Electronic Supplementary Information

Synthesis of 3-halogenated 2,3′-biindoles by a copper-mediated 2,3-difunctionalization of 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. Melting points were measured on an Electrothemal SGW-X4 microscopy digital melting point apparatus and are uncorrected; ^{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 effected at 254 nm; Unless otherwise stated, all the reagents were purchased from commercial sources, used without further purification.

All the reagents were purchased from Bide Pharmatech Ltd. and Energy Chemical. All solvents were purchased from Greagent (Shanghai Titansci incorporated company) and used without further purification. All reactions were heated by metal sand bath (WATTCAS, LAB-500, https://www.wattcas.com). Column chromatography was performed on silica gel (200-300 mesh). Reactions were monitored by using thin layer chromatography (TLC) (Qingdao Jiyida silica gel reagent factory GF254).

2. Substrates preparation.

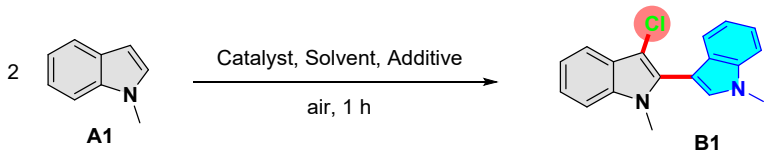
General Procedure for the preparation of *N*-substituted indole derivatives (A2, A4-A34)[1]:

Procedure for 6-chloro-1-methyl-1*H*-indole (**A12**): To a suspended solution of NaH (0.55 g, 65% dispersion in mineral oil, 15.0 mmol) in DMF (5.0 mL), 6-chloro-1*H*-indole (1.51 g, 10.0 mmol) in DMF (5.0 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 (20.0 mL), and extracted with ether (3 × 20.0 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 **A12** 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. Optimization of the reaction conditions. [a]



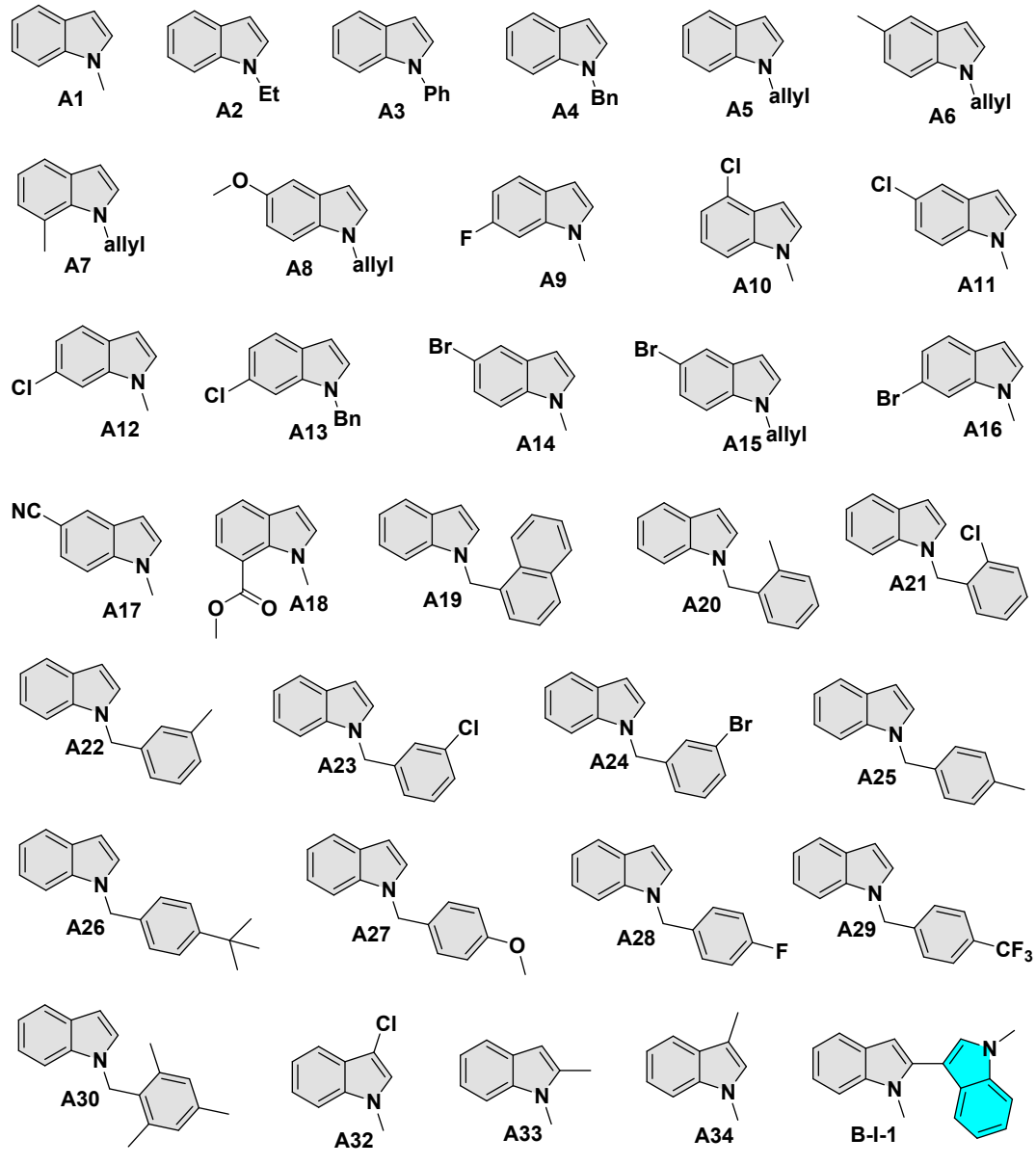
Entry	Catalyst	Solvent	Additive	Isolated yield of **B1** (%)
1.	$CuCl_2$	acetonitrile	NCS	27
2.	CuCl	acetonitrile	NCS	<5
3.	CuBr	acetonitrile	NCS	0
4.	CuI	acetonitrile	NCS	15
5.	$Cu(OAc)_2$	acetonitrile	NCS	20
6.	$Cu(OTf)_2$	acetonitrile	NCS	trace
7.	$FeCl_3$	acetonitrile	NCS	13
8.	$CoCl_2$	acetonitrile	NCS	22
9.	$CuCl_2$	1,4-dioxane	NCS	0
10.	$CuCl_2$	DMF	NCS	16
11.	$CuCl_2$	DMSO	NCS	19
12.	$CuCl_2$	acetone	NCS	0
13.	$CuCl_2$	toluene	NCS	0
14.	$CuCl_2$	acetonitrile	$AlCl_3$	16
15.	$CuCl_2$	acetonitrile	NH_4Cl	trace
16.	$CuCl_2$	acetonitrile	LiCl	10
17.	$CuCl_2$	acetonitrile		(59, **67**, 52) [b]
18.	$CuCl_2$	acetonitrile		54 [c]

[a] Conditions: unless otherwise stated, all the reactions were performed with A1 (0.5 mmol), catalyst (20 mol%), additive (1.0 equiv.), solvent (3.0 mL) at room temperature under air for 1 h; [b] 100 mol%, 120 mol% and 150 mol% of catalysts were used respectively; [c] The reaction was performed for 2 h and 120 mol% of catalyst was used.

4. Typical procedure for the synthesis of B1.

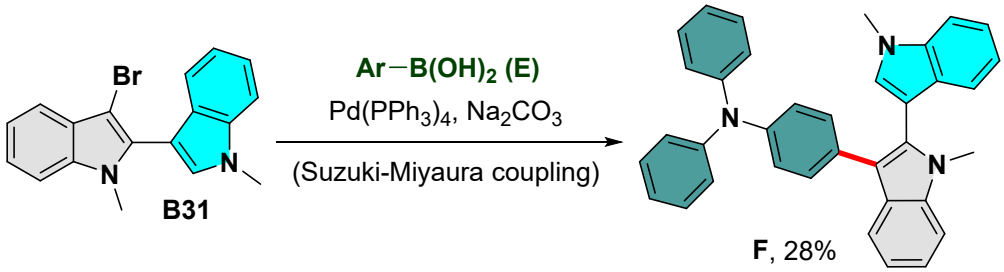
The mixture of 1-methylindole **A1** (65.5 mg, 0.5 mmol), $CuCl_2$ (81.0 mg, 0.6 mmol) in acetonitrile (1.5 mL) was stirred at room temperature for 1 h under air. The resulting mixture was concentrated by removing the solvent under vacuum, and the residue was purified by preparative TLC on silica gel by using petroleum ether/ethyl acetate (20 :1) as the eluent to give **B1** as a yellow solid (49.2 mg, 67% yield).

Scheme S1. **Substrates employed for the synthesis of 3-halogenlated 2,3′-biindoles.**



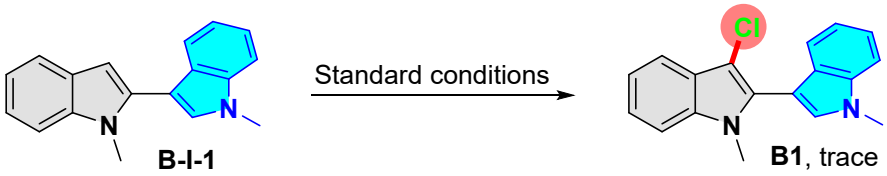
5. Synthetic utility.

The mixture of 3-bromo-1,1'-dimethyl-1*H*,1'*H*-2,3'-biindole **B31** (84.5 mg, 0.25 mmol), (4-(diphenylamino)phenyl)boronic acid (108.0 mg, 0.37 mmol), and Na_2CO_3 (53.0 mg, 0.50 mmol) in toluene: water: ethanol (3 : 2 : 1) was stirred at 125 ℃ for 18 h under N_2. 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 **F** as a yellow solid, (35.0 mg, 28% yield).

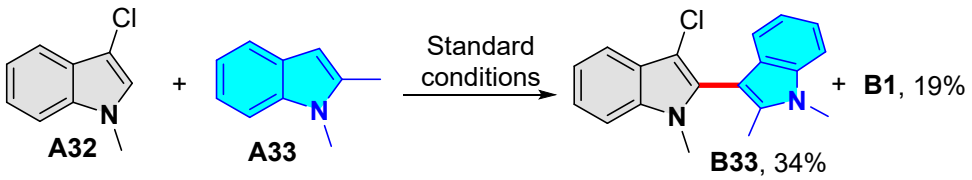


6. Control experiments.

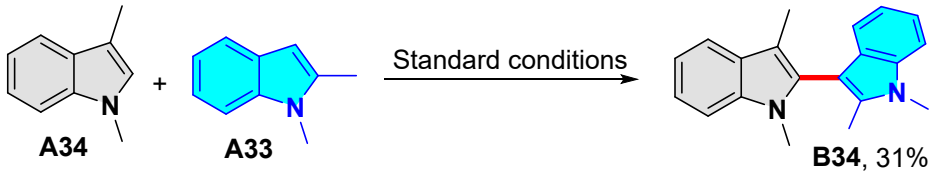
(1) The preparation of **B-I-1** was similar to the literature procedures[2]. Under the optimized reaction conditions, the reaction of **B-I-1** (65.0 mg, 0.5 mmol) was carried. Then, the crude reaction mixture was analyzed by TLC, and only a trace of **B1** was observed.



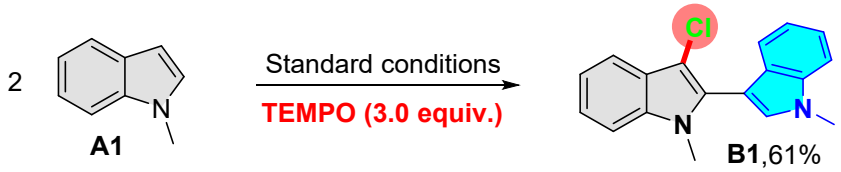
(2) The preparation of **A32** was similar to the literature procedures[3]. Under the optimized reaction conditions, the reaction of **A32** (41.3 mg, 0.25 mmol) and **A33** (36.3 mg, 0.25 mmol) was carried. Then, the reaction mixture was purified by preparative TLC on silica eluting with petroleum ether/ethyl acetate (20:1) to give product **B33** as white solid (26.2 mg, 34% yield) and product **B1** as yellow solid (14.0 mg, 19% yield).



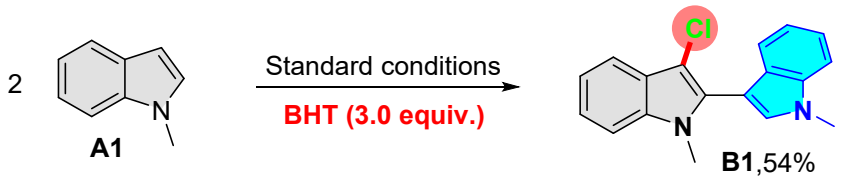
(3) Under the optimized reaction conditions, the reaction of **A34** (36.3 mg, 0.25 mmol) and **A33** (36.3 mg, 0.25 mmol) was carried. Then, the reaction mixture was purified by preparative TLC on silica eluting with petroleum ether/ethyl acetate (20:1) to give product **B34** as white solid (22.3mg, 31% yield).



(4) 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 **B1** as yellow solid (44.8 mg, 61% yield).



(5) Under the optimized reaction conditions, the model reaction was carried out by introducing 3.0 equivalent of BHT (2,6-di-tert-butyl-4-methylphenol). Then, the reaction mixture was purified by preparative TLC on silica eluting with petroleum ether/ethyl acetate (20:1) to give product **B1** as yellow solid (39.7 mg, 54% yield).



7. Single crystal X-ray diffraction of B1.

White block-like single crystals of **B1** 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.

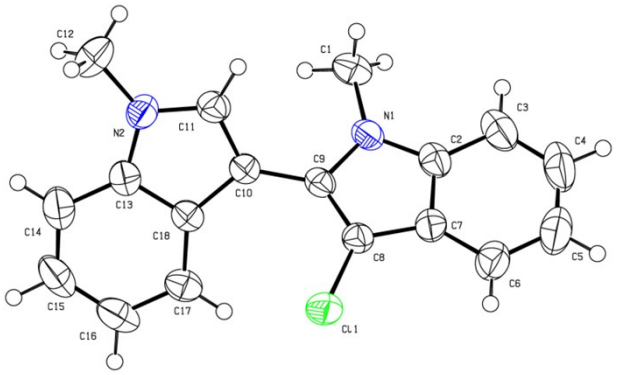


Figure S1. ORTEP drawing of **B1** with the numbering scheme.

Table S2. Crystal data and structure refinement for **B1**.

Identification code	B1	
Empirical formula	$C_{18}H_{15}ClN_2$	
Formula weight	294.77	
Temperature	293(2) K	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 13.1846(10) Å	□= 90°.
	b = 7.7958(7) Å	□= 113.389(9)°.
	c = 15.6184(12) Å	□ = 90°.
Volume	1473.4(2) $Å^3$	
Z	4	
$\rho_{calc}g$	1.329 cm^3	
μ	0.253 mm^{-1}	
F(000)	616.0	
Crystal size	0.22x 0.20 x 0.18 mm^3	
Radiation	MoKα (λ = 0.71073)	
2^{Θ} range for data collection	7.372 to 58.356°	
Index ranges	-16<=h<=12, -5<=k<=9, -19<=l<=19	

Reflections collected	6775
Independent reflections	3375 [R(int) = 0.0292,R(sigma) = 0.0515]
Data / restraints / parameters	3375 / 0 / 192
Goodness-of-fit on F^2	1.070
Final R indices [I>=2σ (I)]	R1 = 0.0608, wR2 = 0.1305
Final R indices (all data)	R1 = 0.0887, wR2 = 0.1473
Largest diff. peak and hole	0.27 and -0.36 e.Å^{-3}

Table S3. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **B1**. U(eq) is defined as 1/3 of of the trace of the orthogonalised U^{ij} tensor.

Atom	*x*	*y*	*z*	U(eq)
N2	9216.7(15)	1892(3)	2641.7(14)	43.6(5)
C10	7394.7(17)	1647(3)	2298.4(14)	35.4(5)
N1	6221.0(15)	1240(3)	3199.6(12)	40.0(5)
C9	6341.4(17)	1771(3)	2394.2(14)	34.7(5)
C2	5161.1(19)	1609(3)	3108.0(16)	41.9(6)
C7	4579.1(18)	2361(3)	2232.5(16)	39.6(5)
C18	7605.9(18)	1081(3)	1503.4(15)	35.7(5)
C8	5344.1(18)	2421(3)	1797.4(15)	37.2(5)
C13	8750.1(18)	1250(3)	1752.8(16)	39.4(5)
C11	8401.8(18)	2123(3)	2959.1(16)	41.3(6)
C17	6947(2)	454(3)	620.0(15)	44.4(6)
C3	4663(2)	1355(4)	3736(2)	60.3(8)
C1	7046(2)	434(4)	4012.2(15)	49.6(6)
C16	7438(2)	39(4)	15.2(17)	57.4(7)
C12	10366(2)	2357(4)	3152(2)	61.7(8)
C14	9245(2)	810(4)	1139.8(19)	55.8(7)
C4	3583(3)	1898(5)	3468(2)	73.1(10)
C6	3488(2)	2901(4)	1985(2)	55.5(7)
C5	3007(2)	2671(5)	2610(2)	71.0(9)
C15	8574(3)	215(4)	281.4(19)	63.3(8)
Cl1	5071.8(5)	3368.9(9)	732.7(4)	49.9(2)

Table S4. Anisotropic Displacement Parameters (Å^2×10^3) for **B1**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N2	35.4(10)	46.2(13)	48.5(12)	-3.3(10)	15.9(9)	-1.5(9)
C10	37.8(11)	35.2(13)	33.8(11)	-0.2(10)	14.9(9)	0.9(9)
N1	44.5(11)	44.8(13)	32.1(10)	-0.9(9)	17.0(8)	-1.2(9)
C9	40.2(12)	34.7(13)	31.1(11)	-4.2(9)	16.1(9)	-4.9(10)
C2	48.8(13)	39.2(14)	43.3(13)	-9.3(11)	24.3(11)	-10.1(11)
C7	37.8(12)	39.3(14)	43.3(13)	-11.0(11)	17.8(10)	-9.1(10)
C18	42.7(12)	30.3(12)	35.0(11)	3.7(9)	16.3(10)	2.7(9)
C8	37.4(11)	39.2(14)	34.6(11)	-3.6(10)	13.9(9)	-4.0(10)
C13	44.5(13)	34.2(13)	43.8(13)	6.4(10)	22.0(11)	5.1(10)
C11	43.4(13)	41.9(15)	37.7(12)	-5.0(10)	15.1(10)	0.2(10)
C17	53.8(14)	39.3(15)	38.0(12)	1.4(11)	16.1(11)	2.1(11)
C3	73.9(19)	65(2)	55.1(16)	-9.4(14)	39.6(15)	-14.6(15)
C1	60.8(15)	49.9(17)	35.6(13)	4.9(12)	16.5(11)	3.0(13)
C16	81(2)	55.2(19)	36.2(13)	0.6(12)	22.9(13)	14.7(15)
C12	37.5(13)	65(2)	74.8(19)	3.1(16)	13.7(13)	-5.0(13)
C14	56.8(16)	60.3(19)	62.6(17)	14.3(14)	36.8(14)	14.4(13)
C4	71(2)	86(3)	87(2)	-19.7(19)	57.9(19)	-21.8(18)
C6	43.8(14)	60.9(19)	63.1(17)	-12.1(14)	22.5(13)	-6.2(13)
C5	48.3(16)	83(3)	92(2)	-20(2)	39.3(17)	-7.3(16)
C15	88(2)	68(2)	50.0(16)	9.8(14)	44.6(16)	25.1(17)
Cl1	46.8(4)	59.5(5)	39.6(3)	8.7(3)	13.2(3)	3.4(3)

Table S5. Bond Lengths for **B1**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N2	C11	1.362(3)	C7	C6	1.398(3)
N2	C13	1.370(3)	C7	C8	1.423(3)
N2	C12	1.451(3)	C18	C17	1.395(3)
C10	C11	1.370(3)	C18	C13	1.407(3)
C10	C18	1.445(3)	C8	Cl1	1.722(2)
C10	C9	1.458(3)	C13	C14	1.399(3)
N1	C2	1.377(3)	C17	C16	1.379(3)
N1	C9	1.392(3)	C3	C4	1.381(4)
N1	C1	1.446(3)	C16	C15	1.392(4)
C9	C8	1.372(3)	C14	C15	1.362(4)

C2	C3	1.395(3)	C4	C5	1.389(5)
C2	C7	1.403(3)	C6	C5	1.372(4)

Table S6. Bond Angles for **B1**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C11	N2	C13	108.36(18)	C17	C18	C13	119.0(2)
C11	N2	C12	124.8(2)	C17	C18	C10	134.4(2)
C13	N2	C12	126.7(2)	C13	C18	C10	106.54(19)
C11	C10	C18	105.66(18)	C9	C8	C7	109.5(2)
C11	C10	C9	125.6(2)	C9	C8	Cl1	126.21(16)
C18	C10	C9	128.66(19)	C7	C8	Cl1	124.02(18)
C2	N1	C9	108.60(18)	N2	C13	C14	129.7(2)
C2	N1	C1	124.06(19)	N2	C13	C18	108.40(18)
C9	N1	C1	127.34(18)	C14	C13	C18	121.9(2)
C8	C9	N1	107.55(18)	N2	C11	C10	111.0(2)
C8	C9	C10	130.5(2)	C16	C17	C18	118.8(2)
N1	C9	C10	121.87(19)	C4	C3	C2	117.4(3)
N1	C2	C3	129.7(2)	C17	C16	C15	120.9(2)
N1	C2	C7	109.16(19)	C15	C14	C13	117.4(2)
C3	C2	C7	121.1(2)	C3	C4	C5	121.9(2)
C6	C7	C2	120.0(2)	C5	C6	C7	118.7(3)
C6	C7	C8	134.8(2)	C6	C5	C4	120.9(3)
C2	C7	C8	105.2(2)	C14	C15	C16	122.0(2)

Table S7. Torsion Angles for **B1**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C2	N1	C9	C8	-1.7(3)	C2	C7	C8	Cl1	-175.36(18)
C1	N1	C9	C8	178.3(2)	C11	N2	C13	C14	179.9(3)
C2	N1	C9	C10	176.4(2)	C12	N2	C13	C14	3.4(4)
C1	N1	C9	C10	-3.6(4)	C11	N2	C13	C18	0.3(3)
C11	C10	C9	C8	132.1(3)	C12	N2	C13	C18	-176.2(2)
C18	C10	C9	C8	-45.3(4)	C17	C18	C13	N2	179.7(2)
C11	C10	C9	N1	-45.5(3)	C10	C18	C13	N2	-0.4(3)
C18	C10	C9	N1	137.1(2)	C17	C18	C13	C14	0.1(4)
C9	N1	C2	C3	-178.4(3)	C10	C18	C13	C14	180.0(2)
C1	N1	C2	C3	1.6(4)	C13	N2	C11	C10	0.0(3)
C9	N1	C2	C7	0.9(3)	C12	N2	C11	C10	176.6(2)
C1	N1	C2	C7	-179.1(2)	C18	C10	C11	N2	-0.3(3)
N1	C2	C7	C6	-178.0(2)	C9	C10	C11	N2	-178.1(2)
C3	C2	C7	C6	1.3(4)	C13	C18	C17	C16	-0.8(4)

N1	C2	C7	C8	0.2(3)	C10	C18	C17	C16	179.4(3)
C3	C2	C7	C8	179.6(2)	N1	C2	C3	C4	178.1(3)
C11	C10	C18	C17	-179.8(3)	C7	C2	C3	C4	-1.0(4)
C9	C10	C18	C17	-2.0(4)	C18	C17	C16	C15	0.9(4)
C11	C10	C18	C13	0.4(3)	N2	C13	C14	C15	-179.1(3)
C9	C10	C18	C13	178.2(2)	C18	C13	C14	C15	0.4(4)
N1	C9	C8	C7	1.9(3)	C2	C3	C4	C5	-0.1(5)
C10	C9	C8	C7	-176.0(2)	C2	C7	C6	C5	-0.4(4)
N1	C9	C8	Cl1	175.76(17)	C8	C7	C6	C5	-178.0(3)
C10	C9	C8	Cl1	-2.1(4)	C7	C6	C5	C4	-0.8(5)
C6	C7	C8	C9	176.6(3)	C3	C4	C5	C6	1.0(5)
C2	C7	C8	C9	-1.3(3)	C13	C14	C15	C16	-0.2(4)
C6	C7	C8	Cl1	2.5(4)	C17	C16	C15	C14	-0.5(5)

Table S8. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **B1**.

Atom	***x***	***y***	***z***	**U(eq)**
H11	8514	2547	3546	50
H17	6190	318	442	53
H3	5043	840	4313	72
H1A	7594	-104	3842	74
H1B	6700	-415	4251	74
H1C	7391	1286	4482	74
H16	7005	-364	-579	69
H12A	10831	1420	3134	93
H12B	10493	2607	3788	93
H12C	10537	3350	2871	93
H14	10003	920	1312	67
H4	3232	1741	3874	88
H6	3097	3407	1408	67
H5	2284	3037	2457	85
H15	8882	-83	-140	76

8. Reference.

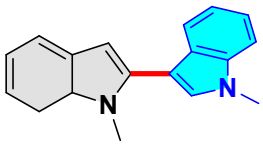
1. X. Hong, Q. Tan, B. Liu and B. Xu, *Angew. Chem., Int. Ed.* 2017, **56**, 1–6.

2. Y. Li, K. Ji, H. Wang, X. Chen, Shaukat Aliand and Y. Liang, *J. Org. Chem*. 2011, **76**, 744–747.

3. J. Yang, S. Liu, J. Zheng and J. Zhou, *Eur. J. Org. Chem*. 2012, **31**, 6248–6259.

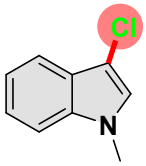
9. Analytic data of the obtained compounds.

(1) 1,1'-dimethyl-1*H*,1'*H*-2,3'-biindole (B-I-1)



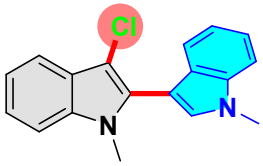
Known compounds, yellow solid, ^{1}H NMR (500 MHz, Chloroform-d) δ 7.74 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.41 (d, *J* = 8.2 Hz, 1H), 7.35 (t, *J* = 7.2 Hz, 1H), 7.24 (m, 3H), 7.18 (t, *J* = 7.4 Hz, 1H), 6.66 (s, 1H), 3.92 (s, 3H), 3.79 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-d) δ 137.98, 136.97, 135.11, 128.44, 128.42, 127.72, 122.35, 121.00, 120.38, 120.23, 120.04, 119.57, 109.55, 109.37, 107.36, 101.43, 33.04, 31.01.

(2) 3-chloro-1-methyl-1*H*-indole (A32)



Known compounds, brownish solid, ^{1}H NMR (500 MHz, Chloroform-d) δ 7.68 (d, *J* = 7.9 Hz, 1H), 7.34–7.29 (m, 2H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.01 (s, 1H), 3.73 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-d) δ 135.88, 125.77, 125.31, 122.66, 119.96, 118.39, 109.58, 104.38, 32.95.

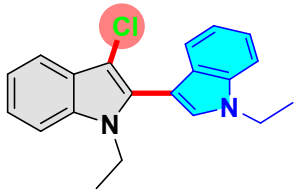
(3) 3-chloro-1,1'-dimethyl-1*H*,1'*H*-2,3'-biindole (B1)



Yellow solid, (49.0 mg, 67% yield), m.p.: 110-112 °C; ^{1}H NMR (500 MHz, Chloroform-d) δ 7.63 (d, *J* = 7.8 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 8.3 Hz, 1H), 7.34 (d, *J* = 8.2 Hz, 1H), 7.30–7.27 (m, 1H), 7.26 (s, 1H), 7.24 (t, *J* = 15 Hz, 1H), 7.19 (t, *J* = 15 Hz, 1H), 7.15 (t, *J* = 15 Hz, 1H), 3.87 (s, 3H), 3.63 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-d) δ 136.93, 136.33, 131.16, 130.24, 127.51, 125.95, 122.30,

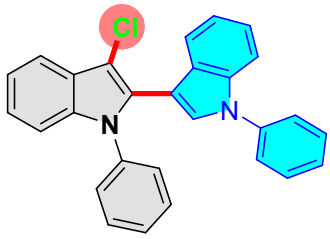
122.22, 120.51, 120.33, 120.10, 117.96, 109.76, 109.58, 103.73, 103.72, 33.18, 31.52. HRMS (ESI): Calcd. for $C_{18}H_{15}ClN_2$ $[M+H]^+$: 295.0996; found: 295.0996.

(4) 3-chloro-1,1'-diethyl-1*H*,1'*H*-2,3'-biindole (B2)



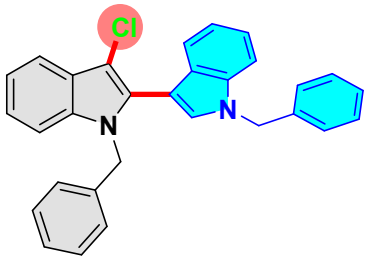
Brownish solid, (45.0 mg, 56% yield); m.p.: 112-115 °C; ^{1}H NMR (500 MHz, Chloroform-d) δ 7.78 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 8.3 Hz, 1H), 7.49 (d, *J* = 8.1 Hz, 1H), 7.41 (s, 1H), 7.40–7.34 (m, 2H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.26 (t, *J* = 8.0 Hz, 1H), 4.33 (q, *J* = 7.3 Hz, 2H), 4.25 (q, *J* = 7.1 Hz, 2H), 1.63 (t, *J* = 7.3 Hz, 3H), 1.26 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, Chloroform-d) δ 136.06, 135.21, 130.44, 128.19, 127.79, 126.37, 122.22, 122.21, 120.55, 120.25, 120.05, 118.16, 109.98, 109.87, 103.97, 41.38, 39.49, 15.53, 15.52. HRMS (ESI): Calcd. for $C_{20}H_{19}ClN_2$ $[M+H]^+$: 323.1309; found: 323.1309.

(5) 3-chloro-1,1'-diphenyl-1*H*,1'*H*-2,3'-biindole (B3)



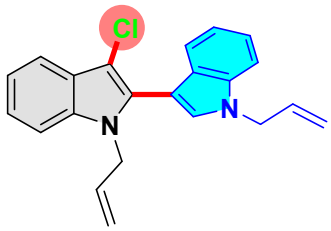
Yellow solid, (41.0 mg, 39% yield); m.p.: 103-105 °C; ^{1}H NMR (500 MHz, Chloroform-d) δ 7.78 (d, *J* = 7.2 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 8.3 Hz, 1H), 7.51–7.48 (m, 2H), 7.39–7.34 (m, 6H), 7.32 (m, 2H), 7.30–7.28 (m, 2H), 7.26 (s, 1H), 7.25–7.22 (m, 1H), 7.16 (d, *J* = 7.2 Hz, 1H), 7.14 (s, 1H). ^{13}C NMR (125 MHz, Chloroform-d) δ 139.13, 138.13, 136.71, 135.86, 129.66, 129.19, 129.10, 127.79, 127.68, 127.36, 126.90, 126.37, 124.49, 123.11, 122.84, 121.34, 121.05, 120.83, 118.09, 110.67, 110.60, 106.61. HRMS (ESI): Calcd. for $C_{28}H_{19}ClN_2$ $[M+H]^+$: 419.1309; found: 419.1309.

(6) 1,1'-dibenzyl-3-chloro-1*H*,1'*H*-2,3'-biindole (B4)



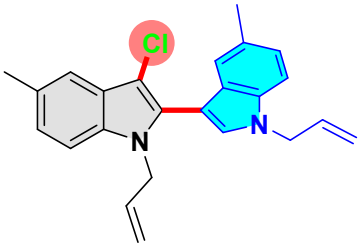
Brownish solid, (70.0 mg, 63% yield), m.p.: 135-137 °C; ^{1}H NMR (500 MHz, Chloroform-d) δ 7.75 (d, *J* = 9.0 Hz, 1H), 7.61 (d, *J* = 7.9 Hz, 1H), 7.38 (d, *J* = 8.2 Hz, 1H), 7.33–7.28 (m, 5H), 7.26–7.24 (m, 2H), 7.22–7.19 (m, 4H), 7.14 (s, 1H), 7.13–7.11 (m, 2H), 6.93–6.91 (m, 2H), 5.34 (s, 4H). ^{13}C NMR (125 MHz, Chloroform-d) δ 138.18, 136.83, 136.43, 135.98, 129.50, 128.88, 128.62, 127.84, 127.71, 127.18, 126.91, 126.04, 122.56, 122.52, 120.66, 120.53, 120.35, 118.10, 110.40, 110.19, 104.28, 50.34, 48.06. HRMS (ESI): Calcd. for $C_{30}H_{23}ClN_2$ $[M+H]^+$: 447.1622; found: 447.1622.

(7) 1,1'-diallyl-3-chloro-1*H*,1'*H*-2,3'-biindole (B5)



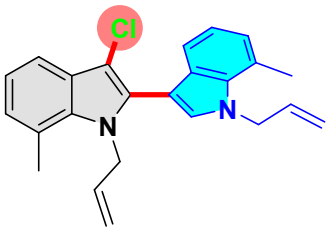
Red solid, (67.0 mg, 78% yield), m.p.: 116-119 °C; ^{1}H NMR (500 MHz, Chloroform-d) δ 7.71 (d, *J* = 7.8 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 8.3 Hz, 1H), 7.36 (d, *J* = 7.9 Hz, 1H), 7.32 (s, 1H), 7.32–7.26 (m, 2H), 7.24 (t, *J* = 7.0 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 6.11–6.03 (m, 1H), 5.91–5.83 (m, 1H), 5.28 (d, *J* = 10.2 Hz, 1H), 5.17 (d, *J* = 17.1 Hz, 1H), 5.12 (d, *J* = 10.4 Hz, 1H), 4.92 (d, *J* = 17.2 Hz, 1H), 4.82 (d, *J* = 5.3 Hz, 2H), 4.72–4.68 (m, 2H). ^{13}C NMR (125 MHz, Chloroform-d) δ 136.32, 135.82, 133.94, 133.08, 130.64, 129.02, 127.71, 126.23, 122.39, 122.37, 120.73, 120.39, 120.26, 118.07, 117.83, 116.46, 110.43, 110.10, 104.10, 49.08, 46.98. HRMS (ESI): Calcd. for $C_{22}H_{19}ClN_2$ $[M+H]^+$: 347.1309; found: 347.1309.

(8) 1,1'-diallyl-3-chloro-5,5'-dimethyl-1*H*,1'*H*-2,3'-biindole (B6)



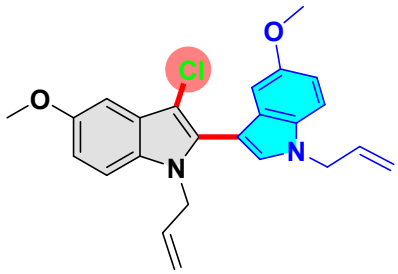
Yellow solid, (31.0 mg, 33% yield); m.p.: 105-107 °C; ^{1}H NMR (500 MHz, Chloroform-d) δ 7.50 (s, 1H), 7.35 (s, 1H), 7.32 (d, *J* = 8.4 Hz, 1H), 7.29 (s, 1H), 7.27 (d, *J* = 8.9 Hz, 1H), 7.15–7.11 (m, 2H), 6.12–6.04 (m, 1H), 5.91–5.84 (m, 1H), 5.28 (d, *J* = 10.3 Hz, 1H), 5.18 (d, *J* = 17.1 Hz, 1H), 5.13 (d, *J* = 10.4 Hz, 1H), 4.93 (d, *J* = 17.2 Hz, 1H), 4.82 (d, *J* = 5.3 Hz, 2H), 4.71–4.67 (m, 2H), 2.55 (s, 3H), 2.47 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-d) δ 134.68, 134.17, 134.06, 133.19, 130.80, 129.72, 129.63, 129.02, 127.97, 126.37, 123.95, 123.87, 120.27, 117.62, 117.60, 116.28, 110.12, 109.72, 103.63, 49.08, 46.99, 21.50, 21.49. HRMS (ESI): Calcd. for $C_{24}H_{23}ClN_2$ $[M+H]^+$: 375.1622; found: 375.1622.

