Supplementary Information

Synthesis and Application of A New Chiral Monodentate Spiro Phosphoramidite Ligand Based on Hexamethyl-1,1'-spirobiindane Backbone in Asymmetric hydroamination/arylation of alkenes

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General Information

All reactions were carried out in oven-dried glassware with magnetic stirring. All reagents were purchased at the commercial quality and used without further purification and all solvents were dried and purified according to standard methods prior to use. NMR spectrums were recorded on a Bruker DPX 400 NMR spectrometer at 400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR, 162 MHz for ^{31}P. The chemical shifts were reported in $CDCl_3$ or DMSO-d_6 with tetramethylsilane (TMS) as internal standard. 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). Infrared spectra were recorded on an ATR-FTIR spectrometer. HRMS were obtained using EI ionization and MS were obtained using ESI ionization. Optical rotations were determined using a Perkin Elmer Model 341 polarimeter at 25 °C. Enantiomeric excesses (ee) were determined by chiral high-performance liquid chromatography. HPLC analysis was performed using Chiralcel columns (Chiralcel OD-H, AD-H, IC-3, IF-3 column). Analytical grade solvents for the column chromatography were used as received. N-Allylurea Substrates **9** were prepared according to the reported procedure (B. A. Hopkins and J. P. Wolfe, *Angew. Chem. Int. Ed.*, 2012, **51**, 9886).

1. Procedure for Synthesis and Resolution of Diols 1

A 500 mL round bottom flask was charged with Bisphenol C (BPC, 51.2 g, 0.2 mol) and methanesulfonic acid (160 mL), and then the mixture was stirred at room temperature for 3 days. Additional 100 mL methanesulfonic acid was added to the reaction system at the forth day and the reaction was continued for another 3 days. The mixture was poured directly into the crushed ice and filtered. The filter cake was washed sequentially with saturated $NaHCO_3$ and hot water. Then, the residue was recrystallized with ethyl acetate/petroleum ether followed by ethanol/water and dried to afford **1** as a white solid (20.6 g, 92% yield).

A solution of **1** (1.68 g, 5 mmol), triethylamine (Et_3N) (3.2 mL, 23 mmol) and 4-dimethyl-aminopyridine (DMAP) (62 mg, 0.5 mmol) in 50 mL methylene chloride was treated over circa 30 minutes with *N*-tosyl-*L*-phenylalanine acid chloride (3.71 g, 11 mmol). The resulting mixture stirred at room temperature overnight then was washed with 1 M hydrochloric acid, brine, dried

with anhydrous sodium sulfate and concentrated in vacuo to afford **2** as a mixture of diastereomeric diester (1:1). After silica gel column chromatography (eluent: methylene chloride / methyl alcohol = 400 / 1), **2a** was obtained in 44% yield, **2b** was obtained in 43% yield.

A solution of **2b** (2.82 g, 3 mmol) and hydrazine hydrate (1.5 mL, 30 mmol, 10 equiv.) in 30 mL THF (1 g / 10 mL) was heated at reflux overnight then concentrated in vacuo, redissolved in methylene chloride, then washed with 4M hydrochloric acid, brine, dried with anhydrous sodium sulfate and concentrated in vacuo followed by flash chromatography to provide (*S*)-**1** as a colorless solid (990 mg, 98% yield). Using **2a** as the starting material in above procedure, (*R*)-**1** was also obtained by the same method in 98% yield.

3. Procedure for Synthesis of Chiral Spiro Phosphoramidite 8.

(*S*)-1 (6.7 g, 20 mmol) was dissolved in methylene chloride (70 mL) under nitrogen, and *N*-bromosuccinimide (NBS, 7.3 g, 41 mmol) was added slowly in several portions at 0 ^{o}C. The yellow solution was stirred at room temperature for additional 2.5 h. Then saturated $NaHSO_3$ (30 mL) was added and stirred for 15 minutes. The organic phase was washed by water, saturated brine in sequence and dried over anhydrous Na_2SO_4. The residue was purified by flash chromatography (ethyl acetate/petroleum ether = 1/30) to give **(*S*)-3** (9.7 g, 98% yield).

To a solution of **(*S*)-3** (7.4 g, 15 mmol) and pyridine (3.7 mL, 45 mmol) in methylene chloride (80 mL), triflic anhydride (6.3 mL, 37.5 mmol) was added dropwise at 0 ^{o}C under a nitrogen atmosphere. The mixture was stirred at room temperature for additional 4.5 h. The resulting solution was diluted with dichloromethane, washed with 5% HCl aqueous, brine, saturated $NaHCO_3$, and brine, and dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by flash chromatography on a silica gel column (ethyl acetate/petroleum ether = 1/50) to obtain the product **(*S*)-4** as a white solid (10.8 g, 95% yield).

Under nitrogen, to a mixture solution of **(*S*)-4** (7.58 g, 10 mmol), $PdCl_2(PPh_3)_2$ (280 mg, 0.4 mmol), and 1,3-bis(diphenylphosphino)propane (210 mg, 0.5 mmol) in DMF (80 mL), triethylamine (17 mL, 120 mmol) was added dropwise at 0℃ followed by the addition of formic acid (3 mL, 80 mmol). After completing addition, the solution was raised to 80 ^{o}C and reacted for 1.5 h. After cooling to room temperature, the resulting mixture was diluted with ethyl acetate and washed sequentially with water, saturated $NaHCO_3$, and brine. The organic layer was dried over

anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography (ethyl acetate / petroleum ether = 1/100) to afford product **(*S*)-5** as a white solid (4.44 g, 96% yield).

Under nitrogen，a mixture of **(*S*)-5** (4.62 g, 10 mmol) in 50 mL THF was cooled to -78℃，tert-butyl lithium (27.5 mL, 44 mmol, 1.6 M in heptane) was added slowly at this temperature followed by additional reaction for another 3 h, anhydrous DMF (4 mL, 50 mmol) was added and continued for another 1 hour at this temperature, then warmed slowly to room temperature and stirred overnight. The reaction was quenched by 1M NH_4Cl aqueous, extracted by diethyl ether and washed by water and brine, then dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography (ethyl acetate / petroleum ether = 1/30) to afford product **(*S*)-6** as a yellow solid (3.31 g, 92% yield).

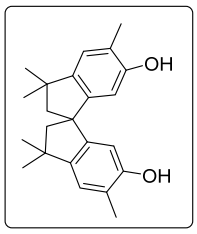
Under nitrogen atmosphere, to a solution of **(*S*)-6** (3.70 g, 8 mmol) in 370 mL methylene chloride, *m*-chloroperbenzoic acid (*m*-CPBA) (6.4 g, 32 mmol, 85% active oxygen content) was added several portions at 0℃ followed by the addition of trifluoroacetic acid (TFA) (1.2 mL, 16 mmol). The mixture was naturally raised to room temperature and stirred overnight. The reaction solution was washed with saturated Na_2SO_3 aqueous, saturated $NaHCO_3$, and brine, and dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was redissolved in 80mL methyl alcohol, 1M NaOH aqueous (32 mL, 32 mmol) was added dropwise at 0℃. After completing addition, the mixture was naturally raised to room temperature and stirred overnight. After removal of the solvent, the residue was redissolved in methylene chloride, acidified by 4M HCl aqueous, washed with brine, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography (ethyl acetate / petroleum ether / glacial acetic acid= 5/100/1) to afford product **(*S*)-7** as a white solid (2.2 g, 82% yield).

At nitrogen atmosphere, to a solution of PCl_3 (5.25 mL, 6 mmol) in 60 mL THF, a solution of lithium bis((R)-1-phenylethyl)amide prepared from bis((R)-1-phenylethyl)amide (6 mmol) and butyllithium (2.4 mL, 6 mmol, 2.5 M solution in hexane) in 30 mL THF at -30℃ was added dropwise at -78℃, the reaction mixture was stirred at this temperature for 1h, naturally raised up to room temperature and stirred overnight, the excess PCl_3 was evaporated in vacuo, then redissolved in 20 mL THF and evaporated in vacuo three times to remove remaining PCl_3, finally THF (10 mL) was added to form a solution of 1,1-dichloro-N,N-bis((R)-1-

phenylethyl)Phosphan-amine.

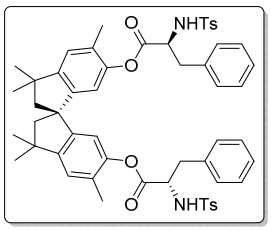
At nitrogen atmosphere, to a solution of diols **(*S*)-7** (336 mg, 1 mmol) in 5 mL THF, Et_3N (1.4 mL, 10 mmol) was added dropwise at 0℃, followed by addition of a freshly prepared 1,1-dichloro-N,N-bis((R)-1-phenylethyl)phosphanamine solution, the reaction mixture was stirred at this temperature for 2h, naturally raised up to room temperature and stirred overnight. The solvent was removed in vaccum and the residue was purified by flash chromatography (Et_3N / petroleum ether = 1/100) to afford product **(*S,R,R*)-8** as white solids (63% yield).

Using **(*R*)-1** as the starting material in above procedures, **(*R,R,R*)-8** was also obtained by the same method.



3,3,3',3',5,5'-hexamethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-6,6'-diol (1)

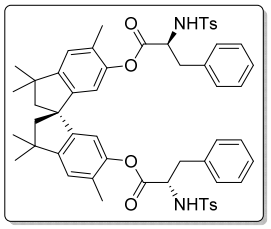
20.1 g, 92% yield; white solid, m.p. 249-250 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 6.91 (s, 2H), 5.84 (s, 2H), 3.93 (s, 2H), 2.29 (d, *J* = 13.0 Hz, 2H), 2.20 (s, 6H), 2.15 (d, *J* = 13.0 Hz, 2H), 1.37 (s, 6H), 1.28 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.18, 150.05, 144.54, 123.55, 122.95, 110.50, 59.40, 57.00, 43.12, 31.88, 30.15, 15.97; IR (film): γ= 3515, 2952, 2862, 1615, 1497, 1411, 1361, 1313, 1288, 1275, 1207, 1149, 1136, 1070, 1014, 886, 858, 758, 668 cm^{-1}; HRMS (EI, GC-TOF): calcd for $C_{23}H_{28}O_2$ 336.2089, found 336.2085.



(*R*)-3,3,3',3',5,5'-hexamethyl-6'-((tosyl-L-phenylalanyl)oxy)-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-6-yl tosyl-L-phenylalaninate (2a)

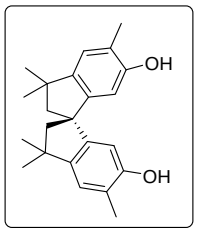
2.07 g, 44% yield; white solid, m.p. 112-114 ^oC; $[\alpha]_D^{20}$ = -5.1 (*c*1.0, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 8.2 Hz, 4H), 7.17 (d, J = 8.1 Hz, 4H), 7.12-6.99 (m, 10H), 6.95 (s, 2H), 5.91 (s, 2H), 5.34 (d, J = 9.1 Hz, 2H), 4.42-4.36 (m, 2H), 3.32-2.94 (m, 4H), 2.32 (s, 6H), 2.27 (d, J =

13.1 Hz, 2H), 2.07 (d, J = 13.1 Hz, 2H), 1.90 (s, 6H), 1.35 (s, 6H), 1.28 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.59, 150.22, 149.20, 148.22, 143.63, 136.93, 134.91, 129.71, 129.54, 128.75, 128.63, 127.24, 127.10, 124.18, 116.89, 77.27, 59.34, 56.92, 56.76, 43.18, 39.88, 31.59, 30.19, 29.72, 21.45, 16.15; IR (film): γ= 3282, 3062, 3028, 2955, 2916, 2865, 1759, 1596, 1485, 1452, 1336, 1268, 1235, 1165, 1115, 1092 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{55}H_{58}N_2O_8S_2Na^+$ $[M\text{-}Na]^+$ 961.3532, found 961.3446.



(*S*)-3,3,3',3',5,5'-hexamethyl-6'-((tosyl-L-phenylalanyl)oxy)-2,2',3,3'-tetrahydro-1,1'-spirobi[inden]-6-yl tosyl-L-phenylalaninate (2b)

2.02 g, 43% yield; white solid, m.p. 105-107 °C; $[\alpha]_D^{20}$ = -79.8 (*c*1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 8.3 Hz, 4H), 7.19 (d, J = 8.1 Hz, 4H), 7.13-7.05 (m, 4H), 7.03-6.92 (m, 8H), 5.95 (s, 2H), 5.29 (d, J = 8.9 Hz, 2H), 4.42-4.37(m, 2H), 3.14 (d, J = 6.1 Hz, 4H), 2.35 (s, 6H), 2.25 (d, J = 13.2 Hz, 2H), 2.08 (d, J = 13.2 Hz, 2H), 1.85 (s, 6H), 1.31 (s, 6H), 1.27 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.43, 150.30, 149.28, 148.18, 143.72, 136.70, 134.71, 129.76, 129.67, 128.57, 128.54, 127.29, 127.18, 124.24, 116.84, 77.27, 59.42, 56.91, 56.34, 43.19, 39.85, 31.50, 30.27, 29.73, 21.49, 15.96; IR (film): γ= 3277, 3062, 3028, 2955, 2925, 2869, 1759, 1596, 1485, 1452, 1339, 1270, 1160, 1117, 1092 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{55}H_{58}N_2O_8S_2Na^+$ $[M\text{-}Na]^+$ 961.3532, found 961.3444.



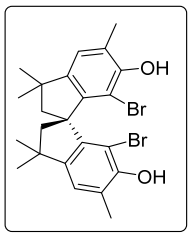
(*S*)-3,3,3',3',5,5'-hexamethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-6,6'-diol [(*S*)-1]

0.99 g, 98% yield; white solid, m.p. 216-218 °C; $[\alpha]_D^{20}$ = -28.7 (*c*1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.85 (s, 2H), 6.03 (s, 2H), 5.63 (s, 2H), 2.28 (d, J = 12.9 Hz, 2H), 2.19 (s, 6H), 2.06 (d, J = 12.9 Hz, 2H), 1.34 (s, 6H), 1.29 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.63, 149.54, 144.62, 124.16, 122.68, 110.03, 59.45, 57.14, 42.92, 31.76, 30.63, 16.12; IR (film): γ=

3289, 2952, 2918, 2863, 1621, 1491, 1467, 1417, 1311, 1286, 1154 cm^{-1}; HRMS (EI, GC-TOF): calcd for $C_{23}H_{28}O_2$ 336.2089, found 336.2091.

(*R*)-3,3,3',3',5,5'-hexamethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-6,6'-diol [(*R*)-1]

0.99 g, 98% yield; white solid, m.p. 216-217 ^oC; $[\alpha]_D^{20}$ = +28.6 (*c*1.0, CH_2Cl_2); HRMS (EI, GC-TOF): calcd for $C_{23}H_{28}O_2$ 336.2089, found 336.2092. Spectroscopic data are identical to (*S*)-**1**.

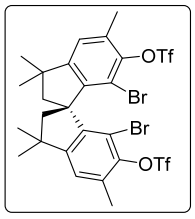


(*S*)-7,7'-dibromo-3,3,3',3',5,5'-hexamethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-6,6'-diol [(*S*)-3]

9.7 g, 98% yield; white solid, m.p. 260-262 ^oC; $[\alpha]_D^{20}$ = 116.2 (*c* 0.6, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 6.87 (s, 2H), 5.57 (s, 2H), 2.46 (d, J = 13.1 Hz, 2H), 2.31 (s, 6H), 2.25 (d, J = 13.0 Hz, 2H), 1.39 (s, 6H), 1.32 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.24, 145.60, 142.67, 124.51, 123.60, 107.15, 60.85, 55.56, 43.06, 32.58, 29.28, 17.12; IR (film): = 3506, 2958, 2928, 2861, 1610, 1558, 1466, 1411, 1382, 1372, 1360, 1325, 1313, 1292, 1268, 1213, 1195, 1159, 1145, 1133, 1080, 1037 cm^{-1}; HRMS (EI, GC-TOF): calcd for $C_{23}H_{26}Br_2O_2$ 492.0300, found 492.0299.

(*R*)-7,7'-dibromo-3,3,3',3',5,5'-hexamethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-6,6'-diol [(*R*)-3]

9.7 g, 98% yield; white solid, m.p. 260-261 ^oC; $[\alpha]_D^{20}$ = -63.1 (*c* 1.0, CH_2Cl_2); HRMS (EI, GC-TOF): calcd for $C_{23}H_{26}Br_2O_2$ 492.0300, found 492.0297. Spectroscopic data are identical to (*S*)-**3**.

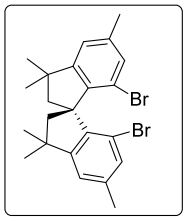


(*S*)-7,7'-dibromo-3,3,3',3',5,5'-hexamethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-6,6'-diyl bis(trifluoromethanesulfonate)[(*S*)-4]

10.8 g, 95% yield; white solid, m.p. 168-170 ^{o}C; $[\alpha]_D^{20}$ = 44.0 (*c*1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (s, 2H), 2.55 (d, J = 13.2 Hz, 2H), 2.45 (s, 6H), 2.30 (d, J = 13.2 Hz, 2H), 1.42 (s, 6H), 1.36 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.73, 145.11, 144.55, 132.61, 124.81, 123.32, 120.13, 116.94, 113.76, 113.36, 61.27, 54.90, 43.43, 32.37, 28.82, 18.17; IR (film): γ= 2962, 2868, 1609, 1555, 1418, 1365, 1318, 1295, 1210, 1137, 1055 cm^{-1}; HRMS (EI, GC-TOF): calcd for $C_{25}H_{24}Br_2O_6S_2F_6$ 755.9285, found 755.9286.

(*R*)-7,7'-dibromo-3,3,3',3',5,5'-hexamethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-6,6'-diyl bis(trifluoromethanesulfonate)[(*R*)-4]

10.7 g, 94% yield; white solid, m.p. 205-207 ^{o}C; $[\alpha]_D^{20}$ = -44.0 (*c*1.0, CH_2Cl_2); HRMS (EI, GC-TOF): calcd for $C_{25}H_{24}Br_2O_6S_2F_6$ 755.9285, found 755.9286. Spectroscopic data are identical to (*S*)-**4**.

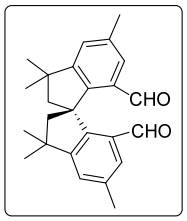


(*S*)-7,7'-dibromo-3,3,3',3',5,5'-hexamethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene][(*S*)-5]

4.44 g, 96% yield; white solid, m.p. 185-187 ^{o}C; $[\alpha]_D^{20}$ = 107.8 (*c*1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (s, 2H), 6.93 (s, 2H), 2.52 (d, J = 13.0 Hz, 2H), 2.33 (s, 6H), 2.24 (d, J = 13.0 Hz, 6H), 1.41 (s, 6H), 1.34 (s, 6H); ^{13}C NMR (100 MHz, CDCl3) δ 154.92, 142.48, 138.93, 131.88, 122.34, 119.14, 59.79, 55.35, 43.43, 32.57, 28.95, 21.01; IR (film): γ= 3425, 3049, 3021, 2961, 2920, 2860, 2724, 1731, 1604, 1557, 1458, 1442, 1380, 1359, 1317, 1292, 1276, 1264, 1223, 1209, 1170, 1142, 1093, 1065 cm^{-1}; HRMS (EI, GC-TOF): calcd for $C_{23}H_{26}Br_2$ 460.0401, found 460.0400.

(*R*)-7,7'-dibromo-3,3,3',3',5,5'-hexamethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene][(*R*)-5]

4.42 g, 95% yield; white solid, m.p. 201-203 ^{o}C; $[\alpha]_D^{20}$ = -107.2 (*c* 1.0, CH_2Cl_2); HRMS (EI, GC-TOF): calcd for $C_{23}H_{26}Br_2$ 460.0401, found 460.0400. Spectroscopic data are identical to (*S*)-**5**.

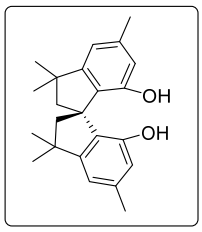


(*S*)-3,3,3',3',5,5'-hexamethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-7,7'-dicarbaldehyde [(*S*)-6]

3.31 g, 92% yield; yellow solid, m.p. 220-222 ^{o}C; $[\alpha]_D^{20}$ = 187.7 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.57 (s, 2H), 7.53 (s, 2H), 7.25 (s, 2H), 2.56 (d, J = 13.2 Hz, 2H), 2.43 (d, J = 13.3 Hz, 2H), 2.41 (s, 6H), 1.45 (s, 6H), 1.40 (s, 6H); ^{13}C NMR (100 MHz, CDCl3) δ 190.54, 153.43, 150.18, 138.27, 130.59, 129.46, 129.24, 59.84, 57.24, 43.43, 32.43, 29.61, 21.17; IR (film): γ= 3359, 2963, 2924, 2866, 1681, 1604, 1573, 1460, 1394, 1383, 1311, 1242, 1162 cm^{-1}; HRMS (EI, GC-TOF): calcd for $C_{25}H_{28}O_2$ 360.2089, found 360.2087.

(*R*)-3,3,3',3',5,5'-hexamethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-7,7'-dicarbaldehyde [(*R*)-6]

3.3 g, 92% yield; yellow solid, m.p. 220-222 ^{o}C; $[\alpha]_D^{20}$ = -181.2 (*c* 1.0, CH_2Cl_2); HRMS (EI, GC-TOF): calcd for $C_{25}H_{28}O_2$ 360.2089, found 360.2089. Spectroscopic data are identical to (*S*)-**6**.



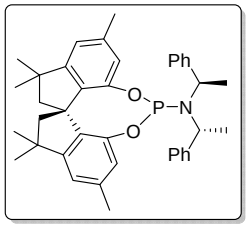
(*S*)-3,3,3',3',5,5'-hexamethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-7,7'-diol [(*S*)-7]

2.2 g, 82% yield; white solid, m.p. 172-174 ^{o}C; $[\alpha]_D^{20}$ = 142.3 (*c*1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, DMSO) δ 6.63 (s, 2H), 6.49 (s, 2H), 4.42 (s, 2H), 2.35 (d, J = 13.4 Hz, 2H), 2.29 (m, 8H), 1.38 (s, 6H), 1.33 (s, 6H); ^{13}C NMR (100 MHz, DMSO) δ 154.01, 152.46, 140.64, 127.12, 116.12, 115.36, 55.92, 53.45, 44.09, 31.88, 29.66, 21.51; IR (film): γ= 3520, 2955, 2925, 2862, 1618, 1585, 1469, 1455, 1447 cm^{-1}; HRMS (EI, GC-TOF): calcd for $C_{25}H_{28}O_4$ 336.2089, found 336.2092.

(*R*)-3,3,3',3',5,5'-hexamethyl-2,2',3,3'-tetrahydro-1,1'-spirobi[indene]-7,7'-diol [(*R*)-7]

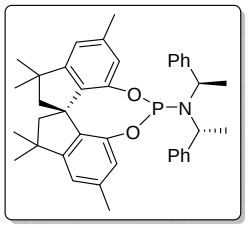
2.2 g, 82% yield; white solid, m.p. 167-168 ^{o}C; $[\alpha]_D^{20}$ = -141.3 (*c* 1.0, CH_2Cl_2); HRMS (EI, GC-TOF): calcd for $C_{25}H_{28}O_4$ 336.2089, found 336.2089. Spectroscopic data are identical to

(*S*)-**7**.



(*S*)-2,4,4,7,7,9-hexamethyl-N,N-bis((R)-1-phenylethyl)-4,5,6,7-tetrahydrodiindeno[7,1-de:1',7'-fg][1,3,2]dioxaphosphocin-12-amine[(*S*,*R*,*R*)-8]

371 mg, 63% yield; white solid, m.p. 62-64 ^{o}C; $[\alpha]_D^{20}$ = -37.8 (*c*1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.15 (m, 6H), 6.98-6.91 (m, 4H), 6.79 (s, 1H), 6.78 (s, 1H), 6.62 (s, 1H), 5.62 (s, 1H), 4.23 (dq, J = 14.1, 7.0 Hz, 2H), 2.43-2.33 (m, 4H), 2.24 (d, J = 12.6 Hz, 1H), 2.07 (d, J = 11.9 Hz, 1H), 1.86 (d, J = 11.9 Hz, 4H), 1.62 (s, 3H), 1.61 (s, 3H), 1.49 (s, 3H), 1.48 (s, 3H), 1.20 (s, 3H), 1.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.17, 152.21, 147.59, 147.53, 146.03, 143.77, 142.79, 138.02, 137.49, 137.22, 135.69, 127.65, 127.02, 127.00, 126.86, 126.67, 125.49, 123.42, 122.95, 122.45, 121.42, 120.84, 120.78, 118.66, 117.99, 117.76, 55.74, 55.21, 54.70, 54.13, 54.02, 41.63, 41.08, 33.84, 33.49, 33.41, 32.58, 30.91, 30.76, 30.48, 30.41, 29.22, 29.15, 29.09, 28.68, 28.65, 28.34, 21.67, 20.22, 19.77, 13.11; ^{31}P NMR (162 MHz, $CDCl_3$) δ 136.78. IR (film): γ= 3415, 3089, 3062, 3037, 2959, 2920, 2852, 1725, 1654, 1609, 1579, 1495, 1450, 1407, 1358, 1321, 1291, 1259, 1231, 1199, 1124, 1098, 1077, 1010 cm^{-1}; HRMS (EI, GC-TOF): calcd for $C_{39}H_{44}NO_2P$ 589.3110, found 589.3109.

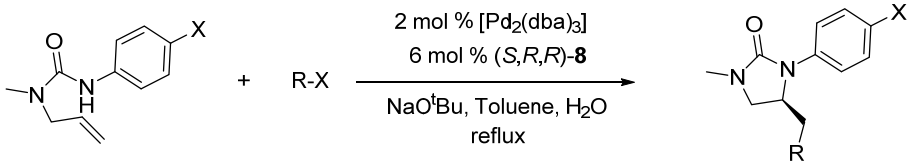


(*R*)-2,4,4,7,7,9-hexamethyl-N,N-bis((R)-1-phenylethyl)-4,5,6,7-tetrahydrodiindeno[7,1-de:1',7'-fg][1,3,2]dioxaphosphocin-12-amine[(*R*,*R*,*R*)-8]

324 mg, 55% yield; white solid, m.p. 85-88 ^{o}C; $[\alpha]_D^{20}$ = 62.4 (*c*1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16-6.95 (m, 10H), 6.80 (s, 1H), 6.77 (s, 1H), 6.73 (s, 1H), 6.46 (s, 1H), 4.26 (s, 2H), 2.43 (d, J = 12.5 Hz, 1H), 2.38 (s, 3H), 2.29 (d, J = 12.7 Hz, 4H), 2.16 (d, J = 12.5 Hz, 1H), 1.92 (d, J = 12.5 Hz, 1H), 1.54 (s, 6H), 1.49 (s, 6H), 1.20 (s, 3H), 1.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.06, 152.66, 147.36, 147.29, 145.04, 144.96, 142.76, 138.03, 137.21, 137.18, 135.80,

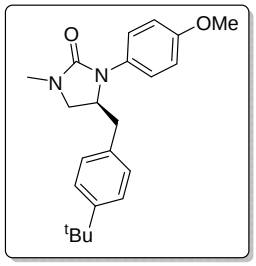
127.15, 127.12, 127.04, 126.68, 125.41, 121.69, 120.84, 120.78, 118.59, 118.57, 118.00, 55.79, 55.16, 55.05, 51.24, 51.10, 41.72, 41.26, 32.47, 30.90, 30.77, 29.27, 29.19, 28.78, 28.68, 28.64, 28.50, 28.34, 21.67, 20.38, 20.27, 20.18, 20.10, 18.78, 13.11; ^{31}P NMR (162 MHz, $CDCl_3$) δ 130.47. IR (film): γ= 3389, 3092, 3062, 3028, 2959, 2920, 2860, 1607, 1583, 1568, 1495, 1452, 1412, 1375, 1360, 1321, 1311, 1289, 1233, 1197, 1126, 1102, 1029, 1012 cm^{-1}; HRMS (EI, GC-TOF): calcd for $C_{39}H_{44}NO_2P$ 589.3110, found 589.3113.

4. General Procedure for Asymmetric hydroamination/arylation of alkenes.



9 **10** **11**

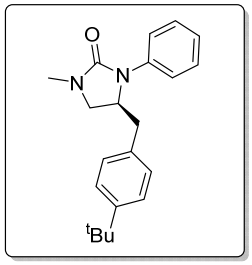
Under a nitrogen atmosphere, $Pd_2(dba)_3$ (0.9 mg, 1μmol), and (*S*,*R*,*R*)-**8** (2 mg, 3μmol) were dissolved in toluene (0.5 mL) in a dry schlenk tube. The mixture was stirred at room temperature for 1 h. Then, the urea substrate **9** (0.05 mmol), the aryl halide **10** (0.1 mmol), NaO^{t}Bu (0.1 mmol), water (0.1mmol, 2 equiv.) and toluene (0.5 mL) were added sequentially and the reaction mixture was stirred at 110 ^oC for 20 h. The mixture was cooled to room temperature and concentrated under reduced pressure, and then it was purified by flash chromatography on silica gel (ethyl acetate/petroleum ether = 1/4 to 1/2) to afford the corresponding product **11**.



(S)-4-(4-(tert-butyl)benzyl)-3-(4-methoxyphenyl)-1-methylimidazolidin-2-one (11a)

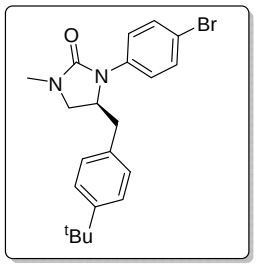
17 mg, 94% yield; orange oil; 54% ee; HPLC analysis: Chiralpak AD-H (hexane/i-PrOH = 85/15, 0.8 mL/min, 198 nm), t_R (major) 10.943 min, t_R (minor) 16.768 min; $[\alpha]_D^{20}$ = -4.7 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.35 (m, 2H), 7.31 (d, J = 8.3 Hz, 2H), 7.06 (d, J = 8.2 Hz, 2H), 6.98-6.89 (m, 2H), 4.44-4.23 (m, 1H), 3.81 (s, 3H), 3.35 (t, J = 8.7 Hz, 1H), 3.17 (dd, J = 8.9, 5.9 Hz, 1H), 3.04 (dd, J = 13.7, 3.5 Hz, 1H), 2.80 (s, 1H), 2.61 (dd, J = 13.7, 9.8 Hz, 1H), 1.30 (s,

9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.05, 156.41, 149.68, 133.55, 131.87, 128.82, 125.56, 123.87, 114.34, 55.49, 55.48, 49.83, 37.81, 34.45, 31.36, 31.19; IR (film): γ= 3471, 3054, 2955, 2903, 2865, 2830, 2039, 1903, 1697, 1611, 1579, 1515, 1491, 1463, 1433, 1403, 1373, 1360, 1319, 1242, 1177, 1152, 1122, 1104, 1036 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{22}H_{29}N_2O_2^+$ (M-H$^+$) 353.2229, found 353.2213.



(*S*)-4-(4-(tert-butyl)benzyl)-1-methyl-3-phenylimidazolidin-2-one(11b)

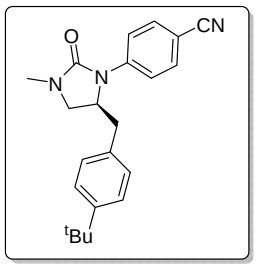
15 mg, 91% yield; white solid; m.p. 56-58°C; 66% ee; HPLC analysis: Chiralpak AD-H (hexane/i-PrOH = 90/10, 0.8 mL/min, 198 nm), t_R (minor) 14.415 min, t_R (major) 16.834 min; $[\alpha]_D^{20}$ = -8.7 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 7.7 Hz, 2H), 7.40-7.36 (m, 2H), 7.32 (d, J = 8.2 Hz, 2H), 7.11-7.08 (m, 3H), 4.67-4.36 (m, 1H), 3.37 (t, J = 8.8 Hz, 1H), 3.20 (dd, J = 8.9, 4.9 Hz, 1H), 3.11 (dd, J = 13.8, 3.3 Hz, 1H), 2.81 (s, 3H), 2.65 (dd, J = 13.8, 9.7 Hz, 1H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.32, 149.77, 138.93, 133.48, 129.00, 128.86, 125.61, 123.43, 120.74, 54.41, 49.39, 37.48, 34.47, 31.36, 31.07; IR (film): γ = 3454, 3058, 3024, 2959, 2865, 1699, 1598, 1500, 1454, 1427, 1401, 1371, 1315, 1268, 1227, 1201, 1177, 1147, 1119, 1079 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{21}H_{26}N_2ONa^+$ (M-Na$^+$) 345.1943, found 345.1903.



(S)-3-(4-bromophenyl)-4-(4-(tert-butyl)benzyl)-1-methylimidazolidin-2-one(11c)

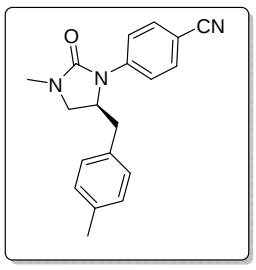
13 mg, 63% yield; orange oil; 79% ee; HPLC analysis: Chiralpak AD-H (hexane/i-PrOH = 90/10, 0.8 mL/min, 198 nm), t_R (major) 11.376 min, t_R (minor) 16.347 min; $[\alpha]_D^{20}$ = -15.7 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.37 (m, 4H), 7.32 (d, J = 8.2 Hz, 2H), 7.10-7.05 (m, 2H),

4.44-4.38 (m, 1H), 3.38 (dd, J = 12.0, 5.6 Hz, 1H), 3.21 (dd, J = 9.0, 4.6 Hz, 1H), 3.06 (dd, J = 13.8, 3.5 Hz, 1H), 2.80 (s, 3H), 2.65 (dd, J = 13.7, 9.4 Hz, 1H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.88, 149.93, 138.11, 133.14, 131.91, 129.00, 128.84, 125.66, 125.61, 121.94, 120.76, 115.94, 54.20, 49.39, 49.22, 37.44, 34.48, 31.36, 31.08, 30.98; IR (film): γ = 3441, 3054, 3019, 2972, 2860, 1901, 1701, 1592, 1515, 1489, 1431, 1403, 1369, 1317, 1268, 1220, 1201, 1143, 1126, 1104, 1074 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{21}H_{26}BrN_2O^+$ (M-H$^+$) 401.1228, found 401.1206.



(S)-4-(5-(4-(tert-butyl)benzyl)-3-methyl-2-oxoimidazolidin-1-yl)benzonitrile(11d)

15 mg, 89% yield; orange solid; m.p. 112-115 °C; 83% ee; HPLC analysis: Chiralpak AD-H (hexane/i-PrOH = 87/13, 1.5 mL/min, 198 nm), t_R (major) 8.499 min, t_R (minor) 13.511 min; $[\alpha]_D^{20}$ = -57.6 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 9.3 Hz, 2H), 7.79 (d, J = 9.3 Hz, 2H), 7.34 (d, J = 8.2 Hz, 2H), 7.10 (d, J = 8.2 Hz, 2H), 4.69-4.42 (m, 1H), 3.48 (t, J = 8.9 Hz, 1H), 3.29 (dd, J = 9.2, 3.1 Hz, 1H), 3.11 (dd, J = 14.0, 3.5 Hz, 1H), 2.83 (s, 3H), 2.76 (dd, J = 14.0, 9.1 Hz, 1H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.75, 150.32, 145.23, 141.91, 132.52, 128.87, 125.81, 125.01, 117.71, 53.77, 48.64, 37.37, 34.51, 31.32, 30.83; IR (film): γ= 3441, 3187, 3118, 3084, 3049, 2959, 2865, 2632, 2430, 1906, 1714, 1592, 1502, 1435, 1401, 1371, 1323, 1261, 1223, 1195, 1111, 1074 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{22}H_{26}N_3O^+$ (M-H$^+$) 348.2076, found 348.2104.



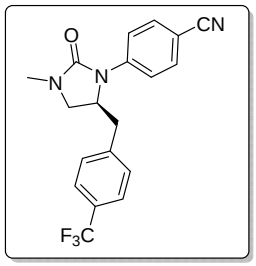
(S)-4-(3-methyl-5-(4-methylbenzyl)-2-oxoimidazolidin-1-yl)benzonitrile (11e)

13 mg, 85% yield; orange solid; m.p. 129-132°C; 87% ee; HPLC analysis: Chiralpak AD-H (hexane/i-PrOH = 90/10, 0.8 mL/min, 198 nm), t_R (major) 28.858 min, t_R (minor) 54.182 min;

$[\alpha]_D^{20}$ = -47.2 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79-7.73 (m, 2H), 7.69-7.59 (m, 2H), 7.14 (d, J = 7.8 Hz, 2H), 7.04 (d, J = 7.9 Hz, 2H), 4.50-4.44 (tt, J = 8.9, 3.4 Hz, 1H), 3.42 (t, J = 8.9 Hz, 1H), 3.25 (dd, J = 9.1, 3.5 Hz, 1H), 3.08 (dd, J = 13.9, 3.2 Hz, 1H), 2.81 (s, 3H), 2.71 (dd, J = 13.9, 9.2 Hz, 1H), 2.34 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.95, 143.24, 136.94, 133.17, 132.54, 129.56, 129.19, 129.06, 128.90, 119.28, 118.56, 105.07, 53.57, 48.54, 37.24, 30.82, 21.07; IR (film): γ= 3398, 3105, 3049, 2916, 2873, 2215, 1717, 1605, 1512, 1493, 1437, 1401, 1373, 1326, 1263, 1227, 1180, 1141, 1119, 1079 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{19}H_{20}N_3O^+$ ($M\text{-}H^+$) 306.1606, found 306.1573.

