Electronic Supplementary Information

Straightforward Access to Novel Indolo[2,3-*b*]indoles via Aerobic Copper-Catalyzed [3 + 2] Annulation of Diarylamines and Indoles

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1. General information.

All the obtained products were characterized by melting points (m.p.), ^{1}H-NMR, ^{13}C-NMR and infrared spectra (IR). Melting points were measured on an Electrothemal SGW-X4 microscopy digital melting point apparatus and are uncorrected; IR spectra were recorded on a FTLA2000 spectrometer; EPR spectra were recorded on a Bruker Elexsys-II E500 CW-EPR spectrometer; ^{1}H-NMR and ^{13}C-NMR spectra were obtained on Bruker-400/500 and referenced to 7.26 ppm for chloroform solvent with TMS as internal standard (0 ppm). Chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane. Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), multiplet (m); TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF254), and visualization was effected at 254 nm; Unless otherwise stated, all the reagents were purchased from commercial sources, used without further purification.

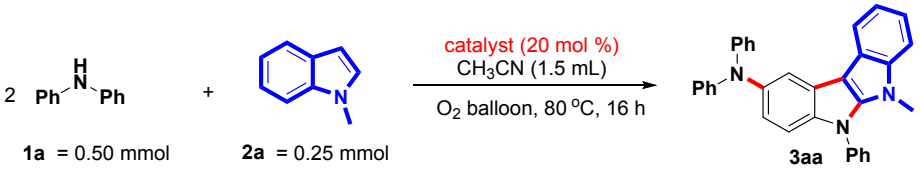
2. Substrates preparation.

General Procedure for preparation of N-substituted indole derivatives (2b-2l)[1]

Procedure for 1,4-dimethyl-1*H*-indole (**2j**): To a suspended solution of NaH (0.55 g, 65% dispersion in mineral oil, 15.0 mmol) in DMF (5 mL), 4-methyl-1*H*-indole (1.31 g, 10.0 mmol) in DMF (5 mL) was added dropwise at 0 °C. The heterogeneous mixture was stirred at 0 °C for 15 min and 1 h at room temperature. The mixture was then cooled to 0 °C, treated with iodomethane (0.83 mL, 13.0 mmol), and allowed to warm to room temperature. After 30 min, the reaction mixture was cooled to 0 °C, quenched with saturated NH_4Cl (20 mL), and extracted with ether (3 × 20 mL). The organic layers were combined, washed with brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The resulting oil was purified by column chromatography on silica gel (petroleum ether) afforded **2j** as a yellow oil. Similarly, the other N-substituted indole derivatives were prepared from their corresponding indoles and halides.

3. Optimization of reaction conditions.

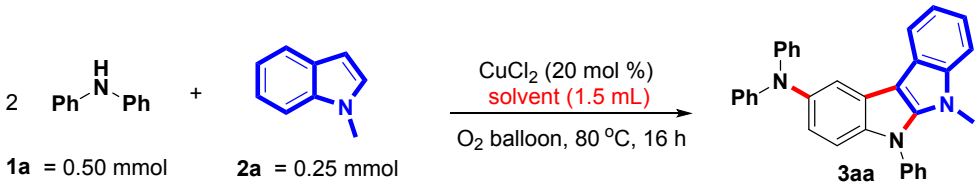
Table S1. Screening of catalyst. [a]



Entry	Catalyst	Yield% of **3aa** [b]
1.	CuCl	trace
2.	**$CuCl_2$**	**18**
3.	$Cu(OTf)_2$	0
4.	CuBr	trace
5.	$CuBr_2$	0
6.	CuI	0
7.	$Cu(OAc)_2$	trace
8.	$Cu(acac)_2$	0
9.	CuF_2	trace
10.	$CuNO_3.3H_2O$	trace
11.	$Cu_4(OH)_6Cl_2$	0
12.	$Cu(BF_4)_2$	0
13.	CuS	0
14.	$CoCl_2$	0

[a] Reaction conditions: unless otherwise stated, all the reactions charged with an O_2 balloon were performed with **1a** (0.50 mmol), **2a** (0.25 mmol), catalyst (20 mol %), CH_3CN (1.5 mL) at 80 °C for 16 h; [b] isolated yield.

Table S2. Screening of solvents. [a]

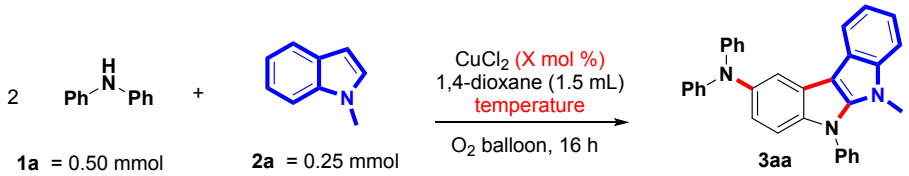


Entry	Solvent	Yield% of **3aa** [b]
1.	CH_3CN	18
2.	*i*-butanol	10
3.	**1,4-dioxane**	**32**
4.	1,3-dioxane	trace
5.	toluene	16
6.	*p*-xylene	24
7.	DMSO	0

8.	DMF	trace
9.	CH_3NO_2	trace
10.	acetone	trace
11.	CH_2Cl_2	trace
12.	NMP	nd
13.	chlorobenzene	23
14.	THF	trace
15.	hexafluoroisopropanol	trace
16.	diethylene glycol dimethyl ether	10
17.	DCE	trace
18.	*n*-butyl acetate	<5

[a] Reaction conditions: unless otherwise stated, all the reactions charged with an O_2 balloon were performed with **1a** (0.50 mmol), **2a** (0.25 mmol), $CuCl_2$ (20 mol %), solvent (1.5 mL) at 80 °C for 16 h; [b] isolated yield.

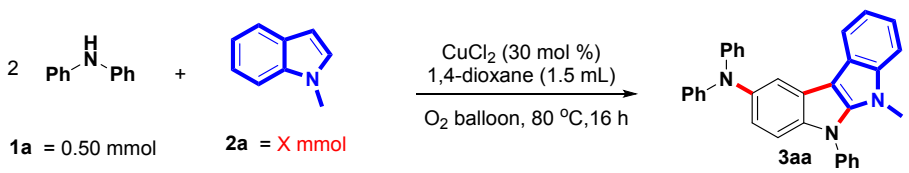
Table S3. Screening of temperature and catalyst loading. [a]



Entry	Temperature	Yield% of **3aa** [b]
1.	100 °C	13
2.	90 °C	17
3.	85 °C	32
4.	**80 °C**	**(32, 40, 28)** [c]
5.	75 °C	31
6.	70 °C	17
7.	60 °C	21
8.	RT.	0

[a] Reaction conditions: unless otherwise stated, all the reactions charged with an O_2 balloon were performed with **1a** (0.50 mmol), **2a** (0.25 mmol), $CuCl_2$ (20 mol %), 1,4-dioxane (1.5 mL) at indicated temperature for 16 h; [b] isolated yield; [c] yields are with respect to the catalyst (20 mol %), (30 mol %) and (40 mol %), respectively.

Table S4. The effect of usage amount of **2a**. [a]

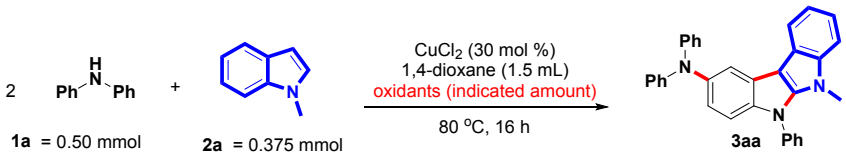


Entry	Usage amount of **2a**	Yield% of **3aa** [b]

1.	0.25 mmol	40
2.	**0.375 mmol**	**47**
3.	0.50 mmol	49

[a] Reaction conditions: unless otherwise stated, all the reactions charged with an O_2 balloon were performed with **1a** (0.50 mmol), **2a** (indicated amount), $CuCl_2$ (30 mol %), 1,4-dioxane (1.5 mL) at 80 °C for 16 h; [b] isolated yield.

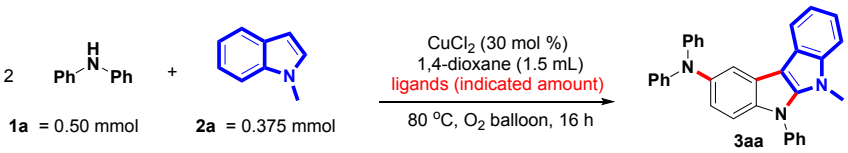
Table S5. Screening of oxidants. [a]



Entry	Oxidants	Yield% of **3aa** [b]
1.	O_2 (balloon)	47
2.	DTBP (2.0 eq.)	31
3.	DTBP (5.0 eq.)	51
4.	TBHP (2.0 eq.)	trace
5.	DCP (2.0 eq.)	21
6.	H_2O_2 (2.0 eq)	0
7.	$PhI(OAc)_2$ (2.0 eq)	0
8.	pyridine-N-oxide (2.0 eq)	0
9.	S_8 (2.0 eq)	32

[a] Reaction conditions: unless otherwise stated, all the reactions were performed with **1a** (0.50 mmol), **2a** (0.375 mmol), $CuCl_2$ (30 mol %), oxidants (indicated amount), 1,4-dioxane (1.5 mL) under N_2 protected at 80 °C for 16 h; [b] isolated yield.

Table S6. Screening of ligands. [a]

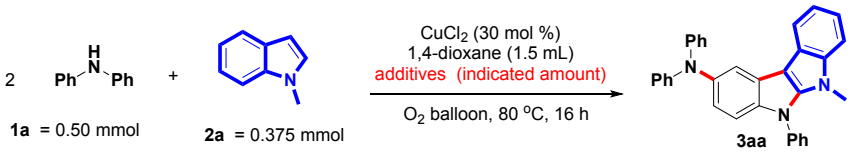


Entry	Ligands	Yield% of **3aa** [b]
1.	-	47
2.	pyridine (1.0 eq.)	trace
3.	pyridine (0.2 eq.)	45
4.	4-methoxypyridine (0.2 eq.)	26
5.	4-dimethylaminopyridine (0.2 eq.)	51
6.	4-cyanopyridine (0.2 eq.)	41
7.	2,2'-bipyridine (0.2 eq.)	<5
8.	1,10-phenanthroline (1.0 eq.)	<5
9.	Ph_3P (0.2 eq.)	50

10.	Ph_2PH (0.2 eq.)	48

[a] Reaction conditions: unless otherwise stated, all the reactions charged with an O_2 balloon were performed with **1a** (0.50 mmol), **2a** (0.375 mmol), $CuCl_2$ (30 mol %), ligands (indicated amount), 1,4-dioxane (1.5 mL) at 80 °C for 16 h; [b] isolated yield.

Table S7. Screening of additives. [a]



Entry	Additive	Yield% of **3aa** [b]
1.	-	47
2.	NaOH (1.0 eq.)	0
3.	Na_2CO_3 (1.0 eq.)	trace
4.	KCO_3 (1.0 eq.)	40
5.	$CsCO_3$ (1.0 eq.)	trace
6.	NaH (1.0 eq.)	trace
7.	*t*-BuONa (1.0 eq.)	0
8.	*t*-BuOK (1.0 eq.)	0
9.	HCl (2.0 eq.)	0
10.	CH_3COOH (0.2 eq.)	trace
11.	*p*-nitrobenzoic acid (1.0 eq.)	9
12.	*p*-toluenesulfonic acid (1.0 eq.)	trace
13.	phenylboronic acid (1.0 eq.)	trace
14.	tetrafluoroboric acid (1.0 eq.)	0
15.	3 Å molecular sieve (20 mg)	60
16.	**3 Å molecular sieve (10 mg)**	**66**
17.	3 Å molecular sieve (5 mg)	45
18.	3 Å molecular sieve (50 mg)	<5
19.	4 Å molecular sieve (20 mg)	51
20.	5 Å molecular sieve (20 mg)	56
21.	NaOTf (1.0 eq.)	52
22.	NaOTf (0.2 eq.)	51
23.	NaOTf (2.0 eq.)	29
24.	$Zn(OTf)_2$ (1.0 eq.)	0
25.	$Er(OTf)_3$ (1.0 eq.)	trace
26.	$Sm(OTf)_3$ (1.0 eq.)	trace
27.	$AlCl_3$ (1.0 eq.)	trace
28.	$FeCl_3$ (1.0 eq.)	trace
29.	$BF_3.OEt_2$ (1.0 eq.)	0
30.	KI (0.2 eq.)	11
31.	NaI (0.2 eq.)	51
32.	LiI (0.2 eq.)	34

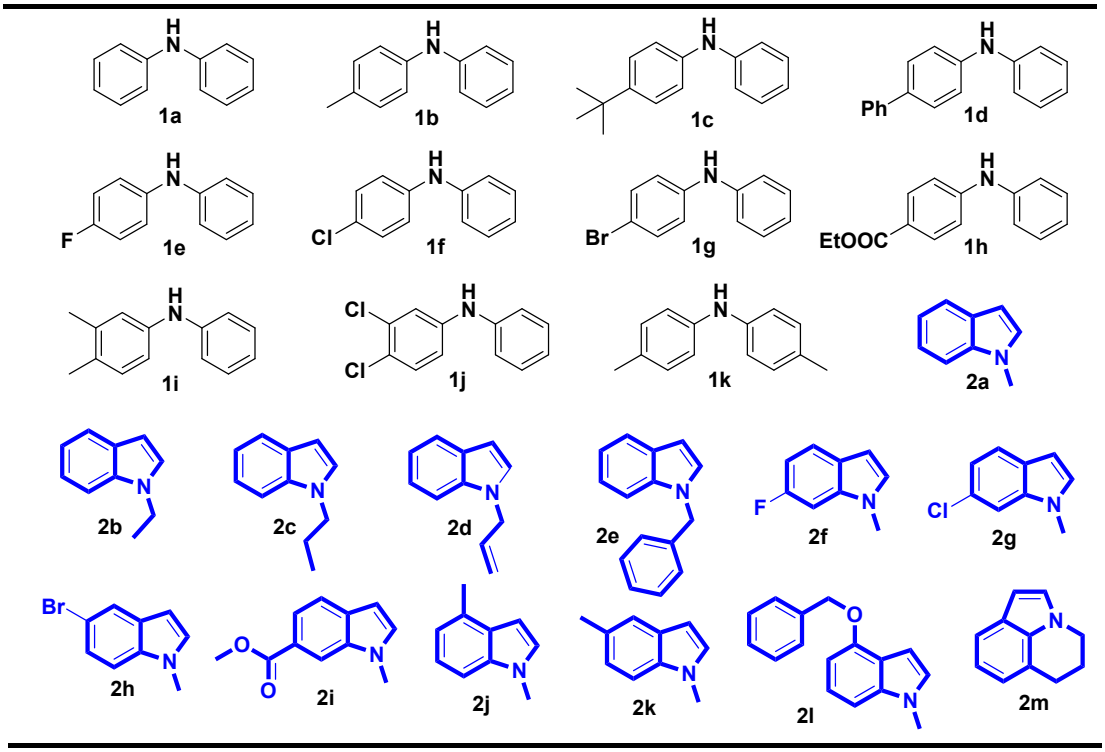
33.	ZnI_2 (0.2 eq.)	trace
34.	$NaIO_4$ (0.2 eq.)	62
35.	NH_4F (0.2 eq.)	48
36.	NH_4Cl (0.2 eq.)	48
37.	NH_4Br (0.2 eq.)	45
38.	NH_4I (0.2 eq.)	53
39.	NH_4I (0.05 eq.)	50
40.	NH_4I (0.3 eq.)	59
41.	NH_4I (0.4 eq.)	39
42.	NH_4I (0.5 eq.)	17
43.	NH_4I (1.0 eq.)	nd
44.	*n*-Bu_4NI (0.2 eq.)	51
45.	*n*-Bu_4NHSO_4 (0.2 eq.)	trace

[a] Reaction conditions: unless otherwise stated, all the reactions charged with an O_2 balloon were performed with **1a** (0.50 mmol), **2a** (0.375 mmol), $CuCl_2$ (30 mol %), additives (indicated amount), 1,4-dioxane (1.5 mL) at 80 °C for 16 h; [b] isolated yield.

4. Typical procedure for the synthesis of 3aa.

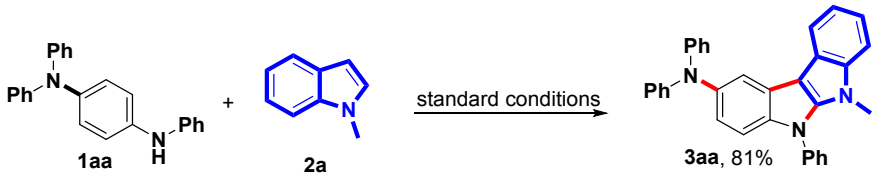
The mixture of diphenylamine **1a** (84.6 mg, 0.5 mmol), 1-methylindole **2a** (49.2 mg, 0.375 mmol), $CuCl_2$ (10.1 mg, 0.075 mmol) and 3 Å molecular sieve (10.0 mg) in 1,4-dioxane (1.5 mL) was stirred at 80 °C for 16 h under O_2 atmosphere (using an O_2 balloon). After being cooled to room temperature, the resulting mixture was concentrated by removing the solvent under vacuum, and the residue was purified by preparative TLC on silica gel by using petroleum ether/ethyl acetate (20 :1) as the eluent to give **3aa** as a brownish solid (76 mg, 66% yield).

Scheme S2. Substrates employed for synthesizing indolo[2,3-*b*]indoles **3**.

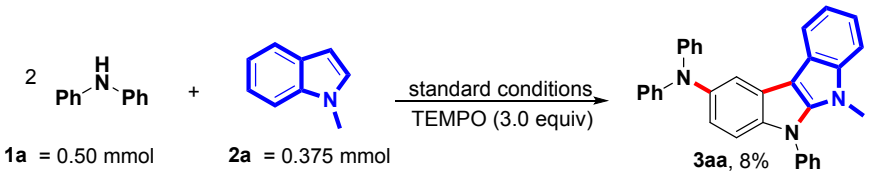


5. Control experiments.

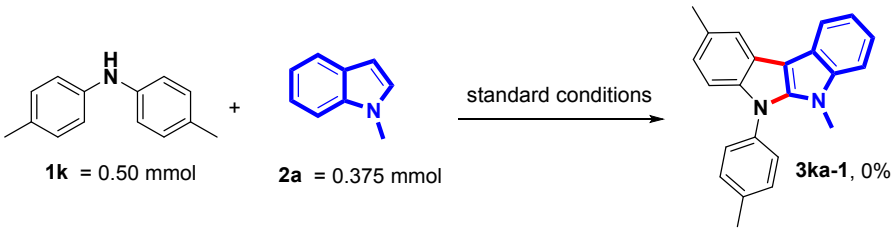
(1) The preparation of **1aa** was similar to the literature procedures.[2] Under the optimized reaction conditions, the reaction of **1aa** (84.0 mg, 0.25 mmol) and N-methylindole **2a** (49.2 mg, 0.375 mmol) was performed. Then, the reaction mixture was purified by preparative TLC on silica eluting with petroleum ether/ethyl acetate (20:1) to give product **3aa** as brownish solid (94 mg, 81% yield).



(2) Under the optimized reaction conditions, the model reaction was carried out by introducing 3.0 equivalent of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy). Then, the reaction mixture was purified by preparative TLC on silica eluting with petroleum ether/ethyl acetate (20:1) to give product **3aa** as brownish solid (9 mg, 8% yield).



(3) Under the optimized reaction conditions, the reaction of diarylamine **1k** and N-methylindole **2a** was carried out, and the crude reaction mixture was analyzed by TLC and GC-MS, which indicated that no **3ka-1** was formed during the reaction.



6. The electron paramagnetic resonance (EPR) experiments.

Under the standard conditions, the mixture of $CuCl_2$ and 3 Å molecular sieves in 1,4-dioxane was treated for 30 min. Then, the reaction solution was taken out by capillary and analyzed by EPR at room temperature. The samples were taken out by an EPR capillary, and then recorded by EPR spectrometer at 298 K. The EPR parameters were set as the following: sweep width 6000 G, center field 3479 G, time constant 39.06 ms, sweep time 40.00 s, microwave power 0.2 mW, modulation amplitude 1.00 G, modulation frequency 100 kHz. As shown in Figure s1, the treatment of $CuCl_2$ and 3 Å molecular sieve under the standard conditions for 30 min exhibited an EPR signal of the copper complex (g = 2.09899) (Figure 1, black line), arising from the coupling of the unpaired electron of Cu^{II} with its nuclear spin (d^9, S = 1/2, I = 3/2).[3] The addition of diphenylamine **1a** to $CuCl_2$ caused a weak radical signal (g = 1.99645), this change is attributed to the single electron transfer from **1a** to Cu^{II} and the formation of Cu^{I} species, which results in an EPR active radical intermediate (red line). Then, the addition of N-methylindole **2a** to $CuCl_2$ did not show a significant change in the signal, suggesting that the reaction initiating with an indolyl radical can be ruled out. As expected, the introduction of both reactants **1a** and **2a** to $CuCl_2$ caused a quick quench of the signal of active radical intermediate (green line), showing that the radical arising from **1a** takes part in the reaction.

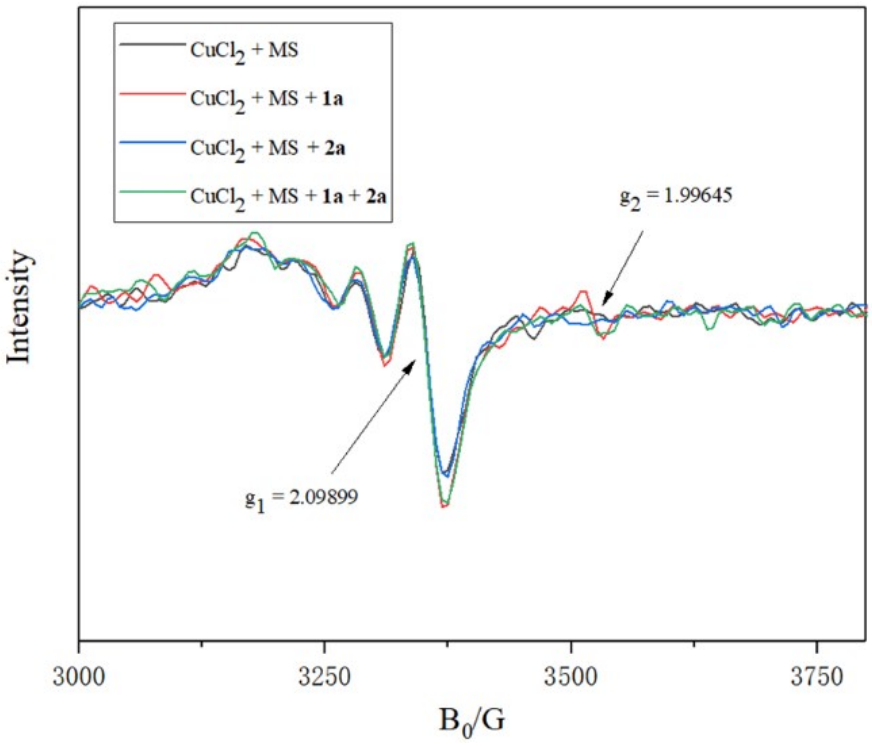


Figure S1. Electron paramagnetic resonance (EPR) spectra.

7. Single crystal X-ray diffraction of 3aa.

Yellow block-like single crystals of **3aa** were grown by layering a dichlormethane solution with *n*-hexane at ambient temperature. X-Ray diffraction data of one these crystals were collected on a R-AXIS SPIDER diffractometer. The measurements were performed with Mo-Kα radiation (λ = 0.71073 Å). Data were collected at 293(2) K, using the *ω*- and *φ*- scans to a maximum θ value of 25.242°. The data were refined by full-matrix least-squares techniques on F^2 with SHELXTL-2014. And the structures were solved by direct methods SHELXS-2014. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included at geometrically idealized positions. And an ORTEP representation of the structure is shown below.

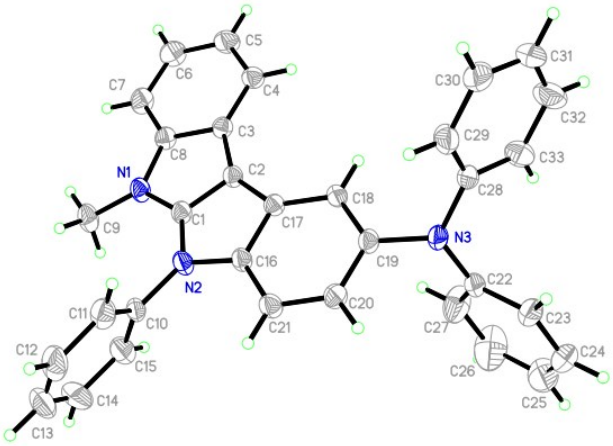


Figure S2. ORTEP drawing of **3aa** with the numbering scheme.

Table S8. Crystal data and structure refinement for **3aa**.

