Supporting Information for

Self-Cyclization vs Dimerization of *o*-Alkenyl Arylisocyanides: Chemodivergent Synthesis of Quinolines and Pyrrolo-fused diindoles

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I. General information

All reagents were purchased from commercial sources and used without further purification, unless otherwise indicated. All reactions were carried out in the sealed tubes and monitored by TLC, which was performed on precoated aluminum sheets of silica gel 60 (F254). The products were purified by flash column chromatography on silica gel (300−400 mesh). Melting points were uncorrected. NMR spectra were obtained on a Varian Inova 400, 500 or a Bruker Avance 400 spectrometer. ^{1}H NMR and ^{13}C NMR were determined with TMS as the internal standard. All chemical shifts are given in ppm. High-resolution mass spectra (HRMS) were obtained using a Bruker microTOF II focus spectrometer (ESI).

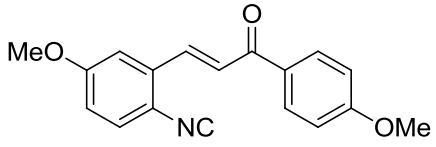
II. Experimental Procedures

2.1 Synthesis of starting materials.

Isocyanides **1** were synthesized according to known literature procedure.[1,2,3]

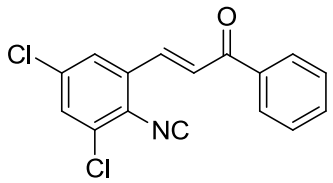
Analytical Data of Substrate 1s and 1t

(*E*)-3-(2-Isocyano-5-methoxyphenyl)-1-(4-methoxyphenyl)prop-2-en-1-one (1s)



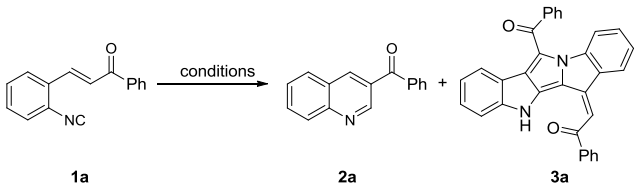
Yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.89 (s, 6H), 6.93 (dd, *J* = 8.0 Hz, *J* = 2.8 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 2.8 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 16 Hz, 1H), 7.94 (d, *J* = 16 Hz, 1H), 8.04 (d, *J* = 8.0 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 55.5, 55.7, 112.4, 113.9, 116.1, 126.4, 129.3, 130.5, 131.0, 132.9, 137.3, 159.8, 163.7, 167.0, 188.3. **HRMS** (ESI-TOF) Calcd for $C_{18}H_{15}NNaO_3^+$ $[M+Na]^+$: 316.0944. Found: 316.0957.

(*E*)-3-(3,5-Dichloro-2-isocyanophenyl)-1-phenylprop-2-en-1-one (1t)



Yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.51-7.55 (m, 3H), 7.62 (d, *J* = 16 Hz, 1H), 7.62-7.66 (m, 2H), 7.94 (d, *J* = 16 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 125.6, 128.0, 128.7, 128.9, 130.7, 133.2, 133.6, 134.5, 135.6, 136.0, 137.1, 175.4, 189.1. **HRMS** (ESI-TOF) Calcd for $C_{16}H_9Cl_2NNaO^+$ $[M+Na]^+$: 323.9953. Found: 323.9947.

2.2 Optimization of reaction conditions.[a]



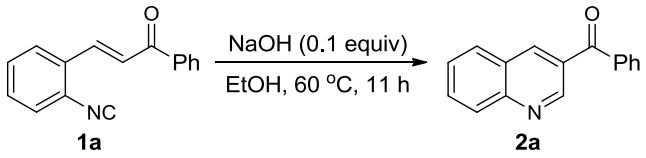
1a **2a** **3a**

Entry	Base (equiv)	Solvent	Temp (℃)	Time (h)	Yield (%)[b]	
					2a	**3a**
1	-	1,4-dioxane	120	4.0	0	36
2	***K_2CO_3 (1.0)***	***1,4-dioxane***	***120***	***4.0***	***0***	***71***
3	K_2CO_3 (2.0)	1,4-dioxane	120	4.0	0	60
4	K_2CO_3 (0.5)	1,4-dioxane	120	4.0	0	62
5	K_2CO_3 (0.3)	1,4-dioxane	120	4.0	0	53
6	DBU (1.0)	1,4-dioxane	120	2.0	ND	ND
7	NaH (1.0)	1,4-dioxane	120	2.0	ND	ND
8	TMG (1.0)	1,4-dioxane	120	1.0	0	33
9	Et_3N (1.0)	1,4-dioxane	120	3.0	0	39
10	K_2CO_3 (1.0)	DMF	120	4.0	0	14
11	K_2CO_3 (1.0)	CH_3CN	120	4.0	0	57
12	K_2CO_3 (1.0)	THF	120	4.0	0	54
13	K_2CO_3 (1.0)	EtOH	120	1.5	65	0
14	K_2CO_3 (1.0)	1,4-dioxane	140	3.0	0	46
15	K_2CO_3 (1.0)	1,4-dioxane	100	6.0	0	66
16	K_2CO_3 (1.0)	1,4-dioxane	80	24	0	61
17	K_2CO_3 (0.3)	EtOH	120	3.0	73	0
18	K_2CO_3 (0.1)	EtOH	120	4.0	74	0
19	K_2CO_3 (0.1)	EtOH	80	12	74	0
20	K_2CO_3 (0.1)	EtOH	60	48	70	0
21	K_2CO_3 (0.1)	EtOH	45	72	60	0
22	***NaOH (0.1)***	***EtOH***	***60***	***11***	***78***	***0***
23	KOH (0.1)	EtOH	60	22	65	0
24	DBU (0.1)	EtOH	60	12	5	0
25	Cs_2CO_3 (0.1)	EtOH	60	22	75	0
26	Ph_3P (0.1)	EtOH	60	11	NR	NR
27	*t*-BuOK (0.1)	EtOH	60	11	68	0
28	NaOH (0.1)	MeOH	60	11	27	0

29	NaOH (0.1)	Toluene	60	11	22	0
30	NaOH (0.1)	DCE	60	11	Trace	0
31	NaOH (0.1)	MeCN	60	11	31	31
32	NaOH (0.1)	THF	60	11	32	37
33	NaOH (0.1), Ag_2CO_3 (0.1)	EtOH	60	11	54	0
34	TBAI (0.1)	EtOH	60	48	NR	NR
35	benzylamine (0.1)	EtOH	60	48	NR	NR

[a]Reaction conditions: **1a** (0.35 mmol) and catalyst, solvent (2.0 mL) in open air. [b]Isolated yields.

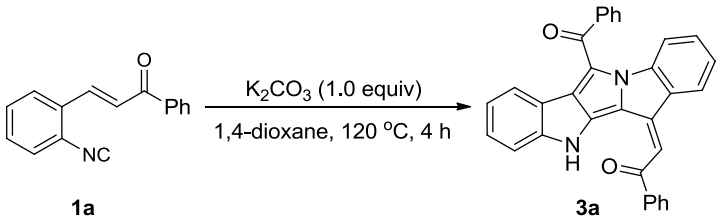
2.3 General procedure for the synthesis of 2a-2q (**2a** as an example):



1a **2a**

To a solution of (*E*)-3-(2-isocyanophenyl)-1-phenylprop-2-en-1-one **1a** (82 mg, 0.35 mmol) in dry EtOH (2 mL) at room temperature was added NaOH (1.4 mg, 0.035 mmol). The mixture was heated to 60 °C and kept stirring until **1a** was completely consumed as indicated by TLC (reaction time, 11 h). Cooled to room temperature, the reaction mixture was poured into 50 mL of saturated aqueous NH_4Cl and extracted with DCM (CH_2Cl_2, 20 mL×3). The combined organics were dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by column chromatography (petroleum ether/EtOAc = 12/1, v/v) to afford the desired product **2a** (64 mg, 78% yield).

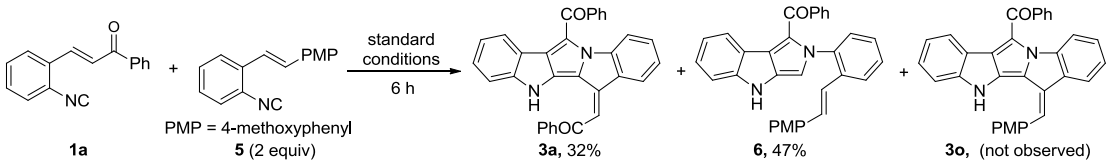
2.4 General procedure for the synthesis of 3a-3l (**3a** as an example):



1a **3a**

To a solution of (*E*)-3-(2-isocyanophenyl)-1-phenylprop-2-en-1-one **1a** (82 mg, 0.35 mmol) in dry 1,4-dioxane (2 mL) at room temperature was added K_2CO_3 (49 mg, 0.35 mmol). The mixture was heated to 120 °C and kept stirring until **1a** was completely consumed as indicated by TLC (reaction time, 4 h). Cooled to room temperature, the reaction mixture was poured into 50 mL of saturated aqueous NH_4Cl and extracted with DCM (CH_2Cl_2, 20 mL×3). The combined organics were dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by column chromatography (petroleum ether/EtOAc = 40/1, v/v) to afford the desired product **3a** (58 mg, 71% yield).

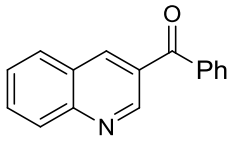
2.5 Control experiments for mechanistic studies.



To a solution of (*E*)-3-(2-isocyanophenyl)-1-phenylprop-2-en-1-one **1a** (47 mg, 0.2 mmol) and (*E*)-1-isocyano-2-(4-methoxystyryl)benzene **5** (94 mg, 0.4 mmol) in dry 1,4-dioxane (2 mL) at room temperature was added K_2CO_3 (28 mg, 0.2 mmol). The mixture was heated to 120 ^oC and kept stirring until **1a** was completely consumed as indicated by TLC (reaction time, 6 h). Cooled to room temperature, the reaction mixture was poured into 50 mL of saturated aqueous NH_4Cl and extracted with DCM (CH_2Cl_2, 20 mL×3). The combined organics were dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by column chromatography (petroleum ether/EtOAc = 40/1 and 12/1 v/v) to afford the desired product **3a** (15 mg, 32% yield) and pyrrolo[3,4-*b*]indole **6** (40 mg, 47% yield), respectively. However, no desired product **3o** was observed under standard conditions, suggesting that the electron-withdrawing group at the double bond in *o*-alkenyl arylisocyanides plays important roles for the formation of pyrrolo-fused biindole derivatives **3**.

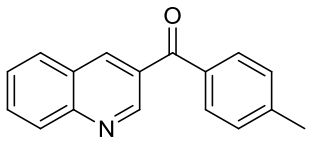
III. Analytical Data of Compounds

Phenyl(quinolin-3-yl)methanone (2a)[4]



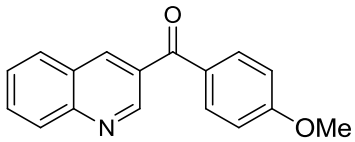
Yield: 64 mg, 78%, yellow solid, m.p. 69−70 ^oC. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.54 (t, *J* = 8.0 Hz, 2H), 7.65 (q, *J* = 8.0 Hz, 2H), 7.83-7.87 (m, 3H), 7.92 (d, *J* = 8.0 Hz, 1H), 8.20 (d, *J* = 8.0 Hz, 1H), 8.56 (d, *J* = 2.0 Hz, 1H), 9.33 (d, *J* = 2.0 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 126.5, 127.5, 128.6, 129.1, 129.4, 129.9, 130.0, 131.8, 133.0, 136.9, 138.7, 149.4, 150.3, 194.8. **HRMS** (ESI-TOF) Calcd for $C_{16}H_{11}NNaO^+$ $[M+Na]^+$: 256.0733. Found: 256.0743.

Quinolin-3-yl(*p*-tolyl)methanone (2b)[5]



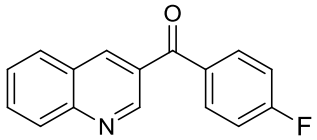
Yield: 63 mg, 72%, yellow solid, m.p. 82−83 ^oC. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.33 (d, *J* = 8.0 Hz, 2H), 7.63 (t, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 2H), 7.84 (t, *J* = 8.0 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 8.19 (d, *J* = 8.0 Hz, 1H), 8.53 (d, *J* = 2.0 Hz, 1H), 9.31 (d, *J* = 2.0 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 21.6, 126.5, 127.4, 129.0, 129.2, 129.4, 130.2, 130.3, 131.6, 134.3, 138.5, 143.9, 149.3, 150.3, 194.4. **HRMS** (ESI-TOF) Calcd for $C_{17}H_{14}NO^+$ $[M+H]^+$: 248.1070. Found: 248.1068.

(4-Methoxyphenyl)(quinolin-3-yl)methanone (2c)[5]



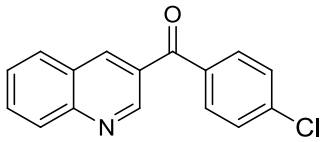
Yield: 64 mg, 69%, yellow solid, m.p. 131−132 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 3.91 (s, 3H), 7.02 (d, *J* = 8.5 Hz, 2H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.85 (t, *J* = 7.5 Hz, 1H), 7.89 (d, *J* = 8.5 Hz, 2H), 7.92 (d, *J* = 8.0 Hz, 1H), 8.19 (d, *J* = 8.0 Hz, 1H), 8.53 (d, *J* = 2.0 Hz, 1H), 9.28 (d, *J* = 2.0 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 55.5, 113.9, 126.6, 127.5, 128.9, 129.4, 129.7, 130.8, 131.5, 132.5, 138.2, 149.2, 150.3, 163.7, 193.4. **HRMS** (ESI-TOF) Calcd for $C_{17}H_{13}NNaO_2^+$ $[M+Na]^+$: 286.0838. Found: 286.0836.

(4-Fluorophenyl)(quinolin-3-yl)methanone (2d)[5]



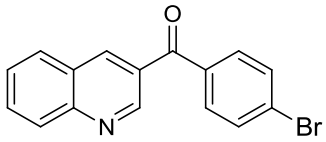
Yield: 64 mg, 72%, yellow solid, m.p. 82−83 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.22 (t, *J* = 8.5 Hz, 2H), 7.65 (t, *J* = 8.0 Hz, 1H), 7.86 (t, *J* = 8.0 Hz, 1H), 7.90-7.93 (m, 3H), 8.20 (d, *J* = 8.5 Hz, 1H), 8.53 (d, *J* = 2.0 Hz, 1H), 9.29 (d, *J* = 2.0 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 115.8 (d, *J* = 21.8 Hz), 126.5, 127.6, 129.1, 129.5, 129.9, 131.9, 132.6 (d, *J* = 9.3 Hz), 133.3 (d, *J* = 2.9 Hz), 138.5, 149.5, 150.1, 165.7 (d, *J* = 254.1 Hz), 193.3. **HRMS** (ESI-TOF) Calcd for $C_{16}H_{10}FNNaO^+$ $[M+Na]^+$: 274.0639. Found: 274.0636.

(4-Chlorophenyl)(quinolin-3-yl)methanone (2e)[6]



Yield: 59 mg, 63%, yellow soild, m.p. 105−106 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.51 (d, *J* = 8.0 Hz, 2H), 7.65 (t, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.86 (t, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 8.19 (d, *J* = 8.0 Hz, 1H), 8.52 (d, *J* = 2.0 Hz, 1H), 9.29 (d, *J* = 2.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 126.5, 127.6, 128.9, 129.1, 129.5, 129.6, 131.3, 131.9, 135.2, 138.6, 139.5, 149.5, 150.0, 193.5. **HRMS** (ESI-TOF) Calcd for $C_{16}H_{10}ClNNaO^+$ $[M+Na]^+$: 290.0343. Found: 290.0338.

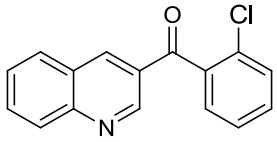
(4-Bromophenyl)(quinolin-3-yl)methanone (2f)[5]



Yield: 83 mg, 76%, white solid, m.p. 115−116 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.66 (t, *J* = 8.5 Hz, 1H), 7.69 (d, *J* = 8.5 Hz, 2H), 7.74 (d, *J* = 8.5 Hz, 2H), 7.87 (t, *J* = 8.5 Hz, 1H), 7.93 (d, *J* = 8.5 Hz, 1H), 8.20 (d, *J* = 8.5 Hz, 1H), 8.53 (d, *J* = 2.0 Hz, 1H), 9.30 (d, *J* = 2.0 Hz, 1H). **^{13}C NMR**

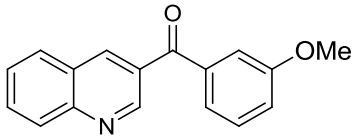
(125 MHz, $CDCl_3$): δ 126.4, 127.7, 128.2, 129.1, 129.5, 129.6, 131.4, 131.9, 132.0, 135.6, 138.7, 149.5, 150.0, 193.8. **HRMS** (ESI-TOF) Calcd for $C_{16}H_{11}BrNO^+$ $[M+H]^+$: 312.0019. Found: 312.0023.

(2-Chlorophenyl)(quinolin-3-yl)methanone (2g)



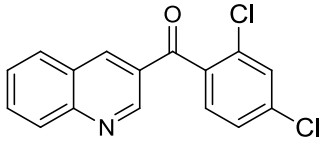
Yield: 68 mg, 73%, yellow solid, m.p. 106−107 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.43-7.50 (m, 2H), 7.53 (d, *J* = 3.2 Hz, 2H), 7.63 (t, *J* = 7.2 Hz, 1H), 7.85-7.91 (m, 2H), 8.19 (d, *J* = 8.8 Hz, 1H), 8.49 (d, *J* = 2.0 Hz, 1H), 9.34 (d, *J* = 2.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 126.6, 126.9, 127.5, 128.8, 129.3, 129.4 (2C), 130.2, 131.3, 131.7, 132.2, 137.5, 139.3, 149.8, 193.8. **HRMS** (ESI-TOF) Calcd for $C_{16}H_{10}ClNNaO^+$ $[M+Na]^+$: 290.0343. Found: 290.0346.

(3-Methoxyphenyl)(quinolin-3-yl)methanone (2h)[3]



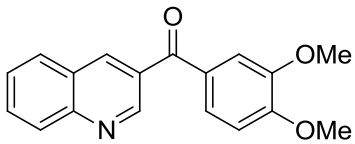
Yield: 68 mg, 74%, yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.86 (s, 3H), 7.16-7.19 (m, 1H), 7.36-7.44 (m, 3H), 7.62 (td, *J* = 6.8 Hz, *J* = 1.2 Hz, 1H), 7.83 (td, *J* = 6.8 Hz, *J* = 1.2 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 8.18 (d, *J* = 8.4 Hz, 1H), 8.55 (d, *J* = 2.0 Hz, 1H), 9.32 (d, *J* = 2.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 55.4, 114.1, 119.3, 122.6, 126.4, 127.4, 129.0, 129.3, 129.4, 129.9, 131.7, 138.2, 138.6, 149.3, 150.2, 159.7, 194.5. **HRMS** (ESI-TOF) Calcd for $C_{17}H_{13}NNaO_2^+$ $[M+Na]^+$: 286.0838. Found: 286.0851.

(2,4-Dichlorophenyl)(quinolin-3-yl)methanone (2i)



Yield: 72 mg, 68%, orange solid, m.p. 81−82 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.43 (m, 2H), 7.53 (s, 1H), 7.63 (t, *J* = 8.0 Hz, 1H), 7.84-7.90 (m, 2H), 8.18 (d, *J* = 8.0 Hz, 1H), 8.47 (d, *J* = 2.0 Hz, 1H), 9.32 (d, *J* = 2.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 126.6, 127.5, 127.7, 128.7, 129.4, 129.5, 130.3, 130.5, 132.4, 132.5, 135.9, 137.4, 139.4, 149.7, 149.9, 192.9. **HRMS** (ESI-TOF) Calcd for $C_{16}H_9Cl_2NNaO^+$ $[M+Na]^+$: 323.9953. Found: 323.9954.

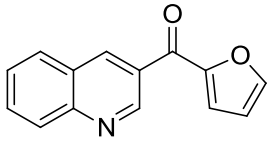
(3,4-Dimethoxyphenyl)(quinolin-3-yl)methanone (2j)



Yield: 78 mg, 76%, yellow solid, m.p. 85−87 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.95 (s, 3H),

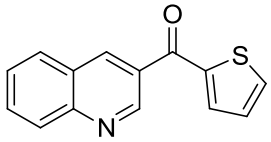
3.97 (s, 3H), 6.93 (d, *J* = 8.4 Hz, 1H), 7.42 (dd, *J* = 8.4 Hz, *J* = 2.0 Hz, 1H), 7.55 (d, *J* = 2.0 Hz, 1H), 7.63 (t, *J* = 8.4 Hz, 1H), 7.84 (td, *J* = 8.4 Hz, *J* = 2.0 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 8.20 (d, *J* = 8.4 Hz, 1H), 8.54 (d, *J* = 2.0 Hz, 1H), 9.29 (d, *J* = 2.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 55.9 (2C), 109.8, 111.7, 125.4, 126.5, 127.4, 128.9, 129.1, 129.6, 130.7, 131.5, 138.1, 148.9, 149.2, 149.9, 153.4, 193.2. **HRMS** (ESI-TOF) Calcd for $C_{18}H_{15}NNaO_3^+$ $[M+Na]^+$: 316.0944. Found: 316.0945.

Furan-2-yl(quinolin-3-yl)methanone (2k)[6]



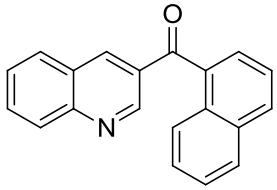
Yield: 69 mg, 88%, brown solid , m.p. 102−103 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 6.69 (dd, *J* = 3.5 Hz, *J* = 1.5 Hz, 1H), 7.41 (d, *J* = 3.5 Hz, 1H), 7.67 (t, *J* = 8.0 Hz, 1H), 7.79 (s, 1H), 7.87 (t, *J* = 8.0 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 8.20 (d, *J* = 8.0 Hz, 1H), 8.86 (d, *J* = 2.5 Hz, 1H), 9.48 (d, *J* = 2.5 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 112.6, 120.7, 126.7, 127.5, 129.2, 129.4, 129.6, 131.9, 138.3, 147.4, 149.5, 149.8, 152.4, 180.3. **HRMS** (ESI-TOF) Calcd for $C_{14}H_9NNaO_2^+$ $[M+Na]^+$: 246.0525. Found: 246.0524.

Quinolin-3-yl(thiophen-2-yl)methanone (2l)[6]



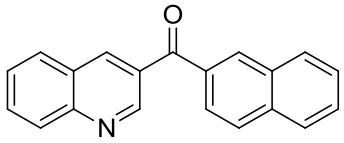
Yield: 67 mg, 80%, yellow soild, m.p. 88−90 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.22 (t, *J* = 5.0 Hz, 1H), 7.65 (t, *J* = 8.5 Hz, 1H), 7.72 (dd, *J* = 3.5 Hz, *J* = 1.0 Hz, 1H), 7.80 (dd, *J* = 5.0 Hz, *J* = 1.0 Hz, 1H), 7.85 (t, *J* = 8.5 Hz, 1H), 7.95 (d, *J* = 8.5 Hz, 1H), 8.19 (d, *J* = 8.5 Hz, 1H), 8.65 (d, *J* = 2.0 Hz, 1H), 9.34 (d, *J* = 2.0 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 126.5, 127.6, 128.3, 128.9, 129.4, 130.6, 131.7, 134.9 (2C), 137.6, 143.1, 149.3, 149.5, 186.0. **HRMS** (ESI-TOF) Calcd for $C_{14}H_9NNaOS^+[M+Na]^+$: 262.0297. Found: 262.0296.

Naphthalen-1-yl(quinolin-3-yl)methanone (2m)[7]



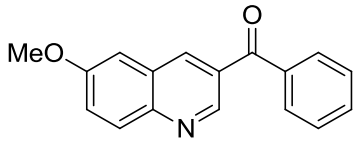
Yield: 73 mg, 73%, yellow soild, m.p. 103−104 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.49-7.58 (m, 4H), 7.63 (dd, *J* = 6.8 Hz, *J* = 1.2 Hz, 1H), 7.78-7.83 (m, 2H), 7.91-7.93 (m, 1H), 8.03 (d, *J* = 8.4 Hz, 1H), 8.19 (d, *J* = 8.4 Hz, 2H), 8.50 (d, *J* = 2.0 Hz, 1H), 9.42 (d, *J* = 2.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 124.2, 125.3, 126.5, 126.6, 127.4, 127.5, 128.3, 128.4, 129.2, 129.3, 130.6, 130.7, 131.9, 133.7, 135.2, 139.4, 150.3, 196.2. **HRMS** (ESI-TOF) Calcd for $C_{20}H_{14}NO^+[M+H]^+$: 284.1070. Found: 284.1071.

Naphthalen-2-yl(quinolin-3-yl)methanone (2n)[7]



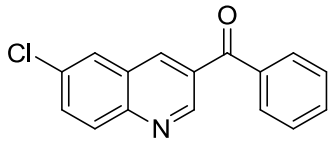
Yield: 77 mg, 77%, yellow solid, m.p. 108−109 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.57 (t, *J* = 8.0 Hz, 1H), 7.64 (t, *J* = 8.0 Hz, 2H), 7.86 (t, *J* = 8.0 Hz, 1H), 7.90-7.93 (m, 3H), 7.99 (s, 2H), 8.22 (d, *J* = 8.0 Hz, 1H), 8.31 (s, 1H), 8.60 (d, *J* = 2.0 Hz, 1H), 9.38 (d, *J* = 2.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 125.4, 126.6, 127.0, 127.5, 127.8, 128.6 (2C), 129.1, 129.4 (2C), 130.4, 131.7, 132.0, 132.2, 134.2, 135.4, 138.7, 149.4, 150.3, 194.7. **HRMS** (ESI-TOF) Calcd for $C_{20}H_{14}NO^+[M+H]^+$: 284.1070. Found: 284.1074.

(6-Methoxyquinolin-3-yl)(phenyl)methanone (2o)[8]



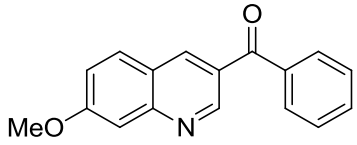
Yield: 65 mg, 70%, yellow solid, m.p. 116−117 °C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 3.93 (s, 3H), 7.14 (d, *J* = 3.0 Hz, 1H), 7.48 (dd, *J* = 9.0 Hz, *J* = 3.0 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 2H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.86 (d, *J* = 9.0 Hz, 2H), 8.07 (d, *J* = 9.0 Hz, 1H), 8.44 (d, *J* = 2.0 Hz, 1H), 9.15 (d, *J* = 2.0 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 55.6, 106.0, 124.7, 127.7, 128.5, 129.9, 130.2, 130.7, 132.9, 137.0, 137.3, 145.6, 147.8, 158.4, 195.0. **HRMS** (ESI-TOF) Calcd for $C_{17}H_{13}NNaO_2^+$ $[M+Na]^+$: 286.0838. Found: 286.0848.

(6-Chloroquinolin-3-yl)(phenyl)methanone (2p)



Yield: 67 mg, 71%, white solid, m.p. 122−124 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.54 (t, *J* = 7.6 Hz, 2H), 7.64-7.68 (m, 1H), 7.74-7.78 (m, 1H), 7.84-7.89 (m, 3H), 8.12 (d, *J* = 7.6 Hz, 1H), 8.44 (d, *J* = 2.0 Hz, 1H), 9.28 (d, *J* = 2.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 127.2, 127.5, 128.7, 129.9, 130.7, 131.0, 132.5, 133.2, 133.4, 136.7, 137.5, 147.7, 150.4, 194.4. **HRMS** (ESI-TOF) Calcd for $C_{16}H_{10}ClNNaO^+$ $[M+Na]^+$: 290.0343. Found: 290.0342.

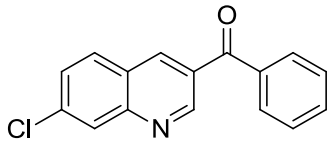
(7-Methoxyquinolin-3-yl)(phenyl)methanone (2q)[9]



Yield: 55 mg, 60%, yellow solid, m.p. 86−87 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 4.00 (s, 3H), 7.28 (dd, *J* = 8.0 Hz, *J* = 2.4 Hz, 1H), 7.49 (d, *J* = 2.4 Hz, 1H), 7.54 (t, *J* = 8.0 Hz, 2H), 7.64 (t, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 2H), 8.49 (d, *J* = 2.0 Hz, 1H), 9.26 (d, *J* = 2.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 55.7, 107.5, 120.9, 121.7, 128.1, 128.5, 129.9,

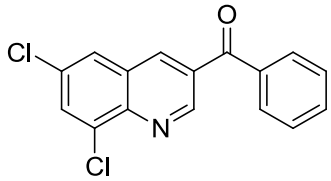
130.2, 132.7, 137.3, 138.5, 150.9, 151.6, 162.7, 194.8. **HRMS** (ESI-TOF) Calcd for $C_{17}H_{13}NNaO_2^+$ $[M+Na]^+$: 286.0838. Found: 286.0837.

(7-Chloroquinolin-3-yl)(phenyl)methanone (2r)[5]



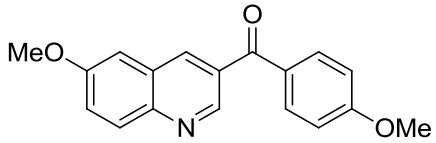
Yield: 56 mg, 60%, white solid, m.p. 97−98 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.55 (t, *J* = 8.0 Hz, 2H), 7.60 (dd, *J* = 8.0 Hz, *J* = 2.0 Hz, 1H), 7.67 (t, *J* = 8.0 Hz, 1H), 7.84-7.87 (m, 3H), 8.18 (d, *J* = 2.0 Hz, 1H), 8.54 (d, *J* = 2.0 Hz, 1H), 9.31 (d, *J* = 2.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 124.9, 128.6 (2C), 128.7, 129.9, 130.2, 133.2, 136.8, 137.9, 138.4, 149.7, 151.4, 194.4. **HRMS** (ESI-TOF) Calcd for $C_{16}H_{10}ClNNaO^+$ $[M+Na]^+$: 290.0343. Found: 290.0336.

(6,8-Dichloroquinolin-3-yl)(phenyl)methanone (2s)



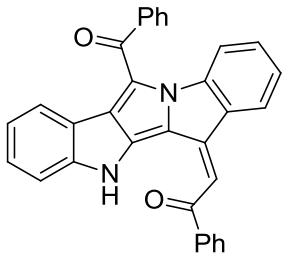
Yield: 97 mg, 92%, white solid, m.p. 123−124 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.56 (t, *J* = 7.6 Hz, 2H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.85-7.87 (m, 3H), 7.94 (d, *J* = 2.0 Hz, 1H), 8.50 (d, *J* = 2.0 Hz, 1H), 9.38 (d, *J* = 2.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 126.7, 128.3, 128.7, 130.1, 131.7, 132.2, 132.9, 133.5, 135.0, 136.4, 137.9, 144.1, 150.9, 193.9. **HRMS** (ESI-TOF) Calcd for $C_{16}H_9Cl_2NNaO^+$ $[M+Na]^+$: 323.9953. Found: 323.9944.

(4-Methoxyphenyl)(6-methoxyquinolin-3-yl)methanone (2t)



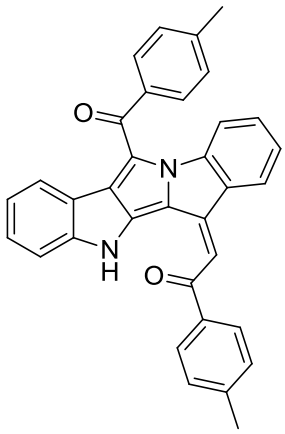
Yield: 69 mg, 67%, white solid, m.p. 134−135 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.91 (s, 3H), 3.94 (s, 3H), 7.01 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 2.8 Hz, 1H), 7.48 (dd, *J* = 8.0 Hz, *J* = 2.8 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 2H), 8.07 (d, *J* = 8.0 Hz, 1H), 8.41 (d, *J* = 2.0 Hz, 1H), 9.10 (d, *J* = 2.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 55.5, 55.6, 106.0, 113.9, 124.4, 127.9, 129.8, 130.8, 131.1, 132.5, 136.8, 145.5, 147.8, 158.4, 163.6, 193.7. **HRMS** (ESI-TOF) Calcd for $C_{18}H_{15}NnaO_3^+$ $[M+Na]^+$: 316.0944. Found: 316.0941.

