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Supplementary Information

Asymmetric synthesis of CF_3- and indole-containing tetrahydro-β carbolines via chiral spirocyclic phosphoric acid-catalyzed *aza*-Friedel-Crafts reaction

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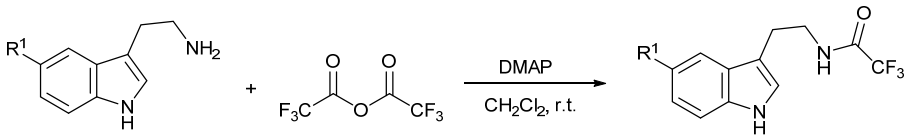
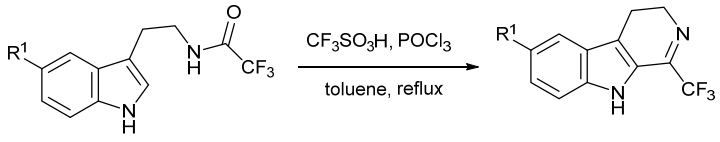
1. General Remarks

All reactions were carried out in oven-dried glassware with magnetic stirring under a nitrogen atmosphere unless otherwise mentioned. All solvents were purified and dried according to standard methods prior to use. ^{1}H NMR spectra were recorded on 400 MHz spectrometer. The chemical shifts were reported relative to internal standard TMS (0) in $CDCl_3$ or 2.5 in DMSO-d_6. The following abbreviations were used to describe peak patterns where appropriate: br=broad, s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet. Coupling constants were reported in Hertz (Hz). ^{13}C NMR spectra were recorded on 100 MHz spectrometer, referred to the internal solvent signals (77.0 for $CDCl_3$ or 40.0 for DMSO-d_6). ^{19}F NMR spectra were recorded on 376 MHz in $CDCl_3$. Infrared spectra were recorded on an ATR-FTIR spectrometer. HRMS were obtained using EI ionization. Optical rotations were determined using a Perkin Elmer Model 341 polarimeter at 20 °C. Enantiomeric excesses (ee) were determined by chiral high-performance liquid chromatography. HPLC analysis was performed using Chiralcel columns (Chiralcel OD-H, AD-H and Chiralpak OOG-4457-EO). Analytical grade solvents for the column chromatography were used as received. The chiral spirocyclic phosphoric acid catalysts were prepared according to the literatures.[1, 2]

2. General Procedure for Synthesis of Dihydro-β-carbolines



To a solution of tryptamine (15 mmol, 1.0 eq.), 4-dimethylaminopyridine (DMAP, 91.5 mg, 0.75 mmol, 0.05 eq.) in dichloromethane (30 mL) was added dropwise trifluoroacetic anhydride (2.5 mL, 18 mmol, 1.2 eq.). The resulting mixture was stirred for 2 h at room temperature in the air. After the reaction was complete, the reaction mixture was washed with saturated brine (30 mL) and extracted with dichloromethane (3x20 mL). The organic layers were dried by anhydrous Na_2SO_4 and concentrated in vacuo. Purification of the residue by flash column chromatography (petroleum ether/ethyl acetate = 6/1) afforded the desired trifluoroacetamide compound.



To a solution of the trifluoroacetamide compounds (10.9 mmol, 1.0 eq.) in toluene (50 mL) was

added phosphorus oxychloride (6.6 mL, 54.5 mmol, 5.0 eq.), trifluorometh anesulfonic acid(1.9 mL, 22 mmol, 2.0 eq.) via syringe in the ice bath. The resulting mixture was refluxed for 5 h under a nitrogen atmosphere. Upon completion the reaction mixture was allowed to cool to room temperature and quenched with water. The pH of aqueous layer was adjusted by the addition sodium hydroxide to pH 10. The resulting solution was extracted four times with EtOAc. Organic layer was washed with brine, dried over anhydrous Na_2SO_4, and solvent was removed in vacuo. Purification of the residue by flash column chromatography (petroleum ether/ethyl acetate = 6/1) afforded the 6-substituted 1-trifluoromethyl-3,4-dihydro-β-carboline **1**.

3,4-dihydro-β-carboline and 1-phenyl-3,4-dihydro-β-carboline were prepared according to the literatures.[3, 4]

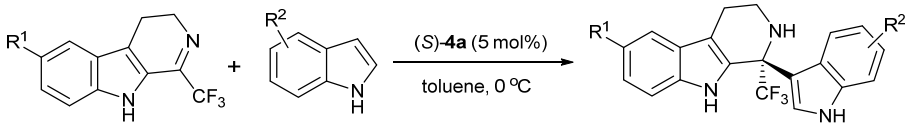
1-(trifluoromethyl)-4,9-dihydro-3H-pyrido[3,4-b]indole (1a): 2.5 g, 71% over yield; yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 7.61 (m, 1H), 7.42 (d, *J* = 8.3 Hz, 1H), 7.35 (m, 1H), 7.19 (m, 1H), 4.14 – 4.04 (m, 2H), 2.97 (t, *J* = 2.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2 (q, *J* = 35 Hz), 137.2, 126.1, 124.8, 123.0, 121.0, 120.2, 120.0, 119.9 (q, *J* = 275 Hz), 112.3, 48.5, 18.9;

6-methyl-1-(trifluoromethyl)-4,9-dihydro-3H-pyrido[3,4-b]indole (1b): 2.1 g, 56% over yield; white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.38 (s, 1H), 7.30 (d, *J* = 8.4 Hz, 1H), 7.17 (m, 1H), 4.12 – 4.00 (m, 2H), 2.98 – 2.89 (m, 2H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2 (q, *J* = 35 Hz), 135.7, 130.4, 128.0, 125.0, 123.1, 119.6, 119.5, 119.9 (q, *J* = 275 Hz), 111.9, 48.57, 21.45, 18.89;

6-methoxy-1-(trifluoromethyl)-4,9-dihydro-3H-pyrido[3,4-b]indole (1c): 1.6 g, 39% over yield; white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.31 (d, *J* = 8.9 Hz, 1H), 7.02 (m, 1H), 6.98 (d, *J* = 2.4 Hz, 1H), 4.21 – 3.98 (m, 2H), 3.87 (s, 3H), 3.03 – 2.79 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 149.0 (q, *J* = 35 Hz), 132.5, 125.1, 123.5, 119.9 (q, *J* = 275 Hz) , 119.4, 117.5, 113.2, 100.4, 55.8, 48.6, 18.9;

6-chloro-1-(trifluoromethyl)-4,9-dihydro-3H-pyrido[3,4-b]indole (1d): 2.9 g, 56% over yield; yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 7.58 (d, *J* = 1.8 Hz, 1H), 7.35 (d, *J* = 8.7 Hz, 1H), 7.29 (m, 1H), 4.28 – 3.92 (m, 2H), 2.94 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9 (q, *J* = 35 Hz), 135.4, 126.7, 126.4, 125.8, 123.9, 119.6, 119.8 (q, *J* = 275 Hz), 119.2, 113.4, 48.5, 18.6;

3. General Procedure for Asymmetric *aza*-Friedel-Crafts Reaction



1 2 3

To a solution of 1-trifluoromethyl-3,4-dihydro-β-carboline **1** (0.05 mmol), indoles **2** (0.06 mmol) in toluene (1 mL) was added catalyst (*S*)-**4a** (0.0025 mmol). The resulting mixture was stirred for the indicated time at ice bath (or at room temperature) under a nitrogen atmosphere. After the reaction was complete, the reaction mixture was then subjected to a silica gel column (petroleum ether/ethyl acetate = 6/1) to afford the desired products (*S*)-**3**.

For scalable preparation of 3e: To a solution of 1-trifluoromethyl-3,4-dihydro-β-carboline **1** (5.88 mmol, 1.4 g), 7-methyl-indole **2e** (7.06 mmol, 0.8 g) in toluene (25 mL) was added catalyst (*S*)-**4a** (0.29 mmol). The resulting mixture was stirred for 48 h at 0 ^{o}C under a nitrogen atmosphere. After the reaction was complete, the reaction mixture was quenched with aq.$NaHCO_3$ and extracted with toluene. The organic layer was washed with brine, dried over Na_2SO_4 and filtrated. After the solvent was removed under reduced pressure, the residue was then subjected to a silica gel column (petroleum ether/ethyl acetate) to afford the desired product **3e** (1.78g, 82% yield, 92% ee). After one recrystallization from EA-Hexane, **3e** was obtained in 70% yield with 95% ee.

(*S*)-(-)-1-(1H-indol-3-yl)-1-(trifluoromethyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3a): 14 mg, 81% yield; white solid; m.p. 189-190°C; 86% ee; HPLC analysis: Chiralpak AD-H (hexane/i-PrOH = 80/20, 0.8 mL/min), t_R (major) 13.048 min, t_R (minor) 18.997 min; $[\alpha]_D^{20}$ = -88.1 (*c* 0.5, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 8.04 (s, 1H), 7.63 (d, *J* = 7.7 Hz, 1H), 7.87 – 7.25 (m, 2H), 7.23 (d, *J* = 8.3 Hz, 1H), 7.21 – 7.11 (m, 4H), 6.95 (t, *J* = 7.4 Hz, 1H), 3.39 – 3.30 (m, 1H), 3.21 – 3.10 (m, 1H), 3.00 – 2.89 (m, 1H), 2.89 – 2.77 (m, 1H), 2.12 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.51 (d, *J* = 5.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.3, 135.9, 128.9, 126.9 (q, *J* = 285 Hz), 126.5, 125.1, 124.6 (d, *J* = 2.3 Hz), 122.8, 122.6, 120.5, 120.4, 119.7, 118.9, 113.3, 113.3, 113.0, 111.4, 60.3 (q, *J* = 28 Hz), 40.4, 22.1; IR (film): γ= 3406, 2953, 2924, 2853, 1457, 1338, 1277, 1245, 1158, 1112, 1013, 903, 744 cm^{-1}; HRMS (EI-TOF): calcd for $C_{20}H_{16}F_3N_3$ 355.1296, found 355.1295.

(*S*)-(-)-1-(7-chloro-1H-indol-3-yl)-1-(trifluoromethyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]i

ndole (3b): 12 mg, 65% yield; yellow solid; m.p. 206-207°C; 91% ee; HPLC analysis: Chiralpak AD-H (hexane/i-PrOH = 90/10, 0.8 mL/min), t_R (major) 28.824min, t_R (minor) 32.785 min; $[\alpha]_D^{20}$ = -67 (*c* 0.2, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 8.01 (s, 1H), 7.63 (d, *J* = 7.7 Hz, 1H), 7.36 – 7.27 (m, 2H), 7.26 – 7.21 (m, 1H), 7.20 – 7.13 (m, 3H), 6.90 (t, *J* = 7.9 Hz, 1H), 6.90 (t, *J* = 7.9 Hz, 1H), 3.43 – 3.31 (m, 1H), 3.21 – 3.11 (m, 1H), 3.01 – 2.91 (m, 1H), 2.91 – 2.80 (m, 1H), 1.62 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.71 (s, 3F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.9, 133.6, 128.6, 126.6, 126.7 (q, *J* = 285 Hz), 126.5, 125.1 (d, *J* = 2.3 Hz), 122.9, 122.0, 121.3, 119.8, 119.4, 118.9, 116.8, 114.7, 113.1, 111.4, 60.4 (q, *J* = 28 Hz), 40.2, 22.1; IR (film): γ= 3409, 1489, 1340, 1318, 1233, 1179, 1083, 1056, 933, 833, 750, 731 cm^{-1}; HRMS (EI-TOF): calcd for $C_{20}H_{15}ClF_3N_3$ 389.0907, found 389.0906.

(*S*)-(-)-1-(5-bromo-1H-indol-3-yl)-1-(trifluoromethyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3c): 17 mg, 79% yield; white solid; m.p. 225-226°C; 80% ee; HPLC analysis: Chiralpak AD-H (hexane/i-PrOH = 80/20, 0.8 mL/min), t_R (major) 13.049 min, t_R (minor) 19.619 min; $[\alpha]_D^{20}$ = -110.3 (*c* 0.4, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 8.07 (s, 1H), 7.69 (s, 1H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.29 – 7.24 (m, 3H), 7.24 – 7.20 (m, 1H), 7.20 – 7.14 (m, 1H), 7.12 (d, *J* = 2.6 Hz, 1H), 3.41 – 3.28 (m, 1H), 3.16 – 3.04 (m, 1H), 2.99 – 2.87 (m, 1H), 2.85 – 2.75 (m, 1H), 1.85 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.05 (s, 3F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.8, 135.1, 128.8, 126.8, 126.7 (q, *J* = 285 Hz), 126.6, 126.1 (d, *J* = 1.4 Hz), 125.7, 123.9 (d, *J* = 1.9 Hz), 123.0, 119.8, 118.9, 113.8, 113.5, 113.0, 112.7, 111.3, 60.7 (q, *J* = 28 Hz), 40.0, 22.1; IR (film): γ= 3411, 2956, 2925, 2852, 1457, 1409, 1290, 1247, 1156, 1114, 1012, 885, 799, 745, 727 cm^{-1}; HRMS (EI-TOF): calcd for $C_{20}H_{15}BrF_3N_3$ 433.0401, found 433.0398.

(*S*)-(-)-1-(7-methoxy-1H-indol-3-yl)-1-(trifluoromethyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3d): 14 mg, 75% yield; gray solid; m.p. 217-218°C; 75% ee; HPLC analysis: Chiralpak AD-H (hexane/i-PrOH = 80/20, 0.8 mL/min), t_R (major) 17.276 min, t_R (minor) 22.935 min; $[\alpha]_D^{20}$ = -40.3 (*c* 0.67, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.04 (s, 1H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.28 (d, *J* = 7.8 Hz, 1H), 7.23 – 7.18 (m, 1H), 7.18 – 7.13 (m, 2H), 6.86 (t, *J* = 8.0 Hz, 1H), 6.75 (d, *J* = 8.2 Hz, 1H), 6.58 (d, *J* = 7.6 Hz, 1H), 3.91 (s, 3H), 3.42 – 3.27 (m, 1H), 3.21 – 3.10 (m, 1H), 3.00 – 2.89 (m, 1H), 2.89 – 2.78 (m, 1H), 2.20 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.60 (s, 3F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.1, 135.9, 128.9, 127.0, 126.9 (q, *J* = 285 Hz),

126.6, 126.4, 124.1 (d, *J* = 2.5 Hz), 122.7, 120.9, 119.6, 118.9, 113.8, 113.0, 112.9, 111.4, 102.2, 60.3 (q, *J* = 28 Hz), 55.3, 40.3, 22.1; IR (film): γ= 3408, 2955, 2925, 2853, 1579, 1499, 1455, 1367, 1263, 1159, 1102, 1051, 1013, 903, 783, 733 cm^{-1}; HRMS (EI-TOF): calcd for $C_{21}H_{18}F_3N_3O$ 385.1402, found 385.1401.

(*S*)-(-)-1-(7-methyl-1H-indol-3-yl)-1-(trifluoromethyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3e): 15 mg, 80% yield; white solid; m.p. 120-121°C; 92% ee; HPLC analysis: Chiralpak AD-H (hexane/i-PrOH = 80/20, 0.8 mL/min), t_R (major) 11.280 min, t_R (minor) 14.278 min; $[\alpha]_D^{20}$ = -107.1 (*c* 0.7, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 8.02 (s, 1H), 7.63 (d, *J* = 7.7 Hz, 1H), 7.30 (d, *J* = 7.9 Hz, 1H), 7.27 – 7.12 (m, 3H), 7.04 (d, *J* = 8.1 Hz, 1H), 6.97 (d, *J* = 7.0 Hz, 1H), 6.92 – 6.83 (m, 1H), 3.43 – 3.28 (m, 1H), 3.24 – 3.11 (m, 1H), 3.00 – 2.90 (m, 1H), 2.90 – 2.78 (m, 1H), 2.46 (s, 3H), 2.04 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.57 (s, 3F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.9, 135.9, 128.9, 127.2 (q, J = 285 Hz), 126.6, 124.7, 124.3 (d, *J* = 2.5 Hz), 123.1, 122.8, 120.8, 120.5, 119.7, 118.9, 118.1, 113.9, 113.0, 111.3, 60.4 (q, *J* = 28 Hz), 40.4, 22.1, 16.6; IR (film): γ= 3410, 2955, 2924, 2853, 1721, 1459, 1377, 1275, 1248, 1158, 1019, 897, 733 cm^{-1}; HRMS (EI-TOF): calcd for $C_{21}H_{18}F_3N_3$ 369.1453, found 369.1449.

(*S*)-(-)-1-(6-methyl-1H-indol-3-yl)-1-(trifluoromethyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3f): 15 mg, 81% yield; white solid; m.p. 224-225°C; 81% ee; HPLC analysis: Chiralpak AD-H (hexane/i-PrOH = 80/20, 0.8 mL/min), t_R (major) 16.709 min, t_R (minor) 27.021 min; $[\alpha]_D^{20}$ = -128 (*c* 0.3, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.26 – 7.13 (m, 2H), 7.11 (s, 2H), 7.06 (d, *J* = 8.3 Hz, 1H), 6.79 (d, *J* = 8.2 Hz, 1H), 3.40 – 3.27 (m, 1H), 3.22 – 3.10 (m, 1H), 3.00 – 2.88 (m, 1H), 2.88 – 2.77 (m, 1H), 2.38 (s, 3H), 2.04 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.70 (s, 3F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 135.9, 132.6, 129.0, 126.9 (q, *J* = 285 Hz), 126.6, 124.0 (d, *J* = 2.3 Hz), 122.9, 122.8, 122.3, 120.1, 119.7, 118.9, 113.3, 112.9, 111.3, 111.2, 60.4 (q, *J* = 28 Hz), 40.3, 22.1, 21.5; IR (film): γ= 3404, 2955, 2924, 2853, 1724, 1534, 1456, 1377, 1278, 1248, 1154, 1108, 1012, 903, 805, 744 cm^{-1}; HRMS (EI-TOF): calcd for $C_{21}H_{18}F_3N_3$ 369.1453, found 369.1449.

(*S*)-(-)-1-(5-methyl-1H-indol-3-yl)-1-(trifluoromethyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3g): 14 mg, 78% yield; yellow solid; m.p. 185-186°C; 75% ee; HPLC analysis: Chiralpak AD-H (hexane/i-PrOH = 80/20, 0.8 mL/min), t_R (major) 14.622 min, t_R (minor) 22.171 min; $[\alpha]_D^{20}$ = -205 (*c* 0.7, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 2H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.31

(d, *J* = 8.0 Hz, 1H),7.22 (t, *J* = 2 Hz, 2H), 7.19 – 7.10 (m, 2H), 7.08 (s, 1H), 7.04 – 6.95 (m, 1H), 3.38 – 3.27 (m, 1H), 3.22 – 3.08 (m, 1H), 2.99 – 2.89 (m, 1H), 2.88 – 2.73 (m, 1H), 2.28 (s, 3H), 2.21 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.68 (s, 3F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.8, 134.7, 129.7, 129.0, 126.9 (q, *J* = 285 Hz), 126.6, 125.2, 125.0, 124.2, 122.9, 122.8, 120.3, 119.7, 118.9, 112.9 (d, *J* = 2.3 Hz), 111.3, 111.0, 60.5 (q, *J* = 28 Hz), 40.3, 22.1, 21.7; IR (film): γ= 3407, 2953, 2924, 2852, 1578, 1455, 1299, 1247, 1155, 1013, 903, 798, 743, 724 cm^{-1}; HRMS (EI-TOF): calcd for $C_{21}H_{18}F_3N_3$ 369.1453, found 369.1454.

(*S*)-(-)-1-(1H-indol-3-yl)-6-methoxy-1-(trifluoromethyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3h): 15 mg, 80% yield; gray solid; m.p. 93-94°C; 85% ee; HPLC analysis: Chiralpak AD-H (hexane/i-PrOH = 85/15, 0.5 mL/min), t_R (major) 44.965 min, t_R (minor) 53.679 min; $[\alpha]_D^{20}$ = -245 (*c* 0.3, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.93 (s, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.23 – 7.13 (m, 4H), 7.06 (d, *J* = 2.4 Hz, 1H), 7.00 – 6.92 (m, 1H), 6.91 – 6.84 (m, 1H), 3.89 (s, 3H), 3.42 – 3.30 (m, 1H), 3.22 – 3.11 (m, 1H), 2.96 – 2.86 (m, 1H), 2.87 – 2.76 (m, 1H), 2.13 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.63 (s, 3F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 136.3, 131.0, 129.7, 126.9 (q, *J* = 285 Hz), 126.9, 125.1, 124.6 (d, *J* = 2.3 Hz), 122.6, 120.5, 120.5, 113.4, 112.9, 112.7, 112.1, 111.3, 100.7, 60.4 (q, *J* = 28 Hz), 56.0, 40.3, 22.2; IR (film): γ= 3407, 2924, 2849, 1626, 1486, 1457, 1338, 1215, 1145, 1114, 1011, 903, 805, 744 cm^{-1}; HRMS (EI-TOF): calcd for $C_{21}H_{18}F_3N_3O$ 385.1402, found 385.14018.

(*S*)-(-)-1-(1H-indol-3-yl)-6-methyl-1-(trifluoromethyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3i): 14 mg, 76% yield; white solid; m.p. 146-147°C; 86% ee; HPLC analysis: Chiralpak AD-H (hexane/i-PrOH = 85/15, 0.5 mL/min), t_R (major) 12.170 min, t_R (minor) 19.392 min; $[\alpha]_D^{20}$ = -105.3 (*c* 0.6, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.95 (s, 1H), 7.41 (s, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.22 – 7.10 (m, 4H), 7.07 – 7.00 (m, 1H), 6.95 (t, *J* = 7.6 Hz, 1H), 3.39 – 3.28 (m, 1H), 3.19 – 3.07 (m, 1H), 2.96 – 2.86 (m, 1H), 2.86 – 2.75 (m, 1H), 2.48 (s, 3H), 1.95 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.54 (s, 3F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.3, 134.2, 129.0, 126.9 (q, *J* = 285 Hz), 126.8, 125.1, 124.6 (d, *J* = 2.5 Hz), 124.4, 122.6, 120.5, 120.5, 118.6, 113.4, 112.5, 111.3, 111.0, 60.4 (q, *J* = 28 Hz), 40.4, 22.1, 21.5; IR (film): γ= 3405, 2953, 2923, 2855, 1619, 1457, 1417, 1337, 1303, 1278, 1246, 1156, 1126, 1016, 903, 800, 745 cm^{-1}; HRMS (EI-TOF): calcd for $C_{21}H_{18}F_3N_3$ 369.1453, found 369.1453.

(*S*)-(-)-6-chloro-1-(1H-indol-3-yl)-1-(trifluoromethyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3j): 14 mg, 72% yield; purple solid; m.p. 108-109°C; 75% ee; HPLC analysis: Chiralpak AD-H (hexane/i-PrOH = 80/20, 0.8 mL/min), t_R (major) 11.874 min, t_R (minor) 17.872 min; $[\alpha]_D^{20}$ = -5.4 (*c* 0.9, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 8.08 (s, 1H), 7.58 (d, *J* = 1.7 Hz, 1H), 7.34 (d, *J* = 8.2 Hz, 1H), 7.23 – 7.11 (m, 4H), 7.06 (d, *J* = 8.1 Hz, 1H), 6.99 – 6.90 (m, 1H), 3.40 – 3.30 (m, 1H), 3.21 – 3.10 (m, 1H), 2.95 – 2.85 (m, 1H), 2.85 – 2.76 (m, 1H), 2.04 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.41 (s, 3F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.2, 134.2, 130.4, 127.6, 126.8 (q, *J* = 285 Hz), 125.4, 125.1, 124.4 (d, *J* = 2.6 Hz), 123.1, 122.7, 120.6, 120.2, 118.5, 113.0, 112.7, 112.4, 111.4, 60.2 (q, *J* = 28 Hz), 40.3, 21.9; IR (film): γ= 3423, 3209, 2953, 2925, 2846, 1724, 1618, 1540, 1458, 1442, 1338, 1290, 1266, 1244, 1157, 1064, 1011, 902, 799, 744 cm^{-1}; HRMS (EI-TOF): calcd for $C_{20}H_{15}ClF_3N_3$ 389.0907, found 389.0902.

(*S*)-(-)-6-methoxy-1-(7-methyl-1H-indol-3-yl)-1-(trifluoromethyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3k): 16 mg,82% yield; purple solid; m.p. 111-112°C; 91% ee; HPLC analysis: Chiralpak AD-H (hexane/i-PrOH = 80/20, 0.8 mL/min), t_R (major) 15.889 min, t_R (minor) 19.589 min; $[\alpha]_D^{20}$ = -14.7 (*c* 2.2, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.92 (s, 1H), 7.18 (m, 2H), 7.06 (d, *J* = 2.4 Hz, 1H), 7.02 (d, *J* = 8.1 Hz, 1H), 6.96 (d, *J* = 7.0 Hz, 1H), 6.92 – 6.83 (m, 2H), 3.88 (s, 3H), 3.41 – 3.26 (m, 1H), 3.22 – 3.09 (m, 1H), 2.96 – 2.86 (m, 1H), 2.86 – 2.76 (m, 1H), 2.45 (s, 3H), 1.86 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.59 (s, 3F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 135.9, 131.0, 129.7, 126.9 (q, *J* = 285 Hz), 126.9, 124.7, 124.3 (d, *J* = 2.6 Hz), 123.1, 120.8, 120.5, 118.1, 113.9, 112.9, 112.7, 112.1, 100.7, 60.4 (q, *J* = 28 Hz), 55.9, 40.4, 22.1, 16.5; IR (film): γ= 3411, 2925, 2846, 1626, 1486, 1456, 1253, 1215, 1138, 1020, 899, 784, 733 cm^{-1}; HRMS (EI-TOF): calcd for $C_{22}H_{20}F_3N_3O$ 399.1558, found 399.1559.

(*S*)-(-)-6-methyl-1-(7-methyl-1H-indol-3-yl)-1-(trifluoromethyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3l): 16 mg, 85% yield; white solid; m.p. 106-107°C; 91% ee; HPLC analysis: Chiralpak AD-H (hexane/i-PrOH = 80/20, 0.8 mL/min), t_R (major) 12.003 min, t_R (minor) 15.484 min; $[\alpha]_D^{20}$ = -45.5 (*c* 1, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.95 (s, 1H), 7.41 (s, 1H), 7.19 – 7.08 (m, 2H), 7.02 (m, 2H), 6.95 (d, *J* = 7.0 Hz, 1H), 6.86 (t, *J* =2 Hz 1H), 3.36 – 3.26 (m, 1H), 3.16 – 3.06 (m, 1H), 2.95 – 2.84 (m, 1H), 2.84 – 2.71 (m, 1H), 2.48 (s, 3H), 2.42 (s, 3H), 2.03 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.47 (d, *J* = 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.8, 134.2, 129.0, 128.9,126.9 (q, *J* = 285 Hz), 126.8, 124.7, 124.3 (d, *J* = 3.3 Hz), 123.1,

120.8, 120.5, 118.6, 118.1, 113.8, 112.9, 112.5, 111.1, 60.4 (q, *J* = 28 Hz), 40.4, 22.1, 21.5, 16.6; IR (film): γ= 3402, 2923, 2849, 1456, 1278, 1154, 1025, 995, 897, 784, 734 cm^{-1}; HRMS (EI-TOF): calcd for $C_{22}H_{20}F_3N_3$ 383.1609, found 383.1606.

(*S*)-(-)-6-chloro-1-(7-methyl-1H-indol-3-yl)-1-(trifluoromethyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3m): 14.5 mg, 72% yield; brown solid; m.p. 199-200°C; 90% ee (**3m** was obtained with 98% ee after one recrystallization from EA-Hexane); HPLC analysis: Chiralpak AD-H (hexane/i-PrOH = 80/20, 0.8 mL/min), t_R (major) 11.006 min, t_R (minor) 16.171 min; $[\alpha]_D^{20}$ = -35.6 (*c* 1.7, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 8.05 (s, 1H), 7.58 (t, *J* = 0.2 Hz 1H), 7.21 (d, *J* = 1.3 Hz, 1H), 7.19 – 7.11 (m, 2H), 6.97 (d, *J* = 6.6 Hz, 1H), 6.93 – 6.82 (m, 2H), 3.40 – 3.29 (m, 1H), 3.20 – 3.09 (m, 1H), 2.94 – 2.85 (m, 1H), 2.85 – 2.75 (m, 1H), 2.45 (s, 3H), 2.02 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.40 (s, 3F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.8, 134.2, 130.4, 127.6, 126.8 (q, *J* = 285 Hz), 125.4, 124.6, 124.0 (d, *J* = 2.9 Hz), 123.2, 123.0, 120.9, 120.6, 118.5, 117.8, 113.5, 112.8, 112.4, 60.2 (q, *J* = 28 Hz), 40.3, 21.9, 16.5; IR (film): γ= 3428, 2956, 2924, 2855, 1715, 1616, 1441, 1290, 1265, 1157, 1108, 1061, 997, 899, 799, 784, 741 cm^{-1}; HRMS (EI-TOF): calcd for $C_{21}H_{17}ClF_3N_3$ 403.1063, found 403.1064.

(*S*)-(-)-1-(7-methoxy-1H-indol-3-yl)-6-methyl-1-(trifluoromethyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3n): 17 mg, 86% yield; white solid; m.p. 196-197°C; 80% ee; HPLC analysis: Chiralpak AD-H (hexane/i-PrOH = 80/20, 0.8 mL/min), t_R (major) 17.159 min, t_R (minor) 22.534 min; $[\alpha]_D^{20}$ = -24.9 (*c* 0.6, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 7.94 (s, 1H), 7.40 (d, *J* = 0.5 Hz, 1H), 7.21 – 7.11 (m, 2H), 7.08 – 7.00 (m, 1H), 6.86 (t, *J* = 8.0 Hz, 1H), 6.76 (d, *J* = 8.2 Hz, 1H), 6.58 (d, *J* = 7.6 Hz, 1H), 3.91 (s, 3H), 3.38 – 3.27 (m, 1H), 3.19 – 3.10 (m, 1H), 2.97 – 2.86 (m, 1H), 2.86 – 2.75 (m, 1H), 2.48 (s, 3H), 2.18 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.65 (s, 3F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.1, 134.2, 129.0, 128.9, 127.0, 126.9 (q, *J* = 285 Hz), 126.8, 126.4, 124.3, 124.1 (d, *J* = 2.2 Hz), 120.9, 118.5, 113.9, 112.9, 112.5, 111.0, 102.2, 60.4 (q, *J* = 28 Hz), 55.3, 40.3, 22.1, 21.5; IR (film): γ= 3408, 2955, 2925, 2853, 1724, 1626, 1578, 1459, 1411, 1377, 1263, 1154, 1051, 943, 900, 799, 783, 733 cm^{-1}; HRMS (EI-TOF): calcd for $C_{22}H_{20}F_3N_3O$ 399.1558, found 399.1552.

(*S*)-(-)-6-methoxy-1-(7-methoxy-1H-indol-3-yl)-1-(trifluoromethyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3o): 14.5 mg, 70% yield; white solid; m.p. 156-157°C; 80% ee; HPLC analysis: Chiralpak OOG-4457-EO (hexane/i-PrOH = 80/20, 0.8 mL/min), t_R (major) 9.556 min,

t_R (minor) 12.767 min; $[\alpha]_D^{20}$ = -40.2 (*c* 1.2, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 7.94 (s, 1H), 7.17 (d, *J* = 8.8 Hz, 2H), 7.05 (d, *J* = 2.4 Hz, 1H), 6.92 – 6.82 (m, 2H), 6.75 (d, *J* = 8.2 Hz, 1H), 6.59 (d, *J* = 7.7 Hz, 1H), 3.91 (s, 3H), 3.88 (s, 3H), 3.40 – 3.27 (m, 1H), 3.22 – 3.10 (m, 1H), 2.96 – 2.86 (m, 1H), 2.86 – 2.76 (m, 1H), 1.71 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.67 (s, 3F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.14, 146.1, 131.0, 129.7, 127.0, 126.9 (q, *J* = 285 Hz), 126.9, 126.4, 124.2, 124.1 (d, *J* = 2.4 Hz), 120.9, 113.8, 112.9, 112.7, 112.1, 102.17 (s), 100.7, 60.4 (q, *J* = 28 Hz), 55.9, 55.3, 40.3, 22.1; IR (film): γ= 3404, 2955, 2924, 2853, 1718, 1626, 1578, 1459, 1377, 1260, 1216, 1151, 1111, 939, 897, 783, 733 cm^{-1}; HRMS (EI-TOF): calcd for $C_{22}H_{20}F_3N_3O_2$ 415.1508, found 415.1505.