Identification code	**3aa**	
Empirical formula	$C_{33}H_{25}N_3$	
Formula weight	463.56	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 10.7120(10) Å	□= 90°.
	b = 26.2639(17) Å	□= 114.352(11)°.
	c = 9.6385(9) Å	□ = 90°.
Volume	2470.4(4) $Å^3$	
Z	4	
Density (calculated)	1.246 Mg/m^3	
Absorption coefficient	0.073 mm^{-1}	
F(000)	976	
Crystal size	0.21 x 0.20 x 0.19 mm^3	
Theta range for data collection	3.740 to 29.441°.	
Index ranges	-13<=h<=13, -34<=k<=35, -11<=l<=12	
Reflections collected	17981	
Independent reflections	5748 [R(int) = 0.0266]	
Completeness to theta = 25.242°	99.7 %	

Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5748 / 0 / 325
Goodness-of-fit on F^2	1.013
Final R indices [I>2sigma(I)]	R1 = 0.0596, wR2 = 0.1387
R indices (all data)	R1 = 0.0923, wR2 = 0.1594
Extinction coefficient	n/a
Largest diff. peak and hole	0.273 and -0.214 e.Å^{-3}

Table S9. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **3aa**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	4078(2)	2507(1)	7554(2)	43(1)
N(2)	2177(1)	2217(1)	5071(2)	43(1)
N(3)	2049(2)	249(1)	2858(2)	44(1)
C(1)	3336(2)	2176(1)	6407(2)	39(1)
C(2)	3830(2)	1685(1)	6689(2)	37(1)
C(3)	4994(2)	1697(1)	8145(2)	38(1)
C(4)	5919(2)	1340(1)	9099(2)	44(1)
C(5)	6902(2)	1497(1)	10496(2)	56(1)
C(6)	6994(2)	2002(1)	10959(2)	61(1)
C(7)	6112(2)	2366(1)	10042(2)	55(1)
C(8)	5113(2)	2213(1)	8643(2)	41(1)
C(9)	4012(2)	3058(1)	7575(3)	56(1)
C(10)	1306(2)	2648(1)	4443(2)	42(1)
C(11)	10(2)	2648(1)	4407(3)	59(1)
C(12)	-839(3)	3068(1)	3766(3)	82(1)
C(13)	-373(4)	3471(1)	3222(3)	95(1)
C(14)	907(4)	3465(1)	3261(3)	89(1)
C(15)	1757(3)	3051(1)	3868(3)	64(1)
C(16)	1923(2)	1726(1)	4440(2)	38(1)
C(17)	2937(2)	1383(1)	5417(2)	36(1)
C(18)	2937(2)	884(1)	4917(2)	38(1)
C(19)	1979(2)	739(1)	3483(2)	40(1)
C(20)	986(2)	1083(1)	2564(2)	45(1)
C(21)	946(2)	1578(1)	3026(2)	44(1)

C(22)	2411(2)	243(1)	1593(2)	43(1)
C(23)	1774(2)	-94(1)	409(2)	56(1)
C(24)	2090(3)	-96(1)	-834(3)	78(1)
C(25)	3028(4)	232(1)	-920(4)	104(1)
C(26)	3675(4)	564(1)	254(5)	123(1)
C(27)	3369(3)	572(1)	1510(3)	83(1)
C(28)	2253(2)	-193(1)	3758(2)	42(1)
C(29)	1427(3)	-289(1)	4507(3)	64(1)
C(30)	1600(3)	-729(1)	5364(3)	77(1)
C(31)	2604(3)	-1074(1)	5473(3)	76(1)
C(32)	3418(3)	-980(1)	4730(3)	74(1)
C(33)	3256(2)	-546(1)	3883(3)	57(1)

Table S10. Bond lengths [Å] and angles [°] for **3aa**.

N(1)-C(1)	1.372(2)
N(1)-C(8)	1.403(2)
N(1)-C(9)	1.449(2)
N(2)-C(1)	1.376(2)
N(2)-C(16)	1.405(2)
N(2)-C(10)	1.431(2)
N(3)-C(28)	1.411(2)
N(3)-C(22)	1.423(2)
N(3)-C(19)	1.435(2)
C(1)-C(2)	1.379(2)
C(2)-C(3)	1.443(2)
C(2)-C(17)	1.442(2)
C(3)-C(4)	1.398(2)
C(3)-C(8)	1.426(2)
C(4)-C(5)	1.386(3)
C(5)-C(6)	1.389(3)
C(6)-C(7)	1.378(3)
C(7)-C(8)	1.391(3)
C(10)-C(15)	1.373(3)
C(10)-C(11)	1.373(3)
C(11)-C(12)	1.399(3)
C(12)-C(13)	1.365(4)

C(13)-C(14)	1.355(4)
C(14)-C(15)	1.382(3)
C(16)-C(21)	1.389(2)
C(16)-C(17)	1.427(2)
C(17)-C(18)	1.395(2)
C(18)-C(19)	1.392(2)
C(19)-C(20)	1.399(3)
C(20)-C(21)	1.380(2)
C(22)-C(27)	1.371(3)
C(22)-C(23)	1.381(3)
C(23)-C(24)	1.373(3)
C(24)-C(25)	1.352(4)
C(25)-C(26)	1.369(5)
C(26)-C(27)	1.378(4)
C(28)-C(29)	1.377(3)
C(28)-C(33)	1.387(3)
C(29)-C(30)	1.387(3)
C(30)-C(31)	1.377(4)
C(31)-C(32)	1.360(4)
C(32)-C(33)	1.370(3)

C(1)-N(1)-C(8)	105.72(14)
C(1)-N(1)-C(9)	128.83(16)
C(8)-N(1)-C(9)	124.61(15)
C(1)-N(2)-C(16)	105.80(13)
C(1)-N(2)-C(10)	129.56(14)
C(16)-N(2)-C(10)	124.50(14)
C(28)-N(3)-C(22)	119.23(14)
C(28)-N(3)-C(19)	120.03(14)
C(22)-N(3)-C(19)	116.79(14)
C(2)-C(1)-N(1)	112.68(15)
C(2)-C(1)-N(2)	112.47(15)
N(1)-C(1)-N(2)	134.77(16)
C(1)-C(2)-C(3)	106.18(15)
C(1)-C(2)-C(17)	106.35(15)
C(3)-C(2)-C(17)	147.43(16)
C(4)-C(3)-C(8)	118.33(16)
C(4)-C(3)-C(2)	136.00(16)

C(8)-C(3)-C(2)	105.64(15)
C(5)-C(4)-C(3)	119.25(18)
C(4)-C(5)-C(6)	121.32(19)
C(5)-C(6)-C(7)	121.16(18)
C(8)-C(7)-C(6)	118.12(19)
C(7)-C(8)-N(1)	128.39(17)
C(7)-C(8)-C(3)	121.81(17)
N(1)-C(8)-C(3)	109.77(14)
C(15)-C(10)-C(11)	120.57(19)
C(15)-C(10)-N(2)	120.25(18)
C(11)-C(10)-N(2)	119.17(19)
C(10)-C(11)-C(12)	118.6(2)
C(13)-C(12)-C(11)	120.3(3)
C(14)-C(13)-C(12)	120.5(2)
C(15)-C(14)-C(13)	120.2(3)
C(14)-C(15)-C(10)	119.8(2)
C(21)-C(16)-C(17)	122.13(16)
C(21)-C(16)-N(2)	127.98(16)
C(17)-C(16)-N(2)	109.61(14)
C(18)-C(17)-C(16)	118.21(15)
C(18)-C(17)-C(2)	135.68(16)
C(16)-C(17)-C(2)	105.75(14)
C(19)-C(18)-C(17)	119.69(16)
C(18)-C(19)-C(20)	120.56(16)
C(18)-C(19)-N(3)	121.17(16)
C(20)-C(19)-N(3)	118.09(15)
C(21)-C(20)-C(19)	121.38(16)
C(20)-C(21)-C(16)	118.00(17)
C(27)-C(22)-C(23)	118.9(2)
C(27)-C(22)-N(3)	121.13(18)
C(23)-C(22)-N(3)	119.96(17)
C(24)-C(23)-C(22)	120.5(2)
C(23)-C(24)-C(25)	120.5(3)
C(26)-C(25)-C(24)	119.4(3)
C(25)-C(26)-C(27)	120.9(3)
C(22)-C(27)-C(26)	119.7(3)
C(29)-C(28)-C(33)	118.27(19)
C(29)-C(28)-N(3)	120.24(17)

C(33)-C(28)-N(3)	121.47(18)
C(30)-C(29)-C(28)	120.6(2)
C(29)-C(30)-C(31)	120.1(2)
C(32)-C(31)-C(30)	119.4(2)
C(31)-C(32)-C(33)	120.9(2)
C(32)-C(33)-C(28)	120.8(2)

Symmetry transformations used to generate equivalent atoms:

Table S11. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **3aa**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	42(1)	32(1)	47(1)	-9(1)	10(1)	-1(1)
N(2)	39(1)	32(1)	45(1)	-6(1)	6(1)	5(1)
N(3)	64(1)	31(1)	42(1)	-7(1)	25(1)	-4(1)
C(1)	38(1)	35(1)	40(1)	-5(1)	10(1)	0(1)
C(2)	36(1)	34(1)	38(1)	-4(1)	12(1)	1(1)
C(3)	36(1)	39(1)	36(1)	-4(1)	13(1)	-2(1)
C(4)	44(1)	44(1)	42(1)	1(1)	14(1)	1(1)
C(5)	49(1)	62(1)	45(1)	4(1)	6(1)	5(1)
C(6)	52(1)	66(2)	46(1)	-10(1)	2(1)	-5(1)
C(7)	51(1)	51(1)	50(1)	-15(1)	9(1)	-7(1)
C(8)	37(1)	42(1)	42(1)	-5(1)	12(1)	-2(1)
C(9)	56(1)	36(1)	69(1)	-14(1)	18(1)	0(1)
C(10)	42(1)	37(1)	40(1)	-7(1)	10(1)	9(1)
C(11)	45(1)	66(1)	59(1)	-14(1)	15(1)	5(1)
C(12)	52(1)	99(2)	75(2)	-24(2)	7(1)	31(1)
C(13)	105(2)	73(2)	72(2)	-7(2)	1(2)	50(2)
C(14)	121(3)	56(2)	80(2)	22(1)	31(2)	23(2)
C(15)	74(2)	50(1)	71(2)	8(1)	32(1)	11(1)
C(16)	37(1)	32(1)	41(1)	-5(1)	11(1)	1(1)
C(17)	35(1)	34(1)	36(1)	-2(1)	12(1)	-1(1)
C(18)	41(1)	32(1)	39(1)	0(1)	15(1)	2(1)
C(19)	46(1)	31(1)	42(1)	-6(1)	18(1)	-4(1)
C(20)	44(1)	41(1)	40(1)	-8(1)	7(1)	-4(1)
C(21)	40(1)	39(1)	44(1)	-2(1)	7(1)	3(1)

C(22)	53(1)	32(1)	44(1)	-2(1)	22(1)	0(1)
C(23)	65(1)	53(1)	48(1)	-10(1)	21(1)	-5(1)
C(24)	114(2)	73(2)	50(1)	-6(1)	37(1)	14(2)
C(25)	179(3)	83(2)	97(2)	12(2)	104(3)	17(2)
C(26)	183(4)	92(2)	162(3)	-21(2)	141(3)	-45(2)
C(27)	112(2)	67(2)	97(2)	-26(2)	70(2)	-37(2)
C(28)	49(1)	33(1)	36(1)	-6(1)	11(1)	-6(1)
C(29)	95(2)	45(1)	72(2)	2(1)	56(1)	7(1)
C(30)	126(2)	59(2)	67(2)	0(1)	62(2)	-7(2)
C(31)	118(2)	51(1)	53(1)	14(1)	28(2)	9(1)
C(32)	75(2)	70(2)	69(2)	25(1)	22(1)	24(1)
C(33)	48(1)	59(1)	58(1)	10(1)	15(1)	8(1)

Table S12. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{3}) for **3aa**.

	x	y	z	U(eq)
H(4A)	5876	1001	8800	53
H(5A)	7513	1259	11136	67
H(6A)	7662	2095	11904	73
H(7A)	6183	2704	10350	66
H(9A)	4659	3182	8540	85
H(9B)	4229	3195	6776	85
H(9C)	3105	3162	7421	85
H(11A)	-295	2376	4800	70
H(12A)	-1727	3071	3711	98
H(13A)	-937	3751	2821	114
H(14A)	1214	3740	2879	107
H(15A)	2632	3047	3886	77
H(18A)	3574	650	5537	46
H(20A)	339	976	1622	54
H(21A)	283	1805	2410	53
H(23A)	1127	-322	455	67
H(24A)	1654	-325	-1624	93
H(25A)	3232	232	-1769	125
H(26A)	4330	787	204	147
H(27A)	3811	801	2298	100

H(29A)	747	-58	4437	76
H(30A)	1037	-791	5867	92
H(31A)	2724	-1368	6050	92
H(32A)	4093	-1213	4797	89
H(33A)	3825	-488	3387	69

Table S13. Hydrogen bonds for **3aa** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

8. Reference

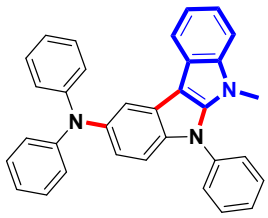
1. X. Hong, Q. Tan, B. Liu and B. Xu, *Angew. Chem., Int. Ed.* 2017, **56**, 1–6.

2. T. Liang, Z. Tan, H. Zhao, X. Chen, H. Jiang and M. Zhang, *ACS Catal*. 2018, **8**, 2242–2246.

3. T. Liang, H. Zhao, L. Gong, H. Jiang and M. Zhang, *Org. Lett.* 2019, **21**, 6736-6740.

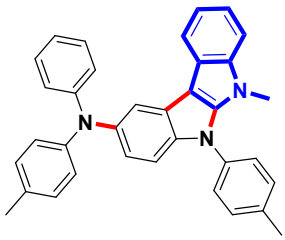
9. Analytic data of the obtained compounds.

(1) 6-methyl-*N*,*N*,5-triphenyl-5,6-dihydroindolo[2,3-*b*]indol-2-amine (3aa)



Brownish solid, (76 mg, 66% yield), m.p.: 224-226 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.68 (d, *J* = 6.8 Hz, 1H), 7.62 (s, 1H), 7.48 – 7.35 (m, 5H), 7.15 (d, *J* = 7.2 Hz, 1H), 7.12 – 6.97 (m, 11H), 6.81 (t, *J* = 7.2 Hz, 3H), 3.32 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 148.84, 145.59, 141.45, 140.24, 138.55, 137.10, 129.89, 129.08, 128.63, 128.10, 123.27, 122.73, 121.64, 121.47, 120.36, 120.12, 119.77, 118.66, 116.97, 111.11, 109.22, 101.27, 30.76. IR (KBr): 3055, 3033, 2929, 1620, 1587, 1454, 787, 752, 694 cm^{-1}. HRMS (ESI): Calcd. for $C_{33}H_{26}N_3$ $[M+H]^+$: 464.2121; found: 464.2122.

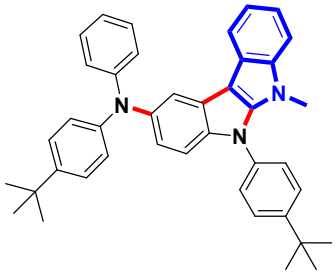
(2) 6-methyl-*N*-phenyl-*N*,5-di-*p*-tolyl-5,6-dihydroindolo[2,3-*b*]indol-2-amine (3ba)



Brownish solid, (56 mg, 46% yield), m.p.: 106-108 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.78 (d, *J* = 6.6 Hz, 1H), 7.69 (s, 1H), 7.41 (d, *J* = 7.2 Hz, 2H), 7.35 (d, *J* = 7.6 Hz, 2H), 7.26 (d, *J* = 7.0 Hz, 1H), 7.17 (t, *J* = 7.0 Hz, 4H), 6.92 – 6.84 (m, 7H), 6.92 – 6.84 (m, 2H), 3.44 (s, 3H), 2.46 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 149.23, 146.30, 145.70, 141.53, 140.23, 138.69, 138.57, 134.41, 131.43, 130.48, 129.78, 128.98, 127.98, 123.65, 123.12, 121.82, 121.71, 120.74, 120.28, 119.98, 119.51, 118.62, 116.70, 111.05, 109.15, 101.05, 30.68, 21.40, 20.89. IR (KBr): 3055, 3025, 2920, 2859, 1621, 1594, 1522, 1508, 1492, 1456, 1313, 1293, 1276, 808, 736, 695 cm^{-1}. HRMS (ESI): Calcd. for $C_{35}H_{30}N_3$ $[M+H]^+$: 492.2434;

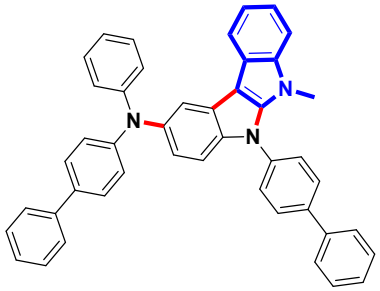
found: 492.2435.

(3) *N*,5-bis(4-(*tert*-butyl)phenyl)-6-methyl-*N*-phenyl-5,6-dihydroindolo[2,3-*b*]indol-2-amine (3ca)



Brownish solid, (66 mg, 46% yield), m.p.: 221-223 °C; ^{1}H NMR (500 MHz, Chloroform-d) δ 7.84 – 7.81 (m, 1H), 7.74 (d, *J* = 2.0 Hz, 1H), 7.63 – 7.58 (m, 2H), 7.52 – 7.48 (m, 2H), 7.32 (dd, *J* = 6.8, 1.9 Hz, 1H), 7.25 – 7.19 (m, 5H), 7.14 (t, *J* = 8.2 Hz, 3H), 7.11 – 7.08 (m, 2H), 6.94 – 6.89 (m, 2H), 3.51 (s, 3H), 1.44 (s, 9H), 1.33 (s, 9H). ^{13}C NMR (125 MHz, Chloroform-d) δ 151.85, 149.15, 146.07, 145.74, 144.49, 141.43, 140.29, 138.71, 134.36, 128.99, 127.63, 126.74, 125.93, 123.17, 122.62, 122.00, 121.76, 120.83, 120.32, 120.00, 119.84, 118.64, 117.05, 111.19, 109.18, 101.15, 35.02, 34.33, 31.62, 31.56, 30.83. IR (KBr): 3055, 3034, 2960, 2902, 2862, 1620, 1594, 1458, 735, 698 cm^{-1}. HRMS (ESI): Calcd. for $C_{41}H_{42}N_3$ $[M+H]^+$: 576.3373; found: 576.3376.

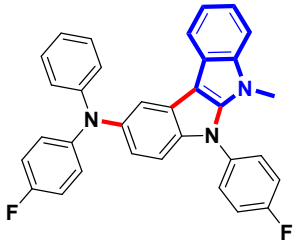
(4) *N*,5-di([1,1'-biphenyl]-4-yl)-6-methyl-*N*-phenyl-5,6-dihydroindolo[2,3-*b*]indol-2-amine (3da)



Brownish solid, (78mg, 51% yield); m.p.: 124-126 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.74 (d, *J* = 8.1 Hz, 3H), 7.63 (d, *J* = 7.7 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 7.7 Hz, 2H), 7.46 – 7.31 (m, 8H), 7.24 – 7.13 (m, 11H), 6.94 – 6.90 (m, 2H), 3.47 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 148.61, 148.22, 145.59,

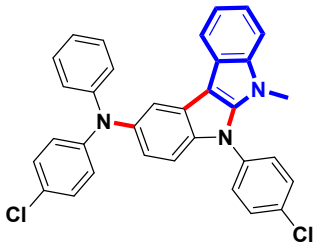
141.48, 141.35, 140.96, 140.31, 139.88, 138.64, 136.17, 133.87, 129.17, 129.14, 128.79, 128.44, 128.32, 128.05, 127.65, 127.24, 126.65, 123.40, 123.18, 122.48, 121.85, 121.66, 120.44, 120.22, 119.84, 118.73, 117.05, 111.25, 109.27, 101.43, 30.91. IR (KBr): 3055, 3028, 2927, 1619, 1593, 1525, 1421, 1371, 808, 763, 695 cm^{-1}. HRMS (ESI): Calcd. for $C_{45}H_{34}N_3$ $[M+H]^+$: 616.2747; found: 616.2748.

(5) *N*,5-bis(4-fluorophenyl)-6-methyl-*N*-phenyl-5,6-dihydroindolo[2,3-*b*]indol-2-amine (3ea)



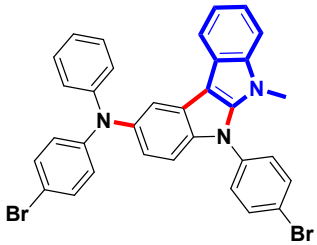
Brownish solid, (69 mg, 55% yield); m.p.: 97-101 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.77 (d, *J* = 6.4 Hz, 1H), 7.66 (s, 1H), 7.57 – 7.47 (m, 2H), 7.24 (t, *J* = 7.8 Hz, 3H), 7.18 (t, *J* = 6.4 Hz, 4H), 7.12 – 7.07 (m, 2H), 7.07 – 6.97 (m, 3H), 6.90 (q, *J* = 11.0, 9.8 Hz, 4H), 3.41 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 162.43 (d, *J* = 249.3 Hz), 158.38 (d, *J* = 241.3 Hz), 149.06, 145.60, 144.90 (d, *J* = 2.5 Hz), 141.73, 140.18, 138.58, 133.07 (d, *J* = 2.1 Hz), 129.99 (d, *J* = 8.7 Hz), 129.13, 125.23 (d, *J* = 7.9 Hz), 123.28, 121.79, 121.55, 121.16, 120.48, 120.28, 119.35, 118.69, 116.95 (d, *J* = 22.8 Hz), 116.49, 115.89 (d, *J* = 22.4 Hz), 110.97, 109.28, 101.23, 30.66. ^{19}F NMR (376 MHz, Chloroform-d) δ -111.76, -121.18. IR (KBr): 3049, 2930, 2875, 2818, 1620, 1594, 1542, 1520, 1309, 736, 694 cm^{-1}. HRMS (ESI): Calcd. for $C_{33}H_{24}F_2N_3$ $[M+H]^+$: 500.1933; found: 500.1930.

(6) *N*,5-bis(4-chlorophenyl)-6-methyl-*N*-phenyl-5,6-dihydroindolo[2,3-*b*]indol-2-amine (3fa)



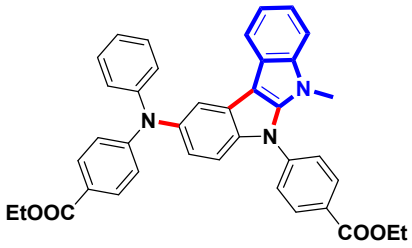
Brownish solid, (68 mg, 51% yield), m.p.: 109-111 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.81 – 7.74 (m, 1H), 7.66 (s, 1H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 7.7 Hz, 2H), 7.27 (d, *J* = 7.5 Hz, 1H), 7.21 (t, *J* = 6.9 Hz, 4H), 7.16 – 7.08 (m, 4H), 7.06 (d, *J* = 8.7 Hz, 1H), 7.02 (d, *J* = 8.1 Hz, 2H), 6.95 (t, *J* = 7.2 Hz, 1H), 6.87 (d, *J* = 8.7 Hz, 1H), 3.45 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 148.38, 147.50, 145.39, 141.38, 140.24, 138.48, 135.67, 134.54, 130.21, 129.33, 129.26, 129.09, 126.11, 123.58, 123.47, 123.10, 122.13, 121.50, 120.56, 120.43, 119.62, 118.76, 116.84, 111.05, 109.33, 101.533, 30.88. IR (KBr): 3080, 3054, 3035, 2927, 1619, 1585, 1539, 1518, 1487, 1307, 1090, 803, 736, 696 cm^{-1}. HRMS (ESI): Calcd. for $C_{33}H_{23}Cl_2N_3$ $[M+H]^+$: 531.1264; found: 531.1260.

(7) *N*,5-bis(4-bromophenyl)-6-methyl-*N*-phenyl-5,6-dihydroindolo[2,3-*b*]indol-2-amine (3ga)



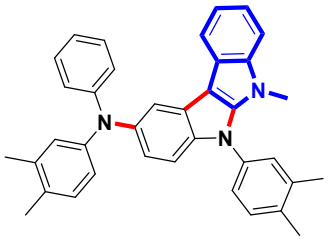
Brownish solid, (96 mg, 62% yield), m.p.: 109-111 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.80 (d, *J* = 7.9 Hz, 1H), 7.76 – 7.66 (m, 3H), 7.43 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 3H), 7.25 – 7.19 (m, 4H), 7.14 (d, *J* = 7.8 Hz, 2H), 7.09 (d, *J* = 8.6 Hz, 1H), 6.99 (d, *J* = 8.6 Hz, 3H), 6.90 (d, *J* = 8.4 Hz, 1H), 3.48 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 147.94, 147.69, 145.01, 140.98, 139.94, 138.11, 135.88, 132.93, 131.71, 129.33, 129.01, 123.50, 123.20, 122.99, 122.19, 122.01, 121.18, 120.29, 120.17, 119.37, 118.49, 116.59, 113.15, 110.79, 109.07, 101.28, 30.68. IR (KBr): 3056, 3033, 2926, 2873, 1619, 1581, 1519, 1399, 802, 736, 696 cm^{-1}. HRMS (ESI): Calcd. for $C_{33}H_{23}Br_2N_3$ $[M+H]^+$: 619.0253; found: 619.0248.

