SUPPORTING INFORMATION

Cascade π-Extended Decarboxylative Annulation Involving Cyclic Diaryliodonium Salts: Site-Selective Synthesis of Phenanthridines and Benzocarbazoles via a Traceless Directing Group Strategy

Zenghui Ye, Yong Li, Kai Xu, Na Chen and Fengzhi Zhang*

College of Pharmaceutical Science, Zhejiang University of Technology, Hangzhou, 310014, P. R. China

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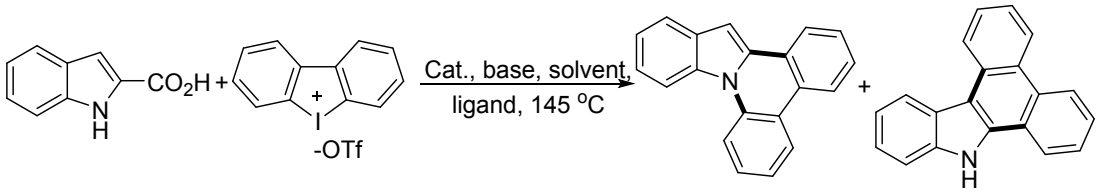
* Corresponding author, zhangfengzhi@zjut.edu.cn

Ⅰ. General information

All reagents were obtained from commercial suppliers and used without further purification. Yields for all compounds were determined by the column chromatography which was generally performed on silica gel (200-300 mesh) using petroleum ether 40-60 (PE)/EtOAc as eluent, and reactions were monitored by thin layer chromatography (TLC) on a glass pate coated with silica gel with fluorescent indicator (GF254) using UV light. The ^{1}H reree and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker ADNANCE III 500 MHz using $CDCl_3$ as solvent with TMS as internal standard. Chemical shifts are given in ppm (δ) referenced to $CDCl_3$ with 7.28 for ^{1}H and 77.03 for ^{13}C, and to DMSO-d_6 with 2.50 for ^{1}H and 39.52 for ^{13}C. Signals are abbreviated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet, and coupling constants are expressed in hertz. Melting points were measured on a SGW® X-4B apparatus and uncorrected. HRMS were recorded on Agilent 6210TOF LC/MS mass spectrometer.

Ⅱ. Conditions optimization of phenanthridine and benzocarbazole.



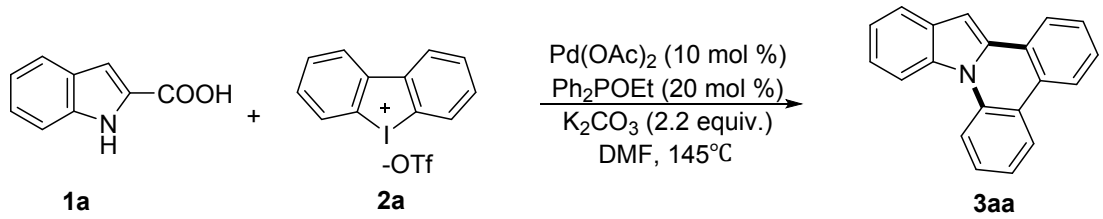
1a **2a** **3aa** **4a**

Entry[a]	**2a** (eq.)	Ligand	Catalyst	Base	Solvent	Yield(%)[b]	
						3aa	**4a**
1	1.1	--	$Pd(OAc)_2$	K_2CO_3	DMF	30	-
2[c]	1.1	-	$Pd(OAc)_2$	K_2CO_3	DMF	40	-
3	1.1	--	--	K_2CO_3	DMF	-	-
4	1.1	--	$Pd(OAc)_2$	--	DMF	-	-
5	1.1	--	$Pd(OAc)_2$	K_2CO_3	DMA	10	-
6	1.1		$Pd(OAc)_2$	K_2CO_3	DMSO	30	-
7	1.1		$Pd(OAc)_2$	K_2CO_3	toluene	19	-
8	1.1		$Pd(OAc)_2$	K_2CO_3	Ac_2O	-	-
9	1.1		$Pd(OAc)_2$	K_2CO_3	dioxane	22	-
10	1.1		$Pd(OAc)_2$	K_2CO_3	DCE	11	-
11	1.1		$Pd(OAc)_2$	Na_2CO_3	DMF	18	-
12	1.1		$Pd(OAc)_2$	Cs_2CO_3	DMF	-	-
13	1.1		$Pd(OAc)_2$	K_3PO_4	DMF	19	-
14	1.1	-	$Pd(OAc)_2$	KOH	DMF	19	-
15	1.1	-	$Pd(OAc)_2$	KO^{t}Bu	DMF	-	-
16	1.1	2,6-Bi(^{t}Bu) pyridine	$Pd(OAc)_2$	K_2CO_3	DMF	15	-
17	1.1	2,2'-Bipyridine	$Pd(OAc)_2$	K_2CO_3	DMF	22	-
18	1.1	1,10-phen	$Pd(OAc)_2$	K_2CO_3	DMF	14	-
19	1.1	PPh_3	$Pd(OAc)_2$	K_2CO_3	DMF	47	-

20	1.1		$Pd(PPh_3)_4$	K_2CO_3	DMF	38	-
21	1.1	PPh_2	$Pd(OAc)_2$	K_2CO_3	DMF	36	-
22	1.1	$P(cy)_3$	$Pd(OAc)_2$	K_2CO_3	DMF	9	-
23	1.1	S-Phos	$Pd(OAc)_2$	K_2CO_3	DMF	6	-
24	1.1	$(p\text{-}MeOC_6H_4)_3P$	$Pd(OAc)_2$	K_2CO_3	DMF	23	-
25	1.1	$(n\text{-}C_8H_{17})_3P$	$Pd(OAc)_2$	K_2CO_3	DMF	26	-
26	1.1	Ph_2POEt	$Pd(OAc)_2$	K_2CO_3	DMF	58	-
27[d]	1.1	Ph_2POEt	$Pd(OAc)_2$	K_2CO_3	DMF	42	-
28[e]	1.1	Ph_2POEt	$Pd(OAc)_2$	K_2CO_3	DMF	55	-
29	1.1	Ph_2POEt	$Pd_2(dba)_3$	K_2CO_3	DMF	38	-
30	1.1	Ph_2POEt	$Pd(dppf)Cl_2$	K_2CO_3	DMF	5	-
31	1.1	Ph_2POEt	$Pd(OAc)_2$	DABCO	DMF	30	-
32	1.1	Ph_2POEt	$Pd(OAc)_2$	Et_3N	DMF	46	-
33[f]	1.1	Ph_2POEt	$Pd(OAc)_2$	K_2CO_3	DMF	43	-
34[g]	1.1	Ph_2POEt	$Pd(OAc)_2$	K_2CO_3	DMF	43	-
35	1.1	Ph_2POEt	$Pd(OAc)_2$ (5mol%)	K_2CO_3	DMF	49	-
36	1.1	Ph_2POEt	$Pd(OAc)_2$ (2.5mol%)	K_2CO_3	DMF	25	-
37[h]	1.1	Ph_2POEt	$Pd(OAc)_2$	K_2CO_3	DMF	66	-
38[i]	1.1	Ph_2POEt	$Pd(OAc)_2$	K_2CO_3	DMF	72	-
39[j]	1.1	Ph_2POEt	$Pd(OAc)_2$	K_2CO_3	DMF	73	-
40[i]	1.3	Ph_2POEt	$Pd(OAc)_2$	K_2CO_3	DMF	73	-
41[i]	1.6	Ph_2POEt	$Pd(OAc)_2$	K_2CO_3	DMF	87	-
42[i]	2.0	Ph_2POEt	$Pd(OAc)_2$	K_2CO_3	DMF	94	-
43	1.1	-	$Pd(OAc)_2$	K_2CO_3	HOAc	-	30
44	2	-	$Pd(OAc)_2$	K_2CO_3	HOAc	-	41
45[i]	2	-	$Pd(OAc)_2$	K_2CO_3	HOAc	-	84
46[j]	2	-	$Pd(OAc)_2$	K_2CO_3	HOAc	-	68
47[i]	2	-	$Pd(OAc)_2$	-	HOAc	-	-
48[i]	2	-	$Pd(OAc)_2$	KOAc	HOAc	-	19
49[i]	2	-	$Pd(OAc)_2$	K_2HPO_4	HOAc	-	31
50[i]	2	Ph_2POEt (10%-20%)	$Pd(OAc)_2$	K_2CO_3	HOAc	-	26-27
51[i]	2	-	$PdCl_2$	K_2CO_3	HOAc	-	20
52[i]	2	-	$Pd_2(dba)_3$	K_2CO_3	HOAc	-	38
53[i]	2	-	$Pd(TFA)_2$	K_2CO_3	HOAc	-	51
54[i]	2	-	$[Ru(p\text{-cymene})Cl_2]_2$	K_2CO_3	HOAc	-	-
55[i]	2	-	$Cu(OAc)_2$	K_2CO_3	HOAc	-	-
56[i]	2	-	$Co(OAc)_2$	K_2CO_3	HOAc	-	-

[a]Reaction condtions: indole-2-carboxylic acid **1a** (0.3 mmol), Pd catalyst (10 mol %), ligand (20 mol %), base (2.2 equiv), solvent (1 mL), 12 h, 145 °C, air atmosphere. [b] Isolated yields. [c] 24h. [d] N_2 atmosphere. [e]O_2 atmosphere. [f] 3.3 eq. base. [g] 1.1 eq. base. [h] 0.75 mL solvent. [i] 2 mL solvent. [j] 3 mL solvent.

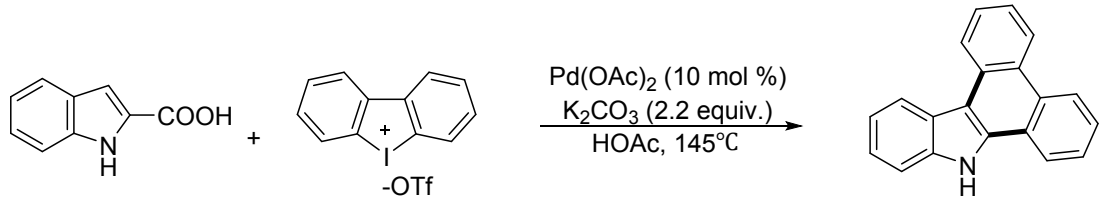
Ⅲ. General procedure to synthesize phenanthridine and benzocarbazole.



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

In a 15 mL thick-walled tube was charged with substrate **1a** (48.3 mg, 0.3 mmol), **2a** (256.9 mg, 0.6 mmol), $Pd(OAc)_2$ (6.8 mg, 0.03 mmol), K_2CO_3 (91.1 mg, 0.66 mmol), ethyl diphenylphosphinite (Ph_2POEt) (13 μL, 0.06 mmol) and DMF (2 mL). The reaction tube was sealed and stirred at 145 °C (pre-heated oil bath) for 12 h. The reaction mixture was then cooled to r.t. and diluted with water (10 mL) before it was extracted with EtOAc (15 mL x 3). The combined organic phase was washed with water (10 mL x 3) and saturated brine (10 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by column chromatography (PE/EA = 500:1) on silica gel to provide the desired indolo[1,2-*f*]phenanthridine **3aa** (75.4 mg, 94%) as a white solid.

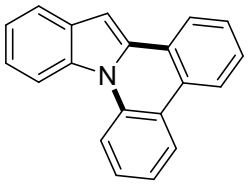
For 1 mmol scale synthesize phenanthridine: In a 30 mL thick-walled tube was charged with substrate **1a** (161.1 mg, 1 mmol), **2a** (513.6 mg, 1.2 mmol), $Pd(OAc)_2$ (22.4 mg, 0.1 mmol), K_2CO_3 (303.6 mg, 2.2 mmol), ethyl diphenylphosphinite (Ph_2POEt) (43.2 μL, 0.2 mmol) and DMF (6 mL). The reaction tube was sealed and stirred at 145 °C (pre-heated oil bath) for 12 h. The reaction mixture was then cooled to r.t. and diluted with water (20 mL) before it was extracted with EtOAc (25 mL x 3). The combined organic phase was washed with water (20 mL x 3) and saturated brine (20 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by column chromatography (PE/EA = 500:1) on silica gel to provide the desired indolo[1,2-*f*]phenanthridine **3aa** (225.0 mg, 84%) as a white solid.



1a **2a** **4a**

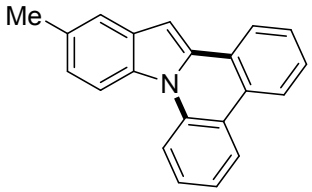
In a 15 mL thick-walled tube was charged with substrate **1a** (48.3 mg, 0.3 mmol), **2a** (256.9 mg, 0.6 mmol), $Pd(OAc)_2$ (6.8 mg, 0.03 mmol), K_2CO_3 (91.1 mg, 0.66 mmol) and HOAc (2 mL). The reaction tube was sealed and stirred at 145 °C (pre-heated oil bath) for 12 h. The reaction mixture was then cooled to r.t. and diluted with water (10 mL) before it was extracted with EtOAc (15 mL x 3). The combined organic phase was washed with water (10 mL x 3) and saturated brine (10 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The residue was purified by column chromatography (PE/EA = 20:1) on silica gel to provide the desired 9*H*-dibenzo[*a*, *c*]carbazole **4a** (66.8 mg, 84%) as a white solid.

Ⅳ. Characterization of the phenanthridine and benzocarbazole.



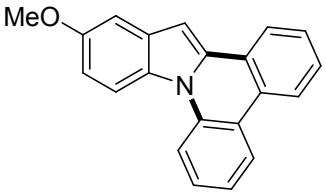
indolo[1,2-*f*]phenanthridine (3aa):

Following the general procedure, **3aa** was purified by PE/EtOAc (500:1) and obtained as a white solid (75.4 mg, 94% yield); Mp =149-150 °C; R_f = 0.40 (PE/EtOAc = 20:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.59 (dd, *J* = 8.4, 1.1 Hz, 1H), 8.46 – 8.39 (m, 1H), 8.37 (dd, *J* = 8.0, 1.5 Hz, 1H), 8.31 – 8.24 (m, 1H), 8.21 – 8.14 (m, 1H), 7.90 – 7.85 (m, 1H), 7.62 (ddd, *J* = 8.5, 7.1, 1.5 Hz, 1H), 7.57 – 7.48 (m, 2H), 7.47 – 7.35 (m, 3H), 7.31 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.0, 135.2, 133.9, 130.4, 128.7, 128.2, 127.8, 126.8, 126.1, 124.1, 124.0, 123.0, 122.4, 122.1, 122.0, 121.8, 121.0, 116.3, 114.2, 96.2. HRMS m/z (ESI): calcd for $C_{20}H_{14}N$ $[M + H]^+$ 268.1121, found 268.1109. The spectra data matched with values reported in the literature.[1, 2]



12-methylindolo[1,2-*f*]phenanthridine (3ab):

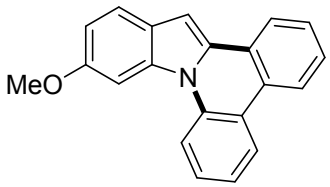
Following the general procedure, **3ab** was purified by PE/EtOAc (500:1) and obtained as a white solid (70.1 mg, 82% yield); Mp = 184-185 °C; R_f = 0.4 (PE/EtOAc = 20:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 (dd, *J* = 8.4, 1.1 Hz, 1H), 8.33 (dd, *J* = 8.1, 1.4 Hz, 1H), 8.27 (d, *J* = 8.7 Hz, 1H), 8.25 – 8.20 (m, 1H), 8.16 – 8.10 (m, 1H), 7.63 (dd, *J* = 2.0, 1.0 Hz, 1H), 7.59 (ddd, *J* = 8.5, 7.1, 1.5 Hz, 1H), 7.53 – 7.47 (m, 2H), 7.35 (ddd, *J* = 8.2, 7.1, 1.1 Hz, 1H), 7.23 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.19 (d, *J* = 0.8 Hz, 1H), 2.57 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ136.0, 135.3, 132.3, 131.2, 130.7, 128.7, 128.1, 127.7, 126.8, 126.2, 124.1, 123.9, 123.7, 122.8, 122.4, 122.0, 120.7, 116.2, 113.9, 95.8, 21.4. The spectra data matched with values reported in the literature.[1]



12-methoxyindolo[1,2-*f*]phenanthridine (3ac):

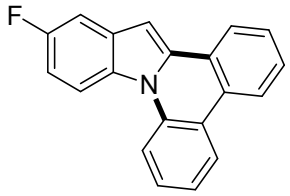
Following the general procedure, **3ac** was purified by PE/EtOAc (20:1) and obtained as a yellow solid (72.3 mg, 81% yield); Mp = 173-174 °C; R_f = 0.20 (PE/EtOAc = 20:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (dd, *J* = 8.5, 1.1 Hz, 1H), 8.36 (dd, *J* = 8.1, 1.5 Hz, 1H), 8.28 (dd, *J* = 13.6, 9.3 Hz, 2H), 8.19 – 8.11 (m, 1H), 7.60 (s, 1H), 7.55 – 7.49 (m, 2H), 7.37 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1H), 7.28 (d, *J* = 2.1 Hz, 1H), 7.22 (s, 1H), 7.04 (dd, *J* = 9.2, 2.6 Hz, 1H),

3.96 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ155.2, 135.9, 135.8, 131.4, 129.1, 128.8, 128.2, 127.8, 126.8, 126.0, 124.1, 124.0, 122.9, 122.4, 121.9, 115.9, 115.1, 112.0, 102.2, 95.9, 55.7. The spectra data matched with values reported in the literature.[1]



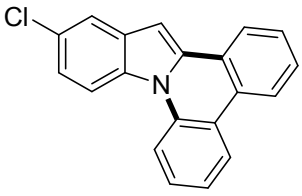
11-methoxyindolo[1,2-*f*]phenanthridine (3ad):

Following the general procedure, **3ad** was purified by PE/EtOAc (20:1) and obtained as a yellow solid (77.6 mg, 87% yield); R_f = 0.20 (PE/EtOAc = 20:1); Mp = 131-132 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42 – 8.37 (m, 1H), 8.25 (dd, *J* = 8.0, 1.3 Hz, 1H), 8.18 – 8.13 (m, 1H), 8.07 – 8.00 (m, 1H), 7.85 (d, *J* = 2.0 Hz, 1H), 7.71 (d, *J* = 8.6 Hz, 1H), 7.54 (ddd, *J* = 8.5, 7.2, 1.4 Hz, 1H), 7.48 – 7.40 (m, 2H), 7.34 – 7.29 (m, 1H), 7.15 (s, 1H), 7.06 (dd, *J* = 8.6, 2.1 Hz, 1H), 4.00 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ156.1, 135.9, 134.5, 134.4, 128.5, 128.1, 127.2, 126.5, 126.4, 124.7, 123.9, 123.6, 122.9, 122.3, 122.2, 121.3, 115.9, 110.8, 99.1, 96.0, 56.0. The spectra data matched with values reported in the literature.[1]



12-fluoroindolo[1,2-*f*]phenanthridine (3ae):

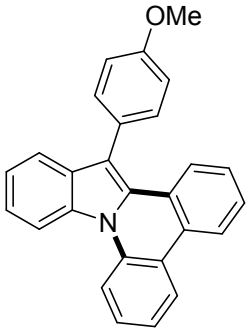
Following the general procedure, **3ae** was purified by PE/EtOAc (500:1) and obtained as a light green solid (77.8 mg, 90% yield). Mp = 132-133 °C; R_f = 0.33 (PE/EtOAc = 20:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.43 – 8.39 (m, 1H), 8.30 (dd, *J* = 8.0, 1.3 Hz, 1H), 8.26 (dd, *J* = 9.2, 4.3 Hz, 1H), 8.22 – 8.18 (m, 1H), 8.10 – 8.05 (m, 1H), 7.56 (ddd, *J* = 8.5, 7.2, 1.5 Hz, 1H), 7.53 – 7.47 (m, 2H), 7.43 (dd, *J* = 9.0, 2.6 Hz, 1H), 7.37 – 7.33 (m, 1H), 7.16 (s, 1H), 7.10 (td, *J* = 9.0, 2.6 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.6 ($J_{C\text{-}F}$ = 239.0 Hz), 136.7, 135.5, 131.2 ($J_{C\text{-}F}$ = 10.4 Hz), 130.5, 128.8, 128.2, 128.1, 126.9, 125.6, 124.2, 124.0, 123.2, 122.4, 121.9, 115.9, 115.0 ($J_{C\text{-}F}$ = 9.8 Hz), 110.0 ($J_{C\text{-}F}$ = 25.4 Hz), 105.5 ($J_{C\text{-}F}$ = 23.0 Hz), 96.0; HRMS m/z (ESI): calcd for $C_{20}H_{13}FN$ $[M + H]^+$ 286.1027, found 286.1027.



12-chloroindolo[1,*2-f*]phenanthridine (3af):

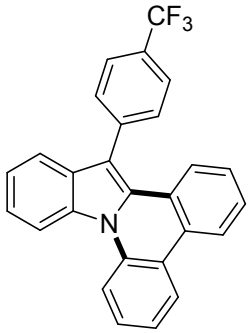
Following the general procedure, **3af** was purified by PE/EtOAc (500:1) and obtained as a white solid (76.0 mg, 84% yield); Mp = 173-174 °C; R_f = 0.4 (PE/EtOAc = 20:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 – 8.40 (m, 1H), 8.34 (dd, *J* = 8.1, 1.5 Hz, 1H), 8.26 (d, *J* = 9.0 Hz,

2H), 8.11 (d, *J* = 9.2 Hz, 1H), 7.77 (d, *J* = 2.1 Hz, 1H), 7.59 (s, 1H), 7.56 – 7.48 (m, 2H), 7.39 (s, 1H), 7.31 (dd, *J* = 9.0, 2.2 Hz, 1H), 7.17 (d, *J* = 0.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ136.5, 135.6, 132.2, 131.5, 128.9, 128.4, 128.3, 127.4, 127.0, 125.7, 124.3, 124.2, 123.4, 122.5, 122.2, 122.1, 120.2, 116.2, 115.1, 95.6; HRMS m/z (ESI) calcd for $C_{20}H_{13}ClN$ $[M + H]^+$ 302.0731, found 302.0734.



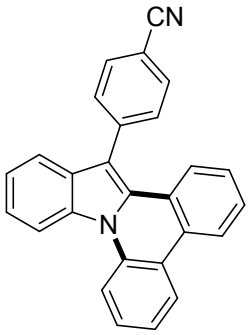
14-(4-methoxyphenyl)indolo[1,2-*f*]phenanthridine (3ag):

Following the general procedure, **3ag** was purified by PE/EtOAc (20:1) and obtained as a yellow solid (104.2 mg, 93% yield); Mp = 198-200 °C; R_f = 0.23 (PE/EtOAc = 20:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (dd, *J* = 8.4, 1.1 Hz, 1H), 8.44 (dd, *J* = 8.6, 0.8 Hz, 1H), 8.35 (dd, *J* = 8.1, 1.5 Hz, 1H), 8.28 – 8.22 (m, 1H), 7.87 – 7.80 (m, 1H), 7.65 – 7.57 (m, 2H), 7.54 – 7.48 (m, 2H), 7.48 – 7.31 (m, 4H), 7.23 – 7.17 (m, 1H), 7.16 – 7.11 (m, 2H), 3.97 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ159.0, 135.9, 132.7, 132.1, 131.7, 128.8, 128.0, 127.7, 127.6, 127.5, 127.0, 125.3, 124.1, 123.1, 122.6, 122.4, 122.3, 121.7, 119.9, 116.5, 114.6, 114.0, 113.5, 55.4; HRMS m/z (ESI) calcd for $C_{27}H_{20}NO$ $[M + H]^+$ 374.1539, found 374.1535.



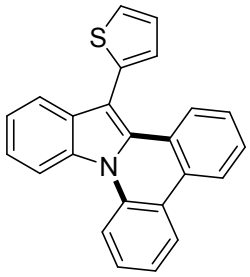
14-(4-(trifluoromethyl)phenyl)indolo[1,2-*f*]phenanthridine (3ah):

Following the general procedure, **3ah** was purified by PE/EtOAc (500:1) and obtained as a white solid (122.2 mg, 99% yield). Mp = 175-176 °C; R_f = 0.38 (PE/EtOAc = 20:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62 (dd, *J* = 8.4, 1.0 Hz, 1H), 8.46 (d, *J* = 8.5 Hz, 1H), 8.37 (dd, *J* = 8.1, 1.4 Hz, 1H), 8.28 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 2H), 7.78 – 7.68 (m, 3H), 7.64 (s, 1H), 7.59 – 7.53 (m, 1H), 7.51 – 7.39 (m, 3H), 7.39 – 7.32 (m, 1H), 7.23 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ140.2, 135.7, 132.8, 131.5, 131.0, 130.4, 129.5 (J_{C-F} = 32.3 Hz), 128.9, 127.9, 127.9, 127.8, 126.3, 126.1 (J_{C-F} = 4.0 Hz), 125.3, 124.4 (J_{C-F} = 272.3 Hz), 124.1, 123.4, 123.0, 122.7, 122.3, 122.2, 119.4, 116.6, 114.2, 112.2.; HRMS m/z (ESI) : calcd for $C_{27}H_{16}F_3N$ $[M + H]^+$ 411.1229, found 411.1231.



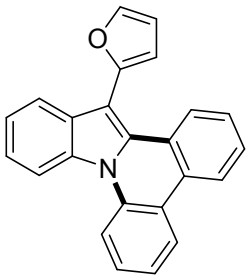
4-(indolo[1,2-*f*]phenanthridin-14-yl)benzonitrile (3ai):

Following the general procedure, **3ai** was purified by PE/EtOAc (500:1) and obtained as a yellow solid (103.9 mg, 94% yield); Mp = 202-203 °C; R_f = 0.18 (PE/EtOAc = 20:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.61 (dd, *J* = 8.4, 1.1 Hz, 1H), 8.46 (d, *J* = 8.6 Hz, 1H), 8.37 (dd, *J* = 8.1, 1.4 Hz, 1H), 8.29 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.92 – 7.83 (m, 2H), 7.77 – 7.70 (m, 2H), 7.69 – 7.61 (m, 2H), 7.57 – 7.51 (m, 1H), 7.51 – 7.40 (m, 3H), 7.40 – 7.33 (m, 1H), 7.23 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ141.6, 132.9, 132.9, 131.9, 130.5, 129.0, 128.1, 128.0, 127.8, 126.0, 125.2, 124.2, 123.6, 123.1, 122.8, 122.3, 122.3, 119.1, 119.1, 116.6, 114.3, 111.1; HRMS m/z (ESI): calcd for $C_{27}H_{16}N_2Na$ $[M + Na]^+$ 391.1206, found 391.1210.



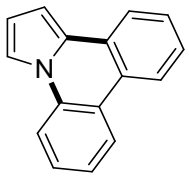
14-(thiophen-2-yl)indolo[1,2-*f*]phenanthridine (3aj):

Following the general procedure, **3aj** was purified by PE/EtOAc (500:1) and obtained as a yellow solid (99.6 mg, 95% yield). Mp = 161-163 °C; R_f = 0.38 (PE/EtOAc = 20:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.61 (dd, *J* = 8.4, 1.1 Hz, 1H), 8.43 (d, *J* = 8.5 Hz, 1H), 8.36 (dd, *J* = 8.1, 1.5 Hz, 1H), 8.28 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.92 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.72 – 7.66 (m, 1H), 7.65 – 7.57 (m, 2H), 7.50 – 7.43 (m, 2H), 7.44 – 7.34 (m, 2H), 7.33 – 7.26 (m, 2H), 7.24 (dd, *J* = 3.4, 1.2 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ135.6, 132.7, 132.2, 128.8, 128.4, 127.9, 127.9, 127.9, 126.9, 126.4, 125.6, 124.1, 123.4, 122.9, 122.4, 122.4, 122.2, 119.9, 116.6, 114.0, 105.3; HRMS m/z (ESI) : calcd for $C_{24}H_{16}NS$ $[M + H]^+$ 350.0998, found 350.1002.



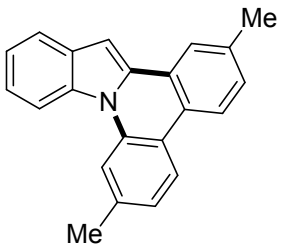
14-(furan-2-yl)indolo[1,2-*f*]phenanthridine (3ak):

Following the general procedure, **3ak** was purified by PE/EtOAc (500:1) and obtained as a brown solid (60.0 mg, 60% yield); Mp = 140-142 °C; R_f = 0.36 (PE/EtOAc = 20:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (dd, *J* = 8.4, 1.1 Hz, 1H), 8.42 (d, *J* = 8.4 Hz, 1H), 8.37 (dd, *J* = 8.1, 1.4 Hz, 1H), 8.28 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.85 – 7.78 (m, 1H), 7.74 – 7.67 (m, 2H), 7.62 (s, 1H), 7.50 (s, 1H), 7.46 (s, 1H), 7.43 – 7.34 (m, 3H), 6.76 – 6.67 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ148.1, 142.3, 135.5, 132.9, 131.0, 128.8, 128.1, 127.9, 126.0, 125.4, 124.1, 123.5, 122.9, 122.5, 122.4, 122.3, 119.9, 116.7, 114.2, 111.6, 110.4, 102.5; HRMS m/z (ESI): calcd for $C_{24}H_{16}NO$ $[M + H]^+$ 334.1226, found 334.1232.



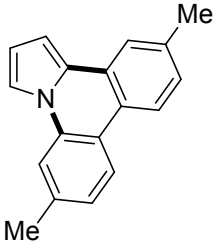
pyrrolo[1,2-*f*]phenanthridine (3al):

Following the general procedure, **3al** was purified by PE/EtOAc (500:1) and obtained as a white solid (63.9 mg, 98% yield); Mp = 131-133 °C; R_f = 0.40 (PE/EtOAc = 20:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 (dd, *J* = 8.1, 1.3 Hz, 1H), 8.27 (dd, *J* = 8.2, 1.1 Hz, 1H), 8.04 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.88 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.80 (dd, *J* = 2.9, 1.5 Hz, 1H), 7.62 – 7.47 (m, 2H), 7.42 (dddd, *J* = 18.7, 8.2, 7.1, 1.3 Hz, 2H), 6.99 (dd, *J* = 3.8, 1.5 Hz, 1H), 6.76 (dd, *J* = 3.8, 2.9 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.2, 129.3, 128.5, 128.1, 126.3, 125.9, 124.8, 124.0, 123.8, 122.8, 122.5, 121.7, 115.0, 113.1, 112.2, 102.0. The spectra data matched with values reported in the literature.[2]



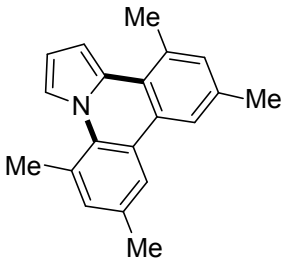
2,7-dimethylindolo[1,2-*f*]phenanthridine (3ba):

Following the general procedure, **3ba** was purified by PE/EtOAc (500:1) and obtained as a white solid (44.3 mg, 50% yield); Mp =132-134 °C; R_f = 0.34 (PE/EtOAc = 20:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.43 (d, *J* = 8.3 Hz, 1H), 8.39 (s, 1H), 8.19 (d, *J* = 8.1 Hz, 1H), 8.11 (d, *J* = 8.2 Hz, 1H), 8.01 – 7.92 (m, 1H), 7.85 (s, 1H), 7.39 (d, *J* = 22.0 Hz, 4H), 7.20 – 7.16 (m, 1H), 2.60 (s, 3H), 2.53 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.5, 137.6, 135.7, 135.6, 134.0, 130.5, 129.2, 125.7, 124.7, 124.2, 124.1, 123.7, 122.2, 121.8, 121.7, 121.0, 119.8, 116.7, 114.3, 95.9, 22.0, 21.5; HRMS m/z (ESI) calcd for $C_{22}H_{18}N$ $[M + H]^+$ 296.1434, found 296.1438.



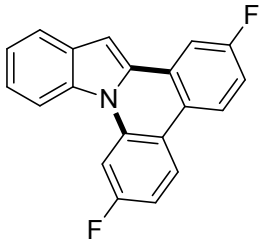
6,11-dimethylpyrrolo[1,2-*f*]phenanthridine (3bb):

Following the general procedure, **3bb** was purified by PE/EtOAc (500:1) and obtained as a light green solid (39.0 mg, 53% yield); Mp = 125-127 °C; R_f = 0.42 (PE/EtOAc = 20:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.2 Hz, 1H), 8.12 (d, *J* = 8.3 Hz, 1H), 7.87 – 7.63 (m, 3H), 7.22 (dddd, *J* = 20.7, 8.2, 1.8, 0.7 Hz, 2H), 6.95 (d, *J* = 3.7 Hz, 1H), 6.73 (d, *J* = 3.2 Hz, 1H), 2.54 (s, 3H), 2.51 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ138.2, 137.5, 132.8, 129.5, 127.3, 125.9, 125.0, 123.6, 122.7, 122.6, 122.2, 119.3, 115.2, 112.9, 112.0, 101.6, 21.7, 21.5; HRMS m/z (ESI): calcd for $C_{18}H_{16}N$ $[M + H]^+$246.1277, found 246.1279.



