Electronic Supplementary Material (ESI) for ChemComm.

Supporting information

for

Chiral Phosphoramide-Catalyzed Enantioselective Synthesis of 2,3'-Diindoylarylmethanes from Indol-2-yl Carbinol and Indole

Shuai Qi,[a,b] Chao-You Liu,[a,b] Jin-Ying Ding[a] and Fu-She Han[a,c,*]

[a] *Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, Jilin 130022, China*

[b] *The University of Chinese Academy of Scicences, Beijing 100864, China*

[c] *Key Lab of Synthetic Chemistry of Natural Substances, Shanghai Institute of Organic Chemistry, CAS, China*

CONTENTS:

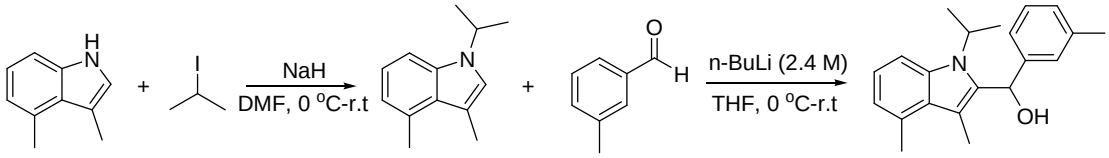
1. General Information

Anhydrous solvents were prepared by distillation according to standard methods. All starting materials were purchased from Alfa or Aldrich and used without further purification. All catalysts were synthesized according to the literatures.[1-12] Unless otherwise noted, the ^{1}H NMR spectra were recorded at 400 MHz or 300 MHz (Bruker AV) and the ^{13}C NMR spectra were recorded at 100 MHz with TMS as internal standard. All shifts are given in ppm. All coupling constants (*J* values) were reported in Hertz (Hz). High resolution mass was measured by using Autoflex III Smartbeam MALDI-TOF, Bruker. HPLC analysis was performed on Waters-Breeze (2487 Dual λ Absorbance Detector and 1525 Binary HPLC Pump, UV detection monitored at 254nm). Chiralpak AD-H and OD-H columns were purchased from Daicel Chemical Industries, LTD. Column chromatography was performed on silica gel with 100–200 mesh.

2. Experimental Section

2.1 Preparation and characterization of indol-2-yl carbinols

The 3-methyl indoles[13]、3-cyclopentyl indole[13] and 3-ethyl indoles[14] were prepared according to known procedures. The general procedure for the preparation of indol-2-yl carbinol substrates was represented by the synthesis of **8a**.

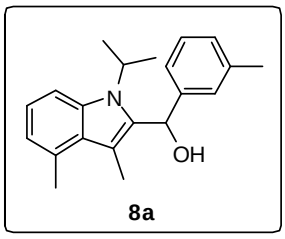


8a

To a DMF solution (15 mL) of 3,4-dimethylindole (1.45 g, 10 mmol) was added NaH (60 percent in mineral oil, 0.8 g, 20 mmol) at 0 °C. The slurry thus formed was gradually warmed to room temperature over a 30 min period. Isopropyl iodide (0.26 g, 15 mmol) was added to the reaction mixture at room temperature and the mixture was stirred for an additional 14 hs. The reaction mixture was then treated with H_2O (15 mL) and extracted with EtOAc (3 x 20 mL). The combined organic extracts were washed with H_2O (3 x 20 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the crude material was purified on silica gel (petroleum:AcOEt = 50:1) to provide

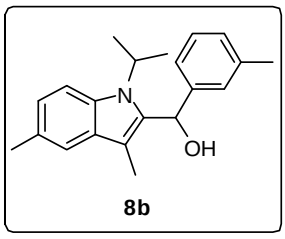
N-isopropyl-3,4-dimethylindole as a colorless oil (1.55 g, 83% yield).

To a solution of N-isopropyl-3,4-dimethylindole (2 mmol, 0.38 g) in dried THF (6 ml) was added *n*-BuLi (2.4 mmol, 2.4 M, 1 ml) at 0 ^{o}C. The mixture was stirred for 3 hs at room temperature. Then *m*-methylbenzaldehyde (0.24 g, 2 mmol) was added slowly, and the resulting mixture was stirred for 12 hs at room temperature. The mixture was carefully quenched with saturated *aq.* NH_4Cl at 0 °C. The organic layer was separated and aqueous layer was extracted with Et_2O twice. The combined organic layer was washed with brine and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by silica-gel column chromatography to give the corresponding alcohol **8a**.



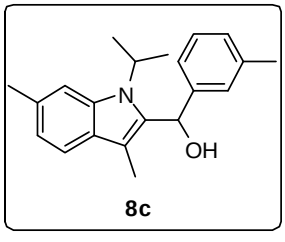
8a

(N-isopropyl-3,4-dimethyl-indol-2-yl)(*m*-tolyl)methanol:[1] H NMR (400 MHz, DMSO) δ 0.87 (d, *J* = 7.2 Hz, 3H), 1.42 (d, *J* = 7.2 Hz, 3H), 2.25 (s, 3H), 2.53 (s, 3H), 2.68 (s, 3H), 4.76 (m, 1H), 6.13 (d, 2H), 6.67 (d, *J* = 7.2 Hz, 1H), 6.88 (t, 1H), 7.05 (m, 3H), 7.17 (d, 1H) 7.25 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (101 MHz, DMSO) δ 143.71, 137.21, 130.89, 128.15, 128.07, 127.41, 127.28, 126.70, 126.11, 122.80, 120.92, 120.00, 110.22, 108.00, 65.02, 47.19, 21.46, 20.85, 20.76, 19.73, 12.04.



8b

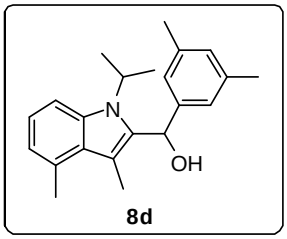
(N-isopropyl-3,5-dimethyl-indol-2-yl)(*m*-tolyl)methanol:[1] H NMR (400 MHz, DMSO) δ 0.88 (d, *J* = 6.8 Hz, 3H), 1.40 (d, *J* = 6.8 Hz, 3H), 2.23 (s, 3H), 2.28 (s, 3H), 2.36 (s, 3H), 4.71 (m, 1H), 6.11 (s, 2H), 6.86 (d, *J* = 8.4 Hz, 1H), 7.04 (m, 3H), 7.17 (m, 1H), 7.28 (s, 1H), 7.30 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (101 MHz, DMSO) δ 143.25, 137.06, 136.87, 132.35, 128.96, 127.82, 126.99, 126.37, 125.86, 122.51, 122.33, 118.47, 111.57, 106.17, 65.25, 46.87, 21.12, 21.02, 20.67, 19.70, 8.68.



8c

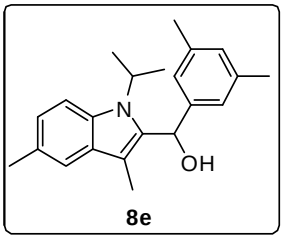
(N-isopropyl-3,6-dimethyl-indol-2-yl)(*m*-tolyl)methanol:[1] H NMR (400 MHz, DMSO) δ 0.91 (d, *J* = 6.8 Hz, 3H), 1.39 (d, *J* = 6.8 Hz, 3H), 2.25 (s, 3H), 2.30 (s, 3H), 2.39 (s, 3H), 4.73 (m, 1H), 6.12 (s, 2H), 6.82 (d, *J* = 8.0 Hz, 1H), 7.06 (m, 3H), 7.18 (t, 1H), 7.24 (s, 1H), 7.39(d, *J* = 8.0 Hz, 1H); ^{13}C

NMR (101 MHz, DMSO) δ 143.64, 137.19, 136.69, 134.74, 130.07, 128.14, 127.30, 127.07, 126.21, 122.87, 119.86, 118.88, 112.06, 106.92, 65.61, 47.21, 22.00, 21.45, 20.90, 19.97, 9.04.



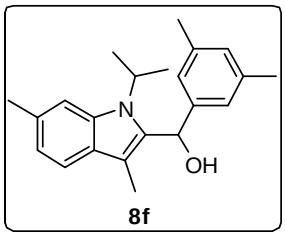
8d

(N-isopropyl-3,4-dimethyl-indol-2-yl)(3,5-dimethylphenyl) methanol: ^{1}H NMR (600 MHz, DMSO) δ 0.89 (d, *J* = 6.6 Hz, 3H), 1.44 (d, *J* = 6.6 Hz, 3H), 2.20 (s, 6H), 2.52 (s, 3H), 2.67 (s, 3H), 4.74 (m, 1H), 6.08 (d, 2H), 6.66 (d, *J* = 7.2 Hz, 1H), 6.85 (m, 4H), 7.25 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (151 MHz, DMSO) δ 143.42, 136.83, 136.74, 130.63, 127.82, 127.11, 123.63, 123.12, 120.63, 119.73, 109.98, 107.68, 64.74, 46.93, 21.11, 21.05, 20.61, 20.49, 19.51, 11.80.



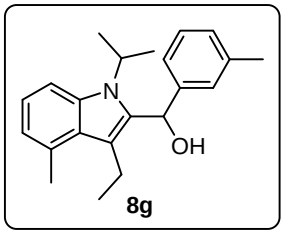
8e

(N-isopropyl-3,5-dimethyl-indol-2-yl)(3,5-dimethylphenyl) methanol: ^{1}H NMR (600 MHz, DMSO) δ 0.92 (d, *J* = 6.6 Hz, 3H), 1.41 (d, *J* = 6.6 Hz, 3H), 2.23 (s, 6H), 2.27 (s, 3H), 2.36 (s, 3H), 4.71 (m, 1H), 6.05 (s, 2H), 6.81 (d, 1H), 6.85 (s, 2H), 6.88 (s, 1H), 7.27 (s, 1H), 7.32 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (151 MHz, DMSO) δ 143.28, 136.81, 132.41, 127.92, 123.63, 123.18, 122.36, 118.55, 111.66, 106.17, 65.29, 46.94, 21.10, 21.05, 20.73, 19.80, 8.77.



8f

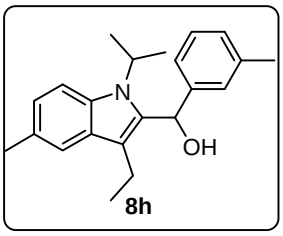
(N-isopropyl-3,6-dimethyl-indol-2-yl)(3,5-dimethylphenyl) methanol: ^{1}H NMR (600 MHz, DMSO) δ 0.82 (d, *J* = 6.8 Hz, 3H), 1.31 (d, *J* = 6.8 Hz, 3H), 2.10 (s, 6H), 2.19 (s, 3H), 2.28 (s, 3H), 4.60 (m, 1H), 5.96 (s, 2H), 6.72 (m, 3H), 6.78 (s, 1H), 7.13 (s, 1H), 7.28 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (151 MHz, DMSO) δ 143.33, 136.80, 136.44, 129.77, 127.84, 126.80, 123.63, 123.20, 119.57, 118.62, 111.82, 106.58, 65.31, 46.94, 21.74, 21.10, 21.05, 20.63, 19.74, 8.80.



8g

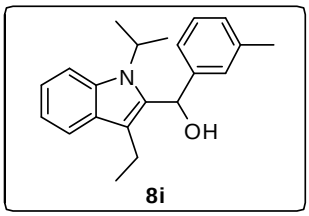
(N-isopropyl-3-ethyl-4-methyl-indol-2-yl)(m-tolyl)methanol: ^{1}H NMR (400 MHz, DMSO) δ 0.89 (d, *J* = 6.8 Hz, 3H), 1.23 (t, 3H), 1.42 (d, *J* = 6.8 Hz, 3H), 2.25 (s, 3H), 2.67 (s, 3H), 2.94 (m, 2H), 4.70 (m, 1H), 6.14 (d, *J* = 3.6 Hz, 1H), 6.18 (d, *J* = 3.6 Hz, 1H), 6.71 (d, *J* = 7.2 Hz, 1H), 6.91 (t, 1H), 7.02 (d, *J* = 7.2 Hz, 1H), 7.07 (d, *J* = 7.2 Hz, 1H), 7.12 (s, 1H), 7.19 (t, 1H), 7.28

(d, *J* = 8.0 Hz, 1H); ^{13}C NMR (101 MHz, DMSO) δ 143.40, 136.91, 136.50, 134.35, 129.92, 127.83, 127.02, 126.06, 125.92, 122.59, 120.46, 120.03, 114.75, 109.97, 64.67, 46.97, 21.15, 20.43, 20.11, 19.34, 18.41, 18.26.



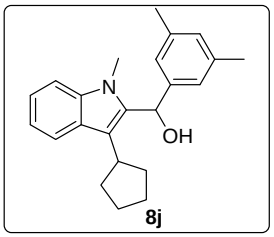
8h

(N-isopropyl-3-ethyl-5-methyl-indol-2-yl)(m-tolyl)methanol: ^{1}H NMR (600 MHz, DMSO) δ 0.88 (d, *J* = 6.6 Hz, 3H), 1.21 (t, 3H), 1.40 (d, *J* = 6.8 Hz, 3H), 2.24 (s, 3H), 2.35 (s, 3H), 2.77 (m, 2H), 4.65 (m, 1H), 6.09 (d, *J* = 3.6 Hz, 1H), 6.14 (d, *J* = 3.6 Hz, 1H), 6.86 (d, *J* = 9.0 Hz, 1H), 7.01 (d, *J* = 7.2 Hz, 1H), 7.04 (d, J = 7.2 Hz, 1H), 7.08 (s, 1H), 7.17 (t, 1H), 7.32 (m, 2H); ^{13}C NMR (151 MHz, DMSO) δ 143.35, 136.92, 136.39, 131.52, 128.70, 127.87, 127.07, 126.34, 126.00, 122.63, 122.32, 118.50, 113.41, 111.79, 65.05, 46.96, 21.21, 21.12, 20.69, 19.66, 17.11, 16.56.



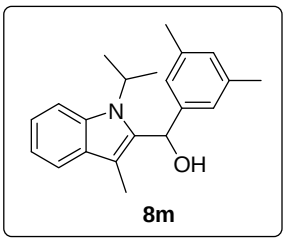
8i

(N-isopropyl-3-ethyl-indol-2-yl)(m-tolyl)methanol: ^{1}H NMR (400 MHz, DMSO) δ 0.91 (d, *J* = 6.8 Hz, 3H), 1.22 (t, 3H), 1.41 (d, *J* = 7.2 Hz, 3H), 2.24 (s, 3H), 2.80 (m, 2H), 4.70 (m, 1H), 6.12 (d, 1H), 6.16 (d, 1H), 7.00 (m, 4H), 7.09 (s, 1H), 7.18 (t, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (101 MHz, DMSO) δ 143.67, 137.37, 136.75, 134.56, 128.30, 128.22, 127.50, 126.38, 123.03, 121.16, 119.29, 118.31, 114.33, 112.44, 65.51, 47.47, 21.61, 21.03, 20.02, 17.49, 16.95.



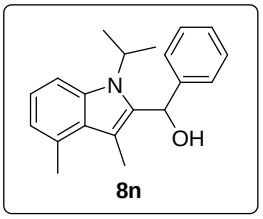
8j

(N-methyl-3-cyclopentyl-indol-2-yl)(3,5-dimethylphenyl) methanol: ^{1}H NMR (600 MHz, DMSO) δ 1.66 (m, 4H), 1.95 (m, 4H), 2.23 (s, 6H), 3.42 (m, 1H), 3.47 (s, 3H), 6.09 (d, 1H), 6.17 (d, 1H), 6.85 (s, 1H), 6.93 (s, 2H), 6.99 (t, 1H), 7.10 (t, 1H), 7.30 (d, *J* = 8.4 Hz, 1H) 7.61 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (151 MHz, DMSO) δ 143.26, 137.36, 136.93, 127.93, 125.11, 123.63, 123.27, 120.90, 119.63, 118.15, 115.14, 109.36, 65.28, 36.59, 33.38, 32.65, 30.68, 26.05, 21.13, 21.05.



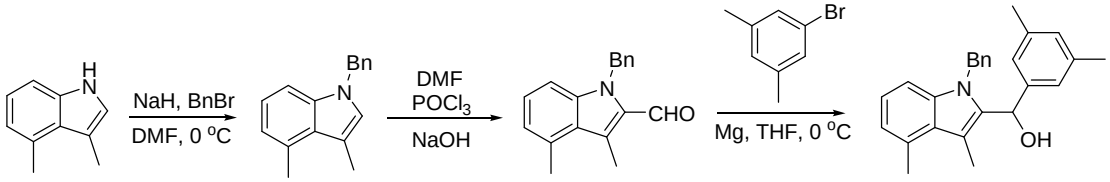
8m

(N-isopropyl-3-methyl-indol-2-yl)(3,5-dimethylphenyl)methanol: ^{1}H NMR (400 MHz, DMSO) δ 0.95 (d, *J* = 7.2 Hz, 3H), 1.44 (d, *J* = 7.2 Hz, 3H), 2.21 (s, 6H), 2.32 (s, 3H), 4.76 (m, 1H), 6.12 (d, 2H), 6.85 (d, 3H), 7.02 (dt, 2H), 7.46 (d, *J* = 7.8 Hz, 1H) 7.51 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (101 MHz, DMSO) δ 143.47, 137.37, 137.11, 134.29, 129.06, 128.16, 123.43, 121.08, 119.16, 118.13, 112.18, 106.99, 65.54, 47.32, 21.36, 20.91, 20.02, 9.02.



8n

(N-isopropyl-3,4-dimethyl-indol-2-yl)(phenyl)methanol: ^{1}H NMR (400 MHz, DMSO) δ 0.82 (d, *J* = 6.8 Hz, 3H), 1.40 (d, *J* = 6.8 Hz, 3H), 2.55 (s, 3H), 2.67(s, 3H), 4.76 (m, 1H), 6.19 (d, 2H), 6.67 (d, *J* = 7.2 Hz, 1H), 6.86 (t, 1H), 7.25 (m, 6H); ^{13}C NMR (101 MHz, DMSO) δ 143.43, 136.73, 130.57, 127.89, 126.46, 126.28, 125.75, 125.28, 120.63, 119.69, 109.88, 107.74, 64.74, 46.88, 20.52, 20.46, 19.35, 11.70.



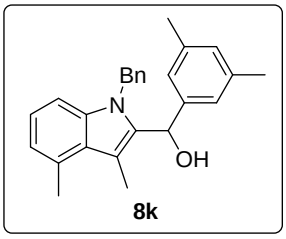
8k

Synthesis of 8k: A solution of 3,4-dimethylindole (1.45 g, 10 mmol) in DMF (15 mL) at 0 °C was treated with NaH (60 percent in mineral oil, 0.8 g, 20 mmol) in 4 portions providing a slurry that was gradually warmed to room temperature over a 30 min period. BnBr (1.70 g, 10 mmol) was added to the reaction mixture slowly at 0 °C and the mixture was stirred for 1 h. The reaction mixture was then treated with H_2O (15 mL) and extracted with AcOEt (3 x 20 mL). The combined organic extracts were washed with H_2O (3 x 20 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the crude material was purified on silica gel (petroleum:AcOEt = 25:1) to provide N-Bn-3,4-dimethylindole as a white solid (2.14 g, 91% yield).

A three-necked flask was charged with N-Bn-3,4-dimethylindole (4 mmol) and DMF (30 mmol). The mixture was stirred and cooled to 0 °C, then the freshly distilled $POCl_3$ (8 mmol) was added dropwise in 10 min. The solution was then heated at 40 °C for 2 hs. Then 2M NaOH aqueous solution (30 mL) was added slowly and the

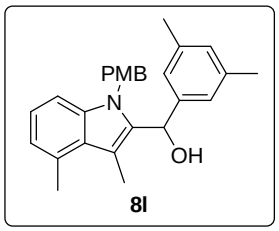
reaction mixture was heated further at 90 °C for 1 h. AcOEt (20 mL) was added to dissolve the solid, and the aqueous layer was extracted with AcOEt (2 × 20 mL). The combined organic phase was washed with brine, dried over Na_2SO_4, separated, evaporated under reduced pressure. The crude material was purified on silica gel (petroleum:AcOEt = 10:1) to provide the N-Bn-3,4-dimethylindole-2-carbaldehyde as a white solid (0.74 g, 70% yield).

To a solution of the 3,5-dimethylphenyl magnesium bromide [prepared from magnesium turnings (1.5 equiv), 1-bromo-3,5-dimethyl benzene (1.5 equiv) and a catalytic amount of I_2 in dry THF] was added dropwise the N-Bn-3,4-dimethylindole-2-carbaldehyde (1 mmol) in dried THF at 0 ^oC through a dropping funnel. The mixture was stirred for 30 min at room temperature. The reaction mixture was then quenched with aq. NH_4Cl solution and extracted with AcOEt. Organic layer was dried over sodium sulfate and the solvent was removed under reduced pressure. The crude material was purified by flash chromatography over silica gel column to provide the indol-2-yl carbinol **8g** as a white solid (0.35 g, 95% yield).



8k

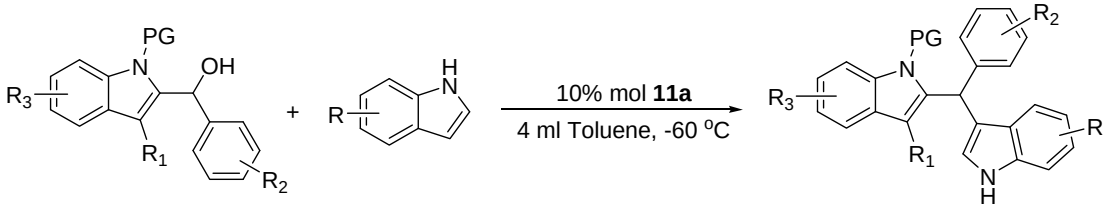
(N-Bn-3,4-dimethyl-indol-2-yl)(3,5-dimethylphenyl)methanol: ^1H NMR (400 MHz, DMSO) δ 2.11 (s, 6H), 2.55 (s, 3H), 2.67 (s, 3H), 5.72 (dd, 2H), 6.05 (d, *J* = 4.0 Hz, 1H), 6.14 (d, *J* = 4.0 Hz, 1H), 6.67 (m, 2H), 6.80 (m, 6H), 7.08 (m, 3H); ^{13}C NMR (101 MHz, DMSO) δ 143.45, 138.88, 137.81, 137.09, 136.86, 130.63, 128.06, 126.64, 126.44, 123.52, 121.50, 120.70, 108.54, 108.33, 65.50, 47.42, 21.30, 20.56, 12.04.



8l

(N-PMB-3,4-dimethyl-indol-2-yl)(3,5-dimethylphenyl)methanol: ^1H NMR (400 MHz, DMSO) δ 2.13 (s, 6H), 2.53 (s, 3H), 2.66 (s, 3H), 3.64 (s, 3H), 5.18 (s, 2H), 6.07 (d, *J* = 4.0 Hz, 1H), 6.13 (d, *J* = 4.0 Hz, 1H), 6.67 (m, 3H), 6.72 (s, 1H), 6.79 (m, 6H); ^{13}C NMR (101 MHz, Acetone) δ 158.29, 143.67, 137.87, 137.21, 136.92, 130.92, 130.69, 128.19, 127.91, 126.78, 123.63, 121.53, 120.73, 113.67, 108.56, 65.63, 55.35, 47.01, 21.42, 20.67, 12.14.

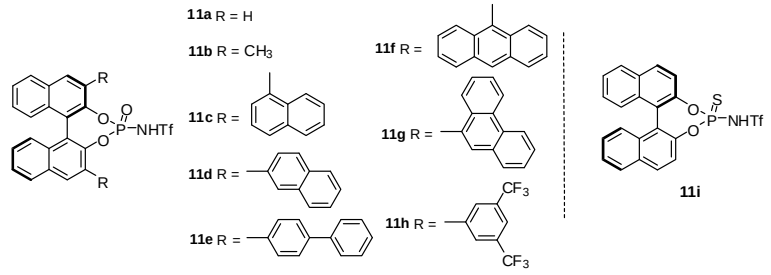
2.3 General procedure and product characterization of the asymmetric reaction



8 **9** **10**

A 10 ml Schlenck tube equipped with a magnetic bar was charged with alcohol **8** (0.1 mmol), indole **9** (0.1 mmol, 1 eq) and catalyst **11a** (4.8 mg, 0.01 mmol) at -60 °C. Then toluene solvent (4 ml) was added and the solution was stirred until the alcohol **8** had disappeared as monitored by TLC. Then one drop of pyridine was added to quench the reaction. The solvent was removed under reduced pressure and the crude mixture was purified by silical gel chromatography to afford the products **10**.

Structures of catalysts



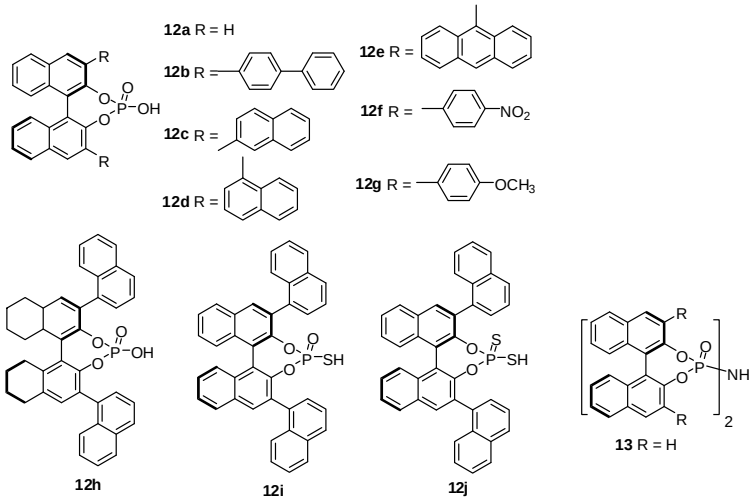
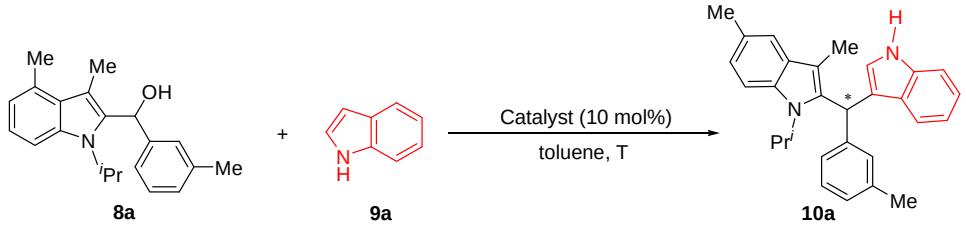
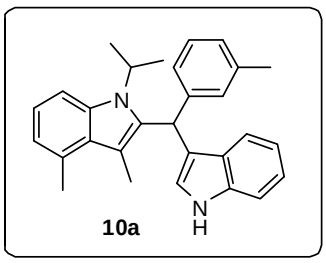


Table S1. Screening of Catalysts.[a]



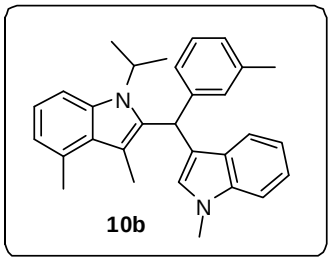
Entry	Catalyst	T (^{o}C)/t (h)	Yield (%)[b]	Ee (%)[c]
1	**11a**	**-60/3**	**92**	**91**
2	**11b**	-60/3	91	-7
3	**11c**	-60/12	77	-12
4	**11d**	-60/12	79	9
5	**11e**	-60/12	82	-6
6	**11f**	-60/12	69	-26
7	**11g**	-60/12	75	-14
8	**11h**	-60/6	94	-15
9	**11i**	-60/12	90	9
10	**12a**	r.t/10	80	2[d]
11	**12b**	r.t/10	85	25
12	**12c**	r.t/10	85	12
13	**12d**	r.t/10	80	3
14	**12e**	r.t/10	55	1
15	**12f**	r.t/10	88	18
16	**12g**	r.t/10	83	17
17	**12h**	r.t/10	84	2
18	**12i**	r.t/10	Trace	
19	**12j**	r.t/10	N.R	
20	**13**	r.t/10	89	10

[a] Reaction reactions: Indol-2-yl carbinol **8a** (0.05 mmol), indole **9a** (0.05 mmol), catalyst (10 mol%) in toluene (2 mL). [b] Isolated yield. [c] The ee value was determined by HPLC on AD-H column. [d] The reaction almost did not proceed at 0 ^{o}C for catalysts **12** and **13**.

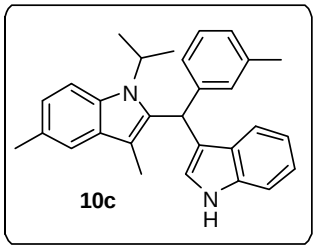


(10a): yield: 92%; ee: 91%; (purifoed by flash column chromatography with petroleum ether and DCM eluents, v/v = 2.5/1); ^{1}H-NMR (d_6-DMSO, 400 MHz) δ (ppm) 1.15 (m, 6H), 2.24 (s, 3H), 2.33 (s, 3H), 2.63 (s, 3H), 4.74 (m, 1H), 6.13 (s, 1H), 6.66 (d, *J* = 6.9 Hz, 1H), 6.80 (s, 1H), 6.88 (m, 2H), 7.05 (m, 5H), 7.20 (t, 1H), 7.28 (d, *J* = 8.1 Hz, 1H), 7.38 (d, *J* =

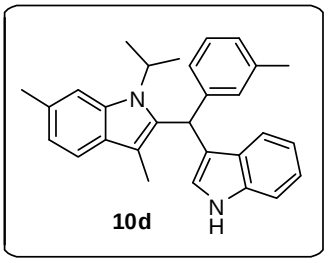
8.1 Hz, 1H), 10.96 (s, 1H); ^{13}C NMR (151 MHz, d_6-Acetone) δ 141.67, 137.04, 136.72, 136.22, 134.33, 129.97, 129.02, 127.67, 127.56, 127.00, 126.39, 125.54, 123.74, 121.13, 119.72, 118.92, 118.35, 115.35, 111.02, 109.57, 46.88, 38.86, 20.23, 19.95, 19.48, 11.31. HRMS calcd. for $C_{29}H_{30}N_2$ (M^+): 406.2409, found: 406.2417; The enantiomeric excess of 91% ee was determined by HPLC [Daicel Chirapak AD-H, hexane/isopropanol = 95/5, flow rate 1 mL/min, T = 30 °C, 254 nm, tR(minor) 6.866 min, tR(major) 9.745 min].



