

Supporting Information for

Substrate-controlled divergent synthesis of polycyclic indoloazepines and indolodiazepines *via* 1,5-hydride shift/7-cyclization cascades

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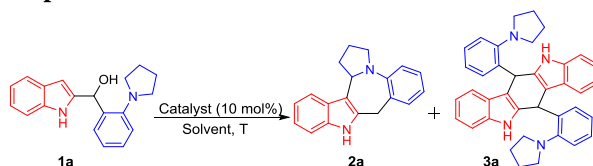
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1. General Information

All reagents and chemicals (AR grade) were purchased from commercial suppliers and used without further purification unless otherwise noticed. Indole-2-carboxaldehydes^{1,2} and *o*-substituted amino bromobenzenes^{3,4} were prepared according to literature. Column chromatography was performed on silica gel (100~200 mesh). All ¹H NMR and ¹⁹F NMR spectra were recorded on a Bruker Avance II 400 MHz and Bruker Avance III 470 MHz, respectively, and ¹³C NMR spectra were recorded on a Bruker Avance II 101 MHz with chemical shifts reported as ppm (in CDCl₃ or *d*₆-DMSO, TMS as internal standard). Data for ¹H NMR are recorded as follows: chemical shift (δ , ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, brs = broad singlet, dd = double doublet, dt = double triplet, coupling constants in Hz, integration). HRMS (ESI) was obtained with a HRMS/MS instrument (LTQ Orbitrap XL TM).

2. Screening of Optimal Reaction Conditions for 2a and 3a

Table S1. Screening of Optimal Reaction Conditions for 2a and 3a^a



Entry	Catalyst	Solvent	T (°C)	t (min)	Yield(%) of 2a ^b	Yield(%) of 3a ^b
1	--	DCE	80	60	--	--
2	Yb(OTf) ₃	DCE	80	15	48	26
3	Cu(OTf) ₂	DCE	80	15	40	25
4	Mg(OTf) ₂	DCE	80	2.5 h	49	35
5	Bi(OTf) ₃	DCE	80	25	54	25
6	Ni(OTf) ₂	DCE	80	3 h	42	31
7	La(OTf) ₃	DCE	80	100	44	30
8	ZnCl ₂	DCE	80	20	35	40
9	FeCl ₃	DCE	80	12	52	18
10	BF ₃ ·Et ₂ O	DCE	80	80	60	17
11	TSOH	DCE	80	5	30	41
12	CSA	DCE	80	7	32	38
13	TfOH	DCE	80	7	32	40
14	TFA	DCE	80	20	39	38
15	DPP	DCE	80	10	37	40
16	BF ₃ ·Et ₂ O	toluene	80	55	28	50
17	BF ₃ ·Et ₂ O	toluene	110	10	35	40
18	BF ₃ ·Et ₂ O	THF	70	25	30	45
19	BF ₃ ·Et ₂ O	MeCN	80	3 h	25	20
20	BF ₃ ·Et ₂ O	EtOH	80	20	trace	40
21	BF ₃ ·Et ₂ O	1,4-dioxane	80	15	65	10
22	BF ₃ ·Et ₂ O	1,4-dioxane	110	2	70	<10
23 ^c	BF ₃ ·Et ₂ O	1,4-dioxane	110	4	70	<10
24 ^d	BF ₃ ·Et ₂ O	1,4-dioxane	110	7	60	trace
25 ^{de}	BF ₃ ·Et ₂ O	1,4-dioxane	110	20	50	trace
26 ^{df}	BF ₃ ·Et ₂ O	1,4-dioxane	110	40	--	--
27	BF ₃ ·Et ₂ O	xylene	110	8	40	37
28	--	xylene	150	30	--	--
29	BF ₃ ·Et ₂ O	xylene	150	1	50	30
30 ^c	BF ₃ ·Et ₂ O	xylene	150	2	61	25
31 ^d	BF ₃ ·Et ₂ O	xylene	150	2	69	20
32 ^{de}	BF ₃ ·Et ₂ O	xylene	150	8	72	19
33 ^{df}	BF ₃ ·Et ₂ O	xylene	150	80	51	37
34 ^{fg}	BF ₃ ·Et ₂ O	xylene	150	80	81	<10
35 ^g	BF ₃ ·Et ₂ O	xylene	150	10	85	trace
36	DPP	toluene	80	6	trace	75
37	DPP	toluene	110	5	<10	70
38	DPP	THF	70	6	trace	69
39	DPP	MeCN	80	50	30	25
40	DPP	EtOH	80	45	trace	45
41	DPP	1,4-dioxane	80	5	trace	65
42	DPP	toluene	70	10	trace	90
43	DPP	THF	60	20	<10	72
44	DPP	1,4-dioxane	70	8	10	60
45	DPP	toluene	50	40	trace	95
46	DPP	toluene	25	36 h	trace	92

^aThe reaction was carried out on a 0.1 mmol scale, catalyst (10 mol%) in 2.0 mL solvent. ^b Isolated yield. ^cSolvent 4.0 mL. ^dSolvent 8.0 mL. ^eCatalyst 5 mol%. ^fCatalyst 1 mol%. ^gSolvent 16.0 mL.

3. General Operation Procedures

General procedure for the synthesis of compounds **1** and **4**

To a solution of *o*-substituted amino bromobenzene (3 mmol) in dry THF (20 mL) was added *n*-BuLi (2.5 M in hexane, 3 mmol) at -78 °C. The reaction mixture was stirred for 2 h at the same temperature, and then 5 mL THF solution of indole-2-carboxaldehyde (1 mmol) was added dropwise to the reaction system. The mixture was stirred for 2 h, and the reaction was quenched by saturated aqueous NH₄Cl. The solution was extracted with ethyl acetate. The organic phase was washed with brine, concentrated in vacuo to give the crude product. After purification by column chromatography on silica gel (ethyl acetate/petroleum ether = 1:5 as eluent), **1** or **4** was obtained.

General procedure for the synthesis of products **2**

2-Indolylmethanol **1** (6.25 mM) and xylene were added to a reaction flask. When the reaction solution is heated up to reflux, BF₃·Et₂O (10 mol%) was added to the reaction. After the reaction was completed (monitored by TLC), the solution was concentrated under reduced pressure to give the residue, which was purified through column chromatography on silica gel (ethyl acetate/petroleum ether = 1/5 as eluent) to afford pure products **2**.

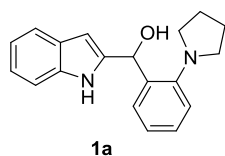
General procedure for the synthesis of products **3**

A reaction tube was charged with **1** (0.2 mmol) and toluene (2 mL), then DPP (10 mmol%) was added at 50 °C. The reaction was stirred at the same temperature until it was completed (monitored by TLC). Then the crude product was purified by column chromatography on silica gel (ethyl acetate/petroleum ether = 1/20 as eluent) to give the product **3**.

General procedure for the synthesis of products **5**

In a tube, **4** (0.1 M) was added in toluene. Then, BF₃·Et₂O (10 mol%) was added at room temperature and the reaction solution was stirred at 80 °C until it was completed (monitored by TLC). The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (ethyl acetate/petroleum ether = 1/10 as eluent) to afford product **5**.

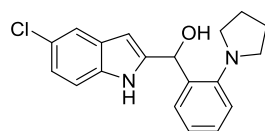
4. Characterization Data



1a

(1H-indol-2-yl)(2-(pyrrolidin-1-yl)phenyl)methanol

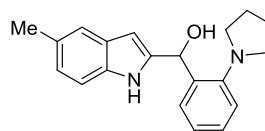
R_f = 0.15 (petroleum ether/EtOAc = 5:1), yellow solid, mp: 124.3-126.3 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.76 (s, 1H), 8.06 (s, 1H), 7.52 (d, J = 7.8 Hz, 1H), 7.34 (dd, J = 8.4, 5.8 Hz, 3H), 7.21-7.10 (m, 3H), 7.07 (t, J = 7.4 Hz, 1H), 6.13 (s, 1H), 6.07 (s, 1H), 3.09-2.85 (m, 4H), 1.96-1.78 (m, 4H); ^{13}C NMR (101 MHz, CDCl_3) δ 148.7, 141.8, 136.5, 136.0, 128.8, 128.7, 128.5, 124.9, 122.1, 121.5, 120.4, 119.6, 111.0, 100.0, 71.5, 53.8, 24.5.



1b

(5-chloro-1H-indol-2-yl)(2-(pyrrolidin-1-yl)phenyl)methanol

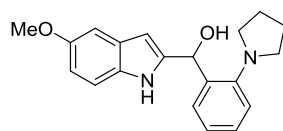
R_f = 0.15 (petroleum ether/EtOAc = 5:1), yellow solid, mp: 218.6-220.1 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.89 (s, 1H), 8.19 (s, 1H), 7.45 (s, 1H), 7.32 (t, J = 3.7 Hz, 2H), 7.24 (s, 1H), 7.17-7.10 (m, 2H), 7.08 (dd, J = 8.6, 2.0 Hz, 1H), 6.08 (s, 1H), 5.98 (s, 1H), 3.02-2.82 (m, 4H), 1.90-1.80 (m, 4H); ^{13}C NMR (101 MHz, CDCl_3) δ 148.7, 143.4, 136.2, 134.3, 129.5, 128.9, 128.7, 125.2, 125.1, 122.3, 121.8, 119.8, 111.9, 99.6, 71.5, 53.8, 24.5.



1c

(5-methyl-1H-indol-2-yl)(2-(pyrrolidin-1-yl)phenyl)methanol

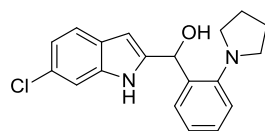
R_f = 0.20 (petroleum ether/EtOAc = 5:1), yellow solid, mp: 151.1-153.0 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.64 (s, 1H), 7.99 (s, 1H), 7.33 (d, J = 5.6 Hz, 3H), 7.27 (s, 1H), 7.17 (d, J = 7.0 Hz, 2H), 7.00 (d, J = 8.2 Hz, 1H), 6.13 (s, 1H), 6.02 (s, 1H), 3.00 (dd, J = 12.9, 6.1 Hz, 4H), 2.45 (s, 3H), 1.94-1.85 (m, 4H); ^{13}C NMR (101 MHz, CDCl_3) δ 148.7, 141.9, 136.6, 134.3, 128.8, 128.7, 124.8, 123.1, 122.0, 120.1, 110.6, 99.6, 71.5, 53.7, 24.5, 21.5.



1d

(5-methoxy-1H-indol-2-yl)(2-(pyrrolidin-1-yl)phenyl)methanol

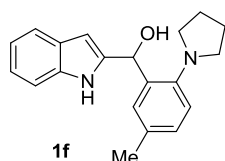
R_f = 0.20 (petroleum ether/EtOAc = 5:1), yellow solid, mp: 130.0-132.3 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.61 (s, 1H), 7.94 (s, 1H), 7.30 (d, J = 3.7 Hz, 2H), 7.21 (d, J = 8.8 Hz, 1H), 7.18-7.08 (m, 2H), 6.97 (s, 1H), 6.80 (dd, J = 8.8, 2.1 Hz, 1H), 6.09 (s, 1H), 5.99 (s, 1H), 3.81 (s, 3H), 3.03-2.88 (m, 4H), 1.91-1.80 (m, 4H); ^{13}C NMR (101 MHz, CDCl_3) δ 154.1, 148.7, 142.6, 136.5, 131.2, 128.9, 128.7, 124.8, 122.0, 111.6, 102.3, 99.9, 71.5, 55.9, 53.8, 24.5.



1e

(6-chloro-1H-indol-2-yl)(2-(pyrrolidin-1-yl)phenyl)methanol

R_f = 0.15 (petroleum ether/EtOAc = 5:1), yellow solid, mp: 59.9-62.1 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.92 (s, 1H), 8.25 (s, 1H), 7.40 (d, J = 8.4 Hz, 1H), 7.34 (d, J = 3.5 Hz, 3H), 7.18-7.13 (m, 2H), 7.03 (dd, J = 8.4, 1.5 Hz, 1H), 6.10 (s, 1H), 6.02 (s, 1H), 3.01-2.89 (m, 4H), 1.87 (dd, J = 12.8, 6.7 Hz, 4H); ^{13}C NMR (101 MHz, CDCl_3) δ 148.6, 142.7, 136.3, 136.2, 128.8, 128.7, 127.2, 127.0, 125.0, 122.3, 121.2, 120.3, 110.9, 100.0, 71.5, 53.8, 24.5.

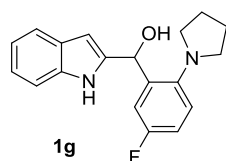


1f

(1H-indol-2-yl)(5-methyl-2-(pyrrolidin-1-yl)phenyl)methanol

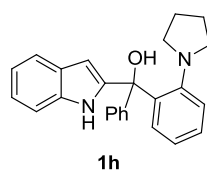
R_f = 0.20 (petroleum ether/EtOAc = 5:1), yellow solid, mp: 80.1-82.0 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.30 (s, 1H), 7.58 (d, J = 7.6 Hz, 1H), 7.43 (s, 1H), 7.30-7.22 (m, 3H), 7.25-7.12 (m, 2H), 6.95 (td, J = 8.3, 2.1 Hz, 1H), 6.77 (d, J = 7.6 Hz, 1H), 6.38 (s, 1H), 3.36 (dt, J = 13.9, 6.9 Hz, 2H), 2.93 (dt, J = 10.9, 4.5 Hz, 2H), 2.25 (s, 3H),

2.05-1.90 (m, 4H); ^{13}C NMR (101 MHz, CDCl_3) δ 148.5, 136.4, 135.5, 134.4, 129.2, 128.7, 128.2, 124.5, 121.7, 120.7, 119.0, 118.6, 111.0, 108.4, 68.6, 52.7, 24.5, 8.7.



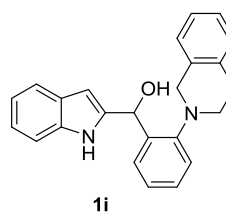
(5-fluoro-2-(pyrrolidin-1-yl)phenyl)(1H-indol-2-yl)methanol

R_f = 0.15 (petroleum ether/EtOAc = 5:1), yellow solid, mp: 99.6-101.4 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.63 (s, 1H), 7.55 (d, J = 7.7 Hz, 1H), 7.37 (d, J = 8.0 Hz, 1H), 7.20-7.08 (m, 3H), 6.98 (dd, J = 10.8, 2.5 Hz, 1H), 6.90-6.73 (m, 2H), 6.14 (d, J = 6.4 Hz, 2H), 3.12-2.89 (m, 4H), 1.94-1.84 (m, 4H); ^{13}C NMR (101 MHz, CDCl_3) δ 162.8(d, J = 248.5 Hz), 150.4(d, J = 8.1 Hz), 141.1, 136.0, 131.6(d, J = 4.0 Hz), 130.2(d, J = 10.1 Hz), 128.3, 121.7, 120.5, 119.7, 111.0, 110.8(d, J = 22.2 Hz), 108.2(d, J = 22.2 Hz), 100.4, 70.2, 53.4, 24.5; ^{19}F NMR (470 MHz, CDCl_3) δ -113.43 (d, J = 33.9 Hz).



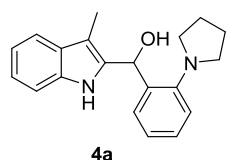
(1H-indol-2-yl)(phenyl)(2-(pyrrolidin-1-yl)phenyl)methanol

R_f = 0.20 (petroleum ether/EtOAc = 5:1), yellow solid, mp: 228.9-230.3 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.76 (s, 1H), 7.53 (d, J = 7.8 Hz, 1H), 7.43-7.28 (m, 8H), 7.21-7.15 (m, 1H), 7.09 (t, J = 7.6 Hz, 2H), 6.88 (dd, J = 7.8, 1.3 Hz, 1H), 5.91 (d, J = 1.3 Hz, 1H), 2.88-2.70 (m, 4H), 1.89-1.78 (m, 4H); ^{13}C NMR (101 MHz, CDCl_3) δ 148.9, 146.4, 143.8, 142.0, 136.1, 129.7, 128.7, 128.0, 127.8, 127.4, 127.3, 125.5, 124.2, 121.7, 120.6, 119.5, 111.1, 103.1, 80.1, 54.6, 24.5.



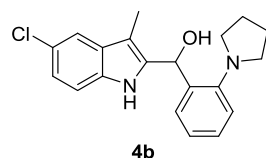
(2-(3,4-dihydroisoquinolin-2(1H)-yl)phenyl)(1H-indol-2-yl)methanol

R_f = 0.15 (petroleum ether/EtOAc = 5:1), yellow solid, mp: 131.0-131.9 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.71 (s, 1H), 7.68 (s, 1H), 7.54 (d, J = 7.7 Hz, 1H), 7.45-7.36 (m, 2H), 7.34-7.26 (m, 3H), 7.23-7.08 (m, 5H), 6.78 (s, 1H), 6.13 (s, 1H), 6.07 (s, 1H), 3.94 (s, 2H), 3.25-3.10 (m, 2H), 3.05-2.85 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 150.6, 142.0, 136.9, 135.8, 134.2, 133.4, 128.9, 128.6, 126.7, 126.6, 126.0, 125.9, 123.0, 121.5, 120.4, 119.7, 111.1, 99.5, 71.5, 55.9, 51.3, 29.5.



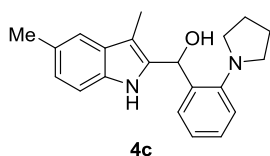
(3-methyl-1H-indol-2-yl)(2-(pyrrolidin-1-yl)phenyl)methanol

R_f = 0.20 (petroleum ether/EtOAc = 5:1), yellow solid, mp: 172.0-172.2 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.35 (s, 1H), 7.62 (d, J = 7.6 Hz, 1H), 7.48 (s, 1H), 7.35-7.27 (m, 3H), 7.21-7.14 (m, 2H), 7.00 (td, J = 8.3, 2.1 Hz, 1H), 6.82 (d, J = 7.6 Hz, 1H), 6.43 (s, 1H), 3.45-3.37 (m, 2H), 3.01-2.94 (m, 2H), 2.30 (s, 3H), 2.10-1.95 (m, 4H); ^{13}C NMR (101 MHz, CDCl_3) δ 148.5, 136.4, 135.5, 134.4, 129.2, 128.7, 128.2, 124.5, 121.7, 120.7, 119.0, 118.6, 111.0, 108.4, 68.6, 52.7, 24.5, 8.67.



(5-chloro-3-methyl-1H-indol-2-yl)(2-(pyrrolidin-1-yl)phenyl)methanol

R_f = 0.20 (petroleum ether/EtOAc = 5:1), yellow solid, mp: 165.5-167.4 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.37 (s, 1H), 7.56 (s, 1H), 7.47 (s, 1H), 7.35-7.29 (m, 2H), 7.23 (d, J = 8.5 Hz, 1H), 7.14 (d, J = 8.6 Hz, 1H), 7.02 (t, J = 7.1 Hz, 1H), 6.79 (d, J = 7.6 Hz, 1H), 6.39(s, 1H), 3.39 (dd, J = 15.3, 6.9 Hz, 2H), 2.97 (dd, J = 9.2, 4.5 Hz, 2H), 2.23 (s, 3H), 2.03 (qt, J = 12.3, 6.0 Hz, 4H); ^{13}C NMR (101 MHz, d_6 -DMSO) δ 148.4, 140.4, 137.4, 134.1, 130.2, 129.0, 128.3, 123.2, 122.9, 120.7, 119.3, 117.5, 113.1, 105.4, 63.6, 53.1, 24.7, 8.7.

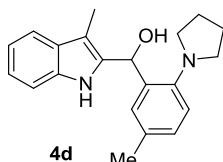


4c

(3,5-dimethyl-1H-indol-2-yl)(2-(pyrrolidin-1-yl)phenyl)methanol

R_f = 0.20 (petroleum ether/EtOAc = 5:1), yellow solid, mp: 155.0-152.3 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.16 (s, 1H), 7.38-7.27 (m, 2H), 7.26 (d, J = 1.2 Hz, 1H), 7.24 (dd, J = 6.2, 2.8 Hz, 1H), 7.18 (d, J = 8.2 Hz, 1H),

7.01-6.92 (m, 2H), 6.78 (d, J = 7.7 Hz, 1H), 6.37 (s, 1H), 3.37 (dt, J = 13.9, 6.9 Hz, 2H), 2.93 (dd, J = 9.2, 4.9 Hz, 2H), 2.47 (s, 3H), 2.22 (s, 3H), 2.04-1.91 (m, 4H); ^{13}C NMR (101 MHz, CDCl_3) δ 148.5, 136.4, 134.5, 133.8, 129.4, 128.6, 128.2, 124.4, 123.3, 120.6, 118.3, 110.6, 108.0, 68.6, 52.7, 24.5, 21.6, 8.6.

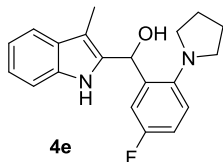


4d

(3-methyl-1H-indol-2-yl)(5-methyl-2-(pyrrolidin-1-yl)phenyl)methanol

R_f = 0.25 (petroleum ether/EtOAc = 5:1), yellow solid, mp: 135.2-137.0 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.24 (s, 1H), 7.73 (s, 1H), 7.59 (d, J = 7.6 Hz, 1H), 7.31 (d, J = 7.9 Hz, 1H), 7.23-7.09 (m, 3H), 7.07 (d, J = 7.9 Hz, 1H), 6.64 (s, 1H), 6.34 (s, 1H), 3.35-3.27 (m, 2H), 2.97-2.88 (m, 2H), 2.26 (s, 3H), 2.18 (s,

3H), 2.03-1.93 (m, 4H); ^{13}C NMR (101 MHz, CDCl_3) δ 146.0, 136.6, 135.6, 134.7, 134.5, 129.3, 128.7, 121.6, 121.2, 118.9, 118.7, 111.1, 108.3, 68.8, 53.2, 24.5, 21.1, 8.8.

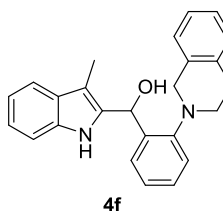


4e

(5-fluoro-2-(pyrrolidin-1-yl)phenyl)(3-methyl-1H-indol-2-yl)methanol

R_f = 0.20 (petroleum ether/EtOAc = 5:1), yellow solid, mp: 148.3-149.6 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.34 (s, 1H), 7.63 (d, J = 7.6 Hz, 1H), 7.34 (d, J = 7.8 Hz, 1H), 7.20 (dt, J = 14.6, 7.1 Hz, 2H), 6.96 (dd, J = 10.8, 1.8 Hz, 1H), 6.82 (t, J = 7.6 Hz, 1H), 6.66 (t, J = 7.1 Hz, 1H), 6.40 (s, 1H), 6.29 (s, 1H), 3.40

(t, J = 7.6 Hz, 2H), 3.01 (d, J = 8.3 Hz, 2H), 2.29 (s, 3H), 2.12-1.96 (m, 4H); ^{13}C NMR (101 MHz, CDCl_3) δ 162.8(d, J = 247.5 Hz), 150.2 (d, J = 8.1 Hz), 135.4, 134.1, 131.3(d, J = 3.0 Hz), 129.70 (d, J = 10.1 Hz), 129.2, 121.8, 119.1, 118.6, 111.0, 110.0(d, J = 21.2 Hz), 108.4, 107.1(d, J = 23.2 Hz), 67.6, 52.3, 24.6, 8.6; ^{19}F NMR (470 MHz, CDCl_3) δ -113.01 (dt, J = 10.8, 7.2 Hz).

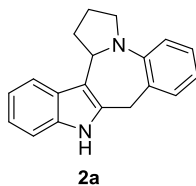


4f

(2-(3,4-dihydroisoquinolin-2(1H)-yl)phenyl)(3-methyl-1H-indol-2-yl)methanol

R_f = 0.20 (petroleum ether/EtOAc = 5:1), yellow solid, mp: 68.7-69.9 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.33 (s, 1H), 7.52 (d, J = 7.1 Hz, 1H), 7.28 (d, J = 3.1 Hz, 2H), 7.18-7.06 (m, 7H), 7.00 (d, J = 7.5 Hz, 1H), 6.87 (d, J = 8.0 Hz, 2H), 6.33 (s, 1H), 4.09 (d, J = 15.0 Hz, 1H), 3.91 (d, J = 15.0 Hz, 1H),

3.31-3.13 (m, 2H), 2.98 (d, J = 4.7 Hz, 2H), 2.15 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 150.7, 137.4, 135.3, 134.8, 134.4, 133.6, 129.4, 129.0, 128.6, 126.8, 126.6, 126.1, 125.9, 122.4, 121.7, 119.1, 118.6, 111.0, 107.9, 68.6, 56.0, 51.2, 29.7, 8.8.

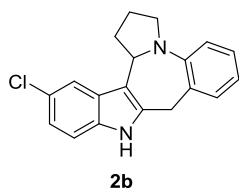


2a

1,2,3,9,10,14c-hexahydrobenzo[6,7]pyrrolo[1',2':1,2]azepino[4,3-b]indole

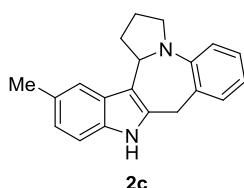
R_f = 0.30 (petroleum ether/EtOAc = 5:1), white solid, mp: 164.0-166.3 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.73 (s, 1H), 7.37 (d, J = 7.6 Hz, 1H), 7.22 (d, J = 7.5 Hz, 2H), 7.17 (d, J = 7.5 Hz, 1H), 7.13-6.99 (m, 3H), 6.93 (td, J = 7.3, 0.9 Hz, 1H), 4.62 (d, J = 15.1 Hz, 1H), 4.05 (t, J = 7.7 Hz, 1H), 3.44-3.35 (m, 2H), 3.27 (t, J =

7.4 Hz, 1H), 2.78-2.66 (m, 1H), 2.07-1.96 (m, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 148.5, 135.0, 134.7, 131.0, 128.1, 127.9, 127.6, 122.5, 121.1, 119.3, 118.7, 118.4, 113.0, 110.6, 61.9, 50.8, 33.1, 33.0, 21.8; HRMS (ESI) for $\text{C}_{19}\text{H}_{19}\text{N}_2$ $[\text{M}+\text{H}]^+$ calcd 275.1543, found 275.1539.



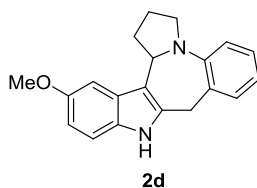
13-chloro-1,2,3,9,10,14c-hexahydrobenzo[6,7]pyrrolo[1',2':1,2]azepino[4,3-b]indole

R_f = 0.30 (petroleum ether/EtOAc = 5:1), light yellow solid, mp: 197.1-199.0 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.76 (s, 1H), 7.30 (s, 1H), 7.23 (t, J = 8.2 Hz, 1H), 7.17 (d, J = 7.9 Hz, 1H), 7.12 (d, J = 8.3 Hz, 2H), 7.02 (dd, J = 8.6, 1.4 Hz, 1H), 6.94 (t, J = 7.2 Hz, 1H), 4.61 (d, J = 15.1 Hz, 1H), 3.97 (t, J = 7.6 Hz, 1H), 3.43-3.30 (m, 2H), 3.26 (t, J = 6.6 Hz, 1H), 2.75-2.62 (m, 1H), 2.05-1.92 (m, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 148.4, 134.3, 133.3, 132.6, 128.9, 128.1, 127.7, 124.9, 122.6, 121.2, 118.8, 117.9, 113.0, 111.4, 61.5, 50.8, 33.0, 21.8; HRMS (ESI) for $\text{C}_{19}\text{H}_{18}\text{ClN}_2$ $[\text{M}+\text{H}]^+$ calcd 309.1153, found 309.1147.



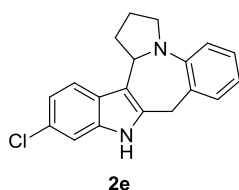
13-methyl-1,2,3,9,10,14c-hexahydrobenzo[6,7]pyrrolo[1',2':1,2]azepino[4,3-b]indole

R_f = 0.35 (petroleum ether/EtOAc = 5:1), light yellow solid, mp: 187.6-189.4 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.68 (s, 1H), 7.28 (t, J = 7.4 Hz, 1H), 7.22 (d, J = 8.2 Hz, 2H), 7.16 (d, J = 7.8 Hz, 2H), 6.97 (dd, J = 14.5, 7.6 Hz, 2H), 4.66 (d, J = 15.0 Hz, 1H), 4.07 (t, J = 8.2 Hz, 1H), 3.52-3.28 (m, 3H), 2.80 (dd, J = 11.4, 5.7 Hz, 1H), 2.47 (s, 3H), 2.14-1.98 (m, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 148.6, 134.8, 133.3, 131.1, 128.4, 128.2, 128.1, 127.5, 122.5, 122.4, 118.6, 118.2, 112.5, 110.2, 62.0, 50.8, 33.1, 33.0, 21.8, 21.6; HRMS (ESI) for $\text{C}_{20}\text{H}_{21}\text{N}_2$ $[\text{M}+\text{H}]^+$ calcd 289.1699, found 289.1692.