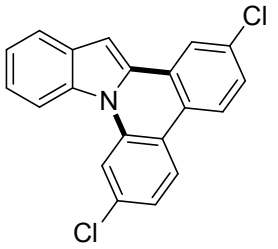
5,7,10,12-tetramethylpyrrolo[1,2-*f*]phenanthridine (3bc):

Following the general procedure, **3bc** was purified by PE/EtOAc (500:1) and obtained as a yellow solid (43.5 mg, 53% yield); R_f = 0.44 (PE/EtOAc = 20:1); Mp = 153-155 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (q, *J* = 1.4 Hz, 2H), 8.00 (s, 1H), 7.21 – 7.16 (m, 2H), 7.05 (dd, *J* = 4.0, 1.4 Hz, 1H), 6.71 (dd, *J* = 4.0, 3.0 Hz, 1H), 2.89 (s, 3H), 2.80 (s, 3H), 2.49 (d, *J* = 4.4 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.4, 133.6, 133.3, 132.5, 132.3, 130.0, 126.8, 125.5, 123.9, 123.6, 122.5, 121.0, 118.8, 110.1, 106.0, 24.6, 24.6, 21.5, 21.0; HRMS m/z (ESI): calcd for $C_{20}H_{20}N$ $[M + H]^+$ 274.1590, found 274.1593.



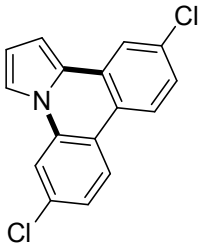
2,7-difluoroindolo[1,2-*f*]phenanthridine (3bd):

Following the general procedure, **3bd** was purified by PE/EtOAc (500:1) and obtained as a light yellow solid (45.4 mg, 57% yield); Mp = 182-184 °C; R_f = 0.29 (PE/EtOAc = 20:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.3 Hz), 8.16 – 8.07 (m), 8.02 (dd, *J* = 9.0, 5.3 Hz), 7.85 – 7.79 (m), 7.65 (dd, *J* = 9.4, 2.6 Hz), 7.45 – 7.35 (m), 7.18 – 7.11 (m), 7.03 (ddd, *J* = 8.8, 7.6, 2.4 Hz); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.7 (d, $J_{C\text{-}F}$ = 247.0 Hz), 162.4 (d, $J_{C\text{-}F}$ = 247.0 Hz), 136.4 (d, $J_{C\text{-}F}$ = 10.2 Hz), 134.3(d, $J_{C\text{-}F}$ = 3.3 Hz), 133.9, 130.2, 127.3 (d, $J_{C\text{-}F}$ = 9.1 Hz), 125.5 (d, $J_{C\text{-}F}$ = 9.9 Hz), 124.5 (d, $J_{C\text{-}F}$ = 8.6 Hz), 122.9, 122.8 (d, $J_{C\text{-}F}$ = 2.4 Hz), 122.4, 121.4, 117.9 (d, $J_{C\text{-}F}$ = 3.0 Hz), 116.0, 114.0, 110.5 (d, $J_{C\text{-}F}$ = 22.1 Hz), 109.7 (d, $J_{C\text{-}F}$ = 23.2 Hz), 103.6, 97.6; HRMS m/z (ESI) : calcd for $C_{20}H_{12}F_2N$ $[M + H]^+$ 304.0932, found 304.0931.



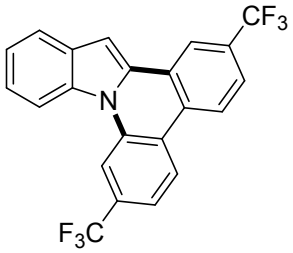
2,7-dichloroindolo[1,2-*f*]phenanthridine (3be):

Following the general procedure, **3be** was purified by PE/EtOAc (500:1) and obtained as a light yellow solid (46.4 mg, 46% yield); Mp =208-210 °C; R_f = 0.34 (PE/EtOAc = 20:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 (d, *J* = 2.0 Hz, 1H), 8.31 (dd, *J* = 8.6, 0.9 Hz, 1H), 8.17 (d, *J* = 8.7 Hz, 1H), 8.10 – 8.07 (m, 2H), 7.86 (ddd, *J* = 7.8, 1.4, 0.7 Hz, 1H), 7.49 – 7.39 (m, 3H), 7.34 (dd, *J* = 8.6, 2.0 Hz, 1H), 7.26 (d, *J* = 0.8 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.4, 128.2, 125.1, 124.0, 123.7, 123.4, 123.0, 122.5, 121.5, 116.4, 114.0, 97.7; HRMS m/z (ESI): calcd for $C_{20}H_{12}Cl_2N$ $[M + H]^+$ 336.0341, found 336.0347.



6,11-dichloropyrrolo[1,2-*f*]phenanthridine (3bf):

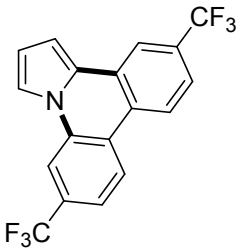
Following the general procedure, **3bf** was purified by PE/EtOAc (500:1) and obtained as a white solid (70.4 mg, 82% yield); Mp = 178-180 °C; R_f= 0.37 (PE/EtOAc = 20:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ8.15 (d, *J* = 8.7 Hz, 1H), 8.06 (d, *J* = 8.7 Hz, 1H), 7.93 (d, *J* = 2.3 Hz, 1H), 7.81 (d, *J* = 2.0 Hz, 1H), 7.70 (dd, *J* = 3.0, 1.4 Hz, 1H), 7.34 (ddd, *J* = 9.0, 7.5, 2.2 Hz, 2H), 6.95 (dd, *J* = 3.8, 1.3 Hz, 1H), 6.76 (t, *J* = 3.4 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.6, 134.4, 133.8, 128.3, 127.5, 126.4, 125.2, 124.4, 124.1, 122.6, 122.4, 119.6, 115.2, 113.9, 113.1, 103.4; HRMS m/z (ESI) calcd for $C_{16}H_{10}Cl_2N$ $[M + H]^+$ 286.0185, found 286.0192. The ^{13}C-NMR of **3bf** is not obvious due to poor solubility.



2,7-bis(trifluoromethyl)indolo[1,2-*f*]phenanthridine (3bg):

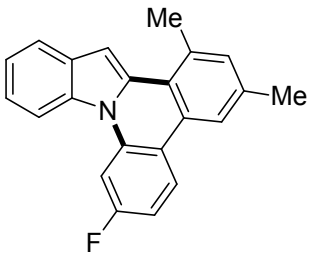
Following the general procedure, **3bg** was purified by PE/EtOAc (500:1) and obtained as a yellow solid (56.8 mg, 47% yield); Mp = 187-189 °C; R_f = 0.4 (PE/EtOAc = 20:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.73 (s, 1H), 8.37 (d, *J* = 8.3 Hz, 1H), 8.32 (s, 1H), 8.27 (t, *J* = 9.3 Hz, 2H), 7.88 (d, *J* = 7.7 Hz, 1H), 7.73 – 7.68 (m, 1H), 7.60 (d, *J* = 8.5 Hz, 1H), 7.50 (ddd, *J* = 8.5, 7.1, 1.3 Hz, 1H), 7.43 (t, *J* = 7.2 Hz, 1H), 7.32 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.4, 133.8 (d, $J_{C\text{-}F}$ = 32.2 Hz), 130.2, 127.1, 126.2, 125.1, 124.2, 124.1 (d, $J_{C\text{-}F}$ = 3.3 Hz),

123.8 (d, $J_{C\text{-}F}$ = 2.0 Hz), 123.7, 123.6, 122.8, 121.8, 121.4 (dd, $J_{C\text{-}F}$ = 4.5 Hz), 119.7 (dd, $J_{C\text{-}F}$ = 4.5 Hz), 113.9, 113.4 (t, $J_{C\text{-}F}$ = 4.3 Hz), 98.4; HRMS m/z (ESI) : calcd for $C_{22}H_{12}F_6N$ [M + H] $^+$ 404.0868, found 404.0874.



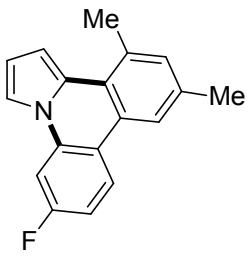
6,11-bis(trifluoromethyl)pyrrolo[1,2-*f*]phenanthridine (3bh):

Following the general procedure, **3bh** was purified by PE/EtOAc (500:1) and obtained as a green solid (44.5 mg, 42% yield); R_f = 0.35 (PE/EtOAc = 20:1); Mp =167-169 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (d, *J* = 8.4 Hz, 1H), 8.28 (d, *J* = 8.5 Hz, 1H), 8.20 (s, 1H), 8.06 (s, 1H), 7.81 (dd, *J* = 2.9, 1.2 Hz, 1H), 7.62 (d, *J* = 8.1 Hz, 2H), 7.04 (dd, *J* = 3.8, 1.2 Hz, 1H), 6.83 – 6.78 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 133.4, 131.3 (d, $J_{C\text{-}F}$ = 33.4 Hz), 131.0 (d, $J_{C\text{-}F}$ = 32.2 Hz), 130.9, 128.2, 126.9, 126.0, 125.1, 123.6, 123.3, 122.9, 122.2 (dd, $J_{C\text{-}F}$ = 3.5 Hz), 120.3 (dd, $J_{C\text{-}F}$ = 3.5 Hz), 120.0 (dd, $J_{C\text{-}F}$ = 3.5 Hz), 114.2, 113.3, 112.4 (dd, $J_{C\text{-}F}$ = 4.5 Hz), 104.0; HRMS m/z (ESI): calcd for $C_{18}H_{10}F_6N$ [M + H] $^+$ 354.0712, found 354.0706.



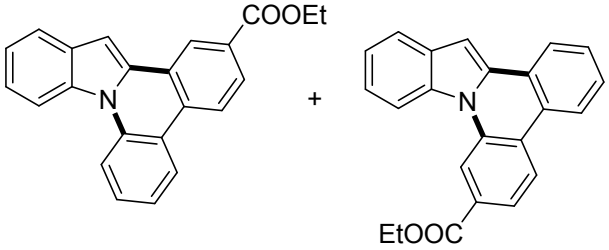
7-fluoro-1,3-dimethylindolo[1,2-*f*]phenanthridine (3bi):

Following the general procedure, **3bi** was purified by PE/EtOAc (500:1) and obtained as a white solid (65.8 mg, 70% yield); Mp = 144-146 ^{o}C; R_f = 0.48 (PE/EtOAc = 20:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (dd, *J* = 8.4, 2.8 Hz, 1H), 8.20 (dd, *J* = 8.8, 6.2 Hz, 1H), 8.16 (dd, *J* = 11.2, 2.4 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 5.0 Hz, 1H), 7.42 (ddd, *J* = 8.6, 7.1, 1.4 Hz, 1H), 7.37 (t, *J* = 7.2 Hz, 1H), 7.28 (d, *J* = 5.5 Hz, 1H), 7.17 (d, *J* = 3.1 Hz, 1H), 7.03 – 6.98 (m, 1H), 2.81 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.7 ($J_{C\text{-}F}$ = 245.7 Hz), 136.8, 136.6 ($J_{C\text{-}F}$ = 11.0 Hz), 135.5, 134.9, 132.8, 132.6, 130.5, 127.9, 126.1 ($J_{C\text{-}F}$ = 9.8 Hz), 122.6, 122.4, 122.0, 121.1, 120.5, 119.0 ($J_{C\text{-}F}$ = 2.8 Hz), 113.8, 110.1 ($J_{C\text{-}F}$ = 22.0 Hz), 103.3 ($J_{C\text{-}F}$ = 27.1 Hz), 101.9, 25.0, 21.5; HRMS m/z (ESI): calcd for $C_{22}H_{17}FN$ [M + H] $^+$ 314.1340, found 314.1339.



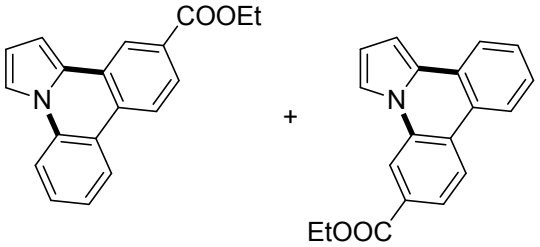
6-fluoro-10,12-dimethylpyrrolo[1,2-*f*]phenanthridine (3bj):

Following the general procedure, **3bj** was purified by PE/EtOAc (500:1) and obtained as a white solid (48.2 mg, 61% yield); R_f = 0.30 (PE/EtOAc = 20:1); Mp = 144-146 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (dd, *J* = 9.0, 6.0 Hz, 1H), 7.92 (s, 1H), 7.71 (dd, *J* = 2.9, 1.1 Hz, 1H), 7.51 (dd, *J* = 10.2, 2.5 Hz, 1H), 7.20 (s, 1H), 7.09 – 7.04 (m, 1H), 7.02 (dd, *J* = 3.9, 1.1 Hz, 1H), 6.80 – 6.77 (m, 1H), 2.77 (s, 3H), 2.49 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.7 (J_{C-F} = 247.0 Hz), 134.9, 134.3 (J_{C-F} = 10.5 Hz), 134.0, 132.3, 129.2, 126.3 (J_{C-F} = 9.5 Hz), 125.6, 122.8, 120.4, 118.4, 112.9, 112.4, 111.4 (J_{C-F} = 22.1 Hz), 107.6, 101.7, (J_{C-F} = 25.2 Hz), 24.7, 21.4; HRMS m/z (ESI): calcd for $C_{18}H_{15}FN$ $[M + H]^+$ 264.1183, found 264.1186.



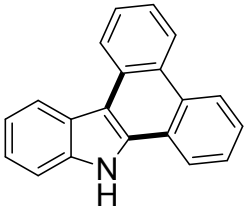
The mixture of ethyl indolo[1,2-*f*]phenanthridine-2-carboxylate (3bk) and ethyl indolo[1,2-*f*]phenanthridine-7-carboxylate (3bk'):

Following the general procedure, inseparable **3bk and 3bk'** were purified by PE/EtOAc (2:1) and obtained as a yellow solid (66.2 mg, 65% yield); R_f = 0.20 (PE/EtOAc = 2:1); HRMS m/z (ESI): calcd for $C_{23}H_{18}NO_2$ $[M + H]^+$ 340.1332, found 340.1332.



The mixture of ethyl pyrrolo[1,2-*f*]phenanthridine-11-carboxylate (3bl) and ethyl pyrrolo[1,2-*f*]phenanthridine-6-carboxylate (3bl'):

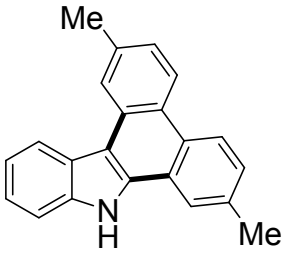
Following the general procedure, inseparable **3bl and 3bl'** were purified by PE/EtOAc (20:1) and obtained as a green solid (65.1 mg, 75% yield); R_f = 0.3 (PE/EtOAc = 20:1); HRMS m/z (ESI): calcd for $C_{19}H_{16}NO_2$ $[M + H]^+$ 290.1176, found 290.1177.



9*H*-dibenzo[*a*, *c*]carbazole(4a):

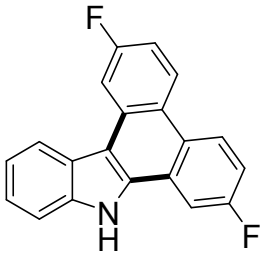
Following the general procedure, **4a** was purified by PE/EtOAc (20:1) and obtained as a white solid (66.8 mg, 84% yield); Mp =194-196 °C; R_f = 0.20 (PE/EtOAc = 20:1); ^{1}H NMR (500 MHz, DMSO-d_6)δ 12.42 (s, 1H), 8.95 – 8.87 (m, 2H), 8.82 (dd, *J* = 8.1, 1.3 Hz, 1H), 8.63 – 8.55 (m, 2H), 7.79 (ddt, *J* = 8.2, 6.9, 1.4 Hz, 2H), 7.73 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 2H), 7.60 (ddd, *J* = 8.4, 7.0, 1.3 Hz, 1H), 7.44 (ddd, *J* = 8.1, 7.1, 1.0 Hz, 1H), 7.34 (ddd, *J* = 8.1,

7.1, 1.1 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 138.5, 134.2, 129.6, 129.3, 127.6, 127.0, 126.5, 126.2, 124.0, 123.7, 123.6, 123.6, 123.4, 122.6, 122.3, 121.4, 120.1, 111.9, 111.3. The spectra data matched with values reported in the literature.[3]



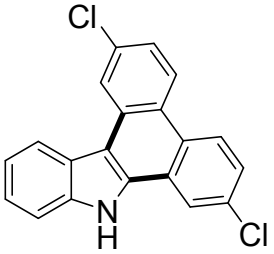
2,7-dimethyl-9*H*-dibenzo[*a, c*]carbazole (4b):

Following the general procedure, **4b** was purified by PE/EtOAc (20:1) and obtained as a white solid (120.2 mg, 88% yield); Mp = 223-226 °C; R_f = 0.20 (PE/EtOAc = 20:1); ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.32 (s, 1H), 8.72 (dd, J = 10.3, 8.5 Hz, 2H), 8.60 (d, J = 8.0 Hz, 1H), 8.57 (d, J = 1.7 Hz, 1H), 8.43 – 8.34 (m, 1H), 7.71 (dt, J = 8.0, 0.8 Hz, 1H), 7.52 (dd, J = 8.6, 1.8 Hz, 1H), 7.46 – 7.37 (m, 2H), 7.33 (ddd, J = 8.1, 7.0, 1.1 Hz, 1H), 2.65 (s, 3H), 2.61 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 138.5, 136.5, 135.8, 134.2, 129.3, 127.3, 124.1, 123.7, 123.6, 123.4, 123.0, 122.3, 121.4, 119.9, 111.1, 21.4, 21.3. **HRMS** m/z (ESI): calcd for $C_{22}H_{18}N$ $[M + H]^+$ 296.1434, found 296.1441.



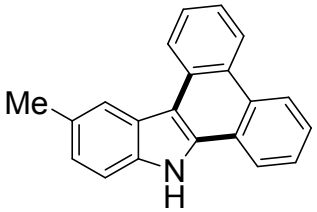
2,7-difluoro-9*H*-dibenzo[*a, c*]carbazole (4c):

Following the general procedure, **4c** was purified by PE/EtOAc (20:1) and obtained as a white solid (30.7 mg, 34% yield); Mp = 230-232 °C; R_f = 0.30 (PE/EtOAc = 10:1); ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.47 (s, 1H), 8.99 – 8.87 (m, 2H), 8.57 (d, J = 8.0 Hz, 1H), 8.44 (dd, J = 10.7, 2.7 Hz, 1H), 8.37 (dd, J = 10.1, 2.7 Hz, 1H), 7.73 (dt, J = 8.1, 0.8 Hz, 1H), 7.62 – 7.54 (m, 1H), 7.52 – 7.39 (m, 2H), 7.35 (ddd, J = 8.1, 7.0, 1.1 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 161.5 (d, $J_{C\text{-}F}$ = 245.2 Hz), 160.9 (d, $J_{C\text{-}F}$ = 244.5 Hz), 138.5, 134.2 (d, $J_{C\text{-}F}$ = 3.3 Hz), 130.4 (d, $J_{C\text{-}F}$ = 8.6 Hz), 127.0 (d, $J_{C\text{-}F}$ = 9.0 Hz), 126.7 (d, $J_{C\text{-}F}$ = 9.2 Hz), 125.8, 124.2, 123.4 (d, $J_{C\text{-}F}$ = 9.2 Hz), 123.2, 122.7, 121.4, 120.4, 115.1 (d, $J_{C\text{-}F}$ = 23.2 Hz), 112.0 (d, $J_{C\text{-}F}$ = 22.6 Hz), 111.9, 111.6 (d, $J_{C\text{-}F}$ = 3.5 Hz), 108.1 (d, $J_{C\text{-}F}$ = 22.0 Hz), 107.1 (d, $J_{C\text{-}F}$ = 22.5 Hz). **HRMS** m/z (ESI): calcd for $C_{20}H_{12}F_2N$ $[M + H]^+$ 304.0932, found 304.0928.



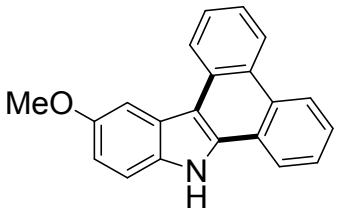
2,7-dichloro-9*H*-dibenzo[*a, c*]carbazole (4d):

Following the general procedure, **4d** was purified by PE/EtOAc (20:1) and obtained as a white solid (33.1 mg, 33% yield); Mp = 228-231 °C; R_f = 0.30 (PE/EtOAc = 10:1); ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.55 (s, 1H), 8.87 (t, *J* = 9.3 Hz, 2H), 8.68 (dd, *J* = 10.6, 2.2 Hz, 2H), 8.51 (d, *J* = 8.0 Hz, 1H), 7.79 – 7.65 (m, 2H), 7.59 (dd, *J* = 8.8, 2.2 Hz, 1H), 7.48 (ddd, *J* = 8.1, 7.0, 1.0 Hz, 1H), 7.37 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 138.5, 133.7, 132.8, 132.2, 130.6, 127.3, 126.6, 126.4, 126.3, 124.3, 124.3, 123.8, 123.7, 122.9, 122.1, 121.6, 121.3, 120.6, 112.0, 111.2. HRMS m/z (ESI): calcd for $C_{20}H_{12}Cl_2N$ [M + H] $^+$ 336.0341, found 336.0345.



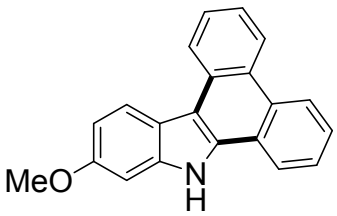
12-methyl-9*H*-dibenzo[*a, c*]carbazole (4e):

Following the general procedure, **4e** was purified by PE/EtOAc (20:1) and obtained as a white solid (70.4 mg, 83% yield); Mp = 235-237 °C; R_f = 0.2 (PE/EtOAc = 20:1); ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.28 (s, 1H), 8.90 (t, *J* = 9.3 Hz, 2H), 8.82 (d, *J* = 8.1 Hz, 1H), 8.57 (d, *J* = 7.9 Hz, 1H), 8.39 (s, 1H), 7.83 – 7.74 (m, 2H), 7.71 (td, *J* = 7.5, 6.9, 1.3 Hz, 1H), 7.64 – 7.55 (m, 2H), 7.27 (dd, *J* = 8.3, 1.4 Hz, 1H), 2.59 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 136.8, 134.3, 129.7, 129.2, 128.7, 127.5, 126.9, 126.3, 126.1, 125.1, 123.9, 123.9, 123.8, 123.4, 122.7, 122.2, 121.1, 111.5, 110.9, 21.5. The spectra data matched with values reported in the literature.[4]



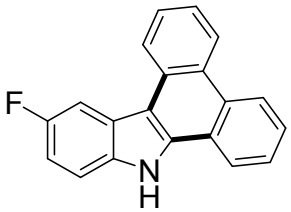
12-methoxy-9*H*-dibenzo[*a, c*]carbazole (4f):

Following the general procedure, **4f** was purified by PE/EtOAc (20:1) and obtained as a white solid (56.5 mg, 64% yield); Mp = 144-146 °C; R_f = 0.20 (PE/EtOAc = 20:1); ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.28 (s, 1H), 8.88 (td, *J* = 8.9, 1.2 Hz, 2H), 8.79 (dd, *J* = 8.1, 1.3 Hz, 1H), 8.57 (dd, *J* = 8.0, 1.3 Hz, 1H), 8.01 (d, *J* = 2.3 Hz, 1H), 7.78 (dddd, *J* = 11.2, 8.1, 7.0, 1.2 Hz, 2H), 7.70 (ddd, *J* = 8.3, 7.0, 1.4 Hz, 1H), 7.64 (d, *J* = 8.8 Hz, 1H), 7.58 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 7.11 (dd, *J* = 8.7, 2.4 Hz, 1H), 3.98 (s, 3H).^{13}C NMR (126 MHz, DMSO-d_6) δ 154.1, 134.7, 133.5, 129.6, 129.2, 127.6, 126.9, 126.4, 126.0, 123.9, 123.9, 123.8, 123.3, 123.3, 122.8, 122.1, 113.2, 112.4, 111.1, 103.9, 55.8. The spectra data matched with values reported in the literature.[4]



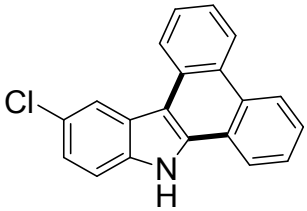
11-methoxy-9*H*-dibenzo[*a, c*]carbazole (4g):

Following the general procedure, **4g** was purified by PE/EtOAc (20:1) and obtained as a white solid (25 mg, 28% yield); Mp = 212-215 °C; R_f = 0.20 (PE/EtOAc = 20:1); **^{1}H NMR** (500 MHz, DMSO-d_6) δ 12.30 (s, 1H), 8.92 – 8.84 (m, 2H), 8.75 (dd, *J* = 8.2, 1.3 Hz, 1H), 8.54 (dd, *J* = 8.1, 1.4 Hz, 1H), 8.43 (d, *J* = 8.7 Hz, 1H), 7.77 (ddt, *J* = 8.1, 6.9, 1.4 Hz, 2H), 7.68 (ddd, *J* = 8.3, 6.9, 1.4 Hz, 1H), 7.58 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.20 (d, *J* = 2.3 Hz, 1H), 6.97 (dd, *J* = 8.7, 2.4 Hz, 1H), 3.91 (s, 3H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 157.1, 139.9, 133.6, 129.3, 128.7, 127.5, 127.0, 126.2, 125.9, 123.9, 123.5, 123.3, 122.7, 122.1, 121.9, 117.8, 111.6, 109.5, 95.1, 55.3. **HRMS** m/z (ESI): calcd for $C_{21}H_{16}NO$ $[M + H]^+$ 298.1226, found 298.1240.



12-fluoro-9*H*-dibenzo[*a, c*]carbazole (4h):

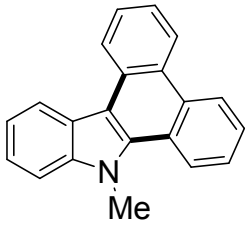
Following the general procedure, **4h** was purified by PE/EtOAc (20:1) and obtained as a white solid (26 mg, 30% yield); Mp = 206-209 °C; R_f = 0.20 (PE/EtOAc = 20:1); ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.52 (s, 1H), 8.89 (ddd, *J* = 13.9, 8.5, 1.2 Hz, 2H), 8.76 (dd, *J* = 8.2, 1.2 Hz, 1H), 8.58 (dd, *J* = 8.0, 1.3 Hz, 1H), 8.37 (dd, *J* = 10.6, 2.5 Hz, 1H), 7.84 – 7.68 (m, 4H), 7.59 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1H), 7.30 (td, *J* = 9.1, 2.5 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 157.4 (d, $J_{C\text{-}F}$ = 231.7 Hz), 135.7, 135.1, 129.6, 129.2, 127.8, 127.1, 126.8, 126.2, 124.0, 123.9, 123.7 (d, $J_{C\text{-}F}$ = 4.5 Hz), 123.6, 123.4, 122.5, 122.3, 112.6(d, $J_{C\text{-}F}$ = 9.2 Hz), 111.6 (d, $J_{C\text{-}F}$ = 25.2 Hz), 111.3 (d, $J_{C\text{-}F}$ = 3.8 Hz), 106.6 (d, $J_{C\text{-}F}$ = 25.0 Hz). The spectra data matched with values reported in the literature.[4]



12-chloro-9*H*-dibenzo[*a, c*]carbazole (4i):

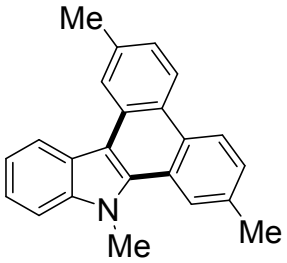
Following the general procedure, **4i** was purified by PE/EtOAc (20:1) and obtained as a white solid (29.8 mg, 35% yield); Mp = 208-211 °C; R_f = 0.20 (PE/EtOAc = 20:1); ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.62 (s, 1H), 8.87 (ddd, *J* = 13.5, 8.5, 1.2 Hz, 2H), 8.76 (dd, *J* = 8.2,

1.2 Hz, 1H), 8.62 – 8.55 (m, 2H), 7.82 – 7.76 (m, 2H), 7.76 – 7.70 (m, 2H), 7.59 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 7.45 (dd, *J* = 8.6, 2.0 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 137.0, 135.3, 129.6, 129.0, 127.8, 127.1, 126.9, 126.3, 124.6, 124.5, 124.0, 123.9, 123.9, 123.5, 123.4, 122.4, 120.5, 113.2, 110.7. The spectra data matched with values reported in the literature.[4]



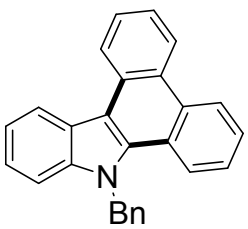
9-methyl-9*H*-dibenzo[*a, c*]carbazole (4j):

Following the general procedure, **4j** was purified by PE/EtOAc (500:1) and obtained as a white solid (106.5 mg,76% yield); Mp = 142-144 °C; R_f = 0.30 (PE/EtOAc = 50:1); ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.02 – 8.97 (m, 1H), 8.90 (td, *J* = 8.2, 1.3 Hz, 3H), 8.68 – 8.64 (m, 1H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.82 – 7.71 (m, 3H), 7.61 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.52 (ddd, *J* = 8.3, 7.0, 1.1 Hz, 1H), 7.39 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 4.45 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 140.4, 134.1, 130.2, 129.2, 127.7, 126.7, 126.3, 126.1, 124.2, 123.9, 123.8, 123.4, 123.3, 123.3, 122.4, 121.5, 120.4, 112.3, 110.4, 34.5. The spectra data matched with values reported in the literature.[3]



2,7,9-trimethyl-9*H*-dibenzo[*a, c*]carbazole (4k):

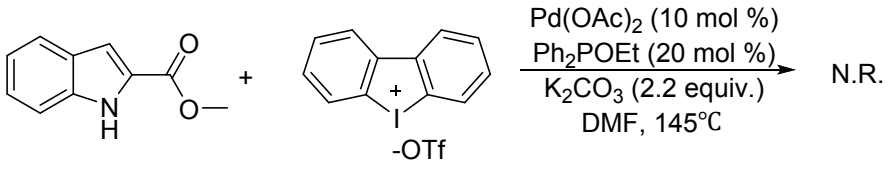
Following the general procedure, **4k** was purified by PE/EtOAc (500:1) and obtained as a white solid (50 mg,33% yield); Mp = 196-198 °C; R_f = 0.30 (PE/EtOAc = 50:1); ^{1}H NMR (500 MHz, $CDCl_3$)δ 8.72 (d, *J* = 8.5 Hz, 1H), 8.65 (d, *J* = 8.0 Hz, 2H), 8.63 (d, *J* = 8.4 Hz, 1H), 8.48 (s, 1H), 7.62 (d, *J* = 8.2 Hz, 1H), 7.54 – 7.51 (m, 1H), 7.51 – 7.48 (m, 1H), 7.45 – 7.39 (m, 2H), 4.42 (s, 3H), 2.70 (s, 3H), 2.65 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.8, 136.6, 135.3, 134.8, 129.7, 128.9, 127.2, 125.2, 124.9, 123.8, 123.6, 123.5, 123.4, 123.2, 122.8, 122.7, 121.8, 120.1, 113.3, 109.5, 34.6, 22.0. The spectra data matched with values reported in the literature.[5]



9-benzyl-9*H*-dibenzo[*a, c*]carbazole (4l):

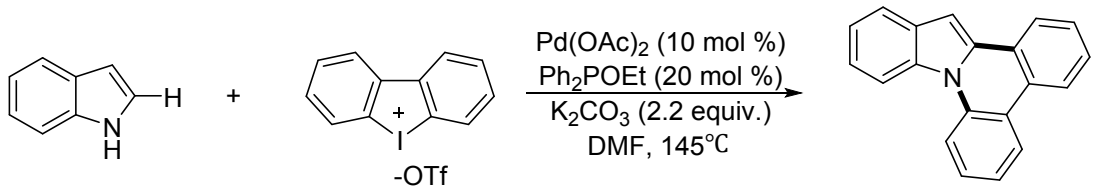
Following the general procedure, **4l** was purified by PE/EtOAc (500:1) and obtained as a white solid (66.2 mg,62% yield); Mp = 198-201 °C; R_f = 0.30 (PE/EtOAc = 50:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.96 (dd, *J* = 8.2, 1.2 Hz, 1H), 8.87 (dd, *J* = 8.4, 1.2 Hz, 1H), 8.81 (dd, *J* = 8.4, 1.2 Hz, 1H), 8.72 – 8.68 (m, 1H), 8.28 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.81 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.64 (ddt, *J* = 8.4, 6.9, 1.4 Hz, 2H), 7.54 – 7.45 (m, 4H), 7.42 – 7.36 (m, 2H), 7.34 (d, *J* = 7.2 Hz, 3H), 6.01 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.3, 137.5, 134.7, 131.0, 129.9, 129.1, 127.5, 127.4, 127.1, 126.4, 126.0, 125.7, 124.2, 124.1, 123.9, 123.9, 123.7, 123.5, 123.2, 122.9, 122.0, 120.9, 114.0, 110.0, 50.2. The spectra data matched with values reported in the literature.[5]

Ⅴ. Control experiment:



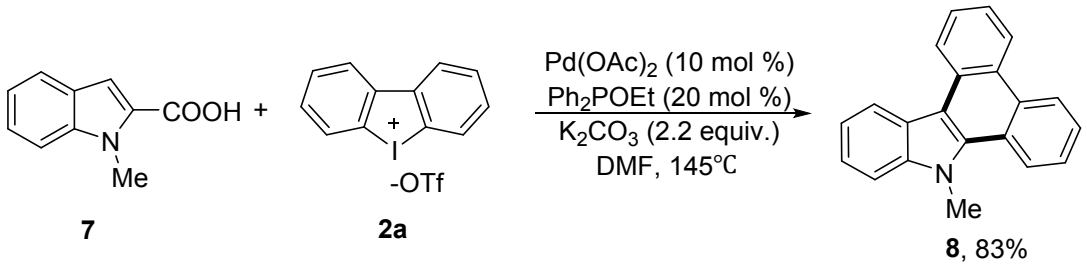
5 **2a**

In a 15 mL thick-walled tube was charged with methyl 1*H*-indole-2-carboxylate **5** (52.6 mg, 0.3 mmol), **2a** (256.9 mg, 0.6 mmol), $Pd(OAc)_2$ (6.8 mg, 0.03 mmol), K_2CO_3 (91.1 mg, 0.66 mmol), ethyl diphenylphosphinite (Ph_2POEt) (13 μL, 0.06 mmol) and DMF (2 mL). The reaction tube was sealed and stirred at 145 °C (pre-heated oil bath) for 12 h. The reaction mixture was then cooled to r.t. and diluted with water (10 mL) before it was extracted with EtOAc (15 mL x 3). No desired product **3aa** was detected by TLC.



