*Supporting Information for*

# Tartrate-derived iminophosphorane catalyzed asymmetric hydroxymethylation of 3-substituted oxindoles with paraformaldehyde

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## Contents

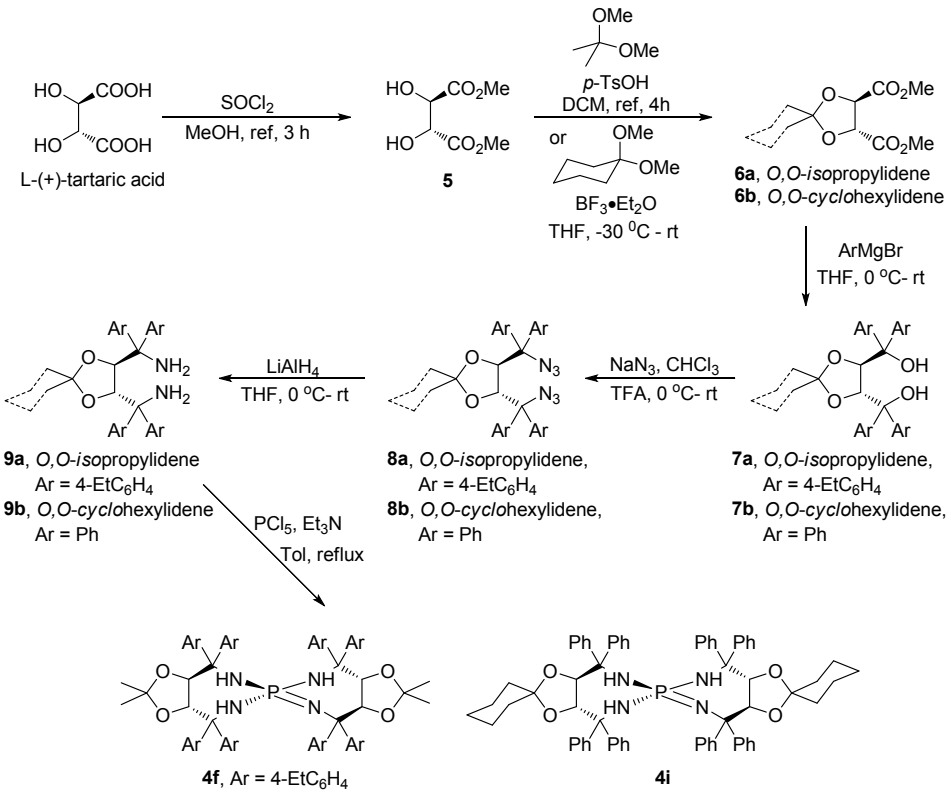
## 1.General information.

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. All the solvents were treated according to general methods. Paraformaldehyde was used as obtained from commercial sources (CAS 30525-89-4, Sinopharm Chemical Reagent Co., Ltd, ≥94.0%). 1,3,5-Trimethylbenzene was from Shanghai Tianlian Chemical Technology Co.,Ltd. (CAS 108-67-8). Flash column chromatography was performed with SiliaFlash®P60 (230–400 mesh, UltraPure SILICA GELS, SiliCycle). $^{1}$H NMR, $^{13}$C NMR, $^{19}$F NMR and $^{31}$P NMR spectra were recorded on a Mercury 300 NMR spectrometer, and TMS was used as a reference. $^{1}$H NMR spectroscopic data are represented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet), coupling constants in hertz (Hz), integration, assignment. $^{13}$C NMR, $^{19}$F NMR and $^{31}$P NMR spectroscopic data are reported in ppm. IR spectra were recorded on a Nicolet iN10 MX spectrometer and are reported in wavenumbers ($cm^{-1}$). High-resolution mass spectra were measured on a Agilent Technologies 6224 TOF LC/MS spectrometer. Enantiomeric excess was measured by HPLC with CHIRALCEL OD-H on an DIONEX UltiMate 3000, ThermoScientific. Optical rotation was measured on an Autopol I, serial number 30575. All melting points were determined using a digital melting point apparatus and were uncorrected.

The starting oxindole derivatives were prepared according to literature procedures.[1] Compounds described in the literature were characterized by comparing their spectral data to the reported values.

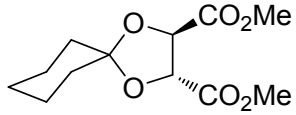
## 2. Experimental Section.

**Chiral iminophosphoranes 4f and 4i were prepared by following the published general procedure.**[2]




***(R,R)*-Dimethyl *O,O*-cyclohexylidenetartrate 6b was synthesized according to literature**

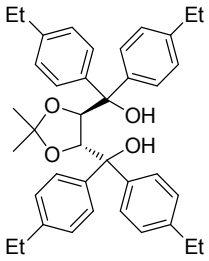
**procedures.**[3]



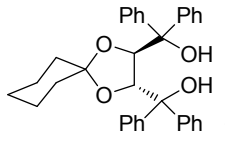
To a solution of L-dimethyl tartrate (9.82 g, 55.1 mmol, 1.5 equiv.) in THF (150 mL) at -30 °C under inert atmosphere was added successively 1,1-dimethoxycyclohexane (5.3 g, 36.75 mmol, 1.0 equiv.) and $BF_3 \cdot Et_2O$ (5.45 mL, 44.1 mmol, 1.2 equiv.) dropwise. The resulting mixture was then stirred for 3 h having the temperature raised from -30 °C to RT. The reaction was then cooled to 0 °C and carefully quenched with sat. aqueous $NaHCO_3$ solution. The organic layer was then separated and the aqueous phase was extracted with EtOAc (3 X 400 mL). The combined organic phases were washed with water (2 X 400 mL) and brine (1 X 400 mL). The combined organic extracts were dried over $Na_2SO_4$, filtered, and concentrated in vacuo to afford a crude oil, which was further purified by flash chromatography (gradient of EtOAc/hexanes 2:98 to 15:85) affording a colorless oil (8.07 g, 31.23 mmol, 85%).[3] $^1$H NMR (300 MHz, $CDCl_3$): δ = 4.76 (s, 2H), 3.76 (s, 6H), 1.69 – 1.50 (m, 8H), 1.42 – 1.28 (m, 2H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 170.52, 114.82, 76.86, 52.93, 35.91, 24.97, 23.88.

**Characterization Data:**

**Characterization data of TADDOL 7a and 7b:**



**7a**, 84% yield, white solid. $[\alpha]^{29}_D$ = -57.5° (*c* = 0.50, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$): δ = 7.45 (d, *J* = 8.1 Hz, 4H), 7.28 (d, *J* = 8.2 Hz, 4H), 7.17 (d, *J* = 8.0 Hz, 4H), 7.11 (d, *J* = 8.2 Hz, 4H), 4.58 (s, 2H), 4.13 (s, 2H), 2.66 (dq, *J* = 22.5, 7.5 Hz, 8H), 1.28 (t, *J* = 7.6 Hz, 6H), 1.22 (t, *J* = 7.6 Hz, 6H), 1.07 (s, 6H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 143.77, 143.50, 143.13, 140.29, 128.86, 127.93, 127.78, 126.94, 109.50, 81.27, 78.17, 28.75, 28.72, 27.44, 15.78, 15.68. IR (KBr): 3303, 3026, 2963, 2931, 2872, 1510, 1455, 1412, 1378, 1369, 1242, 1216, 1168, 1061, 1040, 1018, 887, 827, 756, 617 cm$^{-1}$. HRMS (ESI) Calcd. for $C_{39}H_{50}NO_4^+$ ($[M+NH_4]^+$) 596.3734, found 596.3733.

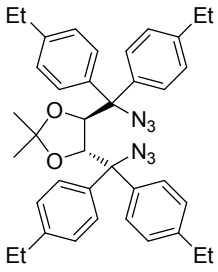


**7b**, 88% yield, white solid. $^1$H NMR (300 MHz, $CDCl_3$): δ = 7.55 – 7.48 (m, 4H), 7.41 – 7.22 (m, 16H), 4.55 (s, 2H), 3.98 (s, 2H), 1.50 – 1.33 (m, 4H), 1.30 – 1.09 (m, 6H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 146.35, 142.90, 128.84, 128.34, 127.94, 127.76, 127.40, 110.16, 80.65, 78.48, 70.85, 36.74, 26.71, 25.28, 24.20. HRMS (ESI) Calcd. for $C_{34}H_{38}NO_4^+$ ($[M+NH_4]^+$) 524.2795, found 524.2796. The spectral data are identical to those in reference 4.

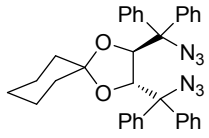
**Synthesis and characterization data of TADDOL-$N_3$ 8a and 8b:**

*Caution!: This reaction should be conducted behind a safety screen in a good hood because hydrazoic acid is very toxic. Care should also be taken in handling sodium azide ($NaN_3$).*

A round-bottomed flask was charged with $CHCl_3$ (31 mL) and sodium azide (9.5 g, 146.4 mmol). The mixture was cooled with an ice-salt bath, then trifluoroacetic acid (TFA, 31 mL) was added to this stirring solution. After 5-10 min, 4-EtPhTADDOL **7a** (14.1 g, 24.4 mmol) dissolved in $CHCl_3$ was added slowly to the stirring mixture with the ice-salt bath. After that, the resulting slurry was stirred at 0 °C. Following, after the reaction was finished detected by TLC, the resulting mixture was poured into ice-water solution with stirring and cautiously neutralized with a slight excess of 12-15% aqueous ammonia solution, then transferred to a separating funnel. The chloroform layer was separated, and the aqueous solution was extracted with 100 mL of $CH_2Cl_2$. The combined organic extracts were washed with 50 mL of water, separated, and dried over anhydrous $Na_2SO_4$. After evaporation of the solvent, the crude residue was purified by column chromatography on silica gel to give TADDOL-$N_3$ **8a**.[2]

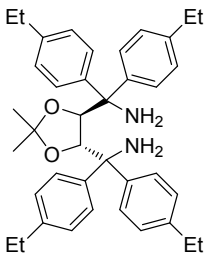



**8a**, 13.5 g, 21.5 mmol, 88% yield, white solid. $[\alpha]^{30}_D$ = -46.2° (*c* = 0.50, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$): δ = 7.27 – 7.11 (m, 16H), 4.92 (s, 2H), 2.73 – 2.56 (m, 8H), 1.30 – 1.17 (m, 12H), 1.09 (s, 6H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 143.79, 143.70, 139.51, 137.77, 129.83, 128.48, 127.70, 127.30, 110.75, 80.83, 73.34, 28.66, 27.73, 15.59, 15.46. IR (KBr): 3026, 2964, 2932, 2873, 2106, 1510, 1460, 1412, 1379, 1370, 1242, 1216, 1165, 1072, 977, 878, 826, 753, 685 $cm^{-1}$. HRMS (ESI) Calcd. for $C_{39}H_{44}N_6O_2K^+$ ($[M+K]^+$) 667.3157, found 667.3109.



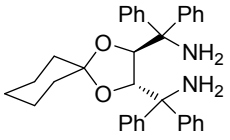

**8b**, 10.7 g, 19.2 mmol, 81% yield, white solid. $^1$H NMR (300 MHz, $CDCl_3$): δ = 7.41 – 7.25 (m, 20H), 4.95 (s, 2H), 1.52 – 1.39 (m, 4H), 1.36 – 1.21 (m, 6H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ: = 142.34, 140.53, 129.86, 128.61, 128.41, 128.03, 127.90, 127.85, 111.08, 80.23, 73.41, 36.98, 25.23, 24.39. HRMS (ESI) Calcd. for $C_{34}H_{32}N_6O_2Na^+$ ($[M+Na]^+$) 579.2479, found 579.2461. The spectral data are identical to those in reference 4.

**Characterization data of TADDOL-$NH_2$ 9a and 9b:**



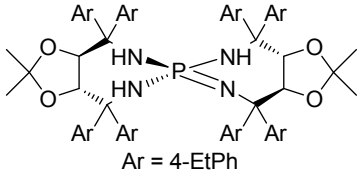

**9a**, 97% yield, white solid. $[\alpha]^{31}_D$ = -46.3° (*c* = 0.53, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$): δ = 7.49 (d, *J* = 7.9 Hz, 4H), 7.20 (d, *J* = 8.0 Hz, 4H), 7.11 (q, *J* = 8.3 Hz, 8H), 4.29 (s, 2H), 2.74 (q, *J* = 15.0, 7.5 Hz, 4H), 2.63 (q, *J* = 14.9, 7.4 Hz, 4H), 2.33 (s, 4H), 1.33 (t, *J* = 7.6 Hz, 6H), 1.24 (t, *J* = 7.6 Hz, 6H), 1.17 (s, 6H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 147.72, 142.79, 142.33, 141.44,

129.38, 127.68, 127.65, 126.92, 107.56, 82.17, 62.35, 28.70, 28.59, 27.49, 15.74, 15.66. IR (KBr): 3248, 3160, 3022, 2962, 2930, 2872, 1584, 1508, 1455, 1411, 1368, 1237, 1172, 1065, 1020, 894, 825, 761, 613 $cm^{-1}$. HRMS (ESI) Calcd. for $C_{39}H_{49}N_2O_2^+$ ([M+H]$^+$) 577.3789, found 577.3788.

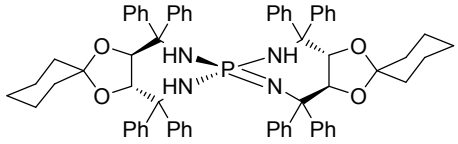


**9b**, 97% yield, white solid. $^1$H NMR (300 MHz, $CDCl_3$): δ = 7.62 – 7.51 (m, 4H), 7.39 – 7.28 (m, 6H), 7.27 – 7.13 (m, 10H), 4.22 (s, 2H), 2.38 (s, 4H), 1.46 (d, *J* = 3.2 Hz, 4H), 1.30 (d, *J* = 5.8 Hz, 6H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 150.40, 144.10, 129.57, 128.22, 127.89, 127.48, 127.24, 127.18, 126.65, 108.03, 81.66, 63.01, 36.85, 25.49, 24.26. HRMS (ESI) Calcd. for $C_{34}H_{37}N_2O_2^+$ ([M+H]$^+$) 505.2850, found 505.2851. The spectral data are identical to those in reference 4.

**Characterization data of iminophosphoranes 4f and 4i:**

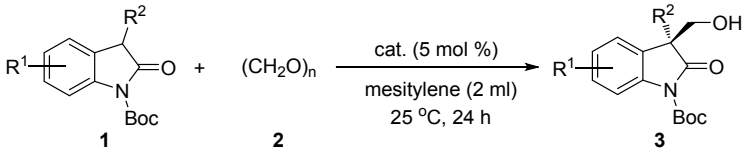



**4f**, 90% yield, white solid. [α]$^{32}_D$ = -88.2° (*c* = 0.53, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$): δ = 7.42 (s, 8H), 7.01 (s, 24H), 4.93 (s, 4H), 3.08 – 2.37 (m, 19H), 1.36 – 0.55 (m, 36H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 146.05, 142.24, 141.71, 129.89, 127.50, 127.14, 126.61, 109.59, 82.76, 77.32, 65.50, 28.42, 27.06, 15.62, 15.20. $^{31}$P NMR (121 MHz, $CDCl_3$): δ = -6.04 (s). IR (KBr): 3363, 3022, 2963, 2931, 2872, 1508, 1456, 1411, 1378, 1240, 1216, 1164, 1061, 1018, 963, 907, 889, 823, 795, 753, 598 $cm^{-1}$. HRMS (MALDI/DHB): Calcd for $C_{78}H_{92}N_4O_4P^+$([M+H]$^+$) 1179.6851, found 1179.6856.



**4i**, 94% yield, white solid. [α]$^{31}_D$ = -74.9° (*c* = 0.59, $CHCl_3$). $^1$H NMR (300 MHz, $CDCl_3$): δ = 7.70 – 6.49 (m, 40H), 4.92 (d, *J* = 61.6 Hz, 4H), 2.80 (s, 3H), 1.58 – 0.58 (m, 20H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 142.20, 138.23, 124.58, 122.72, 122.60, 122.19, 121.80, 121.35, 105.19, 75.83, 71.98, 61.27, 60.22, 31.20, 19.72, 18.60. $^{31}$P NMR (121 MHz, $CDCl_3$): δ = -6.84 (s). IR (KBr): 3361, 3056, 3027, 2932, 2858, 1599, 1493, 1445, 1365, 1278, 1165, 1127, 1099, 1050, 953, 908, 893, 745, 698, 640 $cm^{-1}$. HRMS (MALDI/DHB): Calcd for $C_{62}H_{60}N_4O_4P^+$([M+H]$^+$) 1035.4973, found 1035.4973.

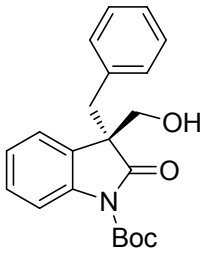
## 3. General procedure for hydroxymethylation of 3-substituted oxindoles with paraformaldehyde.




**1** **2** **3**

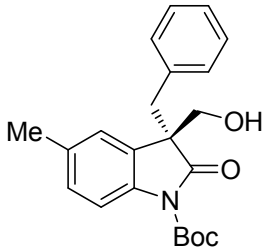
To a tube was added oxindole **1** (0.1 mmol, 1.0 equiv), **cat.** (7.0 mg, 0.005 mmol, 5 mol %) and mesitylene (2 mL) at 25 °C with magnetic stirring. Then paraformaldehyde **2** (9.0 mg, 0.3 mmol, 3.0 equiv) was added to the mixture of oxindole and catalyst. After stirring for 24 h at 25 °C, the reaction mixture was purified directly by silica gel column chromatography to yield product **3**. The *ee* of product **3** was determined by chiral HPLC analysis. The absolute configuration of compound **3** was determined to be "(*S*)" by comparison of the optical rotation value to the reported literature value.[5]

**(*S*)-*tert*-butyl-3-benzyl-3-(hydroxymethyl)-2-oxoindoline-1-carboxylate (3a):**[5]



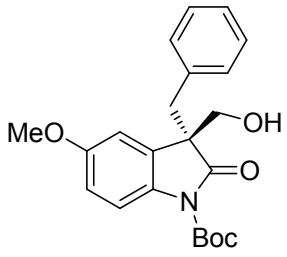

White solid, 34.6 mg, 98% yield, 94% ee; m.p. 107 – 108 ˚C. $[\alpha]^{30}_D$ = + 26.2˚ (*c* = 0.88, $CHCl_3$). Enantiomeric excess was determined by chiral HPLC analysis (CHIRALCEL OD-H, 254 nm, 9:1 hexane/iPrOH, 1.0 mL /min): $t_R$ (major) = 6.52 min, $t_R$ (minor) = 7.38 min. $^1$H NMR (300 MHz, $CDCl_3$): δ = 7.63 (d, *J* = 7.9 Hz, 1H), 7.30 – 7.18 (m, 1H), 7.18 – 6.99 (m, 5H), 6.94 – 6.79 (m, 2H), 4.03 (d, *J* = 10.9 Hz, 1H), 3.87 (d, *J* = 11.0 Hz, 1H), 3.15 (q, *J* = 13.1 Hz, 2H), 2.82 (br s, 1H), 1.55 (s, 9H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 178.17, 148.91, 140.30, 134.98, 130.19, 128.79, 128.27, 128.07, 127.02, 124.44, 123.88, 115.17, 84.49, 66.67, 56.50, 40.35, 28.25. HRMS (ESI): Calcd. for $C_{21}H_{23}NO_4Na$ ($[M+Na]^+$) 376.1519; found 376.1520.

**(*S*)-*tert*-butyl-3-benzyl-3-(hydroxymethyl)-5-methyl-2-oxoindoline-1-carboxylate (3b):**[5]



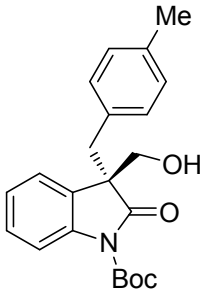

White solid, 35.2 mg, 96% yield, 93% ee; m.p. 82 – 83 ˚C. $[\alpha]^{30}_D$ = - 16.6˚ (*c* = 0.91, $CHCl_3$). Enantiomeric excess was determined by chiral HPLC analysis (CHIRALPAK AD-H, 254 nm, 9:1 hexane/iPrOH, 1.0 mL /min): $t_R$ (major) = 7.72 min, $t_R$ (minor) = 6.77 min. $^1$H NMR (300 MHz, $CDCl_3$): δ = 7.50 (d, *J* = 8.3 Hz, 1H), 7.16 – 6.98 (m, 4H), 6.95 – 6.80 (m, 3H), 4.02 (d, *J* = 10.4 Hz, 1H), 3.86 (d, *J* = 11.1 Hz, 1H), 3.14 (q, *J* = 13.1 Hz, 2H), 2.64 (br s, 1H), 2.33 (s, 3H), 1.55 (s, 9H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 178.37, 148.94, 137.94, 135.03, 134.02, 130.23, 129.30, 128.09, 128.03, 127.01, 124.37, 114.97, 84.33, 66.63, 56.33, 40.31, 28.25, 21.37. HRMS (ESI): Calcd. for $C_{22}H_{25}NO_4Na$ ($[M+Na]^+$) 390.1676; found 390.1676.

**(*S*)-*tert*-butyl-3-benzyl-3-(hydroxymethyl)-5-methoxyl-2-oxoindoline-1-carboxylate (3c):**



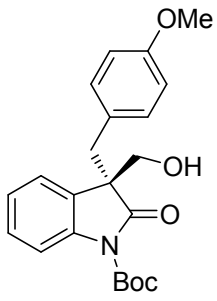

White solid, 35.2 mg, 92% yield, 93% ee; m.p. 100 – 101 ˚C. $[\alpha]^{30}_{D}$ = -20.0˚ (*c* = 1.14, $CHCl_3$). Enantiomeric excess was determined by chiral HPLC analysis (CHIRALPAK AD-H, 254 nm, 9:1 hexane/iPrOH, 1.0 mL /min): $t_R$ (major) = 11.97 min, $t_R$ (minor) = 10.28 min. $^1$H NMR (300 MHz, $CDCl_3$): δ = 7.55 (d, *J* = 8.9 Hz, 1H), 7.17 – 7.02 (m, 3H), 6.96 – 6.84 (m, 2H), 6.75 (dd, *J* = 8.9, 2.6 Hz, 1H), 6.61 (d, *J* = 2.6 Hz, 1H), 4.08 – 3.94 (m, 1H), 3.85 (d, *J* = 11.0 Hz, 1H), 3.74 (s, 3H), 3.23 – 3.04 (m, 2H), 2.71 (d, *J* = 5.0 Hz, 1H), 1.55 (s, 9H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 178.24, 156.76, 148.95, 134.94, 133.64, 130.29, 129.53, 128.10, 127.07, 116.09, 113.47, 110.17, 84.34, 66.55, 56.51, 55.81, 40.21, 28.25. IR (KBr): 3495, 3030, 2979, 2932, 1782, 1728, 1600, 1487, 1455, 1436, 1394, 1369, 1337, 1281, 1248, 1152, 1074, 1036, 1000, 952, 843, 812, 769, 738, 700, 612, 582, 536 $cm^{-1}$. HRMS (ESI): Calcd. for $C_{22}H_{25}NO_5Na$ ($[M+Na]^+$) 406.1625; found 406.1627.

**(*S*)-*tert*–butyl-3-(hydroxymethyl)-3-(4-methylbenzyl) -2-oxoindoline-1-carboxylate (3d):**[5]




White solid, 33.0 mg, 90% yield, 93% ee; m.p. 83 – 84 ˚C. $[\alpha]^{30}_{D}$ = + 31.5˚ (*c* = 0.93, $CHCl_3$). Enantiomeric excess was determined by chiral HPLC analysis (CHIRALPAK AS-H, 254 nm, 9:1 hexane/iPrOH, 1.0 mL /min): $t_R$ (major) = 9.51 min, $t_R$ (minor) = 7.78 min. $^1$H NMR (300 MHz, $CDCl_3$): δ = 7.65 (d, *J* = 8.1 Hz, 1H), 7.29 – 7.20 (m, 1H), 7.18 – 7.05 (m, 2H), 6.88 (d, *J* = 7.8 Hz, 2H), 6.76 (d, *J* = 7.9 Hz, 2H), 4.02 (d, *J* = 10.7 Hz, 1H), 3.86 (d, *J* = 11.1 Hz, 1H), 3.11 (q, *J* = 13.2 Hz, 2H), 2.71 (br s, 1H), 2.21 (s, 3H), 1.57 (s, 9H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 178.31, 148.96, 140.34, 136.50, 131.79, 130.10, 128.79, 128.76, 128.35, 124.41, 123.86, 115.20, 84.49, 66.64, 56.42, 39.89, 28.25, 21.24. HRMS (ESI): Calcd. for $C_{22}H_{25}NO_4Na$ ($[M+Na]^+$) 390.1676; found 390.1674.

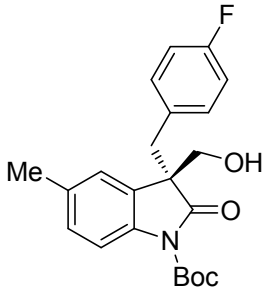
**(S)-*tert*-butyl-3-(hydroxymethyl)-3-(4-methoxybenzyl) -2-oxoindoline-1-carboxylate (3e):**[5]




White solid, 37.7 mg, 97% yield, 91% ee; m.p. 99 – 100 ˚C. $[\alpha]^{30}_{D}$ = + 28.0˚ (*c* = 0.93, $CHCl_3$). Enantiomeric excess was determined by chiral HPLC analysis (CHIRALPAK AS-H, 254

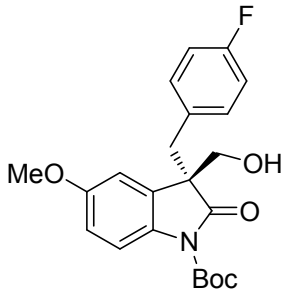
nm, 9:1 hexane/iPrOH, 1.0 mL /min): $t_R$ (major) = 13.67 min, $t_R$ (minor) = 12.41 min. $^1$H NMR (300 MHz, $CDCl_3$): δ = 7.63 (d, *J* = 8.1 Hz, 1H), 7.28 – 7.19 (m, 1H), 7.17 – 7.05 (m, 2H), 6.77 (d, *J* = 8.5 Hz, 2H), 6.60 (d, *J* = 8.4 Hz, 2H), 4.04 – 3.93 (m, 1H), 3.84 (d, *J* = 11.0 Hz, 1H), 3.67 (s, 3H), 3.08 (q, *J* = 13.3 Hz, 2H), 2.78 (br s, 1H), 1.55 (s, 9H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 178.32, 158.56, 148.92, 140.32, 131.21, 128.75, 128.38, 126.94, 124.42, 123.83, 115.20, 113.45, 84.51, 66.58, 56.58, 55.30, 39.45, 28.24. HRMS (ESI): Calcd. for $C_{22}H_{24}FNO_4Na$ ($[M+Na]^+$) 408.1582; found 408.1581. HRMS (ESI): Calcd. for $C_{22}H_{25}NO_5Na$ ($[M+Na]^+$) 406.1625; found 406.1610.

**(*S*)-*tert*-butyl -3-(4-fluorobenzyl)-3-(hydroxymethyl)-5-methyl-2-oxoindoline-1-carboxylate (3f):**




White solid, 36.6 mg, 95% yield, 90% ee; m.p. 93 – 94 ˚C. $[\alpha]^{29}_D$ = - 21.2˚ (*c* = 0.97, $CHCl_3$). Enantiomeric excess was determined by chiral HPLC analysis (CHIRALCEL OD-H, 254 nm, 9:1 hexane/iPrOH, 0.5 mL /min): $t_R$ (major) = 13.78 min, $t_R$ (minor) = 13.34 min. $^1$H NMR (300 MHz, $CDCl_3$): δ = 7.49 (d, *J* = 8.3 Hz, 1H), 7.04 (d, *J* = 8.2 Hz, 1H), 6.93 (s, 1H), 6.85 – 6.69 (m, 4H), 4.04 – 3.93 (m, 1H), 3.85 (d, *J* = 11.0 Hz, 1H), 3.11 (dd, *J* = 37.9, 13.2 Hz, 2H), 2.65 (d, *J* = 5.1 Hz, 1H), 2.33 (s, 3H), 1.54 (s, 9H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 178.22, 162.02 (d, *J* = 245.0 Hz), 148.81, 137.92, 134.17, 131.65 (d, *J* = 8.0 Hz), 130.76 (d, *J* = 3.3 Hz), 129.43, 127.92, 124.19, 115.06, 114.86 (d, *J* = 21.2 Hz), 84.48, 66.56, 56.38, 39.43, 28.22, 21.35. $^{19}$F NMR (282 MHz, $CDCl_3$): δ = -116.38 – -116.51 (m). IR (KBr): 3472, 2981, 2922, 2864, 1778, 1701, 1600, 1508, 1482, 1457, 1394, 1371, 1331, 1312, 1283, 1249, 1219, 1156, 1126, 1107, 1071, 950, 888, 834, 763, 718, 661, 615, 605, 564, 502 $cm^{-1}$. HRMS (ESI): Calcd. for $C_{22}H_{24}FNO_4Na$ ($[M+Na]^+$) 408.1582; found 408.1581.

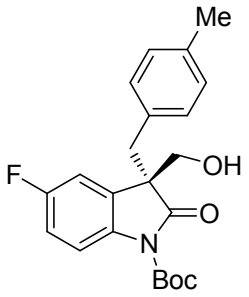
**(*S*)-*tert*-butyl-3-(4-fluorobenzyl)-3-(hydroxymethyl)-5-methoxyl-2-oxoindoline-1-carboxylate (3g):**




White solid, 36.1 mg, 90% yield, 92% ee; m.p. 118 – 119 ˚C. $[\alpha]^{30}_D$ = -28.7˚ (*c* = 1.09, $CHCl_3$). Enantiomeric excess was determined by chiral HPLC analysis (CHIRALPAK AS-H, 254 nm, 9:1 hexane/iPrOH, 1.0 mL /min): $t_R$ (major) = 12.90 min, $t_R$ (minor) = 14.93 min. $^1$H NMR (300 MHz, $CDCl_3$): δ = 7.53 (d, *J* = 8.9 Hz, 1H), 6.88 – 6.80 (m, 2H), 6.79 – 6.70 (m, 3H), 6.67 (d, *J* = 2.6 Hz, 1H), 4.02 – 3.91 (m, 1H), 3.84 (d, *J* = 11.0 Hz, 1H), 3.75 (s, 3H), 3.10 (dd, *J* = 29.2, 13.3 Hz, 2H), 2.77 (d, *J* = 3.9 Hz, 1H), 1.53 (s, 9H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 178.05, 162.03 (d, *J* = 245.2 Hz), 156.85, 148.82, 133.62, 131.68 (d, *J* = 8.0 Hz), 130.68 (d, *J* = 3.3 Hz), 129.43, 116.16, 114.92 (d, *J* = 21.1 Hz), 113.35, 110.17, 84.47, 66.52, 56.67, 55.82, 39.37, 28.22. $^{19}$F NMR (282 MHz,

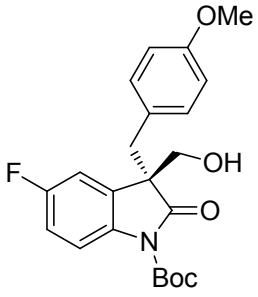
$CDCl_3$): δ = -116.26 – -116.40 (m). IR (KBr): 3494, 3045, 2979, 2933, 2837, 1782, 1730, 1600, 1509, 1485, 1456, 1437, 1394, 1370, 1334, 1282, 1247, 1223, 1152, 1074, 1039, 1000, 953, 840, 766, 736, 611, 583, 551 $cm^{-1}$. HRMS (ESI): Calcd. for $C_{22}H_{24}FNO_5Na$ ([M+Na]$^+$) 424.1531; found 424.1528.

**(*S*)-*tert*–butyl-5-fluoro-3-(hydroxymethyl)-3-(4-methylbenzyl) -2-oxoindoline-1-carboxylate (3h):**




White solid, 36.2 mg, 94% yield, 89% ee; m.p. 110 – 111 ˚C. $[\alpha]^{30}_D$ = + 20.2˚ (*c* = 0.99, $CHCl_3$). Enantiomeric excess was determined by chiral HPLC analysis (CHIRALPAK AD-H, 254 nm, 9:1 hexane/iPrOH, 1.0 mL /min): $t_R$ (major) = 6.08 min, $t_R$ (minor) = 7.20 min. $^1$H NMR (300 MHz, $CDCl_3$): δ = 7.63 (dd, *J* = 8.9, 4.6 Hz, 1H), 6.99 – 6.81 (m, 4H), 6.77 (d, *J* = 7.9 Hz, 2H), 4.02 (d, *J* = 11.0 Hz, 1H), 3.86 (d, *J* = 11.0 Hz, 1H), 3.09 (q, *J* = 13.2 Hz, 2H), 2.66 (br s, 1H), 2.22 (s, 3H), 1.56 (s, 9H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 177.79, 159.90 (d, *J* = 243.6 Hz), 148.87, 136.74, 136.24 (d, *J* = 2.3 Hz), 131.38, 130.44 (d, *J* = 8.1 Hz), 130.00, 128.92, 116.48 (d, *J* = 7.9 Hz), 115.18 (d, *J* = 22.8 Hz), 111.44 (d, *J* = 24.4 Hz), 84.67, 66.51, 56.82, 39.91, 28.22, 21.23. $^{19}$F NMR (282 MHz, $CDCl_3$): δ = -118.13 – -118.26 (m). IR (KBr): 3496, 3131, 3091, 3060, 3013, 2977, 1947, 2913, 2874, 1796, 1711, 1609, 1514, 1479, 1455, 1438, 1396, 1370, 1347, 1306, 1293, 1280, 1246, 1145, 1115, 1099, 1082, 1057, 1028, 1005, 960, 932, 920, 904, 875, 840, 815, 760, 748, 720, 662, 619, 611, 563, 548, 503 $cm^{-1}$. HRMS (ESI): Calcd. for $C_{22}H_{24}FNO_4Na$ ([M+Na]$^+$) 408.1582; found 408.1581.

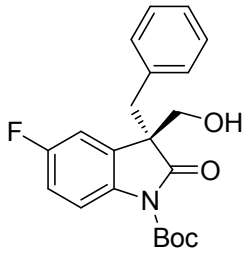
**(S)-*tert*-butyl-5-fluoro-3-(hydroxymethyl)-3-(4-methoxybenzyl) -2-oxoindoline-1-carboxylate (3i):**




White solid, 34.1 mg, 85% yield, 91% ee; m.p. 127 – 128 ˚C. $[\alpha]^{30}_D$ = + 29.1˚ (*c* = 0.81, $CHCl_3$). Enantiomeric excess was determined by chiral HPLC analysis (CHIRALPAK AD-H, 254 nm, 9:1 hexane/iPrOH, 1.0 mL /min): $t_R$ (major) = 8.02 min, $t_R$ (minor) = 9.37 min. $^1$H NMR (300 MHz, $CDCl_3$): δ = 7.61 (dd, *J* = 8.9, 4.6 Hz, 1H), 6.98 – 6.83 (m, 2H), 6.79 (d, *J* = 8.6 Hz, 2H), 6.62 (d, *J* = 8.6 Hz, 2H), 4.00 (d, *J* = 11.0 Hz, 1H), 3.85 (d, *J* = 11.0 Hz, 1H), 3.68 (s, 3H), 3.07 (q, *J* = 13.4 Hz, 2H), 2.68 (br s, 1H), 1.55 (s, 9H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 177.81, 159.91 (d, *J* = 243.5 Hz), 158.69, 148.83, 136.23 (d, *J* = 2.4 Hz), 131.14, 130.48 (d, *J* = 8.1 Hz), 126.52, 116.49 (d, *J* = 7.9 Hz), 115.18 (d, *J* = 22.8 Hz), 113.57, 111.40 (d, *J* = 24.4 Hz), 84.70, 66.46, 56.97, 55.31, 39.48, 28.22. $^{19}$F NMR (282 MHz, $CDCl_3$): δ = -118.09 – -118.25 (m). IR (KBr): 3489, 3094, 3071, 3007, 2982, 2935, 2876, 2839, 2794, 1792, 1706, 1610, 1510, 1481, 1457, 1439, 1394, 1371, 1350, 1301, 1286, 1246,

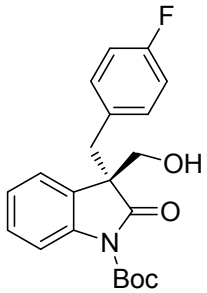
1182, 1144, 1116, 1099, 1083, 1029, 960, 934, 905, 876, 850, 836, 811, 764, 748, 721, 661, 612, 565, 527 $cm^{-1}$. HRMS (ESI): Calcd. for $C_{22}H_{24}FNO_5Na$ ($[M+Na]^+$) 424.1531; found 424.1534.

**(*S*)-*tert*-butyl-3-benzyl-5-fluoro-3-(hydroxymethyl)-2-oxoindoline-1-carboxylate (3j):**



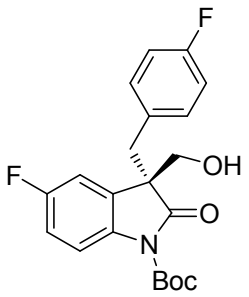

White solid, 35.3 mg, 95% yield, 90% ee; m.p. 102 – 103 ˚C. $[\alpha]^{30}_D$ = + 26.3˚ (*c* = 0.81, $CHCl_3$). Enantiomeric excess was determined by chiral HPLC analysis (CHIRALPAK AD-H, 254 nm, 9:1 hexane/iPrOH, 0.8 mL /min): $t_R$ (major) = 8.98 min, $t_R$ (minor) = 8.14 min. $^1$H NMR (300 MHz, $CDCl_3$): δ = 7.61 (dd, *J* = 8.9, 4.6 Hz, 1H), 7.15 – 7.04 (m, 3H), 6.98 – 6.82 (m, 4H), 4.03 (d, *J* = 11.0 Hz, 1H), 3.89 (d, *J* = 11.0 Hz, 1H), 3.14 (dd, *J* = 30.3, 13.2 Hz, 2H), 2.68 (br s, 1H), 1.55 (s, 9H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 177.67, 159.92 (d, *J* = 243.6 Hz), 148.81, 136.22 (d, *J* = 2.4 Hz), 134.56, 130.31 (d, *J* = 8.1 Hz), 130.10, 128.20, 127.22, 116.47 (d, *J* = 7.9 Hz), 115.24 (d, *J* = 22.8 Hz), 111.43 (d, *J* = 24.4 Hz), 84.71, 66.53, 56.81, 40.34, 28.22. $^{19}$F NMR (282 MHz, $CDCl_3$): δ = -118.08 – -118.20 (m). IR (KBr): 3504, 3085, 3028, 3008, 2971, 2938, 2876, 1775, 1700, 1605, 1583, 1475, 1457, 1396, 1373, 1308, 1285, 1247, 1152, 1124, 1100, 1077, 1034, 955, 935, 902, 864, 838, 743, 704, 660, 611, 565, 534 $cm^{-1}$. HRMS (ESI): Calcd. for $C_{21}H_{22}FNO_4Na$ ($[M+Na]^+$) 394.1425; found 394.1428.

**(*S*)-*tert*-butyl-3-(4-fluorobenzyl)-3-(hydroxymethyl)-2-oxoindoline-1-carboxylate (3k):**[5]



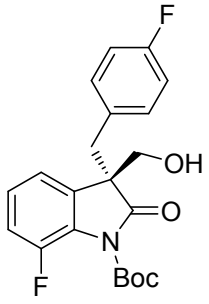

White solid, 35.2 mg, 95% yield, 91% ee; m.p. 102 – 103 ˚C. $[\alpha]^{29}_D$ = + 18.0˚ (*c* = 0.79, $CHCl_3$). Enantiomeric excess was determined by chiral HPLC analysis (CHIRALCEL OD-H, 254 nm, 20:1 hexane/iPrOH, 0.5 mL /min): $t_R$ (major) = 24.88 min, $t_R$ (minor) = 26.93 min. $^1$H NMR (300 MHz, $CDCl_3$): δ = 7.62 (d, *J* = 8.0 Hz, 1H), 7.29 – 7.20 (m, 1H), 7.19 – 7.08 (m, 2H), 6.86 – 6.69 (m, 4H), 3.98 (d, *J* = 6.7 Hz, 1H), 3.86 (d, *J* = 11.0 Hz, 1H), 3.13 (dd, *J* = 35.9, 13.3 Hz, 2H), 2.66 (br s, 1H), 1.56 (s, 9H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 178.05, 162.03 (d, *J* = 245.1 Hz), 148.78, 140.29, 131.64 (d, *J* = 8.0 Hz), 130.68 (d, *J* = 3.3 Hz), 128.96, 128.00, 124.53, 123.68, 115.27, 114.91 (d, *J* = 21.2 Hz), 84.68, 66.56, 56.40, 39.42, 28.22. $^{19}$F NMR (282 MHz, $CDCl_3$): δ = -116.26 – -116.47 (m). HRMS (ESI): Calcd. for $C_{21}H_{22}FNO_4Na$ ($[M+Na]^+$) 394.1425; found 394.1426.

**(*S*)-*tert*-butyl-5-fluoro-3-(4-fluorobenzyl)-3-(hydroxymethyl)-2-oxoindoline-1-carboxylate (3l):**



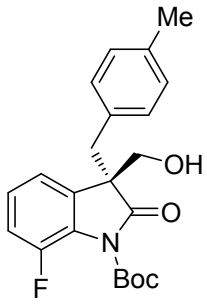
White solid, 37.4 mg, 96% yield, 70% ee; m.p. 104 – 105 ˚C. $[\alpha]^{30}_{D}$ = + 15.2˚ (*c* = 1.18, $CHCl_3$). Enantiomeric excess was determined by chiral HPLC analysis (CHIRALPAK AD-H, 254 nm, 9:1 hexane/iPrOH, 1.0 mL /min): $t_R$ (major) = 6.43 min, $t_R$ (minor) = 7.12 min. $^1$H NMR (300 MHz, $CDCl_3$): δ = 7.59 (dd, *J* = 8.8, 4.8 Hz, 1H), 7.00 – 6.87 (m, 2H), 6.87 – 6.69 (m, 4H), 4.00 (d, *J* = 10.7 Hz, 1H), 3.88 (d, *J* = 11.0 Hz, 1H), 3.11 (dd, *J* = 39.0, 13.3 Hz, 2H), 2.77 (br s, 1H), 1.54 (s, 9H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 177.52, 162.09 (d, *J* = 245.5 Hz), 159.96 (d, *J* = 243.9 Hz), 148.68, 136.19 (d, *J* = 2.3 Hz), 131.55 (d, *J* = 8.0 Hz), 130.32 (d, *J* = 3.3 Hz), 130.18 (d, *J* = 8.1 Hz), 116.56 (d, *J* = 7.9 Hz), 115.35 (d, *J* = 24.1 Hz), 115.05 (d, *J* = 21.3 Hz), 111.30 (d, *J* = 24.4 Hz), 84.87, 66.46, 56.94, 39.47, 28.18. $^{19}$F NMR (282 MHz, $CDCl_3$): δ = -115.94 – -116.11 (m), -117.84 – -117.99 (m). IR (KBr): 3490, 3075, 3012, 2941, 2880, 1777, 1702, 1606, 1512, 1486, 1476, 1463, 1456, 1397, 1385, 1369, 1307, 1249, 1224, 1153, 1076, 1048, 953, 936, 903, 864, 840, 765, 719, 659, 611, 567, 547 cm$^{-1}$. HRMS (ESI): Calcd. for $C_{21}H_{21}F_2NO_4Na$ ($[M+Na]^+$) 412.1331; found 412.1331.

**(*S*)-*tert*-butyl-7-fluoro-3-(4-fluorobenzyl)-3-(hydroxymethyl)-2-oxoindoline-1-carboxylate (3m):**



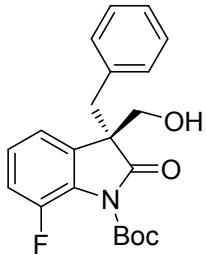
White solid, 35.0 mg, 90% yield, 41% ee; m.p. 103 – 104 ˚C. $[\alpha]^{30}_{D}$ = + 2.8˚ (*c* = 1.06, $CHCl_3$). Enantiomeric excess was determined by chiral HPLC analysis (CHIRALPAK AD-H, 254 nm, 9:1 hexane/iPrOH, 1.0 mL /min): $t_R$ (major) = 9.14 min, $t_R$ (minor) = 7.93 min. $^1$H NMR (300 MHz, $CDCl_3$): δ = 7.20 – 7.10 (m, 1H), 7.08 – 6.94 (m, 2H), 6.82 – 6.69 (m, 4H), 4.03 (d, *J* = 11.1 Hz, 1H), 3.90 (d, *J* = 11.1 Hz, 1H), 3.13 (dd, *J* = 46.7, 13.2 Hz, 2H), 2.78 (br s, 1H), 1.45 (s, 9H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 177.13, 162.10 (d, *J* = 245.2 Hz), 148.82 (d, *J* = 251.5 Hz), 146.94, 131.71 (d, *J* = 1.9 Hz), 131.45 (d, *J* = 8.0 Hz), 130.31 (d, *J* = 3.2 Hz), 127.28 (d, *J* = 9.3 Hz), 125.68 (d, *J* = 7.0 Hz), 119.51 (d, *J* = 3.5 Hz), 117.17 (d, *J* = 20.7 Hz), 115.05 (d, *J* = 21.2 Hz), 84.97, 66.39, 57.76, 39.65, 27.68. $^{19}$F NMR (282 MHz, $CDCl_3$): δ = -116.11 – -116.28 (m), -119.77 (dd, *J* = 11.1, 4.3 Hz). IR (KBr): 3508, 3042, 2984, 2935, 1785, 1710, 1628, 1601, 1509, 1488, 1473, 1393, 1369, 1357, 1303, 1271, 1250, 1221, 1189, 1161, 1148, 1073, 959, 909, 843, 791, 762, 748, 732, 710, 699, 650, 608, 586, 560 cm$^{-1}$. HRMS (ESI): Calcd. for $C_{21}H_{21}F_2NO_4Na$ ($[M+Na]^+$) 412.1331; found 412.1333.