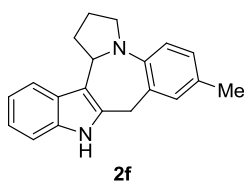
13-methoxy-1,2,3,9,10,14c-hexahydrobenzo[6,7]pyrrolo[1',2':1,2]azepino[4,3-b]indole

R_f = 0.35 (petroleum ether/EtOAc = 5:1), light yellow solid, mp: 196.8-198.3 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.69 (s, 1H), 7.28-7.18 (m, 2H), 7.15 (d, J = 7.8 Hz, 2H), 6.97 (t, J = 7.1 Hz, 1H), 6.88 (s, 1H), 6.79 (d, J = 8.4 Hz, 1H), 4.65 (d, J = 15.0 Hz, 1H), 4.06 (d, J = 7.8 Hz, 1H), 3.87 (s, 3H), 3.50-3.40 (m, 3H), 2.76 (s, 1H), 2.06 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 153.8, 148.5, 134.7, 132.0, 130.2, 128.4, 128.1, 127.5, 122.5, 118.7, 112.8, 111.1, 110.4, 101.3, 61.9, 56.0, 50.8, 33.0, 32.9, 21.8; HRMS (ESI) for $\text{C}_{20}\text{H}_{21}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$ calcd 305.1648, found 305.1645.



12-chloro-1,2,3,9,10,14c-hexahydrobenzo[6,7]pyrrolo[1',2':1,2]azepino[4,3-b]indole

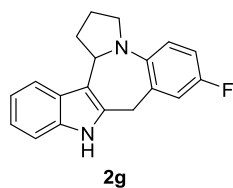
R_f = 0.30 (petroleum ether/EtOAc = 5:1), light yellow solid, mp: 171.4-173.2 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.74 (s, 1H), 7.27-7.20 (m, 3H), 7.16 (dd, J = 13.2, 7.6 Hz, 2H), 7.04-6.87 (m, 2H), 4.62 (d, J = 15.1 Hz, 1H), 4.00 (t, J = 7.5 Hz, 1H), 3.45-3.24 (m, 3H), 2.75-2.59 (m, 1H), 2.09-1.87 (m, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 148.4, 135.3, 134.4, 131.7, 128.1, 127.7, 126.8, 126.5, 122.6, 119.9, 119.2, 118.7, 113.2, 110.5, 61.6, 50.8, 33.0, 32.9, 21.8; HRMS (ESI) for $\text{C}_{19}\text{H}_{18}\text{ClN}_2$ $[\text{M}+\text{H}]^+$ calcd 309.1153, found 309.1143.



7-methyl-1,2,3,9,10,14c-hexahydrobenzo[6,7]pyrrolo[1',2':1,2]azepino[4,3-b]indole

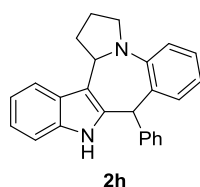
R_f = 0.35 (petroleum ether/EtOAc = 5:1), light yellow solid, mp: 107.1-109.3 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.76 (s, 1H), 7.36 (d, J = 4.0 Hz, 1H), 7.13-6.94 (m, 5H), 6.81 (s, 1H), 4.49 (d, J = 15.1 Hz, 1H), 3.99 (t, J = 7.8 Hz,

1H), 3.42-3.05 (m, 3H), 2.70 (d, $J = 6.8$ Hz, 1H), 2.23 (s, 3H), 2.00 (d, $J = 20.1$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 146.0, 135.1, 134.5, 132.0, 131.1, 129.2, 127.9, 121.1, 119.2, 118.5, 113.0, 110.7, 62.2, 51.0, 33.1, 32.8, 21.9, 20.7; HRMS (ESI) for $\text{C}_{20}\text{H}_{21}\text{N}_2$ $[\text{M}+\text{H}]^+$ calcd 289.1699, found 289.1691.



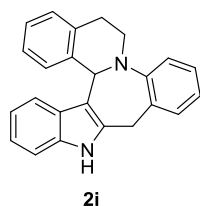
7-fluoro-1,2,3,9,10,14c-hexahydrobenzo[6,7]pyrrolo[1',2':1,2]azepino[4,3-b]indole

$R_f = 0.30$ (petroleum ether/EtOAc = 5:1), light yellow solid, mp: 153.1-154.9 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.77 (s, 1H), 7.39 (d, $J = 7.9$ Hz, 1H), 7.28 (d, $J = 8.0$ Hz, 1H), 7.13-7.03 (m, 3H), 6.88 (dd, $J = 11.2, 2.5$ Hz, 1H), 6.62 (td, $J = 8.2, 2.6$ Hz, 1H), 4.57 (d, $J = 15.1$ Hz, 1H), 4.11 (t, $J = 7.4$ Hz, 1H), 3.46 (d, $J = 15.2$ Hz, 1H), 3.36-3.25 (m, 2H), 2.75 (dt, $J = 7.8, 6.1$ Hz, 1H), 2.10-1.97 (m, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 162.2 (d, $J = 292.8$ Hz), 150.1, 135.0, 130.8, 130.0 (d, $J = 4.0$ Hz), 128.2 (d, $J = 9.1$ Hz), 127.7, 121.2, 119.4, 118.4, 112.6, 110.6, 108.2 (d, $J = 21.2$ Hz), 106.4 (d, $J = 23.2$ Hz), 61.9, 51.0, 33.1, 32.3, 21.7; ^{19}F NMR (470 MHz, CDCl_3) δ -115.02 (dd, $J = 18.4, 7.4$ Hz); HRMS (ESI) for $\text{C}_{19}\text{H}_{18}\text{FN}_2$ $[\text{M}+\text{H}]^+$ calcd 293.1449, found 293.1446.



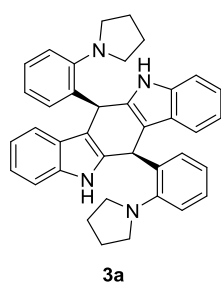
9-phenyl-1,2,3,9,10,14c-hexahydrobenzo[6,7]pyrrolo[1',2':1,2]azepino[4,3-b]indole

$R_f = 0.35$ (petroleum ether/EtOAc = 5:1), light yellow solid, mp: 244.7-246.4 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.84 (s, 1H), 7.46 (d, $J = 7.8$ Hz, 1H), 7.35 (d, $J = 7.3$ Hz, 1H), 7.30 (d, $J = 8.0$ Hz, 1H), 7.23 (d, $J = 7.7$ Hz, 1H), 7.18-7.05 (m, 8H), 6.99 (t, $J = 7.4$ Hz, 1H), 5.04 (s, 1H), 4.18 (t, $J = 8.3$ Hz, 1H), 3.27 (dd, $J = 17.4, 8.7$ Hz, 1H), 2.89 (t, $J = 8.1$ Hz, 1H), 2.77-2.64 (m, 1H), 2.05 (qd, $J = 12.2, 4.4$ Hz, 1H), 1.92-1.82 (m, 1H), 1.72-1.59 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 147.6, 143.0, 137.8, 135.7, 132.3, 129.4, 128.1, 127.8, 127.6, 127.4, 125.8, 122.4, 121.6, 119.9, 119.3, 119.0, 115.3, 110.6, 60.8, 51.1, 50.4, 33.2, 22.0; HRMS (ESI) for $\text{C}_{25}\text{H}_{23}\text{N}_2$ $[\text{M}+\text{H}]^+$ calcd 351.1856, found 351.1854.



5,12,13,17c-tetrahydro-6H-benzo[6,7]indolo[3',2':3,4]azepino[2,1-a]isoquinoline

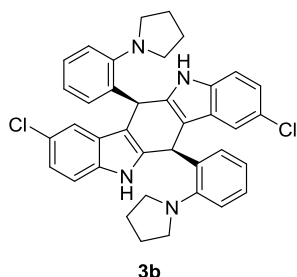
$R_f = 0.35$ (petroleum ether/EtOAc = 5:1), light yellow solid, mp: 89.9-91.4 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.96 (s, 1H), 7.28 (d, $J = 8.0$ Hz, 2H), 7.24-6.90 (m, 9H), 6.80 (t, $J = 7.3$ Hz, 1H), 5.61 (s, 1H), 4.33 (dd, $J = 24.9, 10.2$ Hz, 1H), 3.88-3.60 (m, 3H), 3.30 (dt, $J = 16.4, 8.2$ Hz, 1H), 3.08 (d, $J = 15.7$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 150.1, 139.4, 137.3, 136.2, 134.8, 134.7, 129.7, 128.6, 127.5, 127.0, 126.9, 126.7, 125.8, 122.2, 121.9, 121.0, 119.9, 118.5, 110.8, 110.4, 61.0, 51.1, 32.6, 29.9; HRMS (ESI) for $\text{C}_{24}\text{H}_{21}\text{N}_2$ $[\text{M}+\text{H}]^+$ calcd 337.1699, found 337.1692.



(6R,12R)-6,12-bis(2-(pyrrolidin-1-yl)phenyl)-5,6,11,12-tetrahydroindolo[3,2-b]carbazole

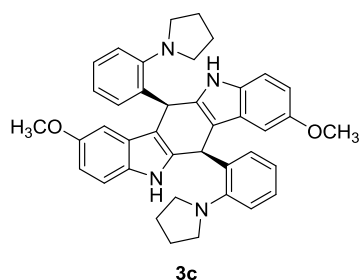
Major: $R_f = 0.20$ (petroleum ether/EtOAc = 20:1), light yellow solid, mp: 261.1-263.2 °C; ^1H NMR (400 MHz, CDCl_3) δ 9.62 (s, 2H), 7.32-7.27 (m, 4H), 7.15-7.05 (m, 6H), 6.91 (t, $J = 7.4$ Hz, 2H), 6.77-6.68 (m, 4H), 6.14 (s, 2H), 3.94-3.73 (m, 4H), 3.35-3.17 (m, 4H), 2.24-2.10 (m, 8H); ^{13}C NMR (101 MHz, CDCl_3) δ 148.4, 140.0, 137.8, 136.4, 129.5, 127.5, 126.2, 124.1, 121.1, 119.1,

119.0, 110.8, 107.4, 53.1, 34.4, 24.8; HRMS (ESI) for $C_{38}H_{37}N_4$ $[M+H]^+$ calcd 549.3013, found 549.3012. Minor: R_f = 0.25 (petroleum ether/EtOAc = 20:1), white solid, mp: 234.6-236.4 °C; 1H NMR (400 MHz, $CDCl_3$) δ 9.11 (s, 1H), 7.29 (d, J = 8.0 Hz, 1H), 7.24 (d, J = 8.0 Hz, 1H), 7.15 (t, J = 7.4 Hz, 1H), 7.06 (dd, J = 11.7, 6.5 Hz, 2H), 6.89 (t, J = 7.5 Hz, 2H), 6.77 (t, J = 7.2 Hz, 1H), 6.23 (s, 1H), 3.74 (s, 2H), 3.32 (s, 2H), 2.12 (d, J = 6.5 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.6, 139.0, 137.5, 136.6, 129.9, 127.6, 126.4, 123.9, 121.1, 119.3, 119.0, 110.8, 108.6, 53.3, 34.3, 24.8; HRMS (ESI) for $C_{38}H_{37}N_4$ $[M+H]^+$ calcd 549.3013, found 549.3015.



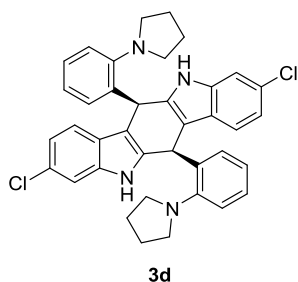
(6R,12R)-2,8-dichloro-6,12-bis(2-(pyrrolidin-1-yl)phenyl)-5,6,11,12-tetrahydroindolo[3,2-b]carbazole

Major: R_f = 0.20 (petroleum ether/EtOAc = 20:1), light yellow solid, mp: 224.0-226.1 °C; 1H NMR (400 MHz, $CDCl_3$) δ 9.87 (s, 2H), 7.33 (d, J = 7.4 Hz, 2H), 7.24-7.14 (m, 4H), 7.11-7.04 (m, 4H), 6.78-6.69 (m, 4H), 6.10 (s, 2H), 3.85 (dd, J = 15.1, 6.2 Hz, 4H), 3.33-3.21 (m, 4H), 2.32-2.10 (m, 8H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.4, 141.3, 137.0, 134.8, 129.2, 127.8, 127.3, 124.6, 124.3, 121.5, 119.4, 118.4, 111.9, 107.1, 53.1, 34.4, 24.8; HRMS (ESI) for $C_{38}H_{35}Cl_2N_4$ $[M+H]^+$ calcd 617.2233, found 617.2218.



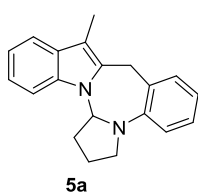
(6R,12R)-2-methoxy-6-(4-methoxy-2-(pyrrolidin-1-yl)phenyl)-12-(2-(pyrrolidin-1-yl)phenyl)-5,6,11,12-tetrahydroindolo[3,2-b]carbazole

Major: R_f = 0.25 (petroleum ether/EtOAc = 20:1), light yellow solid, mp: 161.9-163.2 °C; 1H NMR (400 MHz, $CDCl_3$) δ 9.43 (s, 2H), 7.35 (d, J = 7.7 Hz, 2H), 7.26-7.16 (m, 4H), 6.89 (d, J = 6.8 Hz, 2H), 6.81 (dt, J = 8.0, 4.1 Hz, 4H), 6.65 (d, J = 2.2 Hz, 2H), 6.16 (s, 2H), 3.92-3.80 (m, 4H), 3.73 (d, J = 8.7 Hz, 6H), 3.34 (d, J = 8.8 Hz, 4H), 2.30-2.10 (m, 8H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.5, 148.5, 140.6, 137.6, 131.7, 129.6, 127.5, 126.9, 124.2, 119.1, 111.3, 110.0, 107.8, 102.4, 56.0, 53.2, 34.5, 24.8; HRMS (ESI) for $C_{40}H_{41}N_4O_2$ $[M+H]^+$ calcd 609.3224, found 609.3214.



(6R,12R)-3,9-dichloro-6,12-bis(2-(pyrrolidin-1-yl)phenyl)-5,6,11,12-tetrahydroindolo[3,2-b]carbazole

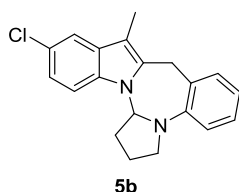
Major: R_f = 0.20 (petroleum ether/EtOAc = 20:1), light yellow solid, mp: 118.2-120.4 °C; 1H NMR (400 MHz, $CDCl_3$) δ 9.83 (s, 2H), 7.37-7.30 (m, 4H), 7.18 (t, J = 7.3 Hz, 2H), 7.04 (dd, J = 8.2, 3.8 Hz, 2H), 6.94 (dd, J = 8.3, 1.8 Hz, 2H), 6.80-6.70 (m, 4H), 6.13 (d, J = 3.5 Hz, 2H), 3.86 (d, J = 6.9 Hz, 4H), 3.34-3.22 (m, 4H), 2.33-2.09 (m, 8H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.4, 140.5, 137.2, 136.8, 129.3, 127.8, 127.1, 124.8, 124.3, 119.8, 119.7, 119.4, 111.0, 107.4, 53.1, 34.4, 24.8; HRMS (ESI) for $C_{38}H_{35}Cl_2N_4$ $[M+H]^+$ calcd 617.2233, found 617.2228.



10-methyl-1,2,3,15a-tetrahydro-9H-benzo[4,5]pyrrolo[2',1':2,3][1,3]diazepino[1,7-a]indole

R_f = 0.15 (petroleum ether/EtOAc = 10:1), light yellow solid, mp: 124.1-126.2 °C; 1H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 7.4 Hz, 1H), 7.31 (d, J = 7.9 Hz, 1H),

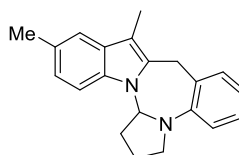
7.18-7.02 (m, 4H), 6.81 (t, $J = 7.4$ Hz, 1H), 6.75 (d, $J = 8.0$ Hz, 1H), 5.92 (dd, $J = 7.5, 3.4$ Hz, 1H), 4.35 (d, $J = 15.6$ Hz, 1H), 4.18 (d, $J = 15.6$ Hz, 1H), 3.40-3.26 (m, 2H), 2.78-2.68 (m, 1H), 2.56 (ddt, $J = 13.6, 10.4, 7.9$ Hz, 1H), 2.27-2.20 (m, 4H), 2.15-2.08 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 145.8, 134.8, 134.4, 129.7, 129.5, 128.4, 127.8, 121.1, 120.7, 118.9, 118.6, 116.1, 110.2, 106.6, 73.4, 48.7, 31.5, 31.0, 22.6, 8.6; HRMS (ESI) for $\text{C}_{20}\text{H}_{21}\text{N}_2$ $[\text{M}+\text{H}]^+$ calcd 289.1699, found 289.1691.



5b

12-chloro-10-methyl-1,2,3,15a-tetrahydro-9H-benzo[4,5]pyrrolo[2',1':2,3][1,3]diazepino[1,7-a]indole

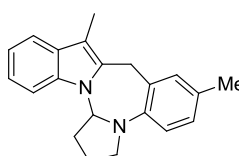
$R_f = 0.15$ (petroleum ether/EtOAc = 10:1), light yellow solid, mp: 181.4-183.0 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.45 (d, $J = 1.9$ Hz, 1H), 7.24-7.14 (m, 3H), 7.07 (dd, $J = 8.8, 2.0$ Hz, 1H), 6.87 (t, $J = 7.4$ Hz, 1H), 6.80 (d, $J = 8.0$ Hz, 1H), 5.89 (dd, $J = 7.5, 3.4$ Hz, 1H), 4.34 (d, $J = 15.6$ Hz, 1H), 4.19 (d, $J = 15.6$ Hz, 1H), 3.45-3.29 (m, 2H), 2.73-2.51 (m, 2H), 2.33-2.12 (m, 5H); ^{13}C NMR (101 MHz, CDCl_3) δ 145.6, 136.3, 132.8, 130.7, 129.7, 128.2, 127.9, 124.6, 121.0, 118.0, 116.2, 111.0, 106.3, 73.4, 48.7, 31.5, 30.9, 22.5, 8.5; HRMS (ESI) for $\text{C}_{20}\text{H}_{20}\text{ClN}_2$ $[\text{M}+\text{H}]^+$ calcd 323.1310, found 323.1307.



5c

10,12-dimethyl-1,2,3,15a-tetrahydro-9H-benzo[4,5]pyrrolo[2',1':2,3][1,3]diazepino[1,7-a]indole

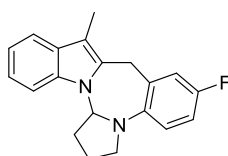
$R_f = 0.20$ (petroleum ether/EtOAc = 10:1), light yellow solid, mp: 117.3-119.5 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.29 (s, 1H), 7.21-7.09 (m, 3H), 6.96 (d, $J = 8.4$ Hz, 1H), 6.82 (t, $J = 7.4$ Hz, 1H), 6.72 (d, $J = 8.0$ Hz, 1H), 5.91 (dd, $J = 7.6, 3.1$ Hz, 1H), 4.36 (d, $J = 15.6$ Hz, 1H), 4.15 (d, $J = 15.7$ Hz, 1H), 3.38-3.22 (m, 2H), 2.80-2.67 (m, 1H), 2.54-2.43 (m, 4H), 2.32-2.22 (m, 4H), 2.12-2.04 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 145.9, 135.1, 132.9, 129.9, 129.8, 128.1, 127.8, 122.6, 120.5, 118.5, 115.9, 110.0, 106.2, 73.2, 48.7, 31.3, 31.1, 22.7, 21.5, 8.7; HRMS (ESI) for $\text{C}_{21}\text{H}_{23}\text{N}_2$ $[\text{M}+\text{H}]^+$ calcd 303.1856, found 303.1856.



5d

7,10-dimethyl-1,2,3,15a-tetrahydro-9H-benzo[4,5]pyrrolo[2',1':2,3][1,3]diazepino[1,7-a]indole

$R_f = 0.20$ (petroleum ether/EtOAc = 10:1), light yellow solid, mp: 77.6-79.1 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.46 (d, $J = 7.4$ Hz, 1H), 7.25 (d, $J = 7.8$ Hz, 1H), 7.10-7.03 (m, 2H), 7.00 (s, 1H), 6.94 (d, $J = 8.0$ Hz, 1H), 6.76 (d, $J = 8.0$ Hz, 1H), 5.69-5.56 (m, 1H), 4.19 (q, $J = 15.1$ Hz, 2H), 3.39-3.25 (m, 2H), 2.62-2.48 (m, 2H), 2.30 (s, 3H), 2.24 (s, 3H), 2.21-2.15 (m, 1H), 2.09-2.03 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 143.4, 134.8, 134.2, 131.2, 130.6, 130.0, 129.5, 128.1, 120.9, 118.9, 118.5, 117.0, 110.1, 106.2, 74.3, 48.9, 32.2, 30.7, 22.2, 20.7, 8.7; HRMS (ESI) for $\text{C}_{21}\text{H}_{23}\text{N}_2$ $[\text{M}+\text{H}]^+$ calcd 303.1856, found 303.1849.

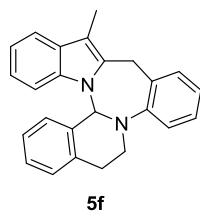


5e

7-fluoro-10-methyl-1,2,3,15a-tetrahydro-9H-benzo[4,5]pyrrolo[2',1':2,3][1,3]diazepino[1,7-a]indole

$R_f = 0.15$ (petroleum ether/EtOAc = 10:1), light yellow solid, mp: 160.4-162.3 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.54-7.45 (m, 1H), 7.36 (d, $J = 8.2$ Hz, 1H), 7.19-6.97 (m, 3H), 6.43 (td, $J = 8.2, 2.5$ Hz, 1H), 6.30 (dd, $J = 11.6, 2.5$ Hz, 1H), 6.19 (dd, $J = 7.7, 2.2$ Hz, 1H), 4.42 (d, $J = 16.1$ Hz, 1H), 4.04 (d, $J = 16.1$ Hz, 1H), 3.30-3.18 (m, 2H), 3.01-2.88 (m, 1H), 2.56-2.32 (m, 2H), 2.28 (s, 3H), 2.19-2.12 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 162.8 (d, $J = 243.4$ Hz), 147.1 (d, $J = 10.1$ Hz), 135.6, 134.0, 131.0 (d, $J = 10.1$ Hz), 129.6, 121.4, 121.1, 119.0, 188.8, 110.3, 107.0, 105.3 (d, $J = 21.2$ Hz), 102.1 (d, $J = 25.3$ Hz), 72.2, 48.6, 30.5,

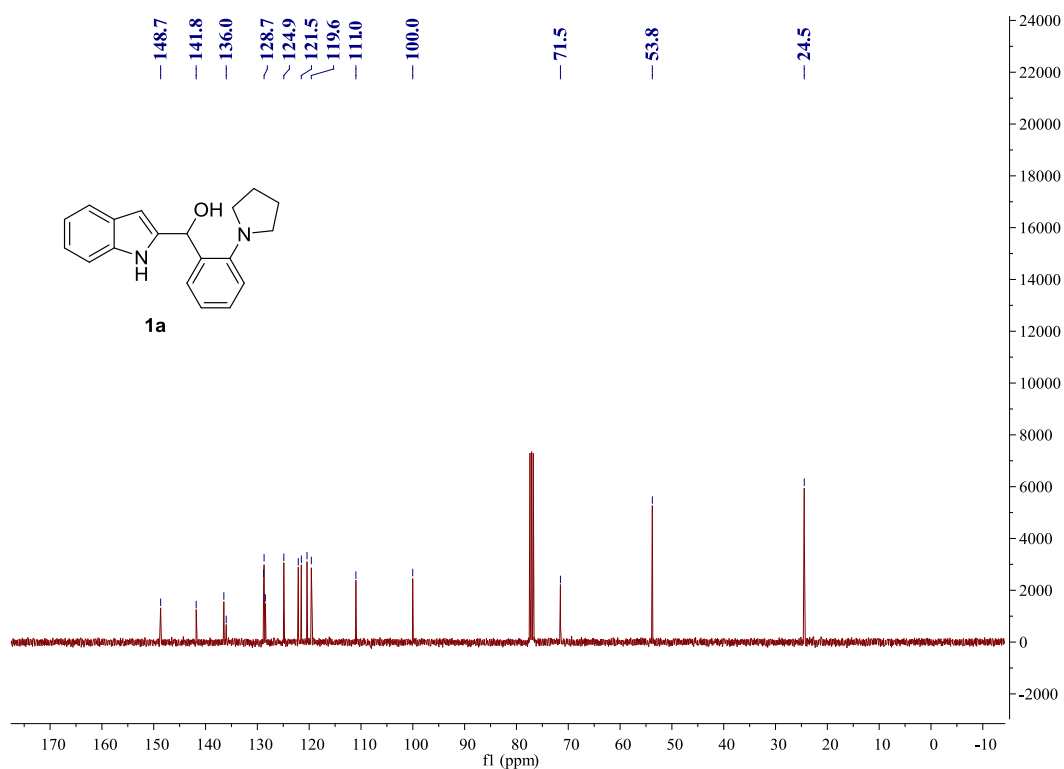
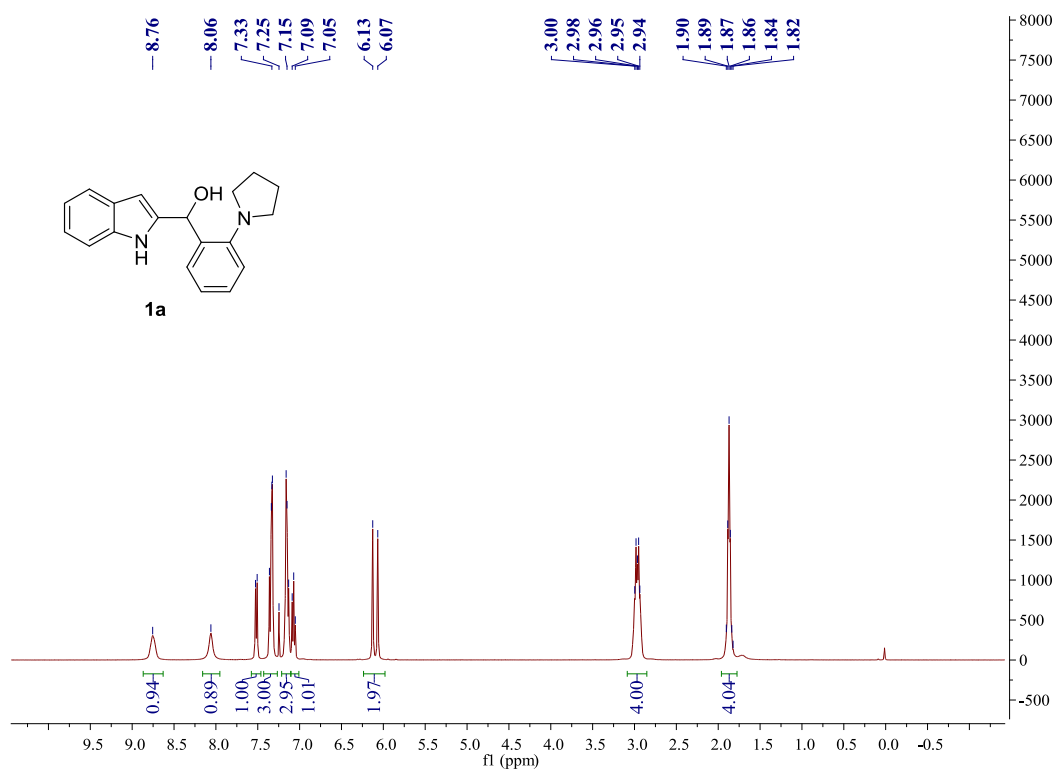
22.9, 8.6; ^{19}F NMR (470 MHz, CDCl_3) δ -115.00 (dt, J = 11.5, 7.4 Hz); HRMS (ESI) for $\text{C}_{20}\text{H}_{20}\text{FN}_2$ $[\text{M}+\text{H}]^+$ calcd 307.1605, found 307.1598.