(8) ethyl 4-(2-((4-(ethoxycarbonyl)phenyl)(phenyl)amino)-6-methylindolo[2,3-*b*]indol-5(6*H*)-yl)benzoate (3ha)



Brownish solid, (47 mg, 31% yield), m.p.: 105-107 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.30 (d, *J* = 7.8 Hz, 2H), 7.87 – 7.78 (m, 3H), 7.72 (s, 1H), 7.66 (d, *J* = 7.9 Hz, 2H), 7.32 – 7.18 (m, 9H), 7.07 (t, *J* = 7.1 Hz, 1H), 7.01 (d, *J* = 8.1 Hz, 2H), 6.94 (d, *J* = 8.7 Hz, 1H), 4.45 (q, *J* = 7.1 Hz, 2H), 4.32 (q, *J* = 7.0 Hz, 2H), 3.51 (s, 3H), 1.45 (t, *J* = 7.3 Hz, 3H), 1.35 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 166.69, 165.76, 152.81, 147.29, 145.18, 141.06, 140.70, 140.38, 138.46, 131.33, 130.85, 130.44, 129.48, 128.53, 128.51, 127.48, 125.18, 123.81, 123.75, 121.50, 121.42, 120.65, 120.13, 118.85, 117.50, 111.23, 109.45, 102.01, 61.60, 60.51, 31.22, 14.55, 14.48. IR (KBr): 3058, 3030, 2978, 2927, 2903, 1710, 1604, 1590, 1490, 1272, 1174, 1103, 807, 768, 697 cm^{-1}. HRMS (ESI): Calcd. for $C_{41}H_{32}N_3O_4$ $[M+H]^+$: 630.2387; found: 630.2380.

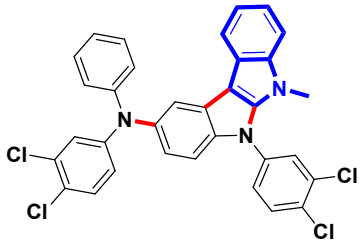
(9) *N*,5-bis(3,4-dimethylphenyl)-6-methyl-*N*-phenyl-5,6-dihydroindolo[2,3-*b*]indol-2-amine (3ia)



Brownish solid, (68 mg, 52% yield); m.p.: 105-107 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.83 (d, *J* = 6.1 Hz, 1H), 7.72 (s, 1H), 7.34 (dd, *J* = 14.4, 7.1 Hz, 4H), 7.25 – 7.17 (m, 4H), 7.10 (d, *J* = 7.0 Hz, 3H), 7.05 – 7.00 (m, 2H), 6.96 – 6.87 (m, 3H), 3.51 (s, 3H), 2.42 (s, 3H), 2.39 (s, 3H), 2.25 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 149.37, 146.57, 145.75, 141.49, 140.25, 138.62, 138.40,

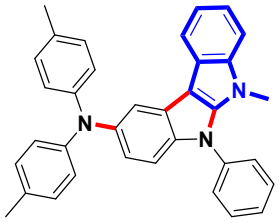
137.34, 137.31, 134.66, 130.86, 130.31, 130.28, 129.09, 128.93, 125.46, 125.09, 123.07, 121.76, 121.68, 121.33, 120.51, 120.25, 119.91, 119.59, 118.63, 116.80, 111.08, 109.12, 100.99, 30.73, 20.05, 19.72, 19.21. IR (KBr): 3054, 3022, 2966, 2918, 2857, 2819, 1610, 1594, 1519, 1492, 1384, 736, 695 cm^{-1}. HRMS (ESI): Calcd. for $C_{37}H_{34}N_3$ $[M+H]^+$: 520.2747; found: 520.2748.

(10) *N*,5-bis(3,4-dichlorophenyl)-6-methyl-*N*-phenyl-5,6-dihydroindolo[2,3-*b*]indol-2-amine (3ja)



Brownish solid, (93 mg, 62% yield), m.p.: 103-105 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.79 (d, *J* = 5.9 Hz, 1H), 7.70 – 7.68 (m, 1H), 7.65 (d, *J* = 5.7 Hz, 1H), 7.42 (d, *J* = 8.5 Hz, 1H), 7.34 – 7.17 (m, 7H), 7.12 (t, *J* = 7.4 Hz, 4H), 7.02 (t, *J* = 7.7 Hz, 1H), 6.89 (d, *J* = 8.7 Hz, 2H), 3.52 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 148.52, 147.62, 145.13, 141.00, 140.28, 138.53, 136.56, 134.06, 133.06, 132.73, 131.65, 130.47, 129.81, 129.68, 129.49, 127.23, 123.92, 123.74, 123.62, 123.12, 122.74, 121.37, 120.80, 120.74, 119.83, 118.90, 117.13, 111.18, 109.47, 101.89, 31.10. IR (KBr): 3058, 3035, 2926, 1619, 1584, 1518, 1492, 1385, 737, 696 cm^{-1}. HRMS (ESI): Calcd. for $C_{33}H_{22}Cl_4N_3$ $[M+H]^+$: 600.0562; found: 600.0567.

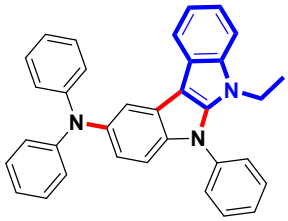
(11) 6-methyl-5-phenyl-*N*,*N*-di-*p*-tolyl-5,6-dihydroindolo[2,3-*b*]indol-2-amine (3ka)



Brownish solid, (64 mg, 52% yield), m.p.: 236-238 °C; ^{1}H NMR (500 MHz,

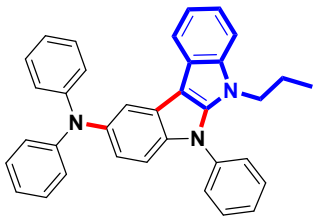
Chloroform-d) δ 7.72 – 7.69 (m, 1H), 7.63 – 7.59 (m, 1H), 7.50 – 7.45 (m, 4H), 7.43 – 7.39 (m, 1H), 7.19 (dd, *J* = 6.4, 2.2 Hz, 1H), 7.14 – 7.08 (m, 3H), 7.07 – 7.01 (m, 1H), 6.99 (dd, *J* = 8.6, 1.9 Hz, 1H), 6.93 (d, *J* = 2.6 Hz, 6H), 6.82 – 6.78 (m, 1H), 3.37 (s, 3H), 2.20 (s, 6H). ^{13}C NMR (125 MHz, Chloroform-d) δ 146.70, 145.62, 142.04, 140.29, 138.27, 137.25, 130.79, 129.89, 129.70, 129.10, 128.58, 128.13, 122.88, 121.75, 120.33, 120.06, 119.31, 118.69, 116.33, 110.96, 109.20, 101.34, 30.81, 20.84. IR (KBr): 3050, 3020, 2919, 2852, 2820, 1609, 1595, 1543, 1422, 807, 740, 703 cm^{-1}. HRMS (ESI): Calcd. for $C_{35}H_{30}N_3$ $[M+H]^+$: 492.2434; found: 492.2435.

(12) 6-ethyl-*N*,*N*,5-triphenyl-5,6-dihydroindolo[2,3-*b*]indol-2-amine (3ab)



Brownish solid, (80 mg, 67% yield); m.p.: 163-165 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.79 (d, *J* = 7.0 Hz, 1H), 7.71 (s, 1H), 7.56 (s, 5H), 7.30 (d, *J* = 7.2 Hz, 1H), 7.20 (t, *J* = 7.2 Hz, 6H), 7.13 (d, *J* = 8.0 Hz, 4H), 7.05 (d, *J* = 8.5 Hz, 1H), 6.92 (t, J = 7.6 Hz, 3H), 3.98 – 3.88 (m, 2H), 1.07 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 148.86, 145.01, 141.40, 139.16, 138.88, 137.31, 129.90, 129.08, 128.92, 128.24, 123.23, 122.72, 121.95, 121.45, 120.30, 120.07, 119.80, 118.77, 116.95, 111.15, 109.43, 101.41, 38.53, 14.54. IR (KBr): 3035, 2980, 2930, 2872, 1621, 1589, 1517, 1388, 800, 772, 694 cm^{-1}. HRMS (ESI): Calcd. for $C_{34}H_{28}N_3$ $[M+H]^+$: 478.2278; found: 478.2282.

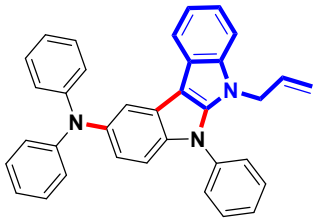
(13) *N*,*N*,5-triphenyl-6-propyl-5,6-dihydroindolo[2,3-*b*]indol-2-amine (3ac)



Brownish solid, (77 mg, 63% yield), m.p.: 192-194 °C; ^{1}H NMR (400 MHz,

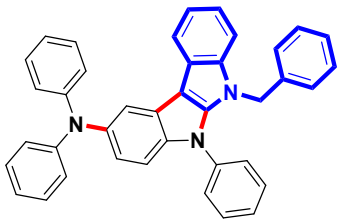
Chloroform-d) δ 7.80 (d, *J* = 6.9 Hz, 1H), 7.71 (s, 1H), 7.64 – 7.69 (m, 5H), 7.31 (d, *J* = 7.1 Hz, 1H), 7.20 (q, *J* = 7.8, 7.2 Hz, 6H), 7.13 (d, *J* = 8.0 Hz, 4H), 7.05 (d, *J* = 8.5 Hz, 1H), 6.92 (t, *J* = 9.7 Hz, 3H), 3.84 (t, *J* = 7.3 Hz, 2H), 1.51 (dt, *J* = 14.5, 7.1 Hz, 2H), 0.59 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 148.88, 145.30, 141.41, 139.56, 138.89, 137.27, 129.86, 129.09, 128.88, 128.45, 123.21, 122.74, 121.75, 121.46, 120.24, 120.01, 119.79, 118.74, 116.96, 111.14, 109.64, 101.29, 45.32, 22.92, 11.20. IR (KBr): 3050, 3034, 2977, 2875, 2851, 1620, 1588, 1515, 1392, 803, 697 cm^{-1}. HRMS (ESI): Calcd. for $C_{35}H_{30}N_3$ $[M+H]^+$: 492.2434; found: 492.2432.

(14) 6-allyl-*N*,*N*,5-triphenyl-5,6-dihydroindolo[2,3-*b*]indol-2-amine (3ad)



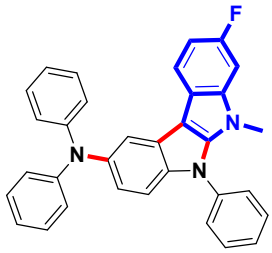
Brownish solid, (56 mg, 46% yield), m.p.: 171-173 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.79 (d, *J* = 7.5 Hz, 1H), 7.71 (s, 1H), 7.63 – 7.42 (m, 5H), 7.24 – 7.10 (m, 11H), 7.06 (d, *J* = 8.6 Hz, 1H), 6.91 (t, *J* = 7.4 Hz, 3H), 5.71 – 5.60 (m, 1H), 4.99 (d, *J* = 10.3 Hz, 1H), 4.67 (d, *J* = 17.1 Hz, 1H), 4.46 (d, J = 2.8 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-d) δ 148.86, 144.99, 141.44, 139.65, 138.64, 137.05, 132.32, 129.77, 129.10, 128.84, 128.29, 123.13, 122.75, 121.90, 121.48, 120.55, 120.23, 119.89, 118.74, 116.98, 111.18, 109.86, 101.51, 46.00. IR (KBr): 3054, 3032, 2922, 2853, 1734, 1618, 1586, 1488, 1321, 785, 753, 695 cm^{-1}. HRMS (ESI): Calcd. for $C_{35}H_{28}N_3$ $[M+H]^+$: 490.2278; found: 490.2284.

(15) 6-benzyl-*N*,*N*,5-triphenyl-5,6-dihydroindolo[2,3-*b*]indol-2-amine (3ae)



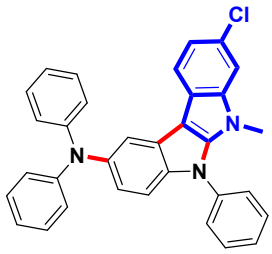
Brownish solid, (59 mg, 44% yield), m.p.: 113-115 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.83 (d, *J* = 7.7 Hz, 1H), 7.74 (s, 1H), 7.43 – 7.34 (m, 3H), 7.29 – 7.24 (m, 3H), 7.20 (t, *J* = 7.3 Hz, 5H), 7.17 – 7.07 (m, 8H), 7.01 (d, *J* = 8.6 Hz, 1H), 6.91 (q, *J* = 8.4, 7.8 Hz, 3H), 6.65 (d, *J* = 7.2 Hz, 2H), 5.11 (s, 2H). ^{13}C NMR (100 MHz, Chloroform-d) δ 148.86, 144.95, 141.45, 140.04, 138.69, 136.95, 136.74, 129.62, 129.11, 128.62, 128.22, 127.38, 126.00, 123.07, 122.78, 121.84, 121.51, 120.65, 120.38, 119.92, 118.81, 116.98, 111.21, 109.77, 101.72, 47.13. IR (KBr): 3055, 3035, 2920, 2852, 2817, 1616, 1587, 1420, 802, 693 cm^{-1}. HRMS (ESI): Calcd. for $C_{39}H_{30}N_3$ $[M+H]^+$: 540.2434; found: 540.2435.

(16) 8-fluoro-6-methyl-*N*,*N*,5-triphenyl-5,6-dihydroindolo[2,3-*b*]indol-2-amine (3af)



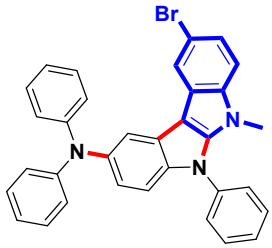
Brownish solid, (64 mg, 53% yield), m.p.: 198-200 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.70 – 7.62 (m, 2H), 7.60 – 7.47 (m, 5H), 7.20 (t, *J* = 7.3 Hz, 4H), 7.13 – 7.07 (m, 5H), 6.98 – 6.90 (m, 5H), 3.40 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 158.87 (d, *J* = 236.1 Hz), 148.93, 145.72(d, *J* = 2.3 Hz), 140.54 (d, *J* = 11.5 Hz), 138.43, 137.10, 129.97, 129.13, 128.77, 128.15, 122.98, 122.87, 121.59, 119.98, 119.02, 118.93, 118.21, 116.82, 111.27, 107.96 (d, *J* = 23.5 Hz), 101.04, 96.78 (d, *J* = 27.2 Hz), 30.97. ^{19}F NMR (376 MHz, Chloroform-d) δ -121.93. IR (KBr): 3058, 3034, 2924, 2851, 1619, 1587, 1414, 800, 695 cm^{-1}. HRMS (ESI): Calcd. for $C_{33}H_{24}FN_3$ $[M+H]^+$: 481.1949; found: 481.1951.

(17) 8-chloro-6-methyl-*N*,*N*,5-triphenyl-5,6-dihydroindolo[2,3-*b*]indol-2-amine (3ag)



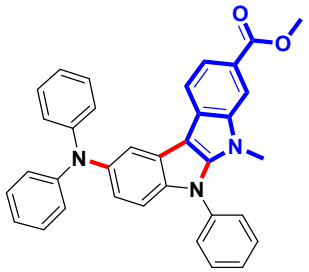
Brownish solid, (52 mg, 42% yield), m.p.: 118-120 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.70 – 7.63 (m, 2H), 7.62 – 7.47 (m, 5H), 7.25 – 7.06 (m, 11H), 6.93 (t, *J* = 6.8 Hz, 3H), 3.43 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 148.92, 145.88, 141.81, 140.80, 138.65, 137.00, 130.02, 129.15, 128.89, 128.22, 125.81, 122.95, 122.92, 121.65, 120.74, 120.31, 120.17, 119.30, 116.95, 111.31, 109.62, 101.18, 30.93. IR (KBr): 3059, 3034, 2924, 1617, 1586, 1418, 795, 694 cm^{-1}. HRMS (ESI): Calcd. for $C_{33}H_{24}ClN_3$ $[M+H]^+$: 497.1653; found: 497.1657.

(18) 9-bromo-6-methyl-*N*,*N*,5-triphenyl-5,6-dihydroindolo[2,3-*b*]indol-2-amine (3ah)



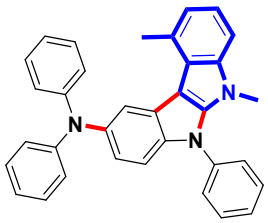
Brownish solid, (72 mg, 53% yield); m.p.: 149-151 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.78 (s, 1H), 7.57 (s, 1H), 7.51 – 7.36 (m, 5H), 7.15 – 7.08 (m, 5H), 7.06 – 6.94 (m, 6H), 6.83 (t, *J* = 7.3 Hz, 3H), 3.29 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 148.88, 146.04, 141.88, 138.98, 138.68, 136.84, 129.99, 129.16, 128.90, 128.19, 123.23, 122.91, 122.64, 121.68, 121.16, 120.22, 116.93, 113.59, 111.27, 110.56, 100.78, 30.82. IR (KBr): 3060, 3033, 2925, 2906, 2854, 2819, 1587, 1419, 807, 695 cm^{-1}. HRMS (ESI): Calcd. for $C_{33}H_{25}BrN_3$ $[M+H]^+$: 542.1226; found: 542.1222.

(19) methyl 9-(diphenylamino)-5-methyl-6-phenyl-5,6-dihydroindolo[2,3-*b*]indole-3-carboxylate (3ai)



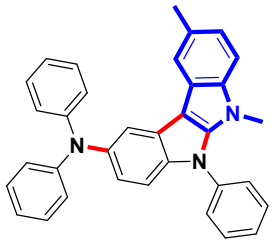
Brownish solid, (29 mg, 22% yield), m.p.: 230-233 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.06 (s, 1H), 7.94 (d, *J* = 8.6 Hz, 1H), 7.78 (d, *J* = 8.3 Hz, 1H), 7.75 – 7.68 (m, 1H), 7.67 – 7.50 (m, 6H), 7.23 (t, *J* = 7.8 Hz, 4H), 7.15 – 7.09 (m, 4H), 6.96 (t, *J* = 7.2 Hz, 3H), 3.95 (s, 3H), 3.54 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 168.36, 148.80, 147.49, 141.97, 139.66, 139.01, 136.63, 130.08, 129.16, 129.09, 128.27, 125.34, 122.89, 122.12, 121.67, 121.30, 120.54, 117.79, 117.19, 111.34, 111.26, 101.78, 52.00, 30.90. IR (KBr): 3057, 3034, 2923, 2815, 1694, 1620, 1596, 1461, 752, 695 cm^{-1}. HRMS (ESI): Calcd. for $C_{35}H_{27}N_3NaO_2$ $[M+Na]^+$: 544.1995; found: 544.2003.

(20) 6,10-dimethyl-*N*,*N*,5-triphenyl-5,6-dihydroindolo[2,3-*b*]indol-2-amine (3aj)



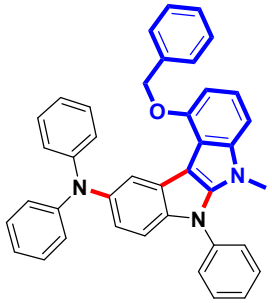
Brownish solid, (72 mg, 60% yield), m.p.: 219-222 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.91 (s, 1H), 7.68 – 7.50 (m, 5H), 7.23 (d, *J* = 7.8 Hz, 4H), 7.19 – 7.10 (m, 7H), 7.01 (d, *J* = 5.4 Hz, 1H), 6.95 (t, *J* = 7.4 Hz, 3H), 3.46 (s, 3H), 2.85 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 148.79, 145.26, 141.35, 140.07, 138.66, 137.18, 129.92, 129.05, 128.72, 128.62, 128.29, 123.25, 122.73, 122.22, 121.51, 121.29, 120.61, 119.55, 117.49, 111.09, 106.80, 101.53, 30.87, 22.18. IR (KBr): 3058, 3032, 2918, 2861, 2818, 1621, 1587, 1421, 1275, 792, 694 cm^{-1}. HRMS (ESI): Calcd. for $C_{34}H_{28}N_3$ $[M+H]^+$: 478.2278; found: 478.2278.

(21) 6,9-dimethyl-*N*,*N*,5-triphenyl-5,6-dihydroindolo[2,3-*b*]indol-2-amine (3ak)



Brownish solid, (73 mg, 61% yield), m.p.: 112-114 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.61 (s, 1H), 7.49 (s, 1H), 7.47 – 7.32 (m, 5H), 7.09 (t, *J* = 7.5 Hz, 4H), 7.02 (d, *J* = 8.3 Hz, 5H), 6.98 (d, *J* = 8.6 Hz, 1H), 6.88 (d, *J* = 8.2 Hz, 1H), 6.80 (q, *J* = 8.3, 7.7 Hz, 3H), 3.29 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 148.96, 145.93, 141.47, 138.75, 138.67, 137.30, 129.86, 129.74, 129.09, 128.55, 128.11, 123.48, 122.78, 121.90, 121.46, 121.36, 119.72, 118.94, 117.02, 111.06, 108.91, 101.12, 30.80, 21.59. IR (KBr): 3051, 3035, 2960, 2923, 1617, 1589, 1491, 805, 694 cm^{-1}. HRMS (ESI): Calcd. for $C_{34}H_{28}N_3$ $[M+H]^+$: 478.2278; found: 478.2275.

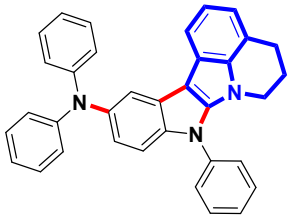
(22) 10-(benzyloxy)-6-methyl-*N*,*N*,5-triphenyl-5,6-dihydroindolo[2,3-*b*]indol-2-amine (3al)



Brownish solid, (60 mg, 42% yield), m.p.: 124-126 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.87 (s, 1H), 7.64 – 7.56 (m, 4H), 7.55 – 7.50 (m, 1H), 7.41 (d, *J* = 7.3 Hz, 2H), 7.21 – 7.10 (m, 9H), 7.05 (d, *J* = 8.1 Hz, 4H), 6.96 (d, *J* = 8.1 Hz, 1H), 6.90 (t, *J* = 7.5 Hz, 3H), 6.78 (d, *J* = 7.9 Hz, 1H), 5.22 (s, 2H), 3.47 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 151.84, 148.95, 144.37, 141.58, 141.04, 138.95, 137.45, 137.43, 129.87, 128.93, 128.62, 128.56, 128.18, 127.96, 127.94, 123.53, 122.50, 121.18, 120.41, 119.34, 112.81, 110.97, 103.22, 103.09, 100.89, 70.85, 31.09. IR (KBr): 3060, 3034, 2949, 2927, 2834, 1588, 1421, 1297, 804, 769, 694 cm^{-1}. HRMS

(ESI): Calcd. for $C_{40}H_{32}N_3O$ $[M+H]^+$: 570.2540; found: 570.2546.