(*Z*)-2-(12-Benzoylpyrrolo[1,2-*a*:3,4-*b*']diindol-6(5*H*)-ylidene)-1-phenylethanone (3a)



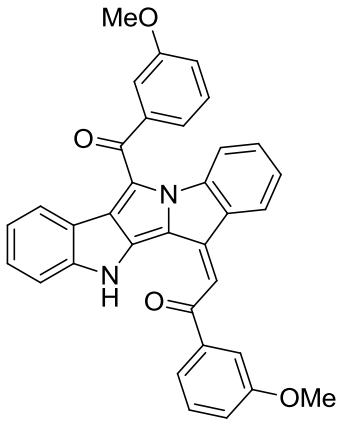
Yield: 58 mg, 71%, purple solid, m.p. 109−110 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.96 (d, *J* = 8.0 Hz, 1H), 6.71 (t, *J* = 7.5 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 7.20 (t, *J* = 8.0 Hz, 1H), 7.32-7.36 (m, 3H), 7.56 (t, *J* = 8.0 Hz, 4H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.70 (t, *J* = 8.0 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 1H), 8.06 (d, *J* = 7.5 Hz, 2H), 8.14 (d, *J* = 7.5 Hz, 2H), 9.87 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 107.8, 111.7, 115.0, 117.9, 119.2, 119.6, 121.4, 122.4, 122.5, 124.3, 126.0, 127.3, 128.1, 128.6, 129.1, 129.8, 131.7, 132.6, 133.2 (2C), 136.4, 136.6, 139.0, 139.5, 141.1, 144.7, 186.4, 189.9. **HRMS** (ESI-TOF) Calcd for $C_{32}H_{20}N_2NaO_2^+$[M+Na]$^+$: 487.1417. Found: 487.1413.

(*Z*)-2-(12-(4-Methylbenzoyl)pyrrolo[1,2-*a*:3,4-*b*']diindol-6(5*H*)-ylidene)-1-(*p*-tolyl)ethanone (3b)



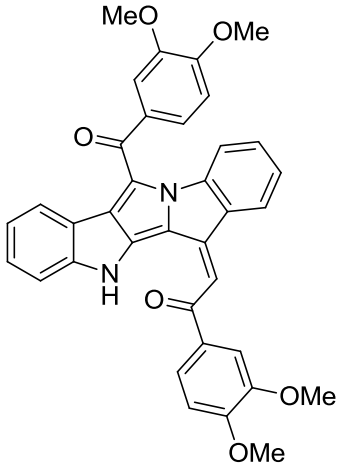
Yield: 43 mg, 50 %, purple solid, m.p. 187−188 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 2.46 (s, 3H), 2.50 (s, 3H), 6.11 (d, *J* = 8.0 Hz, 1H), 6.73 (t, *J* = 7.5 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.30-7.35 (m, 7H), 7.68 (d, *J* = 7.5 Hz, 1H), 7.76 (d, *J* = 7.0 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 2H), 8.03 (d, *J* = 8.5 Hz, 2H), 9.88 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 21.7, 21.8, 107.6, 111.7, 114.9, 117.7, 119.3, 119.5, 121.3, 122.3, 122.5, 124.1, 125.9, 127.1, 128.2, 129.3, 129.7, 130.0, 131.5, 133.3, 136.3, 137.0, 141.0, 143.4, 144.1, 144.7 (2C), 186.1, 189.4. **HRMS** (ESI-TOF) Calcd for $C_{34}H_{24}N_2NaO_2^+$ [M+Na]$^+$: 515.1730. Found: 515.1730.

(*Z*)-2-(12-(3-Methoxybenzoyl)pyrrolo[1,2-*a*:3,4-*b*']diindol-6(5*H*)-ylidene)-1-(3-methoxyphenyl)ethanone (3c)



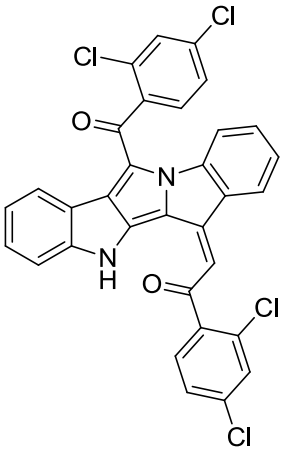
Yield: 46 mg, 50%, purple solid, m.p. 122−123 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.82 (s, 3H), 3.90 (s, 3H), 6.06 (d, *J* = 8.0 Hz, 1H), 6.72 (t, *J* = 8.0 Hz, 1H), 7.05 (t, *J* = 8.0 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 7.17 (t, *J* = 8.0 Hz, 1H), 7.21-7.28 (m, 4H), 7.39 (t, *J* = 8.0 Hz, 2H), 7.57-7.66 (m, 5H), 7.74 (d, *J* = 8.0 Hz, 1H), 9.82 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 55.4 (2C), 107.7, 111.7, 112.6, 113.2, 114.9, 117.9, 118.9, 119.2, 119.6, 120.2, 120.6, 121.2, 122.3, 122.5, 122.8, 124.2, 125.9, 127.3, 129.5, 130.1, 131.5, 133.1, 136.3, 136.4, 140.2, 140.8, 140.9, 144.7, 159.8, 160.1, 185.9, 189.2. **HRMS** (ESI-TOF) Calcd for $C_{34}H_{24}N_2NaO_4^+$ $[M+Na]^+$: 547.1628. Found: 547.1621.

(*Z*)-2-(12-(3,4-Dimethoxybenzoyl)pyrrolo[1,2-*a*:3,4-*b*']diindol-6(5*H*)-ylidene)-1-(3,4-dimethoxyphenyl)ethanone (3d)



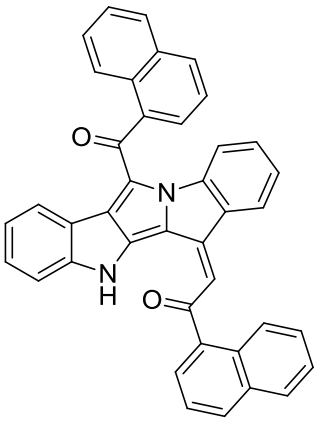
Yield: 64 mg, 62%, purple solid, m.p. 145−146 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.91 (s, 3H), 3.97 (s, 3H), 3.98 (s, 3H), 4.04 (s, 3H), 6.35 (d, *J* = 8.0 Hz, 1H), 6.78 (t, *J* = 8.0 Hz, 1H), 6.93 (dd, *J* = 8.5 Hz, *J* = 4.0 Hz, 2H), 7.10 (t, *J* = 8.0 Hz, 1H), 7.21 (t, *J* = 8.0 Hz, 1H), 7.28-7.35 (m, 3H), 7.66-7.71 (m, 4H), 7.77 (d, *J* = 8.0 Hz, 2H), 9.88 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 56.1 (3C), 107.2, 110.0, 110.5, 110.6, 111.6, 111.7, 114.8, 117.5, 119.4, 119.6, 121.2, 122.1, 122.5, 122.6, 124.1, 125.5, 125.9, 126.9, 131.3, 131.5, 132.7, 133.3, 135.9, 136.2, 140.9, 144.7, 149.2, 149.4, 153.1, 153.7, 184.9, 188.1. **HRMS** (ESI-TOF) Calcd for $C_{36}H_{28}N_2NaO_6^+$ $[M+Na]^+$: 607.1840. Found: 607.1843.

(*Z*)-2-(12-(2,4-Dichlorobenzoyl)pyrrolo[1,2-*a*:3,4-*b*']diindol-6(5*H*)-ylidene)-1-(2,4-dichlorophenyl)ethanone (3e)



Yield: 55 mg, 52%, purple solid, m.p. 148−149 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.66 (d, *J* = 8.0 Hz, 1H), 6.79 (t, *J* = 8.0 Hz, 1H), 7.05 (s, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.41 (t, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 7.5 Hz, 1H), 7.53 (s, 1H), 7.63 (m, 2H), 7.63 (d, *J* = 8.5 Hz, 1H), 7.68 (d, *J* = 8.5 Hz, 1H), 8.16 (d, *J* = 8.5 Hz, 1H), 9.78 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 111.8, 112.0, 115.9, 118.9, 120.3, 121.7, 123.3, 124.7, 126.5, 127.5, 127.6, 128.1, 130.4, 130.8, 131.0, 131.6, 132.4, 132.5, 133.9, 136.4, 136.6, 137.4, 137.6, 138.1, 138.9, 141.4, 144.7, 182.8, 190.2. **HRMS** (ESI-TOF) Calcd for $C_{32}H_{16}C_{l4}N_2NaO_2^+$[M+Na]$^+$: 622.9858. Found: 622.9854.

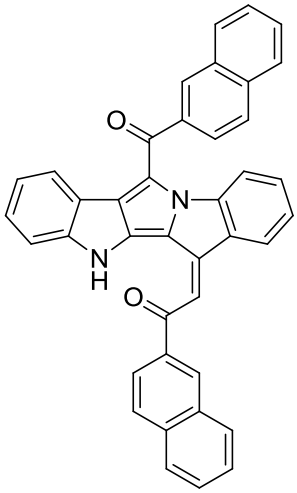
(*Z*)-2-(12-(1-Naphthoyl)pyrrolo[1,2-*a*:3,4-*b*']diindol-6(5*H*)-ylidene)-1-(naphthalen-1-yl)ethanone (3f)



Yield: 57 mg, 57%, purple solid, m.p. 159−160 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.39 (d, *J* = 8.0 Hz, 1H), 6.50 (t, *J* = 8.0 Hz, 1H), 7.11 (q, *J* = 8.0 Hz, 2H), 7.20 (s, 1H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.38 (q, *J* = 8.0 Hz, 1H), 7.53 (t, *J* = 8.0 Hz, 1H), 7.57-7.66 (m, 6H), 7.96 (d, *J* = 8.0 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 8.01-8.05 (m, 2H), 8.09 (d, *J* = 8.0 Hz, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 8.16 (d, *J* = 8.0 Hz, 1H), 8.57-8.61 (m, 2H), 9.89 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 111.7, 112.4, 115.7, 118.5, 119.2, 119.7, 121.5, 122.4, 124.3, 124.4, 124.7, 125.3, 125.5, 125.6, 126.1, 126.5, 126.8, 127.1, 127.6, 127.8, 128.0, 128.5, 128.6, 129.9, 130.2, 132.8, 133.1, 133.9, 134.1, 136.2, 136.4, 136.5, 139.0, 141.5, 144.6, 144.7, 186.7, 193.9. **HRMS** (ESI-TOF) Calcd for $C_{40}H_{24}N_2NaO_2^+$[M+Na]$^+$: 587.1730. Found: 587.1736.

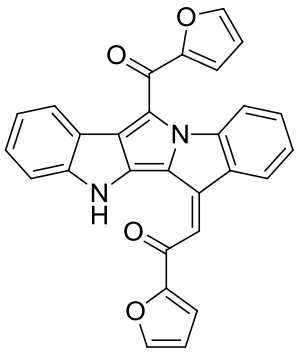
(*Z*)-2-(12-(2-Naphthoyl)pyrrolo[1,2-*a*:3,4-*b*']diindol-6(5*H*)-ylidene)-1-(naphthalen-2-yl)ethan

one (3g)



Yield: 50 mg, 50%, purple solid, m.p. 146−147 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.02 (d, *J* = 8.0 Hz, 1H), 6.52 (t, *J* = 8.0 Hz, 1H), 7.14 (q, *J* = 6.0 Hz, 2H), 7.34 (t, *J* = 8.0 Hz, 2H), 7.49, (s, 1H), 7.53 (t, *J* = 8.0 Hz, 1H), 7.58-7.66 (m, 3H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.97 (t, *J* = 8.0 Hz, 2H), 8.02 (d, *J* = 8.0 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 8.15 (d, *J* = 8.0 Hz, 1H), 8.21 (d, *J* = 8.0 Hz, 1H), 8.66 (d, *J* = 6.0 Hz, 2H), 9.95 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 107.8, 111.8, 115.0, 118.0, 119.3, 119.7, 121.5, 122.4, 122.6, 124.2, 124.3, 125.3, 126.0, 126.8, 126.9, 127.3, 127.8, 127.9, 128.3, 128.5, 128.6, 128.9, 129.4, 129.6, 129.8, 131.7, 132.2, 132.7, 132.8, 133.4, 135.4, 135.7, 136.0, 136.6, 136.7, 136.9, 141.2, 144.9, 186.1, 189.7. **HRMS** (ESI-TOF) Calcd for $C_{40}H_{24}N_2NaO_2^+$[M+Na]$^+$: 587.1730. Found: 587.1733.

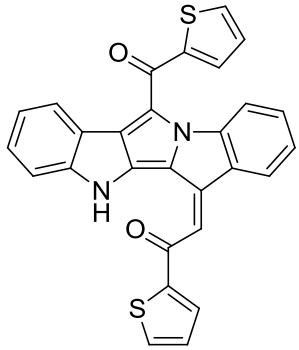
(*Z*)-2-(12-(Furan-2-carbonyl)pyrrolo[1,2-*a*:3,4-*b*']diindol-6(5*H*)-ylidene)-1-(furan-2-yl)ethan one (3h)



Yield: 47 mg, 60%, purple solid, m.p. 166−167 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.57 (dd, *J* = 3.5 Hz, *J* = 1.5 Hz, 1H), 6.67-6.71 (m, 2H), 6.89 (t, *J* = 8.0 Hz, 1H), 7.02 (t, *J* = 8.0 Hz, 1H), 7.05 (s, 1H), 7.23 (q, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 3.5 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 3.5 Hz, 1H), 7.57-7.61 (m, 3H), 7.75 (d, *J* = 1.5 Hz, 1H), 10.00 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 106.8, 111.9, 112.5, 112.9, 114.6, 116.7, 117.6, 119.3, 119.7, 120.6, 121.3, 122.4, 124.2, 126.0, 126.6, 131.5, 132.9, 135.9, 136.6, 140.7, 144.7, 146.3, 147.5, 152.8, 154.7, 172.7, 177.2. **HRMS** (ESI-TOF) Calcd for $C_{28}H_{17}N_2O_4^+$ [M+H]$^+$: 445.1183. Found: 445.1212.

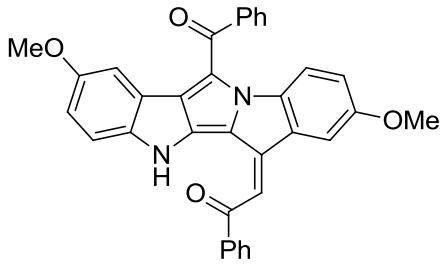
(*Z*)-1-(Thiophen-2-yl)-2-(12-(thiophene-2-carbonyl)pyrrolo[1,2-*a*:3,4-*b*']diindol-6(5*H*)-yliden

e)ethanone (3i)



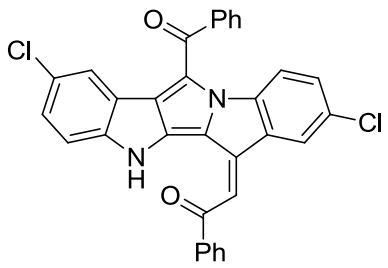
Yield: 35 mg, 42%, purple solid, m.p. 155−156 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.65 (d, *J* = 7.6 Hz, 1H), 6.85 (t, *J* = 7.6 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 7.17-7.25 (m, 4H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.38 (d, *J* = 7.6 Hz, 1H), 7.67-7.70 (m, 3H), 7.85 (d, *J* = 6.2 Hz, 1H), 7.93 (d, *J* = 3.6 Hz, 2H), 9.94 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 107.1, 112.0, 114.7, 117.4, 119.4, 119.7, 121.4, 121.8, 122.3, 124.3, 126.1, 126.7, 128.4, 128.6, 131.1, 131.6, 133.1, 133.4, 134.9, 135.6, 136.1, 136.7, 140.9, 144.1, 144.8, 147.2, 178.0, 181.7. **HRMS** (ESI-TOF) Calcd for $C_{28}H_{16}N_2NaO_2S_2^+$ $[M+Na]^+$: 499.0545. Found: 499.0545.

(*Z*)-2-(12-Benzoyl-2,8-dimethoxypyrrolo[1,2-*a*:3,4-*b*']diindol-6(5*H*)-ylidene)-1-phenylethanone (3j)



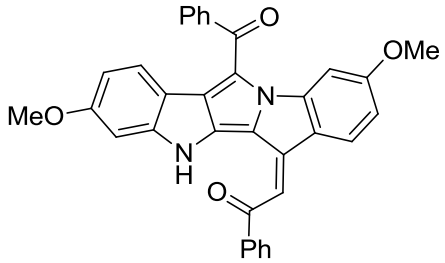
Yield: 50 mg, 54%, purple solid, m.p. 105−106 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.35 (s, 3H), 3.82 (s, 3H), 5.41 (d, *J* = 2.5 Hz, 1H), 6.77 (dt, *J* = 8.5 Hz, *J* = 2.5 Hz, 2H), 7.13-7.16 (m, 3H), 7.49-7.59 (m, 5H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.72 (d, *J* = 8.5 Hz, 1H), 8.03 (d, *J* = 6.0 Hz, 2H), 8.08 (d, *J* = 6.0 Hz, 2H), 9.64 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 55.3, 55.8, 104.7, 107.3, 107.5, 112.3, 115.3, 115.8, 116.3, 118.4, 119.6, 122.2, 126.6, 128.1, 128.6, 129.0, 129.9, 132.5, 132.9, 134.6, 135.2, 136.4, 137.1, 139.4, 139.5 (2C), 153.4, 157.0, 186.1, 189.5. **HRMS** (ESI-TOF) Calcd for $C_{34}H_{25}N_2O_4^+$ $[M+H]^+$: 525.1809. Found: 525.1804.

(*Z*)-2-(12-Benzoyl-2,8-dichloropyrrolo[1,2-*a*:3,4-*b*']diindol-6(5*H*)-ylidene)-1-phenylethanone (3k)



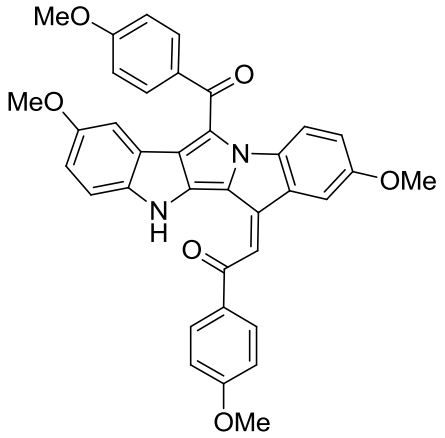
Yield: 52 mg, 55%, purple solid, m.p. 192−193 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.59 (s, 1H), 7.09 (q, *J* = 7.5 Hz, 1H), 7.17-7.21 (m, 3H), 7.52-7.57 (m, 4H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.71 (d, *J* = 7.5 Hz, 1H), 7.74 (d, *J* = 8.5 Hz, 2H), 7.92 (d, *J* = 7.5 Hz, 2H), 8.07 (d, *J* = 7.5 Hz, 2H), 9.85 (s, 1H). **^{13}C NMR** ($CDCl_3$, 125 MHz) δ 108.5, 112.5, 116.3, 117.9, 120.1, 121.4, 122.2, 122.4, 124.9, 126.1, 126.5, 128.2, 128.7, 129.2, 129.5, 130.2, 131.1, 133.0, 133.3, 134.6, 135.0, 136.6, 138.9, 139.0, 139.2, 142.9, 186.1, 189.5. **HRMS** (ESI-TOF) Calcd for $C_{32}H_{19}Cl_2N_2O_2^+$ $[M+H]^+$: 533.0818. Found: 533.0818.

(*Z*)-2-(12-Benzoyl-3,9-dimethoxypyrrolo[1,2-*a*:3,4-*b*']diindol-6(5*H*)-ylidene)-1-phenylethanone (3l)



Yield: 37 mg, 40%, purple solid, m.p. 267−268 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.80 (s, 3H), 3.85 (s, 3H), 5.72 (d, *J* = 8.0 Hz, 1H), 6.30 (d, *J* = 8.0 Hz, 1H), 6.63 (d, *J* = 8.0 Hz, 1H), 6.81 (s, 1H), 7.22 (s, 1H), 7.54-7.68 (m, 8H), 8.01 (d, *J* = 8.0 Hz, 2H), 8.11 (d, *J* = 8.0 Hz, 2H), 9.79 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 55.4, 55.7, 95.9, 100.7, 106.9, 108.1, 110.8, 113.0, 118.9, 121.6, 122.3, 123.4, 125.4, 128.1, 128.4, 128.6, 129.1, 129.7, 132.4, 132.8, 136.5, 137.2, 139.6, 139.8, 143.2, 146.5, 159.2, 163.6, 186.5, 189.7. **HRMS** (ESI-TOF) Calcd for $C_{34}H_{25}N_2O_4^+$ $[M+H]^+$: 525.1809. Found: 525.1802.

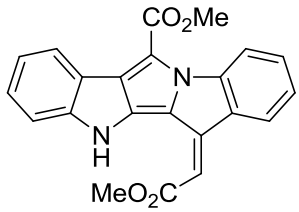
(*Z*)-2-(2,8-Dimethoxy-12-(4-methoxybenzoyl)pyrrolo[1,2-*a*:3,4-*b*']diindol-6(5*H*)-ylidene)-1-(4-methoxyphenyl)ethanone (3m)



Yield: 53 mg, 55%, purple solid, m.p. 226−227 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.42 (s, 3H), 3.88 (s, 3H), 3.90 (s, 3H), 3.92 (s, 3H), 5.68 (d, *J* = 2.4 Hz, 1H), 6.82 (dd, *J* = 8.8 Hz, *J* = 2.4 Hz, 1H), 6.86 (dd, *J* = 8.8 Hz, *J* = 2.4 Hz, 1H), 7.02-7.06 (m, 4H), 7.21-7.25 (m, 3H), 7.74 (d, *J* = 8.8 Hz, 1H), 8.07 (d, *J* = 8.8 Hz, 2H), 8.15 (d, *J* = 8.8 Hz, 2H), 9.66 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 55.1, 55.5, 55.6, 55.9, 104.8, 107.3, 107.4, 112.3, 113.8, 114.3, 115.1, 115.7, 116.2, 118.0, 119.7, 122.1, 126.3, 130.4, 132.2, 132.4, 132.5, 134.8, 135.2, 136.0, 136.9, 139.4, 153.4,

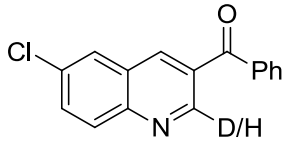
157.0, 163.3, 163.6, 185.0, 188.3. **HRMS** (ESI-TOF) Calcd for $C_{36}H_{29}N_2O_6^+$ $[M+H]^+$: 585.2020. Found: 585.2017.

(*Z*)-Methyl 6-(2-methoxy-2-oxoethylidene)-5,6-dihydropyrrolo[1,2-*a*:3,4-*b*']diindole-12-carboxylate (3n)



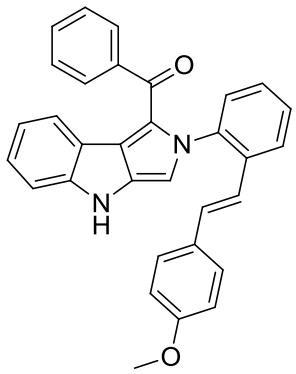
Yield: 20 mg, 30%, orange solid, m.p. 199−200 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.84 (s, 3H), 4.04 (s, 3H), 6.08 (s, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 7.11 (td, *J* = 8.0 Hz, *J* = 2.0 Hz, 1H), 7.28-7.34 (m, 3H), 7.45 (d, *J* = 7.6 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 8.47 (d, *J* = 7.6 Hz, 1H), 9.51 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 51.7 (2C), 102.8, 111.4, 112.9, 115.9, 116.1, 119.5, 119.6, 121.0, 123.2, 124.1, 126.2, 126.8, 131.4, 132.3, 134.5, 136.9, 141.0, 144.8, 160.9, 167.7. **HRMS** (ESI-TOF) Calcd for $C_{22}H_{17}N_2O_4^+$ $[M+H]^+$: 373.1183. Found: 373.1176.

(6-Chloroquinolin-3-yl)(phenyl)methanone (2p/2p-[D])



Yield: 67 mg, 71%, white solid. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.54 (t, *J* = 7.6 Hz, 2H), 7.64-7.68 (m, 1H), 7.74-7.78 (m, 1H), 7.84-7.89 (m, 3H), 8.12 (d, *J* = 7.6 Hz, 1H), 8.44 (d, *J* = 2.0 Hz, 1H).

(*E*)-(2-(2-(4-Methoxystyryl)phenyl)-2,4-dihydropyrrolo[3,4-*b*]indol-1-yl)(phenyl)methanone (6)



Yield: 44 mg, 47%, brown solid, m.p. 177−178 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.74 (s, 3H), 6.21 (d, *J* = 8.0 Hz, 1H), 6.54 (d, *J* = 16 Hz, 1H), 6.72-6.77 (m, 3H), 6.81 (s, 1H), 6.86 (d, *J* = 16 Hz, 1H), 7.14 (t, *J* = 8.0 Hz, 2H), 7.19-7.20 (m, 2H), 7.26-7.31 (m, 3H), 7.36 (t, *J* = 8.0 Hz, 2H), 7.47 (t, *J* = 8.0 Hz, 1H), 7.64 (t, *J* = 8.0 Hz, 2H), 7.78 (dd, *J* = 8.0 Hz, *J* = 1.6 Hz, 2H). **^{13}C NMR**

(100 MHz, $CDCl_3$) δ 55.2, 108.8, 111.1, 113.9, 118.9, 119.7, 121.2, 121.6, 123.0, 123.5, 125.6, 125.7, 127.4, 127.7, 127.8, 128.2, 128.5, 129.3, 129.8, 130.9, 131.6, 133.5, 135.0, 139.4, 139.9, 146.0, 159.3, 184.9. **HRMS** (ESI-TOF) Calcd for $C_{32}H_{25}N_2O_2^+$ $[M+H]^+$: 469.1911. Found: 469.1914.

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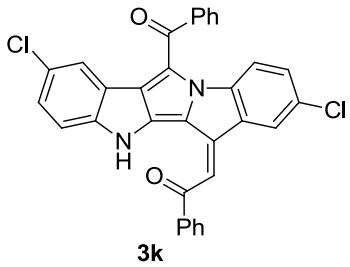
IV. Crystal Data and OPTEP Drawings

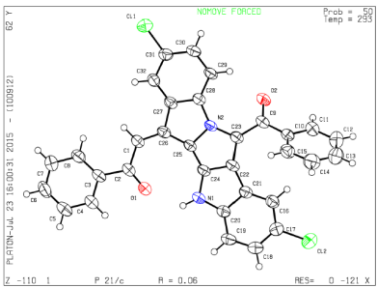
Single-crystal X-ray diffraction data was collected at room temperature on a Oxford Diffraction Gemini R Ultra diffractometer, the X-ray generator using Mo-Kα (λ = 0.71073 Å) radiation with a ω scan technique. The crystal structures were solved by direct method of SHELXS-97[1] and refined by full-matrix least-squares techniques using the SHELXL-97 program. Non-hydrogen atoms were refined anisotropic. CCDC deposition number: 1414910 (**3k**). Data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

(1) Crystal data and OPTEP drawing of compound **3k**

ORTEP drawing:



3k



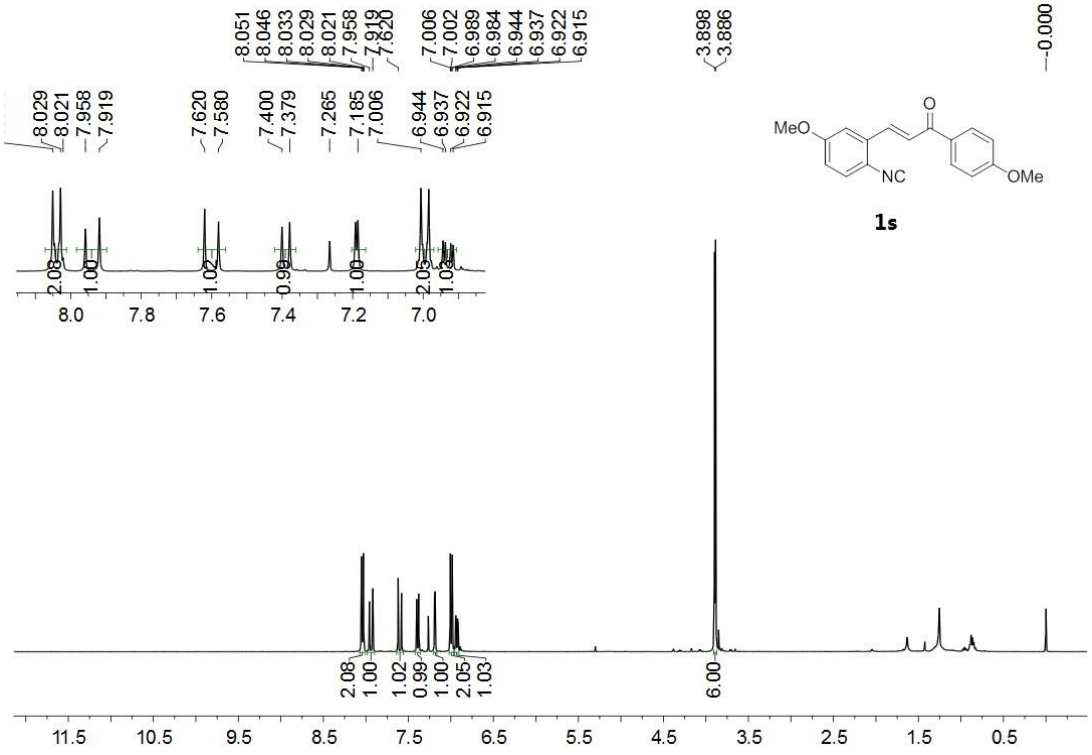
Crystal data:

Empirical formula	$C_{32}H_{18}Cl_2N_2O_2$
Formula weight	533.38
Crystal system	monoclinic
Space group	P 21/c
a (Å)	7.5637(5)
b (Å)	27.8153(18)
c (Å)	11.7714(7)
α (deg)	90.00
β (deg)	96.895(6)
γ (deg)	90.00
Volume ($Å^3$)	2458.6(3)
Z	4
Calculated density (mg/m^3)	1.441
Absorption coefficient (mm^{-1})	0.299
F(000)	1096
Theta range for data collection (deg)	2.80 to 29.250
Reflections collected/unique	4657 / 2799
Goodness-of-fit on F^2	1.021
Final R indices [$I > 2\sigma(I)$]	R1=0.0567, WR2 = 0.1119
R indices (all data)	R1=0.1082, WR2 =0.1335

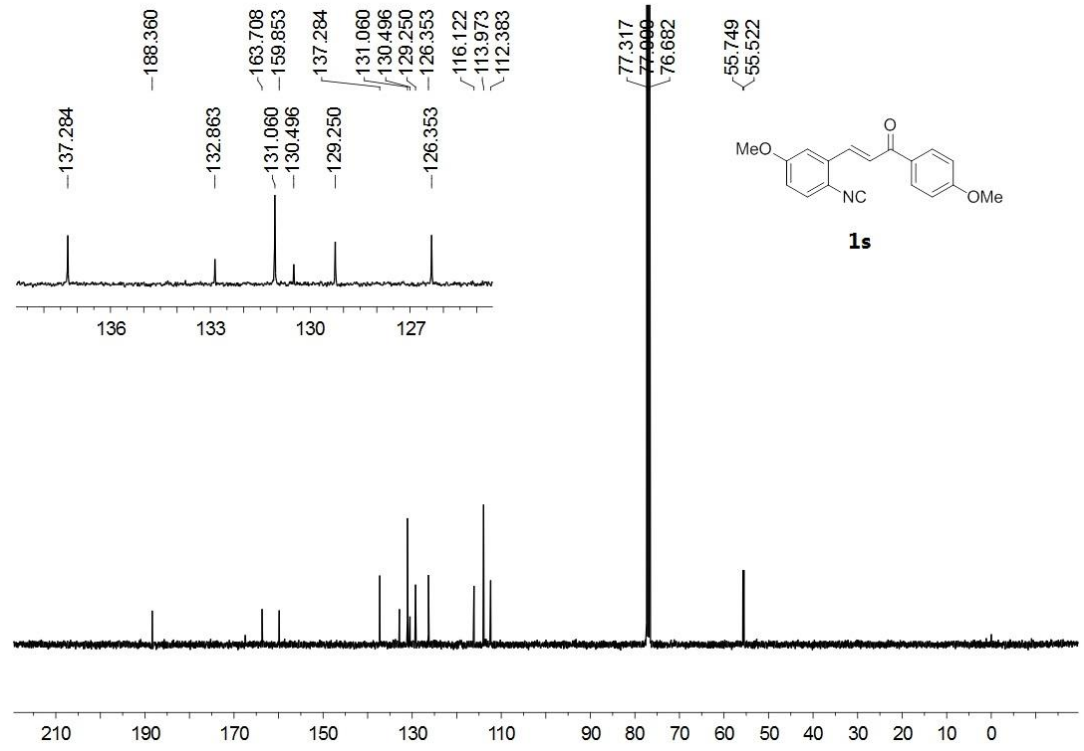
[1] G. M. Sheldrick, *SHELXS-97, Programs for X-ray Crystal Structure Solution*, University of Göttingen, Göttingen, Germany, **1997**.