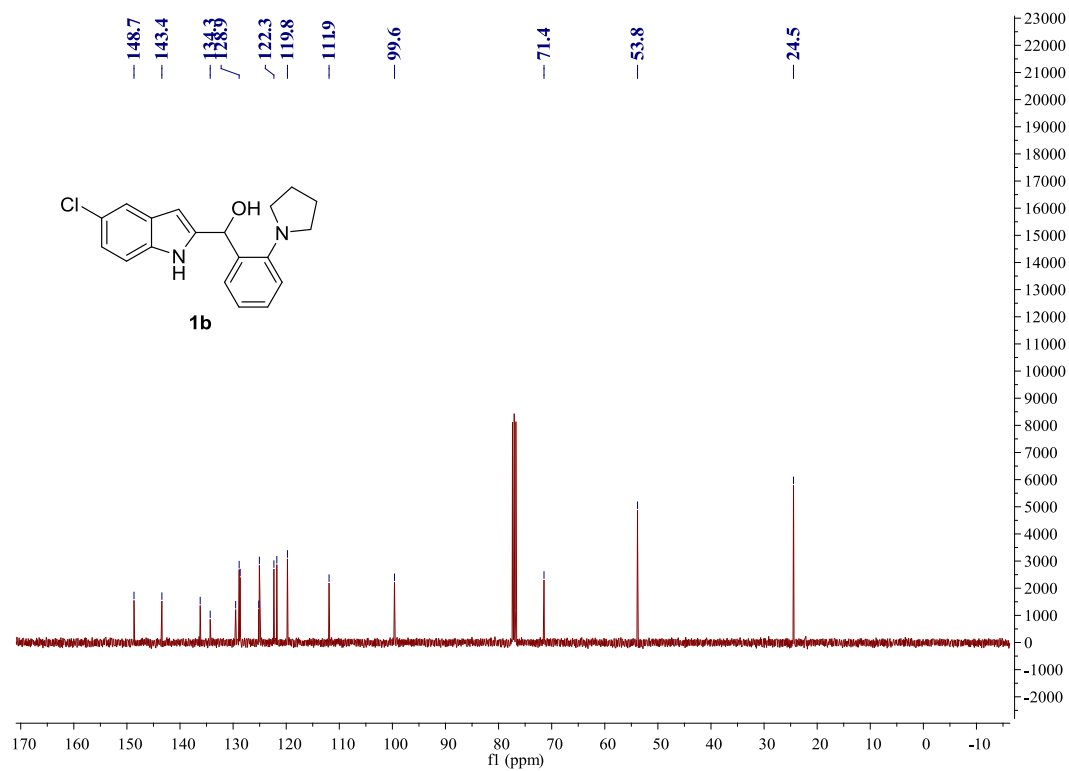
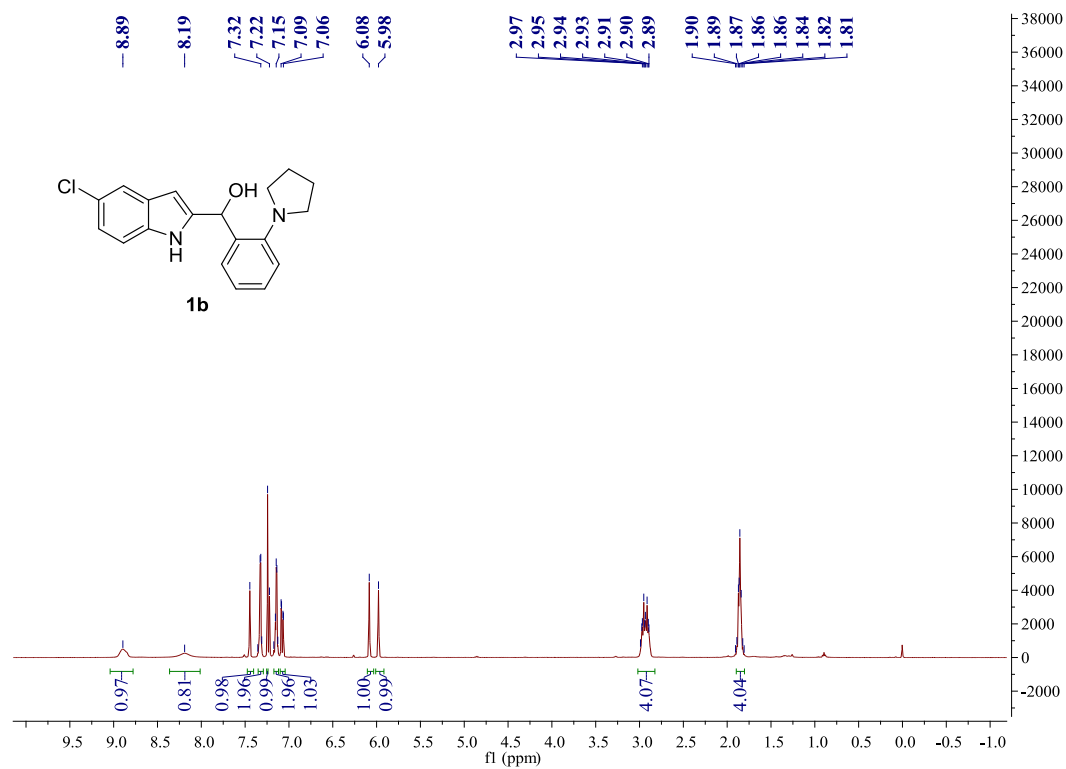


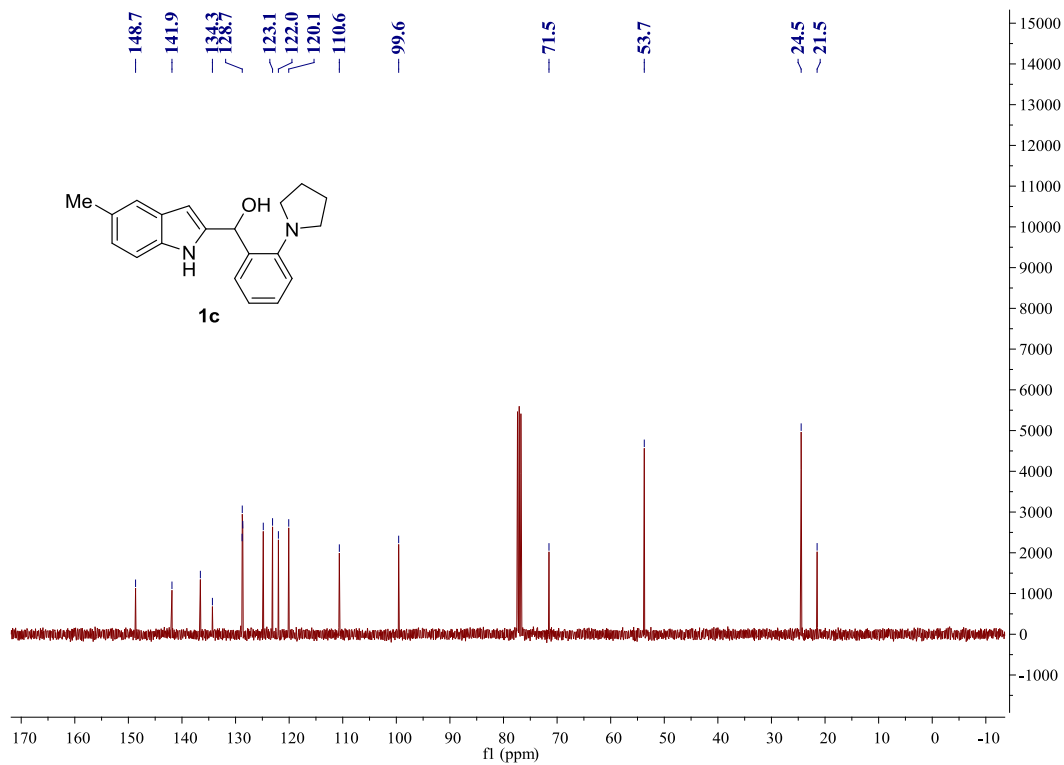
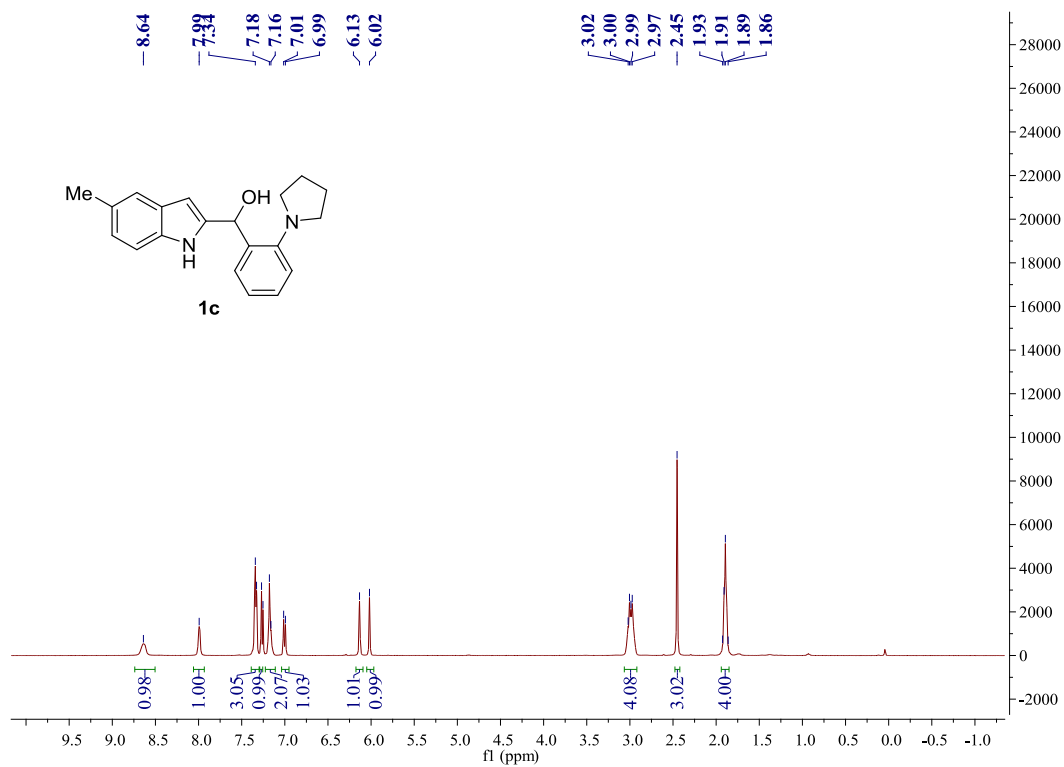
13-methyl-5,18a-dihydro-6H,12H-benzo[6,7]indolo[1',2':3,4][1,3]diazepino[2,1-a]isoquinoline

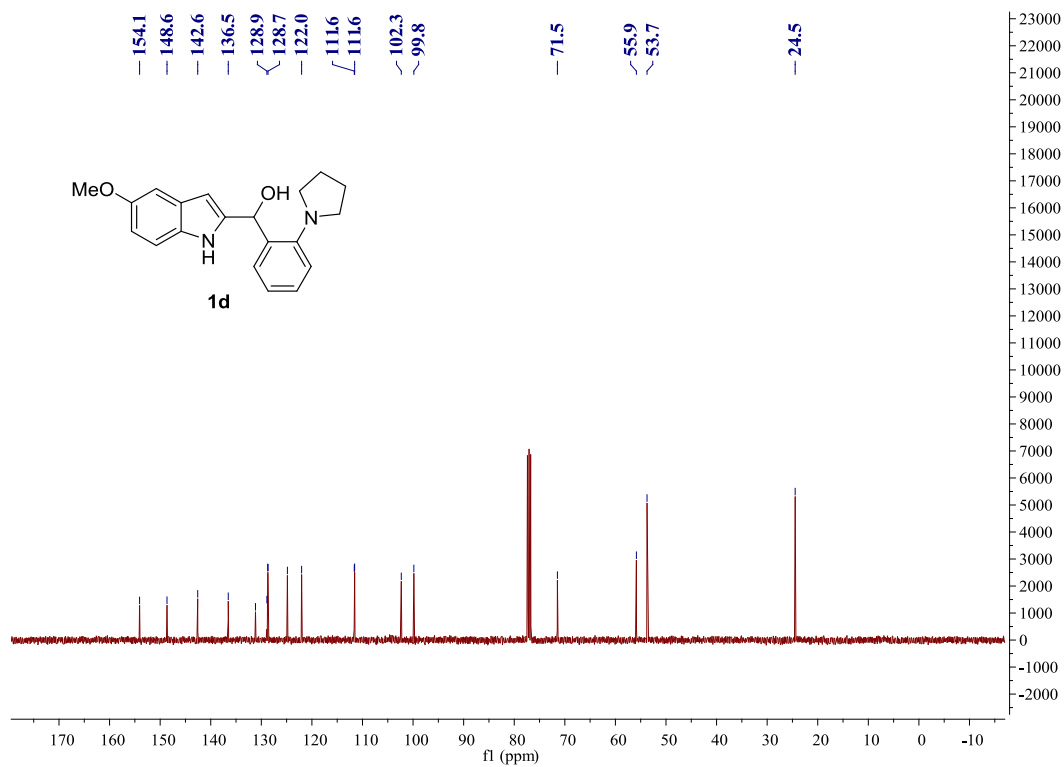
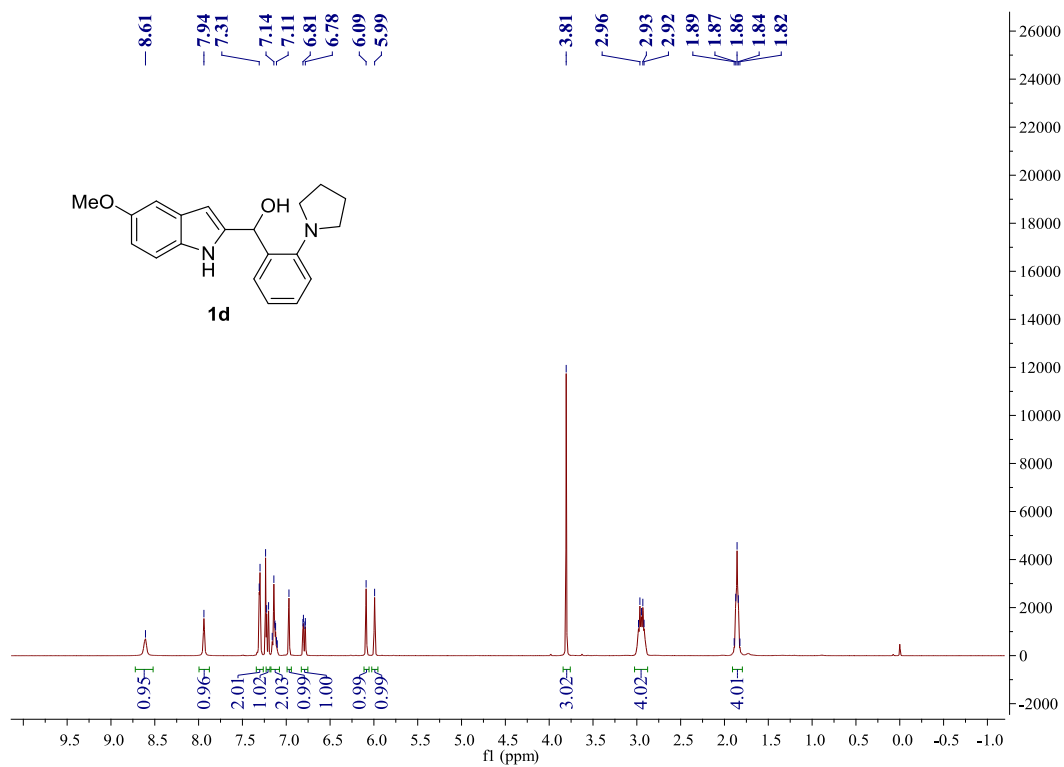
R_f = 0.15 (petroleum ether/EtOAc = 10:1), light yellow solid, mp: 117.3-119.6 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.69-7.16 (m, 8H), 7.07-6.80 (m, 4H), 5.82 (s, 1H), 4.71 (d, J = 16.8 Hz, 1H), 4.21 (d, J = 16.7 Hz, 1H), 3.60 (d, J = 10.8 Hz, 1H), 3.46-3.21 (m, 2H), 2.97 (d, J = 15.8 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 148.7, 137.6, 136.9, 135.6, 132.7, 131.5, 129.5, 129.3, 128.9, 128.8, 128.0, 126.8, 125.7, 121.8, 121.3, 121.0, 118.8, 118.4, 110.8, 107.4, 69.1, 46.7, 31.4, 30.1, 8.8; HRMS (ESI) for $\text{C}_{25}\text{H}_{23}\text{N}_2$ $[\text{M}+\text{H}]^+$ calcd 351.1856, found 351.1849.

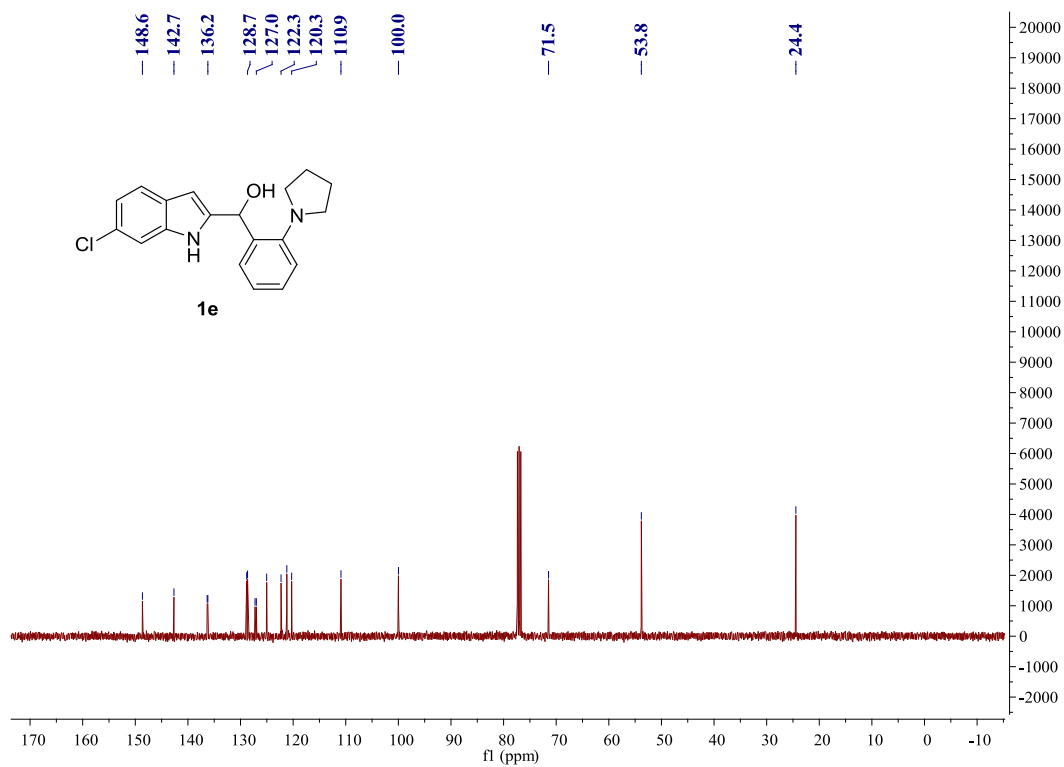
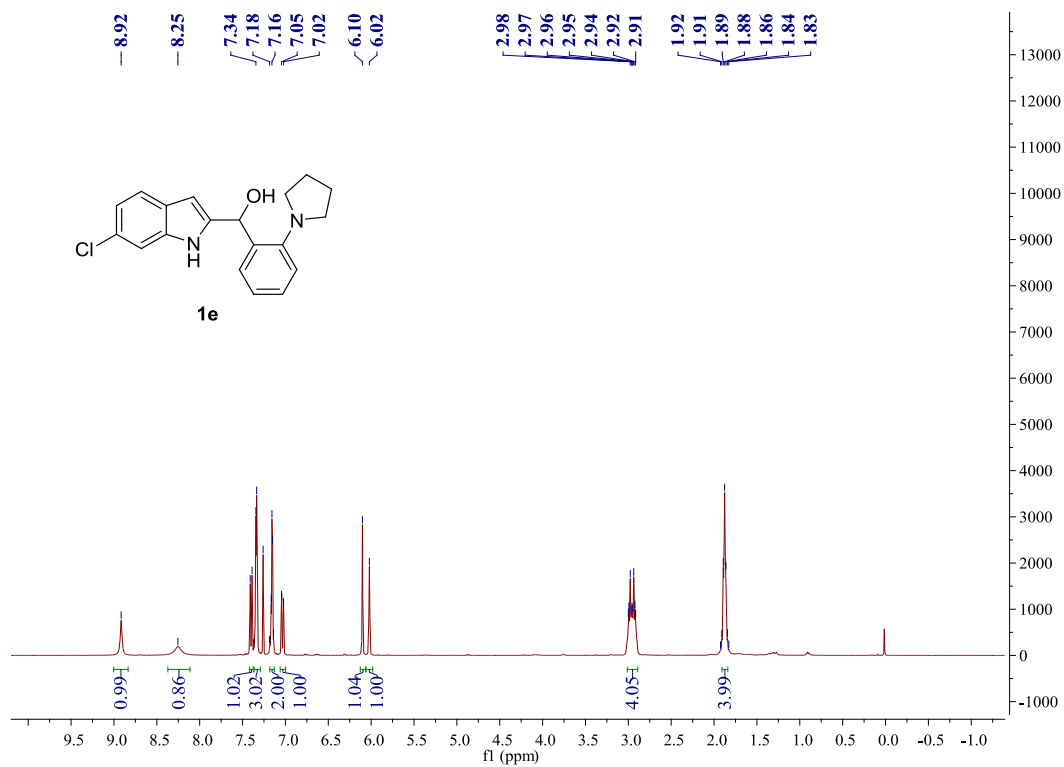
5. Copies of ^1H and ^{13}C NMR Spectra

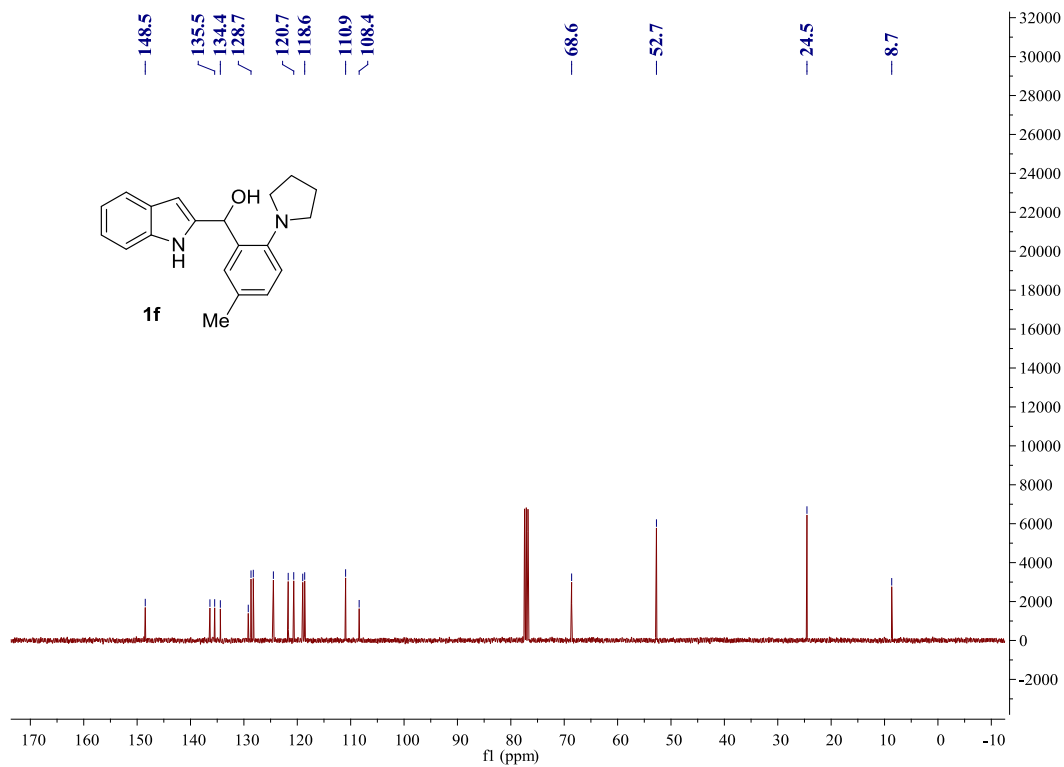
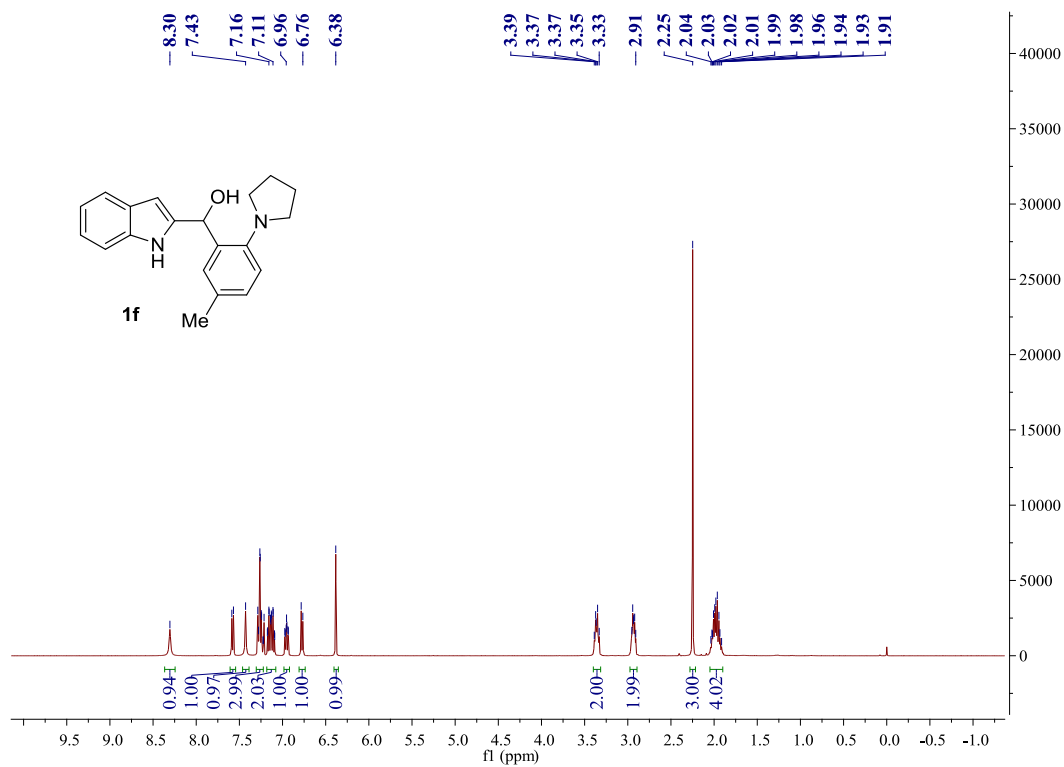


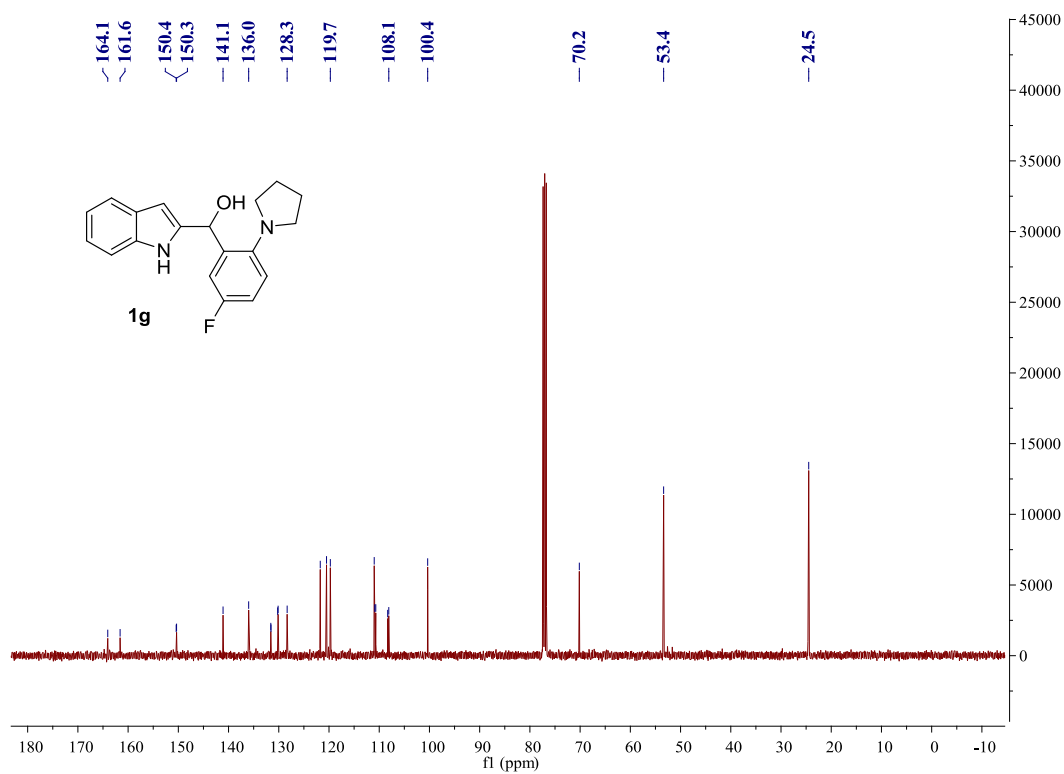
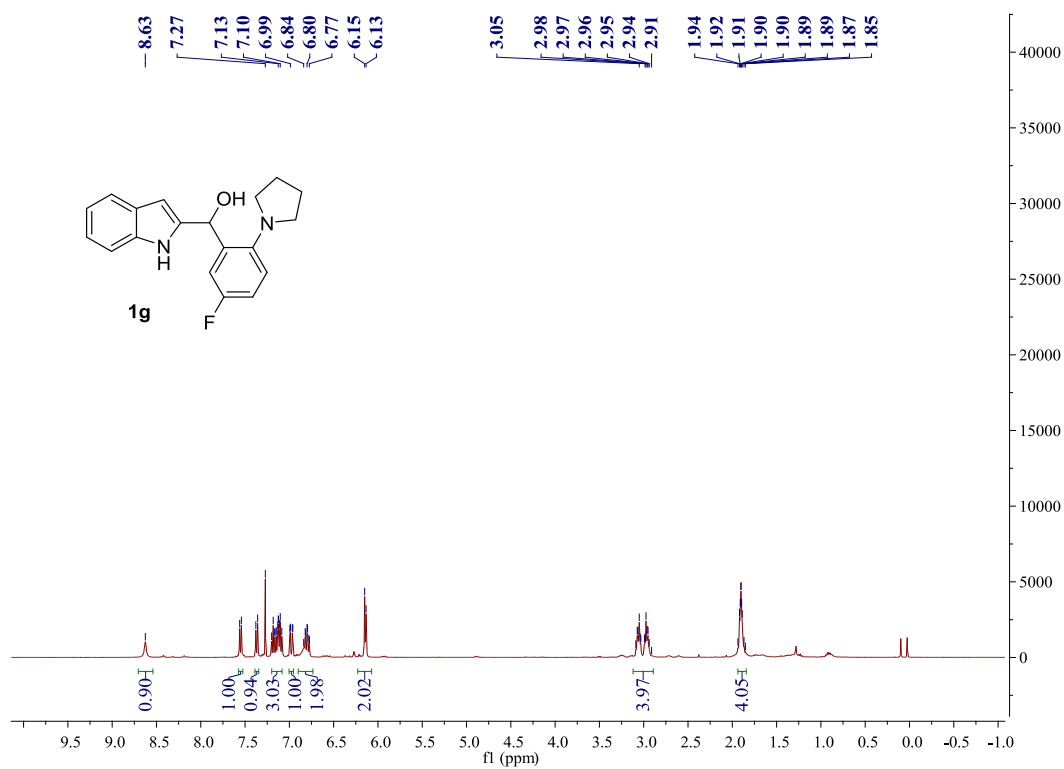