(9) 1,1'-diallyl-3-chloro-7,7'-dimethyl-1*H*,1'*H*-2,3'-biindole (B7)



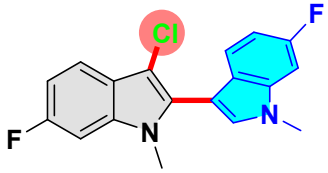
Yellow solid, (26.0 mg, 28% yield), m.p.: 113-117 °C; ^{1}H NMR (500 MHz, Chloroform-d) δ 7.57 (d, *J* = 7.9 Hz, 1H), 7.38 (d, *J* = 7.9 Hz, 1H), 7.26 (s, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.08 (d, *J* = 7.8 Hz, 1H), 7.03–7.02 (m, 2H), 6.18–6.10 (m, 1H), 5.88–5.81 (m, 1H), 5.24 (d, *J* = 10.4 Hz, 1H), 5.04 (d, *J* = 10.5 Hz, 4H), 4.88 (d, *J* = 17.1 Hz, 1H), 4.72 (d, *J* = 17.0 Hz, 1H), 4.61 (d, *J* = 17.2 Hz, 1H), 2.77 (s, 3H), 2.74 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-d) δ 136.67, 136.15, 134.08, 133.22, 132.25, 132.20, 128.30, 125.61, 124.15, 122.08, 121.94, 120.40, 117.69, 117.61, 116.29, 110.27, 109.93, 104.12, 48.90, 46.78, 22.00, 21.92. HRMS (ESI): Calcd. for $C_{24}H_{23}ClN_2$ $[M+H]^+$: 375.1622; found:375.1622.

(10) 1,1'-diallyl-3-chloro-5,5'-dimethoxy-1*H*,1'*H*-2,3'-biindole (B8)



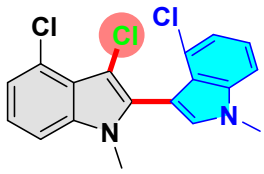
Brownish solid, (21.0 mg, 21% yield), m.p.: 119-121 °C; ^{1}H NMR (500 MHz, Chloroform-d) δ 7.32 (d, *J* = 8.9 Hz, 1H), 7.30 (s, 1H), 7.28 (d, *J* = 8.7 Hz, 1H), 7.16 (d, *J* = 2.4 Hz, 1H), 7.01 (d, *J* = 2.4 Hz, 1H), 6.98–6.94 (m, 2H), 6.12–6.05 (m, 1H), 5.95–5.88 (m, 1H), 5.29 (d, *J* = 10.1 Hz, 1H), 5.21–5.15 (m, 2H), 4.97 (d, *J* = 17.2 Hz, 1H), 4.81 (d, *J* = 5.4 Hz, 2H), 4.69 (s, 2H), 3.95 (s, 3H), 3.83 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-d) δ 154.77, 154.76, 134.12, 133.16, 131.42, 130.94, 129.23, 128.10, 126.50, 117.75, 116.38, 113.02, 112.80, 111.43, 110.88, 103.75, 101.88, 99.31, 55.92, 55.84, 49.27, 47.08. HRMS (ESI): Calcd. for $C_{24}H_{23}ClN_2O_2$ $[M+H]^+$: 407.1520; found: 407.1520.

(11) 3-chloro-6,6'-difluoro-1,1'-dimethyl-1*H*,1'*H*-2,3'-biindole (B9)



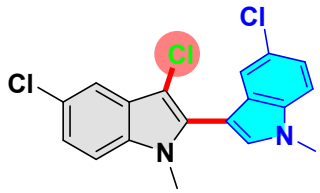
White solid, (59.0 mg, 71% yield); m.p.: 135-139 °C; ^{1}H NMR (500 MHz, Chloroform-d) δ 7.58 (dd, *J* = 8.6, 5.3 Hz, 1H), 7.42 (dd, *J* = 8.7, 5.2 Hz, 1H), 7.26 (s, 1H), 7.10 (dd, *J* = 9.6, 2.2 Hz, 1H), 7.06 (dd, *J* = 9.7, 2.2 Hz, 1H), 7.02–6.95 (m, 2H), 3.86 (s, 3H), 3.61 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-d) δ 161.17 (d, *J* = 8.75 Hz), 159.26 (d, *J* = 8.75 Hz), 137.00 (d, *J* = 11.25 Hz), 136.36 (d, *J* = 12.5 Hz), 130.97 (d, *J* = 3.75 Hz), 130.42 (d, *J* = 2.5 Hz), 123.87, 122.46, 121.31 (d, *J* = 10 Hz), 118.94 (d, *J* = 10 Hz), 109.19 (d, *J* = 23.75 Hz), 108.89 (d, *J* = 25 Hz), 104.03, 103.87, 96.31 (d, *J* = 6.25 Hz), 96.10 (d, *J* = 6.25 Hz), 33.29, 31.59. ^{19}F NMR (471 MHz, Chloroform-d) δ -119.64, -119.83. HRMS (ESI): Calcd. for $C_{18}H_{13}ClFN_2$ $[M+H]^+$: 331.0808; found: 331.0808.

(12) 3,4,4'-trichloro-1,1'-dimethyl-1*H*,1'*H*-2,3'-biindole (B10)



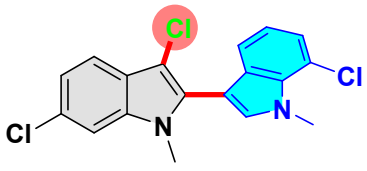
White solid, (53.0 mg, 59% yield), m.p.: 127-133 °C; ^{1}H NMR (500 MHz, Chloroform-d) δ 7.35 (d, *J* = 8.2 Hz, 1H), 7.27 (t, *J* = 5.0 Hz, 1H), 7.26 (d, *J* = 2.7 Hz, 1H), 7.23 (t, *J* = 7.9 Hz, 1H), 7.17–7.15 (m, 3H), 3.92 (s, 3H), 3.56 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-d) δ 138.17, 136.99, 132.12, 131.86, 125.96, 125.36, 125.27, 122.97, 122.39, 121.53, 121.17, 108.59, 108.41, 104.53, 102.45, 33.49, 31.46. HRMS (ESI): Calcd. for $C_{18}H_{13}Cl_3N_2$ $[M+H]^+$: 363.0217; found: 363.0217.

(13) 3,5,5'-trichloro-1,1'-dimethyl-1*H*,1'*H*-2,3'-biindole (B11)



Brownish solid, (67.0 mg, 74% yield), m.p.: 139-143 °C; ^{1}H NMR (500 MHz, Chloroform-d) δ 7.63 (s, 1H), 7.46 (s, 1H), 7.34 (d, *J* = 8.7 Hz, 1H), 7.32 (s, 1H), 7.28 (s, 1H), 7.26 (d, *J* = 3.0 Hz, 1H), 7.24 (d, *J* = 6.7 Hz, 1H), 3.91 (s, 3H), 3.65 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-d) δ 135.36, 134.77, 131.74, 131.49, 128.32, 126.80, 126.52, 126.10, 122.86, 122.75, 119.71, 117.49, 110.94, 110.75, 103.49, 103.06, 33.43, 31.70. HRMS (ESI): Calcd. for $C_{18}H_{13}Cl_3N_2$ $[M+H]^+$: 363.0217; found: 363.0217.

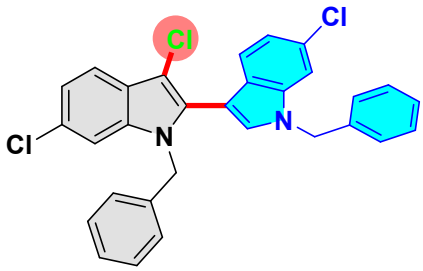
(14) 3,6,6'-trichloro-1,1'-dimethyl-1*H*,1'*H*-2,3'-biindole (B12)



Brownish solid, (66.0 mg, 73% yield), m.p.: 187-189 °C; ^{1}H NMR (500 MHz, Chloroform-d) δ 7.55 (d, *J* = 8.4 Hz, 1H), 7.42 (s, 1H), 7.40 (d, *J* = 8.5 Hz, 1H), 7.36

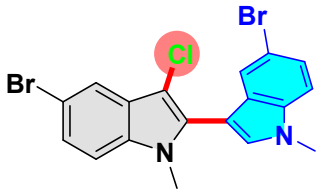
(s, 1H), 7.28 (s, 1H), 7.20–7.15 (m, 2H), 3.88 (s, 3H), 3.61 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-d) δ 137.34, 136.69, 131.17, 130.80, 128.60, 128.43, 125.87, 124.47, 121.31, 121.19, 120.91, 118.96, 109.92, 109.69, 104.19, 103.69, 33.31, 31.56. HRMS (ESI): Calcd. for $C_{18}H_{13}Cl_3N_2$ $[M+H]^+$: 363.0217; found: 363.0217.

(15) 1,1'-dibenzyl-3,6,6'-trichloro-1*H*,1'*H*-2,3'-biindole (B13)



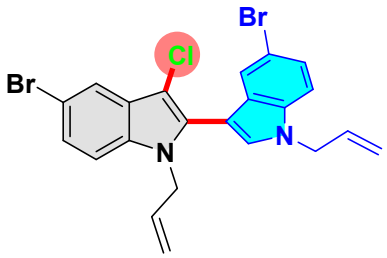
Brownish solid, (102.0 mg, 79% yield), m.p.: 141-144 °C; ^{1}H NMR (500 MHz, Chloroform-d) δ 7.65 (d, *J* = 8.5 Hz, 1H), 7.48 (d, *J* = 8.5 Hz, 1H), 7.39 (s, 1H), 7.36 – 7.35 (m, 3H), 7.31 (s, 1H), 7.26–7.23 (m, 4H), 7.19 (d, *J* = 10.3 Hz, 1H), 7.12–7.10 (m, 2H), 7.09 (s, 1H), 6.90–6.88 (m, 2H), 5.29 (d, *J* = 5.3 Hz, 4H). ^{13}C NMR (125 MHz, Chloroform-d) δ 137.43, 136.81, 136.39, 136.14, 130.86, 129.97, 129.02, 128.80, 128.79, 128.11, 127.48, 126.88, 126.07, 125.84, 124.75, 121.50, 121.43, 121.26, 119.15, 110.32, 110.24, 104.21, 50.44, 48.08. HRMS (ESI): Calcd. for $C_{30}H_{21}Cl_3N_2$ $[M+H]^+$: 515.0843; found: 515.0843.

(16) 5,5'-dibromo-3-chloro-1,1'-dimethyl-1*H*,1'*H*-2,3'-biindole (B14)



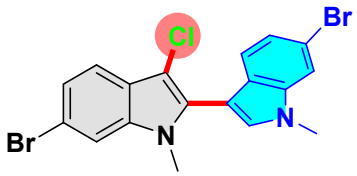
Brownish solid, (76.0 mg, 68% yield), m.p.: 132-135 °C; ^{1}H NMR (500 MHz, Chloroform-d) δ 7.78 (s, 1H), 7.60 (s, 1H), 7.39 (d, *J* = 10.5 Hz, 1H), 7.38–7.35 (m, 1H), 7.29 (t, *J* = 4.3 Hz, 2H), 7.23 (d, *J* = 8.6 Hz, 1H), 3.90 (s, 3H), 3.64 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-d) δ 135.63, 135.05, 131.59, 131.38, 128.93, 127.40, 125.41, 125.31, 122.78, 120.54, 114.03, 113.55, 111.42, 111.22, 103.36, 102.88, 33.42, 31.69. HRMS (ESI): Calcd. for $C_{18}H_{13}Br_2ClN_2$ $[M+H]^+$: 450.9206; found: 450.9206.

(17) 1,1'-diallyl-5,5'-dibromo-3-chloro-1*H*,1'*H*-2,3'-biindole (B15)



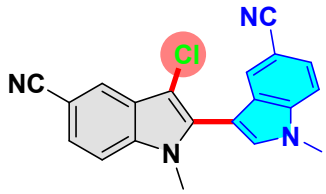
Brownish solid, (102.0 mg, 81% yield); m.p.: 116-117 °C; ^{1}H NMR (500 MHz, Chloroform-d) δ 7.84 (s, 1H), 7.68 (s, 1H), 7.39 (d, *J* = 10.6 Hz, 1H), 7.36 (d, *J* = 10.6 Hz, 1H), 7.33 (s, 1H), 7.30 (d, *J* = 8.7 Hz, 1H), 7.23 (d, *J* = 8.7 Hz, 1H), 6.11 – 6.03 (m, 1H), 5.89–5.82 (m, 1H), 5.33–5.30 (m, 1H), 5.19–5.14 (m, 2H), 4.91–4.86 (m, 1H), 4.83–4.82 (m, 2H), 4.67 (s, 2H). ^{13}C NMR (125 MHz, Chloroform-d) δ 134.98, 134.48, 133.31, 132.52, 131.03, 130.12, 129.09, 127.65, 125.49, 125.48, 123.03, 120.71, 118.19, 116.77, 114.03, 113.70, 111.96, 111.68, 104.23, 103.24, 49.28, 47.05. HRMS (ESI): Calcd. for $C_{22}H_{17}Br_2ClN_2$ $[M+H]^+$: 502.9519; found: 502.9519.

(18) 6,6'-dibromo-3-chloro-1,1'-dimethyl-1*H*,1'*H*-2,3'-biindole (B16)



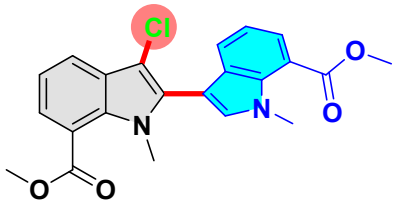
White solid, (77.0 mg, 68% yield), m.p.: 139-141 °C; ^{1}H NMR (500 MHz, Chloroform-d) δ 7.59 (s, 1H), 7.53 (s, 1H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.34 (d, *J* = 8.5 Hz, 1H), 7.32–7.29 (m, 2H), 7.26 (s, 1H), 3.88 (s, 3H), 3.61 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-d) δ 137.73, 137.08, 131.05, 130.73, 126.18, 124.77, 123.77, 123.48, 121.64, 119.31, 116.17, 116.01, 112.95, 112.68, 104.28, 103.68, 33.33, 31.57. HRMS (ESI): Calcd. for $C_{18}H_{13}Br_2ClN_2$ $[M+H]^+$: 450.9206; found: 450.9206.

(19) 3-chloro-1,1'-dimethyl-1*H*,1'*H*-[2,3'-biindole]-5,5'-dicarbonitrile (B17)



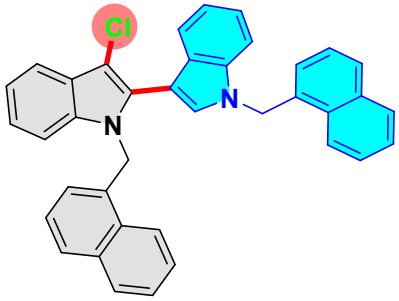
Yellow solid, (61.0 mg, 71% yield), m.p.: 239-243 °C; ^{1}H NMR (500 MHz, Chloroform-d) δ 7.99 (s, 1H), 7.83 (s, 1H), 7.55 (d, *J* = 10.2 Hz, 1H), 7.53–7.50 (m, 2H), 7.46 (s, 1H), 7.44 (d, *J* = 8.6 Hz, 1H), 3.98 (s, 3H), 3.70 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-d) δ 138.44, 137.83, 132.58, 131.85, 126.95, 125.74, 125.67, 125.63, 125.57, 123.77, 120.29, 120.15, 111.01, 110.67, 105.53, 104.10, 103.92, 103.63, 33.60, 31.82. HRMS (ESI): Calcd. for $C_{20}H_{13}ClN_4$ $[M+H]^+$: 345.0901; found: 345.0901.

(20) dimethyl 3-chloro-1,1'-dimethyl-1H,1'H-[2,3'-biindole]-7,7'-dicarboxylate (B18)



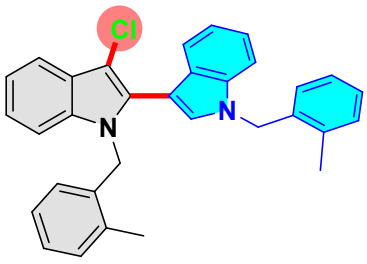
Yellow solid, (60.0 mg, 59% yield), m.p.: 221-224 °C; ^{1}H NMR (500 MHz,) δ 7.34 (d, *J* = 3.9 Hz, 1H), 7.32 (d, *J* = 3.8 Hz, 1H), 7.21 (d, *J* = 2.3 Hz, 2H), 7.18 (s, 1H), 7.04 (d, *J* = 2.4 Hz, 1H), 6.97 (d, *J* = 11.2 Hz, 1H), 3.95 (s, 3H), 3.89 (s, 3H), 3.87 (s, 3H), 3.77 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-d) δ 164.13, 154.82, 154.26, 136.39, 133.34, 132.22, 128.87, 128.67, 128.04, 112.89, 111.03, 110.41, 110.07, 106.89, 102.05, 101.65, 56.04, 55.96, 33.20, 31.09. HRMS (ESI): Calcd. for $C_{22}H_{19}ClN_2O_4$ $[M+H]^+$: 411.1106; found: 411.1106.

(21) 3-chloro-1,1'-bis(naphthalen-1-ylmethyl)-1*H*,1'*H*-2,3'-biindole (B19)



Brownish solid, (85.0 mg, 62% yield), m.p.: 157-159 °C; ^{1}H NMR (500 MHz, Chloroform-d) δ 7.92 (d, *J* = 8.1 Hz, 1H), 7.81–7.72 (m, 5H), 7.69 (d, *J* = 8.3 Hz, 1H), 7.66 (d, *J* = 8.3 Hz, 1H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.2 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.34 – 7.29 (m, 2H), 7.26 (t, *J* = 7.4 Hz, 2H), 7.19–7.13 (m, 3H), 7.06–7.02 (m, 1H), 6.89 (s, 1H), 6.72 (d, *J* = 7.0 Hz, 1H), 6.62 (d, *J* = 7.1 Hz, 1H), 5.71 (s, 2H), 5.62 (s, 2H). ^{13}C NMR (125 MHz, Chloroform-d) δ 136.57, 136.11, 133.53, 133.45, 133.10, 131.24, 128.94, 128.82, 128.71, 128.55, 127.64, 127.60, 126.58, 126.30, 126.25, 125.91, 125.82, 125.54, 125.46, 125.25, 122.87, 122.60, 122.58, 122.28, 122.15, 121.04, 120.59, 120.42, 118.09, 110.37, 110.01, 47.93, 45.73. HRMS (ESI): Calcd. for $C_{38}H_{27}ClN_2$ $[M+H]^+$: 475.1935; found: 475.1935.

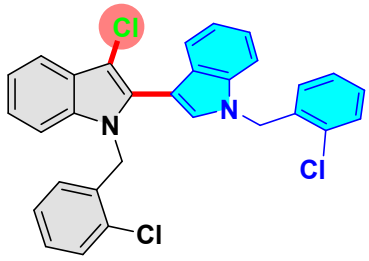
(22) 3-chloro-1,1'-bis(2-methylbenzyl)-1*H*,1'*H*-2,3'-biindole (B20)



Brownish solid, (55.0 mg, 46% yield), m.p.: 138-139 °C; ^{1}H NMR (500 MHz, Chloroform-d) δ 7.78 (d, *J* = 7.5 Hz, 1H), 7.66 (d, *J* = 7.9 Hz, 1H), 7.40 (d, *J* = 8.2 Hz, 1H), 7.32–7.29 (m, 2H), 7.28–7.22 (m, 3H), 7.21–7.18 (m, 2H), 7.14–7.09 (m, 3H), 6.99 (d, *J* = 16.4 Hz, 1H), 6.89 (s, 1H), 6.80 (d, *J* = 7.6 Hz, 1H), 6.52 (d, *J* = 7.7 Hz, 1H), 5.26 (d, *J* = 3.1 Hz, 4H), 2.23 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-d) δ 136.51, 136.04, 135.94, 134.27, 134.10, 130.60, 130.13, 128.70,

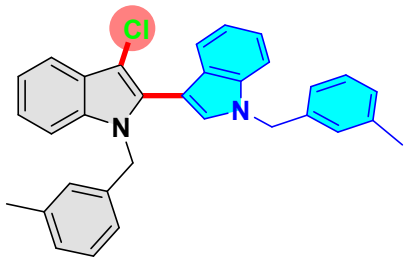
128.09, 127.88, 127.55, 126.97, 126.46, 126.39, 125.21, 122.56, 122.47, 120.92, 120.48, 120.37, 118.08, 110.30, 110.02, 104.16, 48.35, 45.99, 19.06, 18.96. HRMS (ESI): Calcd. for $C_{32}H_{27}ClN_2$ $[M+H]^+$: 475.1935; found: 475.1935.

(23) 3-chloro-1,1'-bis(2-chlorobenzyl)-1*H*,1'*H*-2,3'-biindole (B21)



Red solid, (93.0 mg, 72% yield), m.p.: 141-143 °C; ^{1}H NMR (500 MHz, Chloroform-d) δ 7.79 (d, *J* = 7.4 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.38–7.35 (m, 2H), 7.31 – 7.27 (m, 3H), 7.25–7.22 (m, 3H), 7.18–7.12 (m, 2H), 7.06 (d, *J* = 8.9 Hz, 2H), 6.72 (d, *J* = 7.7 Hz, 1H), 6.57 (d, *J* = 7.7 Hz, 1H), 5.42 (s, 4H). ^{13}C NMR (125 MHz, Chloroform-d) δ 136.41, 135.92, 135.57, 134.25, 132.77, 131.65, 129.67, 129.37, 129.16, 128.98, 128.42, 127.58, 127.36, 127.23, 127.05, 126.28, 122.86, 122.78, 120.86, 120.71, 120.65, 118.22, 110.22, 110.11, 104.30, 47.95, 45.77. HRMS (ESI): Calcd. for $C_{30}H_{21}Cl_3N_2$ $[M+H]^+$: 515.0843; found: 515.0843.

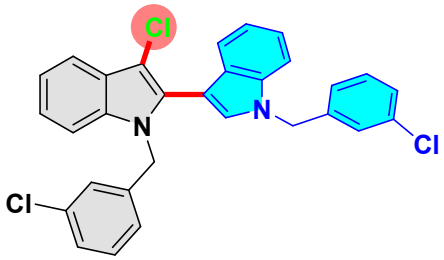
(24) 3-chloro-1,1'-bis(3-methylbenzyl)-1*H*,1'*H*-2,3'-biindole (B22)



White solid, (62.0 mg, 52% yield), m.p.: 150-152 °C; ^{1}H NMR (500 MHz, Chloroform-d) δ 7.78 (d, *J* = 9.0 Hz, 1H), 7.64 (d, *J* = 7.9 Hz, 1H), 7.43 (d, *J* = 8.2 Hz, 1H), 7.34–7.27 (m, 4H), 7.24 (t, *J* = 7.5 Hz, 2H), 7.19 (s, 1H), 7.15–7.11 (m, 2H), 7.04 (d, *J* = 7.5 Hz, 1H), 7.02 (s, 1H), 6.95 (d, *J* = 7.6 Hz, 1H), 6.82 (s, 1H), 6.76 (d, *J* = 7.6 Hz, 1H), 5.34 (d, *J* = 4.5 Hz, 4H), 2.35 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-

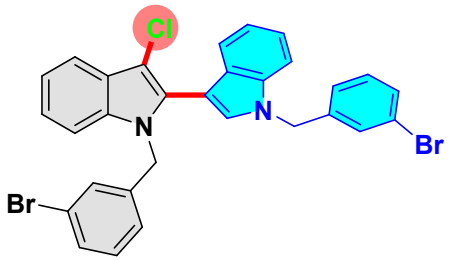
d) δ 138.60, 138.29, 138.12, 136.77, 136.49, 135.98, 129.46, 128.78, 128.62, 128.53, 127.97, 127.75, 127.68, 126.74, 124.05, 123.15, 122.51, 122.48, 120.72, 120.46, 120.31, 118.04, 110.48, 110.20, 104.25, 50.32, 48.06, 21.42, 21.41. HRMS (ESI): Calcd. for $C_{32}H_{27}ClN_2$ $[M+H]^+$: 475.1935; found: 475.1935.

(25) 3-chloro-1,1'-bis(3-chlorobenzyl)-1*H*,1'*H*-2,3'-biindole (B23)



Brownish solid, (89.0 mg, 69% yield), m.p.: 167-169 °C; ^{1}H NMR (500 MHz, Chloroform-d) δ 7.74 (d, *J* = 9.7 Hz, 1H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.30–7.26 (m, 4H), 7.26 (s, 1H), 7.24–7.18 (m, 2H), 7.16 (d, *J* = 9.3 Hz, 2H), 7.13–7.09 (m, 2H), 6.95 (d, *J* = 7.5 Hz, 1H), 6.93 (s, 1H), 6.74 (d, *J* = 7.6 Hz, 1H), 5.30 (d, *J* = 7.3 Hz, 4H). ^{13}C NMR (125 MHz, Chloroform-d) δ 140.17, 138.81, 136.37, 135.89, 134.86, 134.60, 130.26, 129.98, 129.25, 128.19, 127.53, 127.05, 126.20, 124.98, 124.18, 122.86, 120.84, 120.65, 120.62, 118.30, 110.20, 110.10, 104.51, 49.77, 47.56. HRMS (ESI): Calcd. for $C_{30}H_{21}Cl_3N_2$ $[M+H]^+$: 515.0843; found: 515.0843.

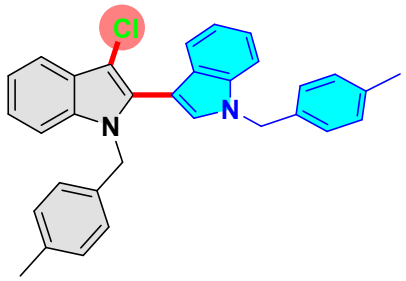
(26) 1,1'-bis(3-bromobenzyl)-3-chloro-1*H*,1'*H*-2,3'-biindole (B24)



Brownish solid, (92.0 mg, 61% yield), m.p.: 150-152 °C; ^{1}H NMR (500 MHz, Chloroform-d) δ 7.72 (d, *J* = 9.8 Hz, 1H), 7.55 (d, *J* = 7.9 Hz, 1H), 7.42 (d, *J* = 7.9 Hz, 1H), 7.33 (d, *J* = 8.3 Hz, 1H), 7.31 (s, 1H), 7.29–7.24 (m, 5H), 7.21–7.15 (m, 2H), 7.09 (s, 2H), 7.03 (t, *J* = 7.8 Hz, 1H), 6.97 (d, *J* = 7.7 Hz, 1H), 6.76 (d, *J* = 7.7 Hz, 1H), 5.28

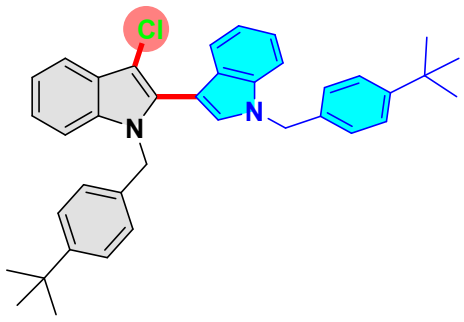
(d, *J* = 7.3 Hz, 4H). ^{13}C NMR (125 MHz, Chloroform-d) δ 140.41, 139.06, 136.36, 135.88, 131.13, 130.56, 130.46, 130.28, 129.97, 129.23, 129.14, 127.67, 126.32, 125.45, 124.65, 123.02, 122.88, 122.78, 120.85, 120.64, 120.62, 118.30, 110.19, 110.09, 104.52, 49.70, 47.50. HRMS (ESI): Calcd. for $C_{30}H_{21}Br_2ClN_2$ $[M+H]^+$: 602.9832; found: 602.9832.

(27) 3-chloro-1,1'-bis(4-methylbenzyl)-1*H*,1'*H*-2,3'-biindole (B25)



Brownish solid, (60.0 mg, 51% yield), m.p.: 139-141 °C; ^{1}H NMR (500 MHz, Chloroform-d) δ 7.74 (d, *J* = 9.0 Hz, 1H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.38 (d, *J* = 8.2 Hz, 1H), 7.30–7.27 (m, 2H), 7.25–7.23 (m, 2H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.13 (d, *J* = 8.2 Hz, 3H), 7.03 (d, *J* = 8.1 Hz, 2H), 7.01 (d, *J* = 7.9 Hz, 2H), 6.82 (d, *J* = 8.0 Hz, 2H), 5.29 (d, *J* = 6.5 Hz, 4H), 2.36 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-d) δ 137.57, 136.75, 136.44, 135.97, 135.17, 133.80, 129.54, 129.47, 129.29, 127.76, 127.03, 126.31, 126.04, 122.49, 122.45, 120.70, 120.47, 120.30, 118.07, 110.50, 110.23, 104.20, 50.16, 47.87, 21.17, 21.10. HRMS (ESI): Calcd. for $C_{32}H_{27}ClN_2$ $[M+H]^+$: 475.1935; found: 475.1935.

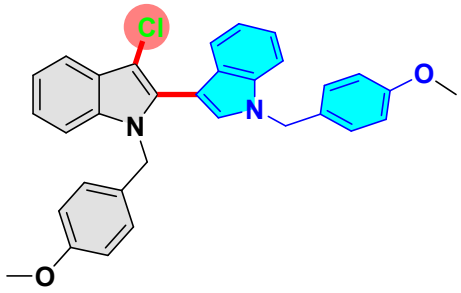
(28) 1,1'-bis(4-(tert-butyl)benzyl)-3-chloro-1*H*,1'*H*-2,3'-biindole (B26)



Brownish solid, (60.0 mg, 43% yield), m.p.: 151-153 °C; ^{1}H NMR (500 MHz, Chloroform-d) δ 7.71 (d, *J* = 9.0 Hz, 1H), 7.56 (d, *J* = 7.9 Hz, 1H), 7.37 (d, *J* = 8.3 Hz,

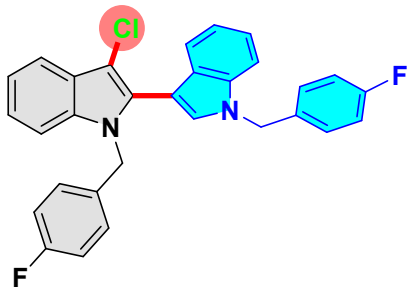
1H), 7.35–7.32 (m, 2H), 7.31–7.29 (m, 1H), 7.25 (d, *J* = 1.9 Hz, 1H), 7.23–7.21 (m, 2H), 7.20–7.18 (m, 2H), 7.18–7.14 (m, 2H), 7.06 (d, *J* = 8.3 Hz, 2H), 6.85 (d, *J* = 8.3 Hz, 2H), 5.30 (d, *J* = 3.0 Hz, 4H), 1.31 (s, 9H), 1.25 (s, 9H). ^{13}C NMR (125 MHz, Chloroform-d) δ 150.82, 150.09, 136.45, 135.96, 135.17, 134.01, 129.62, 127.72, 126.61, 126.28, 125.94, 125.77, 125.47, 122.44, 122.42, 120.66, 120.42, 120.25, 118.05, 110.52, 110.21, 104.26, 50.01, 47.80, 34.57, 34.45, 31.35, 31.34. HRMS (ESI): Calcd. for $C_{38}H_{39}ClN_2$ $[M+H]^+$: 559.2874; found: 559.2874.

(29) 3-chloro-1,1'-bis(4-methoxybenzyl)-1*H*,1'*H*-2,3'-biindole (B27)



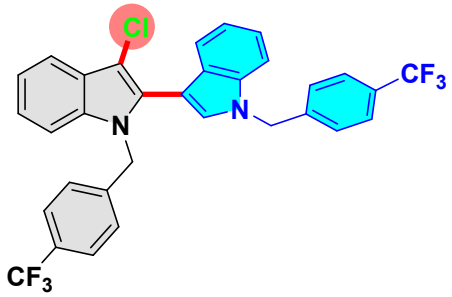
Brownish solid, (73.0 mg, 58% yield), m.p.: 133-136 °C; ^{1}H NMR (500 MHz, Chloroform-d) δ 7.71 (d, *J* = 9.0 Hz, 1H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.39 (d, *J* = 8.2 Hz, 1H), 7.29–7.27 (m, 1H), 7.25–7.16 (m, 4H), 7.10 (s, 1H), 7.07 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 6.81 (d, *J* = 8.7 Hz, 2H), 6.70 (d, *J* = 8.7 Hz, 2H), 5.25 (d, *J* = 4.9 Hz, 4H), 3.80 (s, 3H), 3.74 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-d) δ 159.27, 158.68, 136.39, 135.91, 130.22, 129.30, 128.74, 128.47, 127.74, 127.30, 122.47, 122.43, 120.68, 120.47, 120.28, 118.06, 114.25, 113.97, 110.45, 110.20, 104.18, 55.30, 55.22, 49.84, 47.52. HRMS (ESI): Calcd. for $C_{32}H_{27}ClN_2O_2$ $[M+H]^+$: 507.1833; found: 507.1833.

(30) 3-chloro-1,1'-bis(4-fluorobenzyl)-1*H*,1'*H*-2,3'-biindole (B28)



Brownish solid, (81.0 mg, 67% yield), m.p.: 141-143 °C; ^{1}H NMR (500 MHz, Chloroform-d) δ 7.76 (d, *J* = 8.8 Hz, 1H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.39 (d, *J* = 8.3 Hz, 1H), 7.32–7.27 (m, 4H), 7.24 (d, *J* = 7.1 Hz, 1H), 7.12–7.09 (m, 3H), 7.05–7.01 (m, 2H), 6.91–6.84 (m, 4H), 5.31 (s, 4H). ^{13}C NMR (125 MHz, Chloroform-d) δ 137.11, 136.33, 135.82 (d, *J* = 11.25 Hz), 132.07, 131.74, 131.59, 130.48, 130.01, 129.20, 128.30, 128.60, 127.66 (d, *J* = 8.75 Hz), 126.33, 122.81 (d, J = 3.75 Hz), 121.91, 121.07, 120.72 (d, *J* = 25 Hz), 118.29, 110.17 (d, *J* = 15 Hz), 105.36, 104.46, 49.73, 47.51. ^{19}F NMR (471 MHz, Chloroform-d) δ -114.09, -115.17. HRMS (ESI): Calcd. for $C_{30}H_{21}ClF_2N_2$ $[M+H]^+$: 483.1434; found: 483.1434.