V. Copies of ^{1}H NMR and ^{13}C NMR Spectra

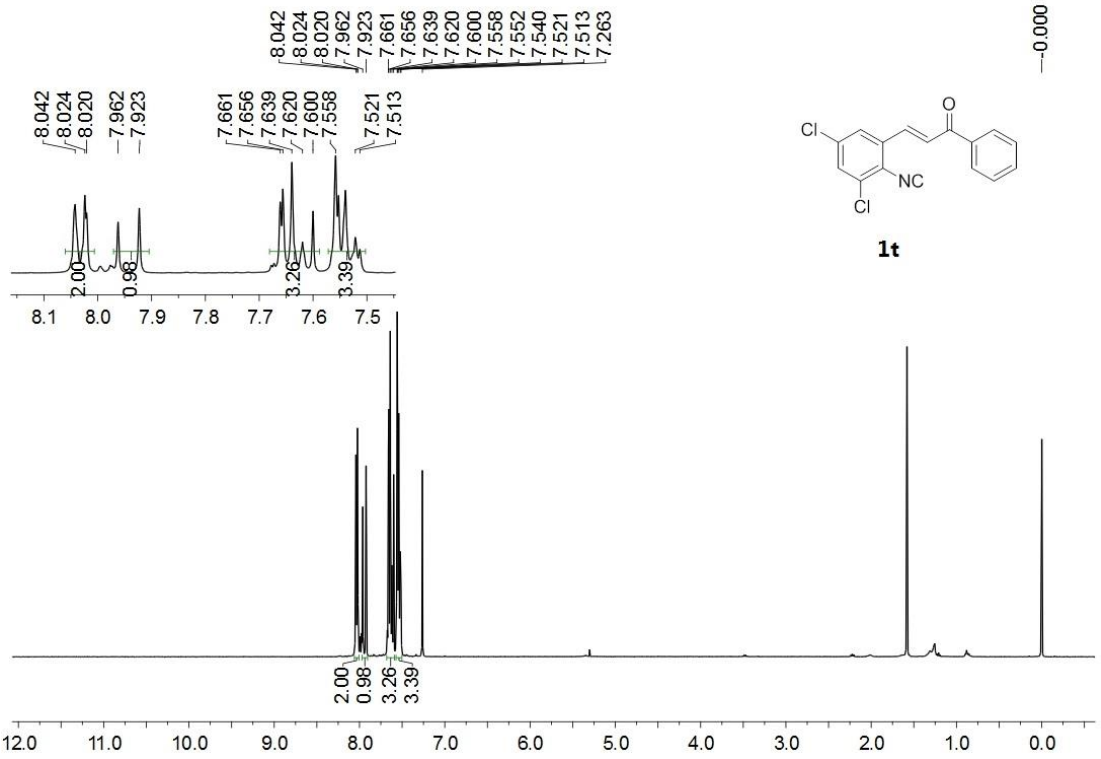
^{1}H NMR (400 MHz, $CDCl_3$) for **1s**



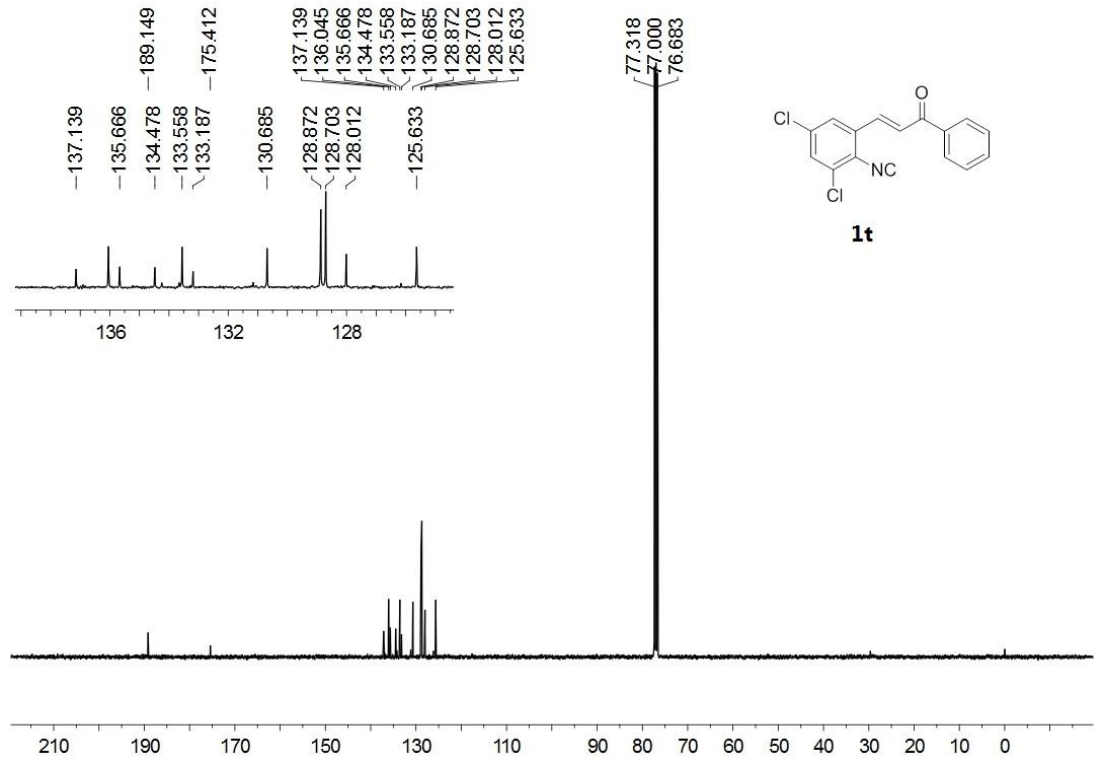
^{13}C NMR (100 MHz, $CDCl_3$) for **1s**



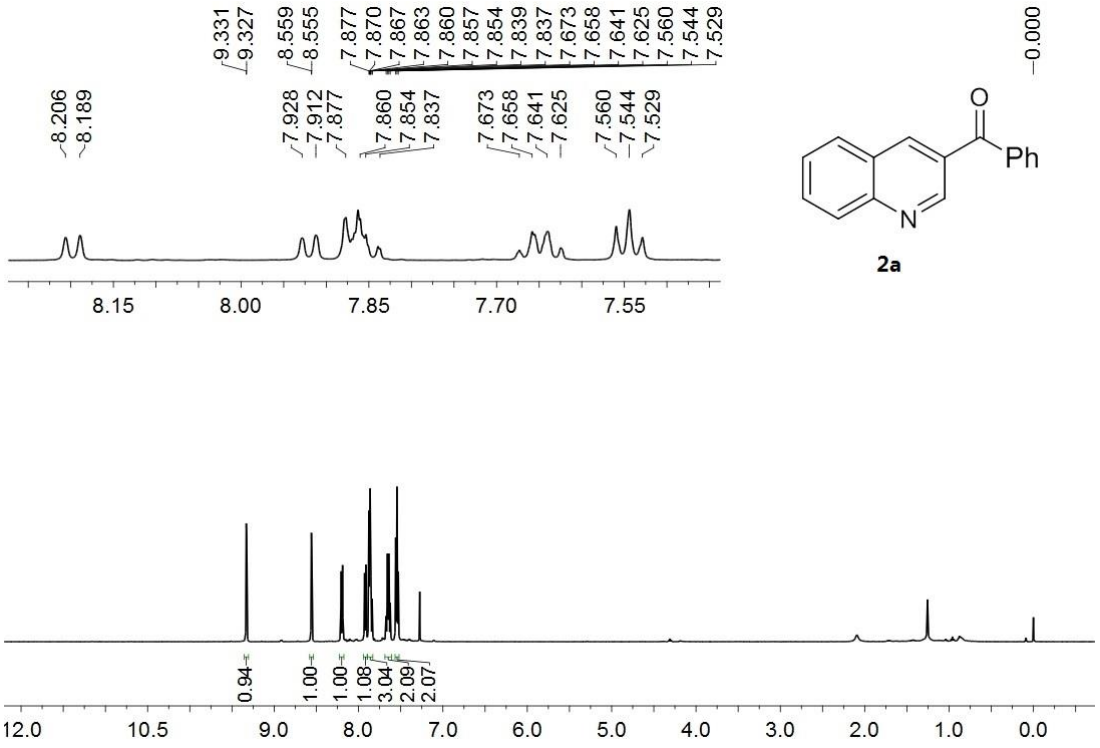
^{1}H NMR (400 MHz, $CDCl_3$) for **1t**



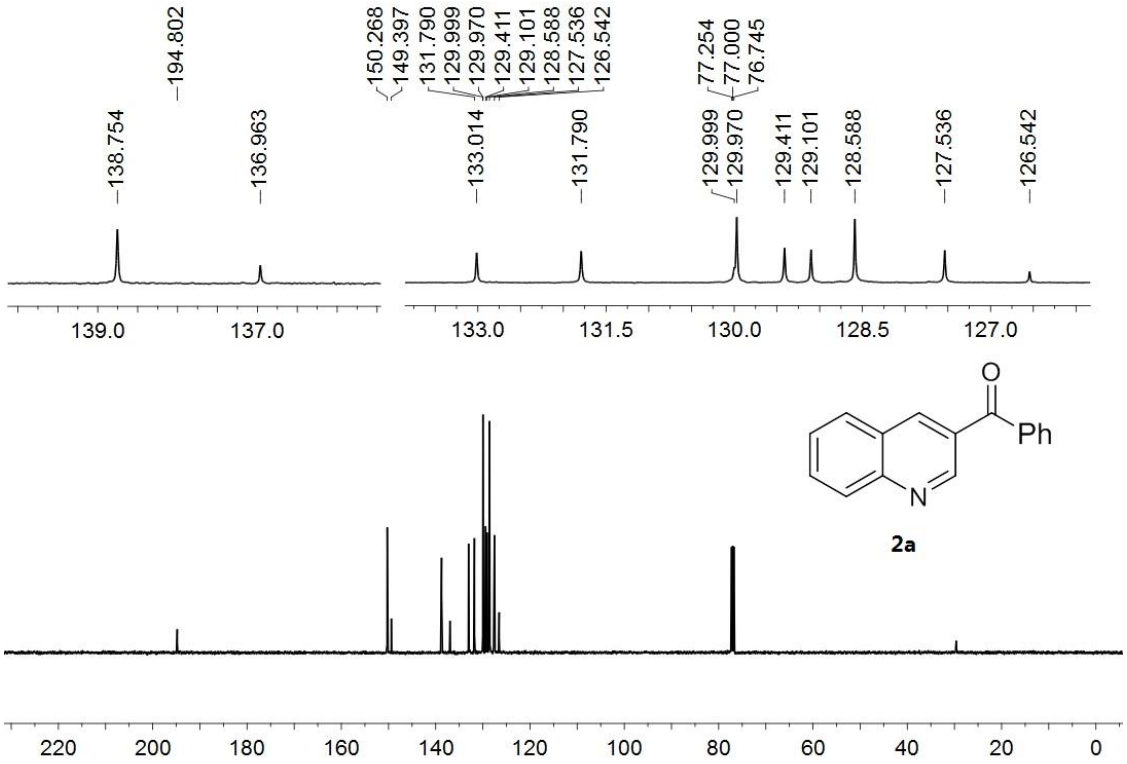
^{13}C NMR (100 MHz, $CDCl_3$) for **1t**



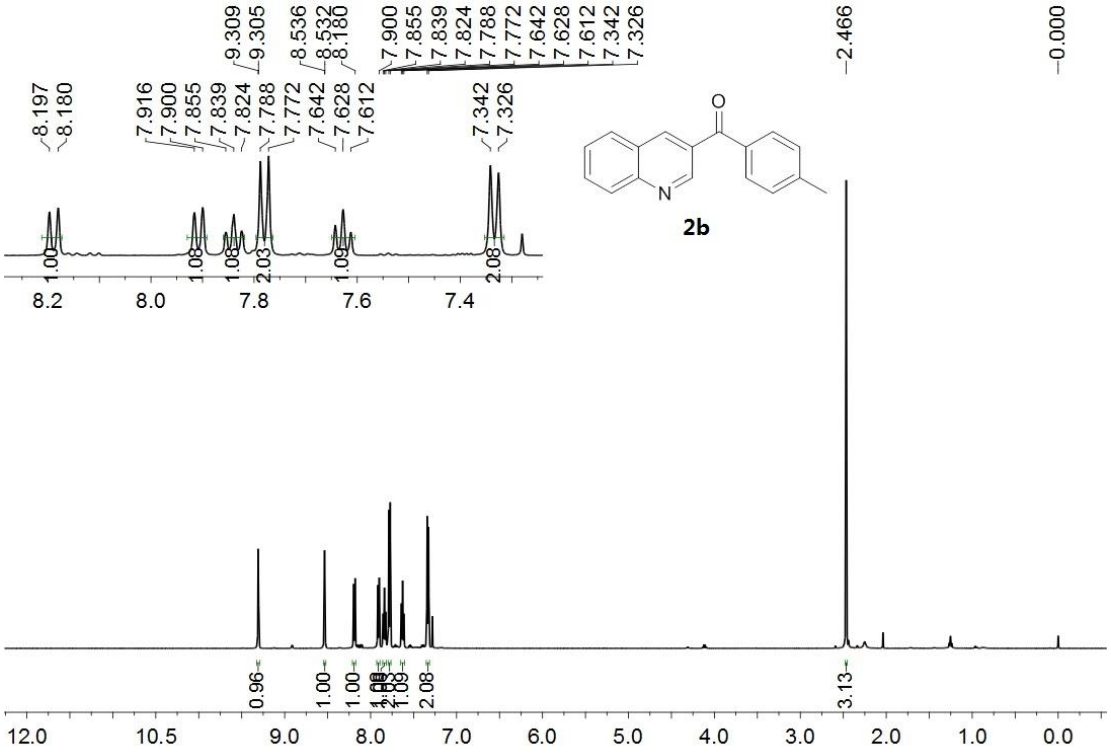
^{1}H NMR (500 MHz, $CDCl_3$) for **2a**



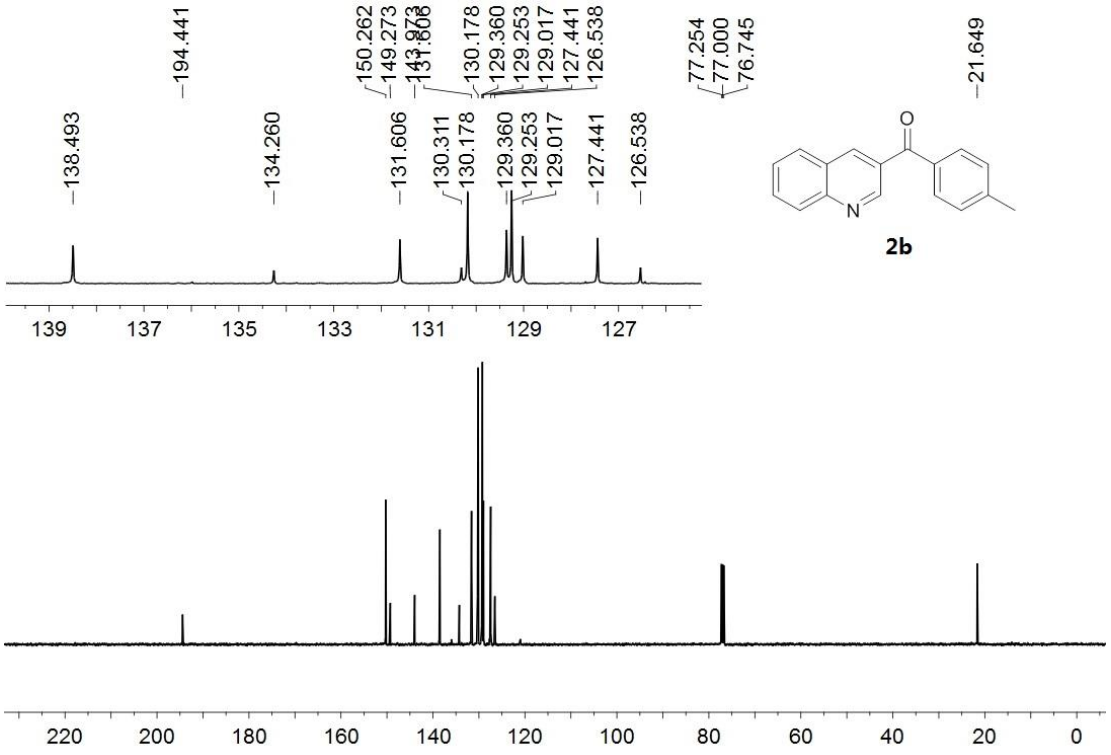
^{13}C NMR (125 MHz, $CDCl_3$) for **2a**



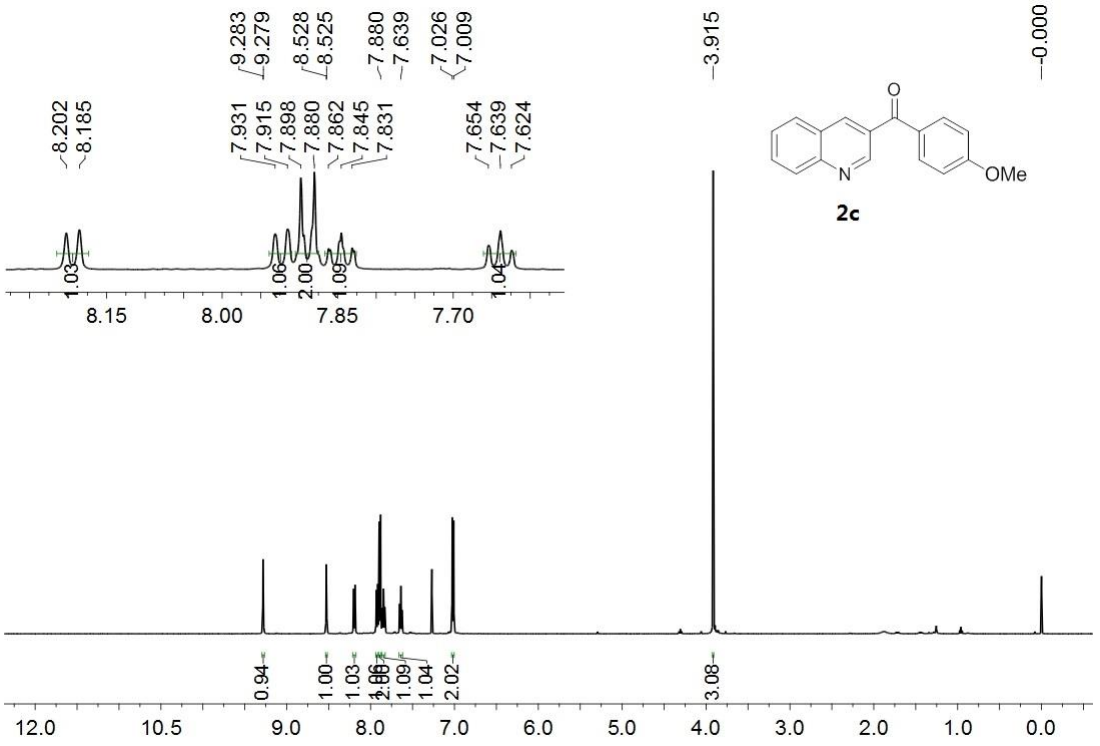
^{1}H NMR (500 MHz, $CDCl_3$) for **2b**



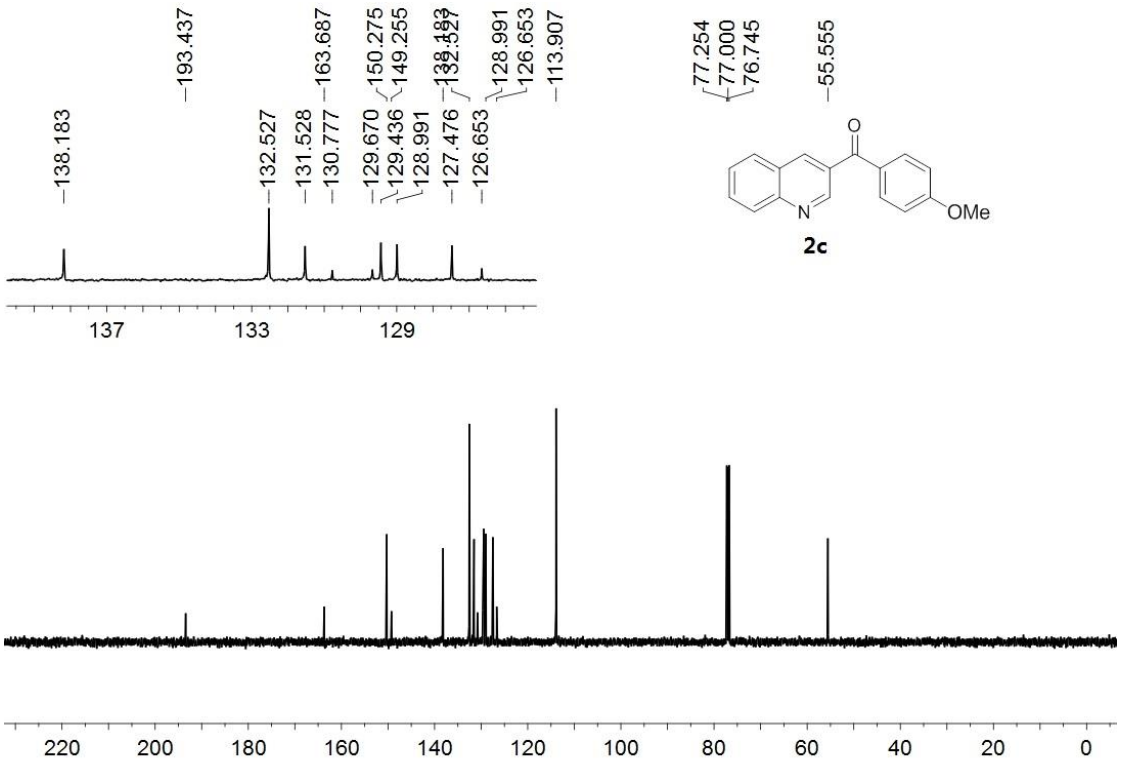
^{13}C NMR (125 MHz, $CDCl_3$) for **2b**



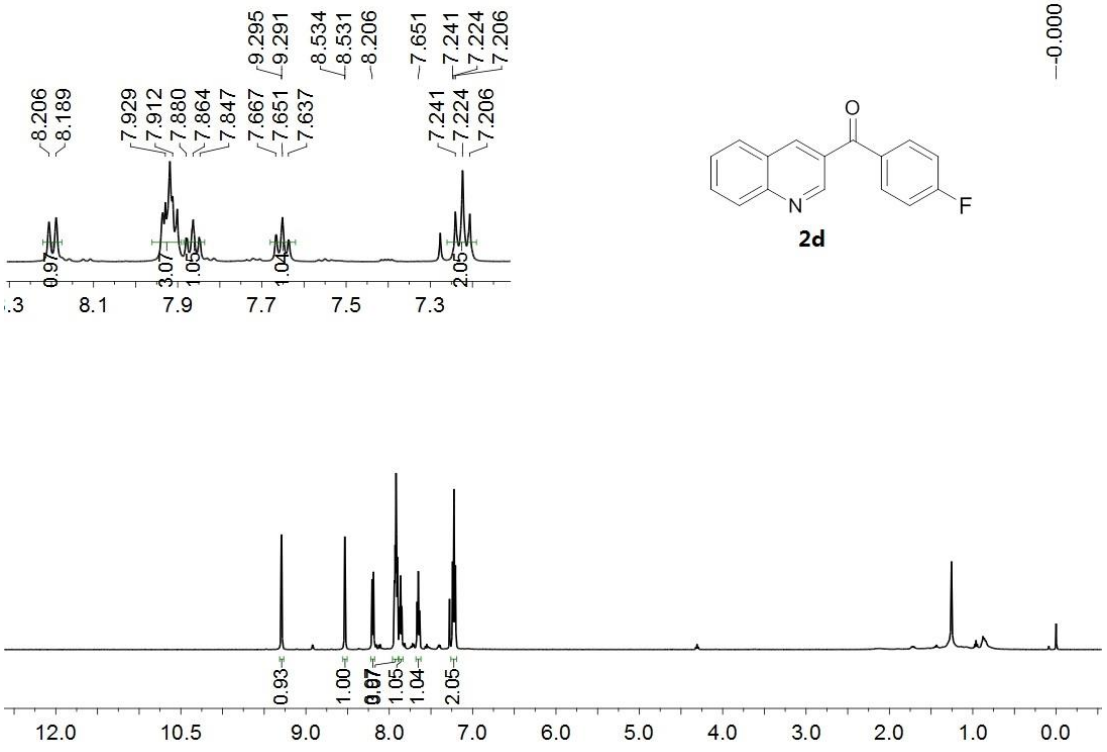
^{1}H NMR (500 MHz, $CDCl_3$) for **2c**



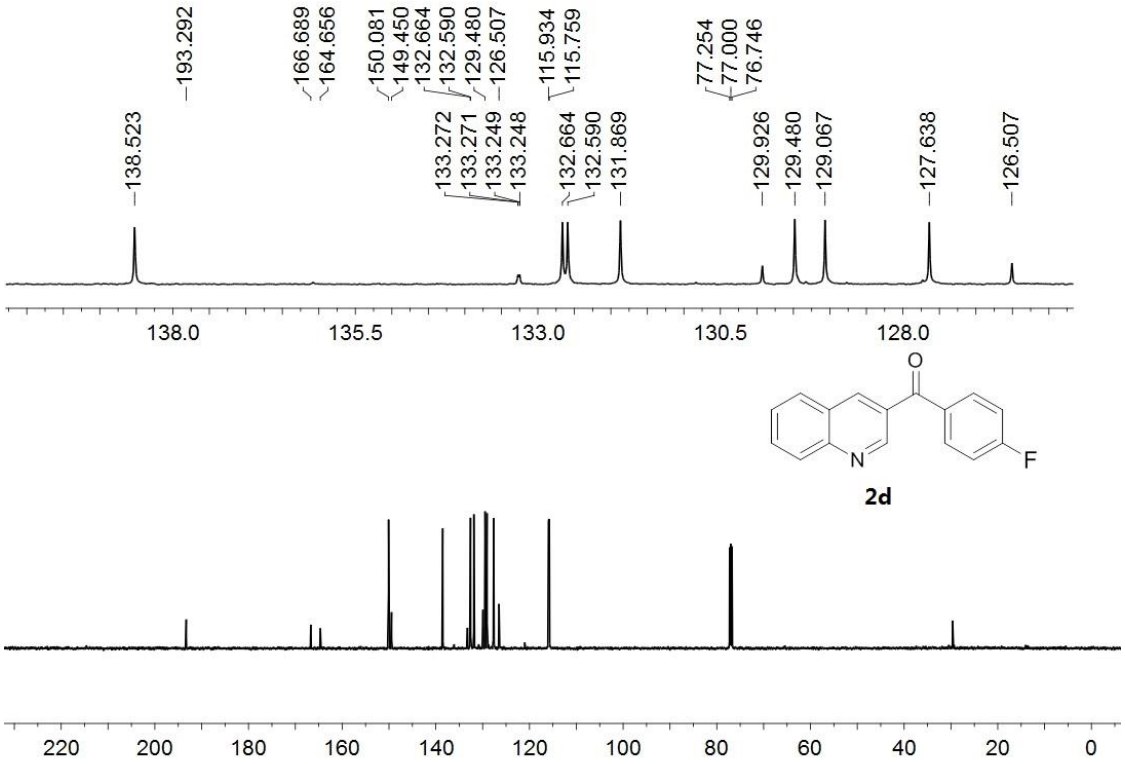
^{13}C NMR (125 MHz, $CDCl_3$) for **2c**



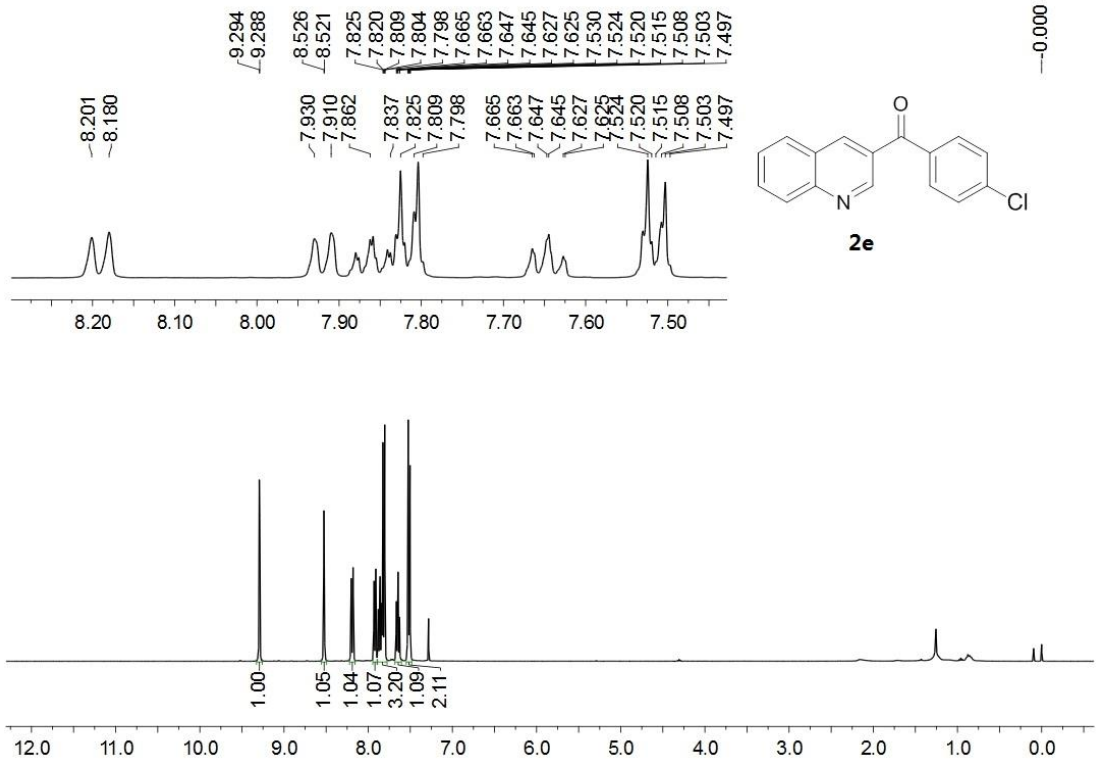
^{1}H NMR (500 MHz, $CDCl_3$) for **2d**



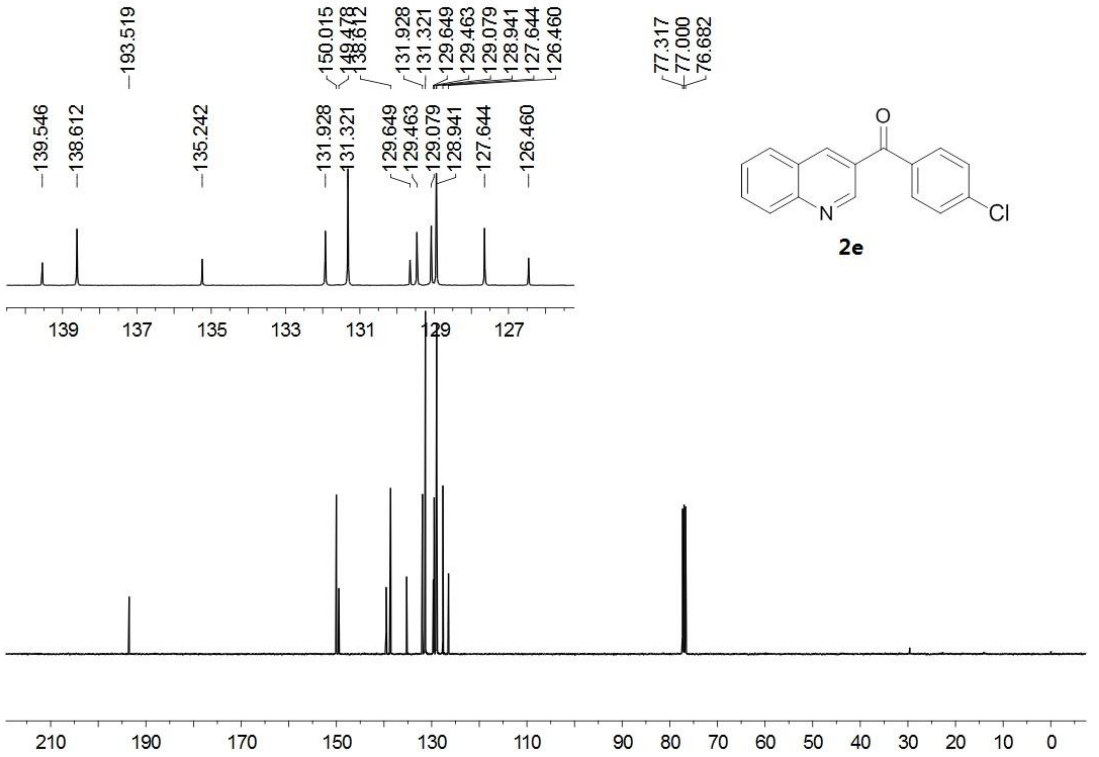
^{13}C NMR (125 MHz, $CDCl_3$) for **2d**