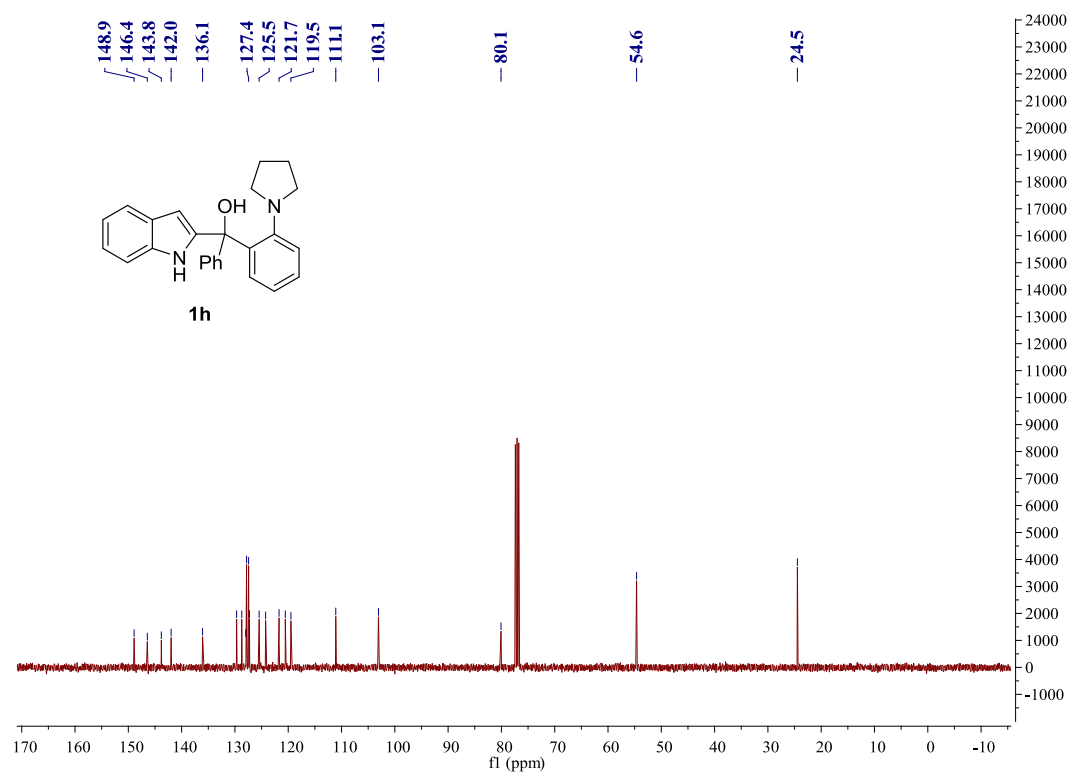
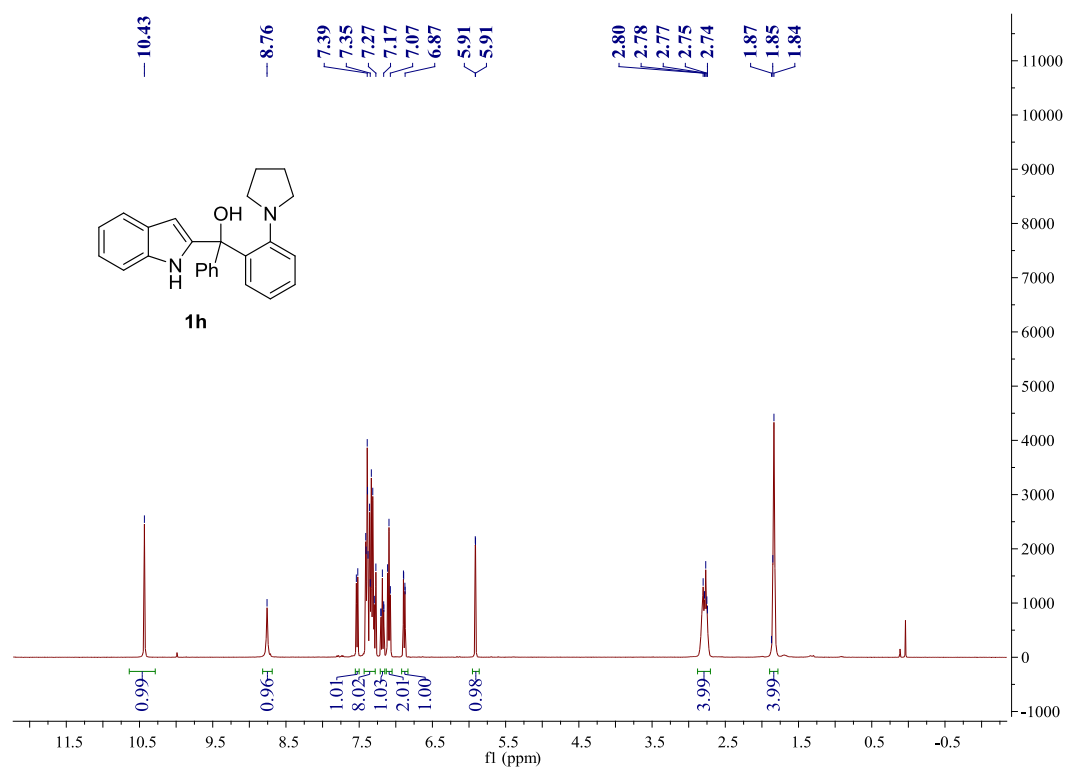


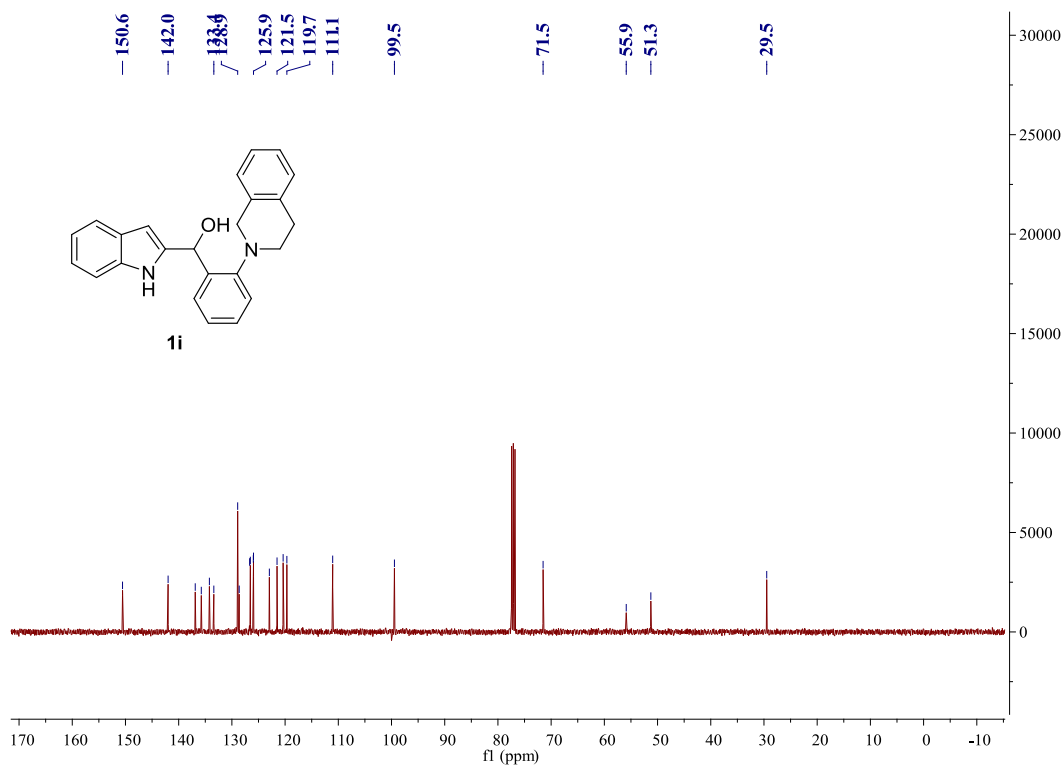
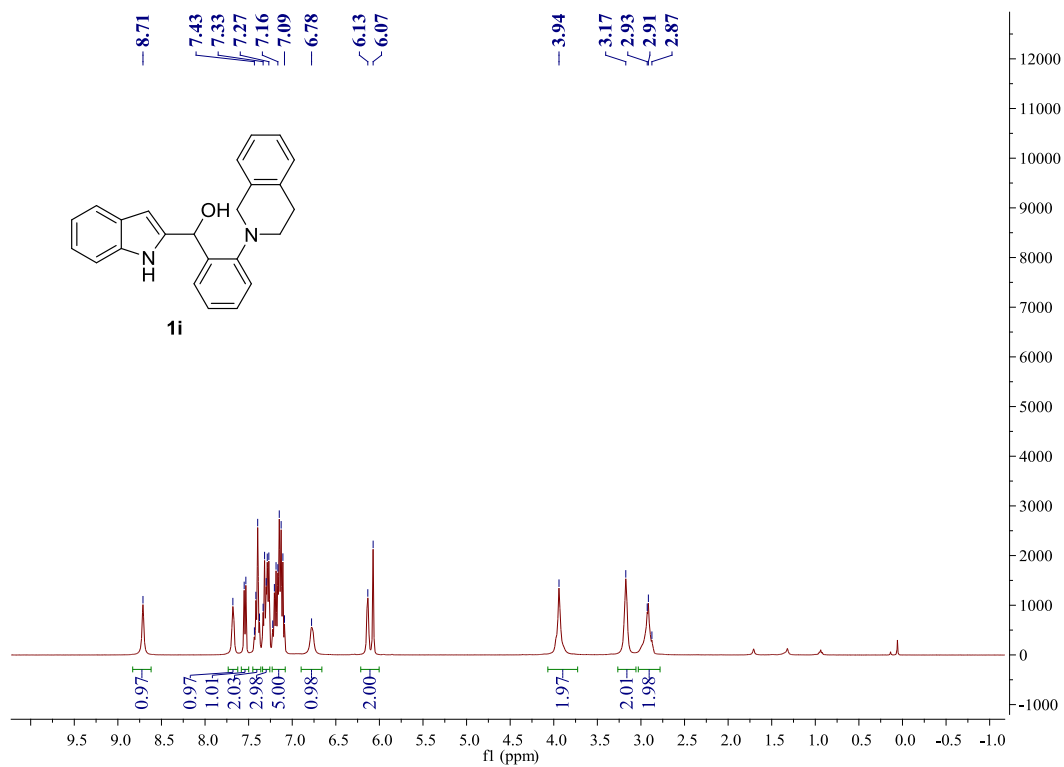


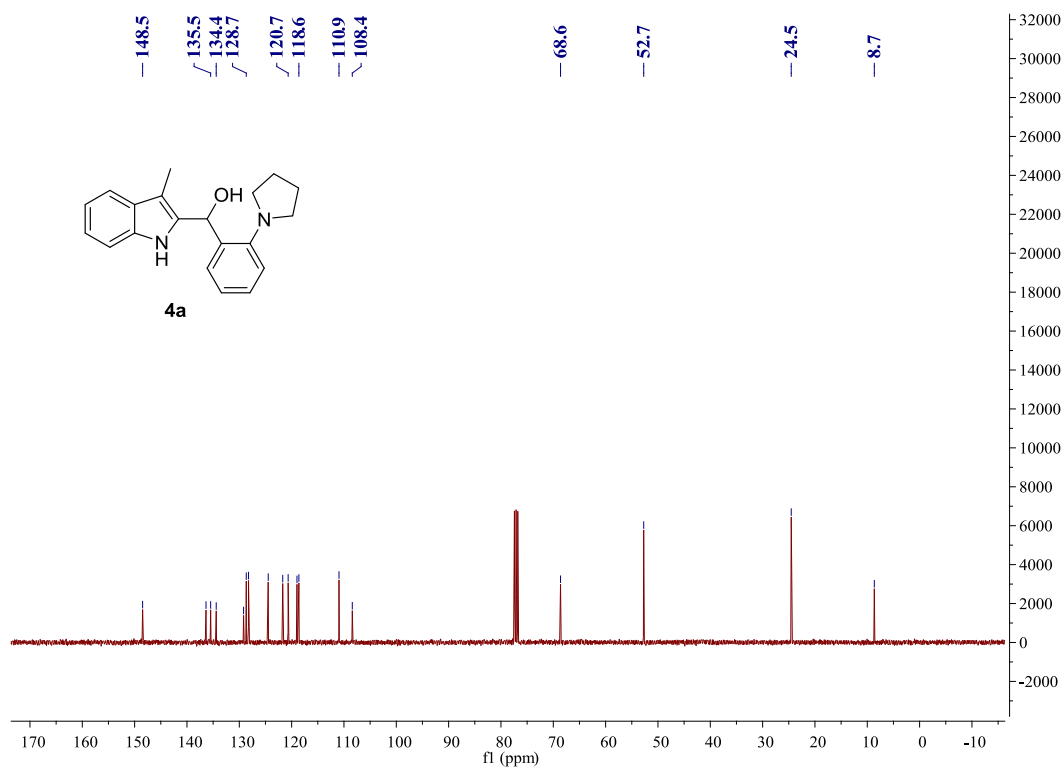
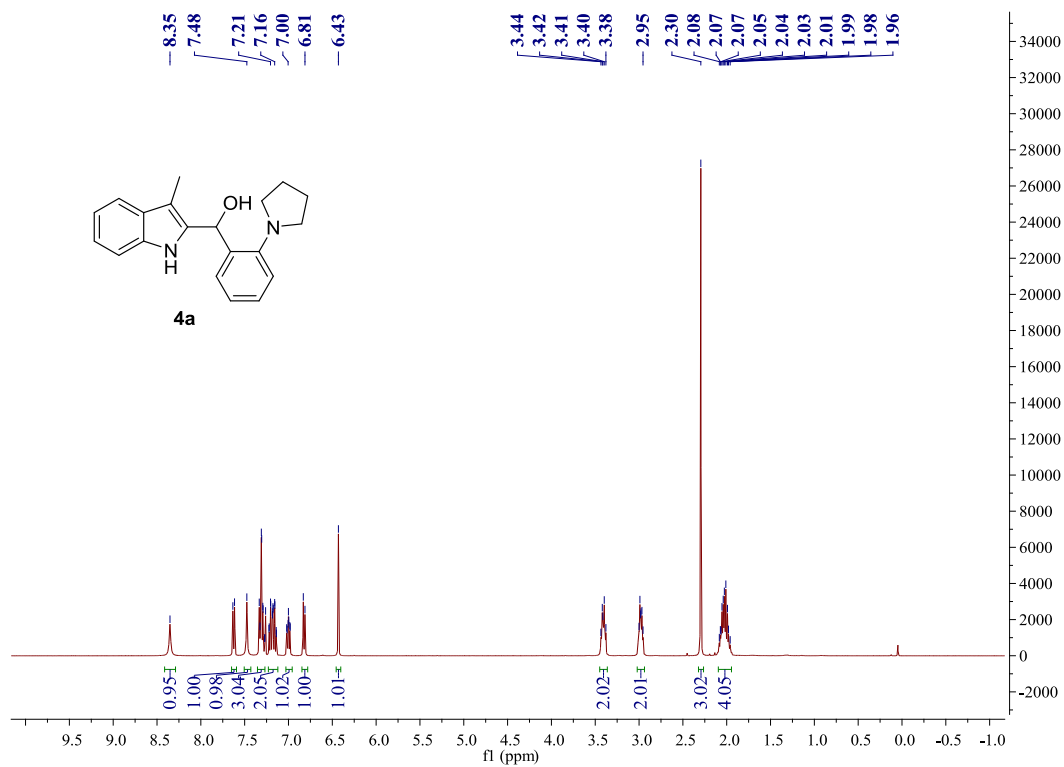


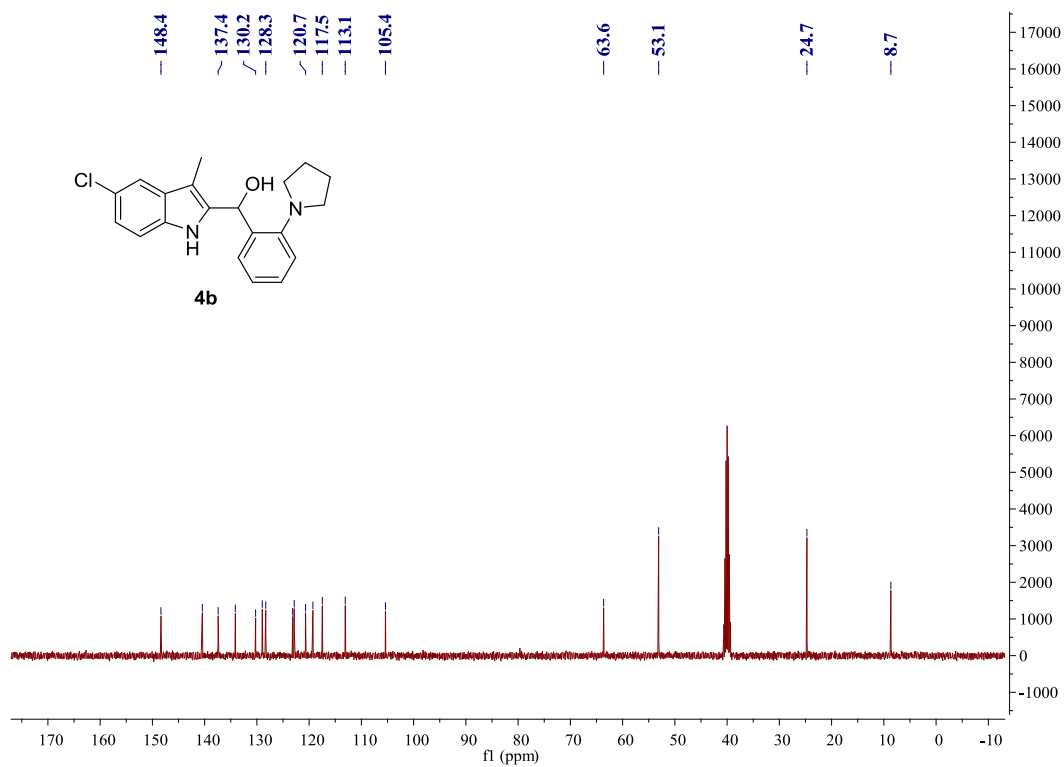
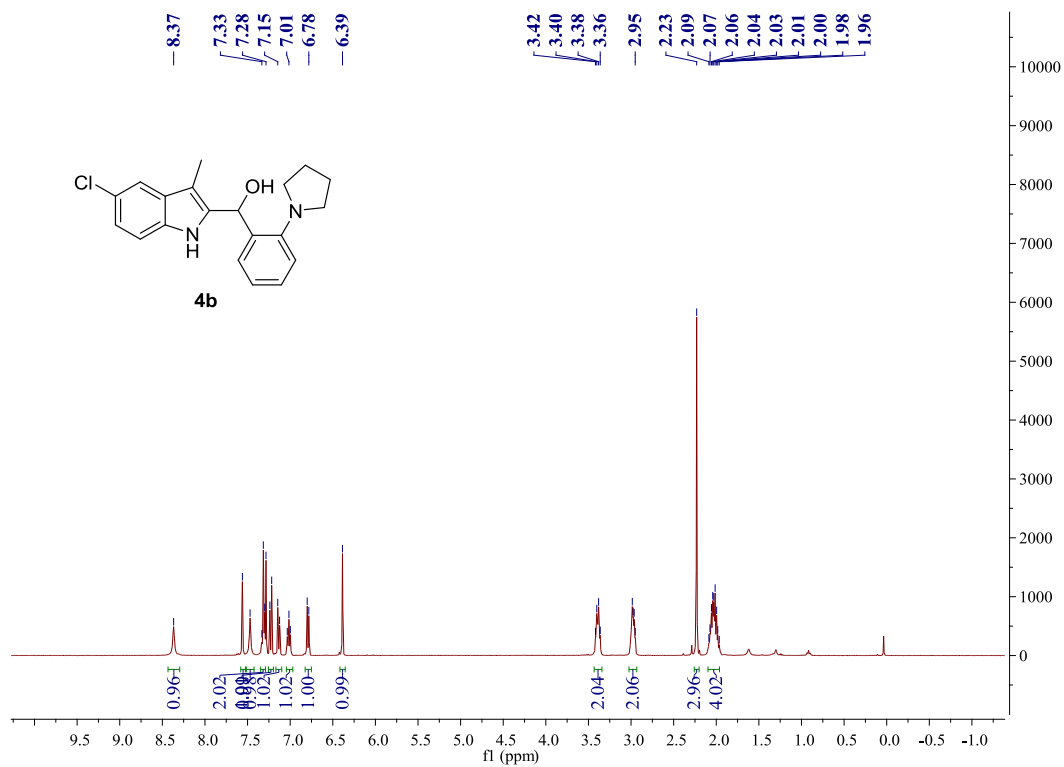


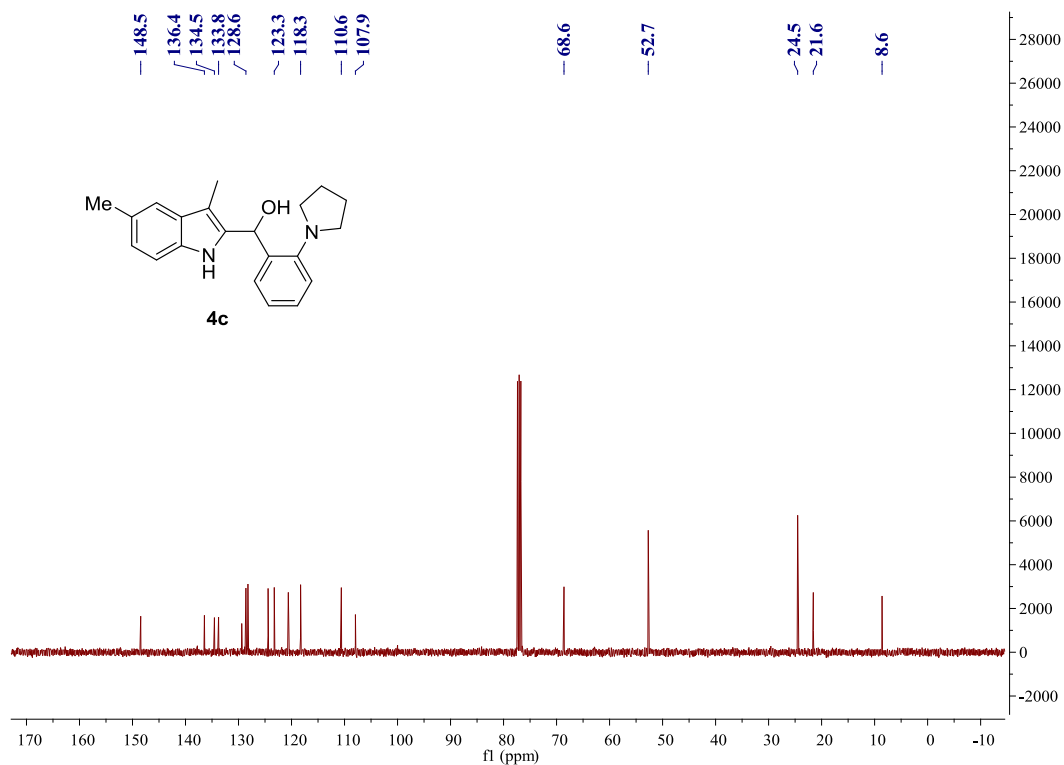
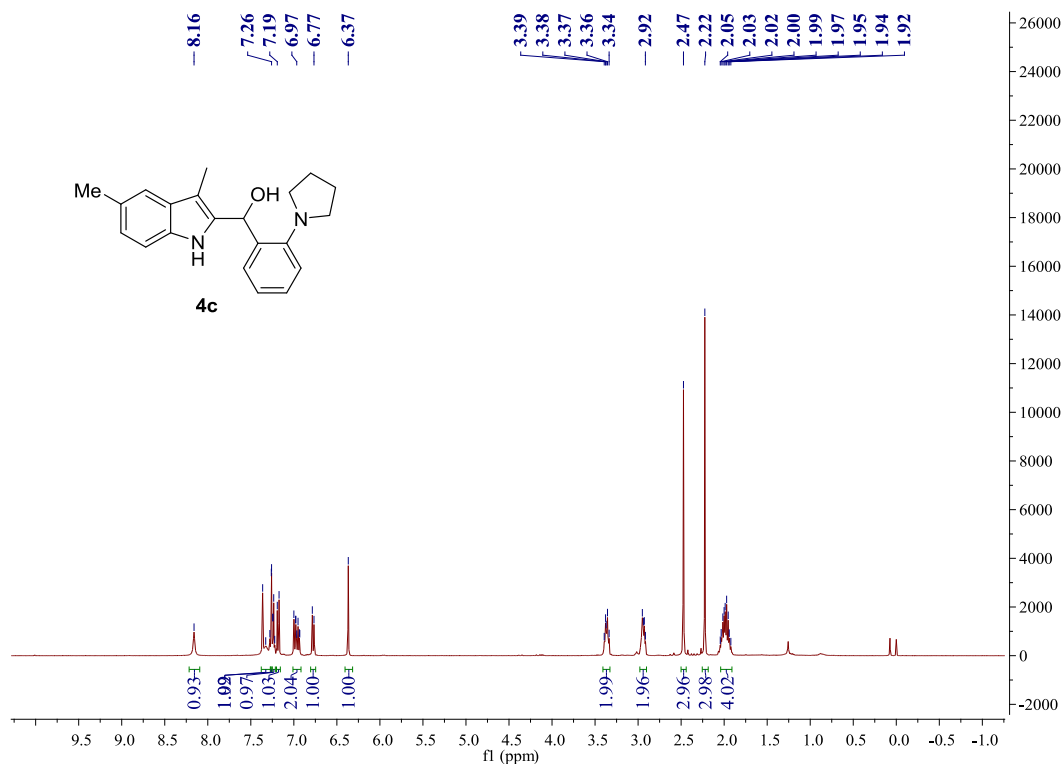


