Electronic Supplementary Material (ESI) for ChemComm.

Exploration of A KI-Catalyzed Oxidation System for Direct Construction of Bispyrrolidino[2,3-b]indolines and Total Synthesis of (+)-WIN 64821

Si-Kai Chen,[†,§] Ju-Song Yang,[†,§] Kun-Long Dai,[†] Fu-Min Zhang,*[,†] Xiao-Ming Zhang,*[,†] and Yong-Qiang Tu.*[,†,‡]

[†]State Key Laboratory of Applied Organic Chemistry and College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, P.R. China

[‡]School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, P.R. China

E-mail: tuyq@lzu.edu.cn; tuyq@sjtu.edu.cn; zhangfm@lzu.edu.cn; zhangxiaom@lzu.edu.cn.

Contents

1. General information

In addition to commercially available extra dry solvents, the solvents used in this work were purified using standard operation and distilled prior to use. Dichloromethane (DCM or CH_2Cl_2), trichloromethane ($CHCl_3$) and 1,2-dichloroethane (DCE) were distilled from CaH_2. Tetrahydrofuran (THF), diethyl ether (Et_2O), benzene and toluene were distilled from sodium. Acetonitrile (CH_3CN) was distilled from phosphorus pentoxide.

All commercial reagents were used without additional purification unless special stated. Air or moisture sensitive operations were conducted under argon atmosphere using oven-dried glassware (150℃).

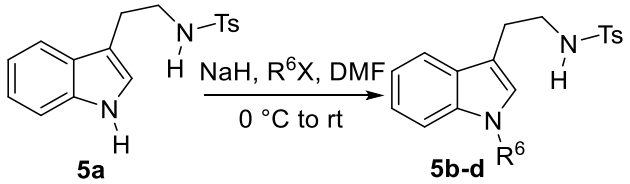
All reactions were monitored by thin-layer chromatography (TLC) visualized by ultraviolet light (254 nm) and the column chromatography purifications of organic compounds were performed via silica gel (200~300 mesh) unless special stated.

^{1}H NMR, **^{13}C NMR** and **^{19}F NMR** spectra were recorded on Bruker AM-600, Bruker AM-400, Varian Mercury-600 or *J*EOL *J*NM-ECS-400. Chemical shift (δ) were quoted in ppm relative to tetramethylsilane or residual protio solvent as internal standard, multiplicities are as indicated: s= singley, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Infrared (**IR**) spectra were recorded on a Nicolet FY-170SX spectrometer. High-resolution mass spectral analysis (**HRMS**) data were determined on a Thermo Scientific Orbitrap Elite spectrometer. **Optical rotations** were detected on RUDOLPH A21202-*J* APTV/GW. **X-ray** diffraction data were collected on Agilent SuperNova Eos diffractometer. Melting points (**m.p.**) were collected on SGW X-4B Micromelting point instrument. High performance liquid chromatography (**HPLC**) analyses were performed using Waters e2695 Separations and 2998 PDA Detector instruments.

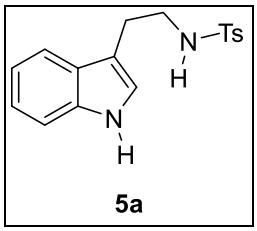
2. Preparations of tryptamine and tryptophol analogues

Tryptamine and tryptophol analogues used in this research are known compounds except **5e**, **5h**, **5g**, **5l**. The syntheses and characterizations of these compounds are all described below:

2.1 Preparation of N_a-substituted tryptamines

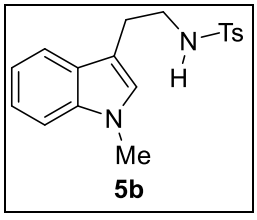


N-(2-(1H-indol-3-yl)ethyl)-4-methylbenzenesulfonamide, **5a**:



Compound **5a** was prepared according to literature's procedure[1] as a pale yellow solid. **m.p.** 99-102℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.24 (s, 1H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 7.6 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 1H), 7.14-7.10 (m, 3H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.82 (d, *J* = 2.4 Hz, 1H), 4.83 (t, *J* = 6.0 Hz, 1H), 3.17 (q, *J* = 6.4 Hz, 2H), 2.83 (t, *J* = 6.8 Hz, 2H), 2.31 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 143.20, 136.35, 136.20, 129.48, 126.75, 126.71, 122.65, 121.81, 119.10, 118.22, 111.31, 111.12, 43.01, 25.24, 21.30; **IR** (KBr) 3406, 3282, 1597, 1316, 1155, 816, 744, 549 cm^{-1}; **HRMS** (ESI) calcd for $[M+Na]^+$ $C_{17}H_{18}N_2NaO_2S$, m/z: 337.0987, found: 337.0973.

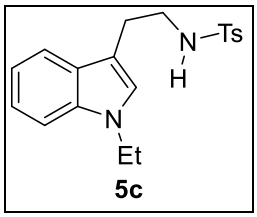
4-methyl-*N*-(2-(1-methyl-1H-indol-3-yl)ethyl)benzenesulfonamide, **5b**:



To a stirred solution of **5a** (2.35g, 7.5 mmol, 1.0 equiv) in DMF (35 mL) at 0℃ was added NaH (0.90 g, 22.5 mmol, 3.0 equiv, 60% dispersion in mineral oil) in portions. The system was reacted at room temperature for 0.5 h, and then cooled to 0℃. A solution of MeI (0.50 mL, 8.25 mmol, 1.1 equiv) in DMF (35 mL) was subsequently added to the reaction mixture dropwise at the same temperature and the reaction mixture was stirred at room temperature for additional 2 h. The resulted reaction system

was carefully quenched with saturated NH_4Cl and extracted with EtOAc (100 mL x 3). The organic layer was washed with water (6 times) and brine, then dried over Na_2SO_4, filtered, and concentrated by vacuo. The residue was purified by flash column chromatography (petrol ether: EtOAc = 8:1 to 6:1) to afford **5b** (2.17 g, 85 % yield) as a white solid. **m.p**. 81-83℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.21-7.10 (m, 4H), 7.00 (t, *J* = 7.2 Hz, 1H), 6.73 (s, 1H), 4.94 (t, *J* = 4.0 Hz, 1H), 3.59 (s, 3H), 3.19 (q, *J* = 6.8 Hz, 2H), 2.84 (t, *J* = 6.8 Hz, 2H), 2.31 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 142.95, 136.85, 136.64, 129.35, 127.18, 127.08, 126.75, 121.43, 118.64, 118.38, 109.86, 109.11, 43.15, 32.28, 25.15, 21.23; **IR** (KBr) 3288, 2928, 1598, 1326, 1159, 815, 740, 550 cm^{-1}; **HRMS** (ESI) calcd for $[M+Na]^+$ $C_{18}H_{20}N_2NaO_2S$, m/z: 351.1143, found: 351.1146.

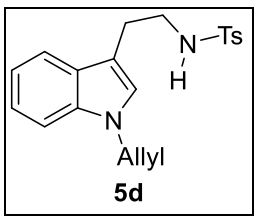
N-(2-(1-ethyl-1H-indol-3-yl)ethyl)-4-methylbenzenesulfonamide, **5c**:



5c

Compound **5c** (2.40 g, 93% yield) was synthesized from **5a** (2.35 g, 7.5 mmol) and EtBr (0.62 mL, 8.25 mmol) as a light yellow oil following the synthetic procedure of **5b**, purified by flash chromatography (petrol ether: EtOAc = 10:1 to 6:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.27 (d, *J* = 8.4 Hz, 1H), 7.20-7.16 (m, 3H), 7.02 (t, *J* = 7.4 Hz, 1H), 6.85 (s, 1H), 4.83 (m, 1H), 4.05 (q, *J* = 7.2 Hz, 2H), 3.24-3.20 (m, 2H), 2.89 (t, *J* = 6.8 Hz, 2H), 2.36 (s, 3H), 1.38 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 143.10, 136.77, 136.04, 129.48, 127.41, 126.90, 125.37, 121.50, 118.79, 118.62, 110.03, 109.30, 43.18, 40.65, 25.37, 21.37, 15.29; **IR** (KBr) 3285, 2931, 1598, 1327, 1159, 816, 742, 551 cm^{-1}; **HRMS** (ESI) calcd for $[M+Na]^+$ $C_{19}H_{22}N_2NaO_2S$, m/z: 365.1300, found: 365.1304.

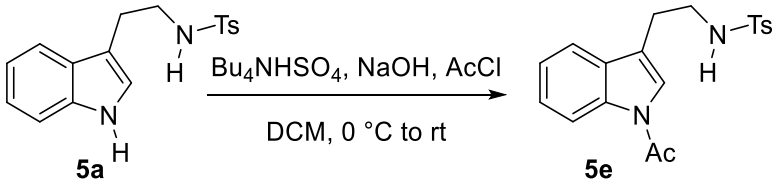
N-(2-(1-allyl-1H-indol-3-yl)ethyl)-4-methylbenzenesulfonamide, **5d**:



5d

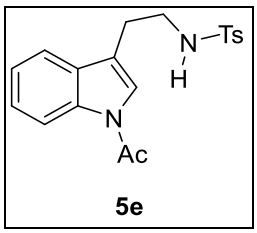
Compound **5d** (2.25 g, 85% yield) was synthesized from **5a** (2.35 g, 7.5 mmol) and allyl bromine (0.71 mL, 8.25 mmol) as a light yellow oil following the synthetic procedure of the **5b**, purified by flash

chromatography (petrol ether: EtOAc = 10:1 to 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.29-7.25 (m, 1H), 7.23-7.17 (m, 3H), 7.07-7.02 (m, 1H), 6.85 (s, 1H), 6.01-5.91 (m, 1H), 5.22-5.18 (m, 1H), 5.11-5.06 (m, 1H), 4.65 (td, *J* = 5.6 Hz, 1.6 Hz, 2H), 4.46 (t, *J* = 8.0 Hz, 1H), 3.26 (q, *J* = 6.4 Hz, 2H), 2.91 (t, *J* = 6.6 Hz, 2H), 2.40 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 143.11, 136.78, 136.43, 133.30, 129.49, 127.48, 126.91, 126.10, 121.69, 119.01, 118.61, 117.25, 110.43, 109.63, 48.57, 43.14, 25.35, 21.38; **IR** (KBr) 3288, 2923, 1598, 1326, 1159, 815, 742, 551 cm^{-1}; **HRMS** (ESI) calcd for $[M+Na]^+$ $C_{20}H_{22}N_2NaO_2S$, m/z: 377.1300, found: 377.1309.



5a **5e**

N-(2-(1-acetyl-1H-indol-3-yl)ethyl)-4-methylbenzenesulfonamide, **5e**:

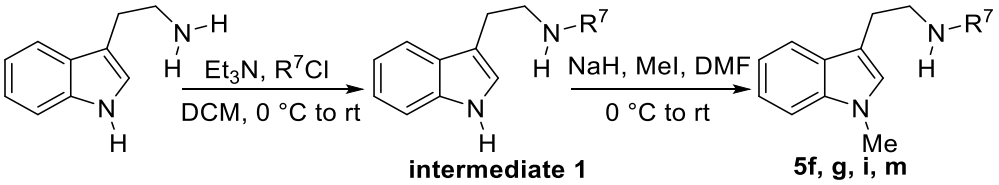


5e

To a solution of **5a** (1.57 g, 5.0 mmol, 1.0 equiv) in DCM (40 mL) was added Bu_4NHSO_4 (0.169 g, 0.25 mmol, 0.05 equiv). The solution was cooled to 0℃ and added NaOH (1.00 g, 12.5 mmol, 2.5 equiv). A solution of AcCl (1.06 mL, 7.5 mmol, 1.5 equiv) in DCM (20 mL) was then added to the reaction system dropwise at 0℃. The resulted mixture was warm to room temperature and stirred for additional 1.5 h, then, quenched with saturated NH_4Cl (aqueous) and extracted with EtOAc (60 mL x 3). The combine organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated by vacuo. The residue was purified by column chromatography (petrol ether: acetone =12:1) to afford 5e (1.57 g, 88 % yield) as a white solid. **m.p.** 130-135℃. **^{1}H NMR** (400 MHz, $CDCl_3$)**:** δ 8.06 (s, 1H), 7.80-7.76 (m, 3H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.20 (td, *J* = 7.2 Hz, 1.2 Hz, 1H), 7.15 (td, *J* = 8.0 Hz, 1.2 Hz, 1H), 7.05 (d, *J* = 2.0 Hz, 1H), 4.06-4.01 (m, 2H), 3.22-3.17 (m, 2H), 2.42 (s, 3H), 2.28 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 170.27, 144.85, 136.73, 136.20, 129.84, 127.47, 127.26, 122.45, 122.14, 119.59, 118.93, 112.18, 111.15, 47.84, 25.98, 24.89, 21.58; **IR** (KBr) 3368, 1675, 1433, 1335, 1164, 746, 542 cm^{-1}; **HRMS** (ESI) calcd for $[M+Na]^+$ $C_{19}H_{20}N_2NaO_3S$, m/z: 379.1087, found: 379.1090.

2.2 Preparation of N_b-substituted tryptamines

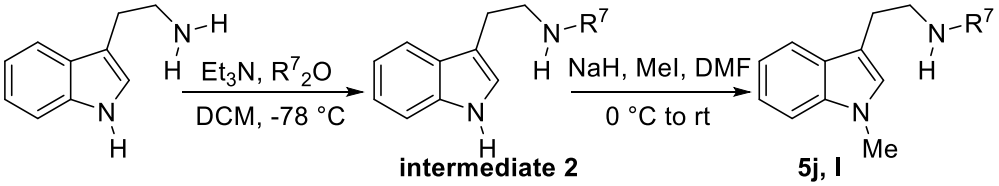
General procedure A:



To a stirred solution of tryptamine (1.0 equiv) in DCM (0.50 M) at 0℃ were added Et_3N (1.2 equiv) and R^7Cl (1.05 equiv) successively. The reaction system was stirred at room temperature for 6 h and then quenched with saturated NH_4Cl. The resulted mixture was extracted with DCM and the organic layer was dried over Na_2SO_4, filtered, and concentrated by vacuo. The residue was recrystallized (Et_2O and petrol ether as eluent) to provide the crude **intermediate 1**.

To a solution of the crude **intermediate 1** (1.0 equiv) above in DMF (0.21 M) at 0℃ was added NaH (3.5 equiv, 60% dispersion in mineral oil). The reaction system was stirred at room temperature for 0.5 h, and then cooled to 0℃. A solution of MeI (1.1 equiv, in DMF) was subsequently added to this reaction mixture. The resulted solution was stirred at room temperature for 6 h, then quenched with saturated NH_4Cl (aqueous) and extracted with EtOAc. The organic layer was washed with water (6 times) and brine, then dried over Na_2SO_4, filtered, and concentrated by vacuo. The residue was purified by column chromatography to afford **5f**, **5g**, **5i** or **5m**.

General procedure B:

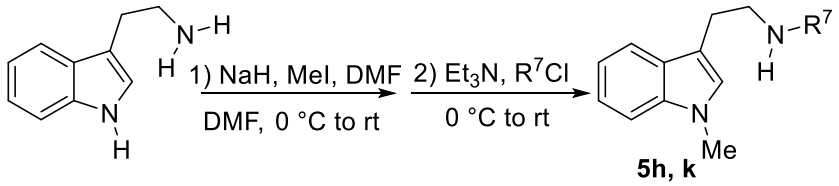


To a solution of tryptamine (1.0 equiv) in DCM (0.63 M) was added Et_3N (3.0 equiv) and then cooled to -78℃. A solution of $R^7{}_2O$ (1.05 equiv) was then added to the reaction system dropwise. The resulted mixture was warm to room temperature and stirred for additional 6 h, then, quenched with water and extracted with DCM. The organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated by vacuo. The resulted residue (crude **intermediate 2**) was used to the next step without further purification.

To a solution of the crude **intermediate 2** (1.0 equiv) above in DMF (0.30 M) at 0℃ was added NaH (3.0 equiv, 60% dispersion in mineral oil). The reaction system was stirred at room temperature for

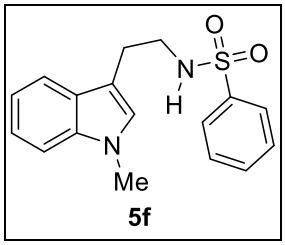
0.5 h, and then cooled to 0℃. A solution of MeI (1.1 equiv, in DMF) was subsequently added to this reactiom mixture. The resulted solution was stirred at room temperature for 6 h, then quenched with saturated NH_4Cl (aqueous), and extracted with EtOAc. The organic layer was washed with water (6 times) and brine, then dried over Na_2SO_4, filtered, and concentrated by vacuo. The residue was purified by column chromatography to afford **5j** or **5l**.

General procedure C:



To a stirred solution of tryptamine (1.0 equiv) in *N*,*N*-dimethylformamide (0.2 M) under 0℃ was added NaH (60% dispersion in mineral oil, 3.0 equiv) portionwise. The reaction mixture was reacted at room temperature for 2 h and cooled to 0℃ again. MeI (1.0 equiv, 0.2 M, in DMF) was then added to the reaction system over 1 h, after which, the system was stirred at 0℃ for additional 3 h. Whereafter, H_2O (the volume is consistent with DMF), Na_2CO_3 (2.0 equiv) and R^7Cl (1.0 equiv) were added to the reaction system successively under 0℃. After stirring under the same temperature for 3 h, R^7Cl (0.50 equiv) was added to the mixture and the system was reacted for additional 1 h. The resulted mixture was extracted with EtOAc and washed with water (6 times). The organic layer was dried with Na_2SO_4 (anhydrous), then filtered and concentrated. The residue was purified by column chromatography to afford **5h** or **5k**.

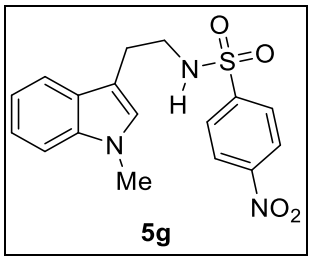
N-(2-(1-methyl-1H-indol-3-yl)ethyl)benzenesulfonamide, **5f:**



Compound **5f** (0.80 g, 51% yield) was synthesized following the general procedure A as a light yellow oil, purified by flash chromatography (petrol ether: EtOAc = 10:1 to 5:1). $R^7Cl = PhSO_2Cl$. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.76 (d, *J* = 7.6 Hz, 2H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.46-7.38 (m, 3H), 7.27 (t, *J* = 8.4 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.80 (s, 1H), 4.50 (t, *J* = 5.6 Hz, 1H), 3.72 (s, 3H), 3.28 (q, *J* = 6.4 Hz, 2H), 2.92 (t, *J* = 6.4 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 139.85,

137.13, 132.47, 128.98, 127.30, 127.26, 126.94, 121.85, 119.03, 118.55, 109.84, 109.35, 43.19, 32.62, 25.40; **IR** (KBr) 3293, 2928, 1615, 1325, 1159, 815, 742, 585 cm^{-1}; **HRMS** (ESI) calcd for $[M+Na]^+$ $C_{17}H_{18}N_2NaO_2S$, m/z: 337.0987, found: 337.0984.

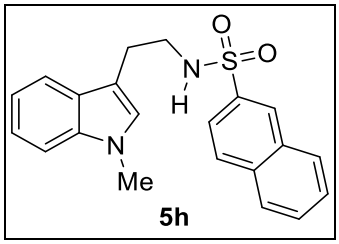
N-(2-(1-methyl-1H-indol-3-yl)ethyl)-4-nitrobenzenesulfonamide, **5g:**



5g

Compound **5g** (1.10 g, 61% yield) was synthesized following the general procedure A as a yellow solid, purified by flash chromatography (petrol ether: EtOAc = 7:1 to 5:1). R^7Cl = *p*-NsCl. **m.p.** 106-108˚C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.08 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 8.8 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.26-7.16 (m, 2H), 7.00 (t, *J* = 7.2 Hz, 1H), 6.81 (s, 1H), 4.60 (t, *J* = 5.4 Hz, 1H), 3.71 (s, 3H), 3.34 (q, *J* = 6.0 Hz, 2H), 2.93 (d, *J* = 6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.68, 145.35, 137.18, 127.85, 127.37, 127.01, 123.86, 122.08, 119.16, 118.36, 109.44, 43.24, 32.62, 25.38; **IR** (KBr) 3307, 2932, 1607, 1529, 1349, 1164, 855, 738, 611 cm^{-1}; **HRMS** (ESI) calcd for $[M+Na]^+$ $C_{17}H_{18}N_3NaO_4S$, m/z: 382.0837, found: 382.0840.

N-(2-(1-methyl-1H-indol-3-yl)ethyl)naphthalene-2-sulfonamide, **5h:**

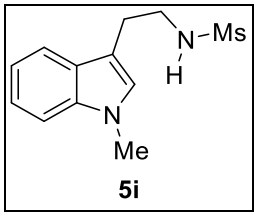


5h

Compound **5h** (2.90 g, 80% yield) was synthesized following the general procedure C as a light yellow oil, purified by flash chromatography (petrol ether: EtOAc = 10:1 to 6:1). R^7Cl = 2-naphthyl-SO_2Cl. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.33 (s, 1H), 7.86-7.79 (m, 3H), 7.68 (dd, *J* = 8.8 Hz, 1.6 Hz, 1H), 7.62-7.53 (m, 2H), 7.32 (d, *J* = 7.6 Hz, 1H), 7.22-7.12 (m, 2H), 6.95 (d, *J* = 7.6 Hz, 1H), 6.73 (s, 1H), 4.76 (t, *J* = 6.0 Hz, 1H), 3.60 (s, 3H), 3.30 (q, *J* = 6.8 Hz, 2H), 2.89 (t, *J* = 6.8 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 137.03, 136.70, 134.65, 132.05, 129.26, 129.15, 128.59, 128.20, 127.80, 127.36, 127.25, 127.21, 122.20, 121.73, 118.90, 118.45, 109.86, 109.24, 43.30, 32.44, 25.36; **IR** (KBr) 3291,

2932, 1325, 817, 741, 549 cm^{-1}; **HRMS** (ESI) calcd for $[M+Na]^+$ $C_{21}H_{20}N_2NaO_2S$, m/z: 387.1143, found: 387.1142.

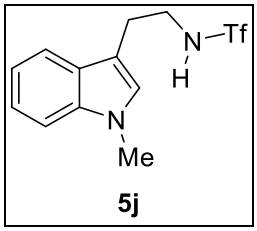
N-(2-(1-methyl-1H-indol-3-yl)ethyl)methanesulfonamide, **5i:**



5i

Compound **5i** (0.65 g, 52% yield) was synthesized following the general procedure A as a pale yellow solid, purified by flash chromatography (petrol ether: EtOAc = 5:1 to 3:1). R^7Cl = MsCl. **m.p.** 101-105˚C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.25 (td, *J* = 7.6 Hz, 0.8 Hz, 1H), 7.12 (td, *J* = 7.4 Hz, 0.8 Hz, 1H), 6.94 (s, 1H), 4.30 (t, *J* = 6.4 Hz, 1H), 3.76 (s, 3H), 3.44 (q, *J* = 6.4 Hz, 2H), 3.04 (t, *J* = 6.4 Hz, 2H), 2.83 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 137.21, 127.41, 127.30, 121.96, 119.14, 118.58, 109.97, 109.46, 43.37, 40.12, 32.68, 25.99; IR (KBr) 3236, 2922, 1615, 1325, 1156, 1071, 737, 521 cm^{-1}; **HRMS** (ESI) calcd for $[M+Na]^+$ $C_{12}H_{16}N_2NaO_2S$, m/z: 275.0830, found: 275.0837.

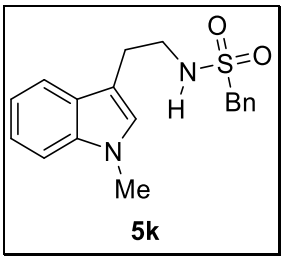
1,1,1-trifluoro-*N*-(2-(1-methyl-1H-indol-3-yl)ethyl)methanesulfonamide, **5j:**



5j

Compound **5j** (1.90 g, 56% yield) was synthesized following the general procedure B as a pale yellow solid, purified by flash chromatography (petrol ether: EtOAc = 20:1 to 5:1). $R^7{}_2O$ = Tf_2O. **m.p.** 52-56˚C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.55 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.29-7.25 (m, 1H), 7.14 (td, *J* = 7.4 Hz, 1.2 Hz, 1H), 6.94 (s, 1H), 3.88 (bs, 1H), 3.78 (s, 3H), 3.60 (q, *J* = 6.4 Hz, 2H), 3.06 (t, *J* = 6.4 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 137.33, 127.45, 127.15, 122.20, 121.25, 119.40, 118.46, 118.06, 109.60, 109.03, 44.51, 32.74, 26.33; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -77.44; **IR** (KBr) 3308, 2936, 1616, 1371 1193, 819, 743, 607 cm^{-1}; **HRMS** (ESI) calcd for $[M+Na]^+$ $C_{12}H_{13}F_3N_2NaO_2S$, m/z: 329.0548, found: 329.0562.

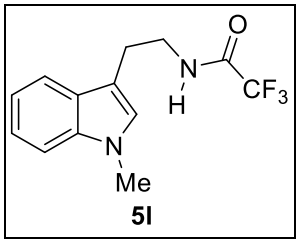
N-(2-(1-methyl-1H-indol-3-yl)ethyl)-1-phenylmethanesulfonamide, **5k:**



5k

Compound **5k** (2.60 g, 79% yield) was synthesized following the general procedure C as a pale yellow oil, purified by flash chromatography (petrol ether: EtOAc = 10:1 to 5:1). $R^7Cl = BnSO_2Cl$. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.53 (d, *J* = 7.6 Hz, 2H), 7.32-7.24 (m, 3H), 7.23-7.17 (m, 4H), 7.13 (td, *J* = 7.4 Hz, 0.8 Hz, 1H), 6.82 (s, 1H), 4.15-4.11 (m, 3H), 3.71(s, 3H), 3.29 (q, *J* = 6.4 Hz, 2H), 2.94 (t, *J* = 6.4 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 137.27, 130.46, 129.33, 128.67, 128.52, 127.36, 127.31, 121.95, 119.12, 118.63, 109.94, 109.43, 58.34, 43.65, 32.59, 26.05; **IR** (KBr) 3308, 2929, 1615, 1156, 1326, 1153, 742, 605 cm^{-1}; **HRMS** (ESI) calcd for $[M+Na]^+$ $C_{18}H_{20}N_2NaO_2S$, m/z: 351.1143, found: 351.1158.

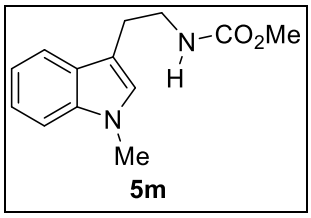
2,2,2-trifluoro-*N*-(2-(1-methyl-1H-indol-3-yl)ethyl)acetamide, **5l:**



5l

Compound **5l** (1.50 g, 75% yield) was synthesized following the general procedure B as a pale yellow solid, purified by flash chromatography (petrol ether: EtOAc = 10:1 to 8:1). $R^7{}_2O = (CF_3CO)_2O$. **m.p.** 90-92˚C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.28-7.23 (m, 1H), 7.15-7.11 (m, 1H), 6.88 (s, 1H), 6.43 (s, 1H), 3.75 (s, 3H), 3.65 (q, *J* = 6.4 Hz, 2H), 3.02 (t, *J* = 6.4 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 157.64, 157.27, 156.90, 156.54, 137.20, 127.38, 126.92, 122.00, 120.10, 119.19, 118.51, 117.24, 114.38, 110.15, 109.46, 40.28, 32.63, 24.59; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -75.97 ; **IR** (KBr) 3318, 2938, 1705, 1474, 1327, 1180, 1160, 741 cm^{-1}; **HRMS** (ESI) calcd for $[M+Na]^+$ $C_{17}H_{18}F_3N_2NaO_2$, m/z: 293.0878, found: 293.0882.

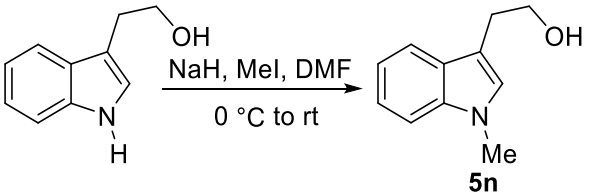
Methyl (2-(1-methyl-1H-indol-3-yl)ethyl)carbamate, **5m**:



5m

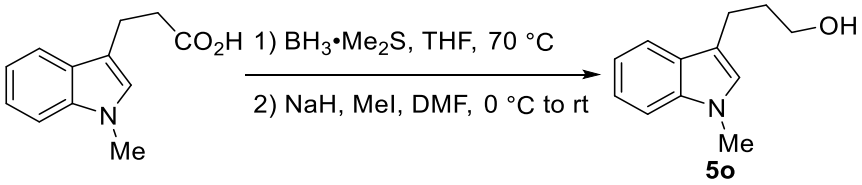
Compound **5m** (1.09 g, 67% yield) was synthesized following the general procedure A as pale yellow solid, purified by flash chromatography (petrol ether: EtOAc = 10:1 to 5:1). R^7Cl = $MeCO_2Cl$. **m.p.** 91-93℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.23 (td, *J* = 6.8 Hz, 0.8 Hz, 1H), 7.11 (td, *J* = 7.6 Hz, 0.8 Hz, 1H), 6.86 (s, 1H), 4.79 (s, 1H), 3.73 (s, 3H), 3.65 (s, 3H), 3.49 (q, *J* = 6.4 Hz, 2H), 2.94 (t, *J* = 6.8 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 156.98, 137.05, 127.62, 126.78, 121.67, 118.85, 118.77, 111.27, 109.22, 51.92, 41.35, 32.56, 25.62; **IR** (KBr) 3333, 2940, 1701, 1533, 1248, 1191, 739, 428 cm^{-1}; **HRMS** (ESI) calcd for $[M+Na]^+$ $C_{13}H_{16}N_2NaO_2$, m/z: 255.1104, found: 255.1098.

2.2 Preparation of *N*-methyl tryptophol and 3-indolepropanol



5n

To a stirred solution of tryptophol (2.50 g, 15.5 mmol, 1.0 equiv) in DMF (20 mL) at 0℃ was added NaH (1.85 g, 46.5 mmol, 3.0 equiv, 60% dispersion in mineral oil) in portions. The system was reacted at room temperature for 30 min, and then cooled to 0℃. A solution of MeI (0.97 mL, 17.1 mmol, 1.1 equiv) in DMF (10 mL) was subsequently added to the reaction mixture dropwise at the same temperature and the reaction mixture was stirred at room temperature for additional 6 h. The resulted reaction system was carefully quenched with saturated NH_4Cl and extracted with EtOAc (100 mL x 3). The organic layer was washed with water (100 mL×8) and brine (100 mL), then dried over Na_2SO_4, filtered, and concentrated by vacuo. The residue was purified by flash column chromatography (petrol ether: EtOAc = 8:1 to 7:1) to afford **5n** (1.80 g, 66% yield) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.60 (d, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 8.4 Hz, 1H), 7.26-7.21 (m, 1H), 7.12 (td, *J* = 7.4 Hz, 1.2 Hz, 1H), 6.94 (s, 1H), 3.88 (t, *J* = 6.4 Hz, 2H), 3.75 (s, 3H) 3.02 (t, *J* = 6.4 Hz, 2H), 1.53 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 137.18, 127.84, 127.27, 121.73, 118.91, 118.88, 110.66, 109.26, 62.74, 32.60, 28.64; **IR** (KBr) 3362, 2931, 1615, 1483, 1045, 740, 428 cm^{-1}; **HRMS** (ESI) calcd for $[M+Na]^+$ $C_{11}H_{13}NNaO$, m/z: 198.0895, found: 198.0902.

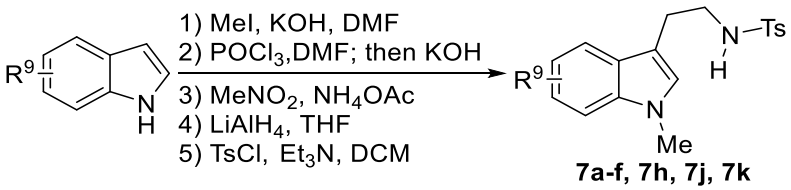


5o

To a solution of 3-indolepropionic acid (1.89 g, 10 mmol, 1.0 equiv) in THF (50 mL) was added BH_3•Me_2S (15 mL, 30 mmol, 3.0 equiv, 2 M in THF) at 0℃. The reaction mixture was stirred at 70℃ for 16 h and then carefully quenched with MeOH at 0℃. The resulted solution was extracted with EtOAc (60 mL x 3), the combined organic layers were washed with brine and then dried over Na_2SO_4, filtered, and concentrated by vacuo. The residue was used for next step directly without further purification.

The residue product above was dissolved in DMF (50 mL) and cooled to 0℃. NaH (1.20 g, 30 mmol, 3.0 equiv, 60% dispersion in mineral oil) was added to the reaction system in one portion, and the mixture was stirred at room temperature for 0.5 h, and then cooled to 0℃. A solution of MeI (1.42 g, 10 mmol, 1.0 equiv) in DMF (50 mL) was subsequently added to the mixture dropwise at 0℃. The reaction system was stirred at the same temperature for 2 h, after which, quenched with saturated NH_4Cl (aqueous). The resulted mixture was extracted with EtOAc (100 mL x 3), the combined organic layers were washed with water (100 mL x 6) and brine and dried over Na_2SO_4, filtered, and concentrated by vacuo. The residue was purified by flash column chromatography (PE: EA=10:1 to 3:1) to afford **5o** in 69% yield as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.59 (d, J = 8.0 Hz, 1H), 7.28 (d, J = 8.0 Hz, 1H), 7.23-7.19 (m, 1H), 7.12-7.07 (m, 1H), 6.84 (s, 1H), 3.73-3.69 (m, 5H), 2.84 (t, J = 7.4 Hz, 2H), 2.00-1.92 (m, 2H), 1.44 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 137.02, 127.79, 126.13, 121.47, 118.93, 118.56, 114.37, 109.11, 62.61, 33.13, 32.52, 21.23; **IR** (KBr) 3361, 2933, 1473, 1326, 1247, 1153, 1062, 740 cm^{-1}; **HRMS** (ESI) calcd for $[M+Na]^+$ $C_{12}H_{15}NNaO$, m/z: 212.1046, found: 212.1043.

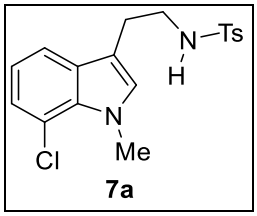
2.3 Preparation of benzene ring-substituted tryptamines



7a-f, 7h, 7j, 7k

Compound **7a-f**,**7h**,**7j**, **7k** were synthesized from corresponding indole over 5 steps according to the literature procedures[2].

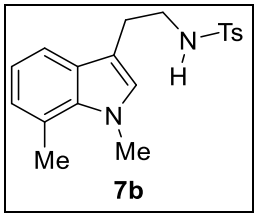
N-(2-(7- chloro-1-methyl-1H-indol-3-yl)ethyl)-4-methylbenzenesulfonamide, **7a**:



7a

Compound **7a** (0.81 g, 38%) was obtained from 7-chloro-indole as a pale yellow solid. **m.p.** 99-102℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.4 Hz, 2H), 7.24 (dd, *J* = 8.0 Hz, 1.2 Hz, 1H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.09 (dd, *J* = 7.6 Hz, 0.8 Hz, 1H), 6.89 (t, *J* = 7.8 Hz, 1H), 6.73 (s, 1H), 4.74 (t, *J* = 6.0 Hz, 1H), 4.01 (s, 3H), 3.21 (q, *J* = 6.4 Hz, 2H), 2.84 (t, *J* = 6.6 Hz, 2H), 2.38 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 143.20, 136.69, 132.24, 130.43, 129.96, 129.48, 126.88, 123.14, 119.66, 117.27, 116.97, 110.17, 43.02, 36.35, 25.13, 21.43; **IR** (KBr) 3274, 2948, 1489, 1315, 1154, 1084, 814, 735, 667 cm^{-1}; **HRMS** (ESI) calcd for $[M+Na]^+$ $C_{18}H_{19}ClN_2NaO_2S$, m/z: 385.0748, found: 385.0745.

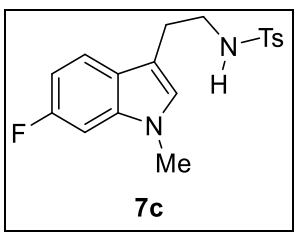
N-(2-(1,7-dimethyl-1H-indol-3-yl)ethyl)-4-methylbenzenesulfonamide, **7b:**



7b

Compound **7b** (0.89 g, 29%) was obtained from 7-methyl-indole as a pale yellow solid. **m.p**. 104-109℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 8.4 Hz, 2H), 7.22-7.19 (m, 3H), 6.90-6.88 (m, 2H), 6.68 (s, 1H), 4.51 (t, *J* = 6.0 Hz, 1H), 3.96 (s, 3H), 3.22 (q, *J* = 6.8 Hz, 2H), 2.86 (t, *J* = 6.8 Hz, 2H), 2.72 (s, 3H), 2.39 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 143.16, 136.84, 135.80, 129.54, 128.91, 128.35, 126.98, 124.38, 121.36, 119.24, 116.58, 109.58 , 43.05, 36.51, 25.23, 21.45, 19.61; **IR** (KBr) 3289, 3046, 2927, 1599, 1321,1159, 1048, 740, 665 cm^{-1}; **HRMS** (ESI) calcd for $[M+Na]^+$ $C_{19}H_{22}N_2NaO_2S$, m/z: 365.1300, found: 365.1285.

N-(2-(6-fluoro-1-methyl-1H-indol-3-yl)ethyl)-4-methylbenzenesulfonamide, **7c:**

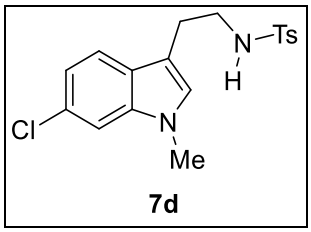


7c

Compound **7c** (2.05 g, 47%) was obtained from 6-fluoro-indole as a white solid. **m.p.** 91-94℃; **^{1}H**

NMR (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 8.4 Hz, 2H), 7.26 (dd, *J* = 5.2 Hz, 3.6 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.90 (dd, *J* = 7.6 Hz, 2.0 Hz, 1H), 6.80-6.74 (m, 2H), 4.75 (t, *J* = 6.0 Hz, 1H), 3.61 (s, 3H), 3.21 (q, *J* = 6.4 Hz, 2H), 2.85 (t, *J* = 6.4 Hz, 2H), 2.38 (s,3H); **^{13}C NMR** (100MHz, $CDCl_3$): δ 161.06, 158.70, 143.20, 137.15, 137.03, 136.71, 129.48, 127.52, 127.49, 126.90, 123.84, 119.35, 119.25, 110.31, 107.64, 107.40, 95.74, 95.48, 43.09, 32.60, 25.23, 21.38; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -120.79; **IR** (KBr) 3286, 3065, 2934, 1624, 1333, 1160, 1069, 737, 667 cm^{-1}; **HRMS** (ESI) calcd for $[M+Na]^+$ $C_{18}H_{19}FN_2NaO_2S$, m/z: 369.1049, found: 369.1056.

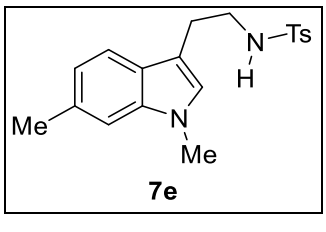
N-(2-(6-chloro-1-methyl-1H-indol-3-yl)ethyl)-4-methylbenzenesulfonamide, **7d**:



7d

Compound **7d** (1.12 g, 17%) was obtained from 6-chloro-indole as a pale yellow solid. **m.p**. 77-79°C; ^{1}H NMR (400 MHz, $CDCl_3$): **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 2.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.99 (dd, *J* = 8.4 Hz, 2.0 Hz, 1H), 6.80 (s, 1H), 4.43 (t, *J* = 6.0 Hz, 1H), 3.68 (s, 3H), 3.23 (q, *J* = 6.4 Hz, 2H), 2.88 (t, *J* = 6.8 Hz, 2H), 2.40 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 143.33, 137.55, 136.76, 129.55, 127.98, 127.93, 126.97, 125.89, 119.68, 119.47, 110.37, 109.38, 43.06, 32.71, 25.29, 21.48; **IR** (KBr) 3286, 3061, 2927, 1613, 1325, 1159, 1067, 737, 667 cm^{-1}; **HRMS** (ESI) calcd for $[M+Na]^+$ $C_{18}H_{19}ClN_2NaO_2S$, m/z: 385.0753, found: 385.0744.

N-(2-(1,6-dimethyl-1H-indol-3-yl)ethyl)-4-methylbenzenesulfonamide, **7e**:

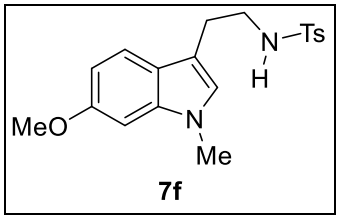


7e

Compound **7e** (374 mg, 32%) was obtained from 6-methyl-indole as a brown oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 8.4 Hz, 2H), 7.25 (s, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.07 (s, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 6.73 (s, 1H), 4.40(t, *J* = 6.0 Hz, 1H), 3.68 (s, 3H), 3.24(q, *J* = 6.8 Hz, 2H), 2.88(t, *J* = 6.4 Hz, 2H), 2.48 (s, 3H), 2.40 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 143.19, 137.61, 136.93, 131.74,

129.56, 127.04, 126.70, 125.19, 120.79, 118.29, 109.80, 109.33, 43.18, 32.54, 25.46, 21.82, 21.49; **IR** (KBr) 3265, 3031, 2918, 1598, 1319,1158, 1065, 756, 667 cm^{-1}; **HRMS** (ESI) calcd for $[M+Na]^+$ $C_{19}H_{22}N_2NaO_2S$, m/z: 365.1300, found: 365.1286.

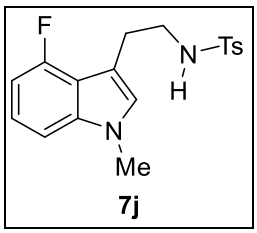
N-(2-(6-methoxy-1-methyl-1H-indol-3-yl)ethyl)-4-methylbenzenesulfonamide, **7f:**



7f

Compound **7f** (3.04 g, 60%) was obtained from 6-methoxyl-indole as a grey solid. **m.p.** 108-110℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 8.4 Hz, 2H), 7.24-7.19 (m, 3H), 6.70 (d, *J* = 9.2 Hz, 3H), 4.48(t, *J* = 5.6 Hz, 1H), 3.86 (s, 3H), 3.65 (s, 3H), 3.22 (q, *J* = 6.4 Hz, 2H), 2.86 (t, *J* = 6.6 Hz, 2H), 2.39 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.52, 143.18, 137.87, 136.80, 129.53, 126.98, 126.09, 121.65, 119.23, 109.95, 108.95, 92.83 , 55.69, 43.11, 32.59, 25.36, 21.45; **IR** (KBr) 3288, 3056, 2937, 1624, 1329,1159, 1068, 736, 667 cm^{-1}; **HRMS** (ESI) calcd for $[M+Na]^+$ $C_{19}H_{22}N_2NaO_3S$, m/z: 381.1249, found: 381.1254.

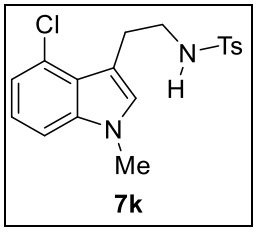
N-(2-(4-fluoro-1-methyl-1H-indol-3-yl)ethyl)-4-methylbenzenesulfonamide, **7j:**



7j

Compound **7j** (1.80 g, 52%) was obtained from 4-fluoro-indole as a white solid. **m.p.** 120-126℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.12-7.06 (m, 1H), 7.02 (d, *J* = 8.0 Hz, 1H), 6.76 (s, 1H), 6.66 (dd, *J* = 10.8 Hz, 7.6 Hz, 1H), 4.46 (bs, 1H), 3.70 (s, 3H), 3.27 (q, *J* = 6.4 Hz, 2H), 2.96 (t, *J* = 6.4 Hz, 2H), 2.38 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 158.16, 155.71, 143.11, 140.08, 139.96, 136.81, 129.48, 127.75, 126.92, 122.25, 122.18, 115.90, 115.70, 108.80, 108.77, 105.48, 105.44, 104.22, 104.03, 43.62, 32.96, 26.48, 21.48; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -123.68; **IR** (KBr) 3282, 2932, 1629, 1319, 1156, 1092, 734, 671 cm^{-1}; **HRMS** (ESI) calcd for $[M+Na]^+$ $C_{18}H_{19}FN_2NaO_2S$, m/z: 369.1043, found: 369.1037.

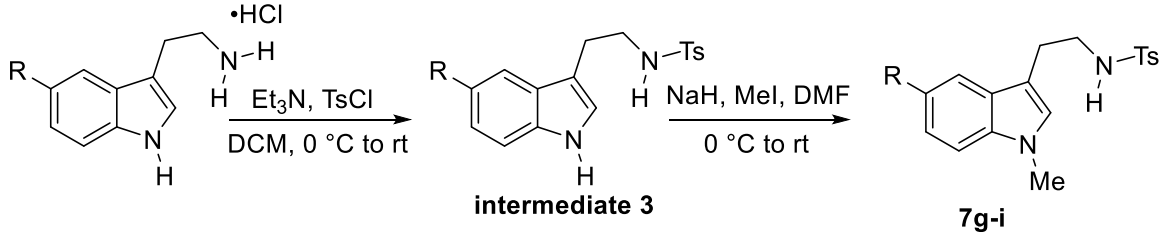
N-(2-(4-chloro-1-methyl-1H-indol-3-yl)ethyl)-4-methylbenzenesulfonamide, **7k**:



7k

Compound **7k** (0.78 g , 54%) was obtained from 4-chloro-indole as a pale yellow solid. **m.p.** 129-132℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 1H), 7.07 (t, *J* = 7.6 Hz, 1H), 6.99 (dd, *J* = 7.2 Hz, 0.4 Hz, 1H), 6.84 (s, 1H), 4.50 (t, *J* = 6.0 Hz, 1H), 3.70 (s, 3H), 3.30 (q, *J* = 6.4 Hz, 2H), 3.11 (t, *J* = 6.4 Hz, 2H), 2.38 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 143.13, 138.66, 136.95, 129.49, 129.09, 126.97, 126.10, 124.07, 122.18, 119.99, 110.47, 108.10, 44.35, 32.87, 26.31, 21.46; **IR** (KBr) 3284, 3061, 2927, 1598, 1321,1158, 1073, 737, 669 cm^{-1}; **HRMS** (ESI) calcd for $[M+Na]^+$ $C_{18}H_{19}ClN_2NaO_2S$, m/z: 385.0753, found: 385.0742.

Compound **7g-i** were synthesized from corresponding tryptamine over 2 steps .

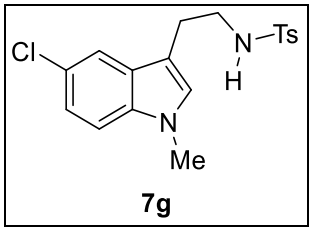


intermediate 3 **7g-i**

To a stirred solution of substituted tryptamine (1.0 equiv) in DCM (0.50 M) at 0℃ were added Et_3N (1.2 equiv) and R^7Cl (1.05 equiv) successively. The reaction system was stirred at room temperature for 6h and then quenched with saturated NH_4Cl. The resulted mixture was extracted with DCM and the organic layer was dried over Na_2SO_4, filtered, and concentrated by vacuo. The residue was recrystallized (Et_2O and petrol ether as eluent) to provide the crude **intermediate 3**.

To a solution of the crude **intermediate 3** (1.0 equiv) above in DMF (0.21 M) at 0℃ was added NaH (3.0 equiv, 60% dispersion in mineral oil). The reaction system was stirred at room temperature for 0.5 h, and then cooled to 0℃. A solution of MeI (1.1 equiv, in DMF) was subsequently added to this reactiom mixture. The resulted solution was stirred at room temperature for 6 h, then quenched with saturated NH_4Cl, and extracted with EtOAc. The organic layer was washed with water (6 times) and brine, then dried over Na_2SO_4, filtered, and concentrated by vacuo. The residue was purified by column chromatography to afford **7g-i**.

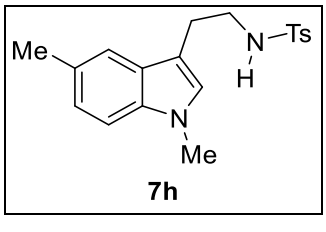
N-(2-(5-chloro-1-methyl-1H-indol-3-yl)ethyl)-4-methylbenzenesulfonamide, **7g:**



7g

Compound **7g** (2.48 g, 91%) was obtained from 5-chloro-tryptamine as a pale yellow solid. **m.p.** 105-107°C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.4 Hz, 2H), 7.26 (dd, *J* = 2.0 Hz, 0.8 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.17-7.10 (m, 2H), 6.83 (s, 1H), 4.66 (t, *J* = 6.0 Hz, 1H), 3.67 (s, 3H), 3.20 (q, *J* = 6.8 Hz, 2H), 2.82 (t, *J* = 6.8 Hz, 2H), 2.40 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 143.43, 136.52, 135.52, 129.66, 128.81, 128.26, 127.00, 124.80, 122.00, 118.03, 110.43, 109.62, 42.96, 32.85, 25.13, 21.57; **IR** (KBr) 3276, 3062, 2926, 1598, 1320, 1159, 1071, 737, 663 cm^{-1}; **HRMS** (ESI) calcd for $[M+Na]^+$ $C_{18}H_{19}ClN_2NaO_2S$, m/z: 385.0753, found: 385.0748.

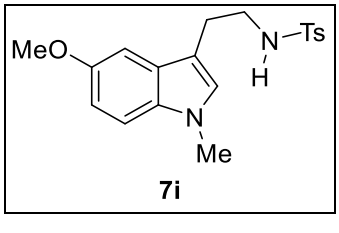
N-(2-(1,5-dimethyl-1H-indol-3-yl)ethyl)-4-methylbenzenesulfonamide, **7h:**



7h

Compound **7h** (1.44 g, 44%) was obtained from 5-methyl-tryptamine as a pale yellow solid. **m.p.** 109-113°C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 6.8 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 1H), 6.76 (s, 1H), 4.53 (bs, 1H), 3.69 (s, 3H), 3.24 (q, *J* = 6.4 Hz, 2H), 2.87 (t, *J* = 6.6 Hz, 2H), 2.41 (s, 3H), 2.40 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 143.20, 136.85, 135.64, 129.58, 128.18, 127.51, 127.45, 127.07, 123.45, 118.27, 109.28, 109.09, 43.16, 32.68, 25.35, 21.52, 21.44; **IR** (KBr) 3261, 3032, 2929, 1599, 1318, 1148, 1064, 738, 668 cm^{-1}; **HRMS** (ESI) calcd for $[M+Na]^+$ $C_{19}H_{22}N_2NaO_2S$, m/z: 365.1300, found: 365.1283.

N-(2-(5-methoxy-1-methyl-1H-indol-3-yl)ethyl)-4-methylbenzenesulfonamide, **7i**:

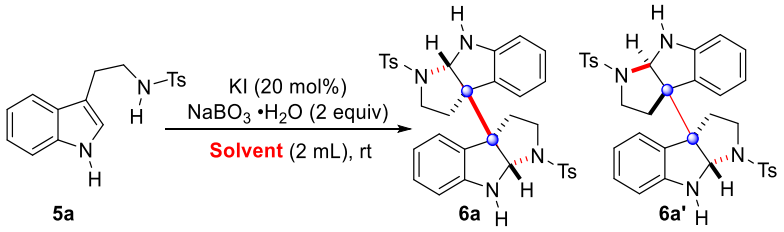


7i

Compound **7i** (1.60 g ,57%) was obtained from 5-methoxyl-tryptamine as a pale yellow solid. **m.p.** 114-116℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.60 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.8 Hz, 1H), 6.85 (dd, *J* = 8.8 Hz, 2.4 Hz, 1H), 6.81 (d, *J* = 2.4 Hz, 1H), 6.76 (s, 1H), 4.66 (t, *J* = 5.6 Hz, 1H), 3.78 (s, 3H), 3.65 (s, 3H), 3.21 (q, *J* = 6.4 Hz, 2H), 2.86 (t, *J* = 6.4 Hz, 2H), 2.37 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 153.81, 143.26, 136.76, 132.55, 129.58, 127.95, 127.62, 127.03, 112.04, 110.16, 109.41, 100.45, 55.88, 43.13, 32.79, 25.39, 21.49; **IR** (KBr) 3285, 3058, 2934, 1598, 1324, 1158, 1066, 736, 665 cm^{-1}; **HRMS** (ESI) calcd for $[M+Na]^+$ $C_{19}H_{22}N_2NaO_3S$, m/z: 381.1249, found: 381.1254.

3. Screening of KI-catalyzed oxidative dimerization conditions

Table S1. Screening of solvents [a]

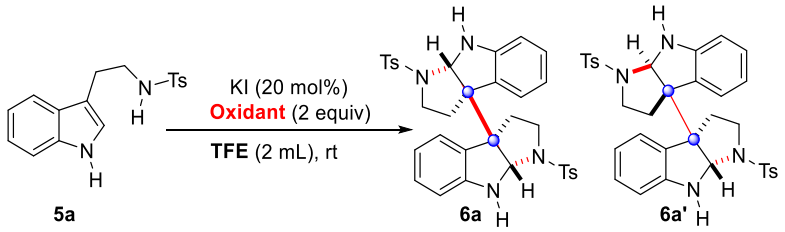


Entry	Solvent	Time[b]	dr[c]	Yield [d]
1	THF	24 h	-	NR[e]
2	DME (1,2-dimethoxyethane)	24 h	-	R.D.[f]
3	Et_2O	24 h	-	NR
4	1,4-dioxane	24 h	-	NR
5	EtOAc	24 h	-	NR
6	CH_3CN	24 h	-	NR
7	Acetone	24 h	-	NR
8	DMF (*N*,*N*-dimethylformamide)	24 h	-	NR
9	CH_2Cl_2	24 h	-	NR
10	$CHCl_3$	24 h	-	NR
11	CCl_4	24 h	-	R.D.
12	DCE (1,2-dichloroethane)	24 h	-	R.D.
13	MeOH	24 h	-	R.D.
14	EtOH	24 h	-	R.D.
15	*i*-PrOH	24 h	-	R.D.
16	TFE (Trifluoroethanol)	1.5 h	1.8:1	64%
17	1,1,1,3,3,3-hexafluoro-2-propanol	2 h	1.7:1	57%
18	H_2O	24 h	-	ND
19	Benzene	24 h	-	R.D.
20	Toluene	24 h	-	R.D.
21	PhCl	24 h	-	R.D.
22	$PhCF_3$	24 h	-	R.D.

[a] Unless otherwise noted, all reactions were carried with **5a** (0.2 mmol), KI (20 mmol%) and $NaBO_3$•$4H_2O$ (2.0 equiv) in 2 mL solvent. [b] The time of which the reaction is completed (monitored by TLC) or the time of which the reaction is quenched (24 h). [c] Determined by ^{1}H NMR. [d] Determined by ^{1}H NMR. [e] Not reacted. [f] Recovery of **5a** and slightly decomposed.

On the basis of our initial efforts, additional solvents were screened to optimize the dimerization reaction of **5a** under the oxidative of $NaBO_3$•$4H_2O$. As shown in Table S1, various ether solvents (entries 1-4), polar solvents (entries 5-8), halogenated alkane solvents (entries 9-12), protic solvents (entries 13-18) and aromatic solvents (entries 19-22) were investigated. According to the results, only polyfluoro substituted alcohol solvent could provide the desired products **6a** and **6a′**, while other solvents screened generally behaved inactive in the catalytic oxidative dimerization of **5a**.

Table S2. Optimization of oxidants [a]

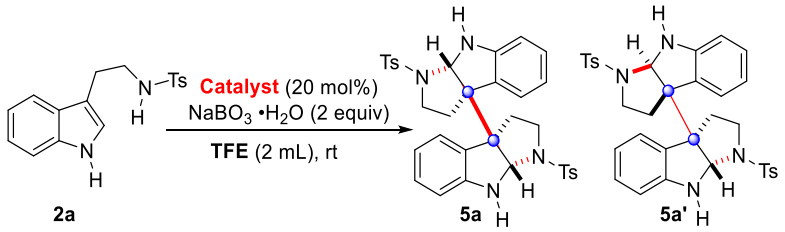


Entry	Oxidant	Time[b]	dr[c]	Yield [d]
1	$NaBO_3•4H_2O$	1.5 h	1.8:1	64%
2	H_2O_2	4 h	1.8:1	44%
3	H_2O_2 (3 equiv)	4 h	1.9:1	40%
4	$^tBuO_2H$ (75% aqueous)	10 h	1.8:1	47%
5	$^tBuO_2H$ (5.5 M in decane)	10 h	1.8:1	53%
6	air	24 h	-	NR[e]
7	O_2 (1atm)	24 h	-	NR
8	*m*-CPBA	10 min	-	ND[f]
9	$^tBuO_2{}^tBu$	24 h	-	NR
10	$^tBuO_2Ac$	24 h	1.9:1	10%
11	Ammonium peroxodisulfate	18 h	1.8:1	43%
12	Sodium carbonate peroxide	24 h	1.9:1	23%
13	potassium peroxodisulfate	24 h	1.8:1	19%
14	Oxone	25 min	-	42%
15	Benzoyl peroxide	10 min	-	trace

[a] Unless otherwise noted, all reactions were carried with **5a** (0.2 mmol), KI (20 mmol%) and oxidant (2.0 equiv) in 2 mL TFE. [b] The time of which the reaction is completed (monitored by TLC) or the time of which the reaction is quenched (24 h). [c] Determined by ^1H NMR. [d] Determined by ^1H NMR. [e] Not reacted. [f] Not dected.

Next, numerous oxidants were also applied to this reaction (Table S2). As a result, most oxidants (entries 1-5, 10-14) were able to drive the desired reactions, giving different reaction yields and similar diastereoselectivities. Among these screenings, $NaBO_3•4H_2O$ was proven to be the optimal (64% yield). Interestingly, both O_2 and $^tBuO_2{}^tBu$ exhibits very low activities, however, *m*-CPBA and Benzoyl peroxide (BPO) were too active in the reaction.

Table S3. Screening of iodide catalysts [a]

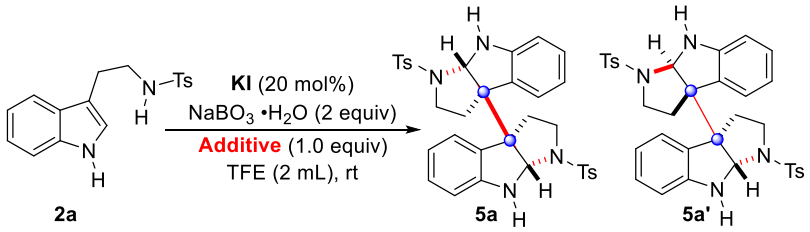


Entry	Catalyst	Time[b]	dr[c]	Yield [d]
1	LiI	3.5 h	1.9:1	64%
2	NaI	2 h	1.9:1	65%
3	KI	1.5 h	1.8:1	64%
4	MgI_2	5.5 h	1.9:1	65%
5	ZnI_2	7 h	1.9:1	61%
6	CuI	24 h	1.9:1	45%
7	AgI	24 h	-	NR[e]
8	$NH_4^+I^-$	1.5 h	1.9:1	63%
9	$PhMe3^+I^-$	2 h	1.8:1	65%
10	$^nBu_4^+I^-$	2 h	1.9:1	62%
11	$Ph_3(i\text{-}Pr)P^+I^-$	2.5 h	1.9:1	63%
12	PhI	24 h	-	NR

[a] Unless otherwise noted, all reactions were carried with **5a** (0.2 mmol), catalyst (20 mmol%) and $NaBO_3$•$4H_2O$ (2.0 equiv) in 2 mL TFE. [b] The time of which the reaction is completed (monitored by TLC) or the time of which the reaction is quenched (24 h). [c] Determined by ^1H NMR. [d] Determined by ^1H NMR. [e] Not reacted.

Subsequently, different iodide catalysts were also screened. Except for silver iodide and iodobenzene, the other selected iodide catalysts could generally promote our target reaction with similar results, although their reaction times were varied. Considering the reaction time and the cost of material, potassium iodide was chosen as the optimal catalyst.

Table S4. Screening of additives [a]

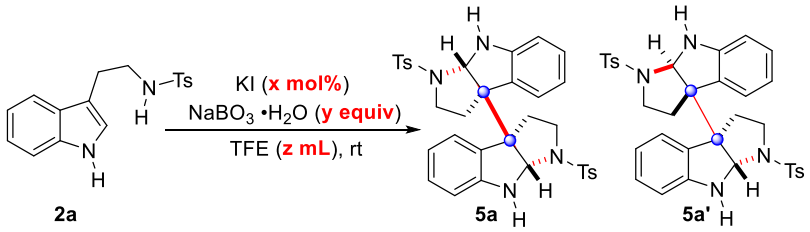


Entry	Additive	Time[b]	dr[c]	Yield [d]
1	3 ÅMS (60 mg)	24 h	2.0:1	32%
2	4 ÅMS (60 mg)	24 h	1.9:1	56%
3	5 ÅMS (60 mg)	2.5 h	1.8:1	64%
4	HCO_2H (60 mg)	1.5 h	1.9:1	43%
5	HOAc	1 h	1.8:1	52%
6	$PhCO_2H$	1.5 h	1.9:1	55%
7	$B(OH)_3$	2 h	1.9:1	58%
8	Phenol	1.5 h	1.8:1	58%
9	4-Methoxyphenol	1.5 h	1.8:1	63%
10	4-Nitrophenol	1.5 h	2.0:1	45%
11	$NaH_2PO_4•2H_2O$	2.5 h	1.9:1	62%
12	Na_2HPO_4	1.5 h	1.7:1	62%
13	NH_4Cl	1 h	1.9:1	60%
14	NH_4OAc	1 h	1.9:1	48%
15	NH_4PF6	1 h	1.9:1	60%
16	$NaHCO_3$	1.5 h	2.0:1	61%
17	KOAc	2 h	2.0:1	38%
18	K_2CO_3	24 h	-	ND[e]

[a] Unless otherwise noted, all reactions were carried with **5a** (0.2 mmol), KI (20 mmol%), additive (1.0 equiv) and $NaBO_3•4H_2O$ (2.0 equiv) in 2 mL TFE. [b] The time of which the reaction is completed (monitored by TLC) or the time of which the reaction is quenched (24 h). [c] Determined by ^1H NMR. [d] Determined by ^1H NMR. [e] Not dected.

Next, we further optimized the target reaction with various additives such as molecular sieves, acids, bases and salts (Table S4). Unfortunately, none of the above screenings gave better results.