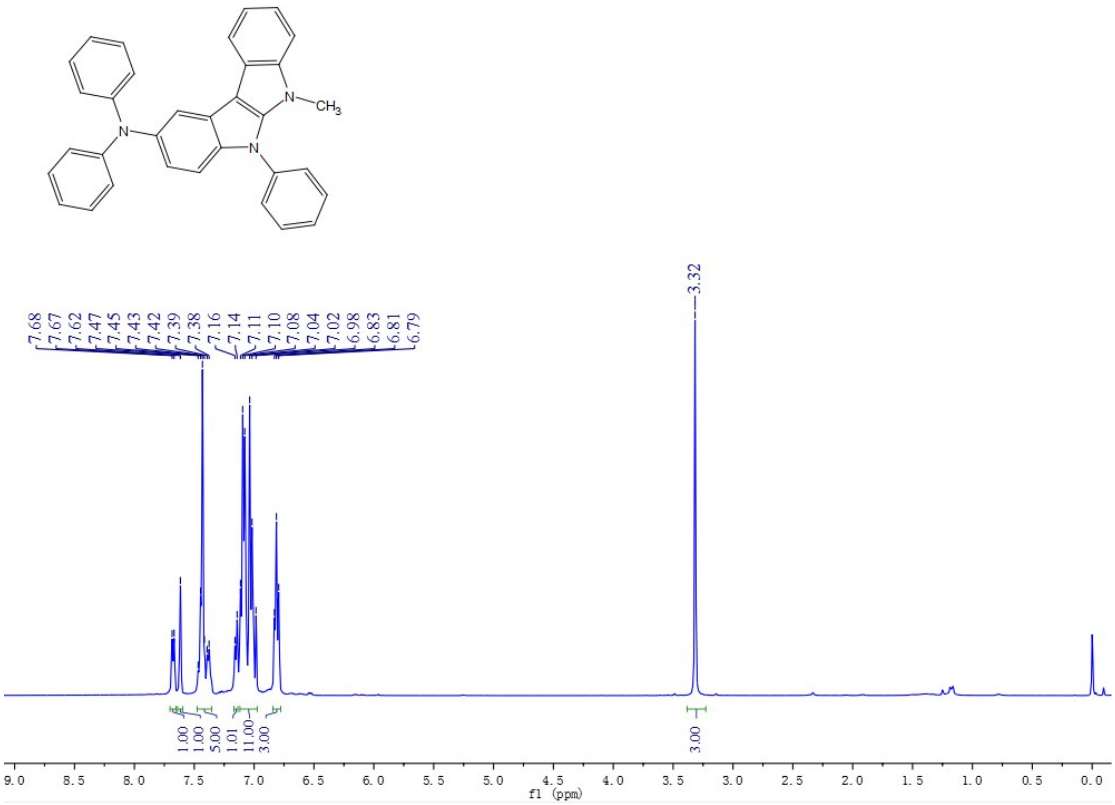
(23)*N*,*N*,8-triphenyl-5,6-dihydro-4*H*,8*H*-indolo[3',2':4,5]pyrrolo[3,2,1-*ij*]quinolin-11-amine (3am)



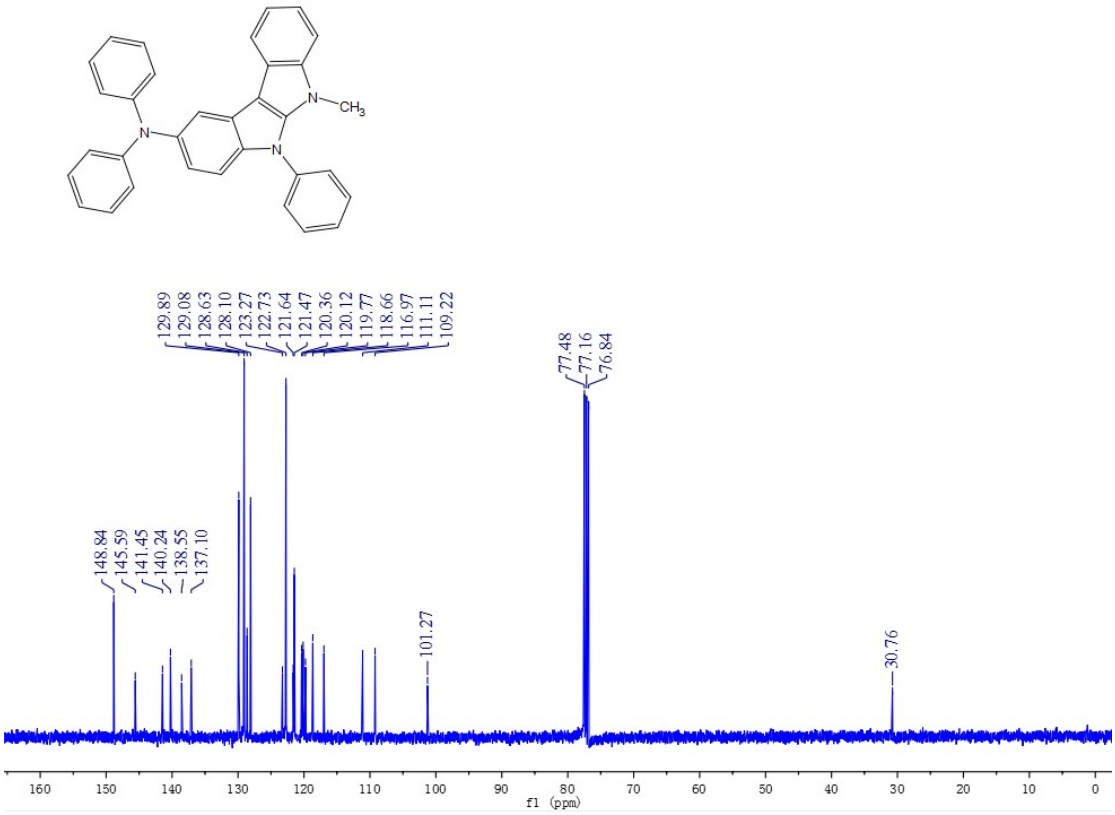
Brownish solid, (49 mg, 40% yield), m.p.: 112-114 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.71 (s, 1H), 7.60 (d, *J* = 4.4 Hz, 5H), 7.55 – 7.49 (m, 1H), 7.25 – 7.10 (m, 10H), 6.94 (t, *J* = 8.5 Hz, 4H), 3.84 (t, *J* = 5.2 Hz, 2H), 2.99 (t, *J* = 5.7 Hz, 2H), 2.20 – 2.11 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-d) δ 148.88, 144.58, 141.36, 137.98, 137.16, 136.59, 129.85, 129.08, 128.35, 127.69, 123.61, 122.72, 121.75, 121.44, 120.18, 119.64, 118.19, 117.17, 116.24, 110.94, 101.20, 43.44, 24.83, 22.86. IR (KBr): 3058, 3033, 2925, 2858, 1618, 1589, 1454, 747, 694 cm^{-1}. HRMS (ESI): Calcd. for $C_{35}H_{28}N_3$ $[M+H]^+$: 490.2278; found:490.2281.

10. NMR spectra of the obtained compounds.

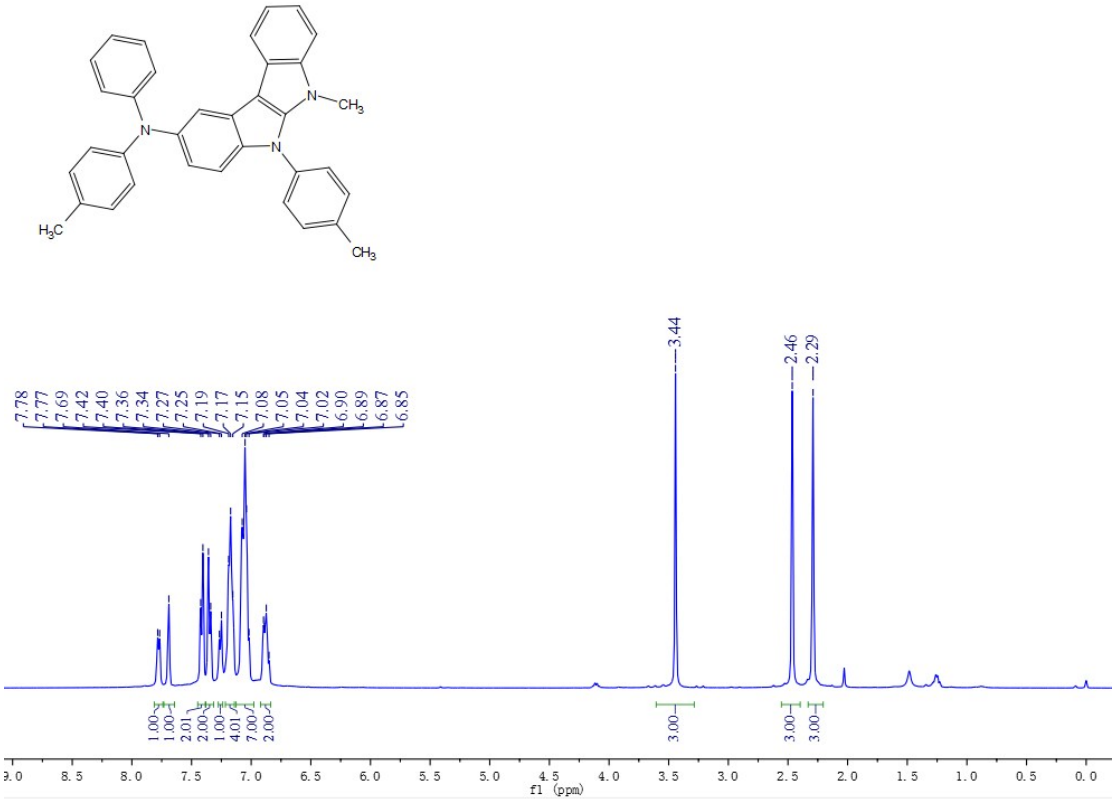
(1) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3aa



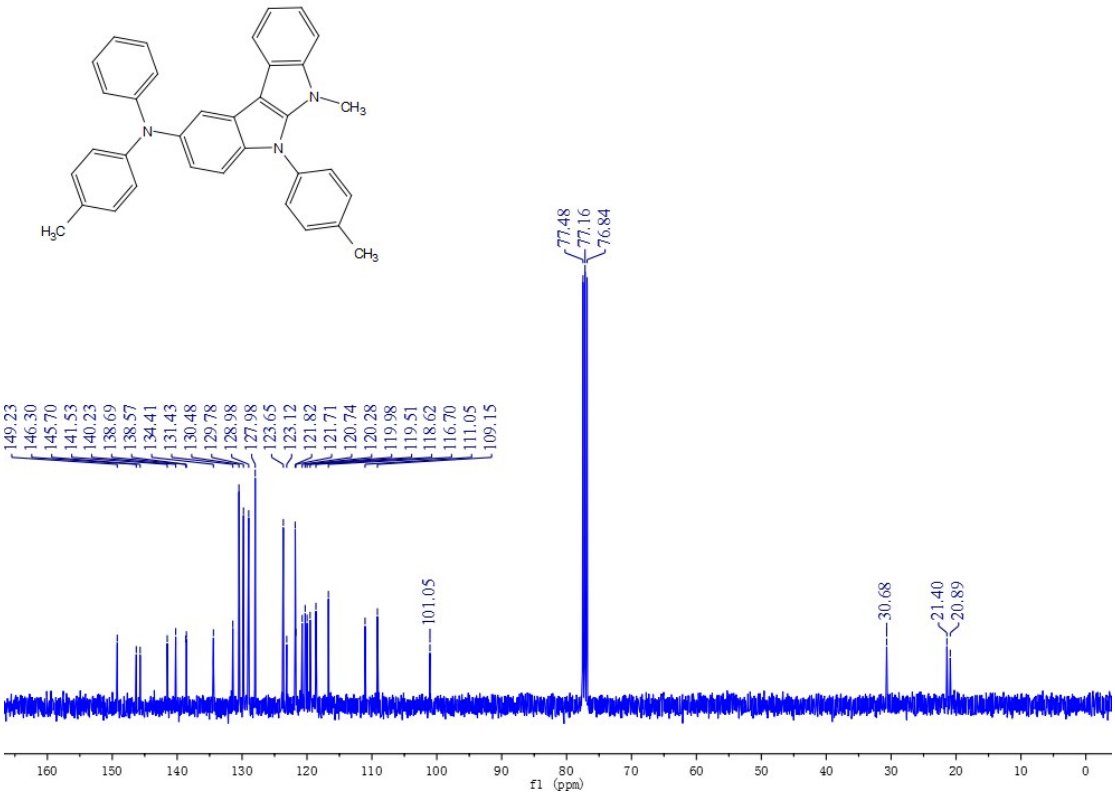
(2) ^{13}C-NMR (100 MHz, $CDCl_3$) spectrum of 3aa



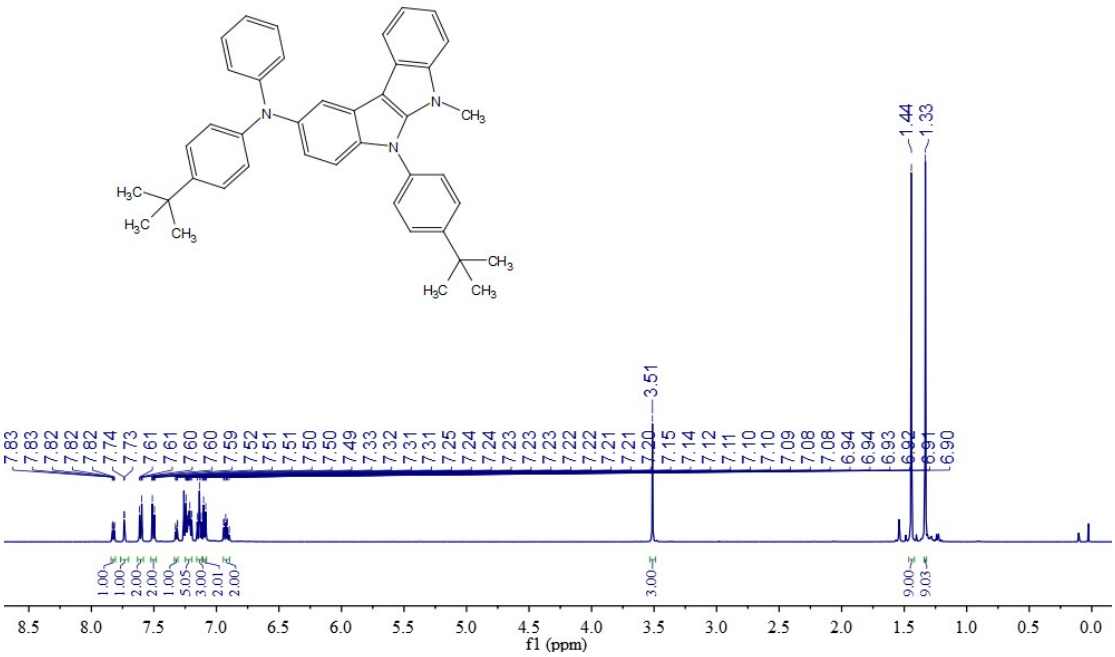
(3) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3ba



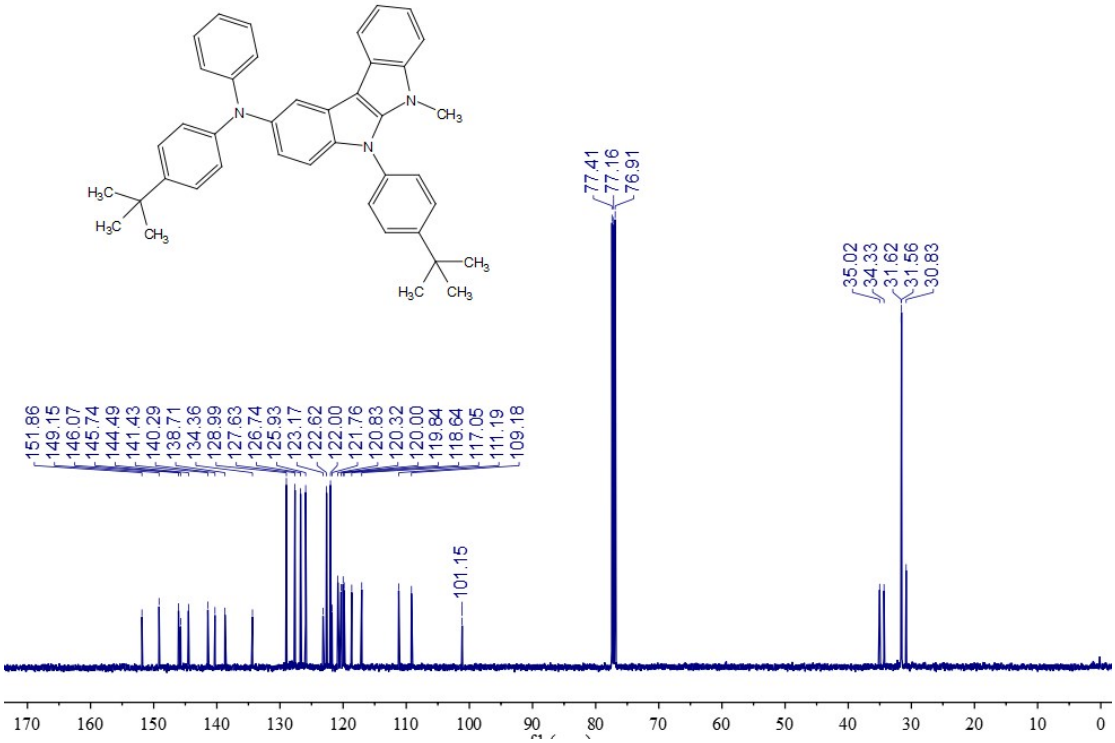
(4) ^{13}C-NMR (100 MHz, $CDCl_3$) spectrum of 3ba



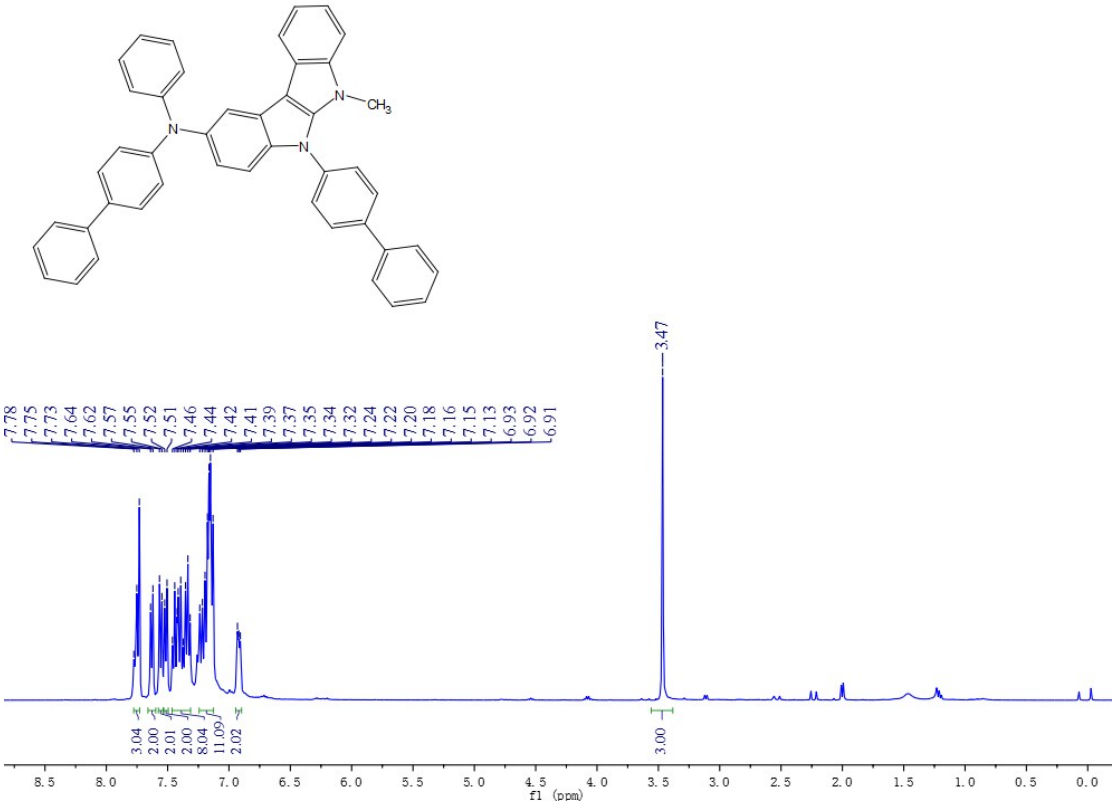
(5) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 3ca



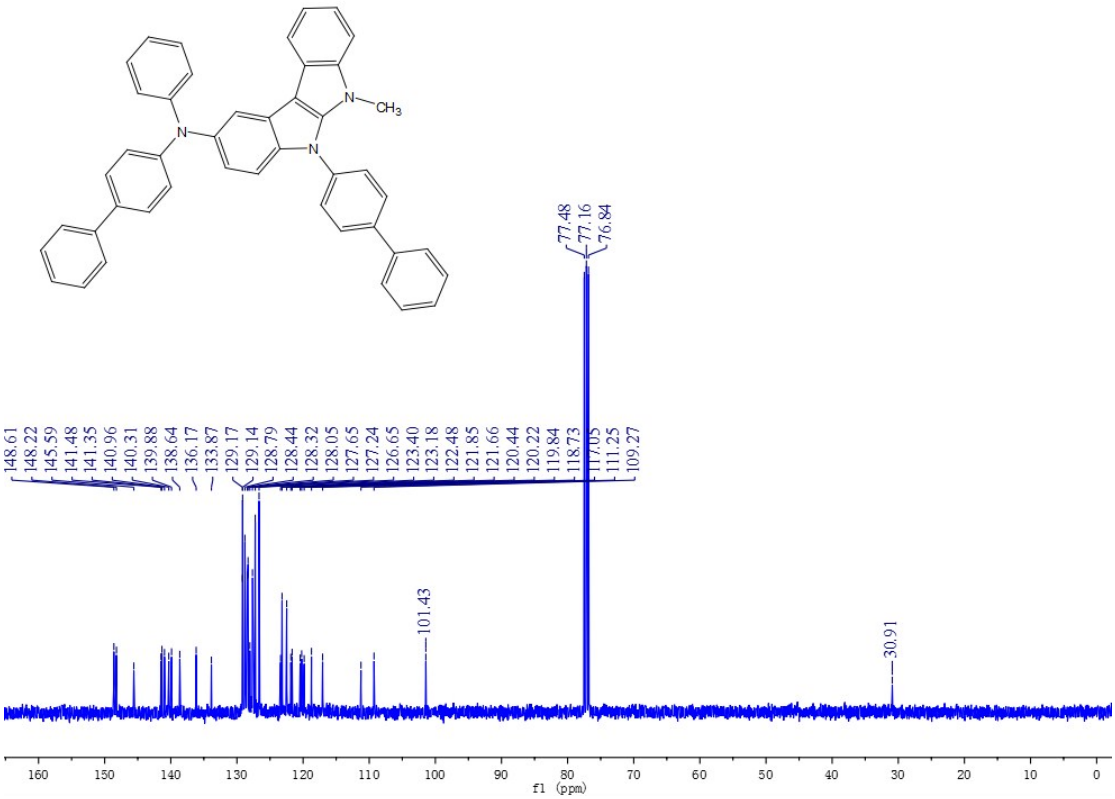
(6) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of 3ca



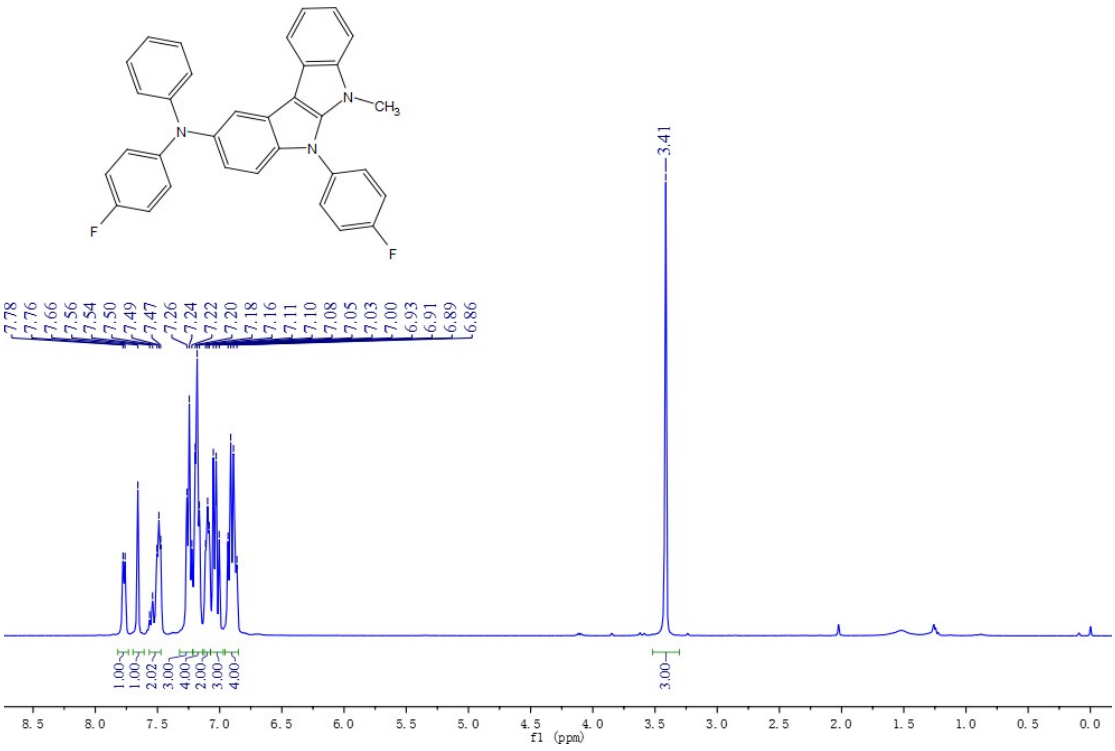
(7) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3da



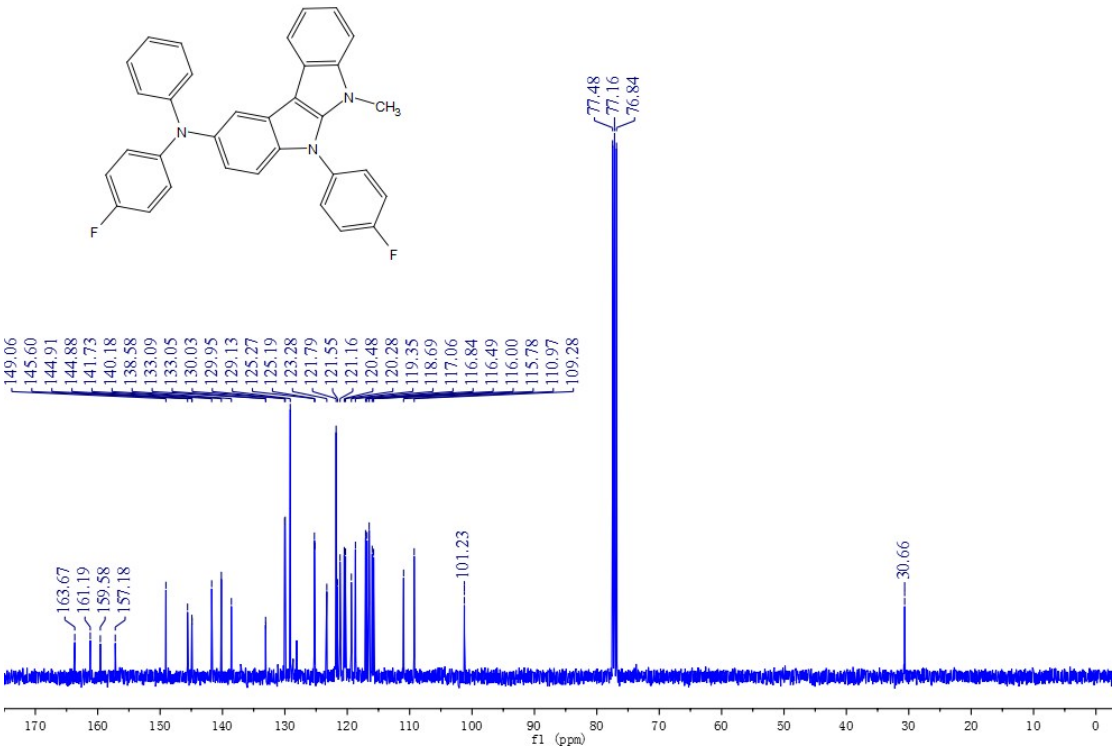
(8) ^{13}C-NMR (100 MHz, $CDCl_3$) spectrum of 3da