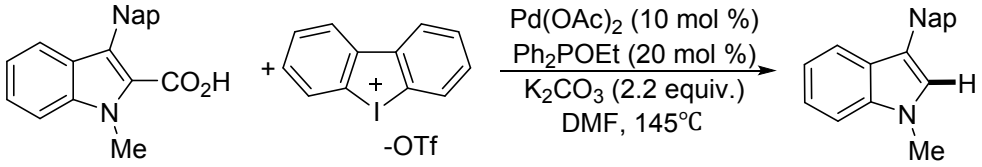
6 **2a** **3aa**, trace

In a 15 mL thick-walled tube was charged with indole **6** (35.2 mg, 0.3 mmol), **2a** (256.9 mg, 0.6 mmol), $Pd(OAc)_2$ (6.8 mg, 0.03 mmol), K_2CO_3 (91.1 mg, 0.66 mmol), ethyl diphenylphosphinite (Ph_2POEt) (13 μL, 0.06 mmol) and DMF (2 mL). The reaction tube was sealed and stirred at 145 °C (pre-heated oil bath) for 12 h. The reaction mixture was then cooled to r.t. and diluted with water (10 mL) before it was extracted with EtOAc (15 mL x 3). Trace product **3aa** was detected by TLC.



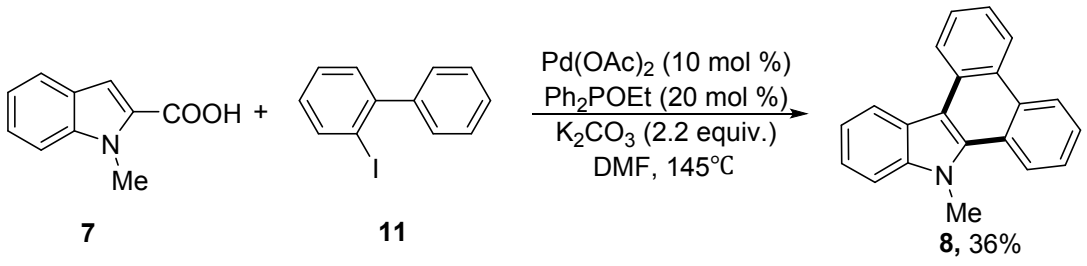
7 **2a** **8**, 83%

In a 15 mL thick-walled tube was charged with 1-methyl-1H-indole-2-carboxylic acid **7** (52.5 mg, 0.3 mmol), **2a** (256.9 mg, 0.6 mmol), $Pd(OAc)_2$ (6.8 mg, 0.03 mmol), K_2CO_3 (91.1 mg, 0.66 mmol), ethyl diphenylphosphinite (Ph_2POEt) (13 μL, 0.06 mmol) and DMF (2 mL). The reaction tube was sealed and stirred at 145 °C (pre-heated oil bath) for 12 h. The reaction mixture was then cooled to r.t. and diluted with water (10 mL) before it was extracted with EtOAc (15 mL x 3). The combined organic phase were washed with water (10 mL x 3) and saturated brine (10 mL), dried over Na_2SO_4, and concentrated in *vacuo*. The residue was purified by column chromatography (PE/EA = 500:1) on silica gel to provide the desired 9-methyl-9*H*-dibenzo[a,c]carbazole **8** as white solid (70.2 mg, 83%).



9 **2a** **10**, 60%

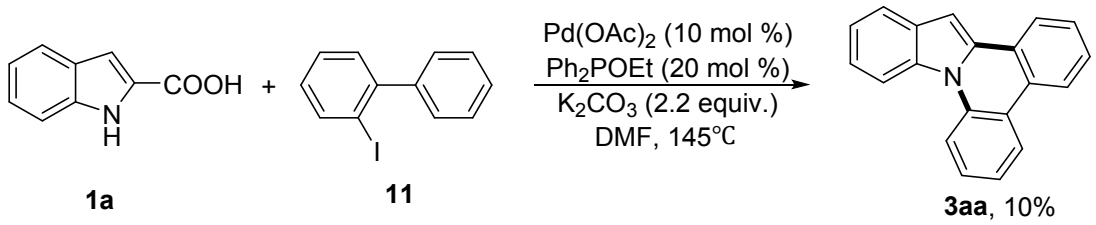
In a 15 mL thick-walled tube was charged with 1-methyl-3-(naphthalen-1-yl)-1*H*-indole-2-carboxylic acid **9** (90.4 mg, 0.3 mmol), **2a** (256.9 mg, 0.6 mmol), $Pd(OAc)_2$ (6.8 mg, 0.03 mmol), K_2CO_3 (91.1 mg, 0.66 mmol), ethyl diphenylphosphinite (Ph_2POEt) (13 μL, 0.06 mmol) and DMF (2 mL). The reaction tube was sealed and stirred at 145 °C (pre-heated oil bath) for 12 h. The reaction mixture was then cooled to r.t. and diluted with water (10 mL) before it was extracted with EtOAc (15 mL x 3). The combined organic phase were washed with water (10 mL x 3) and saturated brine (10 mL), dried over Na_2SO_4, and concentrated in *vacuo*. The residue was purified by column chromatography (PE/EA = 500:1) on silica gel to provide the desired 1-methyl-3-(naphthalen-1-yl)-1*H*-indole **10** as white solid (47 mg, 60%).



7 **11** **8,** 36%

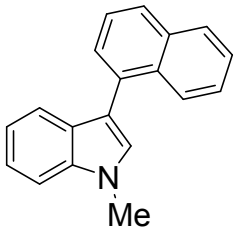
In a 15 mL thick-walled tube was charged with 1-methyl-1*H*-indole-2-carboxylic acid **7** (52.5 mg, 0.3 mmol), 2-iodo-1,1'-biphenyl **11** (105.6 μL, 0.6 mmol), $Pd(OAc)_2$ (6.8 mg, 0.03 mmol), K_2CO_3 (91.1 mg, 0.66 mmol), ethyl diphenylphosphinite (Ph_2POEt) (13 μL, 0.06 mmol) and DMF (2 mL). The reaction tube was sealed and stirred at 145 °C (pre-heated oil

bath) for 12 h. The reaction mixture was then cooled to r.t. and diluted with water (10 mL) before it was extracted with EtOAc (15 mL x 3). The combined organic phase were washed with water (10 mL x 3) and saturated brine (10 mL), dried over Na_2SO_4, and concentrated in *vacuo*. The residue was purified by column chromatography (PE/EA = 500:1) on silica gel to provide the desired 9-methyl-9*H*-dibenzo[*a,c*]carbazole **8** as white solid (30.4 mg, 36%).



1a **11** **3aa**, 10%

In a 15 mL thick-walled tube was charged with substrate **1a** (48.3 mg, 0.3 mmol), 2-iodo-1,1'-biphenyl **11** (105.6 μL, 0.6 mmol), $Pd(OAc)_2$ (6.8 mg, 0.03 mmol), K_2CO_3 (91.1 mg, 0.66 mmol), ethyl diphenylphosphinite (Ph_2POEt) (13 μL, 0.06 mmol) and DMF (2 mL). The reaction tube was sealed and stirred at 145 °C (pre-heated oil bath) for 12 h. The reaction mixture was then cooled to r.t. and diluted with water (10 mL) before it was extracted with EtOAc (15 mL x 3). The combined organic phase were washed with water (10 mL x 3) and saturated brine (10 mL), dried over Na_2SO_4, and concentrated in *vacuo*. The residue was purified by column chromatography (PE/EA = 500:1) on silica gel to provide the desired indolo[1,2-*f*]phenanthridine **3aa** (9 mg, 10%) as a white solid.



1-methyl-3-(naphthalen-1-yl)-1*H*-indole (10)

White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (dd, *J* = 8.4, 1.1 Hz, 1H), 7.95 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.88 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.62 (dd, *J* = 7.0, 1.4 Hz, 1H), 7.57 (dd, *J* = 8.1, 7.0 Hz, 1H), 7.56 – 7.50 (m, 2H), 7.49 – 7.45 (m, 1H), 7.44 (ddd, *J* = 8.3, 6.8, 1.4 Hz, 1H), 7.34 (ddd, *J* = 8.2, 7.0, 1.1 Hz, 1H), 7.27 (s, 1H), 7.16 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 3.94 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.0, 134.0, 133.1, 132.6, 128.2, 128.1, 127.6, 126.9, 126.6, 125. 7, 125.6, 125.6, 121.9, 120.5, 119.6, 115.0, 109.4, 32.9. HRMS m/z (ESI): calcd for $C_{19}H_{16}N$ $[M + H]^+$ 258.1277, found 258.1278.

Refrence:

1. Xie, C.; Zhang, Y.; Huang, Z.; Xu, P., *J. Org. Chem.* **2007**, *72*, 5431-5434.
2. Yan, L.; Zhao, D.; Lan, J.; Cheng, Y.; Guo, Q.; Li, X.; Wu, N.; You, J., *Org. Biomol. Chem.* **2013**, *11*, 7966-7977.
3. Wu, Y.; Peng, X.; Luo, B.; Wu, F.; Liu, B.; Song, F.; Huang, P.; Wen, S., *Org. Biomol. Chem.* **2014**, *12*, 9777-9780.
4. Bhunia, S. K.; Polley, A.; Natarajan, R.; Jana, R., *Chem. Eur. J.* **2015**, *21*, 16786-16791.

5. Kitano, H.; Matsuoka, W.; Ito, H.; Itami, K., *Chem. Sci.*, **2018**, *9*, 7556–7561.

Ⅵ. Crystal data

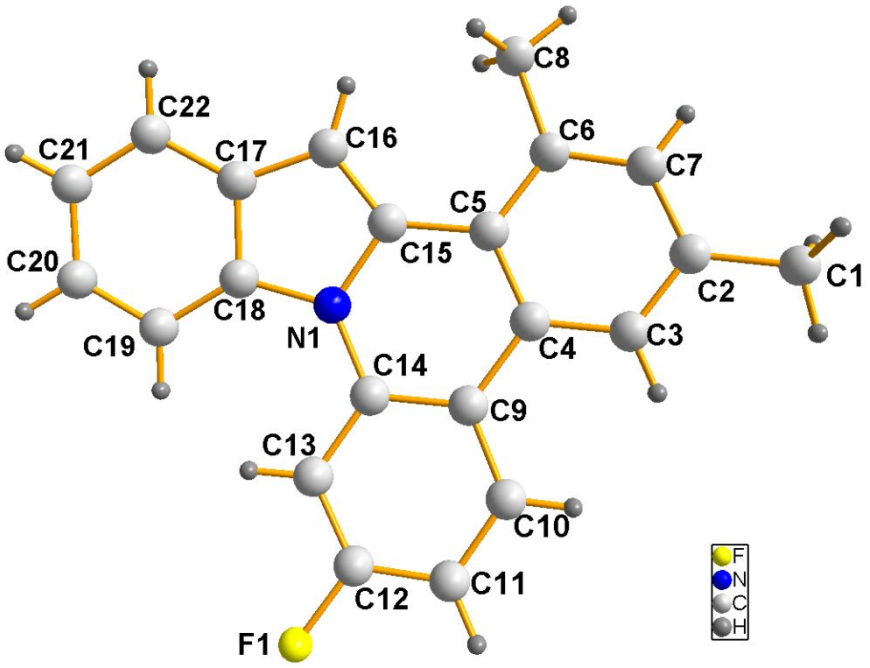
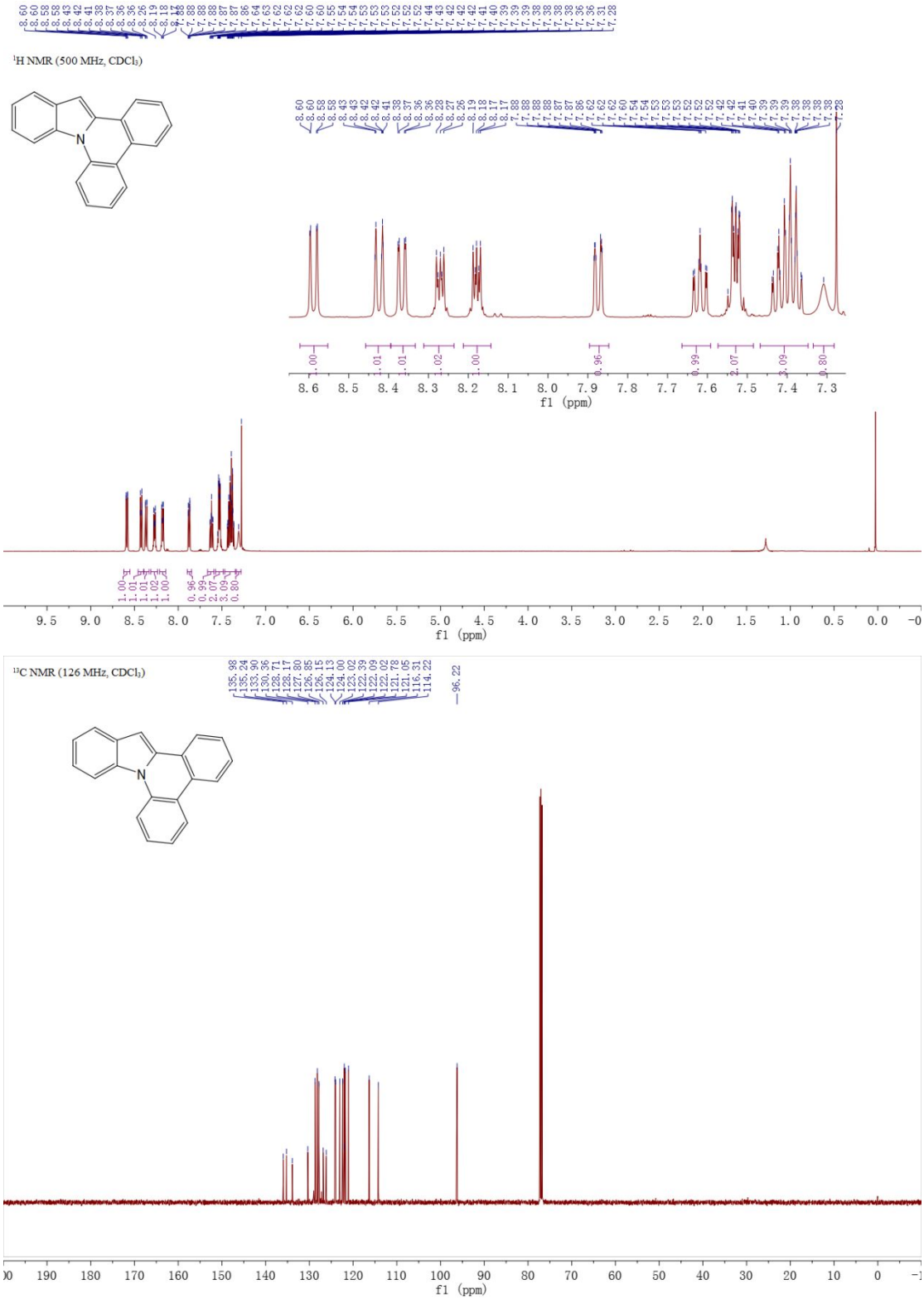


Table S1. Crystal Data and Structure Refinement for 3bi (CCDC 1951128)

Formula	$C_{22}H_{16}FN$
Formula weight	313.36
Temperature/K	288
Crystal system	monoclinic
Space group	P 2 (1)/n
a/Å	10.4961(6)
b/Å	7.6672(5)
c/Å	19.0105(13)
α/°	90
β/°	95.616(6)
γ/°	90
V/Å^3	1522.54(17)
Z	4
D_{calcd}/g·cm^{-3}	1.367
μ/mm^{-1}	0.088
F(000)	656
Crystal size/mm^3	0.30 × 0.30 × 0.20
Radiation	MoKα (λ = 0.71073)
θ range/°	3.30-26.37
Index ranges	-13 ≤ h ≤ 13, -9 ≤ k ≤ 9, -23 ≤ l ≤ 23
Data/restraints/parameters	3108/0/217
R_1[I>2σ(I)][a]	0.0518
wR_2 (all data)[b]	0.1252

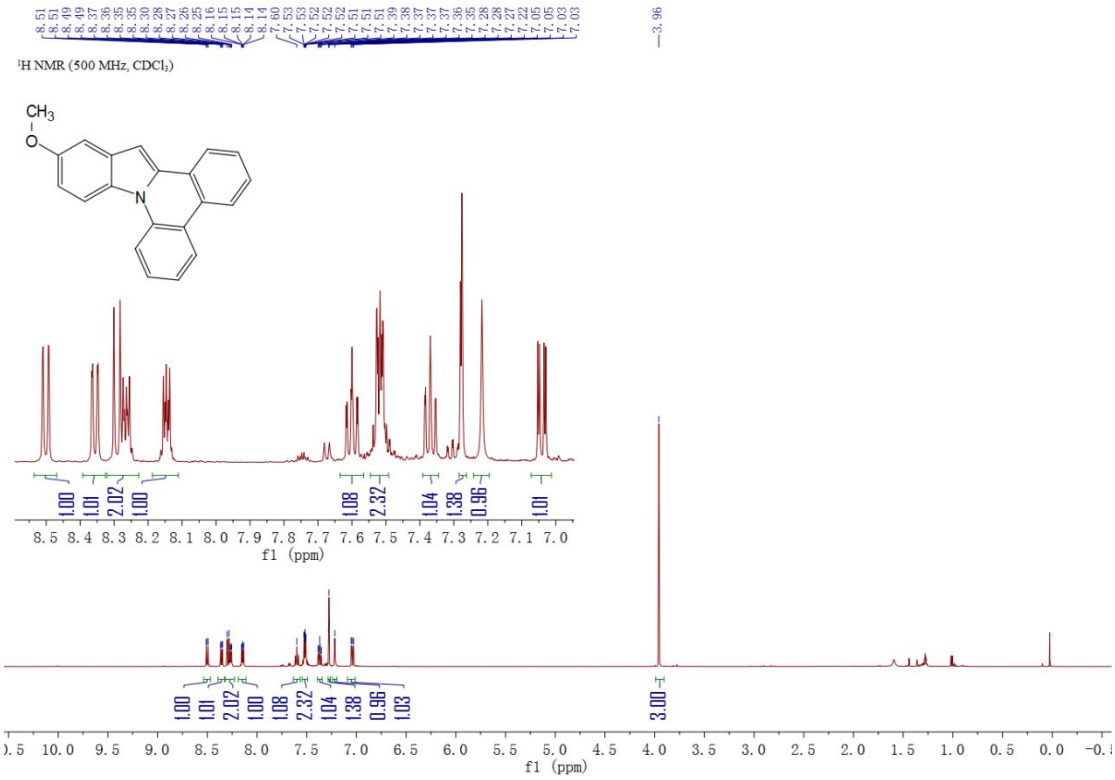
Ⅶ. NMR spectra of all compounds:

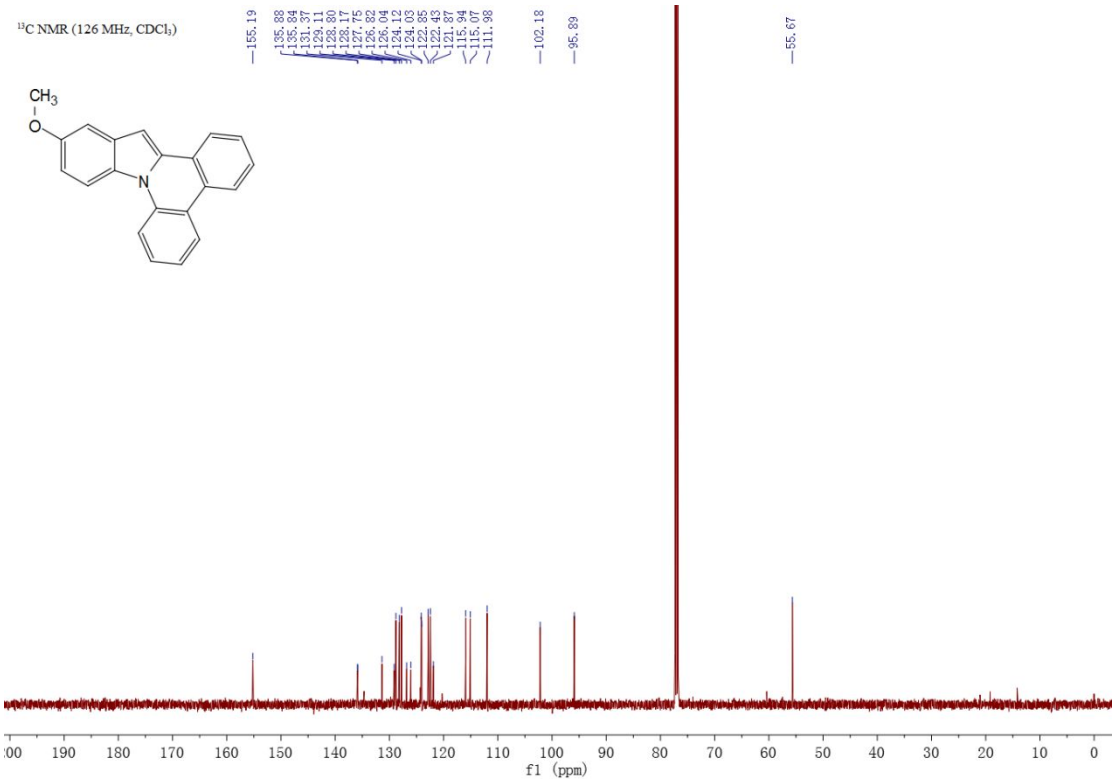
indolo[1,2-*f*]phenanthridine (3aa):



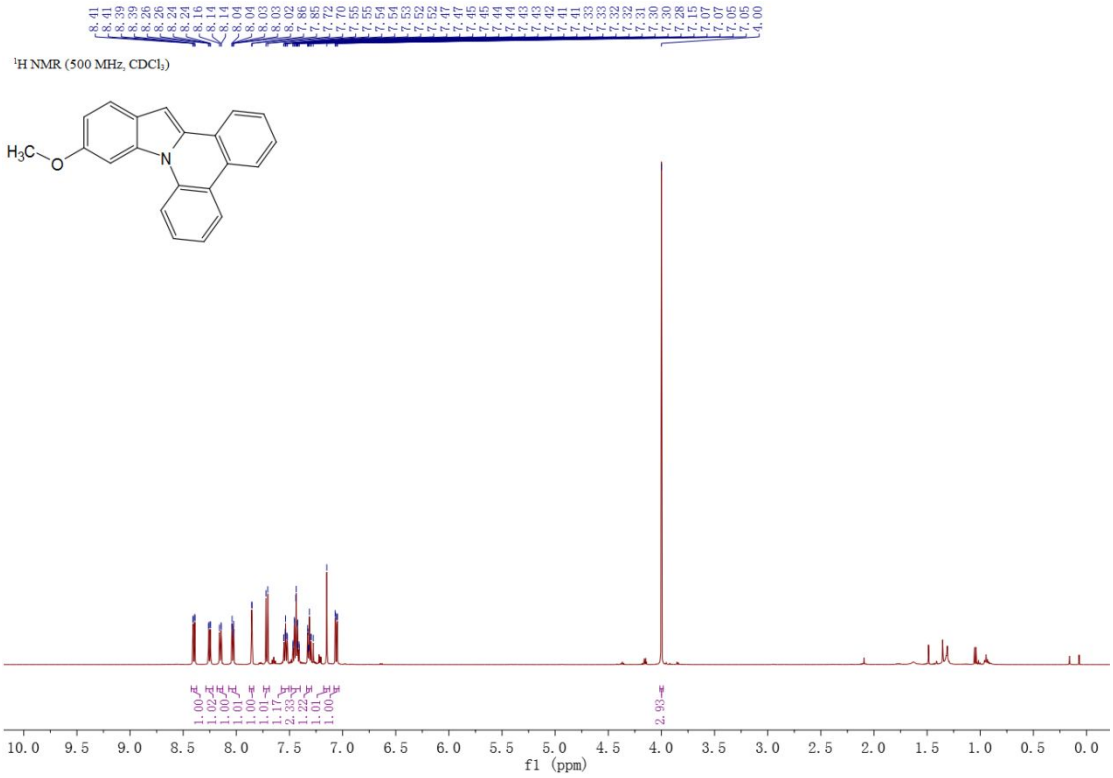
12-methylindolo[1,2-*f*]phenanthridine (3ab)

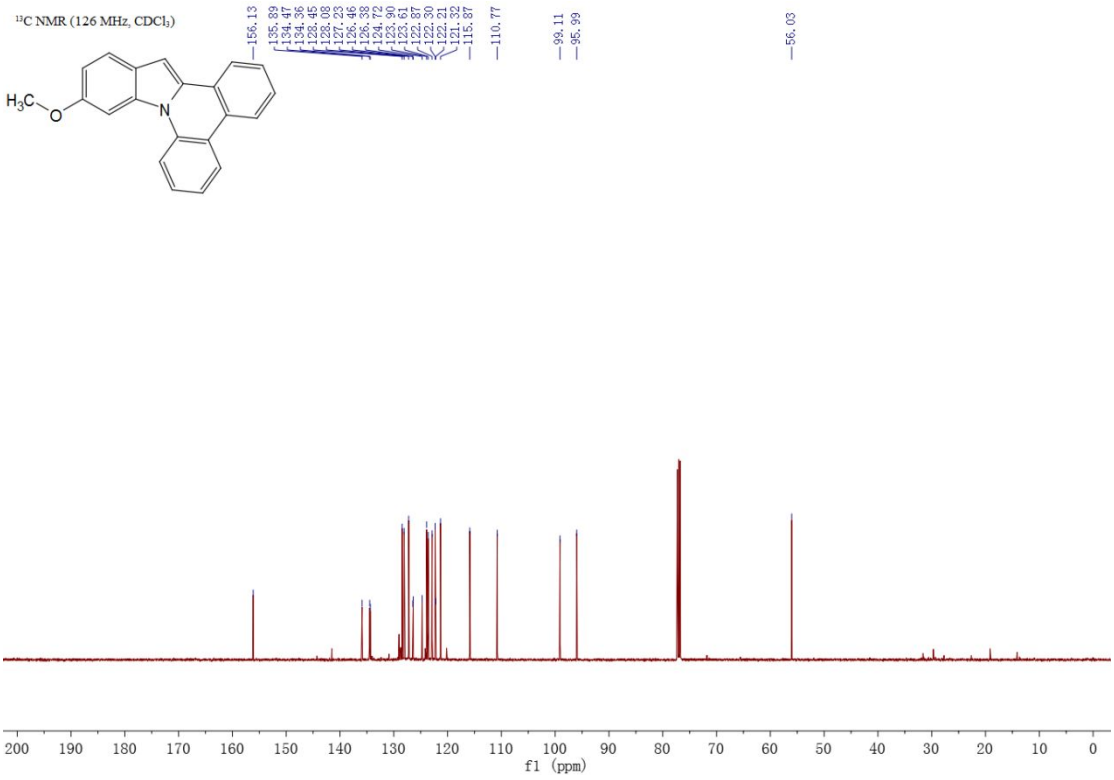
12-methoxyindolo[1,2-*f*]phenanthridine (3ac)



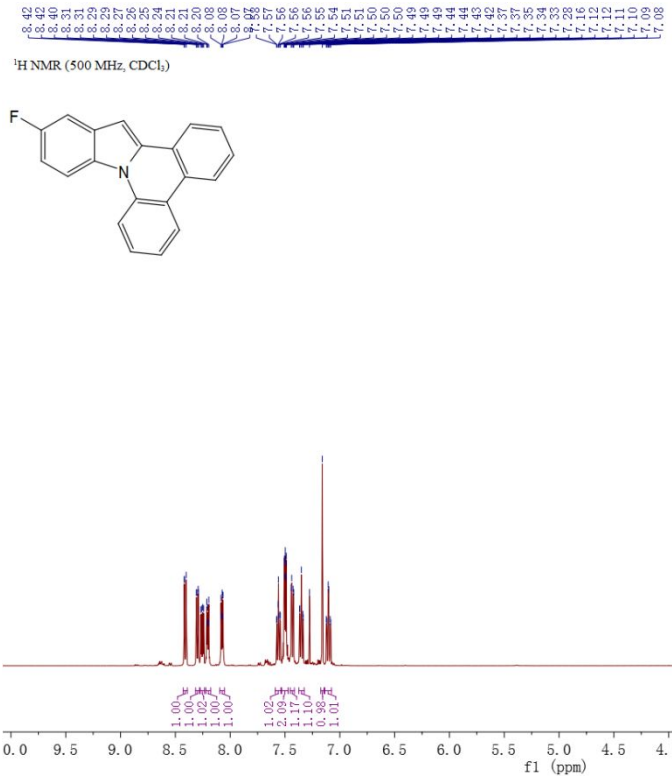


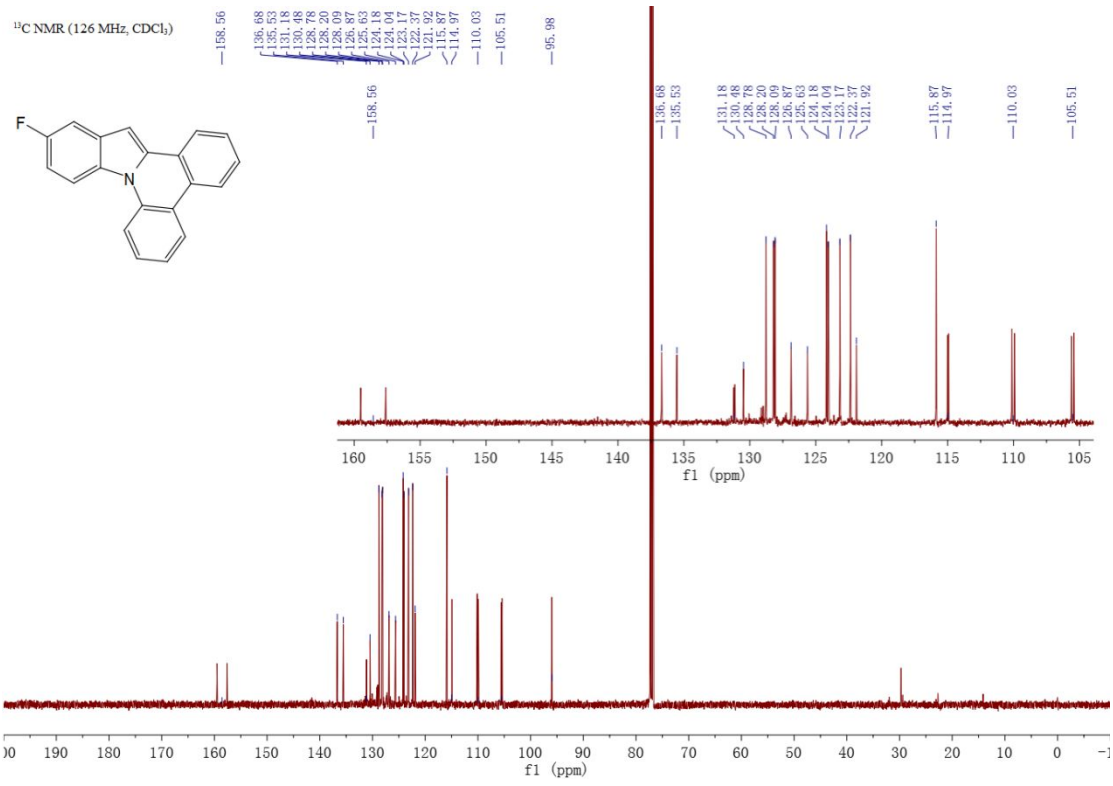
11-methoxyindolo[1,2-*f*]phenanthridine (3ad)