Table S5. Screening of concentrations and the equivalent of reaction components. [a]



Entry	x mol%	y	z	Time[b]	dr[c]	Yield [d]
1	20 mol%	1.0	2 mL (c=0.1 M)	3 h	1.8:1	58%[e]
2	20 mol%	1.1	4 mL (c=0.05 M)	6.5 h	1.8:1	66%[e]
3	20 mol%	1.1	2 mL (c=0.1 M)	2 h	1.8:1	63%[e]
4	20 mol%	1.1	1 mL (c=0.2 M)	2 h	1.8:1	65%[e]
5	20 mol%	1.2	4 mL (c=0.05 M)	6 h	1.8:1	66%
6	20 mol%	1.2	2 mL (c=0.1 M)	2 h	1.8:1	68%
7	20 mol%	1.2	1 mL (c=0.2 M)	2 h	1.9:1	64%
8	20 mol%	1.3	4 mL (c=0.05 M)	4 h	1.8:1	66%
9	20 mol%	1.3	2 mL (c=0.1 M)	2 h	1.8:1	68%
10	20 mol%	1.3	1 mL (c=0.2 M)	2 h	1.8:1	64%
11	20 mol%	1.4	4 mL (c=0.05 M)	3 h	1.8:1	66%
12	20 mol%	1.4	2 mL (c=0.1 M)	2 h	1.8:1	67%
13	20 mol%	1.4	1 mL (c=0.2 M)	1 h	1.8:1	65%
14	20 mol%	1.5	4 mL (c=0.05 M)	2.5 h	1.8:1	67%
15	20 mol%	1.5	2 mL (c=0.1 M)	2 h	1.8:1	68%
16	20 mol%	1.5	4 mL (c=0.2 M)	2 h	1.8:1	65%
17	10 mol%	1.2	2 mL (c=0.1 M)	2 h	1.8:1	68%

[a] Unless otherwise noted, all reactions were carried with **5a** (0.2 mmol), KI (x mmol%) and $NaBO_3$•$4H_2O$ (y equiv) in z mL TFE. [b] The time of which the reaction is completed (monitored by TLC). [c] Determined by ^{1}H NMR. [d] Determined by ^{1}H NMR. [e] The repeatability of these reactions was not good.

Finally, we also carefully screened the concentrations of the reaction and the equivalent of reaction components (Table S5). According to the results, when the concentration of the reaction was chosen as 0.1 M, both 1.0 (entry 1) and 1.1 (entry 3) equivalent of oxidant ($NaBO_3$•$4H_2O$) were able to provide the targeted products with acceptable results, but the repeatability of these reactions was not good. However, when 1.2 equivalent of oxidant (entry 6) was used under this concentration, the desired products could be well obtained with repeatable results (68% yield, 1.8:1 dr). In addition, varying the concentrations (entries 5, 7) of the above reaction could not give a better result, however, when the loading amount of catalyst (KI) was reduced to 10 mol%, the reaction could still provide **6a** and **6a′** with good results (entry 17). According to above screenings (Tables S1-5), we finally obtained the optimal reaction conditions (Table S5, entry 17).

In addition, it is necessary to specifically state that our diastereo ratios is determined by ^{1}HNMR of the crude reaction products, and the yield (NMR) is calibrated with 1,3,5-trimethoxybenzene as an internal standard (Fig. S1).

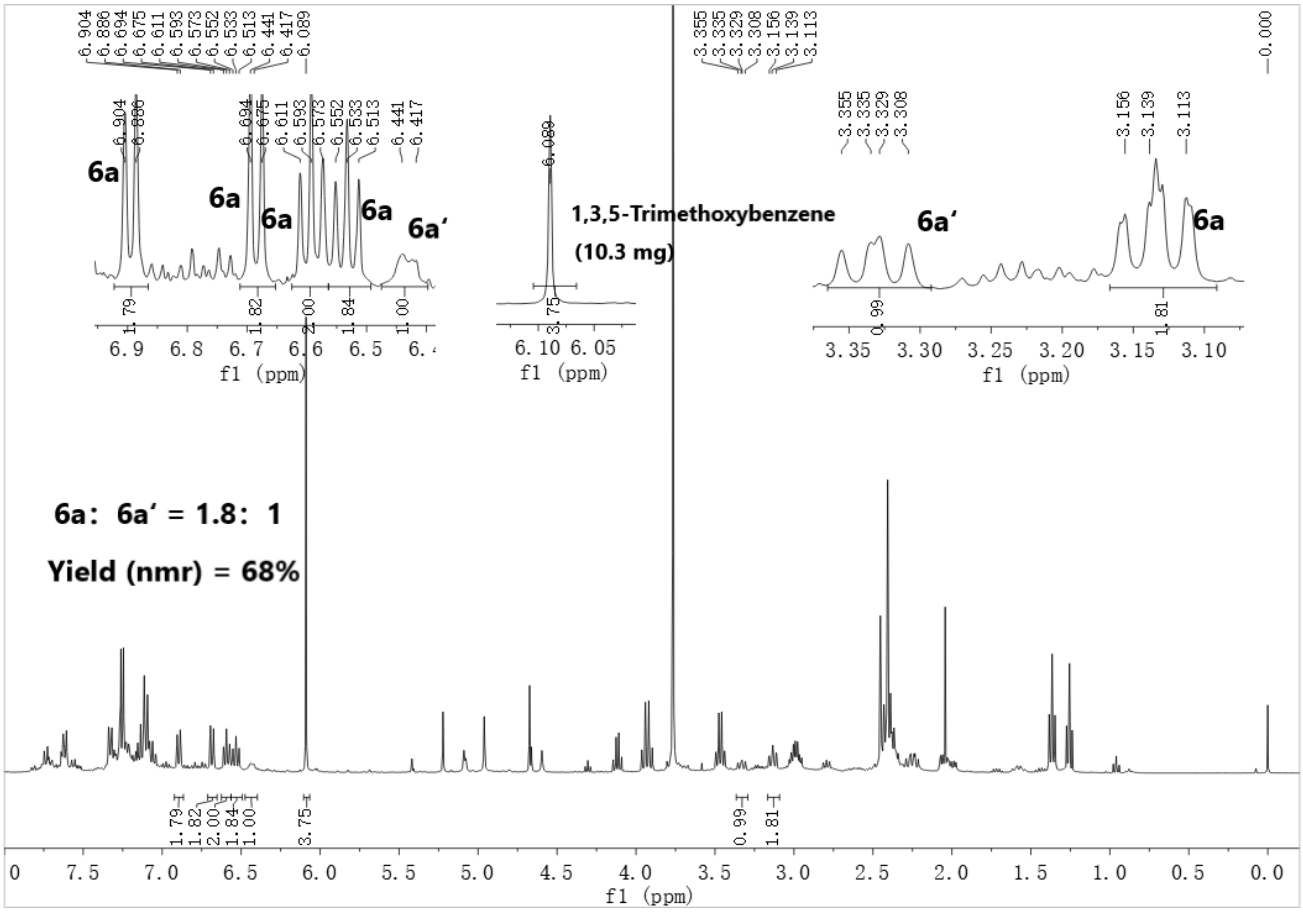
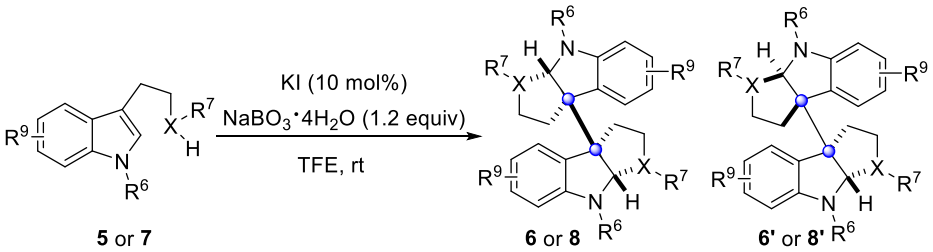


Figure S1. ^{1}H NMR used to identify diastereo ratio and NMR yield of **6a**/**6a'**.

4. KI-catalyzed oxidative dimerization reactions

4.1 General procedure:



To a dry 10 mL reaction tube were added corresponding tryptamine or tryptophol (0.2 mmol), KI (3.3 mg, 10 mol%), TFE (2 mL) and $NaBO_3$•$4H_2O$ (37.0 mg, 1.2 equiv) successively under argon atmosphere. The reaction system was stirred (1500 rmp) at room temperature until TLC indicated that **5** or **7** disappeared (1-3 h). The mixture was then quenched with saturated $Na_2S_2O_3$ (aqueous) and extracted with EtOAc (60 mL). The organic layer was washed with brine (15 mL), dried over Na_2SO_4, filtered, and concentrated by vacuo. The residue was purified by flash column chromatography to afford the dimeric products.

4.2 Exemplificative explanation for the configurational assignments

In our study, most of the diastereomeric product pairs were not easy to be separated into single isomer. In fact, similar situation was also occurred in recent related research.[3] For better configurational assignments of each diastereoisomer (*meso* and racemic C_2-symmetric dimer) of the products, exemplificative explanations based on NMRs, HPLC, X-ray and other experimental data is necessary.

At the beginning of this study, products provided by the KI-catalyzed dimerization of **5a** were purified by column chromatography and identified by NMRs respectively (Figure S2). It's worth noting that the racemic C_2-symmetric dimer **6a** has already been characterized by Xia and co-workers previously (Figure S3).[4] Therefore, our major product showed in Fig. S2-**A** seems to be the C_2-symmetric dimer **6a** and the minor (Fig. S2-**B**) was recognized as the *meso* dimer **6a'** according to the NMR characteristic and the high-resolution mass spectral analysis (**HRMS**) data. Investigating the previous literature[4] in detail, we found that their configuration assignment of compound **6a** was based on the X-ray of a similar compound and the comparison of their NMR spectra. To further confirm this conclusion, we performed a chiral HPLC analysis of compound Fig. S2-**A** (Figure S4). Since the HPLC of this compound exhibits two peaks with equal integral areas, it is identified to be the C_2-symmetric **6a** rather than the meso- **6a'**.

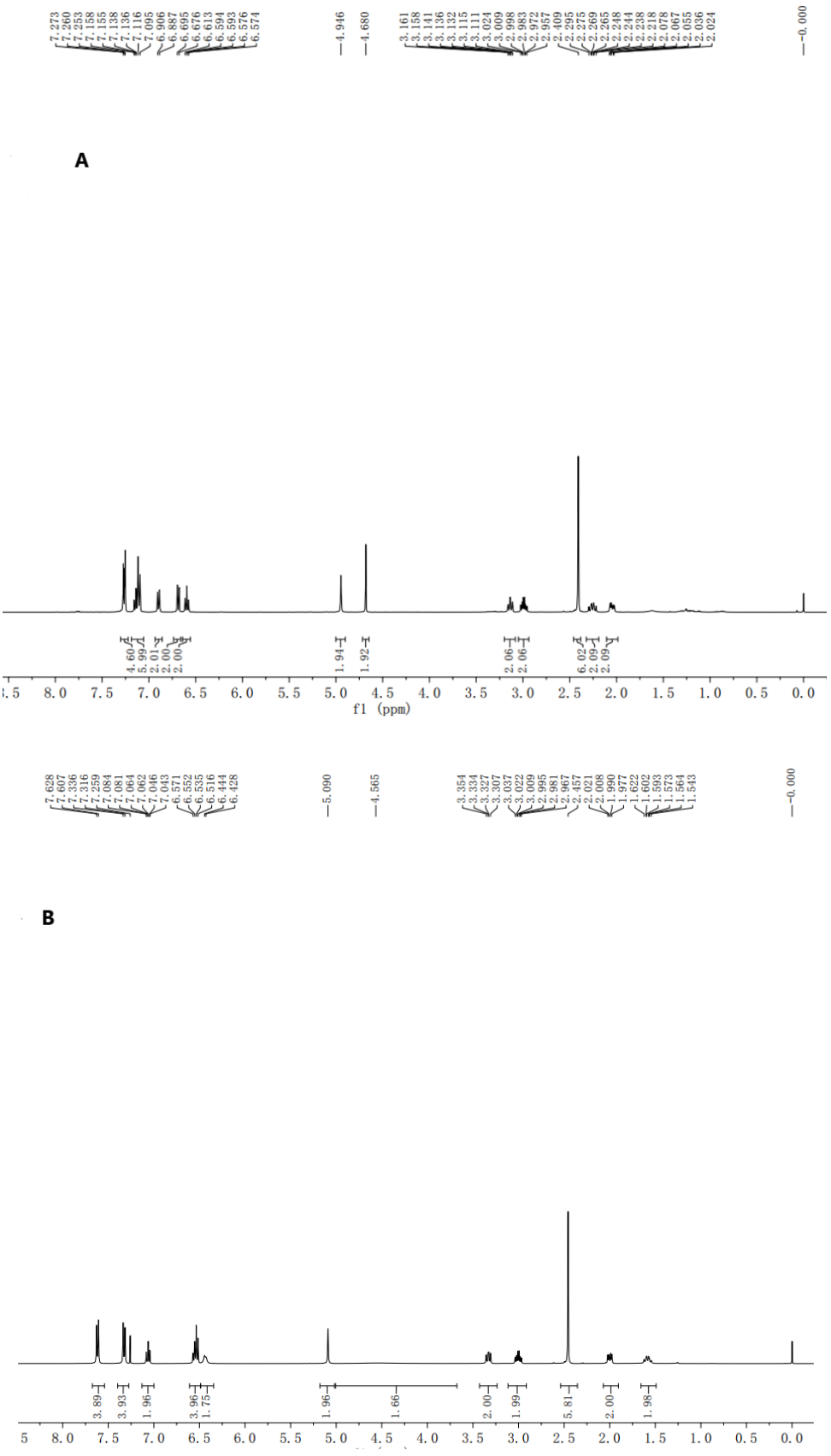


Figure S2. [1]HNMR of the products provided by the KI-catalyzed dimerization of **5a**.

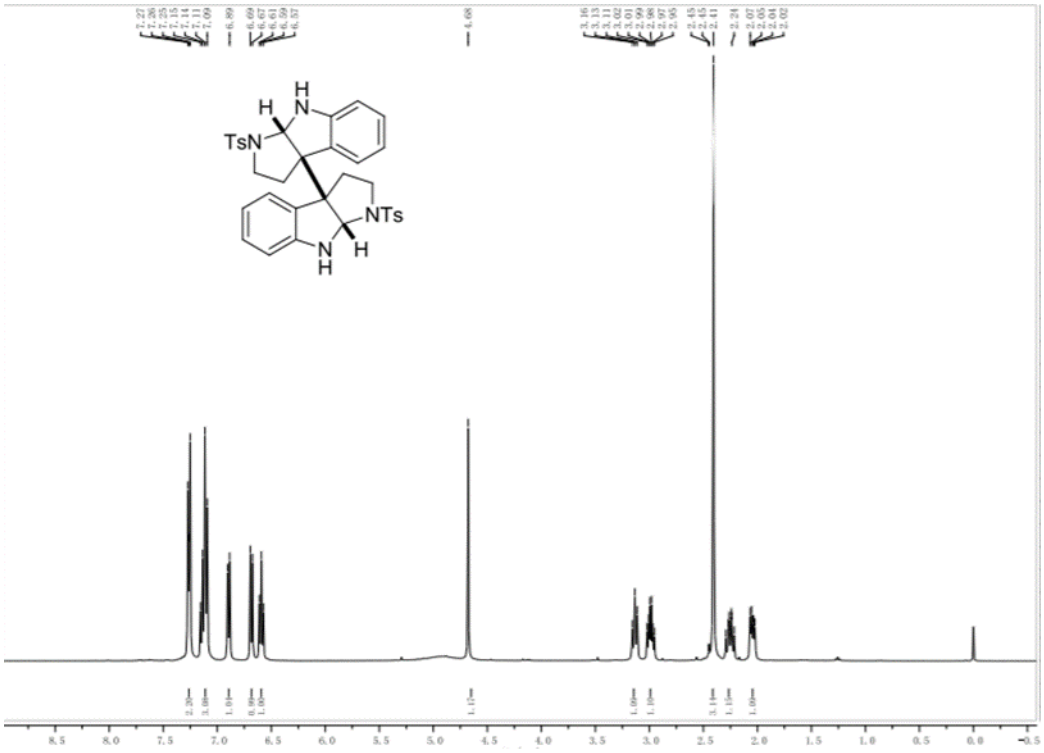
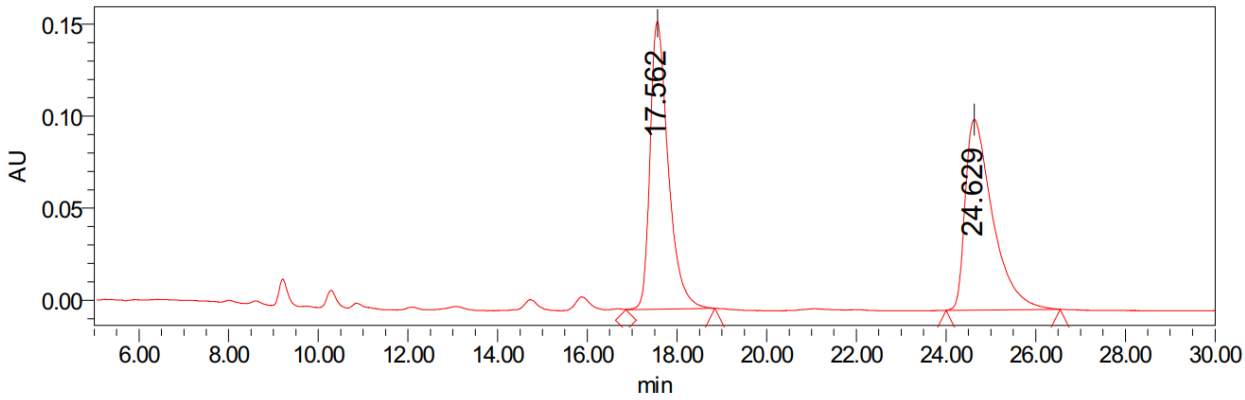


Figure S3. [1]HNMR of **6a** provided by Xia and co-workers.

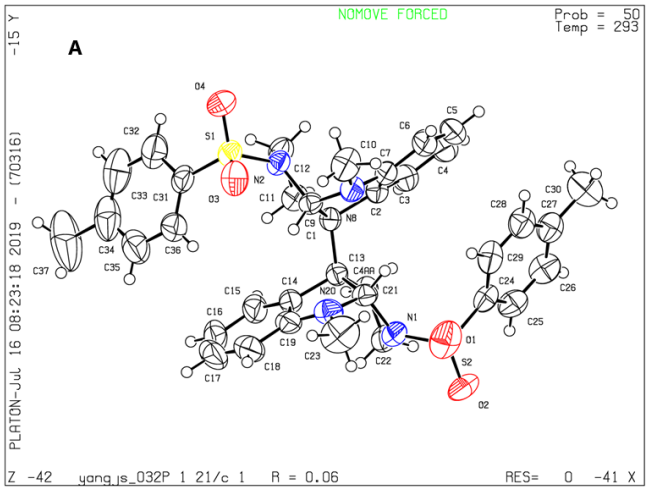


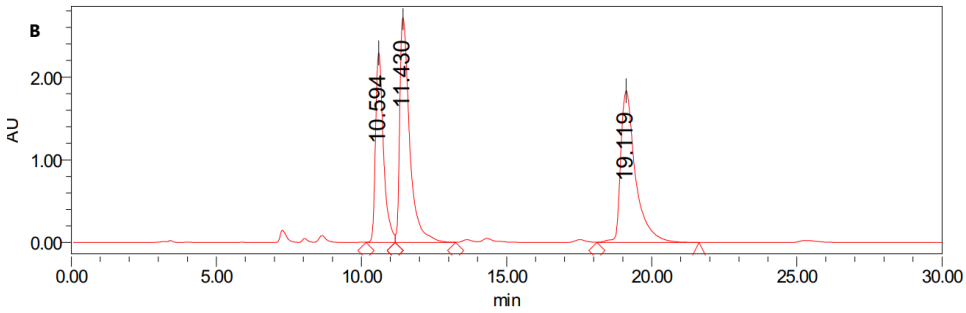
Peak Information:

	RetTime (分钟)	Area (微伏*秒)	Area (%)	Height (微伏)
1	17.562	4397735.242	49.979	156361
2	24.629	4401368.417	50.021	103608

Figure S4. Chiral HPLC analysis of compound from Fig. S2-**A**

Another example supports the configuration assignments of this manuscript is **6b**/**6b'**. The relative configuration of compound **6b** is reported by Liang and co-workers via conversion to (±)-folicanthine.[5] Here, we double-checked this conclusion via X-ray of **6b** (Figure S5-**A**) and chiral HPLC analysis (Figure S5-**B**) of the diastereomeric **6b**/**6b'** mixture.



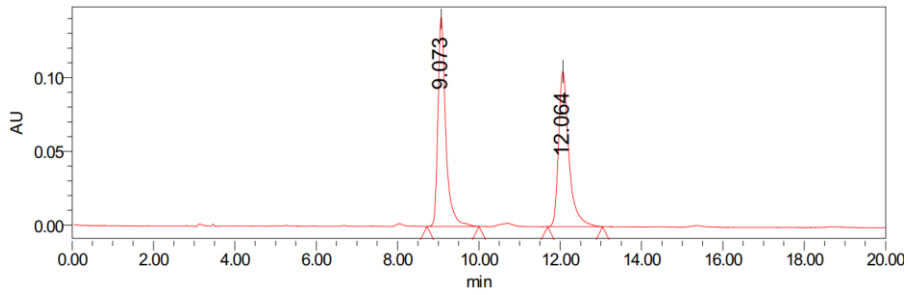


Peak Information:

	RetTime (分钟)	Area (微伏*秒)	Area (%)	Height (微伏)
1	10.594	43681125.499	25.242	2293500
2	11.430	64442274.564	37.239	2716474
3	19.119	64928682.997	37.520	1835340

Figure S5. **A**) X-ray of **6b** and **B**) the chiral HPLC of diastereomeric **6b**/**6b'**

Moreover, compound **8k** which is obtained in high diastereoselectivity (> 20:1 dr) was also subject to chiral HPLC for confirming our configuration assignment. To our delight, this compound exhibits two peaks with equal integral areas, revealing that **8k** is the *C*2-symmetric dimer (Figure S6).



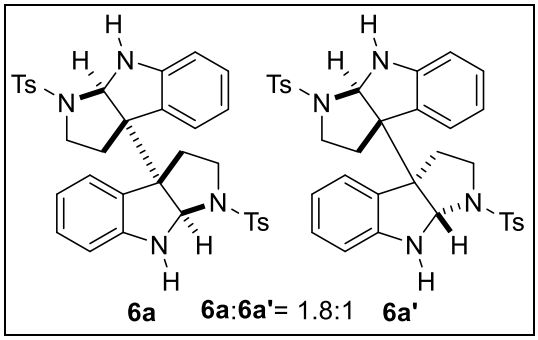
Peak Information:

	RetTime (分钟)	Area (微伏*秒)	Area (%)	Height (微伏)
1	9.073	1895768.020	50.448	141610
2	12.064	1862076.175	49.552	105127

Figure S6. The chiral HPLC of **8k**.

4.3 Characterization of the products:

1,1'-ditosyl-2,2',3,3',8,8a,8',8'a-octahydro-1H,1'H-3a,3'a-bipyrrolo[2,3-b]indole, **6a** and **6a′**:

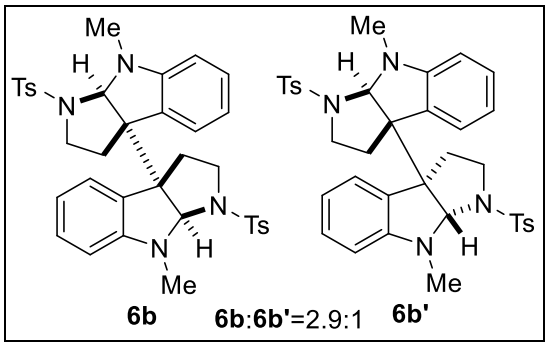


Compound **6a** and **6a′** was obtained (38.9 mg, 62% yield, 1.8:1 dr) via the KI-catalyzed oxidative dimerization of **5a** following the general procedure. Compound **6a** has already been characterized by Xia and co-workers,[4] the configurational assignments of **6a** and **6a′** were confirmed by HPLC spectrum and comparison of the NMRs.

Compound **6a**: White solid; **m.p.** 226-227℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.28-7.25 (m, 4H), 7.16-7.09 (m, 6H), 6.90 (d, *J* = 7.6 Hz, 2H), 6.69 (d, *J* = 7.6 Hz, 2H), 6.62-6.57 (m, 2H), 4.95 (s, 2H), 4.68 (s, 2H), 3.17-3.11 (m, 2H), 3.03-2.95 (m, 2H), 2.41 (s, 6H), 2.30-2.21 (m, 2H), 2.08-2.02 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 150.07, 142.97, 135.41, 129.83, 129.34, 127.37, 126.53, 124.49, 119.06, 110.37, 81.26, 61.33, 46.84, 32.31, 21.52; **IR** (KBr) 3393, 1607, 1467, 1334, 1158, 1031, 737, 662 cm^{-1}; **HRMS** (ESI) calcd for $[M+Na]^+$ $C_{34}H_{34}N_4NaO_4S_2$, m/z: 649.1919, found: 649.1925. Relative configuration of **6a** is confirmed by HPLC (IA-3, Hexane/Isopropanol 70/30, flow rate = 1.0 mL/min, 240 nm): tr_1 =17.56 min; tr_2 = 24.63 min.

Compound **6a′:** White solid; **m.p.** 252-255℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 8.4 Hz, 4H), 7.32 (d, *J* = 8.0 Hz, 4H), 7.06 (td, *J* = 7.8 Hz, 1.2 Hz, 2H), 6.58-6.51 (m, 4H), 6.44 (d, *J* = 6.4 Hz, 2H), 5.09 (s, 2H), 4.57 (bs, 2H), 3.33 (dd, *J* = 10.8 Hz, 8.0 Hz, 2H), 3.00 (td, *J* = 11.2 Hz, 6.0 Hz, 2H), 2.46 (s, 6H), 2.00 (dd, *J* = 12.4 Hz, 5.2 Hz, 2H), 1.58 (td, *J* = 11.6 Hz, 8.0 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 149.78, 143.85, 136.35, 129.86, 129.20, 127.87, 126.83, 123.66, 119.00, 109.77, 80.01, 62.50, 47.13, 33.84, 21.58; **IR** (KBr) 3390, 2952, 1609, 1468, 1335, 1159, 1028, 734, 662 cm^{-1}; **HRMS** (ESI) calcd for $[M+Na]^+$ $C_{34}H_{34}N_4NaO_4S_2$, m/z: 649.1919, found: 649.1918.

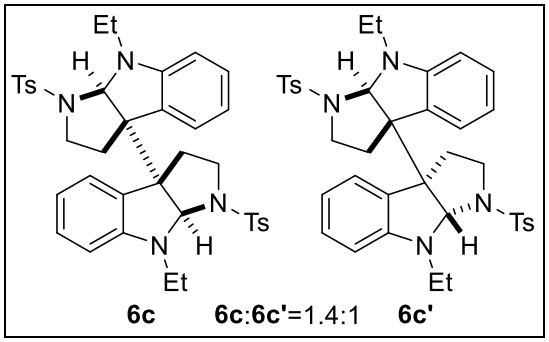
8,8'-dimethyl-1,1'-ditosyl-2,2',3,3',8,8a,8',8'a-octahydro-1H,1'H-3a,3'a-bipyrrolo[2,3-b]indole, **6b** and **6b′:**



Compound **6b** and **6b′** was obtained (60.9 mg, 93% yield, 2.9:1 dr) via the KI-catalyzed oxidative dimerization of **5b** following the general procedure as a white solid. Compound **6b** has already been characterized by Liang and co-workers,[5] the configurational assignments of **6b** and **6b′** were confirmed by HPLC spectrum, X-ray and comparison of the NMRs. Actually, in view of the difficulty in separating the diastereomeric products, most of the configurational assignments of racemic C_2-symmetric and meso dimeric product were established via comparison of the NMRs with **6a**/**6a′** and **6b**/**6b′**. These also proved to be consistent with previous reports[3] (**6n** and **6n′**) and got verified by representative examples mentioned in "section 4.2" of this supporting information.

m.p. 103-105℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 8.4 Hz, 1.43H), 7.38-7.34 (m, 4+1.51H), 7.23-7.19 (m, 6H), 7.07 (t, *J* = 7.8 Hz, 0.77H), 6.84 (d, *J* = 7.2 Hz, 2H), 6.63 (t, *J* = 7.4 Hz, 2H), 6.50-6.44 (m, 2+0.67H), 6.30 (d, *J* = 7.6 Hz, 0.71H), 6.18 (d, *J* = 6.4 Hz, 0.60H), 5.04 (s, 2.0H), 4.99 (s, 0.68H), 3.51 (dd, *J* = 7.2 Hz, 4.8 Hz, 0.70H), 3.22 (dd, *J* = 6.8 Hz, 4.4 Hz, 2H), 2.97 (s, 6H), 2.88-2.80 (m, 0.80H), 2.77-2.69 (m, 3.99H), 2.46 (s, 2.13H), 2.42 (s, 6H), 1.89-1.72 (m, 4+0.62H), 1.41-1.32 (m, 0.77H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 151.60, 151.49, 143.86, 142.94, 136.99, 136.05, 129.93, 129.48, 129.33, 128.27, 127.69, 127.13, 126.99, 124.54, 123.24, 117.69, 117.32, 106.92, 106.57, 87.21, 85.32, 62.06, 60.40, 47.67, 47.44, 34.23, 32.58, 31.57, 31.47, 21.53, 21.49; **IR** (KBr) 3053, 2949, 1604, 1491, 1343, 1157, 1010, 739, 659 cm^{-1}; **HRMS** (ESI) calcd for $[M+Na]^+$ $C_{36}H_{38}N_4NaO_4S_2$, m/z: 677.2232, found: 677.2216. Relative configuration of **6b/6b'** is confirmed by HPLC (IA-3, Hexane/Isopropanol 70/30, flow rate = 1.0 mL/min, 240 nm): tr_1 =10.59 min (**6b'**); tr_2 = 11.43 min (**6b**); tr_3 = 19.12 min (**6b**).

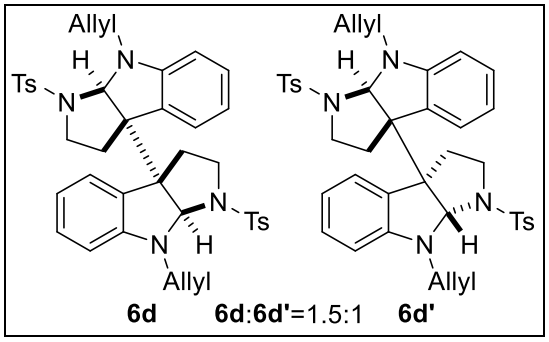
8,8'-diethyl-1,1'-ditosyl-2,2',3,3',8,8a,8',8'a-octahydro-1H,1'H-3a,3'a-bipyrrolo[2,3-b]indole, **6c** and **6c′**:



6c **6c**:**6c'**=1.4:1 **6c'**

Compound **6c** and **6c′** was obtained (61.9 mg, 91% yield, 1.4:1 dr) via the KI-catalyzed oxidative dimerization of **5c** following the general procedure as a pale yellow solid. **m.p.** 191-193°C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.0 Hz, 2.87H), 7.46 (d, *J* = 8.0 Hz, 4H), 7.35 (d, *J* = 8.0 Hz, 2.90H), 7.24 (d, *J* = 8.0 Hz, 4H), 7.15 (m, 2H), 7.06-7.01 (m, 1.23H), 6.87-6.84 (m, 2H), 6.58 (t, *J* = 7.4 Hz, 2H), 6.46 (d, *J* = 7.6 Hz, 2H), 6.41 (t, *J* = 7.2 Hz, 1.25H), 6.33-6.21 (m, 2.21H), 5.29 (s, 3H), 3.62-3.38 (m, 4+2.95H), 3.28-3.22 (m, 2+1.29H), 2.86 (td, *J* = 11.8 Hz, 4.8 Hz, 1.39H), 2.75 (td, *J* = 12.4 Hz, 4.8 Hz, 2H), 2.45 (s, 3.97H), 2.42 (s, 6H), 1.89-1.73 (m, 2+3.37H), 1.46 (bs, 1.39H), 1.25 (t, *J* = 7.0 Hz, 6H), 0.92 (bs, 2+1.35H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 150.46, 150.28, 143.73, 143.08, 137.30, 136.35, 129.92, 129.88, 129.26, 129.13, 128.14, 127.52, 127.26, 127.10, 124.80, 123.67, 116.95, 116.62, 106.32, 105.67, 85.64, 83.36, 62.05, 60.90, 47.31, 47.18, 38.84, 38.29, 35.12, 33.30, 21.51, 12.70, 11.89; **IR** (KBr) 3051, 2972, 1603, 1491, 1344, 1157, 1031, 741, 660 cm^{-1}; **HRMS** (ESI) calcd for $[M+Na]^+$ $C_{38}H_{42}N_4NaO_4S_2$, m/z: 705.2545, found: 705.2527.

8,8'-diallyl-1,1'-ditosyl-2,2',3,3',8,8a,8',8'a-octahydro-1H,1'H-3a,3'a-bipyrrolo[2,3-b]indole, **6d** and **6d′**:

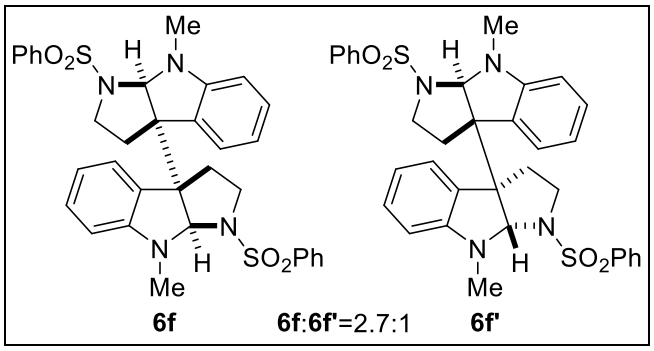


6d **6d**:**6d'**=1.5:1 **6d'**

Compound **6d** and **6d′** was obtained (65.6 mg, 93% yield, 1.5:1 dr) via the KI-catalyzed oxidative dimerization of **5d** following the general procedure as a pale white solid. **m.p.** 113-115°C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.0 Hz, 2.98H), 7.43 (d, *J* = 7.6 Hz, 4H), 7.35 (d, *J* = 6.4 Hz, 2.97H), 7.22 (d, *J* = 8.0 Hz, 4H), 7.13 (t, *J* = 7.6 Hz, 2H), 7.04 (t, *J* = 7.6 Hz, 1.52H), 6.85 (d, *J* = 7.2 Hz, 2H), 6.61 (t, *J* = 7.4 Hz, 2H), 6.52 (d, *J* = 8.0 Hz, 2H), 6.46 (m, 1.45H), 6.33 (d, *J* = 7.6 Hz, 1.57H), 5.94-

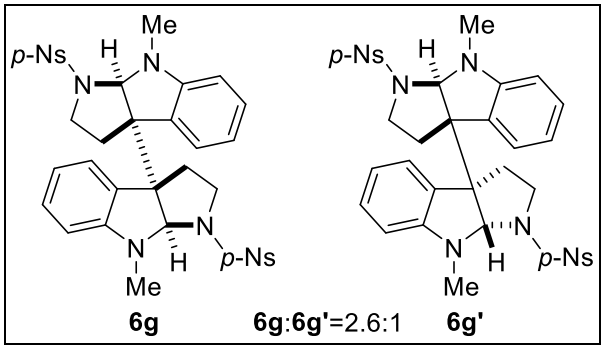
5.84 (m, 2H), 5.29-5.06 (m, 11.98H), 4.31 (dd, *J* = 12.0 Hz, 4.8 Hz, 2H), 4.13 (bs, 1.26H), 3.89 (dd, *J* =11.2 Hz, 5.6 Hz, 2H), 3.75 (d, *J* = 13.6 Hz, 1.36H), 3.49-3.46 (m, 1.36H), 3.26 (dd, *J* = 6.8 Hz, 4.8 Hz, 2H), 2.87 (td, *J* = 12.0 Hz, 4.4 Hz, 1.40H), 2.76 (td, *J* = 11.6 Hz, 4.8 Hz, 2H), 2.45 (s, 3.84H), 2.42 (s, 6H), 1.88-1.73 (m, 4+1.21H), 1.32 (bs, 1.36H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 150.85, 150.68, 143.96, 143.19, 136.98, 136.00, 134.59, 133.96, 130.01, 129.94, 129.18, 129.12, 128.14, 127.70, 127.20, 127.05, 124.68, 123.35, 117.70, 117.32, 116.37, 107.95, 107.04, 86.72, 84.28, 62.13, 60.82, 48.10, 47.41, 47.31, 35.03, 33.14, 21.54; **IR** (KBr) 3056, 2975, 1603, 1489, 1344, 1157, 1051, 741, 660 cm^{-1}; **HRMS** (ESI) calcd for $[M+Na]^+$ $C_{34}H_{34}N_4NaO_4S_2$, m/z: 729.2545, found: 729.2530.

8,8'-dimethyl-1,1'-bis(phenylsulfonyl)-2,2',3,3',8,8a,8',8'a-octahydro-1H,1'H-3a,3'a-bipyrrolo[2,3-b]indole, **6f** and **6f′**:



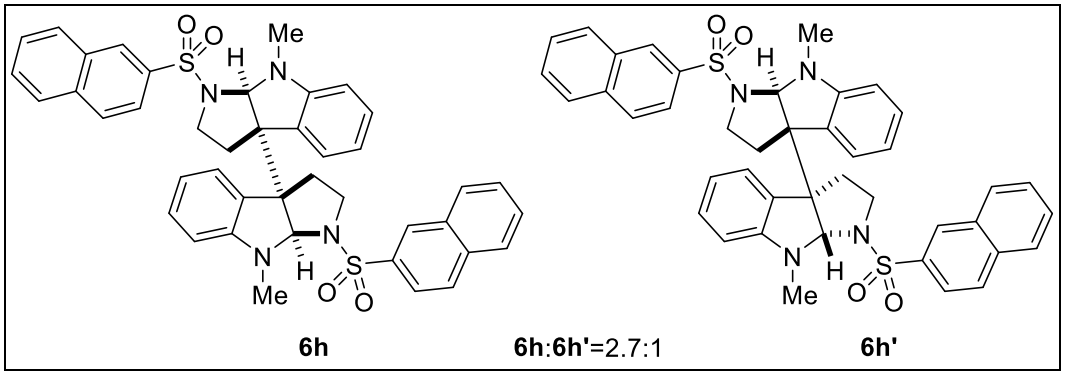
Compound **6f** and **6f′** was obtained (58.9 mg, 93% yield, 2.7:1 dr) via the KI-catalyzed oxidative dimerization of **5f** following the general procedure as pale yellow solid. **m.p.** 123-125°C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 7.6 Hz, 1.55H), 7.74 (t, *J* = 7.2 Hz, 0.85H), 7.58-7.50 (m, 2+1.78H), 7.45-7.39 (m, 8H), 7.23 (t, *J* = 7.6 Hz, 2H), 7.07 (d, *J* = 7.6 Hz, 0.79H), 6.84 (d, *J* = 7.2 Hz, 2H), 6.64 (t, *J* = 7.4 Hz, 2H), 6.51-6.45 (m, 2.74H), 6.31 (d, *J* = 8.0 Hz, 0.73H), 6.21 (d, *J* = 6.0 Hz, 0.63H), 5.06 (s, 2+0.66H), 3.54 (dd, *J* = 7.2 Hz, 4.4 Hz, 0.74H), 3.23 (dd, *J* = 6.8 Hz, 4.8 Hz, 2H), 2.99 (s, 6H), 2.90-2.71 (m, 2+2.94H), 1.92-1.76 (m, 4+0.69H), 1.47-1.42 (m, 0.82H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 151.54, 151.51, 140.08, 139.11, 132.85, 132.21, 129.57, 129.39, 129.28, 128.31, 127.57, 127.13, 127.05, 124.51, 123.32, 117.96, 117.45, 106.99, 106.67, 87.30, 85.42, 62.22, 60.41, 47.65, 47.38, 34.35, 32.58, 31.80, 31.57; **IR** (KBr) 3057, 2947, 1605, 1492, 1344, 1157, 1051, 741, 690 cm^{-1}; **HRMS** (ESI) calcd for $[M+Na]^+$ $C_{34}H_{34}N_4NaO_4S_2$, m/z: 649.1919, found: 649.1916.

8,8'-dimethyl-1,1'-bis((4-nitrophenyl)sulfonyl)-2,2',3,3',8,8a,8',8'a-octahydro-1H,1'H-3a,3'a-bipyrrolo[2,3-b]indole, **6g** and **6g′**:



Compound **6g** and **6g′** was obtained (63.9 mg, 89% yield, 2.6:1 dr) via the KI-catalyzed oxidative dimerization of **5g** following the general procedure as a yellow solid. **m.p.** 127-131℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.35 (d, *J* = 8.8 Hz, 1.54H), 8.16 (d, *J* = 8.8 Hz, 4H), 7.99 (d, *J* = 8.8 Hz, 1.51H), 7.43 (d, *J* = 8.8 Hz, 4H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.11 (t, *J* = 7.8 Hz, 0.83H), 6.75 (d, *J* = 7.2 Hz, 2H), 6.74-6.55 (m, 4+0.78H), 6.36-6.31 (m, 1.47H), 5.22 (s, 0.75H), 4.89 (s, 2H), 3.67 (dd, *J* = 7.2 Hz, 4.0 Hz, 0.81H), 3.27-3.22 (m, 2H), 3.04 (s, 6H), 2.91-2.77 (m, 2+0.98H), 2.62 (s, 2.19H), 2.13 (dd, *J* = 7.2 Hz, 4.8 Hz, 0.84H), 2.01-1.84 (m, 4+0.75H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 151.57, 151.44, 150.06, 149.50, 145.90, 144.63, 130.19, 129.81, 128.17, 128.02, 127.02, 124.70, 124.52, 124.40, 123.61, 118.43, 118.34, 107.60, 107.29, 87.33, 86.03, 62.49, 59.99, 47.70, 47.67, 35.01, 32.79, 32.32, 31.76; **IR** (KBr) 3103, 3057, 2949, 1604, 1492, 1350, 1161, 1091, 740, 686 cm^{-1}; **HRMS** (ESI) calcd for $[M+Na]^+$ $C_{34}H_{32}N_6NaO_8S_2$, m/z: 739.1621, found: 739.1593.

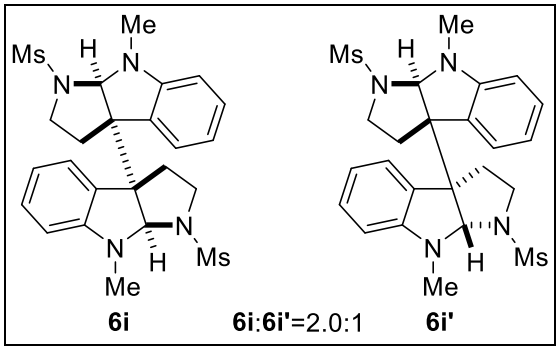
8,8'-dimethyl-1,1'-bis(naphthalen-2-ylsulfonyl)-2,2',3,3',8,8a,8',8'a-octahydro-1H,1'H-3a,3'a-bipyrrolo[2,3-b]indole, **6h** and **6h′**:



Compound **6h** and **6h′** was obtained (65.2 mg, 90% yield, 2.7:1 dr) via the KI-catalyzed oxidative dimerization of **5h** following the general procedure as a white solid. **m.p.** 83-86℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.28 (s, 2+0.60H), 7.98 (d, *J* = 8.4 Hz, 0.77H), 7.93 (d, *J* = 8.0 Hz, 2+0.74H), 7.89 (d, *J* = 8.0 Hz, 2H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 0.74H), 7.68-7.56 (m, 4+2.66H), 7.26 (dd, *J* = 7.2 Hz, 1.6 Hz, 2H), 7.11 (dd, *J* = 7.6 Hz, 0.8 Hz, 2H), 7.05 (dd, *J* = 7.8 Hz, 1.2 Hz,

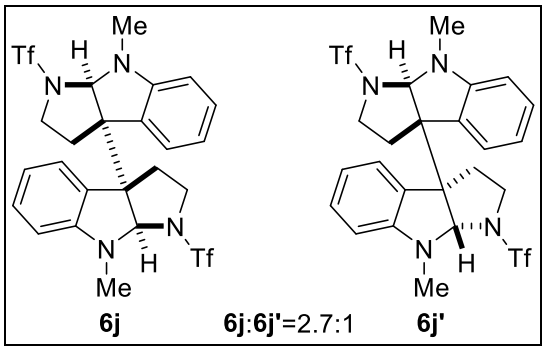
0.73H), 6.77 (d, *J* = 7.2 Hz, 2H), 6.48-6.41 (m, 4+0.79H), 6.30 (d, *J* = 8.0 Hz, 0.74H), 6.14 (d, *J* = 6.4 Hz, 0.69H), 5.21 (s, 0.71H), 5.12 (s, 2H), 3.46 (dd, *J* = 7.2 Hz, 4.4 Hz, 0.74H), 3.30 (dd, *J* = 4.8 Hz, 6.8Hz, 2H), 2.96 (s, 6H), 2.84-2.73 (m, 2+3.37H), 1.87-1.79 (m, 2H), 1.77-1.72 (m, 2H), 1.63-1.59 (m, 1.29H), 1.36-1.22 (m, 1.97H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 151.47, 151.41, 136.63, 135.89, 134.70, 134.59, 132.02, 131.90, 129.93, 129.86, 129.55, 129.37, 129.35, 128.94, 128.87, 128.72, 128.50, 128.25, 128.01, 127.73, 127.70, 127.46, 127.36, 124.32, 123.29, 121.97, 117.66, 117.38, 106.74, 106.64, 87.22, 85.50, 62.14, 60.56, 47.58, 47.47, 34.32, 32.76, 31.80, 31.49; **IR** (KBr) 3057, 2948, 1605, 1340, 1156, 1077, 749, 657 cm^{-1}; **HRMS** (ESI) calcd for $[M+Na]^+$ $C_{42}H_{38}N_4NaO_4S_2$, m/z: 749.2232, found: 749.2201.

8,8'-dimethyl-1,1'-bis(methylsulfonyl)-2,2',3,3',8,8a,8',8'a-octahydro-1H,1'H-3a,3'a-bipyrrolo[2,3-b]indole, **6i** and **6i′**:



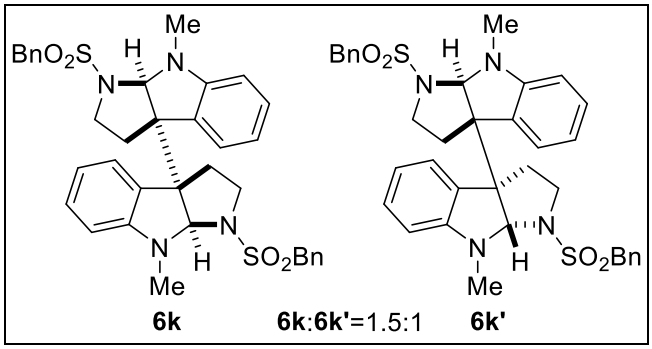
Compound **6i** and **6i′** was obtained (38.5 mg, 77% yield, 2.0:1 dr) via the KI-catalyzed oxidative dimerization of **5i** following the general procedure as a white solid. **m.p.** 243-248℃; **^{1}H NMR** (400 MHz, d_6-DMSO): δ 7.39 (d, *J* = 7.2 Hz, 2H), 7.22 (t, *J* = 7.6 Hz, 2H), 7.12 (d, *J* = 7.6 Hz, 0.99H), 6.71(t, *J* = 7.4 Hz, 2H), 6.63-6.57 (m, 2+0.95H), 6.53 (d, *J* = 8.0 Hz, 1.02H), 5.08 (s, 1.00H), 4.40 (s, 2H), 4.04 (s, 1.22H), 3.62-3.53 (m, 2+0.66H), 3.34 (s, 6H), 2.91 (s, 2.74H), 2.80 (s, 6H), 2.75- 2.53(m, 2+5.44H), 2.34-2.23 (m, 4+0.21H), 2.14 (s, 6H); **^{13}C NMR** (150 MHz, d_6-DMSO): δ 157.15, 156.60, 134.97, 134.57, 134.45, 132.73, 130.78, 128.98, 123.10, 122.65, 112.76, 111.66, 91.21, 90.72, 67.40, 65.82, 53.17, 52.26, 43.39, 40.80, 39.39, 38.17, 37.64, 36.12; **IR** (KBr) 1602, 1493, 1328, 1150, 1085, 764, 601, 518 cm^{-1}; **HRMS** (ESI) calcd for $[M+Na]^+$ $C_{24}H_{30}N_4NaO_4S_2$, m/z: 525.1606, found: 525.1589.

8,8'-dimethyl-1,1'-bis((trifluoromethyl)sulfonyl)-2,2',3,3',8,8a,8',8'a-octahydro-1H,1'H-3a,3'a-bipyrrolo[2,3-b]indole, **6j** and **6j′**:



Compound **6j** and **6j′** was obtained (52.3 mg, 80% yield, 2.7:1 dr) via the KI-catalyzed oxidative dimerization of **5j** following the general procedure as a white solid. **m.p.** 166-170℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.25 (t, *J* = 7.6 Hz, 2H), 7.19-7.14 (m, 2+0.76H), 6.81 (t, *J* = 7.4 Hz, 2H), 6.61 (t, *J* = 7.2 Hz, 0.75H), 6.51 (d, *J* = 7.6 Hz, 2H), 6.39-6.32 (m, 1.28H), 5.27 (s, 0.66H), 4.84 (s, 2H), 3.89-3.83 (m, 0.75H), 3.70 (dd, *J* = 7.2 Hz, 4.0 Hz, 2H), 3.16-3.08 (m, 0.83H), 3.03-2.97 (m, 2H), 2.93 (s, 6H), 2.67-2.59 (m, 2+2.18H), 2.39-2.35 (m, 1.43H), 2.31 (dd, *J* = 7.6 Hz, 4.4 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 150.98, 150.46, 130.47, 130.09, 127.30, 126.20, 124.80, 124.29, 123.56, 121.76, 121.58, 118.77, 118.54, 118.40, 118.37, 115.15, 107.10, 87.64, 86.91, 62.53, 61.14, 48.90, 48.45, 35.04, 33.12, 32.12, 31.75; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -73.52, -75.64; **IR** (KBr) 3057, 2956, 1605, 1343, 1147, 1078, 750, 626, 598 cm^{-1}; **HRMS** (ESI) calcd for $[M+Na]^+$ $C_{24}H_{24}F_6N_4NaO_4S_2$, m/z: 633.1041, found: 633.1015.

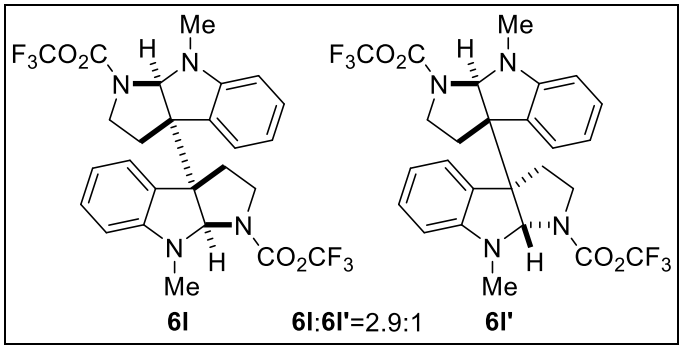
1,1'-bis(benzylsulfonyl)-8,8'-dimethyl-2,2',3,3',8,8a,8',8'a-octahydro-1H,1'H-3a,3'a-bipyrrolo[2,3-b]indole, **6k** and **6k′**:



Compound **6k** and **6k′** was obtained (58.5 mg, 89% yield, 1.5:1 dr) via the KI-catalyzed oxidative dimerization of **5k** following the general procedure as a white solid. **m.p.** 211-213℃; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.31-7.21 (m, 15.77H), 7.19 (d, *J* = 12.6 Hz, 2H), 7.16-7.13 (m, 5.55H), 6.68 (t, *J* = 7.5 Hz, 2H), 6.59-6.55 (m, 2+1.27H), 6.41 (d, *J* = 7.8 Hz, 1.36H), 5.17 (s, 0.85H), 4.85 (s, 2H), 4.19 (q, *J* = 13.2 Hz, 2.74H), 3.77 (q, *J* = 13.2 Hz, 2H), 3.53 (dd, *J* = 7.8 Hz, 4.2 Hz, 2H), 3.40 (t, *J* = 8.4

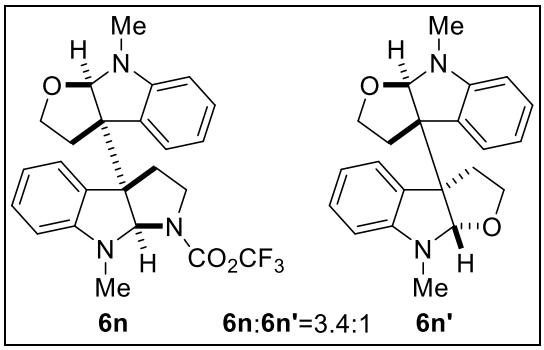
Hz, 1.34H), 3.01 (d, J = 13.2 Hz, 2H), 2.89 (s, 6H), 2.83-2.78 (m, 2H), 2.61-2.51 (m, 2+4.92H), 2.23-2.16 (m, 2+1.50H), 2.10-2.07 (m, 1.35H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 152.11, 151.84, 130.88, 130.72, 130.21, 129.55, 129.21, 128.86, 128.54, 128.52, 128.47, 128.41, 128.37, 127.13, 124.90, 123.82, 118.13, 117.59, 107.68, 106.80, 86.12, 85.91, 62.71, 61.03, 59.40, 56.40, 48.10, 47.50, 34.93, 33.64, 33.42, 31.28; **IR** (KBr) 3059, 2950, 1604, 1338,1150, 1075, 738, 624 cm^{-1}; **HRMS** (ESI) calcd for $[M+Na]^+$ $C_{36}H_{38}N_4NaO_4S_2$, m/z: 677.2232, found: 677.2207.

1,1'-(-8,8'-dimethyl-2,2',3,3',8,8a,8',8'a-octahydro-1H,1'H-[3a,3'a-bipyrrolo[2,3-b]indole]-1,1'-diyl)bis(2,2,2-trifluoroethan-1-one), **6l** and **6l′**:



Compound **6l** and **6l′** was obtained (40.5 mg, 75% yield, 2.9:1 dr) via the KI-catalyzed oxidative dimerization of **5l** following the general procedure as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.19-7.13 (m, 2+0.85H), 7.10 (d, J = 7.2 Hz, 2H), 6.69 (t, J = 7.4 Hz, 2H), 6.60 (t, J = 7.4 Hz, 0.72H), 6.43-6.38 (m, 2+1.31H), 5.50 (s, 0.61H), 5.31 (s, 2H), 3.99-3.94 (m, 0.70H), 3.90-3.85 (m, 2 H), 3.26-3.16 (m, 0.72H), 3.11 (td, J = 11.6 Hz, 5.2 Hz, 2H), 3.00 (s, 6H), 2.72(s, 1.84H), 2.50 (td, J = 12.4 Hz, 7.2 Hz, 2H), 2.38-2.25 (m, 2+1.59H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 156.31, 156.27, 156.07, 156.03, 155.82, 155.78, 155.58, 155.54, 130.05, 129.87, 128.03, 127.21, 123.73, 123.58, 119.05, 118.99, 118.10, 117.91, 117.14, 117.08, 115.23, 115.17, 113.32, 113.26, 107.20, 106.62, 84.18, 83.59, 60.11, 59.21, 45.80, 34.60, 33.62, 33.33, 32.89; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -71.66, -71.67; **IR** (KBr) 3056, 2953, 1606, 1349,1143, 1060, 744, 639 cm^{-1}; **HRMS** (ESI) calcd for $[M+Na]^+$ $C_{26}H_{24}F_6N_4NaO_2$, m/z: 561.1701, found: 561.1691.

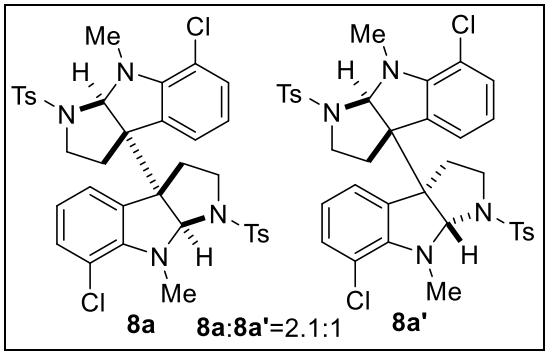
8,8'-dimethyl-2,2',3,3',8,8a,8',8'a-octahydro-3a,3'a-bifuro[2,3-b]indole, **6o** and **6o′**:



Compound **6n** and **6n′** was obtained (32.8 mg, 94% yield, 3.4:1 dr) via the KI-catalyzed oxidative dimerization of **5n** following the general procedure as a colorless oil. Compound **6n** and **6n′** has already been characterized by Ren and co-workers,[3] the configurational assignments of **6n** and **6n′** were confirmed by comparison of the NMRs.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13-7.05 (m, 4+0.50H), 6.60 (t, *J* = 7.2 Hz, 2H), 6.53-6.51 (m, 0.70H), 6.33 (d, *J* = 7.6 Hz, 2H), 6.29 (d, *J* = 7.6 Hz, 0.57H), 5.22 (s, 2H), 5.11 (s, 0.58H), 4.02 (t, *J* = 8.0 Hz, 0.58H), 3.92 (t, *J* = 8.0 Hz, 2H), 3.46-3.40 (m, 0.58H), 3.37-3.30 (m, 2H), 2.92 (s, 6H), 2.72 (s, 1.75H), 2.48-2.39 (m, 2+0.57H), 2.23 (dd, *J* = 7.2 Hz, 4.8 Hz, 0.59H), 2.06 (dd, *J* = 12.0 Hz, 4.8 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 151.88, 151.84, 130.46, 130.28, 128.69, 124.08, 123.86, 116.98, 116.94, 105.02, 104.95, 101.28, 100.72, 66.84, 66.76, 61.35, 60.93, 37.75, 36.76, 30.97, 30.62; **IR** (KBr) 3051, 2942, 1605, 1303, 1156, 1040, 744, 659 cm^{-1}; **HRMS** (ESI) calcd for $[M+Na]^+$ $C_{22}H_{24}N_2NaO_2$, m/z: 371.1735, found: 371.1738.

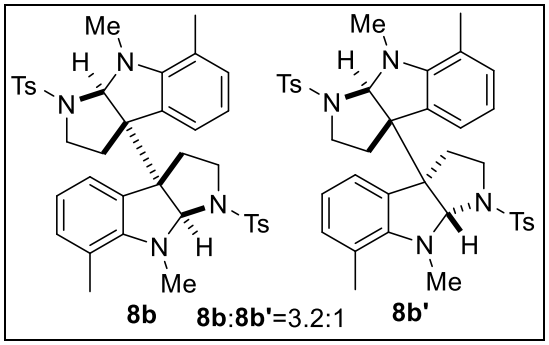
7,7'-dichloro-8,8'-dimethyl-1,1'-ditosyl-2,2',3,3',8,8a,8',8'a-octahydro-1H,1'H-3a,3'a-bipyrrolo[2,3-b]indole, **8a** and **8a′**:



Compound **8a** and **8a′** was obtained (48.5 mg, 68% yield, 2.1:1 dr) via the KI-catalyzed oxidative dimerization of **7a** following the general procedure as a white solid. **m.p.** 86-89°C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.0 Hz, 0.86H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.30-7.26 (m, 2+0.90H), 7.06 (dd, *J* = 8.0 Hz, 1.2 Hz, 1H), 7.03 (dd, *J* = 8.0 Hz, 1.2 Hz, 0.44H), 6.75 (dd, *J* = 7.6 Hz, 1.2 Hz, 1H),

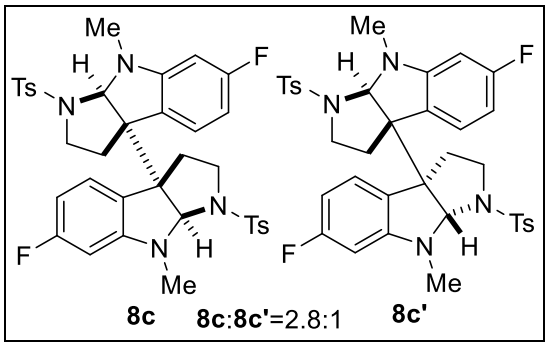
6.59-6.52 (m, 1+0.44H), 6.18 (bs, 0.38H), 5.05 (s, 0.40H), 4.99 (s, 1H), 3.65-3.59 (m, 0.48H), 3.45-3.39 (m, 1H), 3.32 (s, 3H), 2.90 (s, 1.09H), 2.77-2.69 (m, 1+0.46H), 2.42 (s, 3H), 2.41 (s, 1.33H), 2.12-1.93 (m, 2H), 1.82 (dd, *J* = 12.4 Hz, 4.8 Hz, 0.93H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 147.87, 146.62, 143.50, 143.39, 136.83, 136.45, 132.89, 131.65, 131.34, 131.25, 129.86, 129.60, 127.29, 127.18, 123.01, 122.06, 120.29, 119.22, 116.57, 115.17, 88.52, 88.08, 62.52, 60.91, 46.86, 46.64, 37.09, 36.23, 34.53, 33.53, 21.49; **IR** (KBr) 3065, 2949, 1598, 1344, 1159, 1093, 733, 663 cm^{-1}; **HRMS** (ESI) calcd for $[M+Na]^+$ $C_{36}H_{36}Cl_2N_4NaO_4S_2$, m/z: 745.1447, found: 745.1425.

7,7',8,8'-tetramethyl-1,1'-ditosyl-2,2',3,3',8,8a,8',8'a-octahydro-1H,1'H-3a,3'a-bipyrrolo[2,3-b]indole, **8b** and **8b′**:



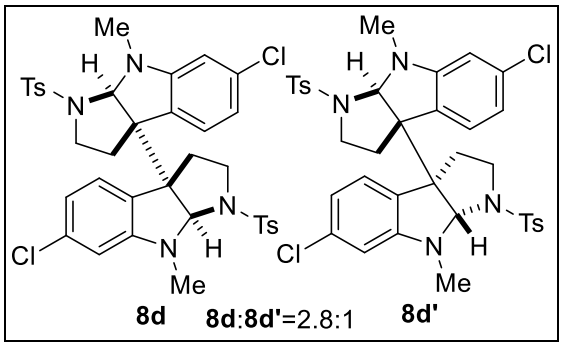
Compound **8b** and **8b′** was obtained (64.1 mg, 94% yield, 3.2:1 dr) via the KI-catalyzed oxidative dimerization of **7b** following the general procedure as a white solid. **m.p.** 105-108℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.4 Hz, 1.34H), 7.48 (d, *J* = 8.0 Hz, 4H), 7.26-7.21 (m, 4+1.60H), 6.90 (d, *J* = 7.2 Hz, 2H), 6.80 (d, *J* = 7.6 Hz, 0.64H), 6.76 (d, *J* = 7.2 Hz, 2H), 6.61 (t, *J* = 7.6 Hz, 2H), 6.52 (bs, 0.48H), 4.98 (bs, 0.62H), 4.86 (s, 2H), 3.64 (dd, *J* = 9.6 Hz, 7.6 Hz, 0.62H), 3.32 (dd, *J* = 10.8 Hz, 7.6 Hz, 2H), 3.20 (s, 6H), 2.79-2.71 (m, 2+1.14H), 2.41 (s, 6H), 2.39 (s, 2.04H), 2.31 (s, 6H), 2.27-2.13 (m, 1.14H), 2.09-1.99 (m, 2+2.47H), 1.83 (dd, *J* = 12.0 Hz, 4.8 Hz, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 149.73, 143.02, 142.86, 137.66, 136.90, 132.62, 131.91, 129.63, 129.29, 129.12, 127.21, 127.15, 122.59, 121.45, 120.02, 119.93, 118.94, 89.25, 89.07, 62.76, 60.54, 46.71, 46.52, 38.62, 37.24, 34.78, 33.34, 21.45, 21.40, 19.20, 18.57; **IR** (KBr) 3054, 2958, 1596, 1340, 1158, 1072, 737, 671 cm^{-1}; **HRMS** (ESI) calcd for $[M+Na]^+$ $C_{38}H_{42}N_4NaO_4S_2$, m/z: 705.2545, found: 705.2510.