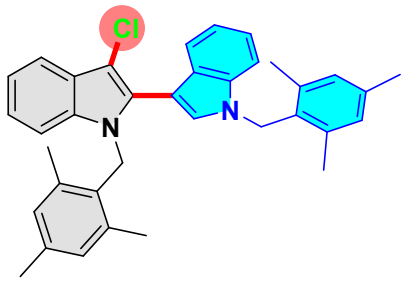
(31) 3-chloro-1,1'-bis(4-(trifluoromethyl)benzyl)-1*H*,1'*H*-2,3'-biindole (B29)



Brownish solid, (96.0 mg, 66% yield), m.p.: 137-139 °C; ^{1}H NMR (500 MHz, Chloroform-d) δ 7.78 (d, *J* = 8.8 Hz, 1H), 7.58 (t, *J* = 8.7 Hz, 3H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.32 – 7.27 (m, 3H), 7.26 – 7.22 (m, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 7.14 (s, 1H), 6.98 (d, *J* = 8.1 Hz, 2H), 5.38 (d, *J* = 5.2 Hz, 4H). ^{13}C NMR (125 MHz, Chloroform-d) δ 142.13, 140.89, 136.40 (d, *J* = 25 Hz), 135.91 (d, *J* = 3.75 Hz), 130.43 (d, *J* = 2.5 Hz), 130.16, 129.77, 129.51, 129.33, 127.68, 127.02, 126.29 (d, *J* = 25 Hz), 125.92 (d, J = 3.75 Hz), 125.63 (d, *J* = 3.75 Hz), 121.03, 120.82, 120.61, 118.42, 110.18 (d, *J* = 11.25 Hz), 105.67, 104.64, 49.81, 47.70. ^{19}F NMR (471 MHz,

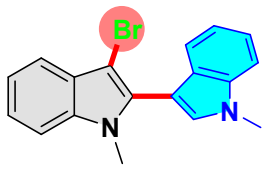
Chloroform-d) δ -62.49, -62.58. HRMS (ESI): Calcd. for $C_{32}H_{21}ClF_6N_2$ $[M+H]^+$: 583.1370; found: 583.1370.

(32) 3-chloro-1,1'-bis(2,4,6-trimethylbenzyl)-1*H*,1'*H*-2,3'-biindole (B30)



Brownish solid, (78.0 mg, 59% yield), m.p.: 136-138 °C; ^{1}H NMR (500 MHz, Chloroform-d) δ 7.69 – 7.59 (m, 3H), 7.42 (t, *J* = 7.7 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.03 (d, *J* = 6.6 Hz, 3H), 6.92 (s, 1H), 6.81 (d, *J* = 19.6 Hz, 3H), 5.38 (s, 4H), 2.40 (s, 3H), 2.33 (s, 6H), 2.28 (s, 3H), 2.04 (s, 6H). ^{13}C NMR (125 MHz, Chloroform-d) δ 138.11, 137.06, 136.73, 135.24, 130.01, 129.58, 129.57, 128.40, 128.30, 128.01, 126.12, 122.23, 122.08, 120.64, 120.60, 119.77, 117.83, 110.95, 109.89, 104.20, 45.18, 44.23, 21.12, 20.92, 20.18, 19.69. HRMS (ESI): Calcd. for $C_{36}H_{35}ClN_2$ $[M+H]^+$: 531.2561; found: 531.2561.

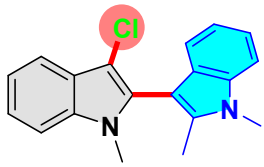
(33) 3-bromo-1,1'-dimethyl-1*H*,1'*H*-2,3'-biindole (B31)



Yellow solid, (57.0 mg, 68% yield), m.p.: 116-119 °C; ^{1}H NMR (500 MHz, Chloroform-d) δ 7.66 (d, *J* = 7.8 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.47 (d, *J* = 8.3 Hz, 1H), 7.41 (d, *J* = 8.1 Hz, 1H), 7.36 (t, *J* = 8.3 Hz, 1H), 7.35 (s, 1H), 7.33 (t, *J* = 8.3 Hz, 1H), 7.29 (t, *J* = 7.8 Hz, 1H), 7.23 (t, *J* = 7.5 Hz, 1H), 3.95 (s, 3H), 3.72 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-d) δ 138.11, 137.06, 136.73, 135.24, 130.01, 129.58, 129.57, 128.40, 128.30, 128.01, 126.12, 122.23, 122.08, 120.64, 120.60, 119.77,

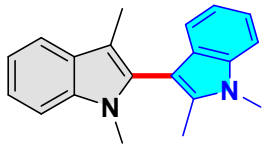
117.83, 110.95, 109.89, 104.20, 45.18, 44.23, 21.12, 20.92, 20.18, 19.69. HRMS (ESI): Calcd. for $C_{18}H_{15}BrN_2$ $[M+H]^+$: 339.0491; found: 339.0491.

(34) 3-chloro-1,1',2'-trimethyl-1*H*,1'*H*-2,3'-biindole (B33)



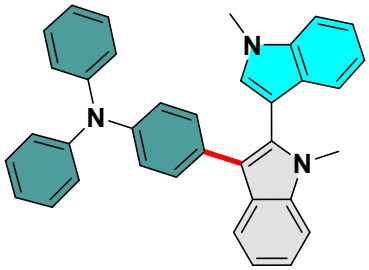
White solid, (26.0 mg, 34% yield), m.p.: 119-121 °C; ^{1}H NMR (500 MHz, Chloroform-d) δ 7.72 (d, *J* = 7.8 Hz, 1H), 7.42 (t, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 7.7 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.28 – 7.25 (m, 2H), 7.17 (t, *J* = 7.9 Hz, 1H), 3.83 (s, 3H), 3.63 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-d) δ 137.74, 136.91, 136.38, 131.51, 127.60, 125.91, 122.12, 121.35, 120.20, 119.93, 119.22, 117.92, 109.53, 109.15, 104.51, 101.48, 31.24, 29.94, 11.66. HRMS (ESI): Calcd. for $C_{19}H_{17}ClN_2$ $[M+H]^+$: 309.1153; found: 309.1153.

(35) 3-chloro-1,1',2'-trimethyl-1*H*,1'*H*-2,3'-biindole (B34)



White solid, (22.0 mg, 31% yield), m.p.: 110-112 °C; ^{1}H NMR (500 MHz, Chloroform-d) δ 7.66 (d, *J* = 7.8 Hz, 1H), 7.39 (t, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 1H), 7.30 – 7.25 (m, 3H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.13 (t, *J* = 7.8 Hz, 1H), 3.83 (s, 3H), 3.56 (s, 3H), 2.37 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-d) δ 137.39, 136.83, 136.79, 131.99, 128.72, 128.26, 121.11, 120.95, 119.85, 119.40, 118.58, 118.45, 109.54, 109.03, 108.88, 103.72, 30.59, 29.89, 11.30, 9.66. HRMS (ESI): Calcd. for $C_{20}H_{20}N_2$ $[M+H]^+$: 289.1699; found: 289.1699.

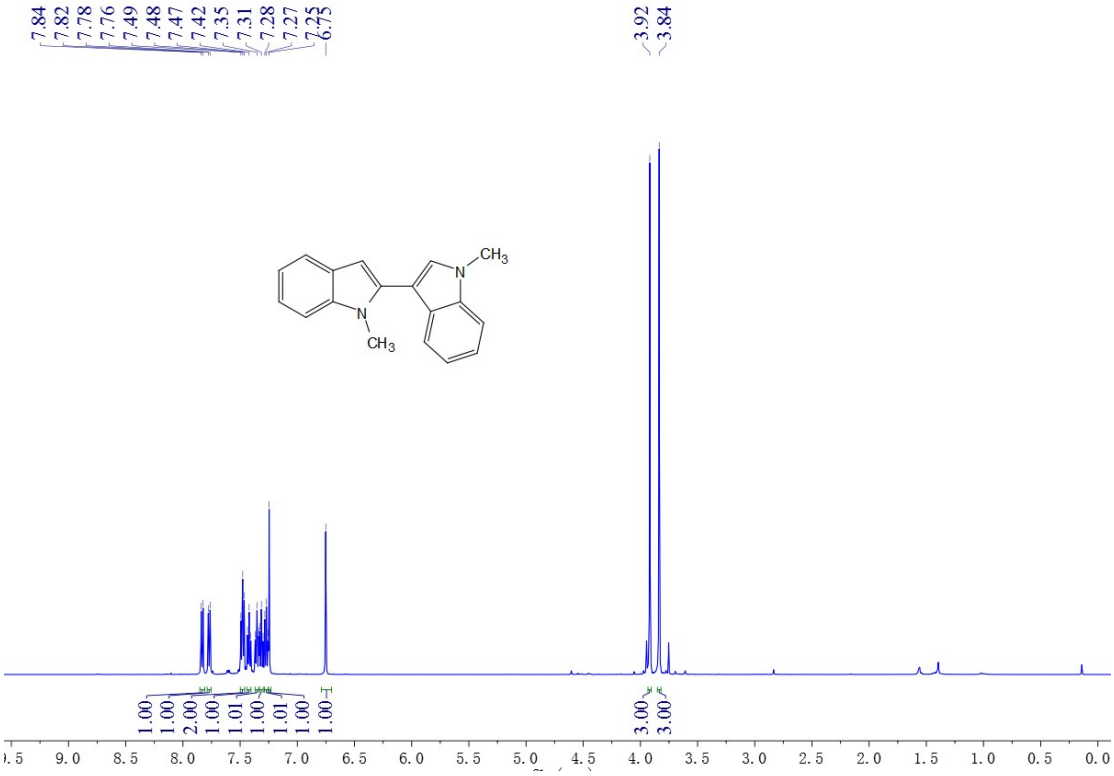
(36) 4-(1,1'-dimethyl-1*H*,1'*H*-[2,3'-biindol]-3-yl)-*N*,*N*-diphenylaniline (F)



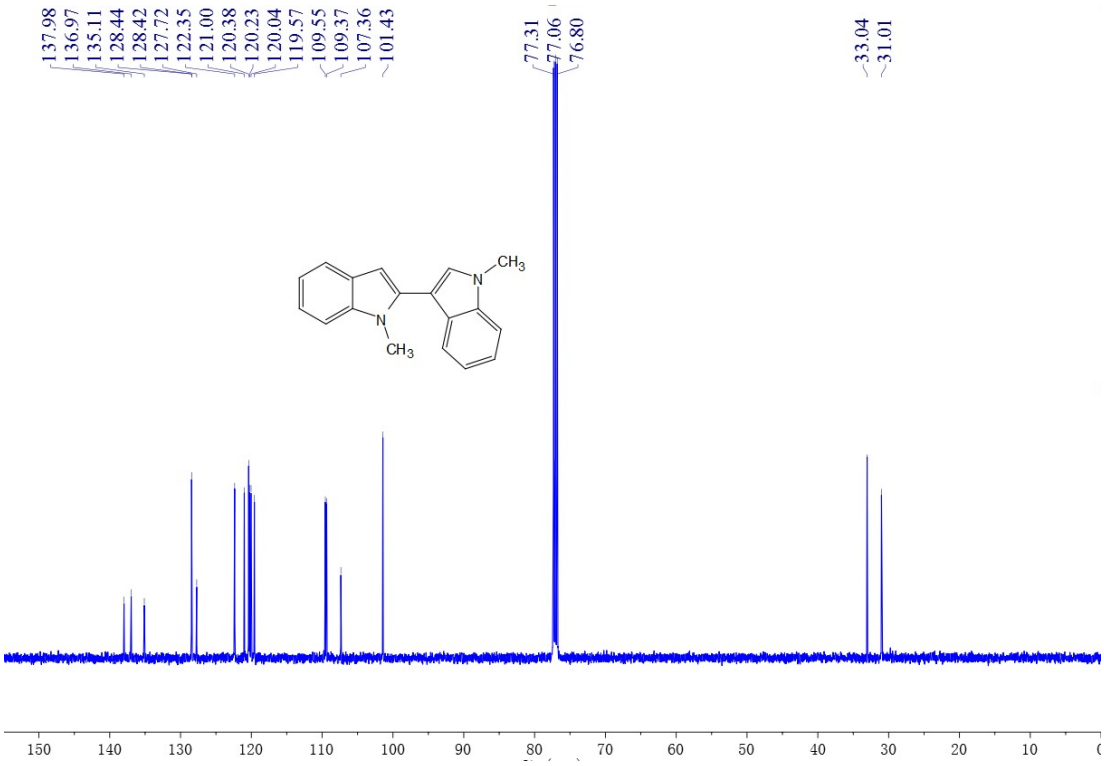
Yellow solid, (35.0 mg, 28% yield), m.p.: 130-132 °C; ^{1}H NMR (500 MHz,) δ 7.88 (d, *J* = 7.9 Hz, 1H), 7.44 (d, *J* = 8.1 Hz, 1H), 7.39 (d, *J* = 8.2 Hz, 1H), 7.32–7.30 (m, 3H), 7.27 (d, *J* = 8.2 Hz, 1H), 7.26 (s, 1H), 7.24–7.22 (m, 5H), 7.12–7.10 (m, 2H), 7.08–7.06 (m, 4H), 6.99–6.94 (m, 4H), 3.88 (s, 3H), 3.71 (s, 3H). ^{13}C NMR (125 MHz, Chloroform-d) δ 147.97, 144.95, 137.50, 136.89, 130.86, 130.14, 129.83, 129.07, 128.19, 127.17, 124.36, 123.83, 122.26, 121.98, 121.66, 120.61, 119.92, 119.82, 119.39, 109.46, 109.42, 105.96, 33.05, 30.83. HRMS (ESI): Calcd. for $C_{36}H_{29}N_3$ $[M+H]^+$: 504.2434; found: 504.2434.

10. NMR spectra of the obtained compounds.

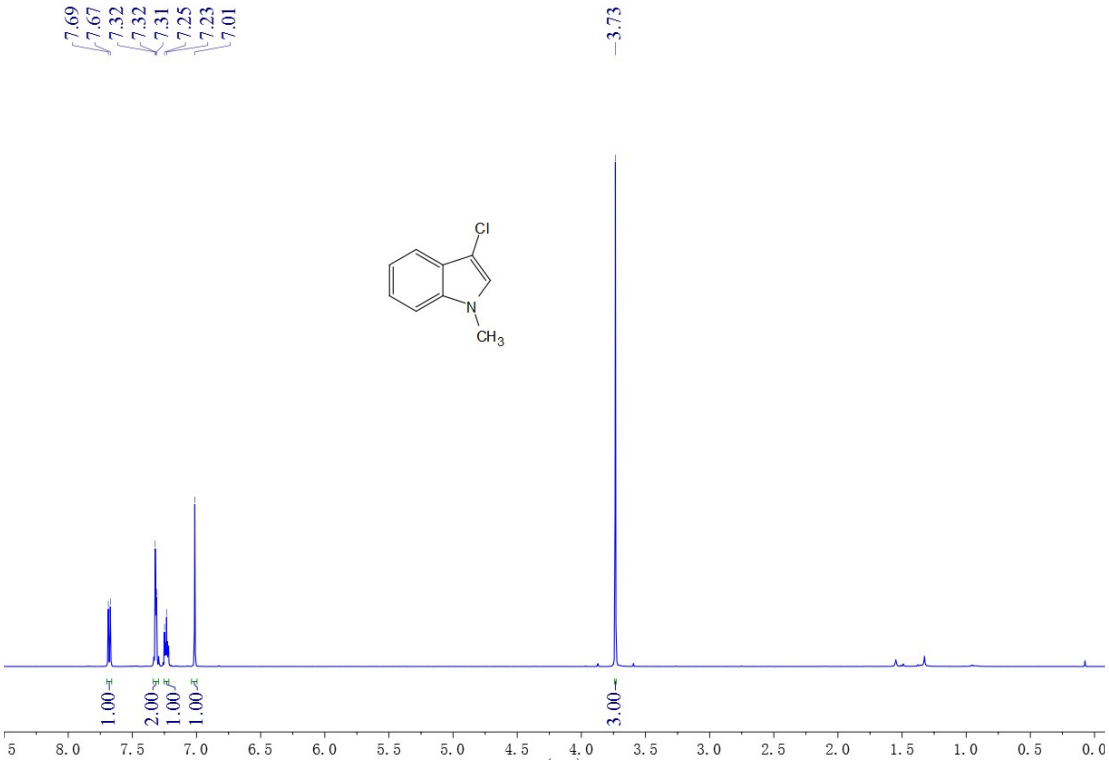
(1) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of B-I-1



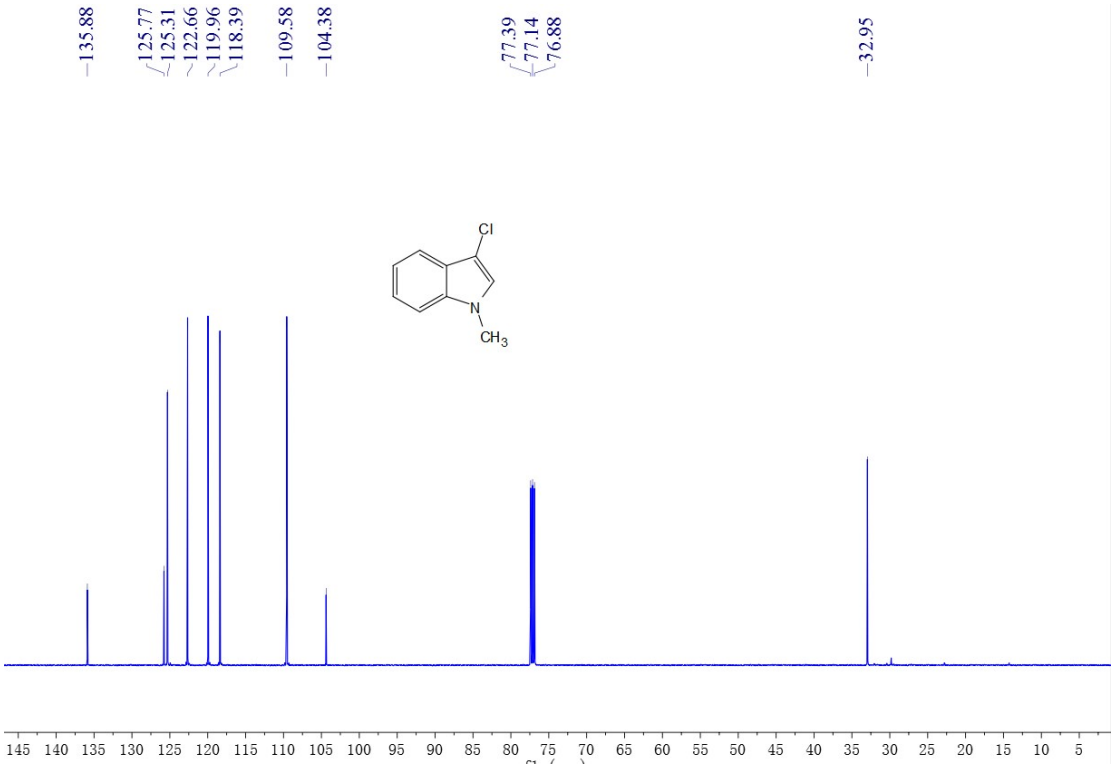
(2) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of B1-1



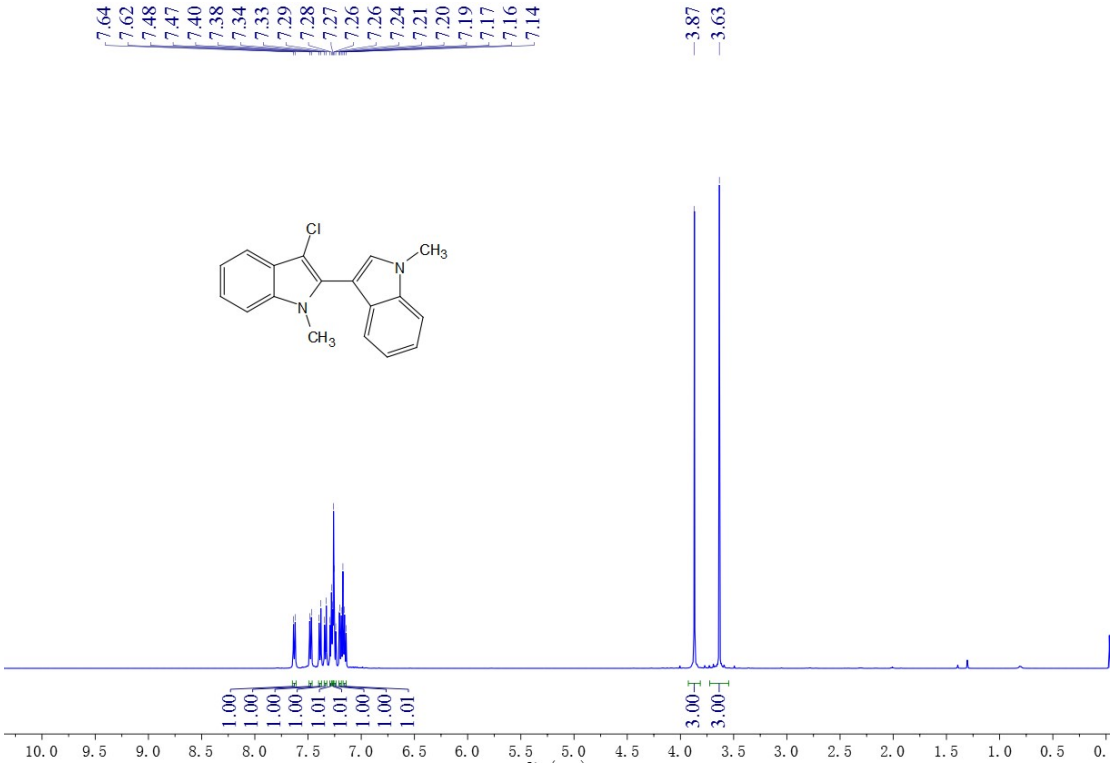
(3) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of A32



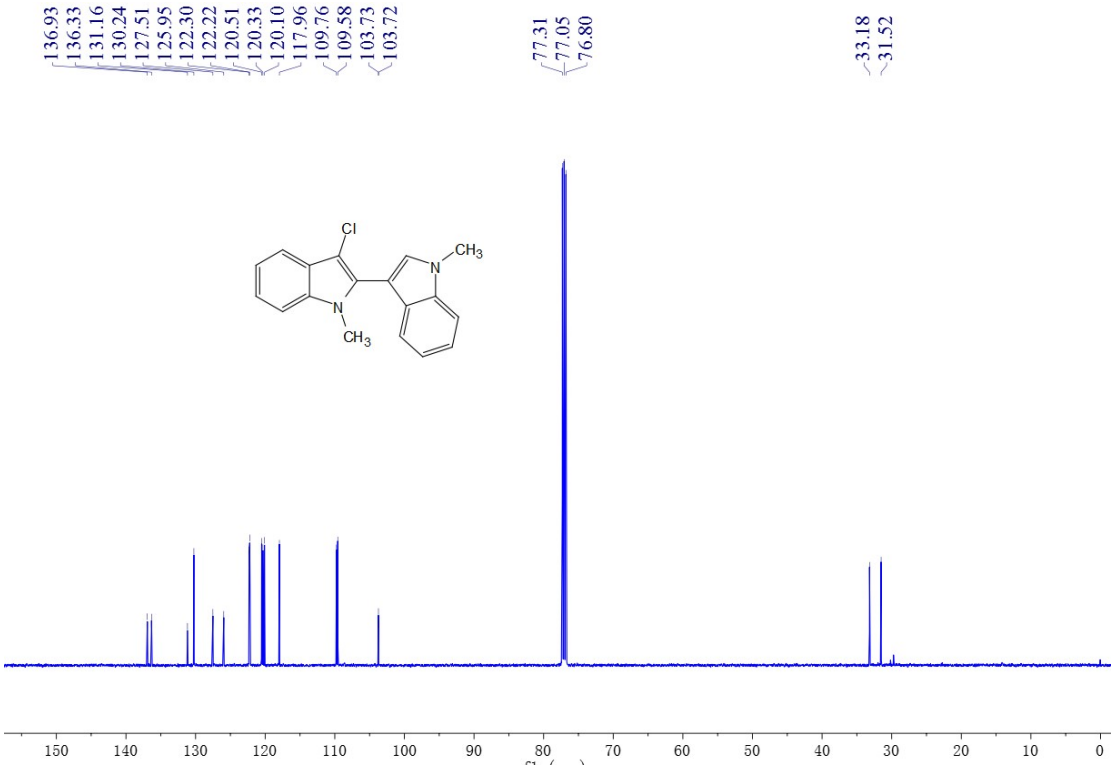
(4) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of A32



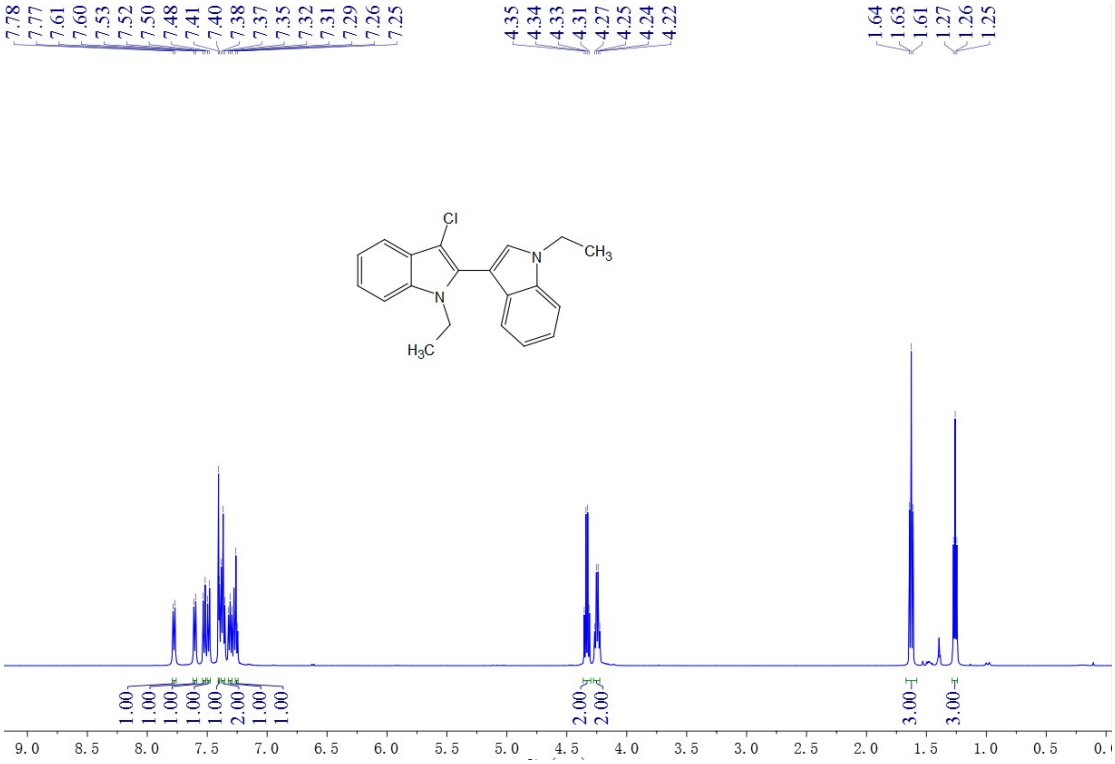
(5) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of B1



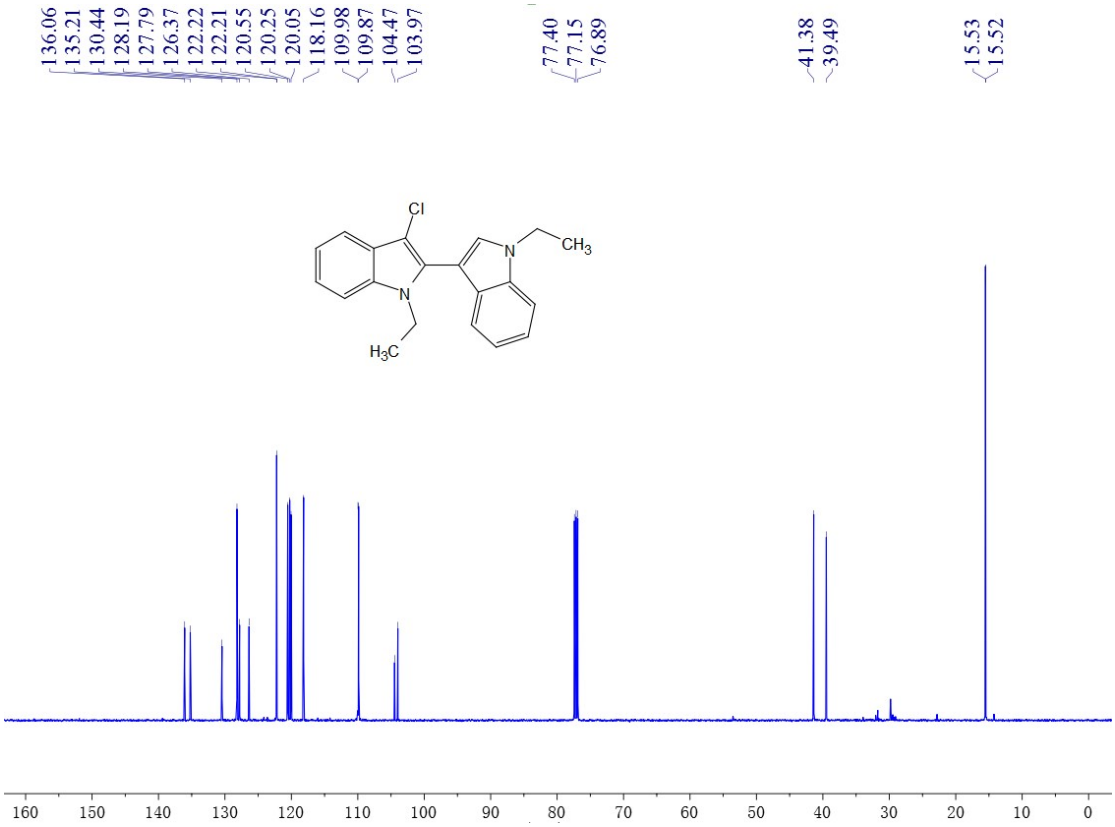
(6) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of B1



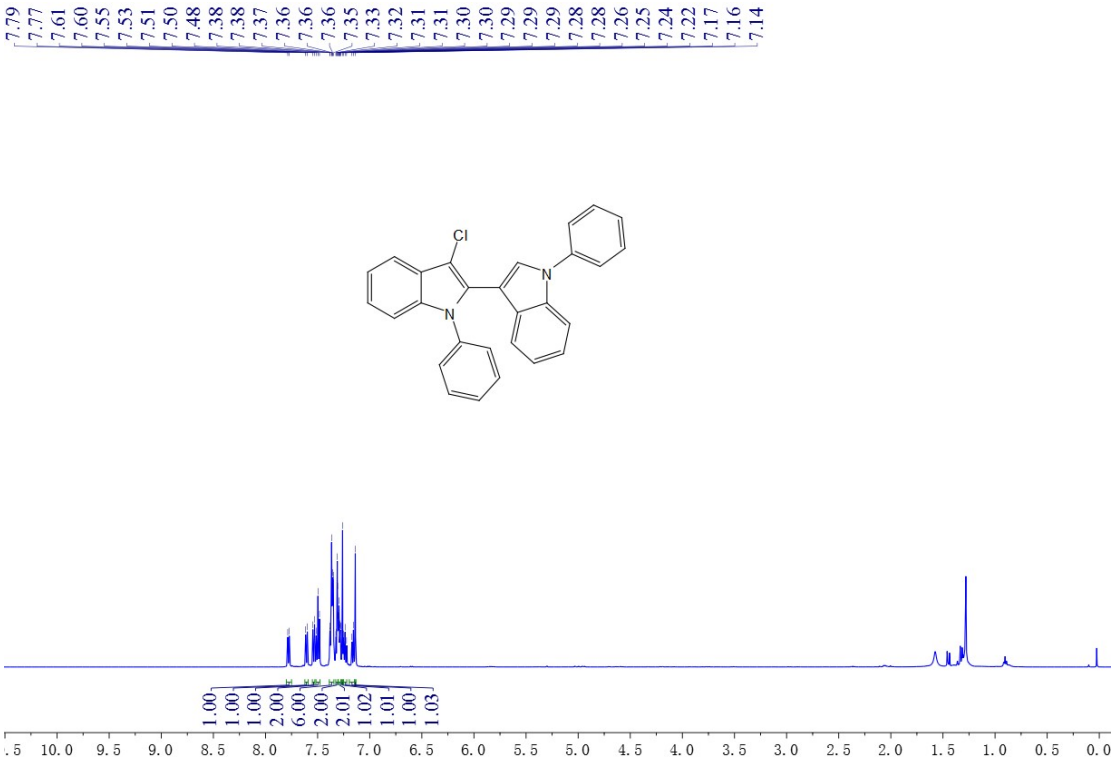
(7) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of B2



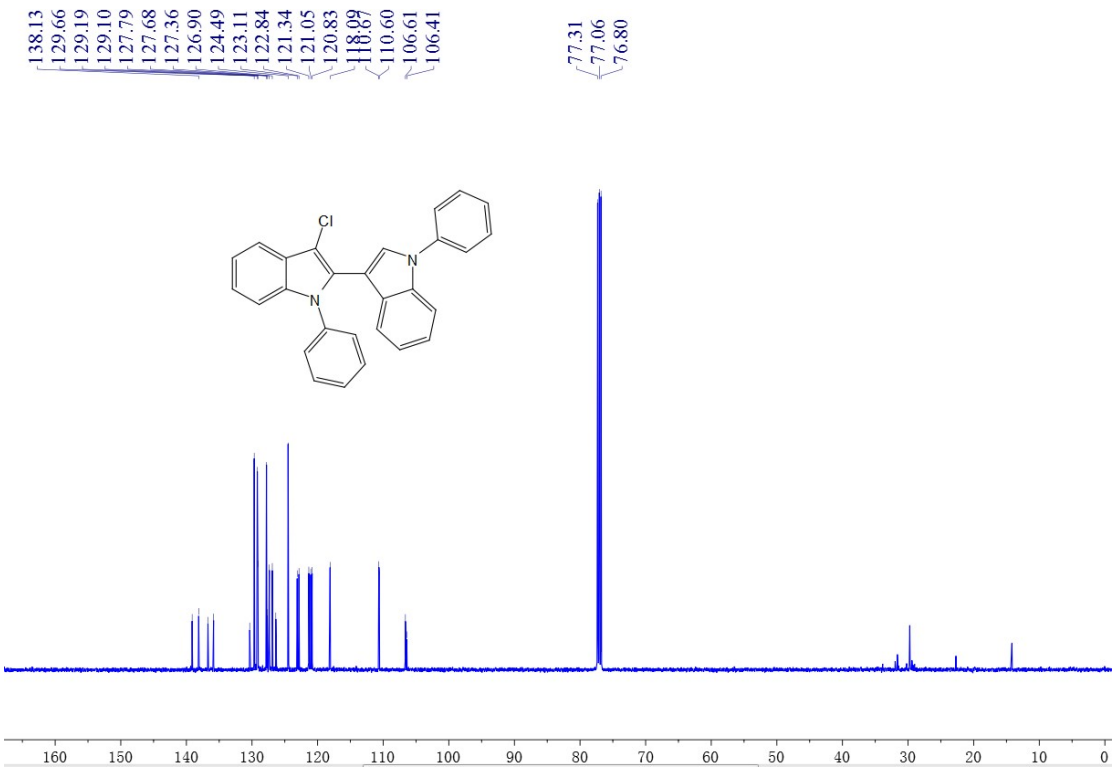
(8) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of B2