(*S*)-(-)-1-(7-chloro-1H-indol-3-yl)-6-methoxy-1-(trifluoromethyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3p): 14.4 mg, 69% yield; yellow solid; m.p. 111-112°C; 89% ee; HPLC analysis: Chiralpak AD-H (hexane/i-PrOH = 80/20, 0.8 mL/min), t_R (minor) 11.598 min, t_R (major) 17.434 min; $[\alpha]_D^{20}$ = -17.8 (*c* 0.8, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.85 (s, 1H), 7.17 (s, 1H), 7.12 (d, *J* = 8.8 Hz, 1H), 7.07 (t, *J* = 7.1 Hz, 2H), 6.98 (d, *J* = 2.3 Hz, 1H), 6.86 – 6.76 (m, 2H), 3.81 (s, 3H), 3.36 – 3.21 (m, 1H), 3.12 – 3.01 (m, 1H), 2.90 – 2.79 (m, 1H), 2.79 – 2.68 (m, 1H), 1.90 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.72 (s, 3F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 133.6, 131.0, 129.3, 126.8 (q, *J* = 285 Hz), 126.9, 126.7, 125.2 (d, *J* = 2.4 Hz), 121.9, 121.3, 119.3, 116.8, 114.7, 113.1, 112.8, 112.1, 100.7, 60.5 (q, *J* = 28 Hz), 55.9, 40.2, 22.1; IR (film): γ= 3413, 2950, 2926, 2852, 1719, 1624, 1565, 1486, 1456, 1435, 1340, 1294, 1263, 1214, 1143, 1116, 1012, 913, 891, 832, 784, 737, 702 cm^{-1}; HRMS (EI-TOF): calcd for $C_{21}H_{17}ClF_3N_3O$ 419.1012, found 419.1015.

(*S*)-(-)-1-(7-chloro-1H-indol-3-yl)-6-methyl-1-(trifluoromethyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3q): 14 mg, 70% yield; yellow solid; m.p. 192-193°C; 90% ee; HPLC analysis: Chiralpak AD-H (hexane/i-PrOH = 80/20, 0.8 mL/min), t_R (major) 12.173 min, t_R (minor) 15.804 min; $[\alpha]_D^{20}$ = -44.8 (*c* 0.4, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.92 (s, 1H), 7.41 (s, 1H), 7.27 – 7.17 (m, 2H), 7.15 (d, *J* = 7.5 Hz, 2H), 7.08 – 7.01 (m, 1H), 6.89 (t, *J* = 7.9 Hz, 1H), 3.41 – 3.28 (m, 1H), 3.19 – 3.06 (m, 1H), 2.97 – 2.86 (m, 1H), 2.86 – 2.75 (m, 1H), 2.48 (s, 3H), 2.04 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.68 (s, 3F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.2, 133.6, 129.1, 128.7, 126.7 (q, J = 285 Hz), 126.8, 126.7, 125.2 (d, *J* = 2.5 Hz), 124.5, 121.9, 121.3, 119.4, 118.6, 116.8, 114.7, 112.6, 111.1, 60.4 (q, *J* = 28 Hz), 40.3, 22.1, 21.5; IR (film): γ= 3370,

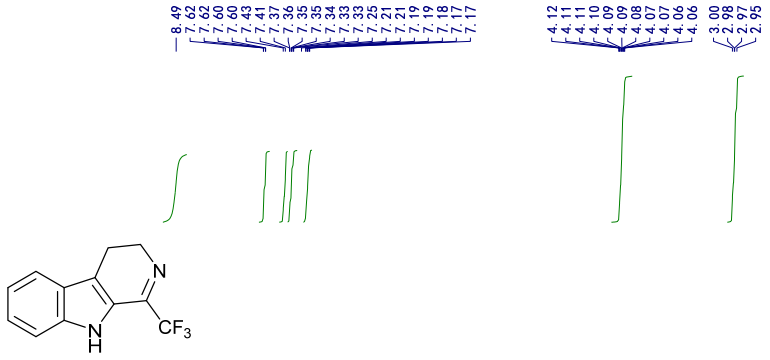
2922, 2846, 1563, 1435, 1339, 1277, 1155, 1084, 1016, 916, 891, 832, 783, 736 cm^{-1}; HRMS (EI-TOF): calcd for $C_{21}H_{17}ClF_3N_3$ 403.1063, found 403.1067.

(*S*)-(-)-6-chloro-1-(7-chloro-1H-indol-3-yl)-1-(trifluoromethyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (3r): 13 mg, 61% yield; yellow solid; m.p. 223-224°C; 87% ee; HPLC analysis: Chiralpak AD-H (hexane/i-PrOH = 90/10, 0.8 mL/min), t_R (major) 29.595 min, t_R (minor) 40.966 min; $[\alpha]_D^{20}$ = -20 (*c* 0.33, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 8.02 (s, 1H), 7.59 (d, *J* = 1.7 Hz, 1H), 7.31 (d, *J* = 1.3 Hz, 1H), 7.23 (d, *J* = 8.6 Hz, 1H), 7.20 – 7.14 (m, 2H), 7.06 (d, *J* = 8.1 Hz, 1H), 6.90 (t, *J* = 7.9 Hz, 1H), 3.44 – 3.32 (m, 1H), 3.24 – 3.12 (m, 1H), 2.97 – 2.78 (m, 2H), 1.83 (s, 3H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.61 (s, 3F); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.2, 133.6, 130.1, 127.6, 126.6 (q, *J* = 285 Hz), 126.6, 125.6, 124.9 (d, *J* = 2.7 Hz), 123.2, 122.1, 121.4, 119.1, 118.6, 116.8, 114.4, 112.9, 112.4, 60.3 (m), 40.11 (q, *J* = 28 Hz), 21.9; IR (film): γ= 3461, 2950, 2917, 1617, 1557, 1435, 1302, 1261, 1224, 1163, 1138, 1100, 1011, 916, 795, 781, 738 cm^{-1}; HRMS (EI-TOF): calcd for $C_{20}H_{14}Cl_2F_3N_3$ 423.0517, found 423.0515.

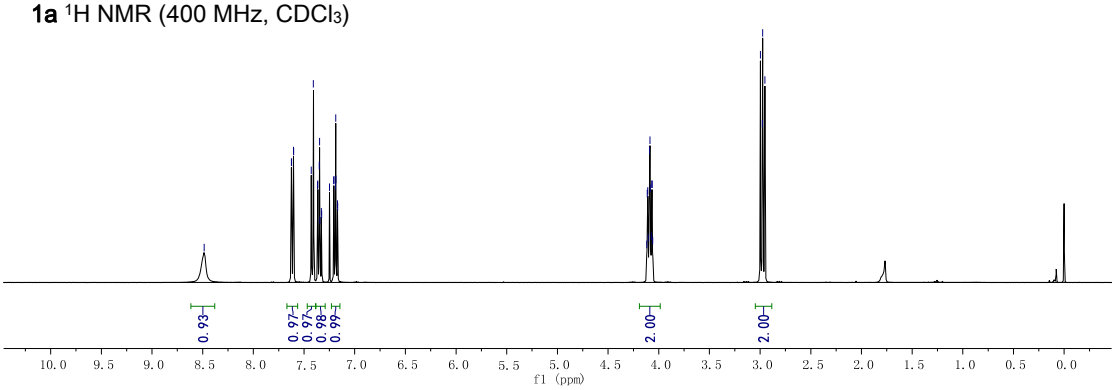
4. References

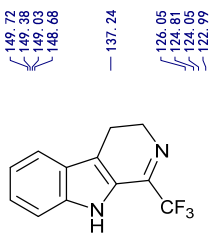
1. F. X. Xu, D. Huang, C. Han, W. Shen, X. F. Lin, Y. G. Wang, *J. Org. Chem.*, **2010**, *75*, 8677-8680.
2. I. Čorić, S. Müller, B. List, *J. Am. Chem. Soc.*, **2010**, *132*, 17370.
3. M. Espinoza-Moraga, J. Caballero, F. Gaube, *Chem. Biol. Drug Des.*, **2012**, *79*, 594-599.
4. Mathieu P. Lalonde, Meredeth A. McGowan, Naomi S. Rajapaksa, *J. Am. Chem. Soc.*, **2013**, *135*, 1891–1894.

5. Copies of NMR and HPLC for Compounds

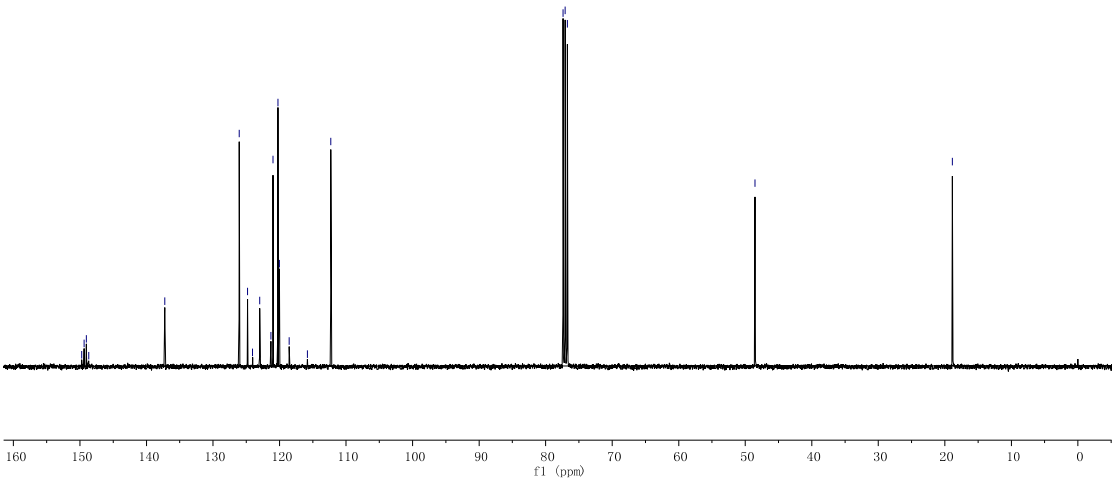


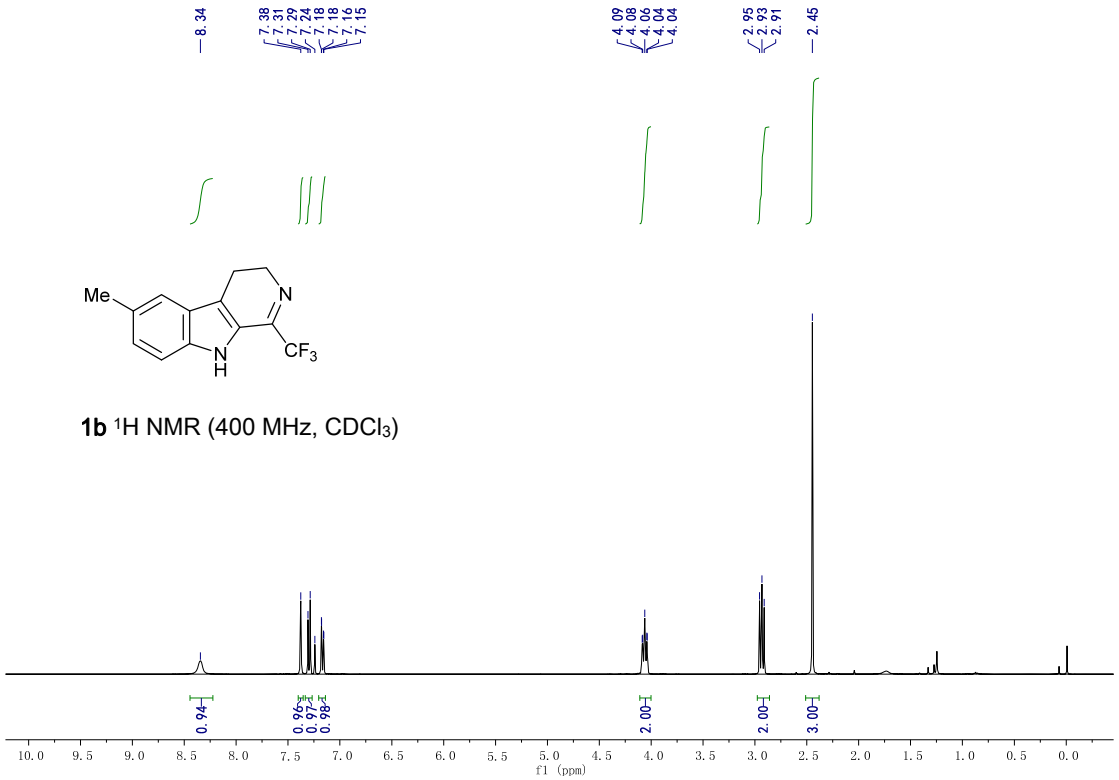
1a ^{1}H NMR (400 MHz, $CDCl_3$)



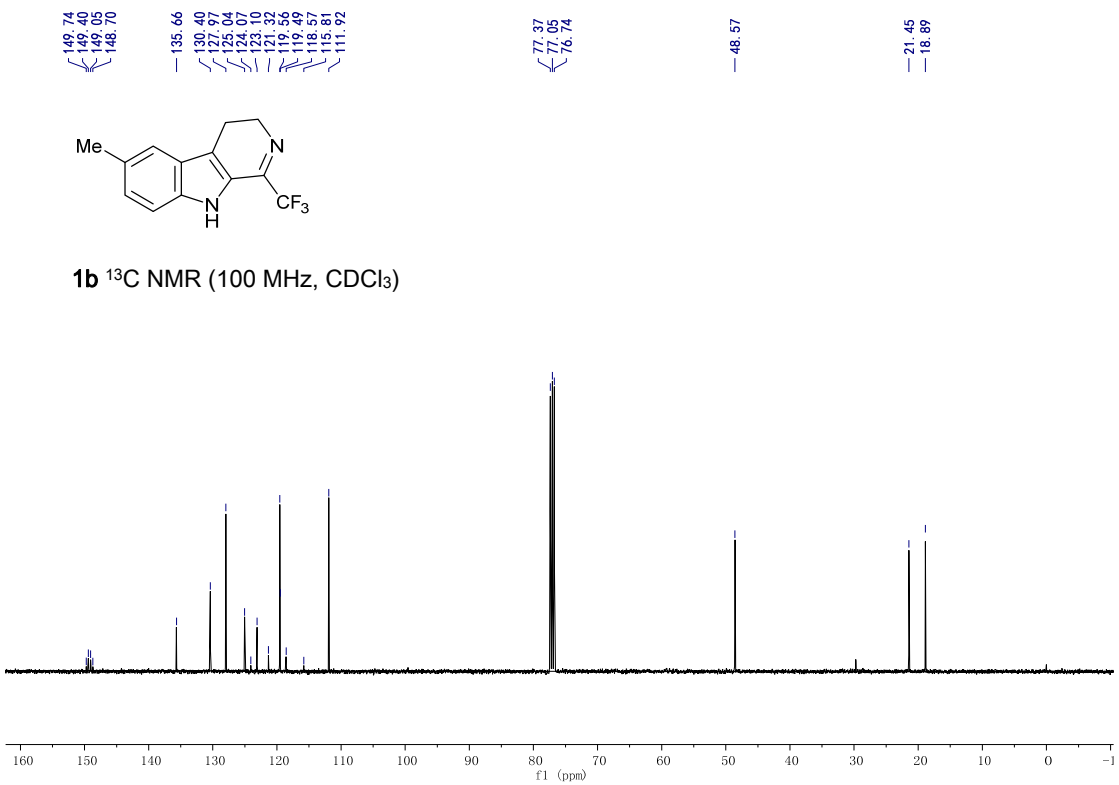


1a ^{13}C NMR (100 MHz, $CDCl_3$)

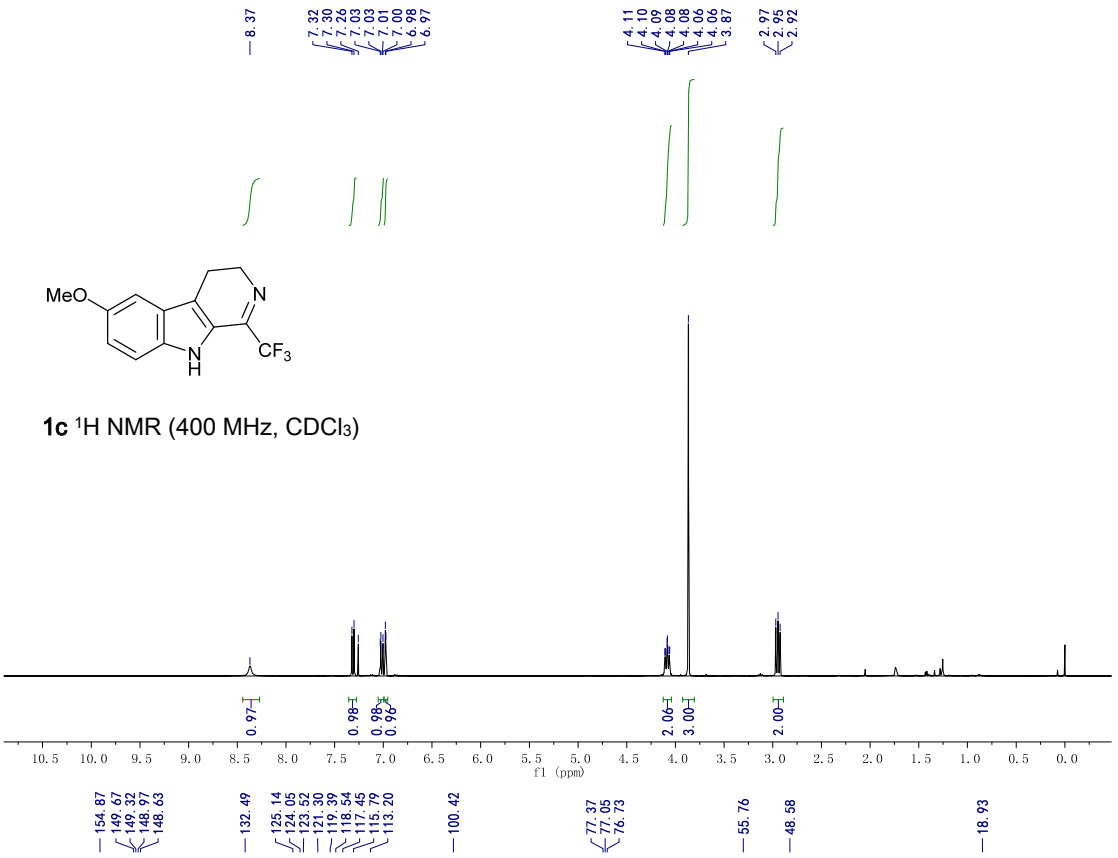




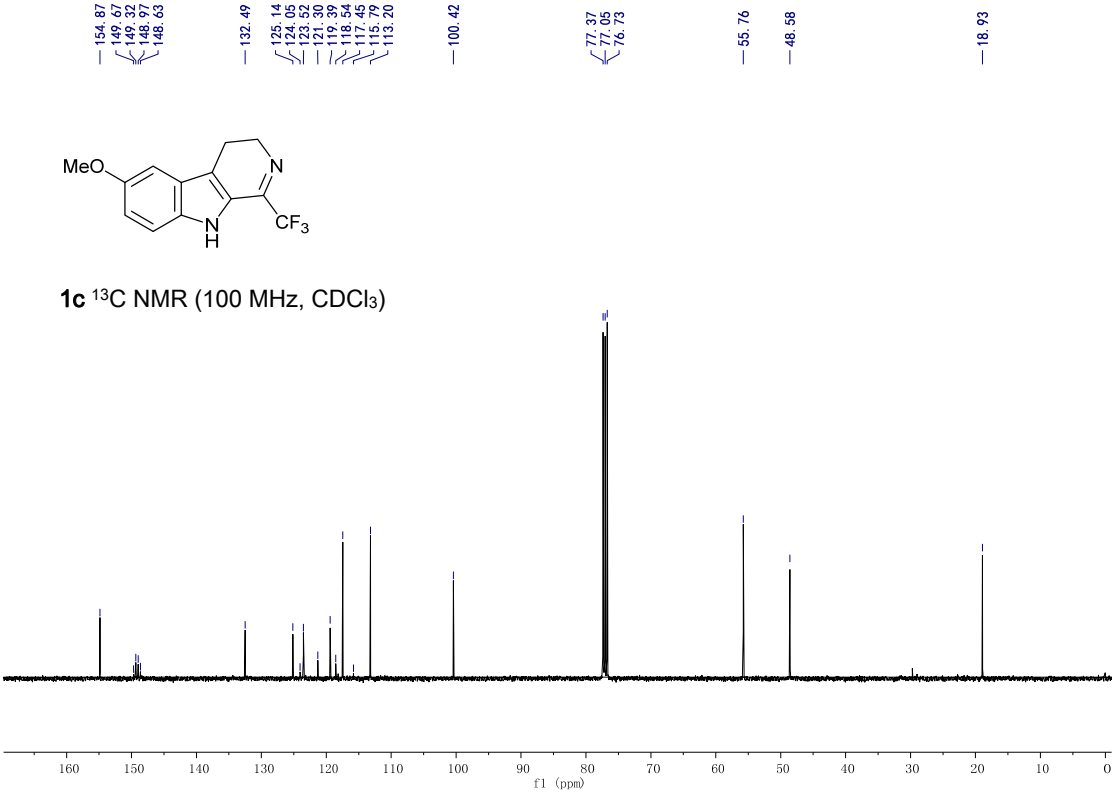
1b ^{1}H NMR (400 MHz, $CDCl_3$)



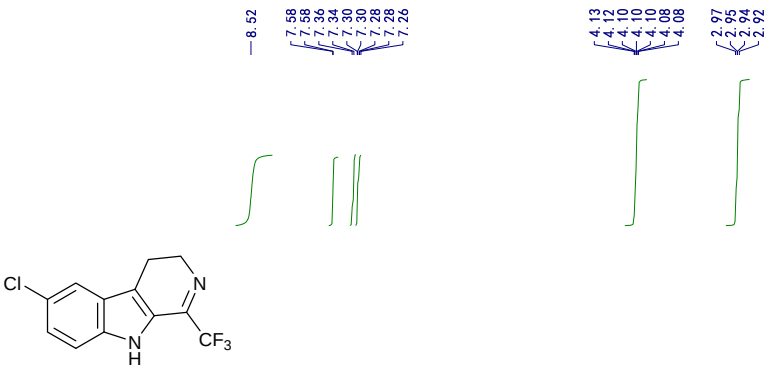
1b ^{13}C NMR (100 MHz, $CDCl_3$)



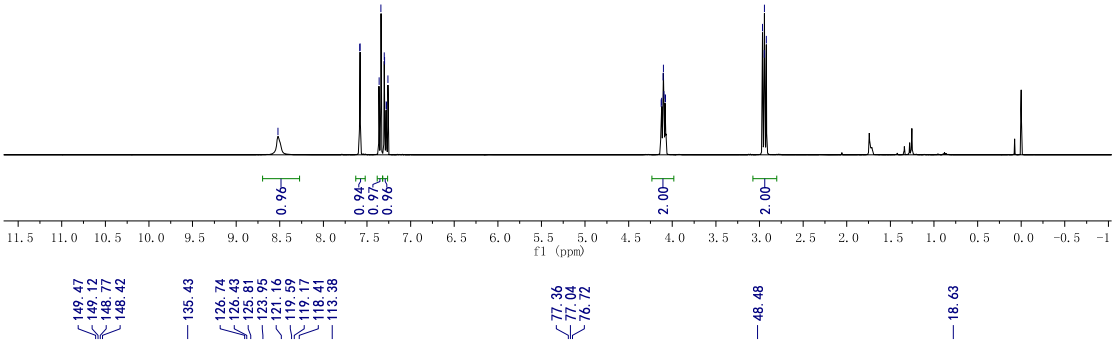
1c ^{1}H NMR (400 MHz, $CDCl_3$)

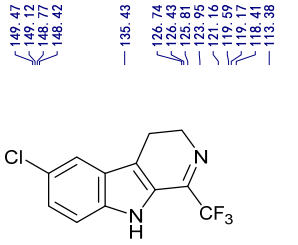


1c ^{13}C NMR (100 MHz, $CDCl_3$)

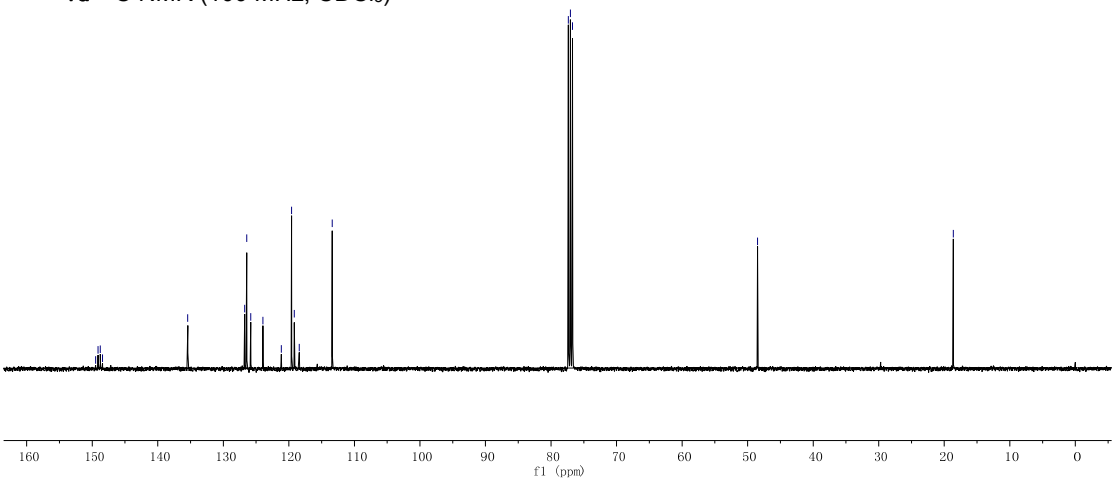


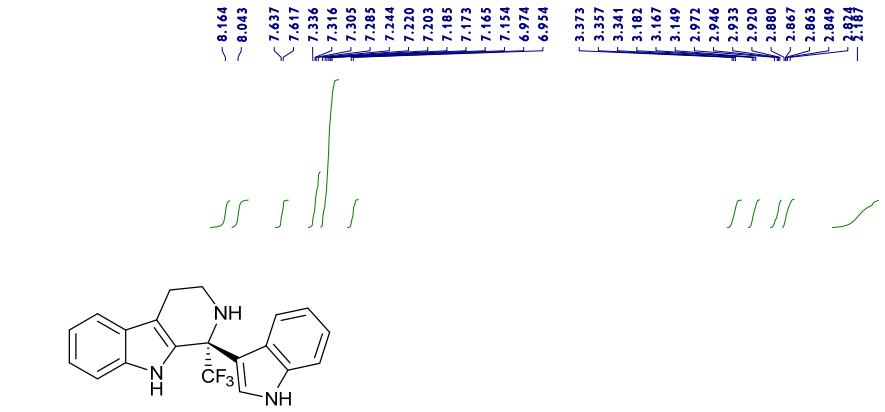
1d ^{1}H NMR (400 MHz, $CDCl_3$)



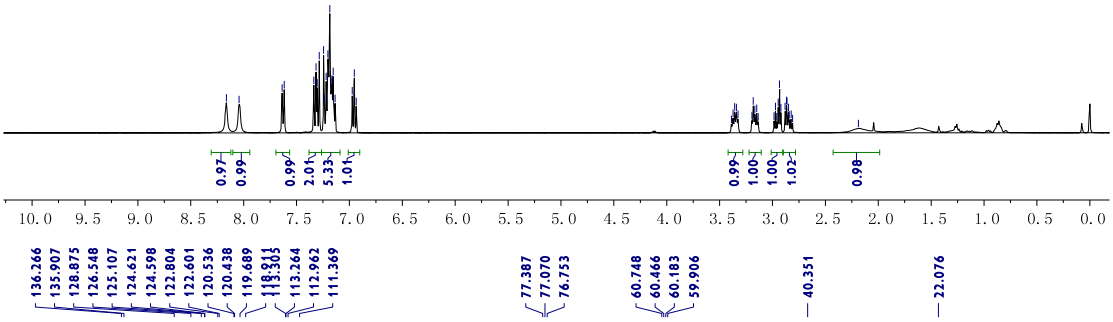


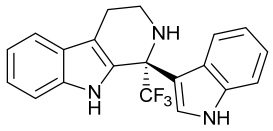
1d ^{13}C NMR (100 MHz, $CDCl_3$)



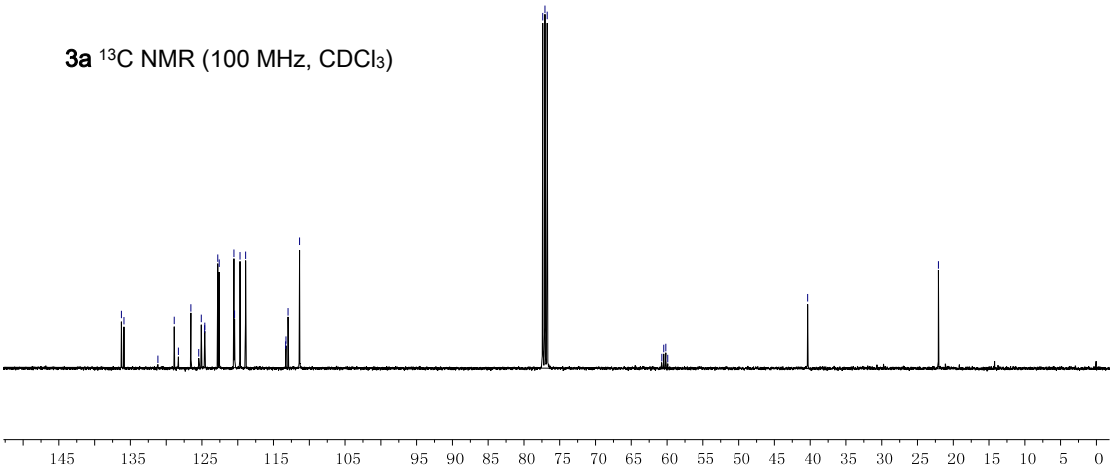


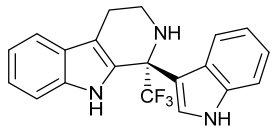
3a ^{1}H NMR (400 MHz, $CDCl_3$)



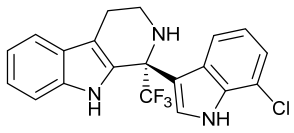


3a ^{13}C NMR (100 MHz, $CDCl_3$)