6,6'-difluoro-8,8'-dimethyl-1,1'-ditosyl-2,2',3,3',8,8a,8',8'a-octahydro-1H,1'H-3a,3'a-bipyrrolo[2,3-b]indole, **8c** and **8c′**:



Compound **8c** and **8c′** was obtained (57.1 mg, 83% yield, 2.8:1 dr) via the KI-catalyzed oxidative dimerization of **7c** following the general procedure as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.0 Hz, 1.46H), 7.41-7.36 (m, 4+1.46H), 7.22 (d, *J* = 8.0 Hz, 4H), 6.66 (dd, *J* = 7.6 Hz, 5.2 Hz, 2H), 6.23-6.13 (m, 4+1.35H),6.02 (d, *J* = 10 Hz, 0.73H), 4.98 (s, 0.73H), 4.96 (s, 2H), 3.54 (dd, *J* = 12.0 Hz, 7.2 Hz, 0.73H), 3.35-3.30 (m, 2H), 2.96 (s, 6H), 2.91-2.74 (m, 2+2.97H), 2.47 (s, 2.07H), 2.44 (s, 6H), 1.80-1.66 (m, 4+0.92H), 1.37-1.30 (m, 0.81H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 165.42, 165.40, 163.81, 163.78, 153.26, 153.18, 153.07, 152.99, 144.12, 143.31, 136.82, 135.99, 130.01, 129.93, 127.11, 126.96, 124.99, 124.92, 123.88, 123.81, 123.55, 122.90, 103.84, 103.69, 103.47, 103.31, 94.97, 94.80, 94.48, 94.30, 87.10, 85.51, 61.60, 60.09, 47.66, 47.63, 34.33, 32.59, 31.43, 31.33, 21.53, 21.46; **^{19}F NMR** (376 MHz, $CDCl_3$): δ -111.89, -112.37; **IR** (KBr) 3061, 2950, 1614, 1345, 1158, 1093, 738, 692 cm^{-1}; **HRMS** (ESI) calcd for $[M+Na]^+$ $C_{36}H_{36}F_2N_4NaO_4S_2$, m/z: 713.2044, found: 713.2016.

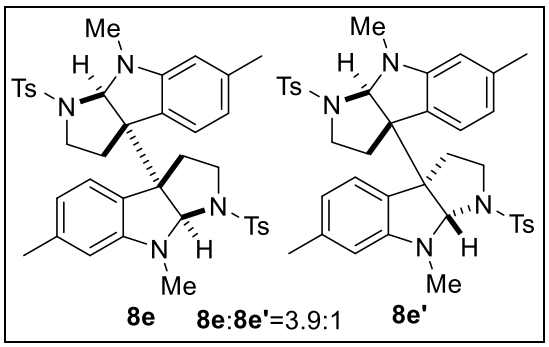
6,6'-dichloro-8,8'-dimethyl-1,1'-ditosyl-2,2',3,3',8,8a,8',8'a-octahydro-1H,1'H-3a,3'a-bipyrrolo[2,3-b]indole, **8d** and **8d′**:



Compound **8d** and **8d′** was obtained (50.3 mg, 70% yield, 2.8:1 dr) via the KI-catalyzed oxidative dimerization of **7d** following the general procedure as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.43 (d, *J* = 8.4 Hz, 0.62H), 7.39-7.34 (m, 2+0.62H), 7.24 (d, *J* = 8.0 Hz, 2H), 6.62 (d, *J* = 8.4 Hz, 1H), 6.50-6.45 (m, 2+0.39H), 6.30 (d, *J* = 1.6 Hz, 0.32H), 6.16 (bs, 0.29H), 5.00 (s, 0.27H), 4.93(s, 1H),

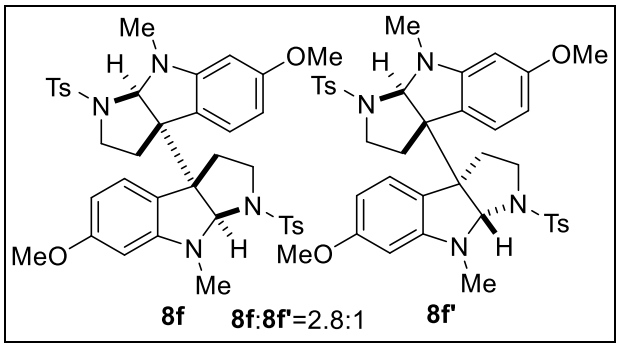
3.54 (dd, *J* = 12.0 Hz, 7.2 Hz, 0.33H), 3.45-3.30 (m, 1H), 2.97(s, 3H), 2.88-2.74 (m, 1+1.26H), 2.47 (s, 0.90H), 2.45 (s, 3H), 1.75-1.68 (m, 2+0.39H), 1.40-1.31(m, 0.42H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 152.66, 152.44, 144.15, 143.33, 136.76, 135.83, 135.51, 135.35, 130.02, 129.94, 126.98, 126.87, 126.65, 126.02, 125.04, 123.89, 117.66, 117.20, 107.26, 106.75, 86.89, 85.27, 61.60, 59.96, 47.62, 34.30, 32.42, 31.43, 31.30, 21.56, 21.51. **IR** (KBr) 3056, 2924, 1600, 1345, 1159, 1092, 739, 660 cm^{-1}; **HRMS** (ESI) calcd for $[M+Na]^+$ $C_{36}H_{36}Cl_2N_4NaO_4S_2$, m/z: 745.1447, found: 745.1421.

6,6',8,8'-tetramethyl-1,1'-ditosyl-2,2',3,3',8,8a,8',8'a-octahydro-1H,1'H-3a,3'a-bipyrrolo[2,3-b]indole, **8e** and **8e′**:



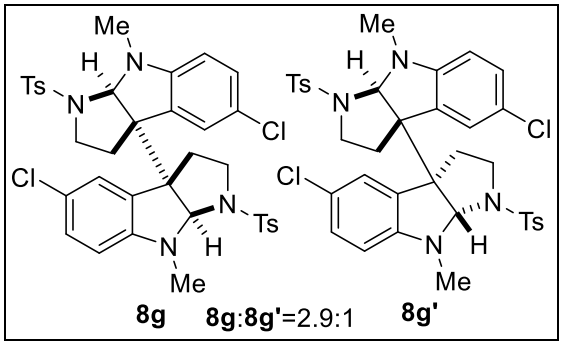
Compound **8e** and **8e′** was obtained (61.6 mg, 90% yield, 3.9:1 dr) via the KI-catalyzed oxidative dimerization of **7e** following the general procedure as a white solid. **m.p.** 188-195℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.0 Hz, 1.02H), 7.36-7.31 (m, 4+1.02H), 7.18 (d, *J* = 8.0 Hz, 4H), 6.70(d, *J* = 7.6 Hz, 2H), 6.43 (d, *J* = 7.6 Hz, 2H), 6.32 (s, 2H), 6.29 (d, *J* = 7.6 Hz, 0.51H), 6.14-6.09 (m, 0.91H), 4.99 (s, 2H), 4.98 (s, 0.51H), 3.48 (dd, *J* = 12.0 Hz, 7.2 Hz, 0.51H), 3.19 (dd, *J* = 11.6 Hz, 7.2 Hz, 2H), 2.96 (s, 6H), 2.88-2.80 (m, 0.57H), 2.78-2.70 (m, 2+1.54H) , 2.45 (s, 1.55H), 2.42 (s, 6H), 2.37 (s, 6H), 2.24 (s, 1.53H), 1.85-1.77 (m, 2H), 1.74-1.67 (m, 2+0.56H), 1.38-1.29 (m, 1.09H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 151.82, 151.71, 143.74, 142.84, 139.27, 139.21, 137.11, 136.16, 129.86, 129.76, 127.16, 127.00, 125.63, 125.04, 124.29, 123.00, 118.49, 118.08, 107.86, 107.45, 87.56, 85.69, 61.86, 60.13, 47.60, 47.42, 34.32, 32.49, 31.60, 31.47, 21.81, 21.64, 21.50; **IR** (KBr) 3046, 2948, 1612, 1343, 1159, 1093, 740, 692 cm^{-1}; **HRMS** (ESI) calcd for $[M+Na]^+$ $C_{38}H_{42}N_4NaO_4S_2$, m/z: 705.2545, found: 705.2516.

6,6'-dimethoxy-8,8'-dimethyl-1,1'-ditosyl-2,2',3,3',8,8a,8',8'a-octahydro-1H,1'H-3a,3'a-bipyrrolo[2,3-b]indole, **8f** and **8f′**:



Compound **8f** and **8f′** was obtained (79% yield, 2.8:1 dr) via the KI-catalyzed oxidative dimerization of **7f** following the general procedure as a white solid. **m.p.** 163-165°C; **^{1}H NMR**[7] (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.0 Hz, 0.30H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.71 (d, *J* = 10.4 Hz, 0.14H), 6.67 (d, *J* = 8.0 Hz, 0.93H), 6.13 (dd, *J* = 8.4 Hz, 2.4 Hz, 1H), 6.06 (d, *J* = 2.0 Hz, 1H), 6.01 (dd, *J* = 8.0 Hz, 1.6 Hz, 0.11H), 5.88 (d, *J* = 2.0 Hz, 0.11H), 5.00 (s, 1H), 4.96 (s, 0.11H), 3.85 (s, 3H), 3.74(s, 0.34H), 3.50 (dd, *J* = 12 Hz, 7.2 Hz, 0.12H), 3.23 (dd, *J* = 11.6 Hz, 6.8 Hz, 1H), 2.97 (s, 3H), 2.91-2.84 (m, 0.23H), 2.81-2.74 (m, 1.25H), 2.46 (s, 0.36H), 2.43 (s, 3H), 1.82-1.67 (m, 2H), 1.35-1.29 (m, 0.27H); **^{13}C NMR**[7] (100 MHz, CD_3CN): δ 162.91, 154.12, 145.81, 144.92, 138.20, 137.56, 131.63, 131.31, 128.27, 128.22, 126.24, 125.36, 121.44, 104.24, 103.63, 94.72, 94.35, 88.94, 87.31, 61.69, 56.36, 49.20, 49.02, 35.23, 33.63, 32.55, 21.99; **IR** (KBr) 2948, 1618, 1597, 1331, 1158, 1091, 748, 659 cm^{-1}; **HRMS** (ESI) calcd for $[M+Na]^+$ $C_{38}H_{42}N_4NaO_6S_2$, m/z: 737.2438, found: 737.2409.

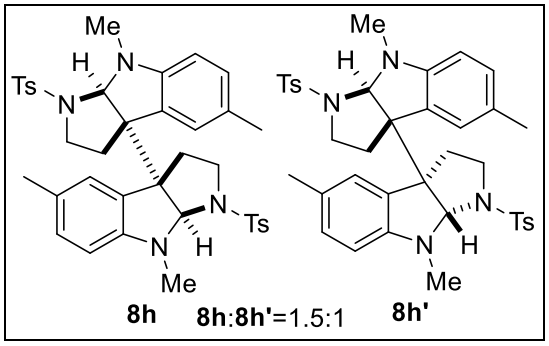
5,5'-dichloro-8,8'-dimethyl-1,1'-ditosyl-2,2',3,3',8,8a,8',8'a-octahydro-1H,1'H-3a,3'a-bipyrrolo[2,3-b]indole, **8g** and **8g′**:



Compound **8g** and **8g′** was obtained (79% yield, 2.9:1 dr) via the KI-catalyzed oxidative dimerization of **7g** following the general procedure as a colorless oil. **^{1}H NMR**[8] (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.0 Hz, 2.58H), 7.39 (d, *J* = 8.0 Hz, 2.58H), 7.22-7.20 (m, 10H), 7.07 (dd, *J* = 8.4 Hz, 2.0 Hz, 1.29H), 6.71 (d, *J* = 2.0 Hz, 2H), 6.48 (d, *J* = 8.4 Hz, 2H), 6.26 (d, *J* = 8.4 Hz, 1.28H), 6.15 (bs, 1.28H), 5.00 (s, 2H), 4.95(s, 1.30H), 3.54 (dd, *J* = 12.0 Hz, 7.2 Hz, 1.29H), 3.23 (dd, *J* = 12.0 Hz, 6.8 Hz, 2H), 3.01 (s, 6H), 2.91-2.77 (m, 2+5.46H), 2.48 (s, 4.00H), 2.45 (s, 6H), 1.78-1.67 (m, 4+1.39H), 1.35-1.28 (m,

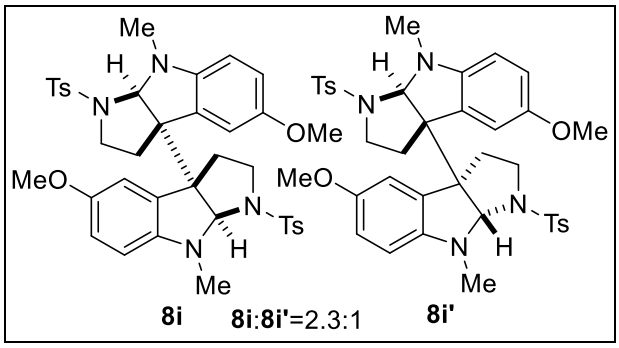
1.86H); **^{13}C NMR**[8] (100 MHz, $CDCl_3$): δ 150.36, 150.06, 144.19, 143.52, 136.79, 135.48, 130.10, 130.06, 129.65, 129.60, 129.42, 129.18, 127.03, 126.92, 124.91, 123.43, 122.63, 122.07, 108.03, 107.33, 87.21, 85.34, 61.98, 59.90, 47.74, 47.44, 34.03, 32.30, 31.64, 31.55, 21.58; **IR** (KBr) 3059, 2925, 1599, 1340, 1159, 1092, 742, 661 cm^{-1}; **HRMS** (ESI) calcd for $[M+Na]^+$ $C_{34}H_{34}Cl_2N_4NaO_4S_2$, m/z: 745.1453, found: 745.1421.

5,5',8,8'-tetramethyl-1,1'-ditosyl-2,2',3,3',8,8a,8',8'a-octahydro-1H,1'H-3a,3'a-bipyrrolo[2,3-b]indole, **8h** and **8h′**:



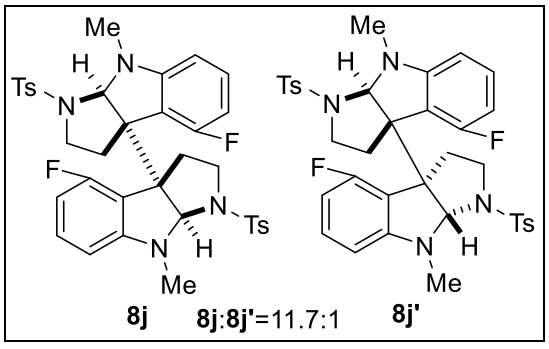
Compound **8h** and **8h′** was obtained (63.3 mg, 93% yield, 1.5:1 dr) via the KI-catalyzed oxidative dimerization of **7h** following the general procedure as a white solid. **m.p.** 219-223℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.0 Hz, 2.77H), 7.35 (d, *J* = 8.0 Hz, 2.87H), 7.32 (d, *J* = 8.0 Hz, 4H), 7.16 (d, *J* = 8.0 Hz, 4H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.87 (d, *J* = 8.0 Hz, 1.35H), 6.61 (s, 2H), 6.41 (d, *J* = 7.6 Hz, 2H), 6.20 (d, *J* = 7.6 Hz, 1.36H), 5.96 (s, 1.24H), 5.07 (s, 2H), 4.95 (s, 1.37H), 3.50 (dd, *J* = 12.0 Hz, 7.6 Hz, 1.37H), 3.19 (dd, *J* = 11.2 Hz, 6.8 Hz, 2H), 2.96 (s, 6H), 2.86 (td, *J* = 12.4 Hz, 4.8 Hz, 1.46H), 2.74 (td, *J* = 11.6 Hz, 4.8 Hz, 2H), 2.68 (s, 3.63H), 2.45 (s, 4.11H), 2.41 (s, 6H), 2.20 (s, 6H), 2.07 (s, 4.11H), 1.85-1.70 (m, 4+1.38H), 1.38-1.30 (m, 1.68H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 149.65, 149.57, 143.73, 142.69, 137.11, 136.14, 129.85, 129.82, 129.50, 128.51, 127.90, 127.12, 127.00, 126.50, 126.44, 125.70, 124.13, 106.86, 106.35, 87.52, 85.71, 62.21, 60.14, 47.67, 47.48, 34.01, 32.37, 31.95, 31.69, 21.50, 21.46, 21.00, 20.63; **IR** (KBr) 3024, 2922, 1598, 1340, 1158, 1092, 754, 658 cm^{-1}; **HRMS** (ESI) calcd for $[M+Na]^+$ $C_{38}H_{42}N_4NaO_4S_2$, m/z: 705.2545, found: 705.2515.

5,5'-dimethoxy-8,8'-dimethyl-1,1'-ditosyl-2,2',3,3',8,8a,8',8'a-octahydro-1H,1'H-3a,3'a-bipyrrolo[2,3-b]indole, **8i** and **8i′**:



Compound **8i** and **8i′** was obtained (52.5 mg, 73% yield, 2.3:1 dr) via the KI-catalyzed oxidative dimerization of **7i** following the general procedure as a white solid. **m.p.** 199-203℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.62 (d, *J* = 8.4 Hz, 4H), 7.36 (d, *J* = 8.0 Hz, 4H), 7.27 (d, *J* = 8.0 Hz, 2.20H), 7.17 (d, *J* = 8.0 Hz, 1.89H), 6.81 (dd, *J* = 8.4 Hz, 2.4 Hz, 0.92H), 6.66 (dd, *J* = 8.4 Hz, 2.4 Hz, 2H), 6.44 (d, *J* = 8.4 Hz, 0.98H), 6.41 (d, *J* = 2.4 Hz, 0.93H), 6.25 (d, *J* = 8.4 Hz, 2H), 5.87 (s, 2H), 5.05 (s, 0.92H), 4.99 (s, 2H), 3.70 (s, 2.78H), 3.55 (s, 6H), 3.52-3.48 (m, 2H), 3.19 (dd, *J* = 11.6 Hz, 6.8 Hz, 0.95H), 2.95 (s, 2.77H), 2.84 (td, *J* = 12.4 Hz, 4.8 Hz, 2H), 2.77-2.69 (m, 6+0.94H), 2.46 (s, 6H), 2.42 (s, 2.78H), 1.84-1.69 (m, 2+2.02H), 1.39-1.25 (m, 2+1.14H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 152.42, 152.39, 146.11, 143.85, 142.93, 137.00, 135.86, 129.90, 129.83, 129.64, 128.99, 127.11, 127.04, 114.55, 114.09, 111.99, 110.48, 107.50, 107.23, 87.98, 86.00, 62.13, 60.19, 56.02, 55.51, 47.62, 47.39, 34.24, 32.47, 32.39, 31.99, 21.54, 21.43; **IR** (KBr) 3057, 2949, 1597, 1344, 1158, 1092, 738, 659 cm^{-1}; **HRMS** (ESI) calcd for $[M+Na]^+$ $C_{38}H_{42}N_4NaO_6S_2$, m/z: 737.2443, found: 737.2411.

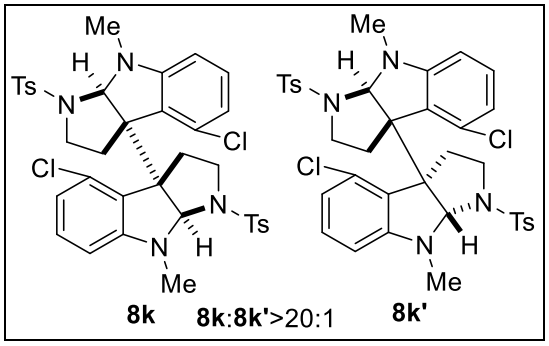
4,4'-difluoro-8,8'-dimethyl-1,1'-ditosyl-2,2',3,3',8,8a,8',8'a-octahydro-1H,1'H-3a,3'a-bipyrrolo[2,3-b]indole, **8j** and **8j′**:



Compound **8j** and **8j′** was obtained (53.9 mg, 72% yield, 11.7:1 dr) via the KI-catalyzed oxidative dimerization of **7j** following the general procedure as a white solid. **m.p.** 215-218℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.28 (d, *J* = 8.4 Hz, 2H), 7.18-7.13 (m, 3H), 6.29-6.24 (m, 2H), 5.14 (s, 1H), 3.32 (dd, *J* = 12.0 Hz, 7.2 Hz, 2H), 3.30 (s, 3H), 2.88 (td, *J* = 11.6 Hz, 4.0 Hz, 1H), 2.42 (s, 3H), 2.26 (dd,

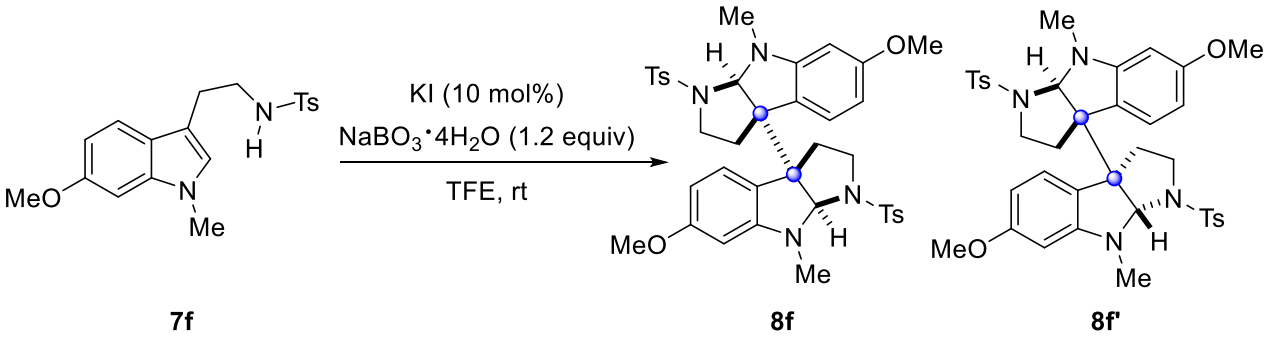
J = 12.4 Hz, 4.4 Hz, 1H), 1.59-1.50 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 160.68, 158.25, 153.89, 153.80, 143.04, 135.81, 131.50, 131.40, 129.88, 126.94, 112.22, 112.06, 105.68, 105.45, 102.87, 102.85, 87.41, 87.39, 61.48, 48.30, 31.63, 31.22, 31.19, 21.53; **IR** (KBr) 3064, 2925, 1595, 1346, 1160, 1093, 743, 658 cm^{-1}; ^{19}F NMR (376 MHz, $CDCl_3$): δ -116.10; **HRMS** (ESI) calcd for $[M+Na]^+$ $C_{36}H_{36}F_2N_4NaO_4S_2$, m/z: 713.2038, found: 713.2020.

4,4'-dichloro-8,8'-dimethyl-1,1'-ditosyl-2,2',3,3',8,8a,8',8'a-octahydro-1H,1'H-3a,3'a-bipyrrolo[2,3-b]indole, **8k** and **8k′**:



Compound **8k** and **8k′** was obtained (33.6 mg, 46% yield, >20:1 dr) via the KI-catalyzed oxidative dimerization of **7k** following the general procedure as a white solid. **m.p.** 198-202℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.19-7.15 (m, 3H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.58 (d, *J* = 8.0 Hz, 1H), 6.45 (d, *J* = 8.0 Hz, 1H), 5.15 (s, 1H), 3.24 (dd, *J* = 11.6 Hz, 6.8 Hz, 1H), 3.02 (s, 3H), 2.87-2.74 (m, 2H), 2.41 (s, 3H), 1.62-1.53 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 153.94, 142.97, 135.25, 131.71, 130.94, 129.87, 126.90, 122.90, 120.19, 105.79, 87.71, 63.19, 48.79, 31.71, 30.80, 21.50; **IR** (KBr) 3057, 2924, 1598, 1341, 1159, 1092, 743, 659 cm^{-1}; **HRMS** (ESI) calcd for $[M+Na]^+$ $C_{36}H_{36}Cl_2N_4NaO_4S_2$, m/z: 745.1453, found: 745.1420. Relative configuration of **8k** is confirmed by HPLC (IA-3, Hexane/Isopropanol 70/30, flow rate = 1.0 mL/min, 240 nm): tr_1 =9.07 min; tr_2 = 12.06 min.

5. Gram-scale of KI-catalyzed oxidative dimerization reactions



To a dry 100 mL reaction round-bottom flask were added tryptamine **7f** (1.00 g, 2.79 mmol, 1.0 equiv), KI (46.3 mg, 0.279 mmol, 0.1 equiv), TFE (28 mL) and $NaBO_3$•$4H_2O$ (515 mg, 3.35 mmol, 1.2 equiv) successively under argon atmosphere. The reaction system was stirred at room temperature until TLC indicated that **7f** disappeared (3h). The mixture was then quenched with saturated $Na_2S_2O_3$ (aqueous) and extracted with EtOAc (60 mL). The organic layer was washed with brine (15 mL), dried over Na_2SO_4, filtered, and concentrated by vacuo. The residue was purified by flash column chromatography (Toluene:EtOAc=200:1 to 60:1) to afford the dimeric products **8f** and **8f′** (69% yield, 2.8:1 dr). The dr of **8f/8f'** were determined by ^{1}H NMR (Fig. S7).

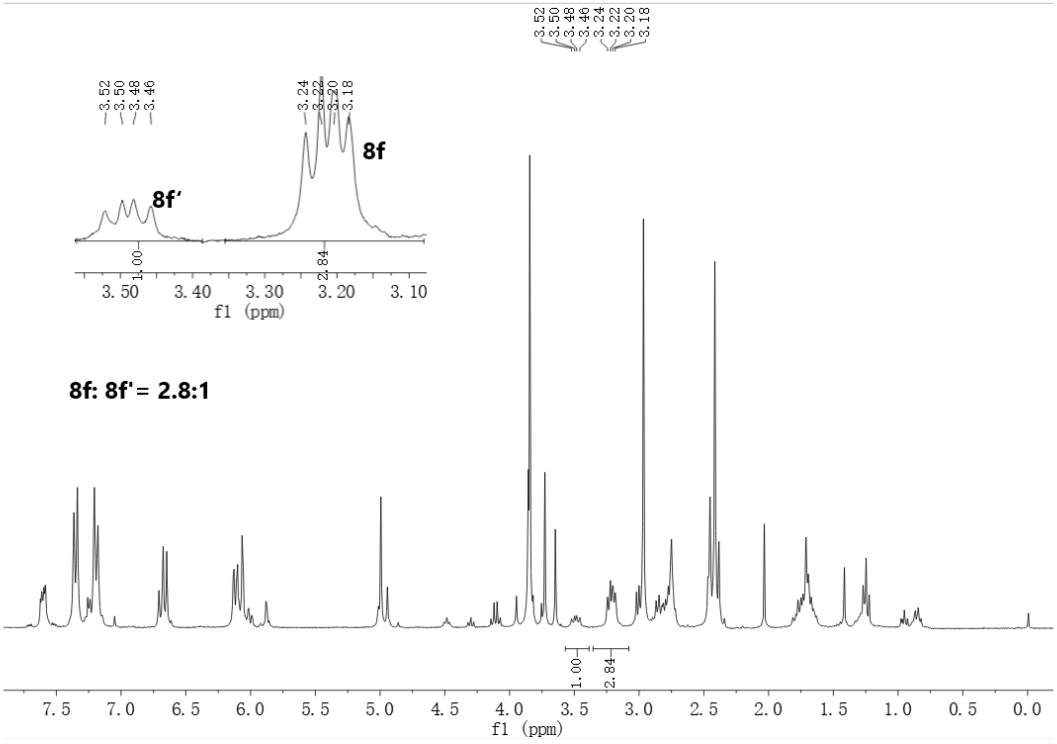
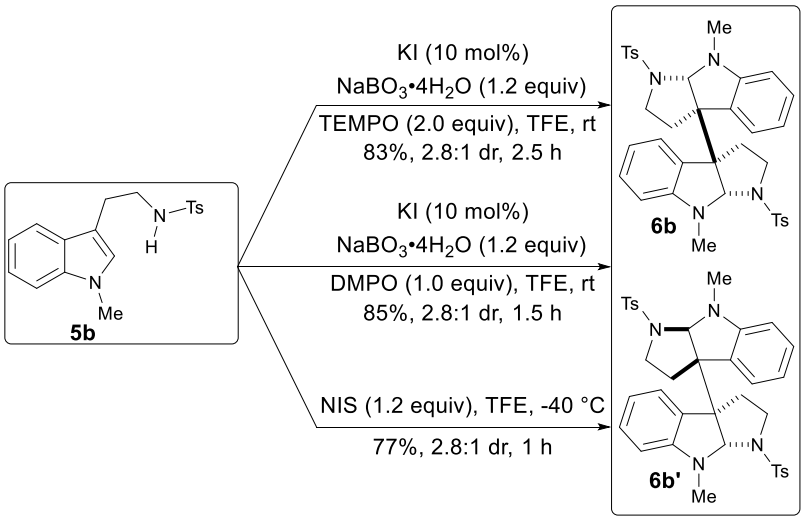
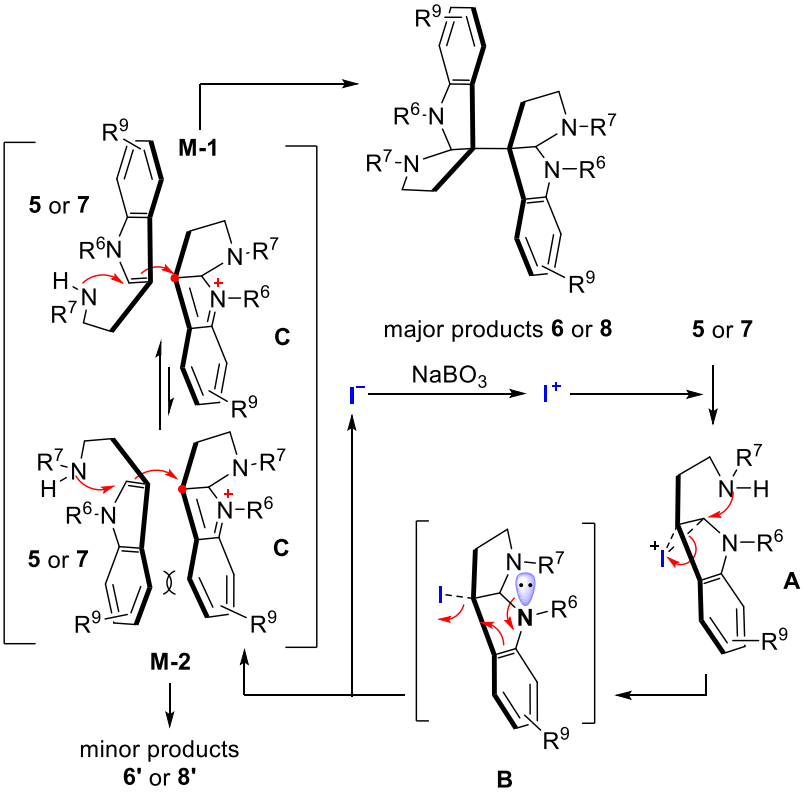


Figure S7. The dr of **8f/8f'** were determined by ^{1}H NMR.

6. Additional description of the proposed mechanism

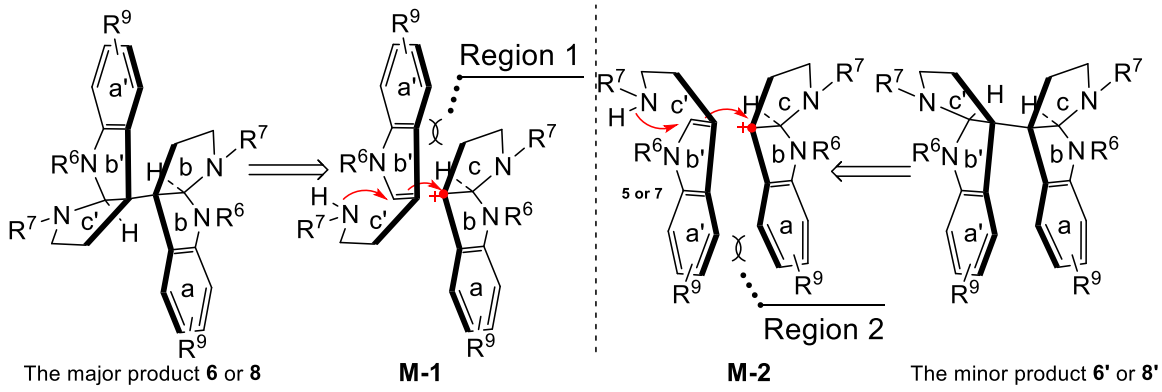


Scheme S1. Control experiments for the mechanistic study.



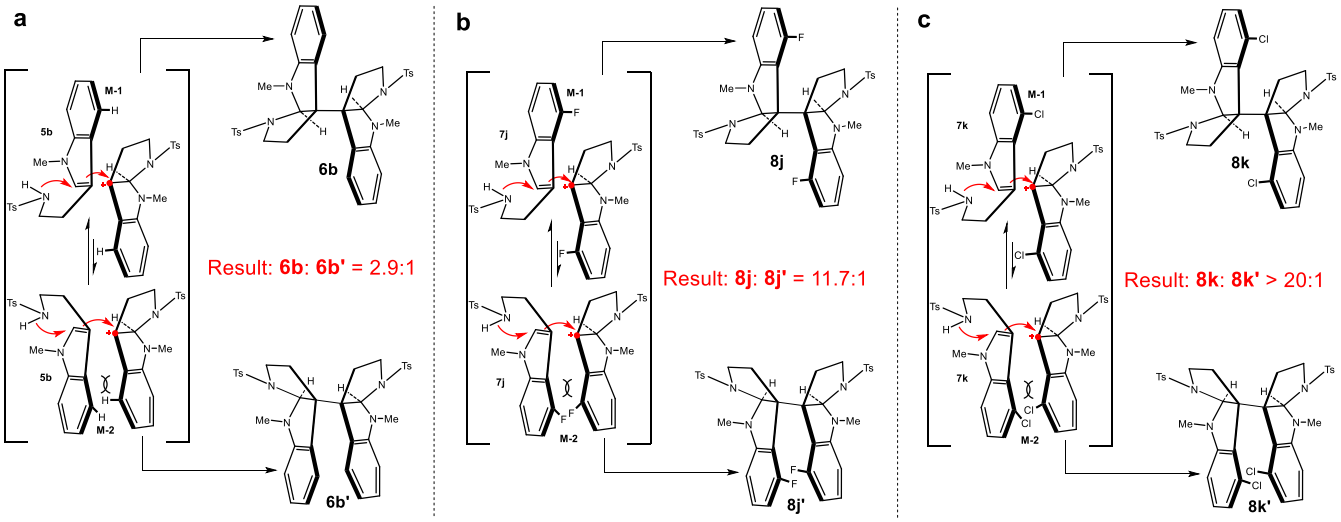
Scheme S2. The plausible mechanism of electrophilic (hypo)iodites "I^+" pathway in our reaction

In our manuscript, we have already elucidated the mechanism (Scheme S2) of the catalytic oxidative coupling/cyclizations reaction according to the control experiments (Scheme S1). Herein, we will make an interpretation of the proposed stereo-control model (Scheme S2) based on our experimental results and previous reports.



Scheme S3. The proposed stereo-control model

According to the proposed model (Scheme S3), the observed major product **6** or **8** could be obtained from stereo-control model **M-1**, while the minor product **6′** or **8′** was generated via **M-2**. Therefore, we suspect that the key to the diastereoselectivity of our reaction lies in the difference in steric hindrance between the above two models. As shown in Scheme S3, the main steric hindrance of **M-1** and **M-2** lie in **Region 1**(the steric hindrance between pyrrolidine "**c**" of the carbocation intermediate and the aromatic ring region of another tryptamine) and **Region 2** (the steric hindrance between aromatic ring region of the carbocation intermediate and the aromatic ring region of another tryptamine) respectively. Since the later behaved to be more hindered than the former, the reaction gives the dimeric **6** or **8** rather than **6′** or **8′** as the major product.

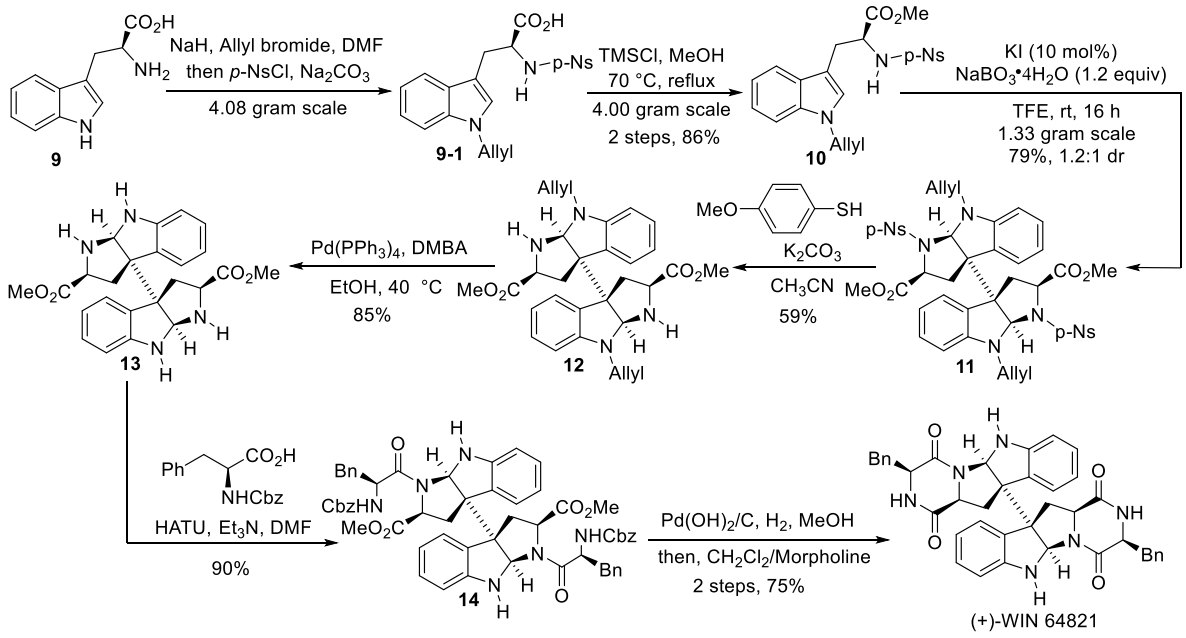


Scheme S4. The observed diastereoselectivity in our reaction

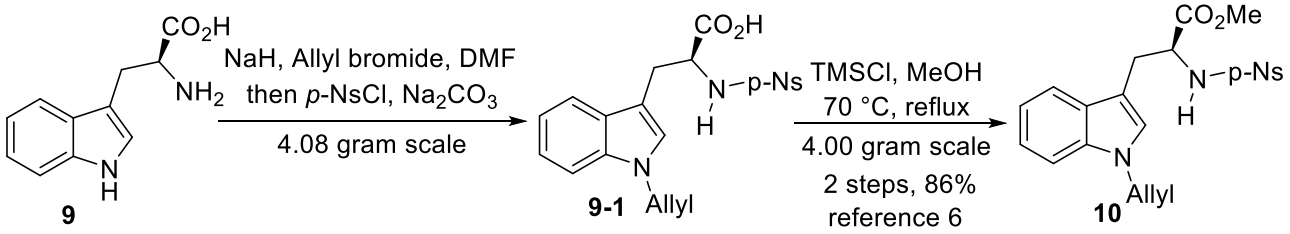
Based on the stereo-control model, the substituents at C_4 of tryptamine substrates might have great influence on the stereoselectivity of the reaction. To further illustrate this model, the reaction of **5b**, **7j** and **7k** were selected for discussion. As shown in Scheme S4, the less hindered C_4-H substituted tryptamine **5b** gave a moderate diastereoselectivity (Scheme S4, **a**, **6b**:**6b′**=2.9:1), while the hindered C_4-F substituted tryptamine **7j** provided good diastereoselectivity (Scheme S4, **b**, **8j**:**8j′**=11.7:1). In

additional, the more hindered C_4-Cl substituted tryptamine **7k** could react to give excellent diastereoselectivity (Scheme S4, **c**, **8k**:**8k′**>20:1). These experimental results could strongly support our speculated stereo-control model.

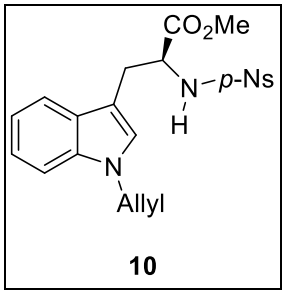
7. Total synthesis of (+)-WIN 64821



Scheme S5. Asymmetric total synthesis of (+)-WIN 64821.



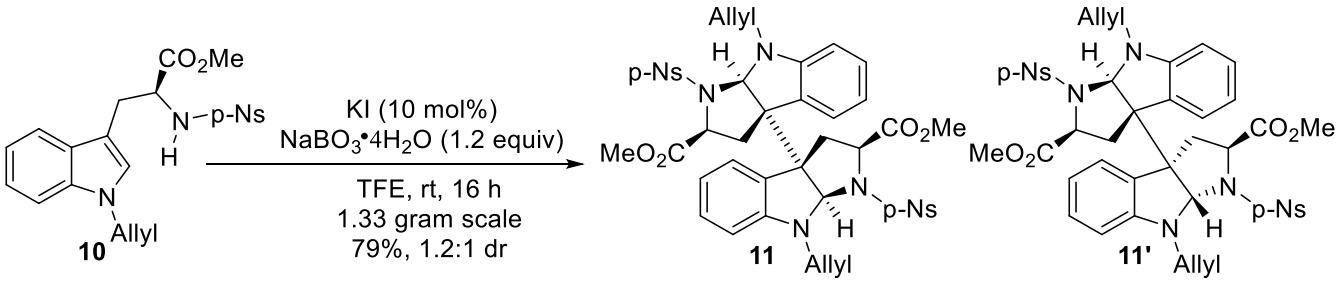
Methyl 1-allyl-N_a-((4-nitrophenyl)sulfonyl)-L-tryptophanate, **10**:



To a stirred solution of L-tryptophane **9** (4.08 g, 20 mmol, 1.0 equiv) in *N*,*N*-dimethylformamide (80 mL) under 0℃ was added NaH (60% dispersion in mineral oil, 2.40 g, 3.0 equiv) portionwise (0.80 g×3). The reaction mixture was reacted at room temperature for 2 h and cooled to 0℃ again. Allyl bromide (1.73 mL, 1.0 equiv, dissolved in 40 mL DMF) was then added to the reaction system over 3 h, after which, the system was stirred at 0℃ for additional 3 h. Whereafter, H_2O (150 mL), Na_2CO_3 (4.24 g, 2.0 equiv) and *p*-NsCl (4.43 g, 1.0 equiv) were added to the reaction system successively under 0℃. After stirring under the same temperature for 3 h, *p*-NsCl (2.22 g, 0.5 equiv) was added to the mixture and the system was reacted for additional 1 hour. Then the reaction mixture was diluted

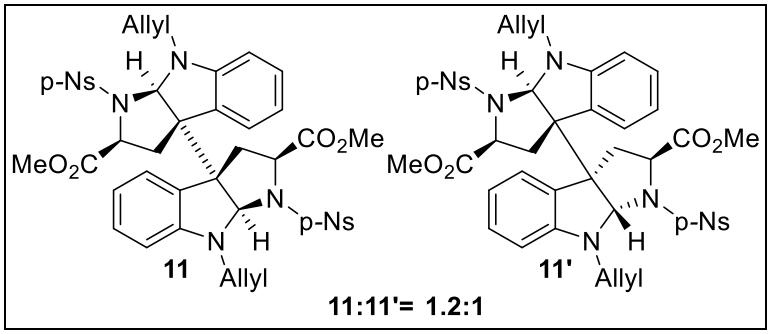
with EtOAc (200 mL) and H_2O (100 mL). The resulted mixture was extracted and the organic layer was extracted again with 200 mL NaOH (aqueous, 0.5 M). All the aqueous layers were combined and carefully acidified with HCl (concentrated, 12 M) to PH 1. Then, the resulted mixture was extracted with EtOAc (400 mL×3). The combined organic layer were wash with 0.1 M HCl (aqueous, 300 mL × 6), dried over Na_2SO_4 (anhydrous), then filtered and concentrated. The resulted solid was recrystallized (CH_2Cl_2 and petrol ether as solvents) to give the crude intermediate **9-1**(7.58 g).

To a solution of the crude intermediate **9-1** (4.00 g, 10 mmol, 1.0 equiv) obtained above in MeOH (60 mL) was added TMSCl (2.66 mL, 2.1 equiv) dropwise over 2 min. The reaction system was refluxed at 70℃ for 1 hour and then cooled to room temperature.[6] Subsequently, the result mixture was concentrated and recrystallized (CH_2Cl_2 and petrol ether as solvents) to give compound **10** (4.07 g, 86% yield over 2 steps) as a green solid. **[α]**$_D^{25}$ -38 (c 0.50, $CHCl_3$); **m.p.** 109-111℃; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 6.8 Hz, 2H), 7.65 (d, *J* = 7.6 Hz, 2H), 7.35 (d, *J* = 7.6 Hz, 1H), 7.14-7.10 (m, 2H), 7.01 (t, *J* = 6.4 Hz, 2H), 6.89 (s, 1H), 5.96-5.88 (m, 1H), 5.61 (s, 1H), 5.19 (d, *J* = 10.0 Hz, 1H), 5.06 (d, *J* = 16.8 Hz, 1H), 4.60 (d, *J* = 3.2 Hz, 2H), 4.27 (s, 1H), 3.67 (s, 3H), 3.28 (d, *J* = 11.2 Hz, 1H), 3.12-3.06 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 171.76, 149.41, 144.91, 136.22, 133.01, 127.66, 127.26, 126.99, 123.48, 122.00, 119.45, 118.38, 117.66, 109.68, 107.82, 56.34, 52.79, 48.62, 28.95; **IR** (KBr) 3352, 3244, 1723, 1521, 1351, 1165, 1090, 738, 682 cm^{-1}; **HRMS** (ESI) calcd for $[M+Na]^+$ $C_{21}H_{21}N_3NaO_6S$, m/z: 466.1049, found: 466.1040;



Dimethyl(2S,2'S,3aR,3'aR,8aS,8'aS)-8,8'-diallyl-1,1'-bis((4-nitrophenyl)sulfonyl)-2,2',3,3',8,8a,8',8'a-octahydro-1H,1'H-[3a,3'a-bipyrrolo[2,3-b]indole]-2,2'-dicarboxylate, **11**

dimethyl(2S,2'S,3aR,3'aS,8aR,8'aS)-8,8'-diallyl-1,1'-bis((4-nitrophenyl)sulfonyl)-2,2',3,3',8,8a,8',8'a-octahydro-1H,1'H-[3a,3'a-bipyrrolo[2,3-b]indole]-2,2'-dicarboxylate, **11′**:

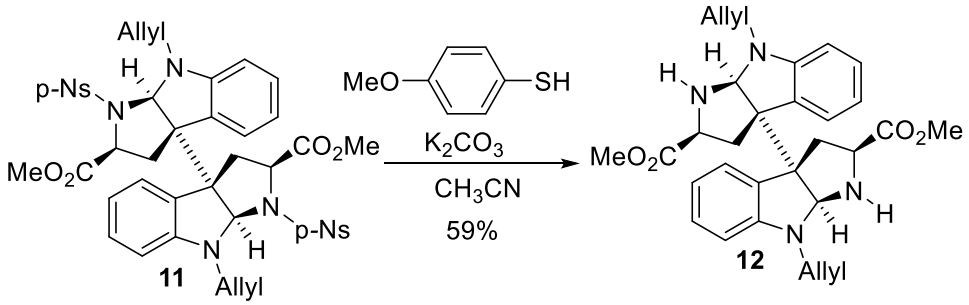


To a 10 mL dry reaction tube were added compound **10** (1.33 g, 3 mmol, 1.0 equiv), KI (49.8 mg, 0.1 equiv), TFE (30 mL) and $NaBO_3$•$4H_2O$ under argon atmosphere at room temperature. The mixture was stirred (1500 rpm) for 16 h and then quenched with saturated $Na_2S_2O_3$ (aqueous). Then TFE was removed under vacuum, and the resulted mixture was extracted with EtOAc (200 mL), the organic layer washed with brine (50 mL) and dried over anhydrous Na_2SO_4, concentrated under vacuum. The crude residue was purified by column chromatography (petrol ether: EtOAc =10: 1 to 1: 1 as eluent) to give the dimeric product **11** (578.4 mg) and **11′** (471.9 mg) with acceptable over-all results (79% yield, 1.2:1 dr).

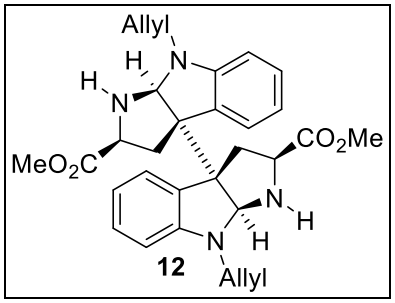
Compound **11**: Yellow solid; **[α]**$_D^{26}$ 54.5 (c 0.22, $CHCl_3$/MeOH= 2:1); **m.p.** 123-126℃; **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.16 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 7.8 Hz, 2H), 7.25 (t, *J* = 7.8 Hz, 1H), 6.74 (d, *J* = 7.2 Hz, 1H), 6.66 (d, *J* = 7.8 Hz, 1H), 6.54 (t, *J* = 7.2 Hz, 1H), 6.06-6.00 (m, 1H), 5.40 (d, *J* = 17.4 Hz, 1H), 5.33 (d, *J* = 10.8 Hz, 1H), 5.24 (s, 1H), 4.36 (dd, *J* = 16.8 Hz, 4.8 Hz, 1H), 4.10 (d, *J* = 8.4 Hz, 1H), 4.04 (dd, *J* = 17.4 Hz, 4.8 Hz, 1H), 3.10 (s, 3H), 2.53 (d, *J* = 12.6 Hz, 1H), 2.30 (dd, *J* = 10.5 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 169.81, 151.08, 149.78, 143.93, 134.09, 130.51, 128.17, 126.12, 125.37, 124.64, 118.03, 117.00, 108.85, 87.53, 61.04, 59.54, 52.43, 48.32, 36.41; **IR** (KBr) 3436, 1746, 1531, 1351, 1166, 739, 618 cm^{-1}; **HRMS** (ESI) calcd for $[M+Na]^+$ $C_{42}H_{40}N_6NaO_{12}S_2$, m/z: 927.2043, found: 907.2033.

Compound **11′**: Yellow solid. **[α]**$_D^{25}$ 48 (c 0.50, $CHCl_3$); **m.p**. 110-114℃; **^{1}H NMR** (400 MHz, CDCl3): δ 8.36 (d, *J* = 8.8 Hz, 2H), 8.22-8.16 (m, 3H), 7.11 (t, *J* = 8.0 Hz, 1H), 7.00 (t, *J* = 8.0 Hz, 1H), 6.82 (bs, 1H), 6.40 (d, *J* = 8.0 Hz, 1H), 6.34 (bs, 1H), 6.26 (d, *J* = 8.0 Hz, 1H), 5.87 (bs, 2H), 5.43 (s, 1H), 5.28-5.20 (m, 2H), 4.91-4.85 (m, 2H), 4.62 (d, *J* = 8.0 Hz, 1H), 4.15-4.01 (m, 2H), 3.86 (s, 3H), 3.30 (bs, 1H), 3.02 (s, 3H), 2.74 (d, *J* = 12.0 Hz, 1H), 2.61 (q, *J* = 7.2 Hz, 1H), 2.32 (t, *J* = 9.8 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 171.01, 169.67, 150.53, 150.31, 150.28, 149.69, 146.85, 145.20, 134.12, 133.64, 129.99, 129.91, 128.87, 127.98, 126.08, 124.82, 124.45, 123.79, 123.46, 119.94, 117.86, 117.79, 117.16, 110.40, 107.59, 87.09, 86.08, 61.90, 61.37, 60.94, 60.27, 53.07, 52.34, 52.27, 47.94, 39.75, 38.38; **IR** (KBr) 3432, 1735, 1531, 1351, 1169, 741, 608 cm^{-1}; **HRMS** (ESI) calcd for $[M+Na]^+$

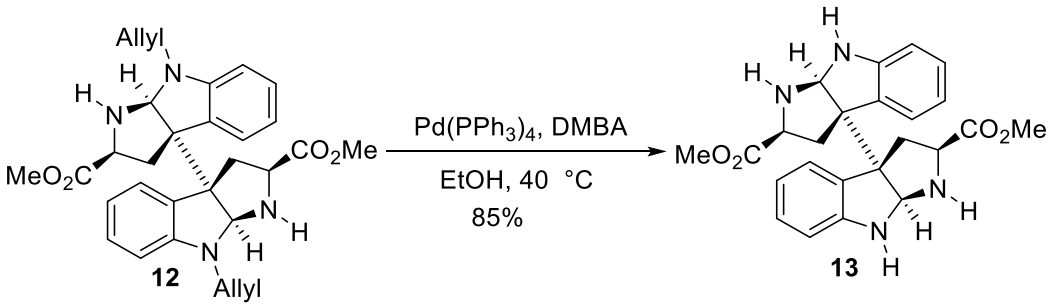
$C_{42}H_{40}N_6NaO_{12}S_2$, m/z: 907.2043, found: 907.2055;



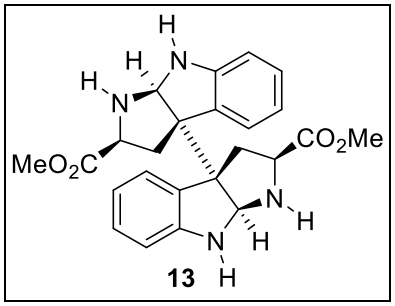
Dimethyl(2S,2'S,3aR,3'aR,8aS,8'aS)-8,8'-diallyl-2,2',3,3',8,8a,8',8'a-octahydro-1H,1'H-[3a,3'a-bipyrrolo[2,3-b]indole]-2,2'-dicarboxylate, **12**:



To a stirred solution of compound **11** (600 mg, 0.68 mmol, 1.0 equiv) in CH_3CN (30 mL) under argon atmosphere at 0°C was added K_2CO_3. Methoxybenzenethiol (279 μL, 4.0 equiv, in 10 mL CH_3CN) was then added to the reaction mixture dropwise over 3 min. Subsequently, the resulted system was stirred at room temperature until the complete conversion of **12** on TLC (about 2 days). The reaction mixture was filtered through a pad of celite (washed by EtOAc and MeOH) and then concentrated under vacuum. The crude residue was purified by column chromatography (petrol ether: EtOAc =2:1 to 1:2, then EtOAc, then CH_2Cl_2: MeOH= 100:1 to 50:1) to give compound **12** (205.7 mg, 59% yield) as a light yellow oil. **[α]**$_D^{25}$ 225 (c 1.00, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.15 (d, *J* = 7.2 Hz, 2H), 7.06 (t, *J* = 7.6 Hz, 2H), 6.60 (t, *J* = 7.6 Hz, 2H), 6.35 (d, *J* = 7.2 Hz, 2H), 6.02-5.92 (m, 2H), 5.33 (dd, *J* = 17.2 Hz, 1.6 Hz, 2H), 5.20 (dd, *J* = 10.0 Hz, 1.2 Hz, 2H), 4.68 (s, 2H), 3.94-3.82 (m, 4H), 3.78 (dd, *J* = 8.0 Hz, 2.0 Hz, 2H), 3.21 (s, 6H), 2.82-2.76 (m, 2H), 2.56 (dd, *J* = 12.4 Hz, 1.6 Hz, 2H), 2.41 (bs, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 174.14, 151.57, 134.70, 129.87, 129.02, 125.55, 116.86, 116.61, 106.30, 85.11, 60.31, 59.93, 51.66, 47.89, 38.86; **IR** (KBr) 3362, 2949, 1735, 1602, 1489, 1255, 748, 666 cm^{-1}; **HRMS** (ESI) calcd for $[M+Na]^+$ $C_{30}H_{35}N_4O_4$, m/z: 515.2658, found: 515.2637;

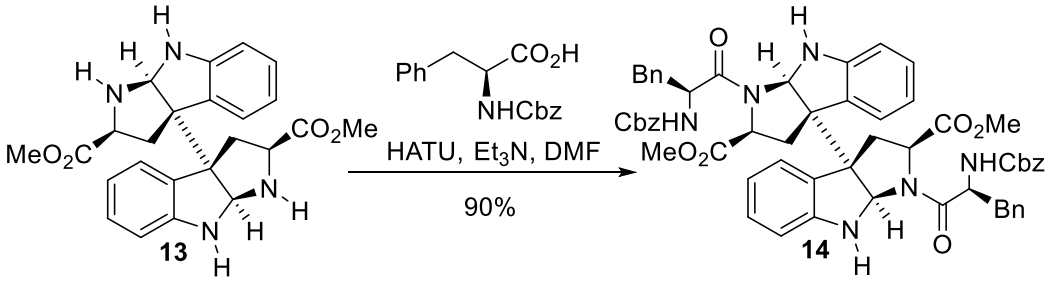


Dimethyl(2S,2'S,3aR,3'aR,8aS,8'aS)-2,2',3,3',8,8a,8',8'a-octahydro-1H,1'H-[3a,3'a-bipyrrolo[2,3-b]indole]-2,2'-dicarboxylate, **13**:

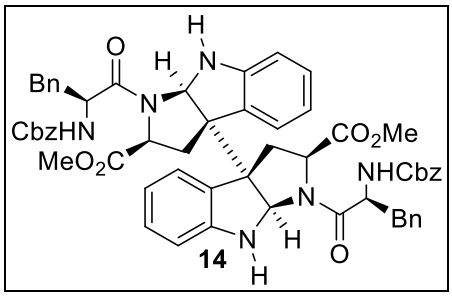


To a stirred solution of compound **12** (311.2 mg, 0.6 mmol, 1.0 equiv) in EtOH (12 mL) under argon atmosphere were added DMBA (188.8 mg, 2.0 equiv) and $Pd(PPh_3)_4$ (69.9 mg, 0.1 equiv). The reaction mixture was degassed with argon and then stirred at 40℃ for about 2 h. The reaction mixture was filtered through a pad of silica gel (washed by CH_2Cl_2 :MeOH = 10:1) and then concentrated under vacuum. The crude residue was purified by column chromatography (CH_2Cl_2: MeOH= 100:1 to 20:1) to give compound **13** (222.7 mg, 85% yield) as a light yellow oil. Compound **13** has already been characterized by Xia and co-workers,[4] and our experimental characterization data is consistent with the literature.

[α]$_D^{26}$ 117 (c 0.14, MeOH); **^{1}H NMR** (400 MHz, CDCl3): δ7.19 (d, *J* = 7.6 Hz, 2H), 7.07 (td, *J* = 8.0 Hz, 0.8 Hz, 2H), 6.72 (td, *J* = 7.2 Hz, 0.4 Hz, 2H), 6.59 (d, *J* = 7.6 Hz, 2H), 4.66 (s, 2H), 3.79 (dd, *J* = 8.4 Hz, 2.4 Hz, 2H), 3.24 (s, 6H), 2.81 (dd, *J* = 12.8 Hz, 8.4 Hz, 2H), 2.58 (dd, *J* = 12.8 Hz, 2.4 Hz, 2H); **^{13}C NMR** (100 MHz, CDCl3): δ 173.89, 151.02, 129.46, 129.04, 125.87, 118.46, 109.83, 80.81, 61.84, 60.02, 51.77, 38.71; **IR** (KBr) 3428, 1638, 1483, 1244, 742, 601 cm^{-1}; **HRMS** (ESI) calcd for $[M+Na]^+$ $C_{24}H_{26}N_4NaO_4$, m/z: 457.1852, found: 457.1859;

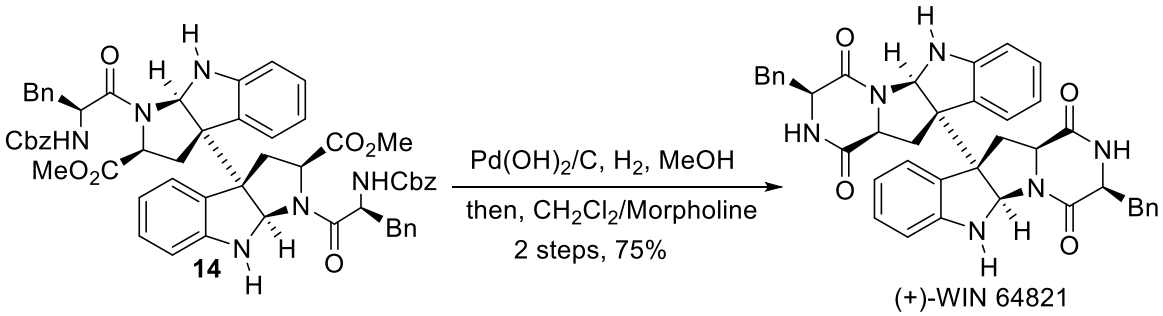


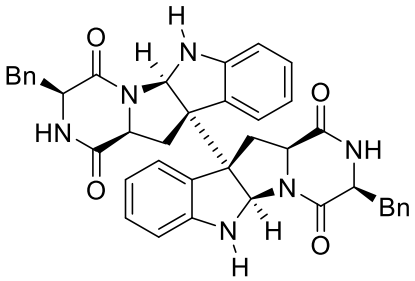
Dimethyl(2S,2'S,3aR,3'aR,8aR,8'aR)-1,1'-bis(((benzyloxy)carbonyl)-L-phenylalanyl)-2,2',3,3',8,8a,8',8'a-octahydro-1H,1'H-[3a,3'a-bipyrrolo[2,3-b]indole]-2,2'-dicarboxylate, **14**:



To a stirred solution of compound **13** (43.6 mg, 0.1 mmol) in *N*,*N*-Dimethylformamide (1.5 mL) under argon atmosphere was added Cbz-L-phenylalanine (89.8 mg, 3.0 equiv). The system was cooled to 0℃ and Et_3N (48.6μL, 3.5 equiv), HATU (114.0 mg, 3.0 equiv) were added successively. The reaction mixture was then stirred at room temperature for 14 h. 3 mL LiCl (aqueous, 5%) was subsequent added to the system, the resulted solution was extracted with EtOAc (30 mL×3). The combined organic layers were washed with 40 mL LiCl (aqueous, 5%) and then dried over anhydrous Na_2SO_4, concentrated under vacuum. The crude residue was purified by column chromatography (petrol ether: EtOAc =10: 1 to 2: 1 as eluent) to give **14** (89.9 mg, 90% yield) as a white solid. Compound **13** has already been characterized by Xia and co-workers,[4] and our experimental characterization data is consistent with the literature.

m.p. 115-118℃; **[α]**$_D^{25}$ 221 (c 0.38, $CHCl_3$); **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.45-7.38 (m, 6H), 7.32-7.28 (m, 12H), 7.19 (d, *J* = 7.2 Hz, 4H), 7.05 (t, *J* = 7.5 Hz, 2H), 6.77 (d, *J* = 7.2 Hz, 2H), 6.62 (t, *J* = 7.2 Hz, 2H), 6.55 (d, *J* = 7.8 Hz, 2H), 5.89 (d, *J* = 9.6 Hz, 2H), 5.09-5.04 (m, 4H), 4.87 (s, 2H), 4.40-4.36 (m, 2H), 3.55 (d, *J* = 9.6 Hz, 2H), 3.14 (dd, *J* = 12.6 Hz, 4.2 Hz, 2H), 2.94 (s, 6H), 2.88 (t, *J* = 11.4 Hz, 2H), 2.06 (d, *J* = 13.2 Hz, 2H), 1.90-1.86 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 171.66, 169.95, 154.94, 150.85, 136.30, 135.51, 129.63, 129.14, 128.98, 128.35, 127.93, 127.58, 126.71, 125.46, 117.95, 109.53, 79.93, 66.68, 59.50, 58.44, 53.69, 52.21, 41.14, 34.73; **IR** (KBr) 3409, 3325, 2925, 1719, 1638, 1449, 1055, 757 cm^{-1}; **HRMS** (ESI) calcd for $[M+Na]^+$ $C_{58}H_{56}N_6NaO_{10}$, m/z: 1019.3956, found: 1019.3996;



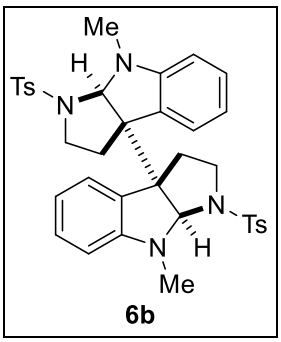


To a solution of compound **14** (89.9 mg, 0.09 mmol, 1.0 equiv) in MeOH (6 mL) was added $Pd(OH)_2/C$ (30 mg). The reaction system was degassed with H_2 and then stirred at H_2 atmosphere (1 atm) for about 1.5 h. Subsequently, the reaction mixture was subject to a pad of silica gel (washed with CH_2Cl_2:MeOH = 5:1) and then concentrated under vacuum. The resulted crude residue was used to the next step without further purification.