(10b): yield: 90%; ee: 9%; (purified by flash column chromatography with petroleum ether and DCM eluents, v/v = 4/1); ^{1}H-NMR (d_6-DMSO, 400 MHz) δ (ppm) 1.15 (m, 6H), 2.23 (s, 3H), 2.33 (s, 3H), 2.63 (s, 3H), 3.71 (s, 3H), 4.71 (m, 1H), 6.12 (s, 1H), 6.66 (d, *J* = 6.9 Hz, 1H), 6.93 (m, 6H), 7.17 (m, 3H), 7.29 (d, *J* = 8.4 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (101 MHz, d_6-Acetone) δ 141.88, 137.45, 137.30, 136.51, 130.23, 129.82, 129.26, 128.39, 127.82, 127.62, 126.65, 125.79, 123.73, 122.45, 121.34, 119.99, 119.42, 118.51, 114.52, 109.79, 109.44, 109.26, 47.13, 38.98, 31.74, 20.48, 20.18, 19.70, 11.60. HRMS calcd. for $C_{30}H_{32}N_2$ (M^+): 420.2565, found: 420.2544; The enantiomeric excess of 9% ee was determined by HPLC [Daicel Chirapak AD-H, hexane/isopropanol = 95/5, flow rate 0.5 mL/min, T = 30 °C, 254 nm, tR(minor) 5.418 min, tR(major) 6.249 min].

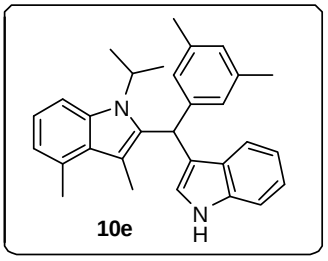


(10c): yield: 93%; ee: 87%; (purified by flash column chromatography with petroleum ether and DCM eluents, v/v = 2.5/1); ^{1}H-NMR (d_6-DMSO, 400 MHz) δ (ppm) 1.20 (m, 6H), 1.85 (s, 3H), 2.24 (s, 3H), 2.35 (s, 3H), 4.70 (m, 1H), 6.05 (s, 1H), 6.68 (s, 1H), 6.86 (t, 2H), 7.05 (m, 5H), 7.19 (t, 2H),7.37 (m, 2H), 10.93 (s, 1H); ^{13}C NMR (151 MHz, d_6-Acetone) δ 141.72, 137.07, 136.75, 136.20, 132.30, 129.87, 129.10, 127.60, 126.98, 126.49, 126.21, 125.60, 123.77, 121.42, 121.12, 118.73, 118.34, 117.66, 115.85, 111.00, 106.31, 46.62, 39.68, 20.24, 20.18, 20.06, 8.01. HRMS calcd. for $C_{29}H_{30}N_2$ (M^+): 406.2409, found: 406.2397; The enantiomeric excess of 87% ee was determined by HPLC [Daicel Chirapak OD-H, hexane/isopropanol = 95/5, flow rate 0.5 mL/min, T = 30 °C, 254 nm, tR(minor) 7.556 min, tR(major) 13.387 min].



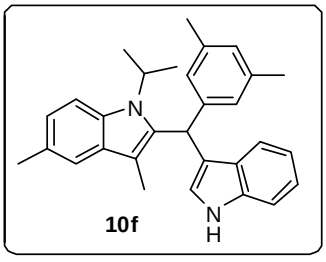
10d

(10d): yield: 91%; ee: 90%; (purified by flash column chromatography with petroleum ether and DCM eluents, v/v = 2.5/1); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm) 1.30 (m, 6H), 1.94 (s, 3H), 2.26 (s, 3H), 2.48 (s, 3H), 4.66 (m, 1H), 6.01 (s, 1H), 6.66 (s, 1H), 6.91 (d, *J* = 8.0 Hz, 1H), 7.01 (m, 3H), 7.06 (s, 1H), 7.16 (m, 2H), 7.28 (m, 2H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.94 (s, 1H); ^{13}C NMR (101 MHz, d_6-Acetone) δ 142.03, 137.32, 137.01, 135.65, 134.57, 129.35, 127.84, 127.24, 126.73, 125.86, 124.03, 121.36, 119.44, 118.99, 118.59, 117.84, 116.16, 111.55, 111.25, 106.93, 46.85, 39.95, 21.05, 20.49, 20.24, 8.28. HRMS calcd. for $C_{29}H_{30}N_2$ (M^+): 406.2409, found: 406.2413; The enantiomeric excess of 89% ee was determined by HPLC [Daicel Chirapak OJ-H, hexane/isopropanol = 97/3, flow rate 0.3 mL/min, T = 30 ^{o}C, 254 nm, tR(minor) 25.029 min, tR(major) 26.567 min].



10e

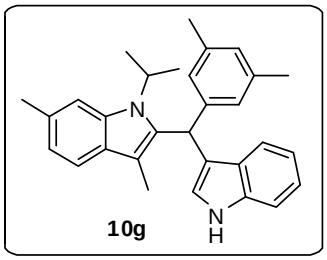
(10e): yield: 92%; ee: 96%; (purified by flash column chromatography with petroleum ether and DCM eluents, v/v = 2.5/1); ^{1}H-NMR (d_6-DMSO, 400 MHz) δ (ppm) 1.11 (m, 6H), 2.19 (s, 3H), 2.35 (s, 6H), 2.63 (s, 3H), 4.74 (m, 1H), 6.09 (s, 1H), 6.66 (d, *J* = 6.2 Hz, 1H), 6.85 (m, 6H), 7.08 (m, 2H), 7.28 (d, *J* = 8.4 Hz, 1H), 7.37 (d, *J* = 7.8 Hz, 1H), 10.95 (s, 1H); ^{13}C NMR (151 MHz, d_6-Acetone) δ 141.54, 136.88, 136.69, 136.23, 134.34, 129.96, 127.68, 127.24, 127.05, 126.80, 126.21, 123.70, 121.10, 119.70, 118.91, 118.33, 115.53, 111.00, 109.57, 107.50, 46.89, 38.80, 20.15, 19.96, 19.80, 19.54, 11.35. HRMS calcd. for $C_{30}H_{32}N_2$ (M^+): 420.2565, found: 420.2551; The enantiomeric excess of 96% ee was determined by HPLC [Daicel Chirapak AD-H, hexane/isopropanol = 95/5, flow rate 0.5 mL/min, T = 30 ^{o}C, 254 nm, tR(minor) 10.586 min, tR(major) 13.643 min].



10f

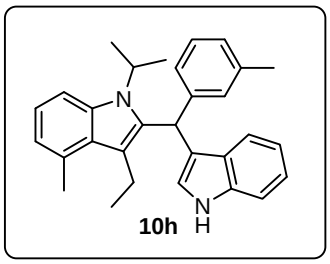
(10f): yield: 92%; ee: 89%; (purified by flash column chromatography with petroleum ether and DCM eluents, v/v = 2.5/1); ^{1}H-NMR (d_6-DMSO, 400 MHz) δ (ppm) 1.19 (m, 6H), 1.87 (s, 3H), 2.19 (s, 6H), 2.35 (s, 3H), 4.70 (m, 1H), 6.01 (s, 1H), 6.70 (s, 1H), 6.85 (m, 5H), 7.06 (m, 2H), 7.20 (s, 1H), 7.36 (d, *J* = 5.1 Hz, 2H), 10.92 (s, 1H); ^{13}C NMR (151 MHz,

d_6-Acetone) δ 141.61, 136.90, 136.71, 136.24, 132.28, 129.86, 127.30, 127.01, 126.25, 126.16, 123.74, 121.35, 121.06, 118.70, 118.29, 117.65, 115.96, 110.96, 46.61, 39.60, 20.13, 19.99, 8.00. HRMS calcd. for $C_{30}H_{32}N_2$ (M^+): 420.2565, found: 420.2552; The enantiomeric excess of 89% ee was determined by HPLC [Daicel Chirapak OD-H, hexane/isopropanol = 9/1, flow rate 0.5 mL/min, T = 30 °C, 254 nm, tR(minor) 8.520 min, tR(major) 12.907 min].



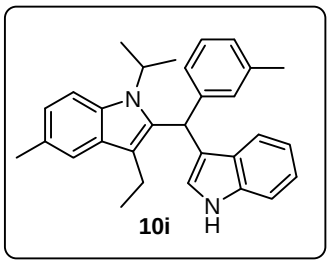
10g

(10g): yield: 94%; ee: 91%; (purified by flash column chromatography with petroleum ether and DCM eluents, v/v = 2.5/1); ^{1}H-NMR (d_6-DMSO, 400 MHz) δ (ppm) 1.21 (m, 6H), 1.87 (s, 3H), 2.19 (s, 6H), 2.38 (s, 3H), 4.70 (m, 1H), 6.00 (s, 1H), 6.70 (s, 1H), 6.81 (m, 5H), 7.06 (m, 2H), 7.28 (m, 2H), 7.37 (d, *J* = 8.1 Hz, 1H), 10.92 (s, 1H); ^{13}C NMR (101 MHz, d_6-Acetone) δ 141.92, 137.15, 136.97, 135.75, 134.31, 129.30, 127.86, 127.56, 127.28, 126.52, 124.01, 121.32, 119.41, 118.97, 118.55, 117.84, 116.28, 111.55, 111.22, 106.67, 46.86, 39.88, 21.04, 20.39, 20.21, 8.30. HRMS calcd. for $C_{30}H_{32}N_2$ (M^+): 420.2565, found: 420.2551; The enantiomeric excess of 91% ee was determined by HPLC [Daicel Chirapak OD-H, hexane/isopropanol = 95/5, flow rate 0.5 mL/min, T = 30 °C, 254 nm, tR(minor) 22.115 min, tR(major) 18.284 min].



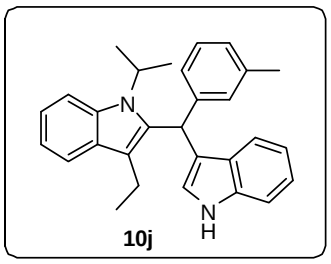
10h

(10h): yield: 91%; ee: 82%; (purifoed by flash column chromatography with petroleum ether and DCM eluents, v/v = 2.5/1); ^{1}H-NMR (d_6-DMSO, 400 MHz) δ (ppm) 0.97 (m, 6H), 1.17 (d, J = 6.0 Hz, 3H), 2.22 (s, 3H), 2.64 (s, 3H), 2.84 (m, 2H), 4.67 (m, 1H), 6.14 (s, 1H), 6.71 (d, J = 6.9 Hz, 1H), 6.81 (s, 1H), 6.90 (m, 2H), 7.08 (m, 6H), 7.30 (d, J = 8.1 Hz, 1H), 7.39 (d, J = 8.1 Hz, 1H), 10.97 (s, 1H); ^{13}C NMR (101 MHz, Acetone) δ 141.56, 136.94, 136.66, 136.32, 134.36, 129.34, 129.10, 127.45, 126.92, 126.62, 126.31, 125.59, 123.77, 121.08, 119.97, 119.54, 119.07, 118.29, 114.98, 114.28, 111.01, 109.58, 47.10, 38.58, 20.15, 19.77, 19.42, 19.18, 18.39, 16.74. HRMS calcd. for $C_{30}H_{32}N_2$ (M^+): 420.2565, found: 420.2552; The enantiomeric excess of 82% ee was determined by HPLC [Daicel Chirapak AD-H, hexane/isopropanol = 95/5, flow rate 0.5 mL/min, T = 30 °C, 254 nm, tR(minor) 12.093 min, tR(major) 16.363 min].



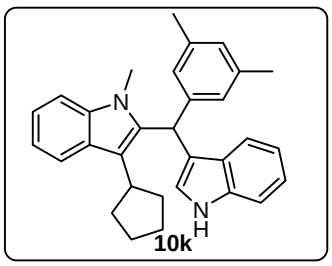
10i

(10i): yield: 88%; ee: 85%; (purifoed by flash column chromatography with petroleum ether and DCM eluents, v/v = 2.5/1); ^{1}H-NMR (d_6-DMSO, 400 MHz) δ (ppm) 0.84 (m, 3H), 1.17 (m, 6H), 2.23 (s, 3H), 2.36 (s, 3H), 2.45 (m, 2H), 4.65 (m, 1H), 6.07 (s, 1H), 6.73 (s, 1H), 6.86 (t, 2H), 6.98 (d, J = 7.5 Hz,1H), 7.08 (m, 4H), 7.19 (t, 1H), 7.25 (s, 1H), 7.37 (t, 2H), 10.94 (s, 1H); ^{13}C NMR (101 MHz, Acetone) δ 141.62, 136.92, 136.67, 135.83, 132.25, 129.11, 128.82, 127.45, 126.88, 126.37, 126.18, 125.56, 123.76, 121.31, 121.07, 118.90, 118.24, 117.78, 115.37, 113.14, 111.12, 110.97, 46.73, 39.29, 20.14, 19.97, 19.70, 16.97, 14.72. HRMS calcd. for $C_{30}H_{32}N_2$ (M^+): 420.2565, found: 420.2557; The enantiomeric excess of 85% ee was determined by HPLC [Daicel Chirapak AD-H, hexane/isopropanol = 95/5, flow rate 0.5 mL/min, T = 30 ^{o}C, 254 nm, tR(minor) 11.580 min, tR(major) 16.663 min].



10j

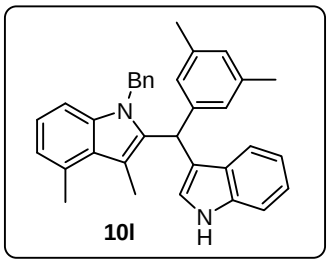
(10j): yield: 94%; ee: 84%; (purified by flash column chromatography with petroleum ether and DCM eluents, v/v = 2.5/1); ^{1}H-NMR (d_6-DMSO, 400 MHz) δ (ppm) 0.85 (t, 3H), 1.19 (m, 6H), 2.23 (s, 3H), 2.51 (m, 2H), 4.69 (m, 1H), 6.10 (s, 1H), 6.74 (d, *J* = 6.2 Hz, 1H), 6.87 (t, 1H), 7.05 (m, 8H), 7.38 (d, *J* = 8.1 Hz, 1H), 7.48 (m, 2H), 10.96 (s, 1H); ^{13}C NMR (101 MHz, d_6-Acetone) δ 141.55, 136.97, 136.68, 135.80, 134.08, 129.13, 128.57, 127.49, 126.86, 126.42, 125.58, 123.83, 121.10, 119.78, 118.88, 118.27, 118.00, 117.51, 115.29, 113.66, 111.41, 111.00, 46.83, 39.31, 20.15, 19.93, 19.67, 16.96, 14.71. HRMS calcd. for $C_{29}H_{30}N_2$ (M^+): 406.2409, found: 406.2398; The enantiomeric excess of 84% ee was determined by HPLC [Daicel Chirapak AD-H, hexane/isopropanol = 95/5, flow rate 0.5 mL/min, T = 30 ^{o}C, 254 nm, tR(minor) 13.091 min, tR(major) 22.664 min].



10k

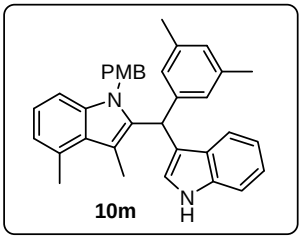
(10k): yield: 95%; ee: 80%; (purified by flash column chromatography with petroleum ether and DCM eluents, v/v = 2.5/1); ^{1}H-NMR (d_6-DMSO, 400 MHz) δ (ppm) 1.34 (m,4H), 1.73 (m, 4H), 2.19 (s, 6H), 3.07 (m, 1H), 3.57 (s, 3H), 6.04 (s, 1H), 6.64 (s, 1H), 6.85 (m, 4H),

6.94 (t, 1H), 7.07 (m, 3H), 7.36 (t, 2H), 7.48 (d, J = 7.8 Hz, 1H), 10.89 (s, 1H); ^{13}C NMR (101 MHz, Acetone) δ 141.98, 137.52, 137.18, 137.04, 127.55, 127.13, 126.47, 126.22, 123.97, 121.38, 120.22, 119.47, 119.18, 118.48, 117.87, 116.26, 115.22, 111.21, 109.41, 109.06, 39.35, 36.89, 32.19, 32.03, 29.76, 25.99, 25.95, 20.39. HRMS calcd. for $C_{31}H_{32}N_2$ (M^+): 432.2565, found: 432.2555; The enantiomeric excess of 80% ee was determined by HPLC [Daicel Chirapak AD-H, hexane/isopropanol = 95/5, flow rate 0.5 mL/min, T = 30 ^{o}C, 254 nm, tR(minor) 13.748 min, tR(major) 15.763 min].



10l

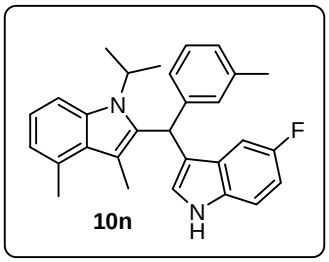
(10l): yield: 95%; ee: 83%; (purified by flash column chromatography with petroleum ether and DCM eluents, v/v = 2.5/1); ^{1}H-NMR (d_6-DMSO, 400 MHz) δ (ppm) 2.11 (s, 3H), 2.12 (s, 6H), 2.61 (s, 3H), 5.32 (s, 2H), 5.81 (s, 1H), 6.60 (s, 1H), 6.70 (m, 3H), 6.85 (m, 6H), 7.05 (m, 2H), 7.18 (m, 3H), 7.34 (d, *J* = 8.1 Hz, 1H)), 10.88 (s, 1H); ^{13}C NMR (101 MHz, d_6-Acetone) δ 141.85, 138.70, 137.28, 137.13, 136.78, 130.29, 128.16, 127.67, 127.24, 126.71, 126.53, 126.06, 124.31, 121.43, 121.00, 120.81, 119.02, 118.67, 116.04, 111.33, 109.17, 107.48, 46.72, 39.69, 20.49, 20.02, 11.40. HRMS calcd. for $C_{34}H_{32}N_2$ (M^+): 468.2565, found: 468.2543; The enantiomeric excess of 83% ee was determined by HPLC [Daicel Chirapak AD-H, hexane/isopropanol = 95/5, flow rate 0.5 mL/min, T = 30 ^{o}C, 254 nm, tR(minor) 14.259 min, tR(major) 17.174 min].



10m

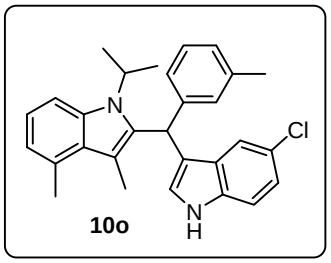
(10m): yield: 91%; ee: 81%; (purified by flash column chromatography with petroleum ether and DCM eluents, v/v = 1.5/1); ^{1}H-NMR (d_6-DMSO, 400 MHz) δ (ppm) 2.09 (s, 3H), 2.13 (s, 6H), 2.60 (s, 3H), 3.66 (s, 3H), 5.24 (s, 2H), 5.82 (s, 1H), 6.59 (s, 1H), 6.73 (m, 9H), 6.89 (m, 2H), 7.04 (t, 1H), 7.11 (d, J = 8.1 Hz, 1H), 7.34 (d, J = 8.1 Hz, 1H)), 10.86 (s, 1H); ^{13}C NMR (101 MHz, Acetone) δ 158.81, 141.93, 137.24, 137.14, 136.81, 130.58, 130.22, 127.60, 127.27, 126.52, 124.26, 121.38, 120.89, 120.71, 119.02, 118.63, 116.15, 113.62, 111.26, 109.14, 107.48, 54.54, 46.20, 39.69, 20.43, 19.93, 11.38. HRMS calcd. for $C_{35}H_{34}N_2O$ (M^+): 498.2671, found: 498.2627; The enantiomeric excess of 81% ee was determined by HPLC [Daicel Chirapak AD-H, hexane/isopropanol = 95/5, flow

rate 1 mL/min, T = 30 °C, 254 nm, tR(minor) 10.111 min, tR(major) 12.127 min].



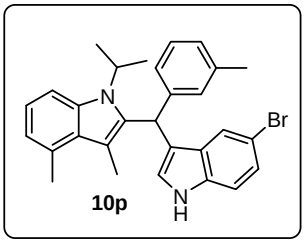
10n

(10n): yield: 91%; ee: 90%; (purified by flash column chromatography with petroleum ether and DCM eluents, v/v = 2.5/1); ^{1}H-NMR (d_6-Acetone, 400 MHz) δ (ppm) 1.24 (m, 6H), 2.26 (s, 3H), 2.39 (s, 3H), 2.68 (s, 3H), 4.83 (m, 1H), 6.17 (s, 1H), 6.69 (d, *J* = 6.8 Hz, 1H), 6.92 (m, 4H), 7.07 (t, 2H), 7.15 (s, 1H), 7.19 (t, 1H), 7.32 (d, *J* = 8.4 Hz, 1H), 7.44 (m, 1H), 10.26 (s, 1H); ^{13}C NMR (101 MHz, d_6-Acetone) δ 158.28, 155.96, 141.56, 137.40, 136.09, 133.55, 130.28, 129.23, 127.89, 126.76, 126.07, 125.71, 120.09, 120.04, 115.89, 112.29, 112.19, 109.60, 109.34, 103.88, 103.64, 47.13, 39.01, 20.47, 20.18, 19.86, 11.55. HRMS calcd. for $C_{29}H_{29}FN_2$ (M^+): 424.2315, found: 424.2309; The enantiomeric excess of 90% ee was determined by HPLC [Daicel Chirapak AD-H, hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 30 °C, 254 nm, tR(minor) 6.869 min, tR(major) 8.879 min].



10o

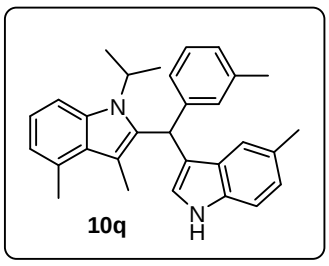
(10o): yield: 93%; ee: 88%; (purified by flash column chromatography with petroleum ether and DCM eluents, v/v = 2.5/1); ^{1}H-NMR (d_6-DMSO, 400 MHz) δ (ppm) 1.16 (m, 6H), 2.24 (s, 3H), 2.30 (s, 3H), 2.63 (s, 3H), 4.71 (m, 1H), 6.14 (s, 1H), 6.67 (d, *J* = 7.2 Hz, 1H), 6.87 (m, 2H), 6.95 (d, 1H), 7.07 (m, 4H), 7.20 (t, 1H), 7.30 (d, *J* = 8.1 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 11.19 (s, 1H); ^{13}C NMR (151 MHz, d_6-Acetone) δ 141.35, 137.17, 135.83, 135.14, 134.40, 130.03, 129.57, 128.98, 128.09, 127.64, 126.53, 125.65, 125.43, 123.68, 121.23, 119.86, 119.80, 118.22, 115.25, 112.51, 109.58, 107.75, 46.87, 38.62, 20.23, 19.94, 19.49, 11.31. HRMS calcd. for $C_{29}H_{29}ClN_2$ (M^+): 440.2019, found: 440.2006; The enantiomeric excess of 88% ee was determined by HPLC [Daicel Chirapak AD-H, hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 30 °C, 254 nm, tR(minor) 6.433 min, tR(major) 8.383 min].



10p

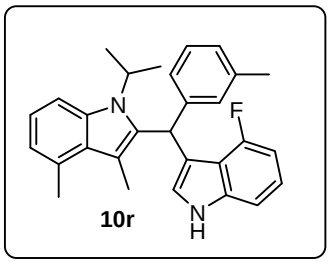
(10p): yield: 93%; ee: 90%; (purified by flash column chromatography with petroleum ether and DCM eluents, v/v = 2.5/1); ^{1}H-NMR (d_6-DMSO, 400 MHz) δ (ppm) 1.17 (m, 6H), 2.24 (s, 3H), 2.30 (s, 3H), 2.63 (s, 3H), 4.70 (m,

1H), 6.14 (s, 1H), 6.67 (d, *J* = 7.2 Hz, 1H), 6.95 (m, 5H), 7.18 (m, 2H), 7.29 (m, 2H), 7.37 (d, *J* = 8.4 Hz, 1H), 11.20 (s, 1H); ^{13}C NMR (151 MHz, d_6-Acetone) δ 141.35, 137.17, 135.86, 135.39, 134.40, 130.04, 128.99, 128.78, 127.64, 126.54, 125.52, 125.42, 123.83, 121.36, 119.88, 119.81, 115.14, 112.98, 111.33, 109.56, 107.76, 46.88, 38.58, 20.25, 19.97, 19.50, 11.35. HRMS calcd. for $C_{29}H_{29}BrN_2$ (M^+): 484.1514, found: 484.1531; The enantiomeric excess of 90% ee was determined by HPLC [Daicel Chirapak AD-H, hexane/isopropanol = 95/5, flow rate 1 mL/min, T = 30 °C, 254 nm, tR(minor) 6.918 min, tR(major) 9.108 min].



10q

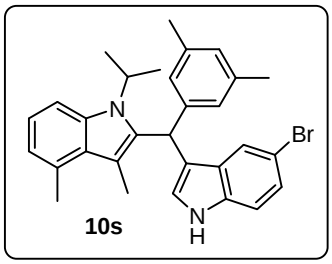
(10q): yield: 90%; ee: 87%; (purified by flash column chromatography with petroleum ether and DCM eluents, v/v = 2.5/1); ^{1}H-NMR (d_6-Acetone, 400 MHz) δ (ppm) 1.15 (s, 3H), 1.33 (d, 3H), 2.25 (s, 3H), 2.30 (s, 3H), 2.39 (s, 3H), 2.68 (s, 3H), 4.85 (m, 1H), 6.18 (s, 1H), 6.70 (d, *J* = 8.4 Hz, 1H), 6.89 (m, 2H), 6.96 (d, 1H), 7.06 (m, 3H), 7.16 (m, 2H), 7.33 (m, 2H), 10.01 (s, 1H); ^{13}C NMR (101 MHz, d_6-Acetone) δ 142.14, 137.24, 136.74, 135.35, 130.21, 129.28, 127.77, 127.54, 127.37, 126.59, 125.76, 124.21, 123.05, 119.97, 118.75, 114.86, 111.04, 109.75, 47.12, 39.00, 20.67, 20.50, 20.22, 19.75, 11.62. HRMS calcd. for $C_{30}H_{32}N_2$ (M^+): 420.2565, found: 420.2544; The enantiomeric excess of 87% ee was determined by HPLC [Daicel Chirapak AD-H, hexane/isopropanol = 95/5, flow rate 0.5 mL/min, T = 30 °C, 254 nm, tR(minor) 12.115 min, tR(major) 15.994 min].



10r

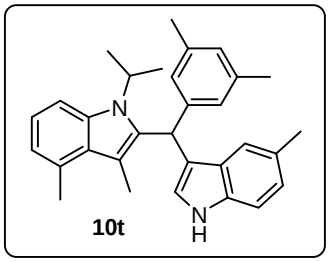
(10r): yield: 92%; ee: 83%; (purified by flash column chromatography with petroleum ether and DCM eluents, v/v = 2.5/1); ^{1}H-NMR (d_6-Acetone, 400 MHz) δ (ppm) 1.20 (m, 6H), 2.15 (s, 3H), 2.22 (s, 3H), 2.59 (s, 3H), 4.72 (m, 1H), 6.21 (s, 1H), 6.65 (m, 3H), 6.88 (m, 2H), 7.03 (m, 3H), 7.19 (m, 2H), 7.31 (d, *J* = 8.4 Hz, 1H), 11.24 (s, 1H); ^{13}C NMR (151 MHz, d_6-Acetone) δ 157.51, 155.88, 142.72, 139.62, 139.55, 137.00, 129.92, 128.68, 127.73, 126.30, 125.11, 124.53, 121.80, 121.75, 119.74, 115.70, 115.57, 114.17, 109.57, 107.52, 103.66, 103.53, 46.68, 39.87, 20.23, 19.99, 19.37, 11.19. HRMS calcd. for $C_{29}H_{29}FN_2$ (M^+): 424.2315, found: 424.2321; The enantiomeric excess of 83% ee was determined by HPLC [Daicel Chirapak AD-H,

hexane/isopropanol = 98/2, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm, tR(minor) 8.798min, tR(major) 12.316 min].



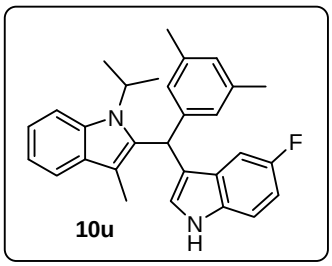
10s

(10s): yield: 96%; ee: 95%; (purified by flash column chromatography with petroleum ether and DCM eluents, v/v = 2.5/1); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm) 1.12 (s, 3H), 1.32 (d, 3H), 2.21 (s, 6H), 2.37 (s, 3H), 2.74 (s, 3H), 4.66 (m, 1H), 6.00 (s, 1H), 6.75 (s, 1H), 6.80 (m, 3H), 6.84 (s, 1H), 6.98 (t, 1H), 7.22 (m, 1H), 7.27 (m, 1H), 7.32 (d, *J* = 8.4 Hz, 1H), 7.47 (s, 1H), 7.98 (s, 1H); ^{13}C NMR (101 MHz, d_6-Acetone) δ 141.49, 137.25, 136.12, 135.61, 134.67, 130.28, 129.09, 127.91, 127.63, 126.39, 125.74, 124.05, 121.59, 120.09, 120.05, 115.58, 113.20, 111.55, 109.80, 107.94, 47.13, 38.78, 20.41, 20.22, 19.84, 11.62. HRMS calcd. for $C_{30}H_{31}BrN_2$ (M^+): 498.1671, found: 498.1656; The enantiomeric excess of 95% ee was determined by HPLC [Daicel Chirapak OD-H, hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm, tR(minor) 10.962 min, tR(major) 13.471 min].

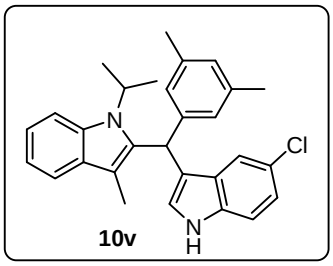


10t

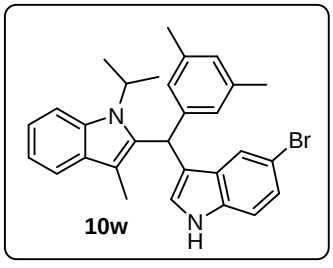
(10t): yield: 87%; ee: 93%; (purified by flash column chromatography with petroleum ether and DCM eluents, v/v = 2.5/1); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm) 1.12 (s, 3H), 1.31 (d, 3H), 2.21 (s, 6H), 2.37 (d, 6H), 2.74 (s, 3H), 4.70 (m, 1H), 6.04 (s, 1H), 6.71 (s, 1H), 6.78 (d, *J* = 6.8 Hz, 1H), 6.85 (m, 3H), 6.99 (m, 2H), 7.13 (s, 1H), 7.24 (d, *J* = 8.4 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.86 (s, 1H); ^{13}C NMR (101 MHz, d_6-Acetone) δ 142.00, 137.07, 136.71, 135.31, 134.71, 130.19, 127.96, 127.59, 127.43, 127.18, 127.04, 126.44, 124.17, 123.02, 119.93, 118.72, 115.04, 111.00, 109.76, 47.12, 38.92, 20.66, 20.40, 20.21, 19.73, 11.63. HRMS calcd. for $C_{31}H_{34}N_2$ (M^+): 434.2722, found: 434.2708; The enantiomeric excess of 93% ee was determined by HPLC [Daicel Chirapak AD-H, hexane/isopropanol = 97/3, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm, tR(minor) 12.911 min, tR(major) 16.557 min].



