H), 3.47 (t,  $J$  = 6.1 Hz, 2H), 2.70 (t,  $J$  = 7.0 Hz, 2H), 2.22 (p,  $J$  = 6.4, 13.1 Hz, 2H).

**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  197.7, 151.2, 136.1, 134.2, 133.4, 131.8, 131.4, 129.2, 127.4, 126.4, 126.2, 126.1, 123.9, 123.3, 123.1, 122.3, 121.4, 121.2, 116.1, 113.3, 99.1, 38.9, 30.6, 21.4.

**IR (Neat, v/cm<sup>-1</sup>)** 3030, 2970, 2938, 1738, 1623, 1589, 1561, 1535, 1494, 1457, 1428, 1366, 1354, 1228, 1217, 1010, 963, 901, 875.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calcd for  $\text{C}_{24}\text{H}_{18}\text{NO}$  336.1383; Found 336.1374.

**9,10-dihydrobenzo[*i*]indolo[1,2-*f*]phenanthridin-7(8*H*)-one (3o):**



Prepared by following procedure A, obtained as pale yellow solid; (19 mg, Yield = 58%), m.p. 148–149 °C,  $R_f$  = 0.5 (ethyl acetate/hexane: 25:75).

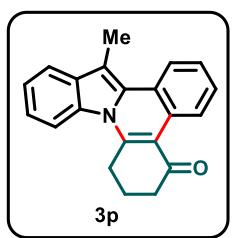
**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  9.23 (d,  $J$  = 9.0 Hz, 1H), 9.11 (d,  $J$  = 8.6 Hz, 1H), 8.23 (d,  $J$  = 8.6 Hz, 1H), 7.97 (d,  $J$  = 7.9 Hz, 1H), 7.92 (d,  $J$  = 8.9 Hz, 2H), 7.87 (s, 1H), 7.70 (t,  $J$  = 8.4 Hz, 1H), 7.61 (t,  $J$  = 7.8 Hz, 1H), 7.47 (t,  $J$  = 7.4 Hz, 1H), 7.39 (t,  $J$  = 7.2 Hz, 1H), 3.79 (t,  $J$  = 6.1 Hz, 2H), 2.83 (t,  $J$  = 6.4 Hz, 2H), 2.37 (p,  $J$  = 6.3, 12.7 Hz, 2H).

**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  197.5, 150.8, 135.8, 133.0, 132.7, 132.0, 129.3, 128.8 (2C), 128.6 (2C), 127.0, 126.4, 126.3, 125.6, 124.2, 123.8, 122.1, 121.2, 116.3, 102.4, 39.1, 31.2, 21.8.

**IR (Neat, v/cm<sup>-1</sup>)** 3054, 2951, 5928, 2850, 1737, 1644, 1585, 1566, 1524, 1464, 1432, 1375, 1335, 1288, 1217, 1182, 1128, 1051, 1007, 986, 912, 895.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calcd for  $\text{C}_{24}\text{H}_{18}\text{NO}$  336.1383; Found 336.1384.

**14-methyl-7,8-dihydroindolo[1,2-*f*]phenanthridin-5(6*H*)-one (3p):**



Prepared by following procedure A, obtained as pale yellow solid; (25 mg, Yield = 82%), m.p. 162–163 °C,  $R_f$  = 0.5 (ethyl acetate/hexane: 26:74).

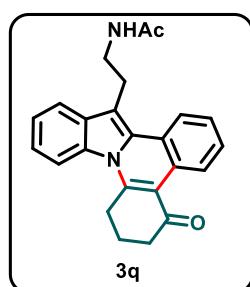
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 9.23 (dd, *J* = 7.8, 1.8 Hz, 1H), 8.23 (dd, *J* = 7.8, 1.7 Hz, 1H), 8.04 (d, *J* = 8.6 Hz, 1H), 7.79 (d, *J* = 7.4 Hz, 1H), 7.52 – 7.47 (m, 2H), 7.46 – 7.42 (m, 1H), 7.36–7.31 (m, 1H), 3.56 (t, *J* = 6.1 Hz, 2H), 2.75 – 2.72 (m, 2H), 2.71 (s, 3H), 2.24 (p, *J* = 12.8, 6.3 Hz, 2H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 197.3, 151.2, 132.6, 132.1, 130.9, 127.3, 126.8, 126.7, 126.5, 126.2, 124.3, 122.9, 121.9, 118.8, 116.2, 113.0, 107.8, 38.8, 30.8, 21.5, 11.8.

**IR (Neat, v/cm<sup>-1</sup>)** 3118, 3037, 2969, 2952, 2875, 1738, 1644, 1585, 1569, 1536, 1476, 1453, 1435, 1394, 1383, 1328, 1247, 1231, 1216, 1181, 1126, 1079, 1053, 1031, 989, 948.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calcd for C<sub>21</sub>H<sub>18</sub>NO 300.1383; Found 300.1381.

#### **N-(2-(5-oxo-5,6,7,8-tetrahydroindolo[1,2-f]phenanthridin-14-yl)ethyl)acetamide (3q):**



Prepared by following procedure A, obtained as pale yellow solid; (28 mg, Yield = 75%), m.p. 224–225 °C, R<sub>f</sub> = 0.2 (ethyl acetate/hexane: 98:02).

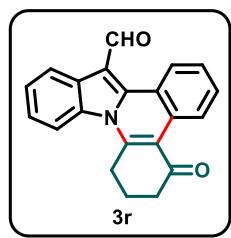
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 9.25 – 9.21 (m, 1H), 8.40 (d, *J* = 7.4 Hz, 1H), 8.12 (d, *J* = 8.6 Hz, 1H), 7.86 (d, *J* = 7.9 Hz, 1H), 7.57 – 7.50 (m, 2H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.8 Hz, 1H), 5.67 (bs, 1H), 3.71 – 3.64 (m, 4H), 3.56 (t, *J* = 7.1 Hz, 2H), 2.75 (t, *J* = 6.6 Hz, 2H), 2.29 (p, *J* = 12.6, 6.2 Hz, 2H), 1.89 (s, 3H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 197.2, 170.6, 150.9, 132.5, 132.4, 131.6, 128.0, 127.3, 126.9, 126.8, 125.6, 123.8, 123.3, 122.4, 118.7, 116.3, 113.6, 109.2, 39.0, 38.8, 31.1, 25.7, 23.3, 21.6.

**IR (Neat, v/cm<sup>-1</sup>)** 3394, 2938, 1658, 1647, 1586, 1513, 1507, 1482, 1451, 1387, 1363, 1321, 1285, 1264, 1195, 1184, 1148, 1114, 1083, 1027, 979, 881.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calcd for C<sub>24</sub>H<sub>23</sub>N<sub>2</sub>O<sub>2</sub> 371.1755; Found 371.1759.

#### **5-oxo-5,6,7,8-tetrahydroindolo[1,2-f]phenanthridine-14-carbaldehyde (3r):**



Prepared by following procedure A, obtained as pale yellow solid; (18 mg, Yield = 56%), m.p. 162–163 °C, R<sub>f</sub> = 0.5 (ethyl acetate/hexane: 23:77).

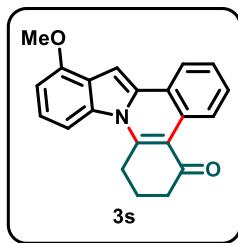
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 10.74 (s, 1H), 9.25 (d, *J* = 8.3 Hz, 1H), 8.70 (d, *J* = 7.9 Hz, 1H), 8.46 (d, *J* = 8.0 Hz, 1H), 8.08 (d, *J* = 8.6 Hz, 1H), 7.72 – 7.68 (m, 1H), 7.59 (t, *J* = 8.1 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.42 – 7.38 (m, 1H), 3.69 (t, *J* = 6.1 Hz, 2H), 2.80 (t, *J* = 6.6 Hz, 2H), 2.32 (p, *J* = 6.5, 12.5 Hz, 2H).

**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  197.2, 185.8, 149.4, 142.3, 133.5, 131.1, 129.7, 128.6, 128.2, 127.8, 127.0, 125.9, 124.0, 123.7, 122.4, 116.2, 116.1, 113.0, 38.8, 31.1, 21.7.

**IR (Neat, v/cm<sup>-1</sup>)** 2923, 2852, 1716, 1660, 1596, 1495, 1452, 1372, 1296, 1238, 1181, 1081.

**HRMS (ESI) m/z:**  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{21}\text{H}_{16}\text{NO}_2$  314.1176; Found 314.1176.

**13-methoxy-7,8-dihydroindolo[1,2-f]phenanthridin-5(6H)-one (3s):**



Prepared by following procedure A, obtained as pale yellow solid; (21 mg, Yield = 68%), m.p. 191-192 °C,  $R_f$  = 0.5 (ethyl acetate/hexane: 25:75).

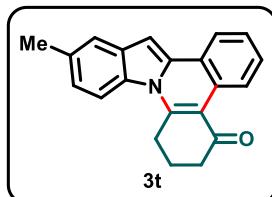
**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  9.19 (d,  $J$  = 8.0 Hz, 1H), 8.09 (d,  $J$  = 7.4 Hz, 1H), 7.66 (d,  $J$  = 8.6 Hz, 1H), 7.51 – 7.42 (m, 2H), 7.38 (s, 1H), 7.21 (t,  $J$  = 8.2 Hz, 1H), 6.80 (d,  $J$  = 7.8 Hz, 1H), 4.03 (s, 3H), 3.61 (t,  $J$  = 6.0 Hz, 2H), 2.74 (t,  $J$  = 6.3 Hz, 2H), 2.27 (t,  $J$  = 6.5, 12.8 Hz, 2H).

**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  197.7, 153.1, 151.0, 135.0, 134.6, 128.1, 127.4, 127.0, 125.9, 125.0, 122.9, 122.5 (2C), 113.9, 109.4, 102.9, 94.1, 55.7, 38.9, 30.6, 21.5.

**IR (Neat, v/cm<sup>-1</sup>)** 3049, 2957, 2835, 1653, 1636, 1596, 1559, 1545, 1473, 1419, 1394, 1331, 1254, 1178, 1102, 1075, 1034, 981, 926.

**HRMS (ESI) m/z:**  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{21}\text{H}_{18}\text{NO}_2$  316.1333; Found 316.1332.

**12-methyl-7,8-dihydroindolo[1,2-f]phenanthridin-5(6H)-one (3t):**



Prepared by following procedure A, obtained as pale yellow solid; (22 mg, Yield = 72%), m.p. 209-210 °C,  $R_f$  = 0.5 (ethyl acetate/hexane: 25:75).

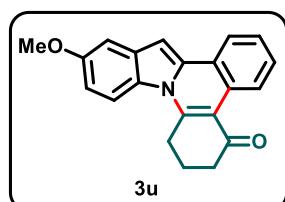
**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  9.23 (dd,  $J$  = 8.3, 0.7 Hz, 1H), 8.04 (dd,  $J$  = 7.8, 1.1 Hz, 1H), 7.92 (d,  $J$  = 8.7 Hz, 1H), 7.55 (s, 1H), 7.51 – 7.47 (m, 1H), 7.46 – 7.42 (m, 1H), 7.13 (s, 1H), 7.11 (dd,  $J$  = 8.8, 1.4 Hz, 1H), 3.57 (t,  $J$  = 6.1 Hz, 2H), 2.73 (t,  $J$  = 6.7 Hz, 2H), 2.52 (s, 3H), 2.27 (p,  $J$  = 12.7, 6.3 Hz, 2H).

**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  197.6, 151.0, 136.3, 133.1, 131.9, 131.9, 128.3, 127.1, 126.9, 126.1, 124.5, 123.3, 123.0, 120.8, 115.9, 113.2, 96.7, 38.9, 30.5, 21.5, 21.4.

**IR (Neat, v/cm<sup>-1</sup>)** 3016, 2949, 2970, 2917, 2867, 1737, 1630, 1594, 1566, 1526, 1487, 1450, 1391, 1327, 1309, 1282, 1247, 1229, 1178, 1129, 1037, 1004, 983, 953, 872.

**HRMS (ESI) m/z:**  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{21}\text{H}_{18}\text{NO}$  300.1383; Found 300.1379.

**12-methoxy-7,8-dihydroindolo[1,2-*f*]phenanthridin-5(6*H*)-one (3u):**



Prepared by following procedure A, obtained as pale yellow solid; (25 mg, Yield = 78%), m.p. 176–177 °C,  $R_f$  = 0.5 (ethyl acetate/hexane: 25:75).

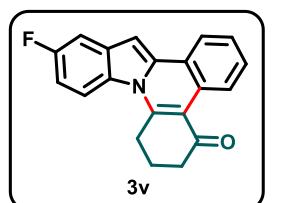
**$^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  9.24 (d,  $J$  = 8.3 Hz, 1H), 8.04 (dd,  $J$  = 7.9, 1.0 Hz, 1H), 7.93 (d,  $J$  = 9.3 Hz, 1H), 7.52 – 7.48 (m, 1H), 7.47 – 7.43 (m, 1H), 7.17 (d,  $J$  = 2.6 Hz, 1H), 7.13 (s, 1H), 6.91 (dd,  $J$  = 9.2, 2.6 Hz, 1H), 3.92 (s, 3H), 3.55 (t,  $J$  = 6.1 Hz, 2H), 2.73 (t,  $J$  = 7.0 Hz, 2H), 2.27 (p,  $J$  = 6.2, 12.5 Hz, 2H).

**$^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  197.6, 156.3, 150.6, 136.9, 132.8, 128.5, 128.3, 127.1, 126.9, 126.1, 124.2, 123.0, 117.1, 113.0, 111.5, 102.1, 96.9, 55.7, 38.9, 30.5, 21.4.

**IR (Neat, v/cm<sup>-1</sup>)** 3122, 2989, 2952, 2938, 2832, 1737, 1633, 1594, 1525, 1487, 1463, 1450, 1396, 1348, 1325, 1292, 1284, 1180, 1087, 1038, 939, 855.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calcd for  $\text{C}_{21}\text{H}_{18}\text{NO}_2$  316.1333; Found 316.1337.

**12-fluoro-7,8-dihydroindolo[1,2-*f*]phenanthridin-5(6*H*)-one (3v):**



Prepared by following procedure A, obtained as pale yellow solid; (19 mg, Yield = 64%), m.p. 220–221 °C,  $R_f$  = 0.5 (ethyl acetate/hexane: 29:71).

**$^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  9.24 (d,  $J$  = 8.4 Hz, 1H), 8.07 (dd,  $J$  = 7.9, 1.1 Hz, 1H), 8.03 (dd,  $J$  = 9.3, 4.2 Hz, 1H), 7.56 – 7.51 (m, 1H), 7.48 (t,  $J$  = 7.5 Hz, 1H), 7.41 (dd,  $J$  = 8.8, 2.6 Hz, 1H), 7.19 (s, 1H), 7.04 (td,  $J$  = 9.0, 2.6 Hz, 1H), 3.61 (t,  $J$  = 6.1 Hz, 2H), 2.76 (t,  $J$  = 7.1 Hz, 2H), 2.31 (p,  $J$  = 6.2, 12.8 Hz, 2H).

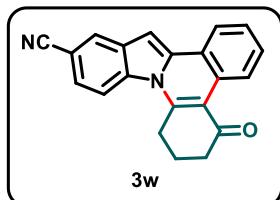
**$^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  197.5, 159.6 (d,  $J$  = 241.2 Hz), 150.4, 137.7 (d,  $J$  = 10.3 Hz), 132.7, 130.2, 128.8, 127.5, 127.1, 126.2, 124.2, 123.2, 117.2 (d,  $J$  = 9.4 Hz), 113.7, 109.7 (d,  $J$  = 25.9 Hz), 105.8 (d,  $J$  = 23.3 Hz), 96.8 (d,  $J$  = 4.4 Hz), 38.9, 30.6, 21.5.

**$^{19}\text{F NMR}$  (470 MHz,  $\text{CDCl}_3$ )**  $\delta$  -119.20.

**IR (Neat, v/cm<sup>-1</sup>)** 3118, 3062, 2941, 287, 1645, 1596, 1578, 1529, 1486, 1467, 1432, 1392, 1361, 1350, 1277, 1247, 1178, 1149, 1127, 1086, 1057, 1006, 982.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calcd for  $\text{C}_{20}\text{H}_{15}\text{FNO}$  304.1133; Found 304.1129.

**5-oxo-5,6,7,8-tetrahydroindolo[1,2-f]phenanthridine-12-carbonitrile (3w):**



Prepared by following procedure A, obtained as pale yellow solid; (16 mg, Yield = 51%), m.p. 290-291 °C,  $R_f$  = 0.5 (ethyl acetate/hexane: 30:70).

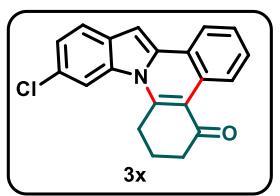
**$^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  9.22 (d,  $J$  = 9.1 Hz, 1H), 8.22 (d,  $J$  = 8.9 Hz, 1H), 8.15 (dd,  $J$  = 5.8, 1.5 Hz, 2H), 7.61 – 7.57 (m, 1H), 7.56 – 7.52 (m, 2H), 7.35 (s, 1H), 3.69 (t,  $J$  = 6.1 Hz, 2H), 2.80 (t,  $J$  = 6.4 Hz, 2H), 2.36 (p,  $J$  = 6.3, 12.8 Hz, 2H).

**$^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  197.5, 149.7, 138.4, 131.2, 129.5, 128.0, 127.4, 126.1 (2C), 124.3, 123.9, 123.5, 119.8, 116.9, 115.2, 106.7, 102.8, 96.9, 38.9, 30.8, 21.5.

**IR (Neat,  $\nu/\text{cm}^{-1}$ )** 3115, 3058, 2973, 2938, 2223, 1651, 1596, 1483, 1455, 1428, 1385, 1322, 1281, 1253, 1209, 1180, 1126, 1088, 1041, 981.

**HRMS (ESI)  $m/z$ :** [M+H]<sup>+</sup> calcd for  $\text{C}_{21}\text{H}_{15}\text{N}_2\text{O}$  311.1179; Found 311.1176.

**11-chloro-7,8-dihydroindolo[1,2-f]phenanthridin-5(6*H*)-one (3x):**



Prepared by following procedure A, obtained as pale yellow solid; (21 mg, Yield = 66%), m.p. 193-194 °C,  $R_f$  = 0.5 (ethyl acetate/hexane: 25:75).

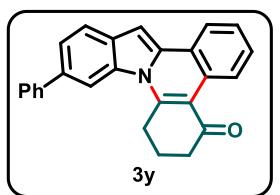
**$^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  9.18 (d,  $J$  = 8.3 Hz, 1H), 7.98 (s, 1H), 7.95 (d,  $J$  = 7.9 Hz, 1H), 7.63 (d,  $J$  = 8.4 Hz, 1H), 7.52 – 7.47 (m, 1H), 7.43 (t,  $J$  = 7.0 Hz, 1H), 7.35 (dd,  $J$  = 8.4, 1.6 Hz, 1H), 7.05 (s, 1H), 3.46 (t,  $J$  = 6.1 Hz, 2H), 2.72 (t,  $J$  = 6.4 Hz, 2H), 2.26 (p,  $J$  = 6.4, 13.0 Hz, 2H).

**$^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  197.4, 150.1, 136.7, 133.4, 129.7, 128.5, 127.4, 127.0, 127.0, 125.8, 124.5, 123.8, 123.0, 121.5, 116.1, 113.9, 96.6, 38.7, 30.3, 21.2.

**IR (Neat,  $\nu/\text{cm}^{-1}$ )** 3026, 2970, 2945, 1738, 1646, 1591, 1563, 1548, 1476, 1450, 1436, 1364, 1328, 1293, 1229, 1216, 1174, 1138, 1075, 1040, 1010, 990, 918, 861.

**HRMS (ESI)  $m/z$ :** [M+H]<sup>+</sup> calcd for  $\text{C}_{20}\text{H}_{15}\text{ClNO}$  320.0837; Found 320.0834.

**11-phenyl-7,8-dihydroindolo[1,2-f]phenanthridin-5(6*H*)-one (3y):**



Prepared by following procedure A, obtained as pale yellow solid; (21 mg, Yield = 58%), m.p. 160-167 °C,  $R_f$  = 0.5 (ethyl acetate/hexane: 25:75).

**$^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  9.24 (d,  $J$  = 7.7 Hz, 1H), 8.29 (s, 1H), 8.13 (dd,  $J$  = 7.8, 1.3 Hz, 1H), 7.87 (d,  $J$  = 8.2 Hz, 1H), 7.70 – 7.64 (m, 3H), 7.55 – 7.47 (m,

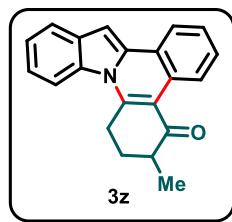
4H), 7.39 (t,  $J$  = 7.4 Hz, 1H), 7.30 (s, 1H), 3.76 (t,  $J$  = 6.1 Hz, 2H), 2.78 (t,  $J$  = 6.4 Hz, 2H), 2.33 (t,  $J$  = 6.0, 11.9 Hz, 2H).

**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  197.6, 151.0, 142.4, 137.0, 135.5, 134.4, 130.8, 130.2, 129.1, 128.6, 127.7, 127.5, 127.2, 127.1, 126.2, 124.8, 123.4, 123.2, 121.3, 115.1, 113.9, 96.9, 38.9, 30.9, 21.6.

**IR (Neat, v/cm<sup>-1</sup>)** 3101, 3026, 2938, 2882, 2839, 1738, 1641, 1591, 1472, 1449, 1434, 1390, 1347, 1283, 1242, 1187, 1139, 1077, 1057, 1024, 918, 856.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calcd for  $\text{C}_{26}\text{H}_{20}\text{NO}$  362.1540; Found 362.1542.

#### 6-methyl-7,8-dihydroindolo[1,2-f]phenanthridin-5(6H)-one (3z):



Prepared by following procedure A, obtained as pale yellow solid; (19 mg, Yield = 65%), m.p. 137-138 °C,  $R_f$  = 0.5 (ethyl acetate/hexane: 22:78).

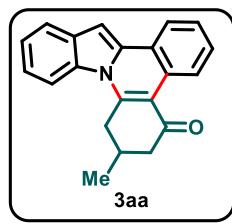
**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  9.20 (d,  $J$  = 8.0 Hz, 1H), 8.13 (t,  $J$  = 7.8 Hz, 2H), 7.82 (d,  $J$  = 7.7 Hz, 1H), 7.53 – 7.45 (m, 2H), 7.41 (t,  $J$  = 7.4 Hz, 1H), 7.32 (t,  $J$  = 7.6 Hz, 1H), 7.28 (s, 1H), 3.85-3.75 (m, 1H), 3.71 – 3.62 (m, 1H), 2.78 – 2.71 (m, 1H), 2.45 – 2.38 (m, 1H), 2.07 – 1.99 (m, 1H), 1.35 (d,  $J$  = 6.7 Hz, 3H).

**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  200.5, 150.0, 136.4, 133.7, 131.6, 128.4, 127.3, 127.0, 126.2, 124.8, 123.4, 123.2, 121.8, 121.2, 116.3, 113.2, 96.9, 41.7, 29.8, 29.2, 15.9.

**IR (Neat, v/cm<sup>-1</sup>)** 3103, 2952, 2851, 1647, 1559, 1469, 1376, 1332, 1274, 1177, 1076, 995, 901, 840, 763.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calcd for  $\text{C}_{21}\text{H}_{18}\text{NO}$  300.1383; Found 300.1386.

#### 7-methyl-7,8-dihydroindolo[1,2-f]phenanthridin-5(6H)-one (3aa):



Prepared by following procedure A, obtained as pale yellow solid; (21 mg, Yield = 69%), m.p. 150-151 °C,  $R_f$  = 0.5 (ethyl acetate/hexane: 25:75).

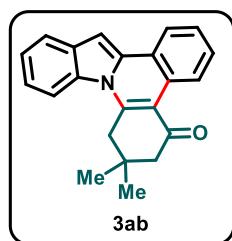
**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  9.25 (d,  $J$  = 8.0 Hz, 1H), 8.09 (dd,  $J$  = 10.1, 4.5 Hz, 2H), 7.81 (d,  $J$  = 7.8 Hz, 1H), 7.53 – 7.50 (m, 1H), 7.47 (td,  $J$  = 7.6, 1.2 Hz, 1H), 7.41 (t,  $J$  = 7.4 Hz, 1H), 7.35 – 7.31 (m, 1H), 7.25 (s, 1H), 3.80 (d,  $J$  = 12.6 Hz, 1H), 3.20 (dd,  $J$  = 16.8, 10.0 Hz, 1H), 2.79 (dd,  $J$  = 12.0, 1.4 Hz, 1H), 2.50 (m, 2H), 1.31 (d,  $J$  = 6.1 Hz, 3H).

**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  197.8, 150.4, 136.4, 133.7, 131.6, 128.5, 127.4, 126.9, 126.1, 124.6, 123.5, 123.1, 121.8, 121.2, 116.4, 113.3, 97.1, 47.0, 38.8, 28.9, 21.4.

**IR (Neat, v/cm<sup>-1</sup>)** 3034, 2953, 2924, 2860, 1737, 1644, 1592, 1569, 1482, 170, 1452, 1391, 1351, 1340, 1290, 1229, 1217, 1169, 1057, 1057, 1024, 971, 911.

**HRMS (ESI)  $m/z$ :** [M+H]<sup>+</sup> calcd for C<sub>21</sub>H<sub>18</sub>NO 300.1383; Found 300.1381.

**7,7-dimethyl-7,8-dihydroindolo[1,2-f]phenanthridin-5(6H)-one (3ab):**



Prepared by following procedure A, obtained as pale yellow solid; (23 mg, Yield = 72%), m.p. 145-146 °C, R<sub>f</sub> = 0.5 (ethyl acetate/hexane: 25:75).

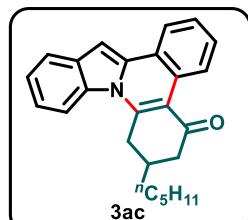
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 9.28 (d, *J* = 8.4 Hz, 1H), 8.09 (d, *J* = 8.6 Hz, 2H), 7.81 (d, *J* = 7.8 Hz, 1H), 7.54 – 7.50 (m, 1H), 7.49 – 7.46 (m, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.34 (dd, *J* = 11.4, 4.2 Hz, 1H), 7.24 (s, 1H), 3.49 (s, 2H), 2.62 (s, 2H), 1.24 (s, 7H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 197.9, 149.2, 136.6, 133.7, 131.7, 129.2, 128.5, 127.4, 126.9, 125.9, 124.7, 123.5, 123.1, 121.7, 121.2, 116.5, 112.6, 97.1, 52.5, 44.3, 32.5, 28.7.

**IR (Neat, v/cm<sup>-1</sup>)** 2970, 2944, 2888, 1721, 1659, 1617, 1597, 1540, 1449, 1425, 1352, 1276, 1216, 1194, 1154, 1135, 1095.

**HRMS (ESI)  $m/z$ :** [M+H]<sup>+</sup> calcd for C<sub>22</sub>H<sub>20</sub>NO 314.1540; Found 314.1541.

**7-pentyl-7,8-dihydroindolo[1,2-f]phenanthridin-5(6H)-one (3ac):**



Prepared by following procedure A, obtained as pale yellow solid; (24 mg, Yield = 67%), m.p. 114-115 °C, R<sub>f</sub> = 0.5 (ethyl acetate/hexane: 25:75).

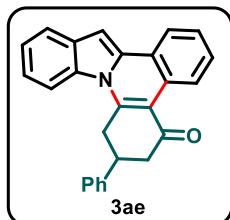
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 9.25 (d, *J* = 8.0 Hz, 1H), 8.10 (d, *J* = 8.1 Hz, 2H), 7.81 (d, *J* = 7.7 Hz, 1H), 7.51 (t, *J* = 8.4 Hz, 1H), 7.47 (t, *J* = 8.0 Hz, 1H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.33 (t, *J* = 8.3 Hz, 1H), 7.26 (s, 1H), 3.83 (dd, *J* = 16.8, 3.4 Hz, 1H), 3.21 (dd, *J* = 16.8, 10.2 Hz, 1H), 2.83 (dd, *J* = 15.7, 2.2 Hz, 1H), 2.48 (dd, *J* = 15.6, 12.9 Hz, 1H), 2.37 – 2.28 (m, 1H), 1.66-1.59 (m, 2H), 1.51-1.44 (m, 2H), 1.39-1.32 (m, 4H), 0.92 (t, *J* = 6.8 Hz, 3H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 197.9, 150.6, 136.4, 133.7, 131.6, 128.5, 127.4, 126.9, 126.1, 124.6, 123.5, 123.1, 121.8, 121.2, 116.3, 113.4, 97.1, 45.3, 37.3, 35.9, 33.7, 31.9, 26.5, 22.7, 14.2.

**IR (Neat, v/cm<sup>-1</sup>)** 3125, 3066, 2958, 2923, 2845, 2845, 1652, 1593, 1539, 1471, 1452, 1391, 1336, 1296, 1247, 1198, 1135, 1053, 960, 837.

**HRMS (ESI)  $m/z$ :** [M+H]<sup>+</sup> calcd for C<sub>25</sub>H<sub>26</sub>NO 356.2009; Found 356.2010.

**7-phenyl-7,8-dihydroindolo[1,2-f]phenanthridin-5(6H)-one (3ae):**



Prepared by following procedure A, obtained as pale yellow solid; (23 mg, Yield = 63%), m.p. 232–233 °C,  $R_f$  = 0.5 (ethyl acetate/hexane: 25:75).

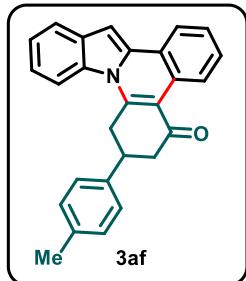
**$^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  9.28 (d,  $J$  = 8.2 Hz, 1H), 8.06 (d,  $J$  = 7.8 Hz, 1H), 7.94 (d,  $J$  = 8.6 Hz, 1H), 7.79 (d,  $J$  = 7.8 Hz, 1H), 7.53 (t,  $J$  = 7.2 Hz, 1H), 7.47 (dd,  $J$  = 15.8, 7.9 Hz, 3H), 7.38 (dd,  $J$  = 15.0, 7.4 Hz, 4H), 7.24 (d,  $J$  = 7.5 Hz, 1H), 7.21 (s, 1H), 3.99 (d,  $J$  = 12.5 Hz, 1H), 3.61 – 3.53 (m, 2H), 3.06 – 2.94 (m, 2H).

**$^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  196.9, 150.1, 142.5, 136.3, 133.6, 131.6, 129.3, 128.5, 127.6, 127.5, 127.0, 127.0, 125.9, 124.6, 123.6, 123.2, 121.9, 121.2, 116.3, 113.3, 97.3, 45.4, 39.6, 38.5.

**IR (Neat,  $\nu/\text{cm}^{-1}$ )** 3027, 3002, 2970, 2945, 1737, 1648, 1634, 1593, 1556, 1481, 1453, 1431, 1371, 1229, 1217, 1144, 1050, 956, 941, 865.

**HRMS (ESI)  $m/z$ :** [M+H]<sup>+</sup> calcd for  $\text{C}_{26}\text{H}_{20}\text{NO}$  362.1540; Found 362.1531.

**7-(*p*-tolyl)-7,8-dihydroindolo[1,2-f]phenanthridin-5(6H)-one (3af):**



Prepared by following procedure A, obtained as pale yellow solid; (26 mg, Yield = 70%), m.p. 194–196 °C,  $R_f$  = 0.5 (ethyl acetate/hexane: 25:75).

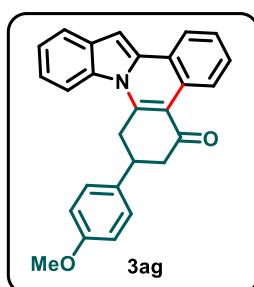
**$^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  9.28 (d,  $J$  = 8.2 Hz, 1H), 8.06 (dd,  $J$  = 7.6, 1.0 Hz, 1H), 7.94 (d,  $J$  = 8.6 Hz, 1H), 7.78 (d,  $J$  = 7.8 Hz, 1H), 7.52 (t,  $J$  = 8.3 Hz, 1H), 7.47 (t,  $J$  = 7.9 Hz, 1H), 7.38 (t,  $J$  = 7.5 Hz, 1H), 7.27 (t,  $J$  = 7.1 Hz, 3H), 7.24 (m, 2H), 7.21 (s, 1H), 3.98 (d,  $J$  = 12.7 Hz, 1H), 3.59 – 3.48 (m, 2H), 3.03 – 2.92 (m, 2H), 2.41 (s, 3H).

**$^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  197.1, 150.2, 139.6, 137.3, 136.4, 133.6, 131.6, 129.9, 128.5, 127.5, 126.9, 126.8, 126.0, 124.6, 123.6, 123.2, 121.9, 121.2, 116.4, 113.3, 97.2, 45.6, 39.2, 38.7, 21.2.

**IR (Neat,  $\nu/\text{cm}^{-1}$ )** 3132, 3019, 2957, 2864, 1737, 1638, 1594, 1556, 1513, 1481, 1454, 1392, 1247, 1198, 1145, 1133, 1053, 943, 922, 867.

**HRMS (ESI)  $m/z$ :** [M+H]<sup>+</sup> calcd for  $\text{C}_{27}\text{H}_{22}\text{NO}$  376.1696; Found 376.1691.

**7-(4-methoxyphenyl)-7,8-dihydroindolo[1,2-f]phenanthridin-5(6H)-one (3ag):**



Prepared by following procedure A, obtained as pale yellow solid; (24 mg, Yield = 61%), m.p. 220-221 °C,  $R_f$  = 0.5 (ethyl acetate/hexane: 24:76).

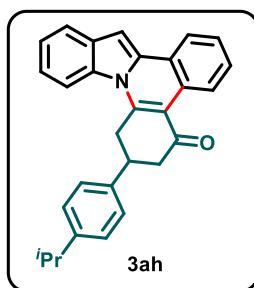
**$^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  9.28 (d,  $J$  = 8.1 Hz, 1H), 8.09 (d,  $J$  = 7.7 Hz, 1H), 7.97 (d,  $J$  = 8.6 Hz, 1H), 7.79 (d,  $J$  = 7.8 Hz, 1H), 7.53 (t,  $J$  = 7.6 Hz, 1H), 7.48 (t,  $J$  = 7.4 Hz, 1H), 7.39 (t,  $J$  = 7.5 Hz, 1H), 7.31 (d,  $J$  = 8.4 Hz, 2H), 7.25 – 7.23 (m, 2H), 6.98 (d,  $J$  = 8.6 Hz, 2H), 4.00 (d,  $J$  = 14.5 Hz, 1H), 3.85 (s, 3H), 3.61-3.49 (m, 2H), 3.04 – 2.93 (m, 2H).

**$^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  197.1, 159.0, 150.2, 136.4, 134.7, 133.6, 131.6, 128.6, 127.9, 127.5, 126.9, 126.0, 124.7, 123.6, 123.2, 121.9, 121.2, 116.3, 114.6, 113.4, 97.3, 55.5, 45.7, 39.0, 38.8.

**IR (Neat,  $\text{v}/\text{cm}^{-1}$ )** 2999, 2973, 2924, 2836, 1738, 1646, 1571, 1530, 1470, 1365, 1229, 1200, 1157, 1141, 1027, 955, 904, 827.

**HRMS (ESI)  $m/z$ :**  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{27}\text{H}_{22}\text{NO}_2$  392.1646; Found 392.1639.

**7-(4-isopropylphenyl)-7,8-dihydroindolo[1,2-f]phenanthridin-5(6H)-one (3ah):**



Prepared by following procedure A, obtained as pale yellow solid; (26 mg, Yield = 65%), m.p. 235-236 °C,  $R_f$  = 0.5 (ethyl acetate/hexane: 25:75).

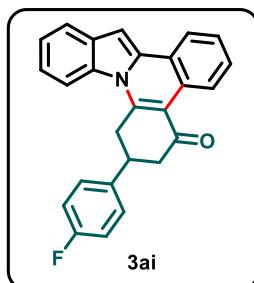
**$^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  9.28 (d,  $J$  = 8.1 Hz, 1H), 8.07 (d,  $J$  = 7.5 Hz, 1H), 7.97 (d,  $J$  = 8.6 Hz, 1H), 7.78 (d,  $J$  = 7.8 Hz, 1H), 7.52 (t,  $J$  = 7.6 Hz, 1H), 7.47 (t,  $J$  = 7.1 Hz, 1H), 7.38 (t,  $J$  = 7.4 Hz, 1H), 7.30 (s, 3H), 7.26-7.20 (m, 3H), 4.03-3.98 (m, 1H), 3.63 – 3.49 (m, 2H), 3.02 – 2.93 (m, 3H), 1.30 (d,  $J$  = 6.9 Hz, 6H).

**$^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  197.1, 150.3, 148.2, 139.9, 136.4, 133.6, 131.6, 128.5, 127.5, 127.3, 127.0, 126.9, 126.0, 124.7, 123.6, 123.2, 121.9, 121.2, 116.4, 113.4, 97.3, 45.6, 39.2, 38.6, 33.9, 24.2.

**IR (Neat,  $\text{v}/\text{cm}^{-1}$ )** 3132, 3019, 2957, 2864, 1737, 1638, 1594, 1556, 1513, 1454, 1392, 1352, 1291, 1247, 1198, 1145, 1133, 1053, 957, 943, 922, 867.

**HRMS (ESI)  $m/z$ :**  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{29}\text{H}_{26}\text{NO}$  404.2009; Found 404.2006.

**7-(4-fluorophenyl)-7,8-dihydroindolo[1,2-f]phenanthridin-5(6H)-one (3ai):**



Prepared by following procedure A, obtained as pale yellow solid; (25 mg, Yield = 65%), m.p. 191-192 °C,  $R_f$  = 0.5 (ethyl acetate/hexane: 25:75).

**$^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  9.24 (d,  $J$  = 8.1 Hz, 1H), 8.01 (d,  $J$  = 7.9 Hz, 1H), 7.88 (d,  $J$  = 8.6 Hz, 1H), 7.76 (d,  $J$  = 7.7 Hz, 1H), 7.50 (t,  $J$  = 8.3 Hz, 1H), 7.45 (t,  $J$  = 7.9 Hz, 1H), 7.38 (t,  $J$  = 7.4 Hz, 1H), 7.32 (dd,  $J$  = 8.5, 5.3 Hz, 2H), 7.25-7.23 (m, 1H), 7.15 (s, 1H), 7.12 (t,  $J$  = 8.6 Hz, 2H), 3.95 – 3.88 (m, 1H), 3.54-3.42 (m, 2H), 2.93 (d,  $J$  = 9.3 Hz, 2H).

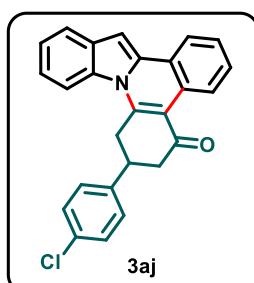
**$^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  196.7, 163.2 (d,  $J$  = 246.10 Hz), 150.0, 138.2 (d,  $J$  = 2.97 Hz), 136.2, 133.5, 131.6, 128.5 (d,  $J$  = 3.19 Hz), 128.5, 127.6, 126.9, 125.8, 124.6, 123.7, 123.2, 122.0, 121.3, 116.2 (d,  $J$  = 6.70 Hz), 116.0, 113.3, 97.3, 45.4, 38.8, 38.6.

**$^{19}\text{F NMR}$  (470 MHz,  $\text{CDCl}_3$ )**  $\delta$  -114.9.

**IR (Neat, v/cm<sup>-1</sup>)** 3034, 2977, 2970, 2942, 1738, 1642, 1594, 1510, 1482, 1469, 1454, 1388, 1353, 1335, 1224, 1158, 1138, 1053, 943, 835.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calcd for  $\text{C}_{26}\text{H}_{19}\text{FNO}$  380.1446; Found 380.1447.

**7-(4-chlorophenyl)-7,8-dihydroindolo[1,2-f]phenanthridin-5(6H)-one (3aj):**



Prepared by following procedure A, obtained as pale yellow solid; (27 mg, Yield = 69%), m.p. 200-201 °C,  $R_f$  = 0.5 (ethyl acetate/hexane: 25:75).

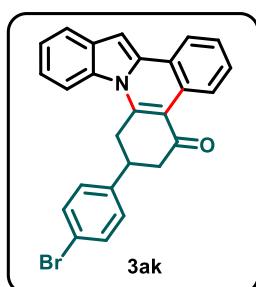
**$^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  9.25 (d,  $J$  = 8.1 Hz, 1H), 8.02 (d,  $J$  = 7.2 Hz, 1H), 7.88 (d,  $J$  = 8.6 Hz, 1H), 7.77 (d,  $J$  = 7.8 Hz, 1H), 7.56 (d,  $J$  = 8.3 Hz, 2H), 7.51 (dd,  $J$  = 11.2, 4.1 Hz, 1H), 7.46 (t,  $J$  = 7.0 Hz, 1H), 7.39 (t,  $J$  = 7.4 Hz, 3H), 7.25 (d,  $J$  = 8.3 Hz, 3H), 7.17 (s, 1H), 3.92 (d,  $J$  = 12.9 Hz, 1H), 3.52 – 3.41 (m, 2H), 2.95-2.89 (m, 2H).

**$^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  196.4, 149.8, 141.4, 136.2, 133.5, 132.3, 131.6, 128.7, 128.6, 127.6, 126.9, 125.8, 124.6, 123.7, 123.2, 122.0, 121.4, 121.3, 116.2, 113.3, 97.4, 45.1, 39.0, 38.3.

**IR (Neat, v/cm<sup>-1</sup>)** 3118, 3058, 3026, 2956, 1737, 1648, 1593, 1469, 1450, 1352, 1319, 1281, 1243, 1143, 1088, 1046, 1013, 957, 827.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calcd for  $\text{C}_{26}\text{H}_{19}\text{ClNO}$  396.1150; Found 396.1151.

**7-(4-bromophenyl)-7,8-dihydroindolo[1,2-f]phenanthridin-5(6H)-one (3ak):**



Prepared by following procedure A, obtained as pale yellow solid; (28 mg, Yield = 64%), m.p. 231-232 °C,  $R_f$  = 0.5 (ethyl acetate/hexane: 25:75).

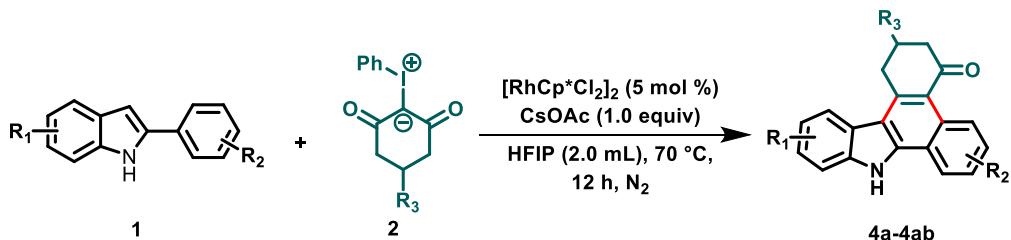
**$^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  9.24 (d,  $J$  = 8.1 Hz, 1H), 8.01 (d,  $J$  = 7.2 Hz, 1H), 7.87 (d,  $J$  = 8.6 Hz, 1H), 7.77 (d,  $J$  = 7.8 Hz, 1H), 7.56 (d,  $J$  = 8.3 Hz, 1H), 7.50 (t,  $J$  = 8.2 Hz, 1H), 7.45 (t,  $J$  = 7.0 Hz, 1H), 7.38 (t,  $J$  = 7.4 Hz, 1H), 7.25 – 7.23 (m, 3H), 7.16 (s, 1H), 3.94-3.87 (m, 1H), 3.51 – 3.42 (m, 1H), 2.95 – 2.89 (m, 2H).

**$^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  196.4, 149.8, 141.4, 136.2, 133.5, 132.3, 131.6, 128.7, 128.6, 127.6, 126.9, 125.8, 124.6, 123.7, 123.2, 122.0, 121.4, 121.3, 116.2, 113.3, 97.4, 45.1, 39.0, 38.3.

**IR (Neat,  $\nu/\text{cm}^{-1}$ )** 3108, 3026, 2970, 2924, 1738, 1649, 1594, 1469, 1450, 1431, 1353, 1281, 1230, 1216, 1160, 1143, 1071, 957.

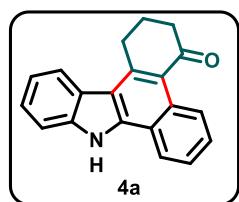
**HRMS (ESI)  $m/z$ :**  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{26}\text{H}_{19}\text{BrNO}$  440.0645; Found 440.0637.

**5. General procedure for product 4:**



**General procedure B:** In a 10 mL oven dried reaction tube with a magnetic stir bar was charged with 2-phenylindole derivatives **1** (0.11 mmol, 1.1 equiv), Iodonium ylide **2** (0.10 mmol, 1.0 equiv),  $[\text{RhCp}^*\text{Cl}_2]_2$  (5 mol %) and CsOAc (1.0 equiv) in 2 mL of HFIP under  $\text{N}_2$  atmosphere. Then the tube was capped with septa and the resulting mixture was stirred at 70 °C on oil bath for 12 h. The reaction completion was monitored by TLC. Upon completion of reaction, the solvent was evaporated under reduced pressure and the crude product was directly purified by a silica gel column chromatography by using ethyl acetate/hexane as the eluent to afford the corresponding product **4**.

**1,2,3,9-tetrahydro-4H-dibenzo[a,c]carbazol-4-one (4a):**



Prepared by following procedure B and obtained as pale yellow solid; (19 mg, Yield = 68%), m.p. 235-236 °C,  $R_f$  = 0.5 (ethyl acetate/hexane: 24:76).

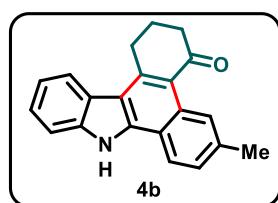
**$^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  9.68 (d,  $J$  = 8.7 Hz, 1H), 9.13 (s, 1H), 8.24 (d,  $J$  = 8.0 Hz, 1H), 8.11 (d,  $J$  = 8.1 Hz, 1H), 7.68 (ddd,  $J$  = 8.5, 6.9, 1.3 Hz, 1H), 7.64 (d,  $J$  = 8.1 Hz, 1H), 7.60 (t,  $J$  = 7.5 Hz, 1H), 7.49 (t,  $J$  = 8.1 Hz, 1H), 7.37 (t,  $J$  = 8.0 Hz, 1H), 3.70 (t,  $J$  = 6.1 Hz, H), 2.87 (t,  $J$  = 6.7 Hz, 2H), 2.35 (p,  $J$  = 6.4, 12.9 Hz, 1H).

**$^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  199.8, 145.6, 139.6, 139.1, 130.8, 128.1, 127.7, 125.3, 124.7, 124.6, 122.3, 121.5, 120.6, 120.5 (2C), 115.6, 111.8, 40.8, 29.5, 22.6.

**IR (Neat, v/cm<sup>-1</sup>)** 3257, 2922, 2850, 1627, 1550, 1507, 1457, 1430, 1378, 1339, 1251, 1180, 1124, 1111, 1038, 1019, 979, 850.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calcd for  $\text{C}_{20}\text{H}_{16}\text{NO}$  286.1227; Found 286.1225.

**6-methyl-1,2,3,9-tetrahydro-4H-dibenzo[a,c]carbazol-4-one (4b):**



Prepared by following procedure B obtained as pale yellow solid; (16 mg, Yield = 53%), m.p. 175-176 °C,  $R_f$  = 0.5 (ethyl acetate/hexane: 25:75).

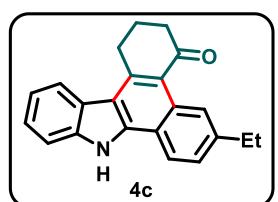
**$^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  9.49 (s, 1H), 9.04 (s, 1H), 8.24 (d,  $J$  = 7.9 Hz, 1H), 8.02 (d,  $J$  = 8.3 Hz, 1H), 7.62 (d,  $J$  = 8.1 Hz, 1H), 7.49 – 7.43 (m, 2H), 7.38 – 7.34 (m, 1H), 3.72 (t,  $J$  = 6.2 Hz, 2H), 2.87 (t,  $J$  = 6.5 Hz, 2H), 2.61 (s, 3H), 2.35 (p,  $J$  = 6.3, 12.9 Hz, 2H).

**$^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  199.9, 145.6, 139.5, 139.2, 137.8, 131.2, 127.6, 127.2, 124.7, 124.7, 122.3, 121.2, 120.6, 120.4, 118.5, 115.2, 111.7, 40.9, 29.6, 22.7, 22.5.

**IR (Neat, v/cm<sup>-1</sup>)** 3288, 2922, 2852, 1718, 1675, 1589, 1487, 1449, 1369, 1284, 1260, 154, 1078, 1020, 991, 889.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calcd for  $\text{C}_{21}\text{H}_{18}\text{NO}$  300.1383; Found 300.1379.

**6-ethyl-1,2,3,9-tetrahydro-4H-dibenzo[a,c]carbazol-4-one (4c):**



Prepared by following procedure B obtained as pale yellow solid; (18 mg, Yield = 58%), m.p. 245-246 °C,  $R_f$  = 0.5 (ethyl acetate/hexane: 30:70).

**$^1\text{H NMR}$  (500 MHz,  $\text{DMSO}-d_6$ )**  $\delta$  12.60 (s, 1H), 9.43 (s, 1H), 8.47 (d,  $J$  = 8.3 Hz, 1H), 8.23 (d,  $J$  = 8.0 Hz, 1H), 7.68 (d,  $J$  = 8.0 Hz, 1H), 7.53 (d,  $J$  = 7.8 Hz, 1H),

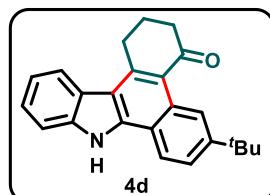
7.46 (t,  $J = 7.5$  Hz, 1H), 7.30 (t,  $J = 7.5$  Hz, 1H), 3.67 (t,  $J = 5.9$  Hz, 2H), 2.82 (q,  $J = 7.5$  Hz, 2H), 2.74 (t,  $J = 6.2$  Hz, 2H), 2.23 (p,  $J = 6.4, 12.6$  Hz, 2H), 1.30 (t,  $J = 7.6$  Hz, 3H).

**$^{13}\text{C}$  NMR (126 MHz, DMSO-*d*<sub>6</sub>)** δ 198.8, 145.6, 143.1, 139.4, 138.7, 130.5, 125.9, 125.5, 124.7, 123.8, 122.2, 122.0, 120.4, 119.2, 118.5, 114.4, 111.8, 40.4, 29.1, 28.9, 22.2, 15.8.

**IR (Neat, v/cm<sup>-1</sup>)** 3185, 3160, 2961, 2927, 2868, 1623, 1617, 1554, 1545, 1457, 1429, 1355, 1329, 1283, 1254, 1189, 1139, 1059, 1019, 903, 880.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calcd for C<sub>22</sub>H<sub>20</sub>NO 314.1540; Found 314.1533.

#### 6-(*tert*-butyl)-1,2,3,9-tetrahydro-4*H*-dibenzo[*a,c*]carbazol-4-one (4d):



Prepared by following procedure B obtained as pale yellow solid; (22 mg, Yield = 65%), m.p. 135-136 °C, R<sub>f</sub> = 0.5 (ethyl acetate/hexane: 30:70).

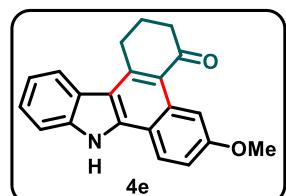
**$^1\text{H}$  NMR (500 MHz, CDCl<sub>3</sub>)** δ 9.79 (d,  $J = 1.1$  Hz, 1H), 9.15 (s, 1H), 8.21 (d,  $J = 8.0$  Hz, 1H), 8.03 (d,  $J = 8.6$  Hz, 1H), 7.67 (dd,  $J = 8.5, 1.4$  Hz, 1H), 7.61 (d,  $J = 8.0$  Hz, 1H), 7.47 (t,  $J = 7.5$  Hz, 1H), 7.36 (t,  $J = 7.5$  Hz, 1H), 3.66 (t,  $J = 6.1$  Hz, 2H), 2.87 (t,  $J = 6.4$  Hz, 2H), 2.33 (p,  $J = 12.5, 6.2$  Hz, 2H), 1.48 (s, 9H).

**$^{13}\text{C}$  NMR (126 MHz, CDCl<sub>3</sub>)** δ 200.4, 151.0, 145.6, 139.0 (2C), 138.5, 131.0, 124.9, 124.8, 124.1, 122.5, 121.0, 120.0, 120.3, 118.1, 115.5, 111.6, 40.9, 35.6, 31.6, 29.5, 22.6.

**IR (Neat, v/cm<sup>-1</sup>)** 3244, 2947, 2862, 1624, 1599, 1554, 1506, 1436, 1355, 1249, 1181, 1124, 1005, 843, 795.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calcd for C<sub>24</sub>H<sub>24</sub>NO 342.1853; Found 342.1849.

#### 6-methoxy-1,2,3,9-tetrahydro-4*H*-dibenzo[*a,c*]carbazol-4-one (4e):



Prepared by following procedure B obtained as pale yellow solid; (18 mg, Yield = 59%), m.p. 234-235 °C, R<sub>f</sub> = 0.5 (ethyl acetate/hexane: 22:78).

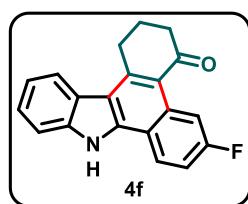
**$^1\text{H}$  NMR (500 MHz, CDCl<sub>3</sub>)** δ 9.35 (d,  $J = 2.5$  Hz, 1H), 9.01 (s, 1H), 8.21 (d,  $J = 8.0$  Hz, 1H), 8.01 (d,  $J = 8.9$  Hz, 1H), 7.60 (d,  $J = 8.0$  Hz, 1H), 7.46 (t,  $J = 7.6$  Hz, 1H), 7.35 (t,  $J = 7.6$  Hz, 1H), 7.24 (d,  $J = 2.6$  Hz, 1H), 4.02 (s, 3H), 3.71 (t,  $J = 6.2$  Hz, 2H), 2.87 (t,  $J = 6.5$  Hz, 2H), 2.35 (p,  $J = 6.3, 13.0$  Hz, 2H).

**$^{13}\text{C}$  NMR (126 MHz, CDCl<sub>3</sub>)** δ 200.0, 159.7, 146.4, 139.7, 139.6, 132.8, 124.7, 124.5, 123.0, 122.1, 120.5, 119.5, 116.9, 115.2, 114.5, 111.6, 107.6, 55.4, 40.9, 29.7, 22.6.

**IR (Neat, v/cm<sup>-1</sup>)** 3291, 3139, 3066, 2990, 2930, 2850, 1734, 1617, 1550, 1507, 1456, 1429, 1375, 1329, 1297, 1246, 1183, 1167, 1066, 1033, 895.

**HRMS (ESI)  $m/z$**  calc. for  $C_{21}H_{18}NO_2 [M+H]^+$  316.1333; Found 316.1332.

**6-fluoro-1,2,3,9-tetrahydro-4H-dibenzo[*a,c*]carbazol-4-one (4f):**



Prepared by following procedure B obtained as pale yellow solid; (14 mg, Yield = 45%), m.p. 291–292 °C,  $R_f$  = 0.5 (ethyl acetate/hexane: 25:75).  
 **$^1H$  NMR (500 MHz, CDCl<sub>3</sub>)** δ 9.52 (dd,  $J$  = 13.5, 2.6 Hz, 1H), 9.06 (s, 1H), 8.25 (d,  $J$  = 8.2 Hz, 1H), 8.11 (dd,  $J$  = 9.0, 5.8 Hz, 1H), 7.64 (d,  $J$  = 8.0 Hz, 1H), 7.50 (t,  $J$  = 7.6 Hz, 1H), 7.42 – 7.36 (m, 2H), 3.74 (t,  $J$  = 6.1 Hz, 2H), 2.87 (t,  $J$  = 6.3 Hz, 2H), 2.37 (p,  $J$  = 6.3, 12.9 Hz, 2H).

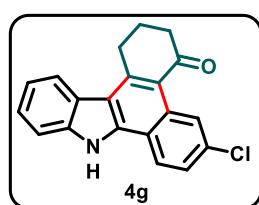
**$^{13}C$  NMR (126 MHz, DMSO-*d*<sub>6</sub>)** δ 194.9, 157.7 (d,  $J$  = 241.67 Hz), 143.2, 135.4, 134.6, 127.5 (d,  $J$  = 10.70 Hz), 121.1, 120.7 (d,  $J$  = 9.66 Hz), 119.7, 118.4, 116.7, 114.6 (d,  $J$  = 4.46 Hz), 113.3, 110.8, 110.8, 110.6, 108.0, 107.6 (d,  $J$  = 25.03 Hz), 36.2, 25.0, 18.1.

**$^{19}F$  NMR (470 MHz, CDCl<sub>3</sub>)** δ -110.9.

**IR (Neat, v/cm<sup>-1</sup>)** 3297, 3134, 3074, 2955, 2852, 1634, 1623, 1564, 1457, 1436, 1354, 1245, 1220, 1133, 1011, 912.

**HRMS (ESI)  $m/z$ :** [M+H]<sup>+</sup> calcd for  $C_{20}H_{15}FNO$  304.1133; Found 304.1136.

**6-chloro-1,2,3,9-tetrahydro-4H-dibenzo[*a,c*]carbazol-4-one (4g):**



Prepared by following procedure B obtained as pale yellow solid; (15 mg, Yield = 48%), m.p. 273–274 °C,  $R_f$  = 0.5 (ethyl acetate/hexane: 25:75).

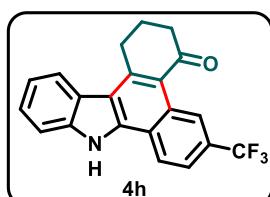
**$^1H$  NMR (500 MHz, DMSO-*d*<sub>6</sub>)** δ 12.80 (s, 1H), 9.70 (d,  $J$  = 2.1 Hz, 1H), 8.59 (d,  $J$  = 8.8 Hz, 1H), 8.28 (d,  $J$  = 8.0 Hz, 1H), 7.72 (dd,  $J$  = 8.7, 2.1 Hz, 2H), 7.51 (t,  $J$  = 8.0 Hz, 1H), 7.35 (t,  $J$  = 8.0 Hz, 1H), 3.70 (t,  $J$  = 6.1 Hz, 2H), 2.77 (t,  $J$  = 6.3 Hz, 2H), 2.26 (p,  $J$  = 12.6, 6.2 Hz, 2H).

**$^{13}C$  NMR (126 MHz, DMSO-*d*<sub>6</sub>)** δ 198.9, 147.1, 139.5, 138.2, 132.6, 130.8, 126.2, 125.6, 125.3, 124.1, 123.6, 122.4, 120.8, 118.6, 118.3, 115.3, 112.0, 40.1, 28.9, 22.0.

**IR (Neat, v/cm<sup>-1</sup>)** 3284, 3059, 2920, 2850, 16217, 1553, 1503, 1456, 1426, 1339, 1251, 1173, 1128, 1086, 867, 791.

**HRMS (ESI)  $m/z$ :** [M+H]<sup>+</sup> calcd for  $C_{20}H_{15}ClNO$  320.0837; Found 320.0841.

**6-(trifluoromethyl)-1,2,3,9-tetrahydro-4H-dibenzo[a,c]carbazol-4-one (4h):**



Prepared by following procedure B obtained as pale yellow solid; (14 mg, Yield = 41%), m.p. 255-256 °C,  $R_f$  = 0.5 (ethyl acetate/hexane: 35:65).

**Note:** A trace amount of unwanted product was observed with product.

**$^1\text{H NMR}$  (500 MHz, DMSO- $d_6$ )**  $\delta$  12.95 (s, 1H), 10.06 (s, 1H), 8.77 (d,  $J$  = 8.6 Hz, 1H), 8.34 (d,  $J$  = 8.5 Hz, 1H), 7.97 (d,  $J$  = 7.7 Hz, 1H), 7.77 (d,  $J$  = 8.1 Hz, 1H), 7.56 (t,  $J$  = 7.6 Hz, 1H), 7.39 (t,  $J$  = 7.5 Hz, 1H), 3.73 (t,  $J$  = 6.0 Hz, 2H), 2.81 (t,  $J$  = 7.2 Hz, 2H), 2.29 (p,  $J$  = 5.8, 12.8 Hz, 2H).

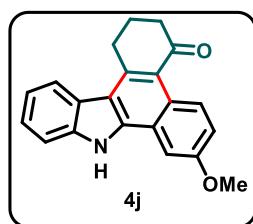
**$^{13}\text{C NMR}$  (126 MHz, DMSO- $d_6$ )**  $\delta$  199.1, 147.1, 139.6, 137.5, 130.1, 128.9, 127.1, 125.9, 125.6, 124.8 (q,  $J$  = 3.34 Hz), 124.65 (q,  $J$  = 230.67 Hz), 123.4 (d,  $J$  = 3.24 Hz), 122.6, 120.9 (d,  $J$  = 4.90 Hz), 120.6, 119.2, 116.5, 112.2, 40.1, 28.9, 22.0.

**$^{19}\text{F NMR}$  (470 MHz, DMSO- $d_6$ )**  $\delta$  -60.43.

**IR (Neat, v/cm<sup>-1</sup>)** 3220, 3194, 3173, 3117, 1622, 1558, 1512, 1456, 1327, 1315, 1289, 1248, 1165, 1117, 1081, 1050, 995, 917.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calcd for C<sub>21</sub>H<sub>15</sub>F<sub>3</sub>NO 354.1101; Found 354.1097.

**7-methoxy-1,2,3,9-tetrahydro-4H-dibenzo[a,c]carbazol-4-one (4j):**



Prepared by following procedure B obtained as pale yellow solid; (18 mg, Yield = 57%), m.p. 152-153 °C,  $R_f$  = 0.5 (ethyl acetate/hexane: 20:80).

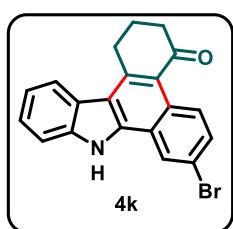
**$^1\text{H NMR}$  (500 MHz, CDCl<sub>3</sub>)**  $\delta$  9.59 (d,  $J$  = 9.5 Hz, 1H), 9.09 (s, 1H), 8.22 (d,  $J$  = 8.0 Hz, 1H), 7.61 (d,  $J$  = 8.1 Hz, 1H), 7.48 (t,  $J$  = 7.6 Hz, 1H), 7.37 – 7.33 (m, 2H), 7.30 (dd,  $J$  = 9.5, 2.7 Hz, 1H), 3.98 (s, 3H), 3.62 (t,  $J$  = 6.2 Hz, 2H), 2.84 (t,  $J$  = 6.4 Hz, 2H), 2.31 (p,  $J$  = 12.8, 6.3 Hz, 2H).

**$^{13}\text{C NMR}$  (126 MHz, CDCl<sub>3</sub>)**  $\delta$  200.2, 157.3, 143.1, 139.0, 137.8, 130.3, 125.8, 125.2, 124.9, 122.7, 121.4, 121.3, 121.0, 118.5, 116.4, 111.6, 100.7, 55.5, 40.8, 29.3, 22.7.

**IR (Neat, v/cm<sup>-1</sup>)** 3251, 3074, 2993, 2854, 1622, 1565, 1513, 1469, 1429, 1388, 1354, 1284, 1228, 1178, 1136, 1092, 1001, 960.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calcd for C<sub>21</sub>H<sub>18</sub>NO<sub>2</sub> 316.1333; Found 316.1327.

### 7-bromo-1,2,3,9-tetrahydro-4H-dibenzo[a,c]carbazol-4-one (4k):



Prepared by following procedure B obtained as pale yellow solid; (15 mg, Yield = 43%), m.p. 289-291 °C,  $R_f$  = 0.5 (ethyl acetate/hexane: 25:75).

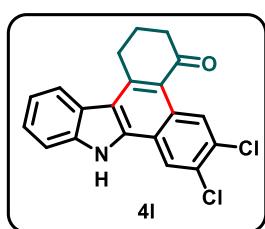
**$^1\text{H NMR}$  (500 MHz, DMSO- $d_6$ )**  $\delta$  12.76 (s, 1H), 9.52 (d,  $J$  = 9.2 Hz, 1H), 8.81 (s, 1H), 8.27 (d,  $J$  = 7.9 Hz, 1H), 7.77 (d,  $J$  = 8.4 Hz, 1H), 7.71 (d,  $J$  = 8.0 Hz, 1H), 7.50 (t,  $J$  = 7.5 Hz, 1H), 7.34 (t,  $J$  = 7.5 Hz, 1H), 3.67 (t,  $J$  = 5.3 Hz, 2H), 2.75 (t,  $J$  = 5.3 Hz, 2H), 2.25 (p,  $J$  = 6.8, 12.3 Hz, 2H).

**$^{13}\text{C NMR}$  (126 MHz, DMSO- $d_6$ )**  $\delta$  198.8, 146.2, 139.5, 137.2, 130.1, 129.7, 128.6, 125.3, 124.2, 123.5, 122.5, 121.7, 120.7, 119.2, 118.6, 115.8, 112.0, 40.1, 28.9, 22.0.

**IR (Neat, v/cm<sup>-1</sup>)** 3315, 3254, 3057, 2936, 1635, 1623, 1581, 1554, 1490, 1426, 1356, 1326, 1255, 1184, 1138, 1081, 107, 979.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calcd for C<sub>20</sub>H<sub>15</sub>BrNO 364.0332; Found 364.0333.

### 6,7-dichloro-1,2,3,9-tetrahydro-4H-dibenzo[a,c]carbazol-4-one (4l):



Prepared by following procedure B obtained as pale yellow solid; (13 mg, Yield = 37%), m.p. 283-284 °C,  $R_f$  = 0.5 (ethyl acetate/hexane: 25:75).

**Note:** A trace amount of unwanted product was observed with product.

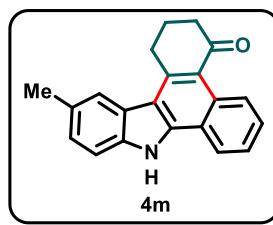
**$^1\text{H NMR}$  (500 MHz, DMSO- $d_6$ )**  $\delta$  12.81 (s, 1H), 9.87 (s, 1H), 8.83 (s, 1H), 8.26 (d,  $J$  = 8.0 Hz, 1H), 7.73 (d,  $J$  = 8.0 Hz, 1H), 7.53 (t,  $J$  = 7.6 Hz, 1H), 7.37 (t,  $J$  = 7.5 Hz, 1H), 3.66 (t,  $J$  = 5.9 Hz, 2H), 2.76 (t,  $J$  = 6.4 Hz, 2H), 2.25 (p,  $J$  = 11.8, 5.7 Hz, 2H).

**$^{13}\text{C NMR}$  (126 MHz, DMSO- $d_6$ )**  $\delta$  199.2, 147.8, 139.9, 137.4, 130.6, 129.5, 129.1, 128.3, 126.0, 123.9, 123.8, 123.0, 121.4, 120.3, 118.4, 116.5, 112.6, 40.4, 29.3, 22.3.

**IR (Neat, v/cm<sup>-1</sup>)** 3259, 3217, 3196, 3134, 3109, 2971, 2906, 1623, 1617, 1542, 1534, 1452, 1419, 1323, 1251, 1164, 1002, 880, 782, 743.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calcd for C<sub>20</sub>H<sub>14</sub>Cl<sub>2</sub>NO 354.0447; Found 354.0438.

### 12-methyl-1,2,3,9-tetrahydro-4H-dibenzo[a,c]carbazol-4-one (4m):



Prepared by following procedure B obtained as pale yellow solid; (16 mg, Yield = 55%), m.p. 204-205 °C,  $R_f$  = 0.5 (ethyl acetate/hexane: 25:75).

**$^1\text{H NMR}$  (500 MHz, CDCl<sub>3</sub>)**  $\delta$  9.67 (d,  $J$  = 8.6 Hz, 1H), 9.02 (s, 1H), 8.09 (d,  $J$  = 8.3 Hz, 1H), 8.04 (s, 1H), 7.69-7.65 (m, 1H), 7.62 – 7.57

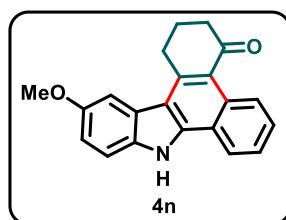
(m, 1H), 7.53 (d,  $J$  = 8.3 Hz, 1H), 7.32 (d,  $J$  = 9.3 Hz, 1H), 3.72 (t,  $J$  = 6.2 Hz, 2H), 2.87 (t,  $J$  = 6.7 Hz, 2H), 2.60 (s, 3H), 2.36 (p,  $J$  = 12.8, 6.3 Hz, 2H).

**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  200.0, 145.6, 138.5, 137.2, 130.9, 130.6, 128.5, 128.0, 126.6, 125.6, 125.05, 122.6, 121.1, 120.3, 120.2, 115.8, 111.2, 40.9, 29.7, 22.7, 22.0.

**IR (Neat, v/cm<sup>-1</sup>)** 3258, 3111, 2945, 2862, 1627, 1558, 1456, 1379, 1307, 1248, 1140, 1038.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calcd for  $\text{C}_{21}\text{H}_{18}\text{NO}$  300.1383; Found 300.1378.

#### 12-methoxy-1,2,3,9-tetrahydro-4*H*-dibenzo[*a,c*]carbazol-4-one (**4n**):



Prepared by following procedure B obtained as pale yellow solid; (19 mg, Yield = 59%), m.p. 192–193 °C,  $R_f$  = 0.5 (ethyl acetate/hexane: 25:75).

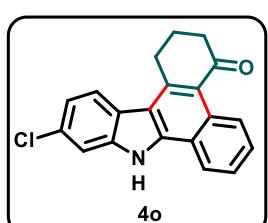
**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  9.65 (d,  $J$  = 8.6 Hz, 1H), 9.08 (s, 1H), 8.07 (d,  $J$  = 8.0 Hz, 1H), 7.70 (s, 1H), 7.66 (t,  $J$  = 7.6 Hz, 1H), 7.58 (t,  $J$  = 7.4 Hz, 1H), 7.52 (d,  $J$  = 8.7 Hz, 1H), 7.13 (dd,  $J$  = 8.7, 1.8 Hz, 1H), 3.97 (s, 3H), 3.66 (t,  $J$  = 6.0 Hz, 2H), 2.86 (t,  $J$  = 6.5 Hz, 2H), 2.34 (p,  $J$  = 12.5, 6.3 Hz, 2H).

**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  199.9, 155.0, 145.6, 139.1, 133.9, 130.9, 128.5, 128.1, 125.7, 125.4, 121.0, 120.3, 120.2, 115.9, 113.8, 112.0, 106.3, 56.4, 40.8, 29.5, 22.6.

**IR (Neat, v/cm<sup>-1</sup>)** 3305, 2954, 2920, 2852, 1709, 1652, 1559, 1512, 1461, 1375, 1264, 1208, 1157, 1109, 1028, 809.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calcd for  $\text{C}_{21}\text{H}_{18}\text{NO}_2$  316.1333; Found 316.1333.

#### 11-chloro-1,2,3,9-tetrahydro-4*H*-dibenzo[*a,c*]carbazol-4-one (**4o**):



Prepared by following procedure B obtained as pale yellow solid; (17 mg, Yield = 52%), m.p. 267–268 °C,  $R_f$  = 0.5 (ethyl acetate/hexane: 25:75).

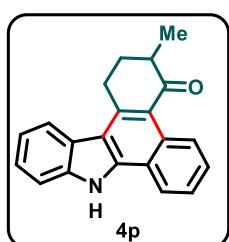
**$^1\text{H}$  NMR (500 MHz,  $\text{DMSO}-d_6$ )**  $\delta$  12.78 (s, 1H), 9.58 – 9.49 (m, 1H), 8.52 – 8.48 (m, 1H), 8.21 (d,  $J$  = 8.5 Hz, 1H), 7.68 – 7.63 (m, 3H), 7.31 (d,  $J$  = 8.4 Hz, 1H), 3.61 (t,  $J$  = 5.6 Hz, 2H), 2.74 (t,  $J$  = 6.5 Hz, 2H), 2.24 (p,  $J$  = 6.2, 11.6 Hz, 2H).

**$^{13}\text{C}$  NMR (126 MHz,  $\text{DMSO}-d_6$ )**  $\delta$  198.8, 145.2, 140.0, 139.0, 130.2, 129.3, 127.8, 127.3, 125.5, 123.6, 122.5, 121.9, 120.6, 120.1, 119.9, 114.5, 111.4, 40.2, 28.7, 22.1.

**IR (Neat, v/cm<sup>-1</sup>)** 3265, 3226, 3196, 3124, 2949, 1630, 1617, 1558, 1545, 1456, 1355, 1325, 1212, 1179, 1142, 1120, 1066, 1041, 980, 919.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calcd for  $\text{C}_{20}\text{H}_{15}\text{ClNO}$  320.0837; Found 320.0828.