To the crude product above were added CH_2Cl_2 (3 mL) and morpholine (0.3 mL). The resulted solution was stirred at room temperature for 2 h, and then quenched with HCl (1 M, 10 mL), extracted with EtOAc (30 mL×3). The combine organic layers were washed with brine, dried over anhydrous Na_2SO_4, concentrated under vacuum. The crude residue was purified by column chromatography (CH_2Cl_2: Acetone =20: 1 to 3: 1 as eluent) to give (+)-WIN 64821 (42.1 mg, 75% yield over 2 steps) as a white solid. (+)-WIN 64821 has already been characterized by Xia and co-workers,[4] and our experimental characterization data is consistent with the literature.

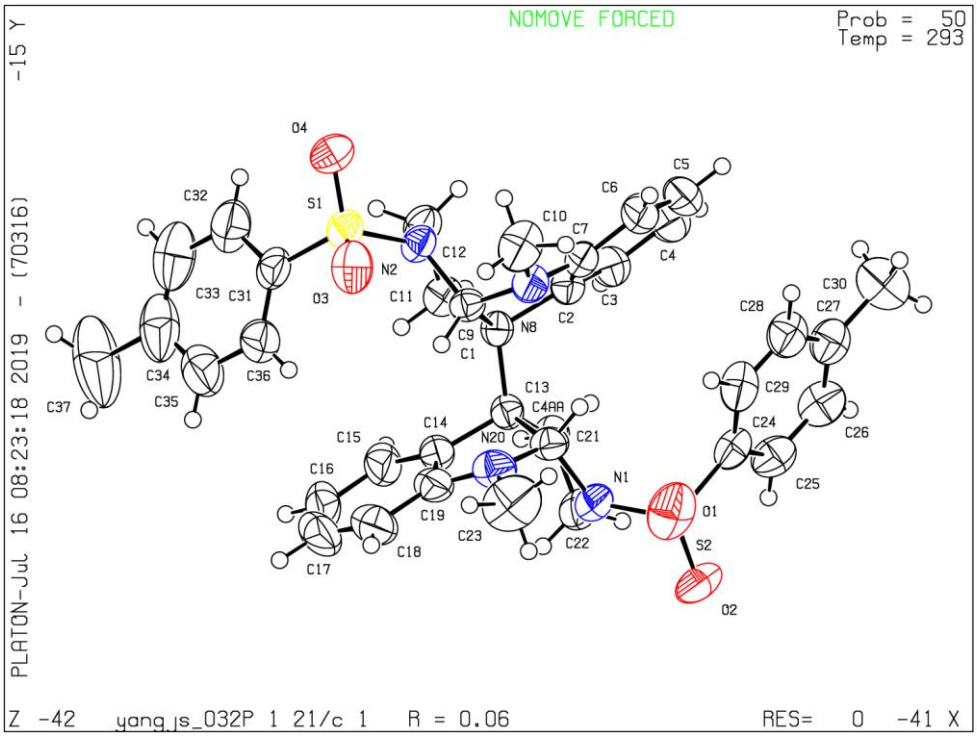
m.p. 175-178℃; **[α]**$_D^{26}$ 228 (c 0.72, MeOH); **^{1}H NMR** (400 MHz, CD_3CN): δ 7.36 (d, *J* = 7.6 Hz, 2H), 7.15-7.11 (m, 12H), 6.75 (t, *J* = 7.6 Hz, 2H), 6.69 (d, *J* = 7.6 Hz, 2H), 6.04 (s, 2H), 5.90 (s, 2H), 4.91 (s, 2H), 4.17 (t, *J* = 5.4 Hz, 2H), 4.08 (t, *J* = 8.6 Hz, 2H), 3.15-3.07 (m, 2H), 3.04-2.97 (m, 4H), 2.53(dd, *J* = 14.4 Hz, 8.0 Hz, 2H); ^{13}C NMR (100 MHz, CD_3CN): δ 169.78, 168.88, 149.98, 137.34, 131.39, 130.29, 130.09, 129.32, 127.60, 126.04, 120.18, 110.40, 80.53, 60.94, 57.73, 56.95, 36.76, 36.07; **IR** (KBr) 3405, 1655, 1459, 1313, 1257, 1096, 702, 603 cm^{-1}; **HRMS** (ESI) calcd for $[M+Na]^+$ $C_{40}H_{36}N_6NaO_4$, m/z: 687.2696, found: 687.2675.

8. Crystals of **6b**



6b

CCDC: 1940250



Datablock: yangJs_0320

Bond precision:	C-C = 0.0055 A		**Wavelength**=0.71000
Cell:	a=16.4849(8)	b=10.3567(3)	c=19.7384(8)
	alpha=90	beta=98.596(5)	gamma=90

Temperature: 293 K

	Calculated	**Reported**
Volume	3332.1(2)	3332.0(2)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C36 H38 N4 O4 S2	C36 H38 N4 O4 S2

Sum formula	C36 H38 N4 O4 S2	C38 H38 N2 O4 S2
Mr	654.82	650.82
Dx,g cm-3	1.305	1.297
Z	4	4
Mu (mm-1)	0.205	0.203
F000	1384.0	1376.0
F000'	1385.52	
h,k,lmax	20,12,24	20,12,24
Nref	6563	6550
Tmin,Tmax	0.964,0.976	0.658,1.000
Tmin'	0.964	

Correction method= # Reported T Limits: Tmin=0.658 Tmax=1.000 AbsCorr = MULTI-SCAN

Data completeness= 0.998 Theta(max)= 25.992

R(reflections)= 0.0579(3838) wR2(reflections)= 0.1617(6550)

S = 0.940 Npar= 419

9. References

[1] H. Zhang, R. B. Hu, N. Liu, S. X. Li, S. D. Yang, *Org. Lett.* **2016**, *18*, 28.

[2] R. S. Klausen, C. R. Kennedy, A. M. Hyde, E. N. Jacobsen, *J. Am. Chem. Soc.* **2017**, *139*, 12299.

[3] H. Ren, J. -R. Song, Z. -Y. Li, W. -D. Pan, *Org. Lett*. **2019**, *21*, 6774-6778.

[4] K. Liang, X. Deng, X. Tong, D. Li, M. Ding, A. Zhou, C. Xia, *Org. Lett*. **2015**, *17*, 206-209.

[5] Y. -X. Li, H. -X. Wang, S. Ali, X. -F. Xia, Y. -M. Liang, *Chem. Commun*. **2012**, *48*, 2343-2345.

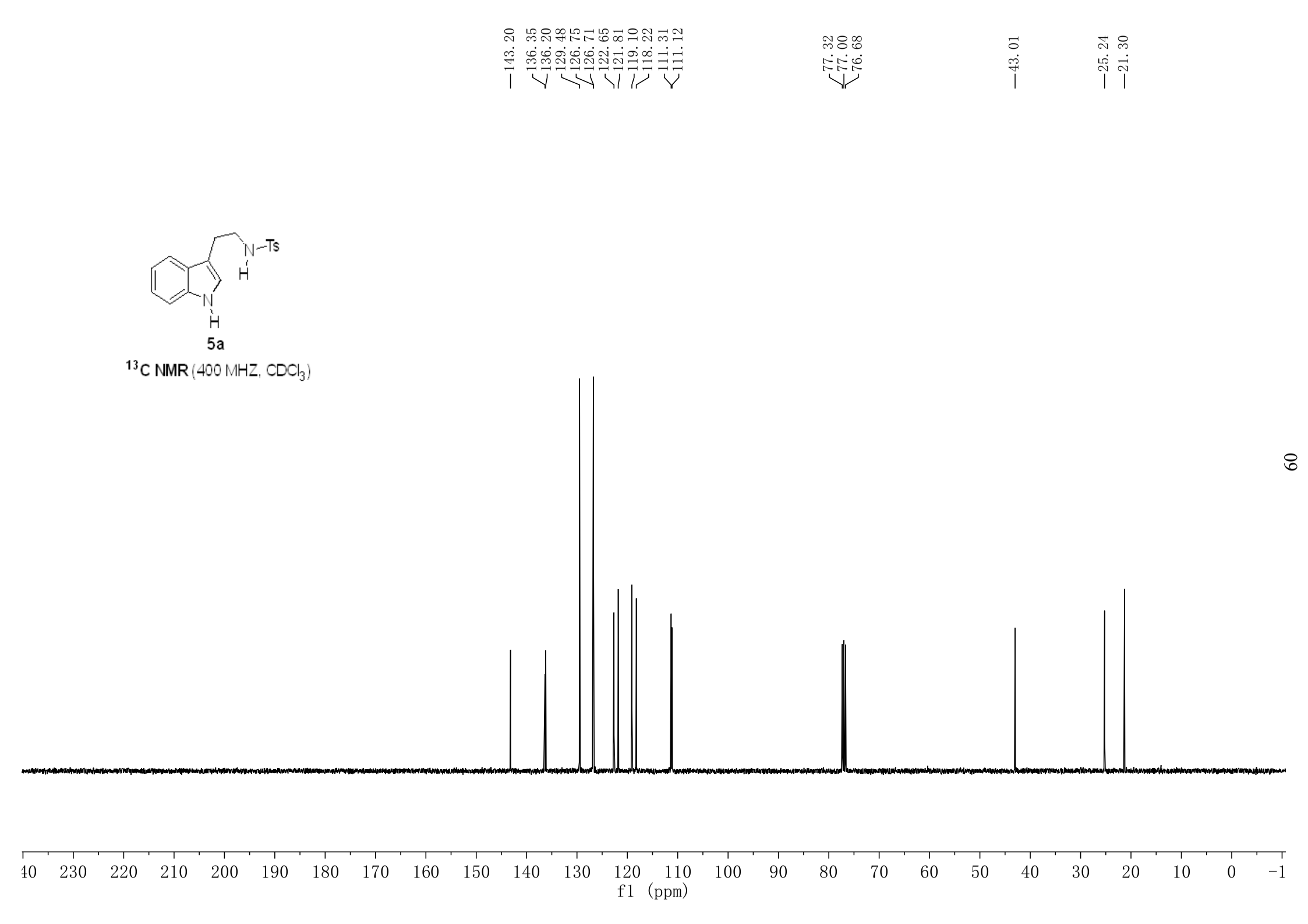
[6] J. Li, Y. Sha, *Molecules* **2008**, *13*, 1111-1119.

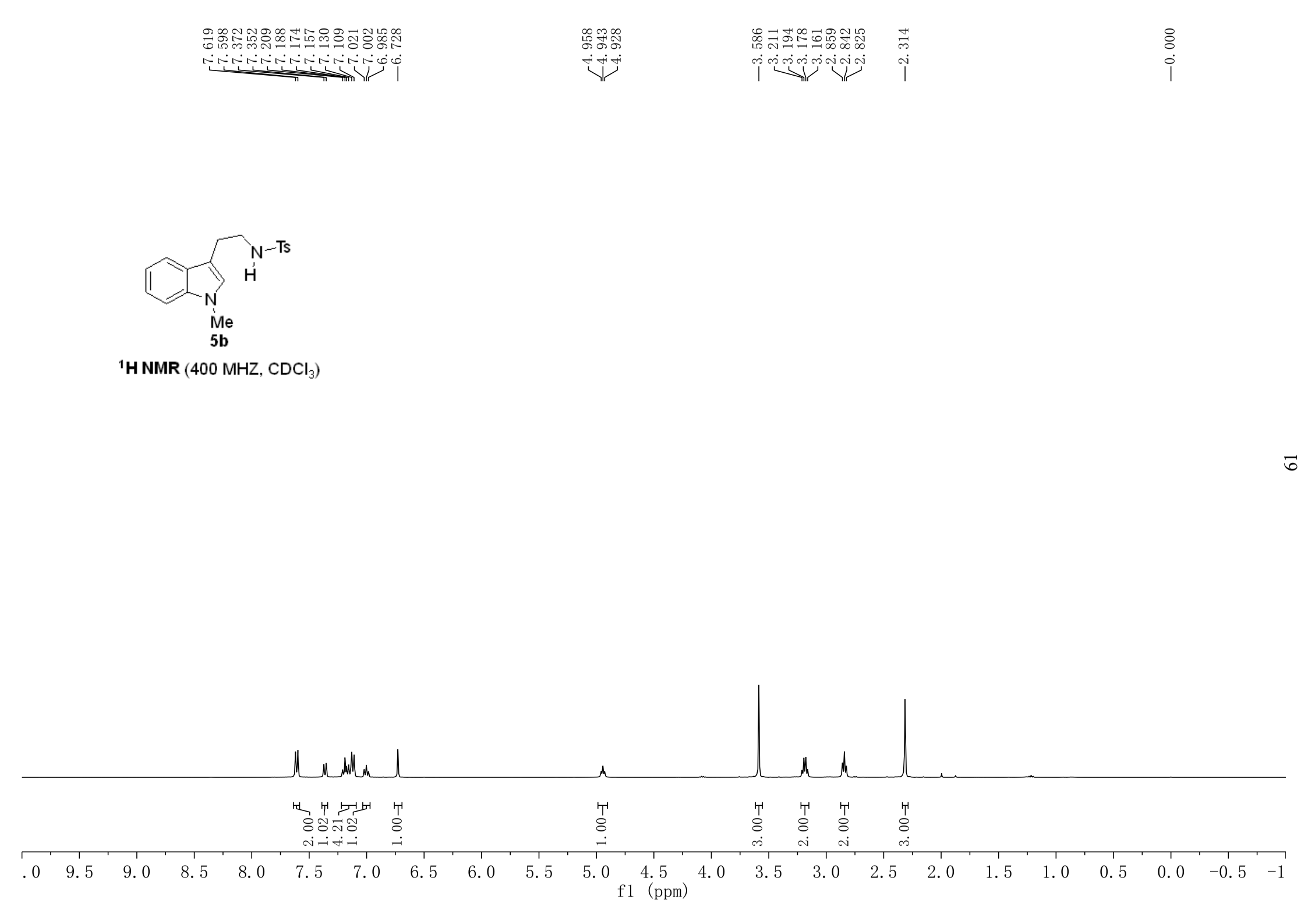
[7] Note: NMR spectra of **8f**/**8f'** here were obtained from the gram-scale dimerization (section 6 of SI) of **7f** (selective collection of the products after column chromatography).

[8] Note: NMR spectra (**8g**/**8g'**) here were obtained from selective collection of the products after column chromatography (trying to separate the **8g** and **8g'**, but failed), The repeatability of the reaction was confirmed by at least three parallel experiments.

10. Copies of NMR

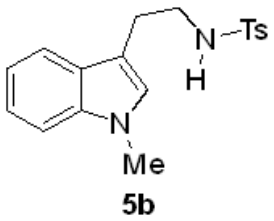
1H NMR (400 MHZ, CDCl3)
5a
N
H
H
N
Ts
8.236
7.591
7.571
7.360
7.341
7.267
7.247
7.132
7.120
7.100
7.019
7.000
6.981
6.827
6.821
4.844
4.829
4.814
3.199
3.183
3.167
3.150
2.844
2.827
2.810
2.309
0.000
1.00
2.00
1.00
1.00
3.00
1.00
1.00
1.00
2.00
2.00
3.00
f1 (ppm)


143.20
136.35
136.20
129.48
126.75
126.71
122.65
121.81
119.10
118.22
111.31
111.12
77.32
77.00
76.68
43.01
25.24
21.30
N
Ts
H
N
H
5a
13C NMR (400 MHZ, CDCl3)
60
40 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)



5b

^{1}H NMR (400 MHZ, $CDCl_3$)



5b

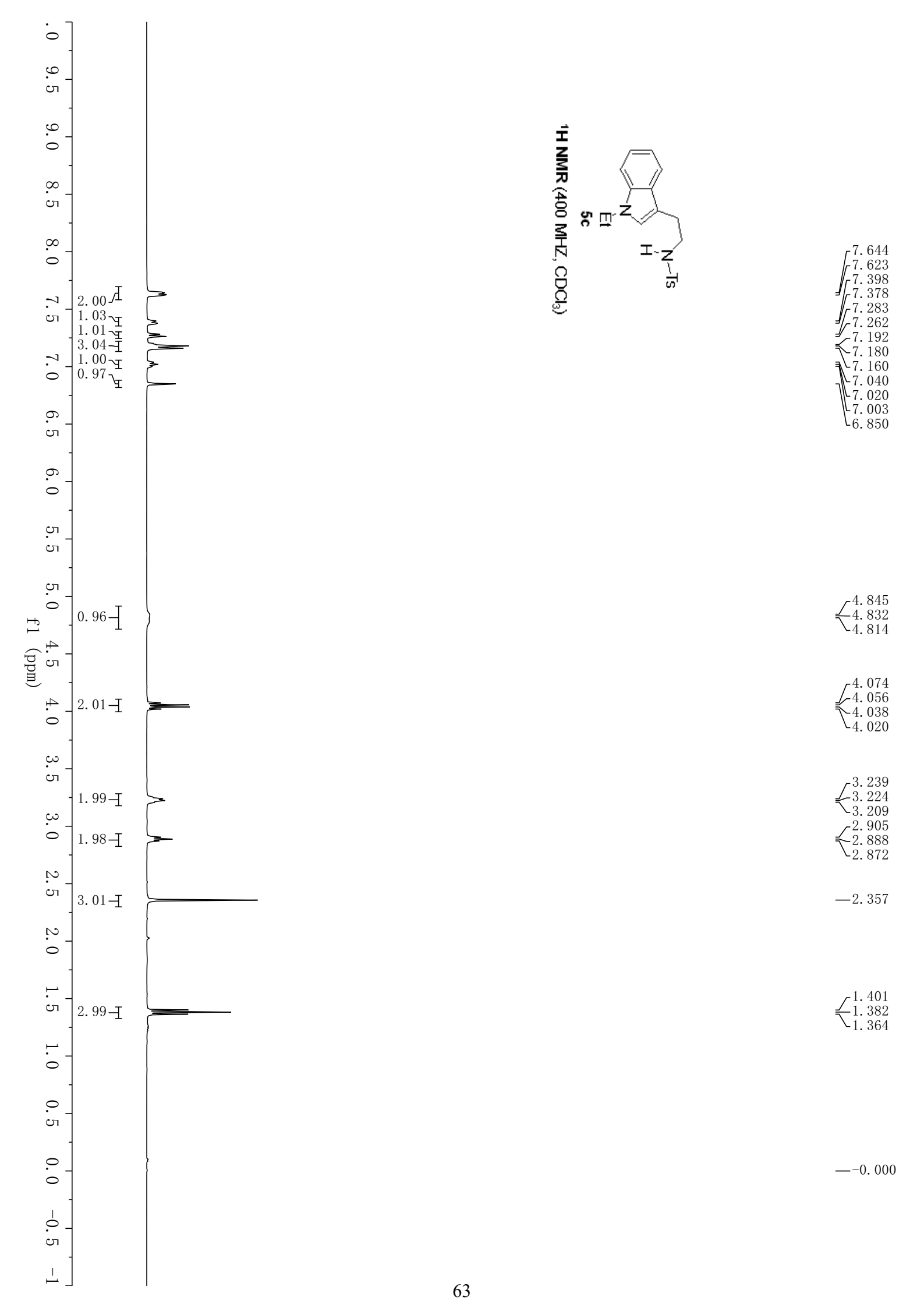
^{13}C **NMR** (100 MHZ, $CDCl_3$)

142.95
136.85
136.64
129.35
127.18
127.08
126.75
121.43
118.64
118.38
109.86
109.11
77.32
77.00
76.68
43.15
32.28
25.15
21.23

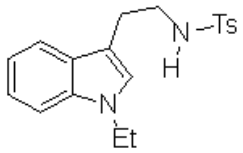
62

40 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −1

f1 (ppm)


¹H NMR (400 MHZ, CDCl₃)
5c
Et
N
H
N—Ts
7.644
7.623
7.398
7.378
7.283
7.262
7.192
7.180
7.160
7.040
7.020
7.003
6.850
4.845
4.832
4.814
4.074
4.056
4.038
4.020
3.239
3.224
3.209
2.905
2.888
2.872
2.357
1.401
1.382
1.364
-0.000
2.00
1.03
1.01
3.04
1.00
0.97
0.96
2.01
1.99
1.98
3.01
2.99
f1 (ppm)

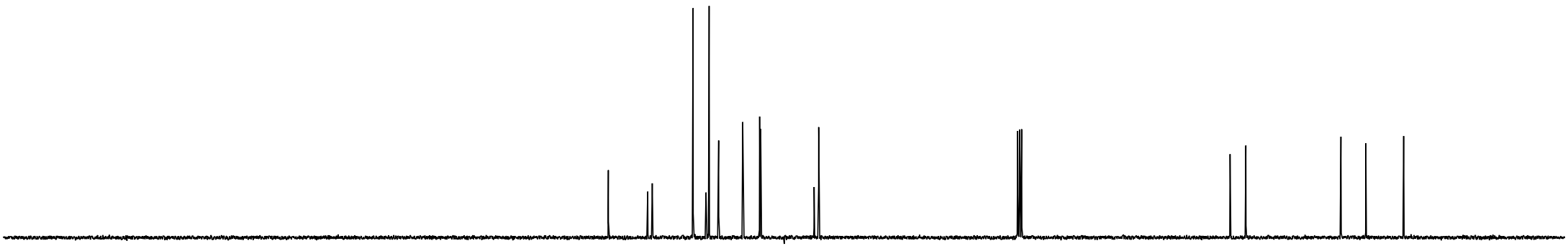
143.10
136.77
136.04
129.48
127.41
126.90
125.37
121.50
118.79
118.62
110.03
109.30
77.32
77.00
76.68
43.18
40.65
25.37
21.37
15.29

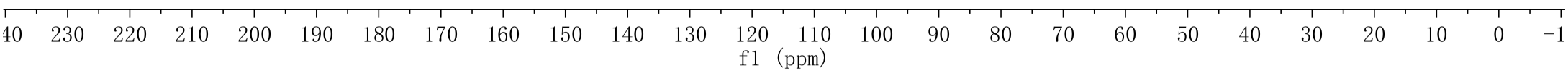


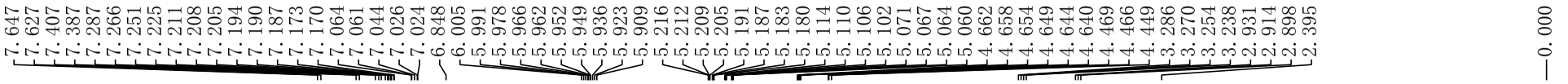
5c

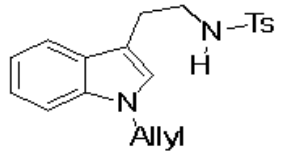
^{13}C NMR (400 MHZ, $CDCl_3$)

64



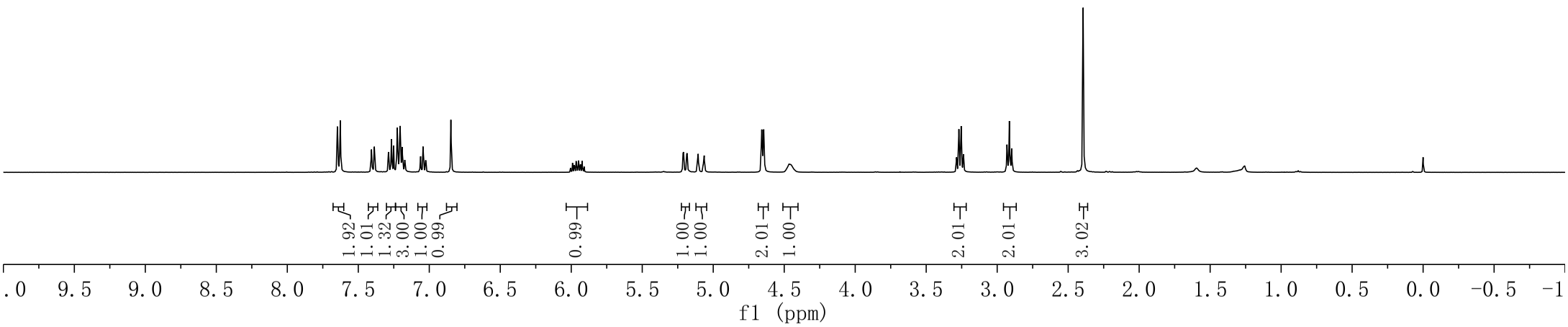


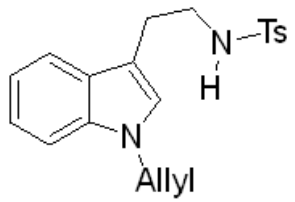




5d

^{1}H NMR (400 MHZ, $CDCl_3$)

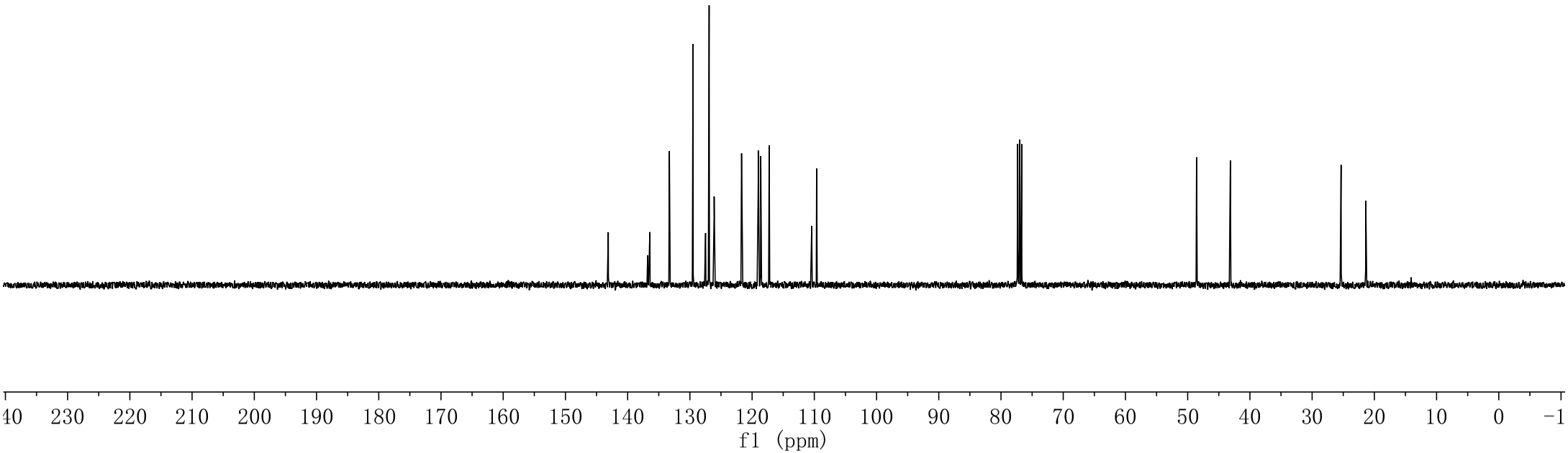


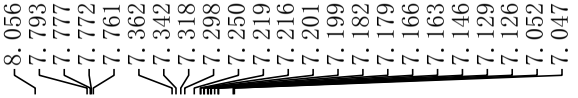


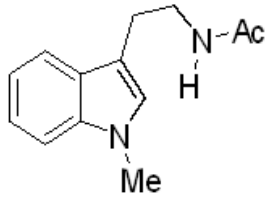
5d

^{13}C NMR (100 MHZ, $CDCl_3$)

143.11
136.78
136.43
133.30
129.49
127.48
126.91
126.10
121.69
119.01
118.61
117.25
110.43
109.63
77.32
77.00
76.68
48.57
43.14
25.35
21.38

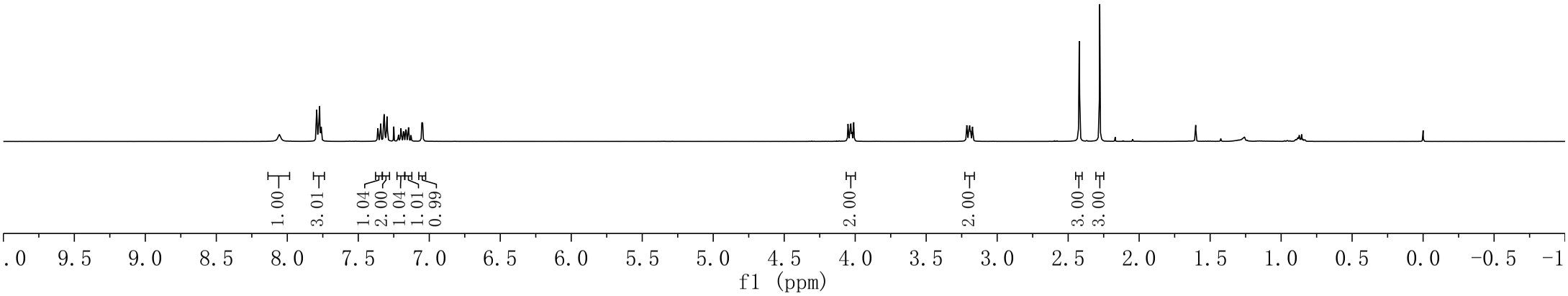


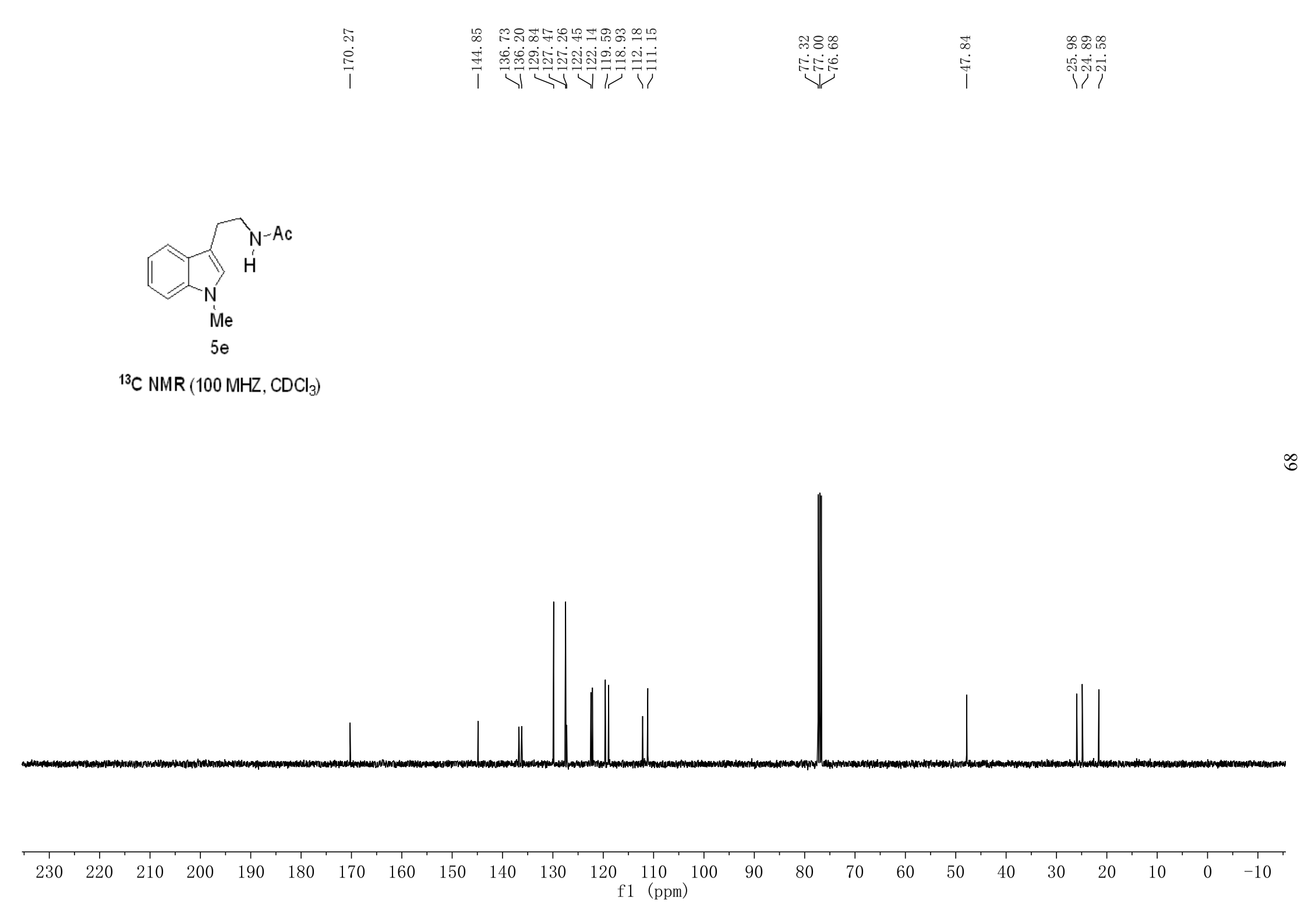




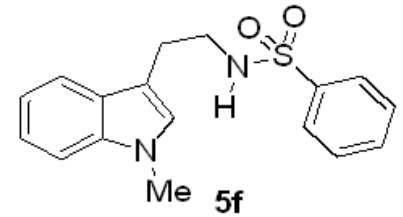
5e

^{1}H NMR (400 MHZ, $CDCl_3$)




170.27
144.85
136.73
136.20
129.84
127.47
127.26
122.45
122.14
119.59
118.93
112.18
111.15
77.32
77.00
76.68
47.84
25.98
24.89
21.58
N-Ac
H
N
Me
5e
13C NMR (100 MHZ, CDCl3)
f1 (ppm)

5f
^{1}H NMR (400 MHZ, CDCl$_3$)
Me
7.766
7.747
7.550
7.531
7.513
7.454
7.434
7.415
7.405
7.385
7.290
7.269
7.249
7.233
7.215
7.195
7.069
7.049
7.032
6.804
4.510
4.496
4.481
3.719
3.299
3.283
3.267
3.251
2.935
2.919
2.902
0.000
2.00
1.14
3.05
1.32
1.01
1.00
1.00
1.01
3.00
2.01
2.01
f1 (ppm)



5f

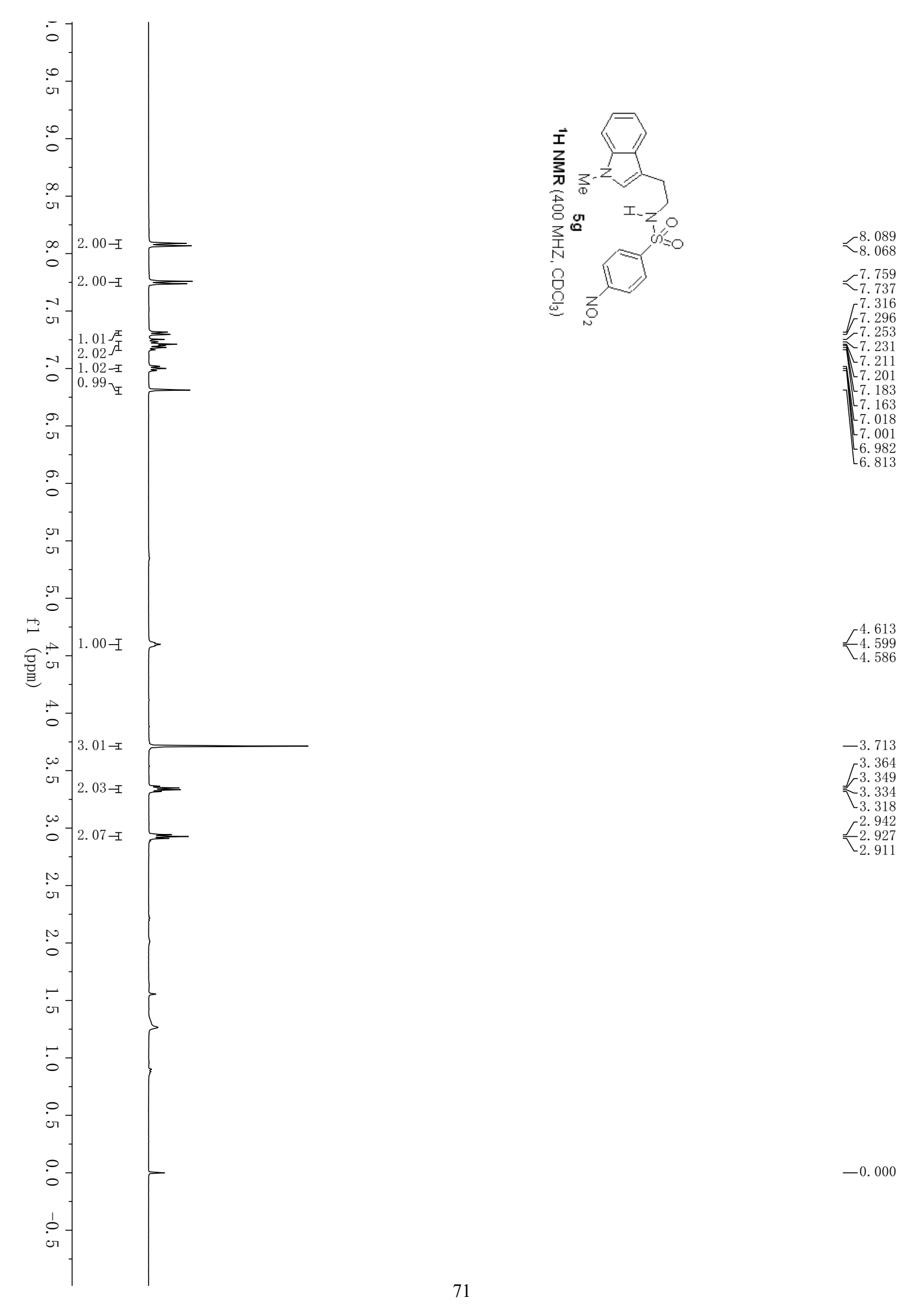
^{13}C **NMR** (100 MHZ, $CDCl_3$)

139.85
137.13
132.47
128.98
127.30
127.26
126.94
121.85
119.03
118.55
109.84
109.35
77.32
77.00
76.68
43.19
32.62
25.40

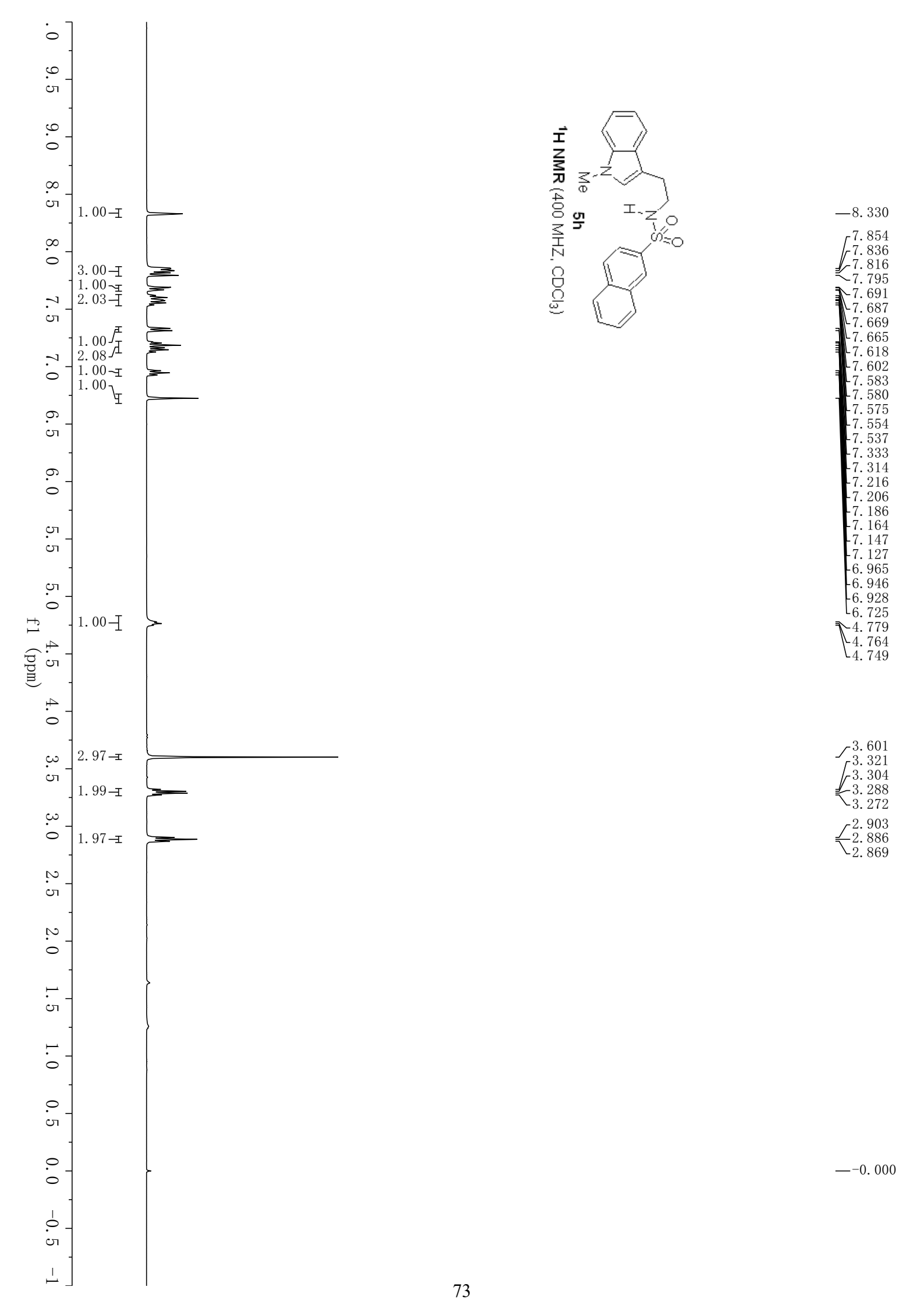
70

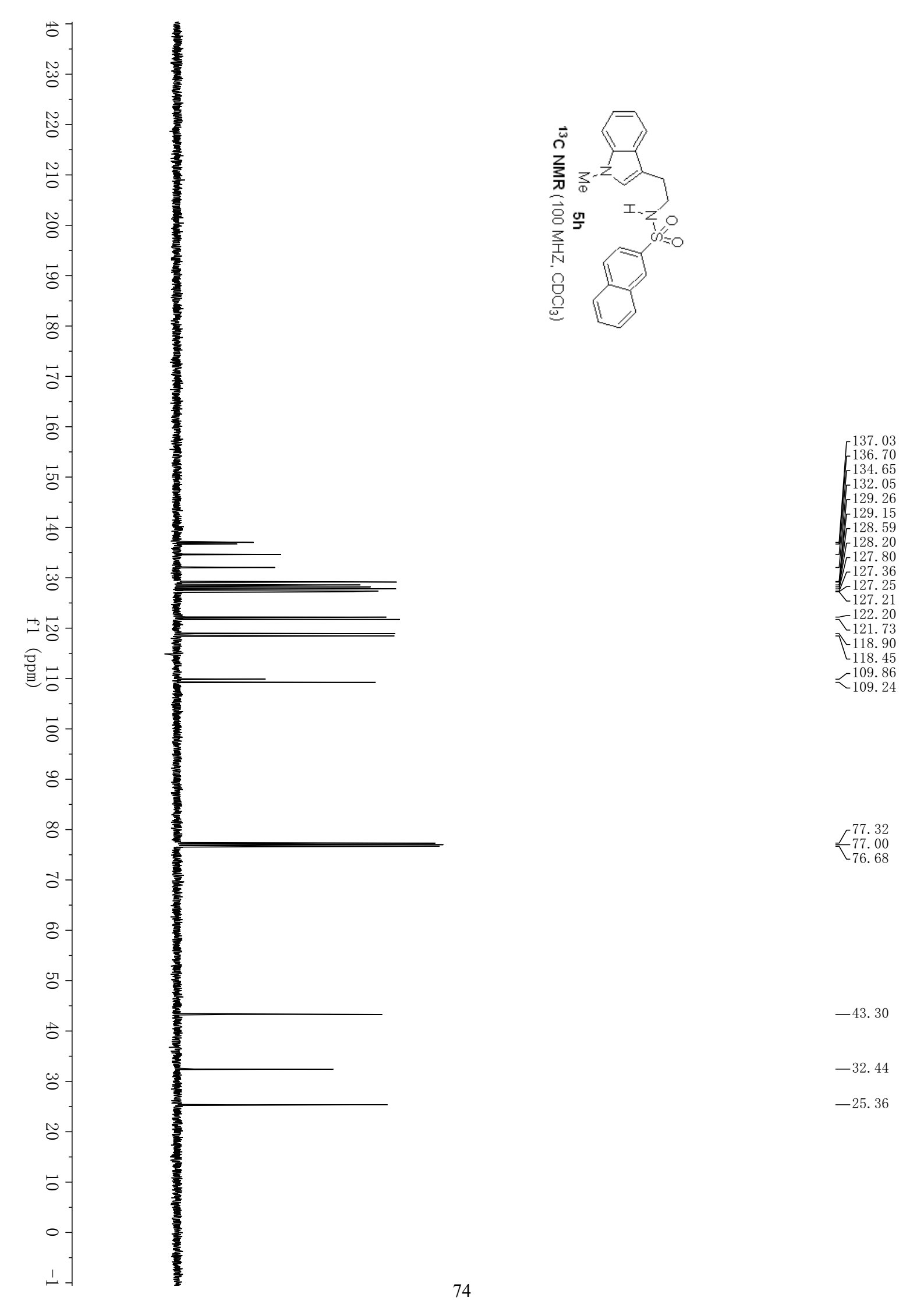
40 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −1

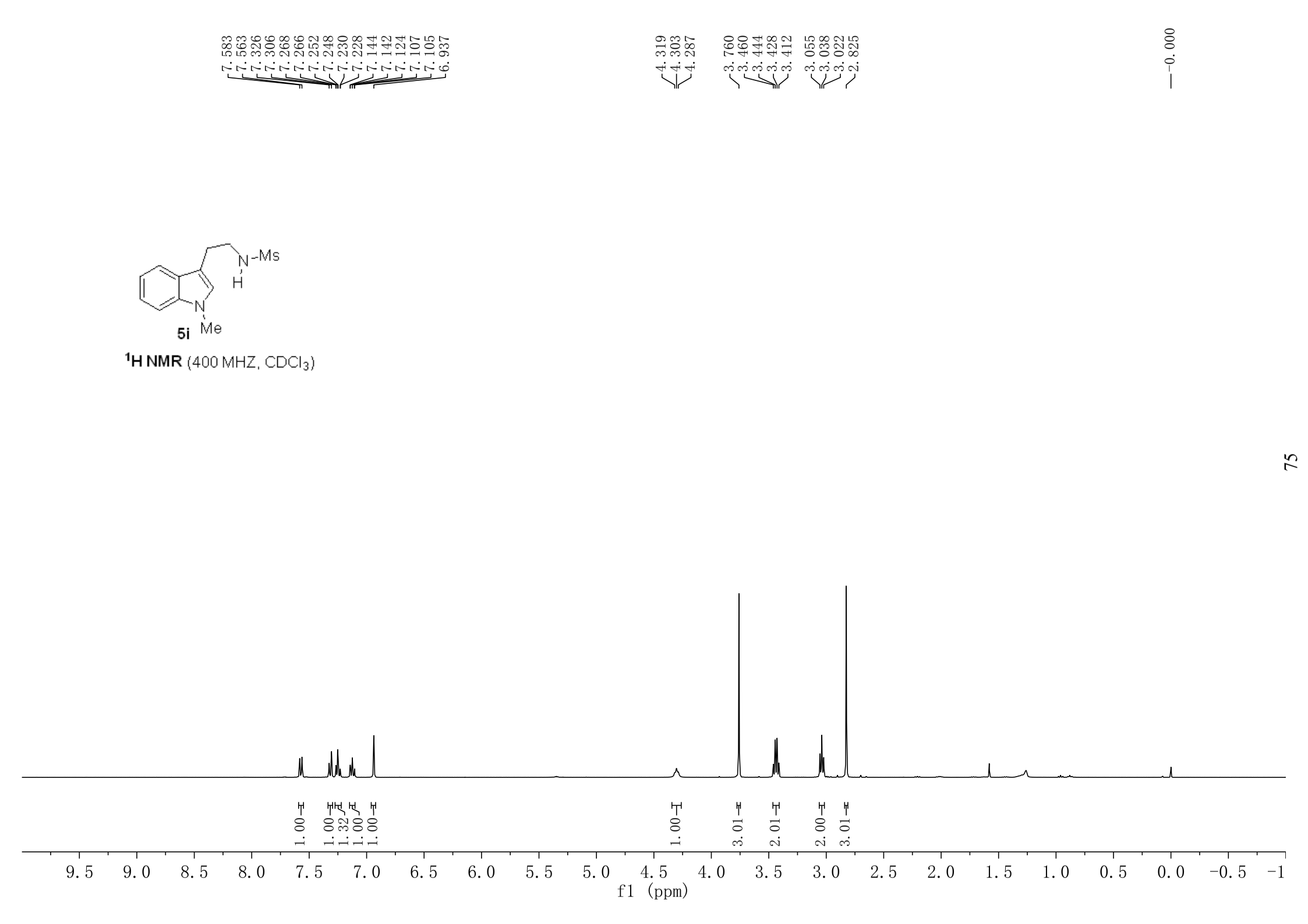
f1 (ppm)


5g
1H NMR (400 MHZ, CDCl3)
Me
H
N
S
O
O
NO2
8.089
8.068
7.759
7.737
7.316
7.296
7.253
7.231
7.211
7.201
7.183
7.163
7.018
7.001
6.982
6.813
4.613
4.599
4.586
3.713
3.364
3.349
3.334
3.318
2.942
2.927
2.911
0.000
2.00
2.00
1.01
2.02
1.02
0.99
1.00
3.01
2.03
2.07
f1 (ppm)

5g
13C NMR (100 MHZ, CDCl3)
Me
H
N
S
O
O
NO2
149.68
145.35
137.18
127.85
127.37
127.01
123.86
122.08
119.16
118.36
109.44
77.32
77.00
76.68
43.24
32.62
25.38
f1 (ppm)

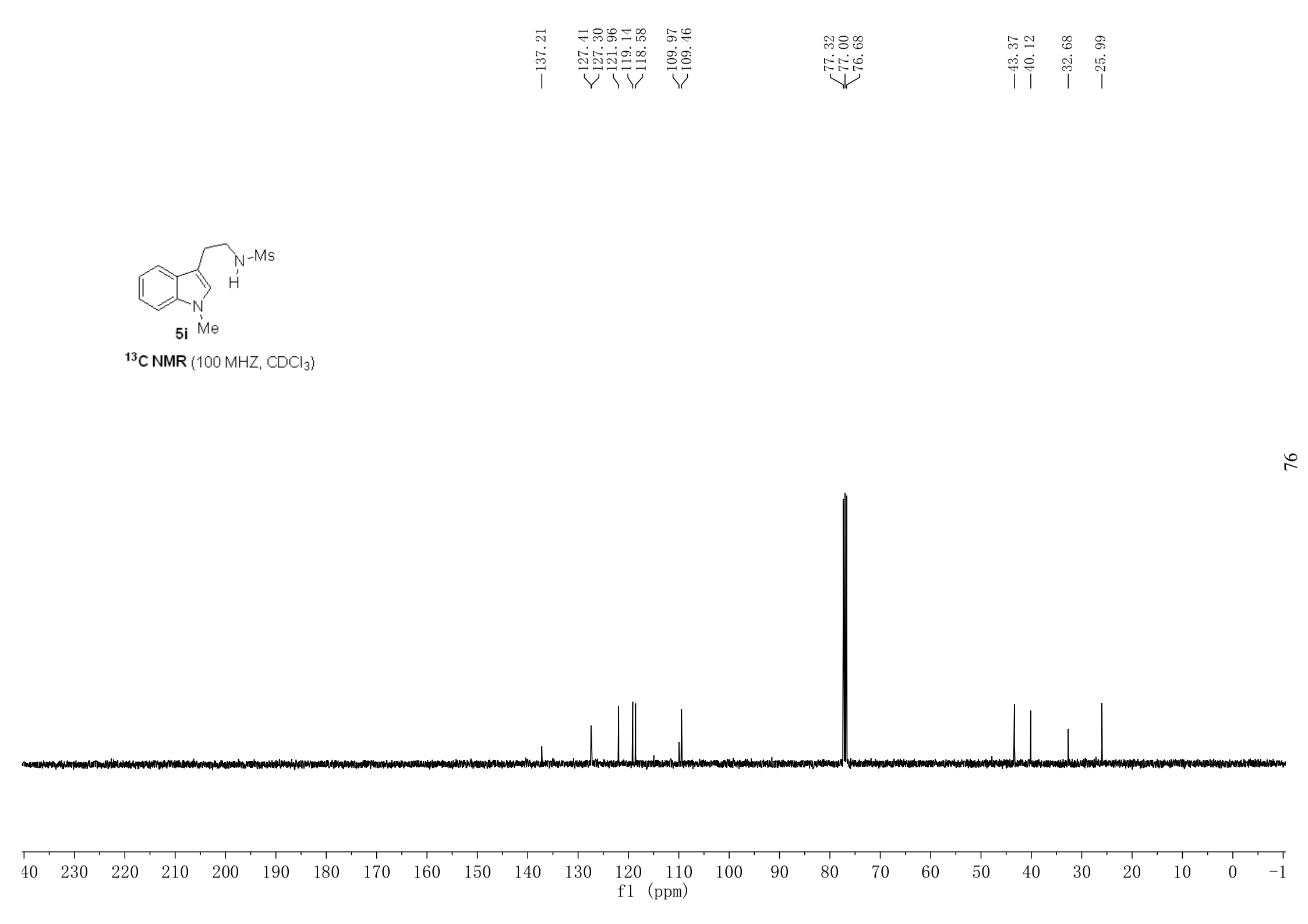

1H NMR (400 MHZ, CDCl3)
5h
Me
8.330
7.854
7.836
7.816
7.795
7.691
7.687
7.669
7.665
7.618
7.602
7.583
7.580
7.575
7.554
7.537
7.333
7.314
7.216
7.206
7.186
7.164
7.147
7.127
6.965
6.946
6.928
6.725
4.779
4.764
4.749
3.601
3.321
3.304
3.288
3.272
2.903
2.886
2.869
-0.000
1.00
3.00
1.00
2.03
1.00
2.08
1.00
1.00
1.00
2.97
1.99
1.97
f1 (ppm)

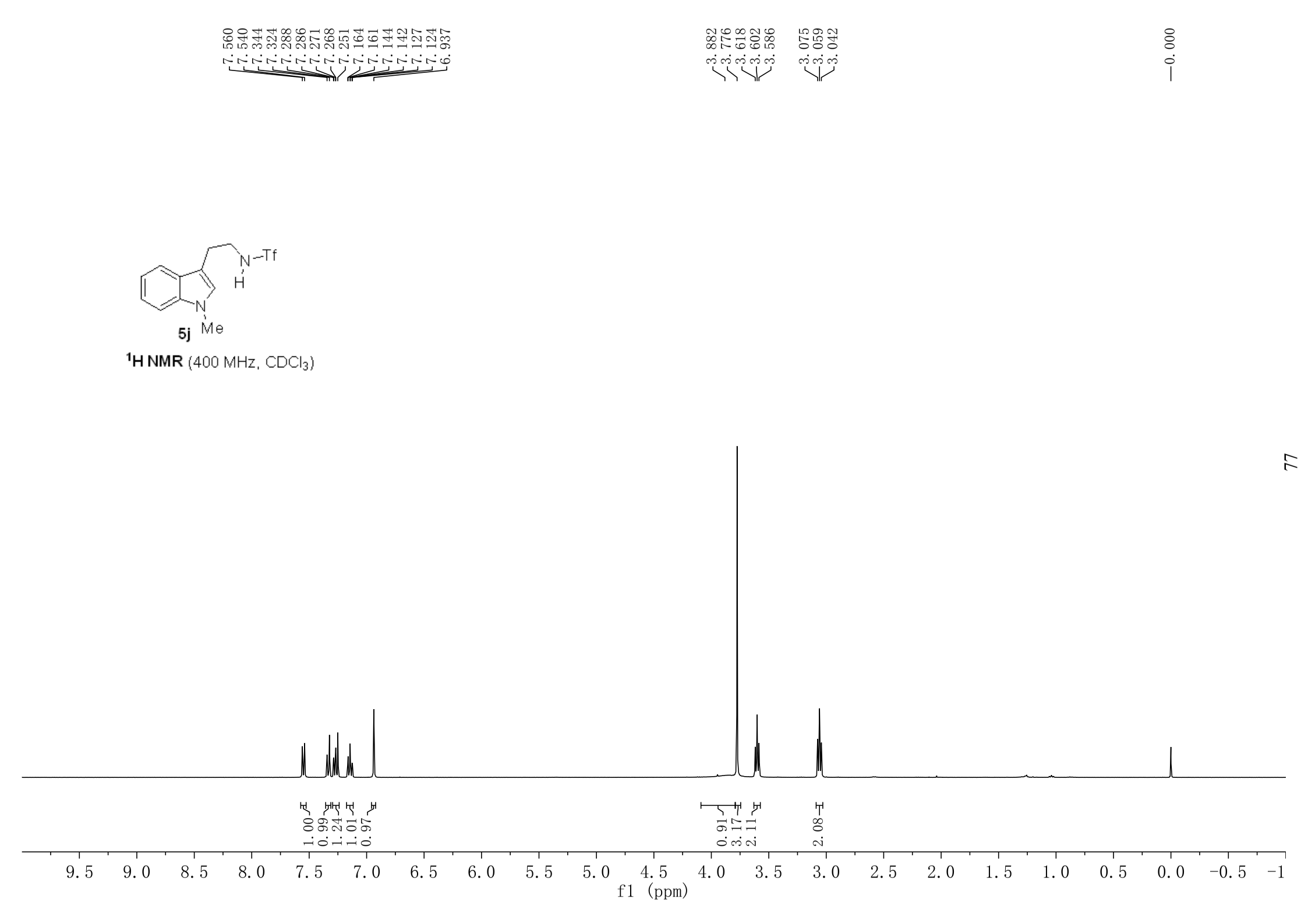

5h
^{13}C NMR (100 MHZ, $CDCl_3$)
Me
N
H
N
S
O
O
137.03
136.70
134.65
132.05
129.26
129.15
128.59
128.20
127.80
127.36
127.25
127.21
122.20
121.73
118.90
118.45
109.86
109.24
77.32
77.00
76.68
43.30
32.44
25.36
f1 (ppm)
40 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

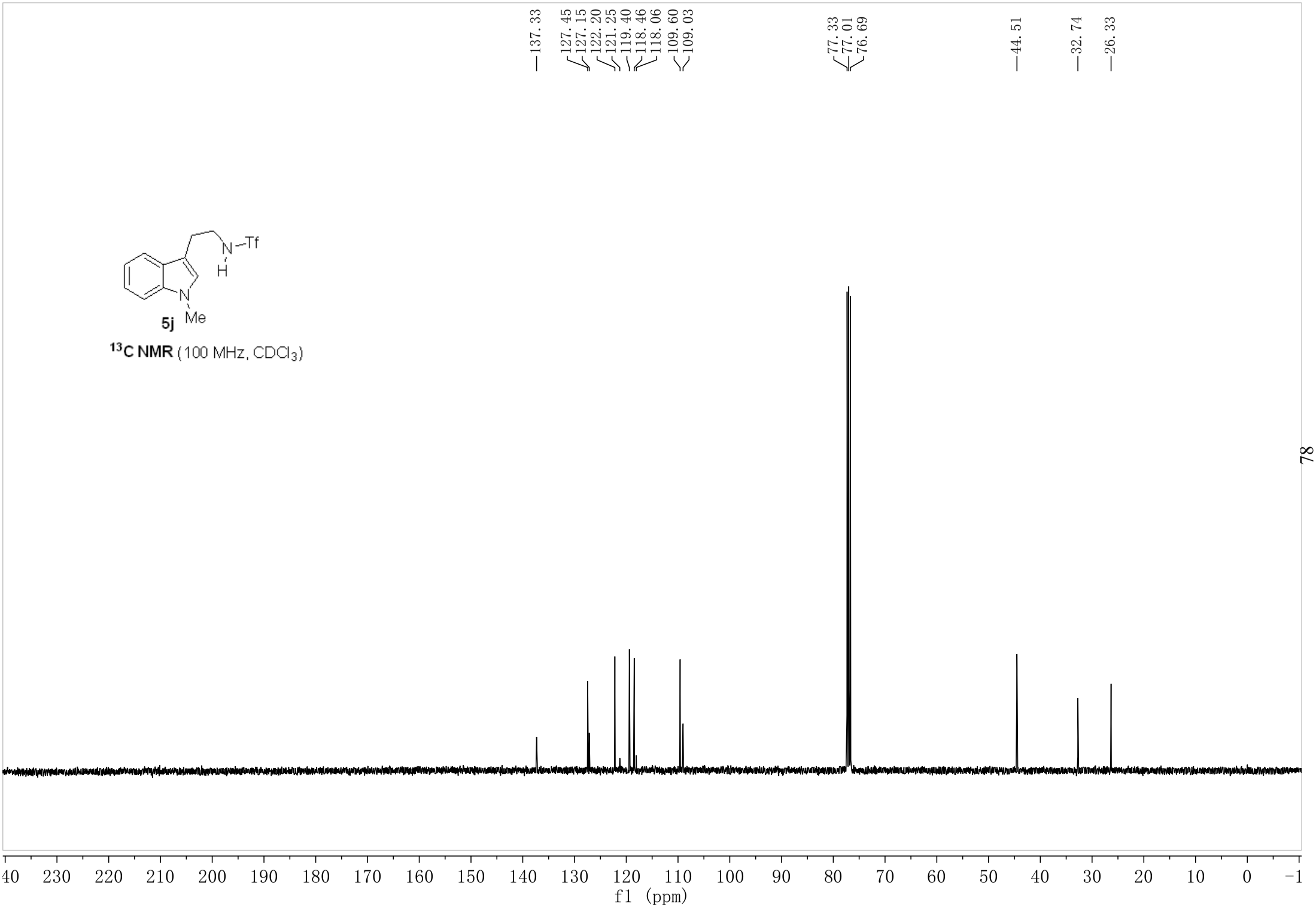


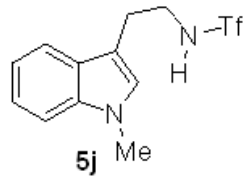
5i

^{1}H NMR (400 MHZ, $CDCl_3$)


137.21
127.41
127.30
121.96
119.14
118.58
109.97
109.46
77.32
77.00
76.68
43.37
40.12
32.68
25.99
N-Ms
H
N
Me
5i
13C NMR (100 MHZ, CDCl3)
76
40 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

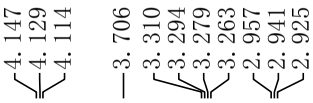

7.560
7.540
7.344
7.324
7.288
7.286
7.271
7.268
7.251
7.164
7.161
7.144
7.142
7.127
7.124
6.937
3.882
3.776
3.618
3.602
3.586
3.075
3.059
3.042
0.000
N
Tf
H
N
Me
5j
1H NMR (400 MHz, CDCl3)
1.00
0.99
1.24
1.01
0.97
0.91
3.17
2.11
2.08
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)
77

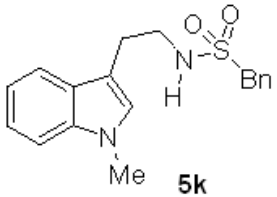

137.33
127.45
127.15
122.20
121.25
119.40
118.46
118.06
109.60
109.03
77.33
77.01
76.69
44.51
32.74
26.33
N
Tf
H
N
Me
5j
13C NMR (100 MHz, CDCl3)
78
40 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)