(10u): yield: 95%; ee: 91%; (purified by flash column chromatography with petroleum ether and DCM eluents, v/v = 2.5/1); ^{1}H-NMR (d_6-DMSO, 400 MHz) δ (ppm) 1.22 (m, 6H), 1.90 (s, 3H), 2.20 (s, 6H), 4.73 (m, 1H), 6.03 (s, 1H), 6.75 (m, 1H), 6.93 (m, 7H), 7.40 (m, 3H), 11.06 (s, 1H); ^{13}C NMR (151 MHz, d_6-Acetone) δ 157.64, 156.10, 141.20, 137.05, 135.80, 133.30, 129.57, 127.47, 127.30, 127.23, 126.21, 125.89, 119.95, 117.88, 117.56, 116.09, 112.00, 111.94, 111.29, 109.27, 109.09, 103.36, 103.20, 46.73, 39.51, 20.13, 19.96, 8.00. HRMS calcd. for $C_{29}H_{29}FN_2$ (M^+): 424.2315, found: 424.2303; The enantiomeric excess of 91% ee was determined by HPLC [Daicel Chirapak AD-H, hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm, tR(minor) 6.745 min, tR(major) 10.297 min].

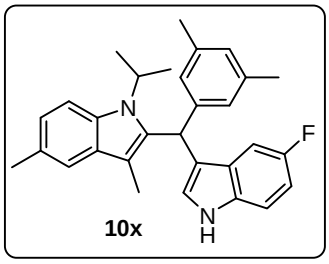


(10v): yield: 91%; ee: 92%; (purified by flash column chromatography with petroleum ether and DCM eluents, v/v = 2.5/1); ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm) 1.35 (m, 6H), 2.00 (s, 3H), 2.26 (d, 6H), 4.70 (m, 1H), 5.98 (s, 1H), 6.72 (s, 1H), 6.86 (s, 2H), 6.90 (s, 1H), 7.15 (m, 3H), 7.28 (d, *J* = 8.4 Hz, 1H), 7.31 (s, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.98 (s, 1H); ^{13}C NMR (101 MHz, d_6-Acetone) δ 141.48, 137.33, 136.03, 135.41, 134.22, 129.85, 128.35, 127.77, 126.48, 125.98, 123.92, 121.48, 120.25, 118.26, 118.16, 117.85, 116.08, 112.76, 111.54, 106.95, 46.97, 39.66, 20.41, 20.28, 8.29. HRMS calcd. for $C_{29}H_{29}ClN_2$ (M^+): 440.2019, found: 440.2008; The enantiomeric excess of 92% ee was determined by HPLC [Daicel Chirapak AD-H, hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm, tR(minor) 5.882 min, tR(major) 9.031 min].



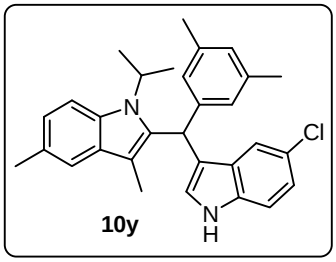
(10w): yield: 93%; ee: 92%; (purified by flash column chromatography with petroleum ether and DCM eluents, v/v = 2.5/1); ^{1}H-NMR (d_6-DMSO, 400 MHz) δ (ppm) 1.23 (m, 6H), 1.88 (s, 3H), 2.20 (s, 6H), 4.73 (m, 1H), 6.06 (s, 1H), 6.81 (m, 3H), 6.89 (s, 1H), 6.99 (m, 2H), 7.18 (m, 1H), 7.27 (s, 1H), 7.36 (d, 1H), 7.43 (d, 1H), 7.47 (d, *J* = 8.1 Hz, 1H), 11.17 (s, 1H); ^{13}C NMR (151 MHz, d_6-Acetone) δ 141.22,

137.06, 135.77, 135.39, 133.93, 129.58, 128.76, 127.50, 126.21, 125.58, 123.79, 121.11, 119.98, 117.89, 117.58, 115.71, 112.95, 111.28, 106.84, 46.70, 39.35, 20.14, 20.01, 8.02. HRMS calcd. for $C_{29}H_{29}BrN_2$ (M^+): 484.1514, found: 484.1508; The enantiomeric excess of 92% ee was determined by HPLC [Daicel Chirapak AD-H, hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 30 ^oC, 254 nm, tR(minor) 5.945 min, tR(major) 9.933 min].



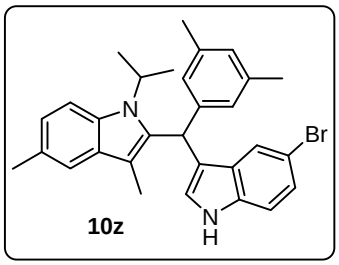
10x

(10x): yield: 94%; ee: 89%; (purified by flash column chromatography with petroleum ether and DCM eluents, v/v = 2.5/1); ^{1}H-NMR (d_6-DMSO, 400 MHz) δ (ppm) 1.25 (m, 6H), 1.86 (s, 3H), 2.20 (s, 6H), 2.35 (s, 3H), 4.68 (m, 1H), 5.99 (s, 1H), 6.73 (m ,1H), 6.87 (m, 6H), 7.21 (s, 1H), 7.37 (m, 2H), 11.04 (s, 1H); ^{13}C NMR (151 MHz, d_6-Acetone) δ 157.63, 156.09, 141.26, 137.02, 135.82, 133.29, 129.83, 127.44, 127.33, 127.26, 126.27, 126.20, 125.83, 121.50, 117.70, 116.21, 111.98, 111.91, 111.03, 109.25, 109.08, 103.38, 103.22, 46.64, 39.50, 20.15, 20.01, 8.03. HRMS calcd. for $C_{30}H_{31}FN_2$ (M^+): 438.2471, found: 438.2466; The enantiomeric excess of 89% ee was determined by HPLC [Daicel Chirapak AD-H, hexane/isopropanol = 95/5, flow rate 0.5 mL/min, T = 30 ^oC, 254 nm, tR(minor) 11.807 min, tR(major) 19.702 min].



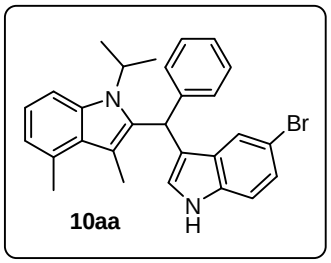
10y

(10y): yield: 94%; ee: 92%; (purified by flash column chromatography with petroleum ether and DCM eluents, v/v = 2.5/1); ^{1}H-NMR (d_6-DMSO, 400 MHz) δ (ppm) 1.20 (m, 6H), 1.84 (s, 3H), 2.19 (s, 6H), 2.35 (s, 3H), 4.68 (m, 1H), 6.02 (s, 1H), 6.84 (m, 5H), 7.06 (m, 2H), 7.20 (s, 1H), 7.38 (t, 2H), 11.14 (s, 1H); ^{13}C NMR (101 MHz, d_6-Acetone) δ 141.54, 137.29, 136.03, 135.40, 132.58, 130.10, 128.36, 127.73, 127.05, 126.45, 125.91, 123.89, 121.78, 121.44, 118.26, 117.96, 116.20, 112.72, 111.27, 106.60, 46.87, 39.64, 20.40, 20.32, 8.29. HRMS calcd. for $C_{30}H_{31}ClN_2$ (M^+): 454.2176, found: 454.2164; The enantiomeric excess of 92% ee was determined by HPLC [Daicel Chirapak OD-H, hexane/isopropanol = 95/5, flow rate 0.5 mL/min, T = 30 ^oC, 254 nm, tR(minor) 11.627 min, tR(major) 19.563 min].



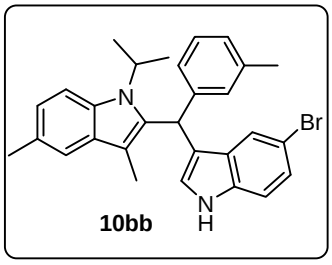
10z

(10z): yield: 97%; ee: 92%; (purified by flash column chromatography with petroleum ether and DCM eluents, v/v = 2.5/1); ^{1}H-NMR (d_6-DMSO, 400 MHz) δ (ppm) 1.20 (m, 6H), 1.84 (s, 3H), 2.19 (s, 6H), 2.35 (s, 3H), 4.68 (m, 1H), 6.02 (s, 1H), 6.82 (m, 5H), 7.18 (m, 2H), 7.25 (s, 1H), 7.36 (t, 2H), 11.15 (s, 1H); ^{13}C NMR (151 MHz, d_6-Acetone) δ 141.28, 137.02, 135.77, 135.38, 132.31, 129.84, 128.79, 127.47, 126.27, 126.19, 125.52, 123.77, 121.52, 121.12, 117.71, 115.83, 112.93, 111.26, 111.01, 106.32, 46.61, 39.34, 20.15, 20.07, 8.04. HRMS calcd. for $C_{30}H_{31}BrN_2$ (M^+): 498.1671, found: 498.1652; The enantiomeric excess of 92% ee was determined by HPLC [Daicel Chirapak AD-H, hexane/isopropanol = 95/5, flow rate 0.5 mL/min, T = 30 ^{o}C, 254 nm, tR(minor) 11.418 min, tR(major) 20.633 min].



10aa

(10aa): yield: 94%; ee: 86%; (purified by flash column chromatography with petroleum ether and DCM eluents, v/v = 2.5/1); ^{1}H-NMR (d_6-DMSO, 400 MHz) δ (ppm) 1.19 (m, 6H), 2.28 (s, 3H), 2.62 (s, 3H), 4.71 (m, 1H), 6.19 (s, 1H), 6.67 (d, *J* = 7.2 Hz, 1H), 6.88 (t, 2H), 7.20 (m, 4H), 7.30 (m, 4H), 7.38 (d, *J* = 8.7 Hz, 1H), 11.21 (s, 1H); ^{13}C NMR (151 MHz, d_6-Acetone) δ 141.49, 135.86, 135.42, 134.41, 130.05, 128.75, 128.34, 127.77, 127.64, 125.81, 125.56, 123.87, 121.37, 119.93, 119.83, 114.95, 113.01, 111.36, 109.58, 107.85, 46.89, 38.64, 19.97, 19.50, 11.32. HRMS calcd. for $C_{28}H_{27}BrN_2$ (M^+): 470.1358, found: 470.1340; The enantiomeric excess of 86% ee was determined by HPLC [Daicel Chirapak AD-H, hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm, tR(minor) 8.715 min, tR(major) 12.133 min].



10bb

(10bb): yield: 92%; ee: 87%; (purified by flash column chromatography with petroleum ether and DCM eluents, v/v = 2.5/1); ^{1}H-NMR (d_6-DMSO, 400 MHz) δ (ppm) 1.21 (m, 6H), 1.83 (s, 3H), 2.24 (s, 3H), 2.35 (s, 3H), 4.69 (m, 1H), 6.07 (s, 1H), 6.76 (s, 1H), 6.85 (d, *J* = 8.1 Hz, 1H), 6.94 (d, *J* = 8.1 Hz, 1H), 7.04 (m, 2H), 7.19 (m, 3H),7.26 (s, 1H), 7.37 (d, *J* = 8.7 Hz, 2H), 11.16 (s, 1H); ^{13}C NMR (101 MHz,

d_6-Acetone) δ 142.10, 137.92, 136.47, 136.13, 133.04, 130.55, 129.78, 129.46, 128.39, 127.36, 127.02, 126.23, 124.53, 122.29, 121.87, 118.42, 116.41, 113.67, 112.02, 111.72, 107.15, 47.32, 40.12, 20.96, 20.89, 20.84, 8.75. HRMS calcd. for $C_{29}H_{29}BrN_2$ (M^+): 484.1514, found: 484.1501; The enantiomeric excess of 87% ee was determined by HPLC [Daicel Chirapak AD-H, hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 30 ^oC, 254 nm, tR(minor) 7.396 min, tR(major) 12.071 min].

References:

(1) D. Uraguchi, M. Terada, *J. Am. Chem. Soc*. 2004, **126**, 5356.

(2) T. Akiyama, H. Morita, J. Itoh, K. Fuchibe, *Org. Lett*. 2005, **7**, 2583.

(3) R. I. Storer, D. E. Carrera, Y. Ni, D. W. C. MacMillan, *J. Am. Chem. Soc*. 2006, **128**, 84.

(4) Q.-X. Guo, H. Liu, C. Guo, S.-W. Luo, Y. Gu, L.-Z. Gong, *J. Am. Chem. Soc*. 2007, **129**, 3790.

(5) X.-H. Chen, W.-Q. Zhang, L.-Z. Gong, *J. Am. Chem. Soc*. 2008, **130**, 5652.

(6) G. Pousse, A. Devineau, J. Blanchet, *Tetrahedron*. 2009, **65**, 10617.

(7) D. Fabbri, G. Delogu, O.-D. Lucchi, *Tetrahedron: Asymmetry*. 1993, **4**, 1591.

(8) D. Nakashima, H. Yamamoto, *J. Am. Chem. Soc*. 2006, **128**, 9626.

(9) A. Berkessel, M. Frauenkron, *Tetrahedron: Asymmetry*. 1996, **7**, 671.

(10) M. Rueping, B.-J. Nachtsheim, W. Ieawsuwan, *Chem. Eur. J*. 2010, **16**, 13116.

(11) M. Rueping, U. Uria, M.-Y. Lin, I. Atodiresei, *J. Am. Chem. Soc*. 2011, **133**, 3732.

(12) K. Wu, Y.-J. Jiang, S.-Q. Zhang, *Chem. Eur. J*. 2013, **19**, 474.

(13) Q. Cai, C. Zheng, S.-L. You, *Angew. Chem. Int. Ed*. 2010, **49**, 8666.

(14) J. F. Quinn, M. E. Bos, W. D. Wulff, *Org. Lett*. 1999, **1**, 161.