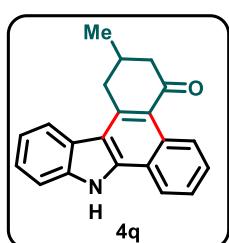
**3-methyl-1,2,3,9-tetrahydro-4H-dibenzo[*a,c*]carbazol-4-one (4p):**



Prepared by following procedure B obtained as pale yellow solid; (17 mg, Yield = 58%), m.p. 221-222 °C,  $R_f$  = 0.5 (ethyl acetate/hexane: 20:80).  
 **$^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )** δ 9.61 (d,  $J$  = 8.7 Hz, 1H), 9.11 (s, 1H), 8.21 (d,  $J$  = 8.0 Hz, 1H), 8.06 (d,  $J$  = 8.1 Hz, 1H), 7.64 (ddd,  $J$  = 8.6, 6.9, 1.4 Hz, 1H), 7.61 (d,  $J$  = 8.1 Hz, 1H), 7.56 (t,  $J$  = 8.0 Hz, 1H), 7.48 (t,  $J$  = 8.1 Hz, 1H), 7.36 (t,  $J$  = 8.0 Hz, 1H), 3.83 – 3.77 (m, 1H), 3.62 – 3.55 (m, 1H), 2.90 – 2.83 (m, 1H), 2.45-2.39 (m, 1H), 2.13-2.04 (m, 1H), 1.37 (d,  $J$  = 6.7 Hz, 3H).  
 **$^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )** δ 203.2, 144.3, 139.0, 138.1, 130.8, 128.2, 127.9, 125.6, 125.6, 124.8, 122.6, 121.1, 121.1, 120.4, 120.1, 115.9, 111.6, 43.3, 30.7, 28.6, 16.1.  
**IR (Neat, v/cm<sup>-1</sup>)** 3331, 2962, 2929, 2867, 2828, 1632, 1558, 1507, 1457, 1338, 1326, 1248, 1163, 1075, 988, 934.

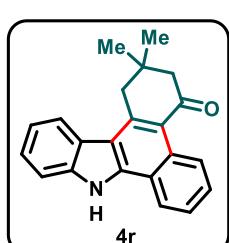
**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calcd for  $\text{C}_{21}\text{H}_{18}\text{NO}$  300.1383; Found 300.1381.

**2-methyl-1,2,3,9-tetrahydro-4H-dibenzo[*a,c*]carbazol-4-one (4q):**



Prepared by following procedure B obtained as pale yellow solid; (19 mg, Yield = 63%), m.p. 168-169 °C,  $R_f$  = 0.5 (ethyl acetate/hexane: 25:75).  
 **$^1\text{H NMR}$  (500 MHz,  $\text{DMSO}-d_6$ )** δ 12.67 (s, 1H), 9.59 (dd,  $J$  = 6.4, 3.4 Hz, 1H), 8.55 (dd,  $J$  = 6.2, 3.2 Hz, 1H), 8.26 (d,  $J$  = 8.0 Hz, 1H), 7.70 (d,  $J$  = 8.0 Hz, 1H), 7.64 (dd,  $J$  = 6.4, 3.3 Hz, 2H), 7.48 (t,  $J$  = 7.6 Hz, 1H), 7.33 (t,  $J$  = 7.5 Hz, 1H), 3.86 (dd,  $J$  = 17.0, 3.7 Hz, 1H), 3.24 (dd,  $J$  = 17.1, 10.0 Hz, 1H), 2.72 (dd,  $J$  = 15.0, 2.6 Hz, 1H), 2.60 – 2.53 (m, 1H), 2.47 – 2.42 (m, 1H), 1.24 (d,  $J$  = 6.4 Hz, 3H).  
 **$^{13}\text{C NMR}$  (126 MHz,  $\text{DMSO}-d_6$ )** δ 198.9, 144.9, 139.4, 138.6, 130.0, 127.5, 127.2, 125.3, 124.8, 123.7, 122.3, 121.9, 120.4, 120.1, 118.9, 114.8, 111.8, 48.2, 36.9, 29.2, 21.1.  
**IR (Neat, v/cm<sup>-1</sup>)** 3109, 2951, 2923, 1653, 1616, 1570, 1507, 1487, 1430, 1339, 1283, 1260, 1138, 1109, 1018, 964.  
**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calcd for  $\text{C}_{21}\text{H}_{18}\text{NO}$  300.1383; Found 300.1387.

**2,2-dimethyl-1,2,3,9-tetrahydro-4H-dibenzo[*a,c*]carbazol-4-one (4r):**



Prepared by following procedure B obtained as pale yellow solid; (18 mg, Yield = 58%), m.p. 171-172 °C,  $R_f$  = 0.5 (ethyl acetate/hexane: 25:75).  
 **$^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )** δ 9.75 (d,  $J$  = 8.6 Hz, 1H), 9.27 (s, 1H), 8.25 (d,  $J$  = 8.0 Hz, 1H), 8.10 (dd,  $J$  = 8.1, 0.8 Hz, 1H), 7.67 (ddd,  $J$  = 8.6, 6.9,

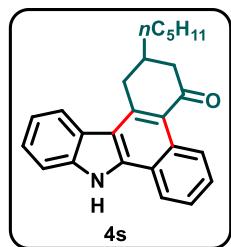
1.4 Hz, 1H), 7.62 (d,  $J$  = 8.1 Hz, 1H), 7.59 – 7.56 (m, 1H), 7.51 – 7.47 (m, 1H), 7.40 – 7.36 (m, 1H), 3.55 (s, 2H), 2.73 (s, 2H), 1.24 (s, 6H).

**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  200.1, 143.7, 139.6, 139.3, 130.5, 127.8, 127.7, 125.2, 124.7, 124.4, 122.4, 121.6, 120.5, 120.4, 119.3, 115.8, 111.8, 54.3, 43.4, 33.1, 28.6.

**IR (Neat, v/cm<sup>-1</sup>)** 3122, 3098, 2957, 2871, 1743, 1684, 1653, 1635, 1575, 1554, 1448, 1369, 1258, 1138, 1071, 999, 930.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calcd for  $\text{C}_{22}\text{H}_{20}\text{NO}$  314.1540; Found 314.1542.

#### 2-pentyl-1,2,3,9-tetrahydro-4H-dibenzo[a,c]carbazol-4-one (4s):



Prepared by following procedure B obtained as pale yellow solid; (22 mg, Yield = 63%), m.p. 215–216 °C,  $R_f$  = 0.5 (ethyl acetate/hexane: 25:75).

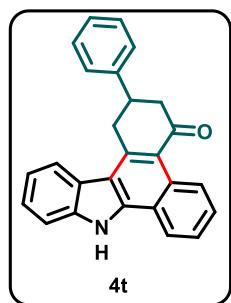
**$^1\text{H}$  NMR (500 MHz, DMSO-*d*<sub>6</sub>)**  $\delta$  12.68 (s, 1H), 9.57 (s, 1H), 8.54 (s, 1H), 8.23 (d,  $J$  = 7.8 Hz, 1H), 7.70 (d,  $J$  = 7.8 Hz, 1H), 7.64 (d,  $J$  = 2.6 Hz, 2H), 7.48 (t,  $J$  = 7.3 Hz, 1H), 7.33 (t,  $J$  = 7.2 Hz, 1H), 3.85 (d,  $J$  = 15.2 Hz, 1H), 3.25 (dd,  $J$  = 16.8, 10.2 Hz, 1H), 2.74 (d,  $J$  = 14.6 Hz, 1H), 2.54 (t,  $J$  = 12.46 Hz, 1H), 2.29 (s, 1H), 1.64 – 1.42 (m, 4H), 1.31 (s, 4H), 0.87 (t,  $J$  = 6.0 Hz, 3H).

**$^{13}\text{C}$  NMR (126 MHz, DMSO-*d*<sub>6</sub>)**  $\delta$  199.4, 145.3, 139.9, 139.1, 130.4, 128.0, 127.6, 125.6, 125.4, 124.2, 122.7, 122.4, 121.0, 120.6, 119.6, 115.3, 112.4, 46.8, 35.7, 35.6, 34.5, 31.9, 26.3, 22.6, 14.5.

**IR (Neat, v/cm<sup>-1</sup>)** 3231, 3190, 3161, 3080, 2953, 2920, 2849, 1631, 1616, 1584, 1559, 1457, 1378, 1339, 1284, 1142, 1019, 953.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calcd for  $\text{C}_{25}\text{H}_{26}\text{NO}$  356.2009; Found 356.2010.

#### 2-phenyl-1,2,3,9-tetrahydro-4H-dibenzo[a,c]carbazol-4-one (4t):



Prepared by following procedure B obtained as pale yellow solid; (20 mg, Yield = 55%), m.p. 157–158 °C,  $R_f$  = 0.5 (ethyl acetate/hexane: 25:75).

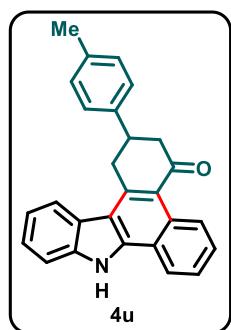
**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  11.46 (s, 1H), 9.71 (t,  $J$  = 9.6 Hz, 1H), 8.43 (t,  $J$  = 9.5 Hz, 1H), 8.15 (dd,  $J$  = 11.4, 8.4 Hz, 1H), 7.70–7.64 (m, 2H), 7.63 – 7.57 (m, 1H), 7.46 – 7.42 (m, 3H), 7.34 – 7.30 (m, 2H), 7.25 (td,  $J$  = 12.3, 6.4 Hz, 2H), 4.22 – 4.12 (m, 1H), 3.74 – 3.62 (m, 2H), 3.16–3.06 (m, 2H).

**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  199.0, 144.6, 143.8, 139.6, 139.4, 130.7, 129.5, 128.9, 127.9, 127.8, 126.9, 126.8, 125.4, 124.8, 124.3, 122.3, 121.7, 120.6, 120.5, 115.4, 111.8, 47.3, 40.4, 37.4.

**IR (Neat, v/cm<sup>-1</sup>)** 3199, 2917, 2849, 1653, 1610, 1550, 1506, 1457, 1433, 1380, 1340, 1257, 1159, 1047, 1022, 994.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calcd for C<sub>26</sub>H<sub>20</sub>NO 362.1540; Found 362.1545.

**2-(*p*-tolyl)-1,2,3,9-tetrahydro-4*H*-dibenzo[*a,c*]carbazol-4-one: (4u):**



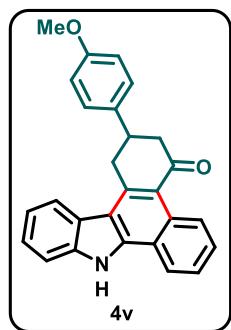
Prepared by following procedure B obtained as pale yellow solid; (19 mg, Yield = 51%), m.p. 276-277 °C, R<sub>f</sub> = 0.5 (ethyl acetate/hexane: 25:75).  
**<sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>)** δ 12.70 (s, 1H), 9.66 – 9.59 (m, 1H), 8.59 – 8.53 (m, 1H), 8.07 (d, J = 8.0 Hz, 1H), 7.70 (d, J = 8.0 Hz, 1H), 7.68 – 7.64 (m, 2H), 7.45 (t, J = 7.5 Hz, 1H), 7.35 (d, J = 7.7 Hz, 2H), 7.25 (t, J = 7.5 Hz, 1H), 7.17 (d, J = 7.6 Hz, 2H), 4.00-3.92 (m, 1H), 3.73-3.64 (m, 1H), 3.62-3.53 (m, 1H), 3.14 – 3.06 (m, 1H), 2.82 (d, J = 13.9 Hz, 1H), 2.29 (s, 3H).

**<sup>13</sup>C NMR (126 MHz, DMSO-d<sub>6</sub>)** δ 198.2, 144.7, 141.0, 139.4, 138.8, 135.7, 130.0, 129.1, 127.7, 127.2, 126.9, 125.4, 124.9, 123.6, 122.1, 122.0, 120.6, 120.2, 118.9, 114.7, 111.9, 46.9, 39.1, 36.7, 20.7.

**IR (Neat, v/cm<sup>-1</sup>)** 3257, 3165, 3121, 3010, 2952, 2919, 2891, 1636, 1617, 1559, 1448, 1419, 1378, 1330, 1283, 1252, 1168, 1048, 953, 810.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calcd for C<sub>27</sub>H<sub>22</sub>NO 376.1696; Found 376.1699.

**2-(4-methoxyphenyl)-1,2,3,9-tetrahydro-4*H*-dibenzo[*a,c*]carbazol-4-one(4v):**



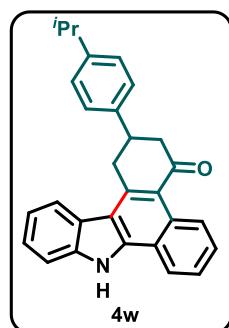
Prepared by following procedure B obtained as pale yellow solid; (19 mg, Yield = 48%), m.p. 226-227 °C, R<sub>f</sub> = 0.5 (ethyl acetate/hexane: 30:70).  
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 9.74 (d, J = 8.6 Hz, 1H), 9.14 (s, 1H), 8.17 (d, J = 8.1 Hz, 1H), 8.12 (d, J = 7.9 Hz, 1H), 7.71 (t, J = 7.4 Hz, 1H), 7.63 (t, J = 7.9 Hz, 2H), 7.48 (t, J = 7.5 Hz, 1H), 7.36 (d, J = 8.6 Hz, 2H), 7.32 (t, J = 7.6 Hz, 1H), 6.98 (d, J = 8.6 Hz, 2H), 4.15-4.09 (m, 1H), 3.86 (s, 3H), 3.67 – 3.57 (m, 2H), 3.12 – 3.06 (m, 2H).

**<sup>13</sup>C NMR (126 MHz, DMSO-d<sub>6</sub>)** δ 198.3, 158.0, 144.9, 139.4, 138.8, 136.1, 130.1, 128.0, 127.7, 127.2, 125.5, 125.0, 123.6, 122.2, 122.0, 120.6, 120.2, 119.0, 114.8, 114.0, 112.0, 55.1, 47.2, 38.7, 36.9.

**IR (Neat, v/cm<sup>-1</sup>)** 3299, 3035, 2924, 2888, 2826, 1635, 1619, 1584, 1558, 1456, 1329, 1288, 1249, 1178, 1035, 952, 826.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calcd for C<sub>27</sub>H<sub>22</sub>NO<sub>2</sub> 392.1646; Found 392.1648.

**2-(4-isopropylphenyl)-1,2,3,9-tetrahydro-4*H*-dibenzo[*a,c*]carbazol-4-one (4w):**



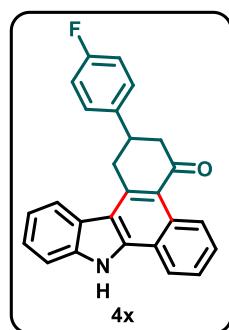
Prepared by following procedure B obtained as pale yellow solid; (23 mg, Yield = 57%), m.p. 192-194 °C,  $R_f$  = 0.5 (ethyl acetate/hexane: 22:78).  
 **$^1\text{H NMR}$  (500 MHz, DMSO-*d*<sub>6</sub>)**  $\delta$  12.73 (s, 1H), 9.65 (dd,  $J$  = 6.6, 3.2 Hz, 1H), 8.59 (dd,  $J$  = 6.5, 2.9 Hz, 1H), 8.11 (d,  $J$  = 8.0 Hz, 1H), 7.72 (d,  $J$  = 8.1 Hz, 1H), 7.70 – 7.66 (m, 2H), 7.47 (t,  $J$  = 7.6 Hz, 1H), 7.41 (d,  $J$  = 8.0 Hz, 2H), 7.29 (d,  $J$  = 7.6 Hz, 1H), 7.25 (d,  $J$  = 8.0 Hz, 2H), 4.05-3.96 (m, 1H), 3.79-3.70 (m, 1H), 3.65-3.56 (m, 1H), 3.19 – 3.10 (m, 1H), 2.92-2.83 (m, 2H), 1.22 (d,  $J$  = 6.9 Hz, 6H).

**$^{13}\text{C NMR}$  (126 MHz, DMSO-*d*<sub>6</sub>)**  $\delta$  198.2, 146.6, 144.8, 141.4, 139.4, 138.8, 130.1, 127.7, 127.2, 126.9, 126.5, 125.5, 124.9, 123.6, 122.2, 122.0, 120.6, 120.2, 118.9, 114.8, 111.9, 47.0, 39.1, 36.6, 33.1, 24.0.

**IR (Neat,  $\nu/\text{cm}^{-1}$ )** 3216, 3164, 3054, 2955, 2955, 2849, 1632, 1616, 1576, 1559, 1424, 1380, 1340, 1283, 1253, 1181, 1141, 1049, 954.

**HRMS (ESI)  $m/z$ :** [M+H]<sup>+</sup> calcd for C<sub>29</sub>H<sub>26</sub>NO 404.2009; Found 404.2000.

**2-(4-fluorophenyl)-1,2,3,9-tetrahydro-4*H*-dibenzo[*a,c*]carbazol-4-one (4x):**



Prepared by following procedure B obtained as pale yellow solid; (13 mg, Yield = 34%), m.p. 160-161 °C,  $R_f$  = 0.5 (ethyl acetate/hexane: 25:75).

**$^1\text{H NMR}$  (500 MHz, CDCl<sub>3</sub>)**  $\delta$  9.72 (d,  $J$  = 8.7 Hz, 1H), 9.64 (s, 1H), 8.20 (d,  $J$  = 7.9 Hz, 1H), 8.14 (d,  $J$  = 8.0 Hz, 1H), 7.71 (t,  $J$  = 7.3 Hz, 1H), 7.64 (dd,  $J$  = 12.5, 7.6 Hz, 2H), 7.48 (t,  $J$  = 7.4 Hz, 1H), 7.39 (q,  $J$  = 8.6 Hz, 4H), 7.32 (t,  $J$  = 7.7 Hz, 1H), 4.17 – 4.10 (m, 1H), 3.70 – 3.59 (m, 2H), 3.11 – 3.06 (m, 2H).

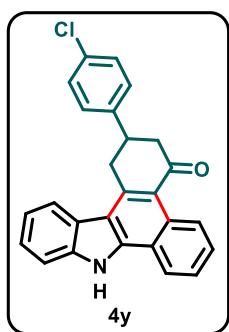
**$^{13}\text{C NMR}$  (126 MHz, CDCl<sub>3</sub>)**  $\delta$  198.7, 162.0 (d,  $J$  = 230.84 Hz), 144.4, 139.5 (d,  $J$  = 26.42 Hz), 130.7, 128.4, 128.3, 128.2, 127.9 (d,  $J$  = 2.33 Hz), 126.8, 125.4, 124.8, 124.3, 122.2, 121.6, 120.6 (d,  $J$  = 4.54 Hz), 119.9, 115.7, 115.5, 115.4, 111.8, 47.4, 39.0, 37.5.

**$^{19}\text{F NMR}$  (470 MHz, CDCl<sub>3</sub>)**  $\delta$  -115.99.

**IR (Neat,  $\nu/\text{cm}^{-1}$ )** 3310, 3055, 2921, 2851, 1700, 1602, 1507, 1457, 1340, 1284, 1201, 1157, 1026, 964, 830.

**HRMS (ESI)  $m/z$ :** [M+H]<sup>+</sup> calcd for C<sub>26</sub>H<sub>19</sub>FNO 380.1446; Found 380.1444.

**2-(4-chlorophenyl)-1,2,3,9-tetrahydro-4*H*-dibenzo[*a,c*]carbazol-4-one (4y):**



Prepared by following procedure B obtained as pale yellow solid; (17 mg, Yield = 43%), m.p. 175-176 °C,  $R_f$  = 0.5 (ethyl acetate/hexane: 32:68).

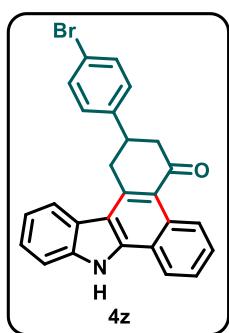
**$^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  9.73 (d,  $J$  = 8.3 Hz, 1H), 9.11 (s, 1H), 8.15 (t,  $J$  = 5.8 Hz, 2H), 7.72 (t,  $J$  = 6.9 Hz, 1H), 7.65 (d,  $J$  = 7.2 Hz, 2H), 7.56 (d,  $J$  = 7.6 Hz, 2H), 7.49 (t,  $J$  = 6.7 Hz, 1H), 7.32 (d,  $J$  = 7.9 Hz, 3H), 4.15-4.09 (m, 1H), 3.67-3.60 (m, 2H), 3.09 (d,  $J$  = 5.0 Hz, 2H).

**$^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  197.8, 144.6, 143.4, 139.4, 138.8, 131.5, 131.3, 130.0, 129.5, 127.6, 127.2, 125.0, 123.6, 122.2, 122.0, 120.2, 119.7, 118.9, 114.7, 112.0, 111.8, 46.5, 38.9, 36.2.

**IR (Neat, v/cm<sup>-1</sup>)** 3266, 3063, 2974, 2924, 2851, 1628, 1559, 1507, 1457, 1330, 1283, 1253, 1146, 1073, 1008, 817.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calcd for  $\text{C}_{26}\text{H}_{19}\text{ClNO}$  396.1150; Found 396.1146.

**2-(4-bromophenyl)-1,2,3,9-tetrahydro-4*H*-dibenzo[*a,c*]carbazol-4-one (4z):**



Prepared by following procedure B obtained as pale yellow solid; (20 mg, Yield = 46%), m.p. 161-163 °C,  $R_f$  = 0.5 (ethyl acetate/hexane: 25:75).

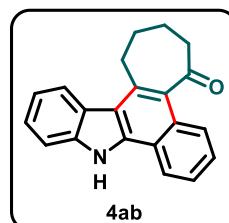
**$^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  10.77 (s, 1H), 9.70 (d,  $J$  = 8.6 Hz, 1H), 8.33 (d,  $J$  = 8.0 Hz, 1H), 8.11 (d,  $J$  = 8.0 Hz, 1H), 7.71-7.62 (m, 2H), 7.60 (t,  $J$  = 7.3 Hz, 1H), 7.44 (t,  $J$  = 7.5 Hz, 1H), 7.39 – 7.34 (m, 3H), 7.31 – 7.24 (m, 2H), 4.16 – 4.08 (m, 1H), 3.68 – 3.59 (m, 2H), 3.12-3.02 (m, 2H).

**$^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  198.6, 144.3, 142.4, 139.5, 139.3, 132.8, 130.8, 129.1, 128.4, 128.1, 128.1, 125.6, 125.1, 124.4, 122.4, 121.4, 120.8, 120.6, 120.1, 115.5, 111.9, 47.2, 40.0, 37.4.

**IR (Neat, v/cm<sup>-1</sup>)** 3215, 3055, 2922, 2850, 1684, 1616, 1559, 1507, 1490, 1456, 1330, 1253, 1091, 1012, 818.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calcd for  $\text{C}_{26}\text{H}_{19}\text{BrNO}$  440.0645; Found 440.0638.

**1,3,4,10-tetrahydrobenzo[*a*]cyclohepta[*c*]carbazol-5(2*H*)-one (4ab):**



Prepared by following procedure A, obtained as pale yellow solid; (19 mg, Yield = 62%), m.p. 192-193 °C,  $R_f$  = 0.5 (ethyl acetate/hexane: 20:85).

**$^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  9.08 (s, 1H), 8.34 – 8.30 (m, 1H), 8.28 (d,  $J$  = 8.0 Hz, 1H), 8.12 – 8.09 (m, 1H), 7.63 (d,  $J$  = 8.1 Hz, 1H), 7.56 – 7.52

(m, 2H), 7.47 (t,  $J$  = 8.0 Hz, 1H), 7.34 (t,  $J$  = 8.0 Hz, 1H), 3.57 (t,  $J$  = 6.7 Hz, 2H), 2.82 (t,  $J$  = 6.0 Hz, 2H), 2.07 (p,  $J$  = 13.4, 6.6 Hz, 2H), 1.84 (p,  $J$  = 12.6, 6.5 Hz, 2H).

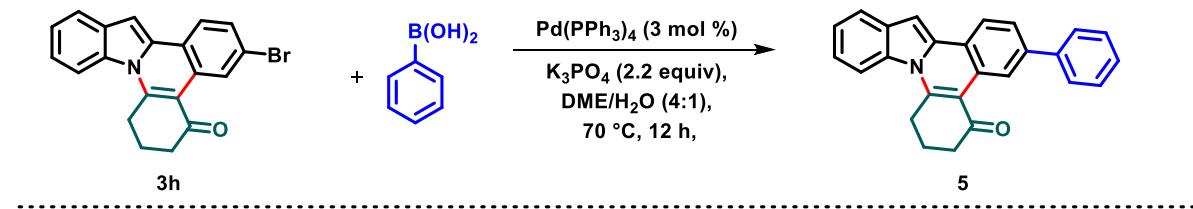
**$^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )**  $\delta$  210.8, 139.1, 136.9, 135.3, 128.9, 128.7, 126.9, 126.1, 125.3, 125.1, 124.3, 122.1, 120.7, 120.6, 119.9, 116.0, 111.6, 42.6, 28.5, 23.4, 21.3.

**IR (Neat, v/cm<sup>-1</sup>)** 3343, 3302, 3279, 2921, 2887, 2857, 1631, 1517, 1456, 1330, 1283, 1262, 1154, 1129, 1046, 1018, 975, 934.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calcd for  $\text{C}_{21}\text{H}_{18}\text{NO}$  300.1383; Found 300.1385.

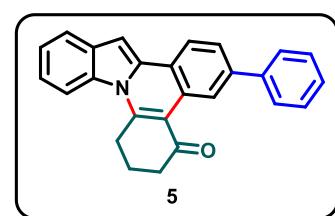
## 7. Synthetic transformations:

### i) Suzuki-Miyaura Coupling:



In a oven-dried 10 mL reaction tube,  $\text{Pd}(\text{PPh}_3)_4$  (3 mol %), potassium triphosphate (0.18 mmol, 2.2 equiv) and DME (2 mL) were taken. The solution was degassed with nitrogen for 10 min. After that, compound **3h** (0.082 mmol, 1.0 equiv), Phenylboronic acid (0.12 mmol, 1.5 equiv) and water (0.5 mL) was added. Then, the reaction tube was capped with septa and allowed to stir at 70 °C in a pre-heated oil bath for the 12 h. The reaction was monitored by TLC and upon completion of the reaction, the reaction mixture was cooled to room temperature and diluted with water (5 mL) and extracted with ethyl acetate (2 x 10 mL). Further, the combined organic layer was washed with brine (10 mL) and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The organic layer was concentrated under reduced pressure and the residue was purified by a silica gel column chromatography using ethyl acetate/hexane as the eluent to afford desired product **5**.<sup>2</sup>

### 3-phenyl-7,8-dihydroindolo[1,2-f]phenanthridin-5(6H)-one (**5**):



Obtained as pale yellow solid; (23 mg, Yield = 78%), m.p. 192–194 °C,  $R_f$  = 0.5 (ethyl acetate/hexane: 20:80).

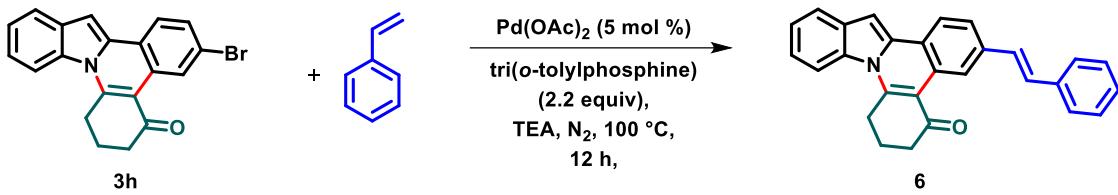
**$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  9.57 (d,  $J$  = 1.7 Hz, 1H), 8.13 (d,  $J$  = 8.3 Hz, 1H), 8.10 (d,  $J$  = 8.6 Hz, 1H), 7.82 (d,  $J$  = 7.8 Hz, 1H), 7.77 (d,  $J$  = 7.2 Hz, 2H), 7.72 (dd,  $J$  = 8.3, 1.8 Hz, 1H), 7.48 (t,  $J$  = 7.7 Hz, 2H), 7.42 (t,  $J$  = 7.4 Hz, 1H), 7.38 (t,  $J$  = 7.4 Hz, 1H), 7.35 – 7.31 (m, 1H), 7.26 (s, 1H), 3.66 (t,  $J$  = 6.1 Hz, 2H), 2.76 (t,  $J$  = 6.3 Hz, 2H), 2.30 (p,  $J$  = 12.8, 6.3 Hz, 2H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 197.7, 151.4, 141.1, 140.9, 136.1, 133.8, 131.7, 129.0, 127.6, 127.5, 126.5 (2C), 126.2, 125.5, 123.7, 123.6, 121.8, 121.2, 116.3, 113.6, 97.2, 39.0, 30.8, 21.5.

**IR (Neat, v/cm<sup>-1</sup>)** 3069, 3029, 2970, 2875, 1737, 1652, 1592, 1565, 1478, 1433, 1389, 1355, 1216, 1174, 1158, 1117, 1025, 986.

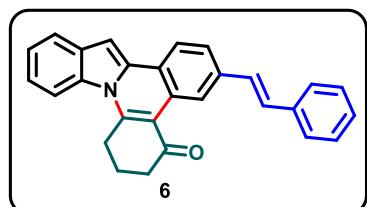
**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calcd for C<sub>26</sub>H<sub>20</sub>NO 362.1540; Found 362.1537.

## ii) Heck coupling reaction:



In a oven dried 10 mL reaction tube, **3h** (0.082 mmol, 1.0 equiv), Pd(OAc)<sub>2</sub> (5 mol %,), tri(*o*-tolyl) phosphine (0.016 mmol, 2.2 equiv) and Et<sub>3</sub>N (1 mL) were taken. The solution was degassed with nitrogen for 10 min. After that, styrene (0.12 mmol, 1.5 equiv) was added and the reaction tube was capped with septa and allowed to stir at 100 °C in a pre-heated oil bath for the 12 h. The reaction was monitored by TLC and upon completion of the reaction, the mixture was quenched with water (2 mL) and extracted with EtOAc (2 x 10 mL). The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated under reduced pressure. Further, the residue was purified by a silica gel column chromatography using ethyl acetate/hexane (30/70) as the eluent to afford desired product **6**.<sup>2</sup>

### (E)-3-styryl-7,8-dihydroindolo[1,2-f]phenanthridin-5(6H)-one (**6**):



Obtained as pale yellow solid; (20 mg, Yield = 63%), m.p. 192–194 °C, R<sub>f</sub> = 0.5 (ethyl acetate/hexane: 25:75).

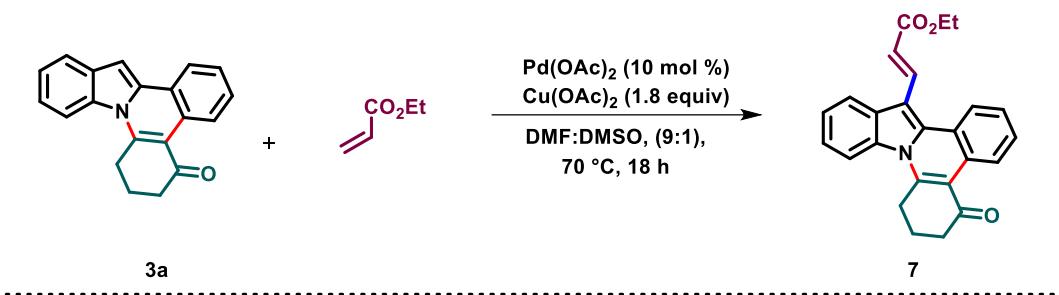
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 9.40 (d, *J* = 1.4 Hz, 1H), 8.09 (d, *J* = 8.6 Hz, 1H), 8.05 (d, *J* = 8.3 Hz, 1H), 7.81 (d, *J* = 7.7 Hz, 1H), 7.66 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.57 (d, *J* = 7.3 Hz, 2H), 7.43–7.37 (m, 3H), 7.34 – 7.28 (m, 2H), 7.25 (bs, 3H), 3.67 (t, *J* = 6.0 Hz, 2H), 2.80 – 2.76 (t, *J* = 6.8 Hz, 2H), 2.32 (p, *J* = 12.6, 6.2 Hz, 2H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 197.8, 151.4, 137.5, 137.3, 136.2, 133.8, 131.8, 129.2, 129.1, 128.9, 127.8, 126.8, 126.4, 125.6, 125.1, 123.9, 123.6, 123.5, 121.9, 121.2, 116.3, 113.4, 97.2, 39.0, 30.8, 21.5.

**IR (Neat, v/cm<sup>-1</sup>)** 3069, 3029, 2970, 2875, 1737, 1652, 1592, 1565, 1478, , 1433, 1389, 1355, 1216, 1174, 1158, 1117, 1025, 986.

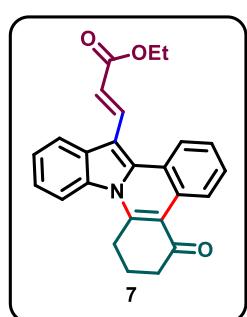
**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calcd for C<sub>26</sub>H<sub>22</sub>NO 388.1696; Found 388.1691.

### iii) Alkenylation:



To a solution of **3a** (0.070 mmol, 1.0 equiv), Pd(OAc)<sub>2</sub> (10 mol %), Cu(OAc)<sub>2</sub> (0.12 mmol, 1.8 equiv) in 2 mL DMF: DMSO (9:1) was added ethyl acrylate (0.070 mmol, 1.0 equiv). Then the contents were stirred at 70 °C for 18 h. completion of reaction was checked by TLC. Upon completion of the reaction, the reaction mixture was extracted with ice-cold water and EtOAc (2x10 mL) the solvent was evaporated under reduced pressure and the residue was purified by a silica gel column chromatography using ethyl acetate/hexane as the eluent to give compound **7**.<sup>3</sup>

#### ethyl (E)-3-(5-oxo-5,6,7,8-tetrahydroindolo[1,2-f]phenanthridin-14-yl)acrylate (7):



Obtained as yellow solid; (19 mg, Yield = 72%), m.p. 192-194 °C, R<sub>f</sub> = 0.5 (ethyl acetate/hexane: 30:70).

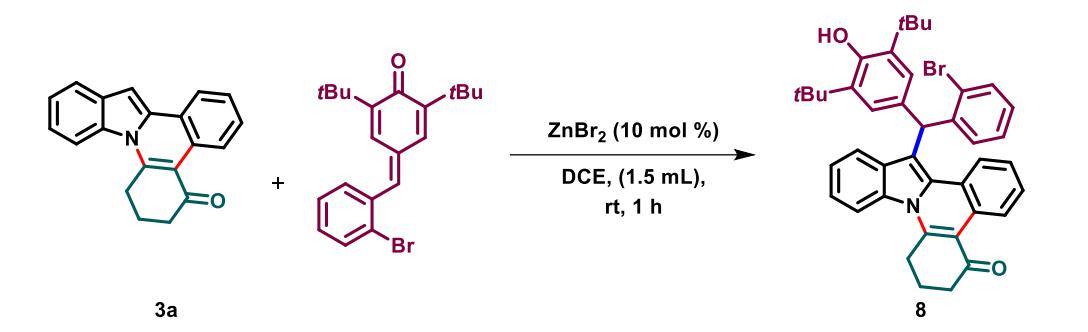
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 9.20 (d, J = 8.3 Hz, 1H), 8.31 (d, J = 16.0 Hz, 1H), 8.12 (d, J = 7.9 Hz, 1H), 8.06 (t, J = 7.2 Hz, 2H), 7.59 – 7.55 (m, 1H), 7.52 (t, J = 7.5 Hz, 1H), 7.46 (t, J = 7.6 Hz, 1H), 7.36 (t, J = 7.5 Hz, 1H), 6.59 (d, J = 16.0 Hz, 1H), 4.37 (q, J = 7.1 Hz, 2H), 3.60 (t, J = 6.0 Hz, 2H), 2.74 (t, J = 6.8 Hz, 2H), 2.27 (p, J = 13.6, 6.2 Hz, 2H), 1.42 (t, J = 7.1 Hz, 3H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 197.1, 167.8, 150.0, 138.0, 135.1, 133.5, 129.6, 129.2, 127.8, 127.7, 126.6, 126.5, 124.9, 124.4, 123.1, 120.2, 120.0, 116.4, 114.7, 108.6, 60.6, 38.8, 30.9, 21.6, 14.6.

**IR (Neat, v/cm<sup>-1</sup>)** 3108, 3060, 2942, 2902, 1701, 1652, 1608, 1596, 1523, 1479, 1454, 1382, 1313, 1272, 1183, 1086.

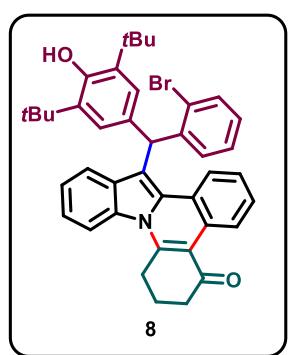
**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calcd for C<sub>25</sub>H<sub>22</sub>NO<sub>3</sub> 384.1595; Found 384.1588.

**iv) 1,6-conjugate addition of **3a** with *p*-quinone methide:**



To a solution of **3a** (0.070 mmol, 1.0 equiv), 4-(2-bromobenzylidene)-2,6-di-*tert*-butylcyclohexa-2,5-dien-1-one (0.070 mmol, 1.0 equiv) in 2 mL DCE was added ZnBr<sub>2</sub> (10 mol %). Then the contents were stirred at room temperature for 1 h. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by a silica gel column chromatography using ethyl acetate/hexane as the eluent to give compound **8**.<sup>3</sup>

**14-((2-bromophenyl)(3,5-di-*tert*-butyl-4-hydroxyphenyl)methyl)-7,8-dihydroindolo[1,2-f]phenanthridin-5(6*H*)-one (**8**):**



Obtained as light yellow solid; (39 mg, Yield = 85%), m.p. 201–202 °C, R<sub>f</sub> = 0.5 (ethyl acetate/hexane: 25:75).

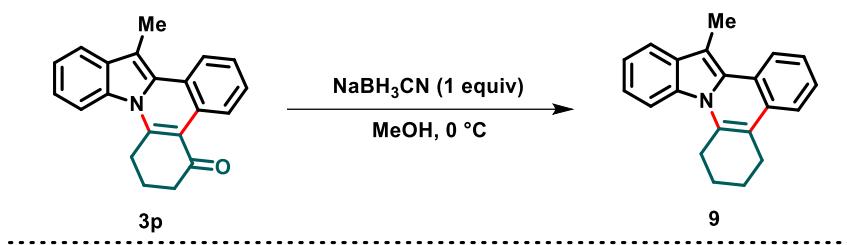
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 9.19 (dd, *J* = 8.3, 1.0 Hz, 1H), 8.13 (d, *J* = 8.7 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.61 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.52 – 7.48 (m, 1H), 7.38 (t, *J* = 8.3 Hz, 1H), 7.26 – 7.22 (m, 2H), 7.19 (td, *J* = 7.6, 1.2 Hz, 1H), 7.13–7.06 (m, 2H), 7.03 (dd, *J* = 8.1, 0.8 Hz, 1H), 6.89 (s, 2H), 6.53 (s, 1H), 5.09 (s, 1H), 3.74 (t, *J* = 6.1 Hz, 2H), 2.79 (t, *J* = 6.7 Hz, 2H), 2.36 – 2.27 (m, 2H), 1.27 (s, 18H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 197.2, 152.5, 150.9, 142.8, 135.9, 133.3, 133.1, 133.0, 132.3, 131.8, 131.5, 128.4, 128.1, 127.6, 127.5, 126.8, 126.4 (2C), 126.3, 126.1 (2C), 125.5, 125.4, 122.7, 121.7, 116.1, 114.5, 113.9, 49.3, 38.9, 34.5, 31.4, 30.5, 21.9.

**IR (Neat, v/cm<sup>-1</sup>)** 3634, 3072, 2954, 2930, 2853, 1713, 1636, 1588, 1515, 1450, 1434, 1394, 1365, 1329, 1289, 1228, 1187, 1115, 1030.

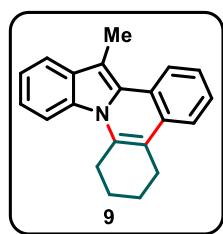
**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calcd for C<sub>41</sub>H<sub>41</sub>BrNO<sub>2</sub> 658.2316; Found 658.2306.

v) Reduction reaction:



To a solution of **3p** (0.1 mmol, 1.0 equiv), in 2 mL methanol at 0 °C was added portion wise NaBH<sub>3</sub>CN (0.1 mmol, 1.0 equiv). Then the contents were stirred at room temperature until the completion of **3p**. Upon completion of the reaction, the reaction mixture quenched with water. Further, the crude material extracted with EtOAc (2 x 10 mL) and combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>. The organic layer was collected and concentrated under reduced pressure, and the residue was purified by a silica gel column chromatography using ethyl acetate/hexane as the eluent to give compound **9**.<sup>2</sup>

**14-methyl-5,6,7,8-tetrahydroindolo[1,2-f]phenanthridine (9):**



Obtained as light green solid; (23 mg, Yield = 80%), m.p. 192–194 °C, R<sub>f</sub> = 0.5 (ethyl acetate/hexane: 30:70).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 8.42 (d, J = 7.5 Hz, 1H), 8.17 (d, J = 8.6 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.68 (d, J = 7.4 Hz, 1H), 7.48 (qd, J = 7.1, 3.5 Hz, 2H), 7.34 (t, J = 7.4 Hz, 1H), 7.25–7.22 (m, 1H), 3.41 (bs, 2H), 2.88 (bs, 2H), 2.85 (s, 3H), 2.05 – 1.94 (m, 4H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 135.2, 131.4, 130.9, 130.4, 130.4, 126.9, 126.6, 126.0, 124.7, 121.8, 120.7, 120.5, 118.3, 115.5, 112.2, 104.8, 30.3, 25.4, 23.1, 22.2, 12.2.

**IR (Neat, v/cm<sup>-1</sup>)** 3062, 3043, 2924, 2854, 1726, 1623, 1599, 1545, 1479, 1382, 1278, 1208, 1122, 1078, 1026.

**HRMS (ESI) m/z:** [M+H]<sup>+</sup> calcd for C<sub>21</sub>H<sub>20</sub>N 286.1591; Found 286.1582.

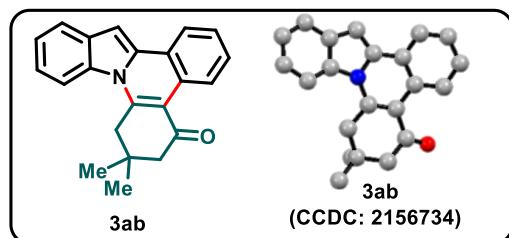
## 8. XRD data

X-ray data for the compounds **3ab** and **4r** were collected at room temperature on a Bruker D8 QUEST instrument with an IμS Mo micro source ( $\lambda$  = 0.71073 Å) and a PHOTON-100 detector. The raw data frames were reduced and corrected for absorption effects using the Bruker Apex 3 software suite programs [1]. The structure was solved using intrinsic phasing method [2] and further refined with the SHELXL [2-3] program and expanded using Fourier

techniques. Anisotropic displacement parameters were included for all non-hydrogen atoms. All H atoms were positioned geometrically and treated as riding on their parent C atoms [C-H = 0.93-0.97 Å, and  $U_{iso}(H) = 1.5U_{eq}(C)$  for methyl H or  $1.2U_{eq}(C)$  for other H atoms].

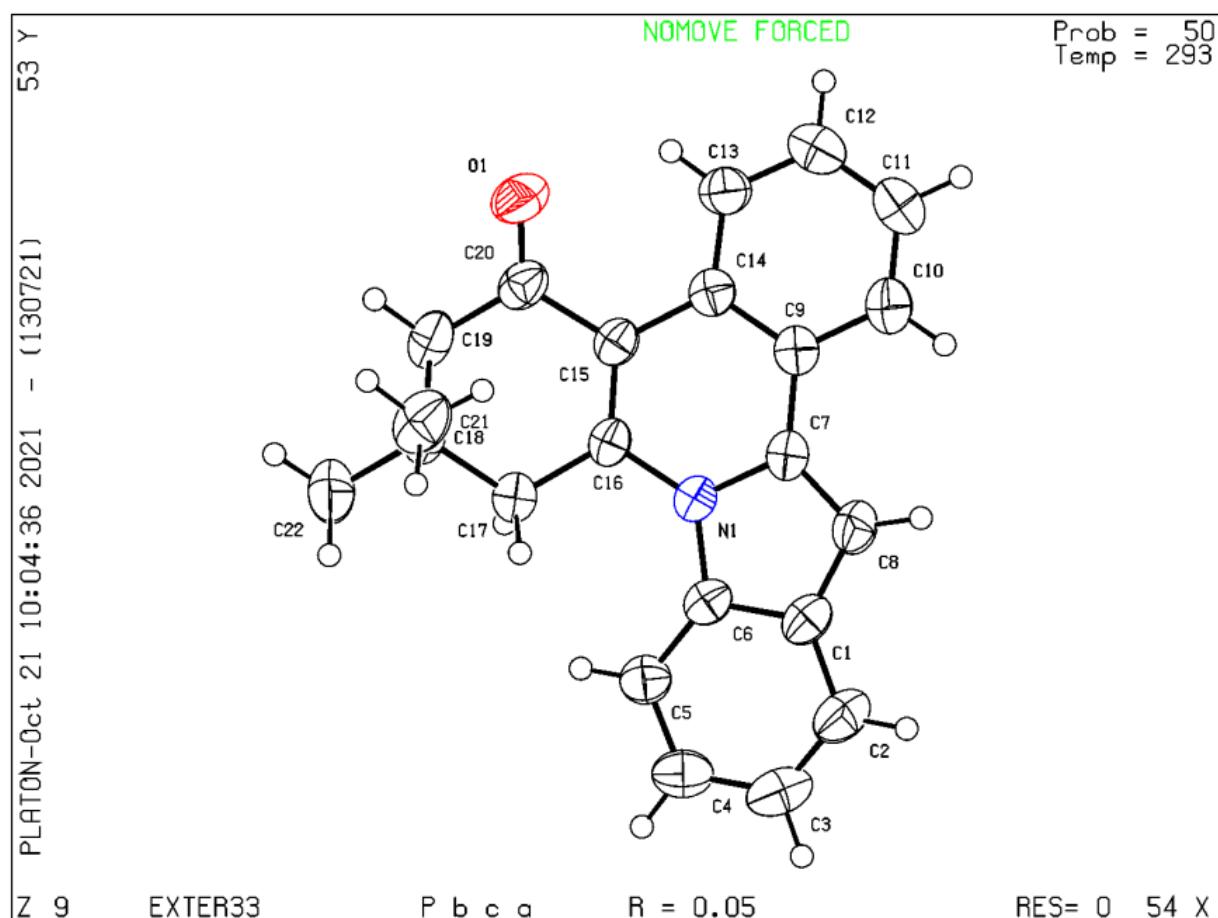
### Sample Preparation for crystal growth for 3ab:

In a 5 mL vial, compound **3ab** was dissolved in 3:1 ratio of  $CDCl_3$  and Hexane solvent (0.6 mL : 0.2 mL). The content kept for the slow evaporation over three days. After three days' pale yellow colour crystals were generated. The generated crystals were collected and send for the X-ray crystallographic analysis.



Colour code: Carbon (Light-gray), Oxygen (Red), Nitrogen (Blue)

CCDC	2156734
Formula	$C_{22}H_{19}NO$
Formula weight	313.4000
Wavelength	0.71073
Temperature (K)	293
Crystal system	Orthorhombic
Space group	P b c a
a (Å)	16.6240 (5)
b (Å)	9.8728 (3)
c (Å)	19.5796 (6)
$\alpha$ (°)	90
$\beta$ (°)	90
$\gamma$ (°)	90
$V$ (cm) <sup>3</sup>	3213.51 (17)
Z	8
Density	1.296
$\mu$ (mm) <sup>-1</sup>	0.079
F (000)	1328.6
No. of ref.	3391
Unique ref.	2353
R1	0.0452
wR2	0.1226
G. O. F.	1.024



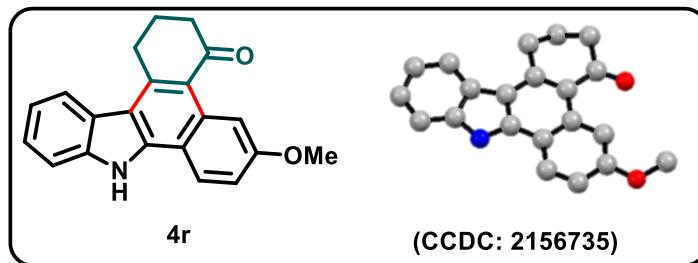
**Fig. 1:** ORTEP drawing of the compound **3ab** showing thermal ellipsoids at the 30% probability level.

Colour code: Carbon (Light-gray), Oxygen (Red), Nitrogen (Blue)

**(b) XRD data of 4r**

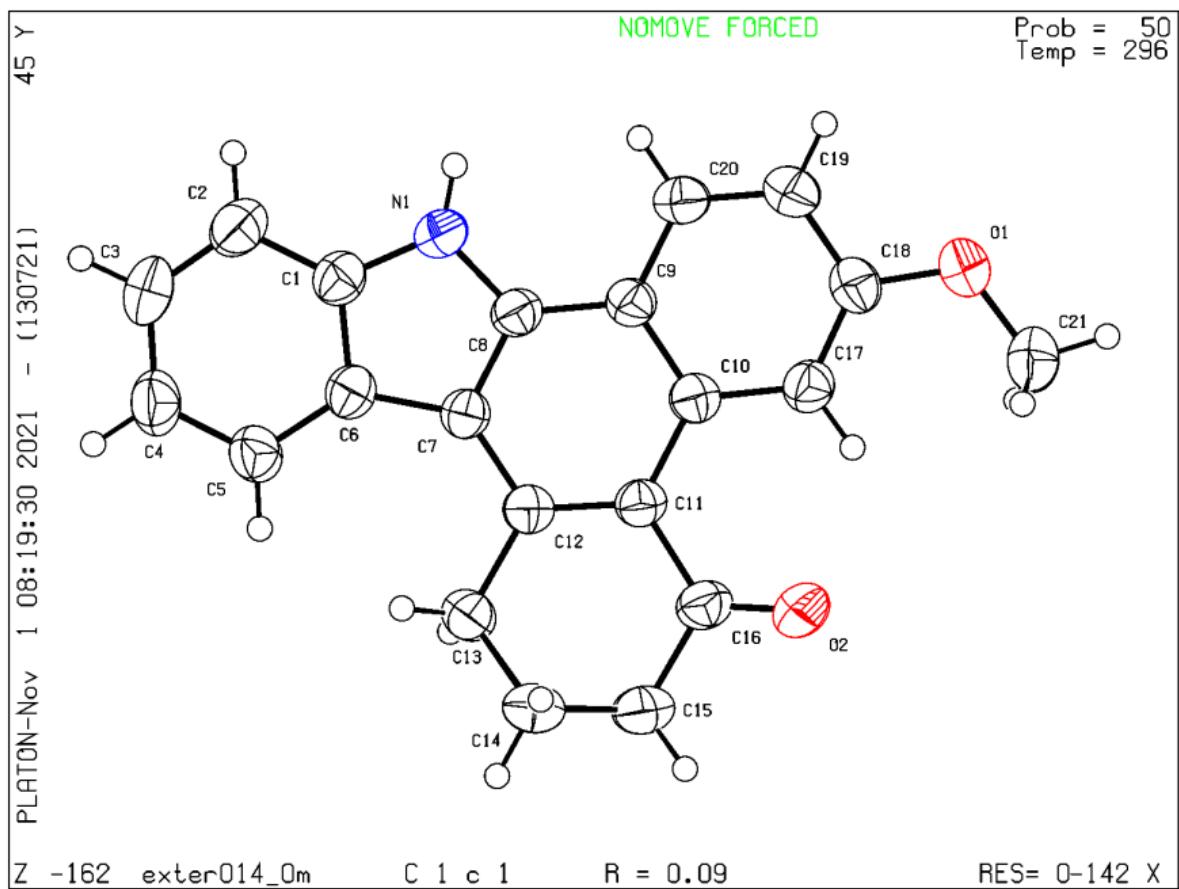
**Sample Preparation for crystal growth for 4r:**

The compound **4r** was dissolved in 3:1 ratio of  $\text{CDCl}_3$  and Hexane solvent (0.6 mL : 0.2 mL). The content kept for the slow evaporation over three days. After three days' crystals were generated. The generated crystals were collected and send for the X-ray crystallographic analysis.



Colour code: Carbon (Light-gray), Nitrogen (Blue), Oxygen (Red)

CCDC	2156735
Formula	$\text{C}_{21}\text{H}_{17}\text{NO}_2$
Formula weight	315.3720
Wavelength	0.71073
Temperature (K)	296
Crystal system	Monoclinic
Space group	C 1 c 1
a ( $\text{\AA}$ )	5.1663 (15)
b ( $\text{\AA}$ )	20.190 (7)
c ( $\text{\AA}$ )	14.945 (5)
$\alpha$ ( $^{\circ}$ )	90
$\beta$ ( $^{\circ}$ )	96.836 (13)
$\gamma$ ( $^{\circ}$ )	90
V ( $\text{cm}^3$ )	1547.8 (8)
Z	4
Density	1.353
$\mu$ ( $\text{mm}^{-1}$ )	0.087
F (000)	664.0
No. of ref.	2695
Unique ref.	2601
R1	0.0937
wR2	0.1845
G. O. F.	1.285



**Fig. 2:** ORTEP drawing of the compound **4r** showing thermal ellipsoids at the 30% probability level.

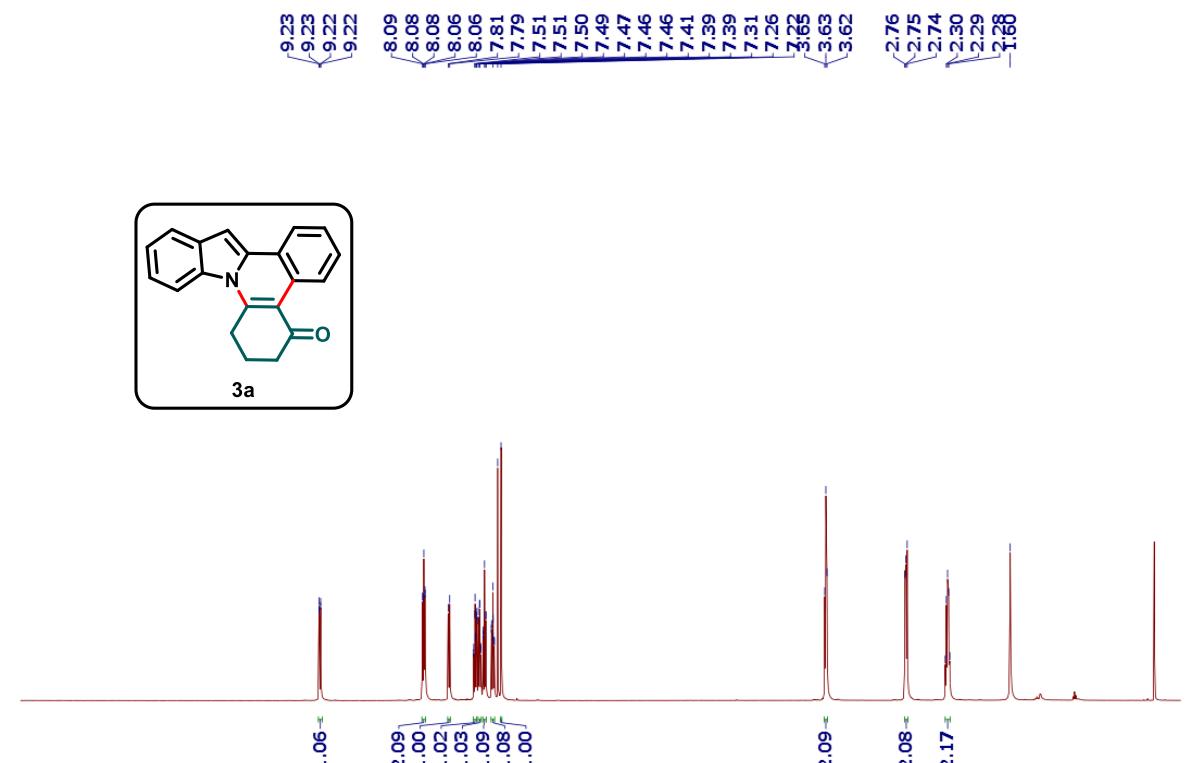
Colour code: Carbon (Light-gray), Oxygen (Red), Nitrogen (Blue)

## **9. References:**

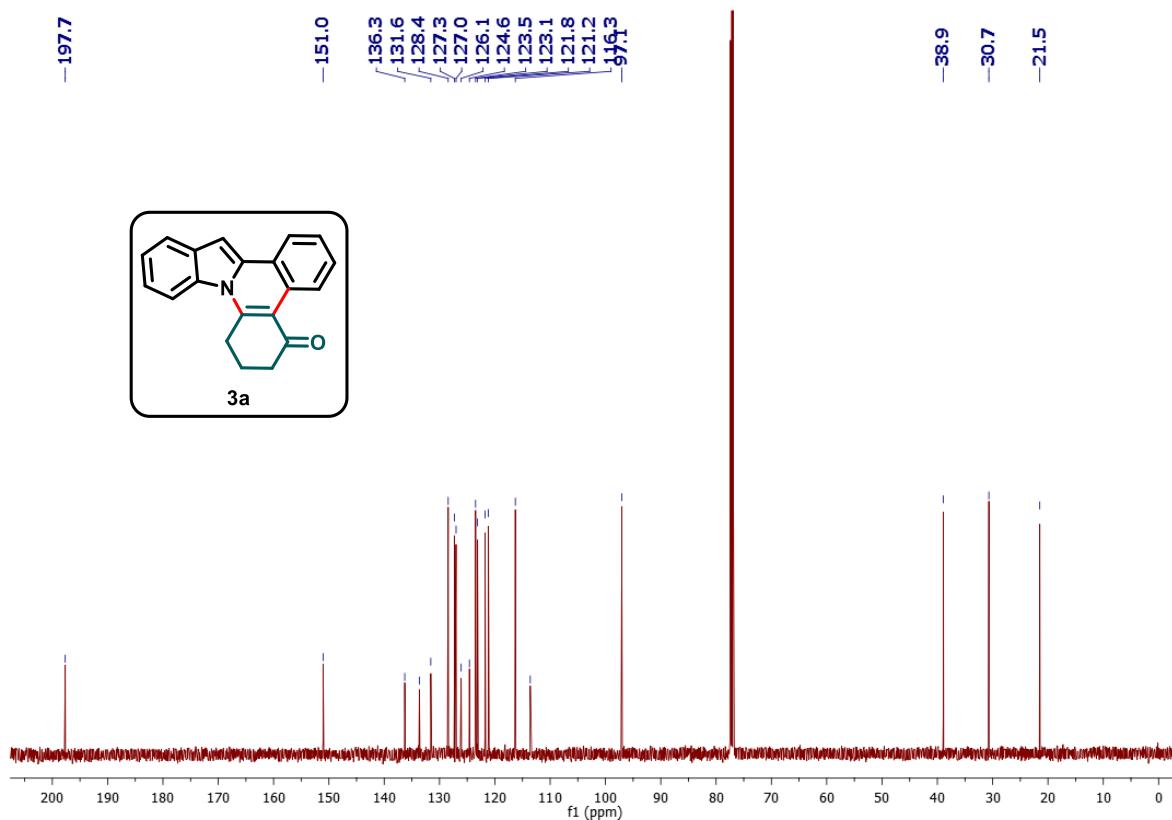
- 1.** (a) Yang, S.D.; Sun, C.L.; Fang, Z.; Li, B.J.; Li, Y.Z.; Shi, Z.J. *Angew. Chem. Int. Ed.* **2008**, 47, 1473-1476. (b) Mao, J.; Wang, Z.; Xu, X.; Liu, G.; Jiang, R.; Guan, H.; Zheng, Z.; Walsh, P.J. *Angew. Chem. Int. Ed.* **2019**, 58, 11033-11038. (c) Markandeya, S.V.; Renuka, C.; Lakshmi, P.K.; Rajesh, A.; Sridhar, C.; Babu, K.R. *Synth. Comm.*, **2018**, 48, 135-145. (d) Xia, X.D.; Xuan, J.; Wang, Q.; Lu, L.Q.; Chen, J.R.; Xiao, W.J. *Adv. Synth. Catal.* **2014**, 356, 2807-2812. (e) Prior, A.M.; Yu, X.; Park, E.J.; Kondratyuk, T.P.; Lin, Y.; Pezzuto, J.M.; Sun, D. *Bioorg. Med. Chem. Lett.* **2017**, 27, 5393–5399. (f) Kraus, G.A.; Guo, H.; Kumar, G.; Pollock III, G.; Carruthers, H.; Chaudhary, D.; Beasley, J. *Synthesis*, **2010**, 8, 1386-1393. (g) Bellezza, D.; Noverges, B.; Fasano, F.; Sarmiento, J.T.; Medio-Simón, M.; Asensio, G. *Eur. J. Org. Chem.* **2019**, 1229-1235. (h) Fu, W.; Yang, K.; Chen, J.; Song, Q. *Org. Biomol. Chem.* **2017**, 15, 8354-8360.
- 2.** (a) Nunewar, S., Kumar, S., Pandhare, H., Nanduri, S. and Kanchupalli, V., *Org. Lett.* **2021**, 23, 4233-4238. (b) Kumar, S., Nunewar, S. and Kanchupalli, V., *Asian J. Org. Chem.*, **2022**, 11, 202100689.
- 3.** Thavaselvan, S. and Parthasarathy, K., *Org. Lett.* **2020**, 22, 3810-3814.

**10. NMR data:**

**7,8-dihydroindolo[1,2-f]phenanthridin-5(6H)-one (3a):**

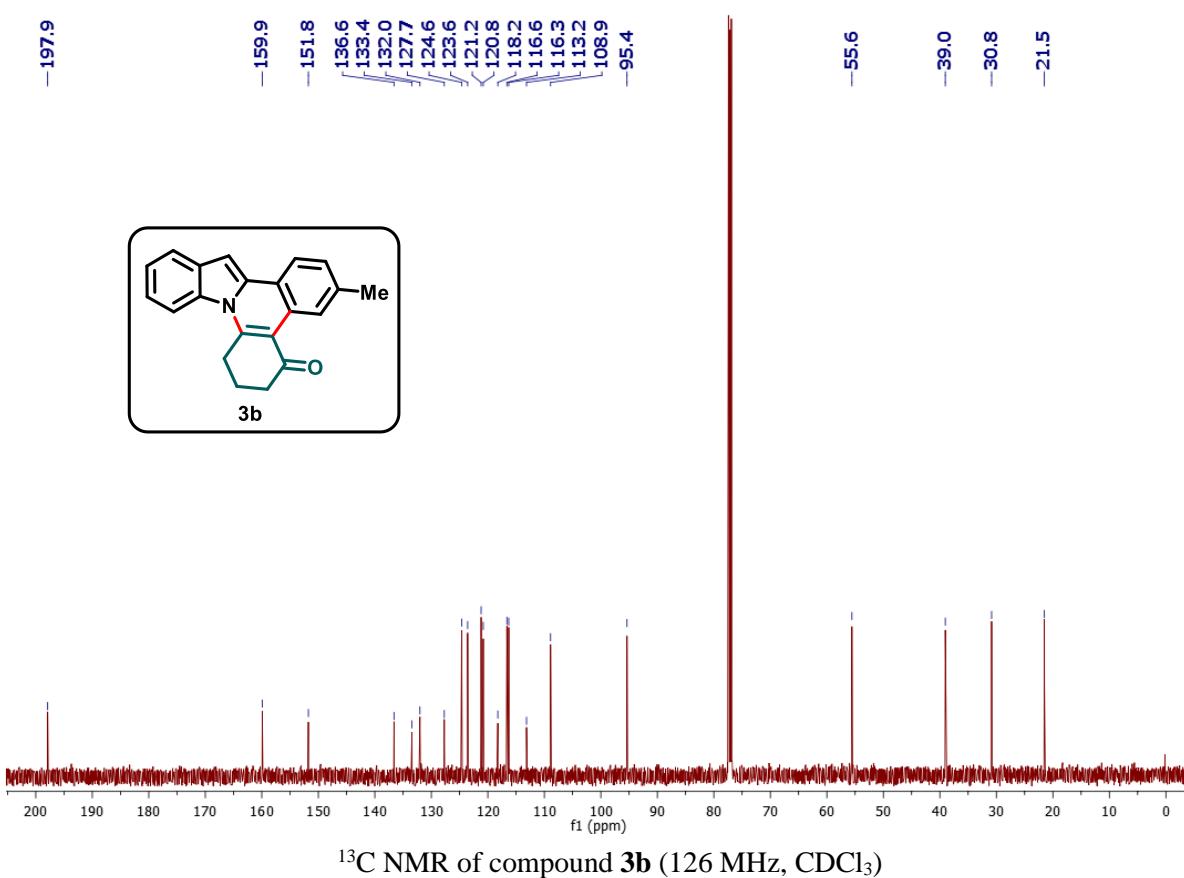
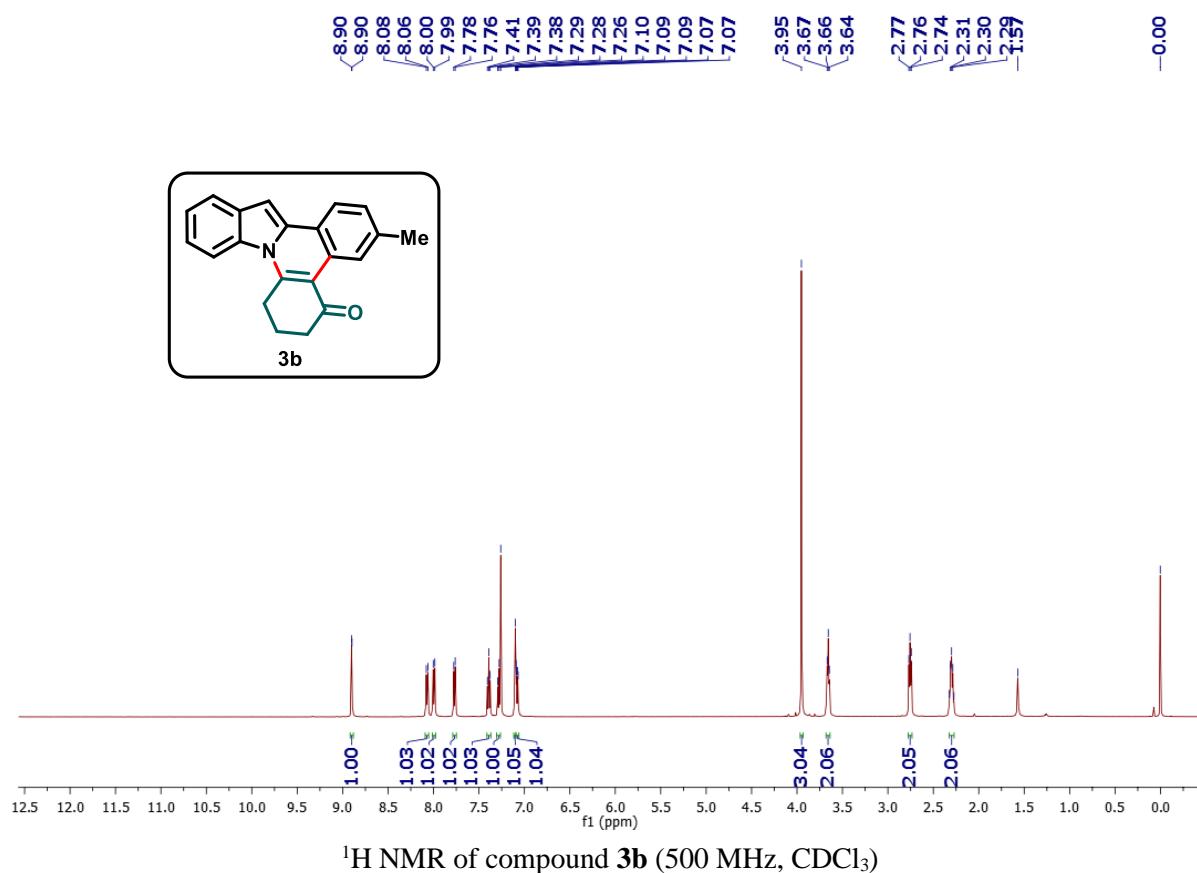


<sup>1</sup>H NMR of compound 3a (500 MHz, CDCl<sub>3</sub>)

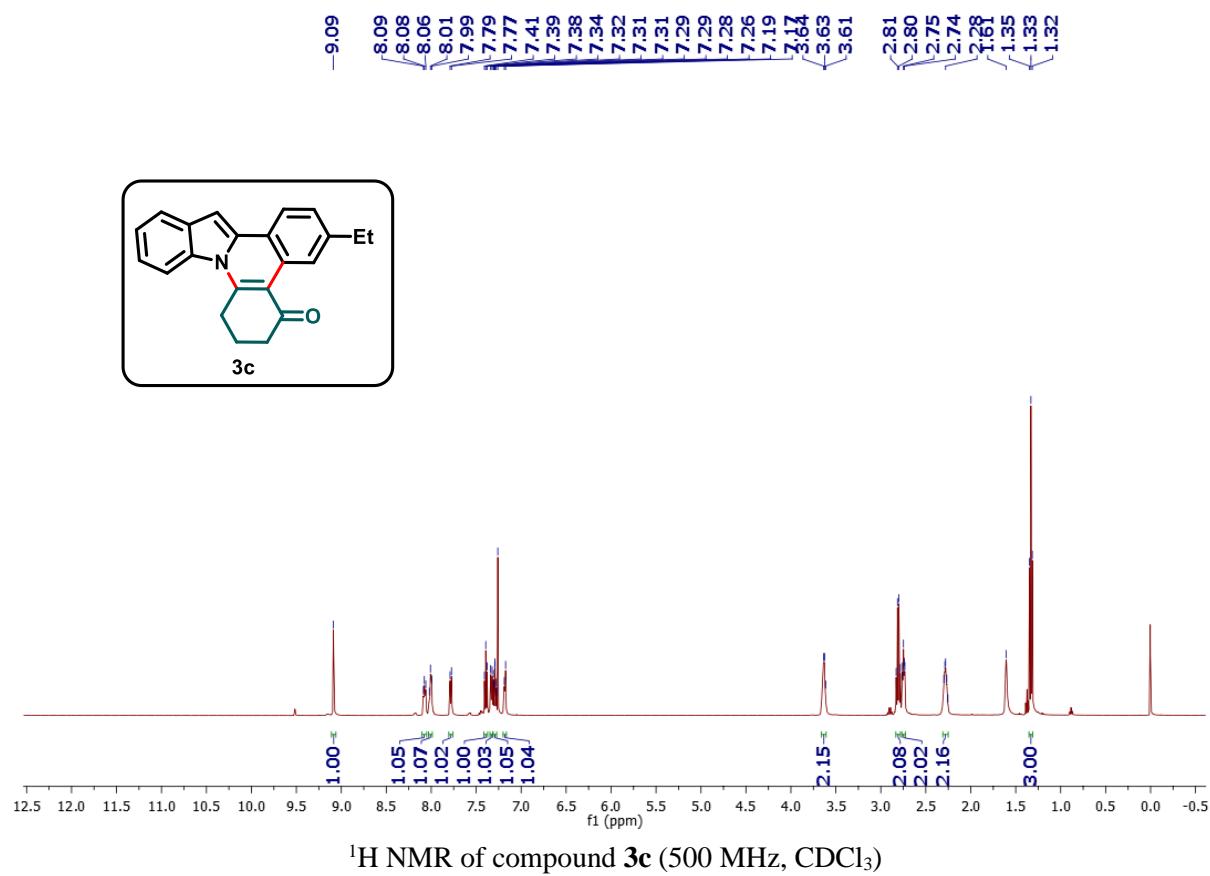


<sup>13</sup>C NMR of compound 3a (126 MHz, CDCl<sub>3</sub>)