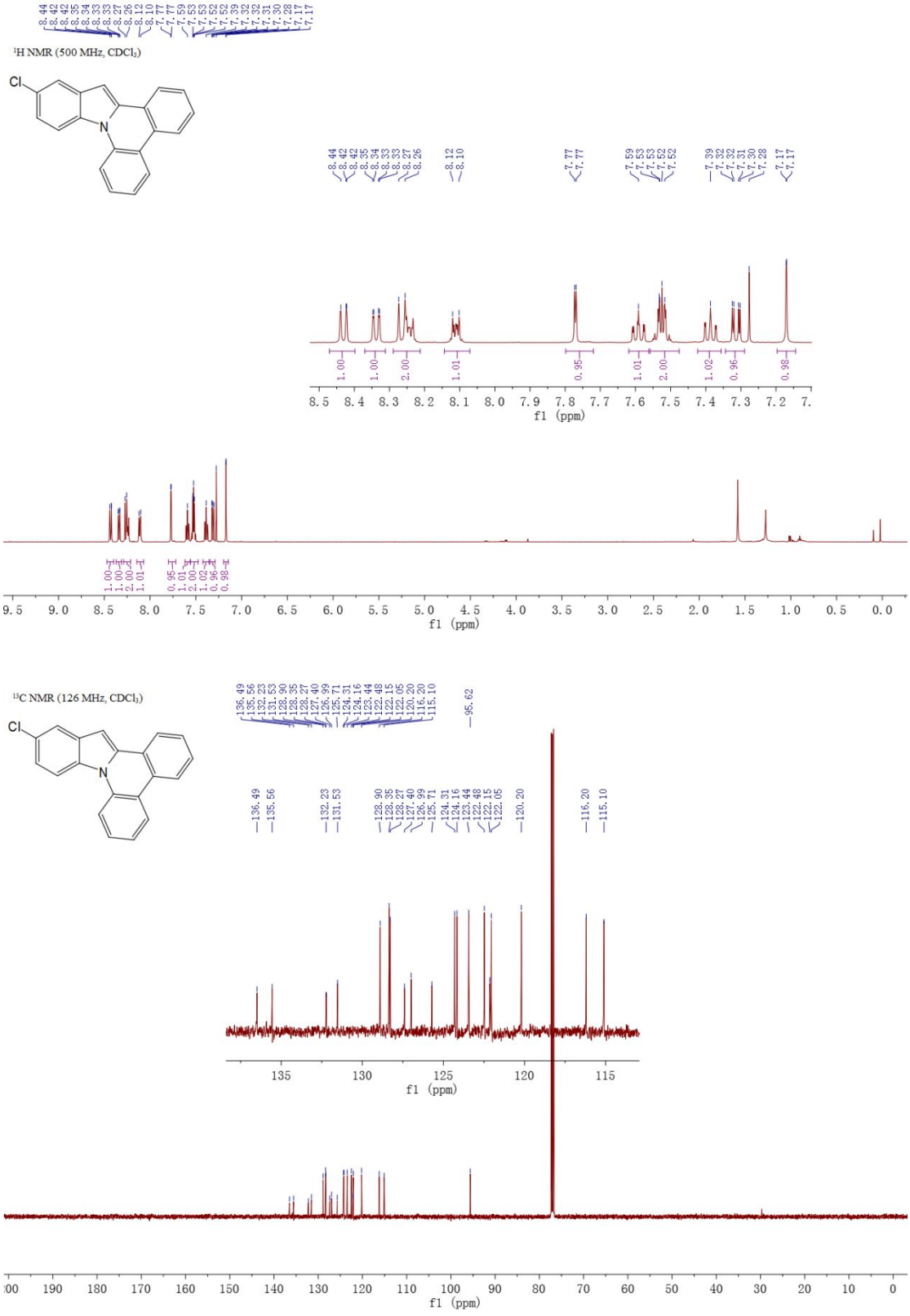


12-fluoroindolo[1,2-*f*]phenanthridine (3ae)

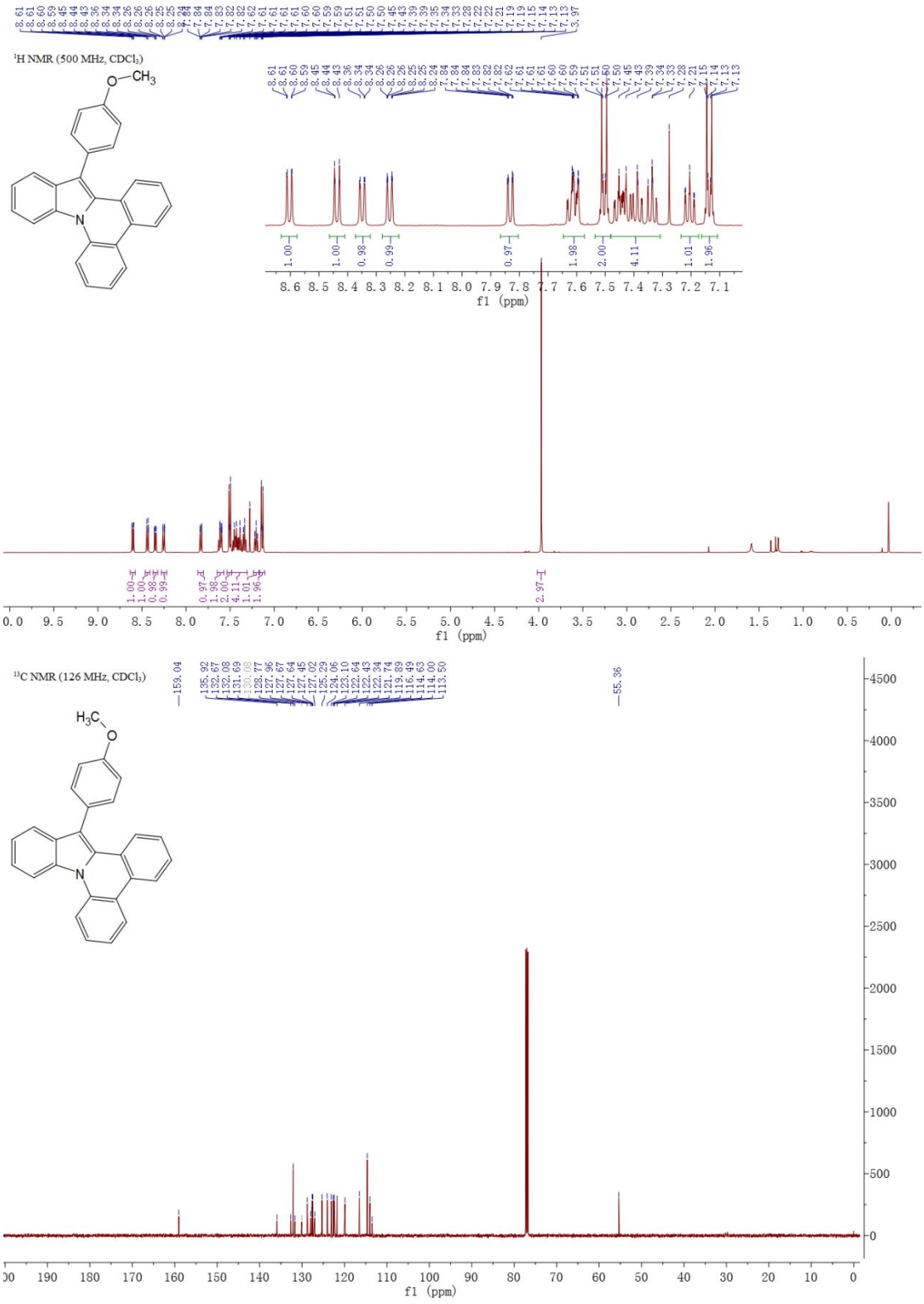




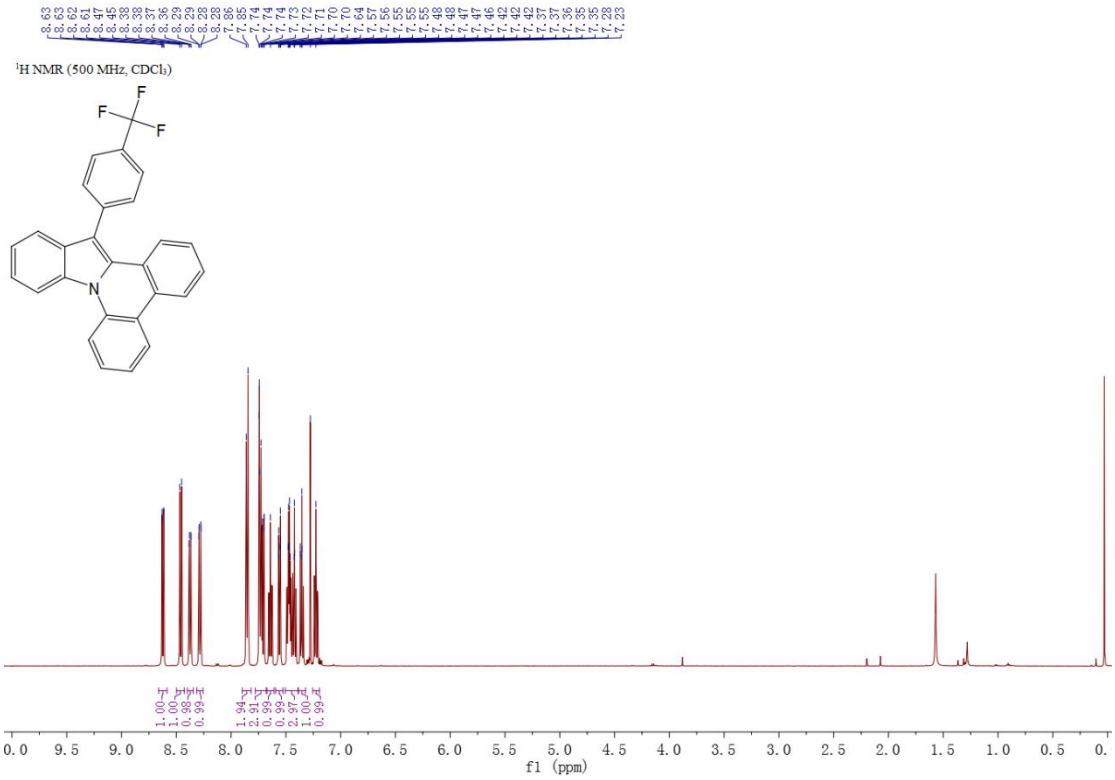
12-chloroindolo[1,2-*f*]phenanthridine (3af)

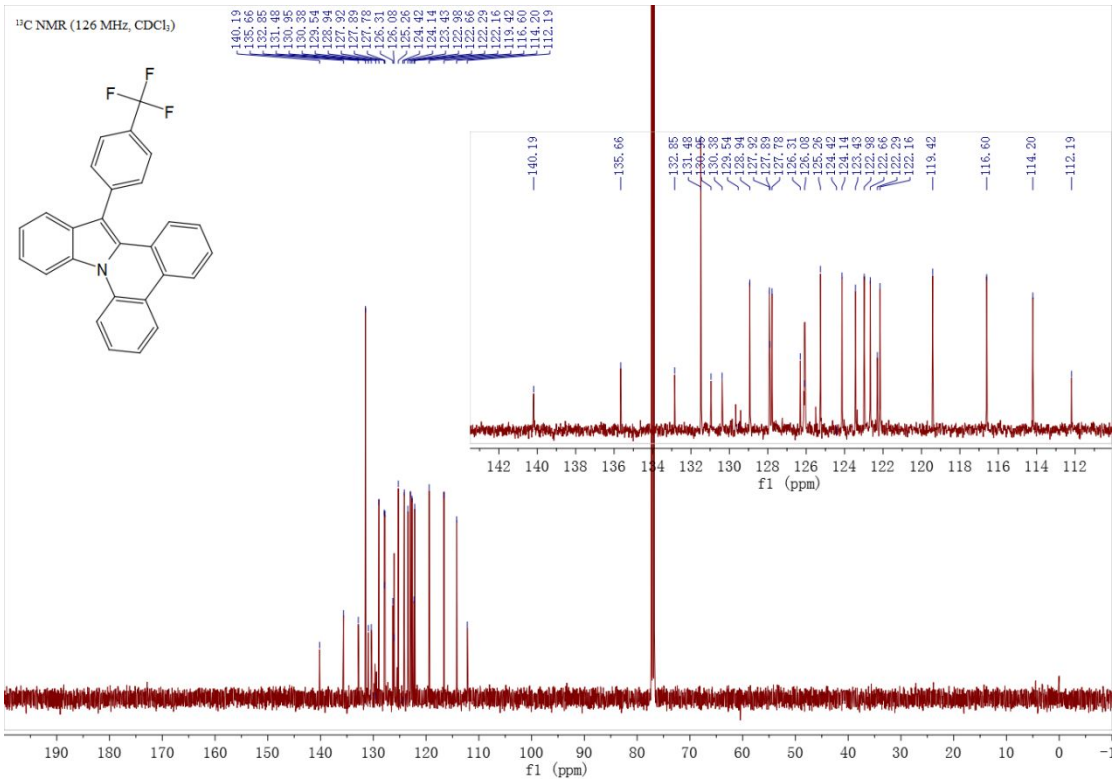


14-(4-methoxyphenyl)indolo[1,2-*f*]phenanthridine (3ag)

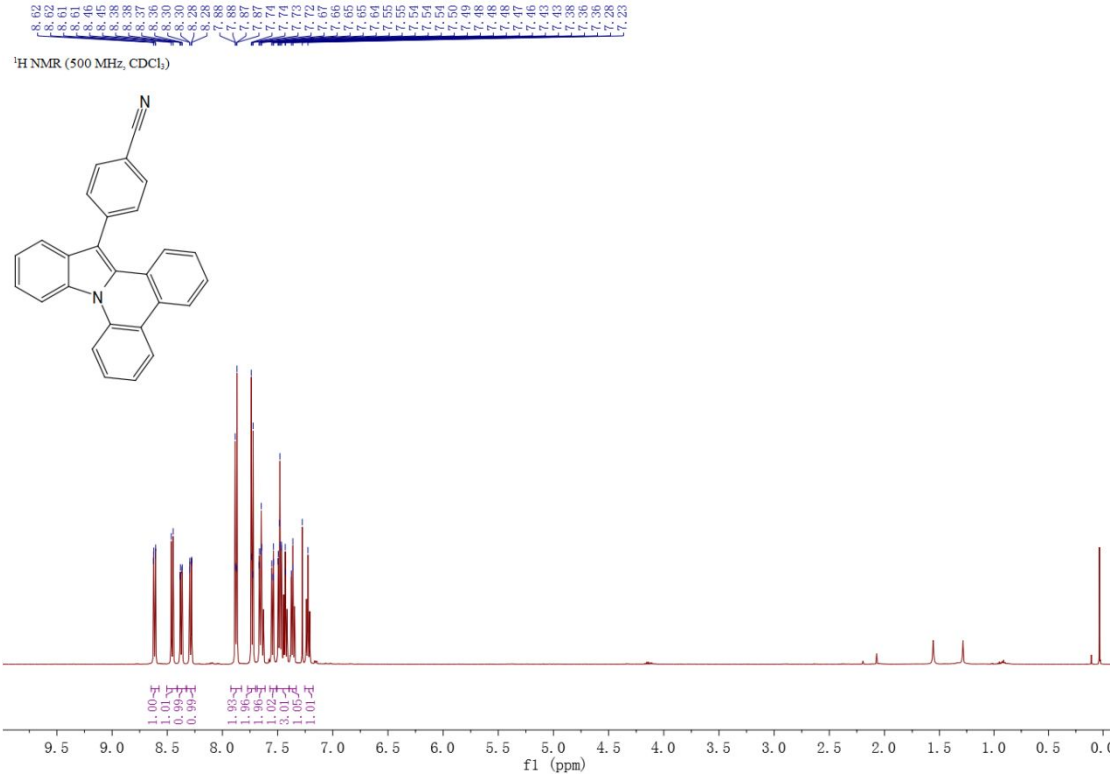


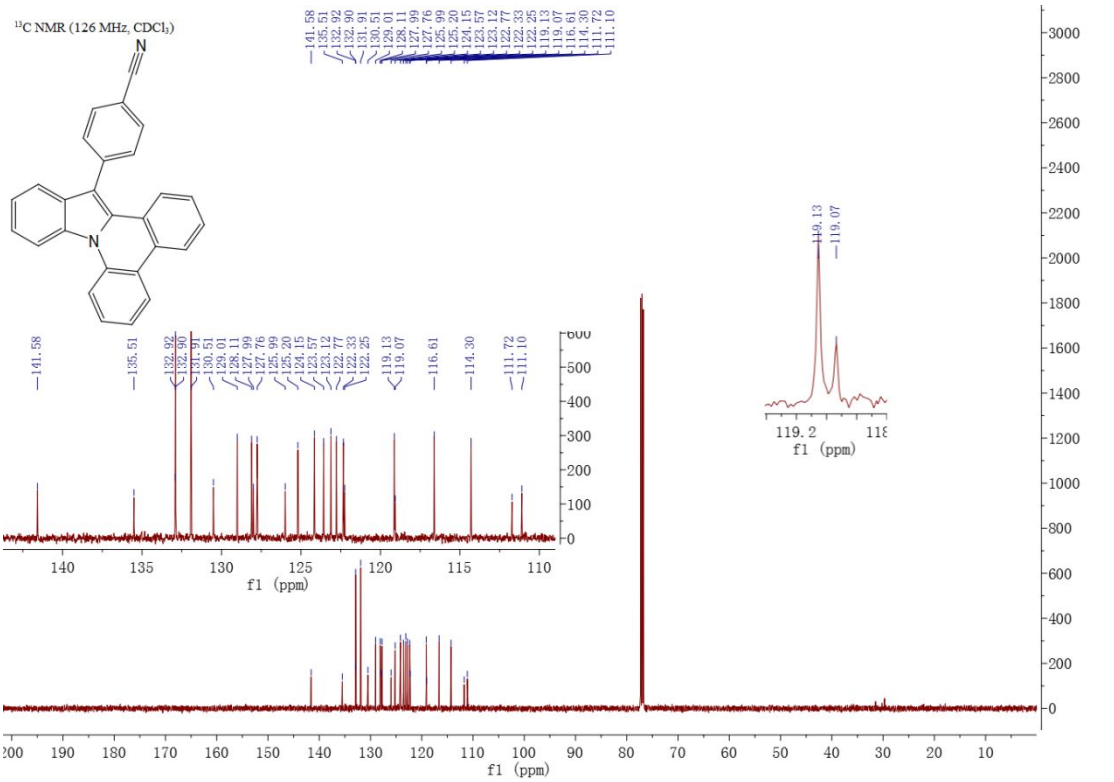
14-(4-(trifluoromethyl)phenyl)indolo[1,2-*f*]phenanthridine (3ah)



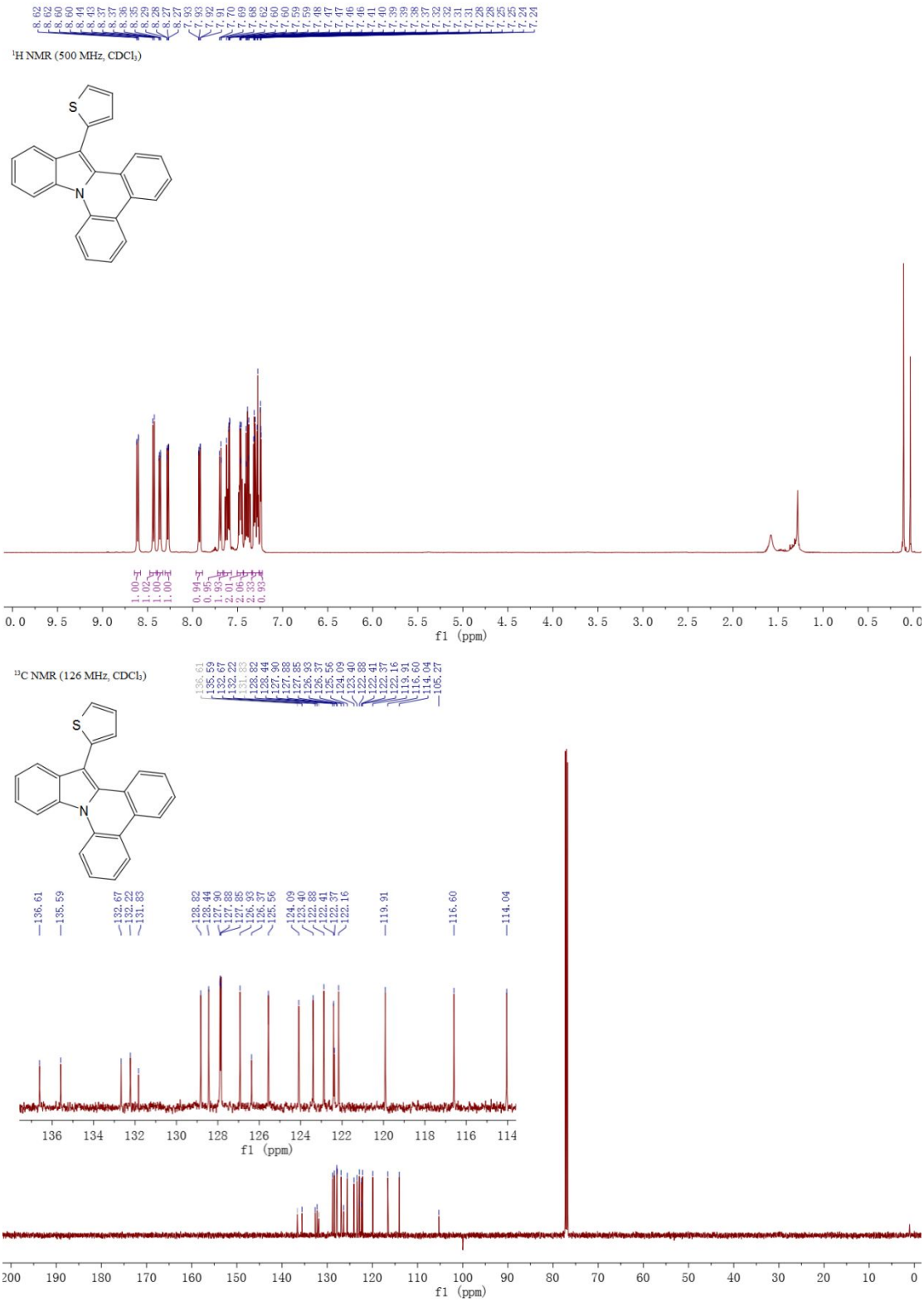


4-(indolo[1,2-*f*]phenanthridin-14-yl)benzonitrile (3ai)

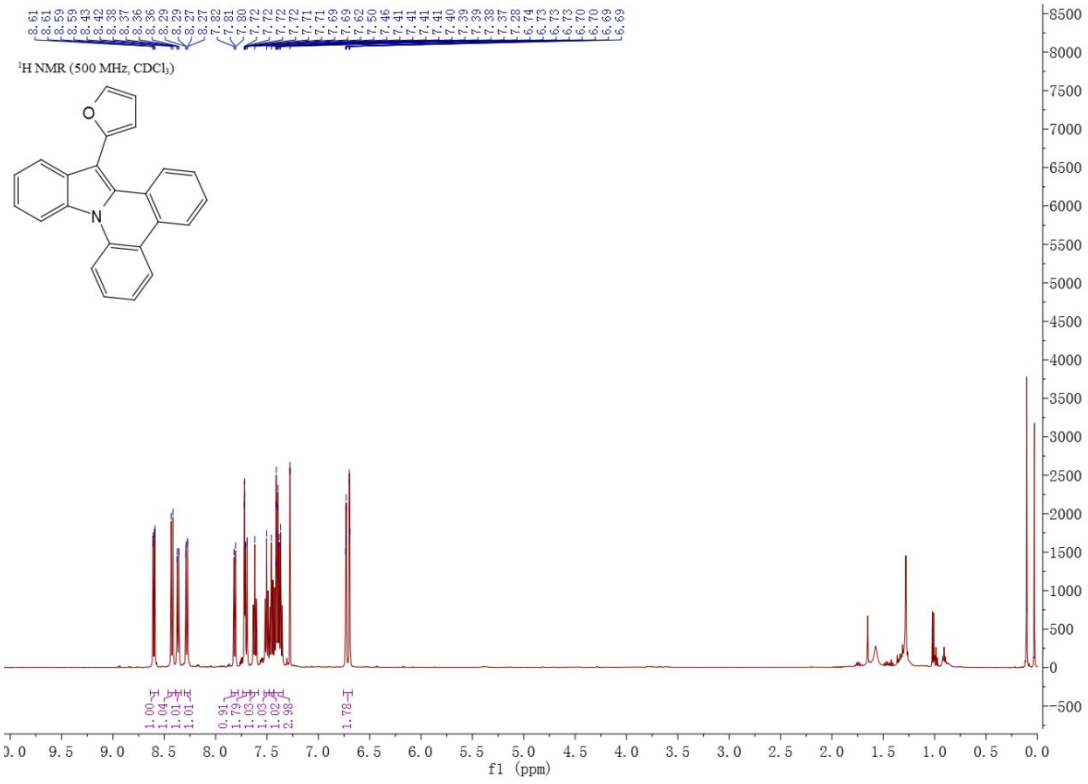


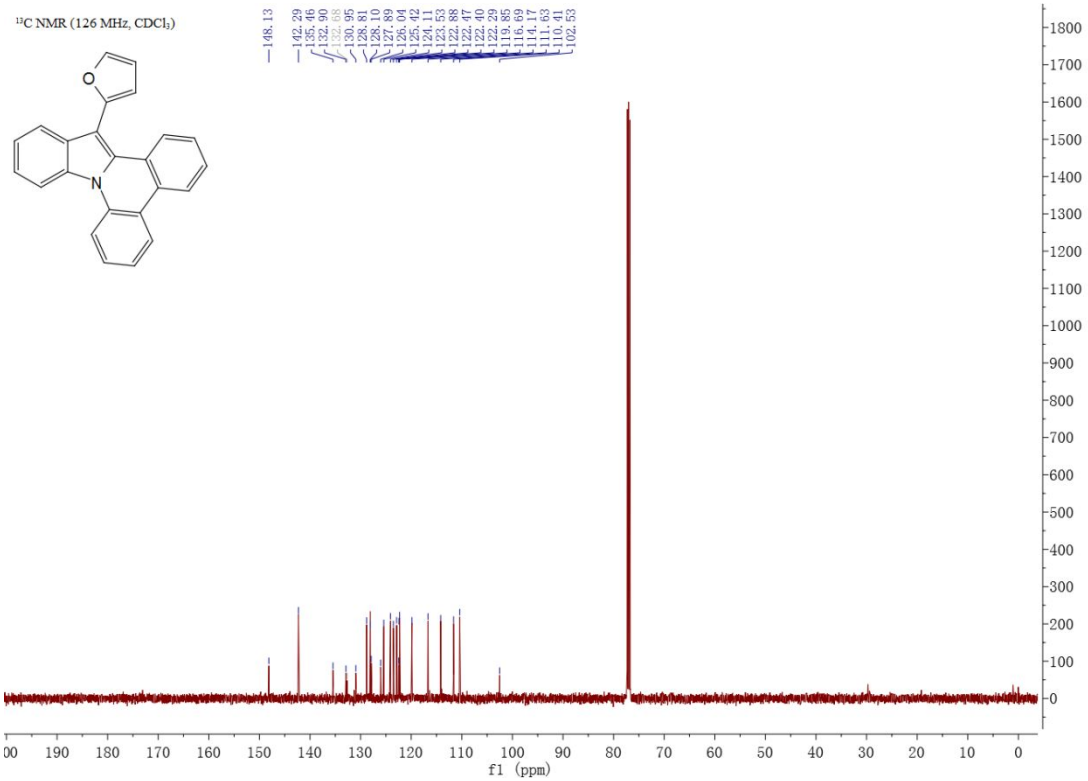


14-(thiophen-2-yl)indolo[1,2-*f*]phenanthridine (3aj):

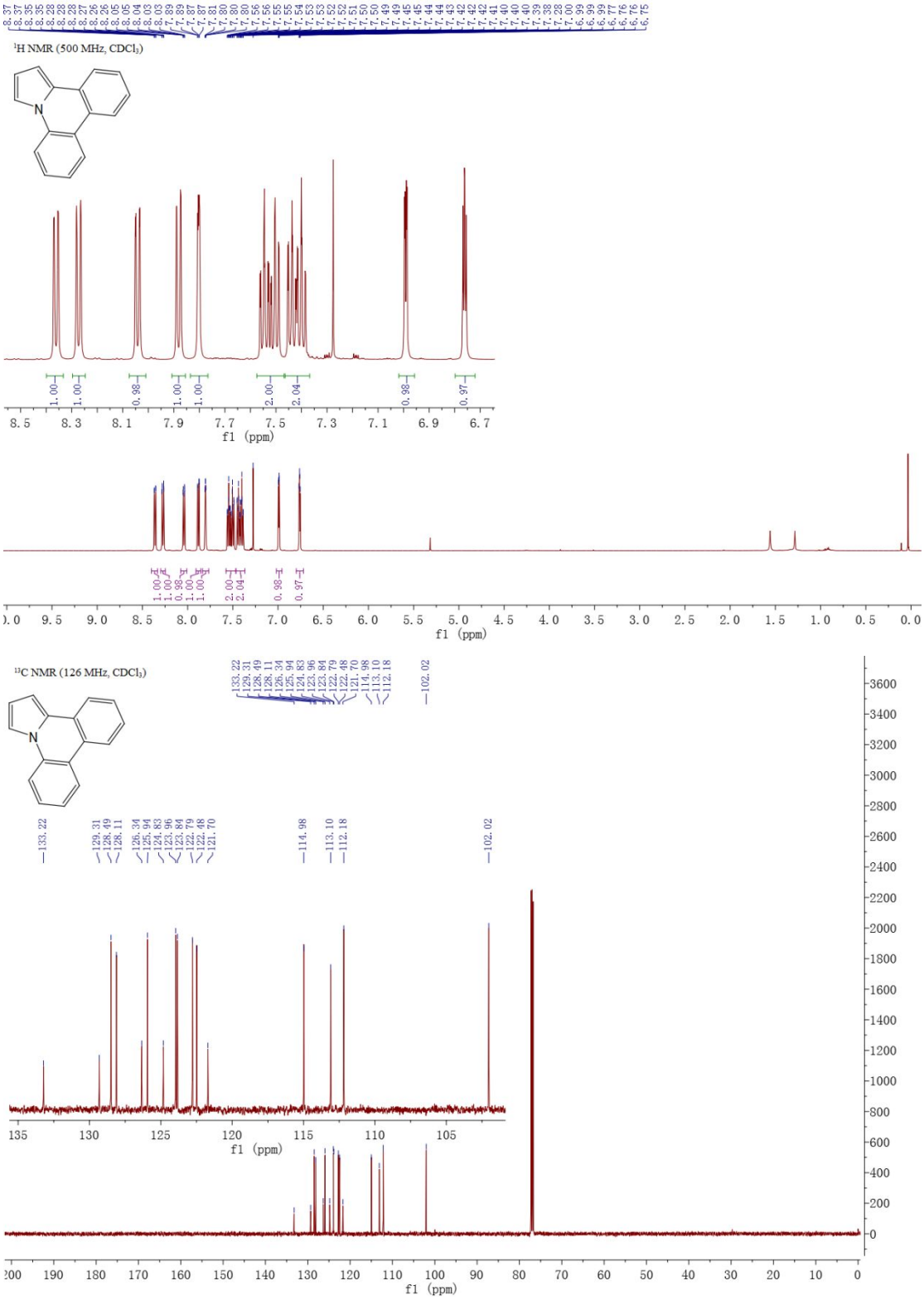


14-(furan-2-yl)indolo[1,2-*f*]phenanthridine (3ak)