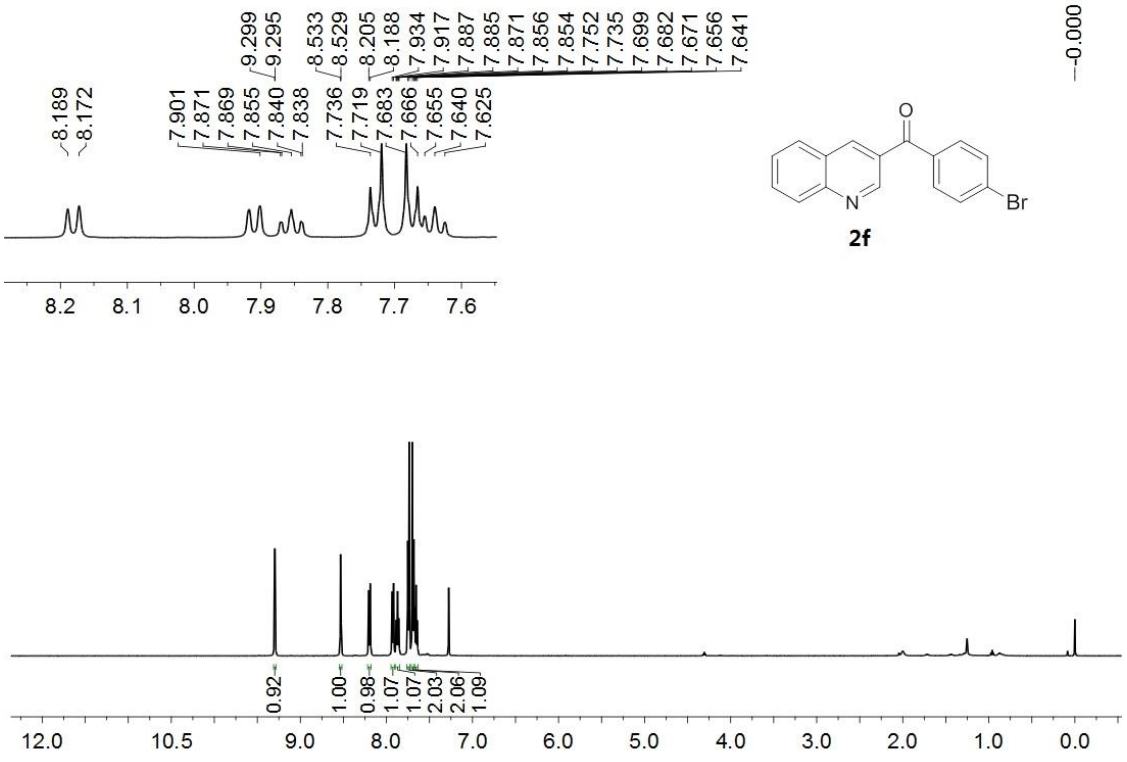
^{1}H NMR (400 MHz, $CDCl_3$) for **2e**



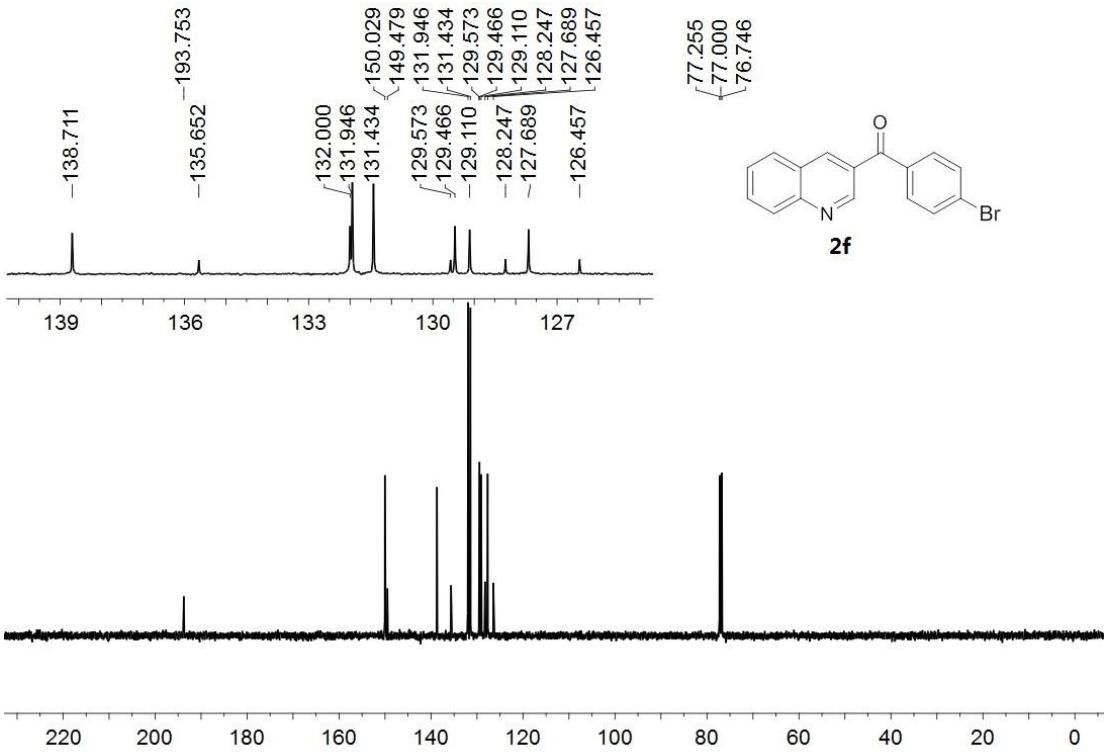
^{13}C NMR (100 MHz, $CDCl_3$) for **2e**



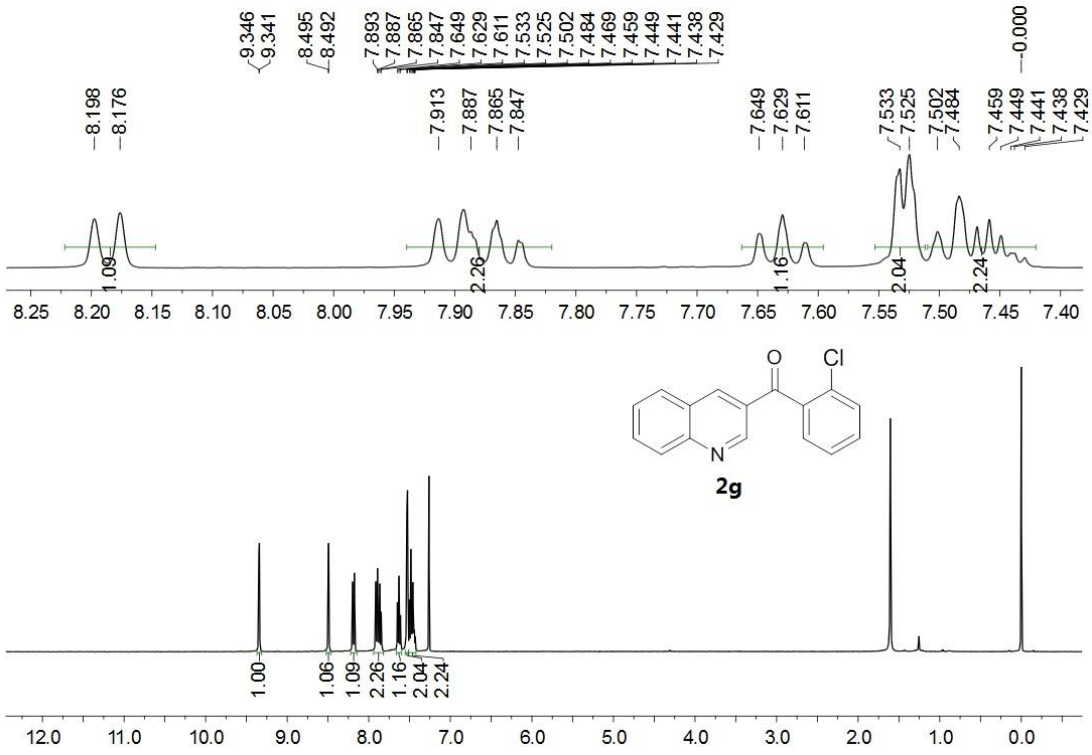
^{1}H NMR (500 MHz, $CDCl_3$) for **2f**



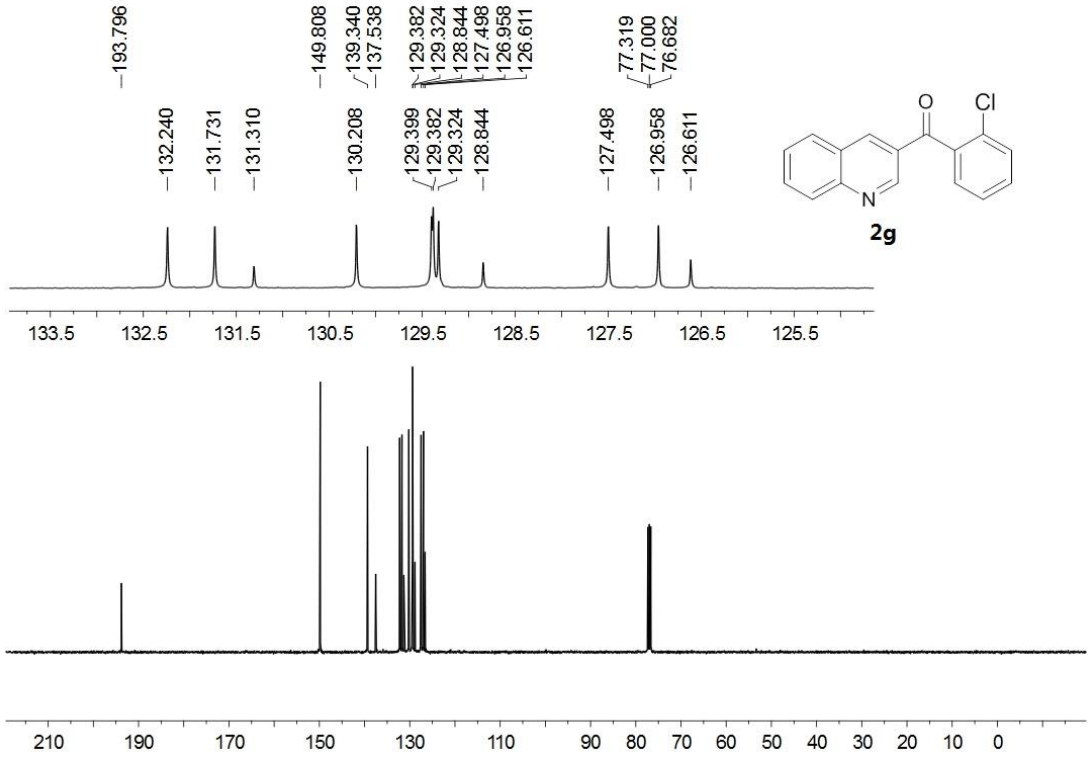
^{13}C NMR (125 MHz, $CDCl_3$) for **2f**



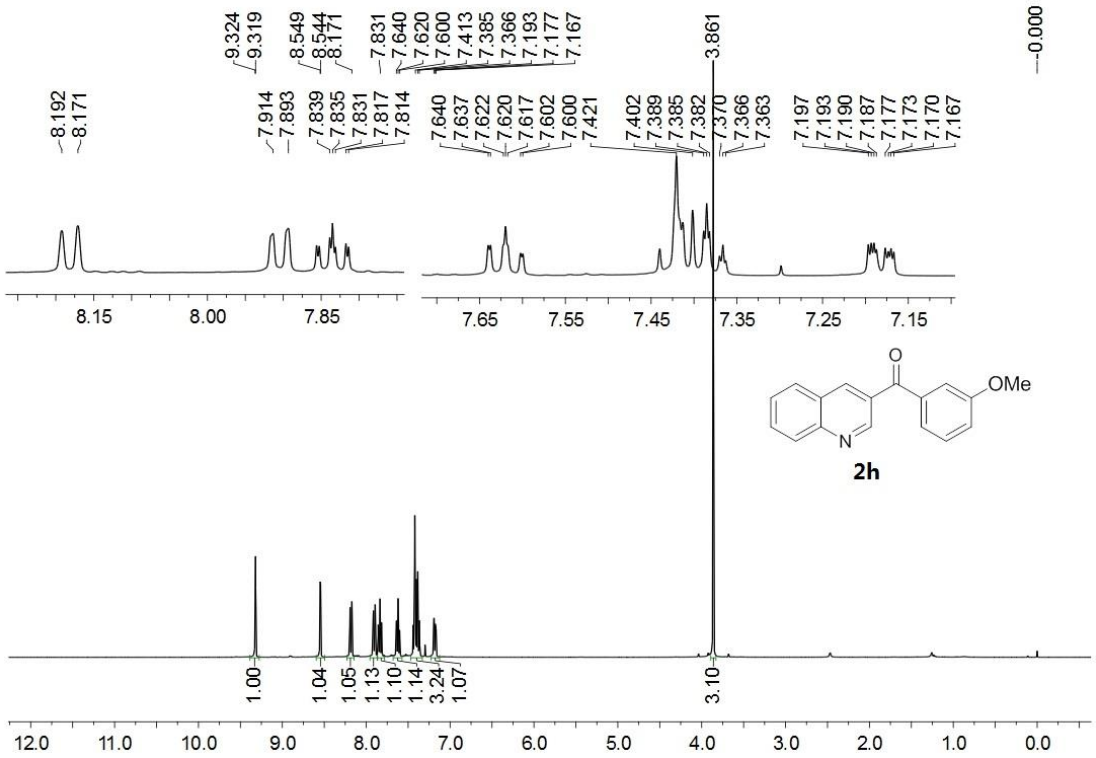
^{1}H NMR (400 MHz, $CDCl_3$) for **2g**



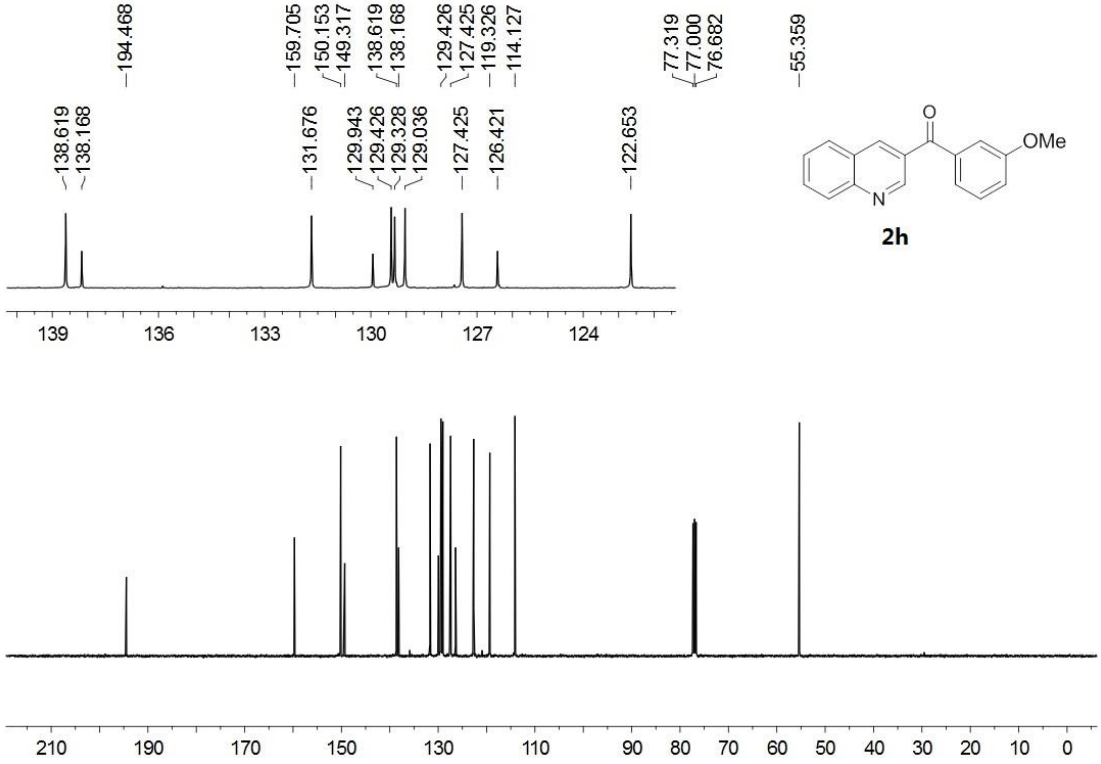
^{13}C NMR (100 MHz, $CDCl_3$) for **2g**



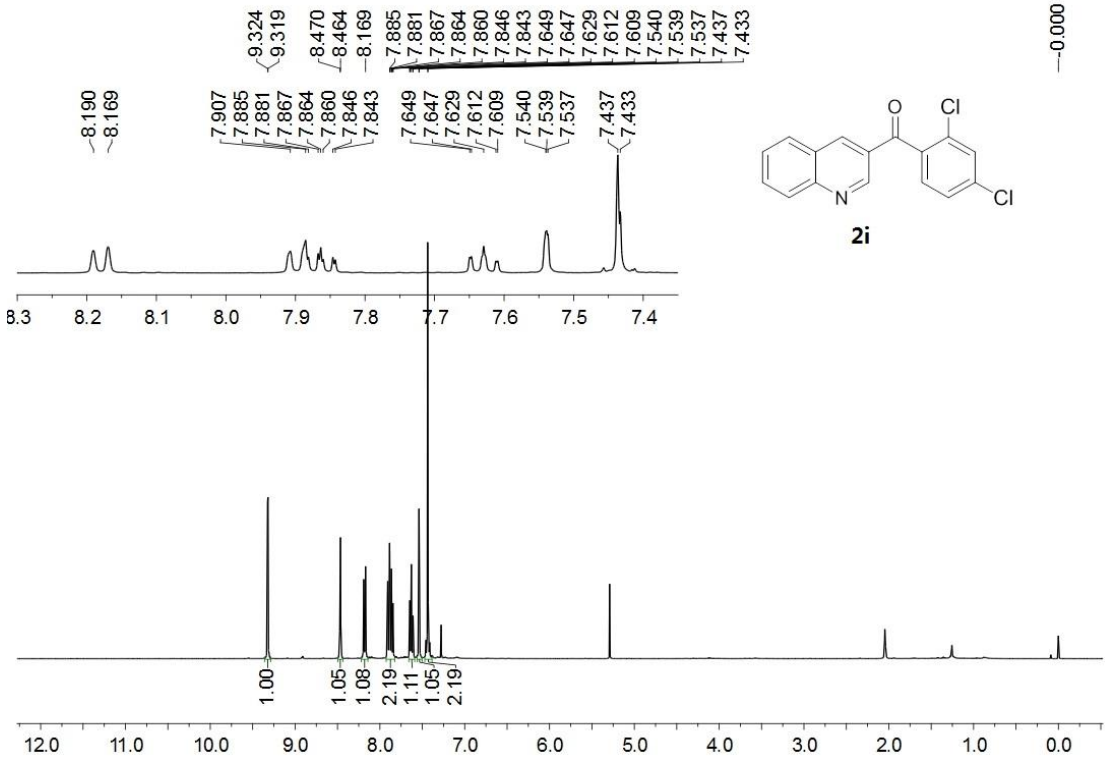
^{1}H NMR (400 MHz, $CDCl_3$) for **2h**



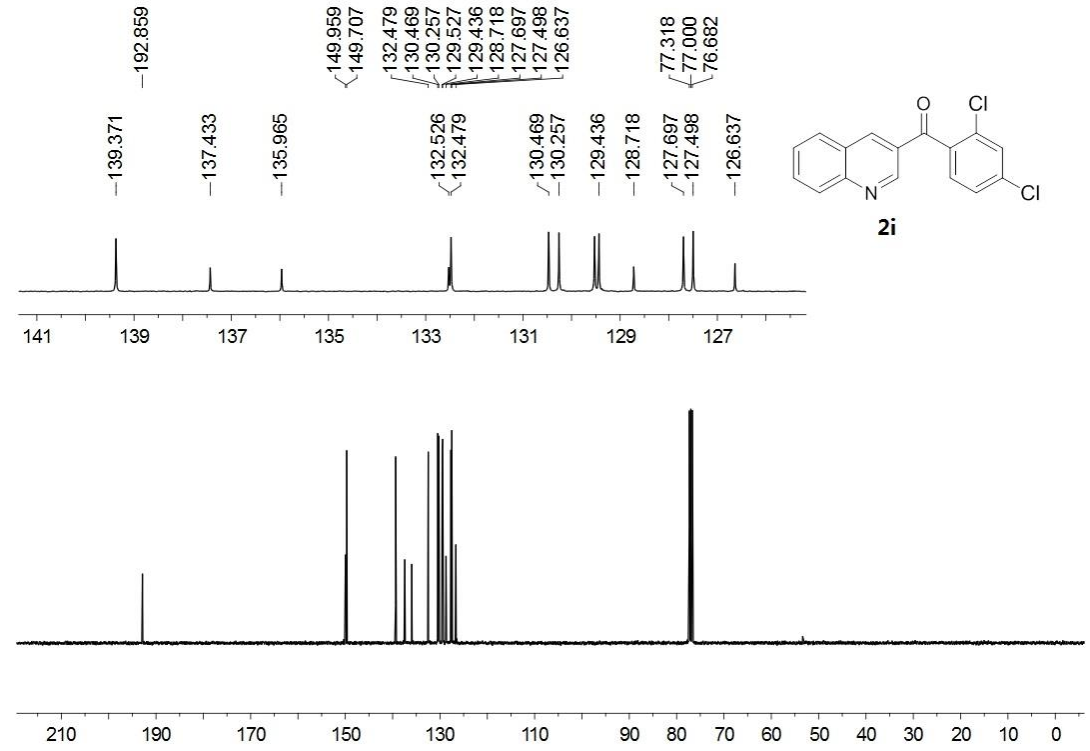
^{13}C NMR (100 MHz, $CDCl_3$) for **2h**



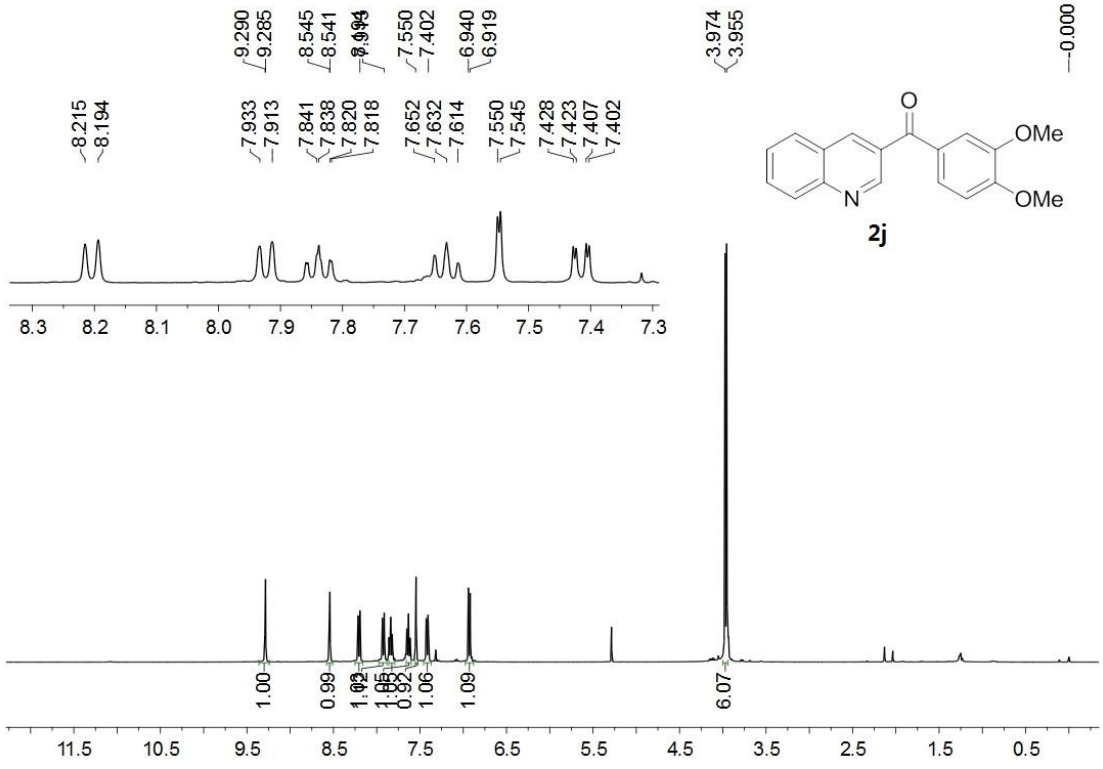
^{1}H NMR (400 MHz, $CDCl_3$) for **2i**



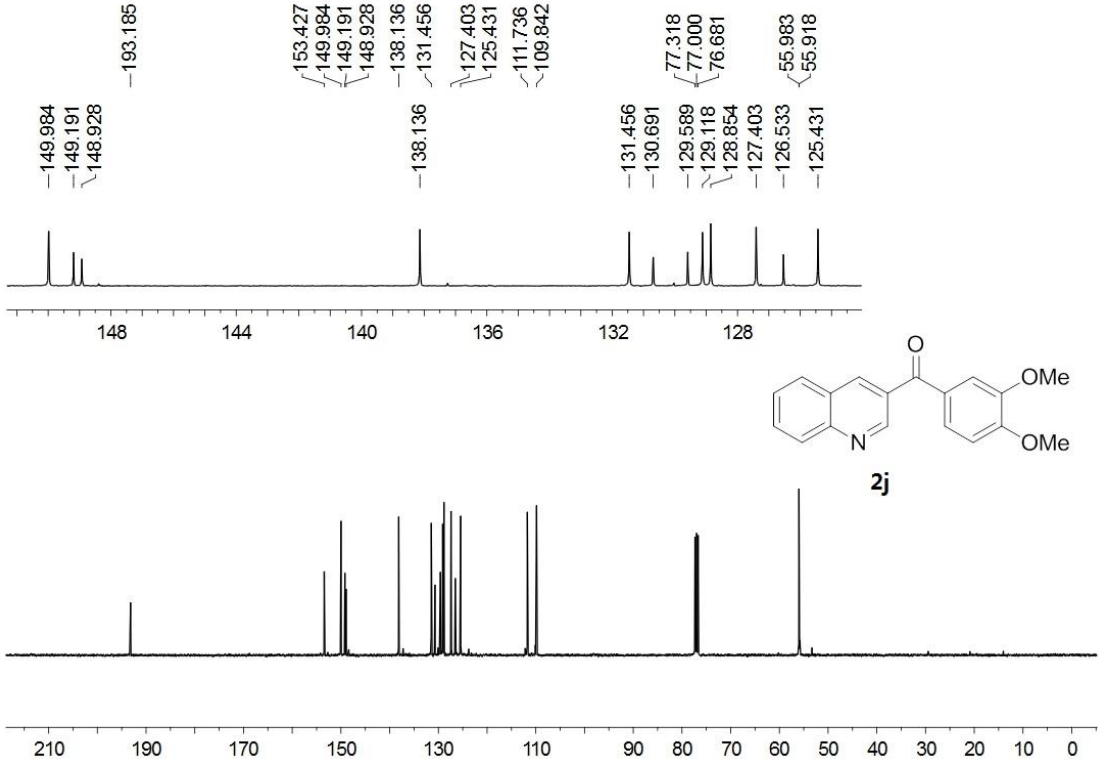
^{13}C NMR (100 MHz, $CDCl_3$) for **2i**



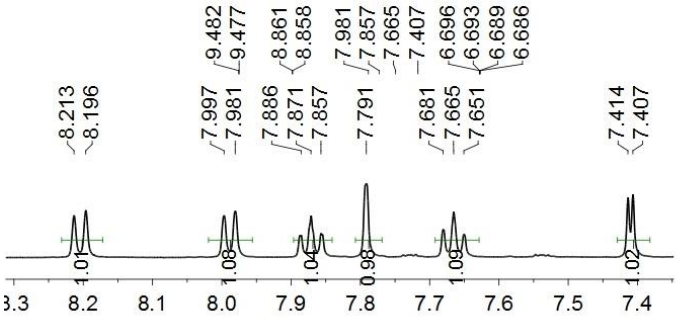
^{1}H NMR (400 MHz, $CDCl_3$) for **2j**

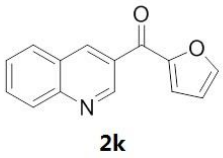


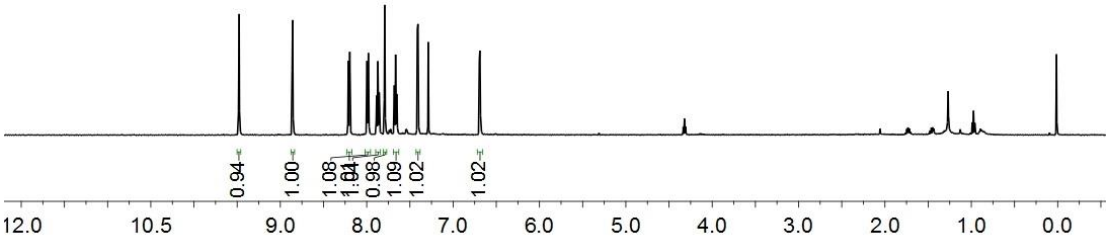
^{13}C NMR (100 MHz, $CDCl_3$) for **2j**



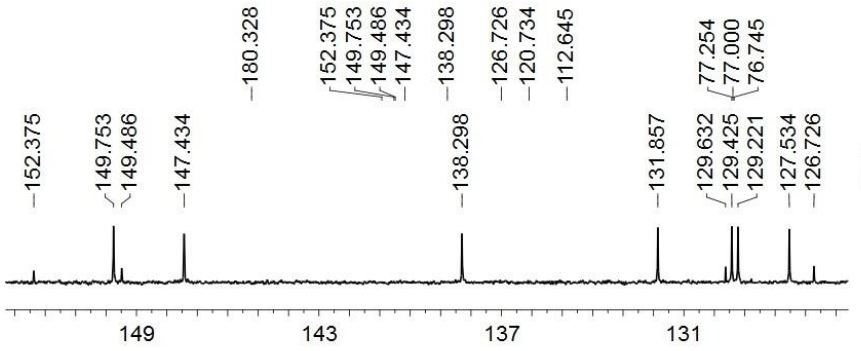
^{1}H NMR (500 MHz, $CDCl_3$) for **2k**