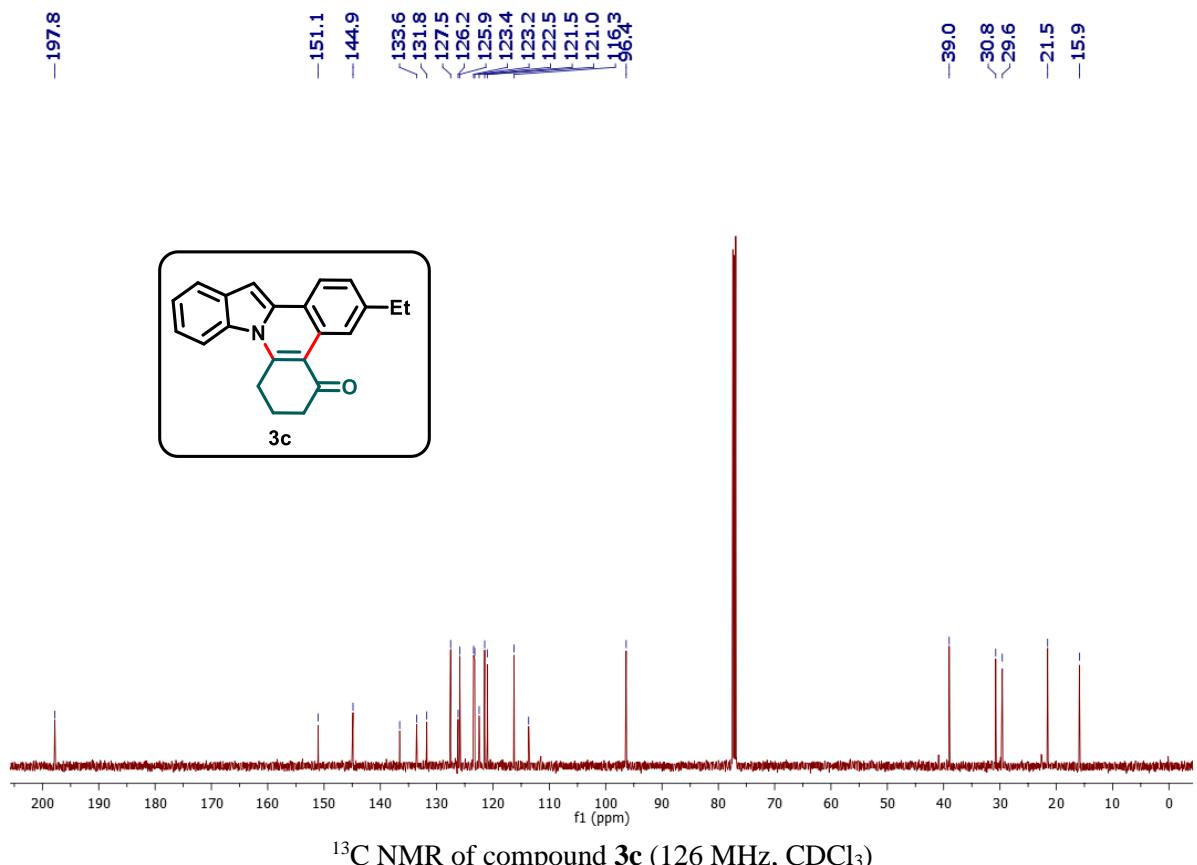
**3-methyl-7,8-dihydroindolo[1,2-f]phenanthridin-5(6H)-one (3b):**



**3-ethyl-7,8-dihydroindolo[1,2-*f*]phenanthridin-5(6*H*)-one (3c):**

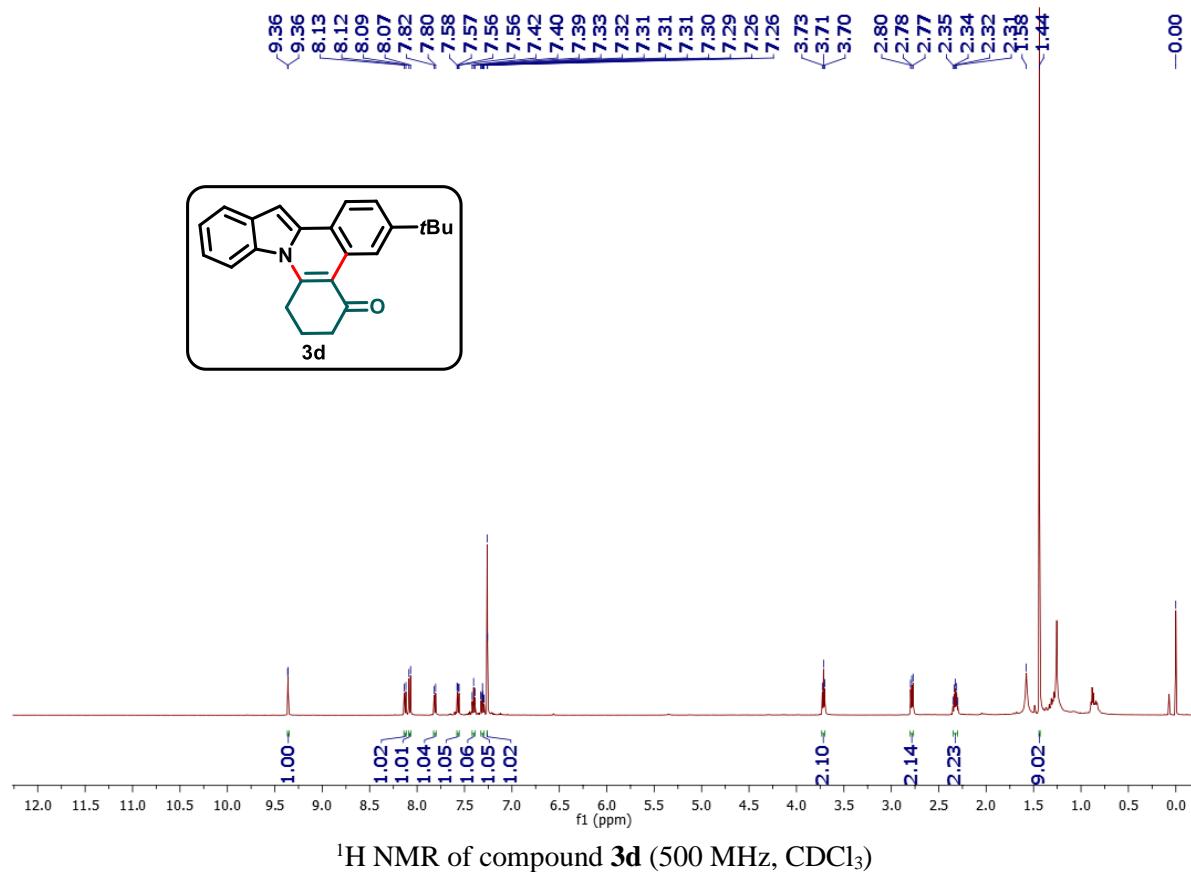


<sup>1</sup>H NMR of compound 3c (500 MHz, CDCl<sub>3</sub>)

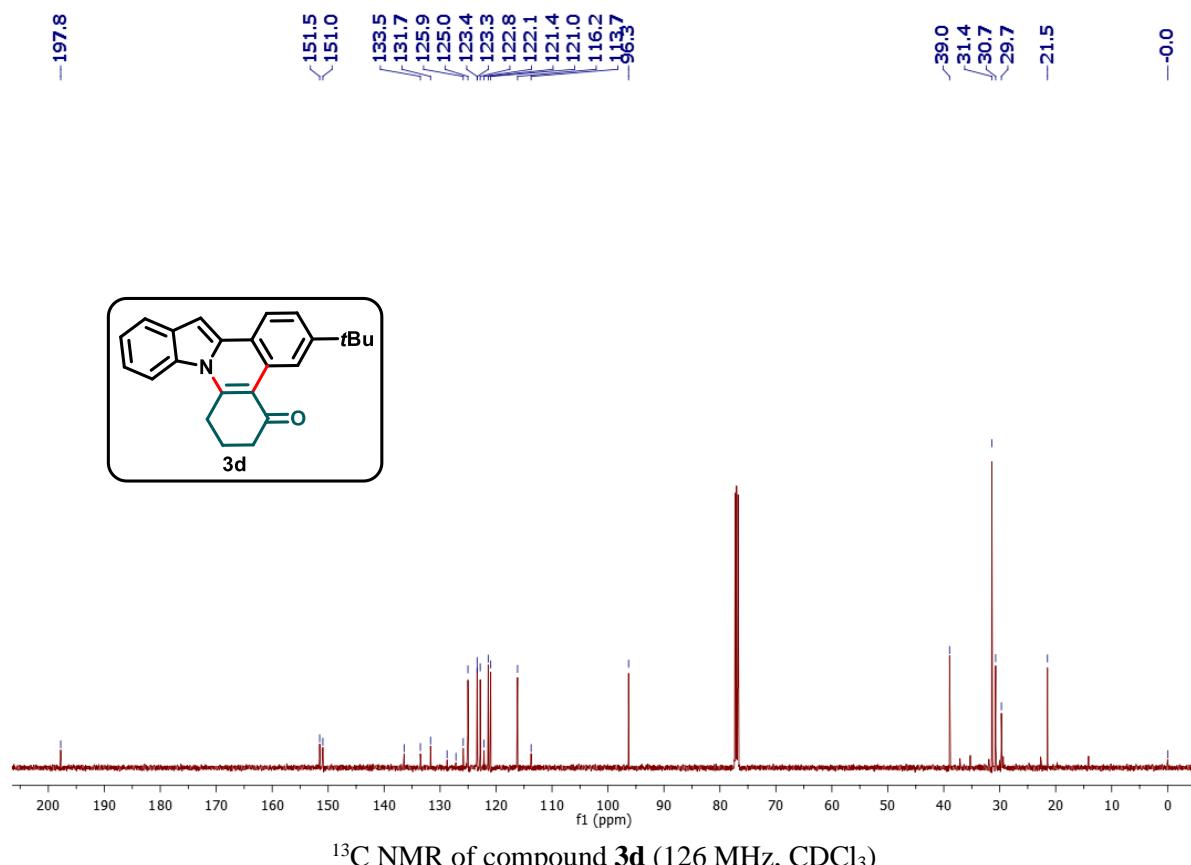


<sup>13</sup>C NMR of compound 3c (126 MHz, CDCl<sub>3</sub>)

**3-(*tert*-butyl)-7,8-dihydroindolo[1,2-*f*]phenanthridin-5(6*H*)-one (**3d**):**

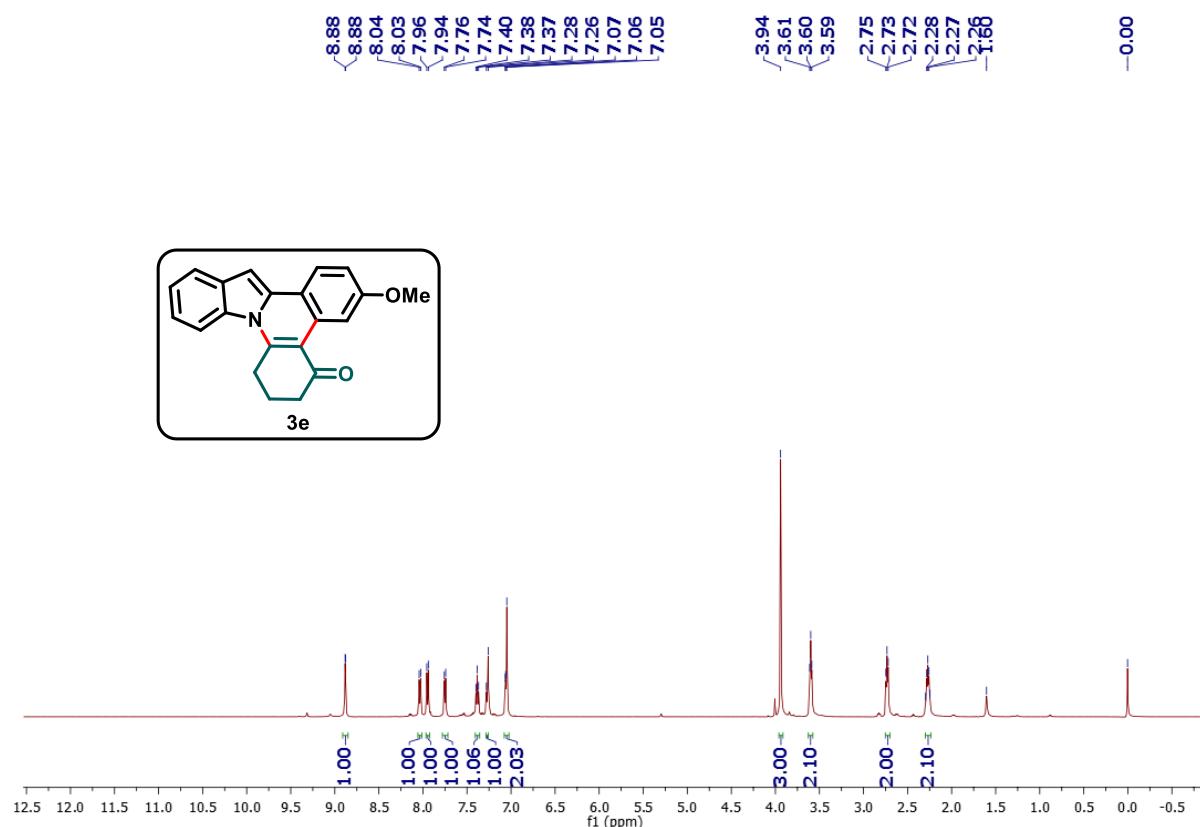


<sup>1</sup>H NMR of compound **3d** (500 MHz, CDCl<sub>3</sub>)

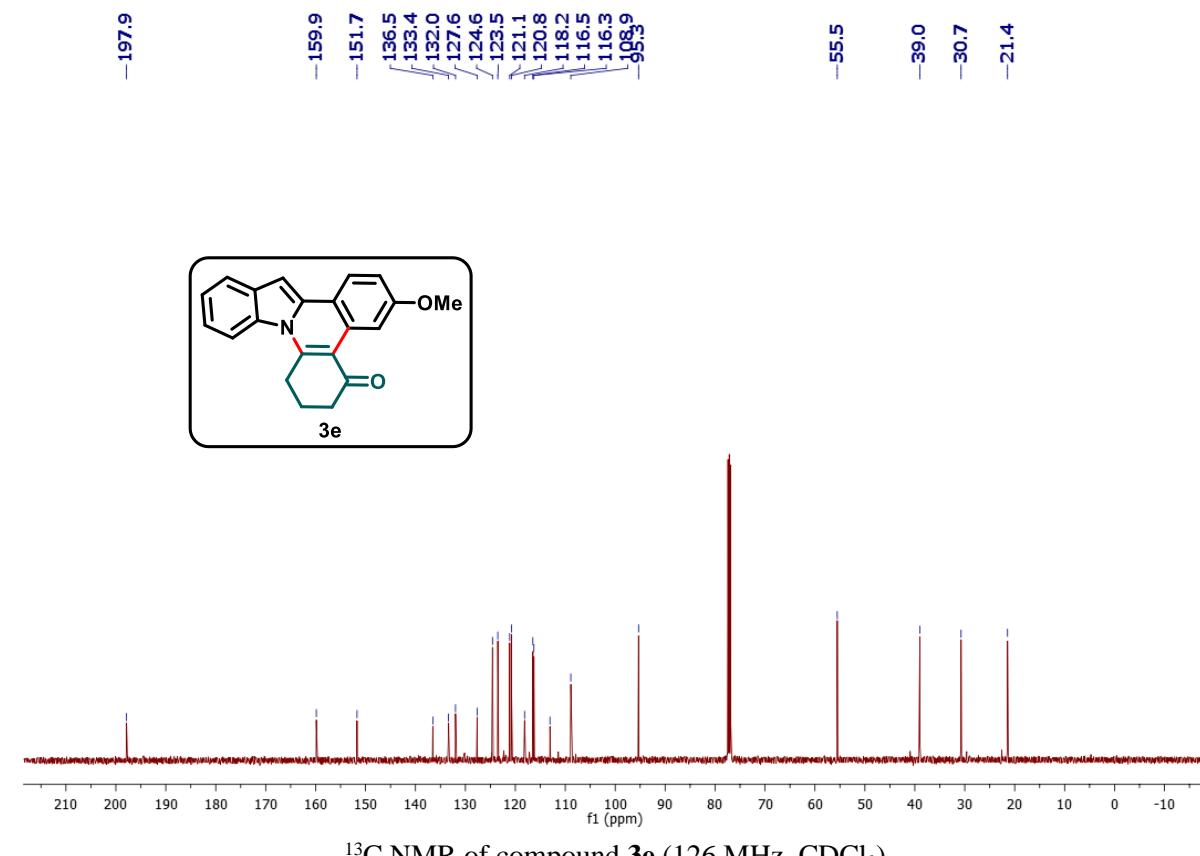


<sup>13</sup>C NMR of compound **3d** (126 MHz, CDCl<sub>3</sub>)

**3-methoxy-7,8-dihydroindolo[1,2-f]phenanthridin-5(6H)-one (3e):**

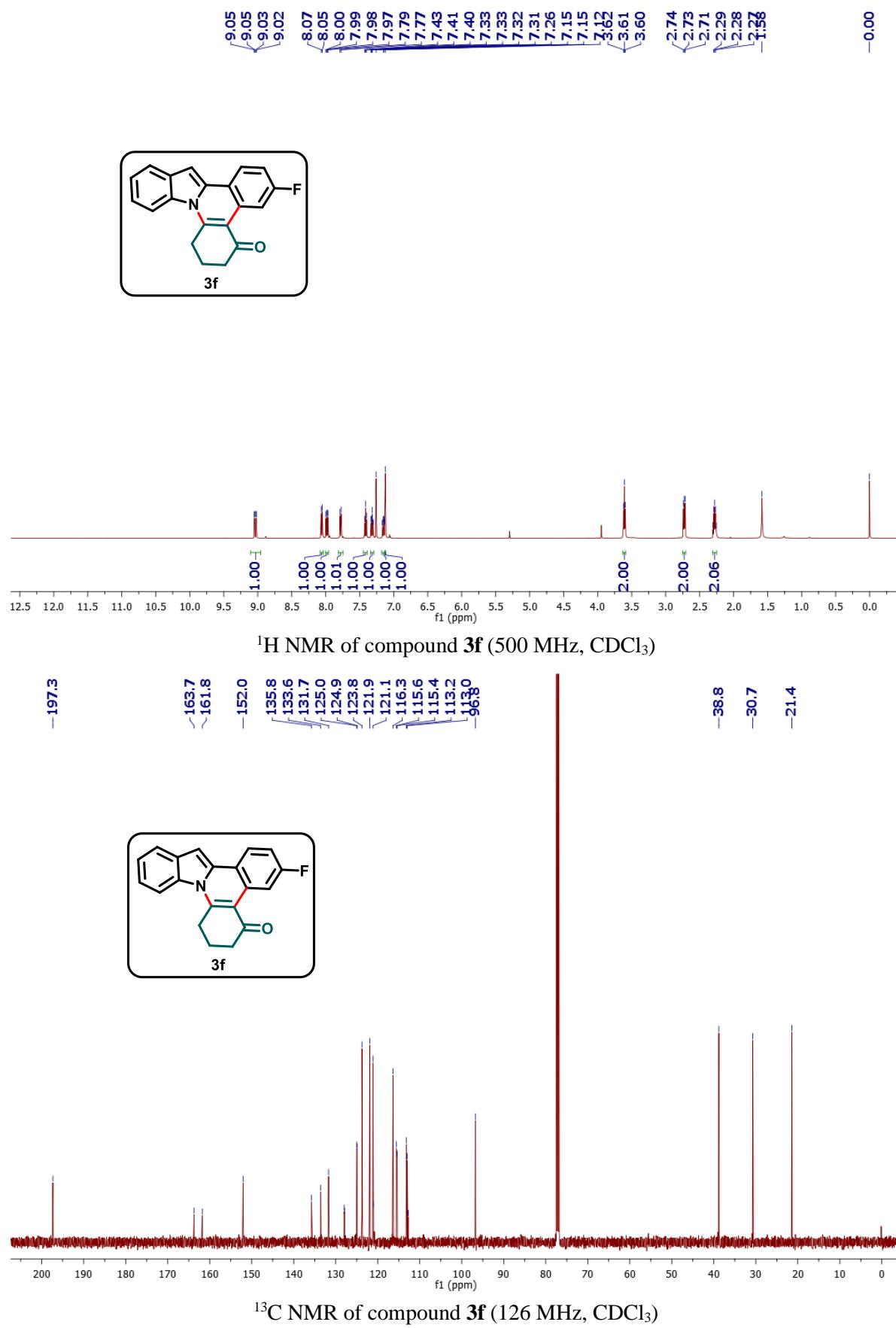


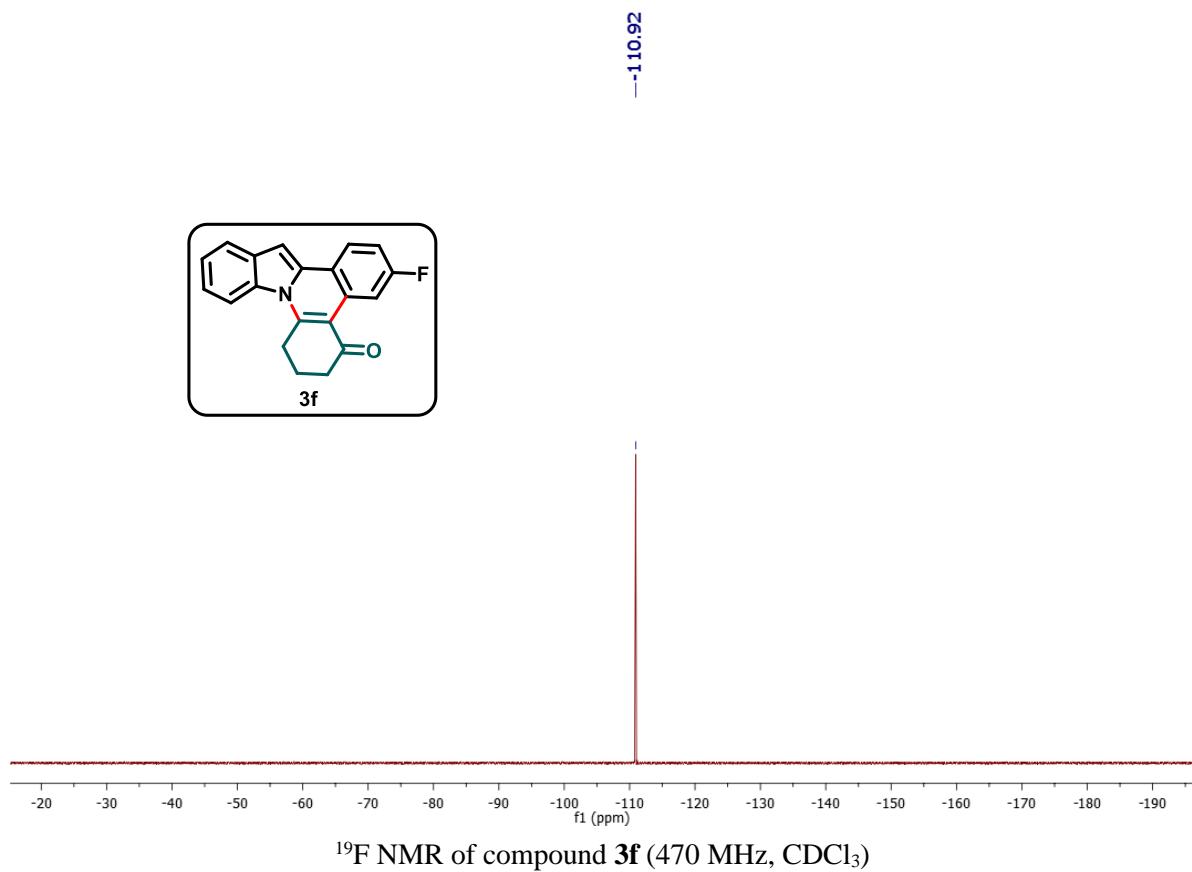
<sup>1</sup>H NMR of compound 3e (500 MHz, CDCl<sub>3</sub>)



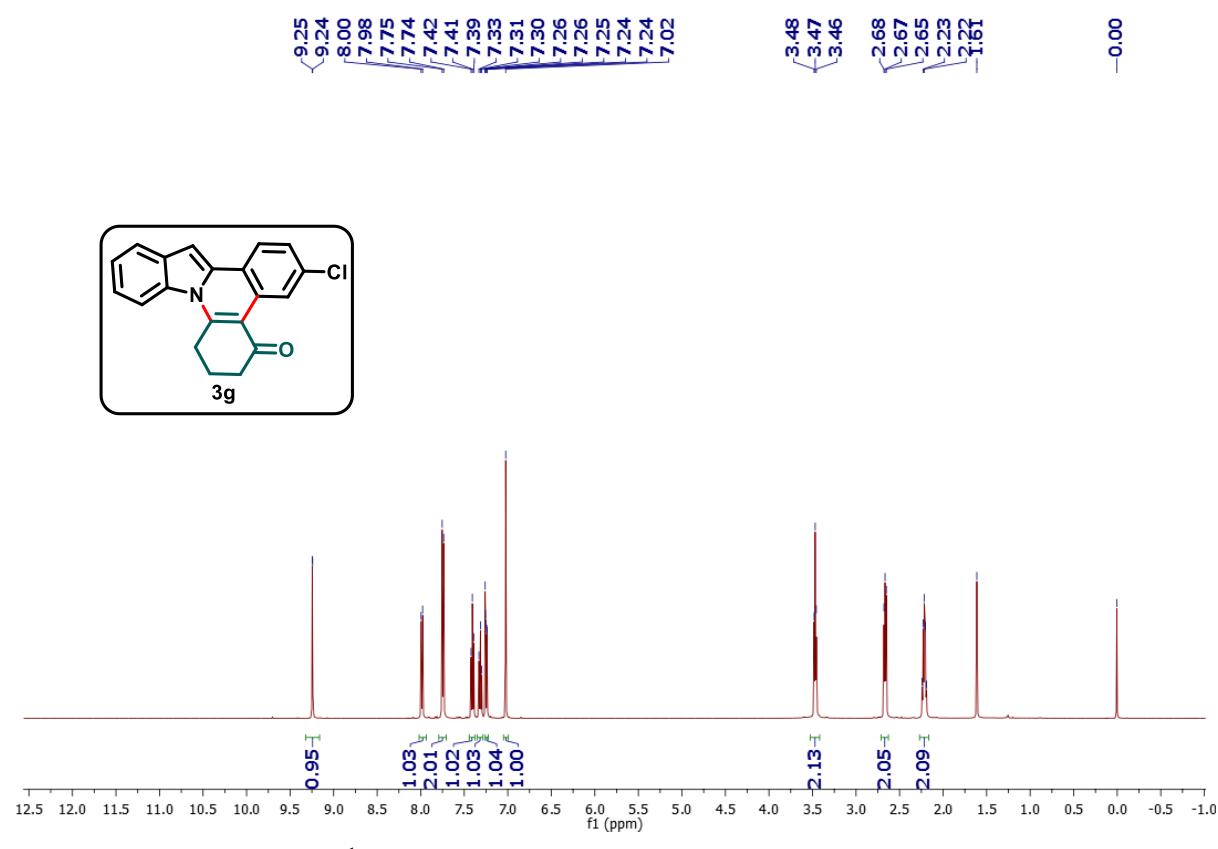
<sup>13</sup>C NMR of compound 3e (126 MHz, CDCl<sub>3</sub>)

**3-fluoro-7,8-dihydroindolo[1,2-*f*]phenanthridin-5(6*H*)-one (3f):**

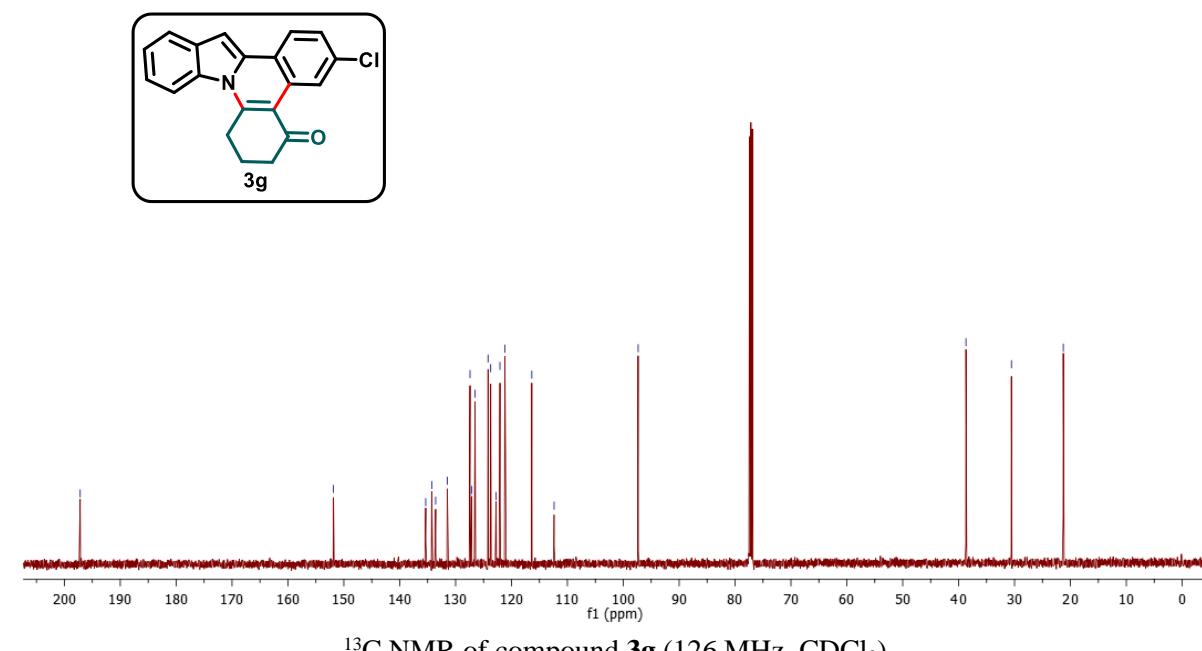
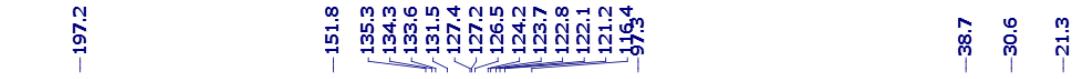




**3-chloro-7,8-dihydroindolo[1,2-f]phenanthridin-5(6H)-one: (3g):**

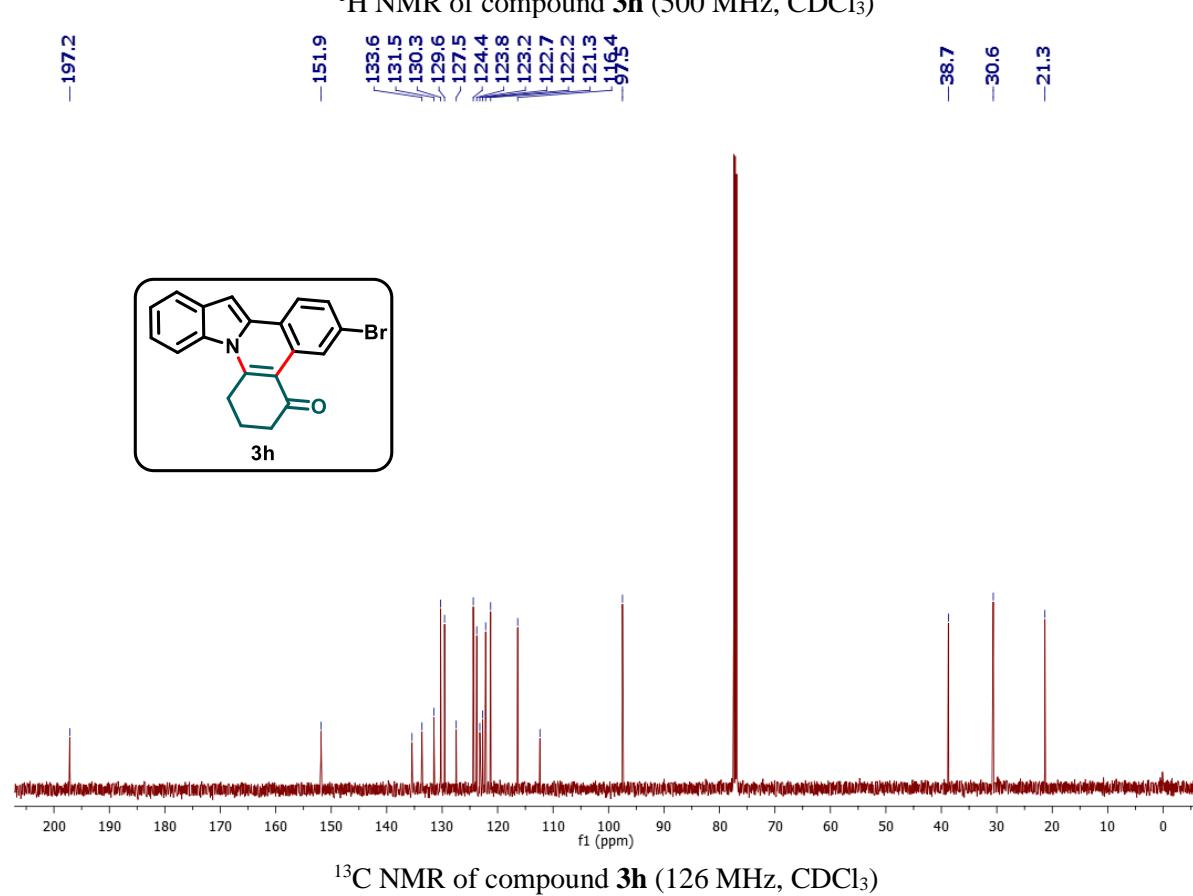
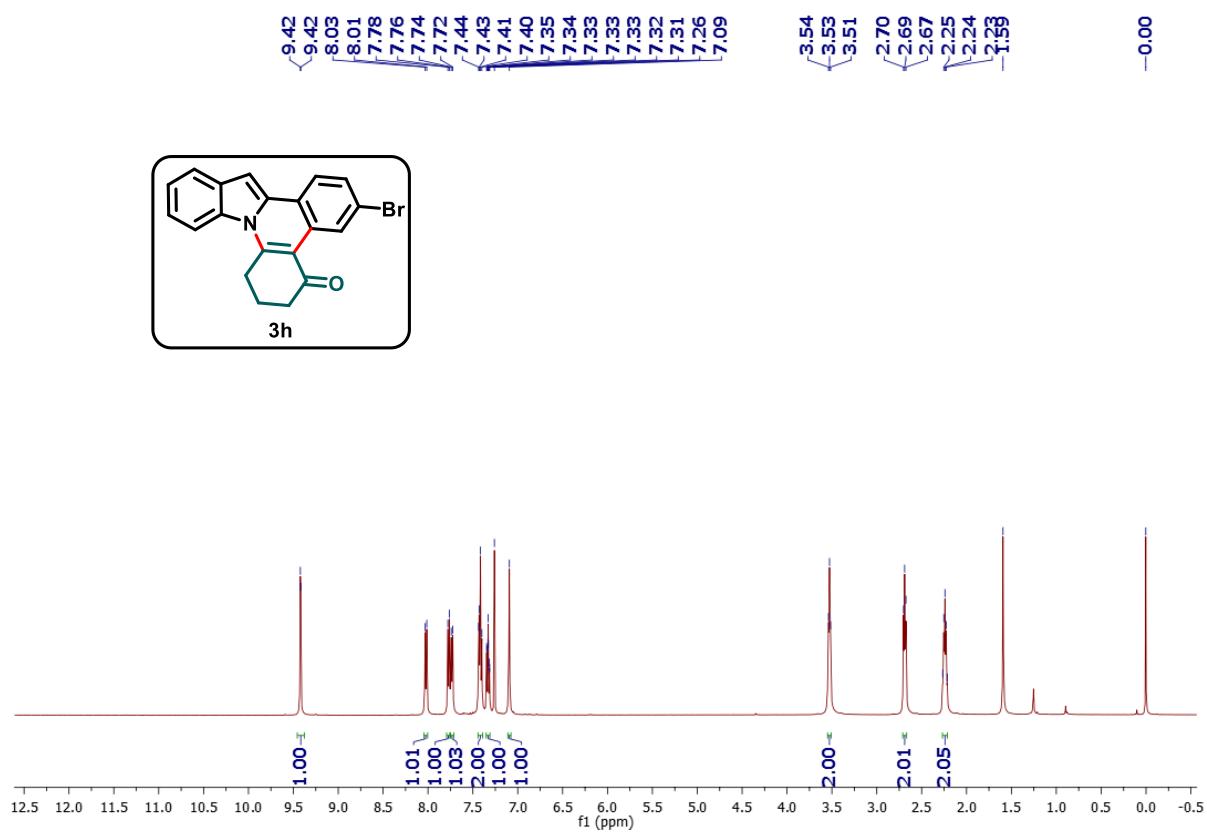


<sup>1</sup>H NMR of compound 3g (500 MHz, CDCl<sub>3</sub>)

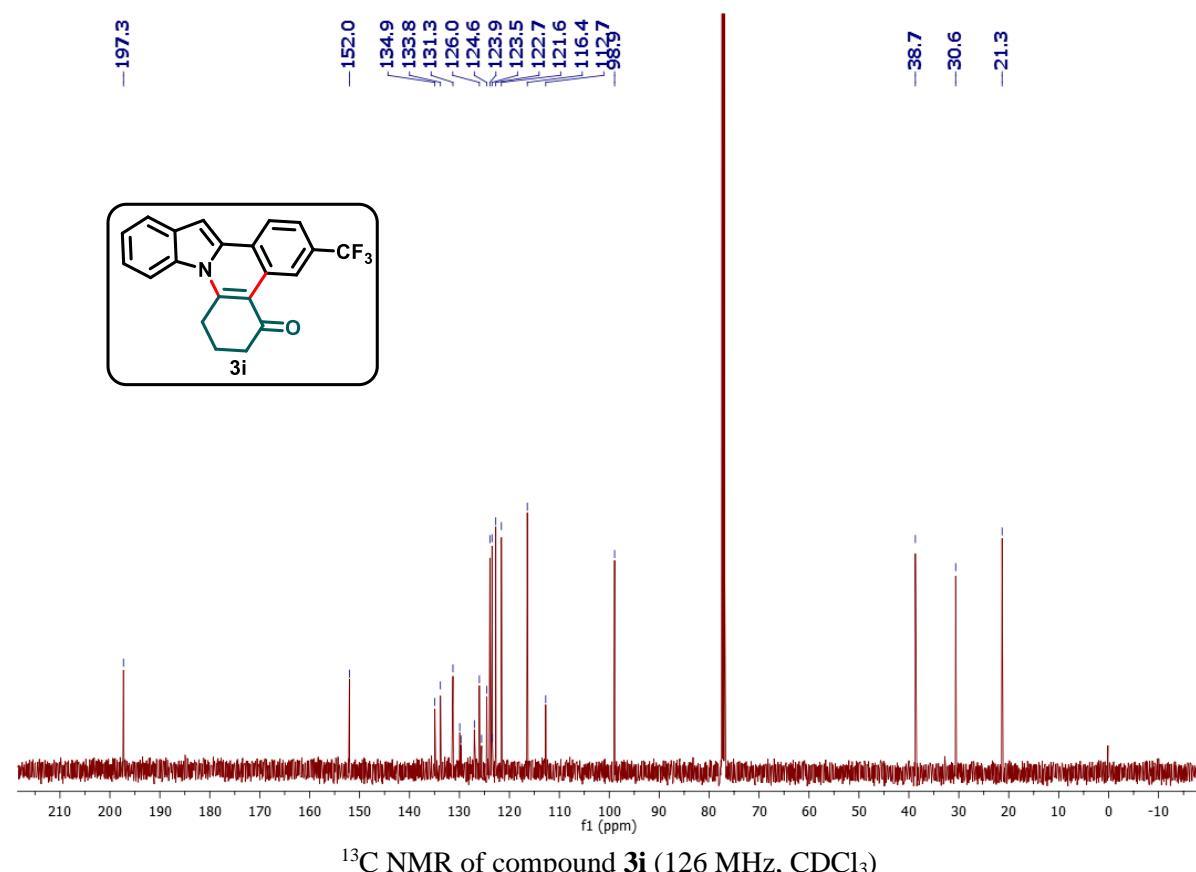
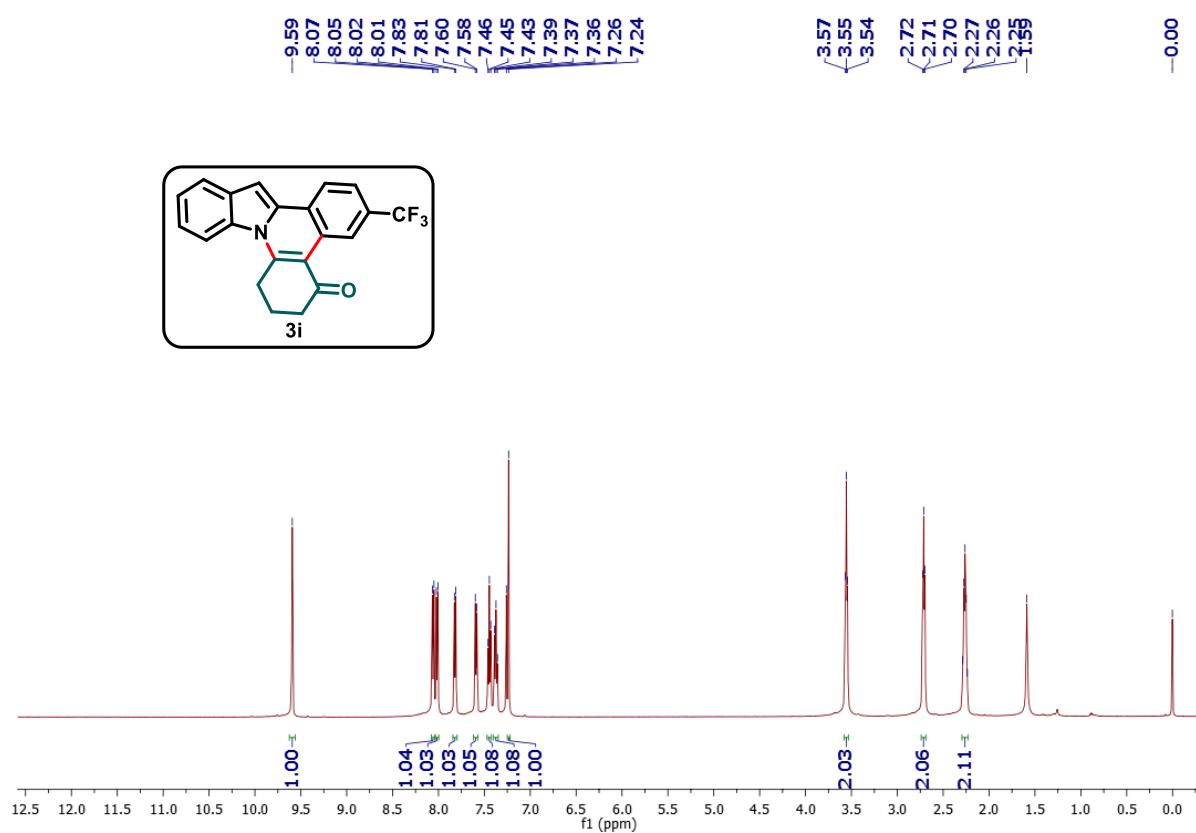


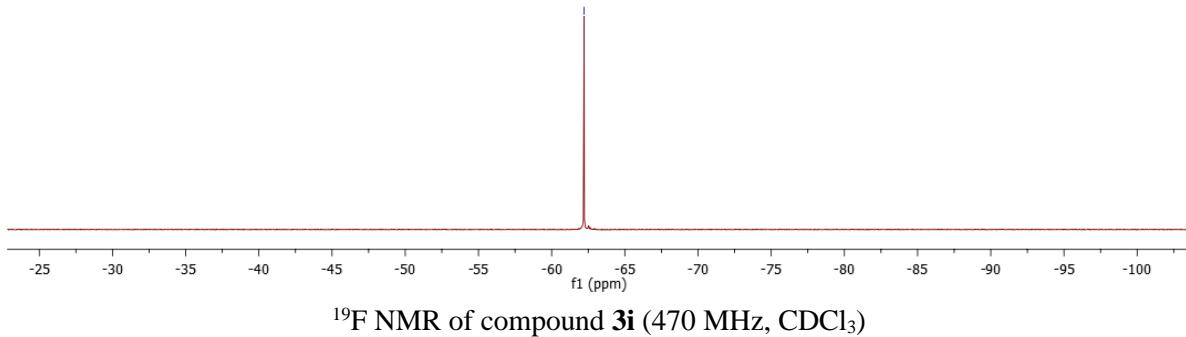
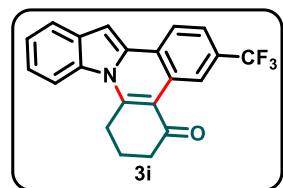
<sup>13</sup>C NMR of compound 3g (126 MHz, CDCl<sub>3</sub>)

**3-bromo-7,8-dihydroindolo[1,2-f]phenanthridin-5(6H)-one (3h):**



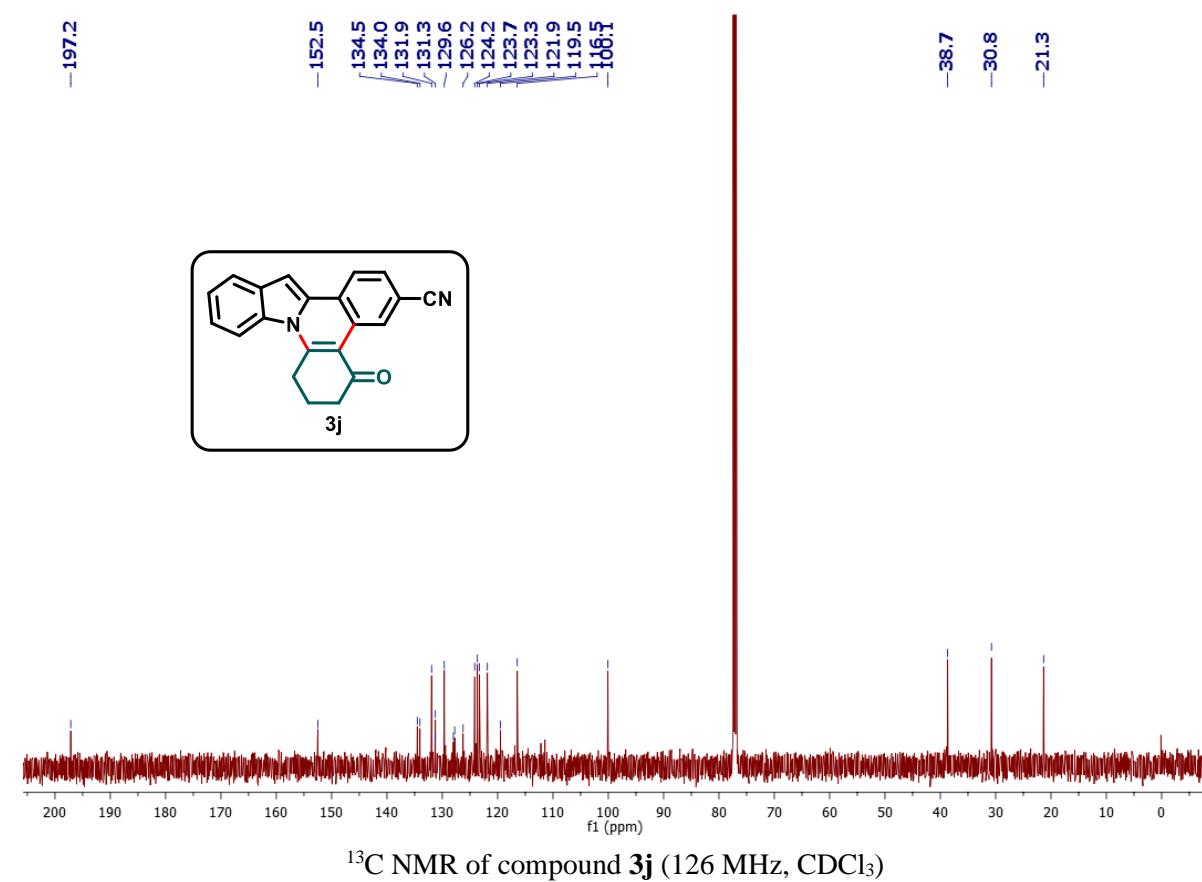
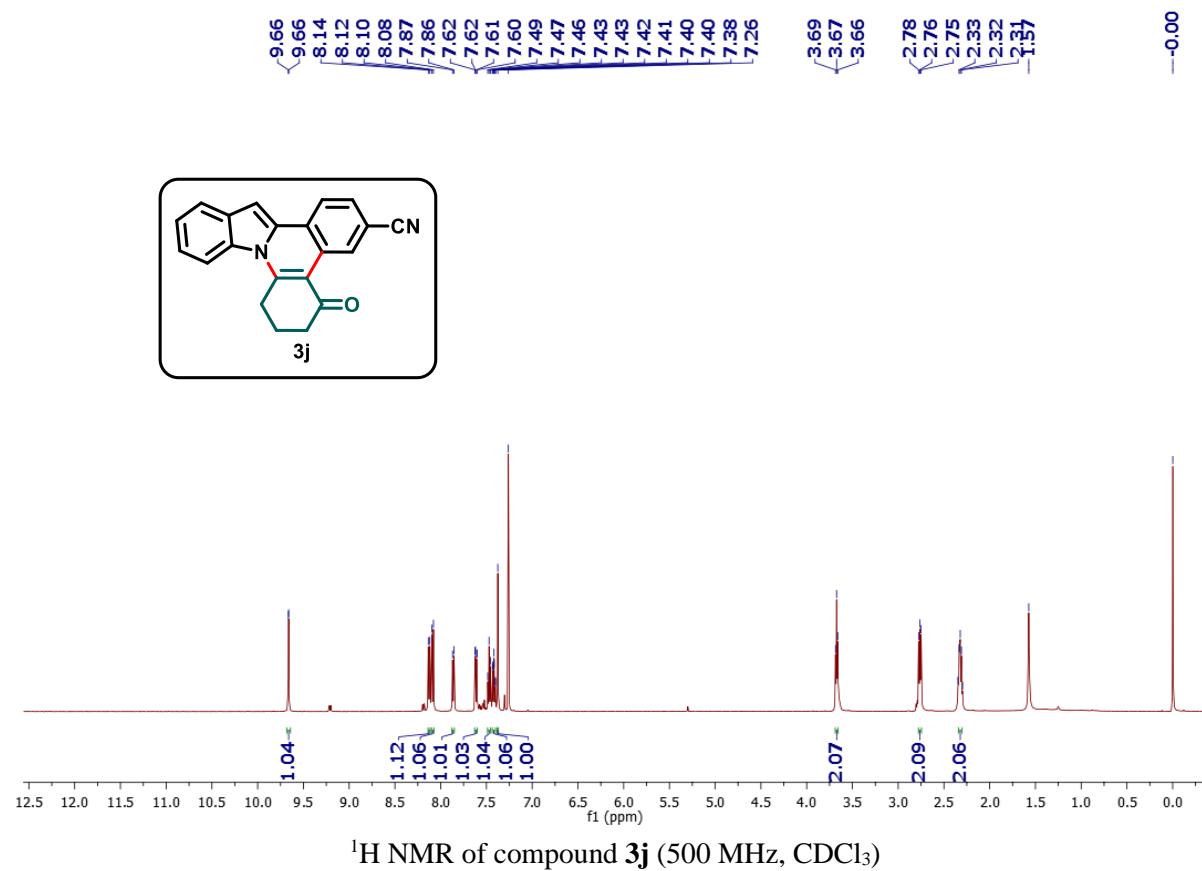
**3-(trifluoromethyl)-7,8-dihydroindolo[1,2-*f*]phenanthridin-5(6*H*)-one(3i):**



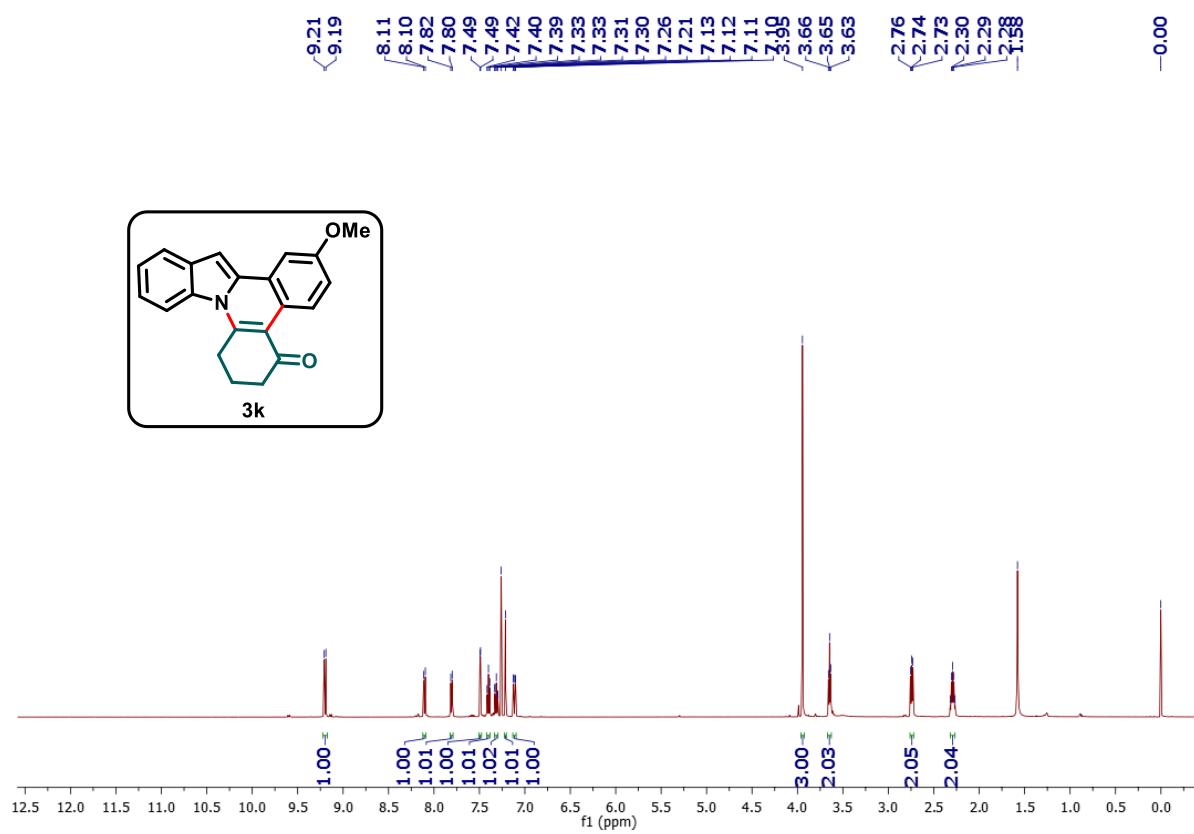


$^{19}\text{F}$  NMR of compound **3i** (470 MHz,  $\text{CDCl}_3$ )

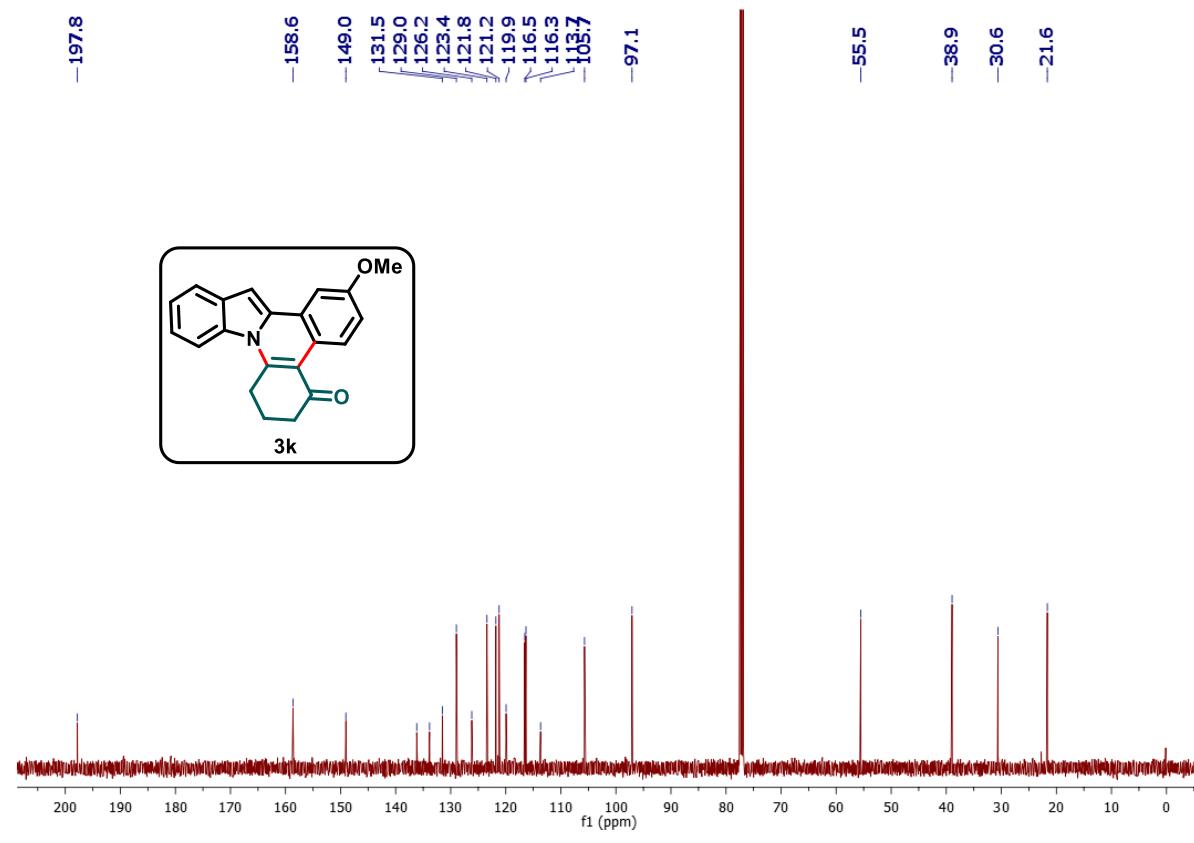
**5-oxo-5,6,7,8-tetrahydroindolo[1,2-*f*]phenanthridine-3-carbonitrile (**3j**):**



**2-methoxy-7,8-dihydroindolo[1,2-f]phenanthridin-5(6H)-one (3k):**

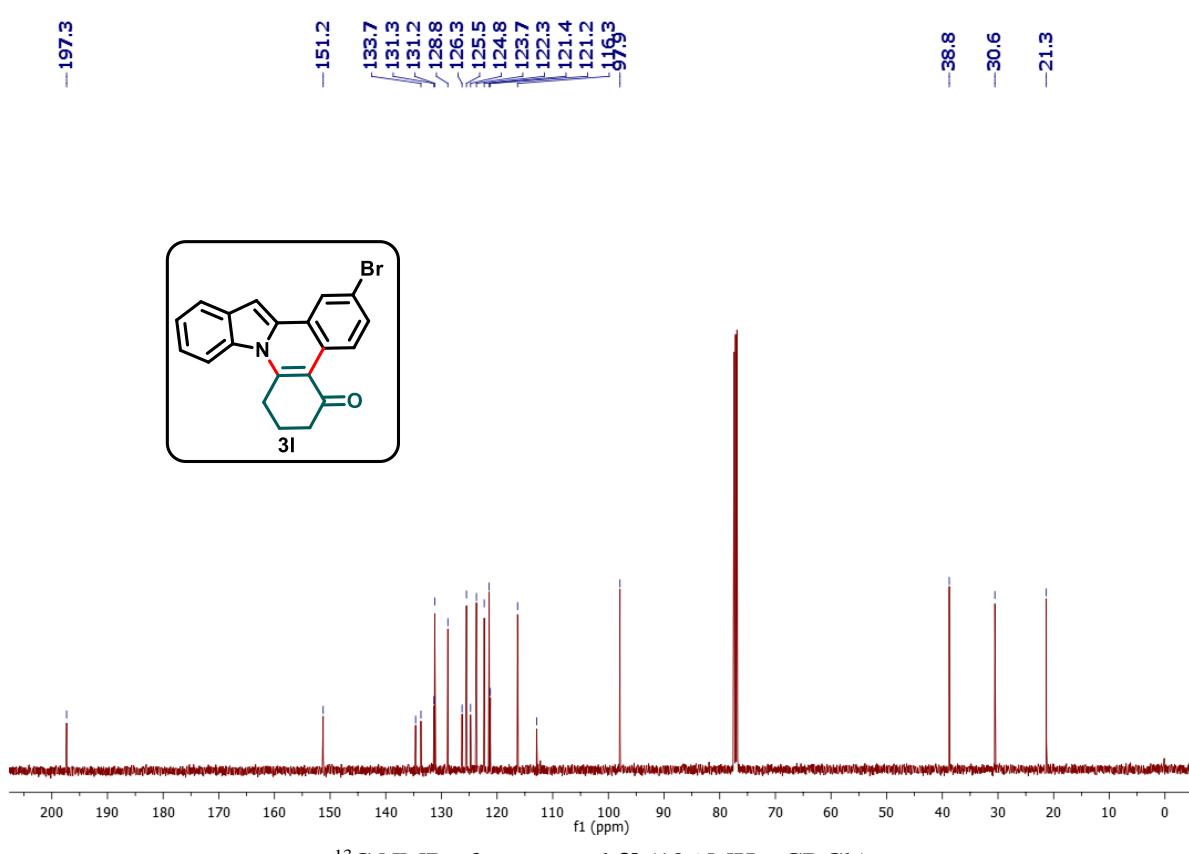
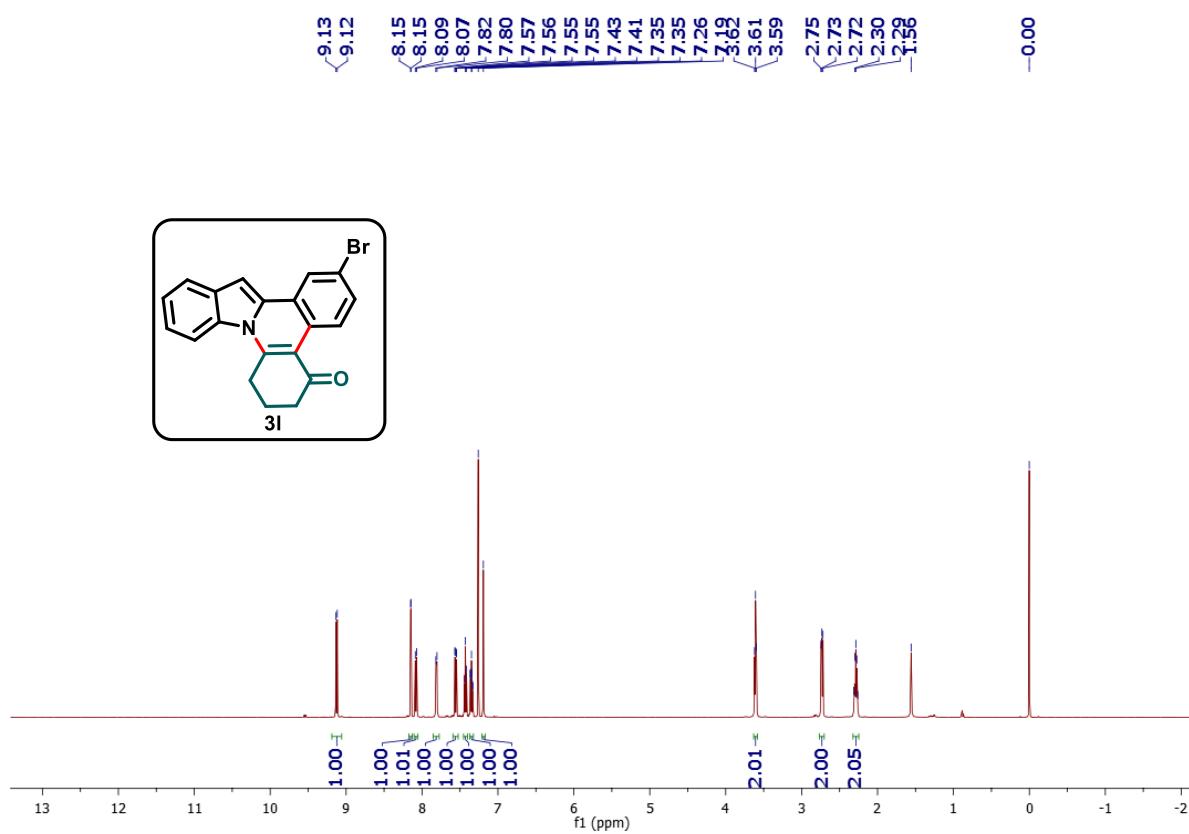


<sup>1</sup>H NMR of compound 3k (500 MHz, CDCl<sub>3</sub>)

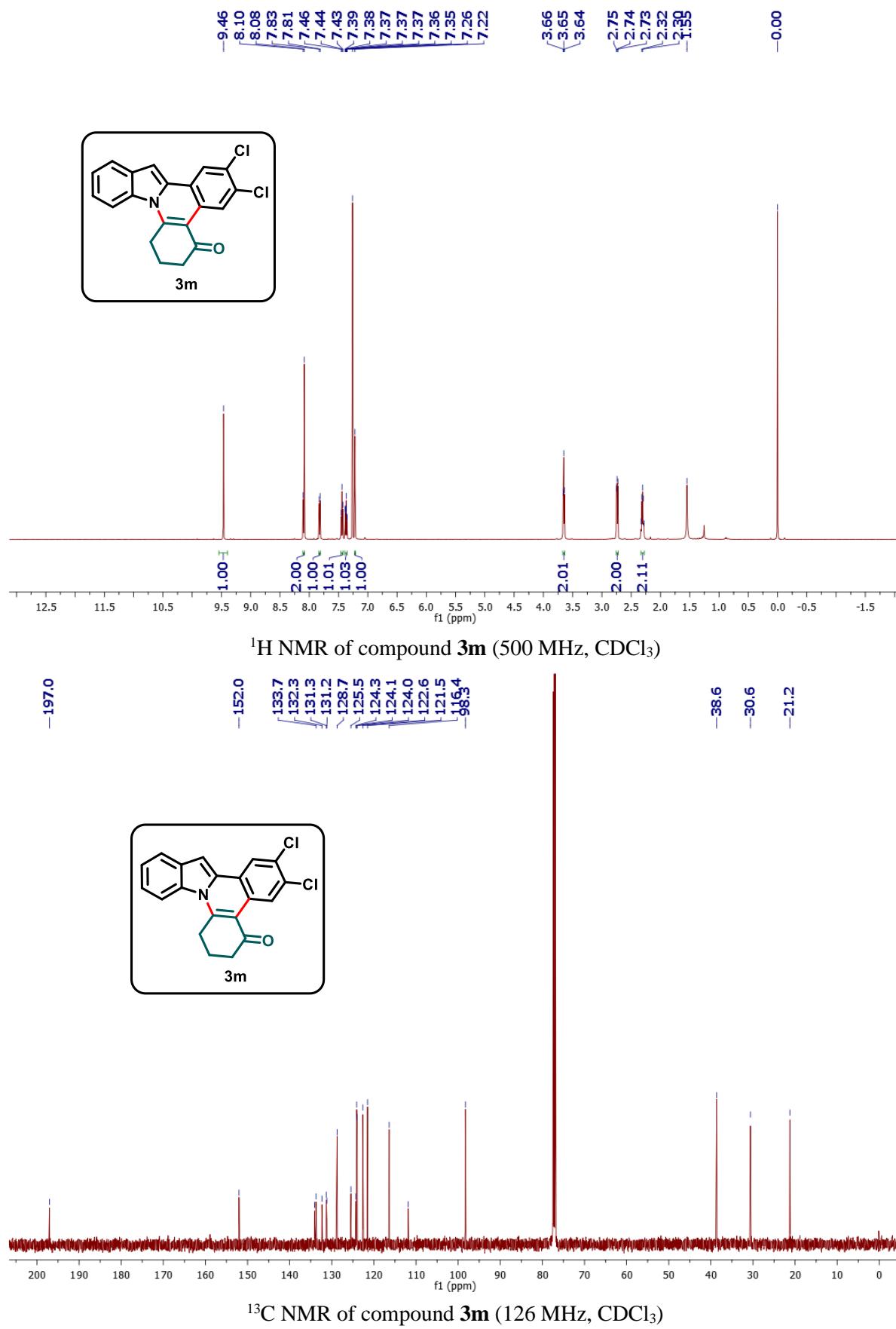


<sup>13</sup>C NMR of compound 3k (126 MHz, CDCl<sub>3</sub>)

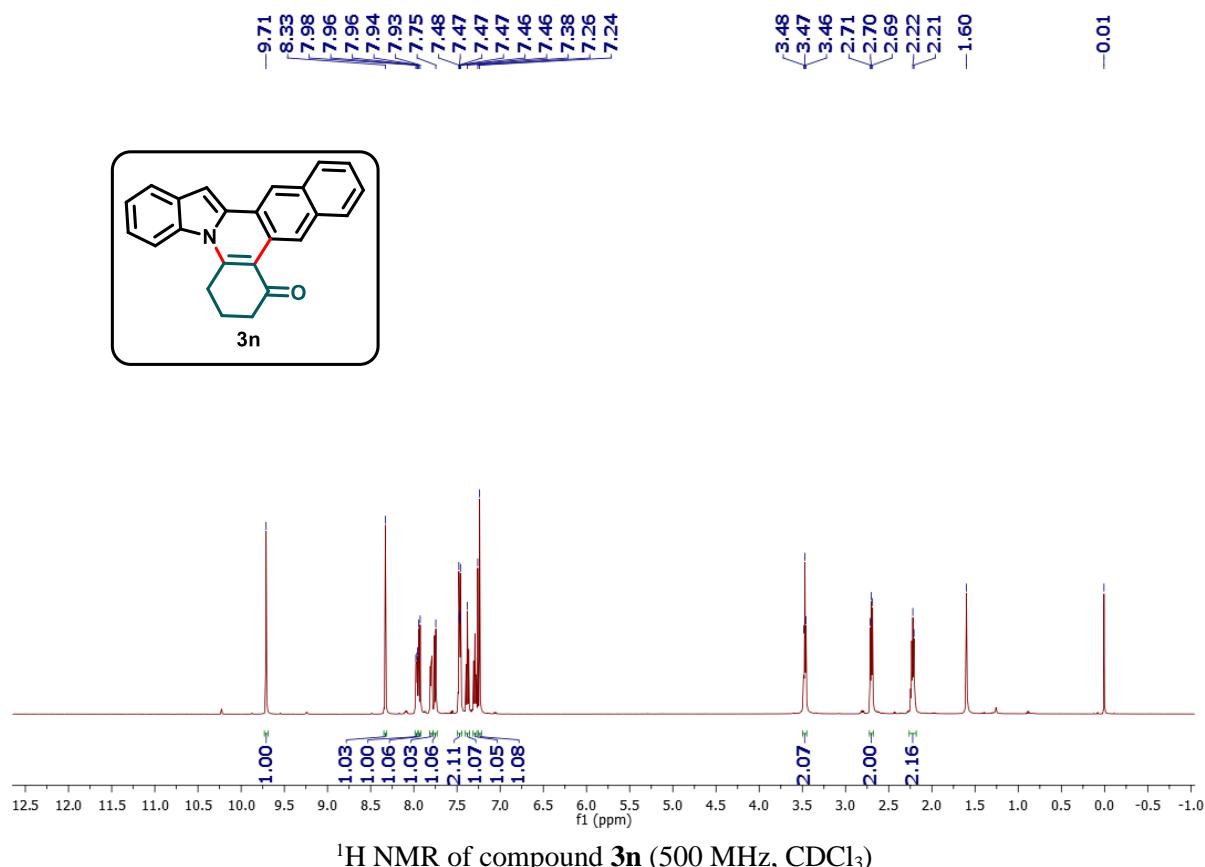
**2-bromo-7,8-dihydroindolo[1,2-f]phenanthridin-5(6H)-one (3l):**