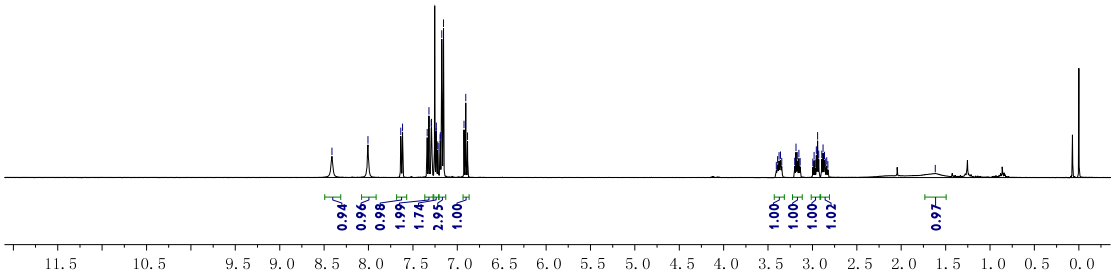


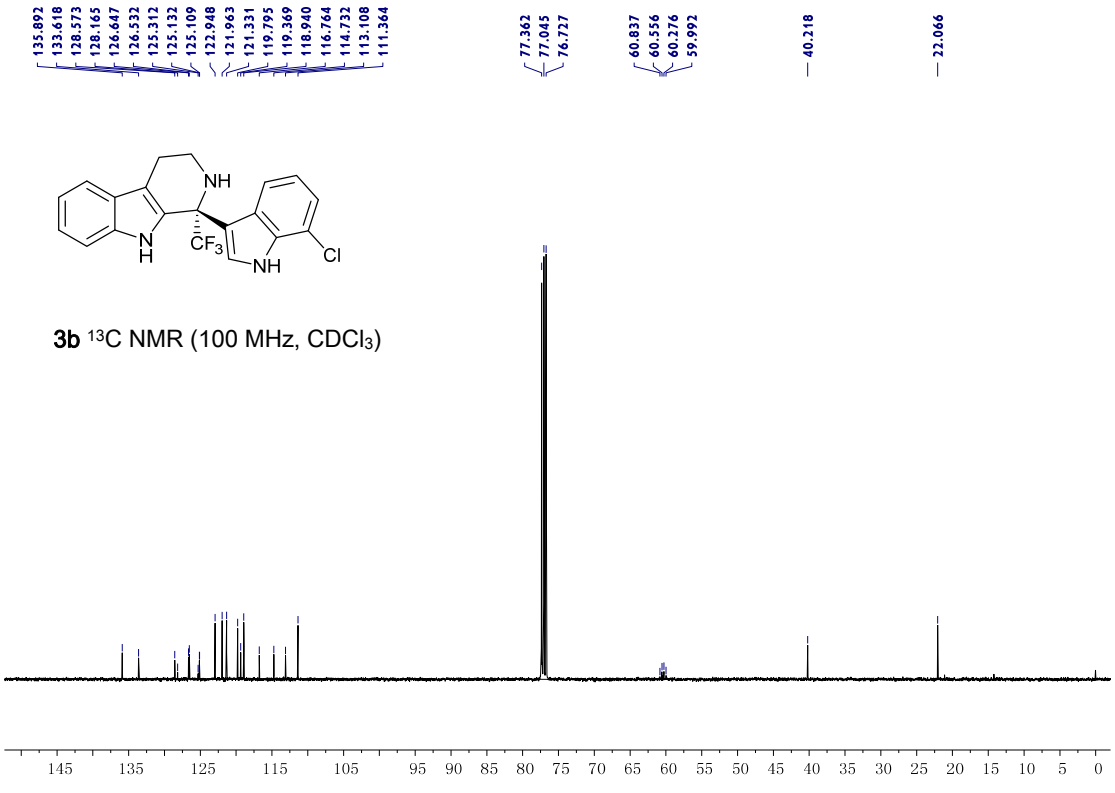


3a ^{19}F NMR (376 MHz, $CDCl_3$)

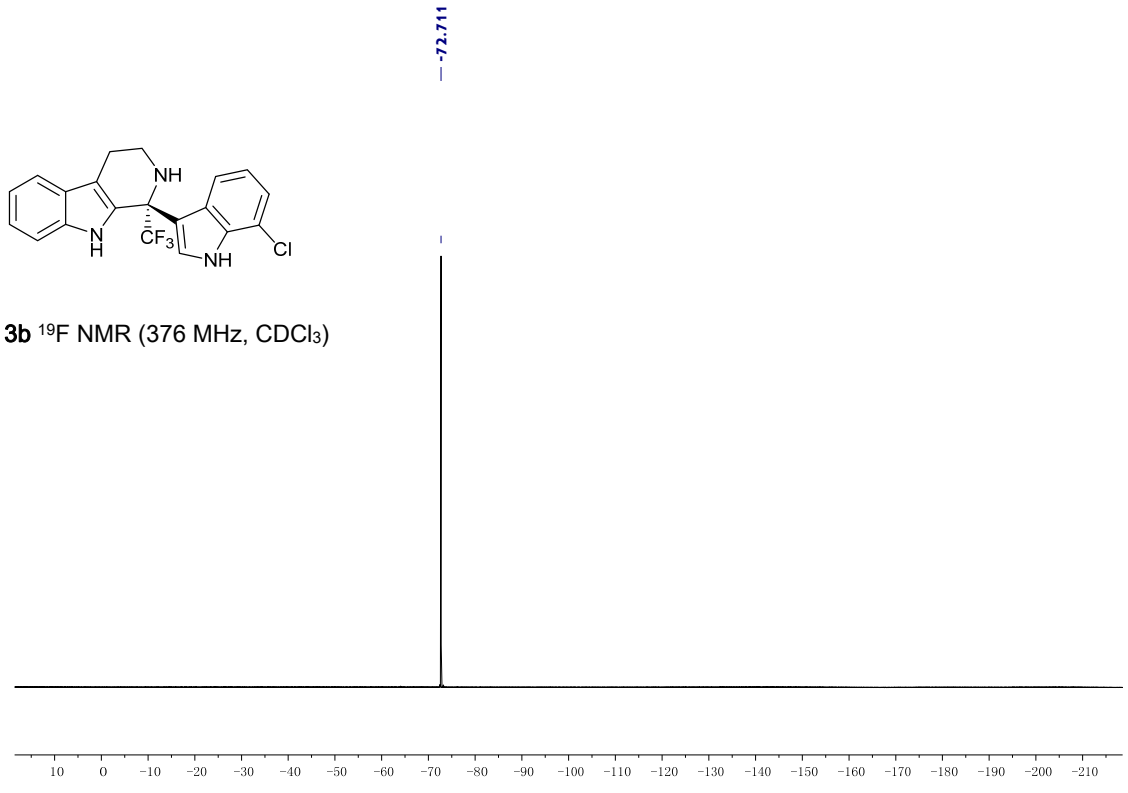


3b ^{1}H NMR (400 MHz, $CDCl_3$)

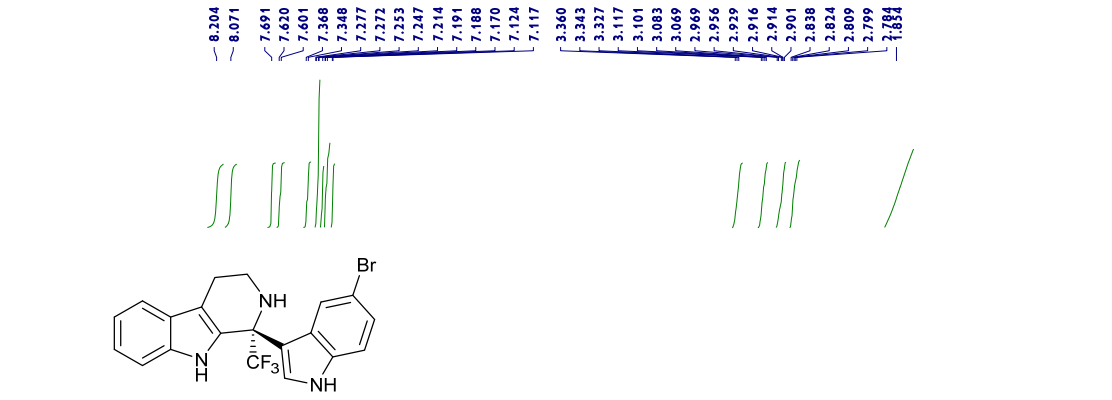




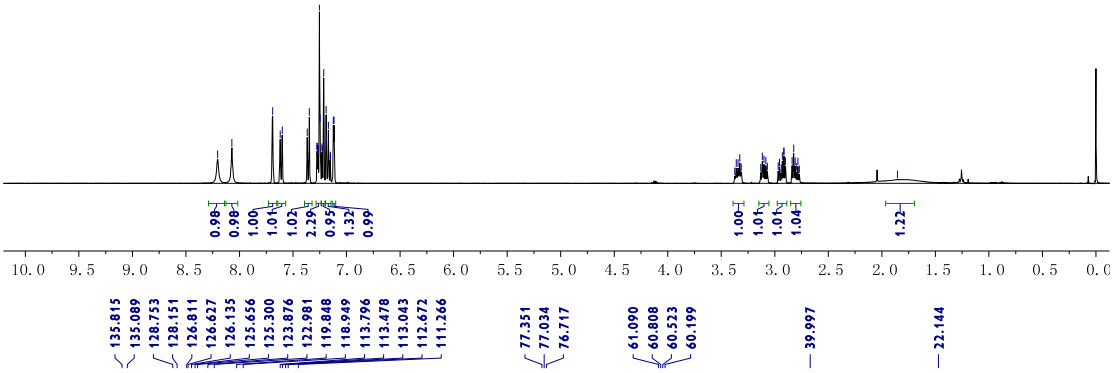
3b ^{13}C NMR (100 MHz, $CDCl_3$)

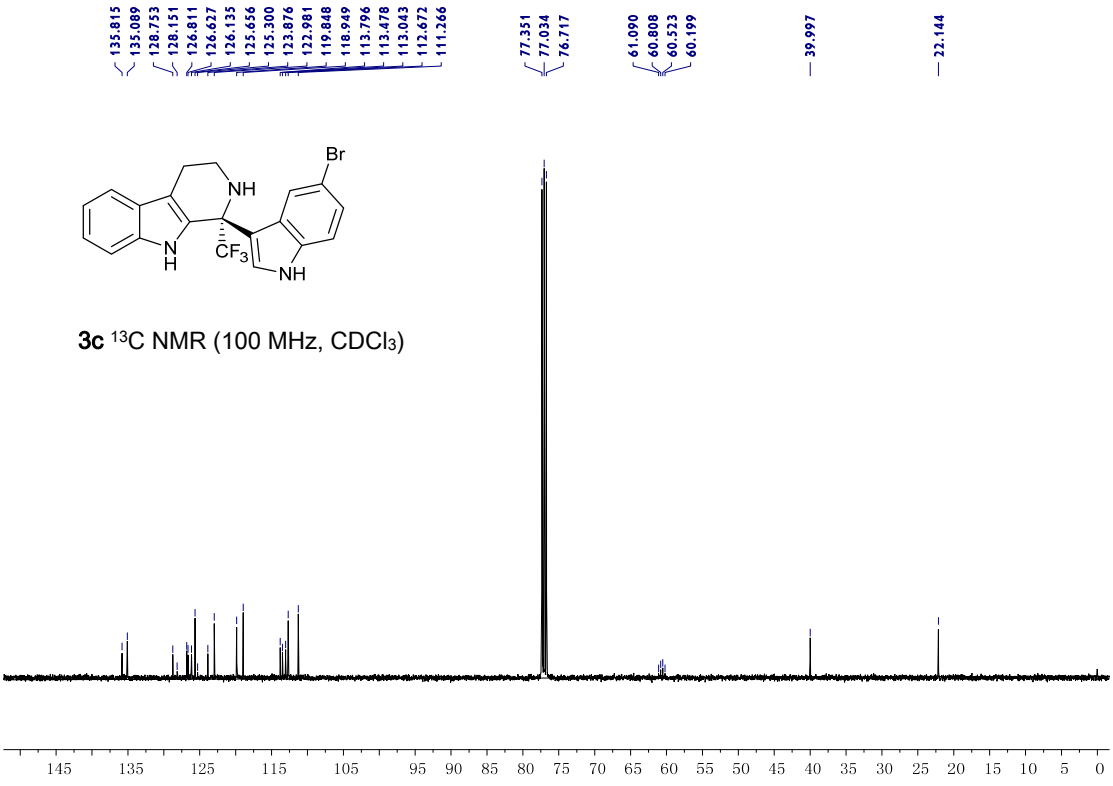


3b ^{19}F NMR (376 MHz, $CDCl_3$)

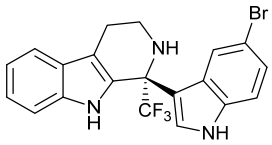


3c ^{1}H NMR (400 MHz, $CDCl_3$)

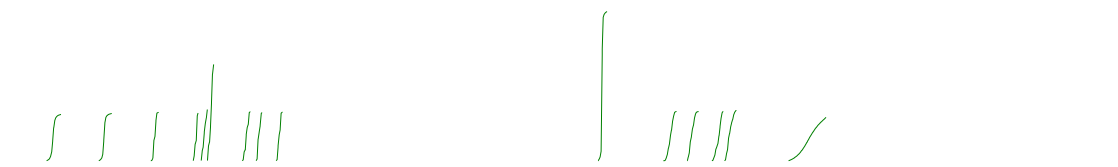


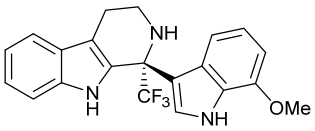


3c ^{13}C NMR (100 MHz, $CDCl_3$)

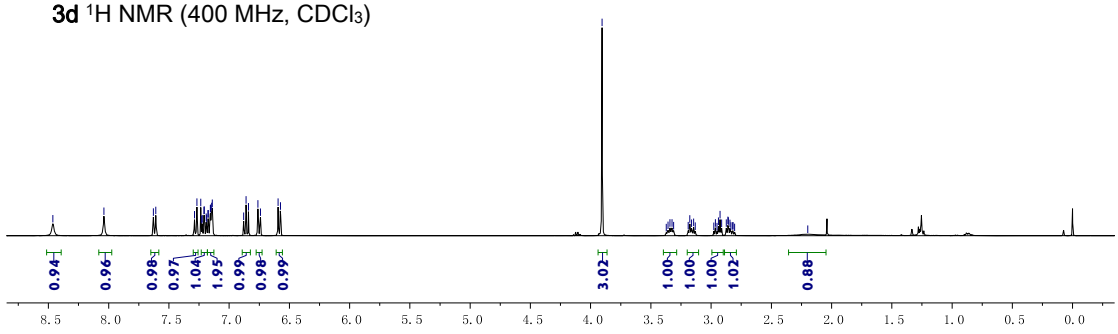


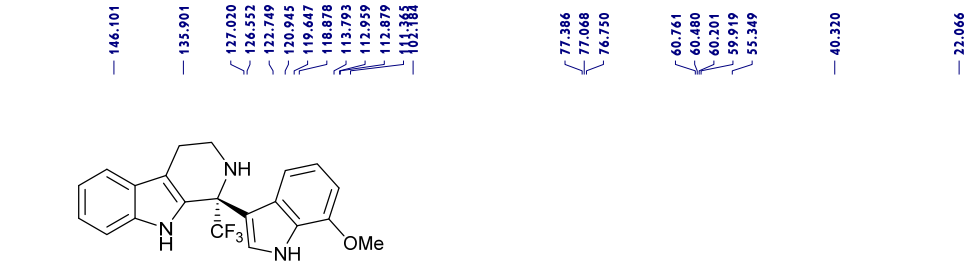
3c ^{19}F NMR (376 MHz, $CDCl_3$)



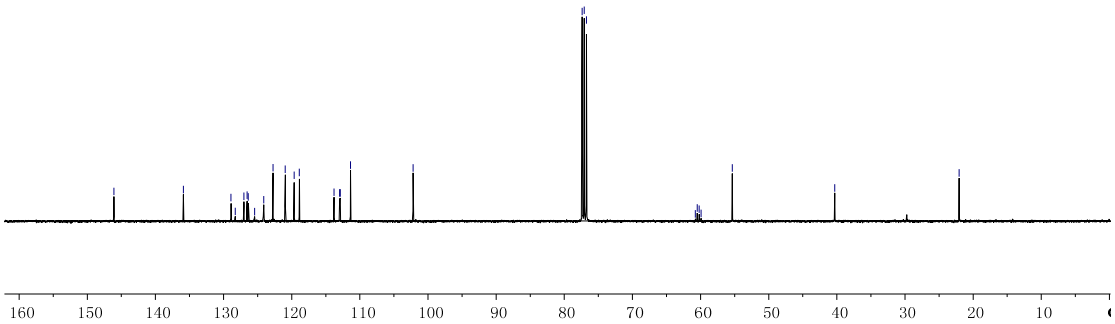


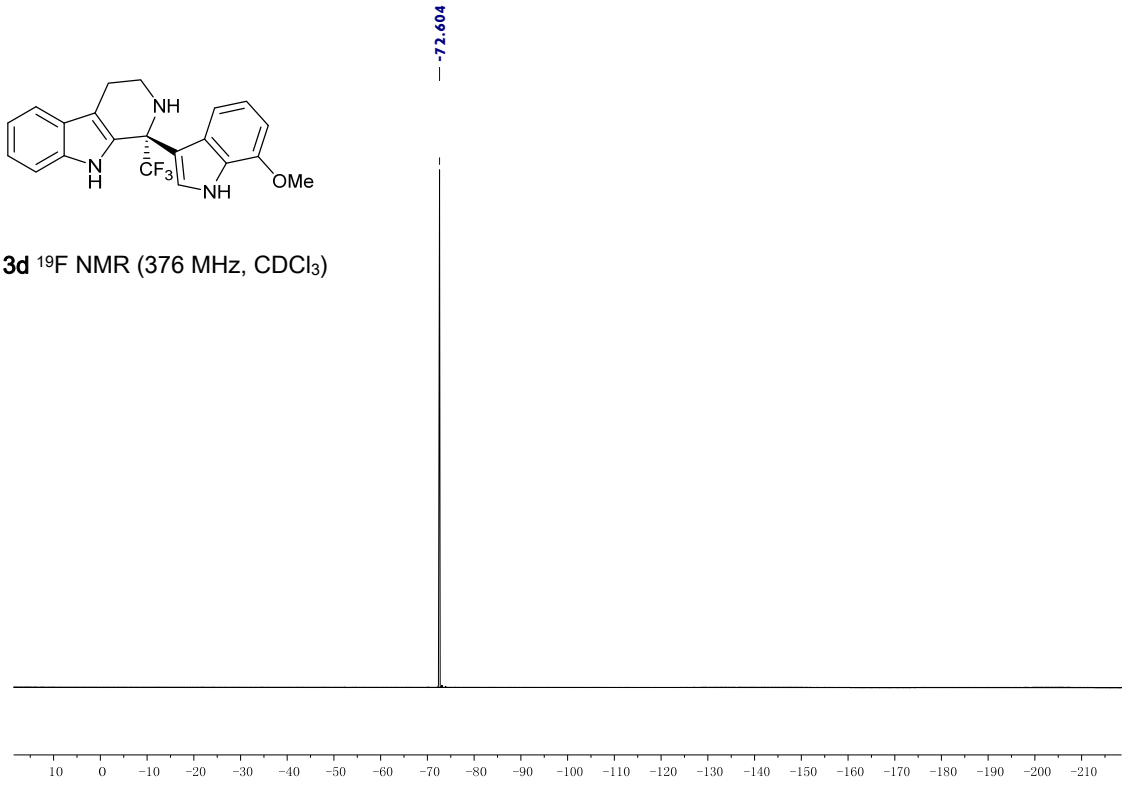
3d ^{1}H NMR (400 MHz, $CDCl_3$)



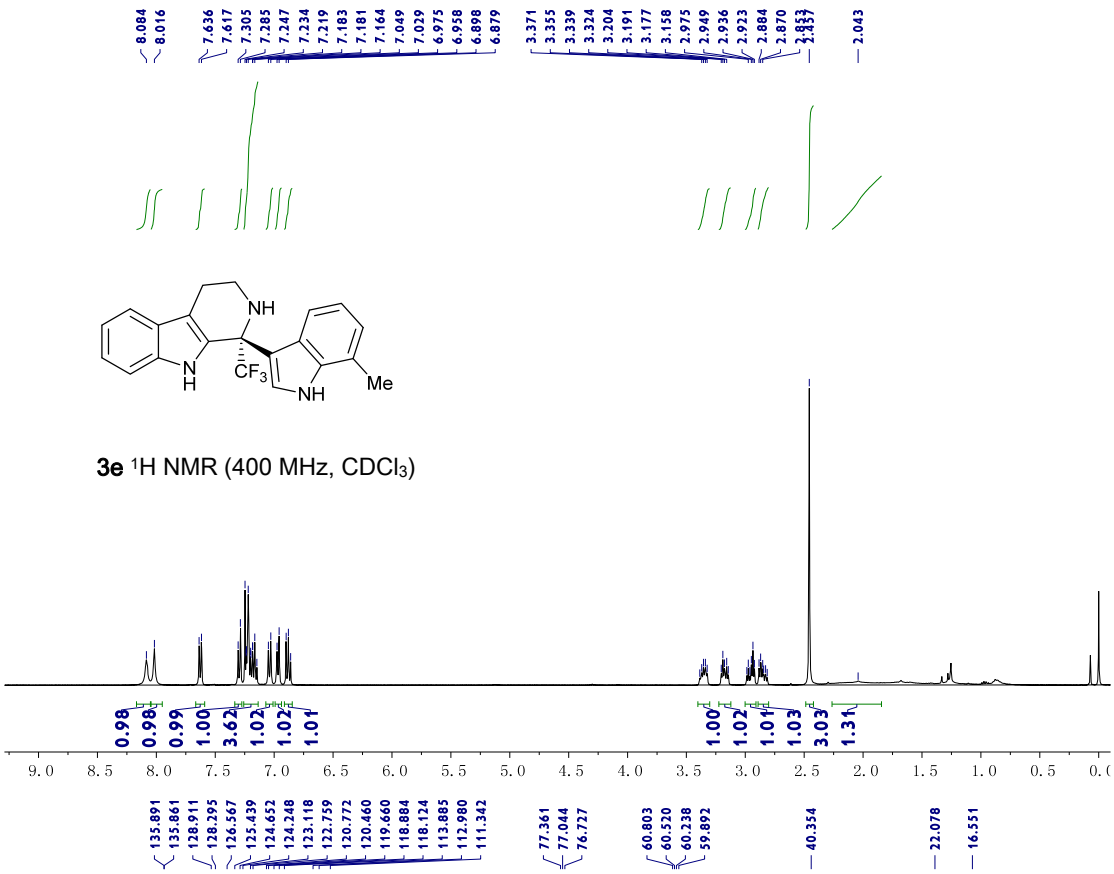


3d ^{13}C NMR (100 MHz, $CDCl_3$)

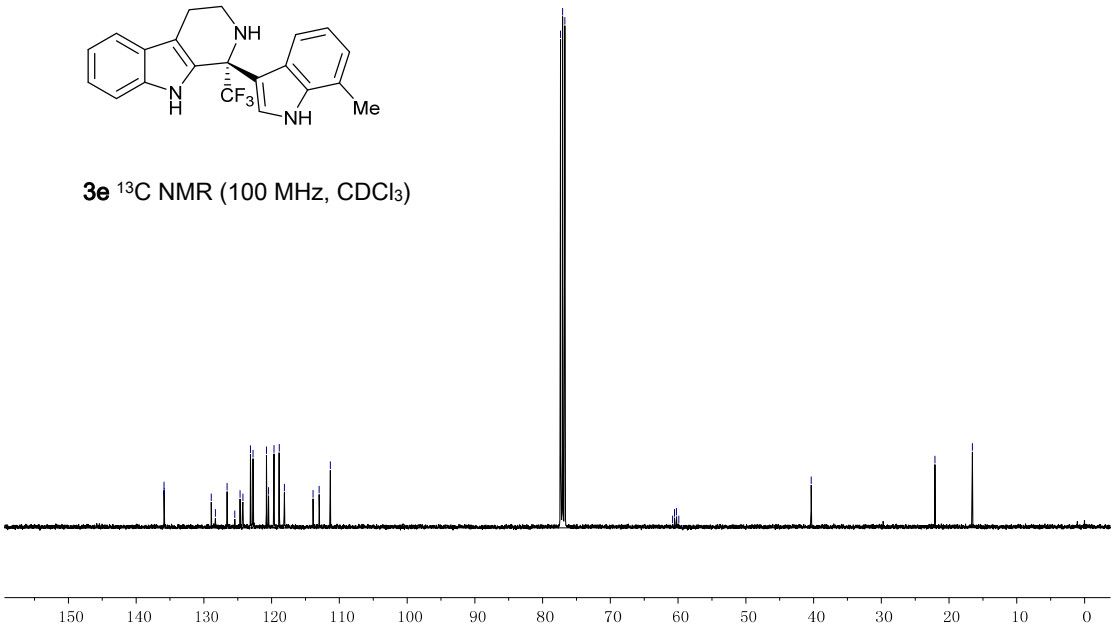




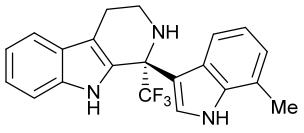
3d ^{19}F NMR (376 MHz, $CDCl_3$)



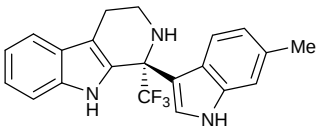
3e ^{1}H NMR (400 MHz, $CDCl_3$)



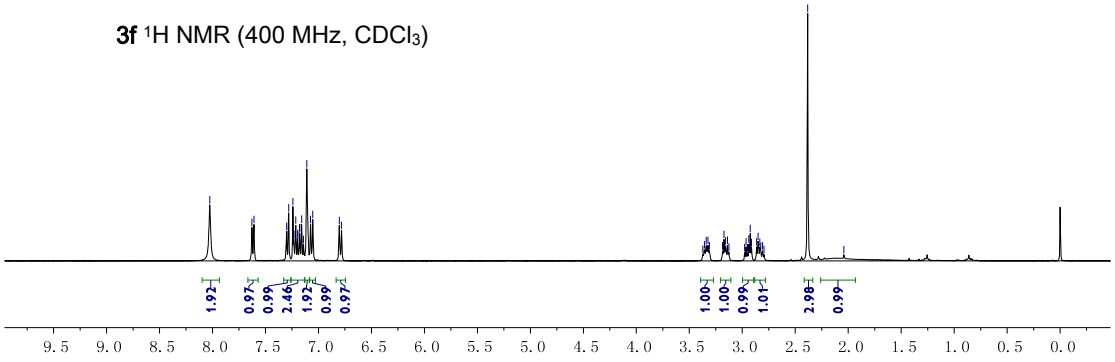
3e ^{13}C NMR (100 MHz, $CDCl_3$)

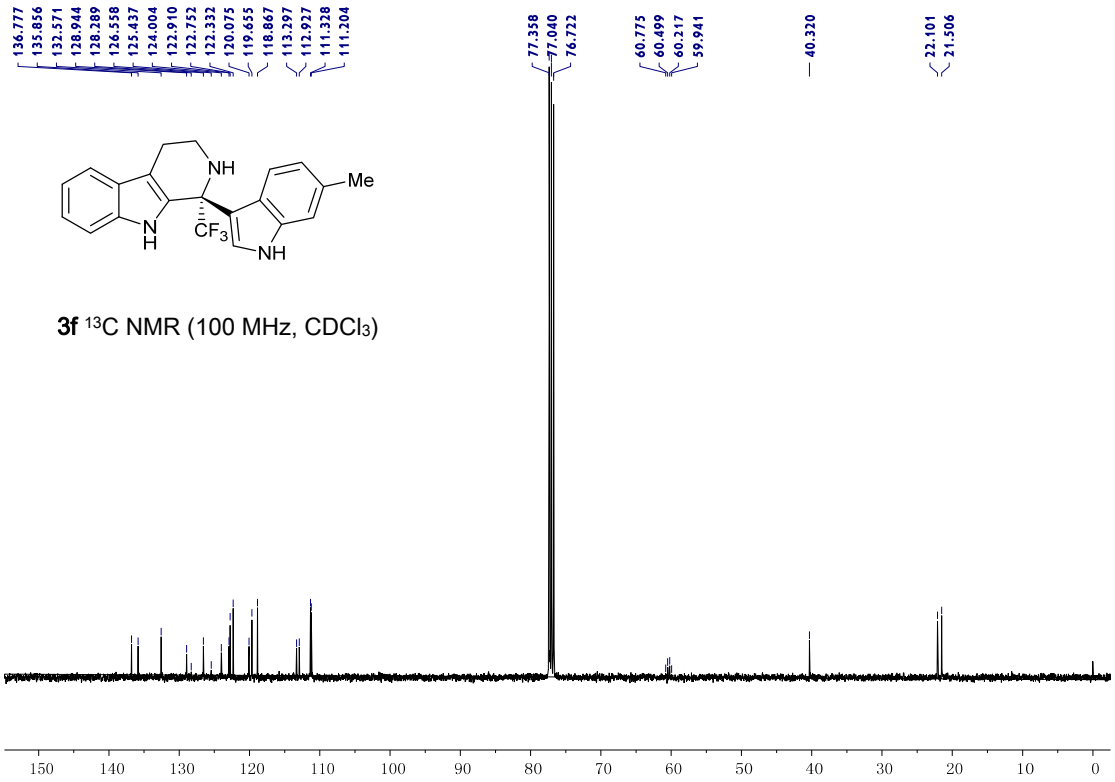


3e ^{19}F NMR (376 MHz, $CDCl_3$)

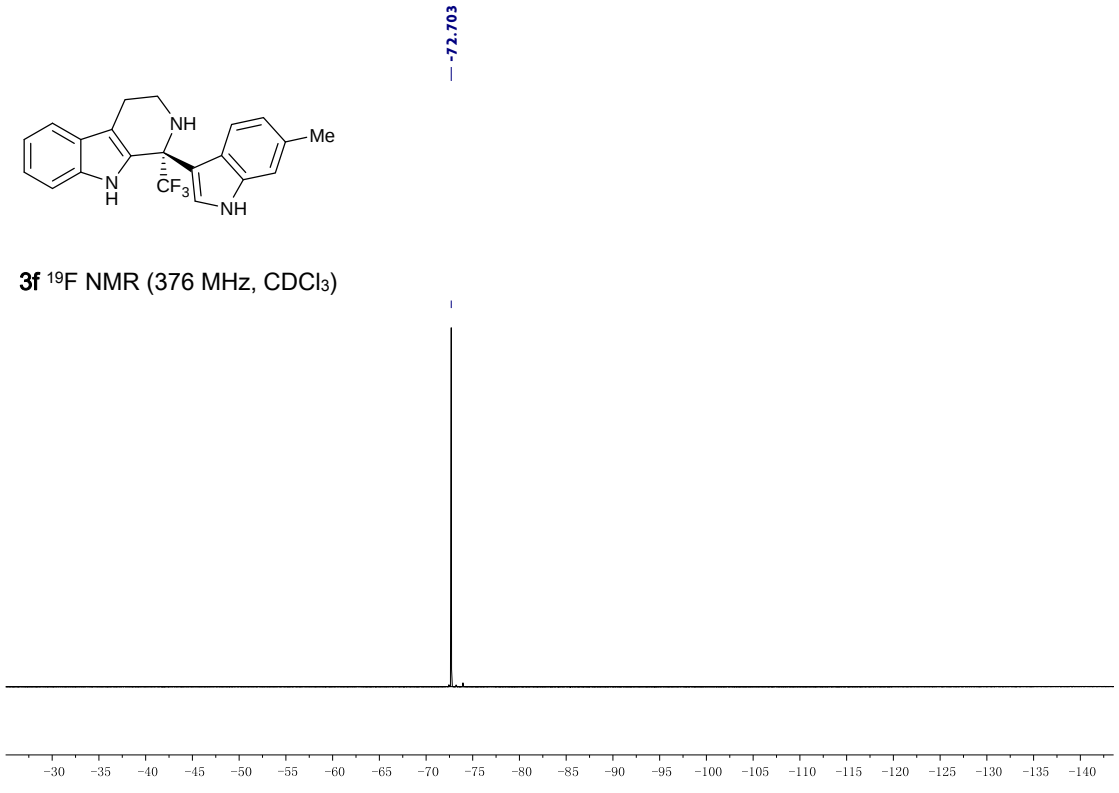


3f ^{1}H NMR (400 MHz, $CDCl_3$)