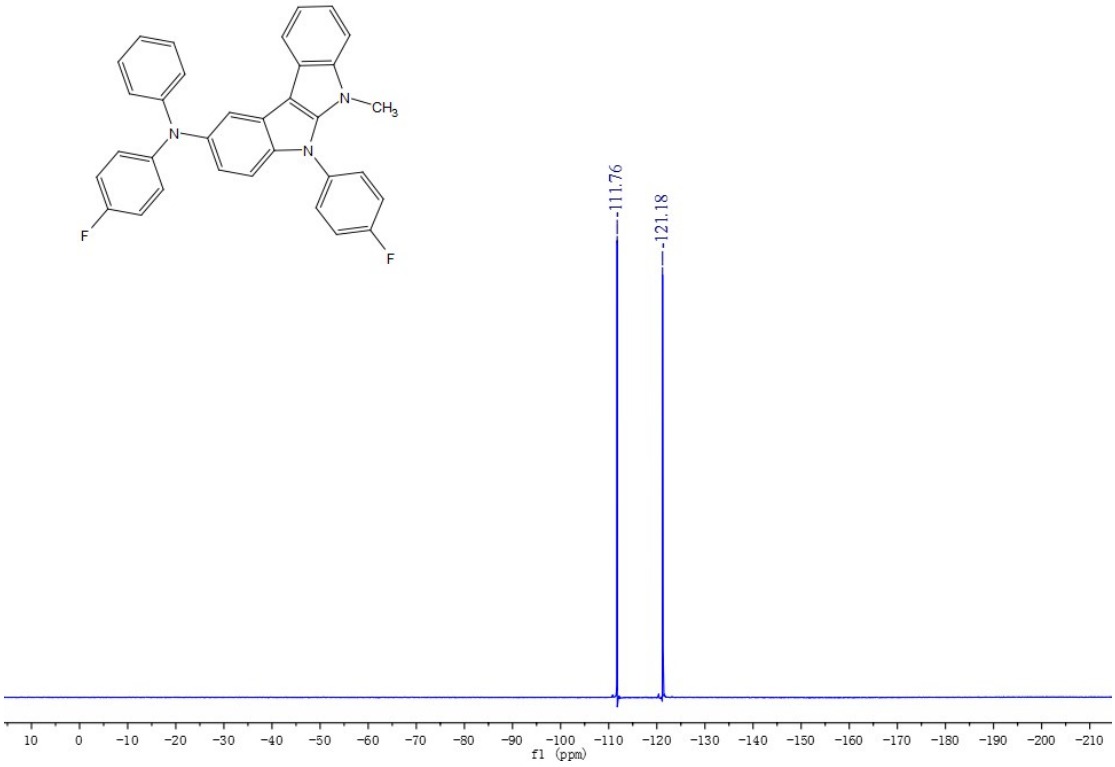
(9) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3ea



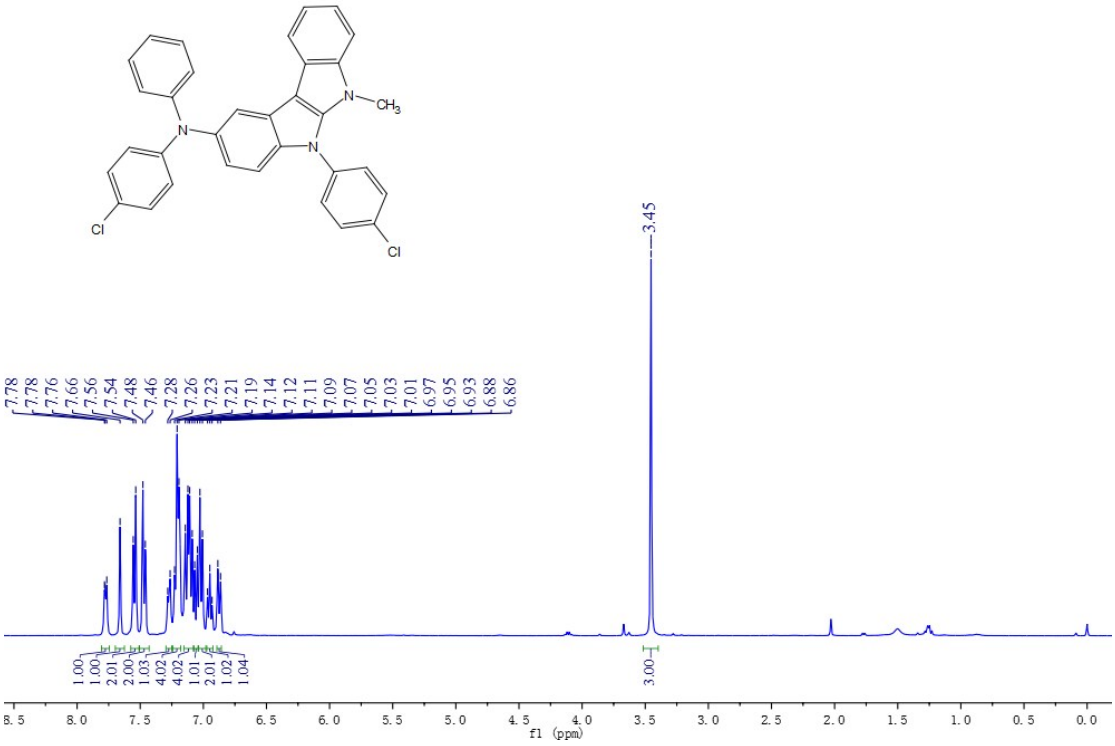
(10) ^{13}C-NMR (100 MHz, $CDCl_3$) spectrum of 3ea



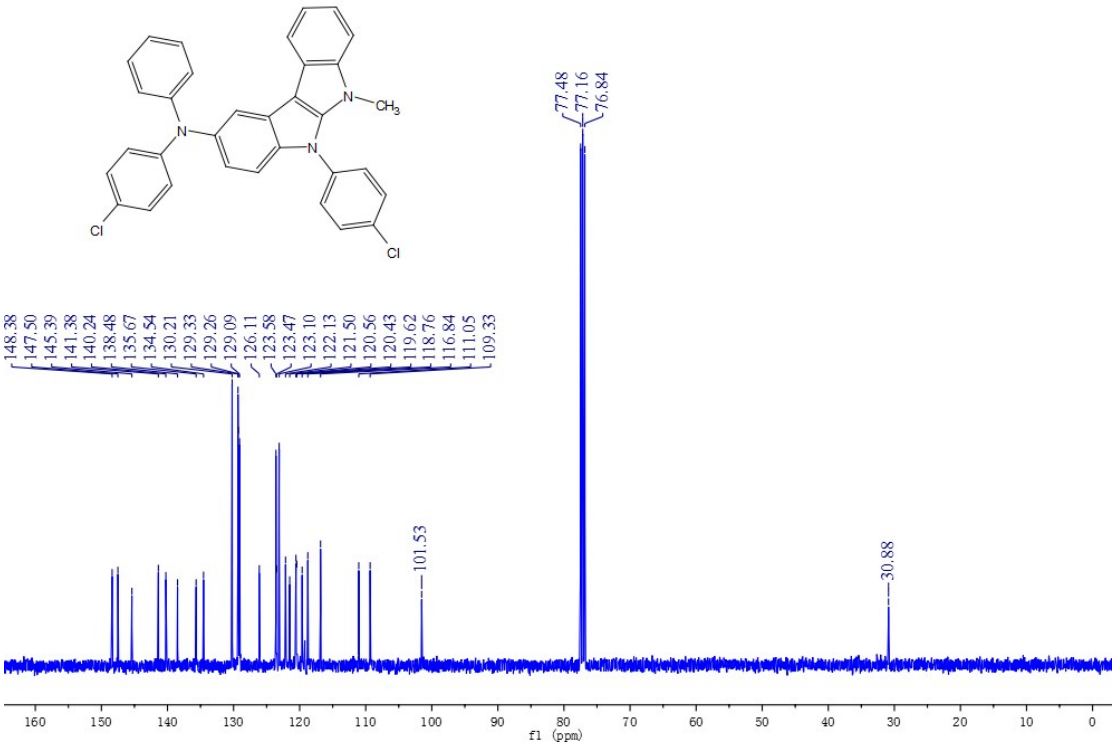
(11) ^{19}F-NMR (400 MHz, $CDCl_3$) spectrum of 3ea



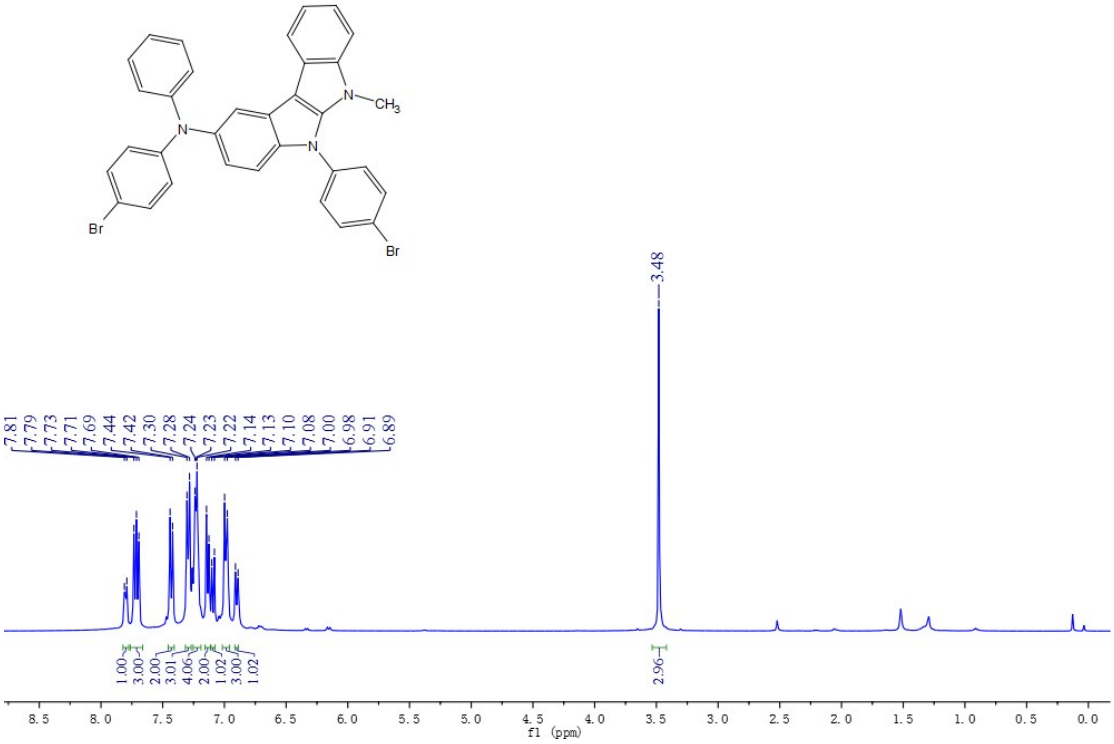
(12) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3fa



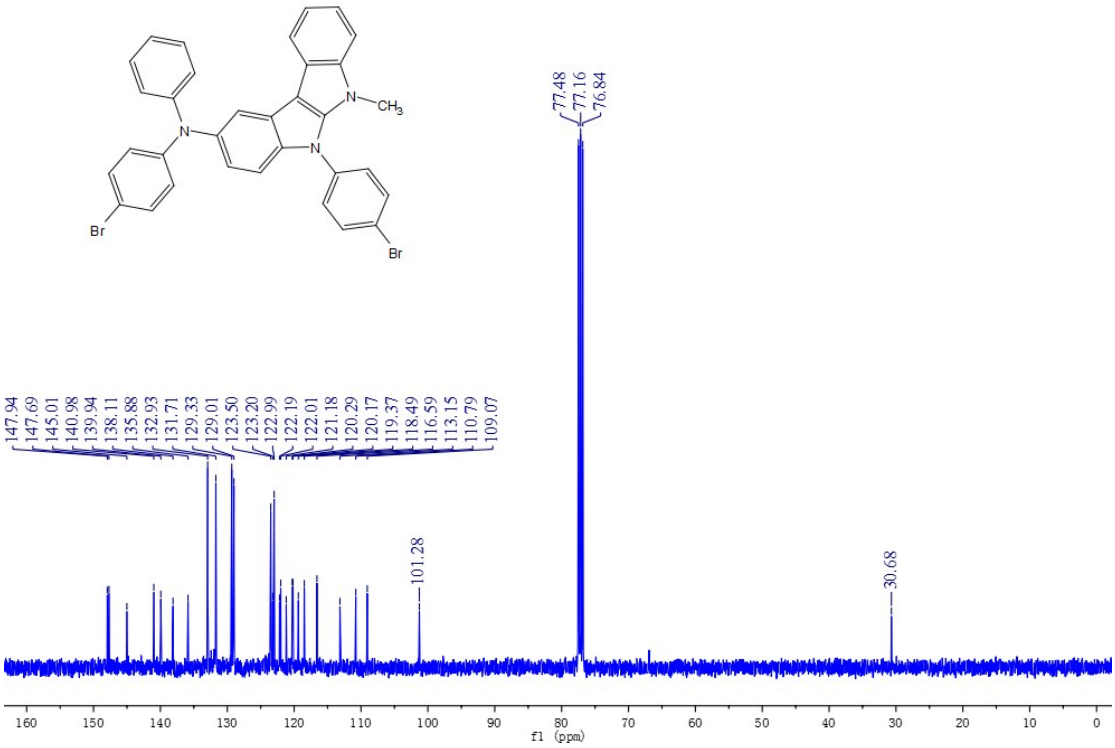
(13) ^{13}C-NMR (100 MHz, $CDCl_3$) spectrum of 3fa



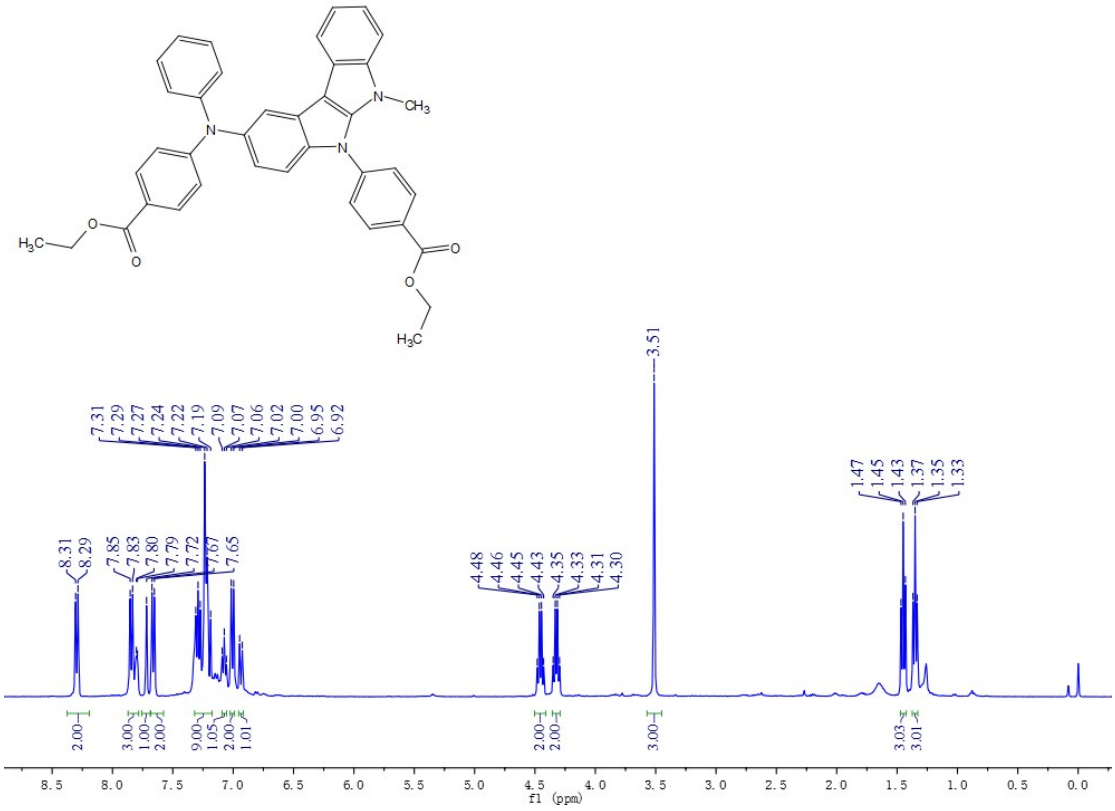
(14) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3ga



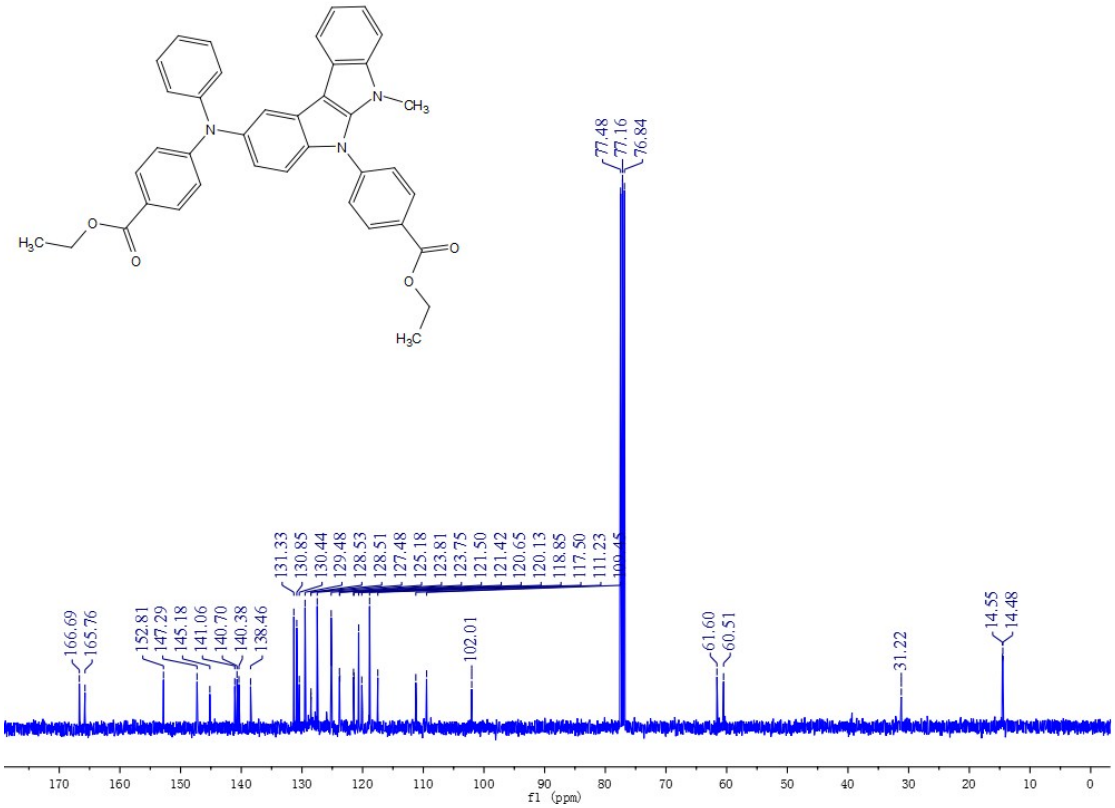
(15) ^{13}C-NMR (100 MHz, $CDCl_3$) spectrum of 3ga



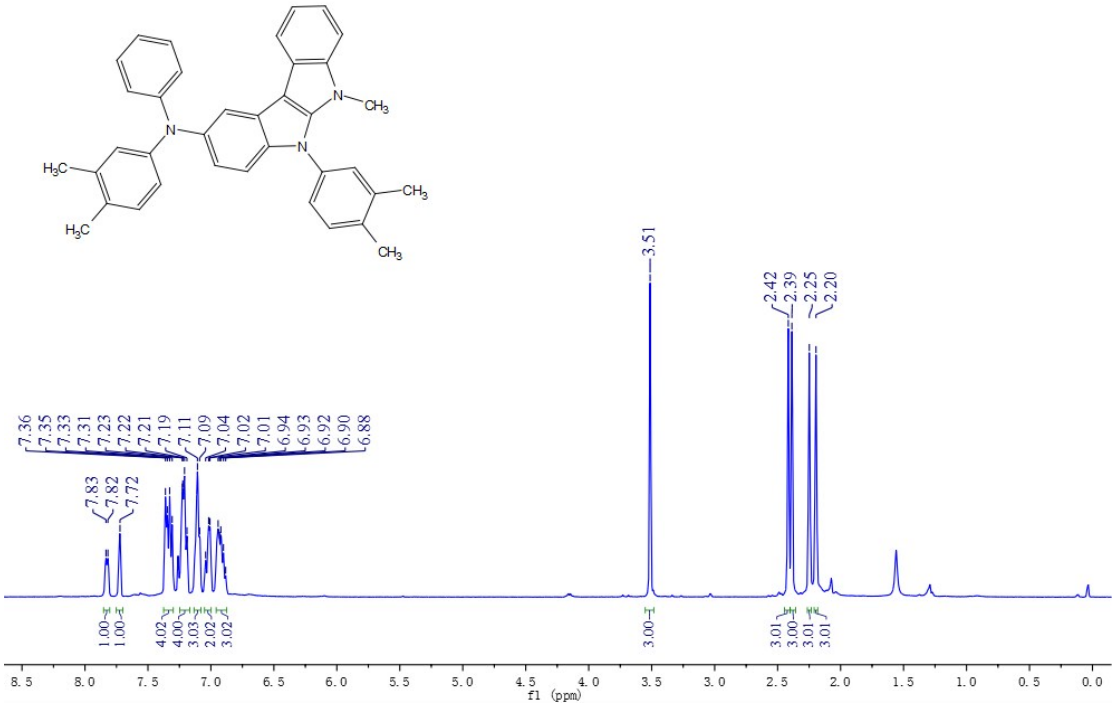
(16) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3ha



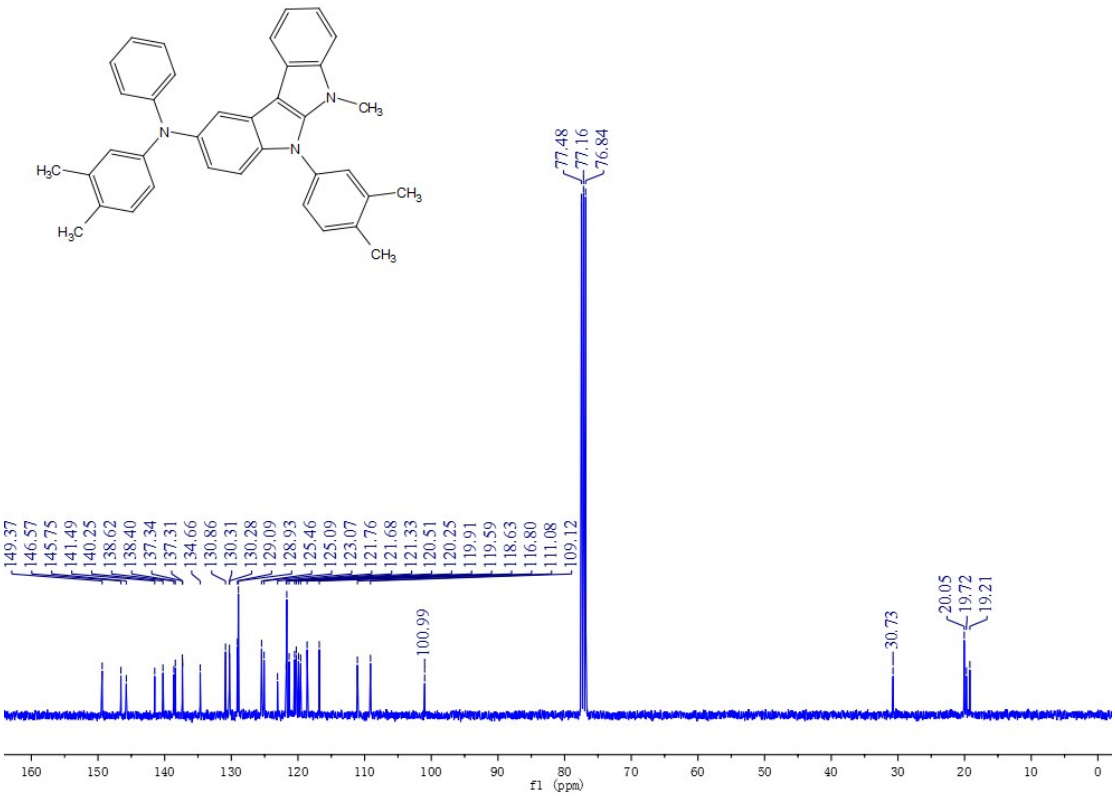
(17) ^{13}C-NMR (100 MHz, $CDCl_3$) spectrum of 3ha



