Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting information

Design of Chiral Ferrocenylphosphine-spiro Phosphonamidite Ligands for Ruthenium-Catalysed Highly Enantioselective Coupling of 1,2-Diols with Amines

Xiao Yi,‡ Yirui Chen,‡ An Huang, Dingguo Song, Jiaying He, Fei Ling* and Weihui Zhong*

College of Pharmaceutical Sciences, Zhejiang University of Technology, Hangzhou 310014, P. R. China

E-mail: lingfei@zjut.edu.cn; *weihuizhong@zjut.edu.cn*

Table of contents

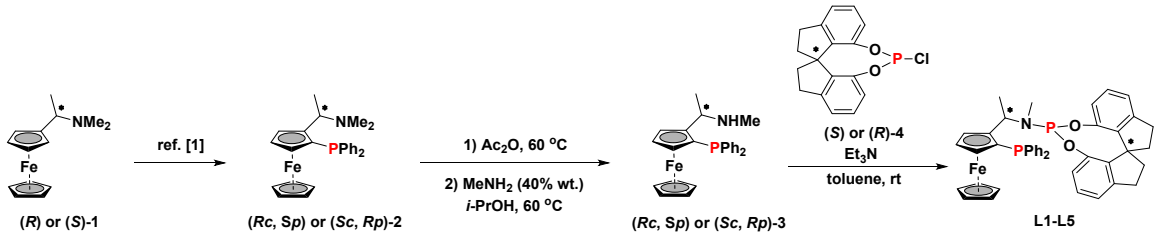
1. General information

Commercial reagents were purchased from Adamas-beta, Aladdin, Bidepharm, Energy Chemical and TCI. 3,3'-diphenyl-SPINOLs were synthesized according to literature.[1] All air-sensitive manipulations were carried out with standard Schlenk techniques under argon. The progress of the reactions was monitored by TLC with silica gel plates, and the visualization was carried out under UV light (254 nm). Melting points were determined using a Büchi B-540 capillary melting point apparatus. Optical rotations were determined using an Rudolph AUTOPOL® V polarimeter. HPLC analyses were performed on Agilent 1100 and Waters e2695 with Daicel chiral columns. NMR spectra were recorded on Bruker Ascend™ (400 MHz for ^{1}H, 100 MHz for ^{13}C, 375 MHz for ^{19}F, 162 MHz for ^{31}P) or Bruker Ascend™ (600 MHz for 1H, 125 MHz for ^{13}C, 565 MHz for ^{19}F, 243 MHz for ^{31}P). Chemical shifts were reported in δ (ppm) referenced to the residual solvent peak of $CDCl_3$ (δ 7.26), DMSO-d_6 (δ 2.50), Acetone-d_6 (δ 2.050) for ^{1}H NMR and $CDCl_3$ (δ 77.0), DMSO-d_6 (δ 40.0), Acetone-d_6 (δ 29.8) for ^{13}C NMR. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). Coupling constants were reported in Hertz (Hz). HRMS spectra were recorded on an electrospray ionization quadrupole time-of-flight (ESI-Q-TOF) mass spectrometer.

2. General procedure for the preparation of SPIROL-derived PPFAPhos

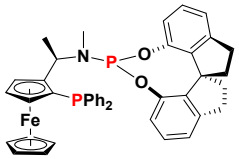
2 were prepared from (*R*) or (*S*)-**1** according to the literatures.[2] A solution of aminophosphine **2** (1 mmol) in acetic anhydride (3 mL) was stirred at 60°C for 2-3 h to afford a homogeneous solution. The excess acetic was removed under reduced pressure. Then, 5 mL of hexane was added, and the solvent was concentrated again. The operation was repeated three times following by adding a solution of 40% wt. methylamine solution (3 mL) in *iso*-propanol (3 mL). The mixture was heated to 60 °C overnight to afford a homogeneous solution. The mixture was cooled to room temperature, and water (4 mL) was added. This resulted in an orange precipitate. The mixture was stirred at ambient temperature for 30 min and the solid was filtered, washed with water, and dried in a nitrogen-purged vacuum oven at 40 °C for 2 days to afford (*Rc*, *Sp*) or (*Sc*, *Rp*)-**3** as an orange solid (~84% two steps).

Chlorophosphite **4** (0.5 mmol) was dissolved in 4.0 mL of dried toluene, which was cooled to 0 °C. A solution of (*Rc*, *Sp*)-**3** or (*Sc*, *Rp*)-**3** (1.0 mmol) and Et_3N (3.0 mmol) in 4.0 mL of toluene was added to above-solution during 30 minutes. The resulting mixture was standing at room temperature overnight. The precipitation was filtrated, and the solid was washed with toluene. The filtrate was collected, and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, hexanes/ethyl acetate = 10/1) to yield **L1-L5**.



Scheme S1. Preparation of SPIROL-derived PPFAPhos

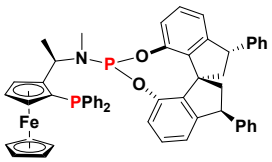
(*Rc*, *Sp*, *S*)-**L1**:



Yellow solid; m.p.= 138-140 °C; 56% yield; $[\alpha]_D^{25}$ = -266.8 (*c* = 0.25, $CHCl_3$); ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.73 – 7.62 (m, 2H), 7.51 – 7.42 (m, 3H), 7.21 – 6.88 (m, 9H), 6.84 (d, *J* = 8.0 Hz, 1H), 5.87 (d, *J* = 7.2 Hz, 1H), 5.28 – 5.15 (m, 1H), 4.59 (d, *J* = 1.0 Hz, 1H), 4.43 (t, *J* = 2.8 Hz, 1H), 4.05 (s, 1H), 3.90 (s, 5H), 3.10 – 2.95 (m, 2H), 2.78 – 2.63 (m, 2H), 2.25 – 2.11 (m, 2H), 1.81 (d, *J* = 7.2 Hz, 3H), 1.78 – 1.67 (m, 2H), 1.57 (d, *J* = 2.8 Hz, 3H); ^{13}C NMR (100 MHz, Acetone-d_6) δ 149.4 (d, $J_{C\text{-}P}$ = 6.0 Hz), 147.8 (d, $J_{C\text{-}P}$ = 7.5 Hz), 145.9 (d, *J* = 2.0 Hz), 145.8, 142.7 (d, $J_{C\text{-}P}$ = 9.5 Hz), 141.5, 140.2 (d, $J_{C\text{-}P}$ = 9.5 Hz), 136.7 (d, $J_{C\text{-}P}$ = 23.0 Hz), 132.5 (d, $J_{C\text{-}P}$ = 16.5 Hz), 130.1, 129.0, 128.9 (d, $J_{C\text{-}P}$ = 8.4 Hz), 128.7 (d, *J* = 2.0 Hz), 128.4 (*d*, $J_{C\text{-}P}$ = 5.0 Hz), 127.9, 122.4, 121.3 (d, *J* = 2.5 Hz), 121.0, 96.4 (dd, $J_{C\text{-}P}$ = 27.5, 14.0 Hz), 76.0 (d, $J_{C\text{-}P}$ = 14.0 Hz), 72.4 (d, $J_{C\text{-}P}$ = 5.5 Hz), 71.2 (dd, $J_{C\text{-}P}$ = 4.5, 2.5 Hz), 70.6, 70.5, 59.4, 52.2 (dd, *J* = 54.5, 9.0 Hz), 38.9, 31.2. 30.9, 24.9 (d, *J* = 7.0 Hz), 19.6; ^{31}P NMR (162 MHz, Acetone-d_6) δ 125.7 (d, *J* = 58.7 Hz), -24.4 (d,

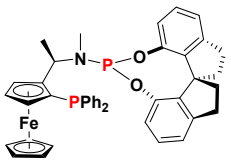
J = 57.7 Hz); HRMS-ESI (m/z): calcd for $C_{42}H_{40}FeNO_2P_2^+$ $[M+H]^+$ 708.1878, found 708.1874.

(*Rc*, *Sp*, *R*)-**L2**:



Yellow solid; m.p.= 160-162 ℃; 61% yield; $[\alpha]_D^{25}$ = -217.5 (c = 0.3, $CHCl_3$); ^{1}H NMR (600 MHz, Acetone-d_6) δ 7.72 – 7.66 (m, 2H), 7.45 (d, J = 4.8 Hz, 3H), 7.35 – 7.27 (m, 8H), 7.25 – 7.15 (m, 8H), 6.92 (t, J = 7.8 Hz, 1H), 6.84 (d, J = 7.8 Hz, 1H), 6.59 (d, J = 7.2 Hz, 1H), 6.51 (d, J = 7.2 Hz, 1H), 6.28 (d, J = 8.0 Hz, 1H), 4.97 – 4.86 (m, 1H), 4.65 (s, 1H), 4.62 – 4.53 (m, 2H), 4.49 (t, J = 2.4 Hz, 1H), 4.18 (s, 1H), 3.90 (s, 5H), 2.83 (dd, J = 12.0, 6.0 Hz, 1H), 2.73 (dd, J = 12.0, 6.0 Hz, 1H), 2.12 – 2.06 (m, 1H), 2.02 – 1.97 (m, 1H), 1.87 (d, J = 4.8 Hz, 3H), 1.66 (d, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, Acetone-d_6) δ 149.8, 149.7 (d, $J_{C\text{-}P}$ = 5.4 Hz), 149.2, 147.2, 147.1, 145.3, 144.6, 142.6 (d, $J_{C\text{-}P}$ = 3.3 Hz), 141.8 (d, $J_{C\text{-}P}$ = 9.6 Hz), 141.3, 140.2 (d, J = 9.6 Hz), 136.4 (d, $J_{C\text{-}P}$ = 23.1 Hz), 133.2 (d, $J_{C\text{-}P}$ = 17.7 Hz), 130.1, 129.5, 129.4, 129.3 (d, $J_{C\text{-}P}$ = 5.4 Hz), 129.0, 128.9 (d, $J_{C\text{-}P}$ = 6.3 Hz), 128.8, 128.4, 127.4, 123.2, 122.6 (d, $J_{C\text{-}P}$ = 5.1 Hz), 121.8, 121.5, 97.3 (dd, $J_{C\text{-}P}$ = 27.6, 10.8 Hz), 76.1 (d, $J_{C\text{-}P}$ = 12.6 Hz), 72.7 (d, $J_{C\text{-}P}$ = 4.8 Hz), 71.5 (t, $J_{C\text{-}P}$ = 4.8 Hz), 70.6, 70.3, 57.7, 50.1, 50.0, 49.7, 29.2, 20.7 (d, $J_{C\text{-}P}$ = 6.0 Hz); ^{31}P NMR (243 MHz, Acetone-d_6) δ 129.2, -25.6; HRMS-ESI (m/z): calcd for $C_{54}H_{48}FeNO_2P_2^+$ $[M+H]^+$ 860.2504, found 860.2497.

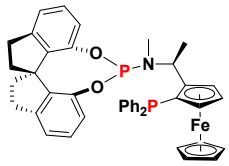
(*Rc*, *Sp*, *R*)-**L3**:



Yellow solid; m.p.= 143-145 ℃; 63% yield; $[\alpha]_D^{25}$ = -176.4 (c = 0.3, $CHCl_3$); ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.72 – 7.63 (m, 2H), 7.44 (d, J = 3.6 Hz, 3H), 7.32 – 7.21 (m, 5H), 7.17 (t, J = 8.0 Hz, 1H), 7.02 (d, J = 7.8 Hz, 1H), 6.94 – 6.86 (m, 2H), 6.76 (d, J = 8.0

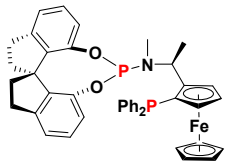
Hz, 1H), 6.16 (d, J = 7.2 Hz, 1H), 4.87 – 4.74 (m, 1H), 4.61 (s, 1H), 4.47 (t, J = 2.4 Hz, 1H), 4.18 (s, 1H), 3.88 (s, 5H), 3.11 – 2.95 (m, 2H), 2.79 – 2.69 (m, 2H), 2.27 – 2.13 (m, 2H), 1.90 – 1.73 (m, 2H), 1.72 (d, J = 4.2 Hz, 3H), 1.68 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, Acetone-d_6) δ 149.9 (d, $J_{C\text{-}P}$ = 5.0 Hz), 147.4 (d, $J_{C\text{-}P}$ = 9.0 Hz), 146.4 (d, $J_{C\text{-}P}$ = 2.0 Hz), 145.7, 143.0 (d, $J_{C\text{-}P}$ = 3.0 Hz), 141.8 (d, $J_{C\text{-}P}$ = 9.0 Hz), 141.1, 140.2 (d, $J_{C\text{-}P}$ = 9.5 Hz), 136.3 (d, $J_{C\text{-}P}$ = 23.0 Hz), 133.1 (d, $J_{C\text{-}P}$ = 18.0 Hz), 130.0, 129.1 (d, $J_{C\text{-}P}$ = 2.0 Hz), 129.0, 128.9, 128.9 (d, $J_{C\text{-}P}$ = 2.0 Hz), 128.8, 128.4, 122.8, 122.2 (d, $J_{C\text{-}P}$ = 5.0 Hz), 121.6 (d, $J_{C\text{-}P}$ = 2.0 Hz), 121.0, 97.4 (dd, $J_{C\text{-}P}$ = 28.0, 11.0 Hz), 75.9 (d, $J_{C\text{-}P}$ = 12.5 Hz), 72.6 (d, $J_{C\text{-}P}$ = 5.0 Hz), 71.4 (t, $J_{C\text{-}P}$ = 5.5 Hz), 70.5, 70.2, 59.5, 53.9 (dd, J = 36.0, 10.5 Hz), 39.0, 38.9, 31.3, 30.9, 29.4, 20.8 (d, J = 7.5 Hz); ^{31}P NMR (162 MHz, Acetone-d_6) δ 129.9 (d, J = 9.8 Hz), -25.7 (d, J = 8.8 Hz); ^{31}P NMR (162 MHz, Acetone) δ 129.9 (d, J = 9.8 Hz), -25.7 (d, J = 8.8 Hz); HRMS-ESI (m/z): calcd for $C_{42}H_{40}FeNO_2P_2^+$ [M+H]$^+$ 708.1878, found 708.1889.

(*Sc*, *Rp*, *R*)-**L4**:



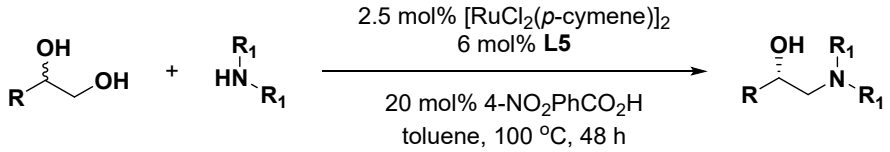
Yellow solid; m.p.= 142-143 ℃; 62% yield; $[\alpha]_D^{25}$ = +257 (c = 0.2, $CHCl_3$); ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.73 – 7.63 (m, 2H), 7.50 – 7.42 (m, 3H), 7.21 – 6.88 (m, 9H), 6.83 (d, J = 8.0 Hz, 1H), 5.87 (d, J = 7.2 Hz, 1H), 5.28 – 5.15 (m, 1H), 4.59 (s, 1H), 4.43 (t, J = 2.8 Hz, 1H), 4.05 (s, 1H), 3.90 (s, 5H), 3.09 – 2.94 (m, 2H), 2.78 – 2.66 (m, 2H), 2.25 – 2.12 (m, 2H), 1.81 (d, J = 7.0 Hz, 3H), 1.77 – 1.67 (m, 2H), 1.56 (d, J = 2.9 Hz, 3H); ^{13}C NMR (100 MHz, Acetone-d_6) δ 149.4 (d, $J_{C\text{-}P}$ = 6.0 Hz), 147.8 (d, $J_{C\text{-}P}$ = 7.5 Hz), 146.0 (d, $J_{C\text{-}P}$ = 2.0 Hz), 145.8, 142.7 (d, $J_{C\text{-}P}$ = 9.5 Hz), 141.5, 140.2 (d, $J_{C\text{-}P}$ = 9.5 Hz), 136.7 (d, $J_{C\text{-}P}$ = 23.0 Hz), 132.5 (d, $J_{C\text{-}P}$ = 16.5 Hz), 130.2, 129.0, 128.9 (d, $J_{C\text{-}P}$ = 8.5 Hz), 128.7 (d, $J_{C\text{-}P}$ = 2.0 Hz), 128.4 (d, $J_{C\text{-}P}$ = 5.0 Hz), 127.9, 122.5, 122.4, 121.3 (d, $J_{C\text{-}P}$ = 2.0 Hz), 121.0, 96.5 (dd, J = 27.5, 14.5 Hz), 76.0 (d, $J_{C\text{-}P}$ = 14.0 Hz), 72.4 (d, J = 5.5 Hz), 71.2 (dd, $J_{C\text{-}P}$ = 4.5, 2.5 Hz), 70.6, 70.5, 59.4, 52.2 (dd, $J_{C\text{-}P}$ = 54.5, 8.5 Hz), 38.9, 31.2, 30.9, 24.9 (d, $J_{C\text{-}P}$ = 7.0 Hz), 19.6; ^{31}P NMR (162 MHz, Acetone-d_6) δ 125.7 (d, J = 58.1 Hz), -24.4 (d, J = 57.8 Hz); HRMS-ESI (m/z): calcd for $C_{42}H_{40}FeNO_2P_2^+$ [M+H]$^+$ 708.1878, found 708.1866.

(*Sc*, *Rp*, *S*)-**L5**:



(*Sc*,*Rp*,*S*)-L4: Yellow solid; m.p.= 146-148 ℃; 61% yield; $[\alpha]_D^{25}$ = +204.6 (*c* = 0.2, $CHCl_3$); ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.71 – 7.64 (m, 2H), 7.46 – 7.41 (m, 3H), 7.32 – 7.21 (m, 5H), 7.17 (t, *J* = 8.0 Hz, 1H), 7.02 (d, *J* = 7.2 Hz, 1H), 6.94 – 6.86 (m, 2H), 6.76 (d, *J* = 8.0 Hz, 1H), 6.16 (d, *J* = 7.2 Hz, 1H), 4.86 – 4.74 (m, 1H), 4.61 (s, 1H), 4.48 (t, *J* = 2.4 Hz, 1H), 4.18 (s, 1H), 3.88 (s, 5H), 3.12 – 2.95 (m, 2H), 2.79 – 2.67 (m, 2H), 2.28 – 2.13 (m, 2H), 1.89 – 1.74 (m, 2H), 1.72 (d, *J* = 4.2 Hz, 3H), 1.69 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, Acetone-d_6) δ 149.9 (d, $J_{C\text{-}P}$ = 5.0 Hz), 147.4 (d, $J_{C\text{-}P}$ = 9.0 Hz), 146.4 (d, $J_{C\text{-}P}$ = 2.0 Hz), 145.7, 142.9 (d, $J_{C\text{-}P}$ = 3.5 Hz), 141.8 (d, $J_{C\text{-}P}$ = 9.0 Hz), 141.1 (d, $J_{C\text{-}P}$ = 1.5 Hz), 140.2 (d, $J_{C\text{-}P}$ = 9.0 Hz), 136.3 (d, *J* = 23.0 Hz), 133.1 (d, $J_{C\text{-}P}$ = 17.5 Hz), 130.0, 129.1 (d, $J_{C\text{-}P}$ = 2.0 Hz), 129.0, 128.9, 128.9 (d, $J_{C\text{-}P}$ = 2.0 Hz), 128.8, 128.4, 122.8, 122.2 (d, $J_{C\text{-}P}$ = 5.0 Hz), 121.6 (d, $J_{C\text{-}P}$ = 2.0 Hz), 121.0, 97.4 (dd, $J_{C\text{-}P}$ = 28.0, 11.0 Hz), 75.9 (d, $J_{C\text{-}P}$ = 12.5 Hz), 72.6 (d, $J_{C\text{-}P}$ = 5.0 Hz), 71.4 (t, $J_{C\text{-}P}$ = 5.0 Hz), 70.5, 70.2, 59.5, 53.9 (dd, $J_{C\text{-}P}$ = 36.5, 10.0 Hz), 39.0, 38.9, 31.3, 30.9, 29.4, 20.8 (d, $J_{C\text{-}P}$ = 7.0 Hz); ^{31}P NMR (162 MHz, Acetone-d_6) δ 129.9 (d, *J* = 9.0 Hz), -25.7 (d, *J* = 9.8 Hz); HRMS-ESI (m/z): calcd for $C_{42}H_{40}FeNO_2P_2^+$ $[M+H]^+$ 708.1878, found 708.1884.

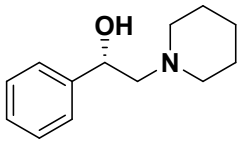
3. General procedure for the Ru-catalyzed enantioselective amination of diols



A sealed tube with magnetic stir bar was charged with diol substrate (0.4 mmol, 2 equiv.), corresponding amine (0.2 mmol, 1equiv.), 4-nitrobenzoic acid (6.68 mg, 0.04 mmol, 0.2 equiv.), [Ru(*p*-cymene)Cl_2]$_2$ (3.0 mg, 0.005mmol, 0.025 equiv.), (*Sc*, *Rp*, *S*)-**L5** (8.6 mg, 0.012 mmol, 0.06 equiv.) and toluene (1mL) subsequently and the reaction mixture was stirred at 100 °C for 48 hours. After cooling to room temperature, washed with saturated sodium bicarbonate and brine, dried over anhydrous sodium sulfate, filtered and concentrated. The crude reaction mixture was purified by flash chromatography or pTLC to afford the desired products.

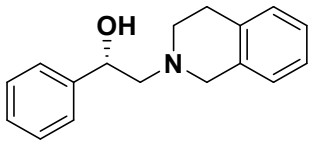
4. Characterization of the products

(*S*)-1-phenyl-2-(piperidin-1-yl)ethanol (3aa)



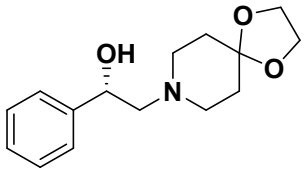
White solid; m.p.= 83-84 ℃; 93% yield, >99% *ee*; $[\alpha]_D^{25}$ = +83.2 (*c* = 1.0, $CHCl_3$) {lit.[3] $[\alpha]_D^{25}$ = +81.5 (*c* = 1.0, $CHCl_3$)}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.22 (m, 5H), 4.71 (dd, *J* = 10.8, 3.6 Hz, 1H), 4.23 (brs, 1H), 2.69 (s, 2H), 2.47 (dd, *J* = 12.4, 3.6 Hz, 1H), 2.44 – 2.23 (m, 3H), 1.69 – 1.54 (m, 4H), 1.53 – 1.36 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 128.3, 127.4, 125.8, 68.6, 66.9, 54.4, 26.1, 24.2; Determined by HPLC analysis [Daicel chiralpak AD-H, *n*-hexane/*i*-PrOH = 98:2, flow rate = 0.5 ml/min, wavelength = 254 nm, *t* (major) = 24.547 min]; HRMS-ESI (m/z): calcd for $C_{13}H_{20}NO^+$ $[M+H]^+$ 206.1539, found 206.1546.

(*S*)-2-(3,4-dihydroisoquinolin-2(1H)-yl)-1-phenylethanol (3ab)



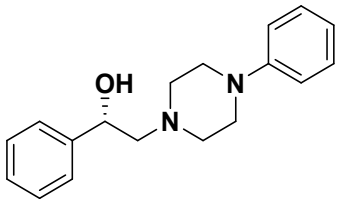
White solid; m.p.= 74-76 ℃; 88% yield, 99% *ee*; $[\alpha]_D^{25}$ = +61.8 (*c* = 0.8, $CHCl_3$); {lit.[3] $[\alpha]_D^{25}$ = 64.0 (*c* = 1.0, $CHCl_3$)} ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.26 (m, 5H), 7.24 – 7.02 (m, 4H), 4.96 – 4.82 (m, 1H), 4.06 (brs, 1H), 3.95 (dd, *J* = 14.8, 6.8 Hz, 1H), 3.70 (dd, *J* = 14.8, 7.6 Hz, 1H), 3.14 – 2.87 (m, 3H), 2.87 – 2.58 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 134.4, 134.2, 128.8, 128.4, 127.6, 126.6, 126.4, 126.0, 125.9, 69.1, 69.1, 66.1, 55.8, 51.0, 29.2; Determined by HPLC analysis [Daicel chiralpak OD-H, *n*-hexane/*i*-PrOH = 90:10, flow rate = 0.5 ml/min, wavelength = 225 nm, *t* (minor) = 17.288 min, *t* (major) = 17.877 min]; HRMS-ESI (m/z): calcd for $C_{17}H_{20}NO^+$ $[M+H]^+$ 254.1539, found 254.1537.

(*S*)-2-(1,4-dioxa-8-azaspiro[4.5]dec-8-yl)-1-phenylethanol (3ac)



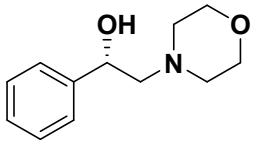
White solid; m.p.= 94-95 °C; 91% yield, 95% *ee*; $[\alpha]_D^{25}$ = +57.3 (*c* = 0.5, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.40 – 7.32 (m, 4H), 7.28 – 7.24 (m, 1H), 4.72 (dd, *J* = 10.8, 3.6 Hz, 1H), 3.96 (s, 4H), 2.90 – 2.80 (m, 2H), 2.56 (dd, *J* = 12.6, 3.6 Hz, 3H), 2.52 – 2.44 (m, 1H), 1.85 – 1.72 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.2, 128.3, 127.5, 125.9, 107.0, 69.0, 65.7, 64.3, 51.3, 34.9; Determined by HPLC analysis [Daicel chiralpak OD-H, *n*-hexane/*i*-PrOH = 95:5, flow rate = 0.8 ml/min, wavelength = 225 nm, *t* (minor) = 14.531 min, *t* (major) = 16.495 min]; HRMS-ESI (m/z): calcd for $C_{15}H_{22}NO_3^+$ $[M+H]^+$ 264.1594, found 264.1592.

(*S*)-1-phenyl-2-(4-phenylpiperazin-1-yl)ethanol (3ad)



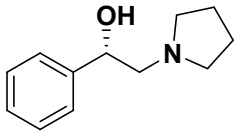
White solid; m.p.= 115-117 °C; 90% yield, 96% *ee*; $[\alpha]_D^{25}$ = +62.7 (*c* = 1.0, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.8 Hz, 2H), 7.37 (t, *J* = 7.8 Hz, 2H), 7.30 (t, *J* = 7.8 Hz, 3H), 6.96 (d, *J* = 8.4 Hz, 2H), 6.89 (t, *J* = 7.2 Hz, 1H), 4.81 (dd, *J* = 10.2, 4.2 Hz, 1H), 3.99 (brs, 1H), 3.33 – 3.20 (m, 4H), 2.97 – 2.90 (m, 2H), 2.70 – 2.52 (m, 4H).^{13}C NMR (150 MHz, $CDCl_3$) δ 151.2, 142.0, 142.0, 129.2, 128.4, 127.6, 125.9, 120.0, 116.2, 68.8, 66.2, 53.1, 49.4; Determined by HPLC analysis [Daicel chiralpak AD-H, *n*-hexane/*i*-PrOH = 85:15, flow rate = 1 ml/min, wavelength = 225 nm, *t* (minor) = 7.893 min, *t* (major) = 9.217 min]; HRMS-ESI (m/z): calcd for $C_{18}H_{23}N_2O^+$ $[M+H]^+$ 283.1805, found 283.1808.

(*S*)-2-morpholino-1-phenylethanol (3ae)



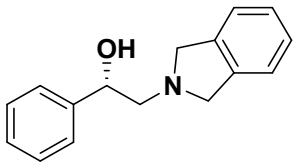
White solid; m.p.= 95-96 ℃; 93% yield, 98% *ee*; $[\alpha]_D^{25}$ = +42.4 (*c* = 0.6, $CHCl_3$) {lit.[4] $[\alpha]_D^{23}$ = -31.7 (*c* = 0.4, $CHCl_3$) (***R***)}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.27 (m, 5H), 4.76 (dd, *J* = 10.4, 3.6 Hz, 1H), 3.92 (brs, 1H), 3.82 – 3.70 (m, 4H), 2.83 – 2.70 (m, 2H), 2.58 – 2.41 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 128.4, 127.6, 125.8, 68.5, 67.0, 66.6, 53.4; Determined by HPLC analysis [Daicel chiralpak OD-H, *n*-hexane/*i*-PrOH = 97:3, flow rate = 0.5 ml/min, wavelength = 225 nm, *t* (minor) = 29.014 min, *t* (major) = 31.165 min]; HRMS-ESI (m/z): calcd for $C_{12}H_{18}NO_2^+$ $[M+H]^+$ 208.1332, found 208.1327.

(*S*)-1-phenyl-2-(pyrrolidin-1-yl)ethanol (3af)



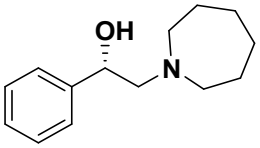
White solid; m.p.= 67-68 ℃; 90% yield, 98% *ee*; $[\alpha]_D^{25}$ = +50.2 (*c* = 1.0, $CHCl_3$) {lit.[3] $[\alpha]_D^{27}$ = +43.8 (*c* = 0.96, MeOH)}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.2 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.29 – 7.24 (m, 1H), 4.70 (dd, *J* = 10.8, 3.2 Hz, 1H), 3.96 (brs, 1H), 2.84 – 2.69 (m, 3H), 2.57 – 2.51 (m, 2H), 2.49 (dd, *J* = 12.4, 3.2 Hz, 1H), 1.87 – 1.75 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.5, 128.3, 127.4, 125.9, 70.7, 64.1, 53.9, 23.7; Determined by HPLC analysis [Daicel chiralpak OD-H, *n*-hexane/*i*-PrOH = 97:3, flow rate = 0.5 ml/min, wavelength = 230 nm, *t* (minor) = 19.733 min, *t* (major) = 22.626 min]; HRMS-ESI (m/z): calcd for $C_{12}H_{18}NO^+$ $[M+H]^+$ 192.1383, found 192.1394.

(*S*)-2-(isoindolin-2-yl)-1-phenylethanol (3ag)



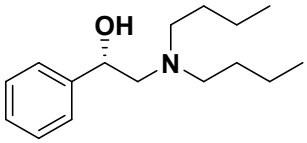
White solid; m.p.= 94-96 °C; 92% yield, 98% *ee*; $[\alpha]_D^{25}$ = +32.4 (*c* = 0.5, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.33 (m, 4H), 7.32 – 7.26 (m, 1H), 7.23 (s, 4H), 4.80 (dd, *J* = 9.6, 4.0 Hz, 1H), 4.17 (d, *J* = 11.0 Hz, 2H), 4.02 (d, *J* = 10.8 Hz, 2H), 2.99 – 2.87 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 139.5, 128.4, 127.6, 127.0, 125.9, 122.3, 70.8, 64.1, 59.1; Determined by HPLC analysis [Daicel chiralpak AD-H, *n*-hexane/*i*-PrOH = 85:15, flow rate = 0.5 ml/min, wavelength = 254 nm, *t* (minor) = 14.411 min, *t* (major) = 16.798 min]; HRMS-ESI (m/z): calcd for $C_{16}H_{18}NO^+$ $[M+H]^+$ 240.1383, found 240.1377.

(*S*)-2-(azepan-1-yl)-1-phenylethanol (3ah)



Colorless oil; 93% yield, 95% *ee*; $[\alpha]_D^{25}$ = +49.7 (*c* = 0.5, $CHCl_3$) {lit.[4] $[\alpha]_D^{27}$ = -41.8 (*c* = 0.6, $CHCl_3$)}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.40 – 7.29 (m, 4H), 7.27 – 7.22 (m, 1H), 4.61 (dd, *J* = 10.8, 3.0 Hz, 1H), 4.33 (brs, 1H), 2.89 – 2.79 (m, 2H), 2.76 (dd, *J* = 12.6, 3.6 Hz, 1H), 2.72 – 2.63 (m, 2H), 2.45 – 2.37 (m, 1H), 1.76 – 1.57 (m, 8H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.6, 128.3, 127.3, 125.9, 69.4, 66.4, 55.6, 28.6, 27.0; Determined by HPLC analysis [Daicel chiralpak AD-H, *n*-hexane/*i*-PrOH = 97:3, flow rate = 0.5 ml/min, wavelength = 230 nm, *t* (minor) = 16.653 min, *t* (major) = 24.148 min]; HRMS-ESI (m/z): calcd for $C_{14}H_{22}NO^+$ $[M+H]^+$ 220.1696, found 220.1688.

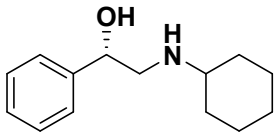
(*S*)-2-(dibutylamino)-1-phenylethanol (3ai)



Yellow oil; 84% yield, 71% *ee*; $[\alpha]_D^{25}$ = +74.6 (*c* = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.30 (m, 4H), 7.28 – 7.22 (m, 1H), 4.63 (dd, *J* = 10.8, 3.6 Hz, 1H), 4.26 (brs, 1H), 2.67 – 2.55 (m, 3H), 2.49 – 2.40 (m, 3H), 1.52 – 1.25 (m, 8H), 0.93 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 128.3, 127.3, 125.8, 69.3, 63.1, 53.7, 29.4, 20.6, 14.1; Determined by HPLC analysis [Daicel chiralpak AD-H, *n*-hexane/*i*-PrOH =

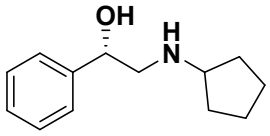
98:2, flow rate = 0.4 ml/min, wavelength = 225 nm, *t* (minor) = 10.255 min, *t* (major) = 11.966 min]; HRMS-ESI (m/z): calcd for $C_{16}H_{28}NO^+$ $[M+H]^+$ 250.2165, found 250.2168.

(*S*)-2-(cyclohexylamino)-1-phenylethanol (3aj)



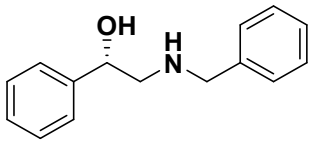
White solid; m.p.= 102-103 ℃; 74% yield, 97% *ee*; $[\alpha]_D^{25}$ = +25.4 (*c* = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.30 (m, 4H), 7.29 – 7.23 (m, 1H), 4.65 (dd, *J* = 9.2, 3.6 Hz, 1H), 2.95 (dt, *J* = 12.0, 2.8 Hz, 1H), 2.76 (brs, 1H), 2.66 (dd, *J* = 12.0, 9.2 Hz, 1H), 2.43 (tt, *J* = 10.4, 3.6 Hz, 1H), 1.89 (d, *J* = 12.0 Hz, 2H), 1.78 – 1.67 (m, 2H), 1.66 – 1.55 (m, 1H), 1.31 – 0.98 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 128.3, 127.4, 125.8, 72.0, 56.5, 54.3, 33.9, 33.6, 26.0, 25.0; Determined by HPLC analysis [Daicel chiralpak IC, *n*-hexane/*i*-PrOH/DEA = 95:5:0.1, flow rate = 1 ml/min, wavelength = 210 nm, *t* (minor) = 9.180 min, *t* (major) = 12.433 min]; HRMS-ESI (m/z): calcd for $C_{14}H_{22}NO^+$ $[M+H]^+$ 220.1696, found 220.1683.

(*S*)-2-(cyclopentylamino)-1-phenylethanol (3ak)



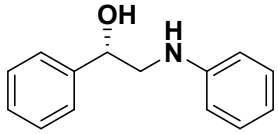
White solid; m.p.= 65-67 ℃; 77% yield, 96% *ee*; $[\alpha]_D^{25}$ = +32.8 (*c* = 0.5, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.30 (m, 4H), 7.29 – 7.23 (m, 1H), 4.75 (dd, *J* = 9.2, 2.4 Hz, 1H), 3.45 (brs, 2H), 3.12 – 3.01 (m, 1H), 2.90 – 2.79 (m, 1H), 2.68 (dd, *J* = 12.0, 9.6 Hz, 1H), 1.85 – 1.46 (m, 6H), 1.38 – 1.21 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.0, 128.3, 127.4, 125.8, 71.8, 59.6, 56.0, 33.0, 32.8, 24.0, 23.9; Determined by HPLC analysis [Daicel chiralpak IC, *n*-hexane/*i*-PrOH/DEA = 95:5:0.1, flow rate = 1 ml/min, wavelength = 210 nm, *t* (minor) = 8.483 min, *t* (major) = 11.776 min]; HRMS-ESI (m/z): calcd for $C_{13}H_{20}NO^+$ $[M+H]^+$ 206.1539, found 206.1531.

(*S*)-2-(benzylamino)-1-phenylethanol (3al)



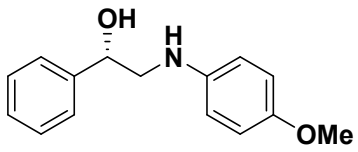
White solid; m.p.= 103-105 °C; 81% yield, 76% *ee*; $[\alpha]_D^{25}$ = +43.6 (*c* = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.23 (m, 10H), 4.73 (dd, *J* = 8.8, 3.6 Hz, 1H), 3.92 – 3.76 (m, 2H), 2.91 (dt, *J* = 12.4, 2.8 Hz, 1H), 2.75 (dd, *J* = 12.4, 9.2 Hz, 1H), 2.65 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 139.8, 128.5, 128.4, 128.1, 127.5, 127.2, 125.8, 71.8, 56.5, 53.5. Determined by HPLC analysis [Daicel chiralpak IC, *n*-hexane/*i*-PrOH/DEA = 95:5:0.1, flow rate = 1 ml/min, wavelength = 210 nm, *t* (minor) = 13.257 min, *t* (major) = 16.547 min]; HRMS-ESI (m/z): calcd for $C_{15}H_{18}NO^+$ $[M+H]^+$ 228.1383, found 228.1378.

(*S*)-1-phenyl-2-(phenylamino)ethanol (3am)



Yellow oil; 57% yield, 95% *ee*; $[\alpha]_D^{25}$ = -6.1 (*c* = 1.0, $CHCl_3$) {lit.[4] $[\alpha]_D^{23}$ = +5.7 (*c* = 1.0, $CHCl_3$) (***R***)}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.33 (m, 4H), 7.33 – 7.26 (m, 1H), 7.18 (t, *J* = 7.8 Hz, 2H), 6.74 (t, *J* = 7.2 Hz, 1H), 6.65 (d, *J* = 7.8 Hz, 2H), 4.87 (dd, *J* = 8.8, 4.0 Hz, 1H), 3.39 (dd, *J* = 13.2, 4.0 Hz, 1H), 3.25 (dd, *J* = 13.2, 8.8 Hz, 1H), 3.20 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 142.0, 129.3, 128.6, 128.0, 125.9, 118.1, 113.5, 72.4, 51.8; Determined by HPLC analysis [Daicel chiralpak AD-H, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1 ml/min, wavelength = 230 nm, *t* (major) = 13.173 min, *t* (minor) = 15.853 min]; HRMS-ESI (m/z): calcd for $C_{14}H_{16}NO^+$ $[M+H]^+$ 214.1226, found 214.1229.

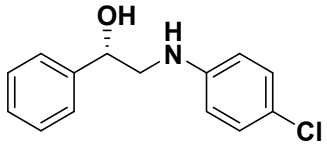
(*S*)-2-(4-methoxyphenylamino)-1-phenylethanol (3an)



Yellow oil; 61% yield, 96% *ee*; $[\alpha]_D^{25}$ = -6.7 (*c* = 1.0, $CHCl_3$) {lit.[4] $[\alpha]_D^{23}$ = +3.1 (*c* = 1.0, $CHCl_3$) (***R***)}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.35 (m, 4H), 7.35 – 7.29 (m, 1H), 6.83

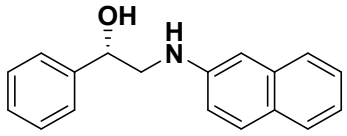
– 6.76 (m, 2H), 6.70 – 6.63 (m, 2H), 4.95 – 4.87 (m, 1H), 3.76 (s, 3H), 3.43 – 3.34 (m, 1H), 3.29 – 3.21 (m, 1H), 3.13 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 142.2, 141.9, 128.6, 128.0, 125.9, 115.1, 114.9, 72.4, 55.8, 53.0; Determined by HPLC analysis [Daicel chiralpak AD-H, *n*-hexane/*i*-PrOH = 85:15, flow rate = 1 ml/min, wavelength = 254 nm, *t* (minor) = 12.884 min, *t* (major) = 14.708 min]; HRMS-ESI (m/z): calcd for $C_{15}H_{18}NO_2^+$ $[M+H]^+$ 244.1332, found 244.1338.

(*S*)-2-(4-chlorophenylamino)-1-phenylethanol (3ao)



White solid; m.p.= 73-74 °C; 51% yield, 98% *ee*; $[\alpha]_D^{25}$ = -17.2 (*c* = 1.0, $CHCl_3$) {lit.[4] $[\alpha]_D^{23}$ = +13.7 (*c* = 1.0, $CHCl_3$) (***R***)}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (d, *J* = 4.8 Hz, 4H), 7.36 – 7.31 (m, 1H), 7.13 (d, *J* = 8.4 Hz, 2H), 6.59 (d, *J* = 8.4 Hz, 2H), 4.91 (dd, *J* = 8.4, 4.2 Hz, 1H), 3.38 (dt, *J* = 13.2, 3.2 Hz, 1H), 3.32 – 3.25 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 146.4, 141.8, 129.2, 128.7, 128.2, 125.9, 122.7, 114.5, 72.5, 51.8; Determined by HPLC analysis [Daicel chiralpak AD-H, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1 ml/min, wavelength = 230 nm, *t* (major) = 16.843 min, *t* (minor) = 18.454 min]; HRMS-ESI (m/z): calcd for $C_{14}H_{15}ClNO^+$ $[M+H]^+$ 248.0837, found 248.0832.

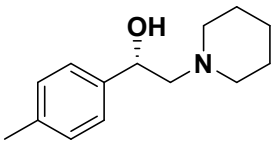
(*S*)-2-(naphthalen-2-ylamino)-1-phenylethanol (3ap)



White solid; m.p.= 76-78 °C; 60% yield, 94% *ee*; $[\alpha]_D^{25}$ = -28.1 (*c* = 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.0 Hz, 1H), 7.59 (t, *J* = 8.8 Hz, 2H), 7.41 – 7.27 (m, 6H), 7.24 – 7.18 (m, 1H), 6.91 – 6.83 (m, 2H), 4.94 (dd, *J* = 8.7, 3.9 Hz, 1H), 3.51 (brs, 1H), 3.47 (dd, *J* = 13.2, 4.0 Hz, 1H), 3.35 (dd, *J* = 13.2, 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 141.9, 135.0, 129.1, 128.6, 128.0, 127.9, 127.6, 126.4, 126.0, 125.9, 122.4, 118.3, 105.7, 72.3, 51.9; Determined by HPLC analysis [Daicel chiralpak IA, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1 ml/min, wavelength = 254 nm, *t* (minor) = 28.247 min, *t*

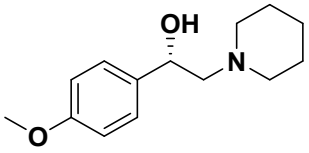
(major) = 31.015 min]; HRMS-ESI (m/z): calcd for $C_{18}H_{18}NO^+$ $[M+H]^+$ 264.1383, found 264.1385.

(*S*)-2-(piperidin-1-yl)-1-*p*-tolylethanol (3ba)



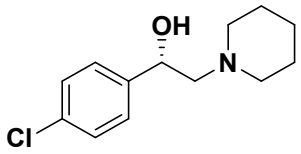
Off white solid; m.p.= 85-86 °C; 90% yield, 97% *ee*; $[\alpha]_D^{25}$ = +27.8 (*c* = 0.5, $CHCl_3$) {lit.[4] $[\alpha]_D^{23}$ = -20.3 (*c* = 0.1, $CHCl_3$) (***R***)}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 (d, *J* = 7.8 Hz, 2H), 7.15 (d, *J* = 7.8 Hz, 2H), 4.69 (dd, *J* = 10.8, 3.6 Hz, 1H), 2.69 (s, 2H), 2.46 (dd, *J* = 12.6, 3.6 Hz, 1H), 2.38 (dd, *J* = 12.6, 10.8 Hz, 3H), 2.33 (s, 3H), 1.70 – 1.53 (m, 4H), 1.51 – 1.41 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.4, 137.0, 129.0, 125.8, 68.5, 67.0, 54.5, 26.1, 24.3, 21.1; Determined by HPLC analysis [Daicel chiralpak AD-H, *n*-hexane/*i*-PrOH = 95:5, flow rate = 1 ml/min, wavelength = 225 nm, *t* (minor) = 7.128 min, *t* (major) = 8.223 min]; HRMS-ESI (m/z): calcd for $C_{14}H_{22}NO^+$ $[M+H]^+$ 220.1696, found 220.1690.

(*S*)-1-(4-methoxyphenyl)-2-(piperidin-1-yl)ethanol (3ca)



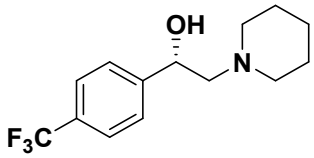
White solid; m.p.= 68-70 °C; 92% yield, 95% *ee*; $[\alpha]_D^{25}$ = +34.1 (*c* = 0.5, $CHCl_3$) {lit.[4] $[\alpha]_D^{23}$ = -29.5 (*c* = 0.4, $CHCl_3$) (***R***)}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 2H), 6.92 – 6.83 (m, 2H), 4.67 (dd, *J* = 10.0, 4.0 Hz, 1H), 3.79 (s, 3H), 2.69 (s, 2H), 2.49 – 2.30 (m, 4H), 1.71 – 1.53 (m, 4H), 1.52 – 1.41 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 134.5, 127.1, 113.7, 68.3, 67.0, 55.3, 54.5, 26.1, 24.3; Determined by HPLC analysis [Daicel chiralpak AD-H, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1 ml/min, wavelength = 230 nm, *t* (minor) = 8.251 min, *t* (major) = 9.408 min]; HRMS-ESI (m/z): calcd for $C_{14}H_{22}NO_2^+$ $[M+H]^+$ 236.1645, found 236.1638.

(*S*)-1-(4-chlorophenyl)-2-(piperidin-1-yl)ethanol (3da)



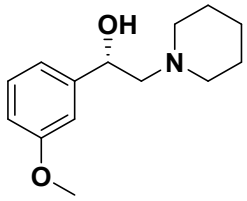
Off white solid; m.p.= 97-98 °C; 93% yield, 97% *ee*; $[\alpha]_D^{25}$ = +38.7 (*c* = 0.5, $CHCl_3$) {lit.[4] $[\alpha]_D^{23}$ = -37.5 (*c* = 0.5, $CHCl_3$) (***R***)}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (s, 4H), 4.68 (dd, *J* = 10.8, 3.6 Hz, 1H), 2.68 (s, 2H), 2.46 (dd, *J* = 12.4, 3.6 Hz, 1H), 2.42 – 2.26 (m, 3H), 1.70 – 1.53 (m, 4H), 1.52 – 1.41 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 132.9, 128.4, 127.2, 68.0, 66.8, 54.4, 26.1, 24.2; Determined by HPLC analysis [Daicel chiralpak AD-H, *n*-hexane/*i*-PrOH = 95:5, flow rate = 1 ml/min, wavelength = 230 nm, *t* (minor) = 7.302 min, *t* (major) = 8.383 min]; HRMS-ESI (m/z): calcd for $C_{13}H_{19}ClNO^+$ $[M+H]^+$ 240.1150, found 240.1153.

(*S*)-2-(piperidin-1-yl)-1-(4-(trifluoromethyl)phenyl)ethanol (3ea)



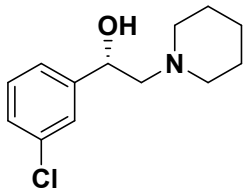
Off white solid; m.p.= 91-93 °C; 81% yield, 93% *ee*; $[\alpha]_D^{25}$ = +44.3 (*c* = 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 4.76 (dd, *J* = 10.8, 3.6 Hz, 1H), 4.35 (brs, 1H), 2.69 (s, 2H), 2.51 (dd, *J* = 12.4, 3.6 Hz, 1H), 2.46 – 2.26 (m, 3H), 1.72 – 1.54 (m, 4H), 1.54 – 1.38 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.7, 129.5 (q, $^2J_{C\text{-}F}$ = 32 Hz), 126.1, 125.3 (q, $^3J_{C\text{-}F}$ = 4 Hz), 124.2 (q, $^1J_{C\text{-}F}$ = 270 Hz), 68.1, 66.6, 54.4, 26.1, 24.2; ^{19}F NMR (375 MHz, $CDCl_3$) δ -62.4; Determined by HPLC analysis [Daicel chiralpak IA, *n*-hexane/*i*-PrOH = 95:5, flow rate = 0.5 ml/min, wavelength = 225 nm, *t* (minor) = 14.738 min, *t* (major) = 16.620 min]; HRMS-ESI (m/z): calcd for $C_{14}H_{19}F_3NO^+$ $[M+H]^+$ 274.1413, found 274.1411.

(*S*)-1-(3-methoxyphenyl)-2-(piperidin-1-yl)ethanol (3fa)



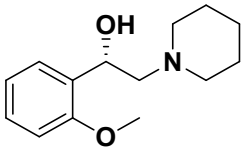
Light yellow oil; 92% yield, 96% *ee*; $[\alpha]_D^{25}$ = +46.2 (*c* = 0.3, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.24 (t, *J* = 8.0 Hz, 1H), 6.99 – 6.90 (m, 2H), 6.80 (dd, *J* = 8.0, 2.4 Hz, 1H), 4.69 (dd, *J* = 10.8, 3.6 Hz, 1H), 3.80 (s, 3H), 2.68 (s, 2H), 2.48 (dd, *J* = 12.4, 3.6 Hz, 1H), 2.43 – 2.30 (m, 3H), 1.72 – 1.52 (m, 4H), 1.53 – 1.38 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 144.3, 129.3, 118.1, 113.0, 111.1, 68.6, 66.9, 55.2, 54.4, 26.1, 24.3; Determined by HPLC analysis [Daicel chiralpak AD-H, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1 ml/min, wavelength = 230 nm, *t* (minor) = 7.839 min, *t* (major) = 9.696 min]; HRMS-ESI (m/z): calcd for $C_{14}H_{22}NO_2^+$ $[M+H]^+$ 236.1645, found 236.1643.

(*S*)-1-(3-chlorophenyl)-2-(piperidin-1-yl)ethanol (3ga)



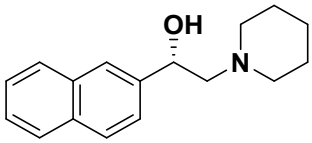
White solid; m.p.= 82-83 °C; 91% yield, 96% *ee*; $[\alpha]_D^{25}$ = +87.6 (*c* = 0.3, $CHCl_3$) {lit.[4] $[\alpha]_D^{23}$ = -83.5 (*c* = 0.2, $CHCl_3$) (***R***)}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 (s, 1H), 7.30 – 7.19 (m, 3H), 4.68 (dd, *J* = 10.8, 3.2 Hz, 1H), 4.22 (s, 1H), 2.68 (s, 2H), 2.53 – 2.45 (m, 1H), 2.42 – 2.28 (m, 3H), 1.72 – 1.54 (m, 4H), 1.52 – 1.40 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 134.2, 129.6, 127.4, 126.0, 124.0, 68.1, 66.7, 54.4, 26.1, 24.2; Determined by HPLC analysis [Daicel chiralpak AD-H, *n*-hexane/*i*-PrOH = 95:5, flow rate = 0.5 ml/min, wavelength = 230 nm, *t* (minor) = 15.621 min, *t* (major) = 18.374 min]; HRMS-ESI (m/z): calcd for $C_{13}H_{19}ClNO^+$ $[M+H]^+$ 240.1150, found 240.1159.

(*S*)-1-(2-methoxyphenyl)-2-(piperidin-1-yl)ethanol (3ha)



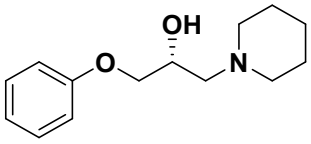
White solid; m.p.= 75-77 °C; 92% yield, 95% *ee*; $[\alpha]_D^{25}$ = +53.7 (*c* = 0.5, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.6 Hz, 1H), 7.23 (td, *J* = 8.0, 1.6 Hz, 1H), 6.98 (t, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 8.4 Hz, 1H), 5.12 (d, *J* = 10.0 Hz, 1H), 3.81 (s, 3H), 2.69 (s, 2H), 2.61 (dd, *J* = 12.4, 3.2 Hz, 1H), 2.45 – 2.25 (m, 3H), 1.69 – 1.53 (m, 4H), 1.51 – 1.40 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 130.8, 127.9, 126.3, 120.7, 110.0, 65.0, 63.6, 55.3, 54.5, 26.2, 24.3; Determined by HPLC analysis [Daicel chiralpak IA, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1 ml/min, wavelength = 225 nm, *t* (minor) = 7.353 min, *t* (major) = 8.819 min]; HRMS-ESI (m/z): calcd for $C_{14}H_{22}NO_2^+$ $[M+H]^+$ 236.1645, found 236.1652.

(*S*)-1-(naphthalen-2-yl)-2-(piperidin-1-yl)ethanol (3ia)



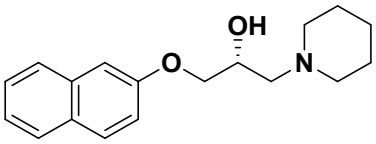
White solid; m.p.= 101-102 °C; 90% yield, 99% *ee*; $[\alpha]_D^{25}$ = +53.8 (*c* = 0.3, $CHCl_3$) {lit.[4] $[\alpha]_D^{23}$ = -48.7 (*c* = 0.4, $CHCl_3$) (***R***)}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 – 7.78 (m, 4H), 7.51 – 7.40 (m, 3H), 4.89 (dd, *J* = 10.4, 3.6 Hz, 1H), 4.35 (brs, 1H), 2.73 (s, 2H), 2.57 (dd, *J* = 12.4, 3.6 Hz, 1H), 2.51 – 2.34 (m, 3H), 1.72 – 1.56 (m, 4H), 1.54 – 1.43 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.9, 133.4, 133.0, 128.0, 127.9, 127.7, 126.0, 125.6, 124.6, 124.0, 68.7, 66.8, 54.5, 26.1, 24.2; Determined by HPLC analysis [Daicel chiralpak OD-H, *n*-hexane/*i*-PrOH = 98:2, flow rate = 0.5 ml/min, wavelength = 254 nm, *t* (minor) = 19.261 min, *t* (major) = 21.778 min]; HRMS-ESI (m/z): calcd for $C_{17}H_{22}NO^+$ $[M+H]^+$ 256.1696, found 256.1694.

(*R*)-1-phenoxy-3-(piperidin-1-yl)propan-2-ol (3ja)



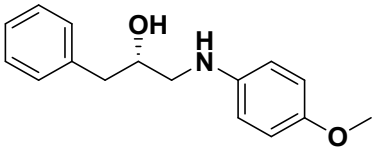
White solid; m.p.= 62-63 °C; 90% yield, 96% *ee*; $[\alpha]_D^{25}$ = -41.2 (*c* = 0.5, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.33 – 7.29 (m, 2H), 7.00 – 6.92 (m, 3H), 4.11 (m, 1H), 4.04 – 3.96 (m, 2H), 2.64 (s, 2H), 2.55 – 2.49 (m, 2H), 2.41 (s, 2H), 1.69 – 1.56 (m, 4H), 1.49 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.9, 129.6, 121.0, 114.7, 70.5, 65.5, 61.3, 54.9, 26.2, 24.4; Determined by HPLC analysis [Daicel chiralpak AD-H, *n*-hexane/*i*-PrOH = 90:10, flow rate = 0.8 ml/min, wavelength = 254 nm, *t* (major) = 15.366 min, *t* (minor) = 18.164 min]; HRMS-ESI (m/z): calcd for $C_{14}H_{22}NO_2^+$ $[M+H]^+$ 236.1645, found 236.1642.