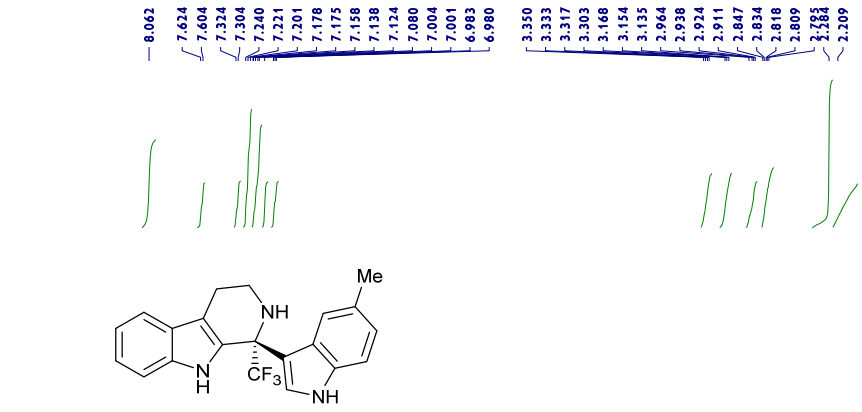




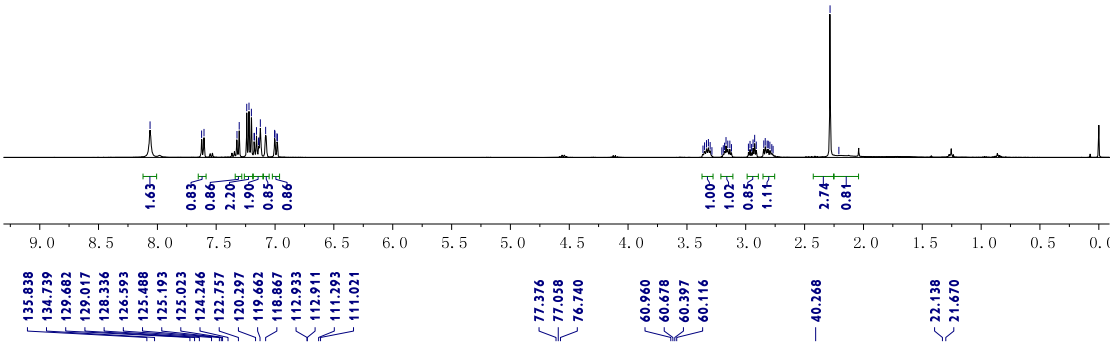
3f ^{13}C NMR (100 MHz, $CDCl_3$)

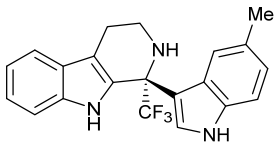


3f ^{19}F NMR (376 MHz, $CDCl_3$)

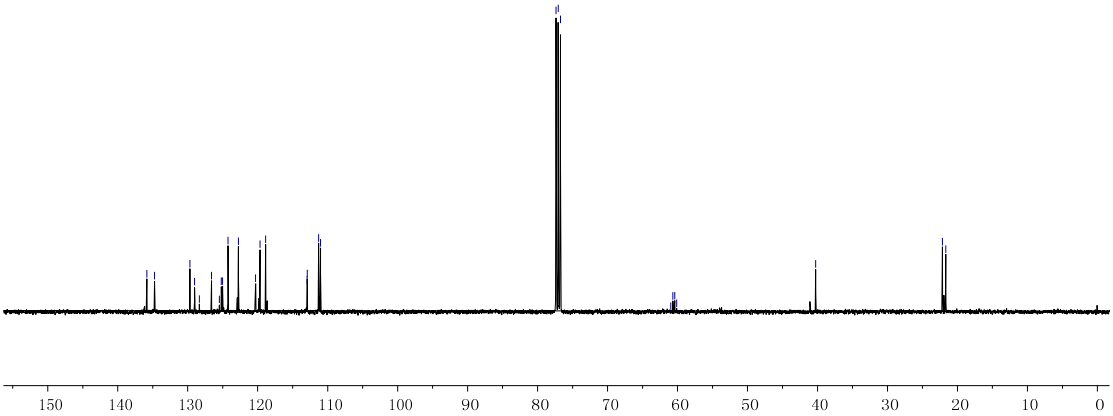


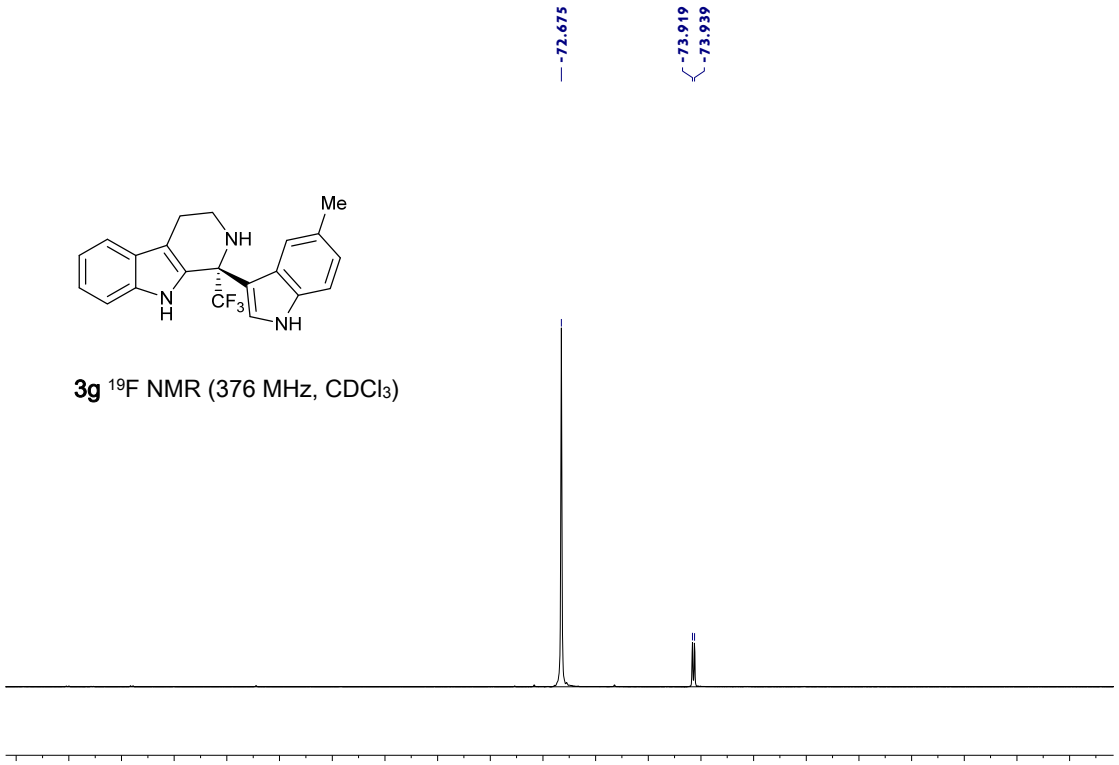
3g ^{1}H NMR (400 MHz, $CDCl_3$)



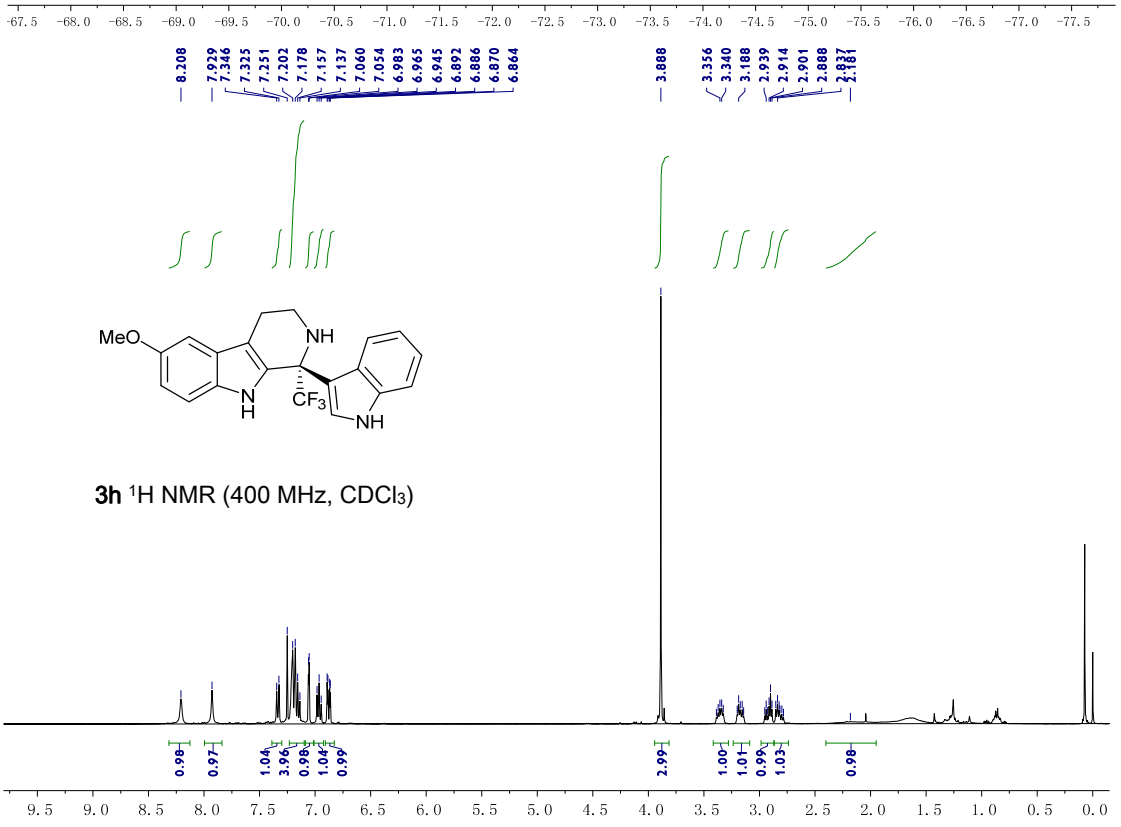


3g ^{13}C NMR (100 MHz, $CDCl_3$)

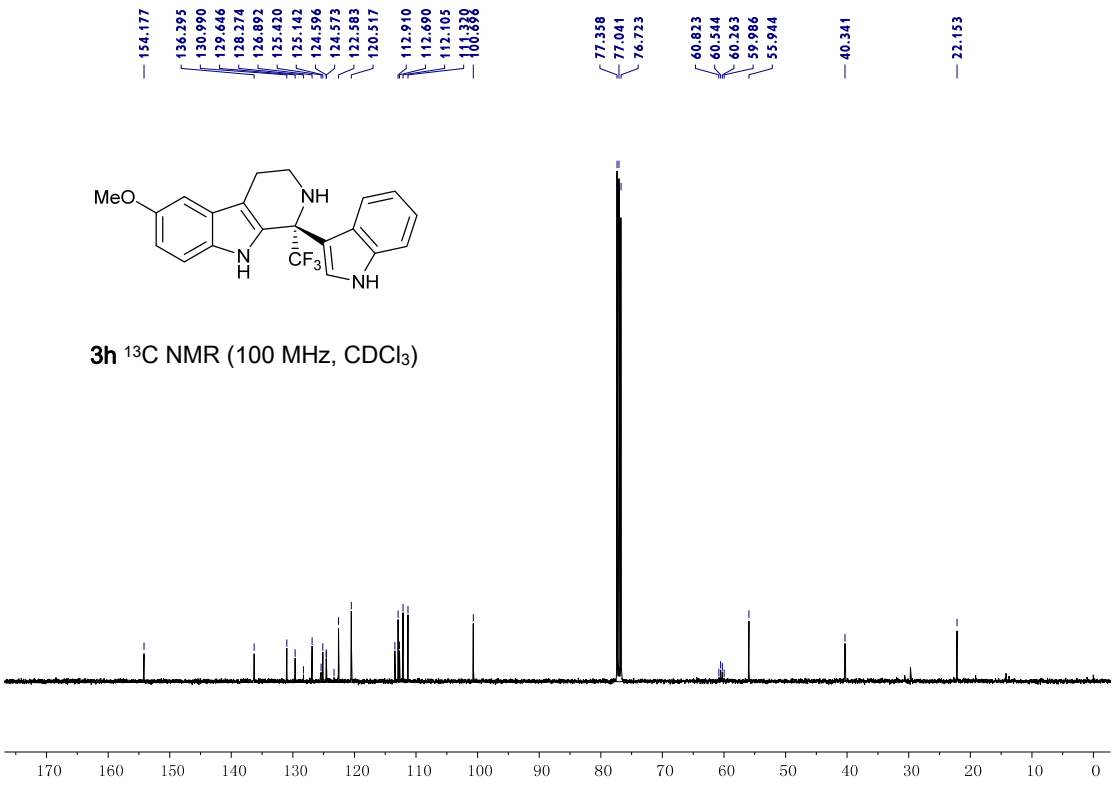




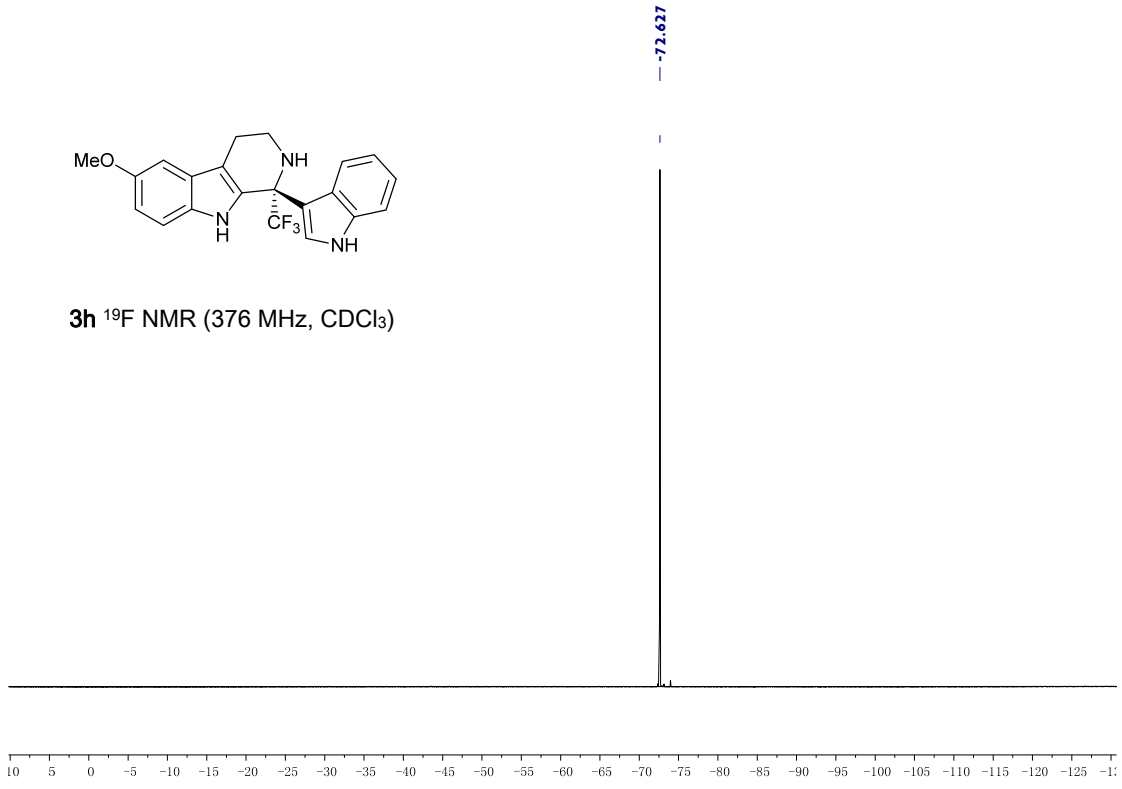
3g ^{19}F NMR (376 MHz, $CDCl_3$)



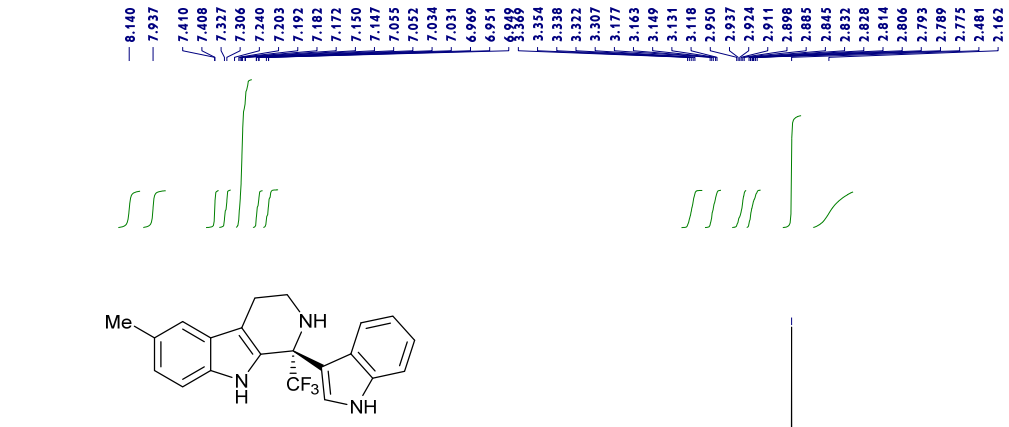
3h ^{1}H NMR (400 MHz, $CDCl_3$)



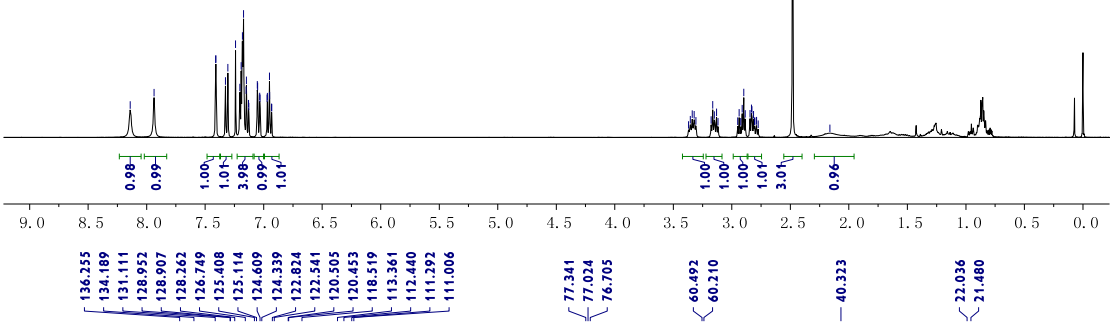
3h ^{13}C NMR (100 MHz, $CDCl_3$)

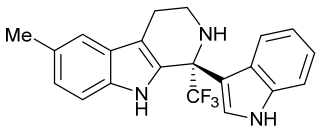


3h ^{19}F NMR (376 MHz, $CDCl_3$)

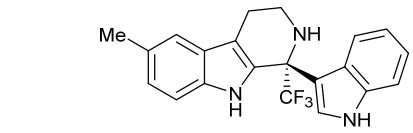


3i ^{1}H NMR (400 MHz, $CDCl_3$)

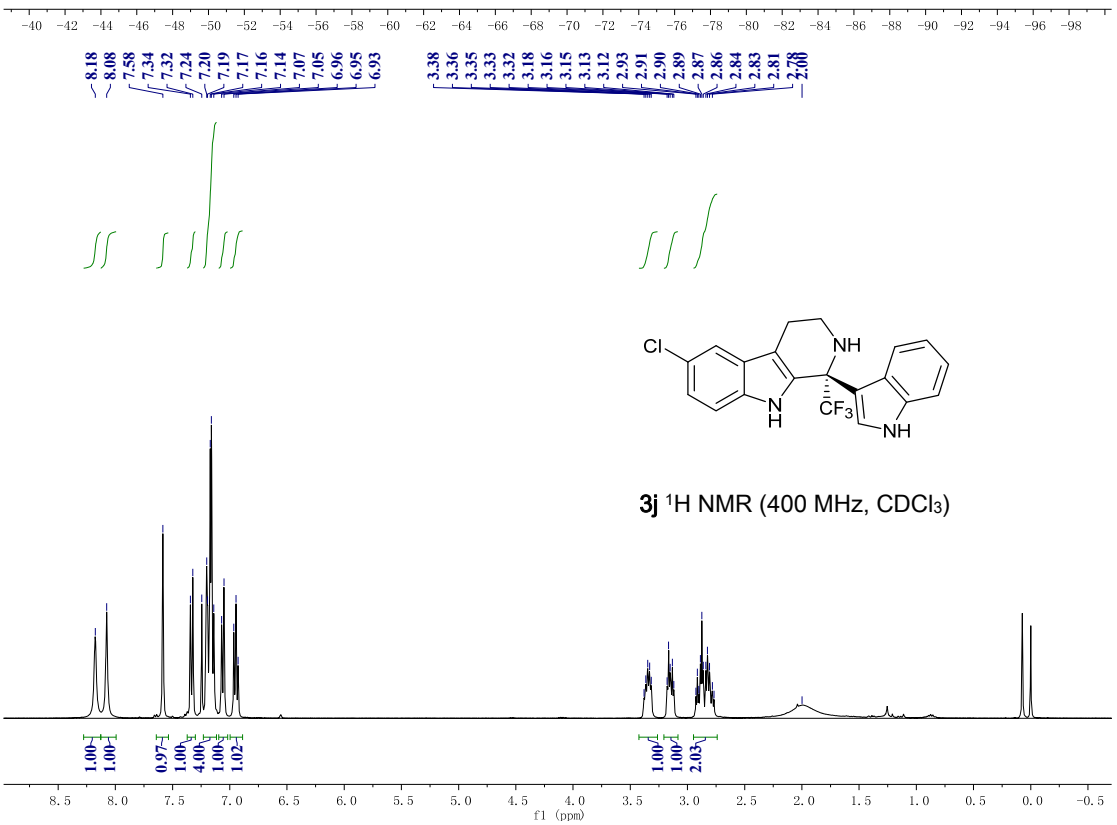




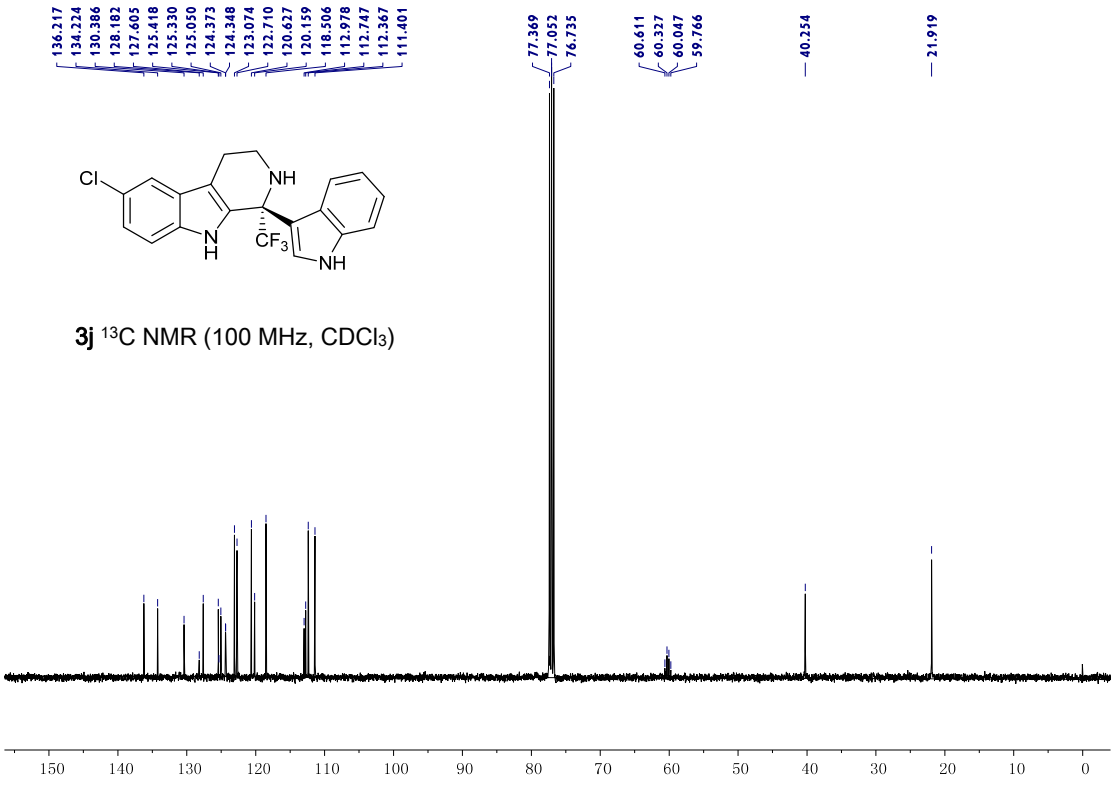
3i ^{13}C NMR (100 MHz, $CDCl_3$)



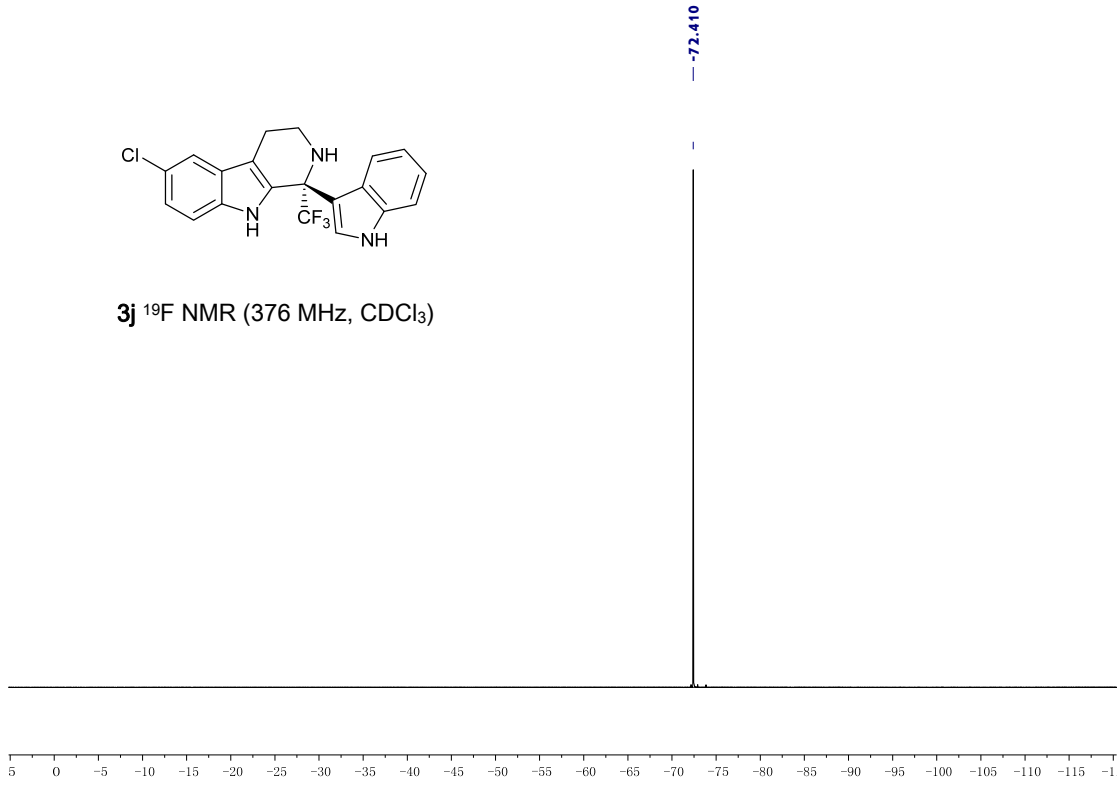
3i ^{19}F NMR (376 MHz, $CDCl_3$)



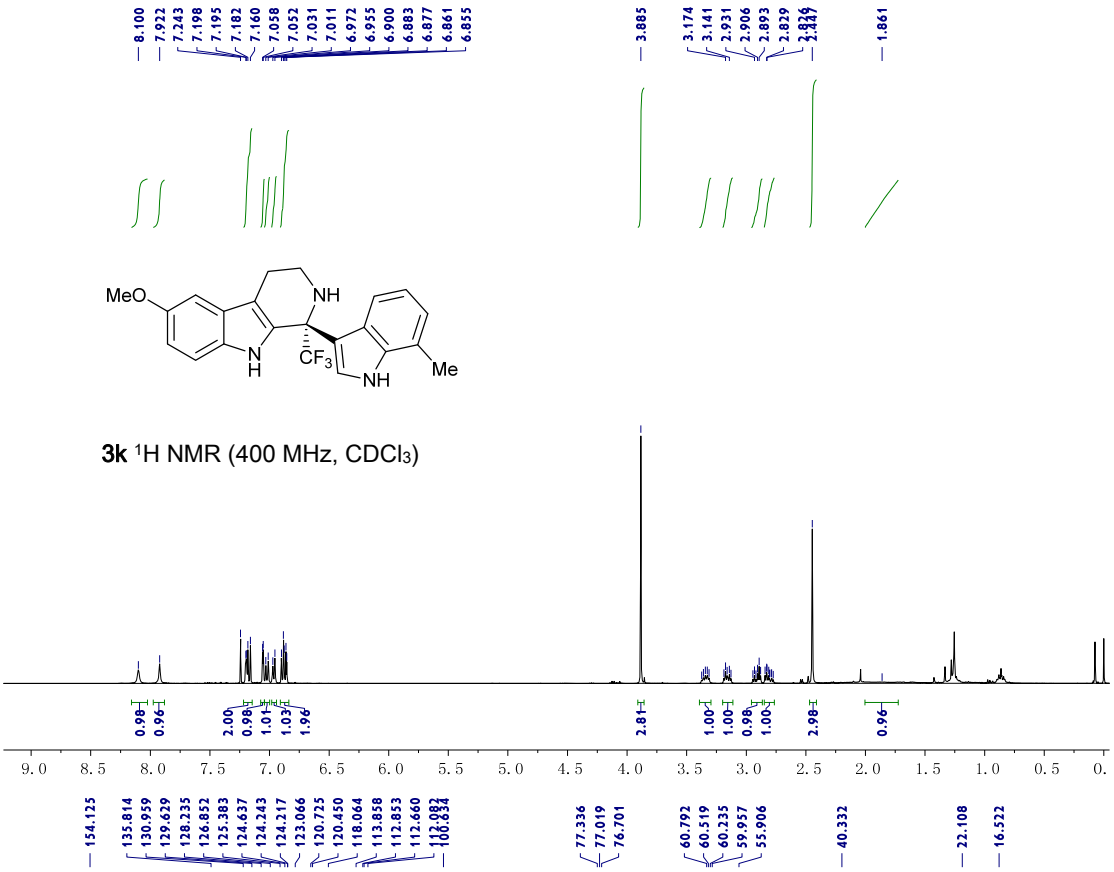
3j ^{1}H NMR (400 MHz, $CDCl_3$)



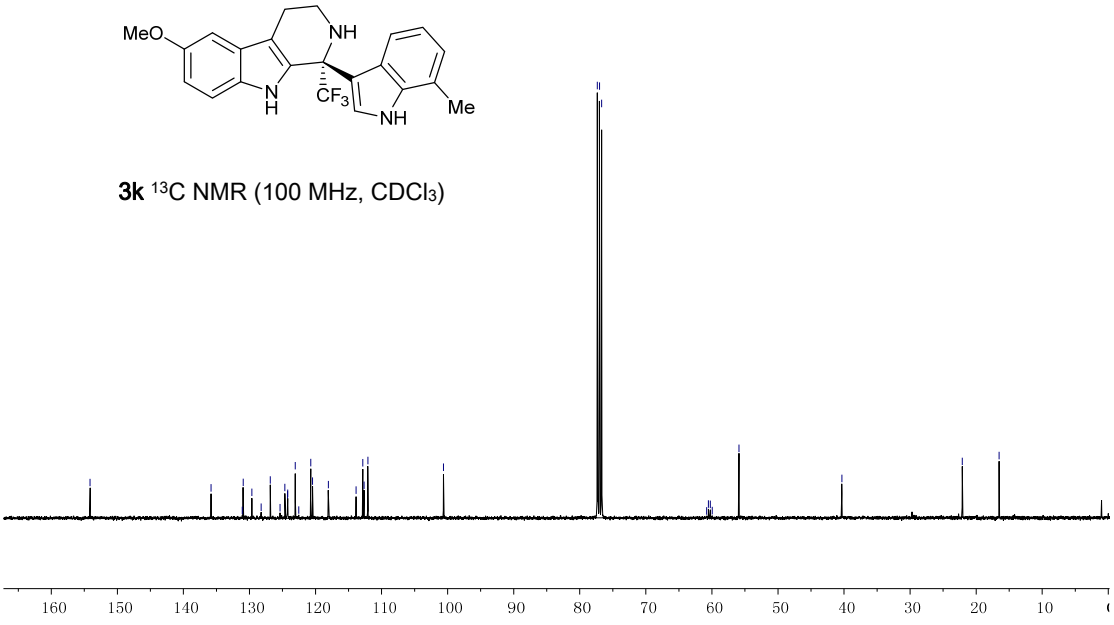
3j ^{13}C NMR (100 MHz, $CDCl_3$)



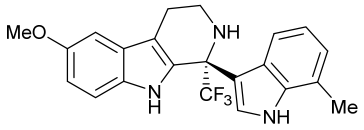
3j ^{19}F NMR (376 MHz, $CDCl_3$)