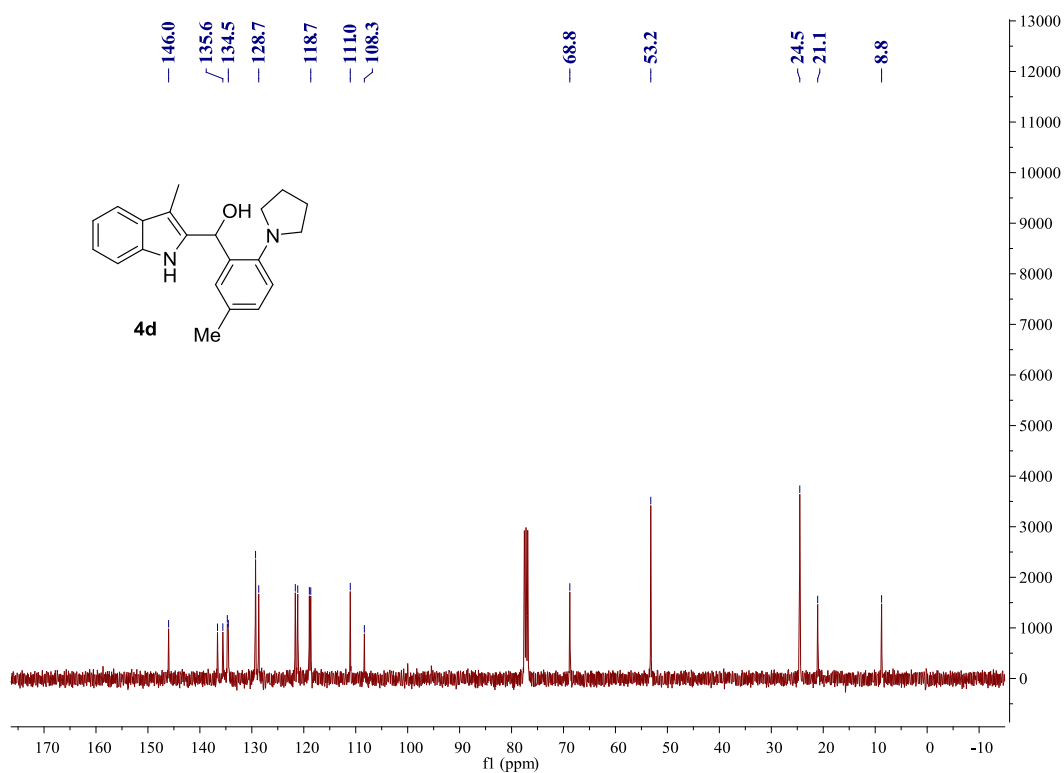
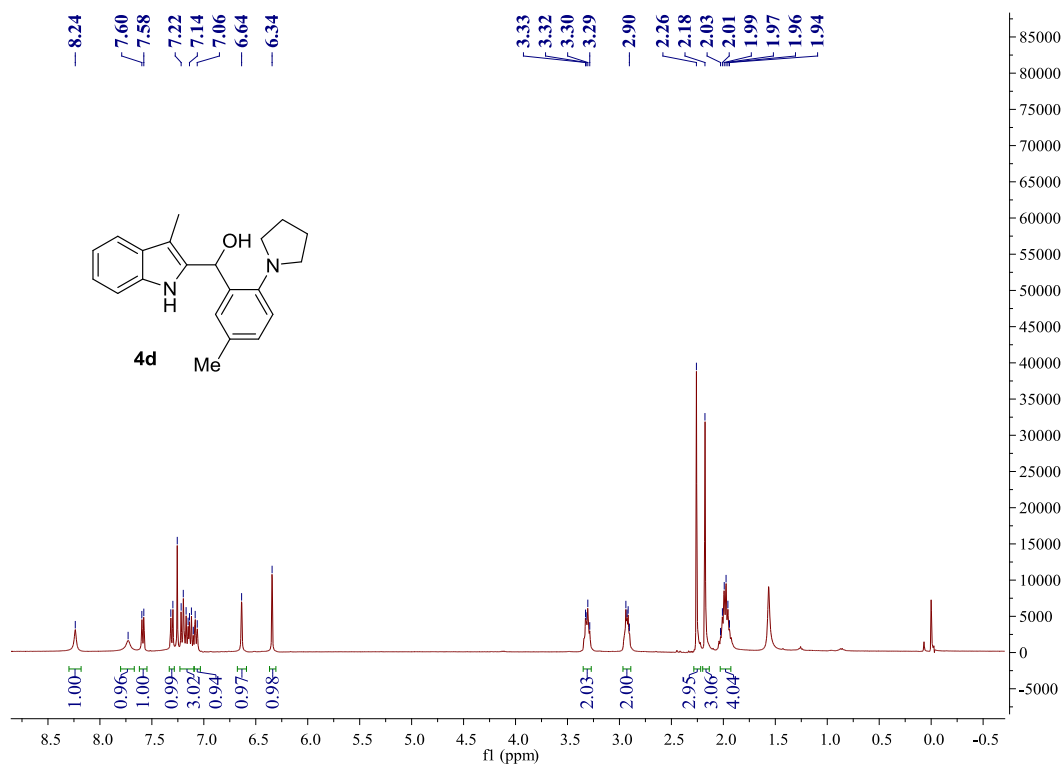


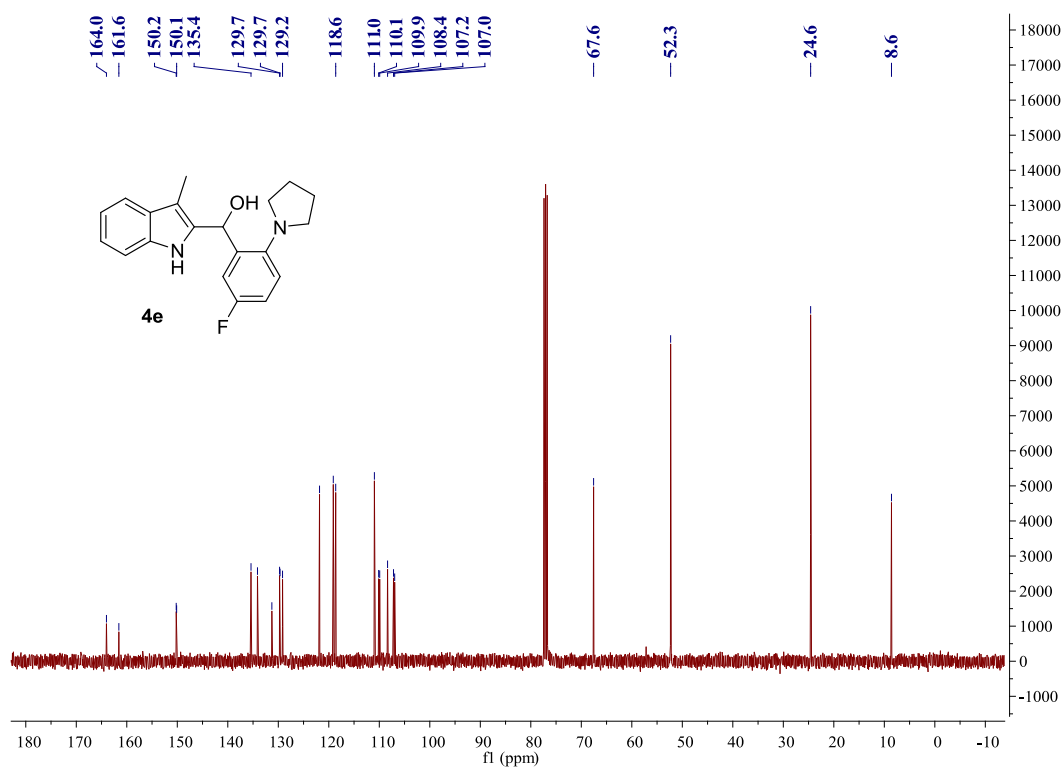
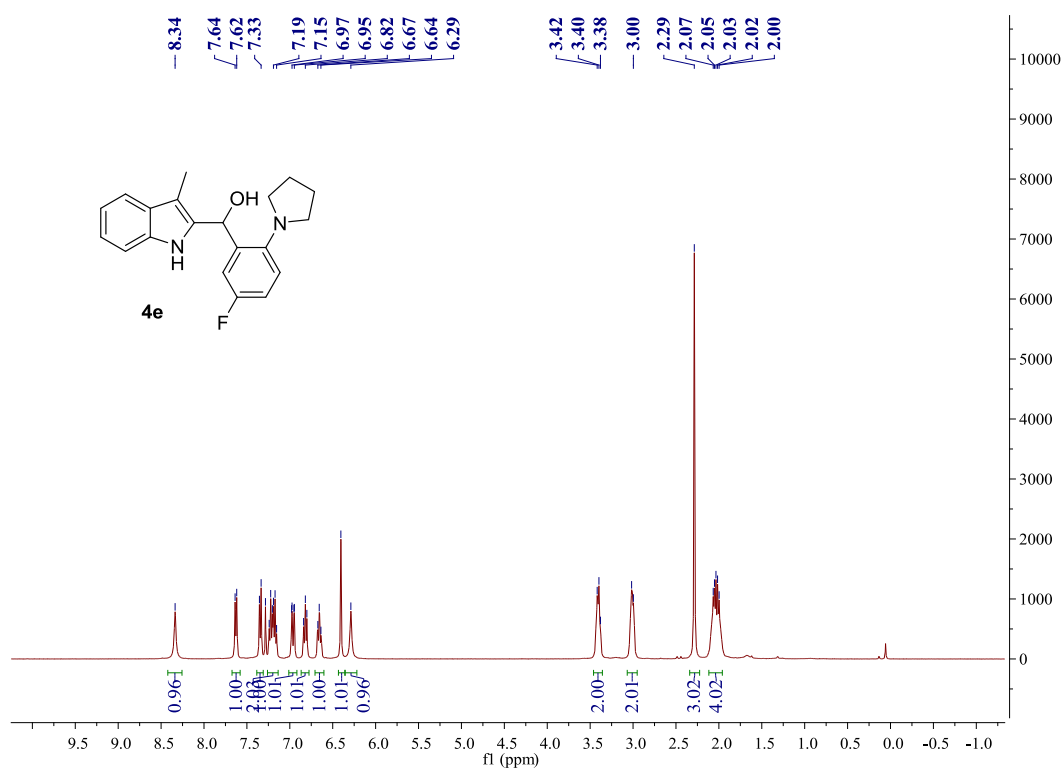


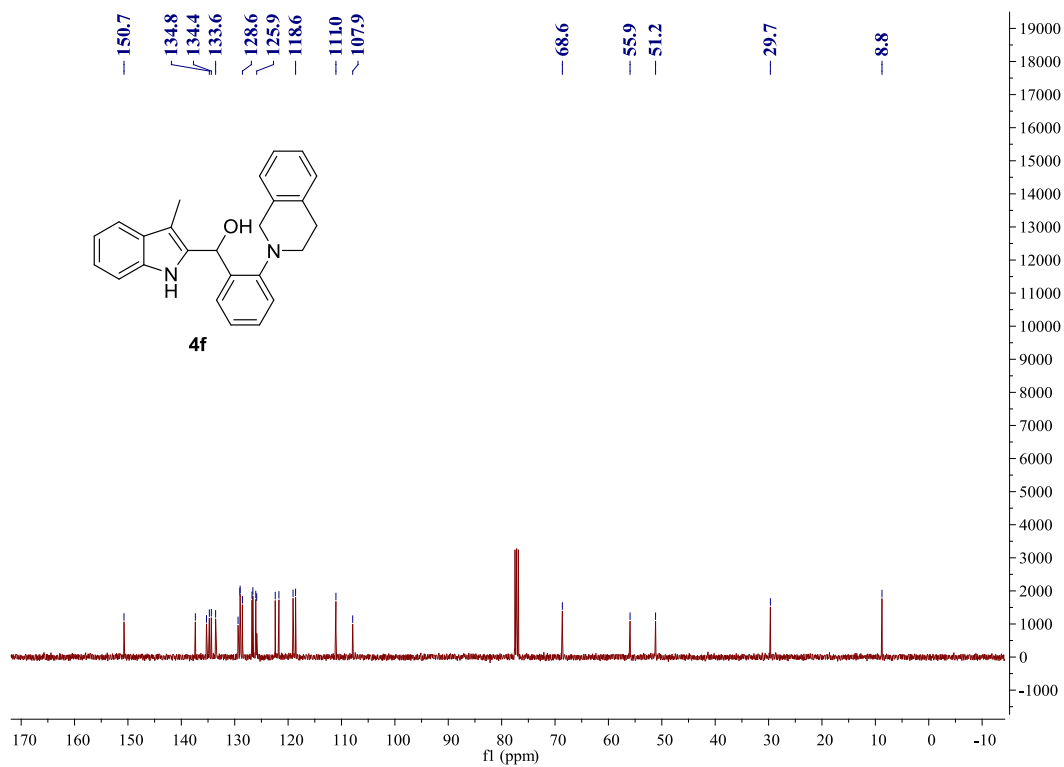
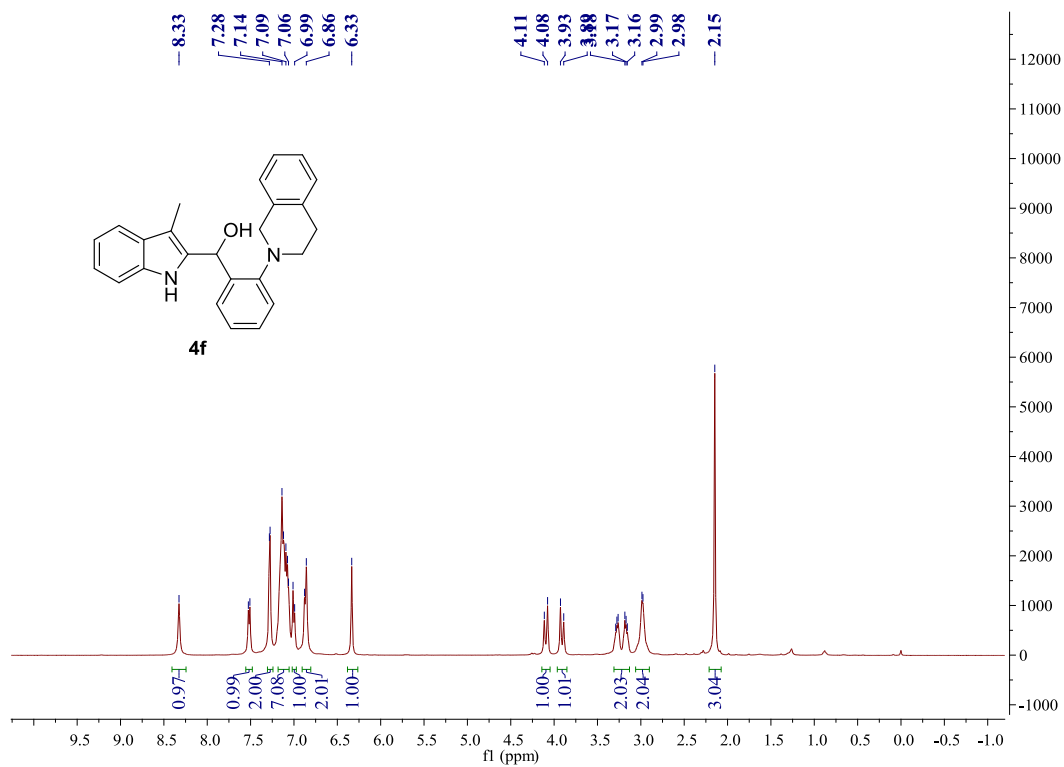


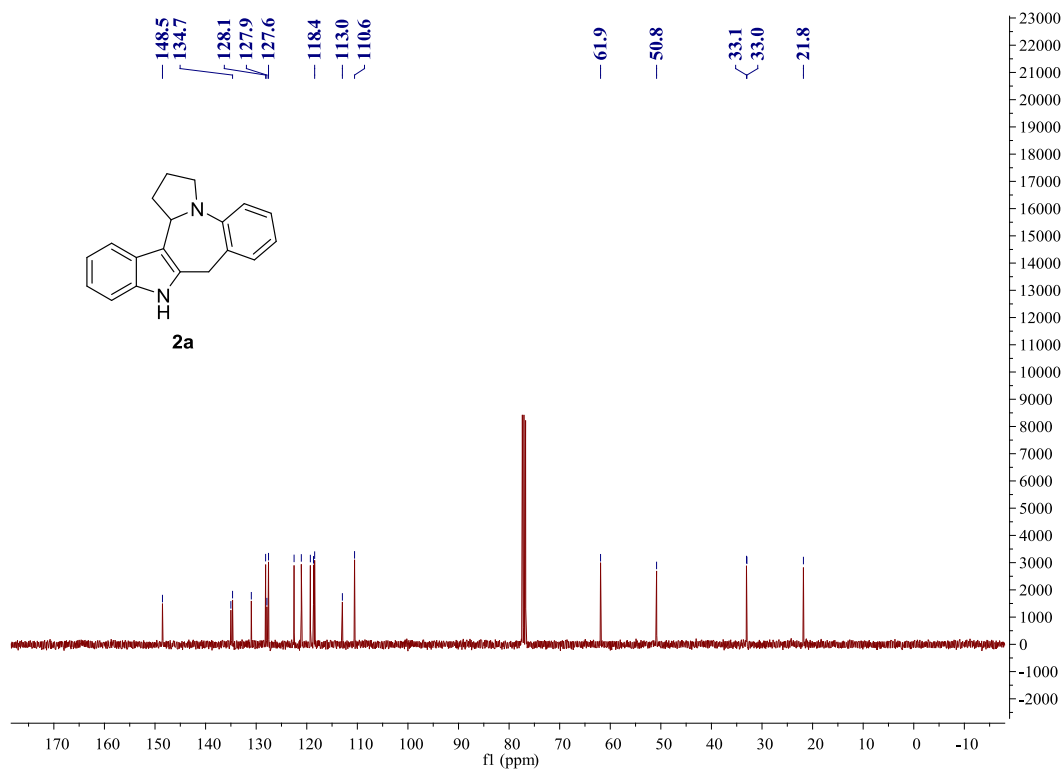
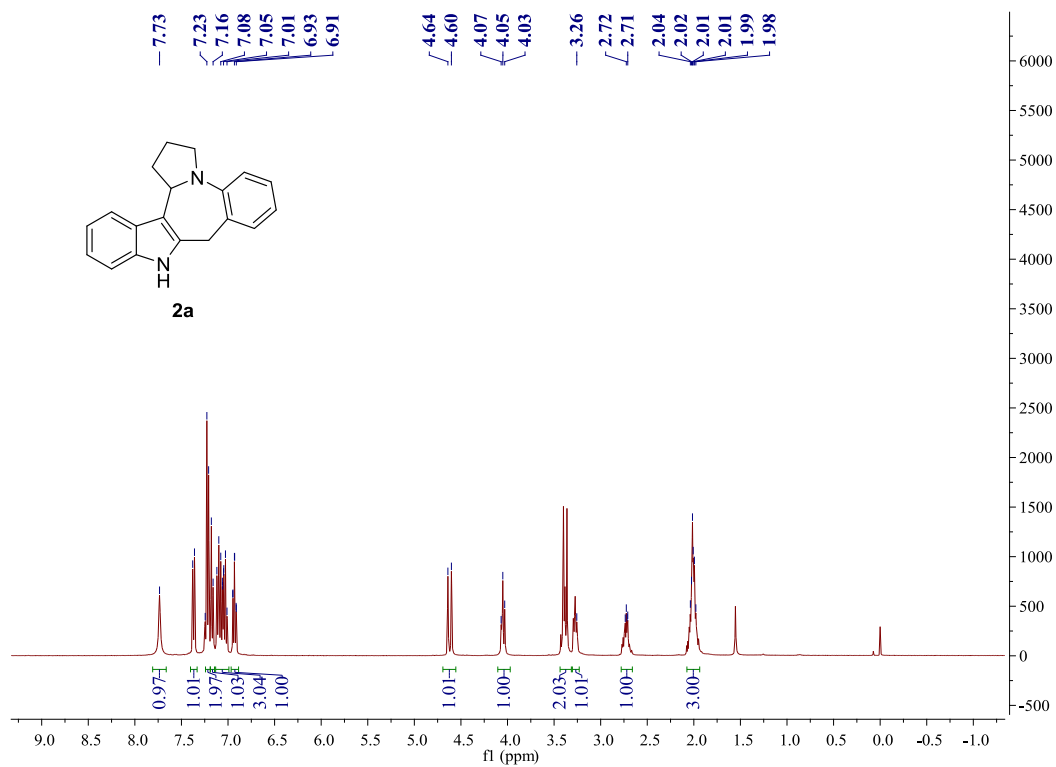


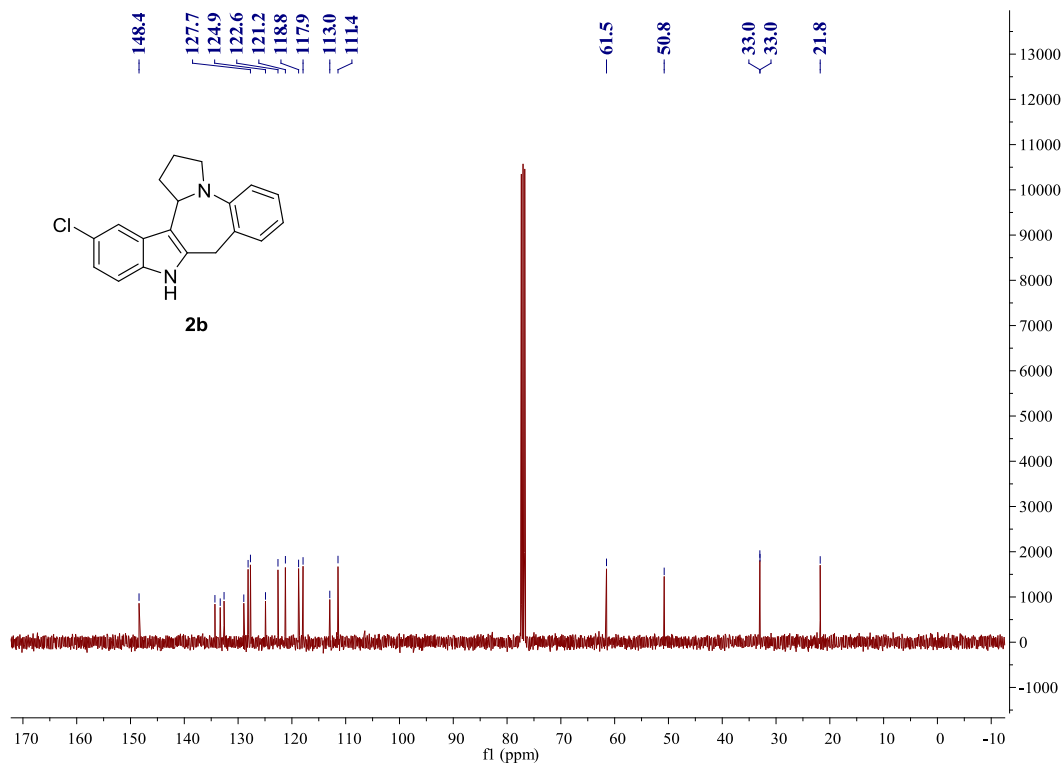
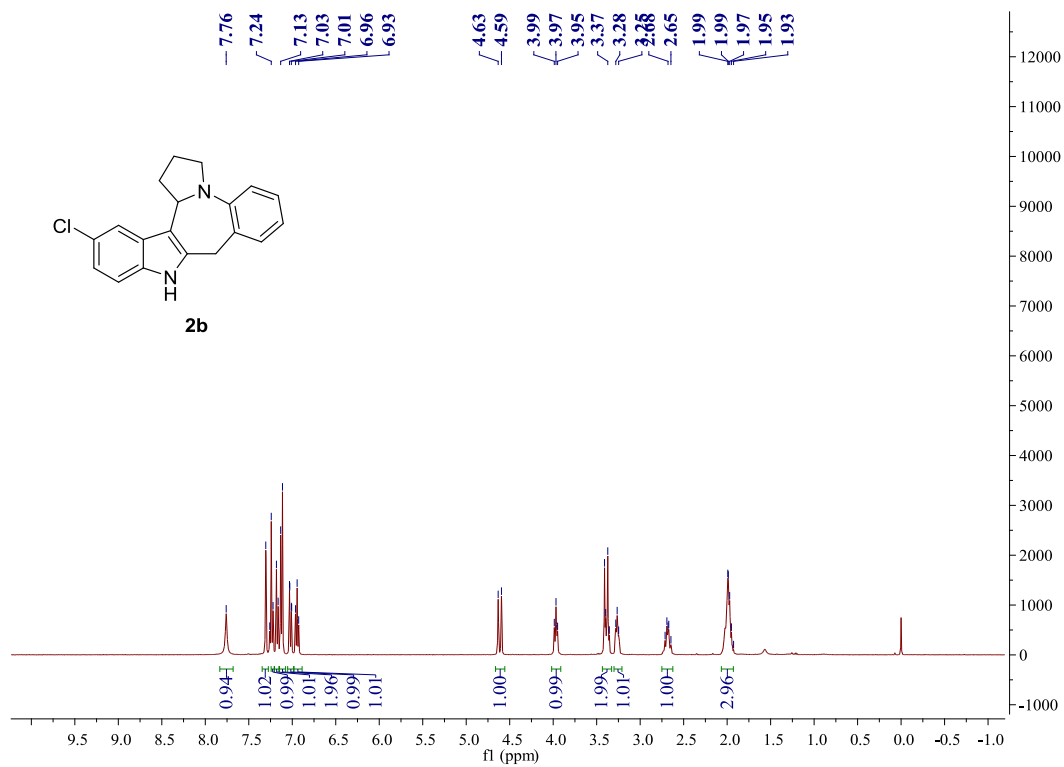


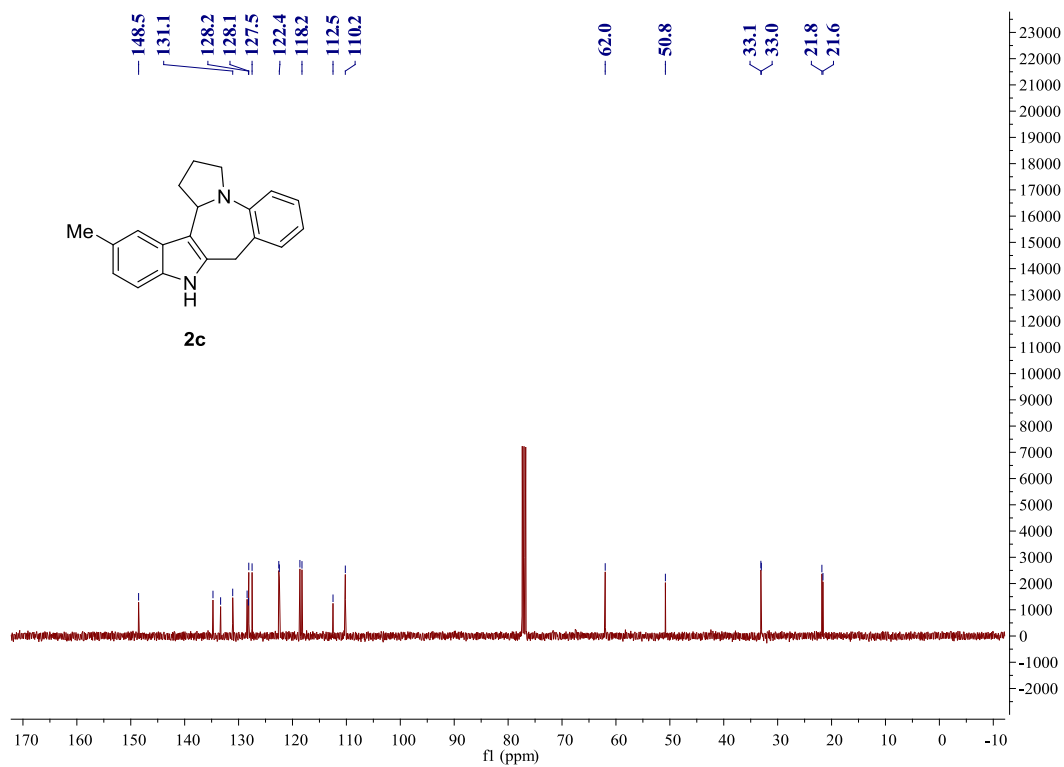
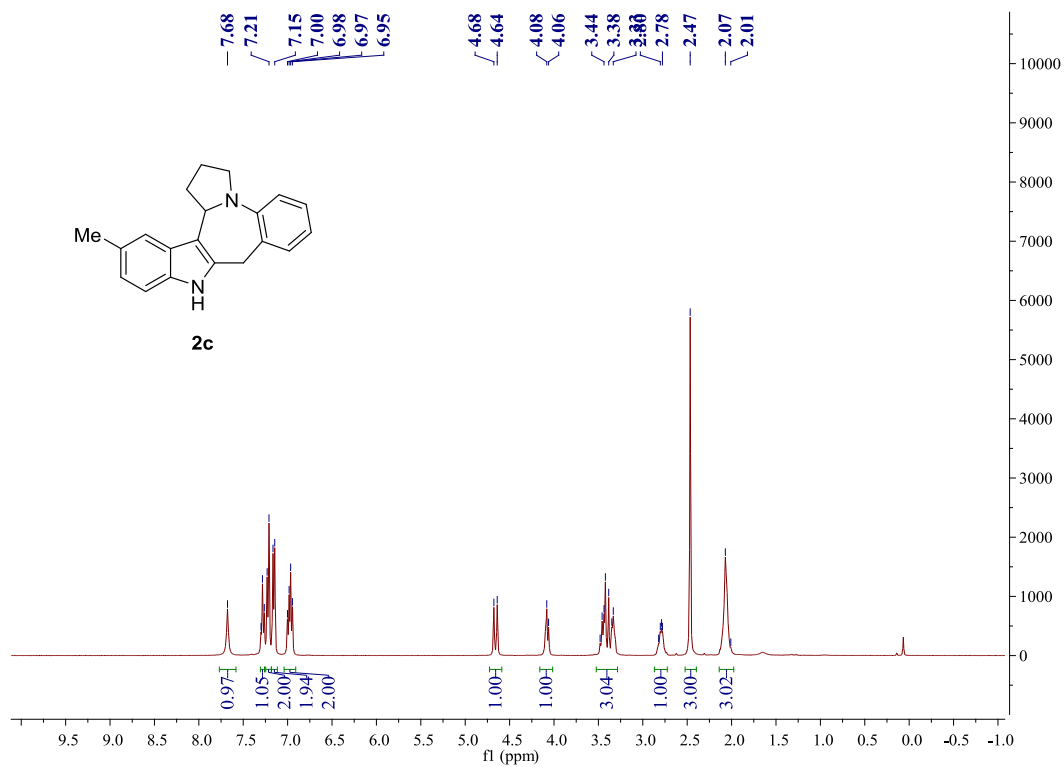