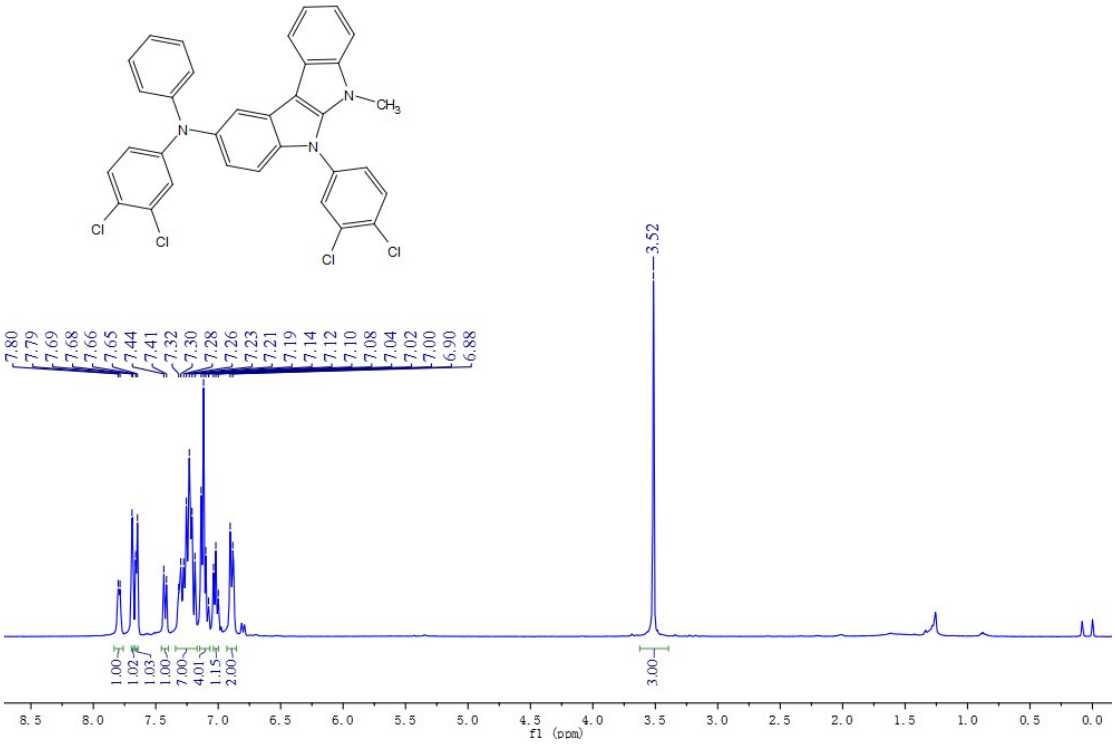
(18) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3ia



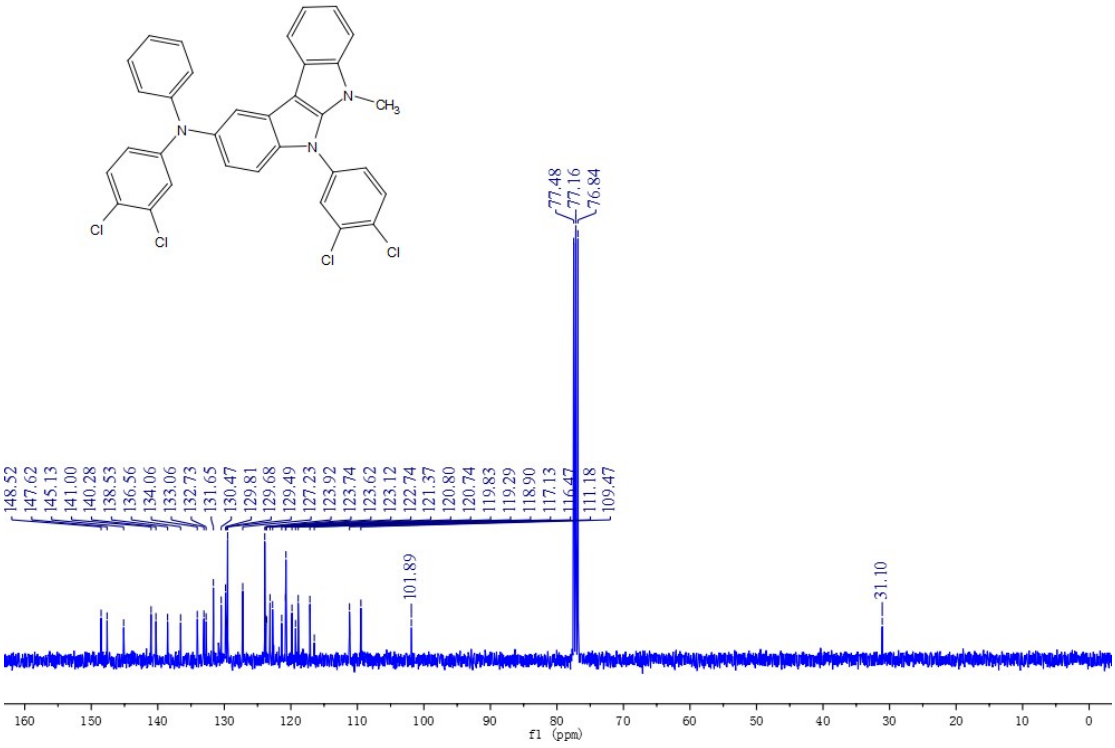
(19) ^{13}C-NMR (100 MHz, $CDCl_3$) spectrum of 3ia



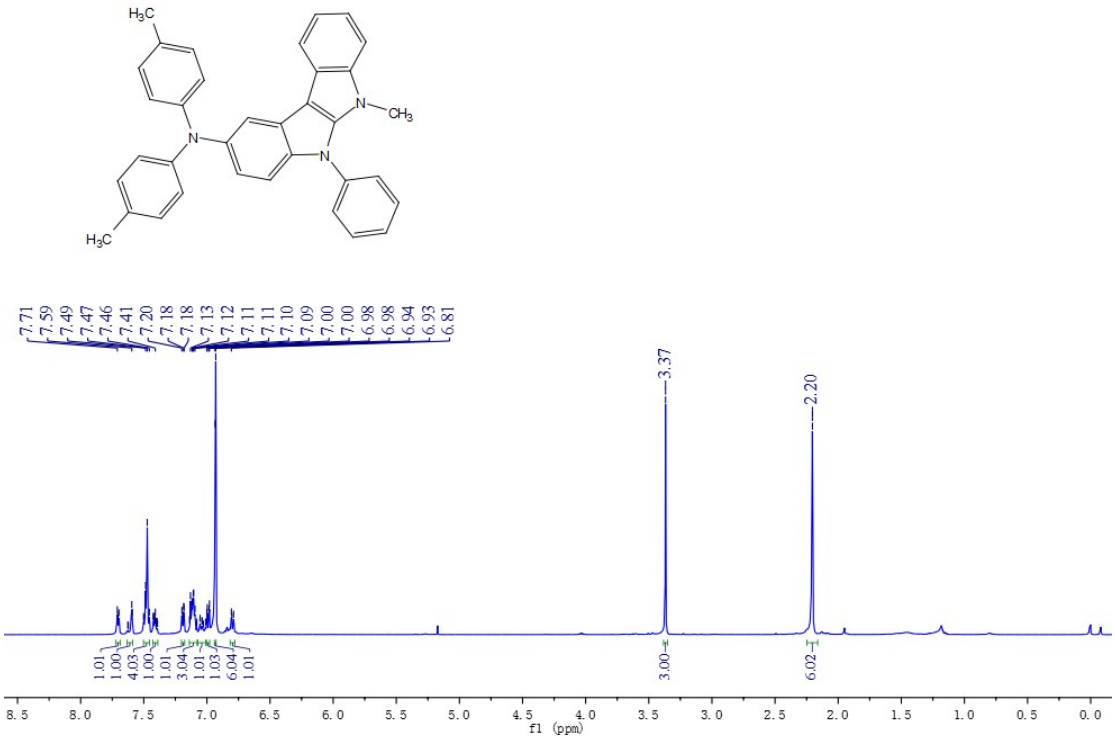
(20) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3ja



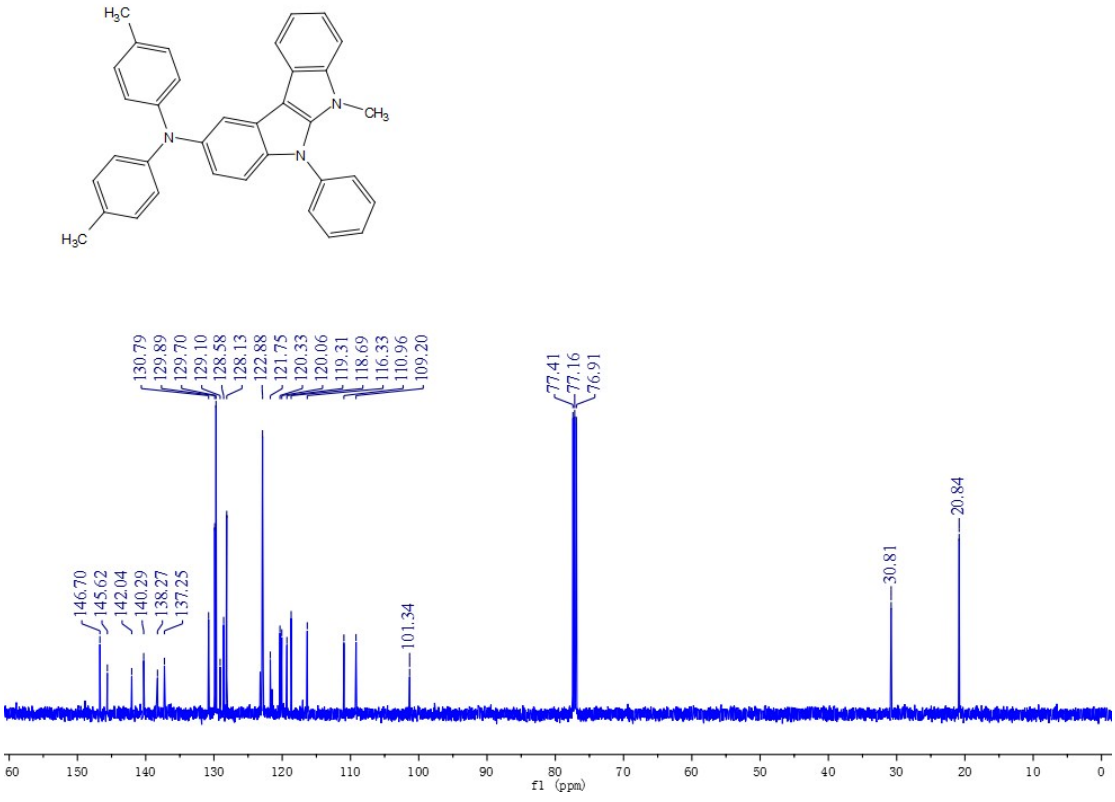
(21) ^{13}C-NMR (100 MHz, $CDCl_3$) spectrum of 3ja



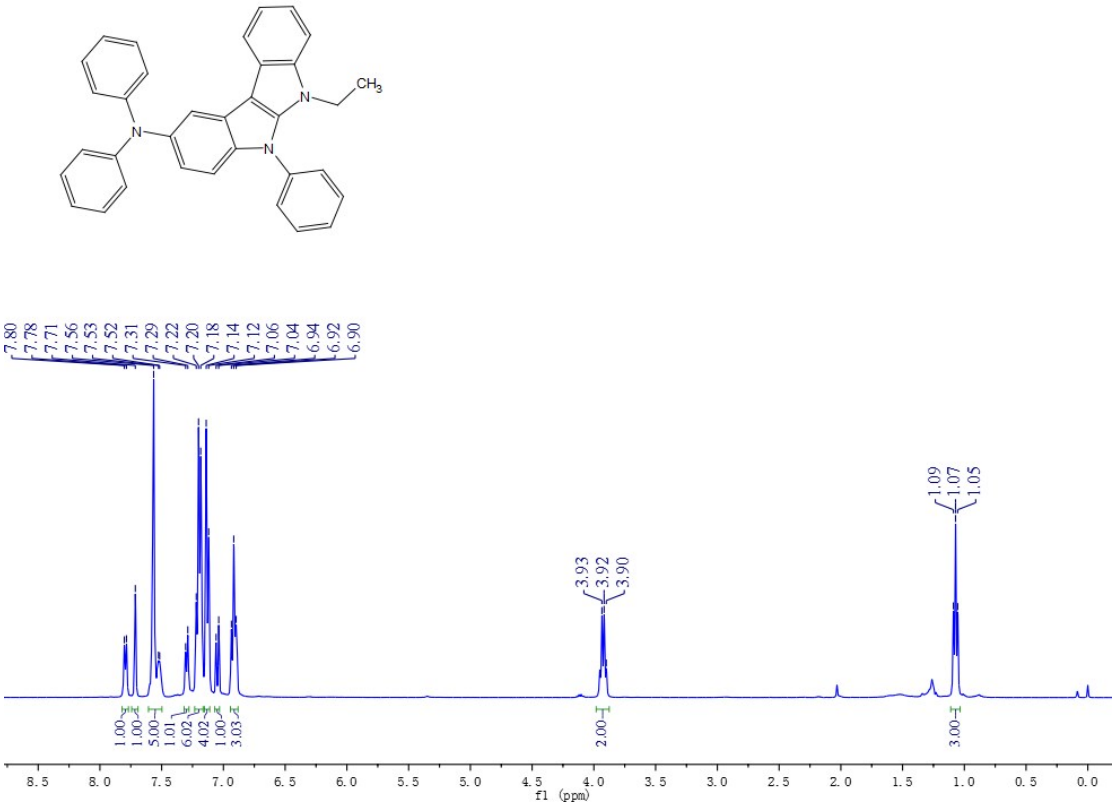
(22) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 3ka



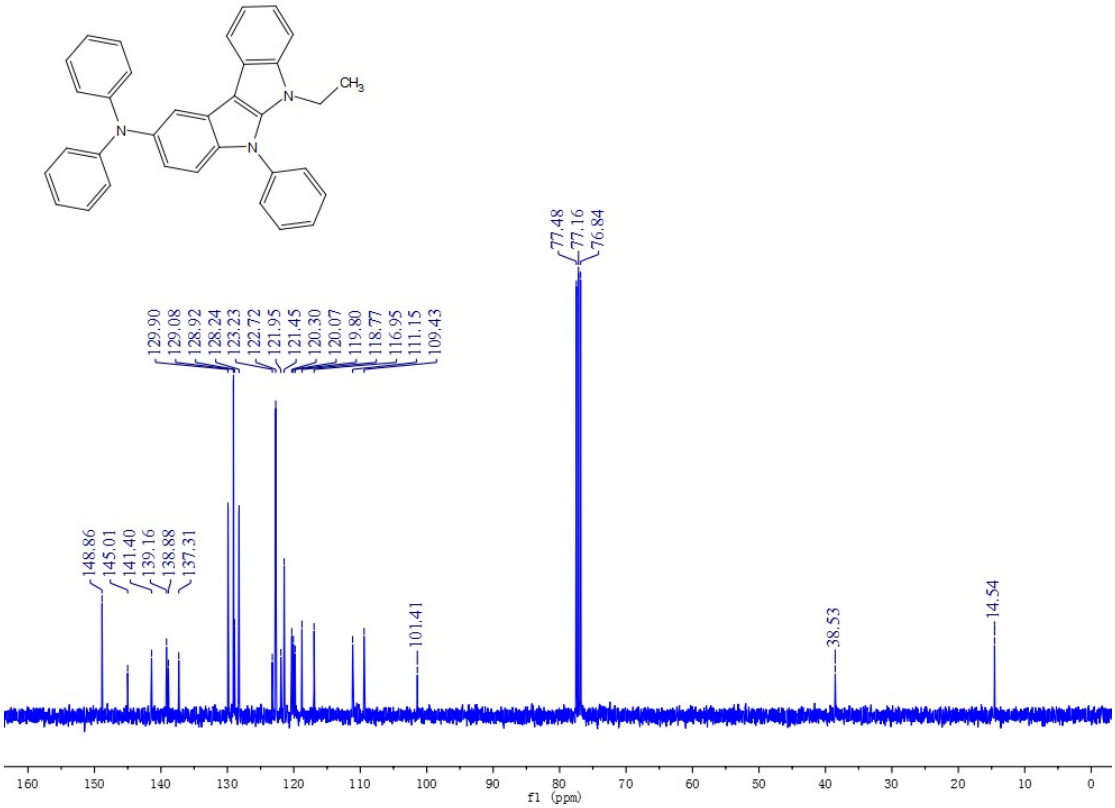
(23) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of 3ka



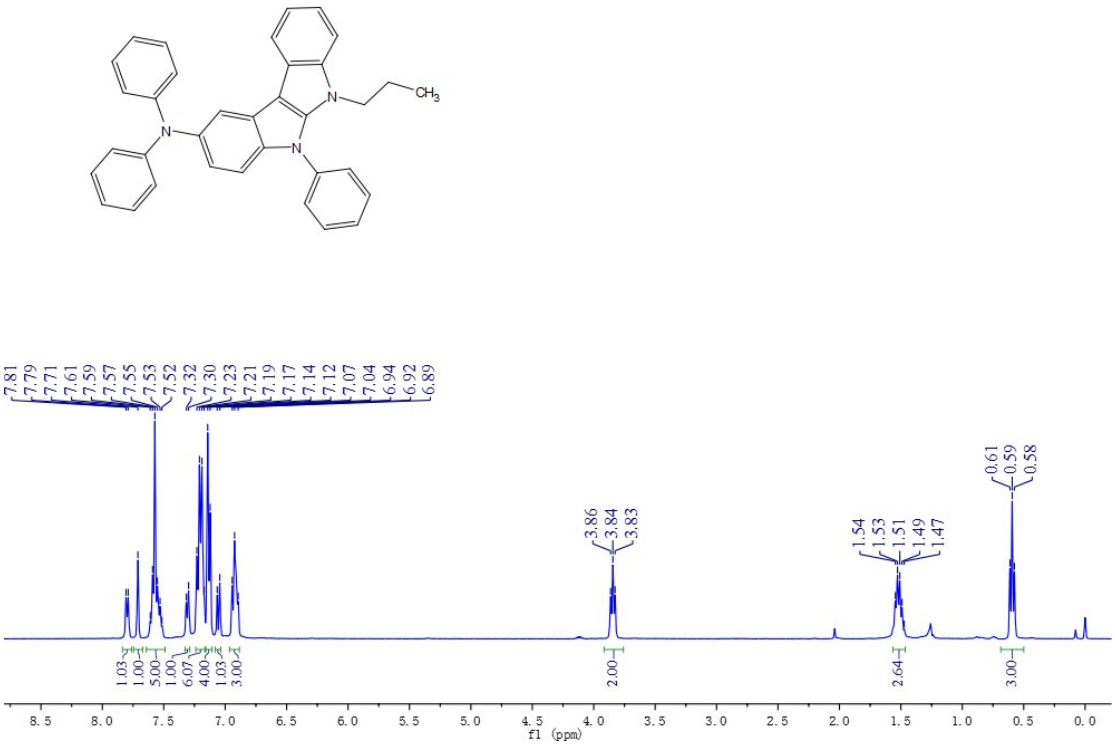
(24) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3ab



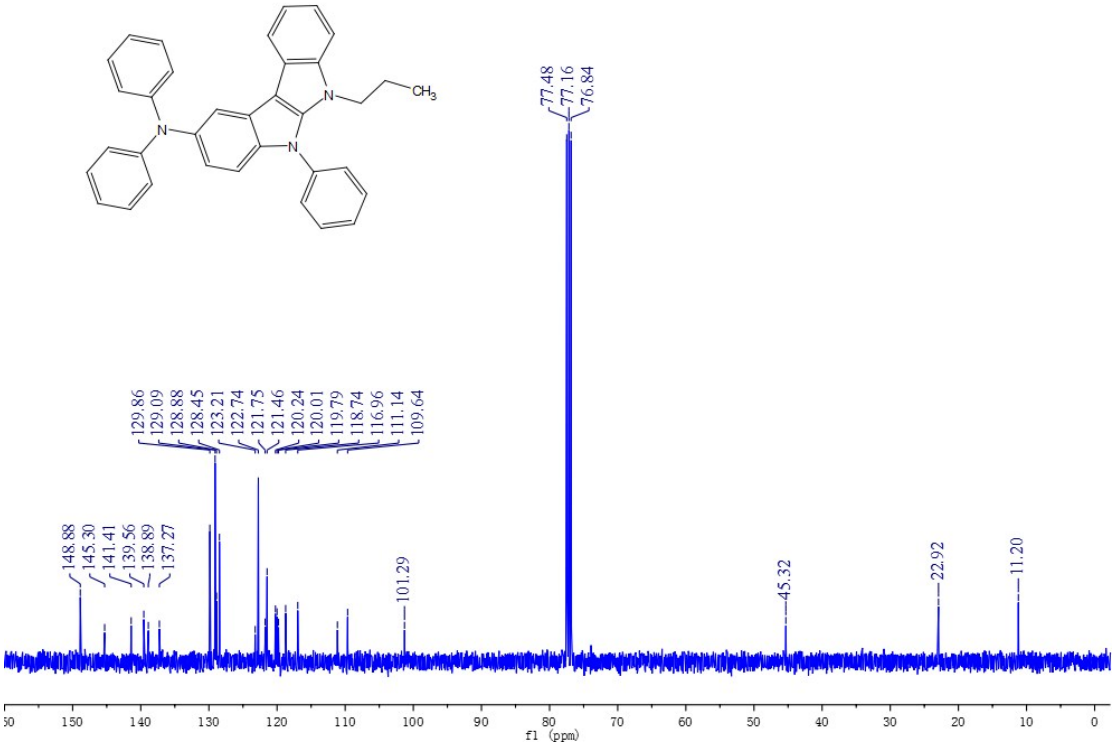
(25) ^{13}C-NMR (100 MHz, $CDCl_3$) spectrum of 3ab



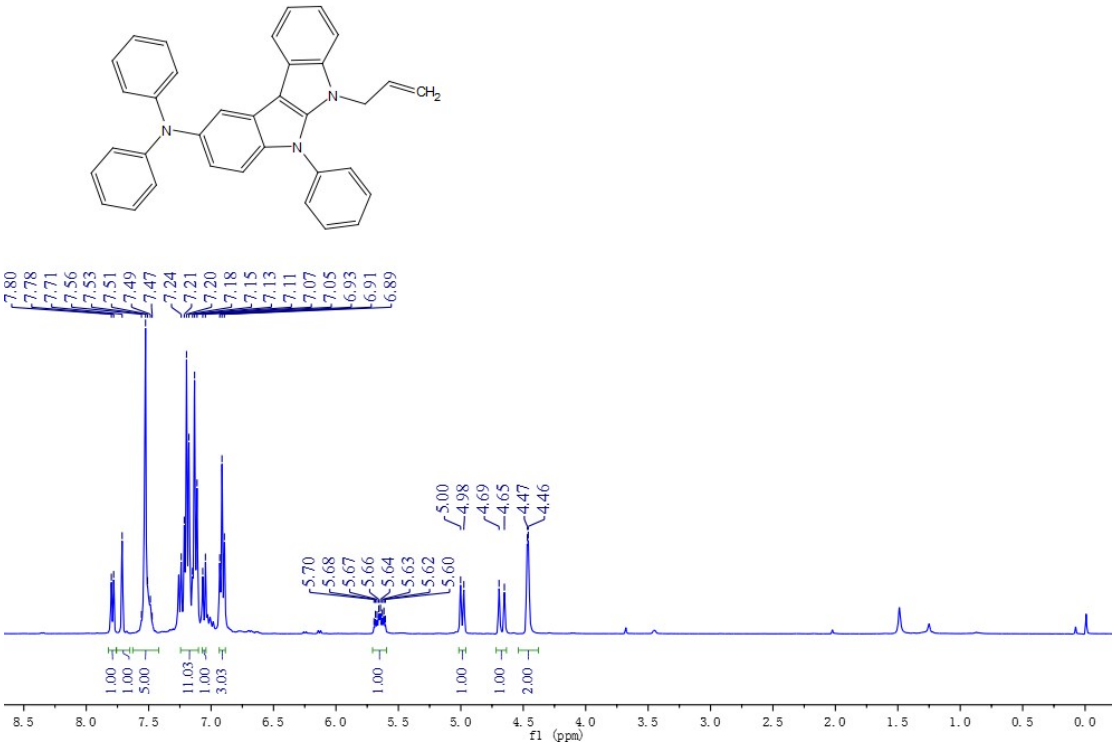
(26) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3ac