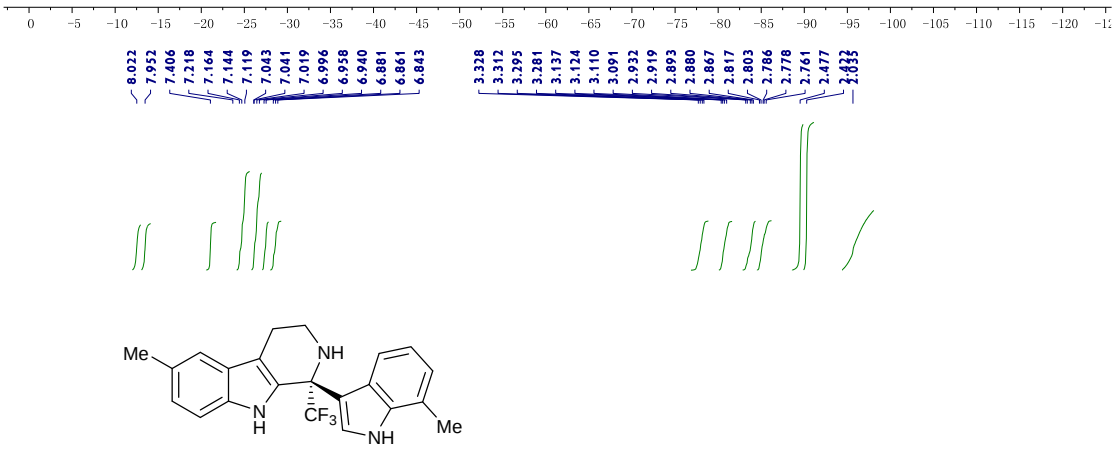
3k ^{1}H NMR (400 MHz, $CDCl_3$)



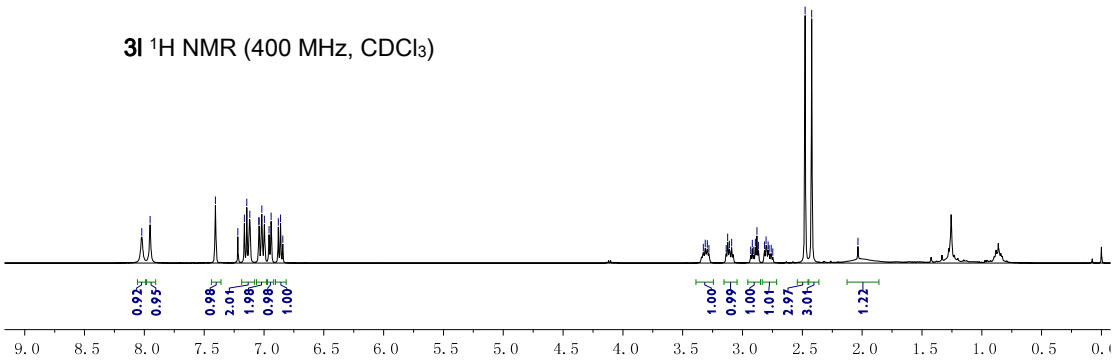
3k ^{13}C NMR (100 MHz, $CDCl_3$)

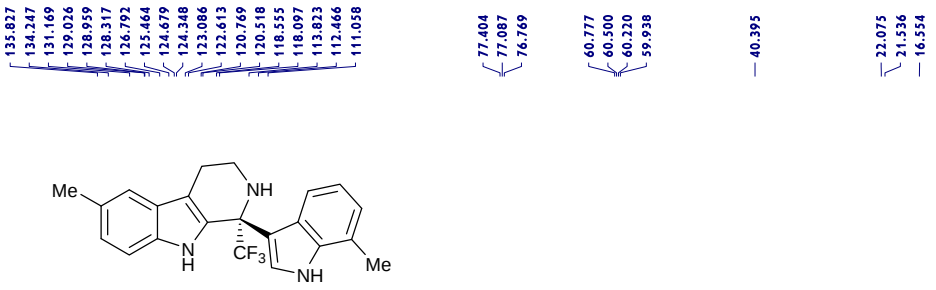


3k ^{19}F NMR (376 MHz, $CDCl_3$)

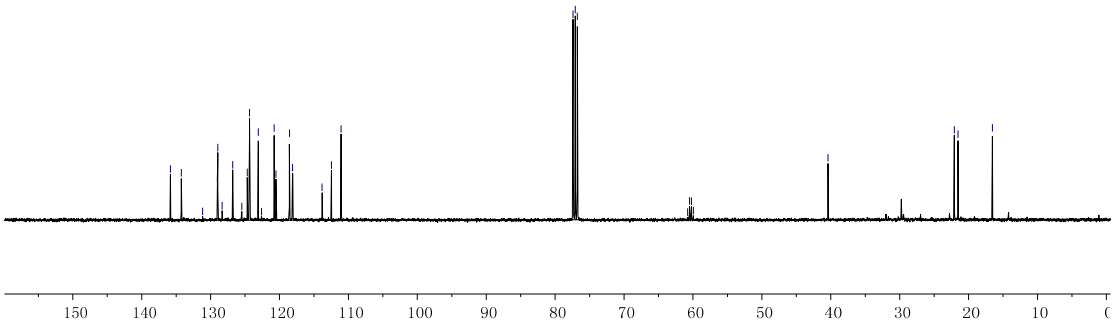


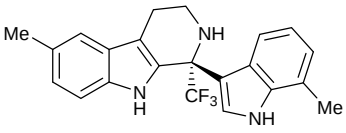
3l ^{1}H NMR (400 MHz, $CDCl_3$)



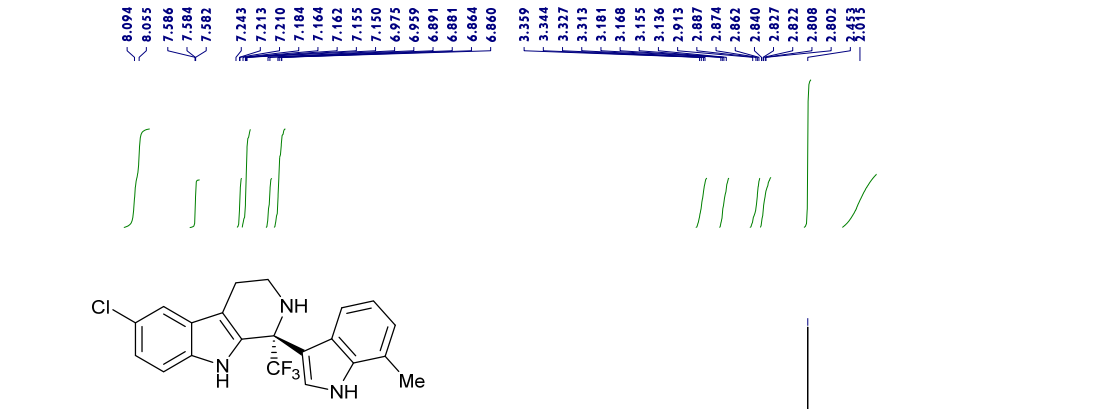


3l ^{13}C NMR (100 MHz, $CDCl_3$)

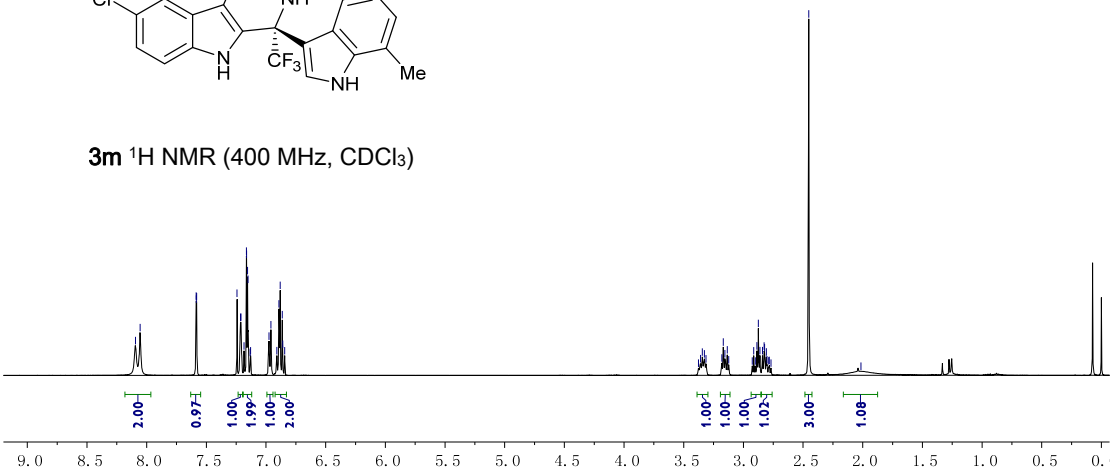


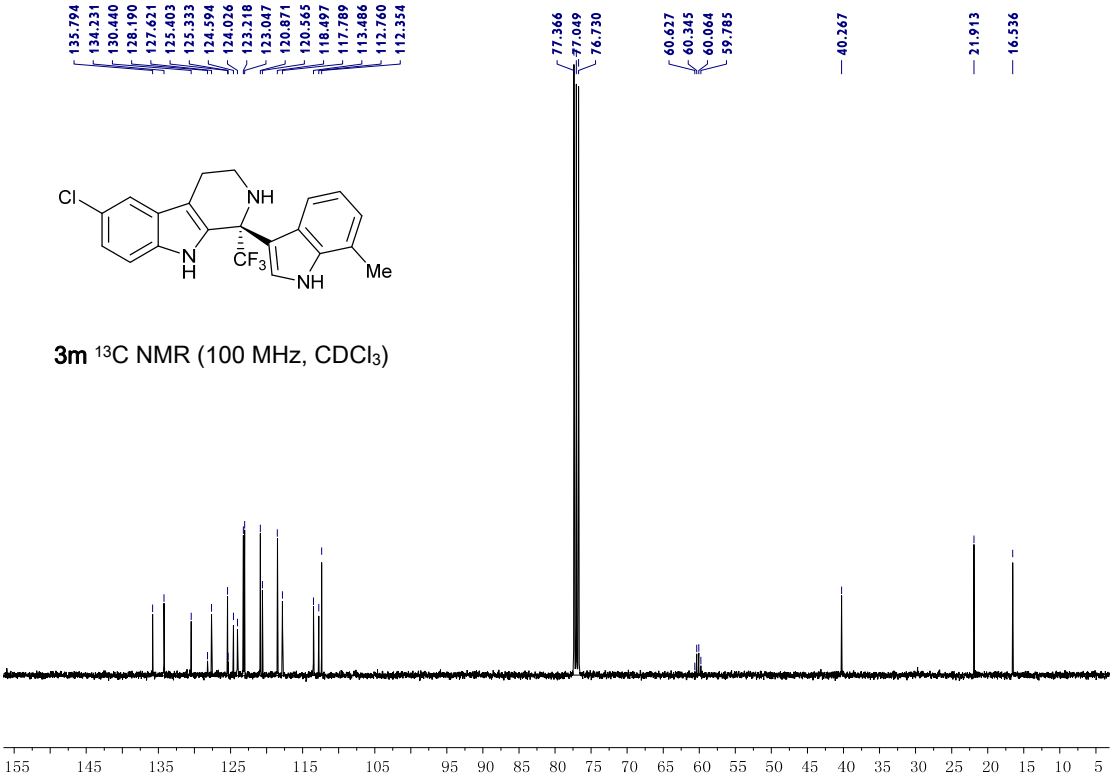


3l ^{19}F NMR (376 MHz, $CDCl_3$)

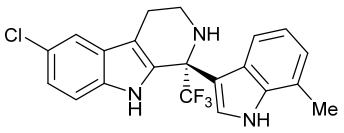


3m ^{1}H NMR (400 MHz, $CDCl_3$)

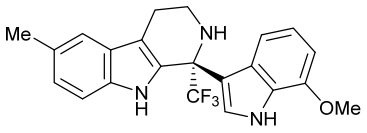




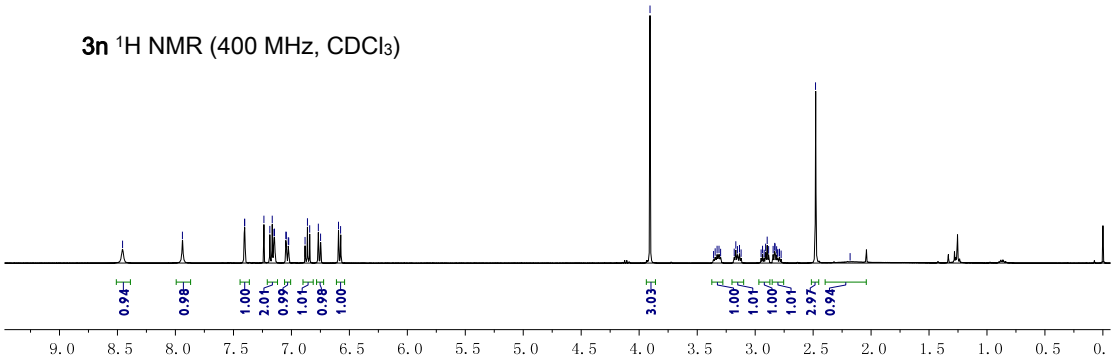
3m ^{13}C NMR (100 MHz, $CDCl_3$)

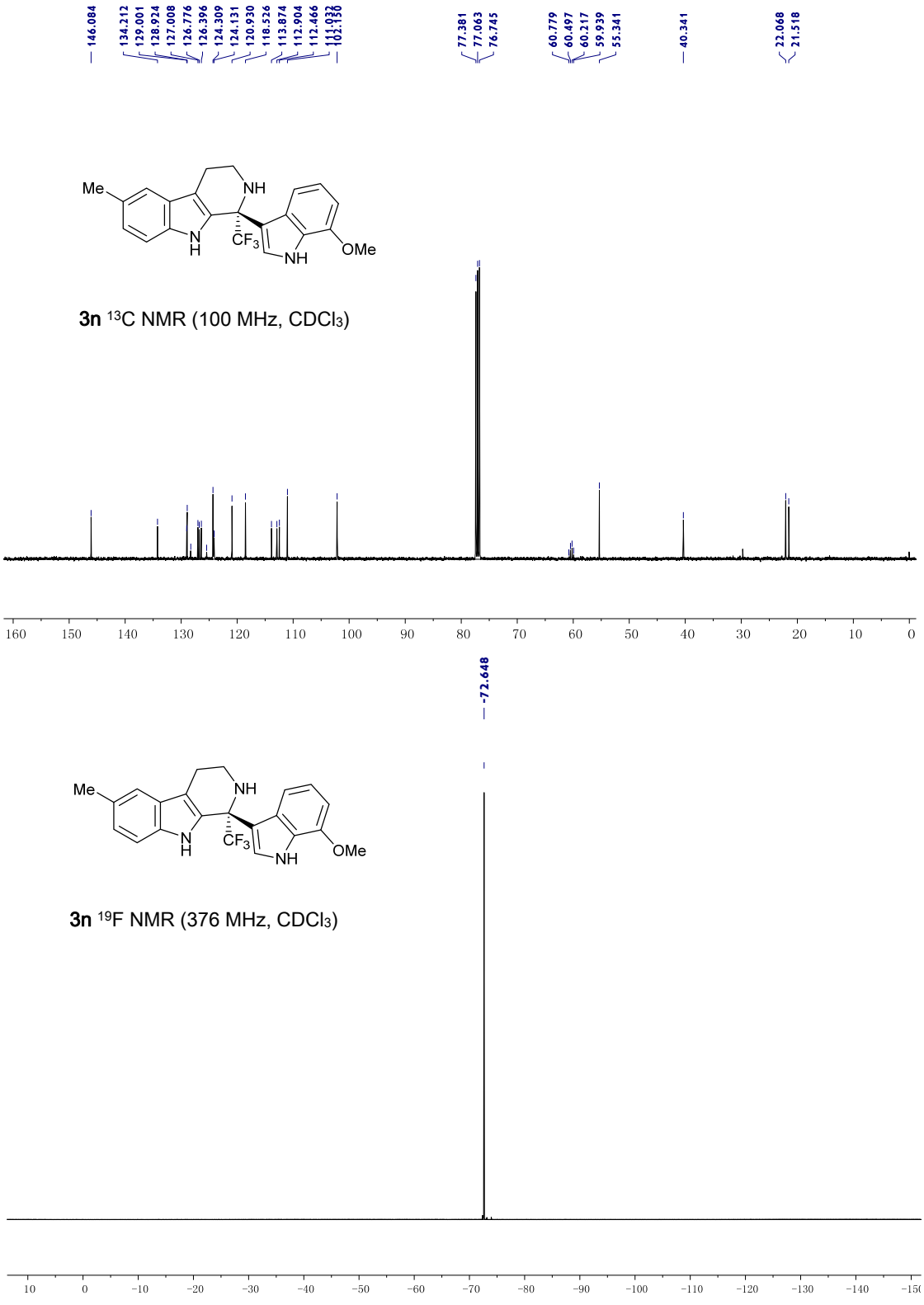


3m ^{19}F NMR (376 MHz, $CDCl_3$)



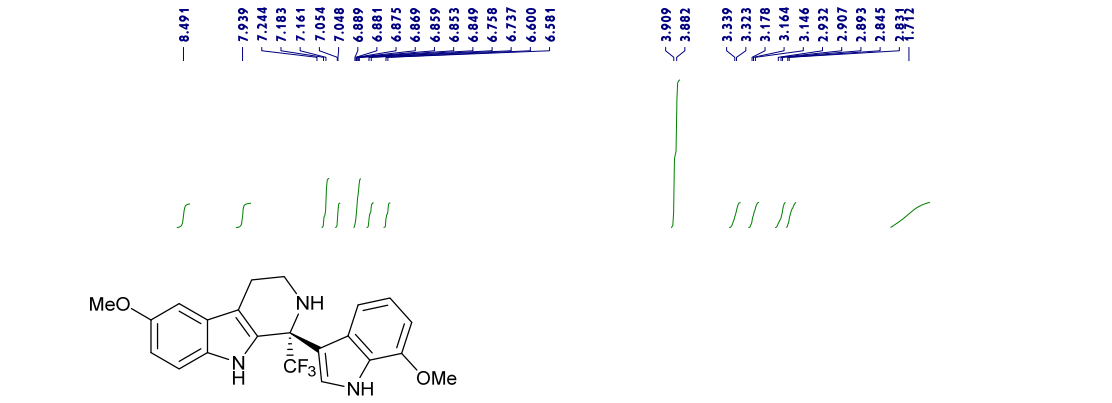
3n ^{1}H NMR (400 MHz, $CDCl_3$)



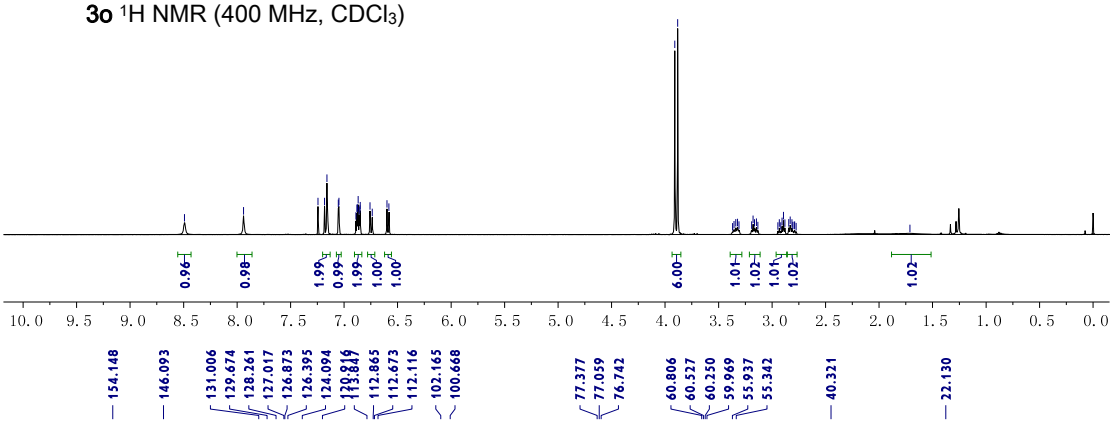


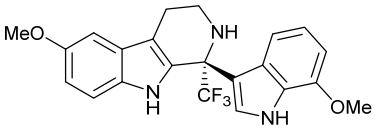
3n ^{13}C NMR (100 MHz, $CDCl_3$)

3n ^{19}F NMR (376 MHz, $CDCl_3$)

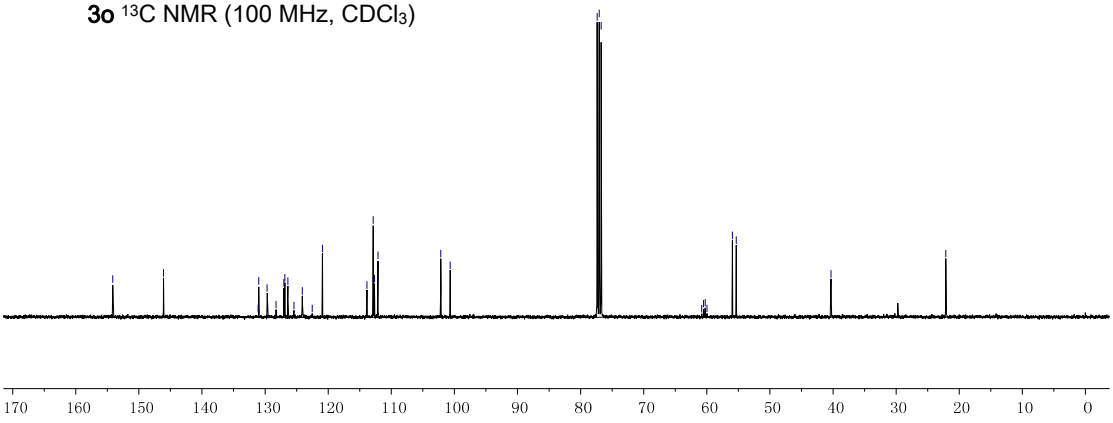


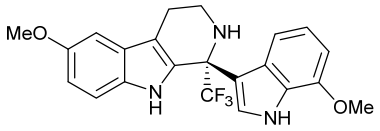
3o ^{1}H NMR (400 MHz, $CDCl_3$)



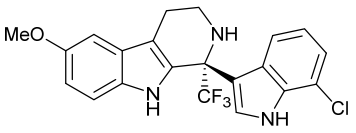


3o ^{13}C NMR (100 MHz, $CDCl_3$)

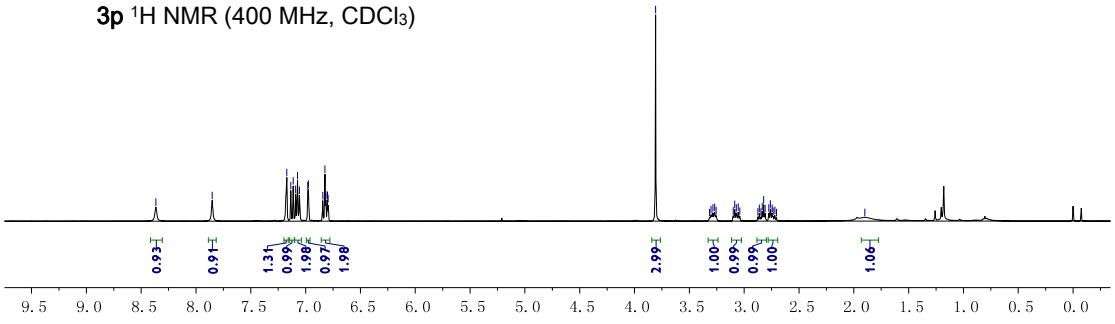


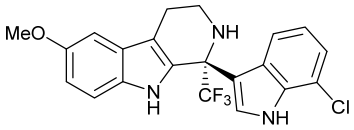


3o ^{19}F NMR (376 MHz, $CDCl_3$)

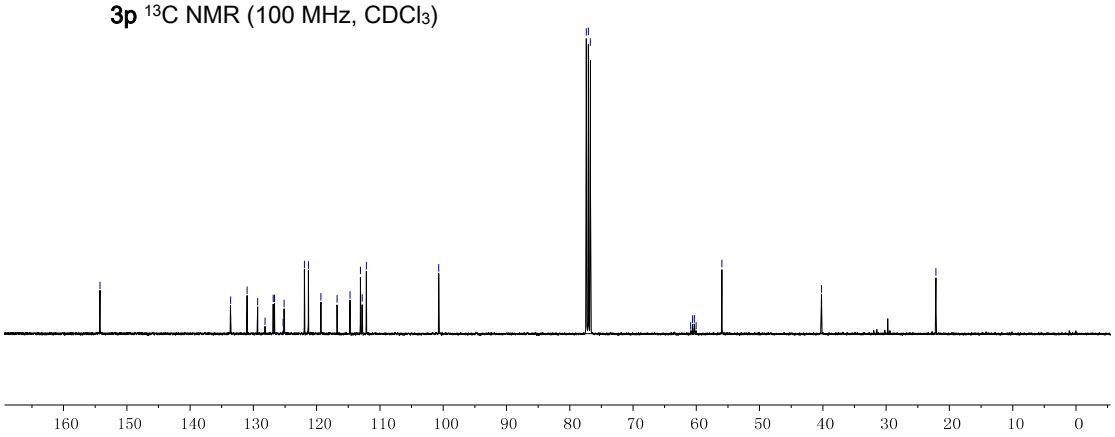


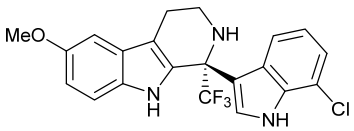
3p ^{1}H NMR (400 MHz, $CDCl_3$)



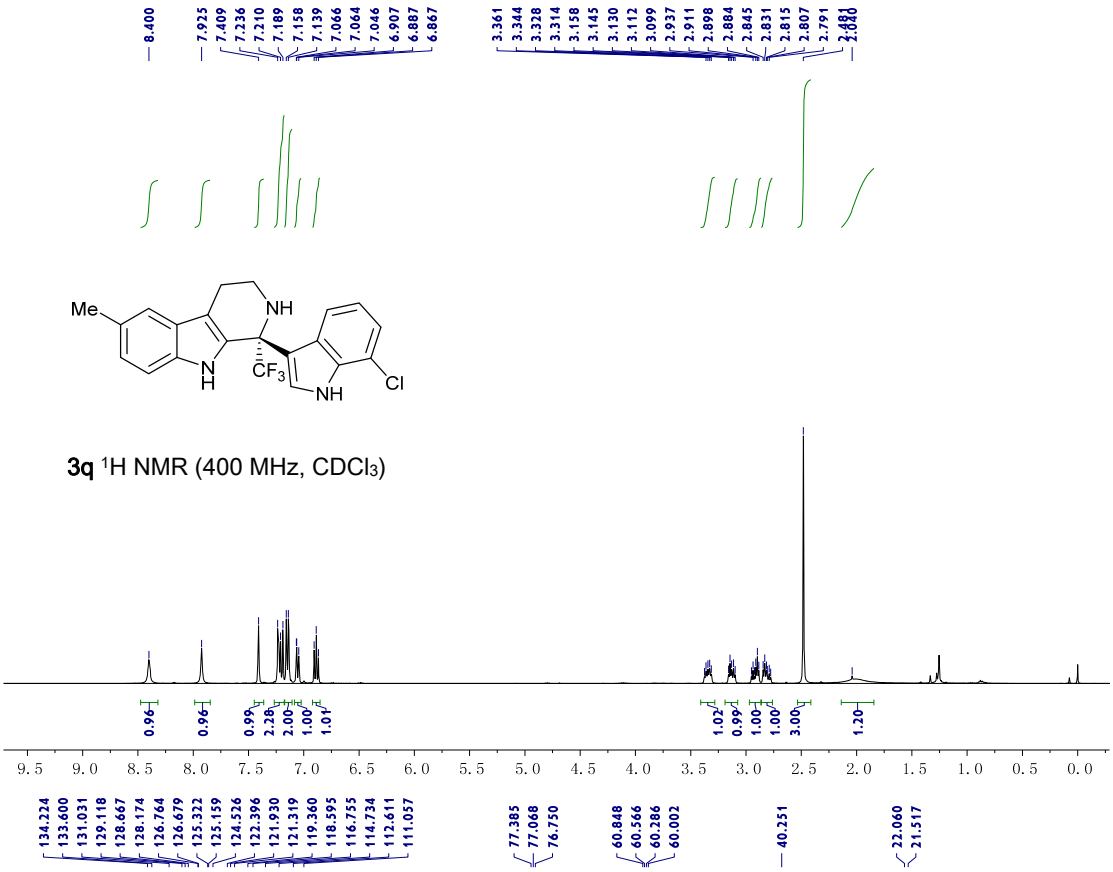


3p ^{13}C NMR (100 MHz, $CDCl_3$)

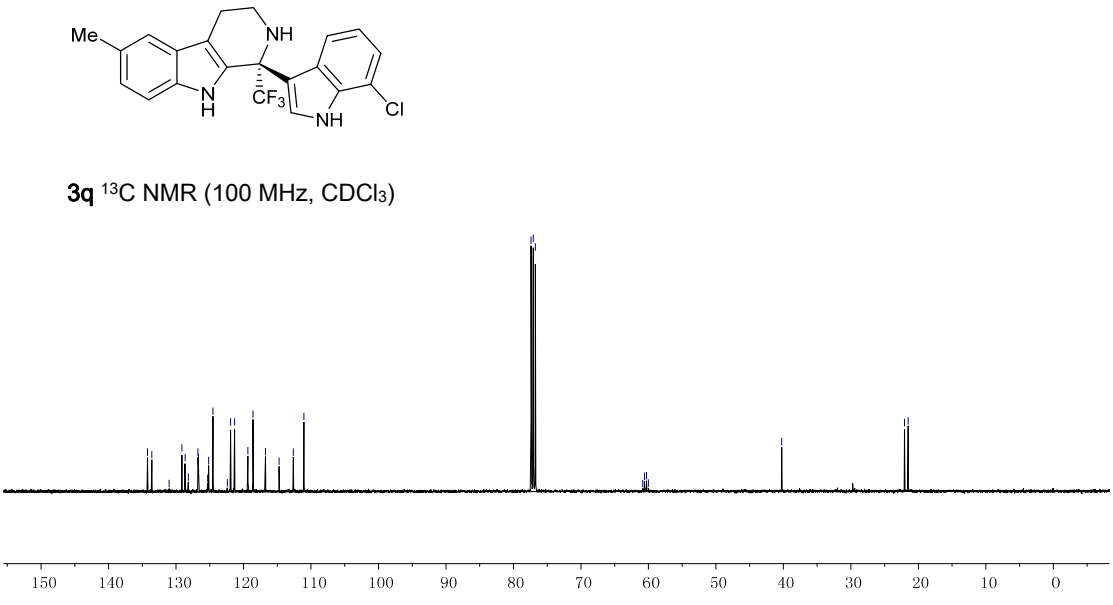




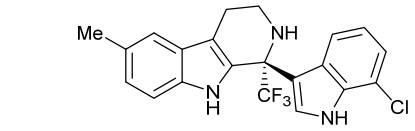
3p ^{19}F NMR (376 MHz, $CDCl_3$)



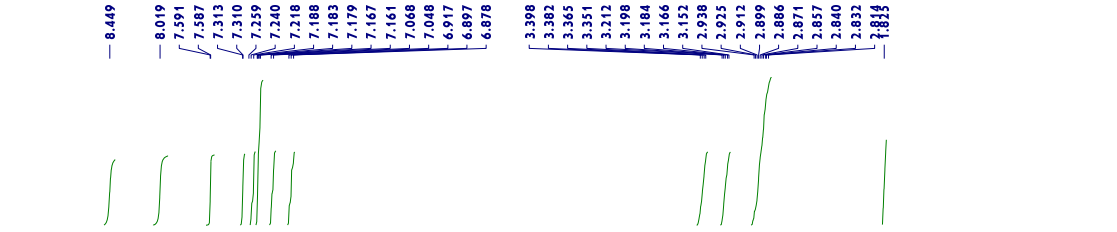
3q ^{1}H NMR (400 MHz, $CDCl_3$)

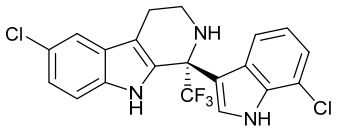


3q ^{13}C NMR (100 MHz, $CDCl_3$)