**(*S*)-*tert*–butyl-7-fluoro-3-(hydroxymethyl)-3-(4-methylbenzyl) -2-oxoindoline-1-carboxylate (3n):**



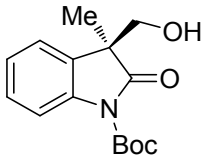

White solid, 34.3 mg, 89% yield, 81% ee; m.p. 112 – 113 ˚C. $[\alpha]^{30}_{D}$ = + 13.6˚ (*c* = 0.93, $CHCl_3$). Enantiomeric excess was determined by chiral HPLC analysis (CHIRALPAK AD-H, 254 nm, 9:1 hexane/iPrOH, 1.0 mL /min): $t_R$ (major) = 9.24 min, $t_R$ (minor) = 7.44 min. $^1$H NMR (300 MHz, $CDCl_3$): δ = 7.19 – 7.08 (m, 1H), 7.05 – 6.93 (m, 2H), 6.88 (d, *J* = 7.8 Hz, 2H), 6.73 (d, *J* = 8.0 Hz, 2H), 4.04 (d, *J* = 11.1 Hz, 1H), 3.89 (d, *J* = 11.1 Hz, 1H), 3.12 (dd, *J* = 36.3, 13.2 Hz, 2H), 2.75 (br s, 1H), 2.21 (s, 3H), 1.46 (s, 9H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 177.41, 148.84 (d, *J* = 251.3 Hz), 147.06, 136.56, 132.02 (d, *J* = 1.9 Hz), 131.45, 129.87, 128.93, 127.27 (d, *J* = 9.3 Hz), 125.55 (d, *J* = 7.0 Hz), 119.64 (d, *J* = 3.5 Hz), 117.01 (d, *J* = 20.7 Hz), 84.69, 66.56, 57.74, 40.05, 27.72, 21.25. $^{19}$F NMR (282 MHz, $CDCl_3$): δ = -119.74 (dd, *J* = 11.1, 4.3 Hz). IR (KBr): 3494, 2982, 2935, 2876, 1789, 1714, 1624, 1596, 1515, 1486, 1465, 1395, 1369, 1355, 1305, 1291, 1278, 1250, 1189, 1146, 1072, 1004, 957, 908, 843, 825, 784, 752, 730, 714, 692, 653, 608, 585, 561, 536 cm$^{-1}$. HRMS (ESI): Calcd. for $C_{22}H_{24}FNO_4Na$ ($[M+Na]^+$) 408.1582; found 408.1581.

**(*S*)-*tert*-butyl-3-benzyl-7-fluoro-3-(hydroxymethyl)-2-oxoindoline-1-carboxylate (3o):**



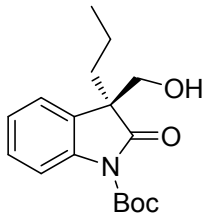

White solid, 33.8 mg, 91% yield, 67% ee; m.p. 99 – 100 ˚C. $[\alpha]^{30}_{D}$ = + 10.4˚ (*c* = 1.05, $CHCl_3$). Enantiomeric excess was determined by chiral HPLC analysis (CHIRALPAK AD-H, 254 nm, 9:1 hexane/iPrOH, 1.0 mL /min): $t_R$ (major) = 10.58 min, $t_R$ (minor) = 8.00 min. $^1$H NMR (300 MHz, $CDCl_3$): δ = 7.18 – 7.04 (m, 4H), 7.04 – 6.94 (m, 2H), 6.91 – 6.81 (m, 2H), 4.05 (d, *J* = 11.0 Hz, 1H), 3.91 (d, *J* = 11.1 Hz, 1H), 3.17 (dd, *J* = 41.6, 13.1 Hz, 2H), 2.61 (br s, 1H), 1.47 (s, 9H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 177.32, 148.82 (d, *J* = 251.4 Hz), 147.02, 134.57, 131.79 (d, *J* = 2.0 Hz), 130.01, 128.23, 127.26 (d, *J* = 9.3 Hz), 127.20, 125.56 (d, *J* = 6.9 Hz), 119.59 (d, *J* = 3.5 Hz), 117.11 (d, *J* = 20.7 Hz), 84.85, 66.57, 57.53, 40.39, 27.76. $^{19}$F NMR (282 MHz, $CDCl_3$): δ = -119.72 (dd, *J* = 11.4, 4.3 Hz). IR (KBr): 3513, 3030, 2983, 2932, 2873, 1784, 1751, 1712, 1626, 1600, 1488, 1455, 1370, 1355, 1297, 1264, 1248, 1195, 1145, 1071, 958, 919, 844, 791, 733, 701, 646, 609, 586, 560 cm$^{-1}$. HRMS (ESI): Calcd. for $C_{21}H_{22}FNO_4Na$ ($[M+Na]^+$) 394.1425; found 394.1427.

**(*S*)-*tert*-butyl-3-(hydroxymethyl)-3-methyl-2-oxoindoline-1-carboxylate (3p):**[5]



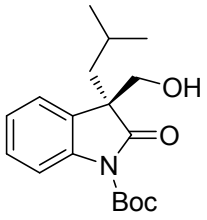

White solid, 25.5 mg, 92% yield, 86% ee; m.p. 82 – 83 ˚C. $[\alpha]^{29}_{D}$ = - 7.6˚ (*c* = 0.85, $CHCl_3$). Enantiomeric excess was determined by chiral HPLC analysis (CHIRALPAK AS-H, 254 nm, 9:1 hexane/iPrOH, 1.0 mL /min): $t_R$ (major) = 6.79 min, $t_R$ (minor) = 6.20 min. $^1$H NMR (300 MHz, $CDCl_3$): δ = 7.81 (d, *J* = 8.1 Hz, 1H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.23 – 7.09 (m, 2H), 3.90 – 3.77 (m, 1H), 3.71 (d, *J* = 10.7 Hz, 1H), 2.73 (br s, 1H), 1.60 (s, 9H), 1.35 (s, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 178.92, 149.37, 139.80, 131.03, 128.67, 124.85, 122.95, 115.33, 84.73, 68.24, 50.97, 28.29, 20.07. HRMS (ESI): Calcd. for $C_{15}H_{19}NO_4Na$ ([M+Na]$^+$) 300.1206; found 300.1208.

**(*S*)-*tert*-butyl-3-(hydroxymethyl)-2-oxo-3-propylindoline-1-carboxylate (3q):**[5]



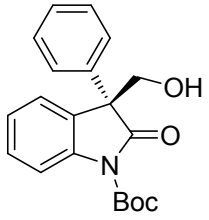

Viscous, 26.6 mg, 87% yield, 74% ee;. $[\alpha]^{30}_{D}$ = + 6.2˚ (*c* = 1.00, $CHCl_3$). Enantiomeric excess was determined by chiral HPLC analysis (CHIRALPAK AS-H, 254 nm, 9:1 hexane/iPrOH, 1.0 mL /min): $t_R$ (major) = 6.46 min, $t_R$ (minor) = 5.20 min. $^1$H NMR (300 MHz, $CDCl_3$): δ = 7.81 (d, *J* = 8.1 Hz, 1H), 7.33 – 7.24 (m, 1H), 7.21 – 7.10 (m, 2H), 3.84 (d, *J* = 10.6 Hz, 1H), 3.72 (d, *J* = 10.8 Hz, 1H), 2.50 (br s, 1H), 1.99 – 1.83 (m, 1H), 1.75 – 1.61 (m, 1H), 1.60 (s, 9H), 1.11 – 0.96 (m, 1H), 0.95 – 0.82 (m, 1H), 0.76 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 178.53, 149.27, 140.55, 129.43, 128.60, 124.77, 123.03, 115.23, 84.65, 67.98, 55.81, 36.31, 28.30, 17.56, 14.36. HRMS (ESI): Calcd. for $C_{17}H_{23}NO_4Na$ ([M+Na]$^+$) 328.1519; found 328.1521.

**(*S*)-*tert*-butyl-3-(hydroxymethyl)-3-isobutyl-2-oxoindoline-1-carboxylate (3r):**




White solid, 25.9 mg, 81% yield, 65% ee; m.p. 76 – 77 ˚C. $[\alpha]^{30}_{D}$ = - 0.4˚ (*c* = 0.86, $CHCl_3$). Enantiomeric excess was determined by chiral HPLC analysis (CHIRALPAK AS-H, 254 nm, 9:1 hexane/iPrOH, 1.0 mL /min): $t_R$ (major) = 5.52 min, $t_R$ (minor) = 4.96 min. $^1$H NMR (300 MHz, $CDCl_3$): δ = 7.84 (d, *J* = 8.1 Hz, 1H), 7.36 – 7.27 (m, 1H), 7.24 – 7.14 (m, 2H), 3.79 (d, *J* = 7.9 Hz, 1H), 3.66 (d, *J* = 10.6 Hz, 1H), 2.53 (br s, 1H), 1.95 (dd, *J* = 14.0, 8.2 Hz, 1H), 1.76 (dd, *J* = 14.0, 5.3 Hz, 1H), 1.63 (s, 9H), 1.44 – 1.27 (m, 1H), 0.67 (t, *J* = 7.0 Hz, 6H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 178.65, 149.33, 140.43, 129.28, 128.61, 124.65, 123.47, 115.29, 84.61, 69.43, 55.19, 42.06, 28.30, 25.15, 24.30, 23.05. IR (KBr): 3476, 3129, 3051, 2975, 2946, 2921, 2894, 2872, 1782, 1705, 1609, 1477, 1462, 1396, 1372, 1356, 1315, 1293, 1254, 1239, 1151, 1090, 1073, 1050, 944, 844, 756, 677, 601, 558, 502 cm$^{-1}$. HRMS (ESI): Calcd. for $C_{18}H_{25}NO_4Na$ ([M+Na]$^+$) 342.1676; found 342.1677.

**(*S*)-*tert*-butyl-3-(hydroxymethyl)-2-oxo-3-phenylindoline-1-carboxylate (3s):**[5]




White solid, 32.6 mg, 96% yield, 30% ee; m.p. 108 – 109 ˚C. $[\alpha]^{29}_{D}$ = - 21.6˚ (*c* = 1.09, $CHCl_3$). Enantiomeric excess was determined by chiral HPLC analysis (CHIRALPAK AD-H, 254 nm, 9:1 hexane/iPrOH, 1.0 mL /min): $t_R$ (major) = 6.97 min, $t_R$ (minor) = 8.52 min. $^1$H NMR (300 MHz, $CDCl_3$): δ = 7.97 (d, *J* = 8.1 Hz, 1H), 7.47 – 7.21 (m, 8H), 4.46 (d, *J* = 10.9 Hz, 1H), 4.18 (d, *J* = 10.9 Hz, 1H), 2.07 (br s, 1H), 1.62 (s, 9H). $^{13}$C NMR (75 MHz, $CDCl_3$): δ = 176.14, 149.36, 140.76, 136.70, 129.23, 129.08, 128.92, 128.30, 127.57, 125.16, 124.89, 115.71, 84.85, 67.96, 59.31, 28.30. HRMS (ESI): Calcd. for $C_{20}H_{21}NO_4Na$ ($[M+Na]^+$) 362.1363; found 362.1364.

## 4. References.

1. (a) Y. Hamashima, T. Suzuki, H. Takano, Y. Shimura and M. Sodeoka, *J. Am. Chem. Soc*. 2005, **127***,* 10164; (b) W. G. Rajeswaran, L. A. Cohen, *Tetrahedron* 1998, **54**, 11375; (c) T. Ishimaru, N. Shibata, J. Nagai, S. Nakamura, T. Toru and S. Kanemasa*, J. Am. Chem. Soc*. 2006, **128***,* 16488.

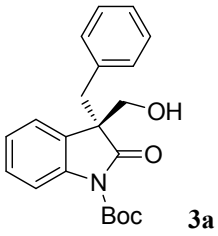
2. X. Gao, J. W. Han and L. M. Wang, *Org. Lett.* 2015, **17**, 4596.

3. (a) N. J. Lajkiewicz, S. P. Roche, B. Gerard and J. A. Porco, Jr. *J. Am. Chem. Soc*. 2012, **134***,* 13108; (b) A. Cuenca, M. Medio-Simon, G. A. Aguilar, D. Weibel, A. K. Beck and D. Seebach, *Helv. Chim.Acta.* 2000, **83**, 3153; (c) B. Gerard, G. Jones II and J. A. Porco Jr., *J. Am. Chem. Soc.* 2004, **126**, 13620.

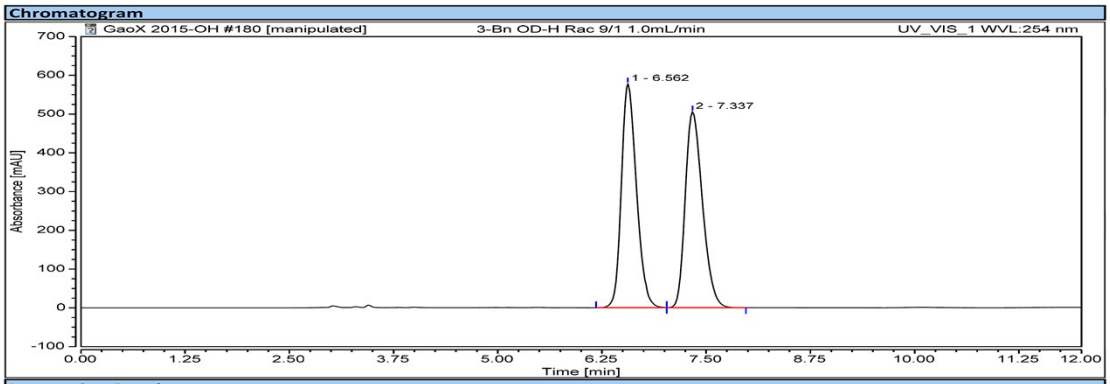
4. L. W. Zou, X. Z. Bao, Y. Y. Ma, Y. M. Song, J. P. Qu and B. M. Wang, *Chem. Commun*. 2014, 5760.

5. X. L. Liu, Y. H. Liao, Z. J. Wu, L. F. Cun, X. M. Zhang and W. C. Yuan, *J. Org. Chem.* 2010, **75**, 4872.

**5. HPLC Spectra for 3 (a-s).**

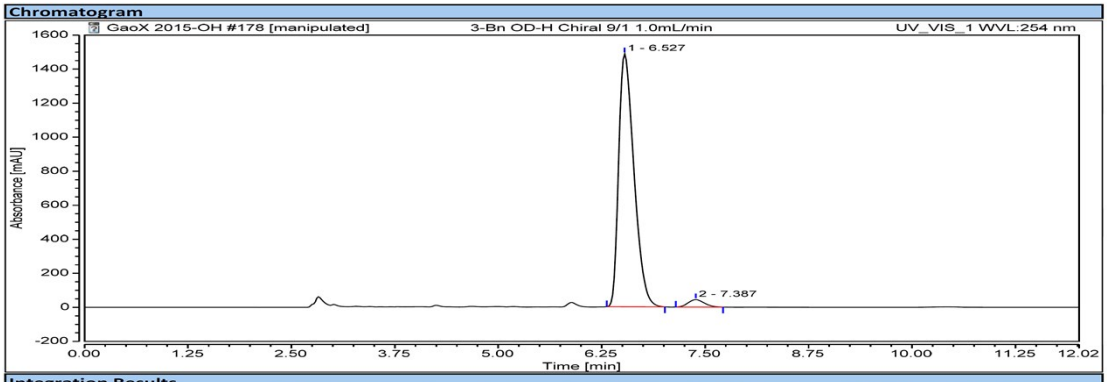



**3a**



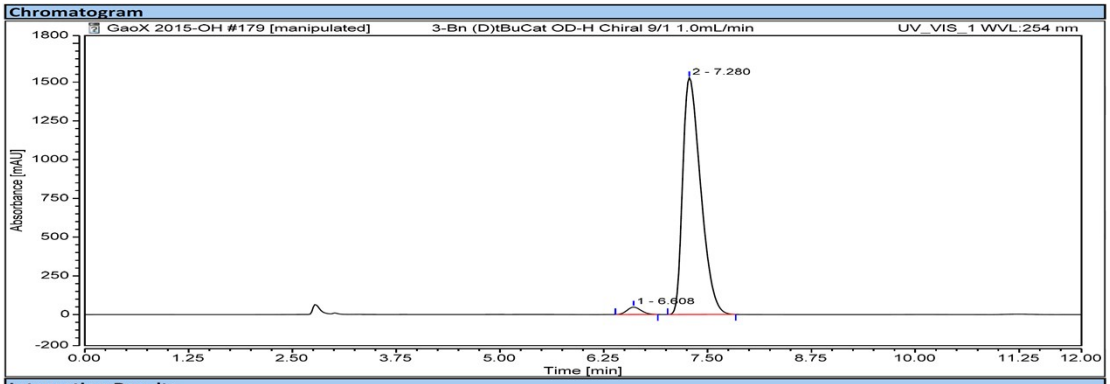

**Integration Results**

| No. | Peak Name | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | Amount mg/l |
|---|---|---|---|---|---|---|---|
| n.a. | toluene | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 1 | | 6.562 | 121.369 | 577.717 | 50.03 | 53.33 | n.a. |
| 2 | | 7.337 | 121.239 | 505.622 | 49.97 | 46.67 | n.a. |
| **Total:** | | | **242.607** | **1083.339** | **100.00** | **100.00** | |



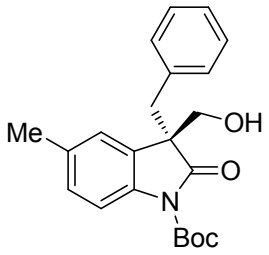

**Integration Results**

| No. | Peak Name | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | Amount mg/l |
|---|---|---|---|---|---|---|---|
| n.a. | toluene | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 1 | | 6.527 | 318.764 | 1487.125 | 97.01 | 97.16 | n.a. |
| 2 | | 7.387 | 9.810 | 43.424 | 2.99 | 2.84 | n.a. |
| **Total:** | | | **328.574** | **1530.549** | **100.00** | **100.00** | |



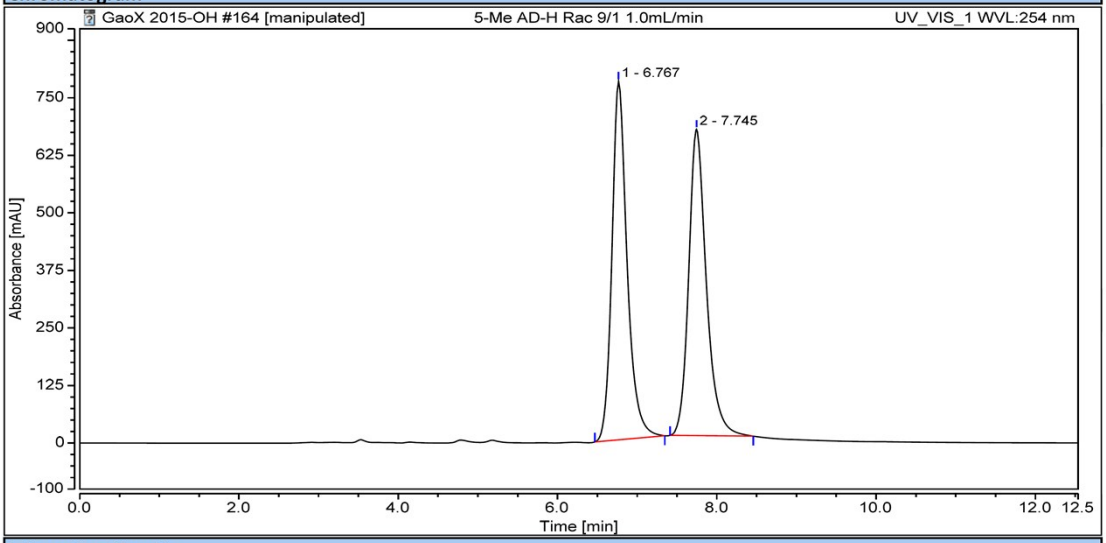

**Integration Results**

| No. | Peak Name | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | Amount mg/l |
|---|---|---|---|---|---|---|---|
| n.a. | toluene | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 1 | | 6.608 | 9.368 | 47.640 | 2.39 | 3.02 | n.a. |
| 2 | | 7.280 | 383.062 | 1528.352 | 97.61 | 96.98 | n.a. |
| **Total:** | | | **392.430** | **1575.992** | **100.00** | **100.00** | |




**3b**

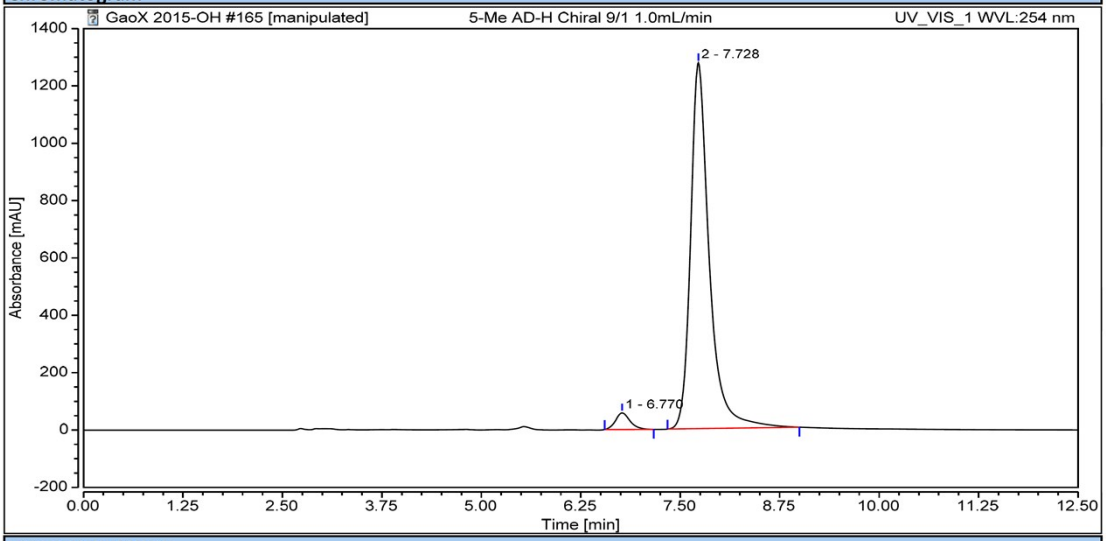
**Chromatogram**




**Integration Results**

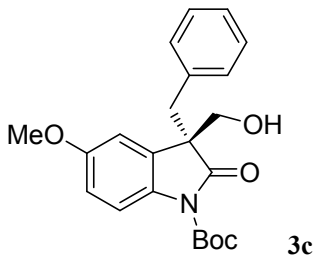
| No. | Peak Name | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | Amount mg/l |
|---|---|---|---|---|---|---|---|
| n.a. | toluene | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 1 | | 6.767 | 171.457 | 778.966 | 50.09 | 53.92 | n.a. |
| 2 | | 7.745 | 170.826 | 665.670 | 49.91 | 46.08 | n.a. |
| **Total:** | | | **342.283** | **1444.635** | **100.00** | **100.00** | |

**Chromatogram**



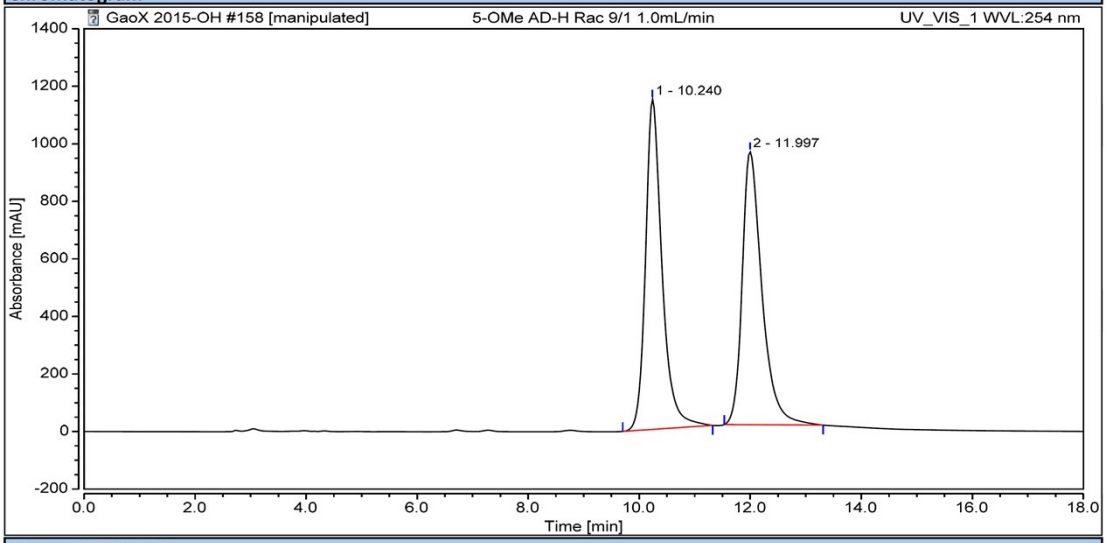

**Integration Results**

| No. | Peak Name | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | Amount mg/l |
|---|---|---|---|---|---|---|---|
| n.a. | toluene | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 1 | | 6.770 | 12.286 | 57.779 | 3.41 | 4.33 | n.a. |
| 2 | | 7.728 | 347.527 | 1276.253 | 96.59 | 95.67 | n.a. |
| **Total:** | | | **359.812** | **1334.032** | **100.00** | **100.00** | |




**3c**

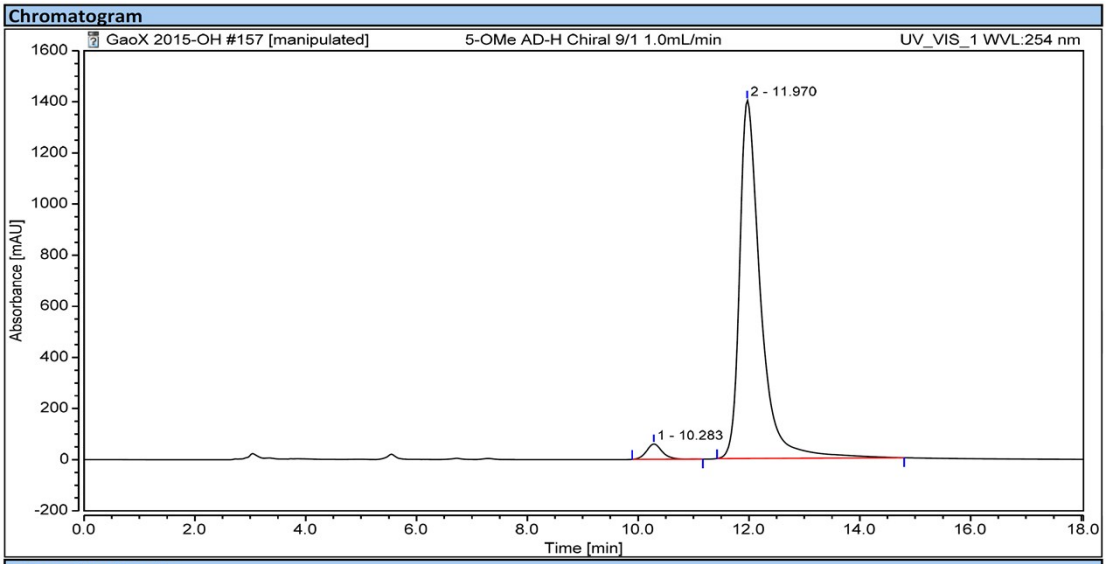
**Chromatogram**




**Integration Results**

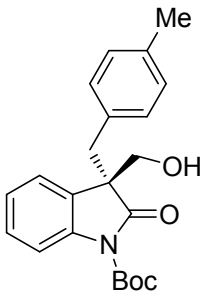
| No. | Peak Name | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | Amount mg/l |
|---|---|---|---|---|---|---|---|
| n.a. | toluene | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 1 | | 10.240 | 396.242 | 1148.056 | 50.31 | 54.75 | n.a. |
| 2 | | 11.997 | 391.423 | 949.005 | 49.69 | 45.25 | n.a. |
| **Total:** | | | **787.665** | **2097.061** | **100.00** | **100.00** | |

**Chromatogram**



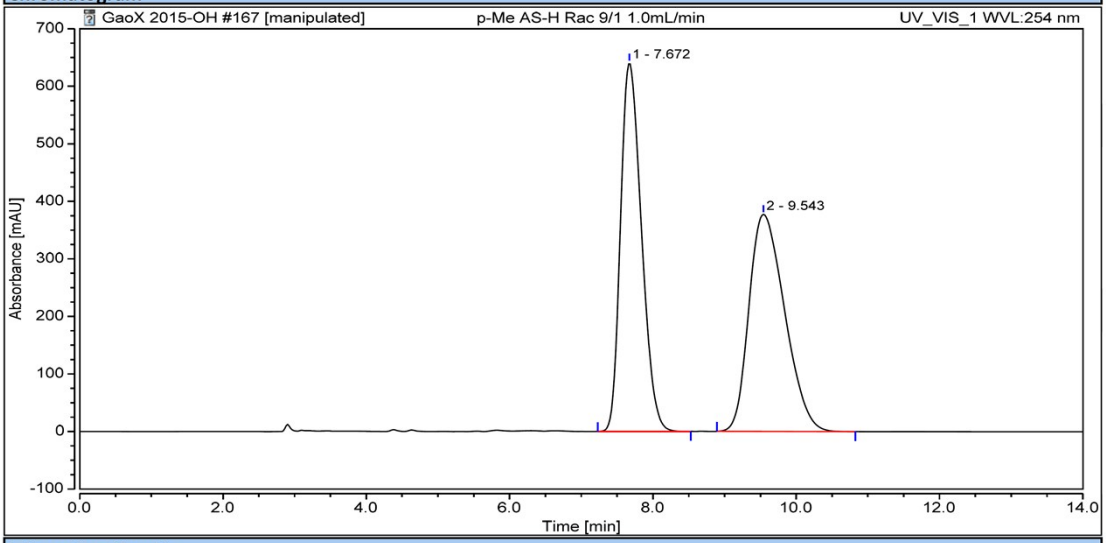

**Integration Results**

| No. | Peak Name | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | Amount mg/l |
|---|---|---|---|---|---|---|---|
| n.a. | toluene | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 1 | | 10.283 | 19.771 | 59.961 | 3.13 | 4.10 | n.a. |
| 2 | | 11.970 | 611.427 | 1401.549 | 96.87 | 95.90 | n.a. |
| **Total:** | | | **631.198** | **1461.509** | **100.00** | **100.00** | |




**3d**

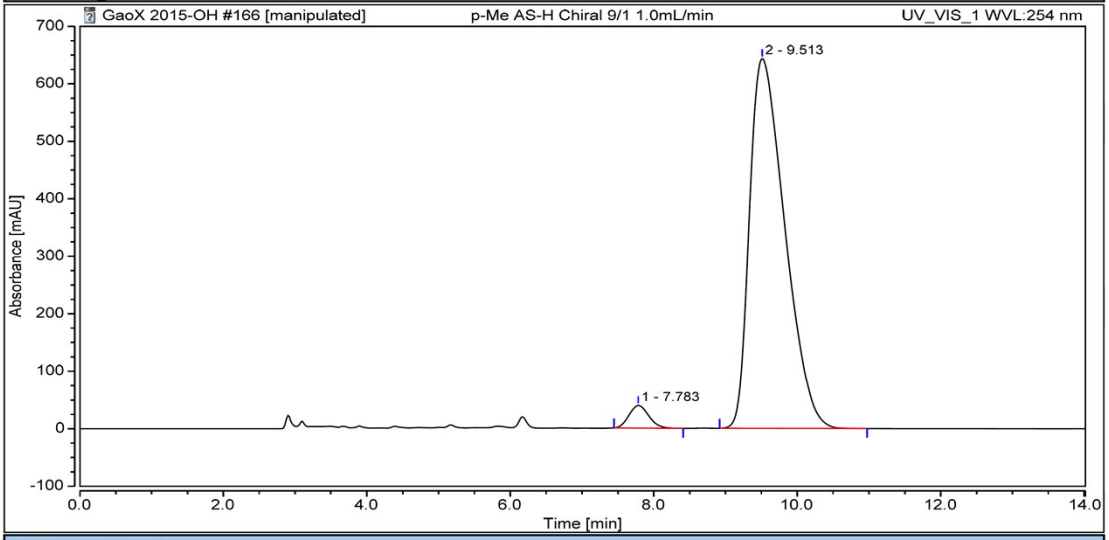
**Chromatogram**




**Integration Results**

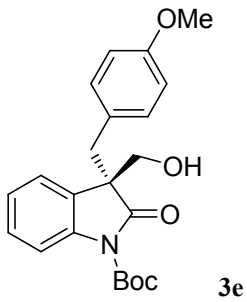
| No. | Peak Name | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | Amount mg/l |
|---|---|---|---|---|---|---|---|
| n.a. | toluene | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 1 | | 7.672 | 216.418 | 640.459 | 49.85 | 62.94 | n.a. |
| 2 | | 9.543 | 217.750 | 377.190 | 50.15 | 37.06 | n.a. |
| **Total:** | | | **434.169** | **1017.649** | **100.00** | **100.00** | |

**Chromatogram**



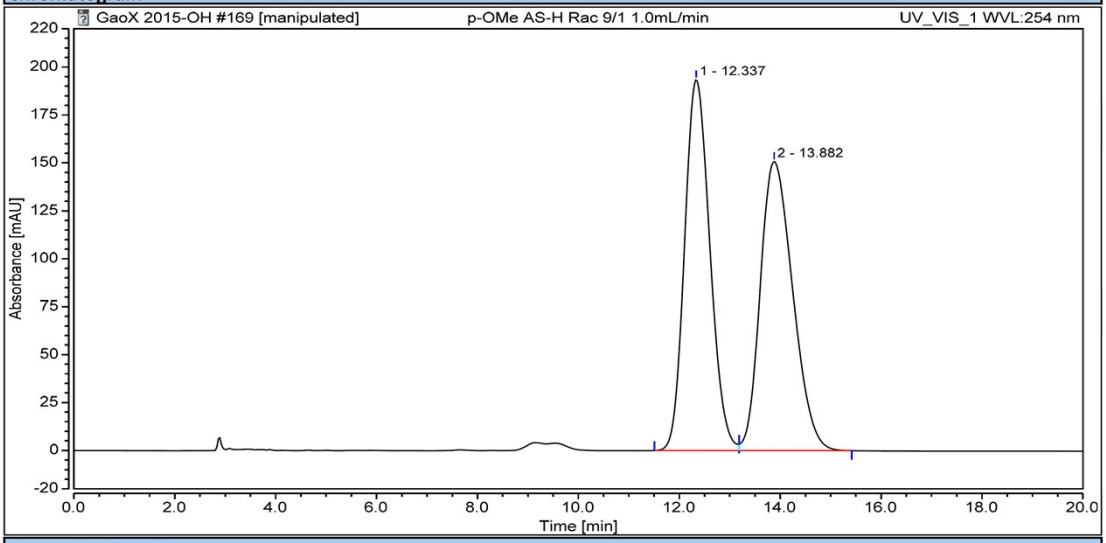

**Integration Results**

| No. | Peak Name | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | Amount mg/l |
|---|---|---|---|---|---|---|---|
| n.a. | toluene | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 1 | | 7.783 | 12.540 | 39.315 | 3.31 | 5.76 | n.a. |
| 2 | | 9.513 | 366.223 | 643.270 | 96.69 | 94.24 | n.a. |
| **Total:** | | | **378.764** | **682.585** | **100.00** | **100.00** | |




**3e**

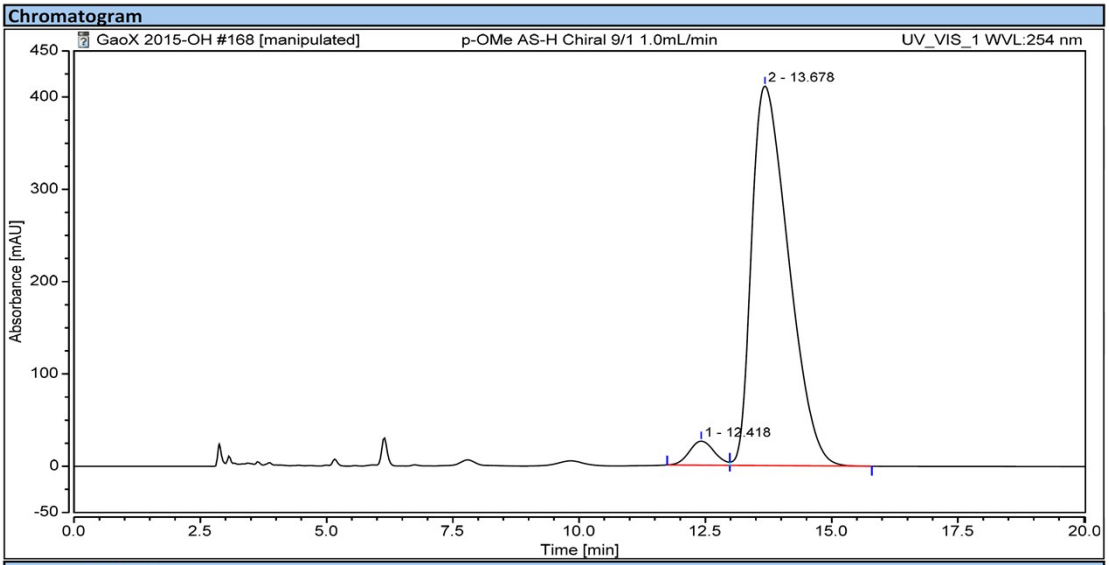
**Chromatogram**




**Integration Results**

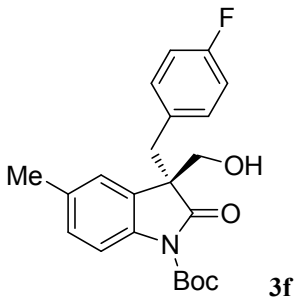
| No. | Peak Name | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | Amount mg/l |
|---|---|---|---|---|---|---|---|
| n.a. | toluene | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 1 | | 12.337 | 112.387 | 193.442 | 49.97 | 56.19 | n.a. |
| 2 | | 13.882 | 112.517 | 150.799 | 50.03 | 43.81 | n.a. |
| **Total:** | | | **224.904** | **344.242** | **100.00** | **100.00** | |

**Chromatogram**



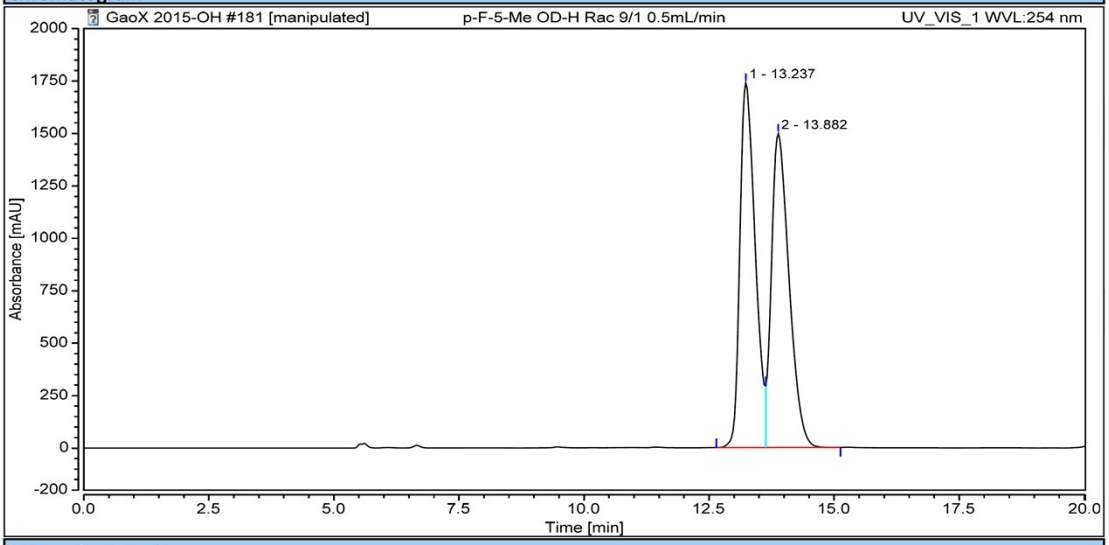

**Integration Results**

| No. | Peak Name | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | Amount mg/l |
|---|---|---|---|---|---|---|---|
| n.a. | toluene | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 1 | | 12.418 | 14.995 | 26.121 | 4.13 | 5.97 | n.a. |
| 2 | | 13.678 | 347.949 | 411.138 | 95.87 | 94.03 | n.a. |
| **Total:** | | | **362.944** | **437.259** | **100.00** | **100.00** | |




**3f**

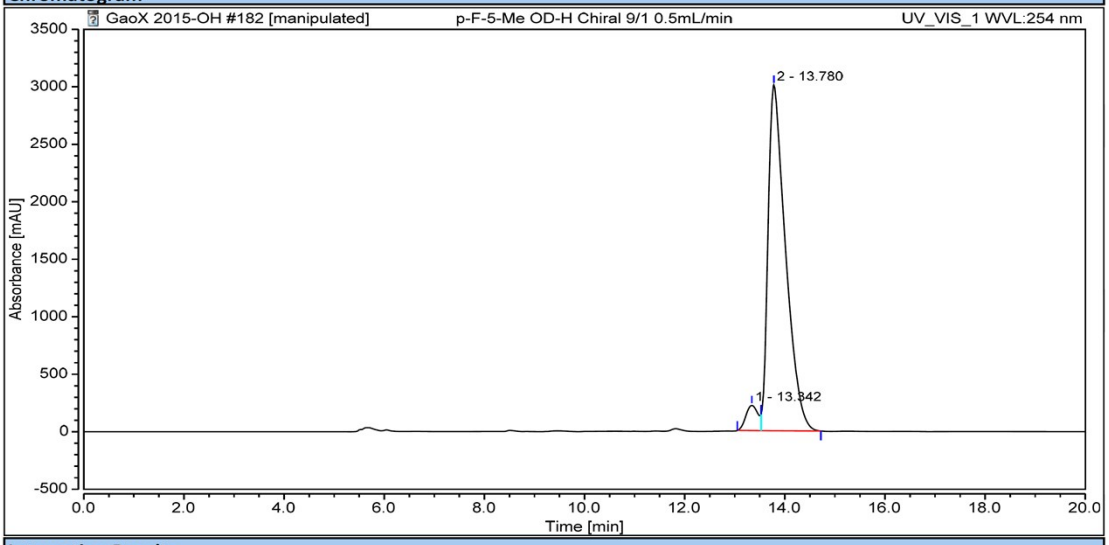
**Chromatogram**




**Integration Results**

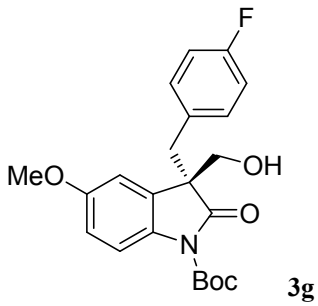
| No. | Peak Name | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | Amount mg/l |
|---|---|---|---|---|---|---|---|
| n.a. | toluene | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 1 | | 13.237 | 615.506 | 1739.032 | 50.14 | 53.75 | n.a. |
| 2 | | 13.882 | 612.071 | 1496.405 | 49.86 | 46.25 | n.a. |
| **Total:** | | | **1227.576** | **3235.437** | **100.00** | **100.00** | |

**Chromatogram**



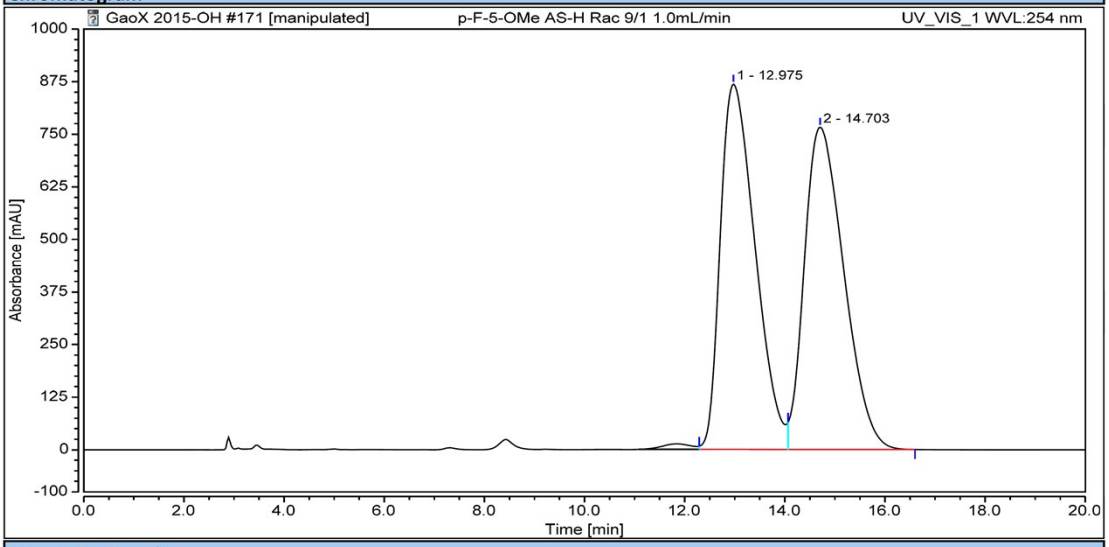

**Integration Results**

| No. | Peak Name | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | Amount mg/l |
|---|---|---|---|---|---|---|---|
| n.a. | toluene | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 1 | | 13.342 | 62.108 | 219.246 | 4.86 | 6.79 | n.a. |
| 2 | | 13.780 | 1215.474 | 3008.503 | 95.14 | 93.21 | n.a. |
| **Total:** | | | **1277.582** | **3227.749** | **100.00** | **100.00** | |