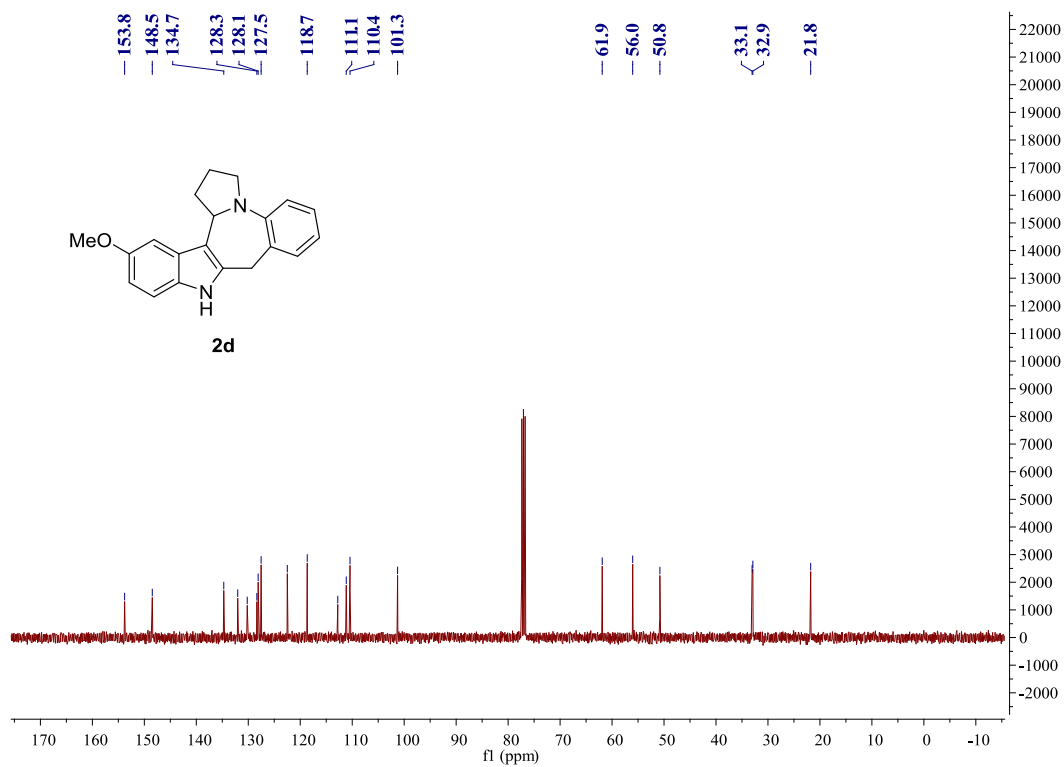
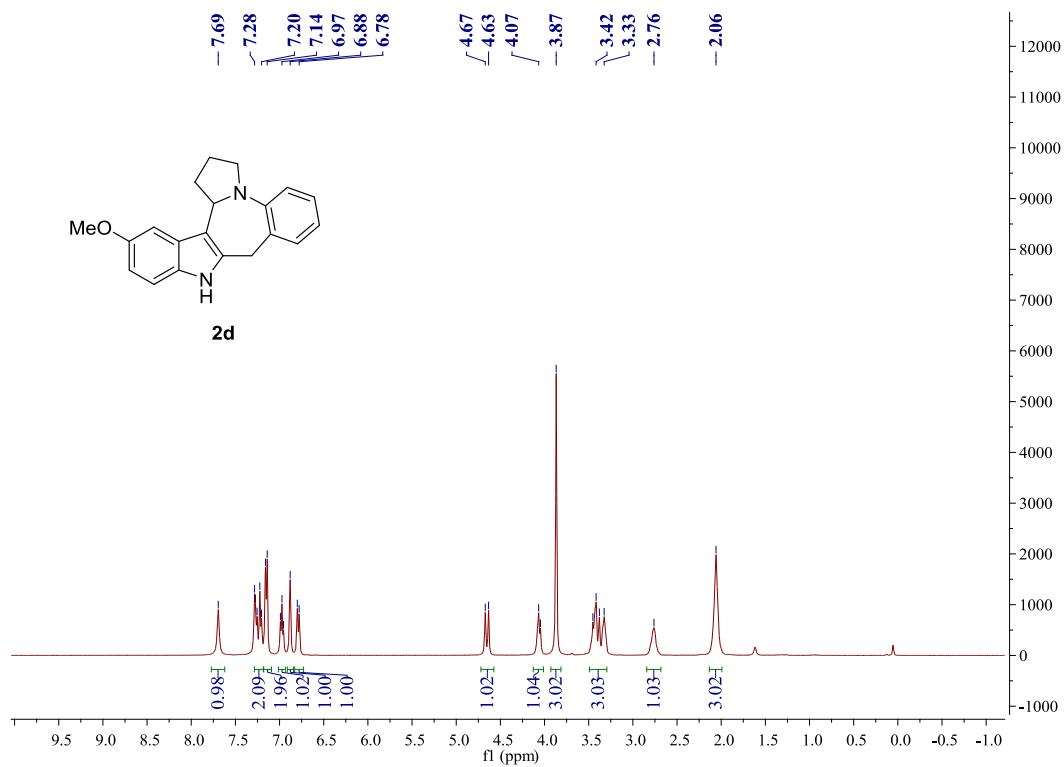


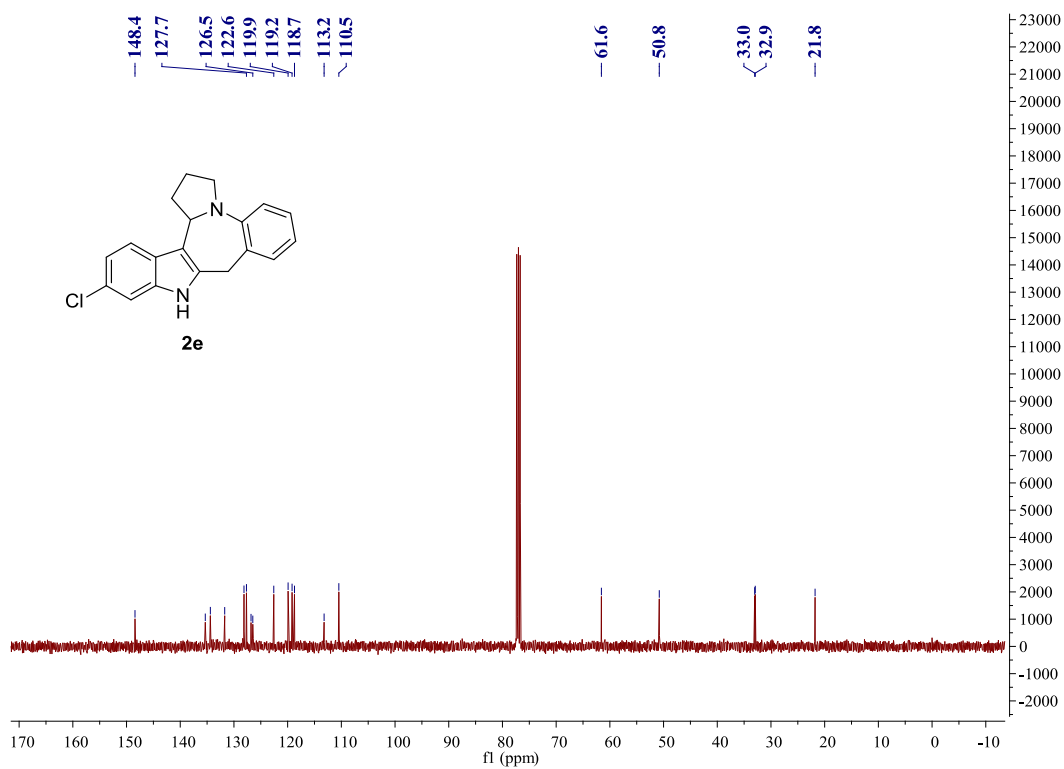
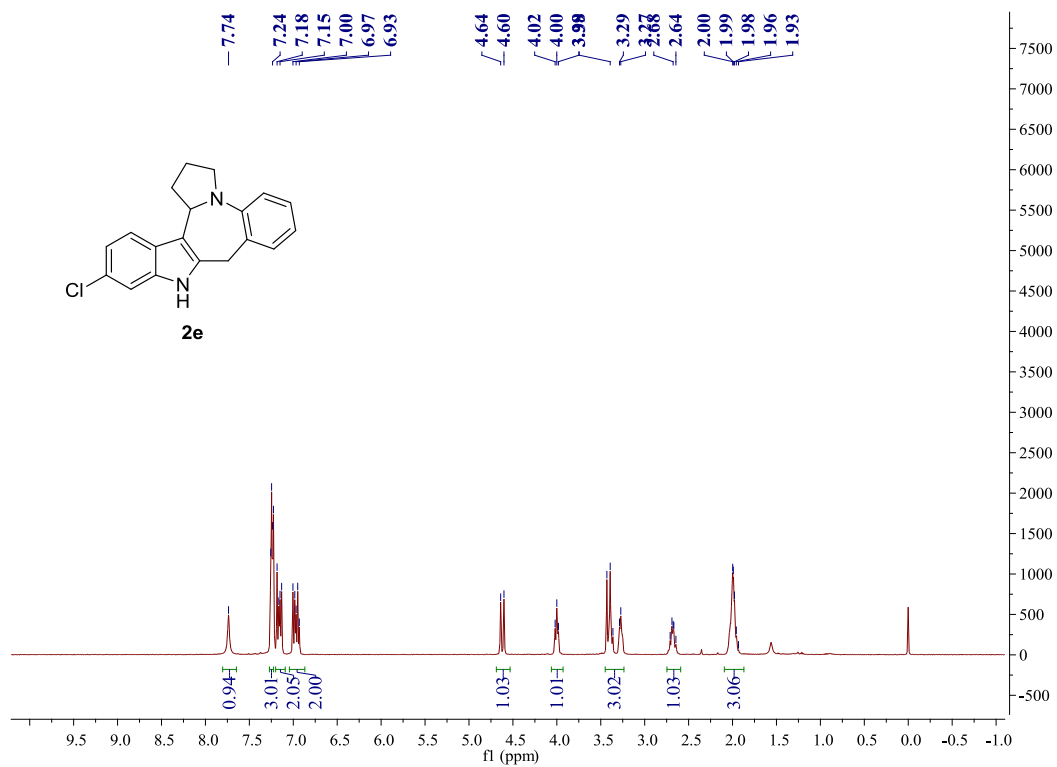


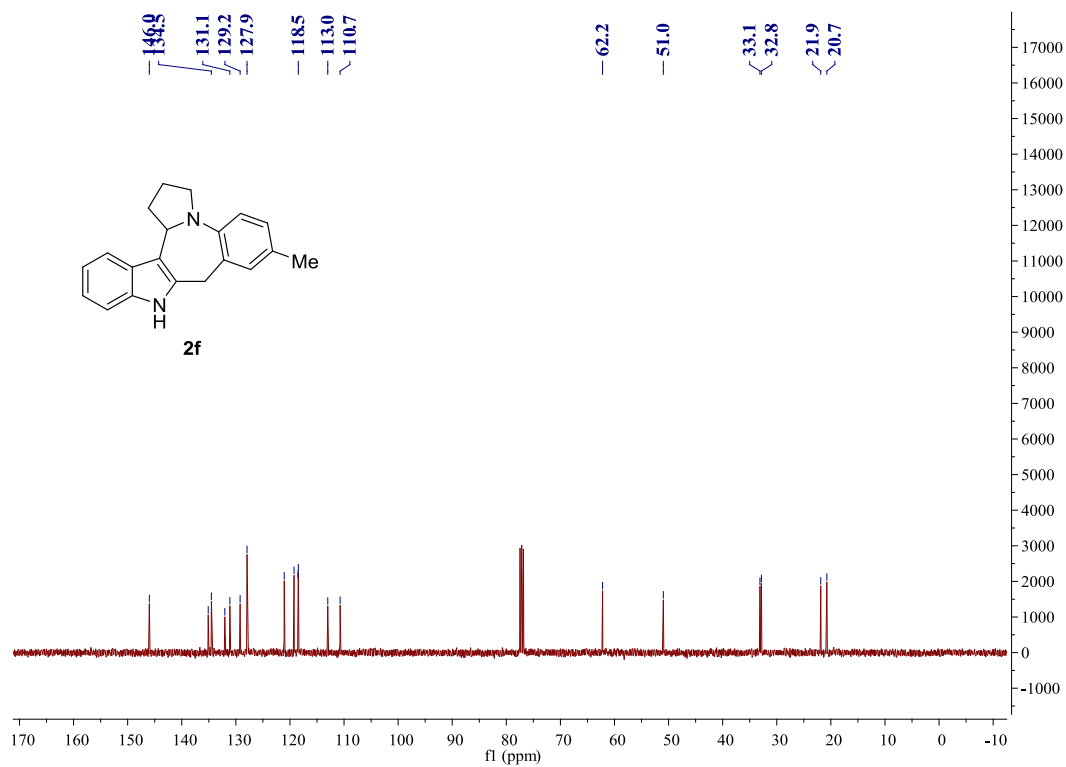
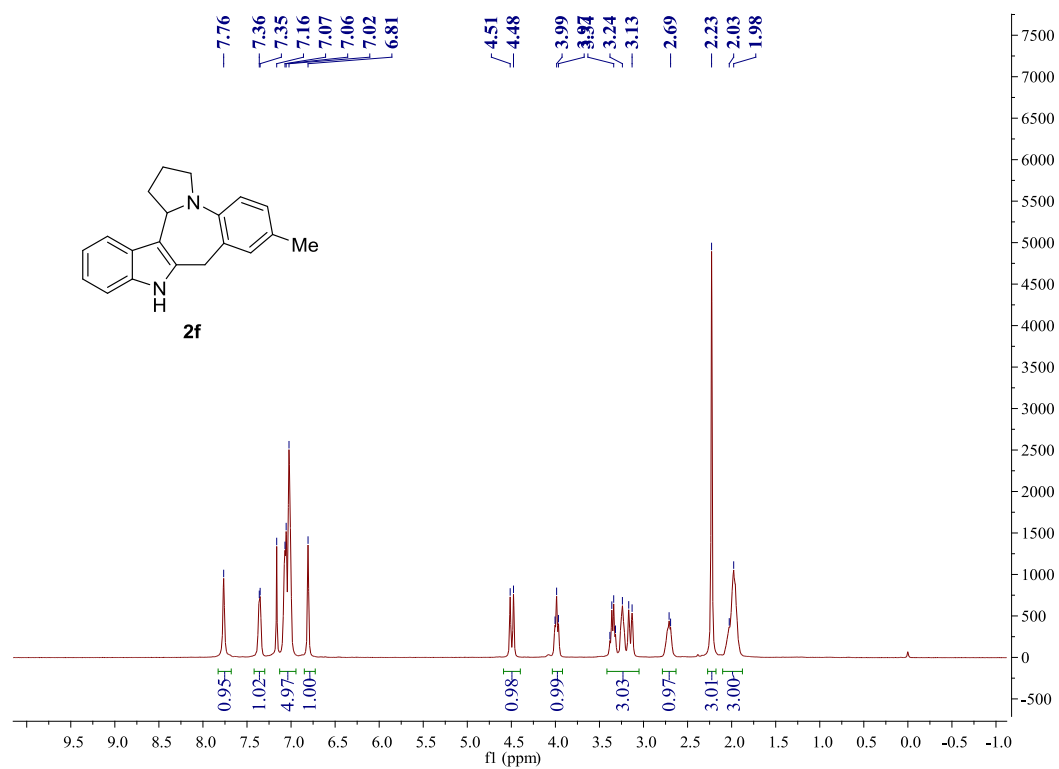


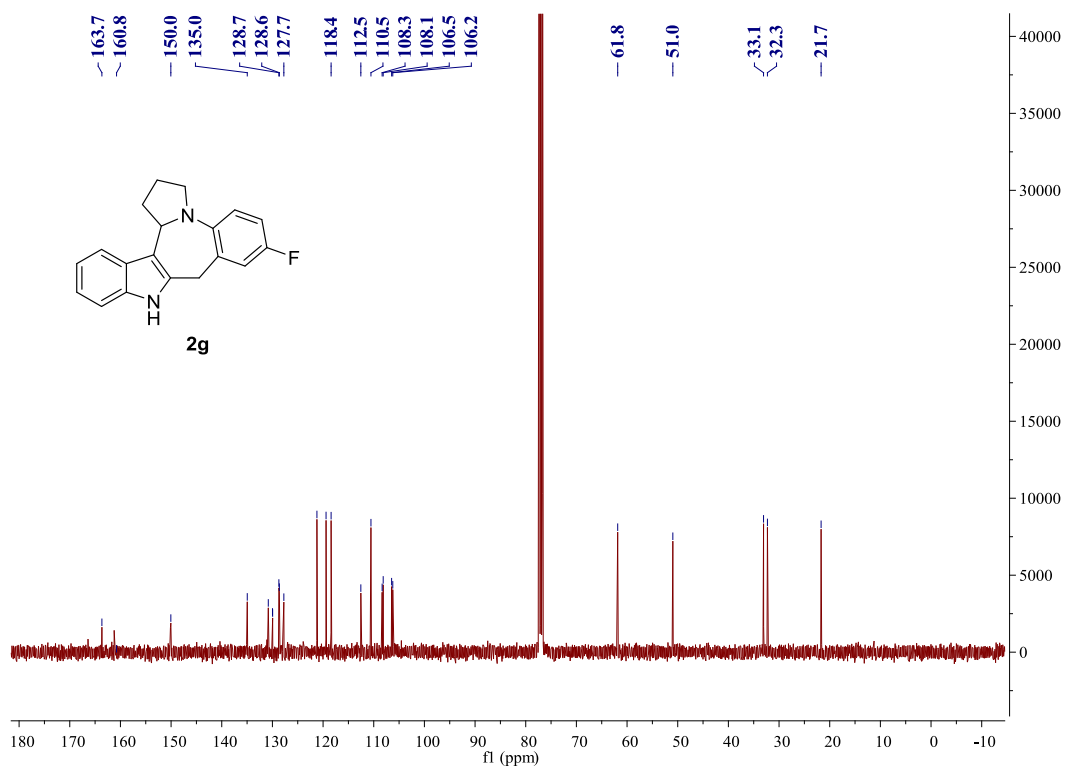
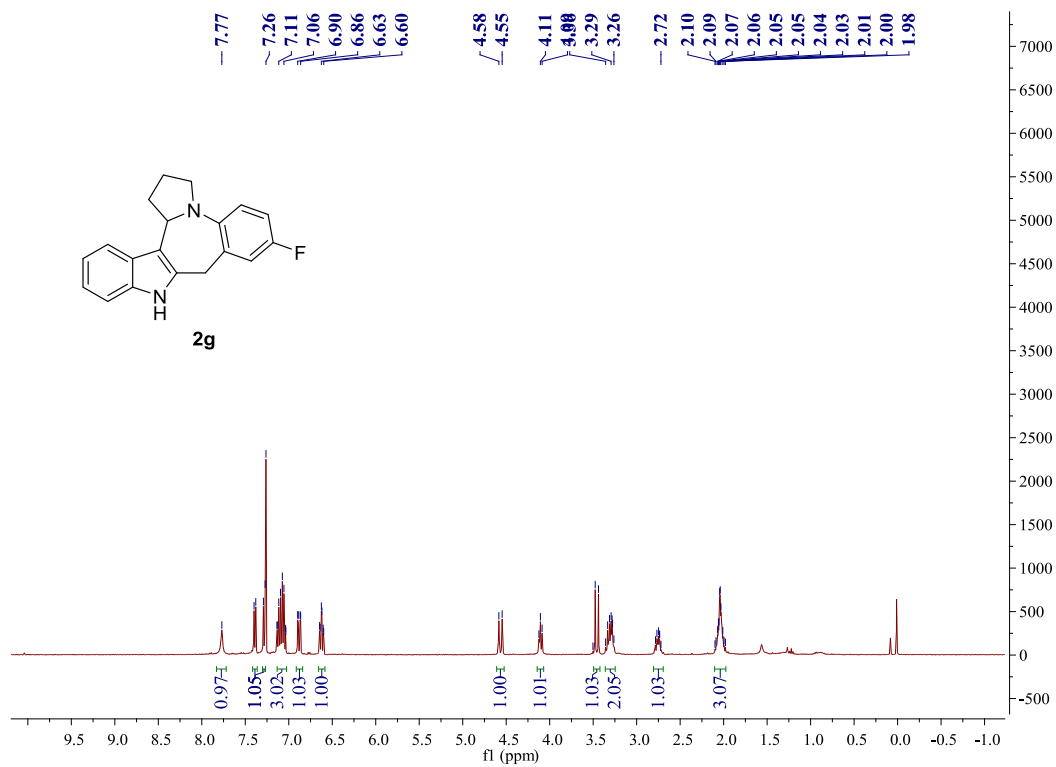


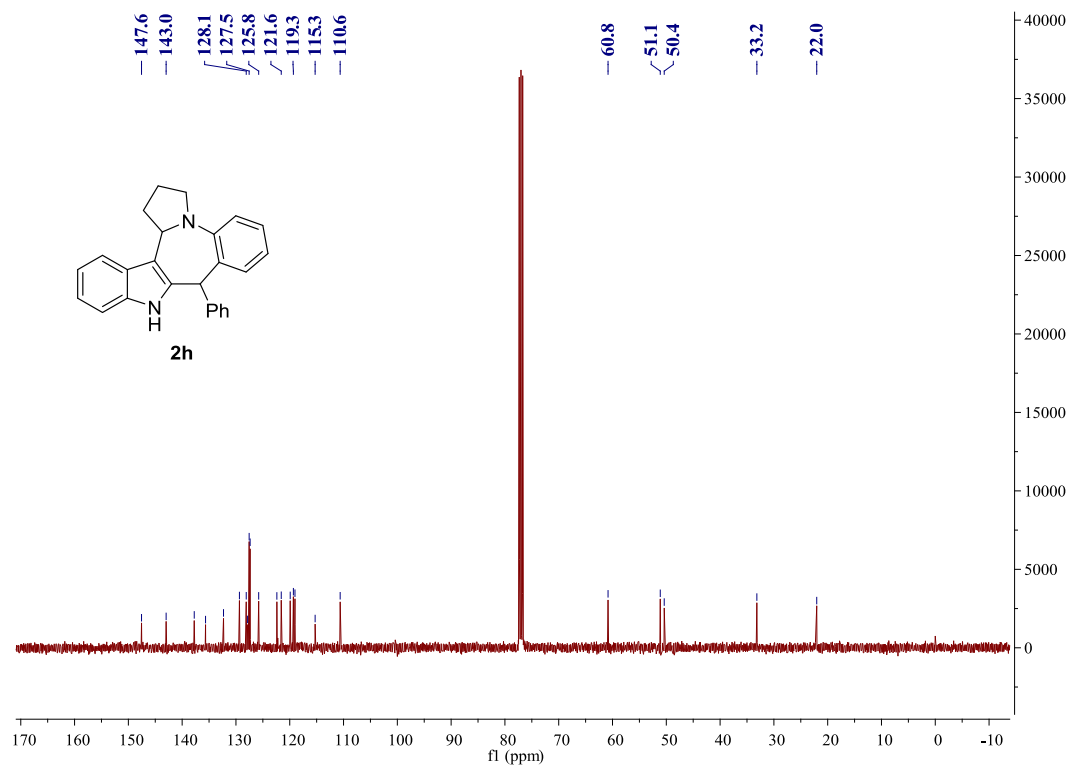
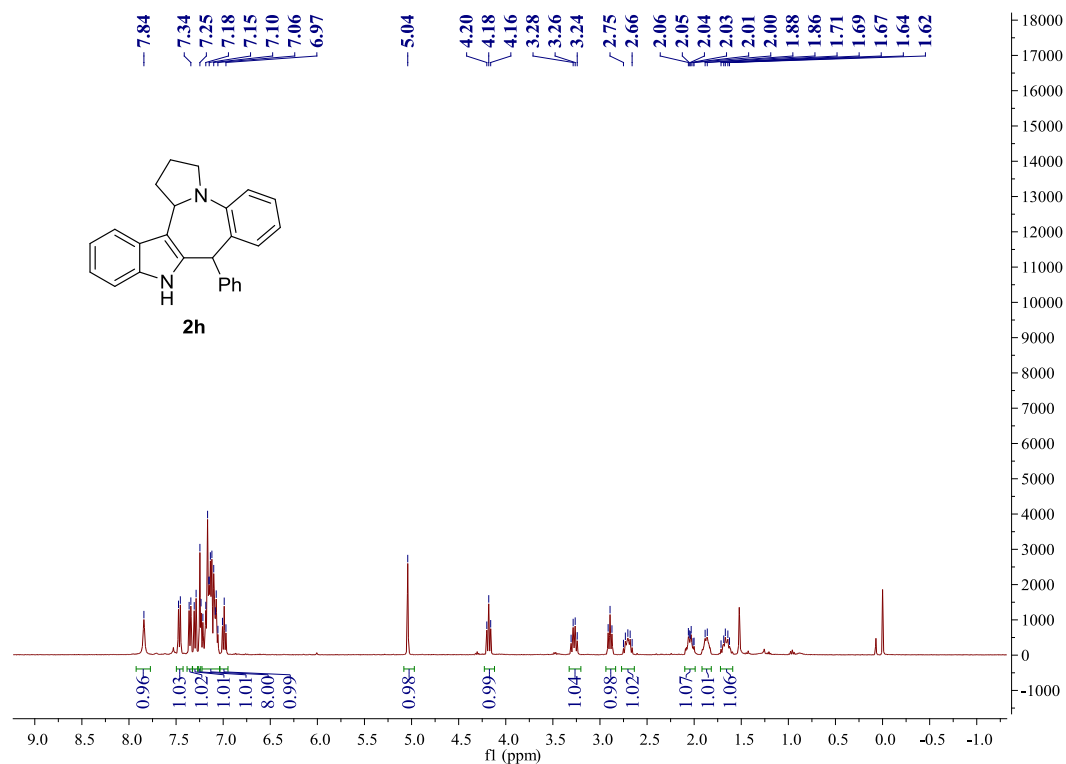


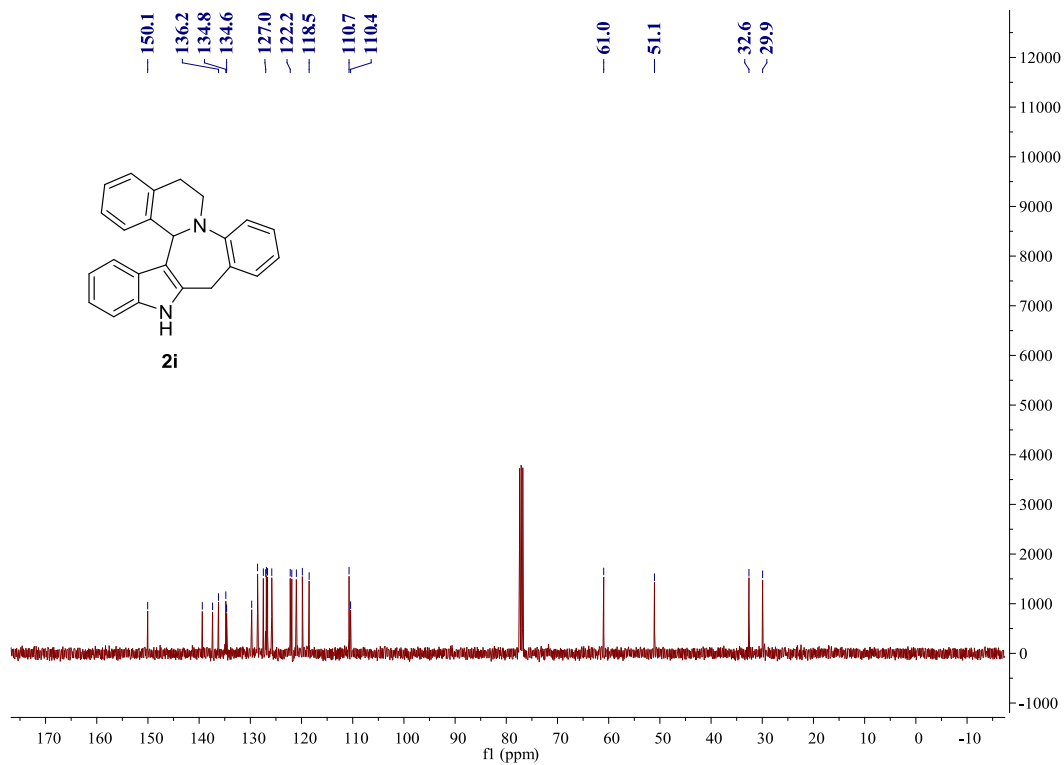
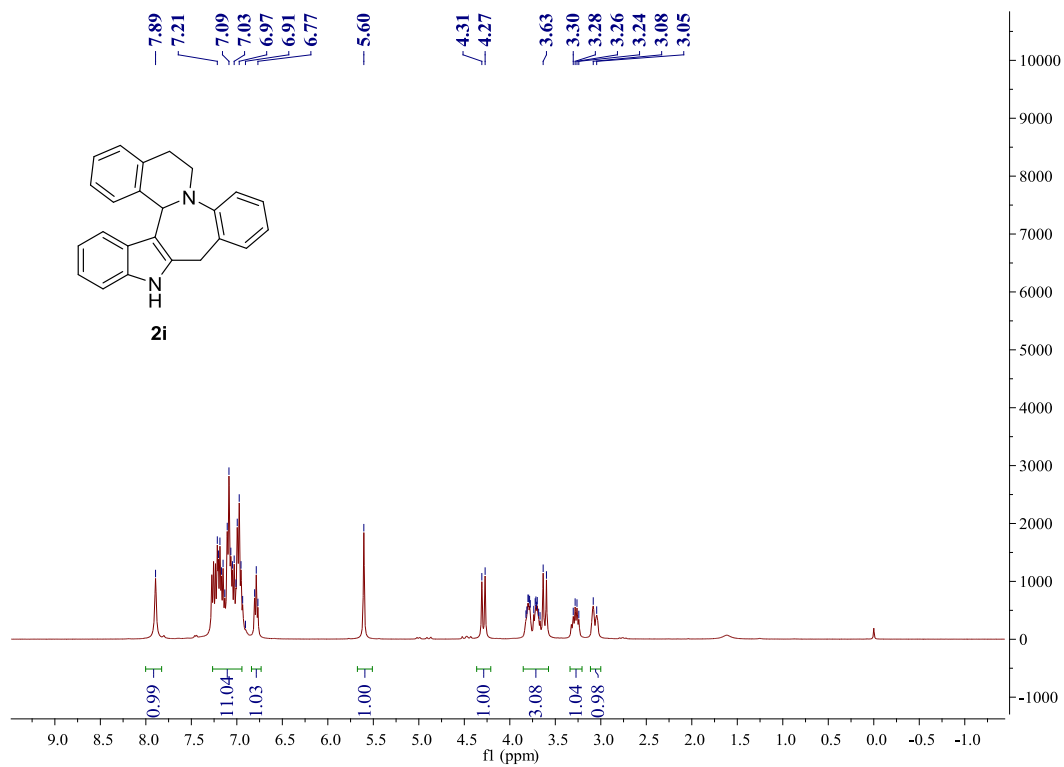