(*R*)-1-(naphthalen-2-yloxy)-3-(piperidin-1-yl)propan-2-ol (3ka)



White solid; m.p.= 76-78 °C; 92% yield, 96% *ee*; $[\alpha]_D^{25}$ = -28.7 (*c* = 0.5, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.80 – 7.68 (m, 3H), 7.43 (t, *J* = 7.2 Hz, 1H), 7.33 (t, *J* = 7.2 Hz, 1H), 7.21 – 7.12 (m, 2H), 4.24 – 4.17 (m, 1H), 4.15 – 4.04 (m, 2H), 2.82 – 2.36 (m, 6H), 1.72 – 1.59 (m, 4H), 1.56 – 1.38 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 156.8, 134.6, 129.5, 129.2, 127.8, 126.9, 126.5, 123.8, 119.0, 106.9, 70.5, 65.3, 61.5, 54.9, 25.9, 24.2; Determined by HPLC analysis [Daicel chiralpak AD-H, *n*-hexane/*i*-PrOH = 85:15, flow rate = 1 ml/min, wavelength = 254 nm, *t* (major) = 8.603 min, *t* (minor) = 9.870 min]; HRMS-ESI (m/z): calcd for $C_{18}H_{24}NO_2^+$ $[M+H]^+$ 286.1802, found 286.1808.

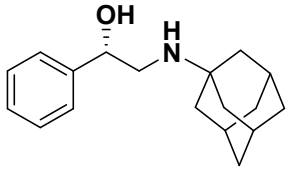
(*S*)-1-((4-methoxyphenyl)amino)-3-phenylpropan-2-ol (3ln)



Off white solid; m.p.= 67-68 °C; 68% yield, 96% *ee*; $[\alpha]_D^{25}$ = -3.2 (*c* = 0.5, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 2H), 7.27 – 7.20 (m, 3H), 6.80 – 6.73 (m, 2H),

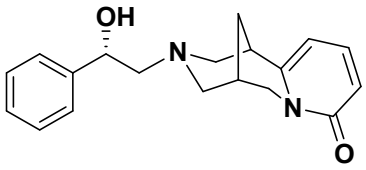
6.63 – 6.56 (m, 2H), 4.08 – 4.02 (m, 1H), 3.74 (s, 3H), 3.24 (dd, *J* = 12.6, 3.6 Hz, 1H), 3.03 (dd, *J* = 12.6, 8.4 Hz, 1H), 2.91 – 2.77 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.6, 142.2, 137.8, 129.4, 128.7, 126.7, 114.9, 71.1, 55.8, 50.7, 41.7; Determined by HPLC analysis [Daicel chiralpak IA, *n*-hexane/*i*-PrOH = 90:10, flow rate = 1 ml/min, wavelength = 230 nm, *t* (minor) = 12.390 min, *t* (major) = 13.989 min]; HRMS-ESI (m/z): calcd for $C_{16}H_{19}NNaO_2^+$ $[M+Na]^+$ 280.1308, found 280.1311.

(*S*)-1-(naphthalen-2-yl)-2-(piperidin-1-yl)ethanol (3aq)



White solid; m.p.= 113-114 °C; 72% yield, 95% *ee*; $[\alpha]_D^{25}$ = +53.7 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.30 (m, 4H), 7.29 – 7.23 (m, 1H), 4.58 (dd, *J* = 8.8, 3.6 Hz, 1H), 2.91 (dd, *J* = 12.0, 3.6 Hz, 1H), 2.67 (brs, 1H), 2.61 (dd, *J* = 12.0, 8.8 Hz, 1H), 2.05 (s, 3H), 1.70 – 1.52 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 128.3, 127.3, 125.8, 72.2, 50.4, 48.2, 43.0, 36.6, 29.5; Determined by HPLC analysis [Daicel chiralpak IC, *n*-hexane/*i*-PrOH/DEA = 95:5:0.1, flow rate = 1 ml/min, wavelength = 210 nm, *t* (minor) = 9.708 min, *t* (major) = 13.174 min]; HRMS-ESI (m/z): calcd for $C_{18}H_{26}NO^+$ $[M+H]^+$ 272.2009, found 272.2007.

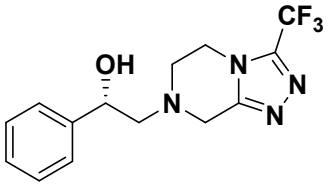
(*S*)-3-(2-oxo-2-phenylethyl)-1,2,3,4,5,6-hexahydro-8H-1,5-methanopyrido[1,2-a][1,5]diazocin-8-one (3ar)



White solid; m.p.= 158-159 °C; 93% yield, 96% *ee*; $[\alpha]_D^{25}$ = +46.4 (*c* = 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.17 (m, 6H), 6.49 – 6.41 (m, 1H), 6.01 (d, *J* = 6.8 Hz, 1H), 4.54 (dd, *J* = 10.0, 3.6 Hz, 1H), 4.12 (d, *J* = 15.6 Hz, 1H), 3.88 (dd, *J* = 15.6, 6.4 Hz, 1H), 3.11 (d, *J* = 10.0 Hz, 1H), 3.02 (s, 2H), 2.87 (d, *J* = 11.2 Hz, 1H), 2.61 (d, *J* = 11.2 Hz, 1H), 2.53 – 2.34 (m, 4H), 2.01 – 1.75 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4,

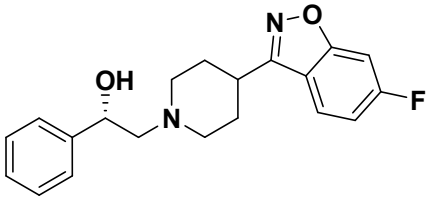
150.5, 141.9, 138.8, 128.2, 127.4, 125.6, 117.0, 104.8, 68.6, 65.5, 61.6, 59.0, 50.0, 35.1, 28.2, 25.8; Determined by HPLC analysis [Daicel chiralpak IB, *n*-hexane/*i*-PrOH = 85:15, flow rate = 1 ml/min, wavelength = 230 nm, *t* (minor) = 24.218 min, *t* (major) = 27.469 min]; HRMS-ESI (m/z): calcd for $C_{19}H_{23}N_2O_2^+$ $[M+H]^+$ 311.1754, found 311.1751.

(*S*)-1-phenyl-2-(3-(trifluoromethyl)-5,6-dihydro-[1,2,4]triazolo[4,3-a]pyrazin-7(8H)-yl)ethanol (3as)



White solid; m.p.= 162-164 °C; 86% yield, 96% *ee*; $[\alpha]_D^{25}$ = +92.6 (*c* = 0.5, $CHCl_3$); ^1H NMR (600 MHz, DMSO-d_6) δ 7.41 – 7.37 (m, 2H), 7.33 (t, *J* = 7.8 Hz, 2H), 7.27 – 7.21 (m, 1H), 5.28 (d, *J* = 4.2 Hz, 1H), 4.87 – 4.81 (m, 1H), 4.14 (t, *J* = 4.8 Hz, 2H), 4.00 (s, 2H), 3.13 – 3.01 (m, 2H), 2.79 – 2.69 (m, 2H).; ^{13}C NMR (150 MHz, DMSO-d_6) δ 152.6, 144.2, 142.3 (q, $^2J_{C\text{-}F}$ = 33 Hz), 128.0, 126.9, 126.1, 118.6 (q, $^1J_{C\text{-}F}$ = 270 Hz), 70.4, 63.9, 48.7, 48.3, 43.0; ^{19}F NMR (565 MHz, DMSO-d_6) δ -61.92; Determined by HPLC analysis [Daicel chiralpak IC, *n*-hexane/*i*-PrOH/DEA = 80:20:0.1, flow rate = 1 ml/min, wavelength = 220 nm, *t* (minor) = 31.253 min, *t* (major) = 35.349 min]; HRMS-ESI (m/z): calcd for $C_{14}H_{16}F_3N_4O^+$ $[M+H]^+$ 313.1271, found 313.1270.

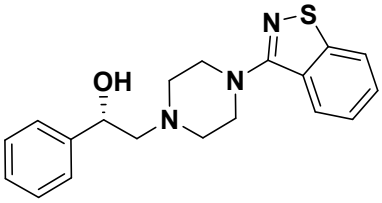
(*S*)-2-(4-(6-fluorobenzo[d]isoxazol-3-yl)piperidin-1-yl)-1-phenylethanol (3at)



White solid; m.p.= 134-136 °C; 85% yield, 94% *ee*; $[\alpha]_D^{25}$ = +105.3 (*c* = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 8.8, 5.2 Hz, 1H), 7.44 – 7.33 (m, 4H), 7.31 – 7.23 (m, 3H), 7.08 (td, *J* = 8.8, 2.0 Hz, 1H), 4.80 (dd, *J* = 10.4, 3.6 Hz, 1H), 4.08 (brs, 1H), 3.34 (d, *J* = 11.6 Hz, 1H), 3.19 – 3.09 (m, 1H), 3.01 (d, *J* = 11.6 Hz, 1H), 2.66 – 2.50 (m, 3H), 2.30 (td, *J* = 11.4, 3.6 Hz, 1H), 2.24 – 2.04 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1

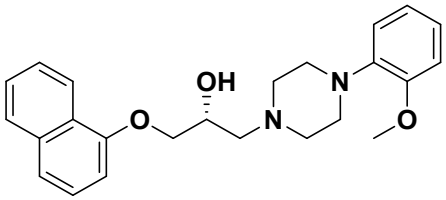
(d, $^{1}J_{C\text{-}F}$ = 250 Hz), 163.9 (d, $^{3}J_{C\text{-}F}$ = 14 Hz), 160.8, 142.0, 128.4, 127.6, 125.9, 122.4 (d, $^{3}J_{C\text{-}F}$ = 11 Hz), 117.2, 112.5 (d, $^{2}J_{C\text{-}F}$ = 25 Hz), 97.5 (d, $^{2}J_{C\text{-}F}$ = 27 Hz), 68.8, 66.5, 54.9, 51.9, 34.2, 30.7, 30.4; ^{19}F NMR (375 MHz, $CDCl_3$) δ -109.4; Determined by HPLC analysis [Daicel chiralpak OD-H, *n*-hexane/*i*-PrOH = 90:10, flow rate = 0.8 ml/min, wavelength = 225 nm, *t* (minor) = 16.092 min, *t* (major) = 18.267 min]; HRMS-ESI (m/z): calcd for $C_{20}H_{22}FN_2O_2^+$ $[M+H]^+$ 341.1660, found 341.1658.

(*S*)-2-(4-(benzo[d]isothiazol-3-yl)piperazin-1-yl)-1-phenylethanol (3au)



White solid; m.p.= 76-78 °C; 83% yield, 95% *ee*; $[\alpha]_D^{25}$ = +82.7 (*c* = 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.52 – 7.44 (m, 1H), 7.43 – 7.33 (m, 5H), 7.32 – 7.26 (m, 1H), 4.82 (dd, *J* = 10.0, 3.6 Hz, 1H), 3.97 (brs, 1H), 3.67 – 3.55 (m, 4H), 3.05 – 2.94 (m, 2H), 2.76 – 2.67 (m, 2H), 2.67 – 2.54 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8, 152.8, 141.9, 128.4, 127.9, 127.6, 125.9, 123.9, 123.8, 120.6, 68.8, 66.3, 52.8, 50.1; Determined by HPLC analysis [Daicel chiralpak AD-H, *n*-hexane/*i*-PrOH = 85:15, flow rate = 1 ml/min, wavelength = 225 nm, *t* (minor) = 15.093 min, *t* (major) = 17.956 min]; HRMS-ESI (m/z): calcd for $C_{19}H_{22}N_3OS^+$ $[M+H]^+$ 340.1478, found 340.1481.

(*R*)-Naftopidil



Off white solid; m.p.= 125-127 °C; 86% yield, 95% *ee*; $[\alpha]_D^{25}$ = -3.2 (*c* = 1.5, MeOH) {lit.[5] $[\alpha]_D^{27}$ = -3.0 (*c* = 1.5, MeOH)}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.30 – 8.25 (m, 1H), 7.82 – 7.77 (m, 1H), 7.52 – 7.45 (m, 2H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.05 – 6.98 (m, 1H), 6.97 – 6.90 (m, 2H), 6.85 (dd, *J* = 16.8, 7.8 Hz, 2H), 4.34 – 4.27 (m, 1H),

4.22 (dd, J = 9.6, 4.8 Hz, 1H), 4.16 (dd, J = 9.6, 4.8 Hz, 1H), 3.86 (s, 3H), 3.13 (s, 4H), 2.97 – 2.88 (m, 2H), 2.75 – 2.67 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.4, 152.3, 141.1, 134.5, 127.5, 126.4, 125.8, 125.6, 125.2, 123.0, 121.9, 121.0, 120.6, 118.2, 111.2, 104.9, 70.6, 65.6, 60.9, 55.4, 53.6, 50.7; Determined by HPLC analysis [Daicel chiralpak AD-H, *n*-hexane/*i*-PrOH/DEA = 80:20:0.1, flow rate = 1 ml/min, wavelength = 230 nm, *t* (major) = 7.246 min, *t* (minor) = 9.285 min]; HRMS-ESI (m/z): calcd for $C_{24}H_{29}N_2O_3^+$ $[M+H]^+$ 393.2173, found 393.2171.

5. DFT calculations

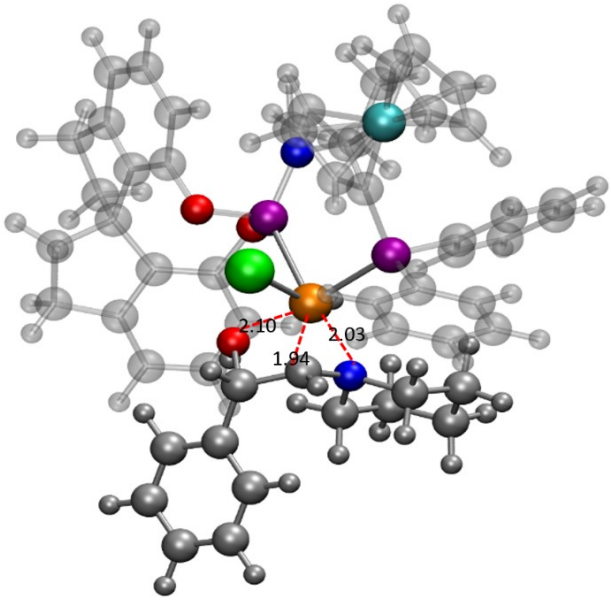
Geometric structures of all species were optimized at T = 298.15 K in gas phase by DFT calculation. DFT calculations were performed using the Gaussian 16 package.[6] All the structures are optimized using the B3LYP functional with the basis set lanl2dz for Ru and Fe,[7] B3LYP/6-311+G (2df, p) for other main group atoms.[8] Vibrational analyses were performed to ensure intermediates to have no imaginary frequencies and the transition state structures to have only one imaginary frequency. Transition state structures were confirmed to connect appropriate reactants or products by intrinsic reaction coordinate (IRC) calculations.[9] Solvent effects were considered using the SMD mode[10] at the B3LYP/6-311+G (d, p) with SDD for Ru and Fe.

Table S3. Calculated energies of transition states.

	Electronic Energy (EE)	EE + Thermal Free Energy Correction	ΔΔG(hatree)	ΔΔG(kcal/mol)
TS(*S*)-1	-9215.375580	-9214.389590	0.013814	8.63375
TS(*R*)-1	-9215.371347	-9214.384910	0.018494	11.55875
TS(*S*)-2	-9215.390462	-9214.403404	0	0
TS(*R*)-2	-9215.373440	-9214.386251	0.017153	10.720625

Coordinates for optimized structures:

TS(*S*)-1



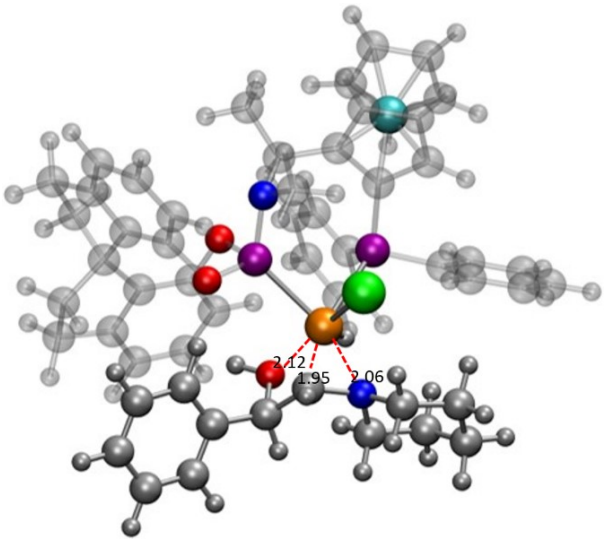
C 2.32883500 -2.04019100 -0.11754800

C	2.68717000	-0.71162600	-0.67361800
C	2.98357900	-0.92722100	-2.10673200
C	2.76142000	-2.32696900	-2.41457900
C	2.40039100	-3.00165700	-1.20579500
C	1.70669000	-2.36420500	1.25852300
C	2.44079000	-3.56491900	1.94485600
N	0.21867500	-2.68872300	1.06589000
P	-0.82236200	-1.38269900	0.46826200
C	-0.38303900	-3.56040200	2.14320700
O	-1.61188900	-2.01838800	-0.94799600
C	-1.96556500	-3.40974100	-0.81556100
C	-1.03843500	-4.41770800	-1.20081500
C	-1.36704100	-5.77793700	-1.05830200
C	-2.60547600	-6.16405100	-0.49820000
C	-3.52931800	-5.16769500	-0.13745900
C	-3.24119100	-3.79435500	-0.33665000
C	-4.90494400	-5.33721300	0.53567600
C	-5.22253000	-3.88905200	1.04490400
C	-4.47789900	-2.93517300	0.01367900
C	-5.42559000	-2.67712800	-1.23308600
C	-6.35258000	-1.49716300	-0.78014100
C	-5.45942700	-0.72059800	0.20726600
C	-4.32151900	-1.49418200	0.56193300
C	-5.64984700	0.57551500	0.71523200
C	-4.67690700	1.11890700	1.58715100
C	-3.50700800	0.39521300	1.89177900
C	-3.29492300	-0.91056500	1.34905400
O	-2.09564700	-1.62444700	1.66795800
P	2.14944300	0.89499900	0.09108500
C	3.09714800	2.17914600	-0.87736700
C	2.87376500	0.87693300	1.81522000
C	1.99496800	0.84830200	2.92459000
C	2.49026400	0.79724000	4.24273400
C	3.87967600	0.77508700	4.47482900
C	4.76558300	0.79659700	3.37977600
C	4.26594300	0.84301100	2.06254900
C	4.09125200	3.01465000	-0.31849900
C	4.74553200	3.97533100	-1.11690100
C	4.41043500	4.11649700	-2.47736400
C	3.40057300	3.30498700	-3.03413000
C	2.74131300	2.34770700	-2.23964000
H	1.83032800	-1.47998500	1.92346800
H	2.06456700	-3.73295300	2.96339300
H	2.31984800	-4.48706100	1.35879600
H	3.51139000	-3.32832000	2.01020300
H	0.05917500	-4.56880400	2.08268500

H	-0.22733000	-3.16035800	3.16544000
H	-1.46750000	-3.64075700	1.96693800
H	-0.06209400	-4.11278100	-1.59826100
H	-0.64069800	-6.54529700	-1.35926600
H	-2.83760400	-7.22646400	-0.34434800
H	-4.87752900	-6.07179000	1.35891900
H	-5.66373600	-5.67756900	-0.19310100
H	-6.30343800	-3.68168000	1.09222400
H	-4.79610600	-3.74568900	2.05240200
H	-4.81722900	-2.36501400	-2.09903700
H	-5.99326700	-3.57912800	-1.51152600
H	-7.26073600	-1.87277400	-0.27343600
H	-6.67702800	-0.86811200	-1.62711800
H	-6.54359000	1.15700200	0.45224300
H	-4.83488500	2.11114400	2.03200400
H	-2.74945500	0.81616000	2.56476400
H	0.90967400	0.85780900	2.75202200
H	1.78928800	0.77335100	5.08853600
H	4.26952000	0.73714500	5.50158100
H	5.85135000	0.77469400	3.54774600
H	4.97535300	0.84819300	1.22903400
H	4.35662800	2.93569000	0.74312400
H	5.51829900	4.61571300	-0.66964000
H	4.92450000	4.86352200	-3.09794000
H	3.12009600	3.42114200	-4.09028000
H	1.92914900	1.73672000	-2.66619100
C	5.81651200	-1.08756700	-0.42934500
C	5.43512100	-2.23209300	0.37678600
C	5.25187800	-3.36670000	-0.52953100
C	5.51256000	-2.88583300	-1.88336200
C	5.86869800	-1.48878100	-1.80662900
Fe	4.06714500	-1.94310300	-0.96378100
H	2.23364900	-4.07417400	-1.10197700
H	2.91049500	-2.79559800	-3.38854300
H	3.18949900	-0.15217600	-2.84143700
H	5.43782900	-2.26461200	1.46626000
H	6.06287300	-0.09106200	-0.06404200
H	5.10376000	-4.40601900	-0.23723800
H	5.51448500	-3.49272700	-2.78908900
H	6.10487400	-0.83888800	-2.65207500
Ru	-0.27550000	1.14837600	-0.09654100
C	-0.06497600	4.59890300	3.10205600
C	-1.26849700	3.65284900	2.82890100
C	-1.61842800	3.61951500	1.31323100
C	0.75083900	4.07094200	0.72417000
C	1.14719800	4.17626600	2.22392500

H	-2.49121900	2.97043800	1.14306400
H	-1.03407100	2.62985300	3.16808200
H	-2.16302700	3.99843600	3.37577200
H	-0.35220700	5.63863300	2.86818700
H	0.21173400	4.55727000	4.16883500
H	1.60214100	3.72732000	0.11217100
H	0.42189300	5.06016000	0.34846000
H	1.54357100	3.20774800	2.56937000
H	1.95743200	4.92169100	2.30410500
H	-1.86160000	4.63639100	0.94927900
C	-0.60224300	2.83442000	-0.99435300
C	-2.04524400	2.55696000	-1.48854800
H	-1.94477100	2.16578100	-2.52823200
O	-2.28675900	1.31575200	-0.66122700
H	-3.01165500	1.49719500	0.03668100
C	-3.17159200	3.61544200	-1.43912700
C	-4.52571200	3.20707800	-1.46038300
C	-2.86189800	4.99517600	-1.47322400
C	-5.55514900	4.16801500	-1.47862100
H	-4.77750500	2.13775200	-1.47163200
C	-3.89317600	5.95321000	-1.50204800
H	-1.81344500	5.32066000	-1.49437900
C	-5.24169200	5.54211900	-1.49688200
H	-6.60463800	3.84289100	-1.49191100
H	-3.64372000	7.02287800	-1.53187300
H	-6.04585700	6.29055000	-1.51804700
N	-0.42622500	3.09090900	0.47726600
H	0.02430700	3.46618400	-1.64180300
Cl	-0.06781100	0.26153300	-2.26309700
H	-0.67947400	0.95086200	1.41768700

TS(*R*)-1



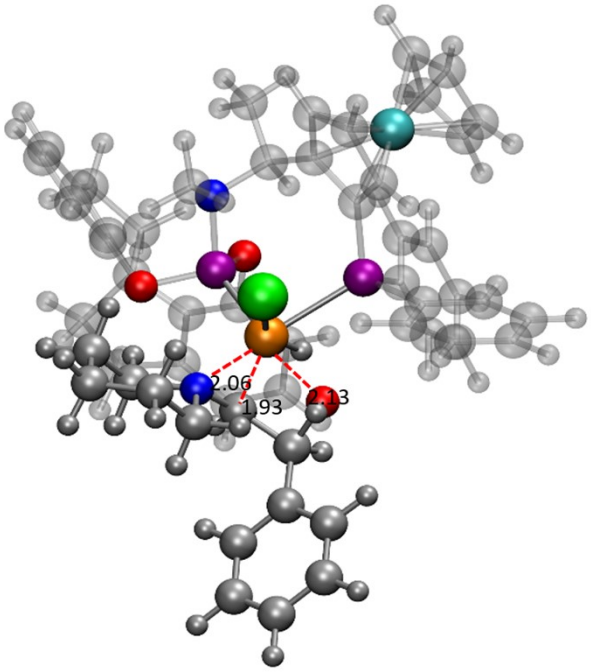
C	2.16446300	-2.40032400	-0.93402300
C	2.87402700	-1.15931700	-0.51468400
C	4.12249900	-1.11972200	-1.30153400
C	4.14709400	-2.23874000	-2.21186100
C	2.98162500	-3.03573900	-1.96756000
C	0.70563000	-2.79624200	-0.63633900
C	0.42765900	-4.31917300	-0.86717300
N	-0.30548600	-2.00199100	-1.47781800
P	-1.00987900	-0.59124200	-0.65302800
C	0.14423800	-1.75775800	-2.89923300
O	-2.59072500	-0.54094400	-1.39942400
C	-3.17619100	-1.84153900	-1.65793800
C	-3.10626400	-2.36441300	-2.98003200
C	-3.61520700	-3.64034600	-3.27723300
C	-4.17120400	-4.44180100	-2.25621700
C	-4.28476700	-3.90879000	-0.96121400
C	-3.85454500	-2.58890300	-0.65975200
C	-4.83668700	-4.60494600	0.29839200
C	-4.39094200	-3.64450600	1.45282800
C	-4.33761000	-2.21504500	0.76662800
C	-5.80326500	-1.59803000	0.74674700
C	-5.95763800	-0.88873800	2.13461000
C	-4.51016700	-0.48748900	2.47411900
C	-3.59516500	-1.17081100	1.63040200
C	-4.06552500	0.43622700	3.43655900
C	-2.67997100	0.68902600	3.55150200
C	-1.76061000	0.06366600	2.68277300
C	-2.21501800	-0.86356800	1.69526100
O	-1.28528900	-1.51766100	0.81794700
P	2.19058500	0.36227500	0.31141900

C	3.68612200	1.46386500	0.19845800
C	2.02223300	0.03033800	2.13939000
C	2.03887900	1.12957400	3.03511900
C	1.84525800	0.93790600	4.41607800
C	1.61236400	-0.35554900	4.92664800
C	1.56532700	-1.45019500	4.04315600
C	1.76397700	-1.25671900	2.66011800
C	4.63132400	1.59377200	1.24084600
C	5.78238900	2.38803800	1.06265800
C	6.01124800	3.04155800	-0.16393000
C	5.08278700	2.89816200	-1.21504400
C	3.92434300	2.11682000	-1.03501500
H	0.44398200	-2.56864700	0.41665700
H	-0.60663900	-4.54822700	-0.57124000
H	0.55530100	-4.59119800	-1.92450800
H	1.11689900	-4.92523400	-0.25980100
H	1.11037200	-1.22540100	-2.97379200
H	0.23095100	-2.73759700	-3.40065600
H	-0.61856400	-1.15959900	-3.42226900
H	-2.63953700	-1.76076400	-3.76852200
H	-3.54634600	-4.02511900	-4.30399500
H	-4.51662700	-5.46124800	-2.47512500
H	-4.42555200	-5.62206400	0.41998700
H	-5.93791100	-4.69234000	0.25421700
H	-5.07922300	-3.66242900	2.31294900
H	-3.38283400	-3.92173700	1.80492600
H	-5.87505800	-0.84997400	-0.05981800
H	-6.57014500	-2.36983200	0.57686100
H	-6.35874100	-1.58138400	2.89767900
H	-6.62935600	-0.01430800	2.08738000
H	-4.77969000	0.95556600	4.08983200
H	-2.31039700	1.39106900	4.31192900
H	-0.68480600	0.26329500	2.77786400
H	2.20911300	2.14614700	2.65560500
H	1.87614500	1.80144800	5.09473700
H	1.46202700	-0.50670100	6.00441100
H	1.37188200	-2.46119700	4.42747600
H	1.71805200	-2.12440300	1.99264900
H	4.48039700	1.07678500	2.19759100
H	6.50663400	2.48574200	1.88316100
H	6.91352900	3.65285900	-0.30359600
H	5.26295400	3.39180100	-2.18003100
H	3.20507900	1.99328100	-1.85978200
C	4.49318500	-2.77564600	1.64923300
C	3.73637200	-3.93991700	1.25684100
C	4.39382700	-4.53758200	0.10466300

C	5.56013300	-3.71928100	-0.21038600
C	5.61263800	-2.62846100	0.75126500
Fe	3.93204800	-2.70936100	-0.29717100
H	2.73502300	-3.96413100	-2.48079800
H	4.95110100	-2.47559100	-2.91001900
H	4.85548400	-0.31617700	-1.28459100
H	2.86157600	-4.33729700	1.77376300
H	4.25284400	-2.11197000	2.48160800
H	4.12960200	-5.48739800	-0.36053700
H	6.32111200	-3.94863300	-0.95616500
H	6.38859400	-1.86437600	0.81662600
Ru	-0.03213300	1.72686900	-0.50052600
C	2.13714800	5.97403600	-0.58606800
C	1.57047200	5.21188700	0.64470600
C	0.11464100	4.73331500	0.37692500
C	0.62256500	4.50591100	-2.06486300
C	2.05678500	5.05972300	-1.84115000
H	-0.27623700	4.19950600	1.25894000
H	2.20281900	4.33693400	0.87300400
H	1.55594500	5.86486000	1.53472100
H	1.55420300	6.89664200	-0.75126400
H	3.18448700	6.26487100	-0.39927600
H	0.61446900	3.77455000	-2.89129700
H	-0.08349300	5.33221600	-2.28082100
H	2.75488500	4.21653500	-1.72672900
H	2.34543900	5.62009000	-2.74720500
H	-0.53466700	5.60316600	0.15177400
C	-1.26094100	3.09502900	-1.14285300
C	-2.28849000	3.21879700	0.01816500
H	-2.26644000	4.20910700	0.52291500
O	-1.52780300	2.26776300	0.90621300
H	-2.12781100	1.64971600	1.45242000
C	-3.77021800	2.91864400	-0.27324000
C	-4.70940500	3.90875300	0.11527600
C	-4.22325000	1.76907900	-0.96264900
C	-6.07521200	3.76394300	-0.18655800
H	-4.36371300	4.80524900	0.64891400
C	-5.59264600	1.63316000	-1.26706900
H	-3.52754200	0.95245700	-1.24528400
C	-6.51934300	2.62474100	-0.88778100
H	-6.78948200	4.54125400	0.11727800
H	-5.93827300	0.74822400	-1.81900300
H	-7.58370800	2.51099500	-1.13685800
N	0.06332200	3.76299500	-0.82515500
H	-1.63017400	3.30754100	-2.15763200
Cl	0.79120700	1.43041100	-2.63819800

H 0.67141000 2.16138600 0.77096300

TS(*S*)-2



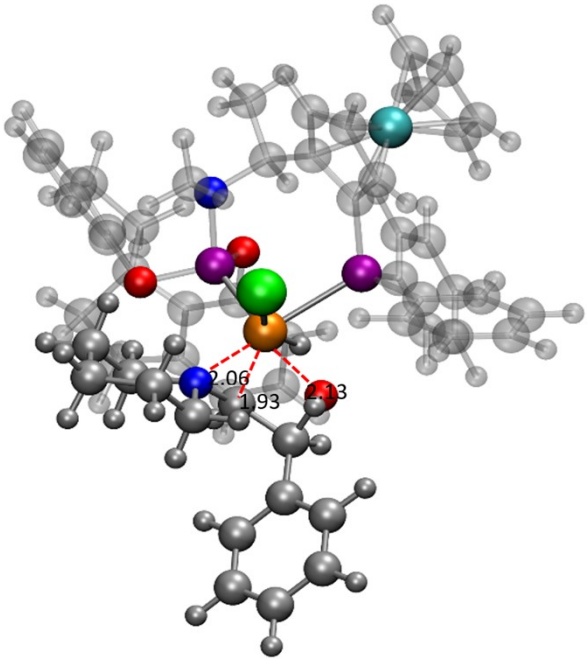
C 1.81067900 -2.50790200 -1.12017000
C 2.59219800 -1.34530800 -0.61397200
C 3.76881800 -1.21275700 -1.49340200
C 3.69586500 -2.21634000 -2.52633600
C 2.53825300 -3.02648200 -2.27920500
C 0.36654800 -2.92054500 -0.75903300
C 0.07439400 -4.42750000 -1.06607500
N -0.70993000 -2.08776900 -1.48469300
P -1.27933300 -0.67263100 -0.53891600
C -0.31552700 -1.70597300 -2.89730700
O -2.93593800 -0.49641600 -1.08844200
C -3.60902100 -1.74592400 -1.36133500
C -3.64302400 -2.25799100 -2.68935300
C -4.26201600 -3.48959600 -2.96566300
C -4.83328700 -4.25540900 -1.92506900
C -4.83874900 -3.73090300 -0.62152300
C -4.28258700 -2.45666100 -0.33897400
C -5.38073300 -4.38126200 0.66648700
C -4.77673200 -3.47663400 1.79497500
C -4.62044700 -2.05103700 1.11391400
C -6.00723300 -1.27958500 1.19862200
C -5.98988100 -0.59513400 2.60656300
C -4.48691800 -0.36516100 2.85463800
C -3.70672700 -1.10352100 1.92725900

C	-3.88893300	0.45696500	3.82492400
C	-2.48100600	0.54172300	3.86883800
C	-1.69413100	-0.13209100	2.91810800
C	-2.29786400	-0.93490100	1.90864500
O	-1.47696900	-1.61416300	0.93500500
P	2.02018400	0.07065600	0.43268000
C	3.55332500	1.13847600	0.49816600
C	1.86503200	-0.48355200	2.20625000
C	1.65256000	-1.82713100	2.58057200
C	1.50699200	-2.17978800	3.93912400
C	1.56826400	-1.19204500	4.93982200
C	1.76309600	0.15635100	4.57478900
C	1.90074100	0.50840200	3.21921800
C	4.51050100	0.96872600	1.52623700
C	5.67993400	1.75422100	1.54895100
C	5.91301400	2.70990700	0.54048400
C	4.97434700	2.86726000	-0.49841500
C	3.80263800	2.08569100	-0.52202400
H	0.17210800	-2.75529200	0.32023200
H	-0.94056600	-4.67693700	-0.72346300
H	0.13684500	-4.63145600	-2.14445000
H	0.79745800	-5.07050500	-0.54170100
H	0.57098200	-1.04428900	-2.95527200
H	-0.11719900	-2.63292500	-3.46038800
H	-1.16483700	-1.18840600	-3.37209000
H	-3.17453300	-1.68712900	-3.50043400
H	-4.27250500	-3.86960200	-3.99641100
H	-5.27066000	-5.24050700	-2.13671900
H	-5.06572800	-5.43480100	0.76198300
H	-6.48607800	-4.35876800	0.68590700
H	-5.41144000	-3.43619000	2.69451000
H	-3.78189600	-3.85450200	2.08577000
H	-6.04722800	-0.51031800	0.40885300
H	-6.86407900	-1.95866100	1.06512300
H	-6.41883600	-1.26022400	3.37869900
H	-6.56230300	0.34845100	2.62224100
H	-4.50397400	1.01693700	4.54218600
H	-1.99168900	1.15448200	4.63806700
H	-0.60303100	-0.04404400	2.94994900
H	1.60274800	-2.61424300	1.82004300
H	1.34565200	-3.23192200	4.21166500
H	1.45946000	-1.46827300	5.99770700
H	1.80654000	0.93650500	5.34725600
H	2.04884700	1.56358500	2.95136100
H	4.35018800	0.22706500	2.31937000
H	6.41183000	1.61354200	2.35631200

H	6.82649700	3.32045700	0.55900700
H	5.15809900	3.59562200	-1.30036500
H	3.08829300	2.17735800	-1.35492100
C	4.33068000	-3.20979000	1.20491900
C	3.53640200	-4.32044100	0.73970200
C	4.09579600	-4.77995900	-0.52106900
C	5.24213300	-3.93088100	-0.82951900
C	5.37921100	-2.95915600	0.24476500
Fe	3.62693600	-2.91095500	-0.66906500
H	2.23435200	-3.88495700	-2.87661700
H	4.43403500	-2.37746900	-3.31321800
H	4.51010500	-0.41736200	-1.43956200
H	2.69754500	-4.77193500	1.27176900
H	4.16273700	-2.65072200	2.12700400
H	3.78499600	-5.66755200	-1.07257100
H	5.94143900	-4.07379200	-1.65323200
H	6.16723700	-2.21080100	0.33924100
Ru	-0.06205900	1.32214500	-0.41311000
C	-2.40648100	3.22684100	-4.10448800
C	-0.99285200	3.65067600	-3.62378000
C	-0.96725200	3.89161800	-2.08619800
C	-2.81453000	2.23914000	-1.76154100
C	-2.86506200	1.98331600	-3.29514400
H	0.05384000	4.18072100	-1.78843900
H	-0.25255700	2.86741200	-3.85939300
H	-0.67961700	4.59037400	-4.11094000
H	-3.12101700	4.05517500	-3.95653700
H	-2.38083600	2.98914600	-5.18108500
H	-3.10093300	1.29767500	-1.24447000
H	-3.49492700	3.06721700	-1.48121100
H	-2.21800800	1.12274900	-3.53583100
H	-3.90293400	1.70955200	-3.55318200
H	-1.65874900	4.70888400	-1.80218200
C	-1.29521600	2.66227200	0.22077700
C	-0.27000800	3.66589900	0.82493100
H	-0.18590200	3.42022900	1.90888500
O	0.98022400	3.06830500	0.21834600
H	1.27985700	3.69695500	-0.52454800
C	-0.38115900	5.20101600	0.65906500
C	0.78743800	5.99674000	0.62179800
C	-1.65085500	5.82292000	0.62053000
C	0.68599200	7.39787100	0.51721200
H	1.77964200	5.52875600	0.68922800
C	-1.74797200	7.22414500	0.52556600
H	-2.56235500	5.21267900	0.67384000
C	-0.58067500	8.01359900	0.46674800

H	1.59840400	8.00945900	0.48528700
H	-2.73734700	7.70150900	0.49739600
H	-0.65881900	9.10695500	0.38982700
N	-1.39115500	2.63143400	-1.28487700
H	-2.26598400	2.60436700	0.73752200
Cl	1.18033700	1.36422900	-2.41621600
H	-0.15016800	1.10598300	1.13445400

TS(*R*)-2



C	1.16232400	-2.64833800	-0.72260400
C	2.20756200	-1.62295800	-0.48120600
C	3.03781900	-1.57631300	-1.70445000
C	2.51061900	-2.53948900	-2.65290200
C	1.39210900	-3.19957000	-2.04586200
C	0.03910400	-3.09067100	0.23605700
C	-0.27451800	-4.61621300	0.00017400
N	-1.31232000	-2.34131900	0.13066900
P	-1.48025000	-0.55882600	0.09226800
C	-2.27454600	-2.99621800	1.11695900
O	-2.77522300	-0.31103900	-1.06400700
C	-3.77012500	-1.35702600	-1.06108500
C	-3.60369900	-2.46731600	-1.93501700
C	-4.52466200	-3.52990500	-1.91528300
C	-5.59511000	-3.53312100	-0.99235400
C	-5.76641800	-2.42776000	-0.14070300
C	-4.89986500	-1.30560800	-0.20703400
C	-6.78913900	-2.25267700	0.99979500

C	-6.18827100	-1.06008500	1.82178500
C	-5.42067700	-0.19027600	0.73678700
C	-6.47775200	0.75138500	0.01409300
C	-6.57318400	2.01474300	0.93400000
C	-5.17388700	2.07867200	1.57559100
C	-4.47093900	0.86218300	1.37051500
C	-4.59301100	3.15753500	2.26529900
C	-3.27323700	3.02941400	2.75147800
C	-2.53515400	1.85889300	2.50244000
C	-3.11553600	0.77061500	1.78737300
O	-2.35542700	-0.43178100	1.61291400
P	2.01802200	-0.12361300	0.57370200
C	3.77831400	0.48308300	0.73186000
C	1.64580700	-0.63736900	2.32653300
C	1.11400200	0.32431000	3.21735400
C	0.86587400	-0.00228000	4.56502500
C	1.15055900	-1.29684400	5.04367400
C	1.69639400	-2.25657200	4.16919700
C	1.94889200	-1.92629400	2.82216000
C	4.58991400	0.07147700	1.81448700
C	5.93511000	0.48264500	1.89167300
C	6.48537600	1.30396200	0.88753100
C	5.67965200	1.72153800	-0.19007400
C	4.33333900	1.31413000	-0.26734700
H	0.40977300	-2.97798700	1.27914400
H	-0.81446400	-5.04903300	0.85179700
H	-0.88056100	-4.74368100	-0.90821100
H	0.66616400	-5.16856600	-0.12077700
H	-2.71602800	-3.89378800	0.65310100
H	-1.76171800	-3.28306700	2.05464500
H	-3.07624300	-2.28954400	1.37267500
H	-2.73429200	-2.48860800	-2.60612900
H	-4.38492000	-4.38152300	-2.59515400
H	-6.27491100	-4.39407500	-0.93556300
H	-6.89054400	-3.16919900	1.60629500
H	-7.79021100	-1.99986300	0.60456000
H	-6.95835500	-0.47448500	2.34868200
H	-5.47029800	-1.44212900	2.56749300
H	-6.09920100	1.03732100	-0.98100300
H	-7.44881500	0.24893600	-0.11673700
H	-7.35371000	1.88764100	1.70675700
H	-6.81191300	2.93097300	0.36667400
H	-5.15629800	4.08655200	2.42672200
H	-2.81088900	3.85473000	3.31007600
H	-1.50206900	1.76497600	2.85959600
H	0.89262200	1.33860200	2.85947500

H	0.45177500	0.75713700	5.24268000
H	0.95574800	-1.55328400	6.09433900
H	1.93535200	-3.26447300	4.53594900
H	2.39696100	-2.67683300	2.16163500
H	4.17658800	-0.56514500	2.60788400
H	6.55428600	0.15812400	2.73941500
H	7.53547000	1.62177000	0.94872800
H	6.09843300	2.37057600	-0.97145800
H	3.68483400	1.66613000	-1.08256600
C	4.35276500	-3.58484200	0.59385500
C	3.32062900	-4.59686600	0.49435400
C	3.34968200	-5.12974500	-0.86656400
C	4.40001100	-4.41710800	-1.58952300
C	5.01465200	-3.47452400	-0.67799200
Fe	3.02679600	-3.24875000	-0.88840200
H	0.82167600	-4.01266800	-2.49674200
H	2.90559400	-2.74306100	-3.64878200
H	3.81749900	-0.84584900	-1.91215400
H	2.71906100	-4.97659600	1.32090300
H	4.59845700	-3.00250500	1.48344700
H	2.79944400	-5.99785100	-1.22948300
H	4.73055400	-4.62324600	-2.60763300
H	5.83481300	-2.79383500	-0.91319700
Ru	0.25623100	1.22466500	-0.57773300
C	-3.49883300	2.79170800	-3.17497700
C	-2.11340300	2.38575300	-3.74807100
C	-0.95365700	3.05349900	-2.95369800
C	-2.36669300	3.11459000	-0.89967300
C	-3.54557800	2.45178700	-1.66041100
H	0.00150700	2.70902800	-3.38220200
H	-1.97881200	1.29183900	-3.69654400
H	-2.01957900	2.69636800	-4.80324200
H	-3.66623200	3.87220900	-3.32901200
H	-4.29609800	2.24737500	-3.70836200
H	-2.38480000	2.84588900	0.17083700
H	-2.40856400	4.21888600	-0.99210200
H	-3.46181000	1.35664200	-1.51055400
H	-4.48454800	2.81084800	-1.20859100
H	-1.01385500	4.15876200	-3.02215700
C	0.11302400	3.14979600	-0.54916500
C	1.39957900	3.55250700	-1.31446400
H	1.24788800	4.05719700	-2.29151600
O	1.84285800	2.10967900	-1.57206900
H	1.72000300	1.86384200	-2.56181500
C	2.46150700	4.31901900	-0.51148800
C	3.30364600	5.23449700	-1.18787600

C	2.60891700	4.14236800	0.88567600
C	4.27815300	5.96241400	-0.47910300
H	3.19050000	5.38385500	-2.27087500
C	3.58407400	4.87071100	1.59233000
H	1.95622500	3.43896500	1.41972100
C	4.41952300	5.78095800	0.91177300
H	4.92430100	6.67410700	-1.01115100
H	3.69147100	4.73142300	2.67675400
H	5.17762100	6.35158900	1.46639000
N	-0.99700300	2.66568200	-1.45567100
H	-0.22443500	3.86752600	0.21314800
Cl	0.30526600	0.05092800	-2.63401100
H	-0.06607200	1.46951200	0.94637900

6. References

[1] L. Yin, J. Xing, Y. Wang, Y. Shen, T. Lu, T. Hayashi, X. Dou, *Angew. Chem. Int. Ed.* **2019**, *58*, 2474-2478.

[2] a) H. Seo, H.-j. Park, B. Y. Kim, J. H. Lee, S. U. Son, Y. K. Chung, *Organometallics* **2003**, *22*, 618-620; b) S. Gischig, A. Togni, *Organometallics* **2004**, *23*, 2479-2487; c) R. T. Stemmler, C. Bolm, *Synlett* **2007**, *2007*, 1365-1370; d) F.-Z. Han, S.-B. Yu, C. Zhang, X.-P. Hu, *Tetrahedron* **2016**, *72*, 2616-2622.

[3] P. Saravanan, A. Bisai, S. Baktharaman, M. Chandrasekhar, V. K. Singh, *Tetrahedron* **2002**, *58*, 4693-4706.

[4] L.-C. Yang, Y.-N. Wang, Y. Zhang, Y. Zhao, *ACS Catal.* **2016**, *7*, 93-97.

[5] M. Kumar, R. I. Kureshy, A. K. Shah, A. Das, N.-u. H. Khan, S. H. R. Abdi, H. C. Bajaj, *J. Org. Chem.* **2013**, *78*, 9076-9084.

[6] Gaussian 16 (Wallingford, CT, 2016).

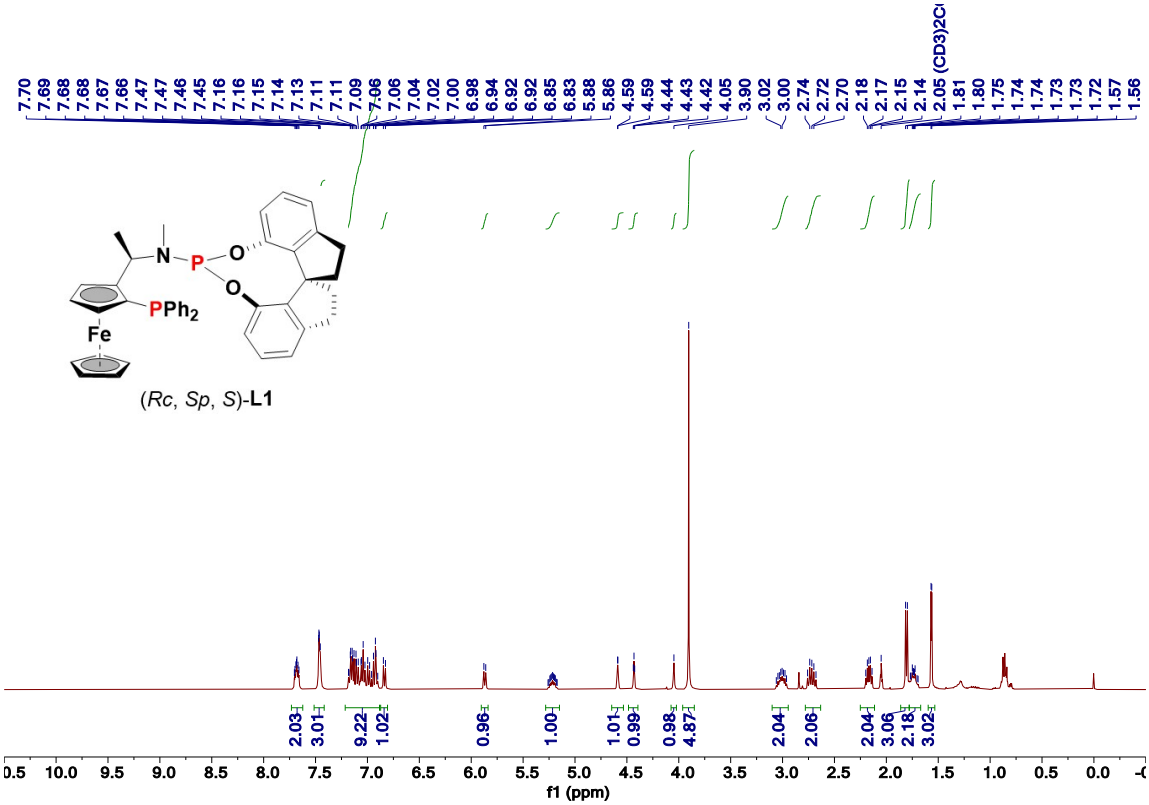
[7] a) M. Dolg, U. Wedig, H. Stoll, H. Preuss, *J. Chem. Phy.* **1987**, *86*, 866-872; b) D. Andrae, U. Häußermann, M. Dolg, H. Stoll, H. Preuß, *Theor. Chem. Acc.* **1990**, *77*, 123-141.

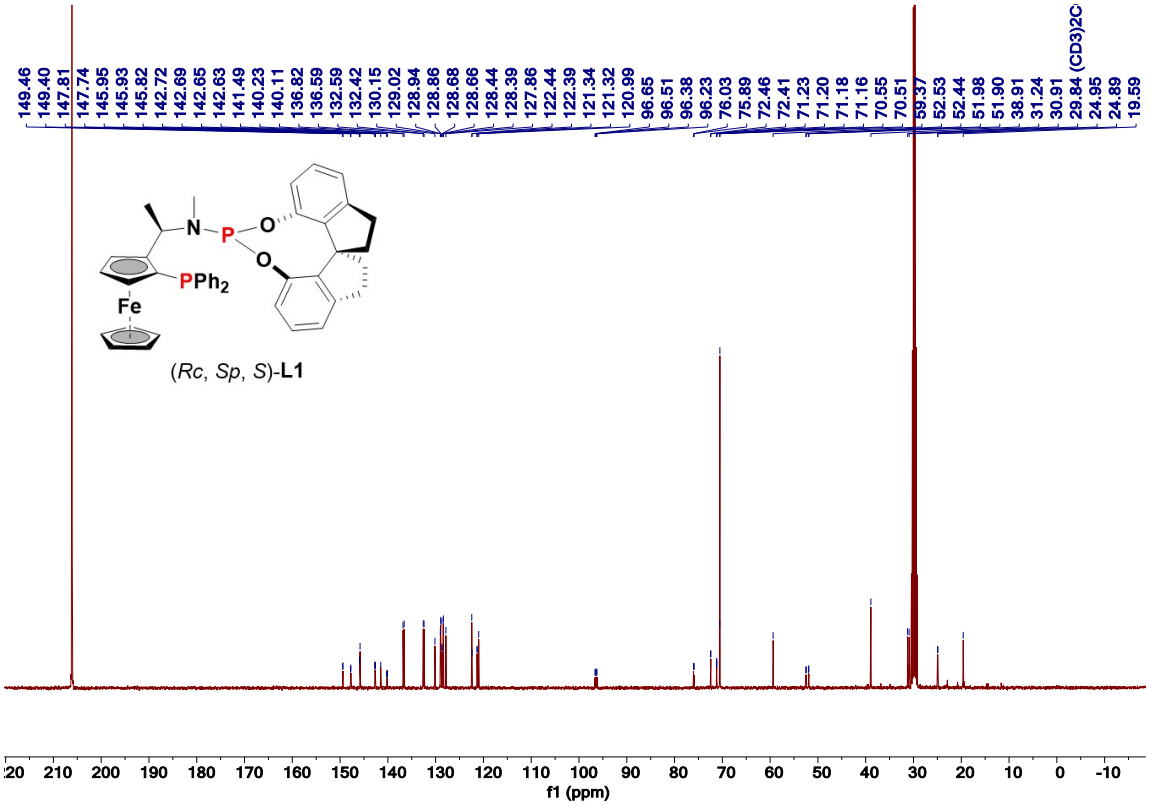
[8] P. J. Hay, W. R. Wadt, *J. Chem. Phy.* **1985**, *82*, 299-310.

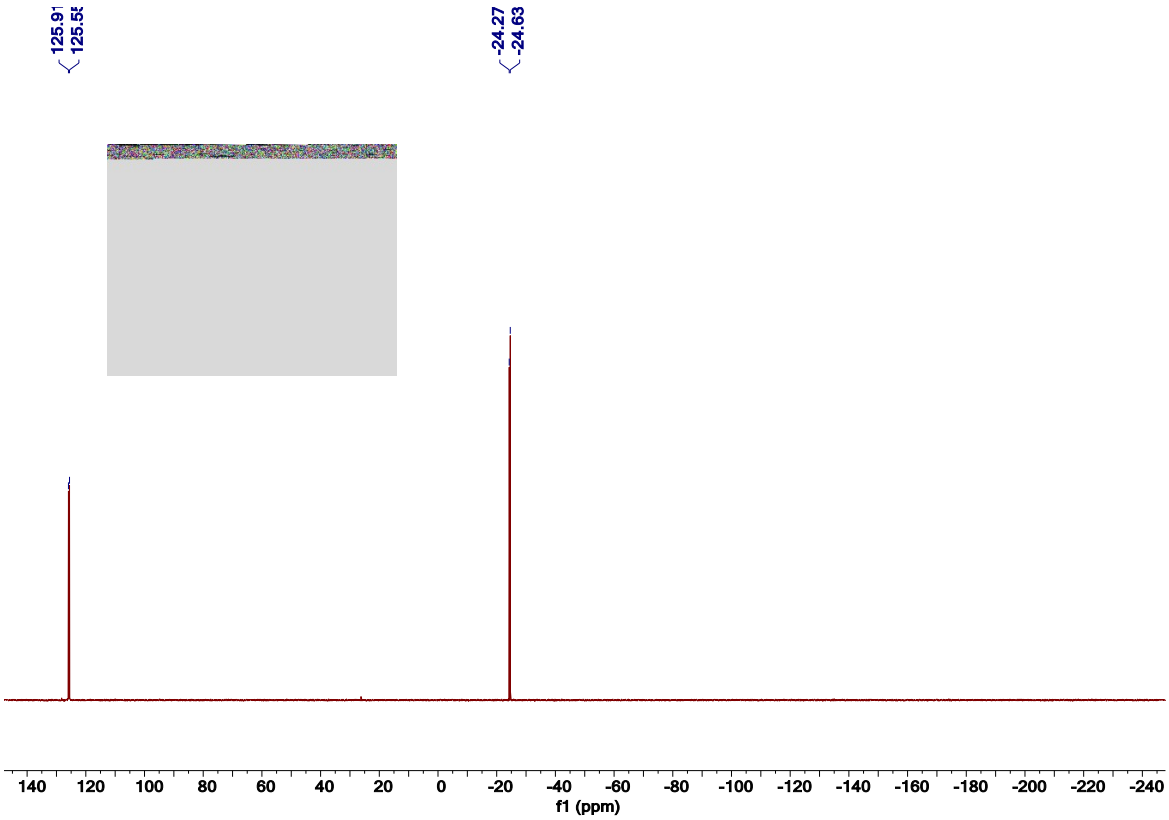
[9] K. Fukui, The path of chemical reactions-the IRC approach. *Acc. Chem. Res.* **1981**, *14,* 363-368.