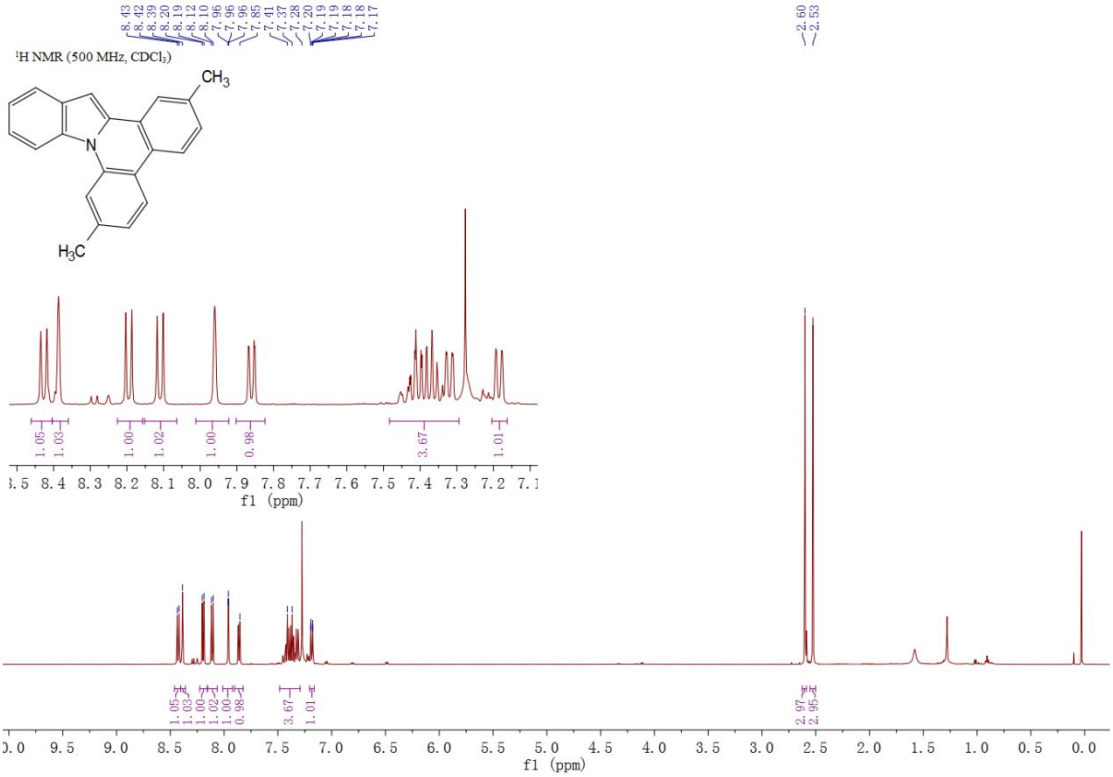


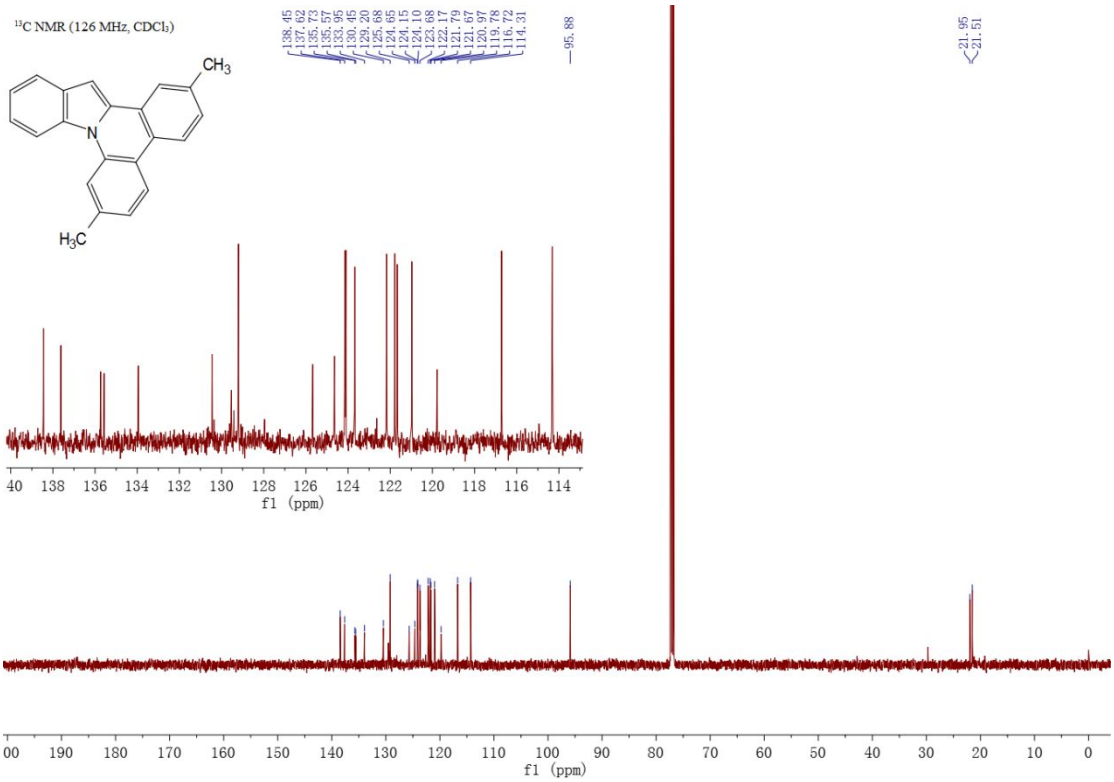


pyrrolo[1,2-*f*]phenanthridine (3al)

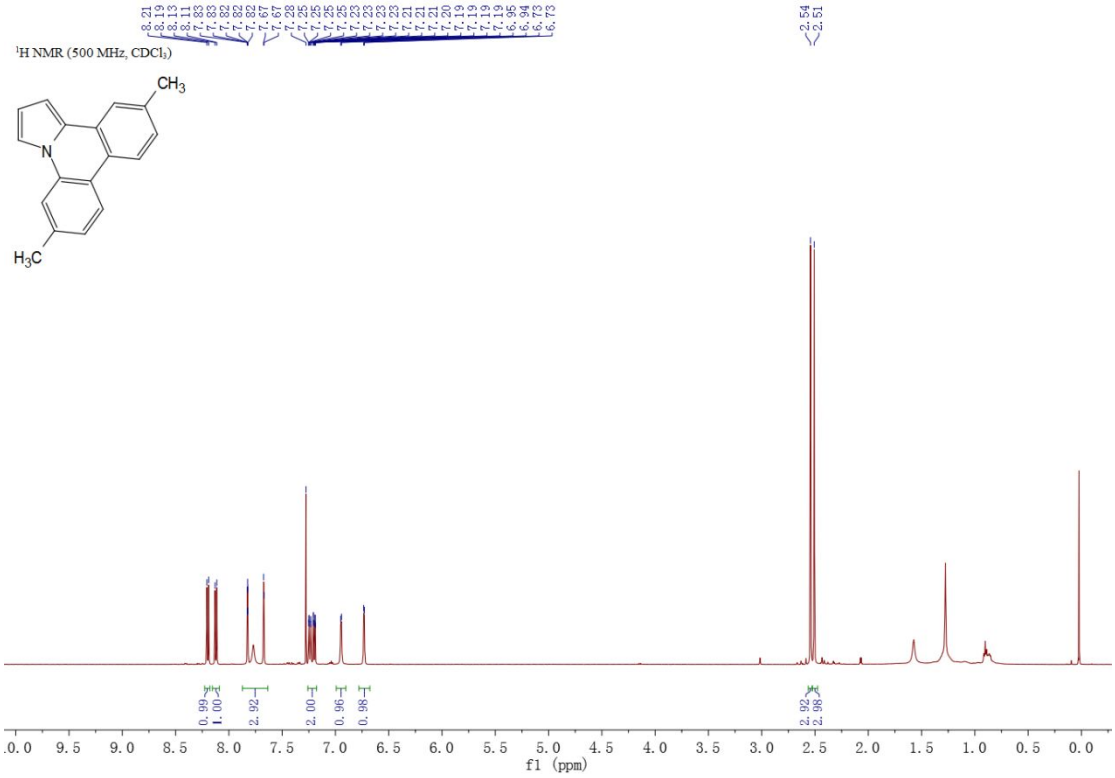


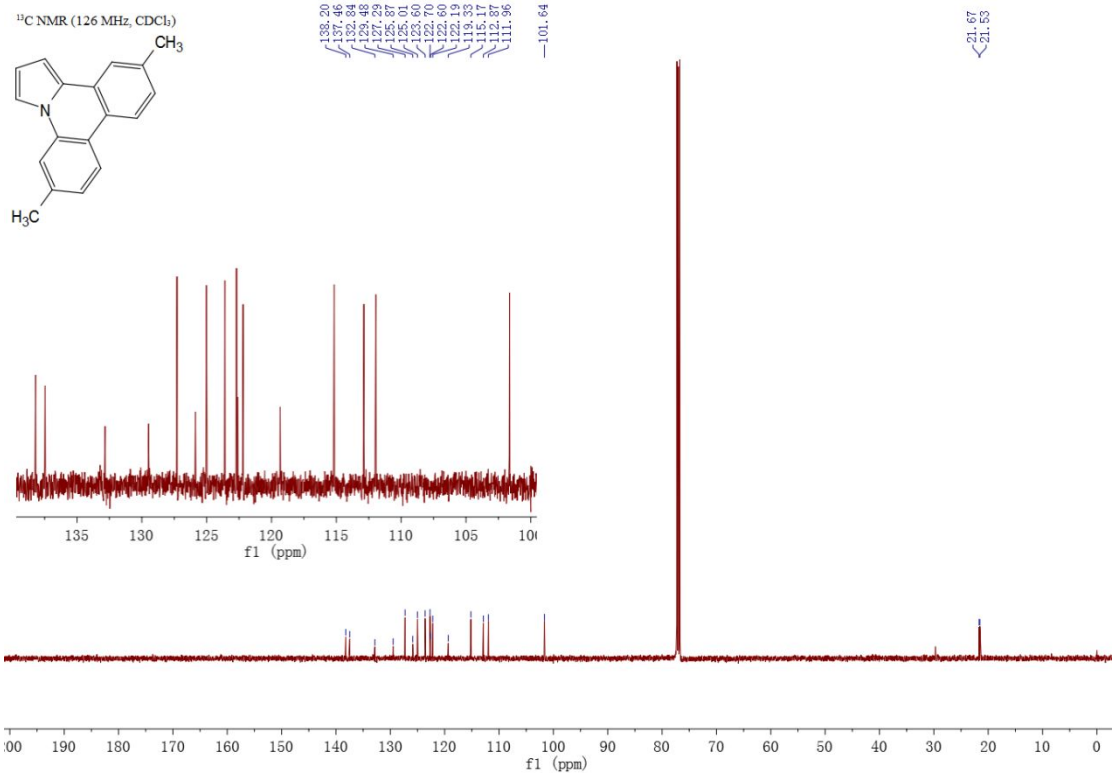
2,7-dimethylindolo[1,2-*f*]phenanthridine (3ba)



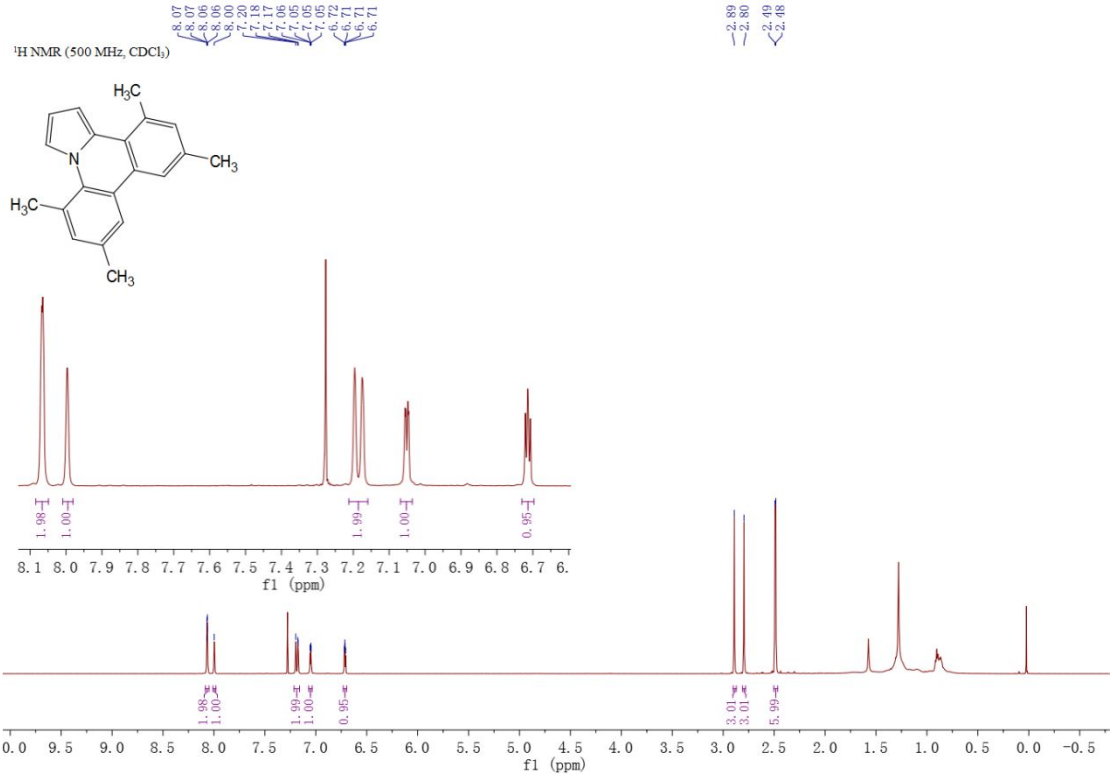


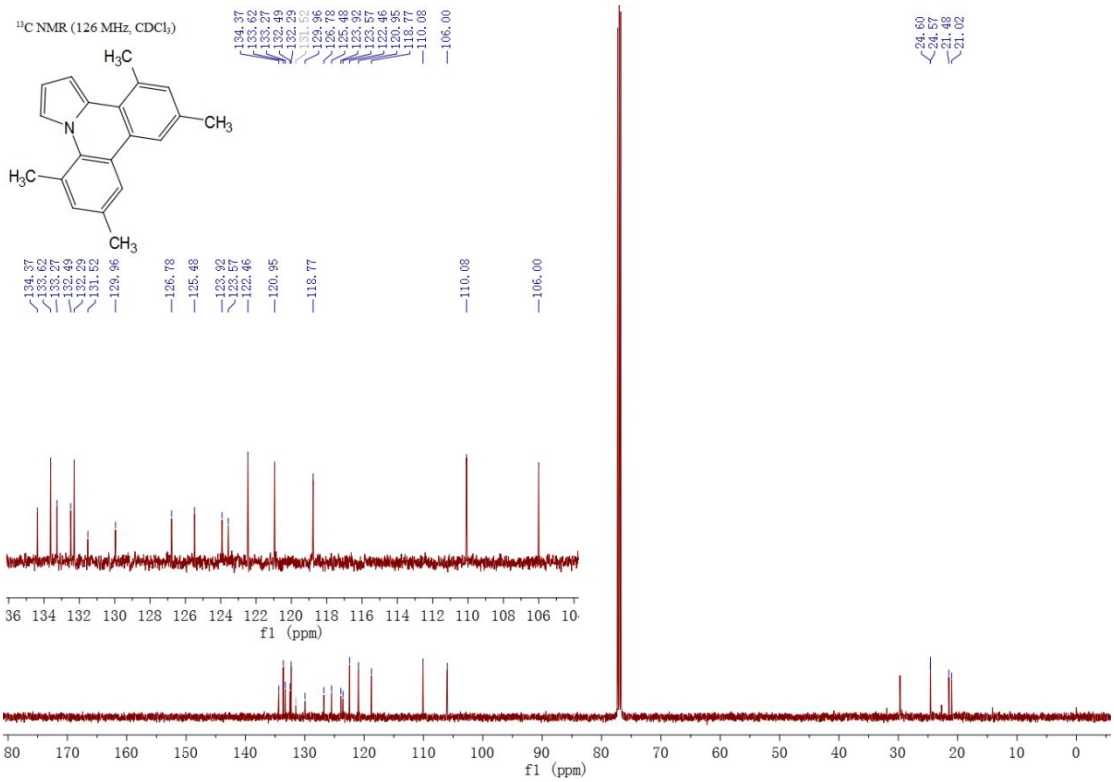
6,11-dimethylpyrrolo[1,2-*f*]phenanthridine (3bb)



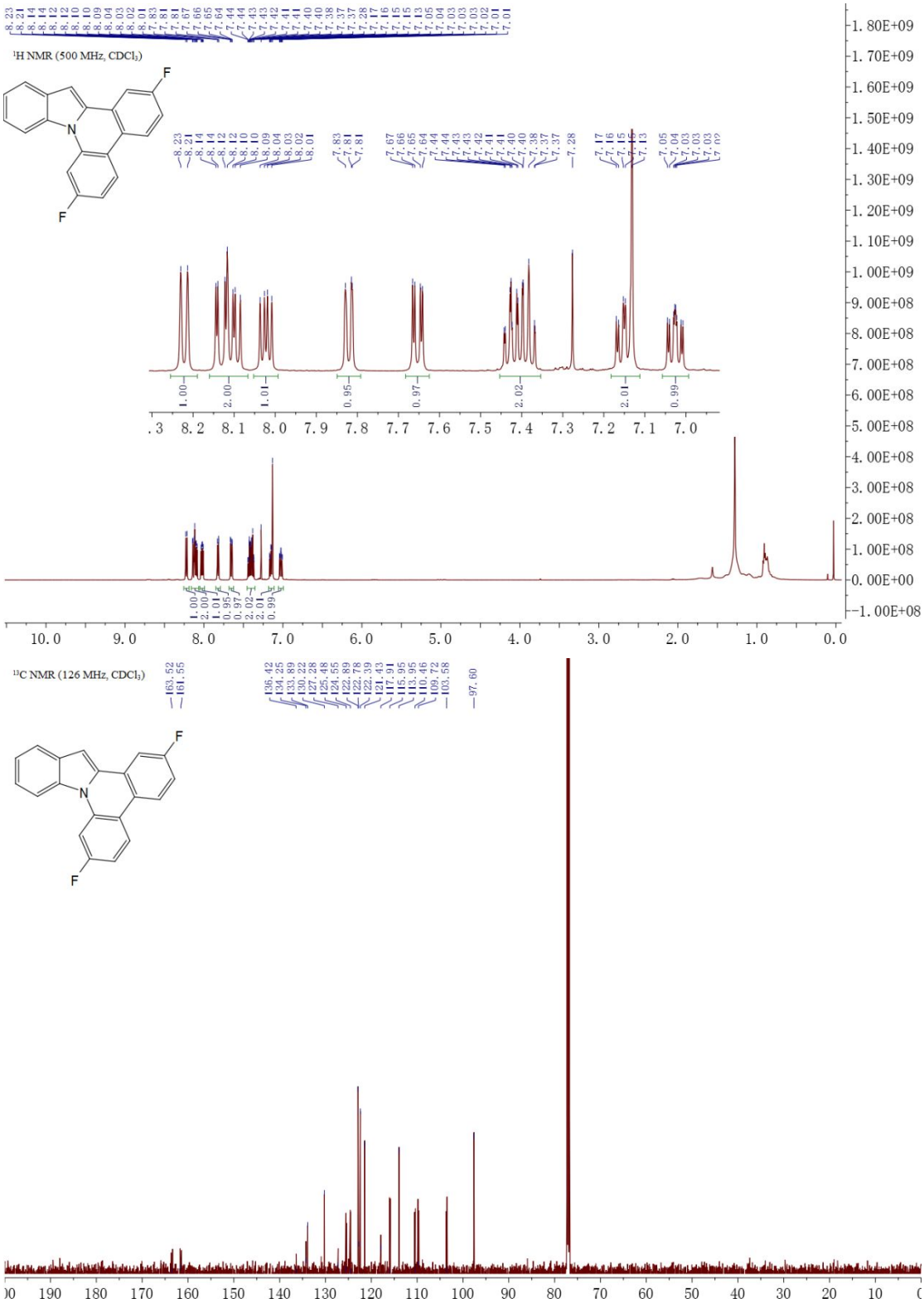


5,7,10,12-tetramethylpyrrolo[1,2-*f*]phenanthridine (3bc)

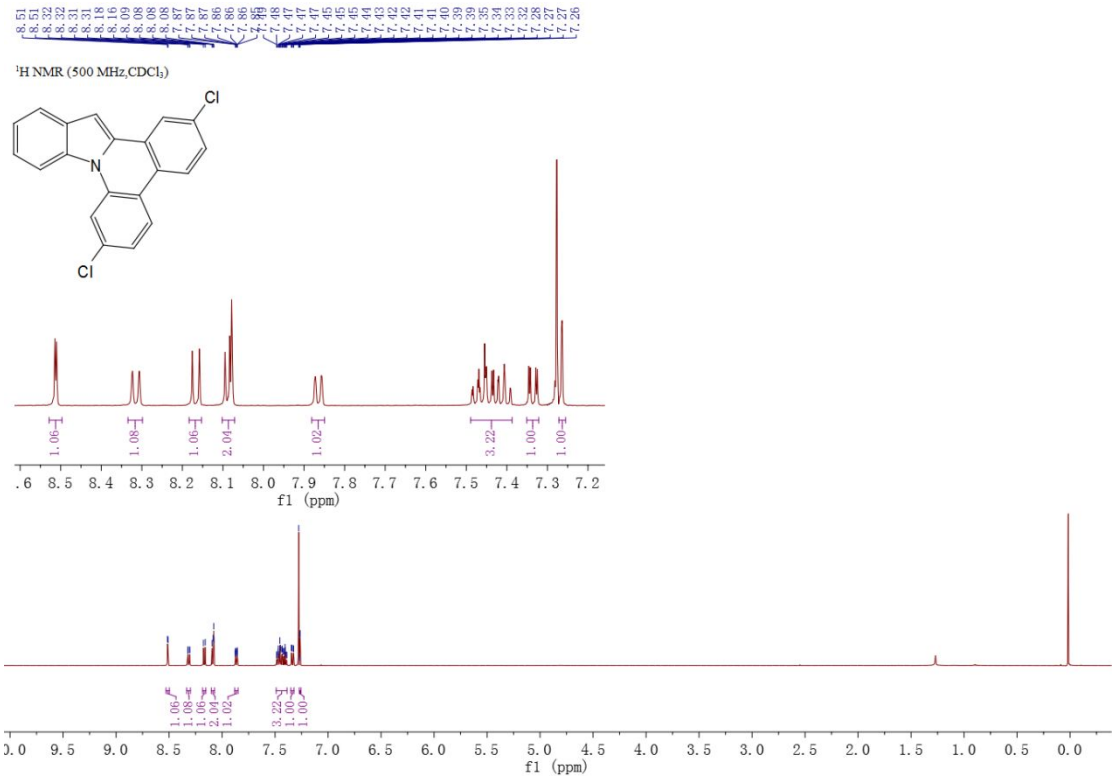


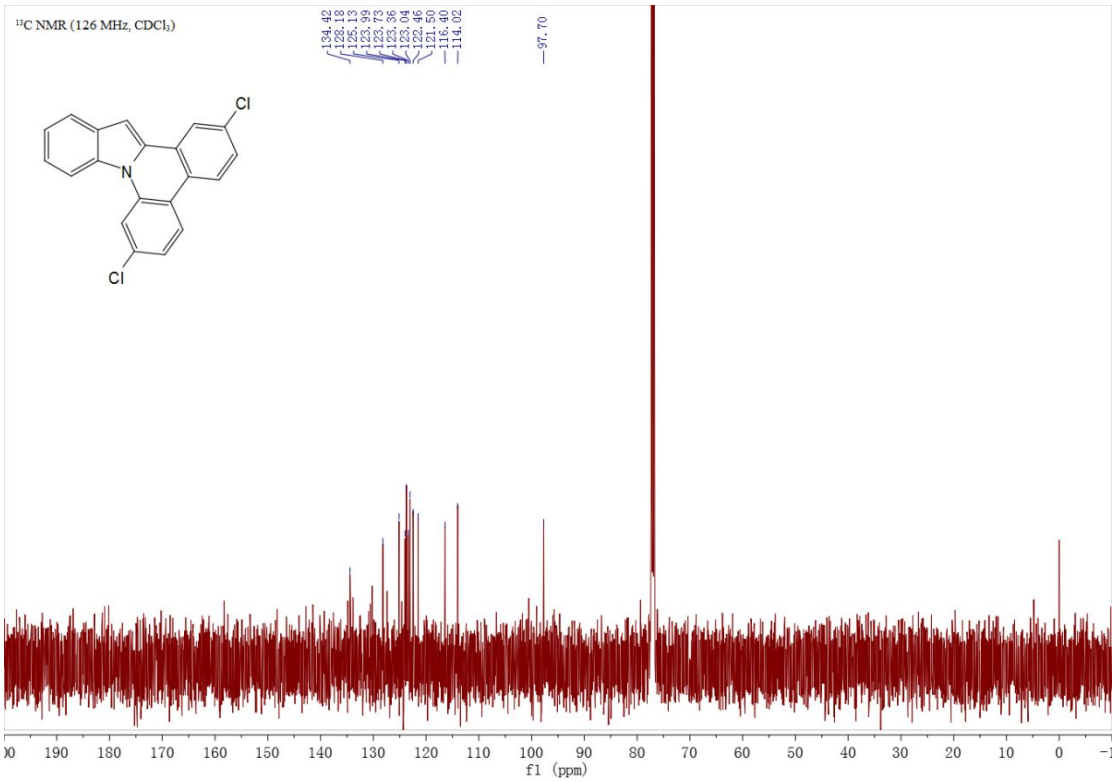


2,7-difluoroindolo[1,2-*f*]phenanthridine (3bd)

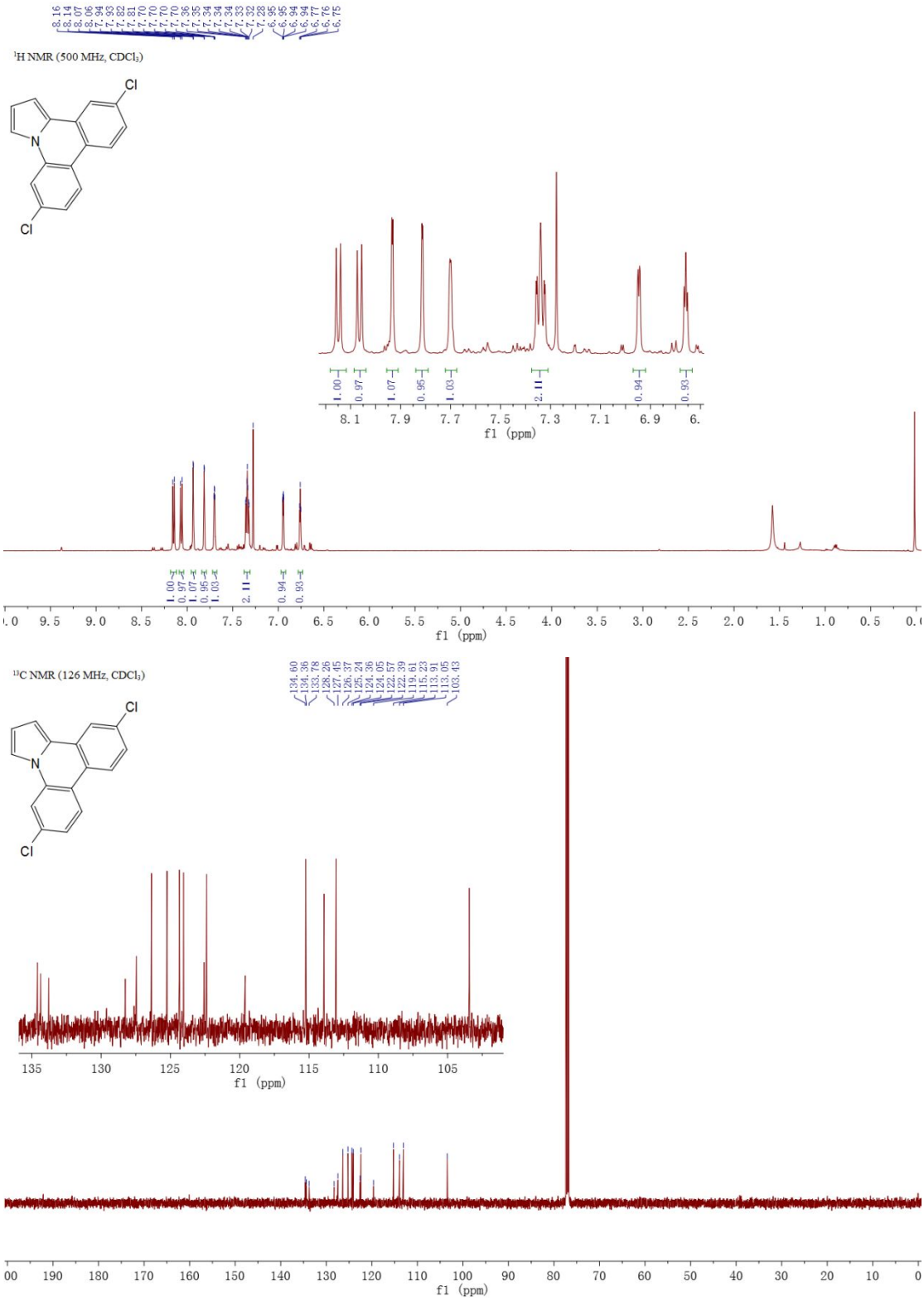


2,7-dichloroindolo[1,2-*f*]phenanthridine (3be)