(S)-4-(5-(4-methoxybenzyl)-3-methyl-2-oxoimidazolidin-1-yl)benzonitrile (11f)

13 mg, 77% yield; orange solid; m.p. 85-87°C; 86% ee; HPLC analysis: Chiralpak AD-H (hexane/i-PrOH = 80/20, 0.8 mL/min, 198 nm), t_R (major) 46.436 min, t_R (minor) 92.794 min; $[\alpha]_D^{20}$ = -18.7 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81-7.71 (m, 2H), 7.70-7.55 (m, 2H), 7.06 (d, J = 8.6 Hz, 2H), 6.96-6.78 (m, 2H), 4.49-4.43 (m, 1H), 3.80 (s, 3H), 3.44 (t, J = 8.9 Hz, 1H), 3.25 (dd, J = 9.1, 3.5 Hz, 1H), 3.04 (dd, J = 14.0, 3.3 Hz, 1H), 2.80 (s, 3H), 2.72 (dd, J = 14.0, 8.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.79, 156.94, 143.27, 133.16, 130.20, 127.50, 119.28, 118.56, 114.26, 105.04, 55.31, 53.56, 48.48, 36.76, 30.81; IR (film): γ= 3394, 3200, 3058, 2998, 2938, 2834, 2219, 1712, 1603, 1579, 1517, 1431, 1403, 1373, 1328, 1246, 1175, 1141, 1122, 1077 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{19}H_{20}N_3O_2^+$ ($M\text{-}H^+$) 344.1375, found 344.1345.



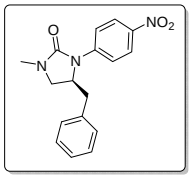
(S)-4-(3-methyl-2-oxo-5-(4-(trifluoromethyl)benzyl)imidazolidin-1-yl)benzonitrile(11g)

12 mg, 63% yield; orange solid; m.p. 115-118°C; 87% ee; HPLC analysis: Chiralpak AD-H (hexane/i-PrOH = 87/13, 1.5 mL/min, 200 nm), t_R (major) 12.421 min, t_R (minor) 22.315 min; $[\alpha]_D^{20}$ = -34.2 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79-7.72 (m, 2H), 7.70-7.62 (m, 2H), 7.59 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 7.9 Hz, 2H), 4.62-4.51 (m, 1H), 3.48 (t, J = 9.0 Hz, 1H), 3.22 (dd, J = 9.2, 3.4 Hz, 1H), 3.15 (dd, J = 14.0, 3.4 Hz, 1H), 2.89 (dd, J = 14.0, 8.7 Hz, 1H), 2.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.77, 142.96, 139.76, 133.25, 129.60, 129.52, 125.80,

125.76, 125.73, 119.10, 118.70, 105.47, 53.02, 48.41, 37.50, 30.78; IR (film): γ= 3398, 3114, 3049, 2916, 2869, 2224, 1712, 1605, 1558, 1512, 1504, 1491, 1433, 1405, 1373, 1326, 1266, 1227, 1177, 1122, 1066 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{19}H_{17}F_3N_3O^+$ ($M\text{-}H^+$) 360.1323, found 360.1304.

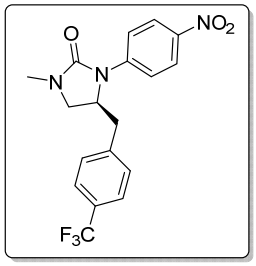
(S)-4-(4-(tert-butyl)benzyl)-1-methyl-3-(4-nitrophenyl)imidazolidin-2-one(11h)

16 mg, 87% yield; orange solid; m.p. 116-118°C; 91% ee; HPLC analysis: Chiralpak AD-H (hexane/i-PrOH = 87/13, 1.5 mL/min, 198 nm), t_R (major) 9.059 min, t_R (minor) 13.217 min; $[\alpha]_D^{20}$ = -147 (*c* 1.0, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 7.80-7.69 (m, 2H), 7.67-7.58 (m, 2H), 7.34 (d, J = 8.3 Hz, 2H), 7.09 (d, J = 8.2 Hz, 2H), 4.52-4.46 (m, 1H), 3.45 (t, J = 8.9 Hz, 1H), 3.27 (dd, J = 9.1, 3.4 Hz, 1H), 3.09 (dd, J = 13.9, 3.5 Hz, 1H), 2.82 (s, 3H), 2.72 (dd, J = 13.9, 9.2 Hz, 1H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.97, 150.22, 143.27, 133.12, 132.65, 128.86, 125.77, 119.27, 118.59, 105.04, 53.58, 48.73, 37.30, 34.50, 31.33, 30.84; IR (film): γ= 3394, 3114, 3049, 2959, 2912, 2865, 2224, 1704, 1601, 1512, 1461, 1424, 1403, 1373, 1356, 1330, 1266, 1225, 1175, 1141, 1119, 1107, 1072 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{21}H_{26}N_3O_3^+$ ($M\text{-}H^+$) 368.1974, found 368.1992.



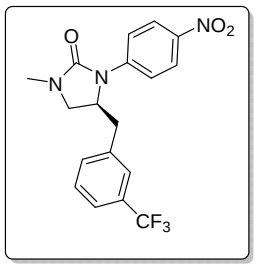
(S)-4-benzyl-1-methyl-3-(4-nitrophenyl)imidazolidin-2-one (11i)

11 mg, 75% yield; orange solid; m.p. 136-138°C; 84% ee; HPLC analysis: Chiralpak AD-H (hexane/i-PrOH = 90/10, 0.8 mL/min, 198 nm), t_R (major) 36.751 min, t_R (minor) 63.701 min; $[\alpha]_D^{20}$ = -116 (*c* 1.0, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 8.35-8.16 (m, 2H), 7.90-7.72 (m, 2H), 7.38-7.31 (m, 2H), 7.31 -7.25 (m, 1H), 7.17 (d, J = 6.9 Hz, 2H), 4.56 (tt, J = 8.8, 3.3 Hz, 1H), 3.48 (t, J = 8.9 Hz, 1H), 3.28 (dd, J = 9.2, 3.1 Hz, 1H), 3.14 (dd, J = 13.9, 3.4 Hz, 1H), 2.87-2.70 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.70, 145.15, 141.97, 135.54, 129.20, 128.93, 127.35, 125.07, 117.69, 53.65, 48.44, 37.74, 30.81; IR (film): γ= 3415, 3118, 3032, 2955, 2925, 2873, 1706, 1596, 1517, 1457, 1433, 1401, 1373, 1358, 1323, 1263, 1225, 1180, 1147, 1115 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{17}H_{18}N_3O_3^+$ ($M\text{-}H^+$) 312.1348, found 312.1352.



(S)-1-methyl-3-(4-nitrophenyl)-4-(4-(trifluoromethyl)benzyl)imidazolidin-2-one (11j)

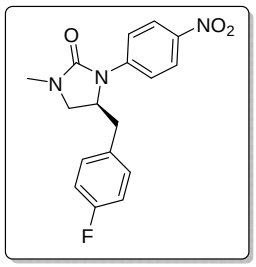
14 mg, 75% yield; orange solid; m.p. 165-167°C; 93% ee; HPLC analysis: Chiralpak AD-H (hexane/i-PrOH = 87/13, 1.5 mL/min, 195nm), t_R (major) 15.231 min, t_R (minor) 26.153 min; $[\alpha]_D^{20}$ = -67.3 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, J = 9.2 Hz, 2H), 7.80 (d, J = 9.3 Hz, 2H), 7.60 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 4.70-4.42 (m, 1H), 3.51 (t, J = 9.0 Hz, 1H), 3.24 (dd, J = 9.3, 3.1 Hz, 1H), 3.18 (dd, J = 14.0, 3.3 Hz, 1H), 2.92 (dd, J = 14.0, 8.7 Hz, 1H), 2.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.57, 144.85, 142.21, 139.60, 129.59, 125.86, 125.83, 125.14, 117.83, 53.20, 48.32, 37.51, 30.79; IR (film): γ= 3398, 3114, 2972, 2925, 2882, 1717, 1596, 1555, 1500, 1487, 1407, 1377, 1349, 1334, 1317, 1278, 1266, 1177, 1160, 1122, 1069 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{18}H_{17}F_3N_3O_3^+$ ($M\text{-}H^+$) 380.1222, found 380.1103.



(S)-1-methyl-3-(4-nitrophenyl)-4-(3-(trifluoromethyl)benzyl)imidazolidin-2-one (11k)

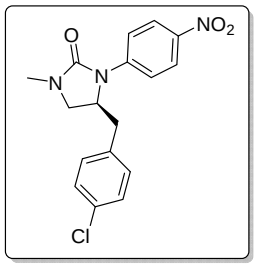
13 mg, 67% yield; orange solid; m.p. 138-140°C; 91% ee; HPLC analysis: Chiralpak AD-H (hexane/i-PrOH = 90/10, 0.8 mL/min, 198nm), t_R (major) 30.434 min, t_R (minor) 51.011 min; $[\alpha]_D^{20}$ = -64.7 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34-8.15 (m, 2H), 8.01-7.67 (m, 2H), 7.55 (d, J = 7.8 Hz, 1H), 7.46 (t, J = 7.7 Hz, 1H), 7.40 (s, 1H), 7.33 (d, J = 7.6 Hz, 1H), 4.74-4.49 (m, 1H), 3.54 (t, J = 9.0 Hz, 1H), 3.25 (dd, J = 9.3, 3.1 Hz, 1H), 3.16 (dd, J = 14.1, 3.6 Hz, 1H), 2.94 (dd, J = 14.1, 8.3 Hz, 1H), 2.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.54, 144.90, 142.17, 136.44, 132.65, 131.39, 131.06, 129.43, 125.85, 125.81, 125.23, 125.10, 124.30, 124.26, 122.52, 117.91, 53.14, 48.40, 37.60, 30.75; IR (film): γ= 3398, 3114, 3080, 2920, 2852, 1708, 1598, 1504, 1487, 1435, 1405, 1381, 1339, 1328, 1308, 1272, 1208, 1192, 1158, 1107, 1094,

1070 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{18}H_{17}F_3N_3O_3^+$ ($M\text{-}H^+$) 380.1222, found 380.1185.



(S)-4-(4-fluorobenzyl)-1-methyl-3-(4-nitrophenyl)imidazolidin-2-one (11l)

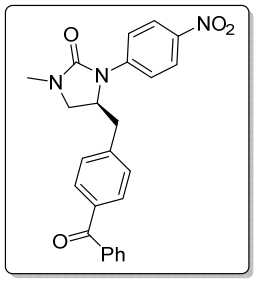
9 mg, 57% yield; orange solid; m.p. 151-152°C; 93% ee; HPLC analysis: Chiralpak AD-H (hexane/i-PrOH = 90/10, 0.8 mL/min, 198nm), t_R (major) 30.658 min, t_R (minor) 58.300 min; $[\alpha]_D^{20}$ = -74.5 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38-8.19 (m, 2H), 7.91-7.71 (m, 2H), 7.24-7.09 (m, 2H), 7.10-6.96 (m, 2H), 4.58-4.52 (m, 1H), 3.50 (t, J = 9.0 Hz, 1H), 3.25 (dd, J = 9.2, 3.2 Hz, 1H), 3.10-3.06 (m, 1H), 2.95-2.76 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.31, 160.86, 156.63, 145.05, 142.04, 131.12, 131.08, 130.74, 130.66, 125.10, 117.71, 115.94, 115.72, 53.44, 48.28, 36.83, 30.77; IR (film): γ= 3402, 3118, 2925, 2882, 2847, 1704, 1596, 1504, 1435, 1403, 1377, 1326, 1266, 1220, 1158, 1141, 1113, 1094, 1074 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{17}H_{17}FN_3O_3^+$ ($M\text{-}H^+$) 330.1254, found 330.1231.



(S)-4-(4-chlorobenzyl)-1-methyl-3-(4-nitrophenyl)imidazolidin-2-one (11m)

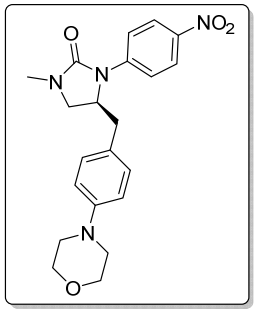
14 mg, 77% yield; orange solid; m.p. 151-154°C; 90% ee; HPLC analysis: Chiralpak AD-H (hexane/i-PrOH = 90/10, 0.8 mL/min, 198nm), t_R (major) 32.805 min, t_R (minor) 59.804 min; $[\alpha]_D^{20}$ = -47.8 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31-8.19 (m, 2H), 7.86-7.75 (m, 2H), 7.37-7.28 (m, 2H), 7.09 (d, J = 8.3 Hz, 2H), 4.58-4.52 (m, 1H), 3.49 (t, J = 9.0 Hz, 1H), 3.24 (dd, J = 9.2, 3.2 Hz, 1H), 3.08 (dd, J = 14.2, 3.5 Hz, 1H), 2.93-2.74 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.60, 144.98, 142.08, 133.87, 133.34, 130.53, 129.07, 125.11, 117.74, 53.31, 48.28, 36.99, 30.79; IR (film): γ= 3394, 3114, 2933, 2877, 1706, 1596, 1495, 1431, 1399, 1375, 1332, 1281, 1263, 1220, 1197, 1180, 1132, 1115, 1096, 1074 cm^{-1}; HRMS (ESI): *m/z* calcd for

$C_{17}H_{16}ClN_3O_3Na^+$ (M-Na^+) 368.0778, found 368.0736.



(S)-4-(4-benzoylbenzyl)-1-methyl-3-(4-nitrophenyl)imidazolidin-2-one (11n)

13 mg, 62% yield; orange solid; m.p. 125-128°C; 83% ee; HPLC analysis: Chiralpak AD-H (hexane/i-PrOH = 90/10, 0.8 mL/min, 198nm), t_R (major) 45.561 min, t_R (minor) 59.945 min; $[\alpha]_D^{20}$ = -35.6 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30-8.21 (m, 2H), 7.88-7.73 (m, 6H), 7.64-7.57 (m, 1H), 7.49 (t, J = 7.6 Hz, 2H), 7.29 (d, J = 8.1 Hz, 2H), 4.78-4.53 (m, 1H), 3.54 (t, J = 8.9 Hz, 1H), 3.29 (dd, J = 9.2, 3.1 Hz, 1H), 3.21 (dd, J = 13.9, 3.5 Hz, 1H), 3.01-2.89 (m, 1H), 2.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.10, 156.60, 144.97, 142.12, 140.35, 137.36, 136.67, 132.64, 130.65, 129.98, 129.21, 128.39, 125.11, 117.84, 53.29, 48.46, 37.79, 30.83; IR (film): γ= 3394, 3299, 3196, 3080, 3058, 2925, 2877, 2628, 2434, 1717, 1654, 1596, 1504, 1433, 1401, 1373, 1328, 1278, 1180, 1113, 1074 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{24}H_{22}N_3O_4^+$ (M-H^+) 416.1610, found 416.1598.

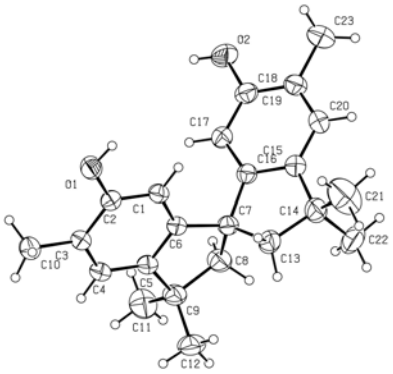


(S)-1-methyl-4-(4-morpholinobenzyl)-3-(4-nitrophenyl)imidazolidin-2-one (11o)

17 mg, 83% yield; orange solid; m.p. 121-124°C; 91% ee; HPLC analysis: Chiralpak AD-H (hexane/i-PrOH = 90/10, 0.8 mL/min, 198nm), t_R (major) 21.899 min, t_R (minor) 30.665 min; $[\alpha]_D^{20}$ = -87.7 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33-8.17 (m, 2H), 7.88-7.70 (m, 2H), 7.06 (d, J = 8.6 Hz, 2H), 6.87 (d, J = 8.6 Hz, 2H), 4.58-4.44 (m, 1H), 3.95-3.79 (m, 4H), 3.47 (t, J = 8.9 Hz, 1H), 3.28 (dd, J = 9.1, 3.2 Hz, 1H), 3.20-3.11 (m, 4H), 3.06 (dd, J = 14.1, 3.4 Hz, 1H), 2.83 (s, 3H), 2.73 (dd, J = 14.0, 8.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.76, 150.49, 145.21, 143.46, 141.95, 137.29, 133.25, 129.99, 126.58, 125.05, 117.72, 115.93, 66.86, 53.81,

49.23, 48.47, 36.84, 30.85; IR (film): γ= 3415, 3123, 2955, 2925, 2856, 1717, 1594, 1504, 1429, 1401, 1377, 1328, 1259, 1235, 1199, 1111, 1066 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{21}H_{25}N_4O_4^+$ ($M\text{-}H^+$) 397.1876, found 397.1866.

5. X-Ray Structure and Crystal Data of (*S*)-1



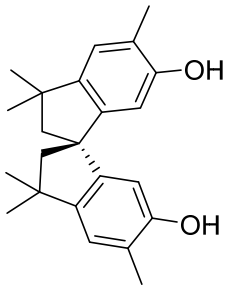


Table S1. Crystal data and structure refinement for (*S*)-1

Bond precision:	C-C = 0.0036 A	Wavelength = 1.54184	
Cell:	a = 10.8110 (4)	b = 11.3987 (3)	c = 11.7982 (4)
	alpha = 90	beta = 104.616(4)	gamma = 90
Temperature:	293 K		
	Calculated	Reported	
Volume	1406.86 (8)	1406.84 (8)	
Space group	P 21	P 1 21 1	
Hall group	P 2yb	P 2yb	
Moiety formula	C23 H28 O2, C6 H14 O	C23 H28 O2, C6 H14 O	
Sum formula	C29 H42 O3	C29 H42 O3	
Mr	438.63	438.63	

Dx, g cm^{-3}	1.035	1.035
Z	2	2
Mu (mm^{-1})	0.504	0.504
F000	480.0	480.0
F000’	481.29	
h,k,lmax	12,13,14	12,13,13
Nref	5057[2666]	4921
Tmin, Tmax	0.785,0.834	0.684,1.000
Tmin’	0.781	

Correction method = # Reported T Limits: Tmin = 0.684 Tmax = 1.000

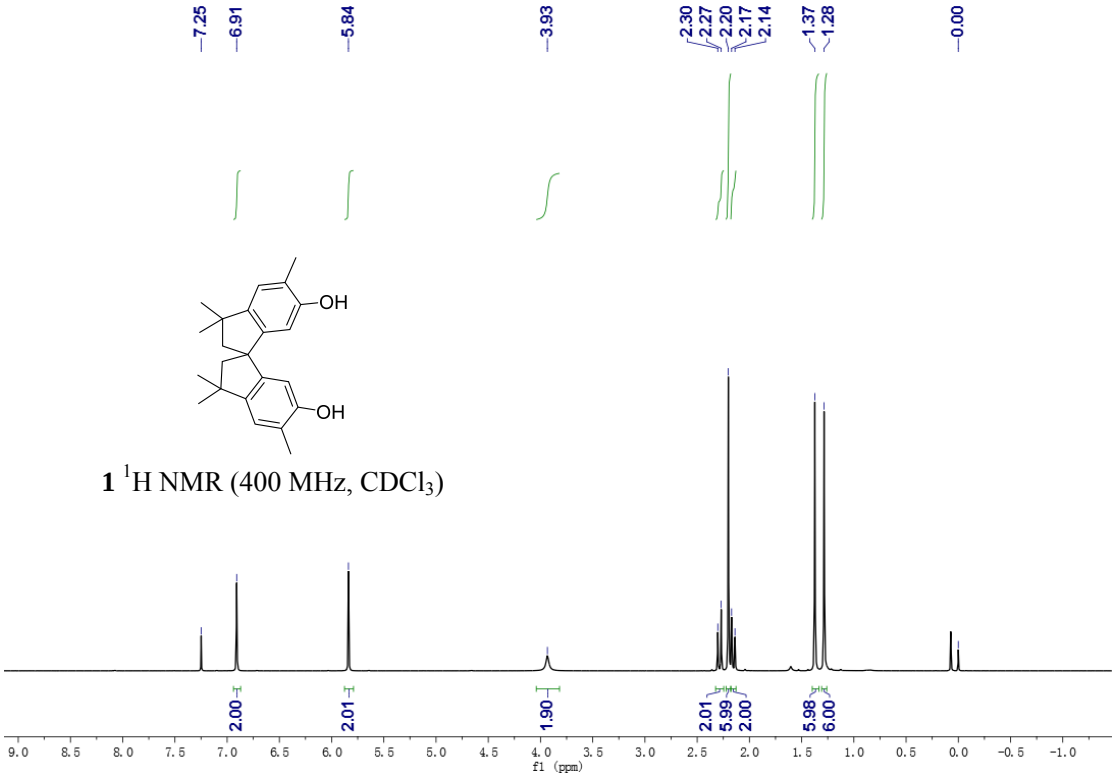
AbsCorr = MULTI-SCAN

Data completeness = 1.85/0.97 Theta (max) = 67.360

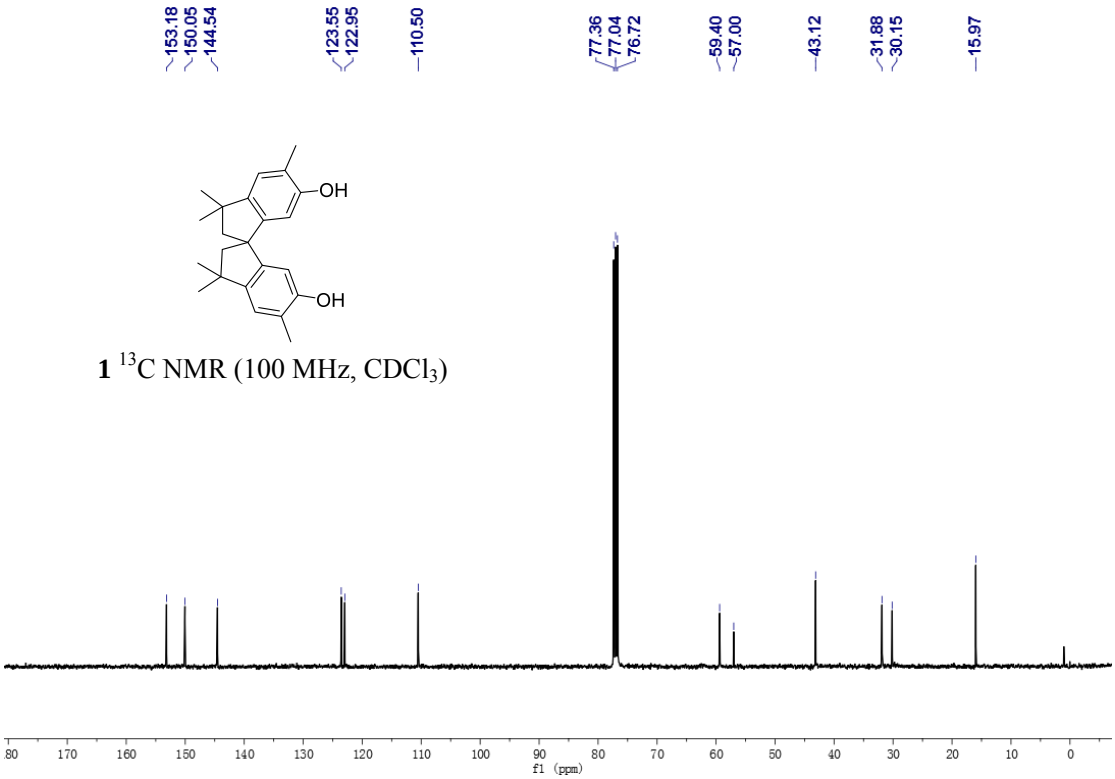
R (reflections) = 0.0466(4155) wR2 (reflections) = 0.1356(4921)

S = 1.029 Npar = 305

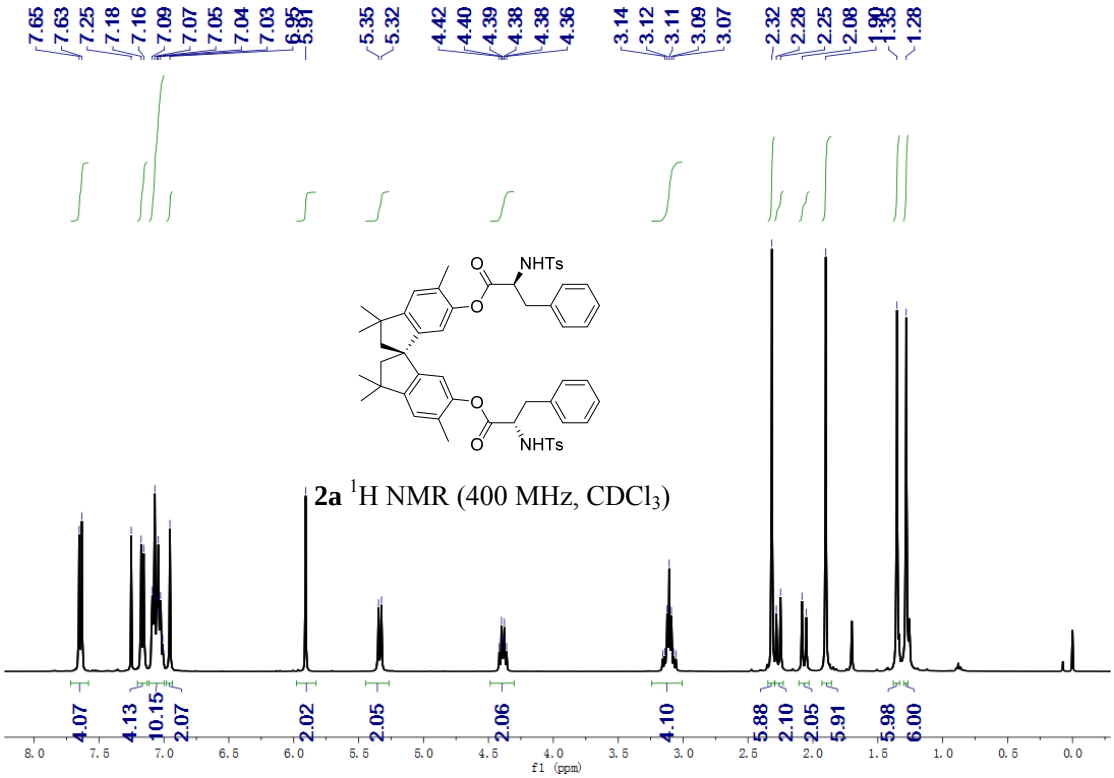
6. Copies of NMR Spectra and HPLC Traces



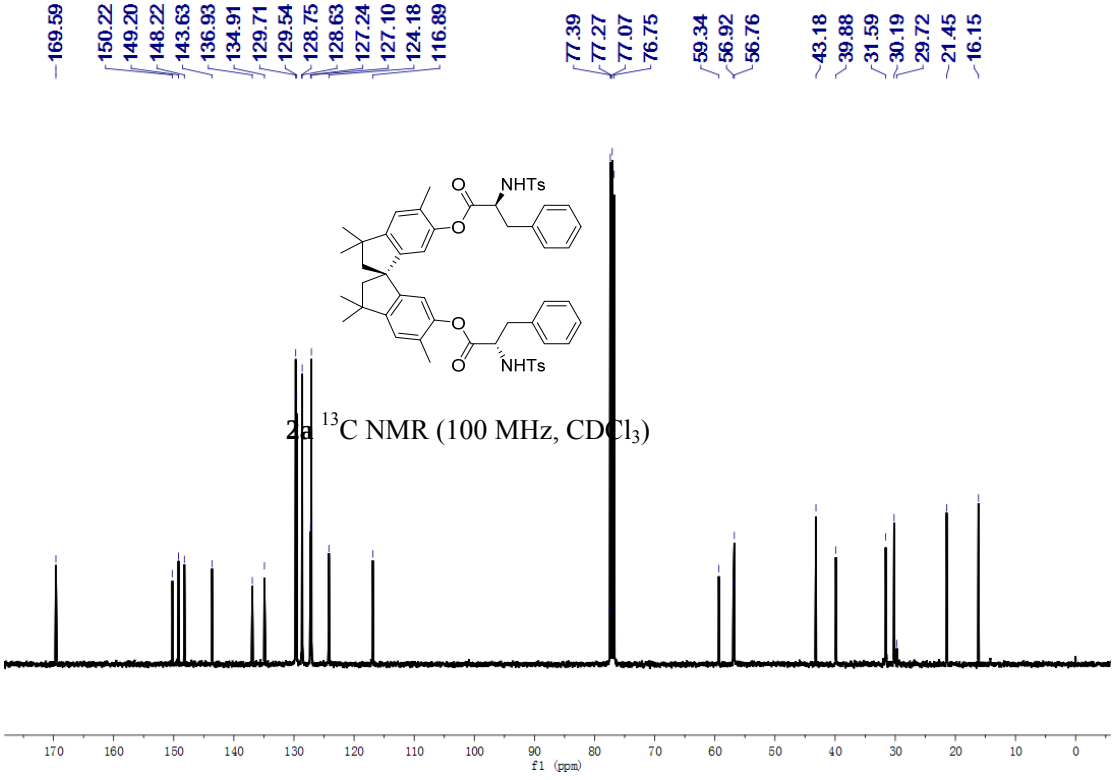
1 ^{1}H NMR (400 MHz, $CDCl_3$)



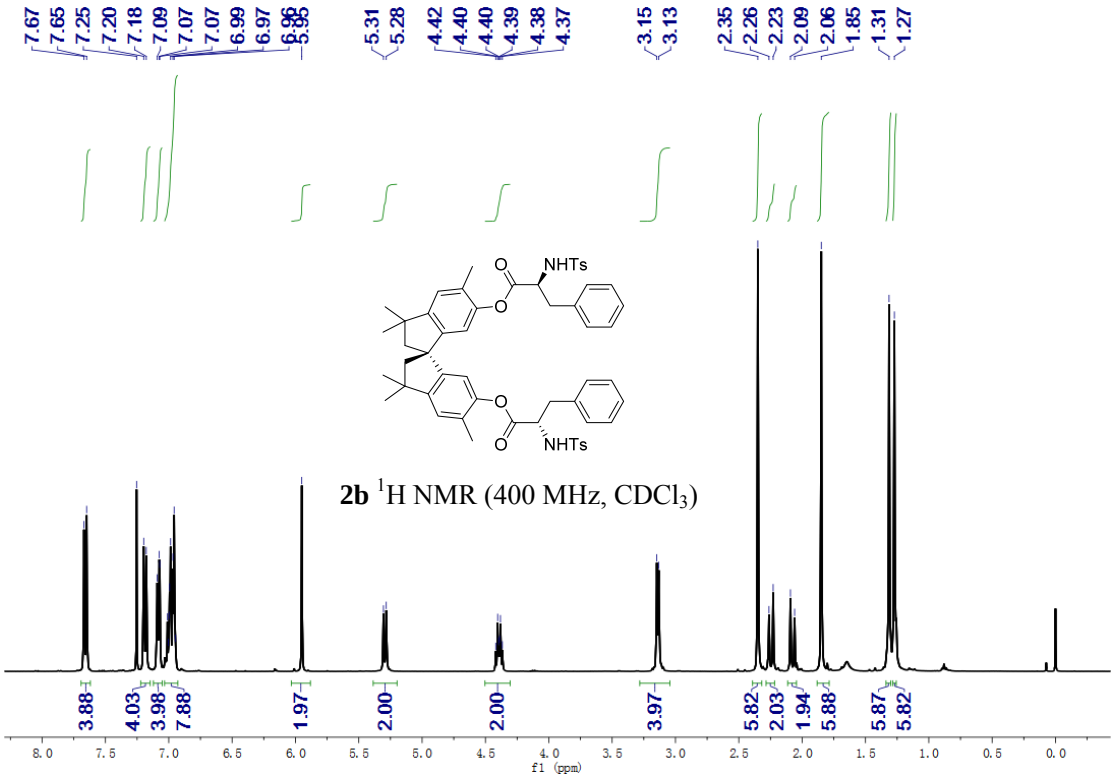
1 ^{13}C NMR (100 MHz, $CDCl_3$)



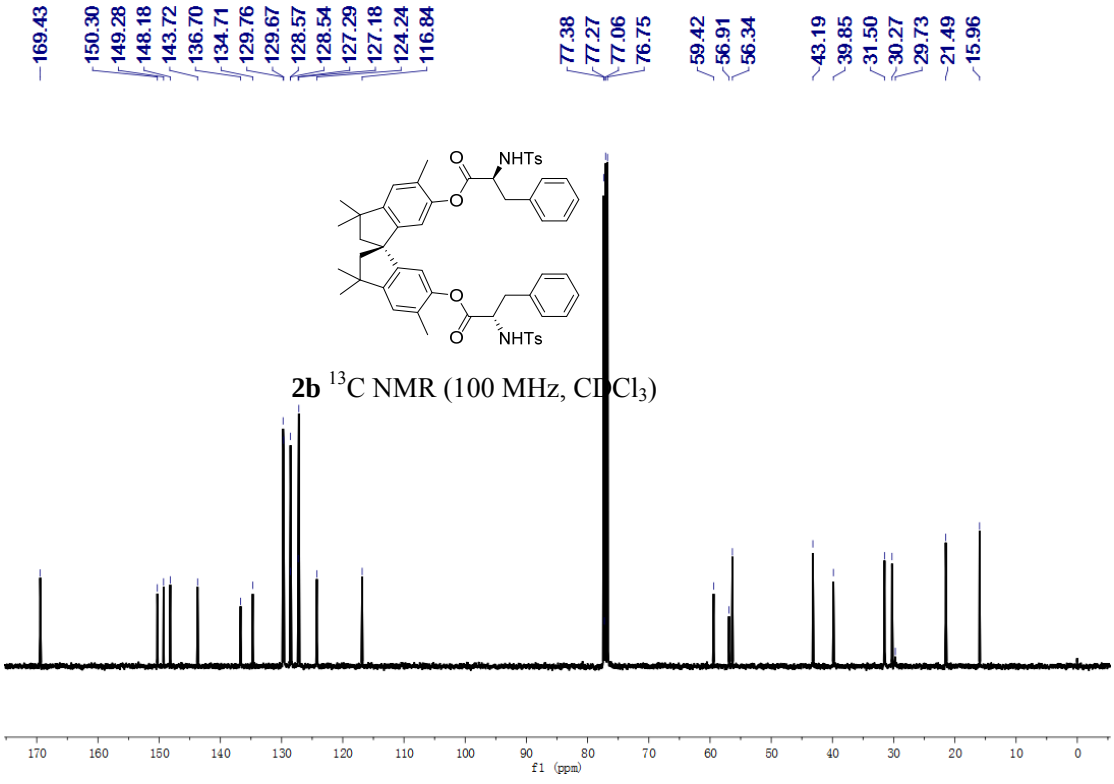
2a ^{1}H NMR (400 MHz, $CDCl_3$)



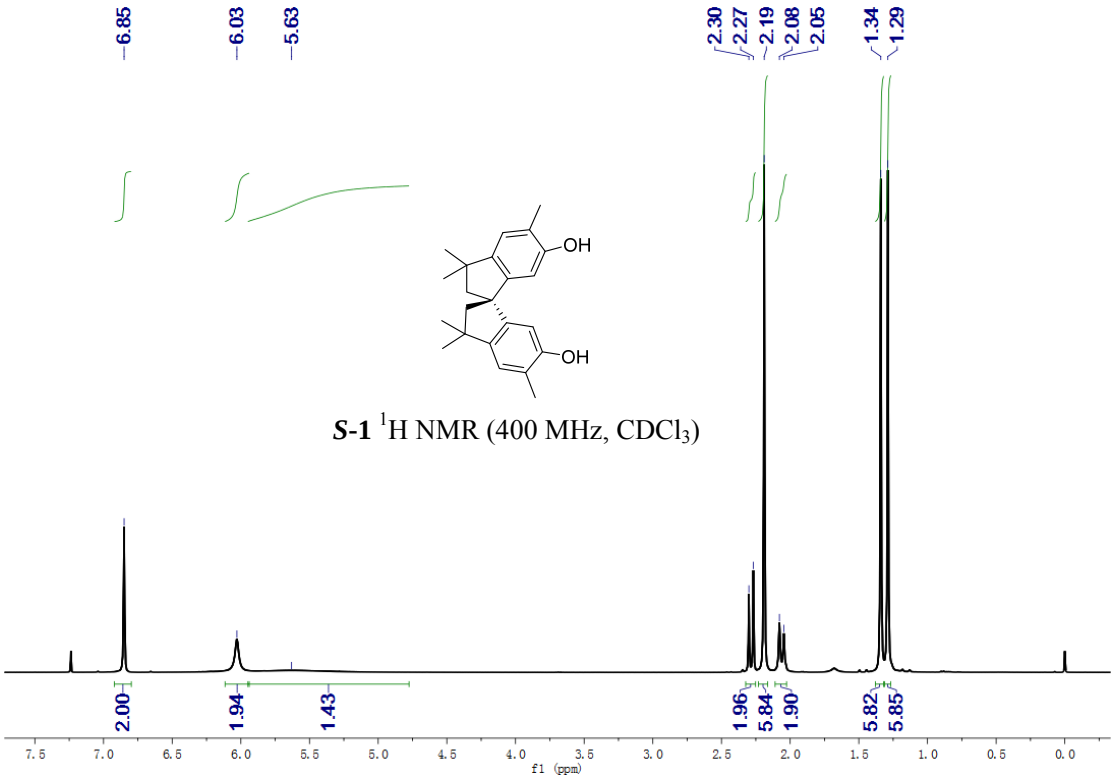
2a ^{13}C NMR (100 MHz, $CDCl_3$)