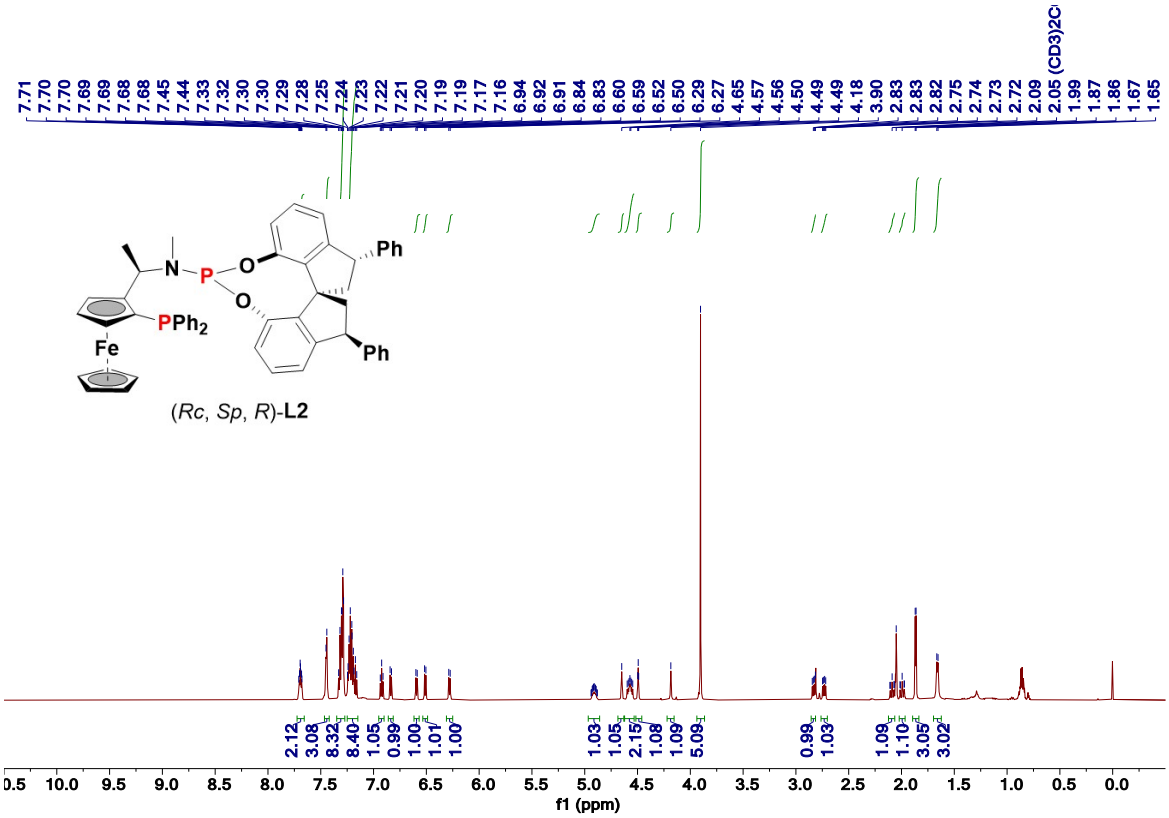
[10] A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B* **2009**, ***113***, 6378-6396.

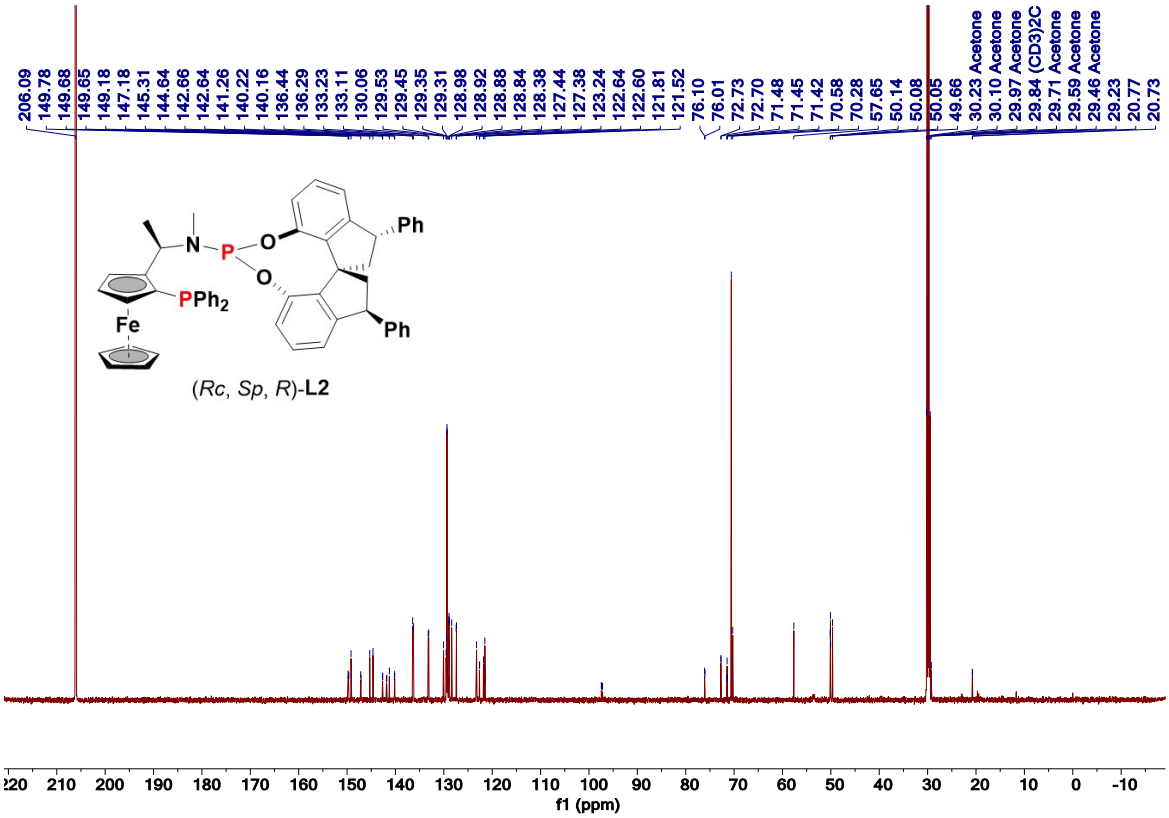
7. NMR spectrum

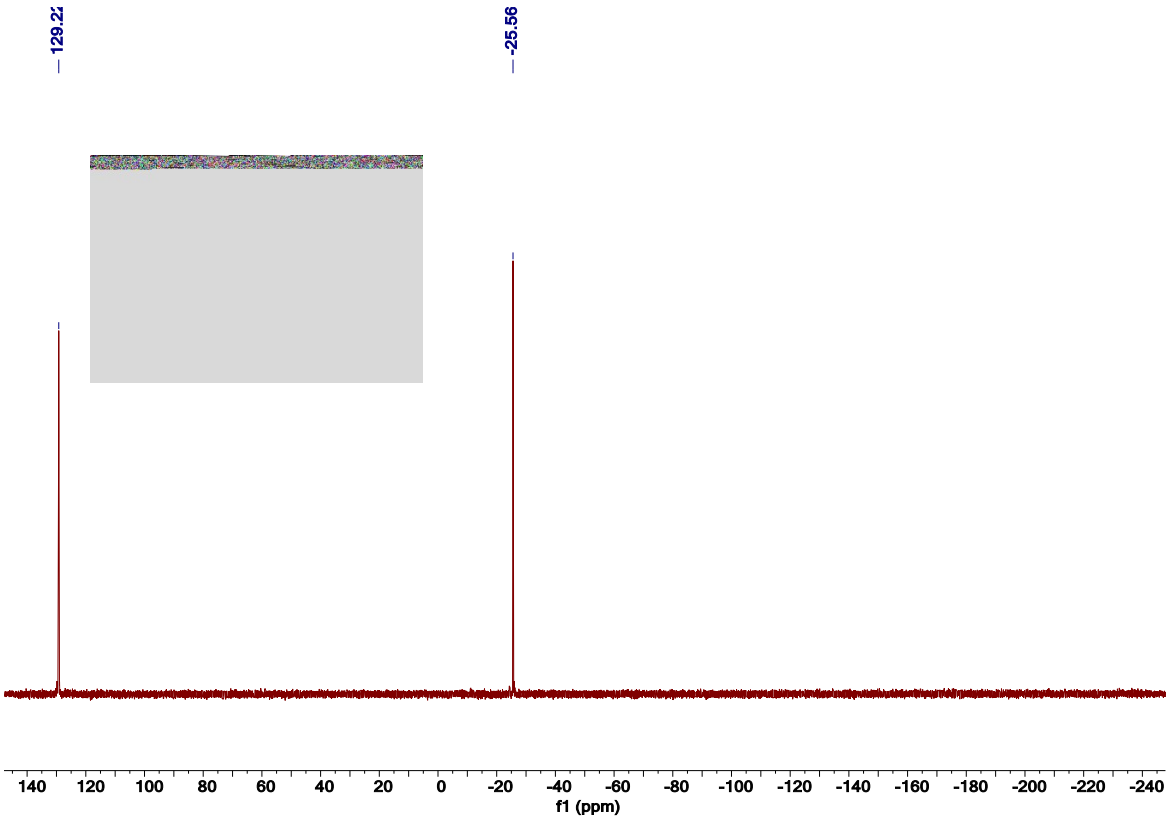


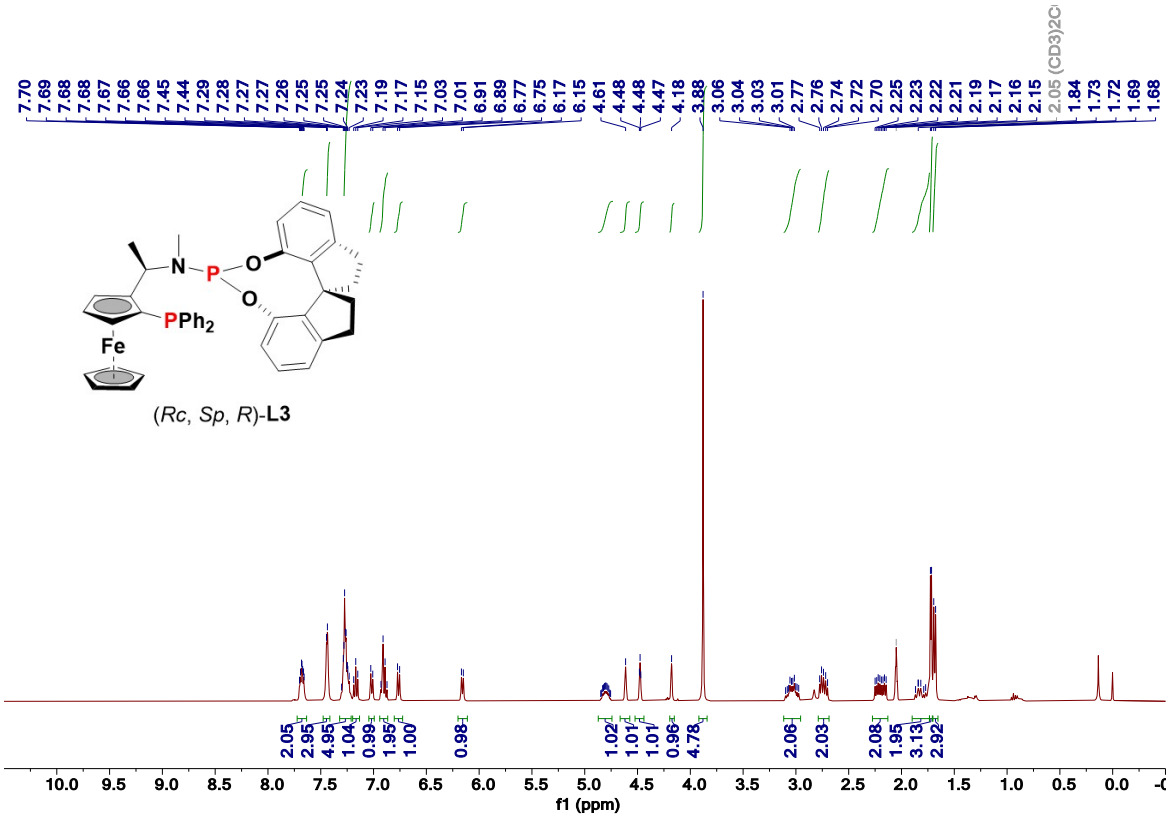


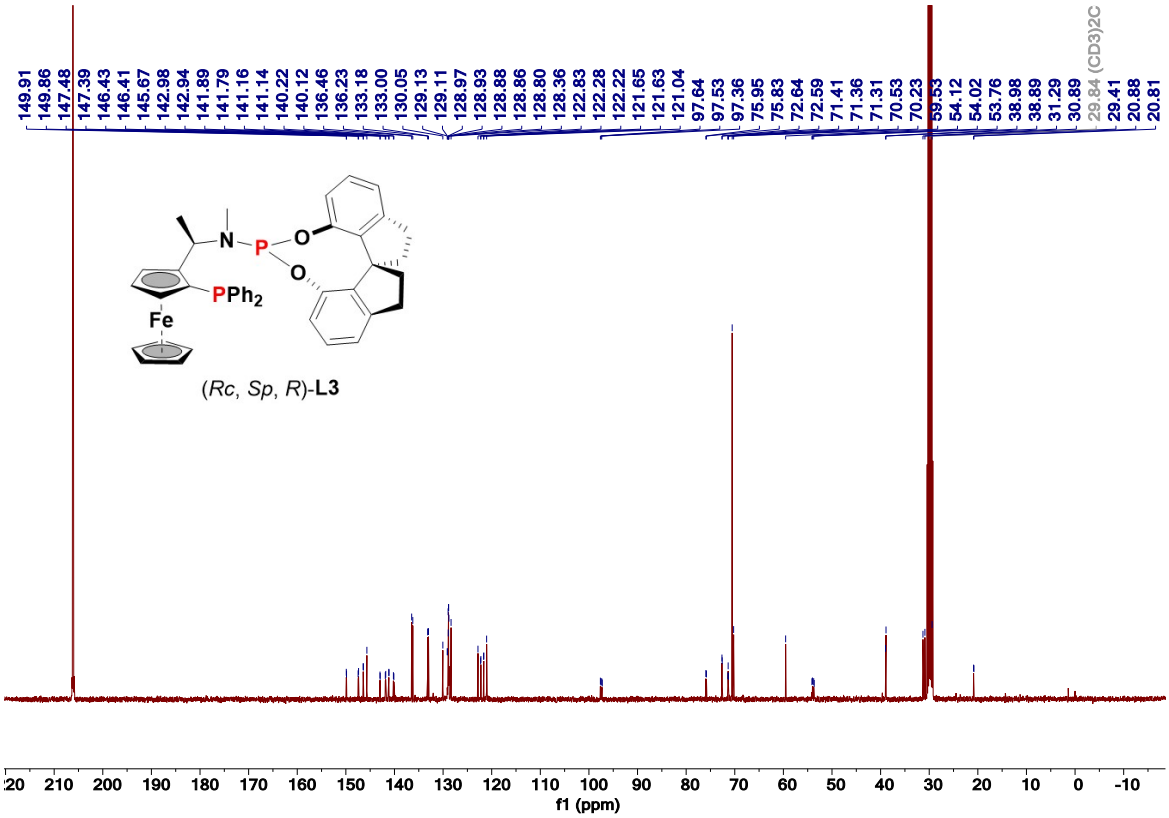

125.91
125.58
-24.27
-24.63
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

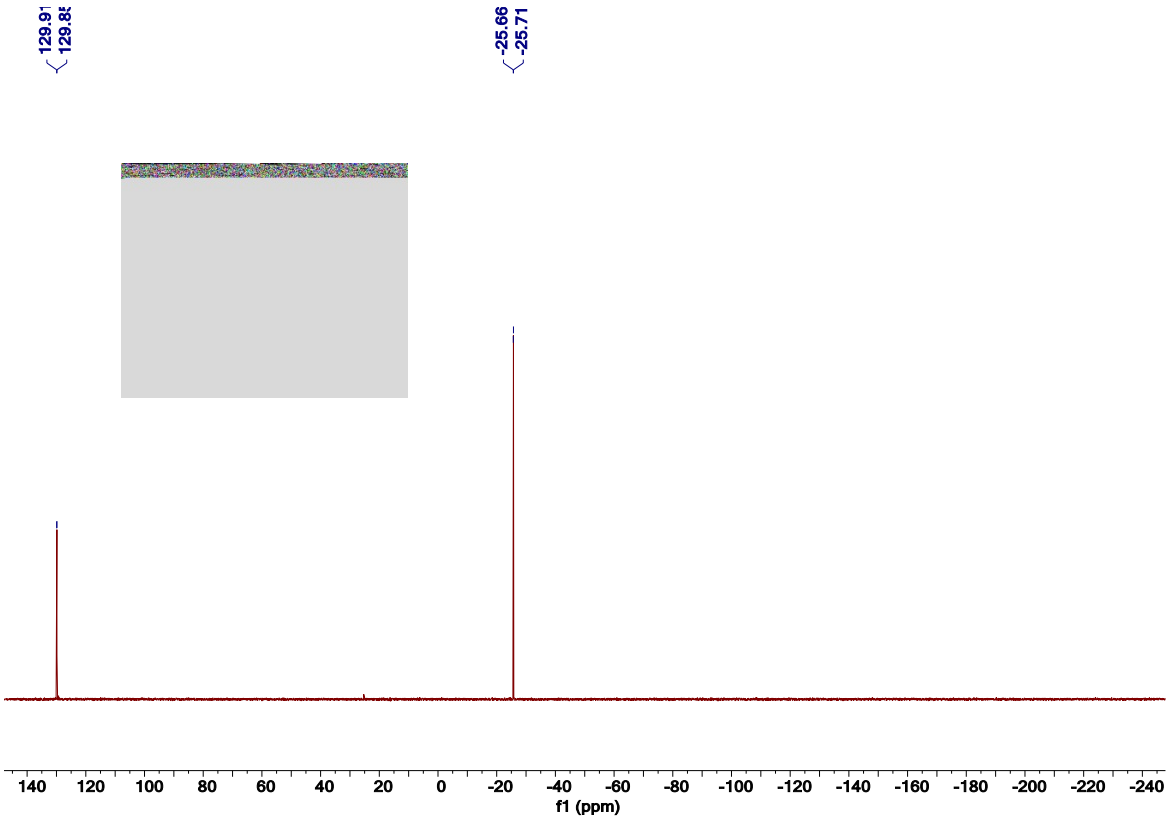

(Rc, Sp, R)-L2
f1 (ppm)

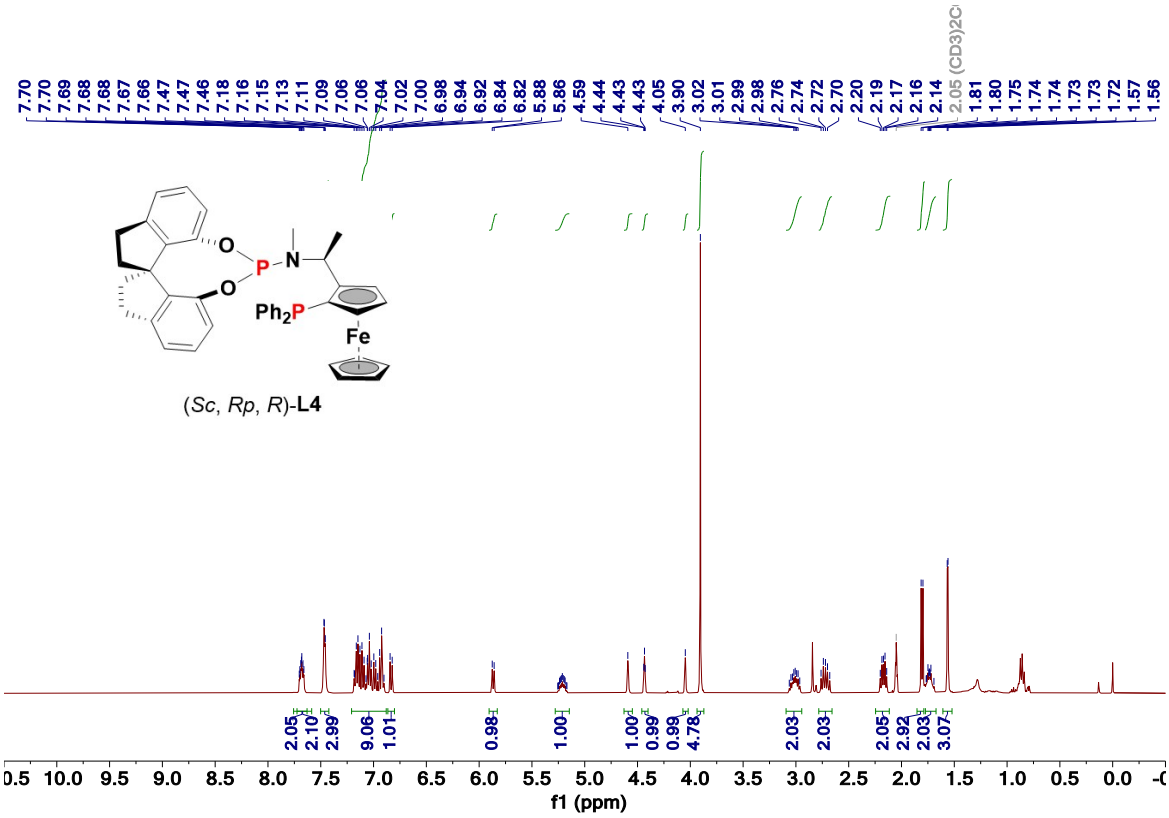

(Rc, Sp, R)-L2
f1 (ppm)

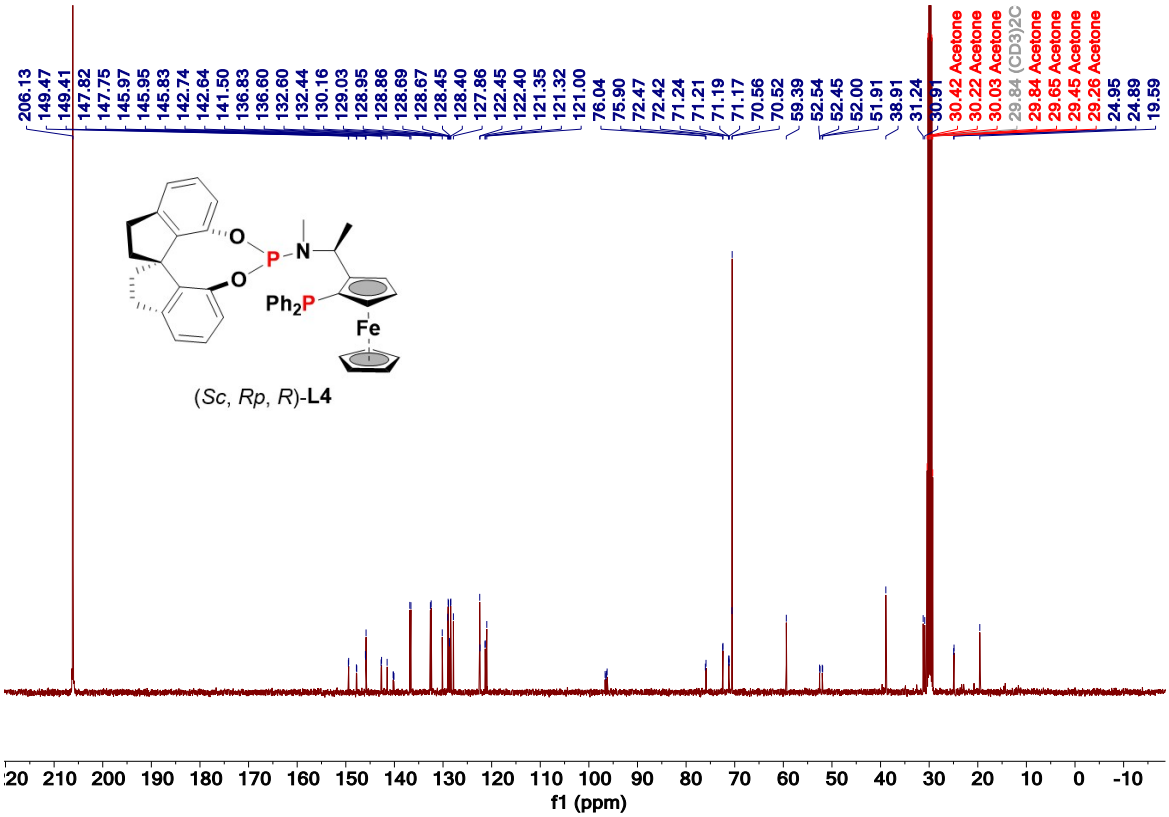

129.2
-25.56
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
f1 (ppm)

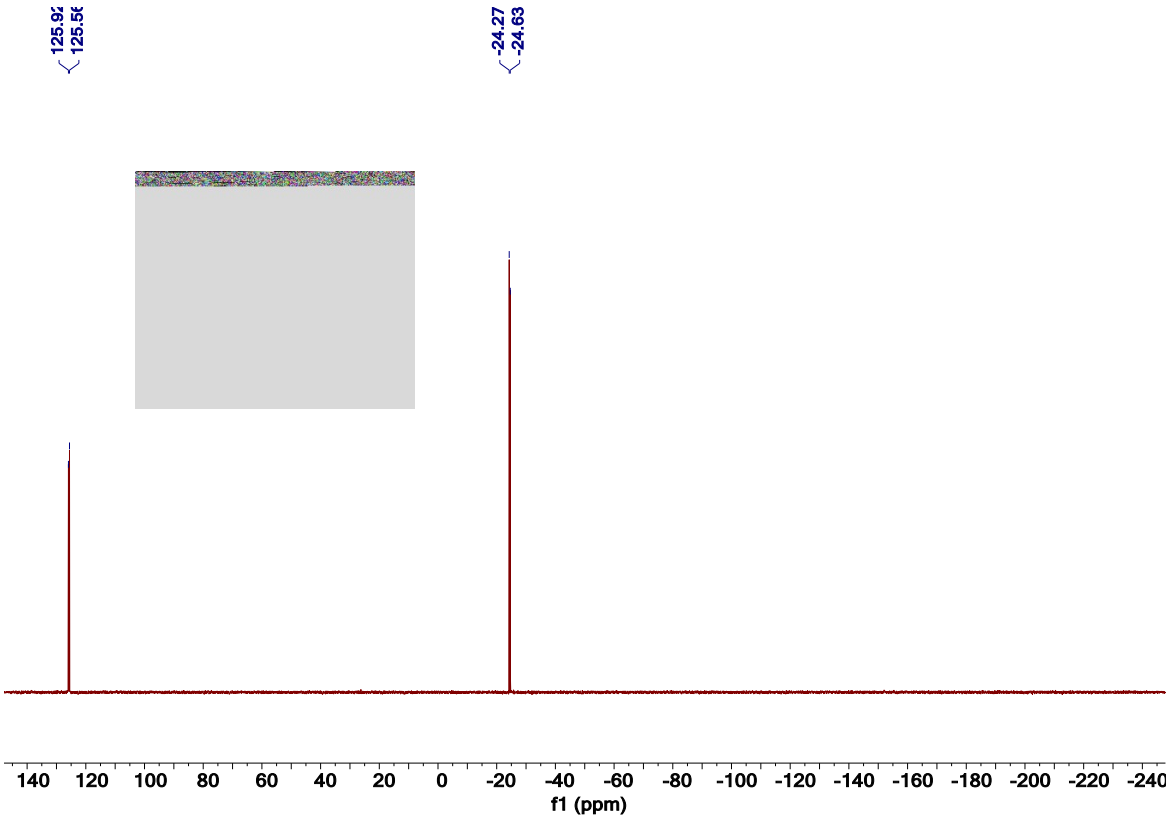

(Rc, Sp, R)-L3
f1 (ppm)

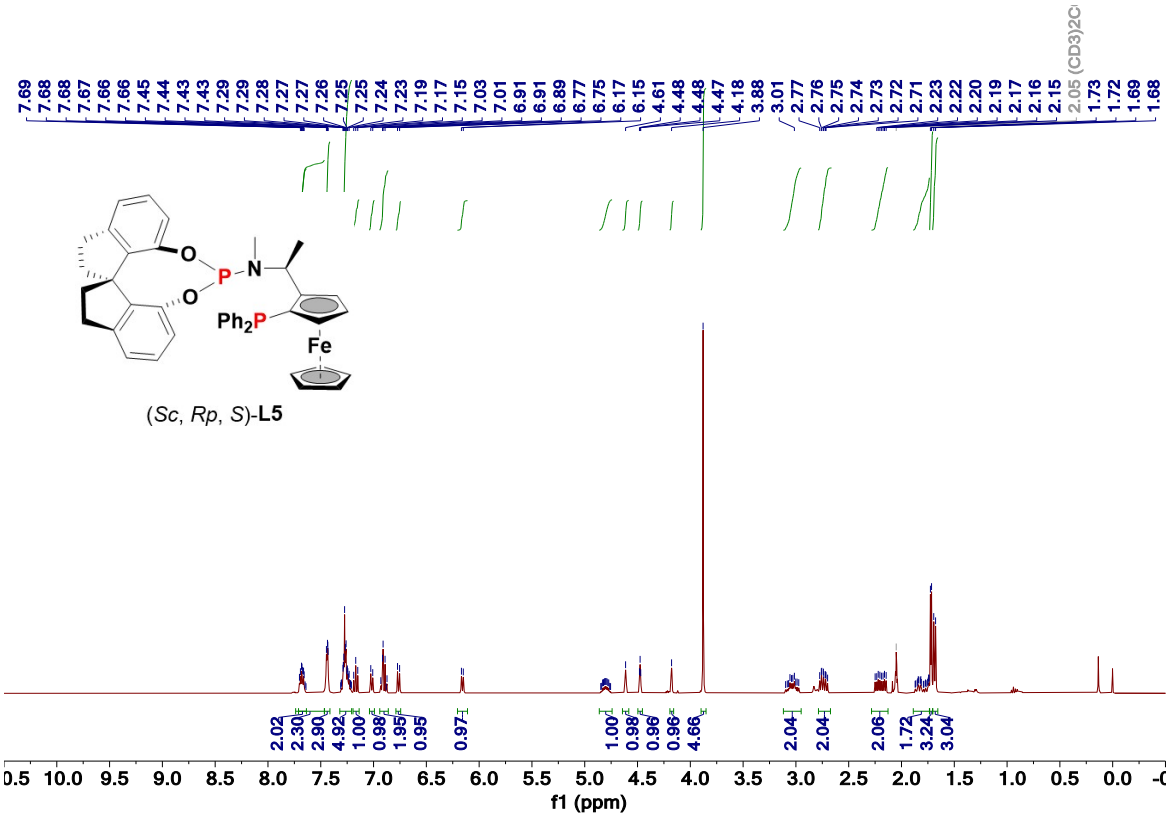

(Rc, Sp, R)-L3
f1 (ppm)

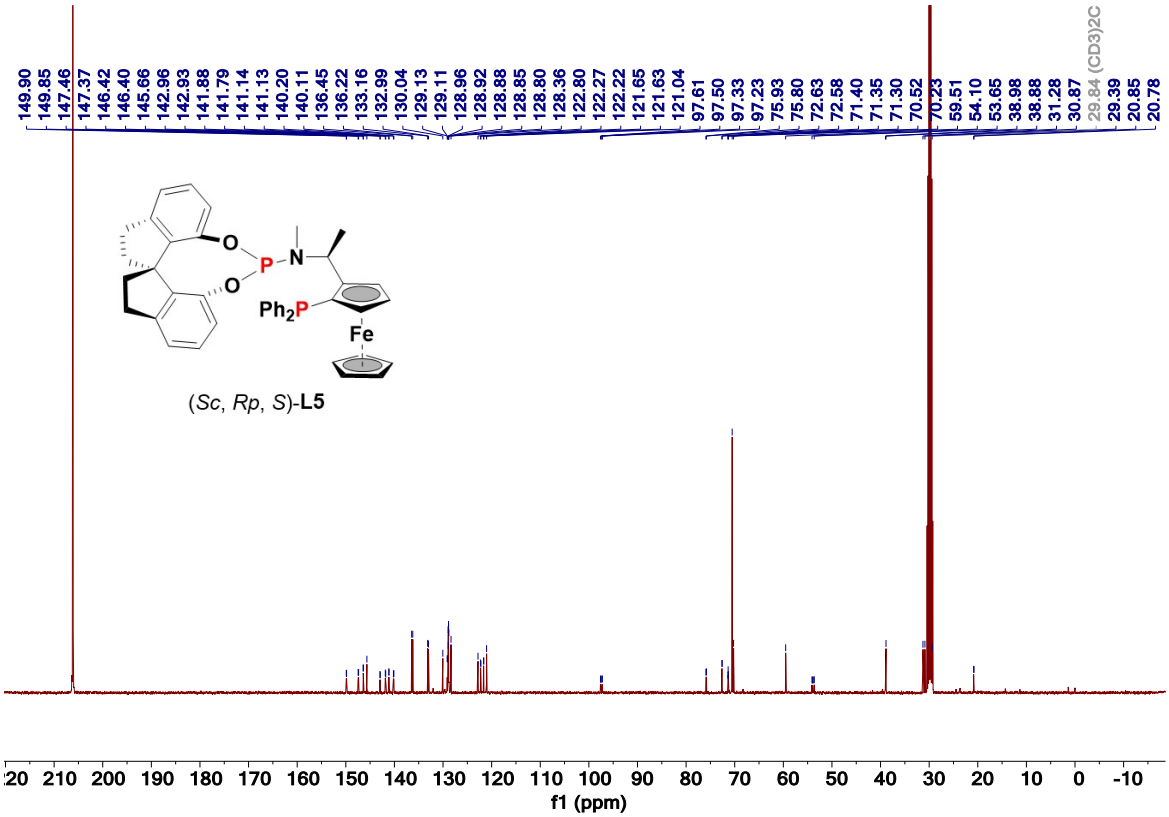

129.91
129.85
-25.66
-25.71
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

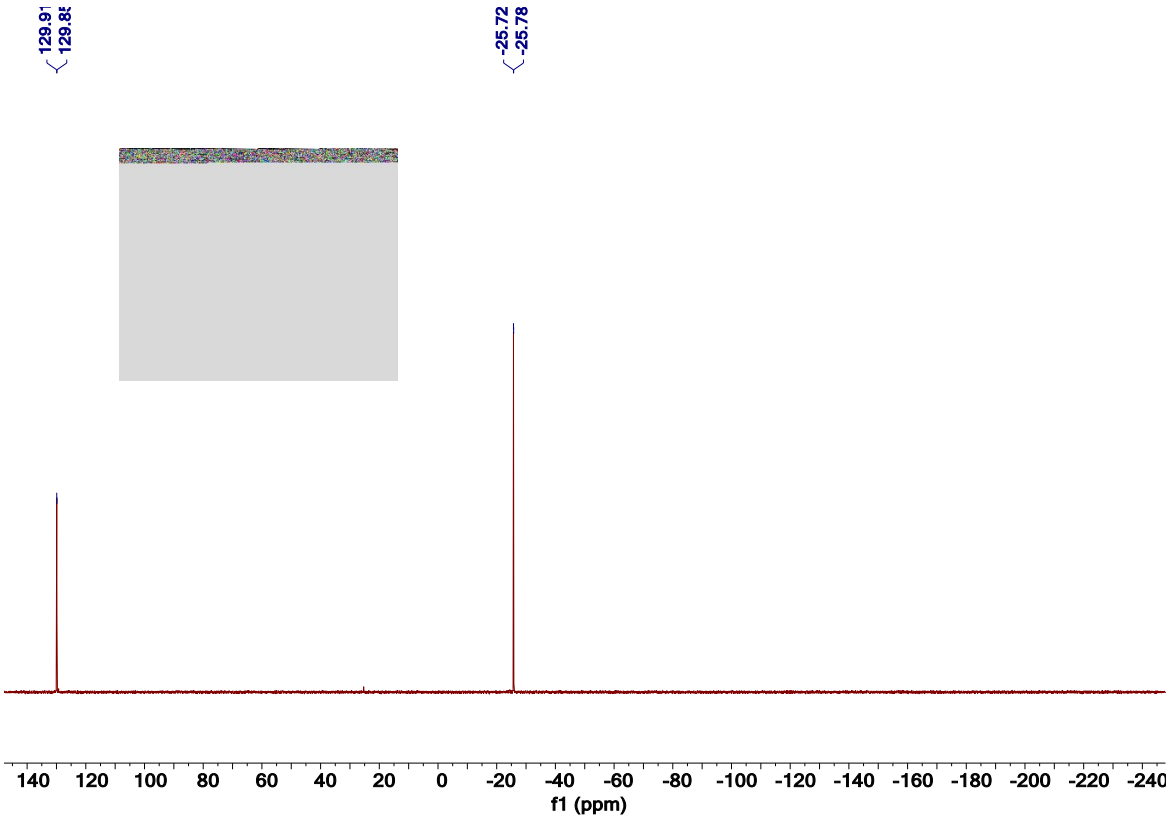

(Sc, Rp, R)-L4
f1 (ppm)

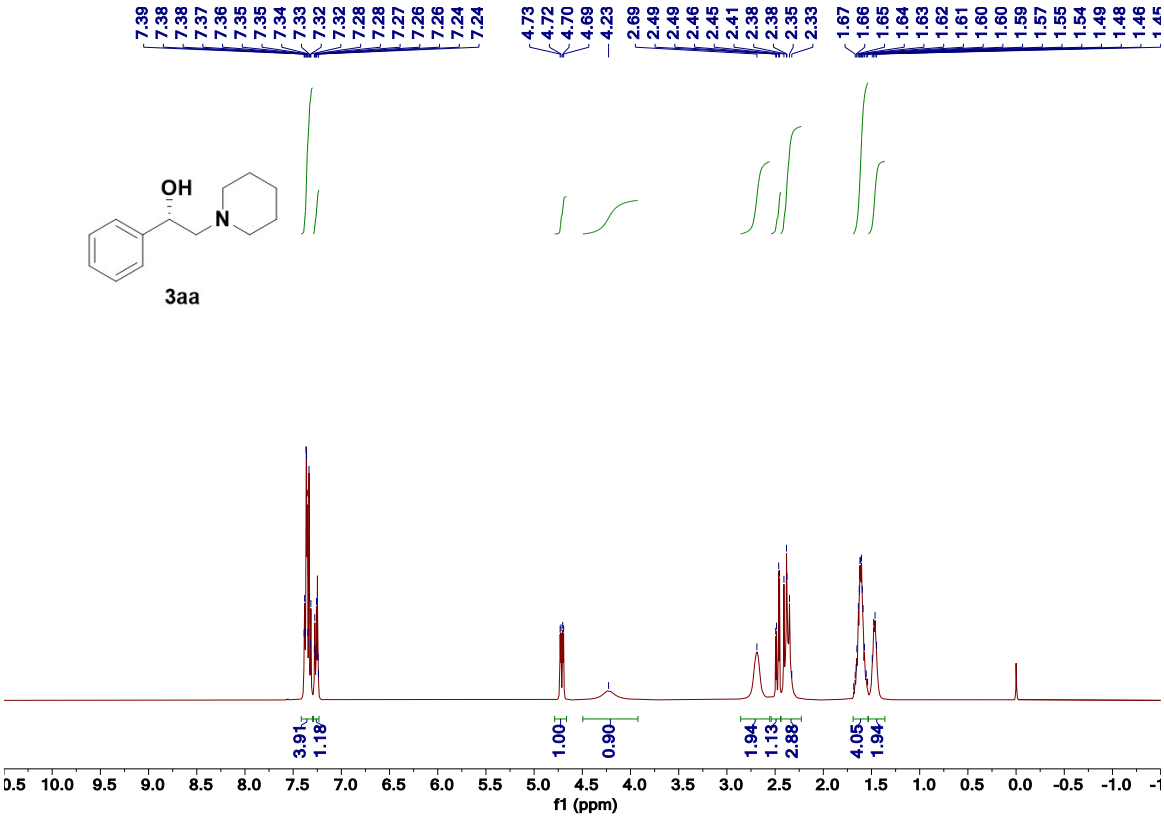

(Sc, Rp, R)-L4
f1 (ppm)

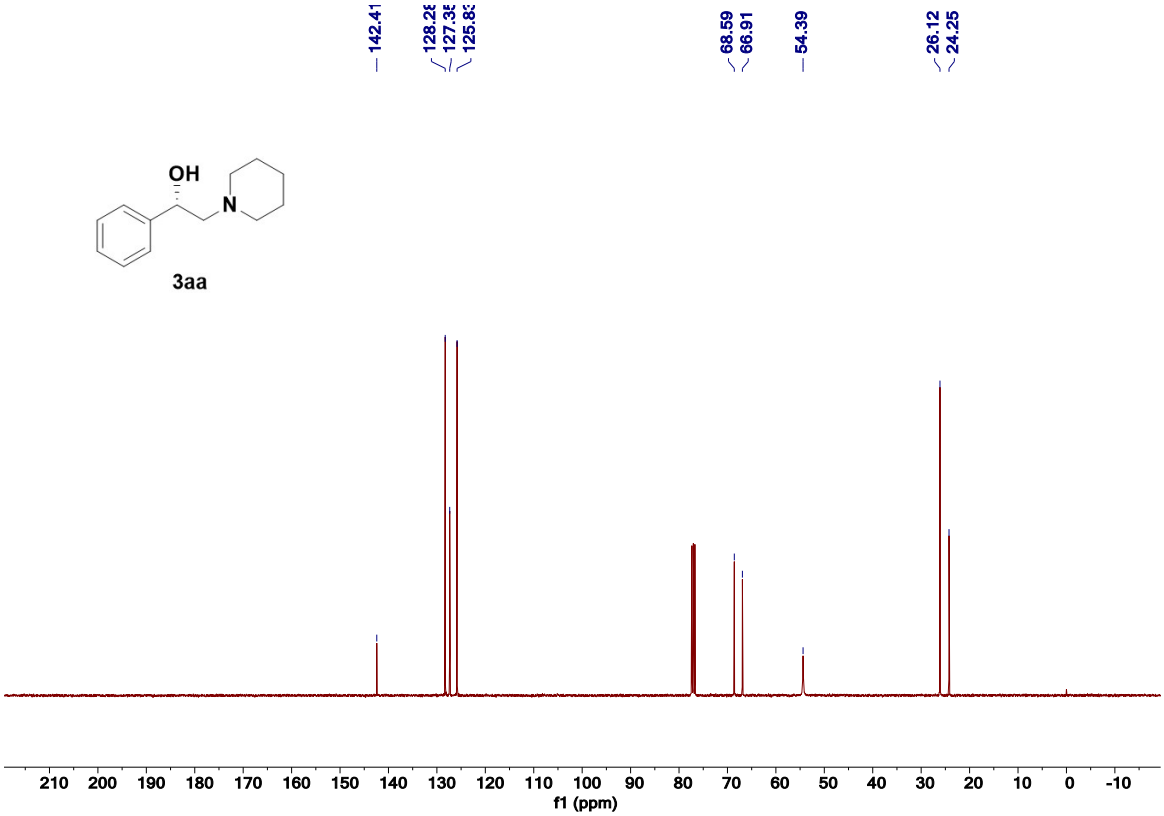

125.92
125.58
-24.27
-24.63
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

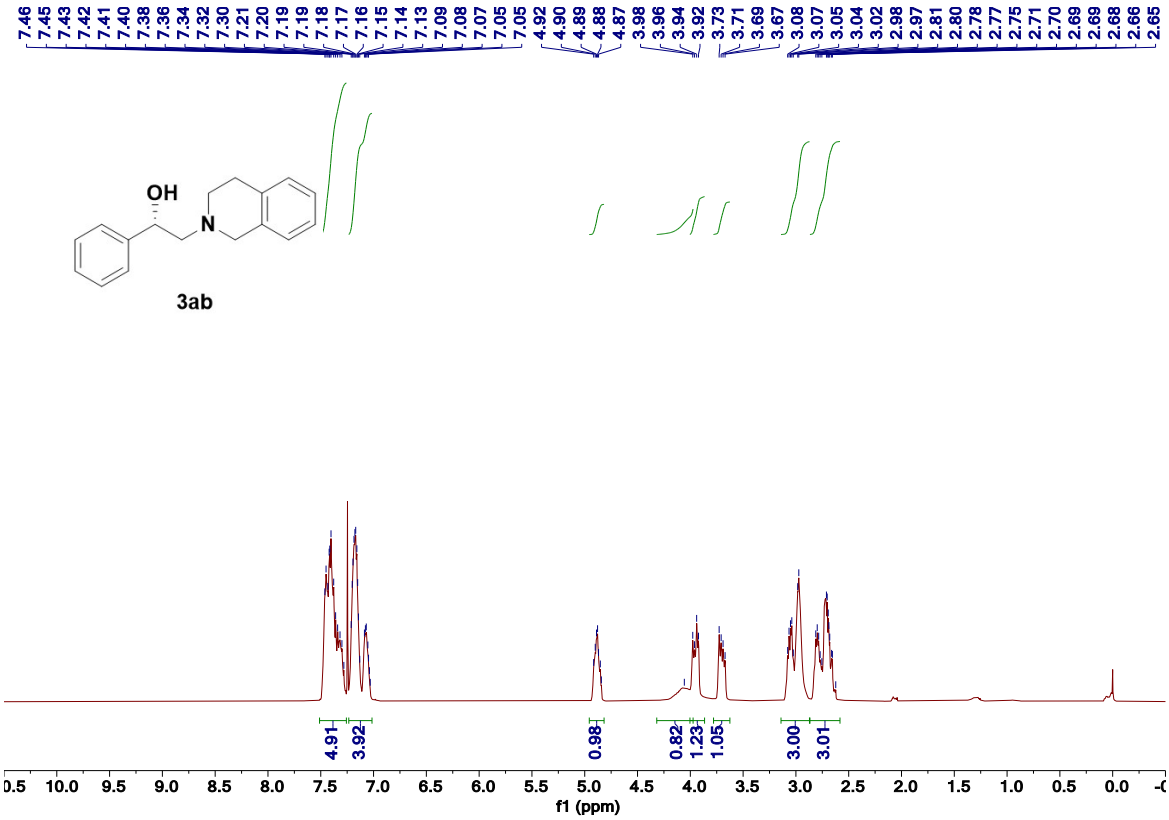

7.69 7.68 7.68 7.67 7.66 7.66 7.45 7.44 7.43 7.43 7.29 7.29 7.28 7.27 7.27 7.26 7.25 7.25 7.24 7.23 7.19 7.17 7.15 7.03 7.01 6.91 6.91 6.89 6.77 6.75 6.17 6.15 4.61 4.48 4.48 4.47 4.18 3.88 3.01 2.77 2.76 2.75 2.74 2.73 2.72 2.71 2.23 2.22 2.20 2.19 2.17 2.16 2.15 2.05 (CD3)2C 1.73 1.72 1.69 1.68
O
P
N
O
Ph2P
Fe
(Sc, Rp, S)-L5
2.02 2.30 2.90 4.92 1.00 0.98 1.95 0.95 0.97 1.00 0.99 0.96 0.96 4.66 2.04 2.04 2.06 1.72 3.24 3.04
f1 (ppm)

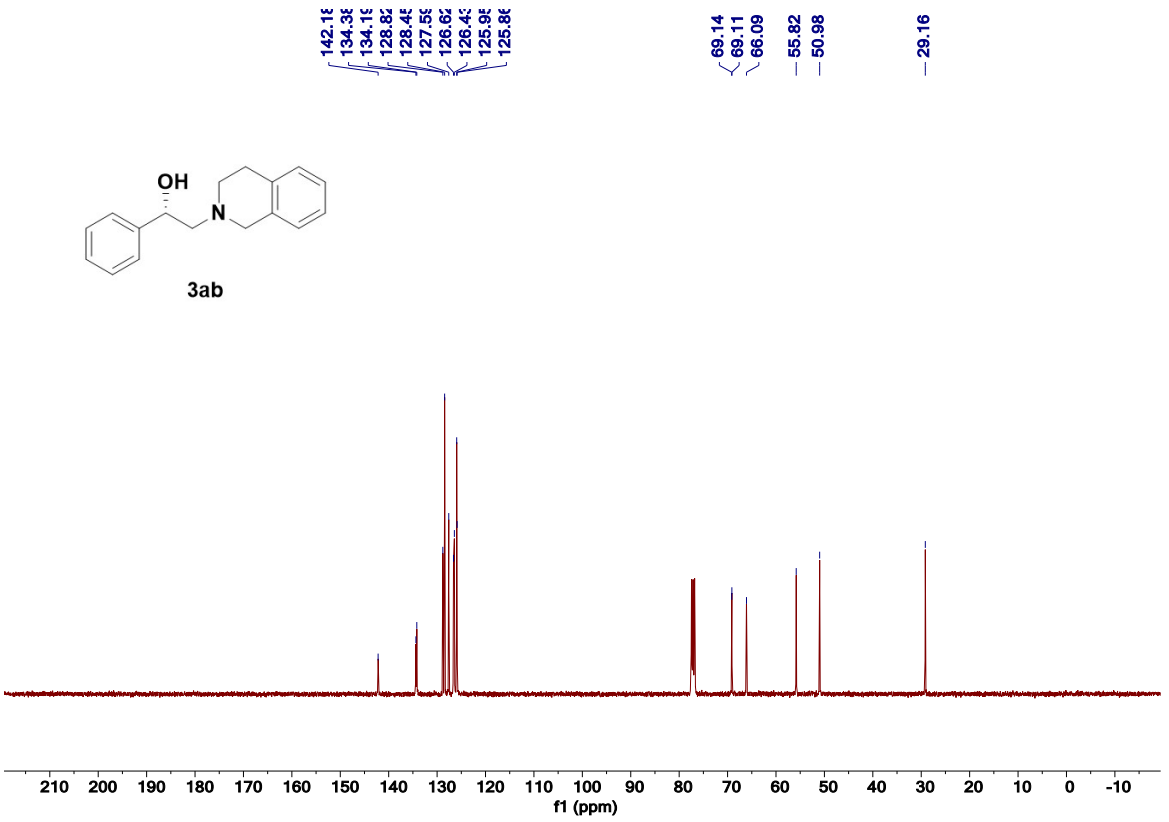

149.90 149.85 147.46 147.37 146.42 146.40 145.66 142.96 142.93 141.88 141.79 141.14 141.13 140.20 140.11 136.45 136.22 133.16 132.99 130.04 129.13 129.11 128.96 128.92 128.88 128.85 128.80 128.36 122.80 122.27 122.22 121.65 121.63 121.04 97.61 97.50 97.33 97.23 75.93 75.80 72.63 72.58 71.40 71.35 71.30 70.52 70.23 59.51 54.10 53.65 38.98 38.88 31.28 30.87 29.84 (CD3)2C 29.39 20.85 20.78
O
P
N
O
Ph2P
Fe
(Sc, Rp, S)-L5
f1 (ppm)

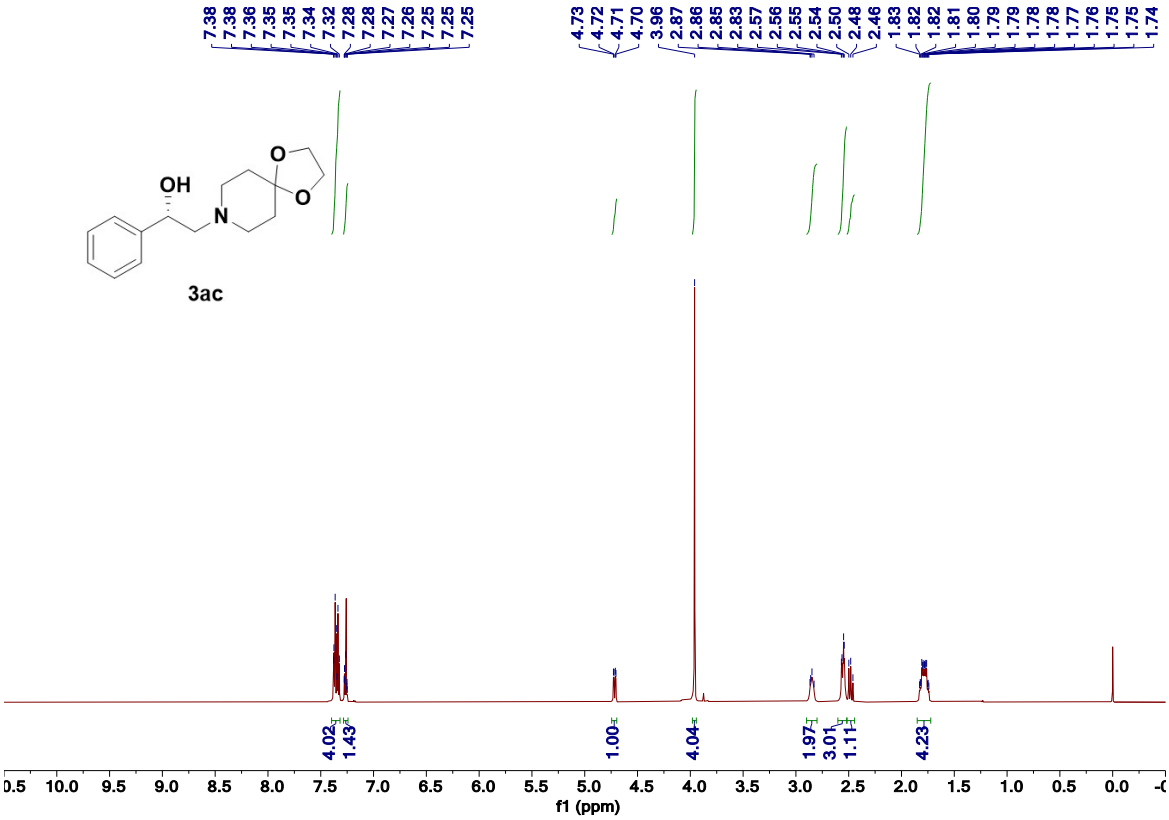

129.91
129.8
-25.72
-25.78
140 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

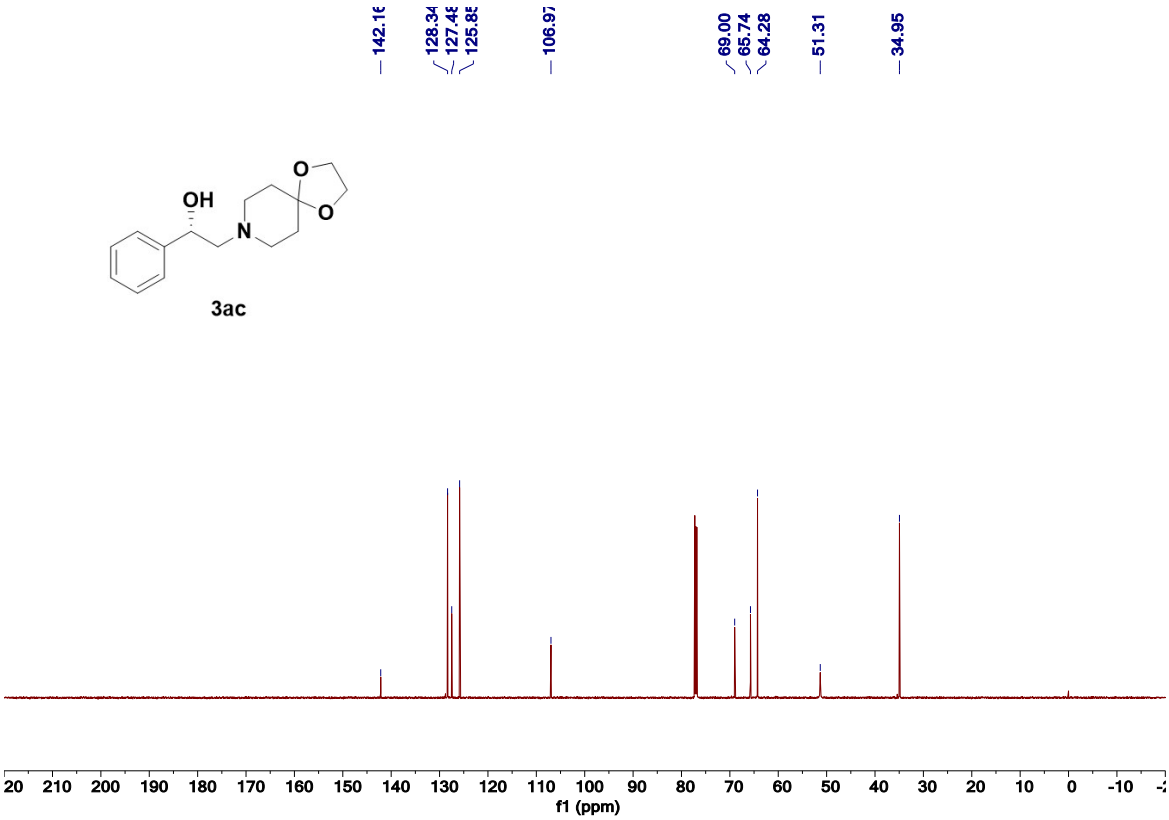

OH
N
3aa
7.39 7.38 7.38 7.37 7.36 7.35 7.35 7.34 7.33 7.32 7.32 7.28 7.28 7.27 7.26 7.26 7.24 7.24
4.73 4.72 4.70 4.69 4.23
2.69 2.49 2.49 2.46 2.45 2.41 2.38 2.38 2.35 2.33
1.67 1.66 1.65 1.64 1.63 1.62 1.61 1.60 1.60 1.59 1.57 1.55 1.54 1.49 1.48 1.46
3.91 1.18 1.00 0.90 1.94 1.13 2.88 4.05 1.94
f1 (ppm)