3 Copies of ^{1}H- and ^{13}C-NMR spectra of products

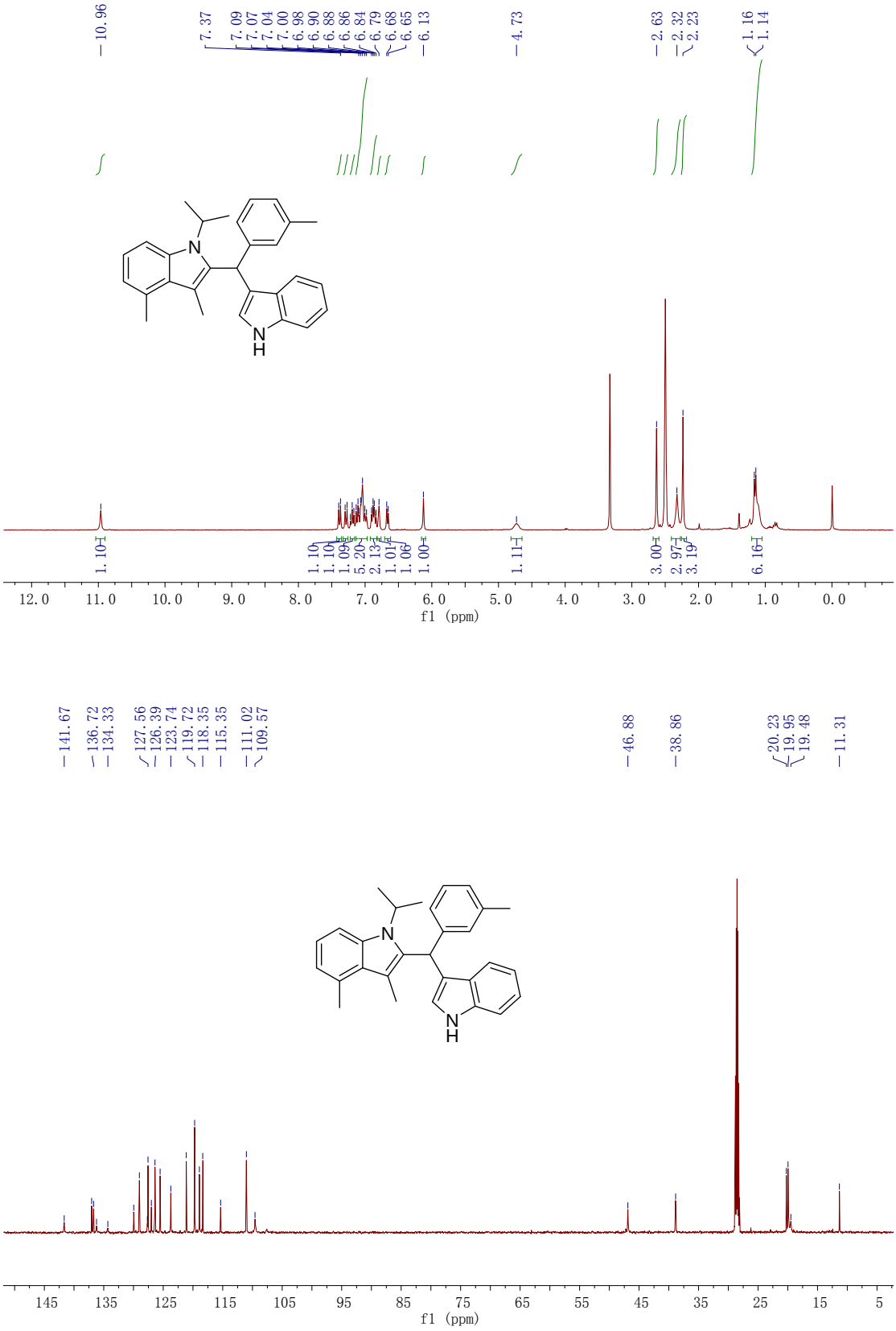


Figure S1. ^{1}H- (upper) and ^{13}C-NMR (bottom) of **10a**

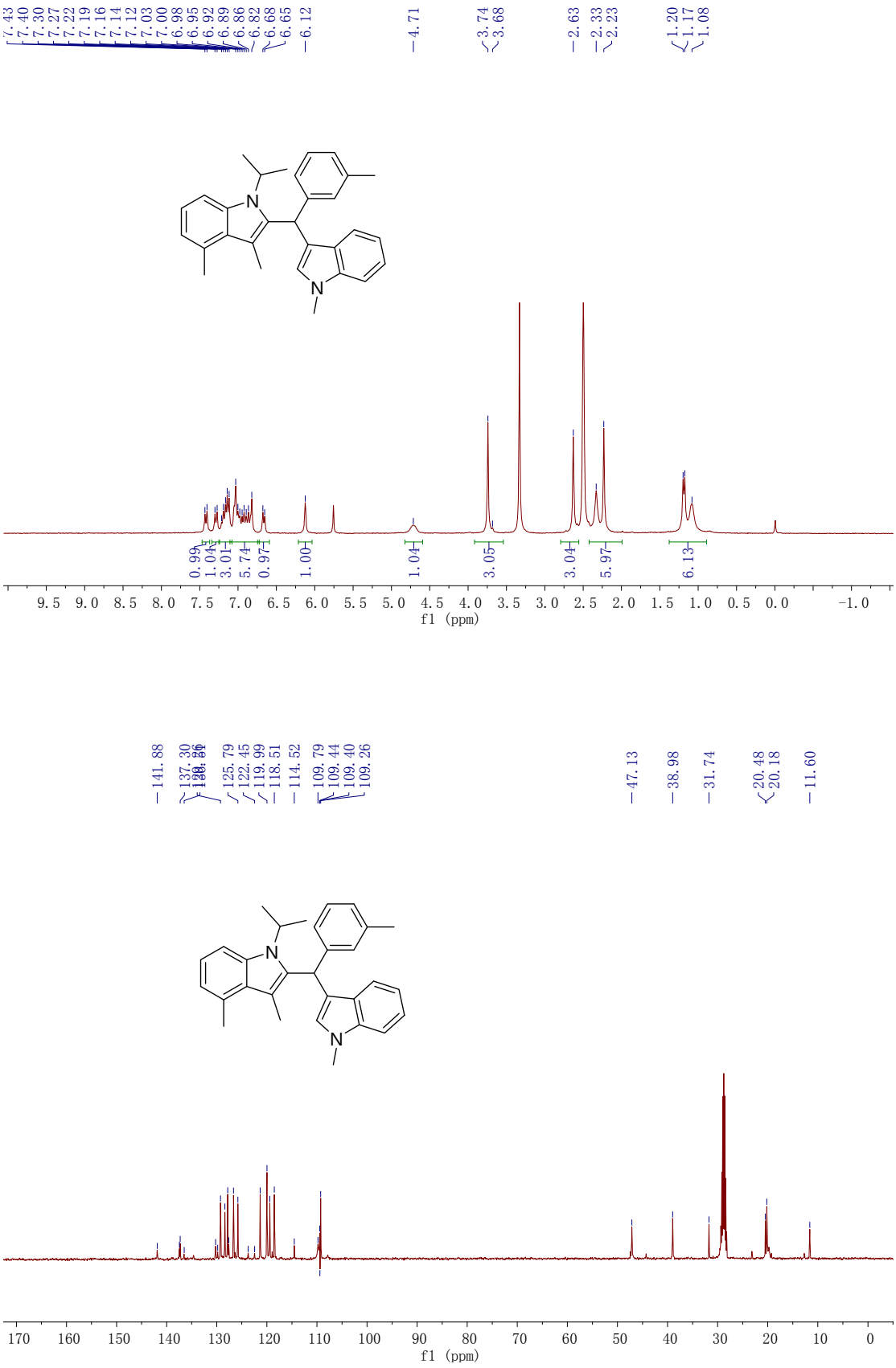


Figure S2. ^{1}H- (upper) and ^{13}C-NMR (bottom) of **10b**

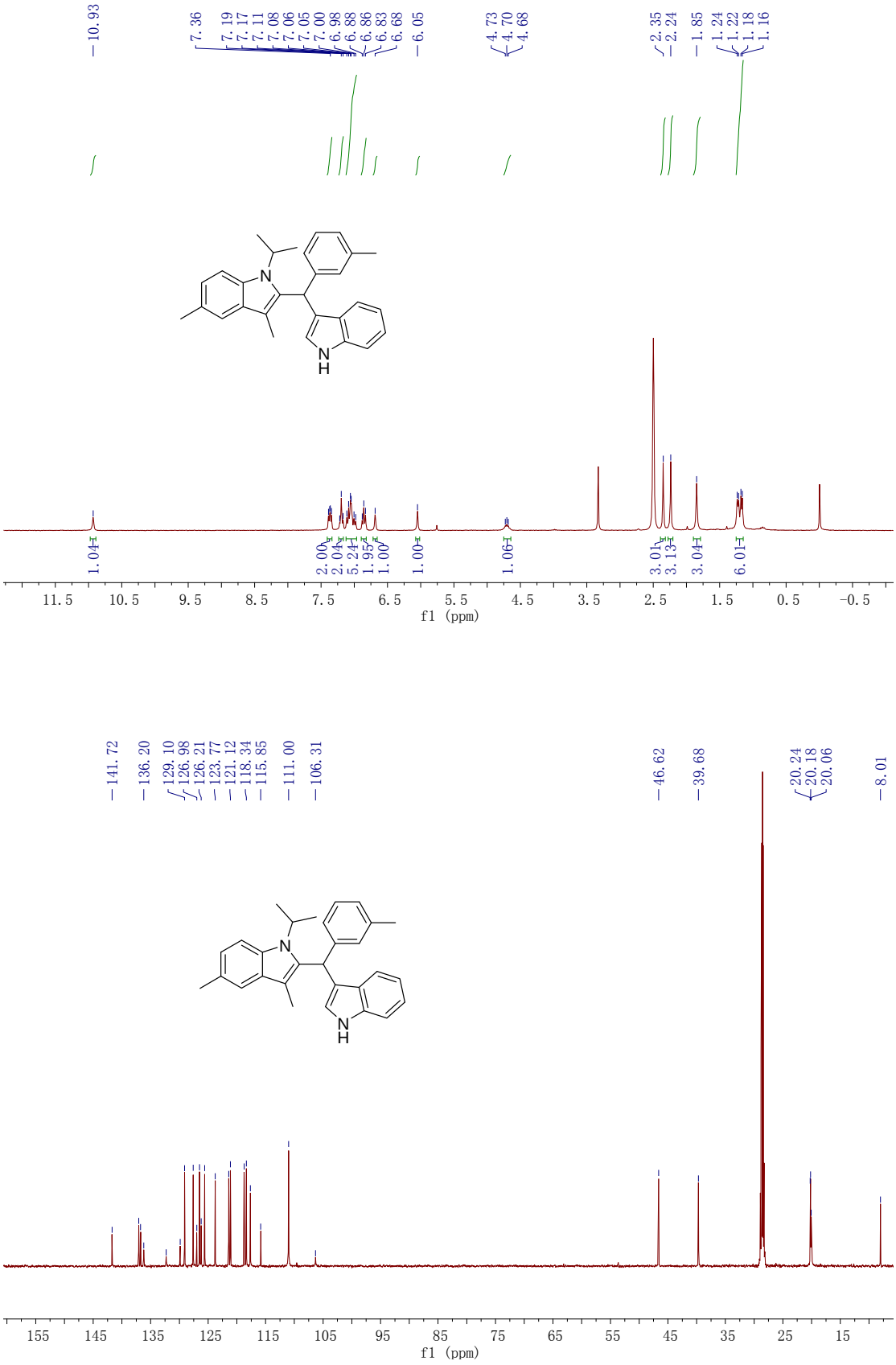


Figure S3. ^{1}H- (upper) and ^{13}C-NMR (bottom) of **10c**

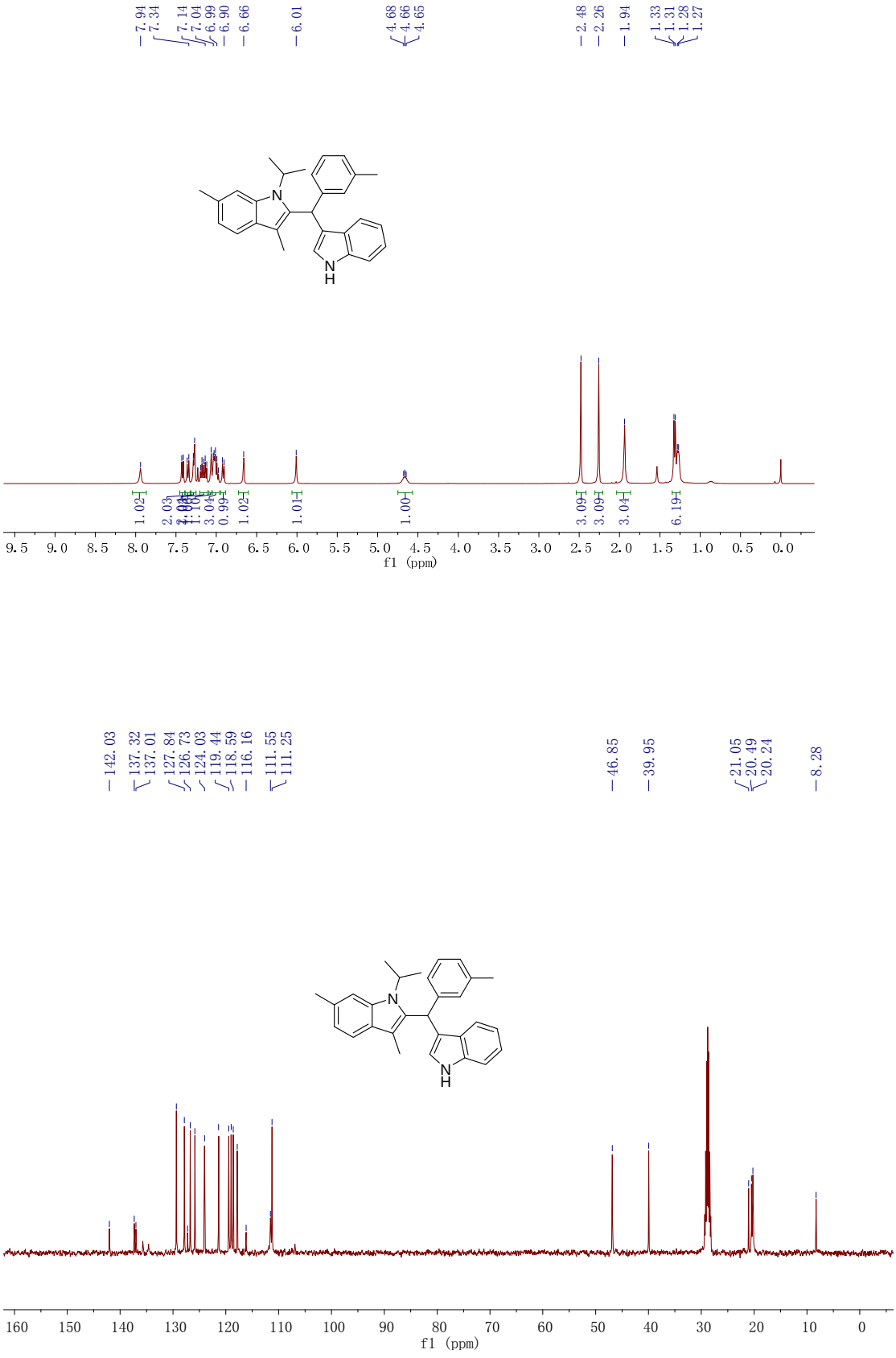


Figure S4. ^{1}H- (upper) and ^{13}C-NMR (bottom) of **10d**

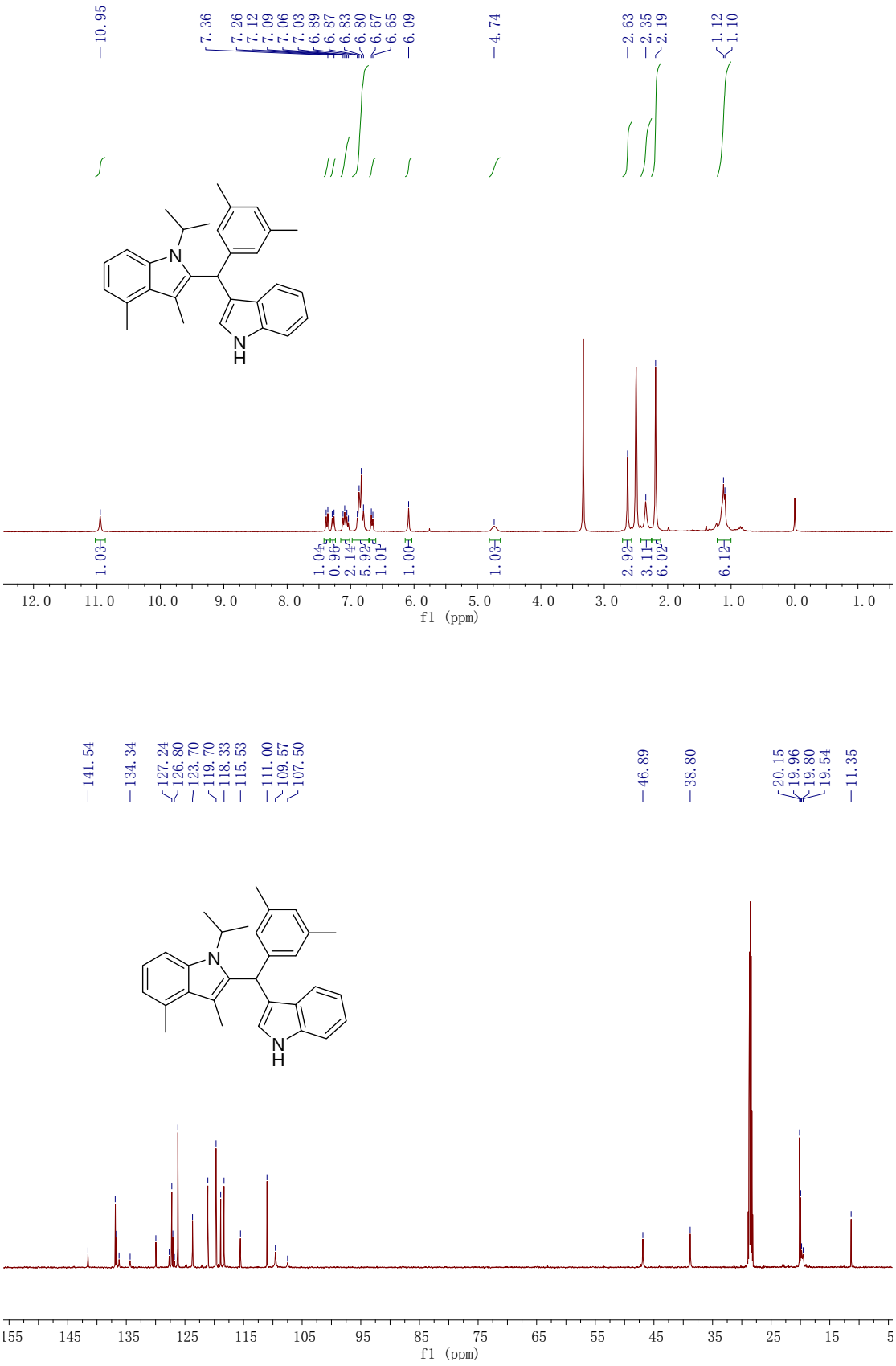


Figure S5. ^{1}H- (upper) and ^{13}C-NMR (bottom) of **10e**

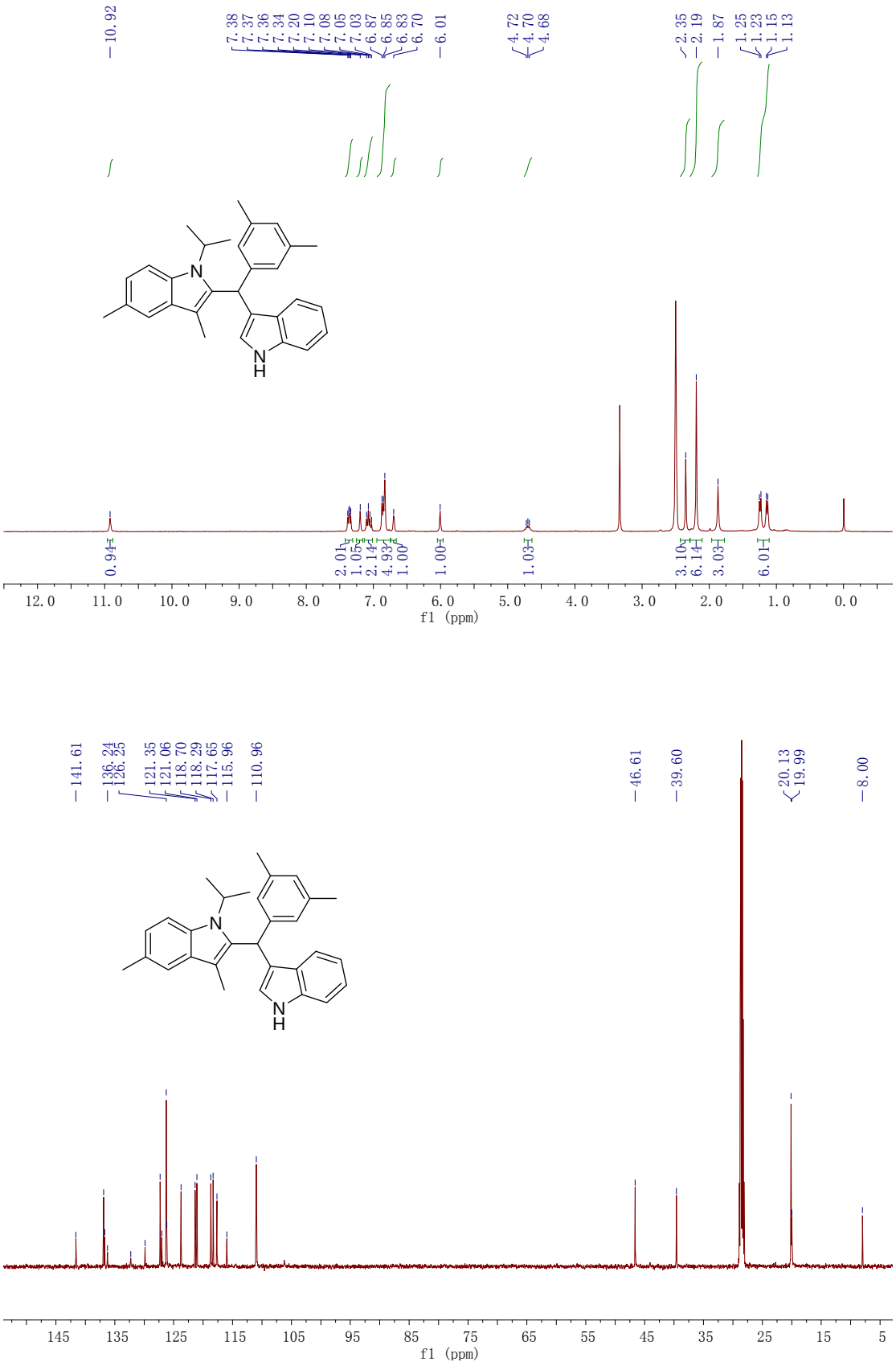


Figure S6. ^{1}H- (upper) and ^{13}C-NMR (bottom) of **10f**

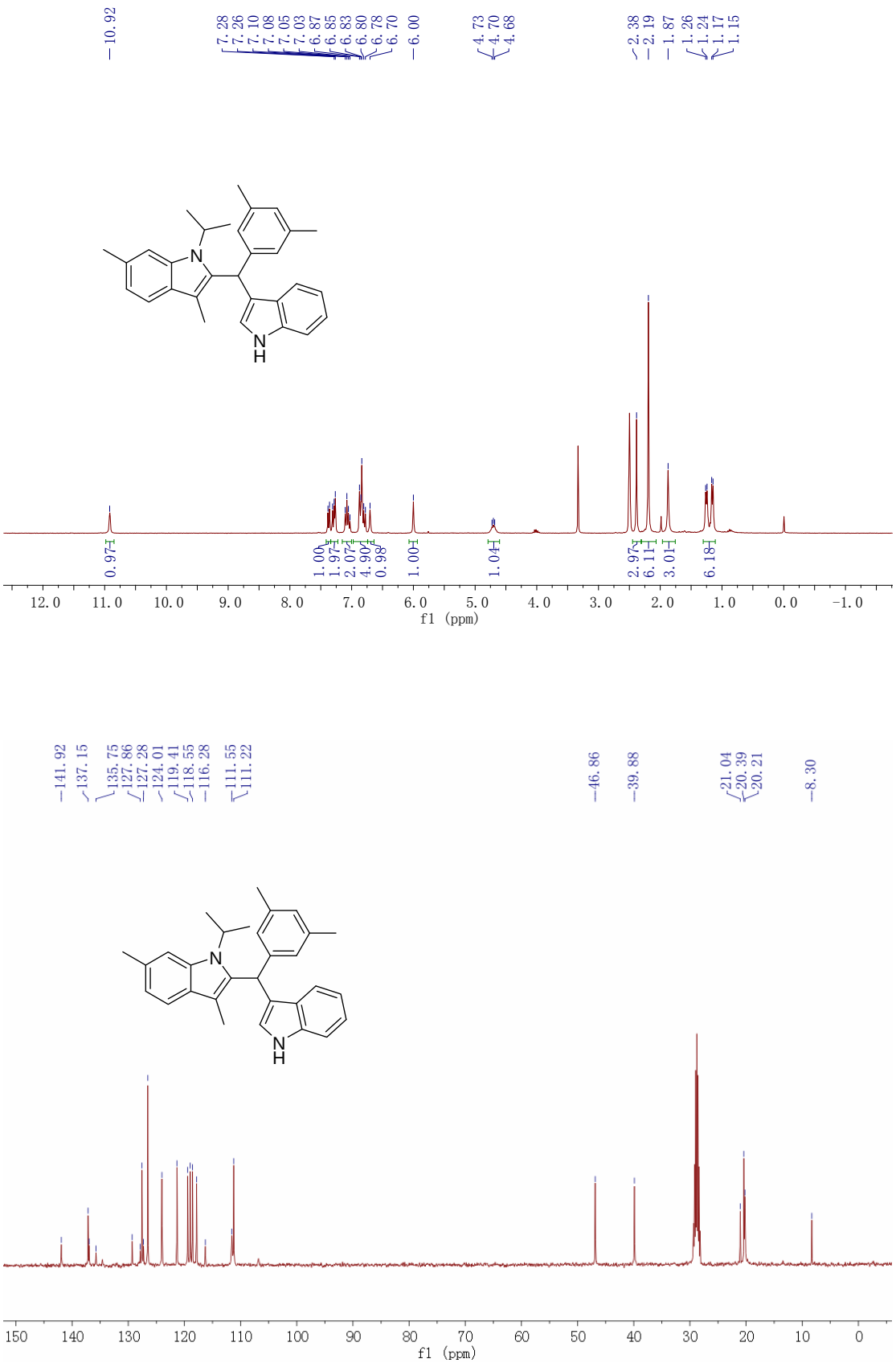


Figure S7. ^{1}H- (upper) and ^{13}C-NMR (bottom) of **10g**

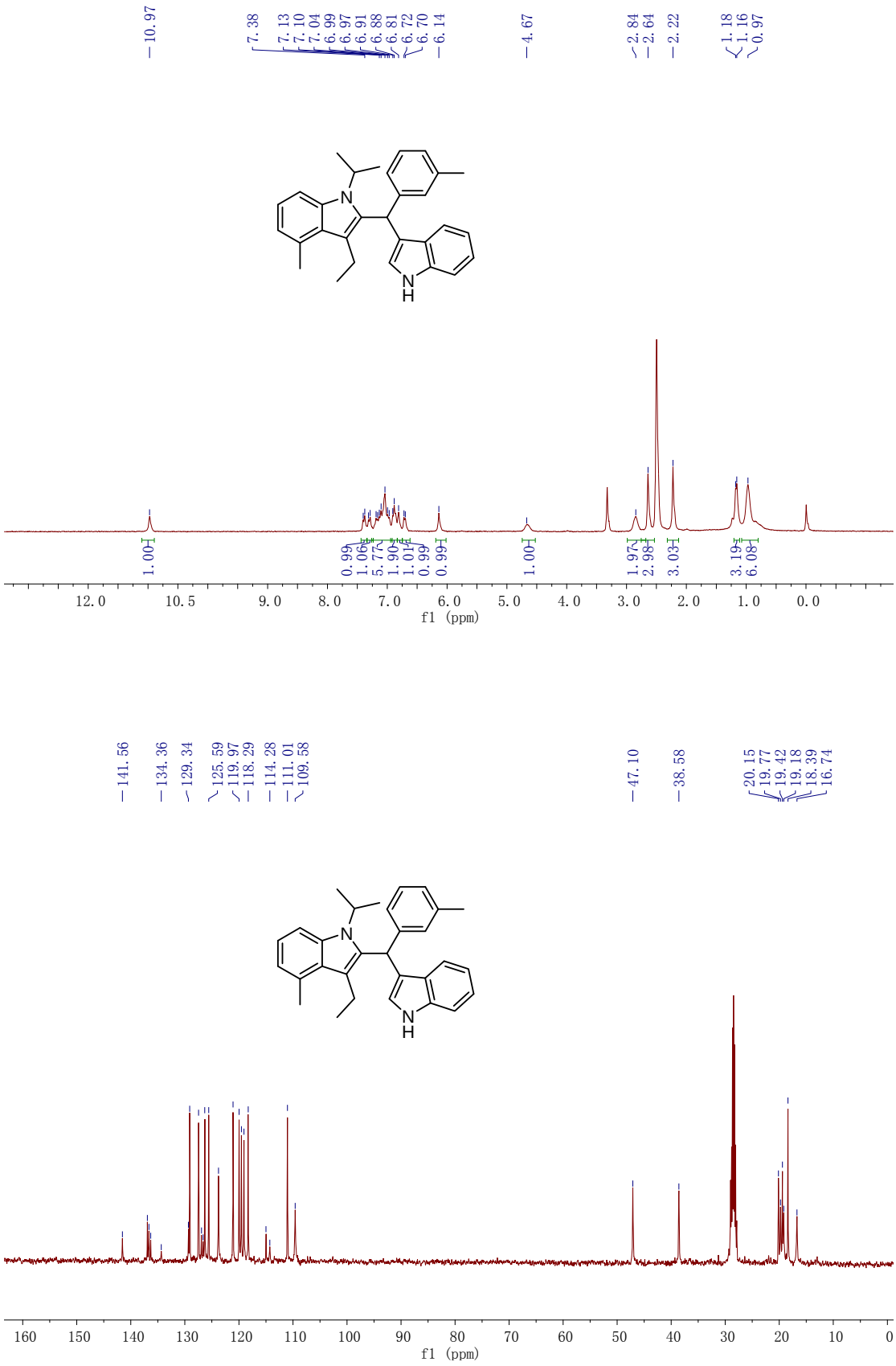


Figure S8. ^{1}H- (upper) and ^{13}C-NMR (bottom) of **10h**

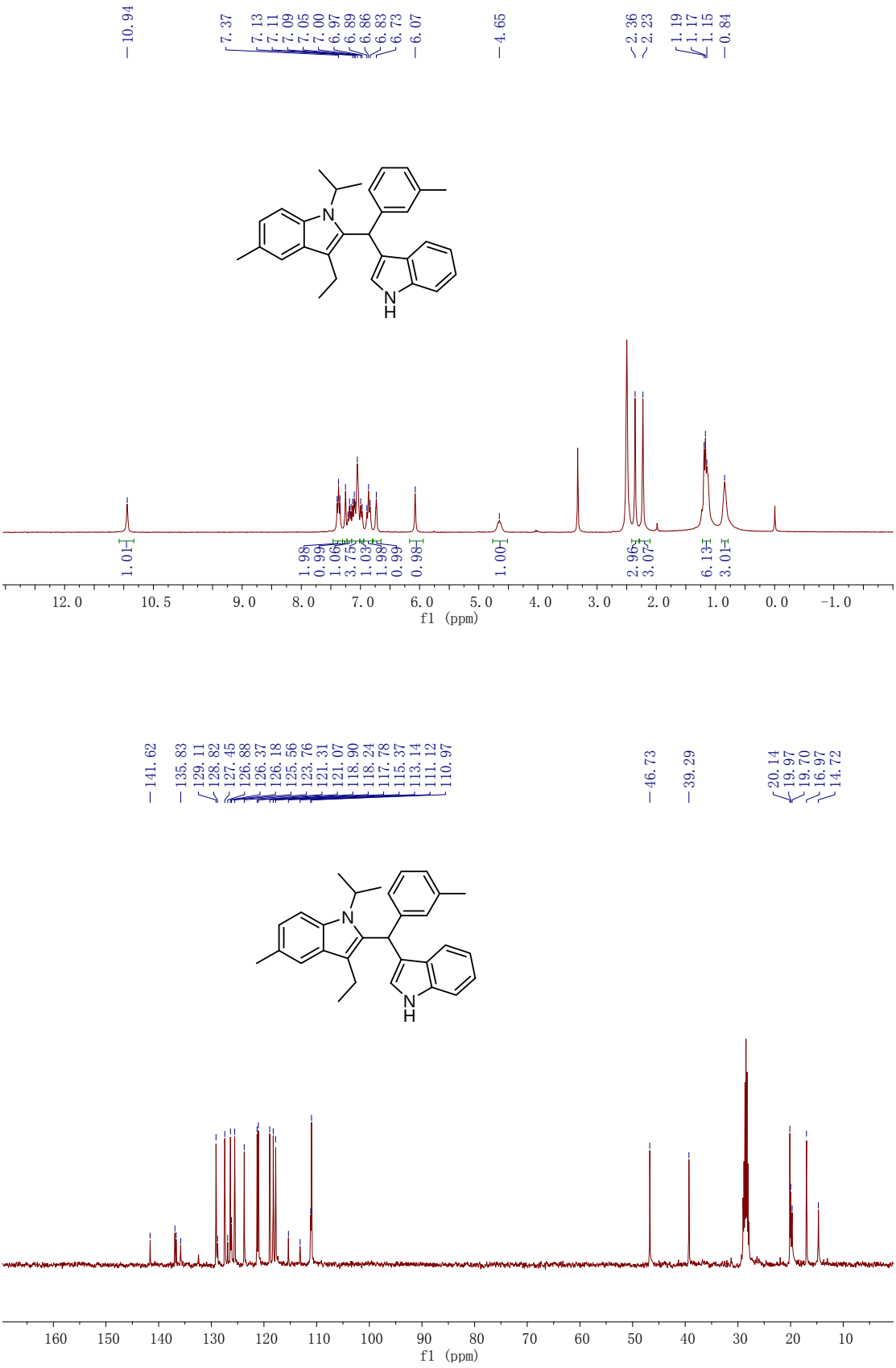


Figure S9. ^{1}H- (upper) and ^{13}C-NMR (bottom) of **10i**