5j

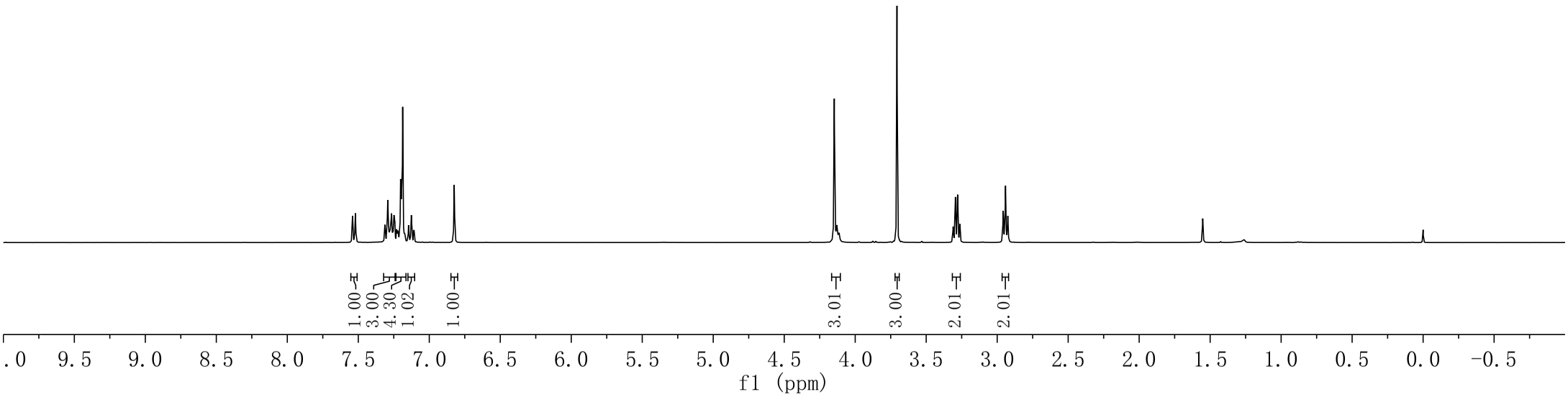
^{19}F NMR (376 MHz, $CDCl_3$)

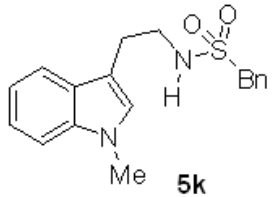




5k

^{1}H NMR (400 MHZ, $CDCl_3$)

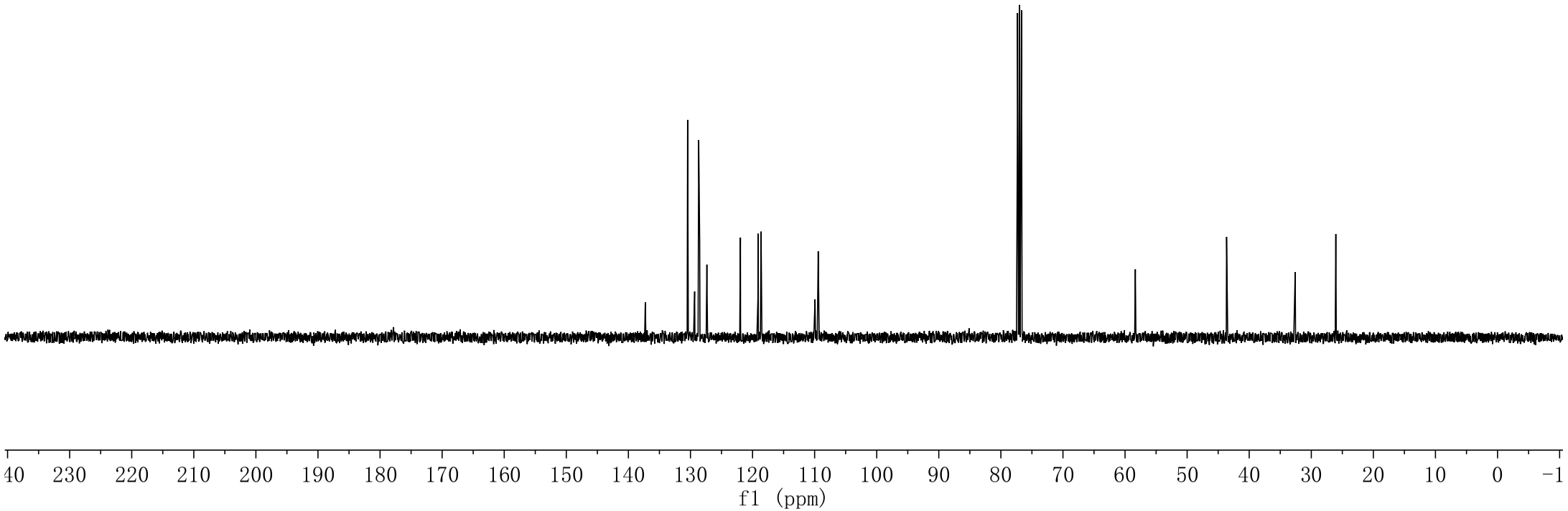


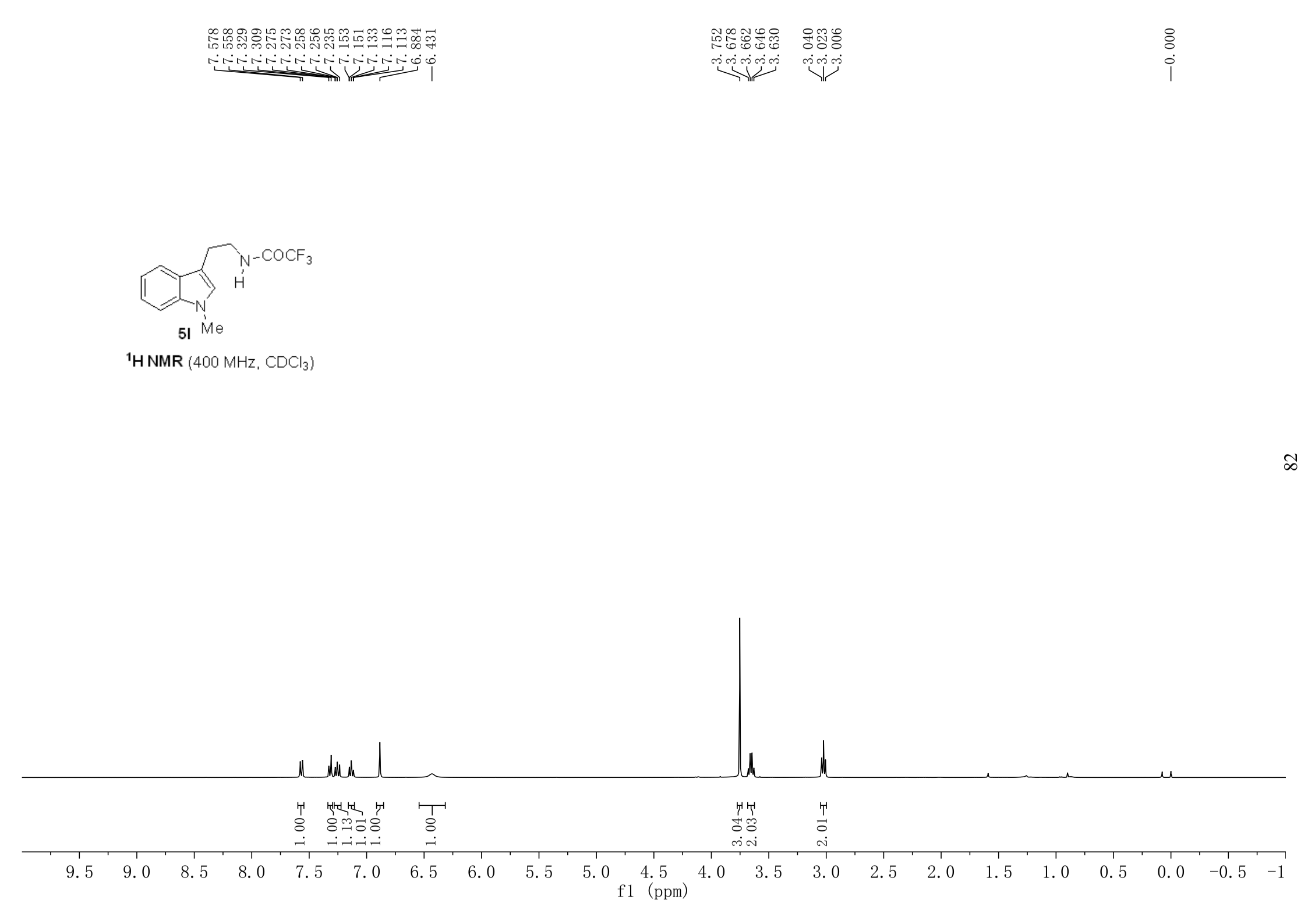


5k

^{13}C NMR (100 MHZ, $CDCl_3$)

137.27
130.46
129.33
128.67
128.52
127.36
127.31
121.95
119.12
118.63
109.94
109.43
77.32
77.00
76.68
58.34
43.65
32.59
26.05

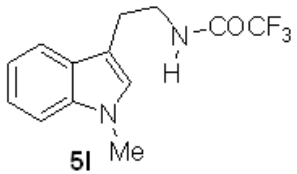




5l

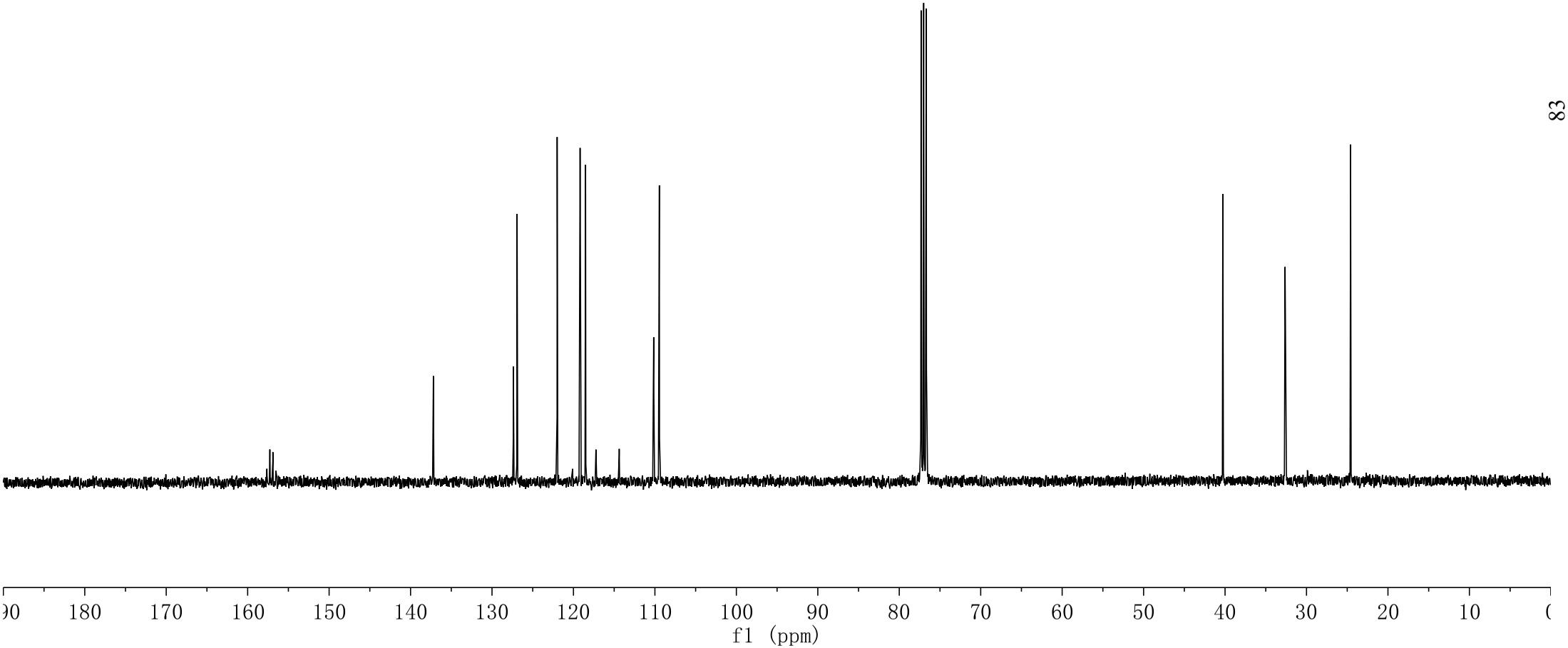
^{1}H NMR (400 MHz, $CDCl_3$)

157.64
157.27
156.90
156.54
137.20
127.38
126.92
122.00
120.10
119.19
118.51
117.24
114.38
110.15
109.46
77.32
77.00
76.68
40.28
32.63
24.59

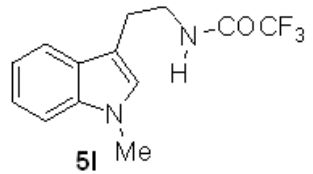


5l

^{13}C NMR (100 MHz, $CDCl_3$)

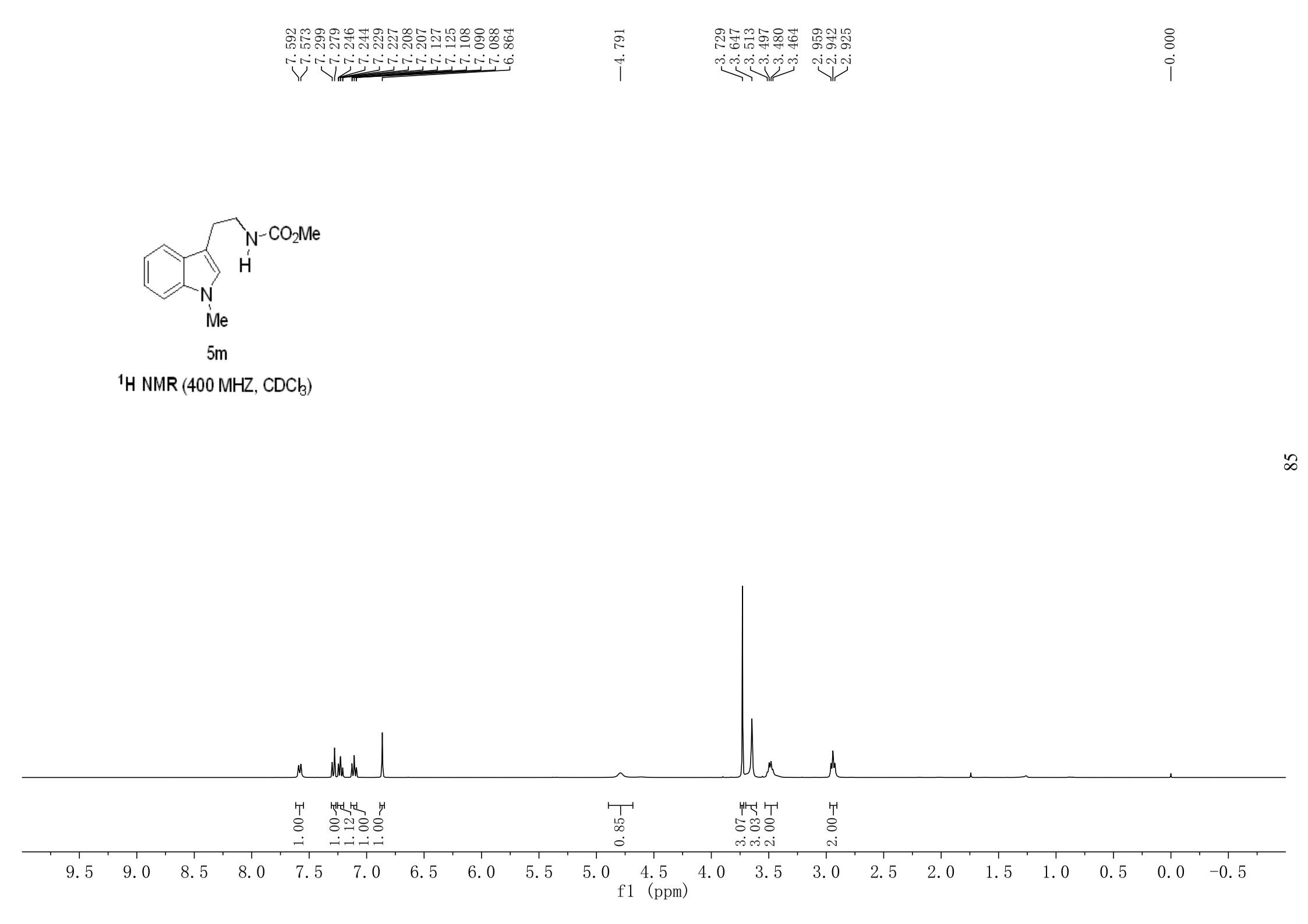


83



5l

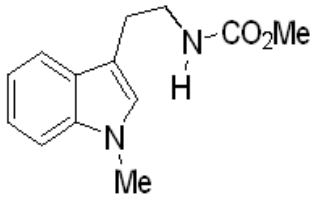
^{19}F NMR (376 MHz, $CDCl_3$)



5m

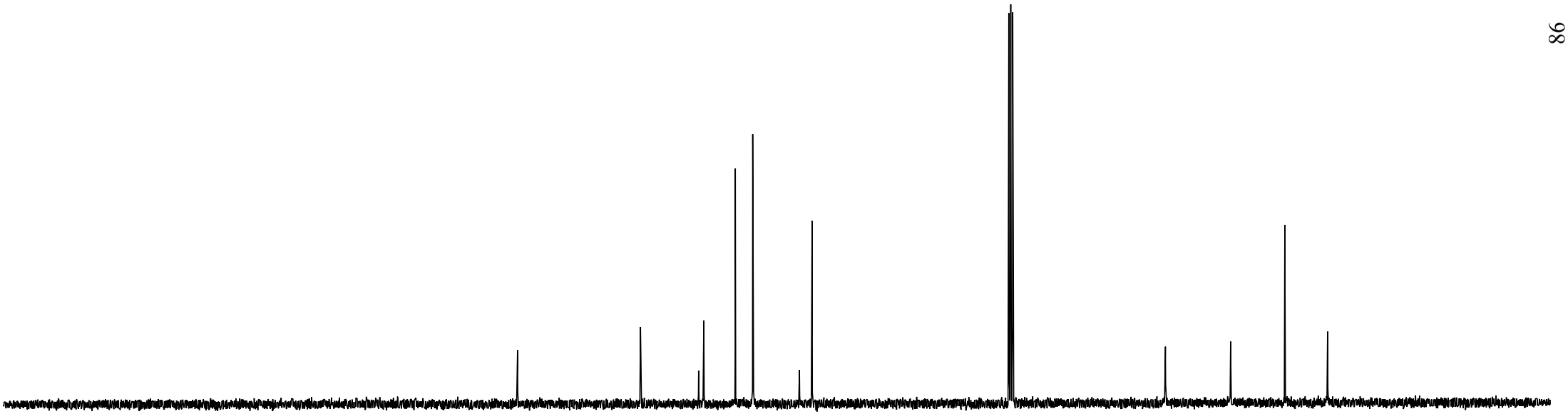
^{1}H NMR (400 MHZ, $CDCl_3$)

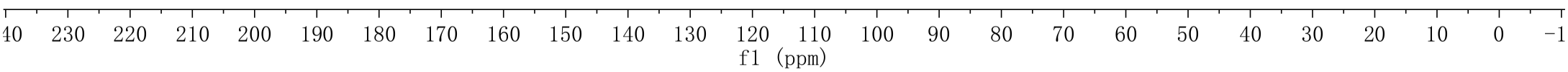
156.98
137.05
127.62
126.78
121.67
118.85
118.77
111.27
109.22
77.32
77.00
76.68
51.92
41.35
32.56
25.62

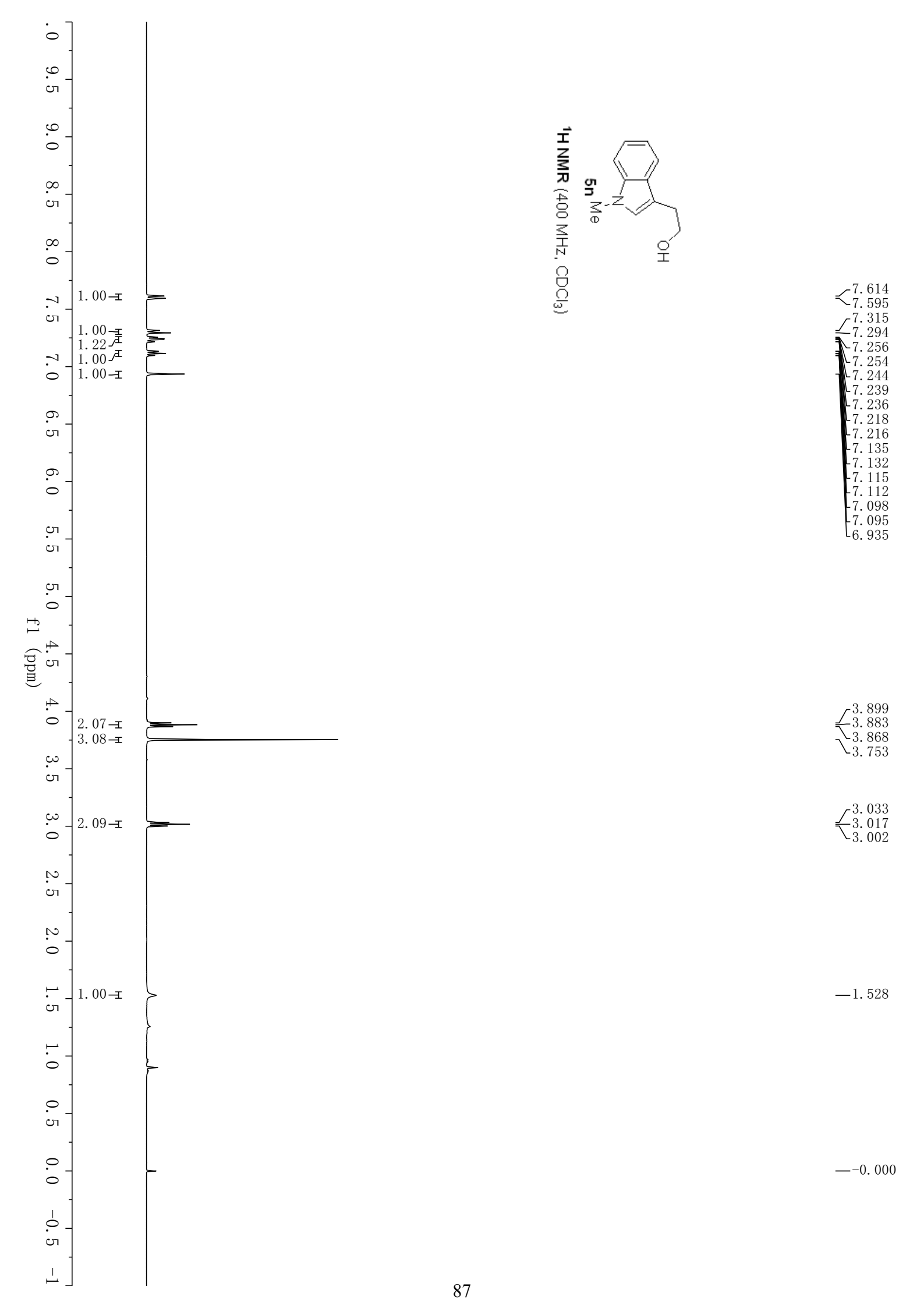


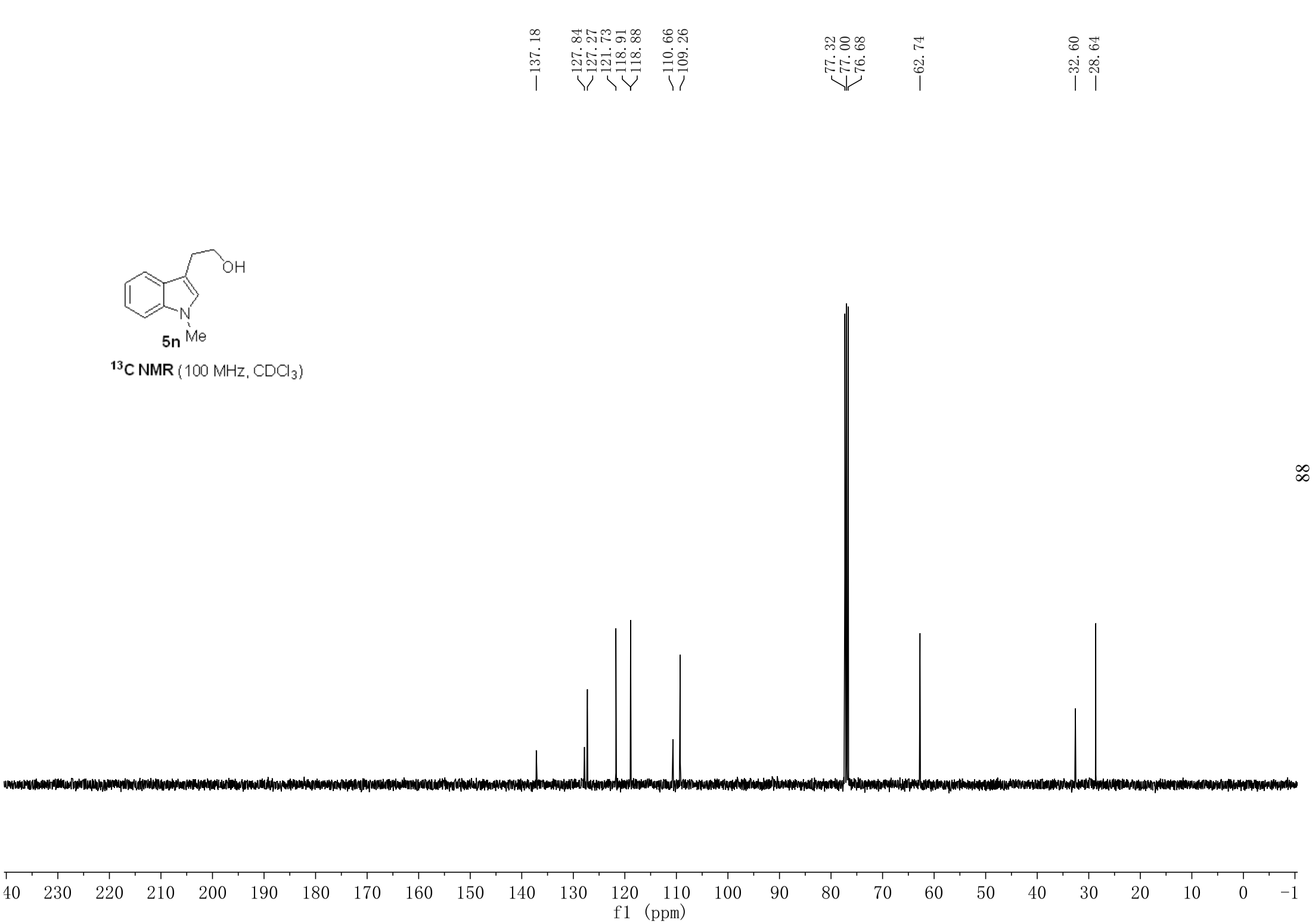
5m

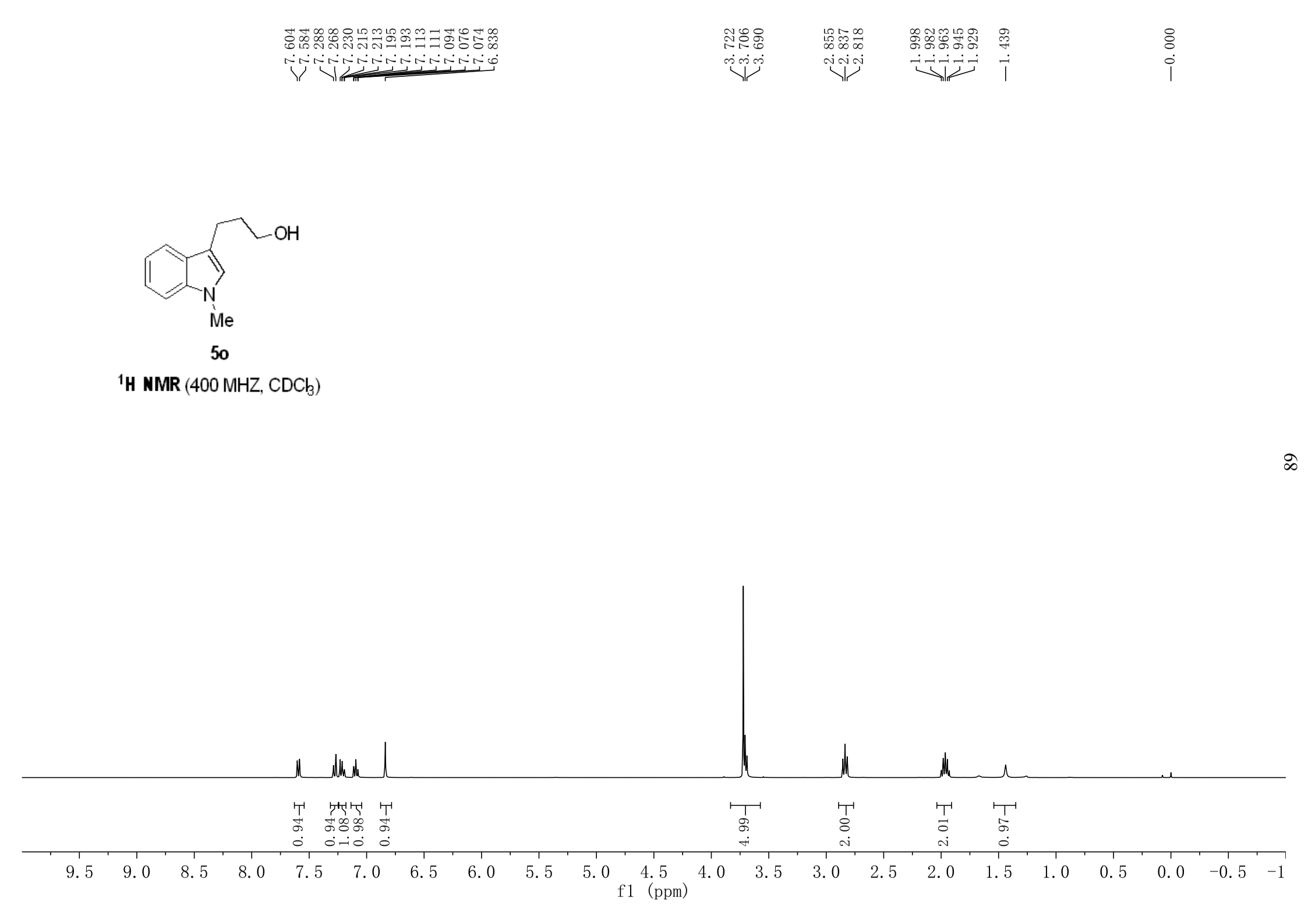
^{13}C NMR (100 MHZ, $CDCl_3$)

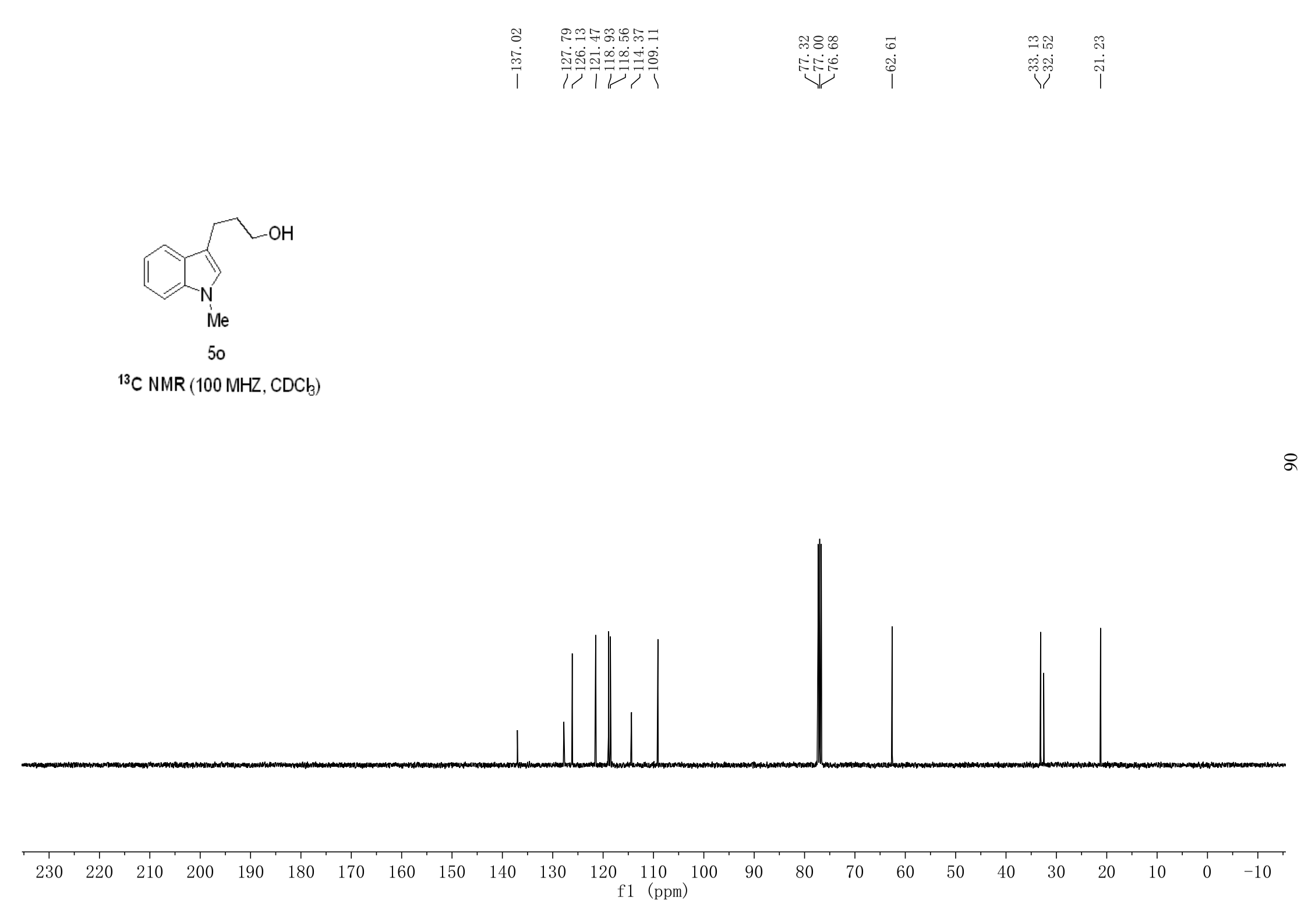


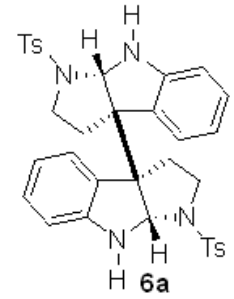



5n
Me
OH
¹H NMR (400 MHz, CDCl₃)
1.00
1.22
1.00
1.00
2.07
3.08
2.09
1.00
7.614
7.595
7.315
7.294
7.256
7.254
7.244
7.239
7.236
7.218
7.216
7.135
7.132
7.115
7.112
7.098
7.095
6.935
3.899
3.883
3.868
3.753
3.033
3.017
3.002
1.528
-0.000
f1 (ppm)


137.18
127.84
127.27
121.73
118.91
118.88
110.66
109.26
77.32
77.00
76.68
62.74
32.60
28.64
OH
N
Me
5n
13C NMR (100 MHz, CDCl3)
88
40 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

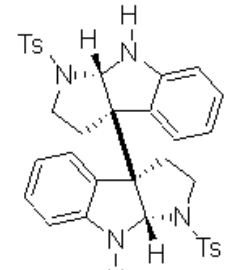

7.604
7.584
7.288
7.268
7.230
7.215
7.213
7.195
7.193
7.113
7.111
7.094
7.076
7.074
6.838
3.722
3.706
3.690
2.855
2.837
2.818
1.998
1.982
1.963
1.945
1.929
1.439
0.000
OH
N
Me
5o
1H NMR (400 MHZ, CDCl3)
0.94
0.94
1.08
0.98
0.94
4.99
2.00
2.01
0.97
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


137.02
127.79
126.13
121.47
118.93
118.56
114.37
109.11
77.32
77.00
76.68
62.61
33.13
32.52
21.23
OH
N
Me
5o
13C NMR (100 MHZ, CDCl3)
90
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



6a

^{1}H NMR (400 MHz, $CDCl_3$)



6a

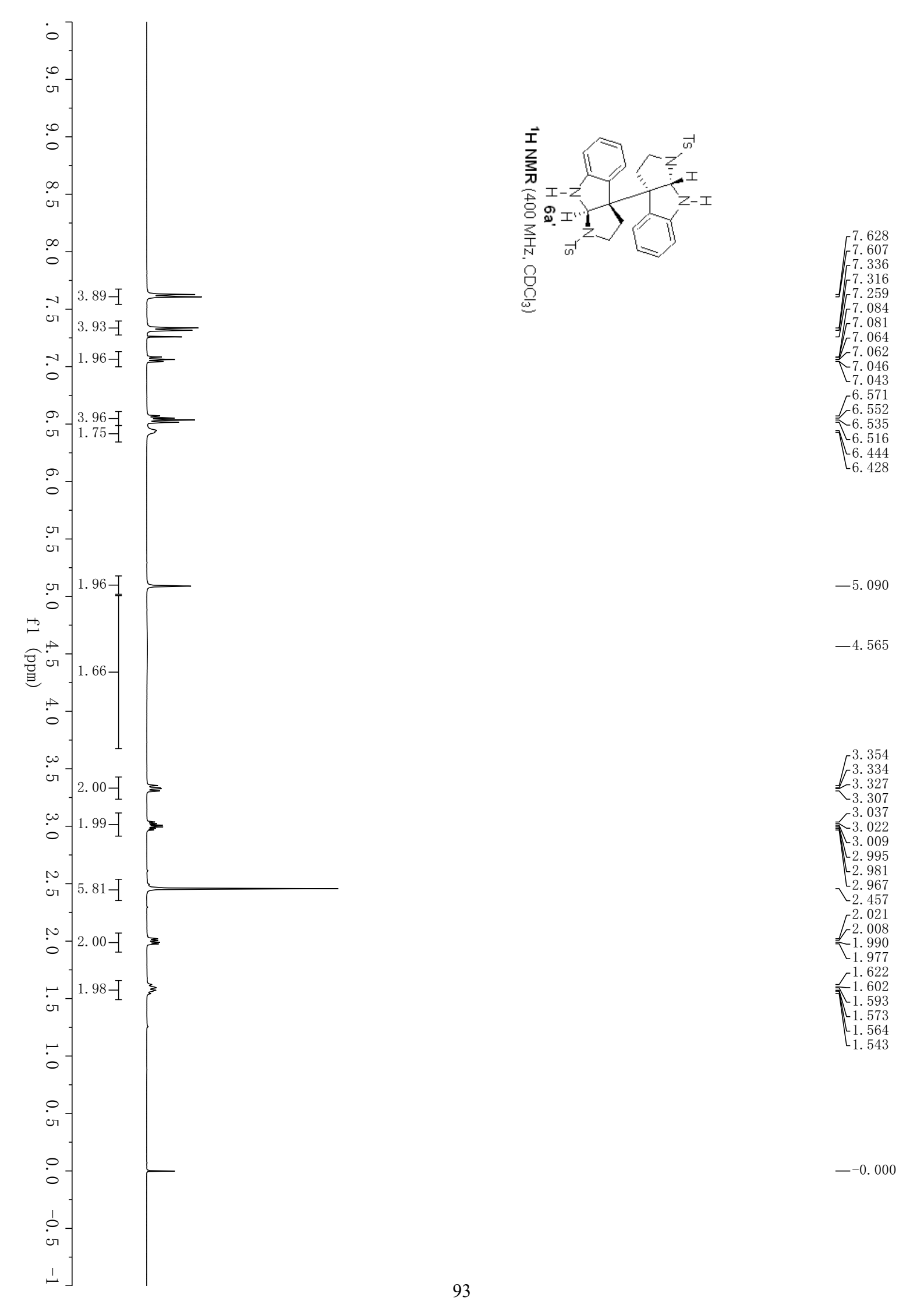
^{13}C NMR (100 MHz, $CDCl_3$)

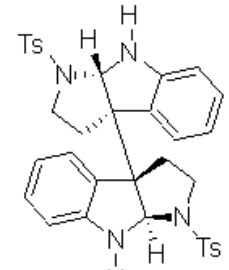
150.07
142.97
135.41
129.83
129.34
127.37
126.53
124.49
119.06
110.37
81.26
77.32
77.00
76.68
61.33
46.84
32.31
21.52

92

40 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −1

f1 (ppm)


1H NMR (400 MHz, CDCl3)
6a'
Ts
Ts
H
H
H
H
7.628
7.607
7.336
7.316
7.259
7.084
7.081
7.064
7.062
7.046
7.043
6.571
6.552
6.535
6.516
6.444
6.428
5.090
4.565
3.354
3.334
3.327
3.307
3.037
3.022
3.009
2.995
2.981
2.967
2.457
2.021
2.008
1.990
1.977
1.622
1.602
1.593
1.573
1.564
1.543
-0.000
3.89
3.93
1.96
3.96
1.75
1.96
1.66
2.00
1.99
5.81
2.00
1.98
f1 (ppm)

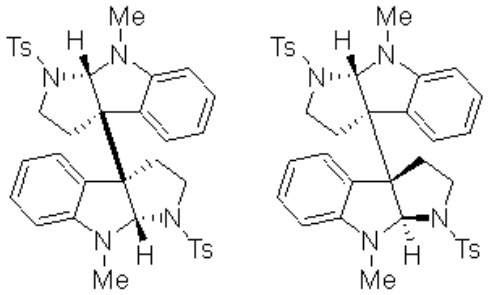


6a'

^{13}C NMR (100 MHz, $CDCl_3$)

149.78
143.85
136.35
129.86
129.20
127.87
126.83
123.66
119.00
109.77
80.01
77.32
77.00
76.68
62.50
47.13
33.84
21.58

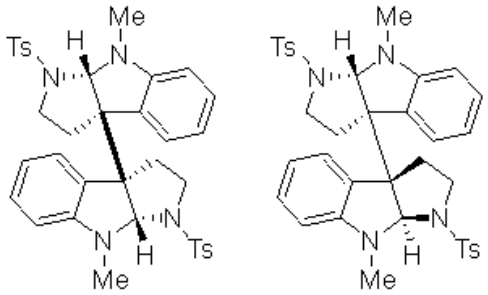
f1 (ppm)



6b **6b'**

^{1}H NMR (400 MHz, $CDCl_3$)

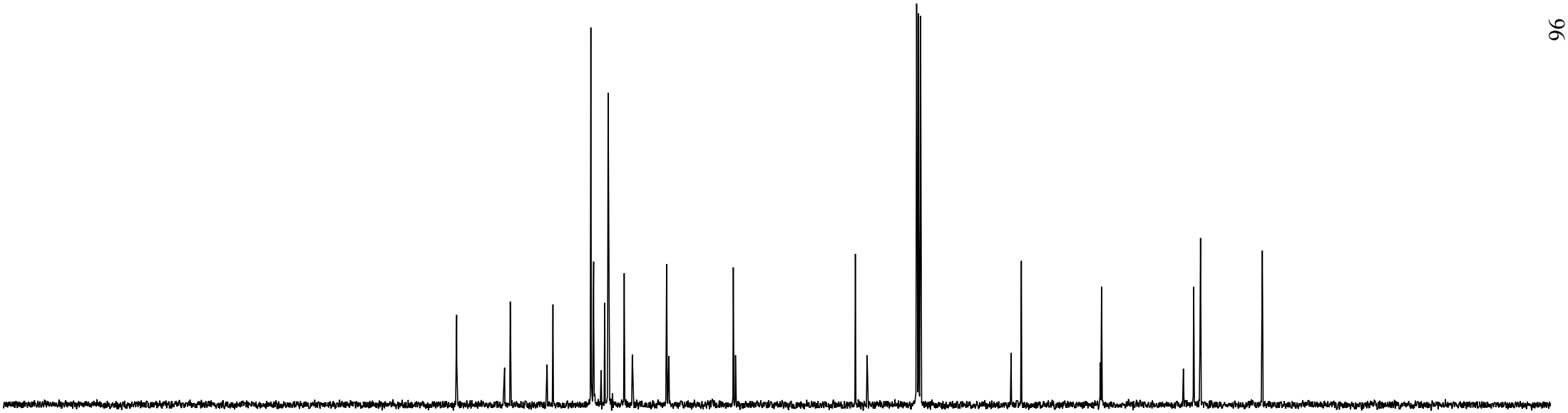
151.60
151.49
143.86
142.94
136.99
136.05
129.93
129.48
129.33
128.27
127.69
127.13
126.99
124.54
123.24
117.69
117.32
106.92
106.57
87.21
85.32
77.32
77.00
76.68
62.06
60.40
47.67
47.44
34.23
32.58
31.57
31.47
21.53
21.49

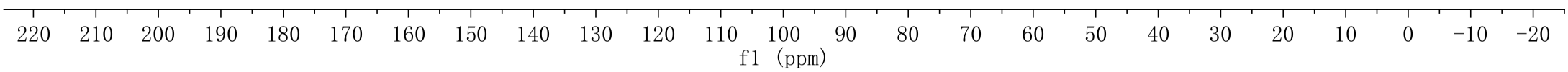


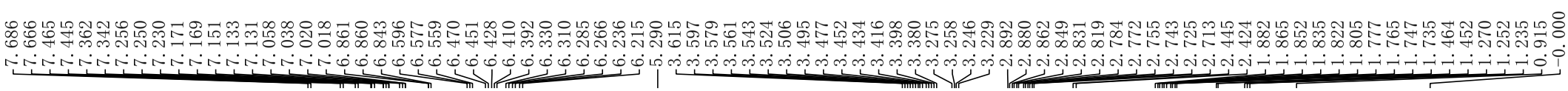
6b

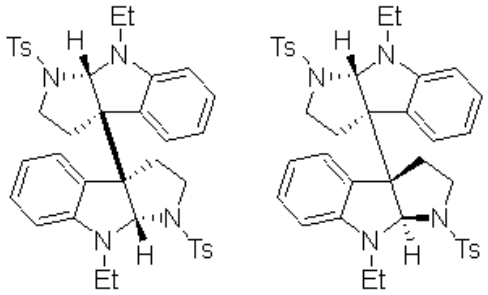
6b'

^{13}C NMR (100 MHz, $CDCl_3$)



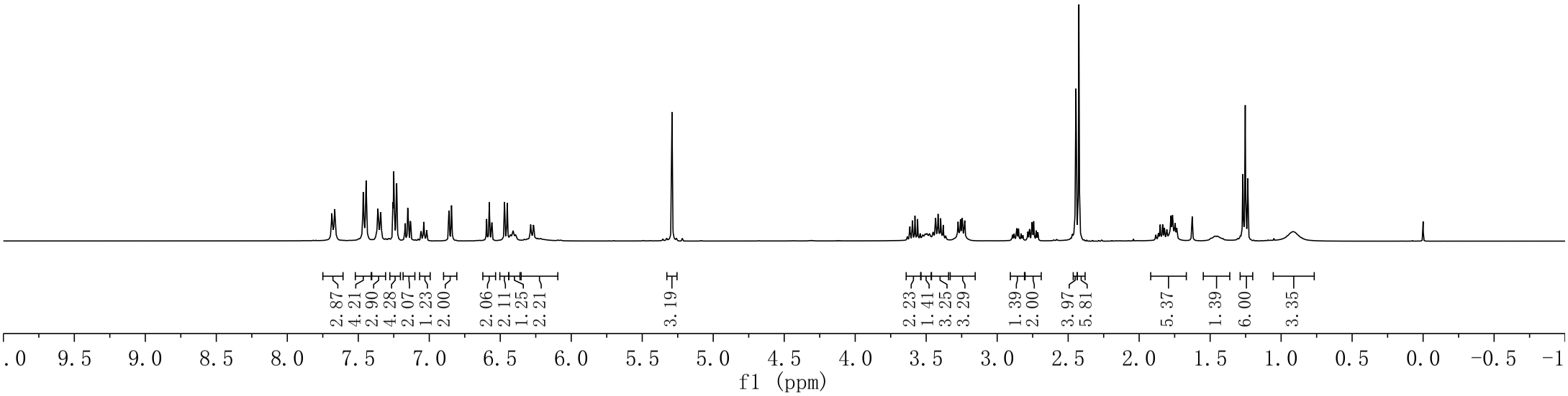


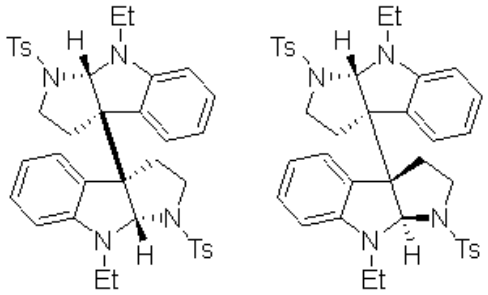




6c **6c'**

^{1}H NMR (400 MHz, $CDCl_3$)

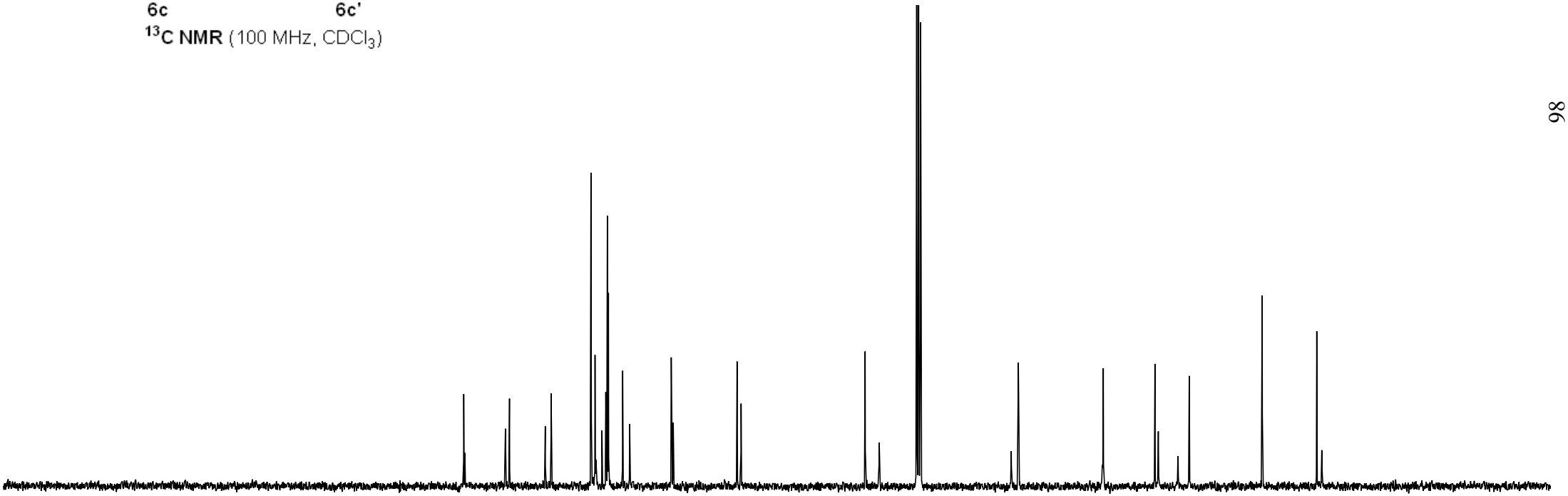


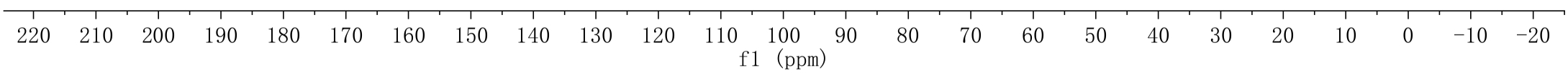


6c **6c'**

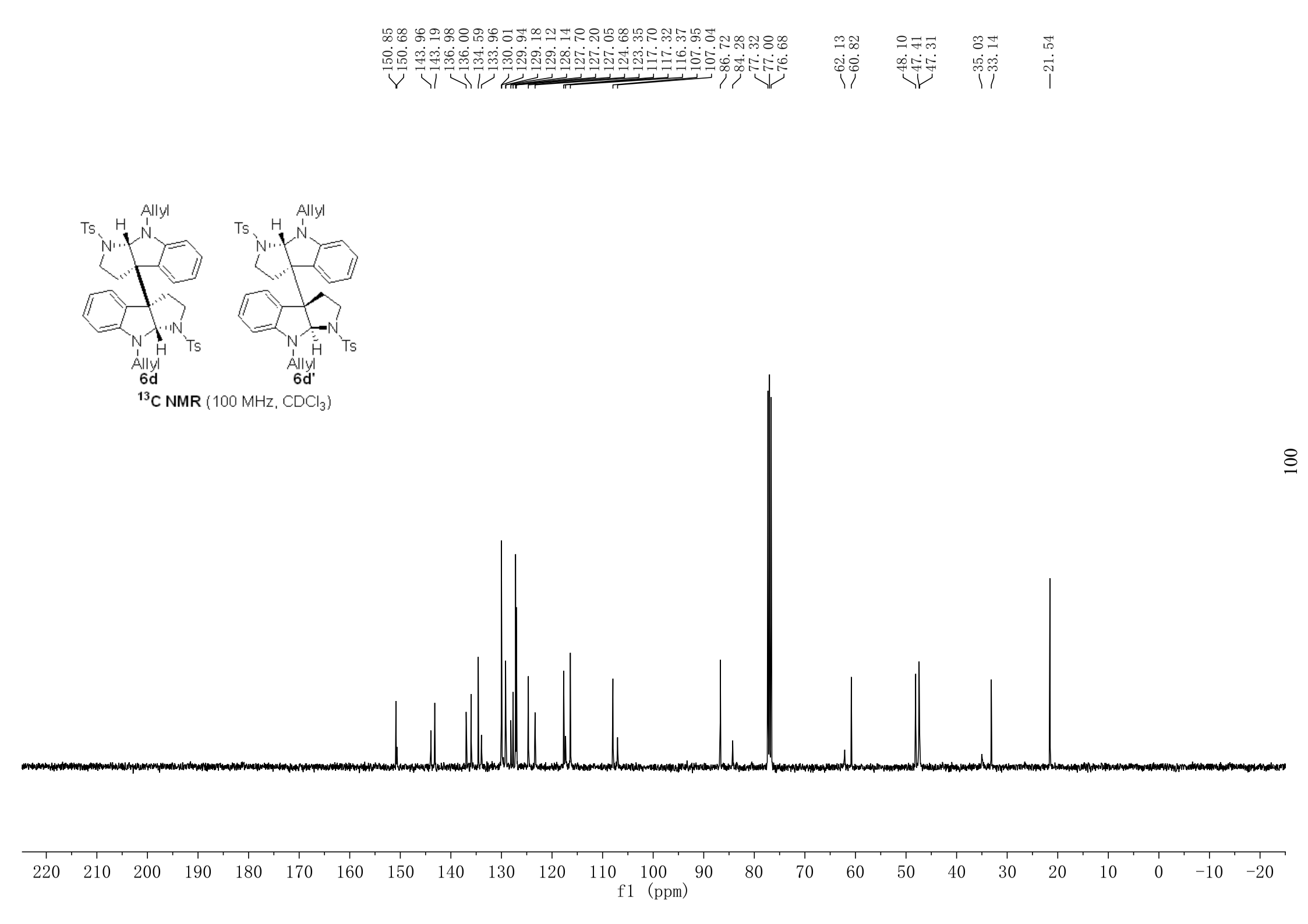
^{13}C NMR (100 MHz, $CDCl_3$)

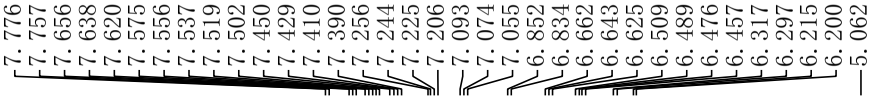
150.46
150.28
143.73
143.08
137.30
136.35
129.92
129.88
129.26
129.13
128.14
127.52
127.26
127.10
124.80
123.67
116.95
116.62
106.32
105.67
85.64
83.36
77.32
77.00
76.68
62.05
60.90
47.31
47.18
38.84
38.29
35.12
33.30
21.51
12.70
11.89

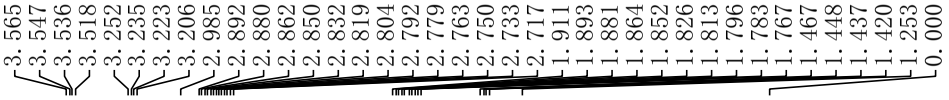


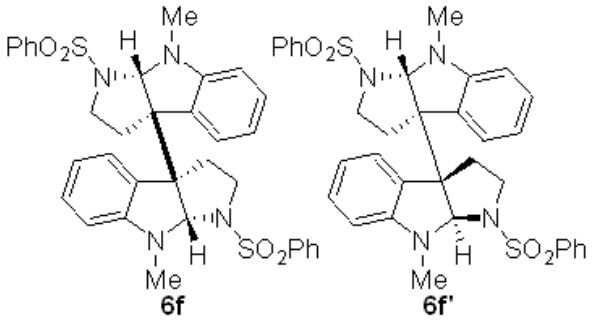


^{1}H NMR (400 MHz, $CDCl_3$)

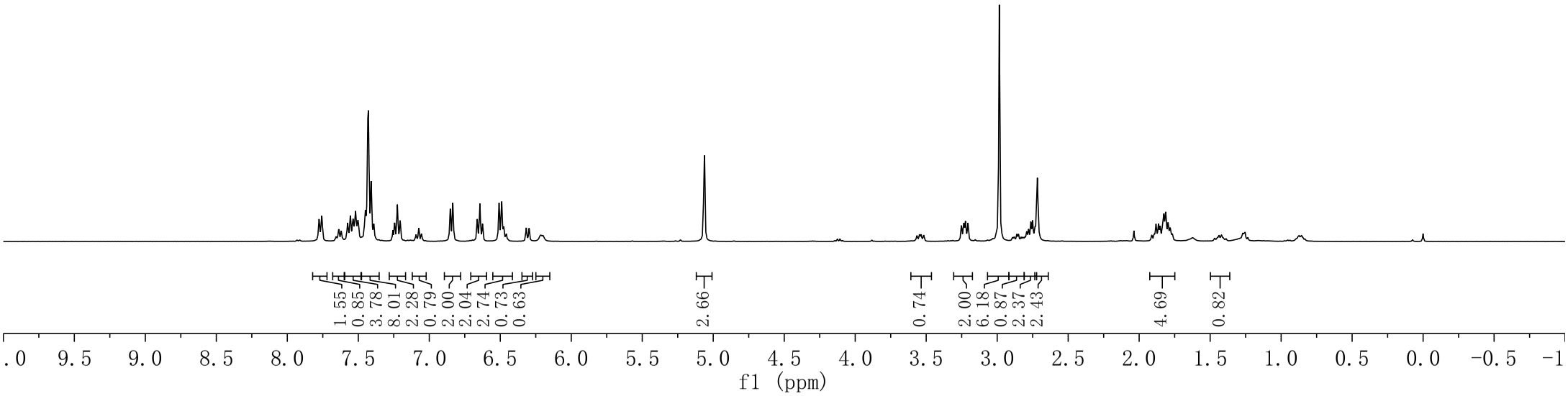

150.85
150.68
143.96
143.19
136.98
136.00
134.59
133.96
130.01
129.94
129.18
129.12
128.14
127.70
127.20
127.05
124.68
123.35
117.70
117.32
116.37
107.95
107.04
86.72
84.28
77.32
77.00
76.68
62.13
60.82
48.10
47.41
47.31
35.03
33.14
21.54
Allyl
Ts
H
N
Allyl
6d
Allyl
Ts
H
N
Allyl
6d'
13C NMR (100 MHz, CDCl3)
100
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)



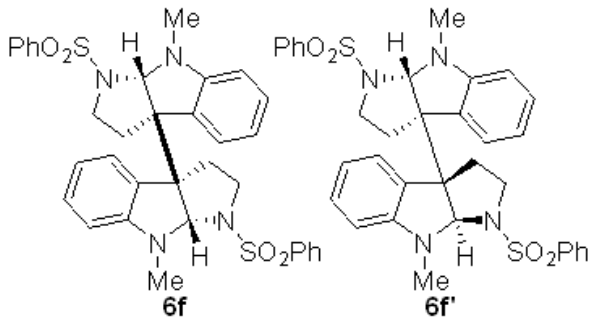




^{1}H NMR (400 MHz, $CDCl_3$)



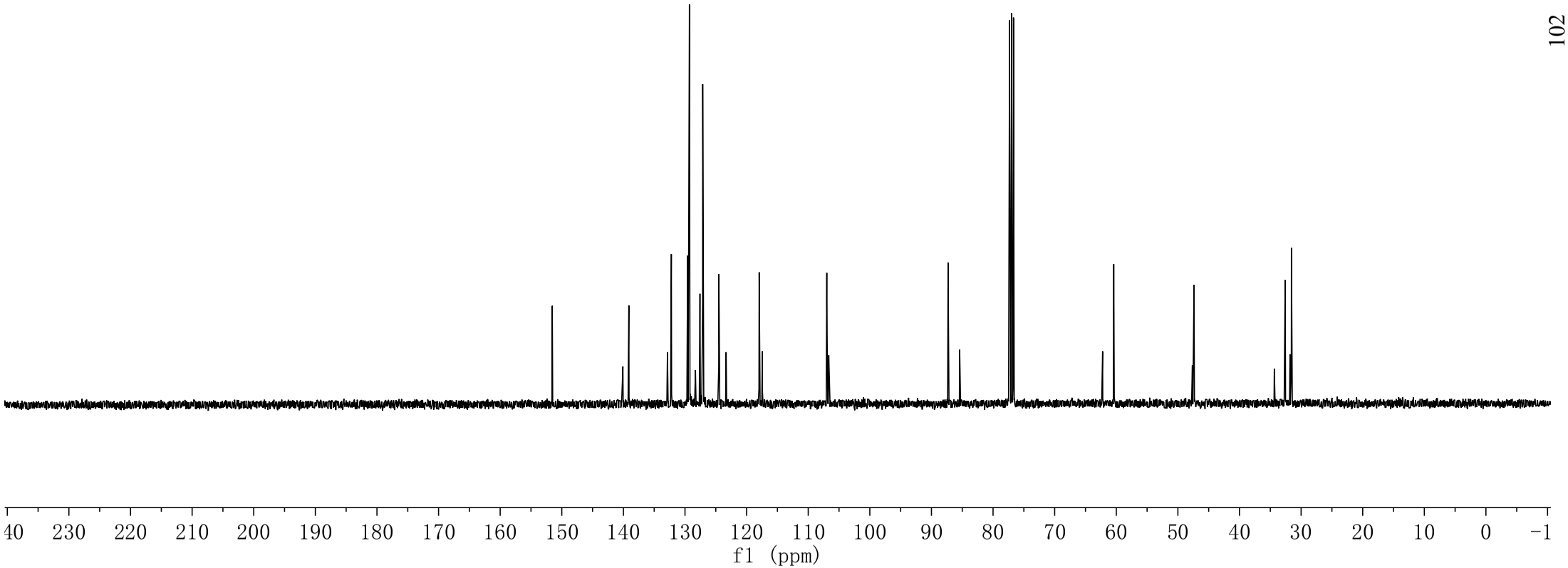
151.54
151.51
140.08
139.11
132.85
132.21
129.57
129.39
129.28
128.31
127.57
127.13
127.05
124.51
123.32
117.96
117.45
106.99
106.67
87.30
85.42
77.32
77.00
76.68
62.22
60.41
47.65
47.38
34.35
32.58
31.80
31.57