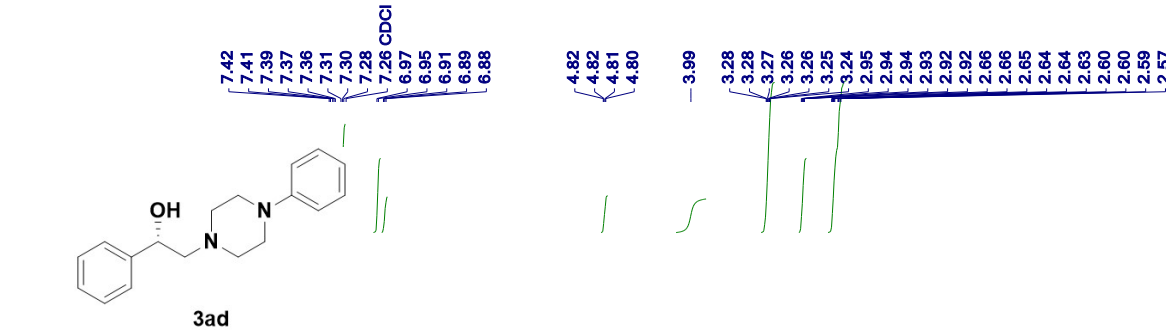

142.41
128.26
127.38
125.85
68.59
66.91
54.39
26.12
24.25
OH
N
3aa
f1 (ppm)


7.46 7.45 7.43 7.42 7.41 7.40 7.38 7.36 7.34 7.32 7.30 7.21 7.20 7.19 7.19 7.18 7.17 7.16 7.15 7.14 7.13 7.09 7.08 7.07 7.05 7.05 4.92 4.90 4.89 4.88 4.87 3.98 3.96 3.94 3.92 3.73 3.71 3.69 3.67 3.08 3.07 3.05 3.04 3.02 2.98 2.97 2.81 2.80 2.78 2.77 2.75 2.71 2.70 2.69 2.69 2.68 2.66 2.65
OH
N
3ab
4.91 3.92 0.98 0.82 1.23 1.05 3.00 3.01
f1 (ppm)

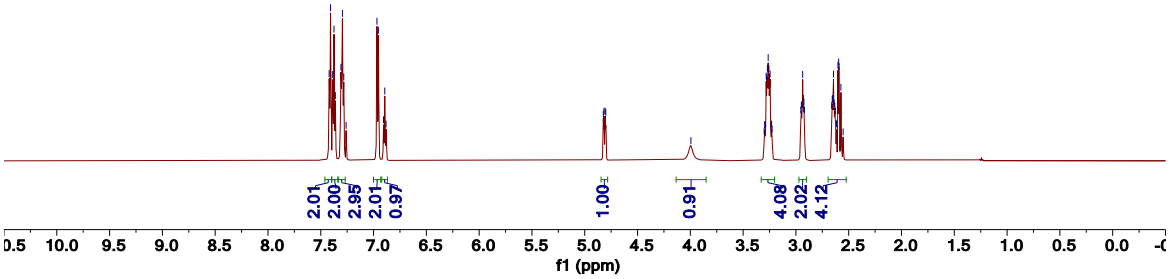

69.14 69.11 66.09 55.82 50.98 29.16
OH
N
3ab
f1 (ppm)

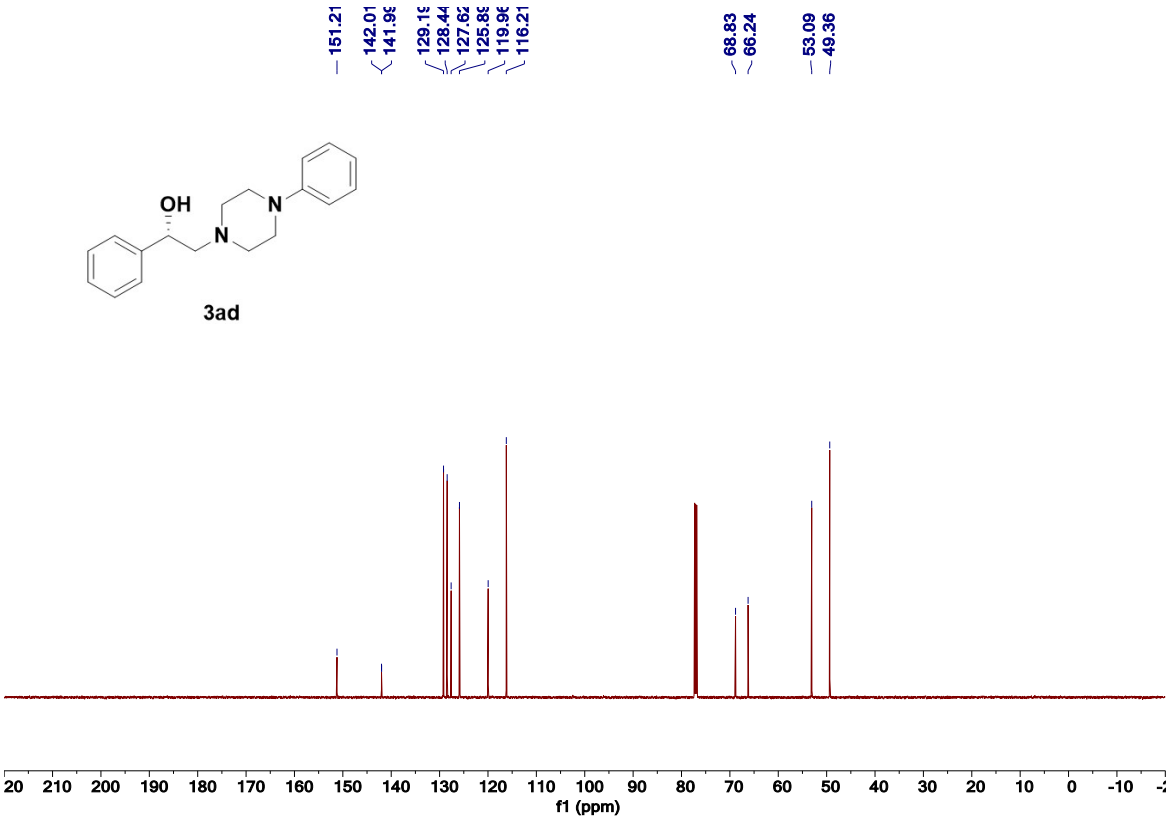

7.38 7.38 7.36 7.35 7.35 7.34 7.32 7.28 7.28 7.27 7.26 7.25 7.25 7.25
4.73 4.72 4.71 4.70 3.96 2.87 2.86 2.85 2.83 2.57 2.56 2.55 2.54 2.50 2.48 2.46 1.83 1.82 1.82 1.81 1.80 1.79 1.79 1.78 1.78 1.77 1.76 1.75 1.75 1.74
OH
N
O
O
3ac
4.02 1.43 1.00 4.04 1.97 3.01 1.11 4.23
f1 (ppm)


142.16
128.34
127.44
125.85
106.97
69.00
65.74
64.28
51.31
34.95
OH
N
O
O
3ac
f1 (ppm)

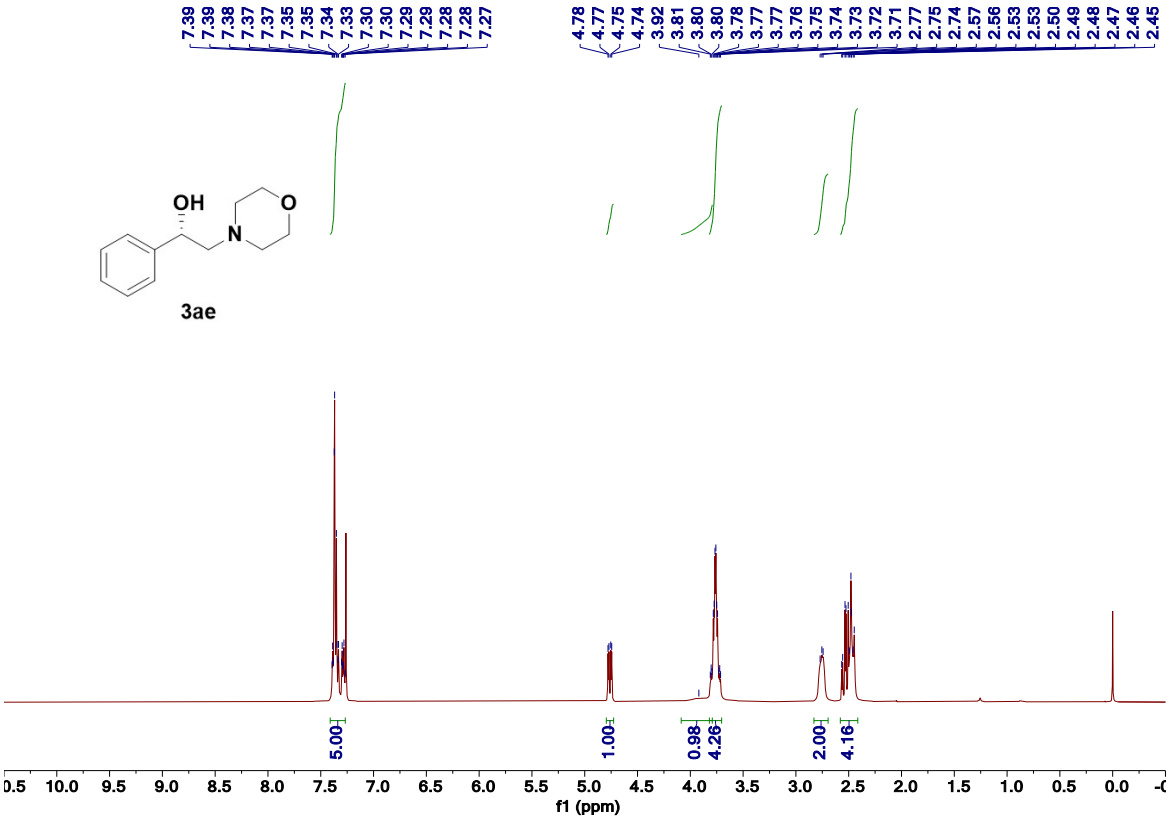

7.42
7.41
7.39
7.37
7.36
7.31
7.30
7.28
7.26 CDCl
6.97
6.95
6.91
6.89
6.88
4.82
4.82
4.81
4.80
3.99
3.28
3.28
3.27
3.26
3.26
3.25
3.24
2.95
2.94
2.94
2.93
2.92
2.92
2.66
2.66
2.65
2.64
2.64
2.63
2.60
2.60
2.59
OH
N
N

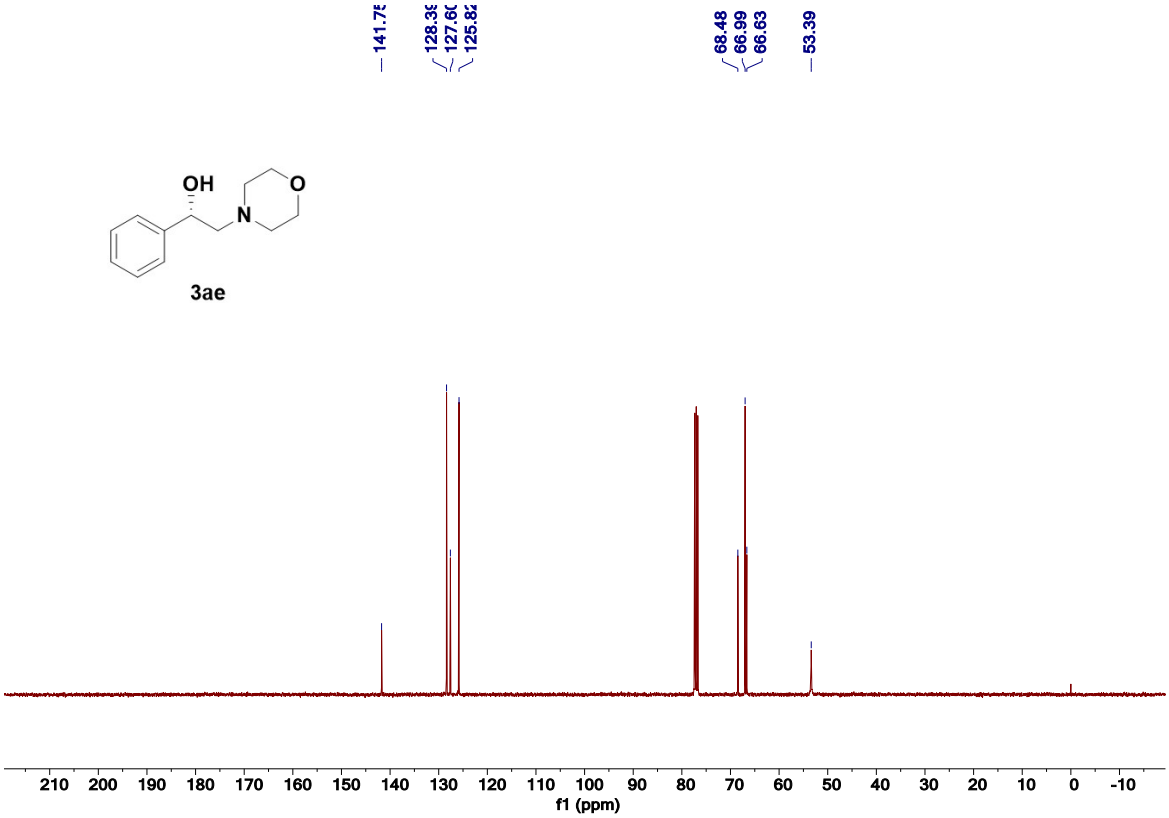
3ad

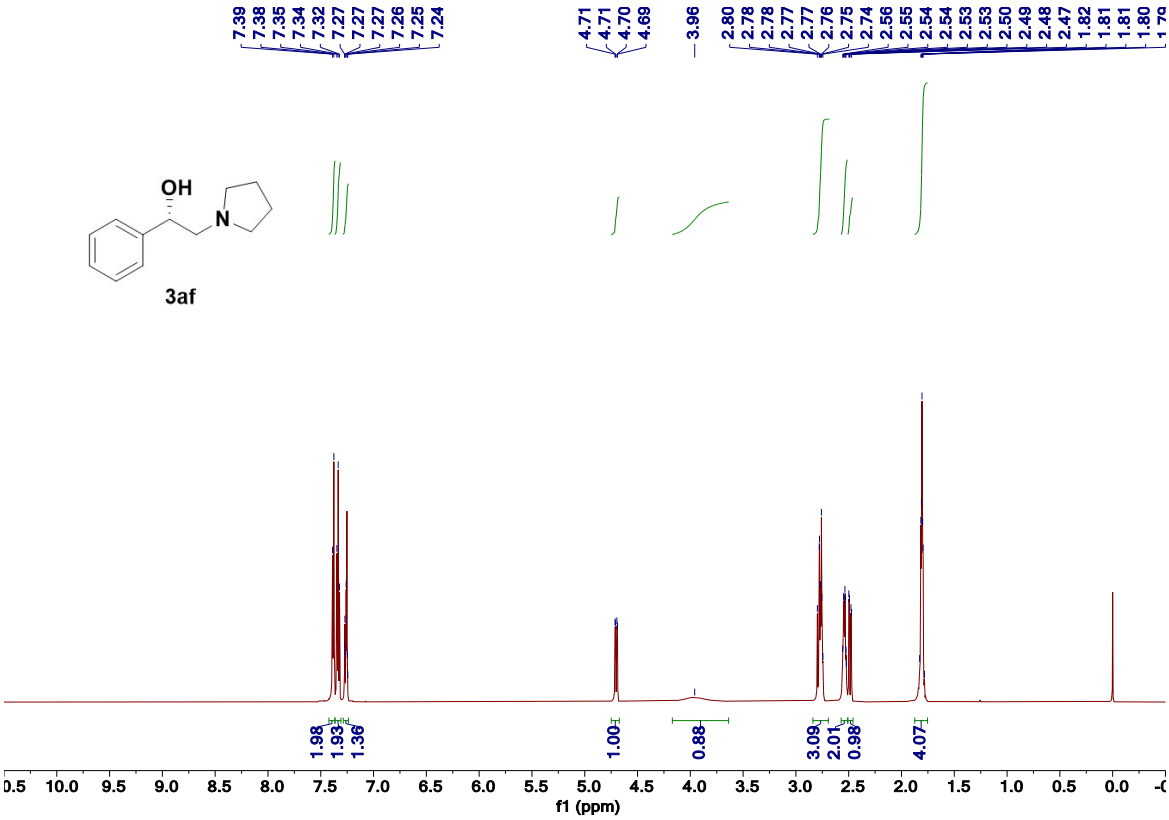

2.01
2.00
2.95
2.01
0.97
1.00
0.91
4.08
2.02
4.12
f1 (ppm)

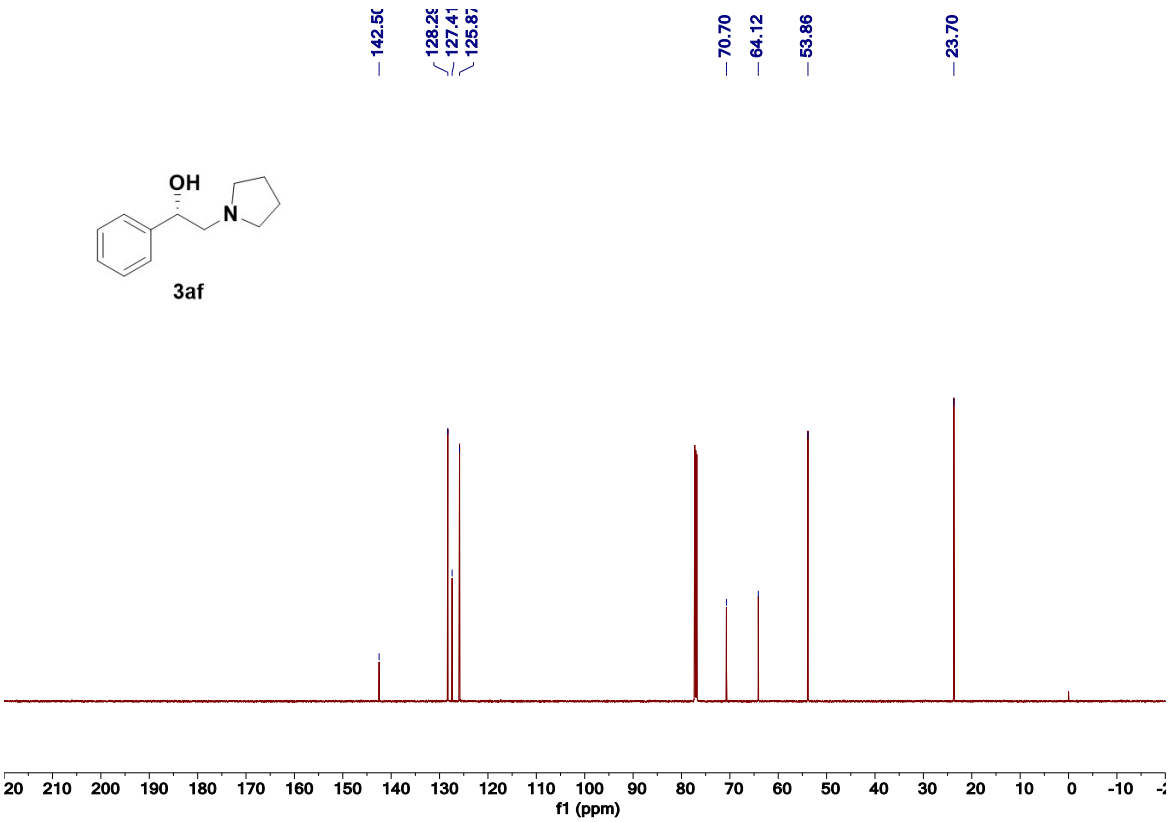

151.21
142.01
141.98
129.15
128.44
127.62
125.88
119.98
116.21
68.83
66.24
53.09
49.36
OH
N
N
f1 (ppm)

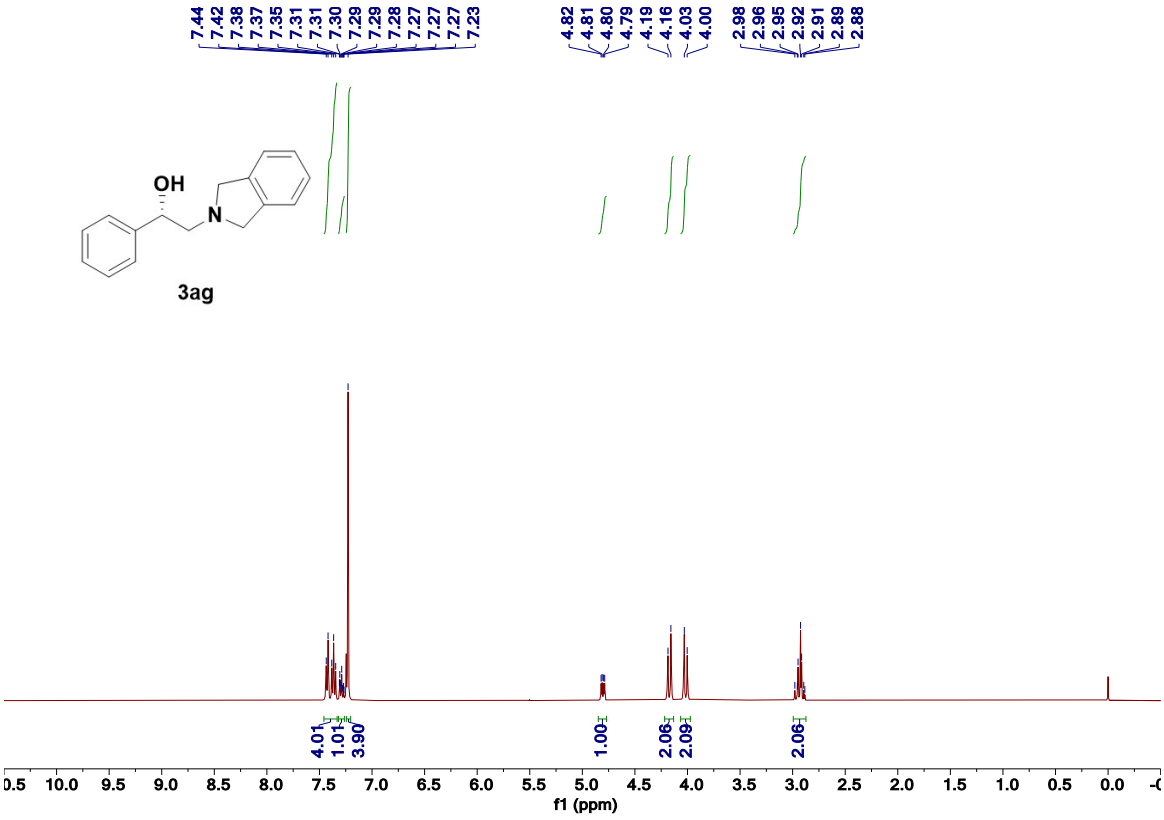
3ad

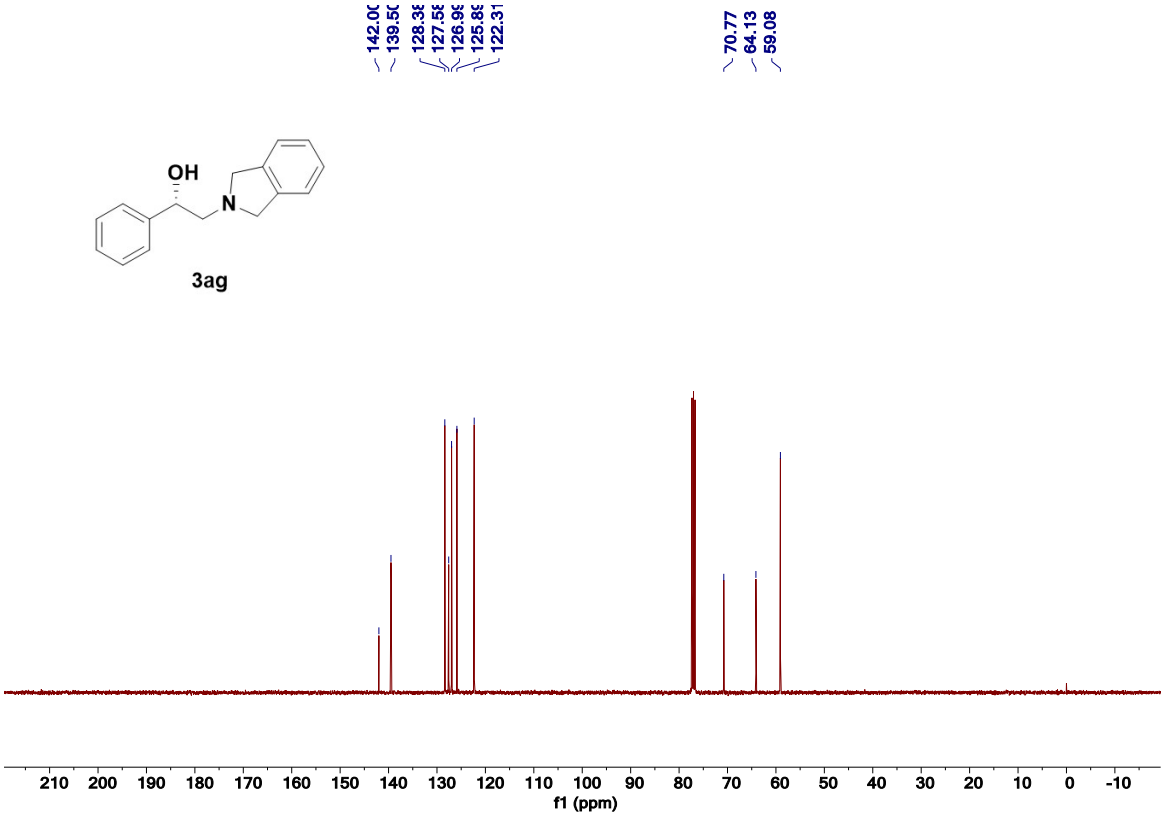

7.39
7.39
7.38
7.37
7.37
7.35
7.35
7.34
7.33
7.30
7.30
7.29
7.29
7.28
7.28
7.27
4.78
4.77
4.75
4.74
3.92
3.81
3.80
3.80
3.78
3.77
3.77
3.76
3.75
3.74
3.73
3.72
3.71
2.77
2.75
2.74
2.57
2.56
2.53
2.53
2.50
2.49
2.48
2.47
2.46
2.45
OH
O
N
3ae
5.00
1.00
0.98
4.26
2.00
4.16
f1 (ppm)

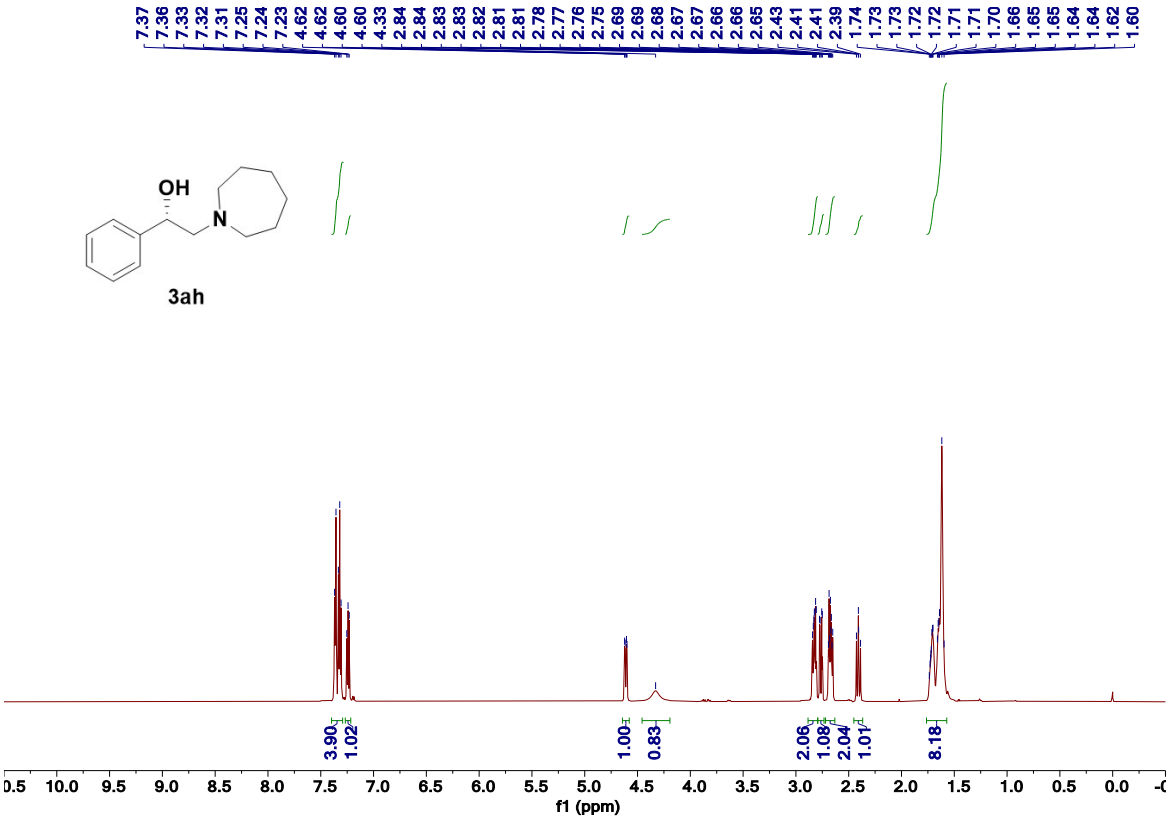

141.7
128.3
127.6
125.8
68.48
66.99
66.63
53.39
OH
O
N
3ae
f1 (ppm)

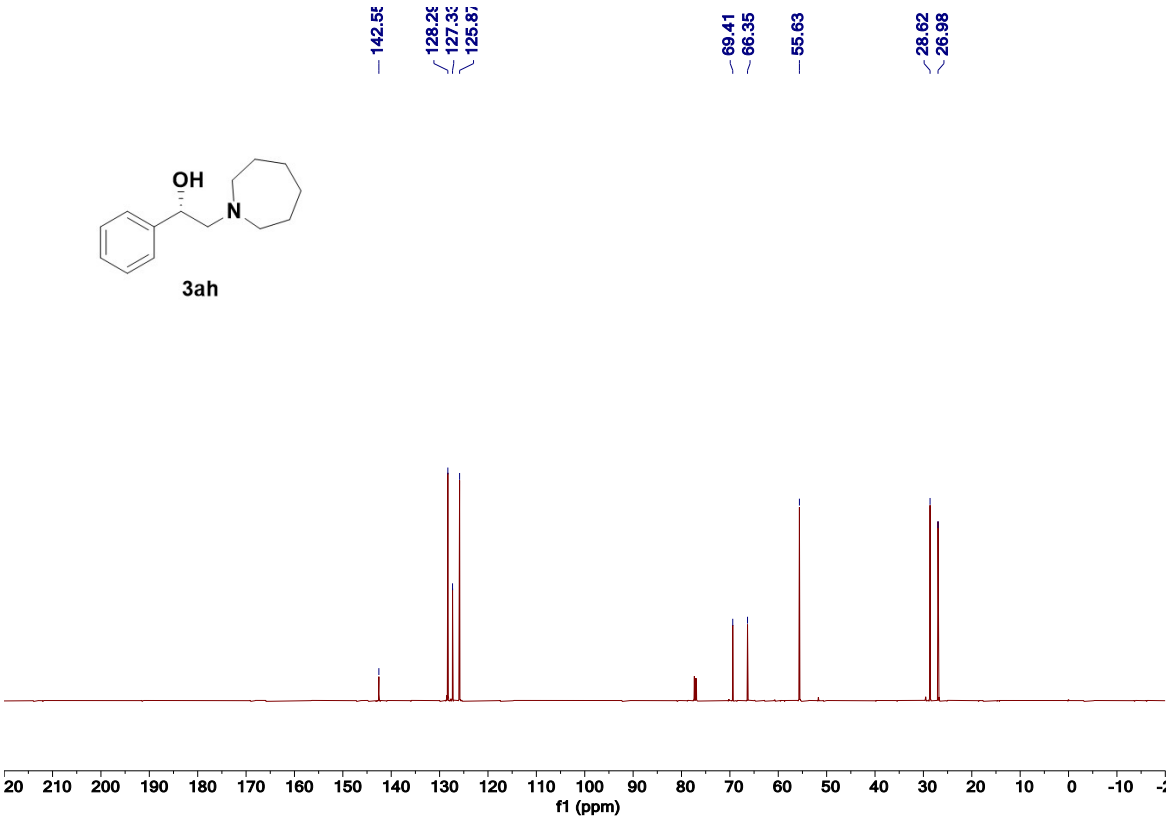

OH
N
3af
f1 (ppm)

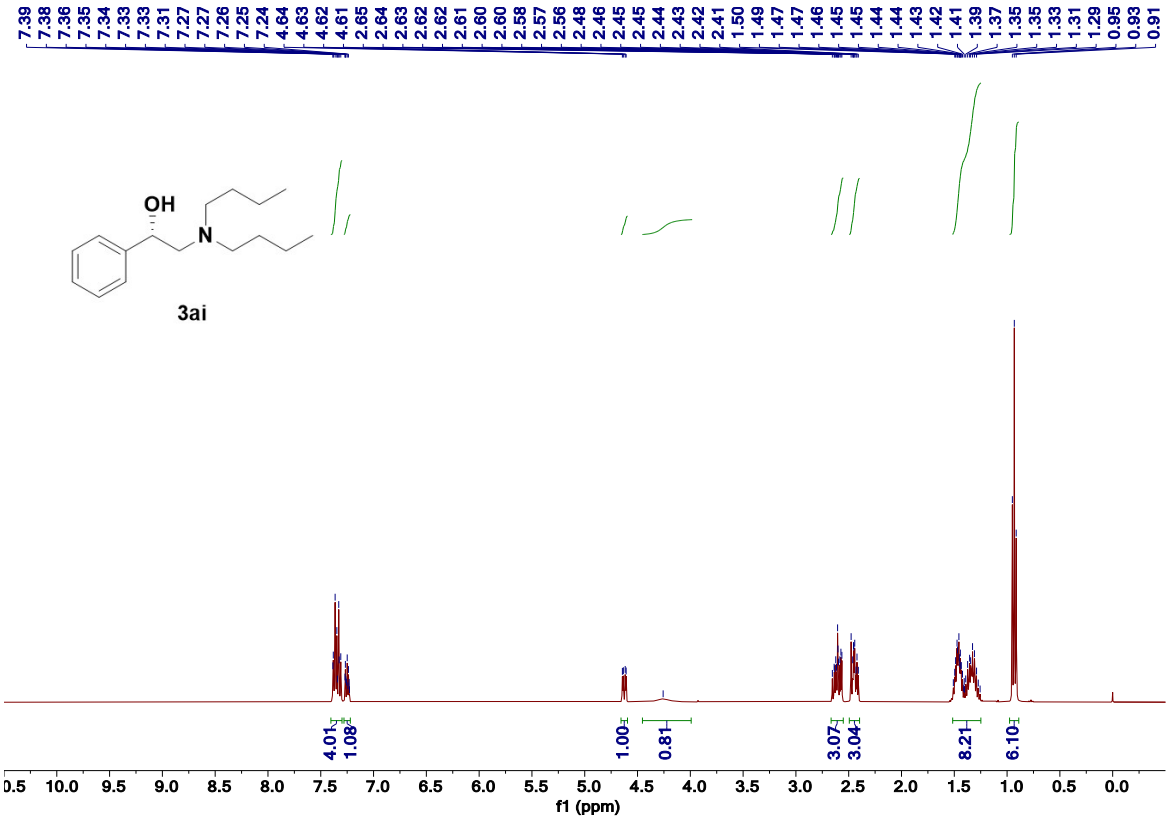

OH
N
3af
f1 (ppm)

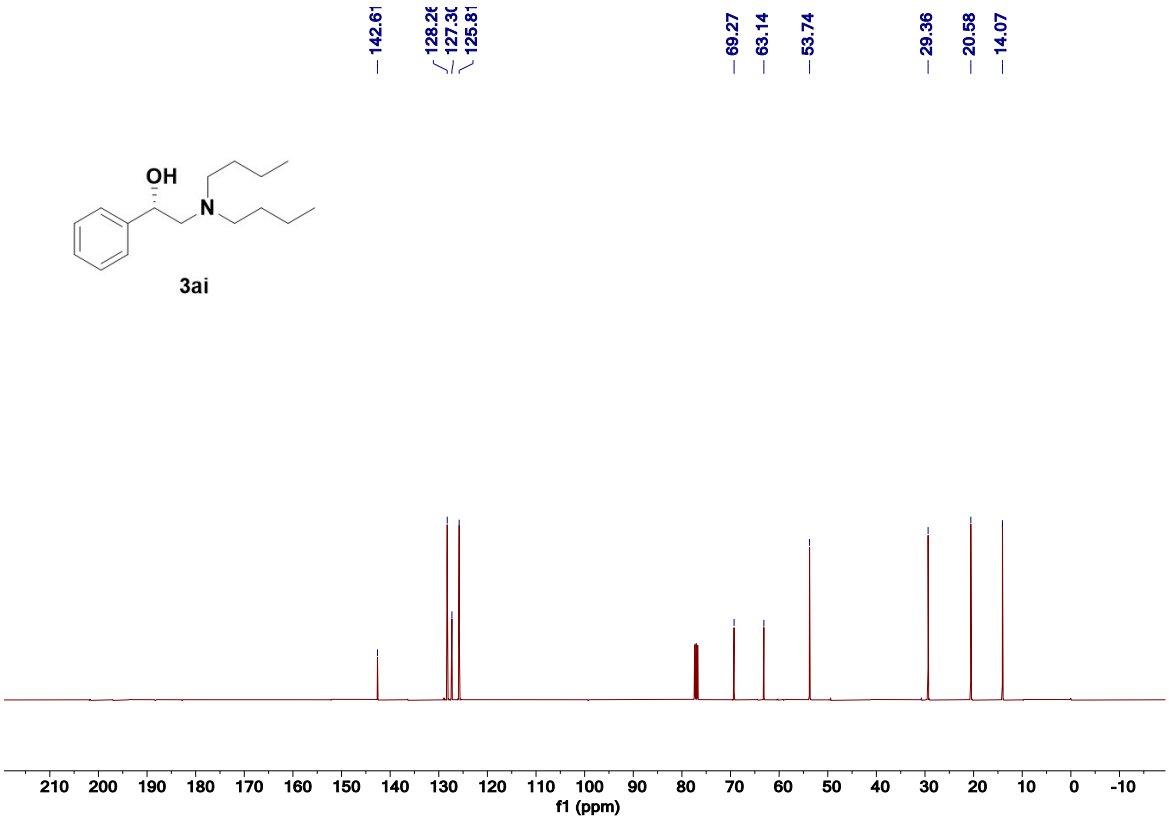

7.44
7.42
7.38
7.37
7.35
7.31
7.31
7.30
7.29
7.29
7.28
7.27
7.27
7.27
7.23
4.82
4.81
4.80
4.79
4.19
4.16
4.03
4.00
2.98
2.96
2.95
2.92
2.91
2.89
2.88
OH
N
3ag
4.01
1.01
3.90
1.00
2.06
2.09
2.06
f1 (ppm)

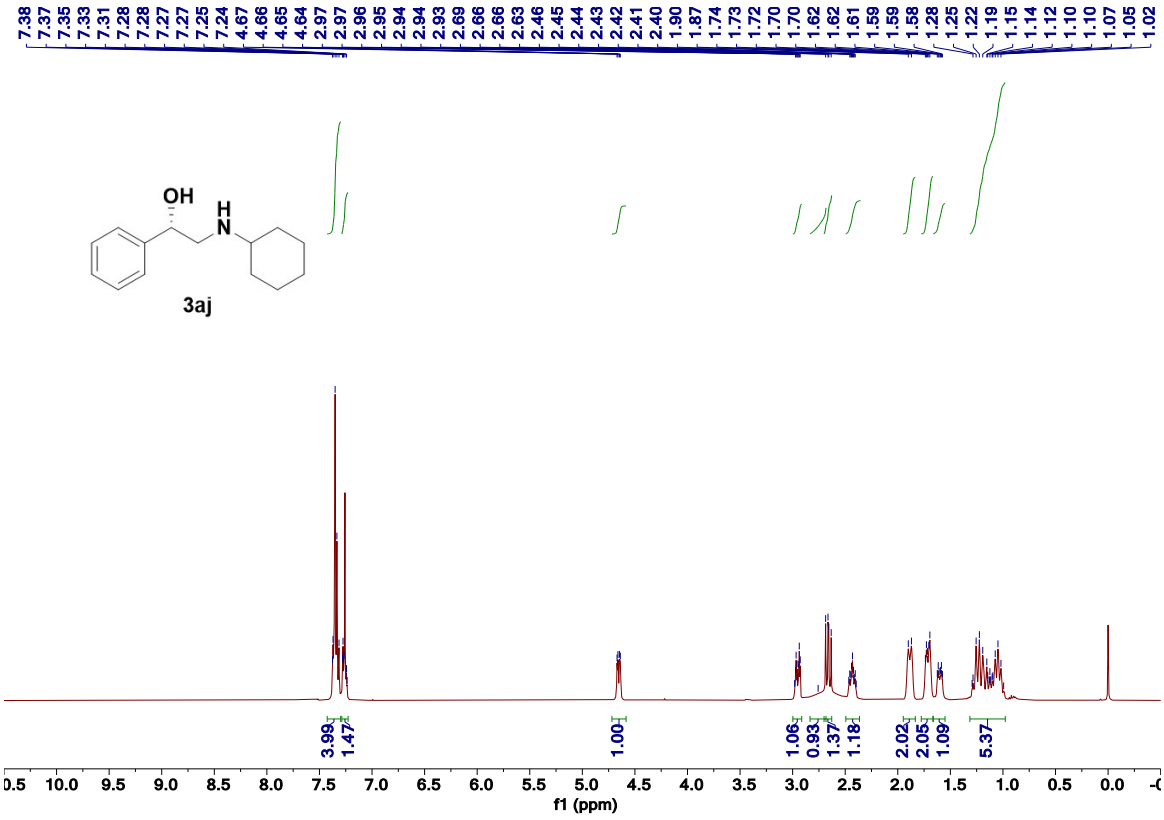

142.0
139.5
128.3
127.5
126.9
125.8
122.3
70.77
64.13
59.08
OH
N
3ag
f1 (ppm)

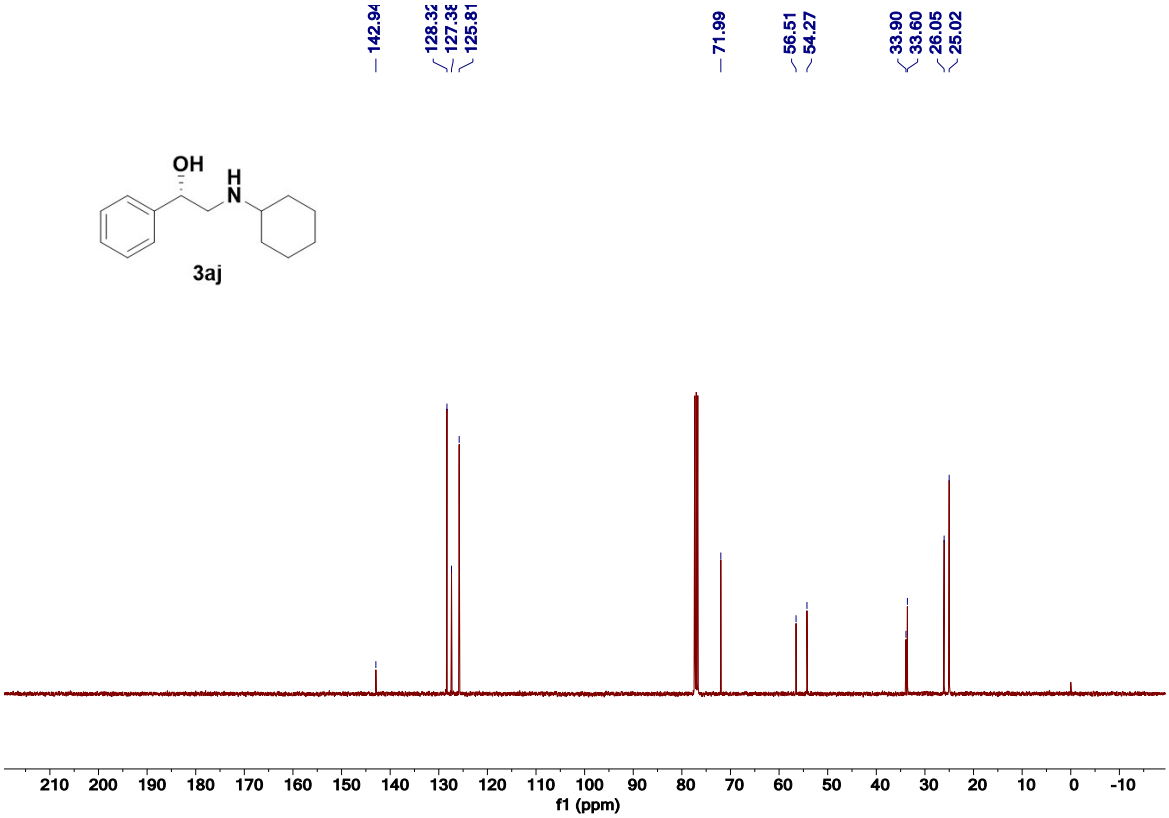

7.37
7.36
7.33
7.32
7.31
7.25
7.24
7.23
4.62
4.62
4.60
4.60
4.33
2.84
2.84
2.83
2.83
2.82
2.81
2.81
2.78
2.77
2.76
2.75
2.69
2.69
2.68
2.67
2.67
2.66
2.66
2.65
2.43
2.41
2.41
2.39
1.74
1.73
1.73
1.72
1.72
1.71
1.71
1.70
1.66
1.65
1.65
1.64
1.64
1.62
1.60
OH
N
3ah
3.90
1.02
1.00
0.83
2.06
1.08
2.04
1.01
8.18
f1 (ppm)

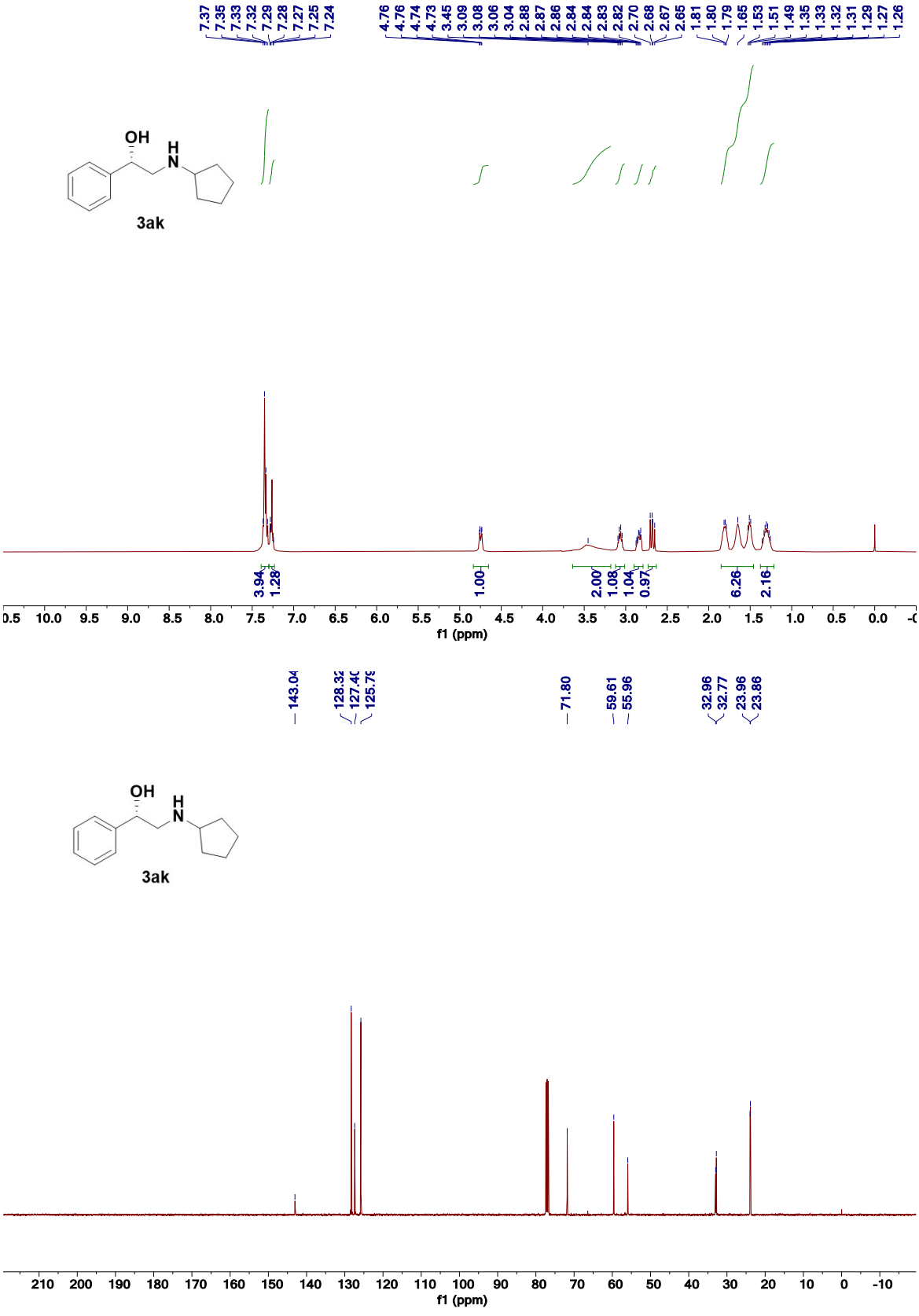

142.58
128.26
127.35
125.87
69.41
66.35
55.63
28.62
26.98
OH
N
3ah
f1 (ppm)

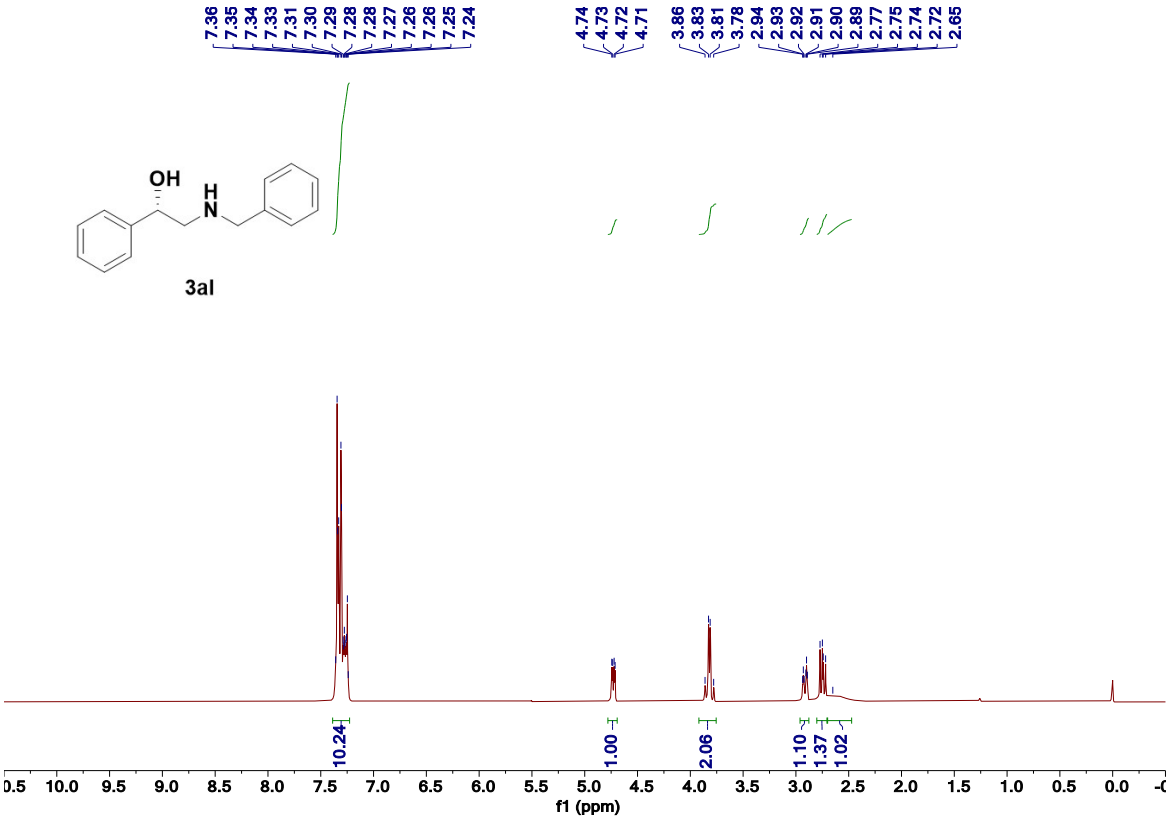

7.39 7.38 7.36 7.35 7.34 7.33 7.33 7.31 7.27 7.27 7.26 7.25 7.24 4.64 4.63 4.62 4.61 2.65 2.64 2.63 2.62 2.62 2.61 2.60 2.60 2.58 2.57 2.56 2.48 2.46 2.45 2.45 2.44 2.43 2.42 2.41 1.50 1.49 1.47 1.47 1.46 1.45 1.45 1.44 1.44 1.43 1.42 1.41 1.39 1.37 1.35 1.35 1.33 1.31 1.29 0.95 0.93 0.91
OH
N
3ai
4.01 1.08 1.00 0.81 3.07 3.04 8.21 6.10
f1 (ppm)