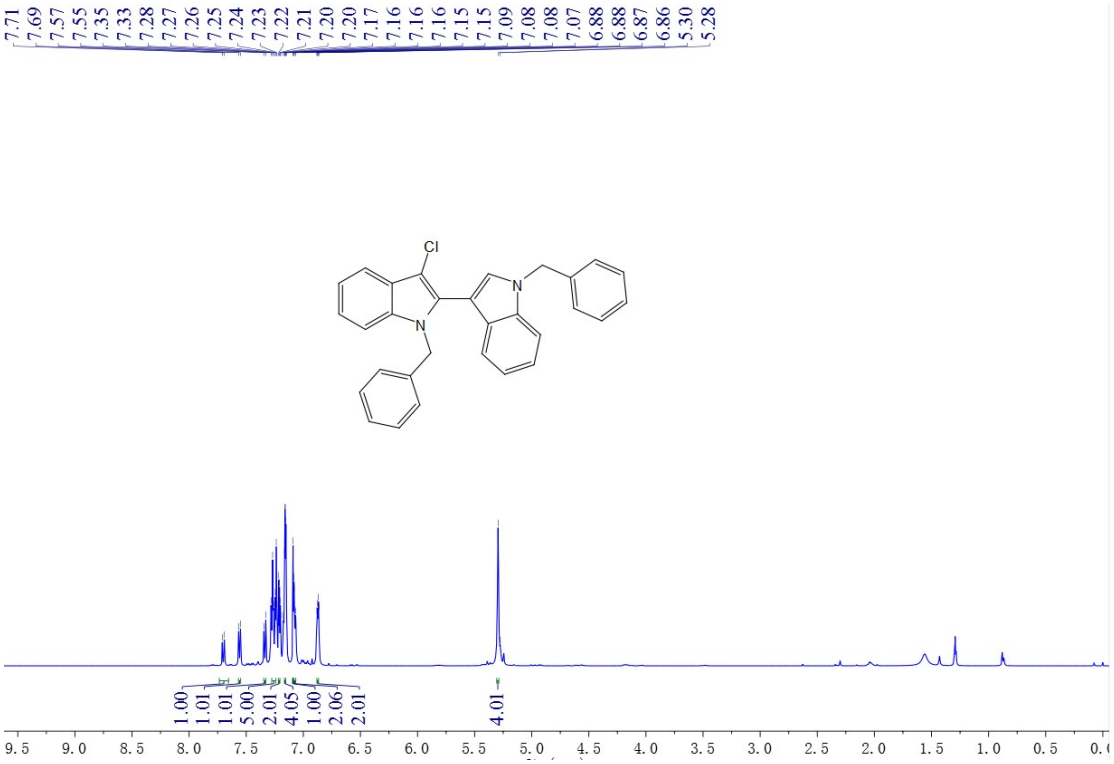
(9) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of B3



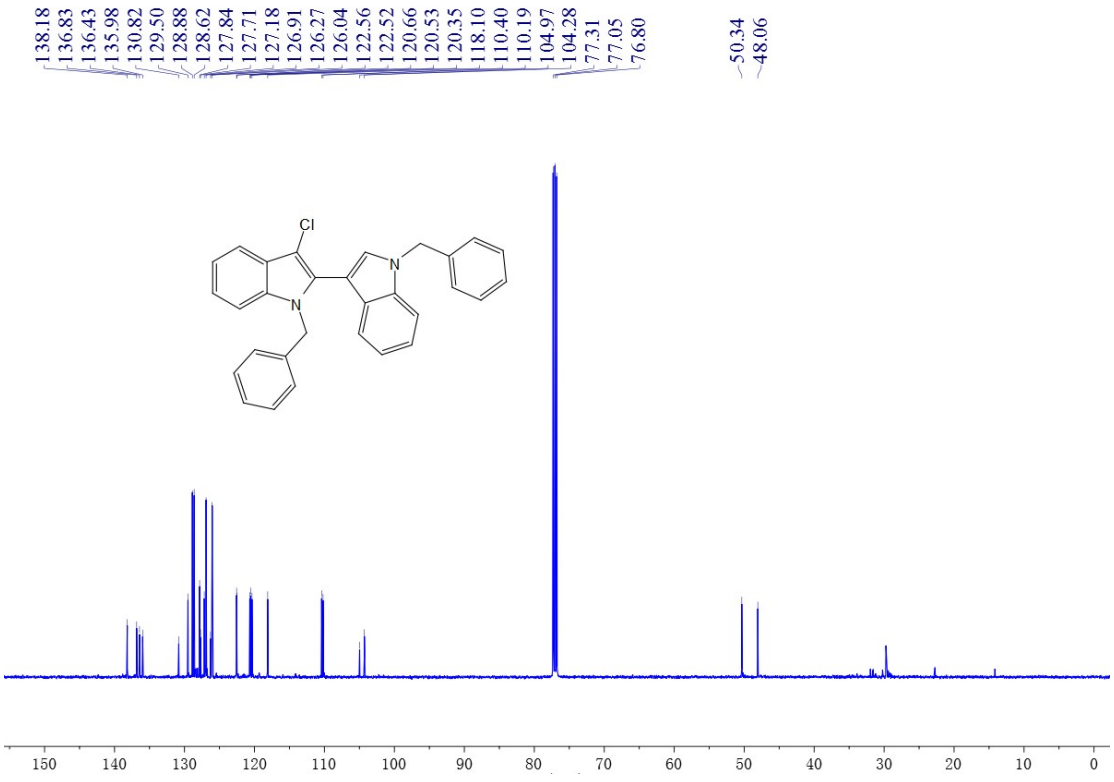
(10) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of B3



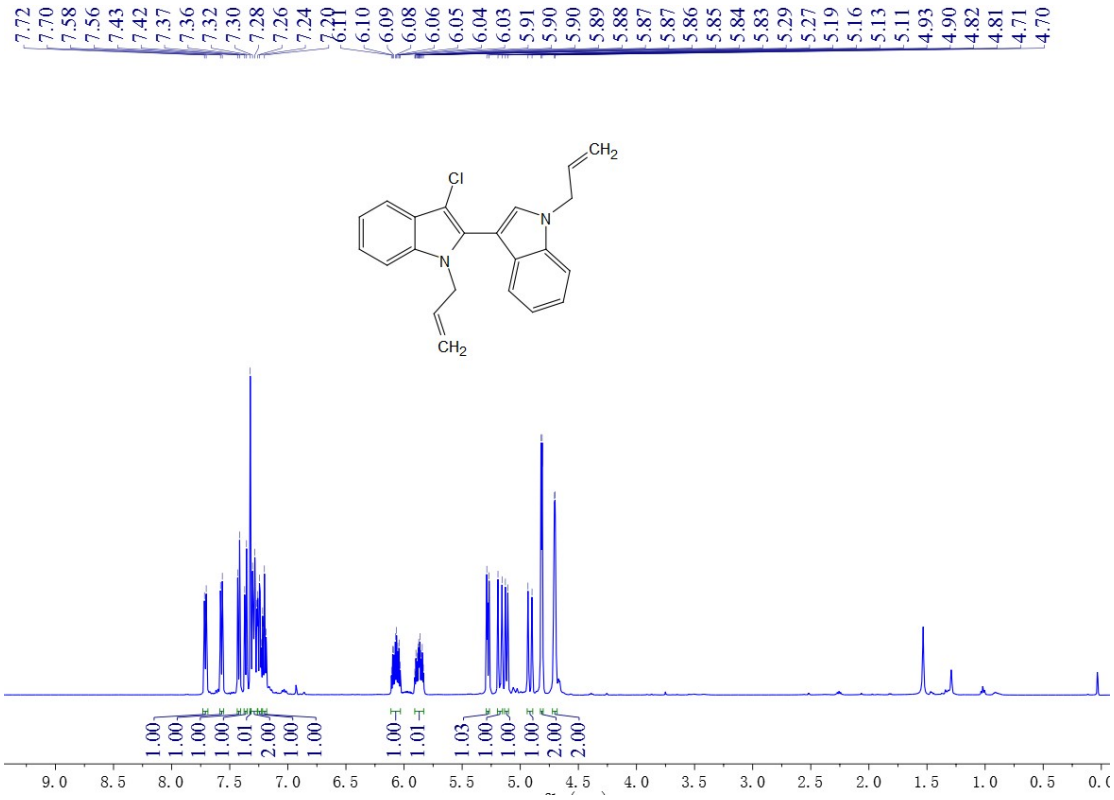
(11) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of B4



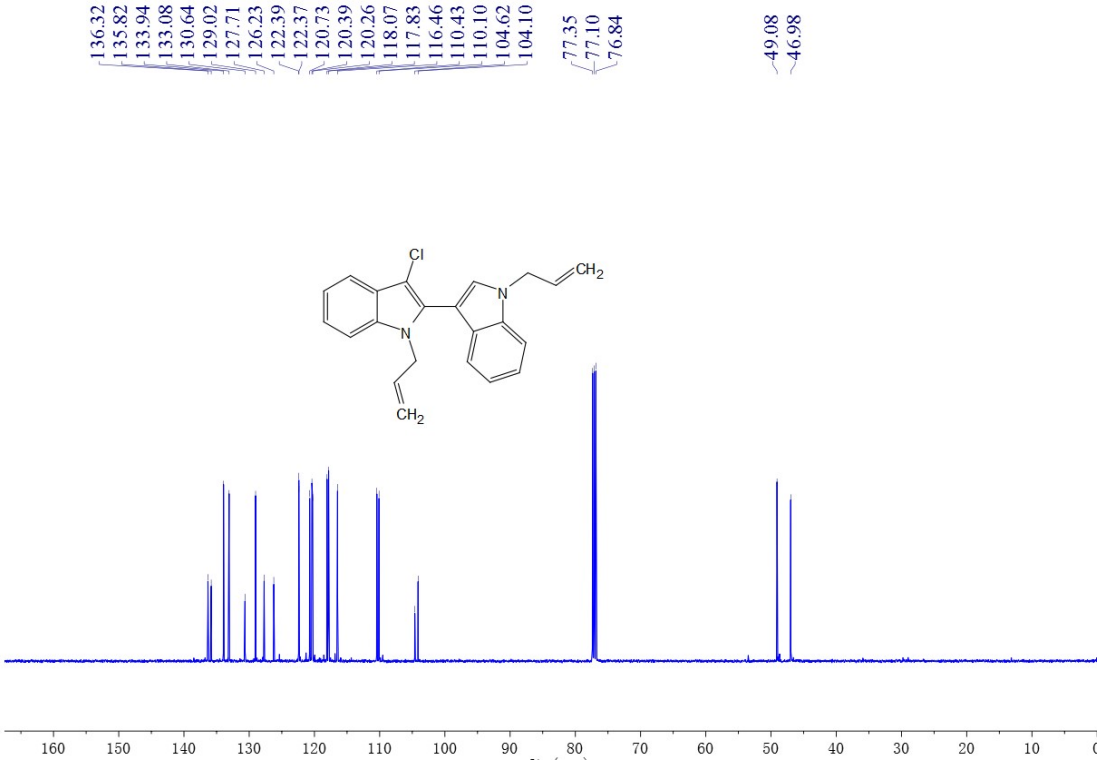
(12) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of B4



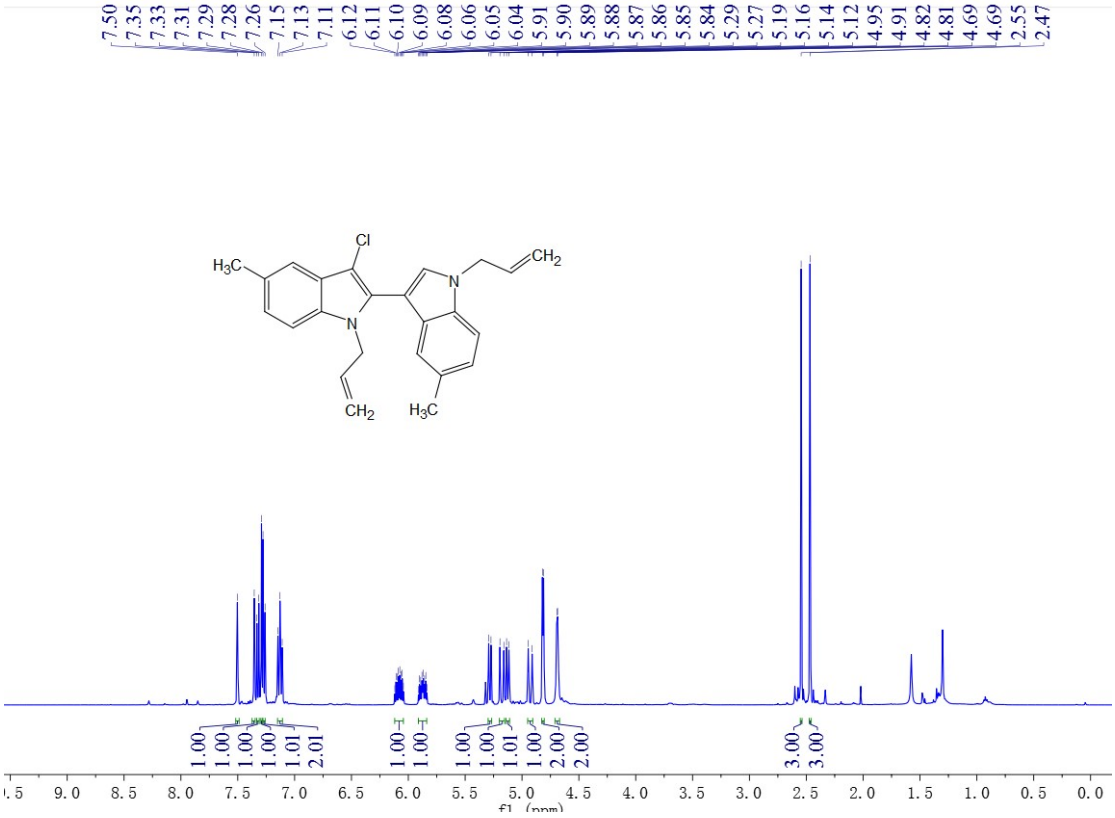
(13) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of B5



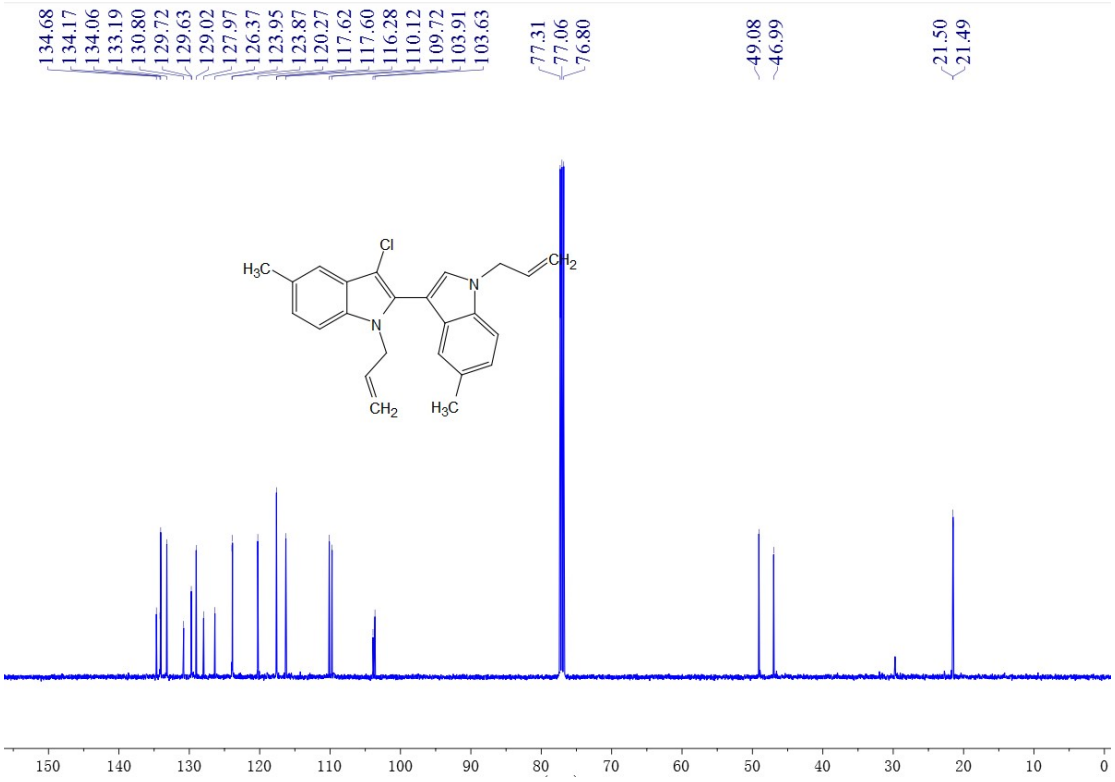
(14) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of B5



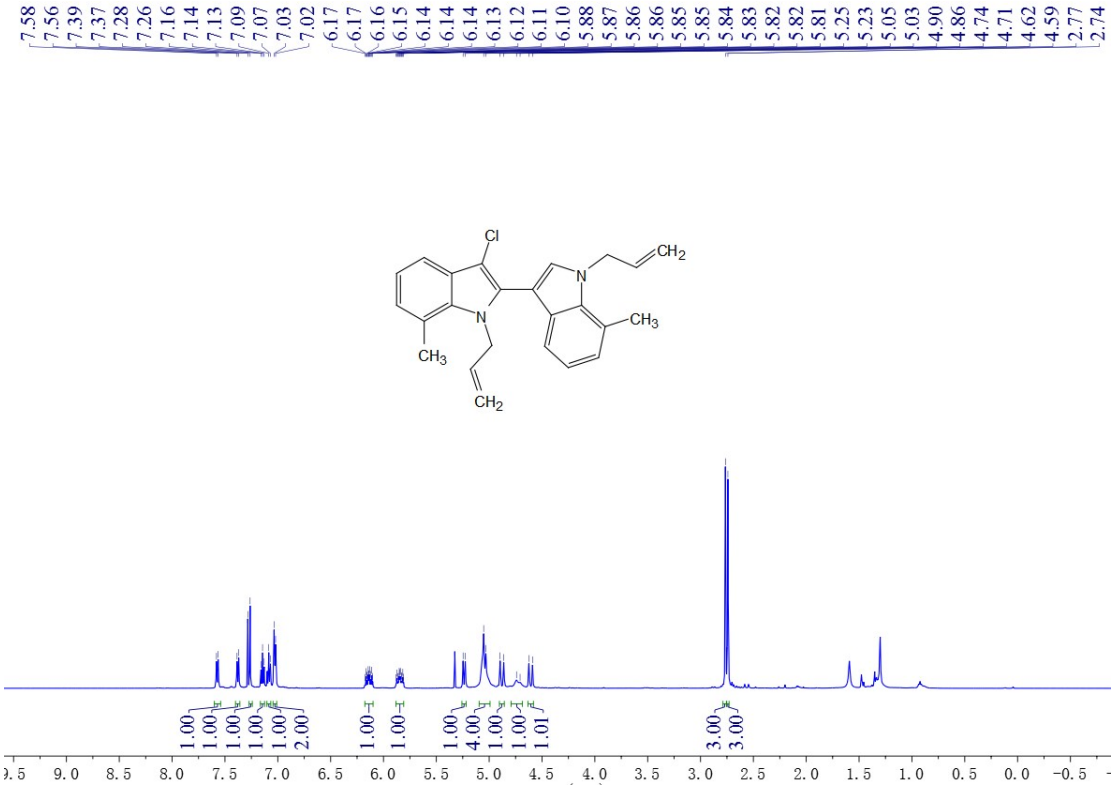
(15) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of B6



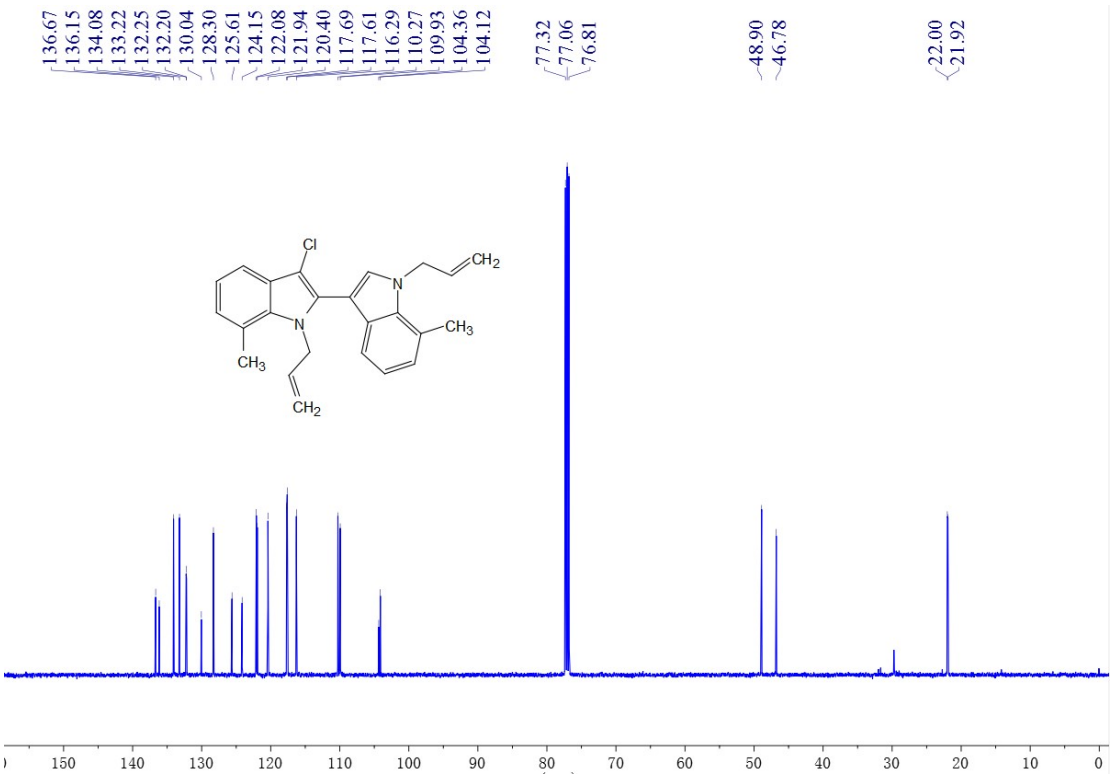
(16) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of B6



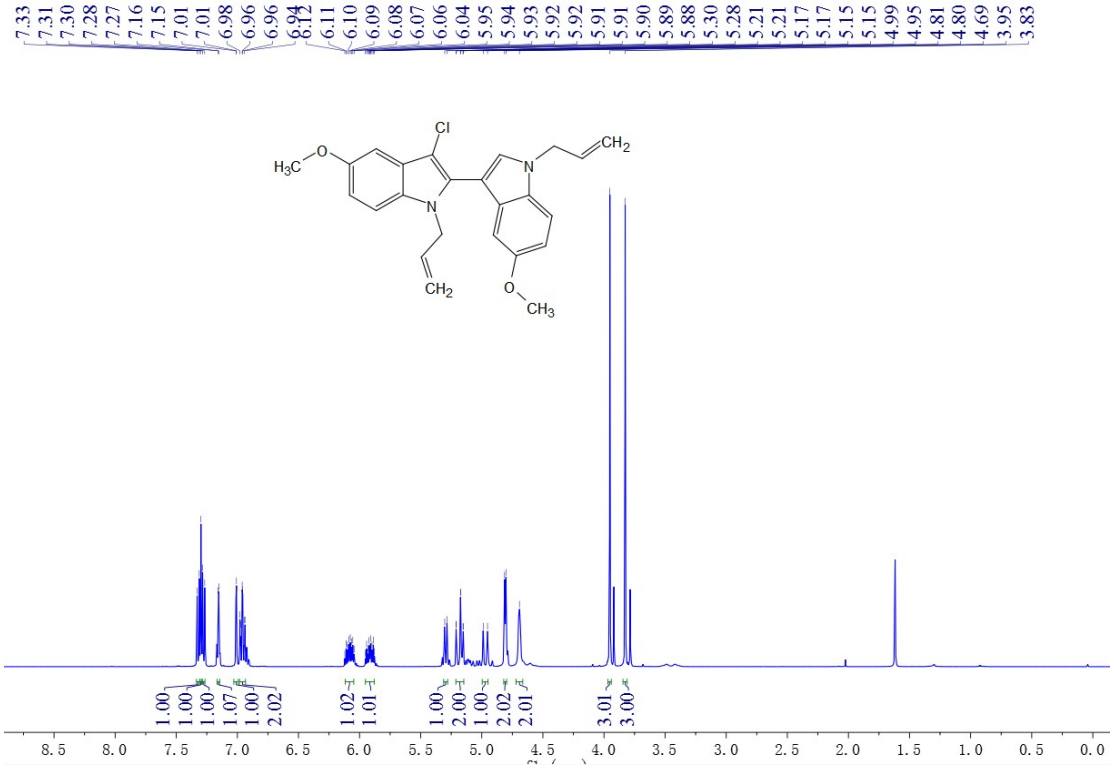
(17) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of B7



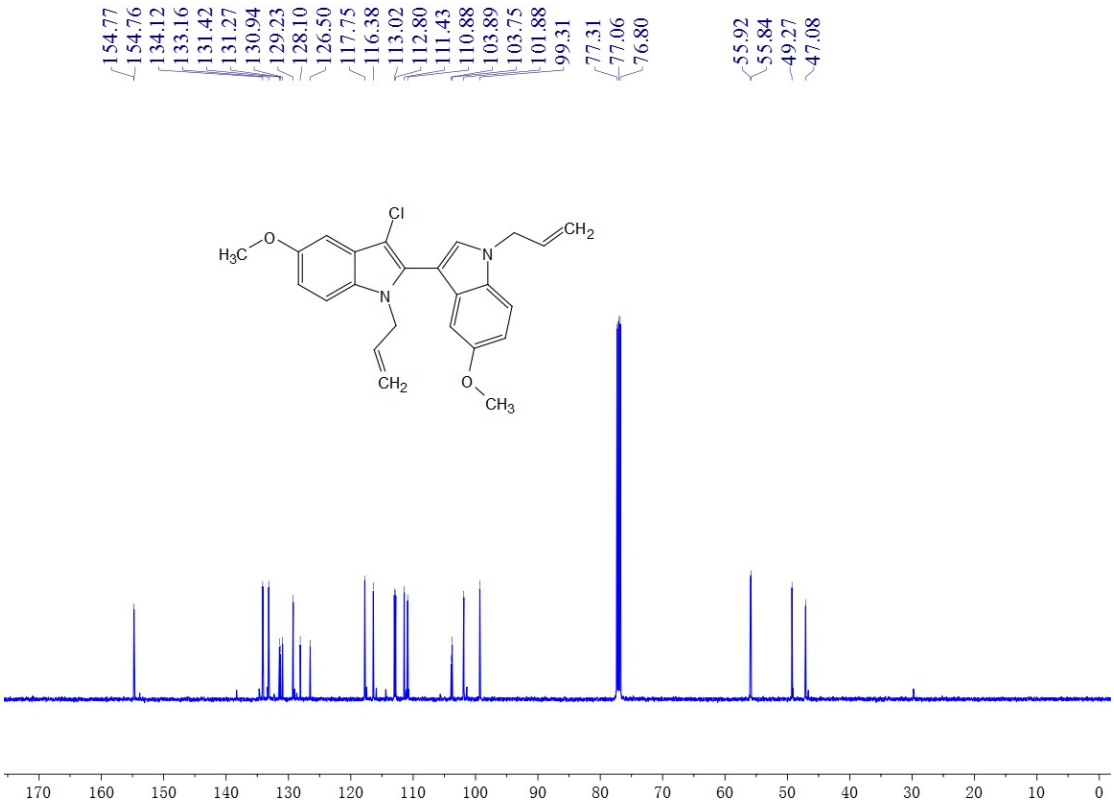
(18) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of B7



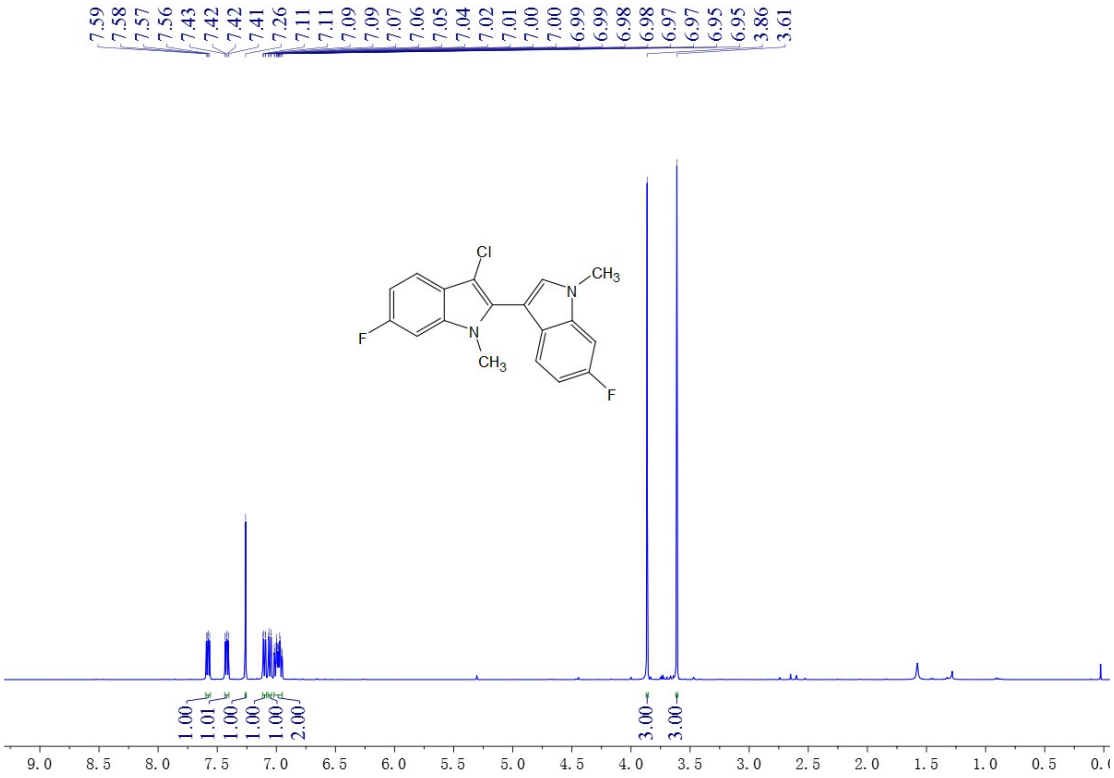
(19) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of B8



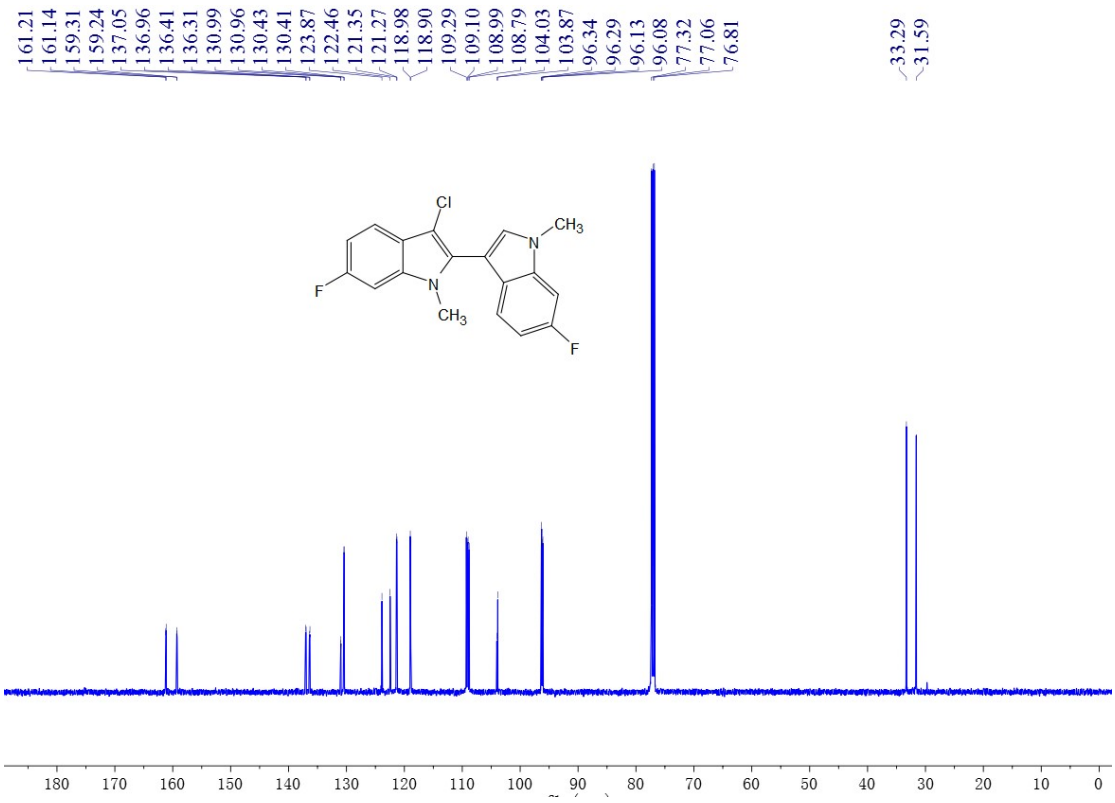
(20) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of B8



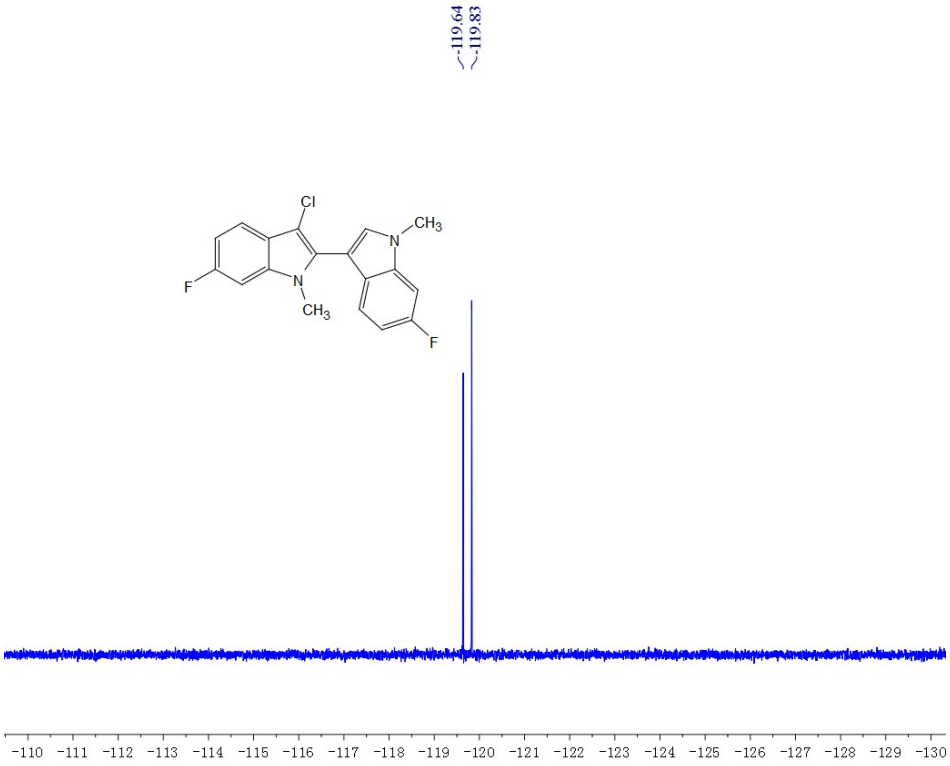
(21) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of B9