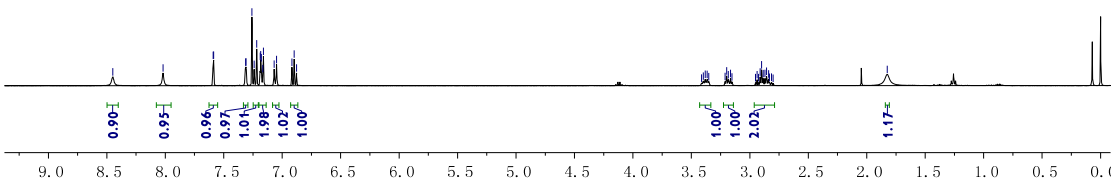


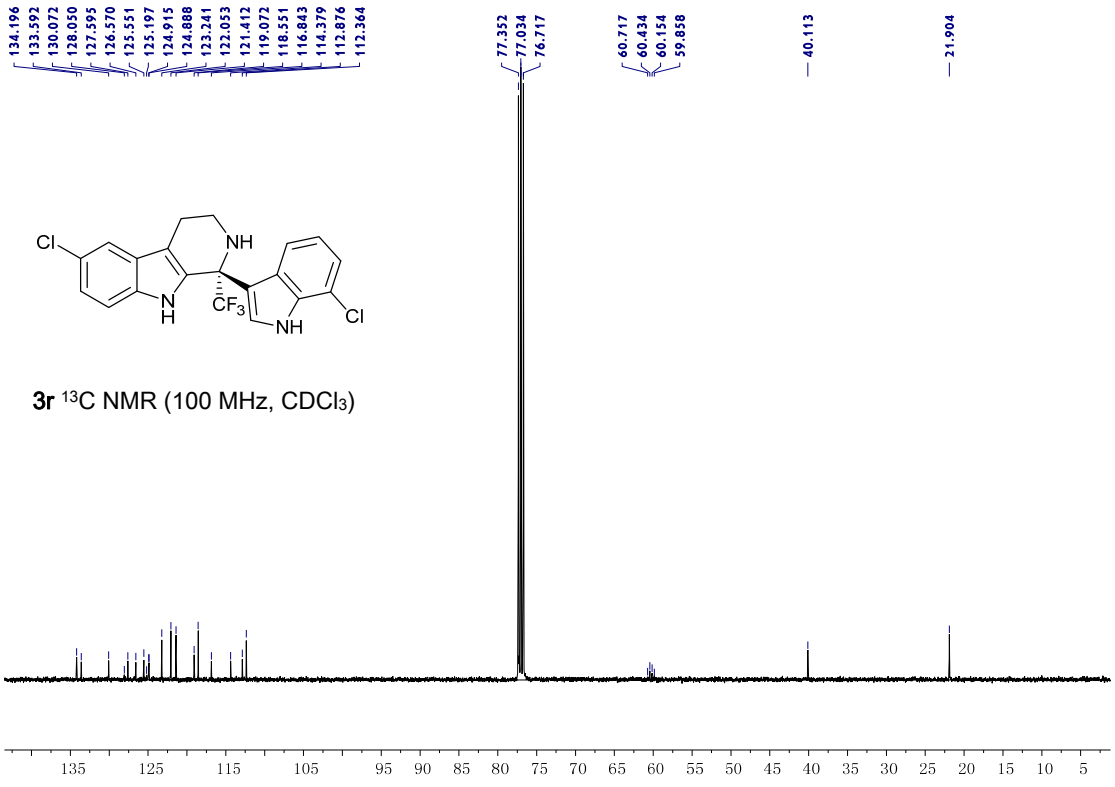
3q ^{19}F NMR (376 MHz, $CDCl_3$)



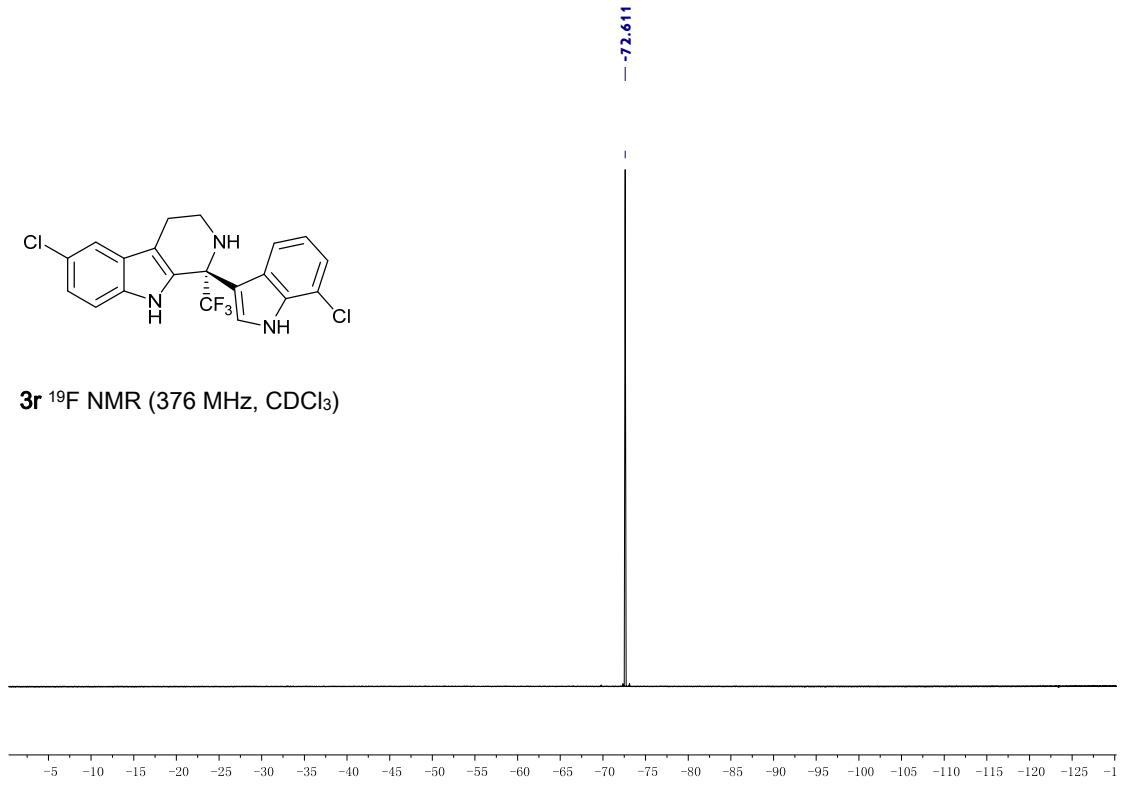


3r ^{1}H NMR (400 MHz, $CDCl_3$)

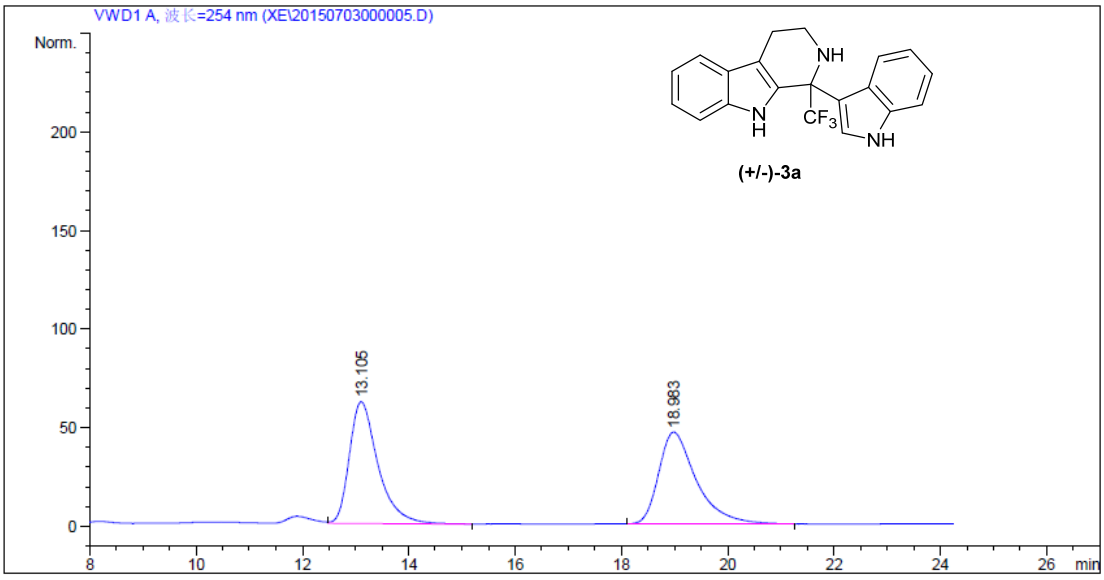




3r ^{13}C NMR (100 MHz, $CDCl_3$)

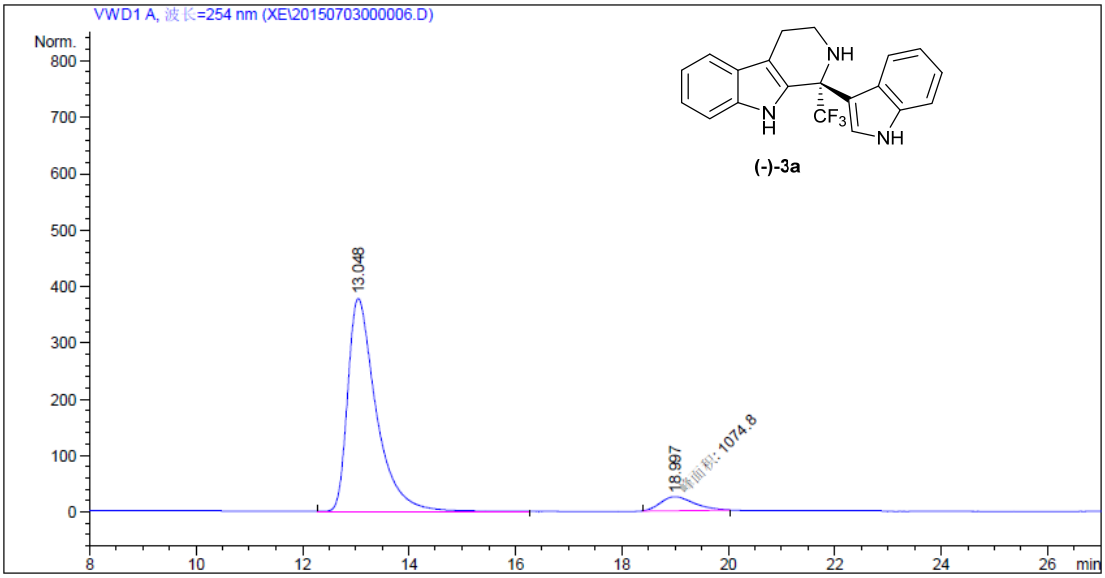


3r ^{19}F NMR (376 MHz, $CDCl_3$)



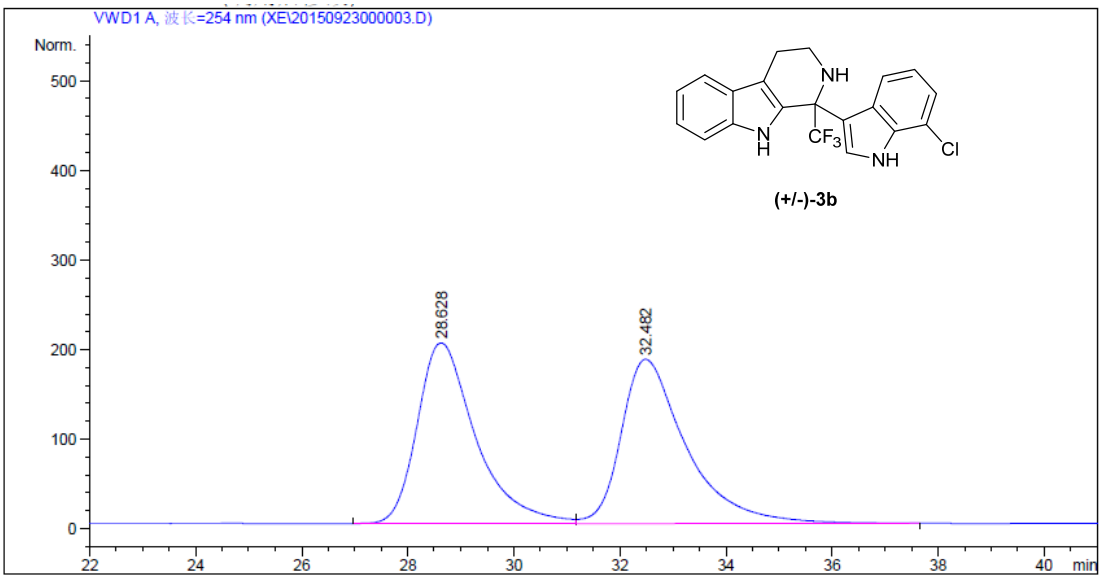
(+/-)-3a

#	[min]		[min]	mAU	*s	[mAU]	%
1	13.105	VB	0.5597	2317.21069		61.81361	49.9288
2	18.983	VV	0.7396	2323.81763		46.78600	50.0712

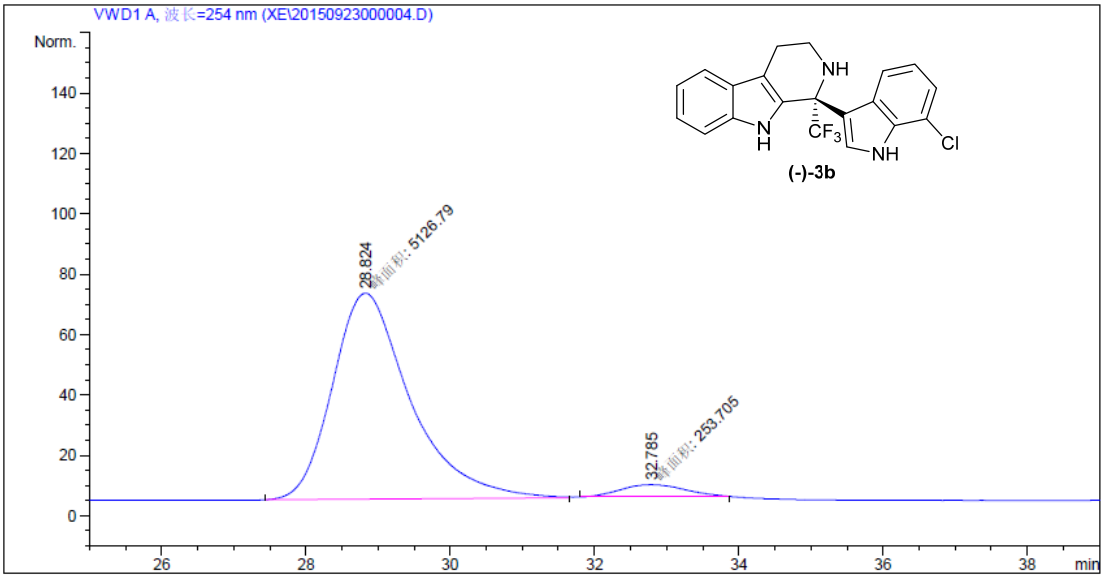


(-)-3a

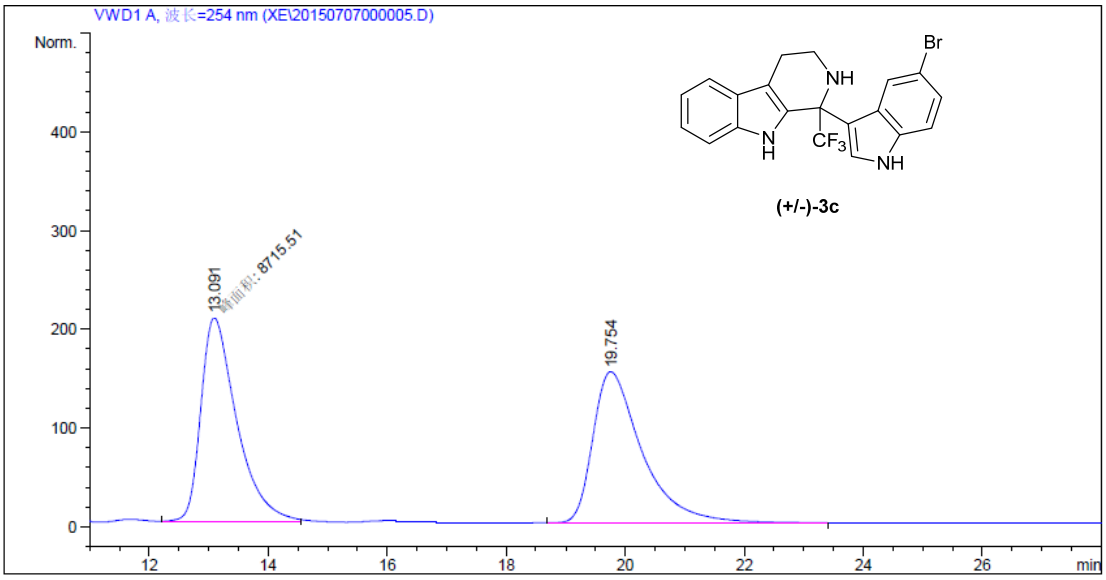
#	[min]		[min]	mAU	*s	[mAU]	%
1	13.048	VB	0.5532	1.40429e4		377.68176	92.8904
2	18.997	MM	0.7234	1074.80066		24.76287	7.1096



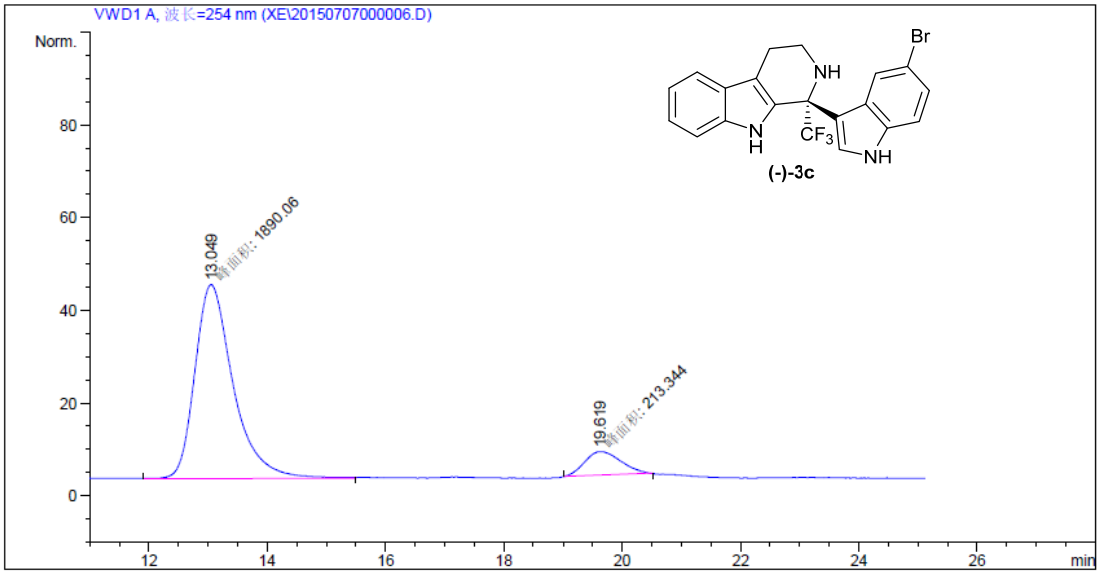
#	[min]		[min]	mAU	*s	[mAU]	%
1	28.628	BV	1.1581	1.54292e4		201.55481	49.6621
2	32.482	VB	1.2517	1.56391e4		183.28769	50.3379



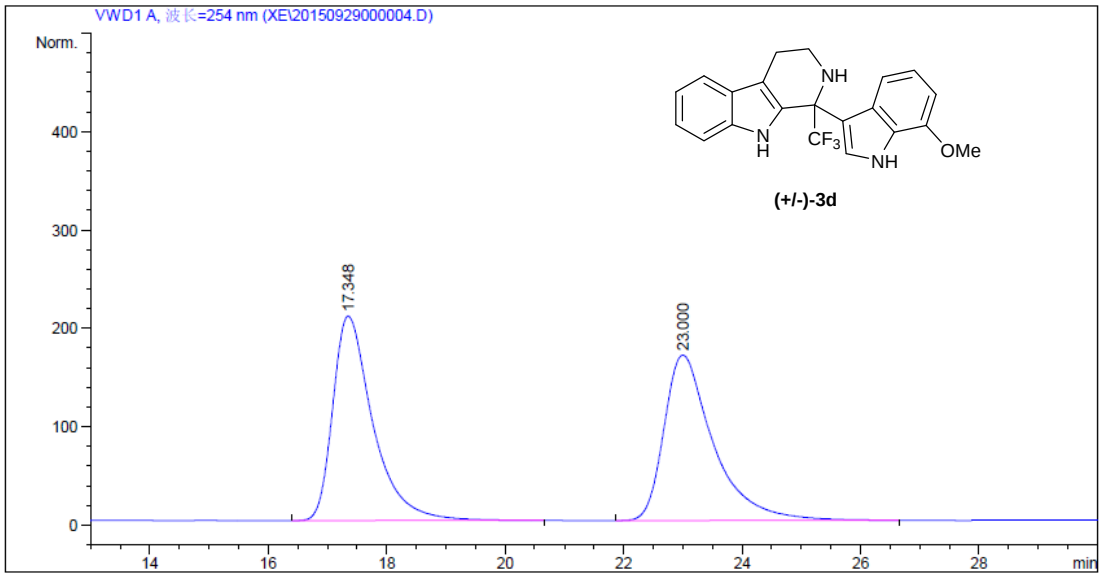
#	[min]		[min]	mAU	*s	[mAU]	%
1	28.824	MM	1.2526	5126.79346		68.21790	95.2847
2	32.785	MM	1.0454	253.70522		4.04487	4.7153



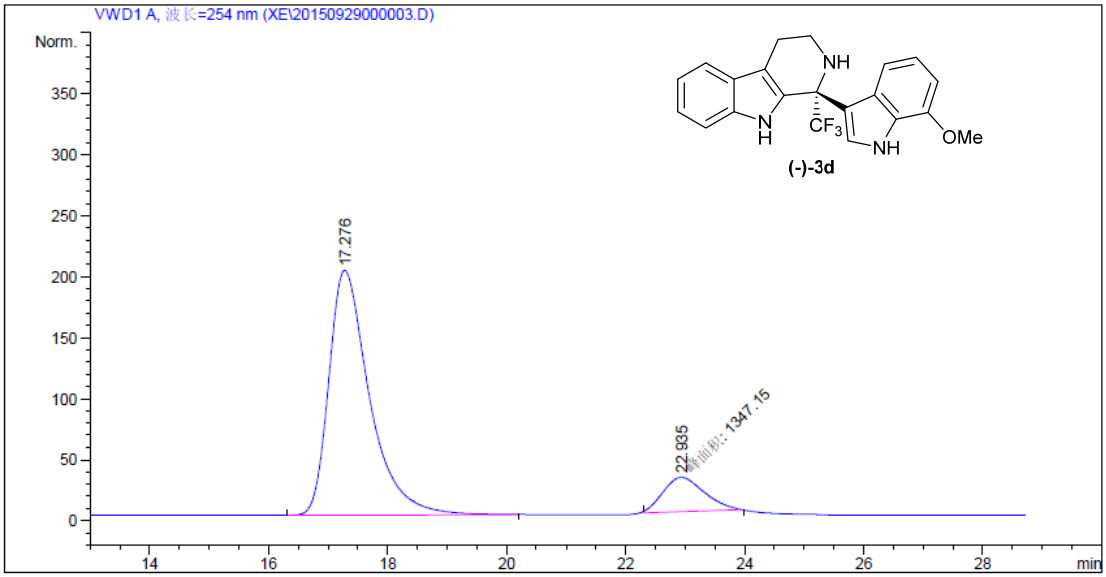
#	[min]		[min]	mAU	*s	[mAU	]	%
1	13.091	MM	0.7010	8715.50781		207.22331		49.4199
2	19.754	BB	0.8613	8920.13379		153.53711		50.5801



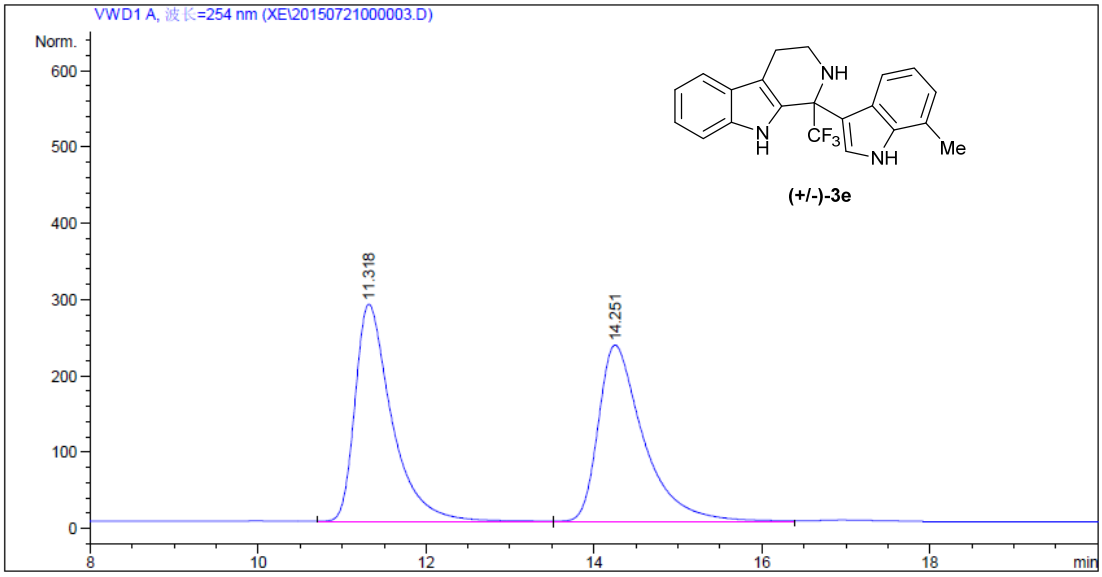
#	[min]		[min]	mAU	*s	[mAU	]	%
1	13.049	MM	0.7527	1890.05725		41.84886		89.8572
2	19.619	MM	0.7006	213.34407		5.07493		10.1428



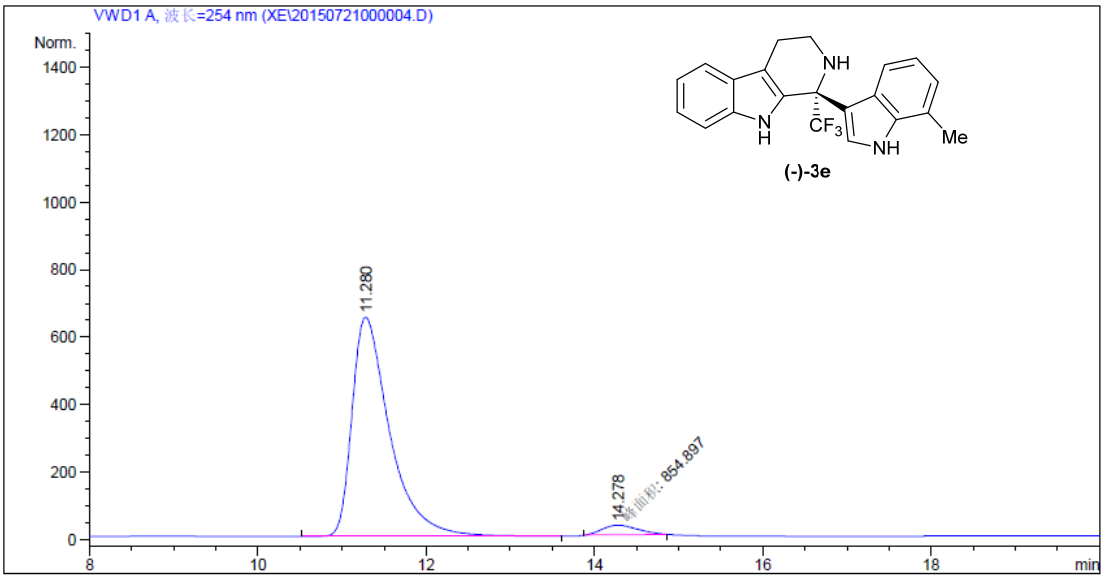
#	[min]		[min]	mAU	*s	[mAU]	%
1	17.348	BB	0.7067	9792.40039	207.92889	50.1071
2	23.000	BB	0.8483	9750.55762	168.16537	49.8929



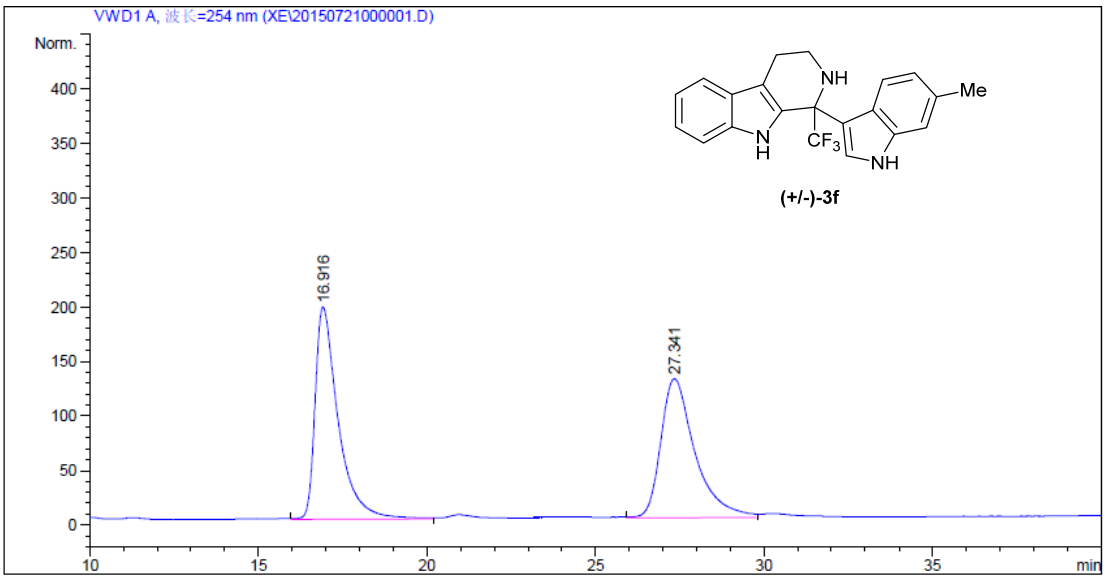
#	[min]		[min]	mAU	*s	[mAU]	%
1	17.276	BB	0.7139	9516.19922	200.50026	87.5992
2	22.935	MM	0.7954	1347.14587	28.22631	12.4008



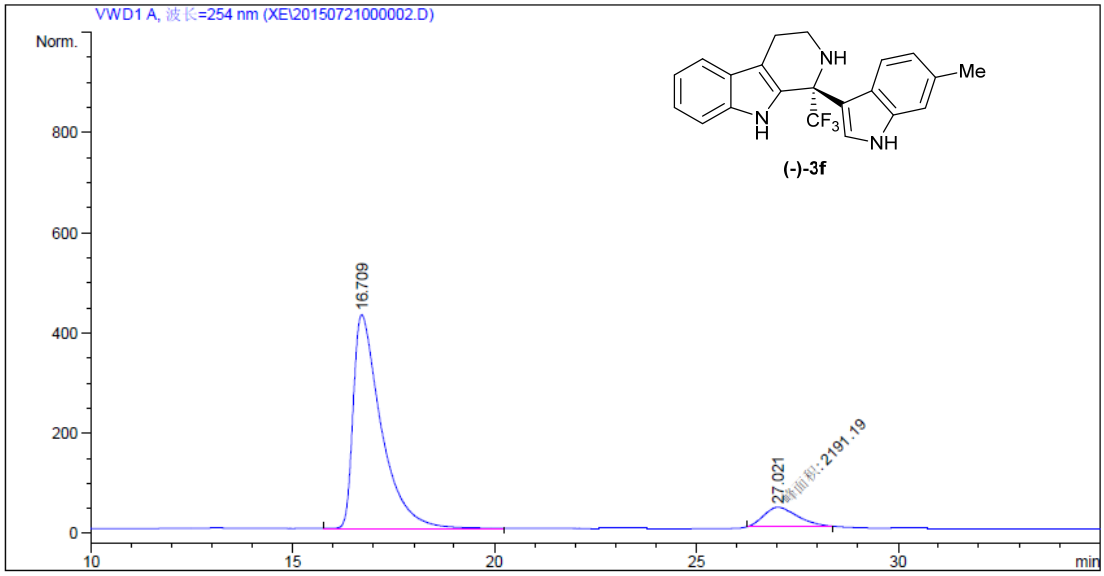
#	[min]		[min]	mAU	*s	[mAU	]	%
1	11.318	VV	0.4546	8684.87402		284.95724		49.9927
2	14.251	VV	0.5578	8687.40332		231.20694		50.0073