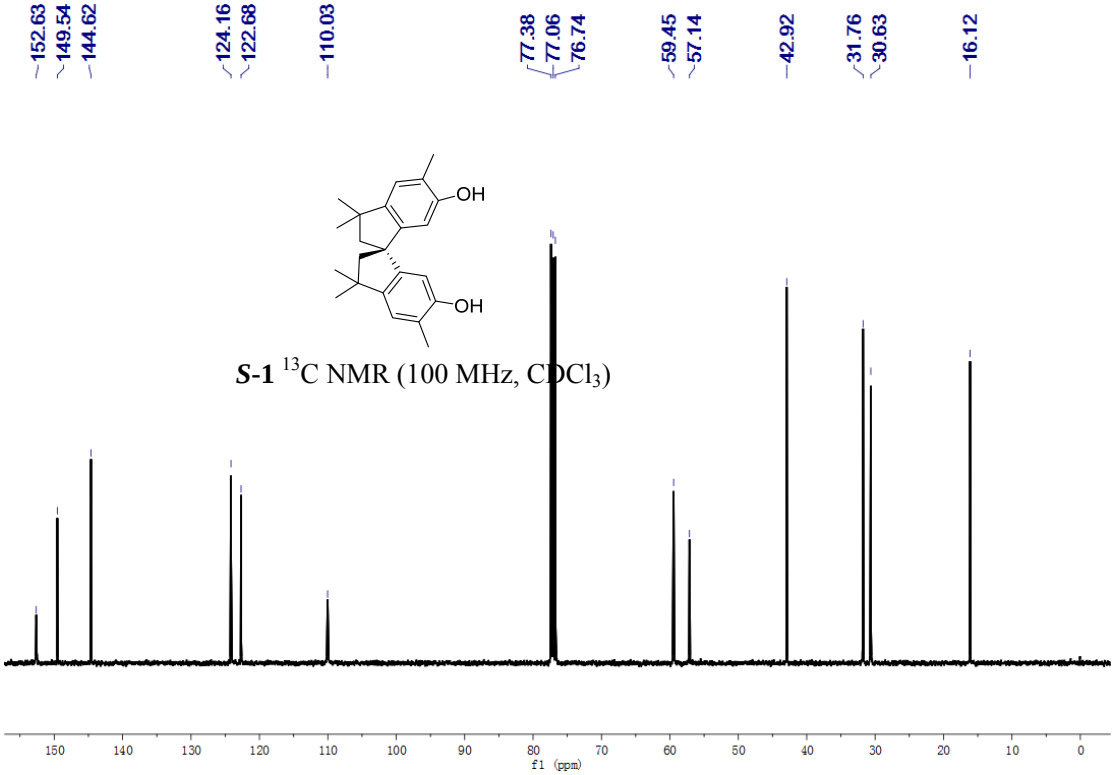
2b ^{1}H NMR (400 MHz, $CDCl_3$)



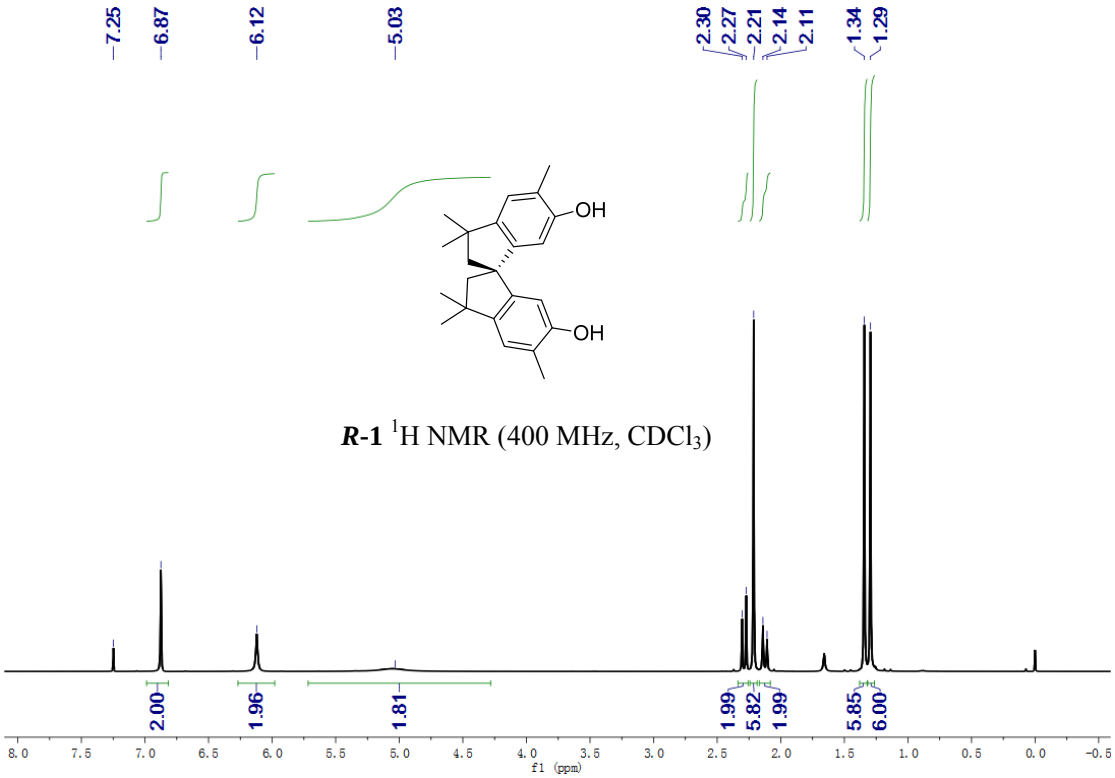
2b ^{13}C NMR (100 MHz, $CDCl_3$)



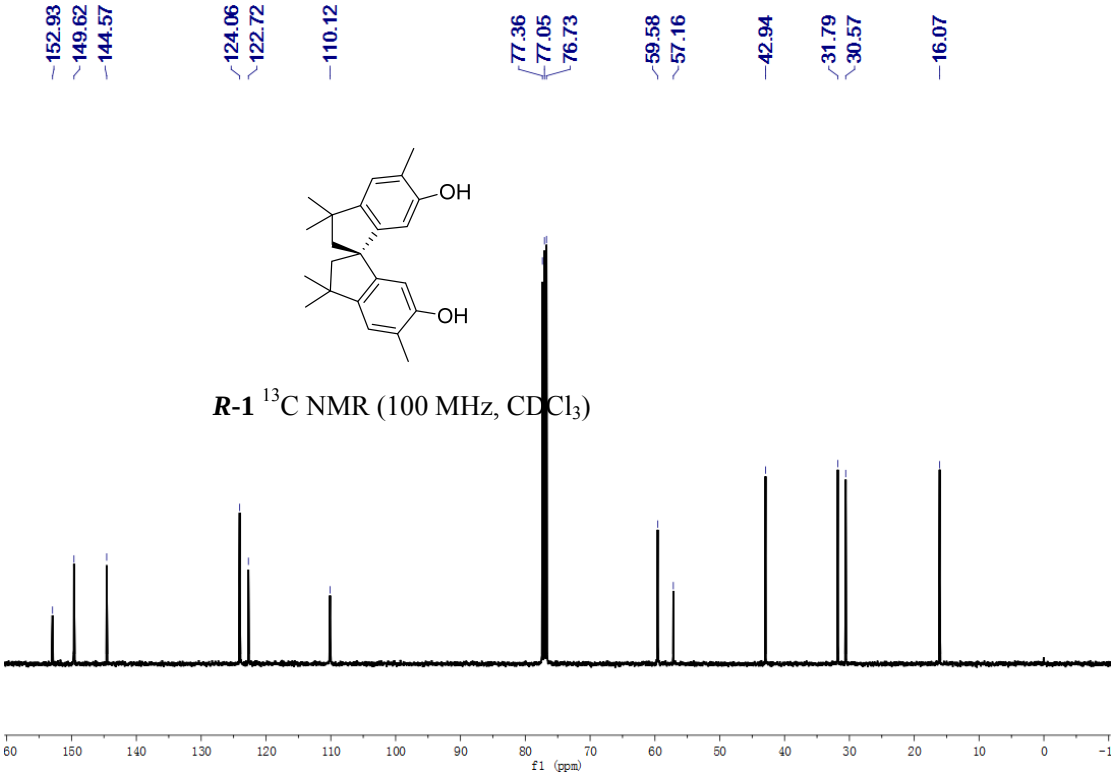
***S*-1** ^{1}H NMR (400 MHz, $CDCl_3$)



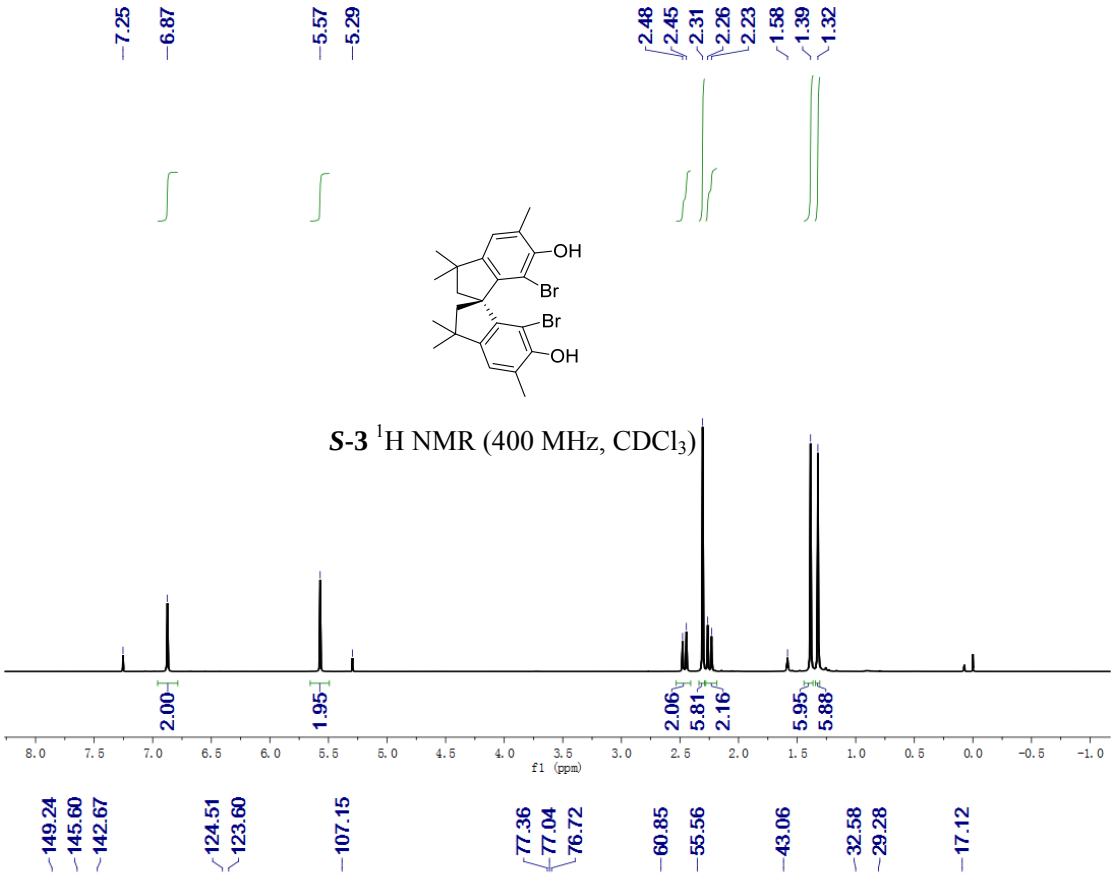
***S*-1** ^{13}C NMR (100 MHz, $CDCl_3$)



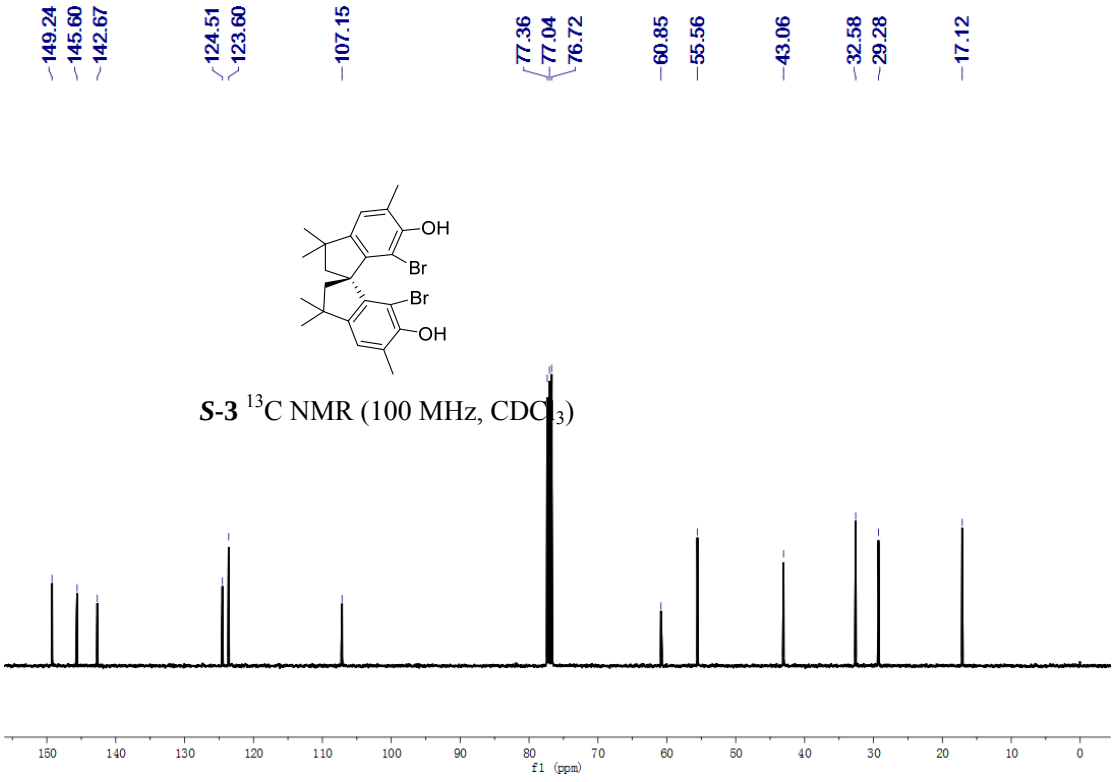
***R*-1** ^{1}H NMR (400 MHz, $CDCl_3$)



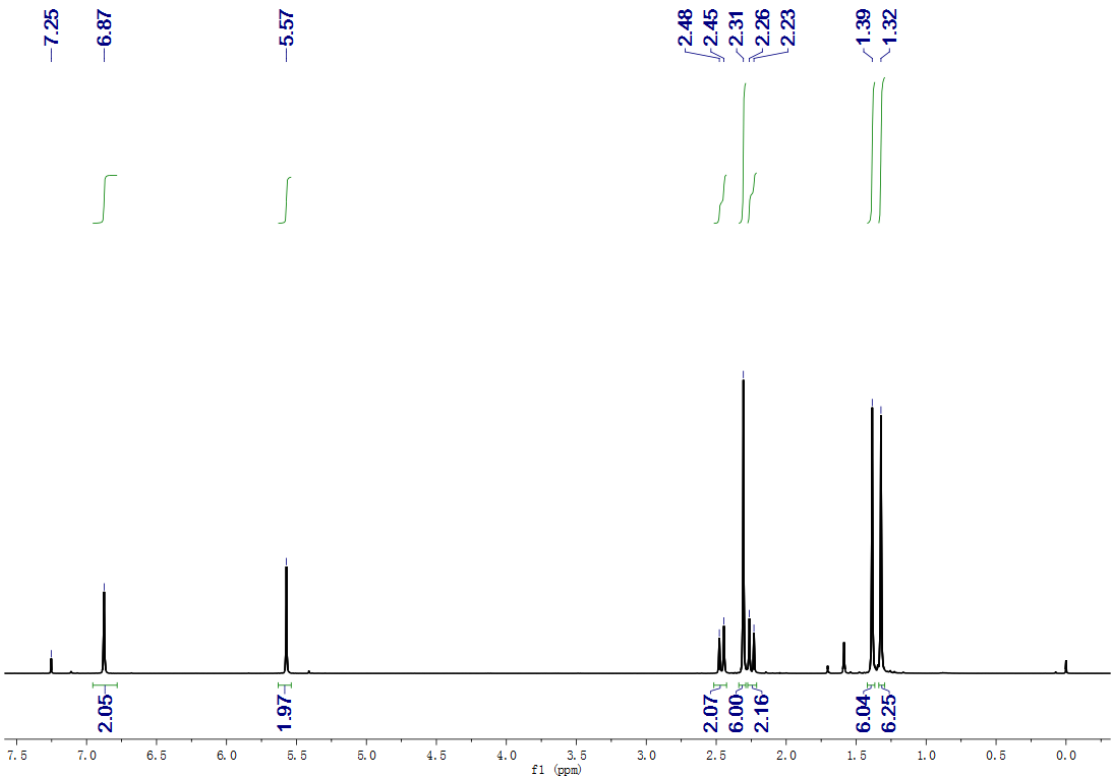
***R*-1** ^{13}C NMR (100 MHz, $CDCl_3$)

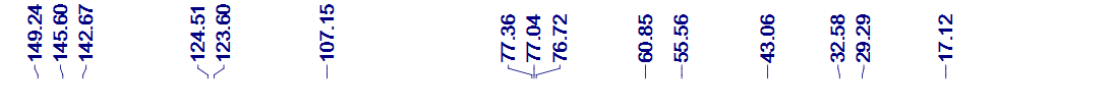


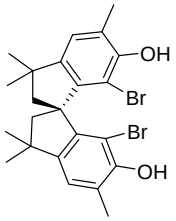
***S*-3** ^{1}H NMR (400 MHz, $CDCl_3$)



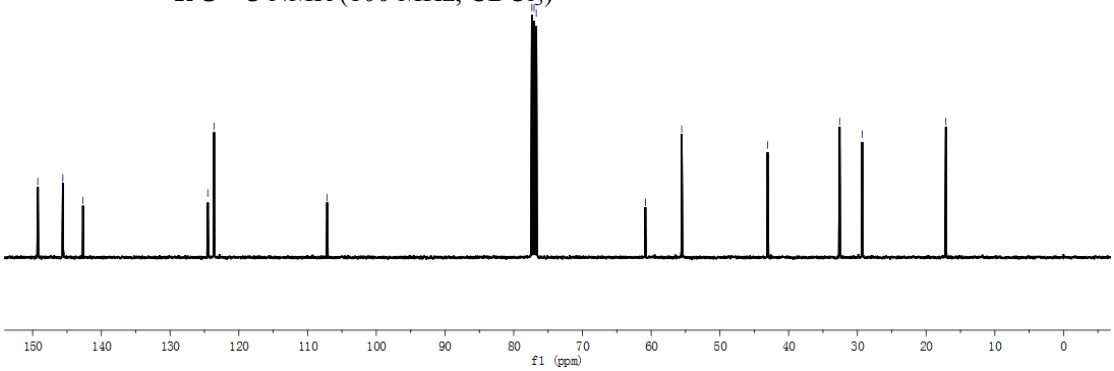
***S*-3** ^{13}C NMR (100 MHz, $CDCl_3$)

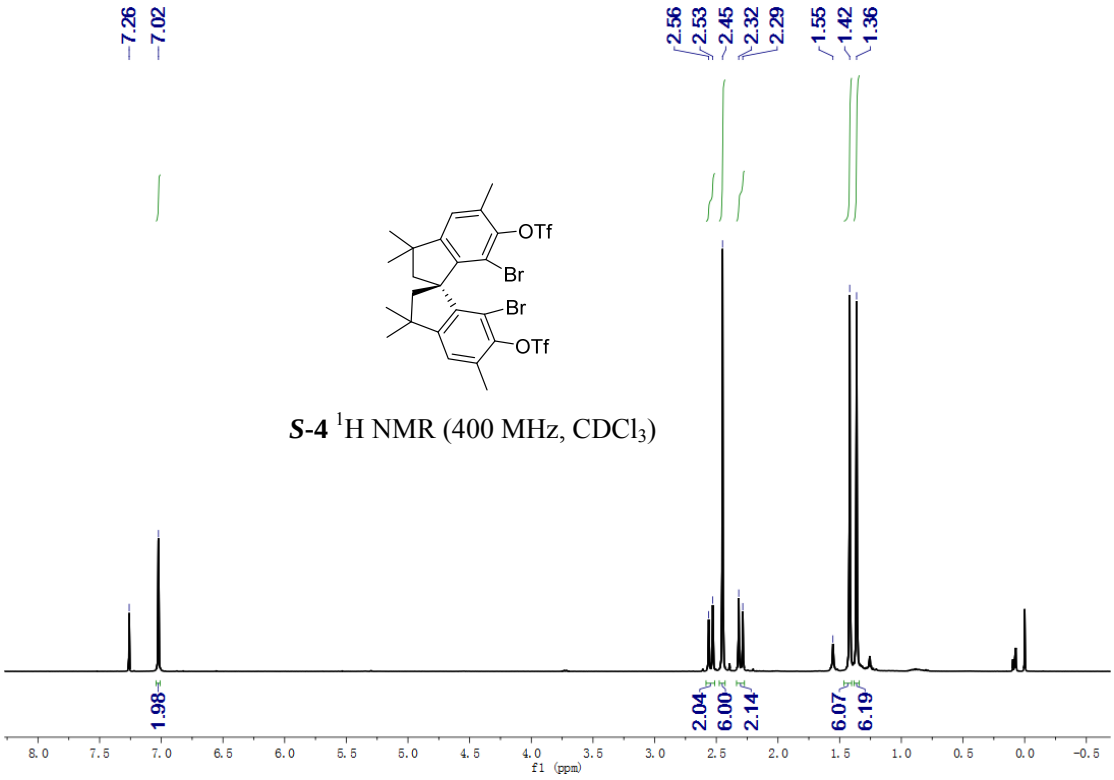




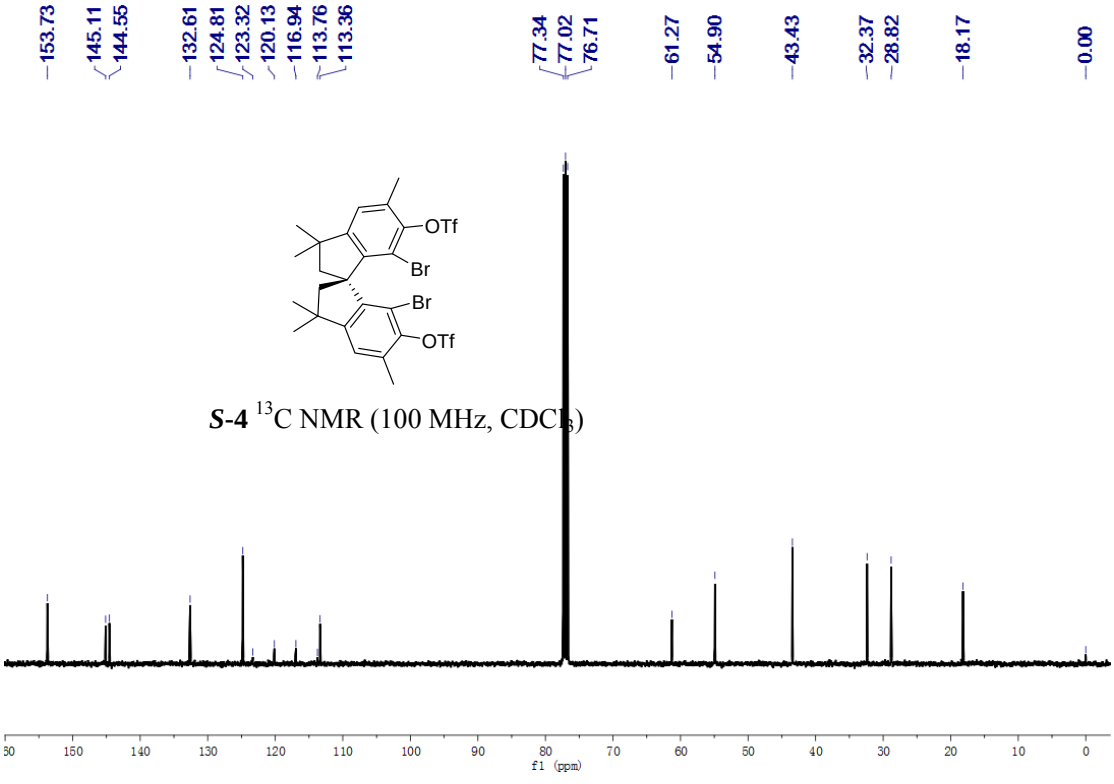


***R*-3** ^{13}C NMR (100 MHz, $CDCl_3$)

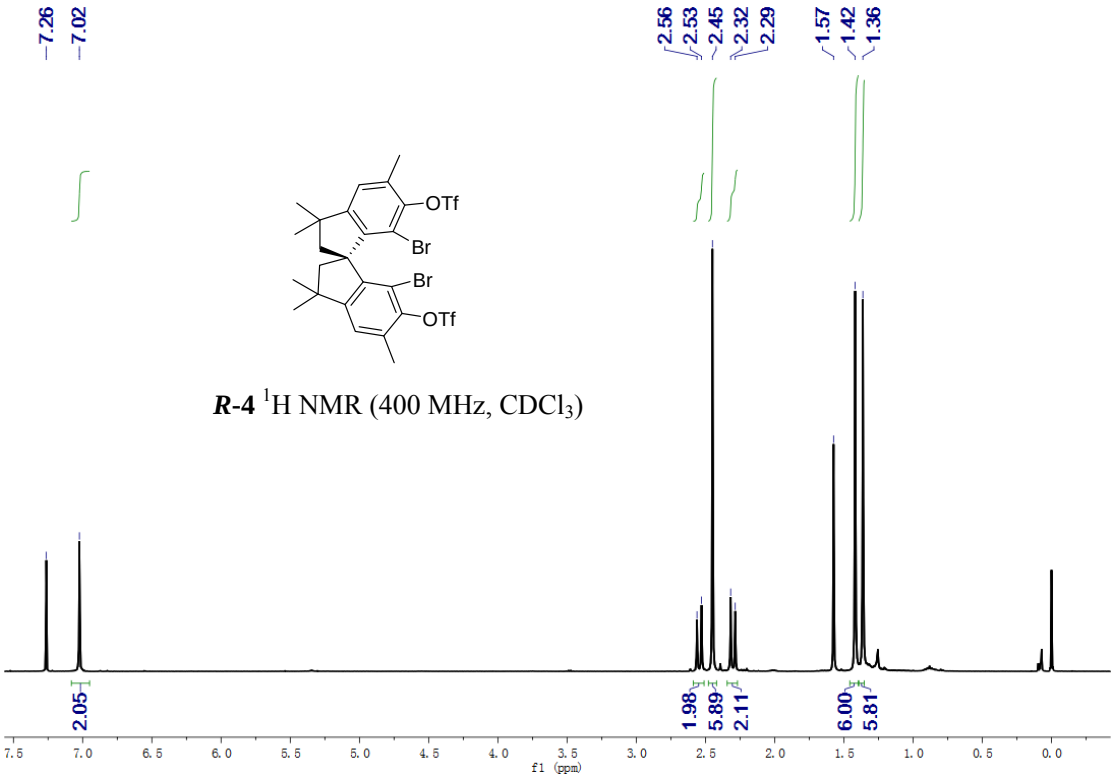




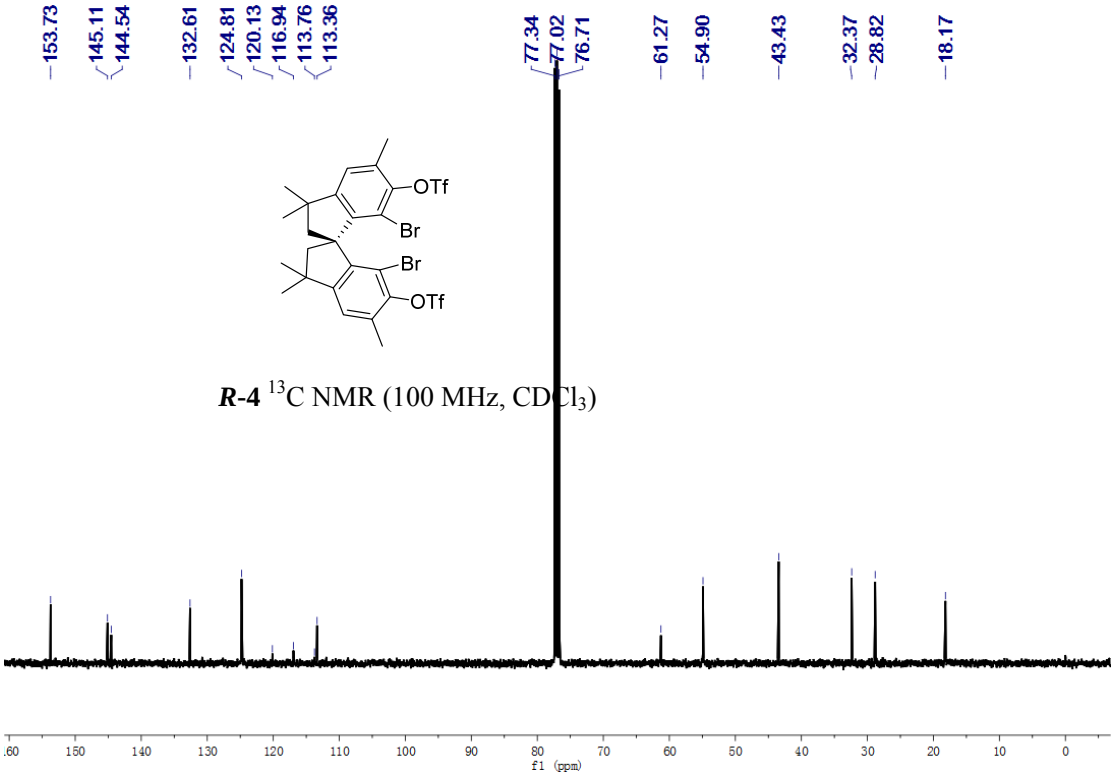
***S*-4** ^{1}H NMR (400 MHz, $CDCl_3$)



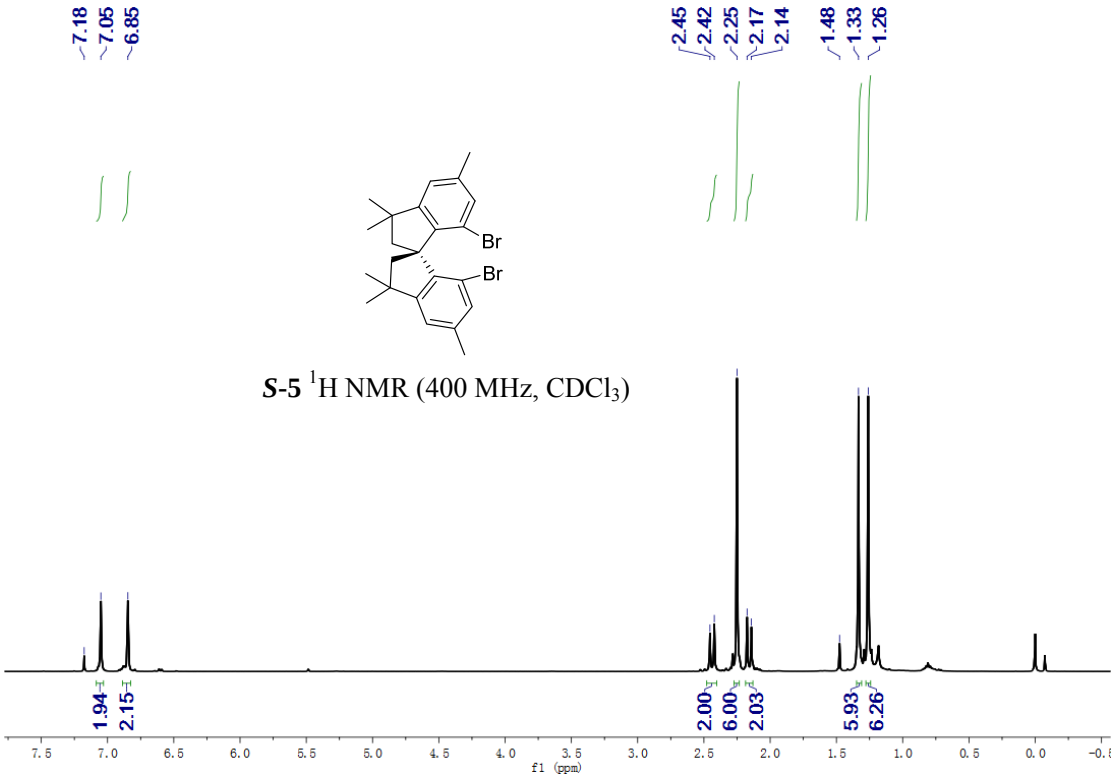
***S*-4** ^{13}C NMR (100 MHz, $CDCl_3$)



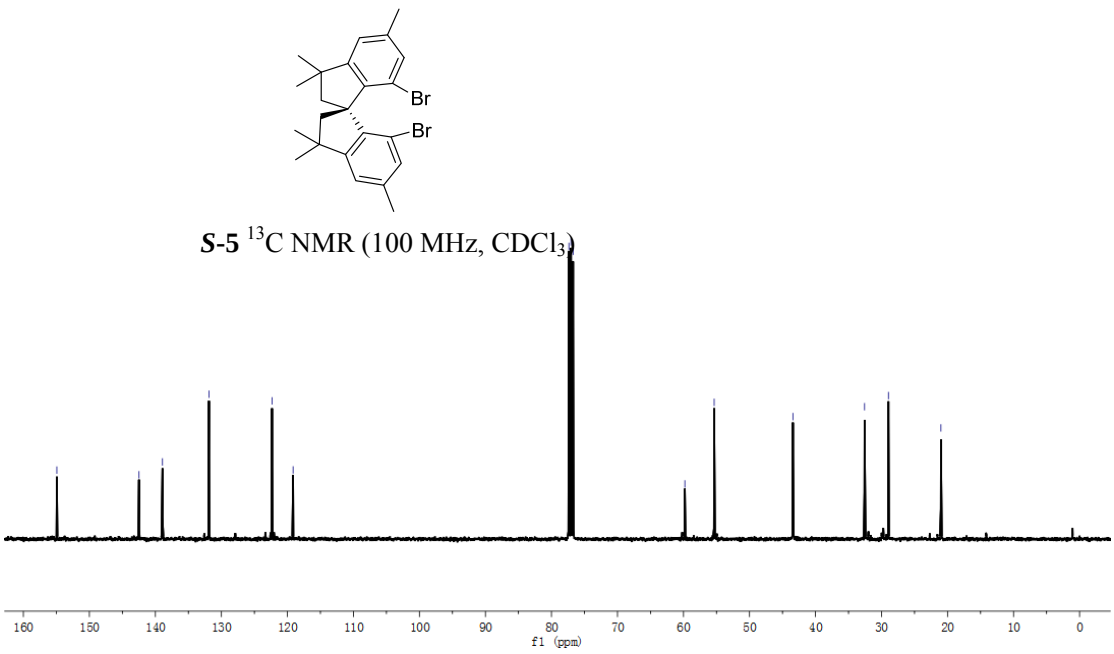
***R*-4** ^{1}H NMR (400 MHz, $CDCl_3$)



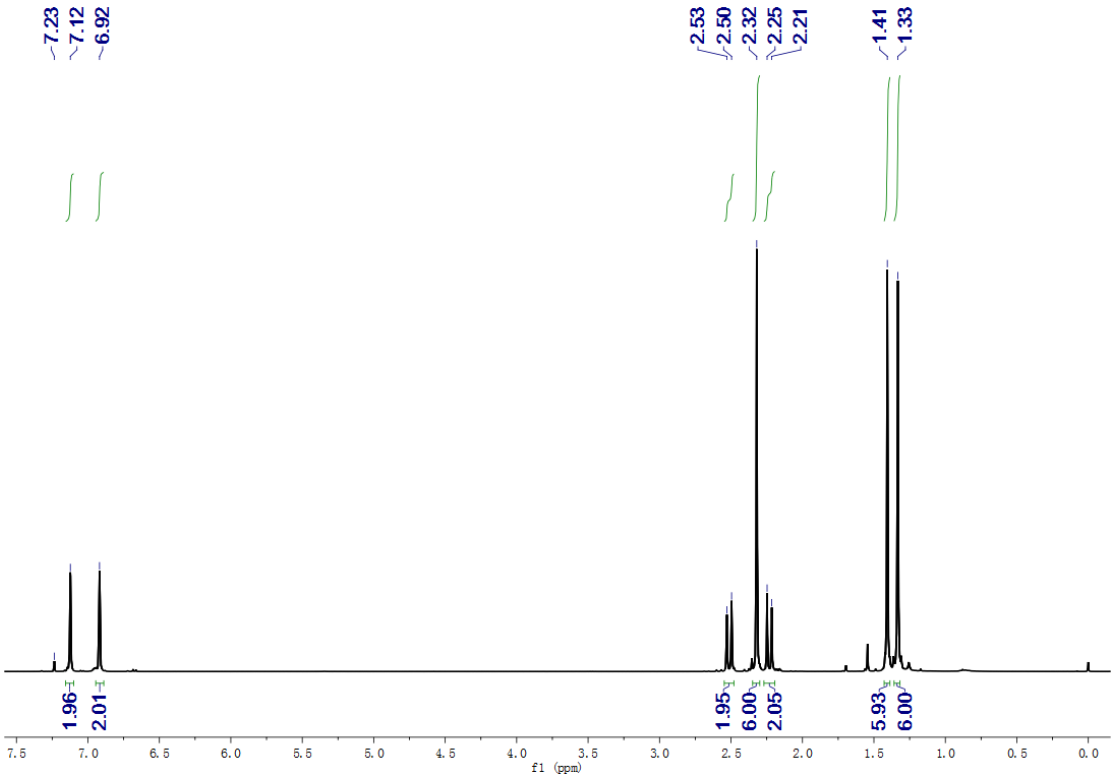
***R*-4** ^{13}C NMR (100 MHz, $CDCl_3$)