**3g**

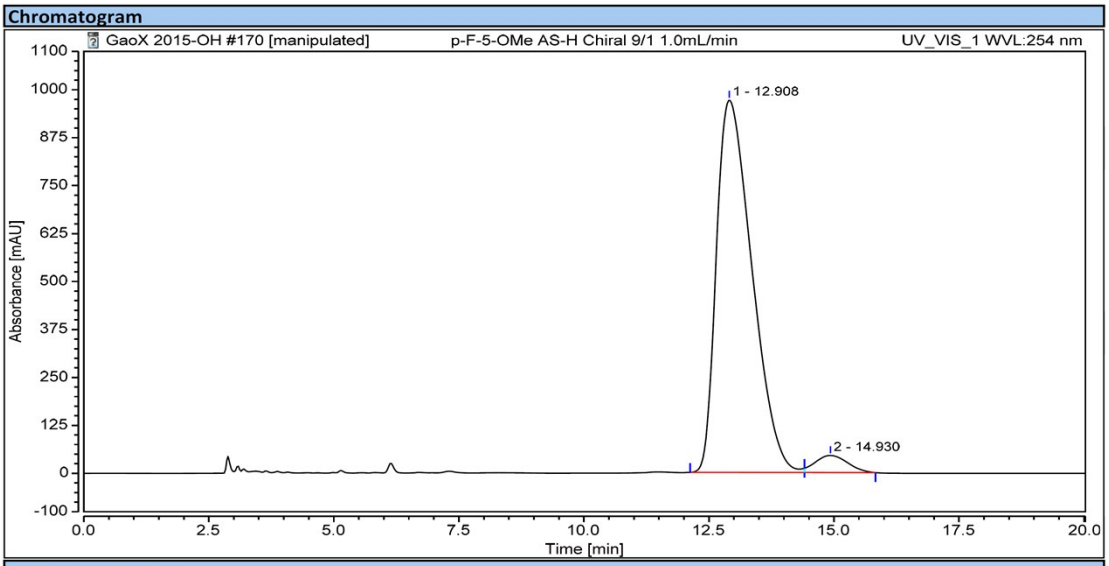
**Chromatogram**




**Integration Results**

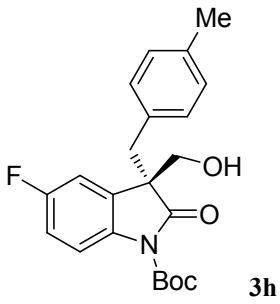
| No. | Peak Name | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | Amount mg/l |
|---|---|---|---|---|---|---|---|
| n.a. | toluene | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 1 | | 12.975 | 699.015 | 867.960 | 49.97 | 53.13 | n.a. |
| 2 | | 14.703 | 699.856 | 765.834 | 50.03 | 46.87 | n.a. |
| **Total:** | | | **1398.871** | **1633.794** | **100.00** | **100.00** | |

**Chromatogram**



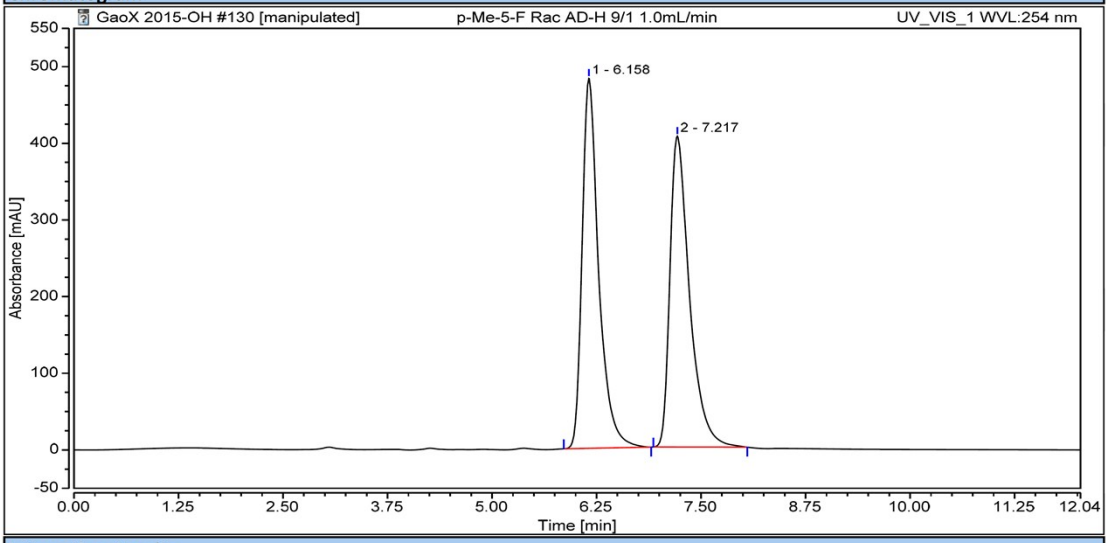

**Integration Results**

| No. | Peak Name | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | Amount mg/l |
|---|---|---|---|---|---|---|---|
| n.a. | toluene | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 1 | | 12.908 | 798.348 | 970.658 | 95.97 | 95.60 | n.a. |
| 2 | | 14.930 | 33.513 | 44.668 | 4.03 | 4.40 | n.a. |
| **Total:** | | | **831.861** | **1015.327** | **100.00** | **100.00** | |




**3h**

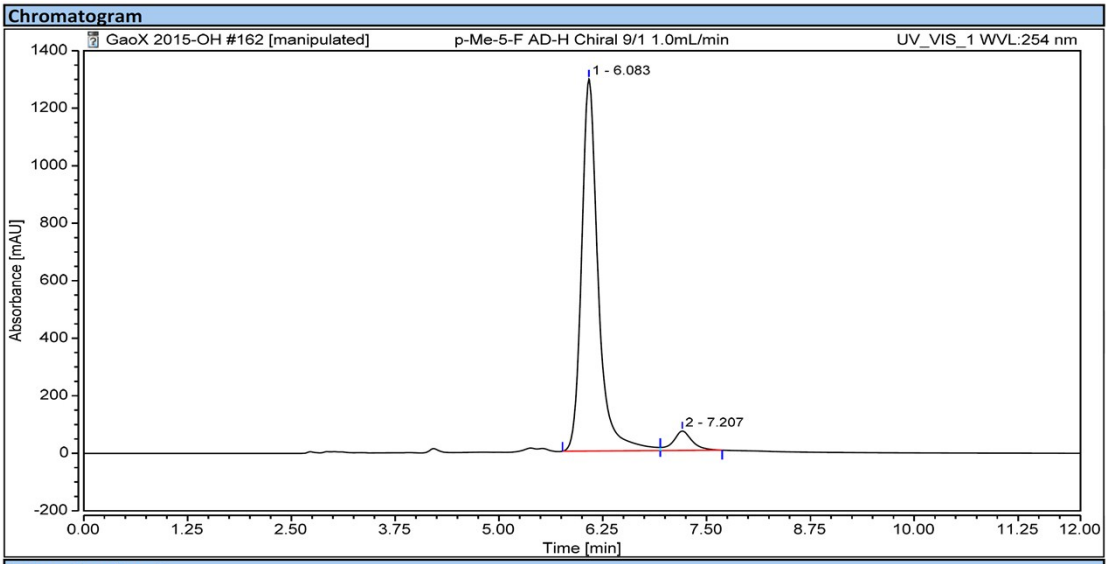
**Chromatogram**




**Integration Results**

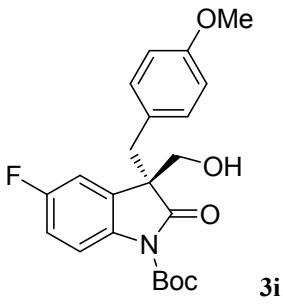
| No. | Peak Name | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | Amount mg/l |
|---|---|---|---|---|---|---|---|
| n.a. | toluene | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 1 | | 6.158 | 110.839 | 482.612 | 50.17 | 54.34 | n.a. |
| 2 | | 7.217 | 110.071 | 405.593 | 49.83 | 45.66 | n.a. |
| **Total:** | | | **220.910** | **888.205** | **100.00** | **100.00** | |

**Chromatogram**



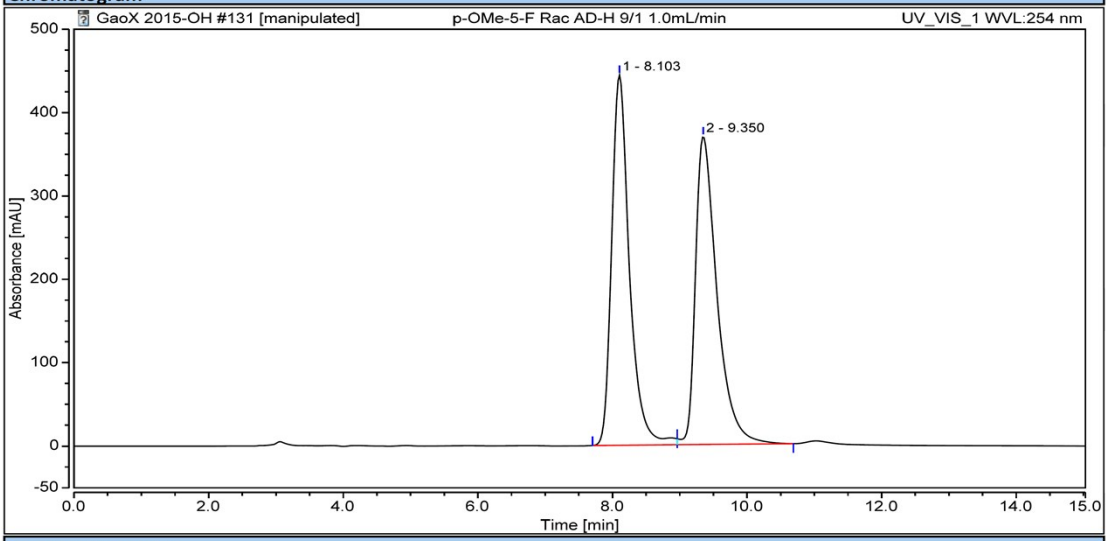

**Integration Results**

| No. | Peak Name | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | Amount mg/l |
|---|---|---|---|---|---|---|---|
| n.a. | toluene | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 1 | | 6.083 | 299.913 | 1293.785 | 94.40 | 95.06 | n.a. |
| 2 | | 7.207 | 17.794 | 67.305 | 5.60 | 4.94 | n.a. |
| **Total:** | | | **317.707** | **1361.090** | **100.00** | **100.00** | |




**3i**

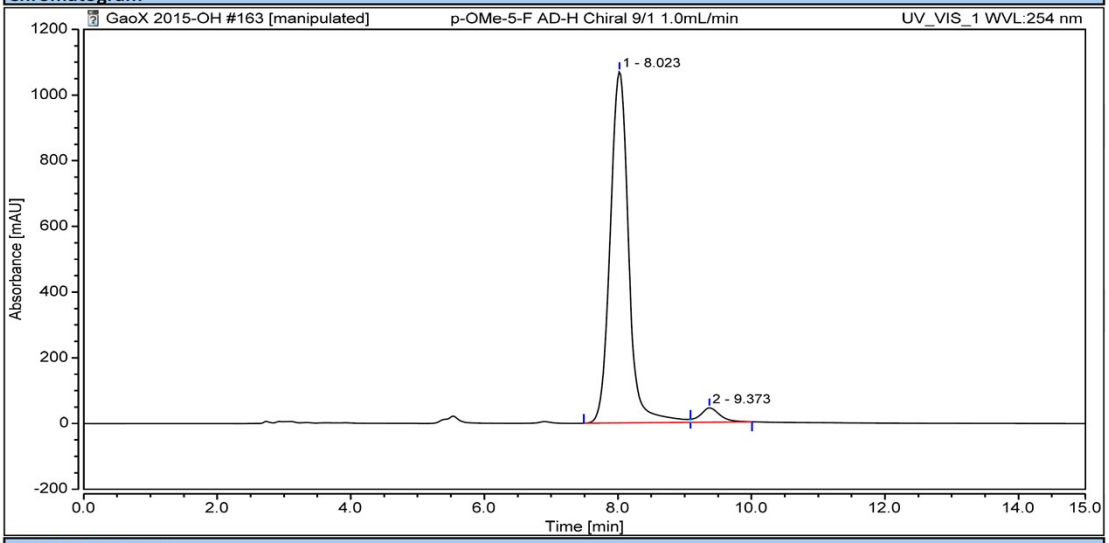
**Chromatogram**




**Integration Results**

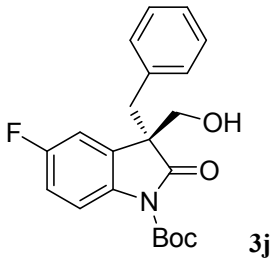
| No. | Peak Name | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | Amount mg/l |
|---|---|---|---|---|---|---|---|
| n.a. | toluene | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 1 | | 8.103 | 136.042 | 444.196 | 49.85 | 54.59 | n.a. |
| 2 | | 9.350 | 136.864 | 369.490 | 50.15 | 45.41 | n.a. |
| **Total:** | | | **272.906** | **813.686** | **100.00** | **100.00** | |

**Chromatogram**



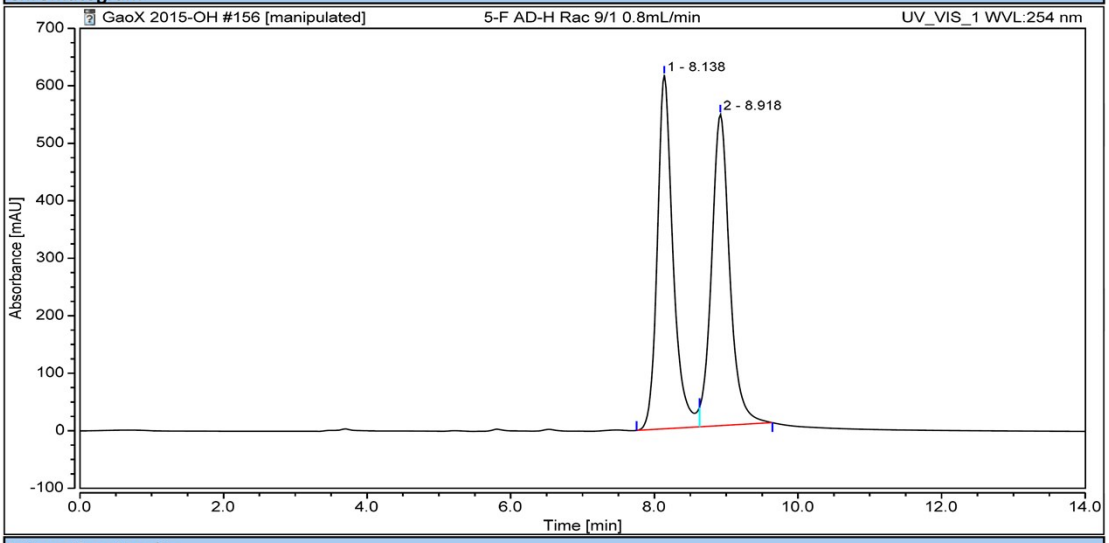

**Integration Results**

| No. | Peak Name | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | Amount mg/l |
|---|---|---|---|---|---|---|---|
| n.a. | toluene | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 1 | | 8.023 | 341.635 | 1069.751 | 95.80 | 96.06 | n.a. |
| 2 | | 9.373 | 14.984 | 43.919 | 4.20 | 3.94 | n.a. |
| **Total:** | | | **356.619** | **1113.670** | **100.00** | **100.00** | |




**3j**

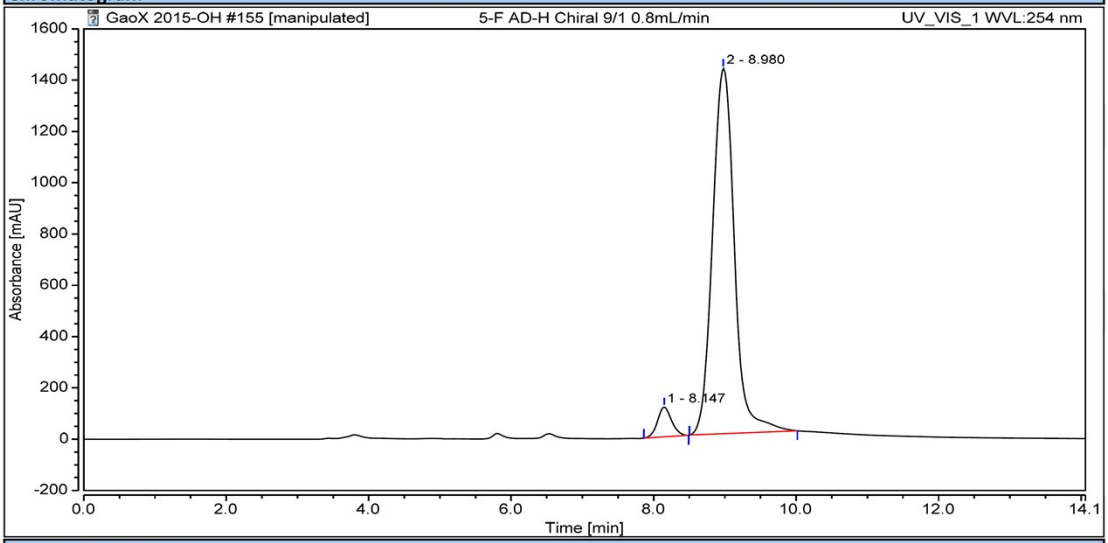
**Chromatogram**




**Integration Results**

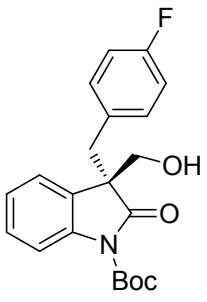
| No. | Peak Name | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | Amount mg/l |
|---|---|---|---|---|---|---|---|
| n.a. | toluene | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 1 | | 8.138 | 156.576 | 614.654 | 49.74 | 53.16 | n.a. |
| 2 | | 8.918 | 158.223 | 541.678 | 50.26 | 46.84 | n.a. |
| **Total:** | | | **314.799** | **1156.332** | **100.00** | **100.00** | |

**Chromatogram**



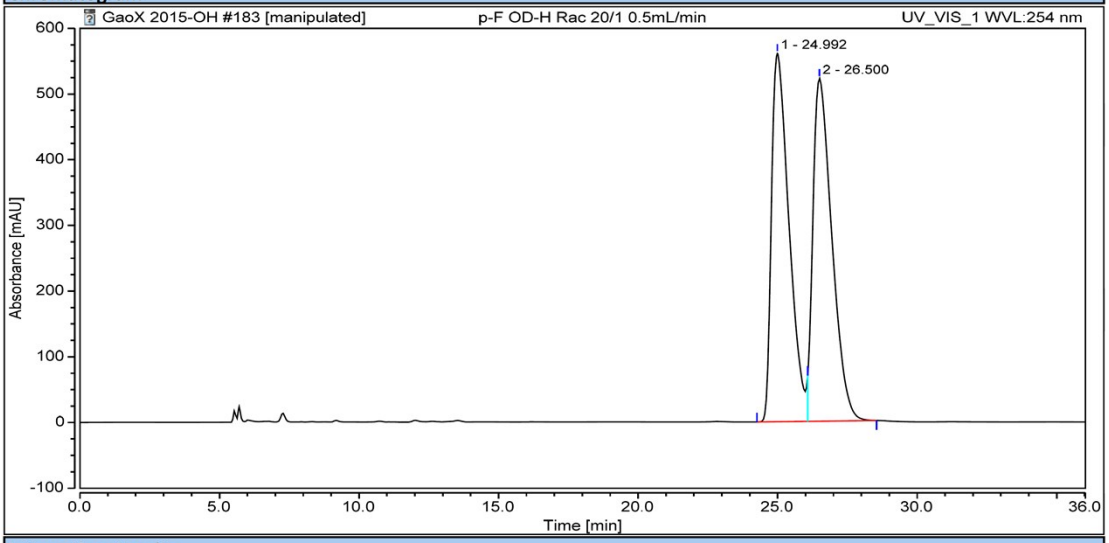

**Integration Results**

| No. | Peak Name | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | Amount mg/l |
|---|---|---|---|---|---|---|---|
| n.a. | toluene | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 1 | | 8.147 | 26.463 | 115.987 | 4.97 | 7.53 | n.a. |
| 2 | | 8.980 | 505.609 | 1424.961 | 95.03 | 92.47 | n.a. |
| **Total:** | | | **532.072** | **1540.948** | **100.00** | **100.00** | |




**3k**

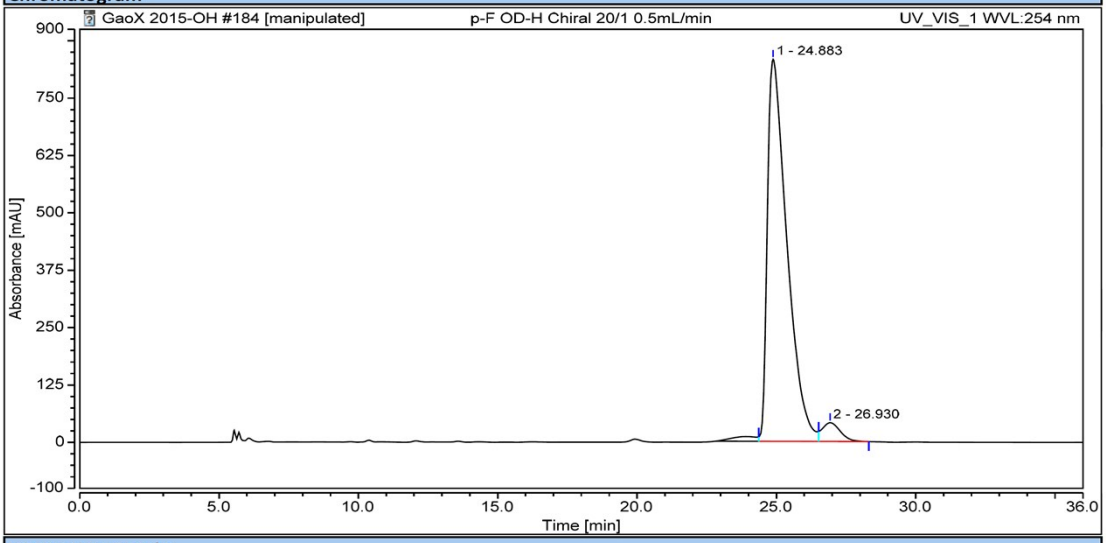
**Chromatogram**




**Integration Results**

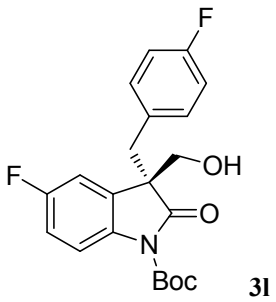
| No. | Peak Name | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | Amount mg/l |
|---|---|---|---|---|---|---|---|
| n.a. | toluene | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 1 | | 24.992 | 409.198 | 560.544 | 49.92 | 51.79 | n.a. |
| 2 | | 26.500 | 410.475 | 521.776 | 50.08 | 48.21 | n.a. |
| **Total:** | | | **819.674** | **1082.320** | **100.00** | **100.00** | |

**Chromatogram**



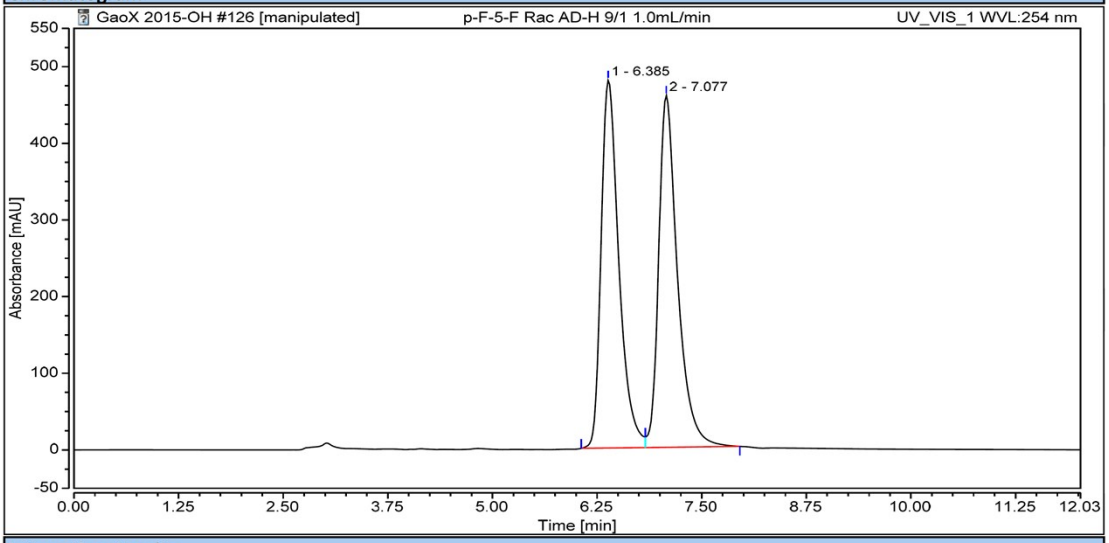

**Integration Results**

| No. | Peak Name | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | Amount mg/l |
|---|---|---|---|---|---|---|---|
| n.a. | toluene | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 1 | | 24.883 | 677.293 | 832.163 | 95.66 | 95.31 | n.a. |
| 2 | | 26.930 | 30.752 | 40.944 | 4.34 | 4.69 | n.a. |
| **Total:** | | | **708.045** | **873.107** | **100.00** | **100.00** | |




**3l**

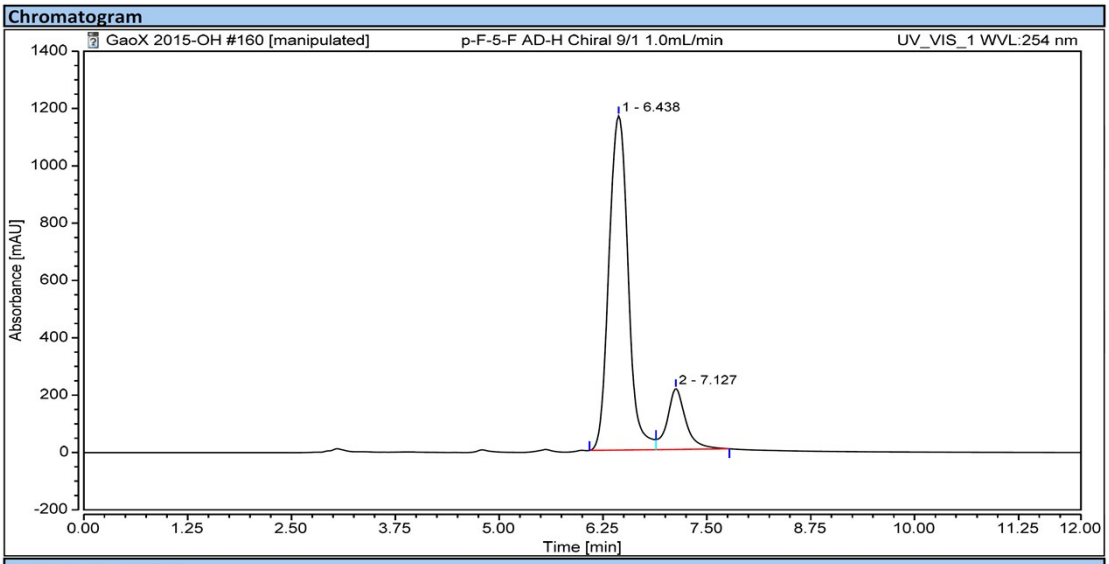
**Chromatogram**




**Integration Results**

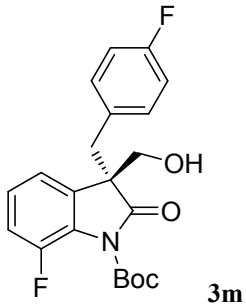
| No. | Peak Name | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | Amount mg/l |
|---|---|---|---|---|---|---|---|
| n.a. | toluene | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 1 | | 6.385 | 118.050 | 480.191 | 49.55 | 51.11 | n.a. |
| 2 | | 7.077 | 120.171 | 459.315 | 50.45 | 48.89 | n.a. |
| **Total:** | | | **238.221** | **939.506** | **100.00** | **100.00** | |

**Chromatogram**



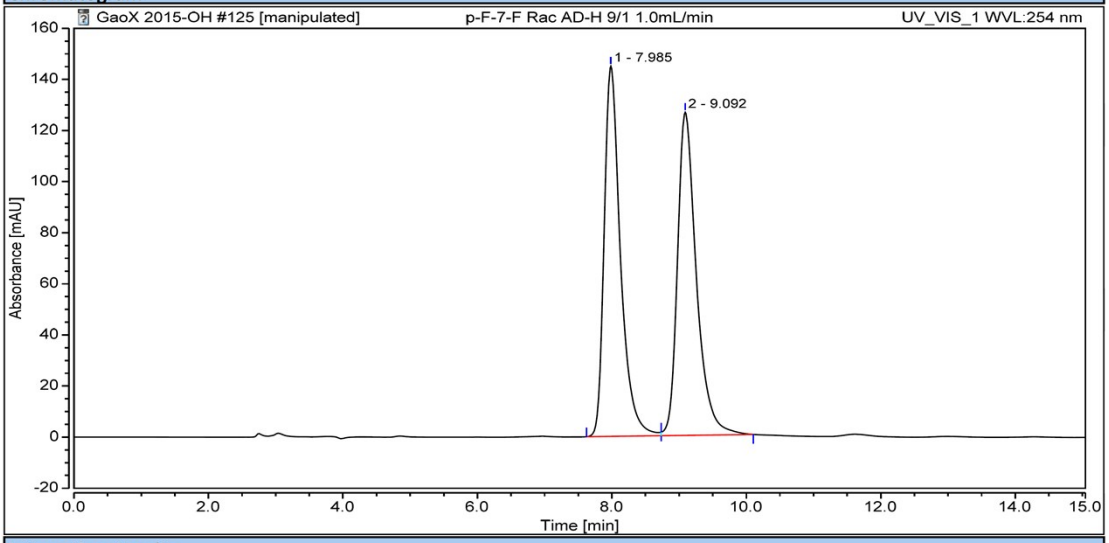

**Integration Results**

| No. | Peak Name | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | Amount mg/l |
|---|---|---|---|---|---|---|---|
| n.a. | toluene | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 1 | | 6.438 | 312.029 | 1166.270 | 85.06 | 84.63 | n.a. |
| 2 | | 7.127 | 54.792 | 211.797 | 14.94 | 15.37 | n.a. |
| **Total:** | | | **366.821** | **1378.066** | **100.00** | **100.00** | |




**3m**

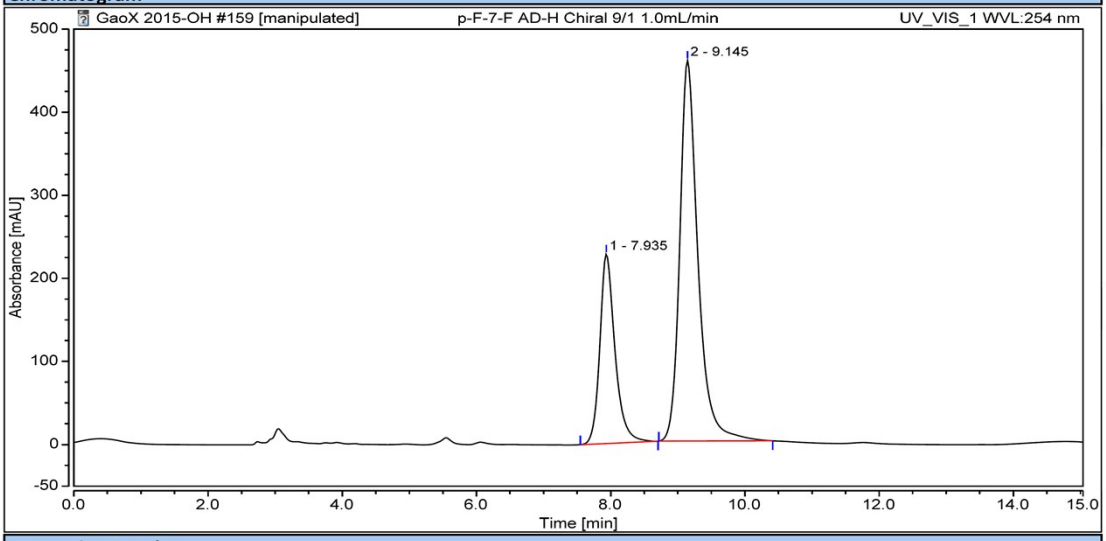
**Chromatogram**




**Integration Results**

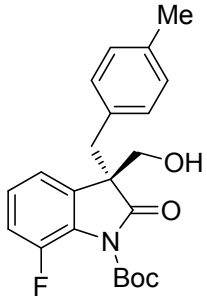
| No. | Peak Name | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | Amount mg/l |
|---|---|---|---|---|---|---|---|
| n.a. | toluene | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 1 | | 7.985 | 40.718 | 144.884 | 49.70 | 53.40 | n.a. |
| 2 | | 9.092 | 41.203 | 126.417 | 50.30 | 46.60 | n.a. |
| **Total:** | | | **81.921** | **271.301** | **100.00** | **100.00** | |

**Chromatogram**



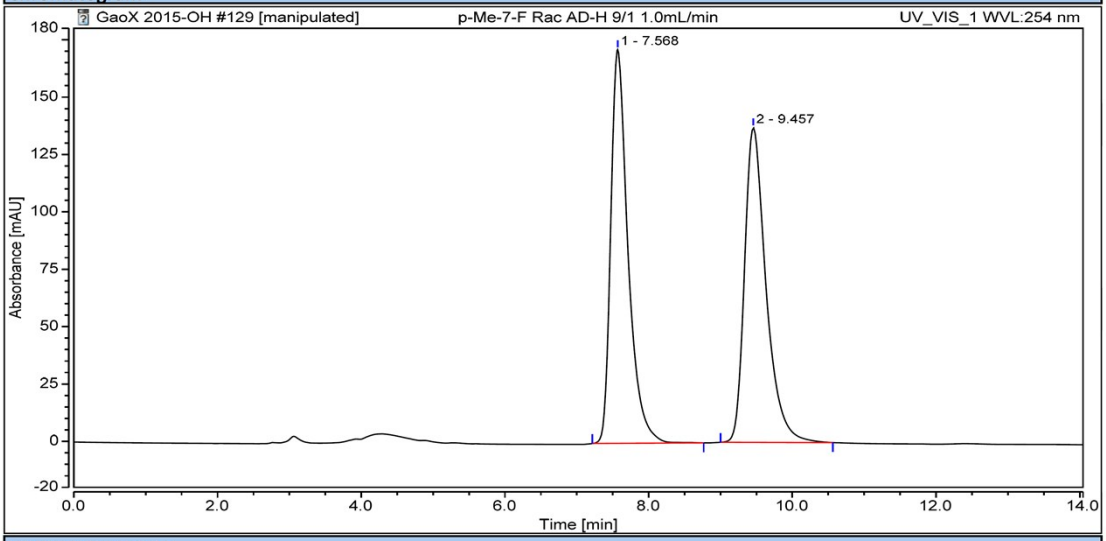

**Integration Results**

| No. | Peak Name | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | Amount mg/l |
|---|---|---|---|---|---|---|---|
| n.a. | toluene | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 1 | | 7.935 | 59.627 | 227.875 | 29.28 | 33.22 | n.a. |
| 2 | | 9.145 | 143.986 | 458.171 | 70.72 | 66.78 | n.a. |
| **Total:** | | | **203.613** | **686.047** | **100.00** | **100.00** | |




**3n**

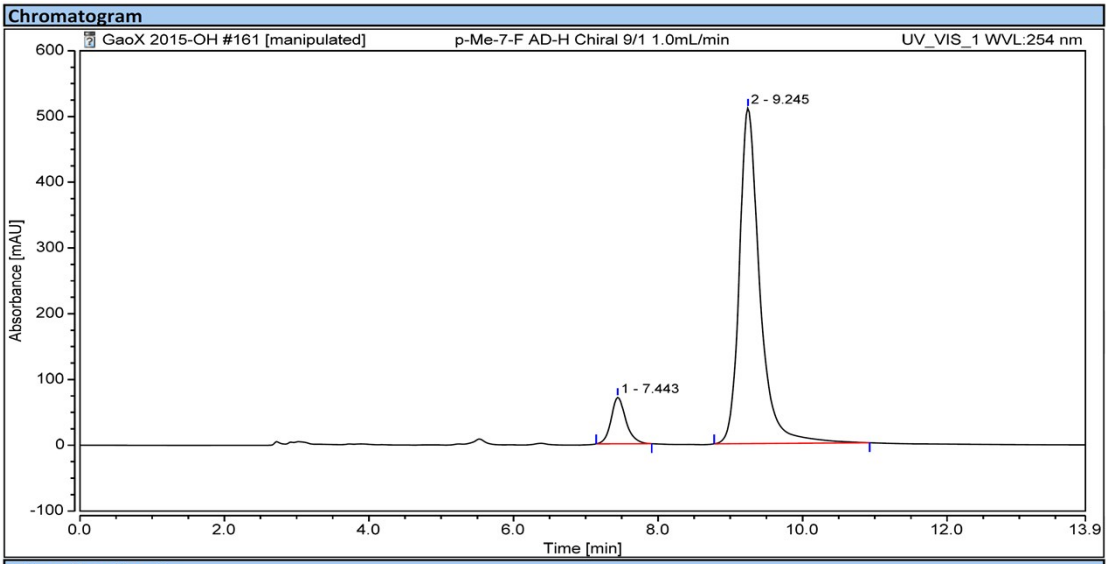
**Chromatogram**




**Integration Results**

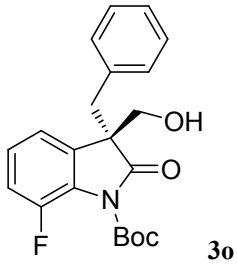
| No. | Peak Name | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | Amount mg/l |
|---|---|---|---|---|---|---|---|
| n.a. | toluene | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 1 | | 7.568 | 47.785 | 171.621 | 50.09 | 55.60 | n.a. |
| 2 | | 9.457 | 47.615 | 137.077 | 49.91 | 44.40 | n.a. |
| **Total:** | | | **95.400** | **308.697** | **100.00** | **100.00** | |

**Chromatogram**



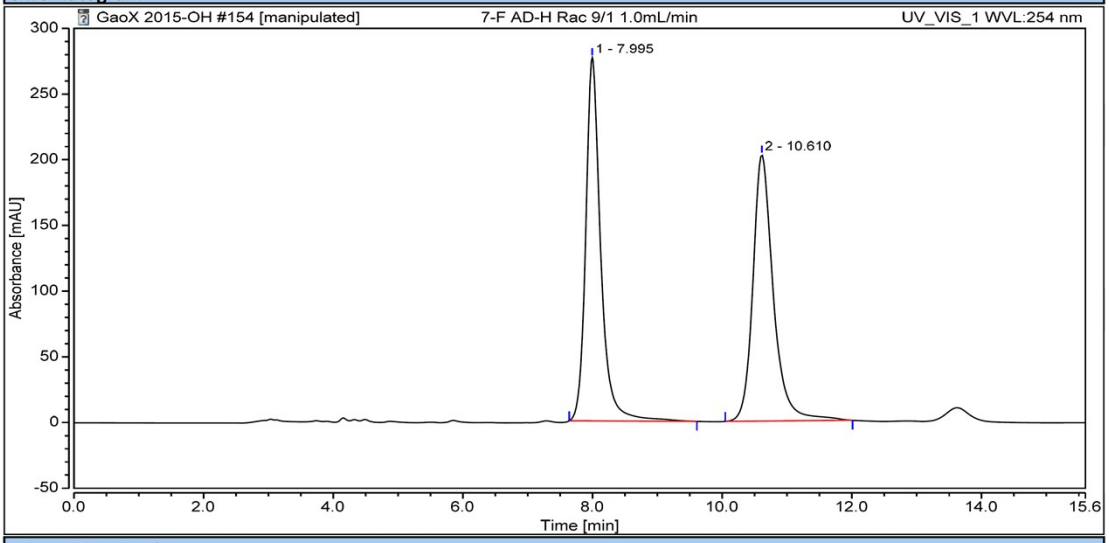

**Integration Results**

| No. | Peak Name | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | Amount mg/l |
|---|---|---|---|---|---|---|---|
| n.a. | toluene | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 1 | | 7.443 | 16.831 | 70.581 | 9.14 | 12.15 | n.a. |
| 2 | | 9.245 | 167.338 | 510.204 | 90.86 | 87.85 | n.a. |
| **Total:** | | | **184.169** | **580.785** | **100.00** | **100.00** | |




**3o**

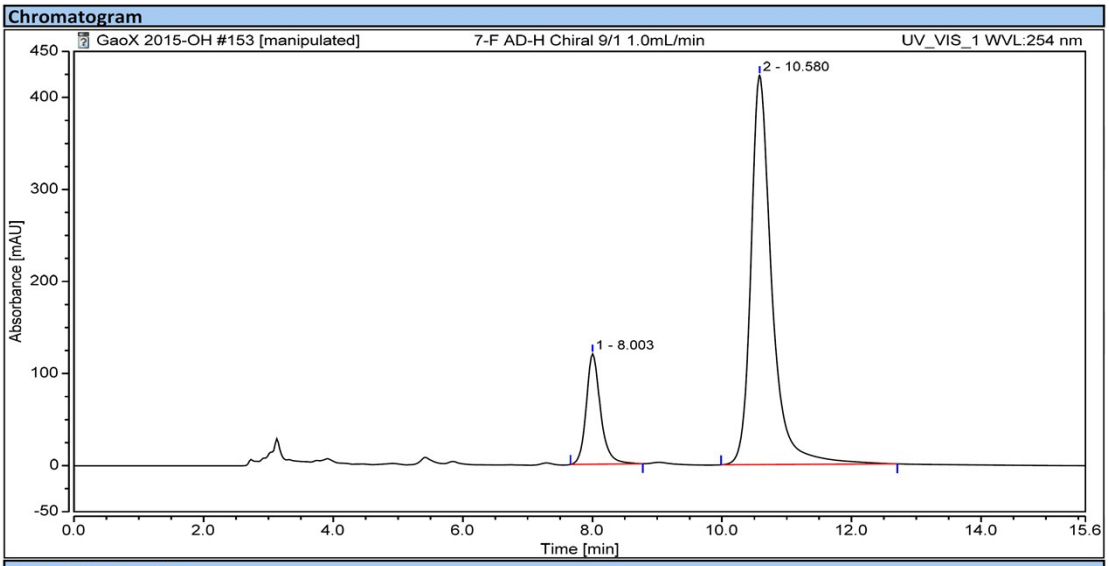
**Chromatogram**




**Integration Results**

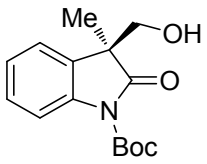
| No. | Peak Name | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | Amount mg/l |
|---|---|---|---|---|---|---|---|
| n.a. | toluene | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 1 | | 7.995 | 74.105 | 276.548 | 49.97 | 57.70 | n.a. |
| 2 | | 10.610 | 74.195 | 202.710 | 50.03 | 42.30 | n.a. |
| **Total:** | | | **148.300** | **479.258** | **100.00** | **100.00** | |