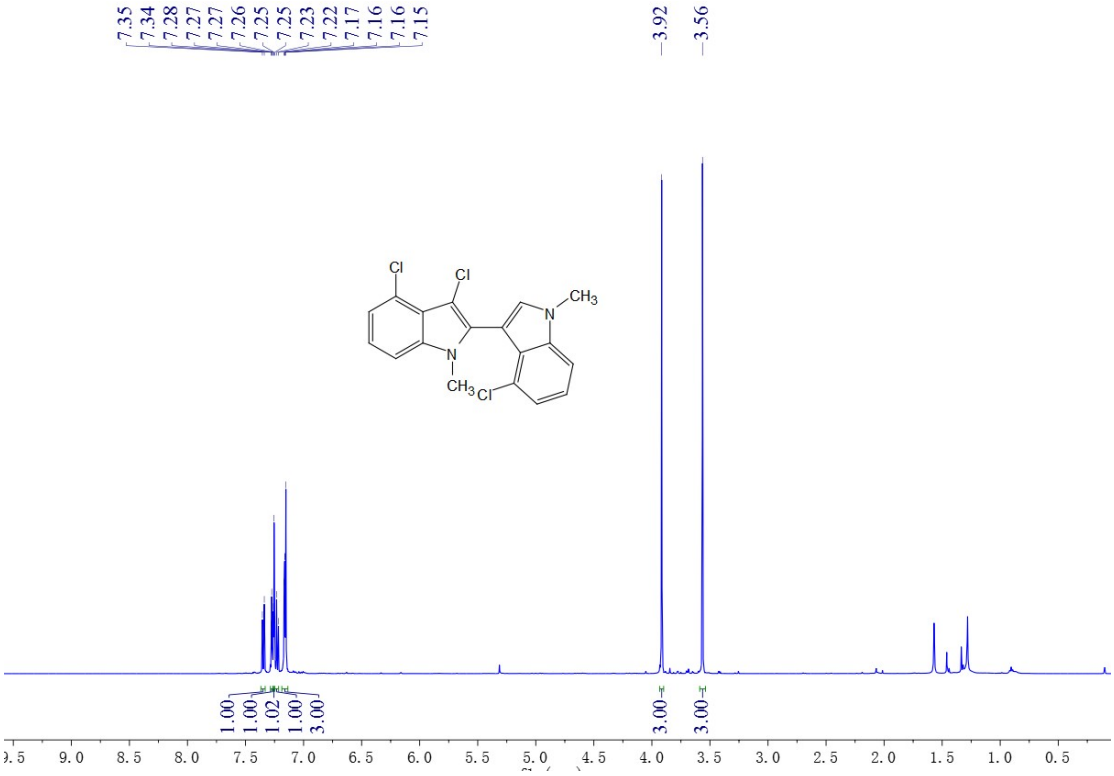
(22) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of B9



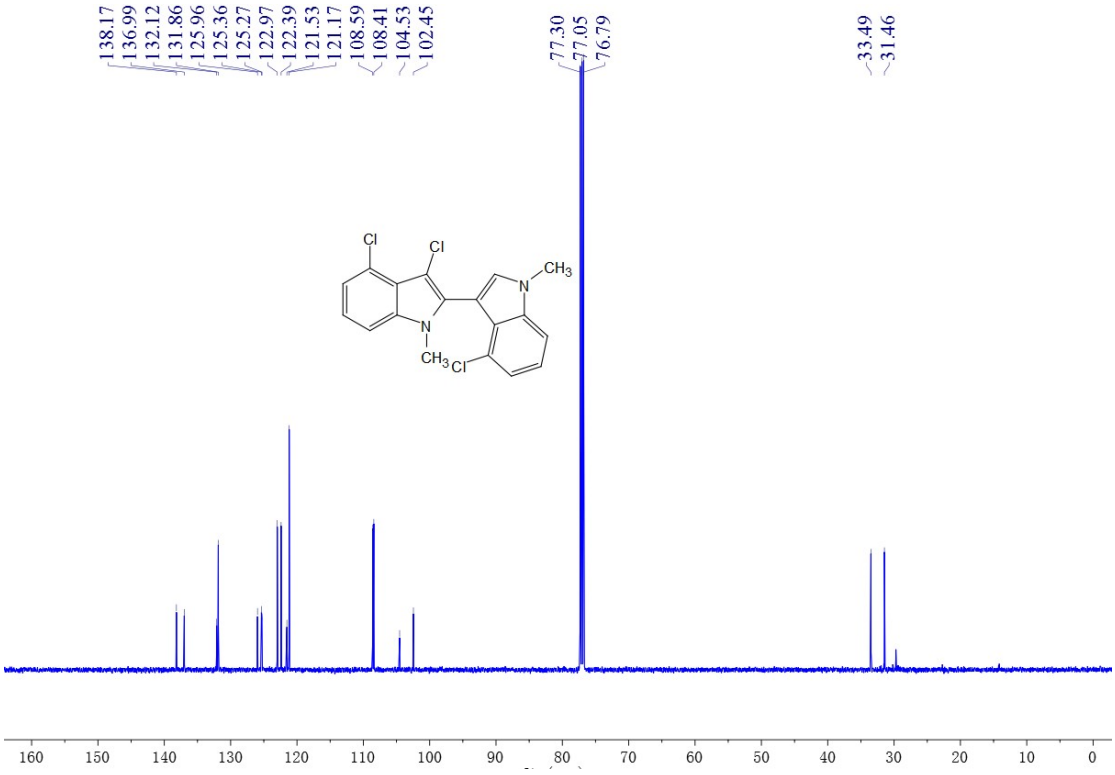
(23) ^{19}F-NMR (471 MHz, $CDCl_3$) spectrum of B9



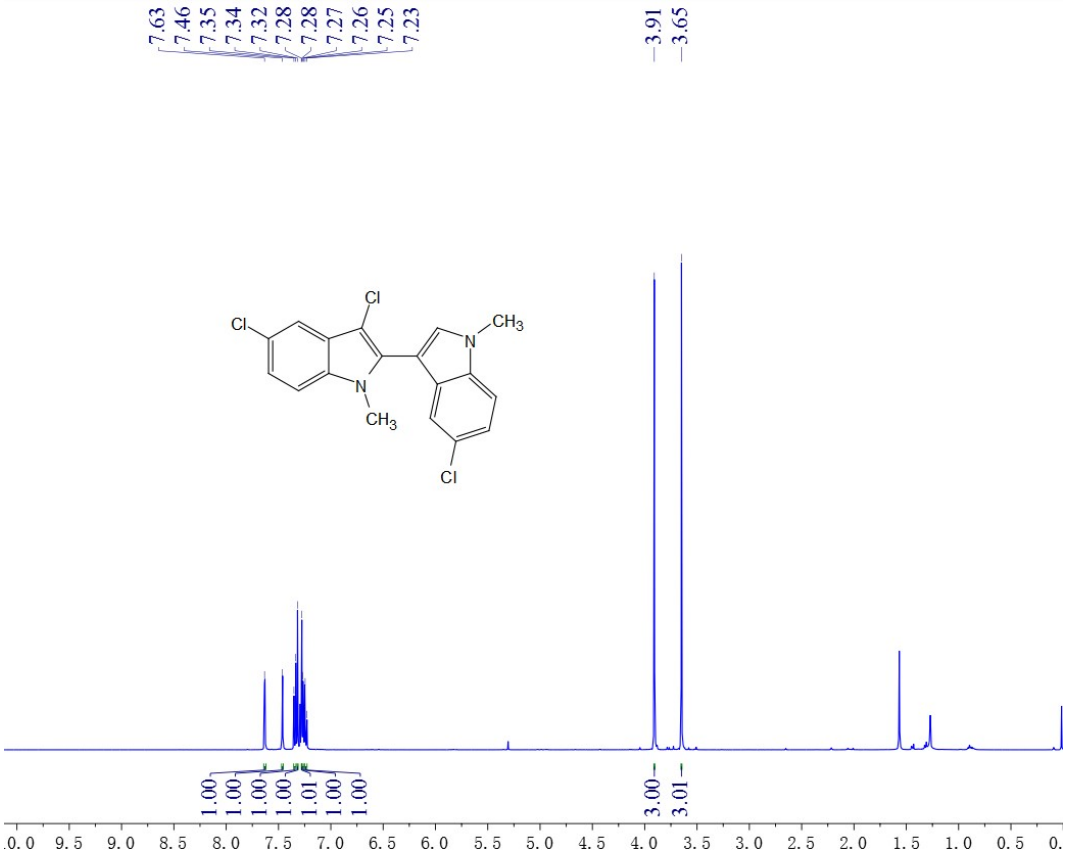
(24) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of B10



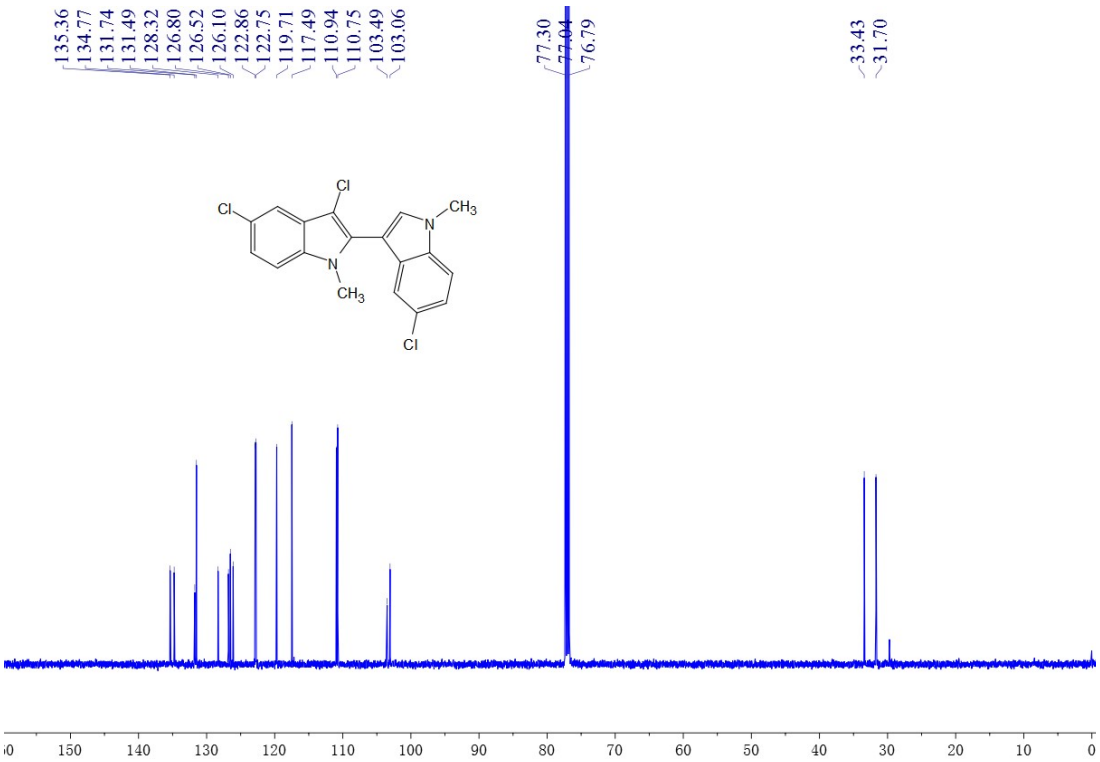
(25) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of B10



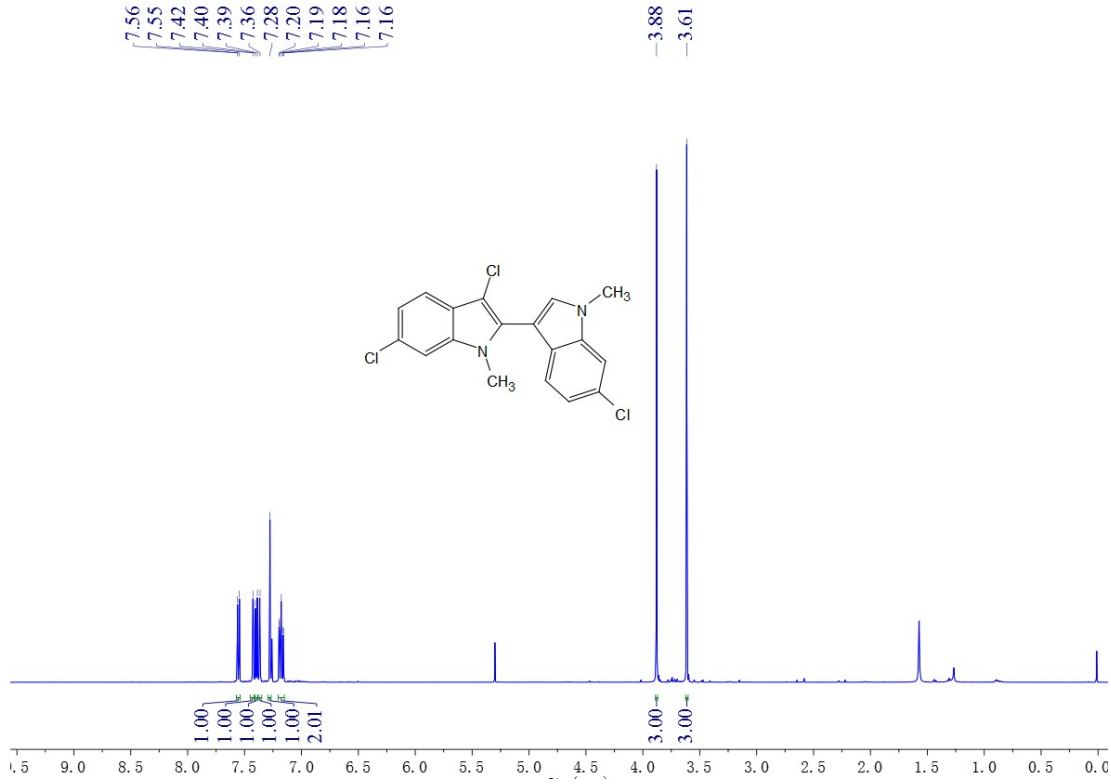
(26) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of B11



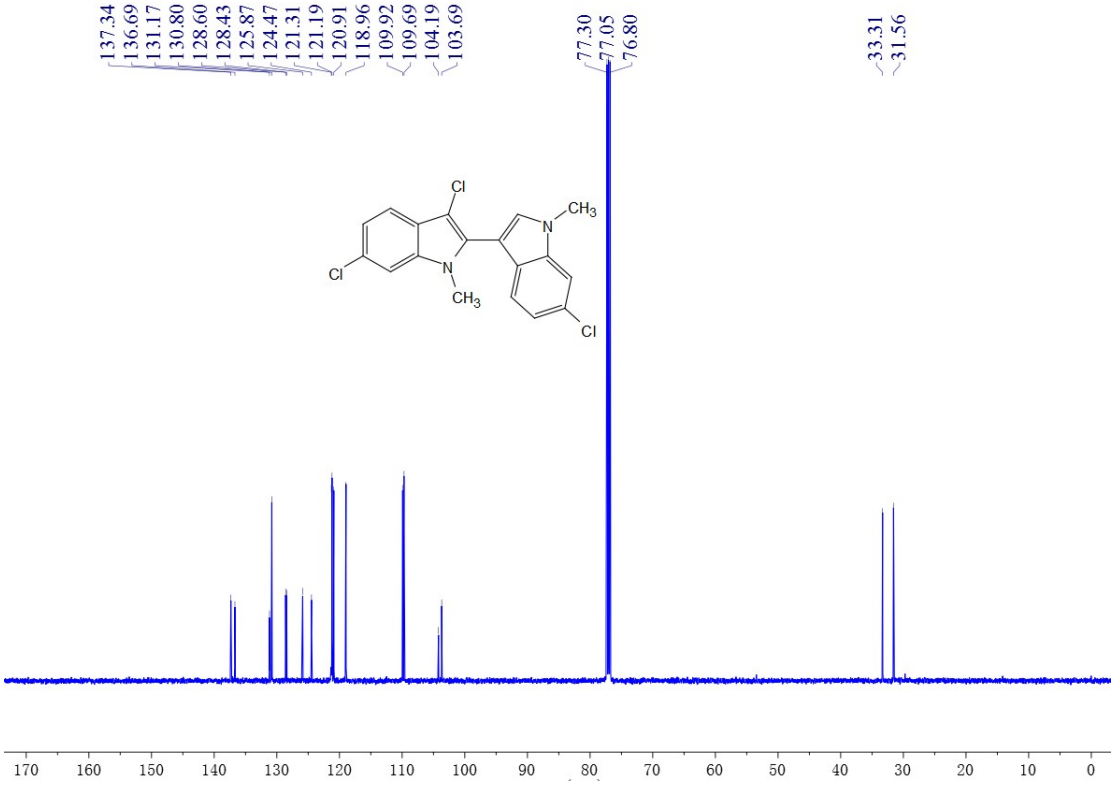
(27) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of B11



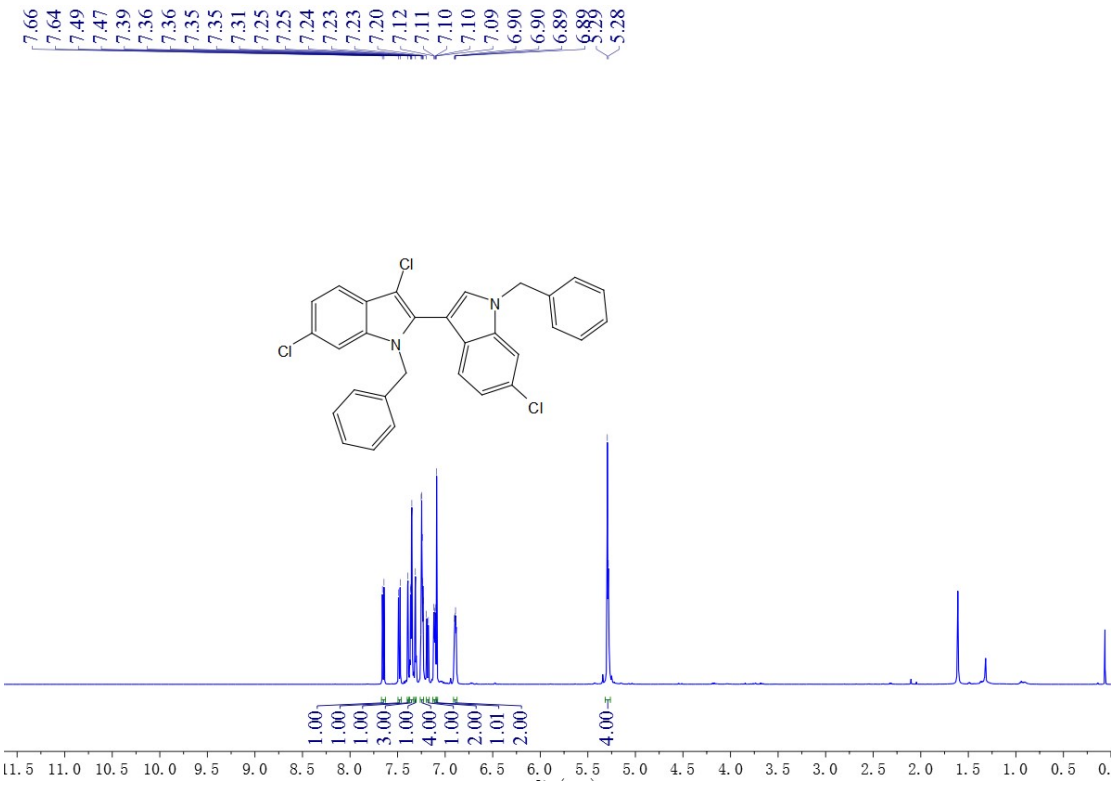
(28) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of B12



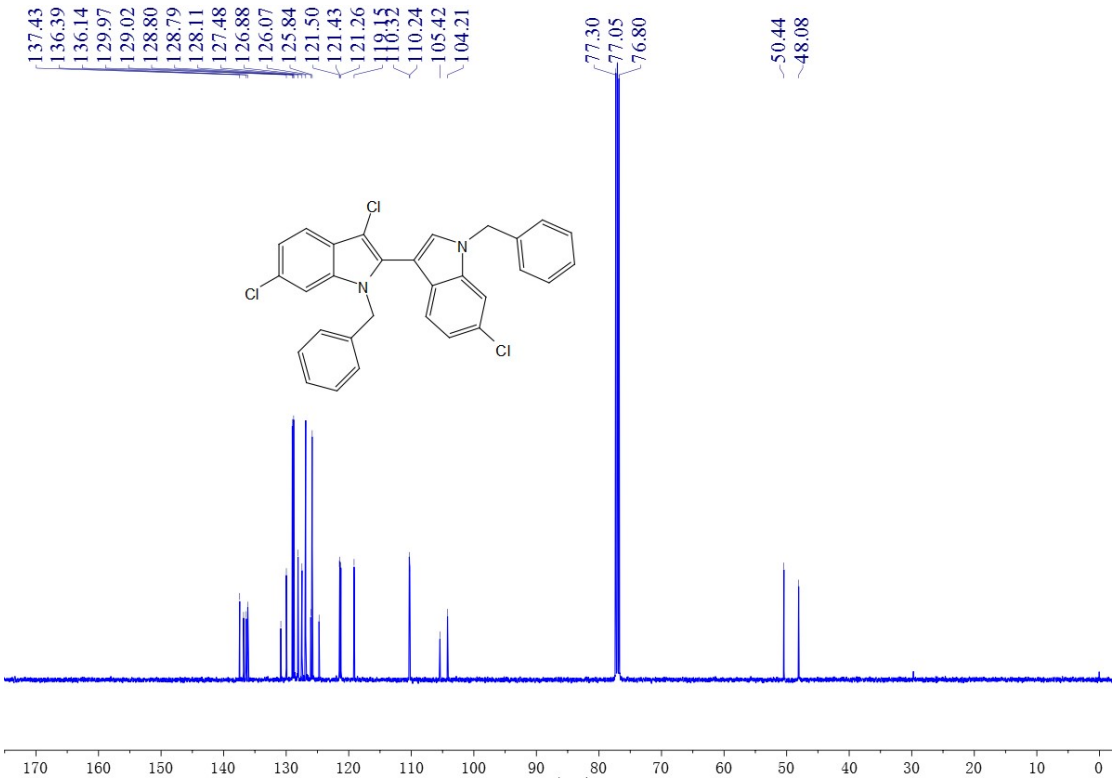
(29) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of B12



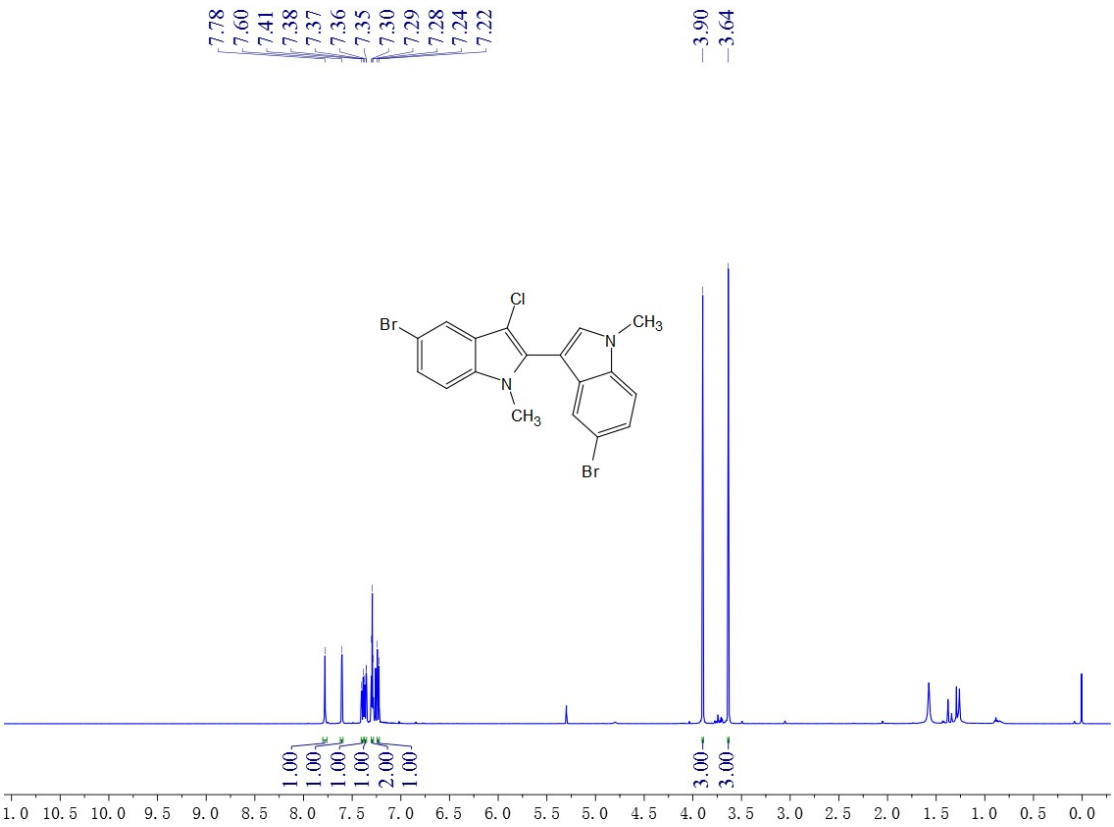
(30) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of B13



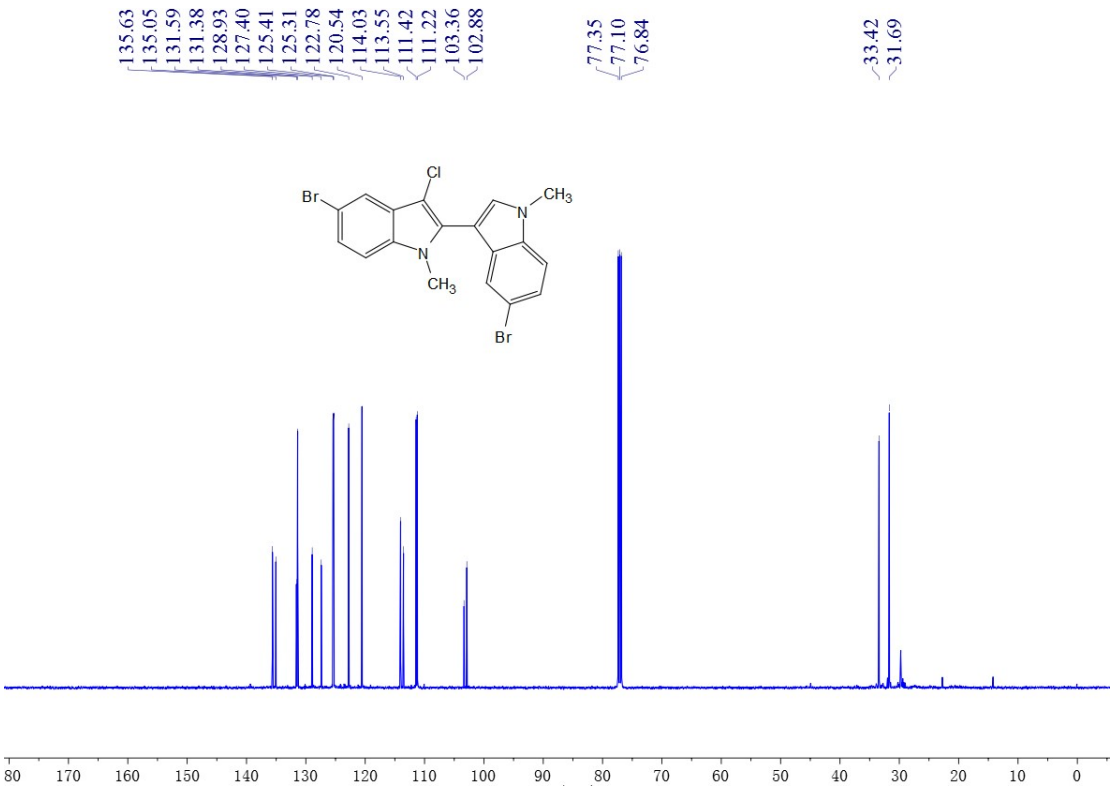
(31) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of B13



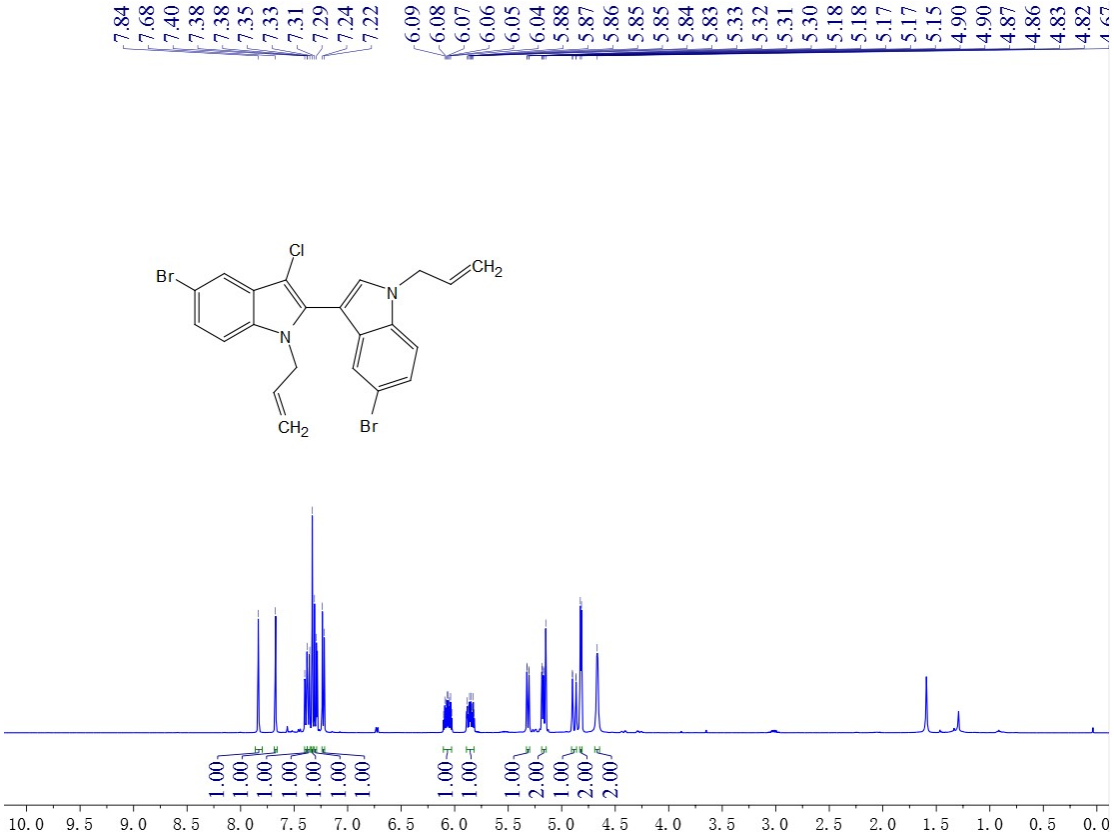
(32) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of B14



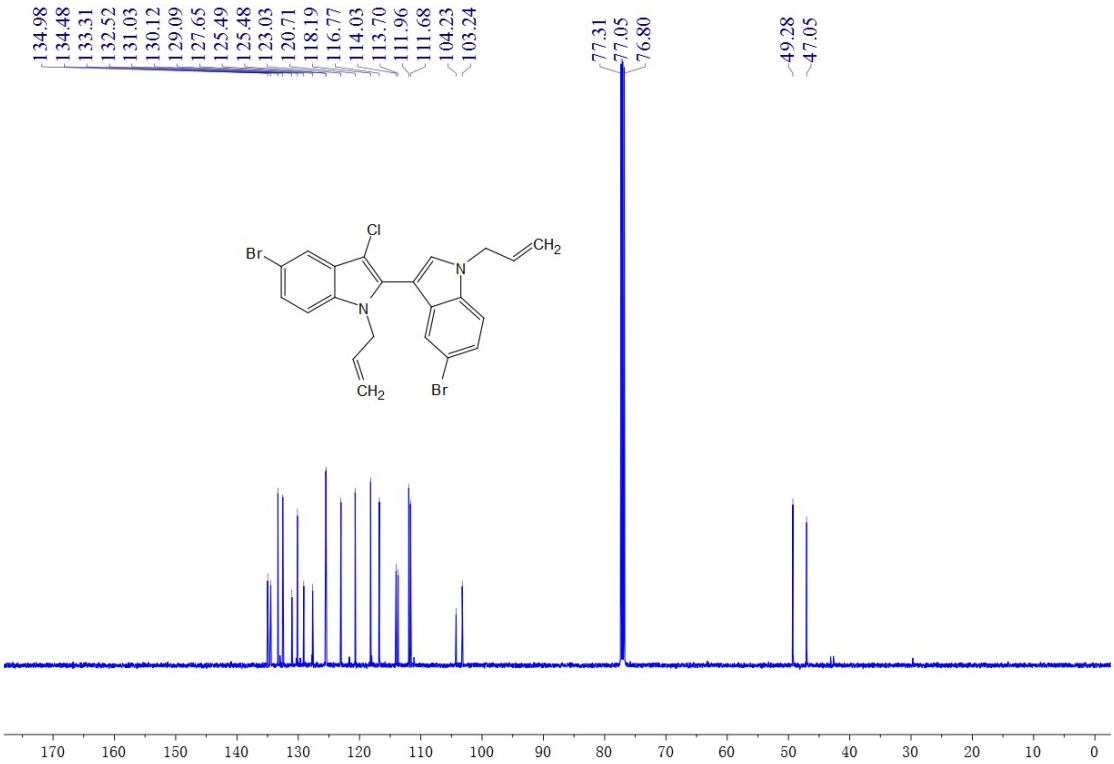
(33) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of B14



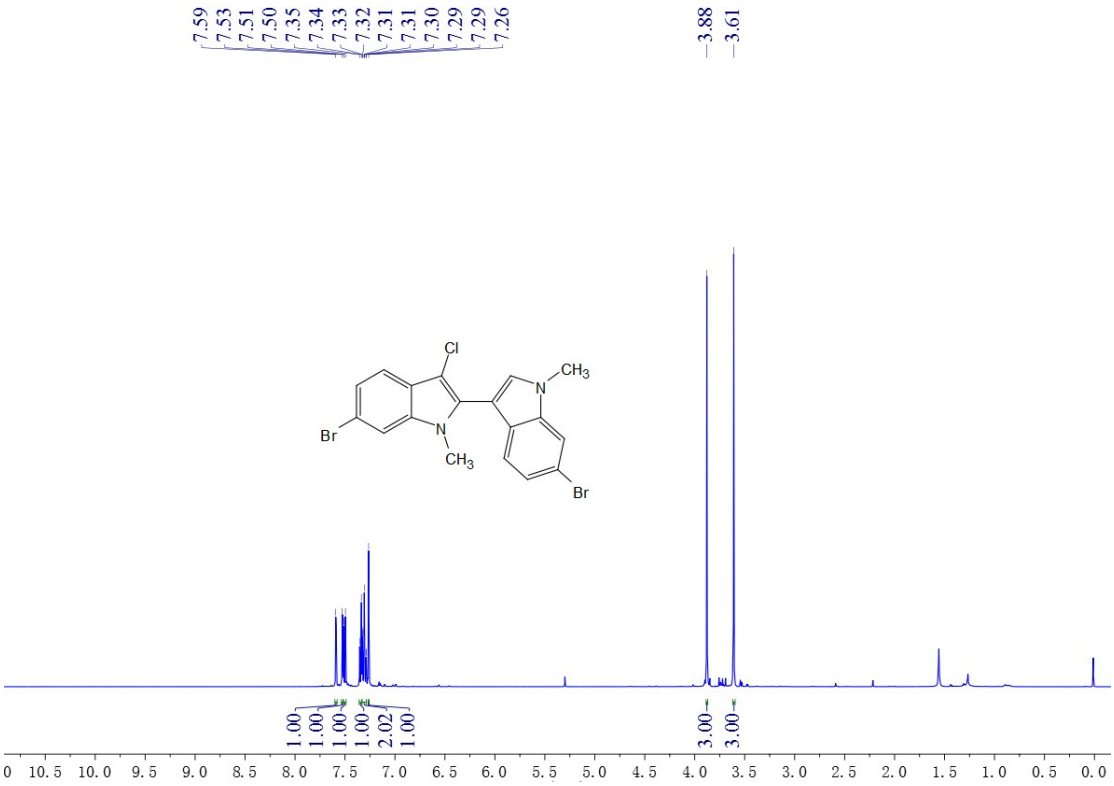
(34) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of B15