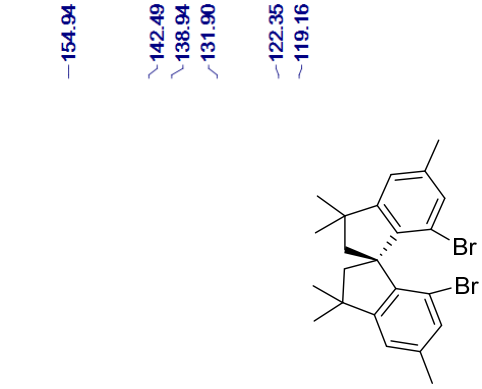


***S*-5** ^{1}H NMR (400 MHz, $CDCl_3$)

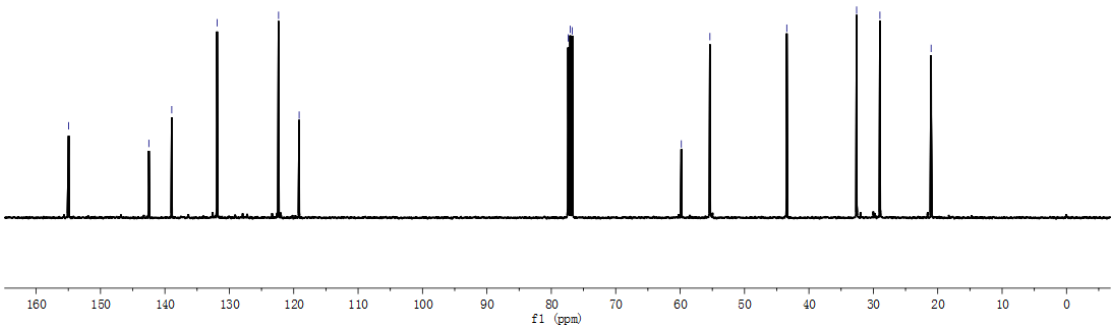


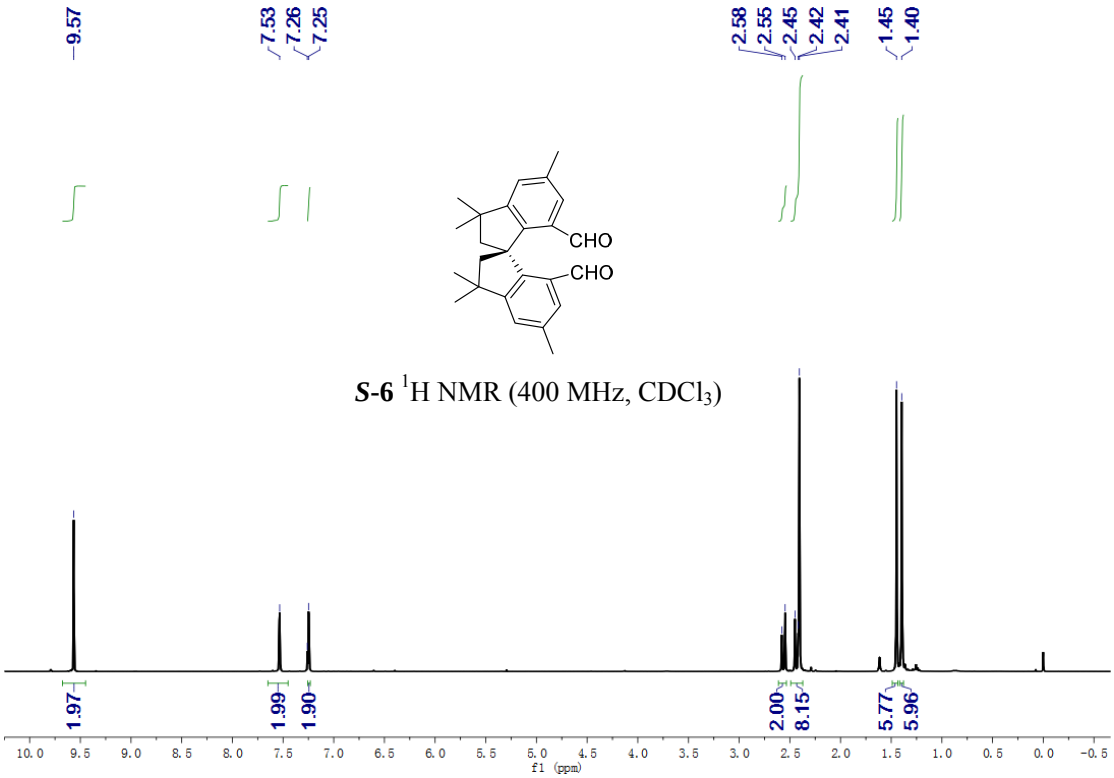
***S*-5** ^{13}C NMR (100 MHz, $CDCl_3$)



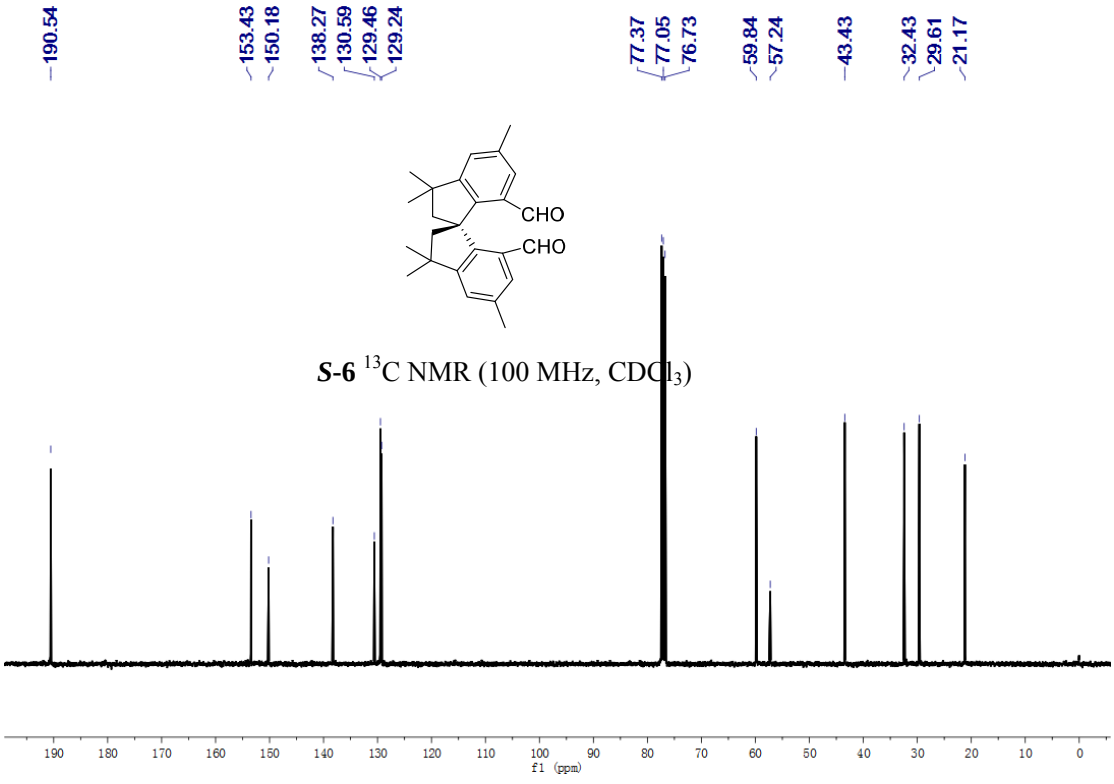


***R*-5** ^{13}C NMR (100 MHz, $CDCl_3$)

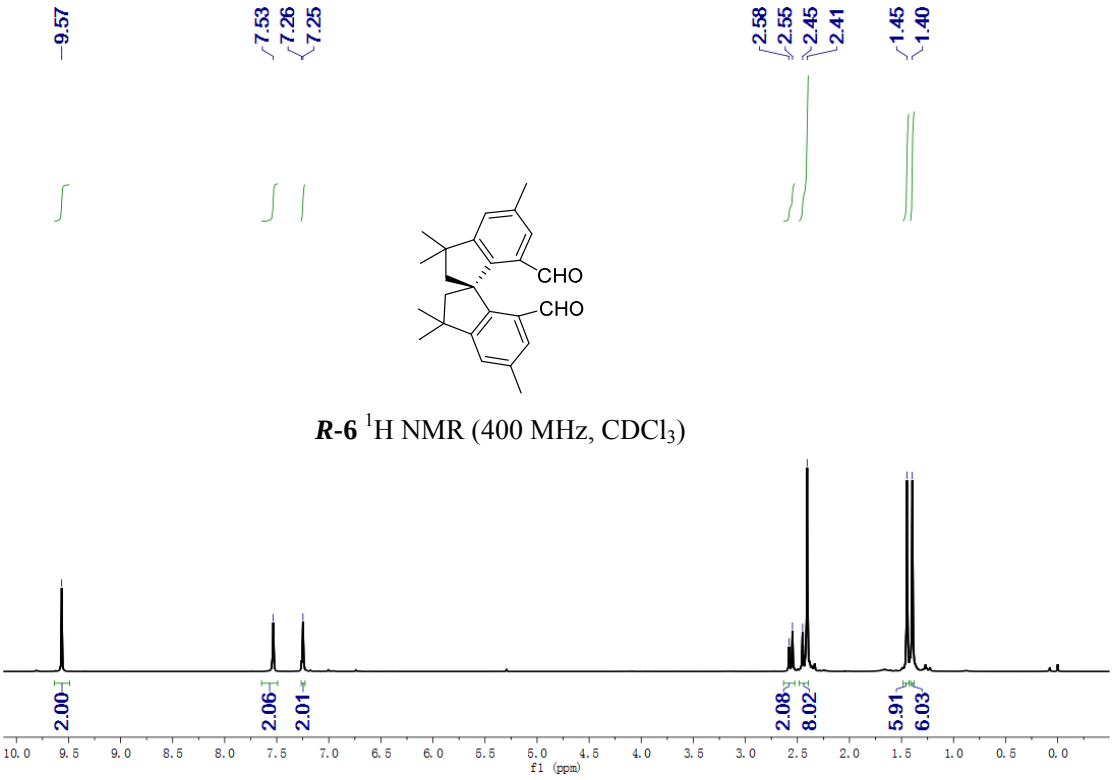




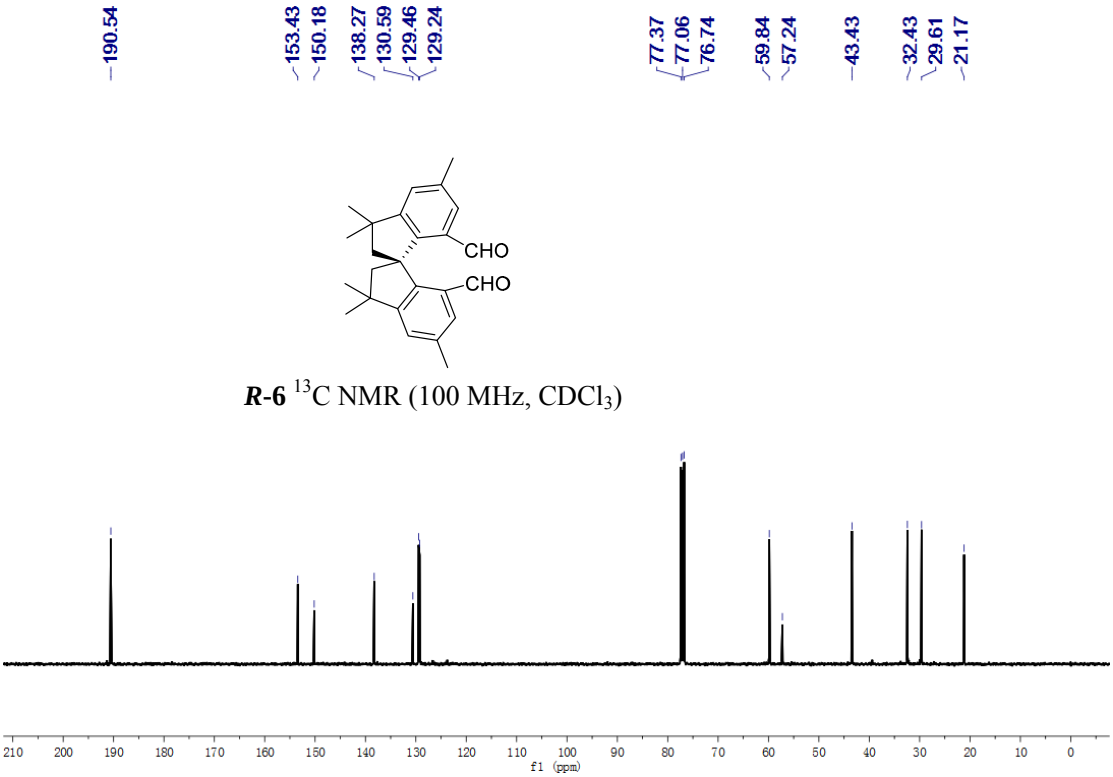
***S*-6** ^{1}H NMR (400 MHz, $CDCl_3$)



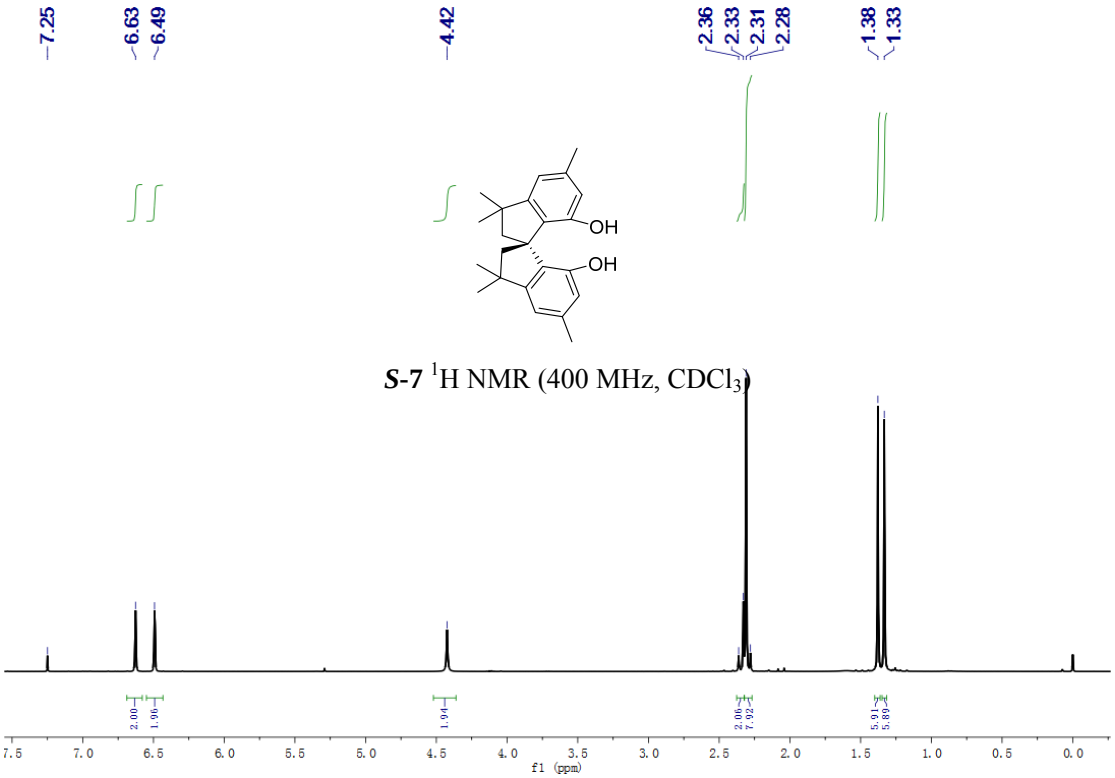
***S*-6** ^{13}C NMR (100 MHz, $CDCl_3$)



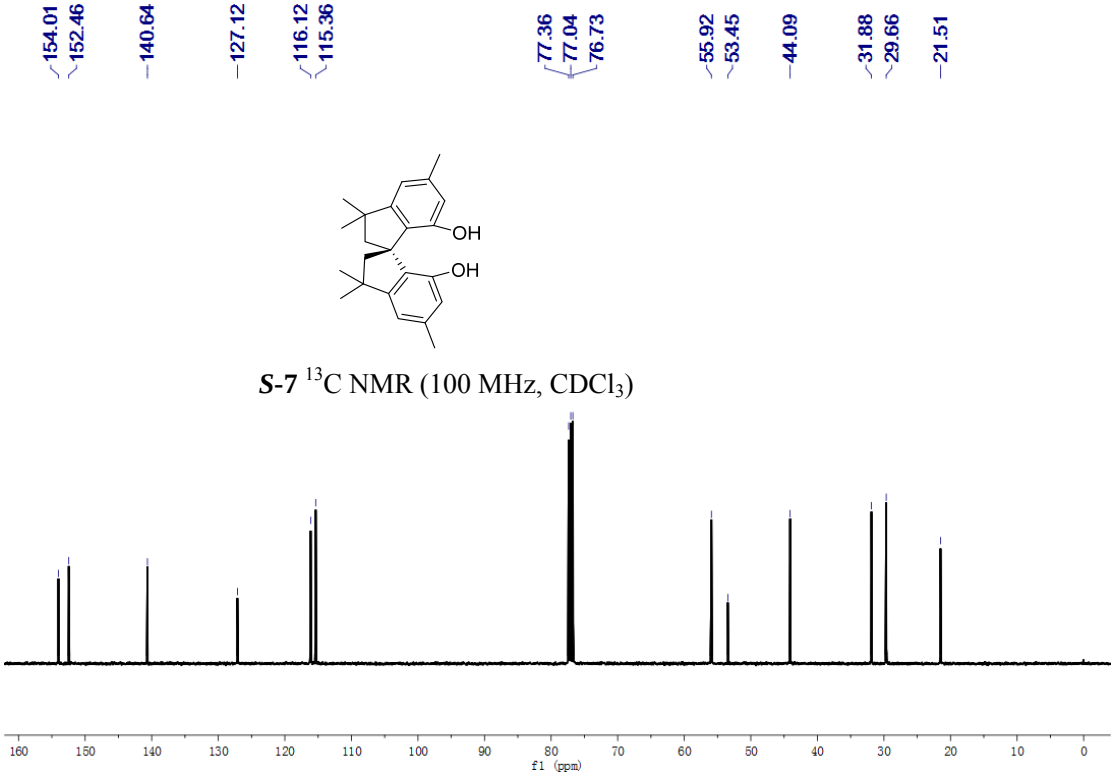
***R*-6** ^{1}H NMR (400 MHz, $CDCl_3$)



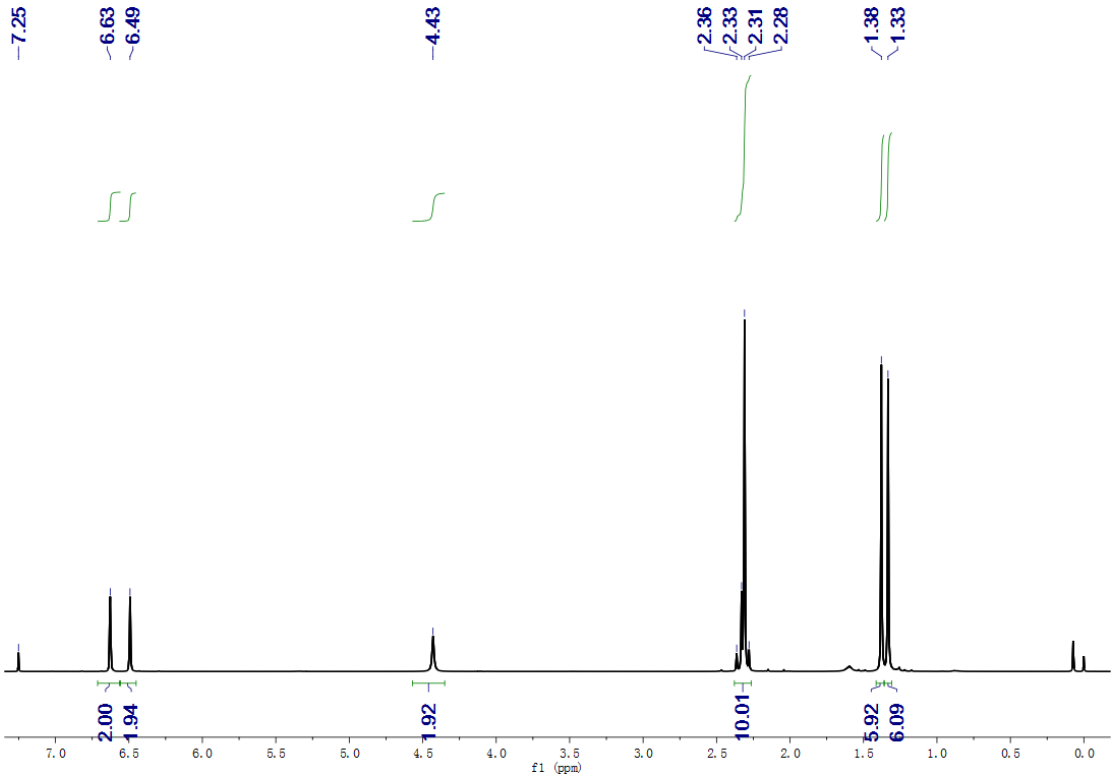
***R*-6** ^{13}C NMR (100 MHz, $CDCl_3$)

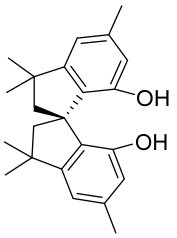


***S*-7** ^{1}H NMR (400 MHz, $CDCl_3$)

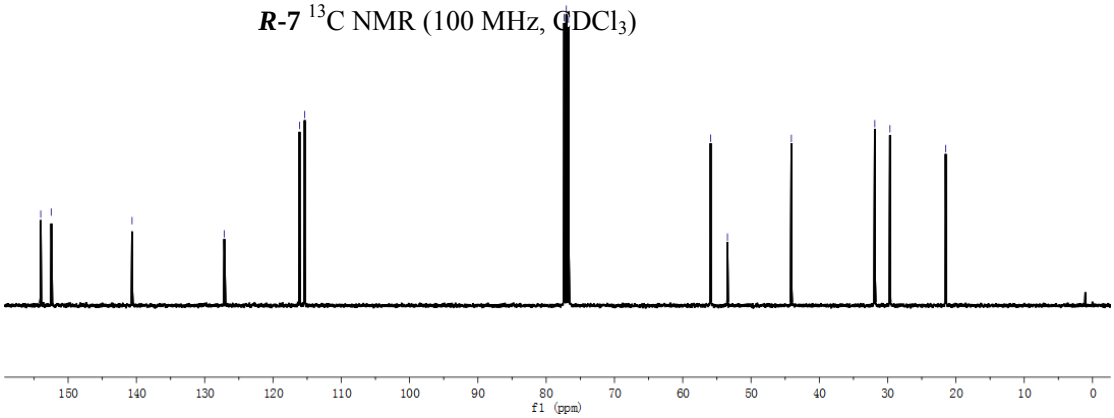


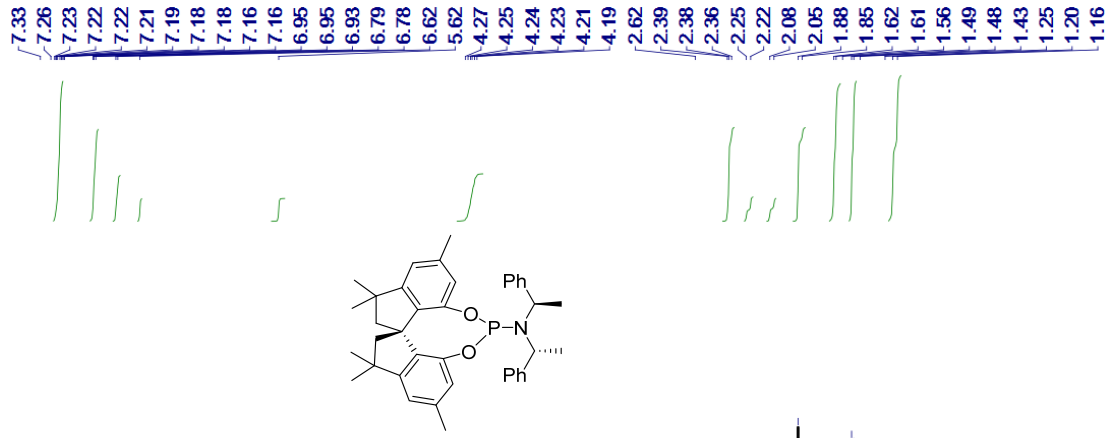
***S*-7** ^{13}C NMR (100 MHz, $CDCl_3$)



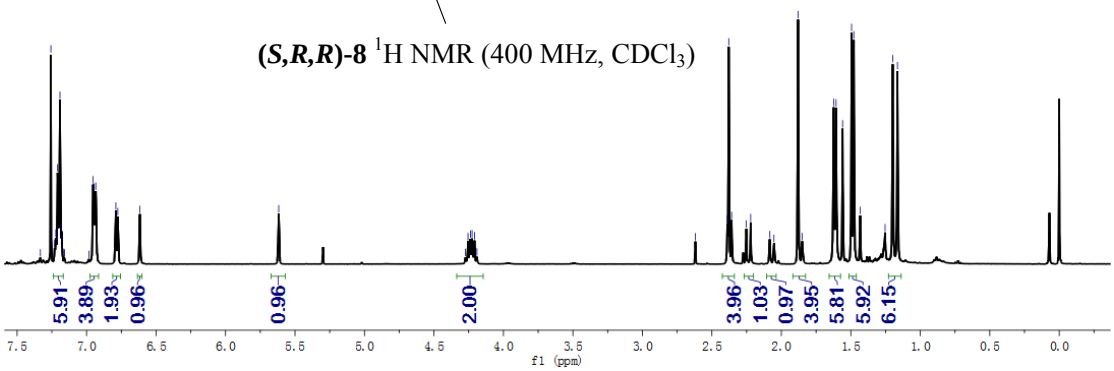


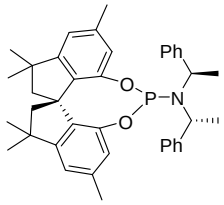
***R*-7** ^{13}C NMR (100 MHz, $CDCl_3$)



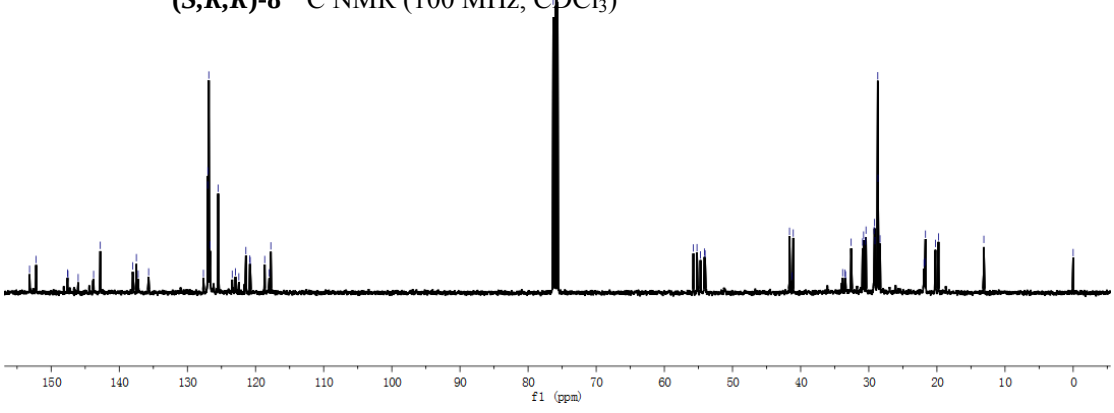


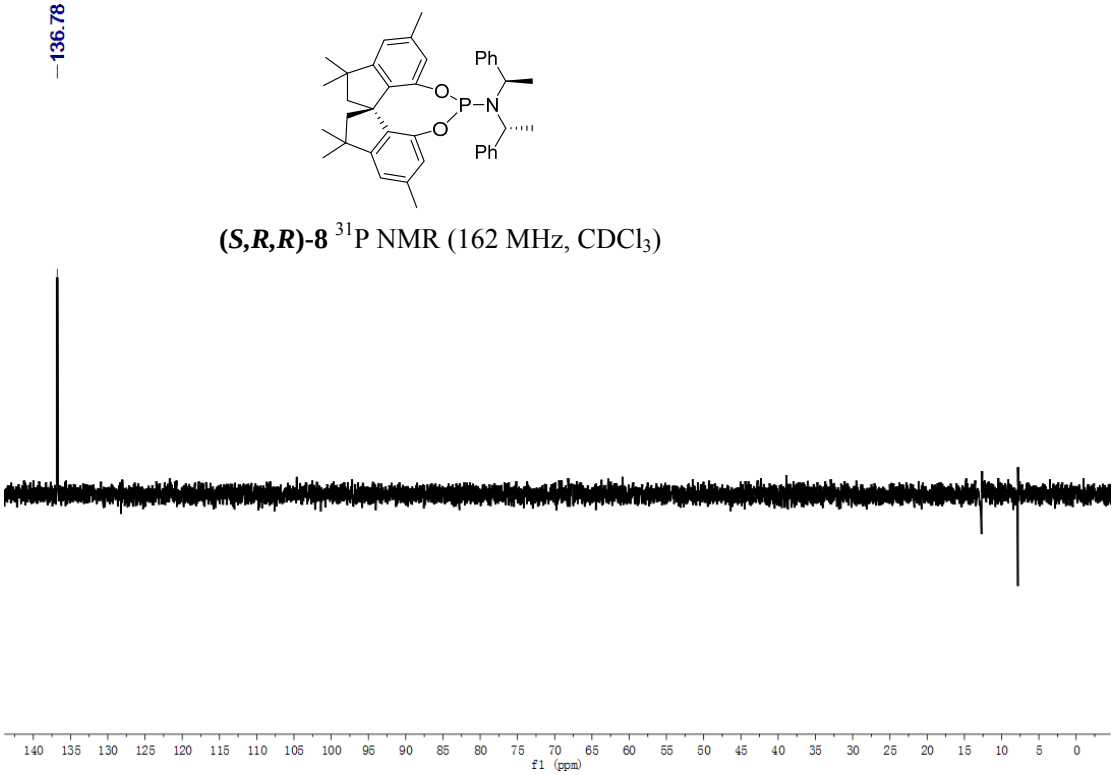
(*S*,*R*,*R*)-8 ^{1}H NMR (400 MHz, $CDCl_3$)



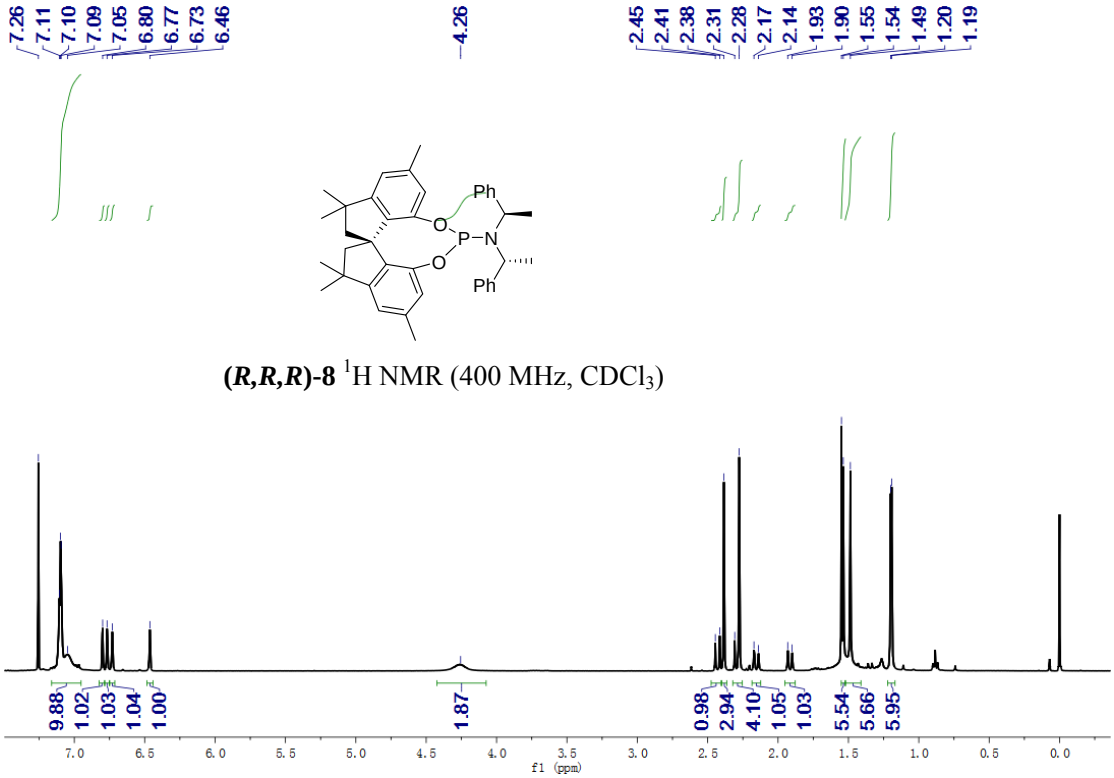


(*S*,*R*,*R*)-8 ^{13}C NMR (100 MHz, $CDCl_3$)

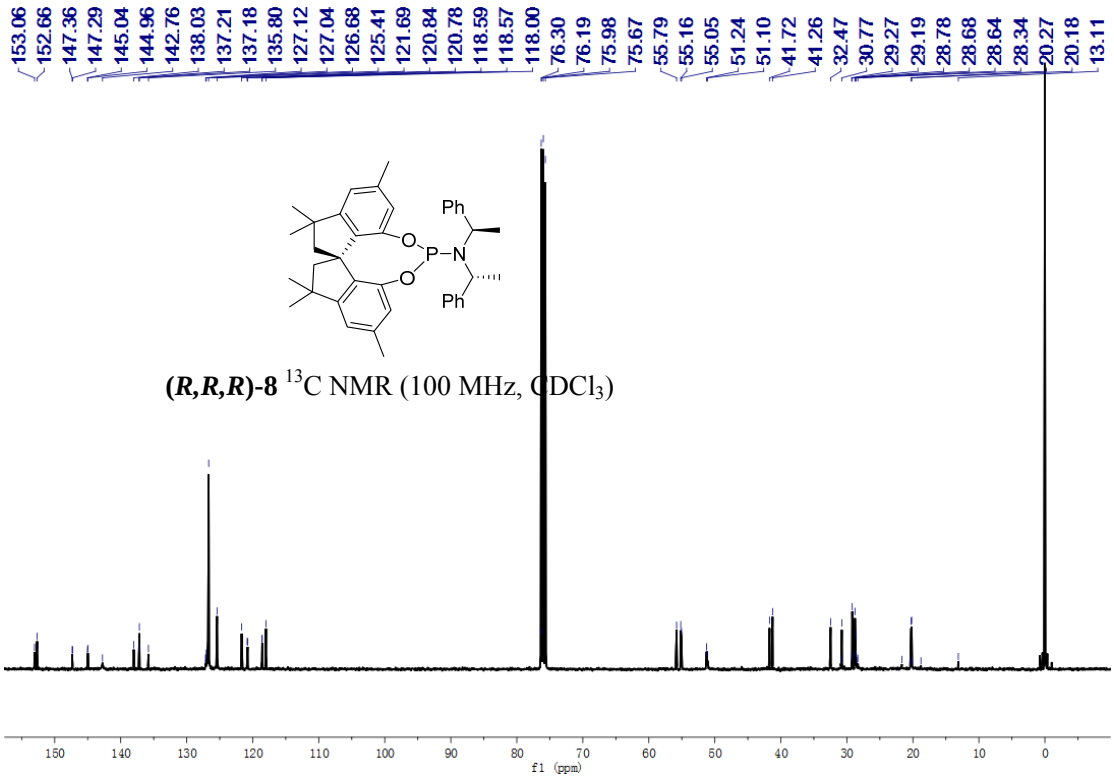




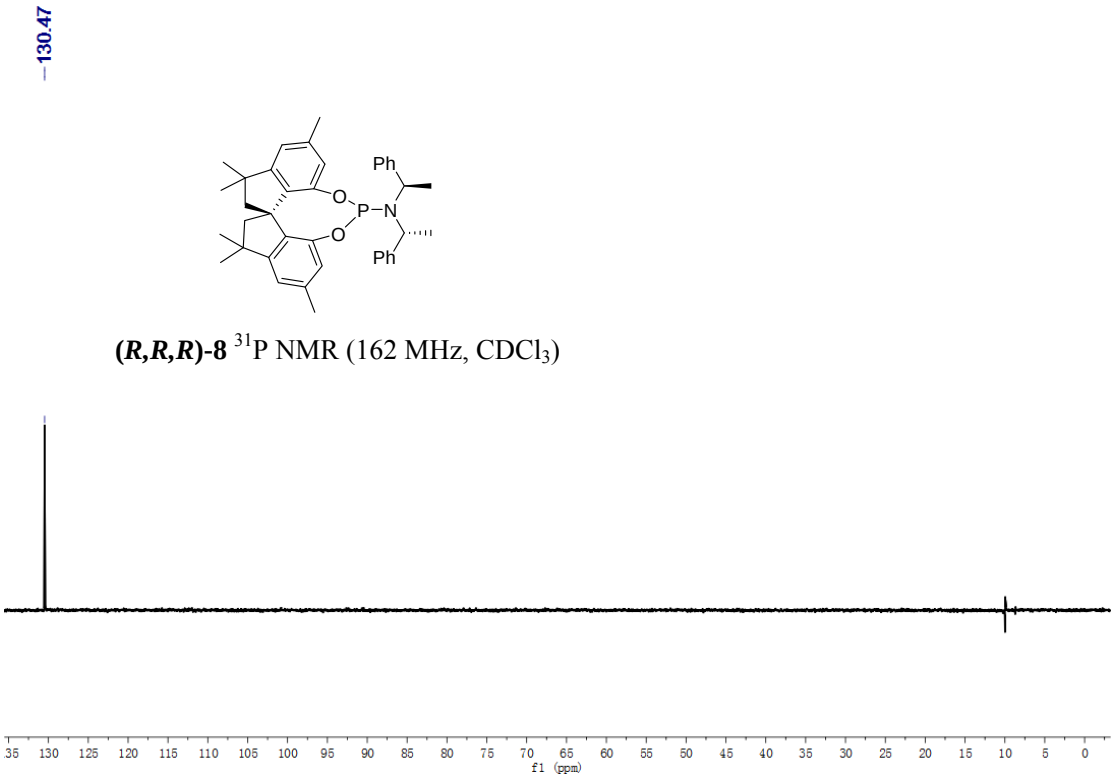
(*S,R,R*)-8 ^{31}P NMR (162 MHz, $CDCl_3$)