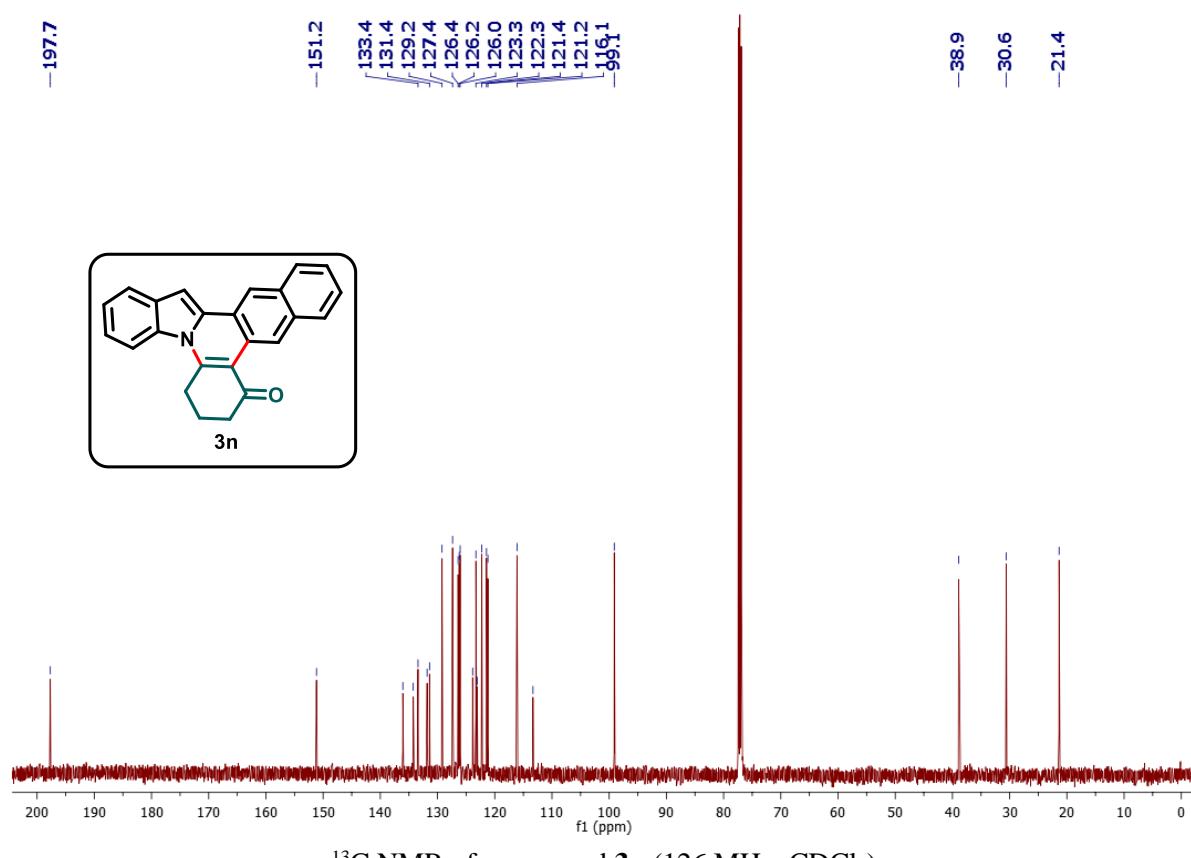
**2,3-dichloro-7,8-dihydroindolo[1,2-*f*]phenanthridin-5(6*H*)-one (3m):**



**7,8-dihydrobenzo[*j*]indolo[1,2-*f*]phenanthridin-9(6*H*)-one (3n):**

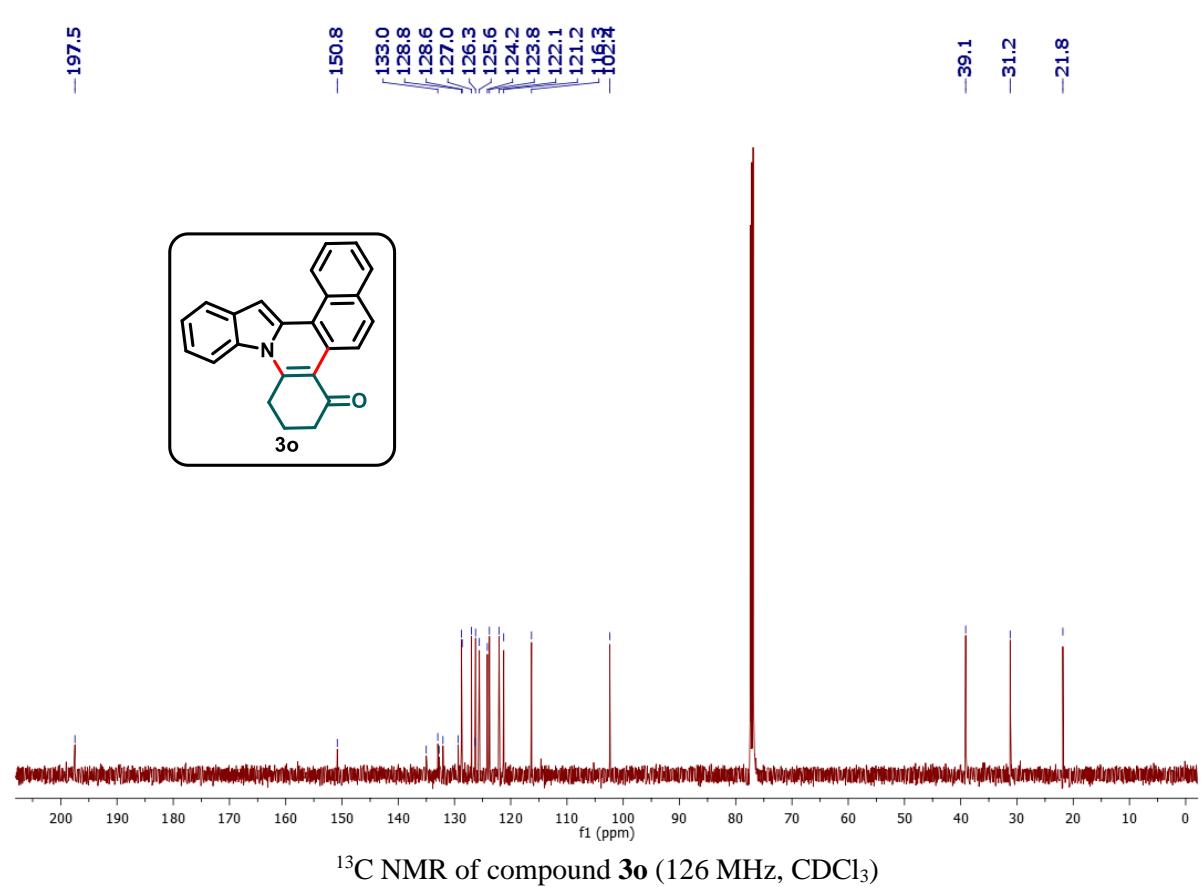
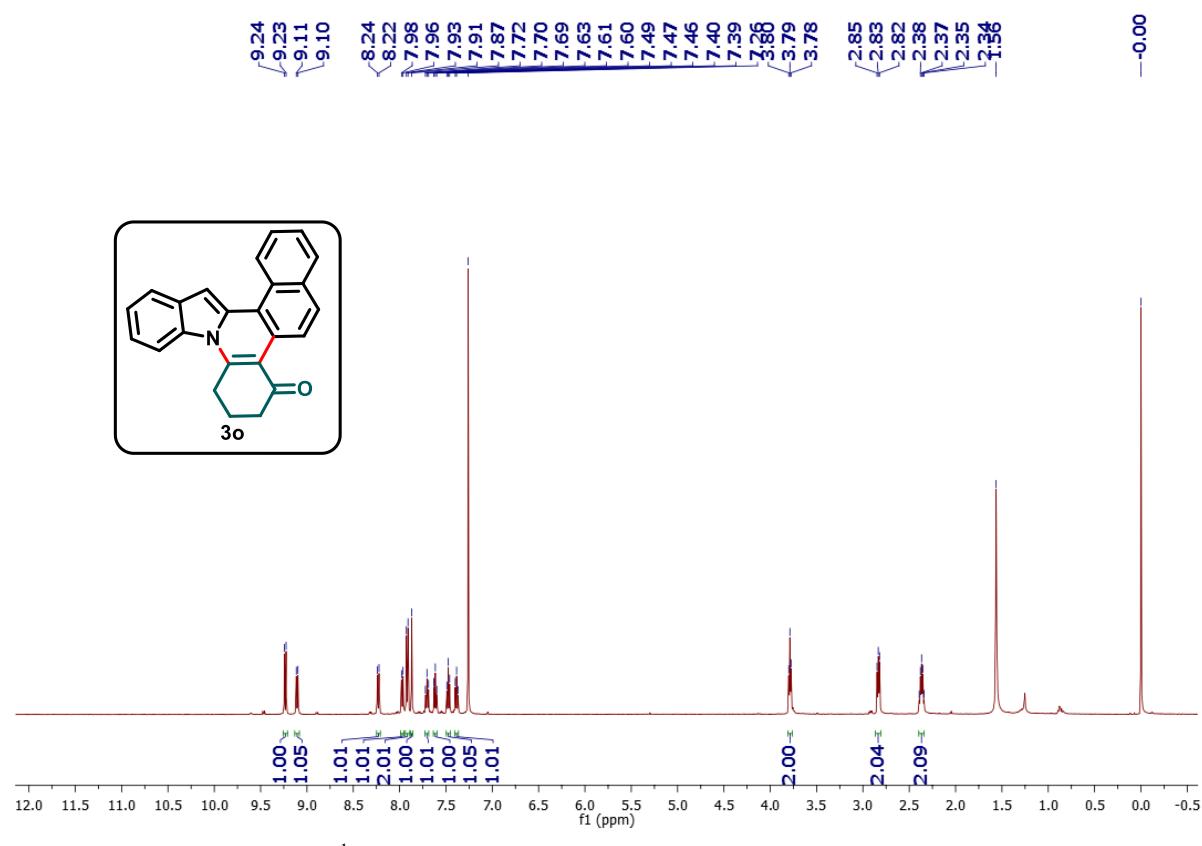


<sup>1</sup>H NMR of compound 3n (500 MHz, CDCl<sub>3</sub>)

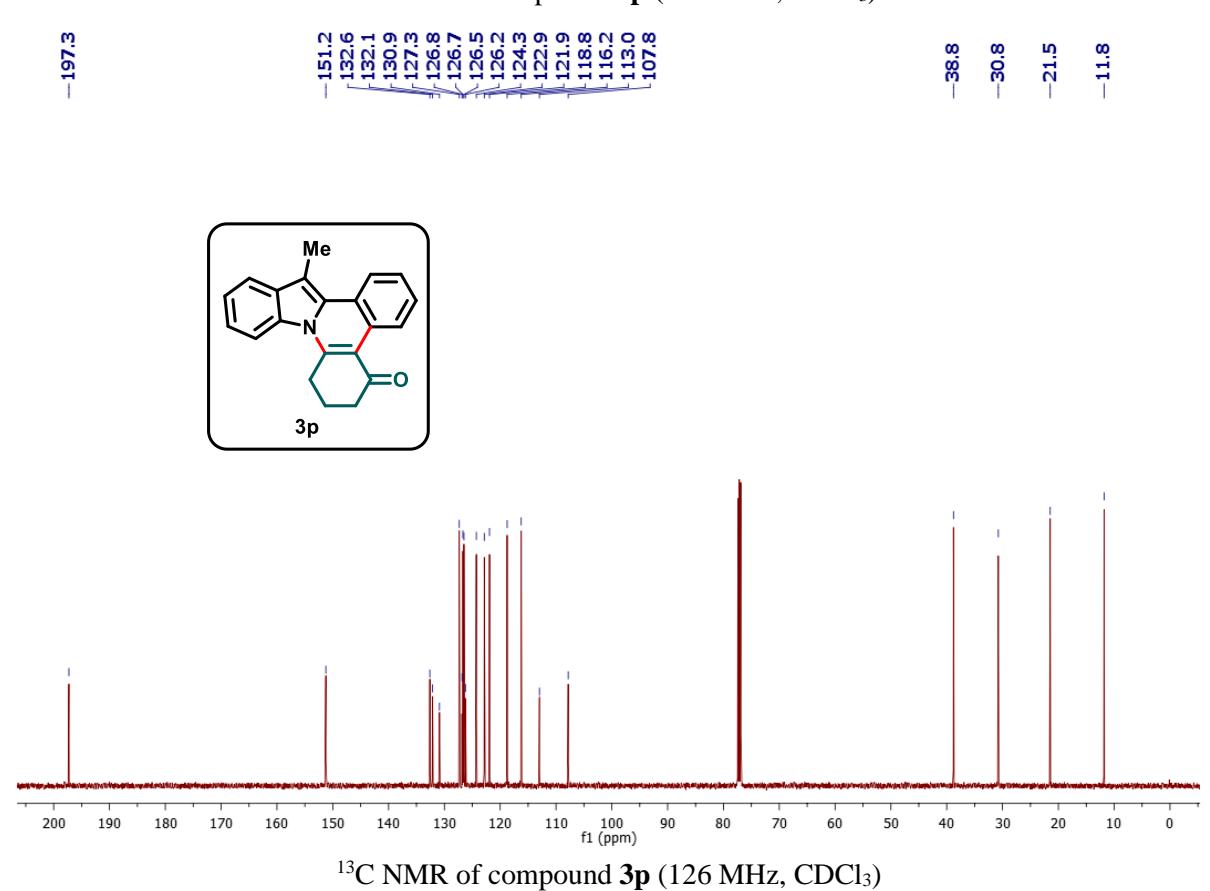
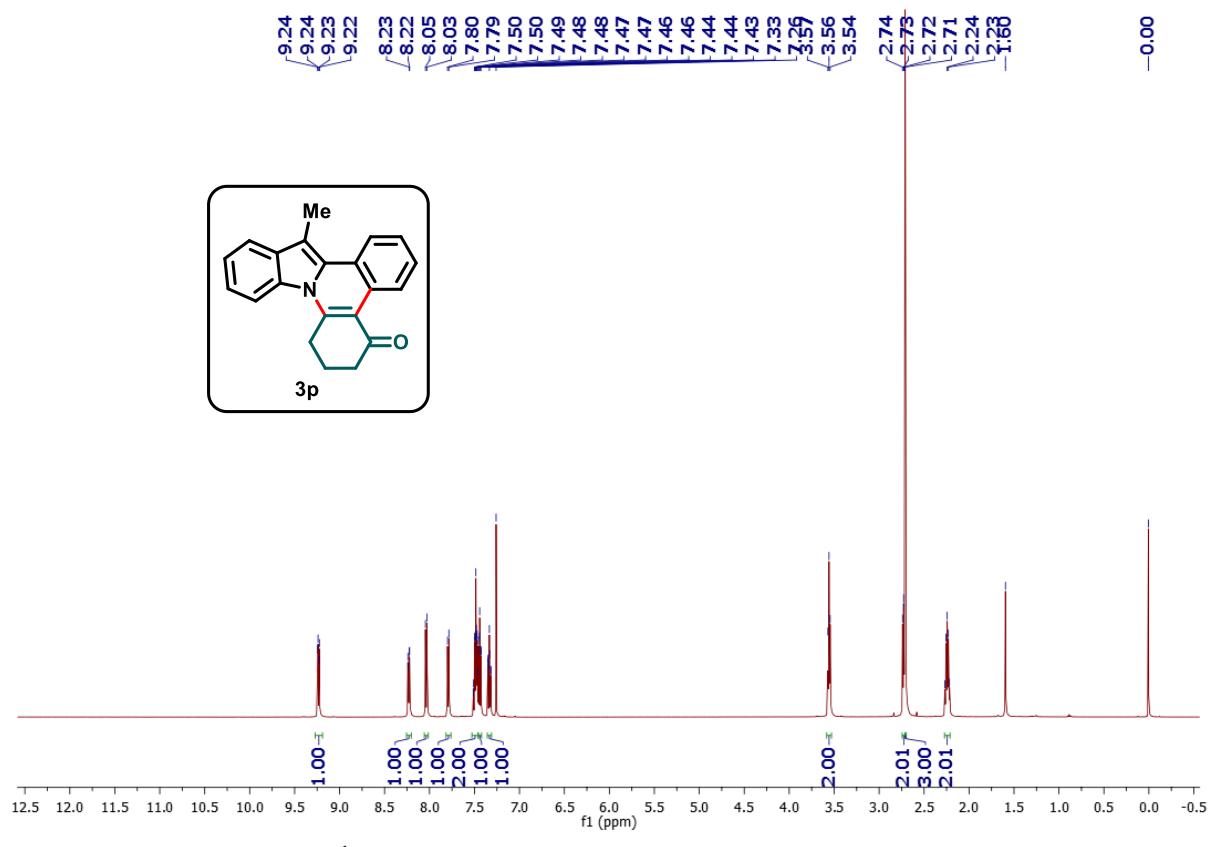


<sup>13</sup>C NMR of compound 3n (126 MHz, CDCl<sub>3</sub>)

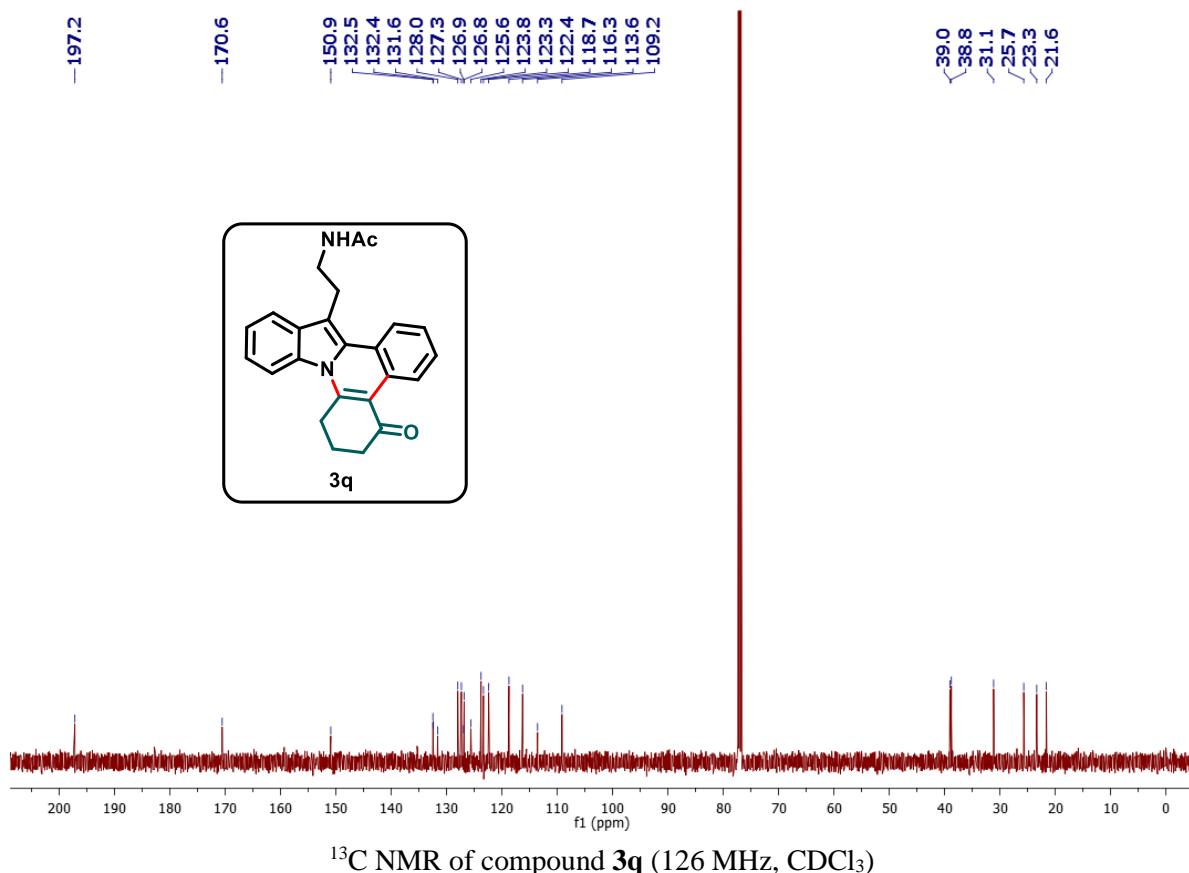
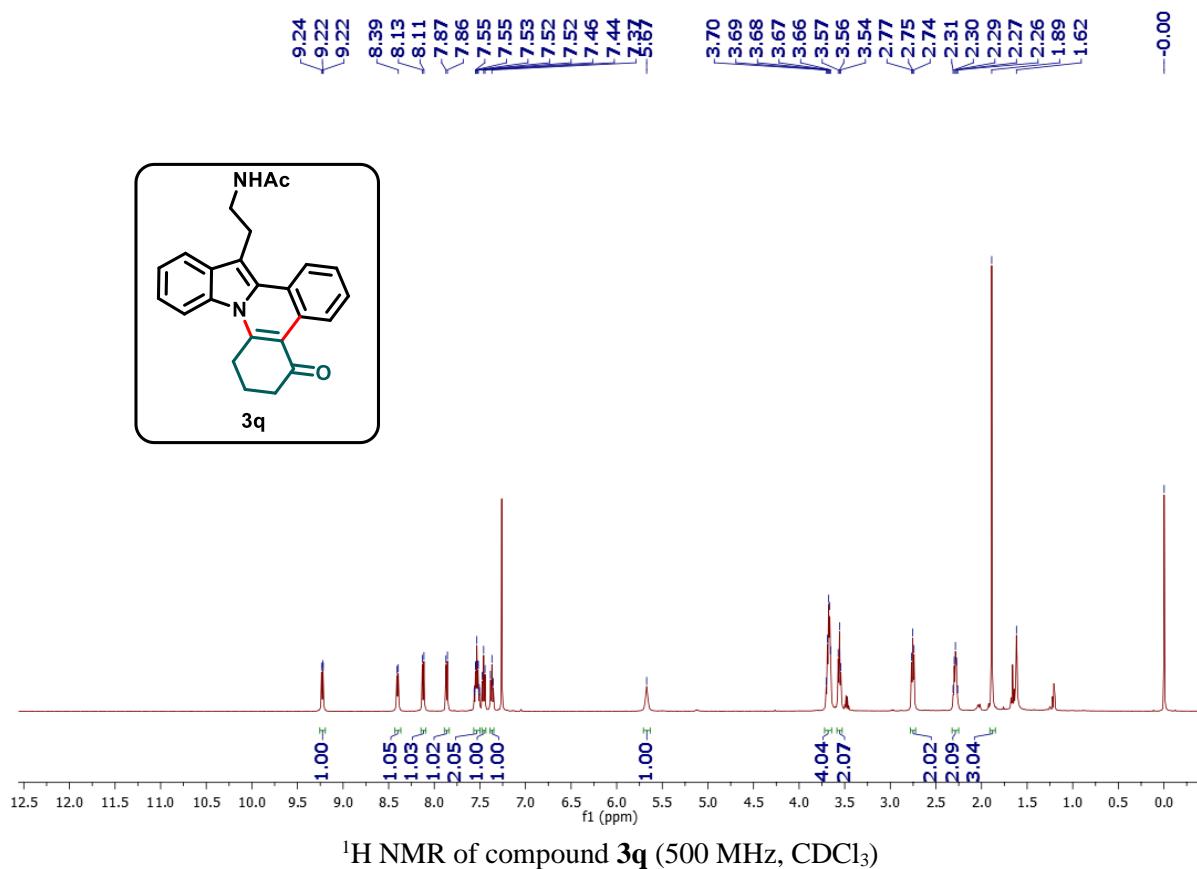
**9,10-dihydrobenzo[*i*]indolo[1,2-*f*]phenanthridin-7(8*H*)-one (**3o**):**



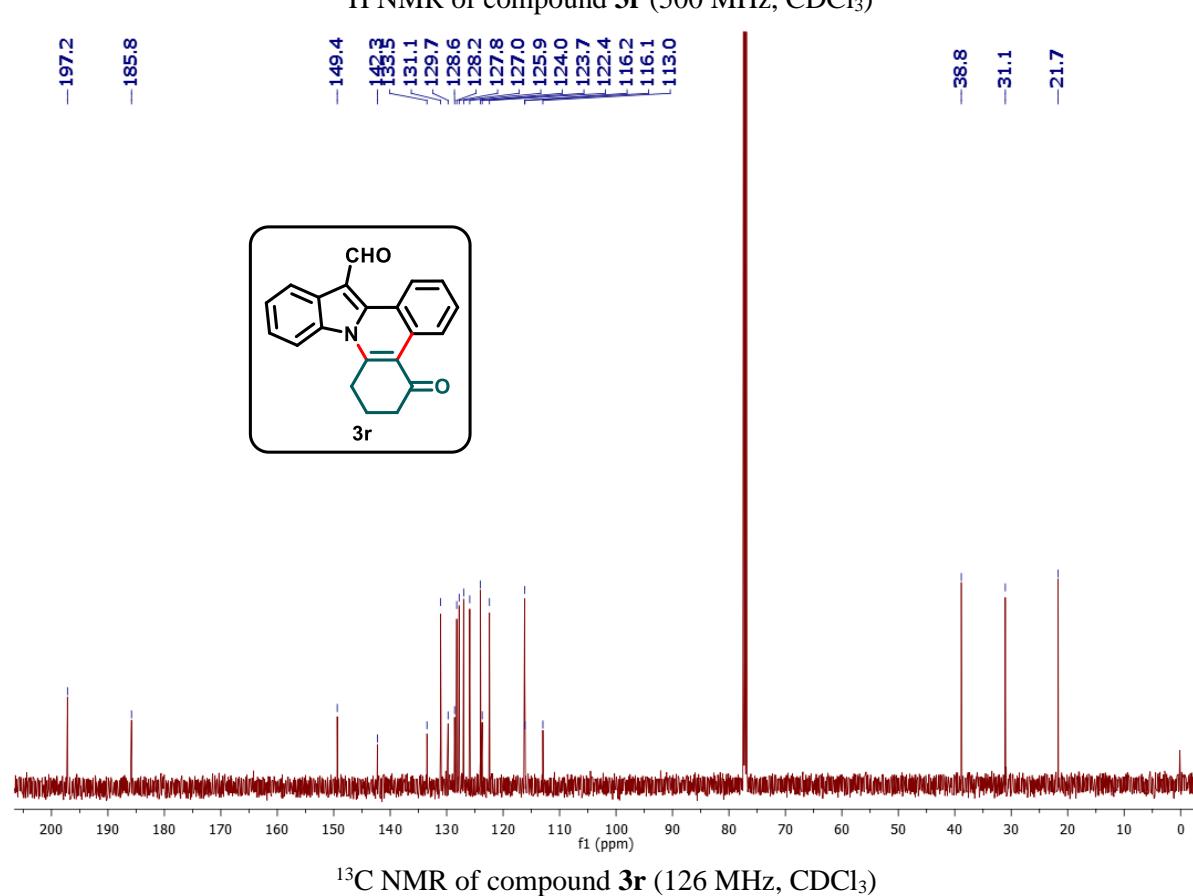
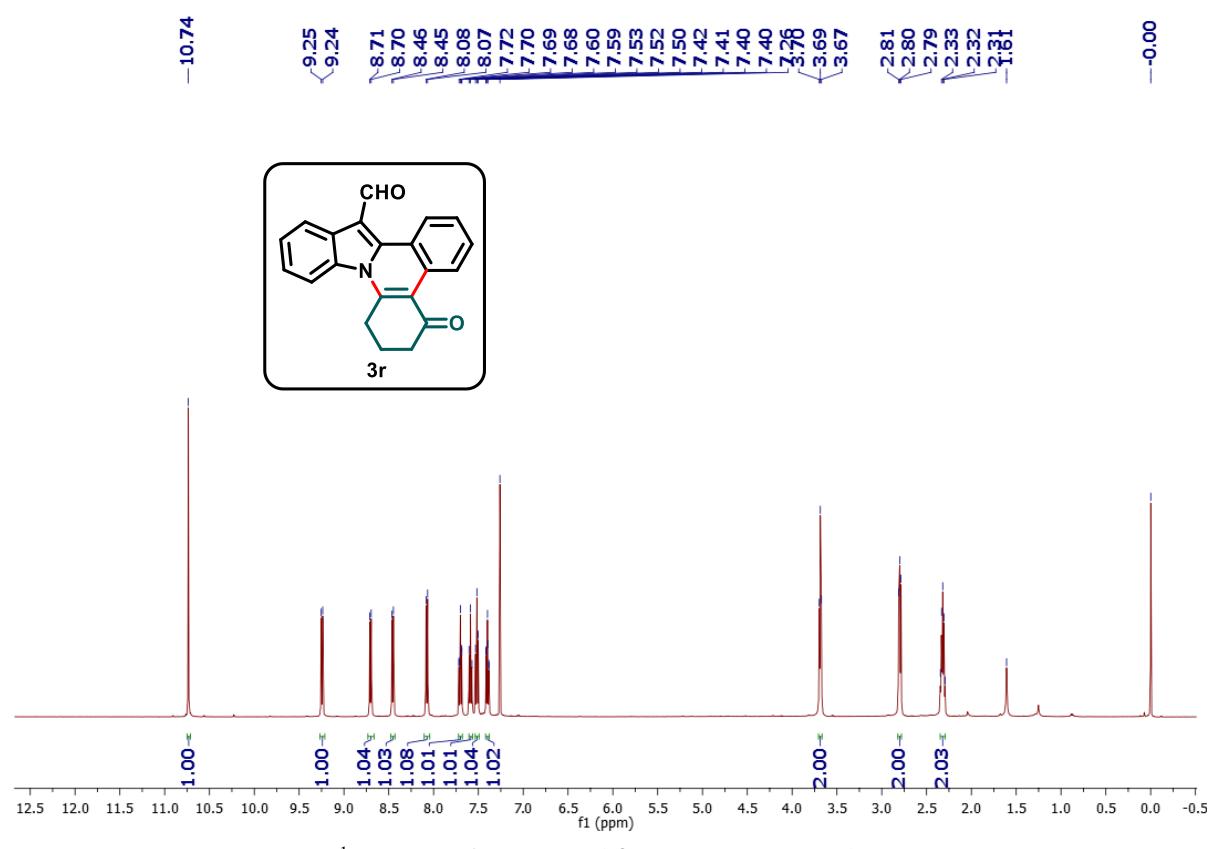
**14-methyl-7,8-dihydroindolo[1,2-f]phenanthridin-5(6H)-one (3p):**



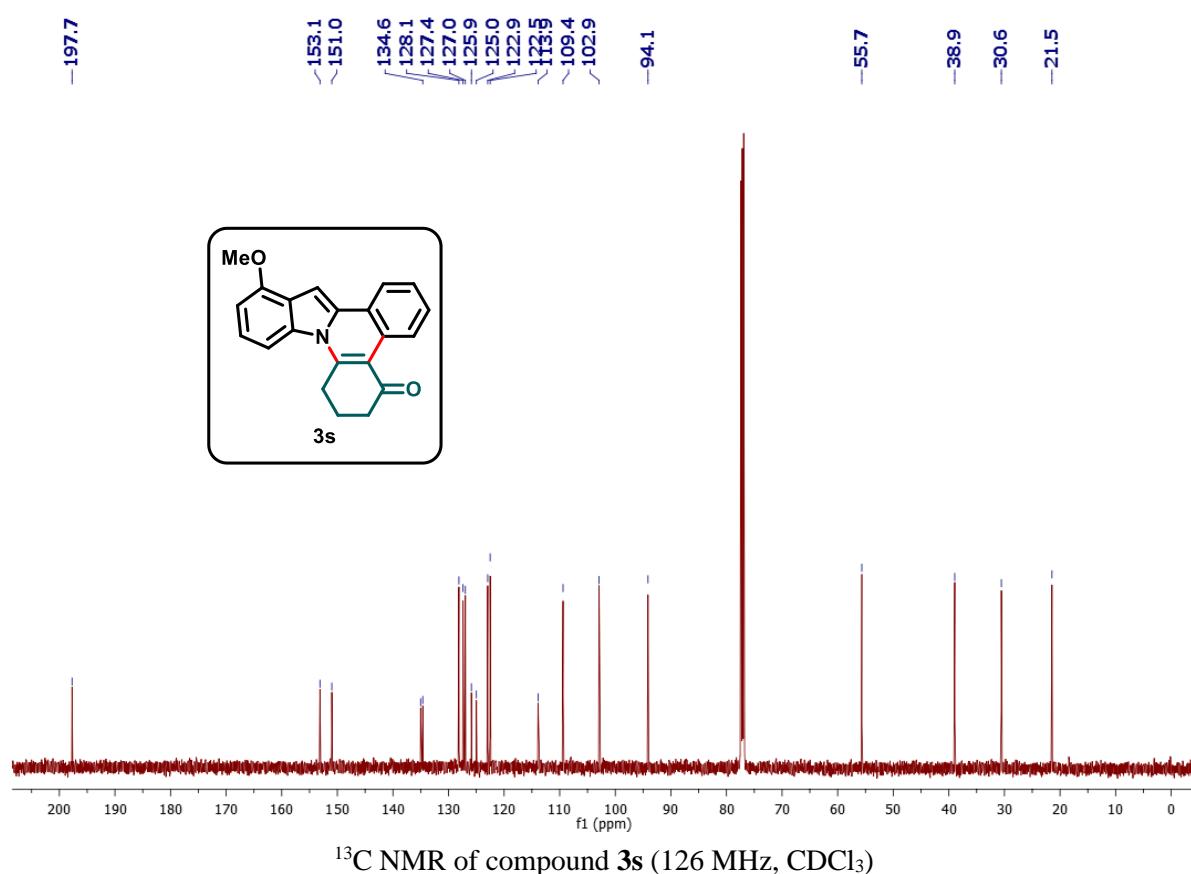
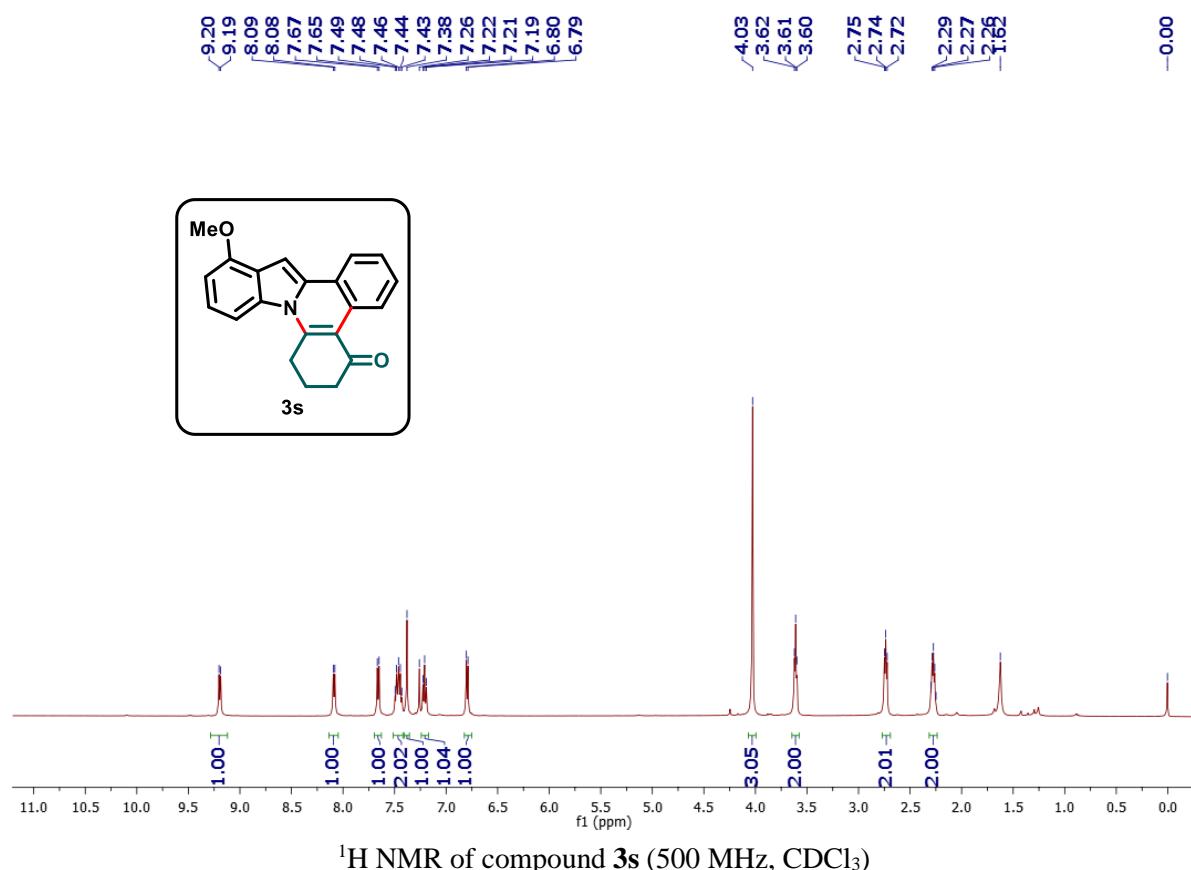
***N*-(2-(5-oxo-5,6,7,8-tetrahydroindolo[1,2-*f*]phenanthridin-14-yl)ethyl)acetamide (3q):**



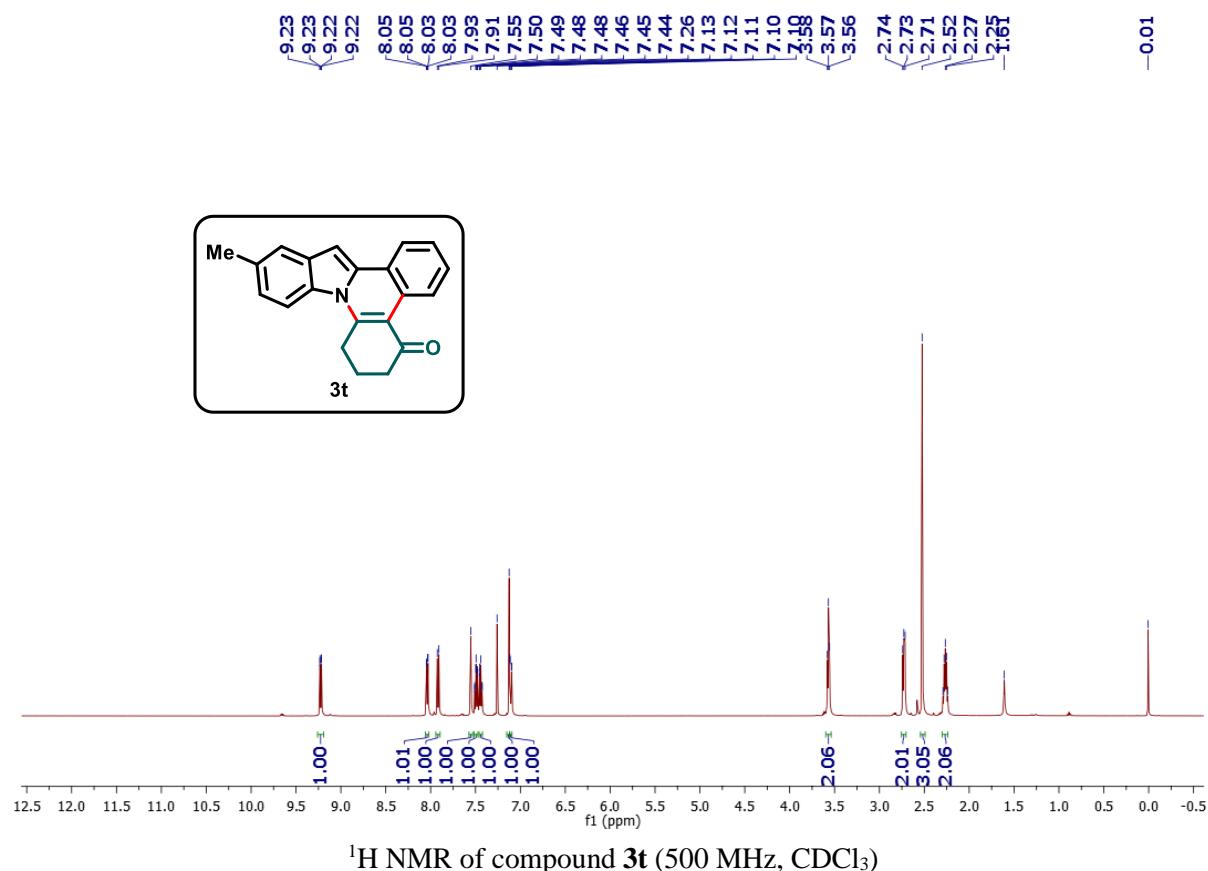
**5-oxo-5,6,7,8-tetrahydroindolo[1,2-*f*]phenanthridine-14-carbaldehyde (3r):**



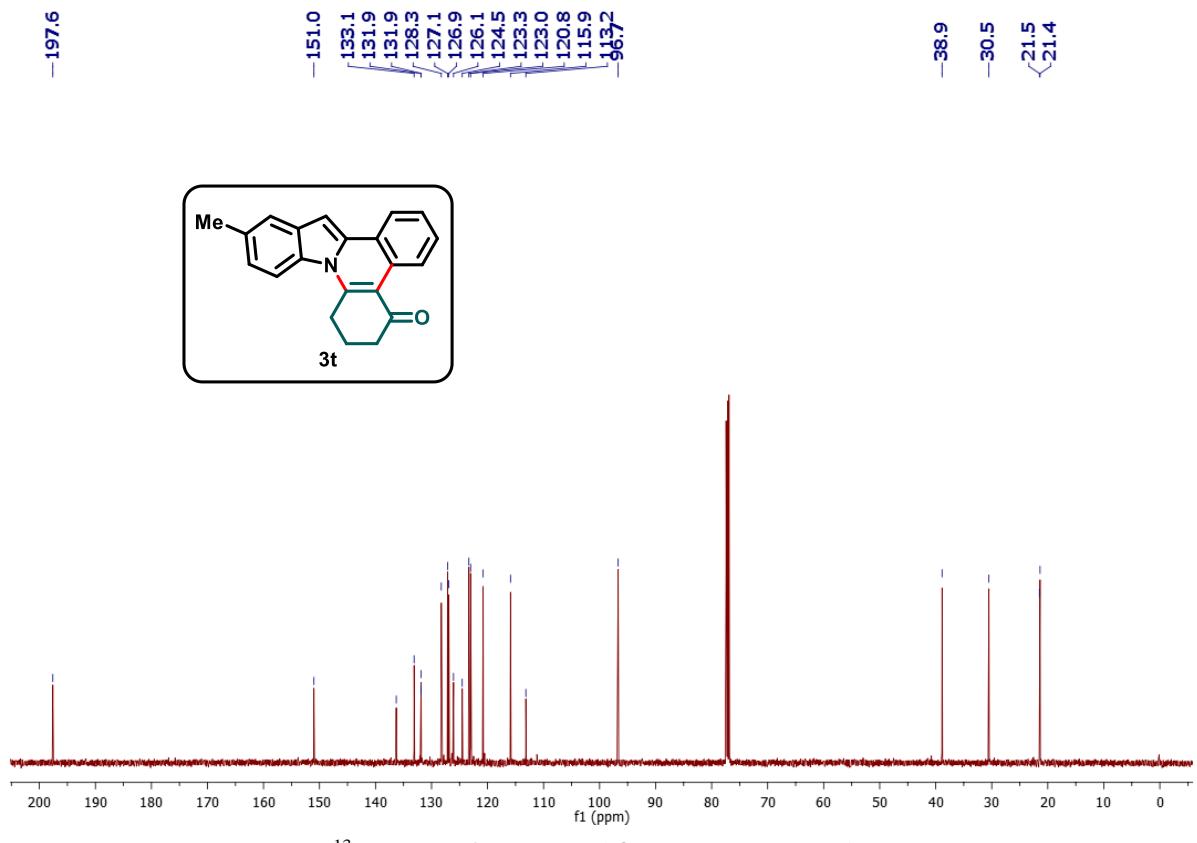
**13-methoxy-7,8-dihydroindolo[1,2-*f*]phenanthridin-5(6*H*)-one (3s):**



**12-methyl-7,8-dihydroindolo[1,2-*f*]phenanthridin-5(6*H*)-one (3t):**

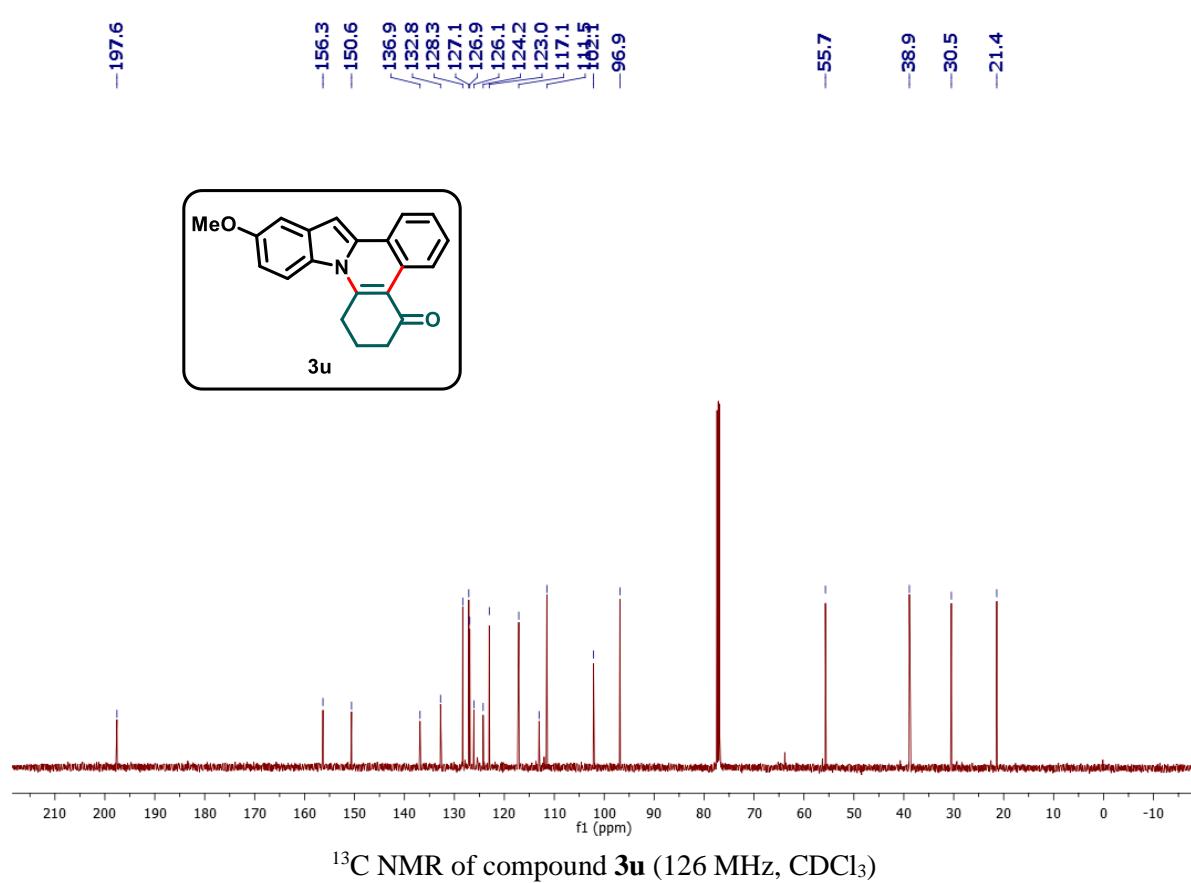
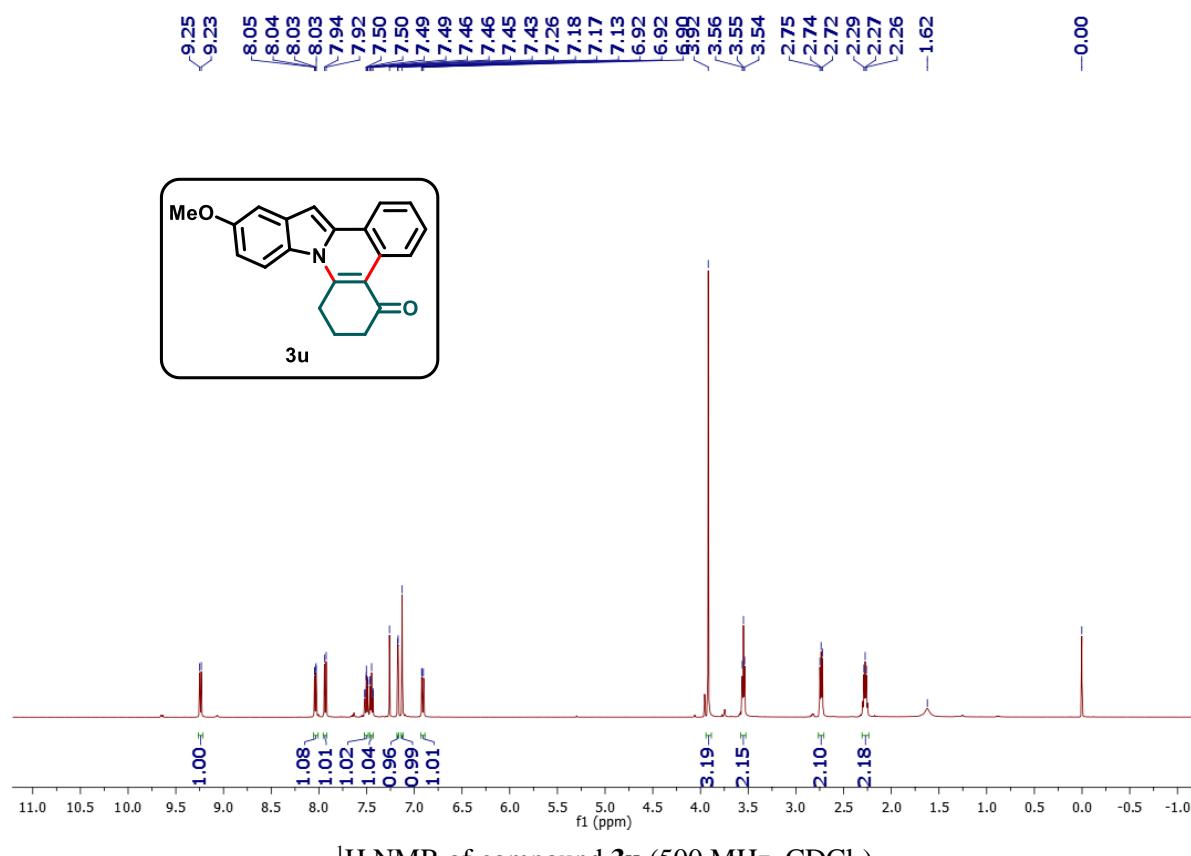


<sup>1</sup>H NMR of compound 3t (500 MHz, CDCl<sub>3</sub>)

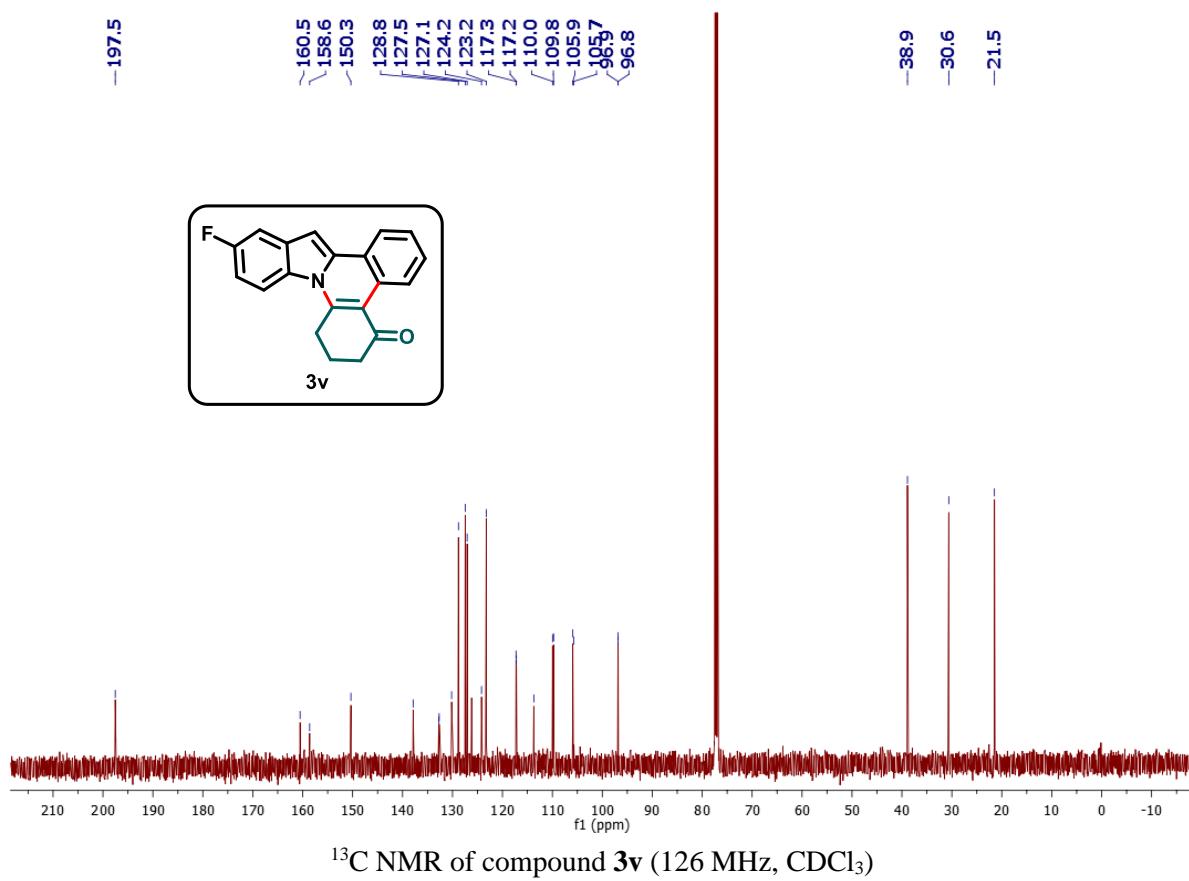
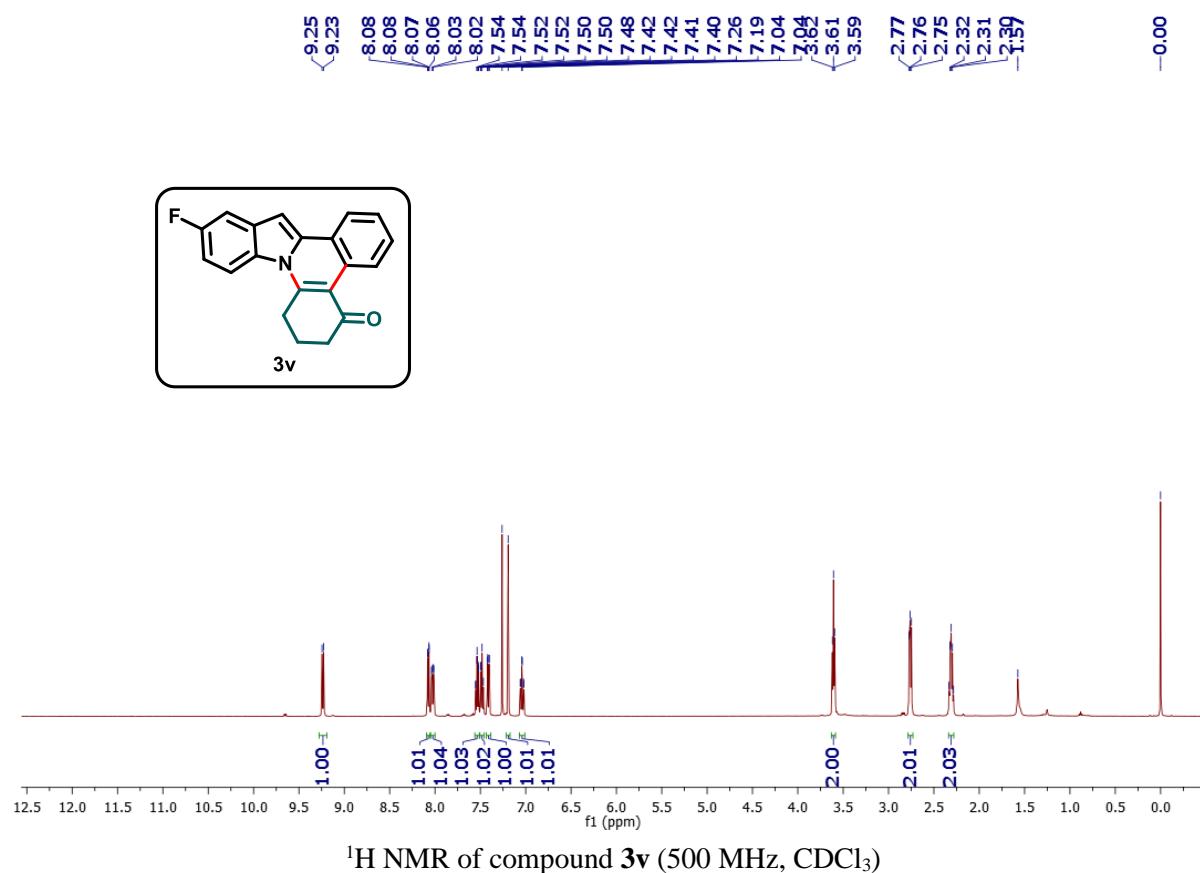


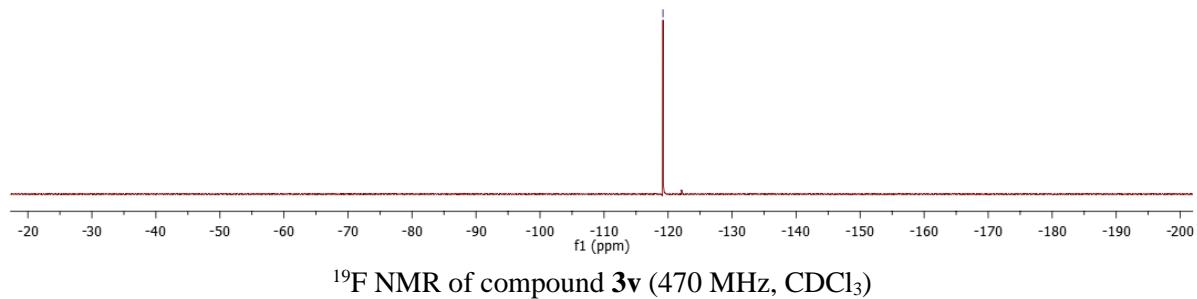
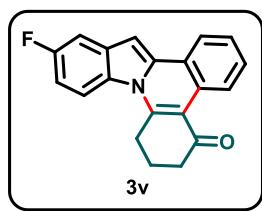
<sup>13</sup>C NMR of compound 3t (126 MHz, CDCl<sub>3</sub>)

**12-methoxy-7,8-dihydroindolo[1,2-*f*]phenanthridin-5(6*H*)-one (**3u**):**



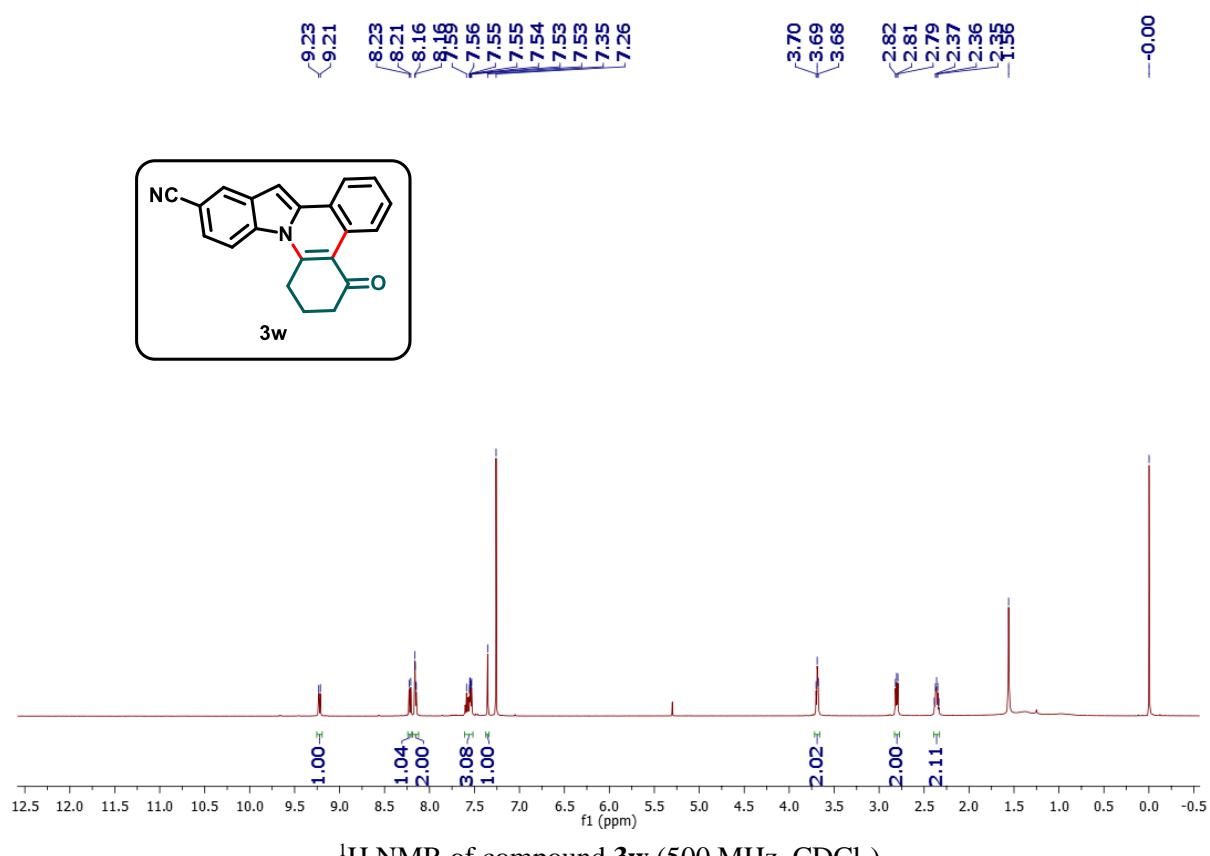
**12-fluoro-7,8-dihydroindolo[1,2-f]phenanthridin-5(6H)-one (3v):**



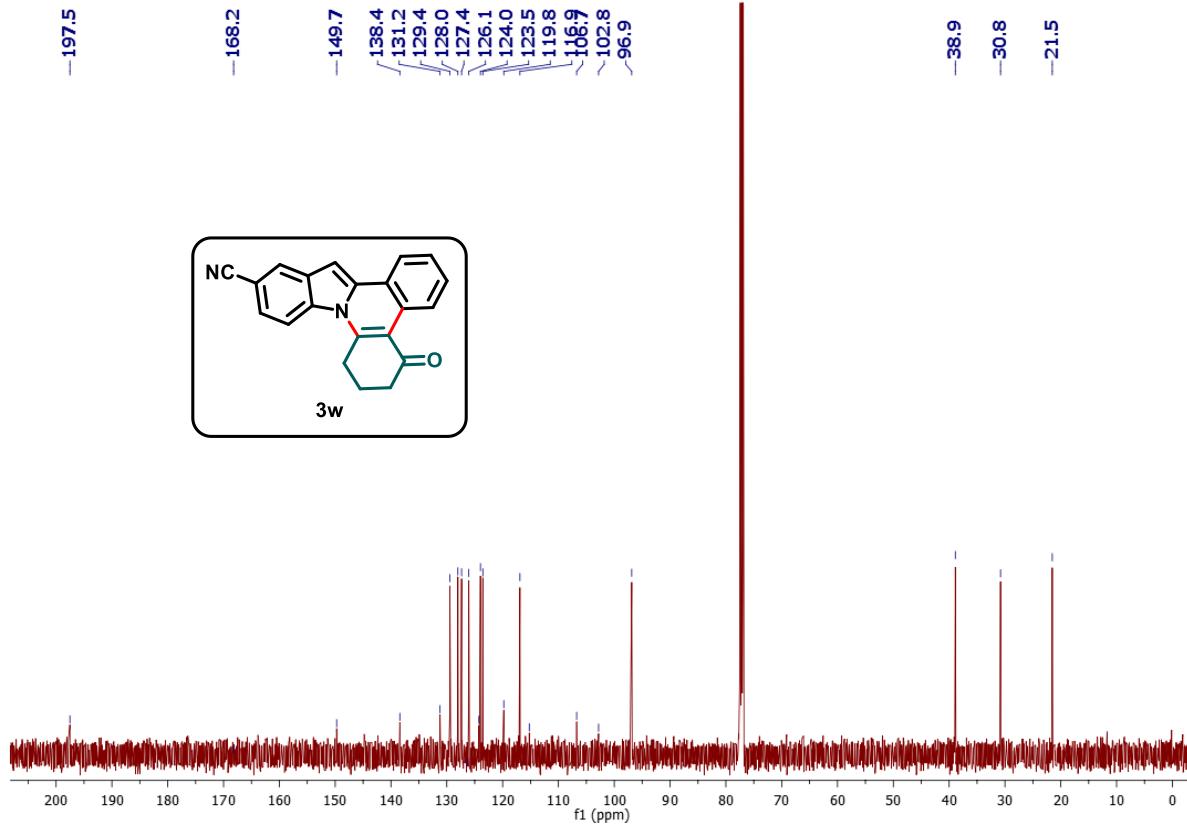


$^{19}\text{F}$  NMR of compound **3v** (470 MHz,  $\text{CDCl}_3$ )

**5-oxo-5,6,7,8-tetrahydroindolo[1,2-*f*]phenanthridine-12-carbonitrile (3w):**

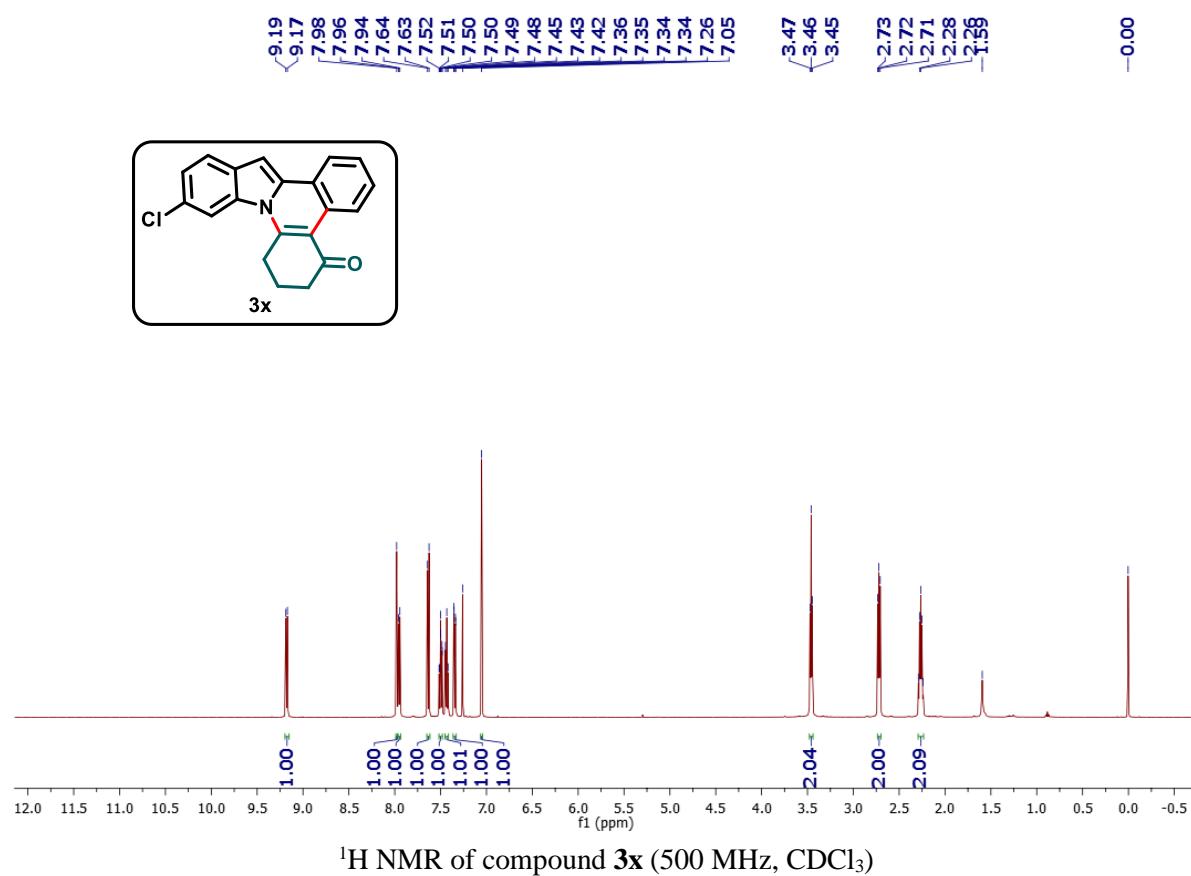


<sup>1</sup>H NMR of compound 3w (500 MHz, CDCl<sub>3</sub>)

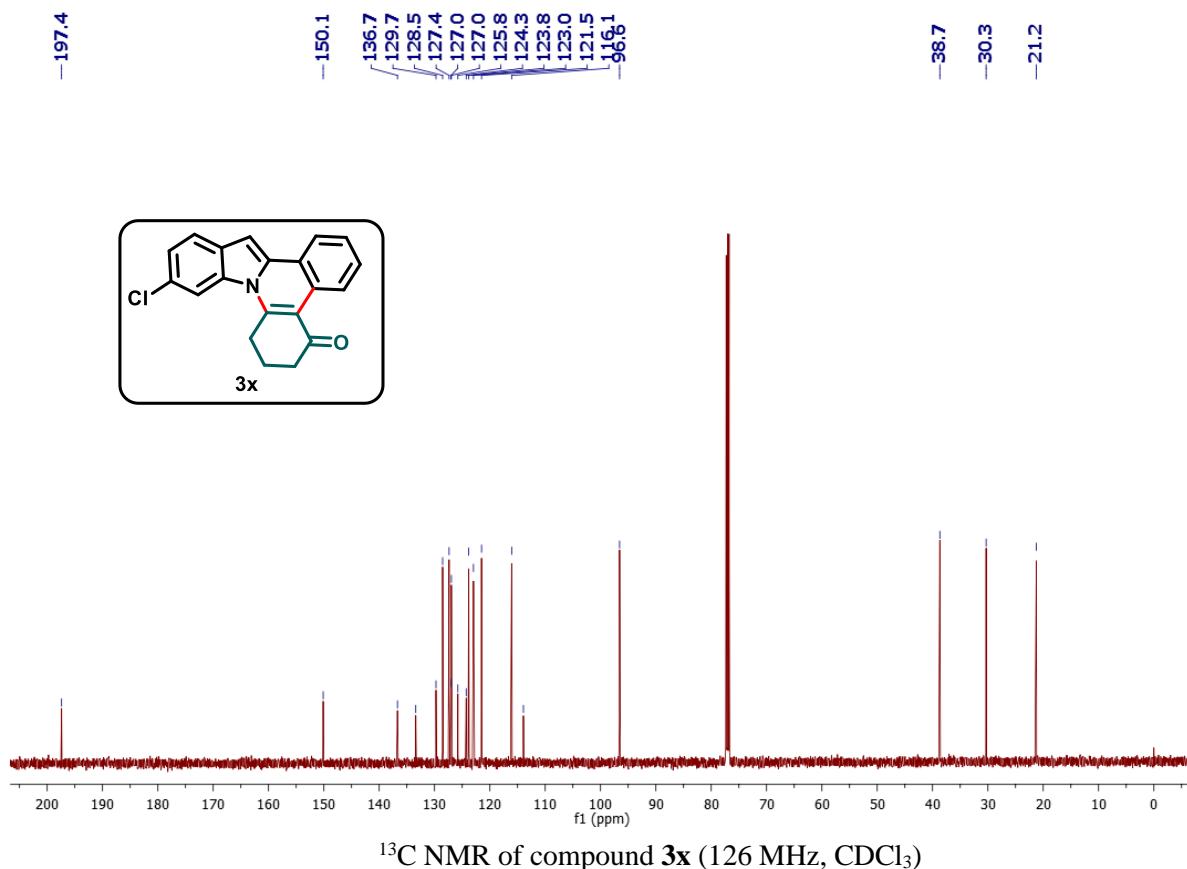


<sup>13</sup>C NMR of compound 3w (126 MHz, CDCl<sub>3</sub>)