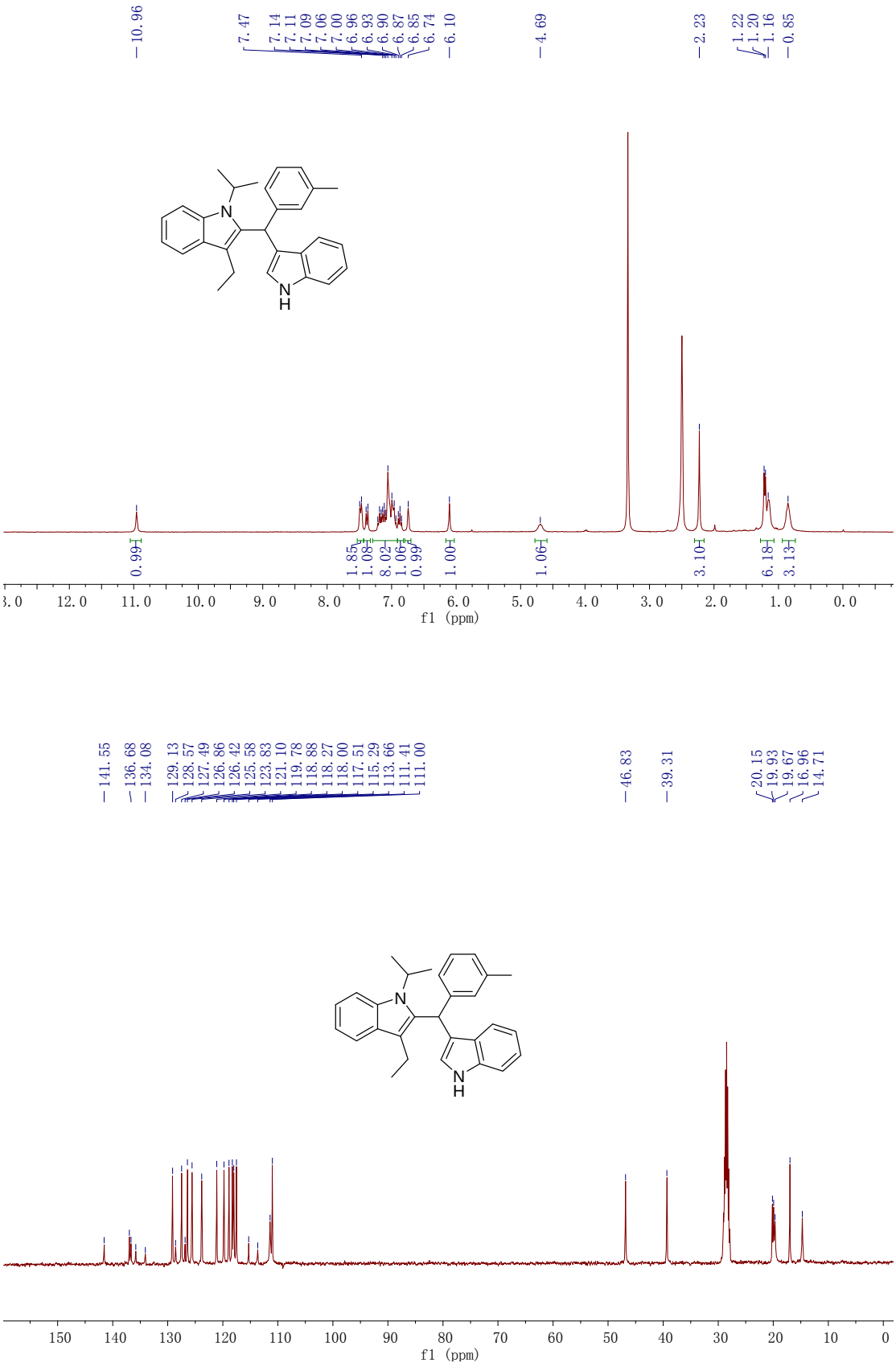


Figure S10. ^{1}H- (upper) and ^{13}C-NMR (bottom) of **10j**

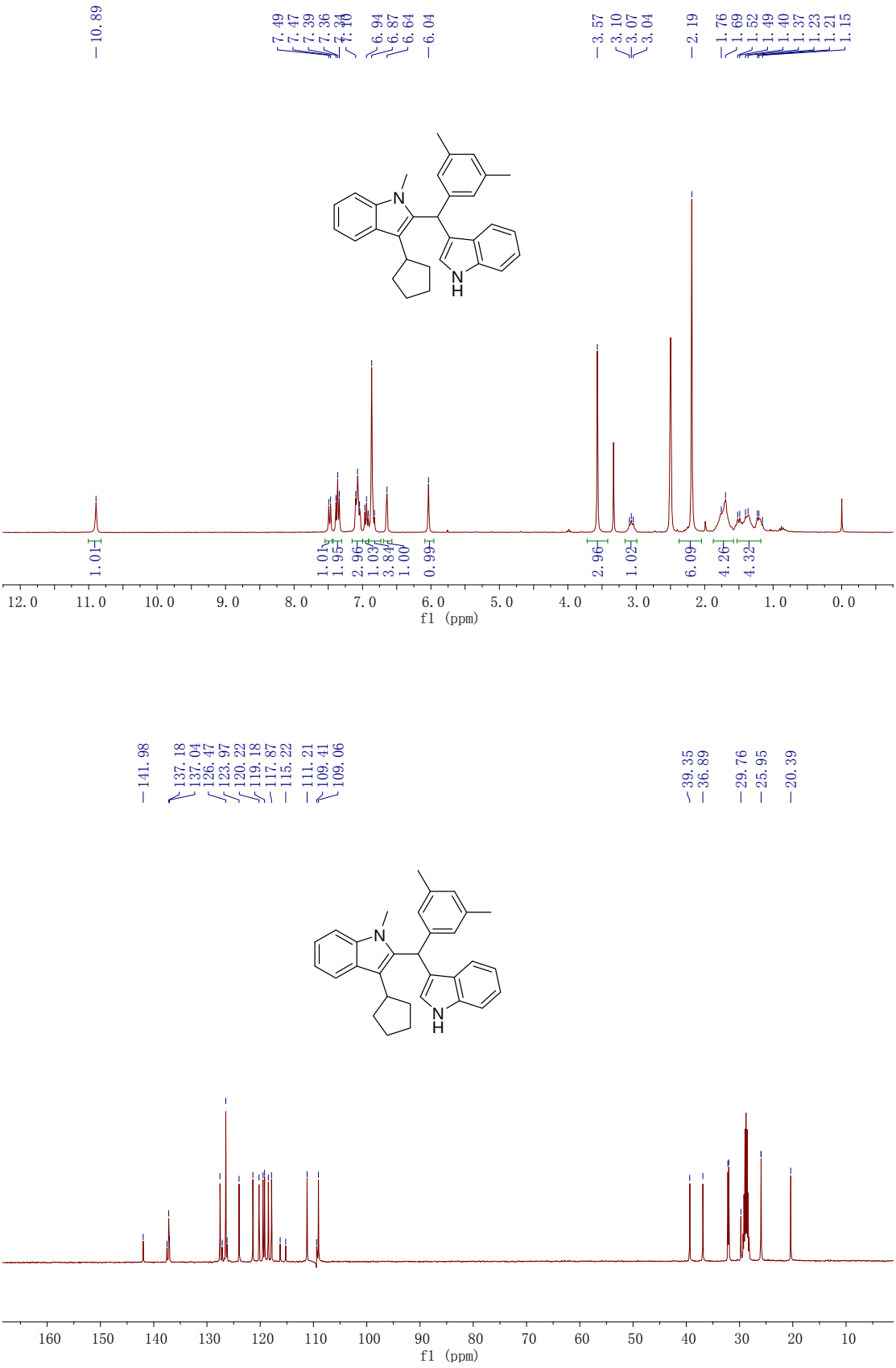


Figure S11. ^{1}H- (upper) and ^{13}C-NMR (bottom) of **10k**

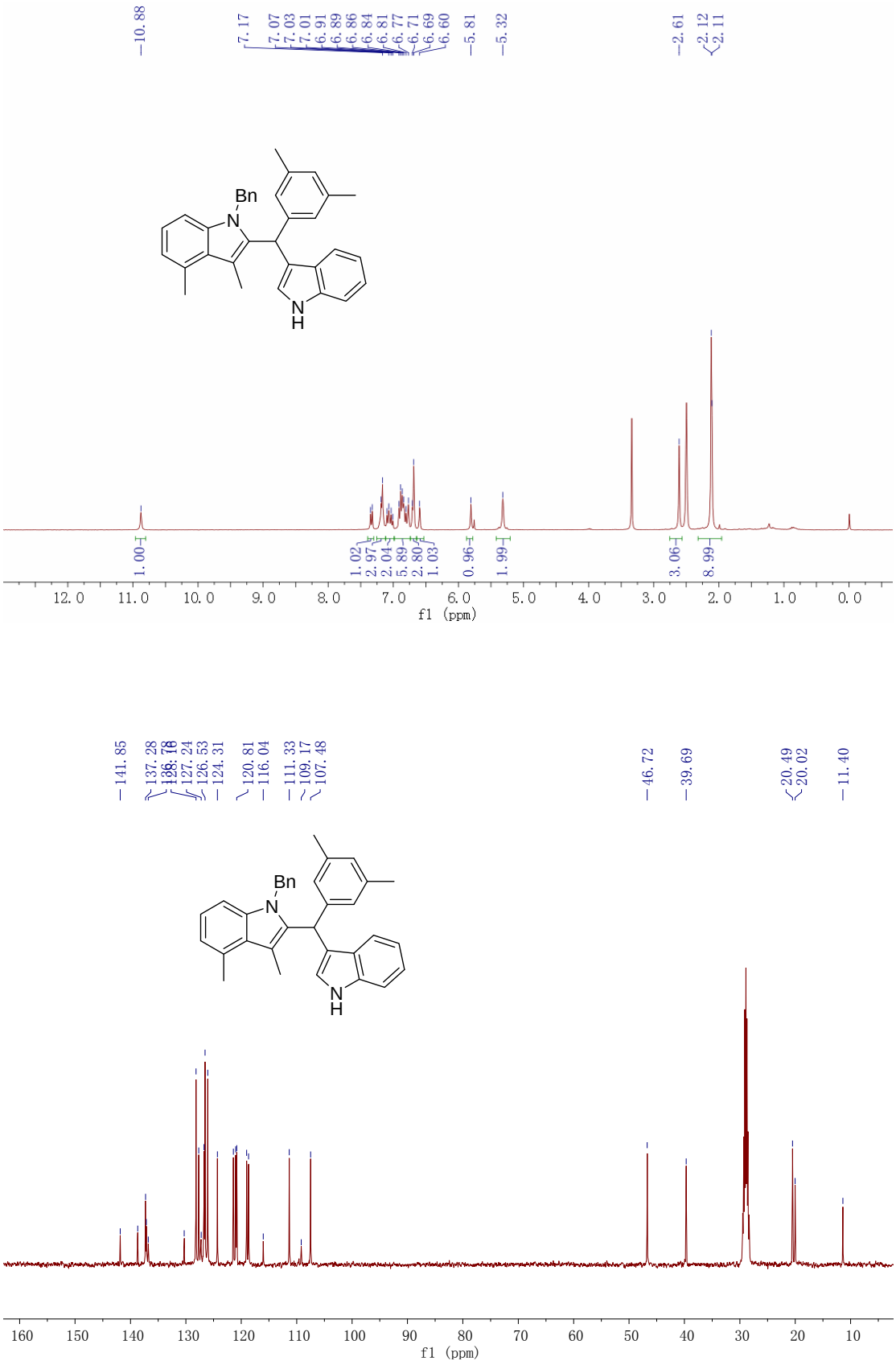


Figure S12. ^{1}H- (upper) and ^{13}C-NMR (bottom) of **10l**

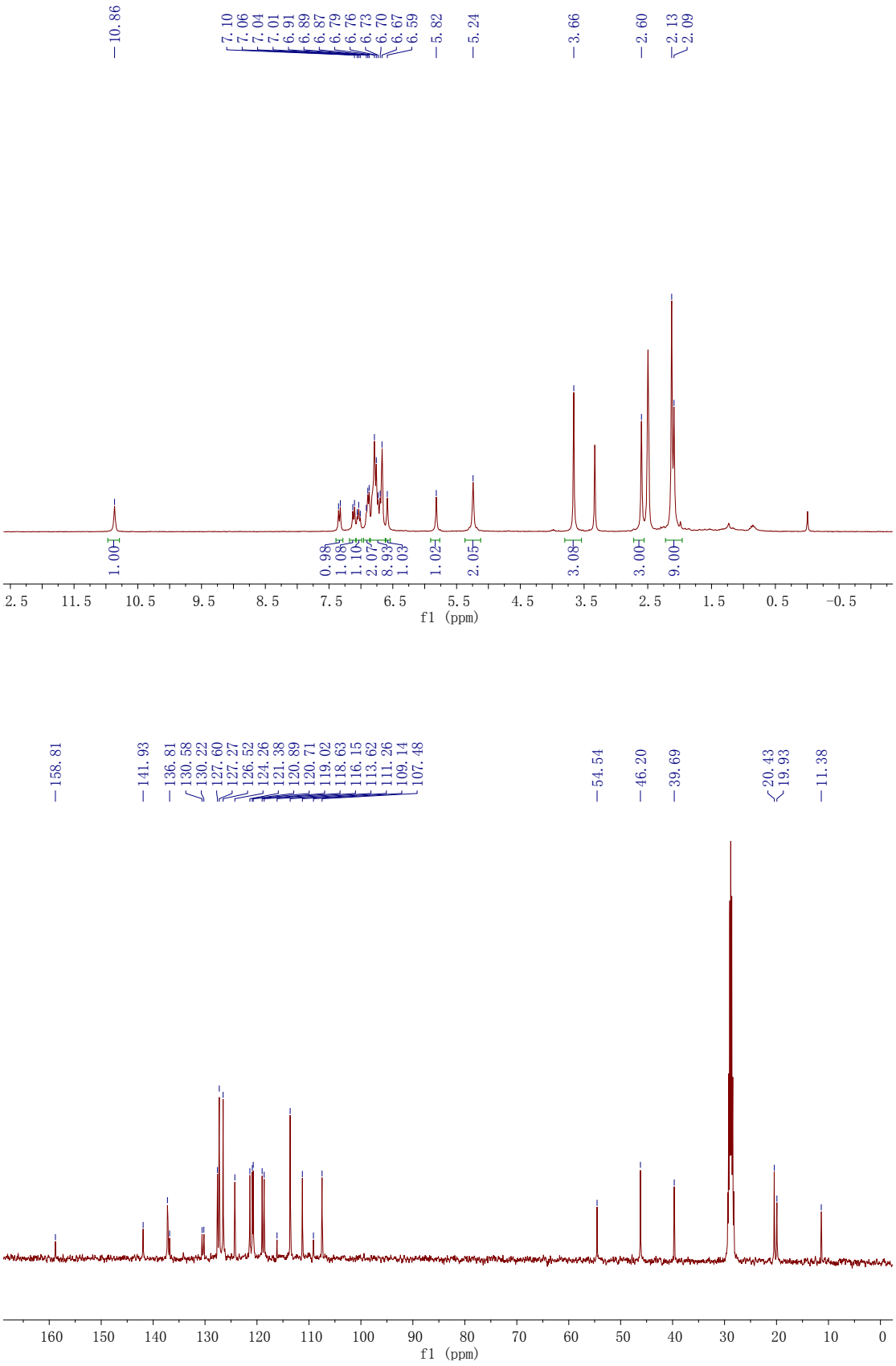


Figure S13. ^{1}H- (upper) and ^{13}C-NMR (bottom) of **10m**

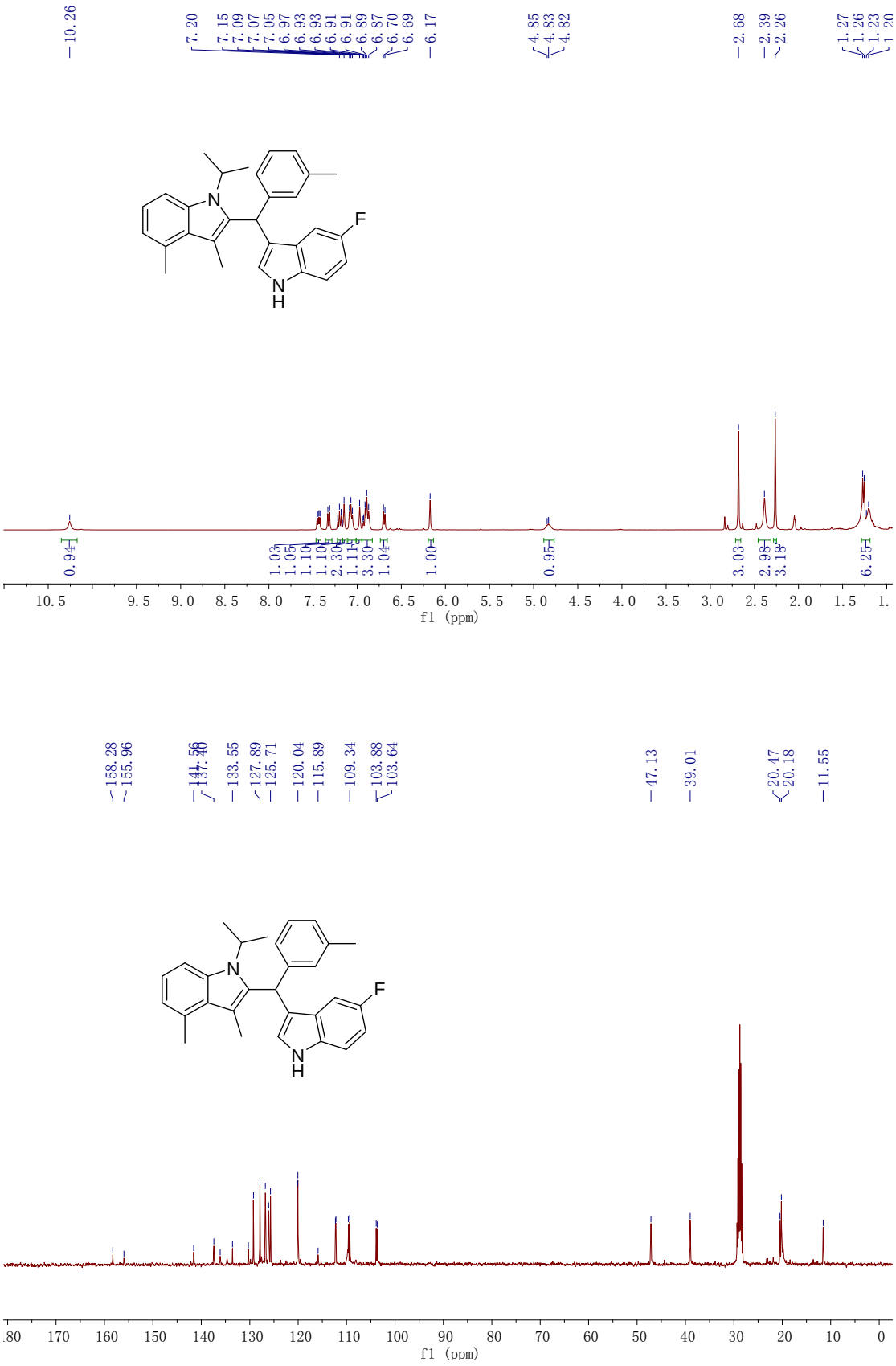


Figure S14. ^{1}H- (upper) and ^{13}C-NMR (bottom) of **10n**

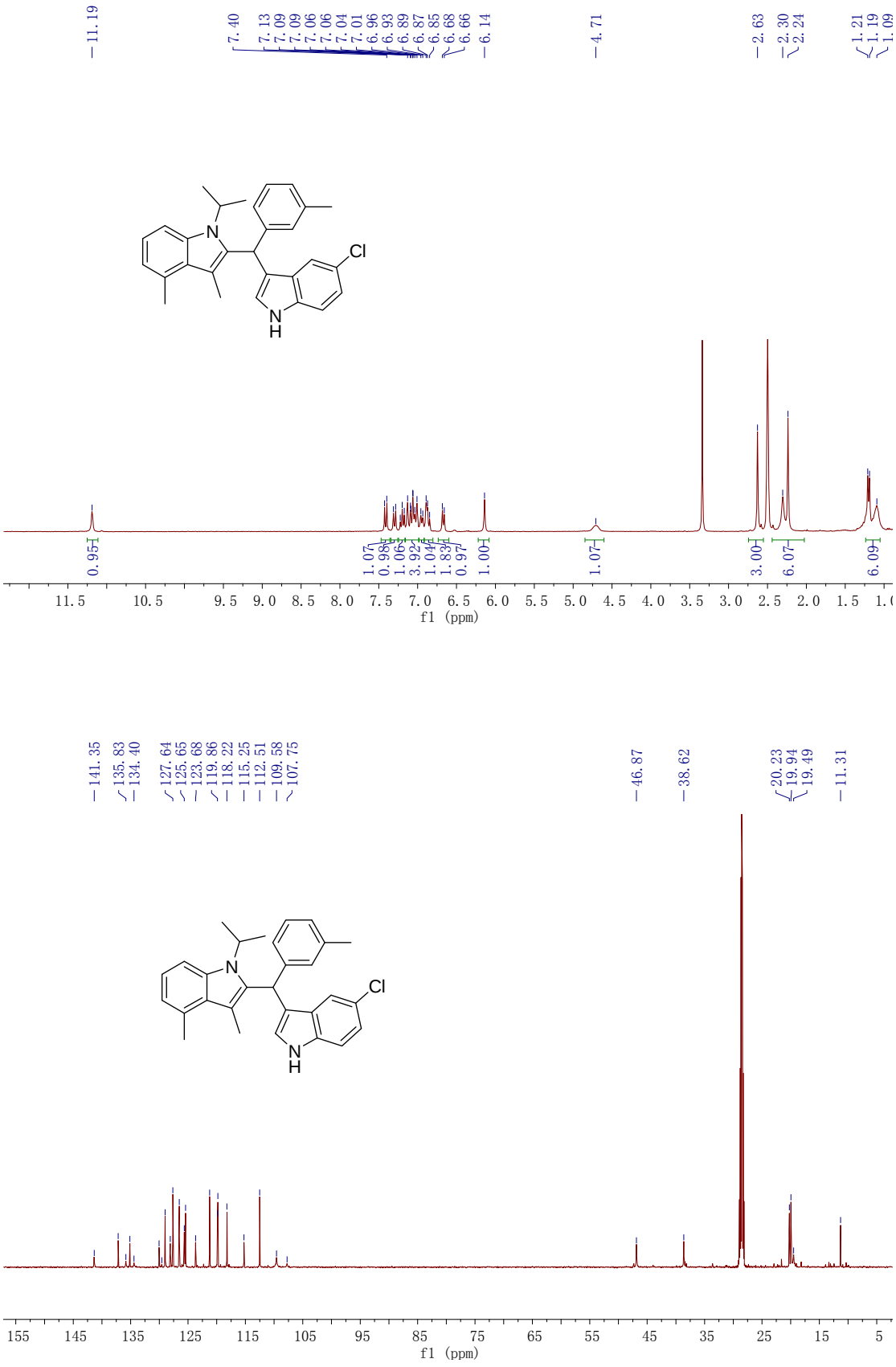


Figure S15. ^{1}H- (upper) and ^{13}C-NMR (bottom) of **10o**

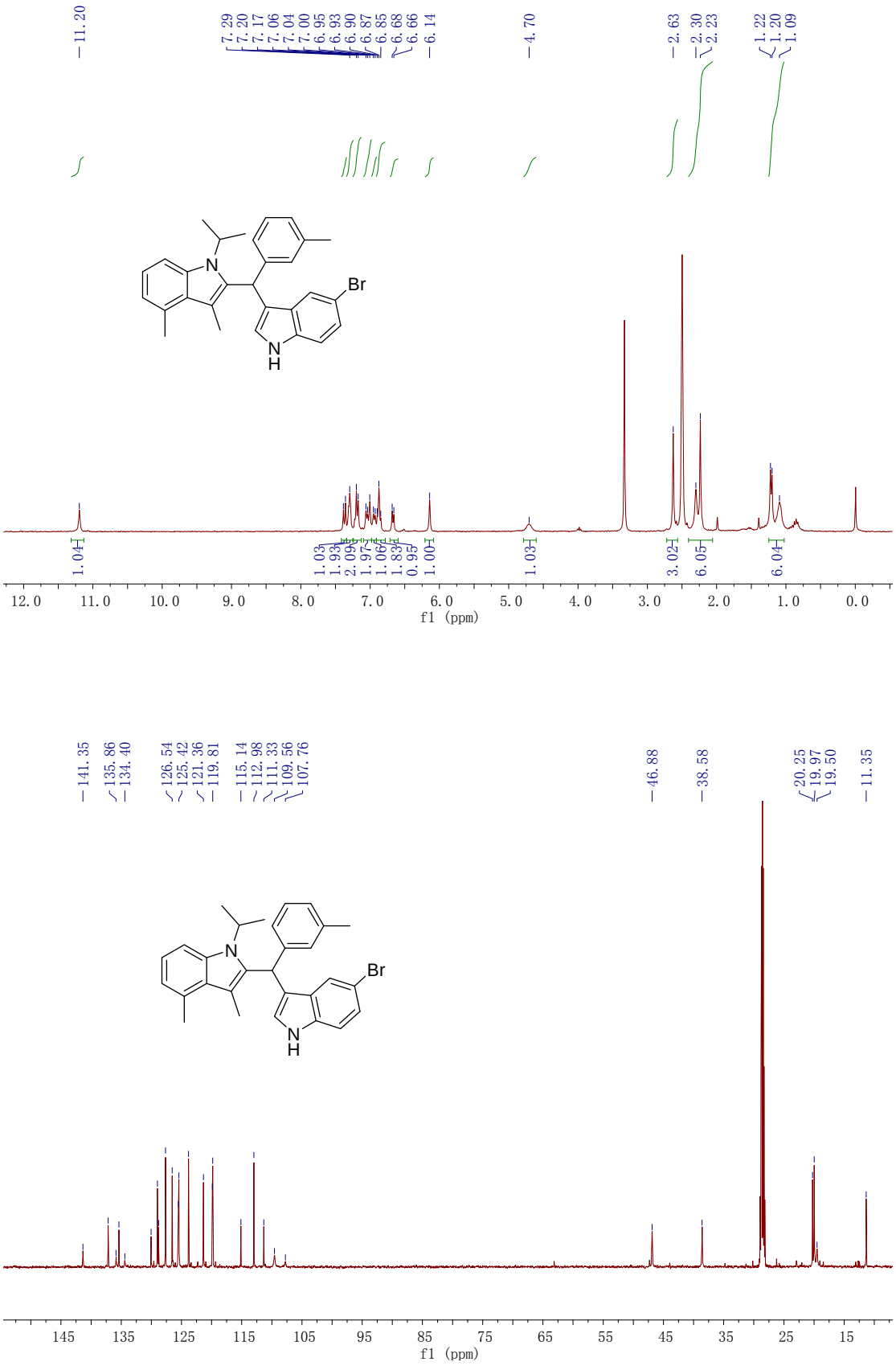


Figure S16. ^{1}H- (upper) and ^{13}C-NMR (bottom) of **10p**

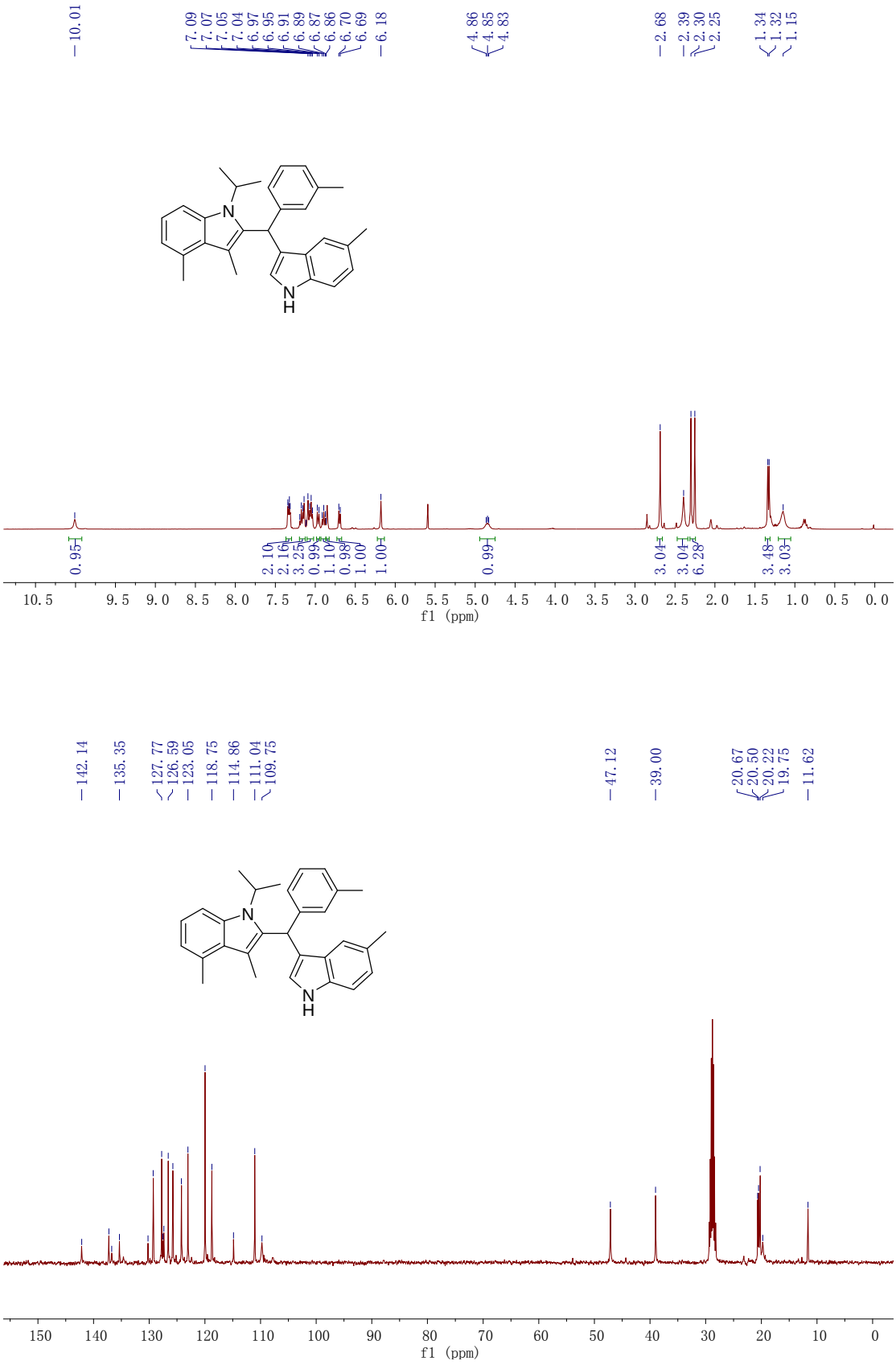


Figure S17. ^{1}H- (upper) and ^{13}C-NMR (bottom) of **10q**

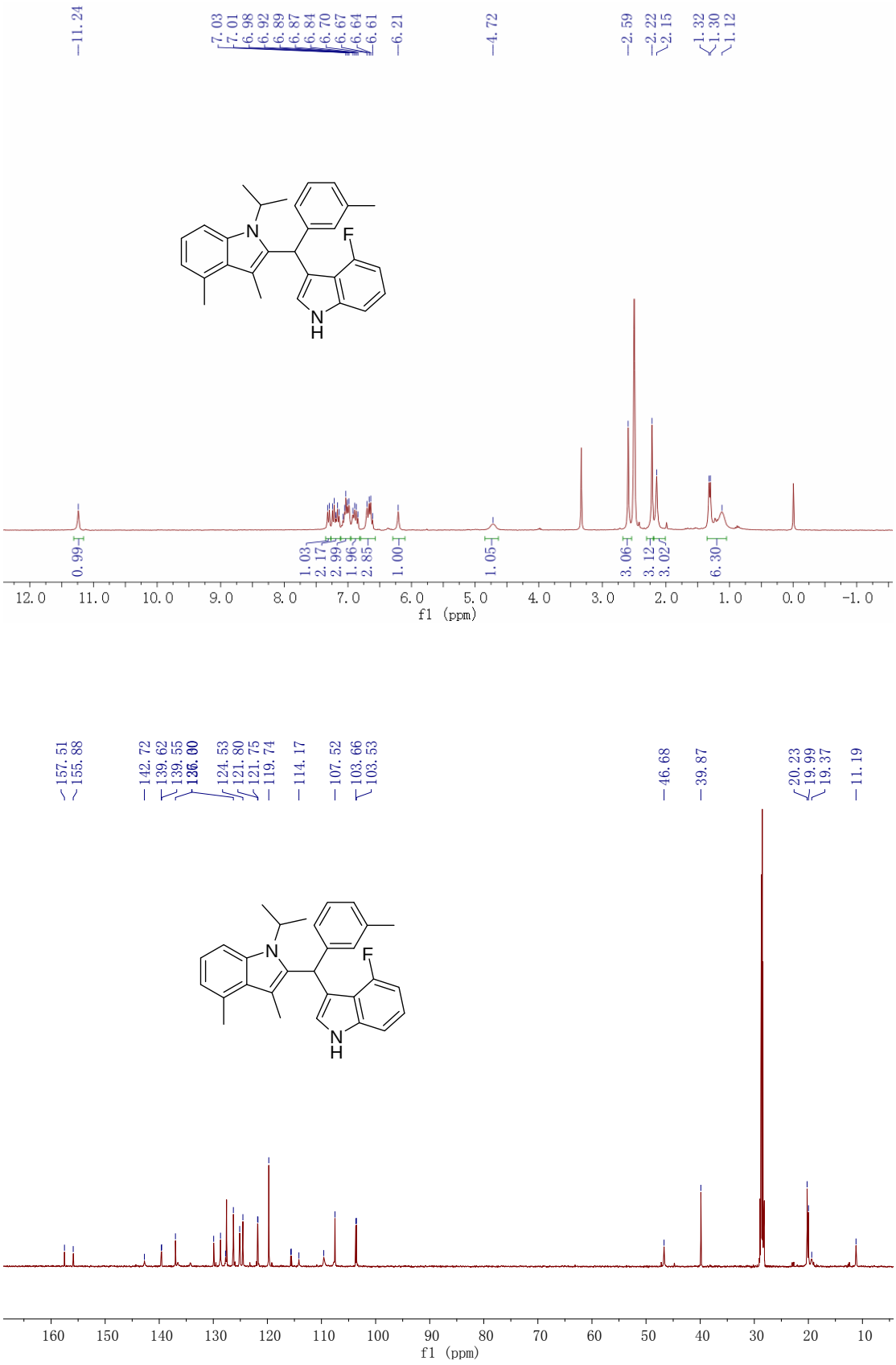


Figure S18. ^{1}H- (upper) and ^{13}C-NMR (bottom) of **10r**

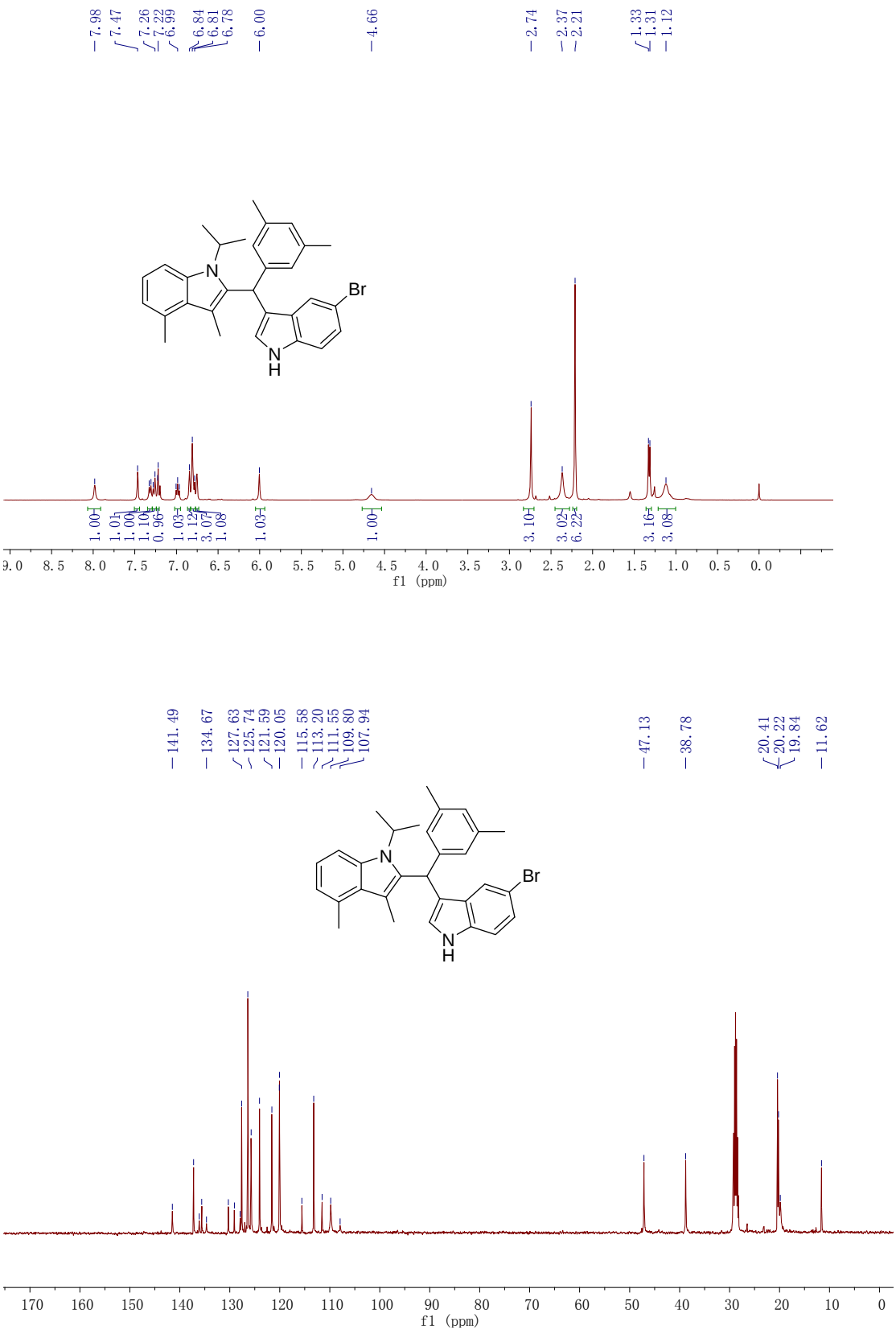