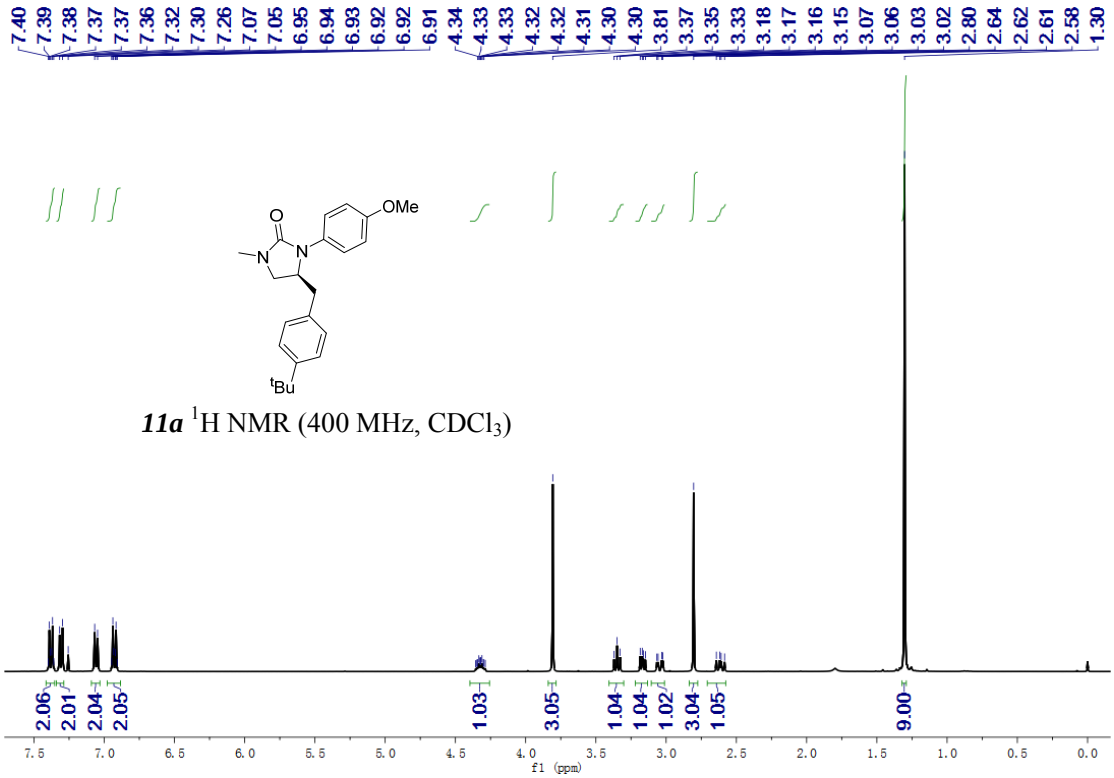
(*R,R,R*)-8 ^{1}H NMR (400 MHz, $CDCl_3$)



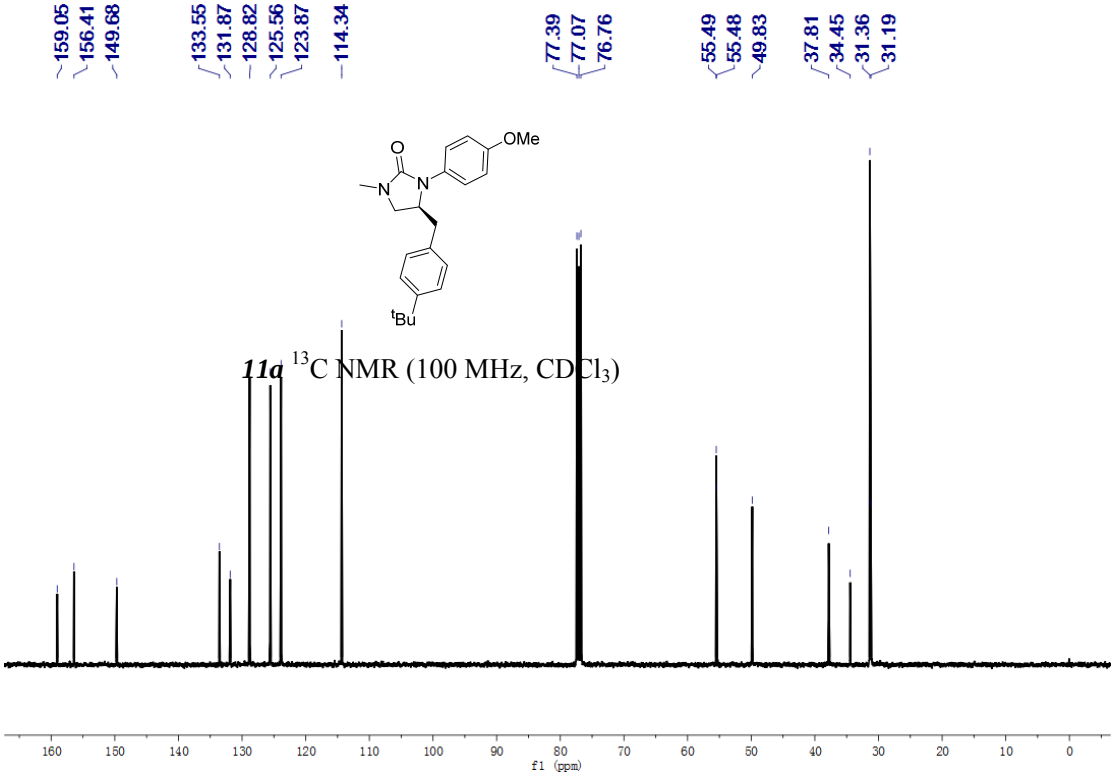
(*R*,*R*,*R*)-8 ^{13}C NMR (100 MHz, $CDCl_3$)



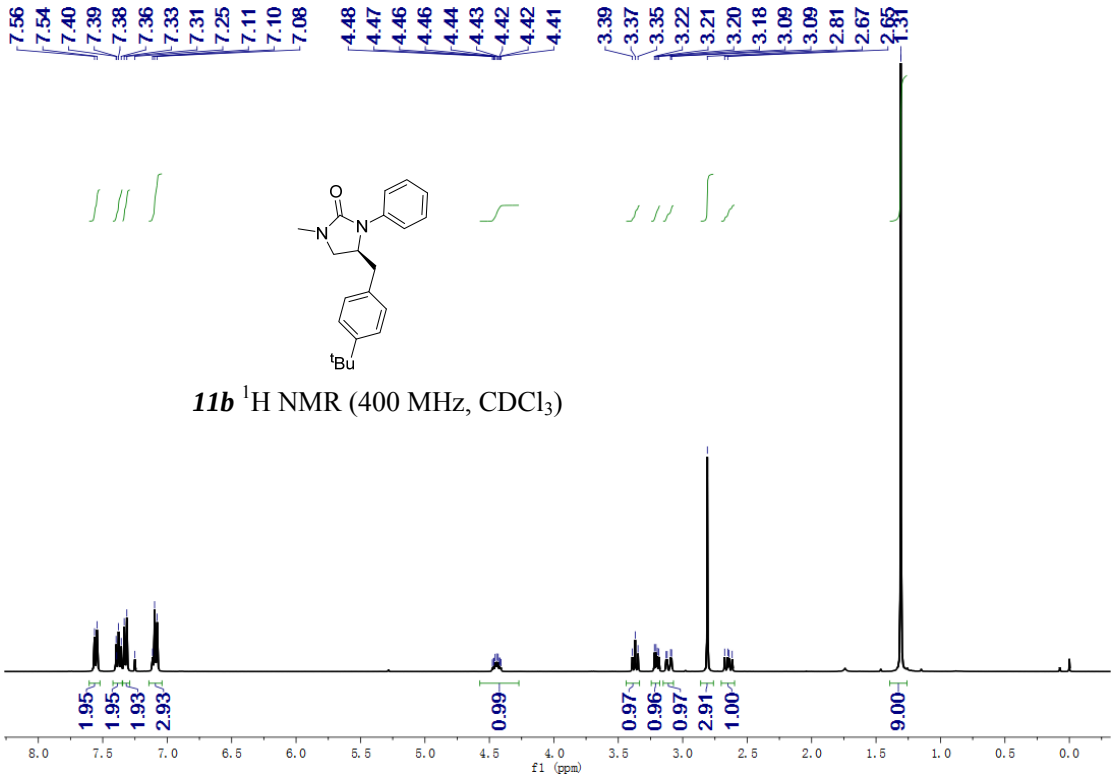
(*R*,*R*,*R*)-8 ^{31}P NMR (162 MHz, $CDCl_3$)



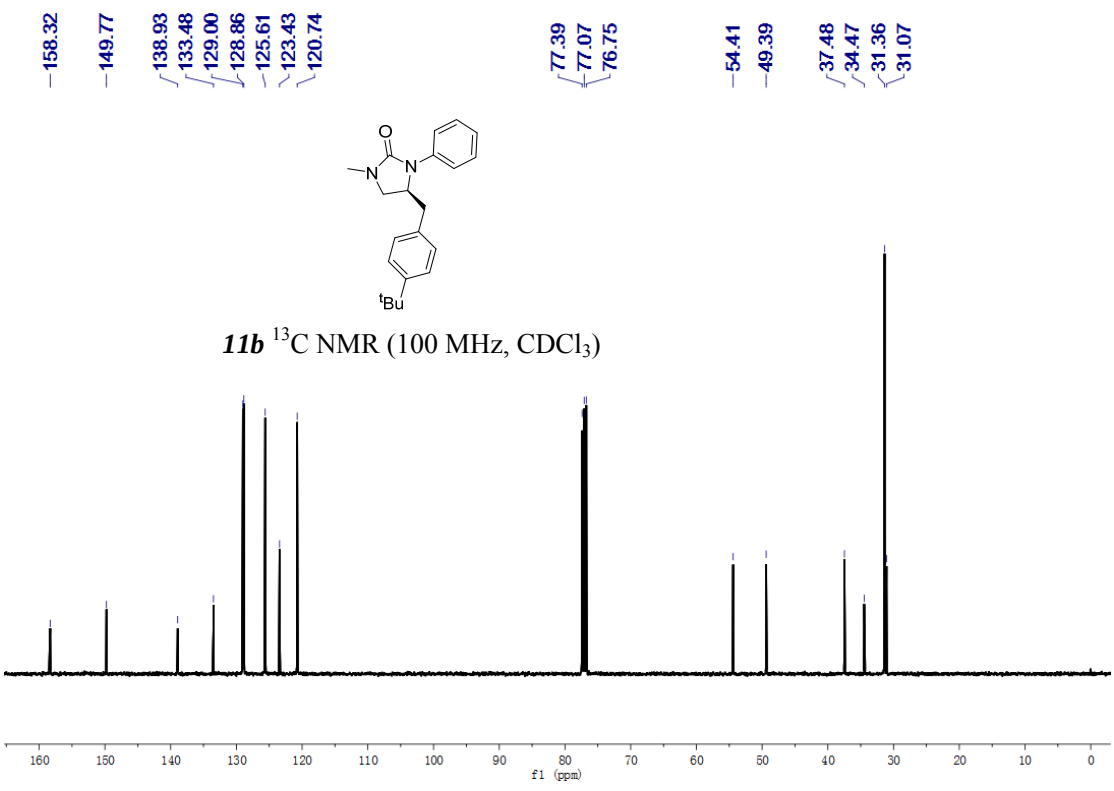
11a ^{1}H NMR (400 MHz, $CDCl_3$)



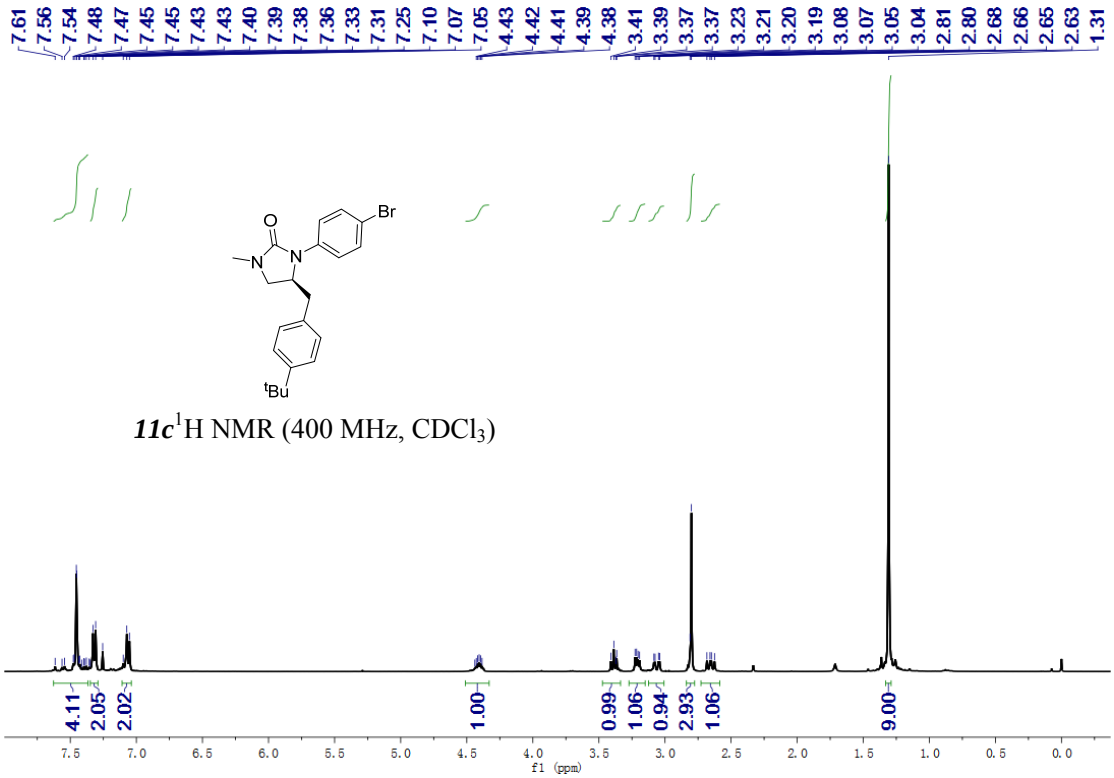
11a ^{13}C NMR (100 MHz, $CDCl_3$)



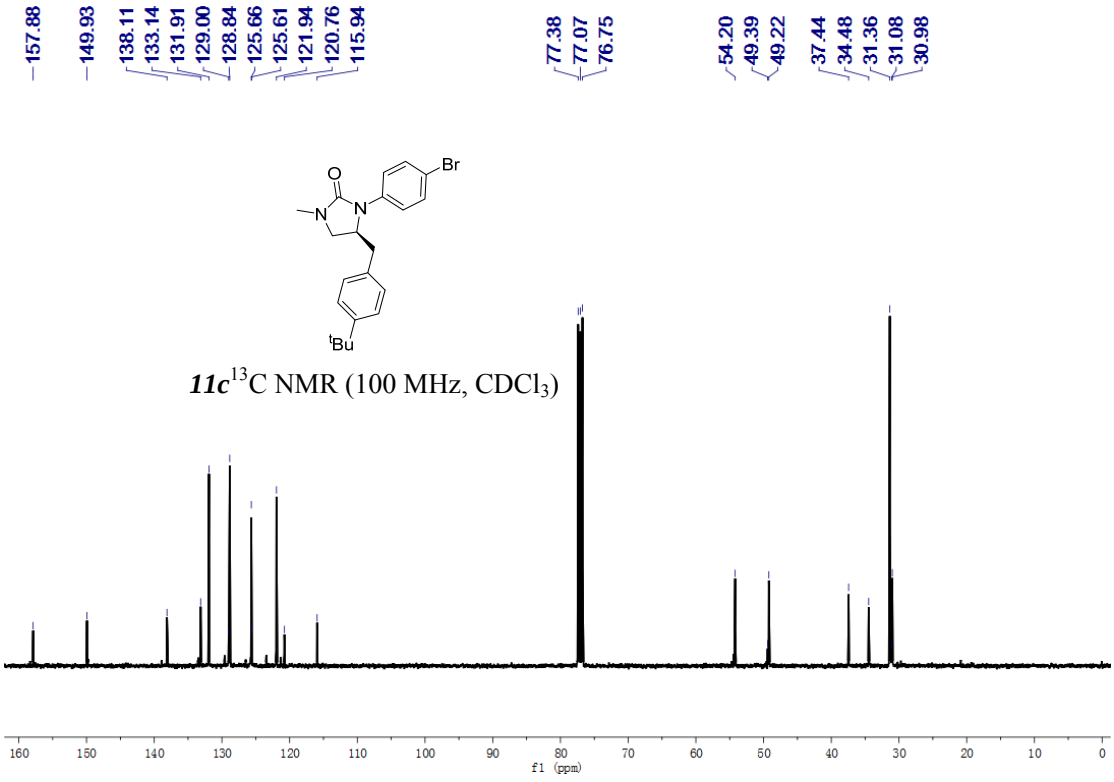
11b ^{1}H NMR (400 MHz, $CDCl_3$)



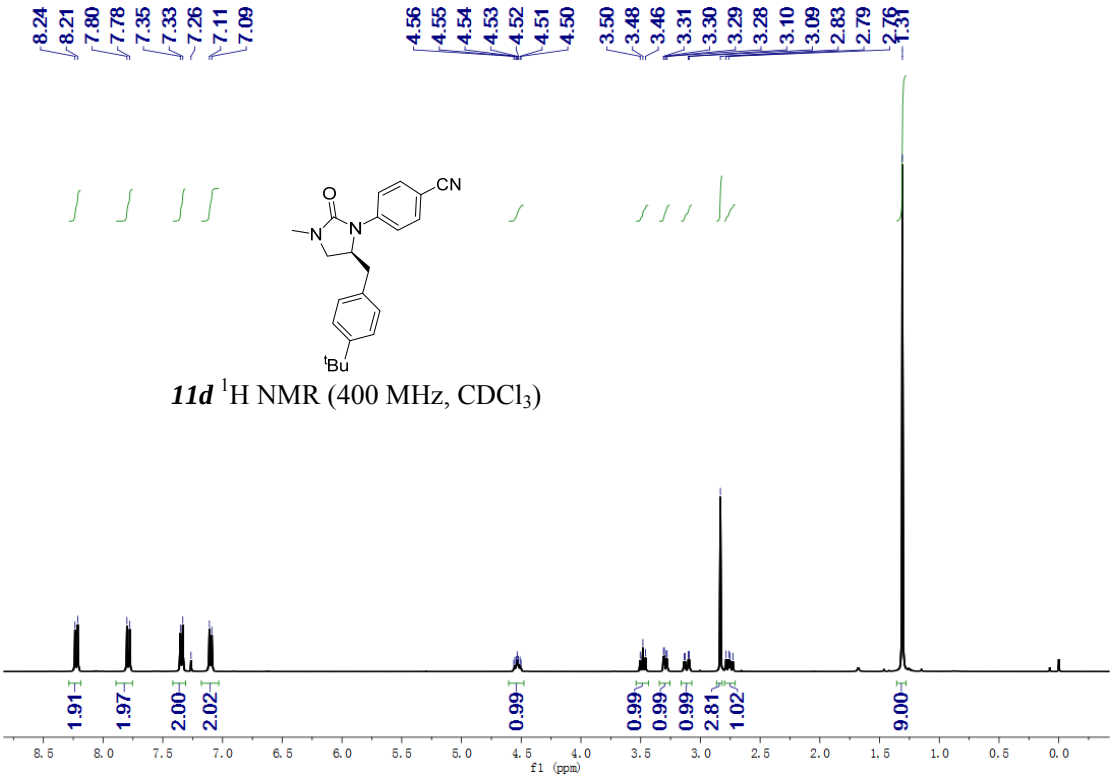
11b ^{13}C NMR (100 MHz, $CDCl_3$)



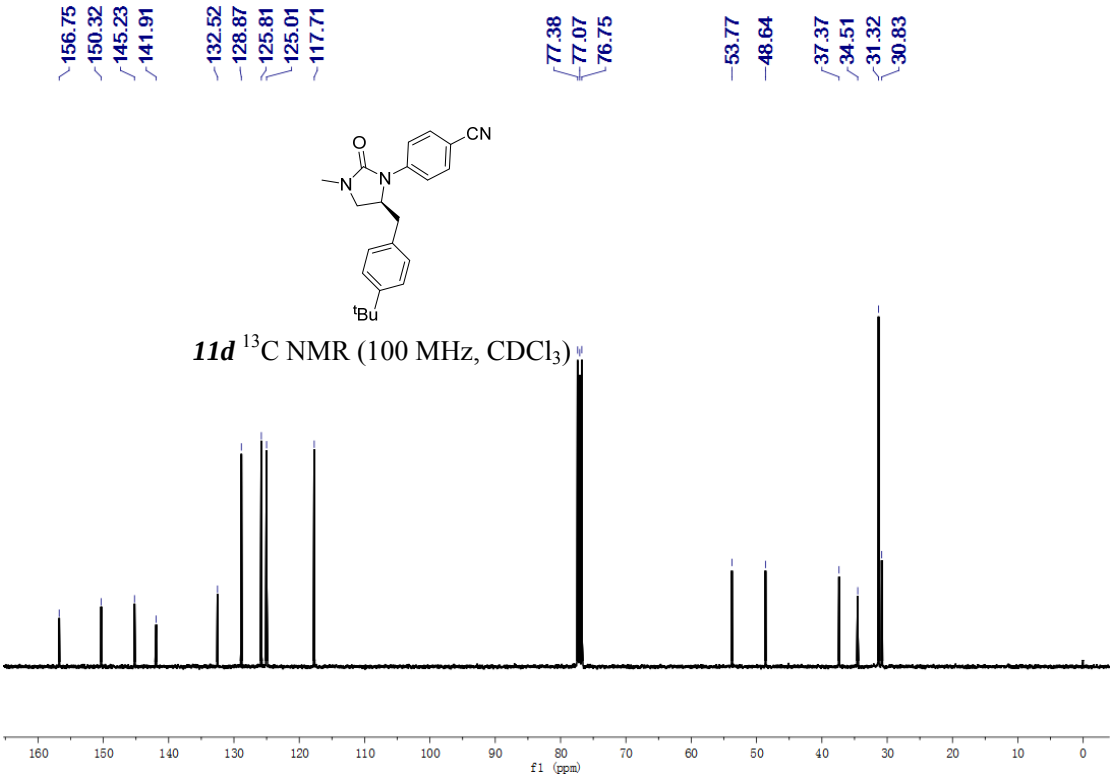
11c ^{1}H NMR (400 MHz, $CDCl_3$)



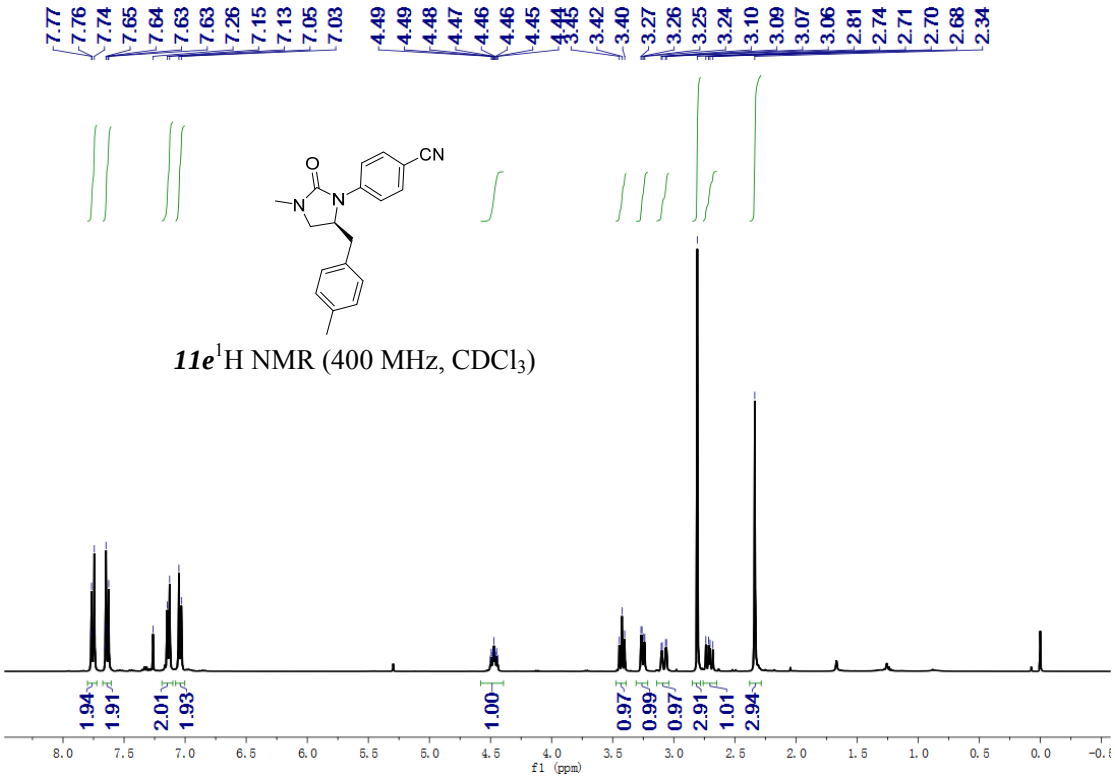
11c ^{13}C NMR (100 MHz, $CDCl_3$)



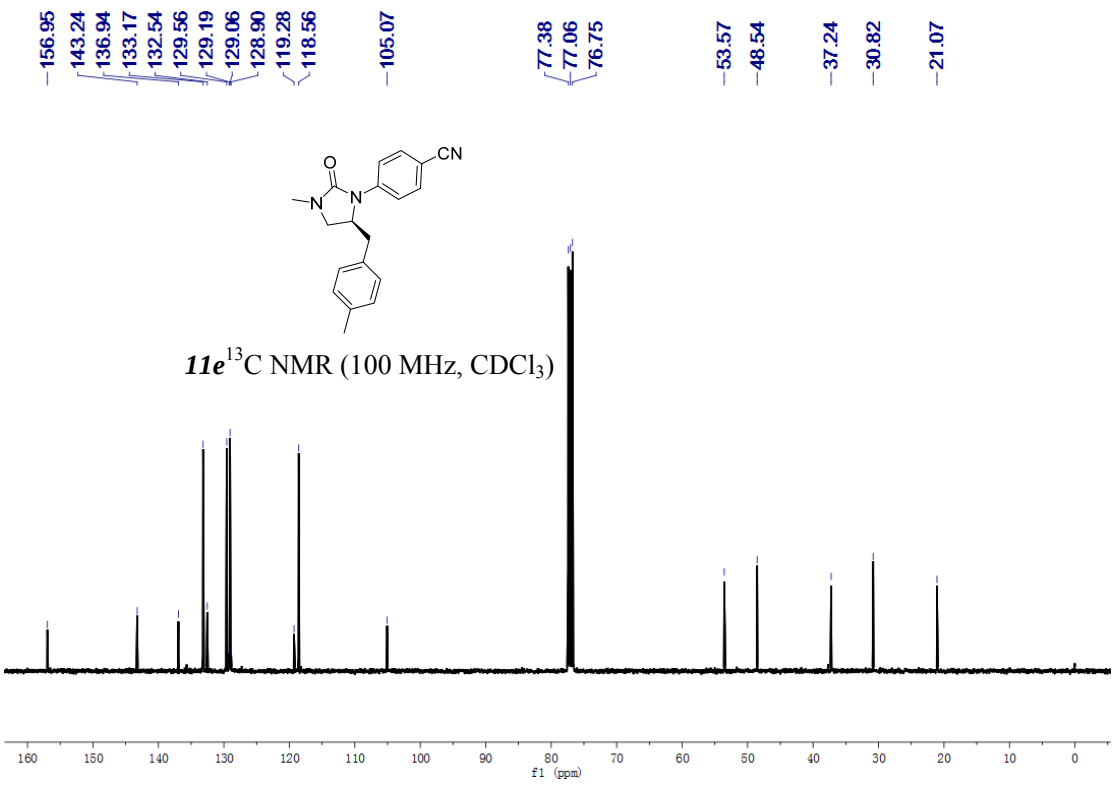
11d ^{1}H NMR (400 MHz, $CDCl_3$)



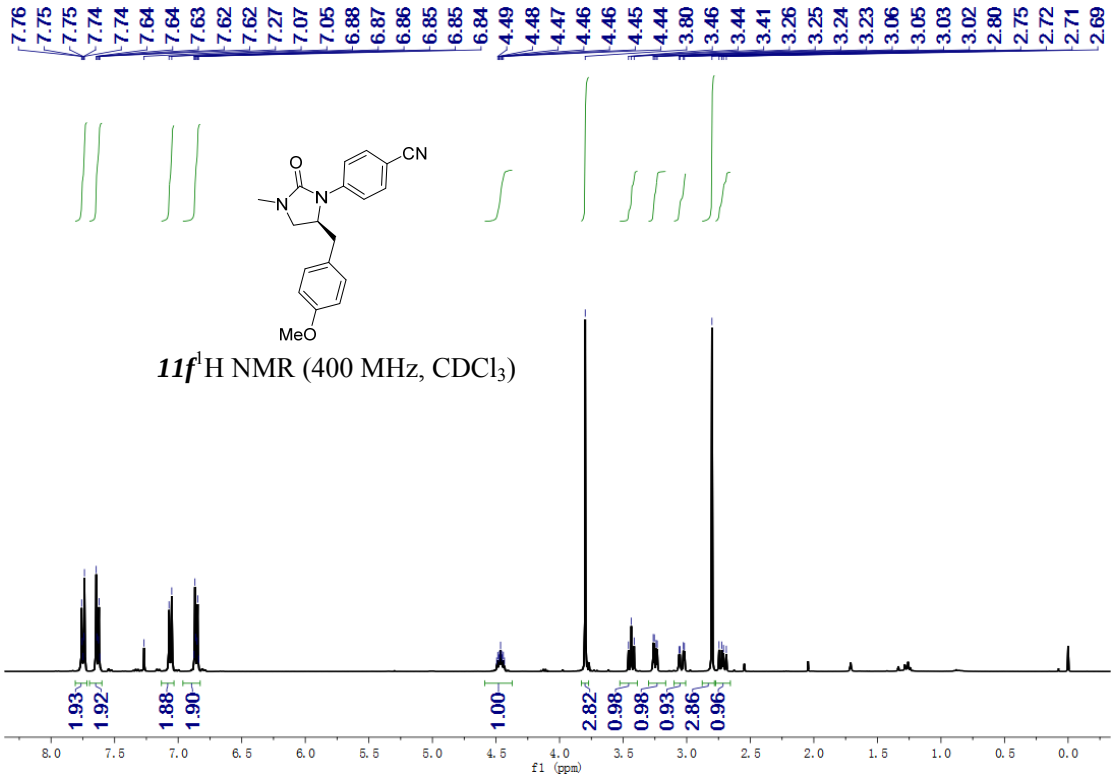
11d ^{13}C NMR (100 MHz, $CDCl_3$)



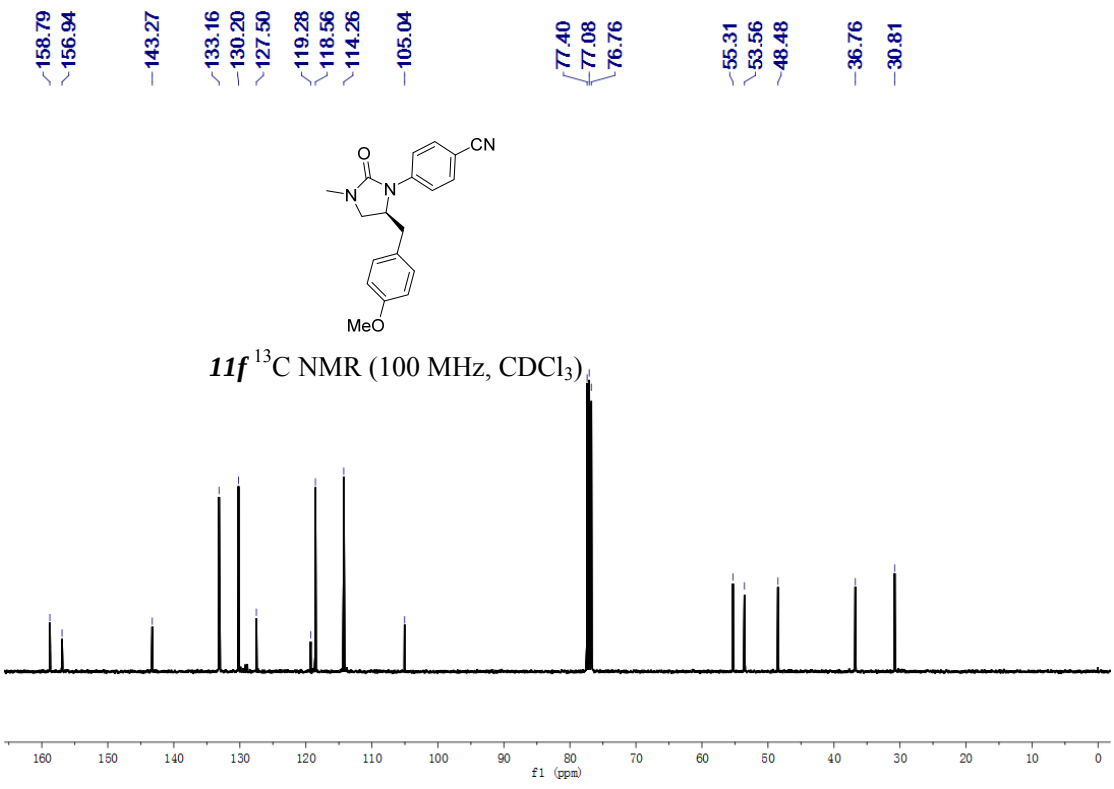
11e ^{1}H NMR (400 MHz, $CDCl_3$)



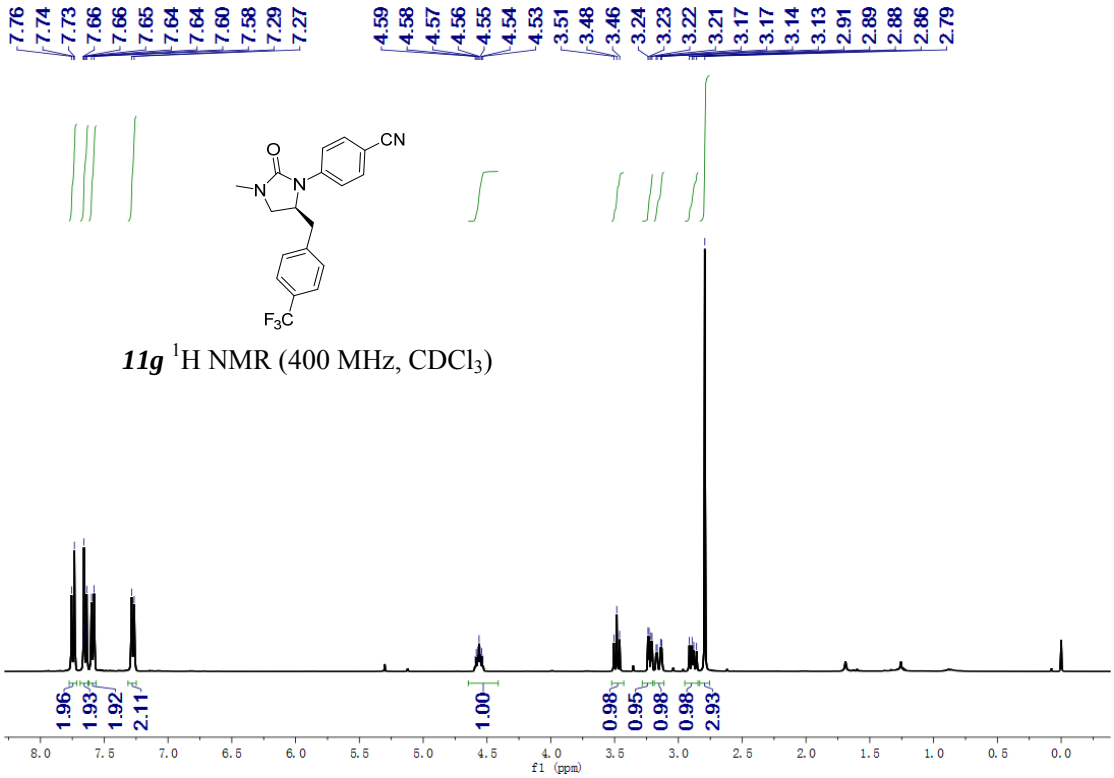
11e ^{13}C NMR (100 MHz, $CDCl_3$)



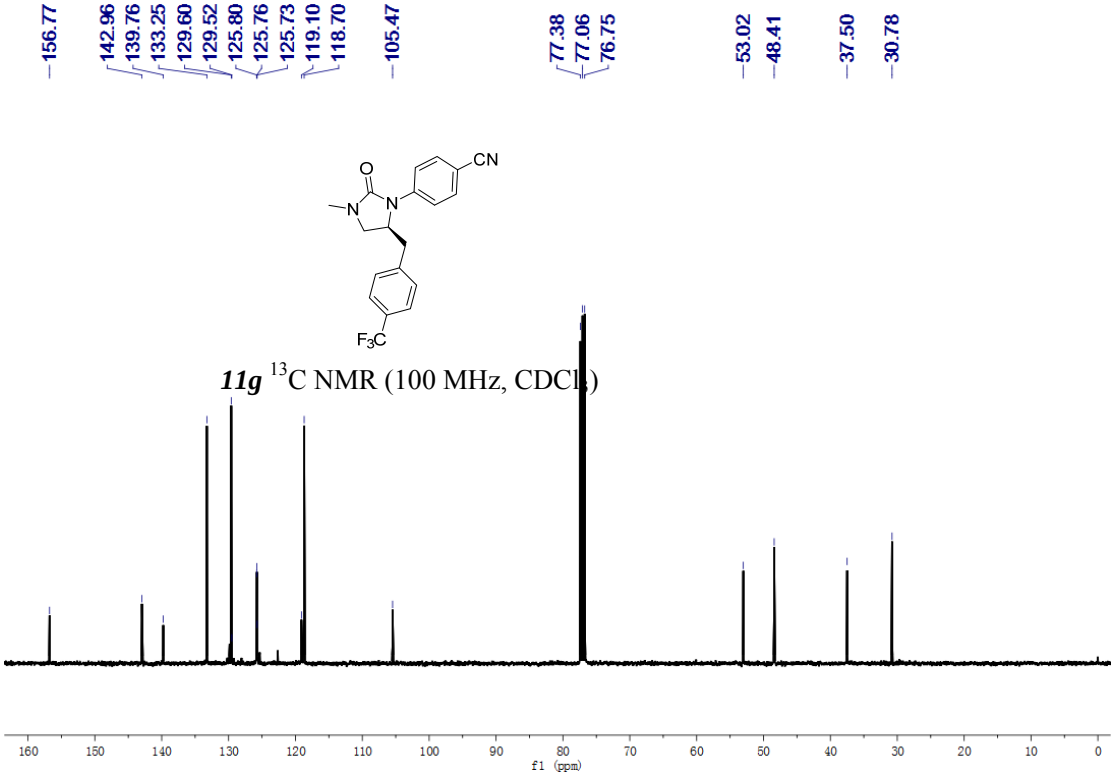
11f ^{1}H NMR (400 MHz, $CDCl_3$)