**Chromatogram**



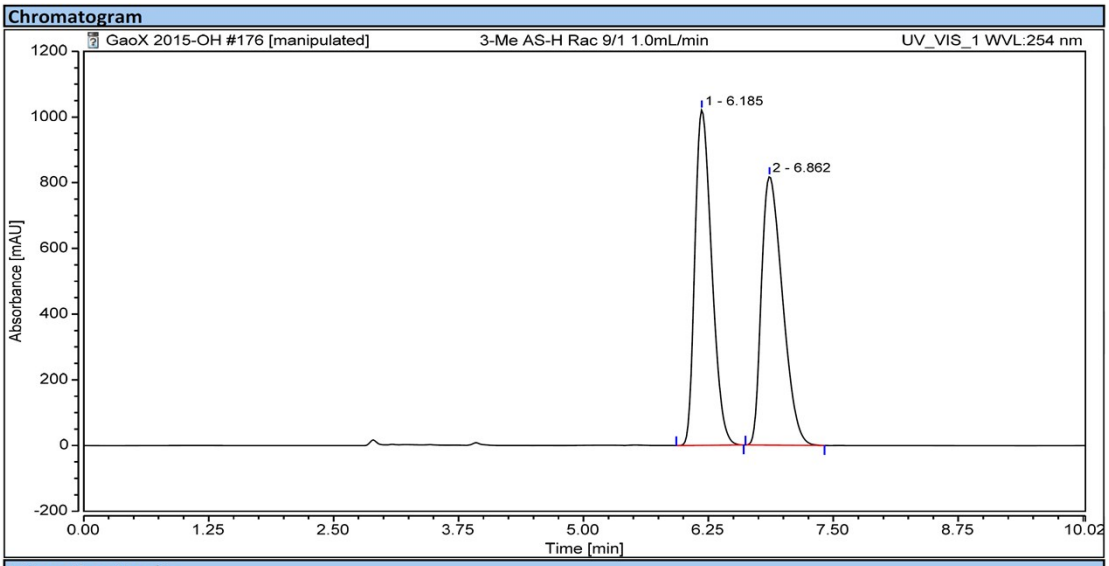

**Integration Results**

| No. | Peak Name | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | Amount mg/l |
|---|---|---|---|---|---|---|---|
| n.a. | toluene | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 1 | | 8.003 | 30.680 | 119.902 | 16.23 | 22.09 | n.a. |
| 2 | | 10.580 | 158.374 | 422.938 | 83.77 | 77.91 | n.a. |
| **Total:** | | | **189.054** | **542.840** | **100.00** | **100.00** | |




**3p**

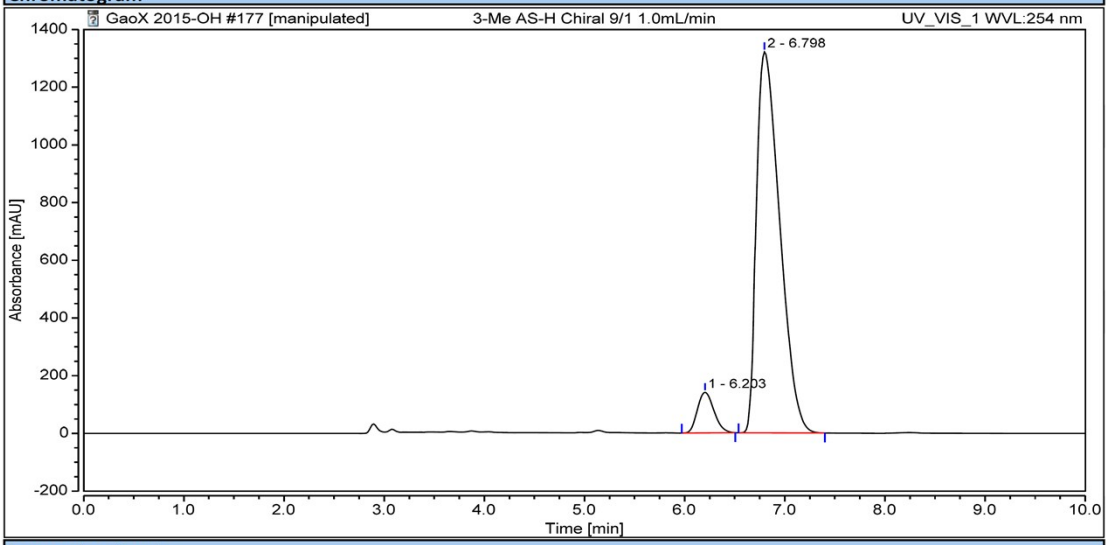
**Chromatogram**




**Integration Results**

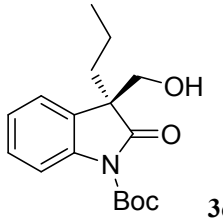
| No. | Peak Name | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | Amount mg/l |
|---|---|---|---|---|---|---|---|
| n.a. | toluene | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 1 | | 6.185 | 199.524 | 1021.405 | 49.88 | 55.53 | n.a. |
| 2 | | 6.862 | 200.444 | 817.924 | 50.12 | 44.47 | n.a. |
| **Total:** | | | **399.967** | **1839.329** | **100.00** | **100.00** | |

**Chromatogram**



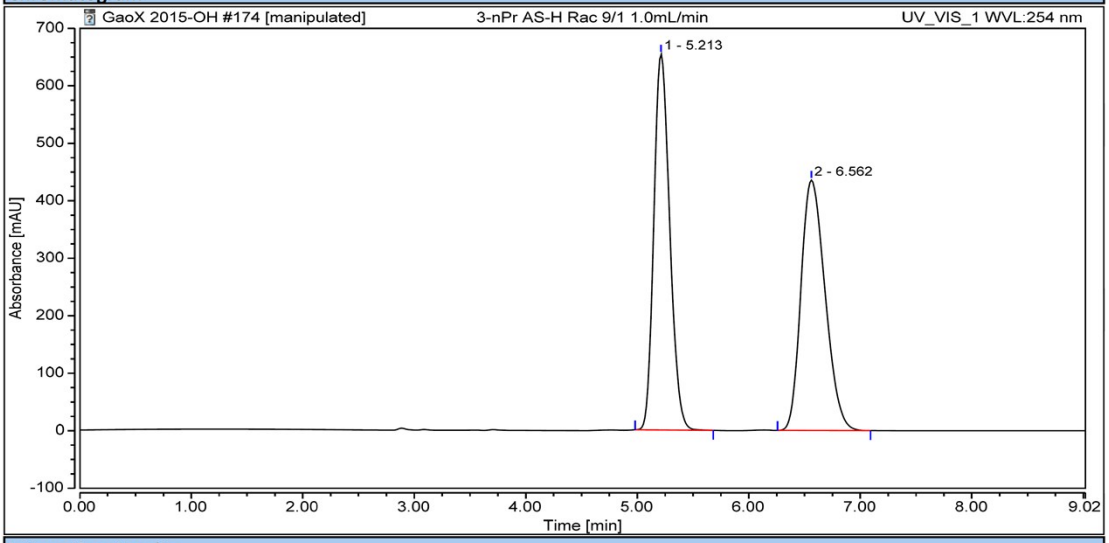

**Integration Results**

| No. | Peak Name | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | Amount mg/l |
|---|---|---|---|---|---|---|---|
| n.a. | toluene | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 1 | | 6.203 | 26.853 | 140.382 | 7.02 | 9.61 | n.a. |
| 2 | | 6.798 | 355.669 | 1321.004 | 92.98 | 90.39 | n.a. |
| **Total:** | | | **382.522** | **1461.386** | **100.00** | **100.00** | |




**3q**

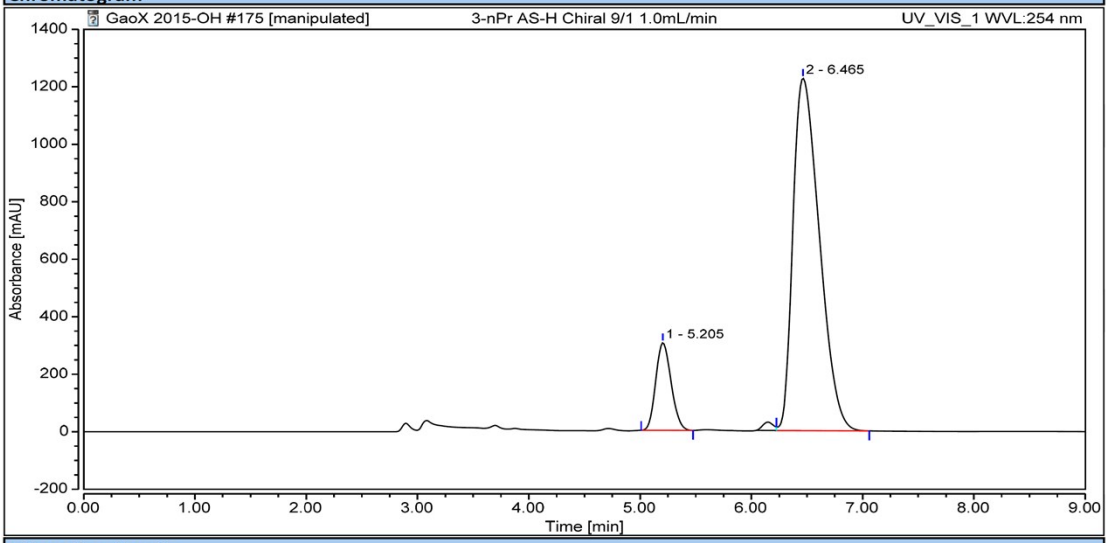
**Chromatogram**




**Integration Results**

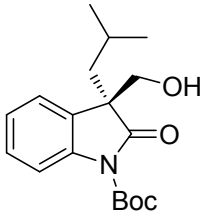
| No. | Peak Name | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | Amount mg/l |
|---|---|---|---|---|---|---|---|
| n.a. | toluene | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 1 | | 5.213 | 107.959 | 654.153 | 49.70 | 60.03 | n.a. |
| 2 | | 6.562 | 109.269 | 435.562 | 50.30 | 39.97 | n.a. |
| **Total:** | | | **217.227** | **1089.714** | **100.00** | **100.00** | |

**Chromatogram**



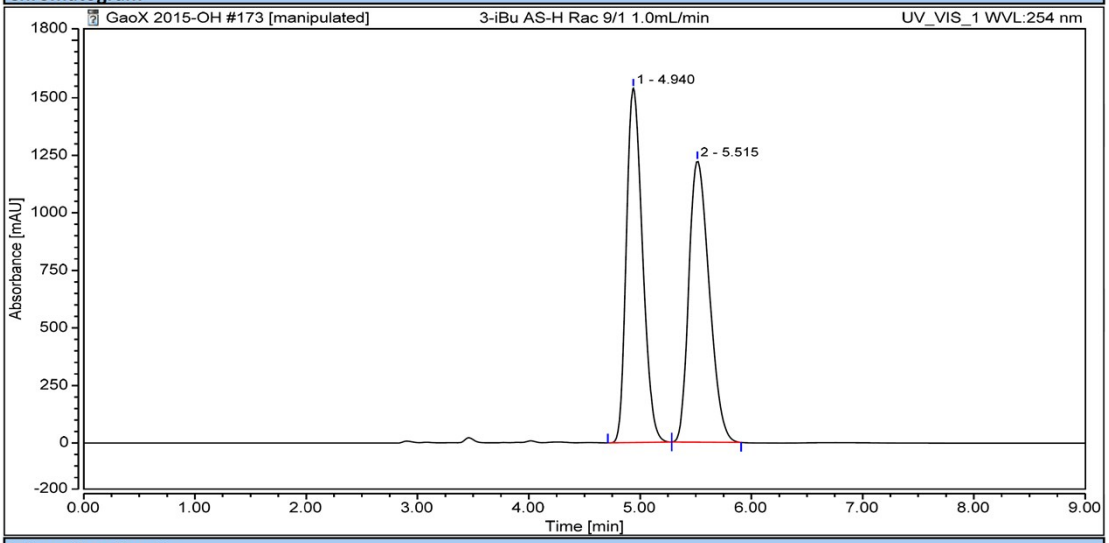

**Integration Results**

| No. | Peak Name | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | Amount mg/l |
|---|---|---|---|---|---|---|---|
| n.a. | toluene | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 1 | | 5.205 | 48.848 | 304.571 | 12.66 | 19.90 | n.a. |
| 2 | | 6.465 | 336.866 | 1225.922 | 87.34 | 80.10 | n.a. |
| **Total:** | | | **385.713** | **1530.493** | **100.00** | **100.00** | |




**3r**

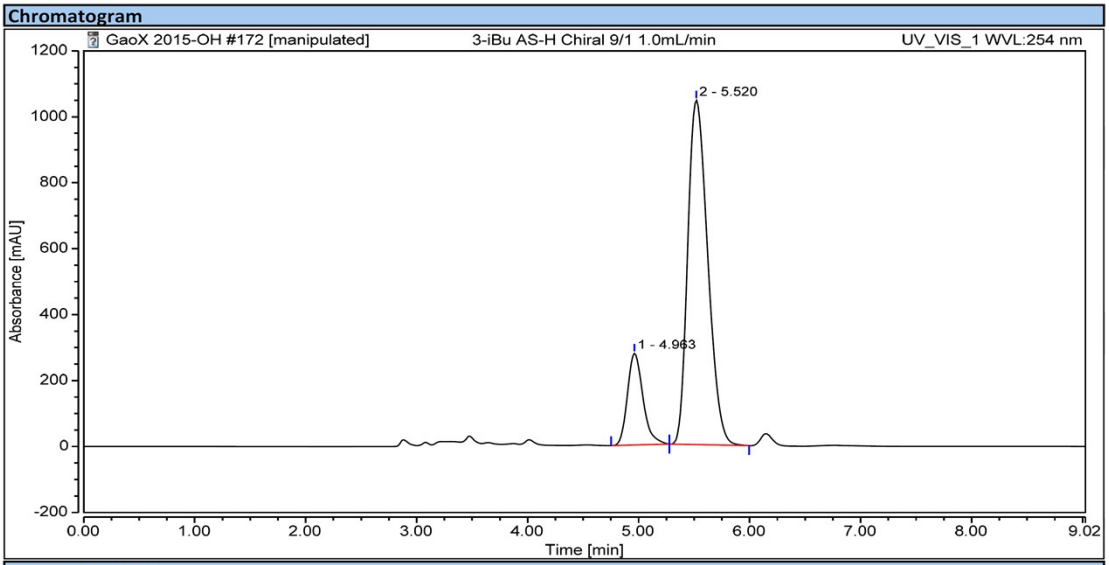
**Chromatogram**




**Integration Results**

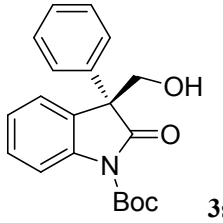
| No. | Peak Name | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | Amount mg/l |
|---|---|---|---|---|---|---|---|
| n.a. | toluene | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 1 | | 4.940 | 258.661 | 1539.836 | 49.90 | 55.75 | n.a. |
| 2 | | 5.515 | 259.739 | 1222.120 | 50.10 | 44.25 | n.a. |
| **Total:** | | | **518.400** | **2761.955** | **100.00** | **100.00** | |

**Chromatogram**



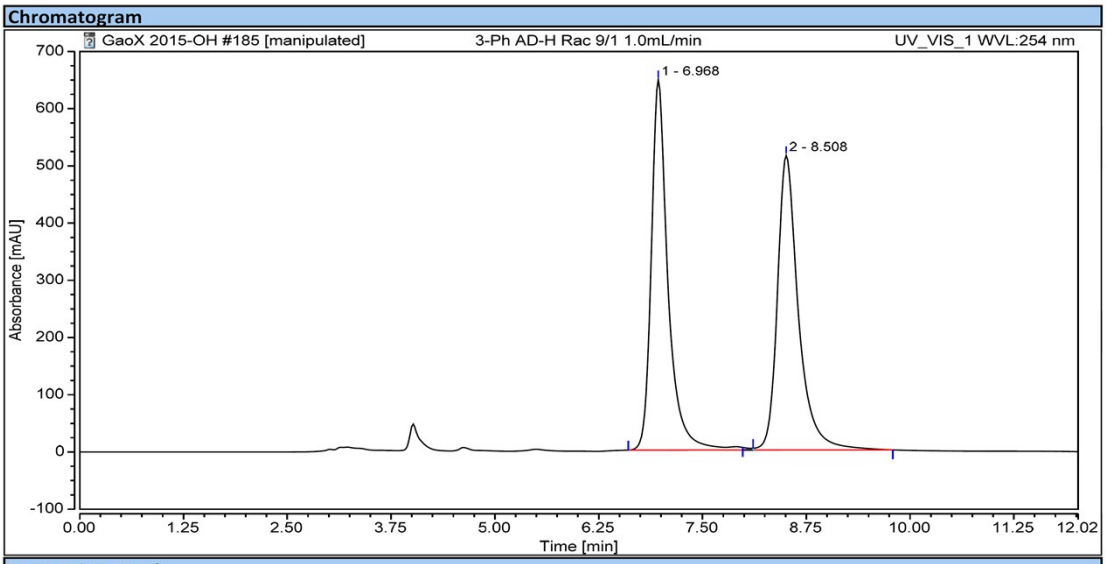

**Integration Results**

| No. | Peak Name | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | Amount mg/l |
|---|---|---|---|---|---|---|---|
| n.a. | toluene | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 1 | | 4.963 | 45.149 | 278.121 | 17.15 | 21.03 | n.a. |
| 2 | | 5.520 | 218.039 | 1044.662 | 82.85 | 78.97 | n.a. |
| **Total:** | | | **263.188** | **1322.783** | **100.00** | **100.00** | |




**3s**

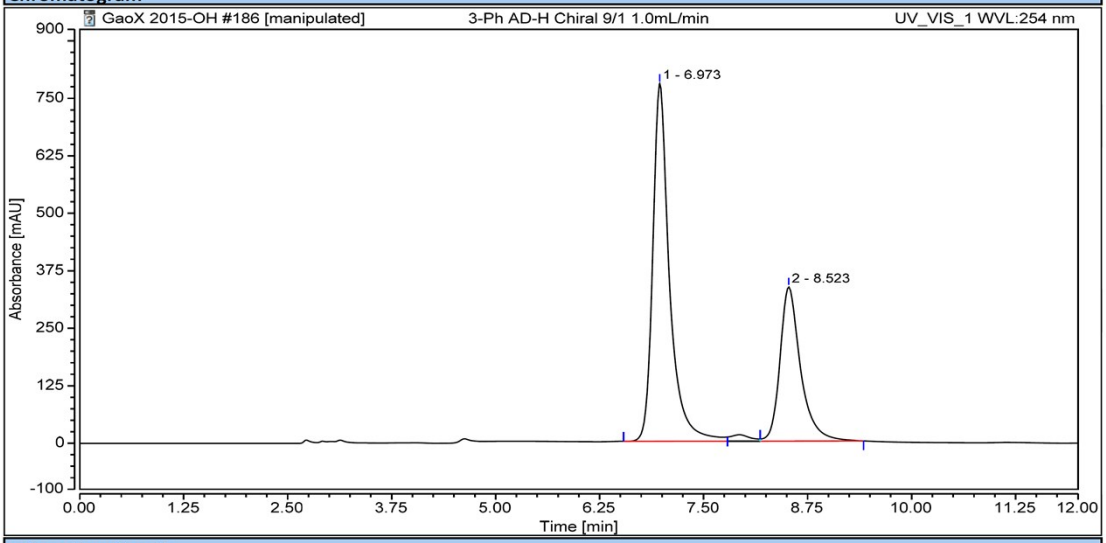
**Chromatogram**




**Integration Results**

| No. | Peak Name | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | Amount mg/l |
|---|---|---|---|---|---|---|---|
| n.a. | toluene | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 1 | | 6.968 | 151.239 | 647.535 | 50.00 | 55.71 | n.a. |
| 2 | | 8.508 | 151.246 | 514.772 | 50.00 | 44.29 | n.a. |
| **Total:** | | | **302.485** | **1162.306** | **100.00** | **100.00** | |

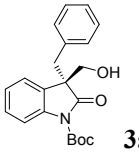
**Chromatogram**



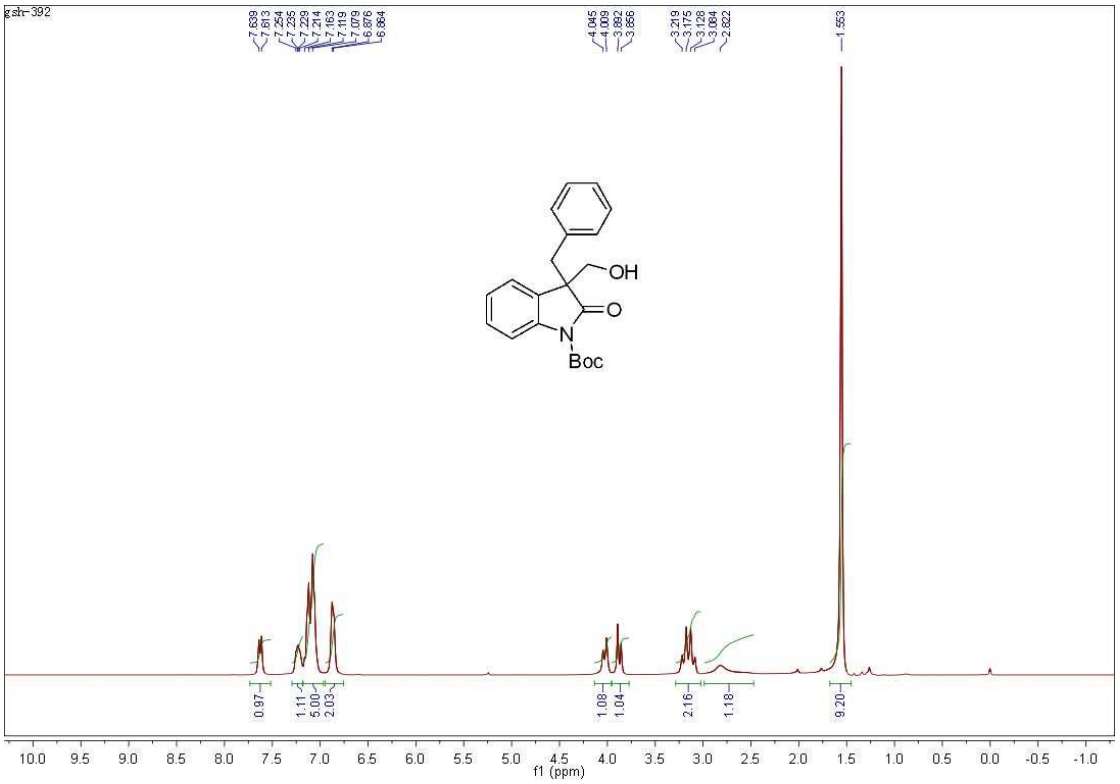

**Integration Results**

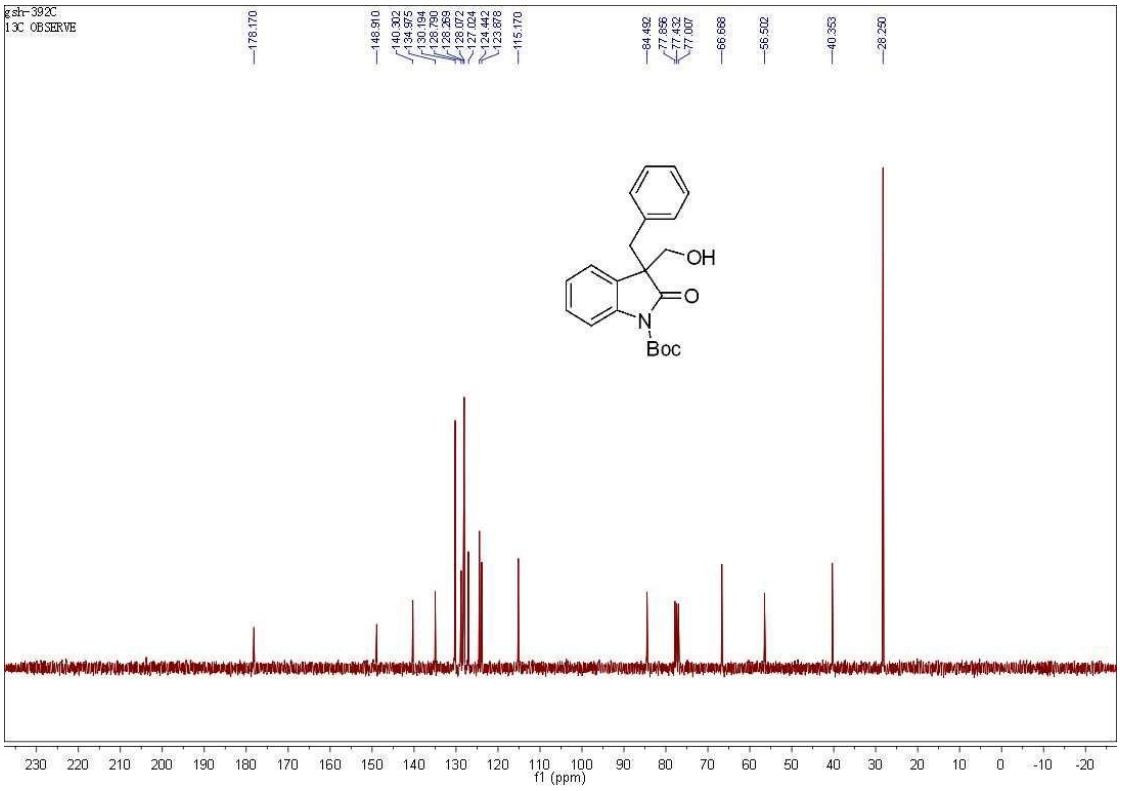
| No. | Peak Name | Retention Time min | Area mAU*min | Height mAU | Relative Area % | Relative Height % | Amount mg/l |
|---|---|---|---|---|---|---|---|
| n.a. | toluene | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| 1 | | 6.973 | 181.809 | 778.088 | 65.42 | 69.90 | n.a. |
| 2 | | 8.523 | 96.093 | 335.112 | 34.58 | 30.10 | n.a. |
| **Total:** | | | **277.902** | **1113.201** | **100.00** | **100.00** | |

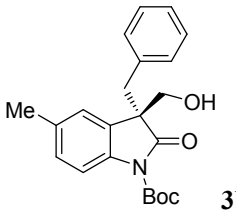
## 6. NMR Spectra for 3(a-s), 7(a, b), 8(a, b), 9(a, b) and 4(f, i).



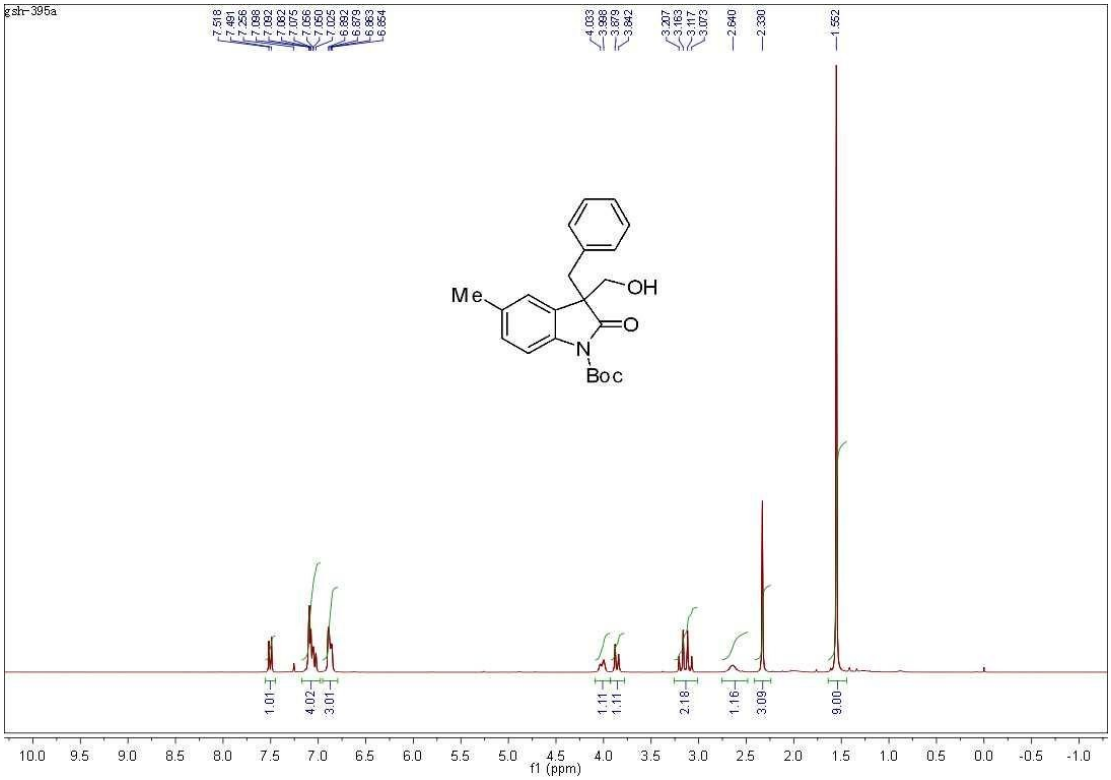

**3a**

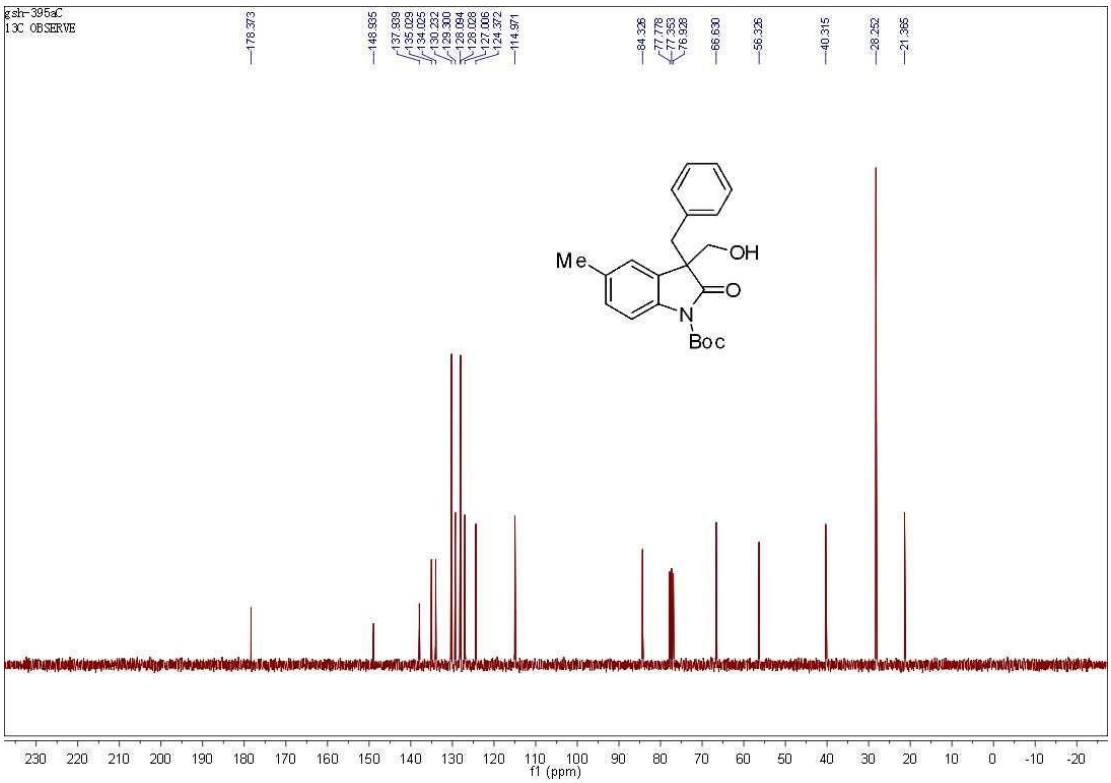

gsh-392
OH
O
N
Boc
f1 (ppm)

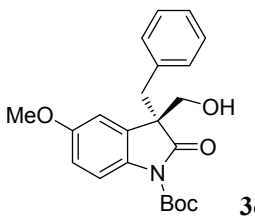

gsh-392C
13C OBSERVE
OH
O
N
Boc
f1 (ppm)


Me
OH
O
N
Boc

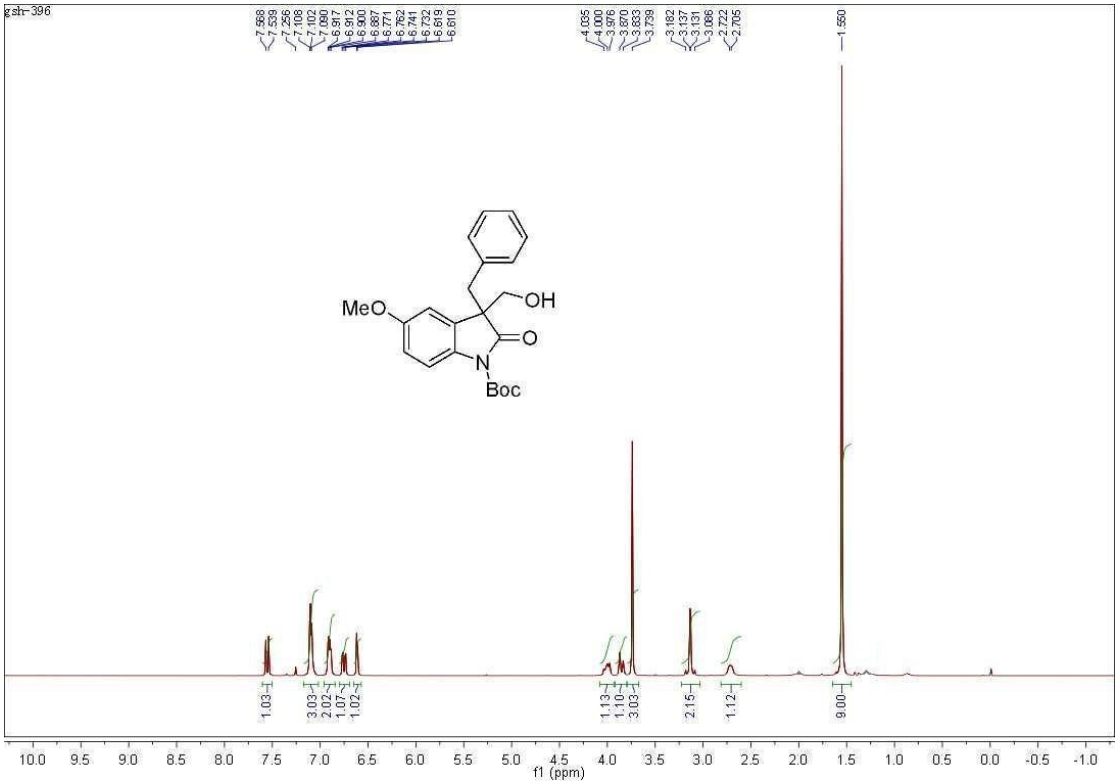
**3b**

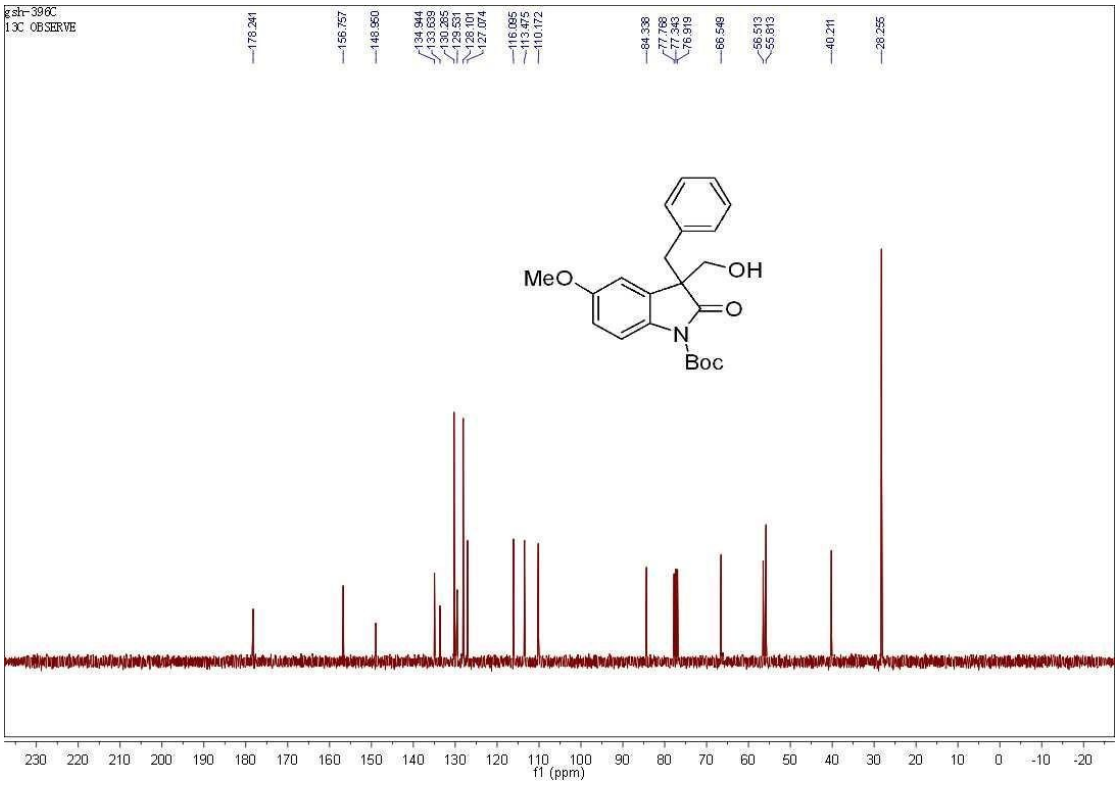

gsh-395a
7.518
7.491
7.256
7.088
7.082
7.075
7.056
7.050
7.025
6.892
6.879
6.863
6.854
4.033
3.998
3.879
3.842
3.207
3.163
3.117
3.073
2.640
2.330
1.552
Me
OH
O
N
Boc
1.01
4.02
3.01
1.11
1.11
2.18
1.16
3.09
9.00
f1 (ppm)

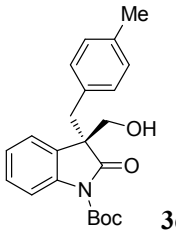

gsh-395aC
13C OBSERVE
178.373
148.935
137.939
135.029
134.055
130.232
129.300
128.094
128.028
127.006
124.372
114.971
64.326
77.778
77.353
76.928
66.630
56.335
40.315
28.252
21.365
Me
OH
O
N
Boc
f1 (ppm)


MeO
OH
O
N
Boc

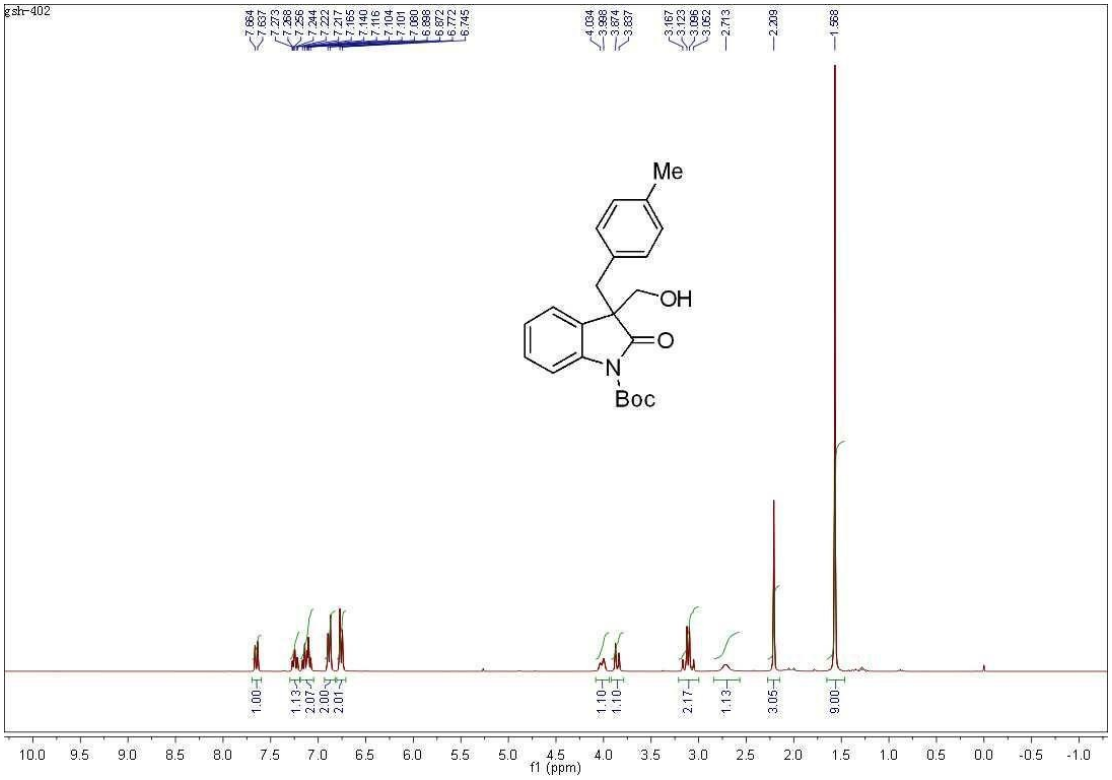
**3c**

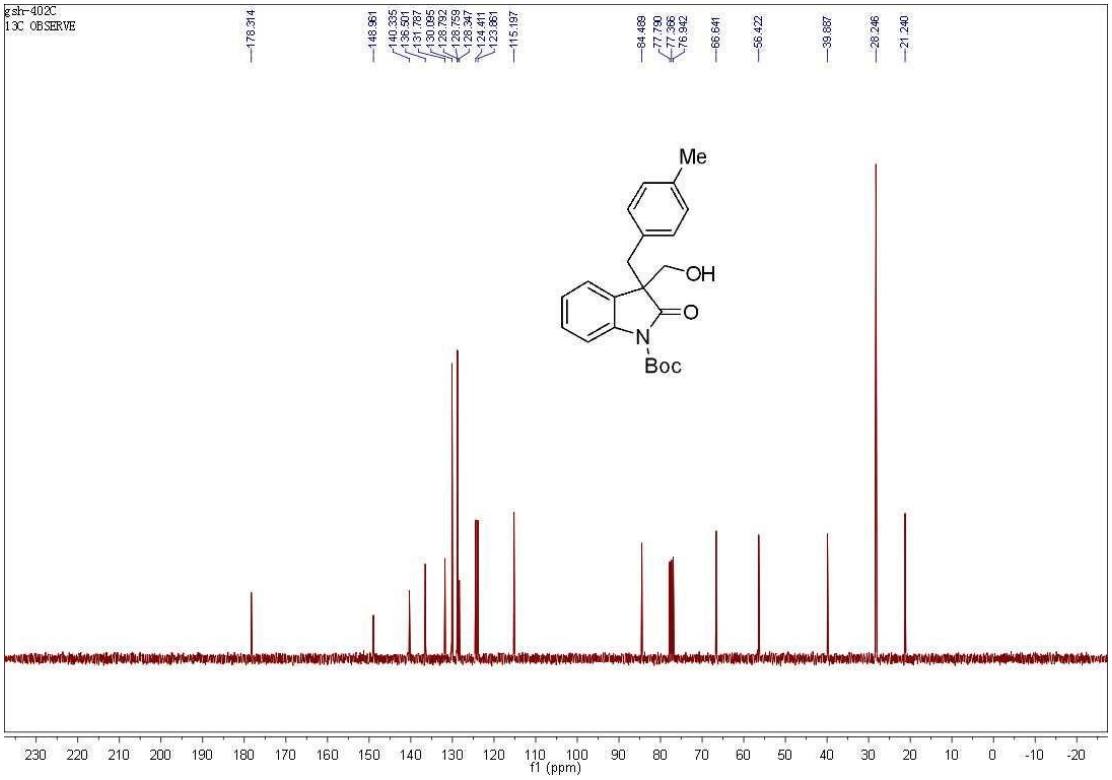

gsh-396
MeO
OH
O
N
Boc
f1 (ppm)

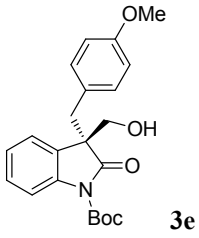

gsh-396C
13C OBSERVE
MeO
OH
O
N
Boc
f1 (ppm)