Figure S19. ^{1}H- (upper) and ^{13}C-NMR (bottom) of **10s**

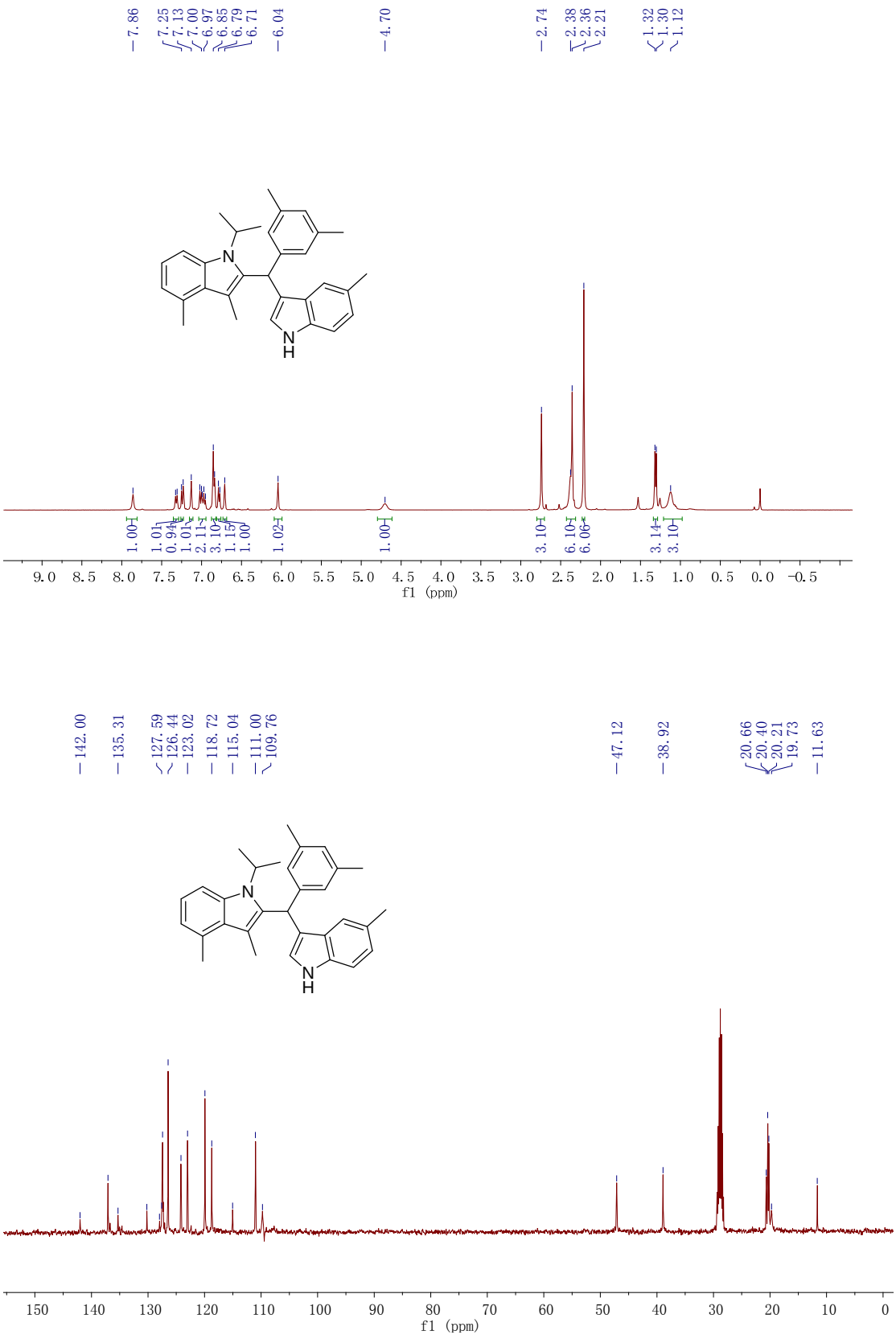


Figure S20. ^{1}H- (upper) and ^{13}C-NMR (bottom) of **10t**

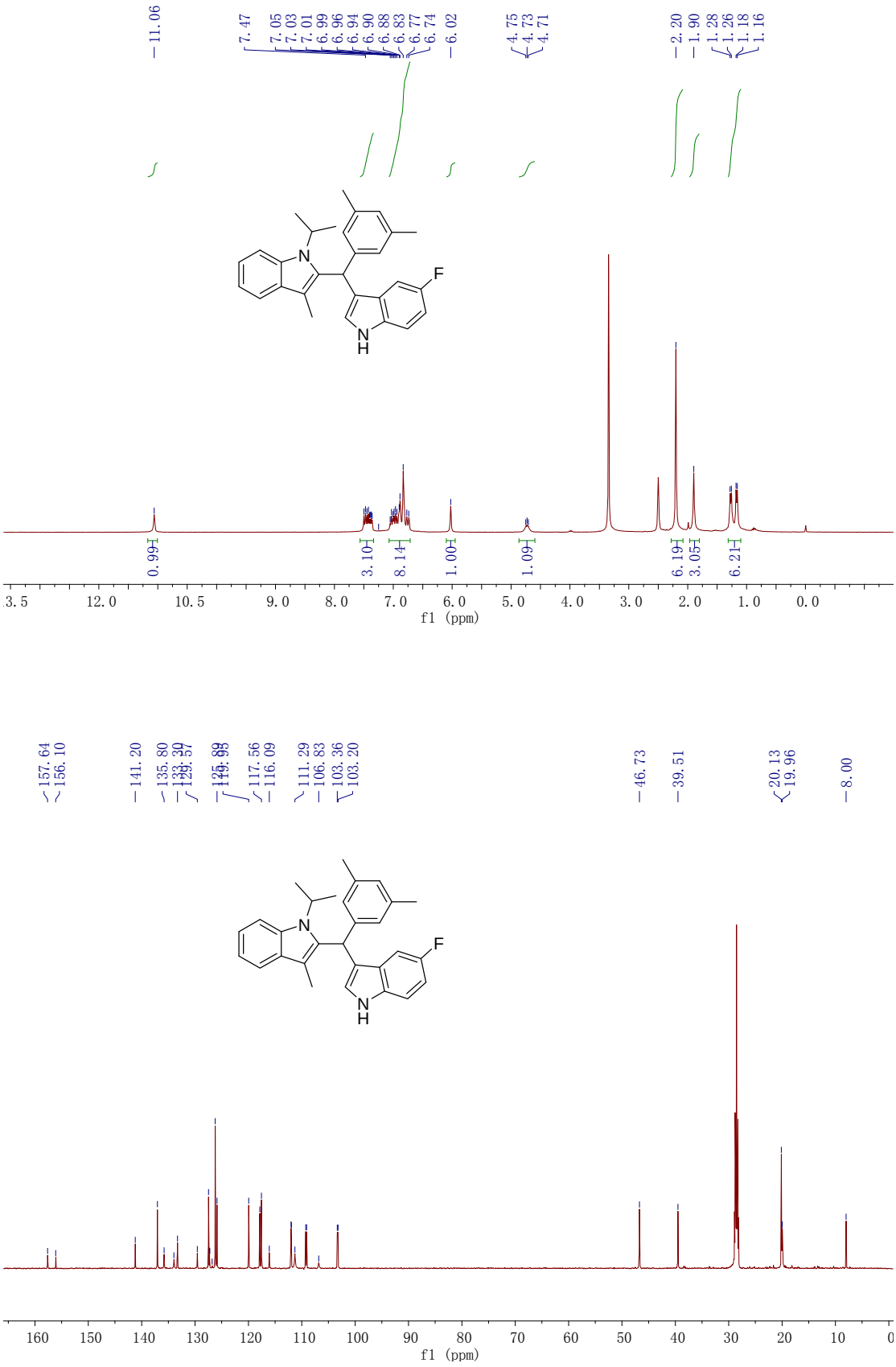


Figure S21. ^{1}H- (upper) and ^{13}C-NMR (bottom) of **10u**

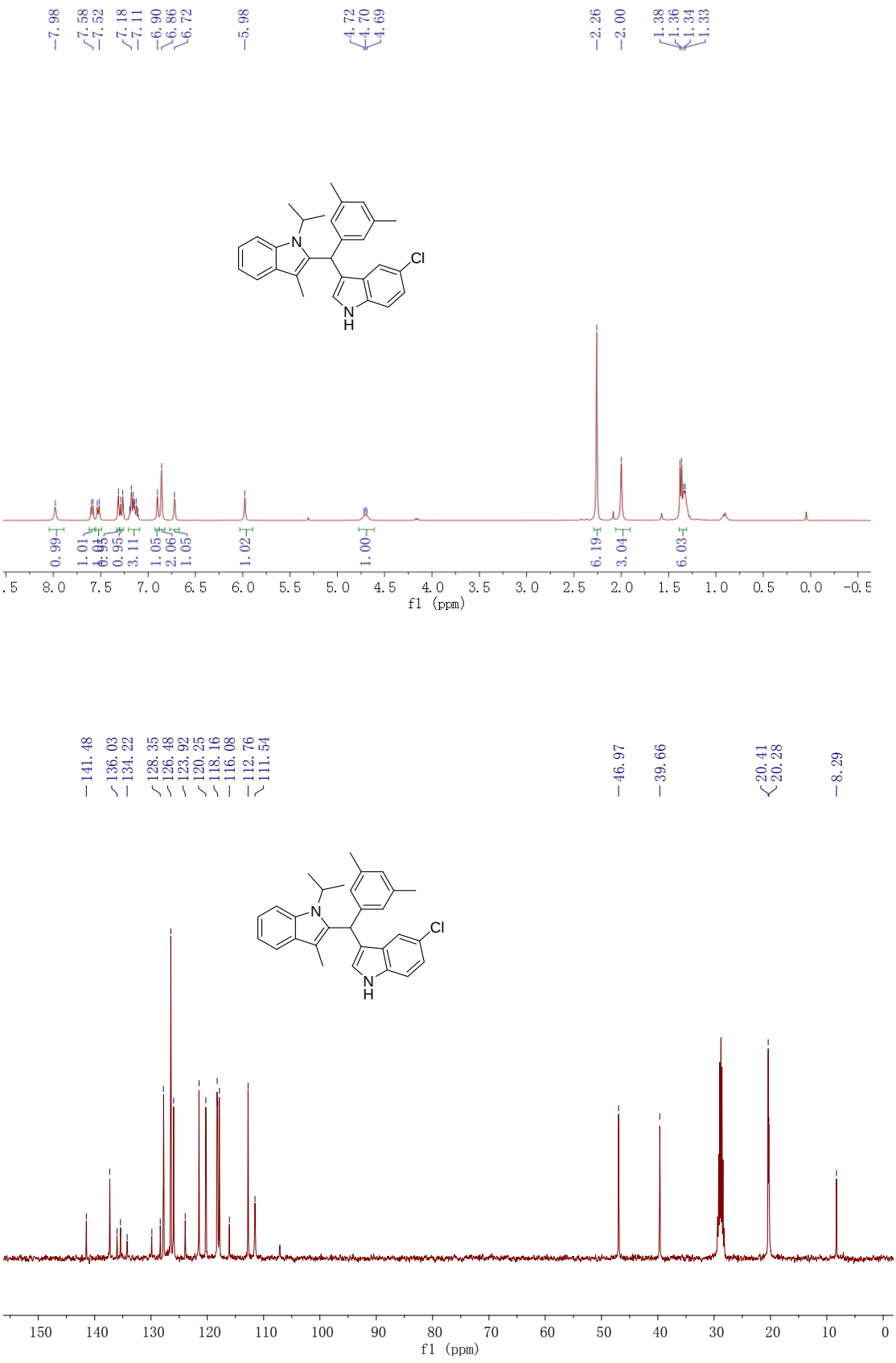


Figure S22. ^{1}H- (upper) and ^{13}C-NMR (bottom) of **10v**

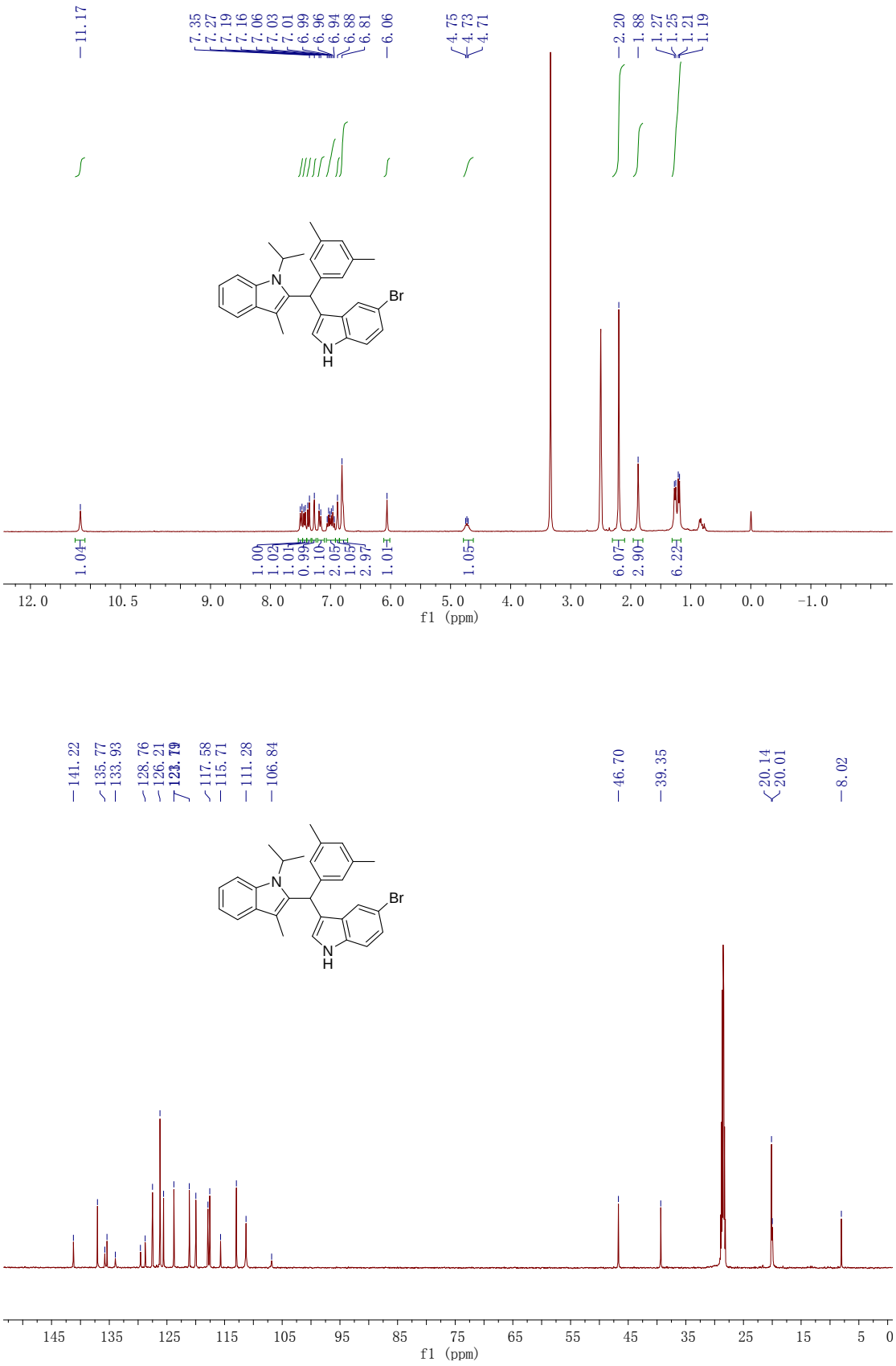


Figure S23. ^{1}H- (upper) and ^{13}C-NMR (bottom) of **10w**

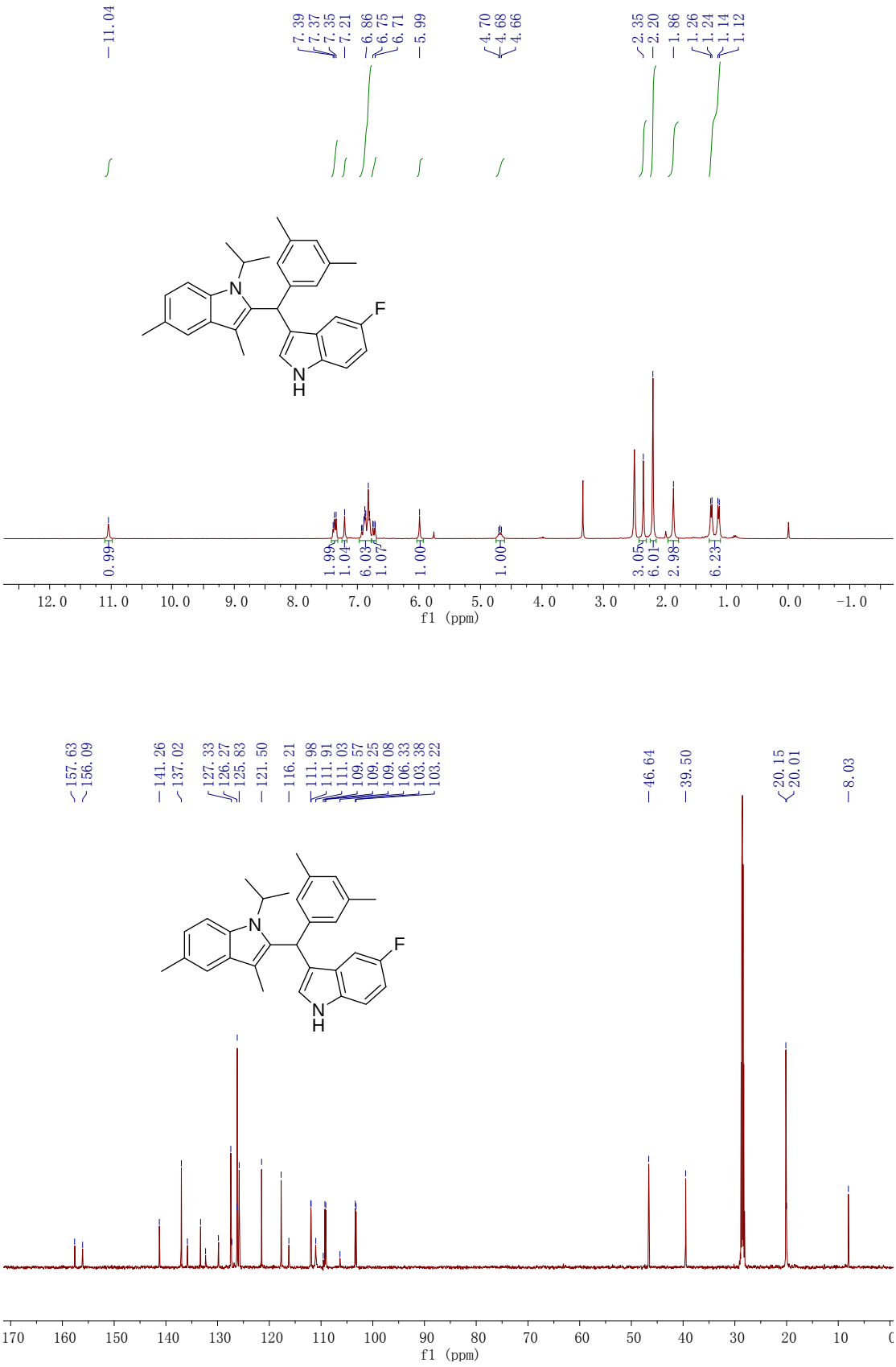


Figure S24. ^{1}H- (upper) and ^{13}C-NMR (bottom) of **10x**

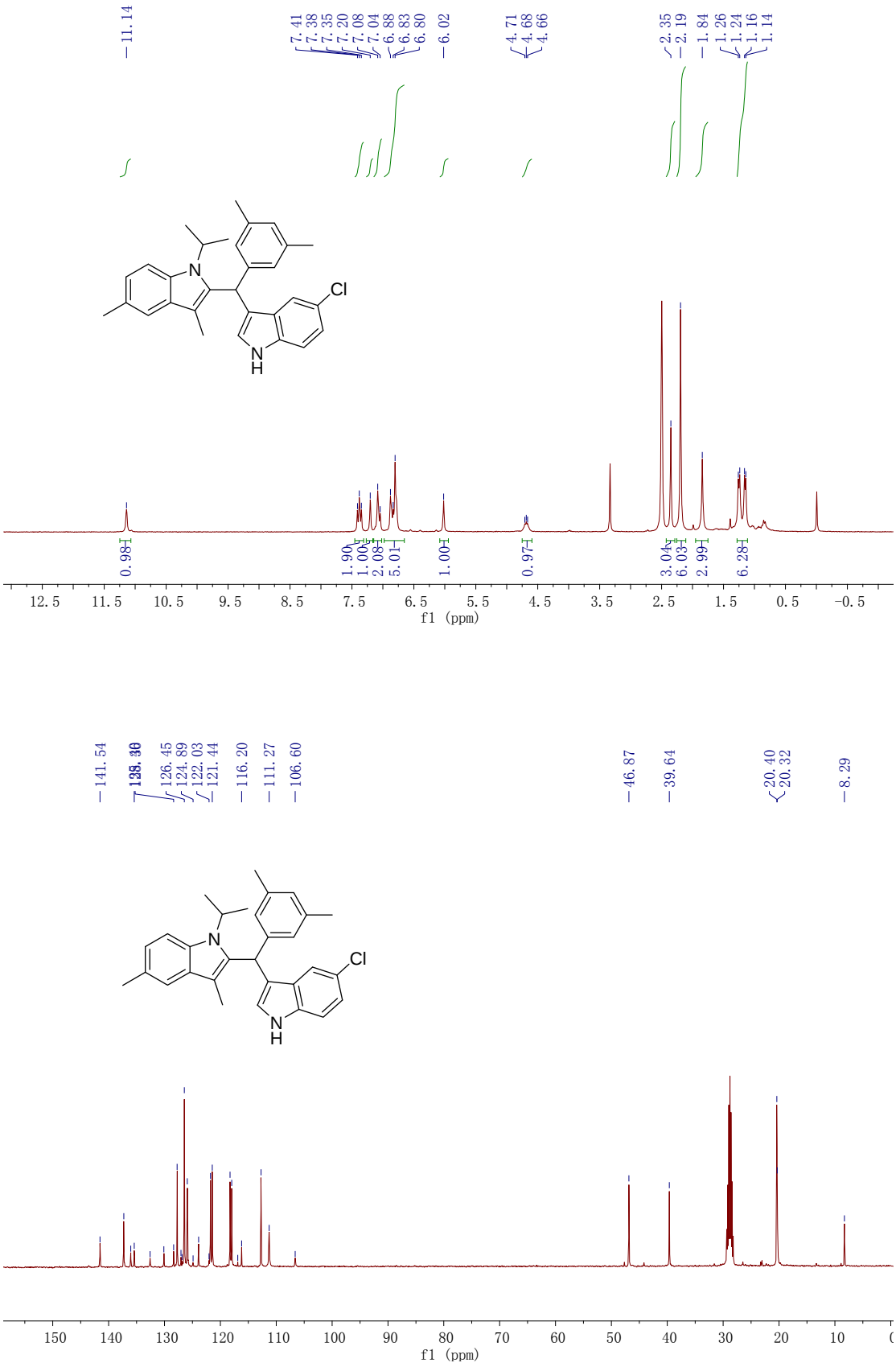


Figure S25. ^{1}H- (upper) and ^{13}C-NMR (bottom) of **10y**

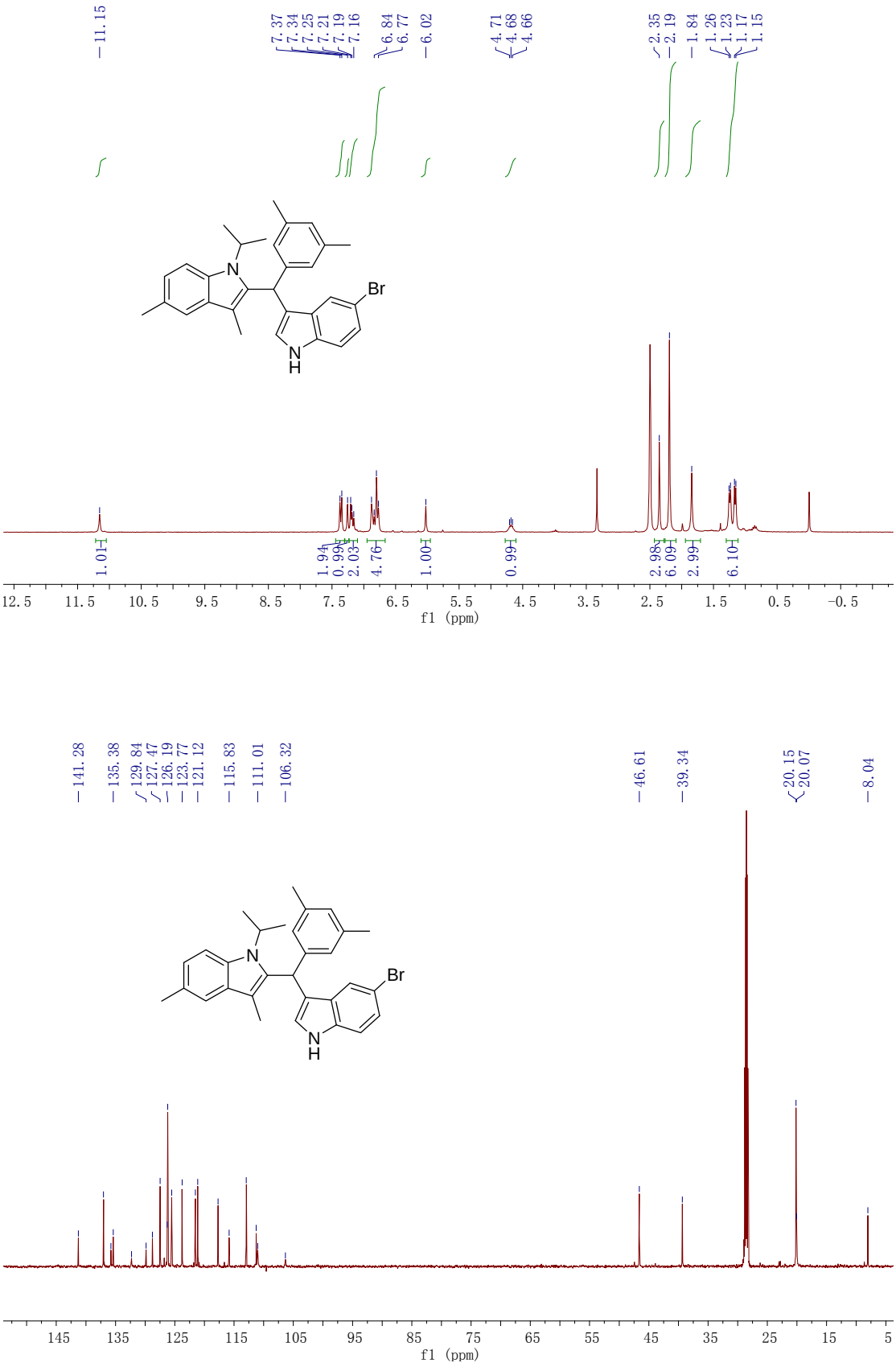


Figure S26. ^{1}H- (upper) and ^{13}C-NMR (bottom) of **10z**

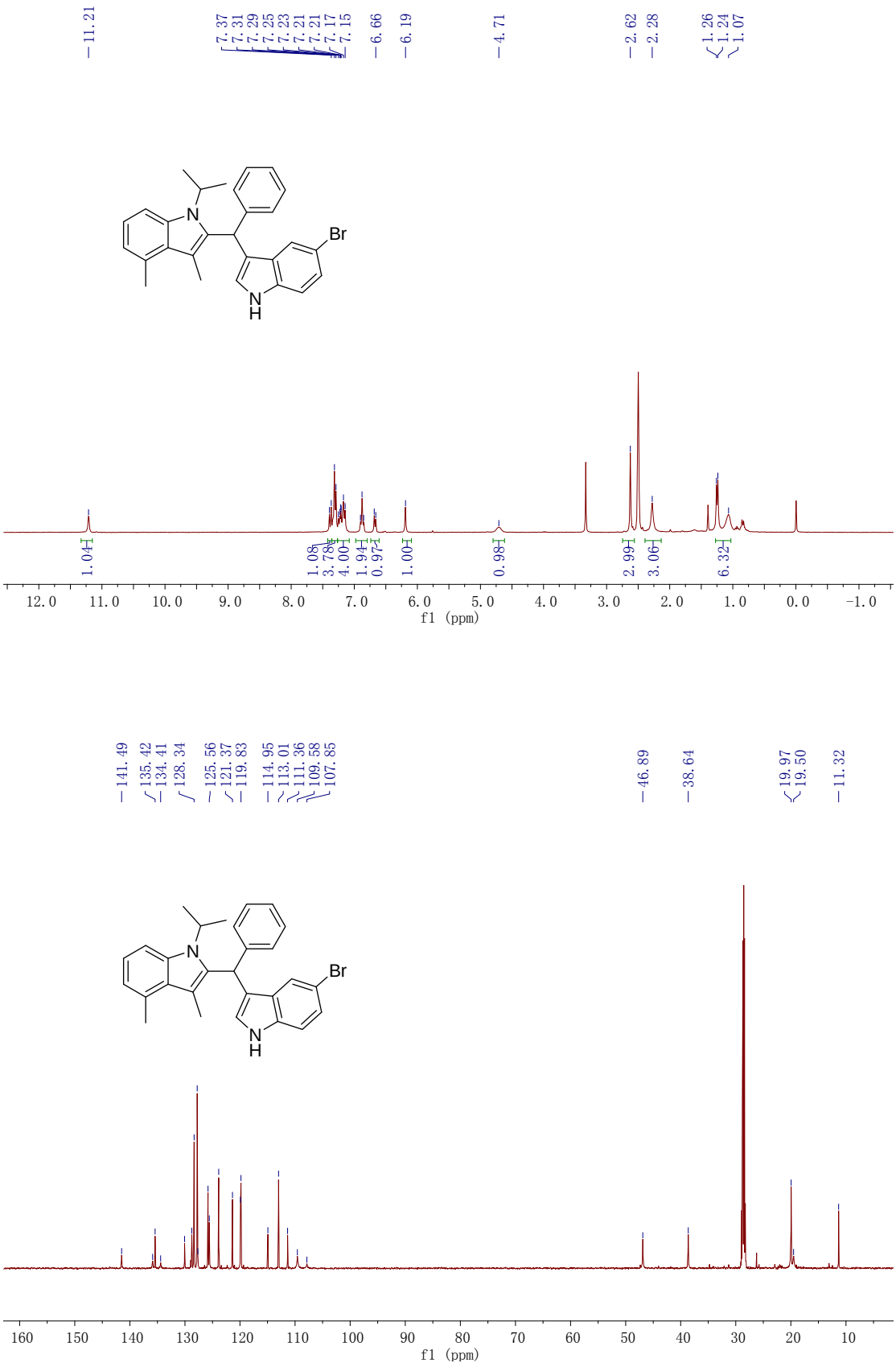


Figure S27. ^{1}H- (upper) and ^{13}C-NMR (bottom) of **10aa**

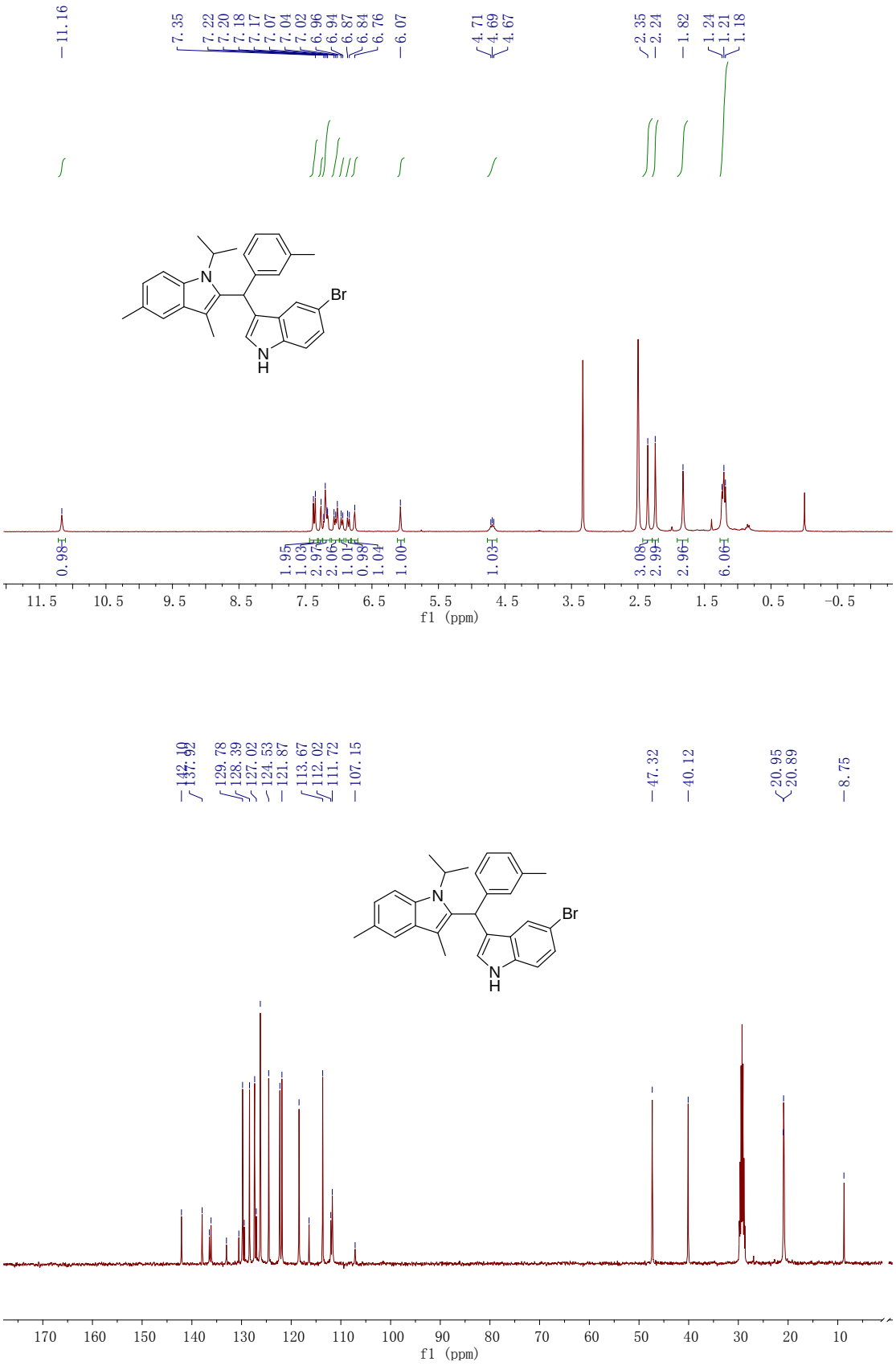
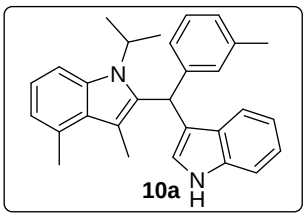
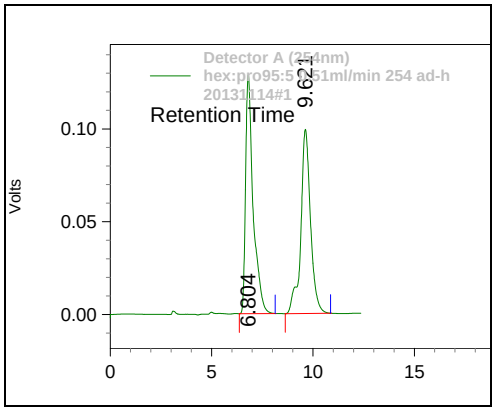