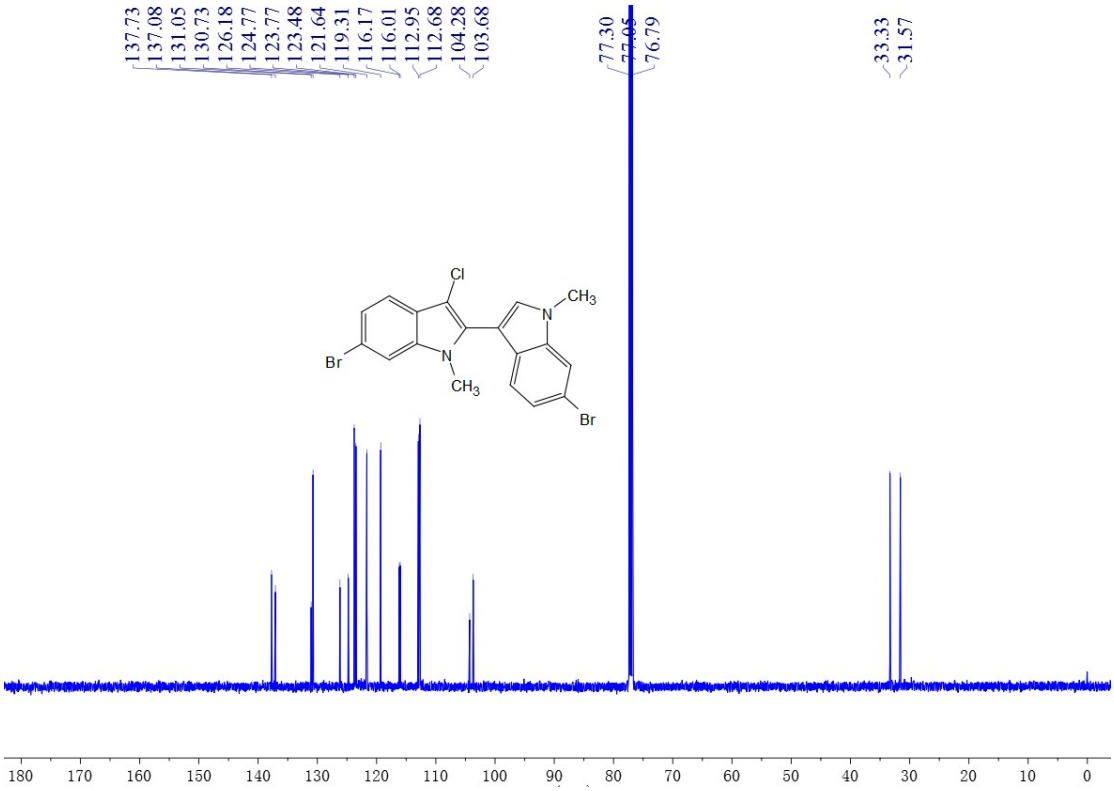
(35) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of B15



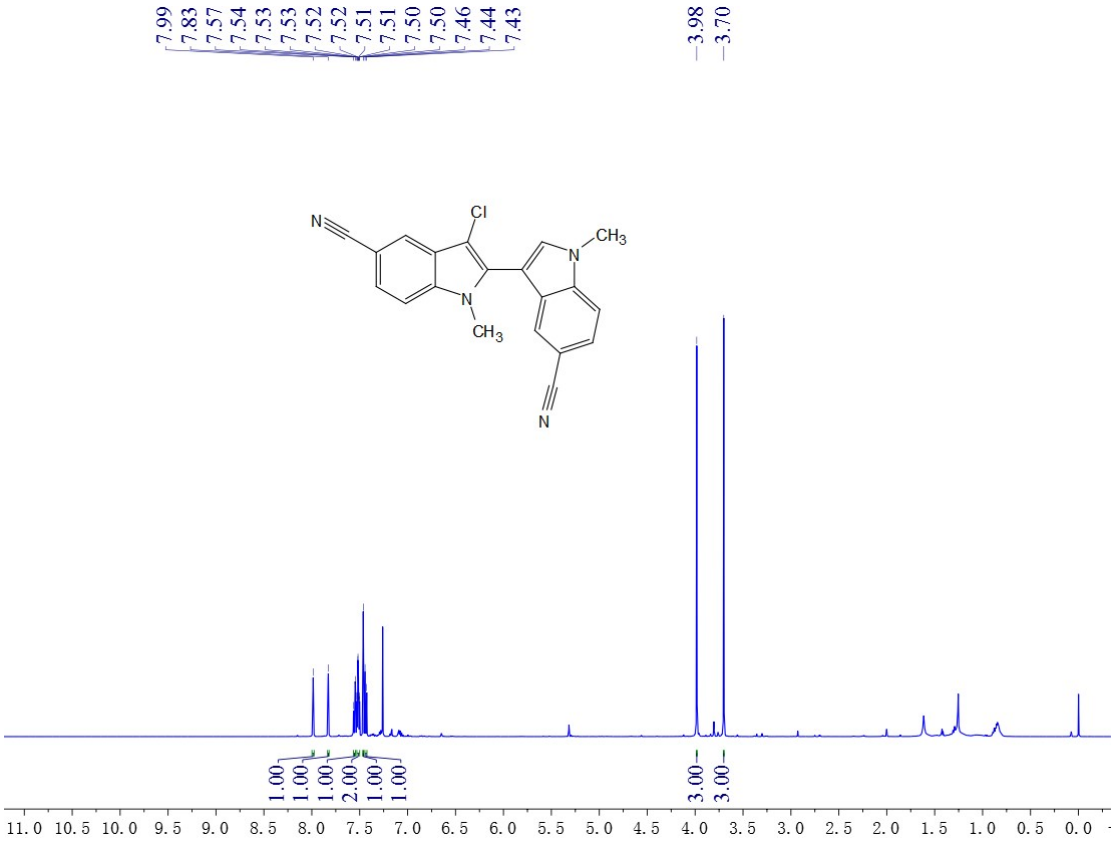
(36) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of B16



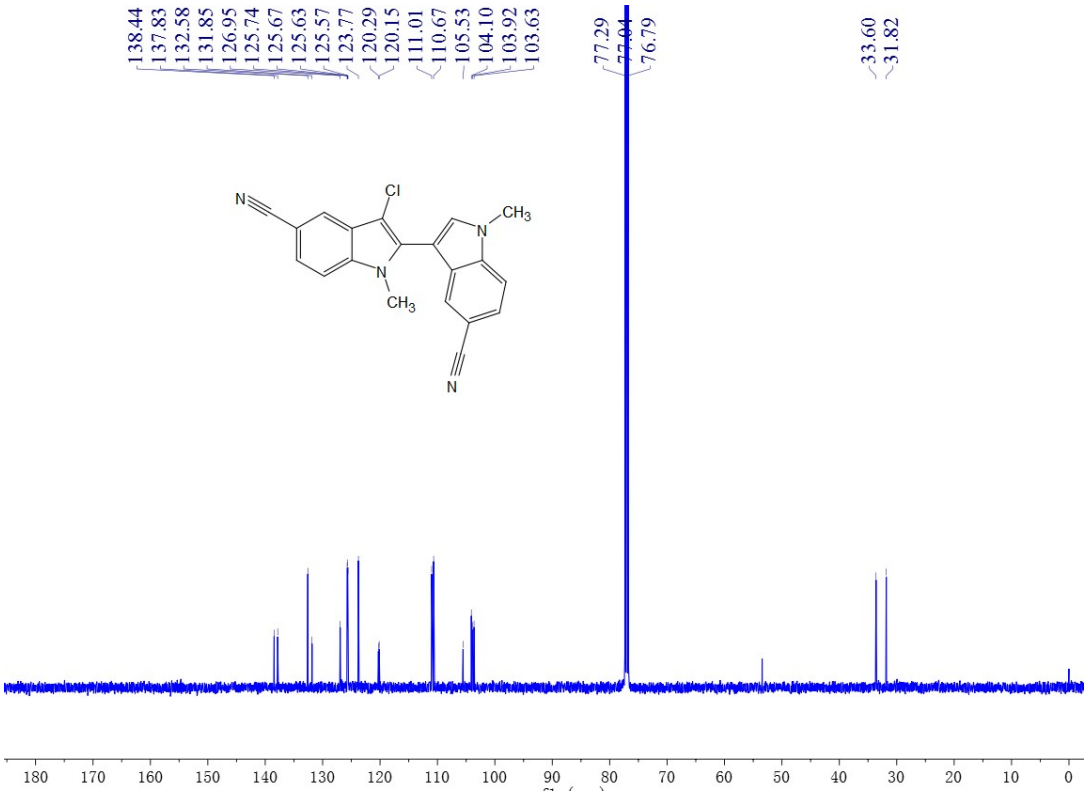
(37) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of B16



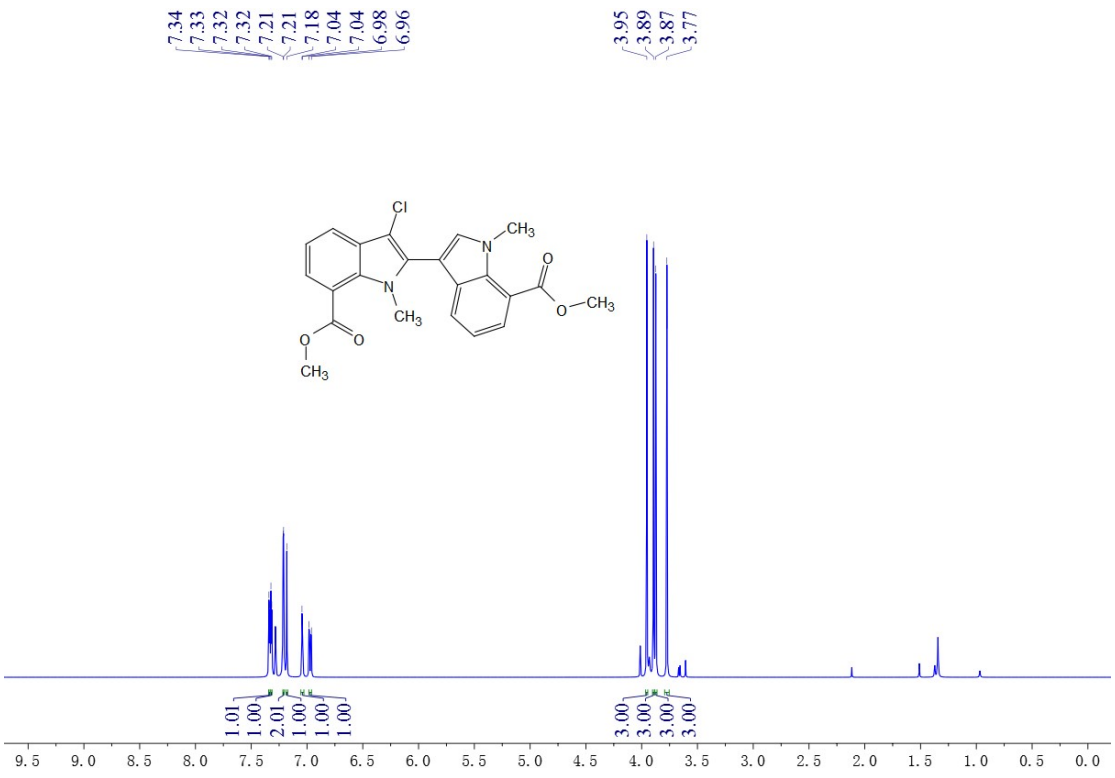
(38) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of B17



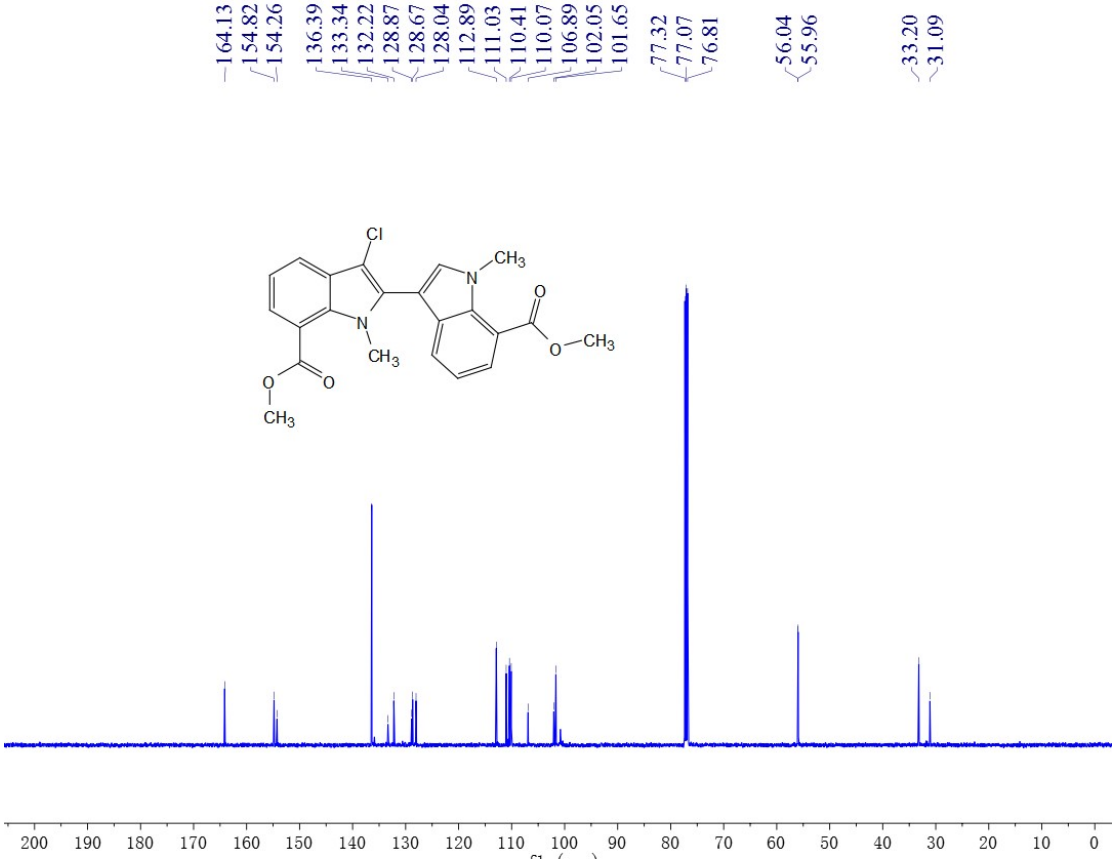
(39) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of B17



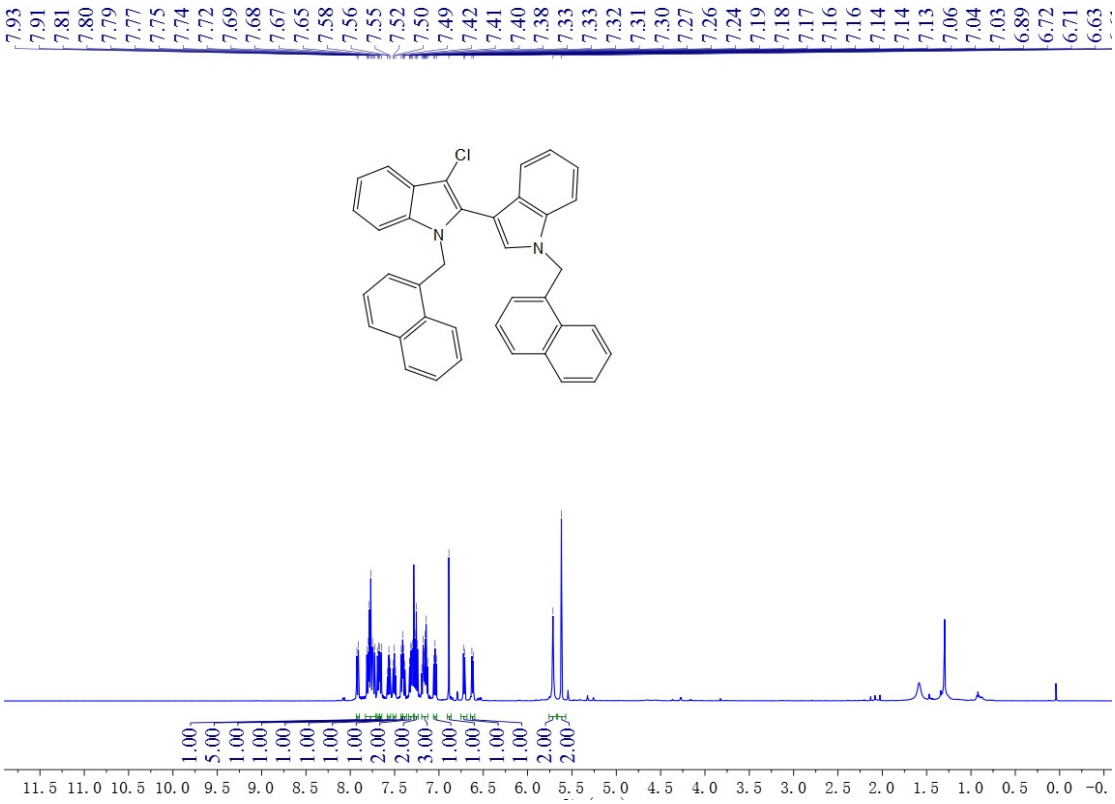
(40) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of B18



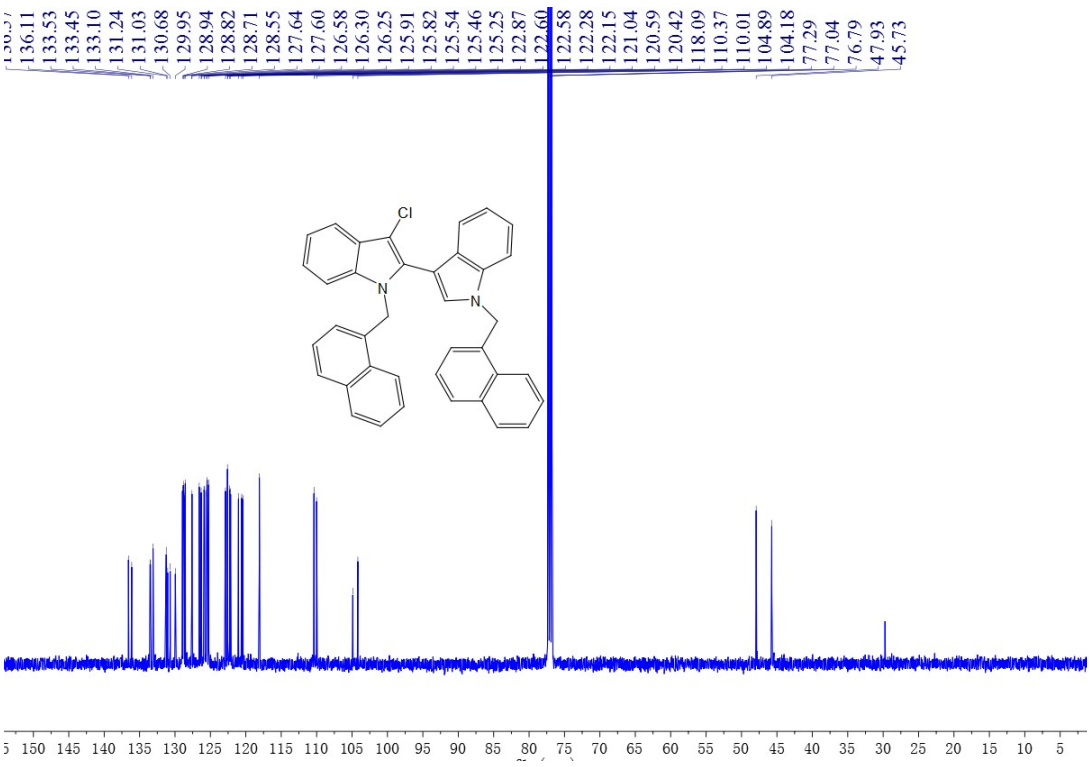
(41) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of B18



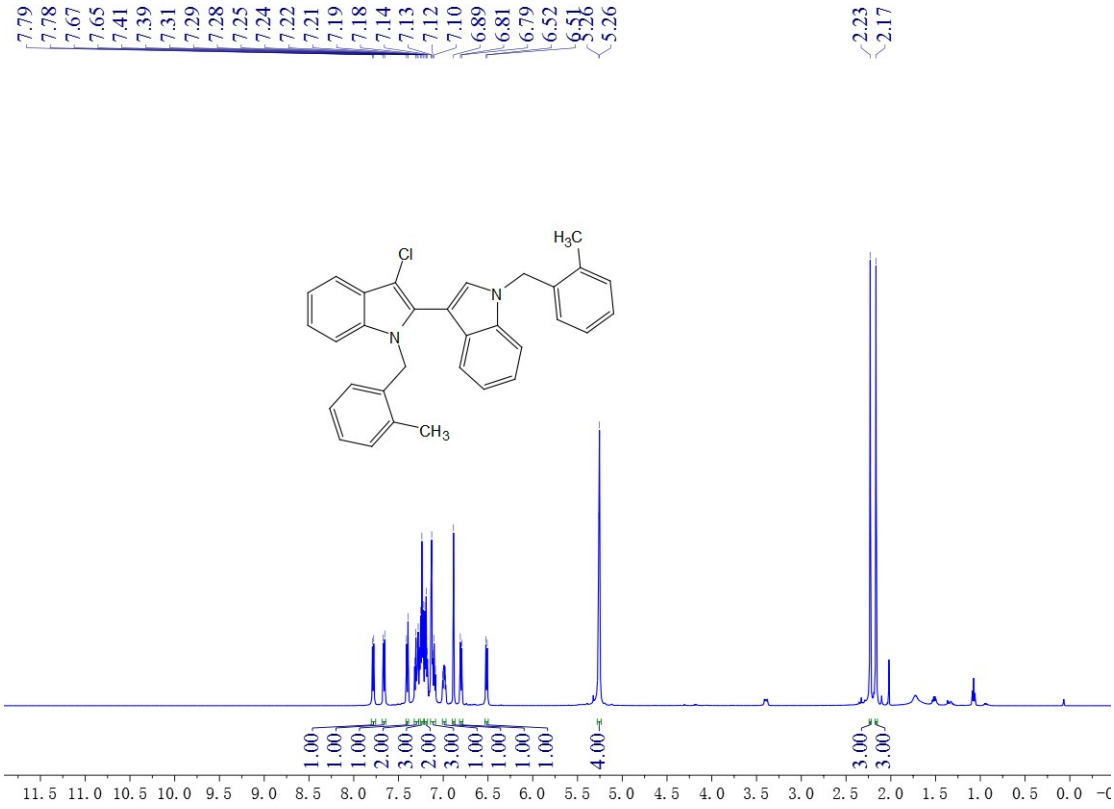
(42) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of B19



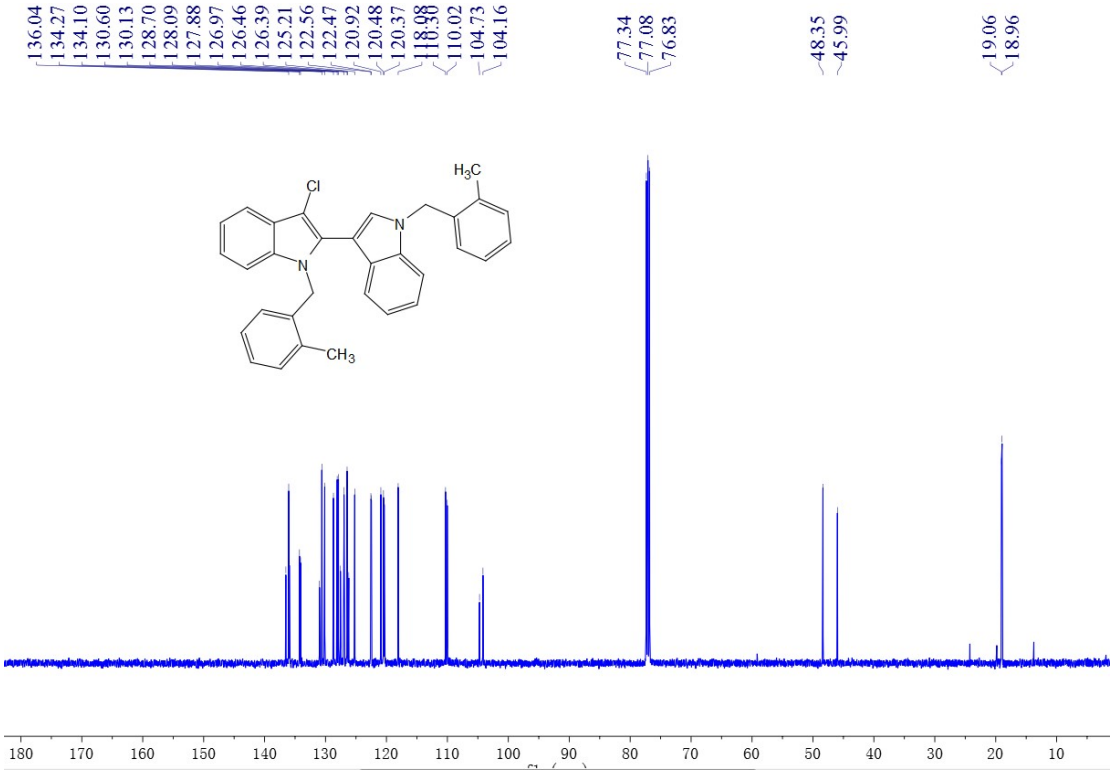
(43) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of B19



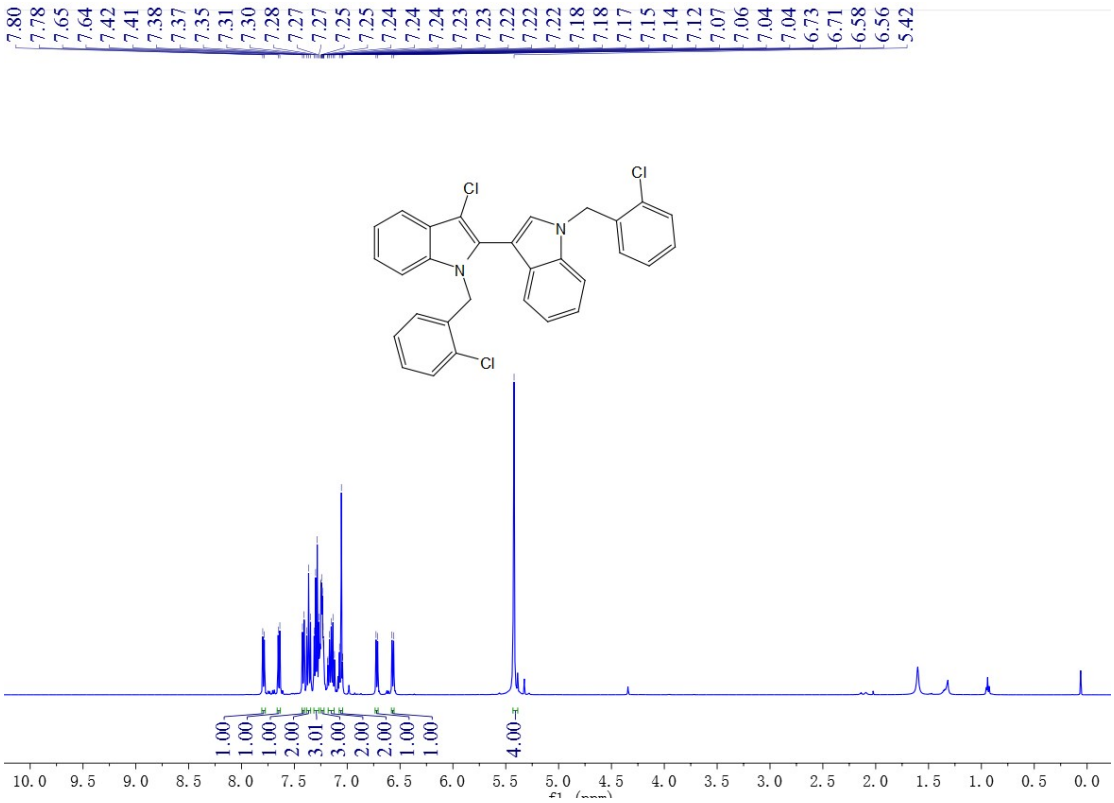
(44) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of B20



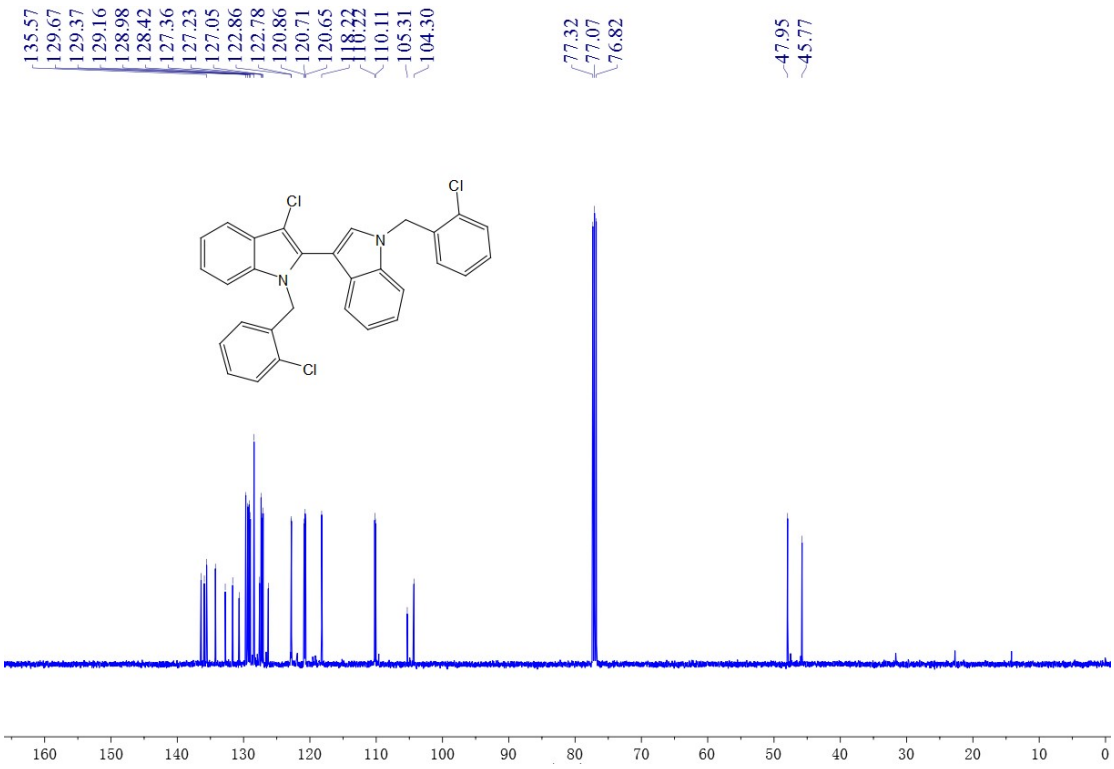
(45) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of B20



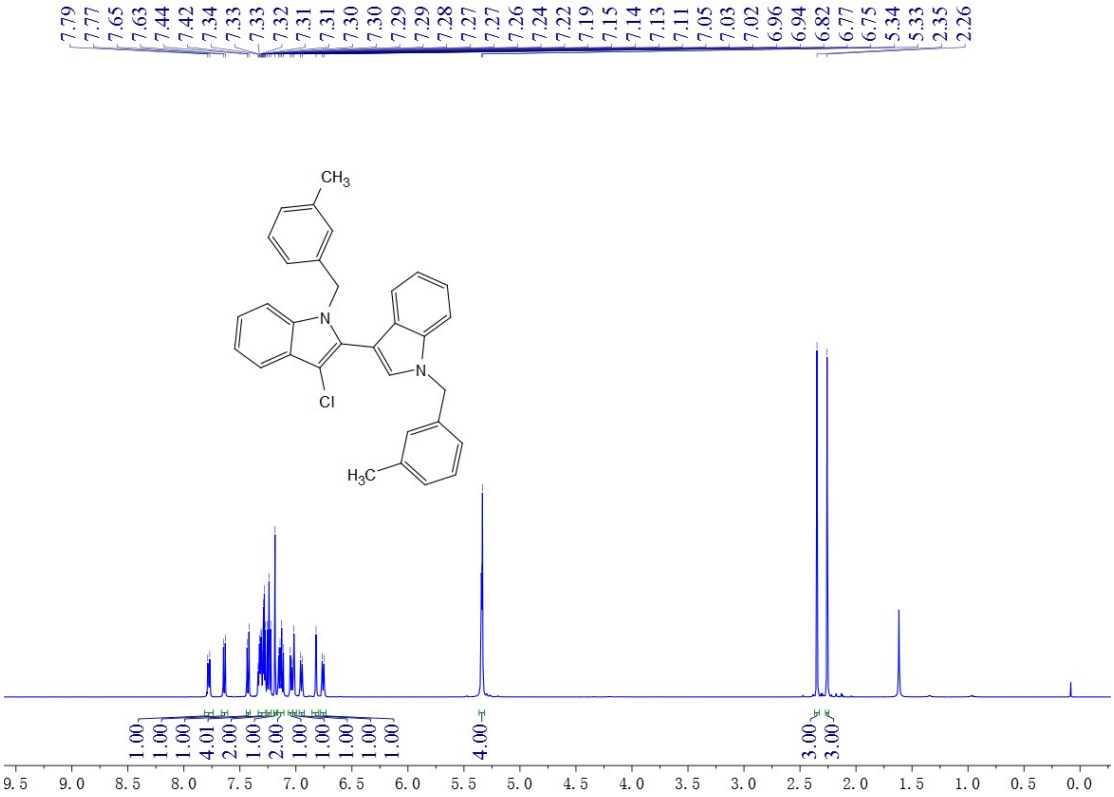
(46) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of B21