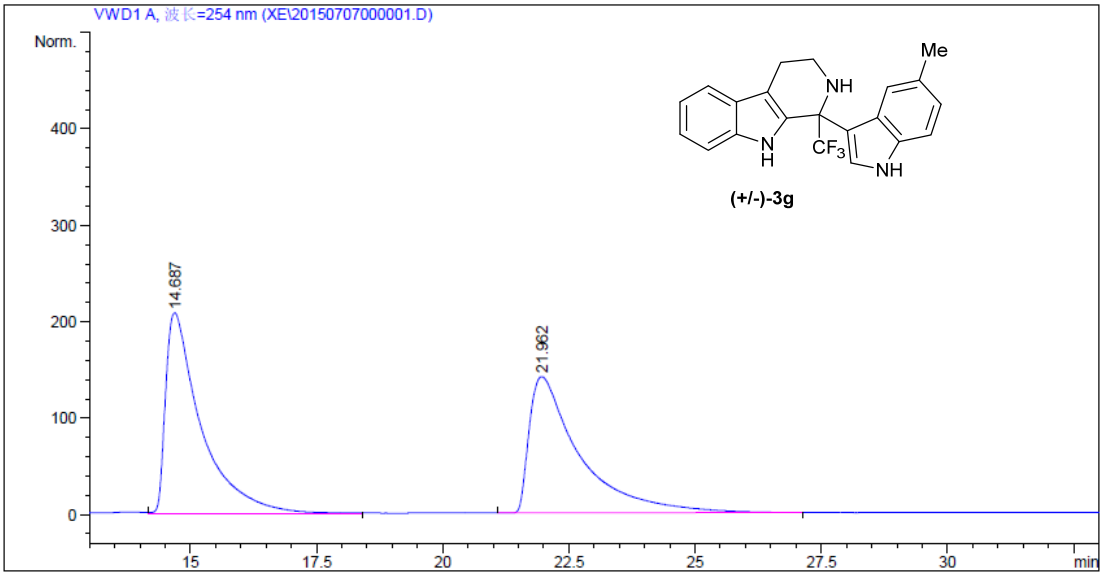
#	[min]		[min]	mAU	*s	[mAU	]	%
1	11.280	VV	0.4707	2.01975e4		649.27106		95.9392
2	14.278	MM	0.4942	854.89703		28.82949		4.0608



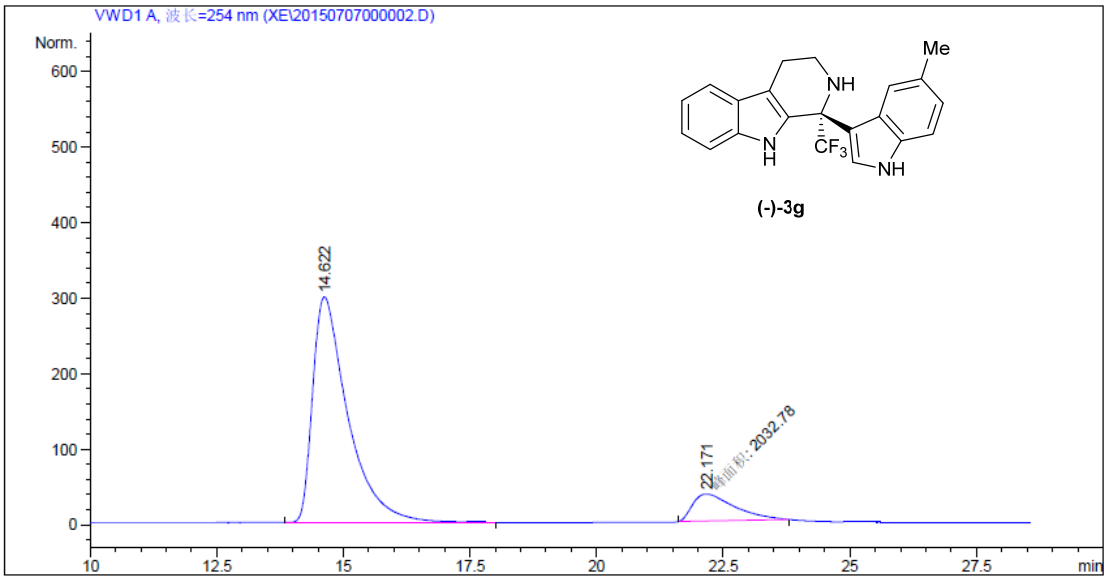
#	[min]		[min]	mAU	*s	[mAU	]	%
1	16.916	VV	0.7015	9274.59961		194.62943		50.7091
2	27.341	VV	1.0463	9015.21289		127.49264		49.2909



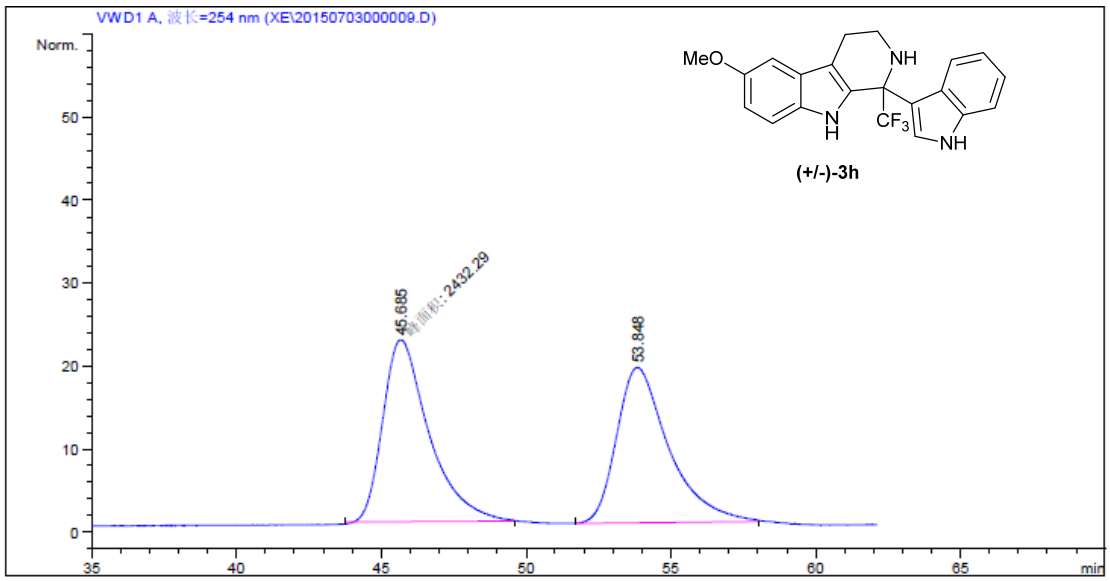
#	[min]		[min]	mAU	*s	[mAU	]	%
1	16.709	VV	0.7160	2.06752e4		427.21902		90.4174
2	27.021	MM	0.9530	2191.19409		38.31918		9.5826



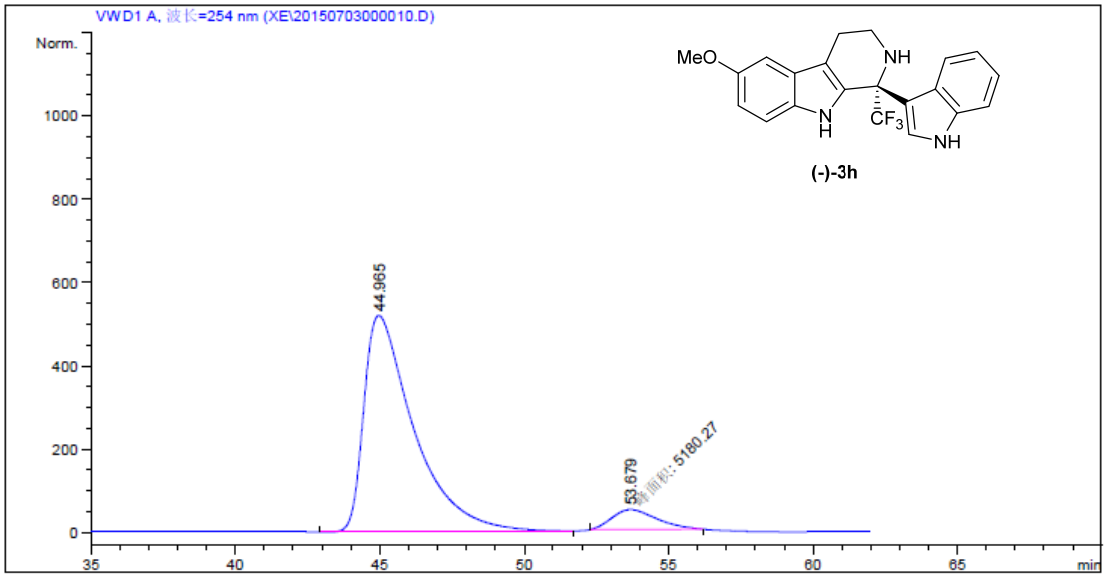
#	[min]		[min]	mAU	*s	[mAU	]	%
1	14.687	VB	0.7004	1.01545e4		208.05898		50.7159
2	21.962	VB	0.9894	9867.80762		141.32053		49.2841



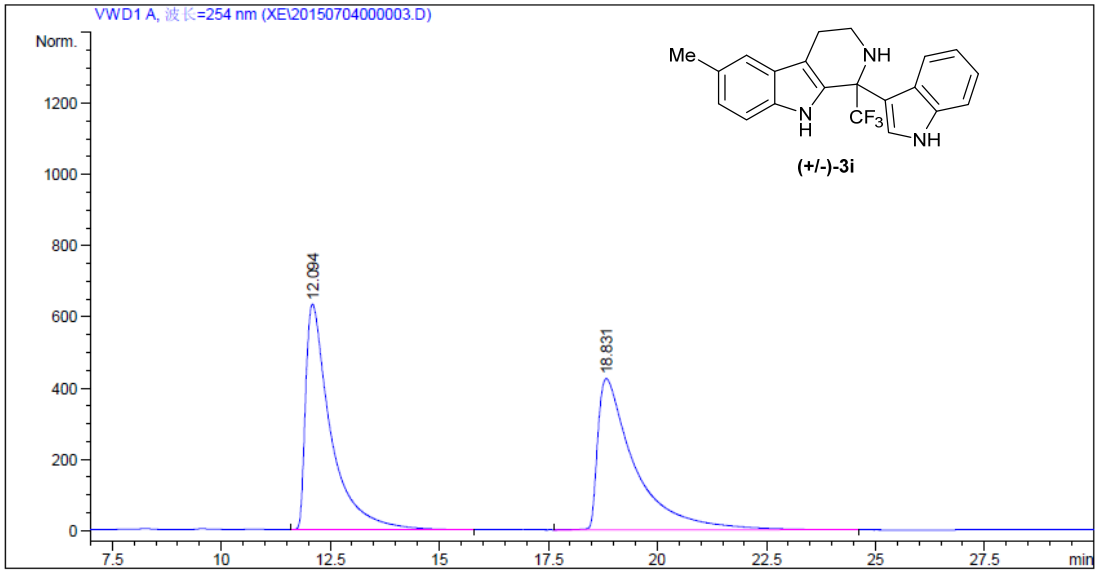
#	[min]		[min]	mAU	*s	[mAU	]	%
1	14.622	VB	0.7192	1.44455e4		298.36206		87.6639
2	22.171	MM	0.9512	2032.78210		35.61833		12.3361



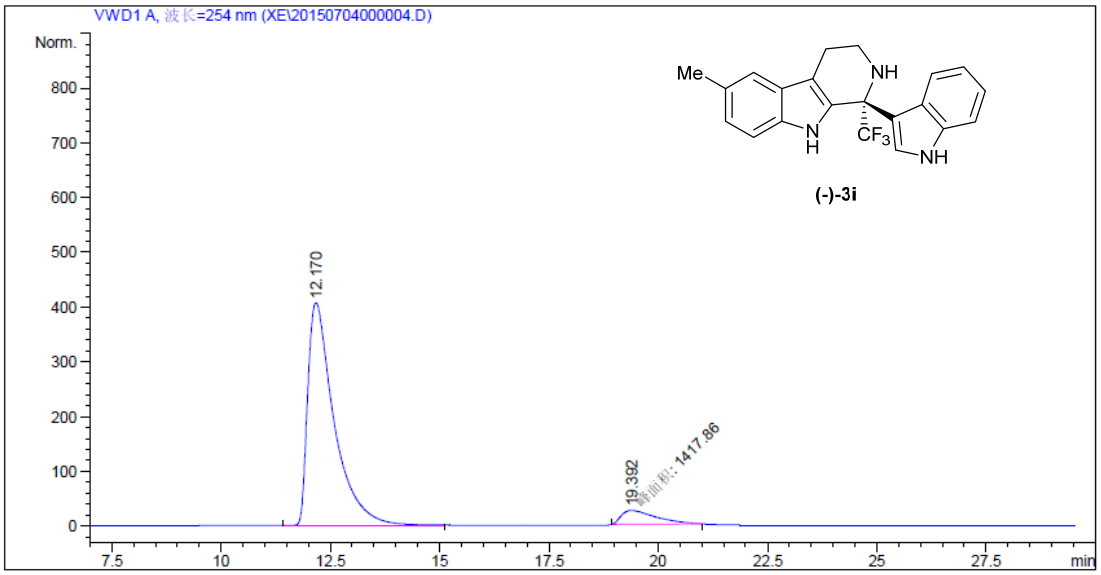
#	[min]		[min]	mAU	*s	[mAU]	%
1	45.685	MM	1.8485	2432.28564		21.93066	50.8639
2	53.848	BB	1.5680	2349.65894		18.73512	49.1361



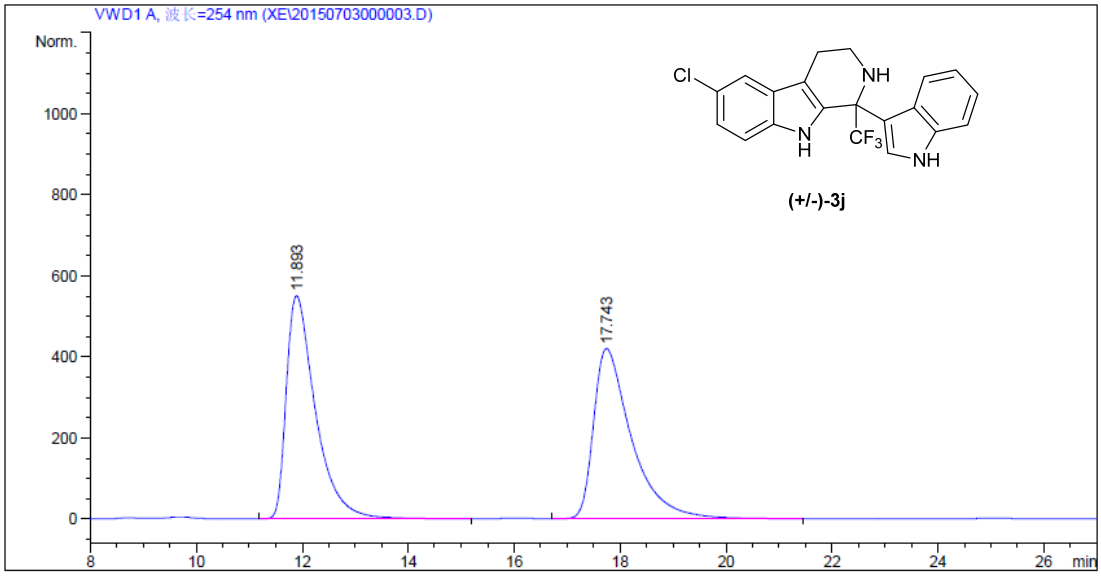
#	[min]		[min]	mAU	*s	[mAU]	%
1	44.965	VB	1.7554	6.33055e4		519.93408	92.4360
2	53.679	MM	1.8044	5180.26611		47.84729	7.5640



#	[min]		[min]	mAU *s	[mAU]	%
1	12.094	VV	0.5793	2.54962e4	634.76239	50.2475
2	18.831	VB	0.8388	2.52450e4	424.88431	49.7525

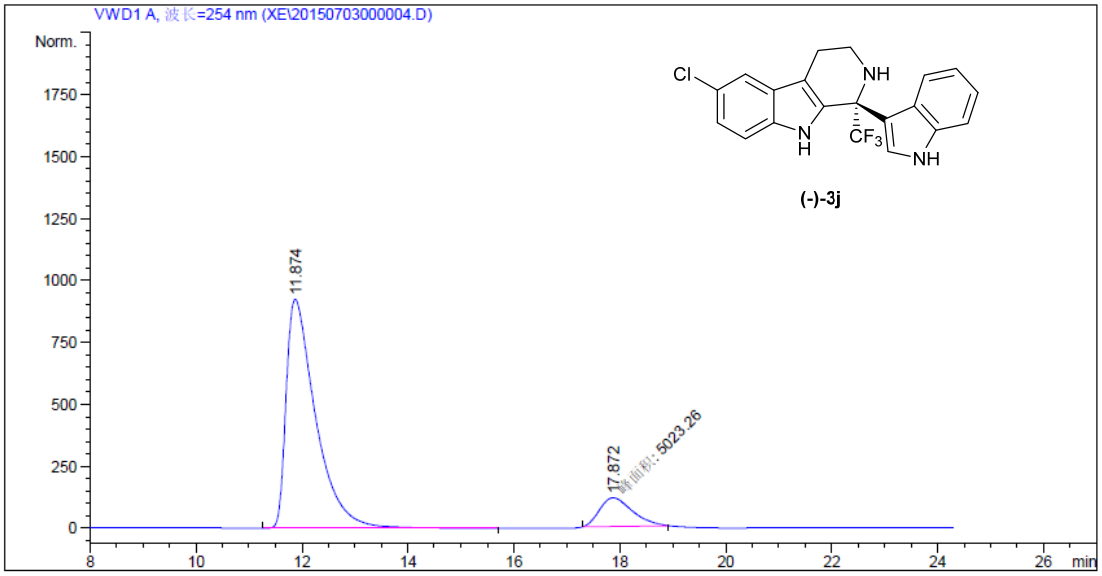


#	[min]		[min]	mAU *s	[mAU]	%
1	12.170	VV	0.6199	1.70298e4	406.44199	92.3142
2	19.392	MM	0.9241	1417.85522	25.57308	7.6858



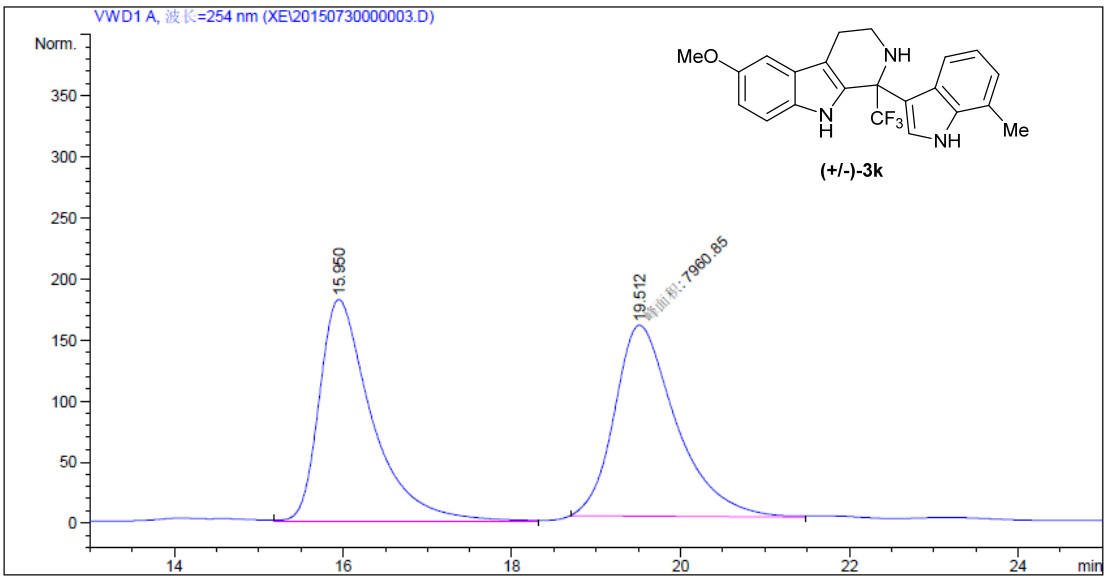
(+/-)-3j

#	[min]		[min]	mAU *s	[mAU]	%
1	11.893	VB	0.5740	2.10181e4	549.94574	50.1411
2	17.743	VB	0.7355	2.08998e4	419.54880	49.8589

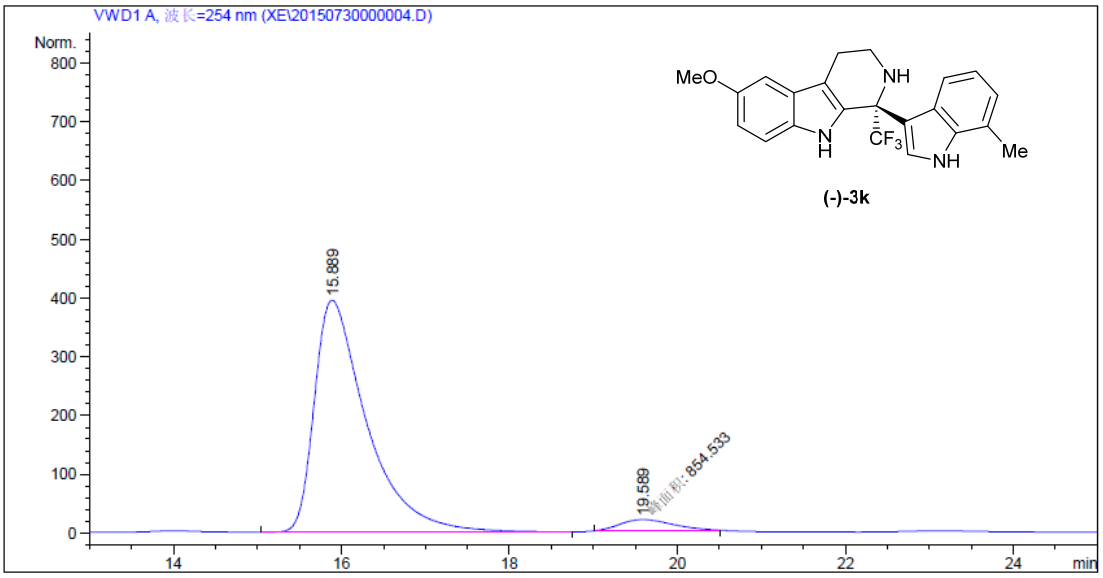


(-)-3j

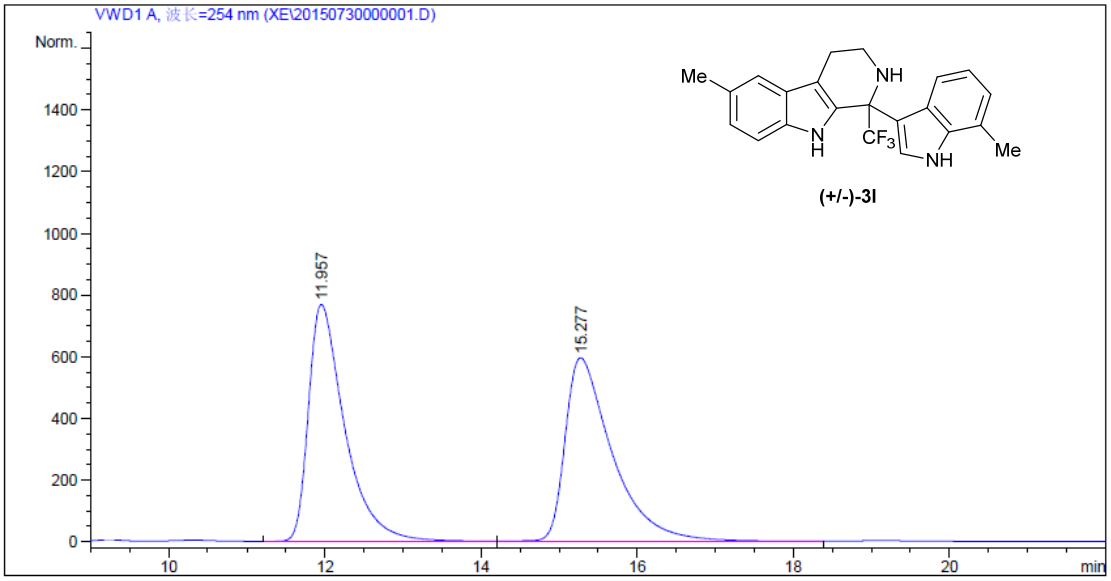
#	[min]		[min]	mAU *s	[mAU]	%
1	11.874	BV	0.5769	3.57473e4	923.36774	87.6792
2	17.872	MM	0.7217	5023.25928	116.00944	12.3208



#	[min]		[min]	mAU	*s	[mAU	]	%
1	15.950	VV	0.6409	7838.77881		181.44501		49.6137
2	19.512	MM	0.8482	7960.84766		156.42931		50.3863

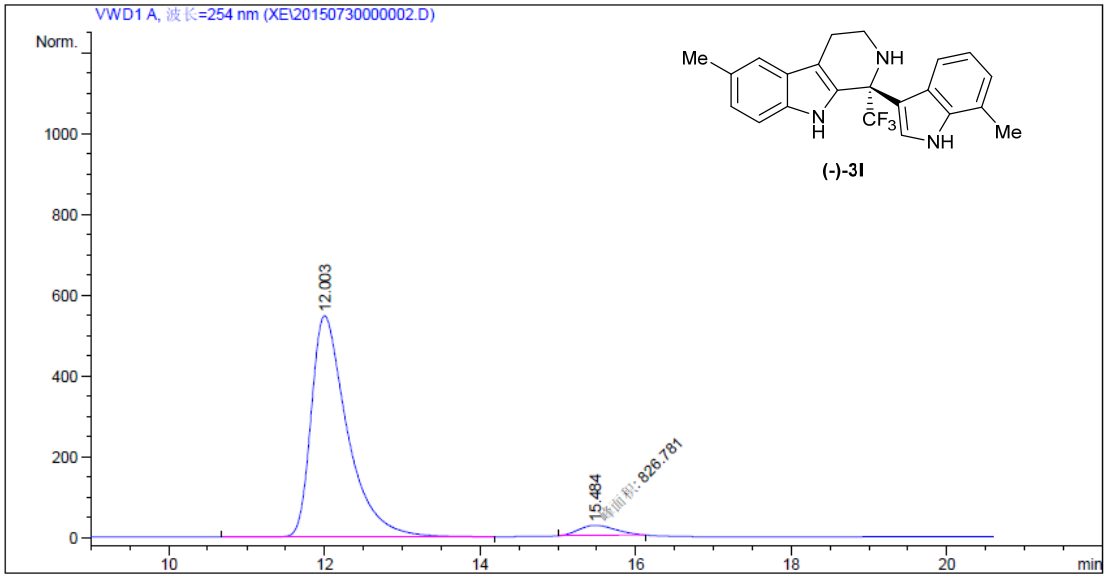


#	[min]		[min]	mAU	*s	[mAU	]	%
1	15.889	VV	0.6413	1.71762e4		394.98169		95.2607
2	19.589	MM	0.7428	854.53326		19.17427		4.7393



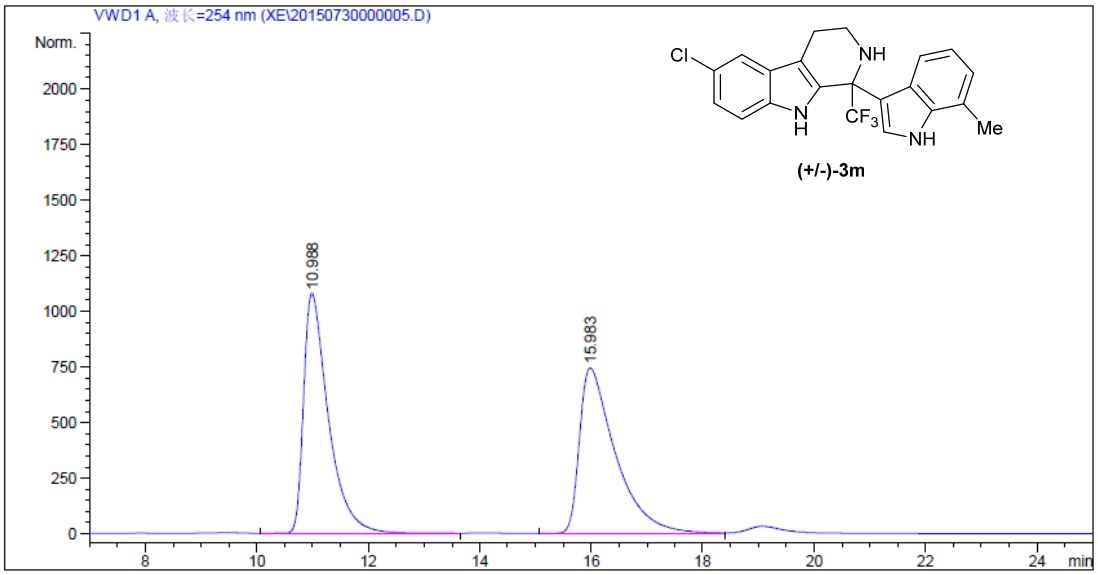
(+/-)-3l

#	[min]		[min]	mAU	*s	[mAU	]	%
1	11.957	VV	0.4828	2.48723e4		767.77832		49.7882
2	15.277	VV	0.6231	2.50840e4		594.72913		50.2118



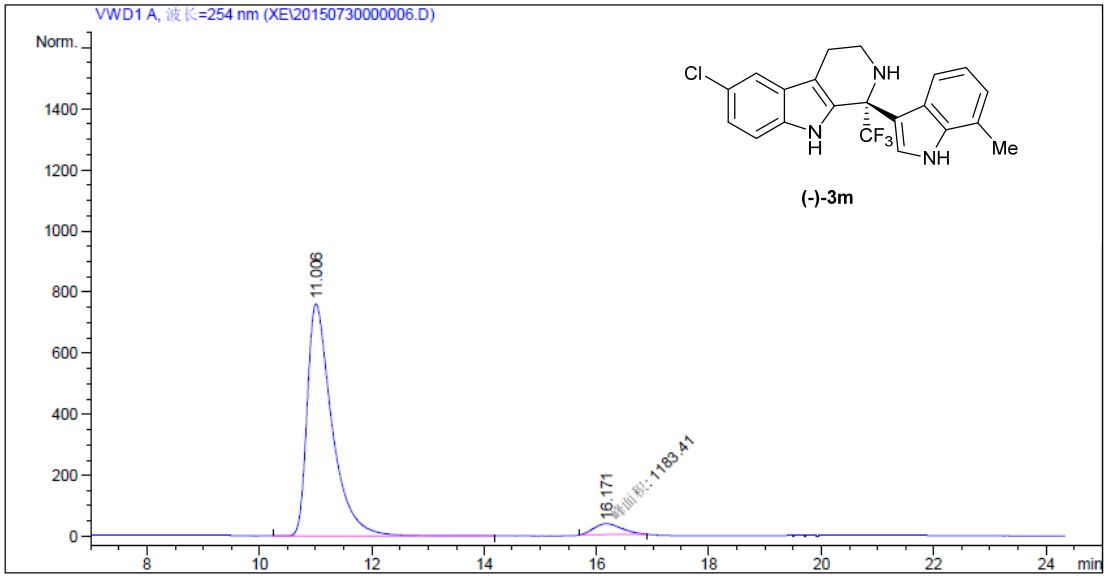
(-)-3l

#	[min]		[min]	mAU	*s	[mAU	]	%
1	12.003	VV	0.4828	1.77511e4		547.88940		95.5496
2	15.484	MM	0.5453	826.78094		25.26896		4.4504