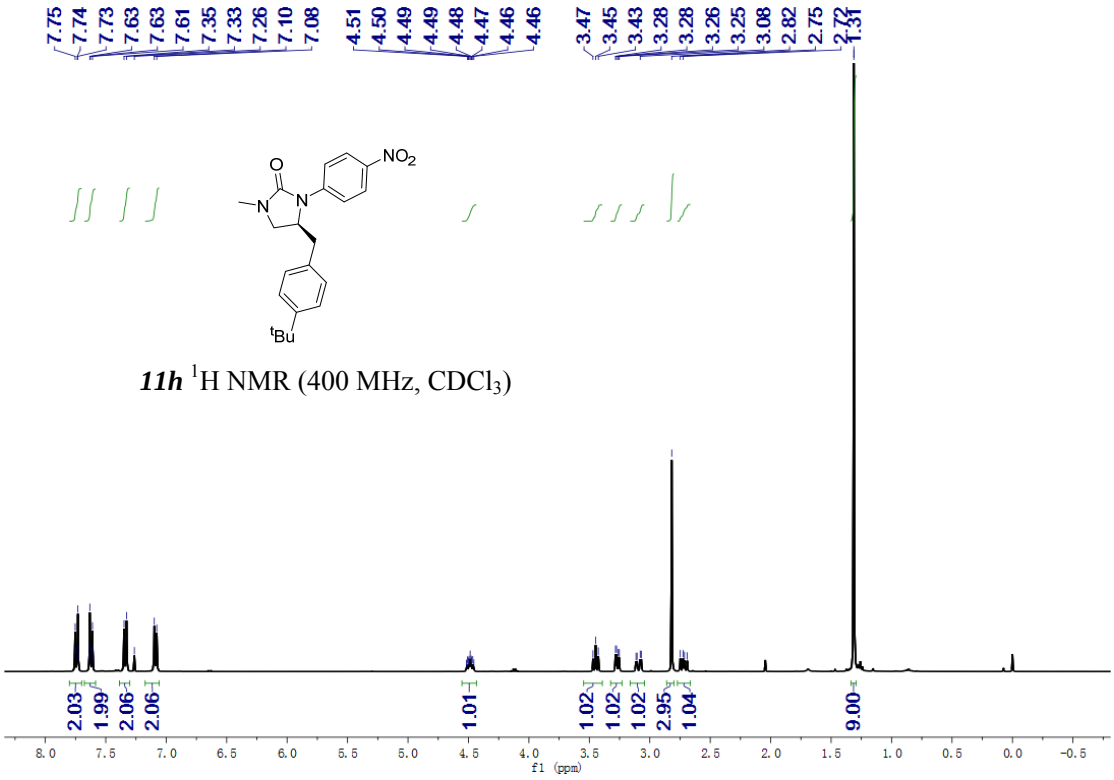
11f ^{13}C NMR (100 MHz, $CDCl_3$)



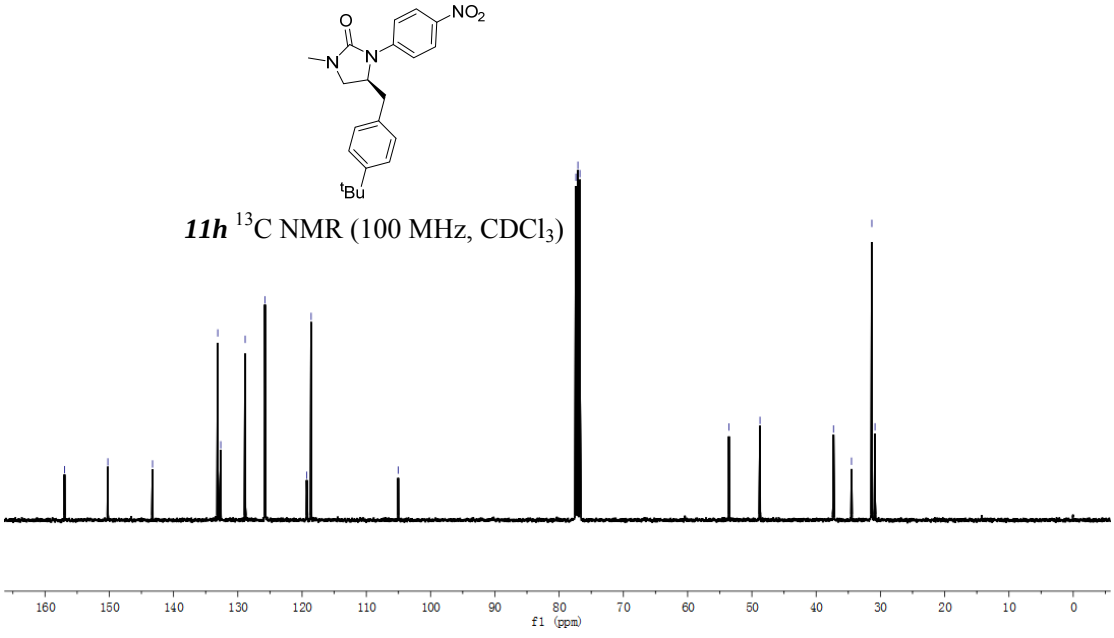
11g ^{1}H NMR (400 MHz, $CDCl_3$)



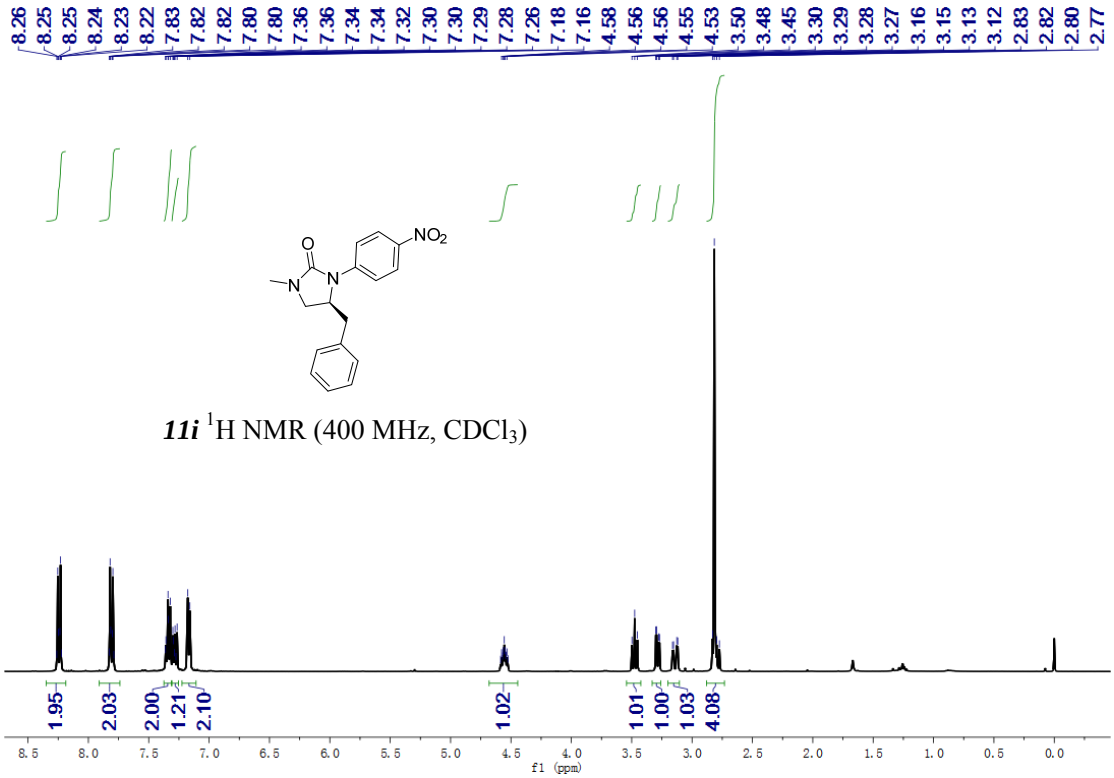
11g ^{13}C NMR (100 MHz, $CDCl_3$)



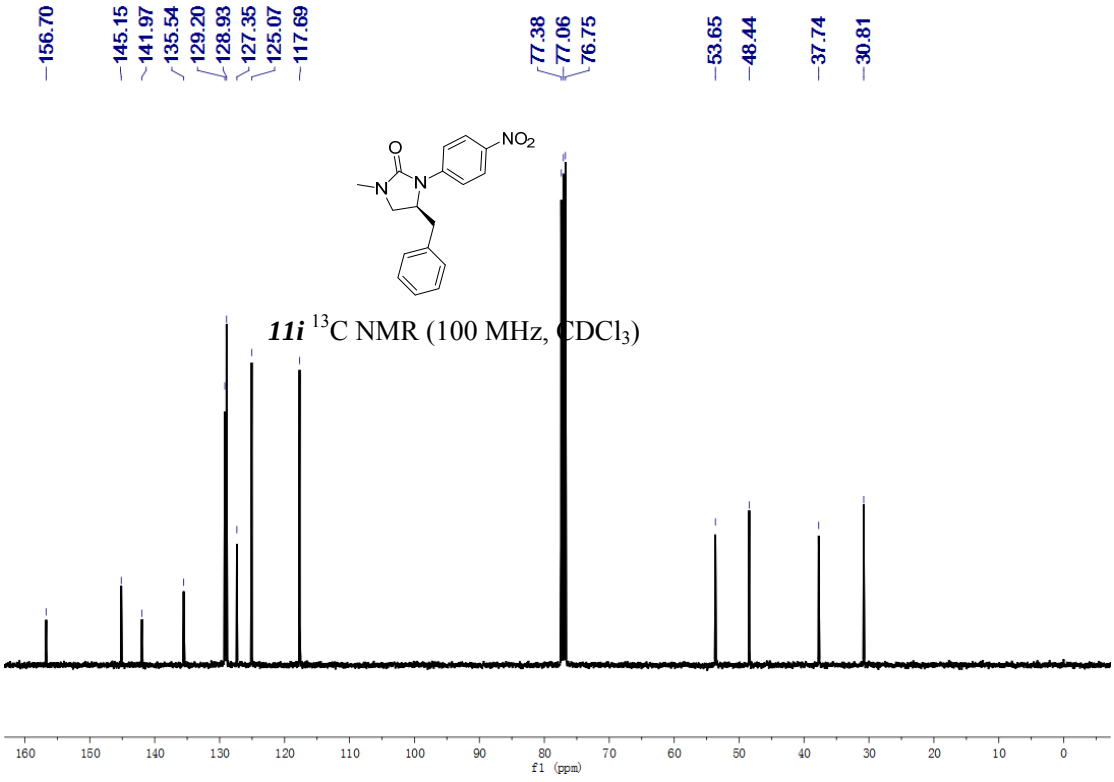
11h ^{1}H NMR (400 MHz, $CDCl_3$)



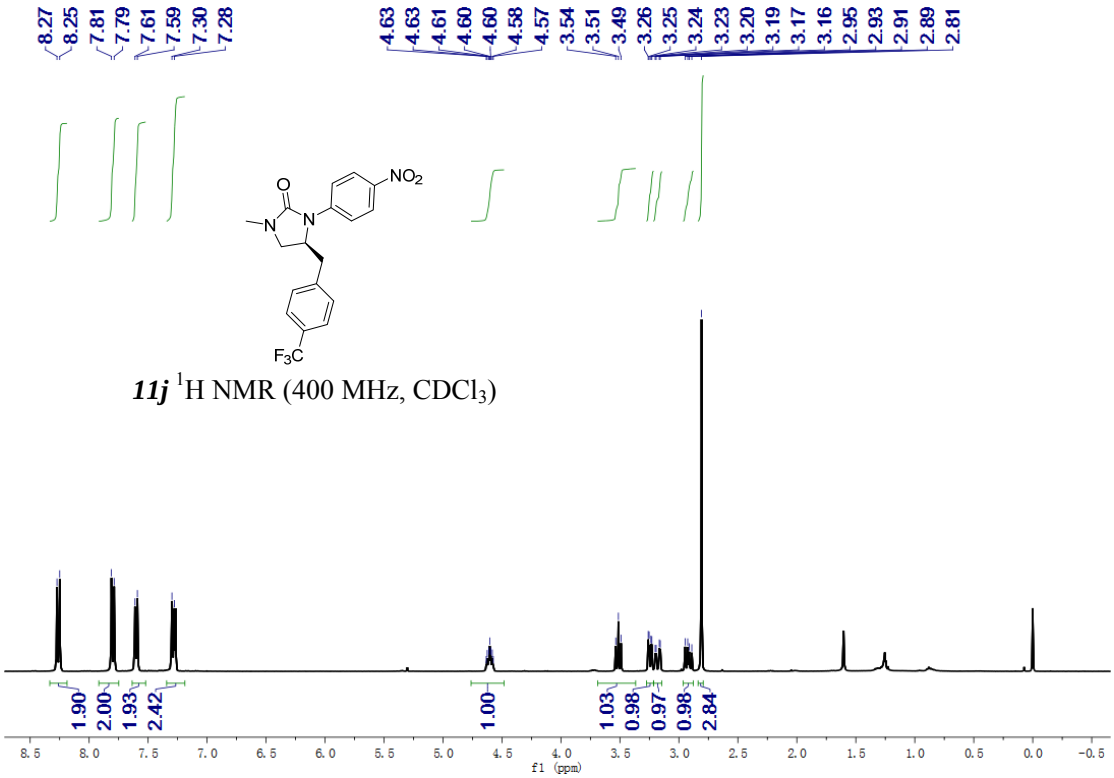
11h ^{13}C NMR (100 MHz, $CDCl_3$)



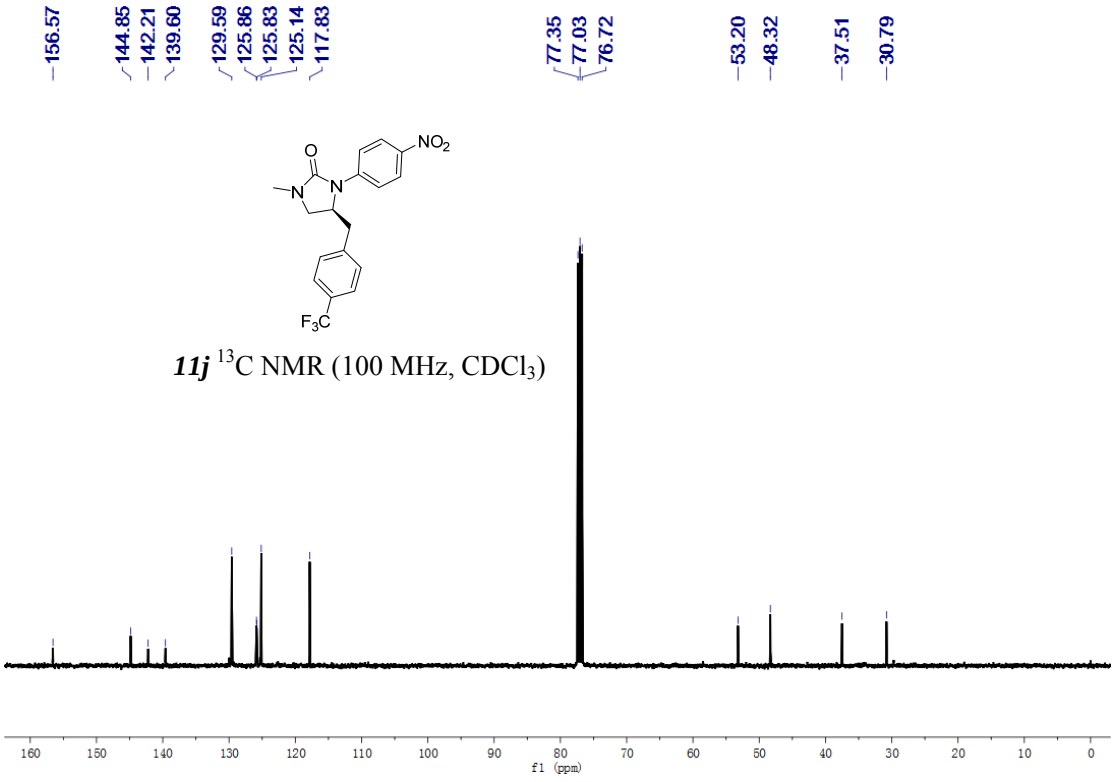
11i ^{1}H NMR (400 MHz, $CDCl_3$)



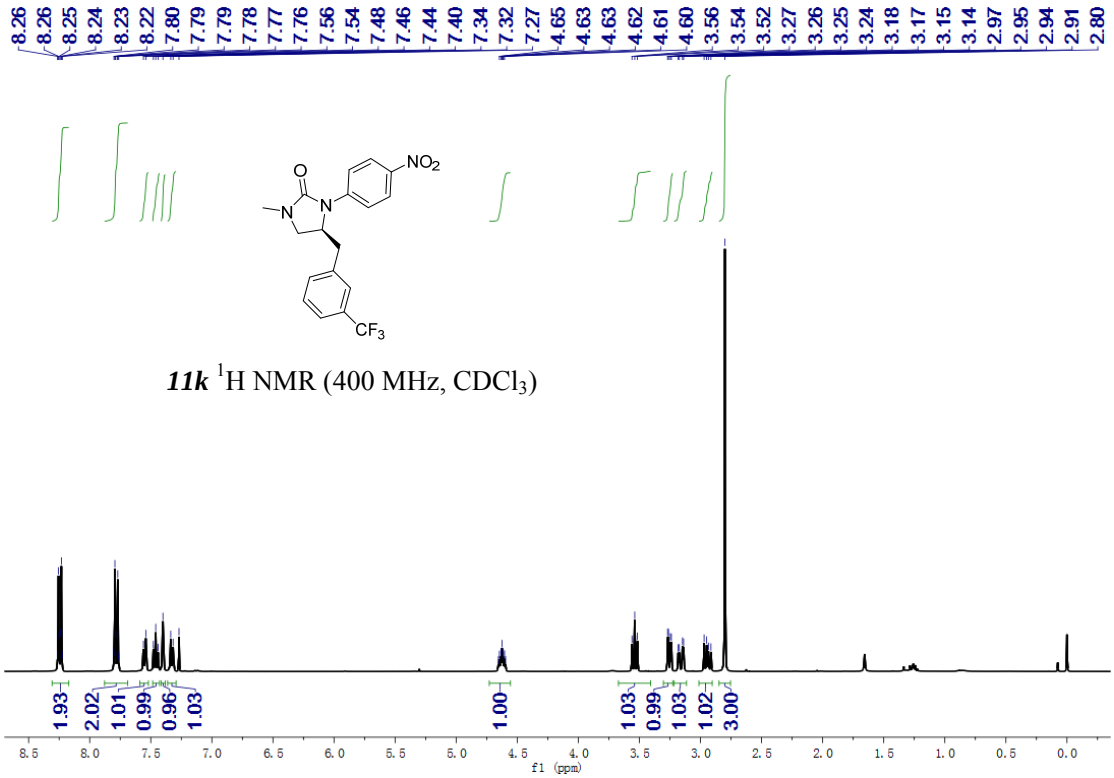
11i ^{13}C NMR (100 MHz, $CDCl_3$)



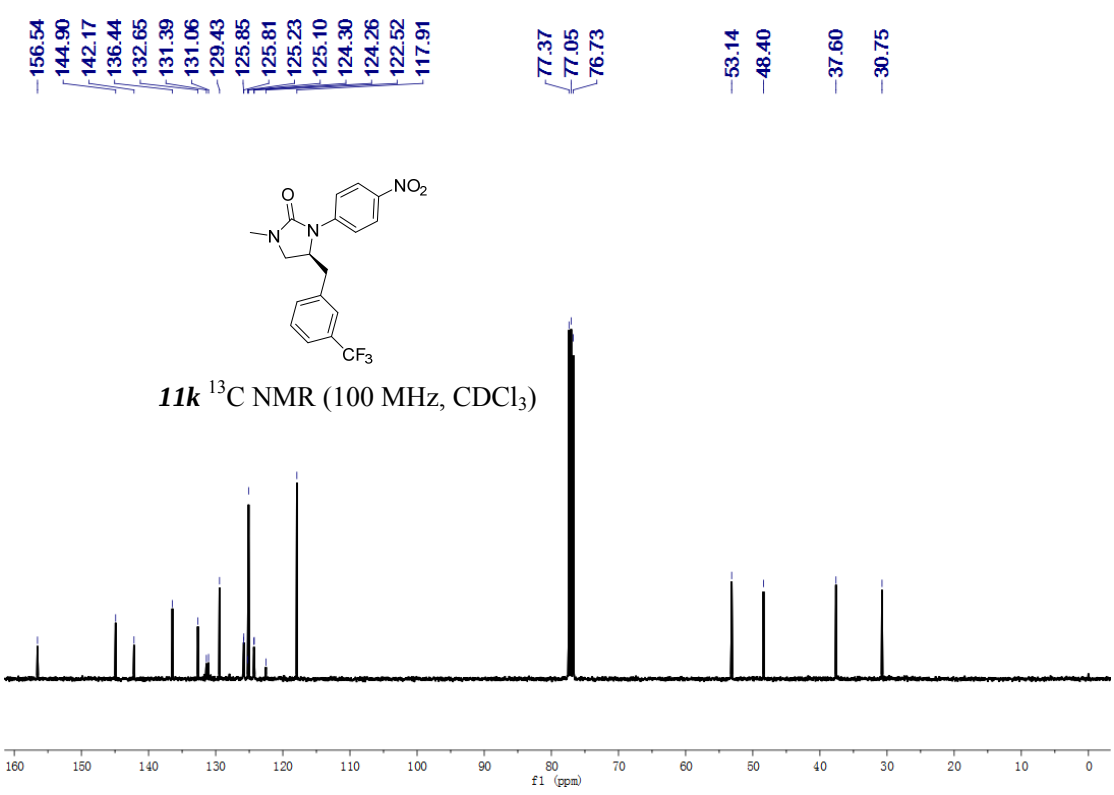
11j ^{1}H NMR (400 MHz, $CDCl_3$)



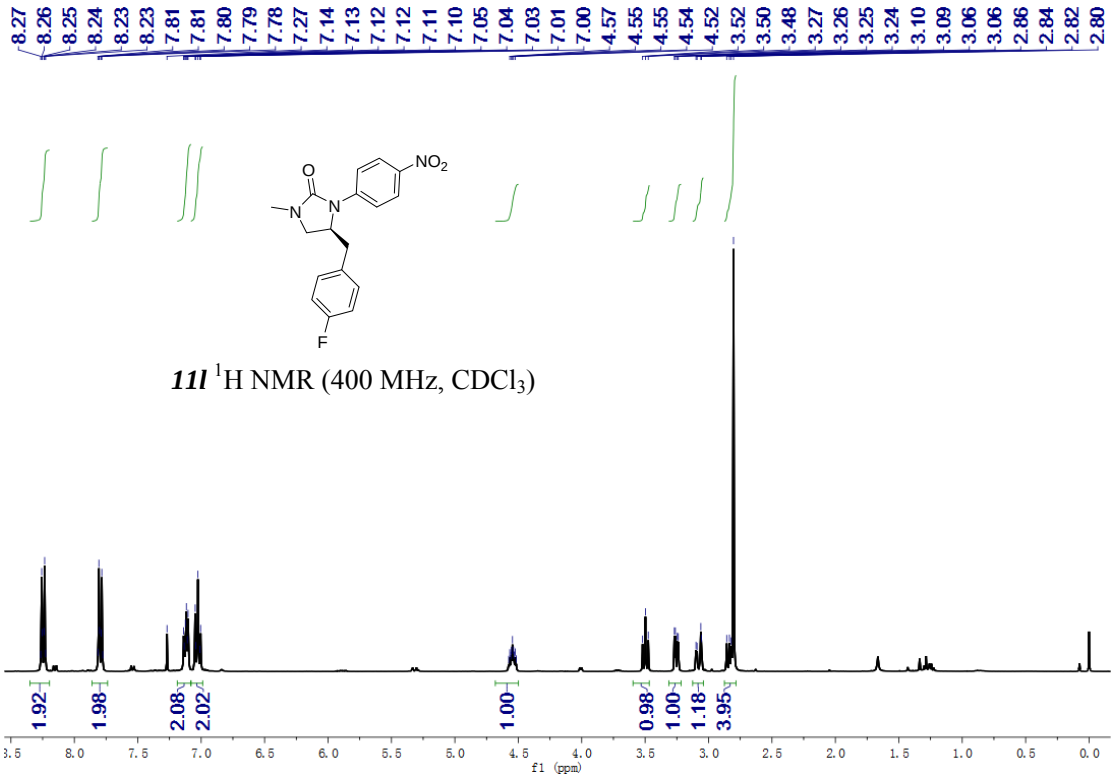
11j ^{13}C NMR (100 MHz, $CDCl_3$)



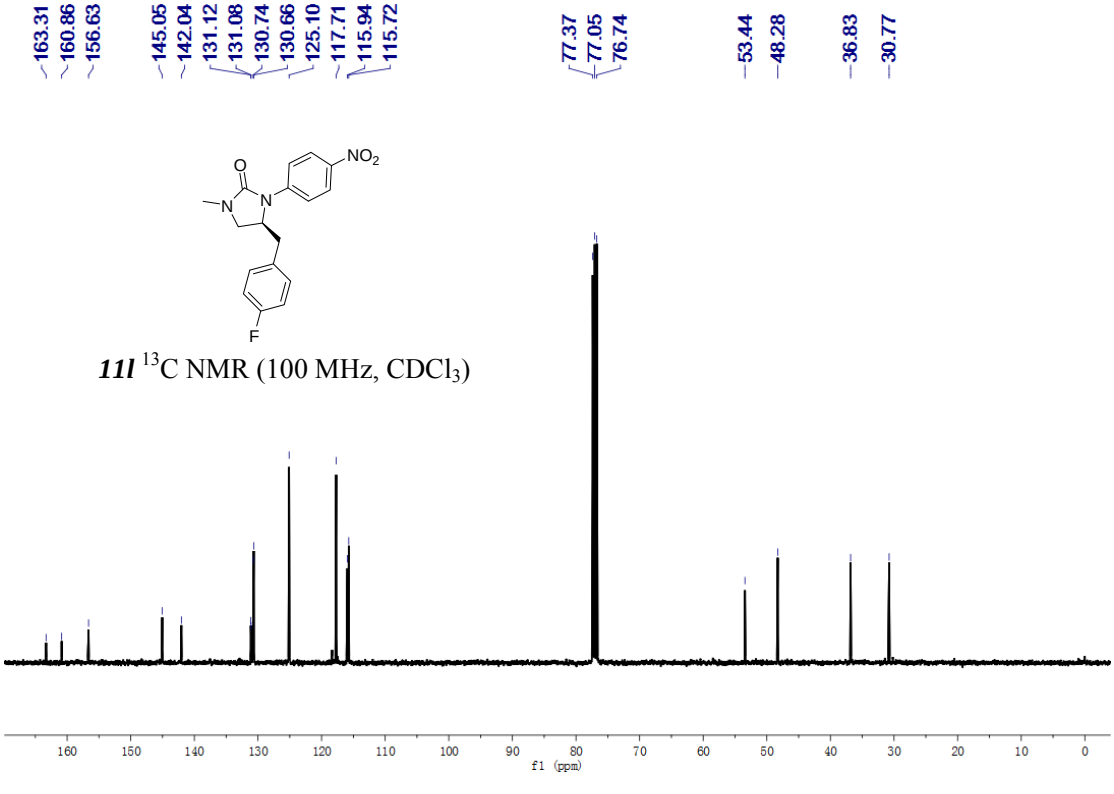
11k ^{1}H NMR (400 MHz, $CDCl_3$)



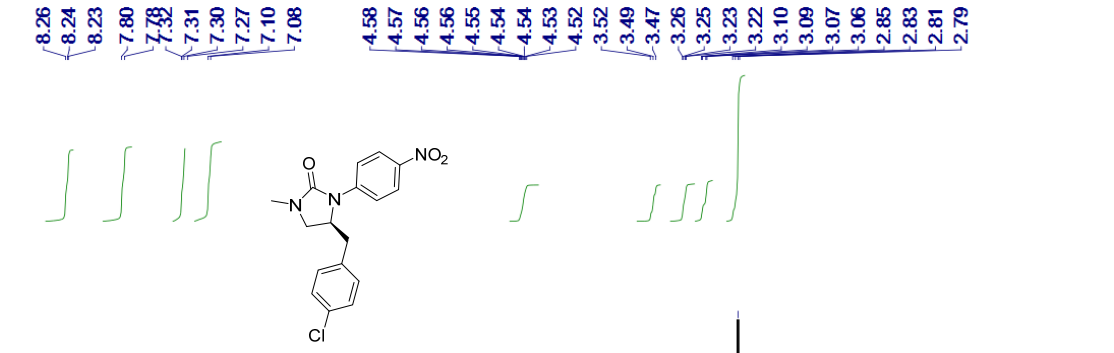
11k ^{13}C NMR (100 MHz, $CDCl_3$)



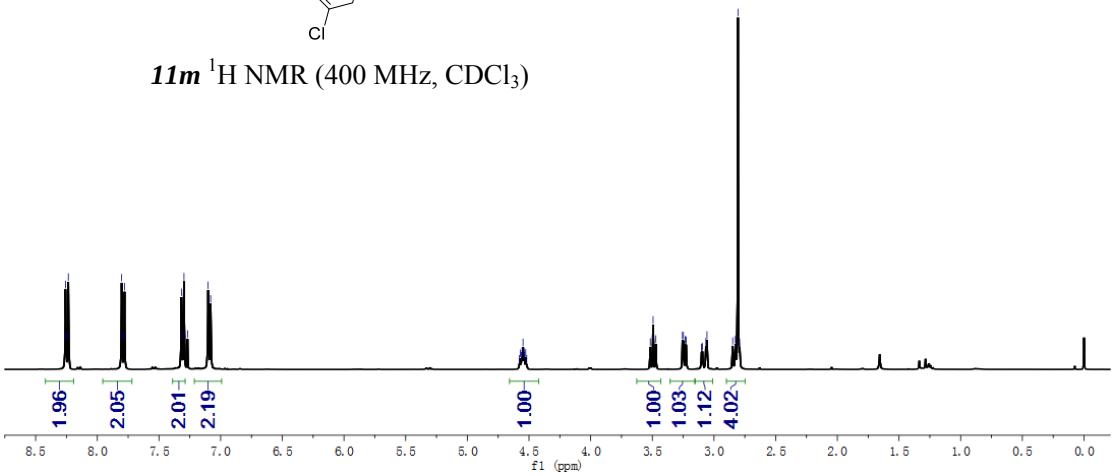
11l ^{1}H NMR (400 MHz, $CDCl_3$)

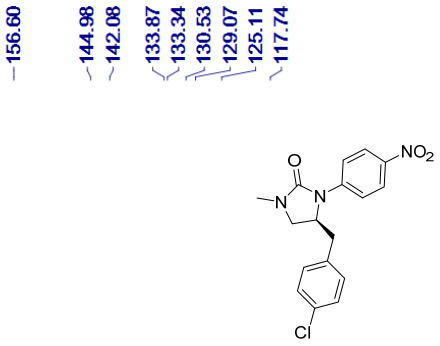


11l ^{13}C NMR (100 MHz, $CDCl_3$)

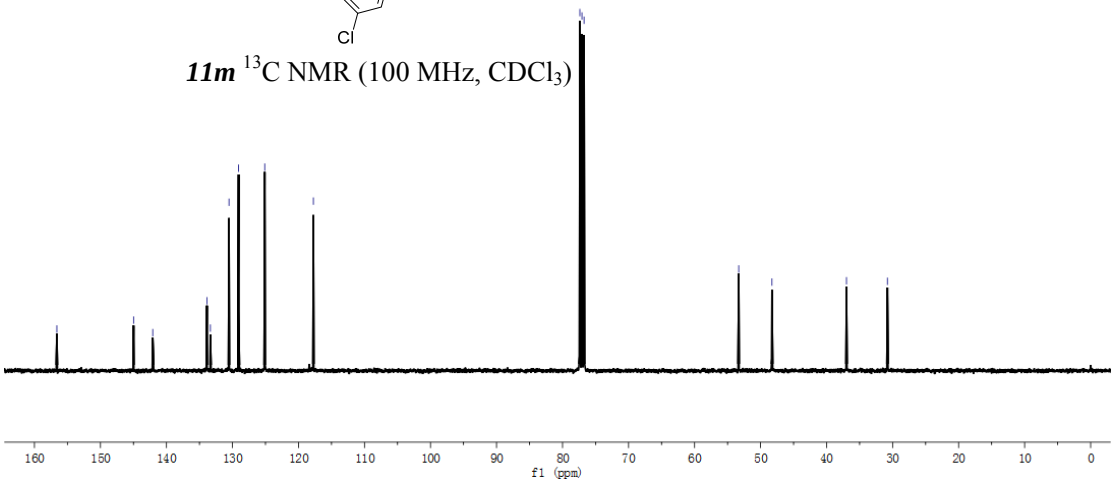


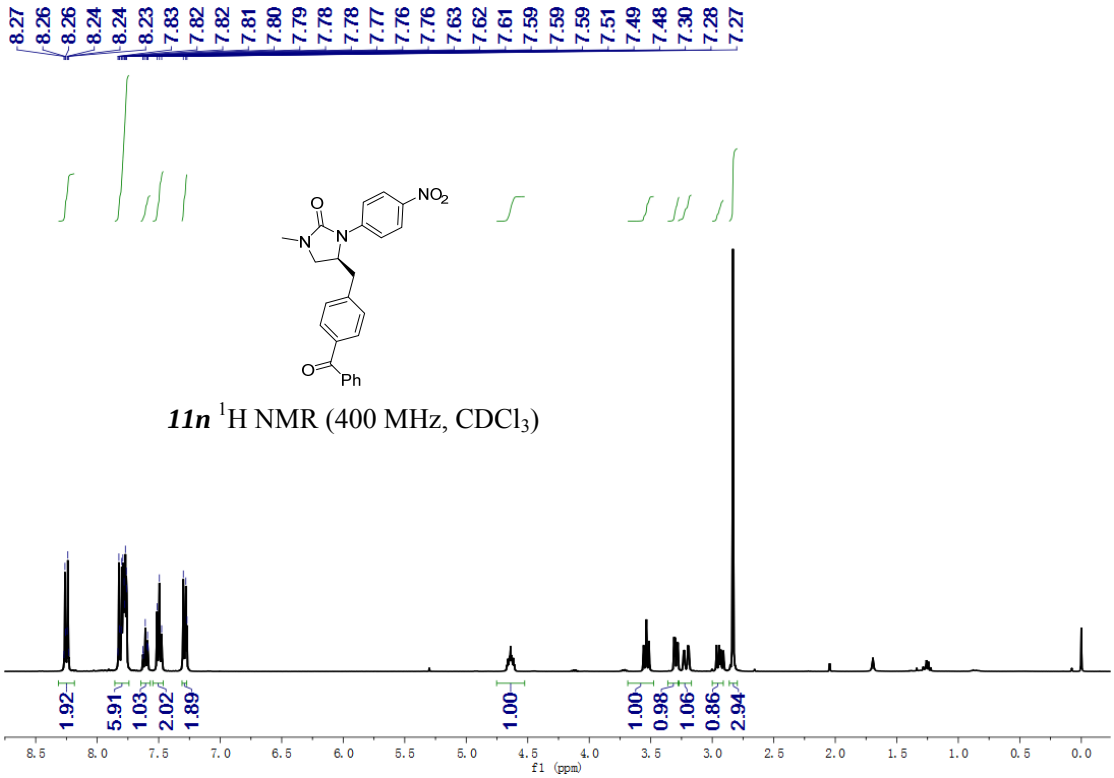
11m ^{1}H NMR (400 MHz, $CDCl_3$)



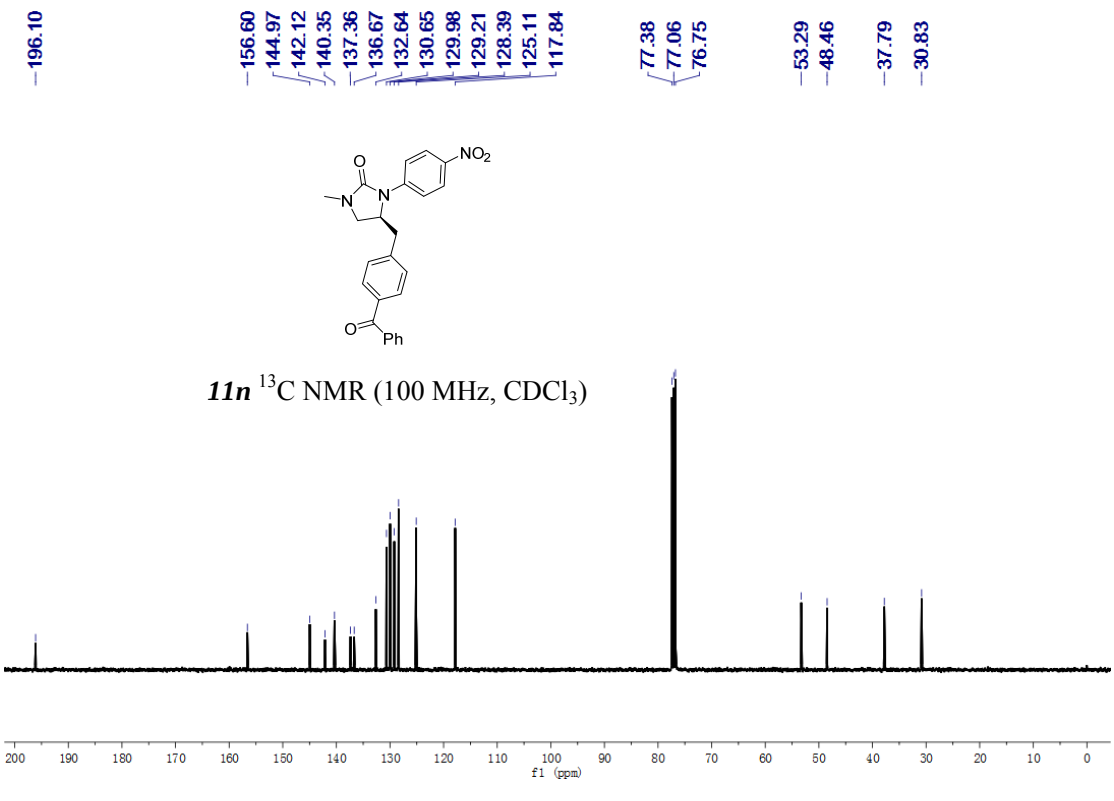


11m ^{13}C NMR (100 MHz, $CDCl_3$)