Me
OH
O
N
Boc

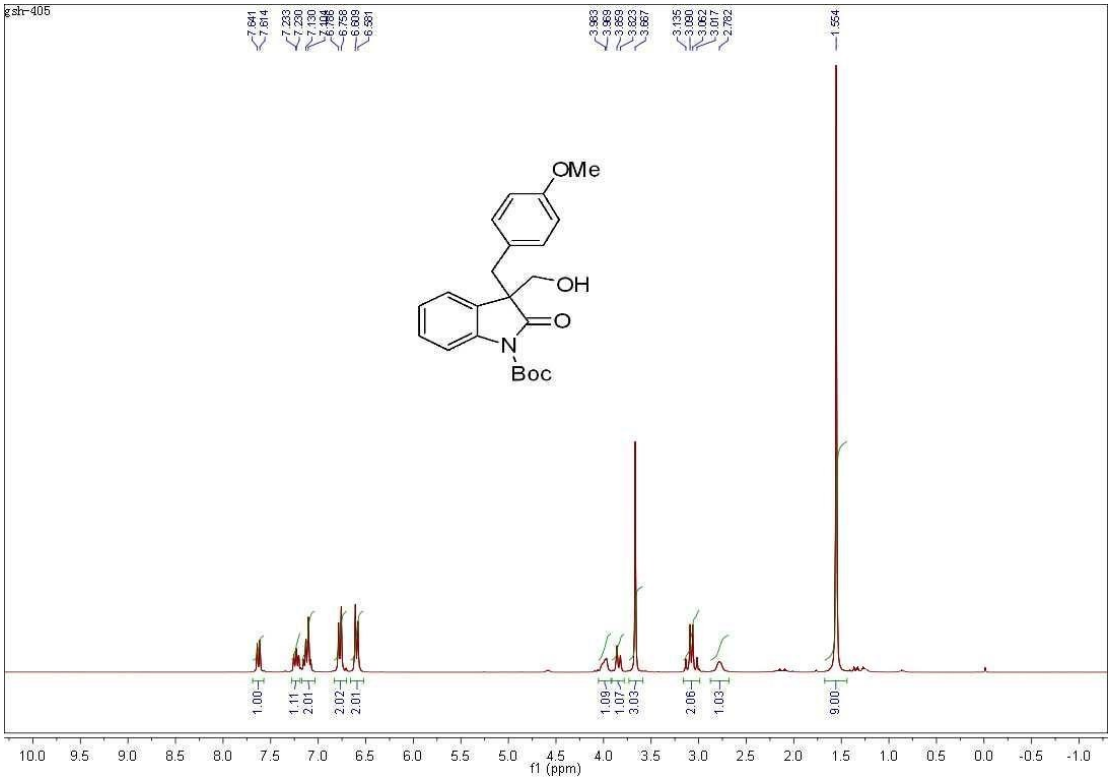
**3d**

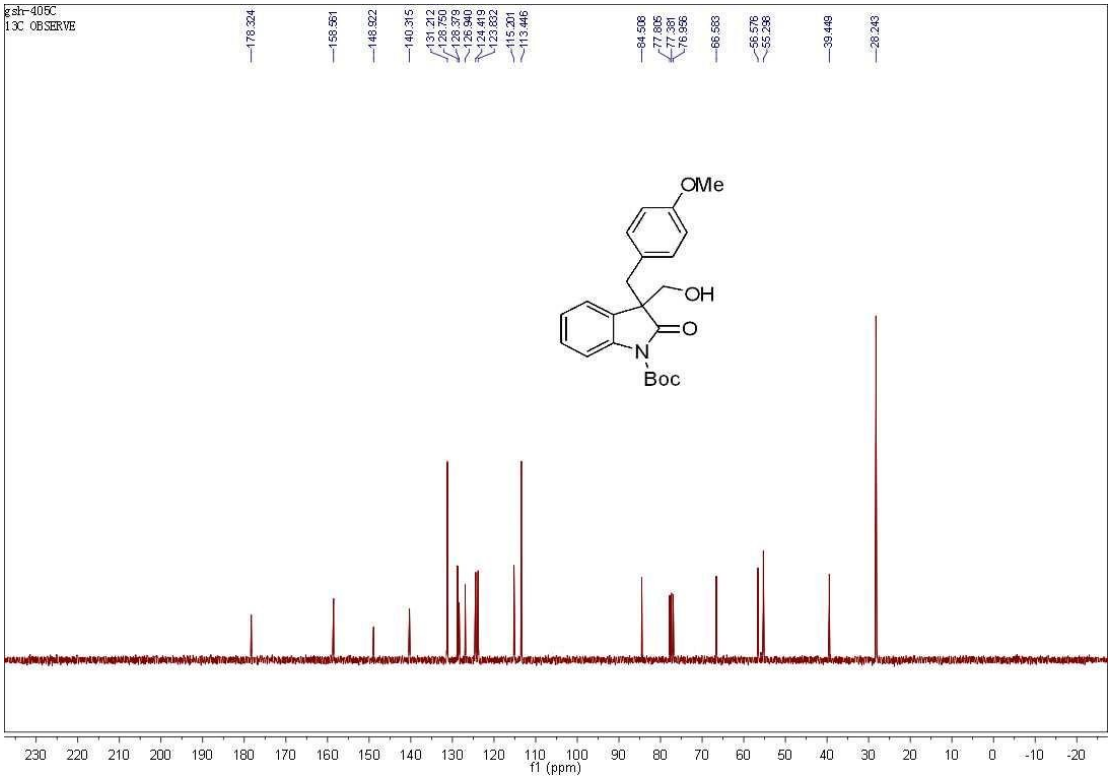

gsh-402
7.664
7.637
7.273
7.268
7.256
7.244
7.222
7.217
7.165
7.140
7.116
7.104
7.101
7.080
6.898
6.872
6.772
6.745
4.094
3.998
3.874
3.837
3.167
3.123
3.096
3.052
2.713
2.209
1.568
Me
OH
O
N
Boc
1.00
1.13
2.07
2.00
2.01
1.10
1.10
2.17
1.13
3.05
9.00
f1 (ppm)

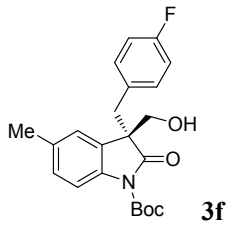

gsh-402C
13C OBSERVE
178.314
148.961
140.335
136.501
131.787
130.085
128.792
128.759
128.347
124.411
123.861
115.197
64.489
77.790
77.396
76.942
66.641
56.422
39.887
28.246
21.240
Me
OH
O
N
Boc
f1 (ppm)


OMe
OH
O
N
Boc

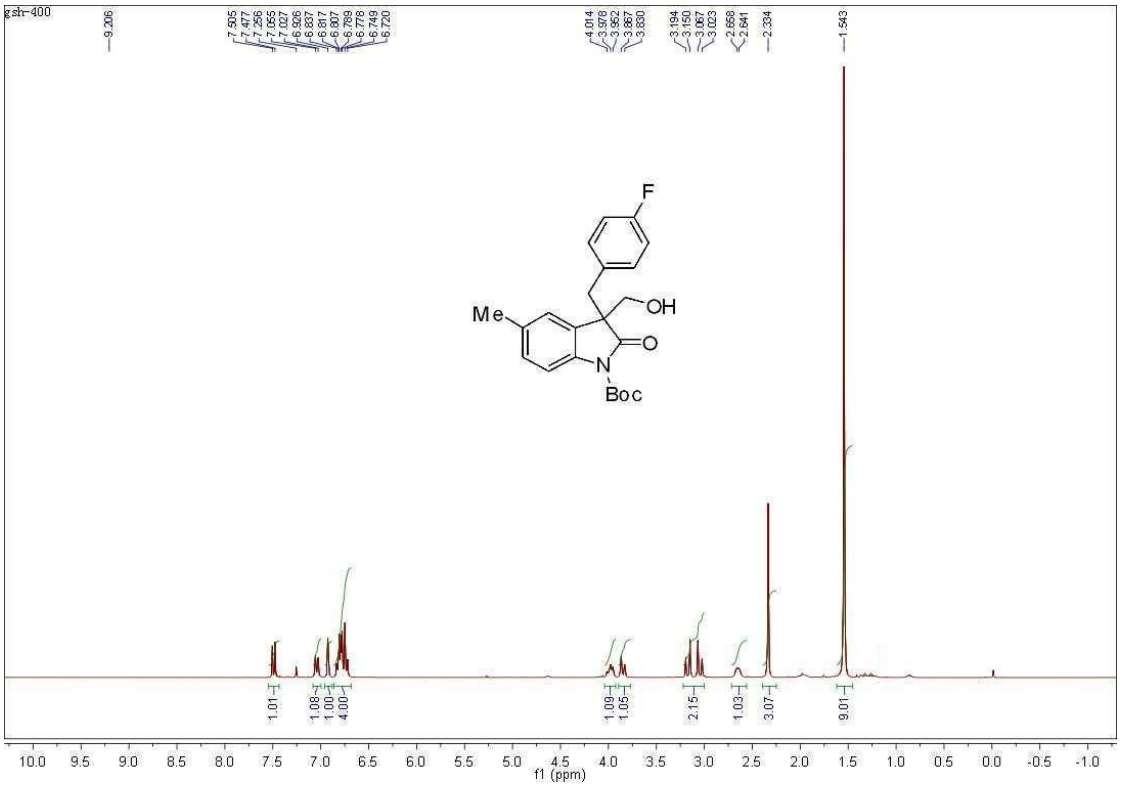
**3e**

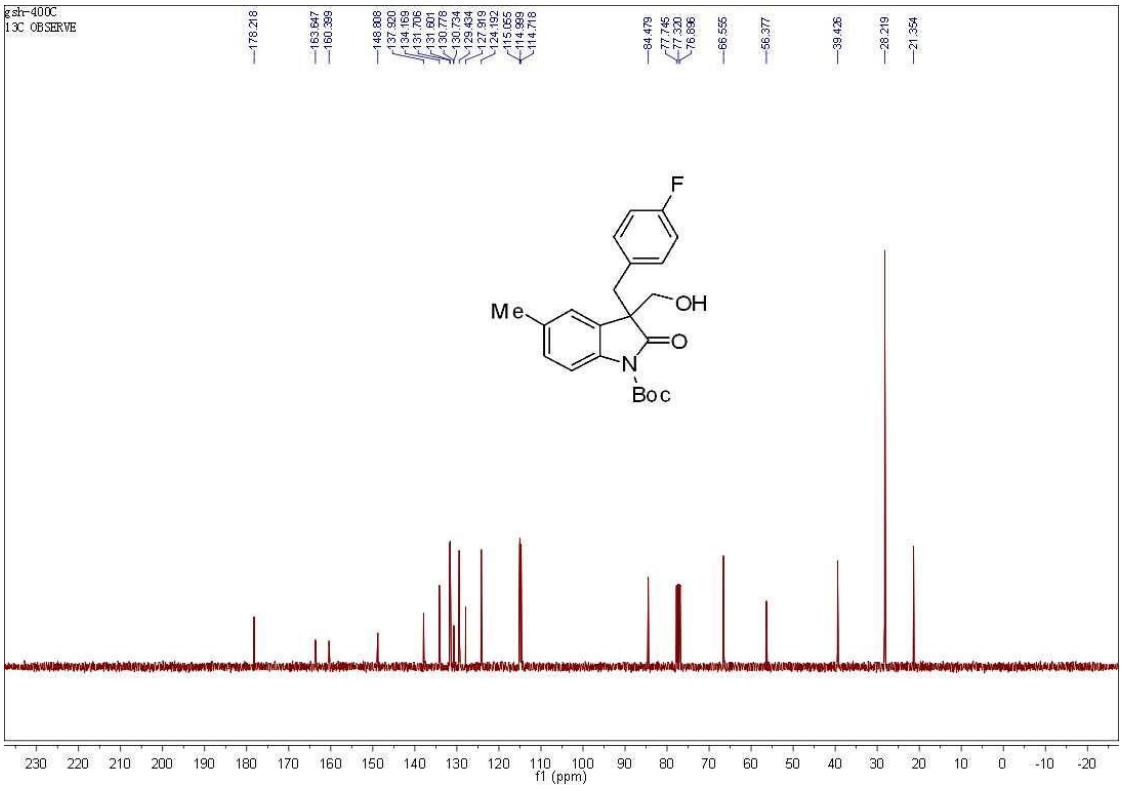

gsh-405
7.641
7.614
7.233
7.230
7.130
6.758
6.609
6.581
3.983
3.969
3.869
3.823
3.687
3.135
3.090
3.062
3.017
2.782
1.554
OMe
OH
O
N
Boc
1.00
1.11
2.01
2.02
2.01
1.09
1.07
3.03
2.06
1.03
9.00
f1 (ppm)

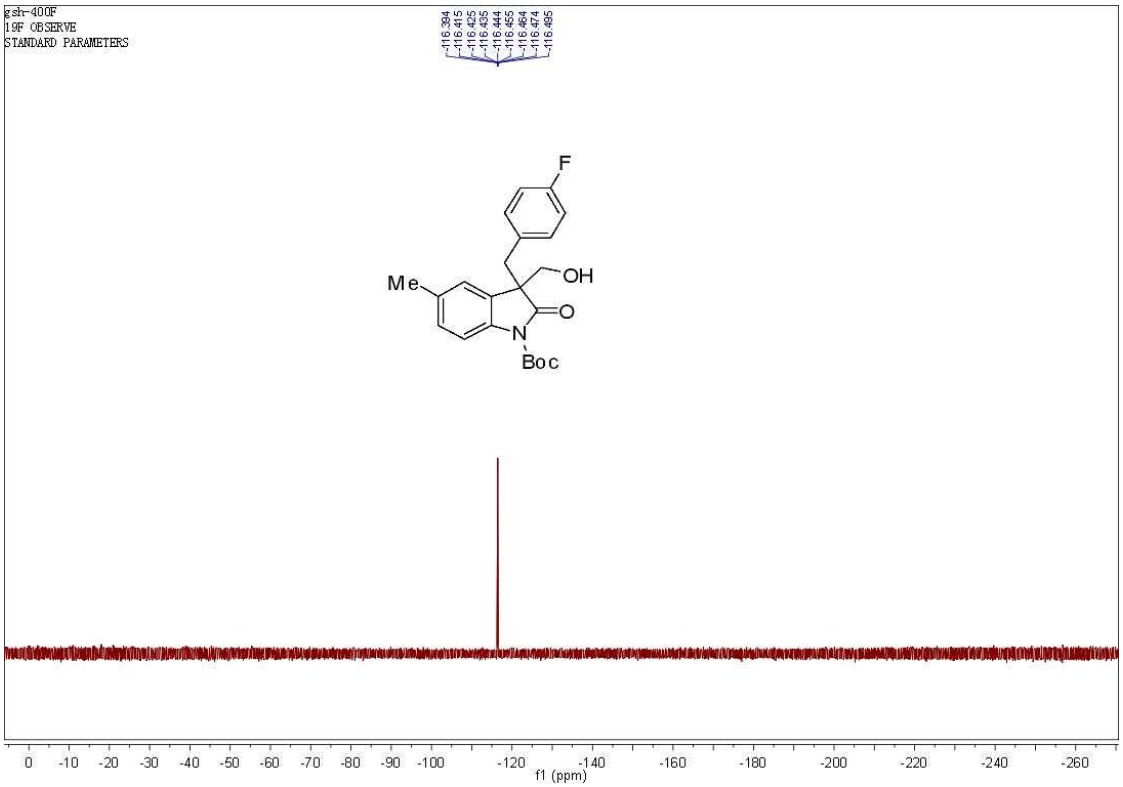

gsh-405C
13C OBSERVE
178.324
158.561
148.922
140.315
131.212
128.750
128.379
126.940
124.419
123.832
115.201
113.446
64.508
77.805
77.381
76.956
66.583
56.576
55.286
39.449
28.243
OMe
OH
O
N
Boc
f1 (ppm)

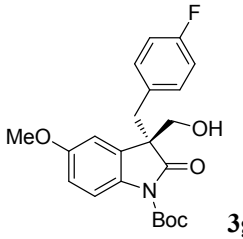

F
Me
OH
O
N
Boc

**3f**

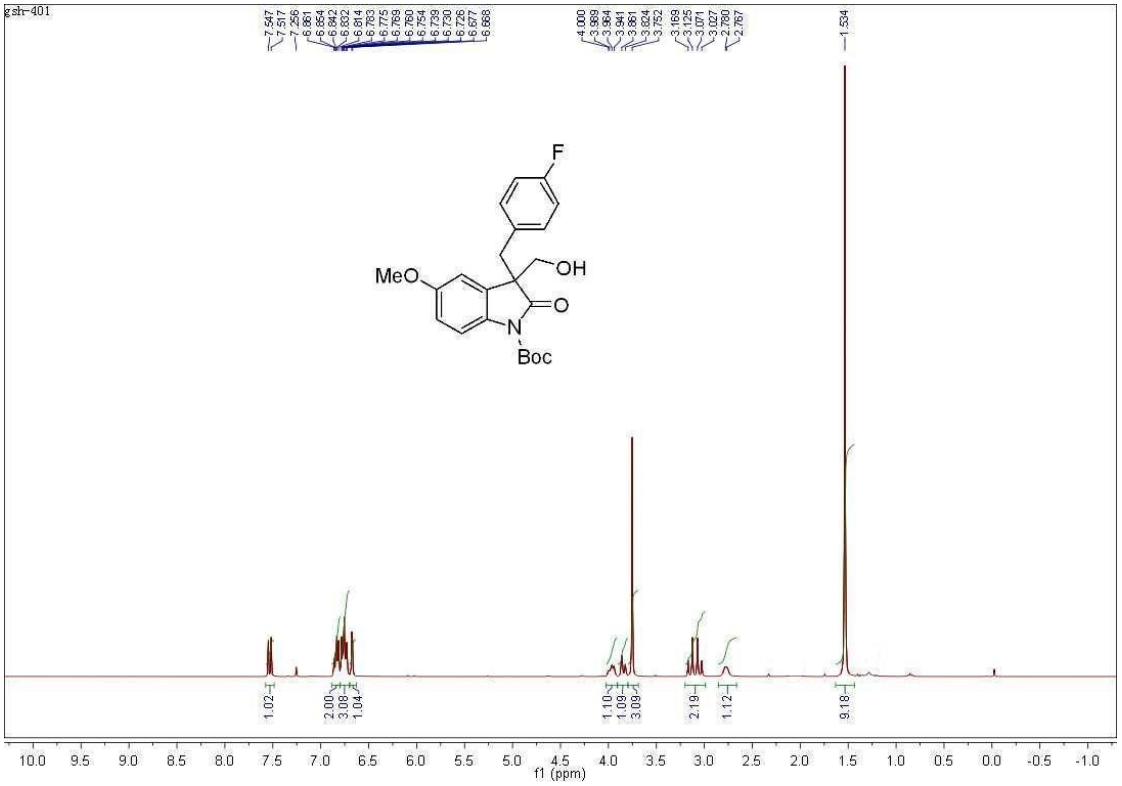

gsh-400
F
Me
OH
O
N
Boc
f1 (ppm)

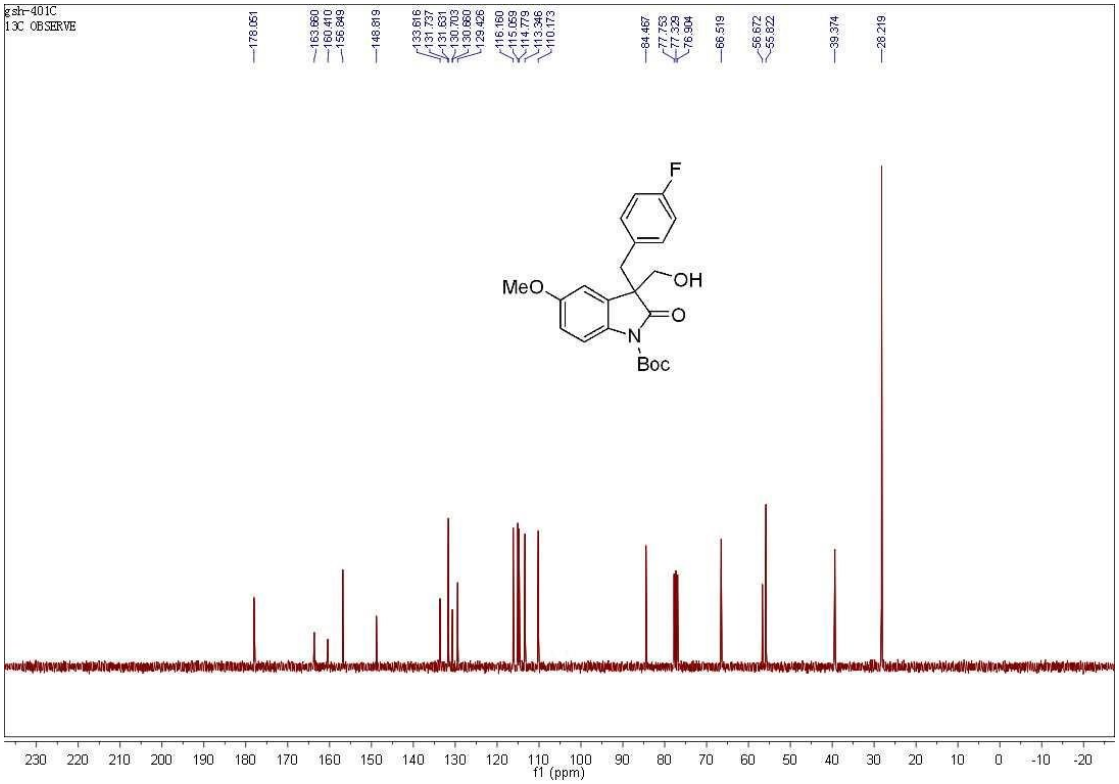

gsh-400C
13C OBSERVE
F
Me
OH
O
N
Boc
f1 (ppm)

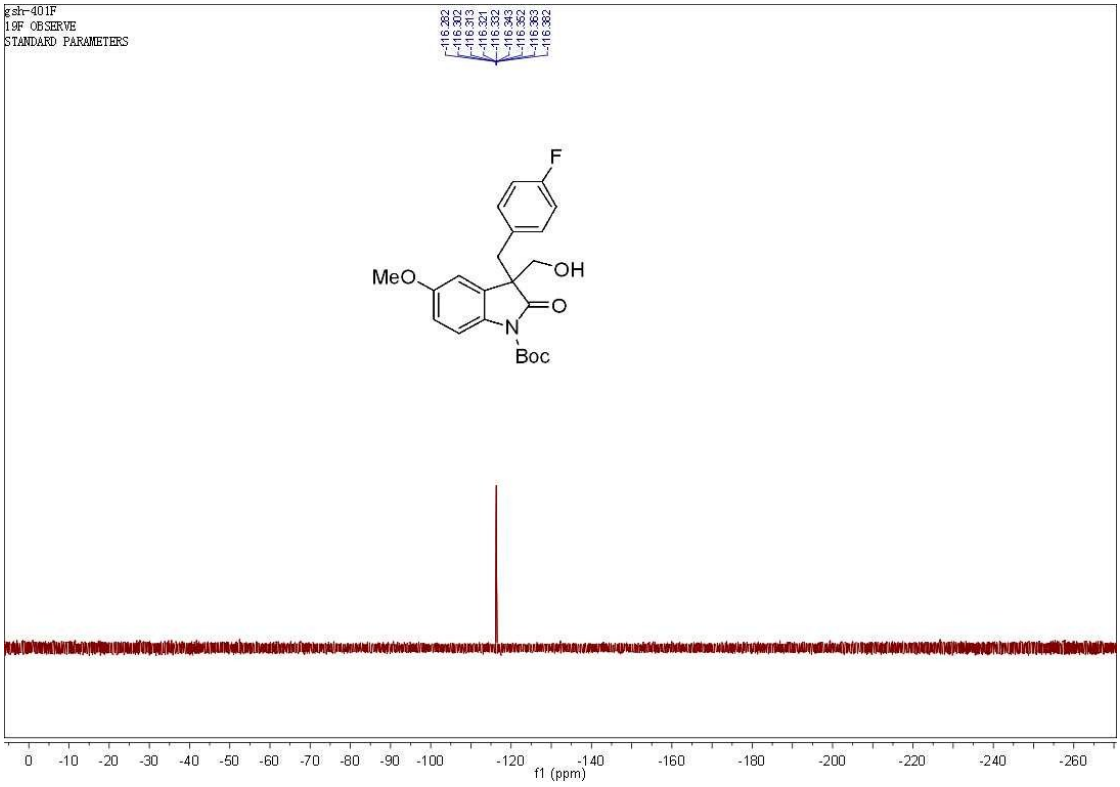

gsh-400F
19F OBSERVE
STANDARD PARAMETERS
-116.394
-116.415
-116.425
-116.435
-116.444
-116.455
-116.464
-116.474
-116.485
F
Me
OH
O
N
Boc
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200 -220 -240 -260
f1 (ppm)

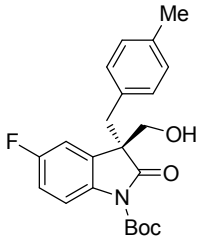

F
MeO
OH
O
N
Boc

**3g**

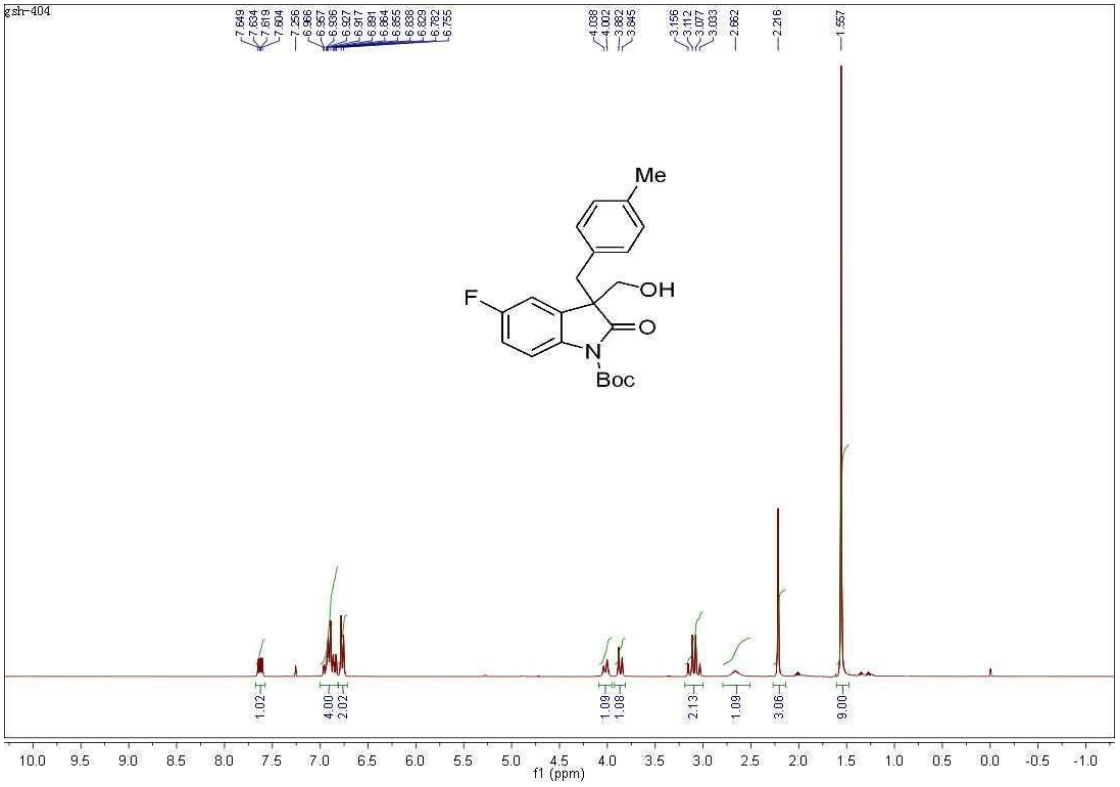

gsh-401
7.547
7.537
7.256
6.861
6.854
6.842
6.832
6.814
6.783
6.775
6.769
6.760
6.754
6.739
6.730
6.726
6.677
6.668
4.000
3.989
3.964
3.941
3.861
3.804
3.752
3.169
3.155
3.071
3.027
2.780
2.767
1.534
F
MeO
OH
O
N
Boc
1.02
2.00
3.08
1.04
1.10
1.09
3.09
2.19
1.12
9.18
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

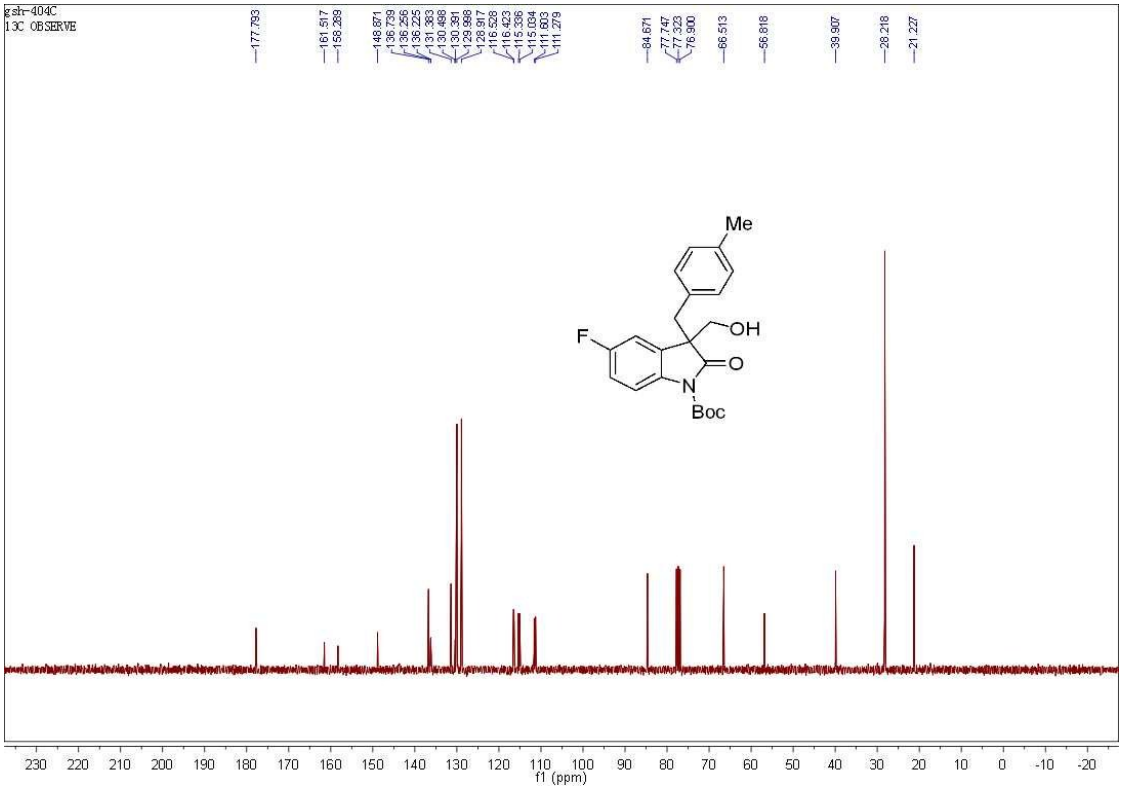

gsh-401C
13C OBSERVE
178.051
163.660
160.410
156.849
148.819
133.616
131.737
131.631
130.703
130.660
129.426
116.160
115.059
114.779
113.346
110.173
84.467
77.753
77.329
76.904
66.519
56.672
55.822
39.374
28.219
F
MeO
OH
O
N
Boc
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

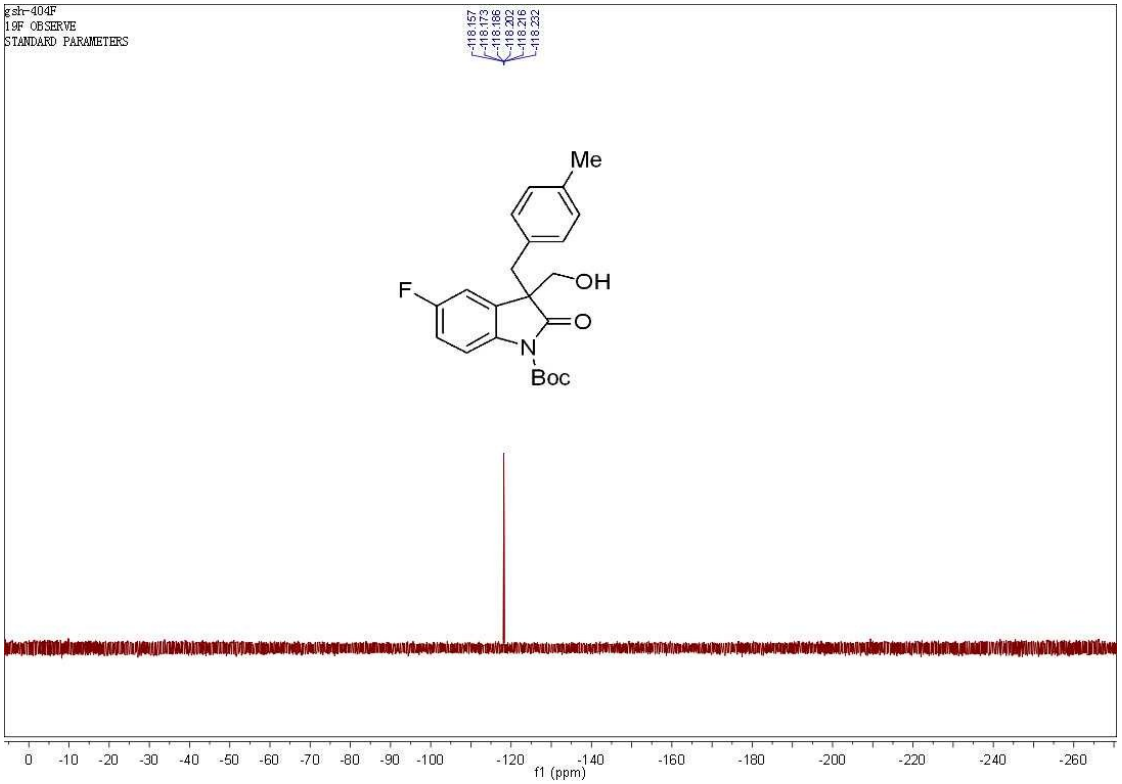

gsh-401F
19F OBSERVE
STANDARD PARAMETERS
-116.282
-116.302
-116.313
-116.321
-116.332
-116.343
-116.352
-116.363
-116.382
F
MeO
OH
O
N
Boc
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200 -220 -240 -260
f1 (ppm)

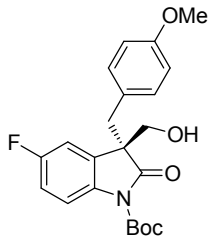

Me
F
OH
O
N
Boc

**3h**

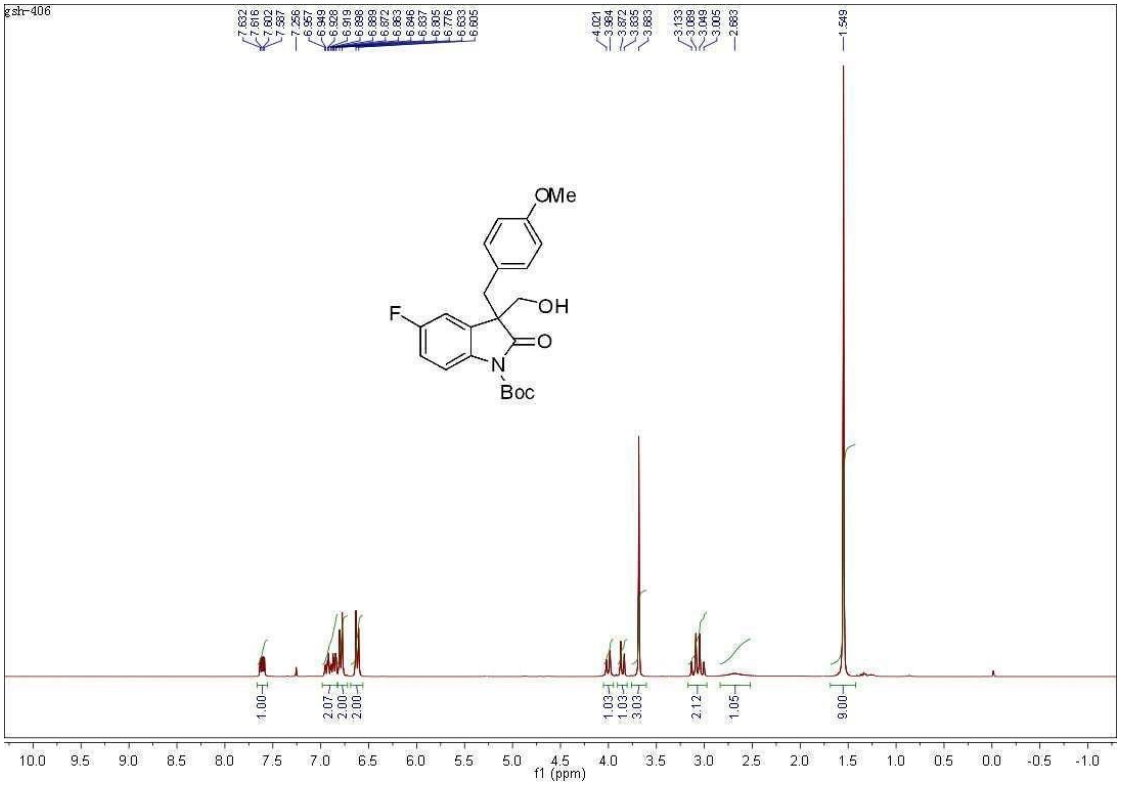

gsh-404
7.649
7.634
7.619
7.604
7.256
6.966
6.957
6.936
6.927
6.917
6.881
6.864
6.855
6.838
6.829
6.782
6.755
4.038
4.002
3.892
3.882
3.845
3.156
3.111
3.077
3.033
2.662
2.216
1.557
Me
F
OH
O
N
Boc
1.02
4.00
2.02
1.09
1.08
2.13
1.09
3.06
9.00
f1 (ppm)

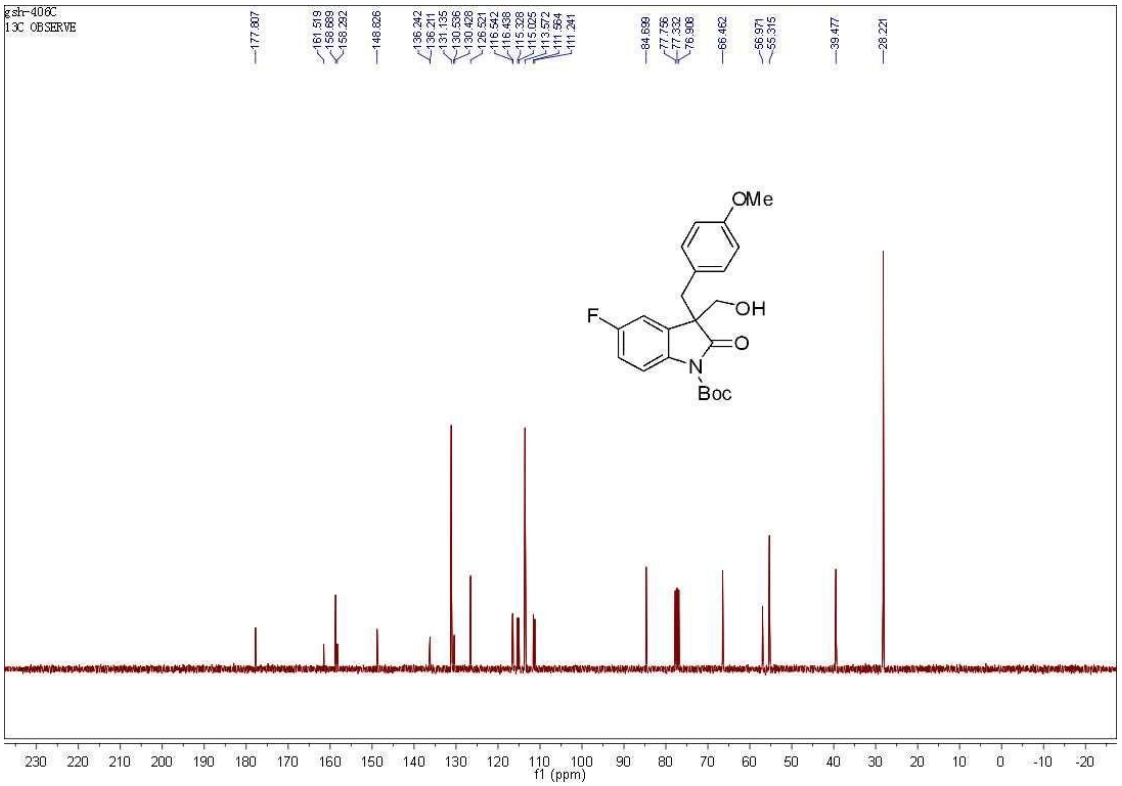

gsh-404C
13C OBSERVE
177.793
161.517
158.289
148.671
136.739
136.256
136.225
131.383
130.488
130.391
129.988
128.917
116.528
116.453
115.369
115.034
111.803
111.279
84.671
77.747
77.323
76.900
66.513
56.818
39.907
28.218
21.227
Me
F
OH
O
N
Boc
f1 (ppm)

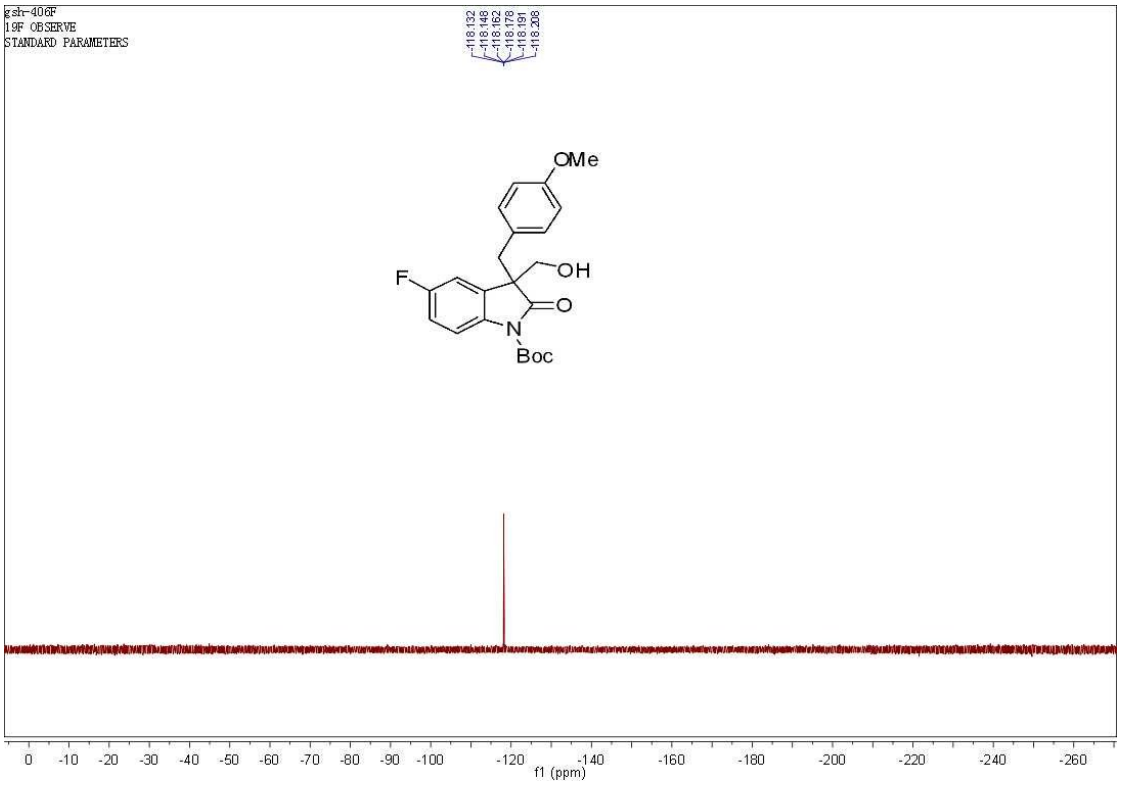

gsh-404F
19F OBSERVE
STANDARD PARAMETERS
-118.157
-118.173
-118.186
-118.202
-118.216
-118.232
Me
OH
F
O
N
Boc
f1 (ppm)

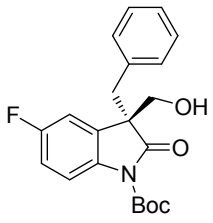

OMe
OH
F
O
N
Boc

**3i**

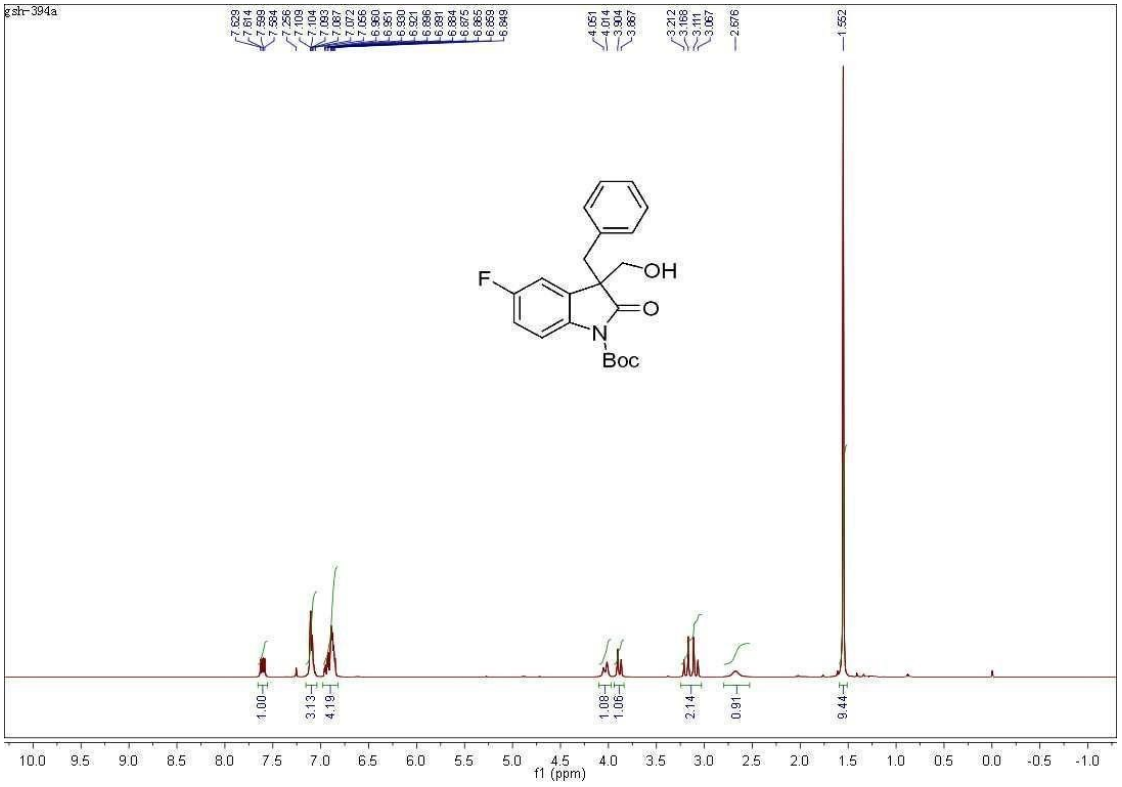

gsh-406
7.632
7.616
7.602
7.587
7.256
6.567
6.549
6.538
6.519
6.888
6.889
6.872
6.863
6.846
6.837
6.795
6.776
6.633
6.605
4.021
3.884
3.872
3.855
3.663
3.133
3.089
3.049
3.005
2.663
1.549
OMe
OH
F
O
N
Boc
1.00
2.07
2.00
2.00
1.03
1.03
3.03
2.12
1.05
9.00
f1 (ppm)