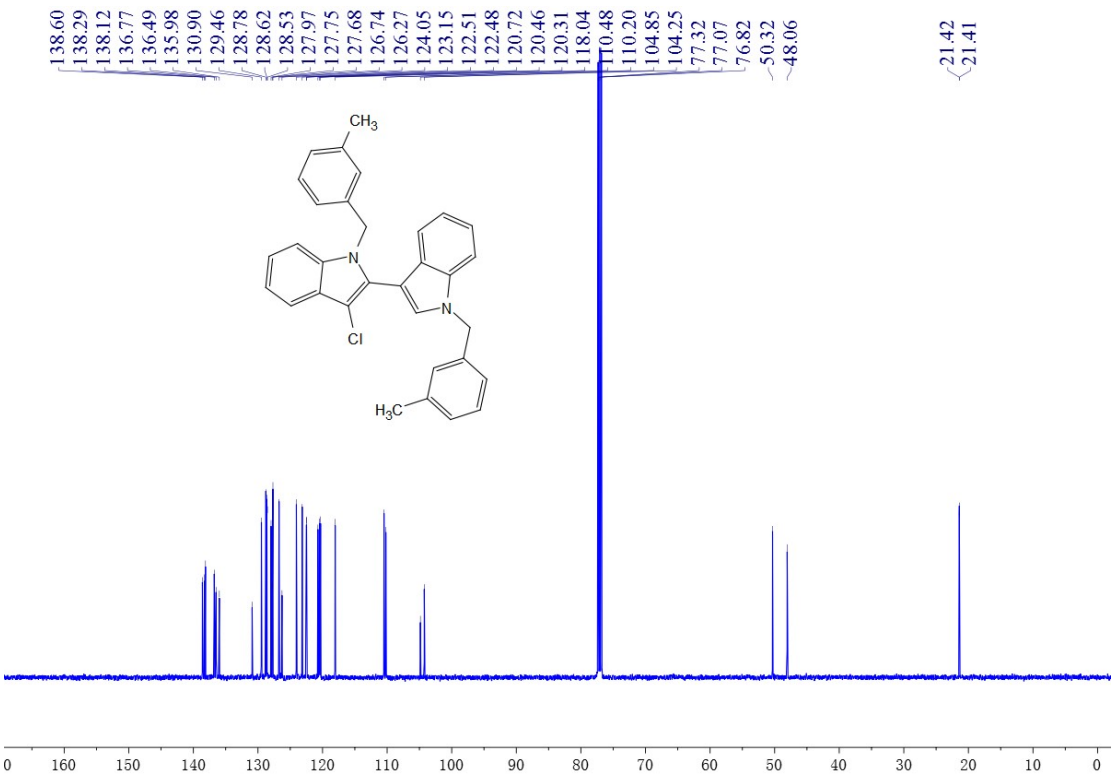
(47) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of B21



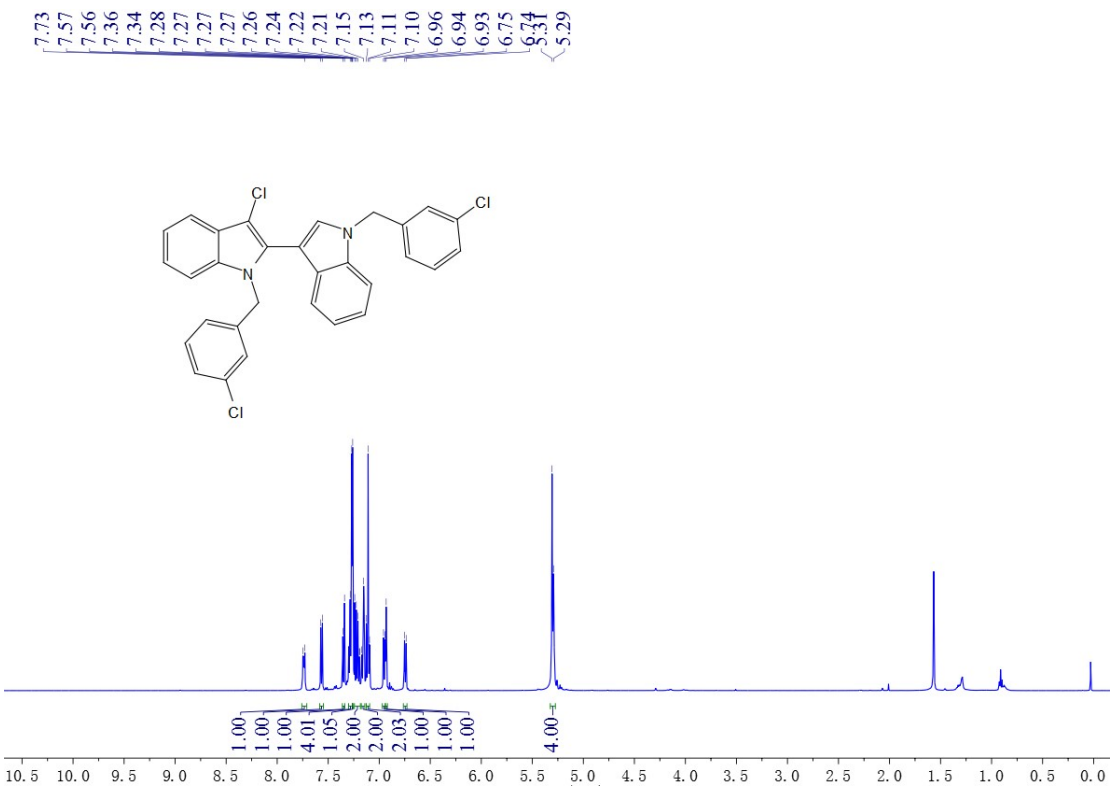
(48) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of B22



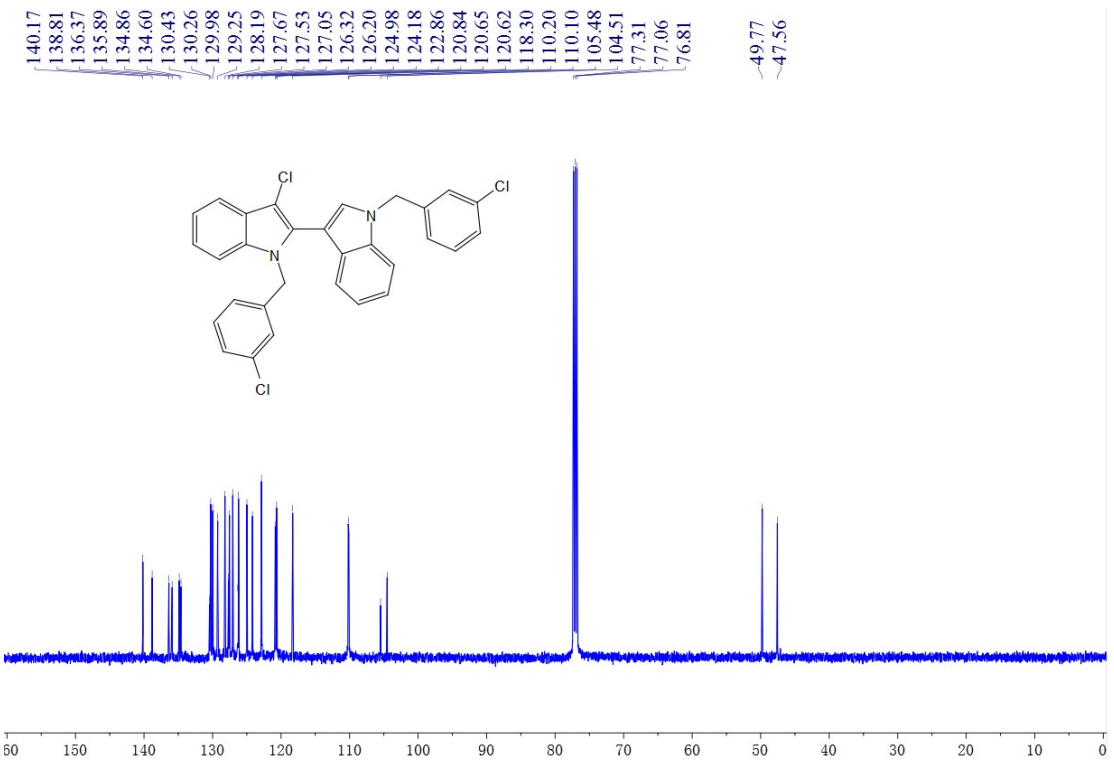
(49) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of B22



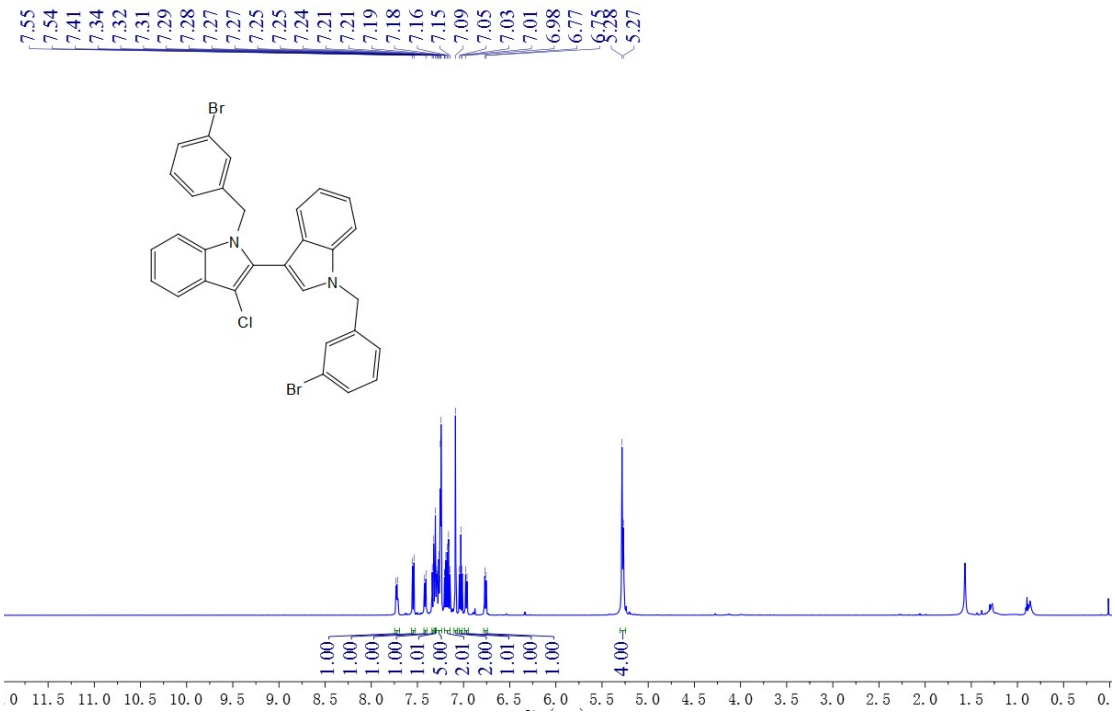
(50) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of B23



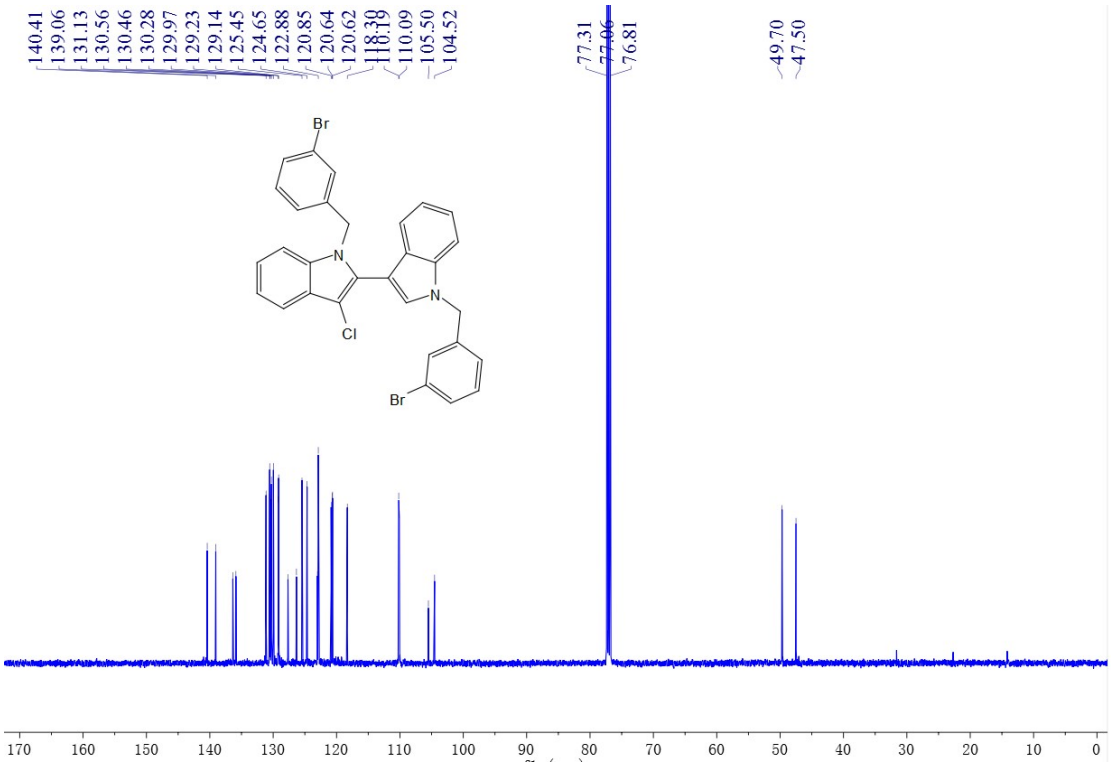
(51) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of B23



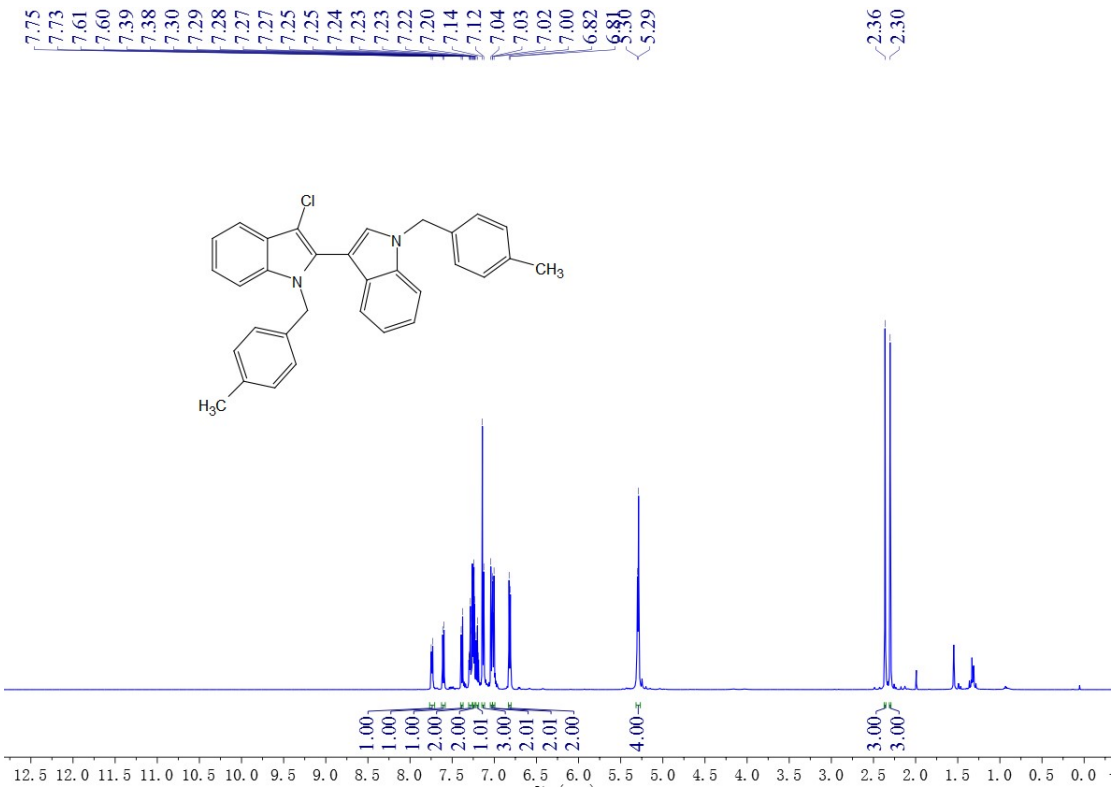
(52) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of B24



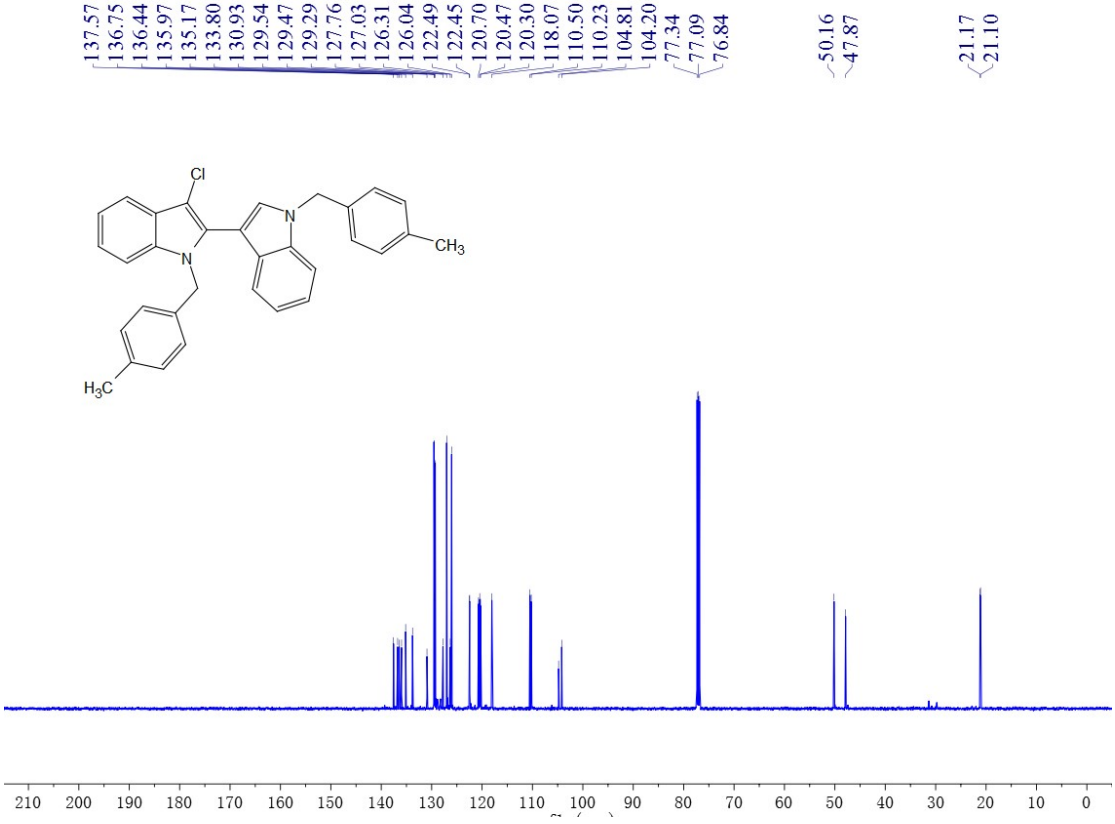
(53) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of B24



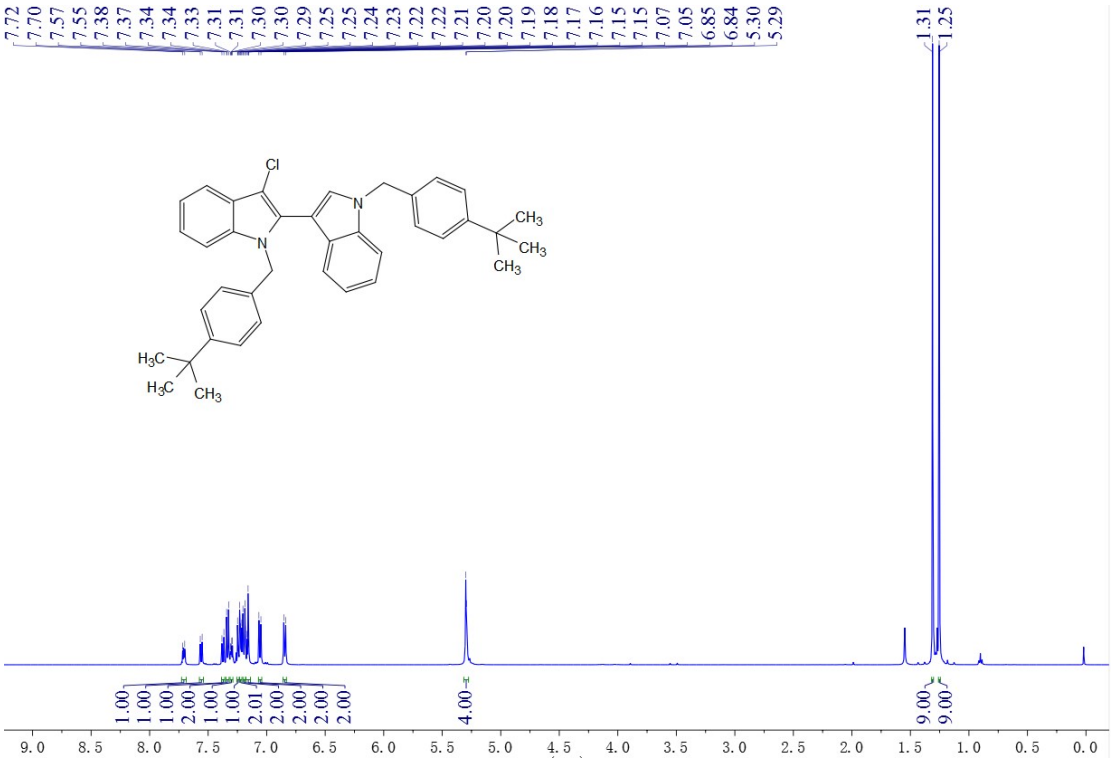
(54) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of B25



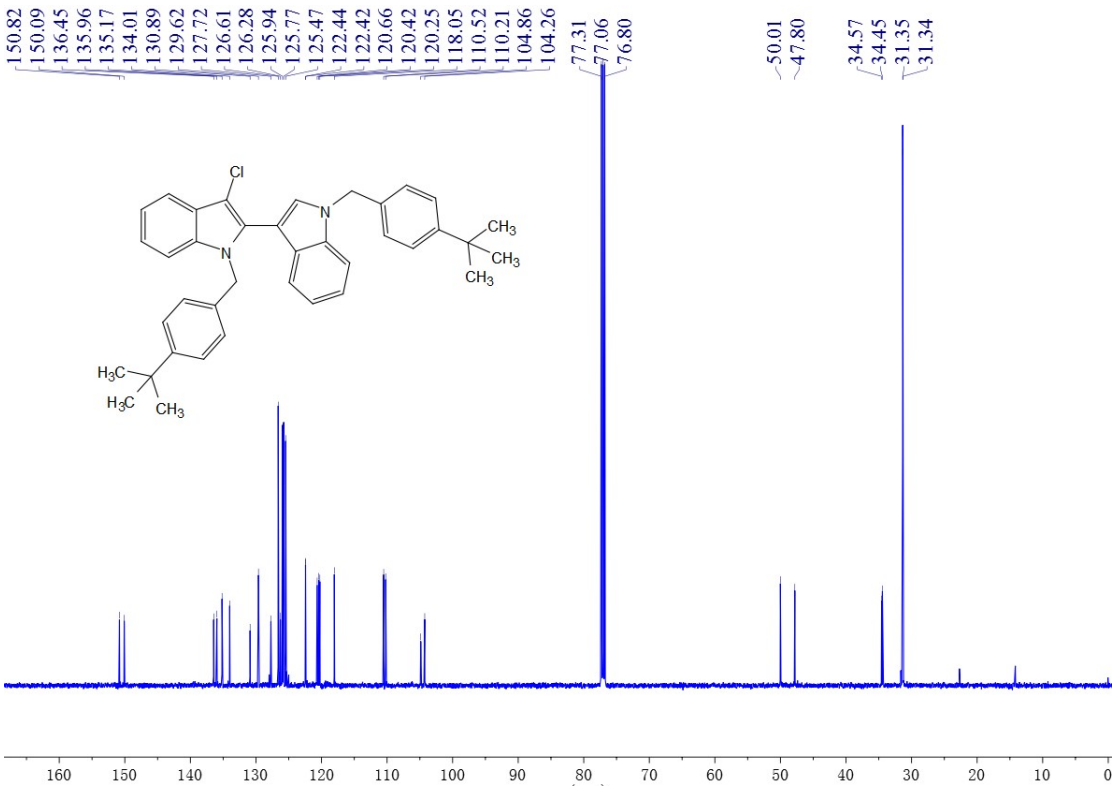
(55) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of B25



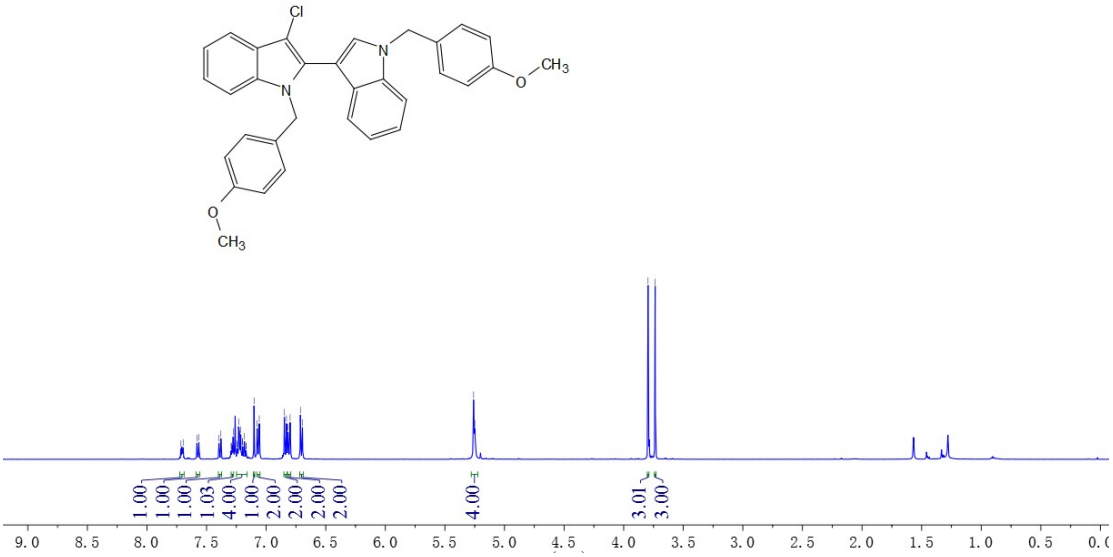
(56) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of B26



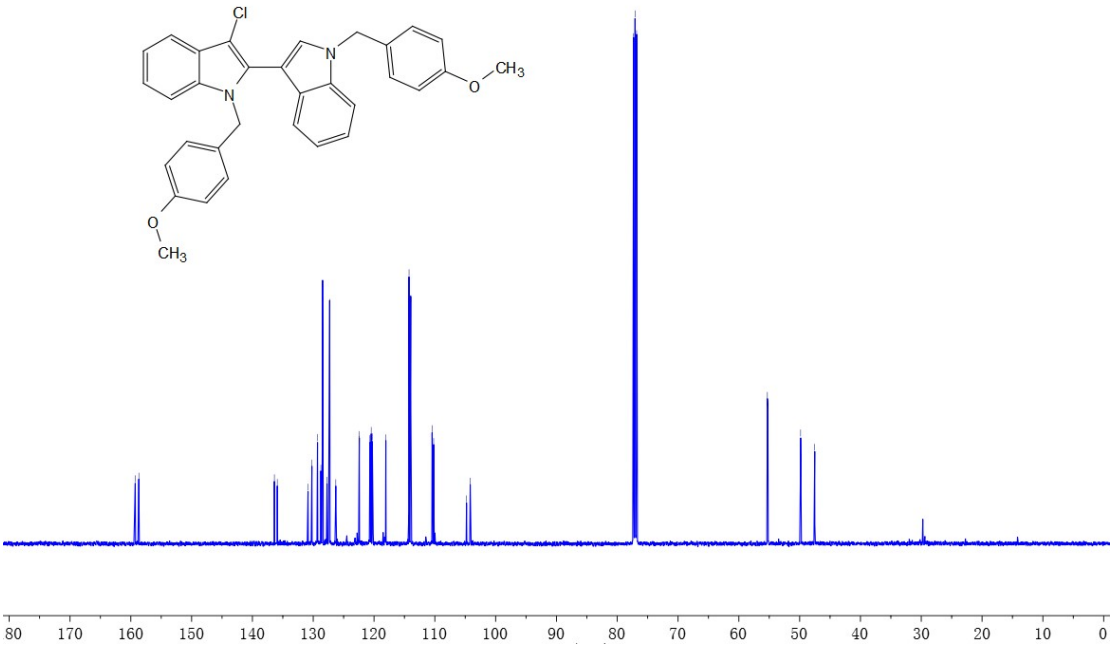
(57) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of B26



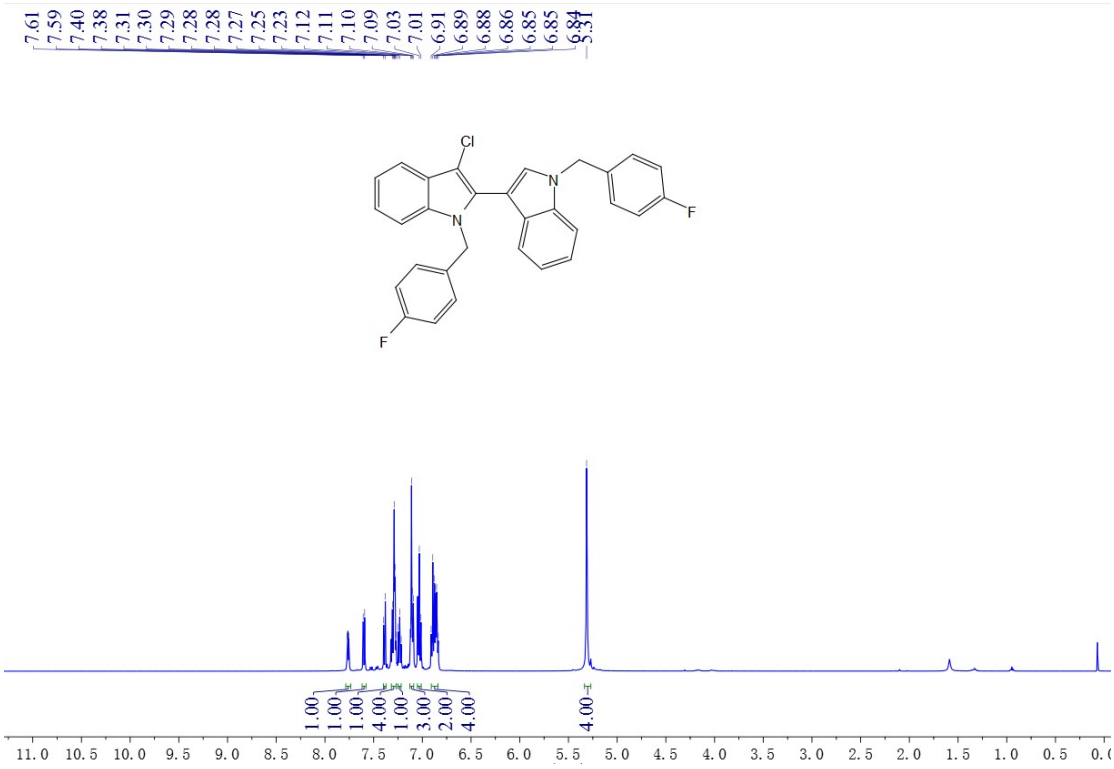
(58) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of B27



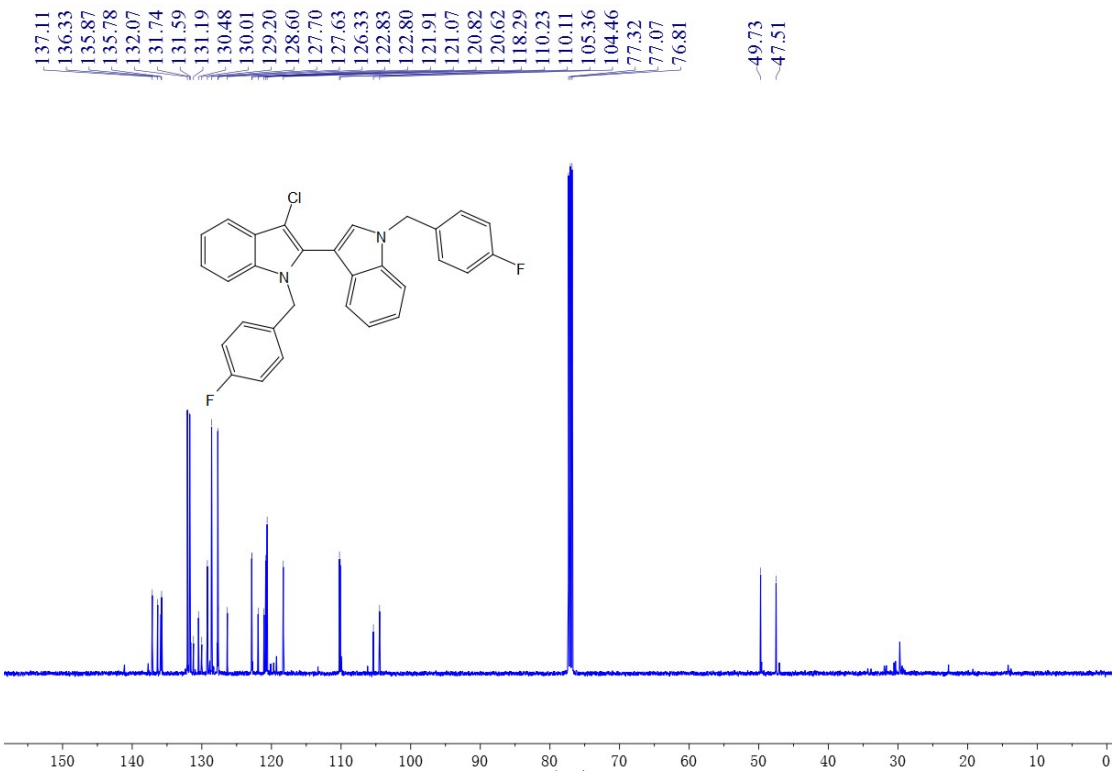
(59) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of B27