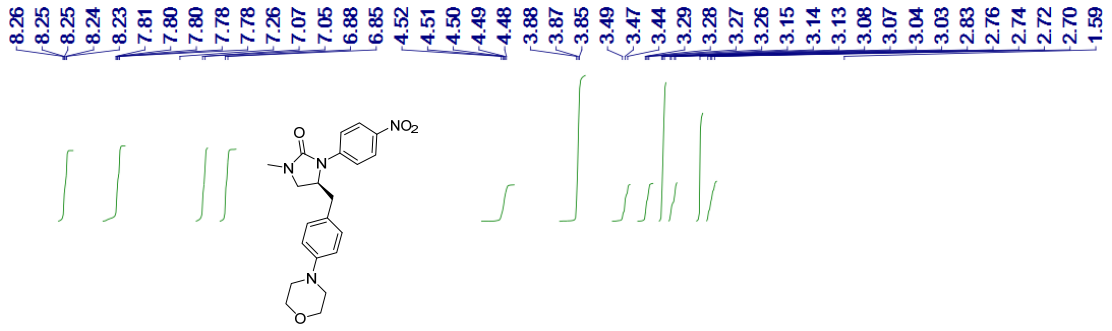




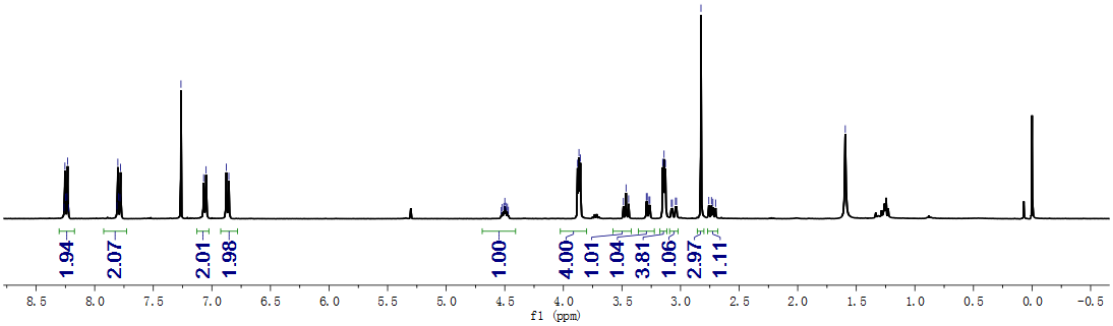
11n ^{1}H NMR (400 MHz, $CDCl_3$)

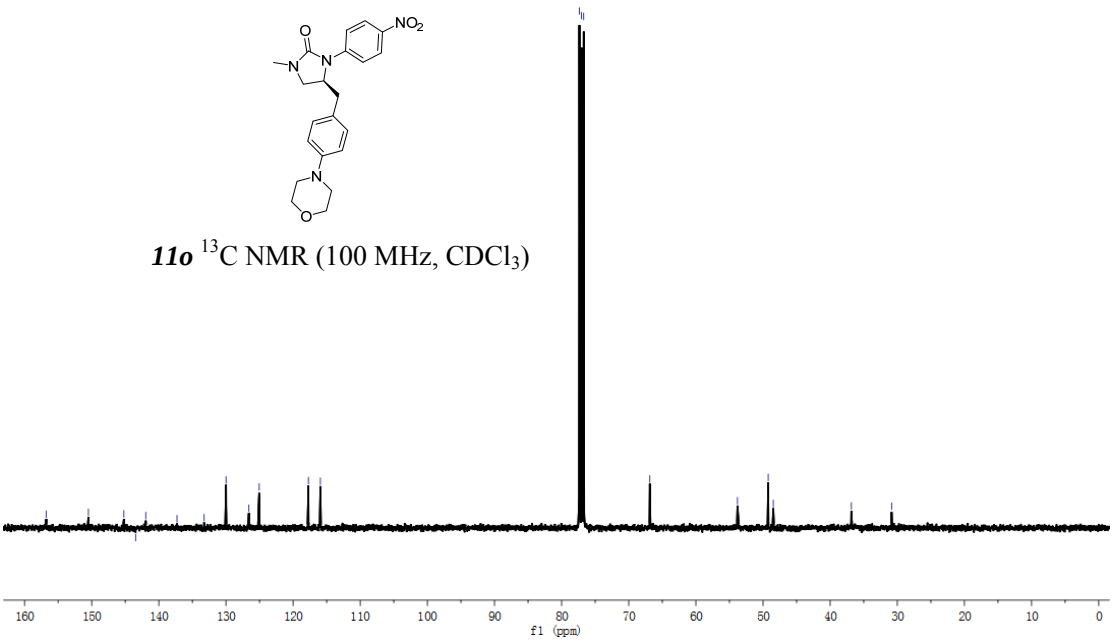


11n ^{13}C NMR (100 MHz, $CDCl_3$)

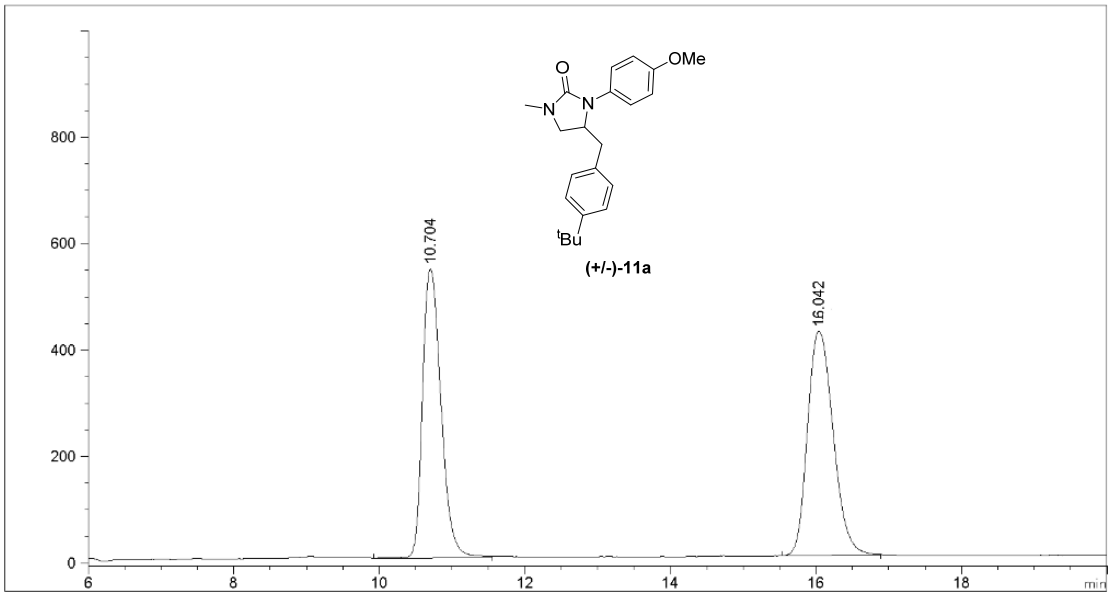


11o ^{1}H NMR (400 MHz, $CDCl_3$)

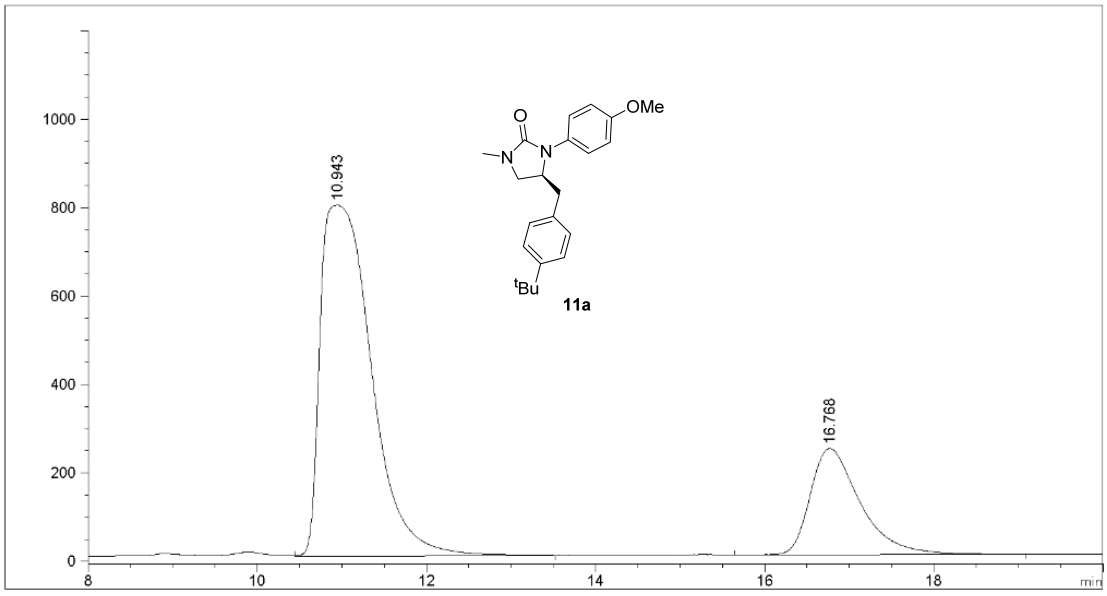




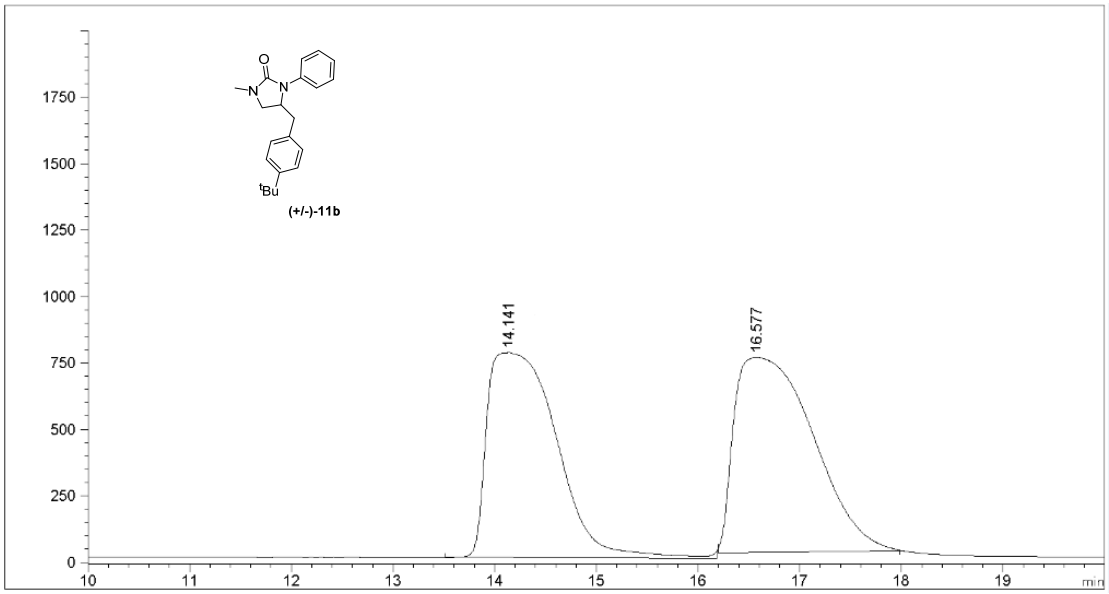
11o ^{13}C NMR (100 MHz, $CDCl_3$)



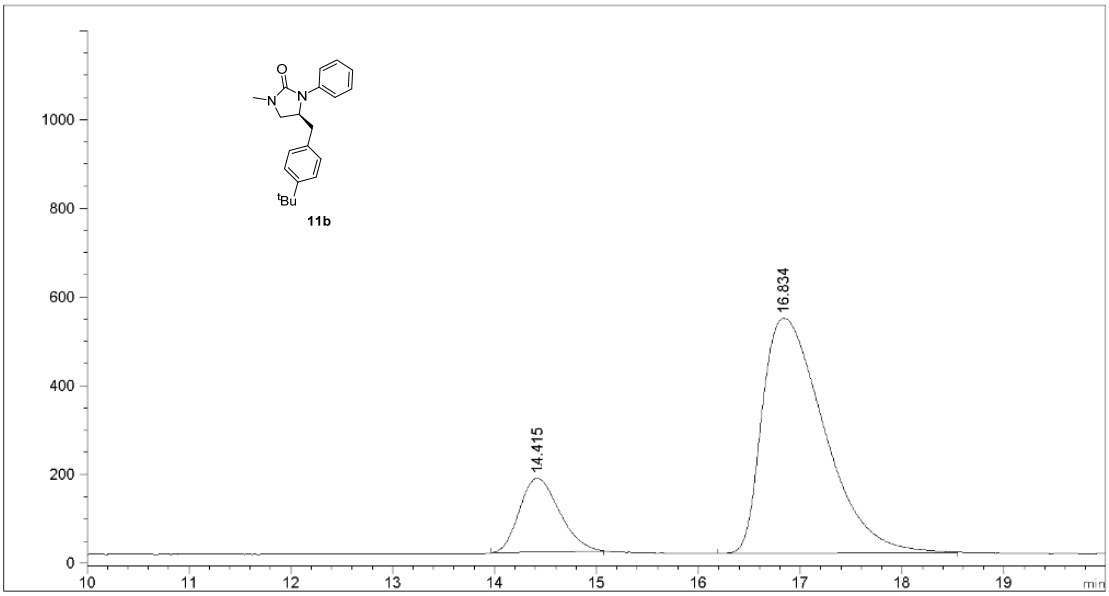
#	[min]		[min]	mAU	*s	[mAU]	%
1	10.704	BV	0.2799	9643.78809	543.21844	48.3284	
2	16.042	MM	0.4082	1.03109e4	420.97690	51.6716	



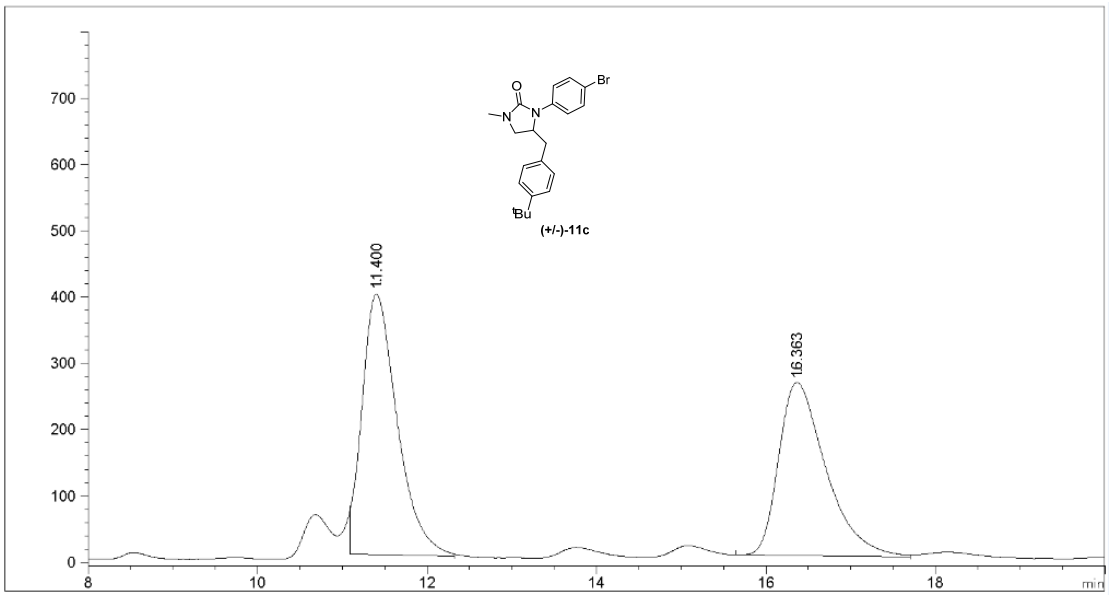
#	[min]		[min]	mAU	*s	[mAU]	%
1	10.943	VB	0.6676	3.33225e4	793.36615	77.0245	
2	16.768	VB	0.6167	9939.72656	240.22475	22.9755	



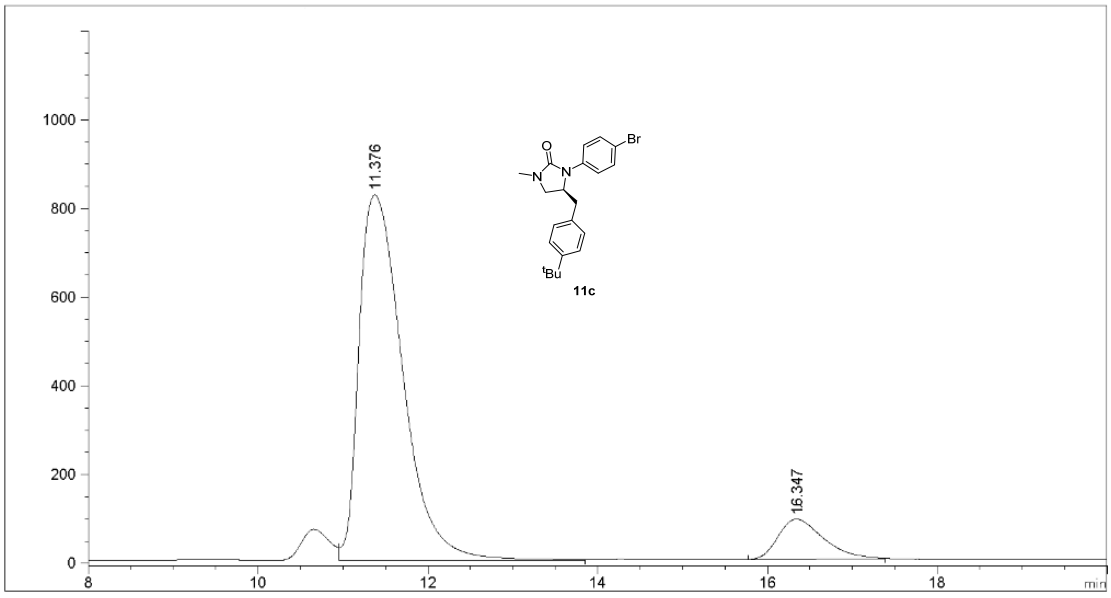
#	[min]		[min]	mAU	*s	[mAU]	%
1	14.141	MM	0.7920	3.66286e4		770.79053	48.0469
2	16.577	MM	0.8995	3.96066e4		733.83783	51.9531



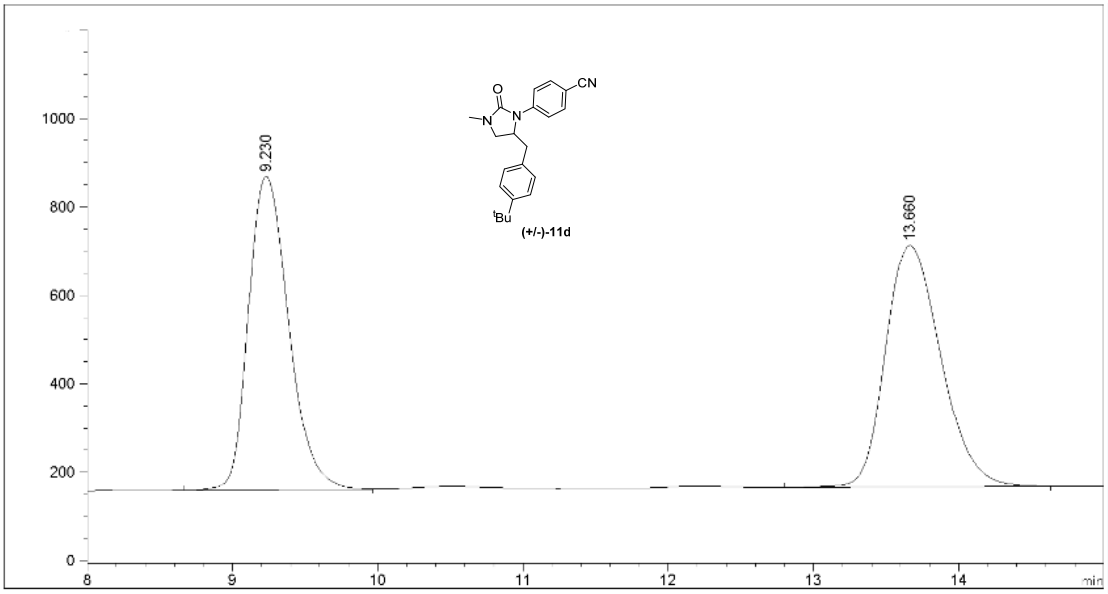
#	[min]		[min]	mAU	*s	[mAU]	%
1	14.415	MM	0.4544	4545.66113		166.73798	16.8886
2	16.834	BV	0.6376	2.23699e4		528.91541	83.1114



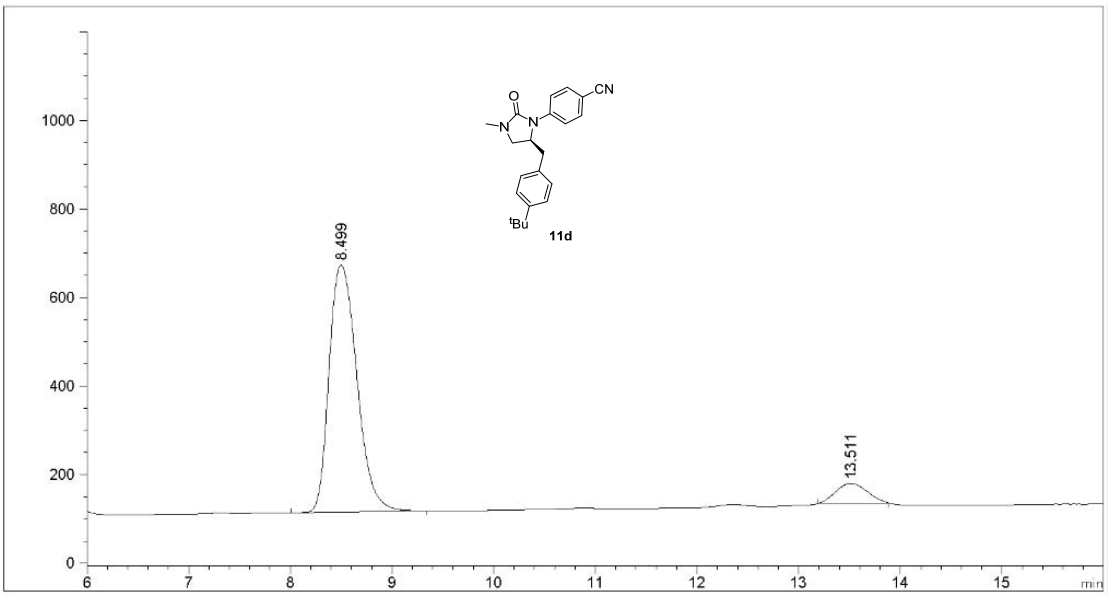
#	[min]		[min]	mAU	*s	[mAU]	%
1	11.400	MM	0.4789	1.13012e4		393.28790	52.8052
2	16.363	MM	0.6452	1.01005e4		260.91779	47.1948



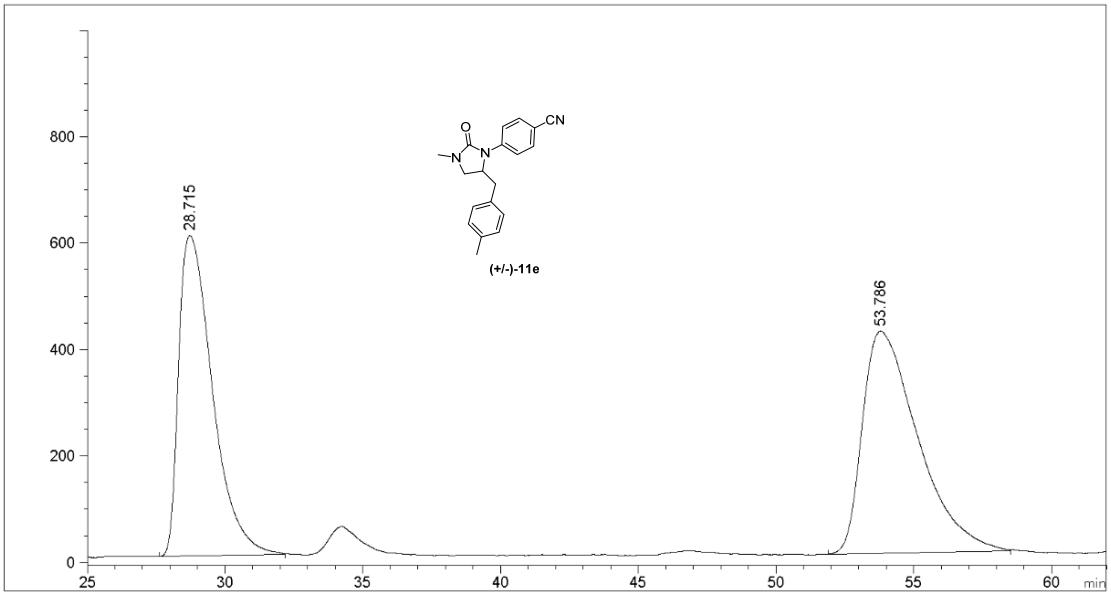
#	[min]		[min]	mAU	*s	[mAU]	%
1	11.376	VV	0.5630	2.94841e4		824.09589	89.6943
2	16.347	MM	0.6202	3387.65112		91.03527	10.3057



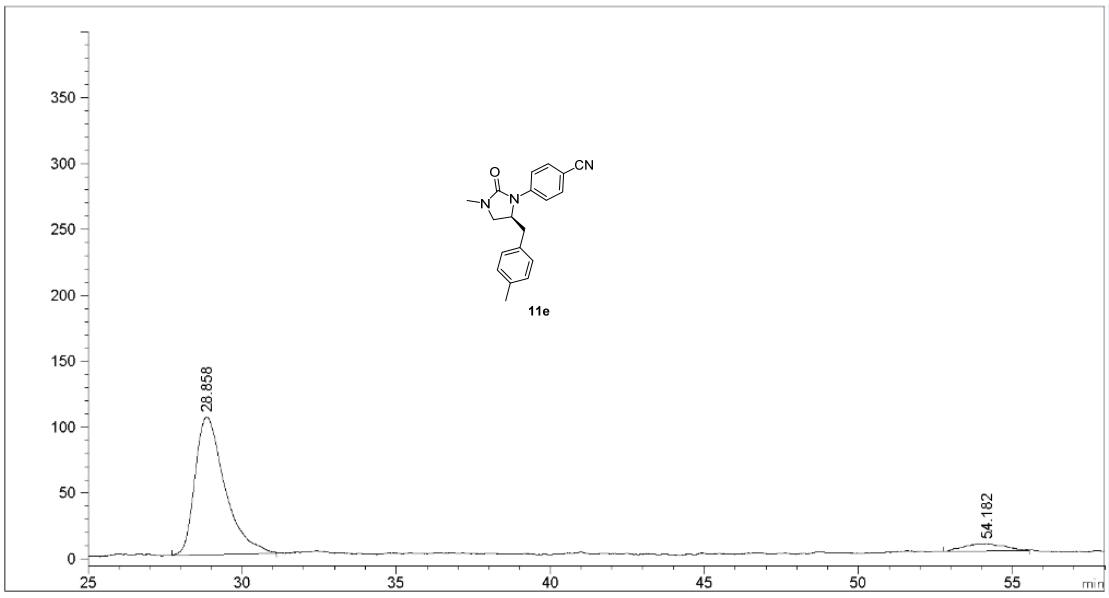
#	[min]		[min]	mAU	*s	[mAU]	%
1	9.230	BV	0.3031	1.36398e4		708.80237	48.5509
2	13.660	BV	0.4167	1.44540e4		545.85229	51.4491



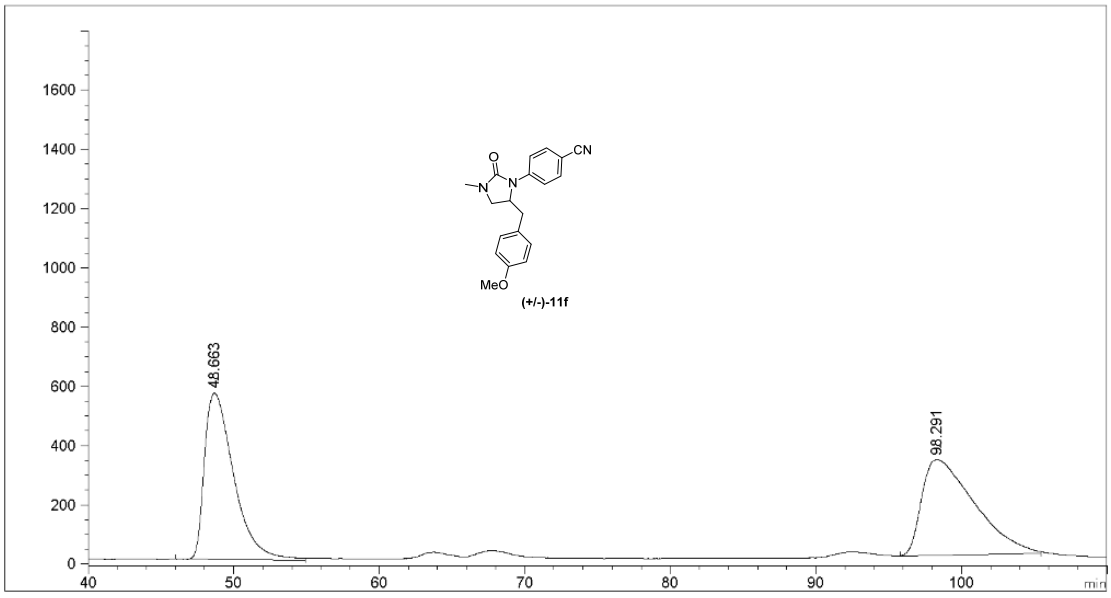
#	[min]		[min]	mAU	*s	[mAU]	%
1	8.499	BV	0.3021	1.06129e4		557.76428	91.7069
2	13.511	MM	0.3545	959.72766		45.12719	8.2931



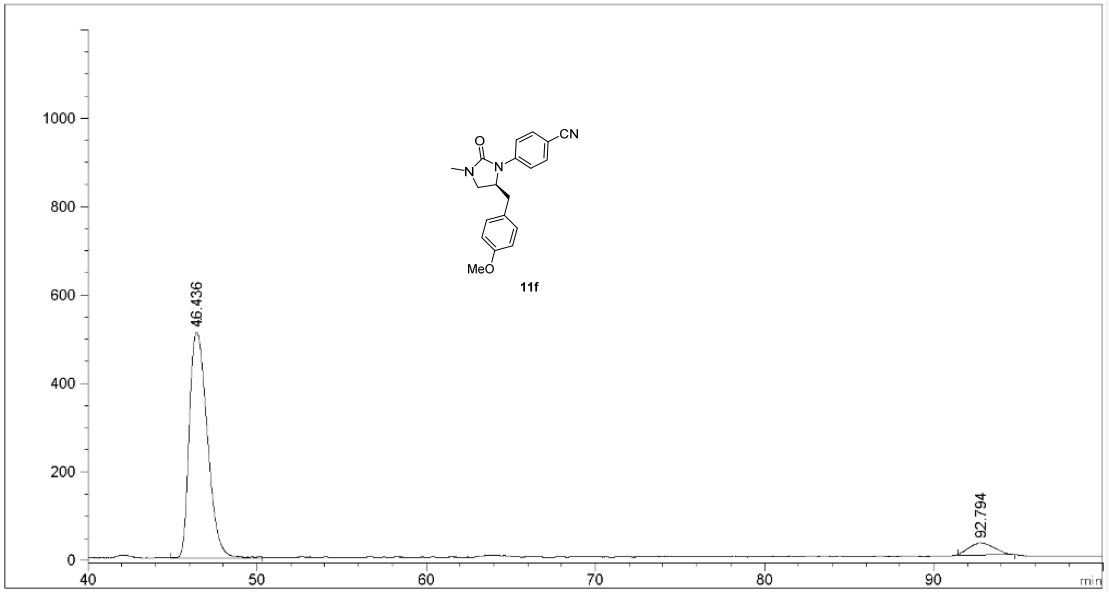
#	[min]		[min]	mAU	*s	[mAU	]	%
1	28.715	BV	1.0119	5.14054e4		602.23364		46.7909
2	53.786	VV	1.6442	5.84566e4		417.37531		53.2091



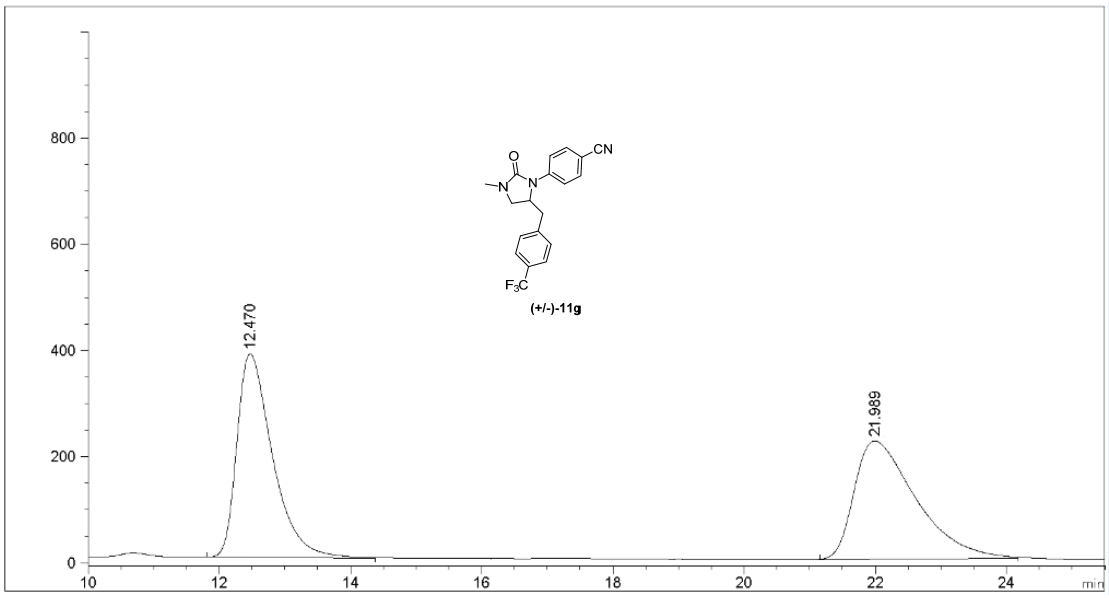
#	[min]		[min]	mAU	*s	[mAU	]	%
1	28.858	MM	1.1230	7064.65234		104.84964		93.4146
2	54.182	MM	1.5281	498.03595		5.43195		6.5854



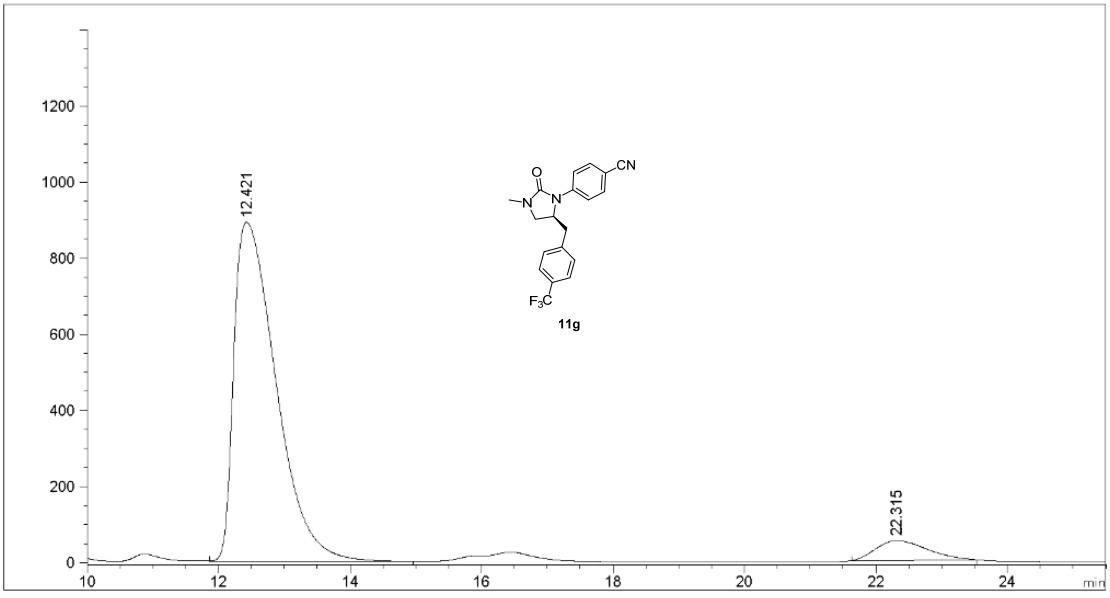
#	[min]		[min]	mAU	*s	[mAU]	%
1	48.663	MM	2.3302	7.85509e4		561.82837	49.0526
2	98.291	MM	4.2099	8.15853e4		322.98798	50.9474