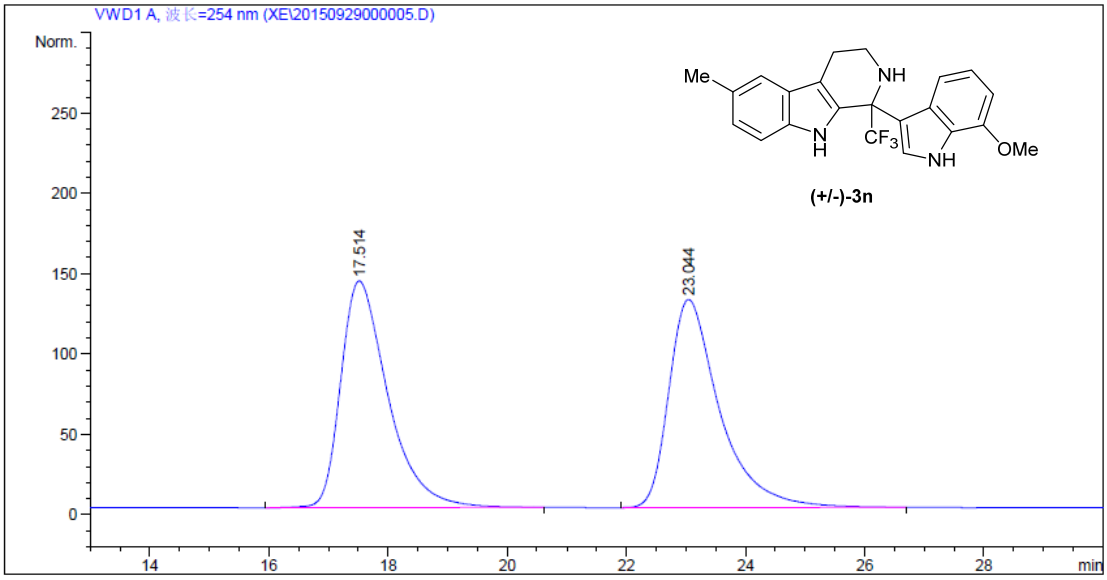
(+/-)-3m

#	[min]		[min]	mAU	*s	[mAU	]	%
1	10.988	VV	0.4644	3.35467e4		1079.76123		50.0059
2	15.983	VV	0.6568	3.35387e4		744.20361		49.9941



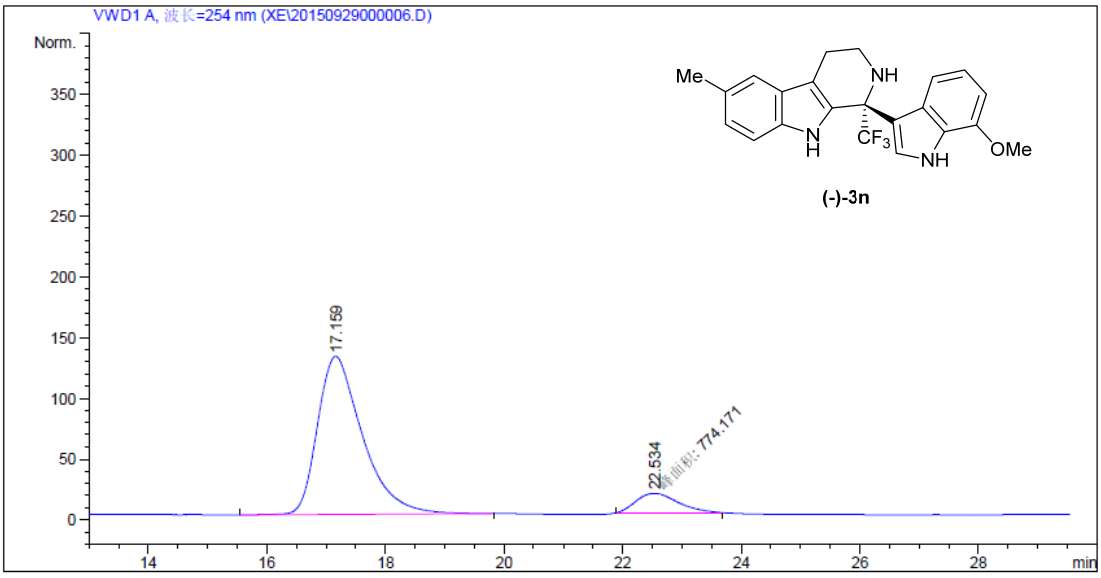
(-)-3m

#	[min]		[min]	mAU	*s	[mAU	]	%
1	11.006	VV	0.4564	2.33004e4		760.52673		95.1666
2	16.171	MM	0.5656	1183.40564		34.87301		4.8334



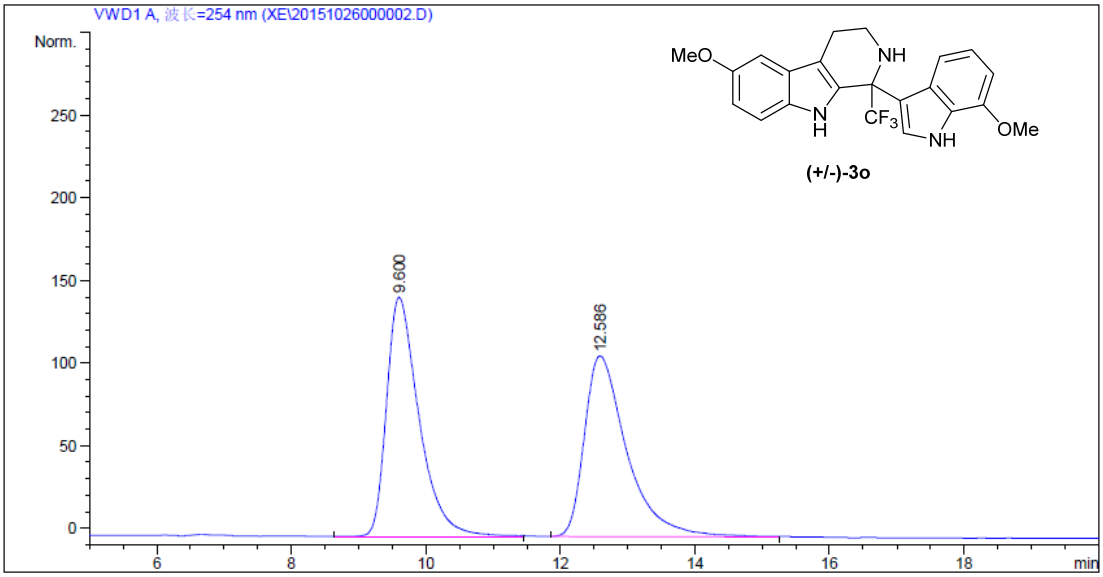
(+/-)-3n

#	[min]		[min]	mAU	*s	[mAU]	%
1	17.514	BB	0.8487	7765.08398	141.11661	50.2645
2	23.044	BB	0.8929	7683.36035	129.54201	49.7355

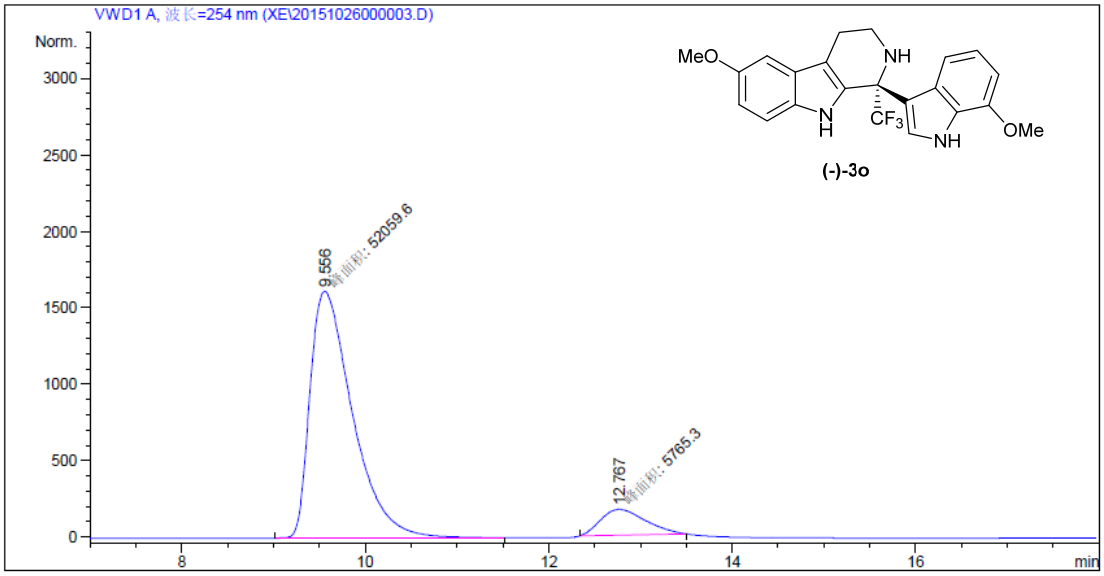


(-)-3n

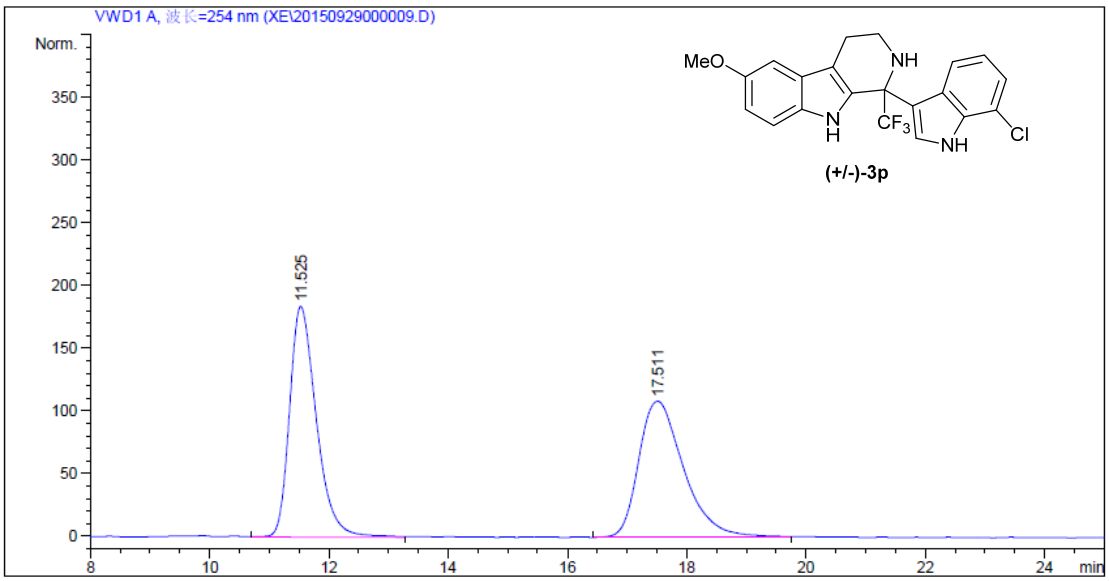
#	[min]		[min]	mAU	*s	[mAU]	%
1	17.159	BB	0.7895	6843.82275	129.88455	89.8376
2	22.534	MM	0.8174	774.17053	15.78443	10.1624



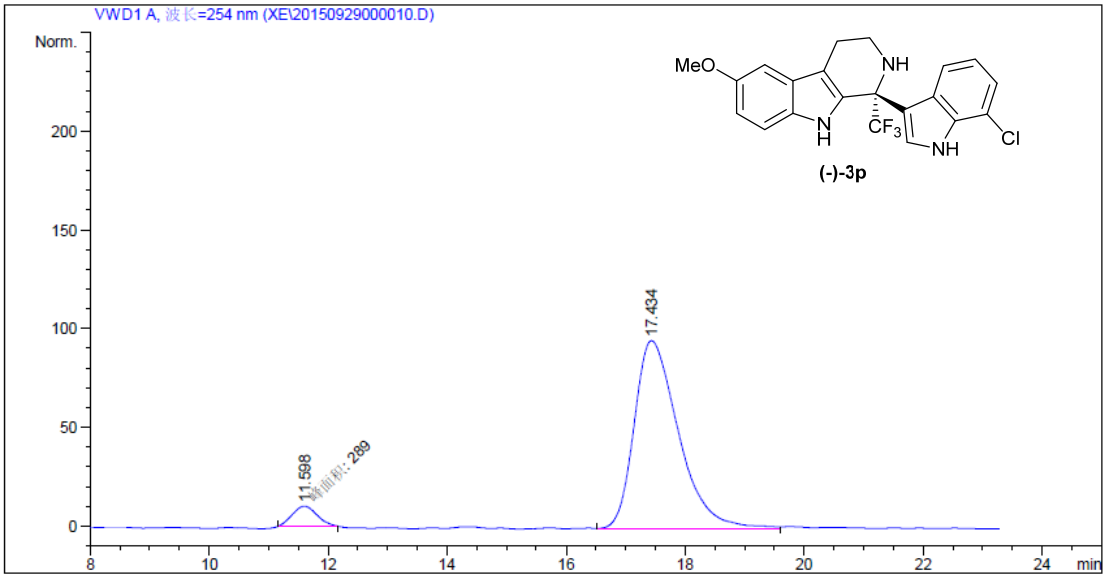
#	[min]		[min]	mAU *s	[mAU]	%
1	9.600	VB	0.5030	4868.78223	144.78682	50.3416
2	12.586	BB	0.6609	4802.70459	109.36222	49.6584



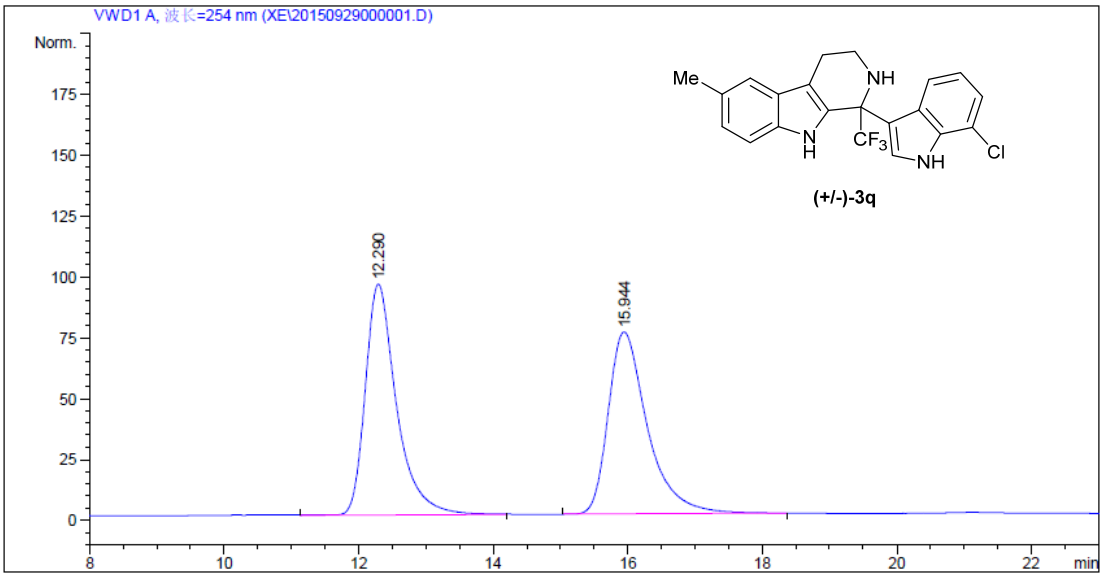
#	[min]		[min]	mAU *s	[mAU]	%
1	9.556	MM	0.5380	5.20596e4	1612.78088	90.0297
2	12.767	MM	0.5688	5765.30469	168.92665	9.9703



#	[min]		[min]	mAU	*s	[mAU	]	%
1	11.525	VV	0.4787	5763.13086		184.14456		50.2020
2	17.511	VV	0.7942	5716.74170		108.68918		49.7980

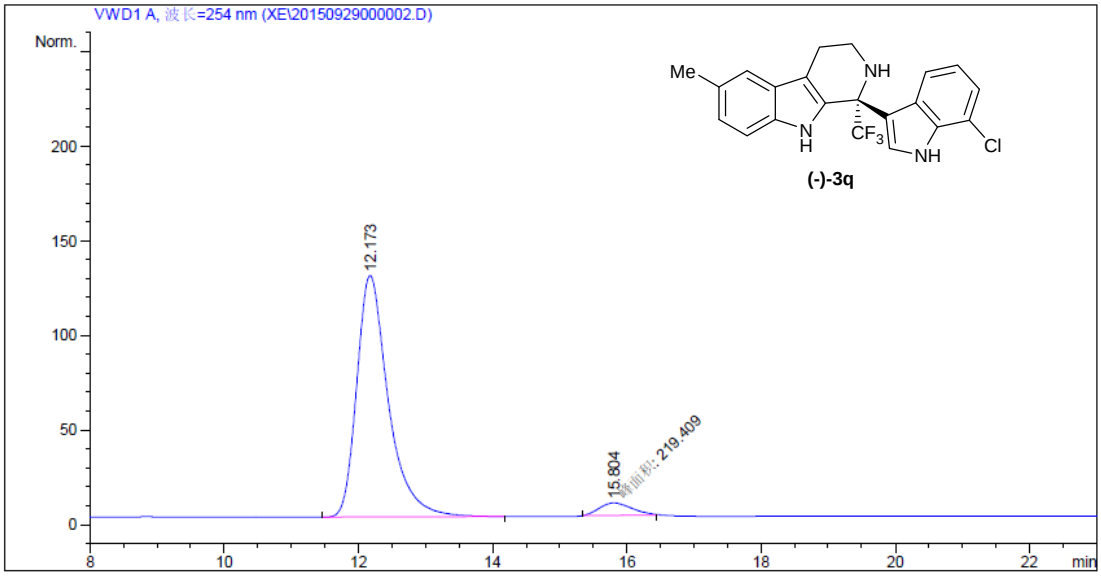


#	[min]		[min]	mAU	*s	[mAU	]	%
1	11.598	MM	0.4775	288.99982		10.08676		5.4870
2	17.434	VV	0.7978	4977.99951		95.43887		94.5130



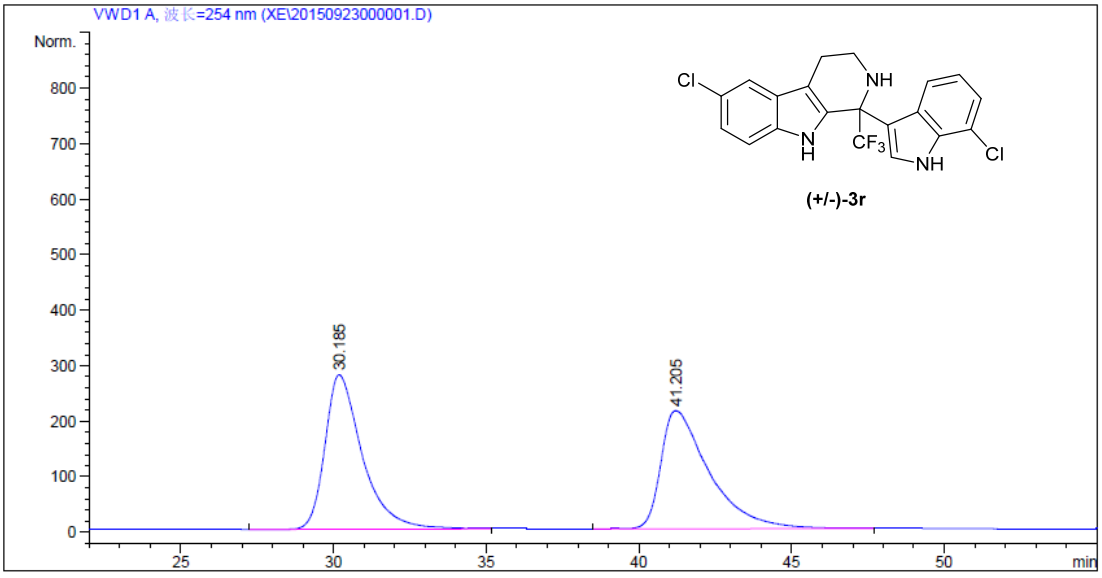
(+/-)-3q

#	[min]		[min]	mAU	*s	[mAU]	%
1	12.290	VB	0.4797	3048.13086	94.85743	50.0648
2	15.944	BB	0.6113	3040.24585	74.76701	49.9352

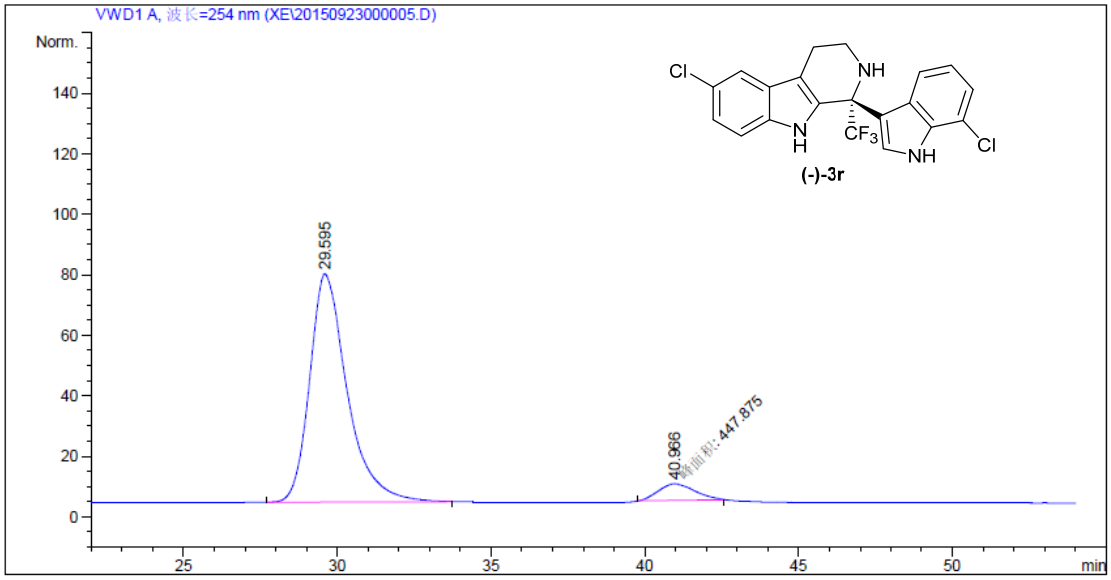


(-)-3q

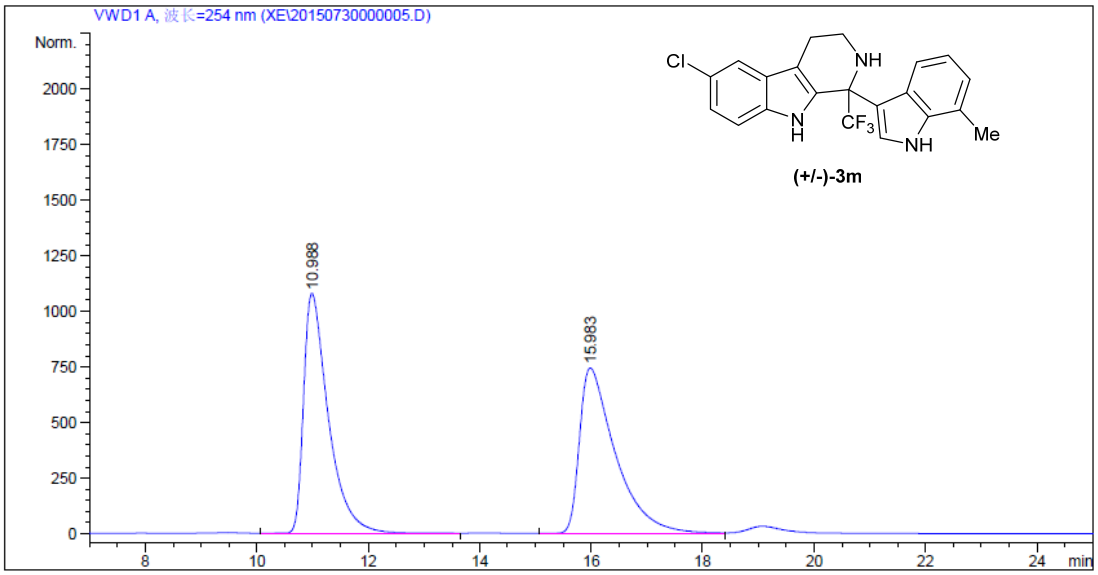
#	[min]		[min]	mAU	*s	[mAU]	%
1	12.173	BB	0.4897	4179.72754	127.66871	95.0124
2	15.804	MM	0.5574	219.40929	6.56106	4.9876



#	[min]		[min]	mAU	*s	[mAU	]	%
1	30.185	BB	1.2816	2.37387e4		278.01398		50.3099
2	41.205	BB	1.5253	2.34462e4		212.61732		49.6901

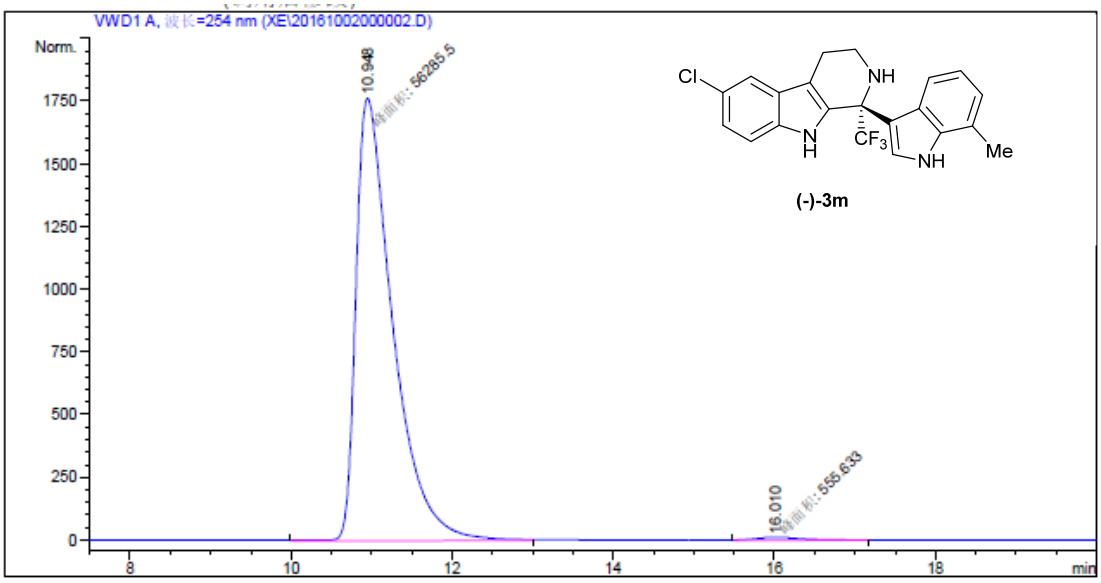


#	[min]		[min]	mAU	*s	[mAU	]	%
1	29.595	BB	1.2643	6406.29004		75.45031		93.4656
2	40.966	MM	1.3576	447.87543		5.49851		6.5344

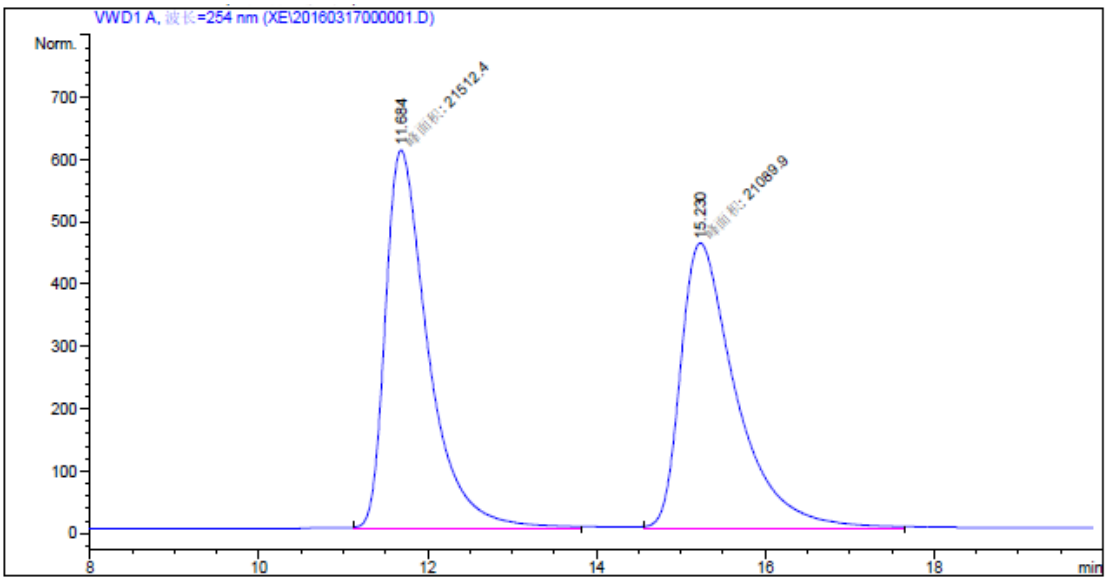


#	[min]		[min]	mAU	*s	[mAU]	%
1	10.988	VV	0.4644	3.35467e4		1079.76123	50.0059
2	15.983	VV	0.6568	3.35387e4		744.20361	49.9941

After one recrystallization from EA-Hexane

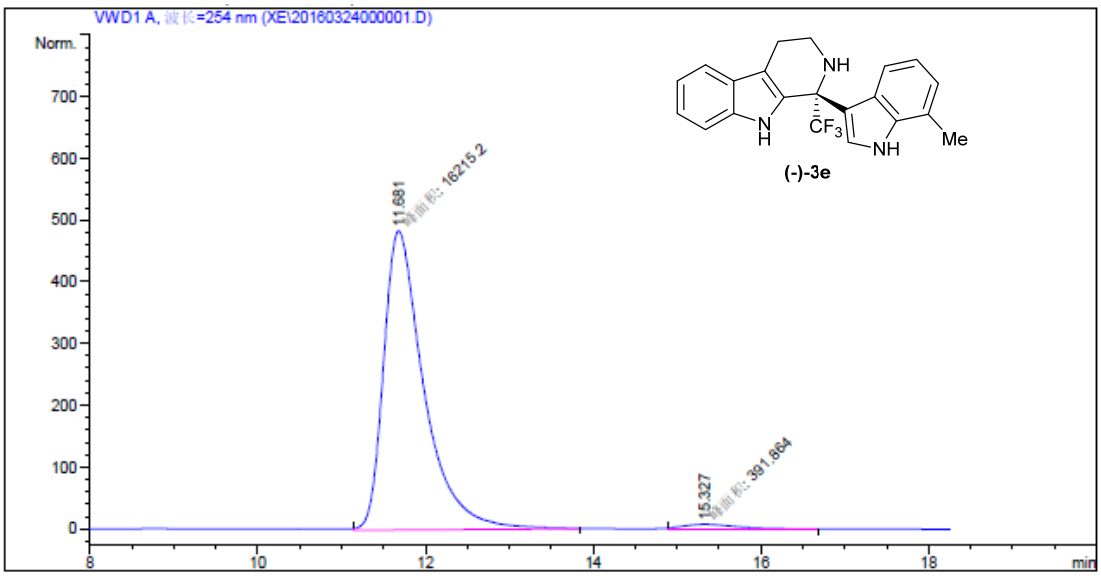


#	[min]		[min]	mAU	*s	[mAU]	%
1	10.948	MM	0.5314	5.62855e4		1765.43481	99.0225
2	16.010	MM	0.7839	555.63281		11.81282	0.9775



#	[min]		[min]	mAU *s	[mAU]	%
1	11.684	MM	0.5898	2.15124e4	607.88580	50.4958
2	15.230	MM	0.7661	2.10899e4	458.81381	49.5042

After one recrystallization from EA-Hexane



#	[min]		[min]	mAU *s	[mAU]	%
1	11.681	MM	0.5583	1.62152e4	484.02579	97.6404
2	15.327	MM	0.7944	391.86407	8.22114	2.3596