6f

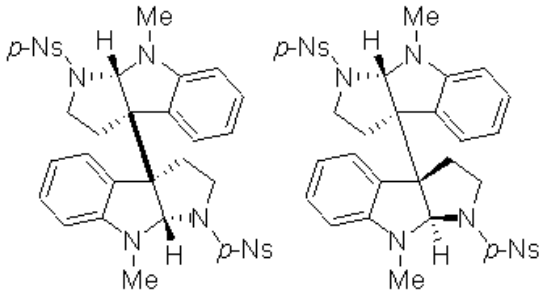
6f'

^{13}C NMR (100 MHz, $CDCl_3$)



6g
6g'
^{1}H NMR (400 MHz, CDCl$_3$)
p-Ns
Me
H
N
1.54
3.87
1.51
3.88
2.04
0.83
2.01
3.52
1.18
1.47
0.75
1.93
0.81
2.08
6.00
2.98
2.19
0.84
4.75
f1 (ppm)
8.362
8.340
8.167
8.145
7.997
7.975
7.439
7.417
7.371
7.352
7.333
7.262
7.134
7.114
7.095
6.754
6.736
6.637
6.617
6.598
6.580
6.569
6.550
6.356
6.329
6.309
5.219
4.893
3.693
3.675
3.665
3.647
3.268
3.254
3.241
3.235
3.228
3.222
3.042
2.906
2.893
2.875
2.863
2.850
2.836
2.822
2.808
2.796
2.779
2.619
2.152
2.140
2.122
2.110
2.003
1.984
1.972
1.954
1.942
1.919
1.902
1.878
1.865
1.849

151.57
151.44
150.06
149.50
145.90
144.63
130.19
129.81
128.17
128.02
127.02
124.70
124.52
124.40
123.61
118.43
118.34
107.60
107.29
87.33
86.03
77.32
77.00
76.68
62.49
59.99
47.70
47.67
35.01
32.79
32.32
31.76



6g

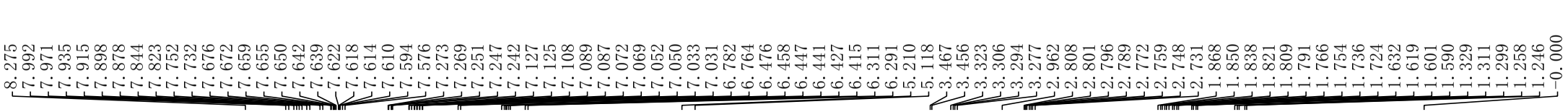
6g'

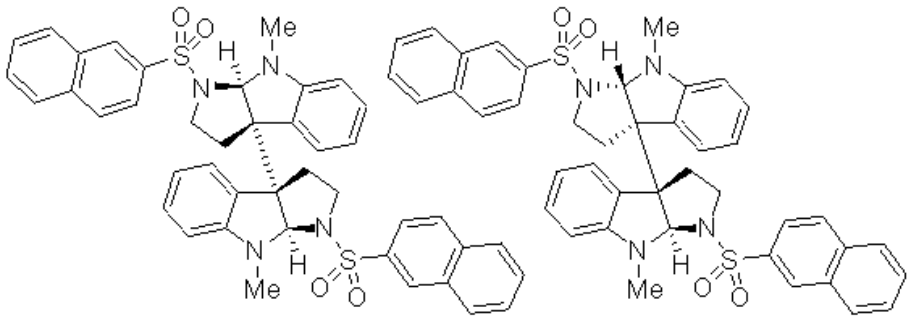
^{13}C NMR (100 MHz, $CDCl_3$)

104

40 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −1

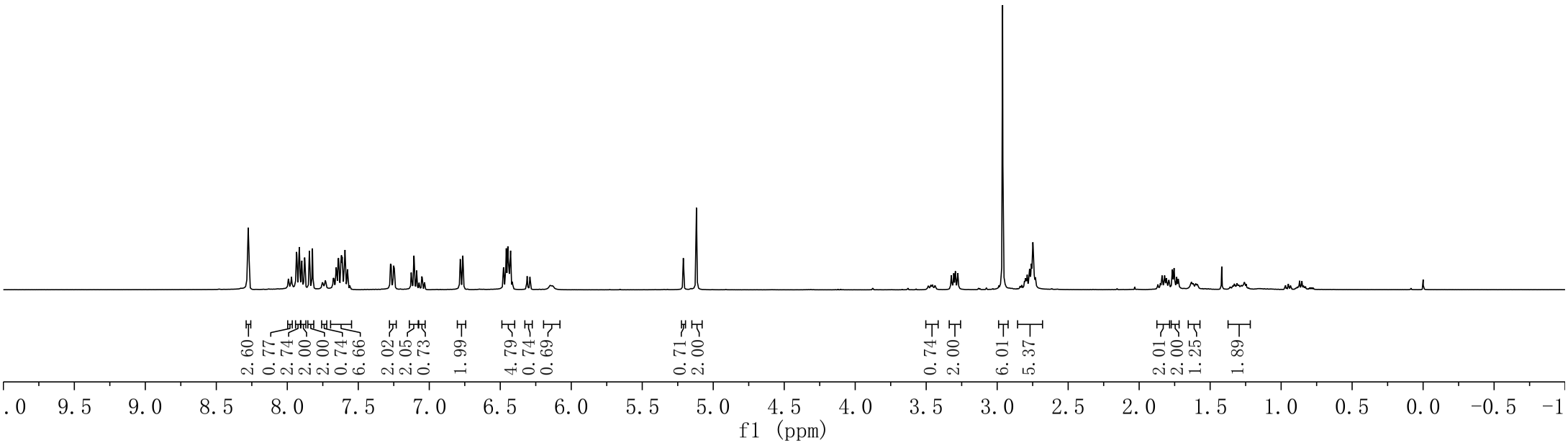
f1 (ppm)





6h **6h'**

^{1}H NMR (400 MHz, $CDCl_3$)



151.47
151.41
136.63
135.89
134.70
134.59
132.02
131.90
129.93
129.86
129.55
129.37
129.35
128.94
128.87
128.72
128.50
128.25
128.01
127.73
127.70
127.46
127.36
124.32
123.29
121.97
117.66
117.38
106.74
106.64

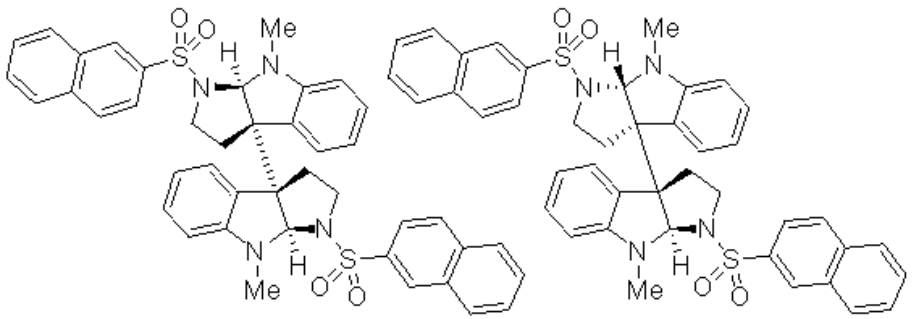
87.22
85.50

77.21
77.00
76.79

62.14
60.56

47.58
47.47

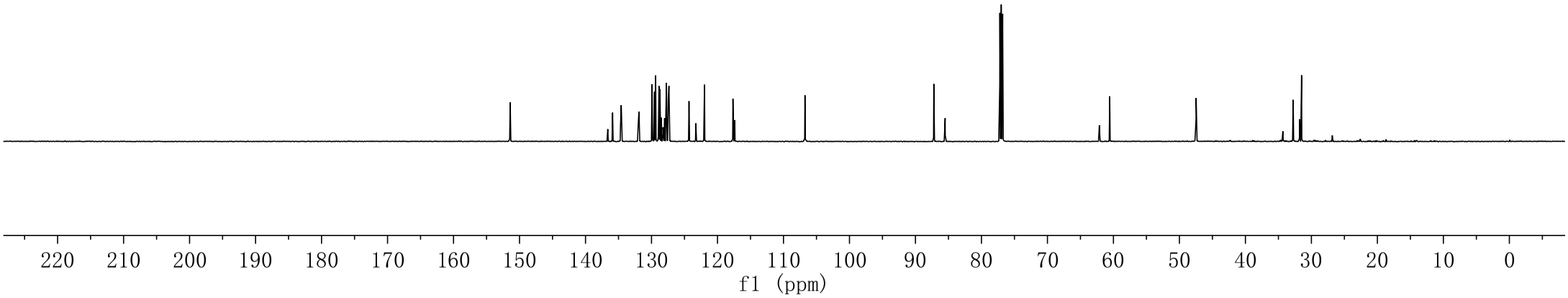
34.32
32.76
31.80
31.49

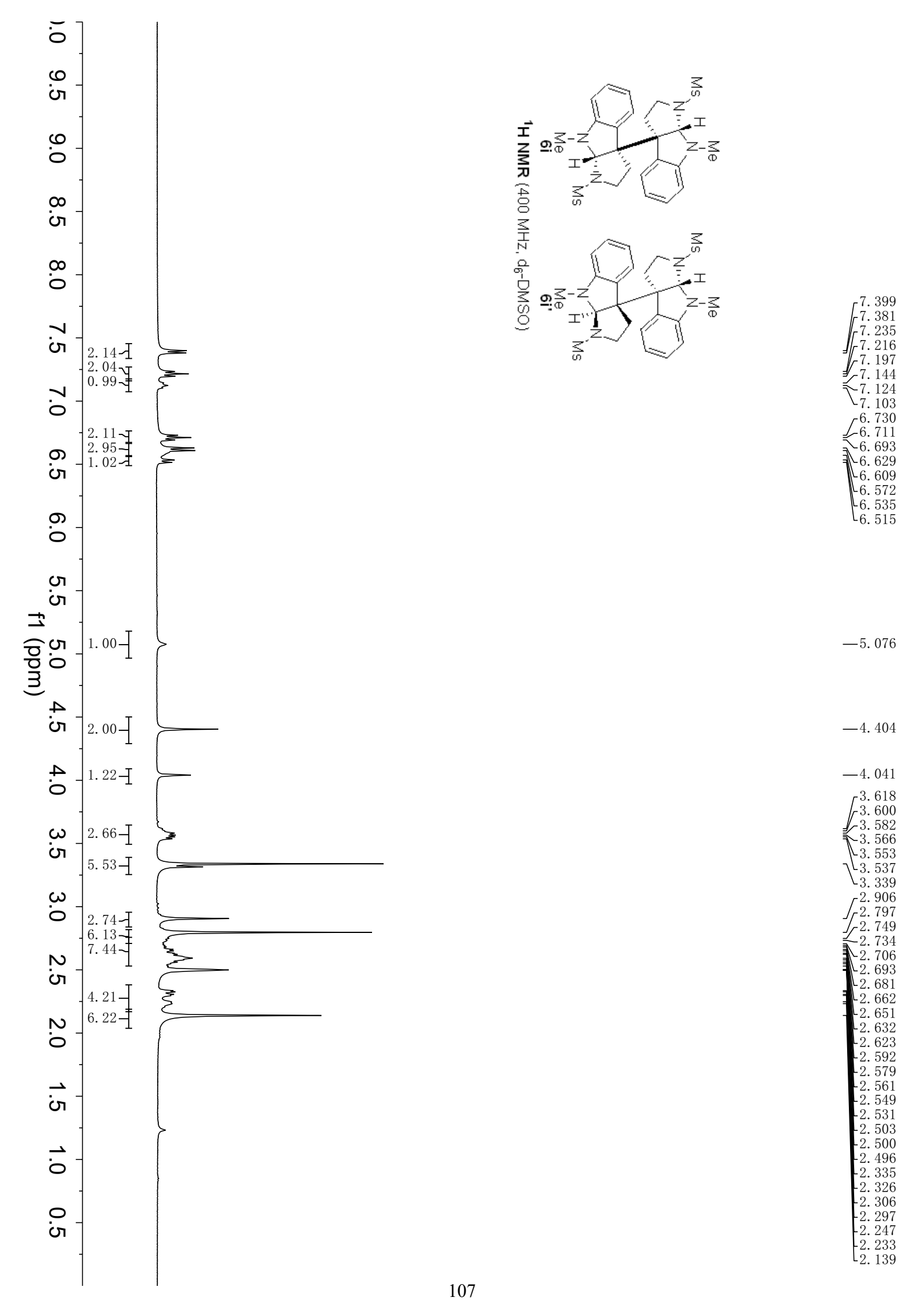


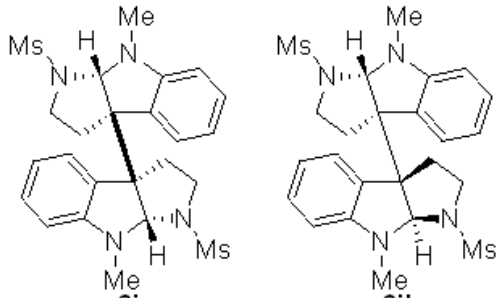
6h **6h'**

^{13}C NMR (150 MHz, $CDCl_3$)

106




Ms
N
H
Me
N
Me
N
H
N
Ms
6i
Ms
N
H
Me
N
Me
N
H
N
Ms
6i'
^{1}H NMR (400 MHz, d_6-DMSO)
f1 (ppm)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
2.14
2.04
0.99
2.11
2.95
1.02
1.00
2.00
1.22
2.66
5.53
2.74
6.13
7.44
4.21
6.22
7.399
7.381
7.235
7.216
7.197
7.144
7.124
7.103
6.730
6.711
6.693
6.629
6.609
6.572
6.535
6.515
5.076
4.404
4.041
3.618
3.600
3.582
3.566
3.553
3.537
3.339
2.906
2.797
2.749
2.734
2.706
2.693
2.681
2.662
2.651
2.632
2.623
2.592
2.579
2.561
2.549
2.531
2.503
2.500
2.496
2.335
2.326
2.306
2.297
2.247
2.233
2.139



6i

6i'

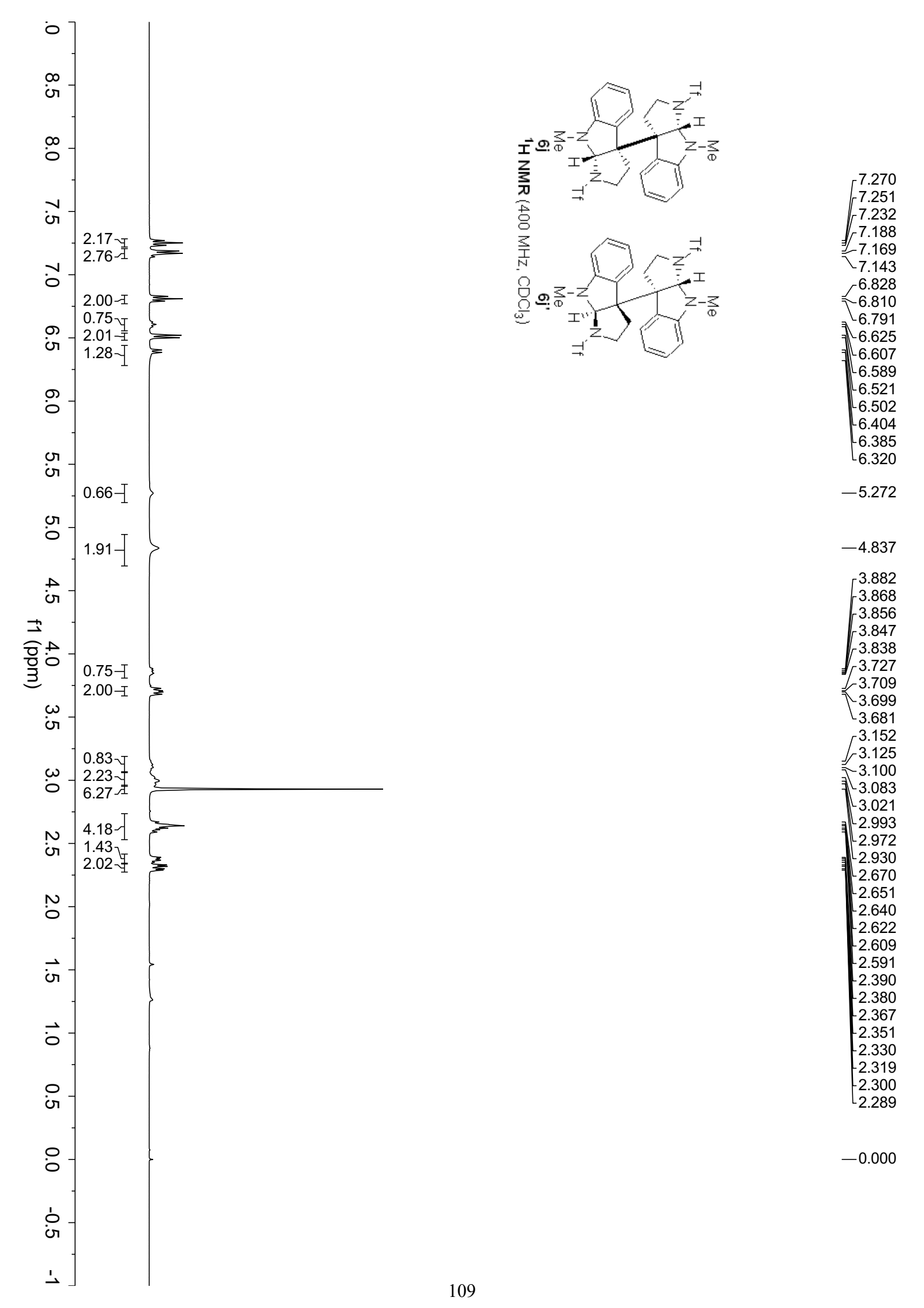
^{13}**C NMR** (400 MHz, d_6-DMSO)

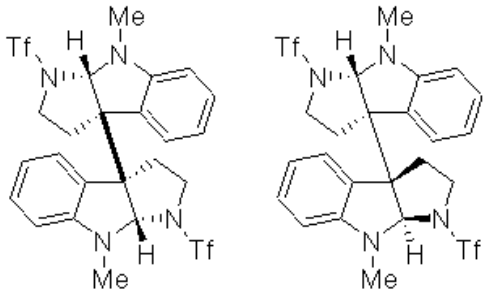
157.15
156.60
134.97
134.57
134.45
132.73
130.78
128.98
123.10
122.65
112.76
111.66
91.21
90.72
67.40
65.82
53.17
52.26
45.28
45.16
45.02
44.88
44.74
44.61
44.47
44.33
43.39
40.80
39.39
38.17
37.64
36.12

108

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)


6j
1H NMR (400 MHz, CDCl3)
6j'
2.17
2.76
2.00
0.75
2.01
1.28
0.66
1.91
0.75
2.00
0.83
2.23
6.27
4.18
1.43
2.02
f1 (ppm)
7.270
7.251
7.232
7.188
7.169
7.143
6.828
6.810
6.791
6.625
6.607
6.589
6.521
6.502
6.404
6.385
6.320
5.272
4.837
3.882
3.868
3.856
3.847
3.838
3.727
3.709
3.699
3.681
3.152
3.125
3.100
3.083
3.021
2.993
2.972
2.930
2.670
2.651
2.640
2.622
2.609
2.591
2.390
2.380
2.367
2.351
2.330
2.319
2.300
2.289
0.000

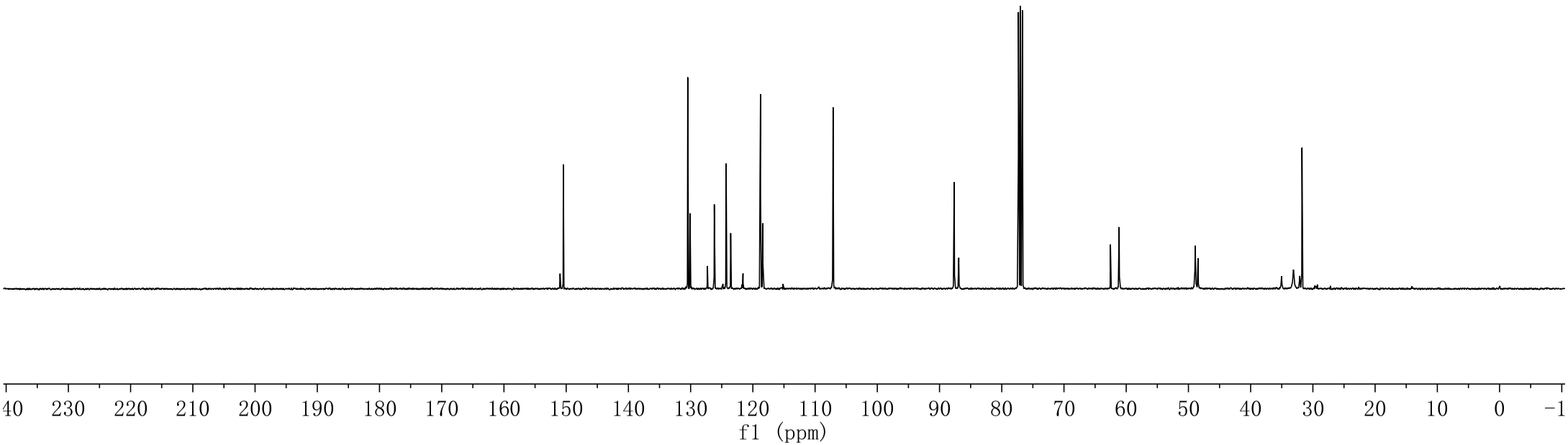


6j **6j'**

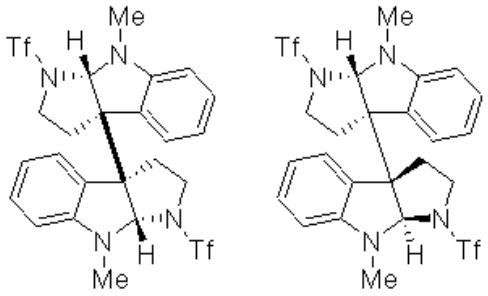
^{13}C NMR (100 MHz, $CDCl_3$)

150.98
150.46
130.47
130.09
127.30
126.20
124.80
124.29
123.56
121.76
121.58
118.77
118.54
118.40
118.37
115.15
107.10
87.64
86.91
77.32
77.00
76.68
62.53
61.14
48.90
48.45
35.04
33.12
32.12
31.75

110



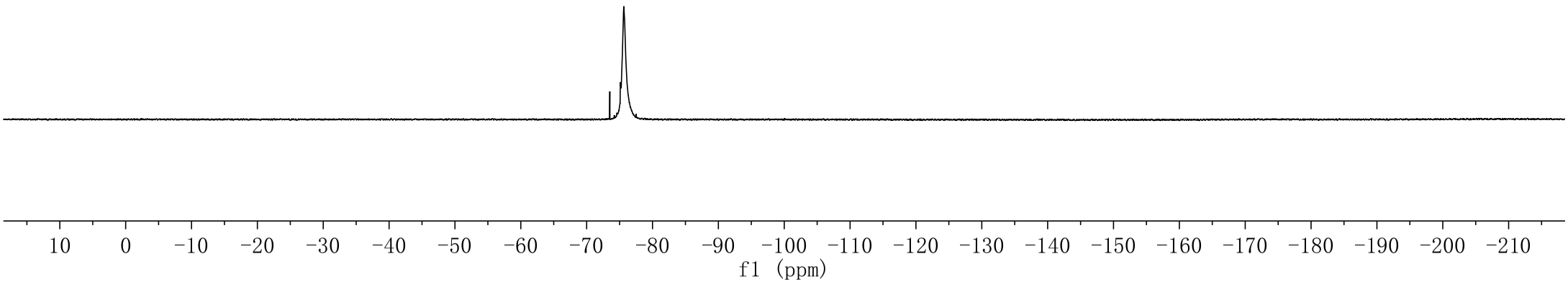
−73.517
−75.639

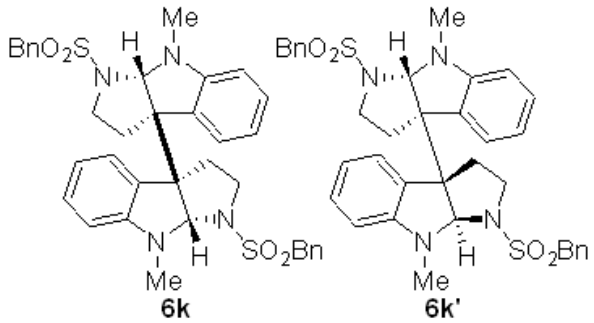


6j

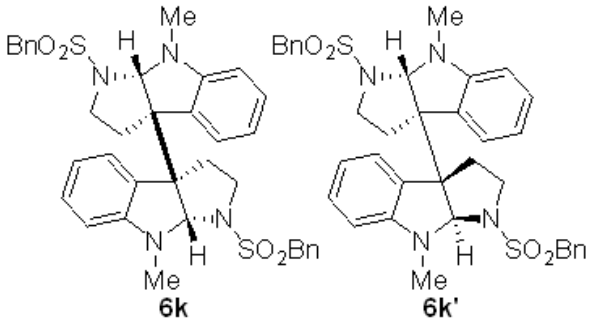
6j'

^{19}F NMR (376 MHz, $CDCl_3$)



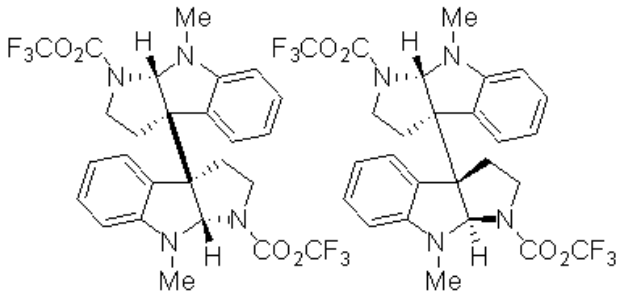


^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (150 MHz, $CDCl_3$)

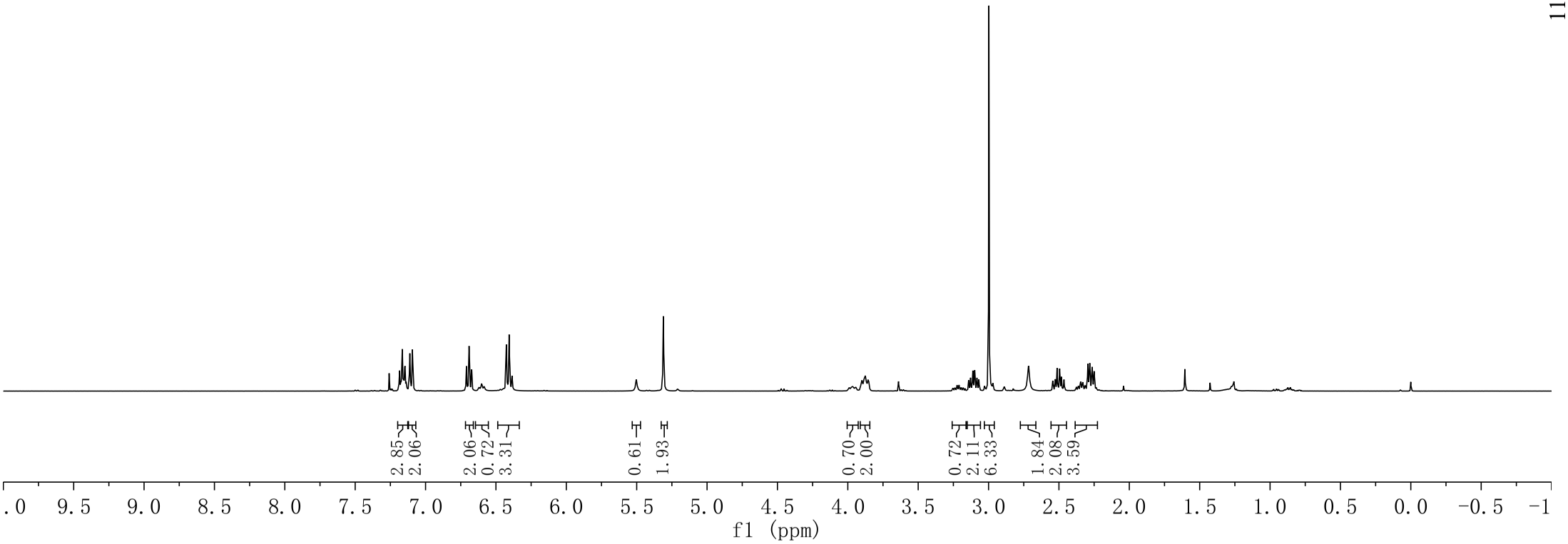
7.259
7.187
7.184
7.174
7.165
7.157
7.148
7.146
7.138
7.112
7.094
6.709
6.691
6.672
6.620
6.602
6.583
6.426
6.406
6.385
5.503
5.311
3.989
3.971
3.965
3.944
3.903
3.899
3.880
3.876
3.857
3.853
3.253
3.239
3.224
3.209
3.195
3.180
3.167
3.141
3.128
3.112
3.098
3.082
3.069
2.998
2.716
2.544
2.526
2.513
2.495
2.483
2.464
2.376
2.362
2.345
2.331
2.314
2.294
2.281
2.264
2.250
0.000



6l

6l'

^{1}H NMR (400 MHz, $CDCl_3$)



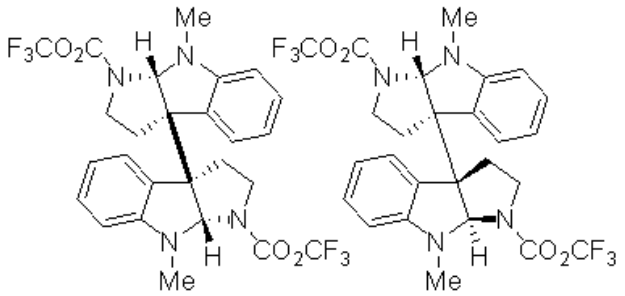
156.31
156.27
156.07
156.03
155.82
155.78
155.58
155.54
130.05
129.87
128.03
127.21
123.73
123.58
119.05
118.99
118.10
117.91
117.14
117.08
115.23
115.17
113.32
113.26
107.20
106.62

84.18
83.59
77.21
77.00
76.79

60.11
59.21

45.80

34.60
33.62
33.33
32.89

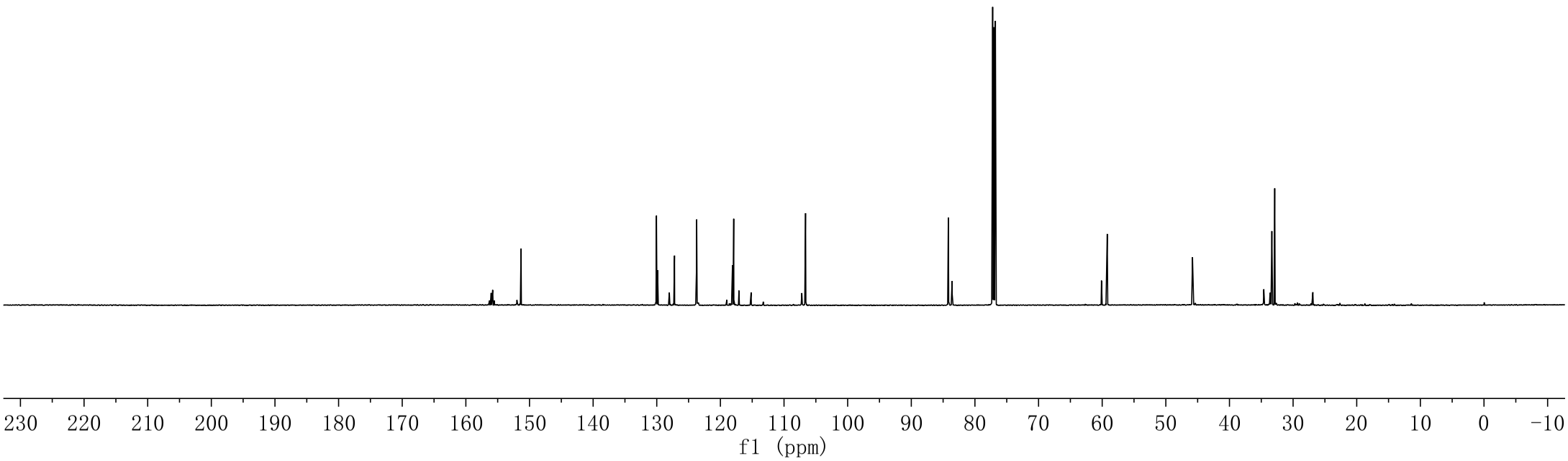


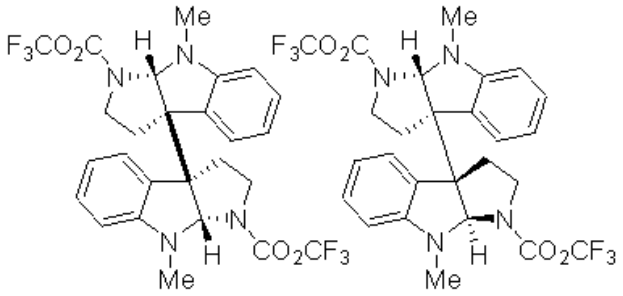
6l

6l'

^{13}C NMR (150 MHz, $CDCl_3$)

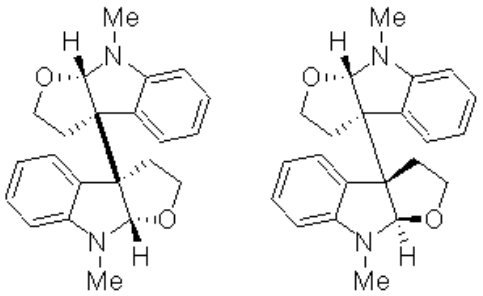
115





6l **6l'**

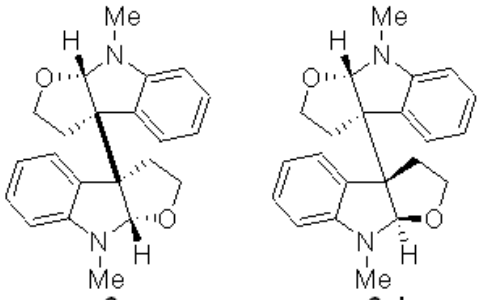
^{19}F NMR (376 MHz, $CDCl_3$)



6n **6n'**

^{1}H NMR (400 MHz, $CDCl_3$)

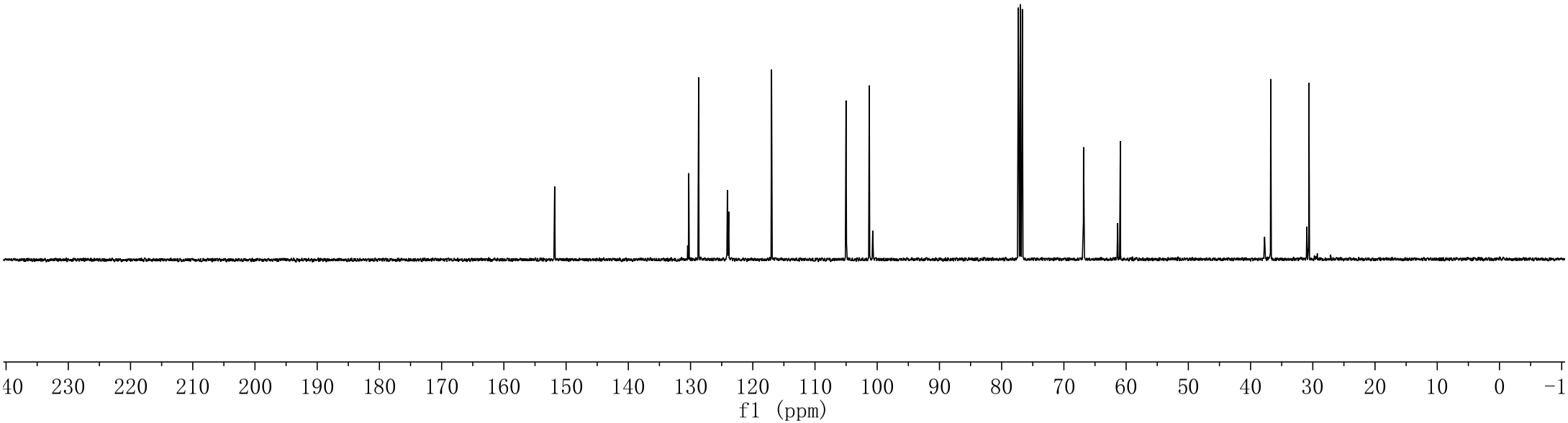
151.88
151.84
130.46
130.28
128.69
124.08
123.86
116.98
116.94
105.02
104.95
101.28
100.72
77.32
77.00
76.68
66.84
66.76
61.35
60.93
37.75
36.76
30.97
30.62

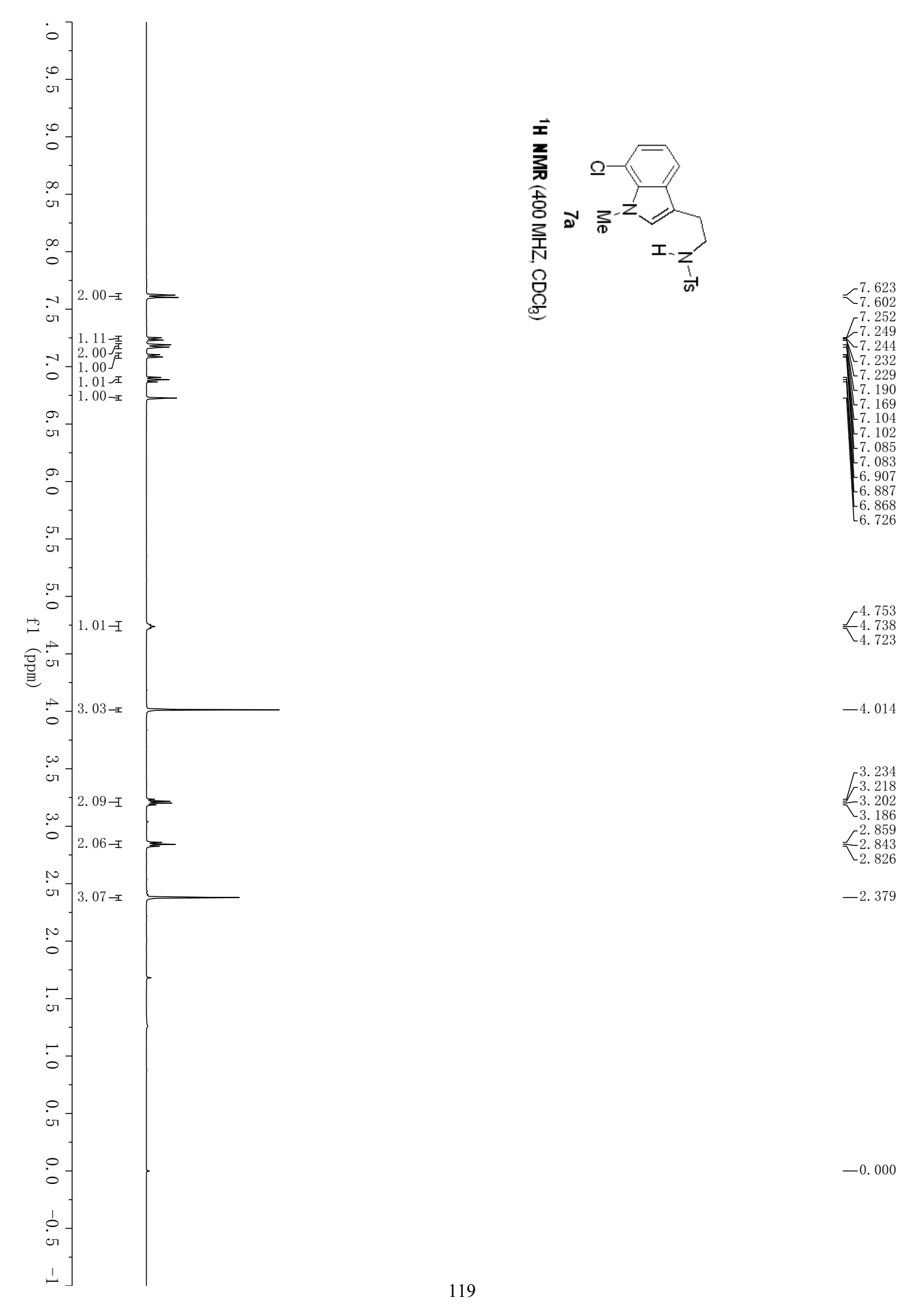


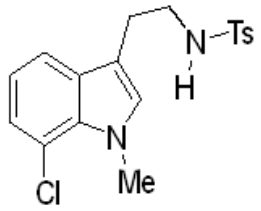
6n

6n'

^{13}C NMR (100 MHz, $CDCl_3$)




¹H NMR (400 MHZ, CDCl3)
7a
Cl
Me
N
H
N
Ts
7.623
7.602
7.252
7.249
7.244
7.232
7.229
7.190
7.169
7.104
7.102
7.085
7.083
6.907
6.887
6.868
6.726
4.753
4.738
4.723
4.014
3.234
3.218
3.202
3.186
2.859
2.843
2.826
2.379
0.000
2.00
1.11
2.00
1.00
1.01
1.00
1.01
3.03
2.09
2.06
3.07
f1 (ppm)



7a

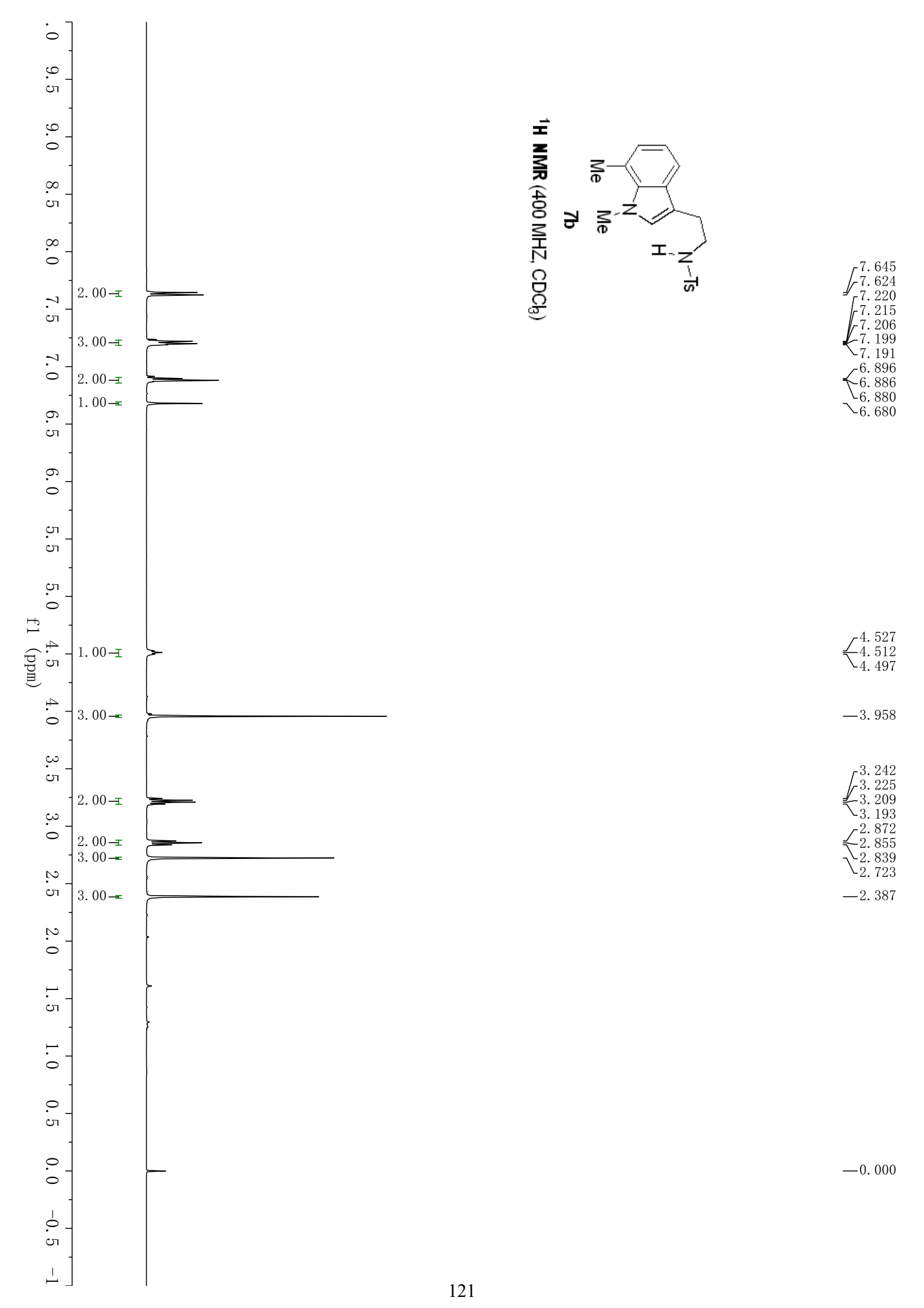
^{13}C NMR (100 MHZ, $CDCl_3$)

143.20
136.69
132.24
130.43
129.96
129.48
126.88
123.14
119.66
117.27
116.97
110.17
77.32
77.00
76.68
43.02
36.35
25.13
21.43

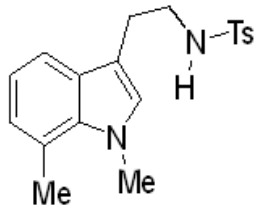
120

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)


¹H NMR (400 MHZ, CDCl3)
7b
Me
Me
N
H
N
Ts
7.645
7.624
7.220
7.215
7.206
7.199
7.191
6.896
6.886
6.880
6.680
4.527
4.512
4.497
3.958
3.242
3.225
3.209
3.193
2.872
2.855
2.839
2.723
2.387
0.000
2.00
3.00
2.00
1.00
1.00
3.00
2.00
2.00
3.00
3.00
f1 (ppm)

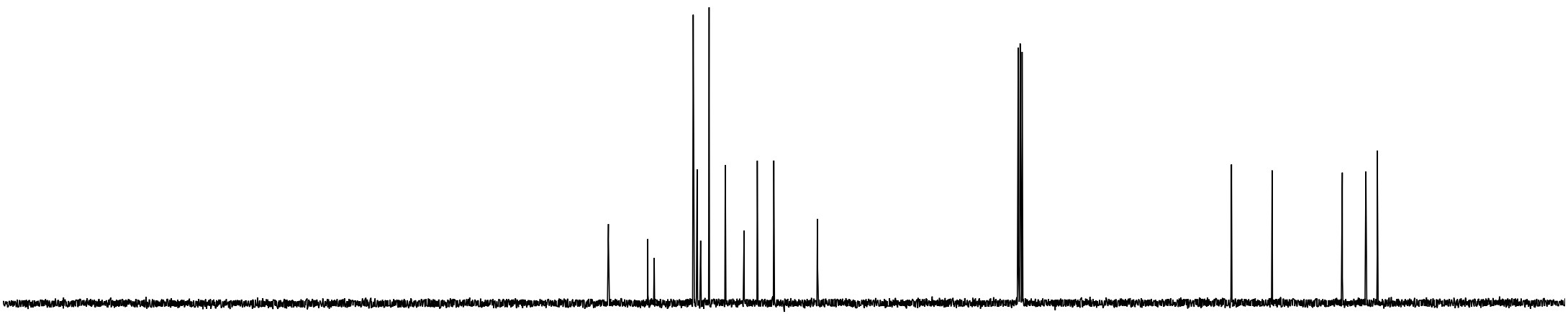
143.16
136.84
135.80
129.54
128.91
128.35
126.98
124.38
121.36
119.24
116.58
109.58
77.32
77.00
76.68
43.05
36.51
25.23
21.45
19.61

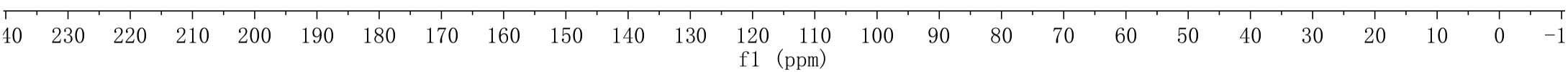


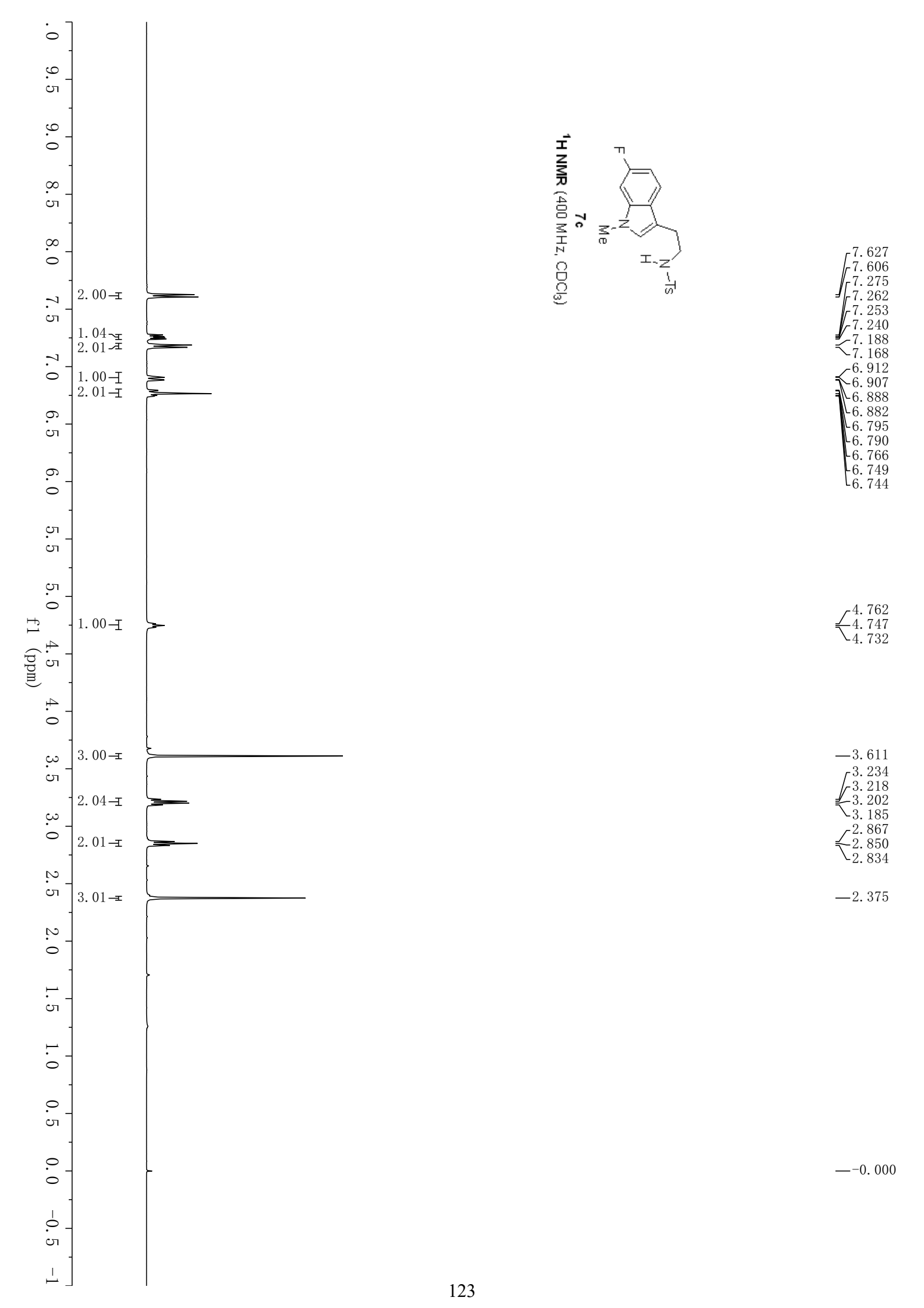
7b

^{13}C NMR (100 MHZ, $CDCl_3$)

122






7c
1H NMR (400 MHz, CDCl3)
F
N
Me
H
N
Ts
7.627
7.606
7.275
7.262
7.253
7.240
7.188
7.168
6.912
6.907
6.888
6.882
6.795
6.790
6.766
6.749
6.744
4.762
4.747
4.732
3.611
3.234
3.218
3.202
3.185
2.867
2.850
2.834
2.375
-0.000
2.00
1.04
2.01
1.00
2.01
1.00
3.00
2.04
2.01
3.01
f1 (ppm)

7c
13C NMR (100 MHz, CDCl3)
F
N
Me
H
N
Ts
161.06
158.70
143.20
137.15
137.03
136.71
129.48
127.52
127.49
126.90
123.84
119.35
119.25
110.31
107.64
107.40
95.74
95.48
77.32
77.00
76.68
43.09
32.60
25.23
21.38
f1 (ppm)

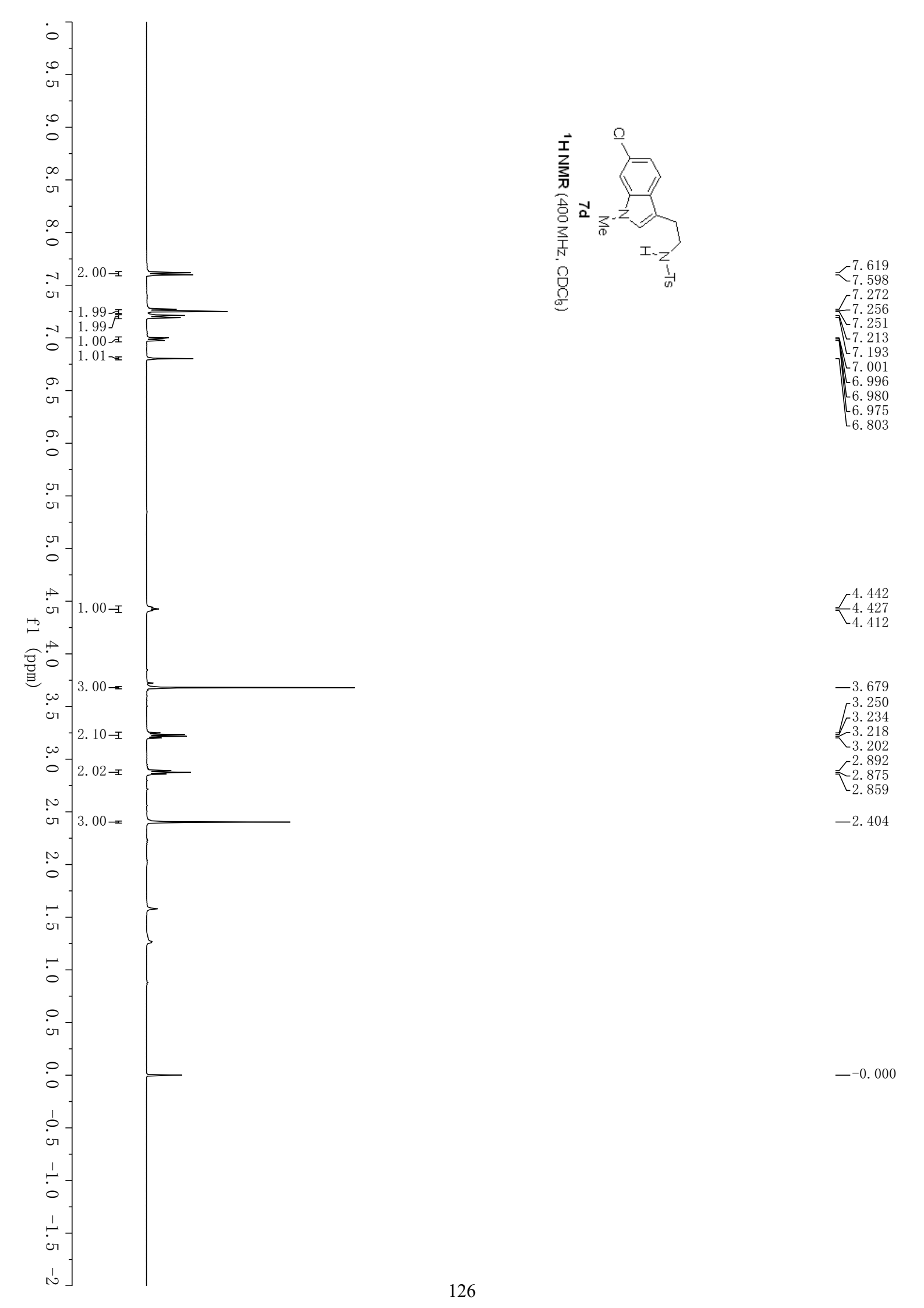
7c

^{19}F NMR (376 MHz, $CDCl_3$)

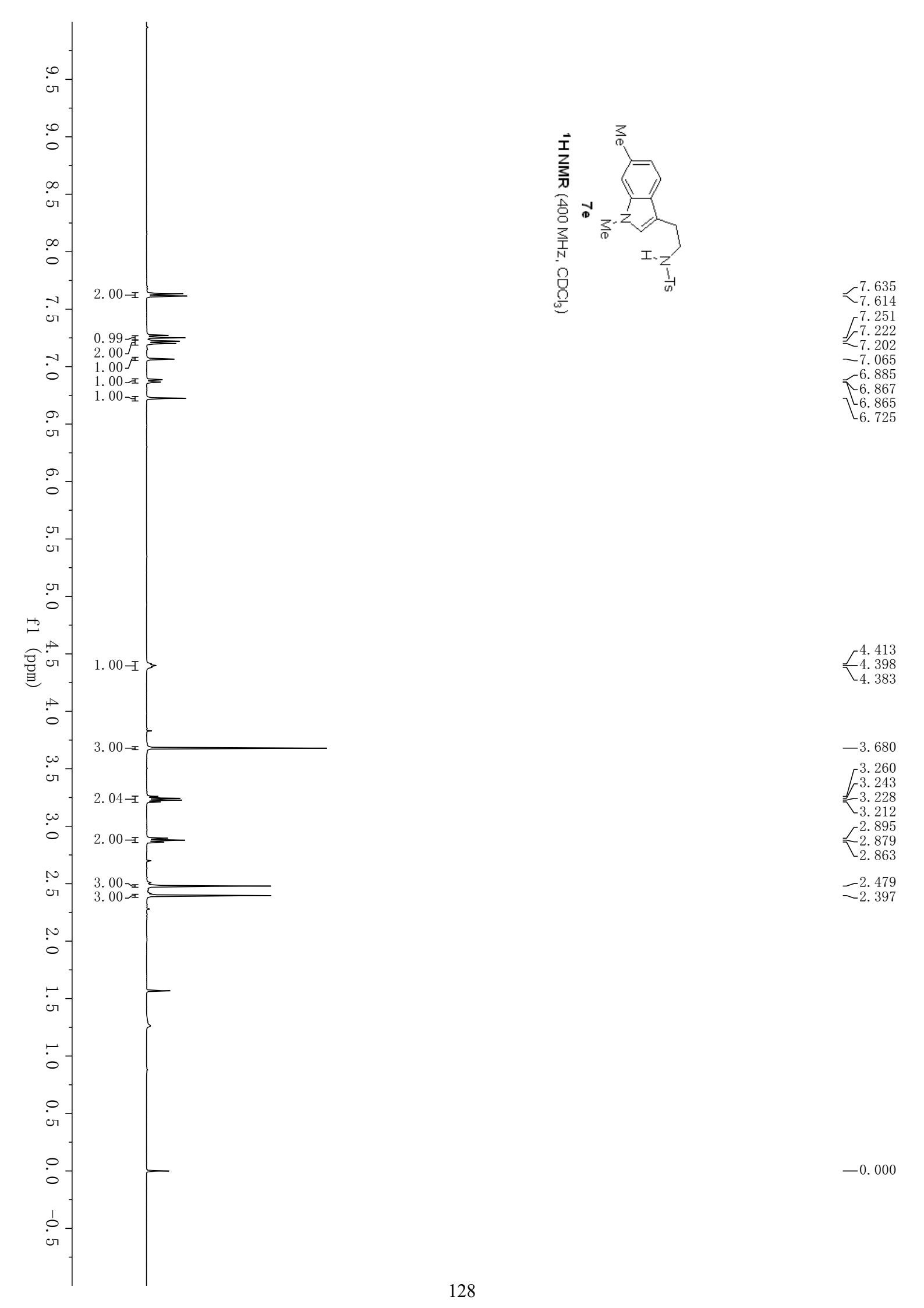
—-120.790

10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210

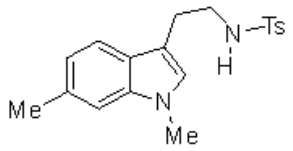
f1 (ppm)


Cl
N
Me
H
N
Ts
7d
1H NMR (400 MHz, CDCl3)
2.00
1.99
1.99
1.00
1.01
1.00
3.00
2.10
2.02
3.00
7.619
7.598
7.272
7.256
7.251
7.213
7.193
7.001
6.996
6.980
6.975
6.803
4.442
4.427
4.412
3.679
3.250
3.234
3.218
3.202
2.892
2.875
2.859
2.404
-0.000
f1 (ppm)

7d
^{13}C NMR (100 MHz, CDCl$_3$)
Cl
N
Me
H
N
Ts
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
143.33
137.55
136.76
129.55
127.98
127.93
126.97
125.89
119.68
119.47
110.37
109.38
77.32
77.00
76.68
43.06
32.71
25.29
21.48


Me
N
Me
H
N
Ts
7e
1H NMR (400 MHz, CDCl3)
2.00
0.99
2.00
1.00
1.00
1.00
1.00
3.00
2.04
2.00
3.00
3.00
7.635
7.614
7.251
7.222
7.202
7.065
6.885
6.867
6.865
6.725
4.413
4.398
4.383
3.680
3.260
3.243
3.228
3.212
2.895
2.879
2.863
2.479
2.397
0.000
f1 (ppm)

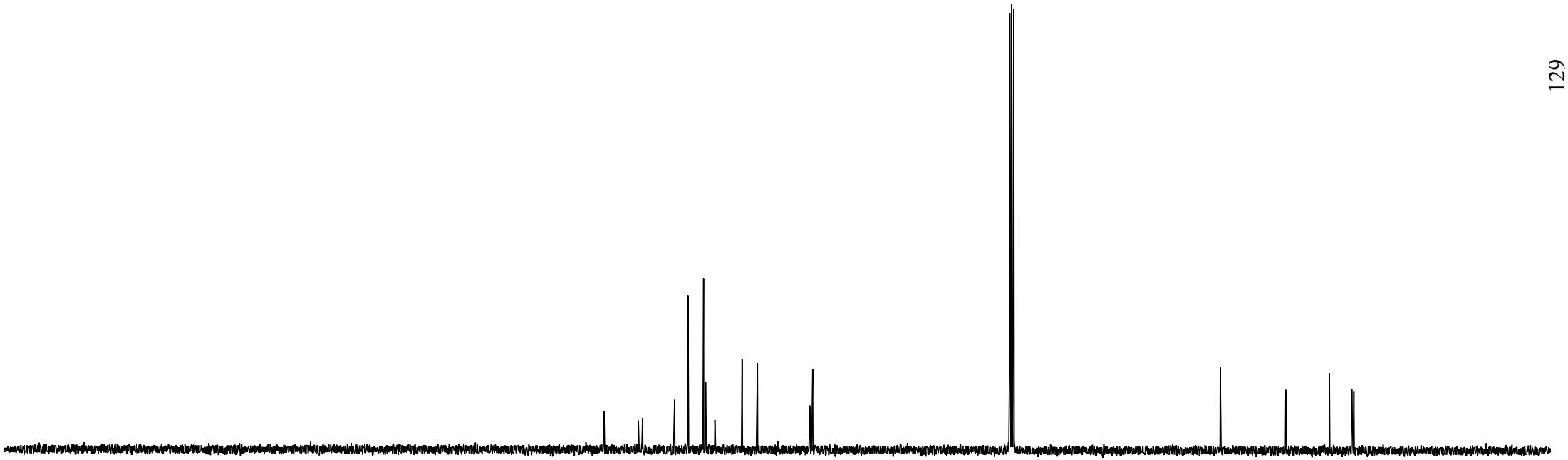
143.19
137.61
136.93
131.74
129.56
127.04
126.70
125.19
120.79
118.29
109.80
109.33
77.34
77.02
76.70
43.18
32.54
25.46
21.82
21.49