**11-chloro-7,8-dihydroindolo[1,2-f]phenanthridin-5(6H)-one (3x):**

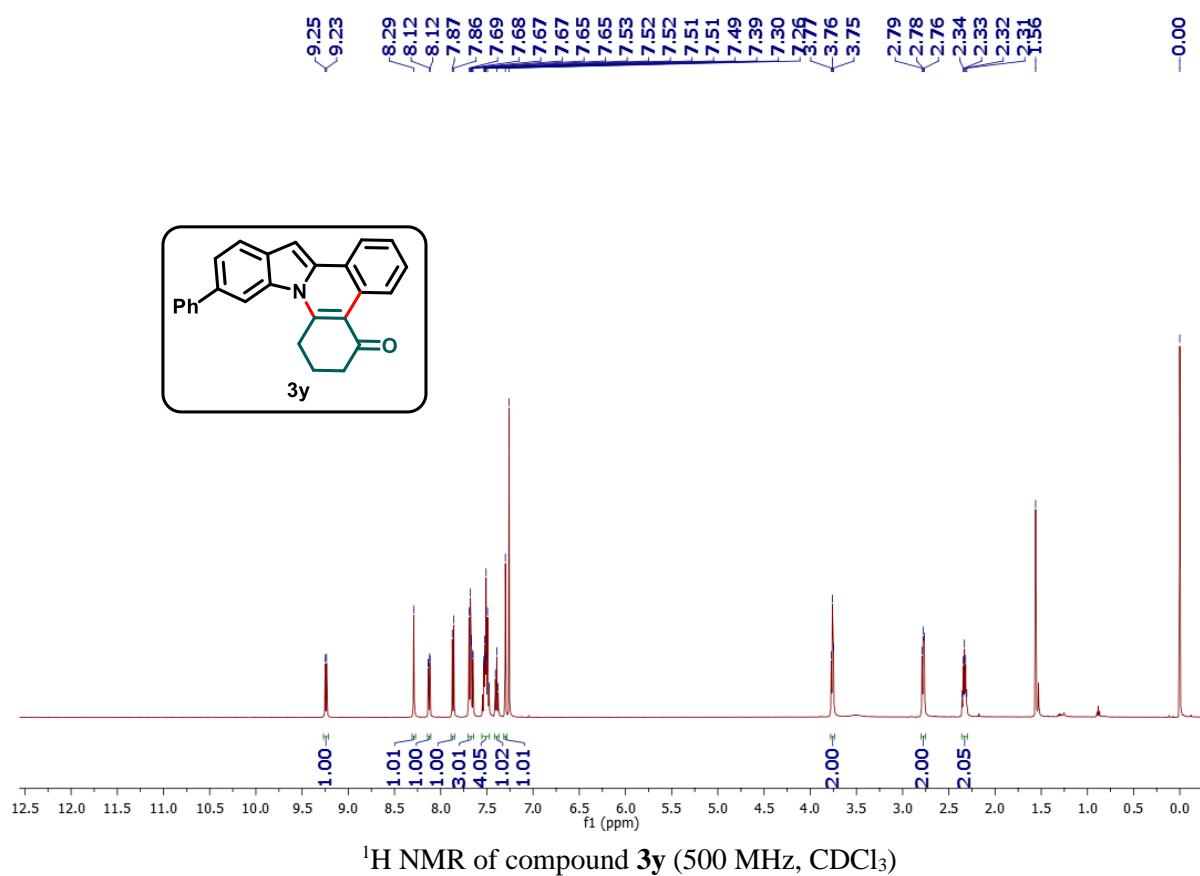


<sup>1</sup>H NMR of compound 3x (500 MHz, CDCl<sub>3</sub>)

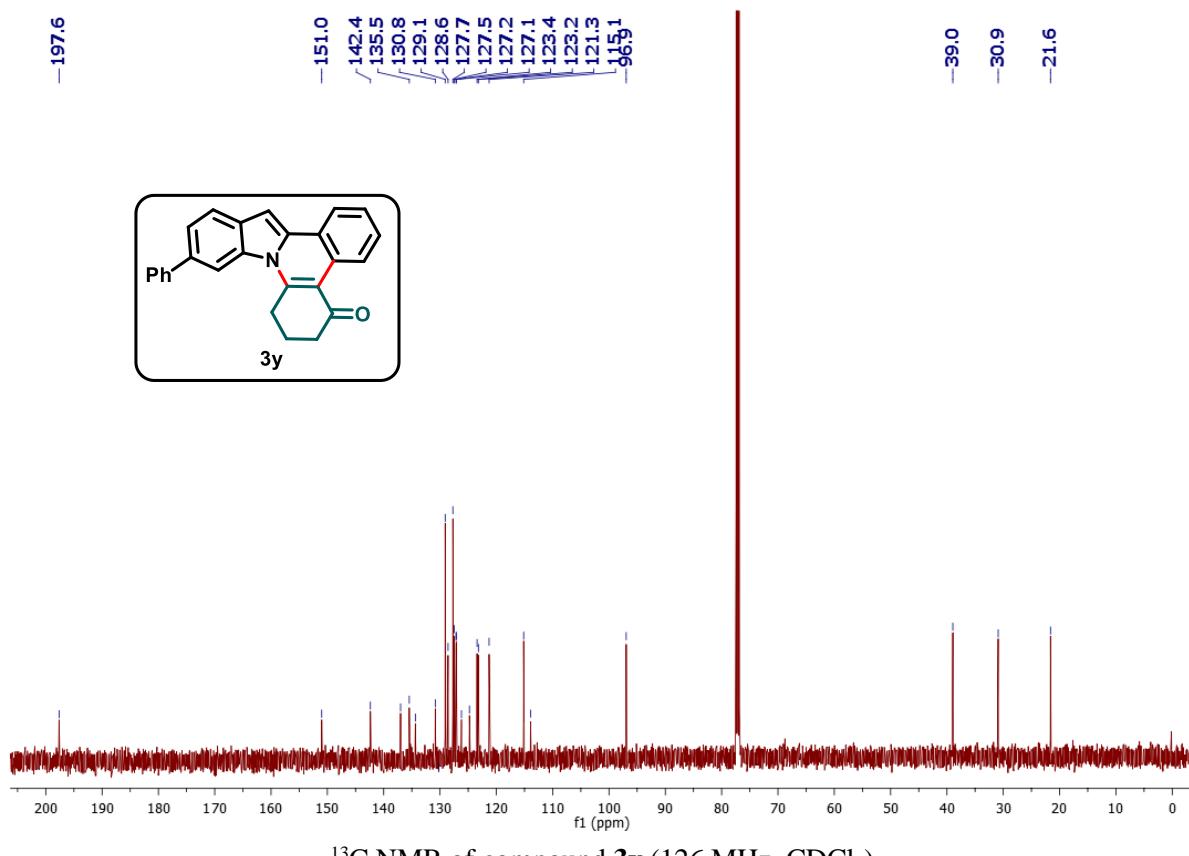


<sup>13</sup>C NMR of compound 3x (126 MHz, CDCl<sub>3</sub>)

**11-phenyl-7,8-dihydroindolo[1,2-*f*]phenanthridin-5(6*H*)-one (**3y**):**

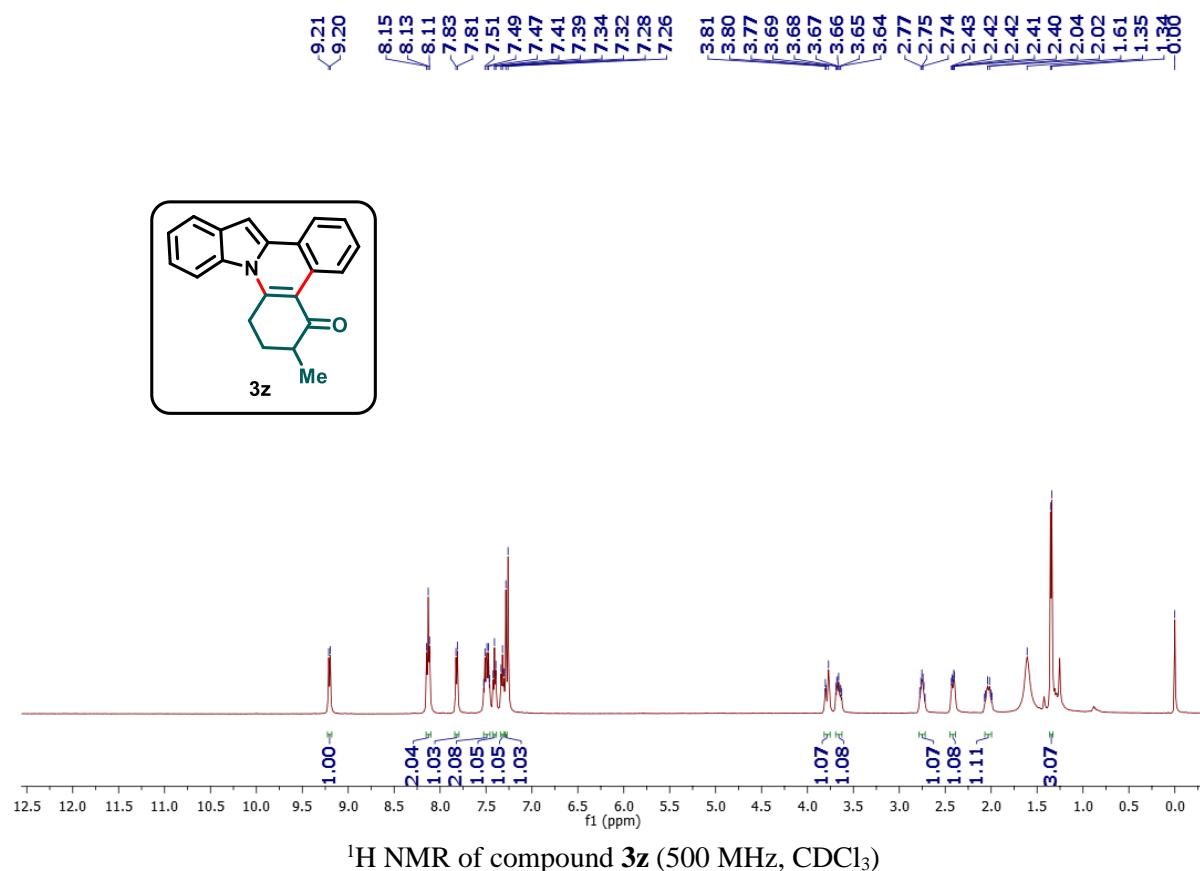


<sup>1</sup>H NMR of compound **3y** (500 MHz, CDCl<sub>3</sub>)

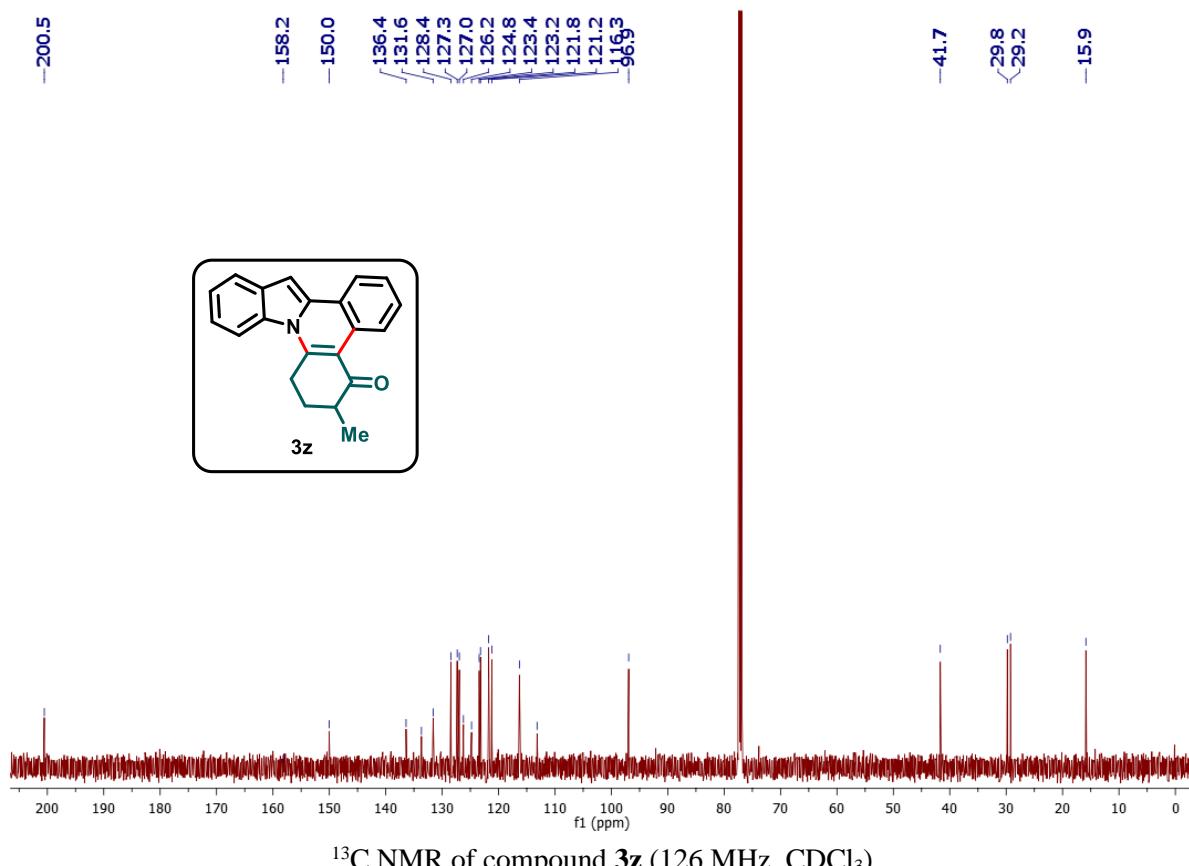


<sup>13</sup>C NMR of compound **3y** (126 MHz, CDCl<sub>3</sub>)

**6-methyl-7,8-dihydroindolo[1,2-f]phenanthridin-5(6H)-one (3z):**

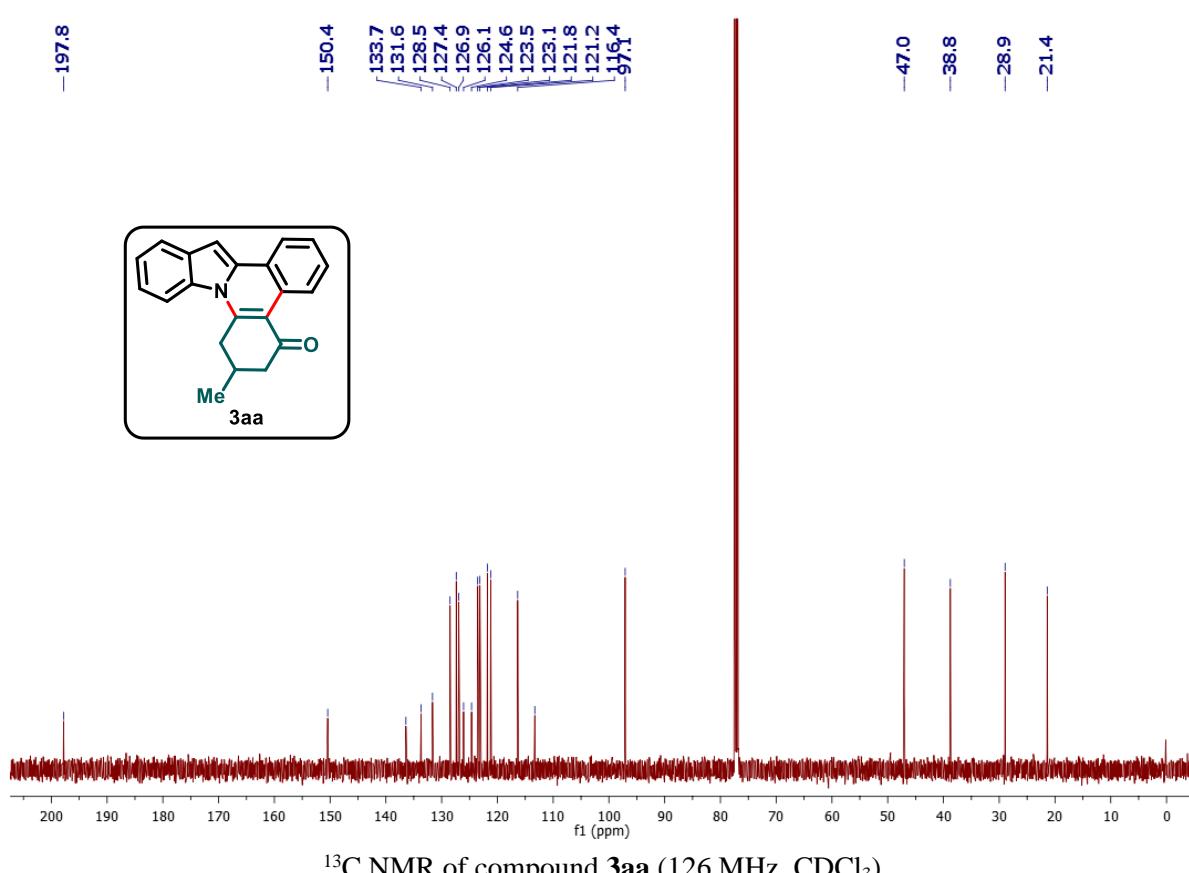
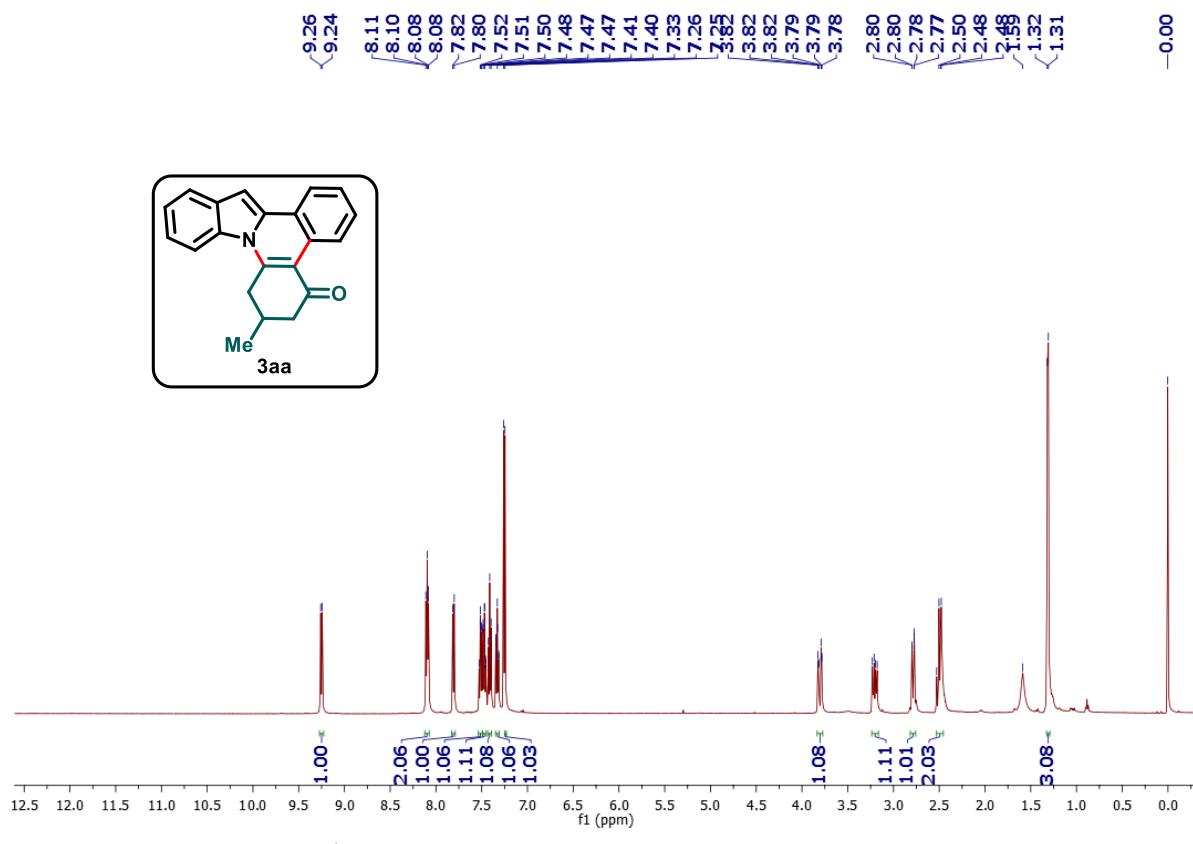


<sup>1</sup>H NMR of compound **3z** (500 MHz, CDCl<sub>3</sub>)

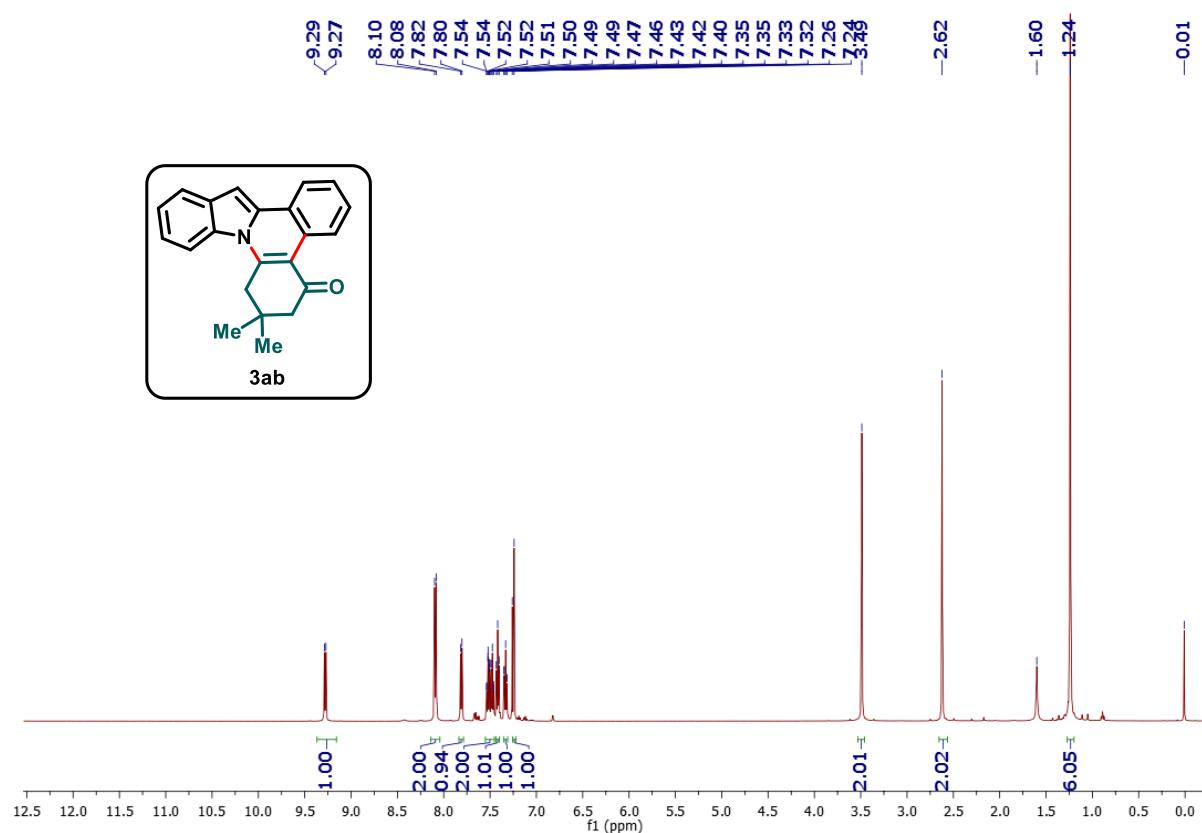


<sup>13</sup>C NMR of compound **3z** (126 MHz, CDCl<sub>3</sub>)

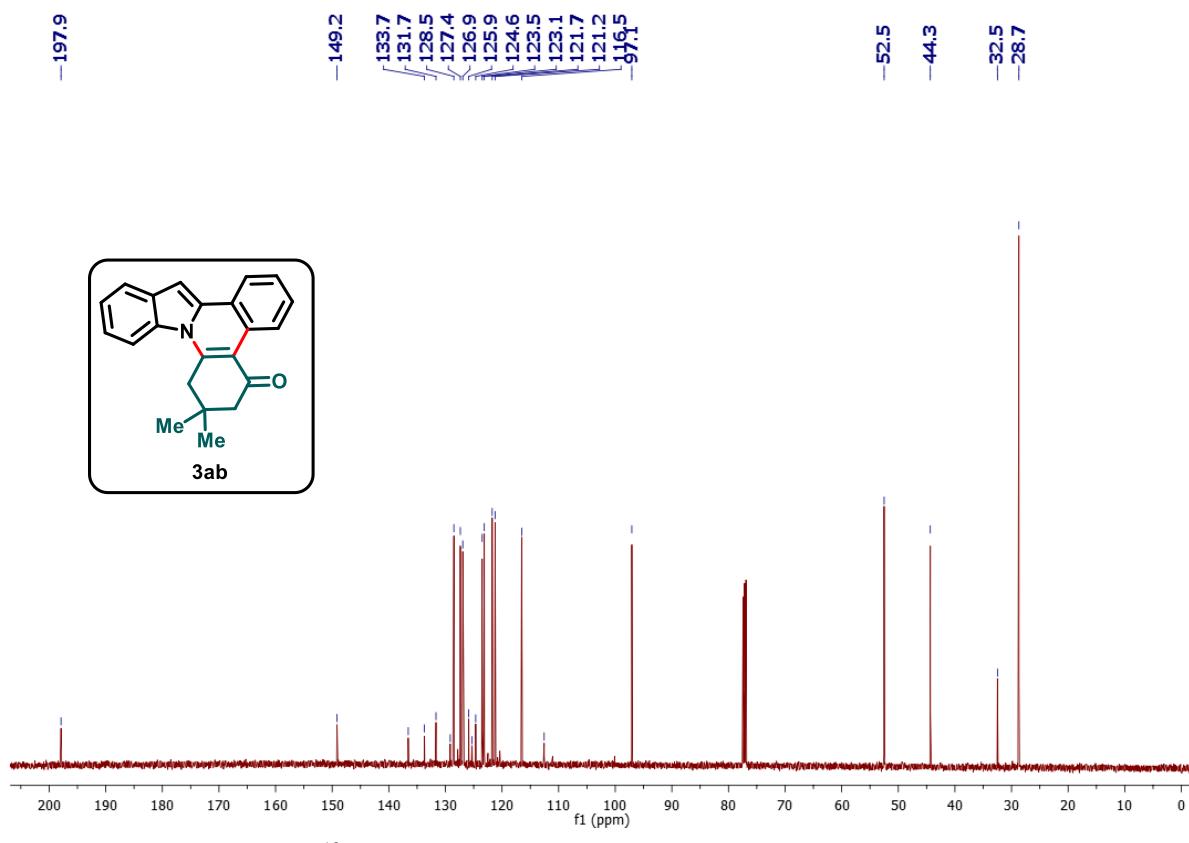
**7-methyl-7,8-dihydroindolo[1,2-f]phenanthridin-5(6H)-one (3aa):**



**7,7-dimethyl-7,8-dihydroindolo[1,2-f]phenanthridin-5(6H)-one (3ab):**

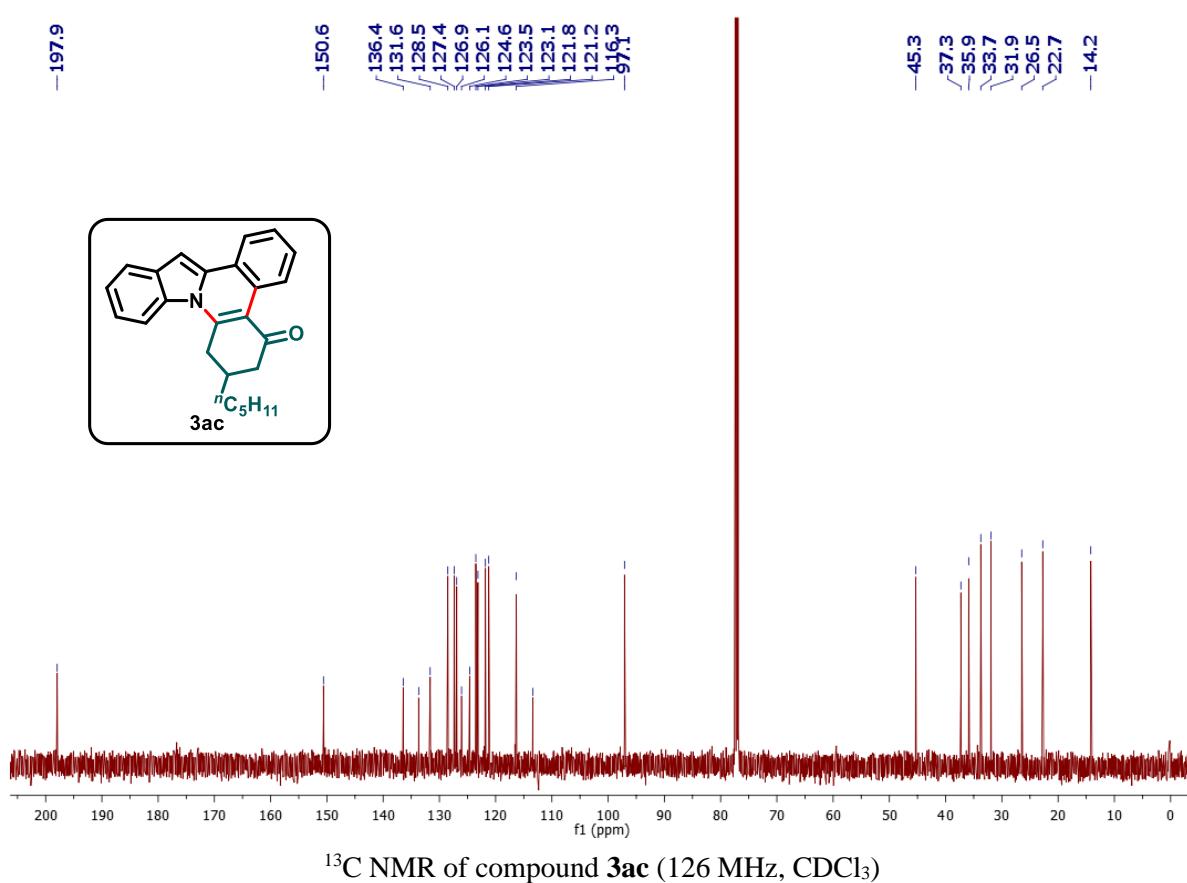
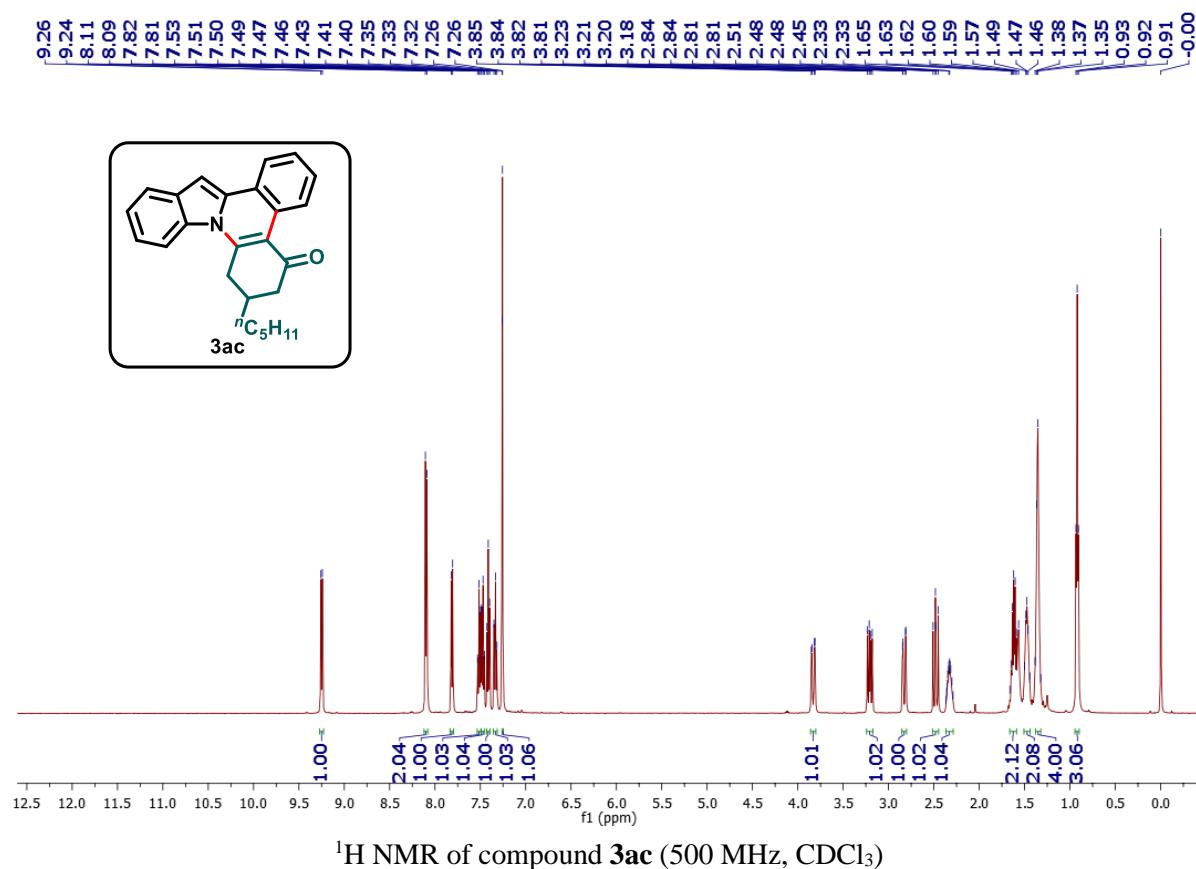


<sup>1</sup>H NMR of compound 3ab (500 MHz, CDCl<sub>3</sub>)

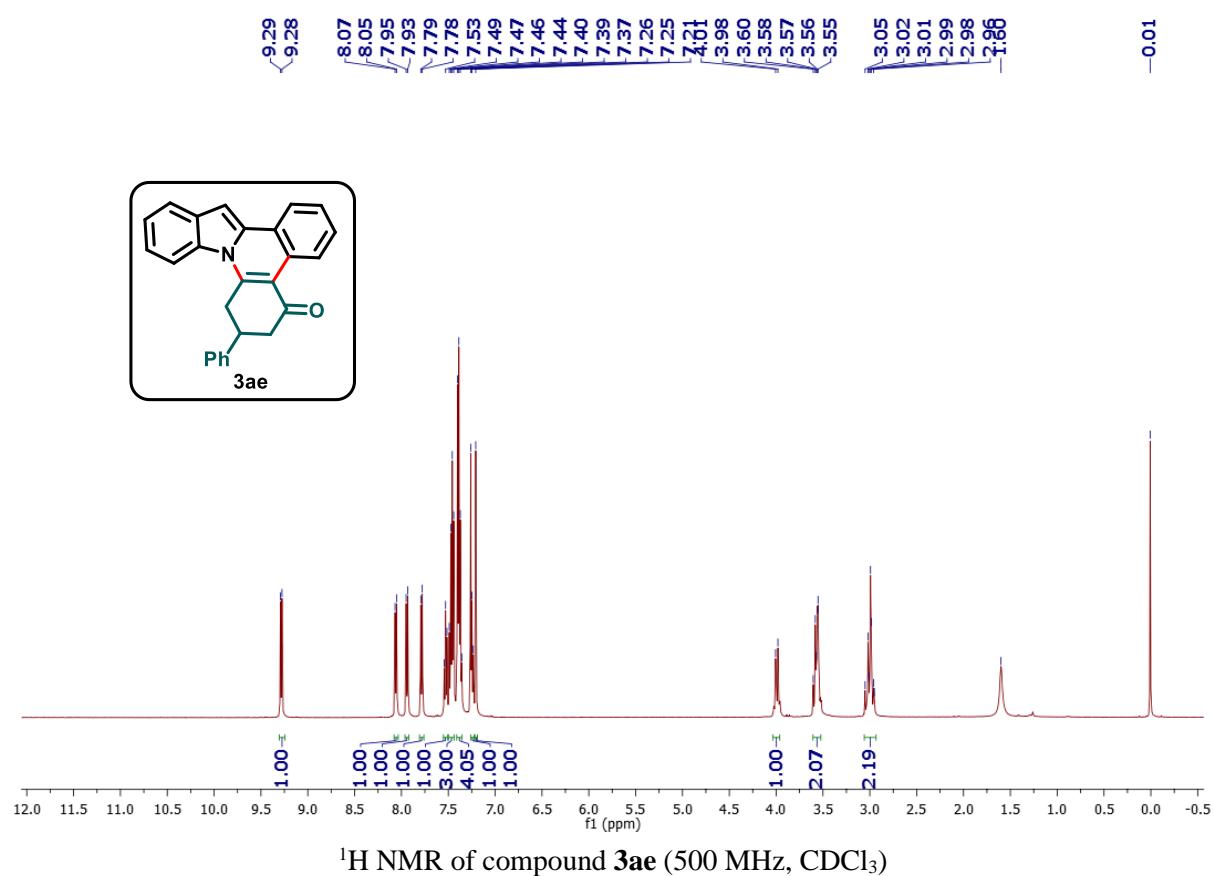


<sup>13</sup>C NMR of compound 3ab (126 MHz, CDCl<sub>3</sub>)

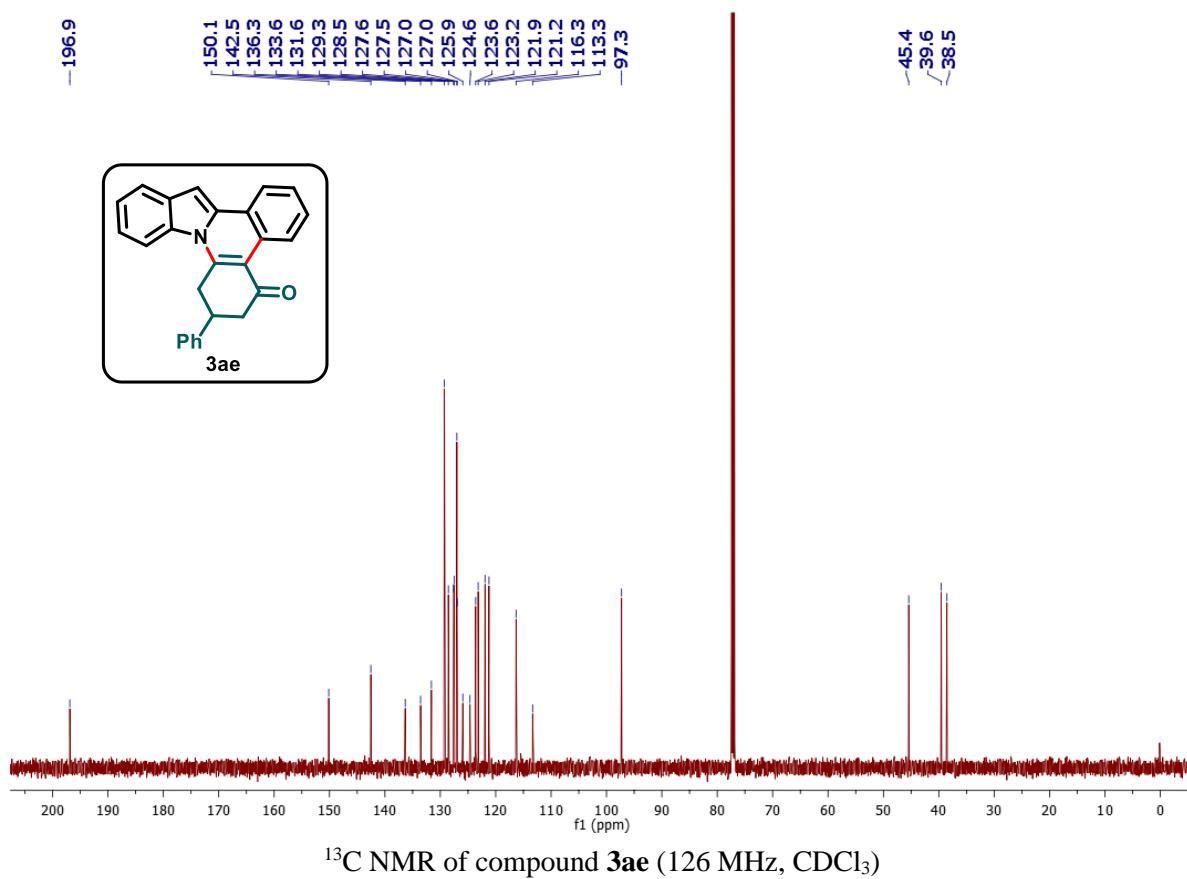
**7-pentyl-7,8-dihydroindolo[1,2-f]phenanthridin-5(6H)-one (3ac):**



**7-phenyl-7,8-dihydroindolo[1,2-f]phenanthridin-5(6H)-one (3ae):**

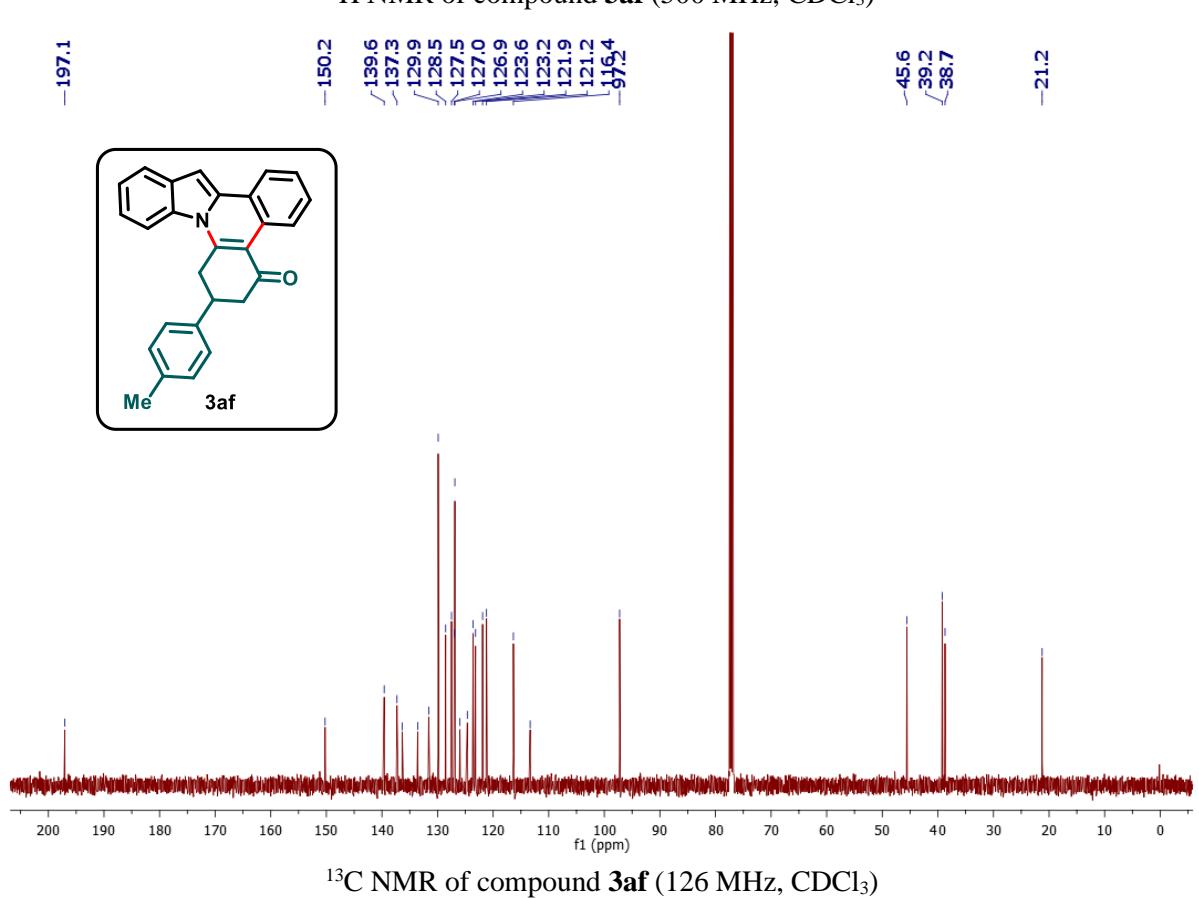
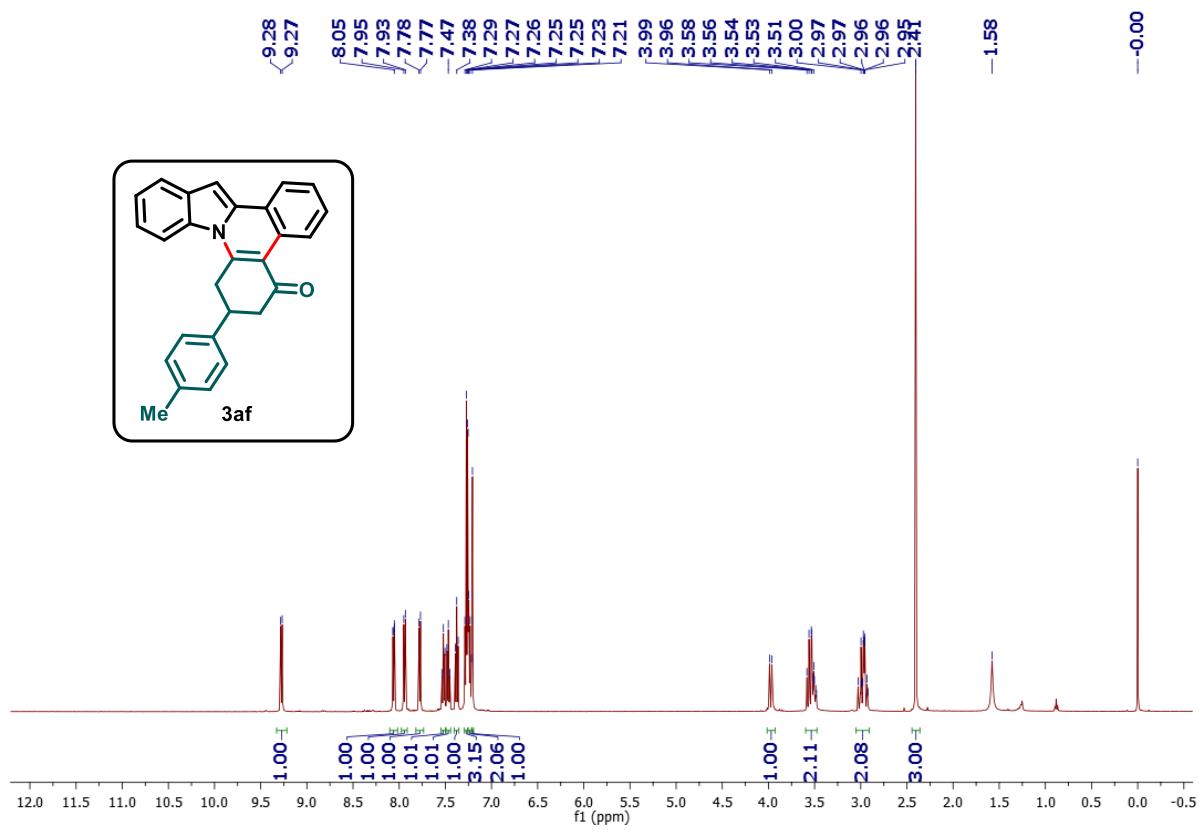


<sup>1</sup>H NMR of compound 3ae (500 MHz, CDCl<sub>3</sub>)

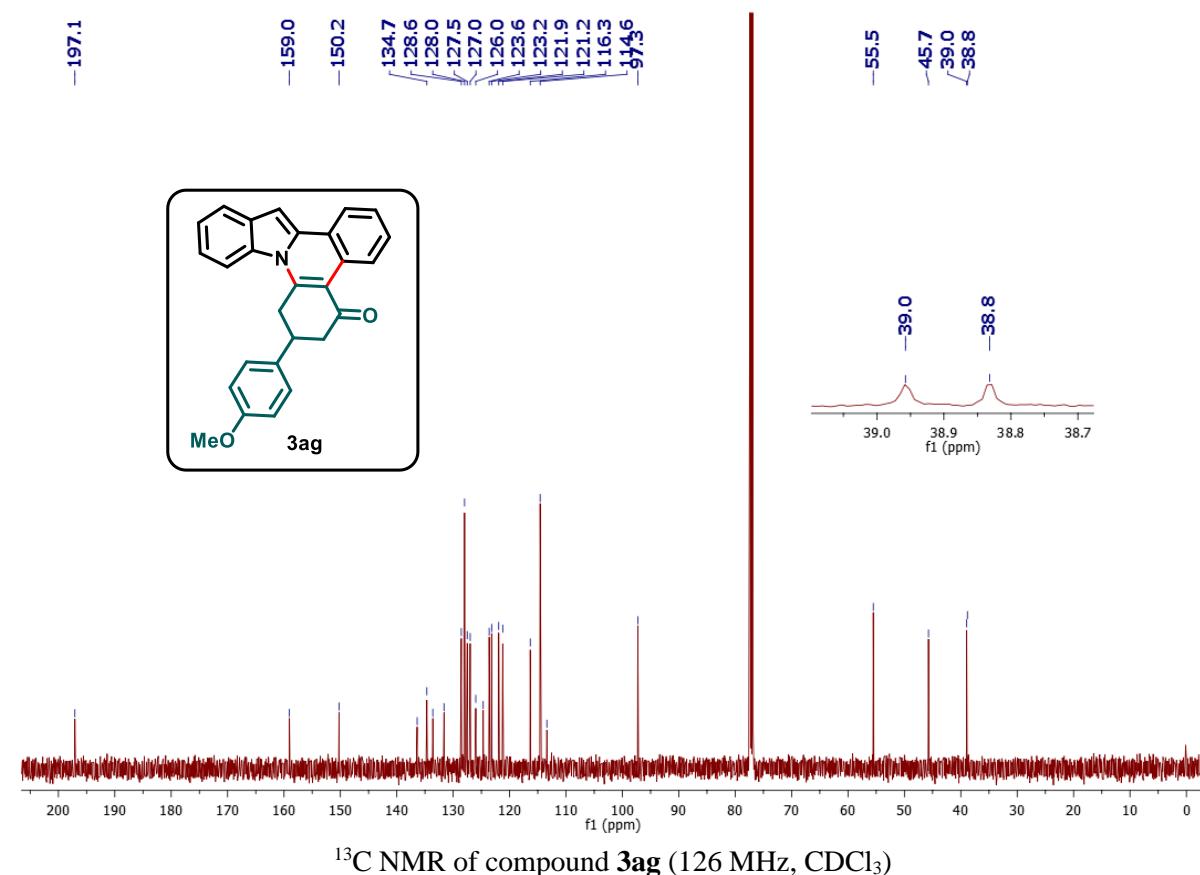
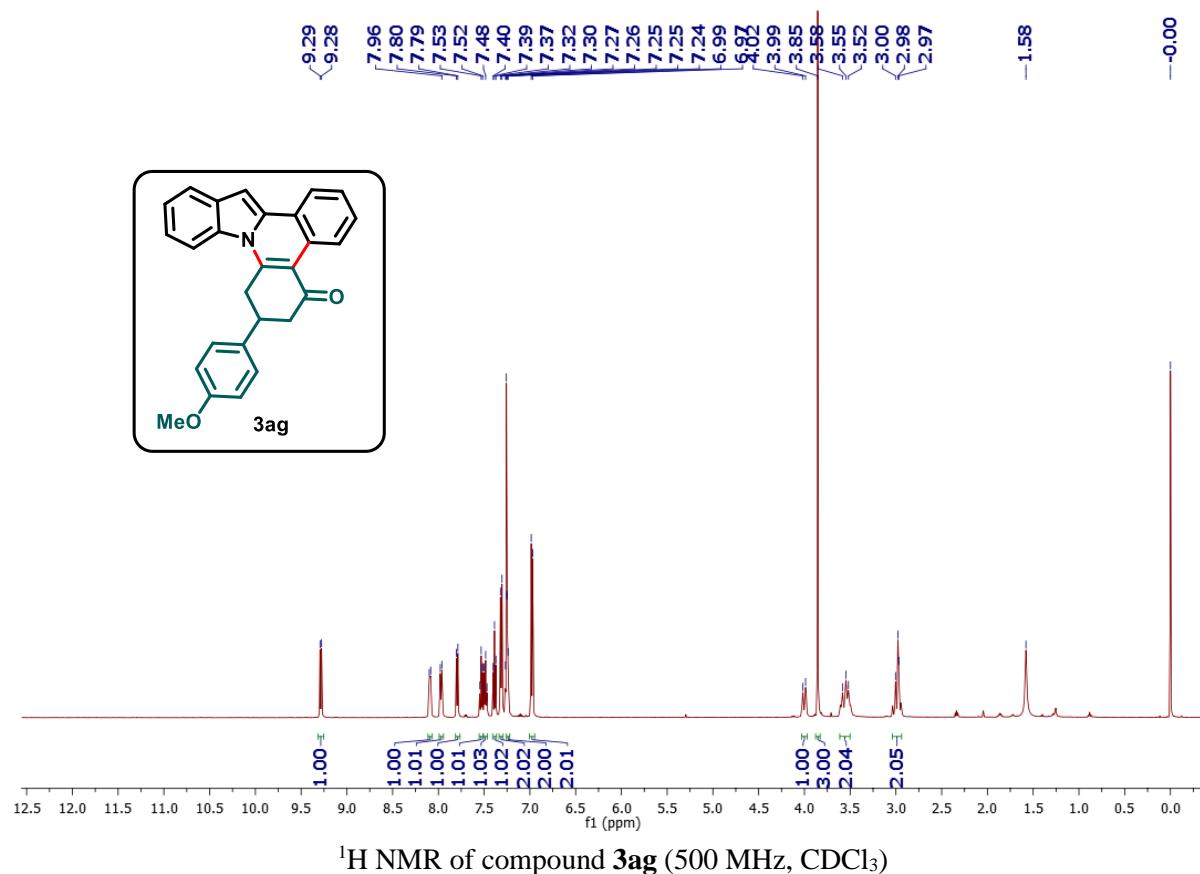


<sup>13</sup>C NMR of compound 3ae (126 MHz, CDCl<sub>3</sub>)

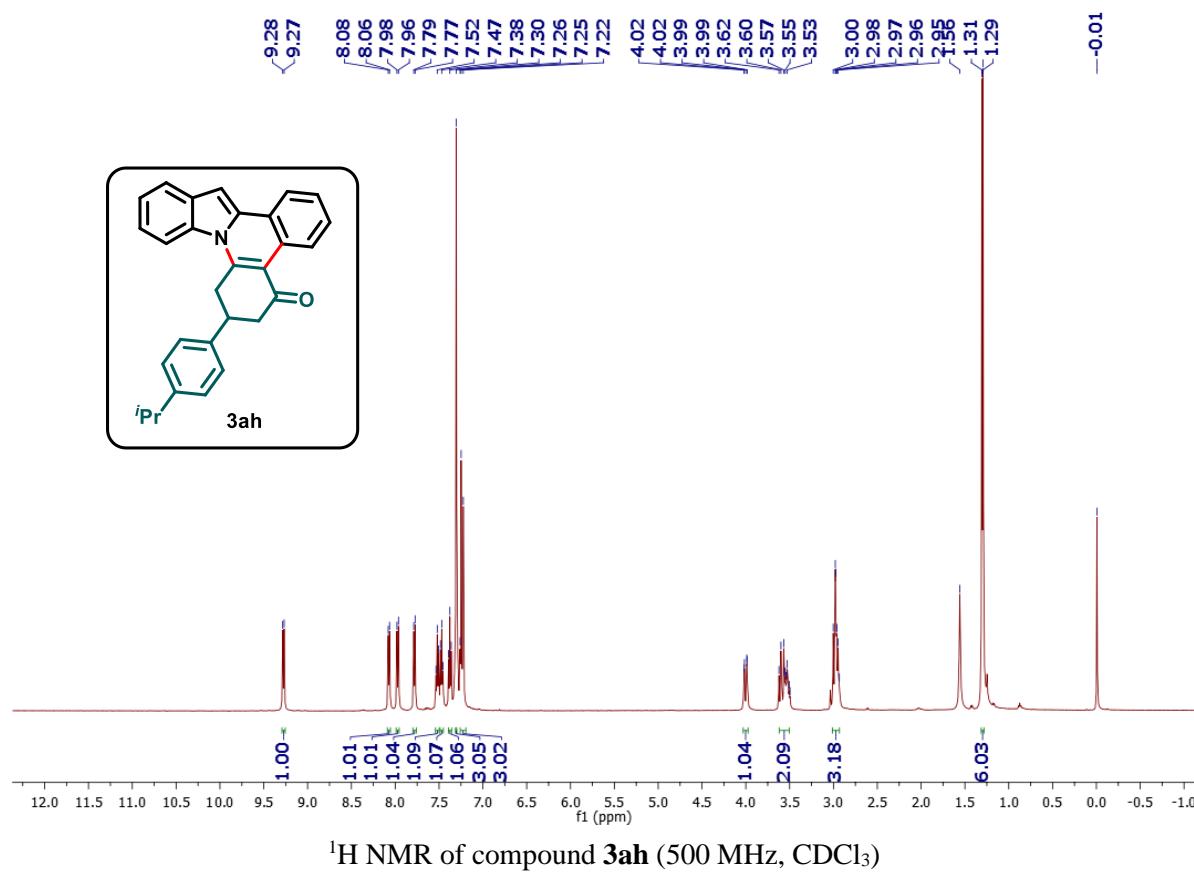
**7-(*p*-tolyl)-7,8-dihydroindolo[1,2-*f*]phenanthridin-5(6*H*)-one (3af):**



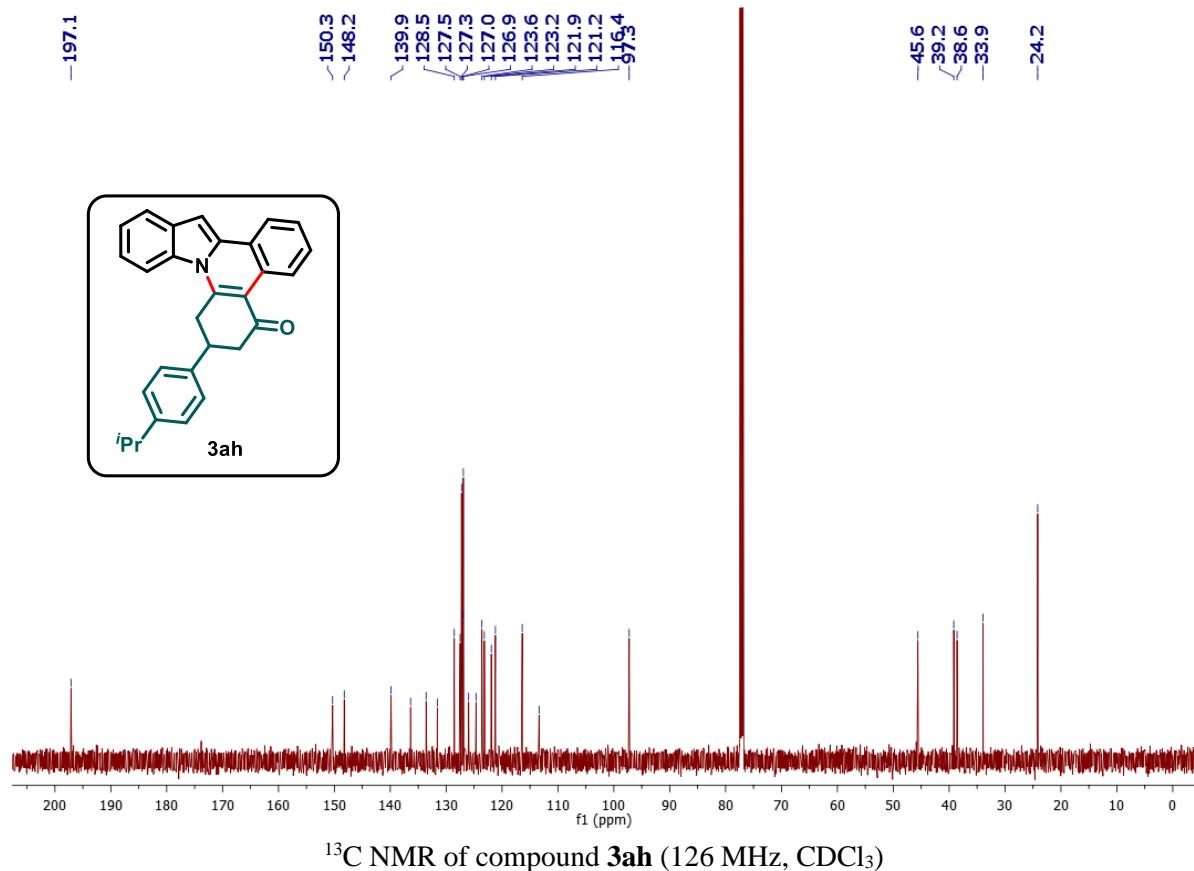
**7-(4-methoxyphenyl)-7,8-dihydroindolo[1,2-f]phenanthridin-5(6H)-one (3ag):**



**7-(4-isopropylphenyl)-7,8-dihydroindolo[1,2-f]phenanthridin-5(6H)-one (3ah):**

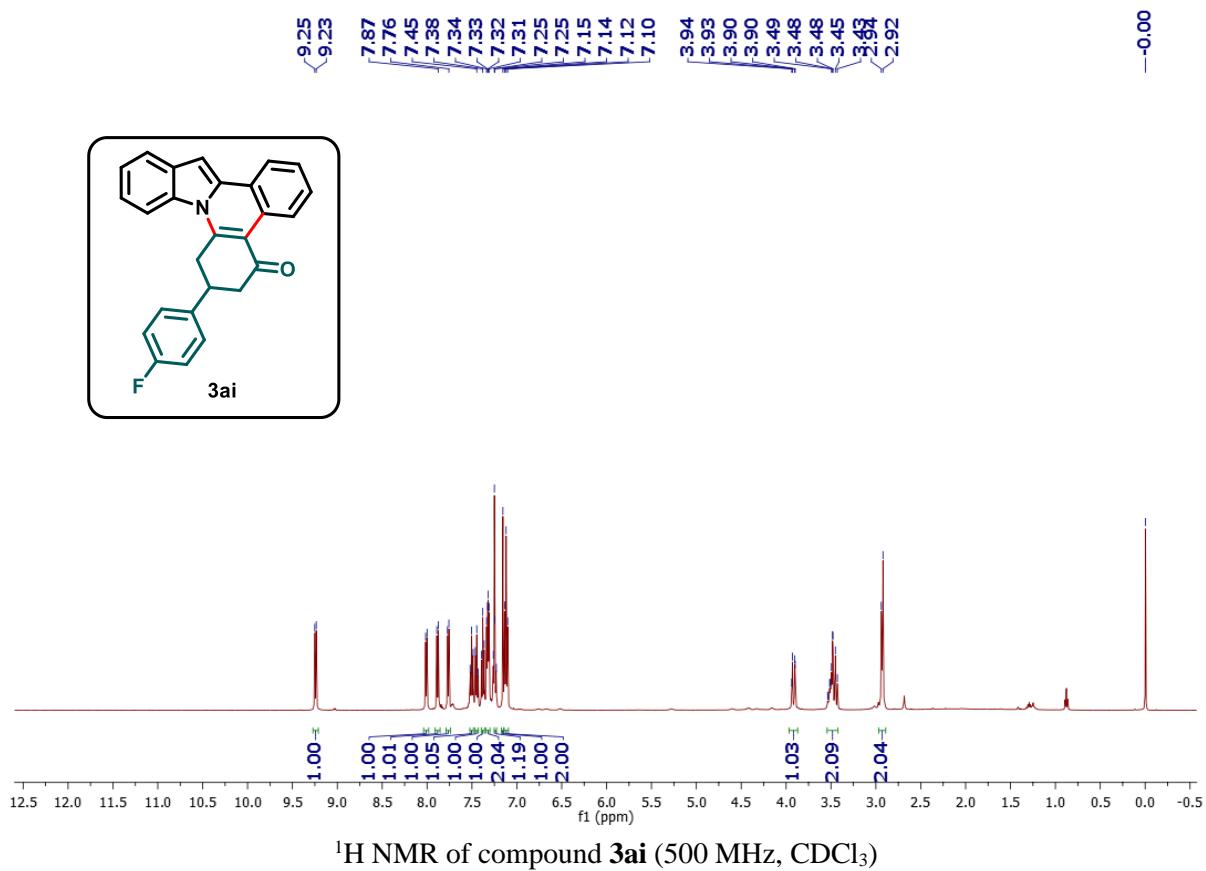


<sup>1</sup>H NMR of compound 3ah (500 MHz, CDCl<sub>3</sub>)

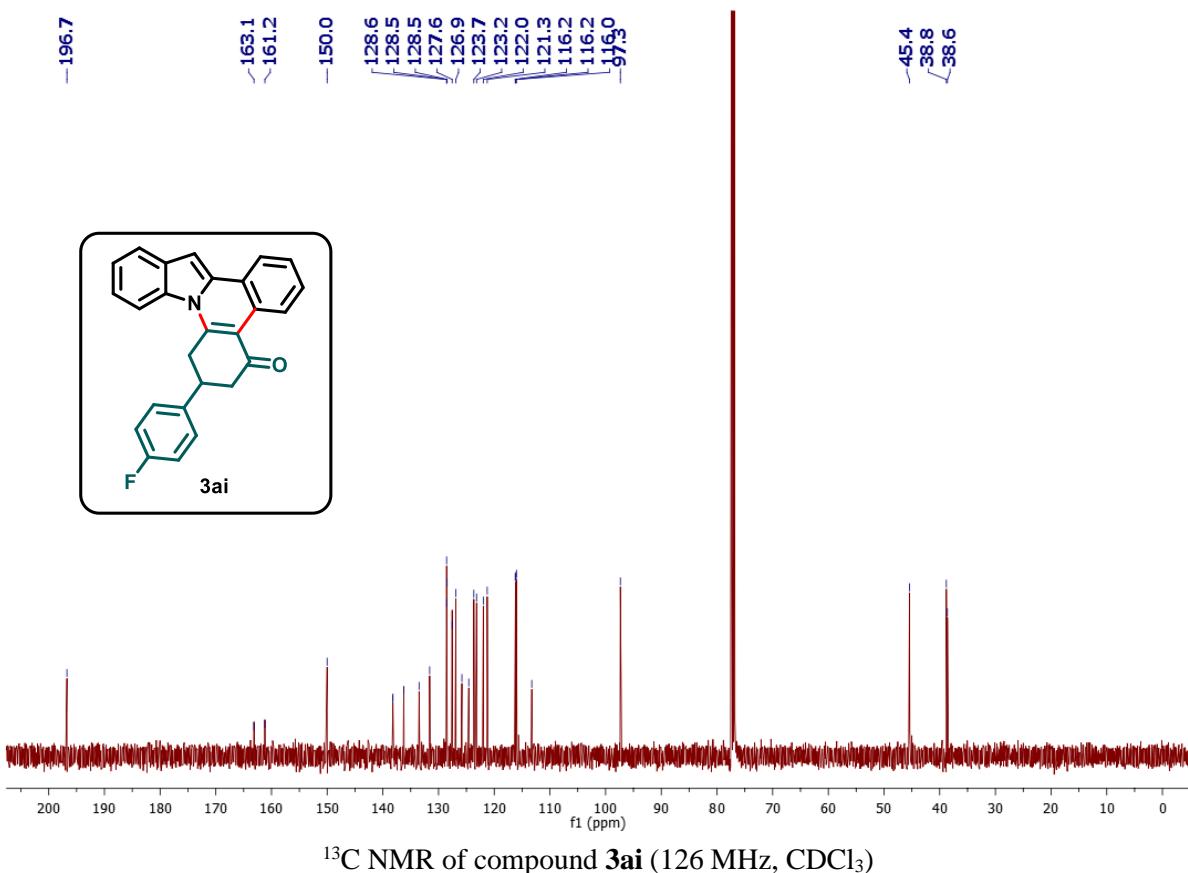


<sup>13</sup>C NMR of compound 3ah (126 MHz, CDCl<sub>3</sub>)

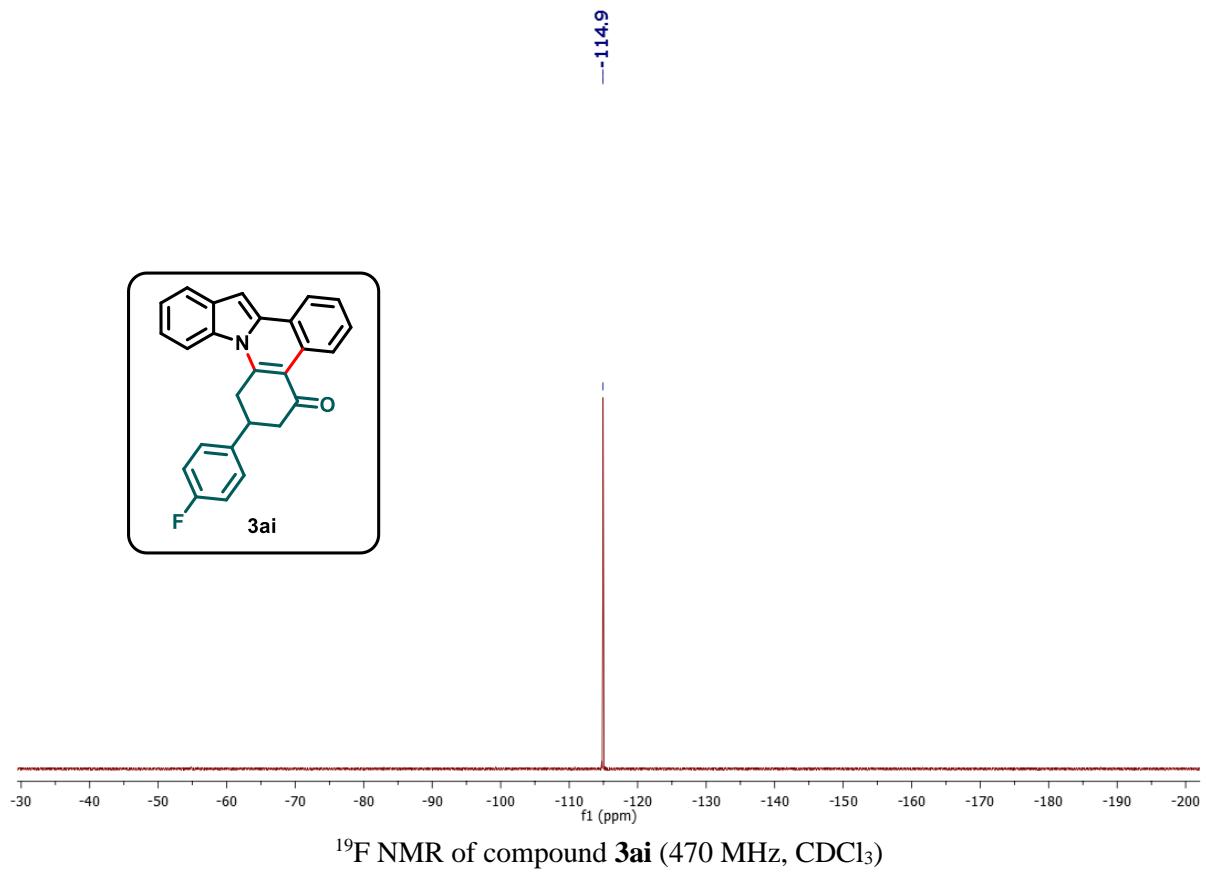
**7-(4-fluorophenyl)-7,8-dihydroindolo[1,2-f]phenanthridin-5(6H)-one (3ai):**



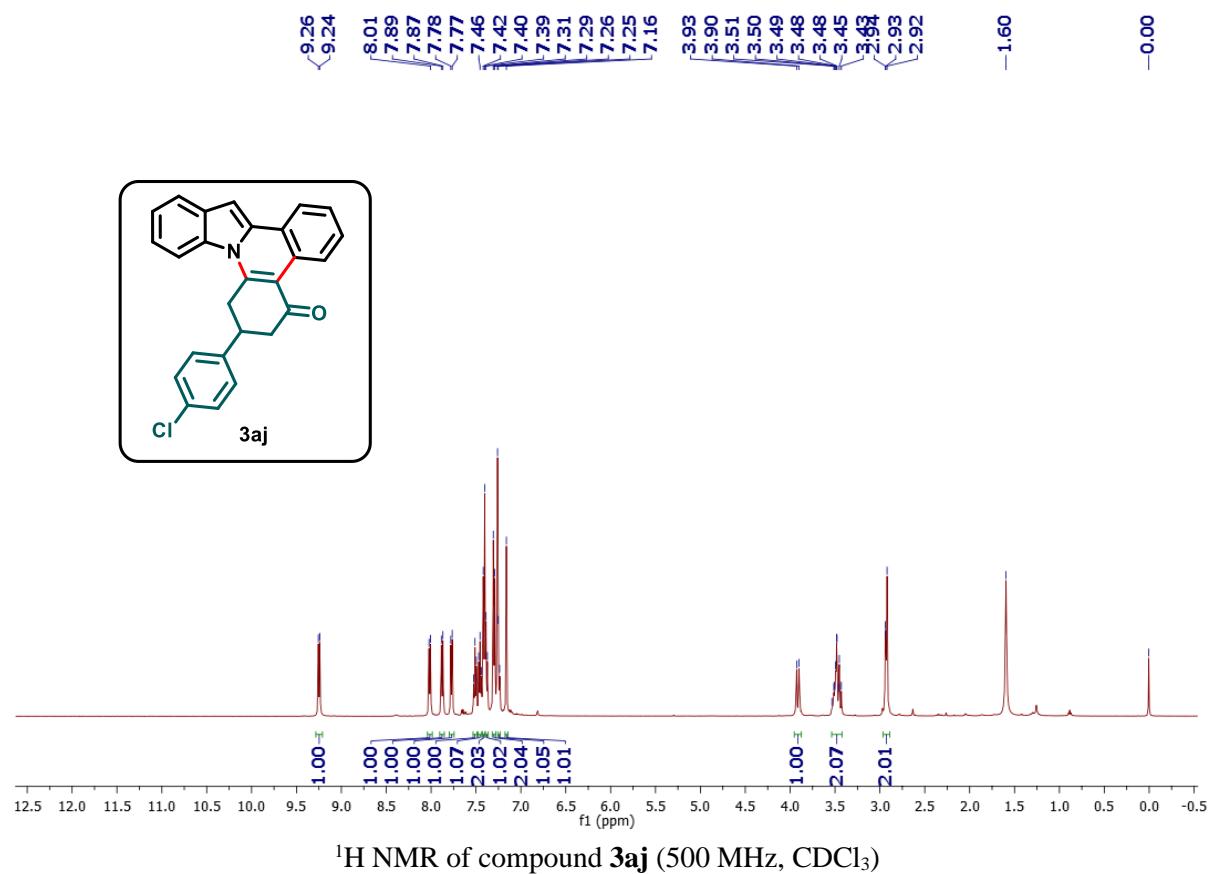
<sup>1</sup>H NMR of compound 3ai (500 MHz, CDCl<sub>3</sub>)