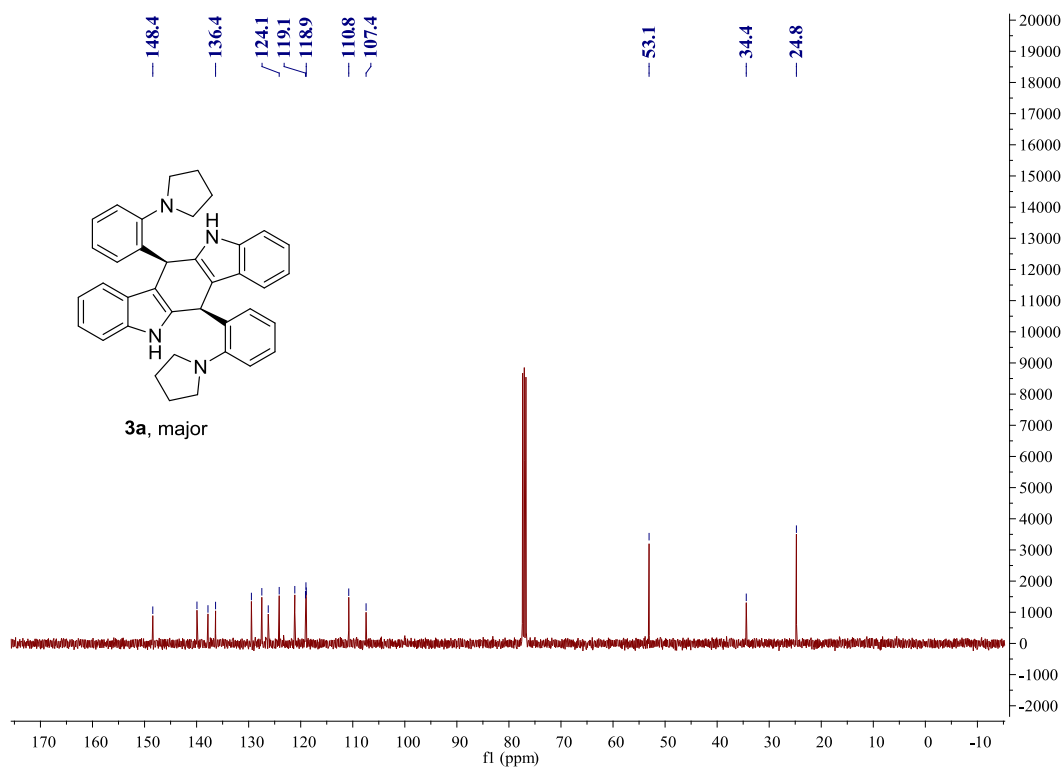
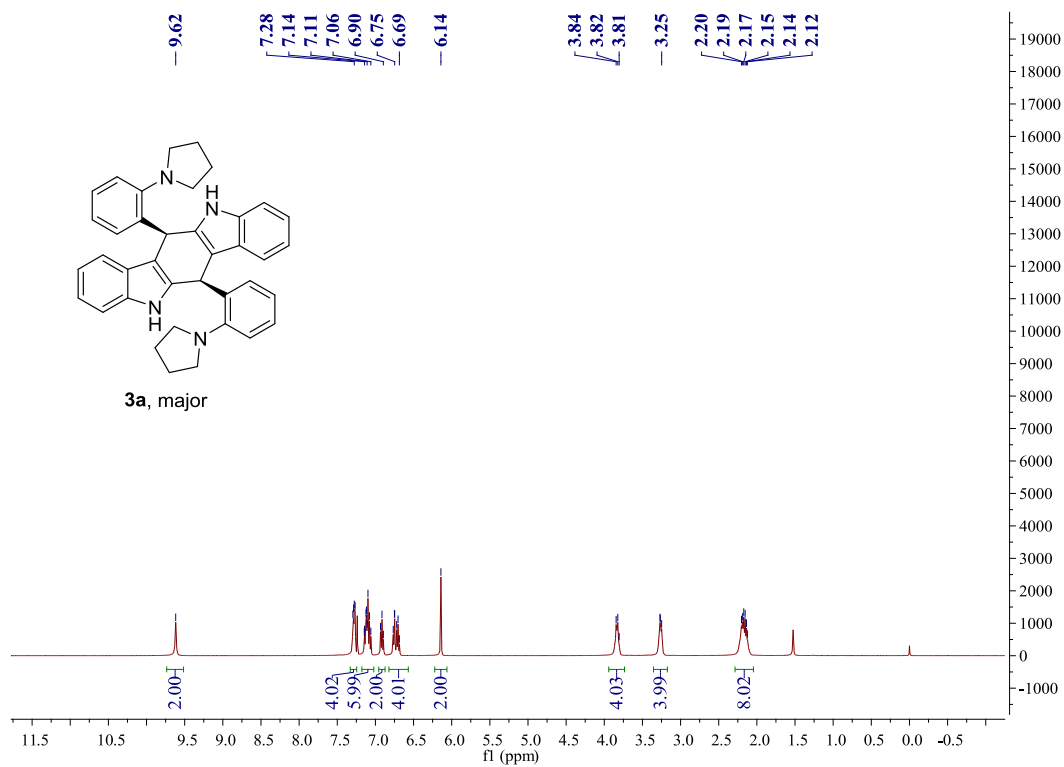


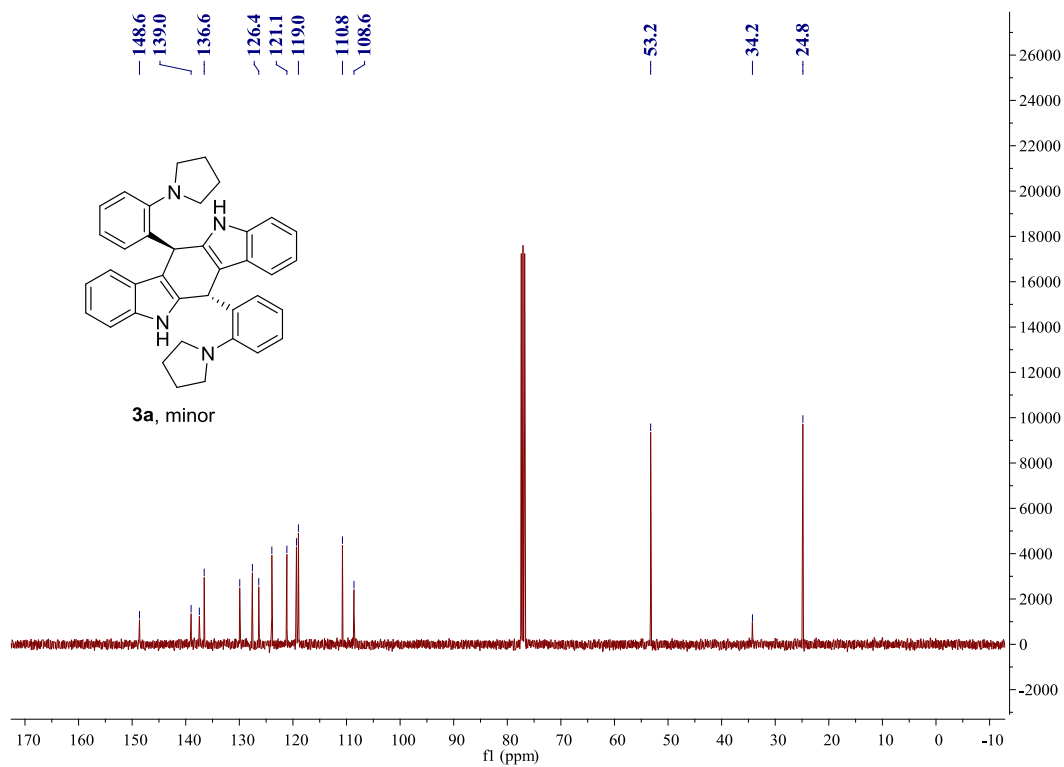
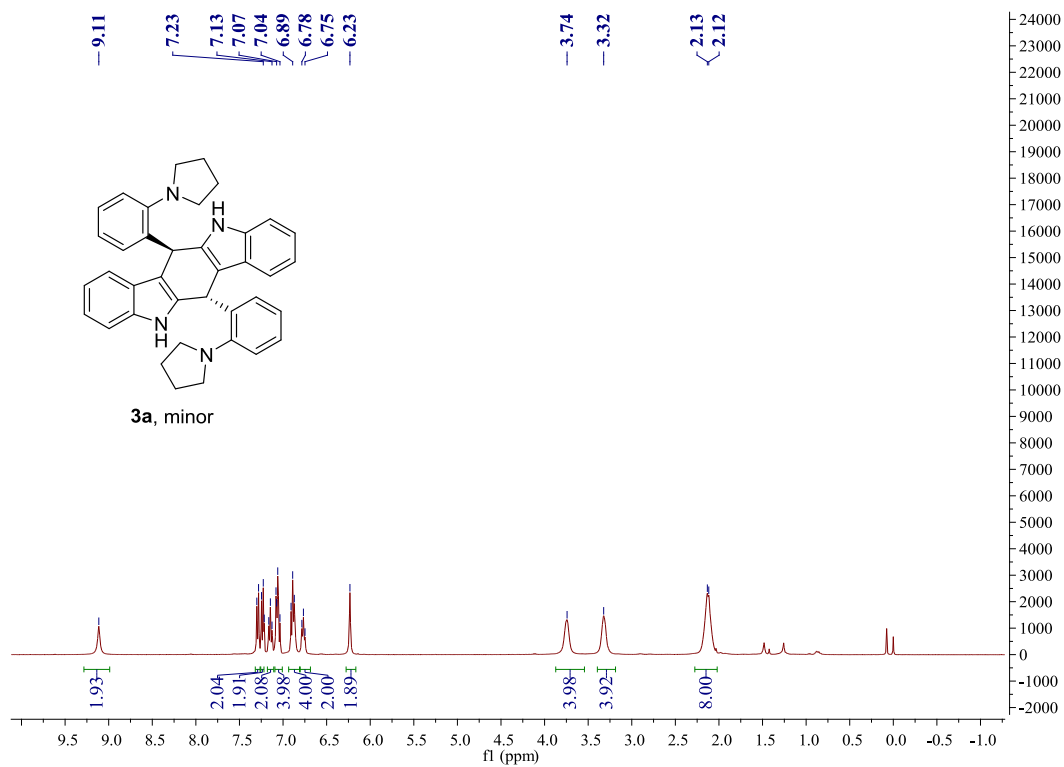


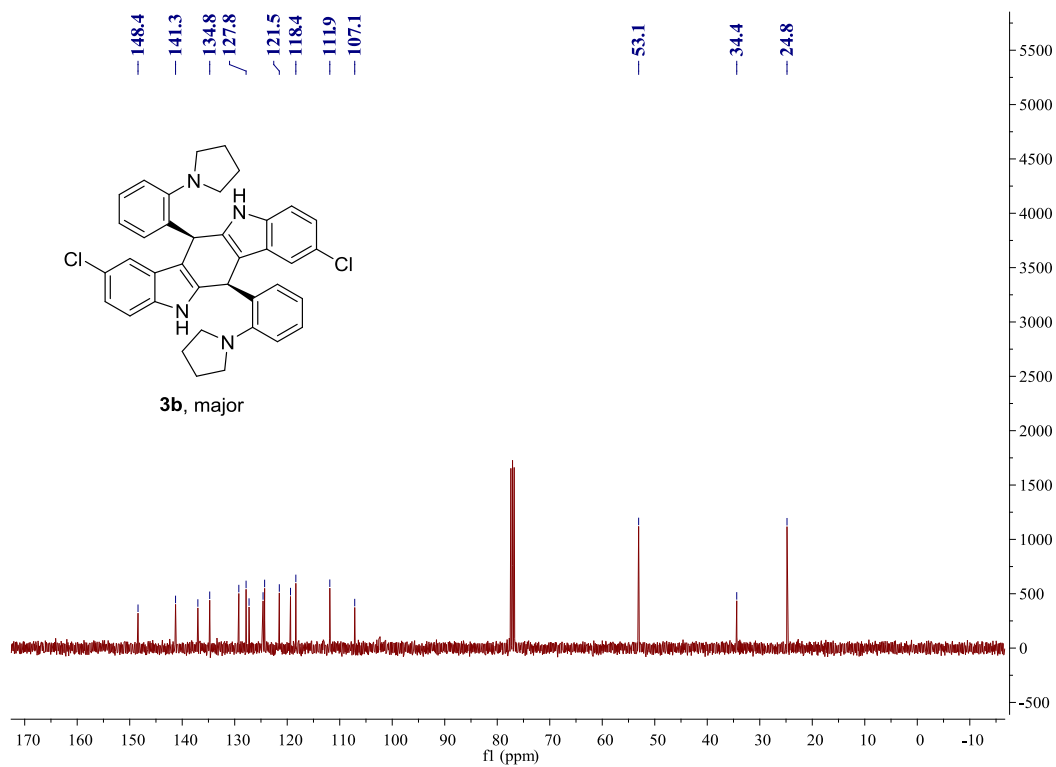
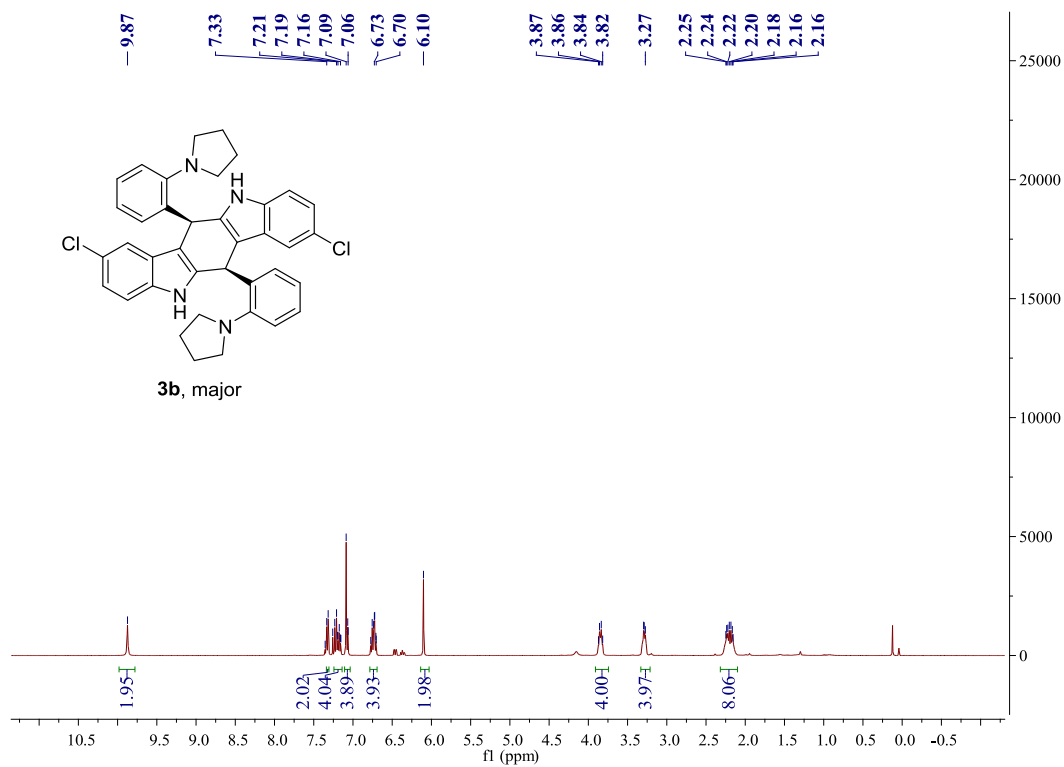


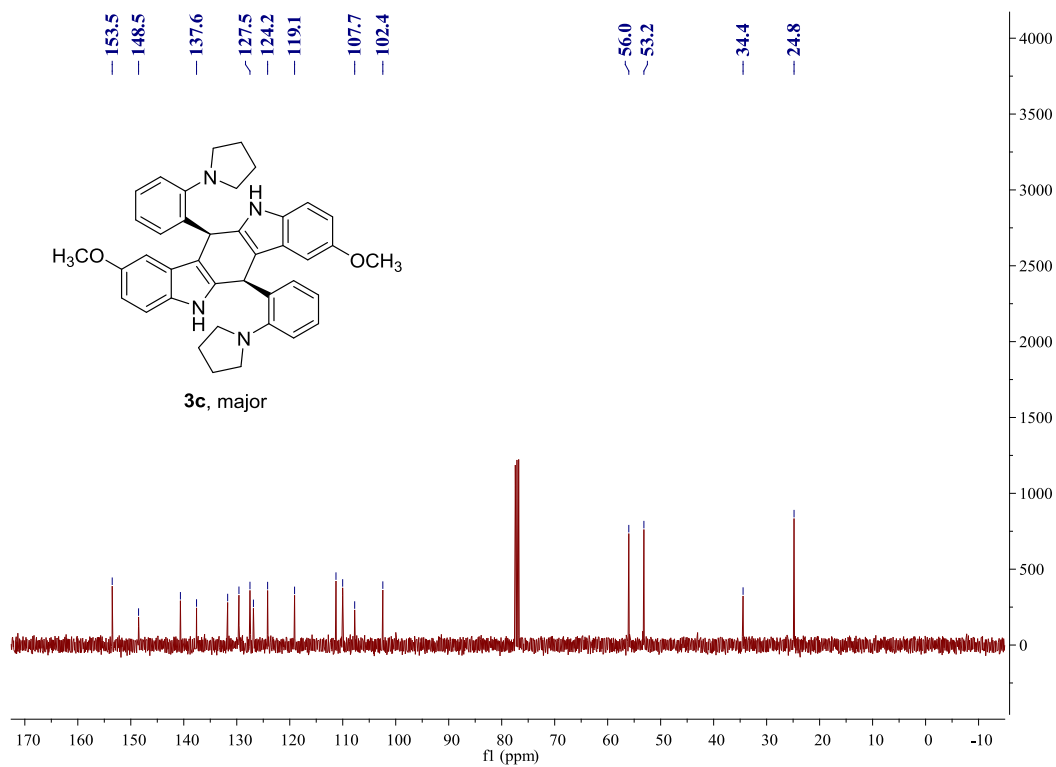
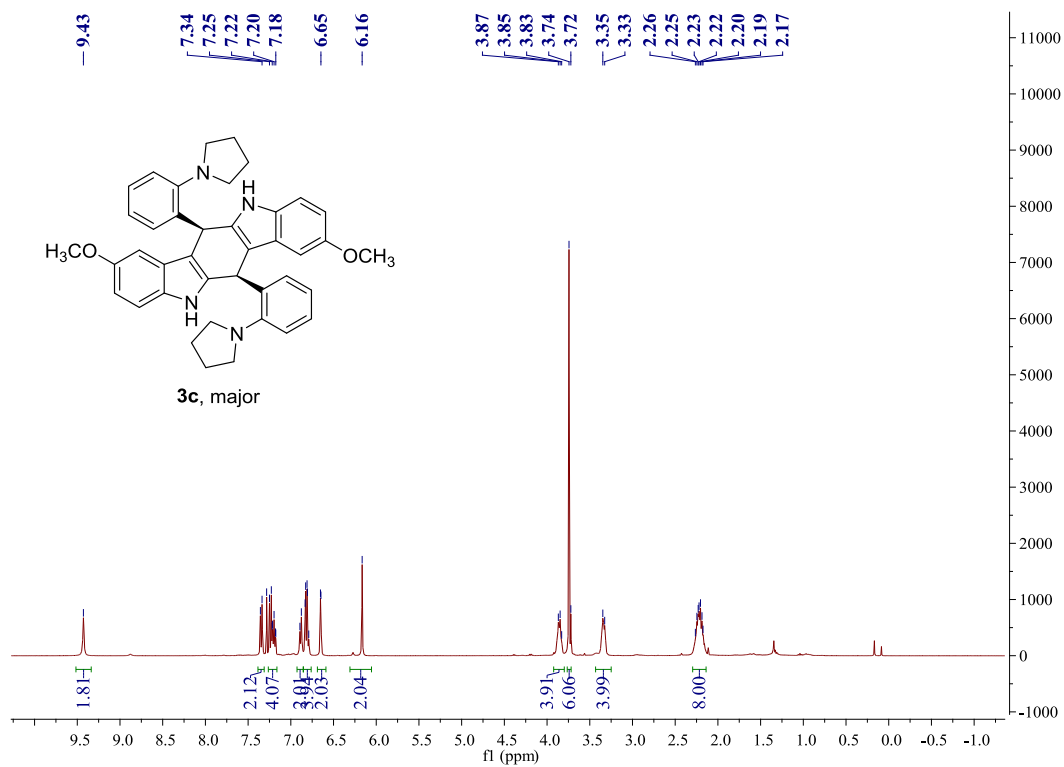


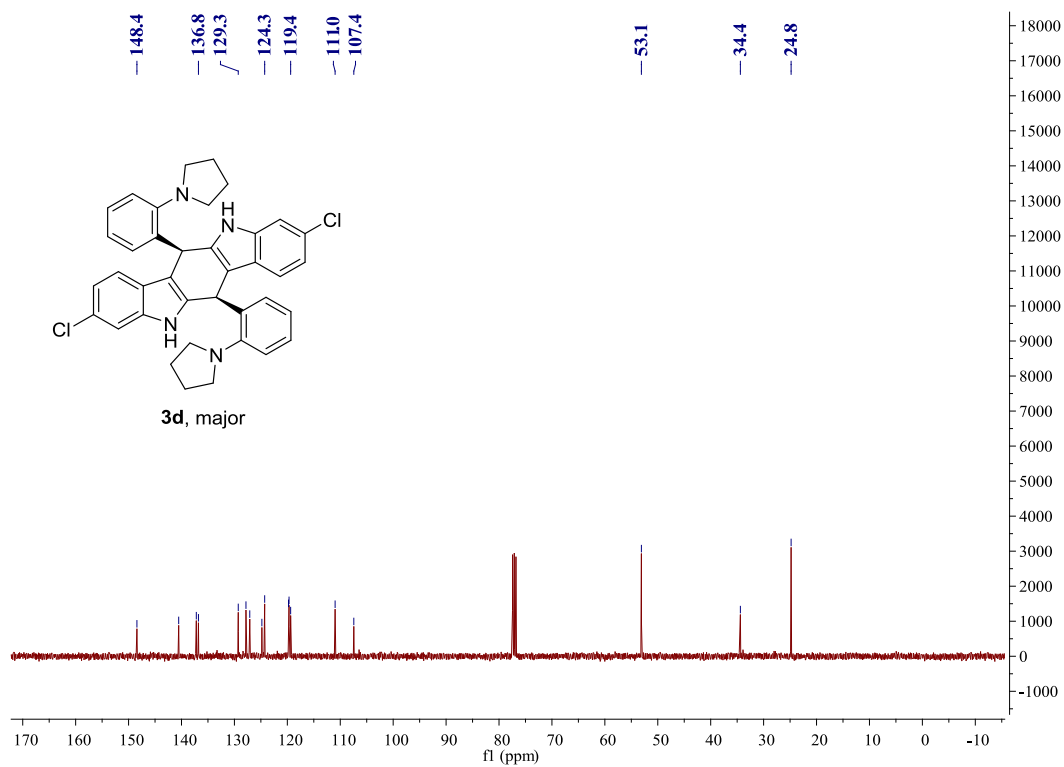
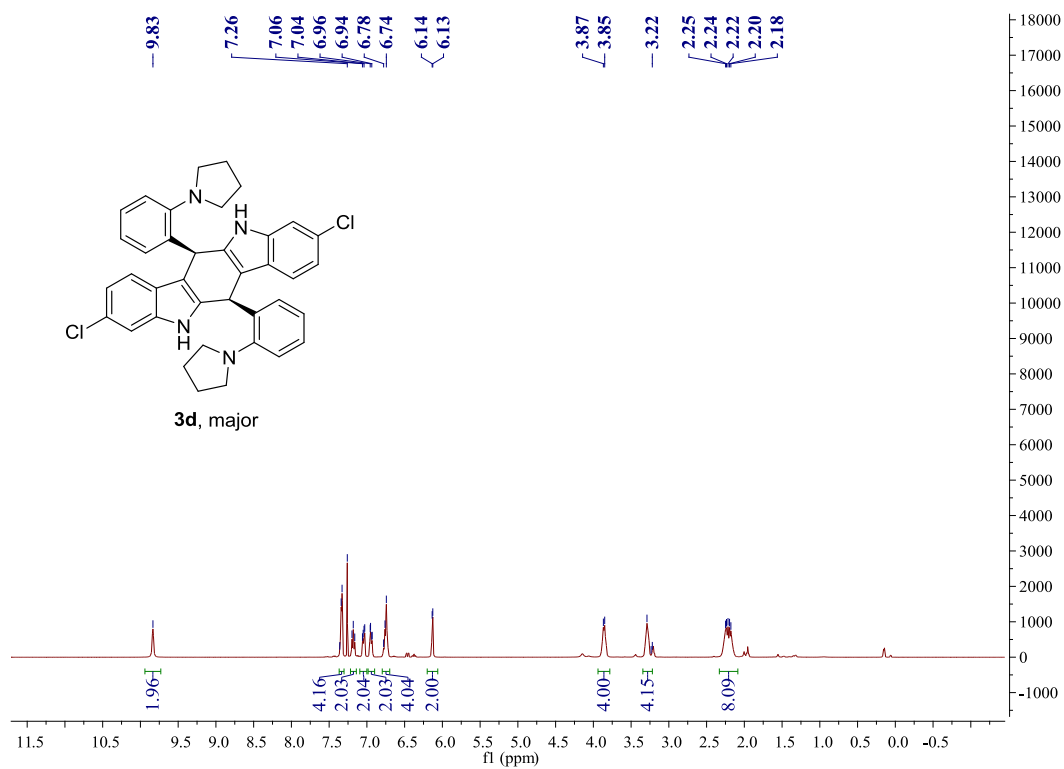