Figure S28. ^{1}H- (upper) and ^{13}C-NMR (bottom) of **10bb**

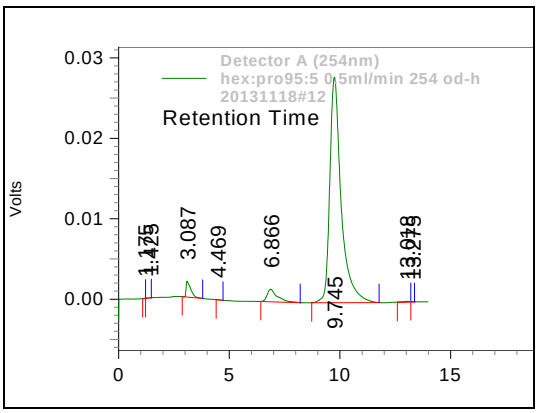
4. Copies of HPLC and integration area



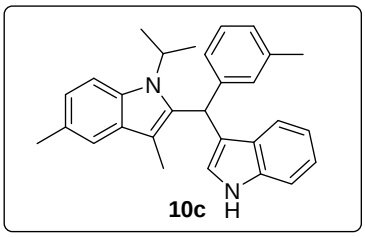
10a



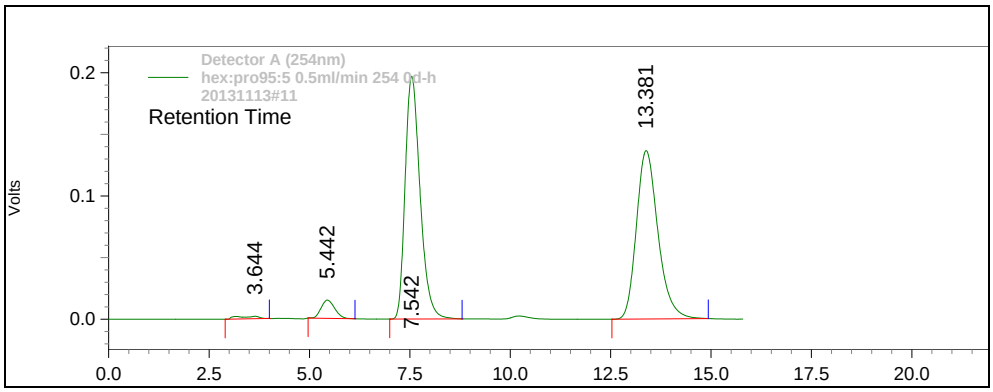
Peak	RT (min)	Area (V*sec)	Area %	Height (V)	Height %
1	6.804	3340329	50.24	127891	56.36
2	9.621	3307836	49.76	99039	43.64



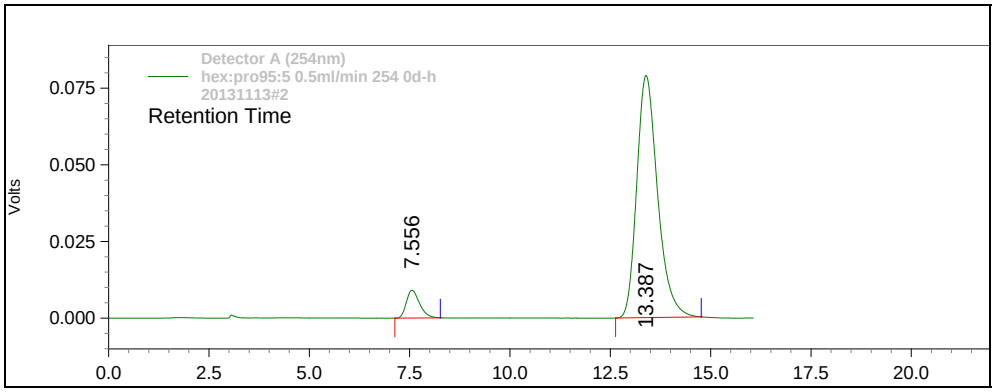
Peak	RT (min)	Area (V*sec)	Area %	Height (V)	Height %
1	6.866	44633	4.27	1547	5.23
2	9.745	1001268	95.73	28023	94.77



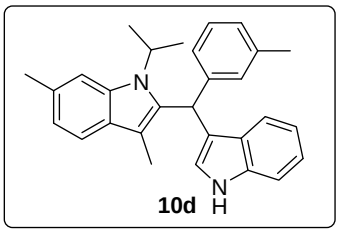
10c



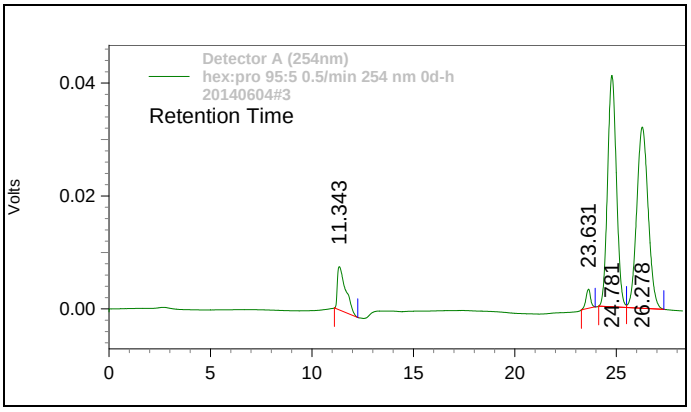
Peak	RT (min)	Area (V*sec)	Area %	Height (V)	Height %
1	7.542	5097802	49.74	196901	59.00
2	13.381	5150500	50.26	136778	41.00



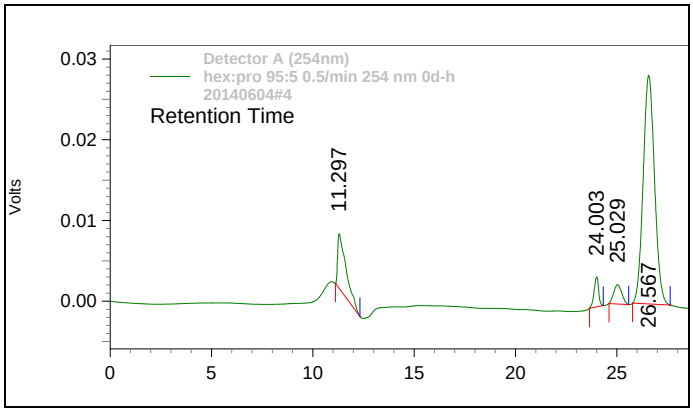
Peak	RT (min)	Area (V*sec)	Area %	Height (V)	Height %
1	7.556	203028	6.64	9048	10.28
2	13.387	2855285	93.36	78936	89.72



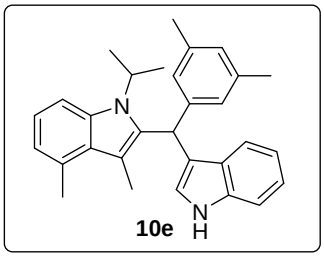
10d



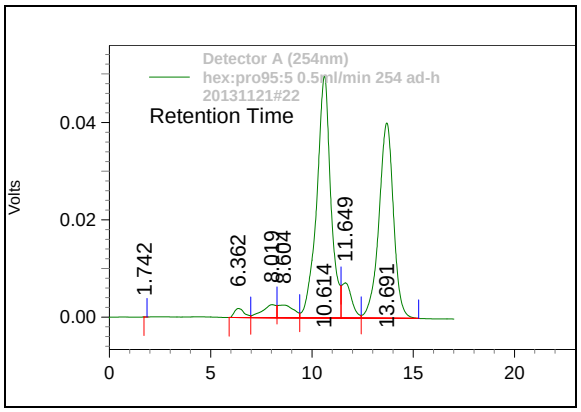
Peak	RT (min)	Area (V*sec)	Area %	Height (V)	Height %
1	24.781	1241689	49.68	40980	56.09
2	26.278	1257920	50.32	32075	43.91



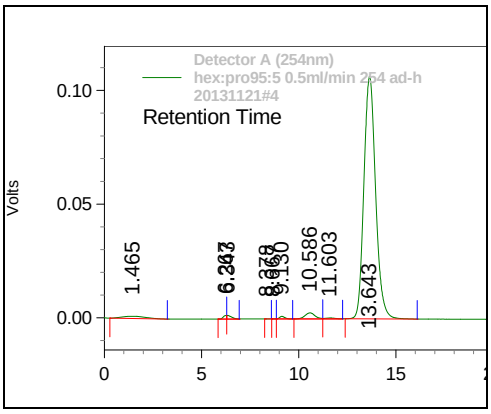
Peak	RT (min)	Area (V*sec)	Area %	Height (V)	Height %
1	25.029	66091	5.65	2375	7.74
2	26.567	1104281	94.35	28316	92.26



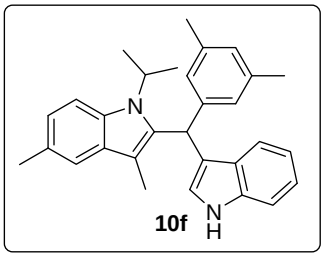
10e



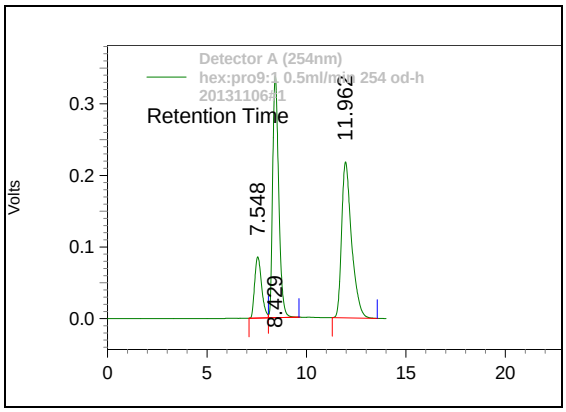
Peak	RT (min)	Area (V*sec)	Area %	Height (V)	Height %
1	10.614	2107905	51.16	49757	55.33
2	13.691	2012341	48.84	40173	44.67



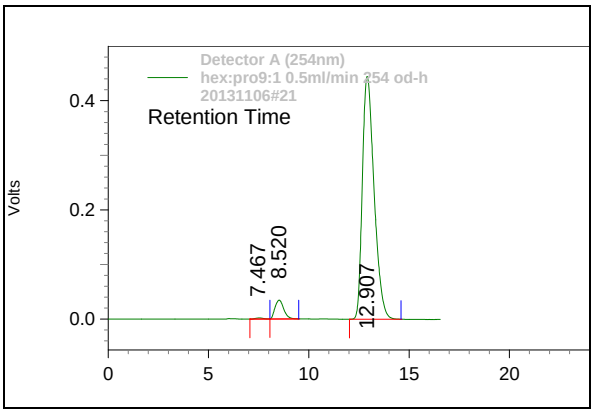
Peak	RT (min)	Area (V*sec)	Area %	Height (V)	Height %
1	10.586	93292	2.05	2650	2.43
2	13.643	4468305	97.95	106595	97.57



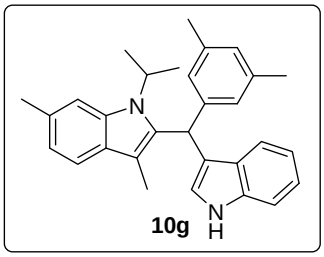
10f



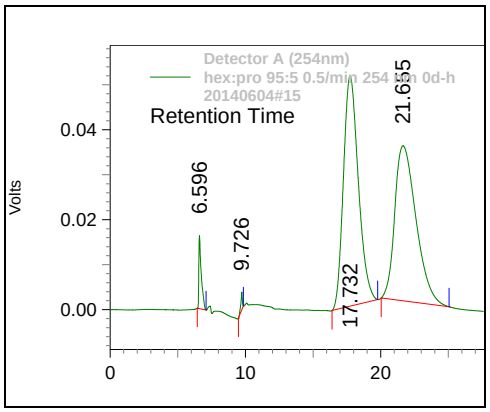
Peak	RT (min)	Area (V*sec)	Area %	Height (V)	Height %
1	8.429	7158409	49.28	337628	60.78
2	11.962	7367088	50.72	217823	39.22



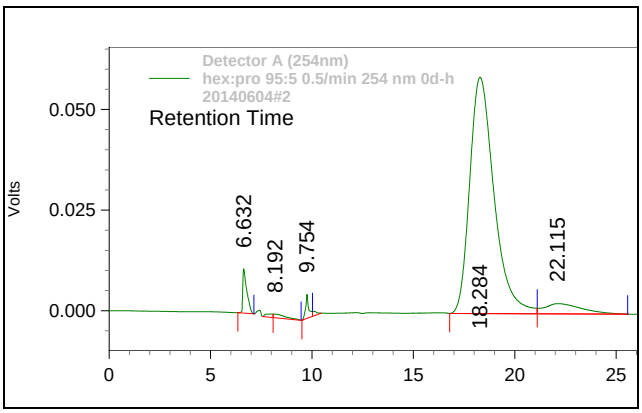
Peak	RT (min)	Area (V*sec)	Area %	Height (V)	Height %
1	8.520	1051394	5.48	34616	7.22
2	12.907	18127975	94.52	444844	92.78



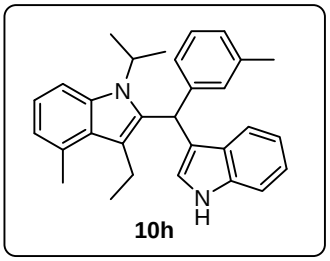
10g



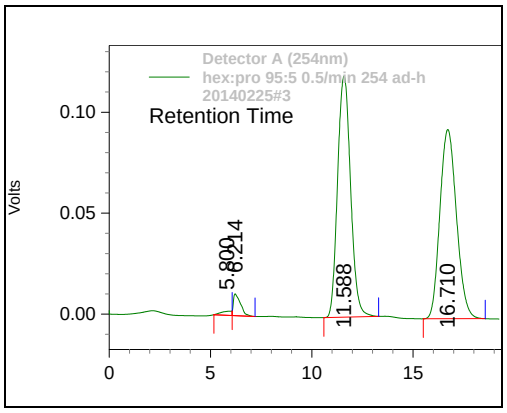
Peak	RT (min)	Area (V*sec)	Area %	Height (V)	Height %
1	17.732	3920907	50.30	51161	59.75
2	21.655	3873538	49.70	34461	40.25c



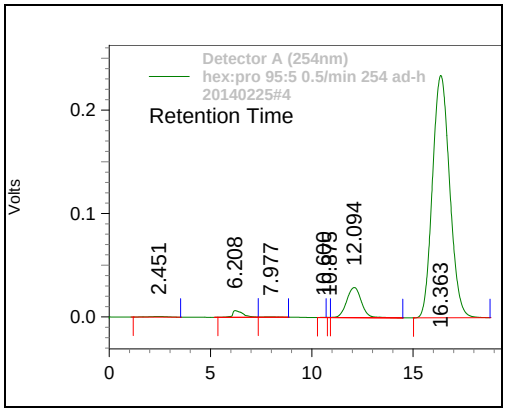
Peak	RT (min)	Area (V*sec)	Area %	Height (V)	Height %
1	18.284	4910811	95.60	58695	95.85
2	22.115	226004	4.40	2540	4.15



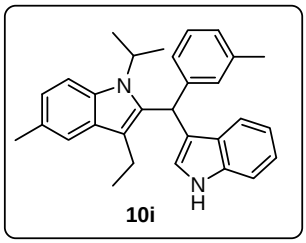
10h



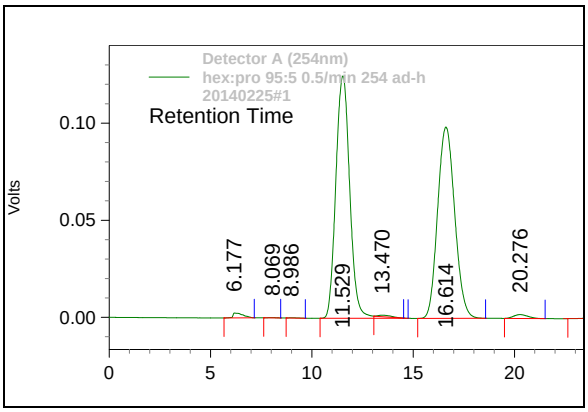
Peak	RT (min)	Area (V*sec)	Area %	Height (V)	Height %
1	11.588	5336205	50	119379	56.03
2	16.710	5334533	50	93698	43.97



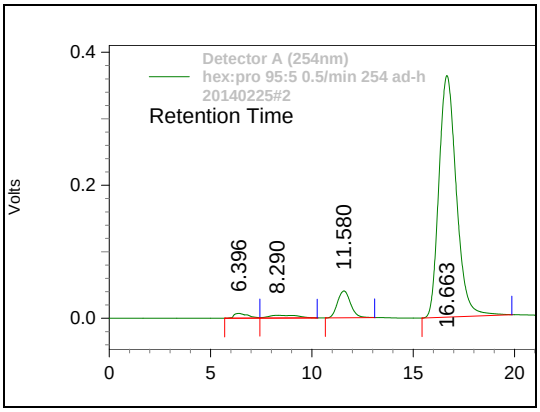
Peak	RT (min)	Area (V*sec)	Area %	Height (V)	Height %
1	12.093	1399710	9.21	28707	10.93
2	16.363	13797070	90.79	233965	89.07



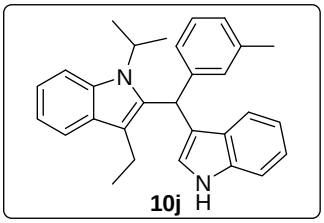
10i



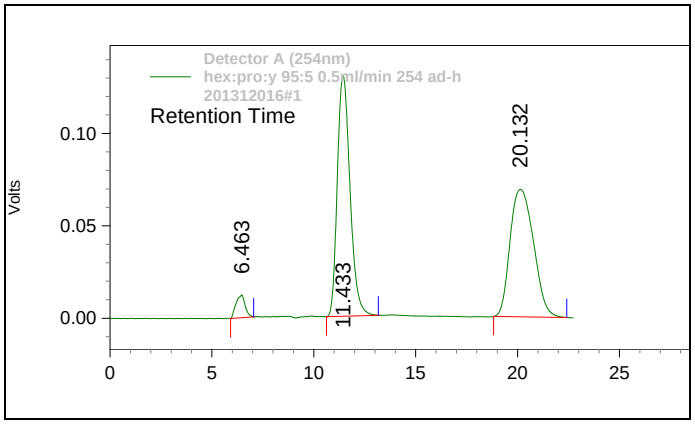
Peak	RT (min)	Area (V*sec)	Area %	Height (V)	Height %
1	11.529	5838800	50.29	124155	55.78
2	16.615	5759997	49.71	98471	44.22



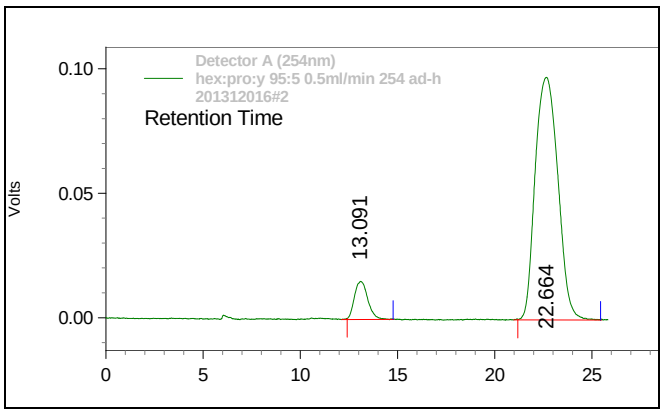
Peak	RT (min)	Area (V*sec)	Area %	Height (V)	Height %
1	11.580	1801671	7.67	40327	10.01
2	16.663	21699262	92.33	362831	89.99



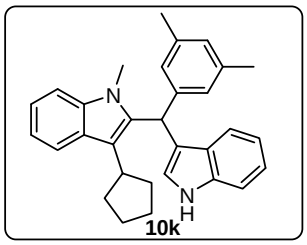
10j



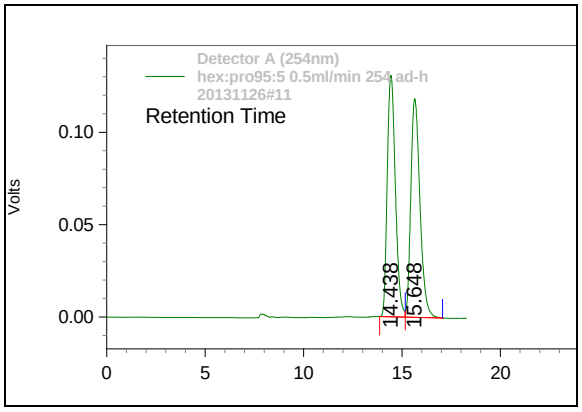
Peak	RT (min)	Area (V*sec)	Area %	Height (V)	Height %
1	11.433	5655267	50.53	130186	65.41
2	20.132	5536943	49.47	69042	34.59



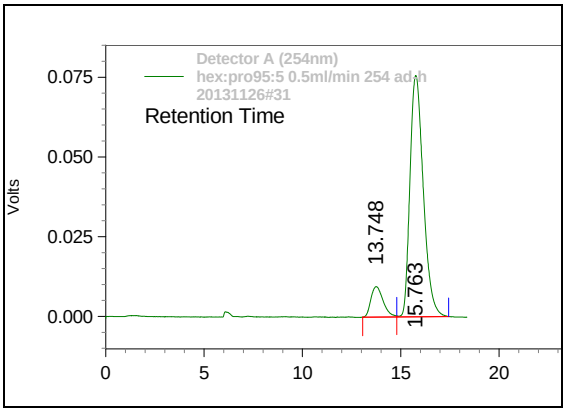
Peak	RT (min)	Area (V*sec)	Area %	Height (V)	Height %
1	13.091	726223	8.08	15324	13.58
2	22.664	7931997	91.92	97522	86.42



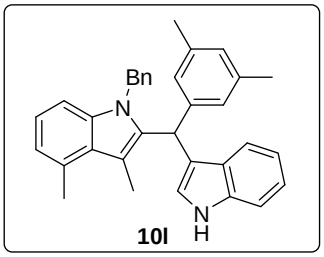
10k



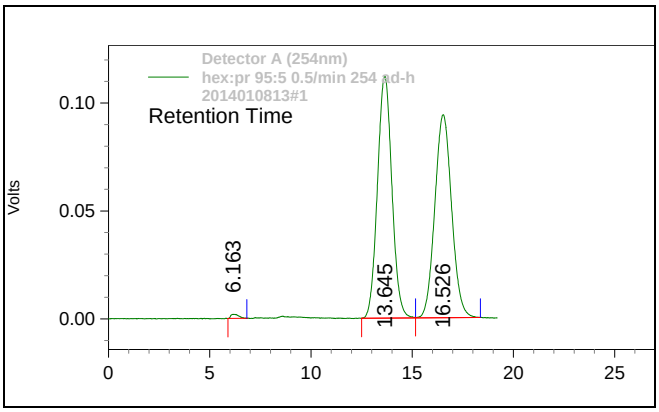
Peak	RT (min)	Area (V*sec)	Area %	Height (V)	Height %
1	14.438	3756953	49.50	130242	52.41
2	15.648	3832944	50.50	118286	47.59



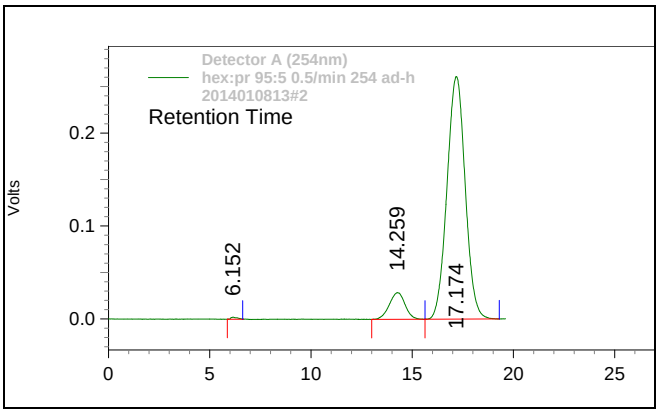
Peak	RT (min)	Area (V*sec)	Area %	Height (V)	Height %
1	13.748	404326	10.20	9561	11.23
2	15.763	3559065	89.80	75579	88.77



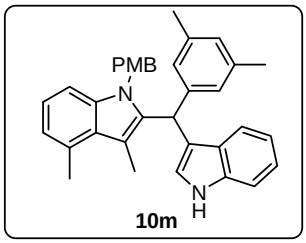
10l



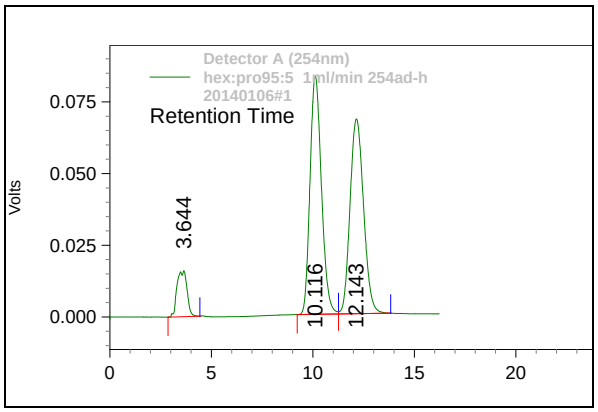
Peak	RT (min)	Area (V*sec)	Area %	Height (V)	Height %
1	13.645	5553044	50.45	112058	54.08
2	16.526	5433344	49.55	94040	45.92



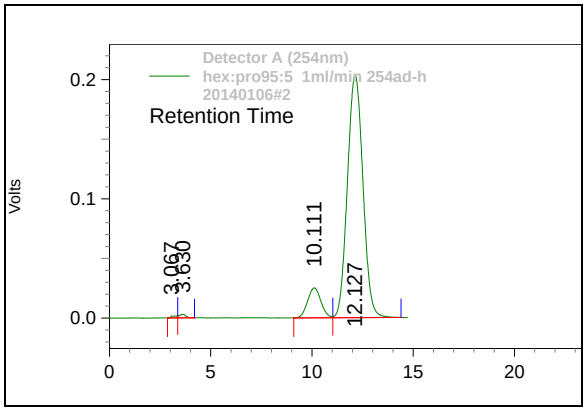
Peak	RT (min)	Area (V*sec)	Area %	Height (V)	Height %
1	14.259	1561685	8.63	28792	9.94
2	17.174	16527045	91.37	260758	90.06



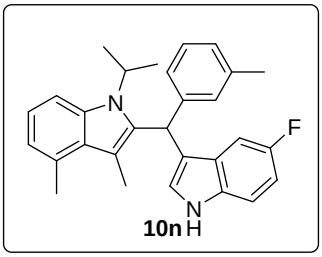
10m



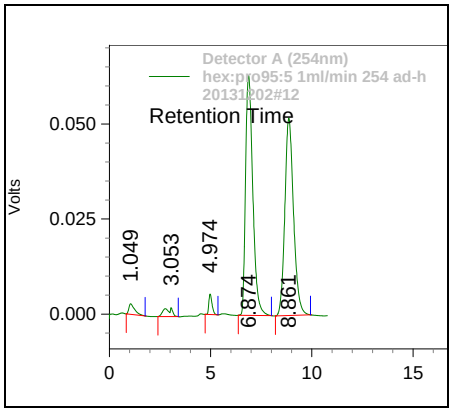
Peak	RT (min)	Area (V*sec)	Area %	Height (V)	Height %
1	10.116	3250995	50.77	83077	55.02
2	12.143	3152313	49.23	67906	44.98



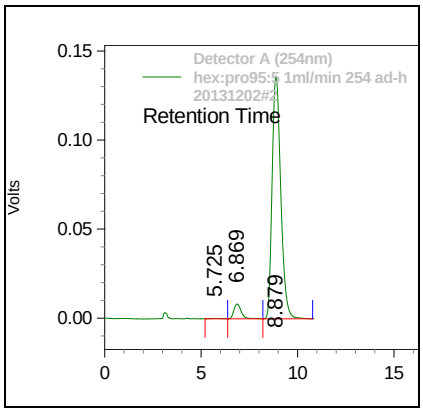
Peak	RT (min)	Area (V*sec)	Area %	Height (V)	Height %
1	10.111	1150780	9.52	25106	10.99
2	12.127	10933386	90.48	203310	89.01



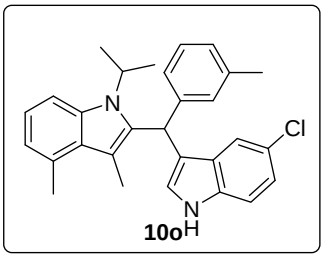
10n



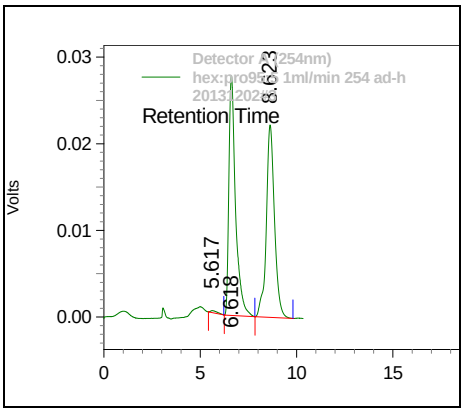
Peak	RT (min)	Area (V*sec)	Area %	Height (V)	Height %
1	6.874	1578044	50.09	63164	54.78
2	8.861	1568737	49.91	52.021	45.22



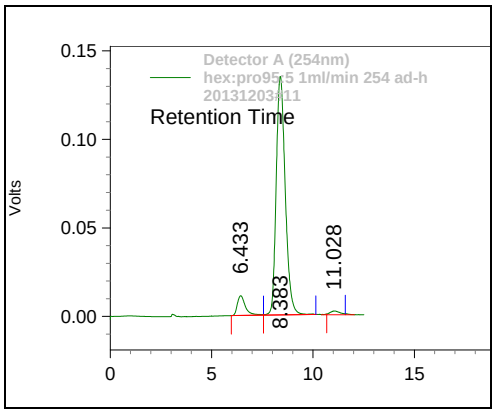
Peak	RT (min)	Area (V*sec)	Area %	Height (V)	Height %
1	6.869	222416	4.95	8280	5.72
2	8.879	4268602	95.05	136393	94.28