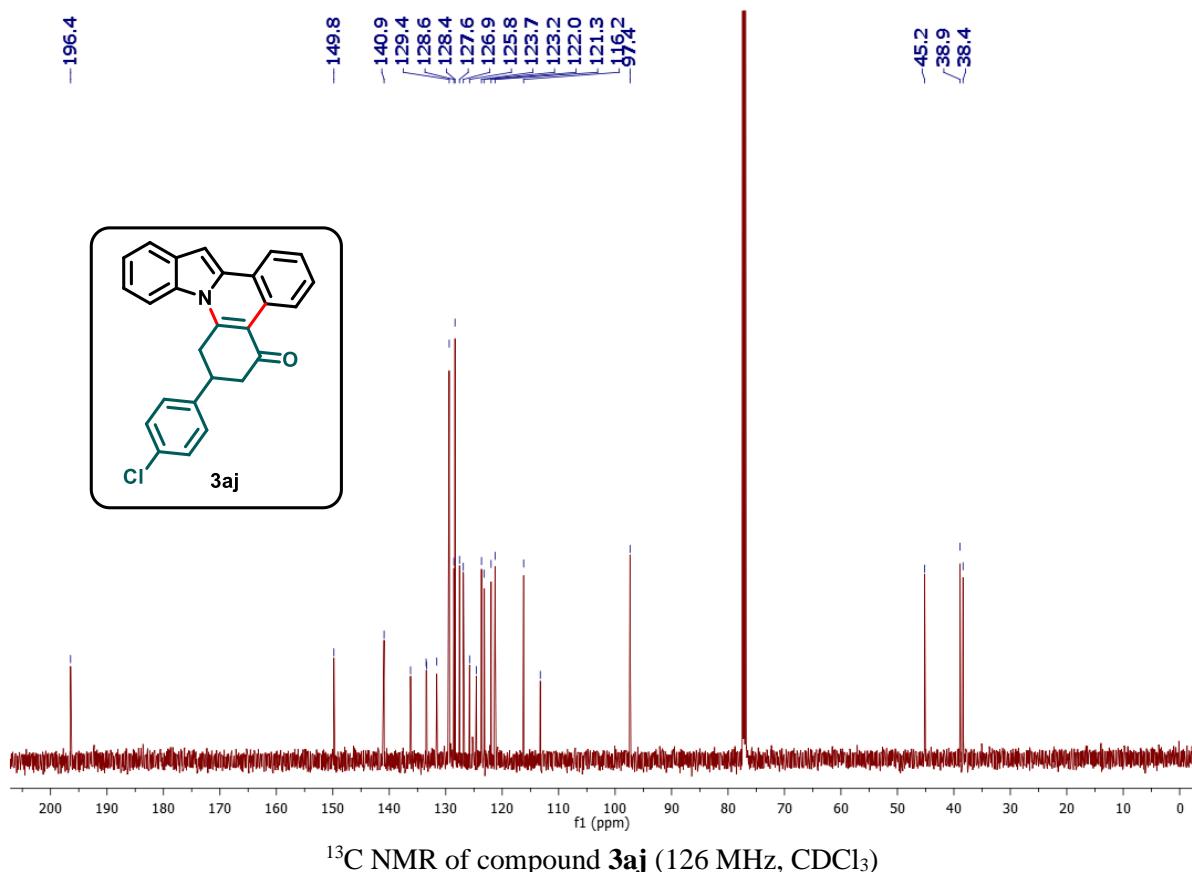
<sup>13</sup>C NMR of compound 3ai (126 MHz, CDCl<sub>3</sub>)



**7-(4-chlorophenyl)-7,8-dihydroindolo[1,2-f]phenanthridin-5(6H)-one (3aj):**

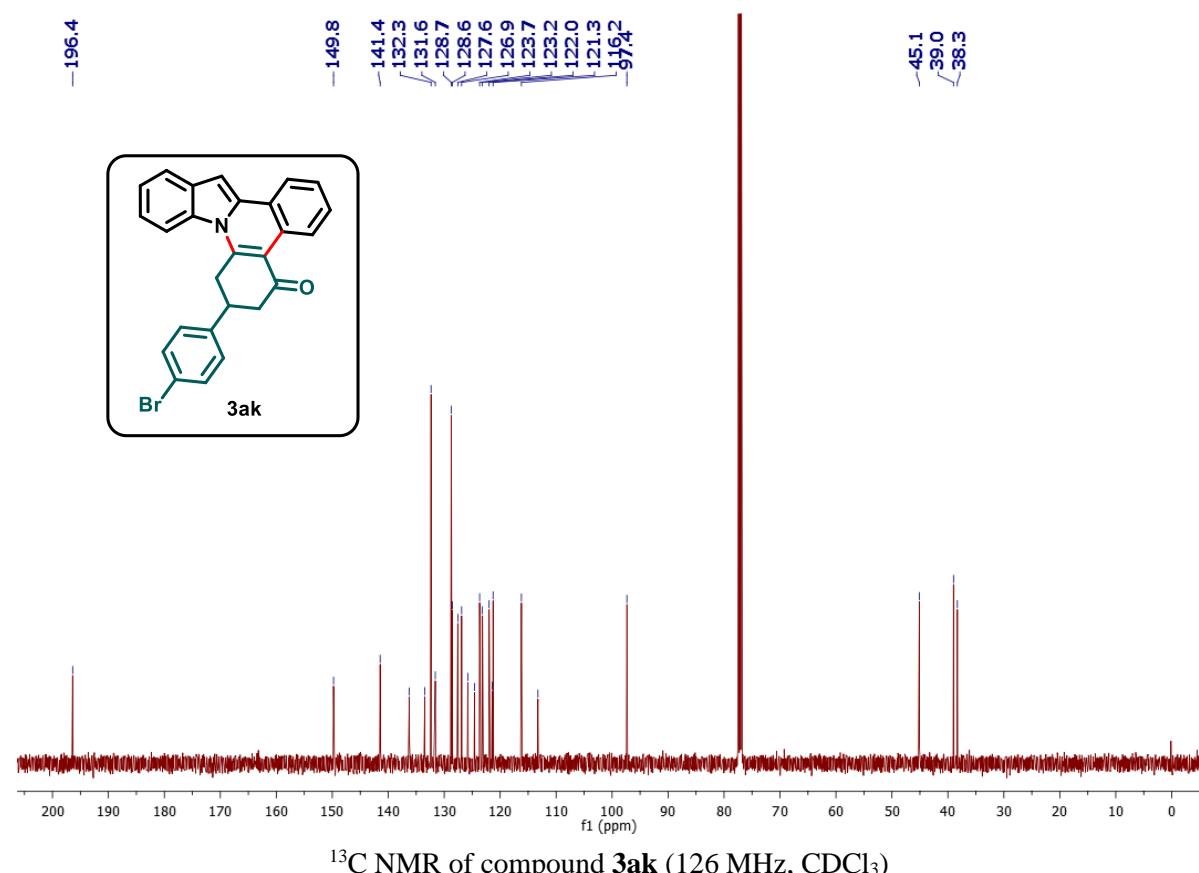
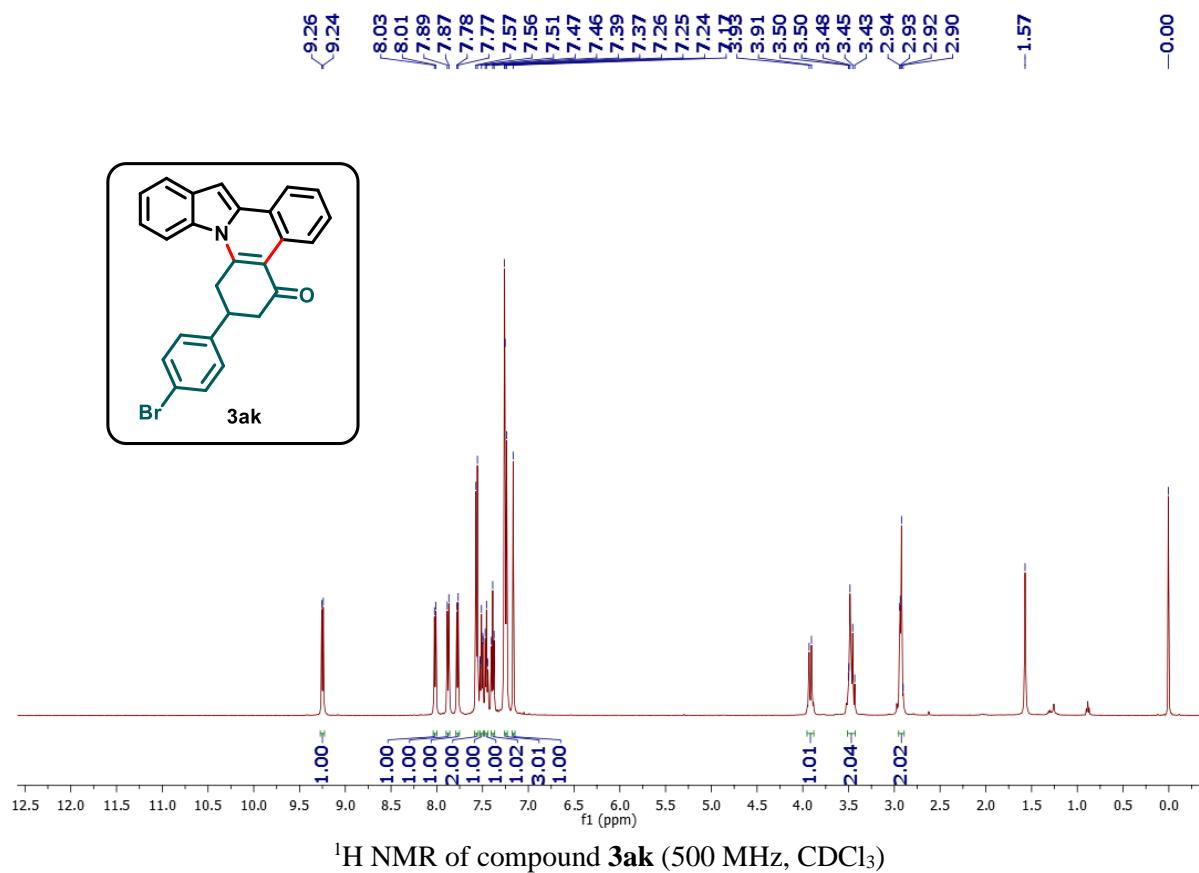


<sup>1</sup>H NMR of compound 3aj (500 MHz, CDCl<sub>3</sub>)

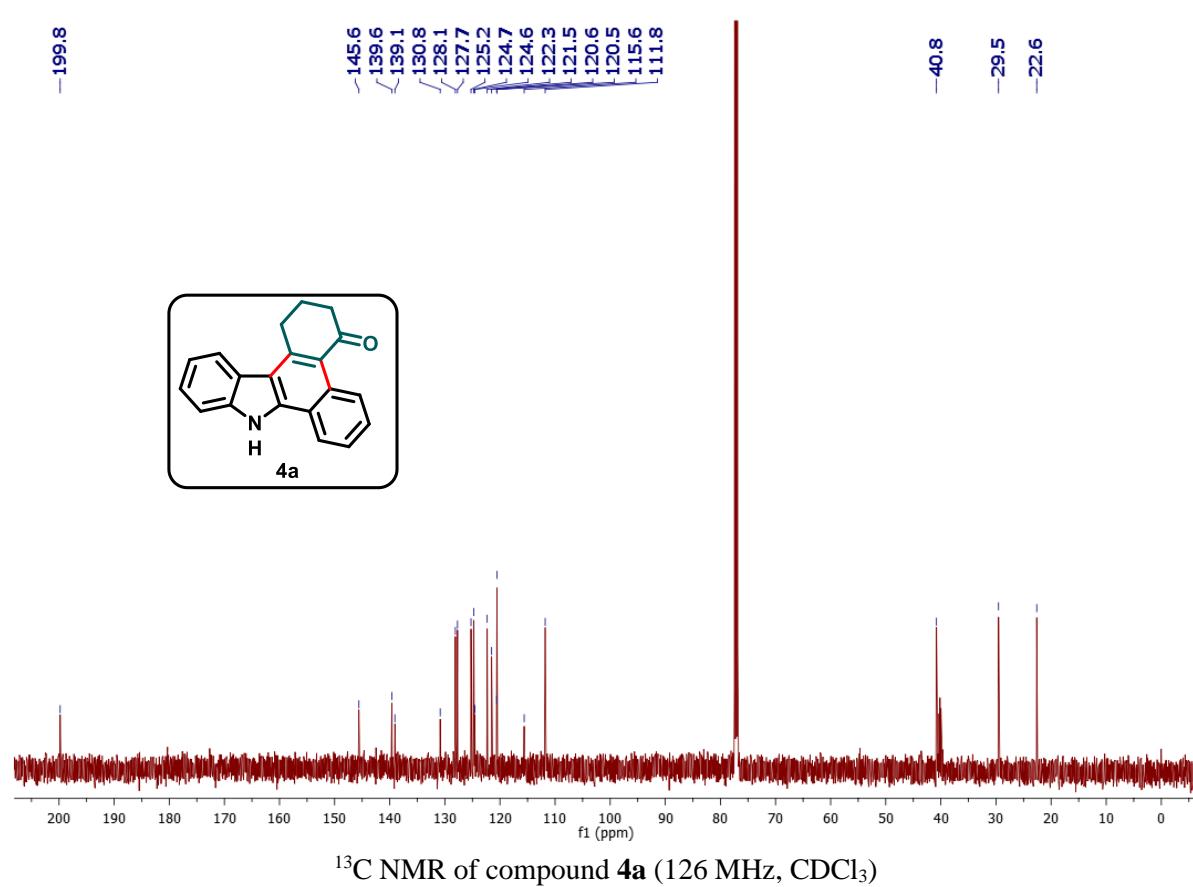
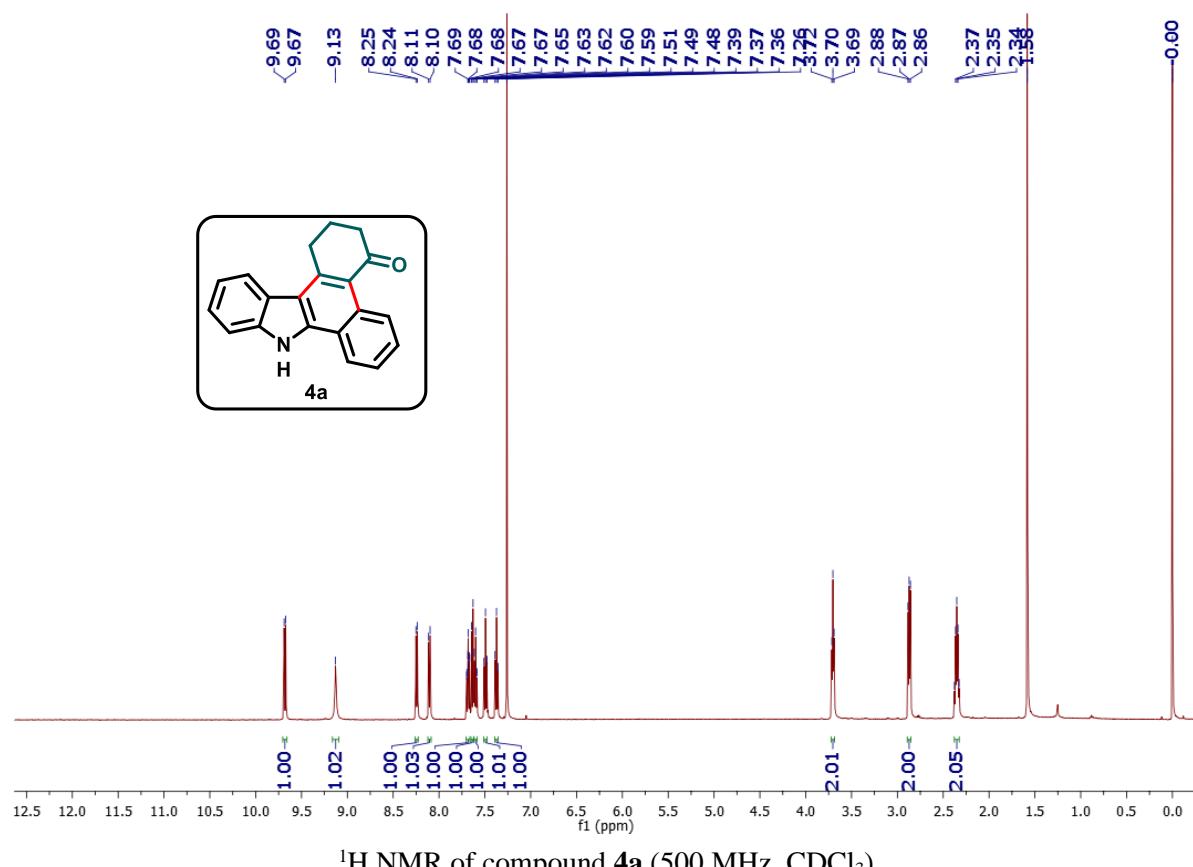


<sup>13</sup>C NMR of compound 3aj (126 MHz, CDCl<sub>3</sub>)

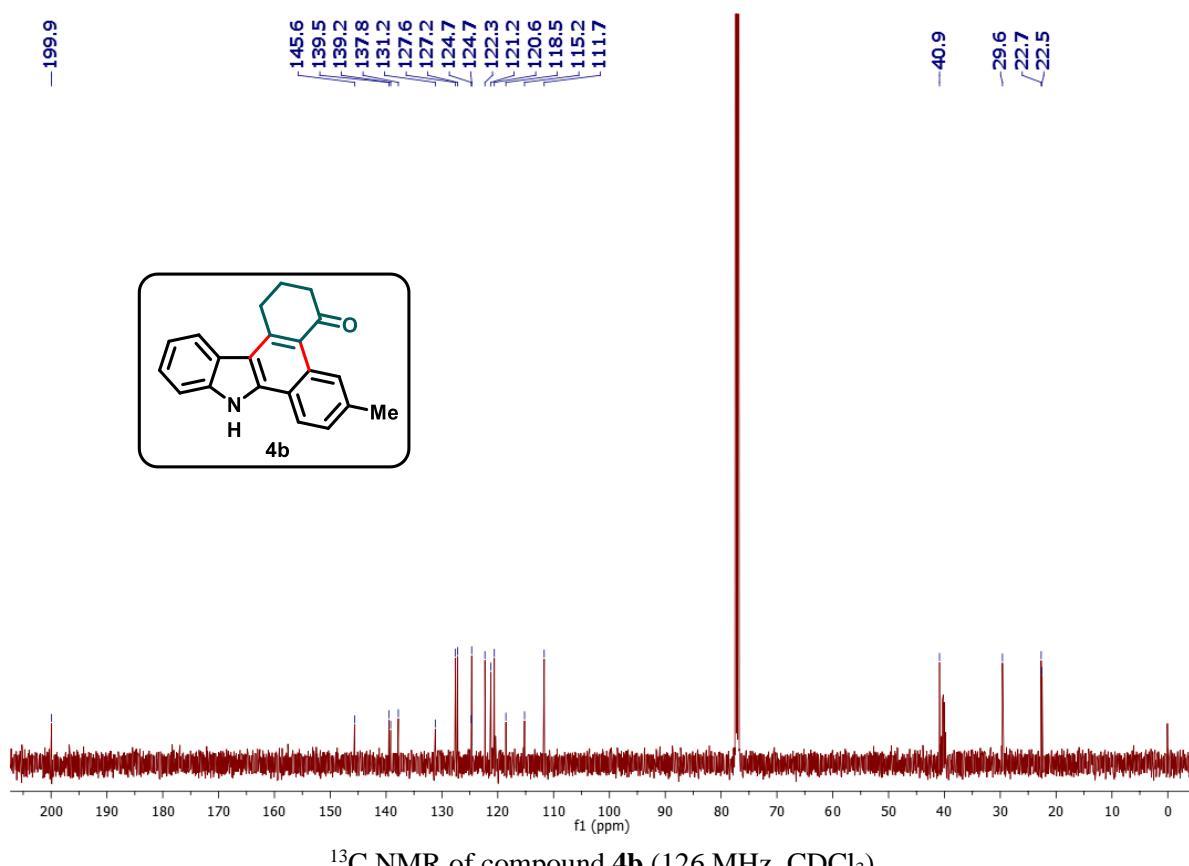
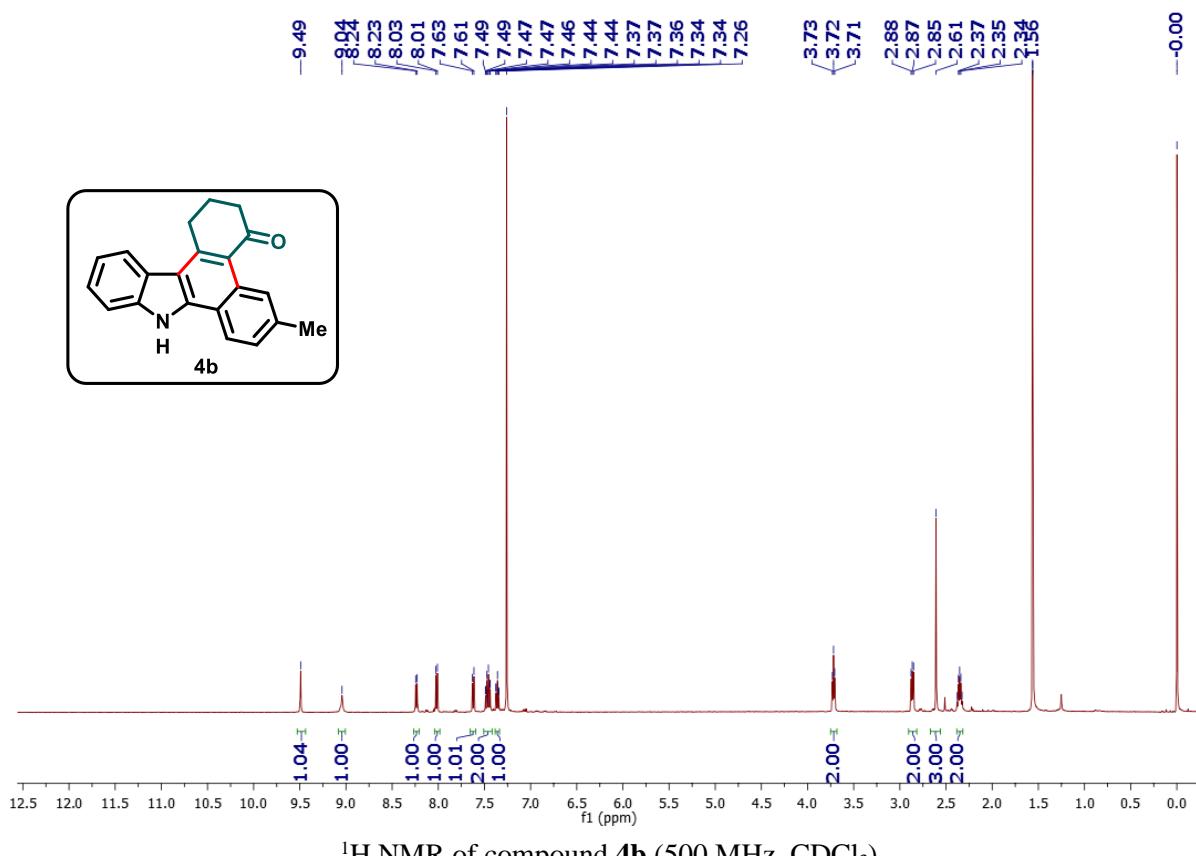
**7-(4-bromophenyl)-7,8-dihydroindolo[1,2-f]phenanthridin-5(6H)-one (3ak):**



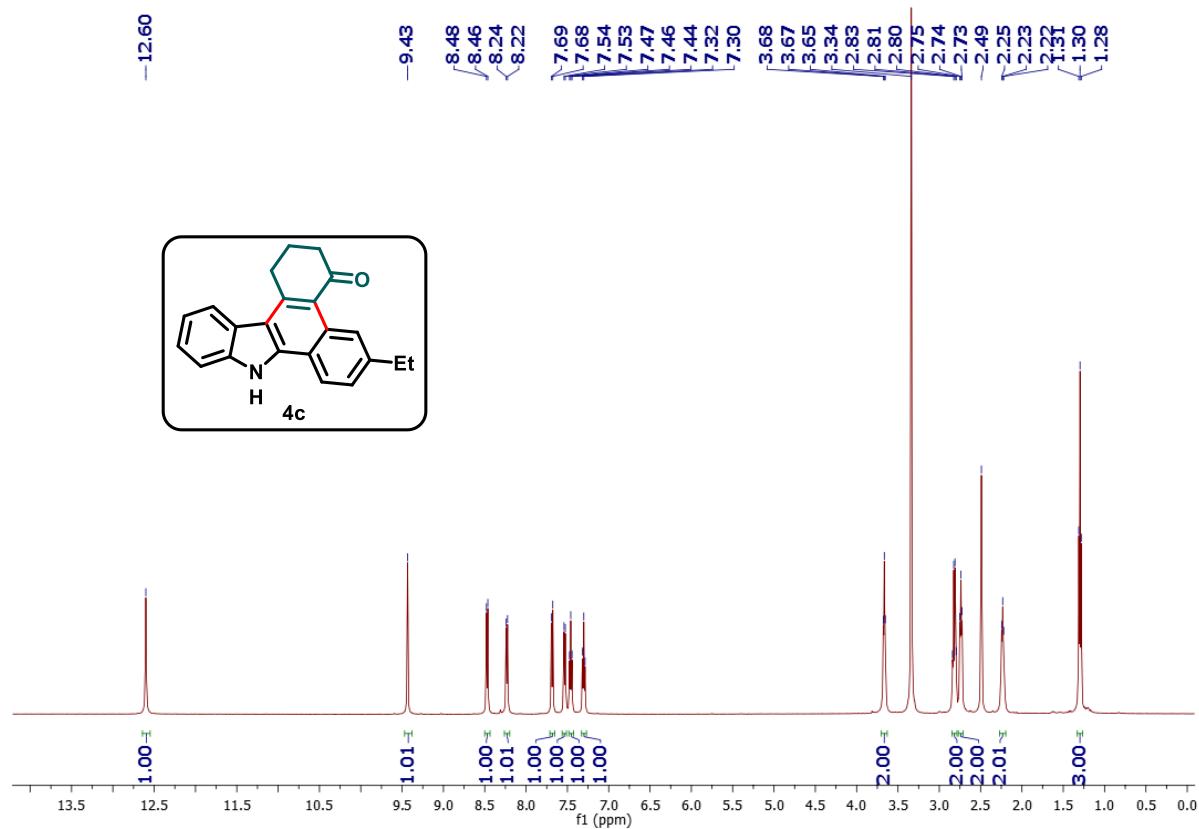
**1,2,3,9-tetrahydro-4H-dibenzo[*a,c*]carbazol-4-one (**4a**):**



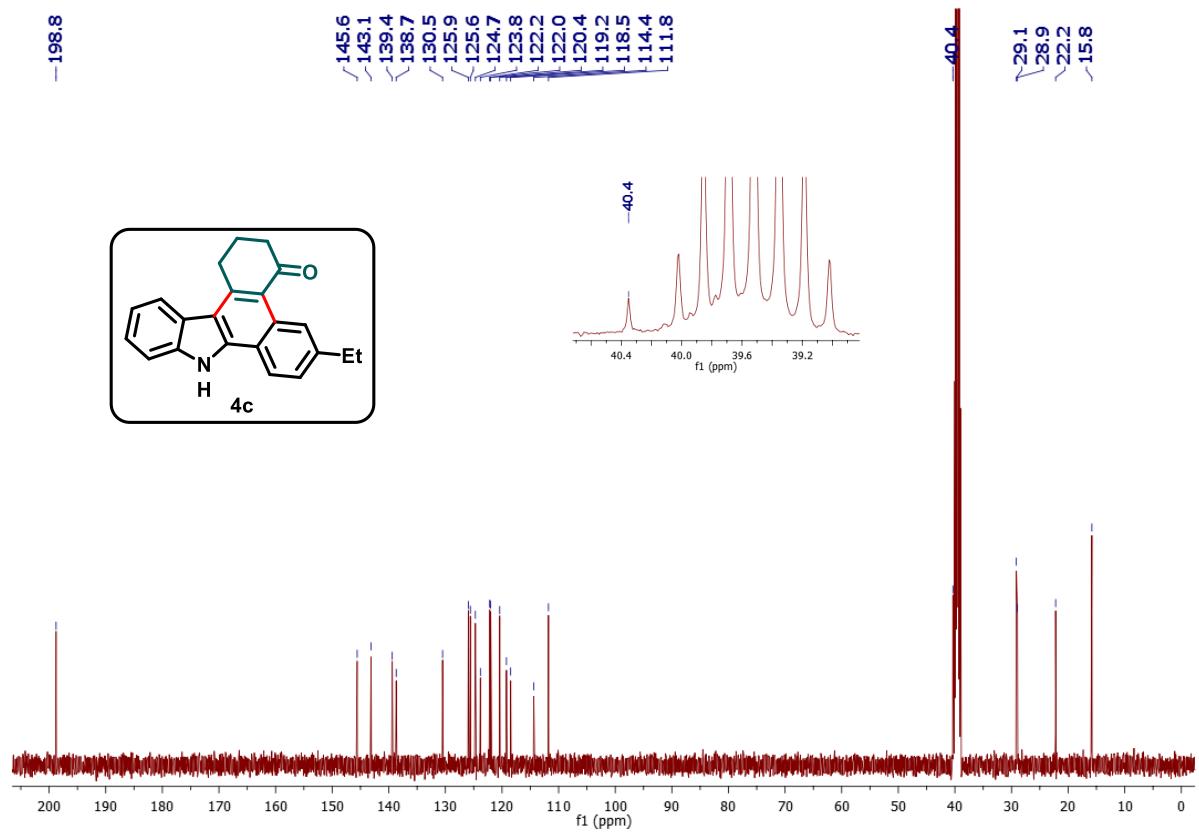
**6-methyl-1,2,3,9-tetrahydro-4H-dibenzo[*a,c*]carbazol-4-one (**4b**):**



**6-ethyl-1,2,3,9-tetrahydro-4H-dibenzo[*a,c*]carbazol-4-one (**4c**):**

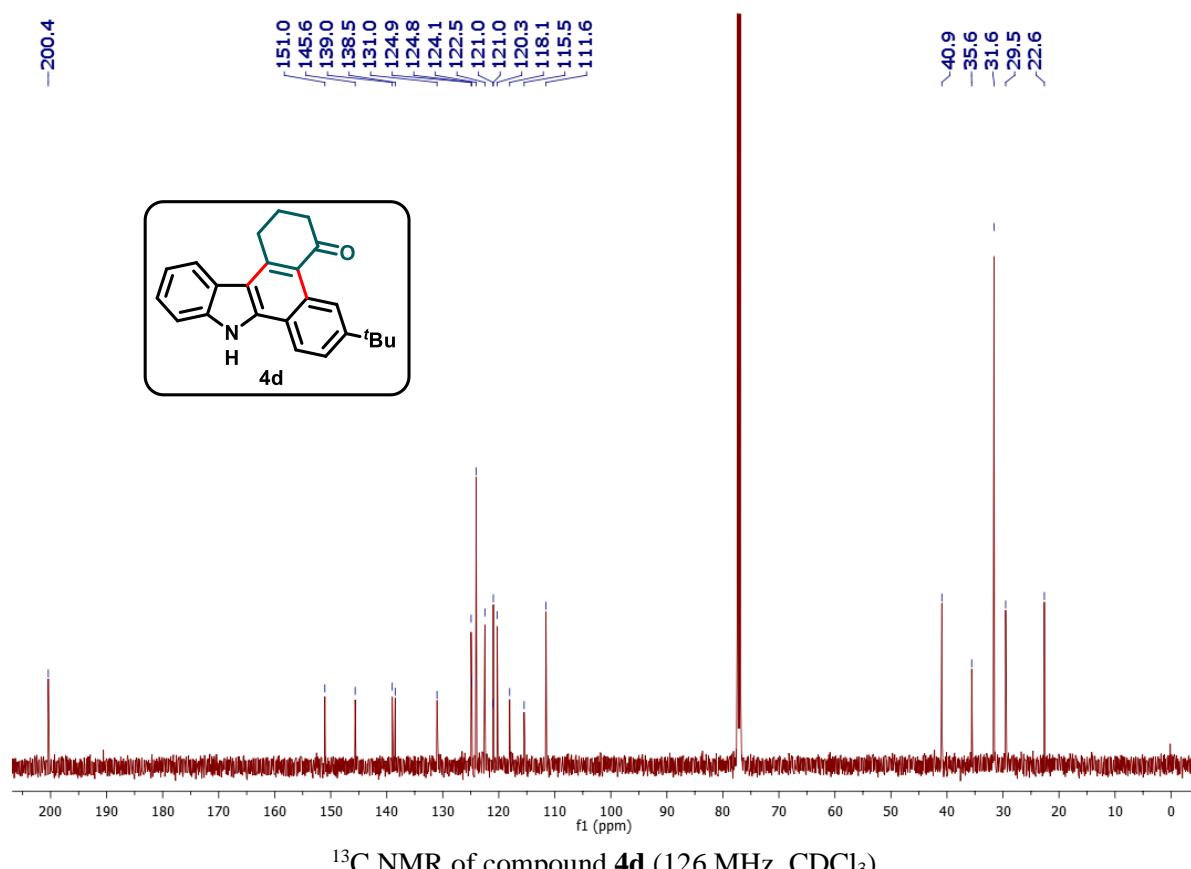
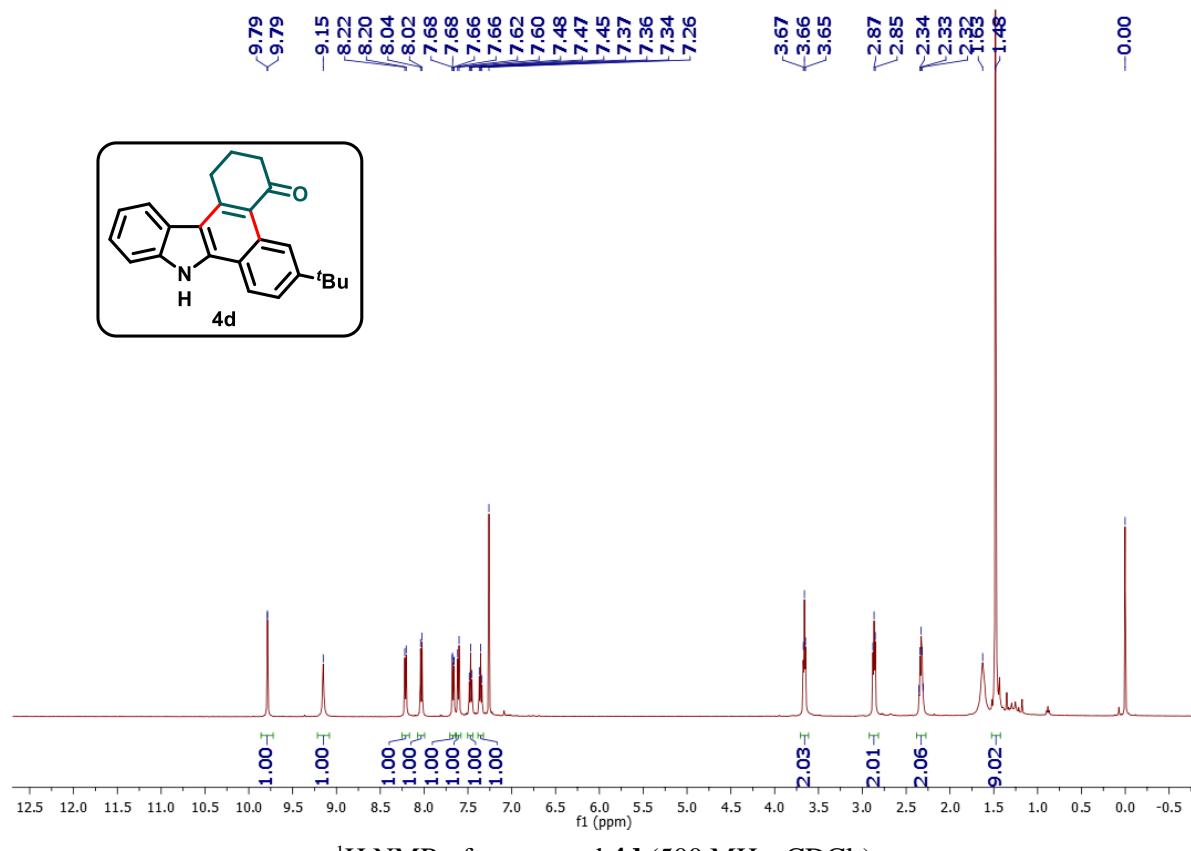


<sup>1</sup>H NMR of compound **4c** (500 MHz, DMSO-*d*<sub>6</sub>)

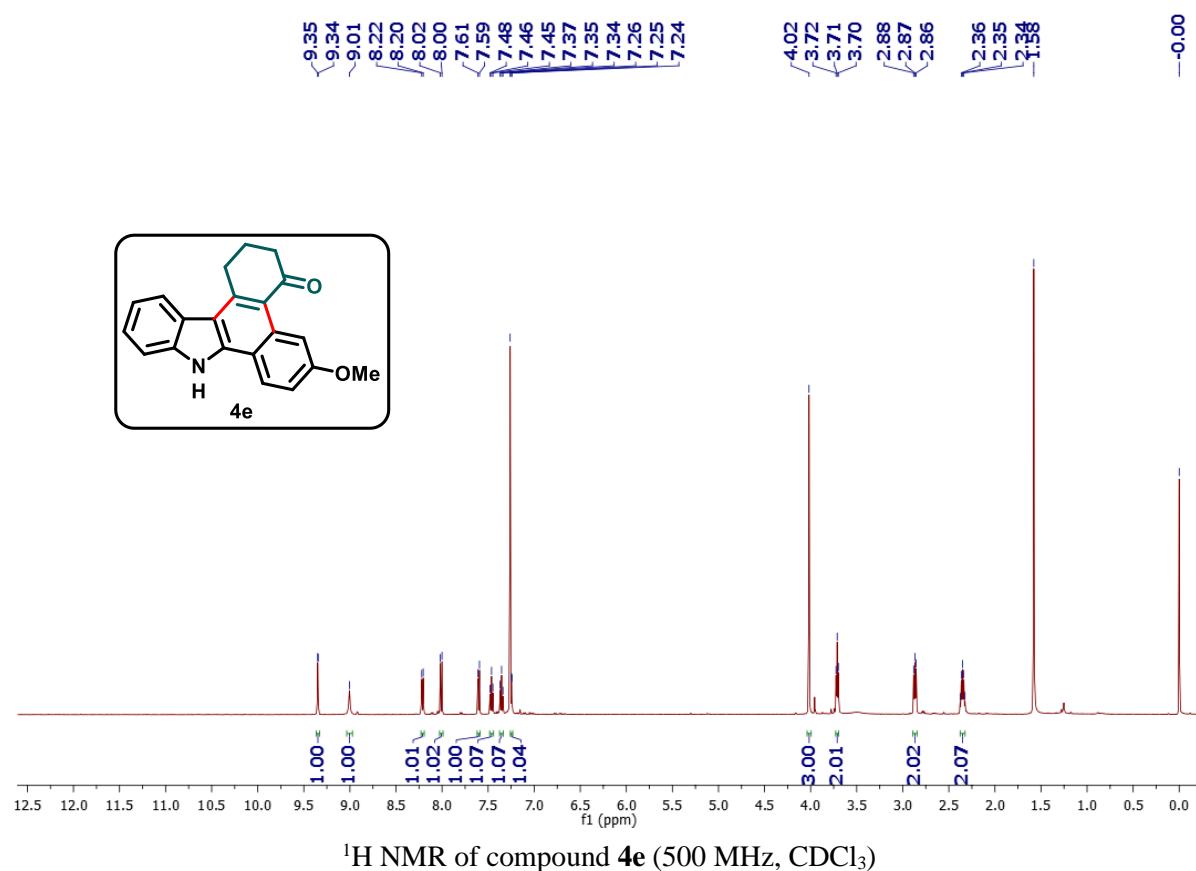


<sup>13</sup>C NMR of compound **4c** (126 MHz, DMSO-*d*<sub>6</sub>)

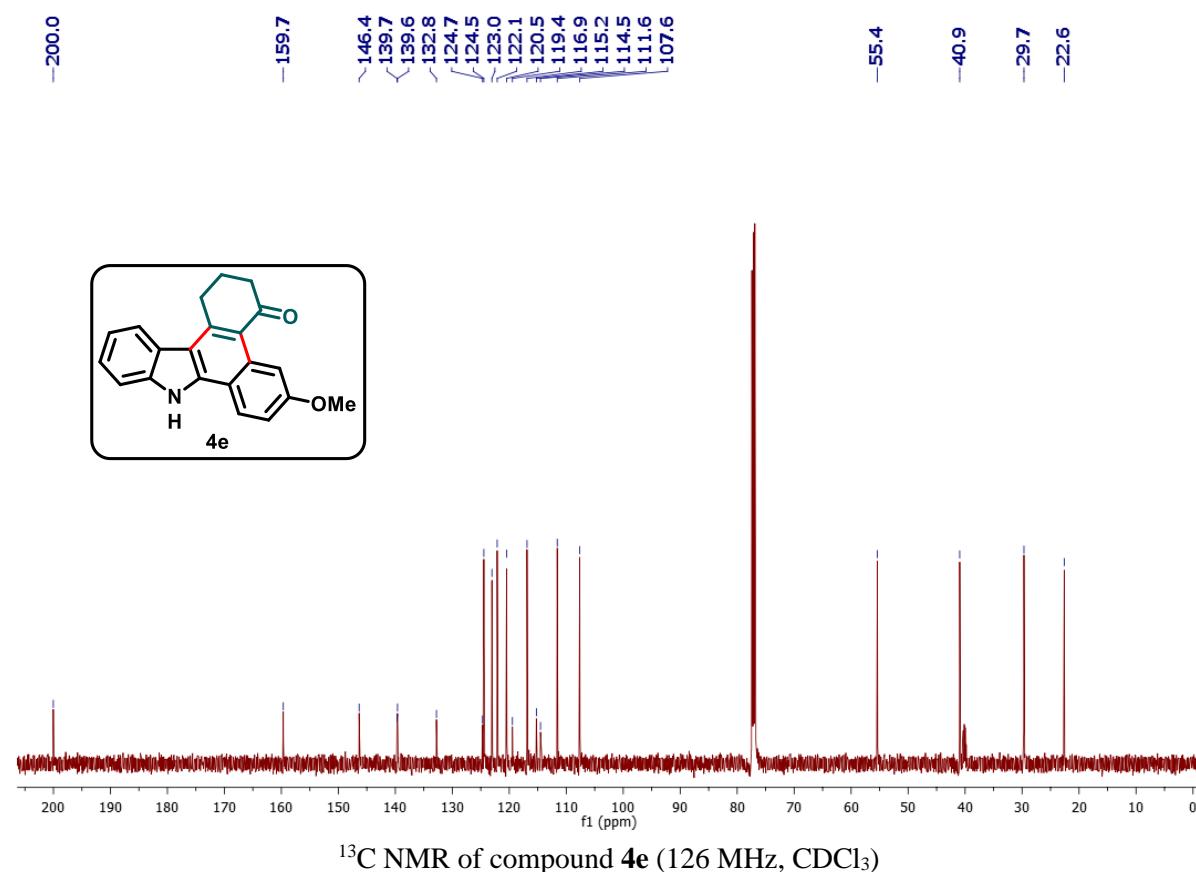
**6-(*tert*-butyl)-1,2,3,9-tetrahydro-4*H*-dibenzo[*a,c*]carbazol-4-one (**4d**):**



**6-methoxy-1,2,3,9-tetrahydro-4H-dibenzo[*a,c*]carbazol-4-one(4e):**

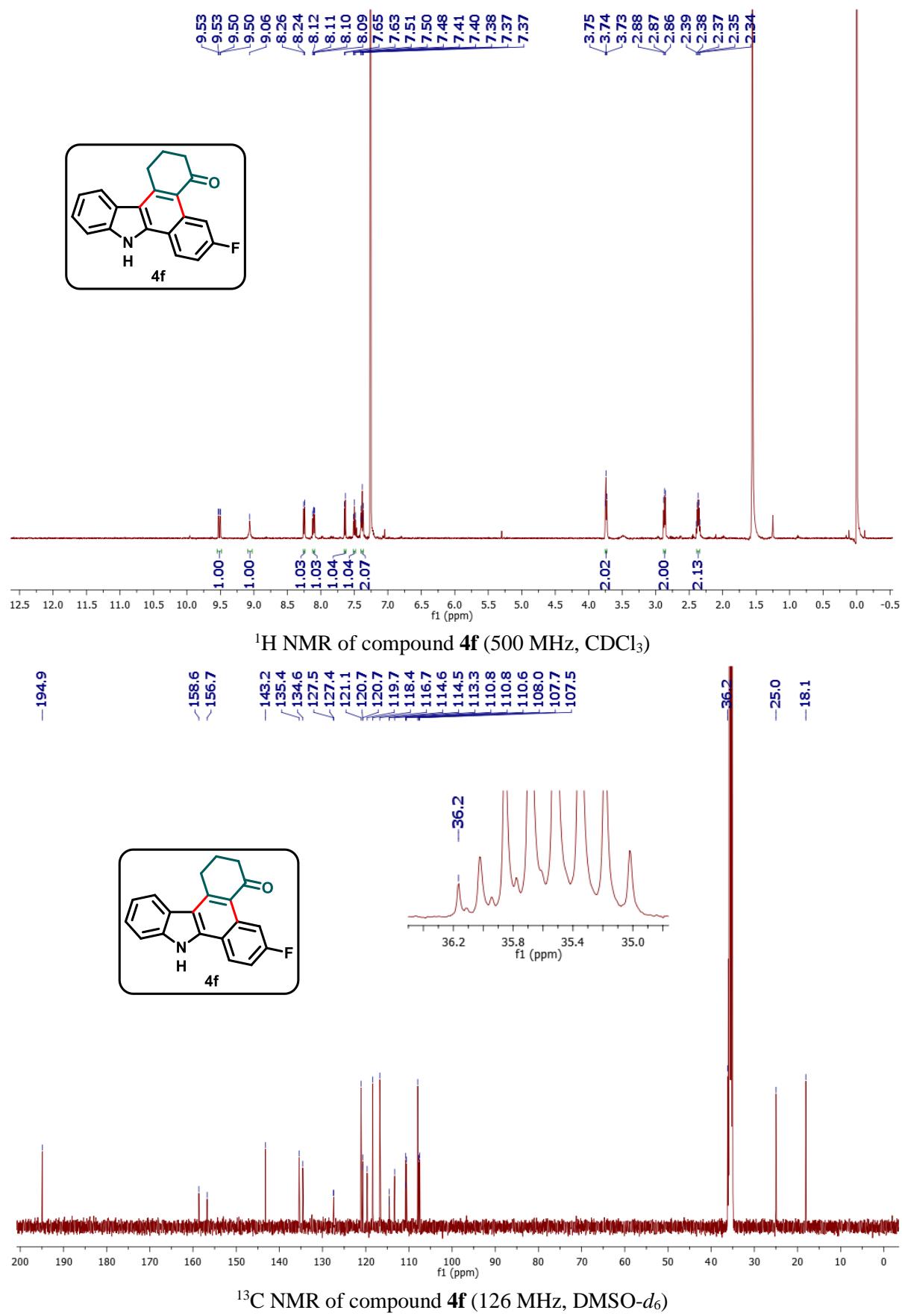


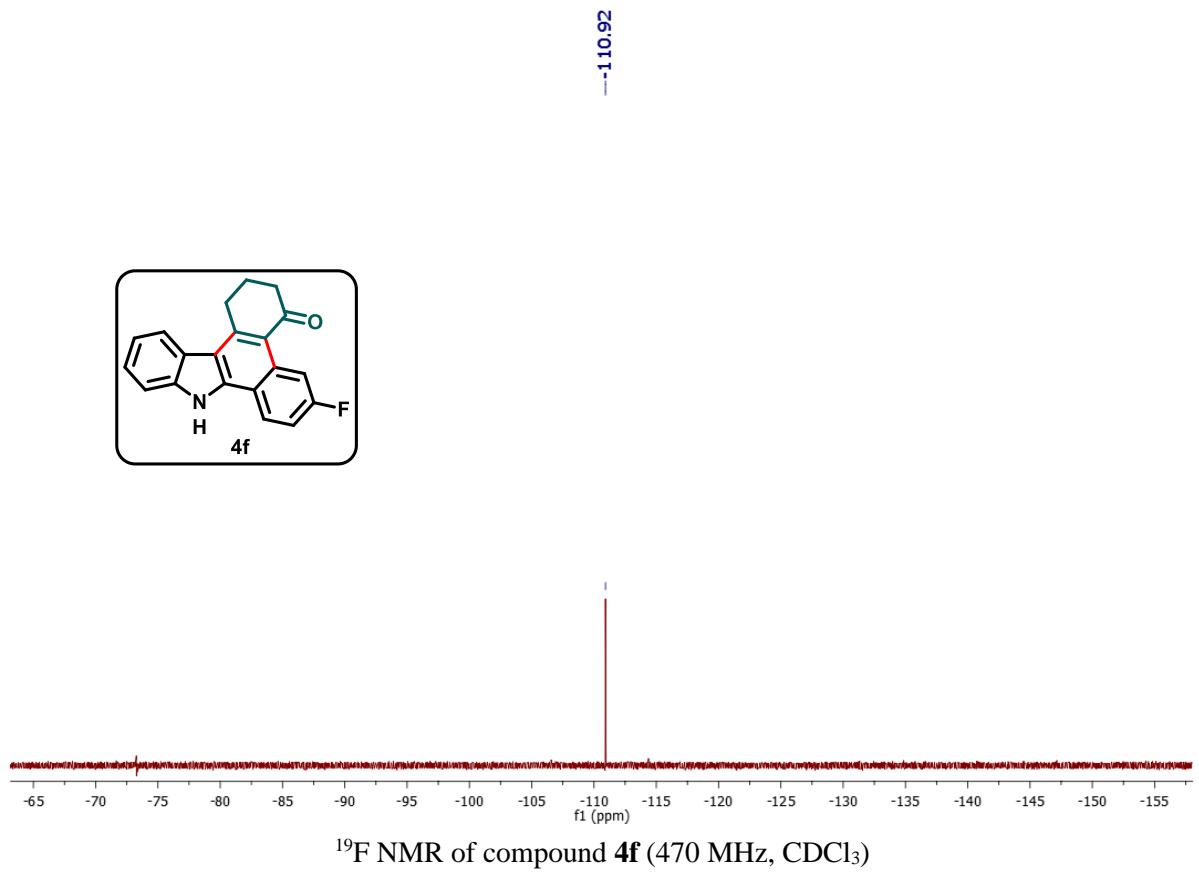
<sup>1</sup>H NMR of compound 4e (500 MHz, CDCl<sub>3</sub>)



<sup>13</sup>C NMR of compound 4e (126 MHz, CDCl<sub>3</sub>)

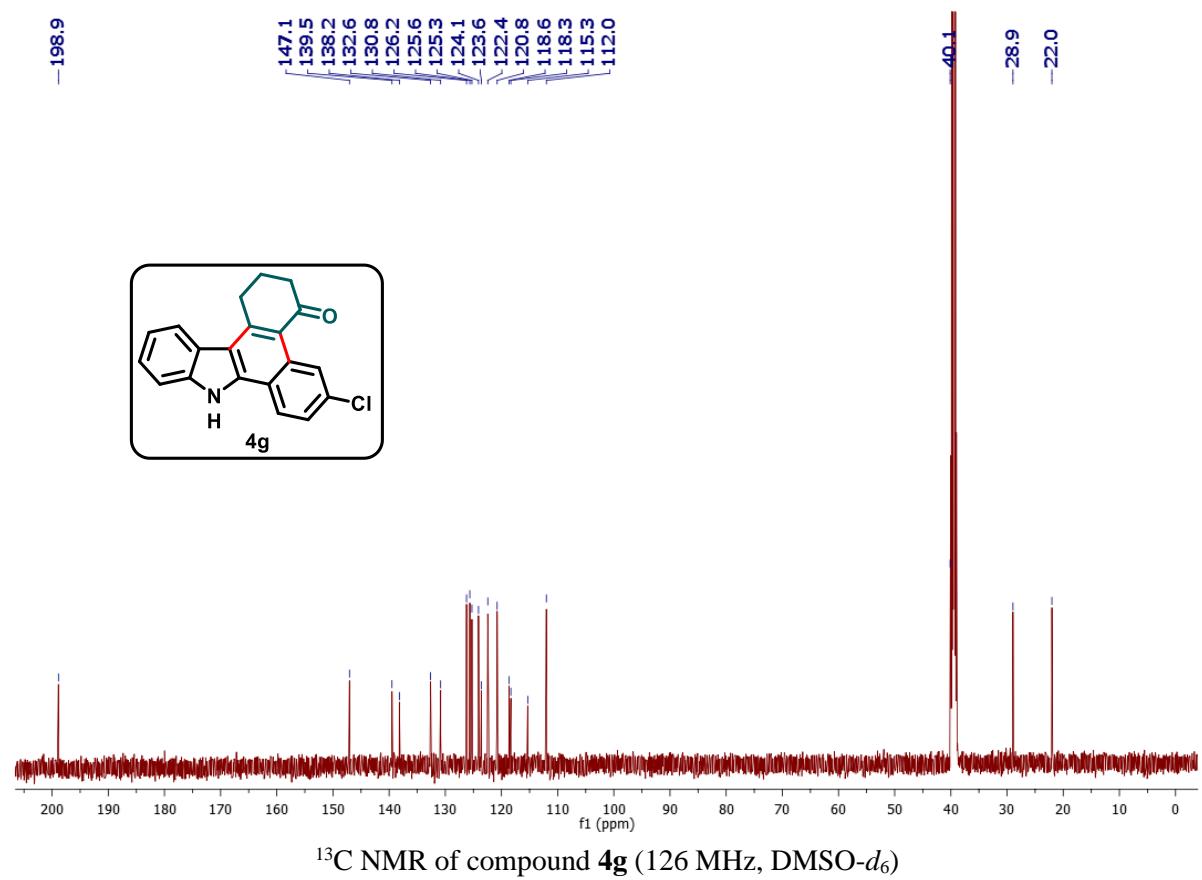
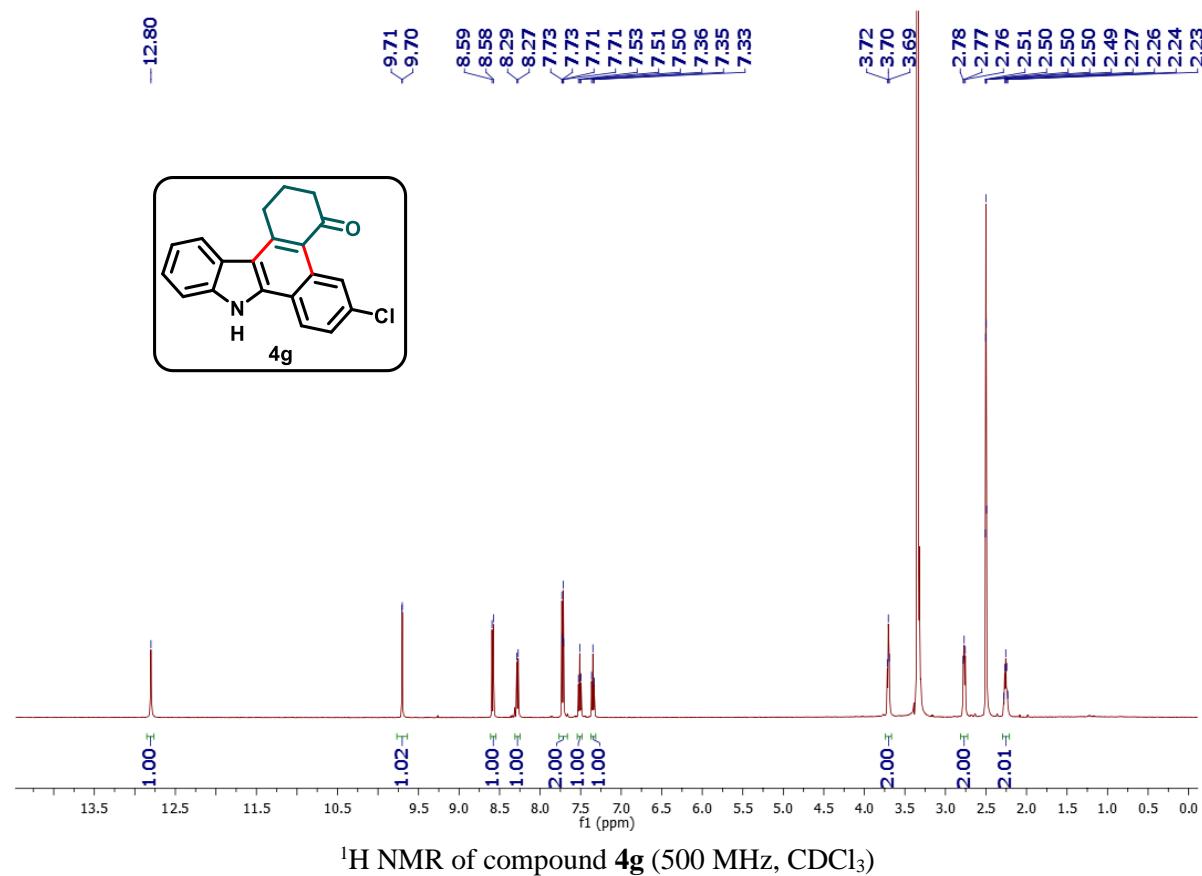
**6-fluoro-1,2,3,9-tetrahydro-4H-dibenzo[*a,c*]carbazol-4-one (**4f**):**



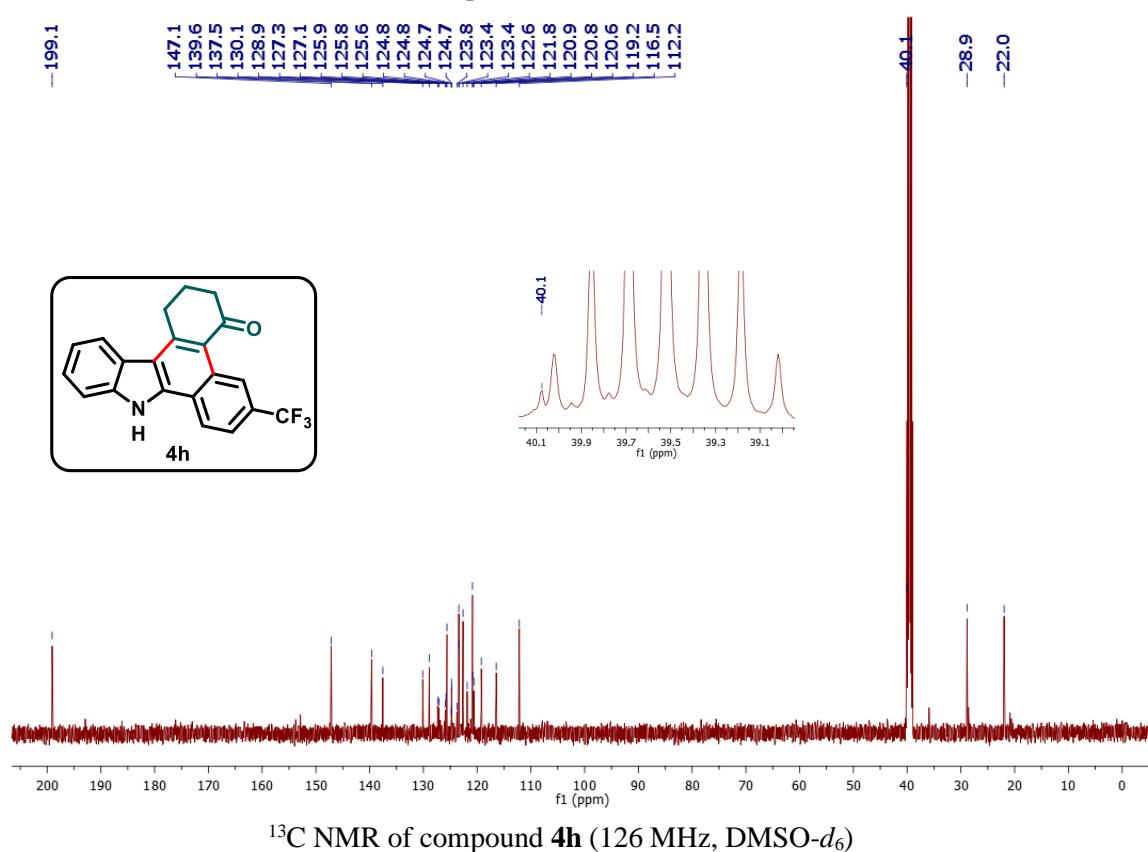
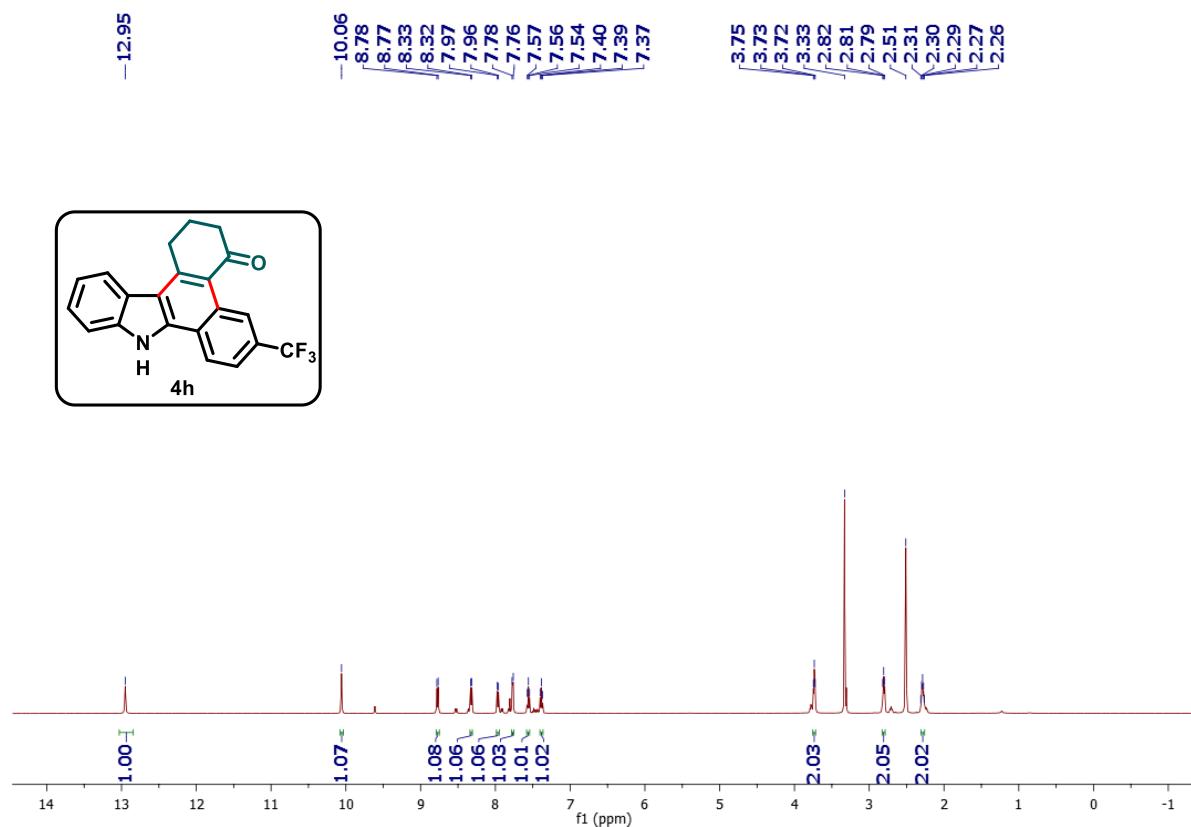


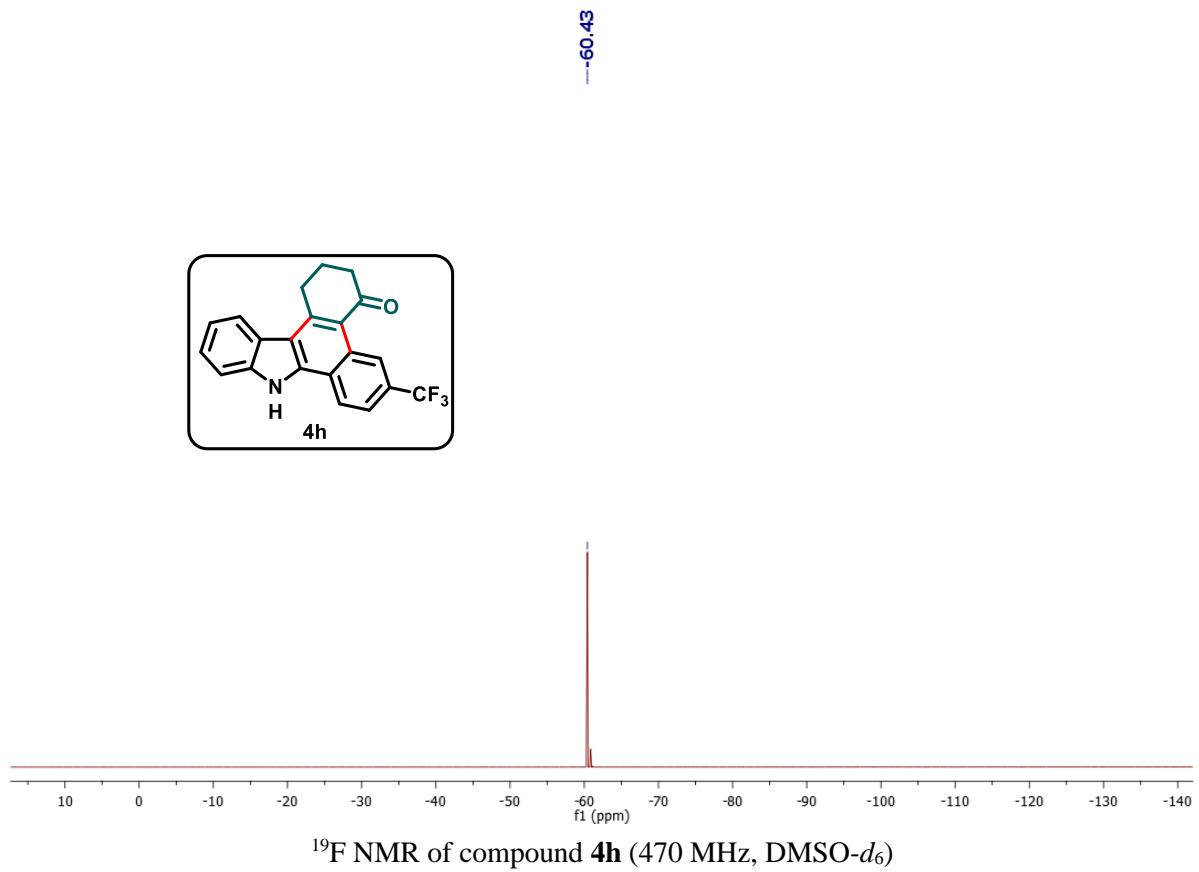
$^{19}\text{F}$  NMR of compound **4f** (470 MHz,  $\text{CDCl}_3$ )

**6-chloro-1,2,3,9-tetrahydro-4*H*-dibenzo[*a,c*]carbazol-4-one (4g):**

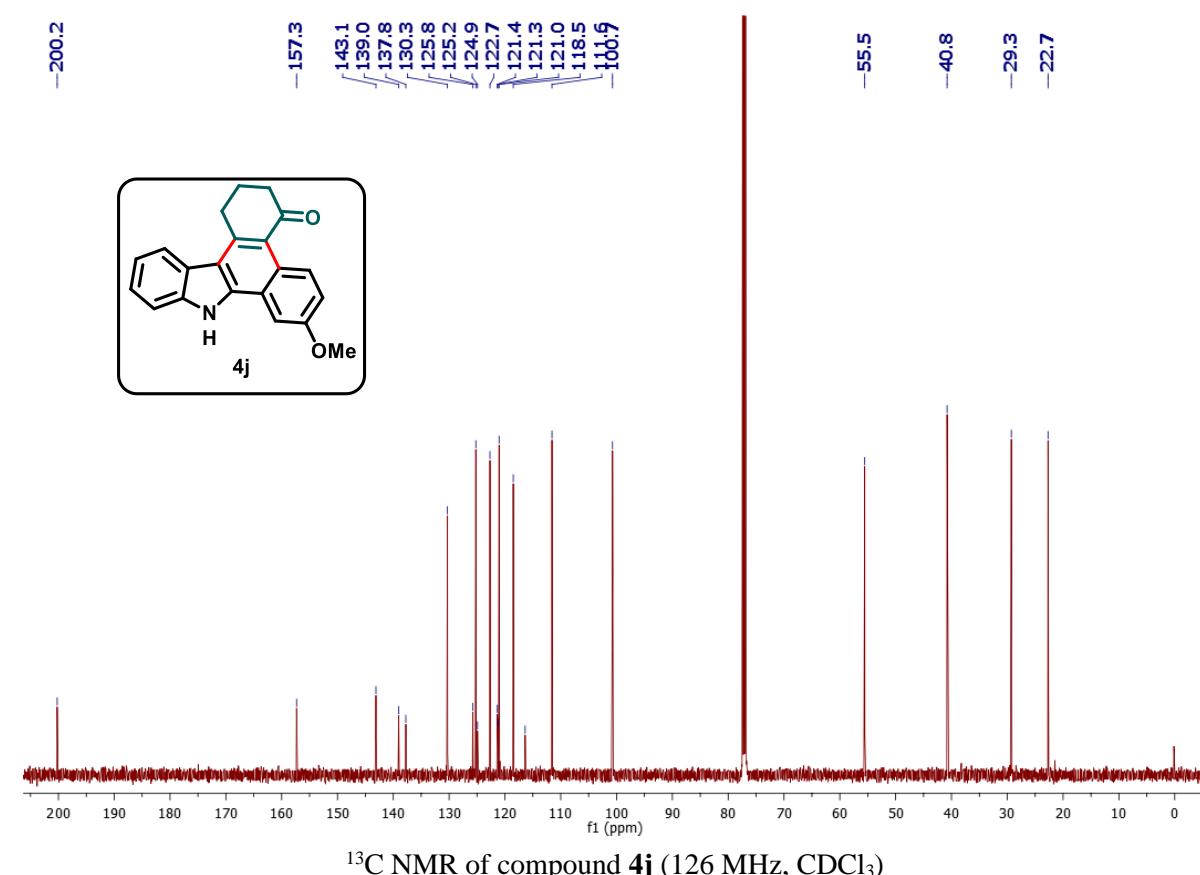
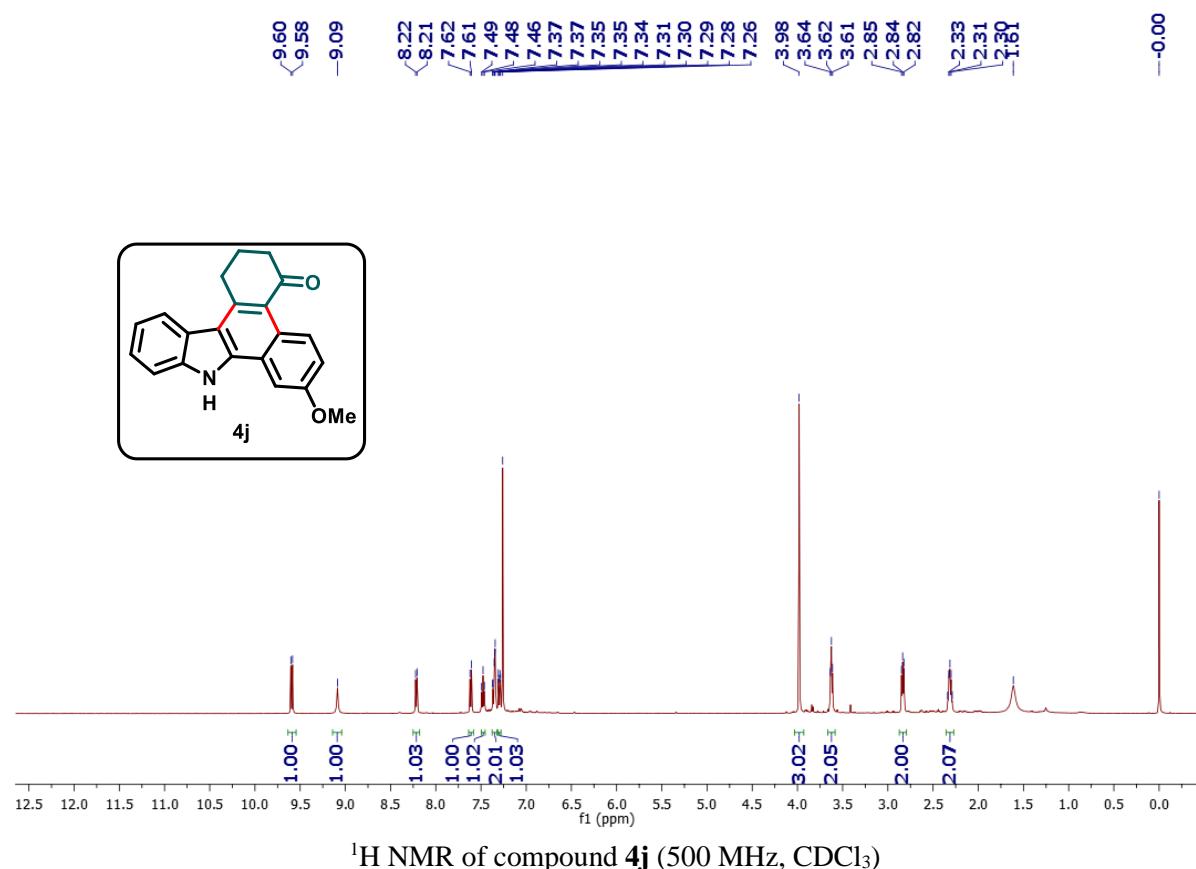