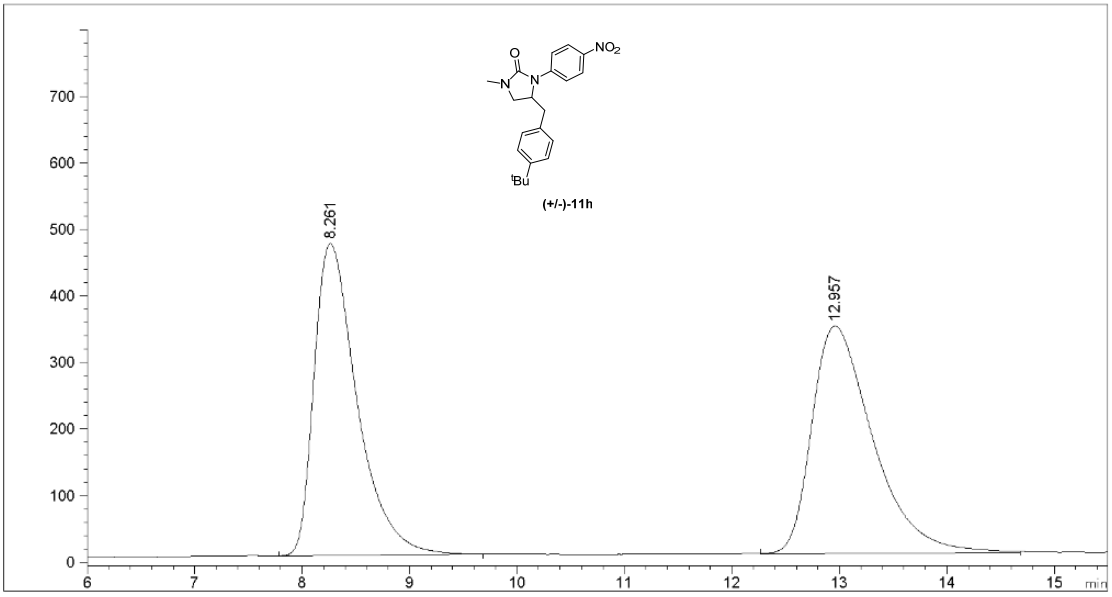
#	[min]		[min]	mAU	*s	[mAU]	%
1	46.436	MM	1.2370	3.79815e4		511.74658	92.9972
2	92.794	MM	1.7425	2860.03662		27.35528	7.0028



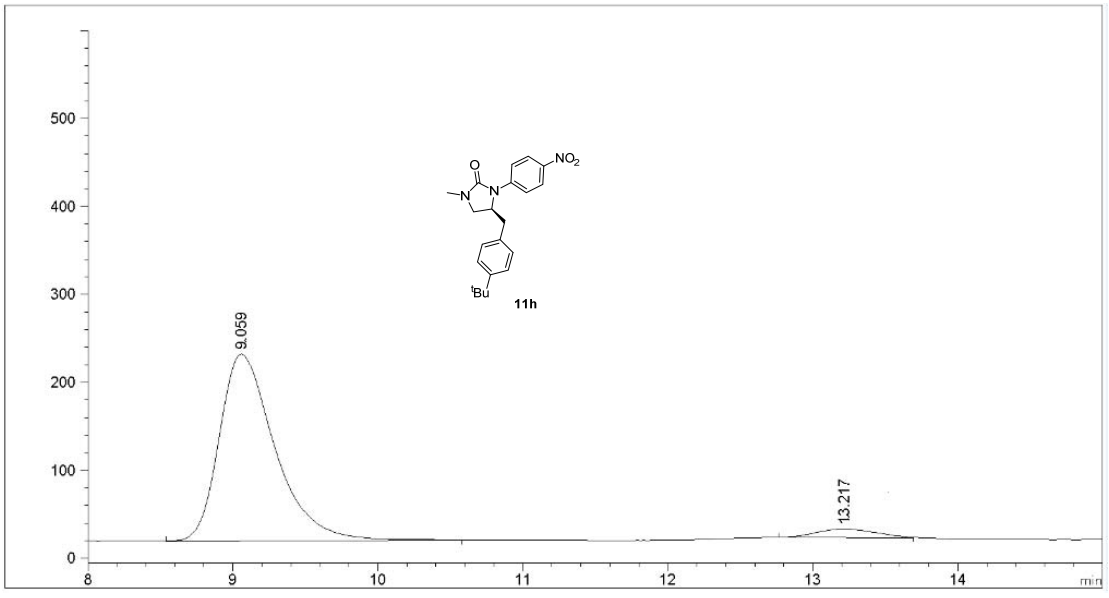
#	[min]		[min]	mAU	*s	[mAU]	%
1	12.470	VV	0.5669	1.44611e4		383.22980	49.7309
2	21.989	MM	1.0907	1.46176e4		223.36343	50.2691



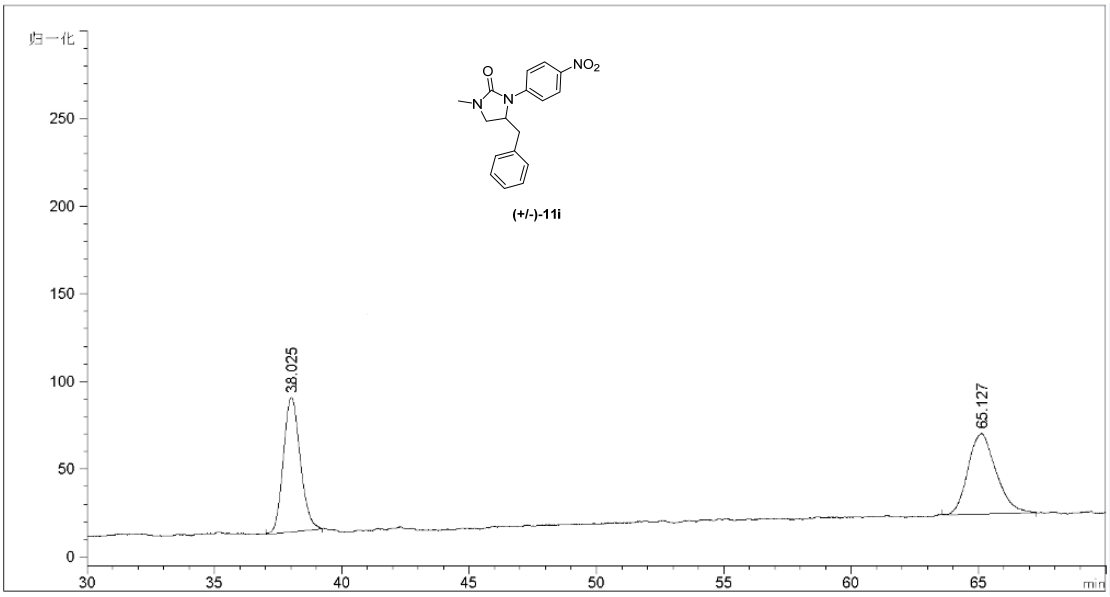
#	[min]		[min]	mAU	*s	[mAU]	%
1	12.421	VB	0.6887	3.96973e4		891.01099	93.3621
2	22.315	MM	0.8981	2822.40503		52.37597	6.6379



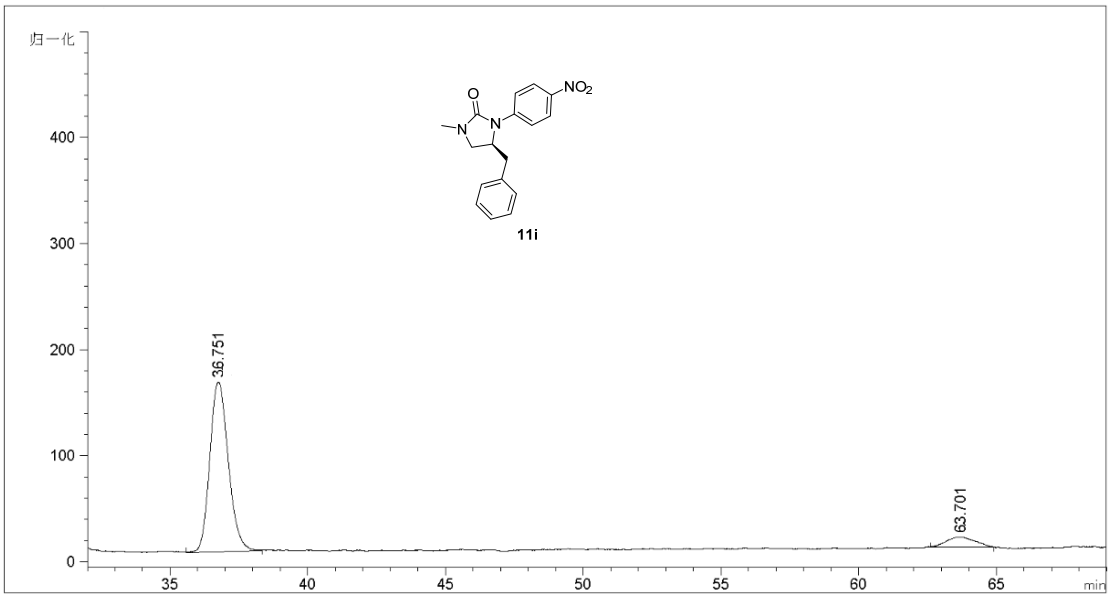
#	[min]		[min]	mAU	*s	[mAU]	%
1	8.261	VV	0.4203	1.30251e4		468.73694	49.1540
2	12.957	VV	0.6016	1.34735e4		341.45874	50.8460



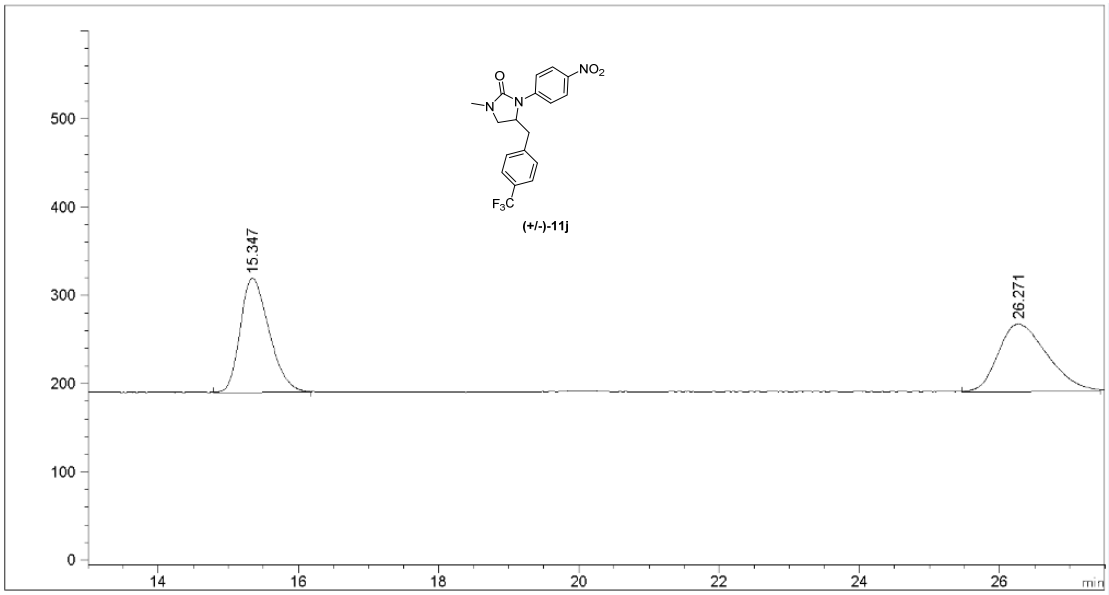
#	[min]		[min]	mAU	*s	[mAU]	%
1	9.059	MM	0.4461	5688.40967		212.53671	95.5494
2	13.217	MM	0.4514	264.96176		9.78396	4.4506



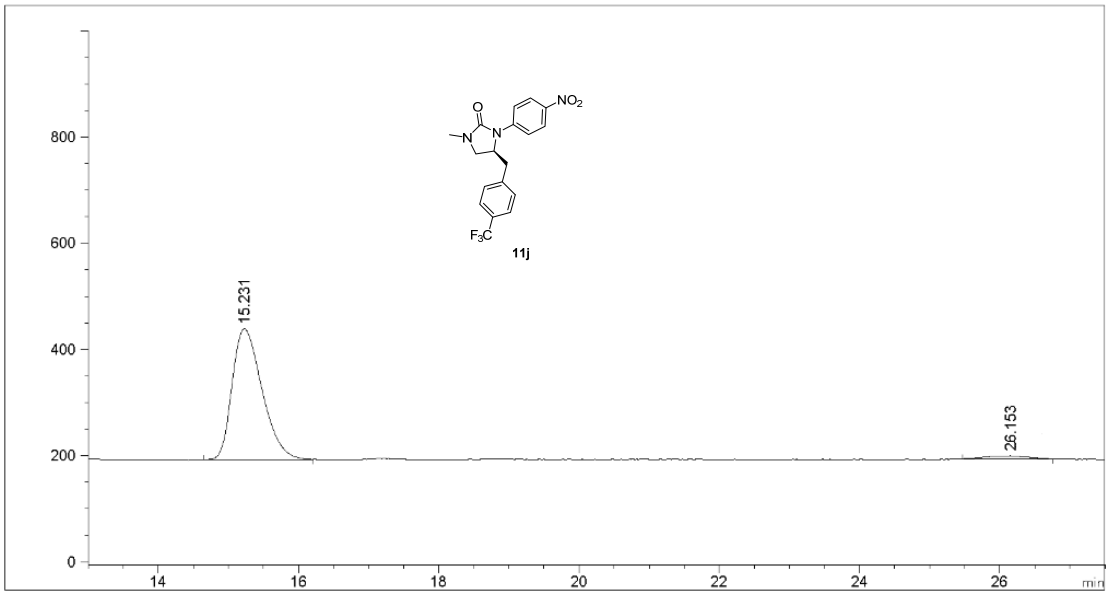
#	[min]		[min]	mAU *s	[mAU]	%
1	38.025	MM	0.7704	3532.52417	76.42620	49.9466
2	65.127	MM	1.2815	3540.07520	46.04067	50.0534



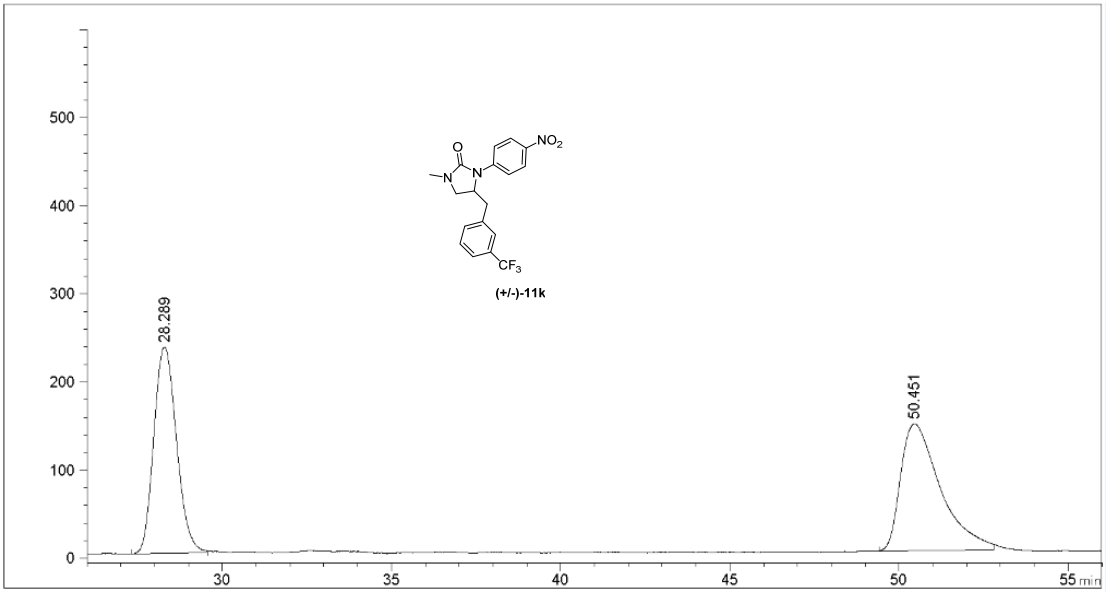
#	[min]		[min]	mAU *s	[mAU]	%
1	36.751	MM	0.7768	7451.81201	159.88284	91.9416
2	63.701	MM	1.1685	653.12500	9.31603	8.0584



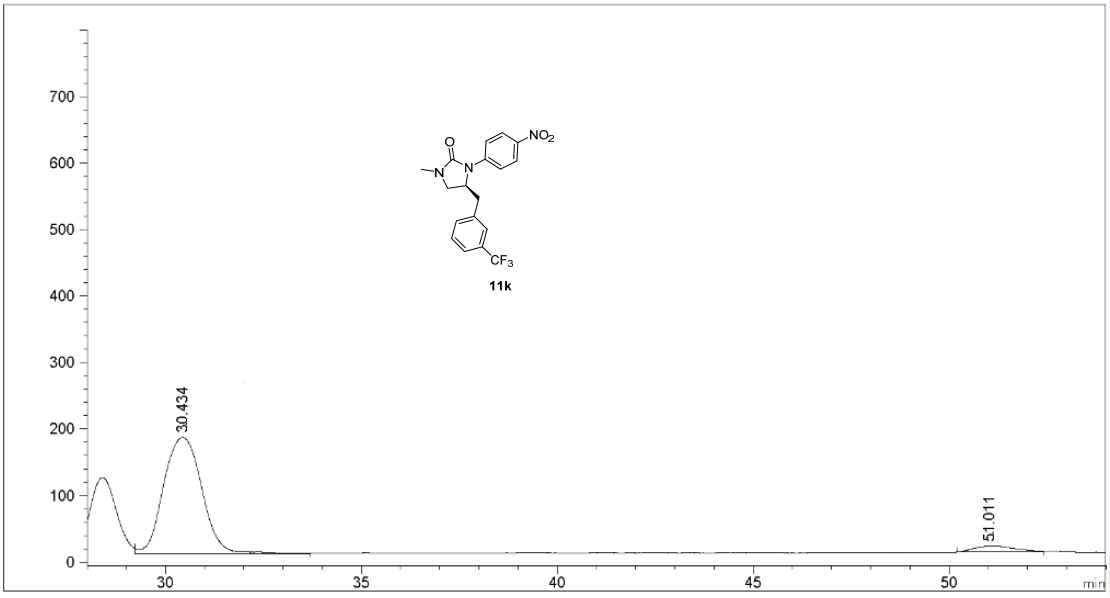
#	[min]		[min]	mAU	*s	[mAU]	%
1	15.347	VV	0.4274	3697.25732	129.04695	49.8205
2	26.271	VV	0.5880	3723.89575	76.73042	50.1795



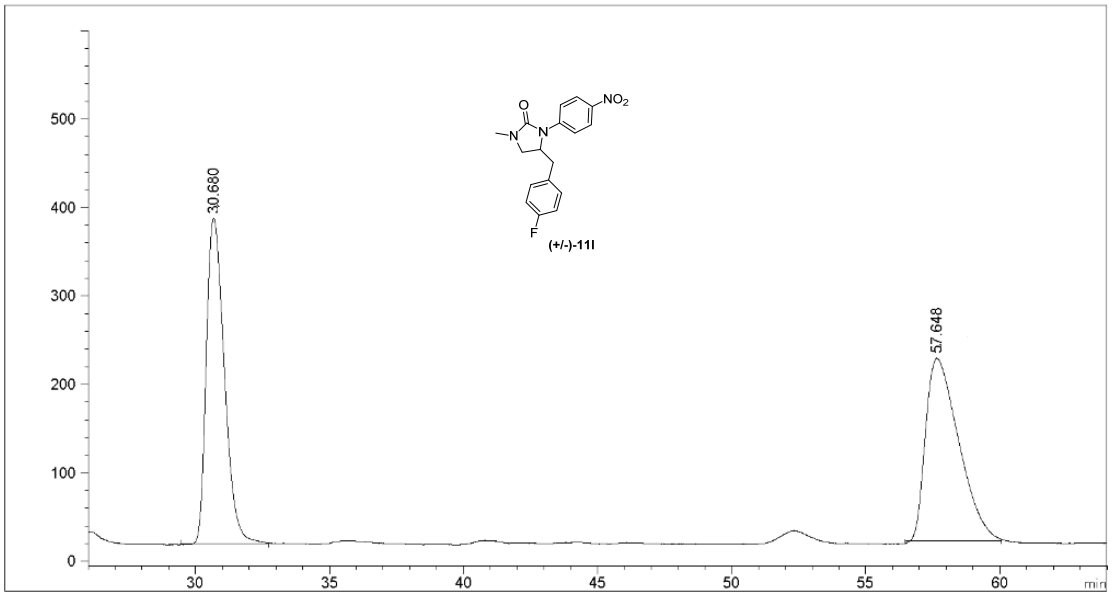
#	[min]		[min]	mAU	*s	[mAU]	%
1	15.231	VV	0.4444	7343.04883	247.00500	96.4242
2	26.153	MM	0.7341	272.30786	6.18219	3.5758



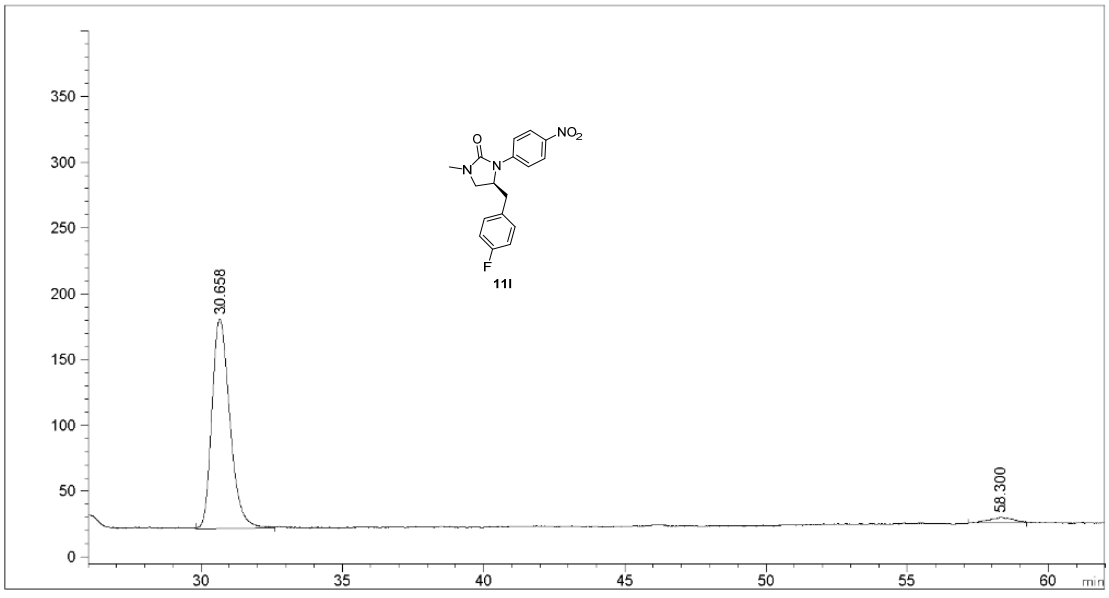
#	[min]		[min]	mAU	*s	[mAU]	%
1	28.289	BV	0.6746	1.09334e4		234.06154	48.2069
2	50.451	VV	0.9620	1.17467e4		144.20877	51.7931



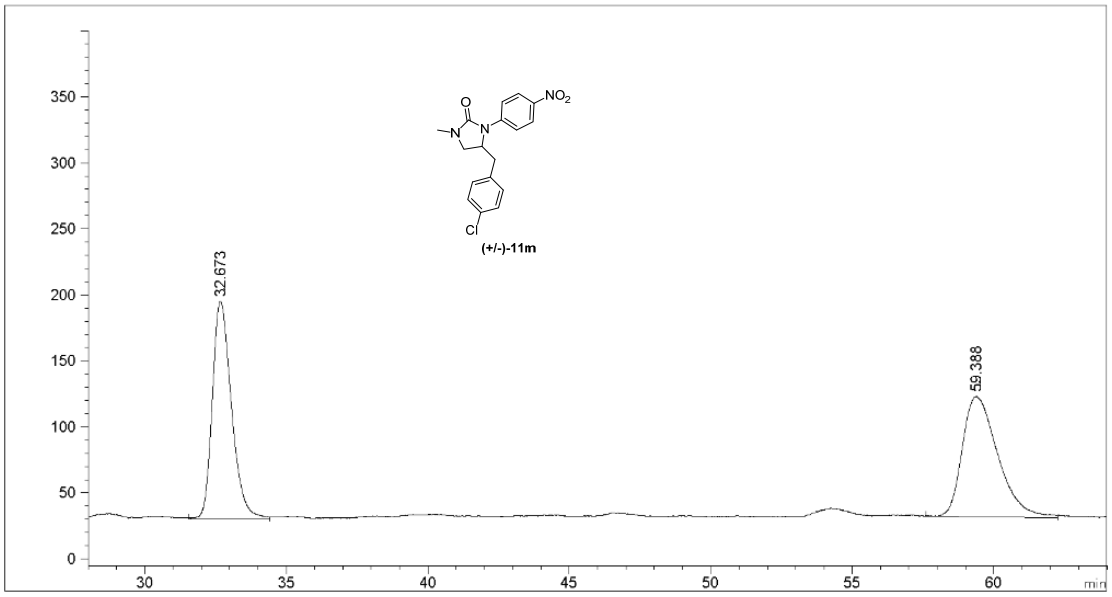
#	[min]		[min]	mAU	*s	[mAU]	%
1	30.434	MM	1.1406	1.19744e4		174.96997	95.2239
2	51.011	MM	1.1429	600.59918		8.75836	4.7761



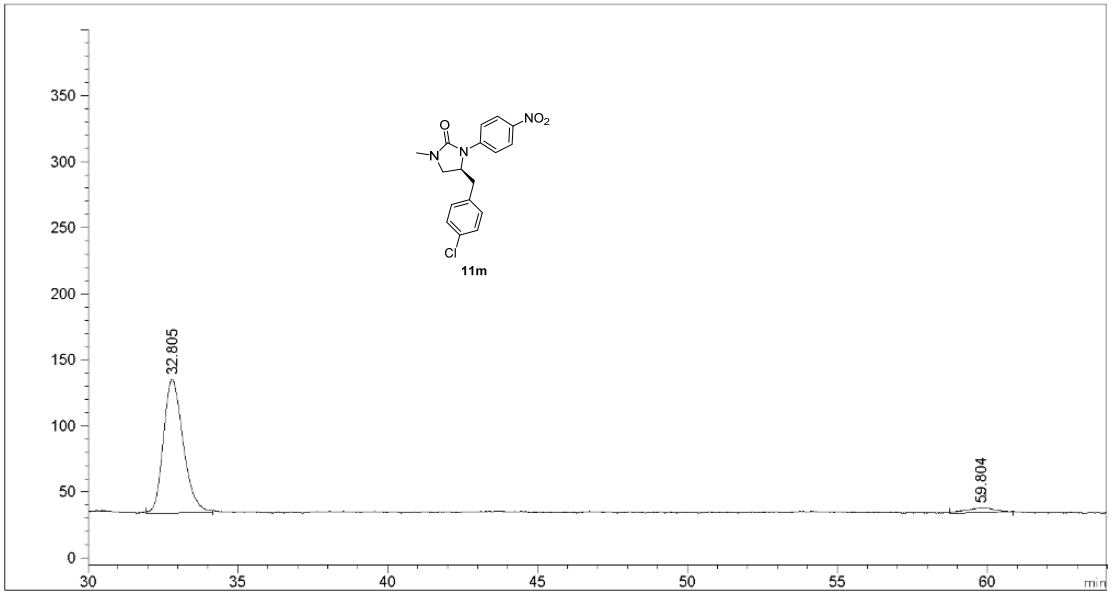
#	[min]		[min]	mAU *s	[mAU]	%
1	30.680	MM	0.7780	1.71611e4	367.65256	49.2081
2	57.648	MM	1.4310	1.77135e4	206.30650	50.7919



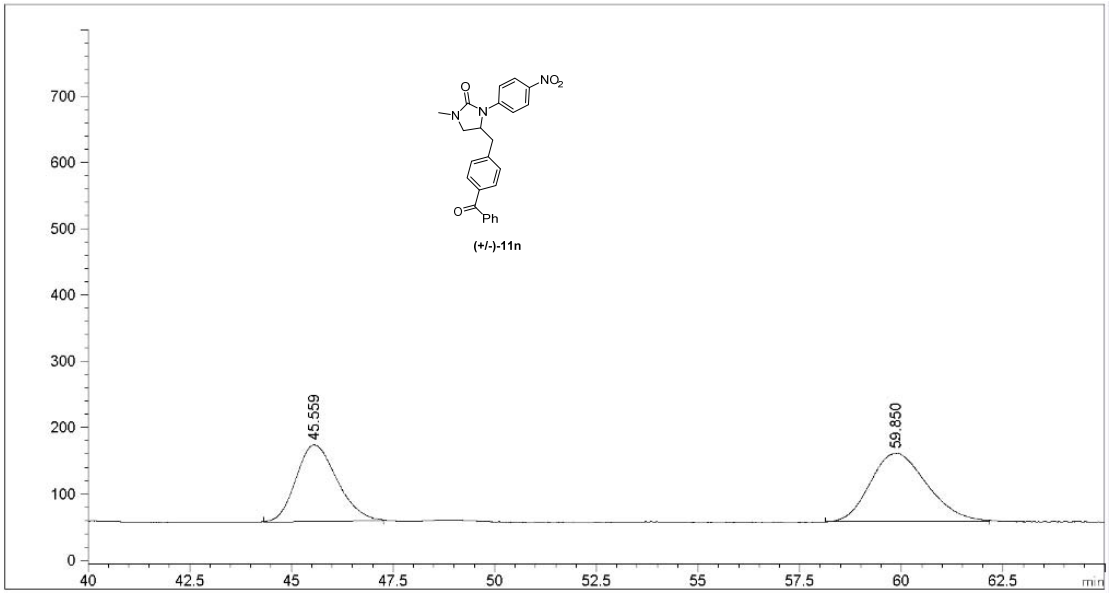
#	[min]		[min]	mAU *s	[mAU]	%
1	30.658	MM	0.7420	7099.71826	159.46674	96.4265
2	58.300	MM	1.0335	263.10733	4.24310	3.5735



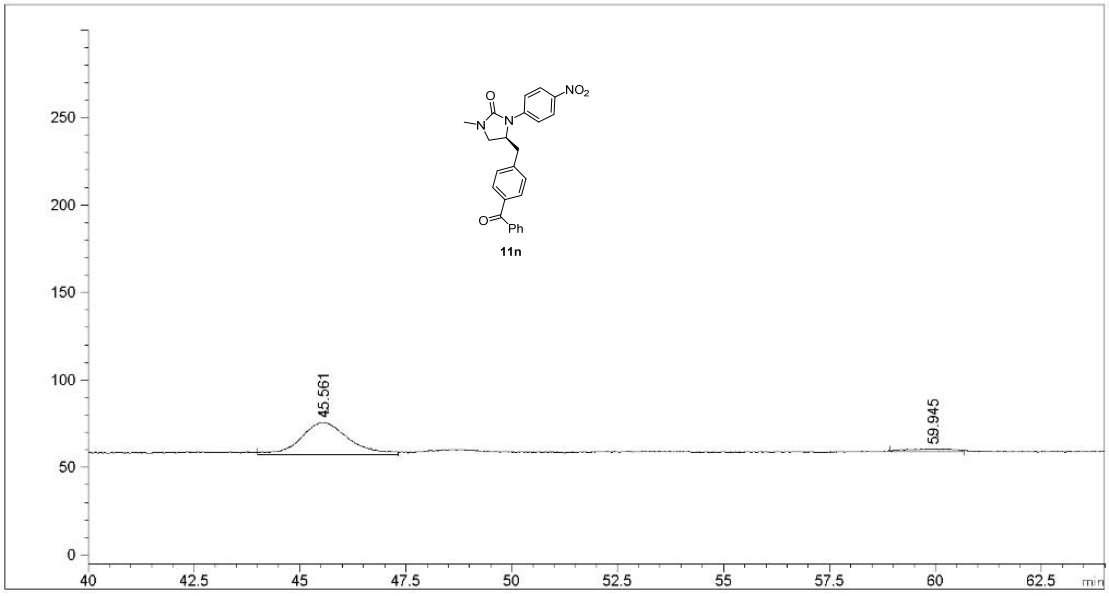
#	[min]		[min]	mAU *s	[mAU]	%
1	32.673	MM	0.7875	7802.50000	165.12625	49.5750
2	59.388	MM	1.4520	7936.27246	91.09553	50.4250



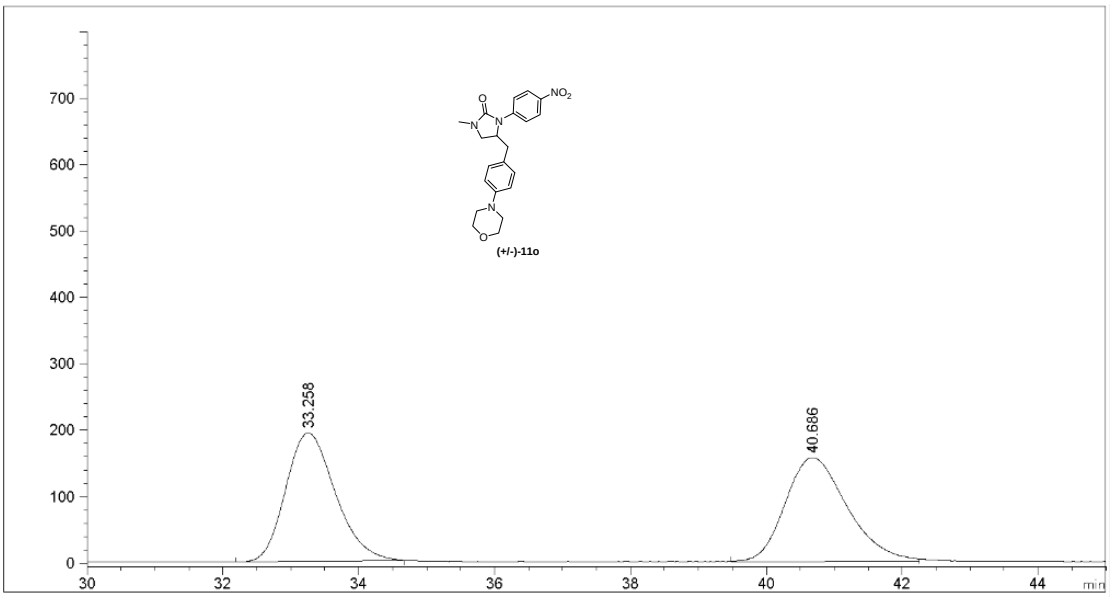
#	[min]		[min]	mAU *s	[mAU]	%
1	32.805	MM	0.7683	4679.75586	101.52327	94.9892
2	59.804	MM	1.0900	246.86284	3.77451	5.0108



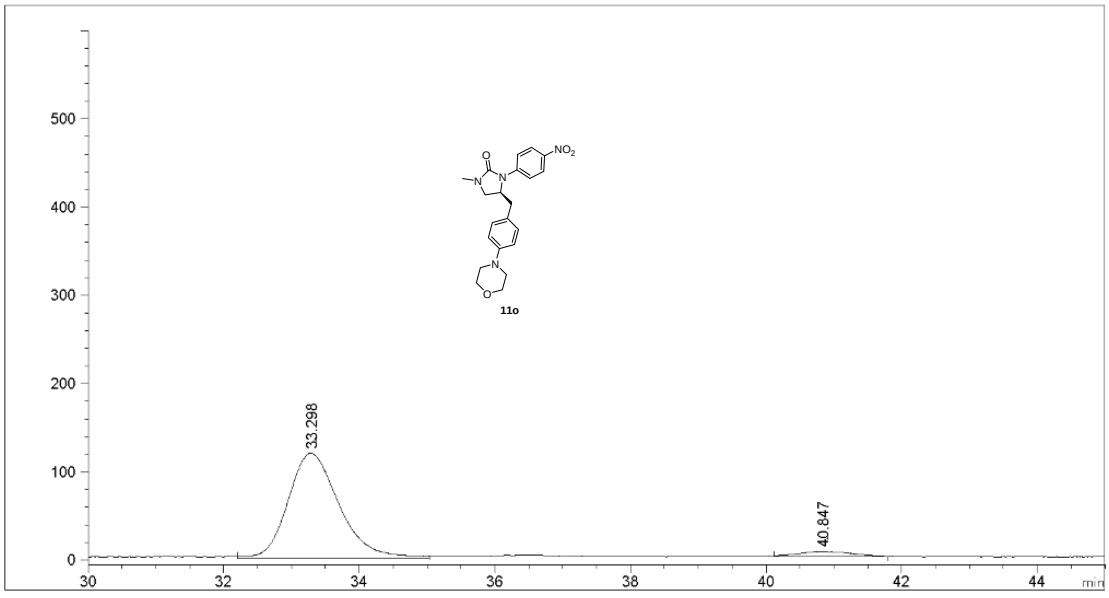
#	[min]		[min]	mAU	*s	[mAU]	%
1	45.559	VV	0.8762	8150.68848		115.83702	45.1771
2	59.850	MM	1.6090	9890.94531		102.45132	54.8229



#	[min]		[min]	mAU	*s	[mAU]	%
1	45.561	MM	1.3021	1439.33777		18.42388	91.4506
2	59.945	MM	1.3018	134.55878		1.72277	8.5494



#	[min]		[min]	mAU	*s	[mAU]	%
1	33.258	VV	0.6825	9872.51367	193.99809	49.9992	
2	40.686	VV	0.8028	9872.83789	156.21901	50.0008	



#	[min]		[min]	mAU	*s	[mAU]	%
1	33.298	MM	0.8757	6245.24121	118.86828	95.4746	
2	40.847	MM	0.9141	296.02017	5.39723	4.5254	