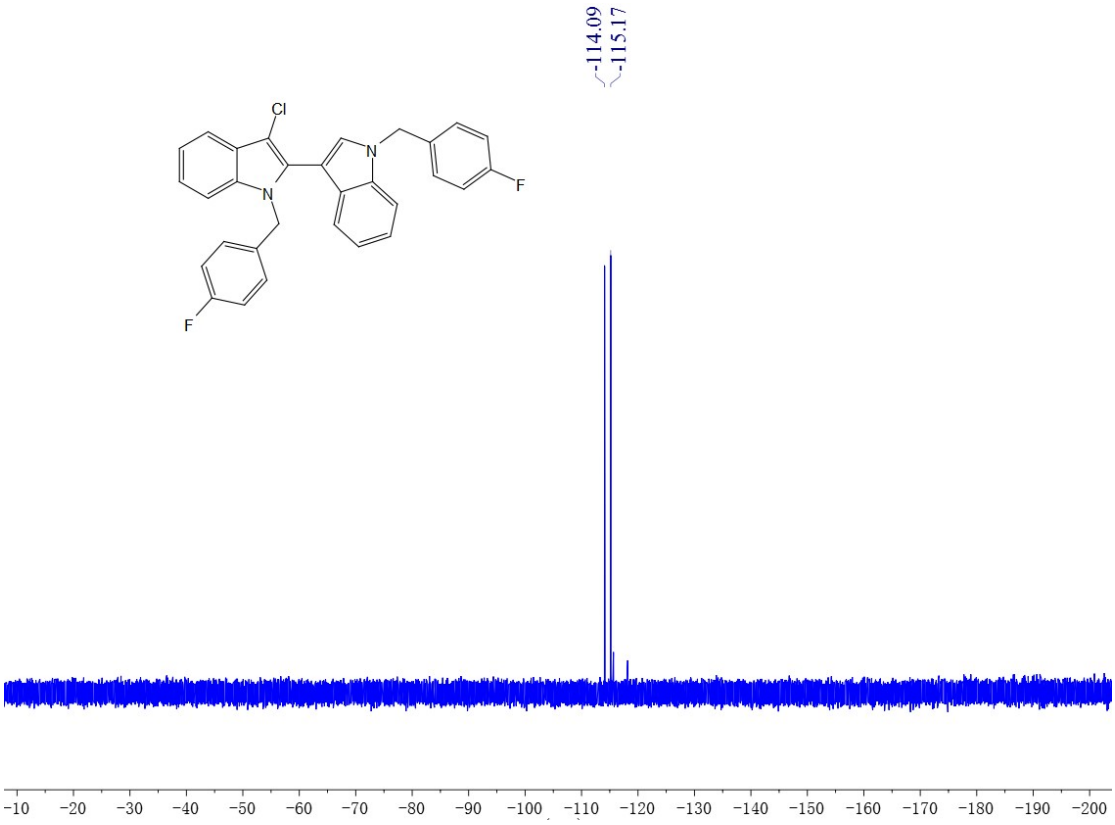
(60) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of B28



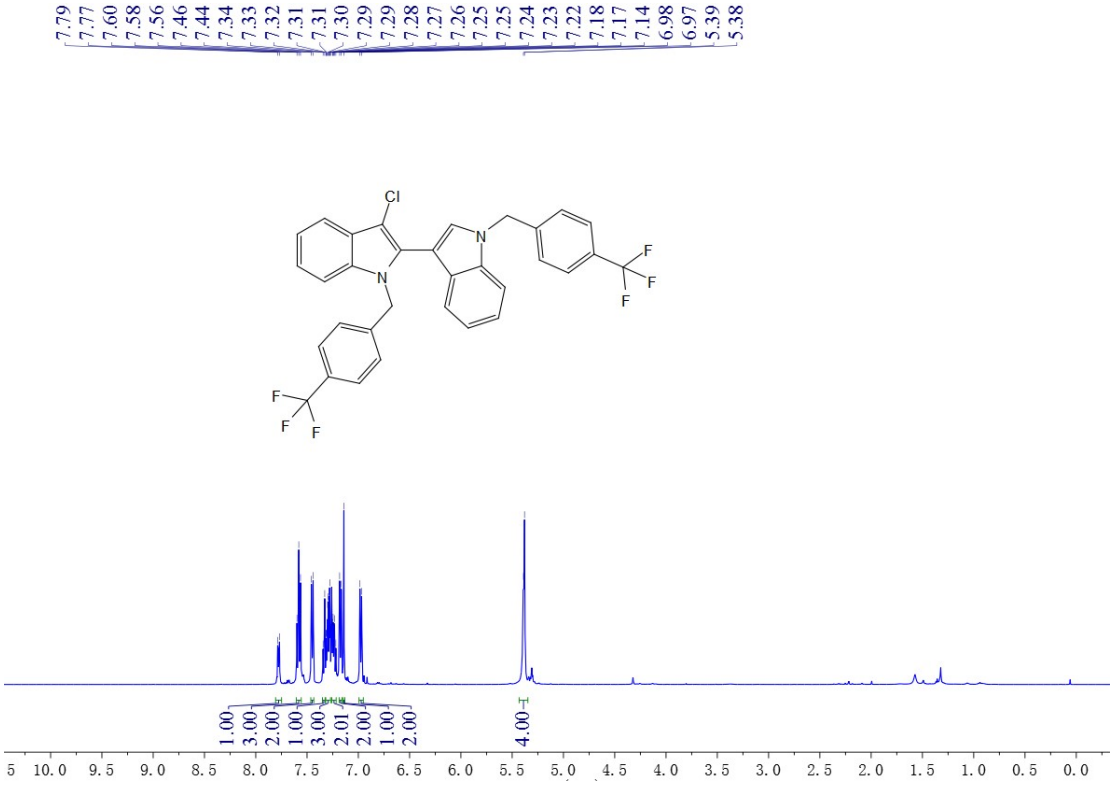
(61) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of B28



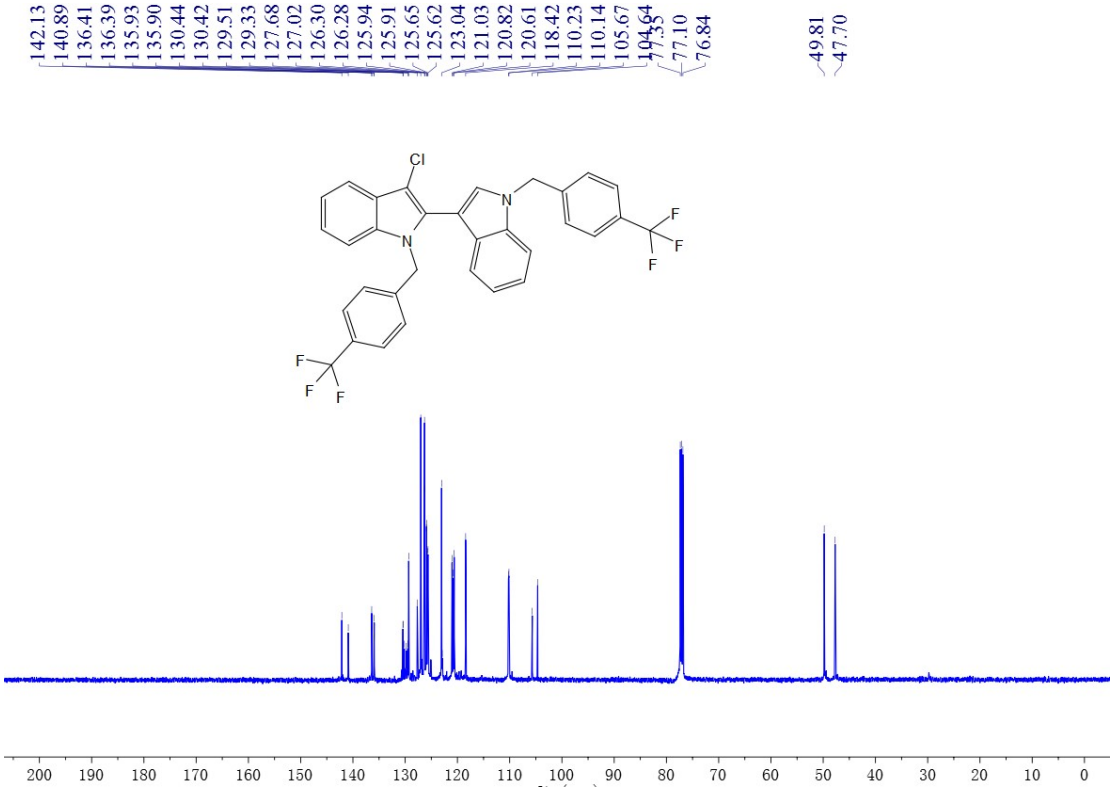
(62) ^{19}F-NMR (471 MHz, $CDCl_3$) spectrum of B28


-114.09
-115.17
Cl
N
N
F
F
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200

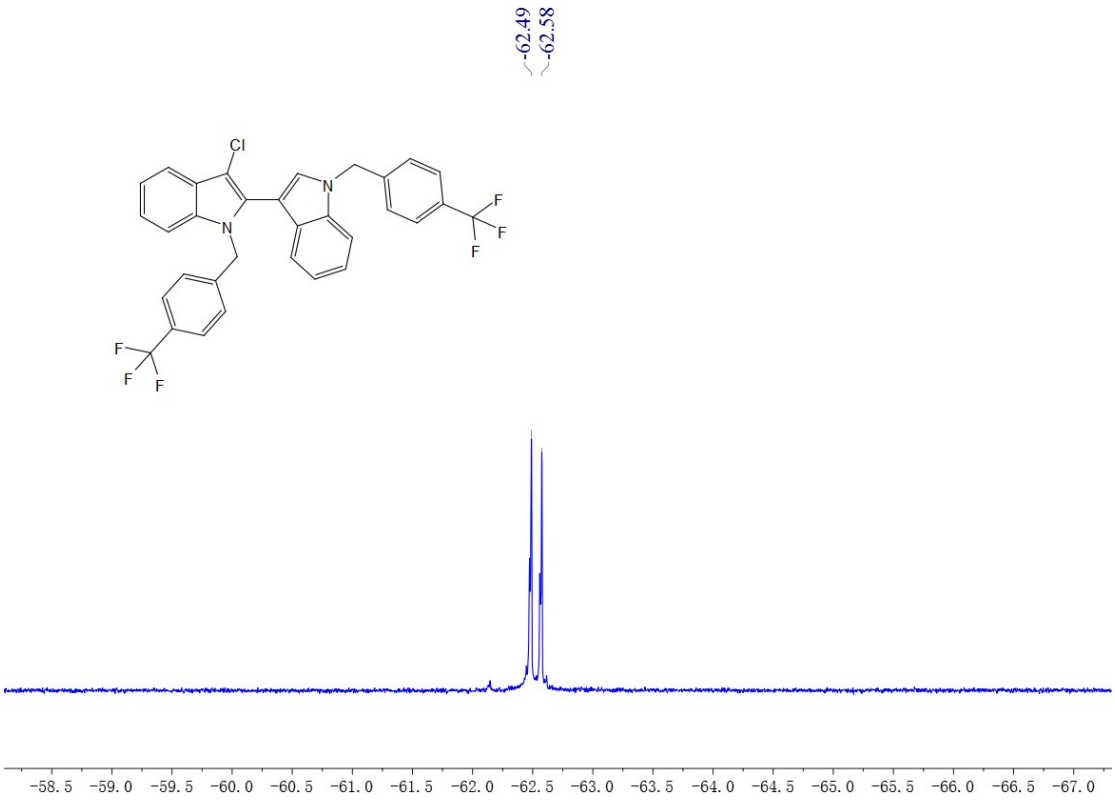
(63) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of B29



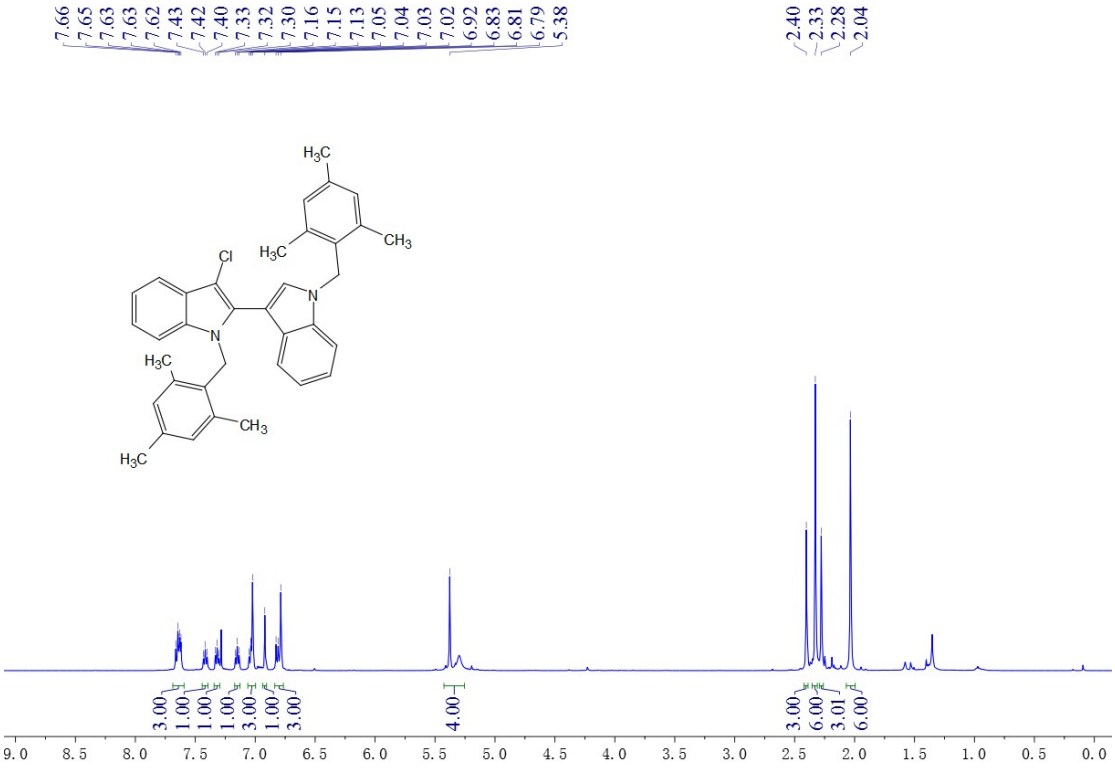
(64) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of B29



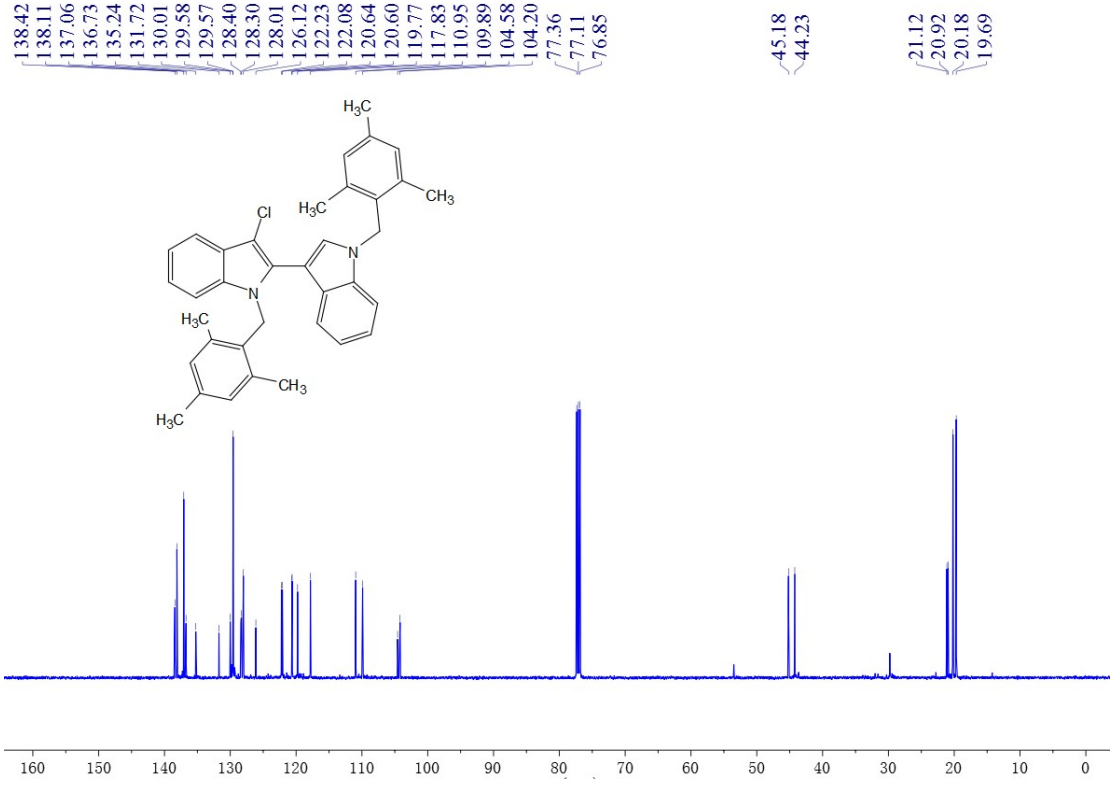
(65) ^{19}F-NMR (471 MHz, $CDCl_3$) spectrum of B29



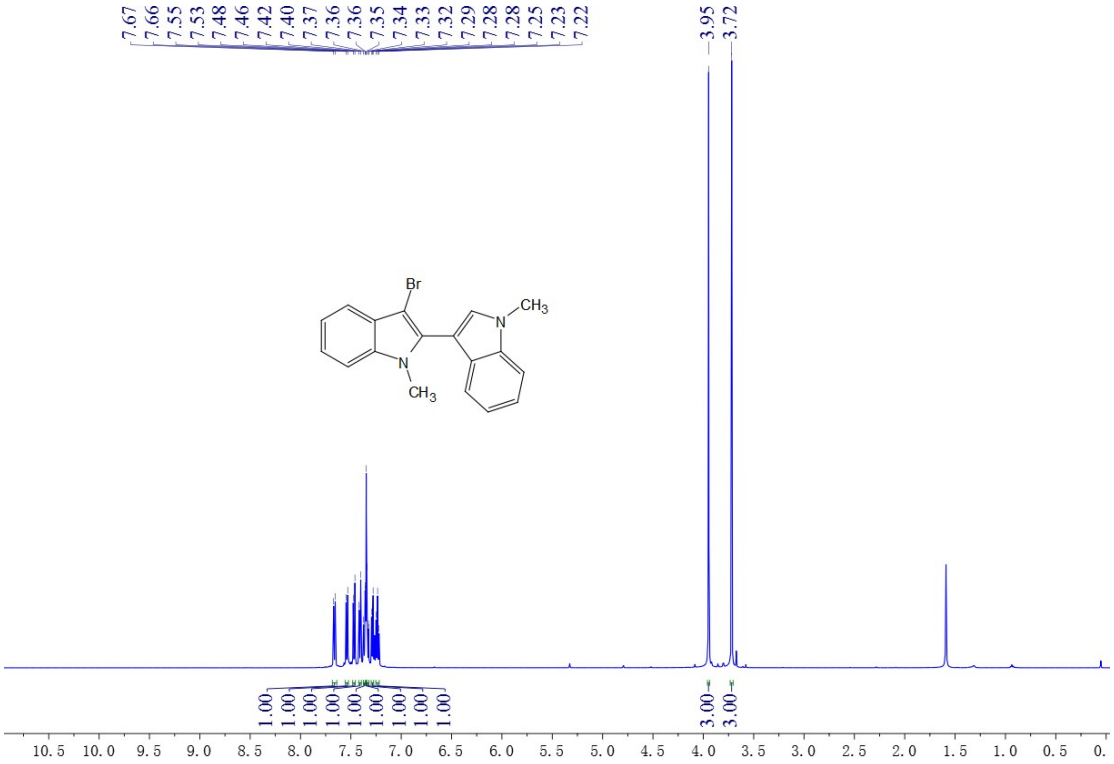
(66) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of B30



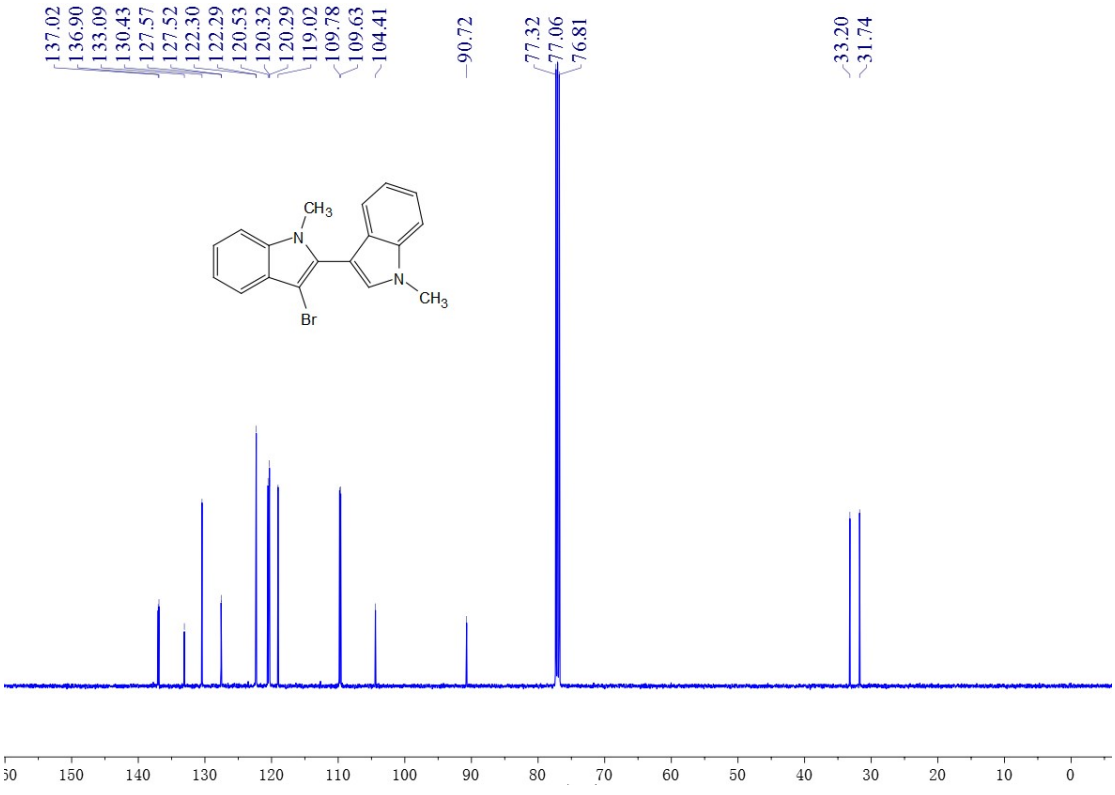
(67) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of B30



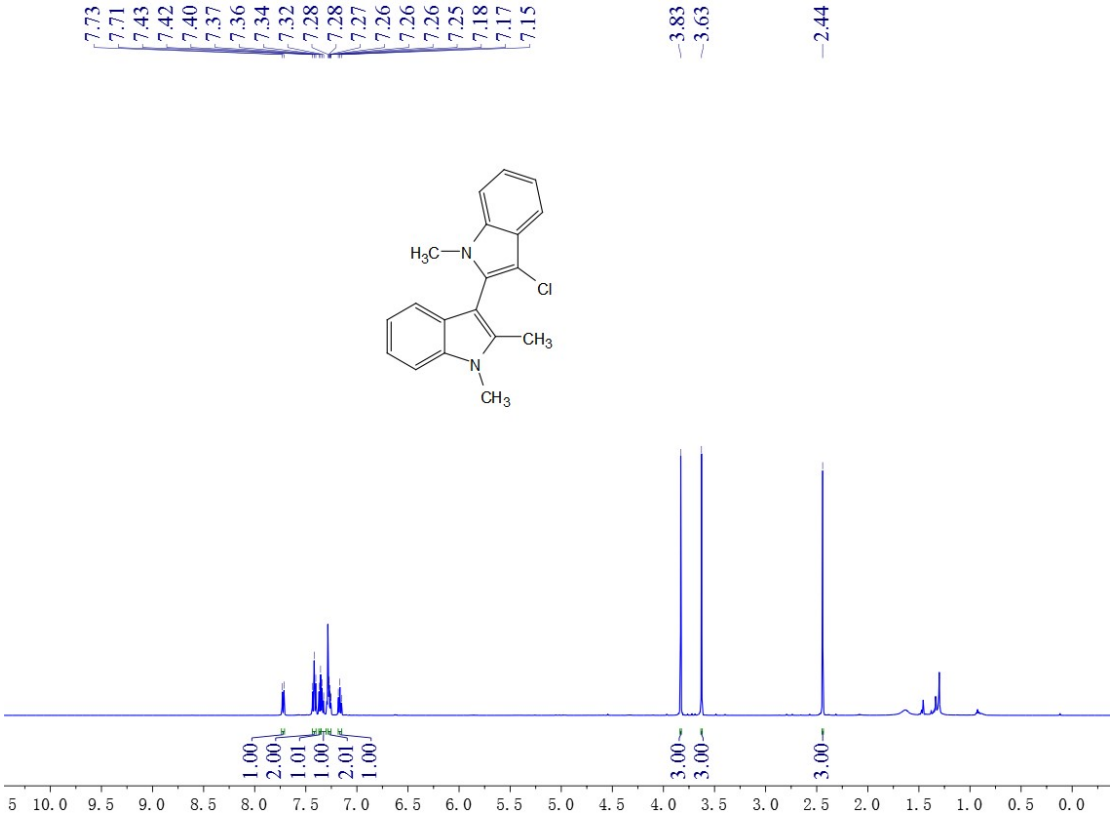
(68) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of B31



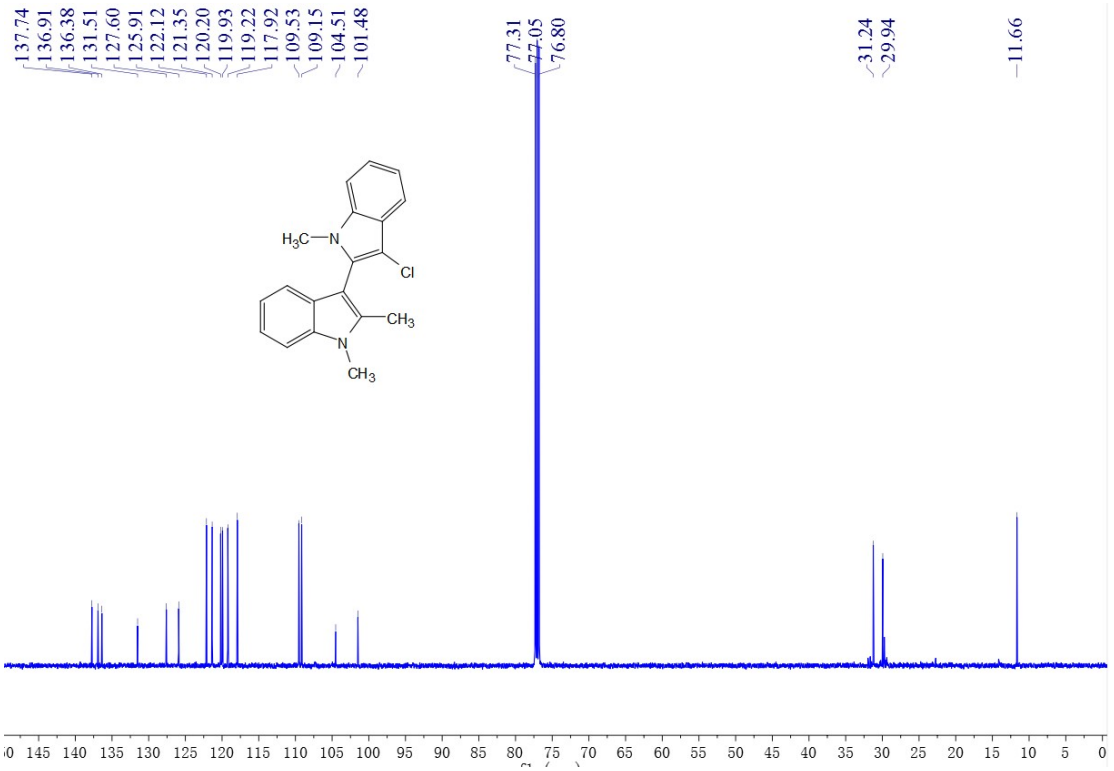
(69) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of B31



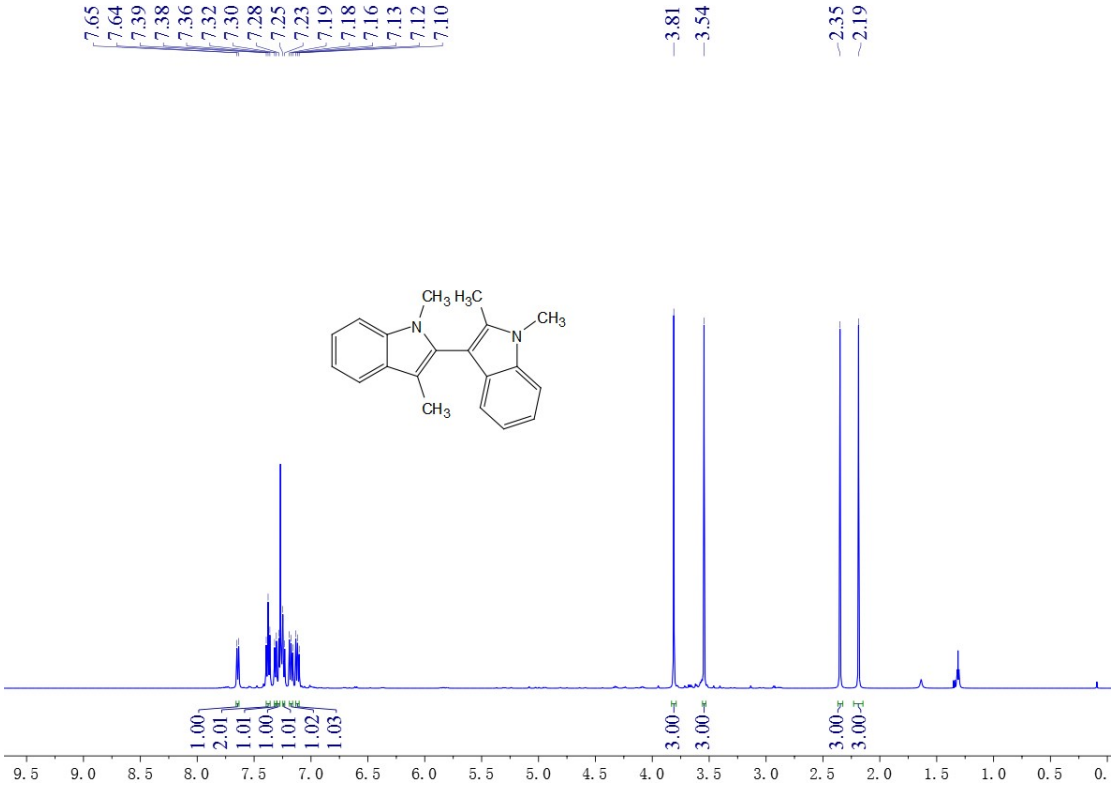
(70) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of B33



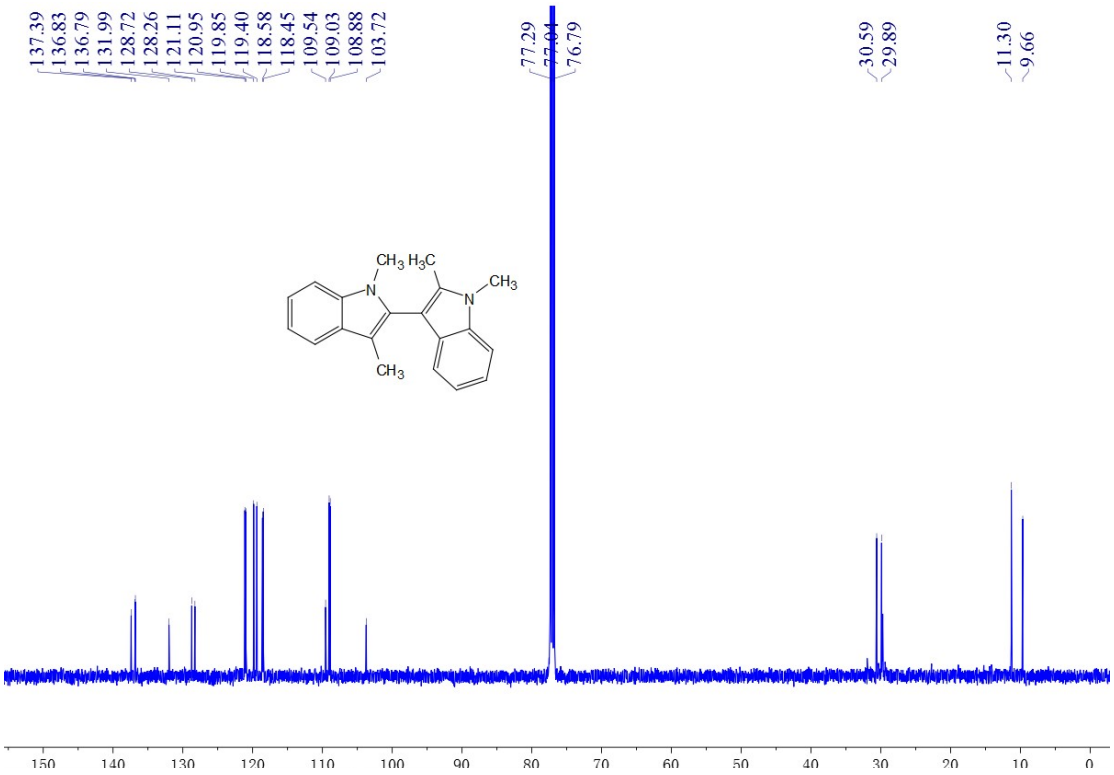
(71) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of B33



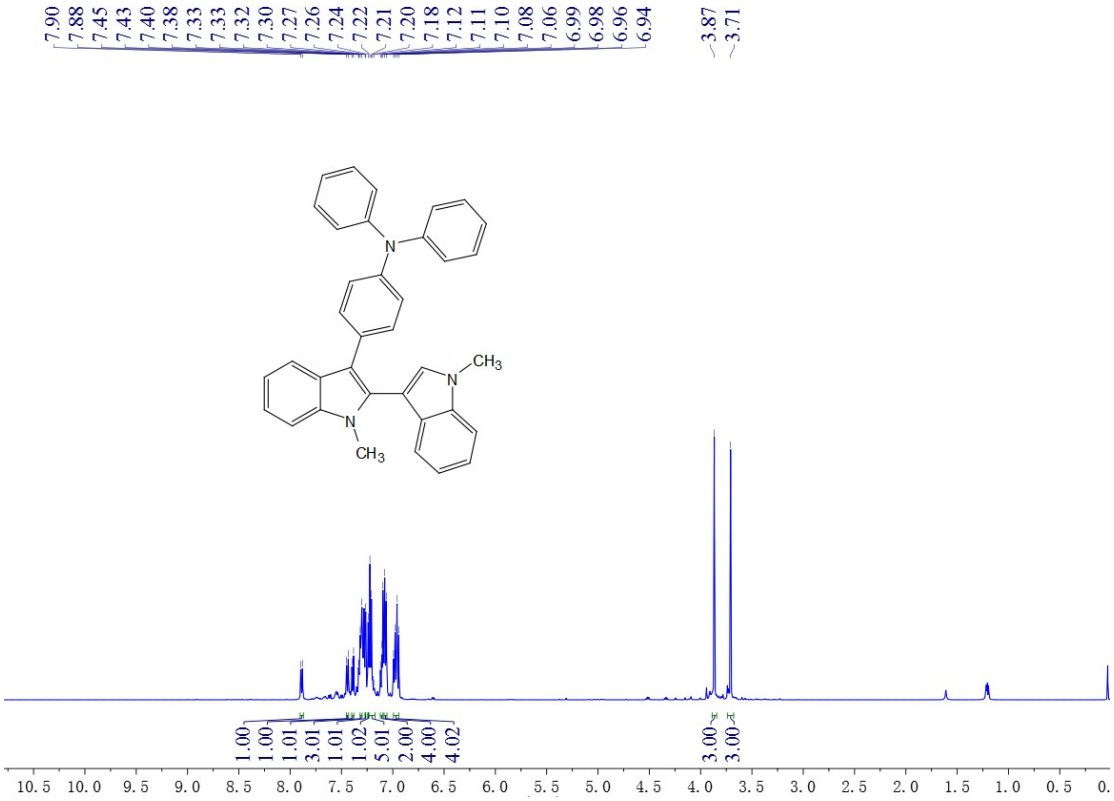
(72) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of B34



(73) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of B34



(74) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of F



(75) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of F