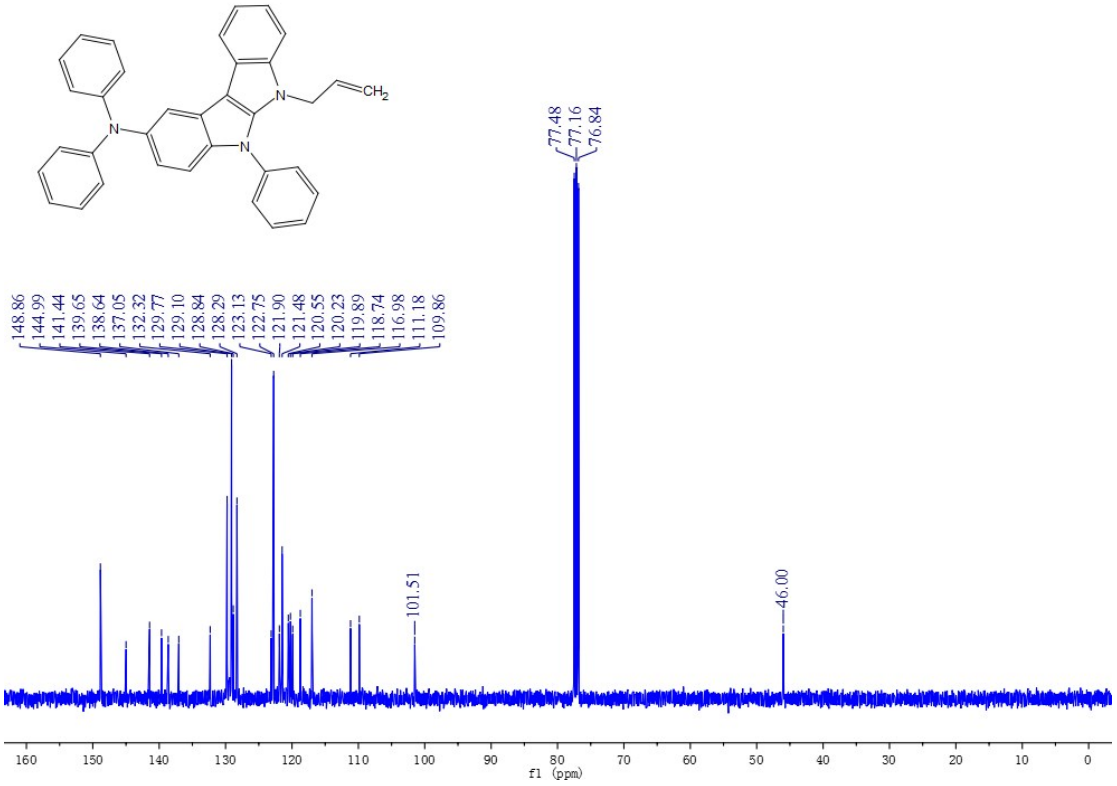
(27) ^{13}C-NMR (100 MHz, $CDCl_3$) spectrum of 3ac



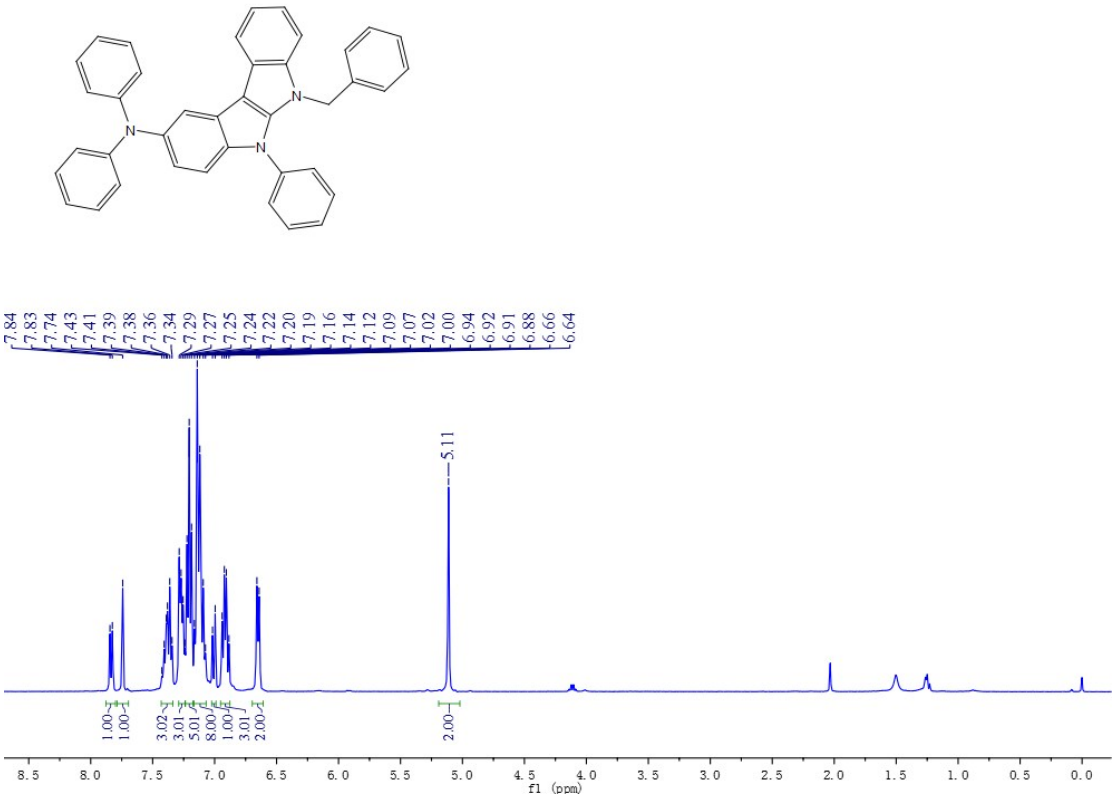
(28) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3ad



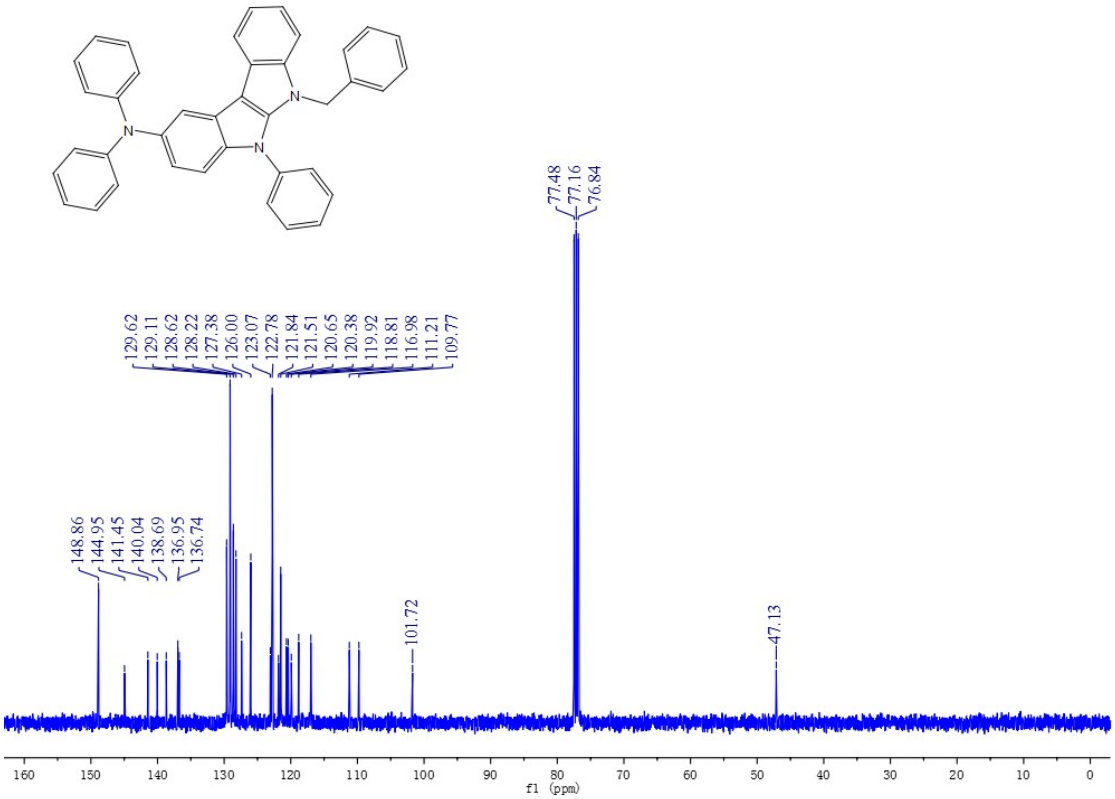
(29) ^{13}C-NMR (100 MHz, $CDCl_3$) spectrum of 3ad



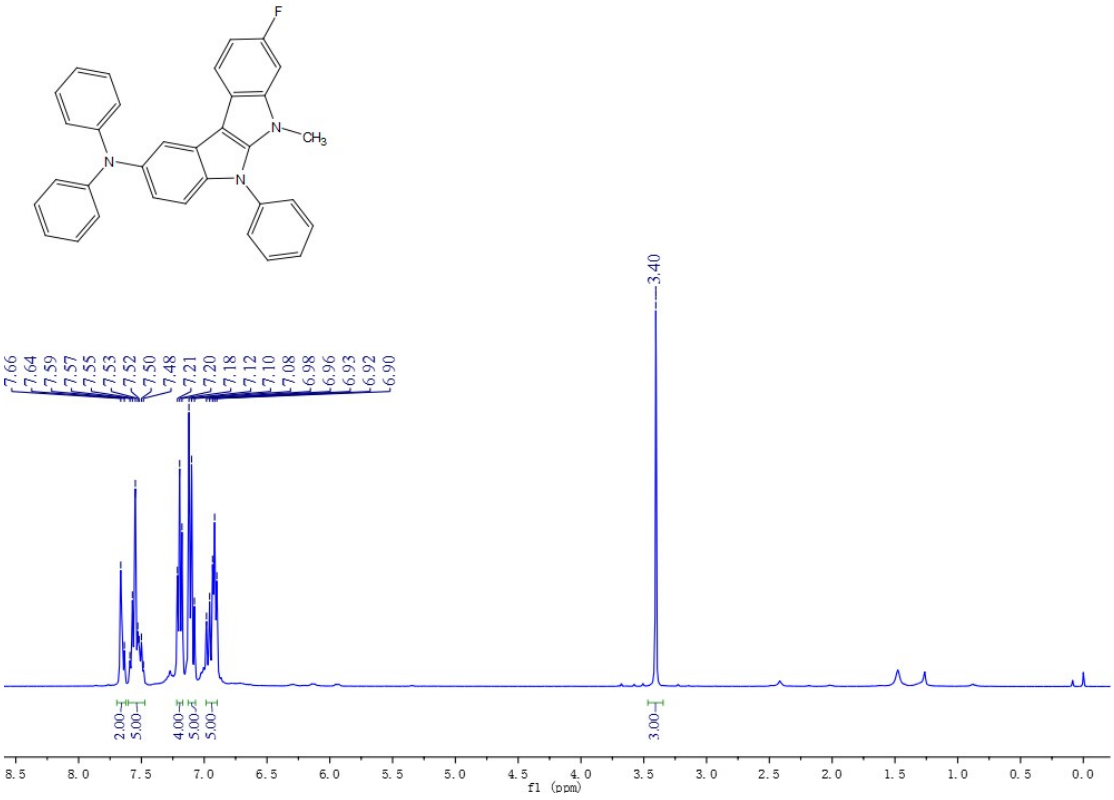
(30) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3ae



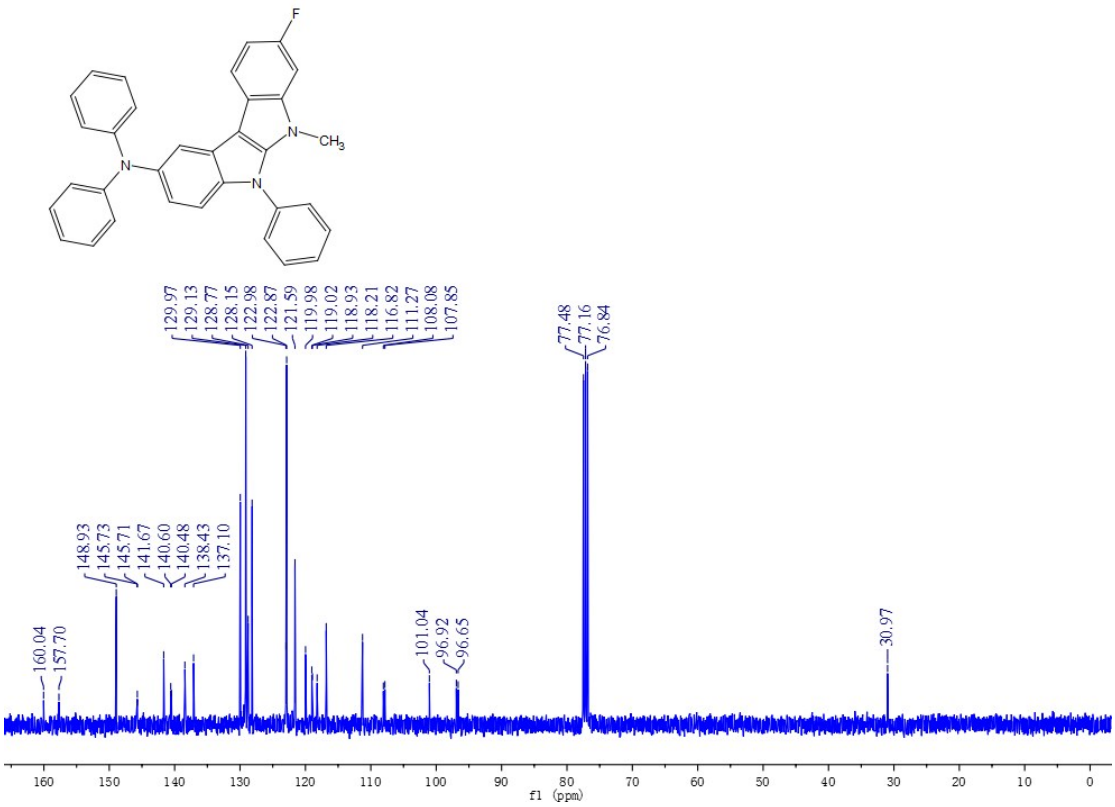
(31) ^{13}C-NMR (100 MHz, $CDCl_3$) spectrum of 3ae



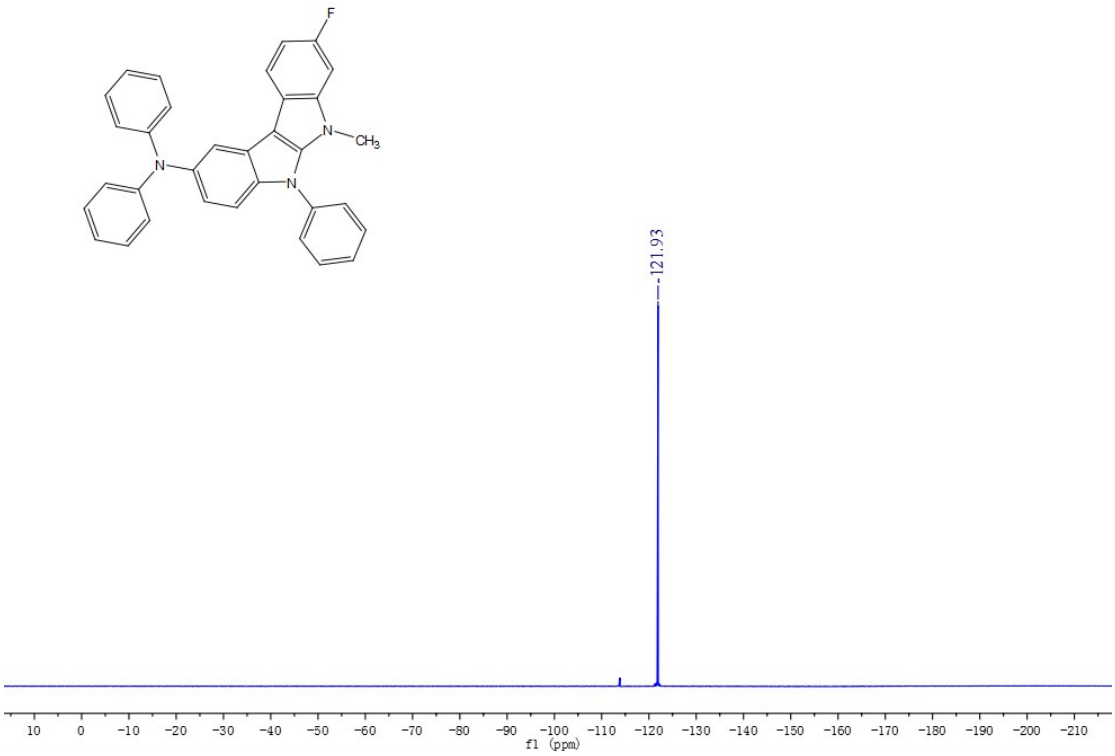
(32) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3af



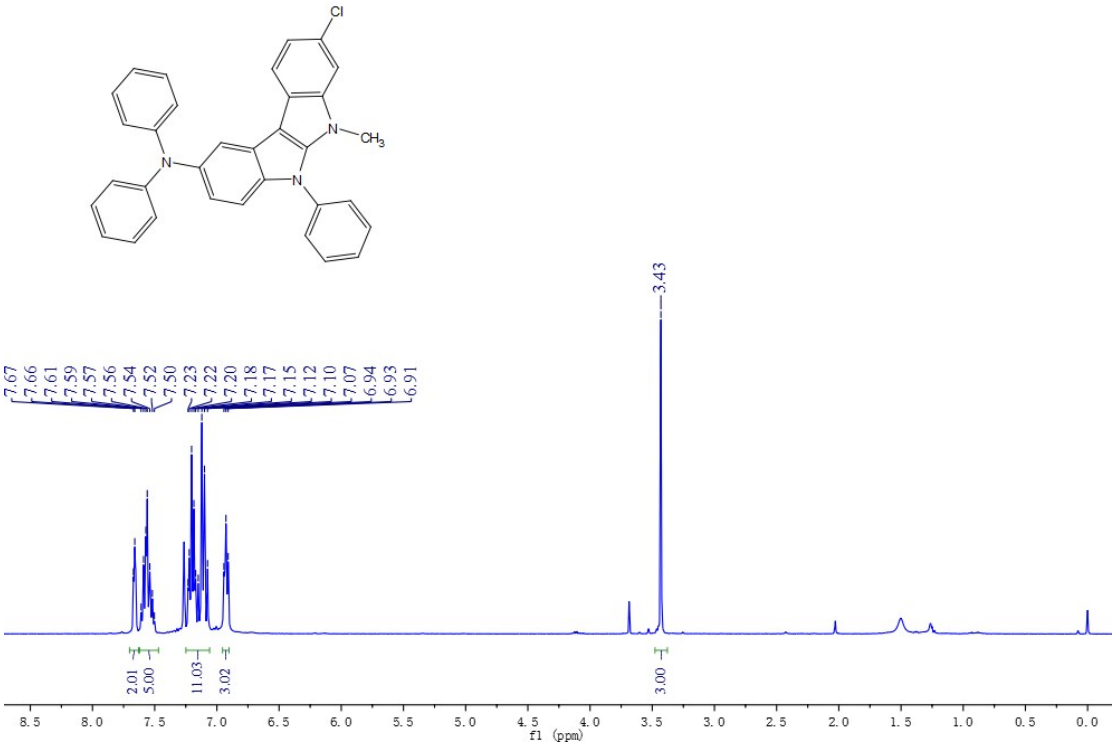
(33) ^{13}C-NMR (100 MHz, $CDCl_3$) spectrum of 3af



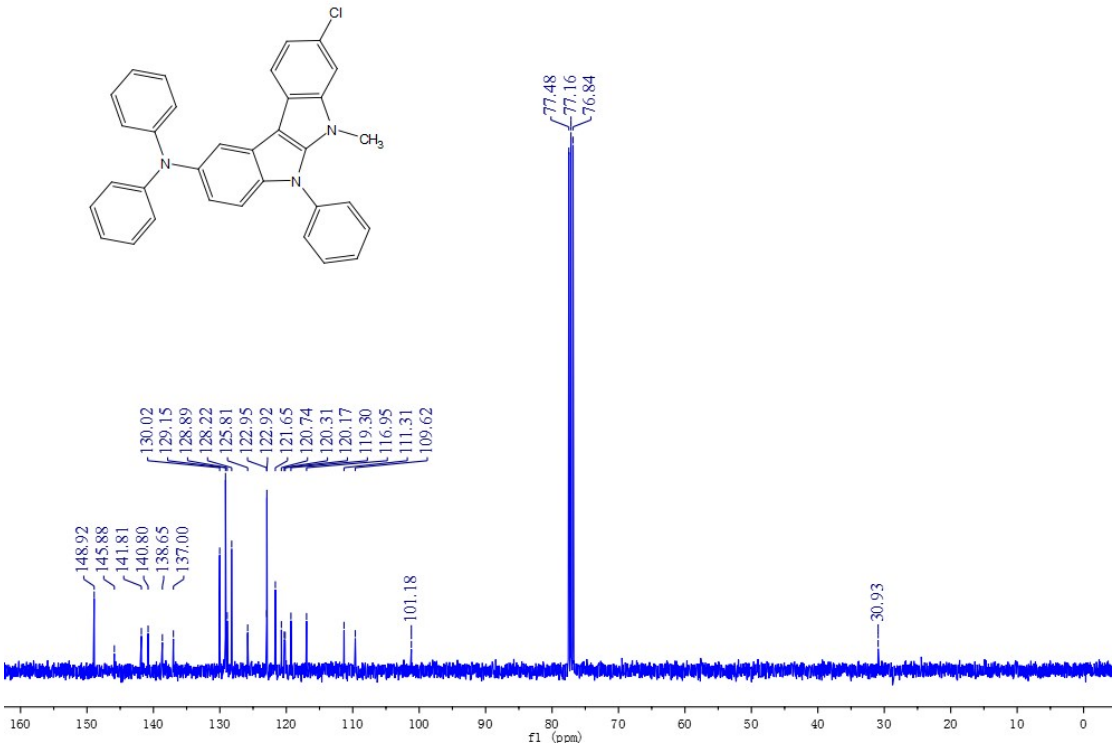
(34) ^{19}F-NMR (376 MHz, $CDCl_3$) spectrum of 3af



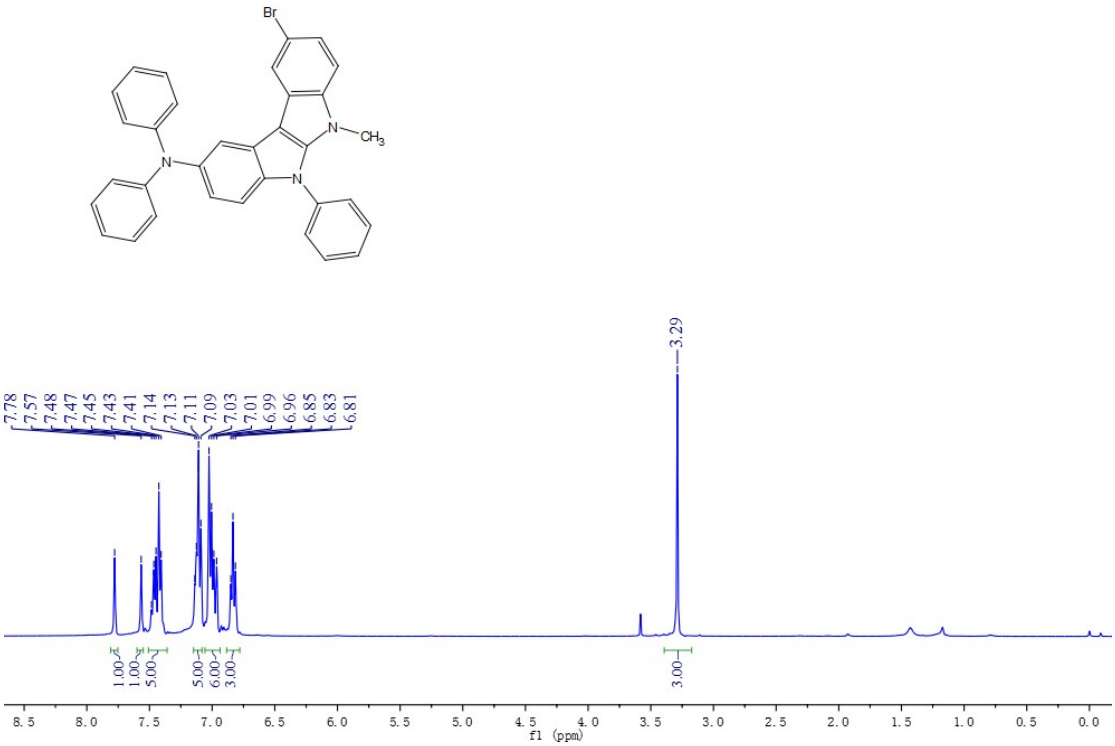
(35) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3ag



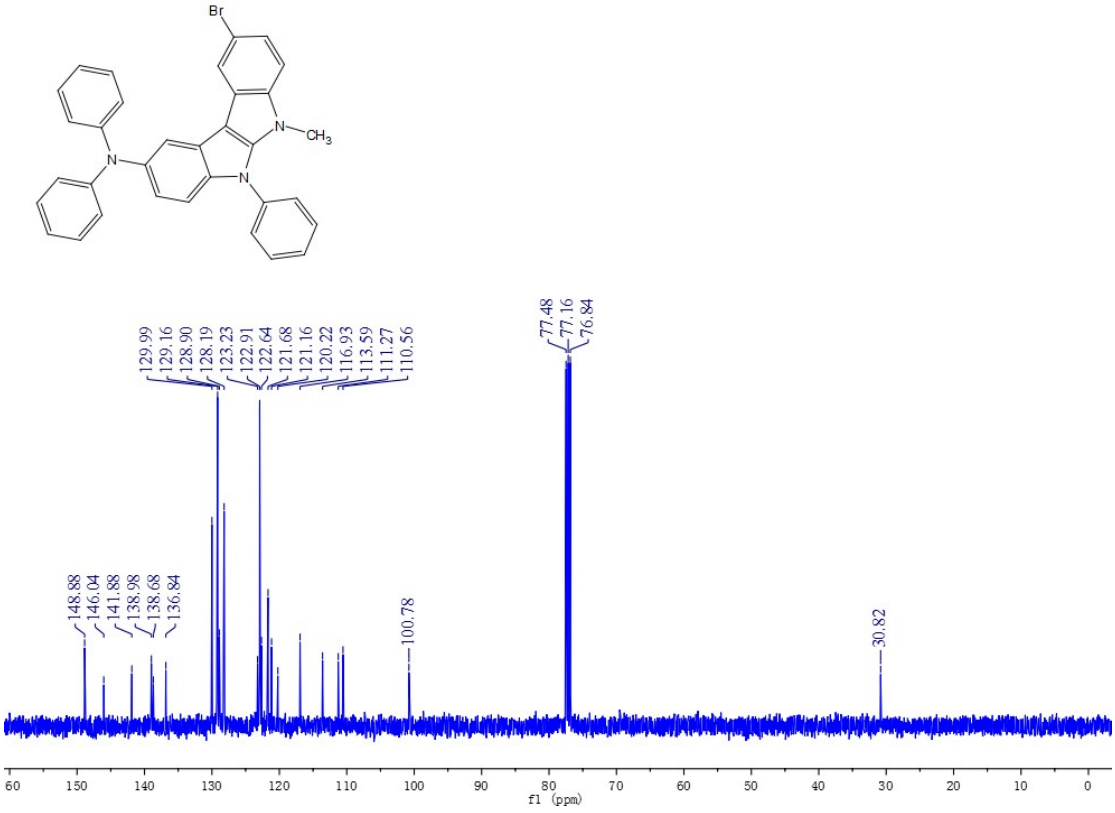
(36) ^{13}C-NMR (100 MHz, $CDCl_3$) spectrum of 3ag