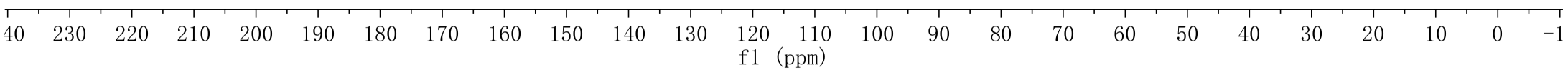


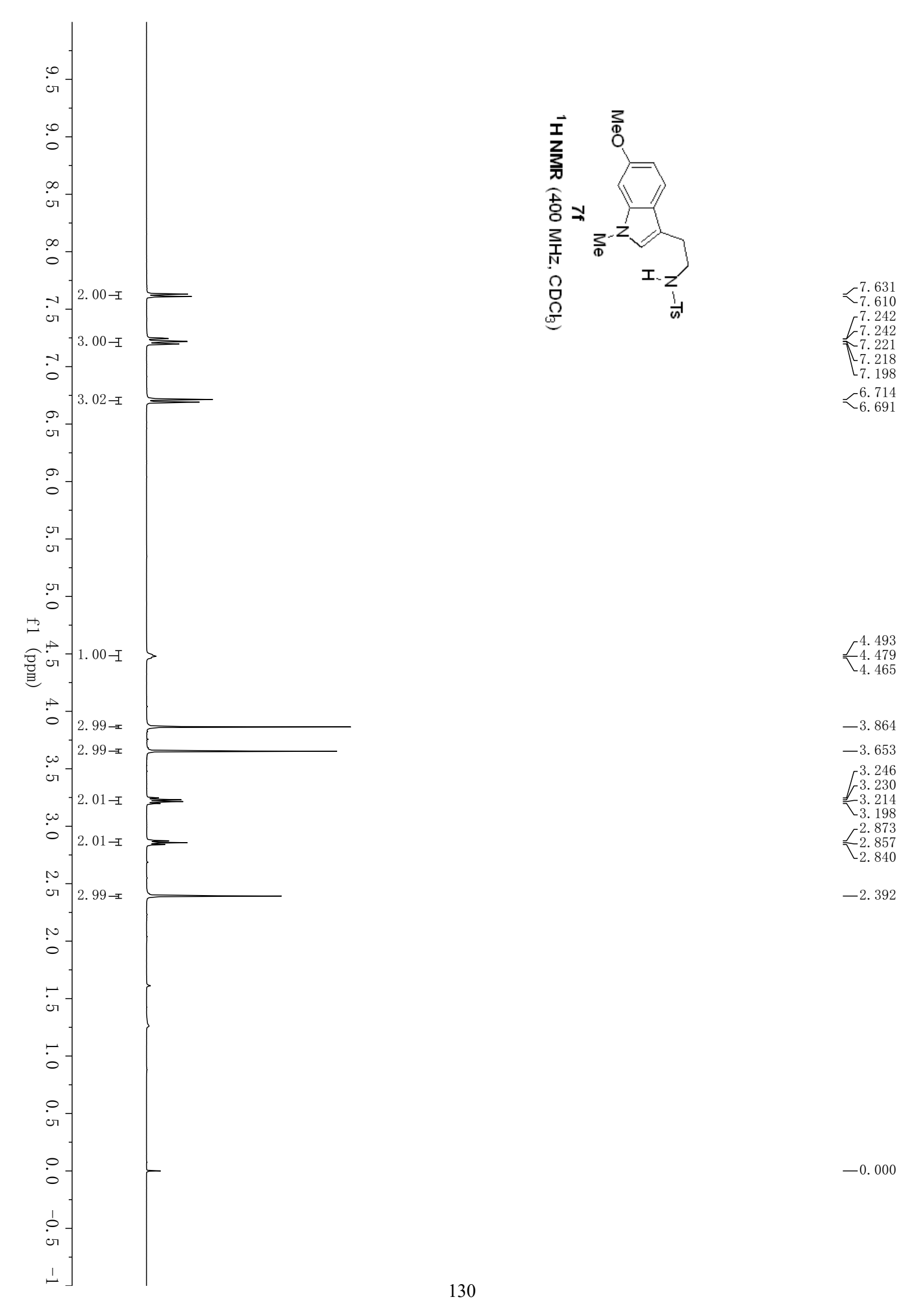
7e

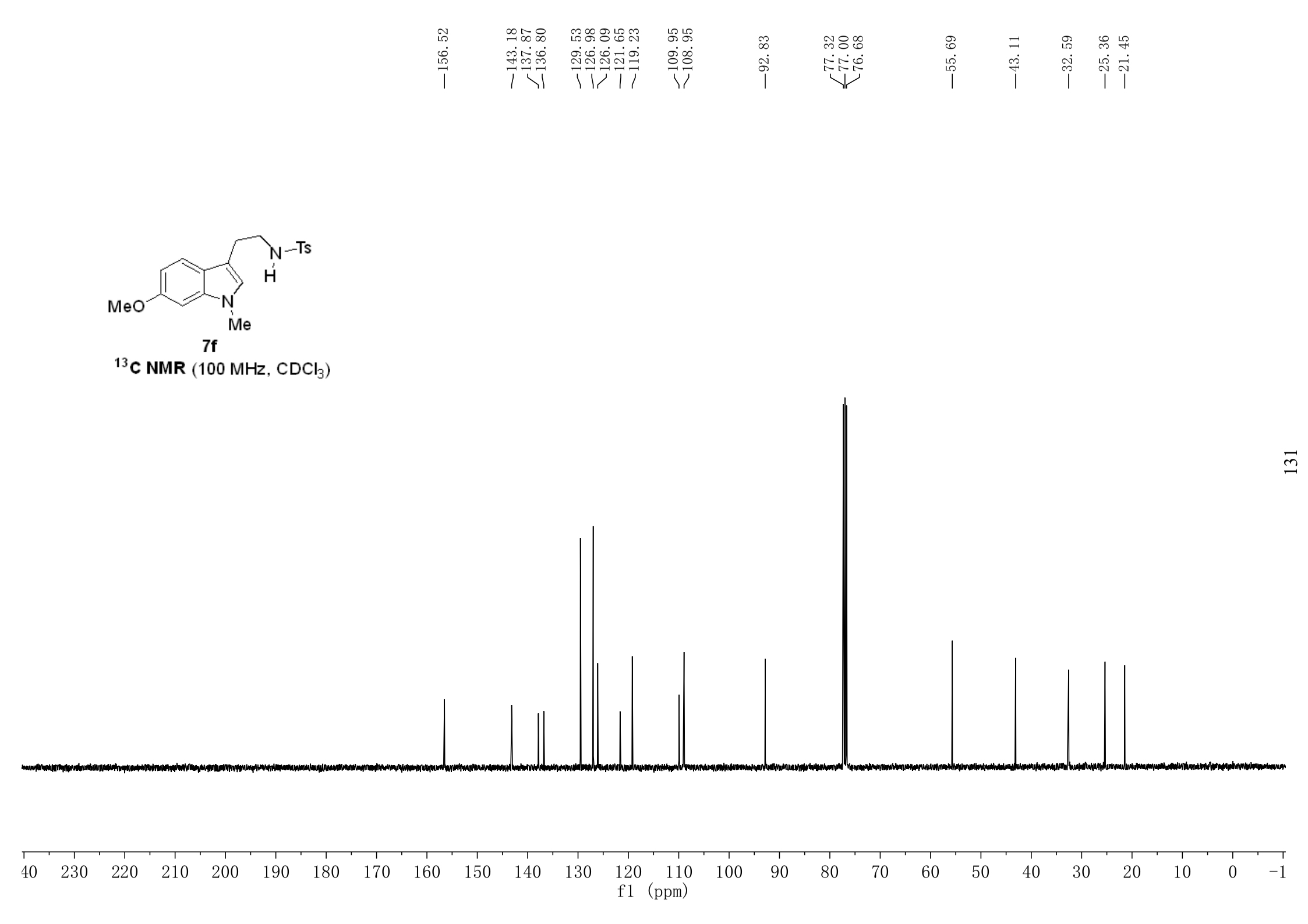
^{13}C NMR (100 MHz, $CDCl_3$)

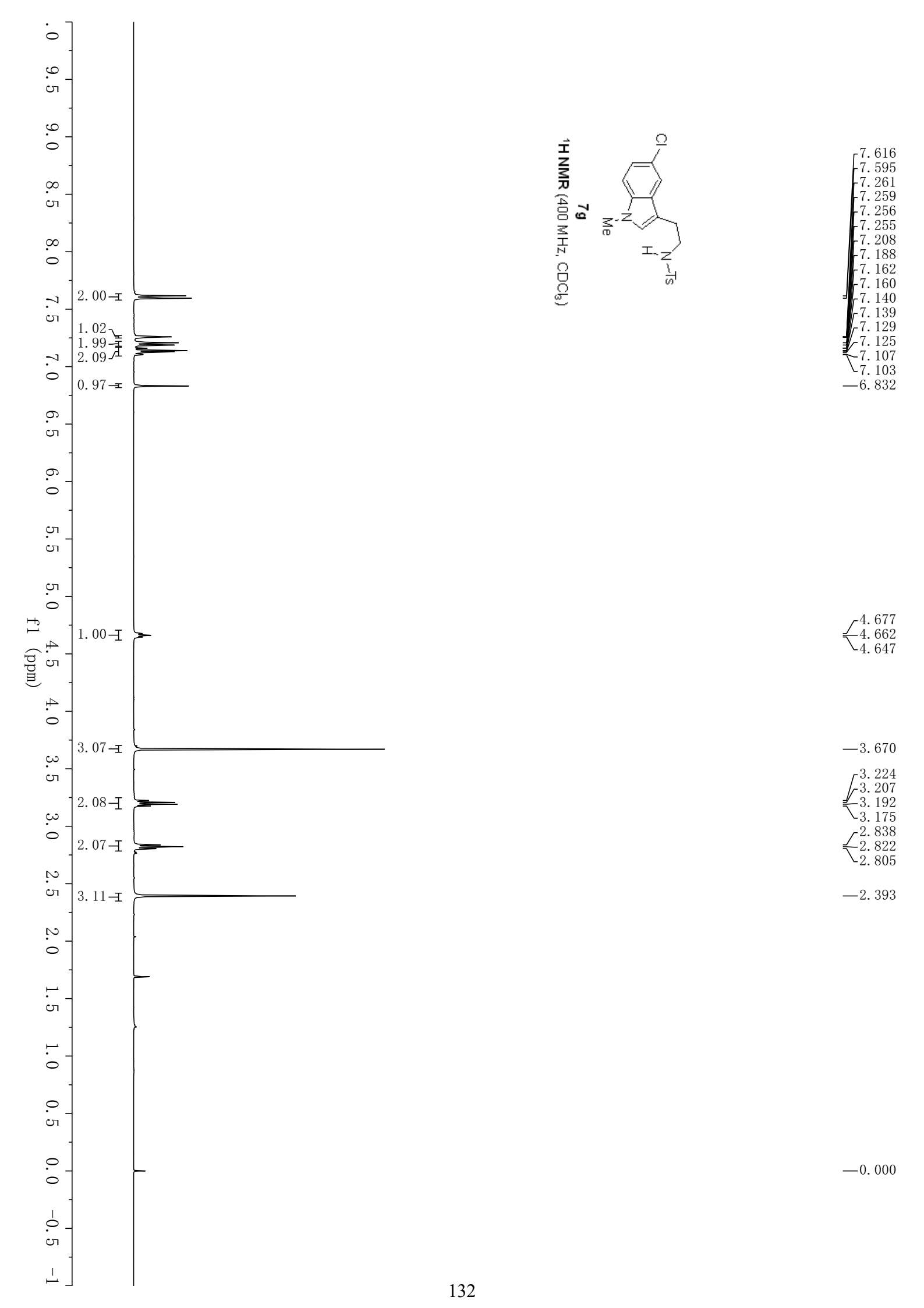
129



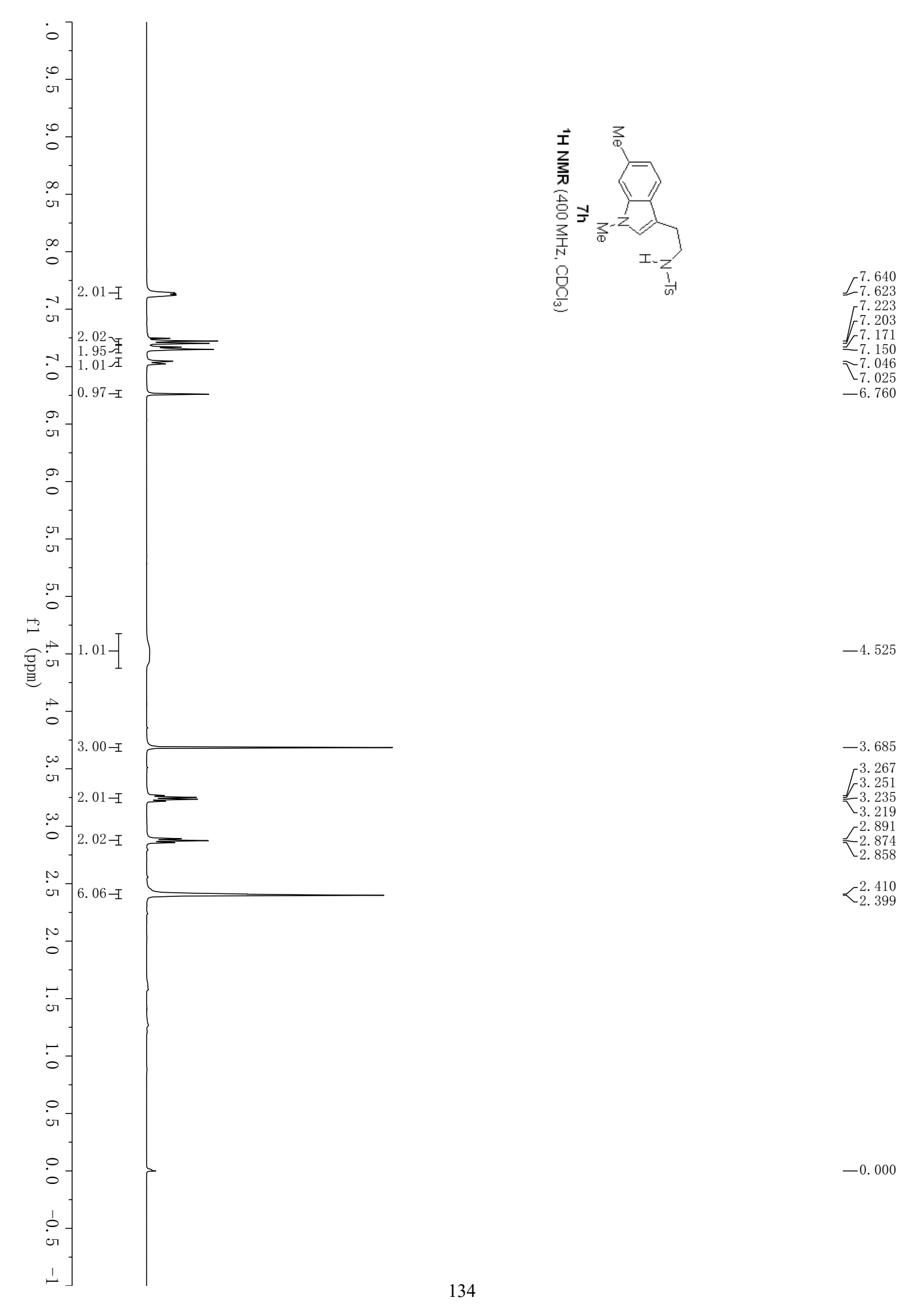



7f
^{1}H NMR (400 MHz, CDCl$_3$)
MeO
Me
N
H
N
Ts
2.00
3.00
3.02
1.00
2.99
2.99
2.01
2.01
2.99
7.631
7.610
7.242
7.242
7.221
7.218
7.198
6.714
6.691
4.493
4.479
4.465
3.864
3.653
3.246
3.230
3.214
3.198
2.873
2.857
2.840
2.392
0.000
f1 (ppm)

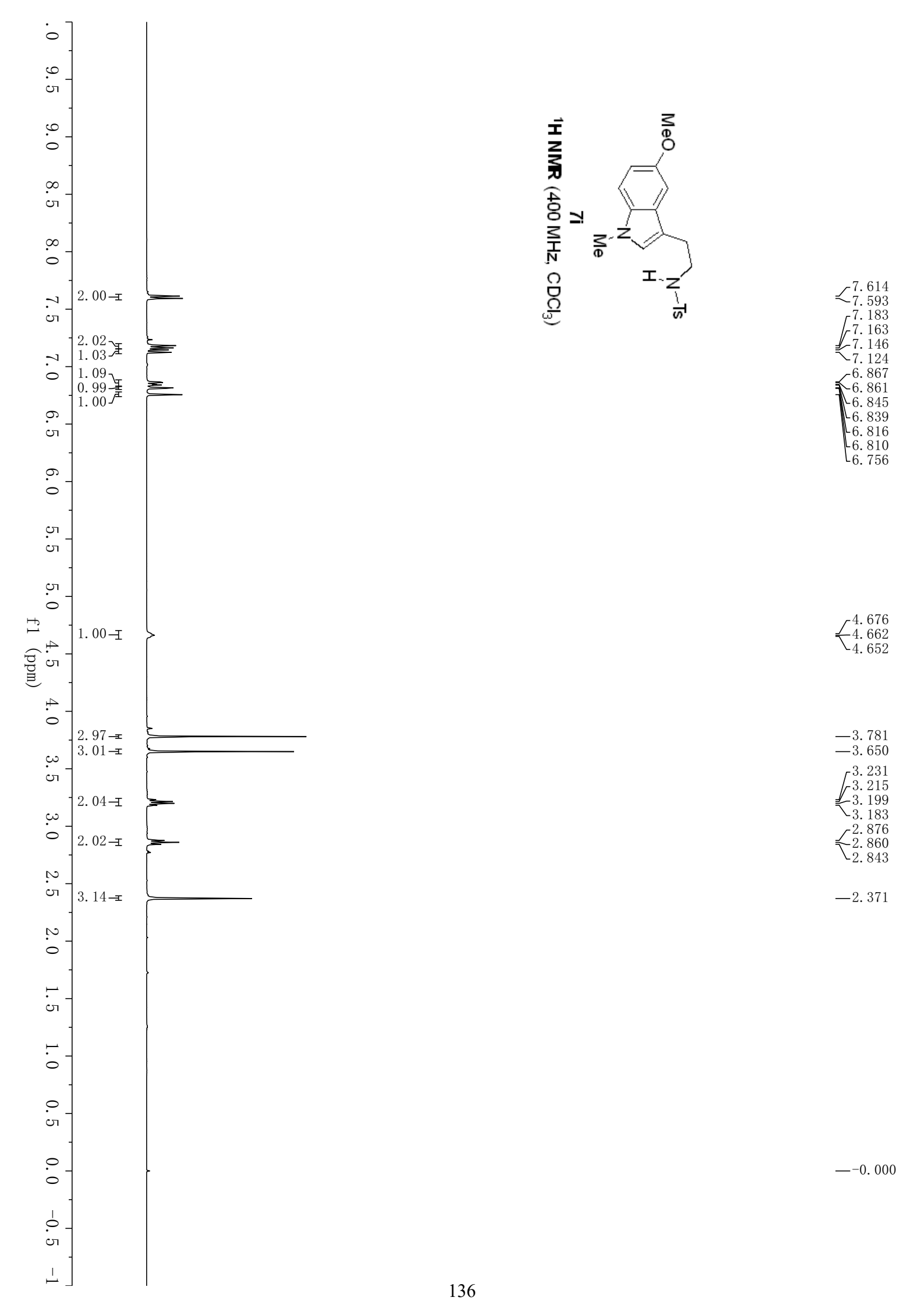

156.52
143.18
137.87
136.80
129.53
126.98
126.09
121.65
119.23
109.95
108.95
92.83
77.32
77.00
76.68
55.69
43.11
32.59
25.36
21.45
N
Ts
H
MeO
N
Me
7f
13C NMR (100 MHz, CDCl3)
131
40 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


7g
¹H NMR (400 MHz, CDCl₃)
Cl
N
Me
H
N
Ts
7.616
7.595
7.261
7.259
7.256
7.255
7.208
7.188
7.162
7.160
7.140
7.139
7.129
7.125
7.107
7.103
6.832
4.677
4.662
4.647
3.670
3.224
3.207
3.192
3.175
2.838
2.822
2.805
2.393
0.000
2.00
1.02
1.99
2.09
0.97
1.00
3.07
2.08
2.07
3.11
f1 (ppm)

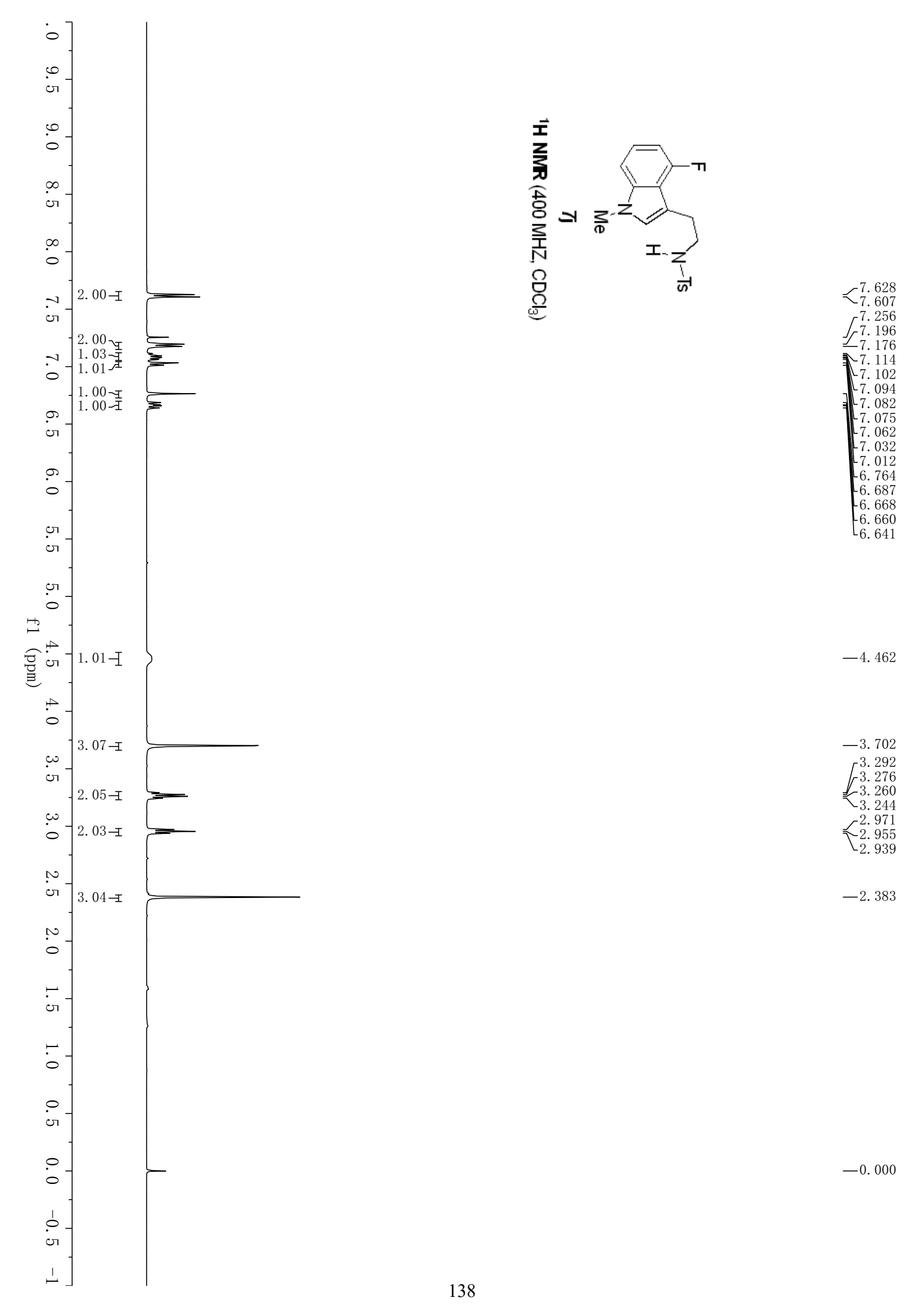
7g
13C NMR (100 MHz, CDCl3)
Cl
N
Me
H
N
Ts
143.43
136.52
135.52
129.66
128.81
128.26
127.00
124.80
122.00
118.03
110.43
109.62
77.42
77.10
76.78
42.96
32.85
25.13
21.57
f1 (ppm)


7h
1H NMR (400 MHz, CDCl3)
Me
N
Me
H
N
Ts
2.01
2.02
1.95
1.01
0.97
1.01
3.00
2.01
2.02
6.06
7.640
7.623
7.223
7.203
7.171
7.150
7.046
7.025
6.760
4.525
3.685
3.267
3.251
3.235
3.219
2.891
2.874
2.858
2.410
2.399
0.000
f1 (ppm)

7h
^{13}C NMR (100 MHz, CDCl$_3$)
Me
N
Me
H
N
Ts
143.20
136.85
135.64
129.58
128.18
127.51
127.45
127.07
123.45
118.27
109.28
109.09
77.37
77.05
76.73
43.16
32.68
25.35
21.52
21.44
f1 (ppm)


MeO
N
Me
H
N
Ts
7i
¹H NMR (400 MHz, CDCl3)
2.00
2.02
1.03
1.09
0.99
1.00
1.00
2.97
3.01
2.04
2.02
3.14
7.614
7.593
7.183
7.163
7.146
7.124
6.867
6.861
6.845
6.839
6.816
6.810
6.756
4.676
4.662
4.652
3.781
3.650
3.231
3.215
3.199
3.183
2.876
2.860
2.843
2.371
-0.000
f1 (ppm)

MeO
N
Me
H
N
Ts
7l
^{13}C NMR (100 MHz, $CDCl_3$)
153.81
143.26
136.76
132.55
129.58
127.95
127.62
127.03
112.04
110.16
109.41
100.45
77.44
77.12
76.81
55.88
43.13
32.79
25.39
21.49
f1 (ppm)

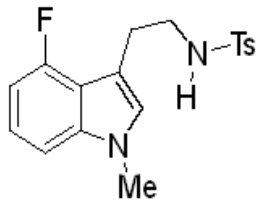

F
N
Me
H
N
Ts
7j
¹H NMR (400 MHZ, CDCl3)
2.00
2.00
1.03
1.01
1.00
1.00
1.01
3.07
2.05
2.03
3.04
7.628
7.607
7.256
7.196
7.176
7.114
7.102
7.094
7.082
7.075
7.062
7.032
7.012
6.764
6.687
6.668
6.660
6.641
4.462
3.702
3.292
3.276
3.260
3.244
2.971
2.955
2.939
2.383
0.000
f1 (ppm)

^{13}C NMR (100 MHZ, $CDCl_3$)

7j

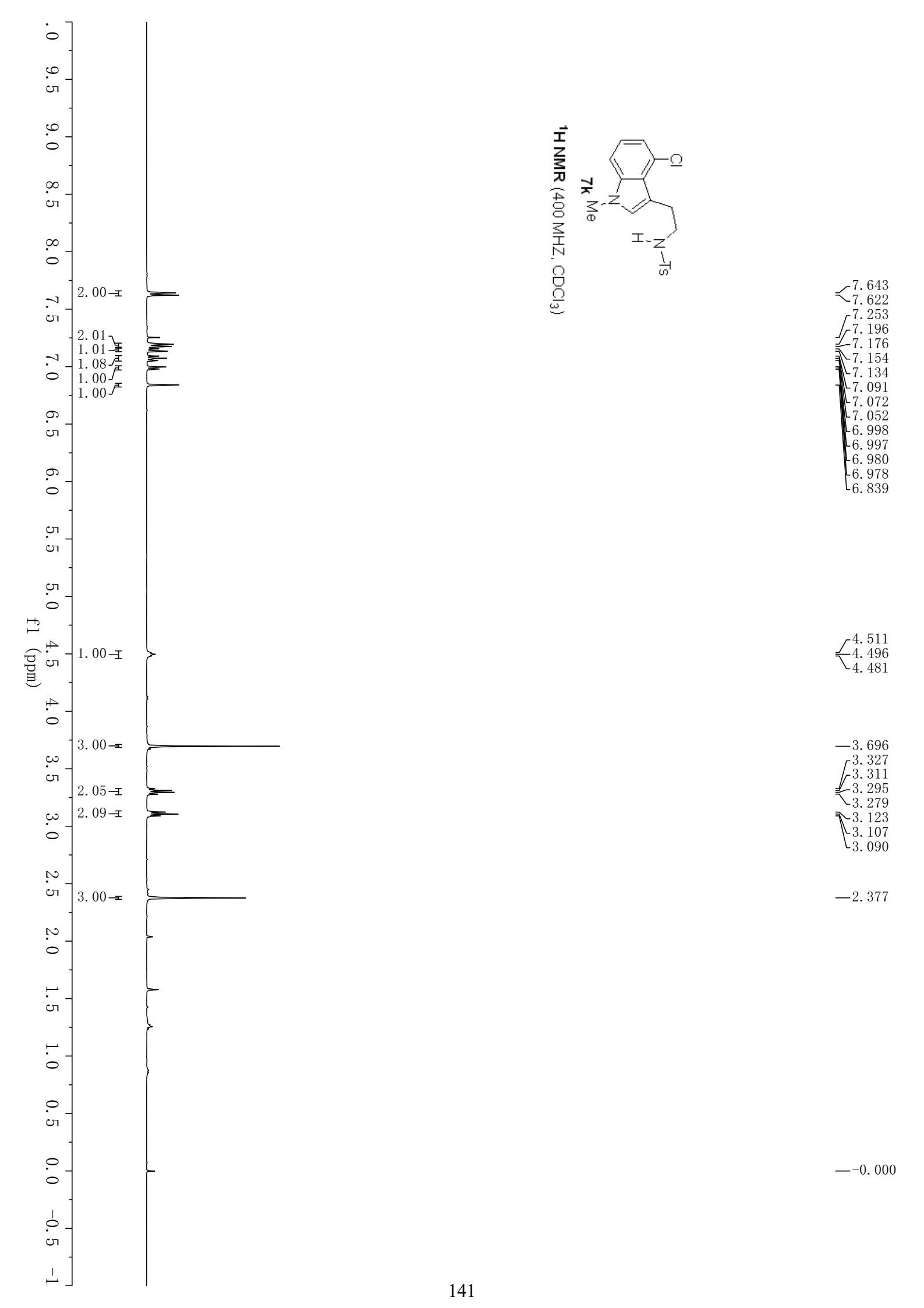
158.16
155.71
143.11
140.08
139.96
136.81
129.48
127.75
126.92
122.25
122.18
115.90
115.70
108.80
108.77
105.48
105.44
104.22
104.03
77.32
77.00
76.68
43.62
32.96
26.48
21.48

f1 (ppm)

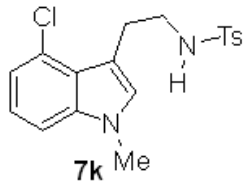


7j

^{19}F NMR (376 MHZ, $CDCl_3$)


¹H NMR (400 MHZ, CDCl₃)
7k
Me
Cl
N
H
N—Ts
7.643
7.622
7.253
7.196
7.176
7.154
7.134
7.091
7.072
7.052
6.998
6.997
6.980
6.978
6.839
4.511
4.496
4.481
3.696
3.327
3.311
3.295
3.279
3.123
3.107
3.090
2.377
-0.000
2.00
2.01
1.01
1.08
1.00
1.00
1.00
3.00
2.05
2.09
3.00
f1 (ppm)

143.13
138.66
136.95
129.49
129.09
126.97
126.10
124.07
122.18
119.99
110.47
108.10
77.32
77.00
76.68
44.35
32.87
26.31
21.46



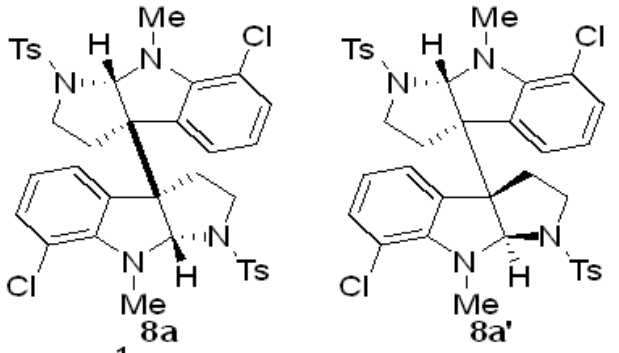
7k

^{13}C NMR (100 MHZ, $CDCl_3$)

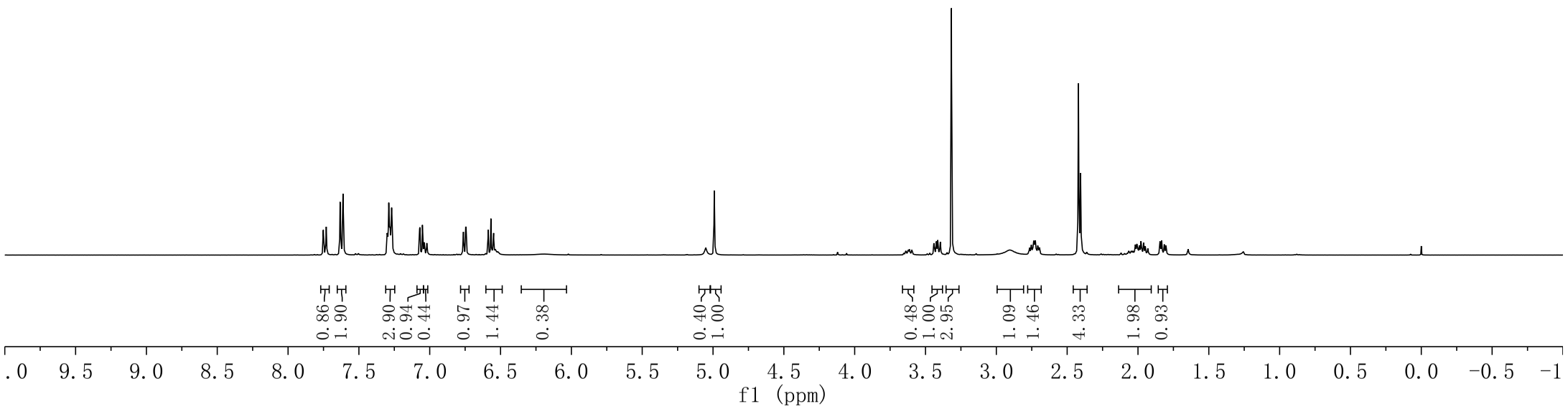
142

40 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −1

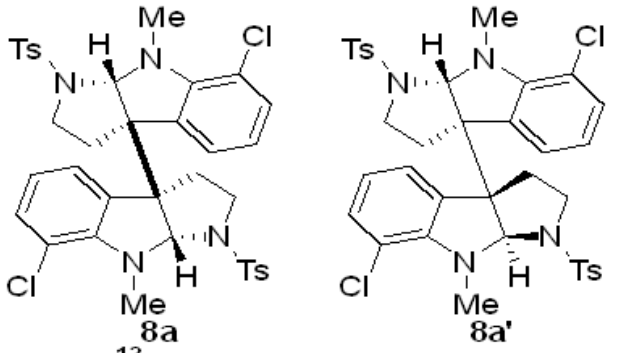
f1 (ppm)



^{1}H NMR (400 MHz, $CDCl_3$)



147.87
146.62
143.50
143.39
136.83
136.45
132.89
131.65
131.34
131.25
129.86
129.60
127.29
127.18
123.01
122.06
120.29
119.22
116.57
115.17
88.52
88.08
77.32
77.00
76.68
62.52
60.91
46.86
46.64
37.09
36.23
34.53
33.53
21.49

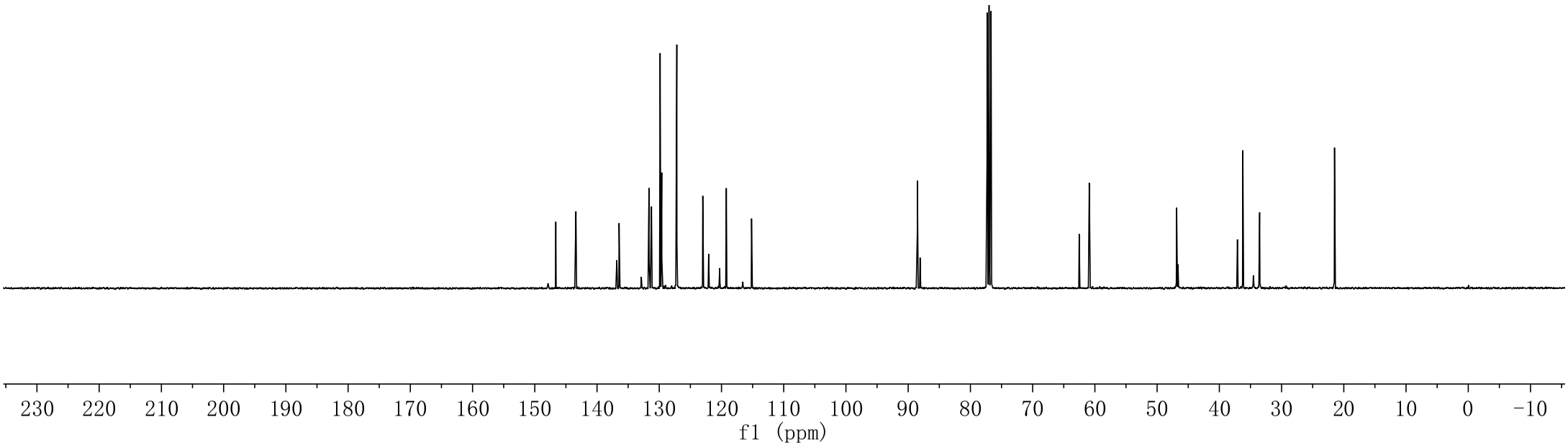


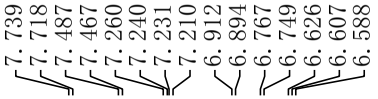
8a

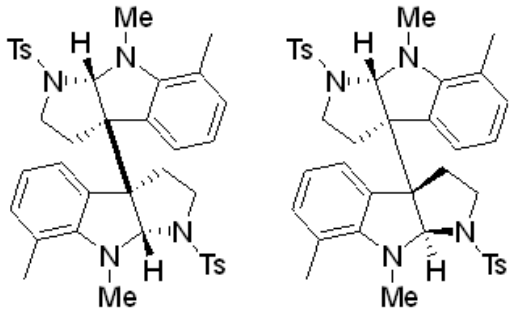
8a'

^{13}C **NMR** (100 MHz, $CDCl_3$)

144



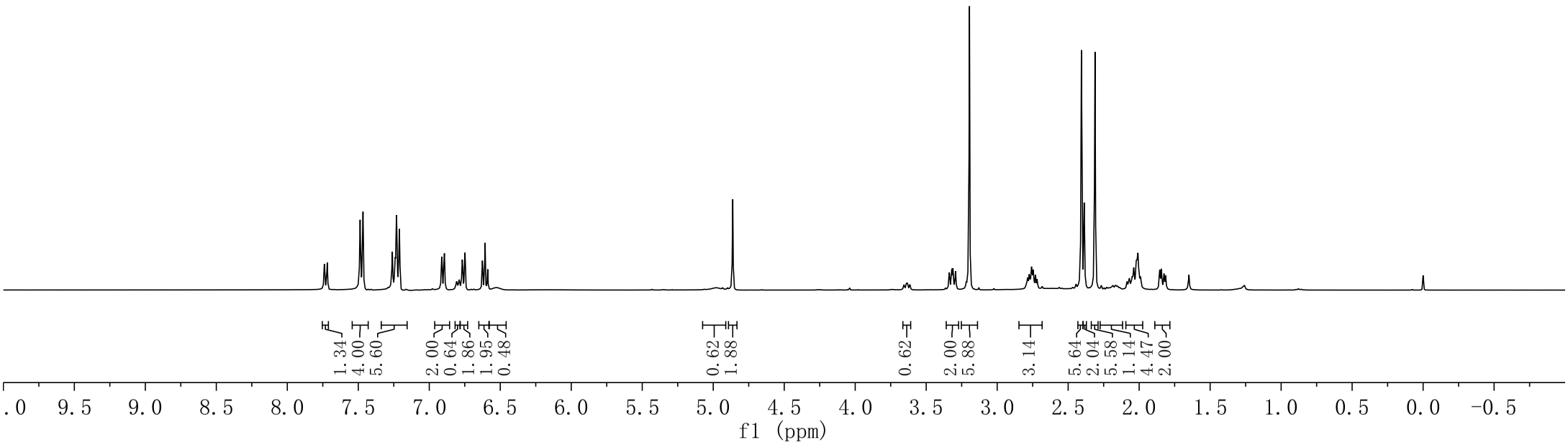




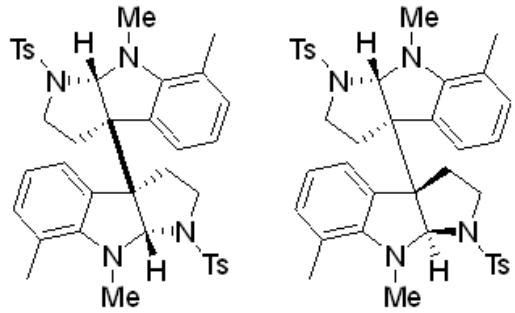
8b **8b'**

^{1}H NMR (100 MHz, CDCl3)

145



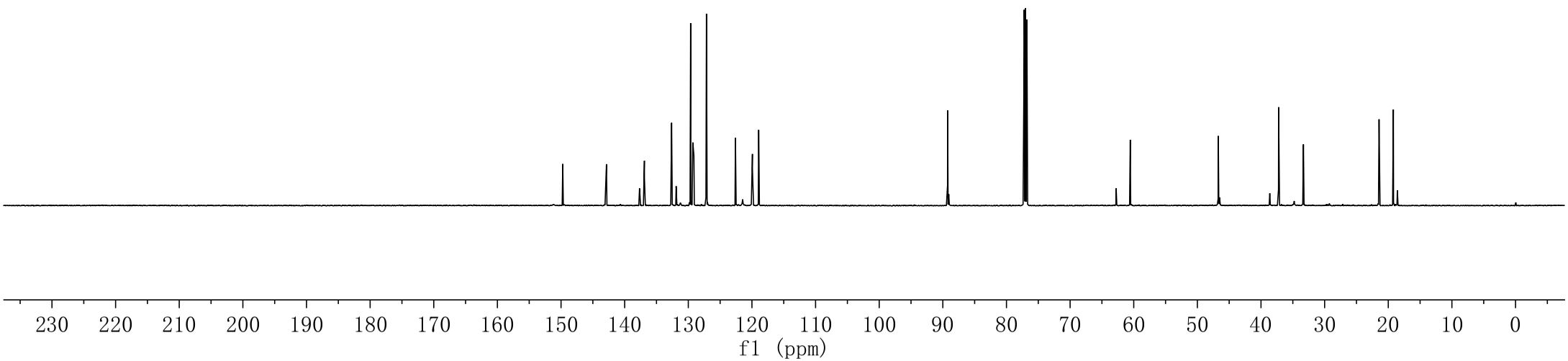
149.73
143.02
142.86
137.66
136.90
132.62
131.91
129.63
129.29
129.12
127.21
127.15
122.59
121.45
120.01
119.93
118.94
89.25
89.07
77.21
77.00
76.79
62.76
60.54
46.71
46.52
38.62
37.24
34.78
33.34
21.45
21.40
19.20
18.57

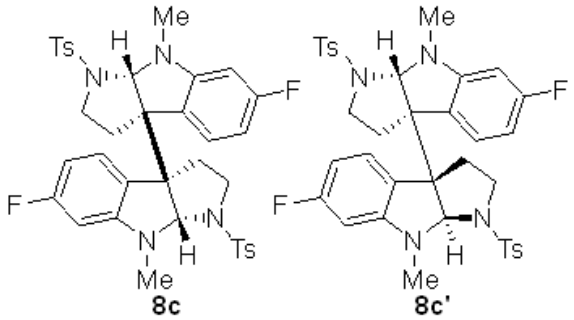


8b

8b'

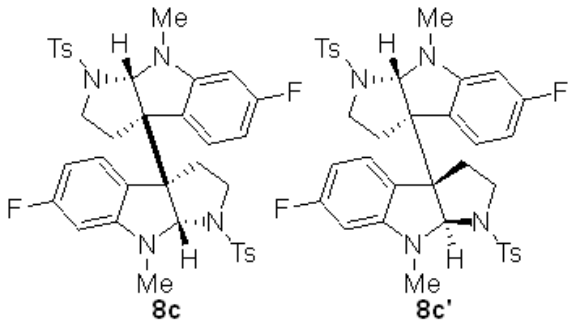
^{13}C NMR (150 MHz, CDCl3)





^{1}H NMR (400 MHz, $CDCl_3$)

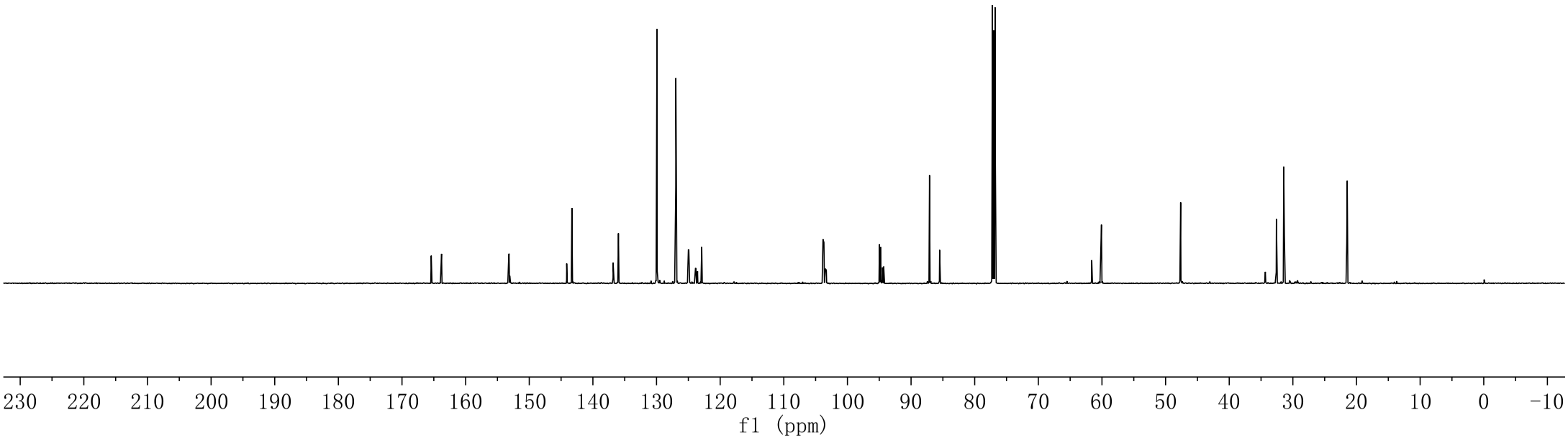
165.42
165.40
163.81
163.78
153.26
153.18
153.07
152.99
144.12
143.31
136.82
135.99
130.01
129.93
126.96
124.99
124.92
123.88
123.81
123.55
122.90
103.84
103.69
103.47
103.31
94.97
94.80
94.48
94.30
87.10
85.51
77.21
77.00
76.79
61.60
60.09
47.66
47.63
34.33
32.59
31.43
31.33
21.53
21.46

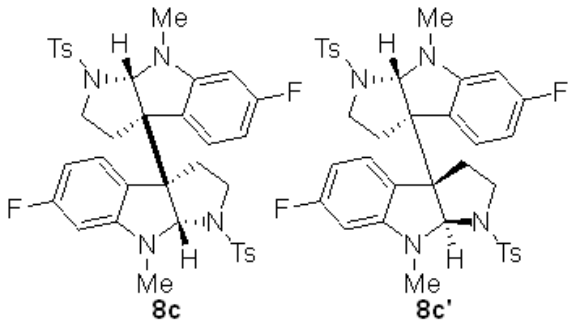


8c **8c'**

^{13}C NMR (150 MHz, $CDCl_3$)

148

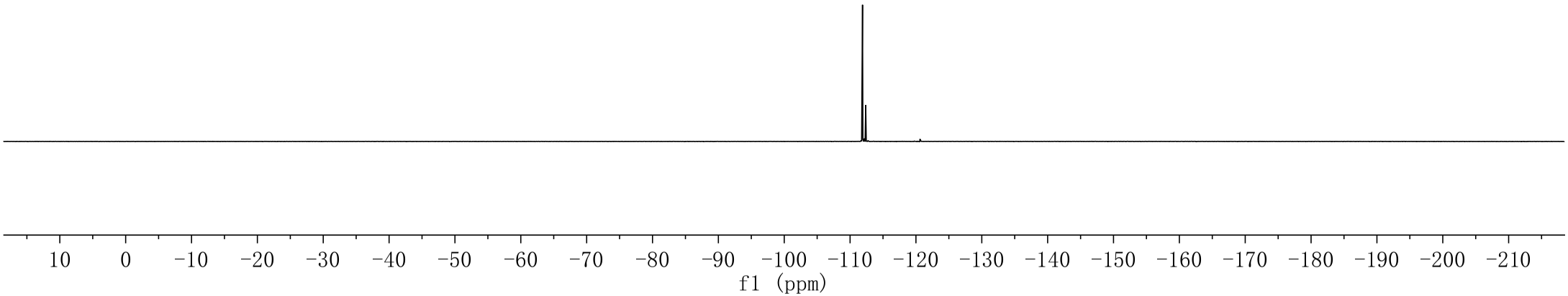


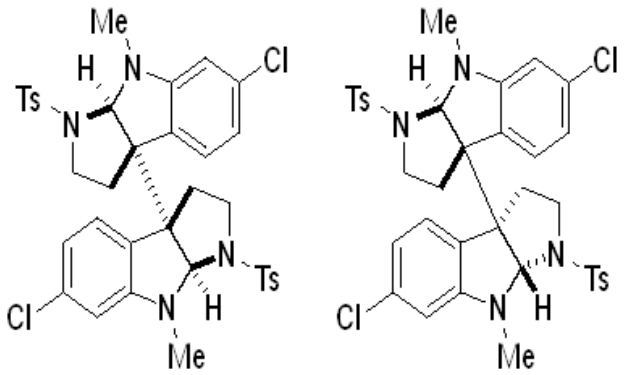


8c **8c'**

^{19}F NMR (376 MHz, $CDCl_3$)

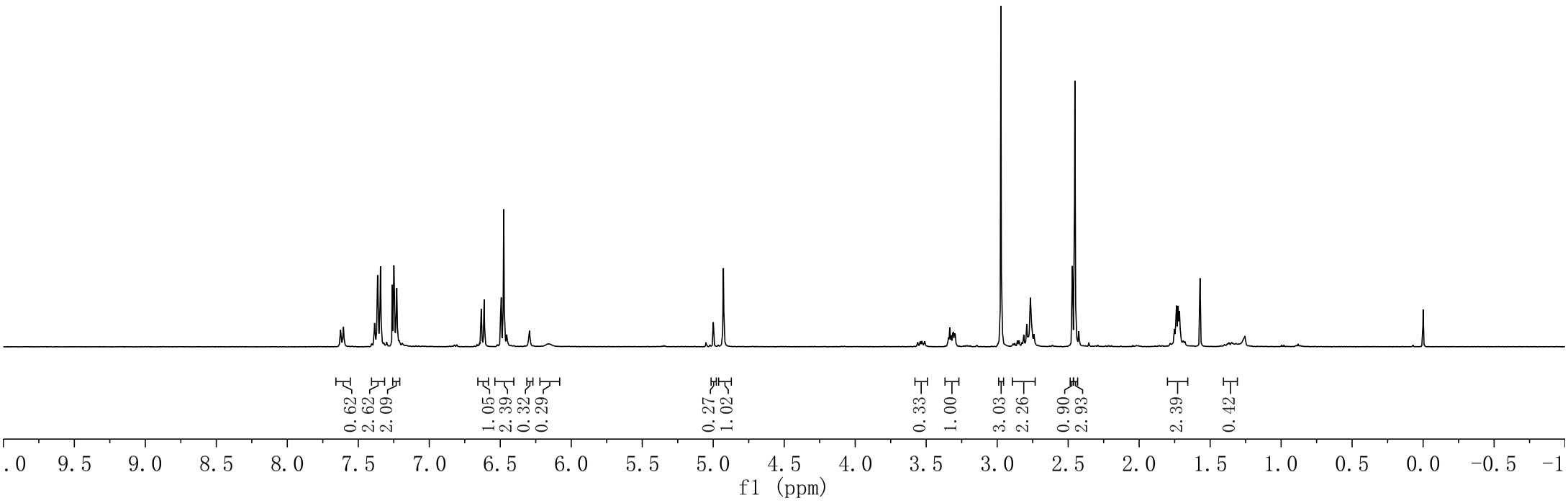
-111.89
-112.37

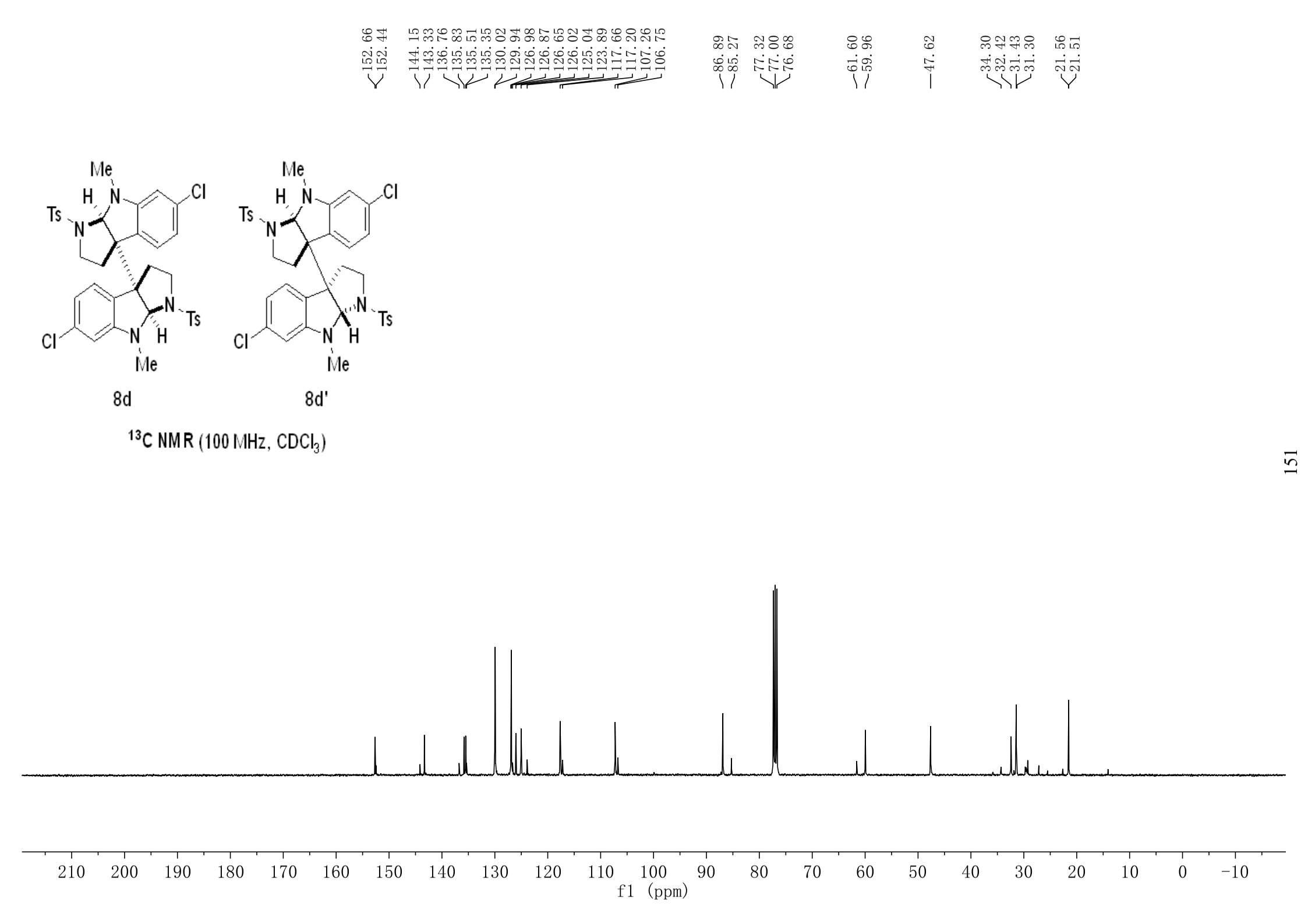


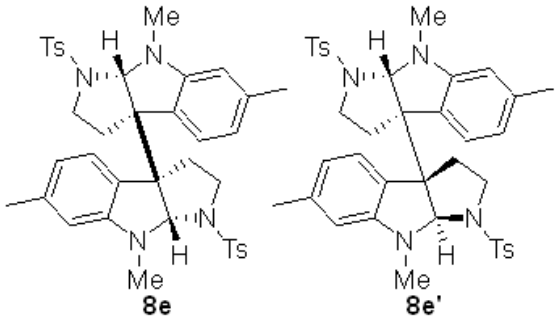


8d 8d'

^{1}H NMR (400 MHz, $CDCl_3$)



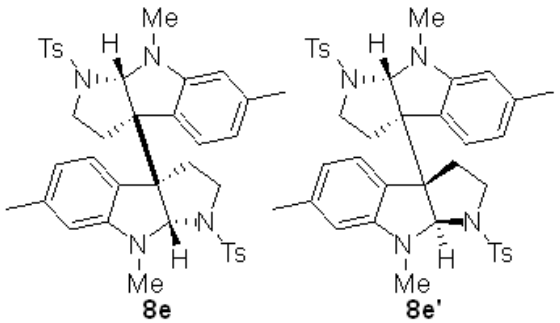

152.66
152.44
144.15
143.33
136.76
135.83
135.51
135.35
130.02
129.94
126.98
126.87
126.65
126.02
125.04
123.89
117.66
117.20
107.26
106.75
86.89
85.27
77.32
77.00
76.68
61.60
59.96
47.62
34.30
32.42
31.43
31.30
21.56
21.51
Me
H
N
Cl
Ts
N
N
Ts
Cl
N
H
Me
8d
8d'
13C NMR (100 MHz, CDCl3)
151
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



8e **8e'**

^{1}H NMR (400 MHz, $CDCl_3$)

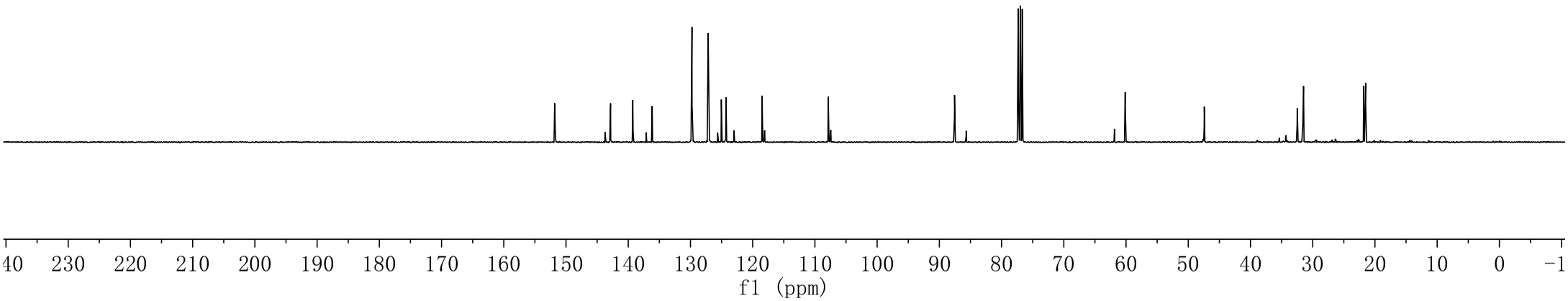
151.82
151.71
143.74
142.84
139.27
139.21
137.11
136.16
129.86
129.76
127.16
127.00
125.63
125.04
124.29
123.00
118.49
118.08
107.86
107.45
87.56
85.69
77.32
77.00
76.68
61.86
60.13
47.60
47.42
34.32
32.49
31.60
31.47
21.81
21.64
21.50

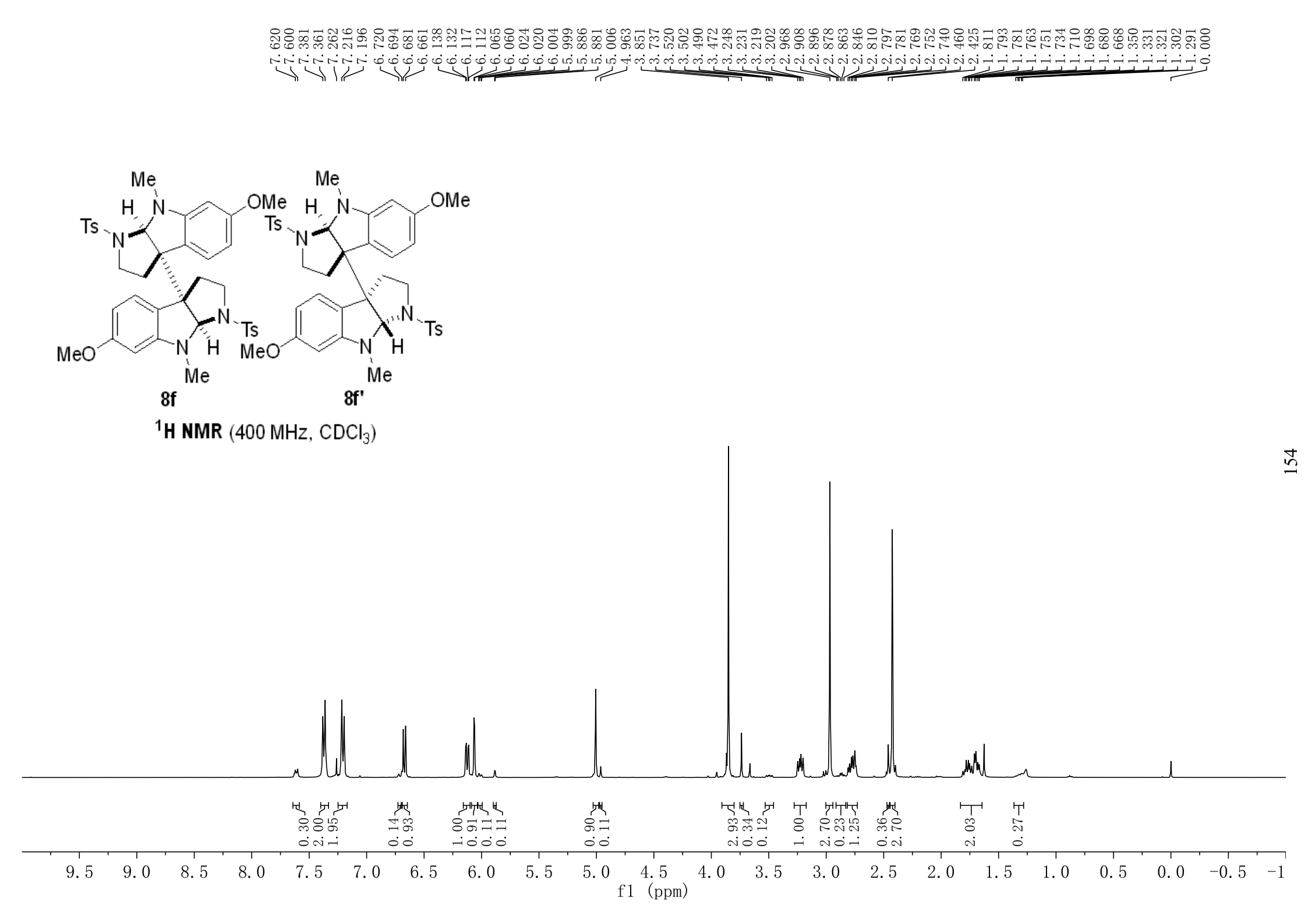


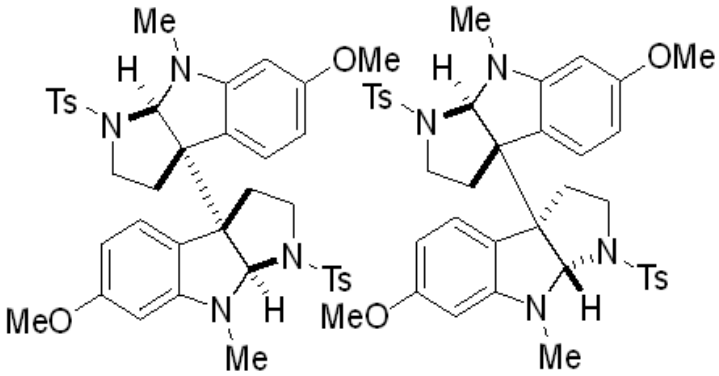
8e **8e'**

^{13}C NMR (100 MHz, $CDCl_3$)