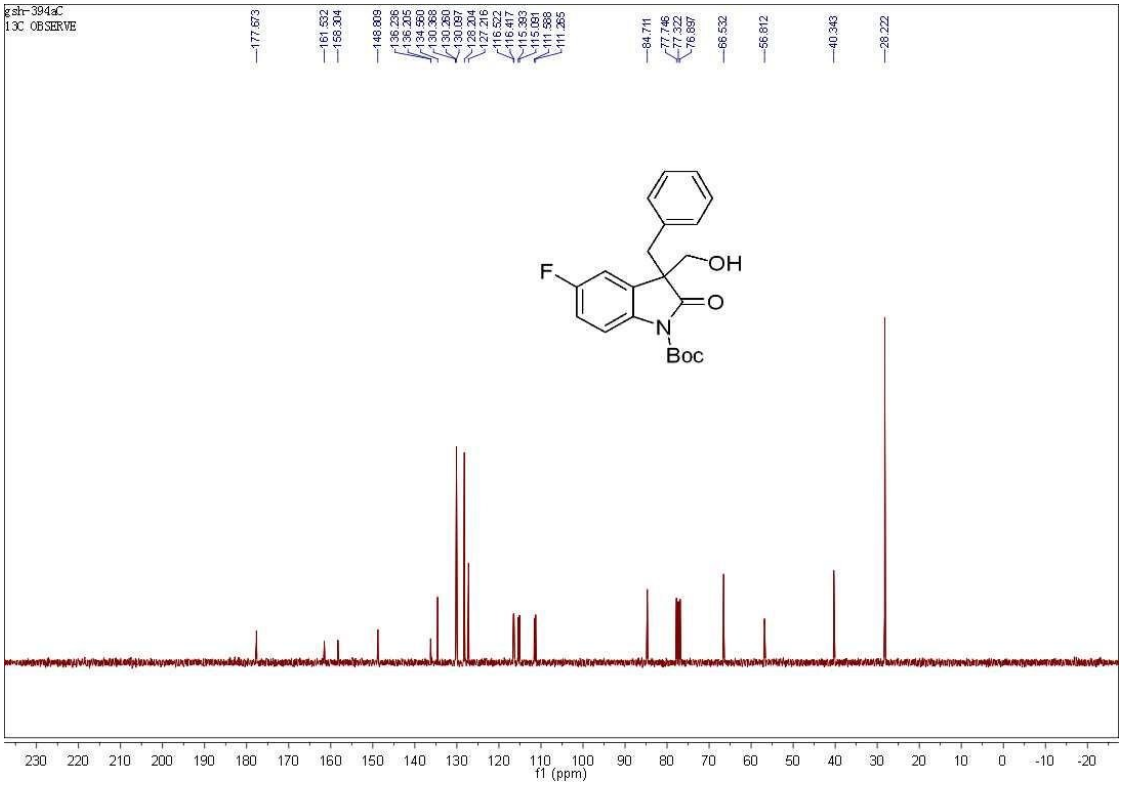

gsh-406C
13C OBSERVE
177.807
161.519
158.889
158.292
148.826
136.242
136.211
131.135
130.536
130.428
126.521
116.542
116.458
115.338
115.025
113.572
111.564
111.241
84.699
77.756
77.332
76.906
66.462
56.971
55.315
39.477
28.221
OMe
OH
F
O
N
Boc
f1 (ppm)

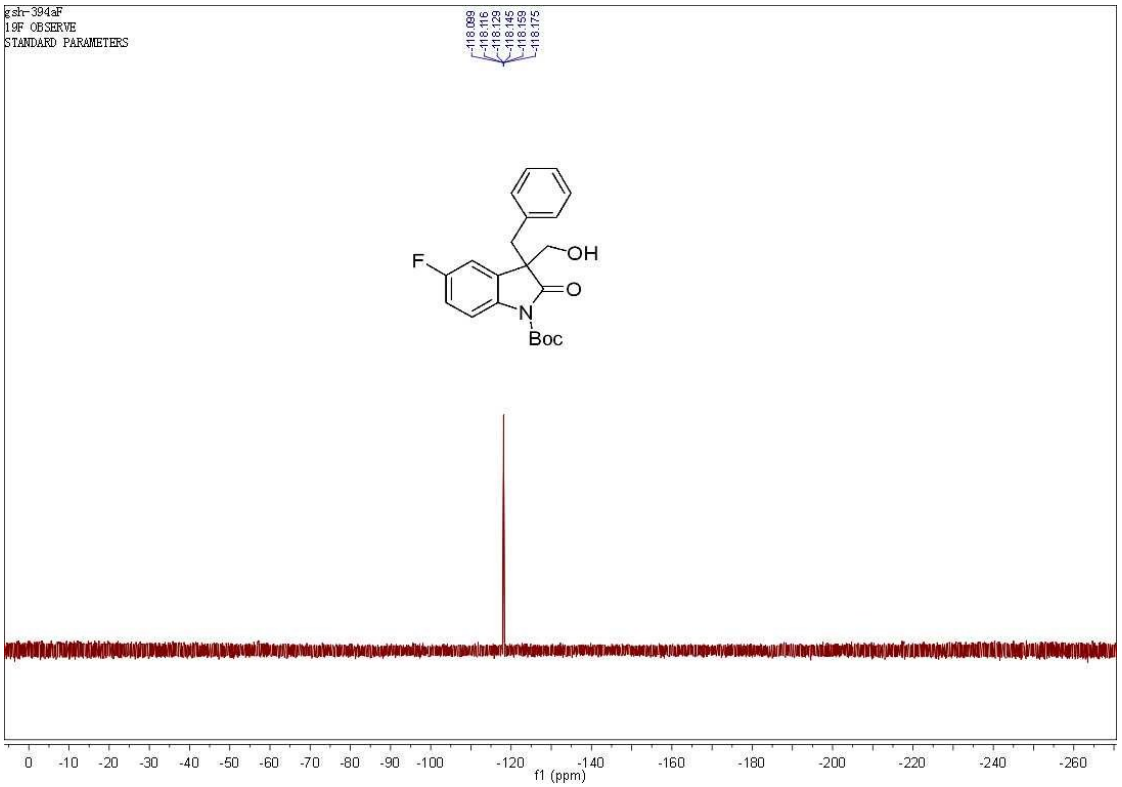

gsh-406F
19F OBSERVE
STANDARD PARAMETERS
-118.132
-118.148
-118.162
-118.178
-118.191
-118.208
OMe
OH
F
O
N
Boc
f1 (ppm)

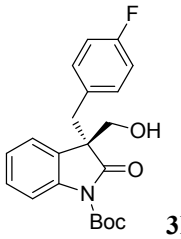

F
OH
O
N
Boc

**3j**

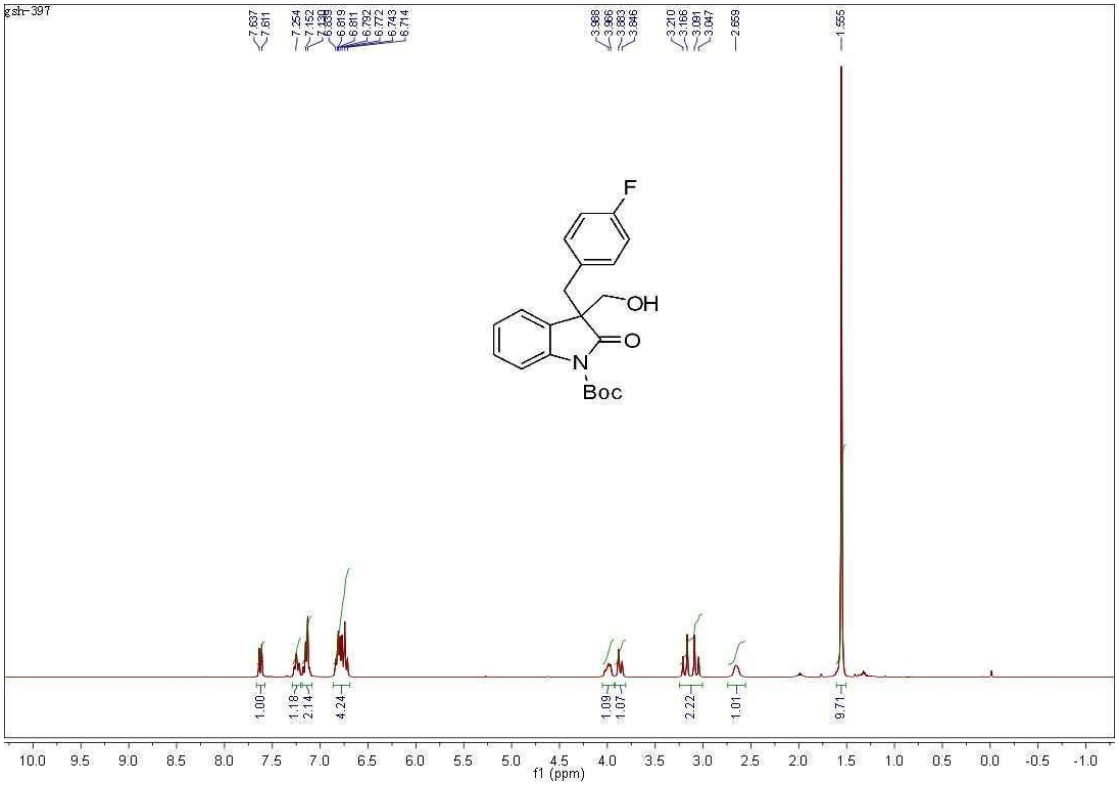

gsh-394a
7.629
7.614
7.599
7.584
7.256
7.109
7.104
7.093
7.087
7.072
7.056
6.960
6.951
6.930
6.921
6.896
6.891
6.884
6.875
6.865
6.855
6.849
4.051
4.014
3.994
3.957
3.212
3.166
3.111
3.067
2.676
1.552
F
OH
O
N
Boc
1.00
3.13
4.19
1.08
1.06
2.14
0.91
9.44
f1 (ppm)

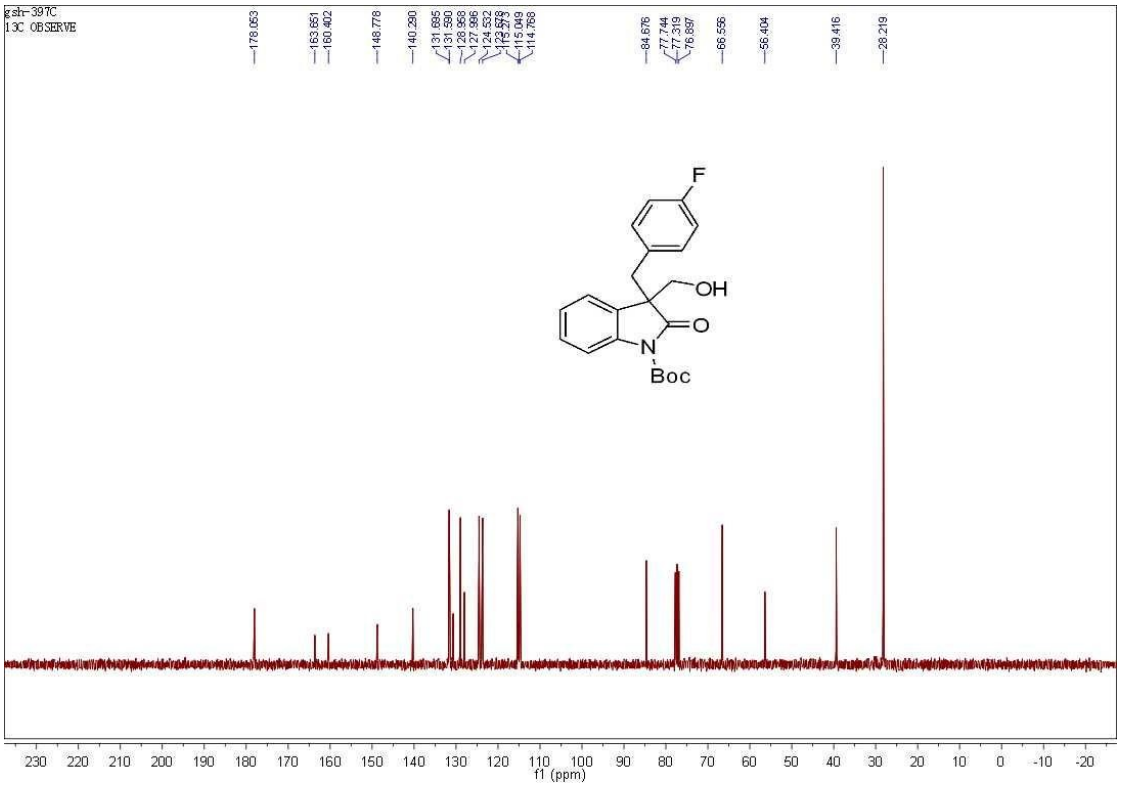

gsh-394aC
13C OBSERVE
177.673
161.522
158.304
148.809
136.726
135.205
134.560
130.368
130.280
130.097
128.204
127.216
116.522
116.417
115.393
115.281
111.588
111.285
84.711
77.746
77.322
76.897
68.532
58.812
40.343
28.222
F
OH
O
N
Boc
f1 (ppm)

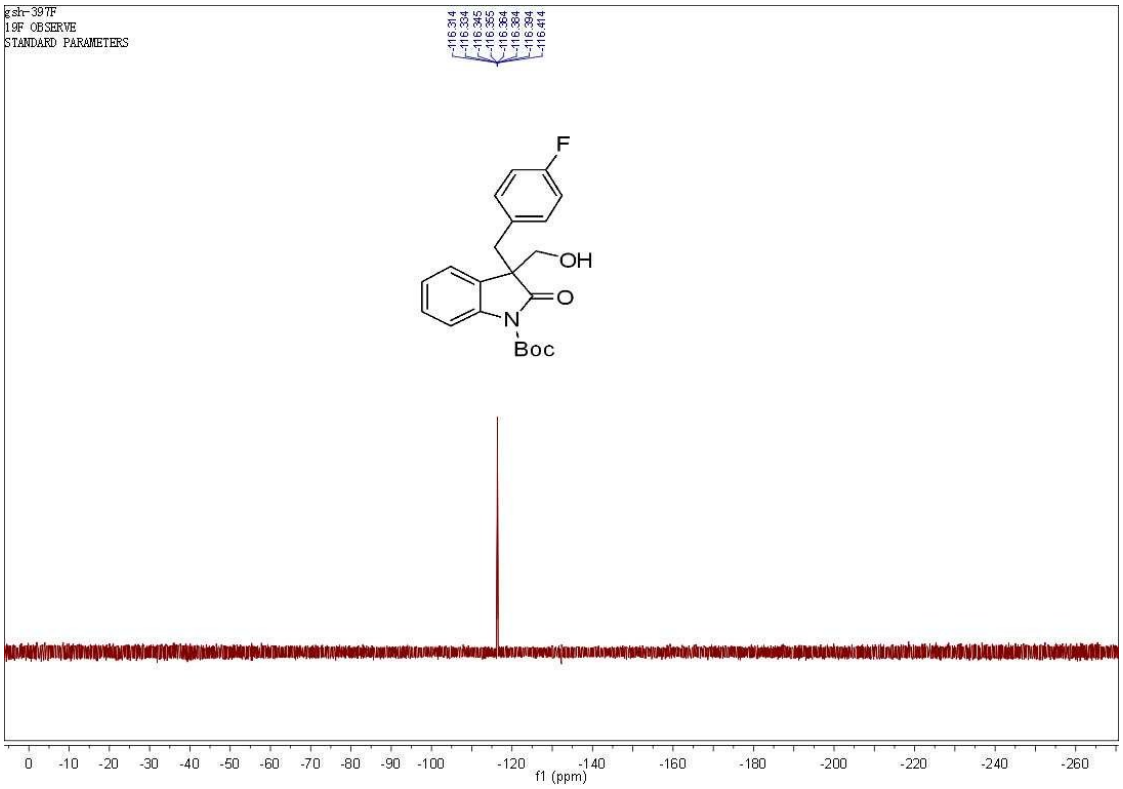

gsh-394aF
19F OBSERVE
STANDARD PARAMETERS
-118.099
-118.116
-118.129
-118.145
-118.159
-118.175
F
OH
O
N
Boc
f1 (ppm)

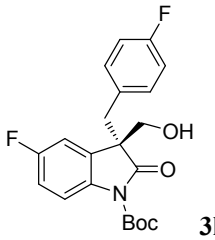

F
OH
O
N
Boc

**3k**

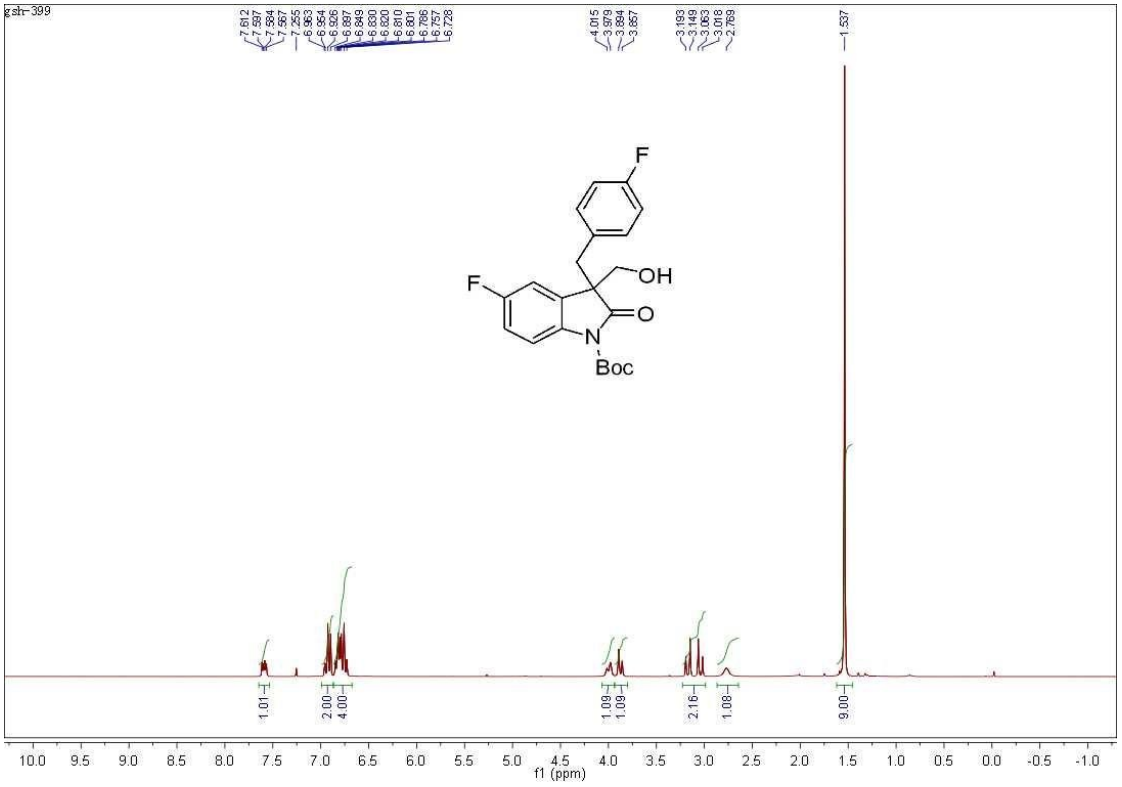

gsh-397
7.627
7.611
7.554
7.532
7.139
6.839
6.819
6.811
6.792
6.772
6.743
6.714
3.888
3.866
3.883
3.846
3.210
3.166
3.091
3.047
2.659
1.555
F
OH
O
N
Boc
1.00
1.18
2.14
4.24
1.09
1.07
2.22
1.01
9.71
f1 (ppm)

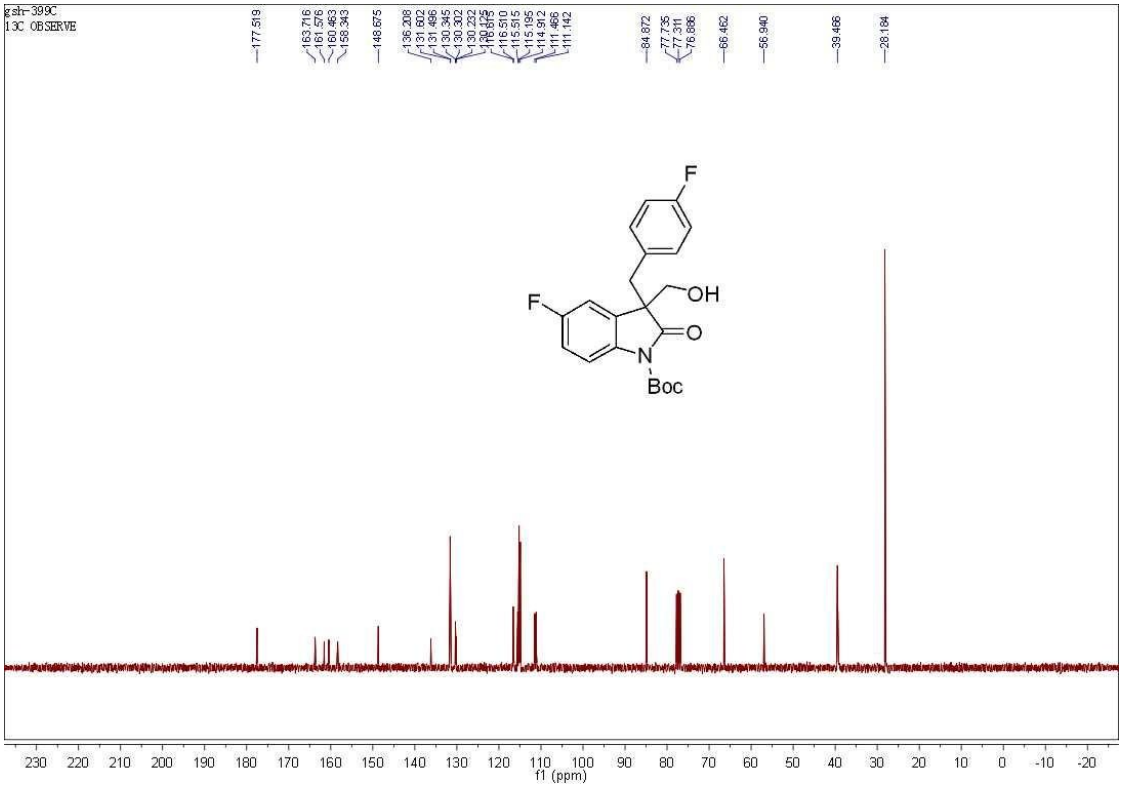

gsh-397C
13C OBSERVE
178.053
163.851
160.402
148.778
140.290
131.695
131.590
128.958
127.996
124.532
84.676
77.744
77.319
76.897
68.556
56.404
39.416
28.219
F
OH
O
N
Boc
f1 (ppm)

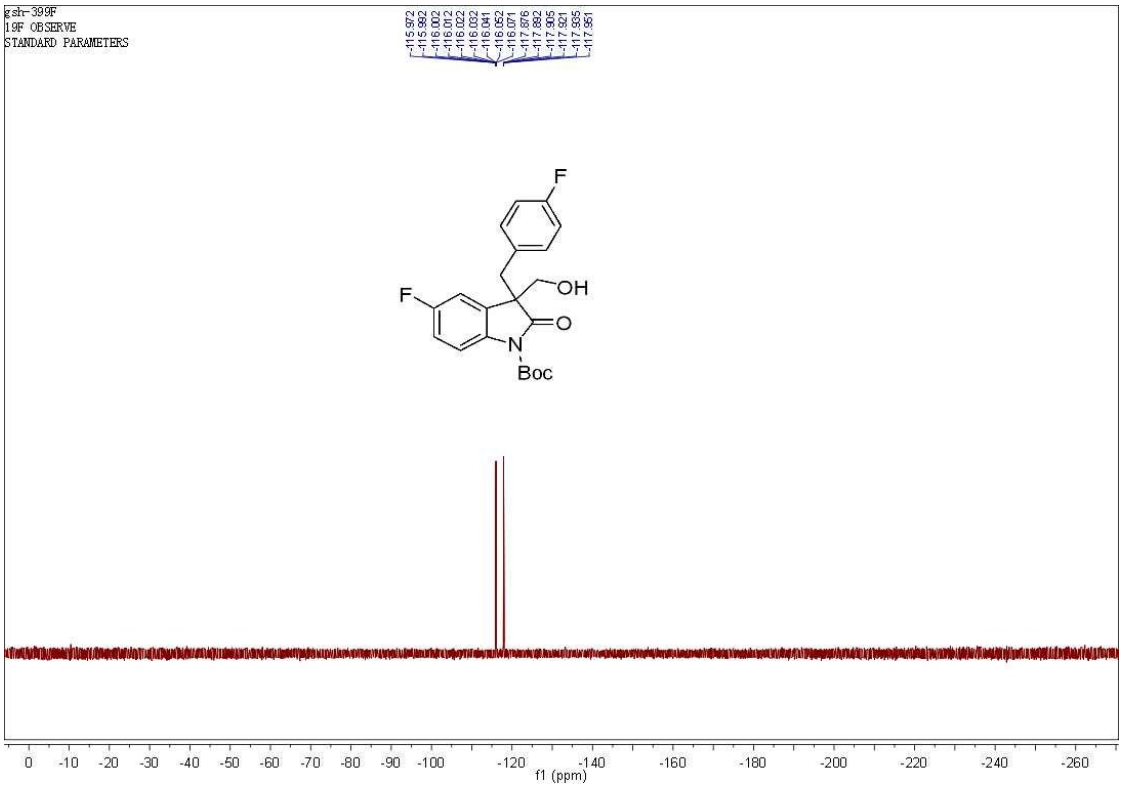

gsh-397F
19F OBSERVE
STANDARD PARAMETERS
-116.314
-116.334
-116.345
-116.355
-116.364
-116.384
-116.394
-116.414
F
OH
O
N
Boc
f1 (ppm)

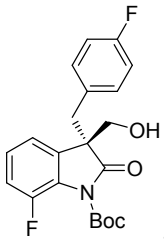

F
F
OH
O
N
Boc

**3l**

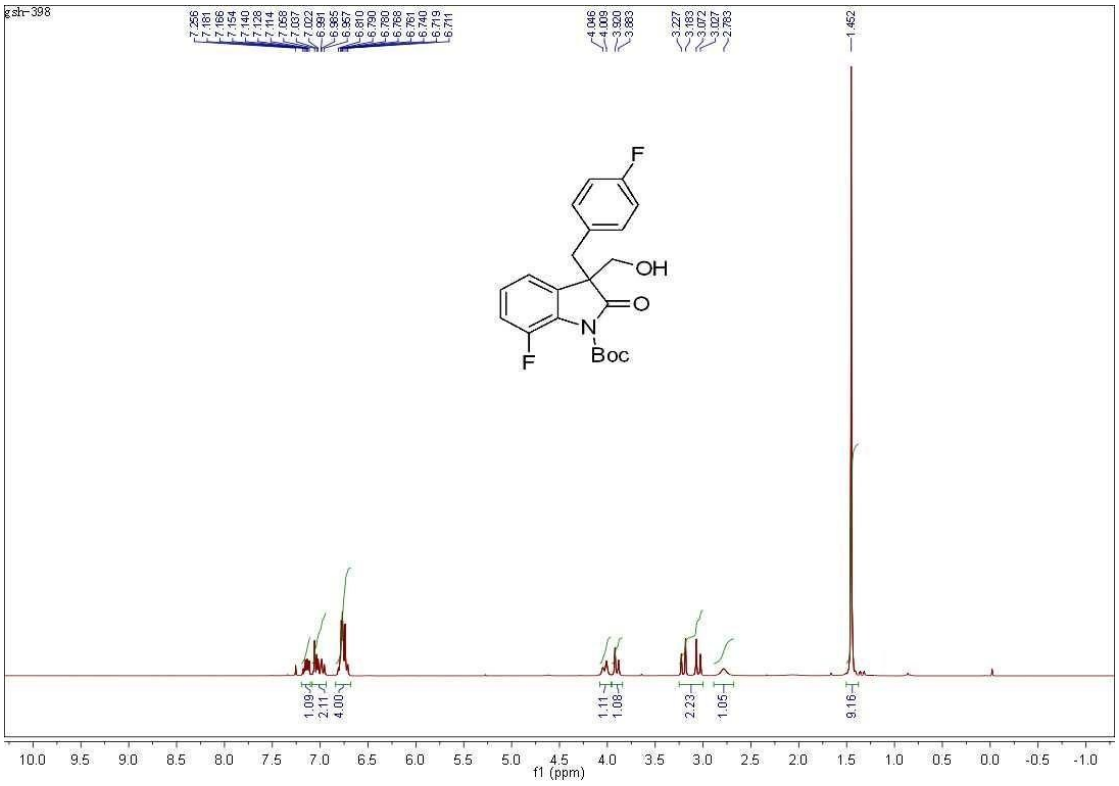

gsh-399
7.612
7.597
7.584
7.567
7.555
6.963
6.954
6.926
6.897
6.849
6.830
6.820
6.810
6.801
6.766
6.757
6.728
4.015
3.979
3.884
3.857
3.193
3.149
3.063
3.018
2.769
1.537
F
F
OH
O
N
Boc
1.01
2.00
4.00
1.09
1.09
2.16
1.08
9.00
f1 (ppm)

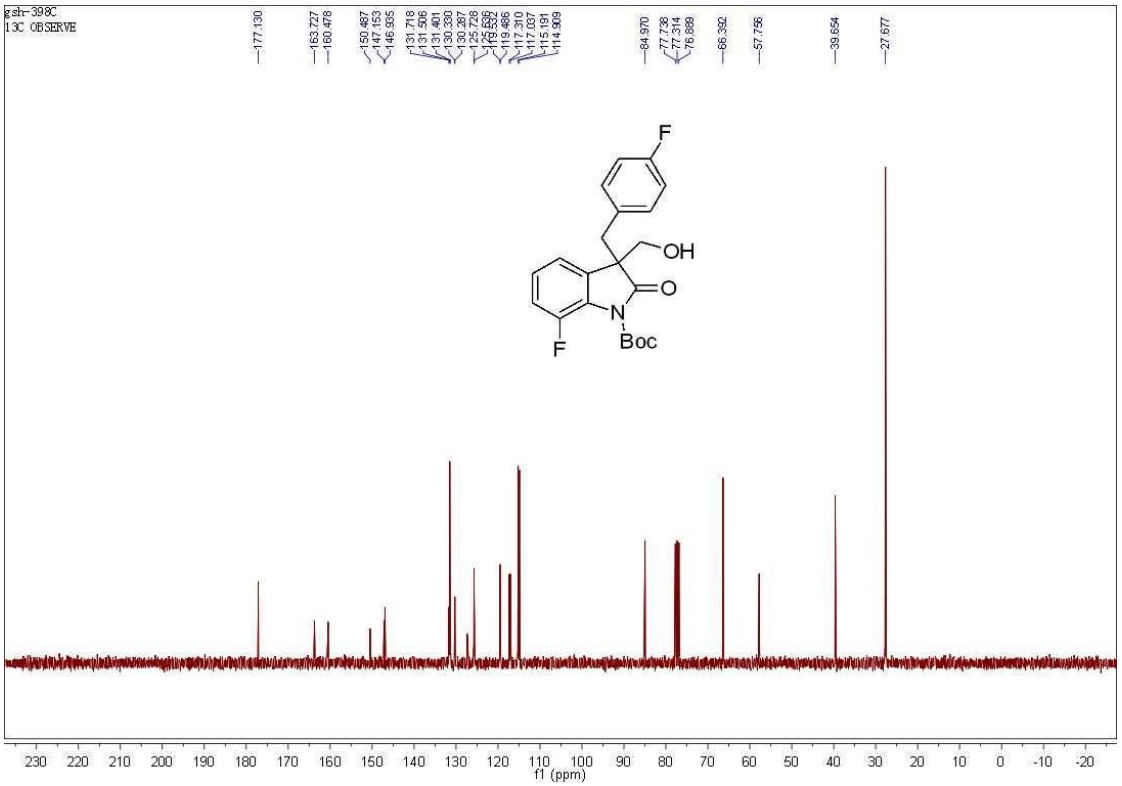

gsh-399C
13C OBSERVE
177.519
163.716
161.576
160.463
158.343
148.675
136.208
131.602
131.486
130.345
130.302
130.232
116.510
115.515
115.195
114.912
111.466
111.142
84.872
77.735
77.311
76.886
66.462
56.940
39.466
28.184
F
F
OH
O
N
Boc
f1 (ppm)

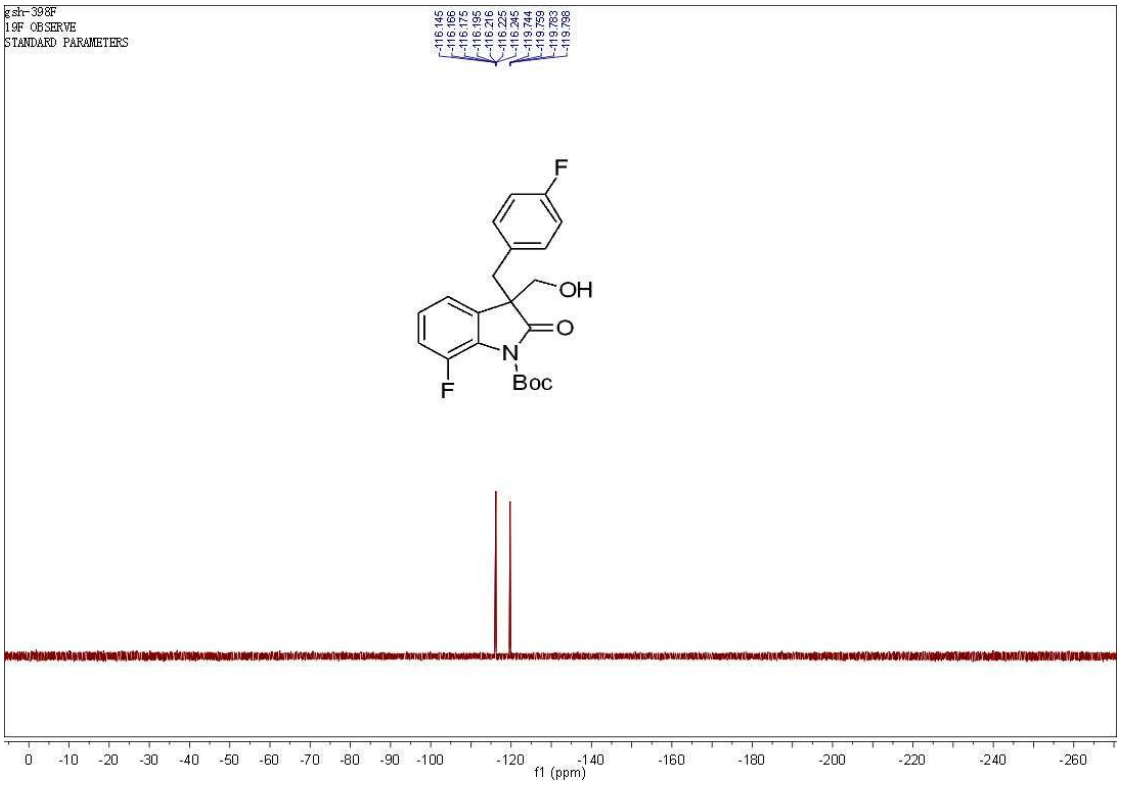

gsh-399F
19F OBSERVE
STANDARD PARAMETERS
F
OH
O
N
Boc
F
f1 (ppm)

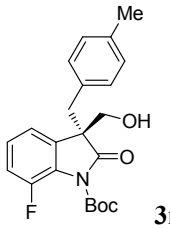

F
OH
O
N
Boc
F

**3m**

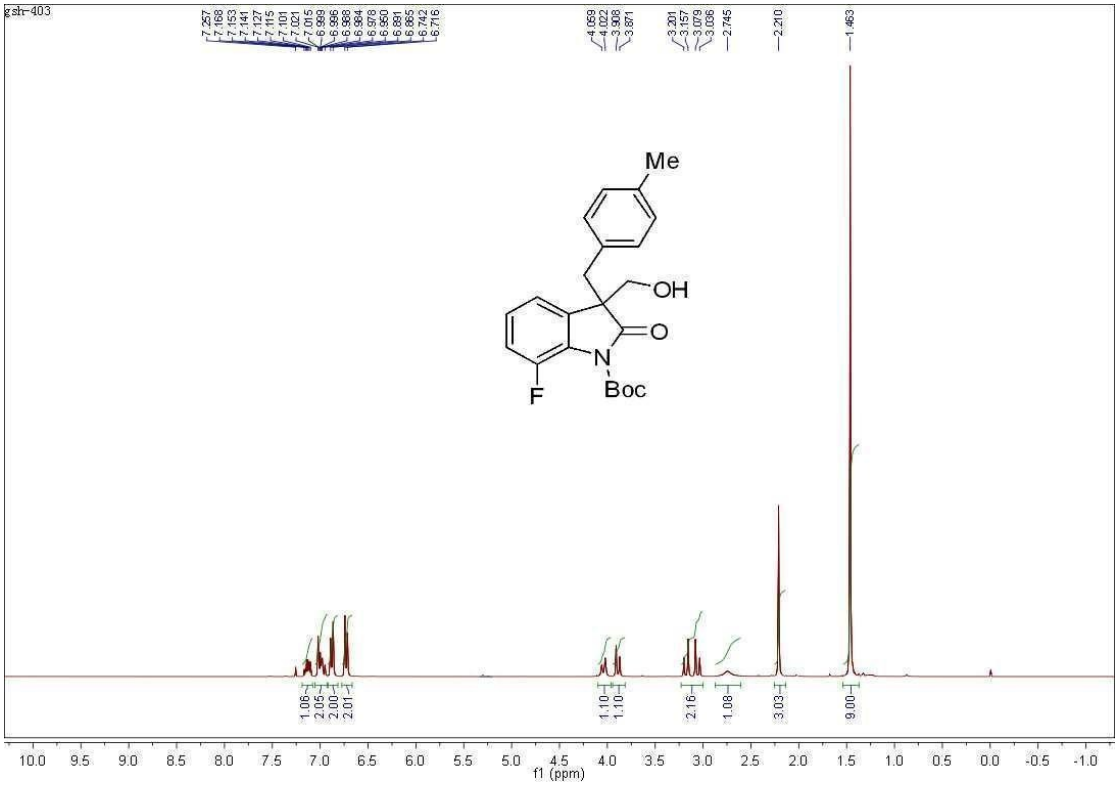

gsh-398
F
OH
O
N
Boc
F
f1 (ppm)

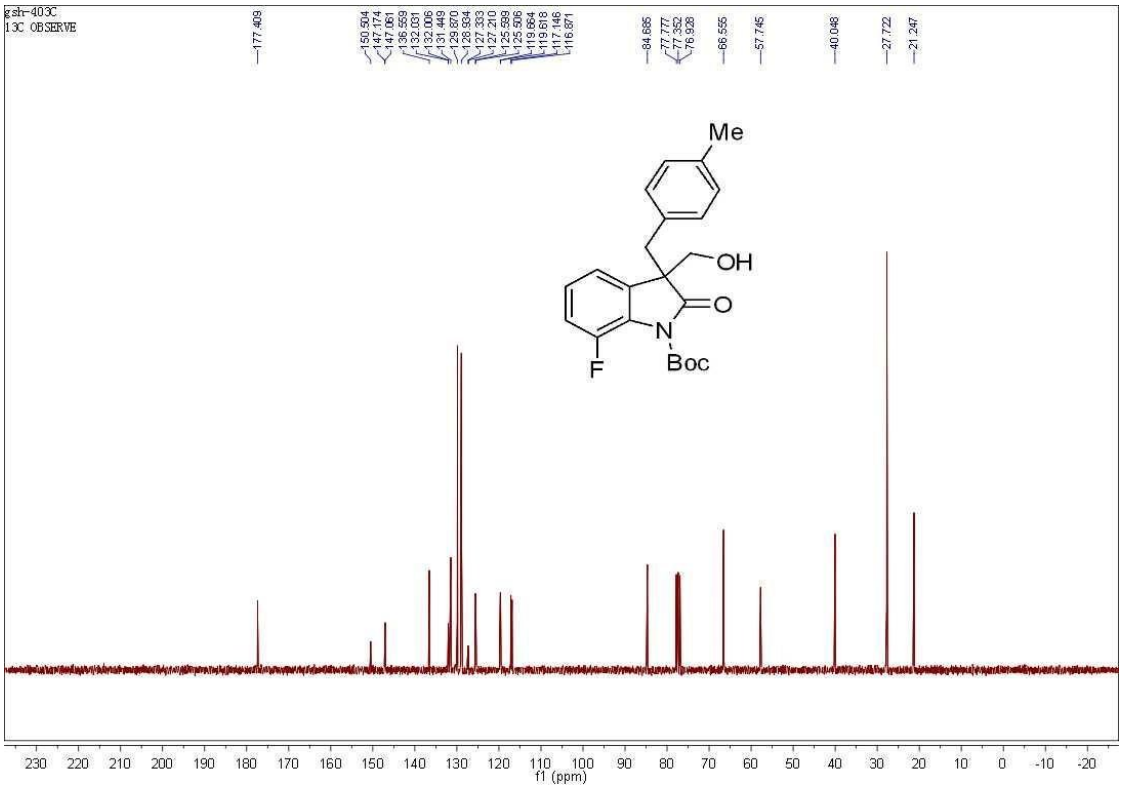

gsh-398C
13C OBSERVE
177.130
163.727
160.478
150.487
147.153
146.935
131.718
131.606
131.491
130.330
130.287
125.728
125.636
119.486
117.310
117.037
115.191
114.909
84.970
77.738
77.314
76.889
66.392
57.756
39.654
27.677
F
OH
O
N
Boc
F
f1 (ppm)

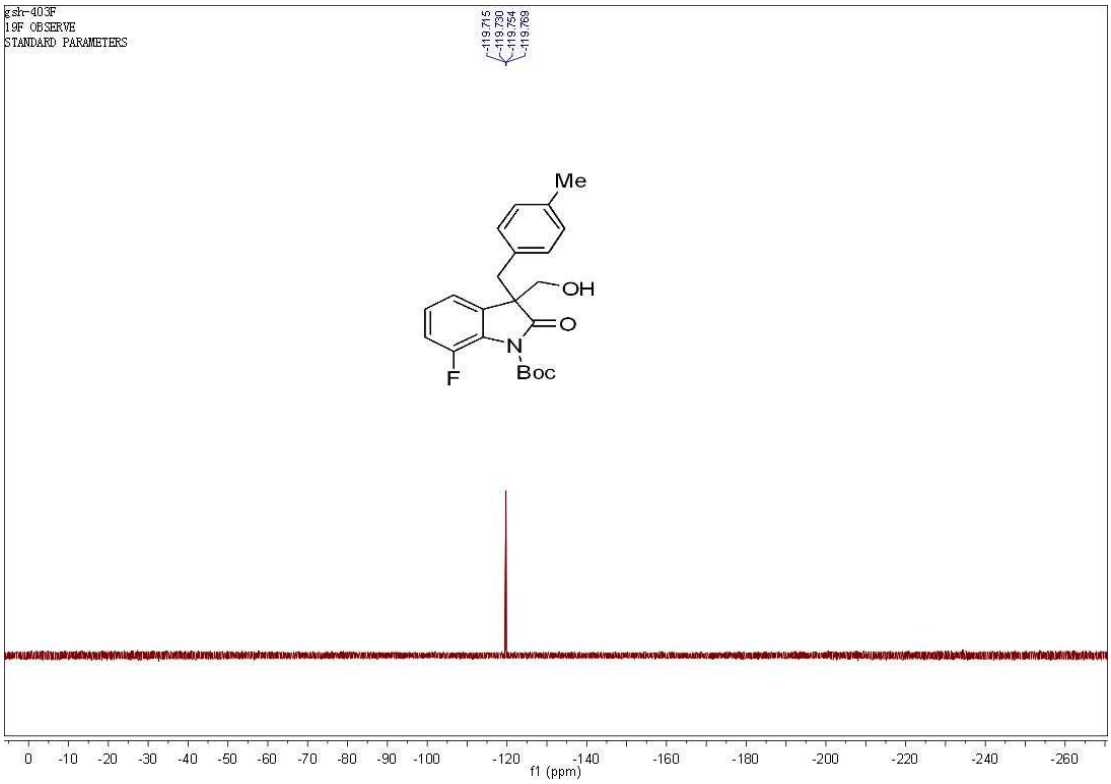

gsh-398F
19F OBSERVE
STANDARD PARAMETERS
-116.145
-116.166
-116.175
-116.195
-116.216
-116.225
-116.245
-119.744
-119.759
-119.783
-119.798
F
OH
O
N
Boc
F
f1 (ppm)