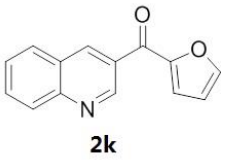


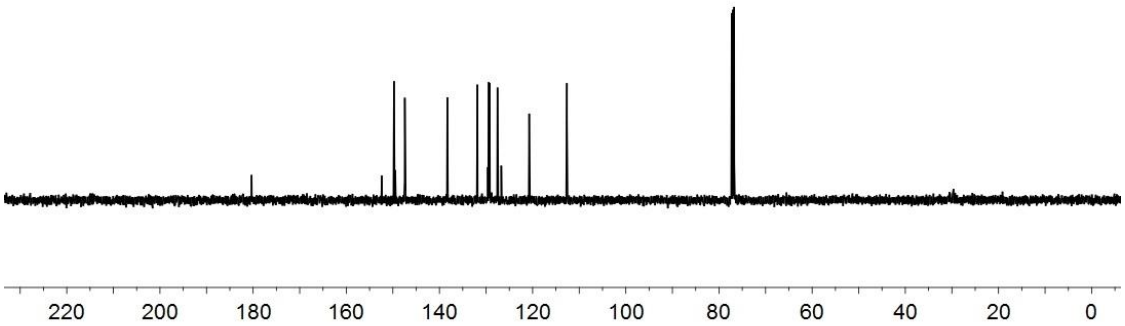




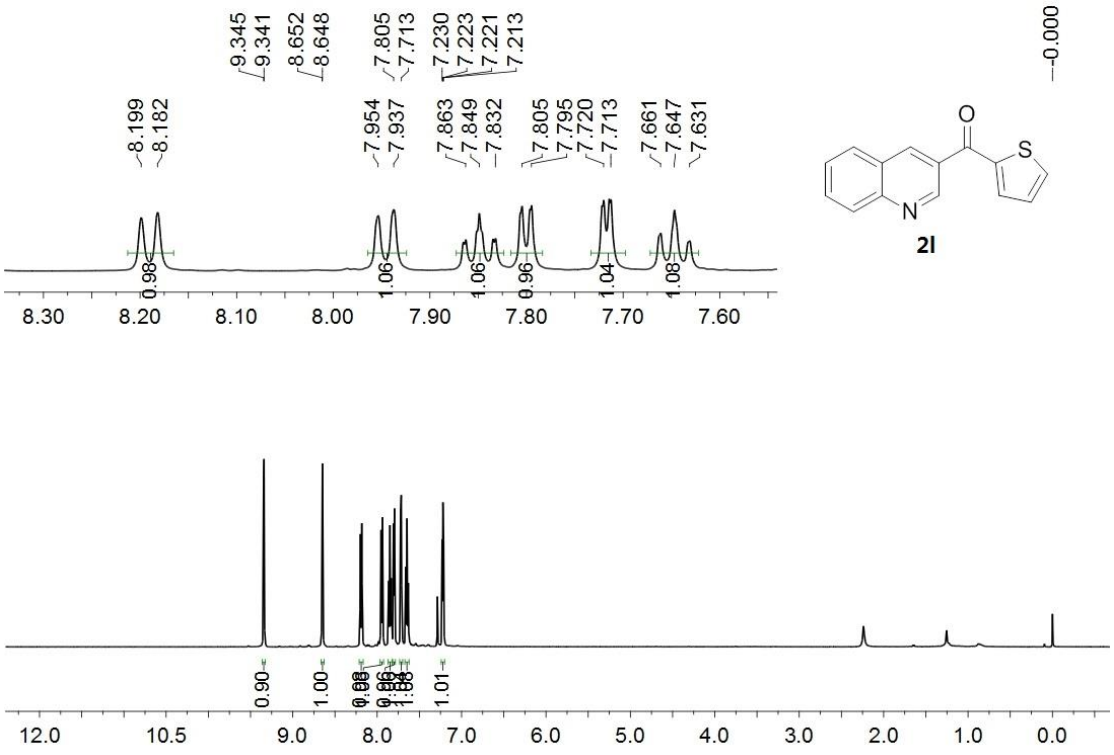
^{13}C NMR (125 MHz, $CDCl_3$) for **2k**



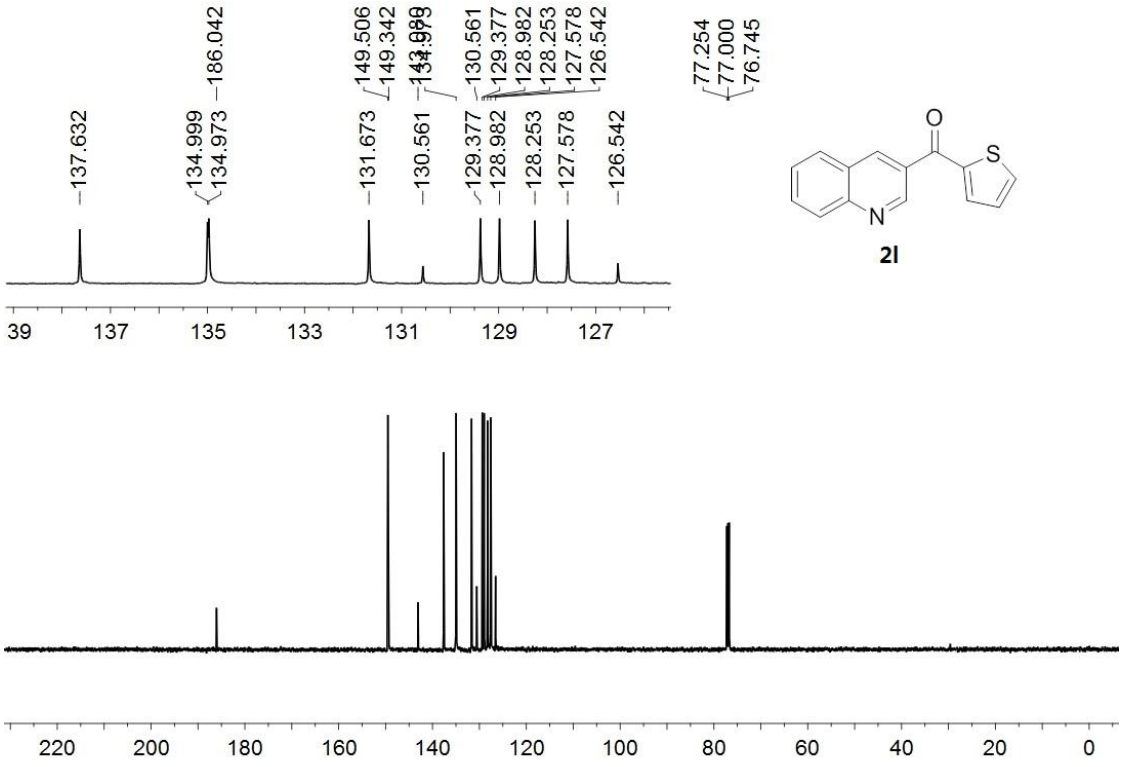




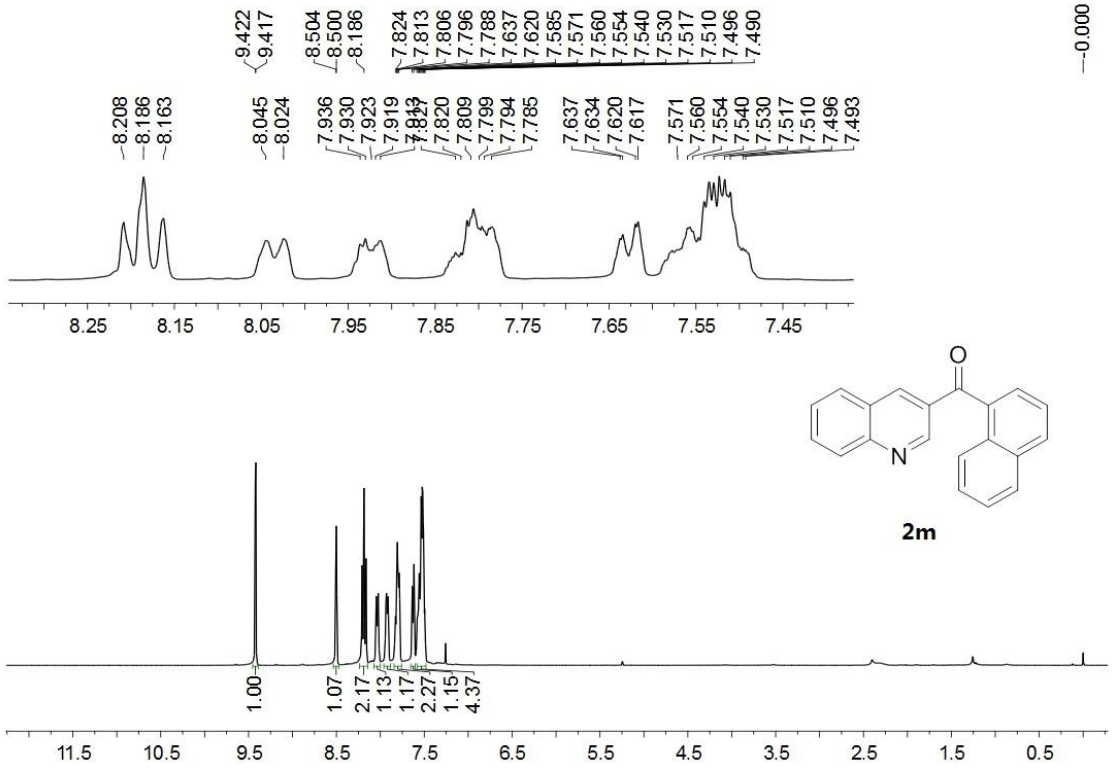
^{1}H NMR (500 MHz, $CDCl_3$) for **2l**



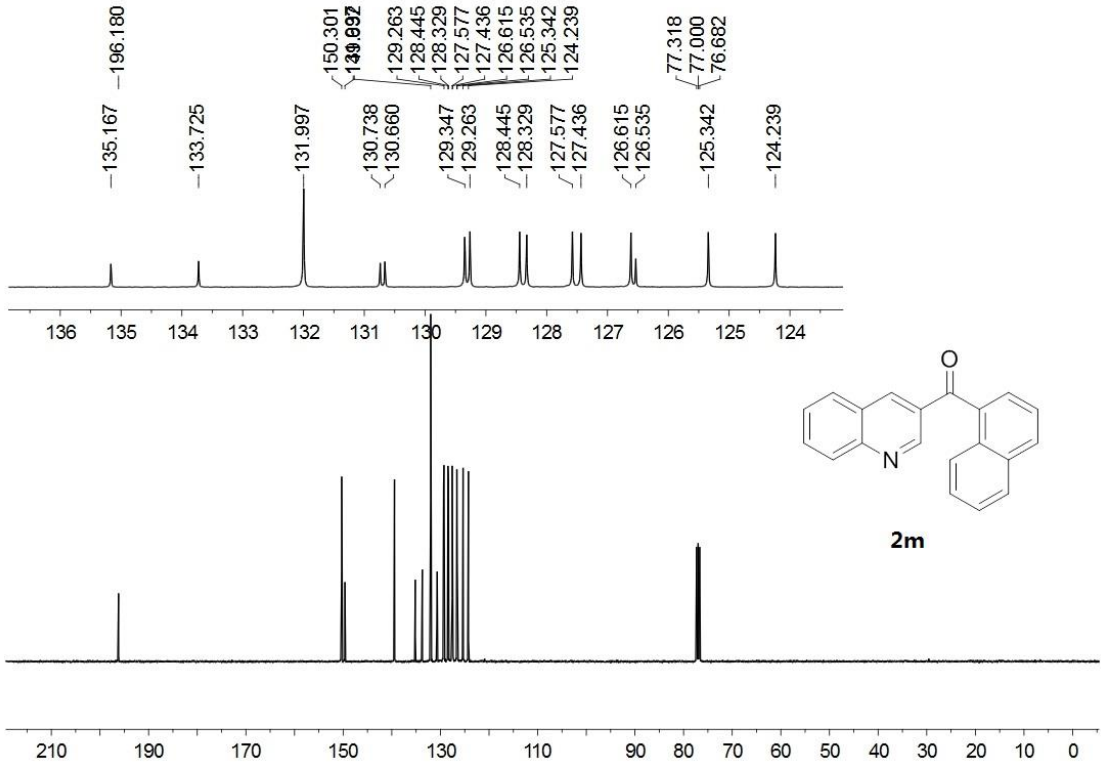
^{13}C NMR (125 MHz, $CDCl_3$) for **2l**



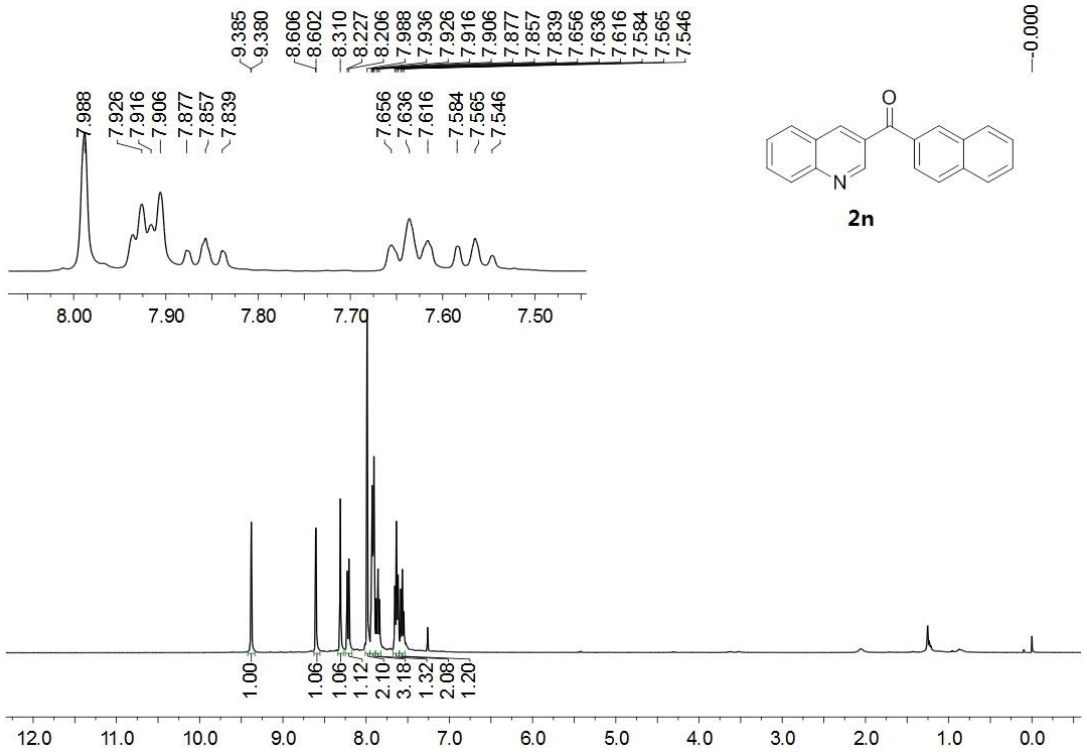
^{1}H NMR (400 MHz, $CDCl_3$) for **2m**



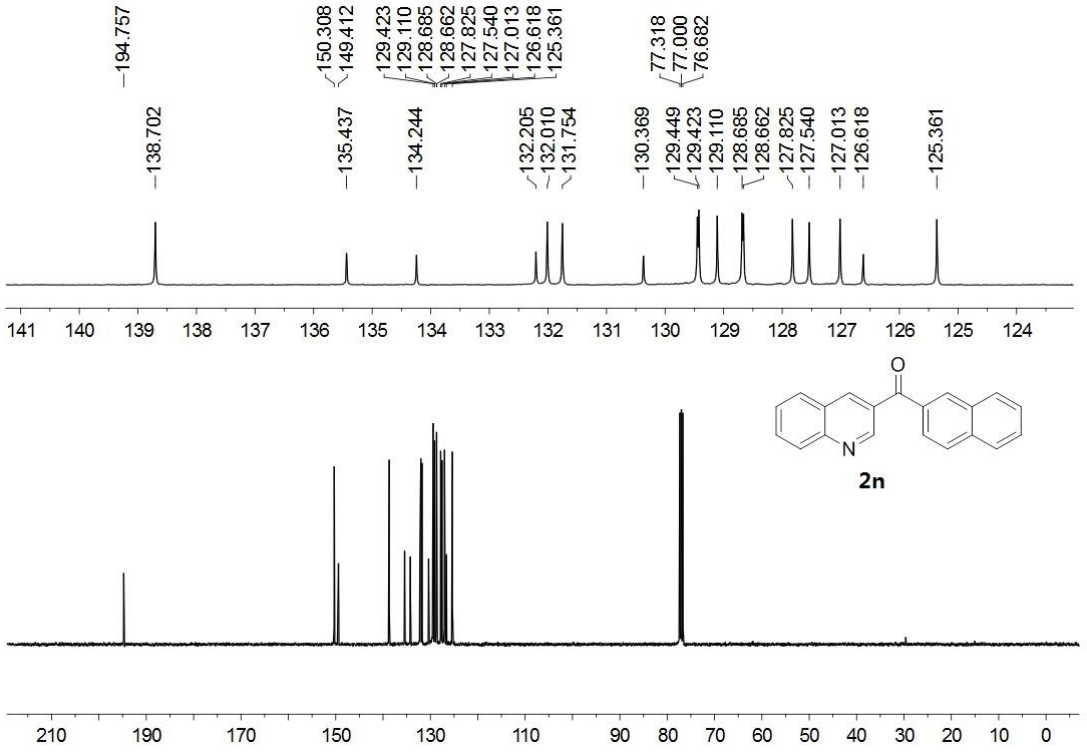
^{13}C NMR (100 MHz, $CDCl_3$) for **2m**



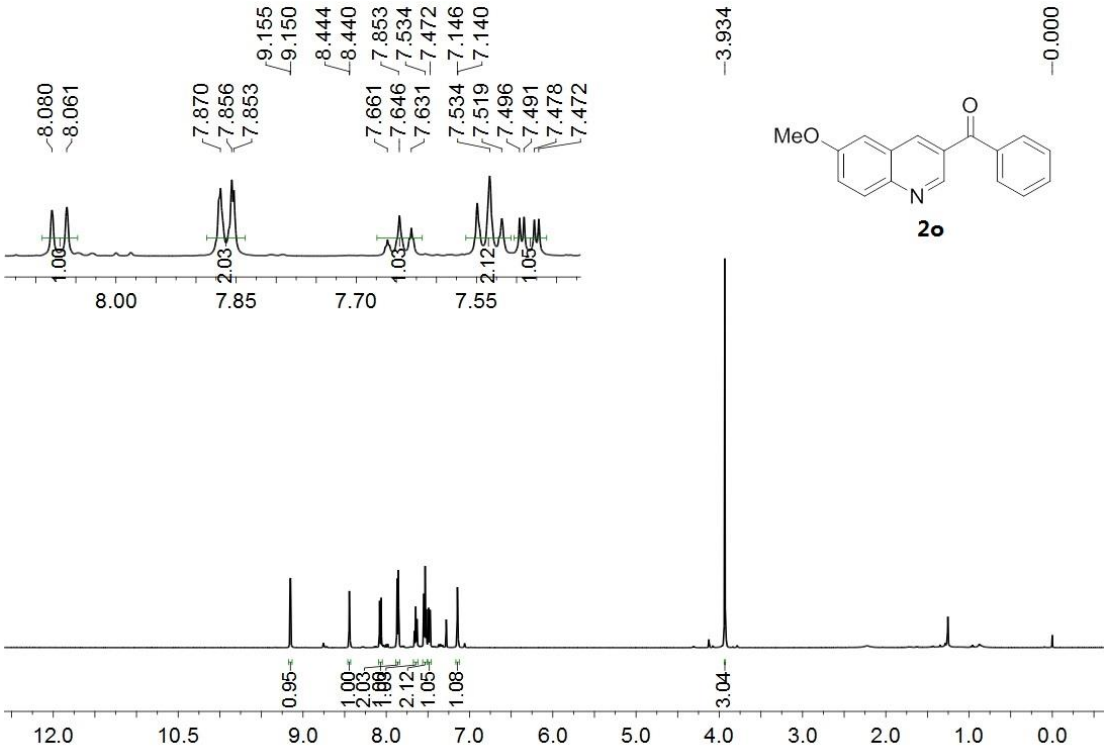
^{1}H NMR (400 MHz, $CDCl_3$) for **2n**



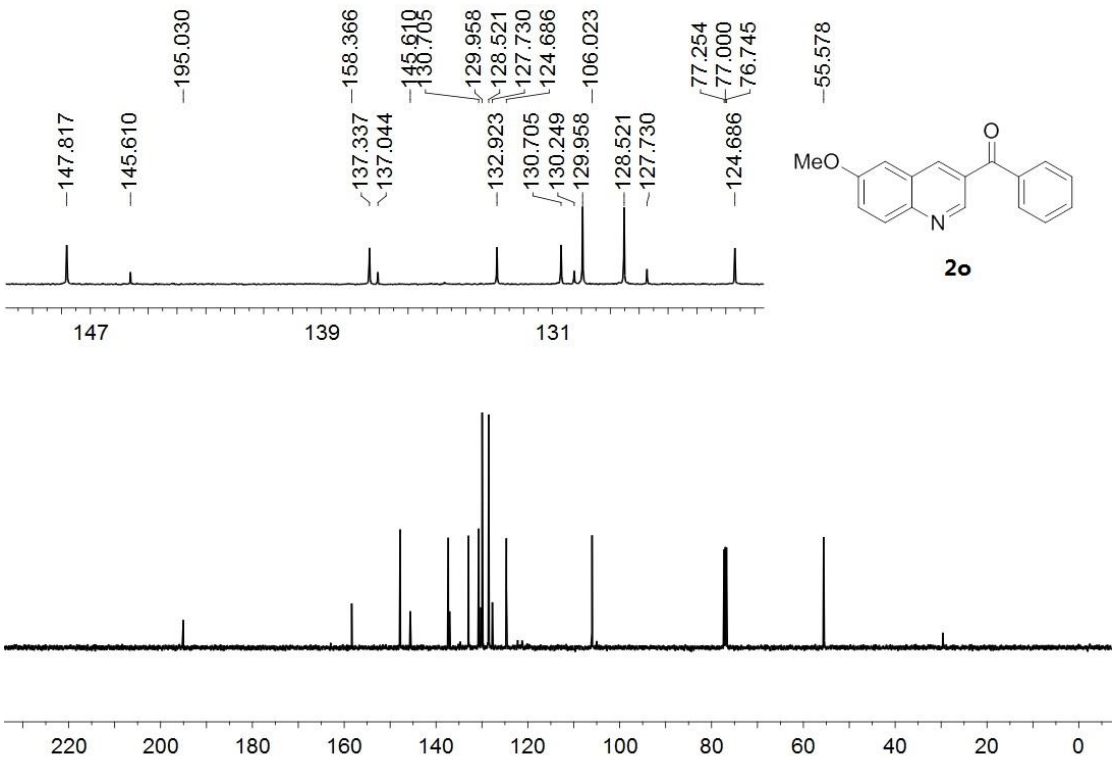
^{13}C NMR (100 MHz, $CDCl_3$) for **2n**



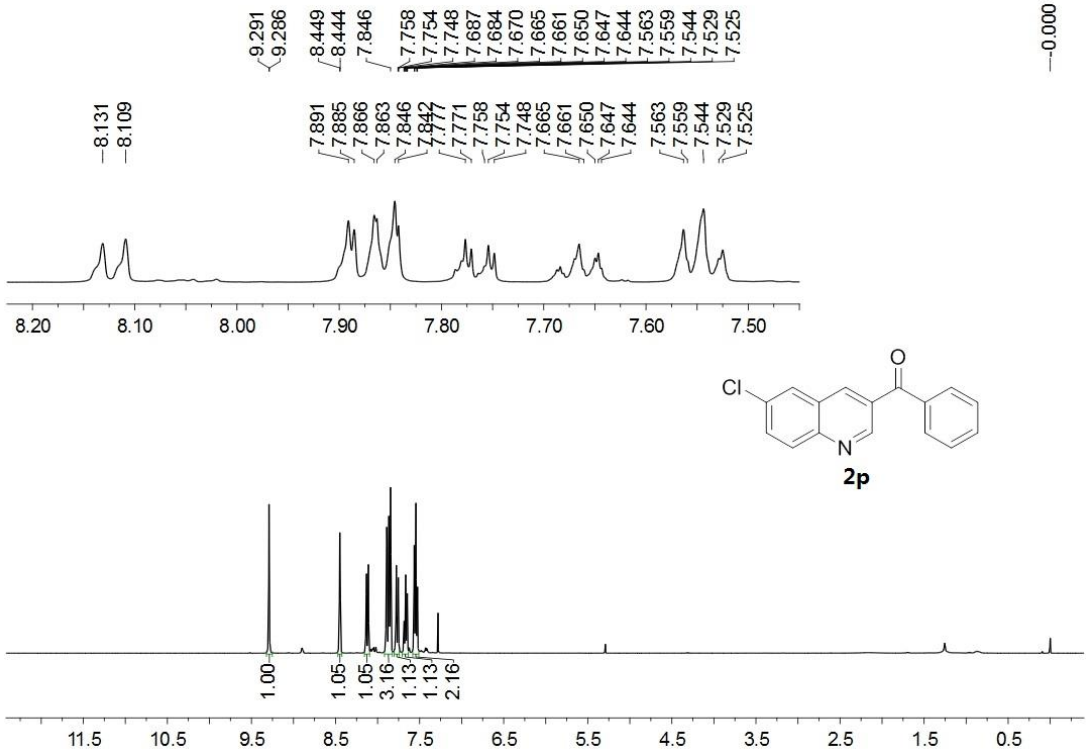
^{1}H NMR (500 MHz, $CDCl_3$) for **2o**



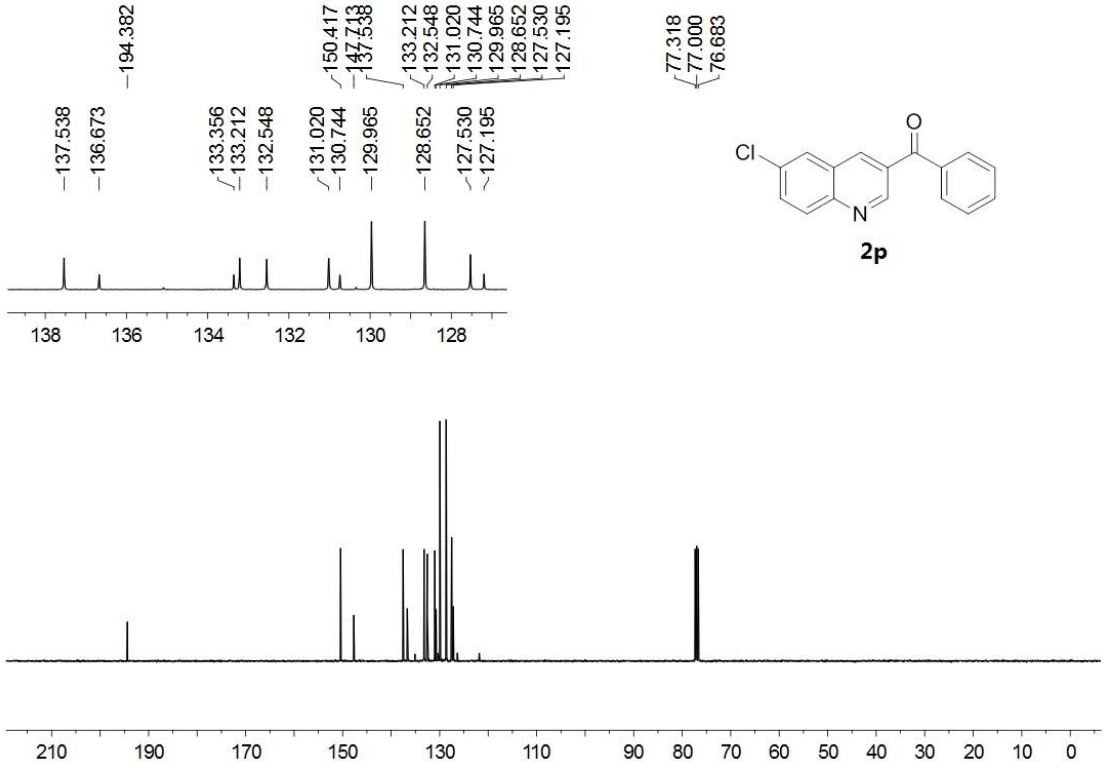
^{13}C NMR (125 MHz, $CDCl_3$) for **2o**



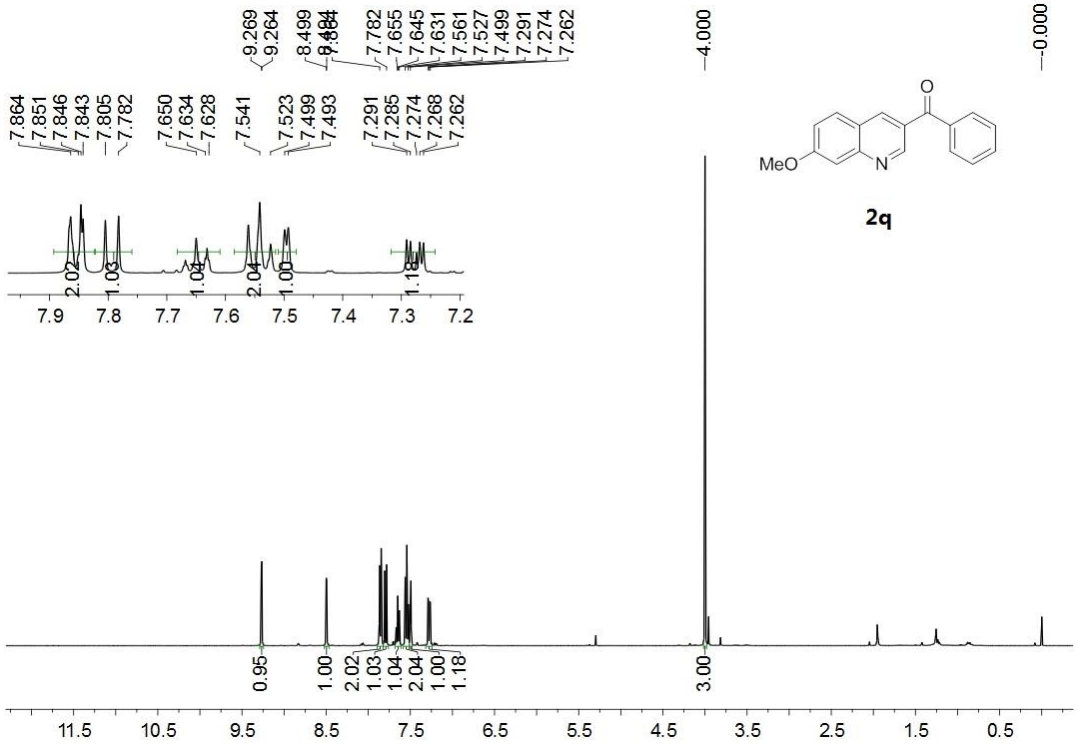
^{1}H NMR (400 MHz, $CDCl_3$) for **2p**



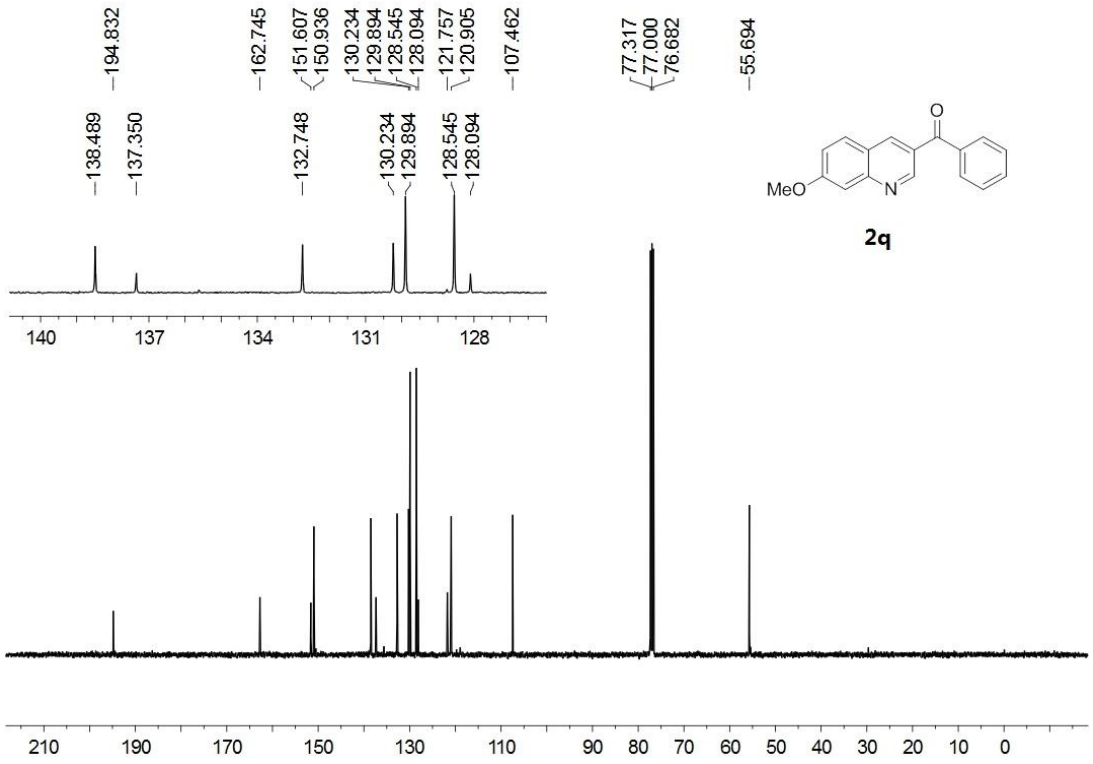
^{13}C NMR (100 MHz, $CDCl_3$) for **2p**