**6-(trifluoromethyl)-1,2,3,9-tetrahydro-4H-dibenzo[*a,c*]carbazol-4-one (**4h**):**

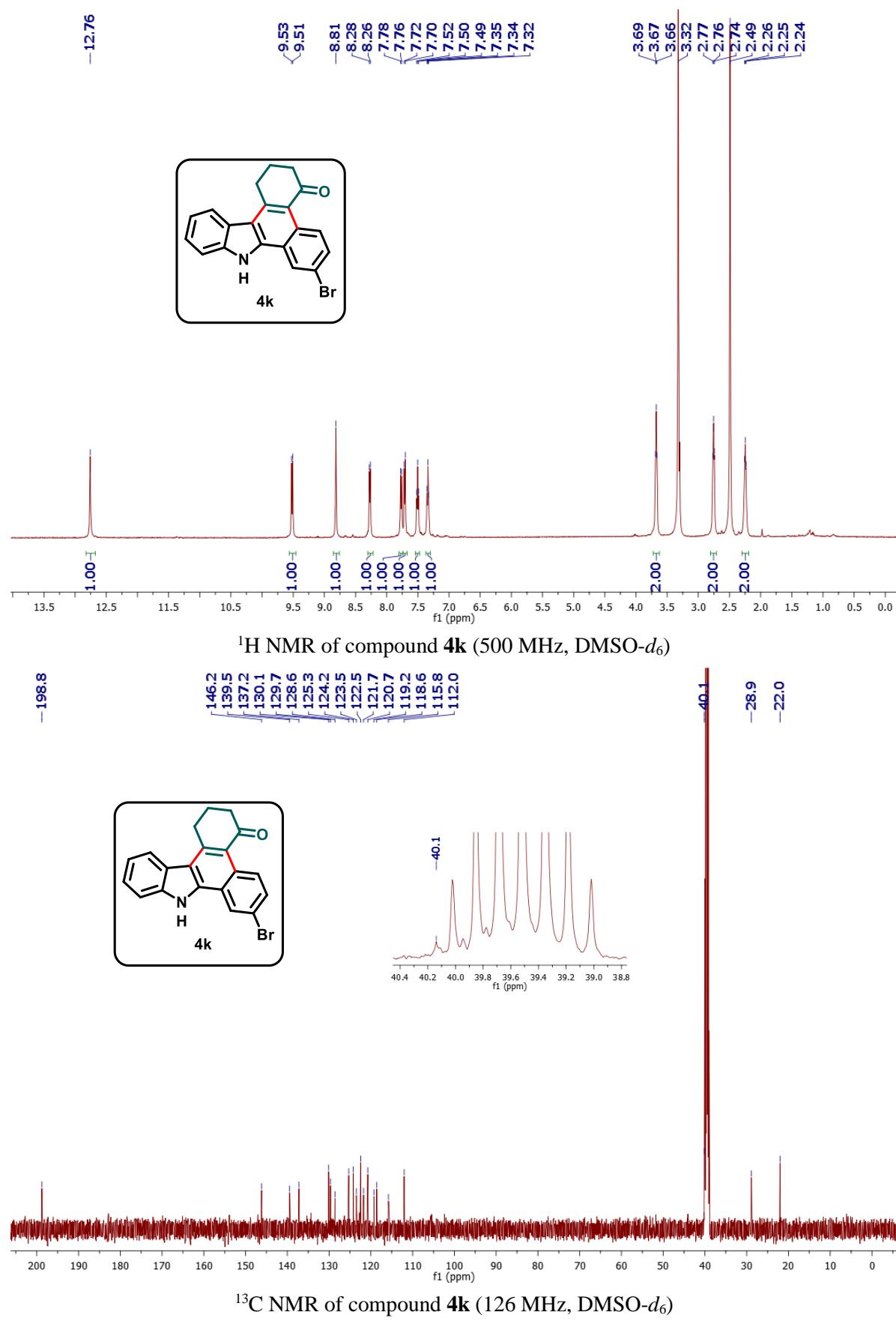




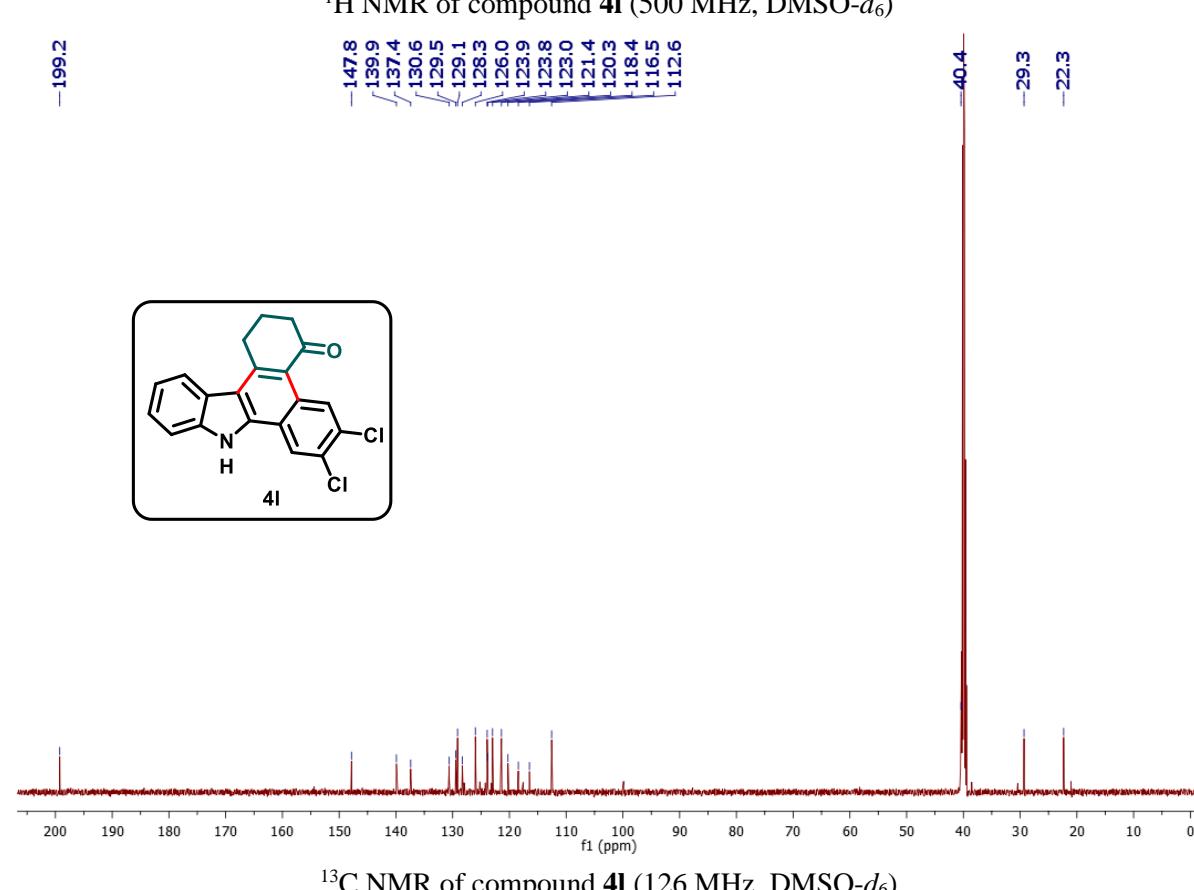
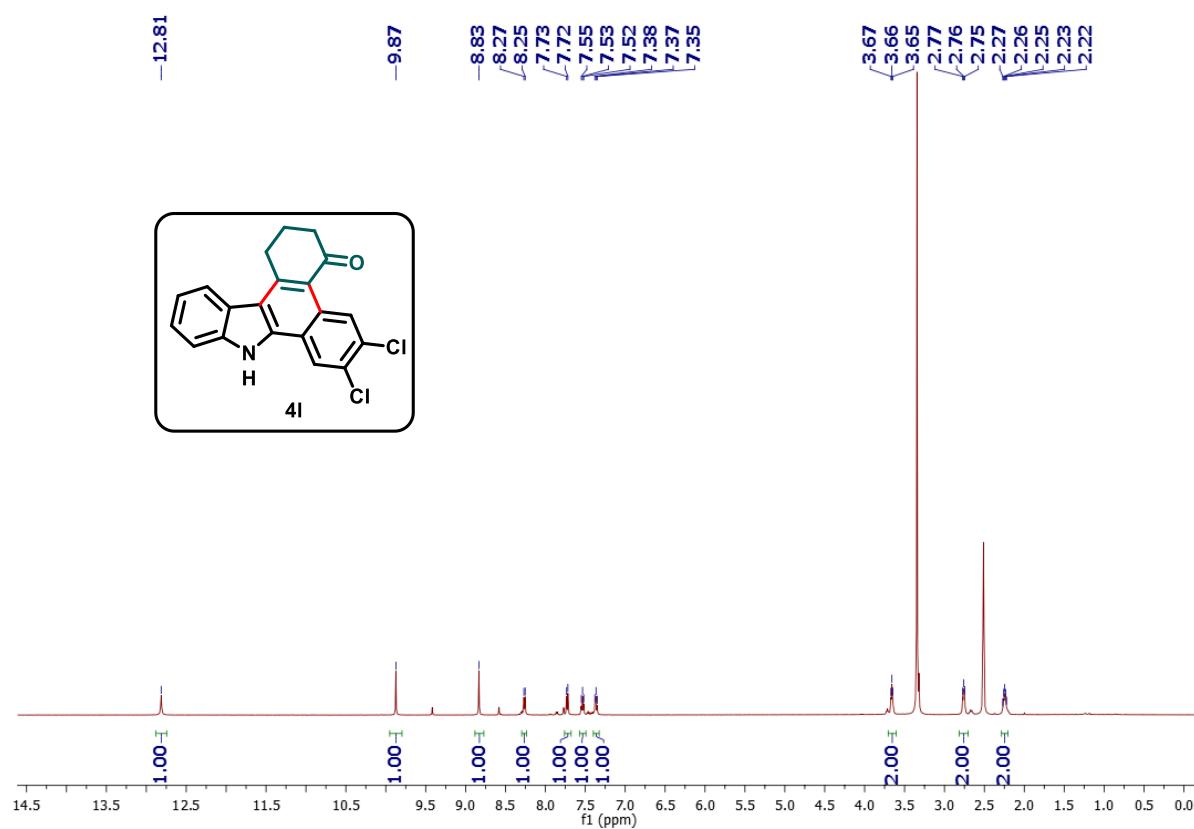
**7-methoxy-1,2,3,9-tetrahydro-4*H*-dibenzo[*a,c*]carbazol-4-one (**4j**):**



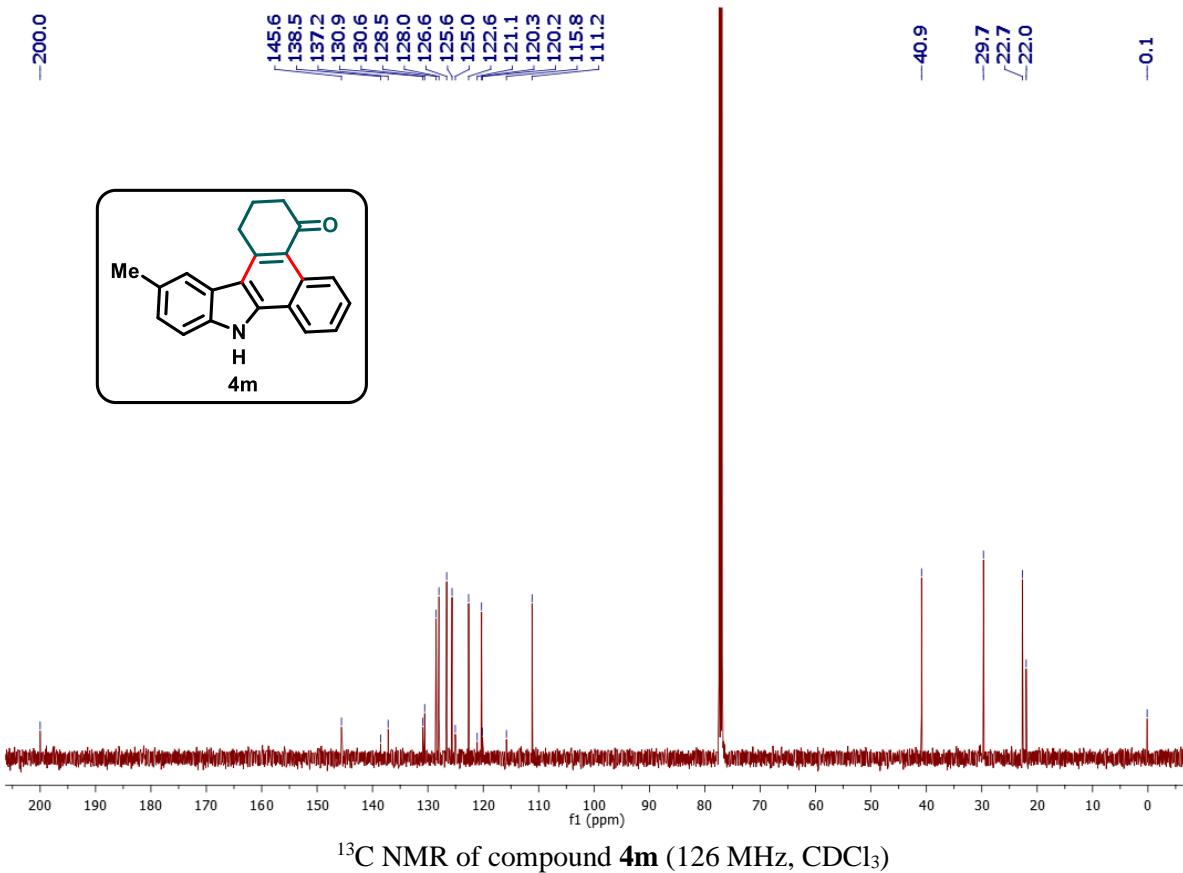
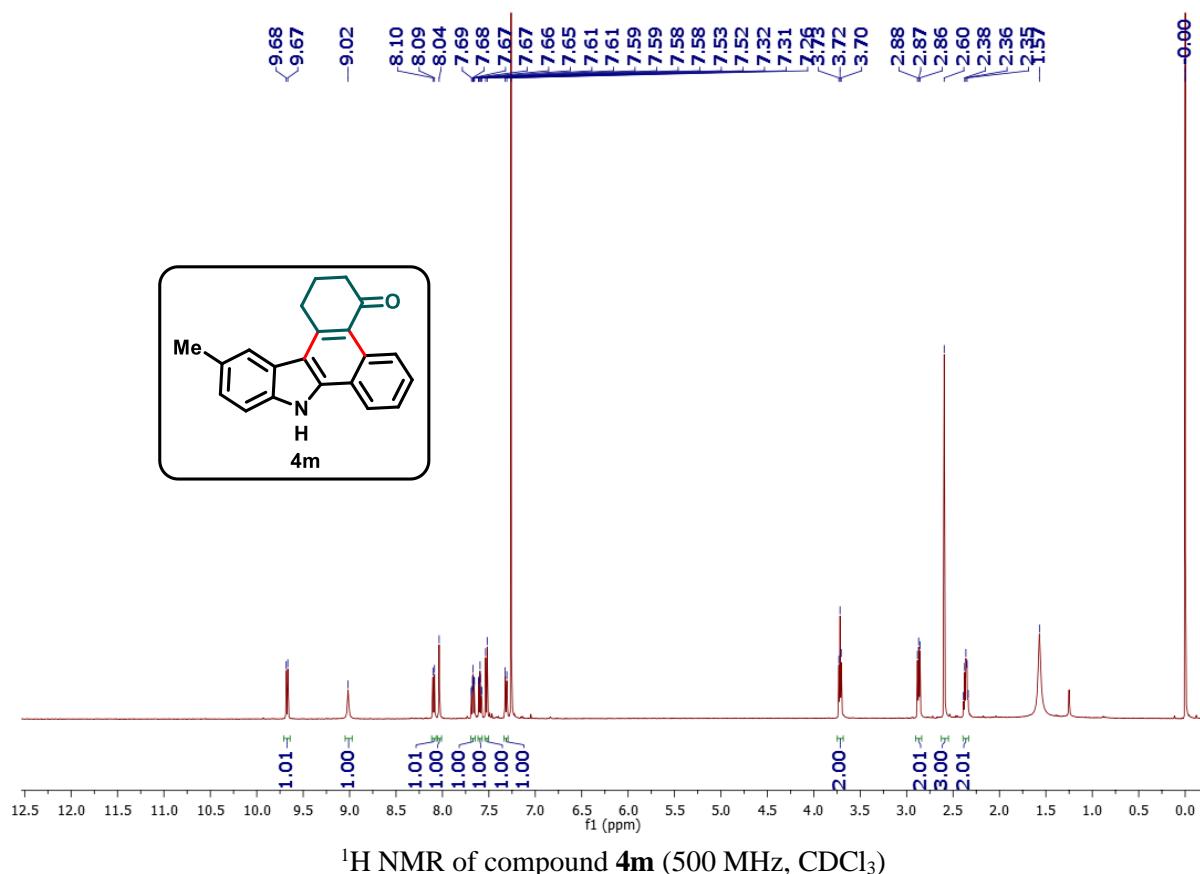
**7-bromo-1,2,3,9-tetrahydro-4*H*-dibenzo[*a,c*]carbazol-4-one (**4k**):**



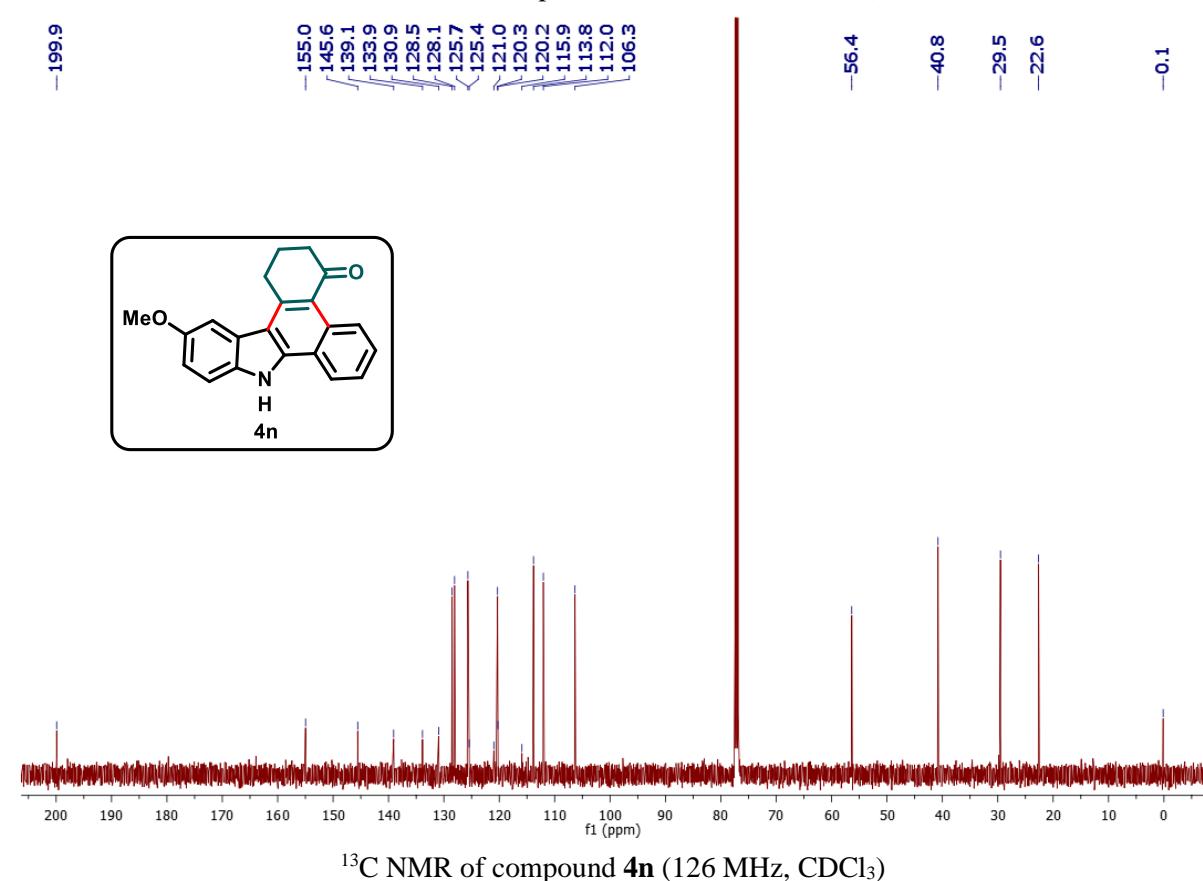
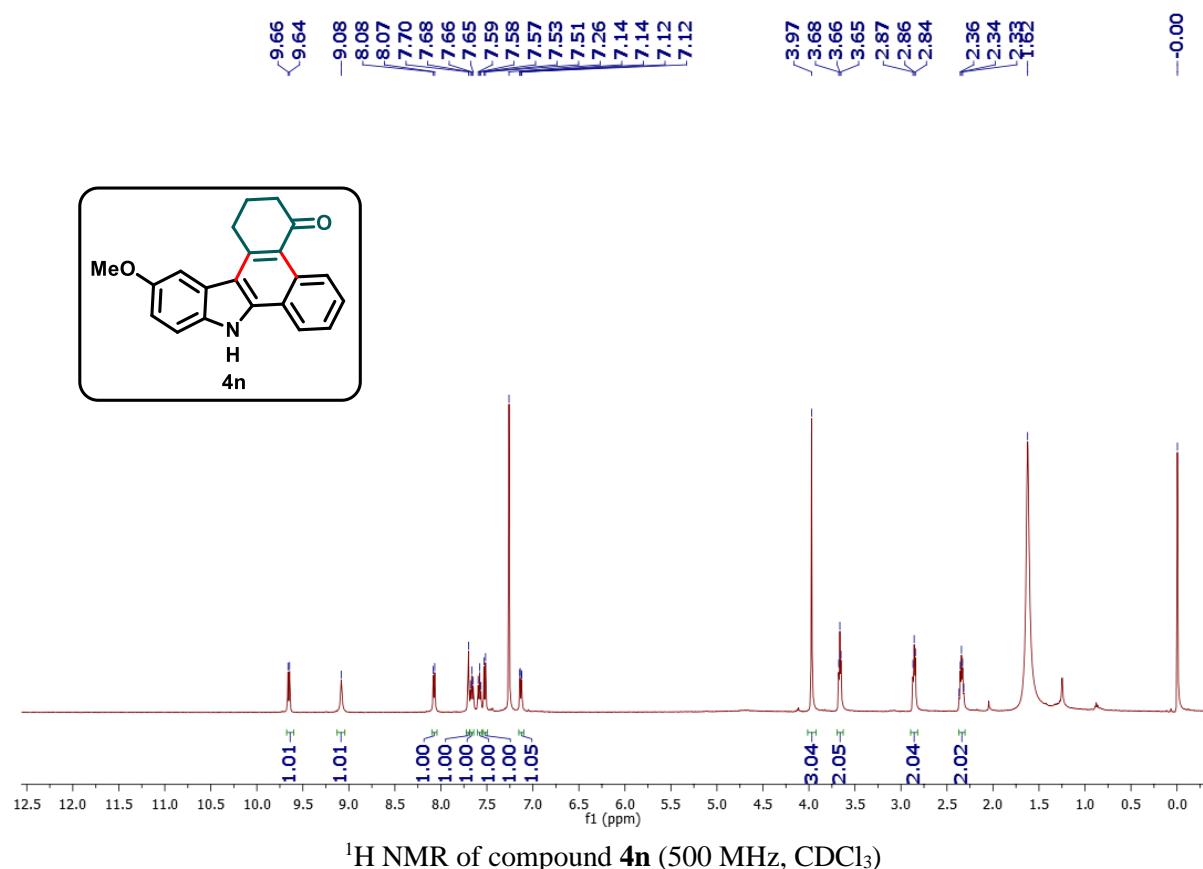
**6,7-dichloro-1,2,3,9-tetrahydro-4*H*-dibenzo[*a,c*]carbazol-4-one (**4l**):**



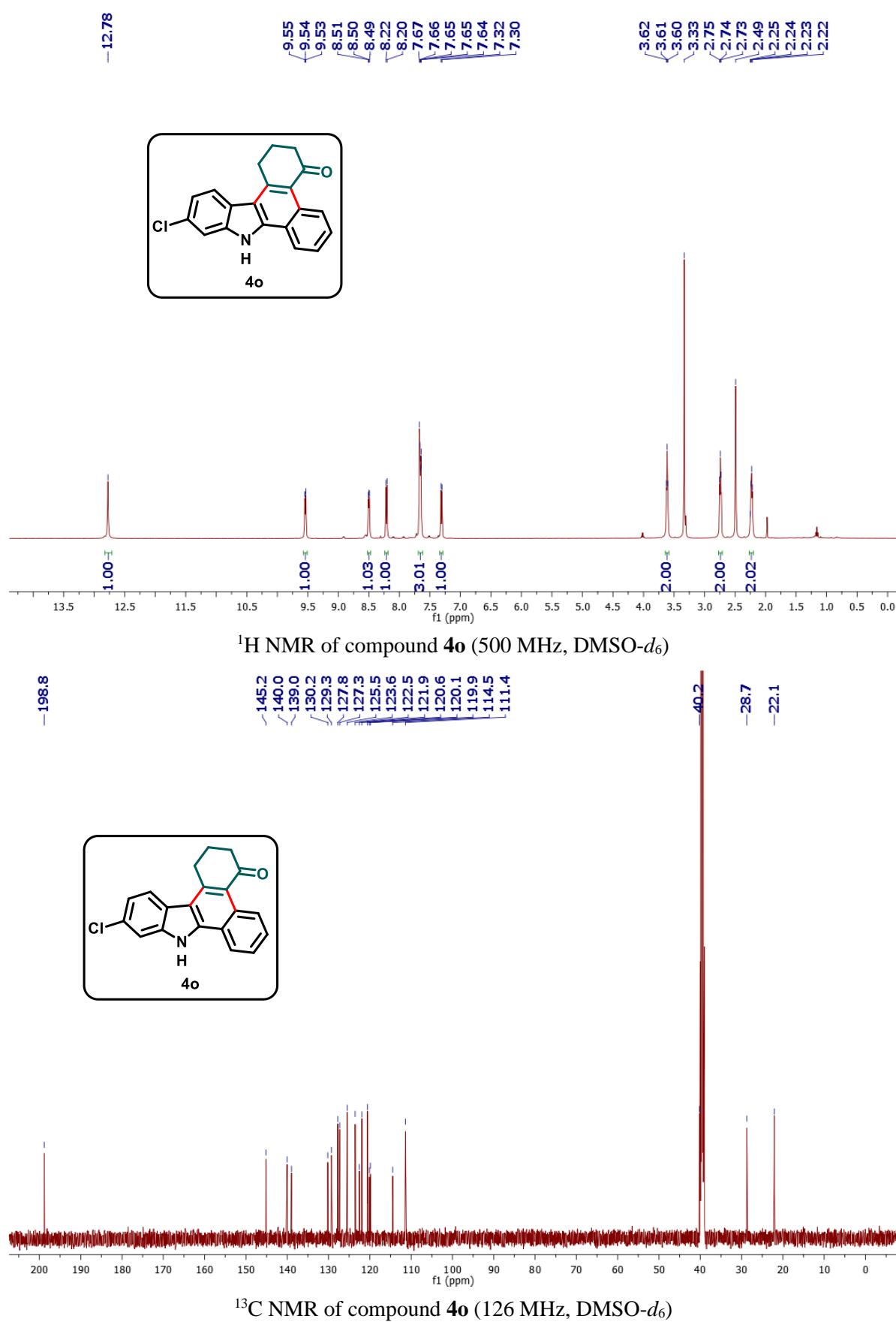
**12-methyl-1,2,3,9-tetrahydro-4*H*-dibenzo[*a,c*]carbazol-4-one (**4m**):**



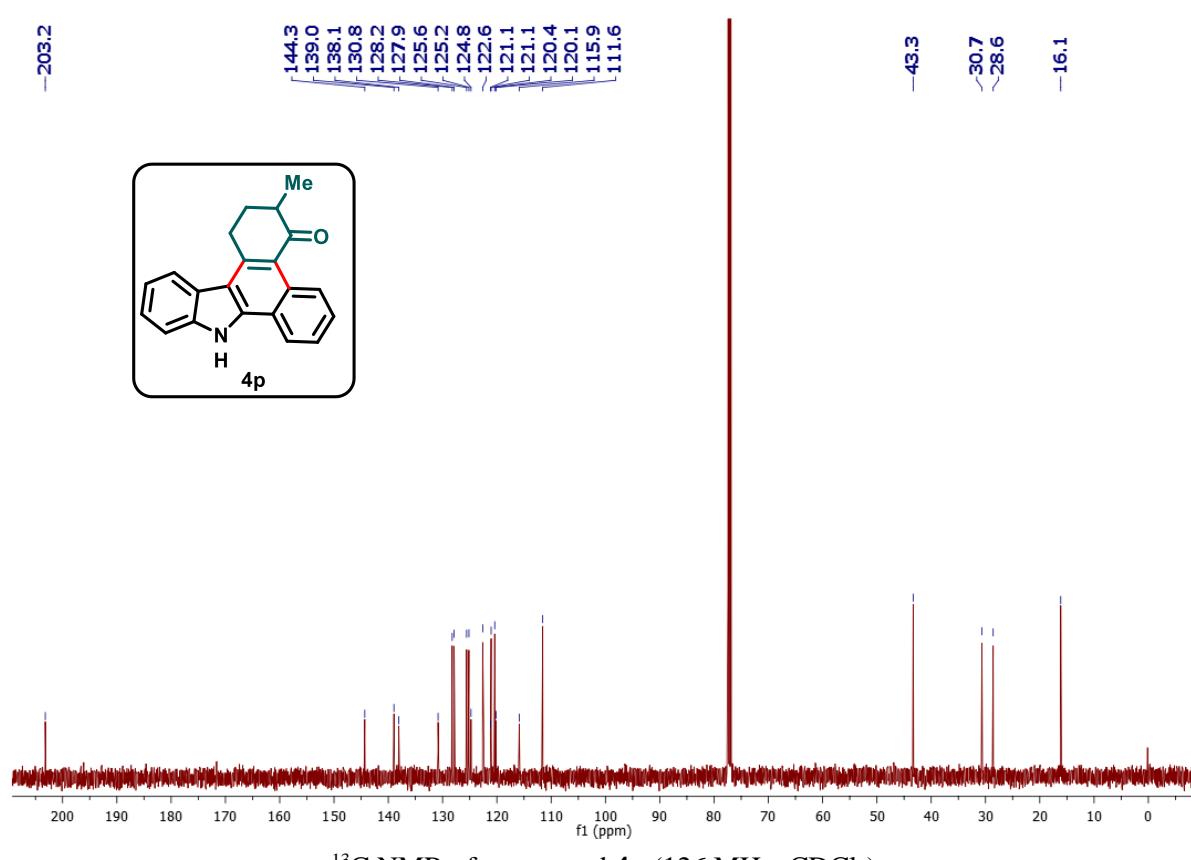
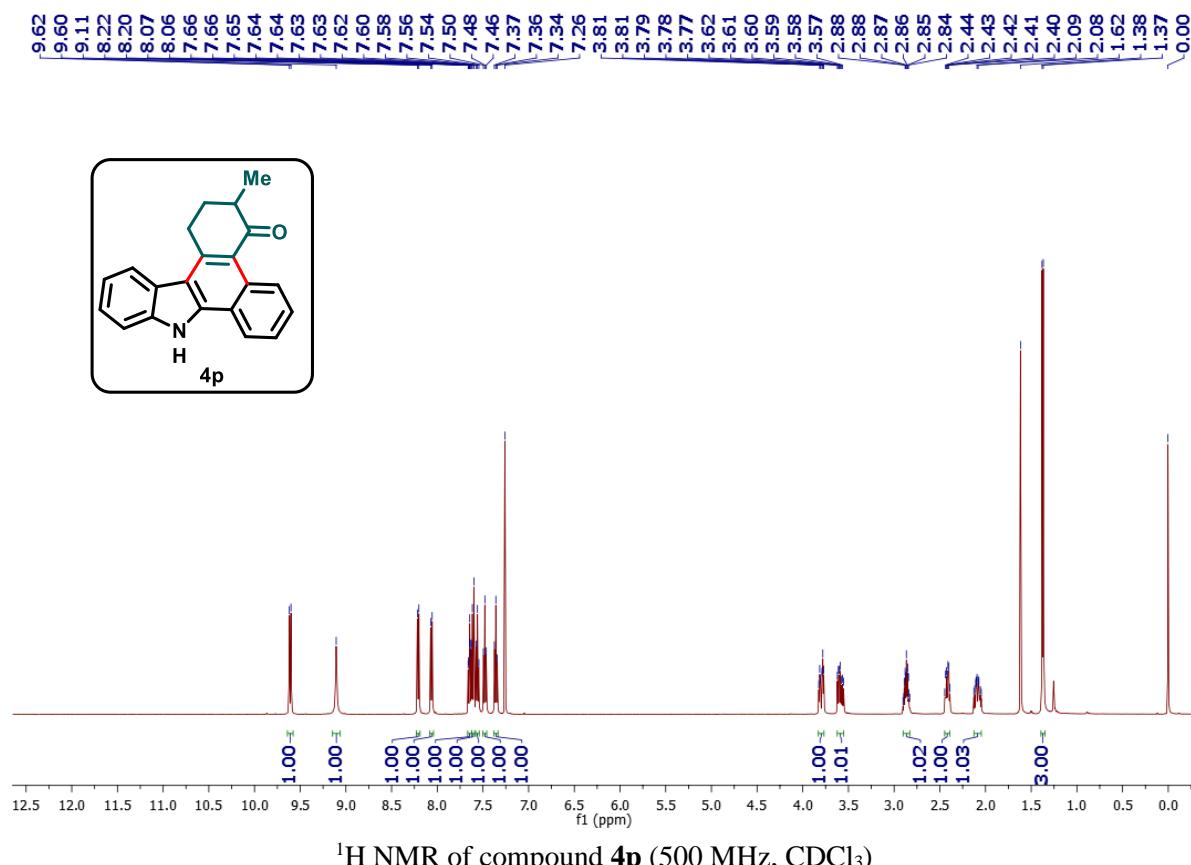
**12-methoxy-1,2,3,9-tetrahydro-4H-dibenzo[*a,c*]carbazol-4-one (**4n**):**



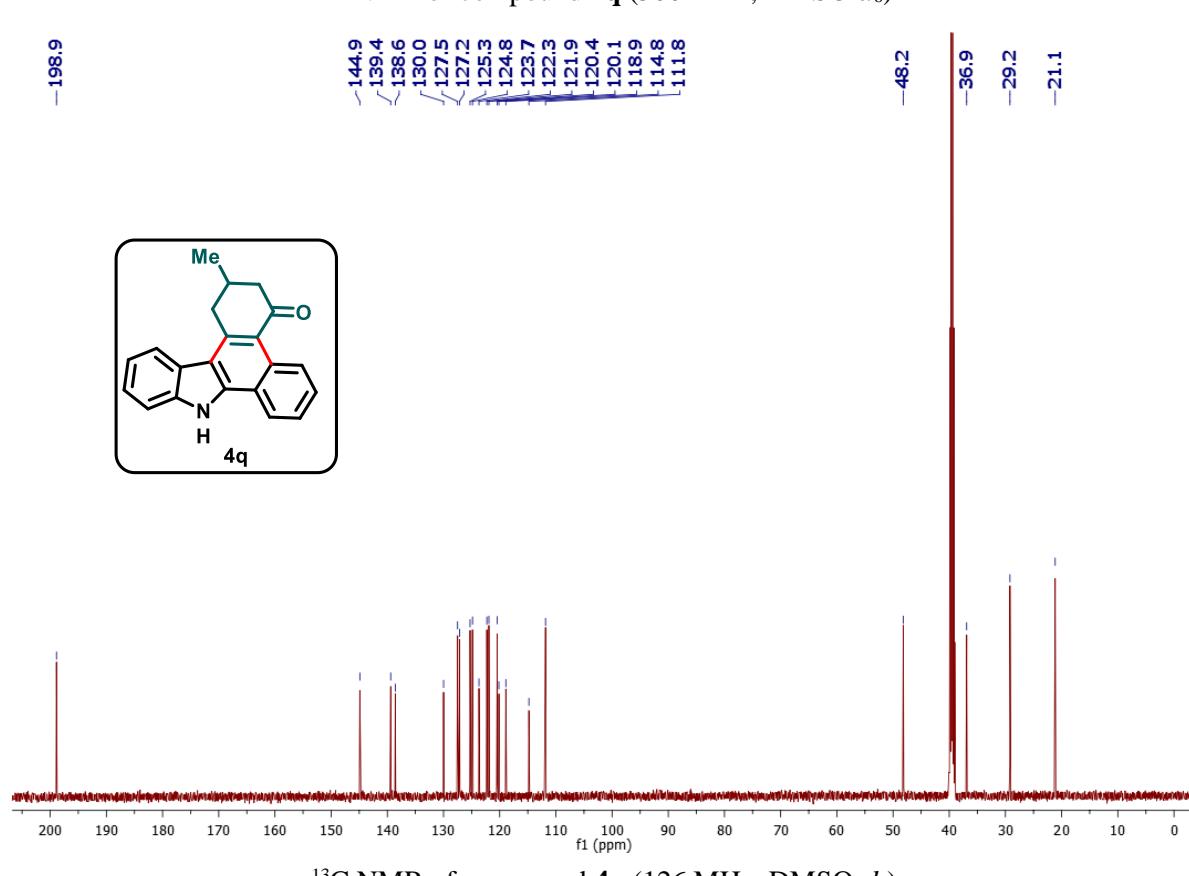
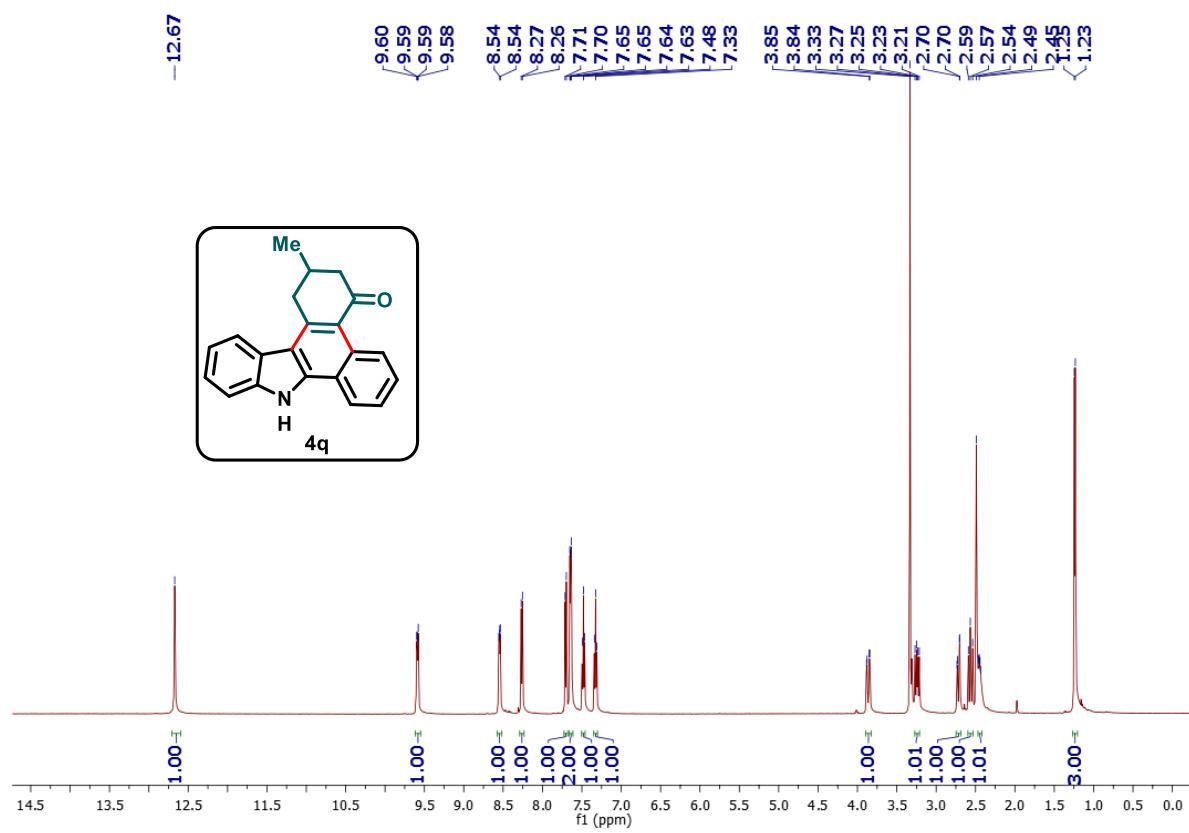
**11-chloro-1,2,3,9-tetrahydro-4*H*-dibenzo[*a,c*]carbazol-4-one (**4o**):**



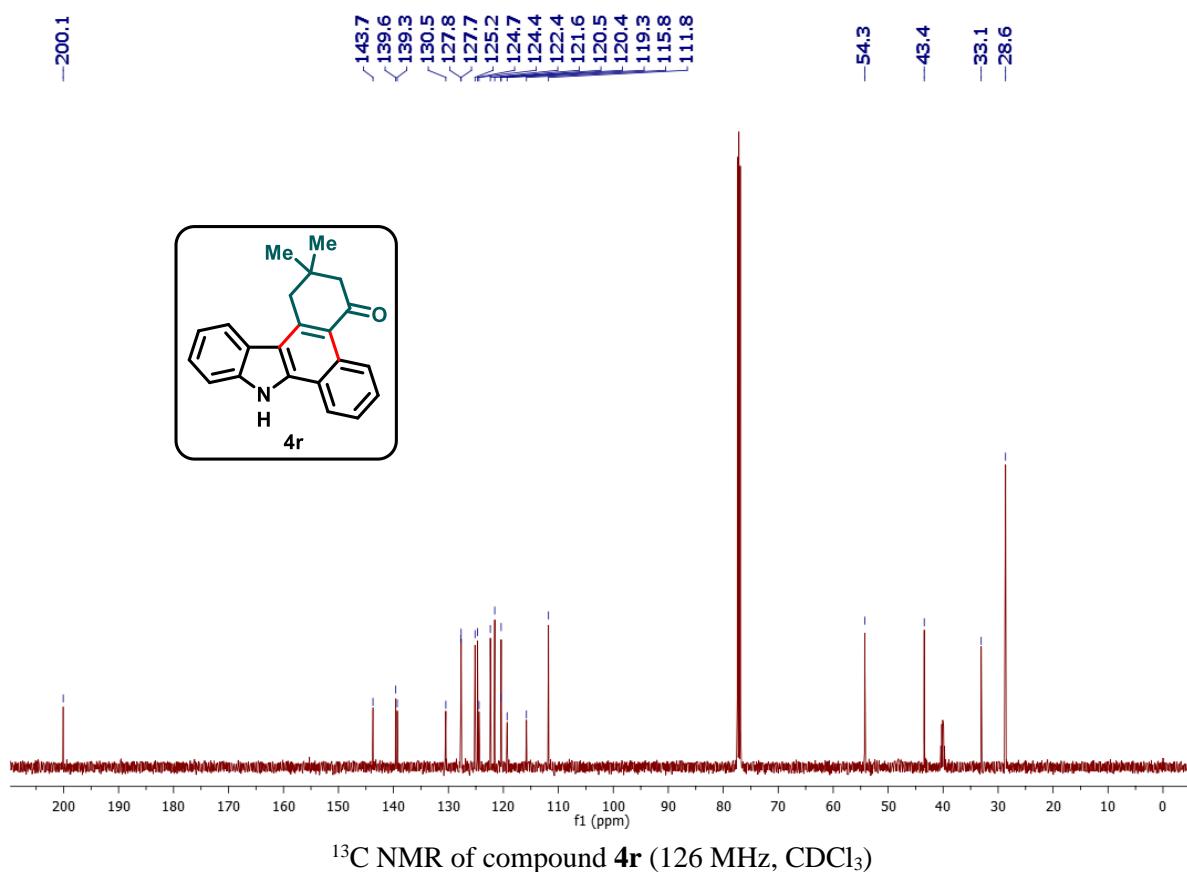
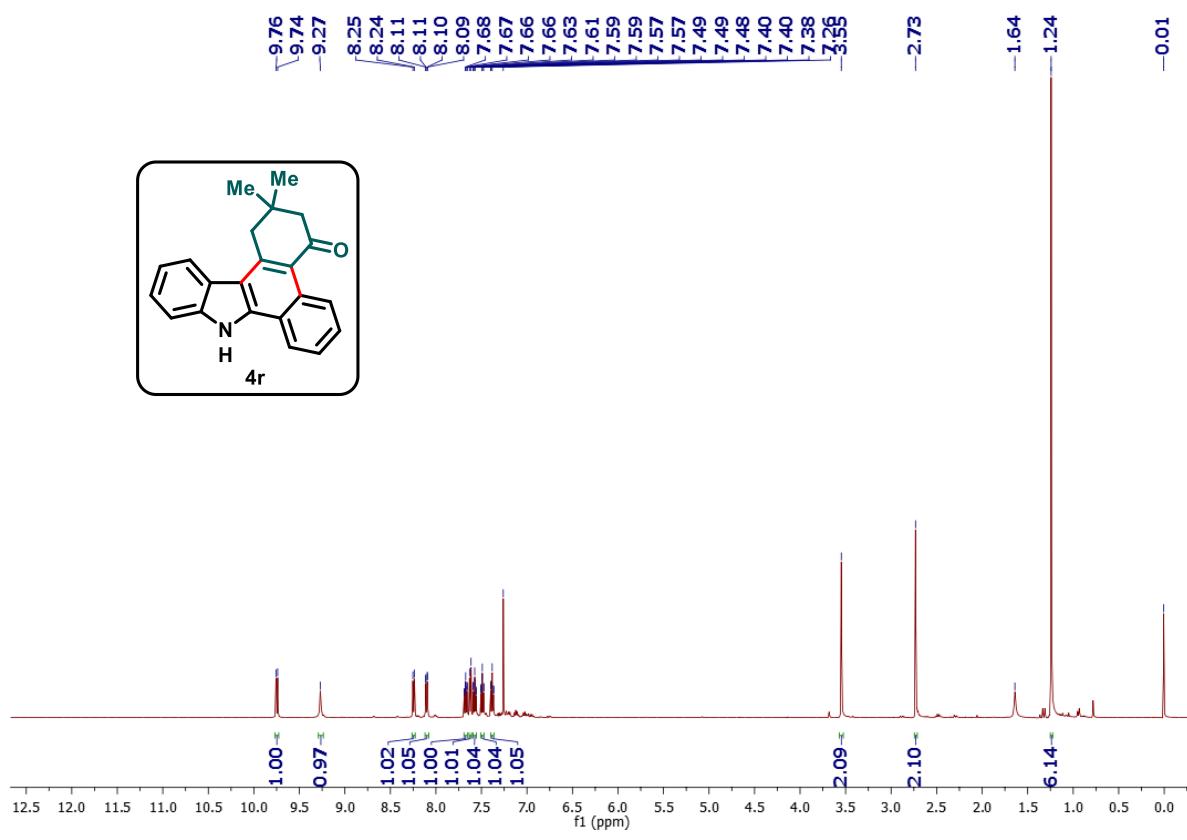
**3-methyl-1,2,3,9-tetrahydro-4H-dibenzo[*a,c*]carbazol-4-one (**4p**):**



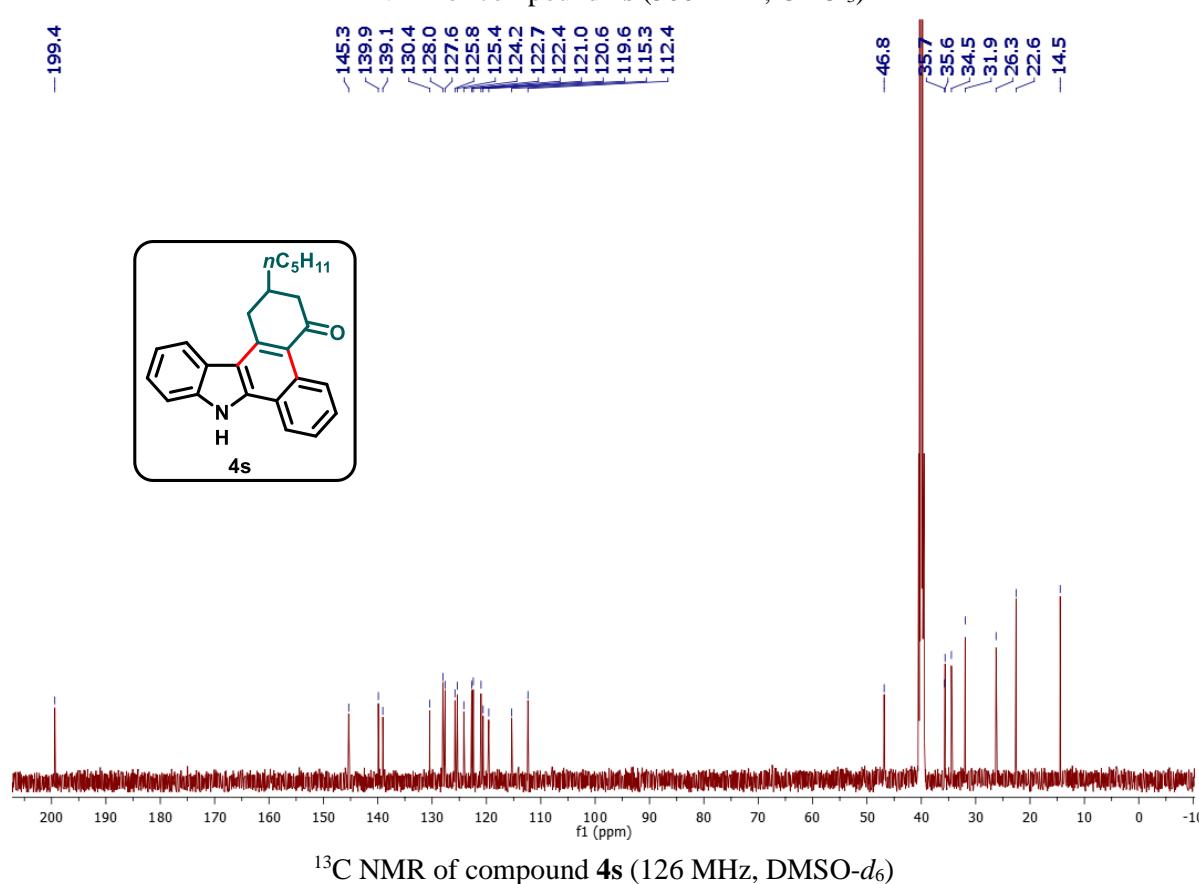
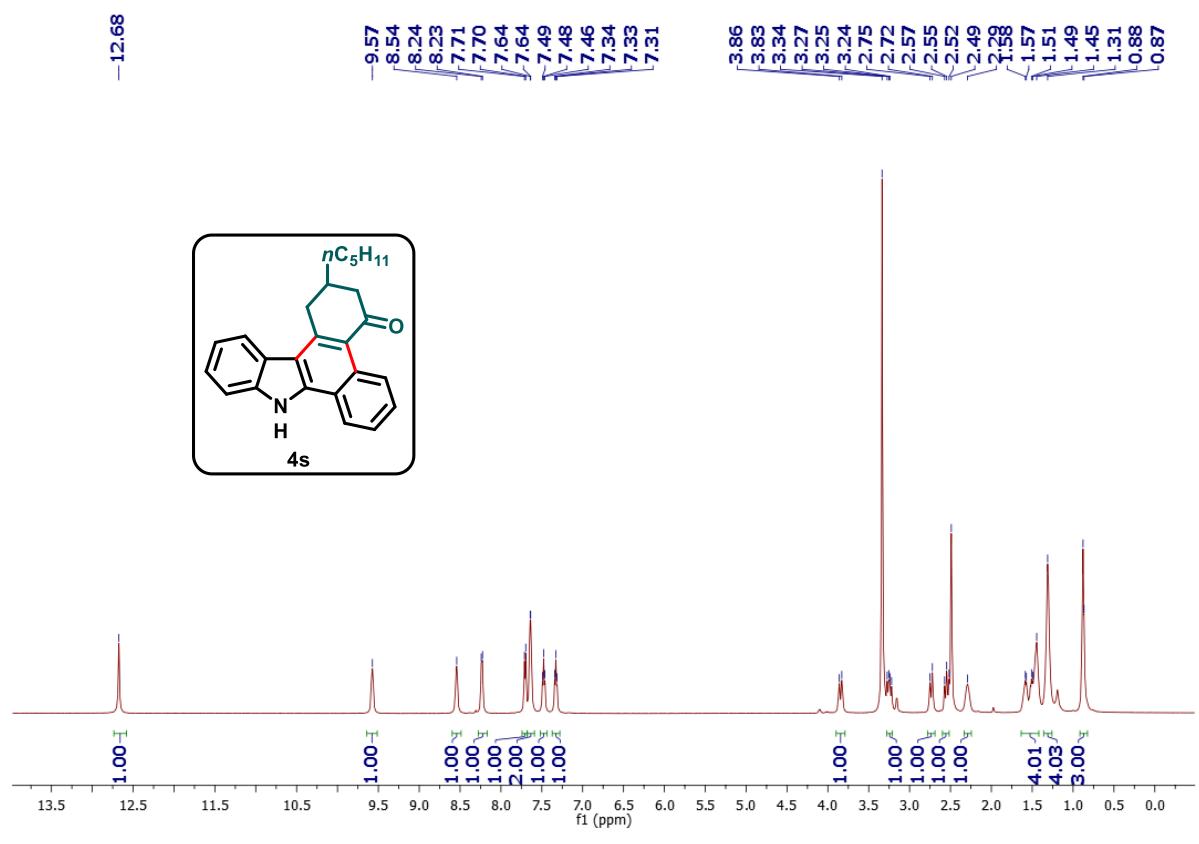
**2-methyl-1,2,3,9-tetrahydro-4H-dibenzo[*a,c*]carbazol-4-one (**4q**):**



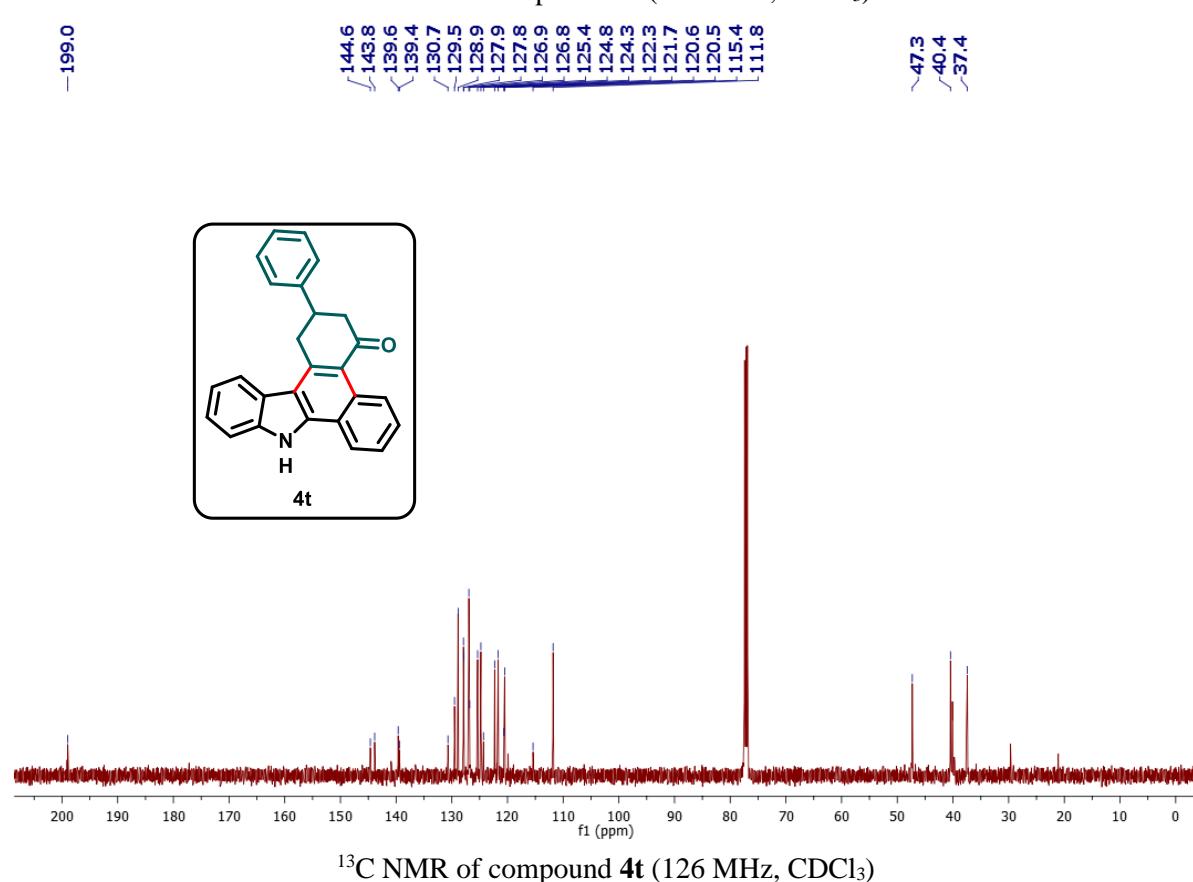
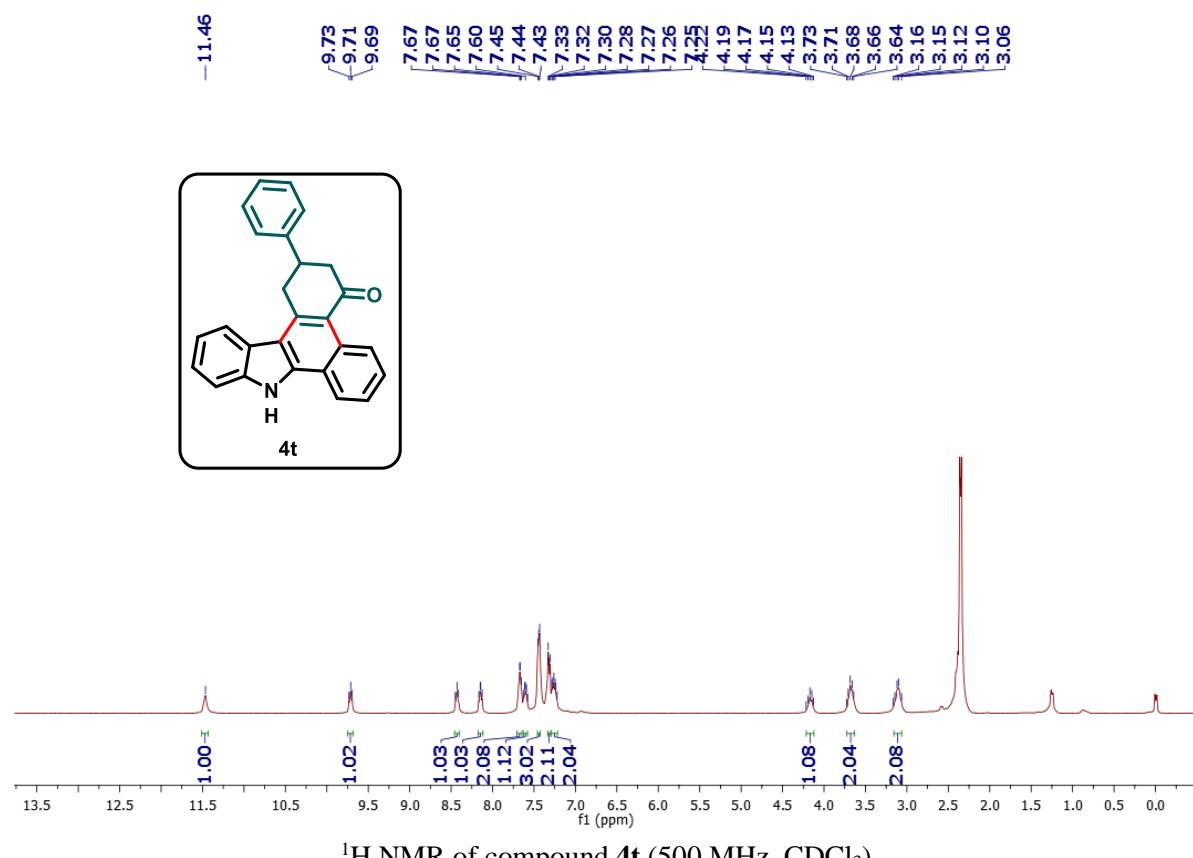
**2,2-dimethyl-1,2,3,9-tetrahydro-4H-dibenzo[*a,c*]carbazol-4-one (**4r**):**



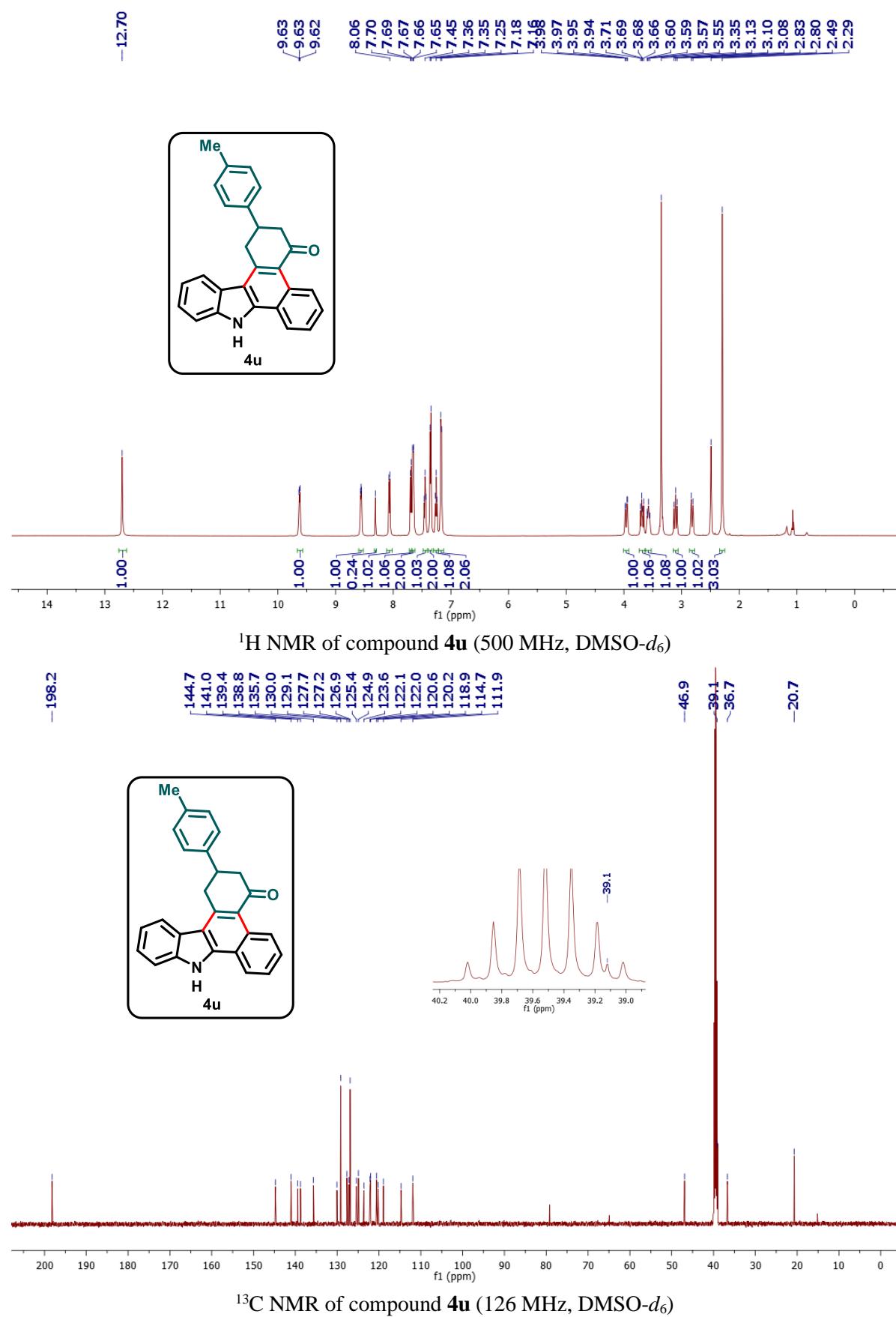
**2-pentyl-1,2,3,9-tetrahydro-4H-dibenzo[*a,c*]carbazol-4-one (4s):**



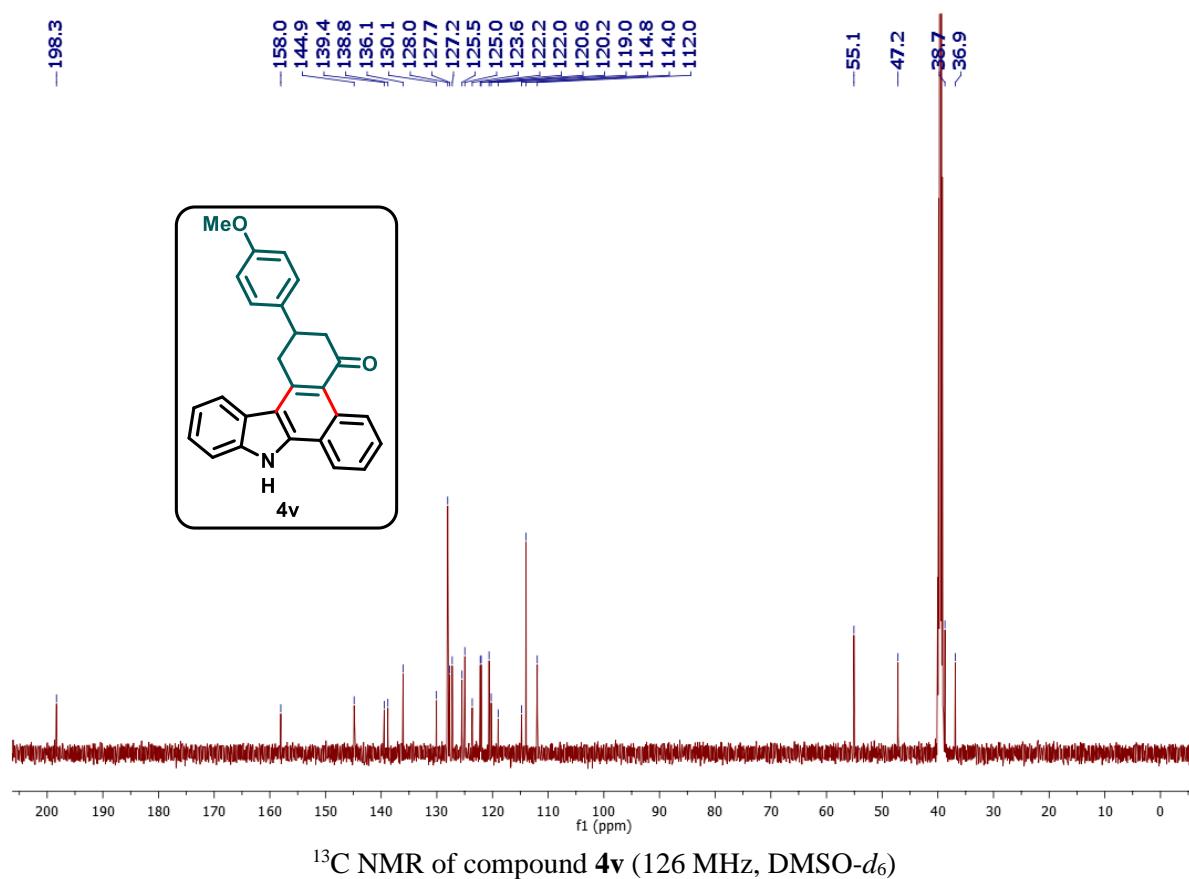
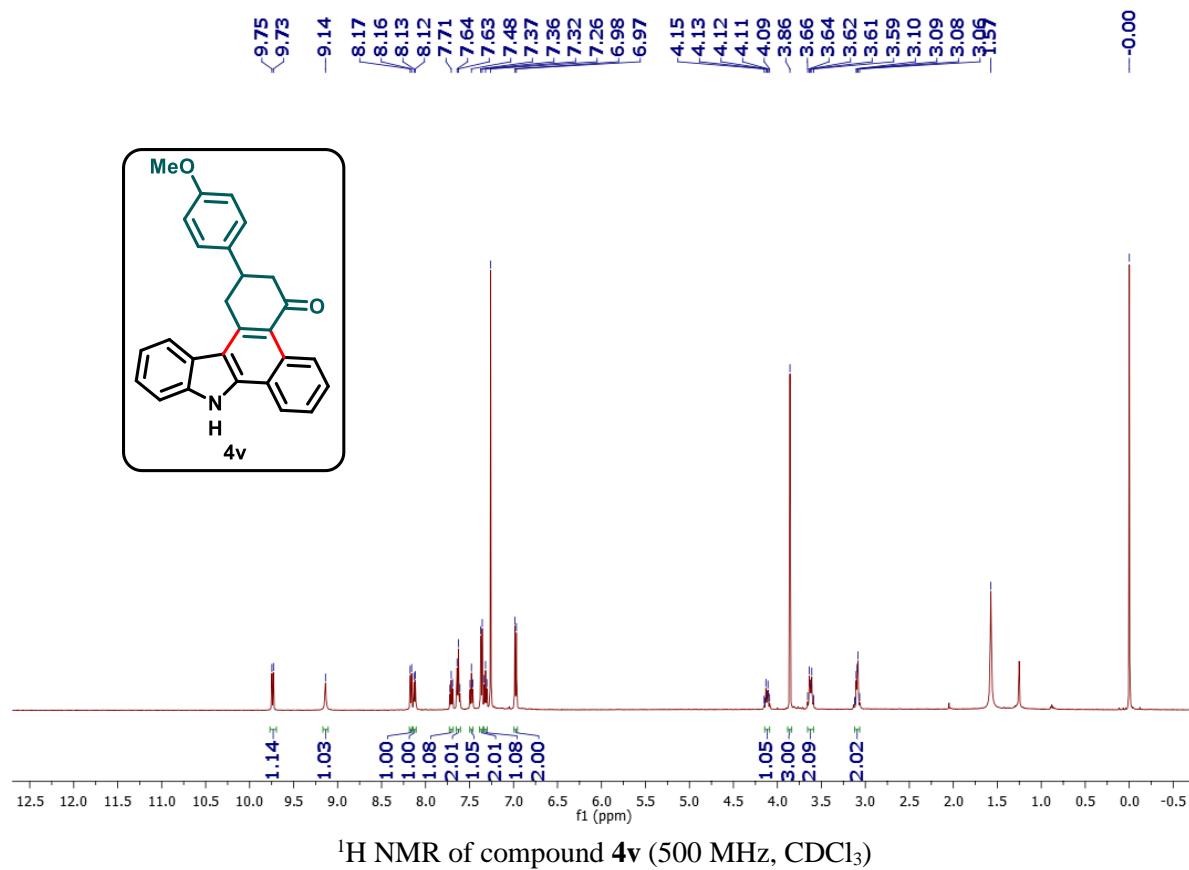
**2-phenyl-1,2,3,9-tetrahydro-4H-dibenzo[*a,c*]carbazol-4-one (**4t**):**