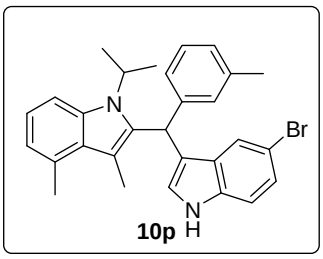
10o



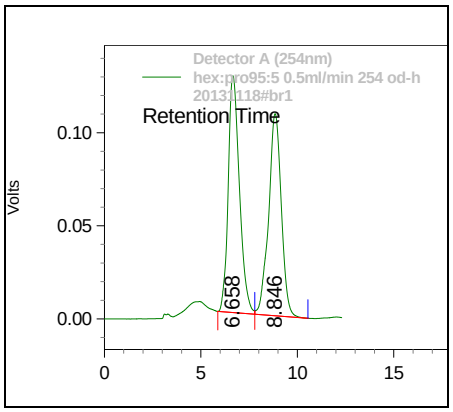
Peak	RT (min)	Area (V*sec)	Area %	Height (V)	Height %
1	6.618	666328	50.30	27634	55.40
2	8.623	657562	49.70	22206	44.60



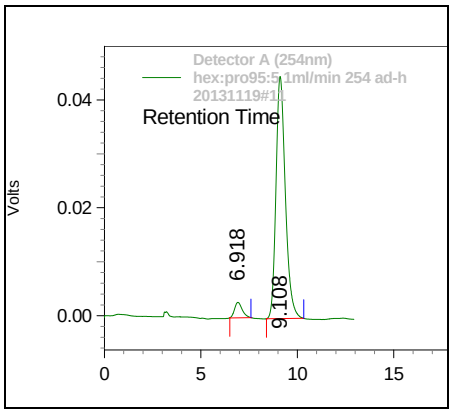
Peak	RT (min)	Area (V*sec)	Area %	Height (V)	Height %
1	6.433	283602	6.23	11114	7.62
2	8.383	4268602	93.77	134679	92.38



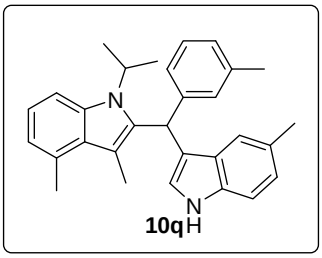
10p



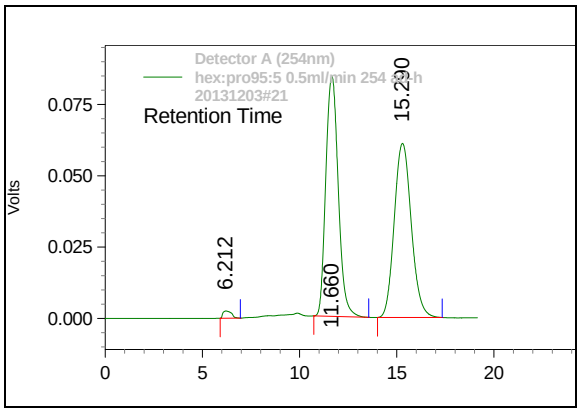
Peak	RT (min)	Area (V*sec)	Area %	Height (V)	Height %
1	6.658	5173634	50.96	127083	53.93
2	8.846	4978259	49.04	108573	46.07



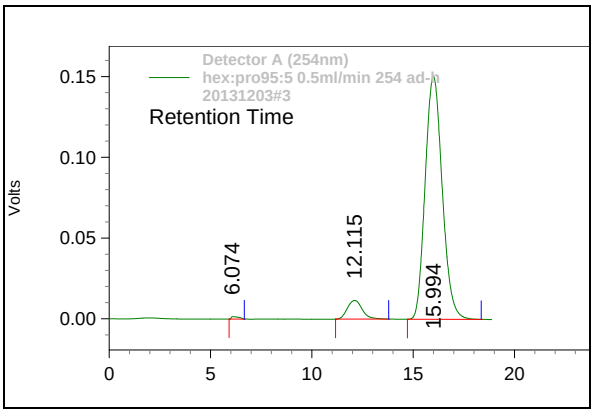
Peak	RT (min)	Area (V*sec)	Area %	Height (V)	Height %
1	6.918	83532	5.20	2908	6.08
2	9.108	1523685	94.80	44893	93.92



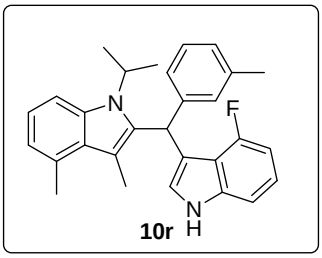
10q



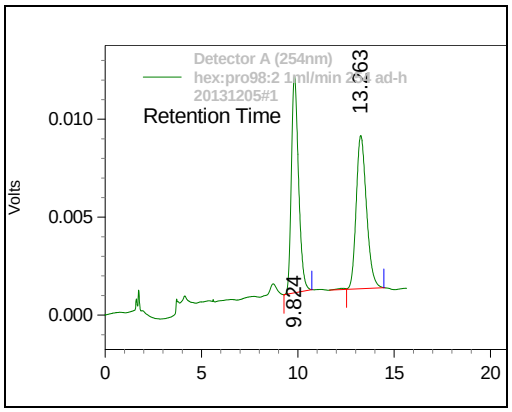
Peak	RT (min)	Area (V*sec)	Area %	Height (V)	Height %
1	11.660	3764516	50.27	84262	57.99
2	15.290	3723998	49.73	61032	42.01



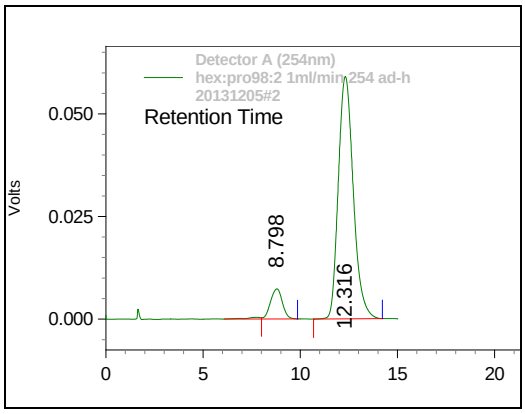
Peak	RT (min)	Area (V*sec)	Area %	Height (V)	Height %
1	12.115	592047	6.30	11585	7.15
2	15.994	8808823	93.70	150346	92.85



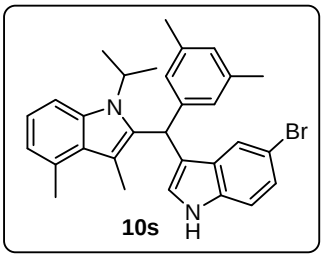
10r



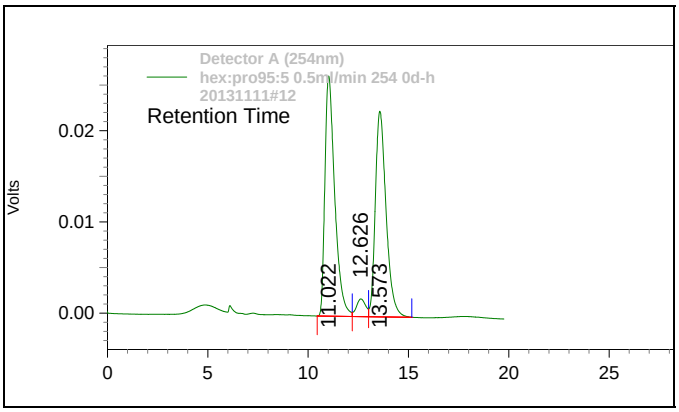
Peak	RT (min)	Area (V*sec)	Area %	Height (V)	Height %
1	9.824	286322	49.63	11070	58.58
2	13.263	290558	50.37	7828	41.42



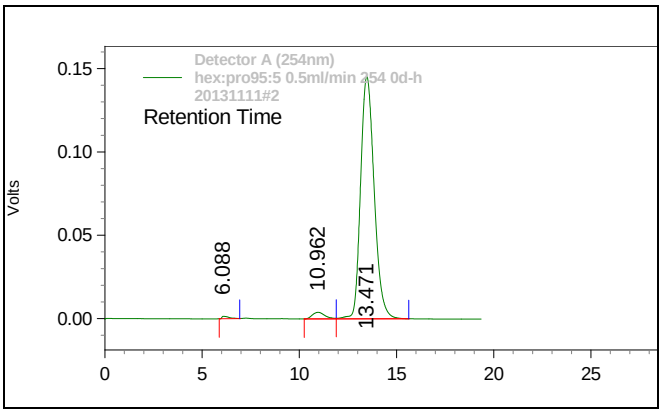
Peak	RT (min)	Area (V*sec)	Area %	Height (V)	Height %
1	8.798	308107	8.49	7312	11.02
2	12.316	3196123	91.51	59063	88.98



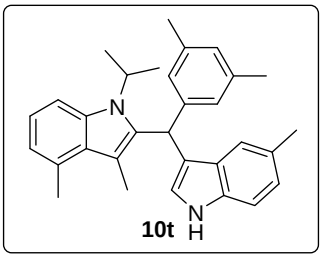
10s



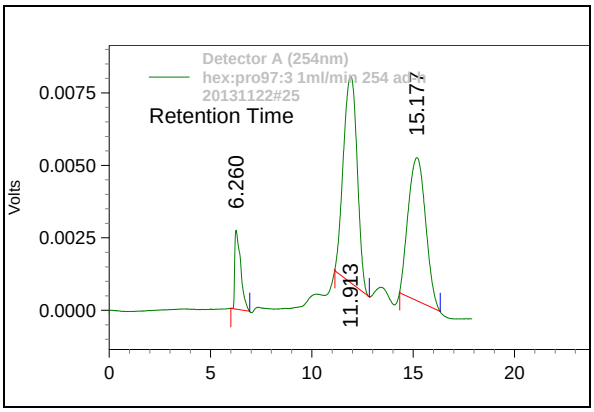
Peak	RT (min)	Area (V*sec)	Area %	Height (V)	Height %
1	11.022	898573	51.59	26318	53.87
2	13.573	843023	48.41	22537	46.13



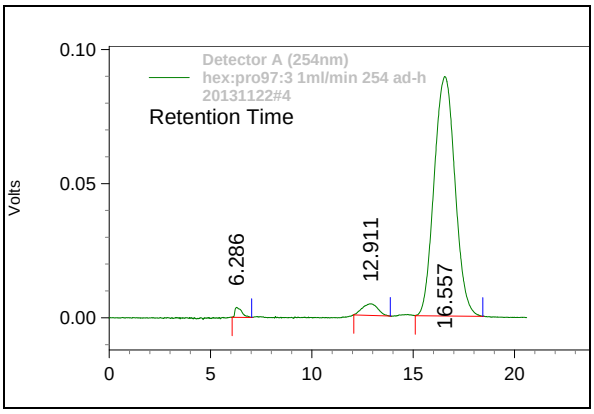
Peak	RT (min)	Area (V*sec)	Area %	Height (V)	Height %
1	10.962	175861	2.43	3940	2.64
2	13.471	7067869	97.57	145388	97.36



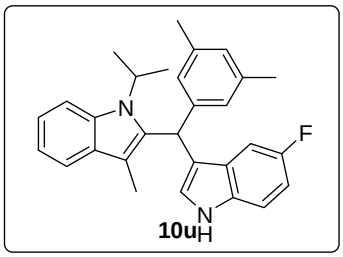
10t



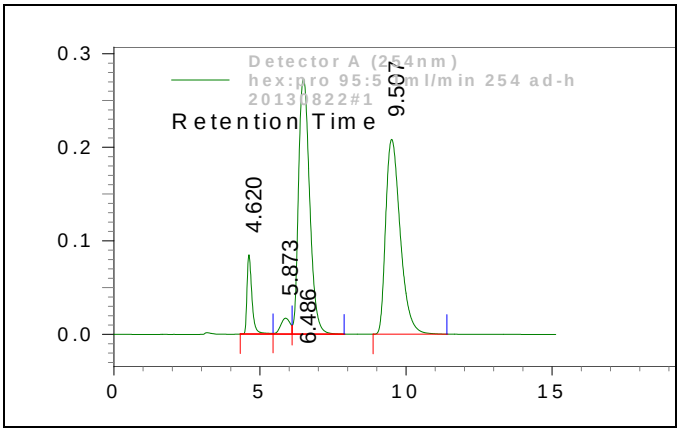
Peak	RT (min)	Area (V*sec)	Area %	Height (V)	Height %
1	11.913	316025	51.78	7128	59.10
2	15.177	294250	48.22	4933	40.90



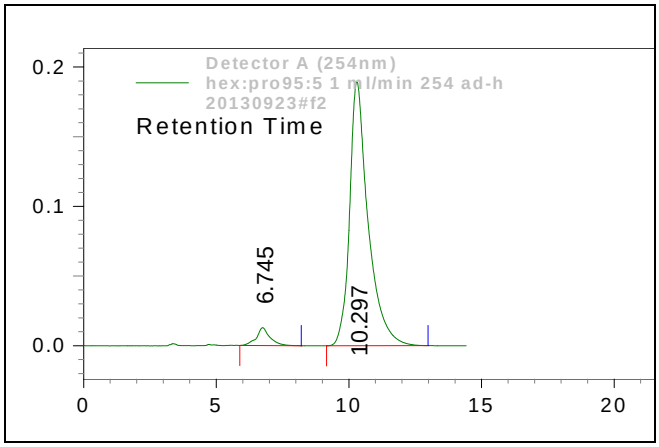
Peak	RT (min)	Area (V*sec)	Area %	Height (V)	Height %
1	12.911	232210	3.51	5251	5.52
2	16.557	6380734	96.49	89810	94.48



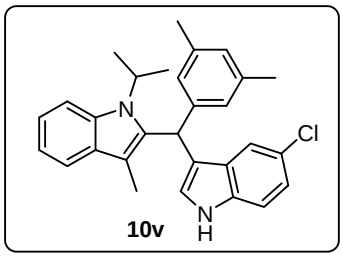
10u



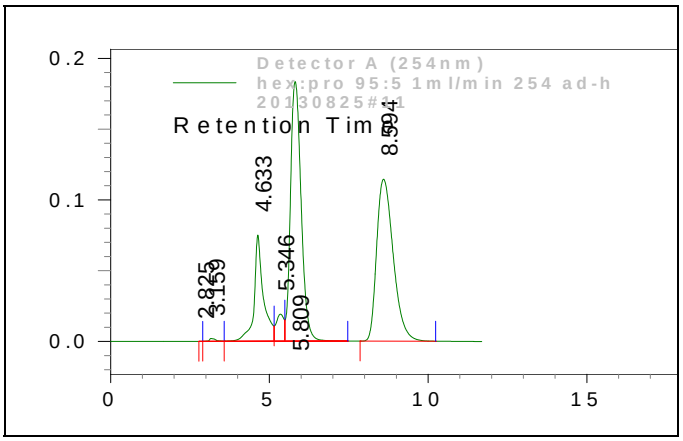
Peak	RT (min)	Area (V*sec)	Area %	Height (V)	Height %
1	6.486	7233718	50.03	272810	56.69
2	9.507	7224270	49.97	208406	43.31



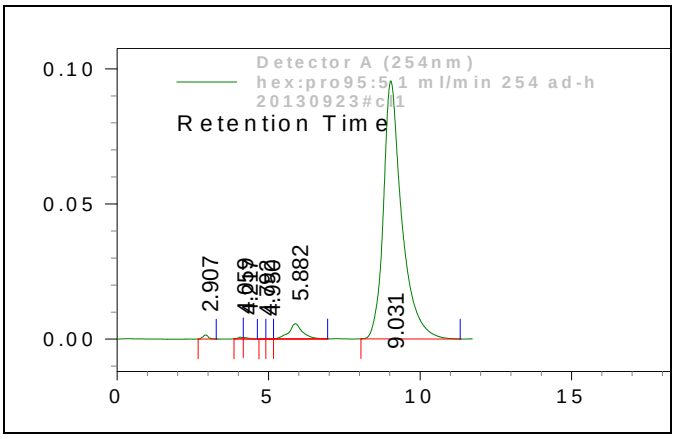
Peak	RT (min)	Area (V*sec)	Area %	Height (V)	Height %
1	6.745	450587	4.66	12780	6.32
2	10.297	9213258	95.34	189452	93.68



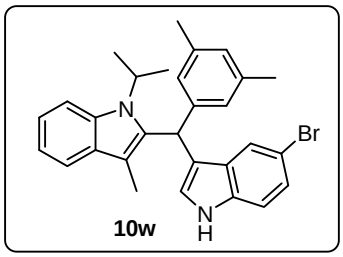
10v

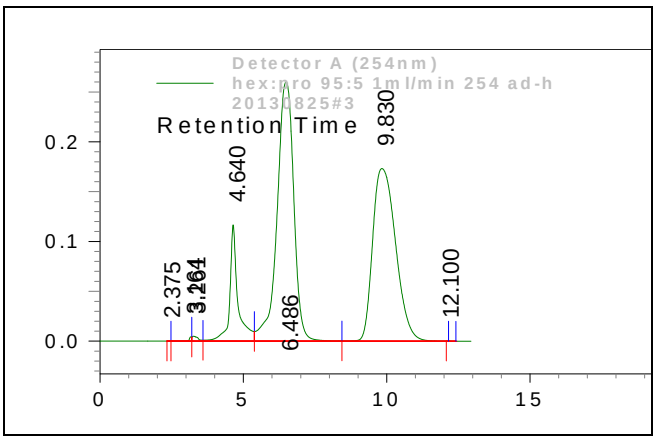


Peak	RT (min)	Area (V*sec)	Area %	Height (V)	Height %
1	5.809	4279950	50.73	183428	61.58
2	8.594	4156263	49.27	114418	38.42

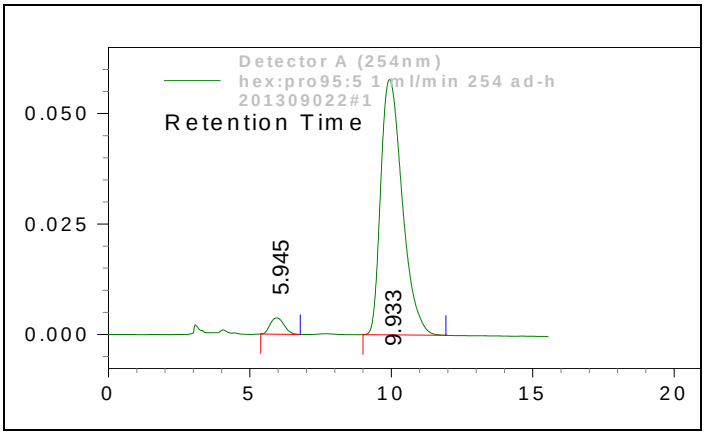


Peak	RT (min)	Area (V*sec)	Area %	Height (V)	Height %
1	5.882	172245	4.10	5581	5.52
2	9.031	40283389	95.90	95507	94.48

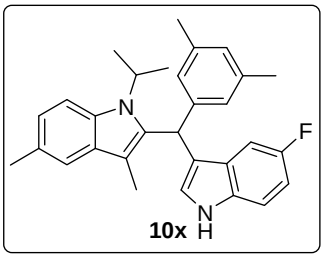




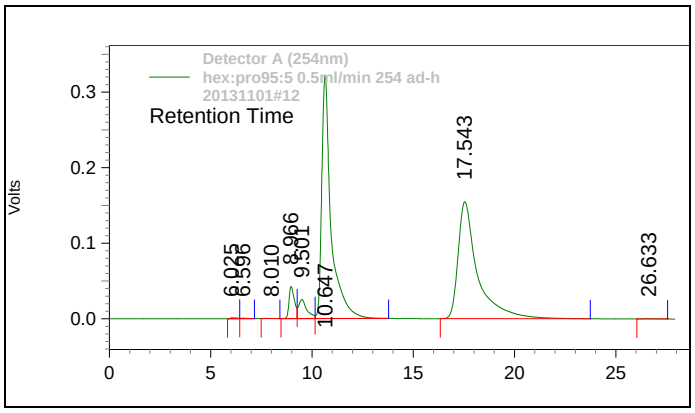
Peak	RT (min)	Area (V*sec)	Area %	Height (V)	Height %
1	6.486	10561589	51.45	260000	60.00
2	9.830	9964604	48.55	173224	40.00



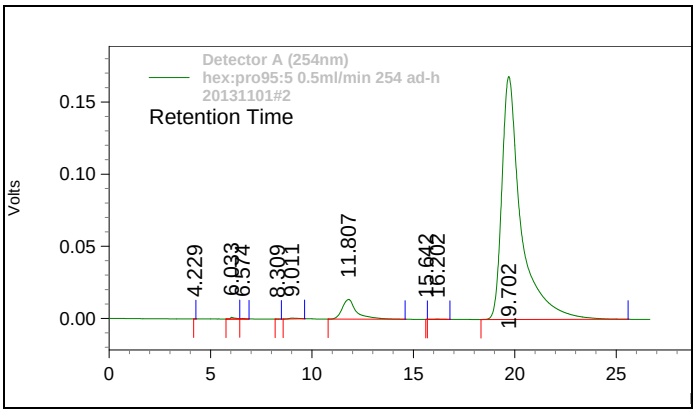
Peak	RT (min)	Area (V*sec)	Area %	Height (V)	Height %
1	5.945	125563	3.94	3658	5.96
2	9.933	3060191	96.06	57772	94.04



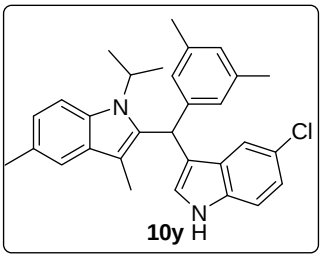
10x



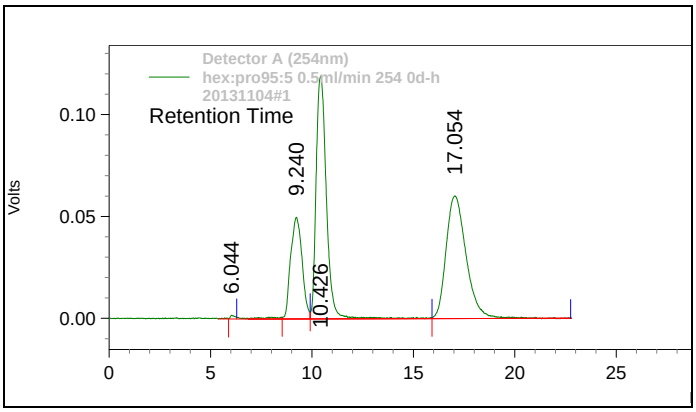
Peak	RT (min)	Area (V*sec)	Area %	Height (V)	Height %
1	10.467	10302661	49.99	320844	67.46
2	17.543	10306443	50.01	154795	32.54



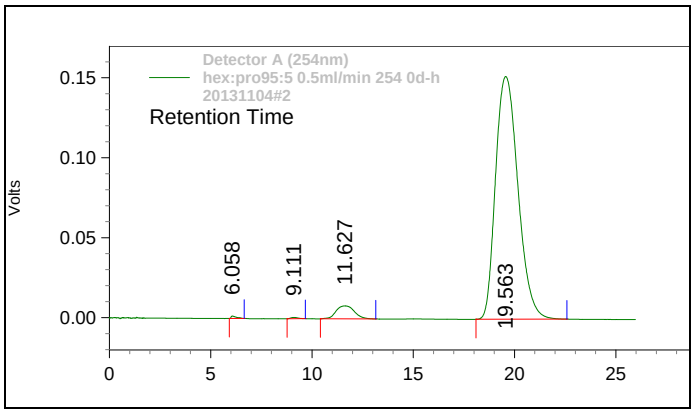
Peak	RT (min)	Area (V*sec)	Area %	Height (V)	Height %
1	11.807	675106	5.75	13657	7.50
2	19.702	11056829	94.25	168427	92.50



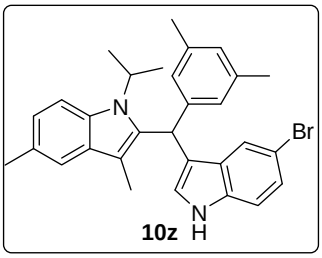
10y



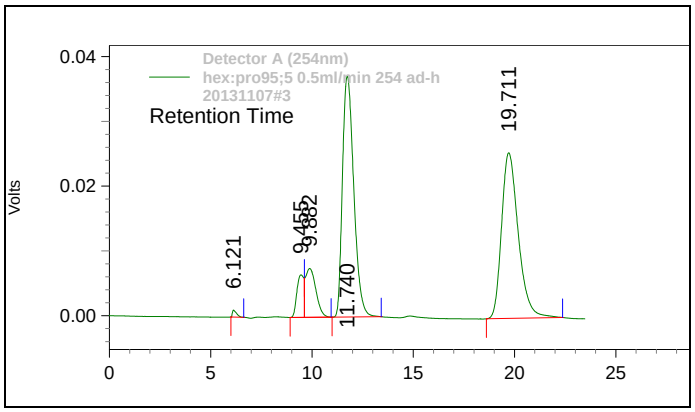
Peak	RT (min)	Area (V*sec)	Area %	Height (V)	Height %
1	10.426	4136150	50.48	119179	66.44
2	17.054	4057745	49.52	60205	33.56



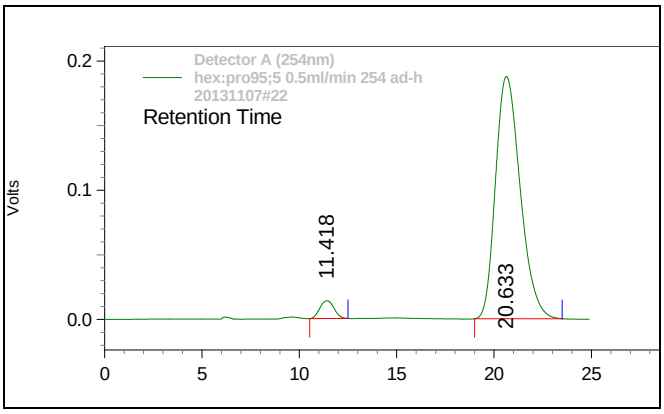
Peak	RT (min)	Area (V*sec)	Area %	Height (V)	Height %
1	11.627	509765	4.11	8086	5.06
2	19.563	11697732	95.89	151832	94.94



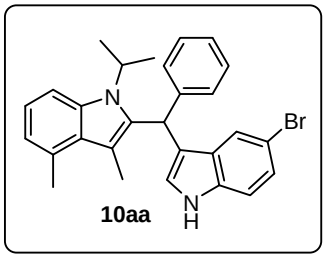
10z



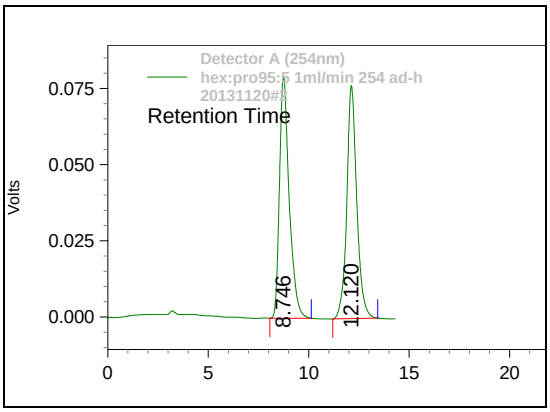
Peak	RT (min)	Area (V*sec)	Area %	Height (V)	Height %
1	11.740	1446553	49.59	37224	59.27
2	19.711	1470709	50.41	25581	40.73



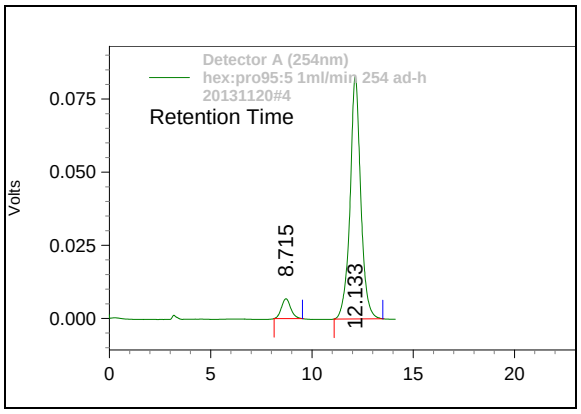
Peak	RT (min)	Area (V*sec)	Area %	Height (V)	Height %
1	11.418	697866	4.05	13740	6.83
2	20.633	16540791	95.95	187359	93.17



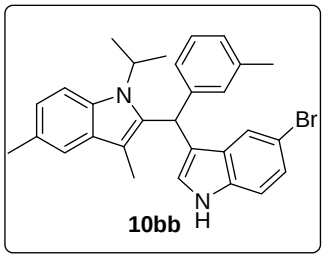
10aa



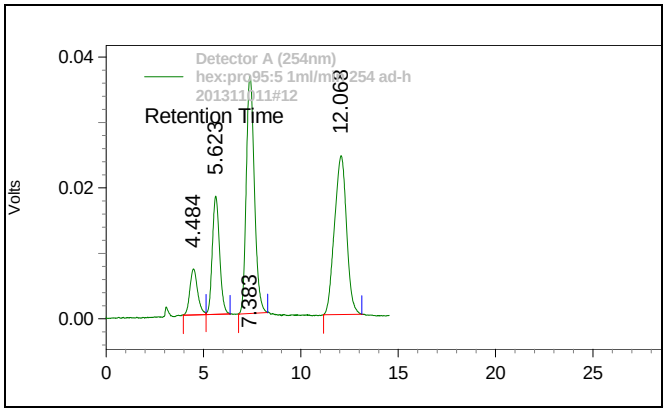
Peak	RT (min)	Area (V*sec)	Area %	Height (V)	Height %
1	8.746	2678658	50.22	79461	50.98
2	12.120	2655137	49.78	76421	49.02



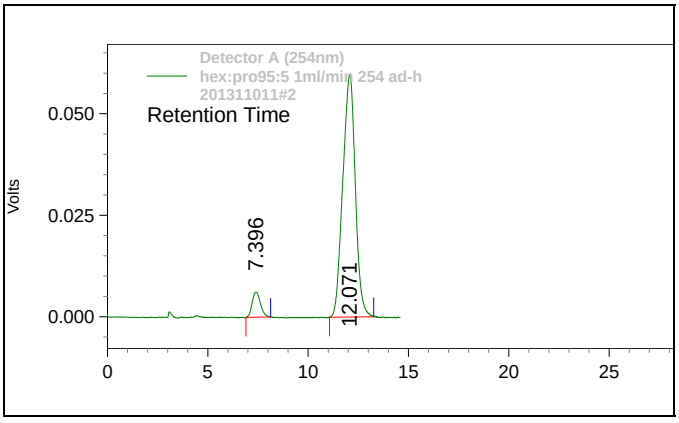
Peak	RT (min)	Area (V*sec)	Area %	Height (V)	Height %
1	8.715	288623	6.89	8120	7.42
2	12.133	3901444	93.11	101276	92.58



10bb



Peak	RT (min)	Area (V*sec)	Area %	Height (V)	Height %
1	7.383	1067932	50.58	36472	60.05
2	12.068	1043341	49.42	24263	39.95



Peak	RT (min)	Area (V*sec)	Area %	Height (V)	Height %
1	7.396	177703	6.42	6185	9.42
2	12.071	2589930	93.58	59507	90.58