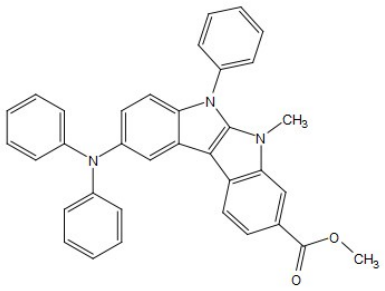
(37) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3ah

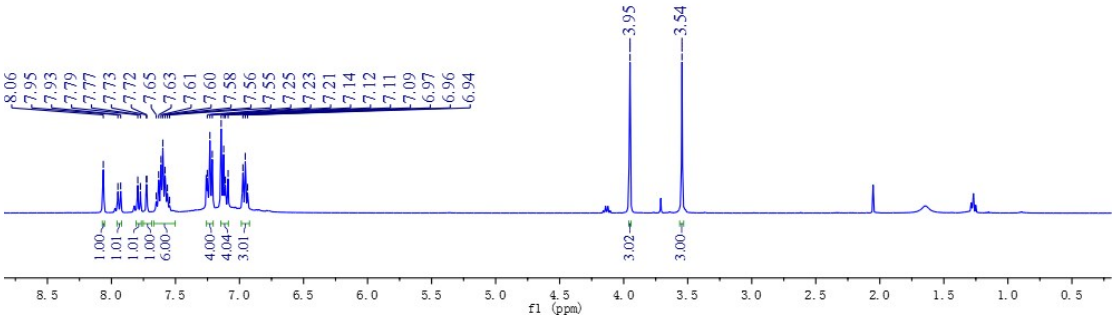


(38) ^{13}C-NMR (100 MHz, $CDCl_3$) spectrum of 3ah

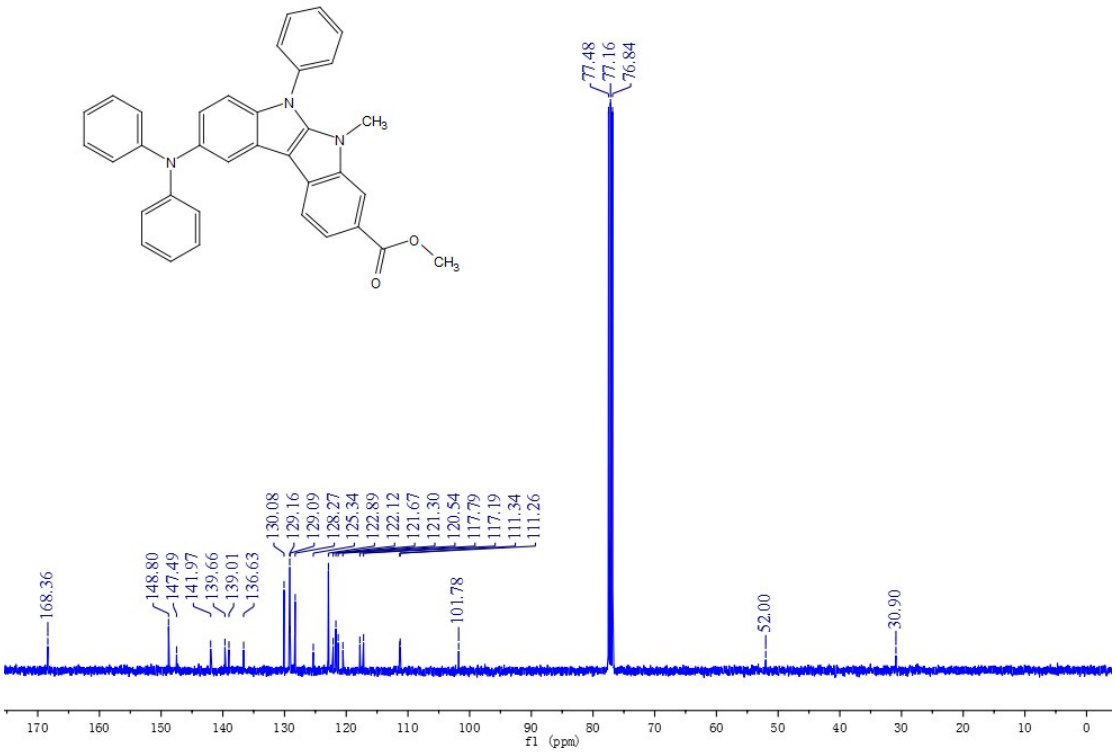


(39) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3ai

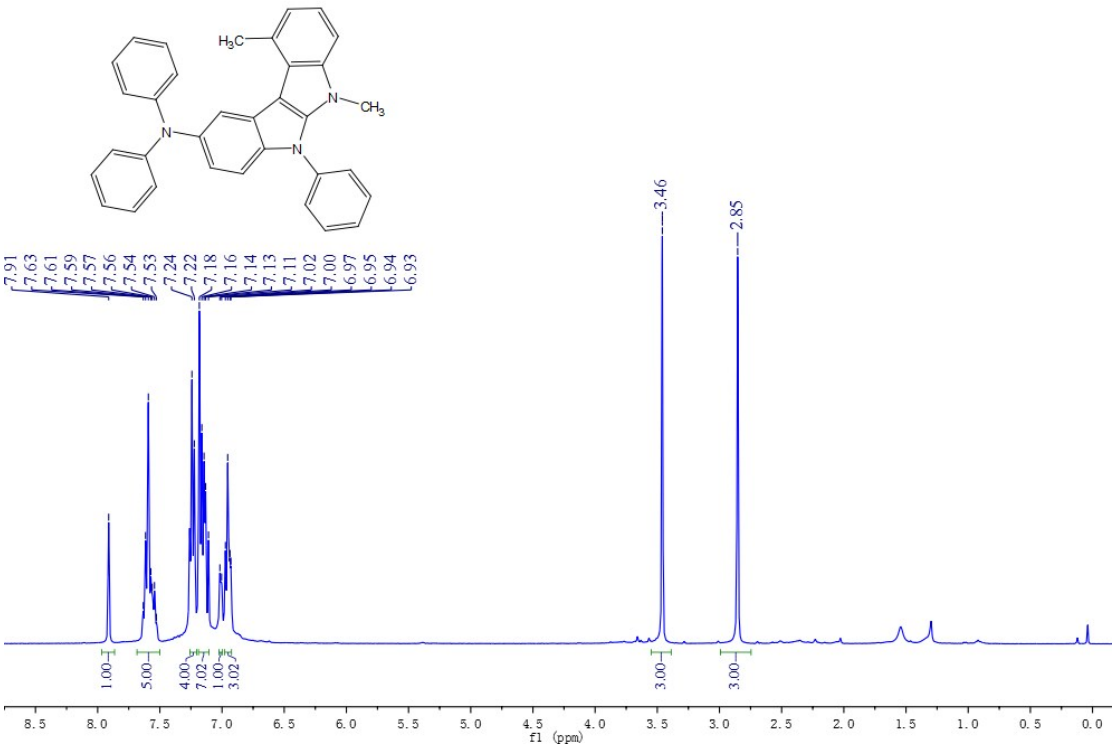




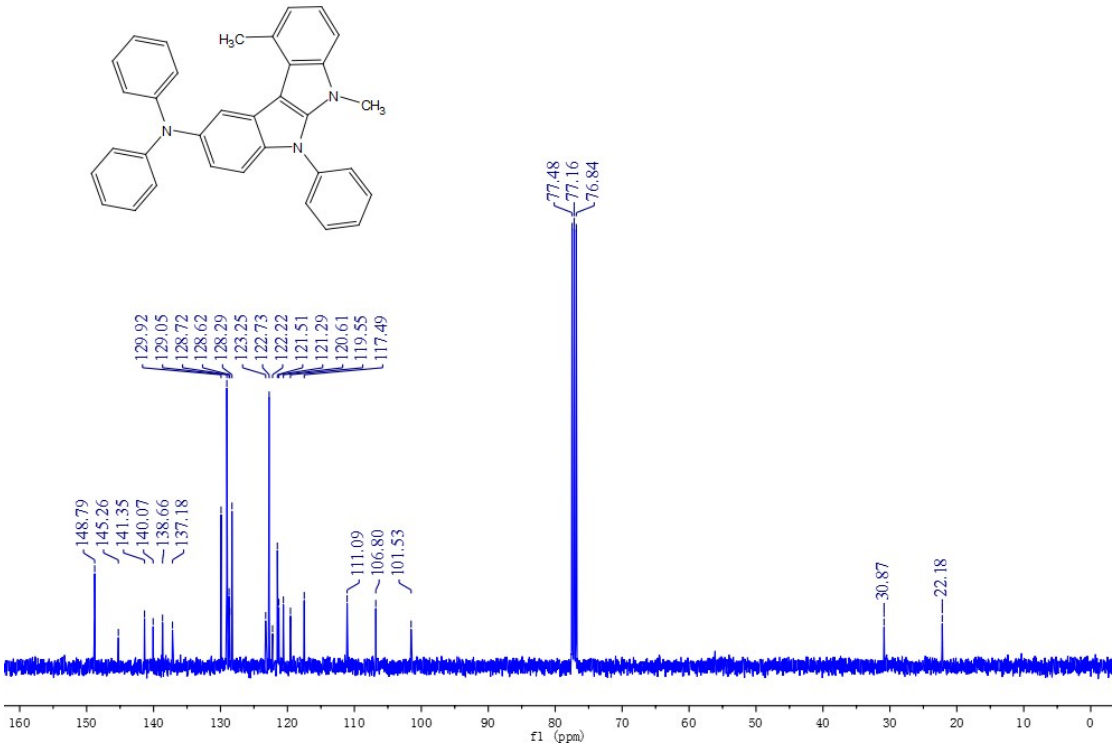
(40) ^{13}C-NMR (100 MHz, $CDCl_3$) spectrum of 3ai



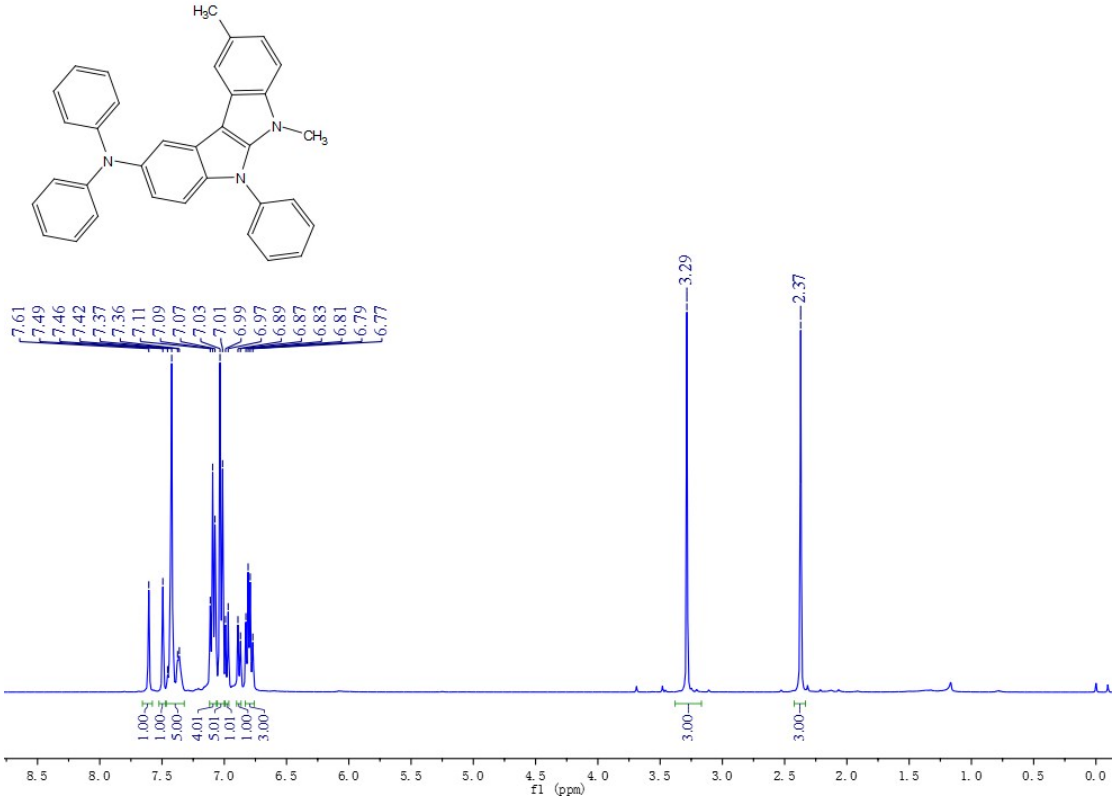
(41) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3aj



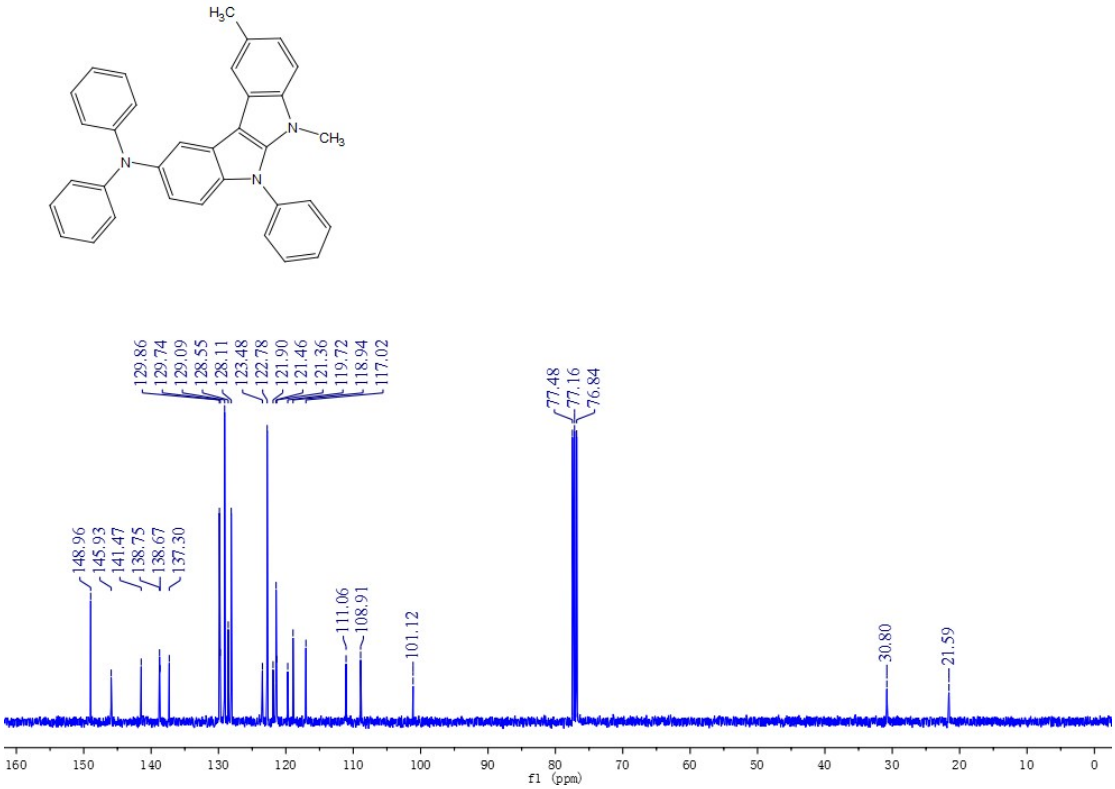
(42) ^{13}C-NMR (100 MHz, $CDCl_3$) spectrum of 3aj



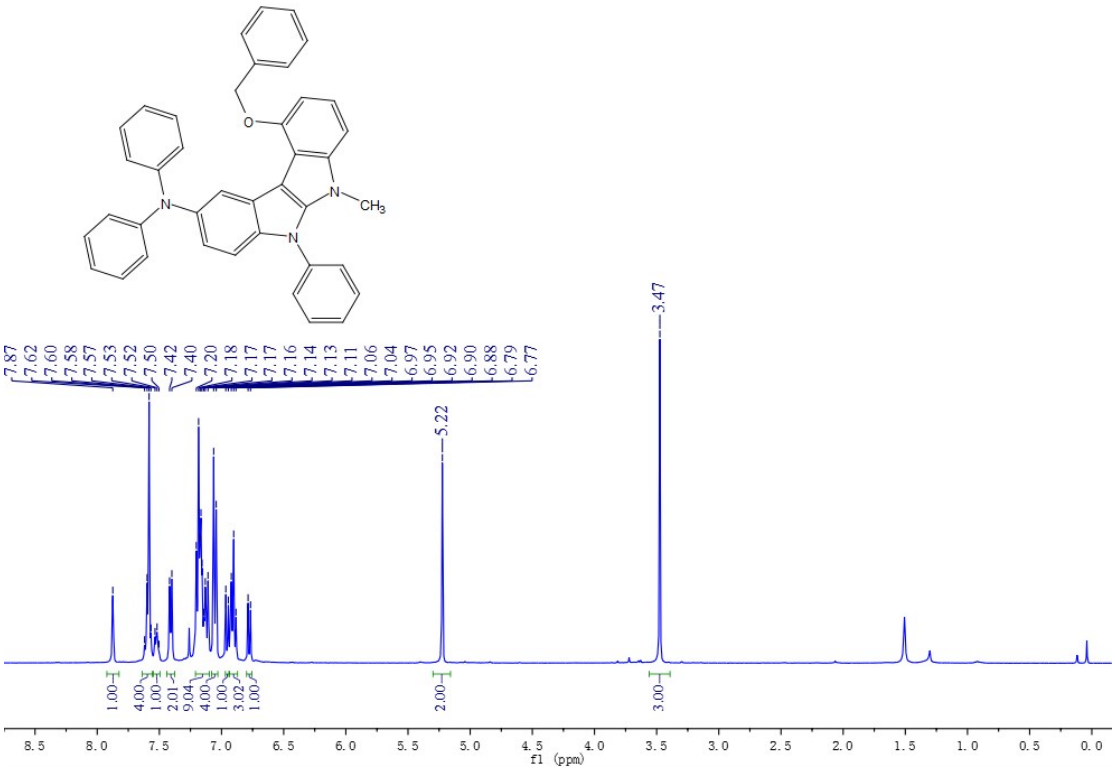
(43) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3ak



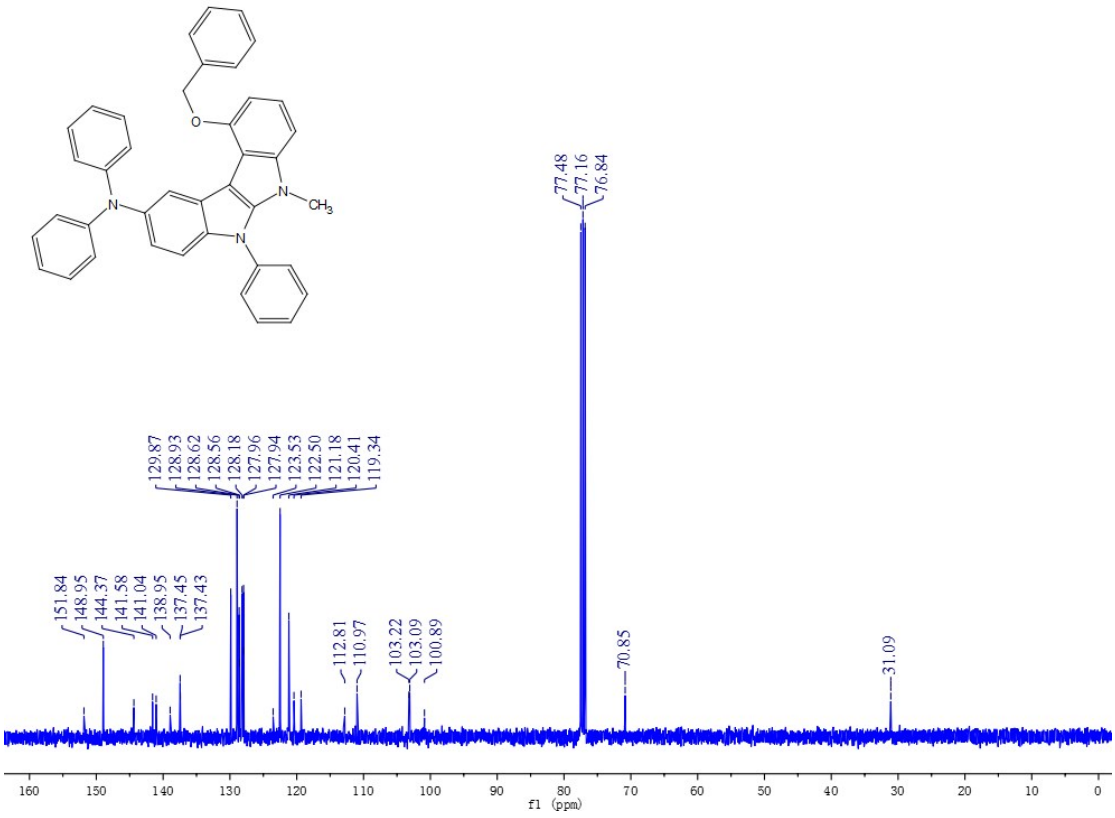
(44) ^{13}C-NMR (100 MHz, $CDCl_3$) spectrum of 3ak



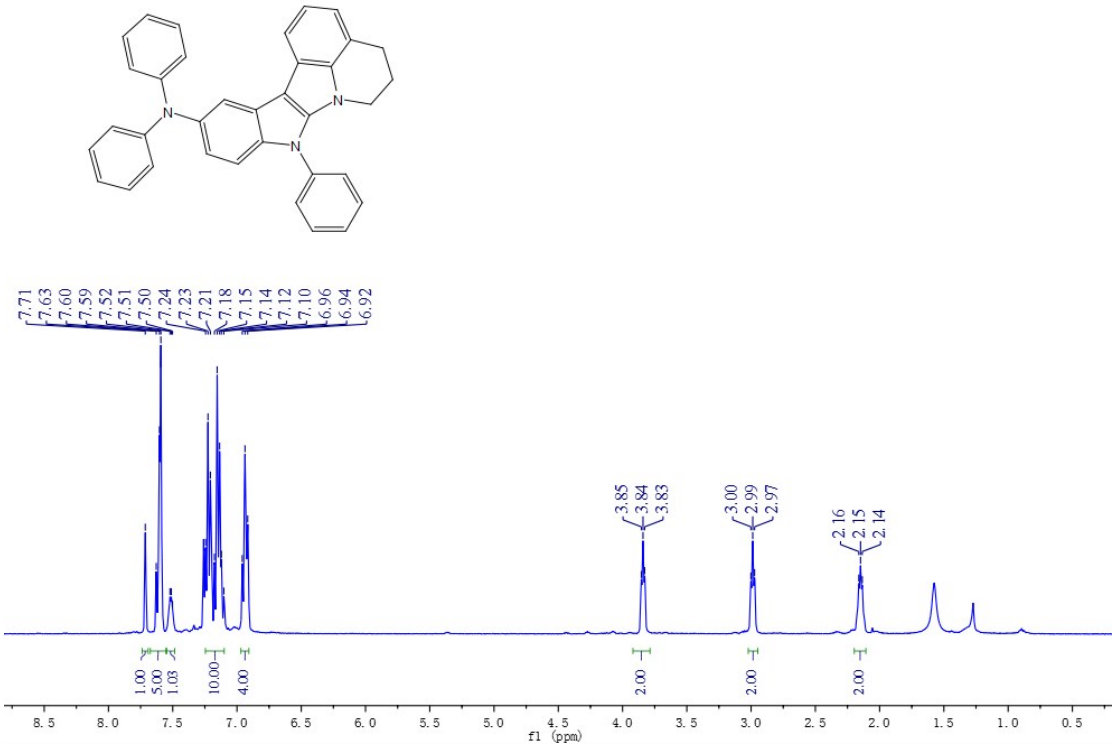
(45) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3al



(46) ^{13}C-NMR (100 MHz, $CDCl_3$) spectrum of 3al



(47) ^{1}H-NMR (400 MHz, $CDCl_3$) spectrum of 3am



(48) ^{13}C-NMR (100 MHz, $CDCl_3$) spectrum of 3am