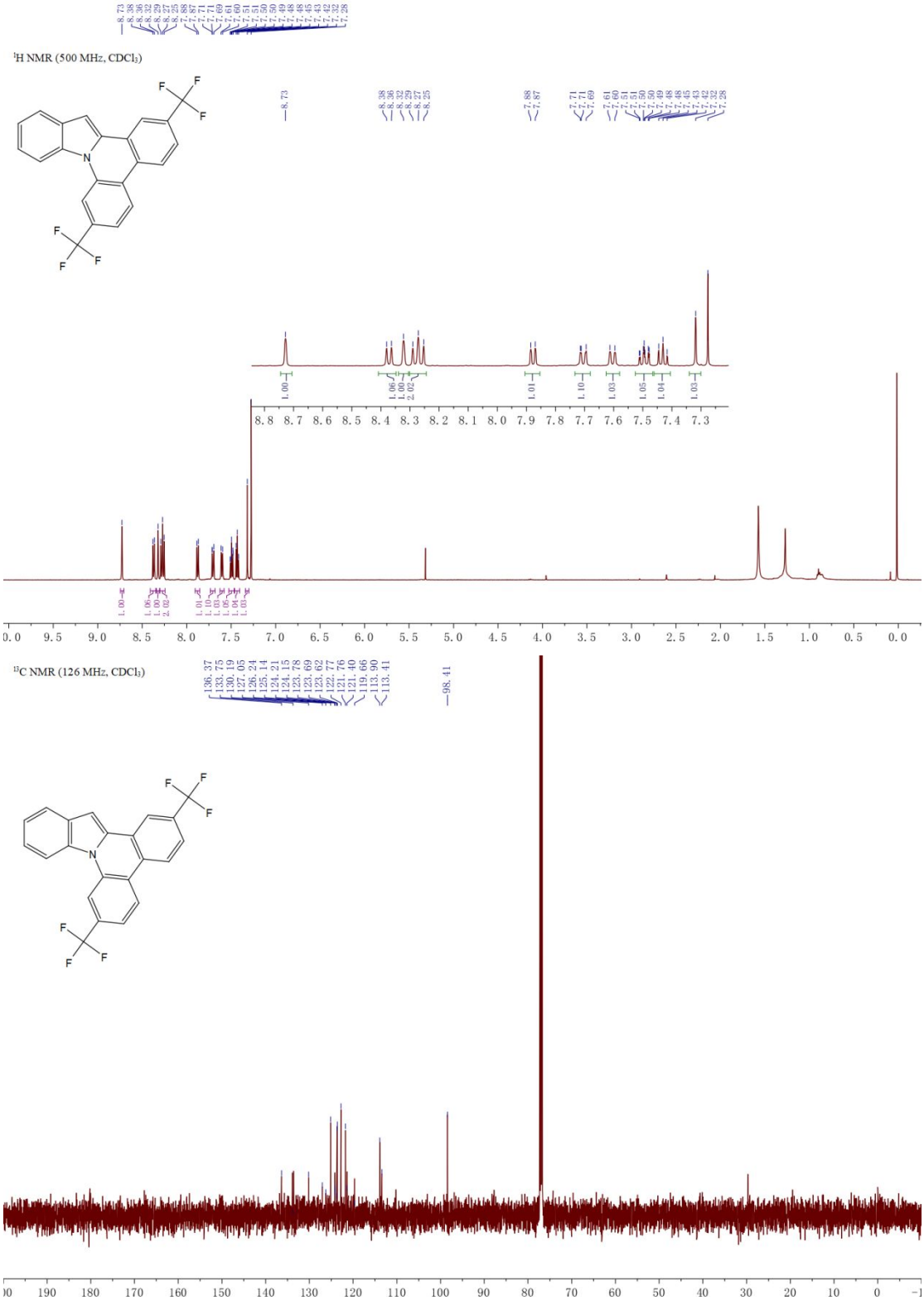




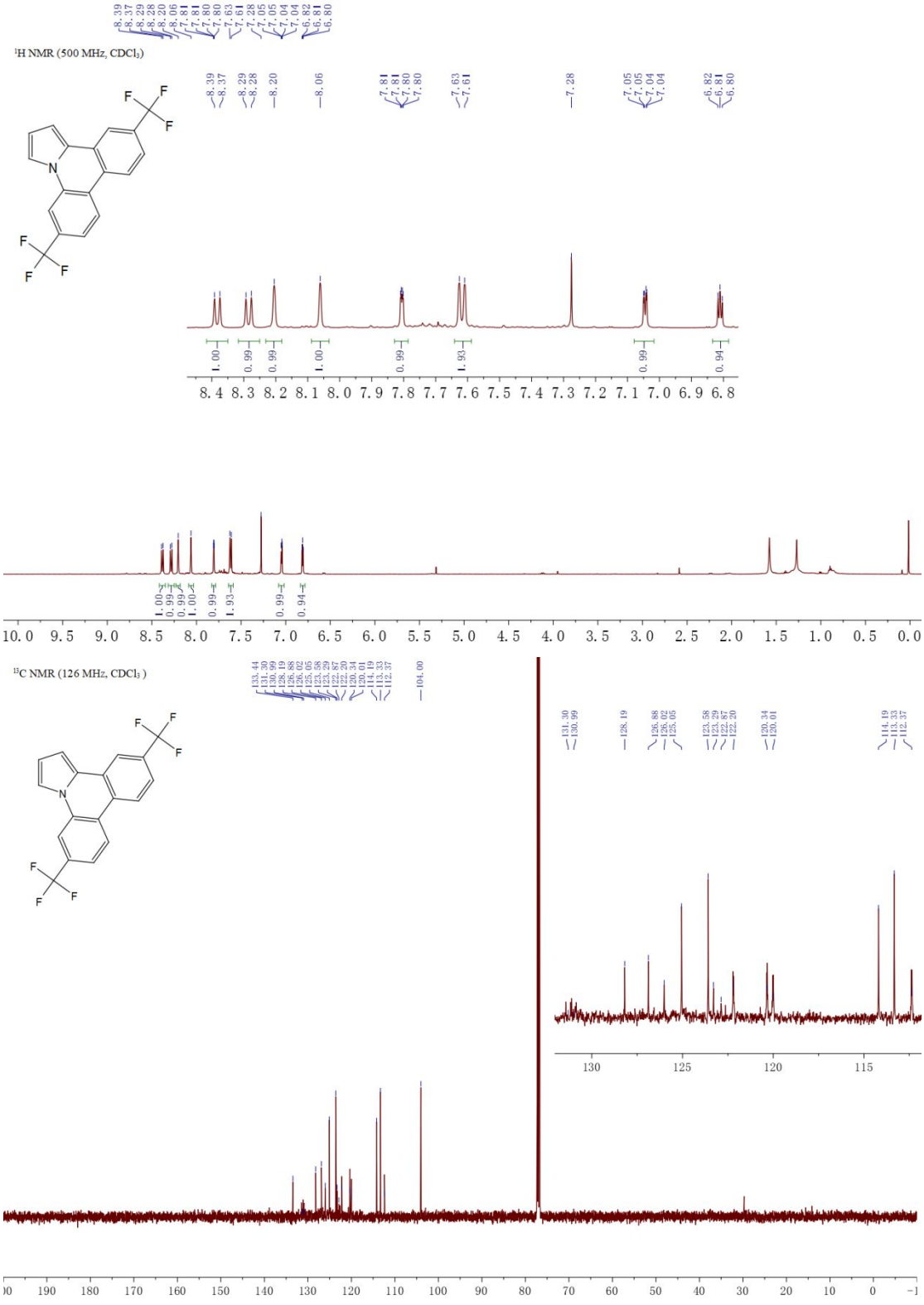
6,11-dichloropyrrolo[1,2-*f*]phenanthridine (3bf)



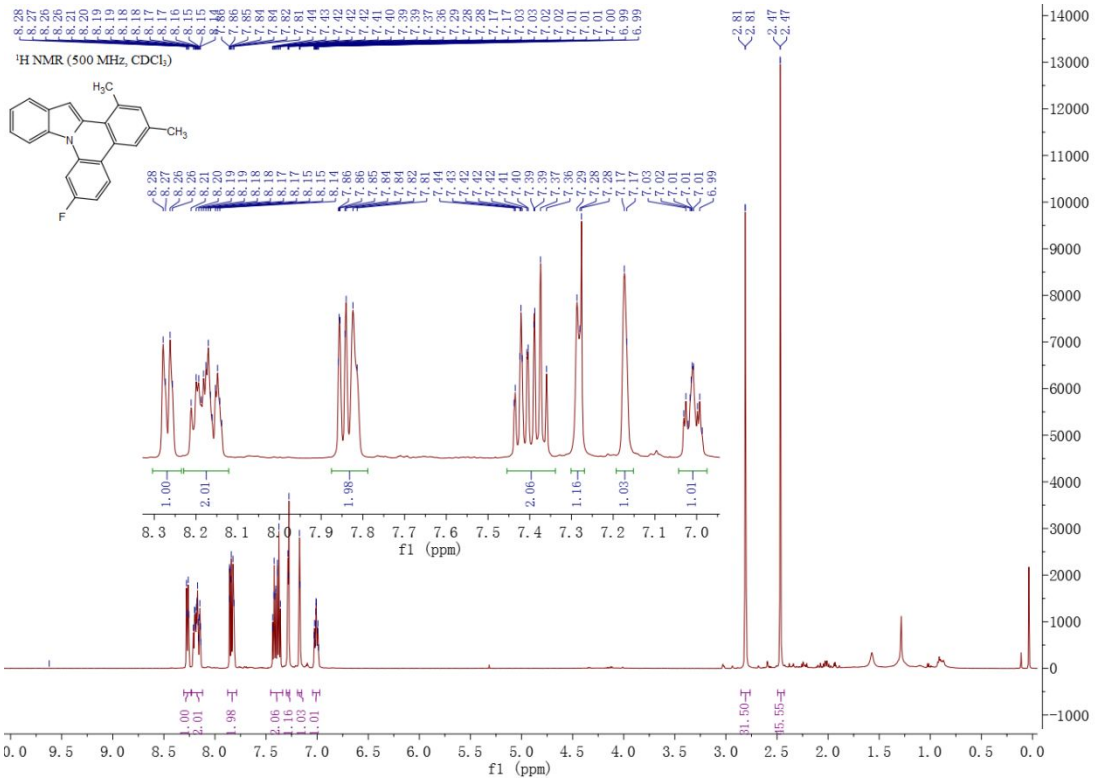
2,7-bis(trifluoromethyl)indolo[1,2-*f*]phenanthridine (3bg)

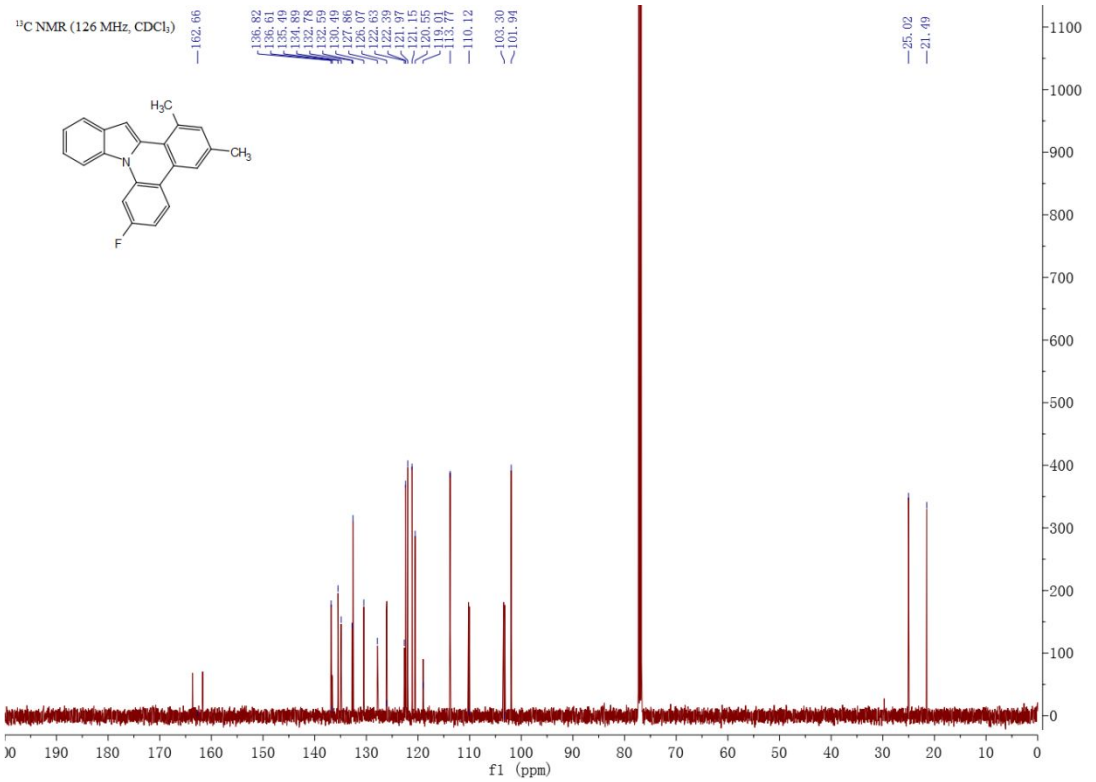


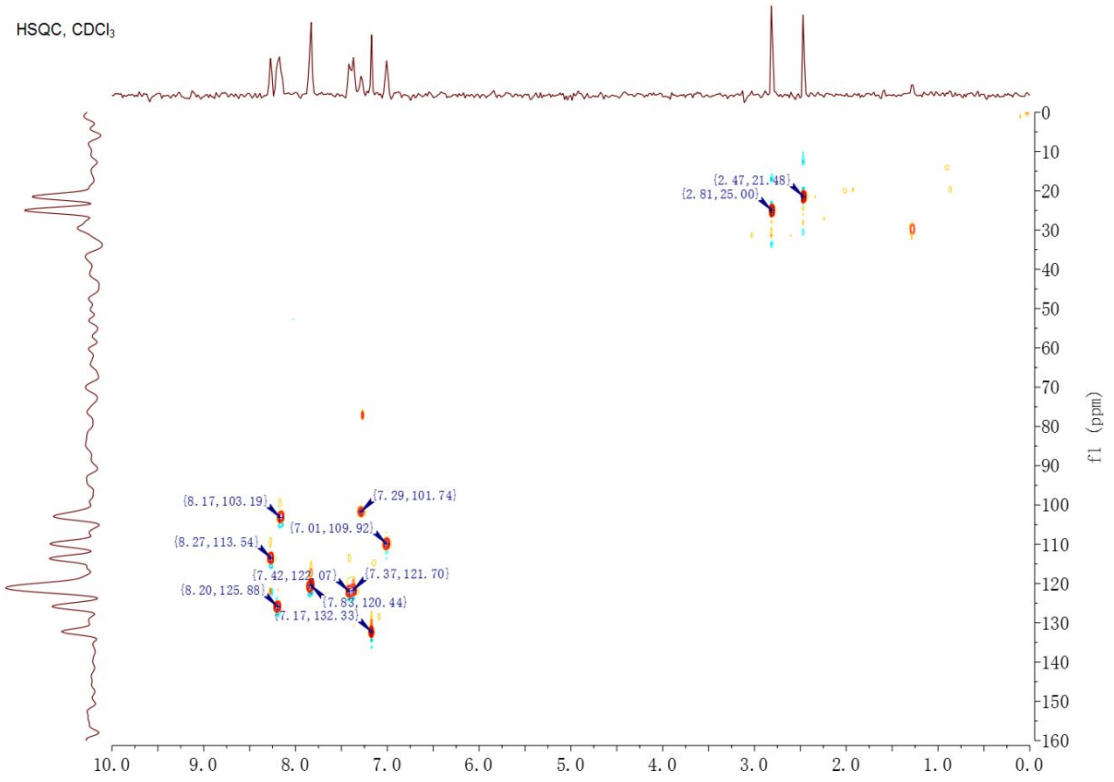
6,11-bis(trifluoromethyl)pyrrolo[1,2-*f*]phenanthridine (3bh)

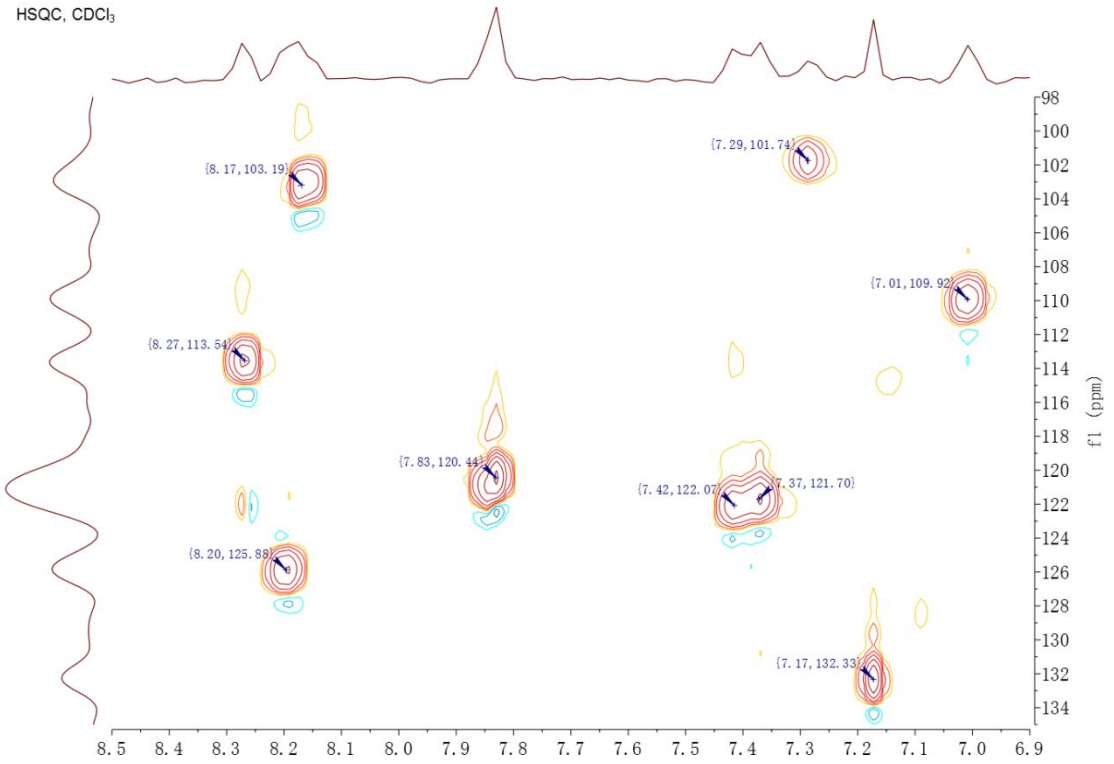


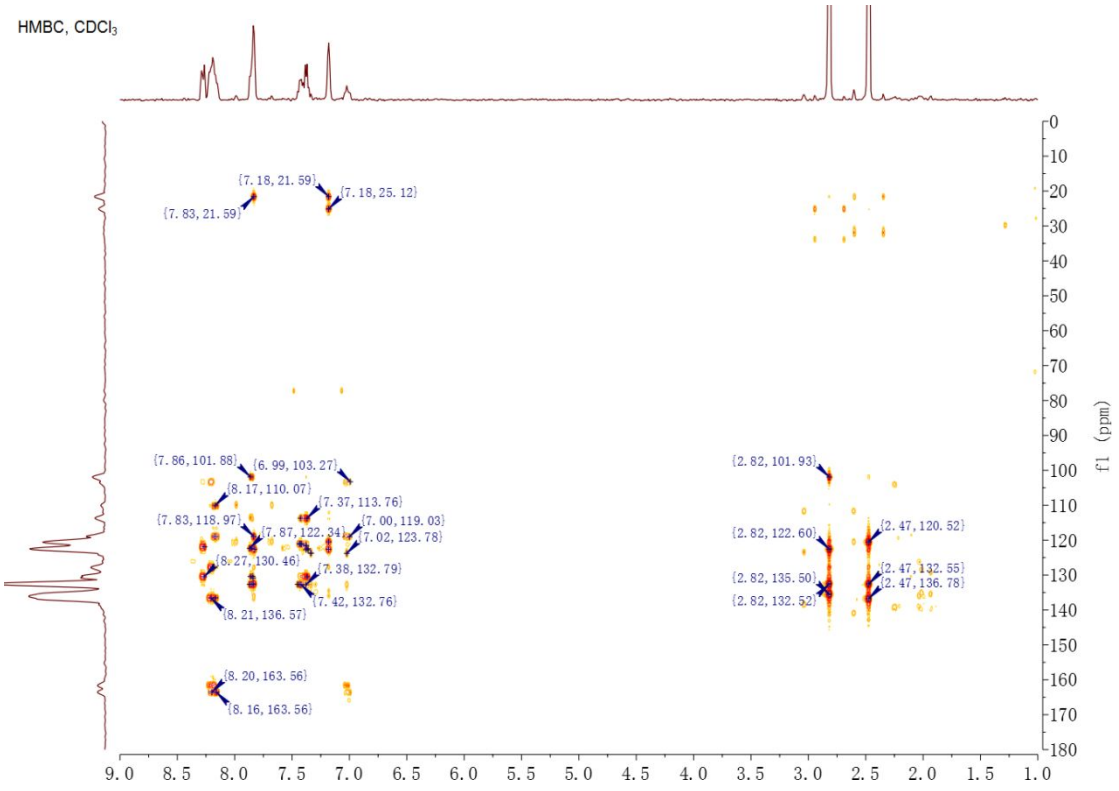
7-fluoro-1,3-dimethylindolo[1,2-*f*]phenanthridine (3bi):

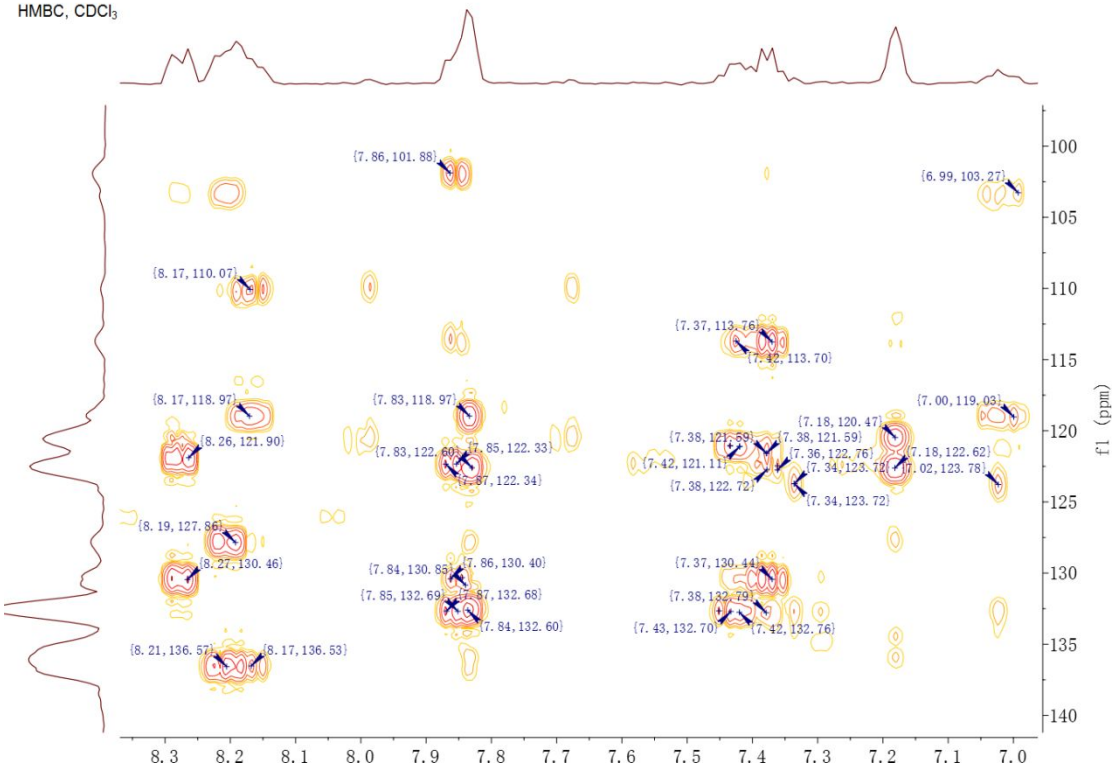


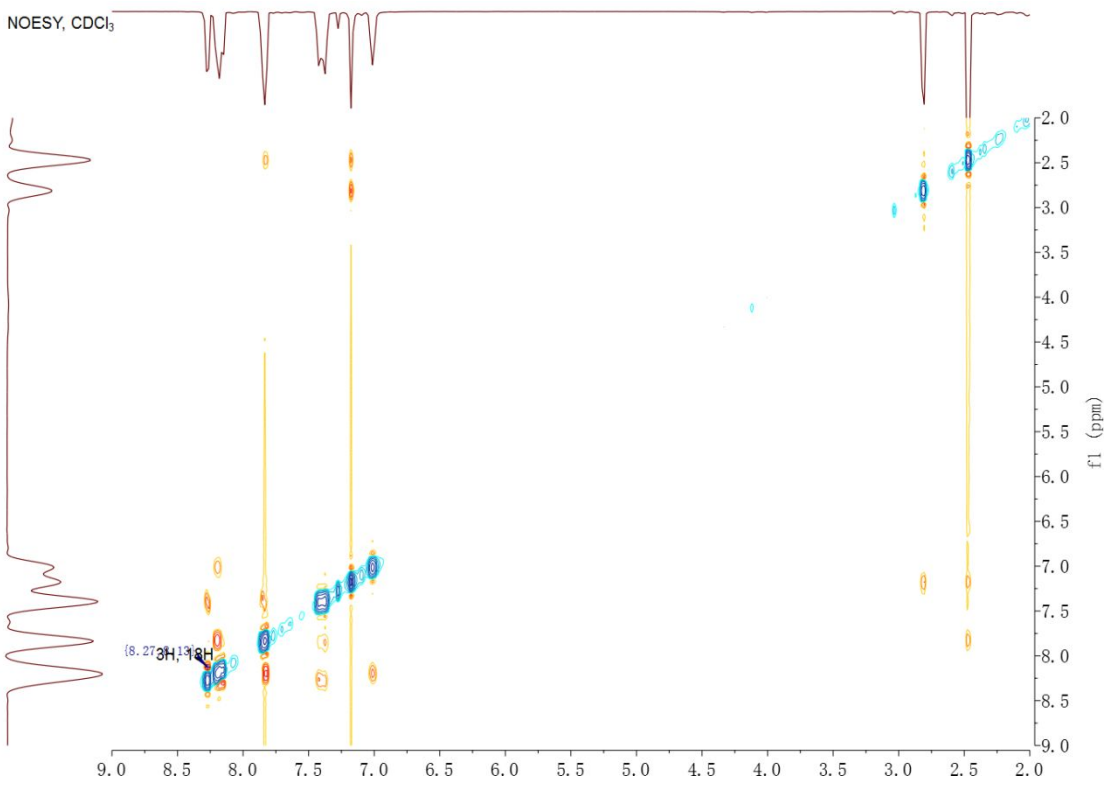


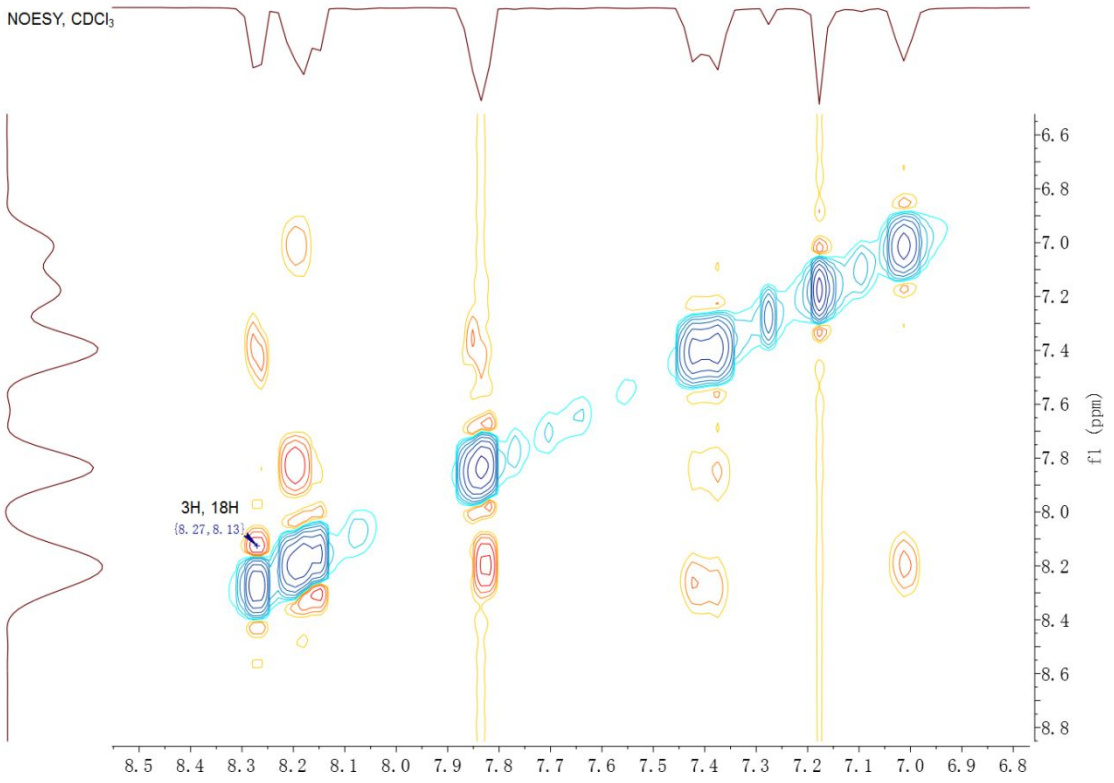

HSQC, CDCl3
{2.47,21.48}
{2.81,25.00}
{8.17,103.19}
{7.29,101.74}
{7.01,109.92}
{8.27,113.54}
{7.42,122.07}
{7.37,121.70}
{8.20,125.88}
{7.83,120.44}
{7.17,132.33}
f1 (ppm)
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0

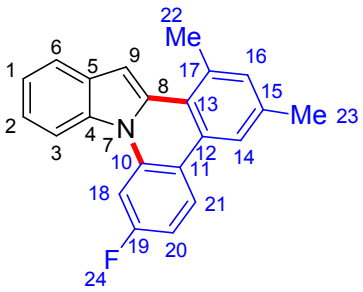

HSQC, CDCl3
{8.17,103.19}
{7.29,101.74}
{7.01,109.92}
{8.27,113.54}
{7.83,120.44}
{7.42,122.07}
{7.37,121.70}
{8.20,125.88}
{7.17,132.33}
f1 (ppm)
8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9


HMBC, CDCl3
f1 (ppm)


HMBC, CDCl3
f1 (ppm)

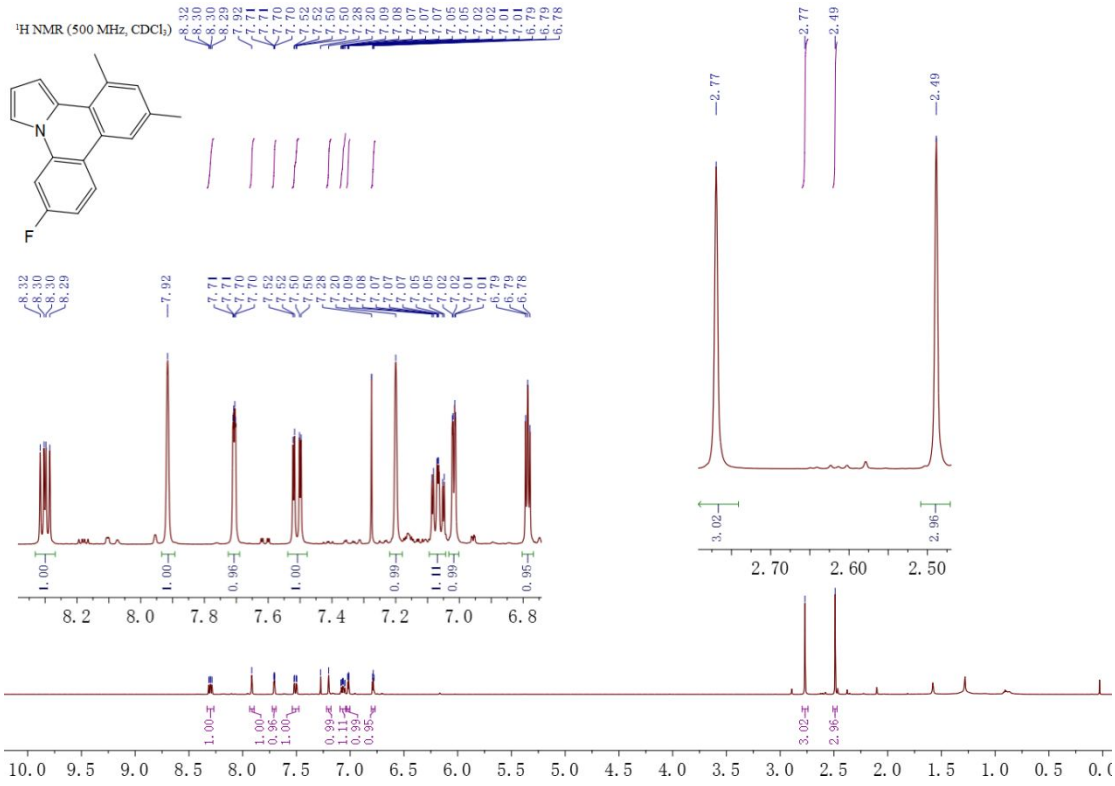

NOESY, CDCl3
3H, 18H
{8.27, 8.13}
f1 (ppm)

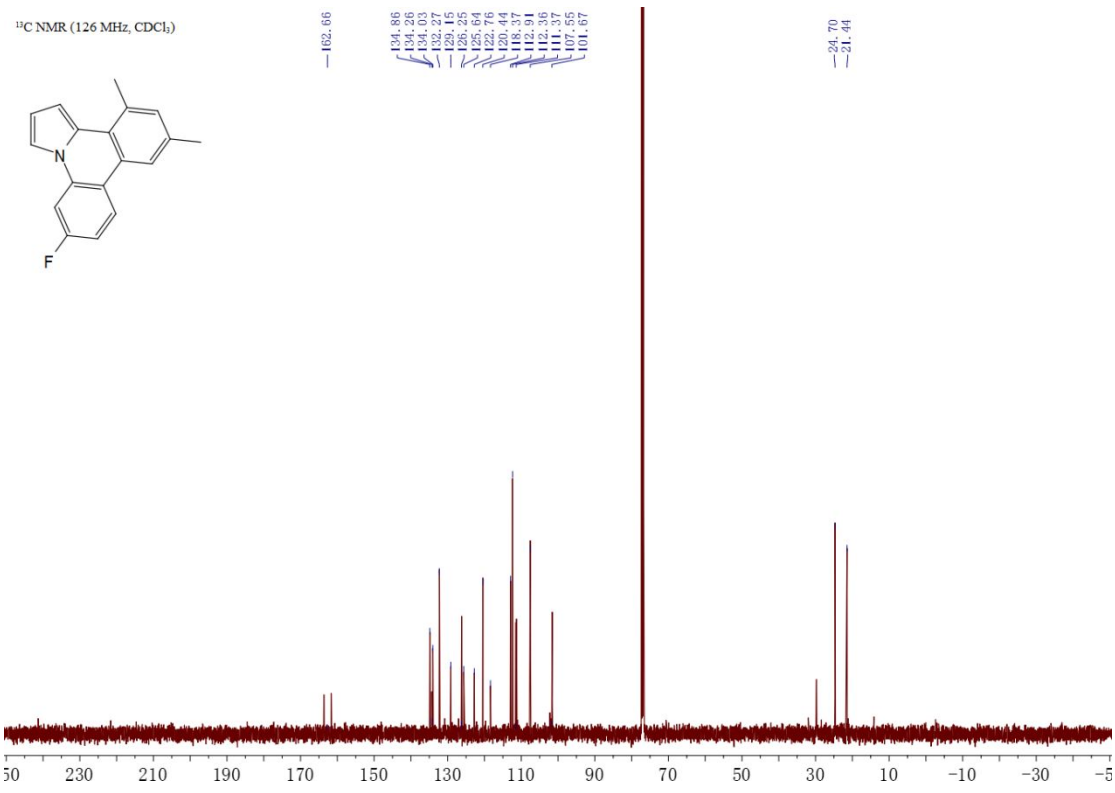

NOESY, CDCl3
3H, 18H
{8.27, 8.13}
f1 (ppm)