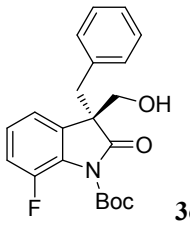

Me
OH
O
N
Boc
F

**3n**

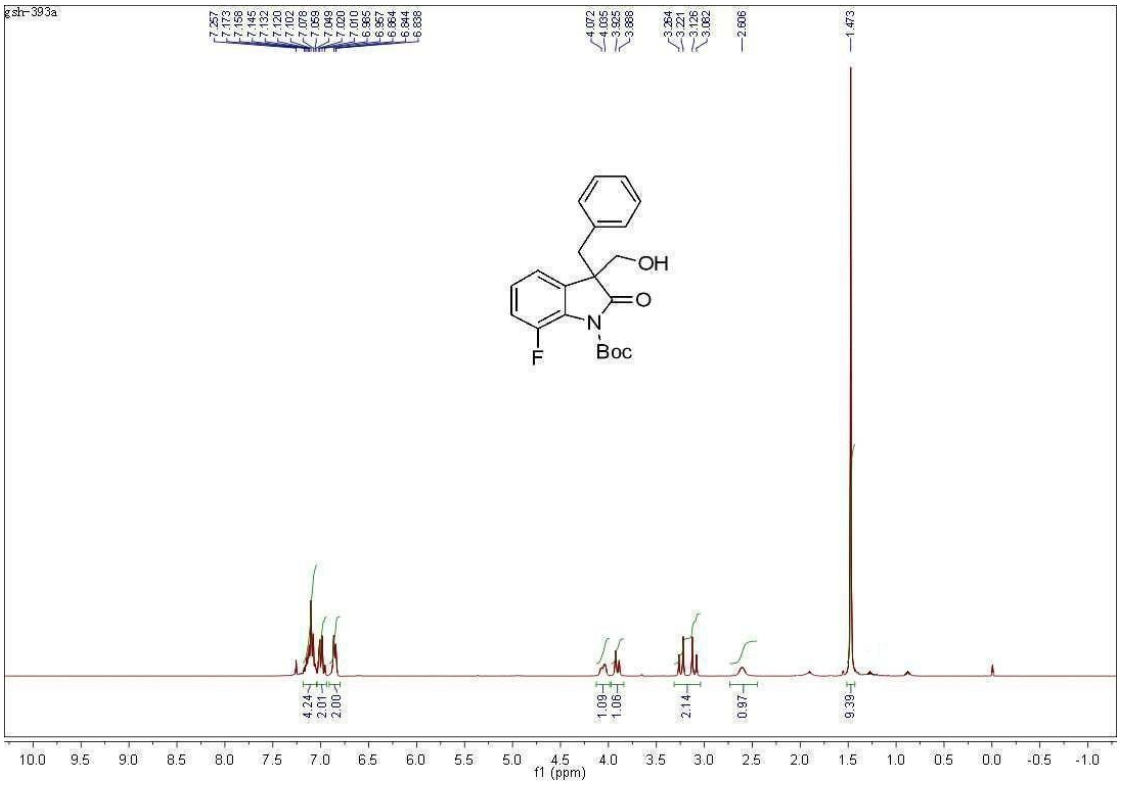

gsh-403
Me
OH
O
N
Boc
F
f1 (ppm)

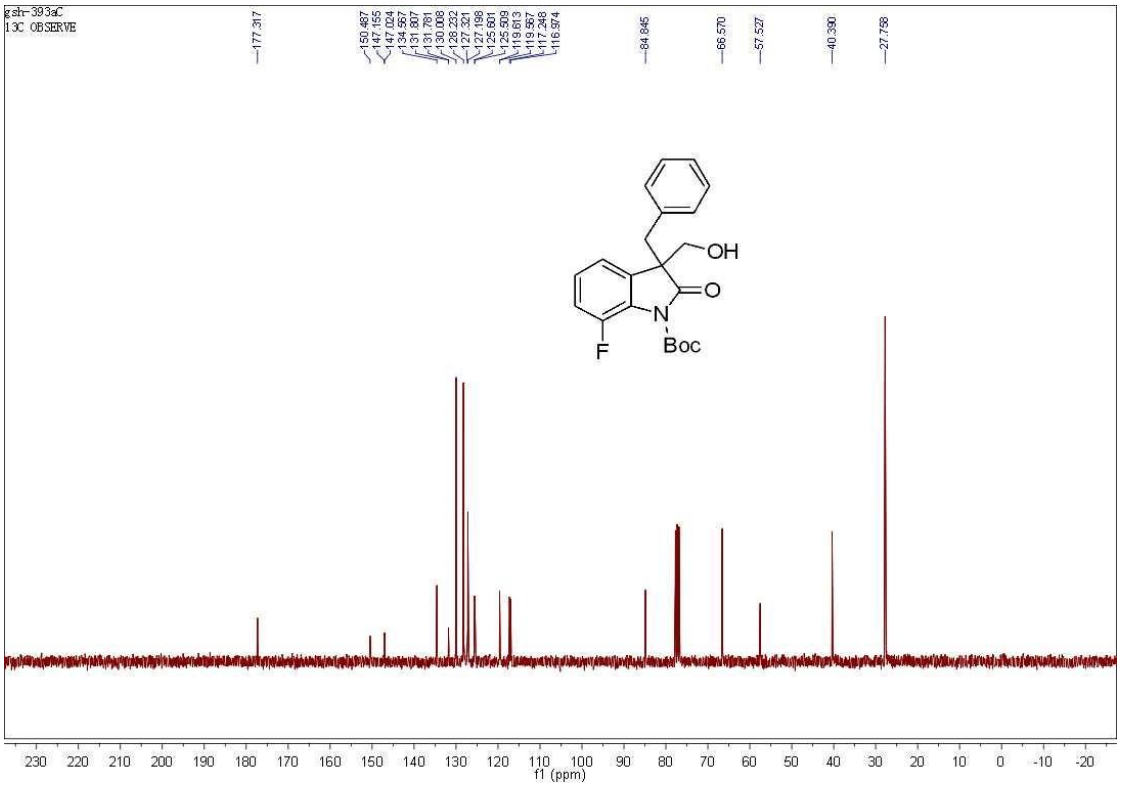

gsh-403C
13C OBSERVE
Me
OH
O
N
Boc
F
f1 (ppm)

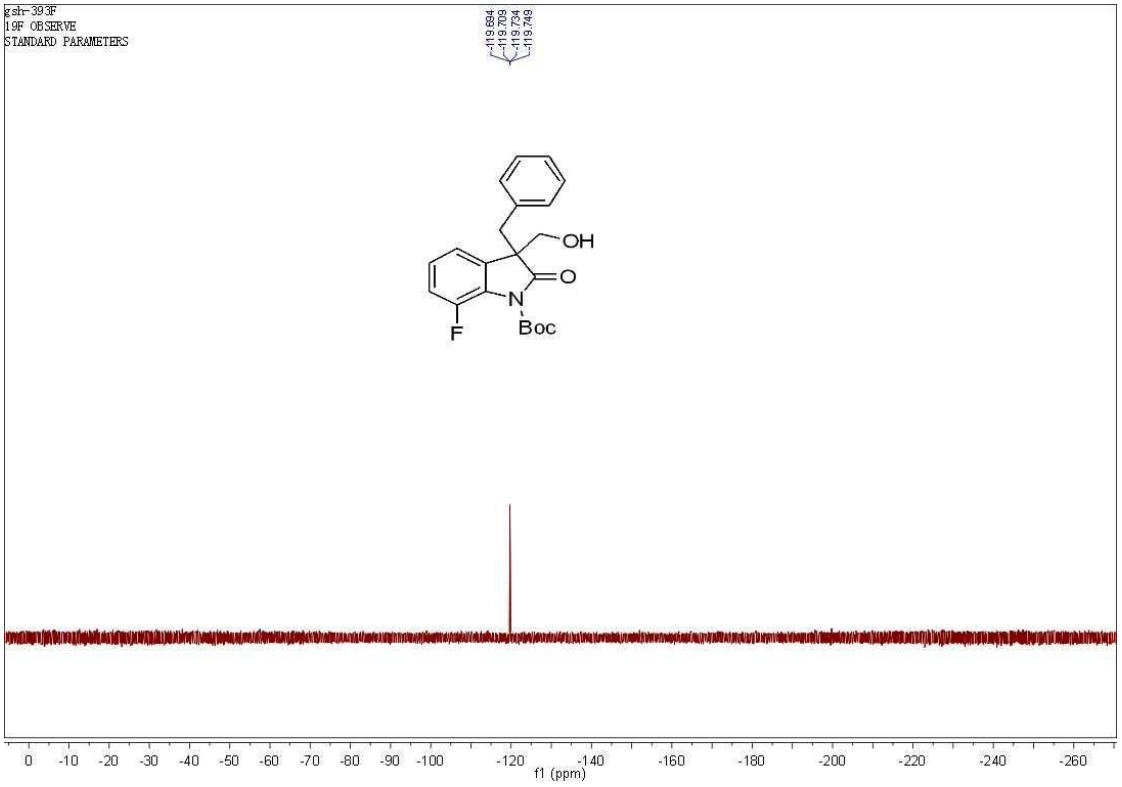

gsh-403F
19F OBSERVE
STANDARD PARAMETERS
-119.715
-119.730
-119.754
-119.769
Me
OH
O
N
Boc
F
f1 (ppm)

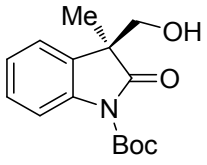

OH
O
N
Boc
F

**3o**

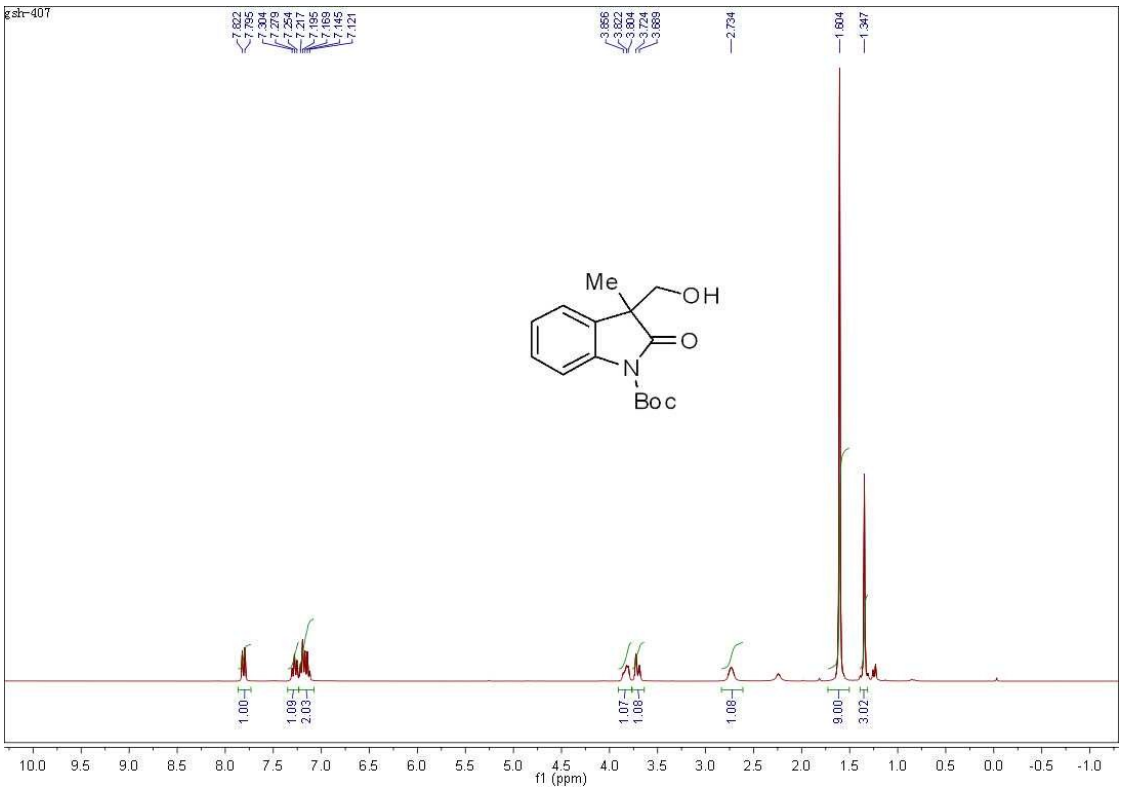

gsh-393a
7.357
7.173
7.168
7.145
7.132
7.120
7.102
7.078
7.059
7.049
7.000
6.865
6.857
6.844
6.838
4.072
4.025
3.925
3.888
3.264
3.221
3.126
3.082
2.606
1.473
OH
O
N
Boc
F
4.24
2.01
2.00
1.09
1.06
2.14
0.97
9.39
f1 (ppm)

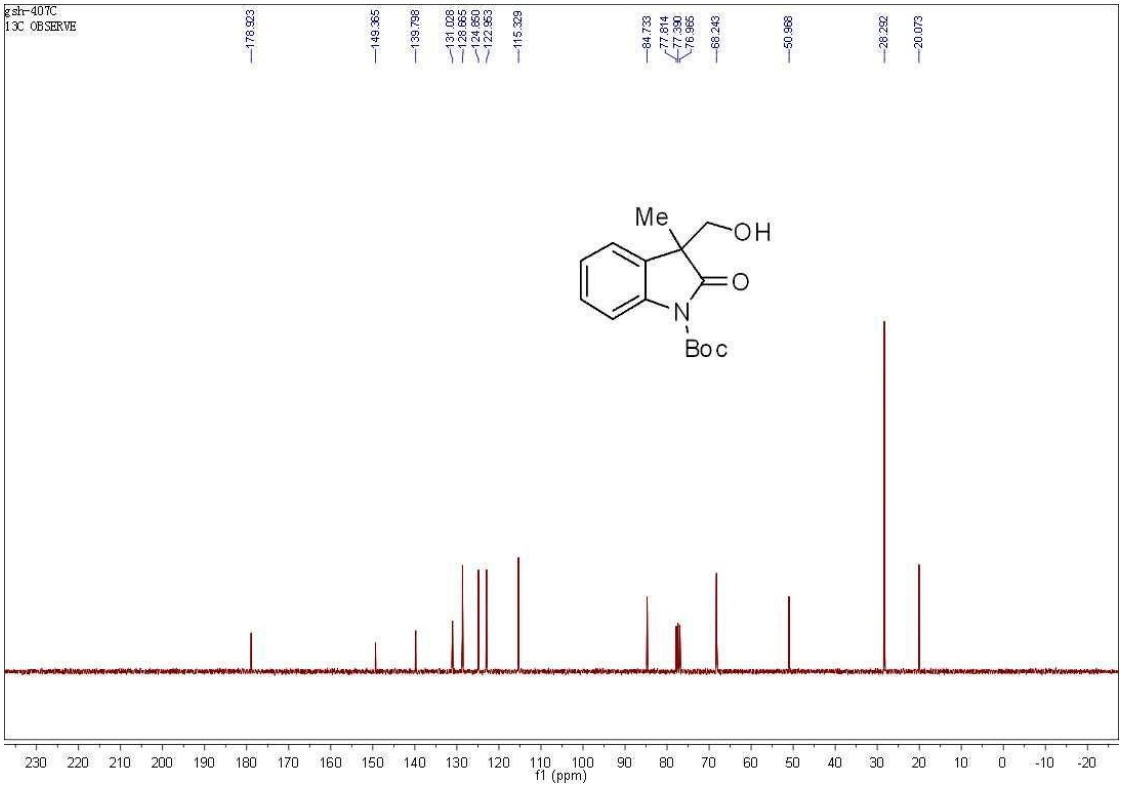

gsh-393aC
13C OBSERVE
177.317
150.487
147.155
147.024
134.567
131.807
131.781
130.008
128.232
127.321
127.198
125.951
125.909
119.613
119.567
117.248
116.974
84.845
66.570
57.527
40.390
27.758
OH
O
N
Boc
F
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

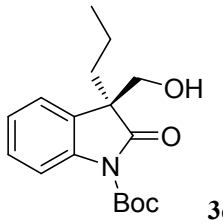

gsh-393F
19F OBSERVE
STANDARD PARAMETERS
-119.684
-119.709
-119.734
-119.749
OH
O
N
Boc
F
0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200 -220 -240 -260
f1 (ppm)


Me
OH
O
N
Boc

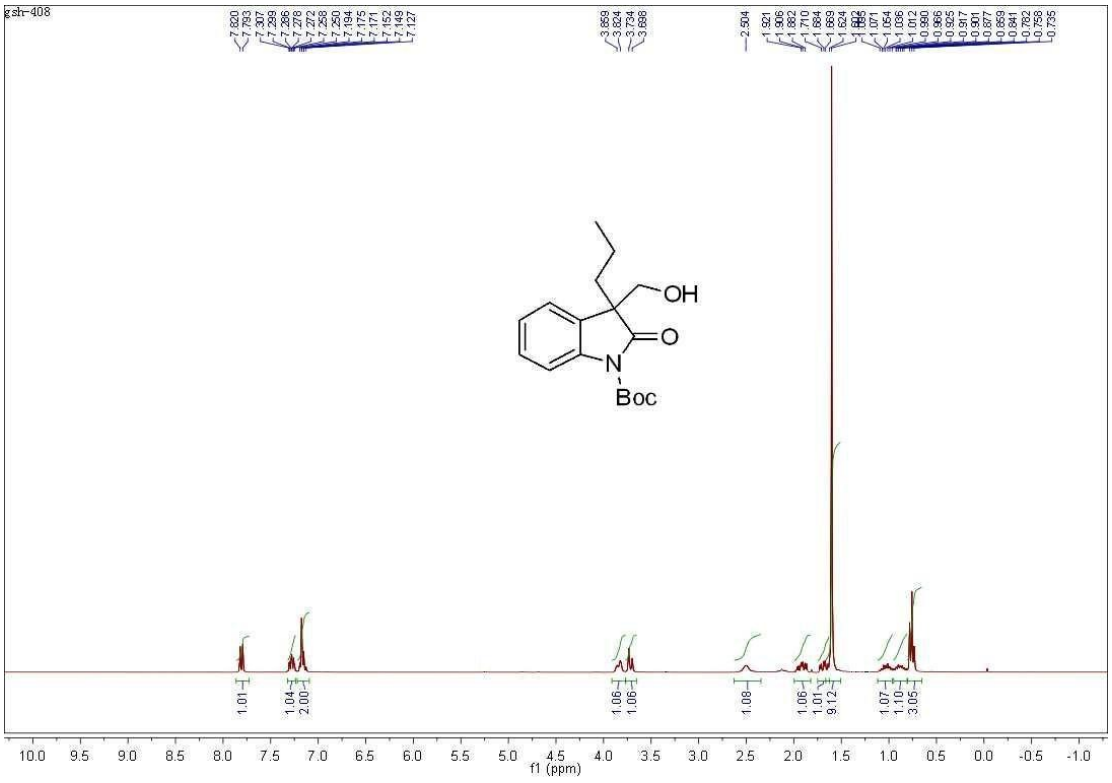
**3p**

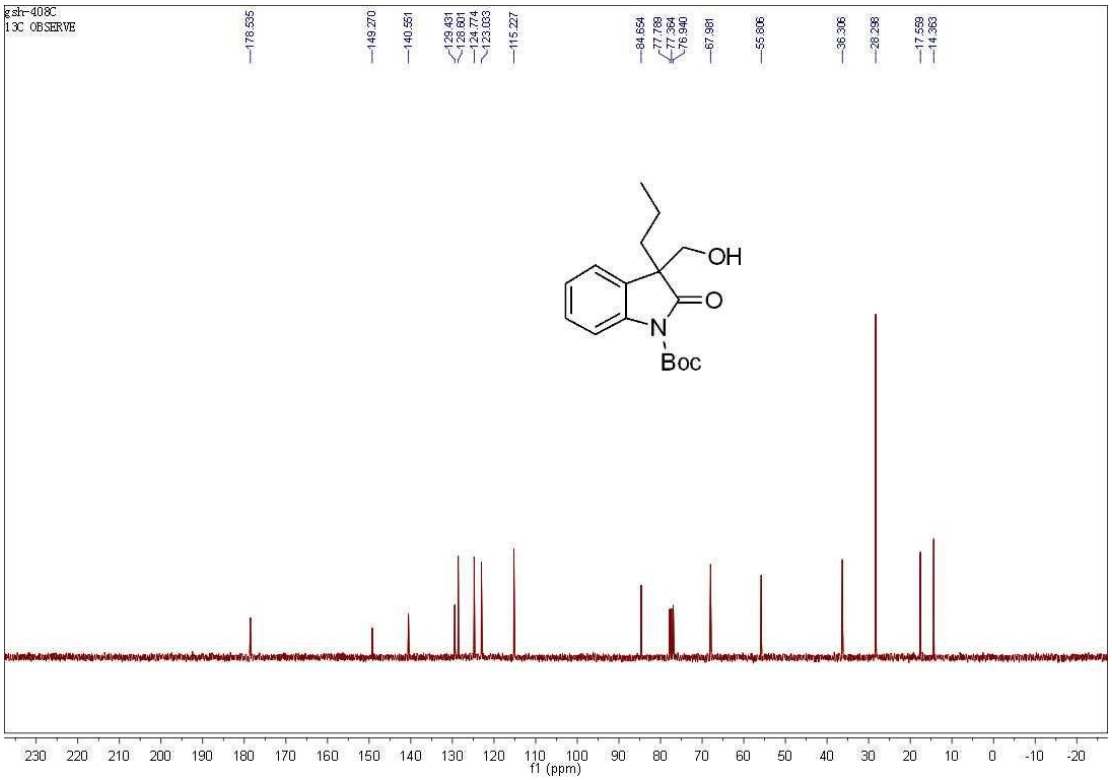

gsh-407
7.822
7.795
7.304
7.279
7.254
7.217
7.195
7.169
7.145
7.121
3.856
3.837
3.804
3.724
3.689
2.734
1.604
1.347
Me
OH
O
N
Boc
1.00
1.09
2.03
1.07
1.08
1.08
9.00
3.02
f1 (ppm)

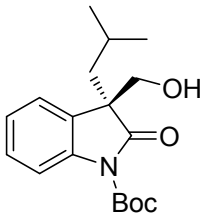

gsh-407C
13C OBSERVE
178.923
149.365
139.798
131.008
128.665
124.650
122.953
115.329
84.733
77.814
77.390
76.965
68.243
50.988
28.292
20.073
Me
OH
O
N
Boc
f1 (ppm)


OH
O
N
Boc

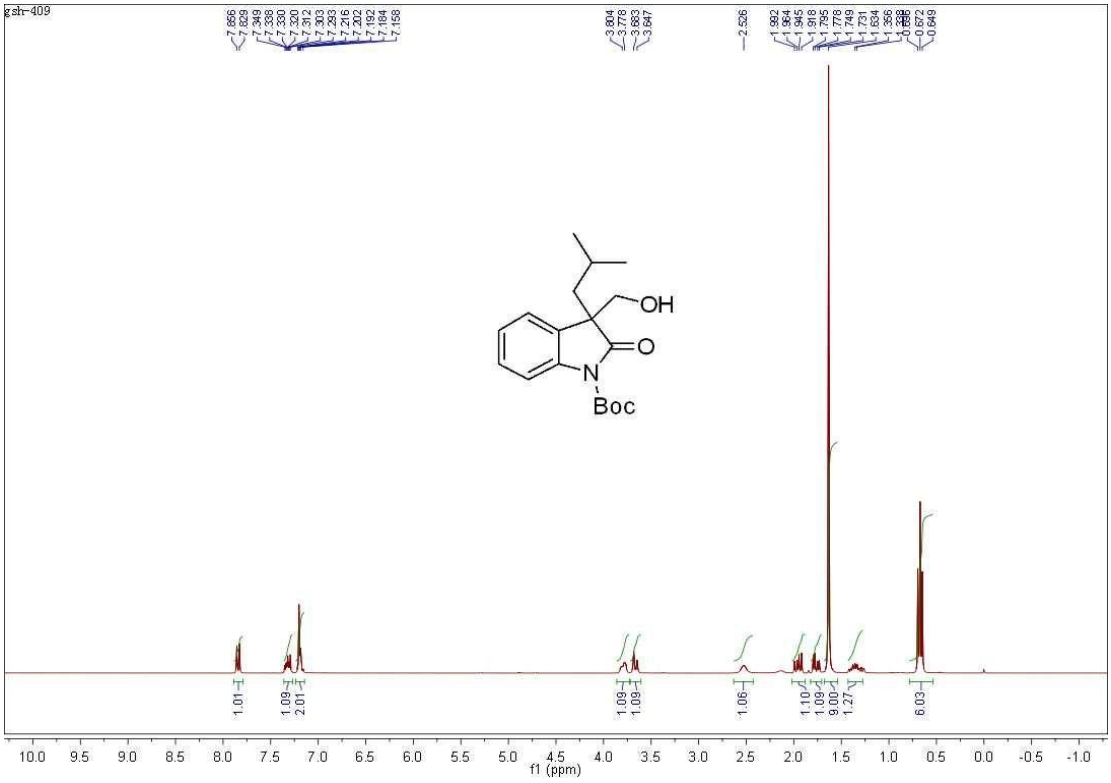
**3q**

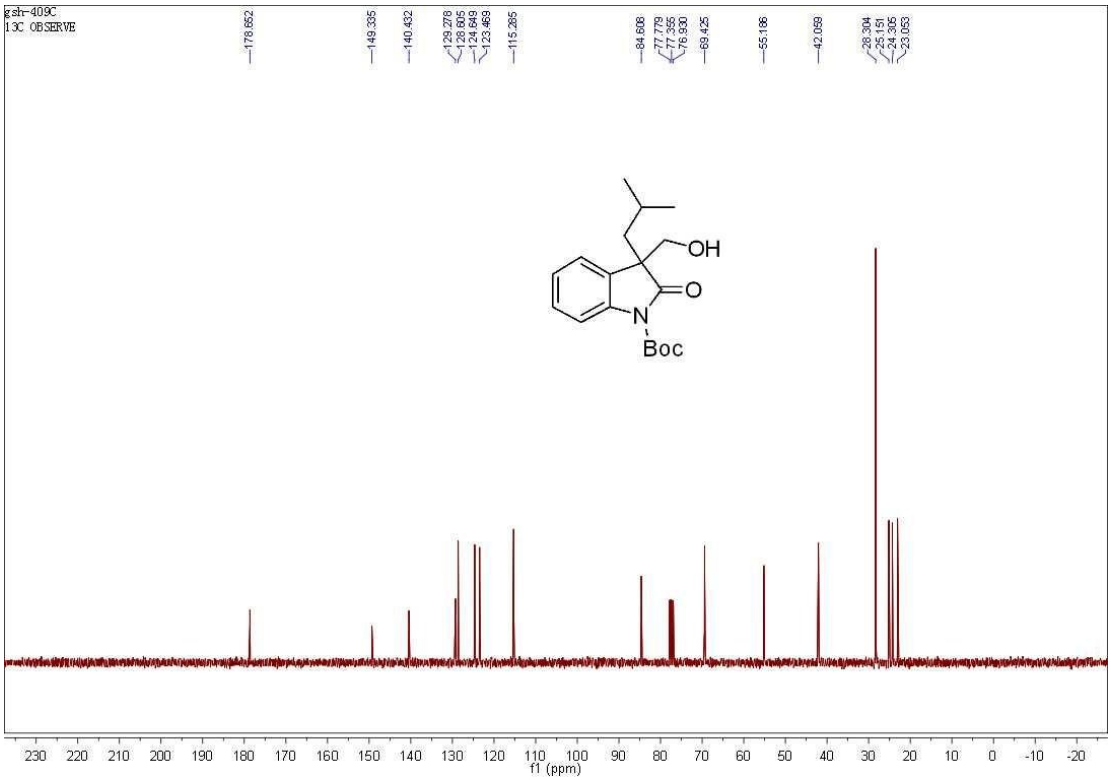

gsh-408
OH
O
N
Boc
f1 (ppm)

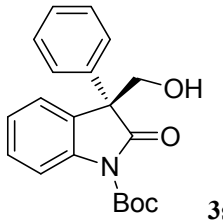

gsh-408C
13C OBSERVE
OH
O
N
Boc
f1 (ppm)


OH
O
N
Boc

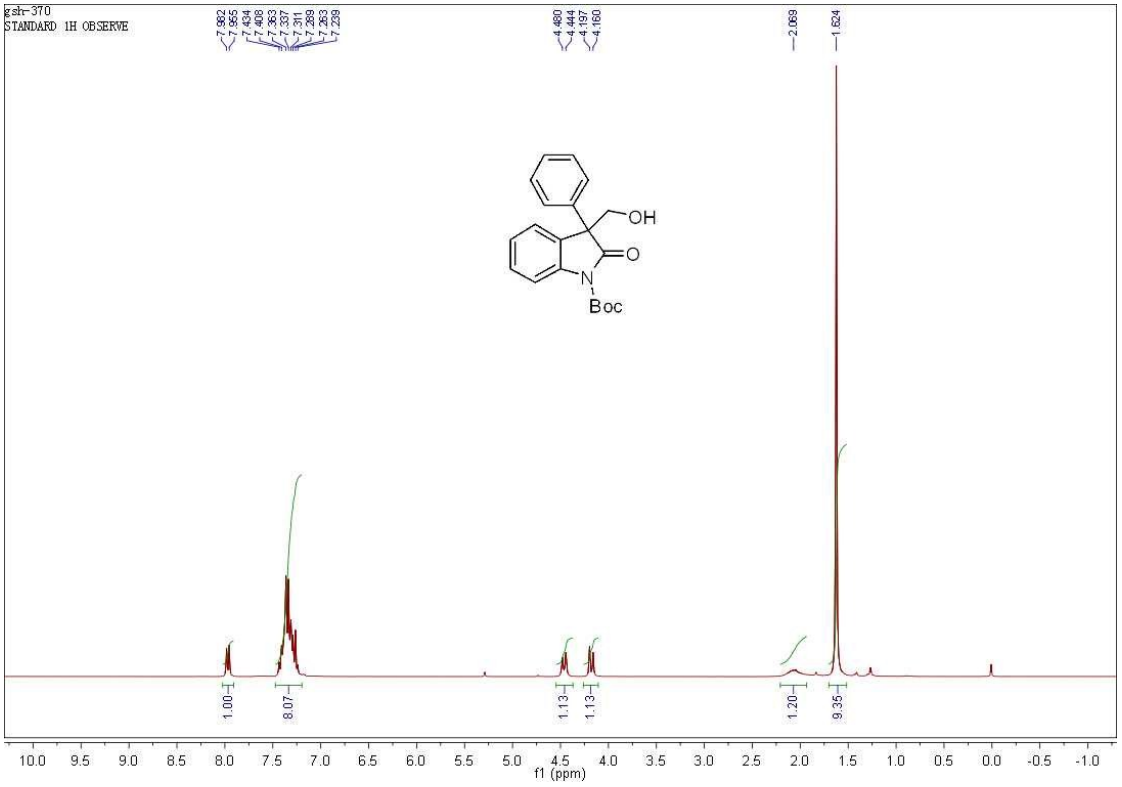
**3r**

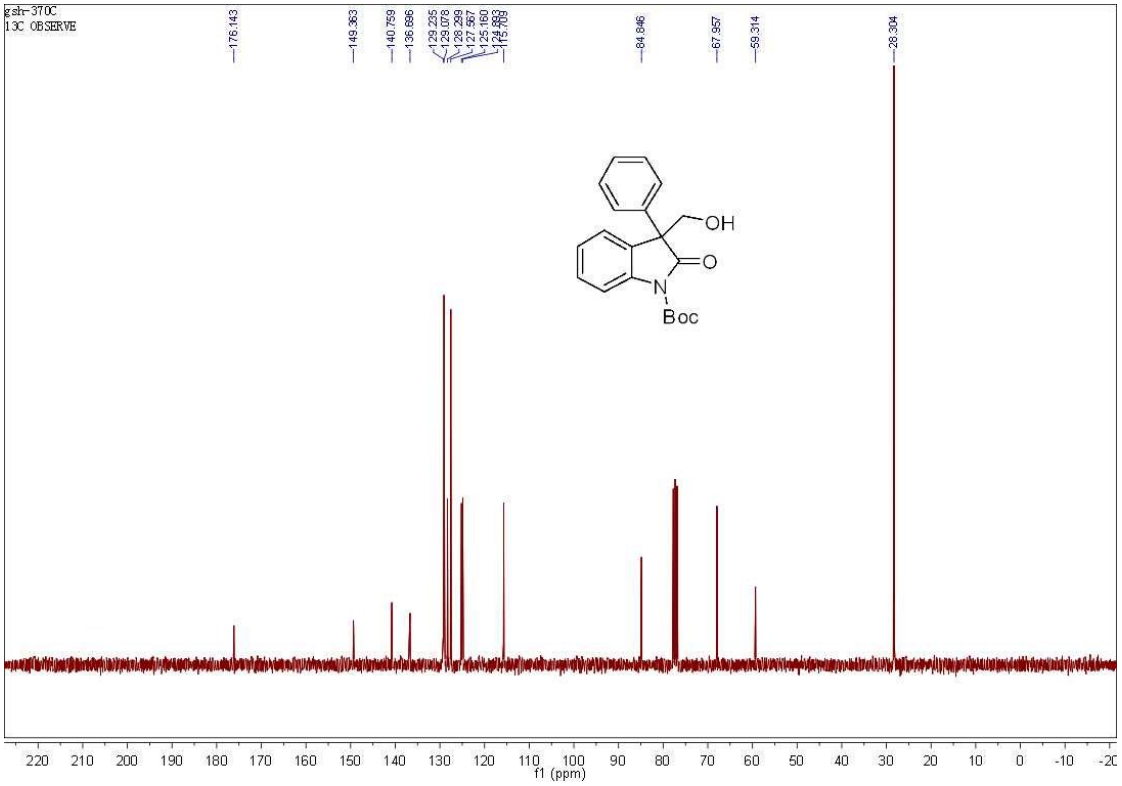

gsh-409
OH
O
N
Boc
f1 (ppm)

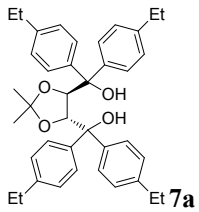

gsh-409C
13C OBSERVE
OH
O
N
Boc
f1 (ppm)


OH
O
N
Boc

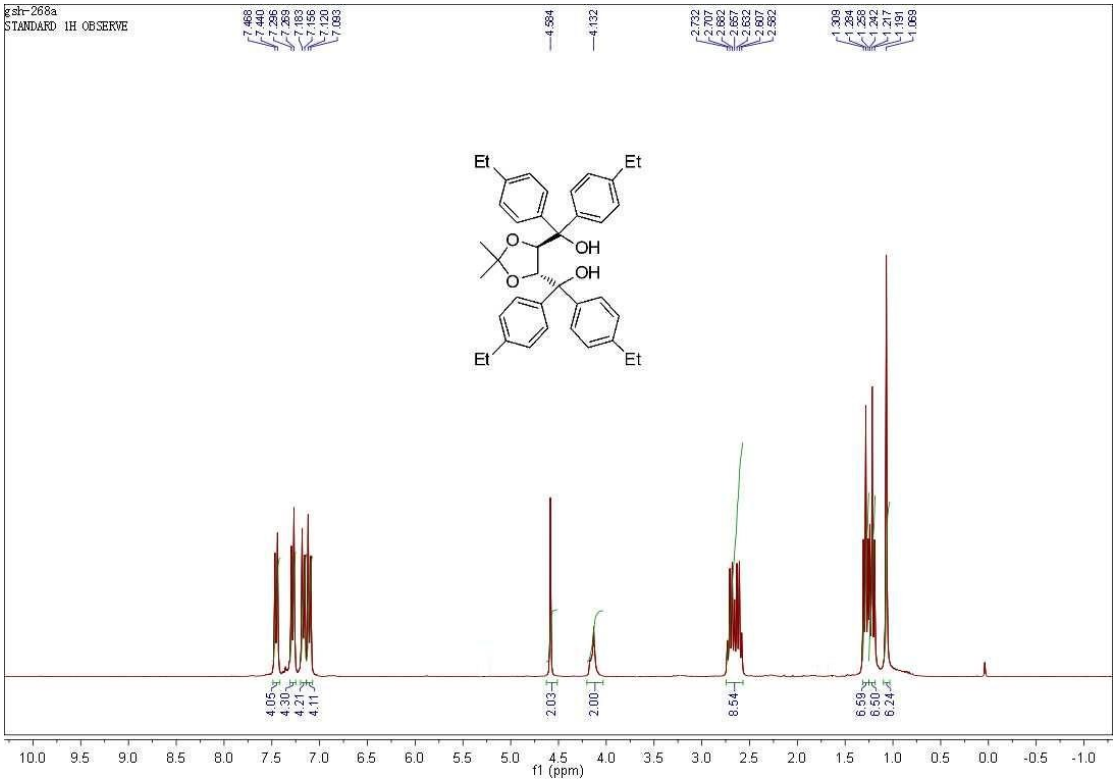
**3s**

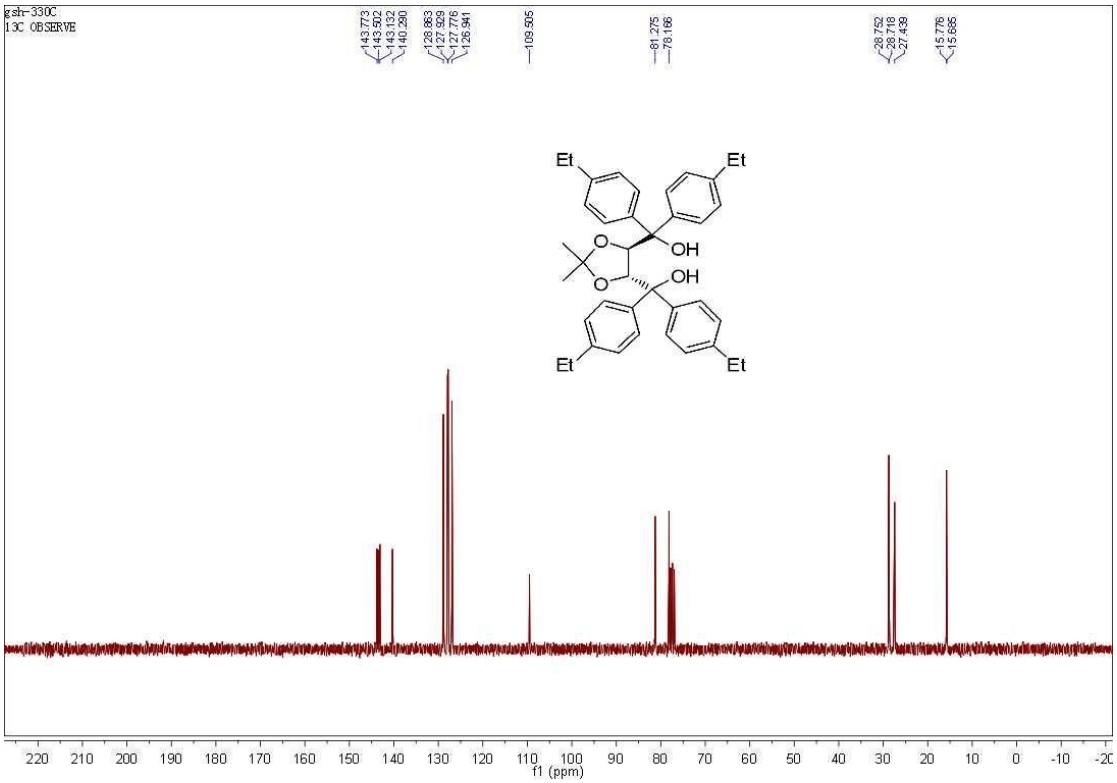

gsh-370
STANDARD 1H OBSERVE
7.982
7.955
7.434
7.408
7.363
7.337
7.311
7.289
7.263
7.239
4.460
4.444
4.197
4.160
2.069
1.624
OH
O
N
Boc
1.00
8.07
1.13
1.13
1.20
9.35
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

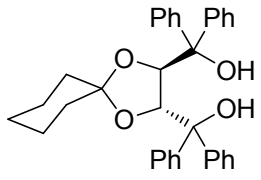

gsh-370C
13C OBSERVE
176.143
149.363
140.759
136.686
129.235
129.078
128.299
127.567
125.160
84.846
67.957
59.314
28.304
OH
O
N
Boc
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


Et
Et
OH
OH
Et
Et

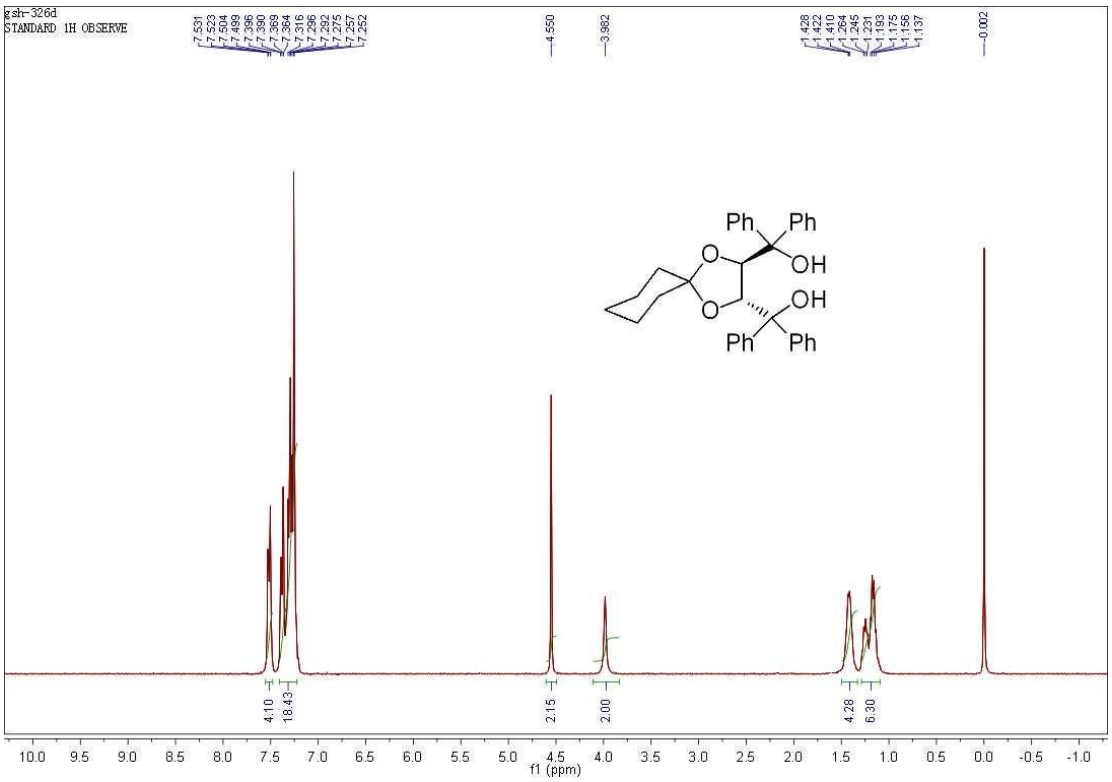
**7a**

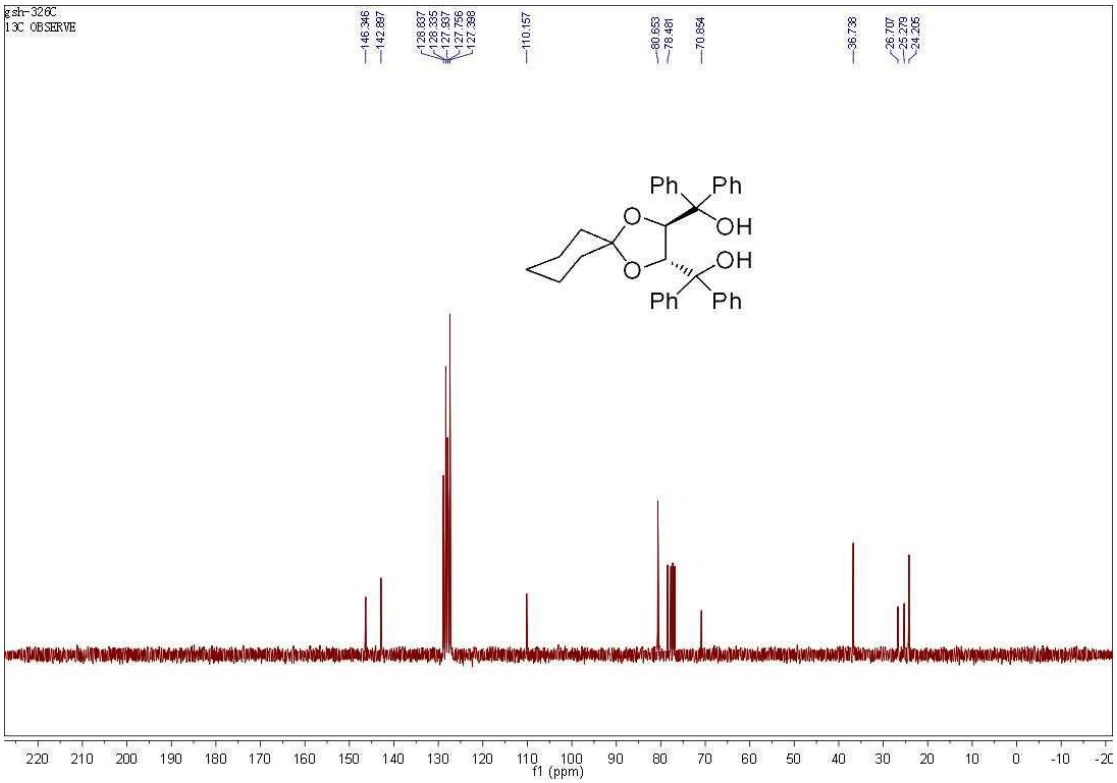

gsh-268a
STANDARD 1H OBSERVE
7.468
7.440
7.296
7.269
7.183
7.156
7.103
7.083
4.504
4.132
2.732
2.707
2.682
2.657
2.632
2.607
2.582
1.309
1.284
1.258
1.242
1.217
1.191
1.169
4.05
4.30
4.21
4.11
2.03
2.00
8.54
6.59
6.50
6.24
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