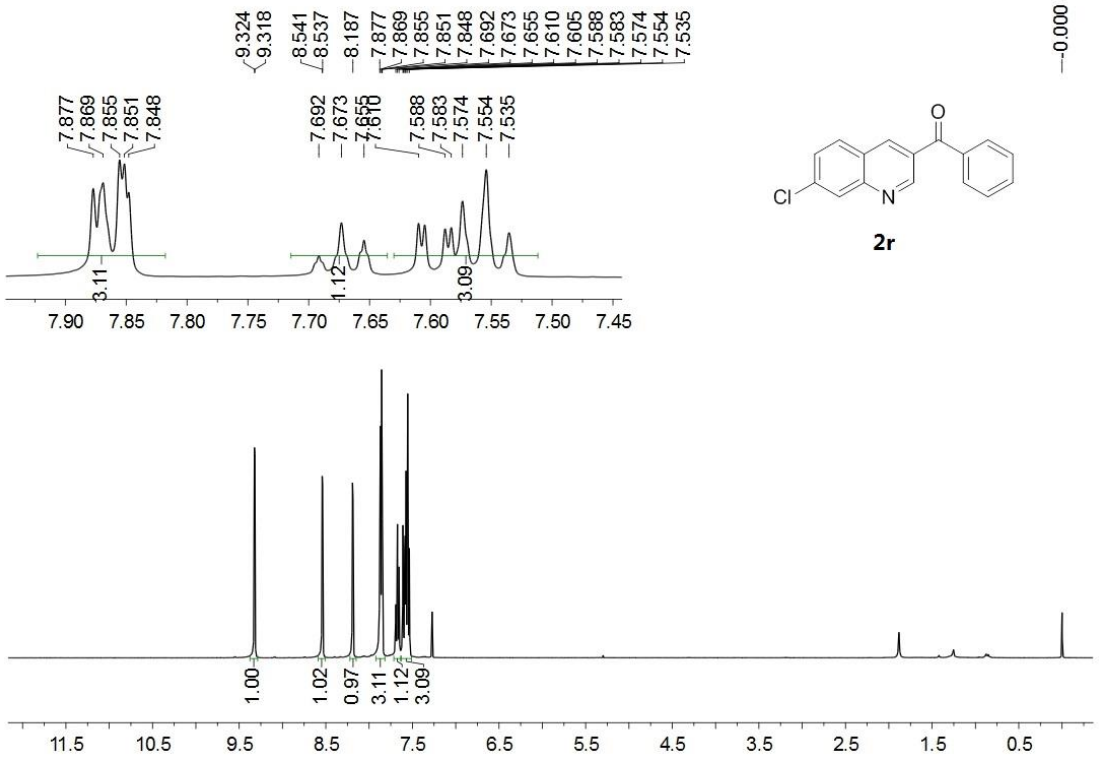
^{1}H NMR (400 MHz, $CDCl_3$) for **2q**



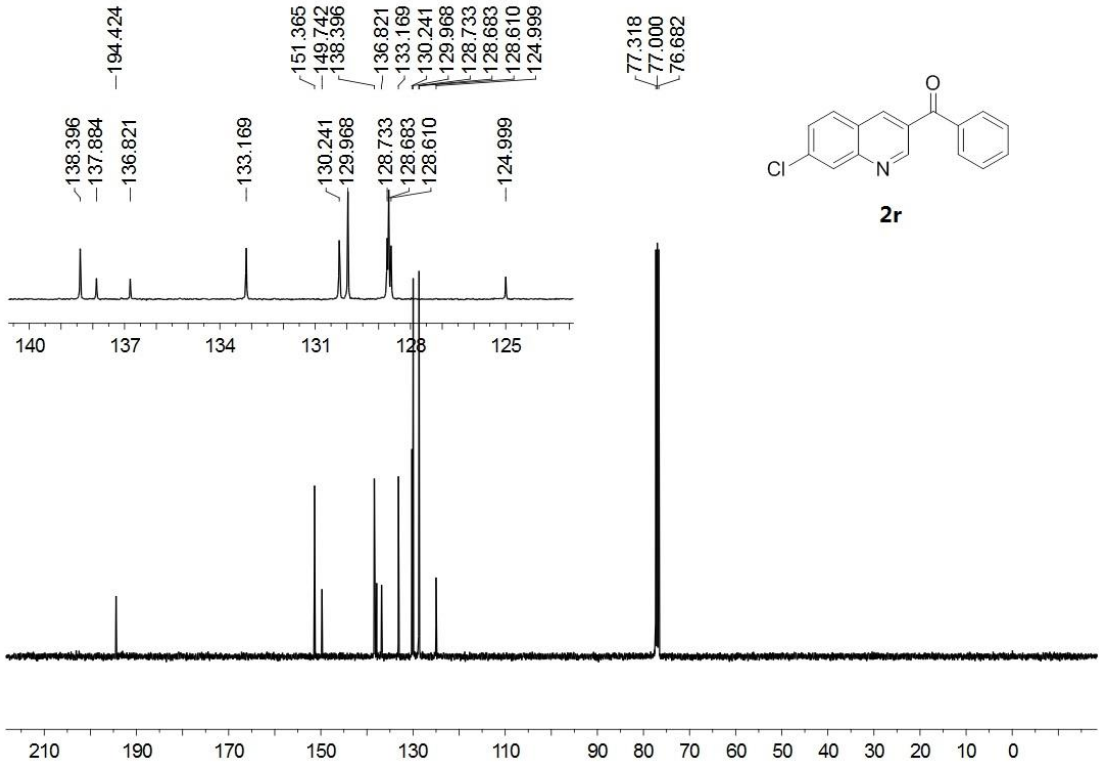
^{13}C NMR (100 MHz, $CDCl_3$) for **2q**



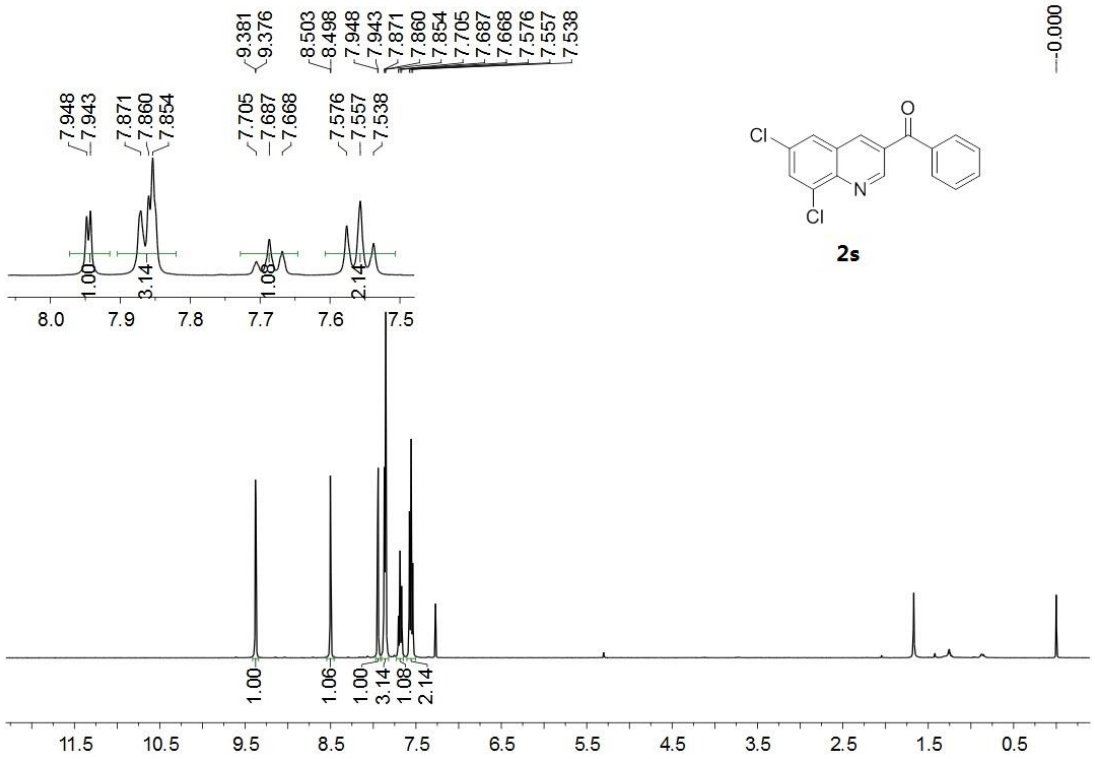
^{1}H NMR (400 MHz, $CDCl_3$) for **2r**



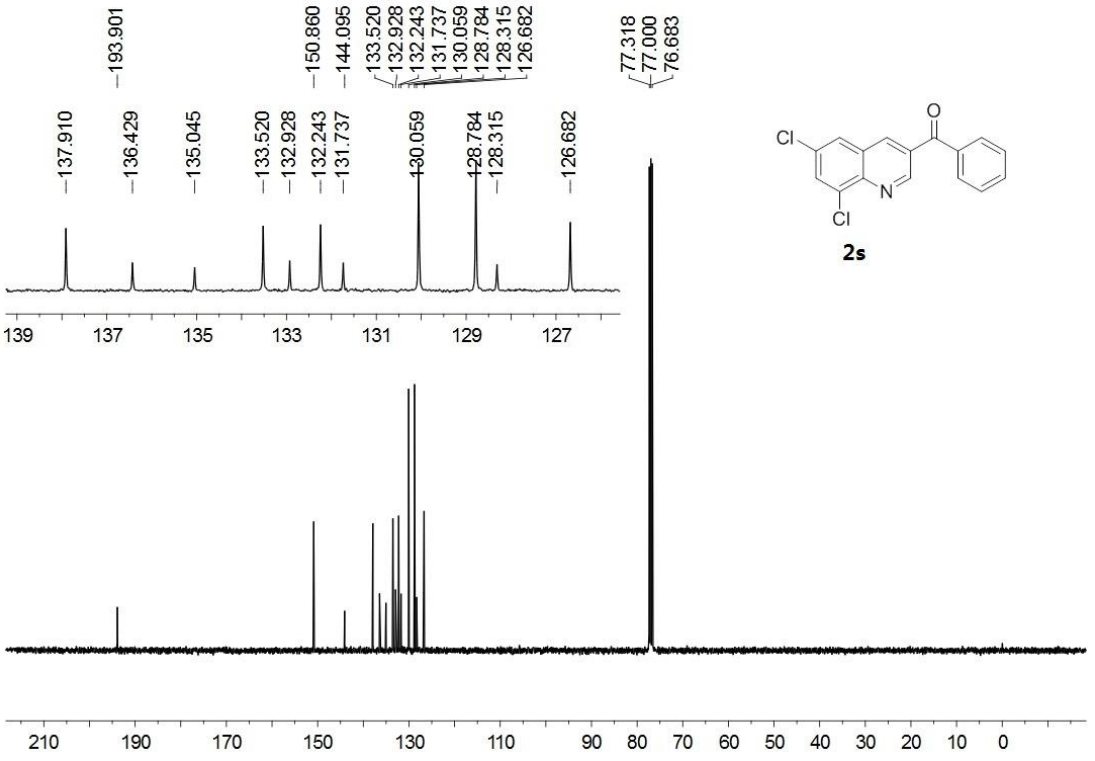
^{13}C NMR (100 MHz, $CDCl_3$) for **2r**



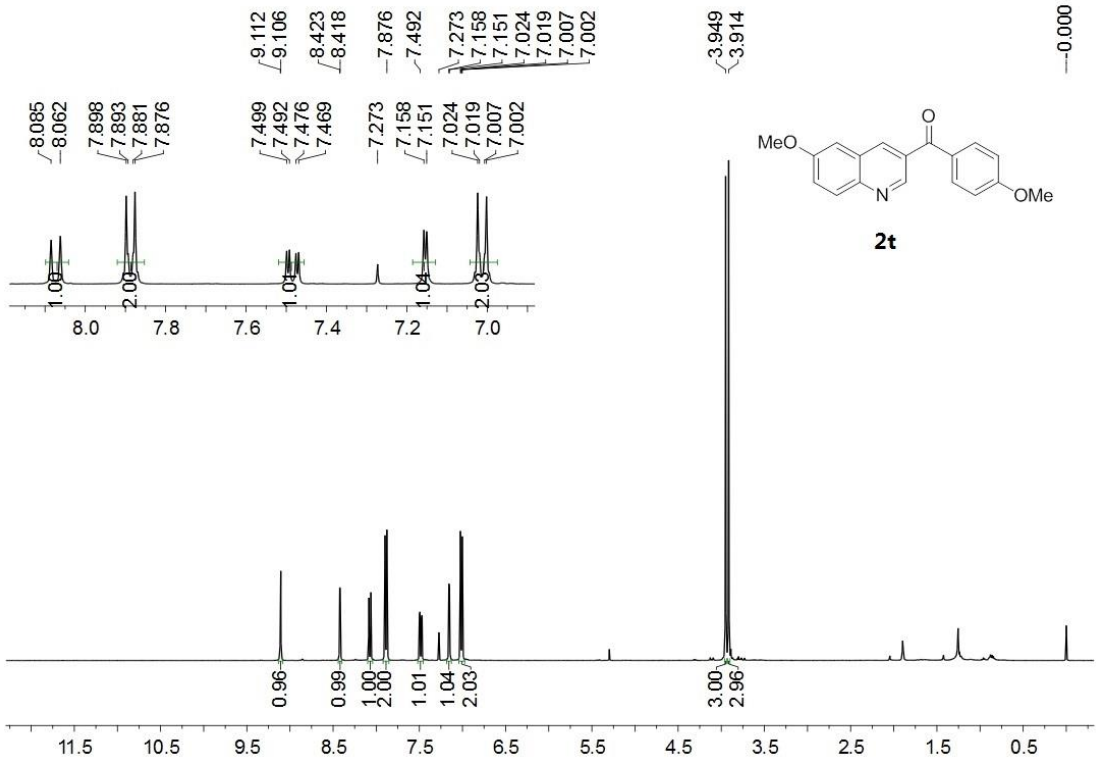
^{1}H NMR (400 MHz, $CDCl_3$) for **2s**



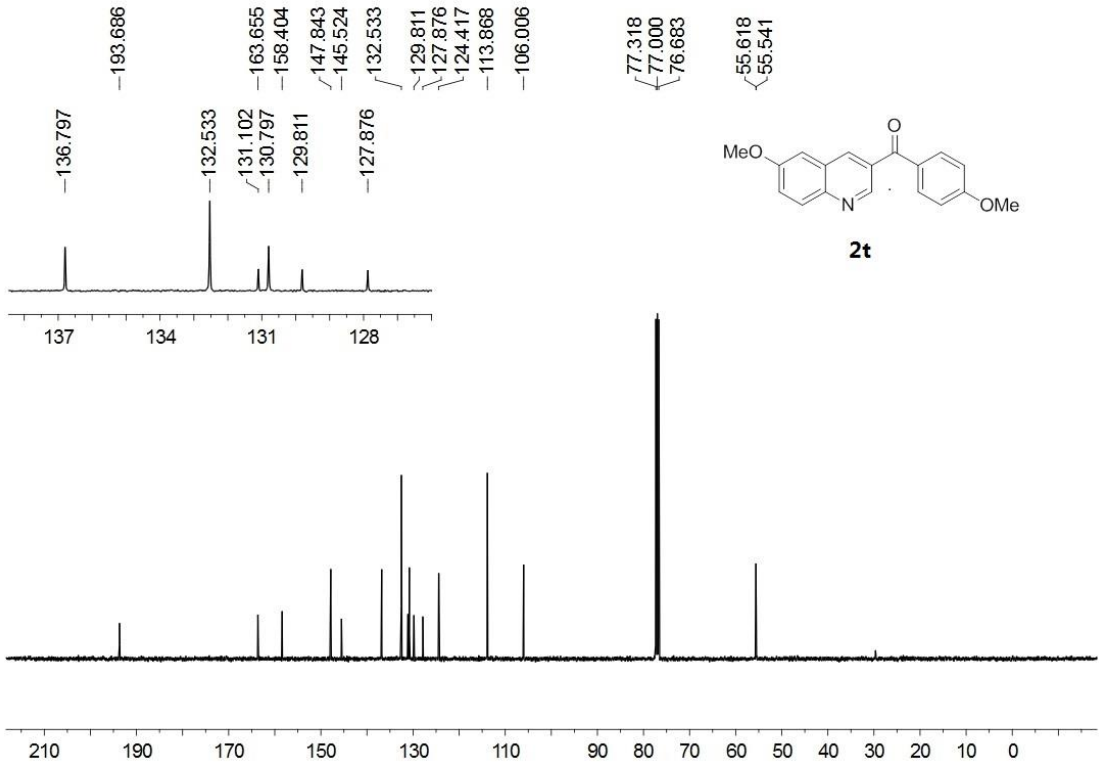
^{13}C NMR (100 MHz, $CDCl_3$) for **2s**



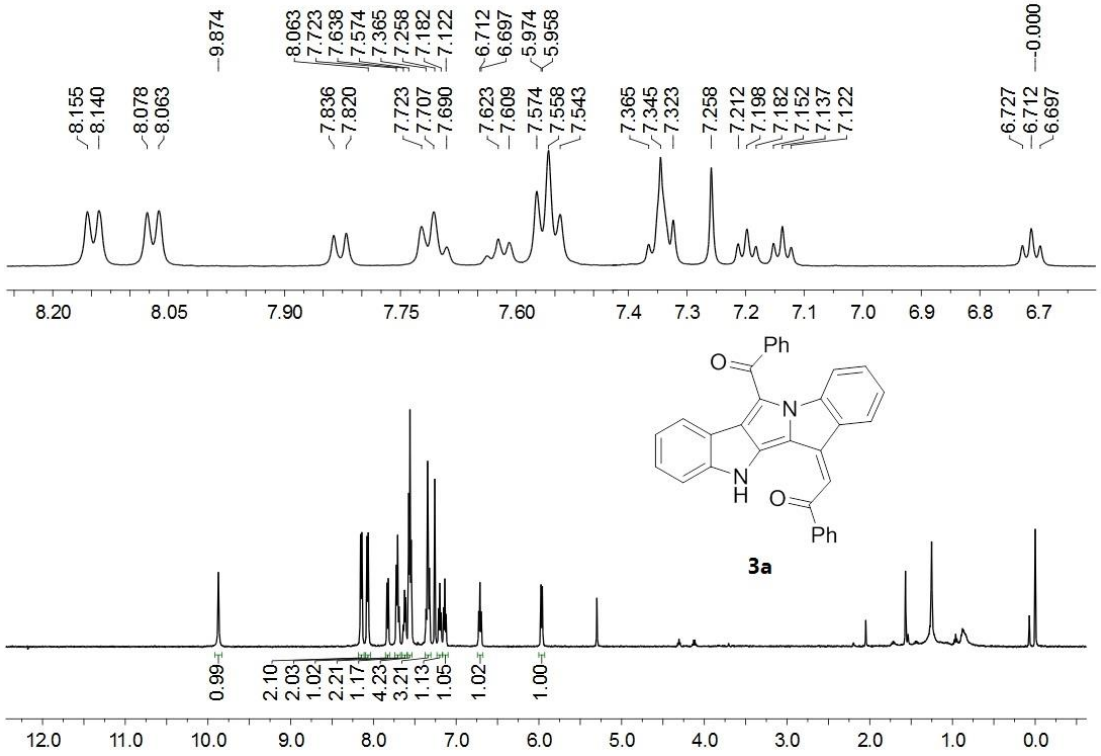
^{1}H NMR (400 MHz, $CDCl_3$) for **2t**



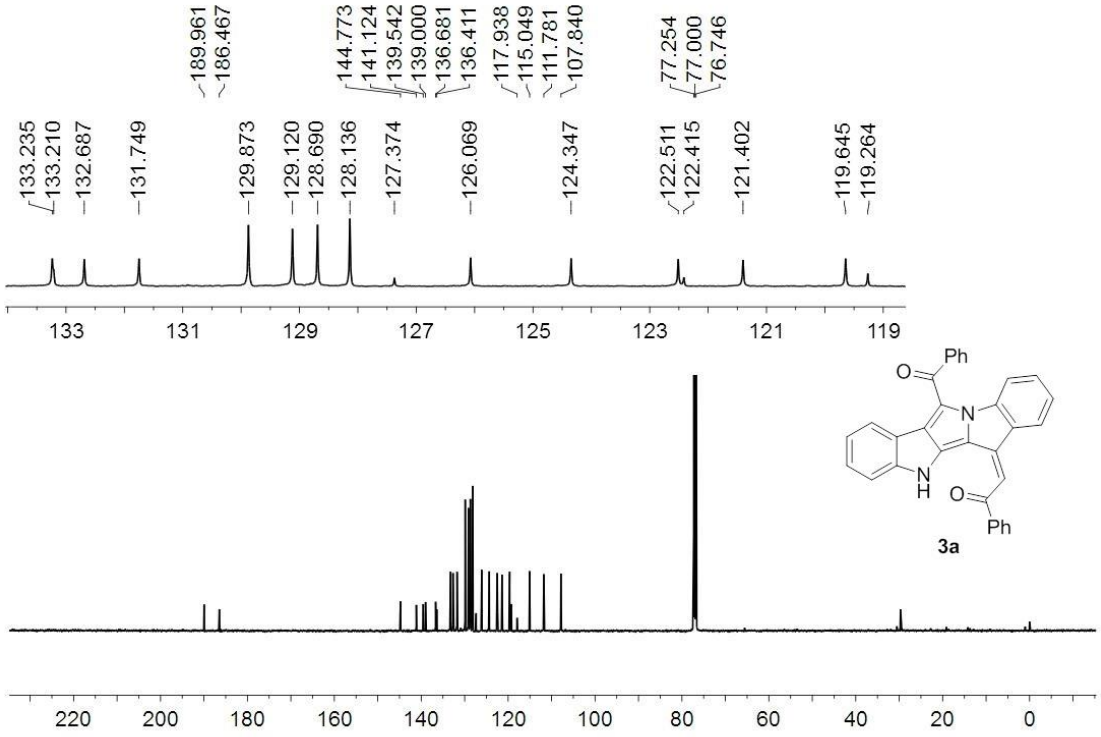
^{13}C NMR (100 MHz, $CDCl_3$) for **2t**



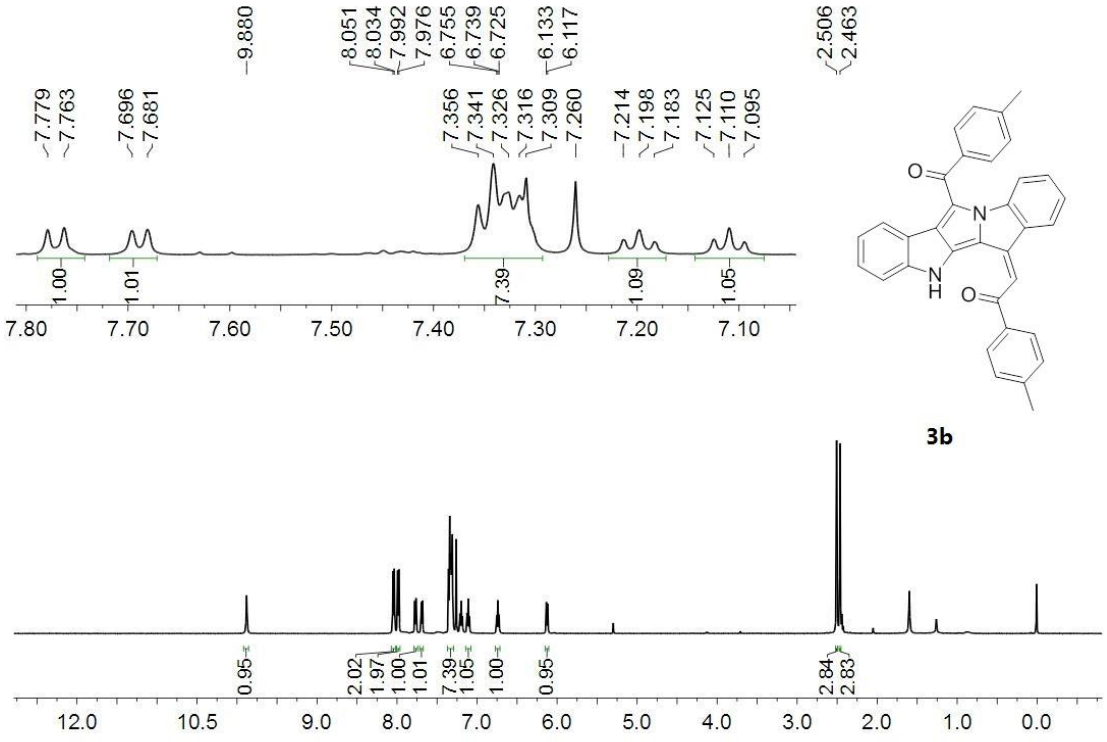
^{1}H NMR (500 MHz, $CDCl_3$) for **3a**



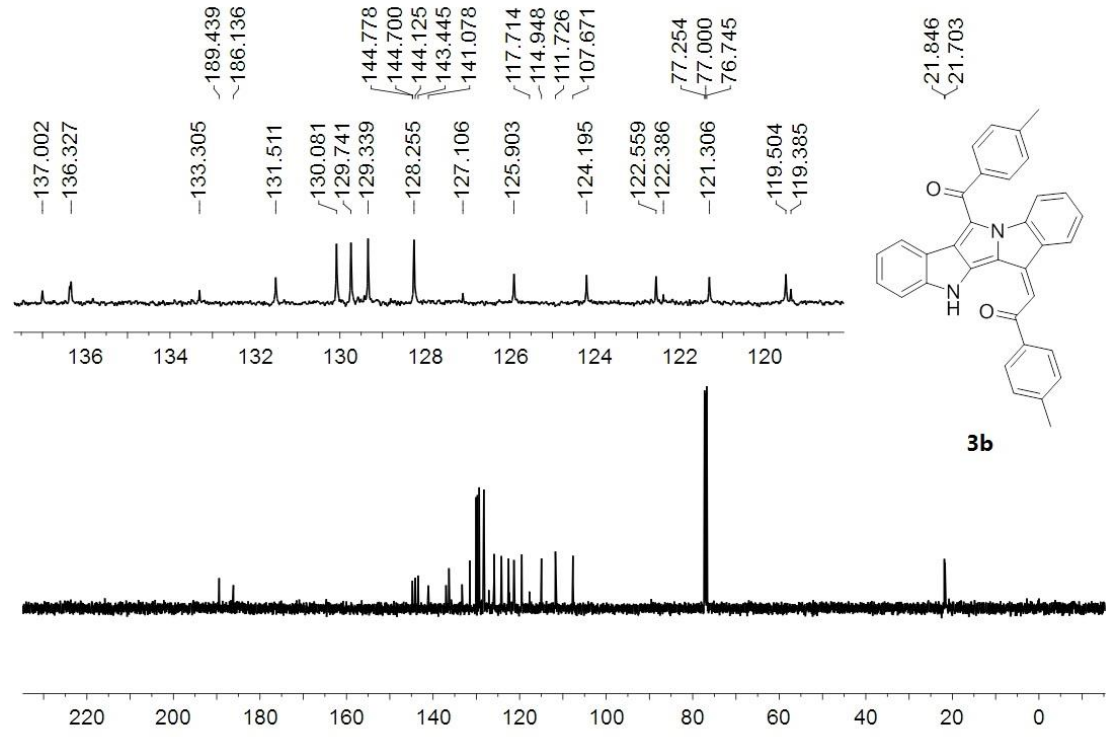
^{13}C NMR (125 MHz, $CDCl_3$) for **3a**



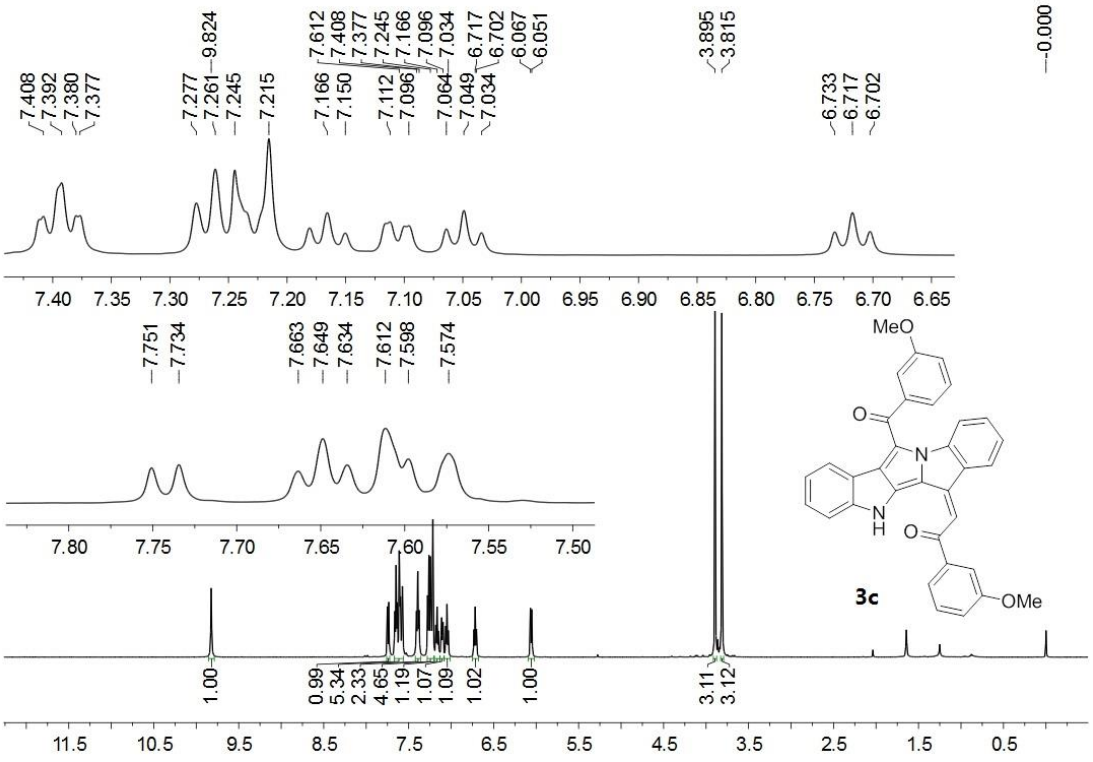
^{1}H NMR (500 MHz, $CDCl_3$) for **3b**



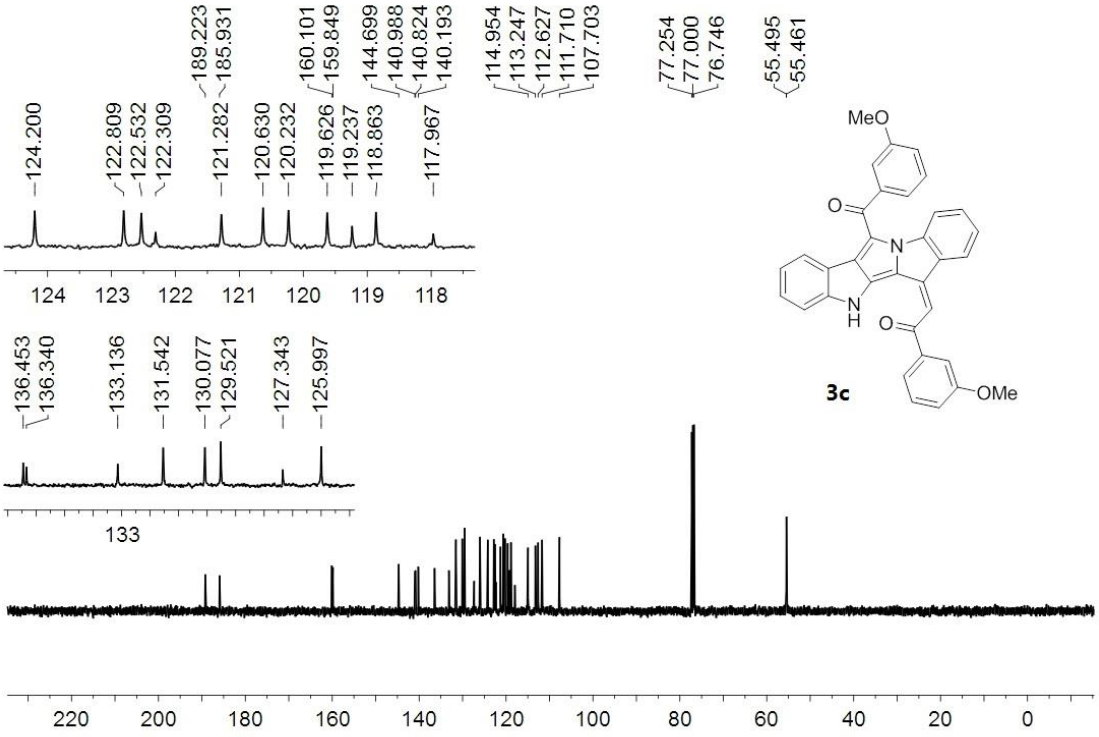
^{13}C NMR (125 MHz, $CDCl_3$) for **3b**