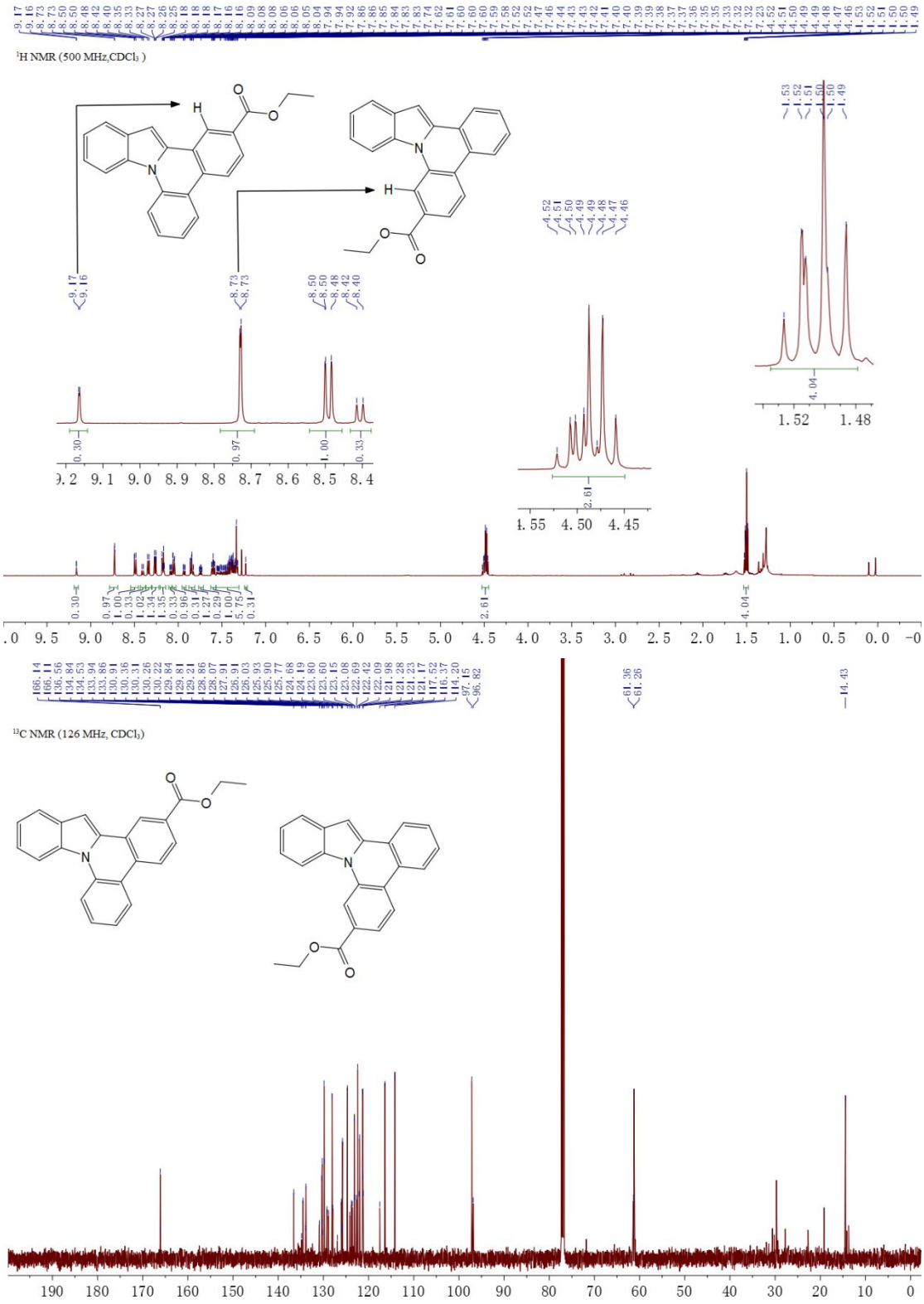
Number	^{1}H	^{13}C
1	7.85 (1H, d, *J* = 8.0 Hz)	121.2
2	7.42 (1H, ddd, *J* = 8.6, 7.1, 1.4 Hz)	122.4
3	8.27 (1H, dd, *J* = 8.4, 2.8 Hz)	113.8
4	-	130.5
5	-	**132.8**
6	7.37 (1H, t, *J* = 7.2 Hz)	122.0
7	-	-
8	-	**134.9**
9	7.28 (1H, d, *J* = 5.5 Hz)	101.9
10	-	136.6
11	-	119.0
12	-	127.9
13	-	122.6
14	7.82 (1H, d, *J* = 5.0 Hz)	120.6
15	-	**136.8**
16	7.17 (1H, d, *J* = 3.1 Hz)	132.6
17	-	**135.5**
18	8.16 (1H, dd, *J* = 11.2, 2.4 Hz)	103.3
19	-	162.7
20	7.03 – 6.98 (1H, m)	110.1
21	8.20 (1H, dd, *J* = 8.8, 6.2 Hz)	126.1
22	2.81 (3H, s)	25.0
23	2.47 (3H, s)	21.5

6-fluoro-10,12-dimethylpyrrolo[1,2-*f*]phenanthridine (3bj)

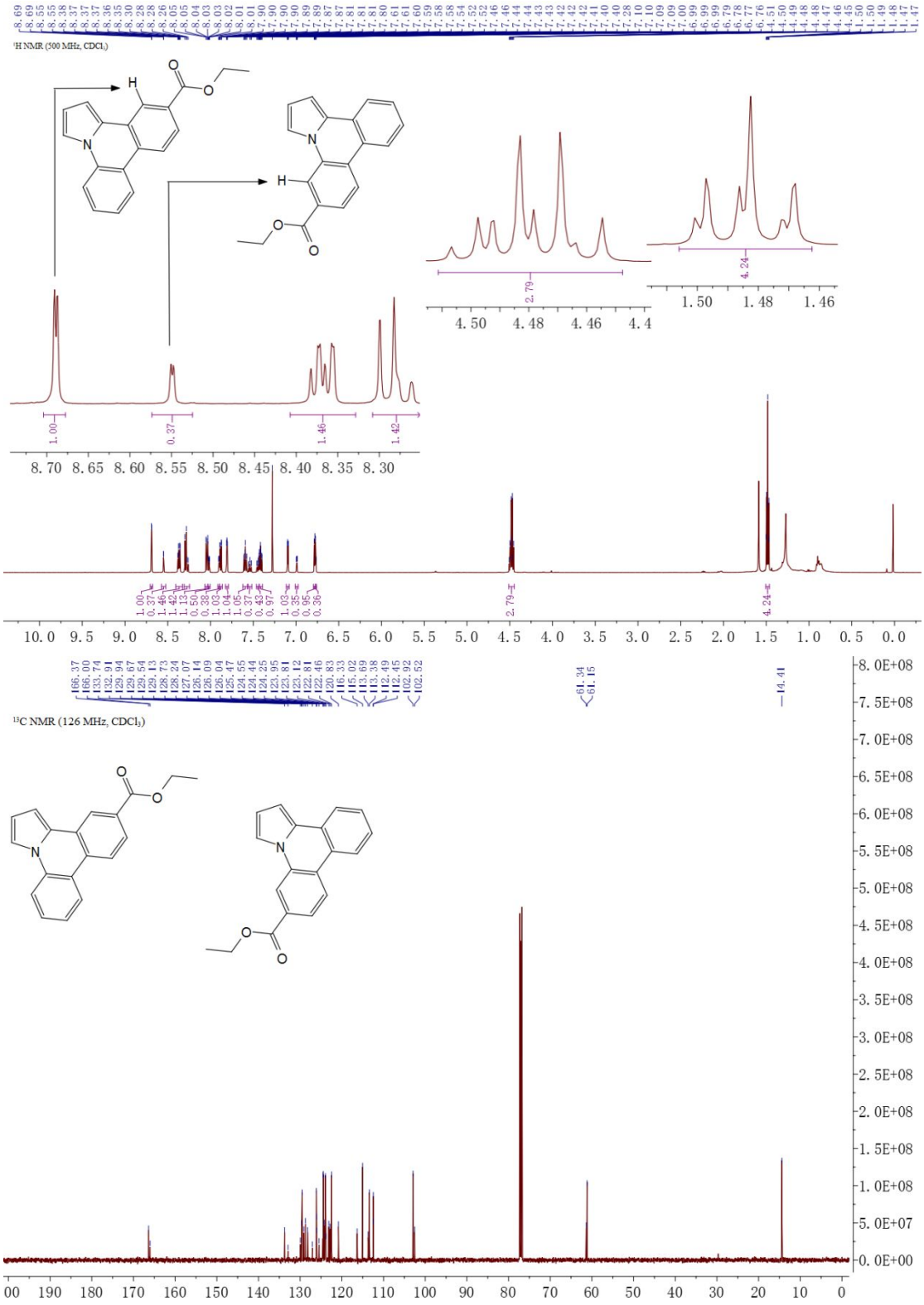




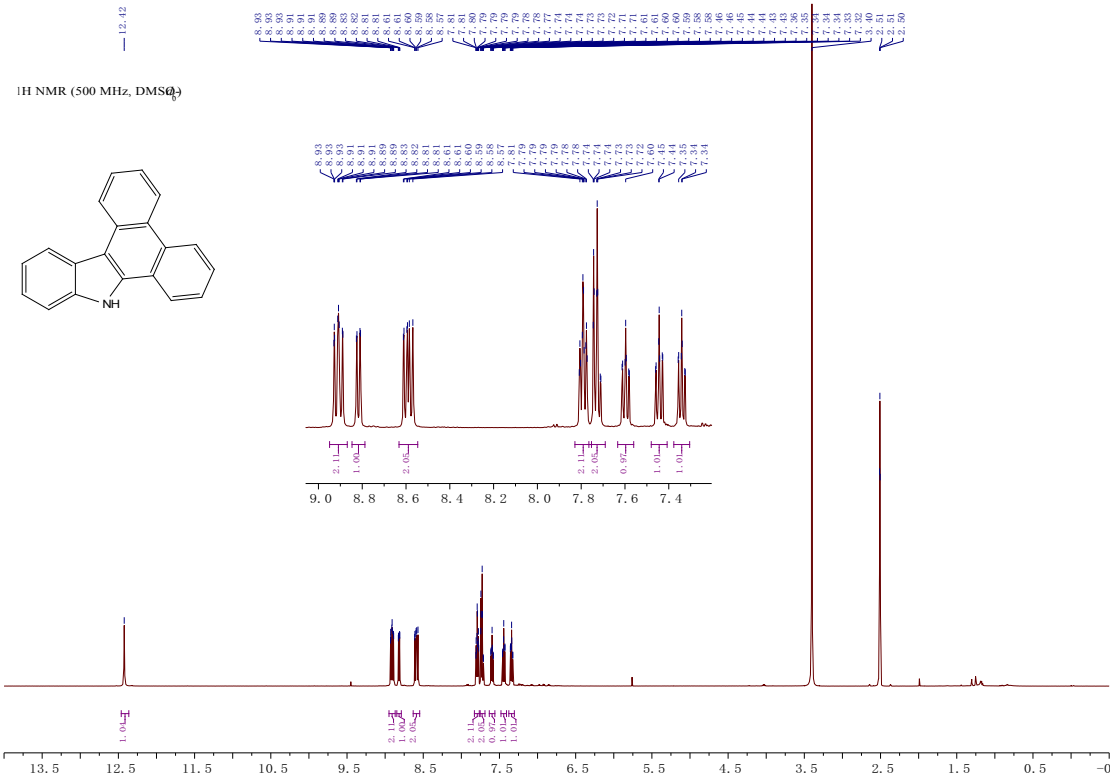
The mixture of ethyl indolo[1,2-*f*]phenanthridine-2-carboxylate (3bk) and ethyl indolo[1,2-*f*]phenanthridine-7-carboxylate (3bk')

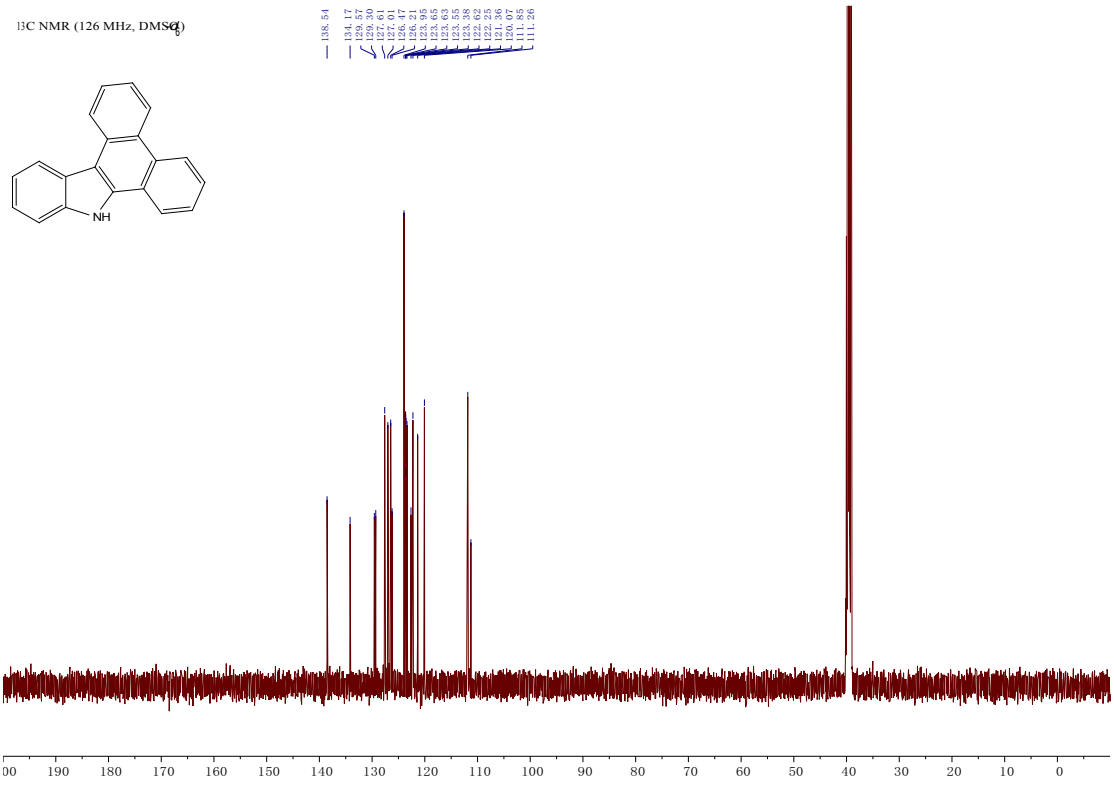


The mixture of ethyl pyrrolo[1,2-*f*]phenanthridine-11-carboxylate (3bl) and ethyl pyrrolo[1,2-*f*]phenanthridine-6-carboxylate (3bl')

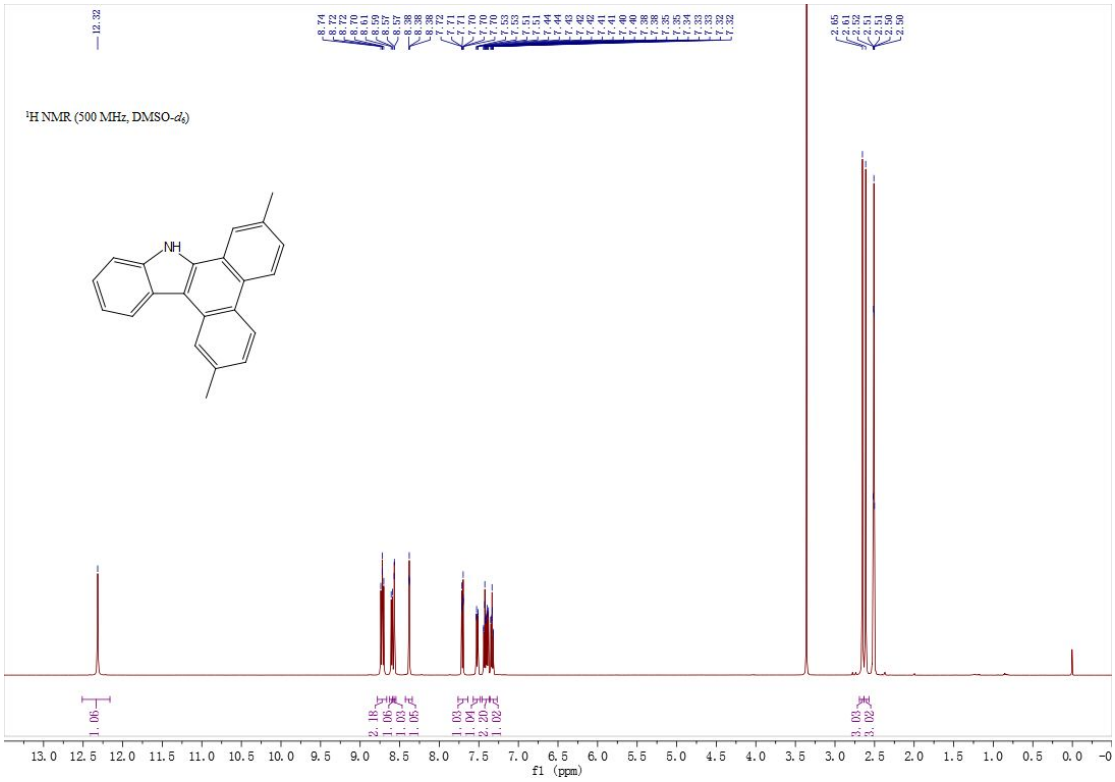


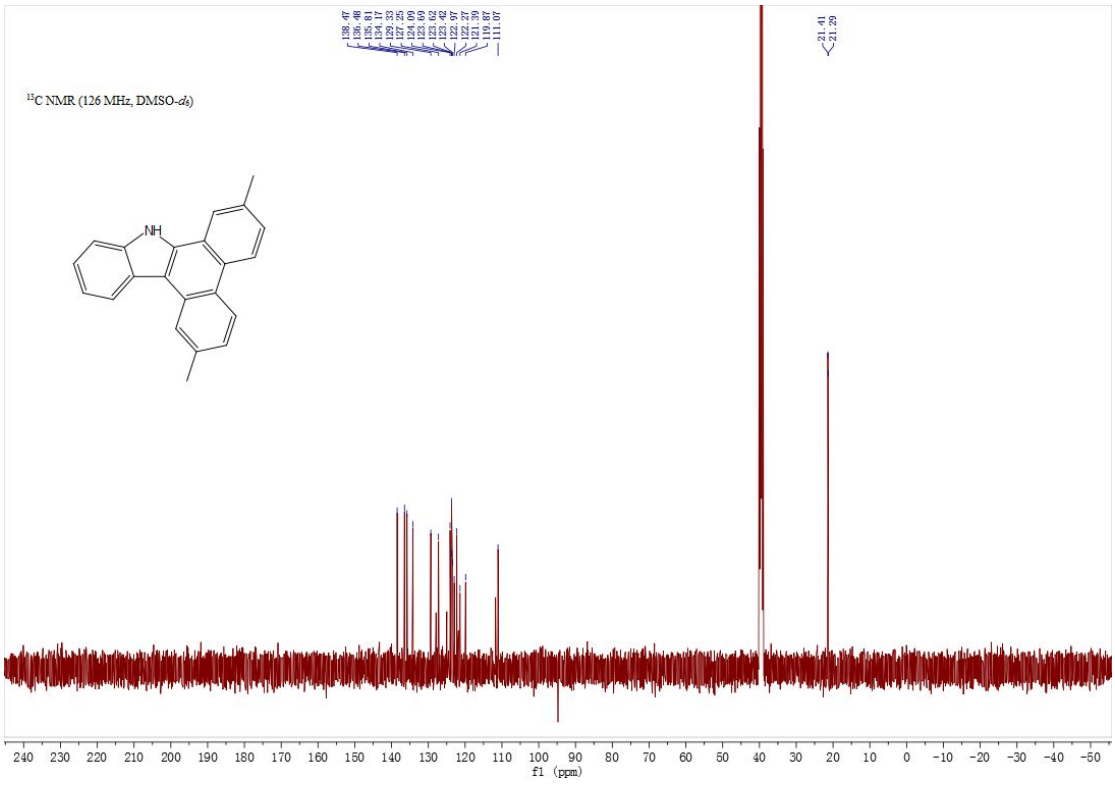
9*H*-Dibenzo[*a*,*c*]carbazole(4a):



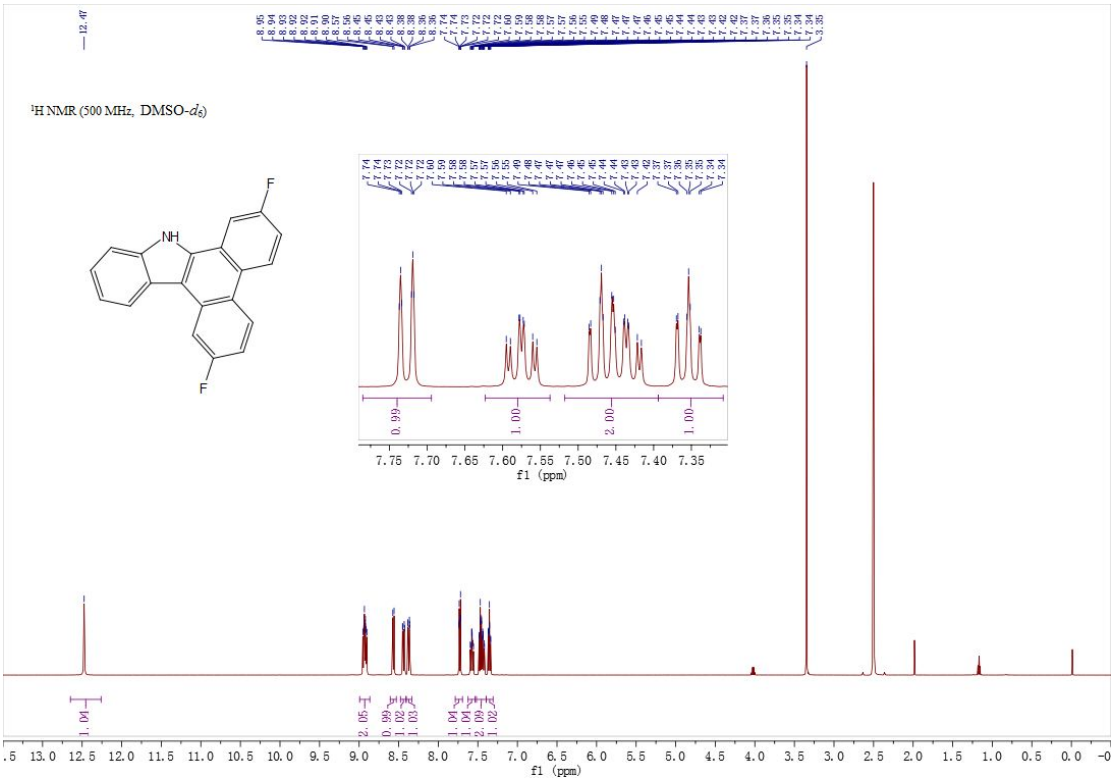


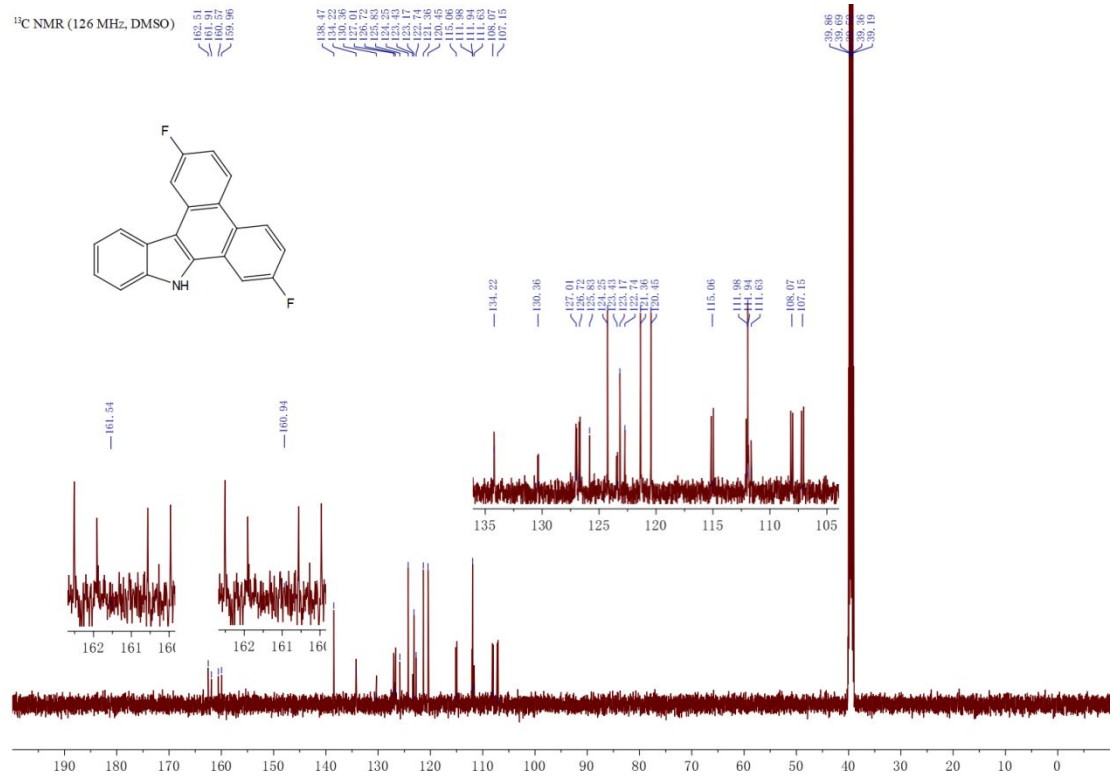
2,7-dimethyl-9*H*-dibenzo[*a*,*c*]carbazole (4b):



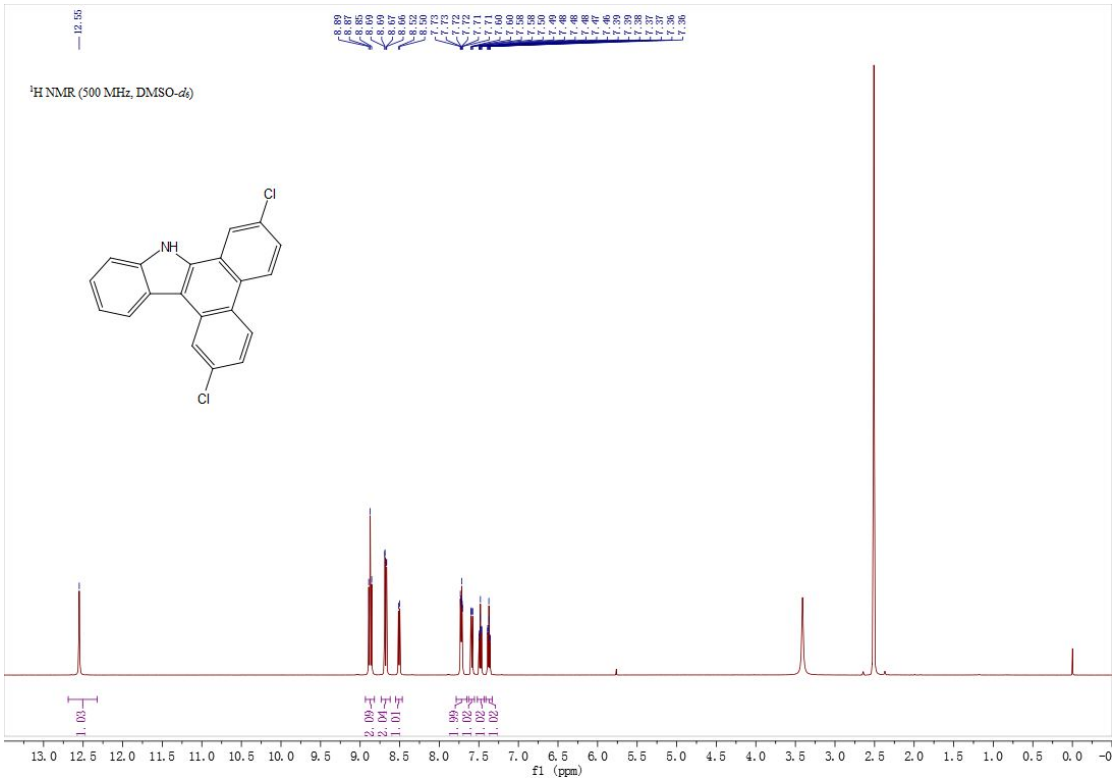


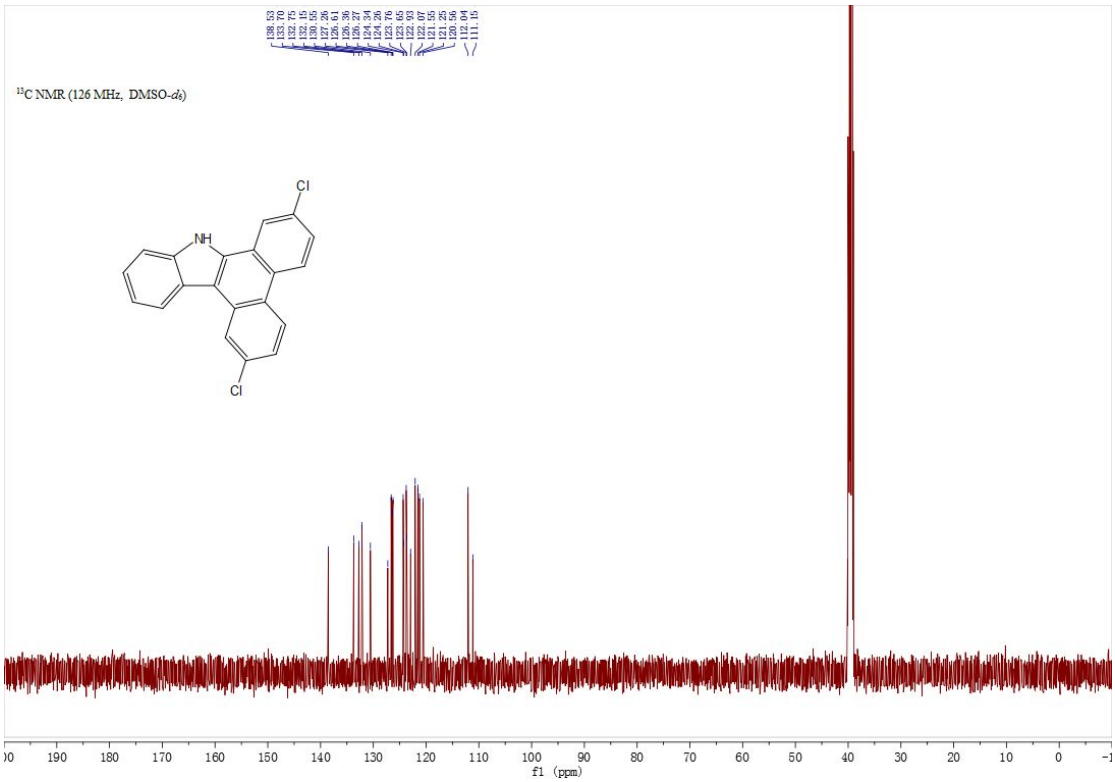
2,7-difluoro-9*H*-dibenzo[*a,c*]carbazole (4c):