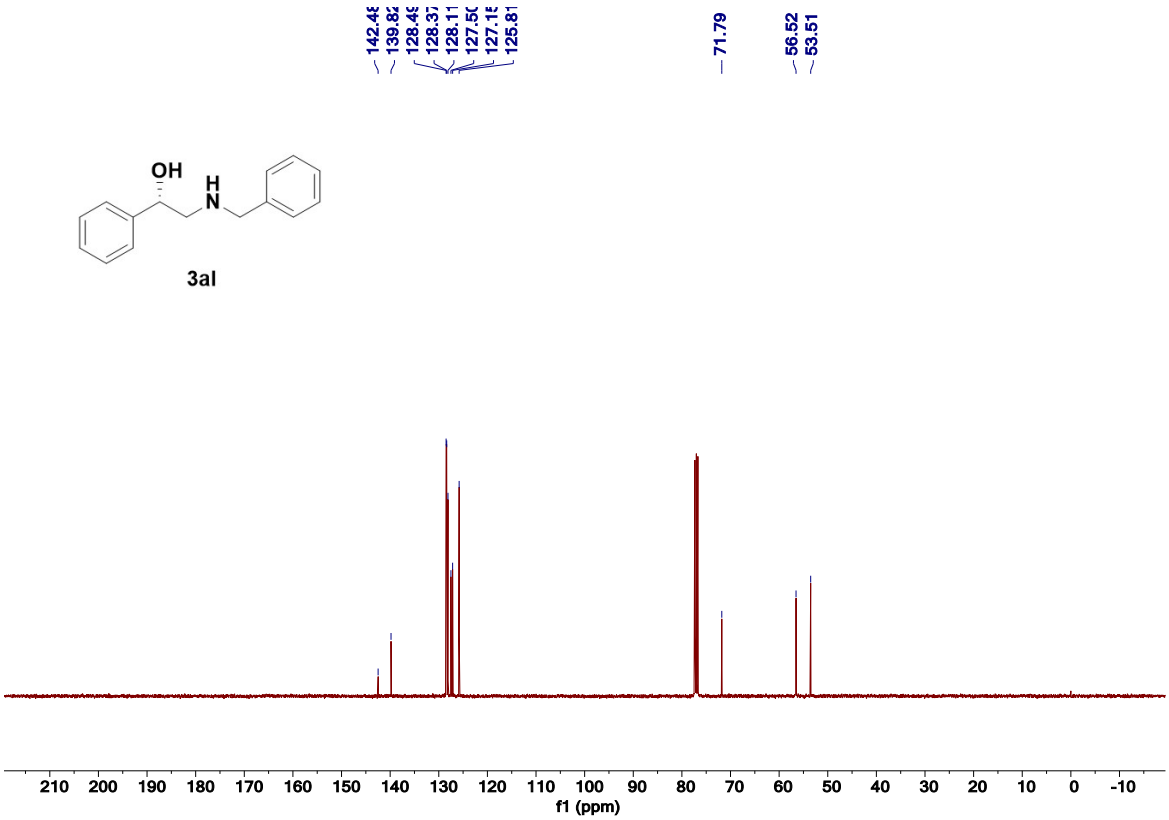

142.61 128.26 127.30 125.81 69.27 63.14 53.74 29.36 20.58 14.07
OH
N
3ai
f1 (ppm)

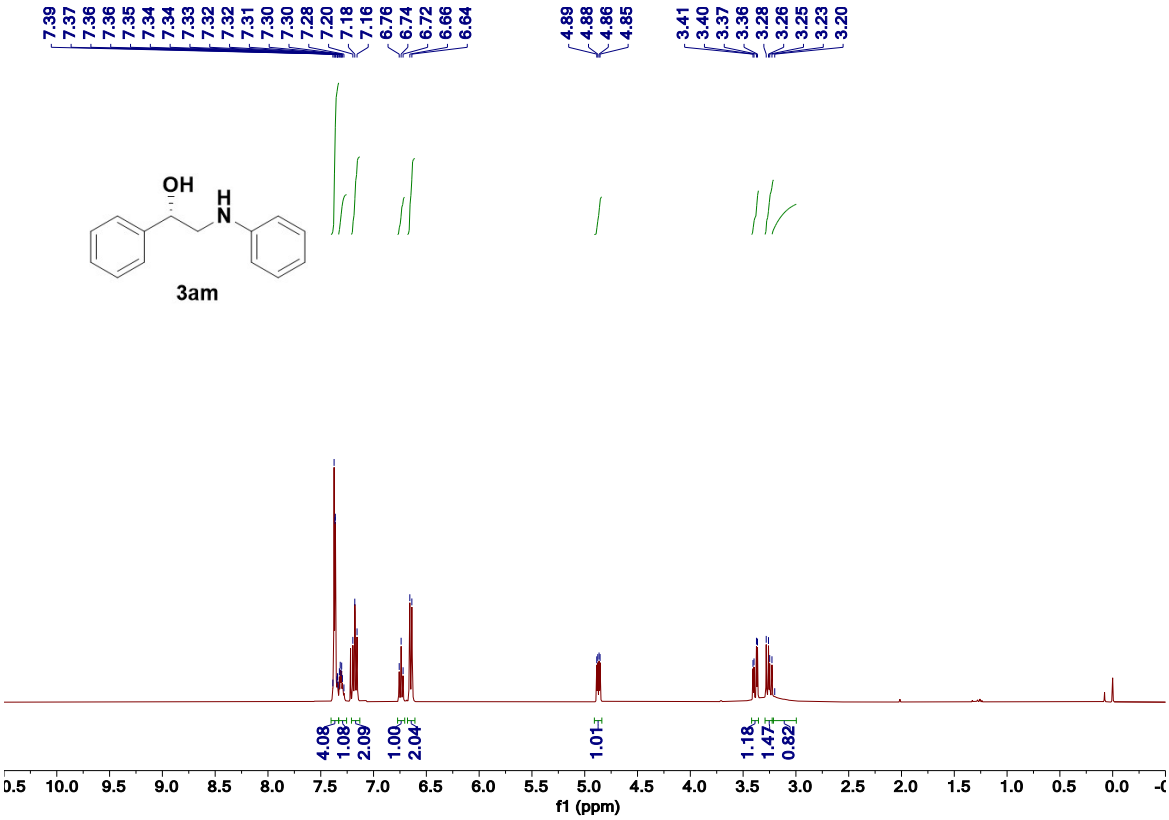

7.38 7.37 7.35 7.33 7.31 7.28 7.28 7.27 7.27 7.25 7.24 4.67 4.66 4.65 4.64 2.97 2.97 2.96 2.95 2.94 2.94 2.93 2.69 2.66 2.66 2.63 2.46 2.45 2.44 2.43 2.42 2.41 2.40 1.90 1.87 1.74 1.73 1.72 1.70 1.70 1.62 1.62 1.61 1.59 1.59 1.58 1.28 1.25 1.22 1.19 1.15 1.14 1.12 1.10 1.10 1.07 1.05 1.02
OH
H
N
3aj
3.99 1.47 1.00 1.06 0.93 1.37 1.18 2.02 2.05 1.09 5.37
f1 (ppm)

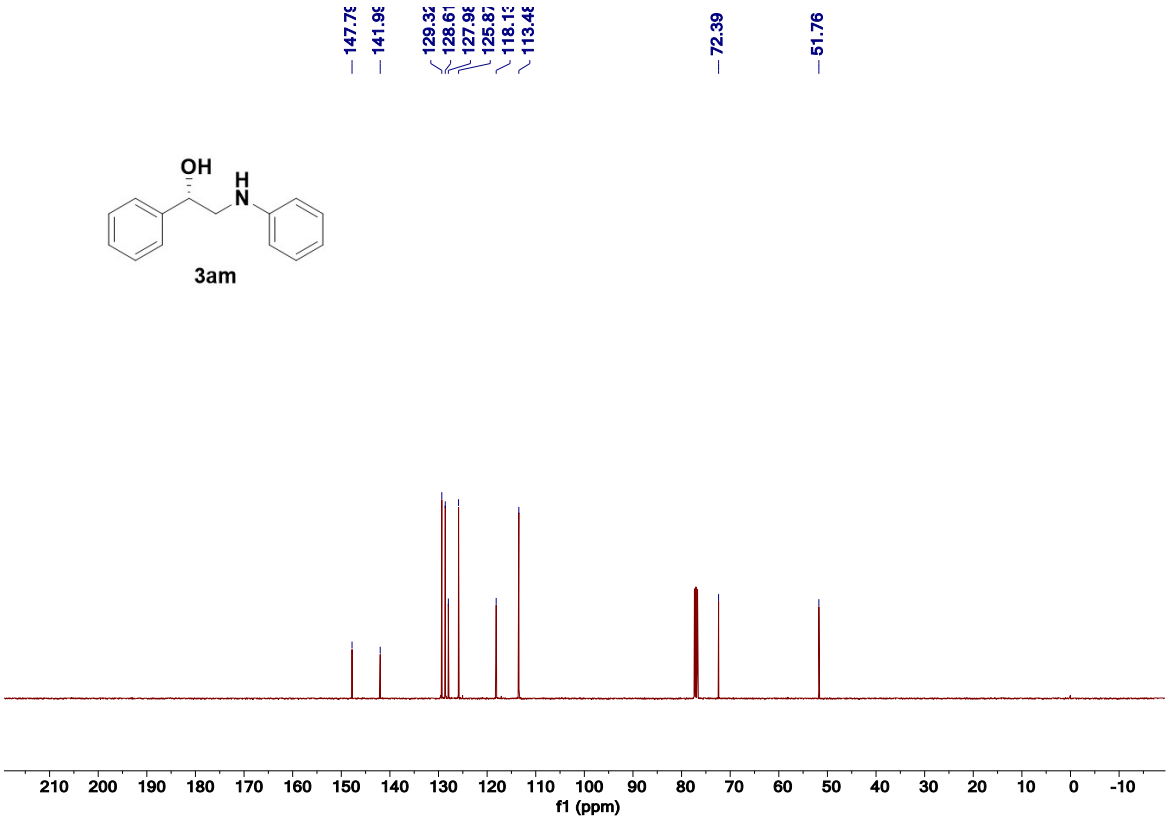

142.94 128.32 127.38 125.81 71.99 56.51 54.27 33.90 33.60 26.05 25.02
OH
H
N
3aj
f1 (ppm)

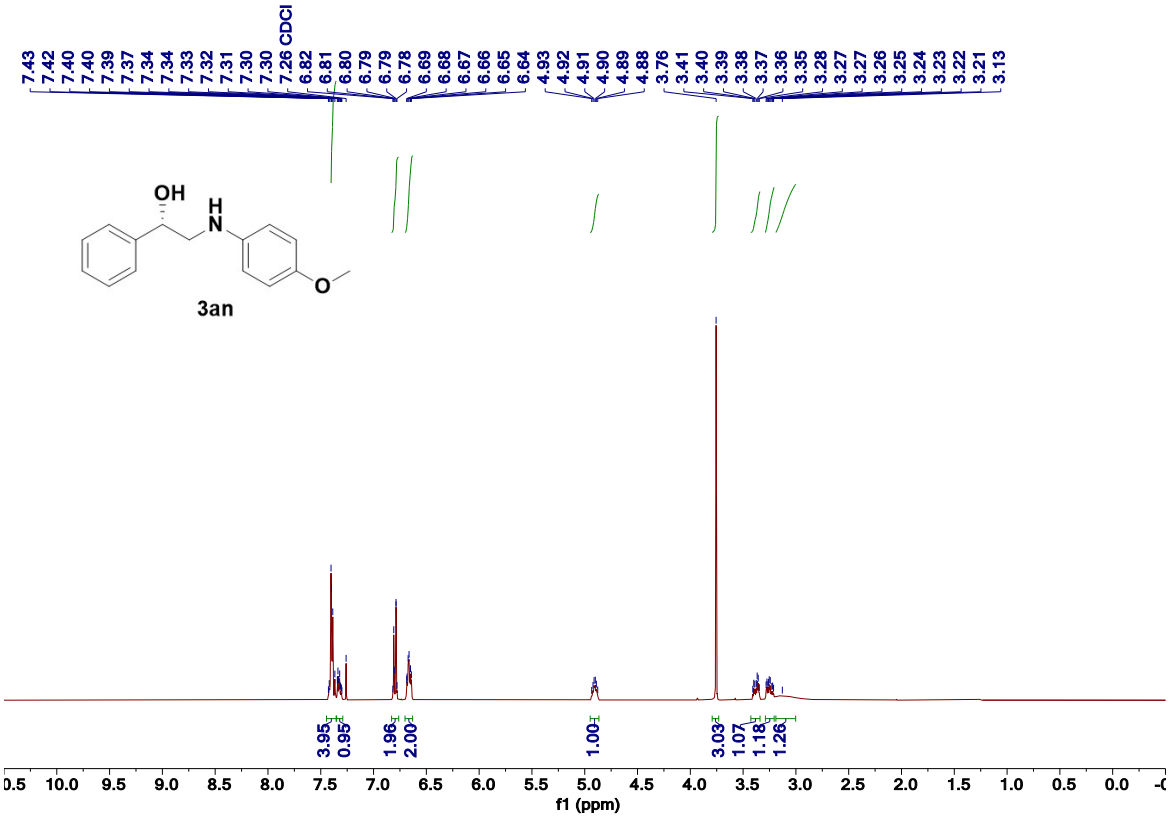

7.37 7.35 7.33 7.32 7.29 7.28 7.27 7.25 7.24
4.76 4.76 4.74 4.73 3.45 3.09 3.08 3.06 3.04 2.88 2.87 2.86 2.84 2.84 2.83 2.82 2.70 2.68 2.67 2.65 1.81 1.80 1.79 1.65 1.53 1.51 1.49 1.35 1.33 1.32 1.31 1.29 1.27 1.26
OH
H
N
3ak
3.94 1.28 1.00 2.00 1.08 1.04 0.97 6.26 2.16
f1 (ppm)
143.04 128.32 127.44 125.75 71.80 59.61 55.96 32.96 32.77 23.96 23.86
OH
H
N
3ak
f1 (ppm)

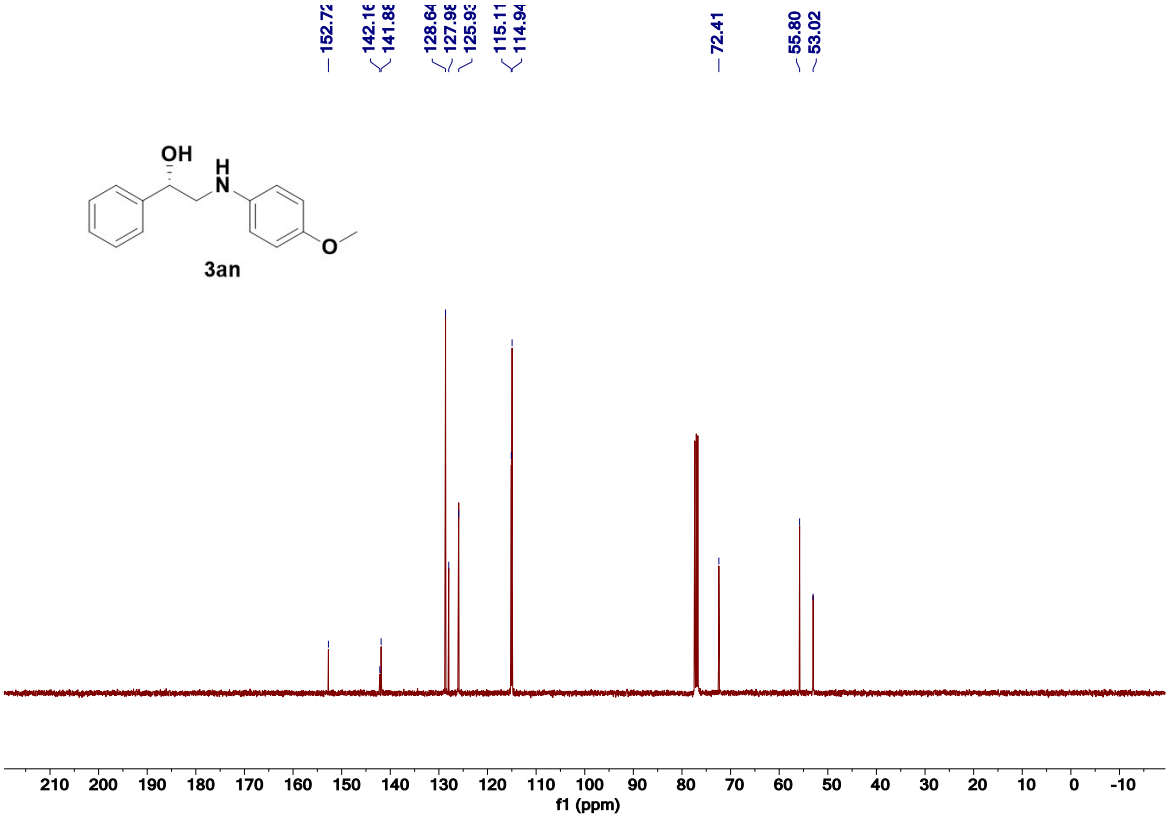

7.36
7.35
7.34
7.33
7.31
7.30
7.29
7.28
7.28
7.27
7.26
7.26
7.25
7.24
4.74
4.73
4.72
4.71
3.86
3.83
3.81
3.78
2.94
2.93
2.92
2.91
2.90
2.89
2.77
2.75
2.74
2.72
2.65
OH
H
N
3al
10.24
1.00
2.06
1.10
1.37
1.02
f1 (ppm)

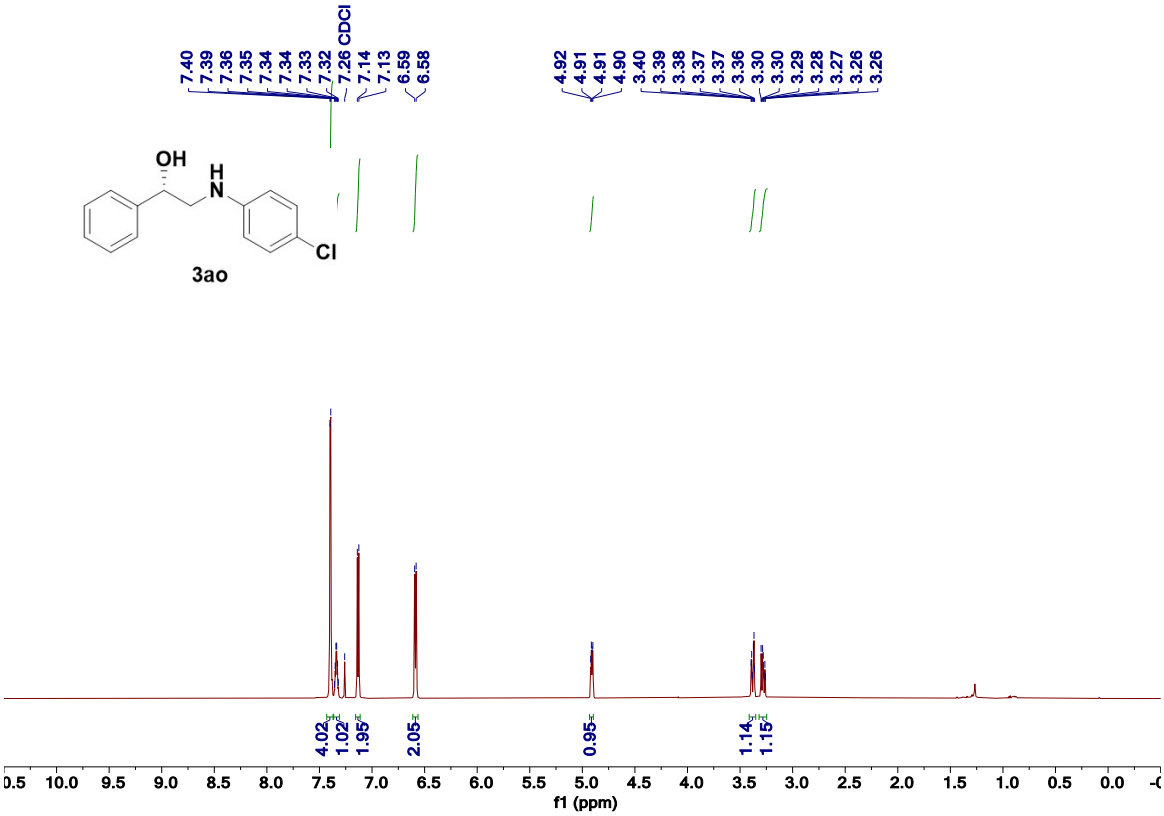

142.44
139.82
128.45
128.37
128.11
127.56
127.18
125.81
71.79
56.52
53.51
OH
H
N
3al
f1 (ppm)

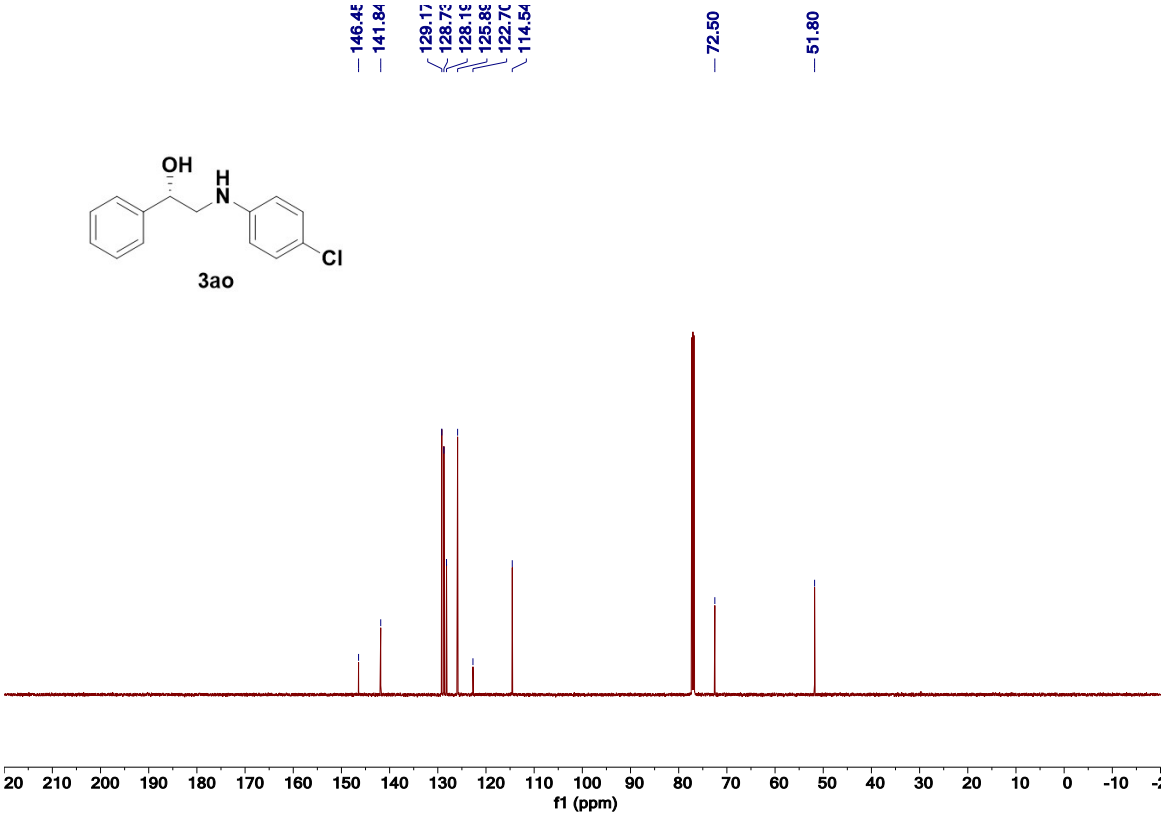

7.39
7.37
7.36
7.36
7.35
7.34
7.34
7.33
7.32
7.32
7.31
7.30
7.30
7.28
7.20
7.18
7.16
6.76
6.74
6.72
6.66
6.64
4.89
4.88
4.86
4.85
3.41
3.40
3.37
3.36
3.28
3.26
3.25
3.23
3.20
OH
H
N
3am
4.08
1.08
2.09
1.00
2.04
1.01
1.18
1.47
0.82
f1 (ppm)

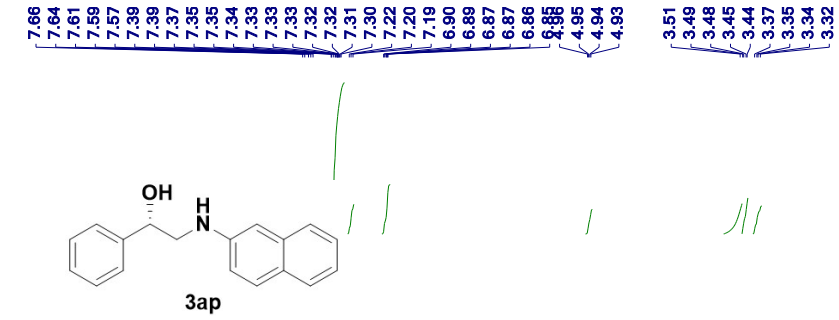

147.7
141.9
129.3
128.6
127.9
125.8
118.1
113.4
72.39
51.76
OH
H
N
3am
f1 (ppm)

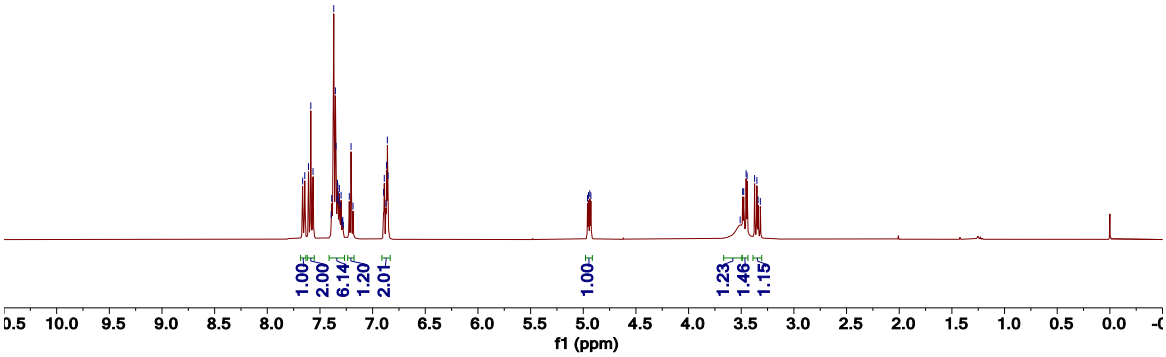

7.43 7.42 7.40 7.40 7.39 7.37 7.34 7.34 7.33 7.32 7.31 7.30 7.30 7.26 CDCl 6.82 6.81 6.80 6.79 6.79 6.78 6.69 6.68 6.67 6.66 6.65 6.64 4.93 4.92 4.91 4.90 4.89 4.88 3.76 3.41 3.40 3.39 3.38 3.37 3.36 3.35 3.28 3.27 3.27 3.26 3.25 3.24 3.23 3.22 3.21 3.13
OH
H
N
O
3an
3.95 0.95 1.96 2.00 1.00 3.03 1.07 1.18 1.26
f1 (ppm)


152.72 142.16 141.88 128.64 127.98 125.83 115.11 114.94 72.41 55.80 53.02
OH
H
N
O
3an
f1 (ppm)

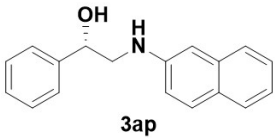

7.40
7.39
7.36
7.35
7.34
7.34
7.33
7.32
7.26 CDCl
7.14
7.13
6.59
6.58
4.92
4.91
4.91
4.90
3.40
3.39
3.38
3.37
3.37
3.36
3.30
3.30
3.29
3.28
3.27
3.26
3.26
OH
H
N
Cl
3ao
4.02
1.02
1.95
2.05
0.95
1.14
1.15
f1 (ppm)

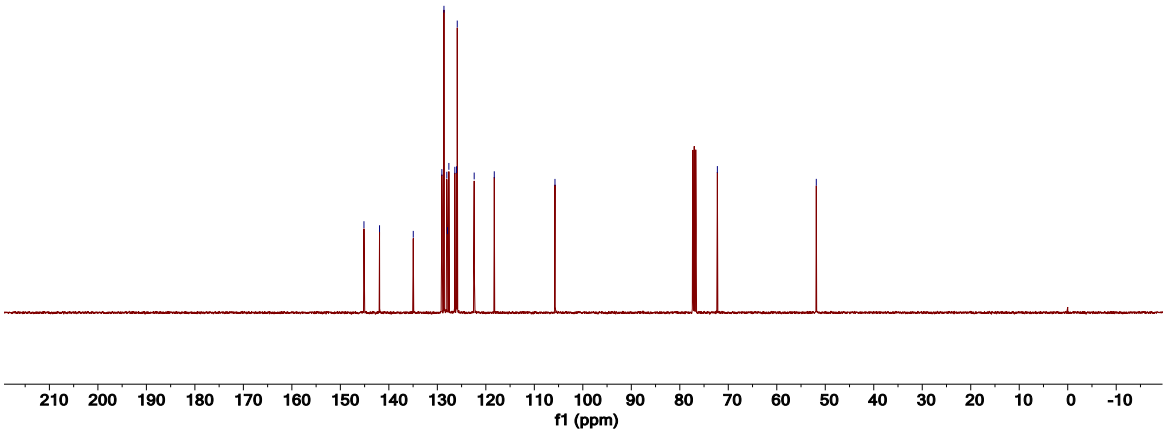

146.45
141.84
129.17
128.72
128.15
125.85
122.70
114.54
72.50
51.80
OH
H
N
Cl
3ao
f1 (ppm)

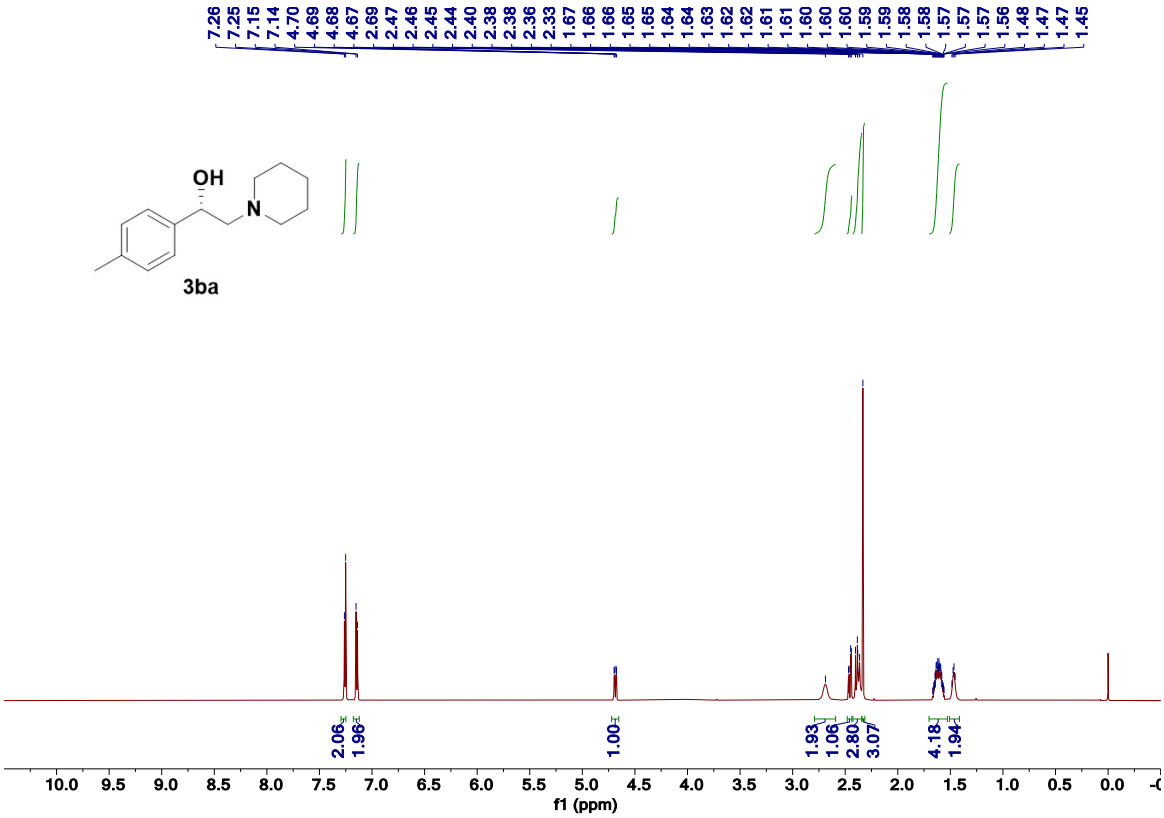

7.66
7.64
7.61
7.59
7.57
7.39
7.39
7.37
7.35
7.35
7.34
7.33
7.33
7.33
7.32
7.32
7.31
7.30
7.22
7.20
7.19
6.90
6.89
6.87
6.87
6.86
6.85
4.95
4.94
4.93
3.51
3.49
3.48
3.45
3.44
3.37
3.35
3.34
3.32
OH
H
N
3ap

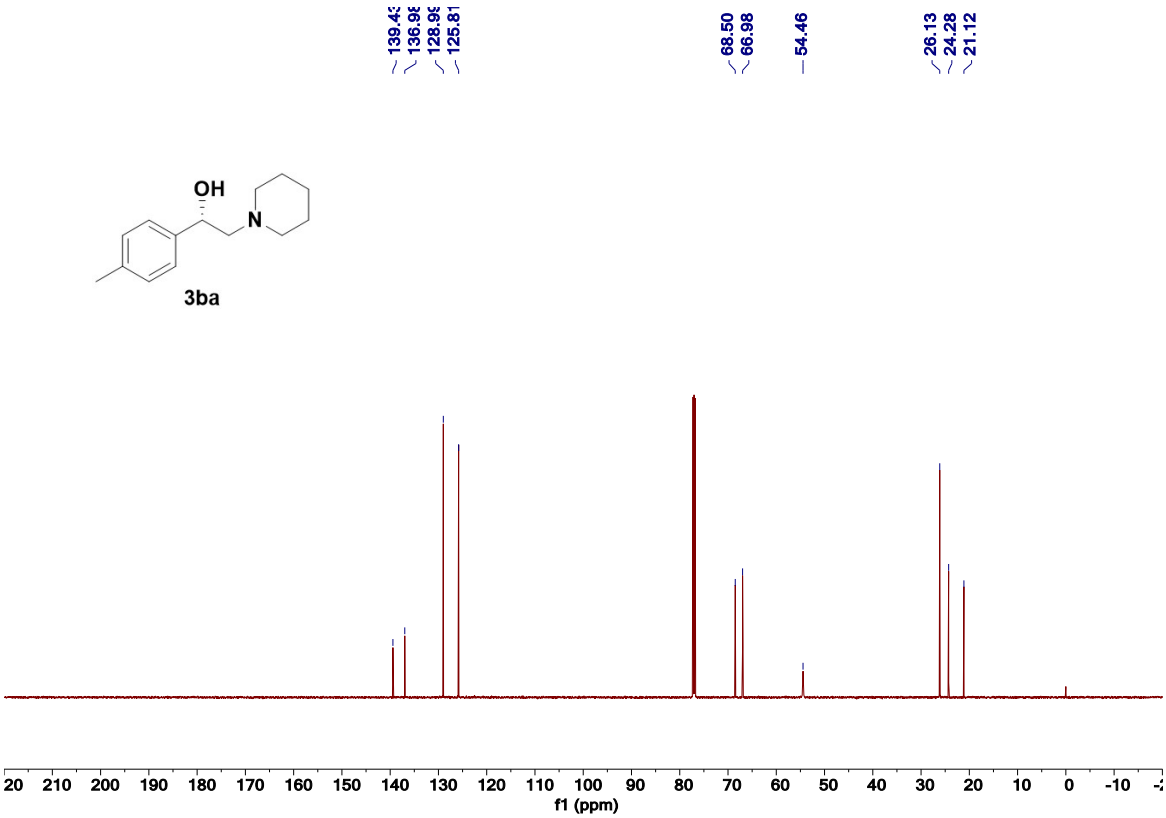

1.00
2.00
6.14
1.20
2.01
1.00
1.23
1.46
1.15
f1 (ppm)

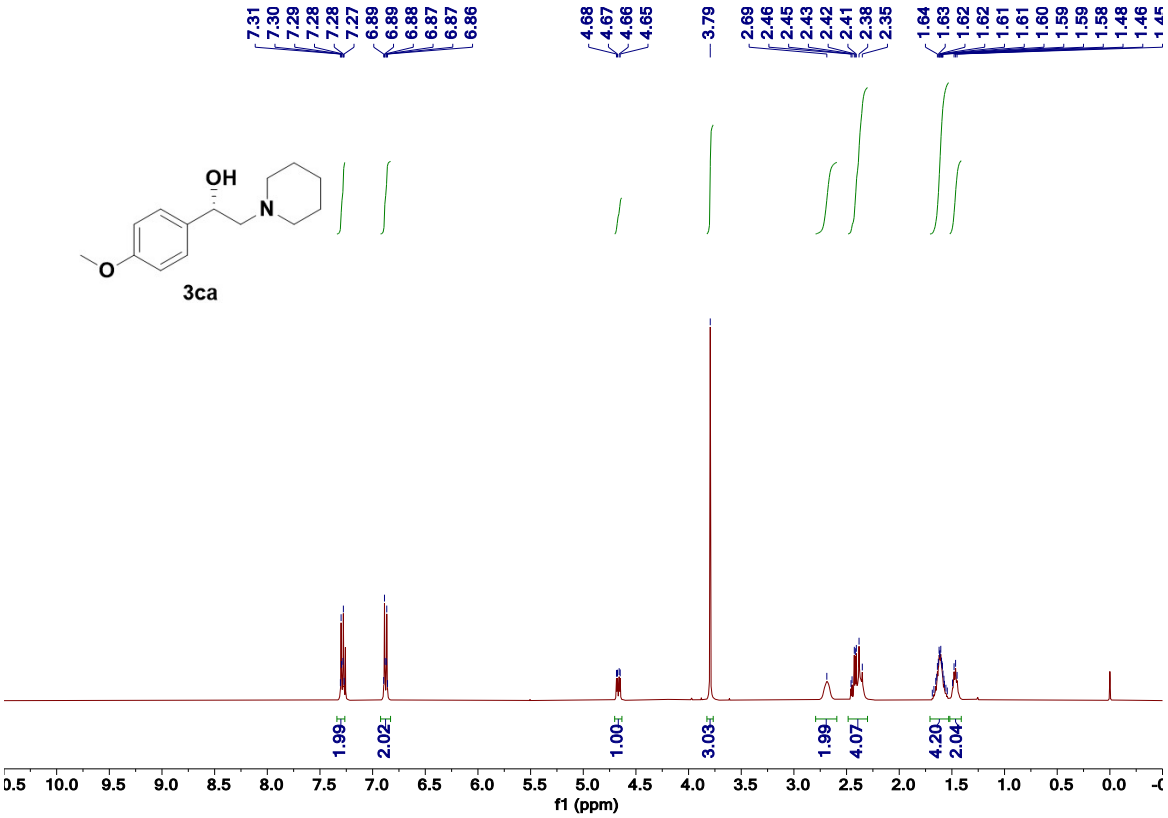

145.13
141.92
134.96
129.07
128.64
128.04
127.91
127.62
126.35
126.04
125.88
122.44
118.26
105.74
72.25
51.85

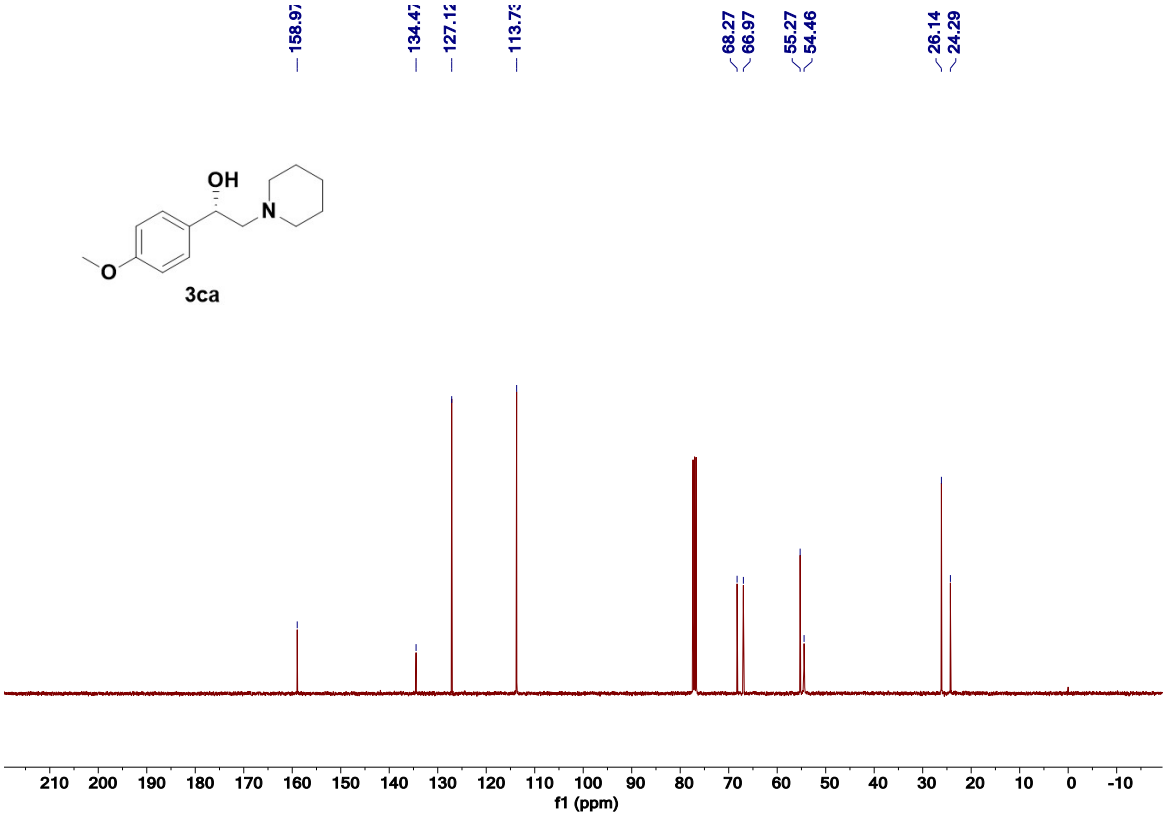

OH
H
N
3ap

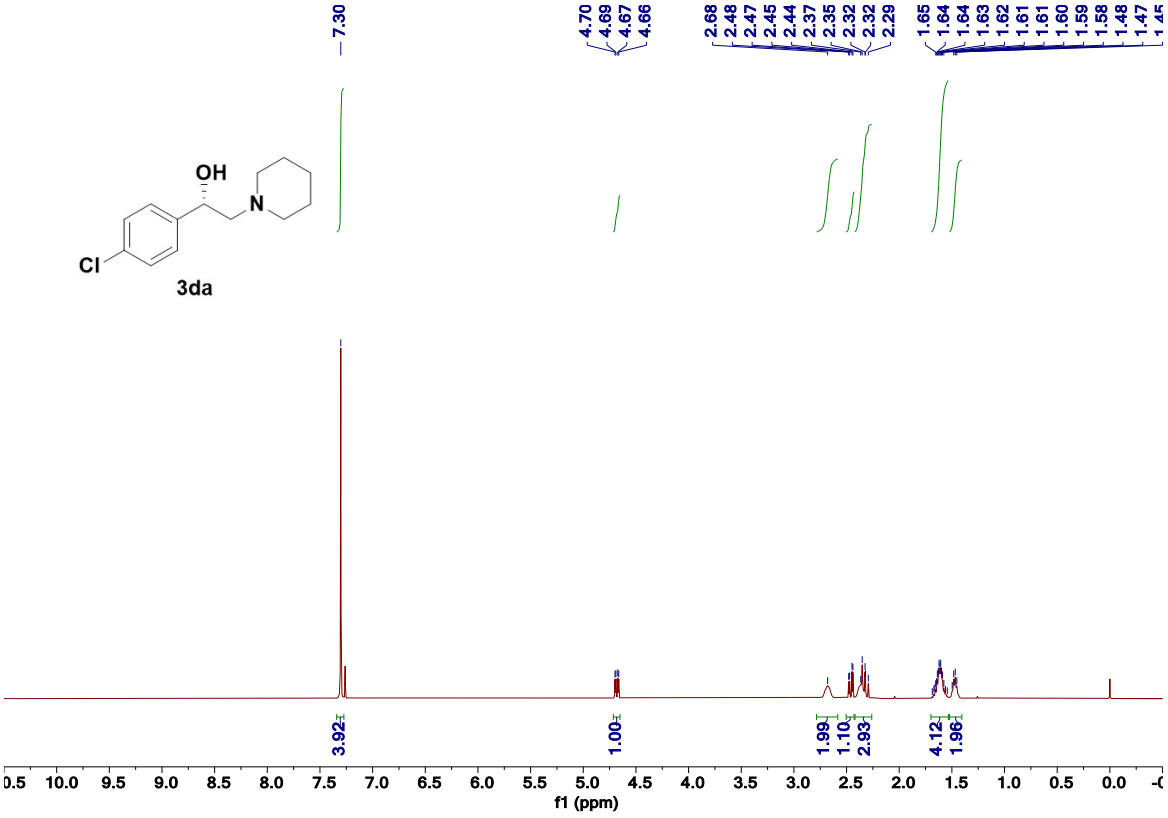

f1 (ppm)

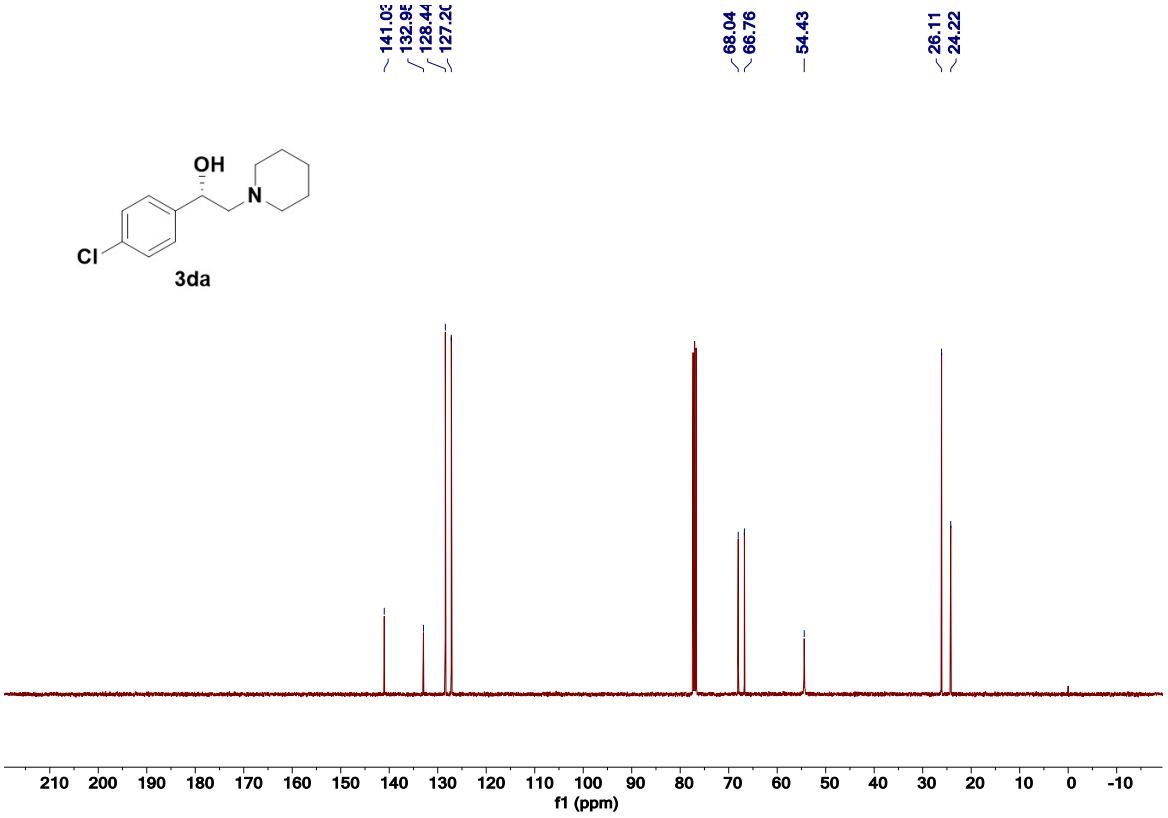

7.26 7.25 7.15 7.14 4.70 4.69 4.68 4.67 2.69 2.47 2.46 2.45 2.44 2.40 2.38 2.38 2.36 2.33 1.67 1.66 1.66 1.65 1.65 1.64 1.64 1.63 1.62 1.62 1.61 1.61 1.60 1.60 1.60 1.59 1.59 1.58 1.58 1.57 1.57 1.57 1.56 1.48 1.47 1.47 1.45
OH
N
3ba
2.06 1.96 1.00 1.93 1.06 2.80 3.07 4.18 1.94
f1 (ppm)

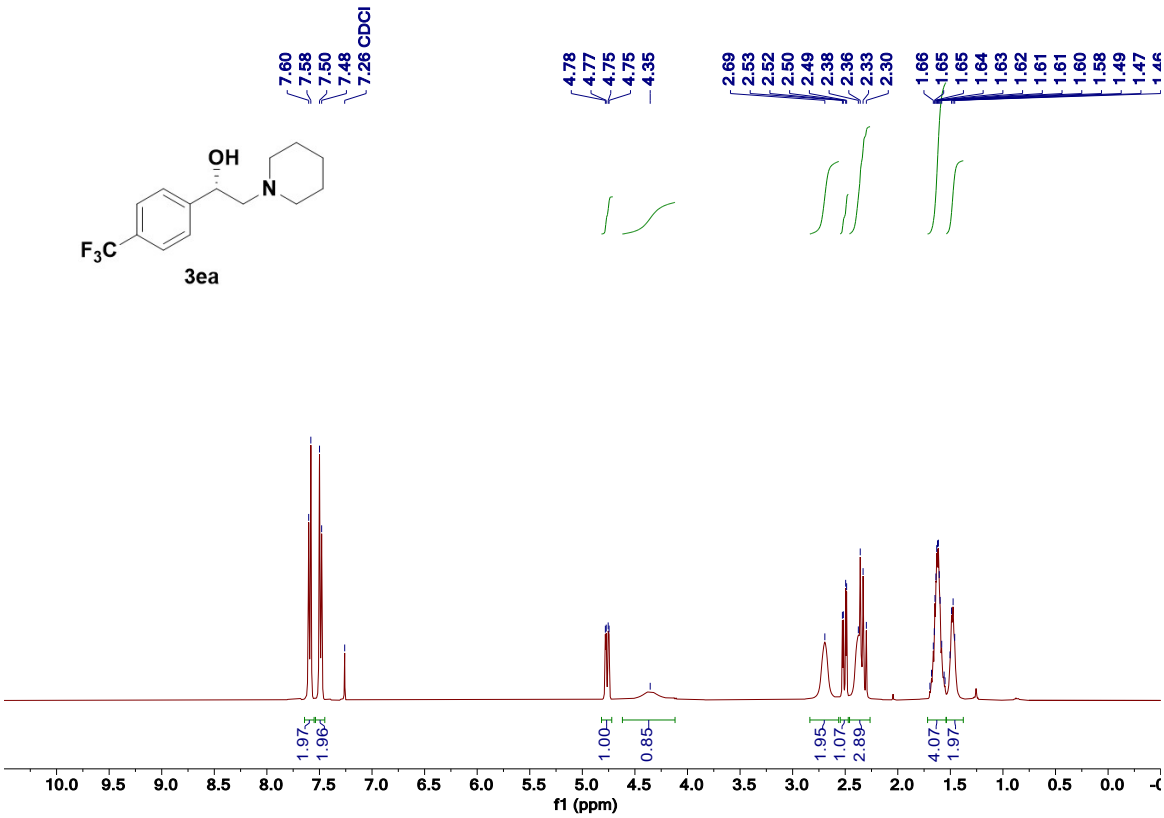

139.43 136.98 128.96 125.81 68.50 66.98 54.46 26.13 24.28 21.12
OH
N
3ba
f1 (ppm)

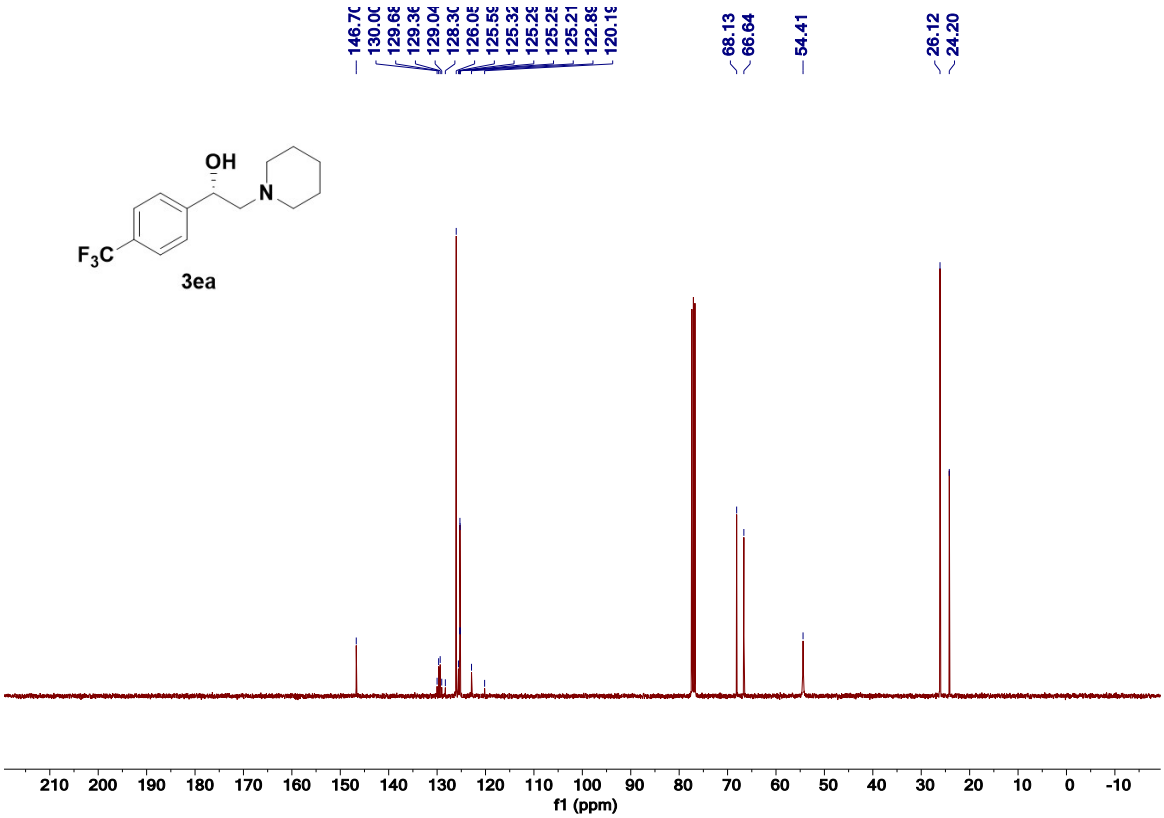

7.31
7.30
7.29
7.28
7.28
7.27
6.89
6.89
6.88
6.87
6.87
6.86
4.68
4.67
4.66
4.65
3.79
2.69
2.46
2.45
2.43
2.42
2.41
2.38
2.35
1.64
1.63
1.62
1.62
1.61
1.61
1.60
1.59
1.59
1.58
1.48
1.46
OH
N
O
3ca
1.99
2.02
1.00
3.03
1.99
4.07
4.20
2.04
f1 (ppm)

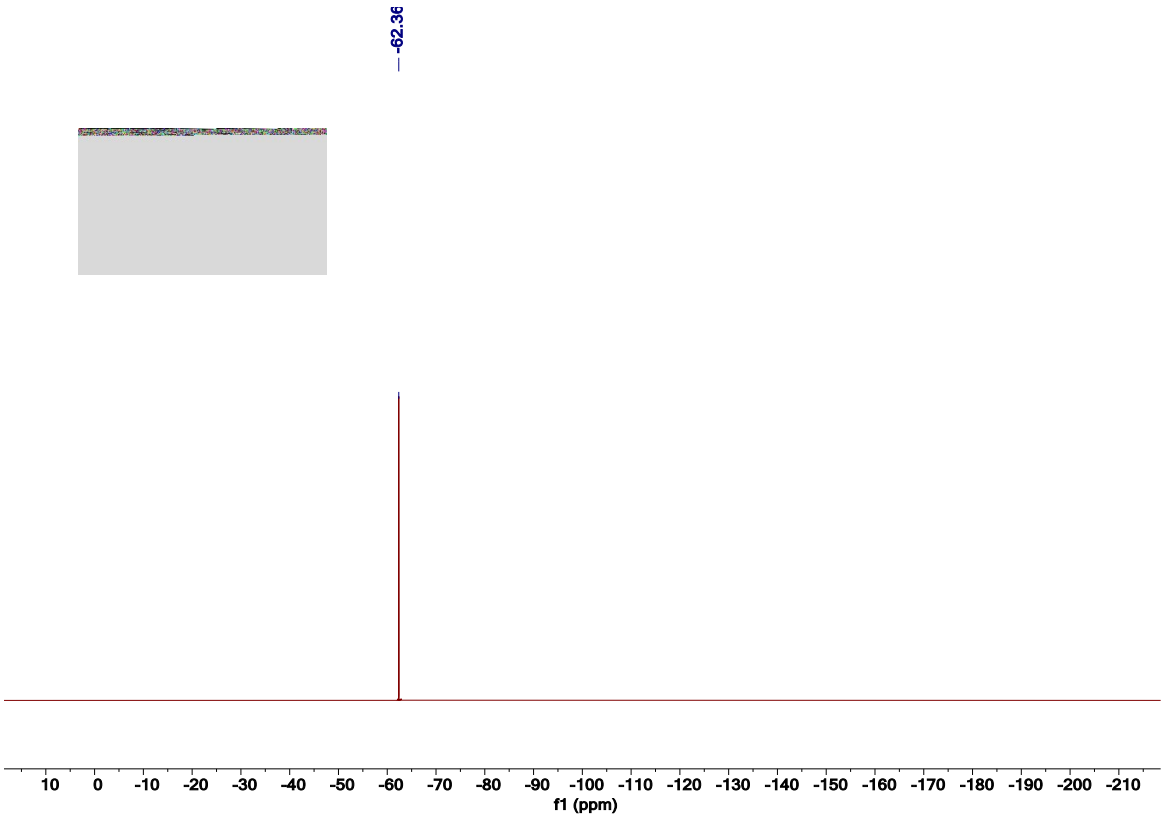

158.97
134.47
127.12
113.73
68.27
66.97
55.27
54.46
26.14
24.29
OH
N
O
3ca
f1 (ppm)