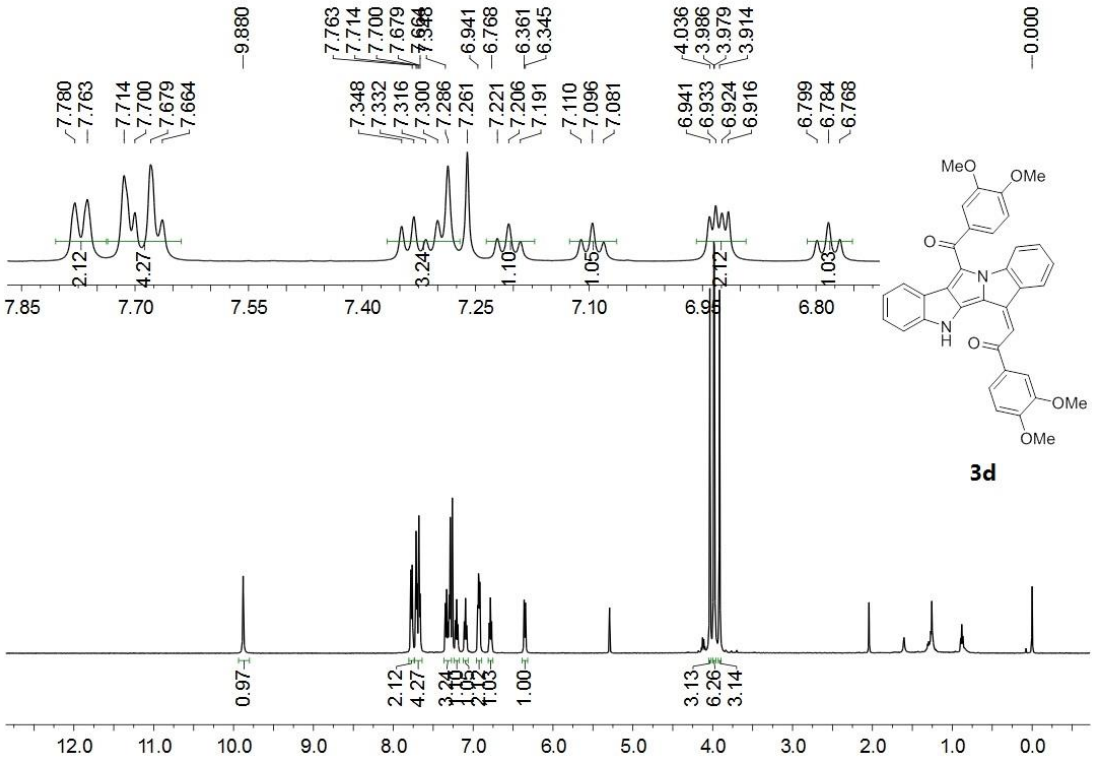
^{1}H NMR (500 MHz, $CDCl_3$) for **3c**



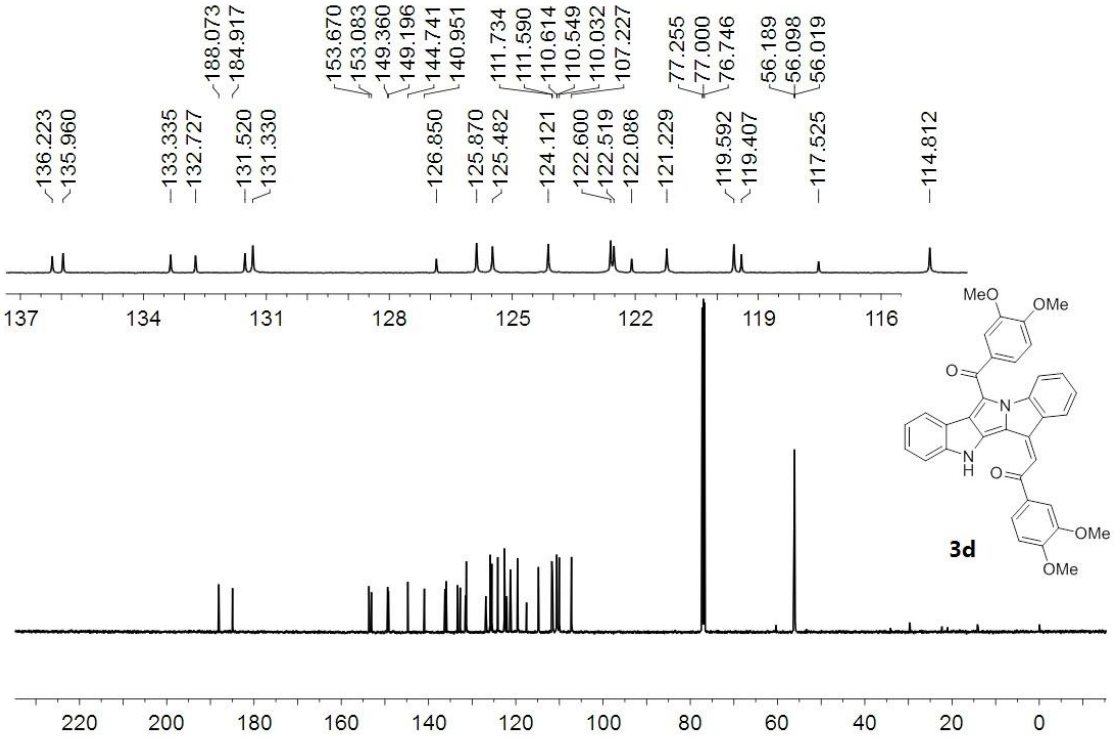
^{13}C NMR (125 MHz, $CDCl_3$) for **3c**



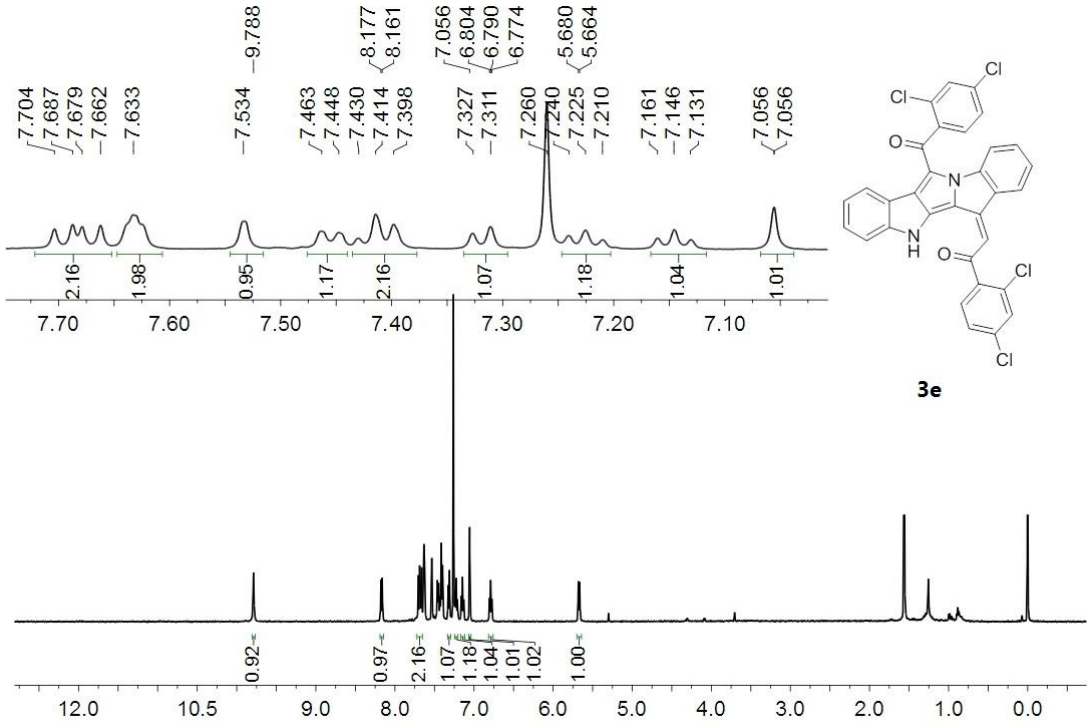
^{1}H NMR (500 MHz, $CDCl_3$) for **3d**



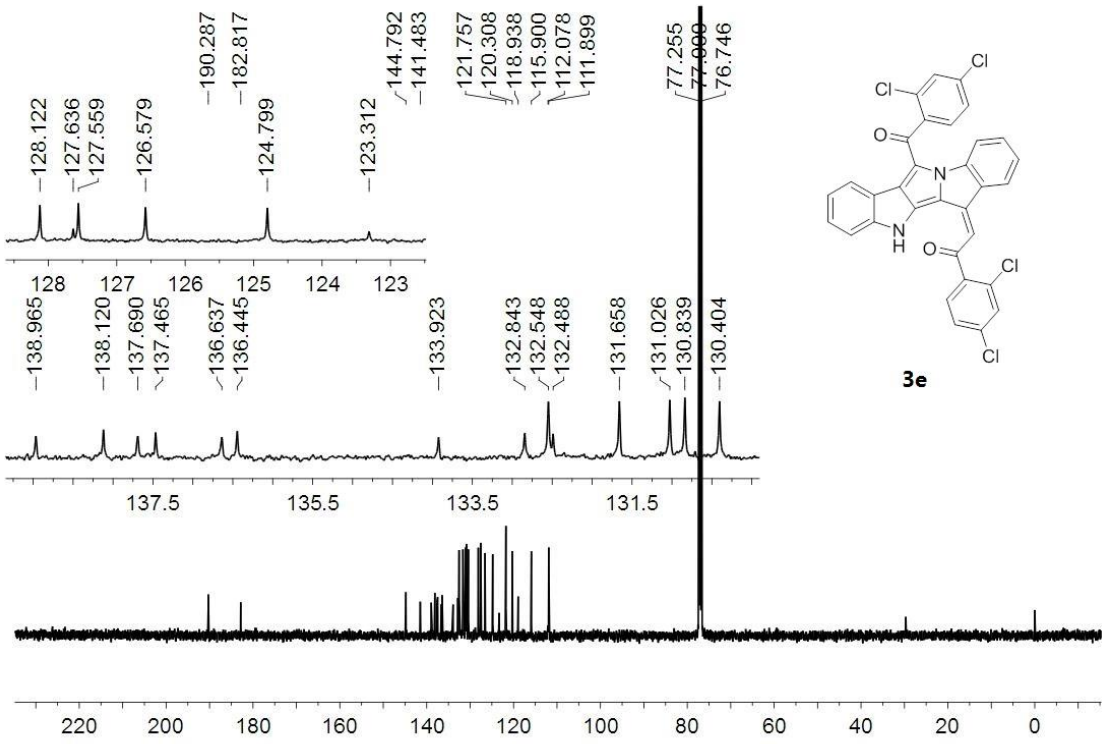
^{13}C NMR (125 MHz, $CDCl_3$) for **3d**



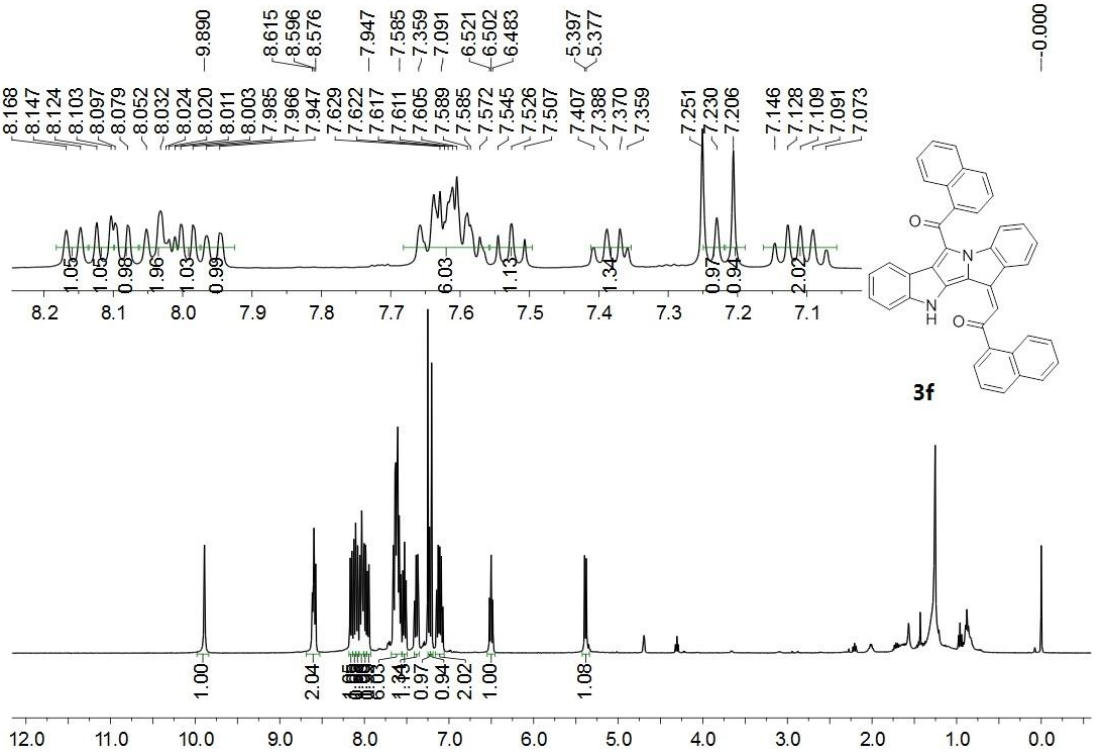
^{1}H NMR (500 MHz, $CDCl_3$) for **3e**



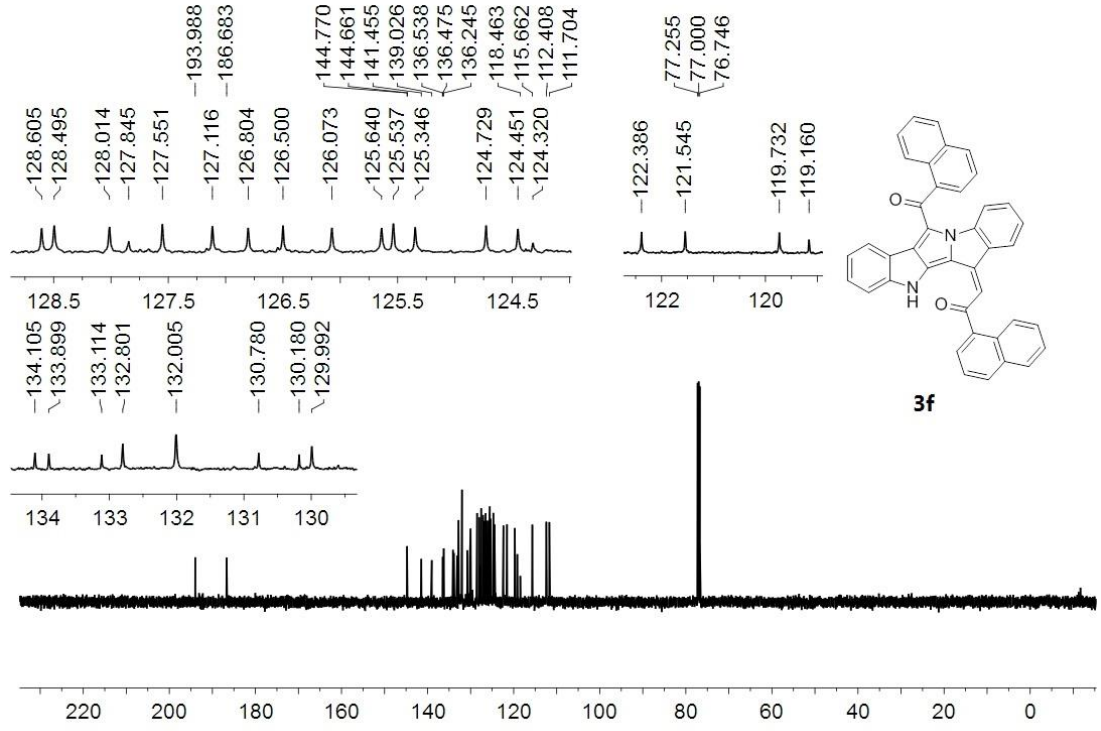
^{13}C NMR (125 MHz, $CDCl_3$) for **3e**



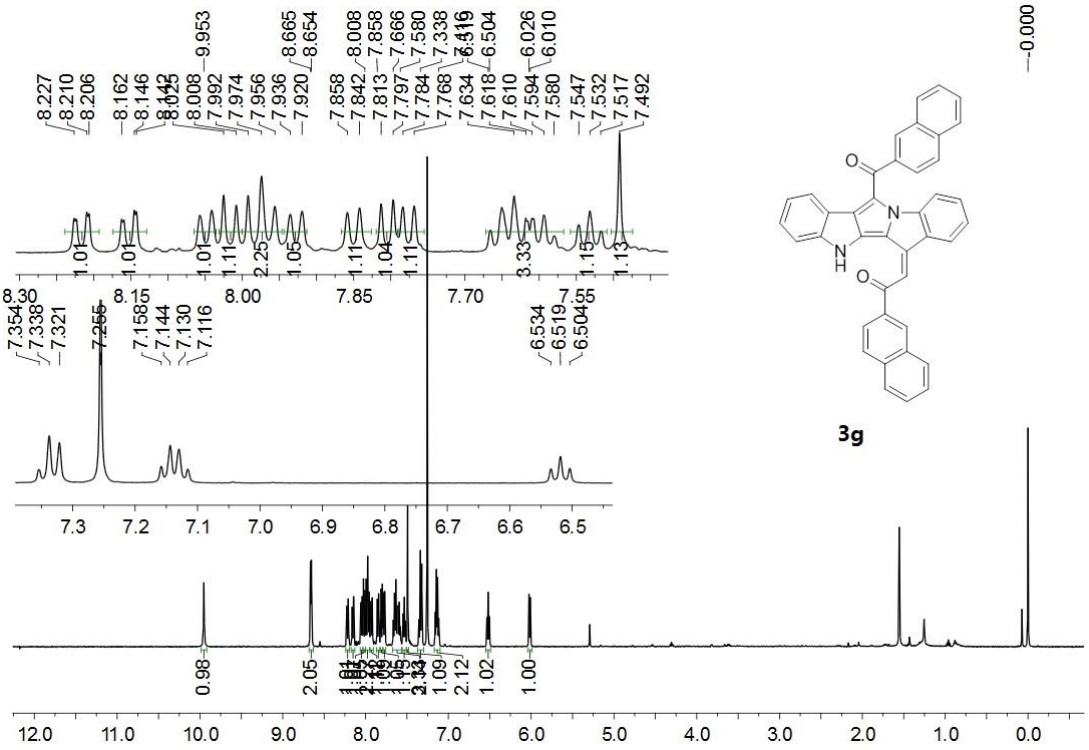
^{1}H NMR (400 MHz, $CDCl_3$) for **3f**



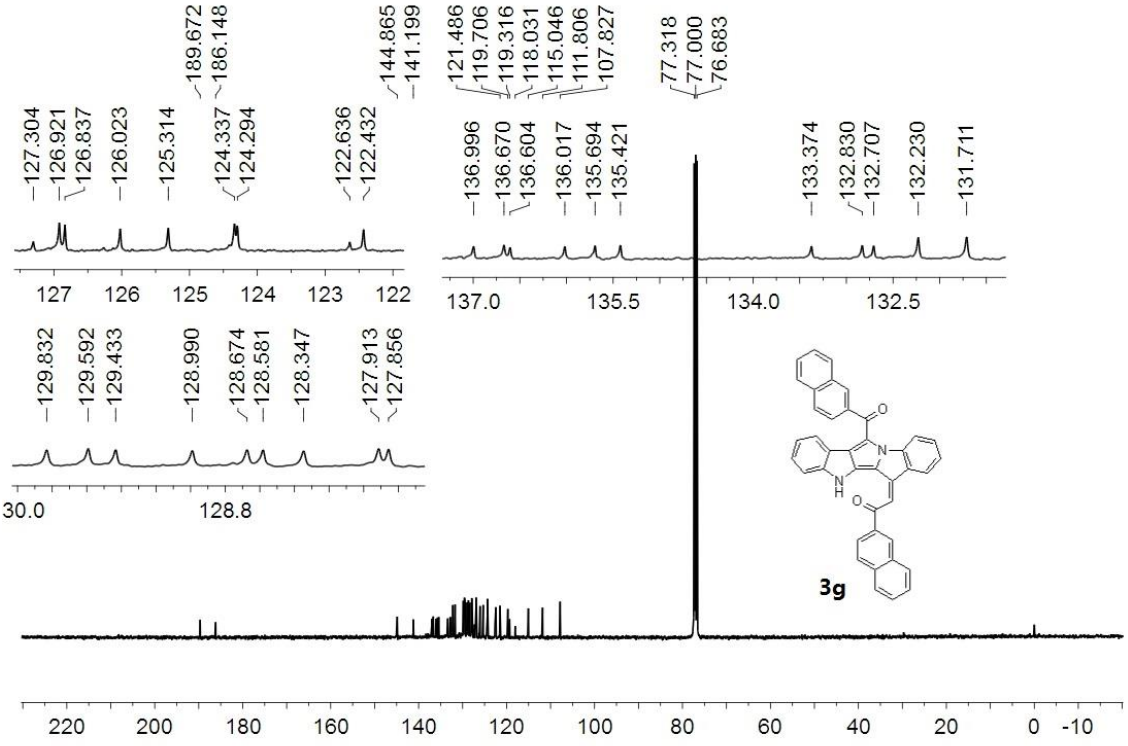
^{13}C NMR (125 MHz, $CDCl_3$) for **3f**



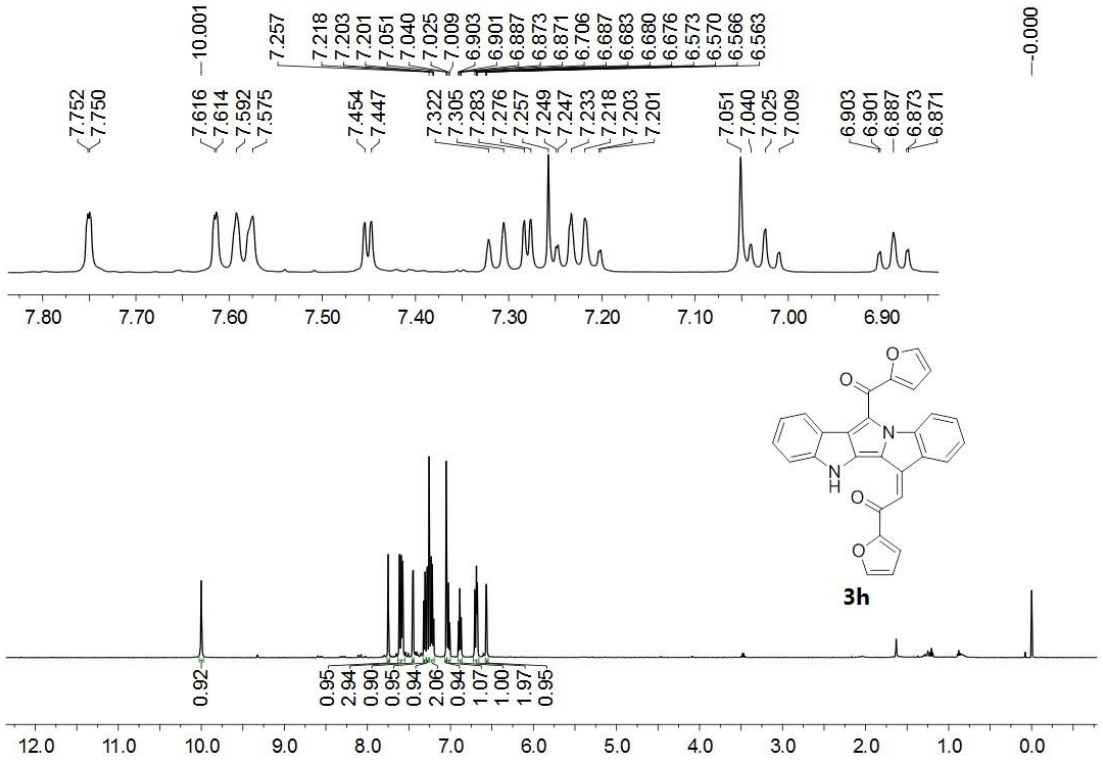
^{1}H NMR (500 MHz, $CDCl_3$) for **3g**



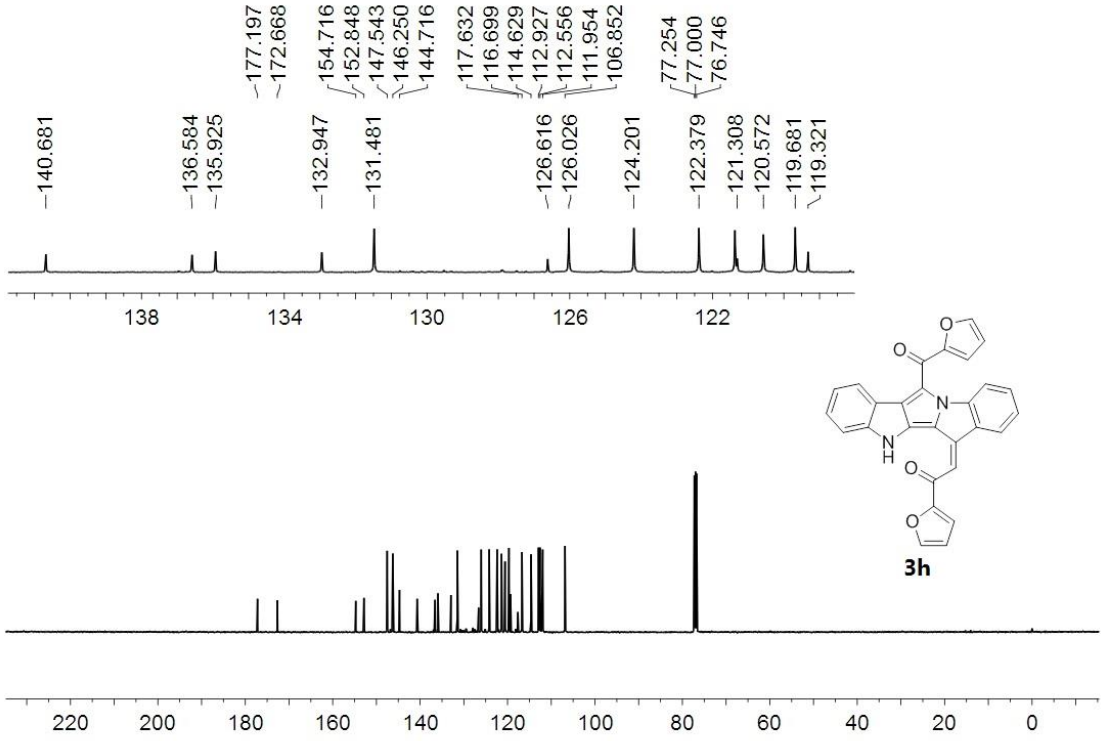
^{13}C NMR (125 MHz, $CDCl_3$) for **3g**



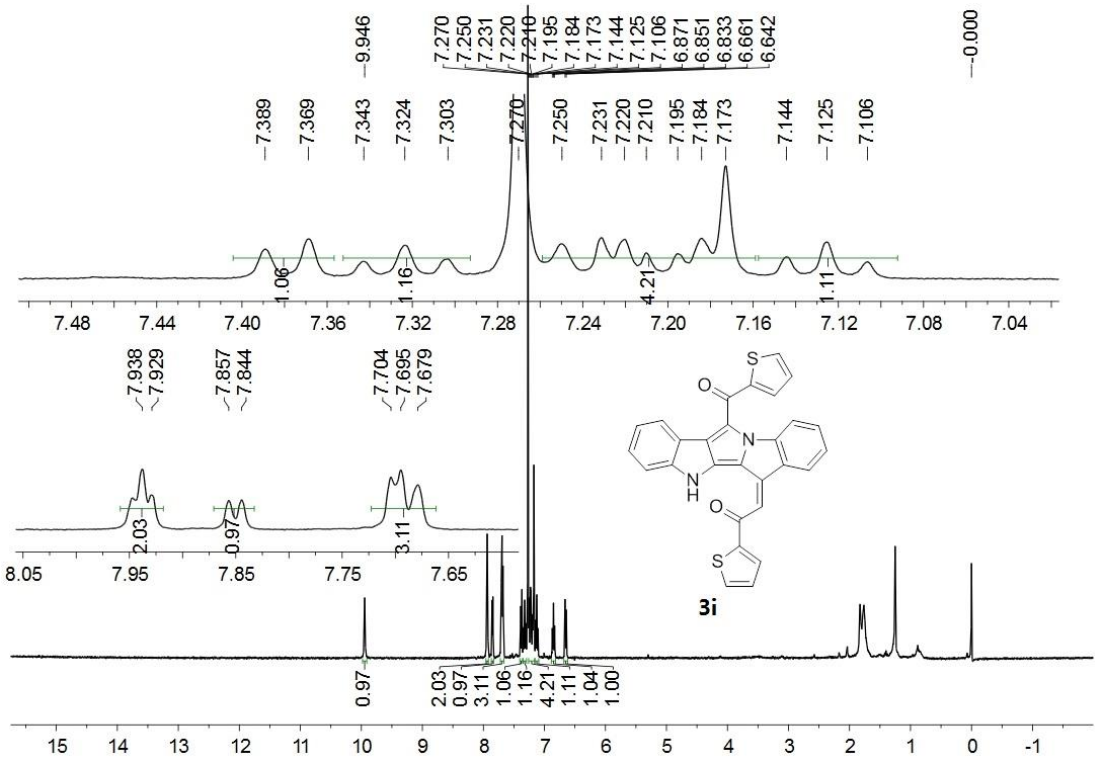
^{1}H NMR (500 MHz, $CDCl_3$) for **3h**



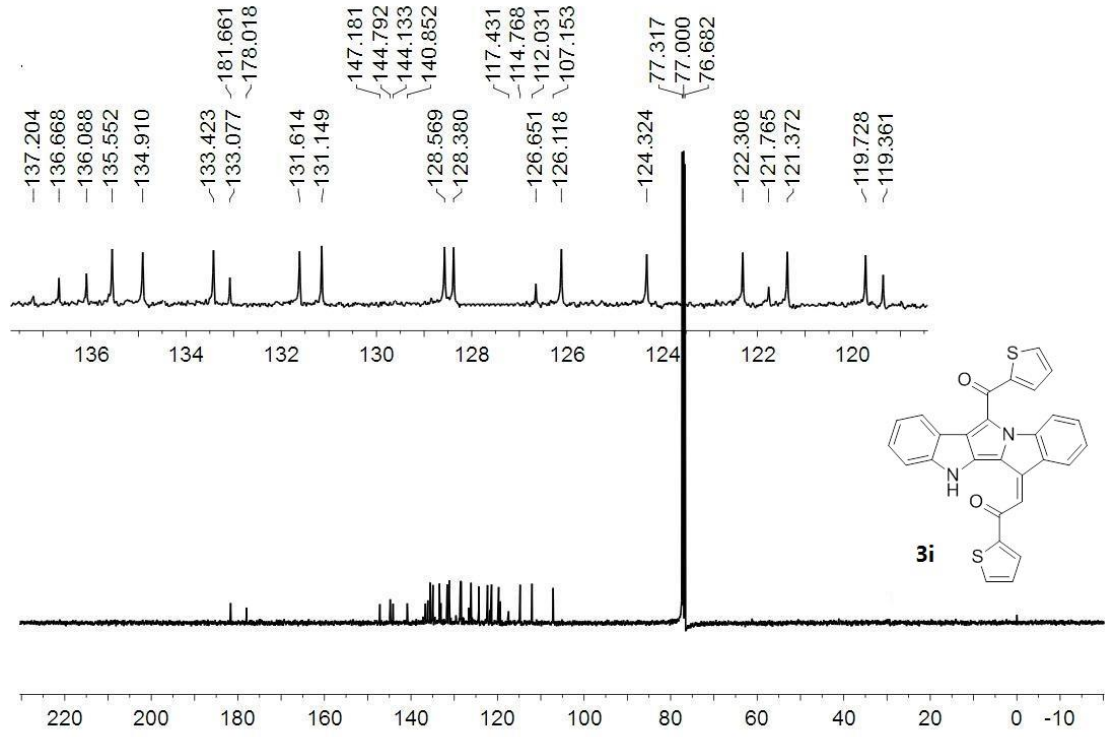
^{13}C NMR (125 MHz, $CDCl_3$) for **3h**