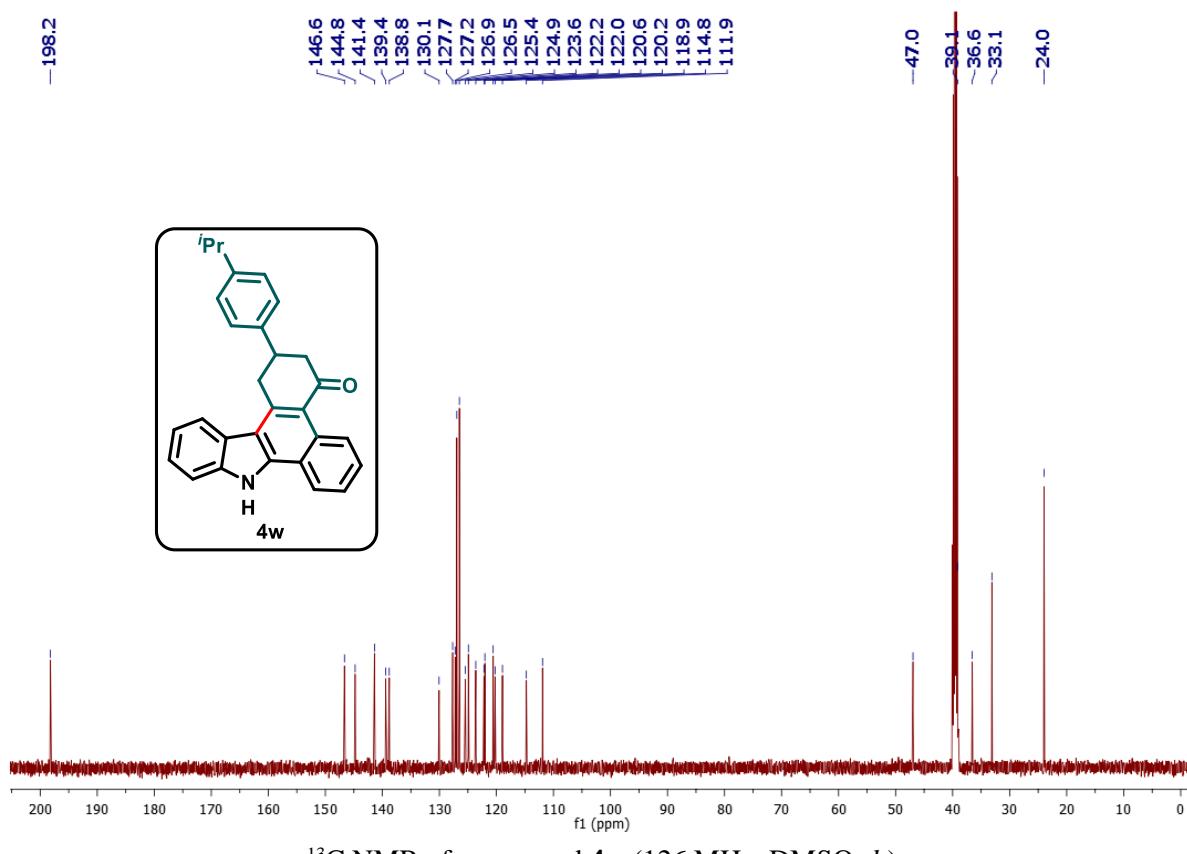
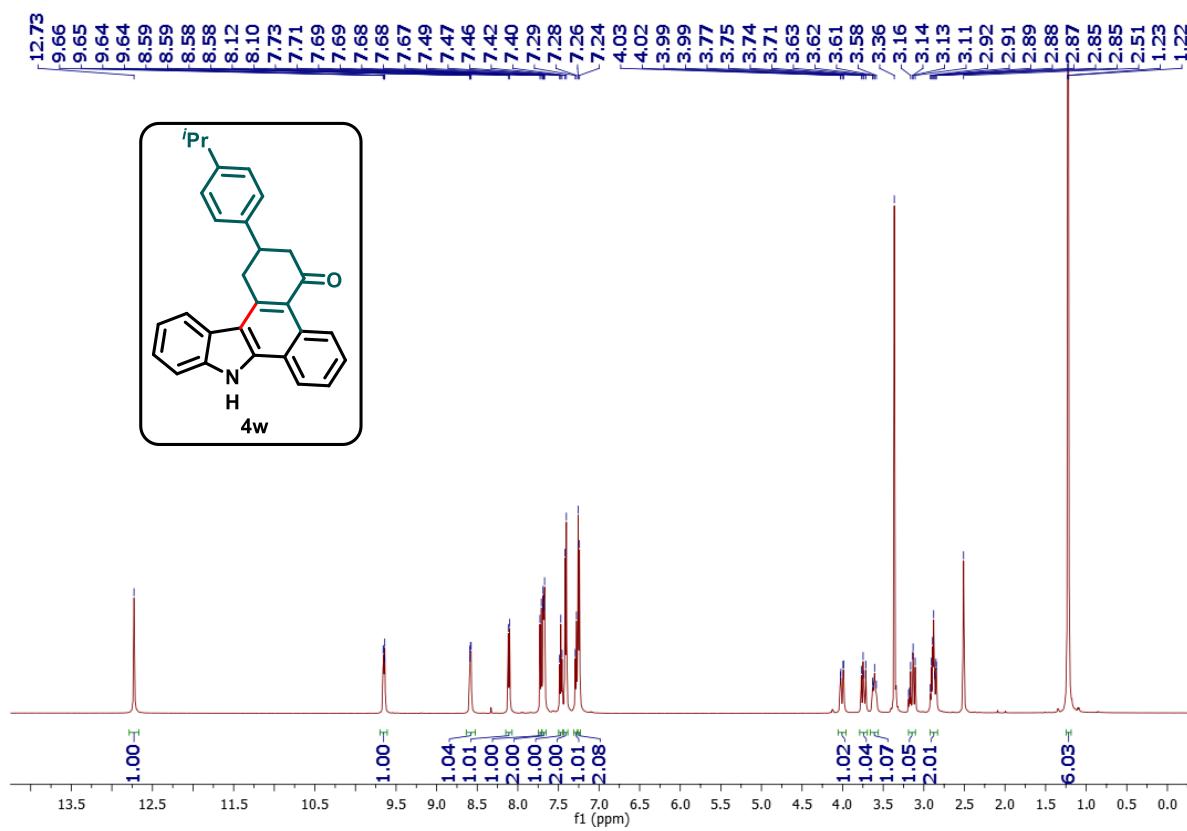
**2-(*p*-tolyl)-1,2,3,9-tetrahydro-4*H*-dibenzo[*a,c*]carbazol-4-one (**4u**):**



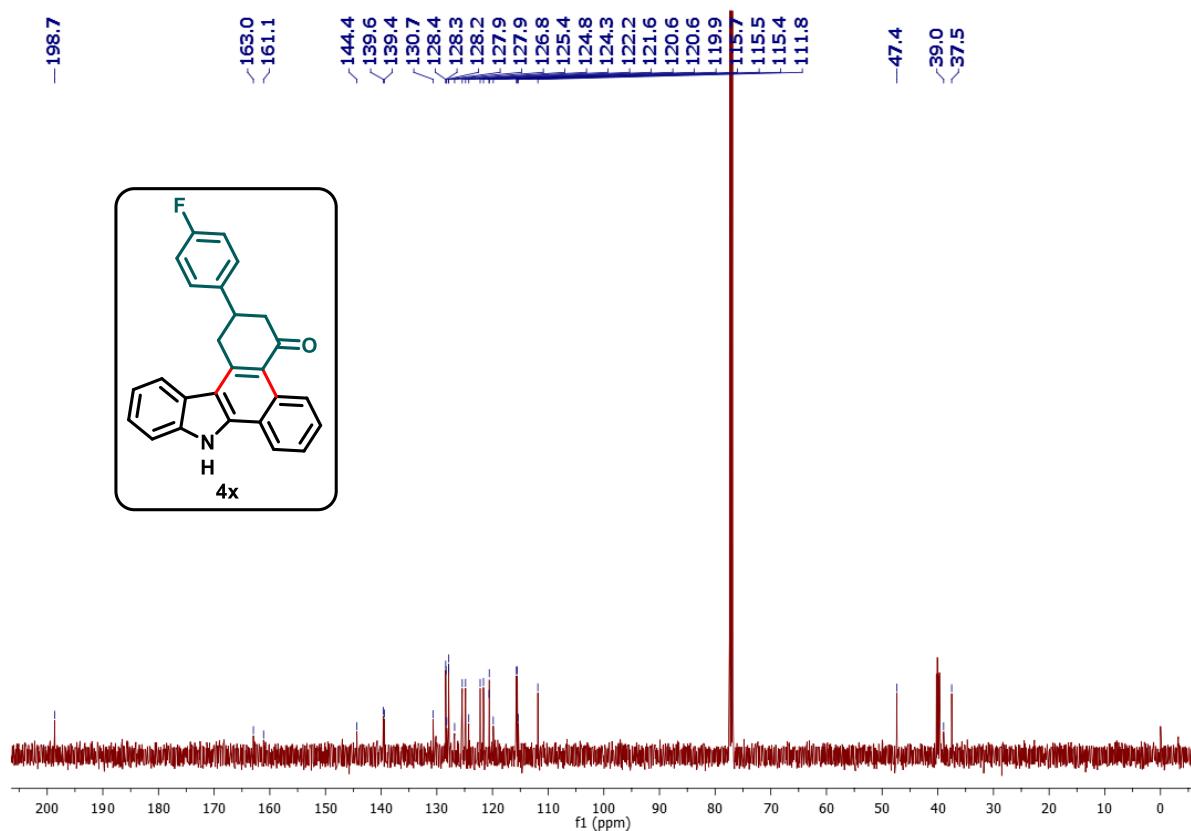
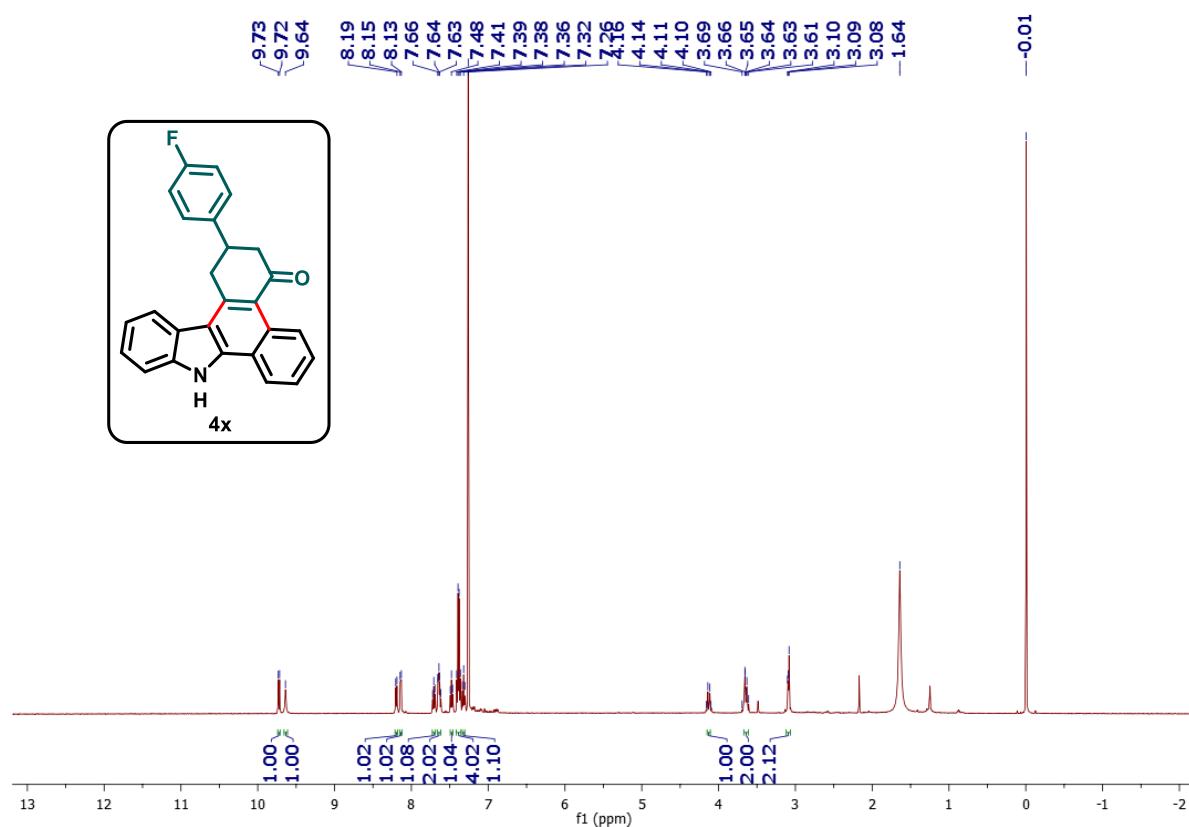
**2-(4-methoxyphenyl)-1,2,3,9-tetrahydro-4H-dibenzo[*a,c*]carbazol-4-one (**4v**):**



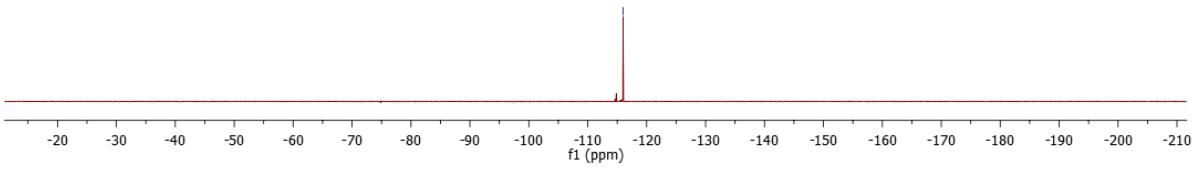
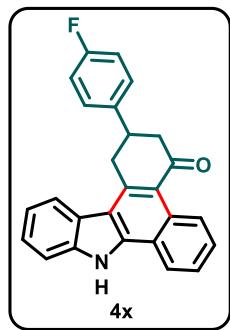
**2-(4-isopropylphenyl)-1,2,3,9-tetrahydro-4H-dibenzo[*a,c*]carbazol-4-one (**4w**):**



**2-(4-fluorophenyl)-1,2,3,9-tetrahydro-4H-dibenzo[*a,c*]carbazol-4-one (**4x**):**

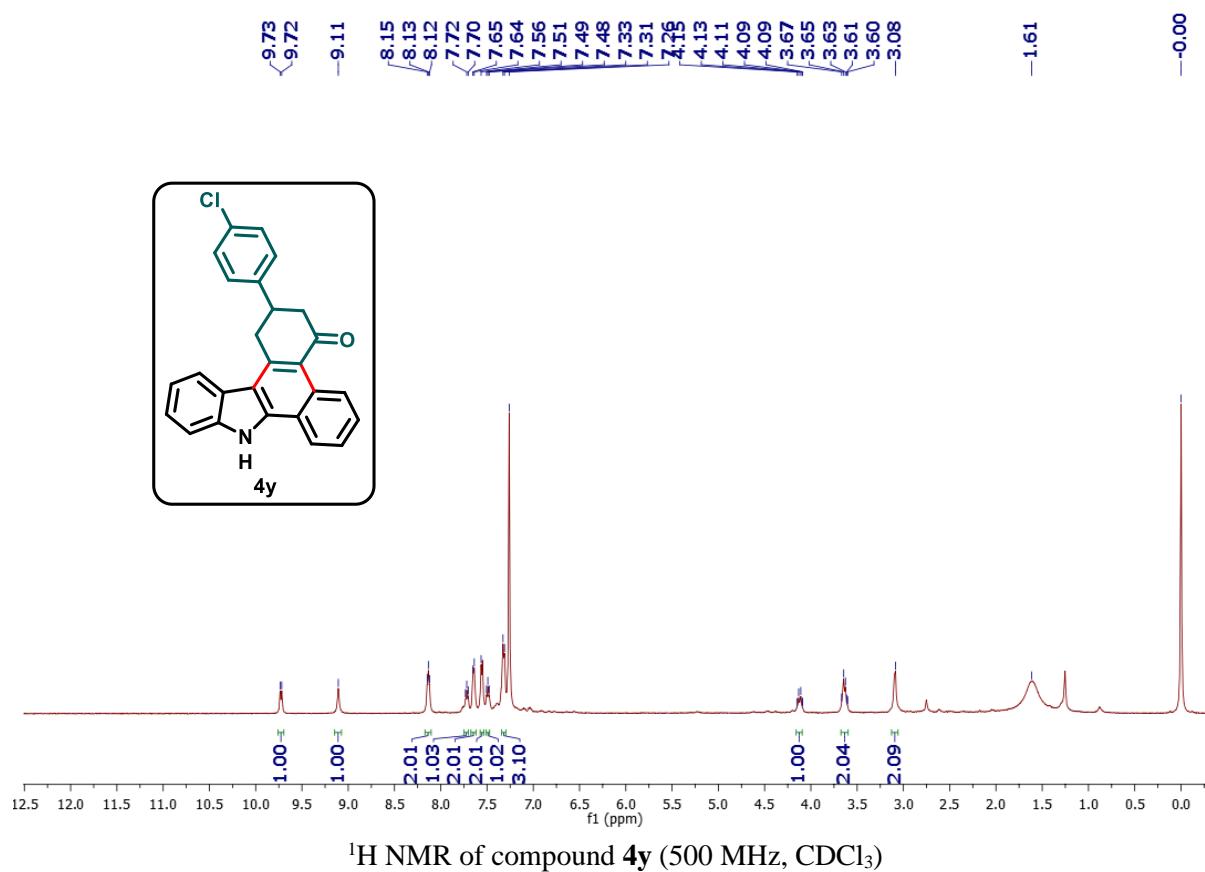


-115.99

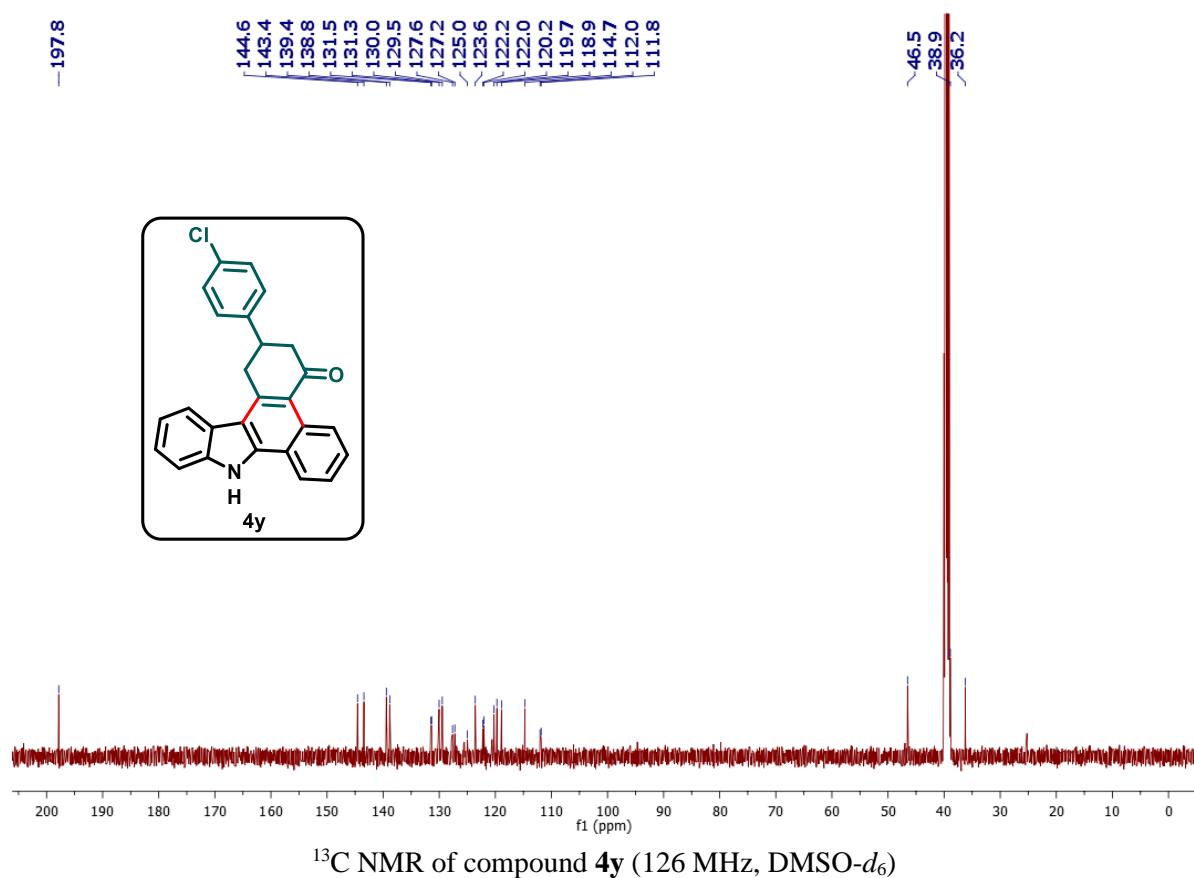


<sup>19</sup>F NMR of compound **4x** (470 MHz,  $\text{CDCl}_3$ )

**2-(4-chlorophenyl)-1,2,3,9-tetrahydro-4*H*-dibenzo[*a,c*]carbazol-4-one (**4y**):**

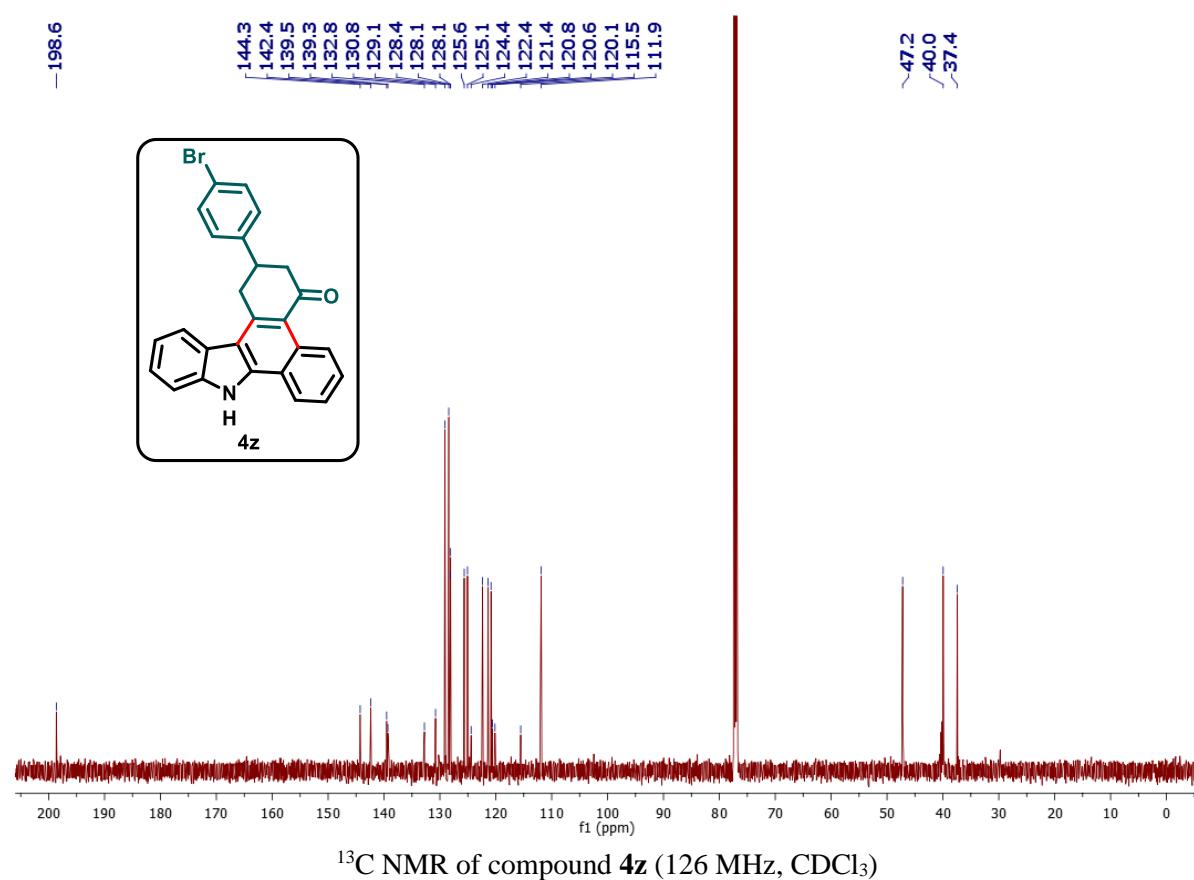
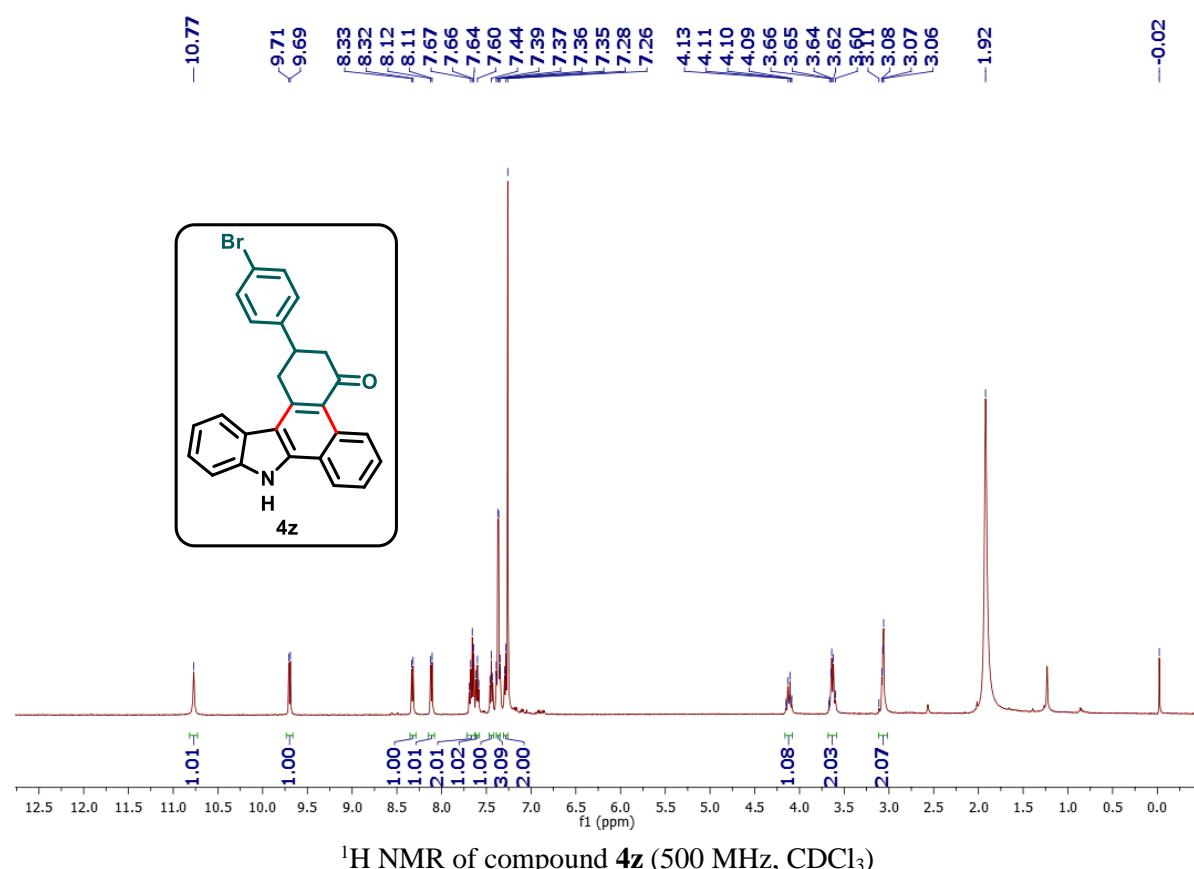


<sup>1</sup>H NMR of compound **4y** (500 MHz, CDCl<sub>3</sub>)

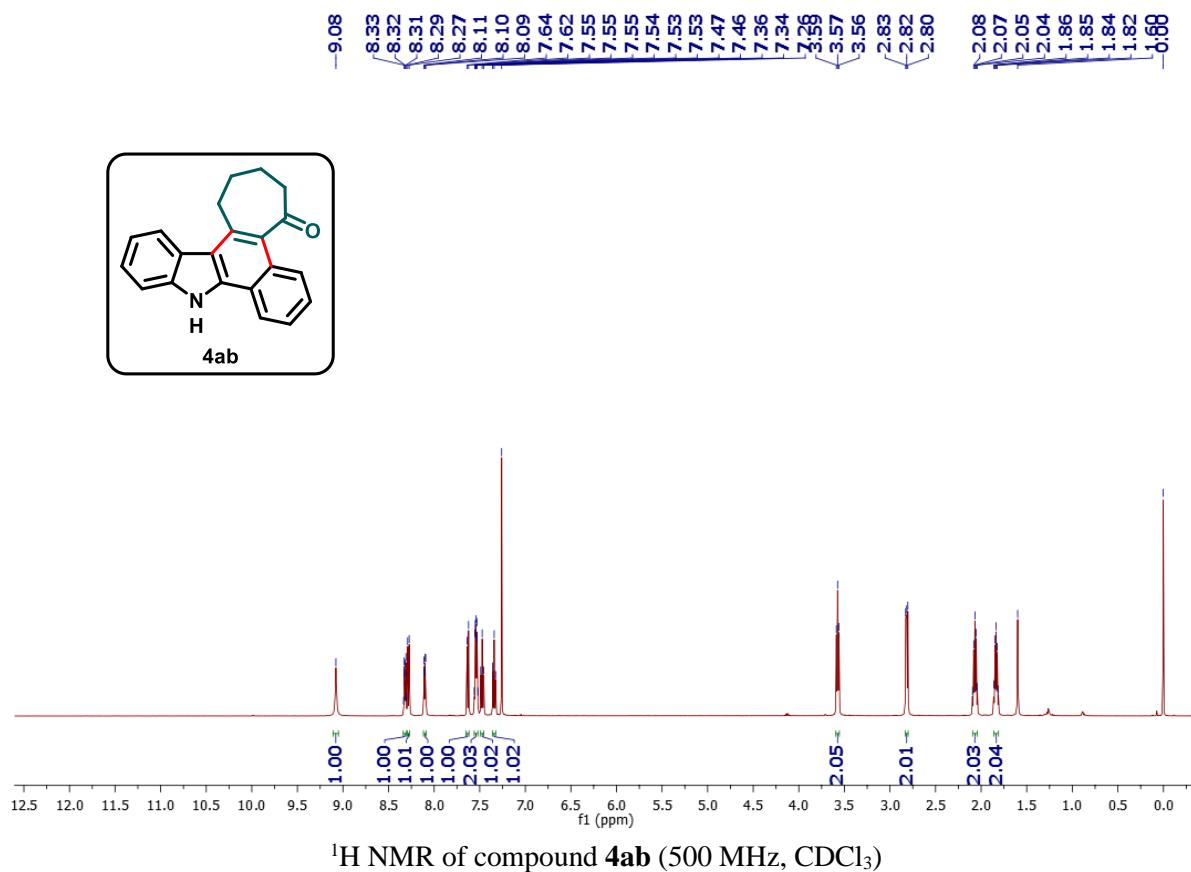


<sup>13</sup>C NMR of compound **4y** (126 MHz, DMSO-*d*<sub>6</sub>)

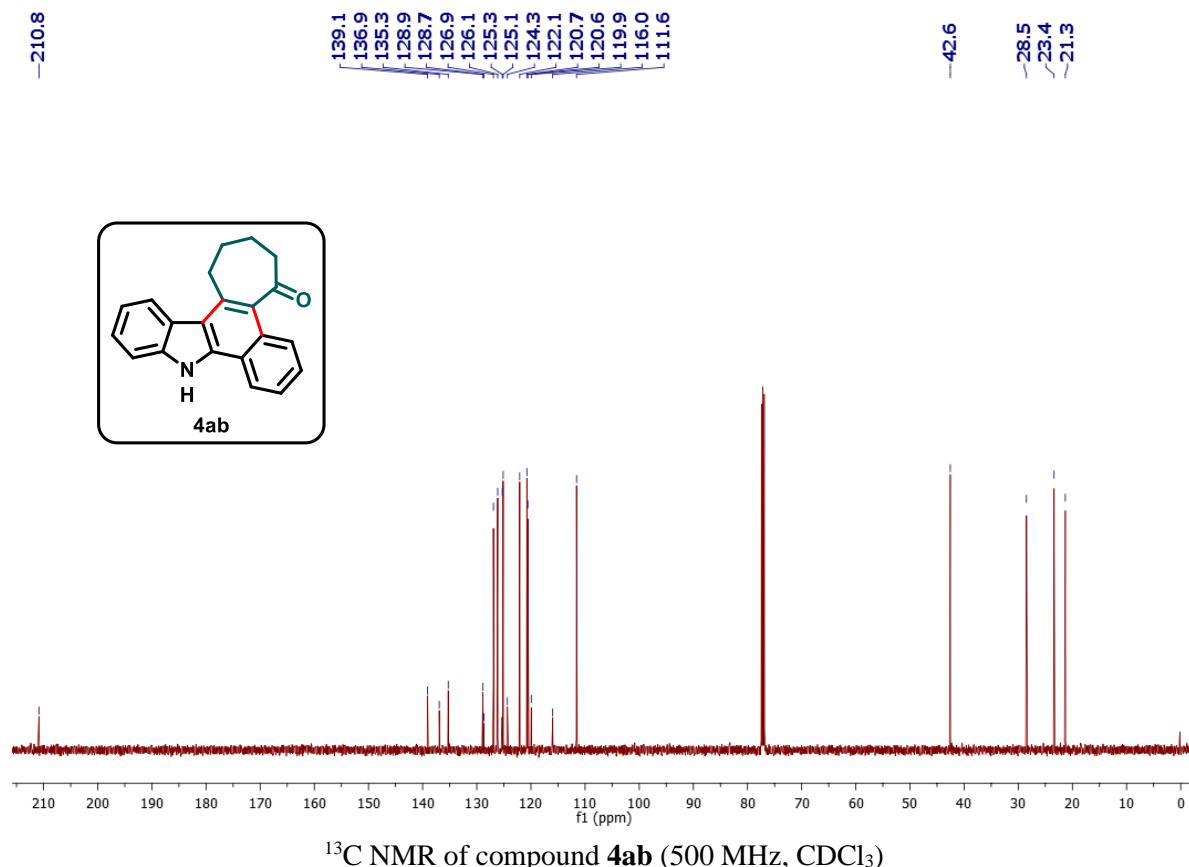
**2-(4-bromophenyl)-1,2,3,9-tetrahydro-4H-dibenzo[*a,c*]carbazol-4-one (**4z**):**



**1,3,4,10-tetrahydrobenzo[*a*]cyclohepta[*c*]carbazol-5(2*H*)-one (**4ab**):**

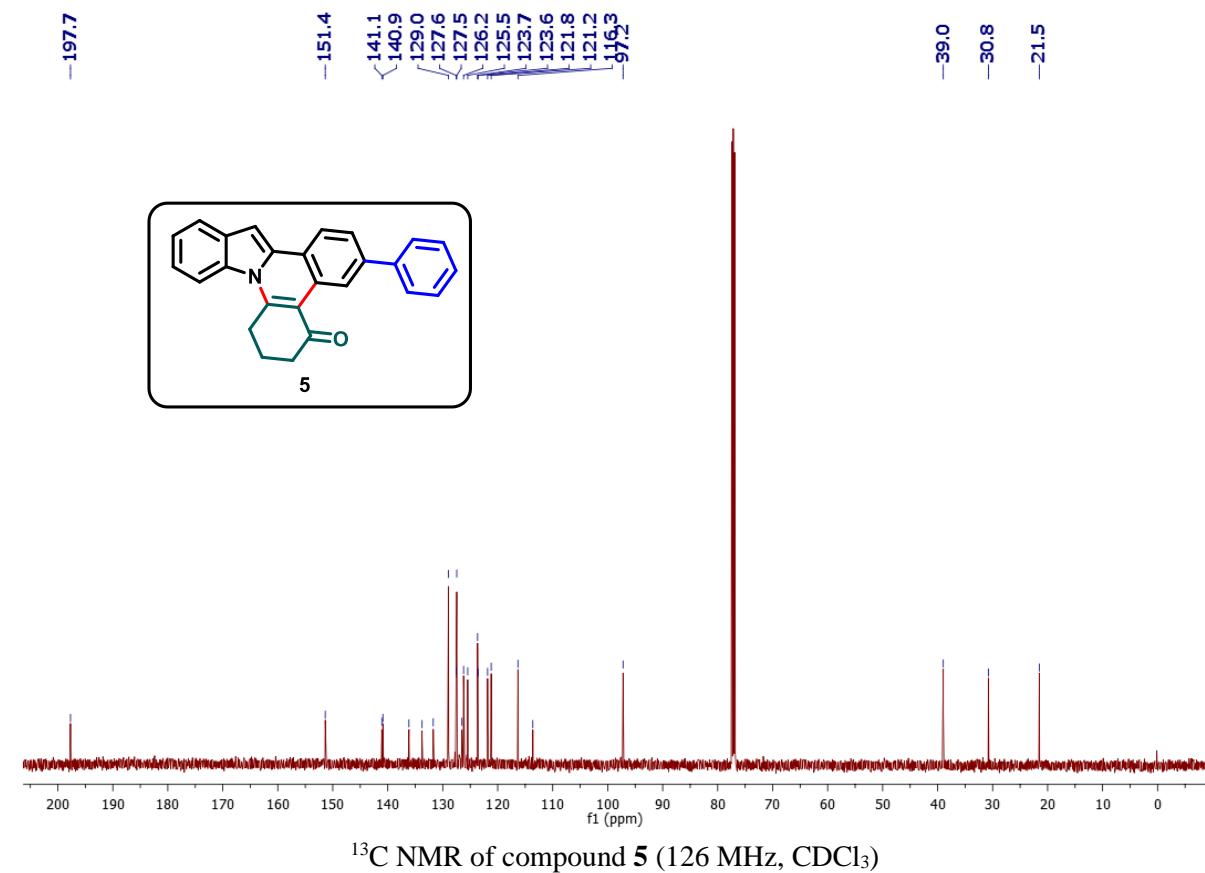
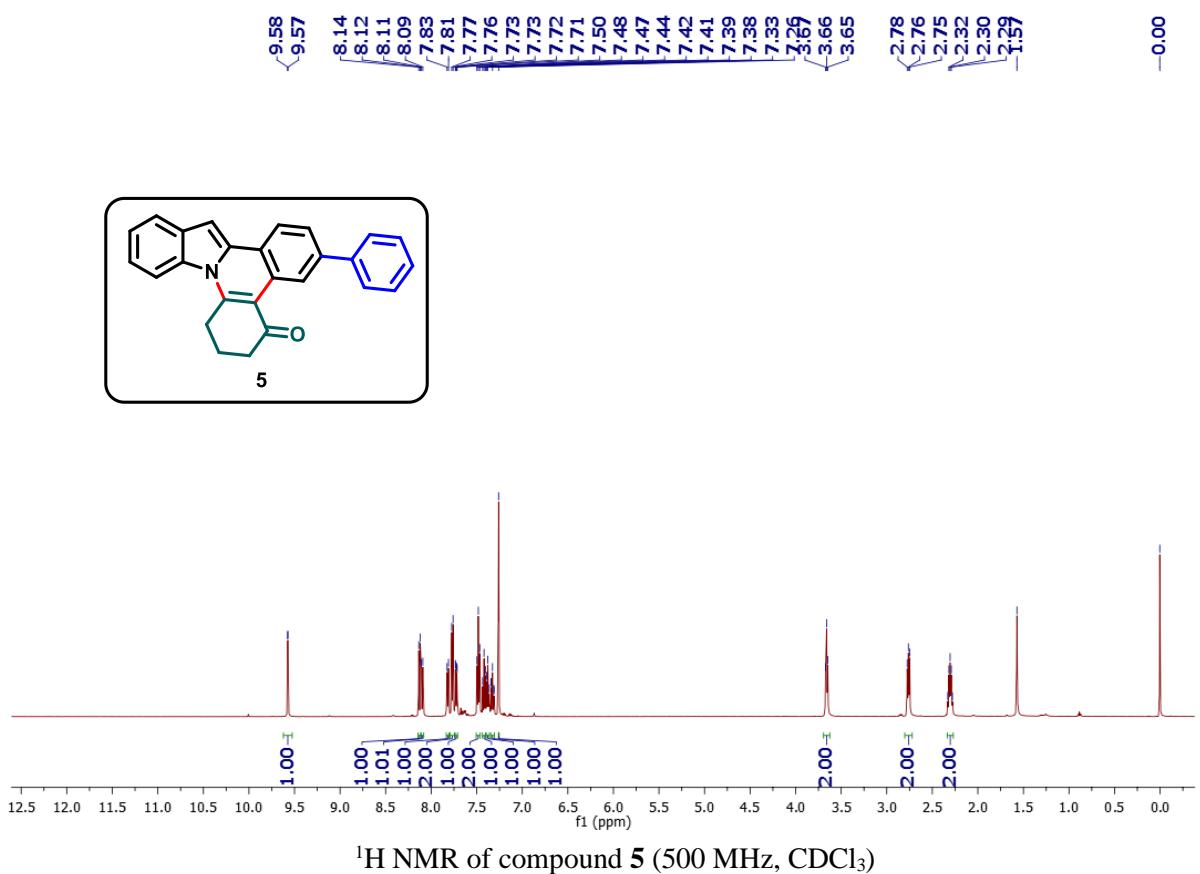


<sup>1</sup>H NMR of compound **4ab** (500 MHz, CDCl<sub>3</sub>)

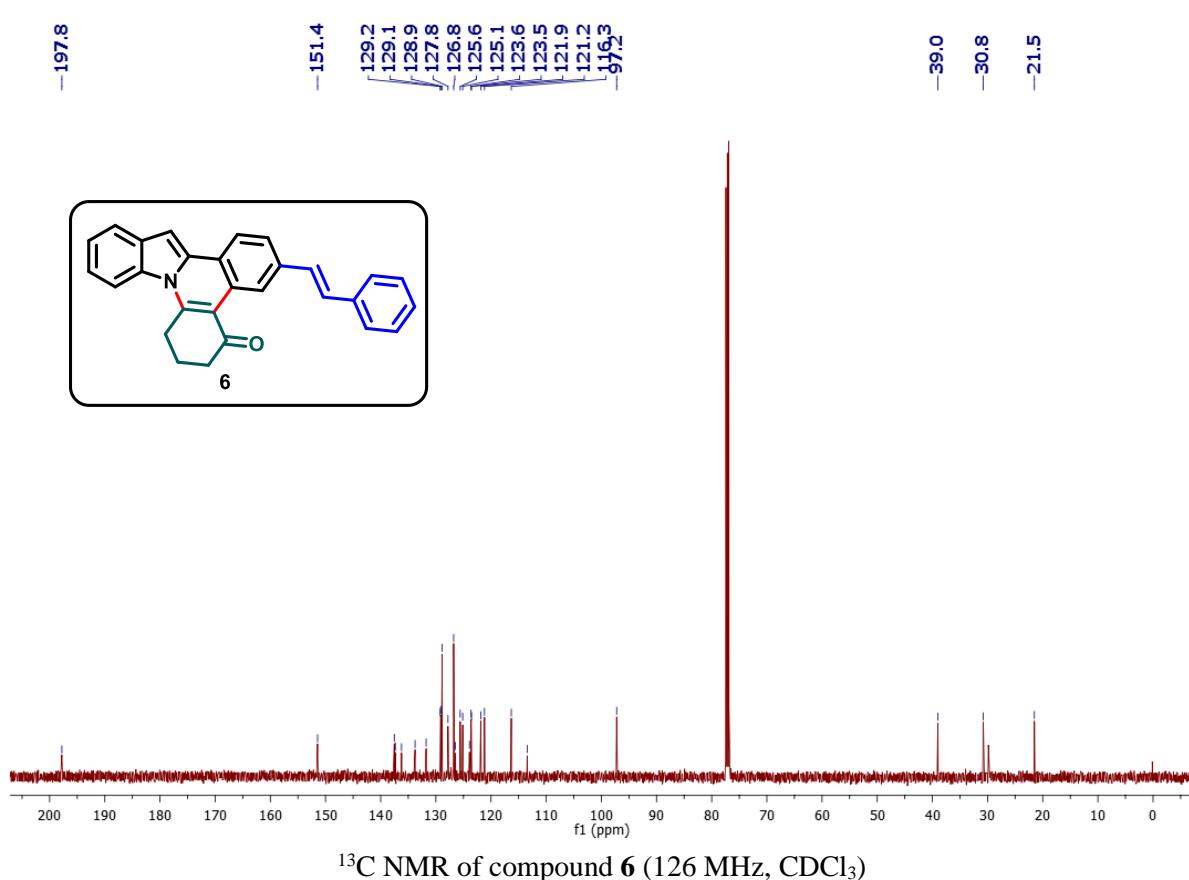
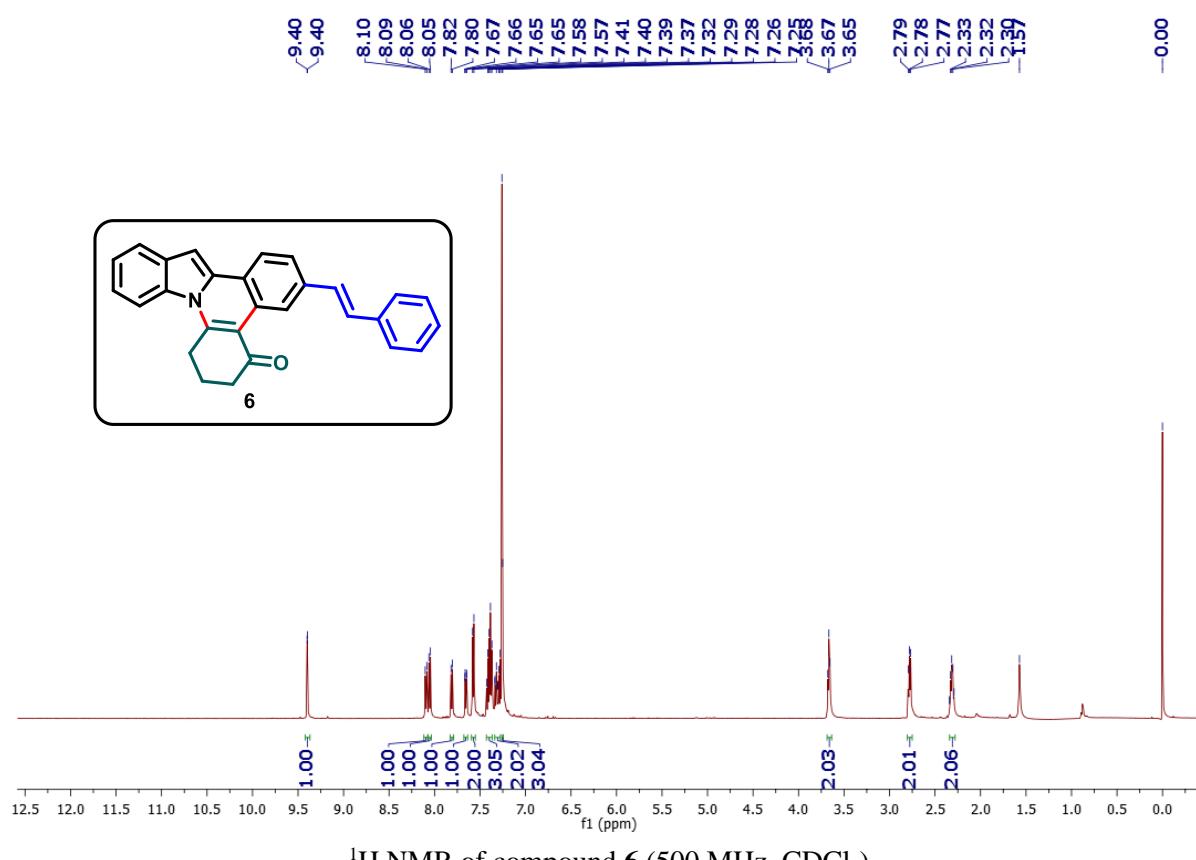


<sup>13</sup>C NMR of compound **4ab** (500 MHz, CDCl<sub>3</sub>)

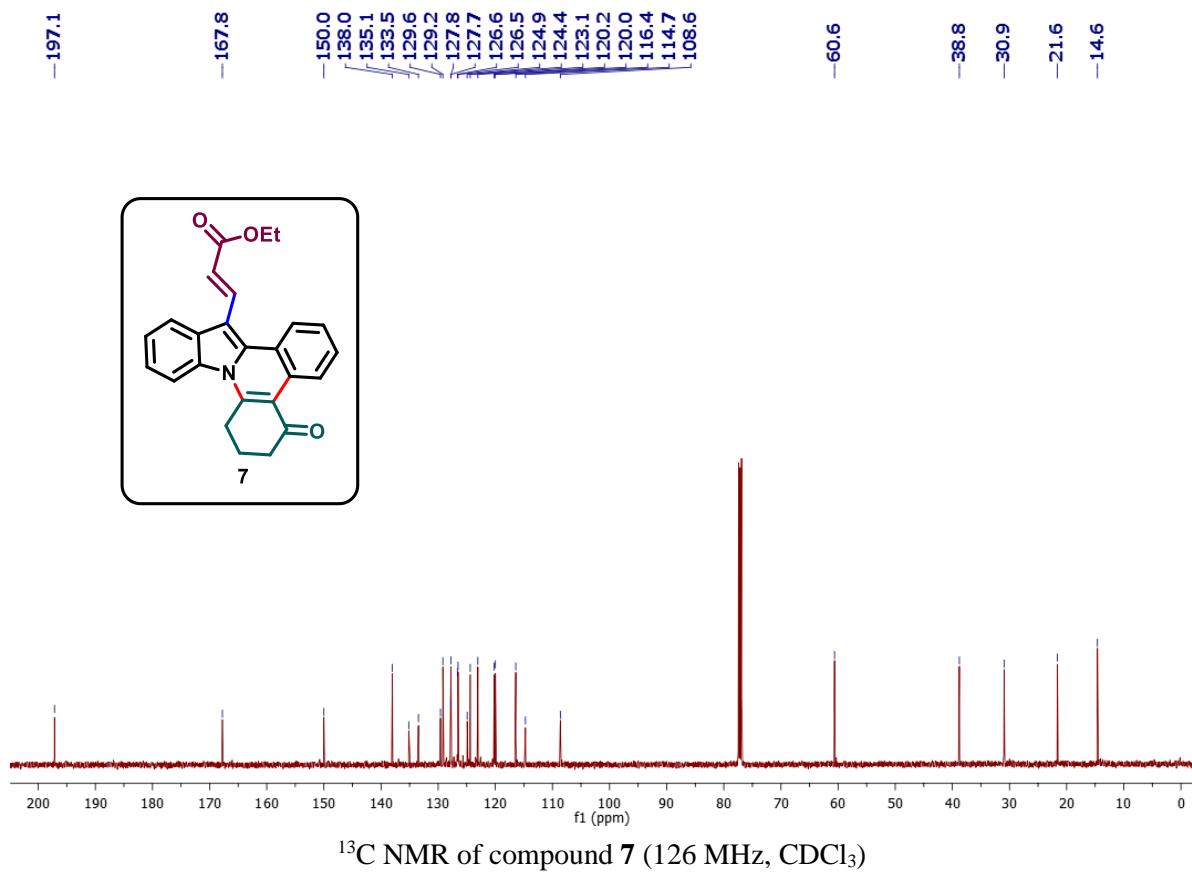
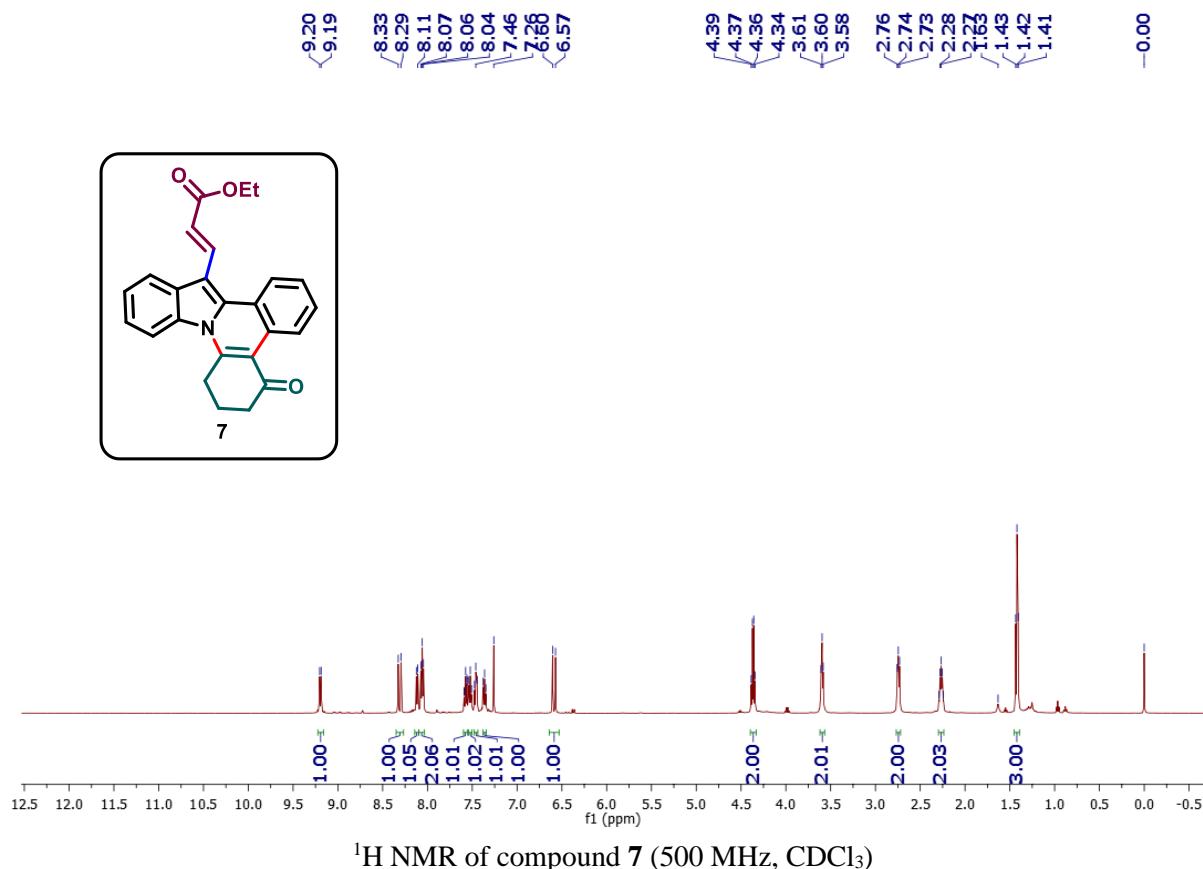
**3-phenyl-7,8-dihydroindolo[1,2-f]phenanthridin-5(6H)-one (5):**



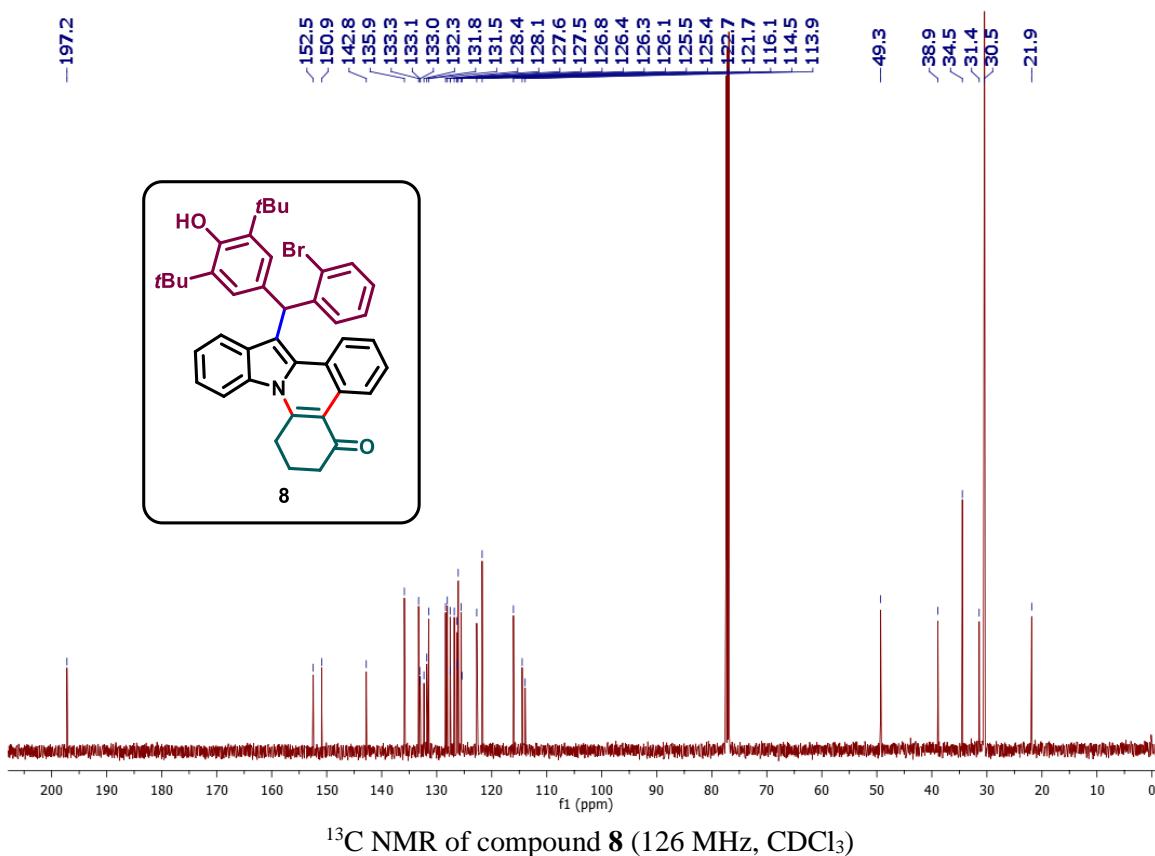
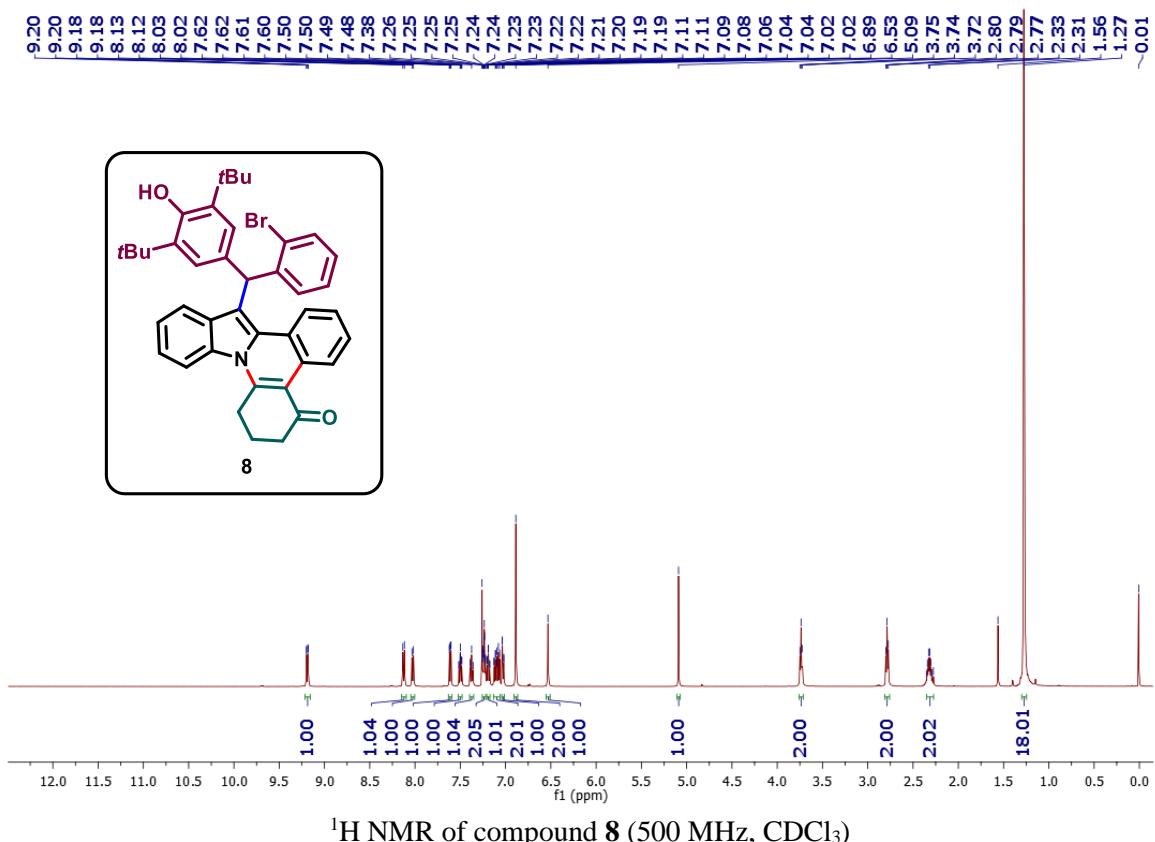
**(E)-3-styryl-7,8-dihydroindolo[1,2-f]phenanthridin-5(6H)-one (6):**



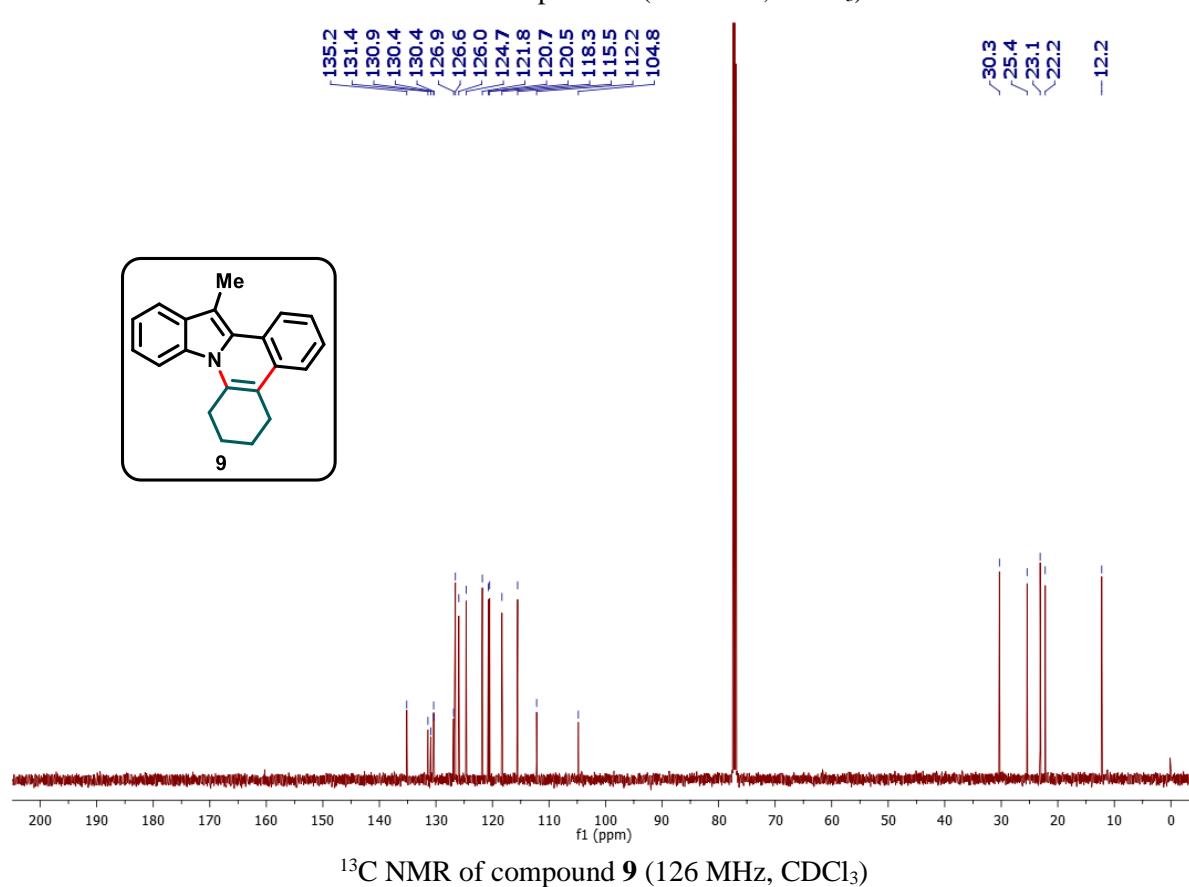
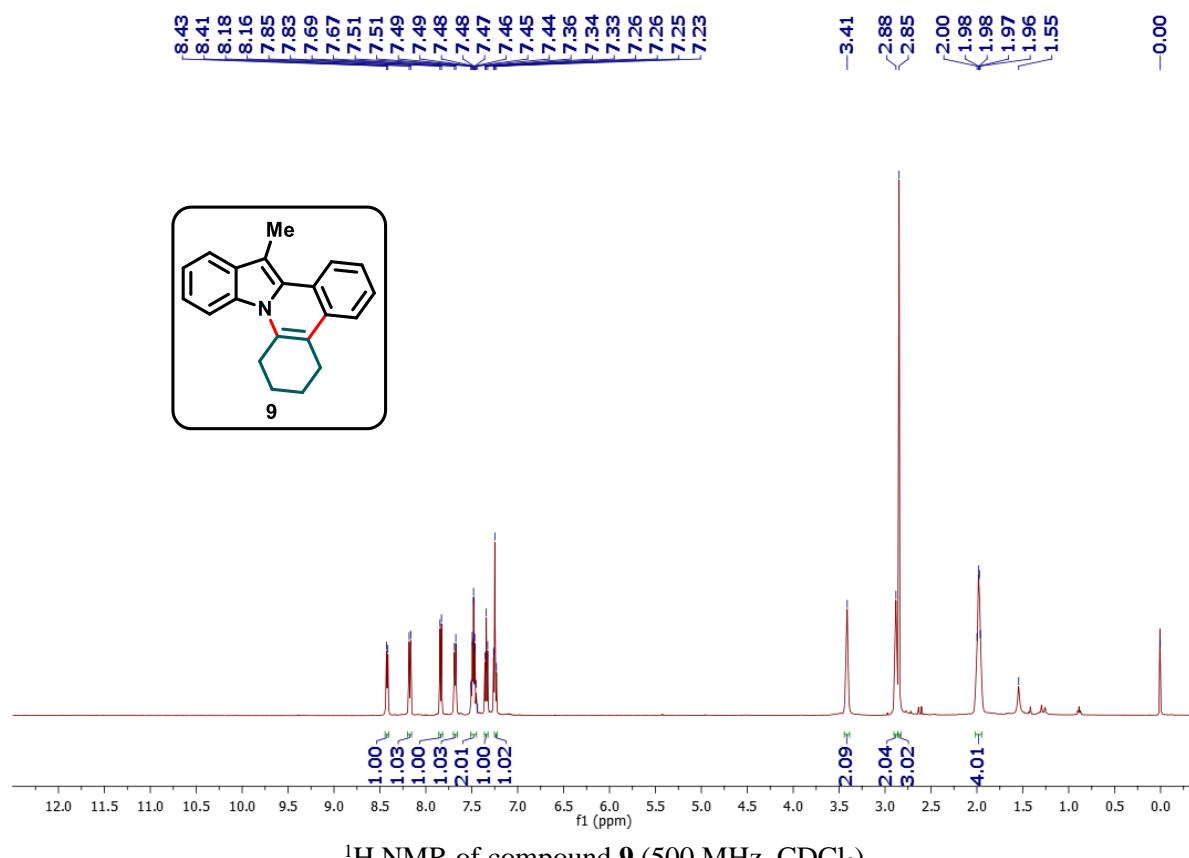
**ethyl (E)-3-(5-oxo-5,6,7,8-tetrahydroindolo[1,2-*f*]phenanthridin-14-yl)acrylate (7):**



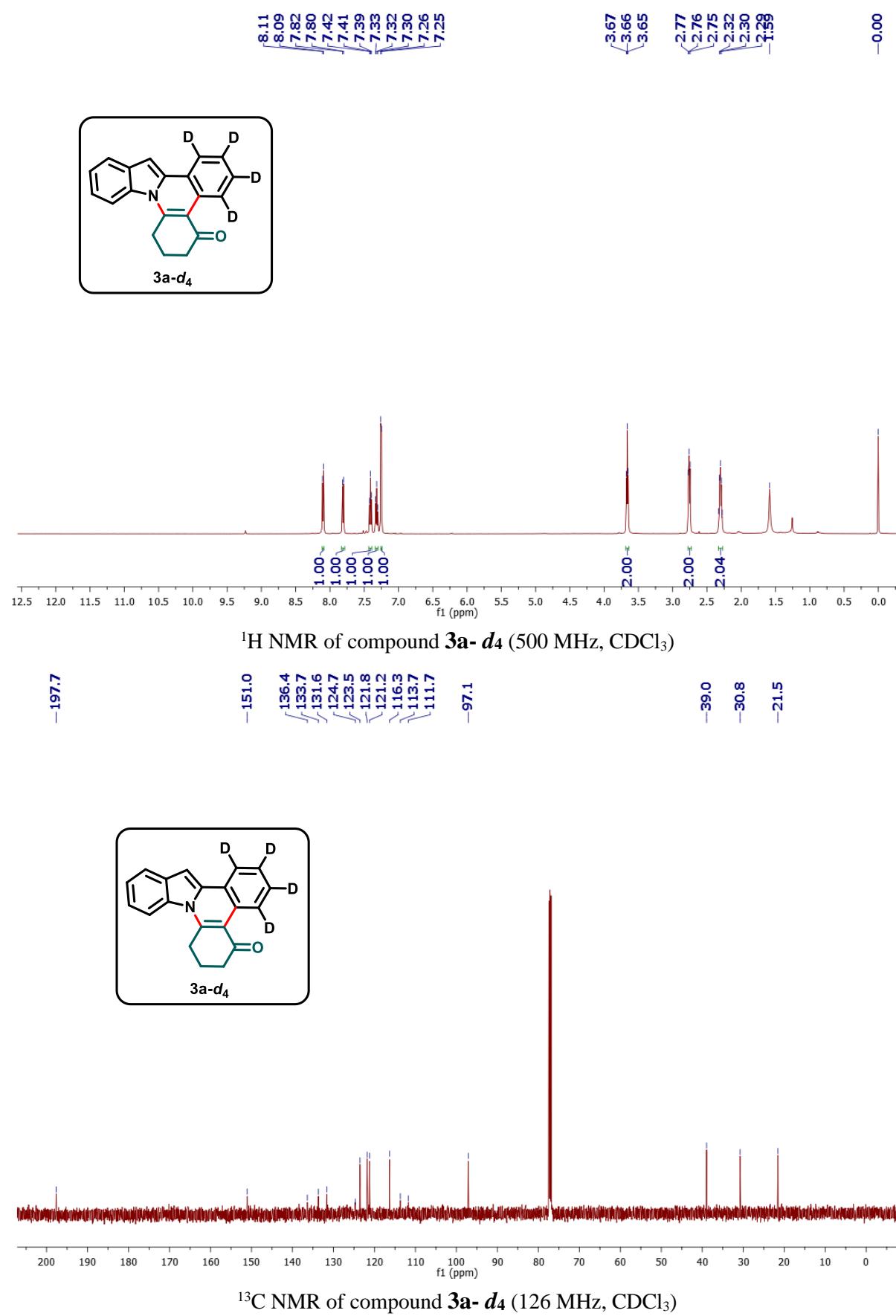
**14-((2-bromophenyl)(3,5-di-tert-butyl-4-hydroxyphenyl)methyl)-7,8-dihydroindolo[1,2-f]phenanthridin-5(6*H*)-one (8):**



**14-methyl-5,6,7,8-tetrahydroindolo[1,2-f]phenanthridine (9):**



**7,8-dihydroindolo[1,2-f]phenanthridin-5(6H)-one-1,2,3,4-d<sub>4</sub> (3a- d<sub>4</sub>):**



**1,2,3,9-tetrahydro-4*H*-dibenzo[*a,c*]carbazol-4-one-5,6,7,8-*d*<sub>4</sub> (**4a-d**<sub>4</sub>):**