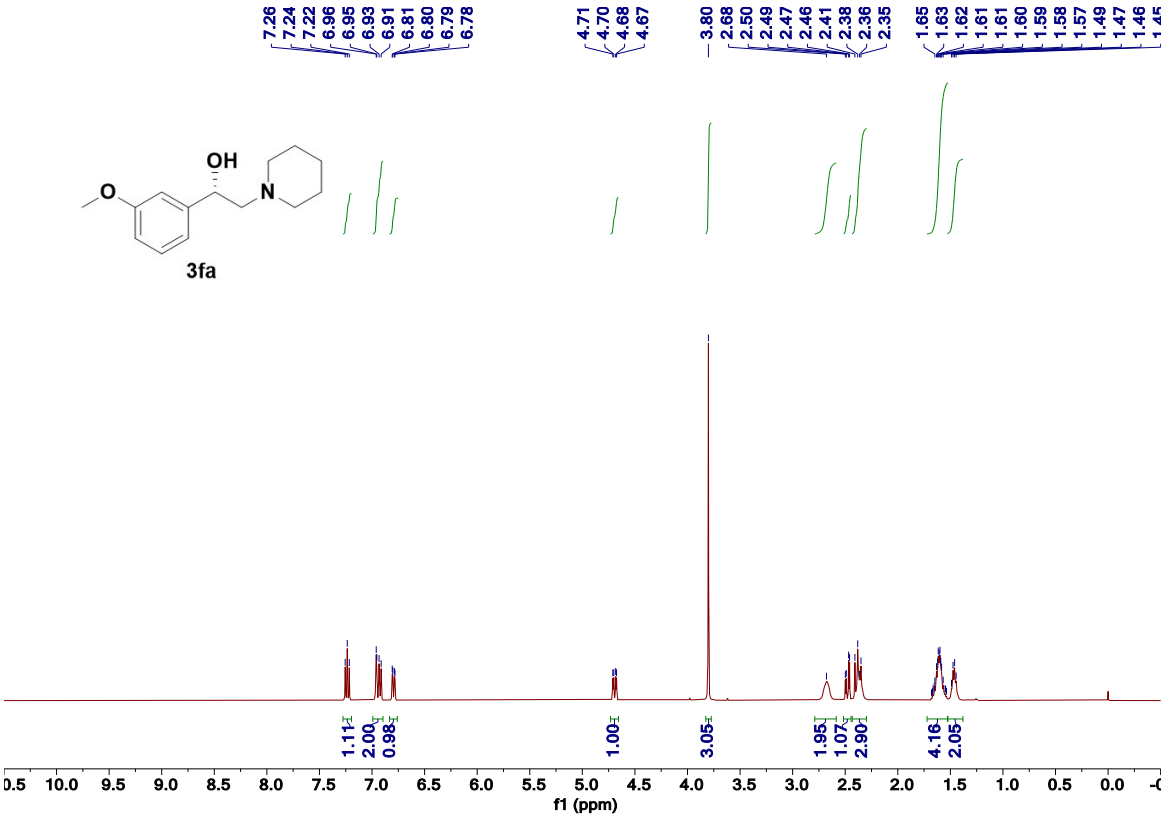

7.30
4.70
4.69
4.67
4.66
2.68
2.48
2.47
2.45
2.44
2.37
2.35
2.32
2.32
2.29
1.65
1.64
1.64
1.63
1.62
1.61
1.61
1.60
1.59
1.58
1.48
1.47
OH
N
Cl
3da
3.92
1.00
1.99
1.10
2.93
4.12
1.96
f1 (ppm)

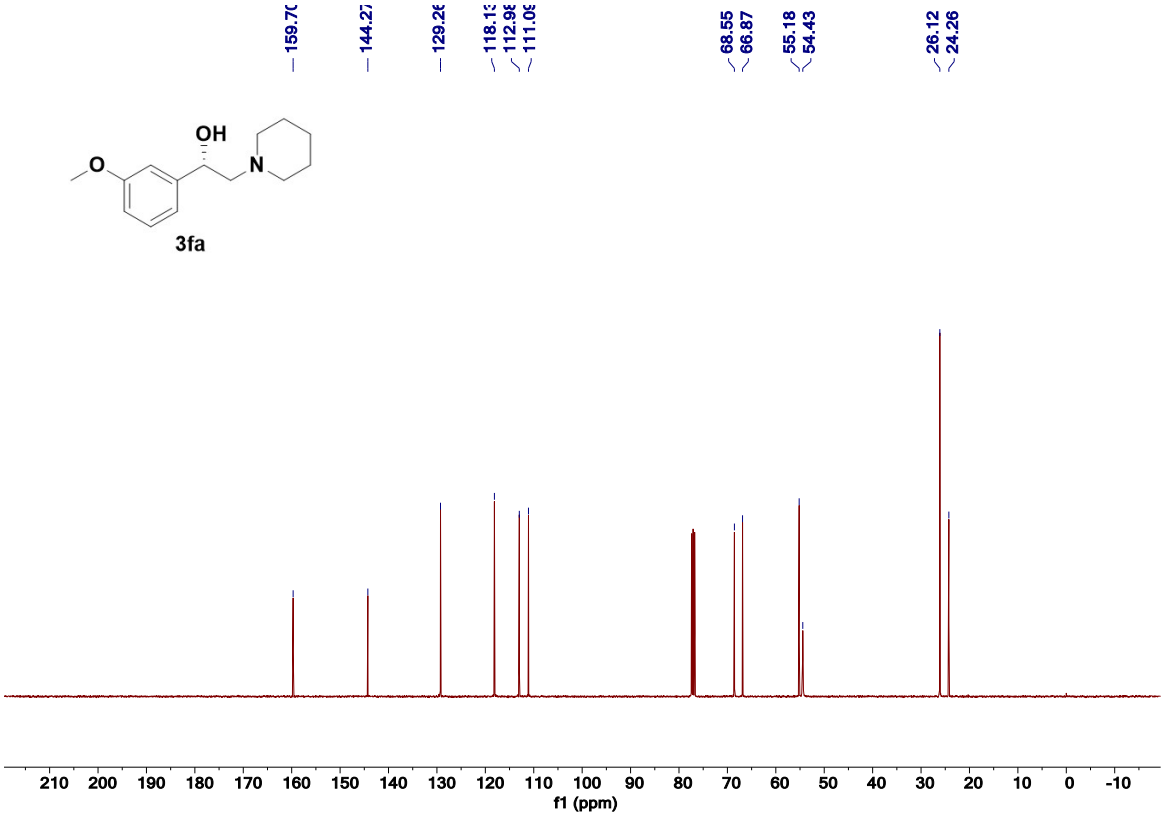

141.03
132.98
128.44
127.20
68.04
66.76
54.43
26.11
24.22
OH
N
Cl
3da
f1 (ppm)

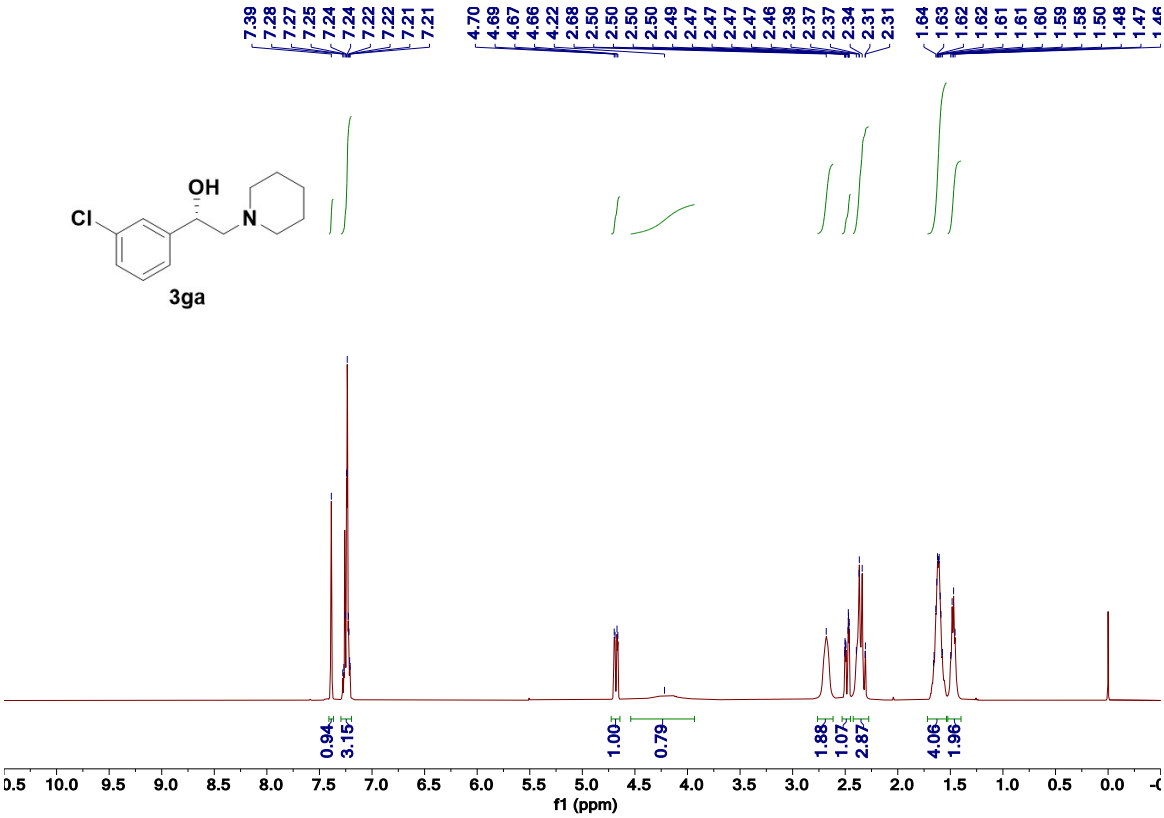

7.60
7.58
7.50
7.48
7.26 CDCl
4.78
4.77
4.75
4.75
4.35
2.69
2.53
2.52
2.50
2.49
2.38
2.36
2.33
2.30
1.66
1.65
1.65
1.64
1.63
1.62
1.61
1.61
1.60
1.58
1.49
1.47
OH
N
F3C
3ea
1.97
1.96
1.00
0.85
1.95
1.07
2.89
4.07
1.97
f1 (ppm)

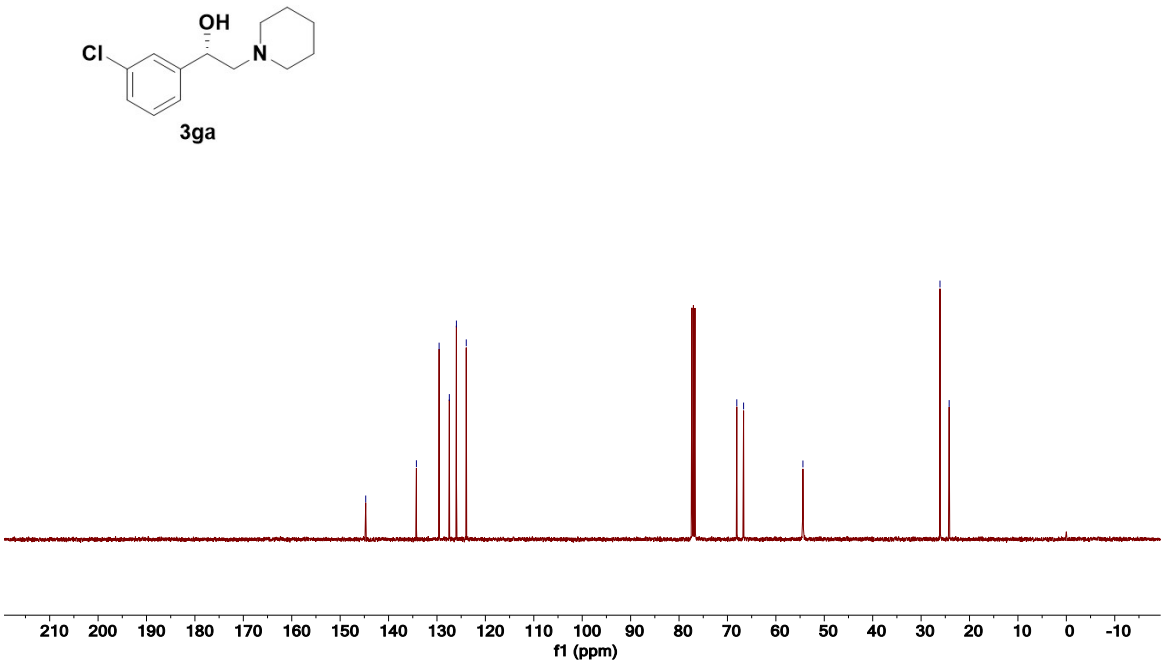

146.7
130.0
129.6
129.3
129.0
128.3
126.0
125.5
125.3
125.2
125.2
125.2
122.8
120.1
68.13
66.64
54.41
26.12
24.20
OH
N
F3C
3ea
f1 (ppm)

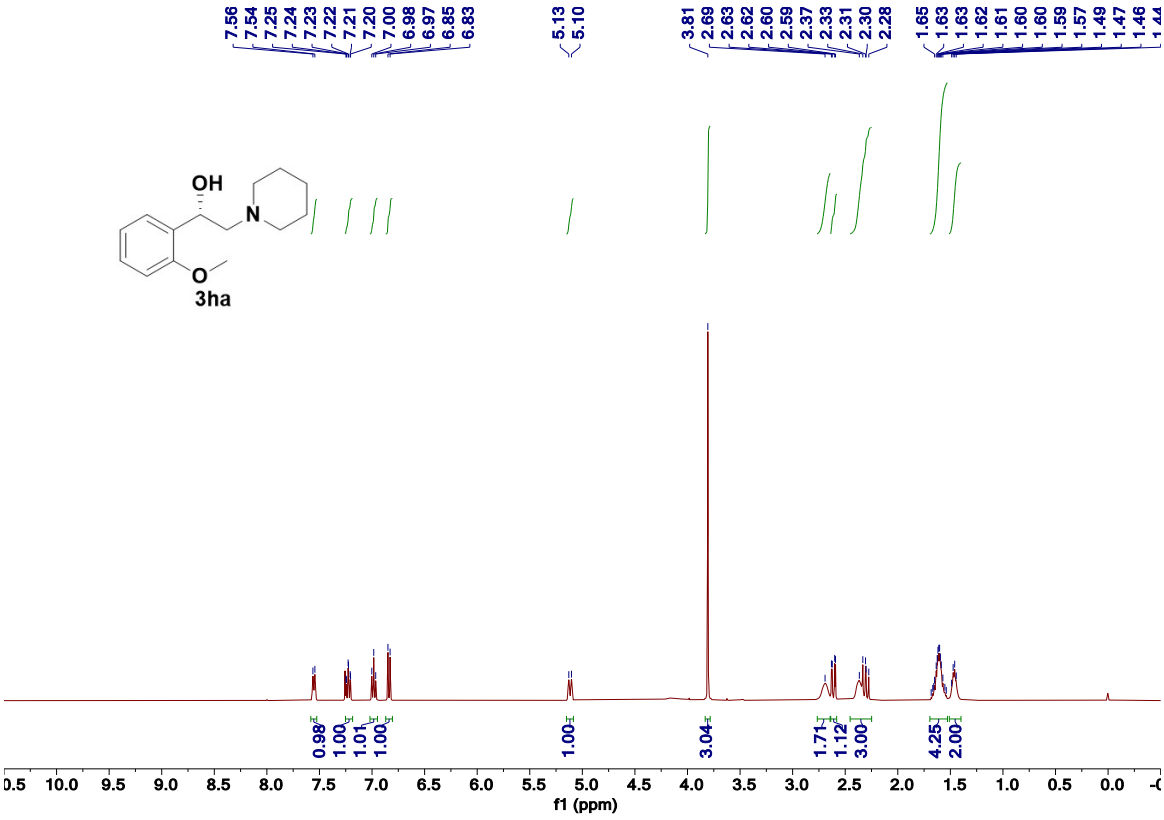

-62.36
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

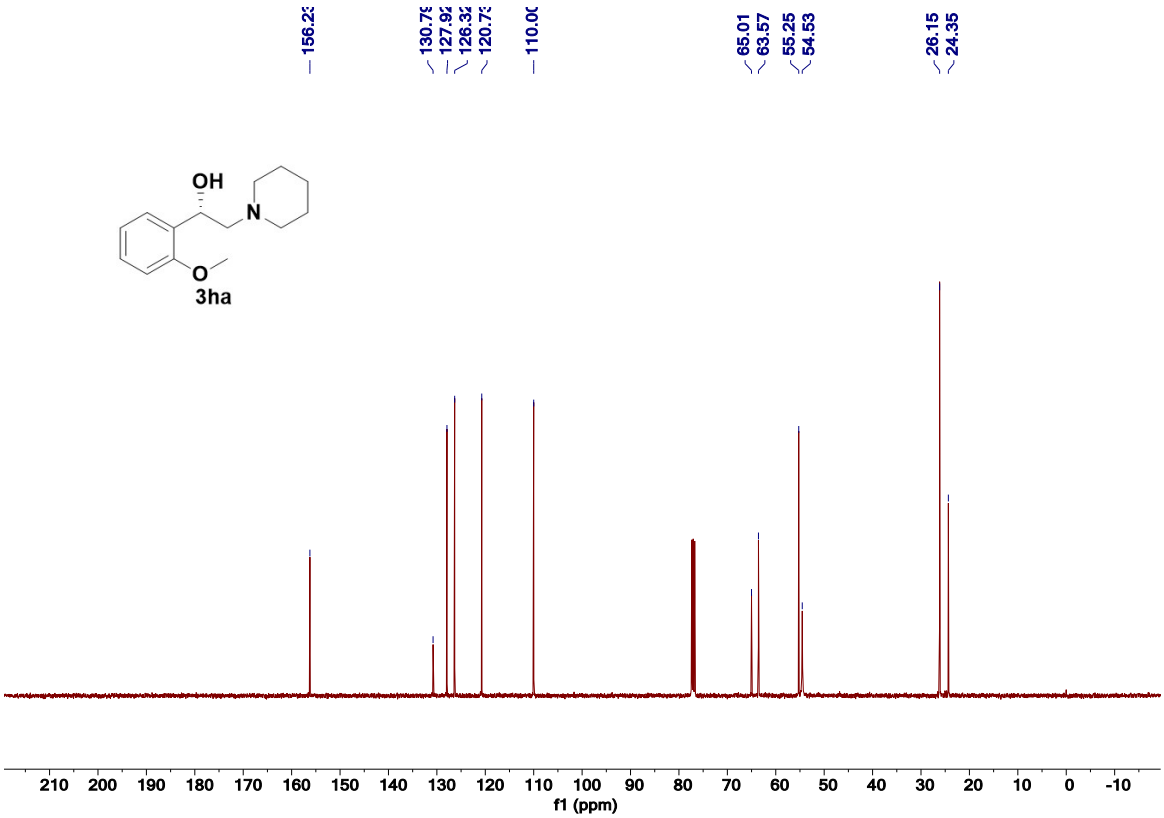

7.26
7.24
7.22
6.96
6.95
6.93
6.91
6.81
6.80
6.79
6.78
4.71
4.70
4.68
4.67
3.80
2.68
2.50
2.49
2.47
2.46
2.41
2.38
2.36
2.35
1.65
1.63
1.62
1.61
1.61
1.60
1.59
1.58
1.57
1.49
1.47
1.46
OH
O
N
3fa
1.11
2.00
0.98
1.00
3.05
1.95
1.07
2.90
4.16
2.05
f1 (ppm)

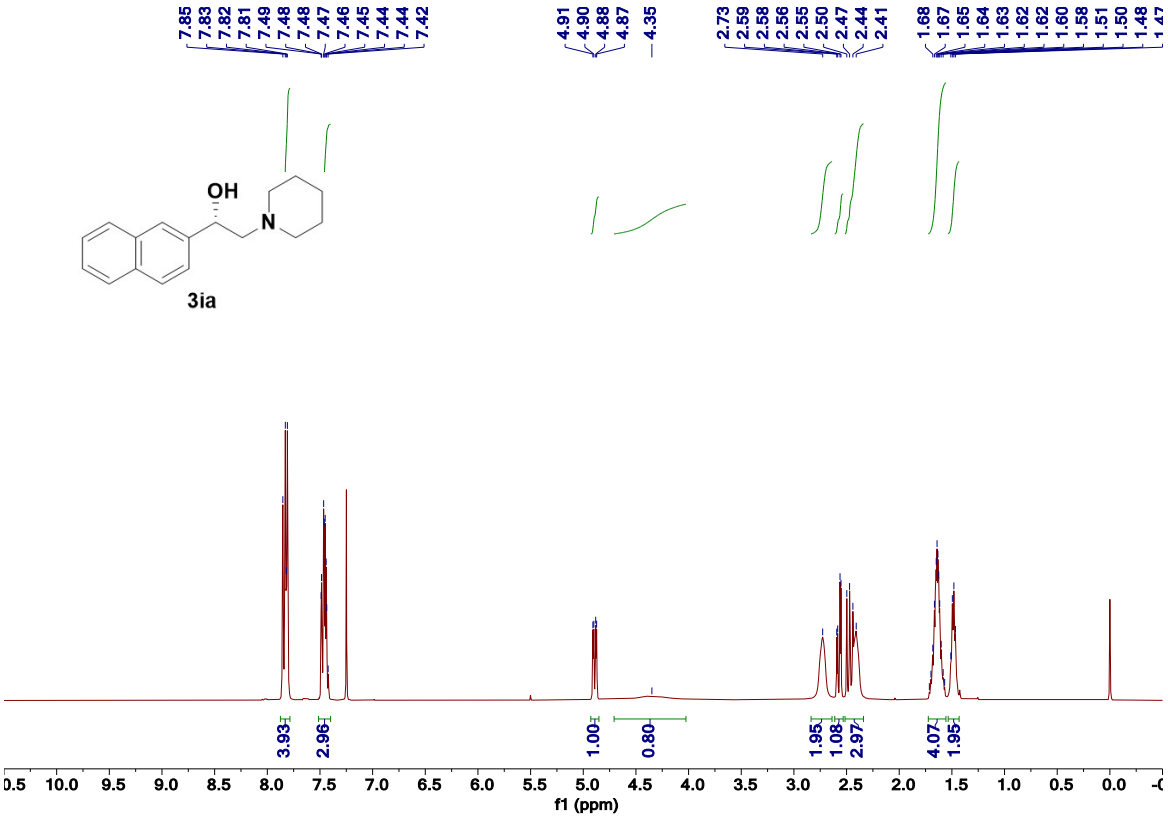

159.7
144.2
129.2
118.1
112.9
111.0
68.55
66.87
55.18
54.43
26.12
24.26
OH
O
N
3fa
f1 (ppm)

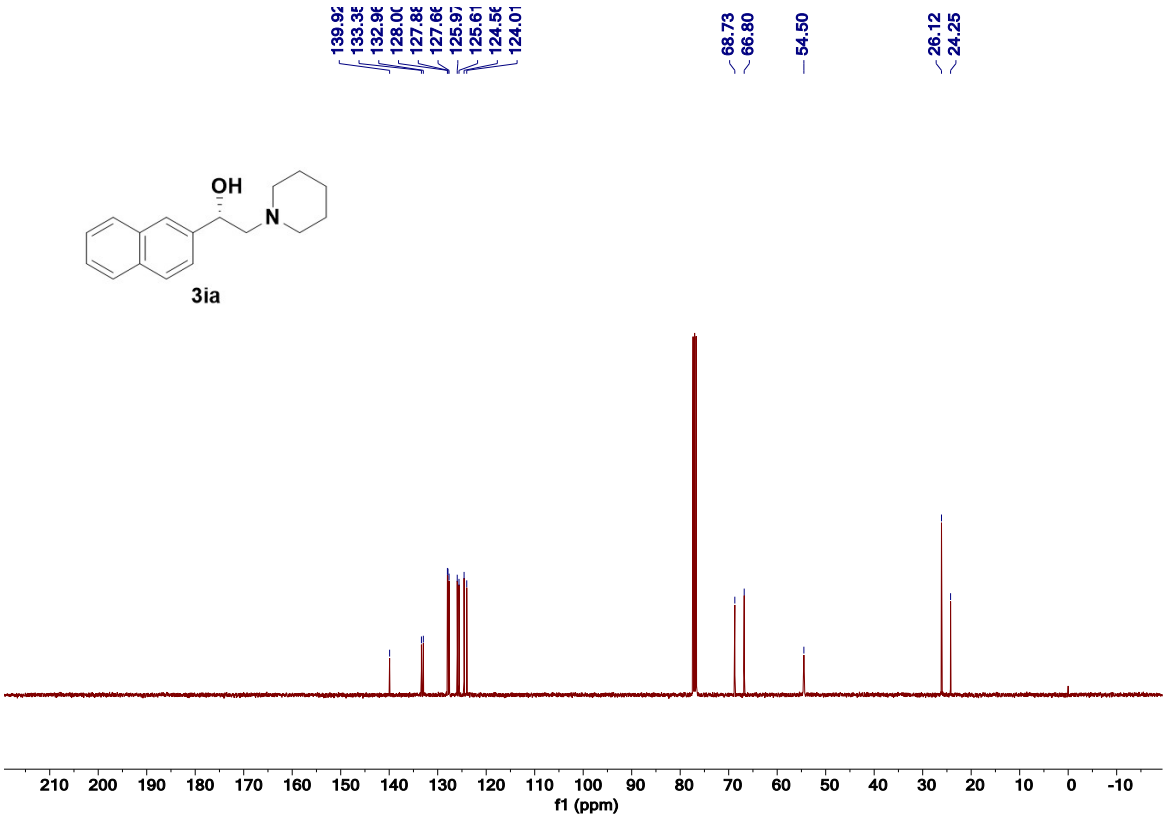

OH
Cl
N
3ga
f1 (ppm)

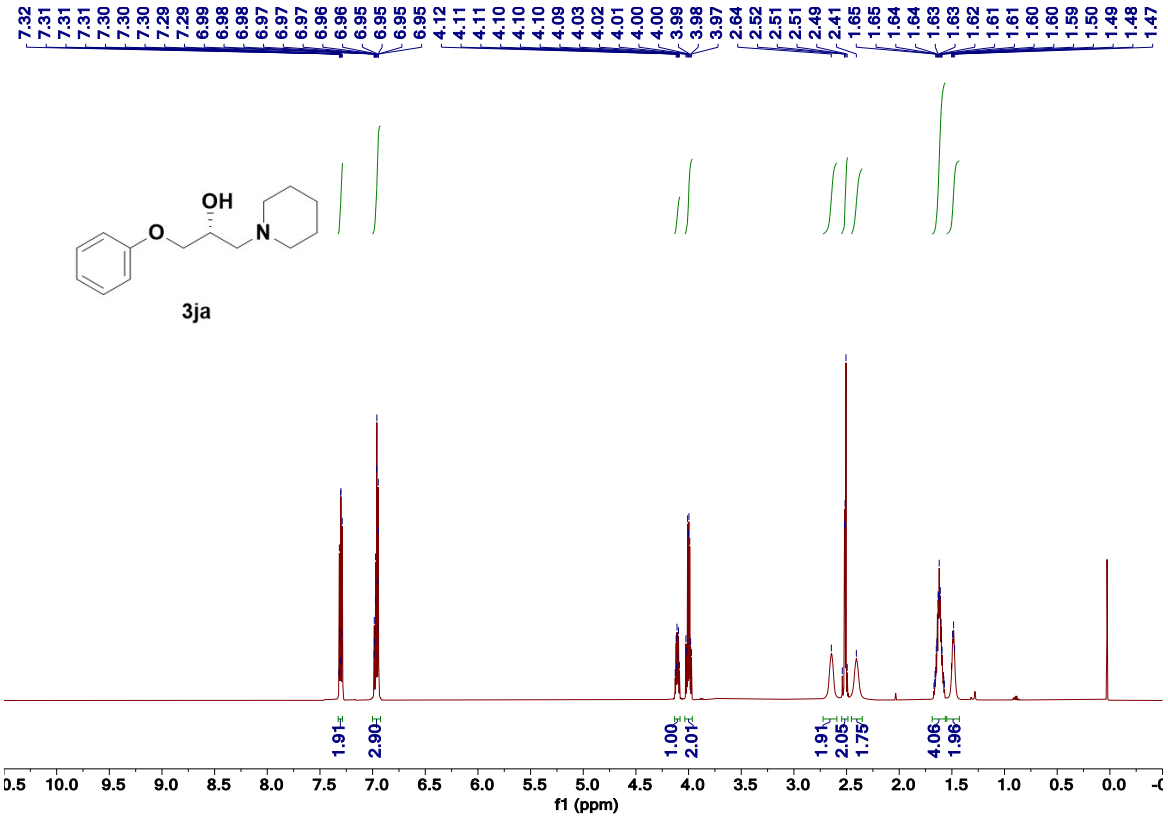

OH
Cl
N
3ga
f1 (ppm)

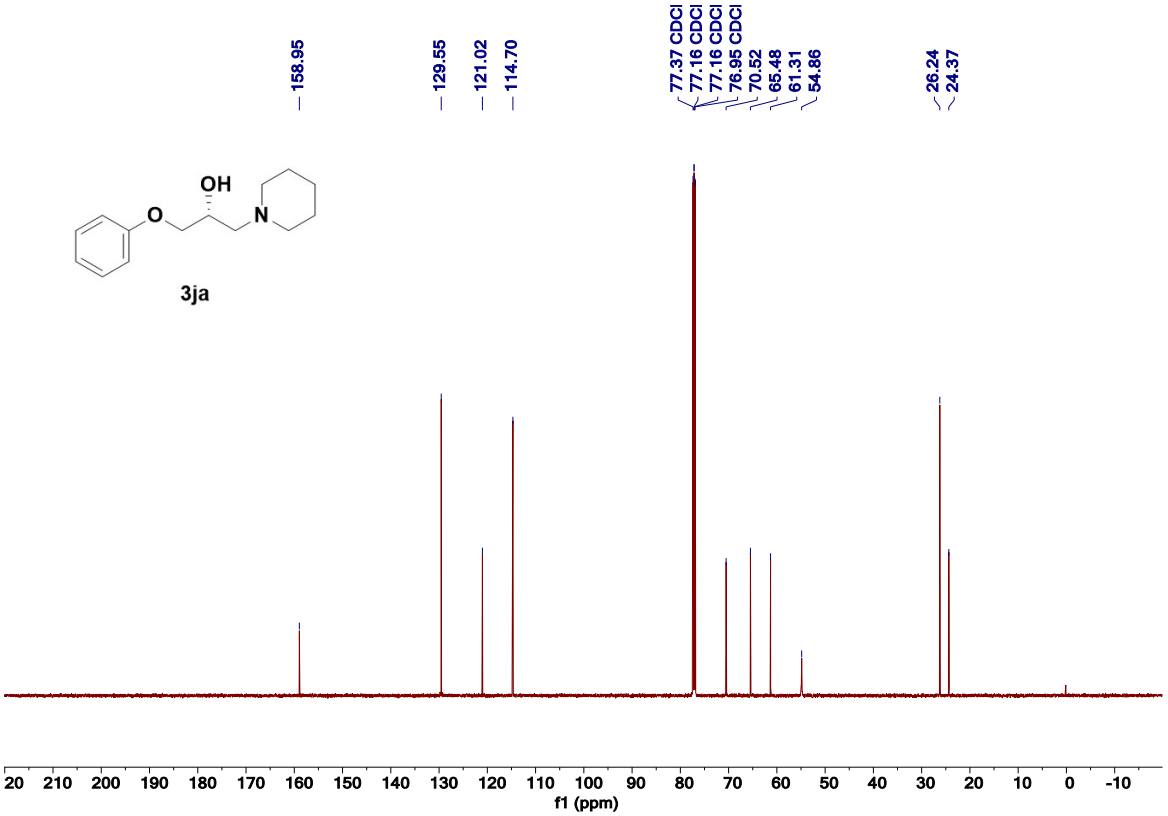

7.56
7.54
7.25
7.24
7.23
7.22
7.21
7.20
7.00
6.98
6.97
6.85
6.83
5.13
5.10
3.81
2.69
2.63
2.62
2.60
2.59
2.37
2.33
2.31
2.30
2.28
1.65
1.63
1.63
1.62
1.61
1.60
1.60
1.59
1.57
1.49
1.47
1.46
OH
N
O
3ha
0.98
1.00
1.01
1.00
1.00
3.04
1.71
1.12
3.00
4.25
2.00
f1 (ppm)

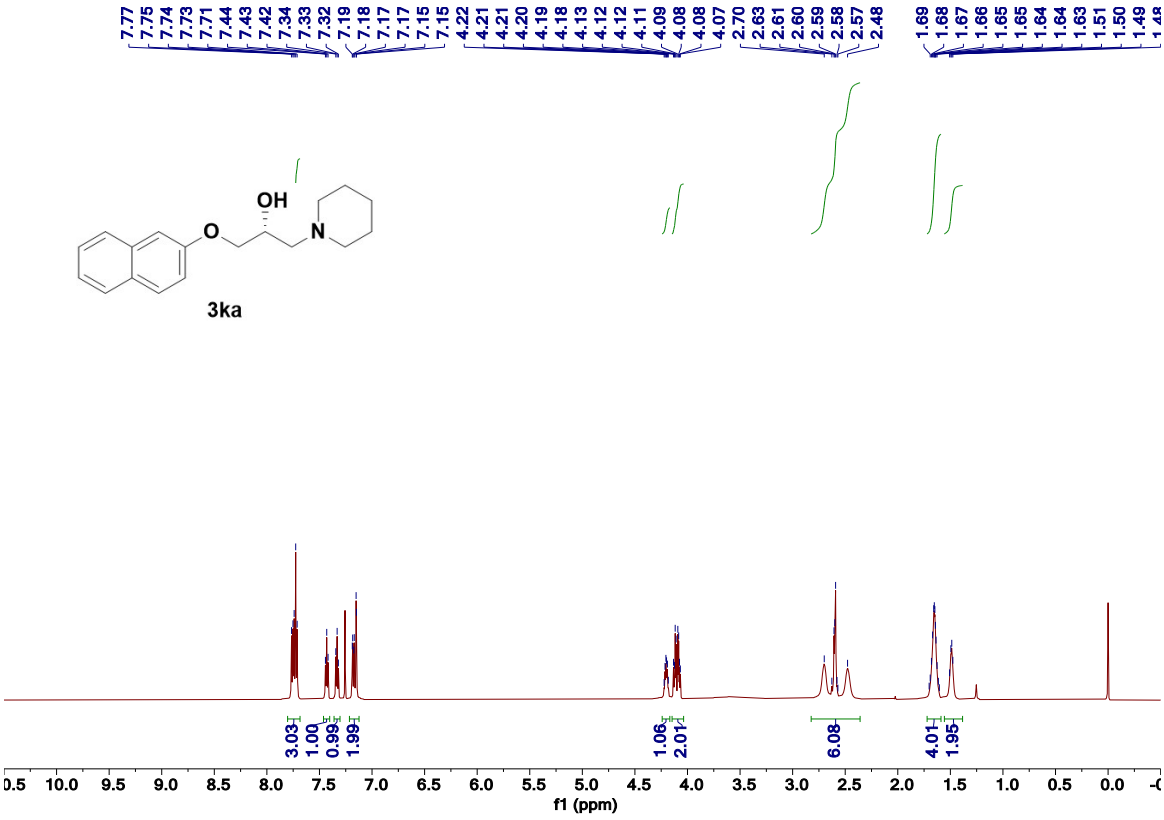

156.23
130.78
127.92
126.32
120.72
110.00
65.01
63.57
55.25
54.53
26.15
24.35
OH
N
O
3ha
f1 (ppm)

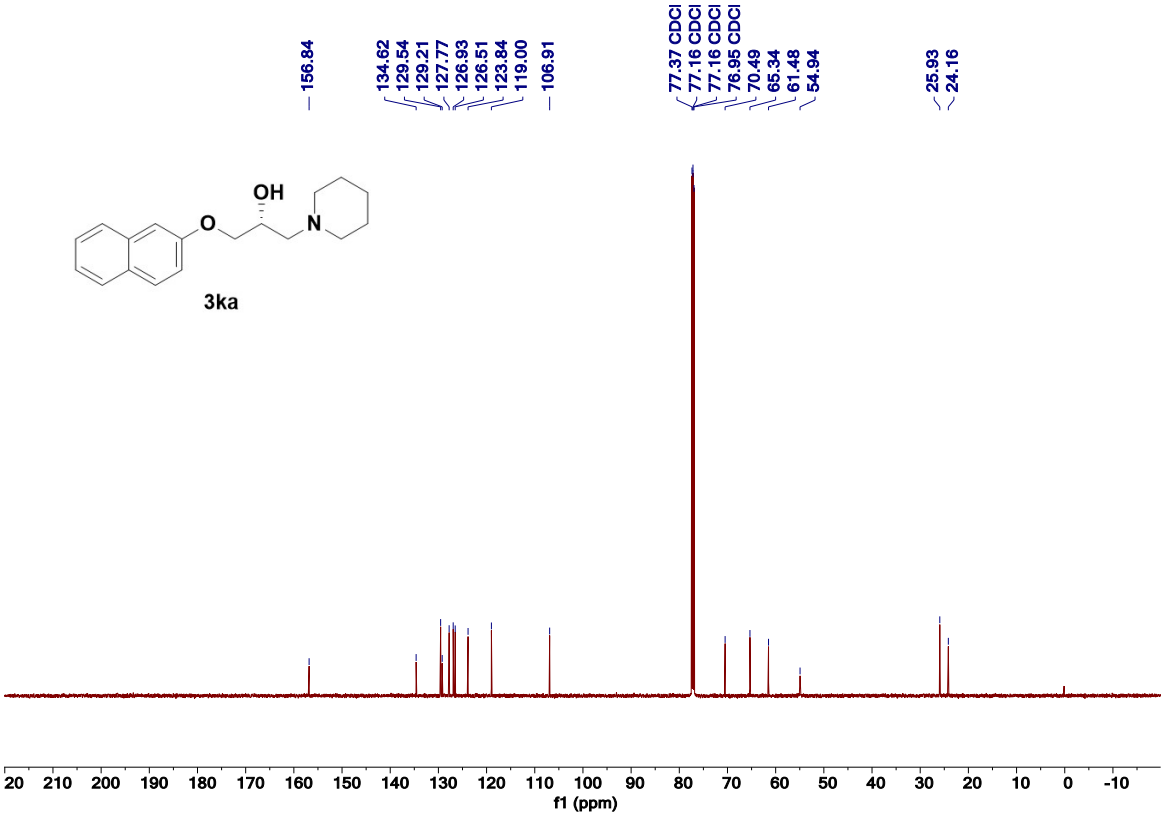

7.85
7.83
7.82
7.81
7.49
7.48
7.48
7.47
7.46
7.45
7.44
7.44
7.42
4.91
4.90
4.88
4.87
4.35
2.73
2.59
2.58
2.56
2.55
2.50
2.47
2.44
2.41
1.68
1.67
1.65
1.64
1.63
1.62
1.62
1.60
1.58
1.51
1.50
1.48
OH
N
3ia
3.93
2.96
1.00
0.80
1.95
1.08
2.97
4.07
1.95
f1 (ppm)

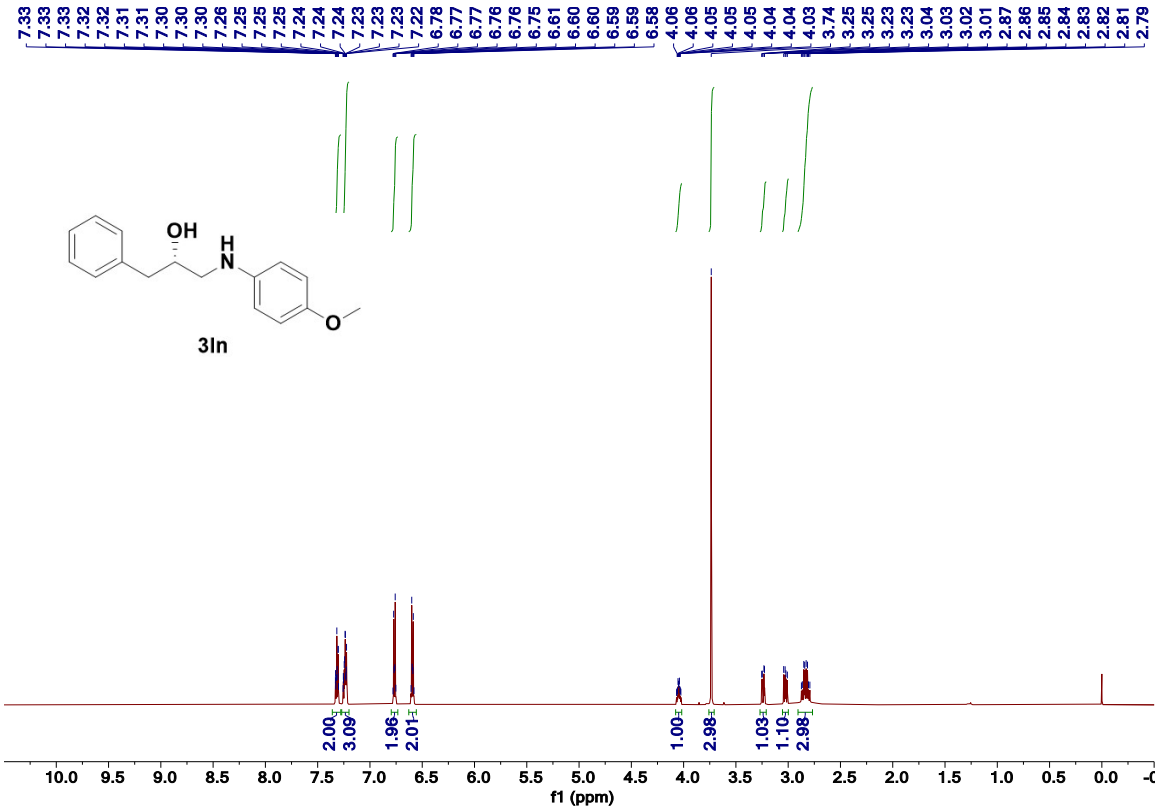

139.92
133.38
132.96
128.0
127.88
127.68
125.97
125.61
124.56
124.01
68.73
66.80
54.50
26.12
24.25
OH
N
3ia
f1 (ppm)

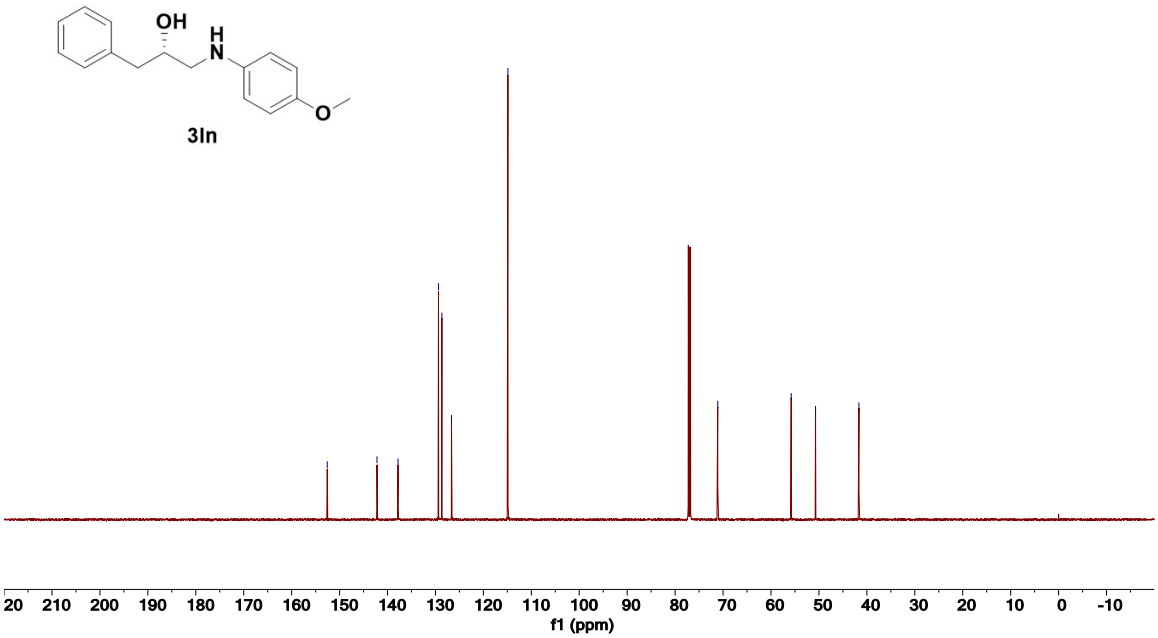

7.32 7.31 7.31 7.31 7.30 7.30 7.30 7.29 7.29 6.99 6.98 6.98 6.97 6.97 6.97 6.96 6.96 6.96 6.95 6.95 6.95 6.95
4.12 4.11 4.11 4.10 4.10 4.10 4.09 4.03 4.02 4.01 4.00 4.00 4.00 3.99 3.98 3.97
2.64 2.52 2.51 2.51 2.49 2.41 1.65 1.65 1.64 1.64 1.63 1.63 1.62 1.61 1.61 1.60 1.60 1.59 1.50 1.49 1.48 1.47
OH
O
N
3ja
1.91 2.90 1.00 2.01 1.91 2.05 1.75 4.06 1.96
f1 (ppm)

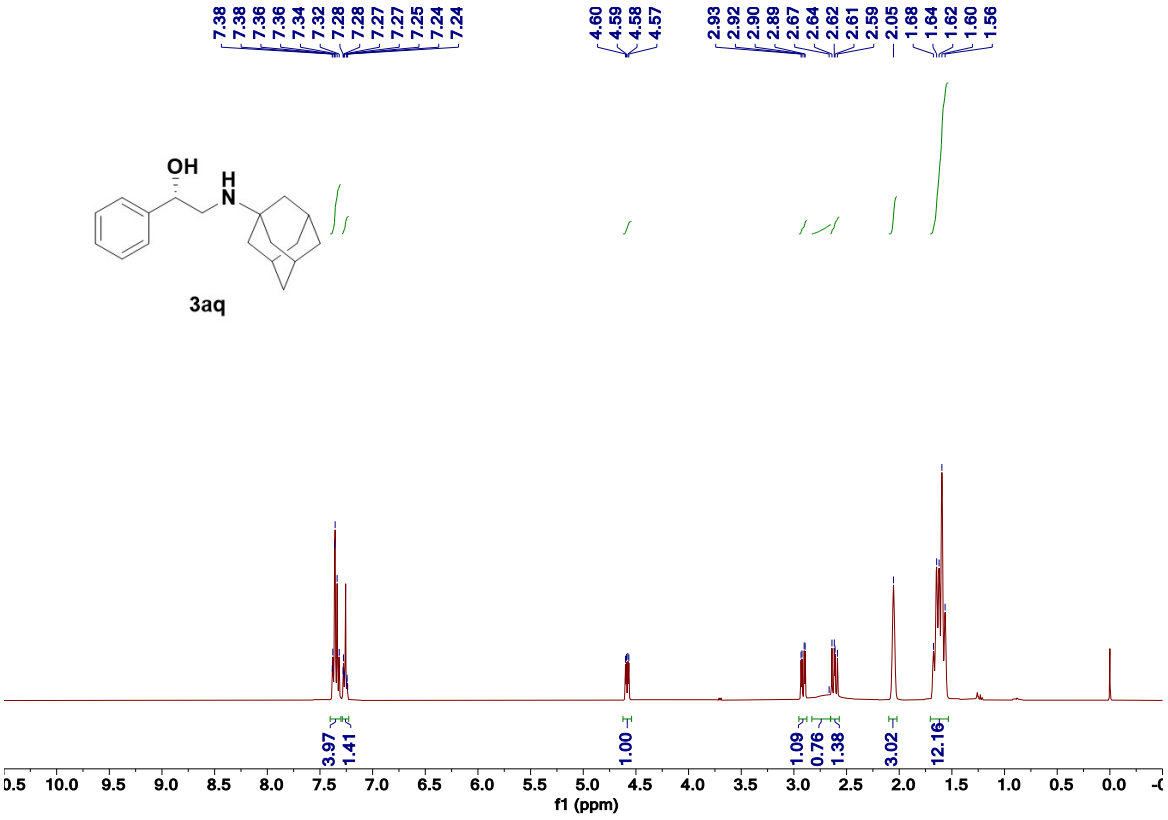

158.95
129.55
121.02
114.70
77.37 CDCl
77.16 CDCl
77.16 CDCl
76.95 CDCl
70.52
65.48
61.31
54.86
26.24
24.37
OH
O
N
3ja
f1 (ppm)

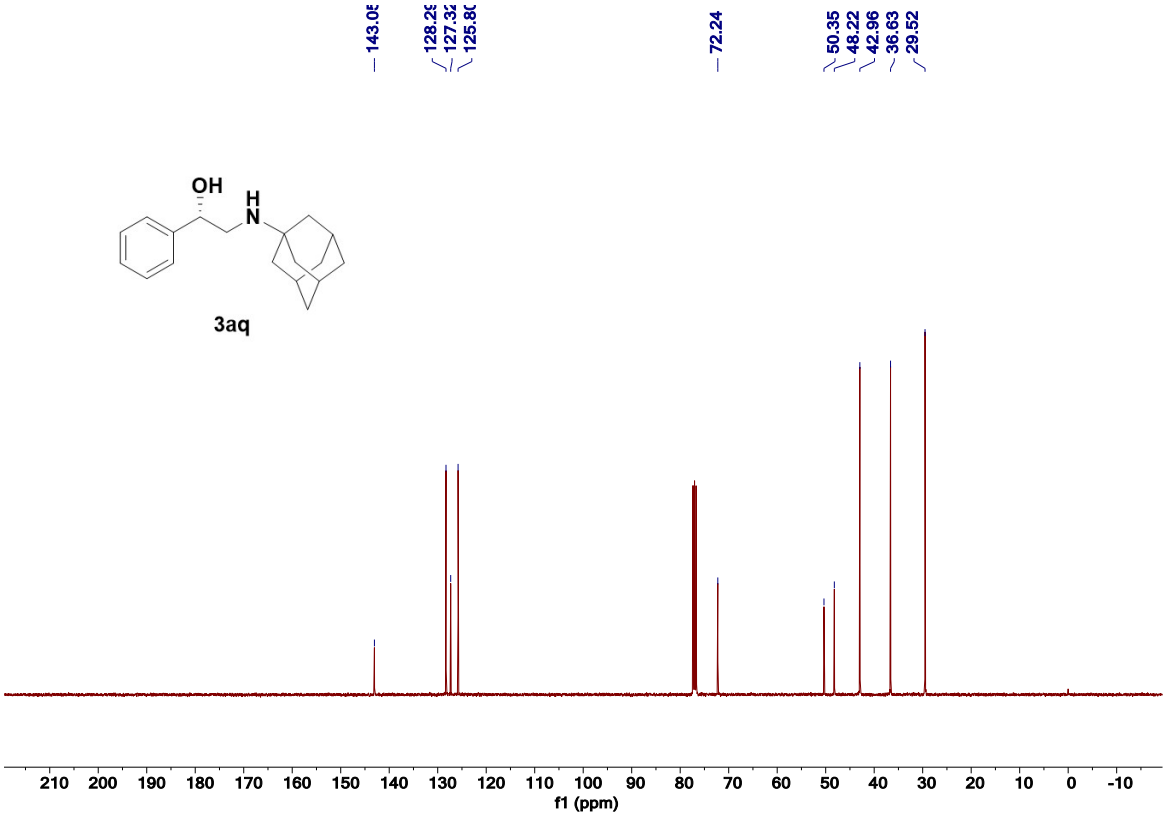

7.77
7.75
7.74
7.73
7.71
7.44
7.43
7.42
7.34
7.33
7.32
7.19
7.18
7.17
7.17
7.15
7.15
4.22
4.21
4.21
4.20
4.19
4.18
4.13
4.12
4.12
4.11
4.09
4.08
4.08
4.07
2.70
2.63
2.61
2.60
2.59
2.58
2.57
2.48
1.69
1.68
1.67
1.66
1.65
1.65
1.64
1.64
1.63
1.51
1.50
1.49
OH
O
N
3ka
3.03
1.00
0.99
1.99
1.06
2.01
6.08
4.01
1.95
f1 (ppm)

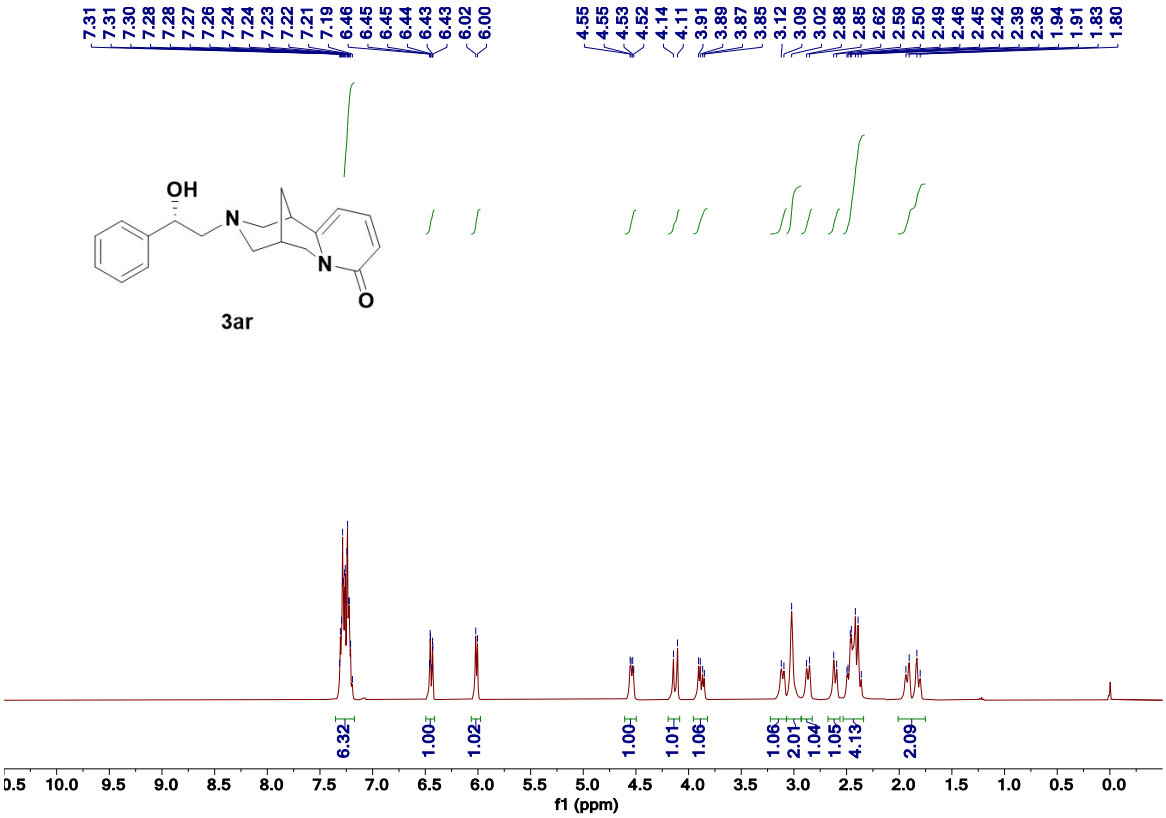

156.84
134.62
129.54
129.21
127.77
126.93
126.51
123.84
119.00
106.91
77.37 CDCl
77.16 CDCl
77.16 CDCl
76.95 CDCl
70.49
65.34
61.48
54.94
25.93
24.16
OH
O
N
3ka
f1 (ppm)