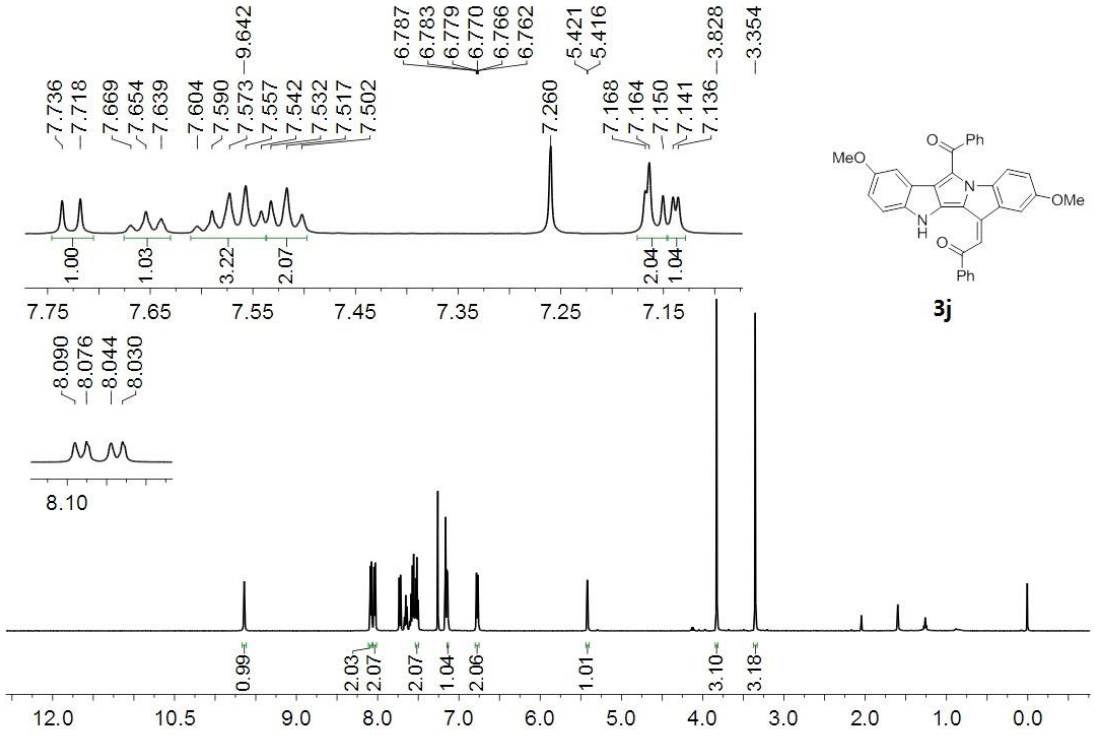
^{1}H NMR (400 MHz, $CDCl_3$) for **3i**



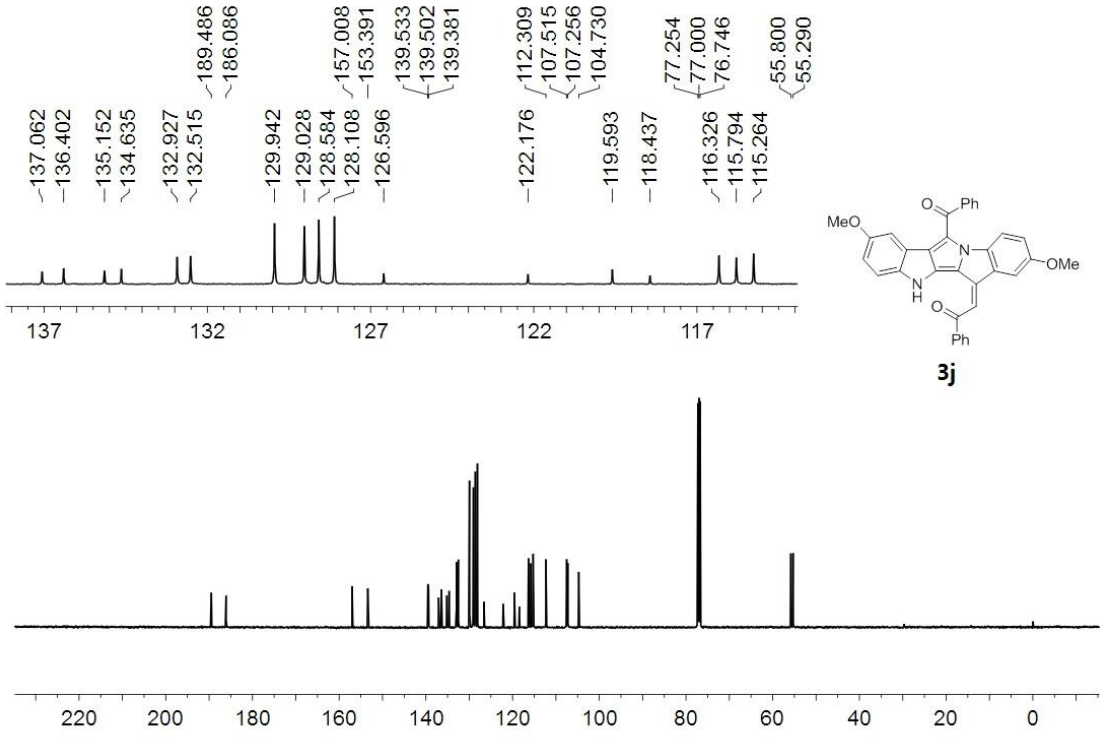
^{13}C NMR (100 MHz, $CDCl_3$) for **3i**



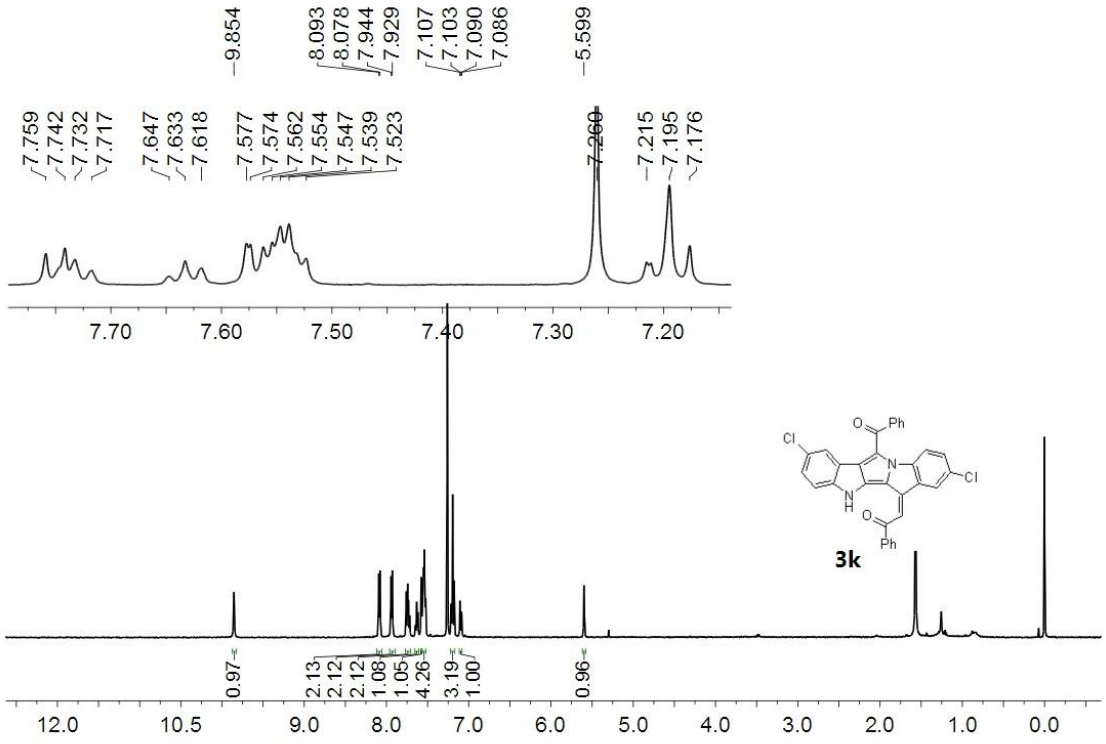
^{1}H NMR (500 MHz, $CDCl_3$) for **3j**



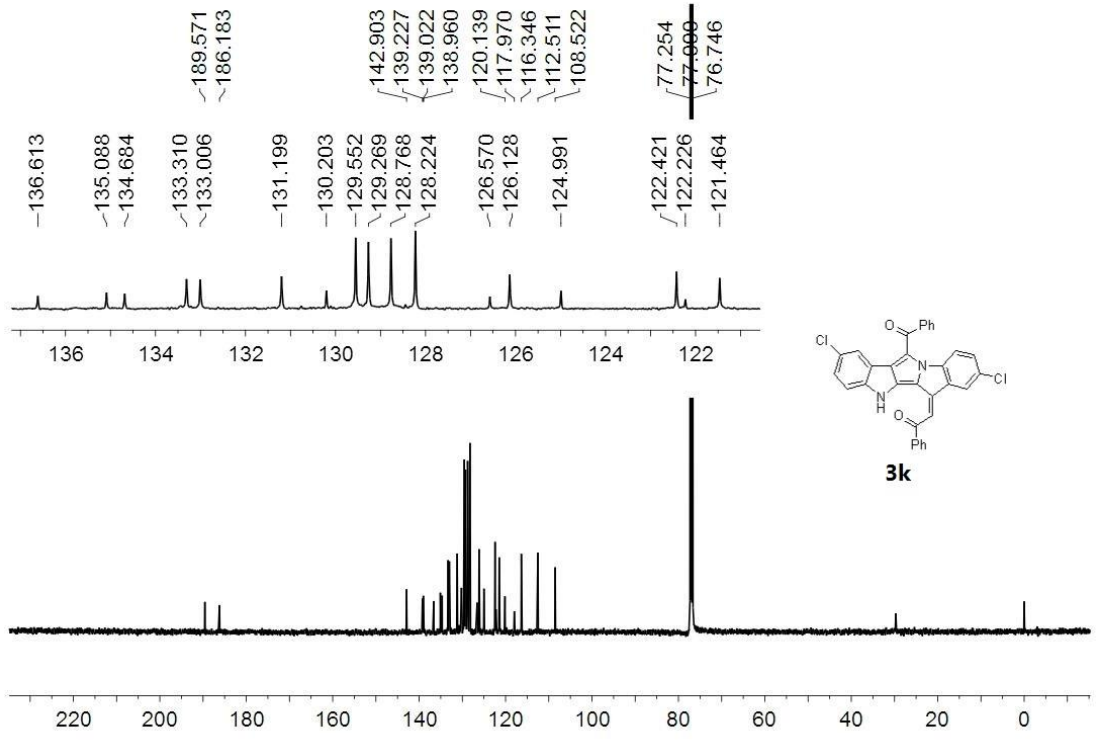
^{13}C NMR (125 MHz, $CDCl_3$) for **3j**



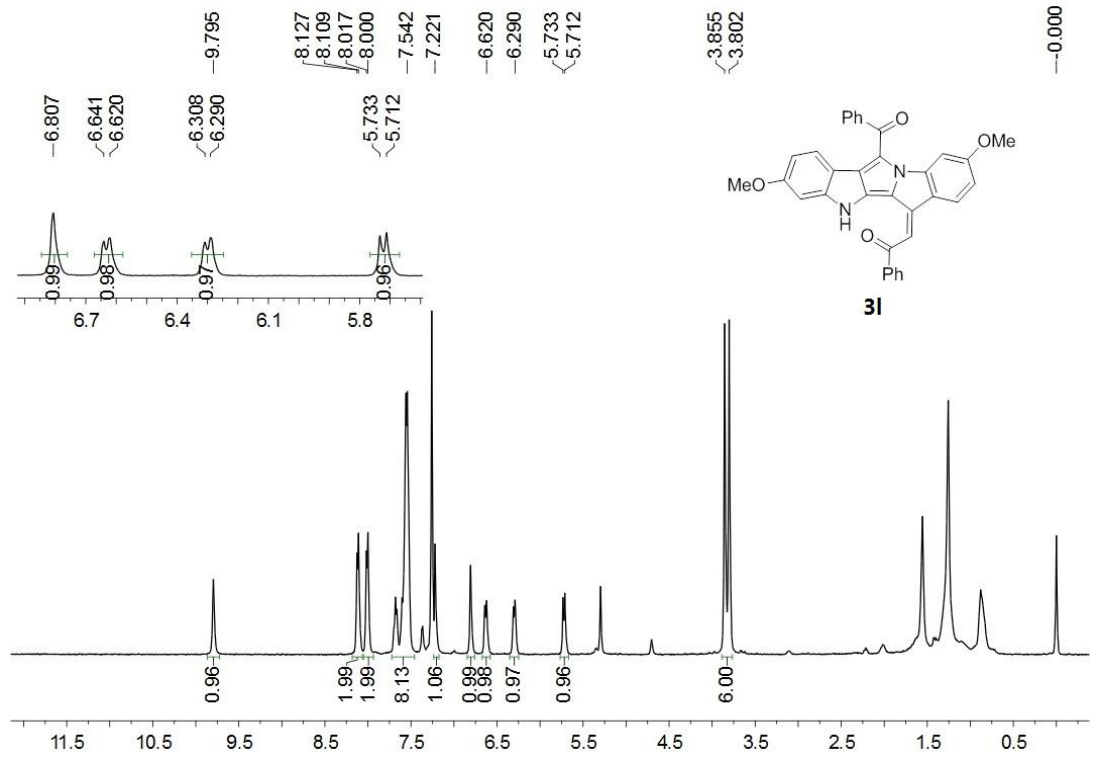
^{1}H NMR (500 MHz, $CDCl_3$) for **3k**



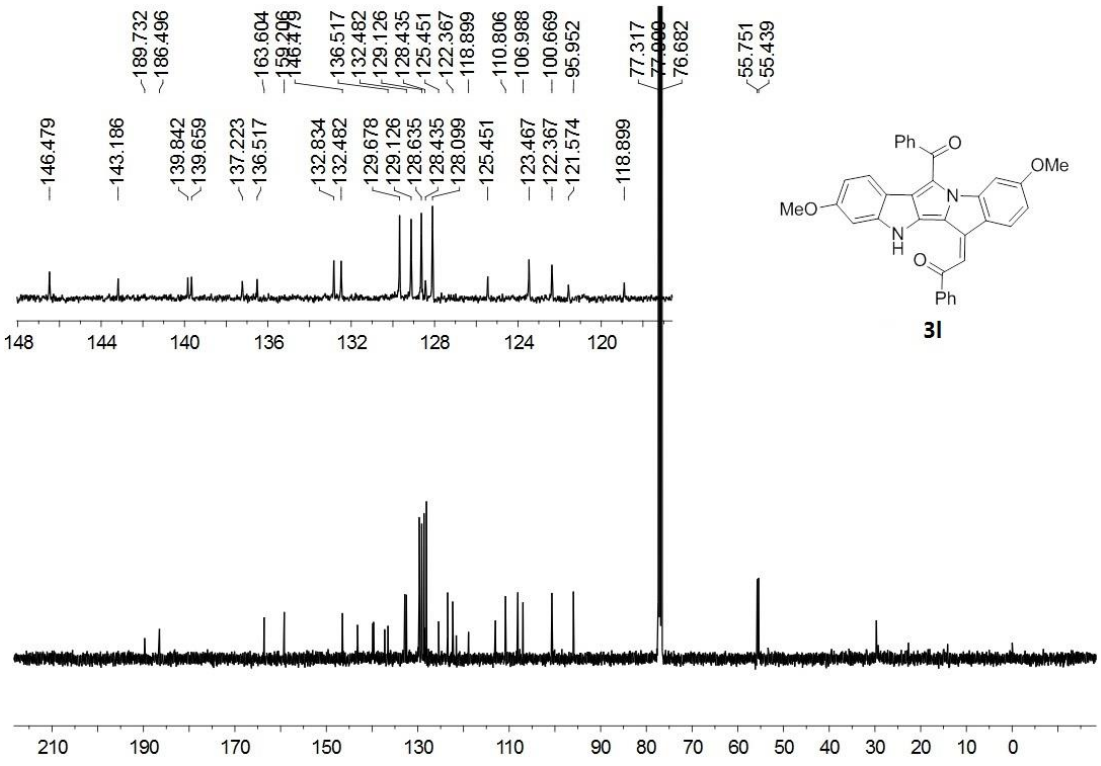
^{13}C NMR (125 MHz, $CDCl_3$) for **3k**



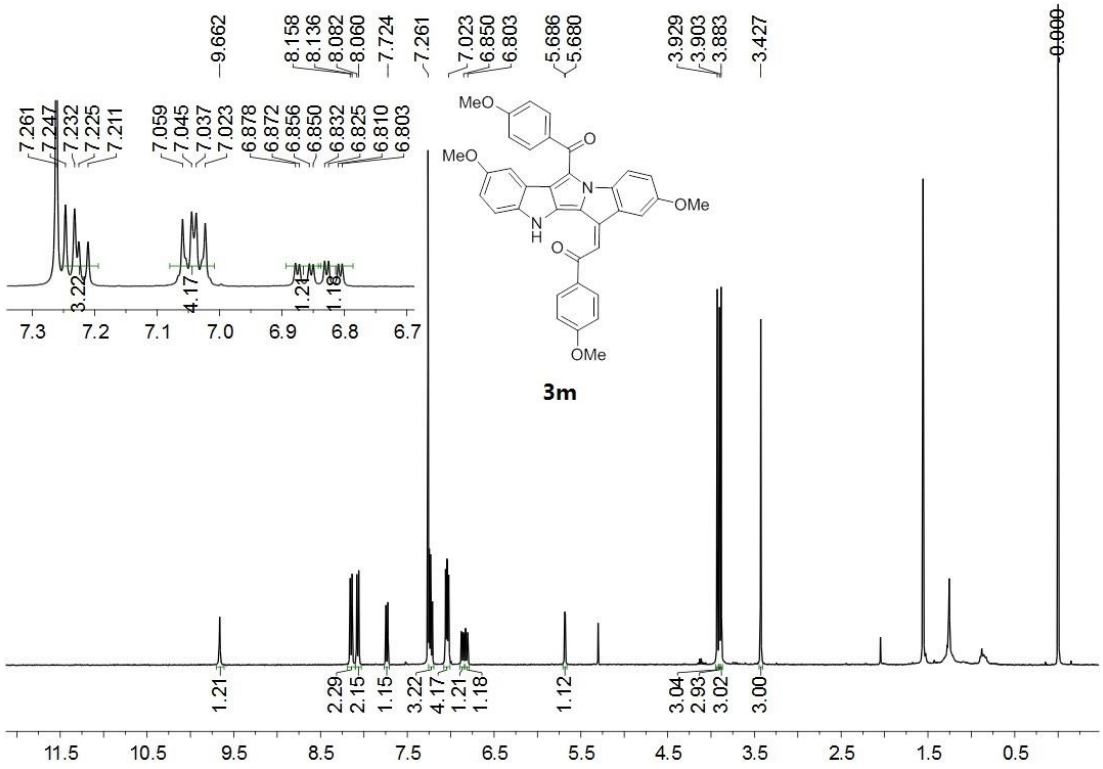
^{1}H NMR (400 MHz, $CDCl_3$) for **3l**



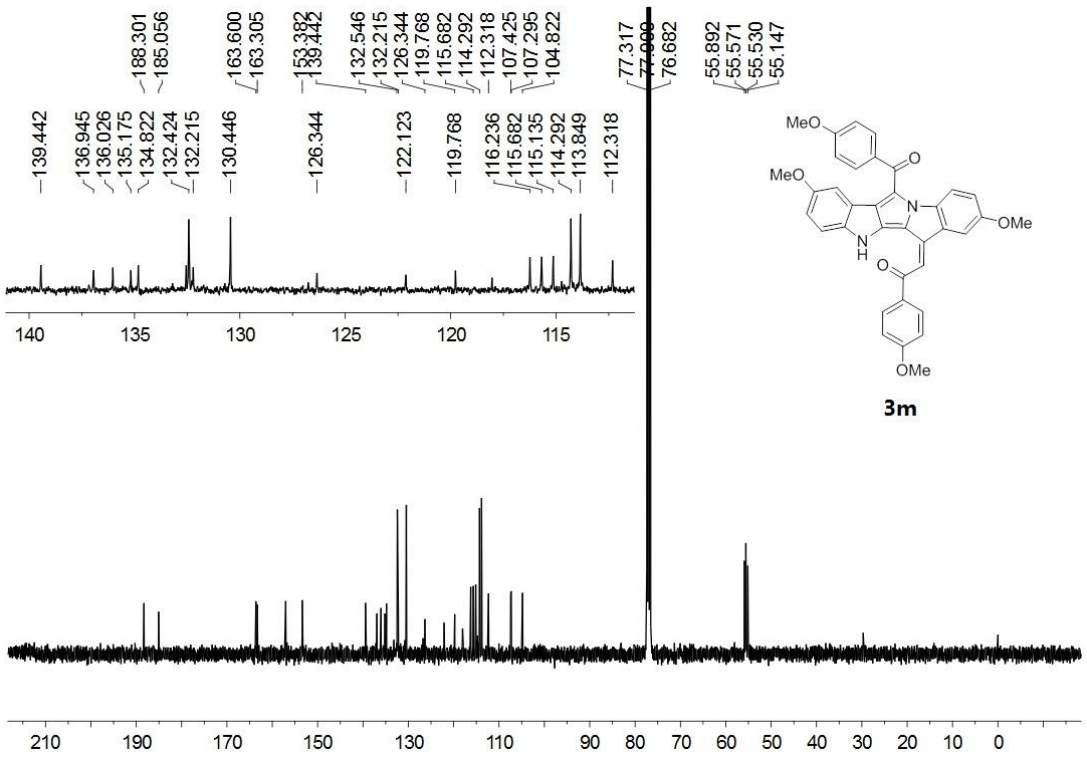
^{13}C NMR (100 MHz, $CDCl_3$) for **3l**



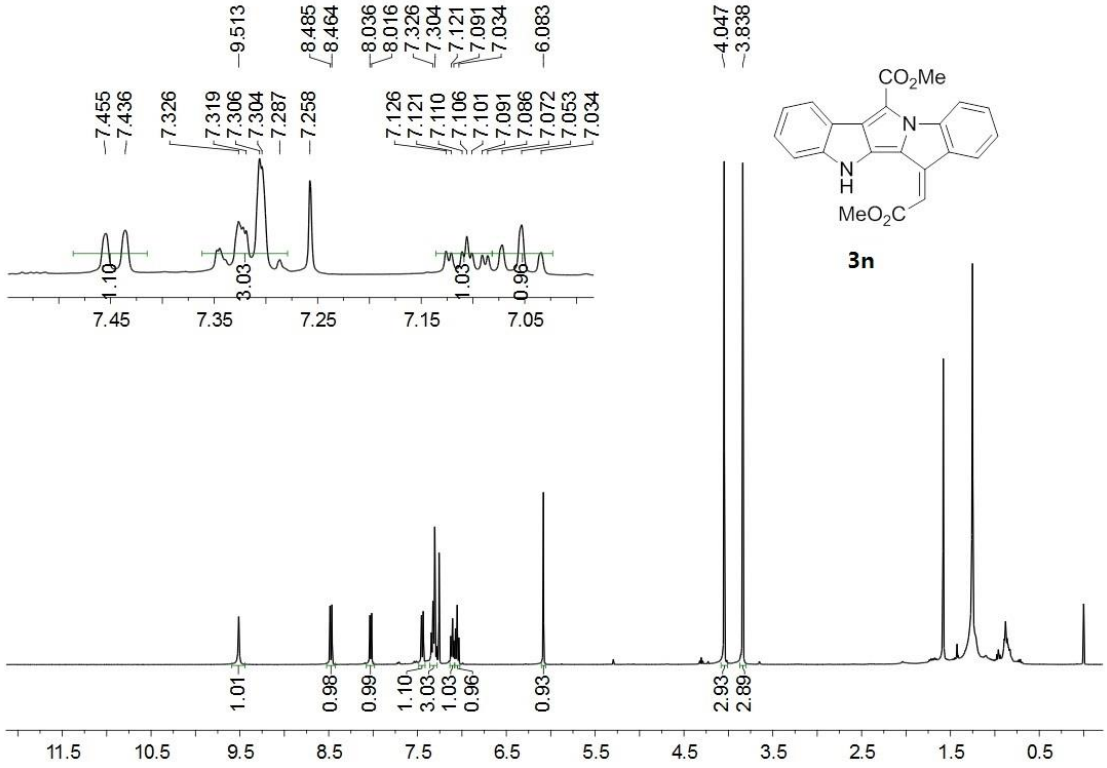
^{1}H NMR (400 MHz, $CDCl_3$) for **3m**



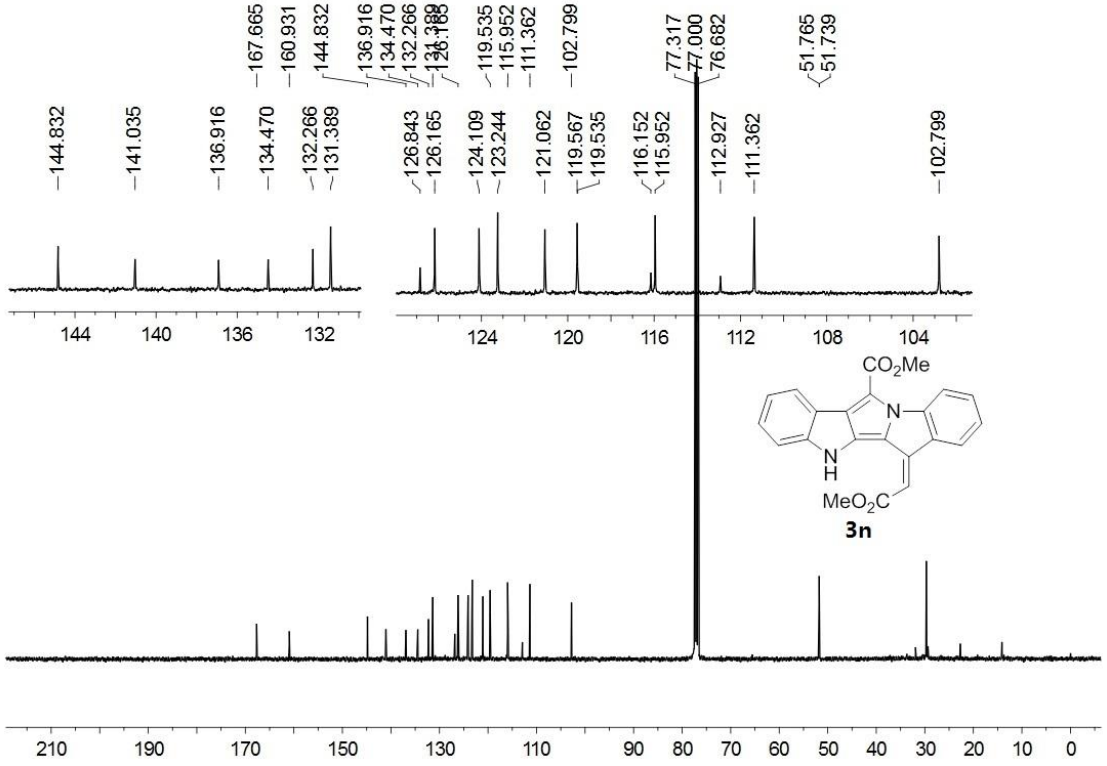
^{13}C NMR (100 MHz, $CDCl_3$) for **3m**



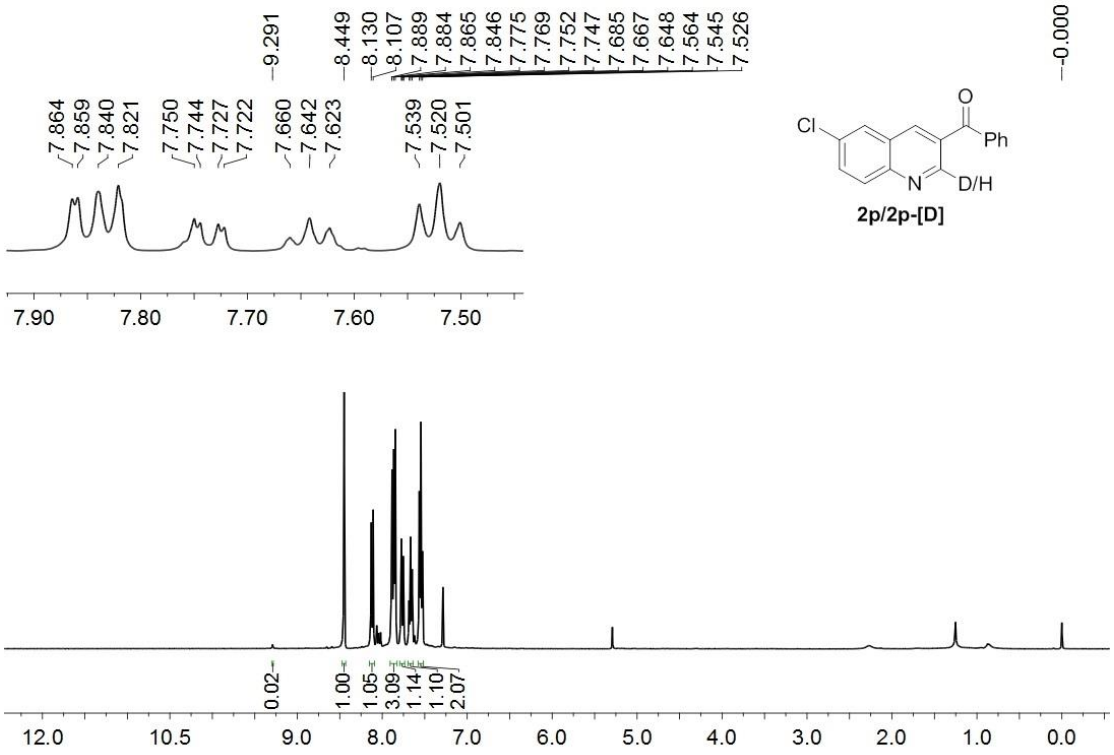
^{1}H NMR (400 MHz, $CDCl_3$) for **3n**



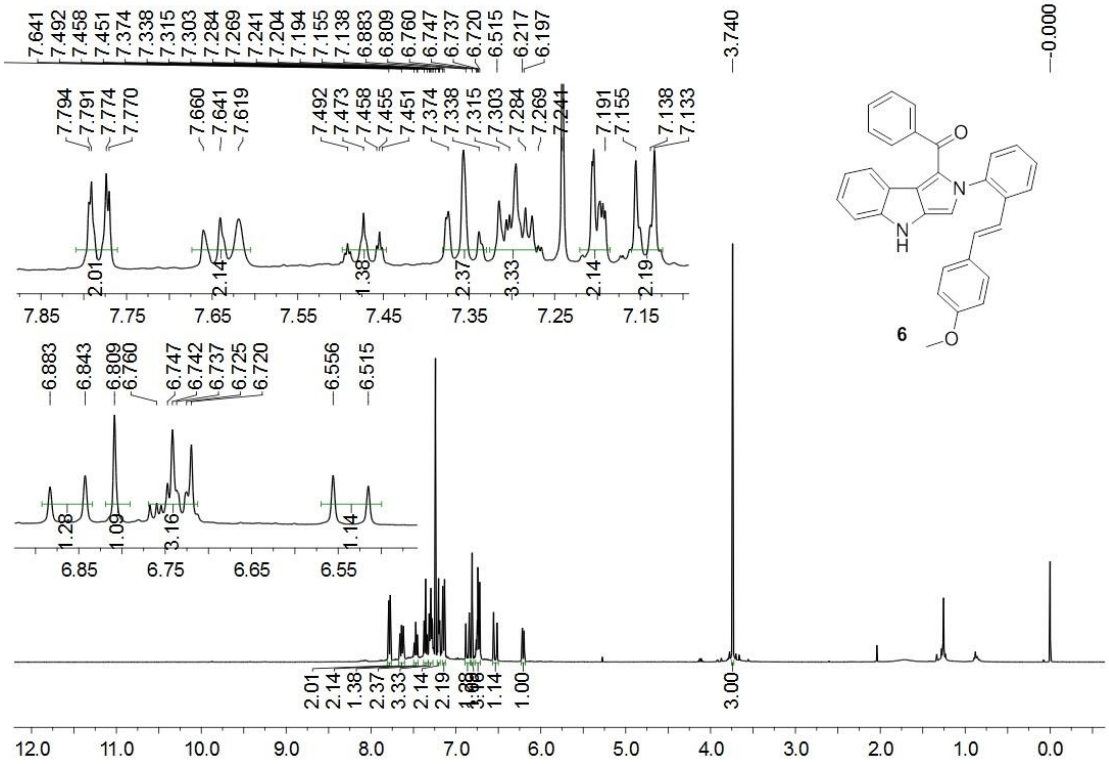
^{13}C NMR (100 MHz, $CDCl_3$) for **3n**



^{1}H NMR (400 MHz, $CDCl_3$) for **2p/2p-[D]**



^{1}H NMR (400 MHz, $CDCl_3$) for **6**



^{13}C NMR (100 MHz, $CDCl_3$) for **6**