153

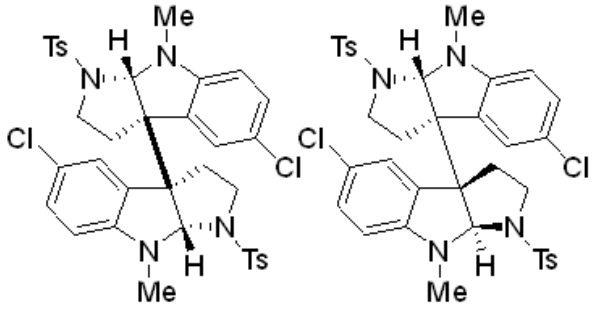



7.620
7.600
7.381
7.361
7.262
7.216
7.196
6.720
6.694
6.681
6.661
6.138
6.132
6.117
6.112
6.065
6.060
6.024
6.020
6.004
5.999
5.886
5.881
5.006
4.963
3.851
3.737
3.520
3.502
3.490
3.472
3.248
3.231
3.219
3.202
2.968
2.908
2.896
2.878
2.863
2.846
2.810
2.797
2.781
2.769
2.752
2.740
2.460
2.425
1.811
1.793
1.781
1.763
1.751
1.734
1.710
1.698
1.680
1.668
1.350
1.331
1.321
1.302
1.291
0.000
Me
H
N
OMe
Ts
N
MeO
N
H
Me
8f
8f'
1H NMR (400 MHz, CDCl3)
154
0.30
2.00
1.95
0.14
0.93
1.00
0.91
0.11
0.11
0.90
0.11
2.93
0.34
0.12
1.00
2.70
0.23
1.25
0.36
2.70
2.03
0.27
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)



8f **8f'**

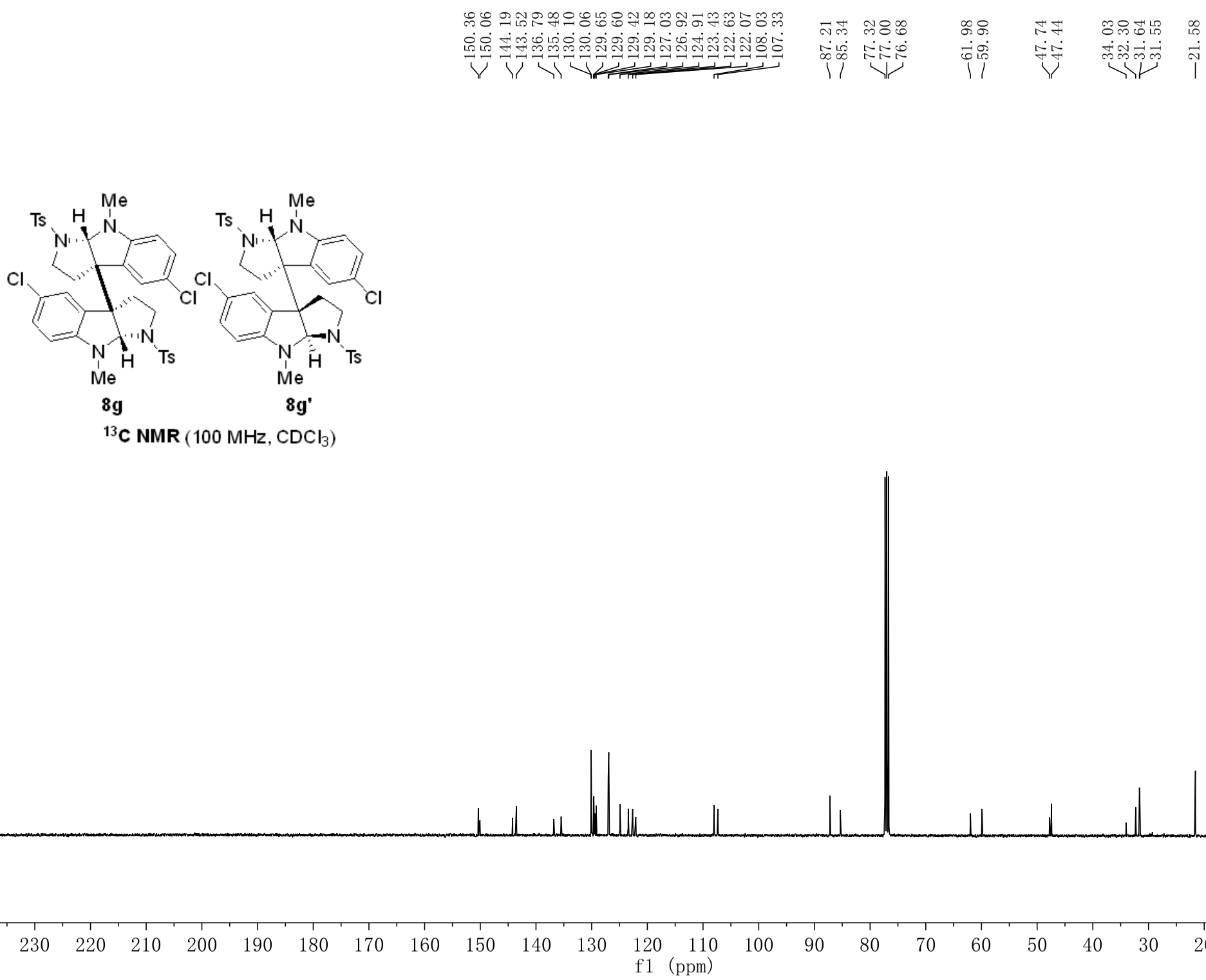
^{13}**C NMR** (100 MHz, CD_3CN)

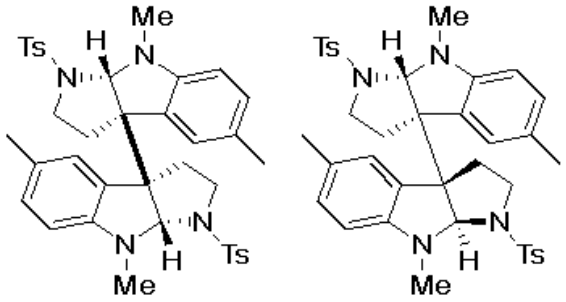


8g

8g'

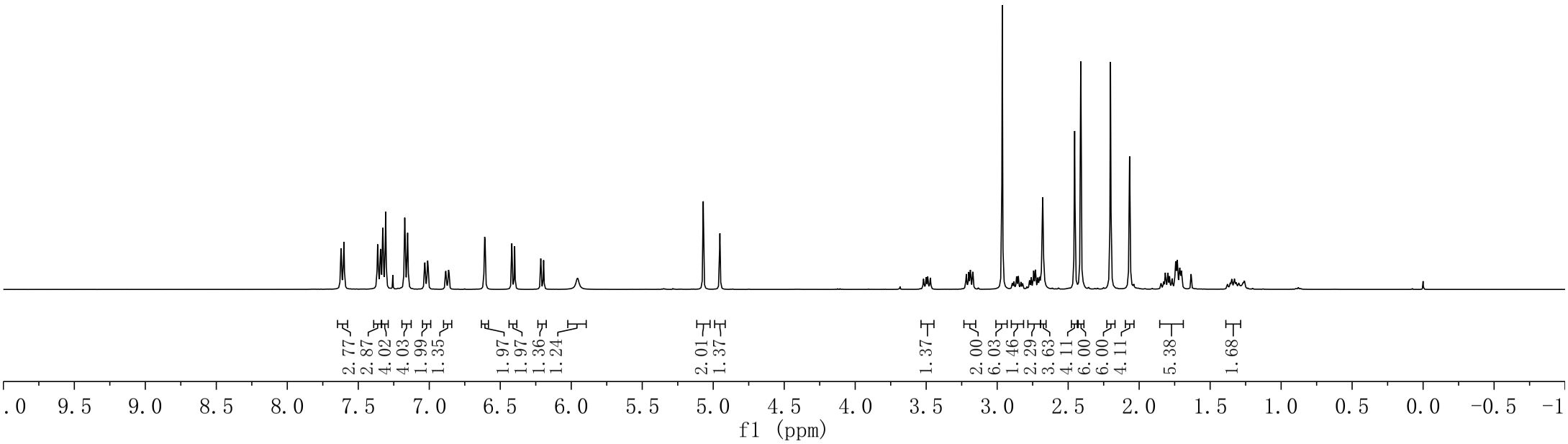
^{1}H NMR (400 MHz, $CDCl_3$)


150.36
150.06
144.19
143.52
136.79
135.48
130.10
130.06
129.65
129.60
129.42
129.18
127.03
126.92
124.91
123.43
122.63
122.07
108.03
107.33
87.21
85.34
77.32
77.00
76.68
61.98
59.90
47.74
47.44
34.03
32.30
31.64
31.55
21.58
157
Me
Ts
H
N
Cl
Cl
N
Ts
N
H
Me
8g
8g'
13C NMR (100 MHz, CDCl3)
40 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −1
f1 (ppm)

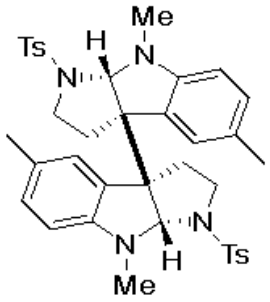


8h **8h'**

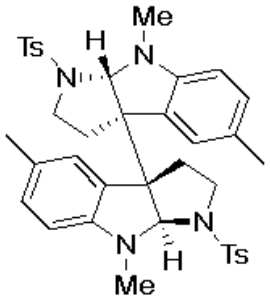
^{1}H NMR (400 MHz, $CDCl_3$)



149.65
149.57
143.73
142.69
137.11
136.14
129.85
129.82
129.50
128.51
127.90
127.12
127.00
126.50
126.44
125.70
124.13
106.86
106.35
87.52
85.71
77.32
77.00
76.68
62.21
60.14
47.67
47.48
34.01
32.37
31.95
31.69
21.50
21.46
21.00
20.63

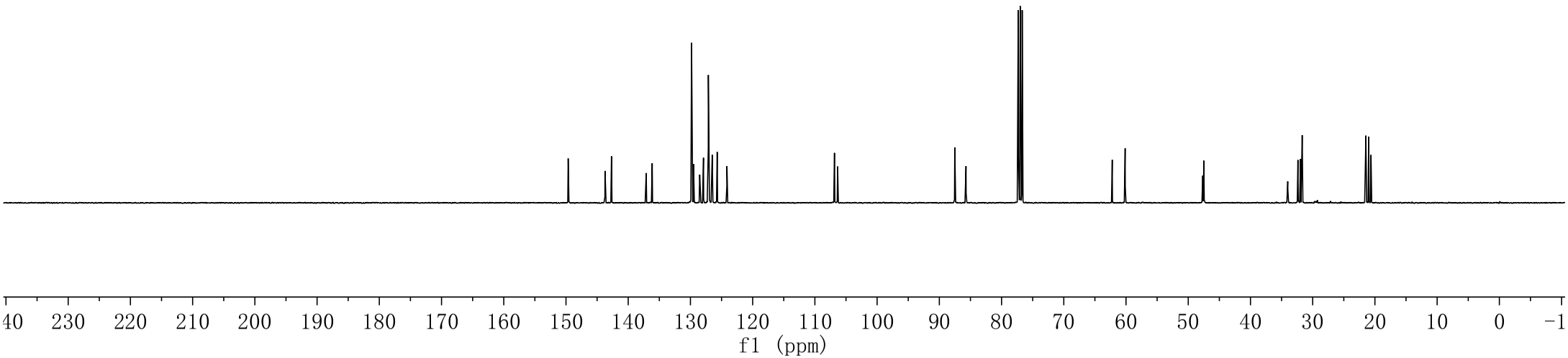


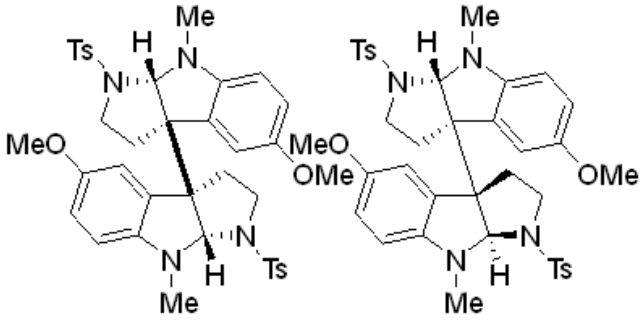
8h



8h'

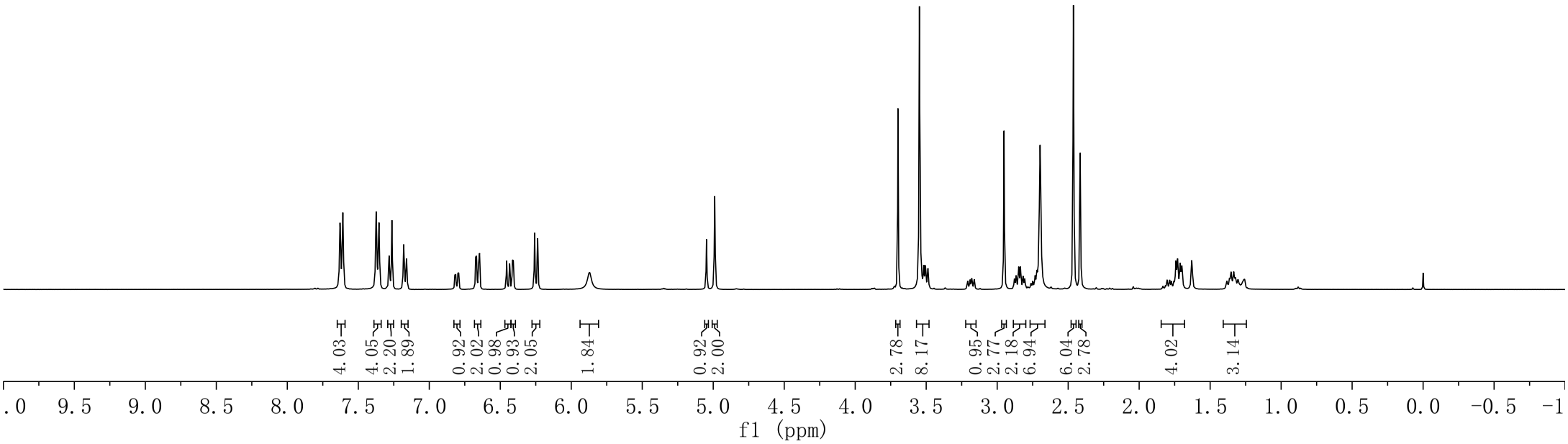
^{13}C NMR (100 MHz, $CDCl_3$)



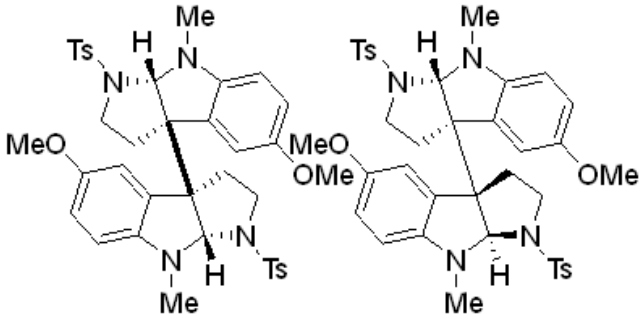


8i **8i'**

^{1}H NMR (400 MHz, $CDCl_3$)

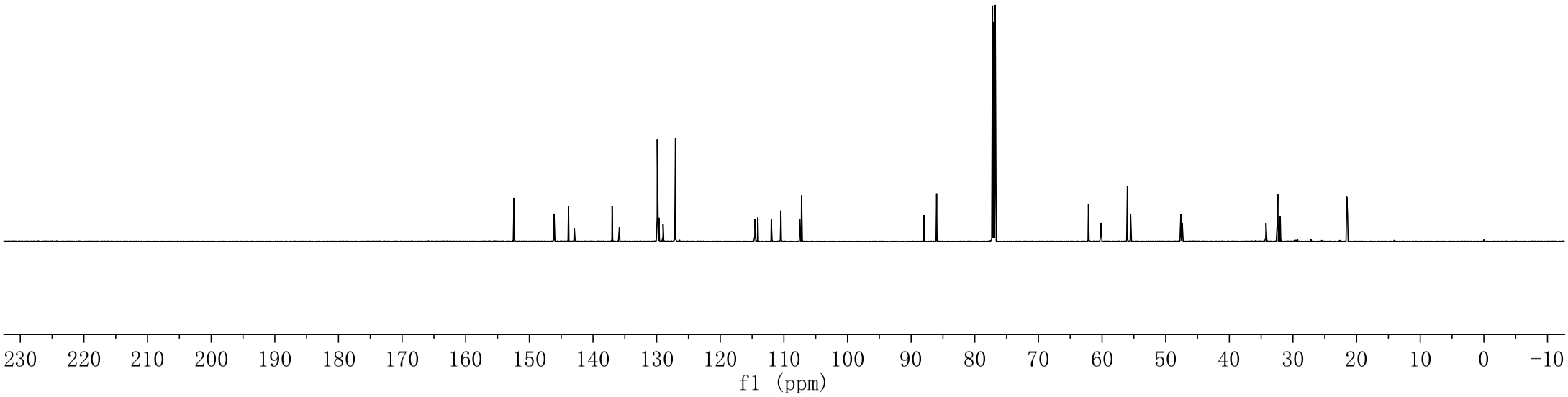


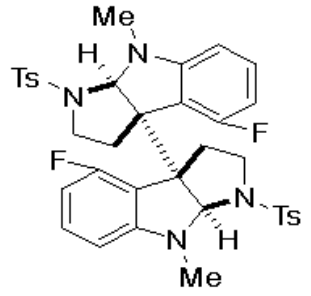
152.42
152.39
146.11
143.85
142.93
137.00
135.86
129.90
129.83
129.64
128.99
127.11
127.04
114.55
114.09
111.99
110.48
107.50
107.23
87.98
86.00
77.21
77.00
76.79
62.13
60.19
56.02
55.51
47.62
47.39
34.24
32.47
32.39
31.99
21.54
21.43



8i **8i'**

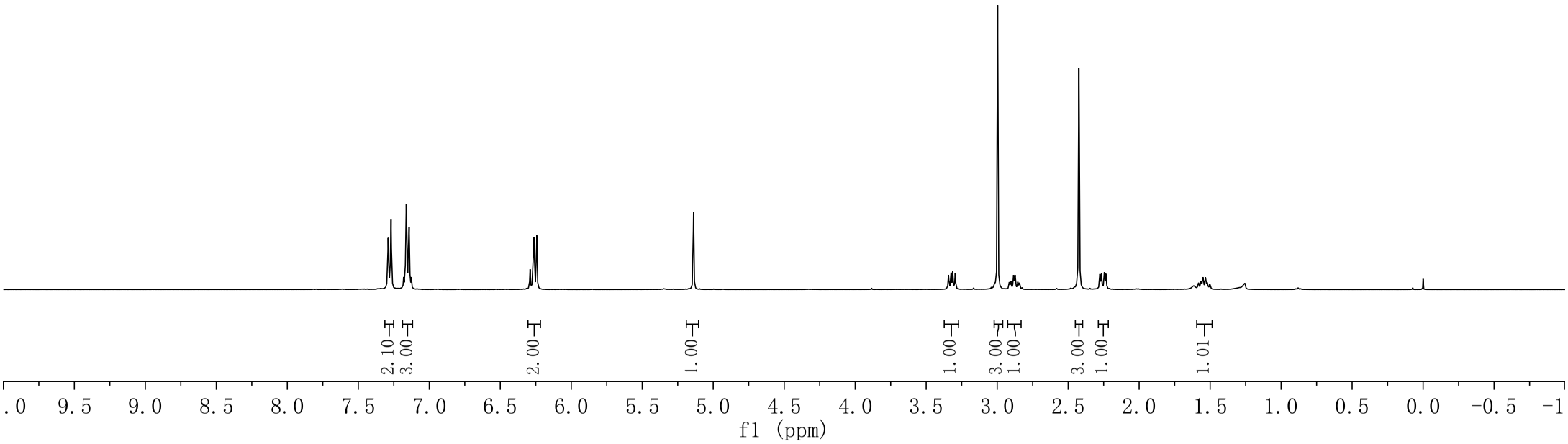
^{13}**C NMR** (150 MHz, $CDCl_3$)



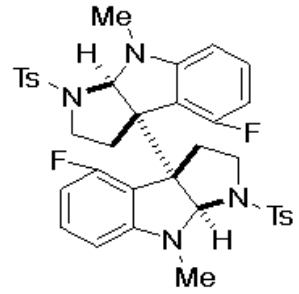


8j

^{1}H NMR (400 MHz, $CDCl_3$)



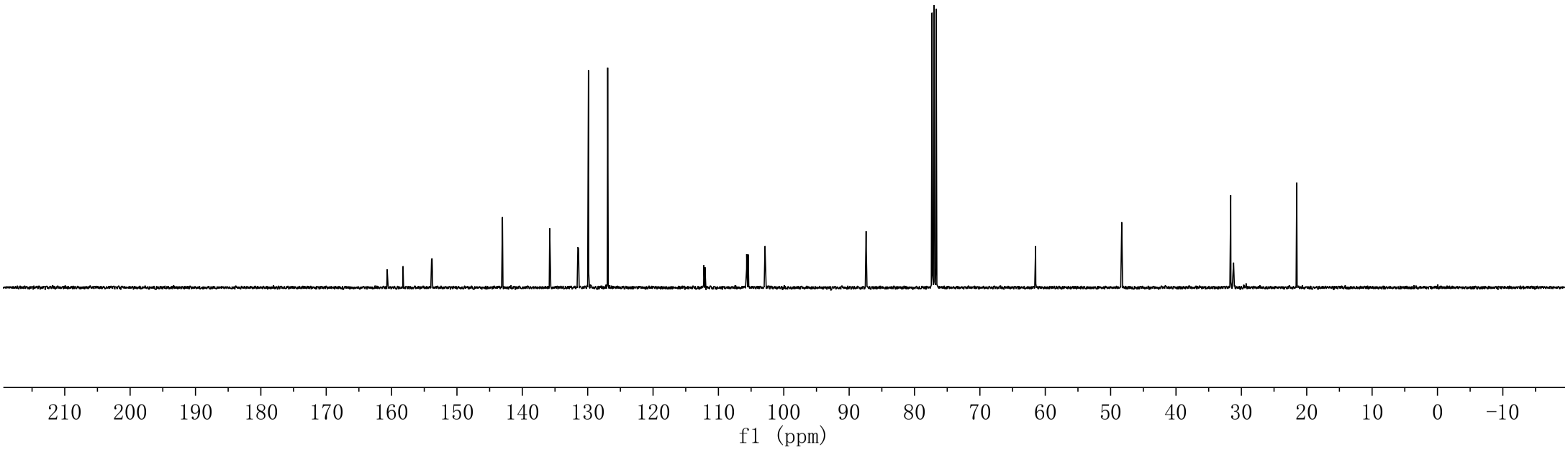
160.68
158.25
153.89
153.80
143.04
135.81
131.50
131.40
129.88
126.94
112.22
112.06
105.68
105.45
102.87
102.85
87.41
87.39
77.32
77.00
76.68
61.48
48.30
31.63
31.22
31.19
21.53

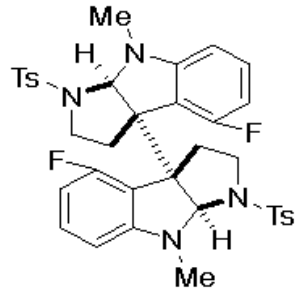


8j

^{13}**C NMR** (100 MHz, $CDCl_3$)

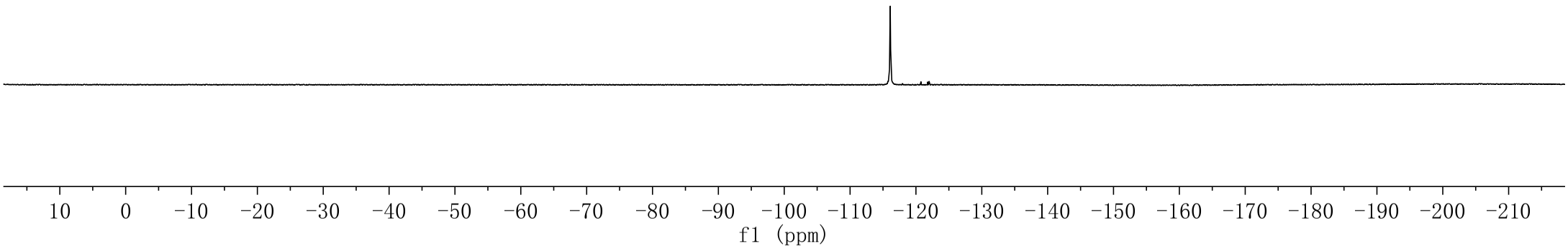
163

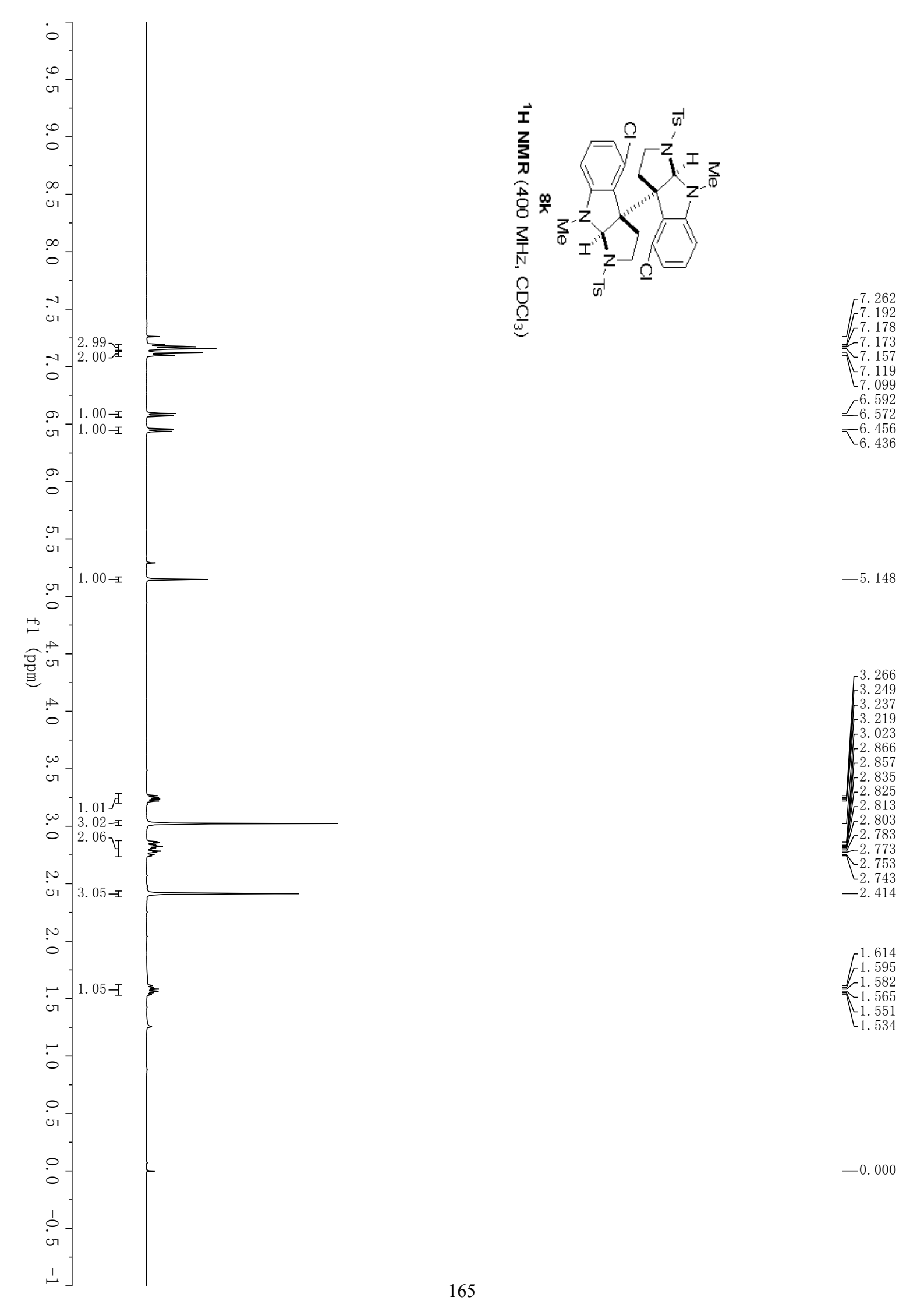


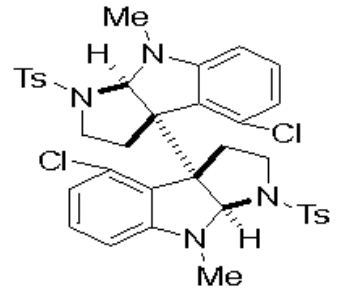


8j

^{19}F NMR (376 MHz, $CDCl_3$)




8k
^{1}H NMR (400 MHz, CDCl$_3$)
Ts
N
H
Me
N
Cl
Cl
N
Me
H
N
Ts
f1 (ppm)
2.99
2.00
1.00
1.00
1.00
1.01
3.02
2.06
3.05
1.05
7.262
7.192
7.178
7.173
7.157
7.119
7.099
6.592
6.572
6.456
6.436
5.148
3.266
3.249
3.237
3.219
3.023
2.866
2.857
2.835
2.825
2.813
2.803
2.783
2.773
2.753
2.743
2.414
1.614
1.595
1.582
1.565
1.551
1.534
0.000

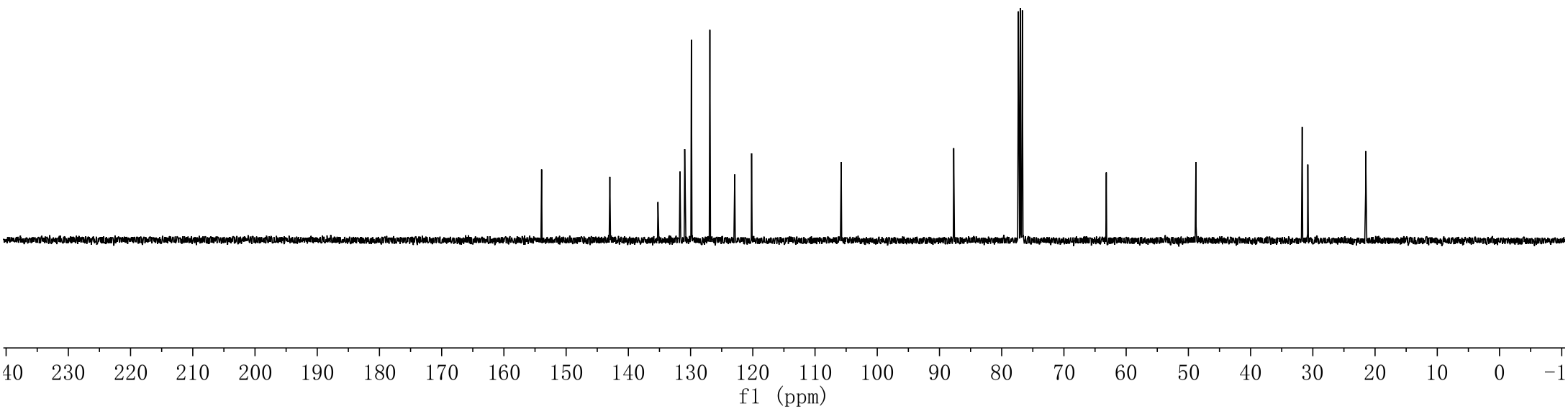


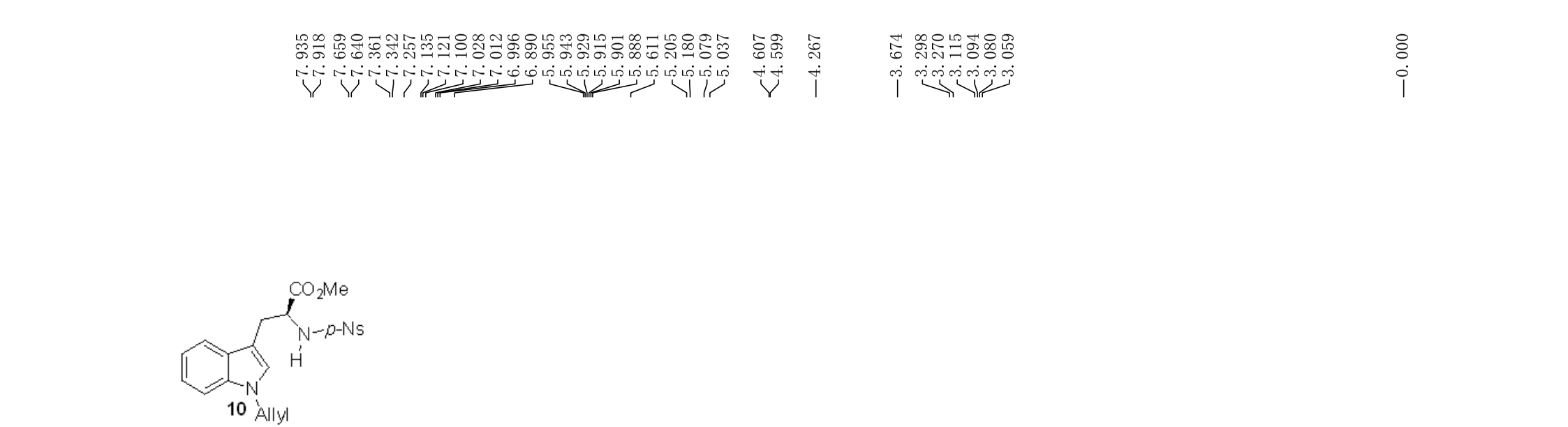
8k

^{13}C **NMR** (100 MHz, $CDCl_3$)

153.94
142.97
135.25
131.71
130.94
129.87
126.90
122.90
120.19
105.79
87.71
77.32
77.00
76.68
63.19
48.79
31.71
30.80
21.50

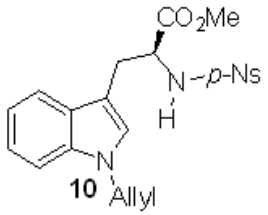
166





^{1}H NMR Spectum (400 MHZ, $CDCl_3$)

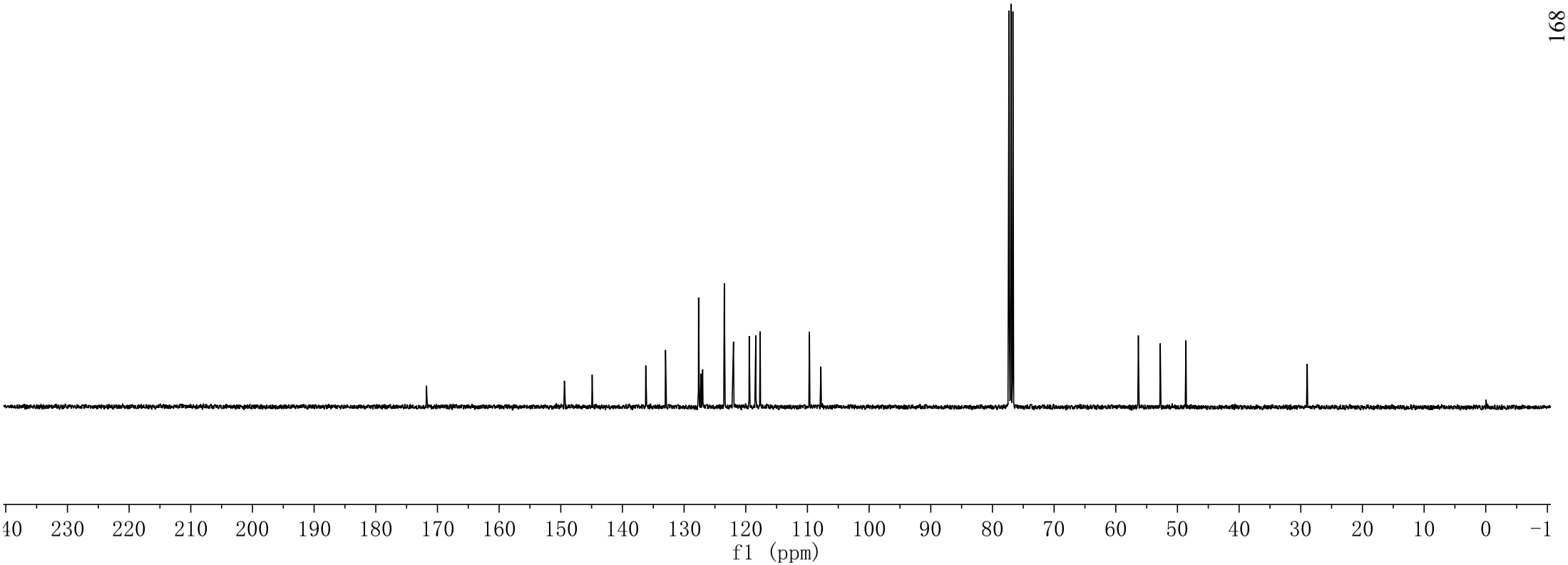
171.76
149.41
144.91
136.22
133.01
127.66
127.26
126.99
123.48
122.00
119.45
118.38
117.66
109.68
107.82
77.32
77.00
76.68
56.34
52.79
48.62
28.95

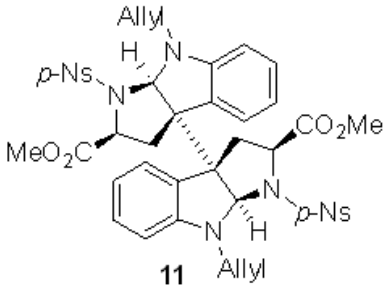


10

^{13}C NMR Spectum (100 MHZ, $CDCl_3$)

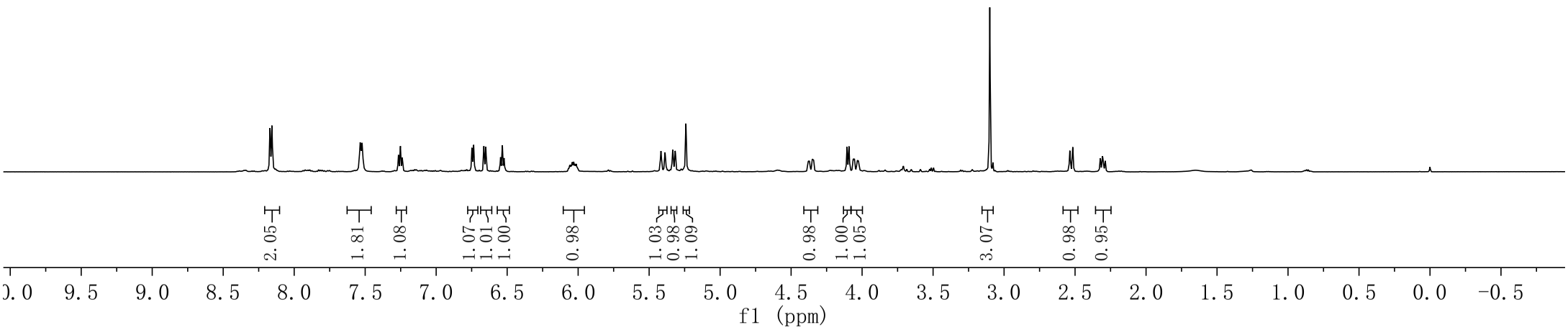
168

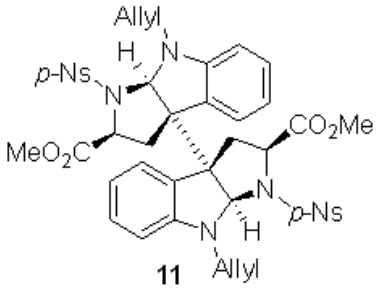




11

^{1}H NMR Spectum (600 MHZ, $CDCl_3$)

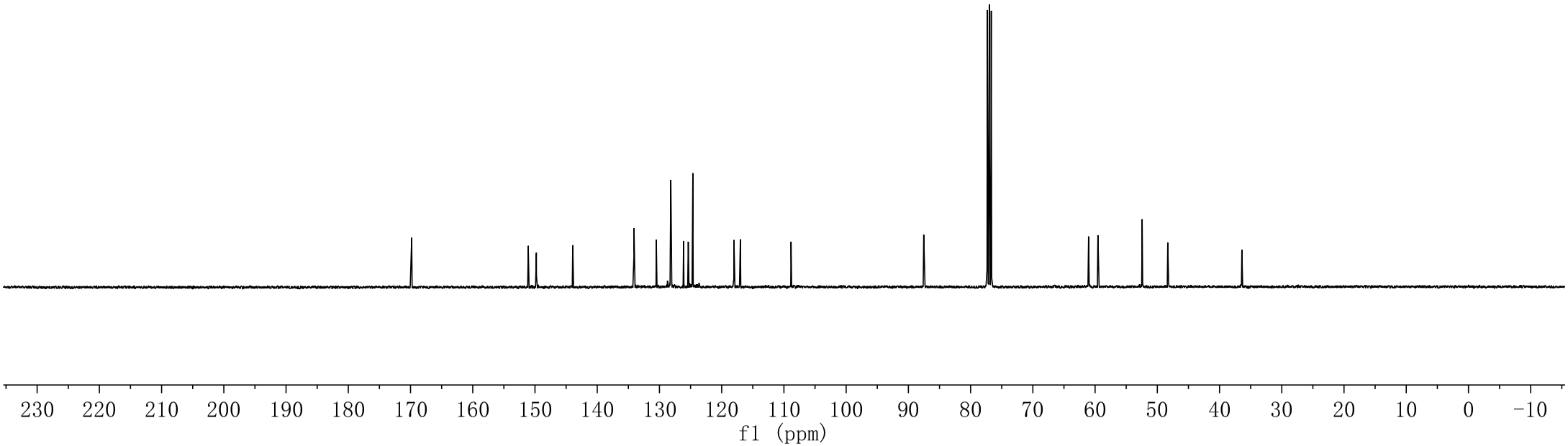


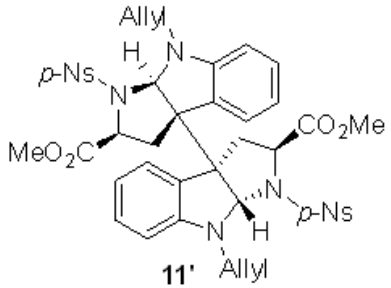


11

^{13}C NMR Spectum (100 MHZ, $CDCl_3$)

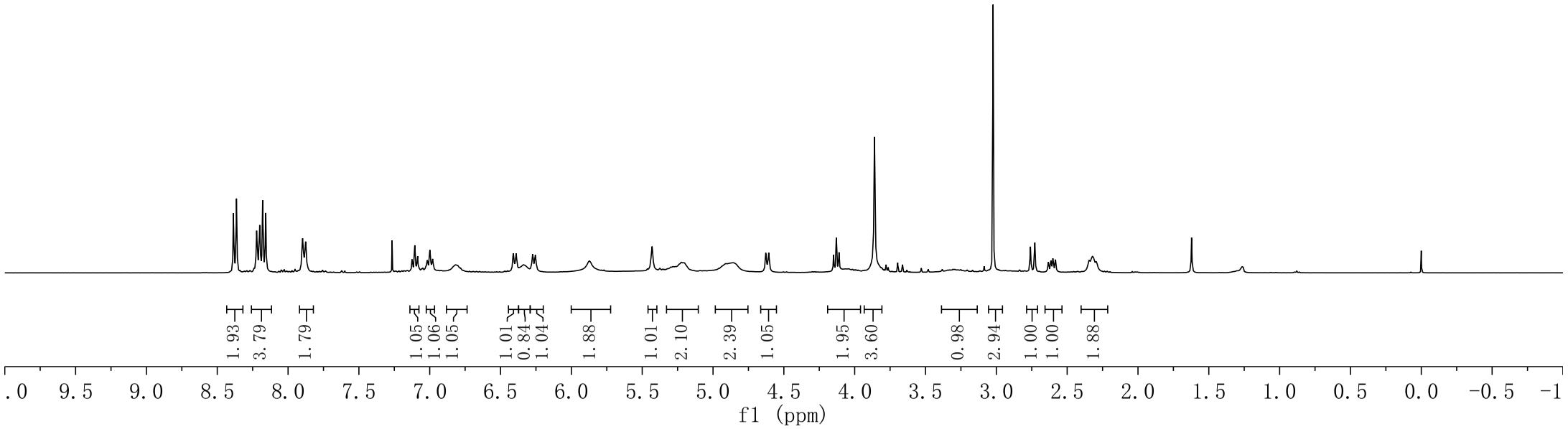
169.81
151.08
149.78
143.93
134.09
130.51
128.17
126.12
125.37
124.64
118.03
117.00
108.85
87.53
77.32
77.00
76.68
61.04
59.54
52.43
48.32
36.41

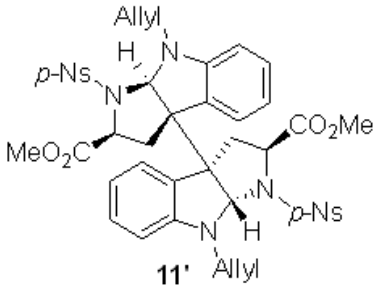




11'

^{1}H NMR Spectum (400 MHZ, $CDCl_3$)





11'

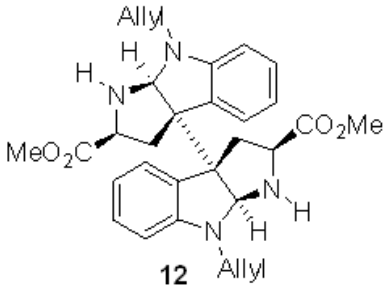
^{13}C NMR Spectum (100 MHZ, $CDCl_3$)

171.01
169.67
150.53
150.31
150.28
149.69
146.85
145.20
134.12
133.64
129.99
129.91
128.87
127.98
126.08
124.82
124.45
123.79
123.46
119.94
117.86
117.79
117.16
110.40
107.59
87.09
86.08
77.32
77.00
76.68
61.90
61.37
60.94
60.27
53.07
52.34
52.27
47.94
39.75
38.38

172

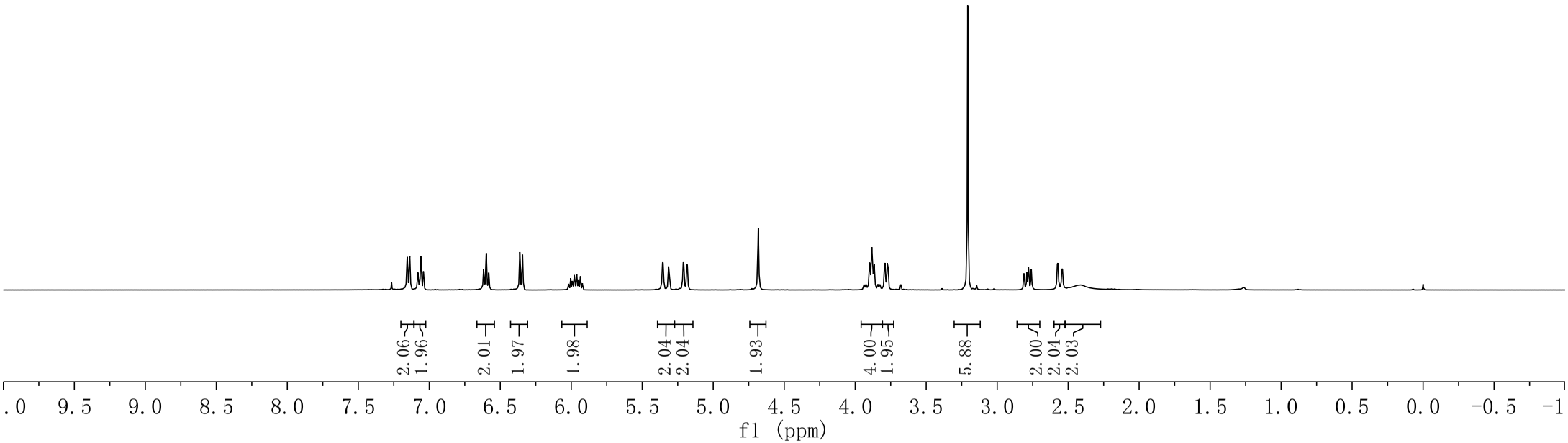
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

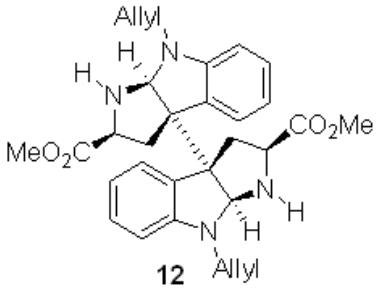
f1 (ppm)



12

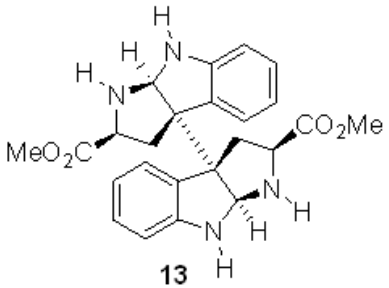
^{1}H NMR Spectum (400 MHZ, $CDCl_3$)





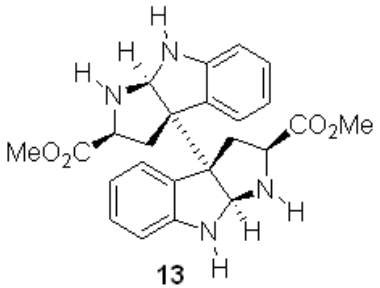
12

^{13}C NMR Spectum (100 MHZ, $CDCl_3$)



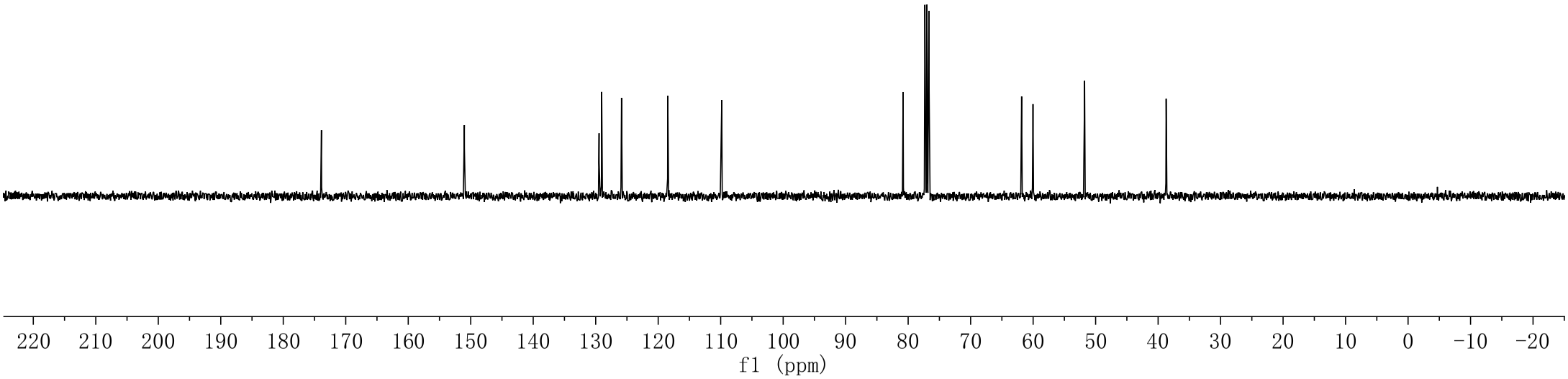
13

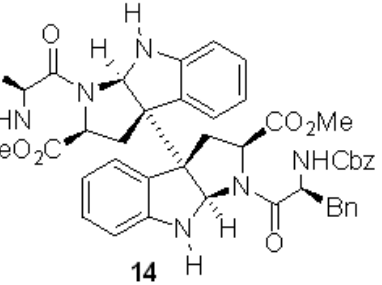
^{1}H NMR Spectum (400 MHZ, $CDCl_3$)



13

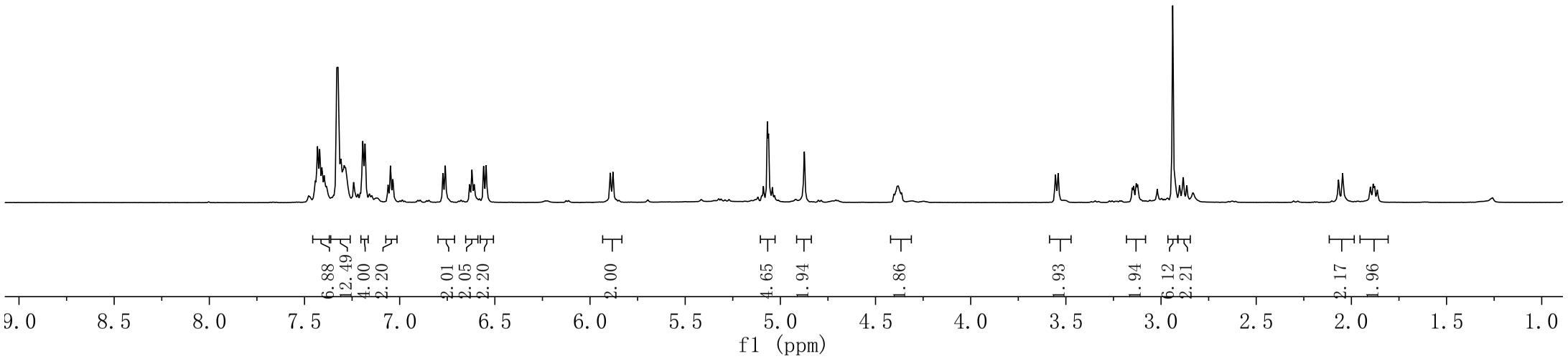
^{13}C NMR Spectum (100 MHZ, $CDCl_3$)



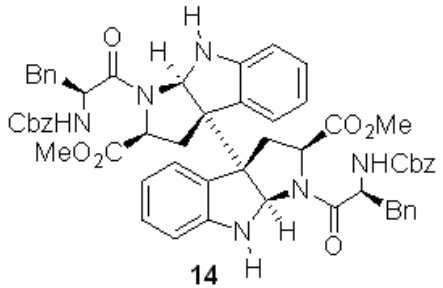


14

^{1}H NMR Spectum (600 MHZ, $CDCl_3$)

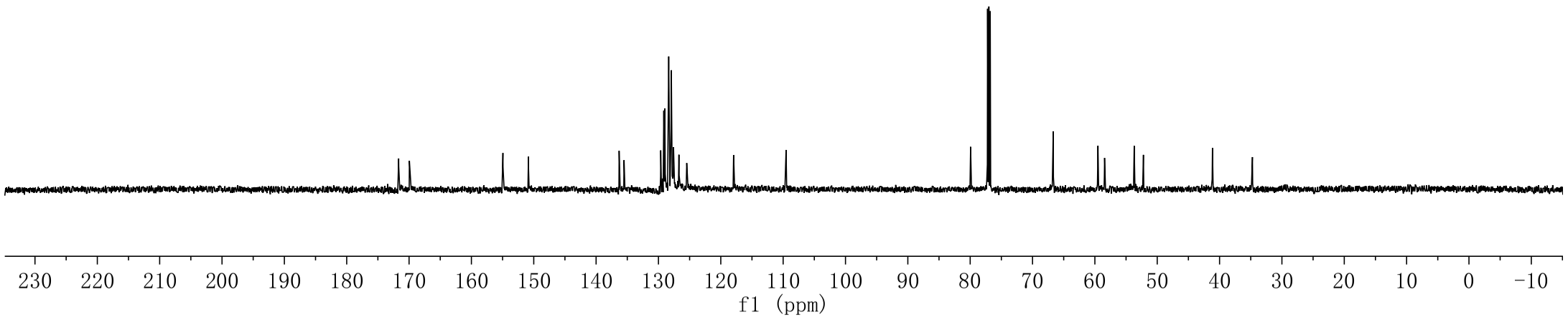


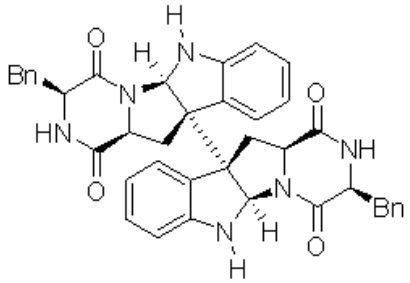
171.66
169.95
154.94
150.85
136.30
135.51
129.63
129.14
128.98
128.35
127.93
127.58
126.71
125.46
117.95
109.53
79.93
77.21
77.00
76.79
66.68
59.50
58.44
53.69
52.21
41.14
34.73



14

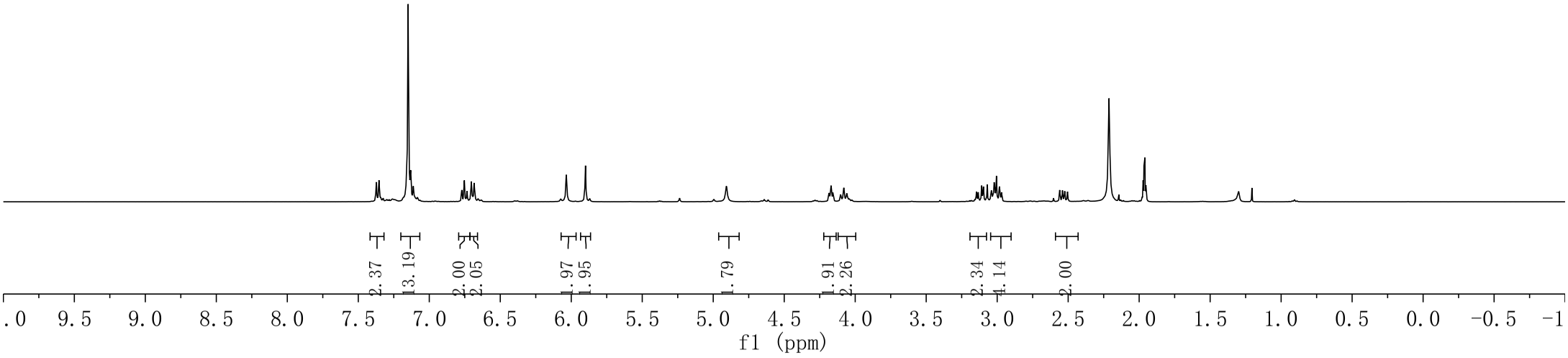
^{13}C NMR Spectum (150 MHZ, $CDCl_3$)

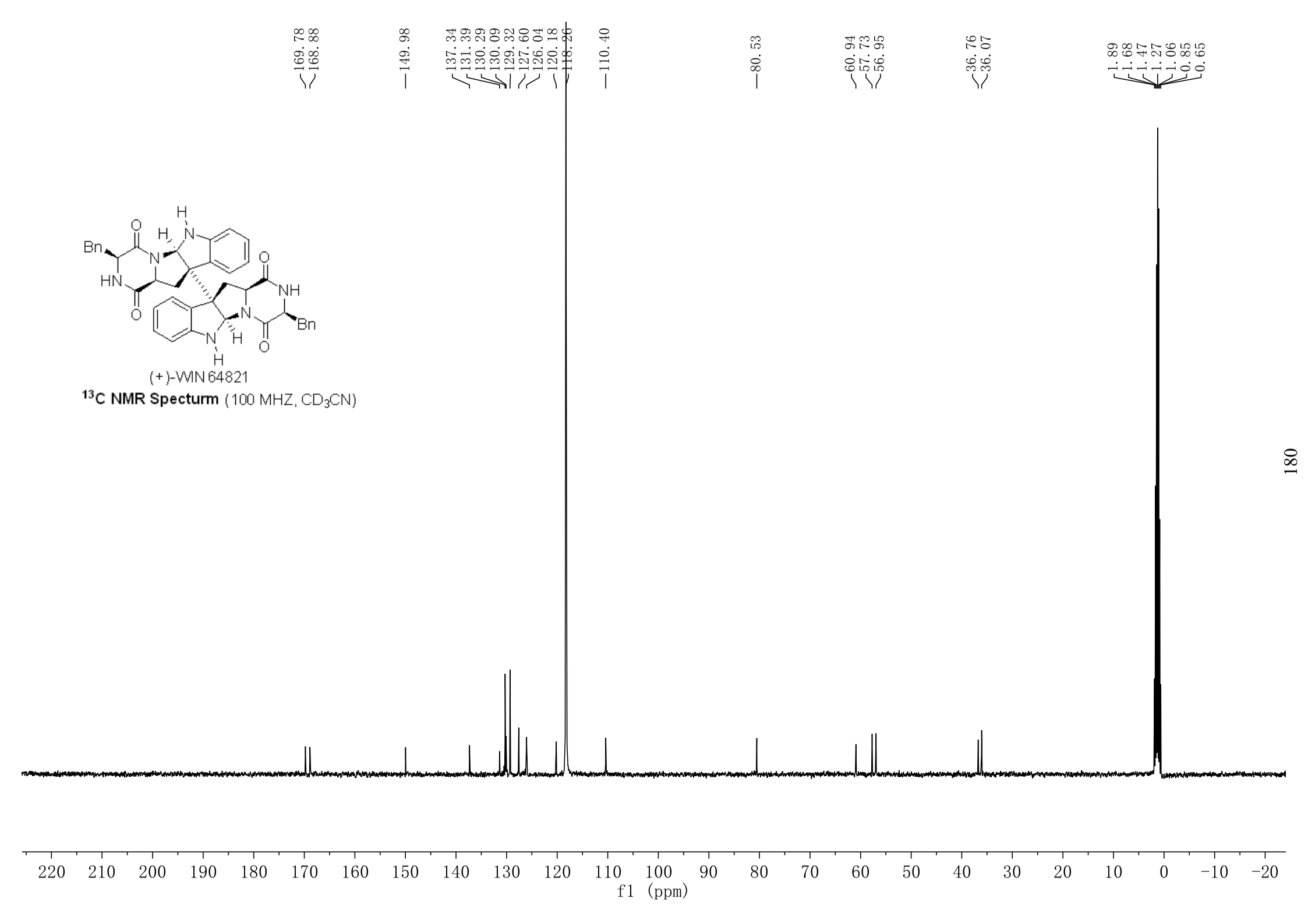




(+)-WIN 64821

^{1}H NMR Specturm (400 MHZ, CD_3CN)





(+)-WIN 64821

^{13}C NMR Specturm (100 MHZ, CD_3CN)