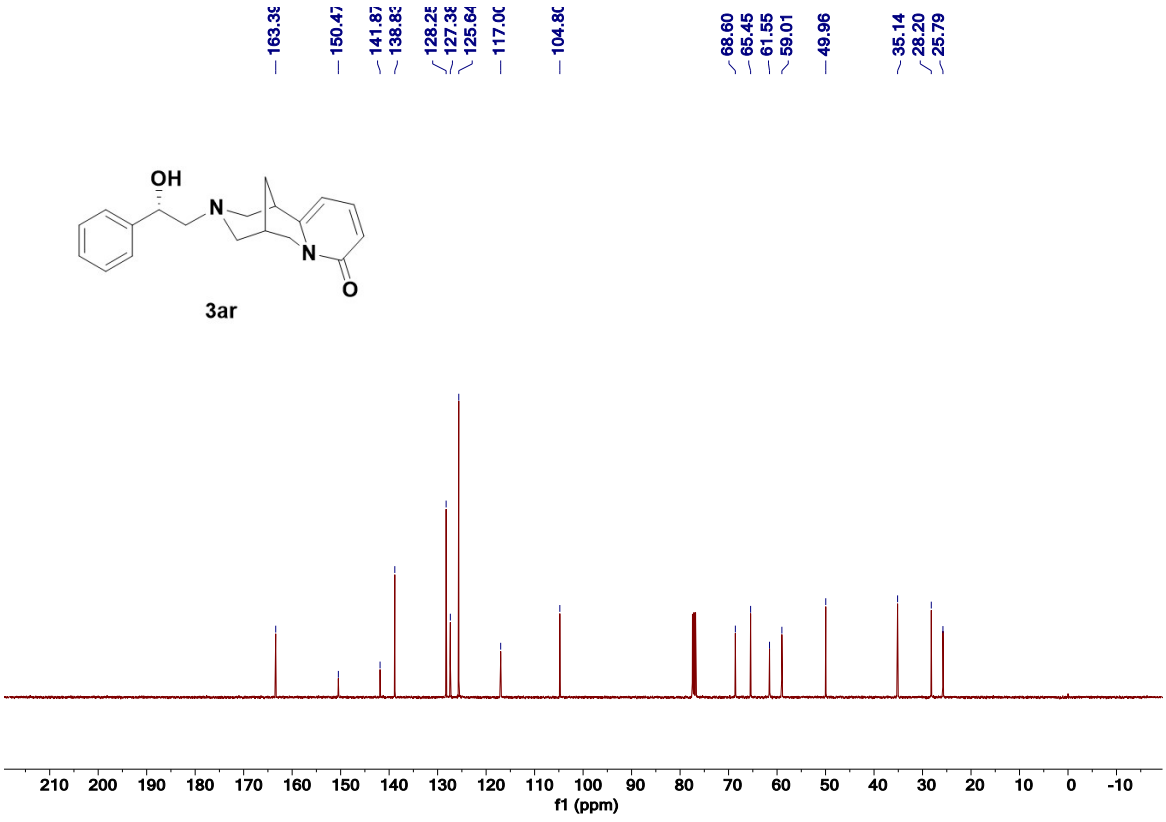

OH
H
N
O
3ln
f1 (ppm)

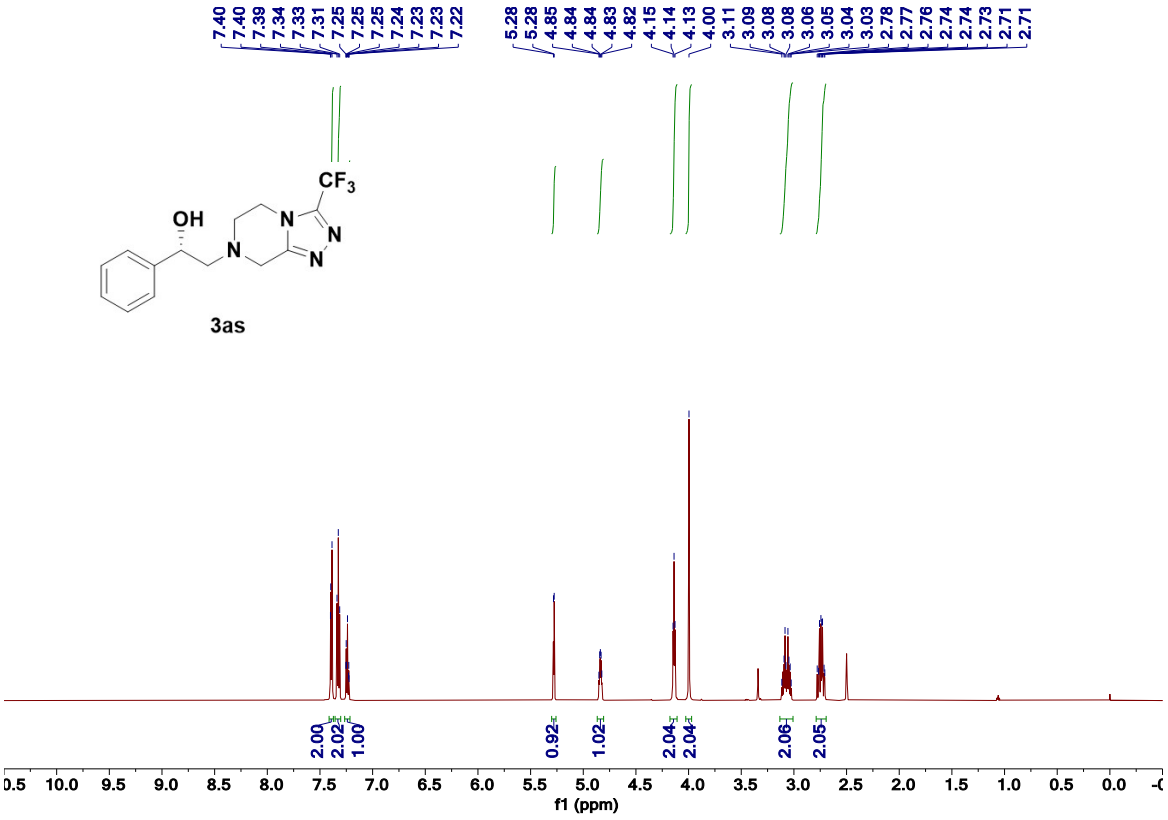

OH
H
N
O
3ln
f1 (ppm)

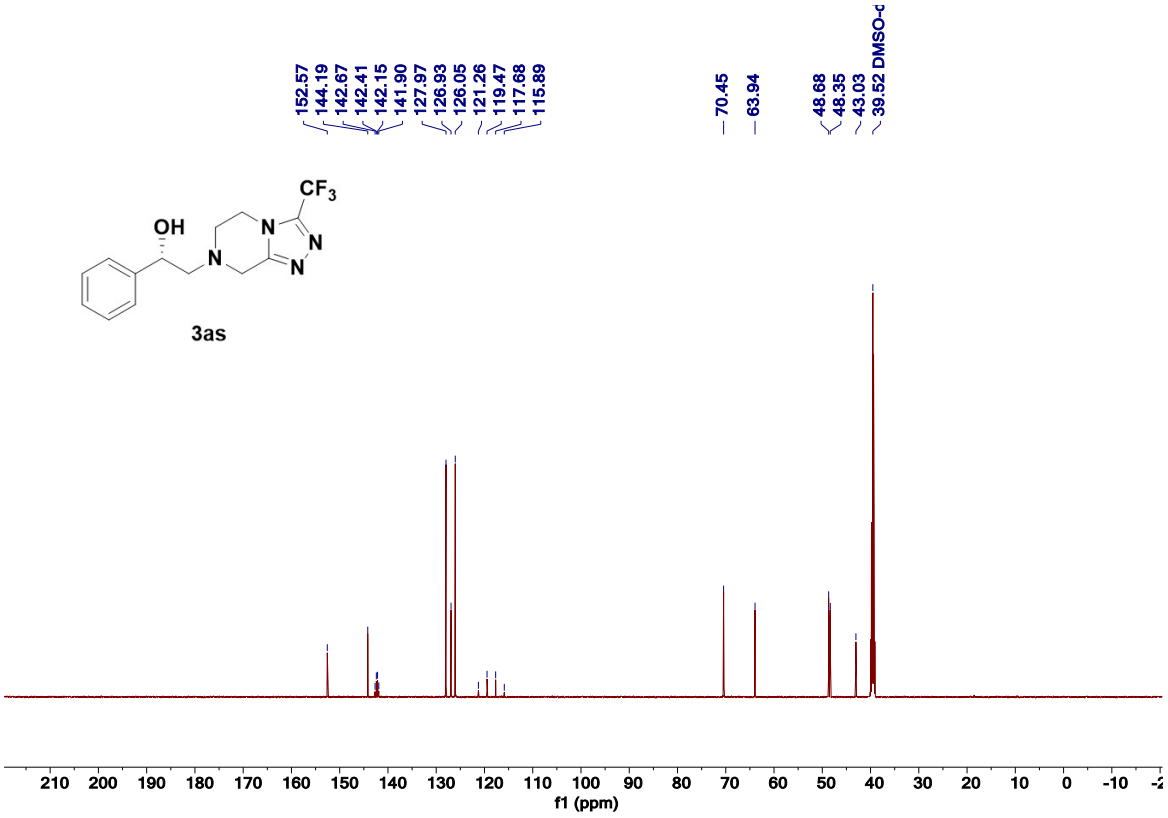

7.38
7.38
7.36
7.36
7.34
7.32
7.28
7.28
7.27
7.27
7.25
7.24
7.24
4.60
4.59
4.58
4.57
2.93
2.92
2.90
2.89
2.67
2.64
2.62
2.61
2.59
2.05
1.68
1.64
1.62
1.60
1.56
OH
H
N
3aq
3.97
1.41
1.00
1.09
0.76
1.38
3.02
12.16
f1 (ppm)

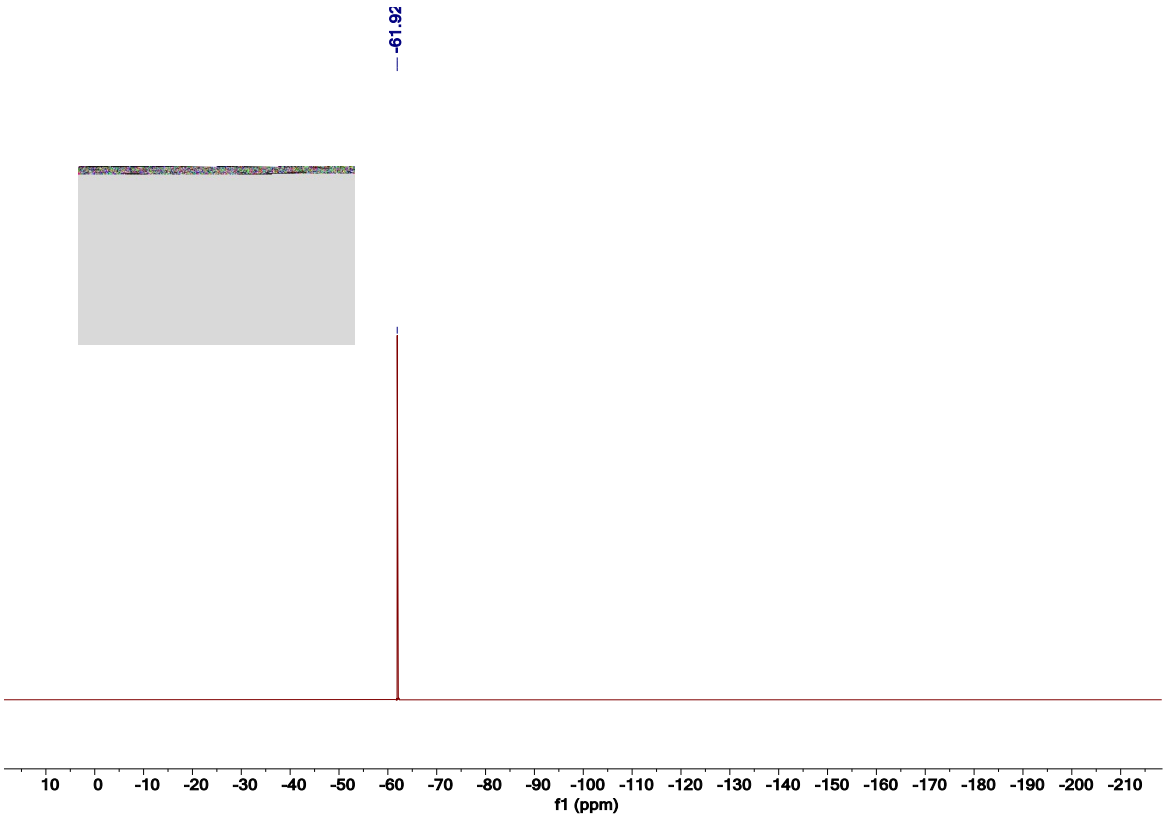

143.0
128.2
127.3
125.8
72.24
50.35
48.22
42.96
36.63
29.52
OH
H
N
3aq
f1 (ppm)

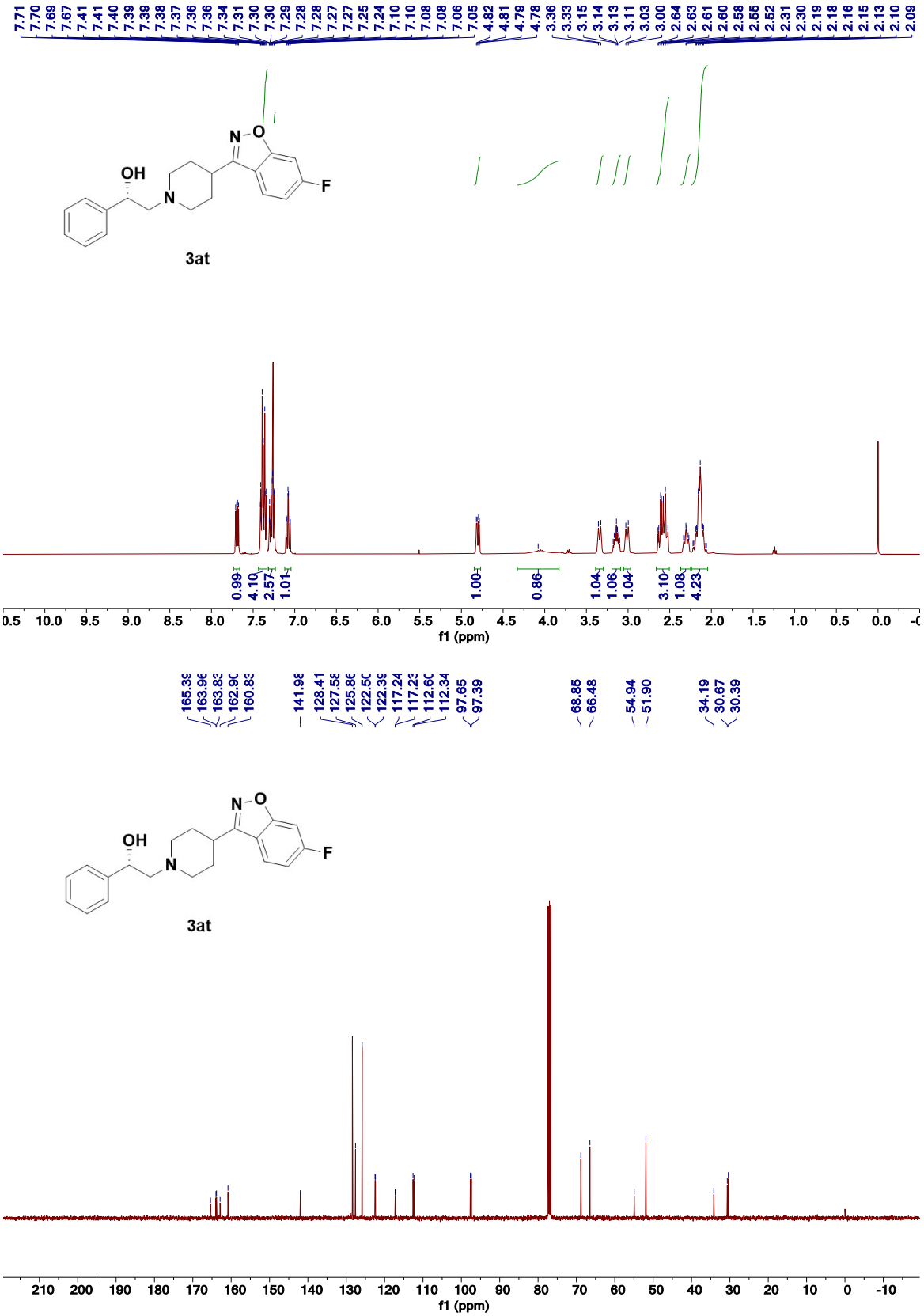

7.31 7.31 7.30 7.28 7.28 7.27 7.26 7.24 7.24 7.23 7.22 7.21 7.19 6.46 6.45 6.45 6.44 6.43 6.43 6.02 6.00
4.55 4.55 4.53 4.52 4.14 4.11 3.91 3.89 3.87 3.85 3.12 3.09 3.02 2.88 2.85 2.62 2.59 2.50 2.49 2.46 2.45 2.42 2.39 2.36 1.94 1.91 1.83 1.80
OH
N
N
O
3ar
6.32 1.00 1.02 1.00 1.01 1.06 1.06 2.01 1.04 1.05 4.13 2.09
f1 (ppm)

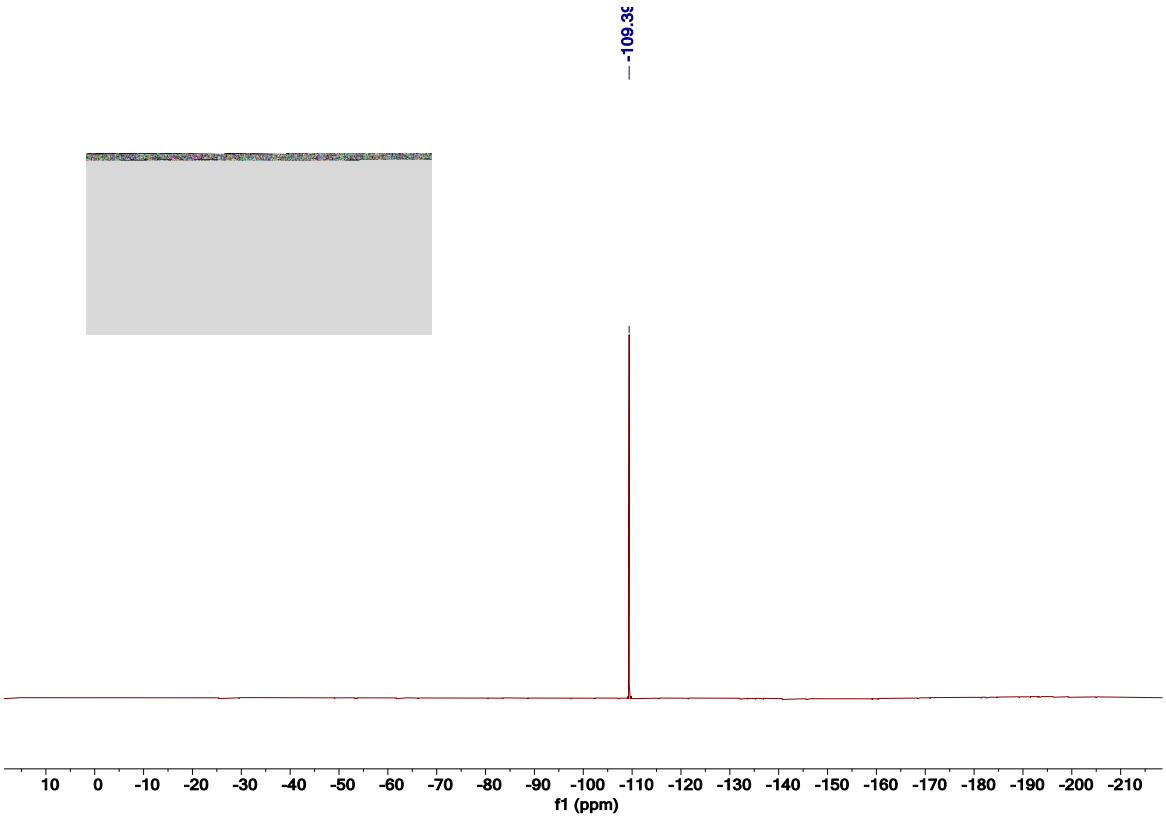

163.3 150.4 141.8 138.8 128.2 127.3 125.6 117.0 104.8 68.60 65.45 61.55 59.01 49.96 35.14 28.20 25.79
OH
N
N
O
3ar
f1 (ppm)

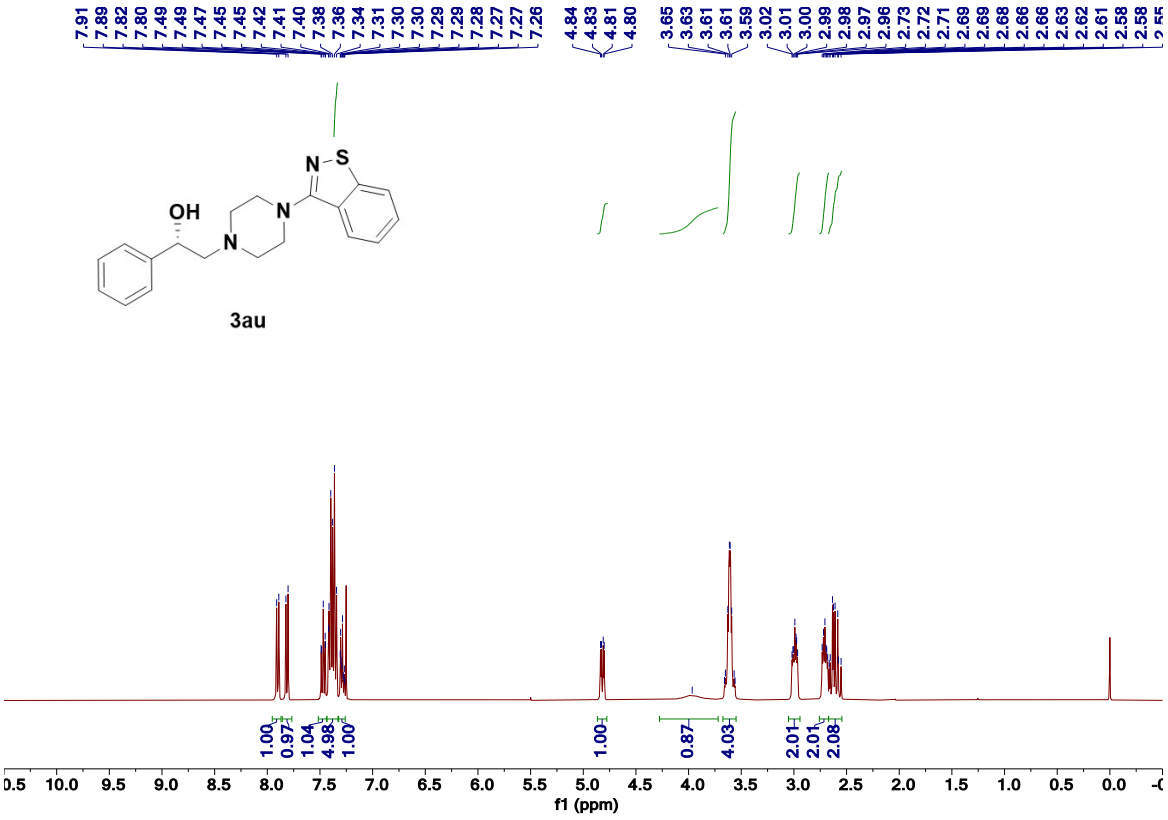

7.40
7.40
7.39
7.34
7.33
7.31
7.25
7.25
7.25
7.24
7.23
7.23
7.22
5.28
5.28
4.85
4.84
4.84
4.83
4.82
4.15
4.14
4.13
4.00
3.11
3.09
3.08
3.08
3.06
3.05
3.04
3.03
2.78
2.77
2.76
2.74
2.74
2.73
2.71
2.71
CF3
OH
N
N
N
N
3as
2.00
2.02
1.00
0.92
1.02
2.04
2.04
2.06
2.05
f1 (ppm)

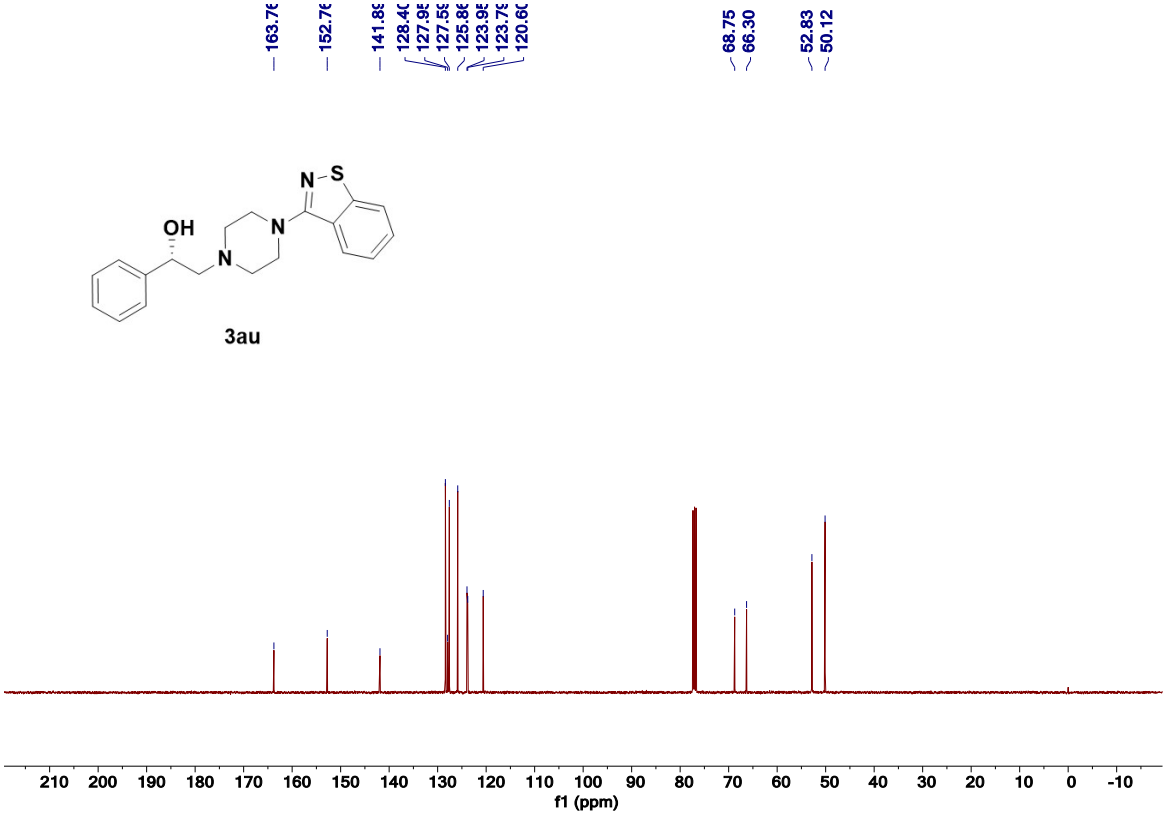

152.57
144.19
142.67
142.41
142.15
141.90
127.97
126.93
126.05
121.26
119.47
117.68
115.89
70.45
63.94
48.68
48.35
43.03
39.52 DMSO-d
CF3
OH
N
N
N
N
3as
f1 (ppm)

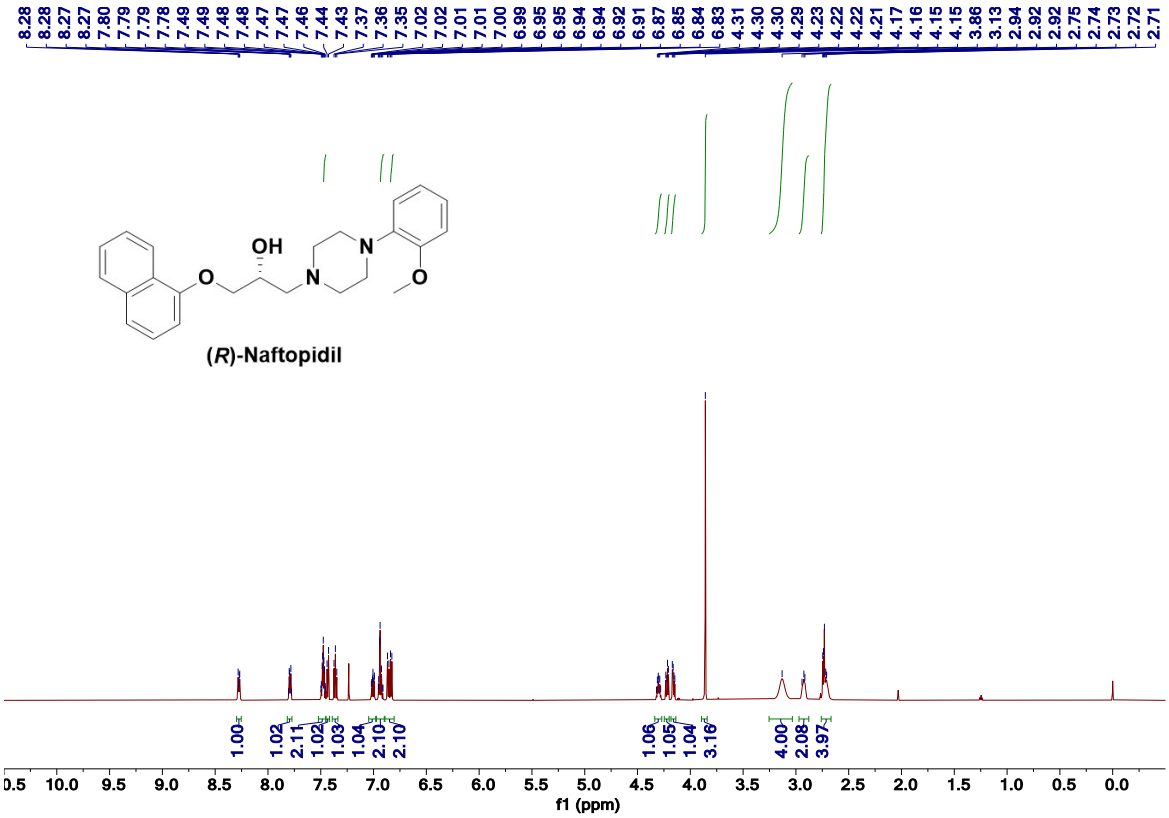

-61.92
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

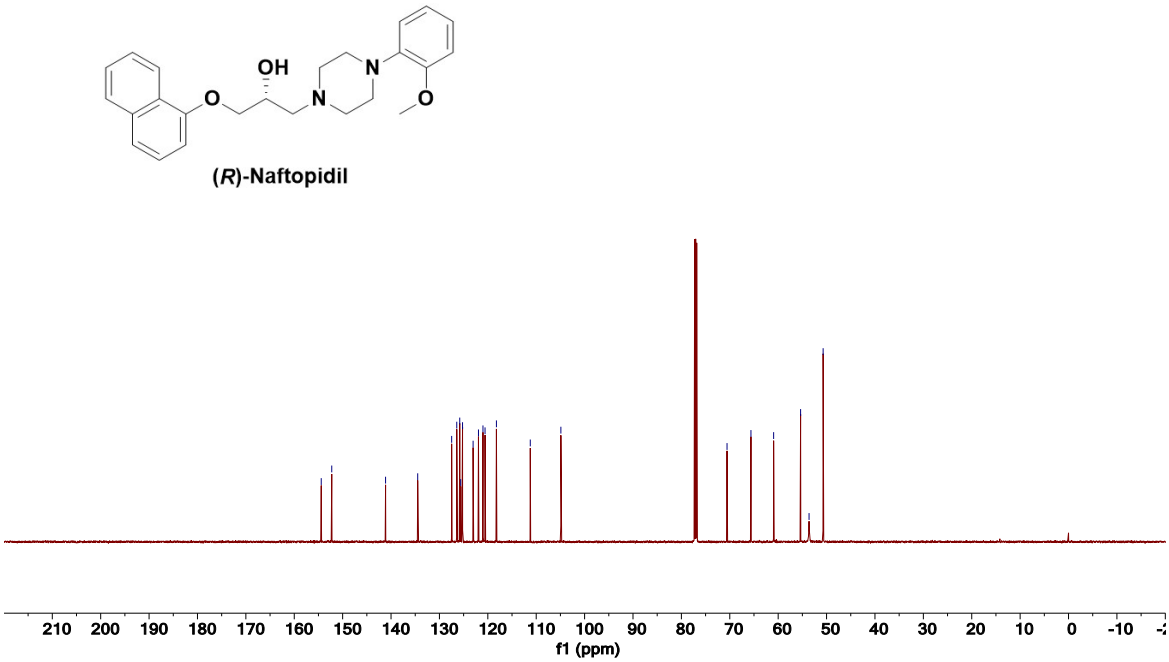

7.71 7.70 7.69 7.67 7.41 7.41 7.40 7.39 7.39 7.38 7.37 7.36 7.36 7.34 7.31 7.30 7.30 7.29 7.28 7.28 7.27 7.27 7.25 7.24 7.10 7.10 7.08 7.08 7.06 7.05 4.82 4.81 4.79 4.78 3.36 3.33 3.15 3.14 3.13 3.11 3.03 3.00 2.64 2.63 2.61 2.60 2.58 2.55 2.52 2.31 2.30 2.19 2.18 2.16 2.15 2.13 2.10 2.09
OH
N
O
N
F
3at
0.99 4.10 2.57 1.01 1.00 0.86 1.04 1.06 1.04 3.10 1.08 4.23
f1 (ppm)
165.3 163.9 163.8 162.9 160.8 141.9 128.41 127.5 125.8 122.5 122.3 117.24 117.22 112.6 112.34 97.65 97.39 68.85 66.48 54.94 51.90 34.19 30.67 30.39
OH
N
O
N
F
3at
f1 (ppm)


-109.3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

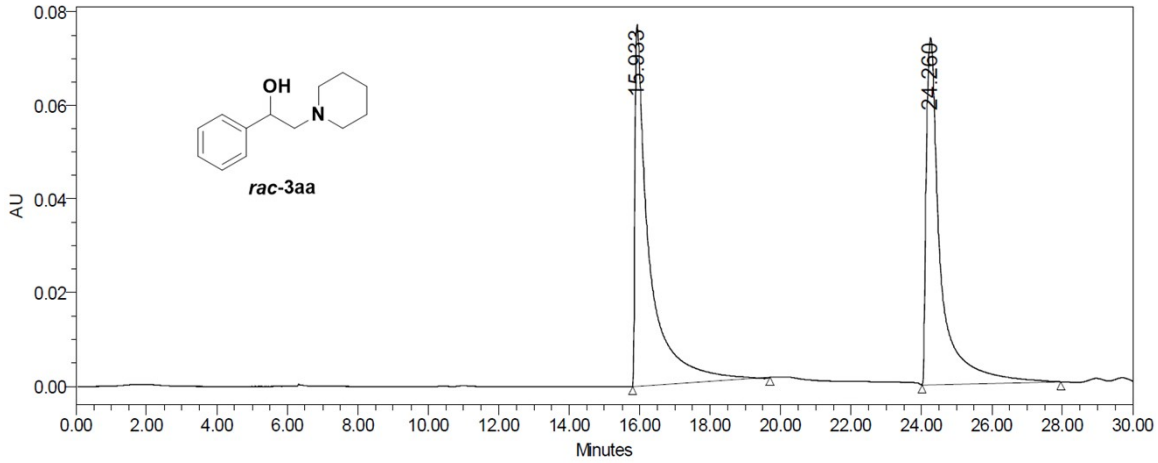

7.91 7.89 7.82 7.80 7.49 7.49 7.47 7.45 7.45 7.42 7.41 7.40 7.38 7.36 7.34 7.31 7.30 7.30 7.29 7.29 7.28 7.27 7.27 7.26
4.84 4.83 4.81 4.80
3.65 3.63 3.61 3.61 3.59
3.02 3.01 3.00 2.99 2.98 2.97 2.96 2.73 2.72 2.71 2.69 2.69 2.68 2.66 2.66 2.63 2.62 2.61 2.58
N S
OH
N
N
3au
1.00 0.97 1.04 4.98 1.00 1.00 0.87 4.03 2.01 2.01 2.08
f1 (ppm)


163.7
152.7
141.8
128.4
127.9
127.5
125.8
123.9
123.7
120.6
68.75
66.30
52.83
50.12
N S
OH
N
N
3au
f1 (ppm)


OH
N
N
O
O
(R)-Naftopidil
f1 (ppm)

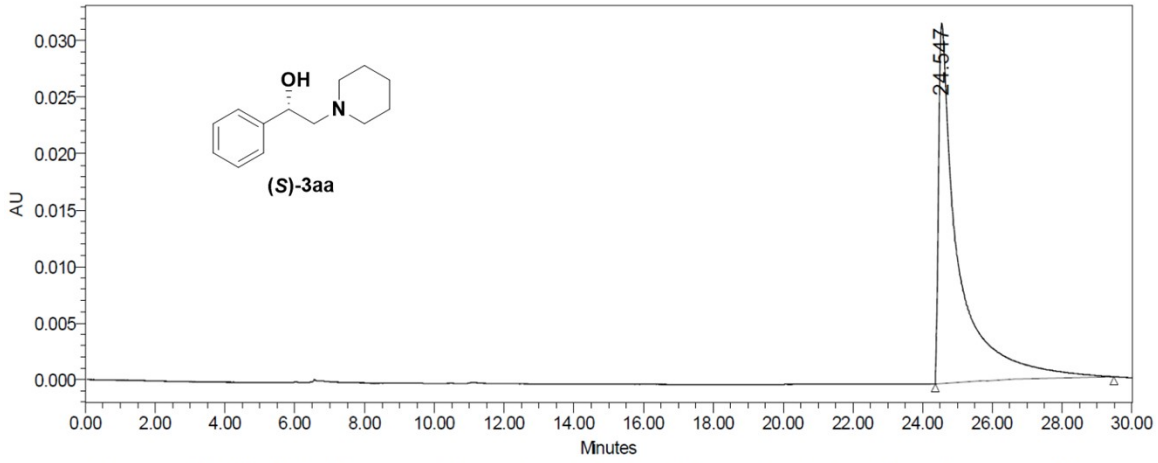

OH
N
N
O
O
(R)-Naftopidil
f1 (ppm)

8. HPLC charts of the products



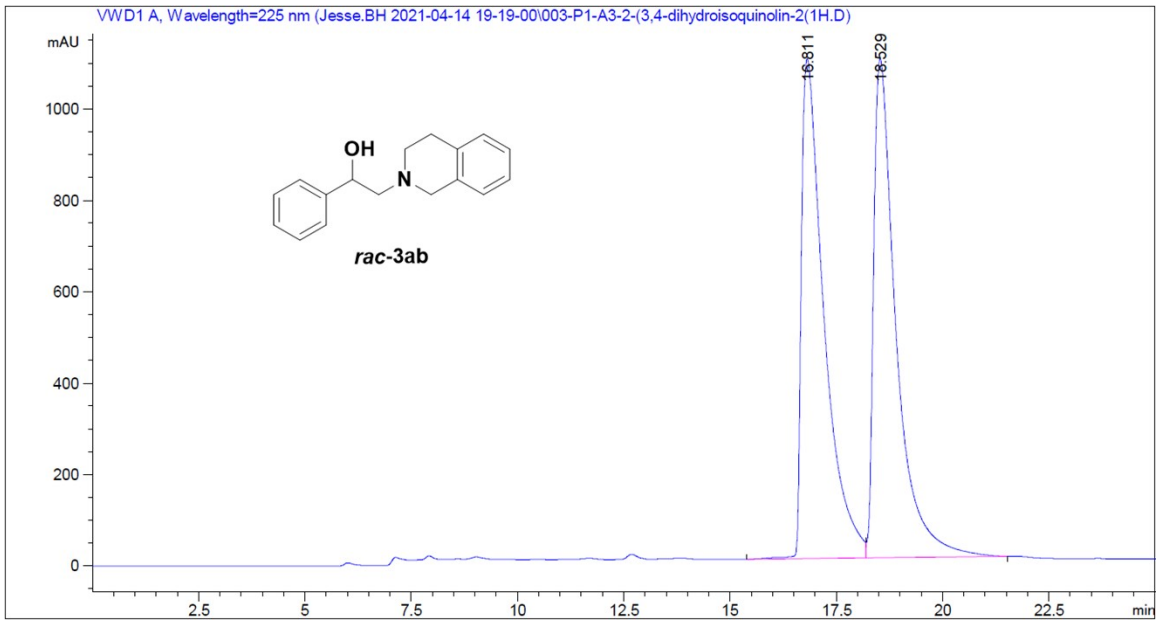
Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 1399; Processing Method: Default

Peak#	Ret. Time	Area	Height	Area %
1	15.933	2191115	77116	50.93
2	24.260	2110704	73983	49.07

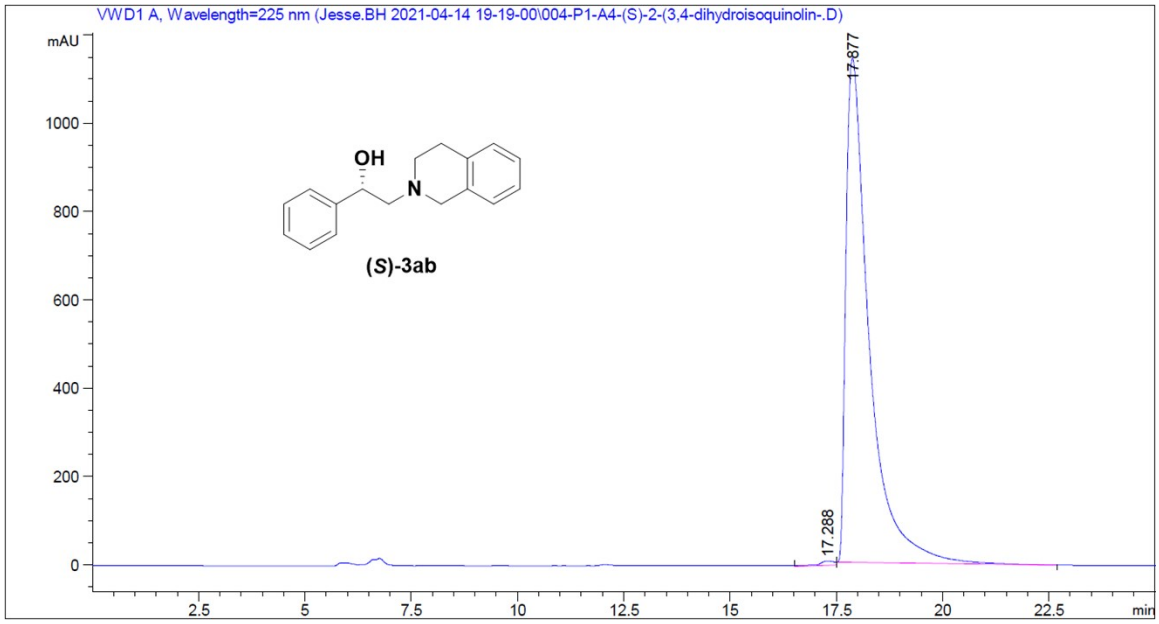


Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 1401; Processing Method: Default

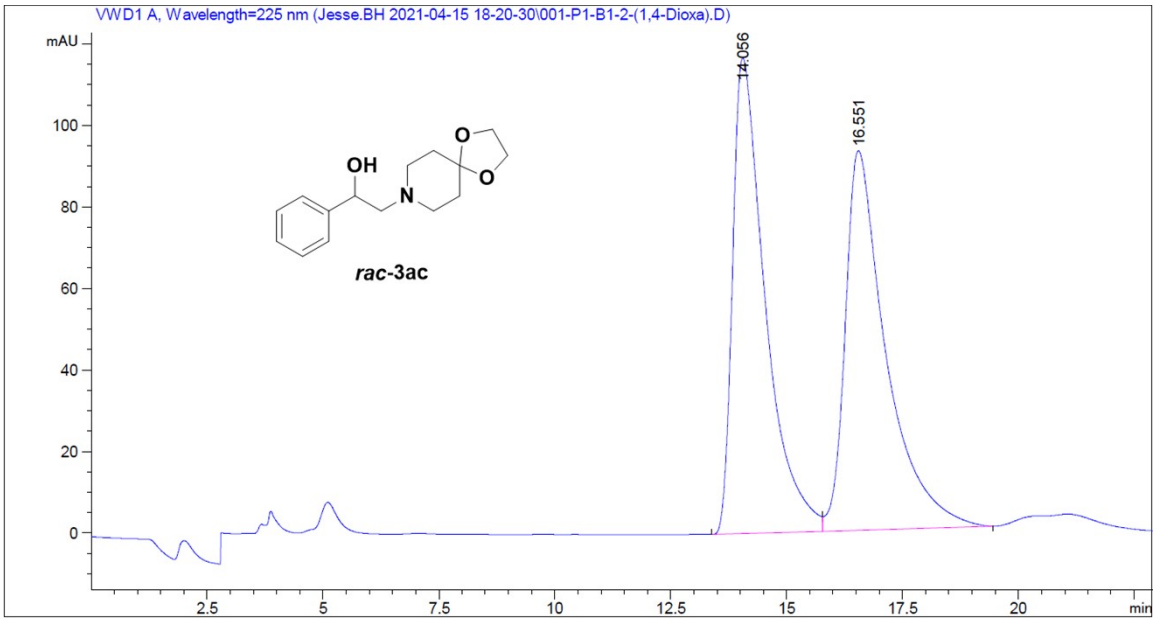
Peak#	Ret. Time	Area	Height	Area %
1	/	/	/	/
2	24.547	1241599	31656	100.00



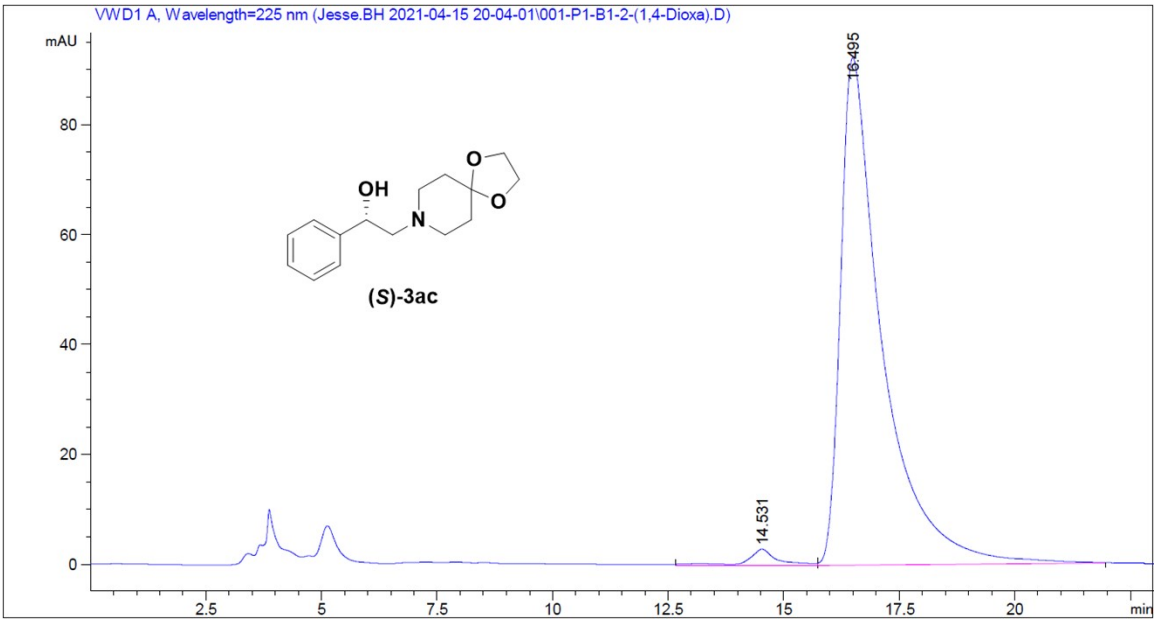
Peak#	Ret. Time	Area	Height	Area %
1	16.811	40343325	1094313	50.19
2	18.529	40042264	1092448	49.81



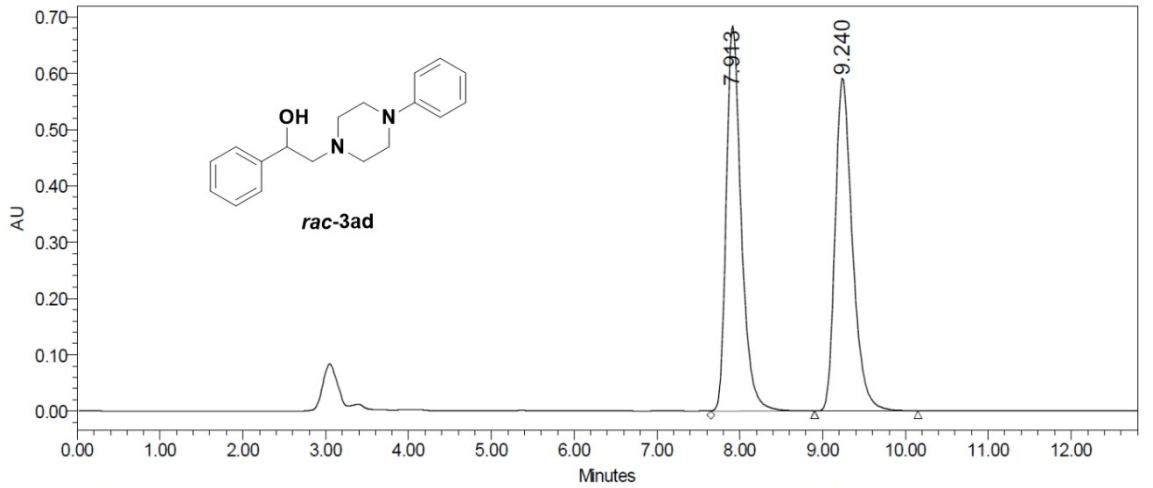
Peak#	Ret. Time	Area	Height	Area %
1	17.288	246823	9379	0.57
2	17.877	43381238	1143067	99.43



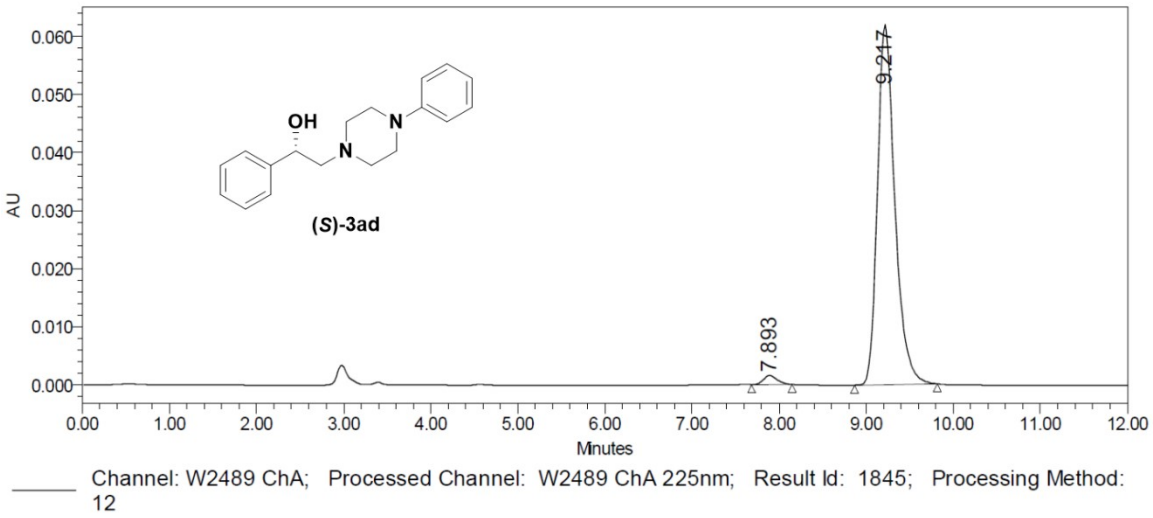
Peak#	Ret. Time	Area	Height	Area %
1	14.056	5695201	116730	50.02
2	16.551	5691900	93104	49.98



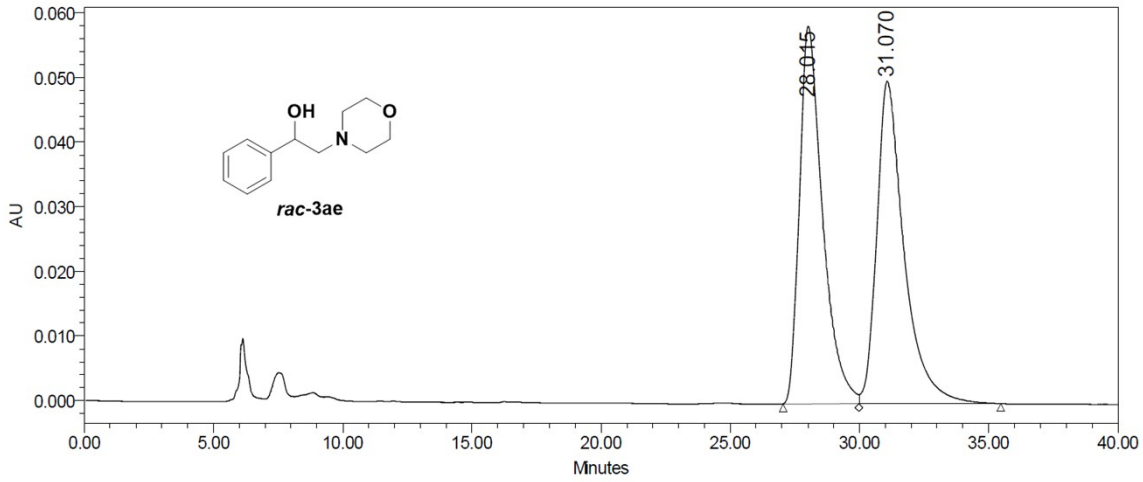
Peak#	Ret. Time	Area	Height	Area %
1	14.531	141120	2983	2.37
2	16.495	5810070	92313	97.63



Peak#	Ret. Time	Area	Height	Area %
1	7.913	8599325	685200	50.12
2	9.240	8559744	592439	49.88