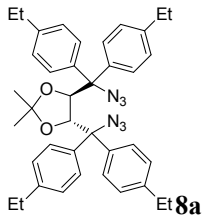

gsh-330C
13C OBSERVE
143.773
143.502
143.132
140.290
128.863
127.529
127.176
126.941
109.505
81.275
78.166
28.752
28.718
27.439
15.776
15.685
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)


Ph
Ph
O
OH
O
OH
Ph
Ph

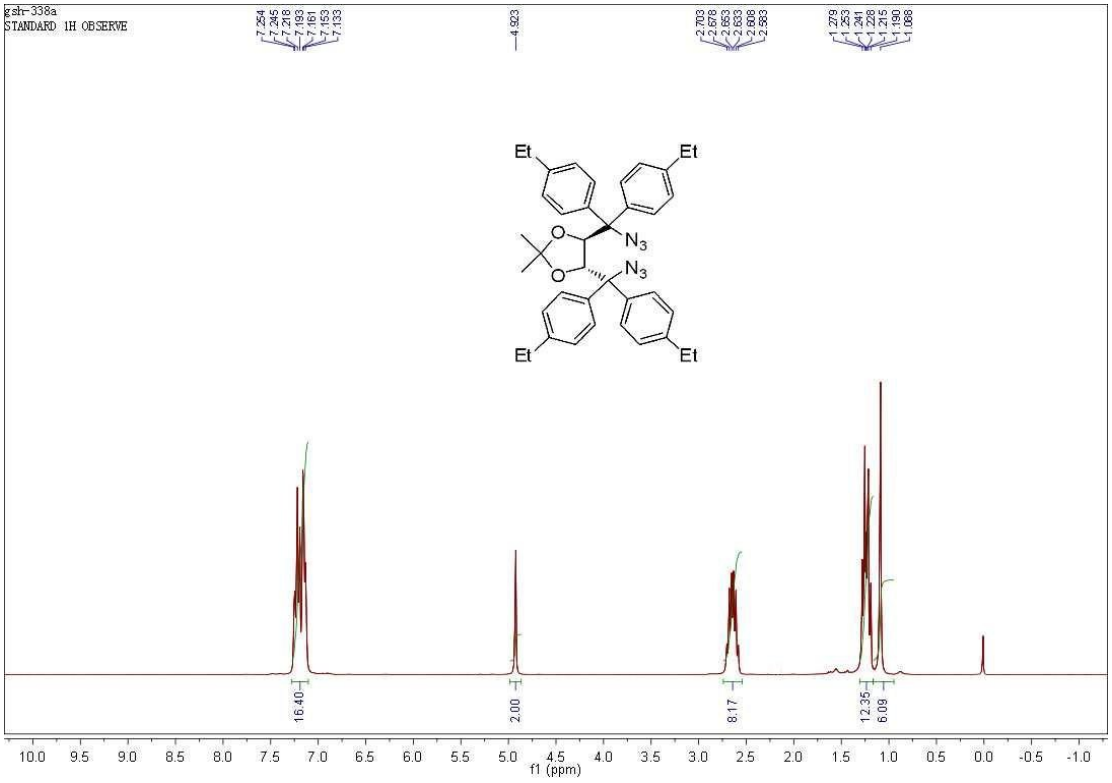
**7b**

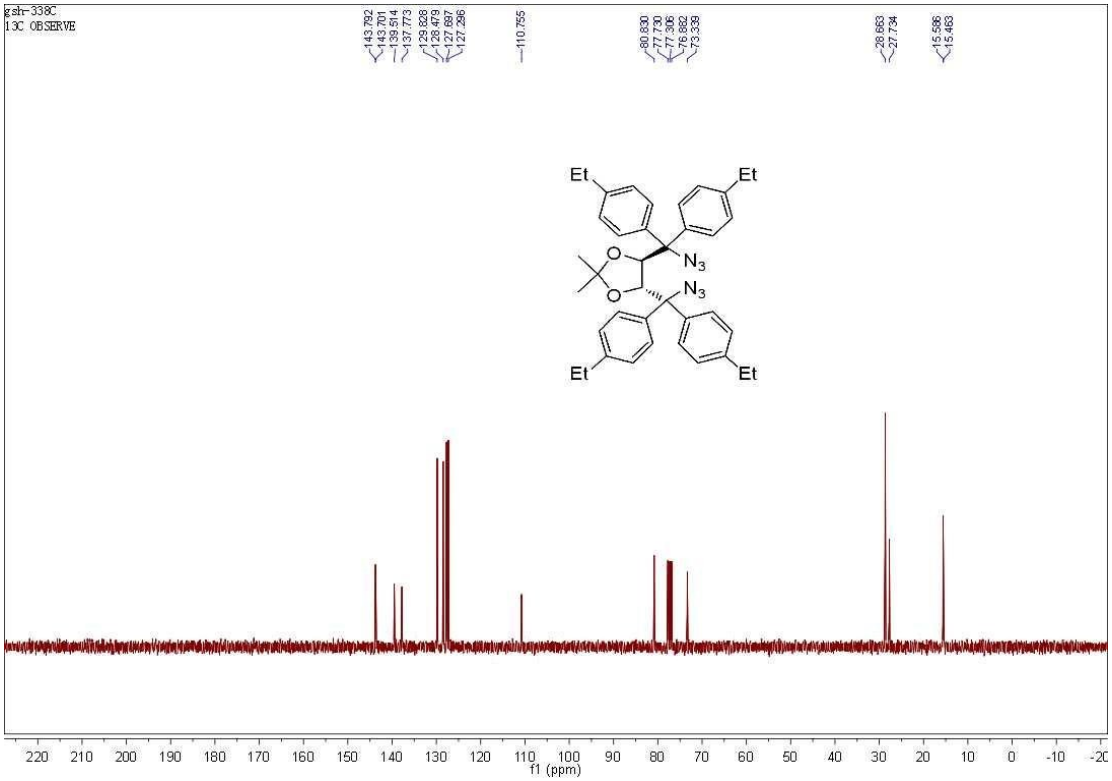

gsh-326d
STANDARD 1H OBSERVE
7.531
7.523
7.504
7.499
7.396
7.390
7.389
7.364
7.316
7.296
7.292
7.275
7.257
7.252
4.550
3.982
1.428
1.422
1.410
1.264
1.245
1.231
1.193
1.175
1.156
1.137
0.002
4.10
18.43
2.15
2.00
4.28
6.30
f1 (ppm)

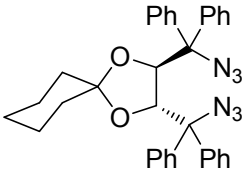

gsh-326C
13C OBSERVE
146.346
142.897
128.837
128.335
127.937
127.756
127.398
110.157
80.653
78.481
70.854
36.738
26.707
25.279
24.205
f1 (ppm)


Et
Et
O
N3
N3
O
Et
Et

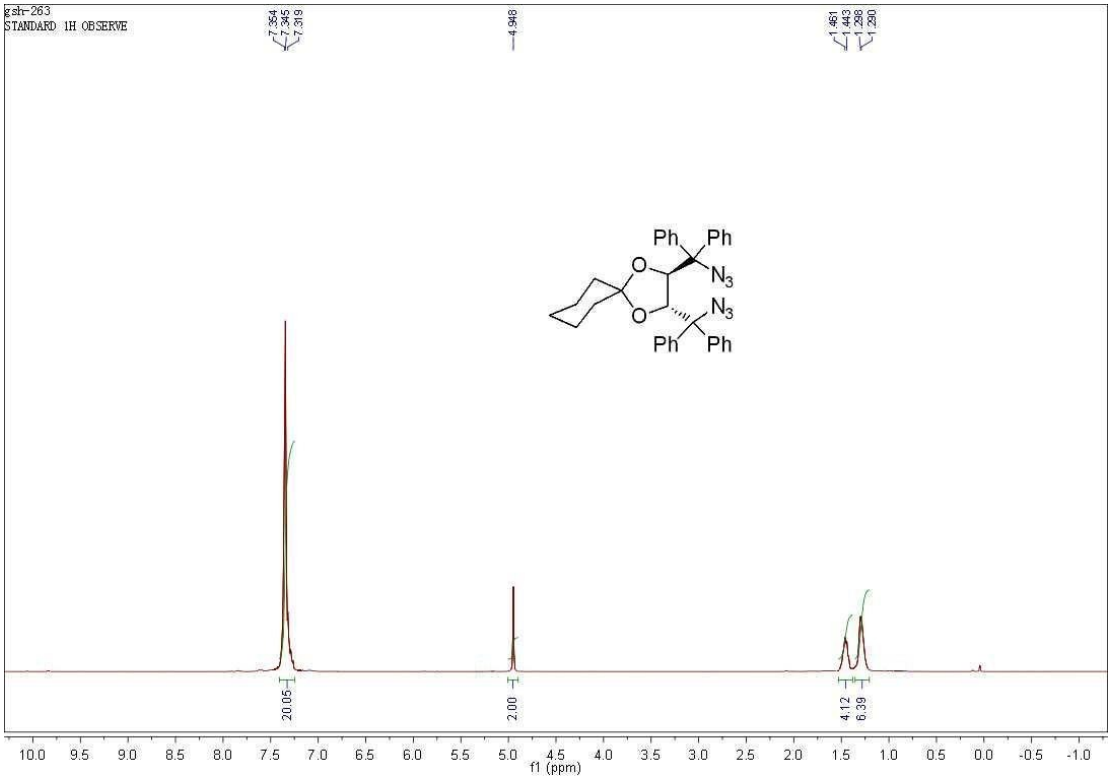
**8a**

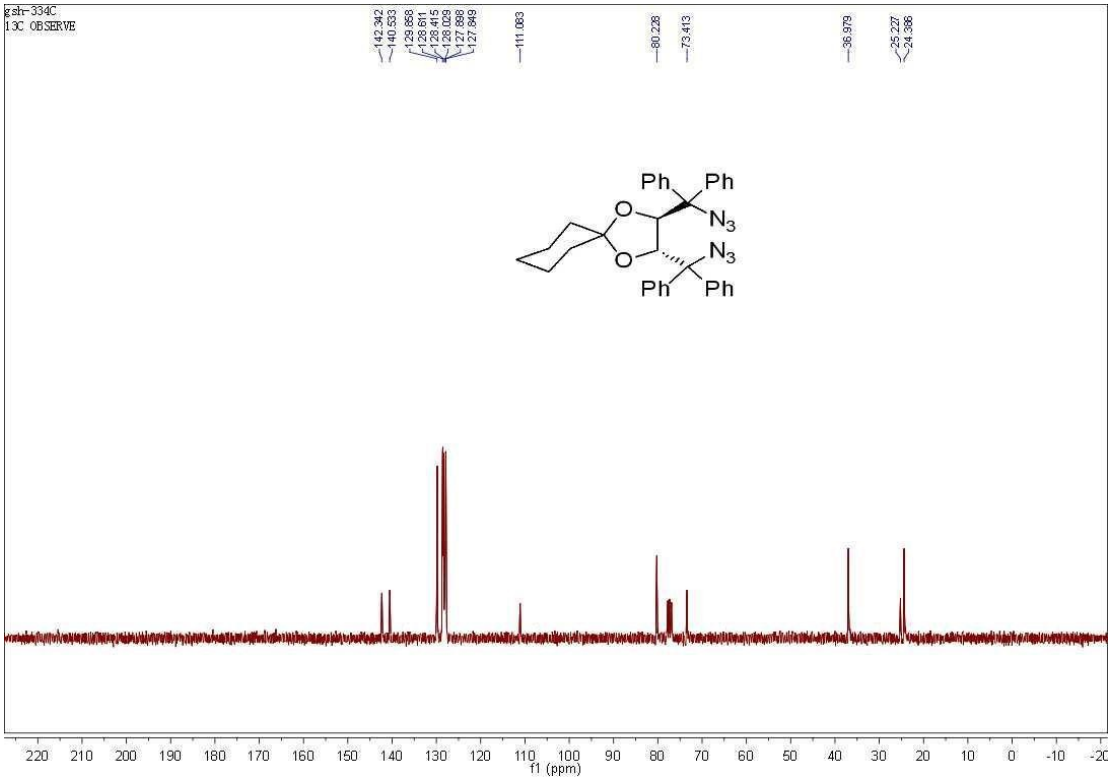

gsh-338a
STANDARD 1H OBSERVE
7.254
7.245
7.218
7.193
7.161
7.153
7.133
4.923
2.703
2.678
2.653
2.633
2.608
2.583
1.279
1.253
1.241
1.228
1.215
1.190
1.088
Et
Et
N3
N3
Et
Et
16.40
2.00
8.17
12.35
6.09
f1 (ppm)

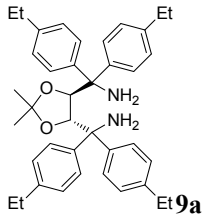

gsh-338C
13C OBSERVE
143.792
143.701
139.914
137.773
129.628
128.469
127.897
127.296
110.755
80.830
77.730
77.306
76.882
73.339
28.663
27.734
15.586
15.463
Et
Et
N3
N3
Et
Et
f1 (ppm)


Ph
Ph
O
N3
N3
O
Ph
Ph

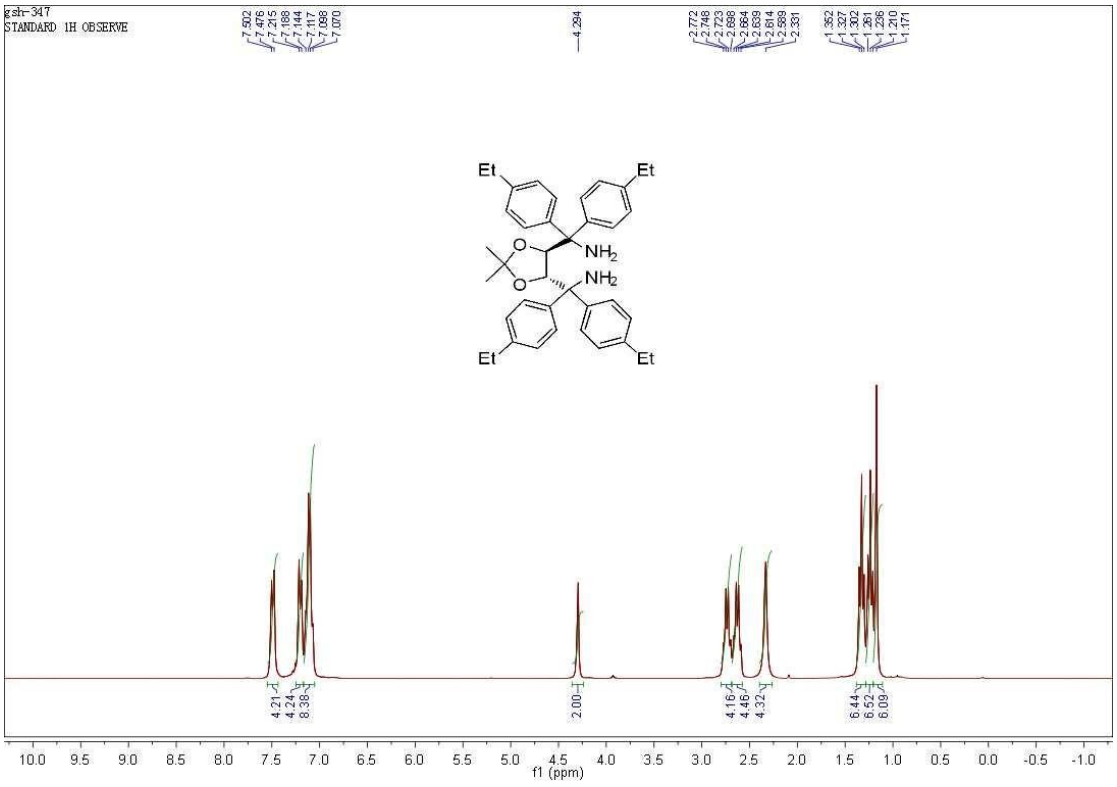
**8b**

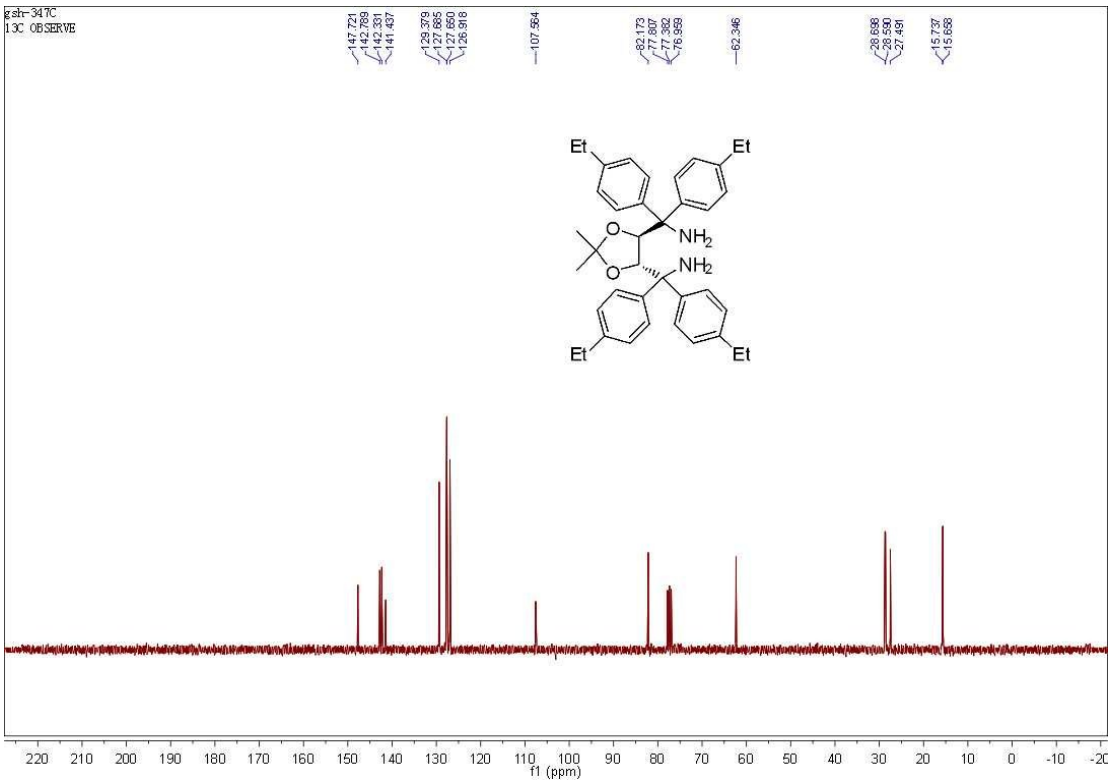

gsh-263
STANDARD 1H OBSERVE
7.354
7.345
7.319
4.946
1.461
1.443
1.298
1.280
20.05
2.00
4.12
6.39
f1 (ppm)

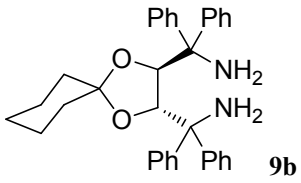

gsh-334C
13C OBSERVE
142.342
140.533
129.868
128.611
128.415
128.029
127.898
127.849
111.063
80.228
73.413
36.979
25.227
24.386
f1 (ppm)


Et
Et
O
NH2
NH2
O
Et
Et

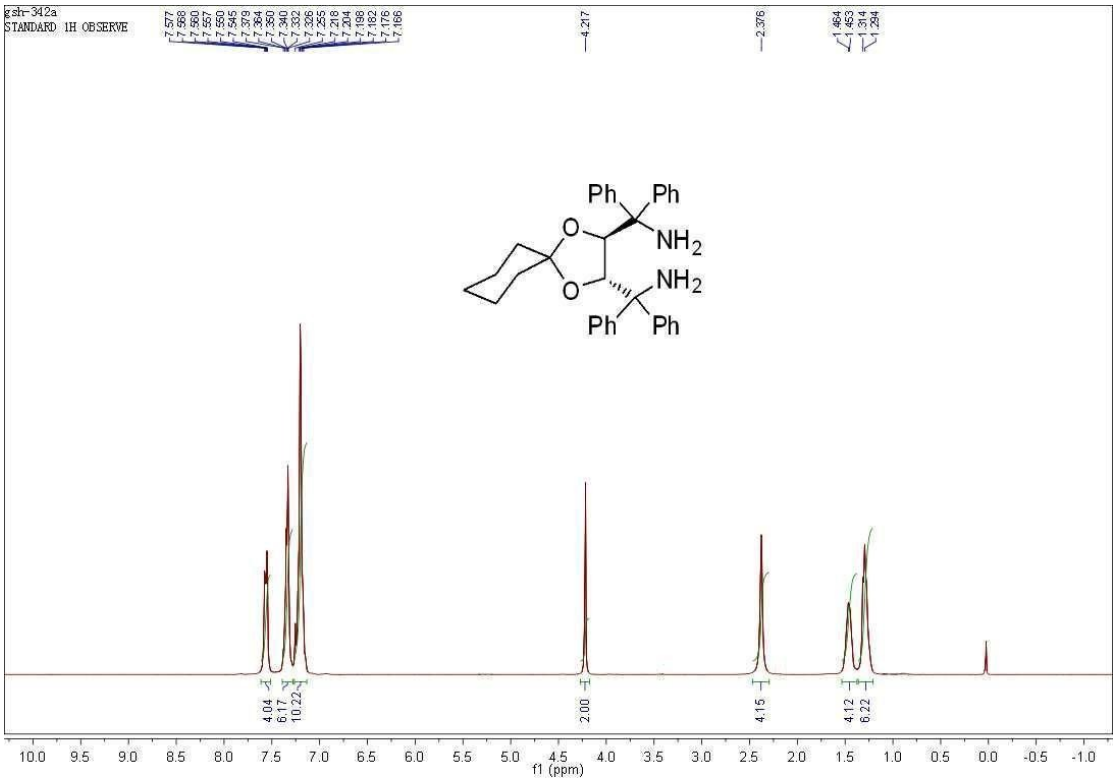
**9a**

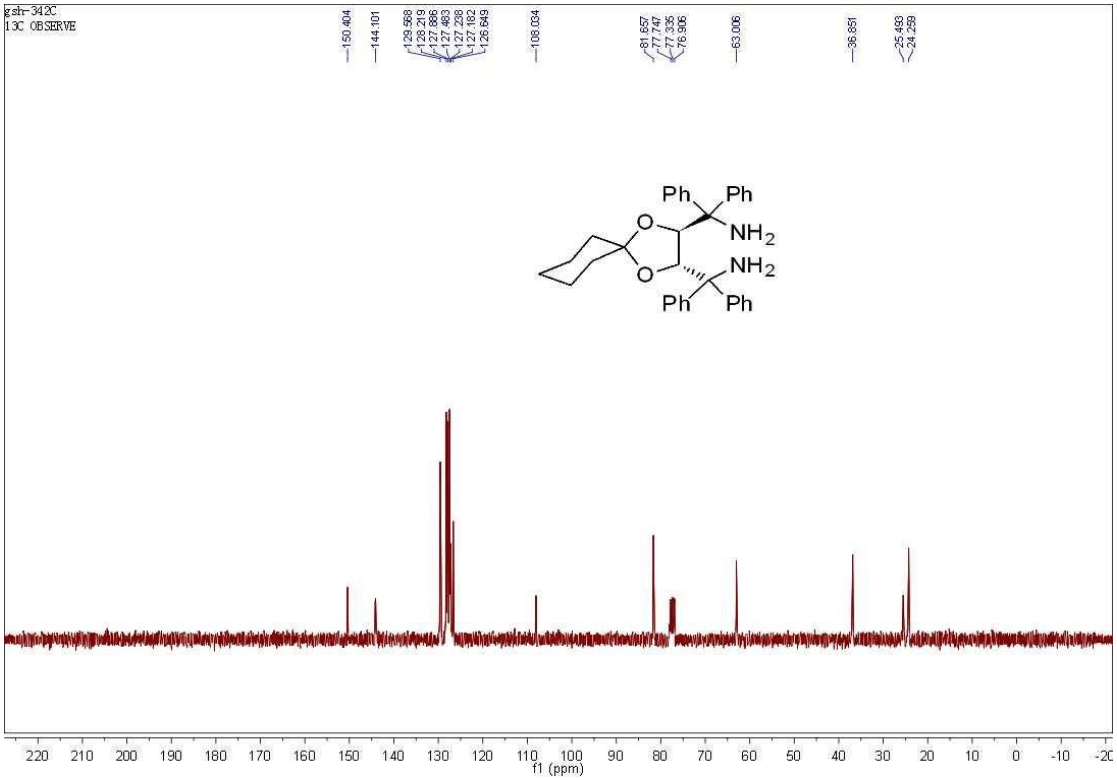

gsh-347
STANDARD 1H OBSERVE
7.502
7.476
7.215
7.188
7.144
7.117
7.097
7.070
4.294
2.772
2.748
2.723
2.698
2.664
2.639
2.614
2.589
2.331
1.352
1.327
1.302
1.261
1.236
1.210
1.171
4.21
4.24
8.38
2.00
4.16
4.46
4.32
6.44
6.52
6.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

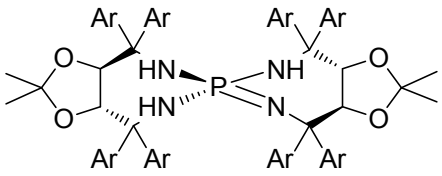

gsh-347C
13C OBSERVE
147.721
142.759
142.331
141.437
129.379
127.865
127.660
126.918
107.964
82.173
77.807
77.382
76.959
62.346
28.698
28.590
27.491
15.737
15.658
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


Ph
Ph
O
NH2
NH2
O
Ph
Ph

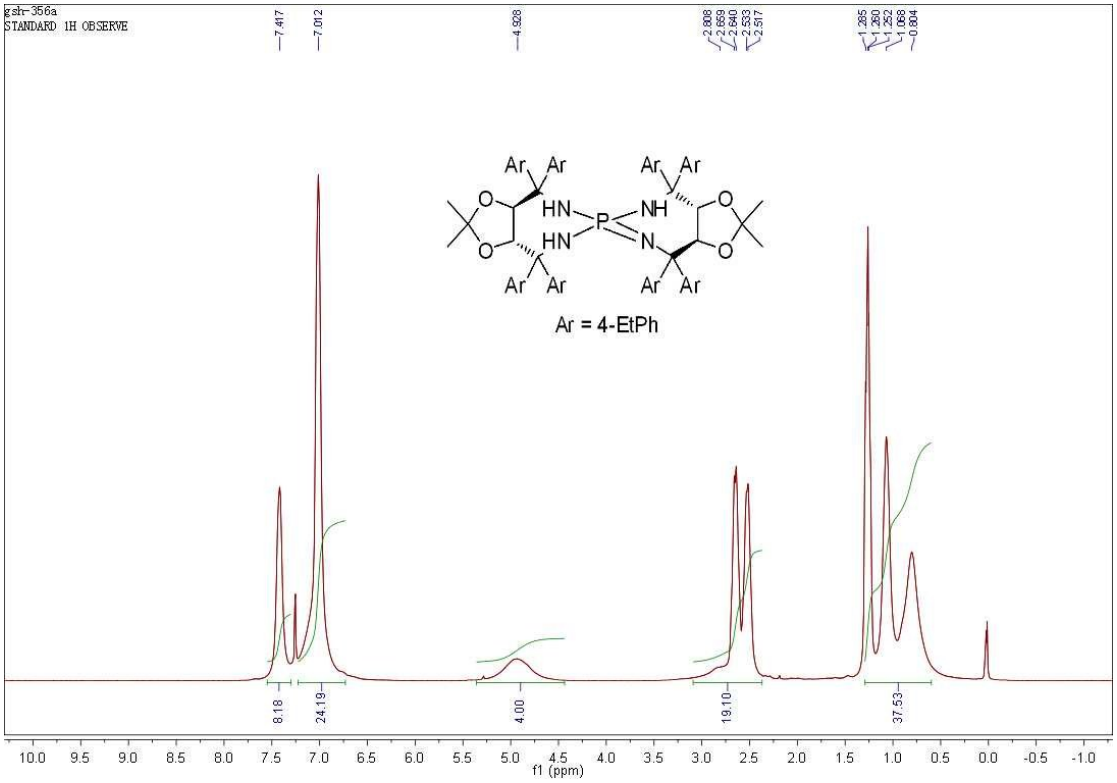
**9b**

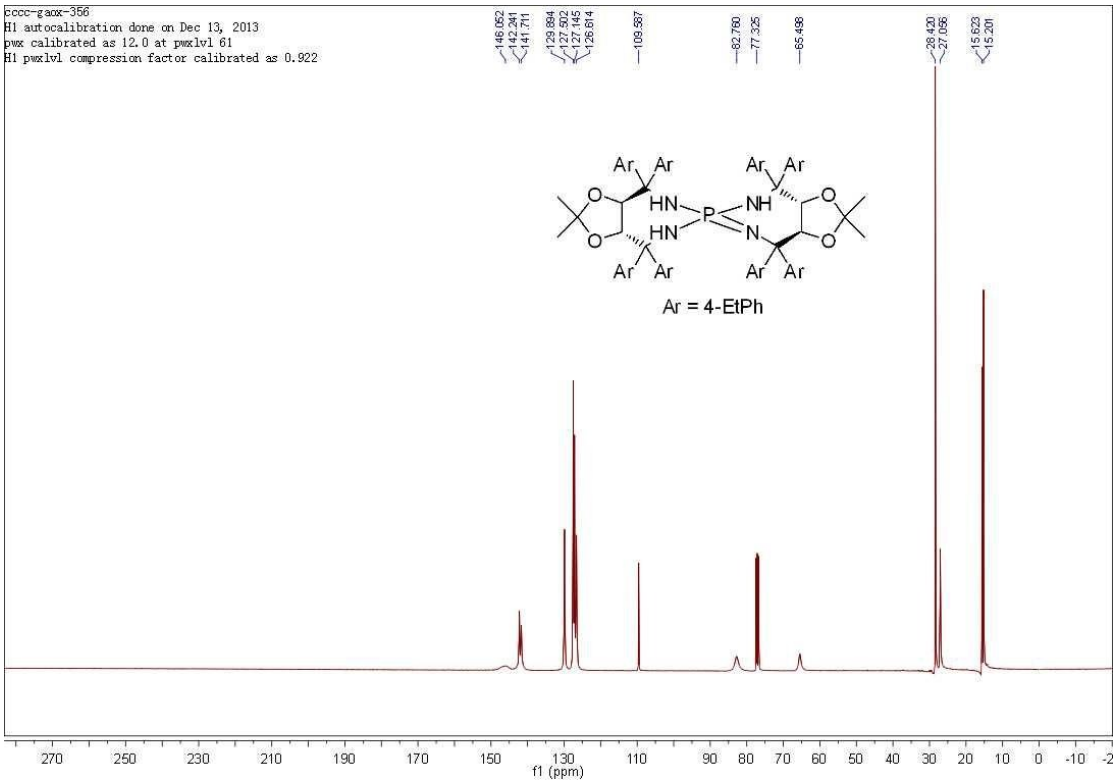

gsh-342a
STANDARD 1H OBSERVE
7.577
7.568
7.560
7.557
7.550
7.545
7.379
7.364
7.360
7.340
7.332
7.306
7.255
7.218
7.204
7.198
7.182
7.176
7.166
4.217
2.376
1.464
1.453
1.314
1.294
Ph
Ph
O
NH2
NH2
O
Ph
Ph
4.04
6.17
10.22
2.00
4.15
4.12
6.22
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

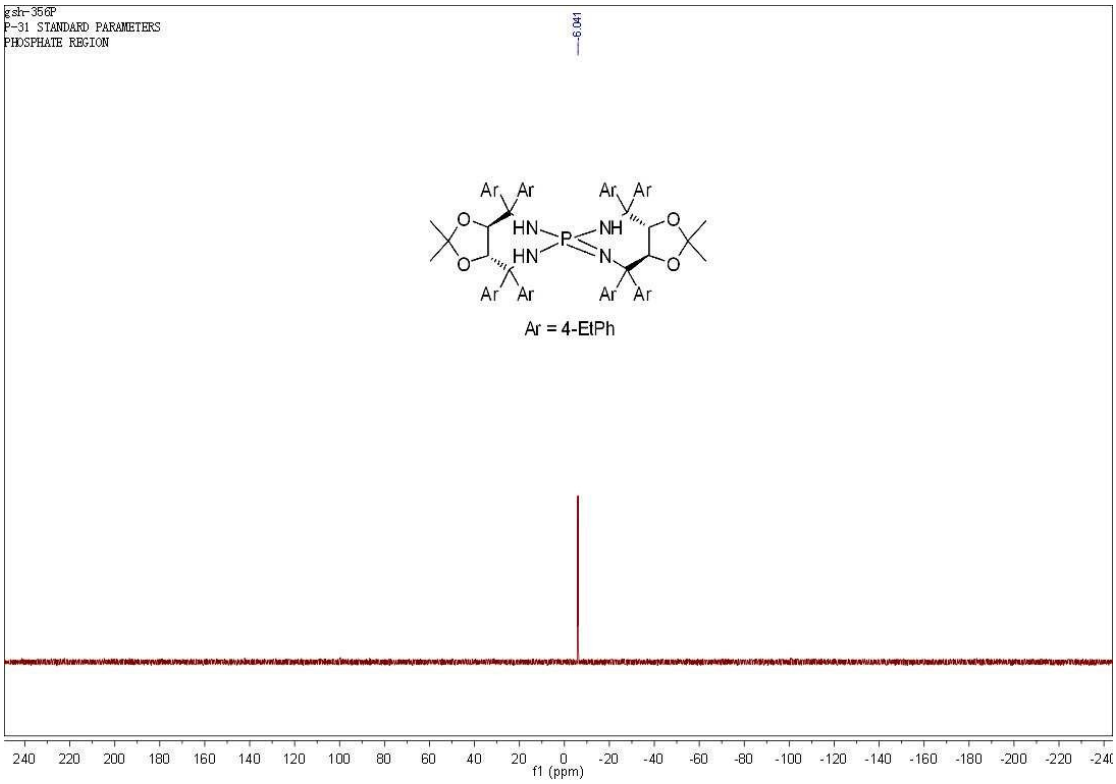

gsh-342C
13C OBSERVE
150.404
144.101
129.568
129.219
127.886
127.483
127.238
127.182
126.649
108.034
81.657
77.747
77.335
76.906
63.006
36.851
25.493
24.259
Ph
Ph
O
NH2
NH2
O
Ph
Ph
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

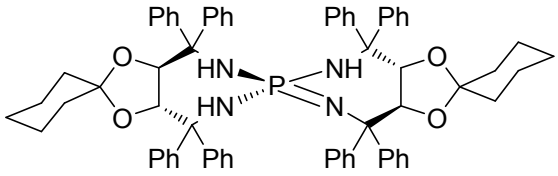

Ar
Ar
HN
HN
P
NH
N
O
O
Ar = 4-EtC6H4

**4f**

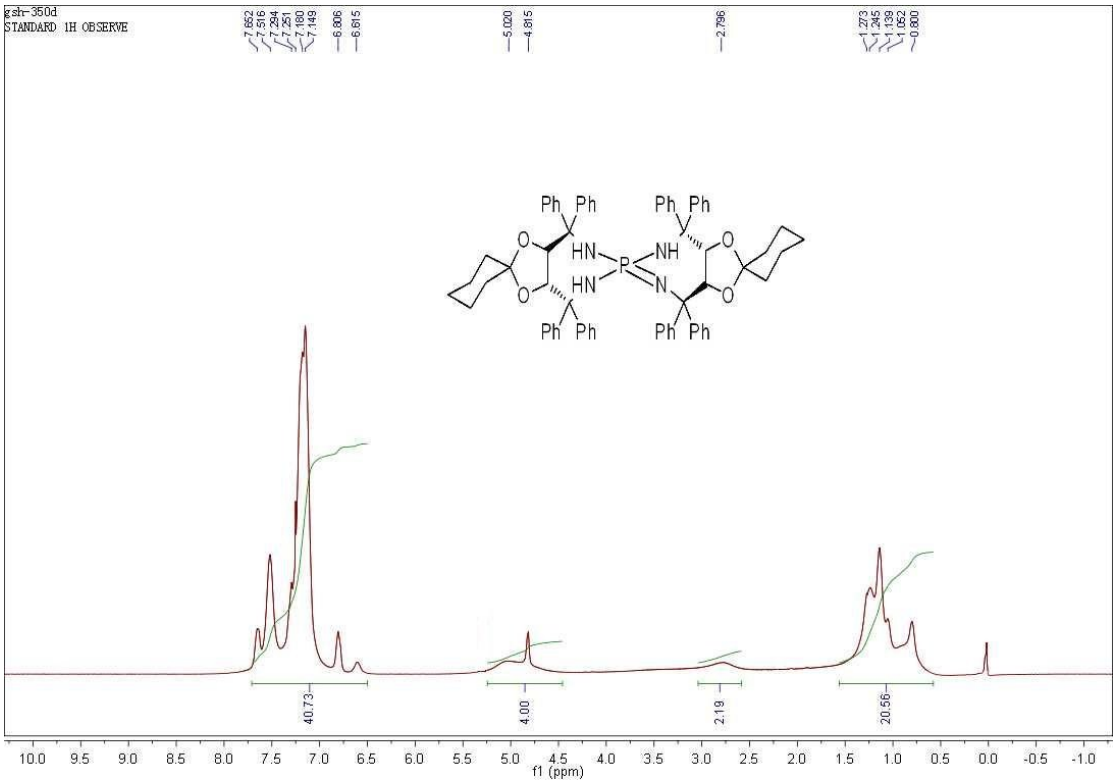

gsh-356a
STANDARD 1H OBSERVE
Ar = 4-EtPh
f1 (ppm)

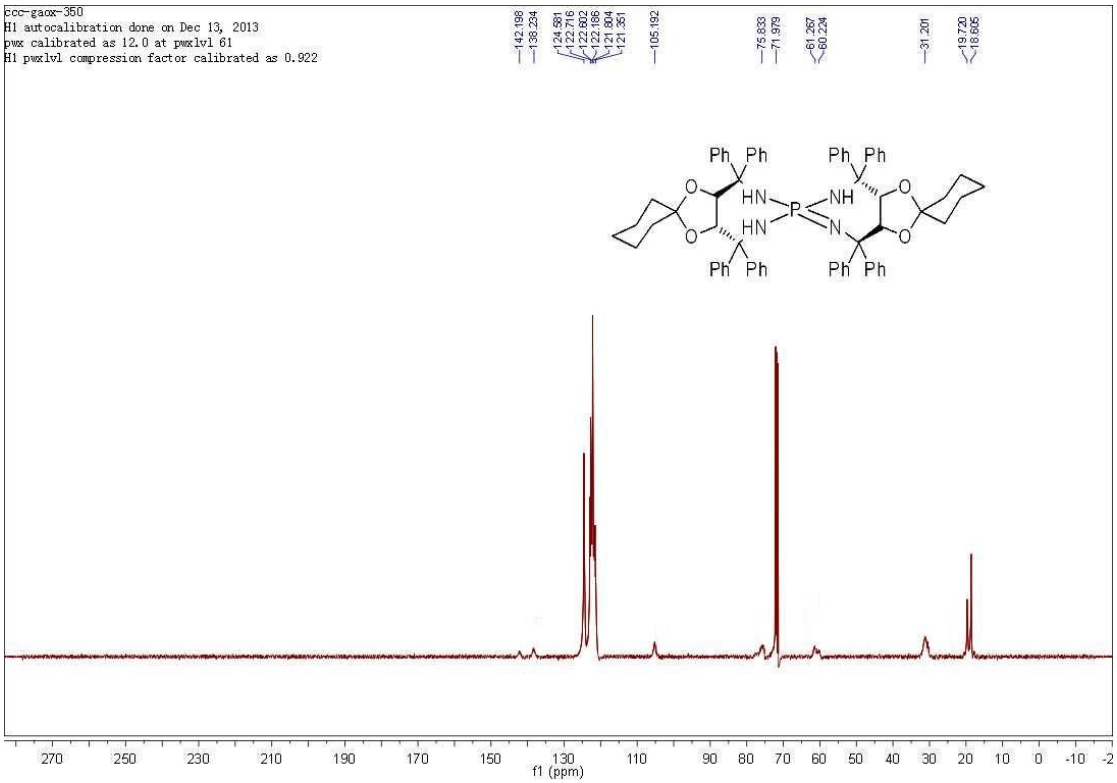

cccc-gaox-356
H1 autocalibration done on Dec 13, 2013
pwx calibrated as 12.0 at pwxlvl 61
H1 pwxlvl compression factor calibrated as 0.922
Ar = 4-EtPh
f1 (ppm)

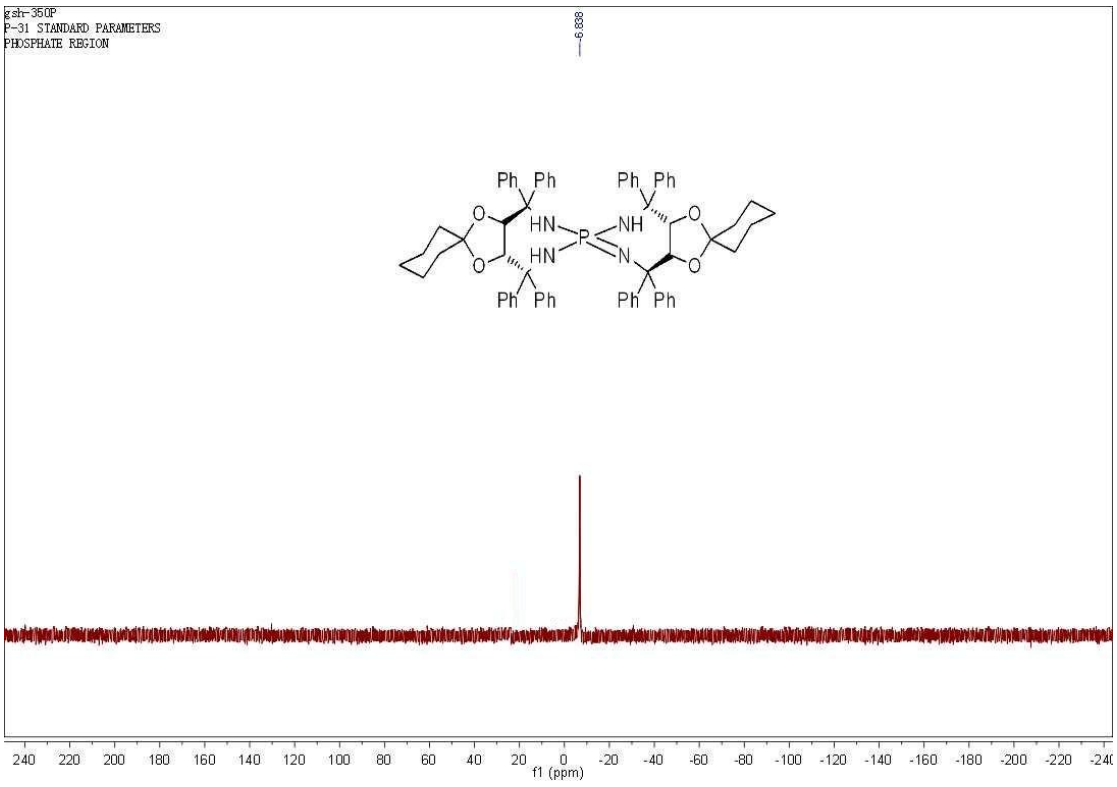

gsh-356P
P-31 STANDARD PARAMETERS
PHOSPHATE REGION
6.041
Ar = 4-EtPh
f1 (ppm)



**4i**


gsh-350d
STANDARD 1H OBSERVE
7.852
7.516
7.294
7.251
7.160
7.149
6.806
6.615
5.020
4.815
2.796
1.273
1.245
1.139
1.052
0.800
40.73
4.00
2.19
20.56
f1 (ppm)


ccc-gaox-350
H1 autocalibration done on Dec 13, 2013
pwx calibrated as 12.0 at pwxlvl 61
H1 pwxlvl compression factor calibrated as 0.922
142.198
138.234
124.581
122.716
122.602
122.186
121.804
121.351
105.192
75.833
71.979
61.257
60.224
31.201
19.720
18.605
Ph Ph
Ph Ph
HN
NH
P
HN
N
Ph Ph
Ph Ph
O
O
O
O
f1 (ppm)


gsh-360P
P-31 STANDARD PARAMETERS
PHOSPHATE REGION
6.838
Ph Ph
Ph Ph
HN
NH
P
HN
N
Ph Ph
Ph Ph
O
O
O
O
f1 (ppm)