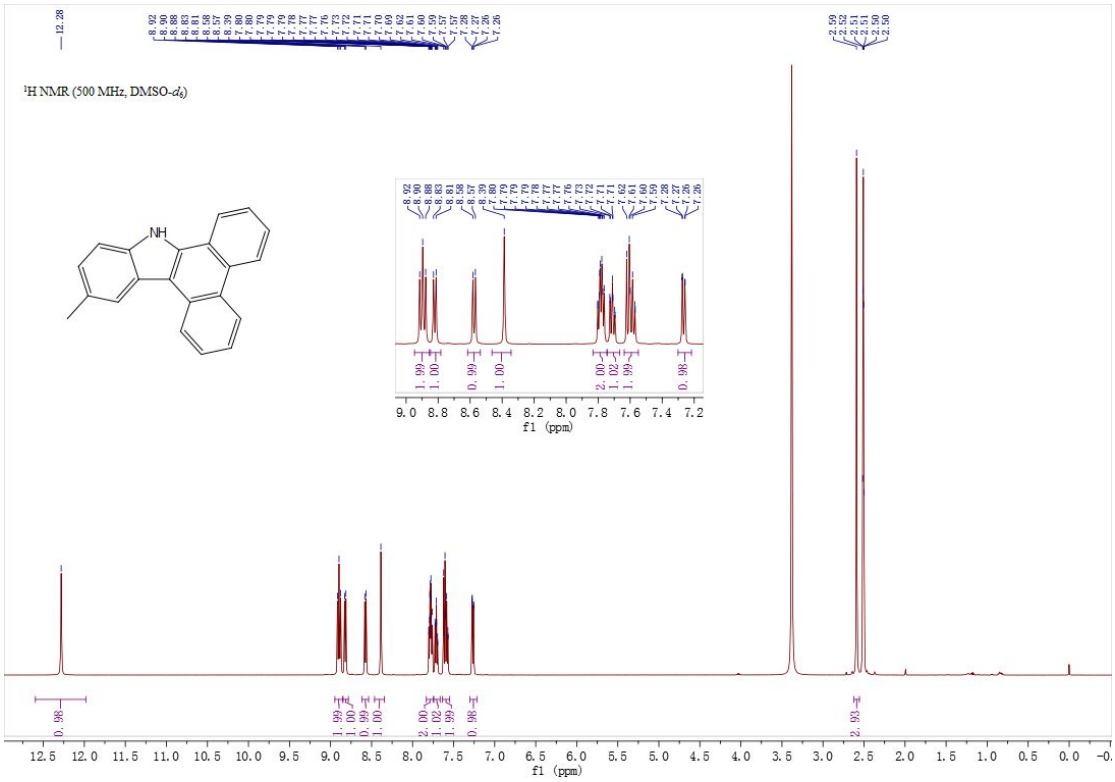


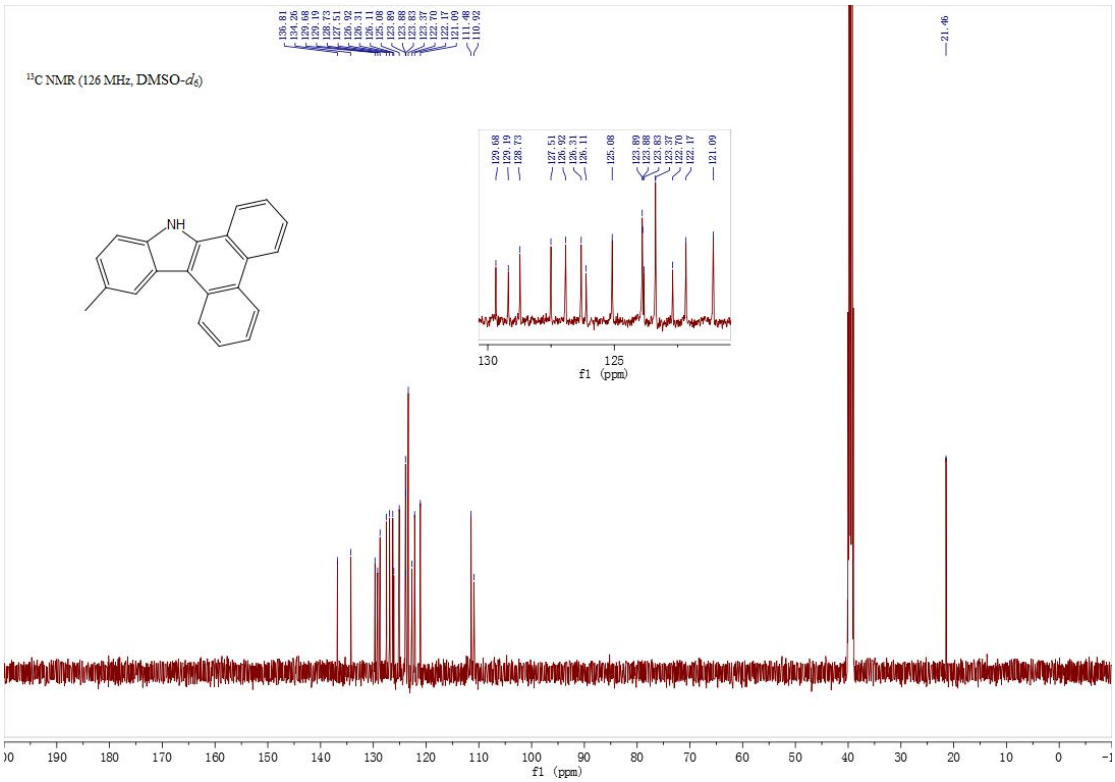
2,7-dichloro-9*H*-dibenzo[*a*,*c*]carbazole(4d):



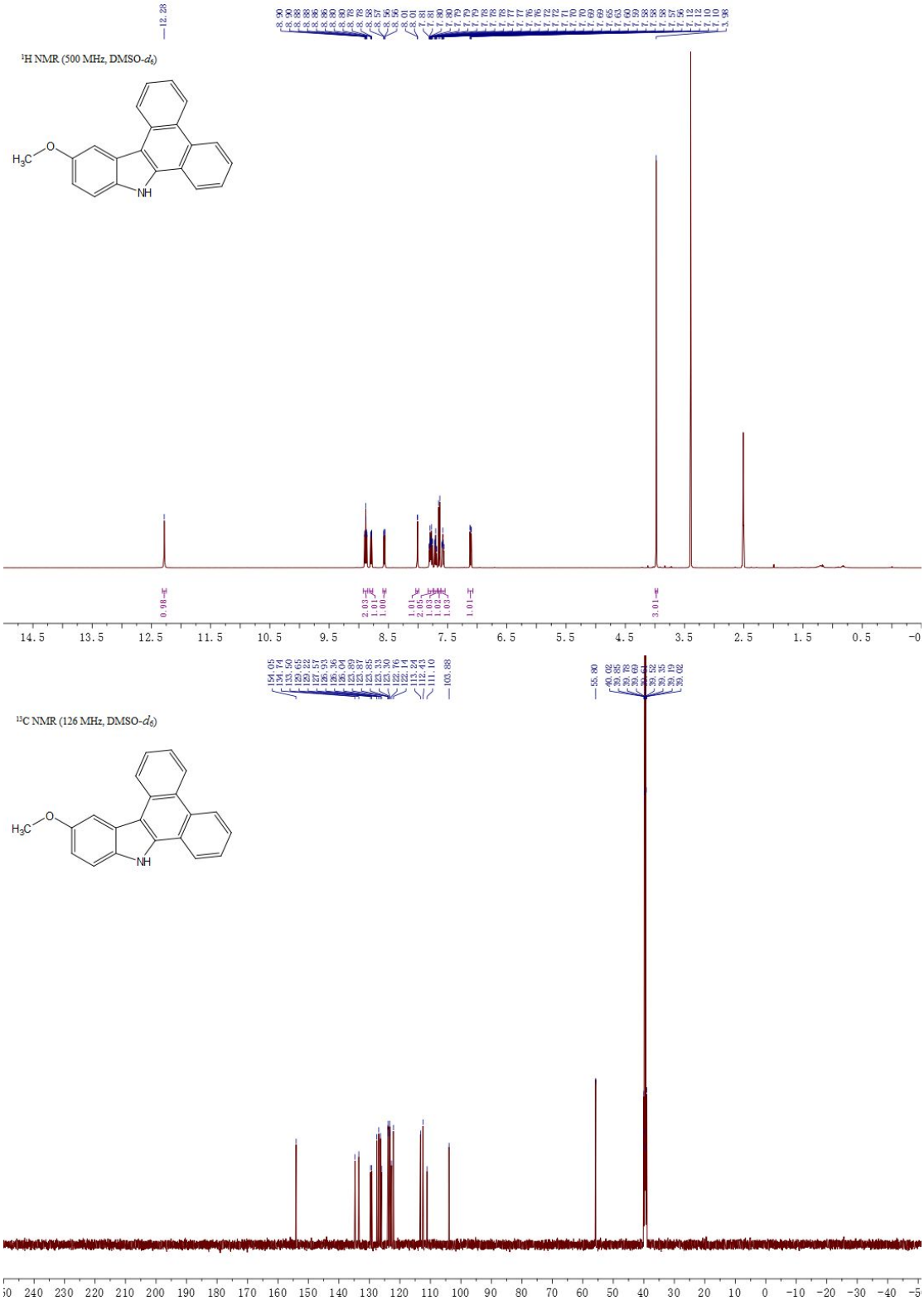


12-methyl-9*H*-dibenzo[*a*,*c*]carbazole (4e):

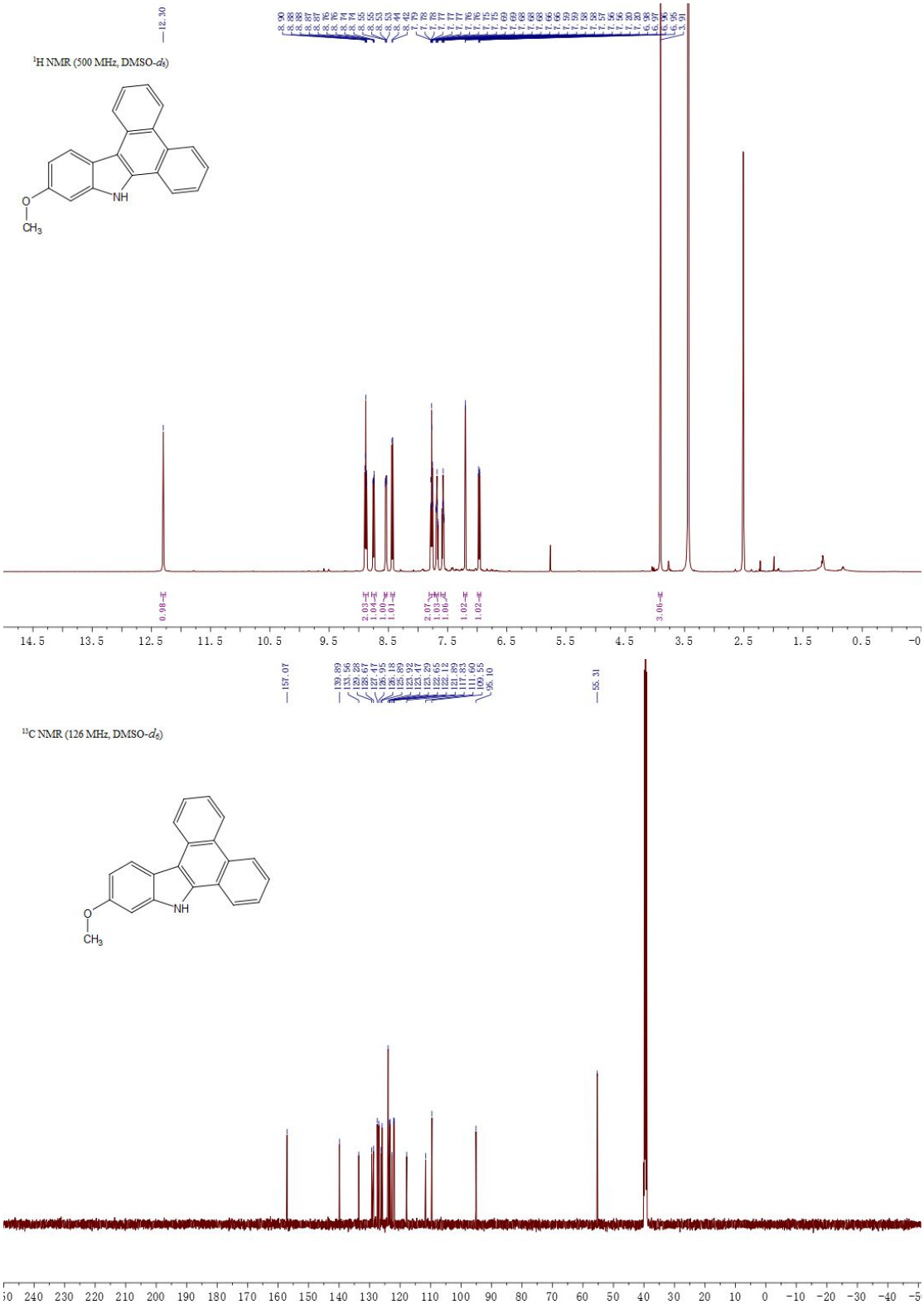




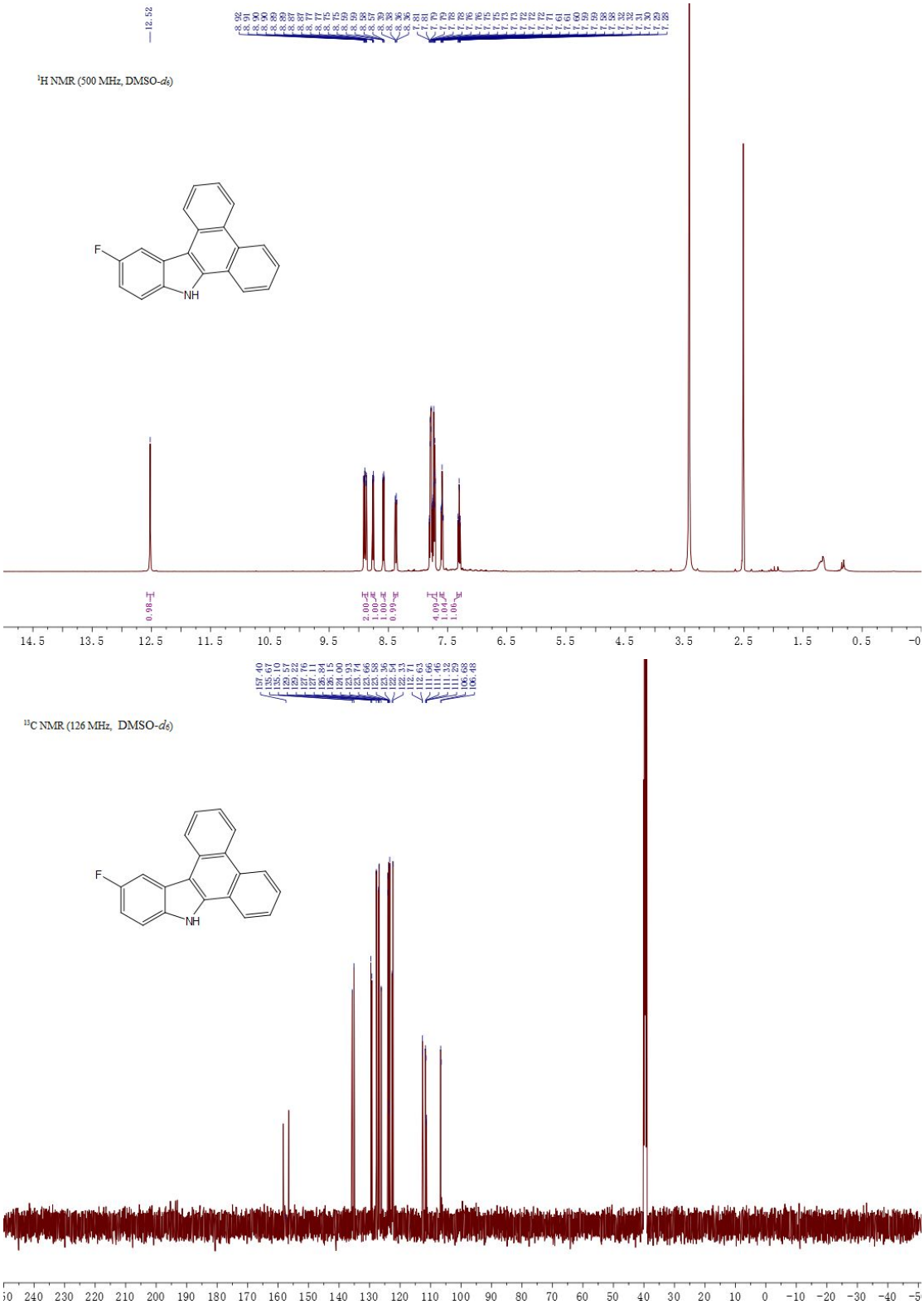
12-methoxy-9*H*-dibenzo[*a*,*c*]carbazole (4f):



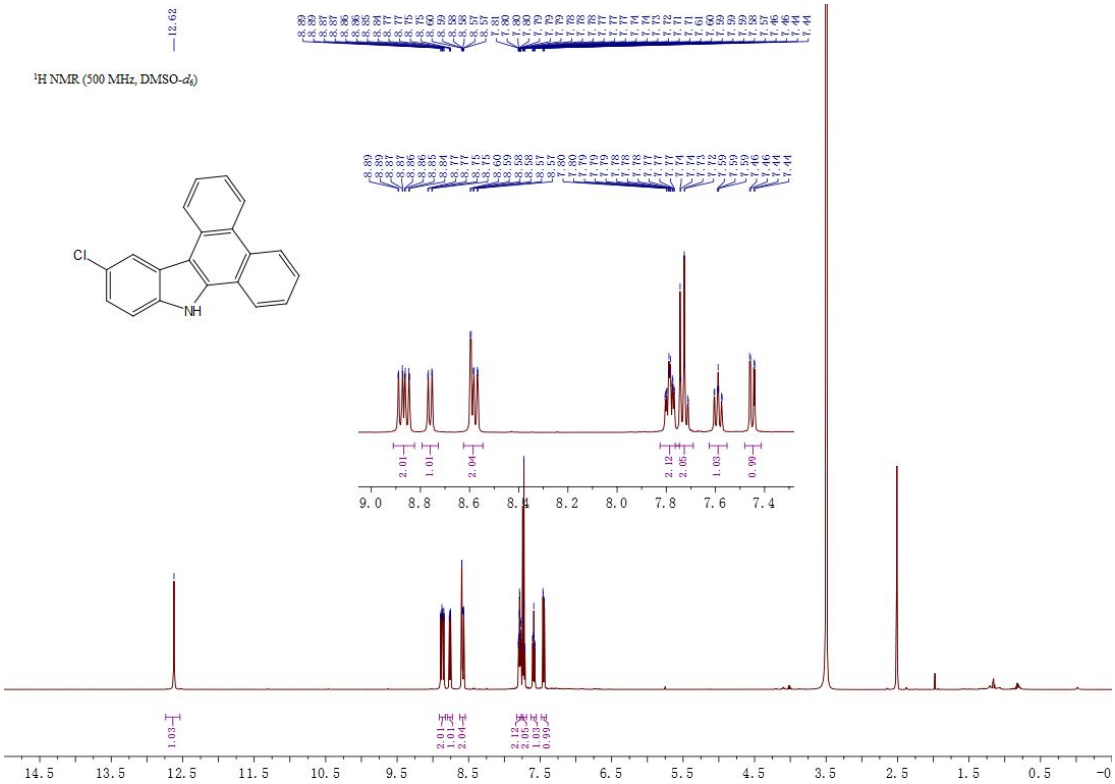
11-methoxy-9*H*-dibenzo[*a*,*c*]carbazole (4g):

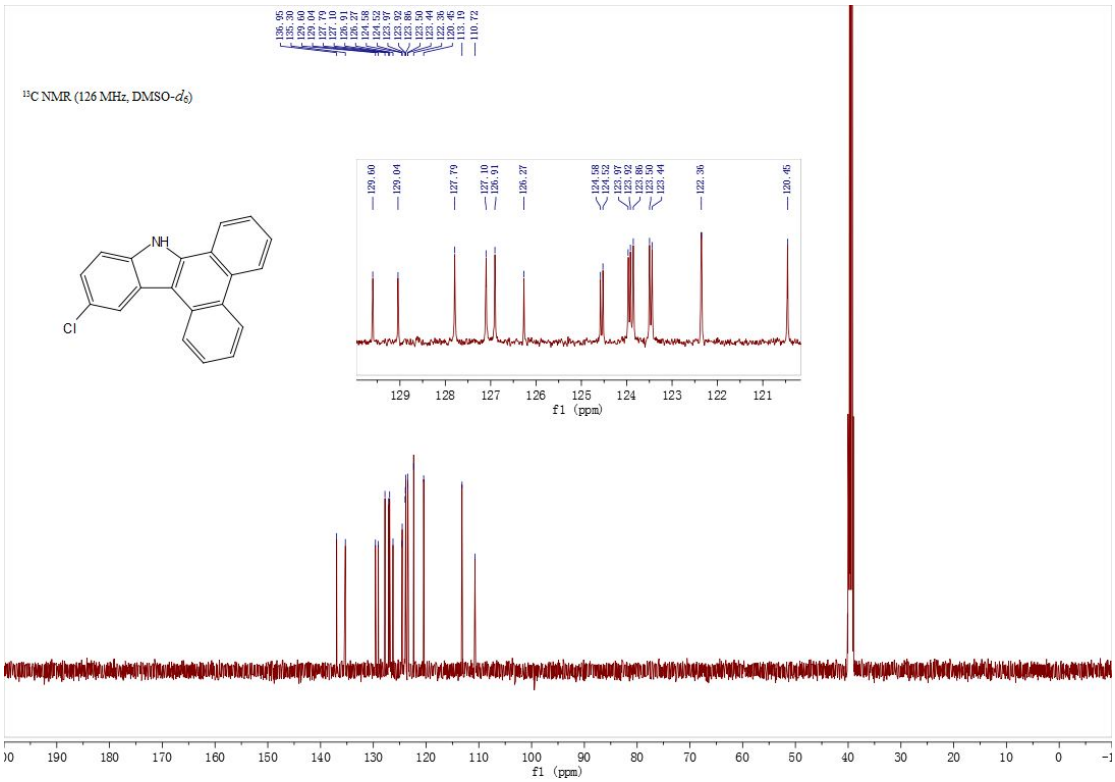


12-fluoro-9*H*-dibenzo[*a*,*c*]carbazole (4h):

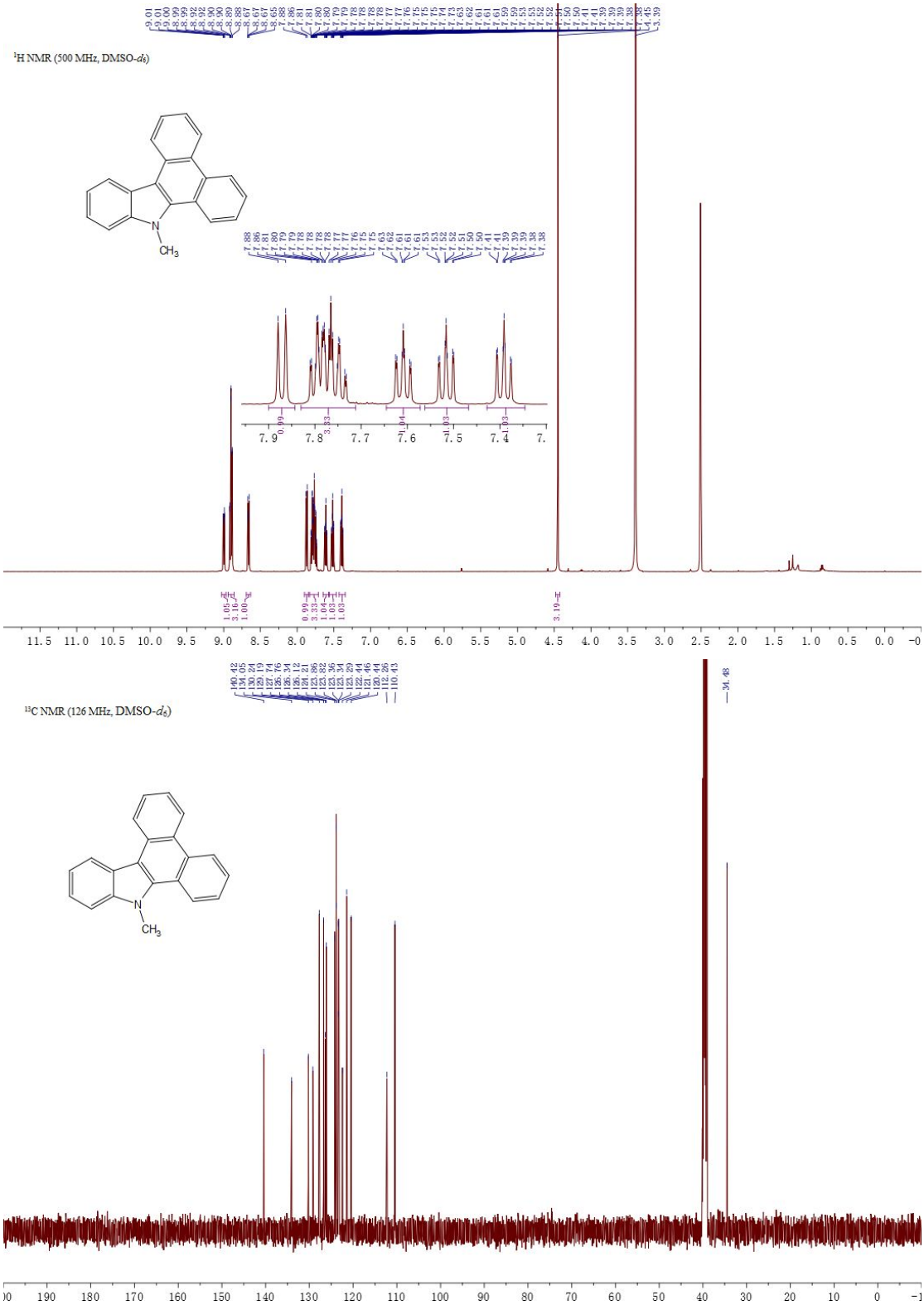


12-chloro-9*H*-dibenzo[*a*,*c*]carbazole (4i):

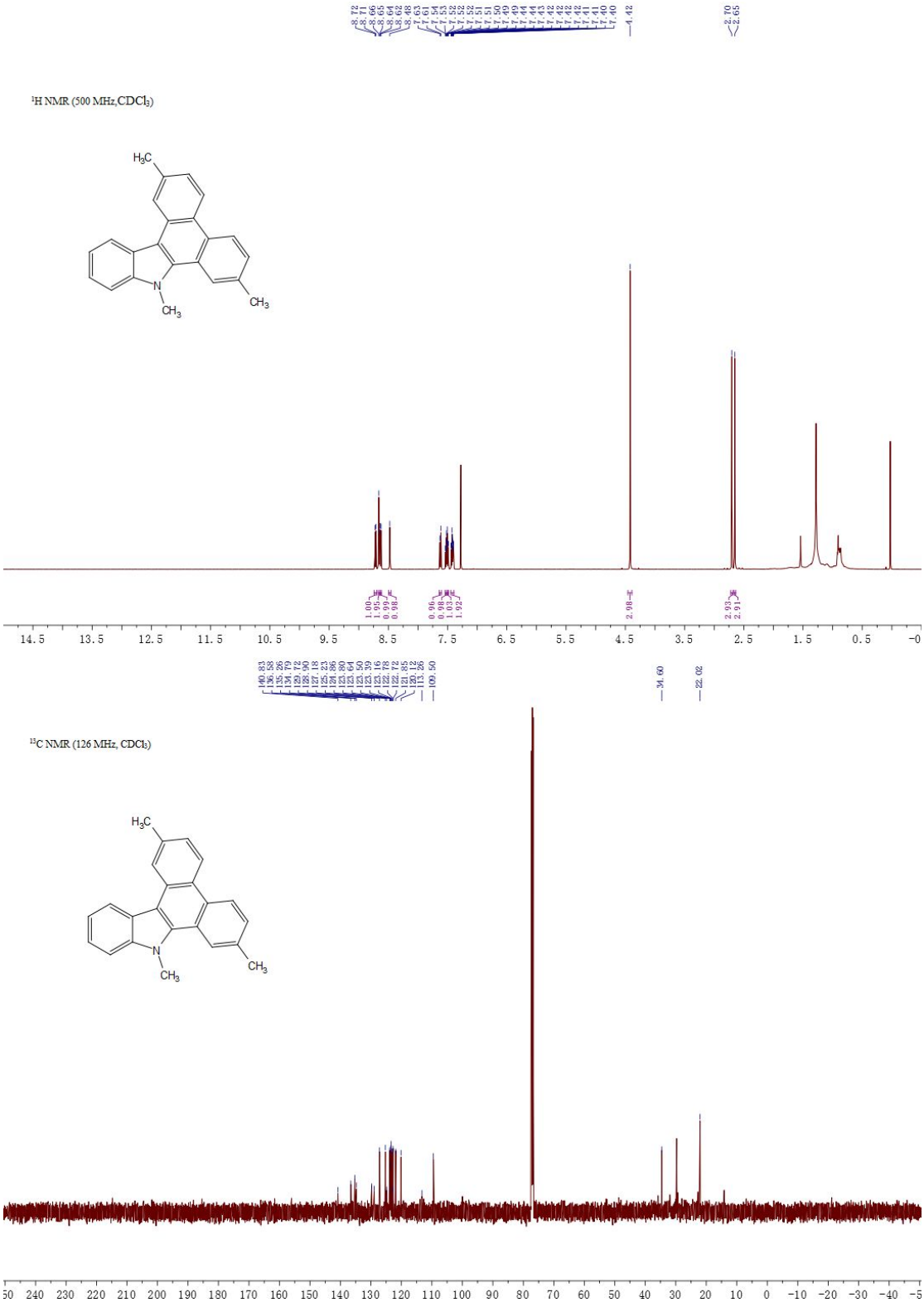




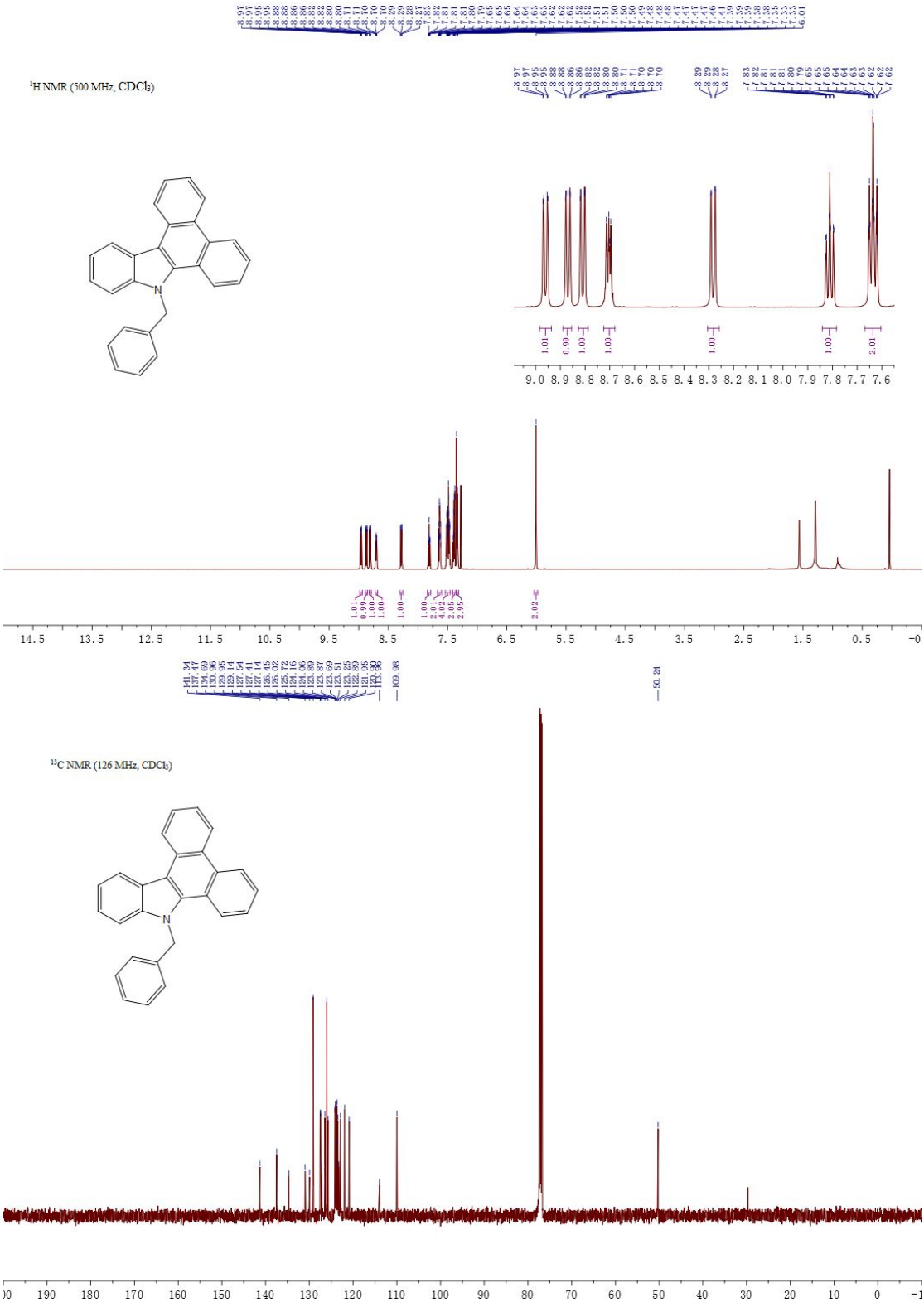
9-methyl-9*H*-dibenzo[*a*,*c*]carbazole (4j):



2,7,9-trimethyl-9*H*-dibenzo[*a*,*c*]carbazole (4k):



9-benzyl-9*H*-dibenzo[*a*,*c*]carbazole (4l):



1-methyl-3-(naphthalen-1-yl)-1*H*-indole (10)