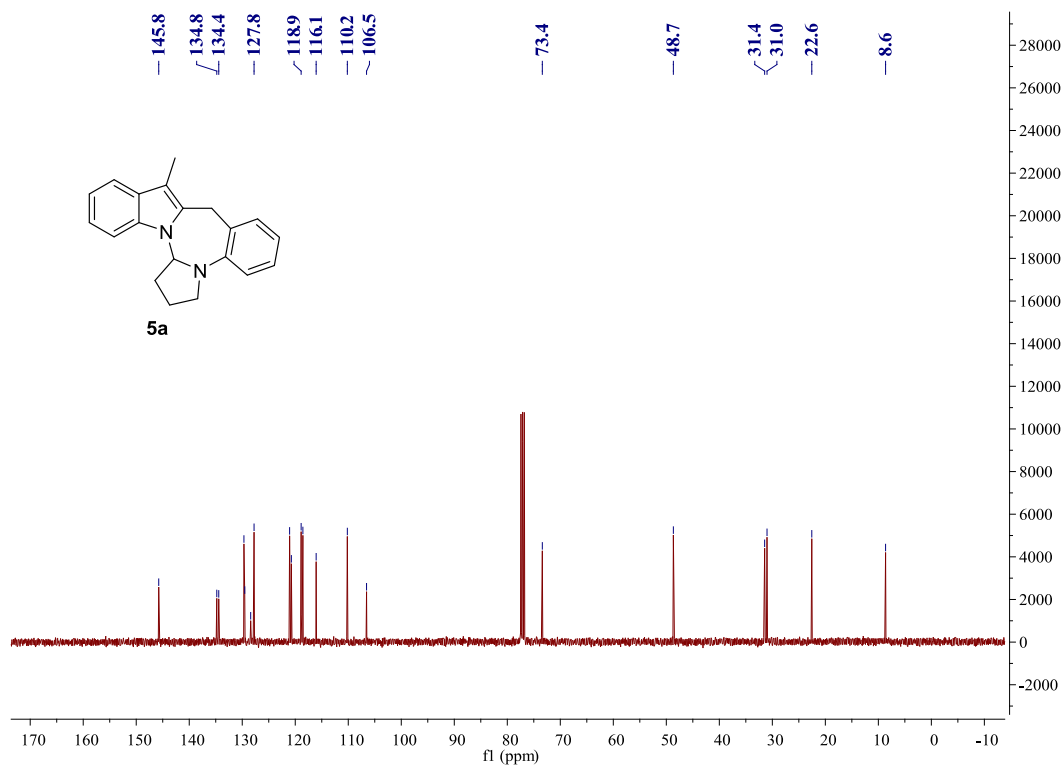
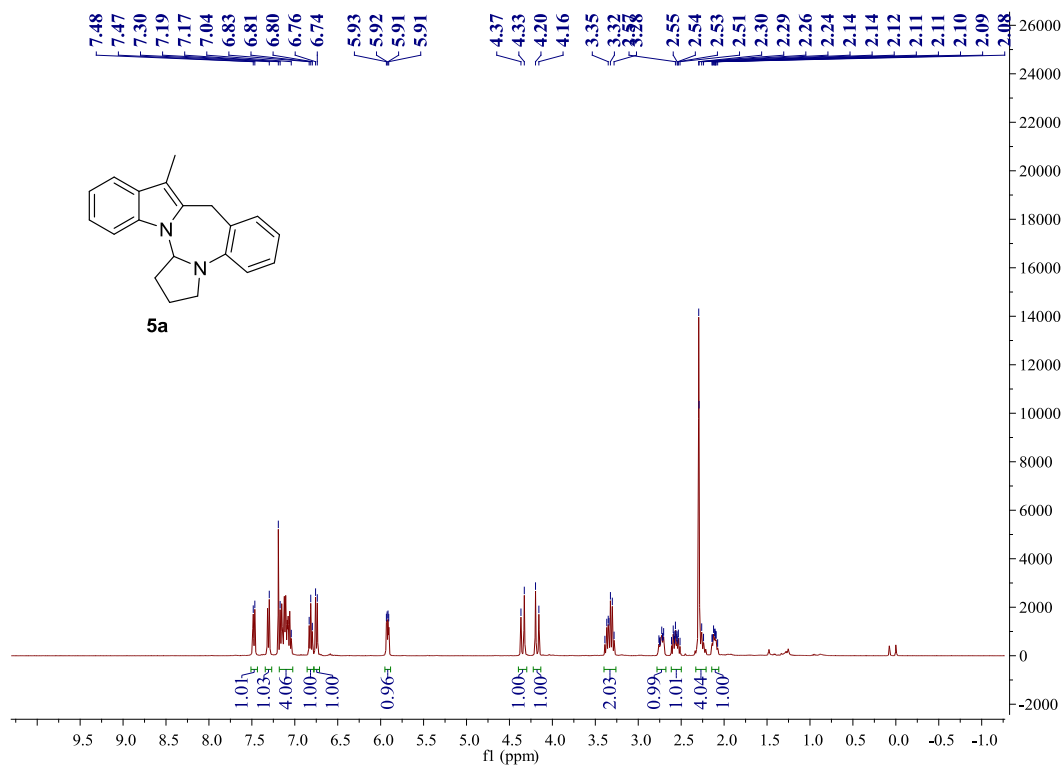


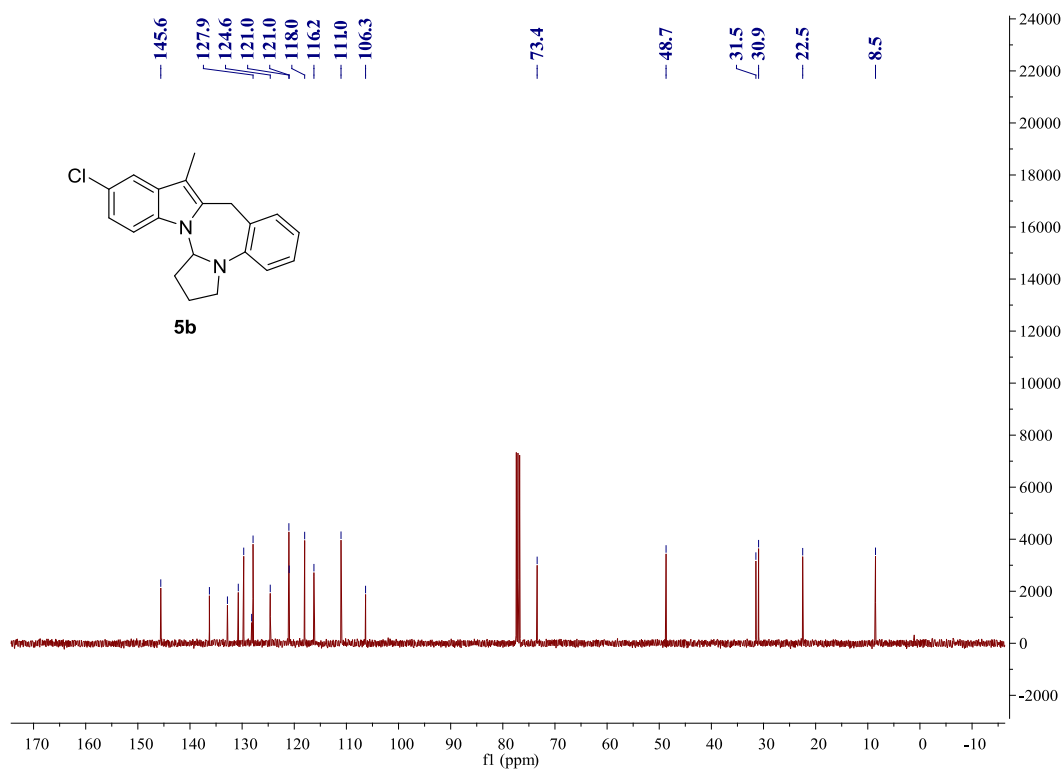
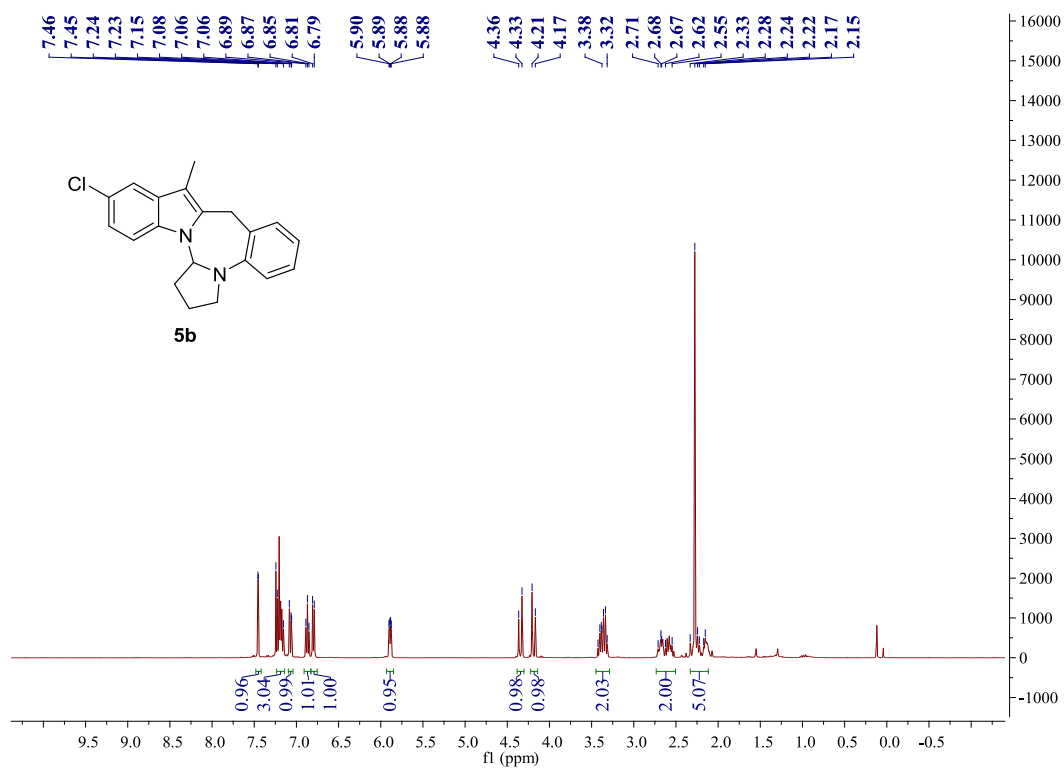


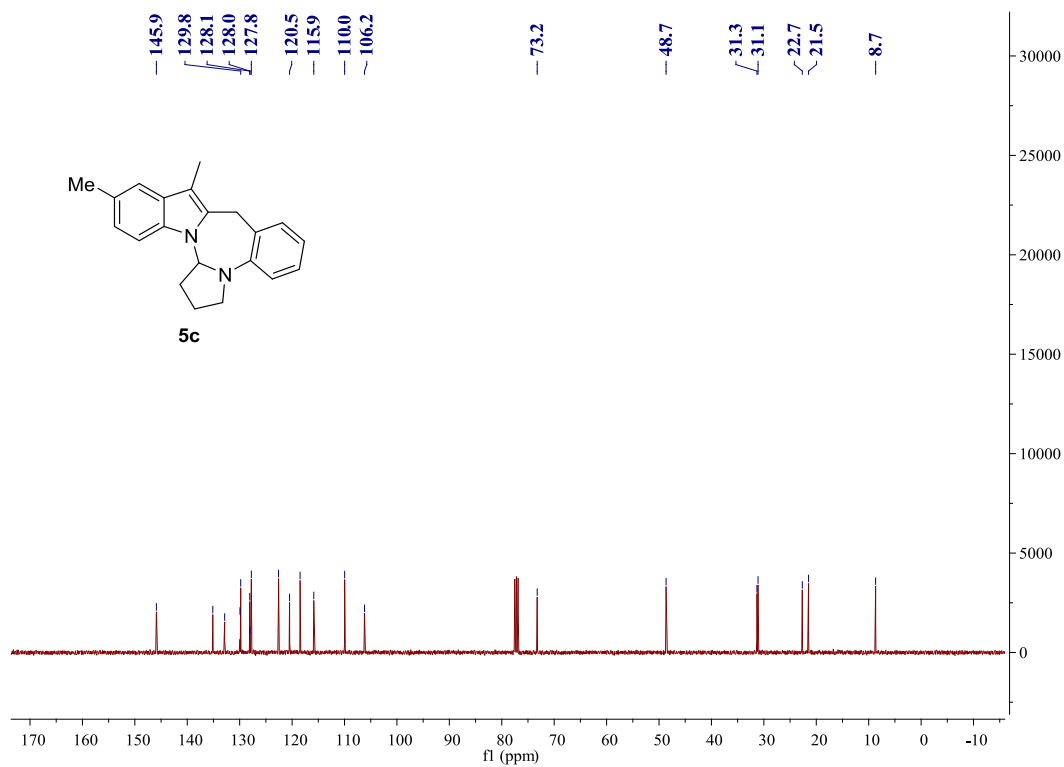
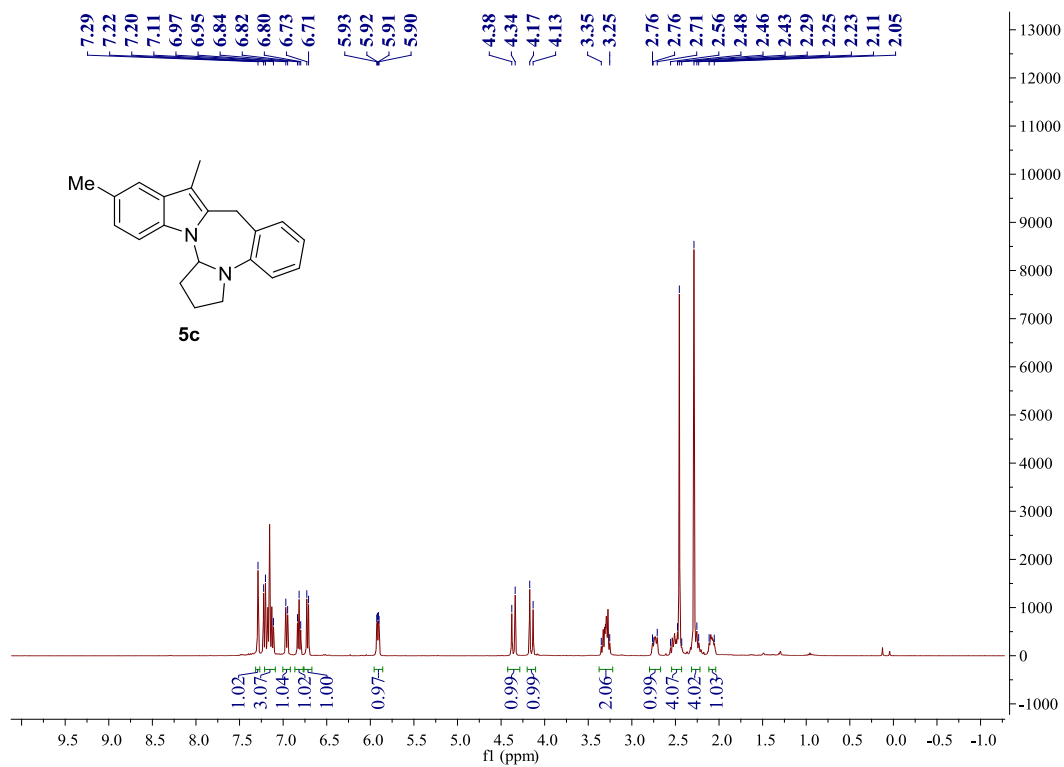


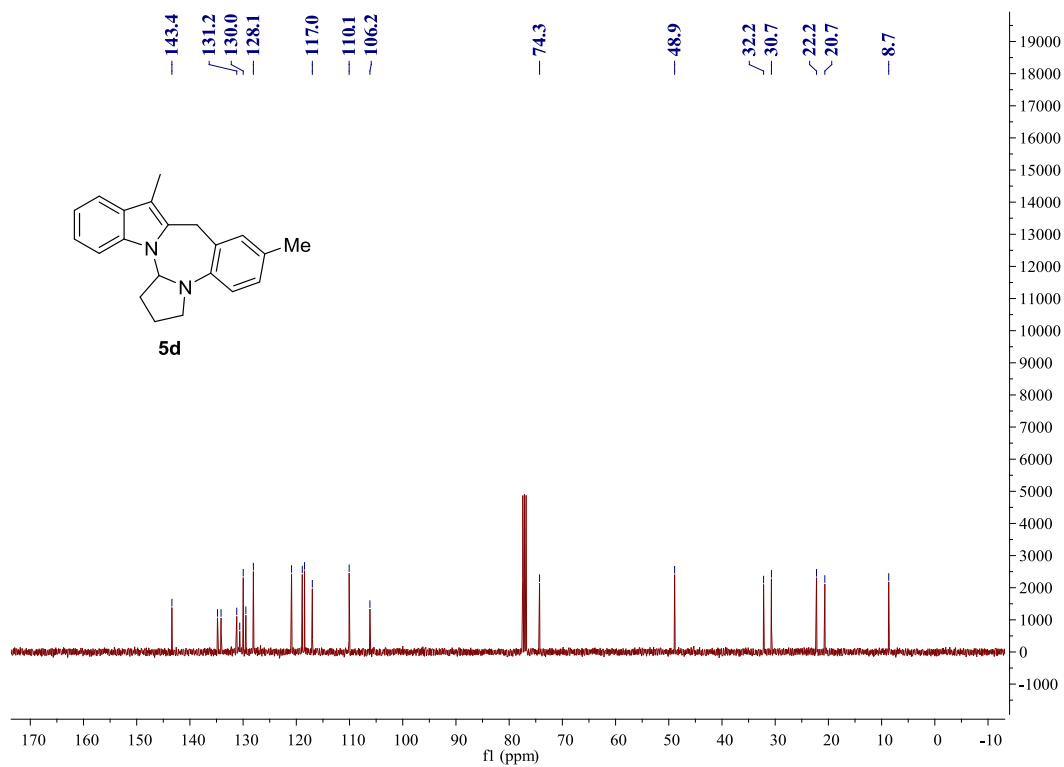
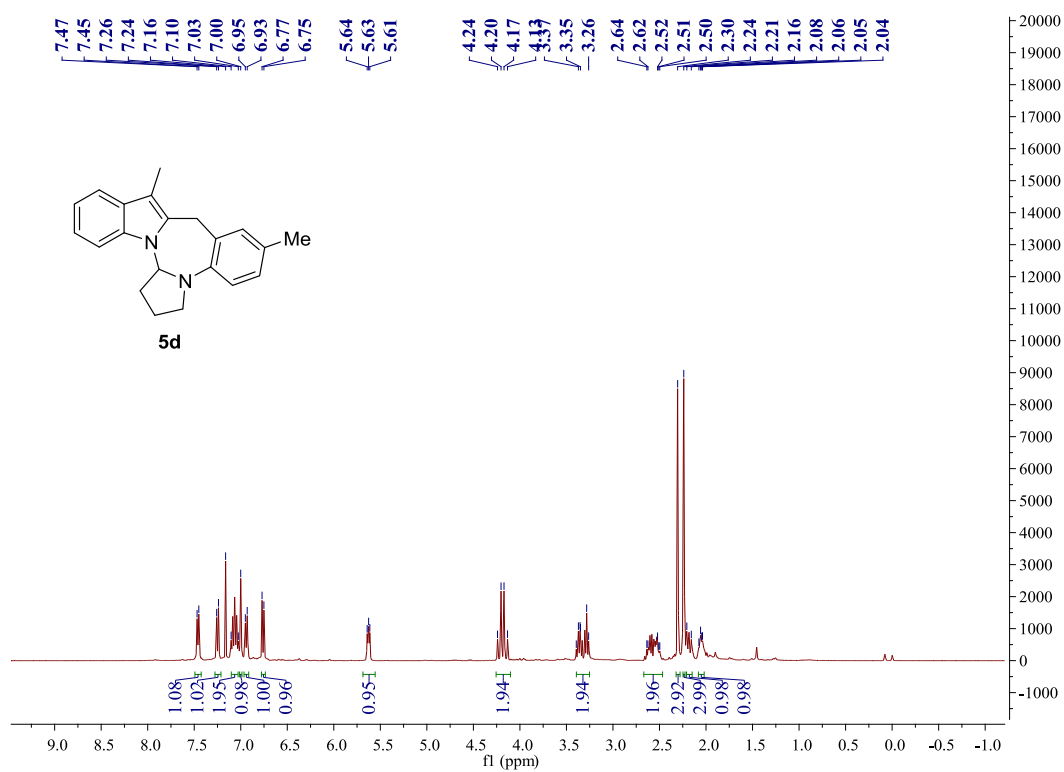


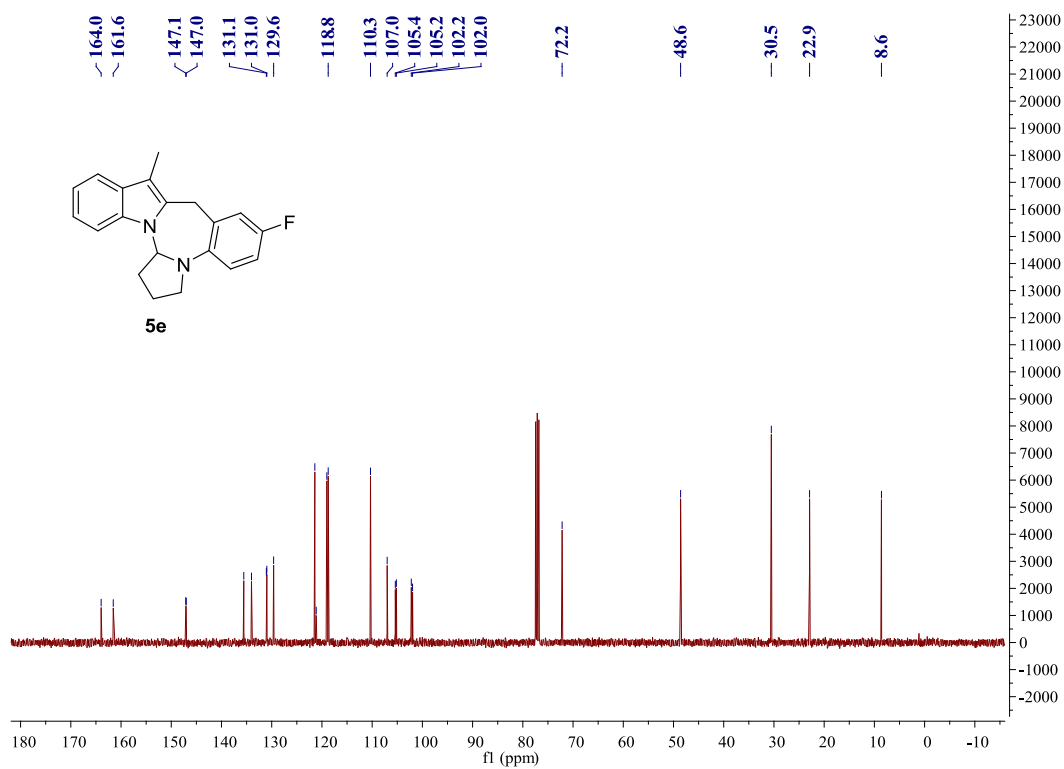
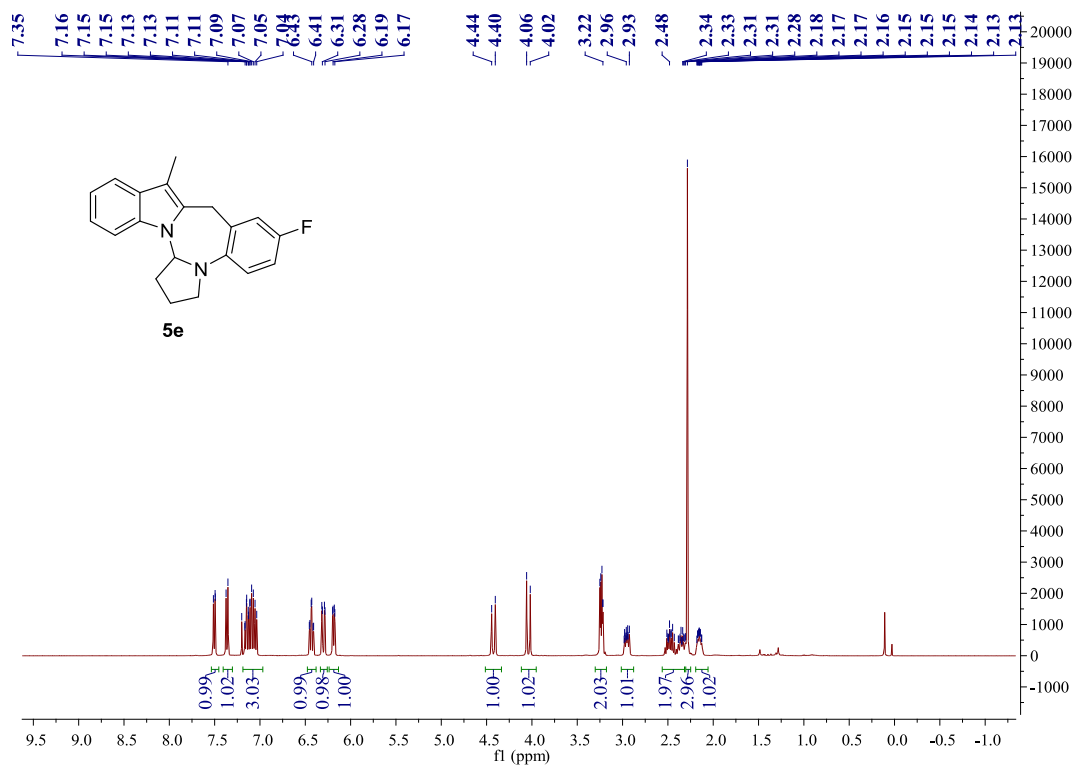


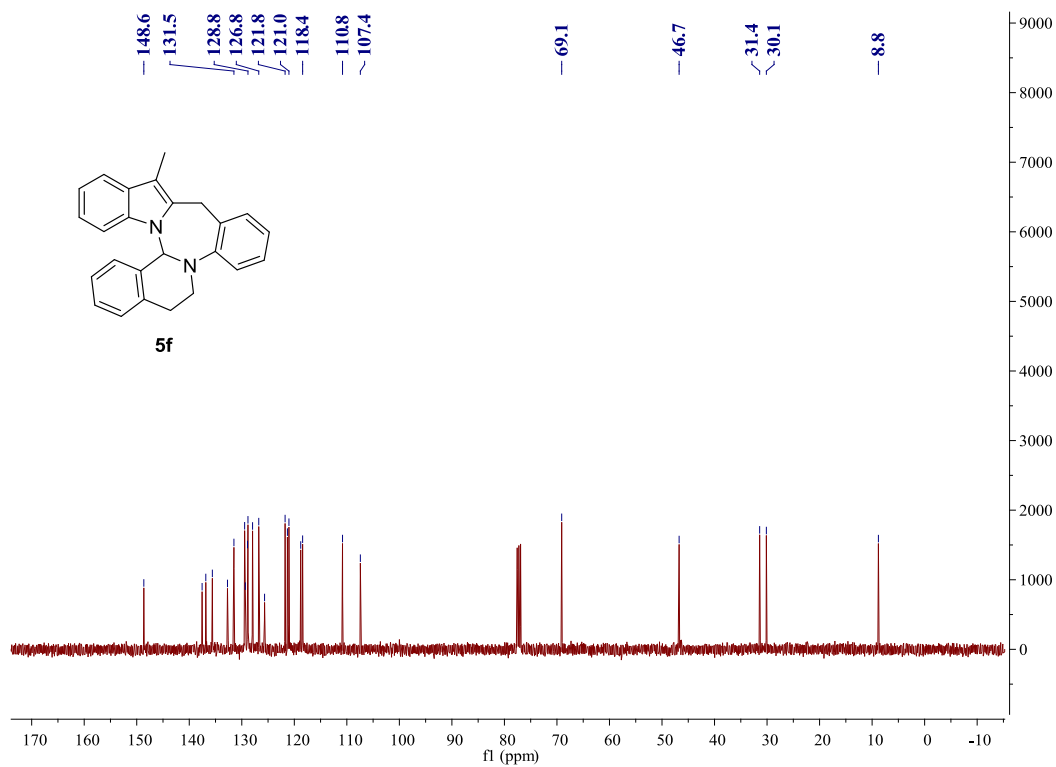
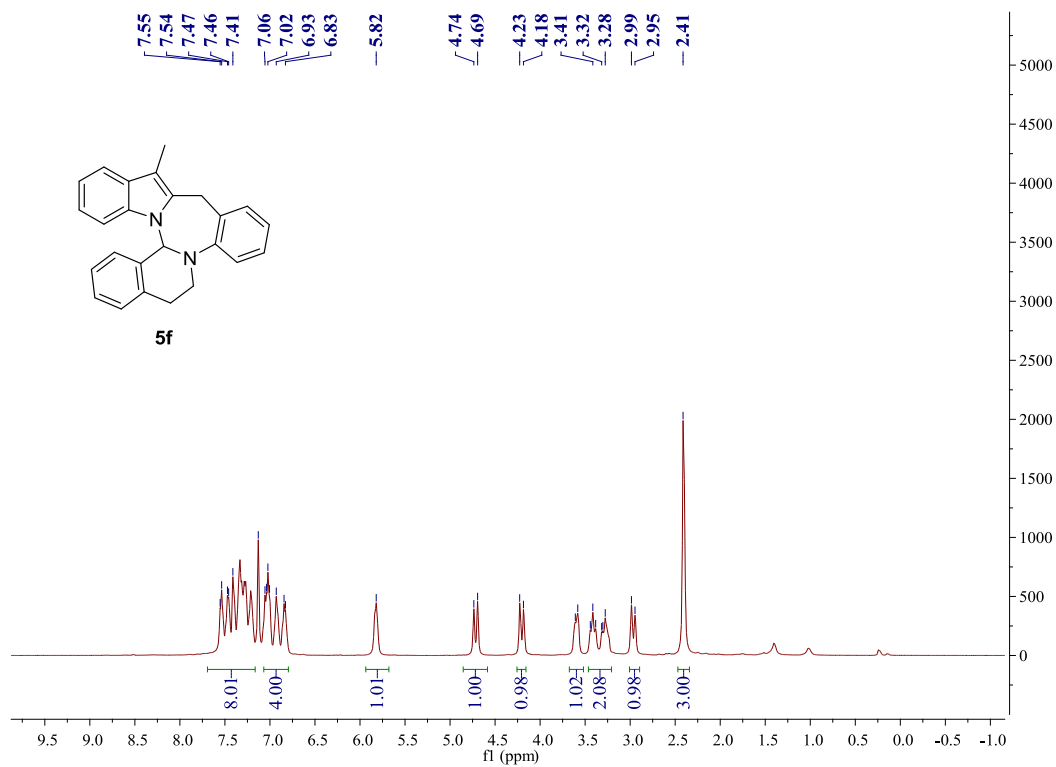












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