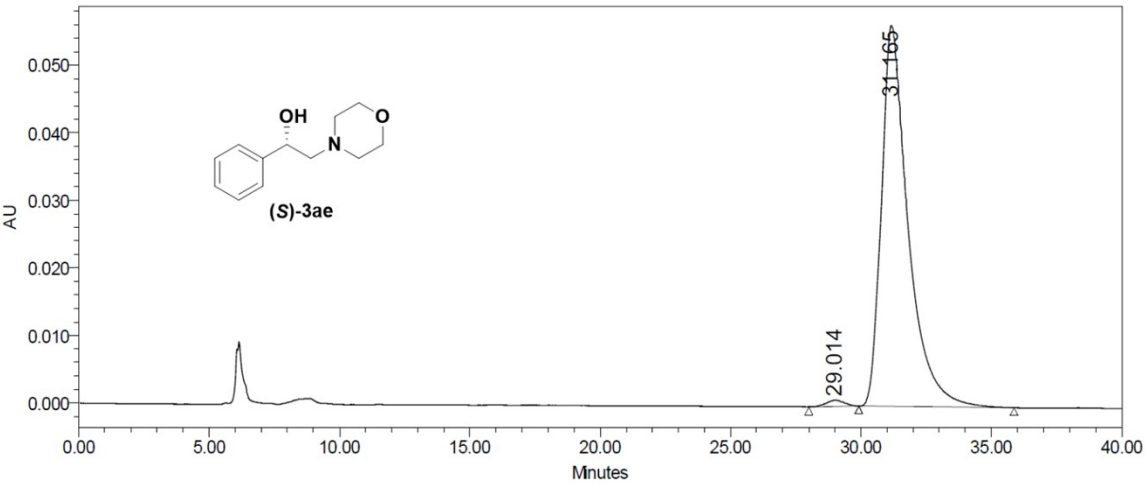


Peak#	Ret. Time	Area	Height	Area %
1	7.893	16963	1541	1.93
2	9.217	861706	61915	98.07



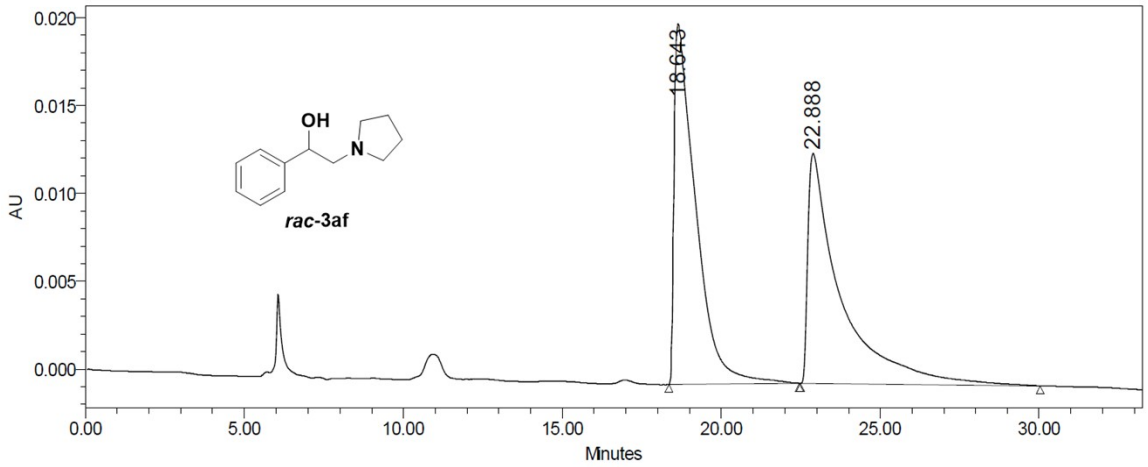
Channel: W2489 ChA; Processed Channel: W2489 ChA 225nm; Result Id: 1487; Processing Method: 2

Peak#	Ret. Time	Area	Height	Area %
1	28.015	3620783	58443	49.58
2	31.070	3682646	49911	50.42



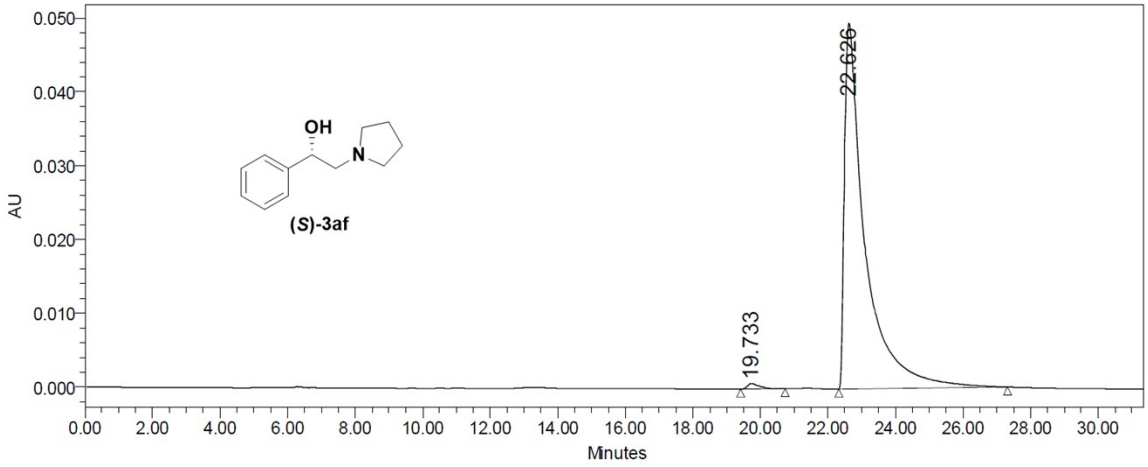
Channel: W2489 ChA; Processed Channel: W2489 ChA 225nm; Result Id: 1495; Processing Method: 2

Peak#	Ret. Time	Area	Height	Area %
1	29.014	44408	922	1.09
2	31.165	4035979	56405	98.91



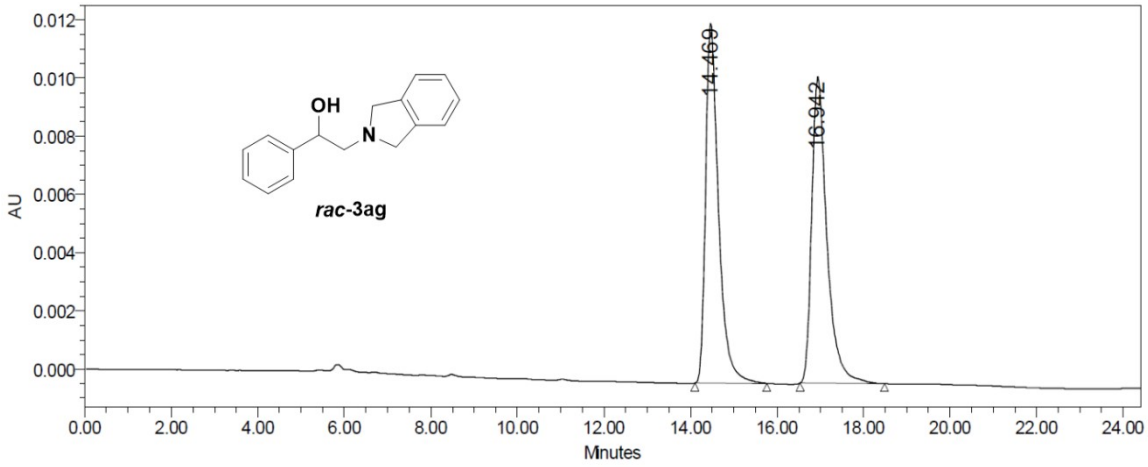
Channel: W2489 ChB; Processed Channel: W2489 ChB 230nm; Result Id: 1638; Processing Method: 12

Peak#	Ret. Time	Area	Height	Area %
1	18.643	970929	20524	50.88
2	22.888	937321	13076	49.12



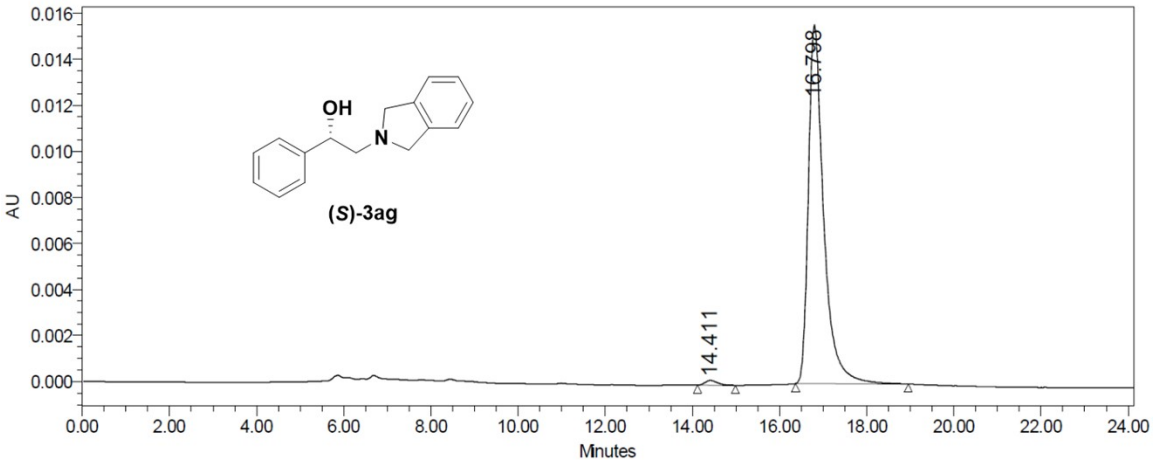
Channel: W2489 ChA; Processed Channel: W2489 ChA 230nm; Result Id: 1654; Processing Method: 122

Peak#	Ret. Time	Area	Height	Area %
1	19.733	18415	727	0.87
2	22.626	2094398	49599	99.13



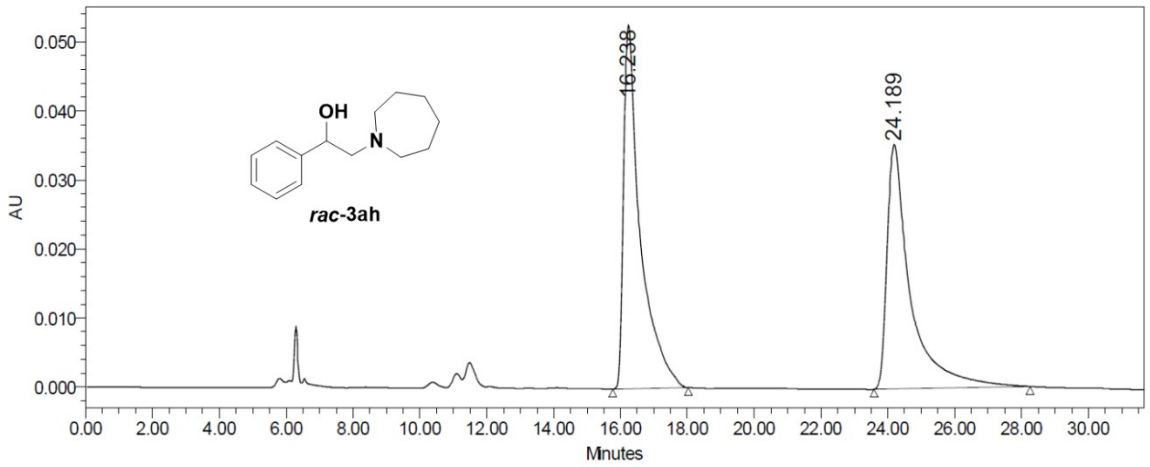
Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 1725; Processing Method: RAC

Peak#	Ret. Time	Area	Height	Area %
1	14.469	255855	12354	50.06
2	16.942	255219	10536	49.94



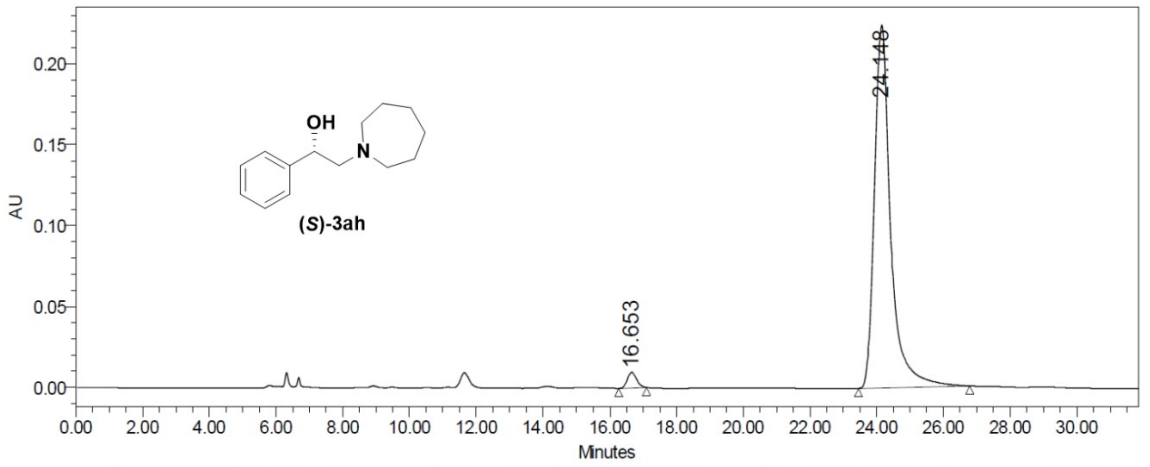
Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 1733; Processing Method: 11111

Peak#	Ret. Time	Area	Height	Area %
1	14.411	4073	210	1.06
2	16.798	380010	15587	98.94



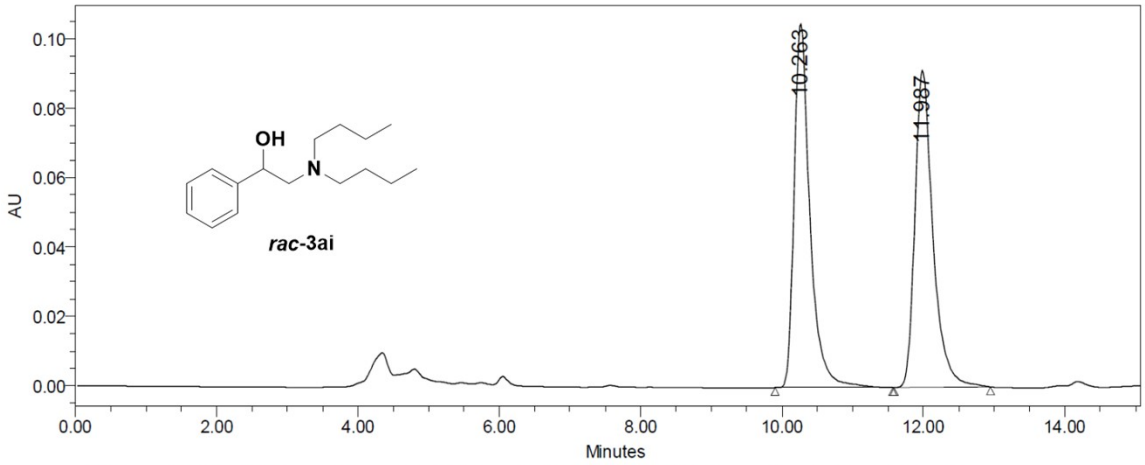
Channel: W2489 ChA; Processed Channel: W2489 ChA 230nm; Result Id: 1677; Processing Method: 1222

Peak#	Ret. Time	Area	Height	Area %
1	16.238	1745839	52697	50.43
2	24.189	1716067	35413	49.57



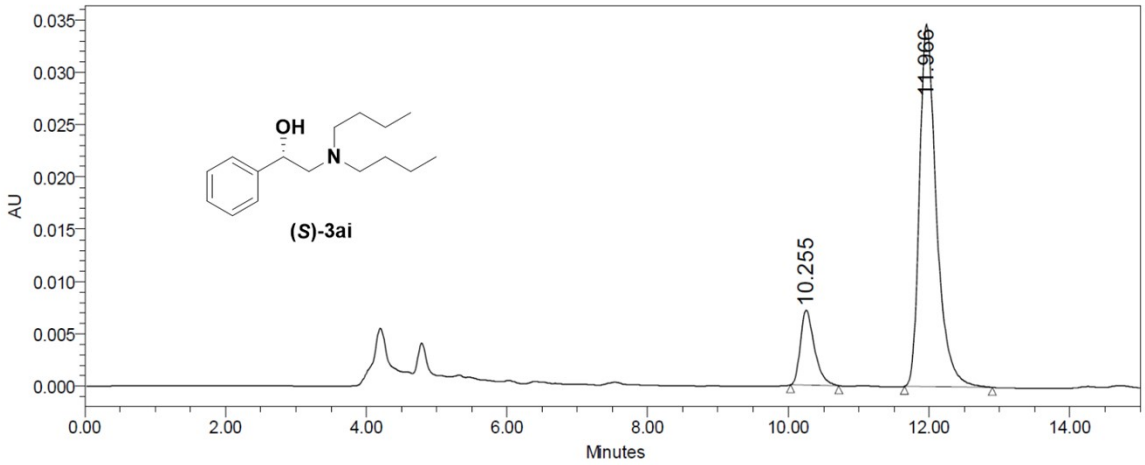
Channel: W2489 ChA; Processed Channel: W2489 ChA 230nm; Result Id: 1695; Processing Method: 1111

Peak#	Ret. Time	Area	Height	Area %
1	16.653	183741	9676	2.37
2	24.148	7575695	224152	97.63



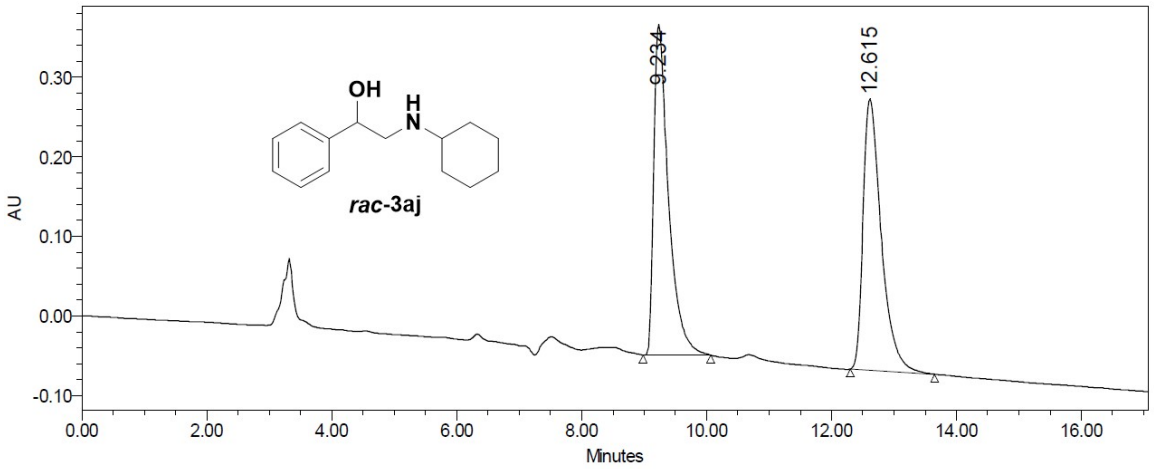
Channel: W2489 ChA; Processed Channel: W2489 ChA 225nm; Result Id: 1794; Processing Method: 12

Peak#	Ret. Time	Area	Height	Area %
1	10.263	1632234	104873	50.14
2	11.987	1623392	91479	49.86



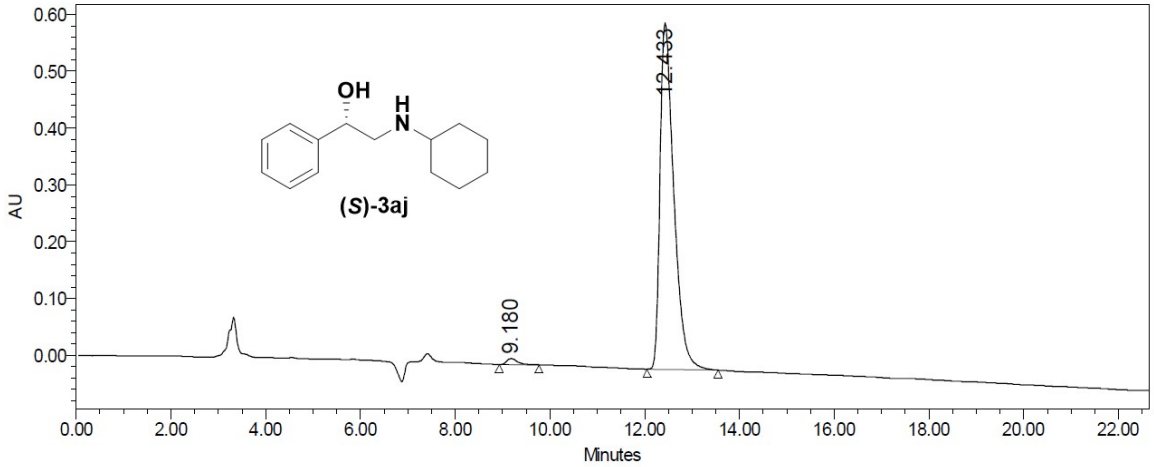
Channel: W2489 ChA; Processed Channel: W2489 ChA 225nm; Result Id: 1802; Processing Method: 12

Peak#	Ret. Time	Area	Height	Area %
1	10.255	99357	7184	14.63
2	11.966	579942	34635	85.37



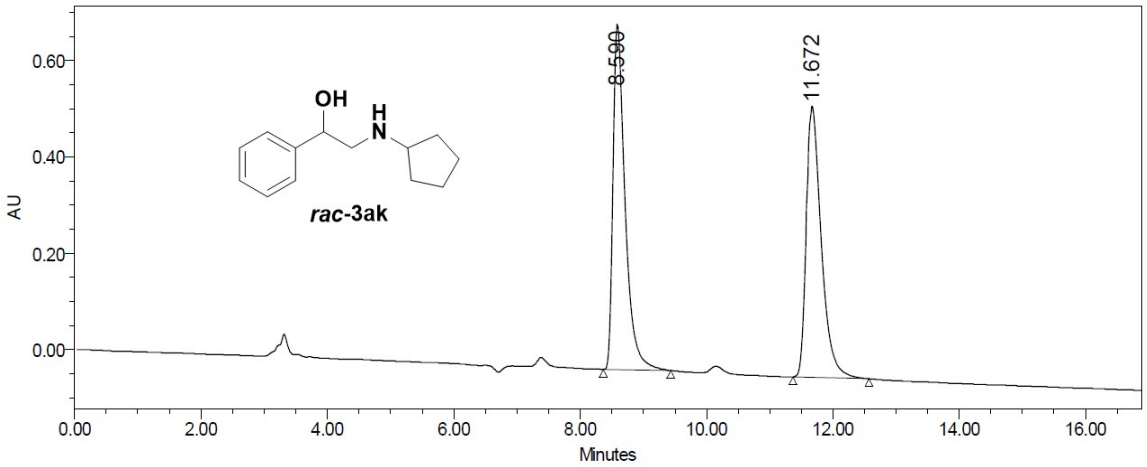
Channel: W2489 ChB; Processed Channel: W2489 ChB 210nm; Result Id: 3012; Processing Method: HEXNH

Peak#	Ret. Time	Area	Height	Area %
1	9.234	6781615	415262	49.64
2	12.615	6880494	341178	50.36



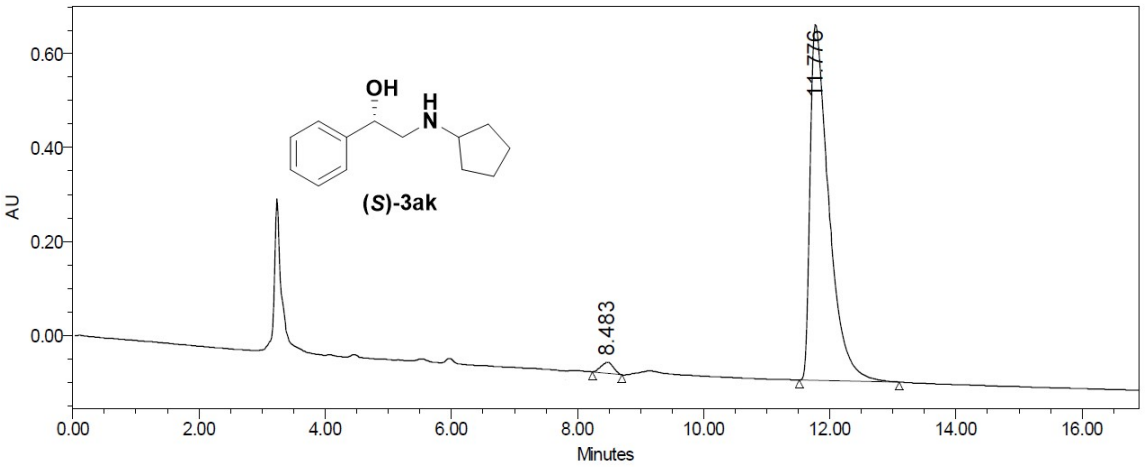
Channel: W2489 ChB; Processed Channel: W2489 ChB 210nm; Result Id: 3014; Processing Method: HEXNH

Peak#	Ret. Time	Area	Height	Area %
1	9.180	172508	10658	1.37
2	12.433	12398046	609903	98.63



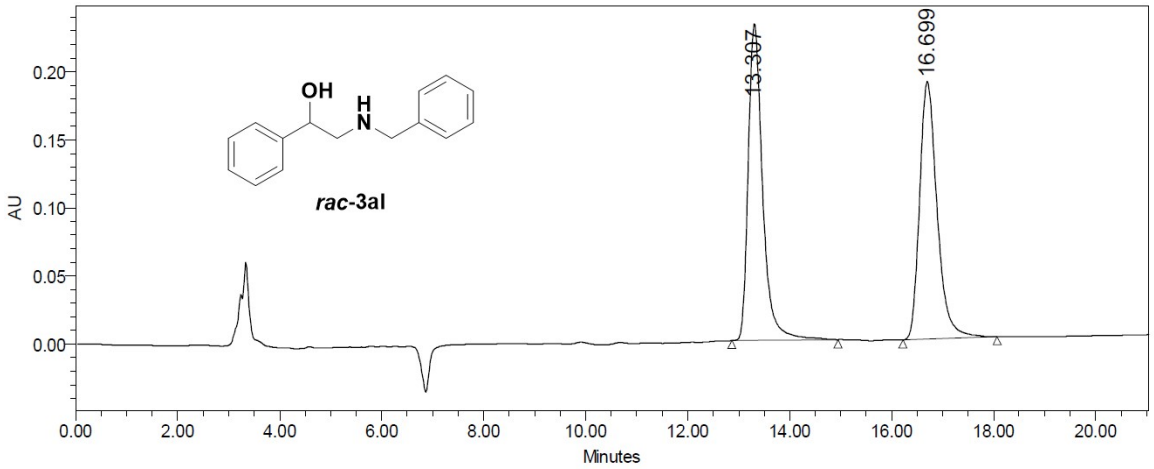
Channel: W2489 ChB; Processed Channel: W2489 ChB 210nm; Result Id: 3069; Processing Method: pent

Peak#	Ret. Time	Area	Height	Area %
1	8.590	9399922	718776	49.97
2	11.672	9412793	563787	50.03



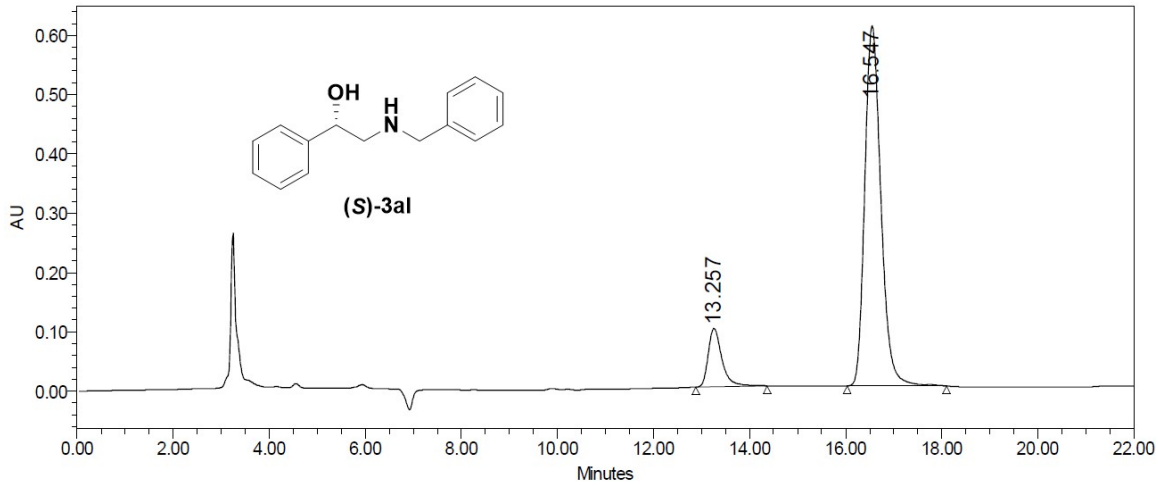
Channel: W2489 ChA; Processed Channel: W2489 ChA 210nm; Result Id: 3084; Processing Method: pent

Peak#	Ret. Time	Area	Height	Area %
1	8.483	324114	23991	2.04
2	11.776	15585993	759857	97.96



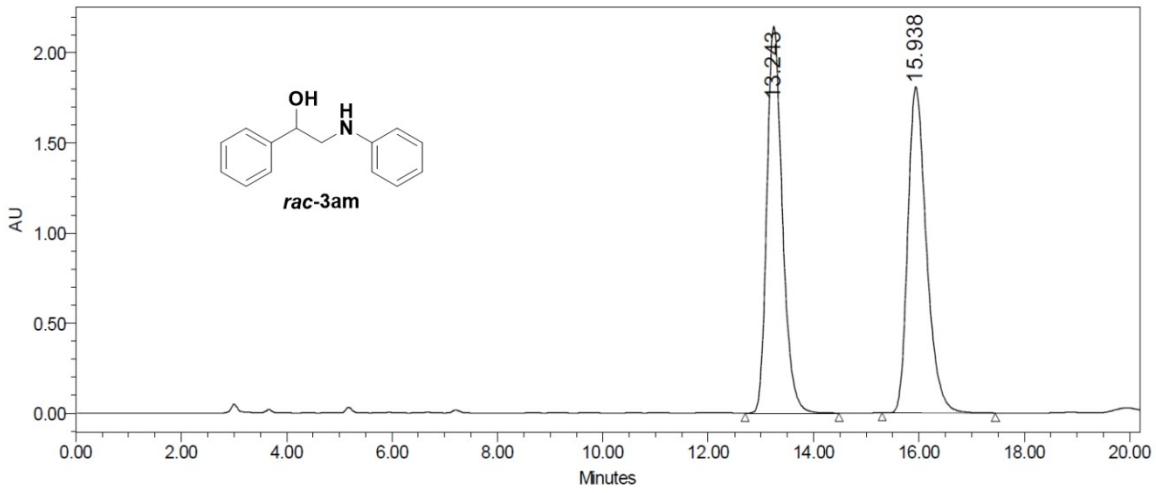
Channel: W2489 ChA; Processed Channel: W2489 ChA 210nm; Result Id: 3216; Processing Method: RAC

Peak#	Ret. Time	Area	Height	Area %
1	13.307	4555751	232631	50.25
2	16.699	4509557	189124	49.75

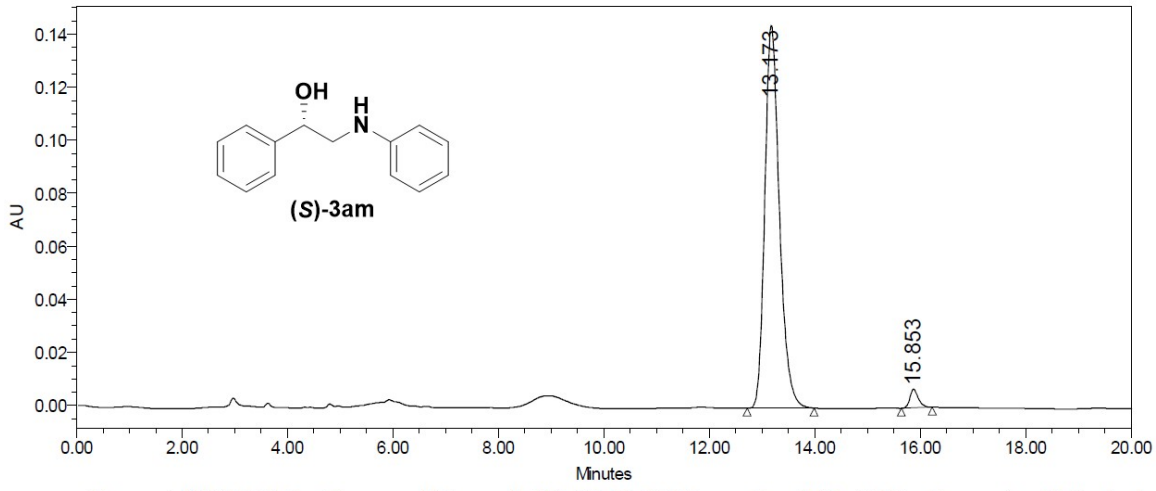


Channel: W2489 ChA; Processed Channel: W2489 ChA 210nm; Result Id: 3214; Processing Method: S

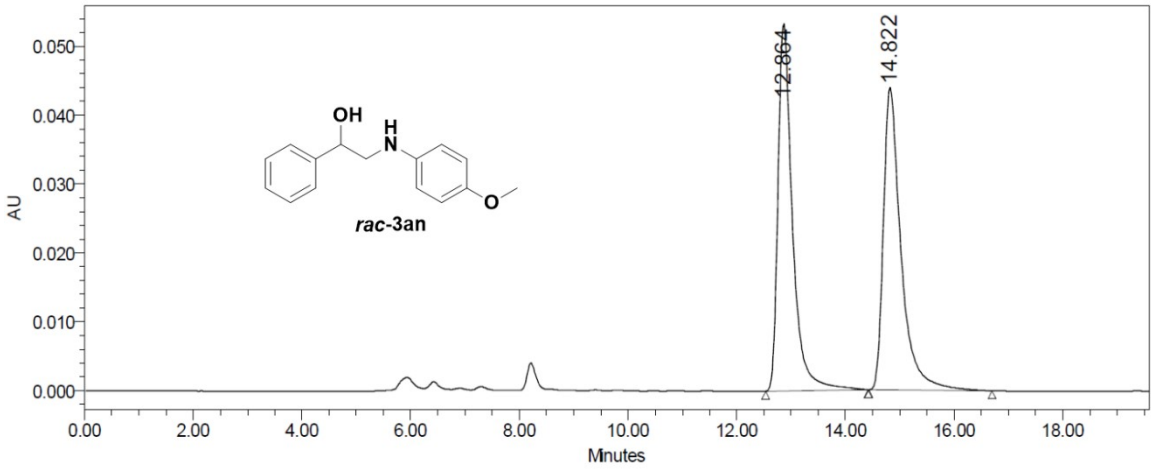
Peak#	Ret. Time	Area	Height	Area %
1	13.257	1949819	98422	12.12
2	16.547	14143942	607802	87.88



Peak#	Ret. Time	Area	Height	Area %
1	13.243	43889641	2149111	49.67
2	15.938	44471319	1812974	50.33

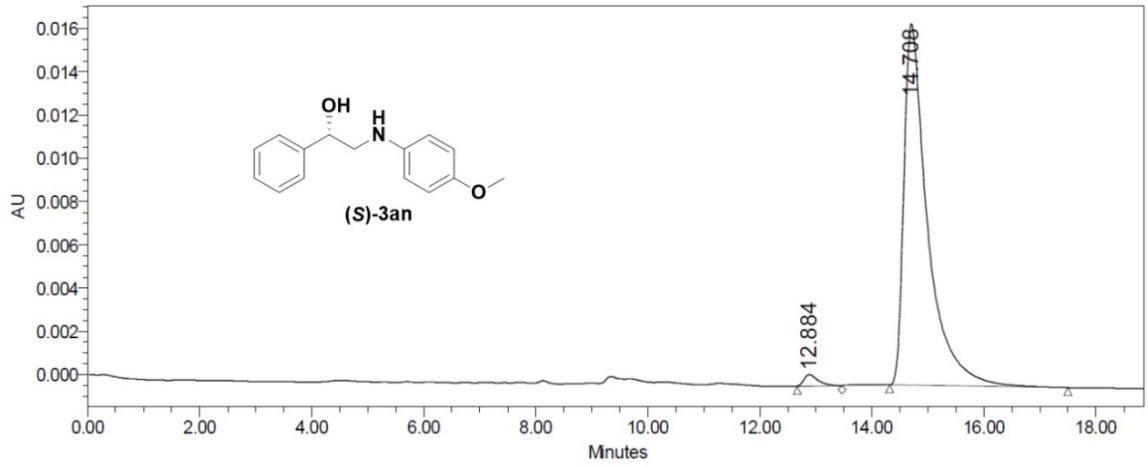


Peak#	Ret. Time	Area	Height	Area %
1	13.173	2775256	144530	97.25
2	15.853	78347	7034	2.75



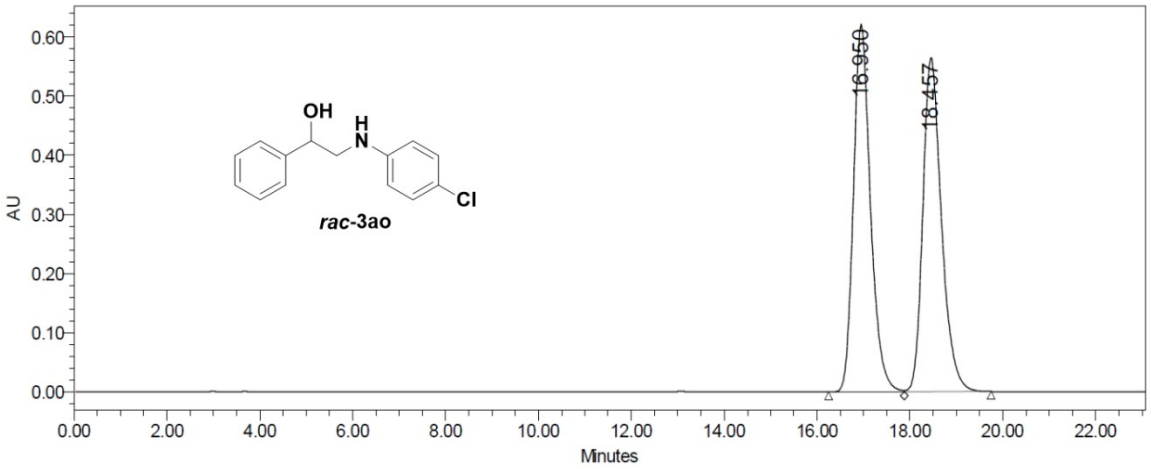
Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 2156; Processing Method: RAC

Peak#	Ret. Time	Area	Height	Area %
1	12.864	988622	53293	50.02
2	14.822	987841	43949	49.98



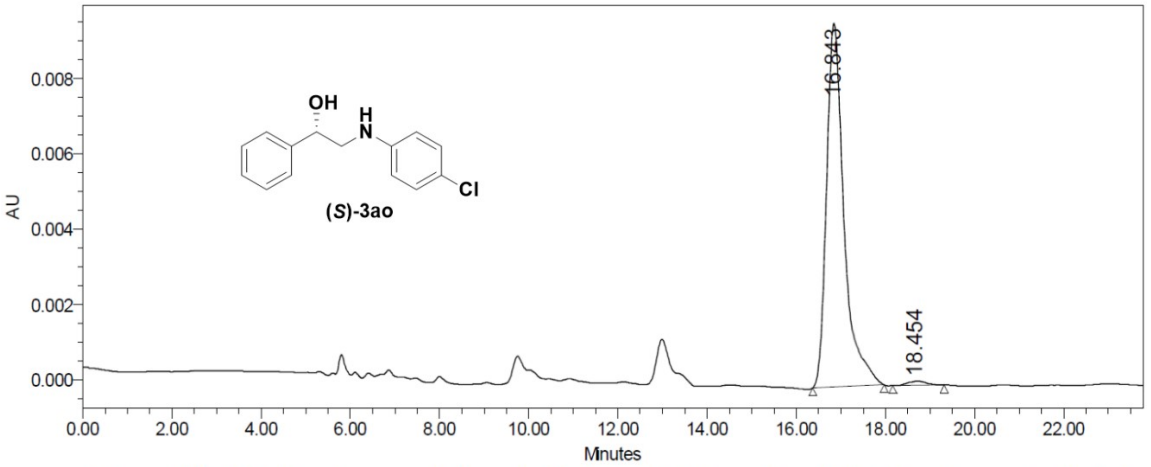
Channel: W2489 ChB; Processed Channel: W2489 ChB 254nm; Result Id: 2158; Processing Method:

Peak#	Ret. Time	Area	Height	Area %
1	12.884	9249	537	1.85
2	14.708	490747	16718	98.15



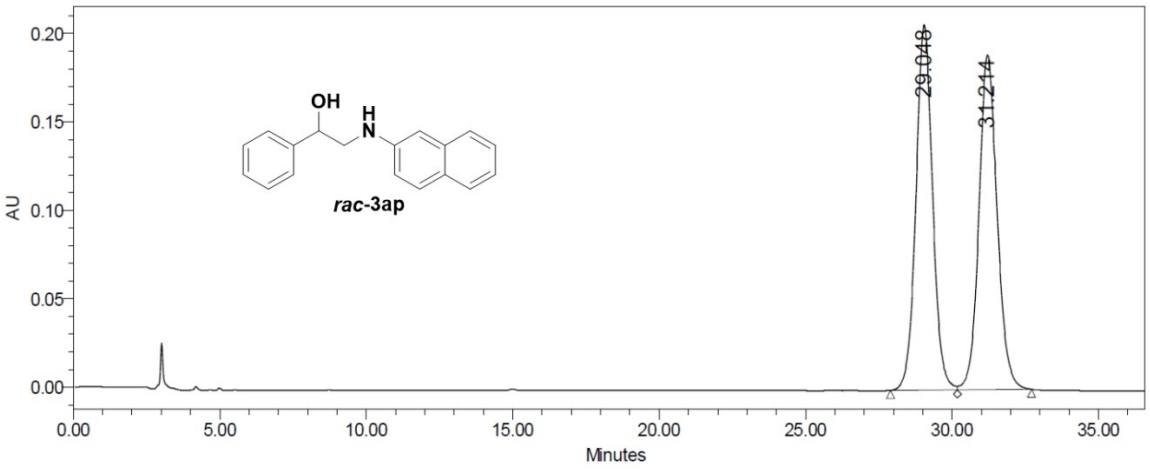
Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 2184; Processing Method: 1212

Peak#	Ret. Time	Area	Height	Area %
1	16.950	15791178	621707	49.97
2	18.457	15809796	565225	50.03



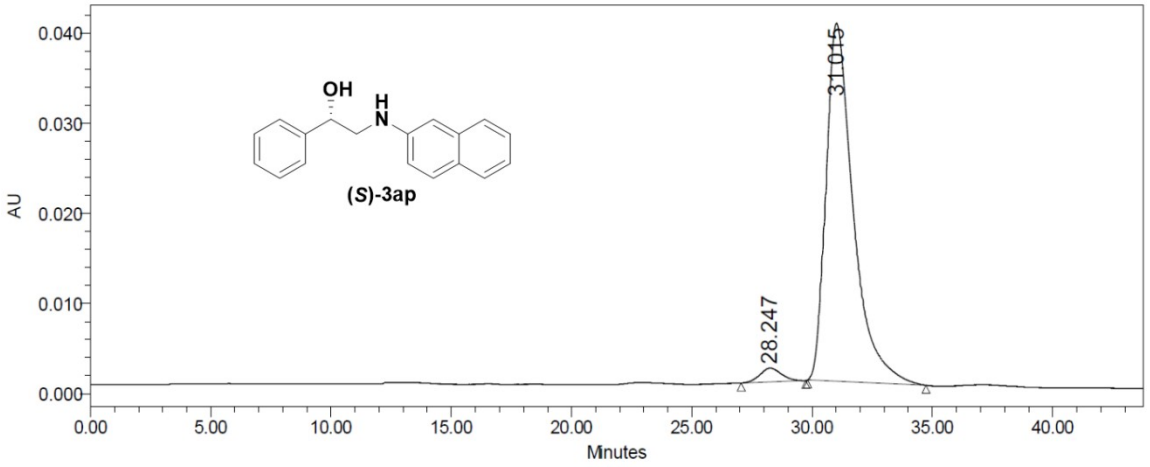
Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 2181; Processing Method: 1212

Peak#	Ret. Time	Area	Height	Area %
1	16.843	261551	9653	98.80
2	18.454	3174	110	1.20



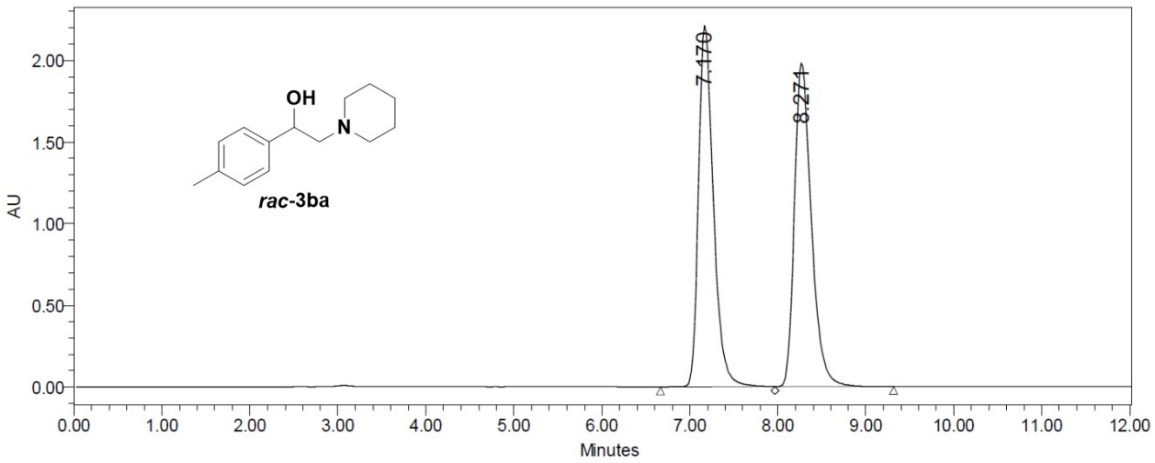
Channel: W2489 ChB; Processed Channel: W2489 ChB 254nm; Result Id: 1984; Processing Method: 33

Peak#	Ret. Time	Area	Height	Area %
1	29.048	8194001	206796	49.98
2	31.214	8201197	189459	50.02



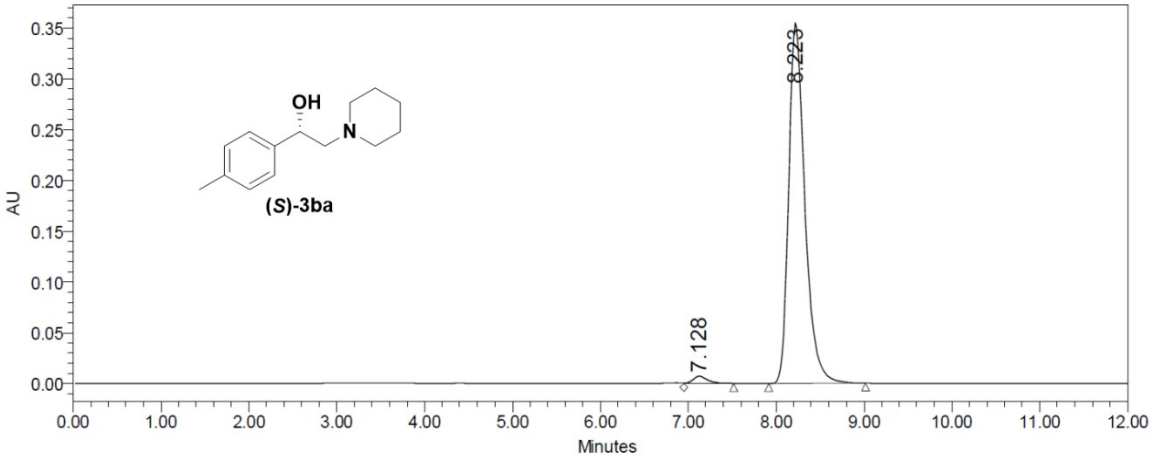
Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 1986; Processing Method: 33

Peak#	Ret. Time	Area	Height	Area %
1	28.247	96087	1541	2.99
2	31.015	3116389	39731	97.01



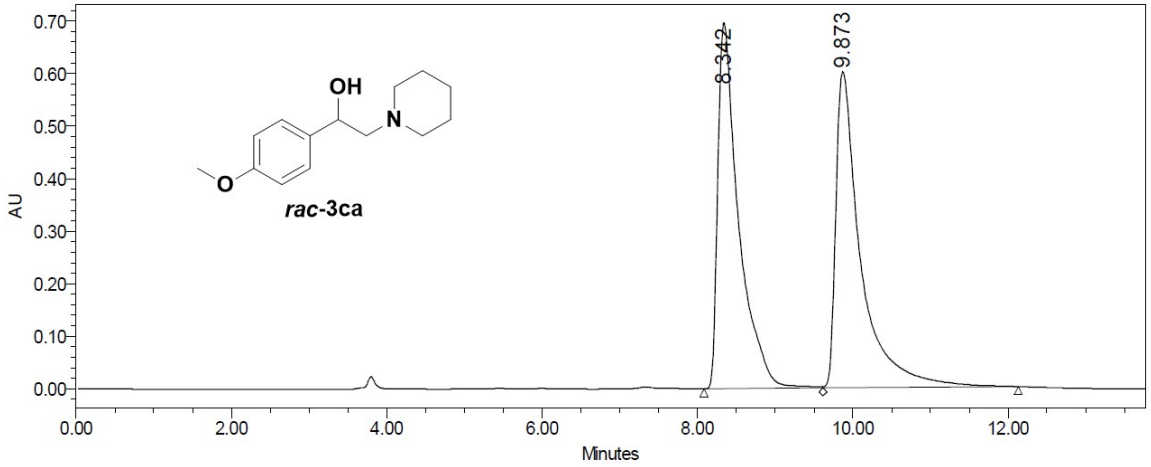
Channel: W2489 ChB; Processed Channel: W2489 ChB 225nm; Result Id: 1902; Processing Method: 13

Peak#	Ret. Time	Area	Height	Area %
1	7.170	26099302	2211637	49.60
2	8.271	26523886	1982857	50.40



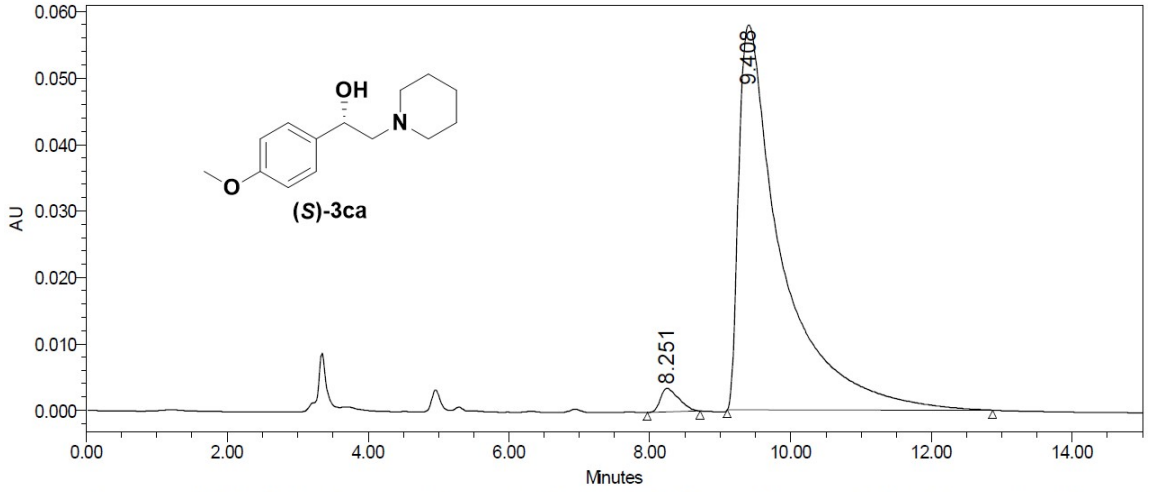
Channel: W2489 ChB; Processed Channel: W2489 ChB 225nm; Result Id: 1900; Processing Method: 13

Peak#	Ret. Time	Area	Height	Area %
1	7.128	80596	7091	1.75
2	8.223	4536564	355663	98.25



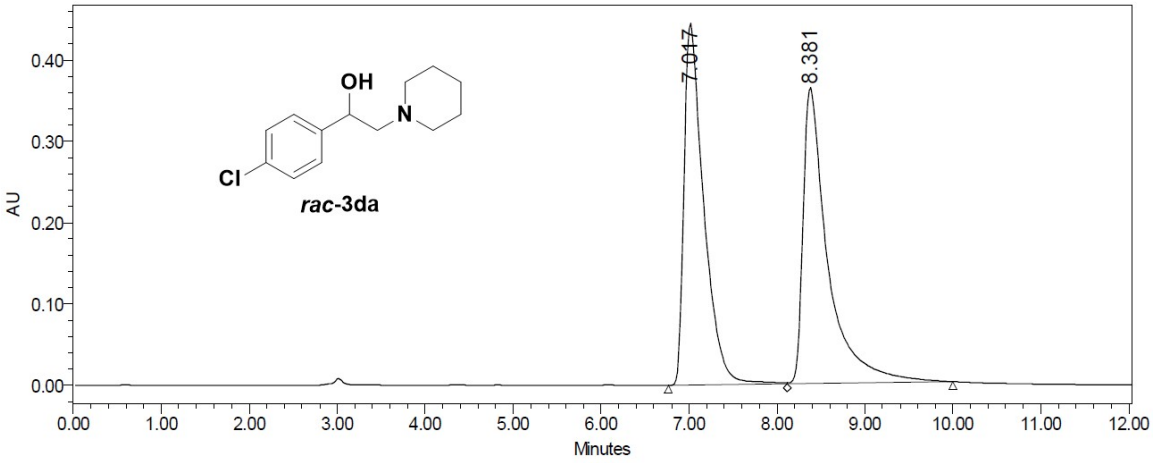
Channel: W2489 ChB; Processed Channel: W2489 ChB 230nm; Result Id: 2435; Processing Method: RAC

Peak#	Ret. Time	Area	Height	Area %
1	8.342	13008327	699925	49.32
2	9.873	13367405	603971	50.68



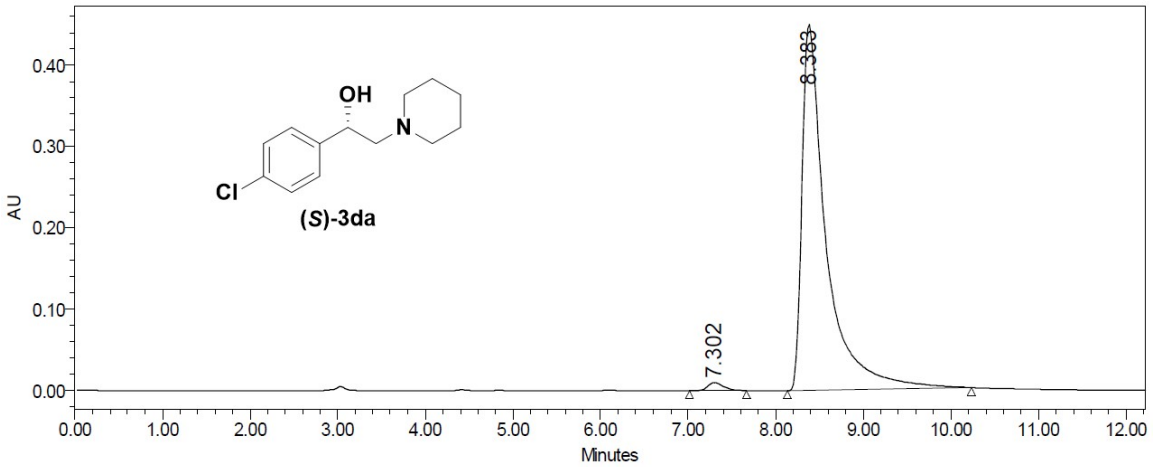
Channel: W2489 ChB; Processed Channel: W2489 ChB 230nm; Result Id: 2399; Processing Method: S

Peak#	Ret. Time	Area	Height	Area %
1	8.251	63752	3534	2.53
2	9.408	2452402	57984	97.47



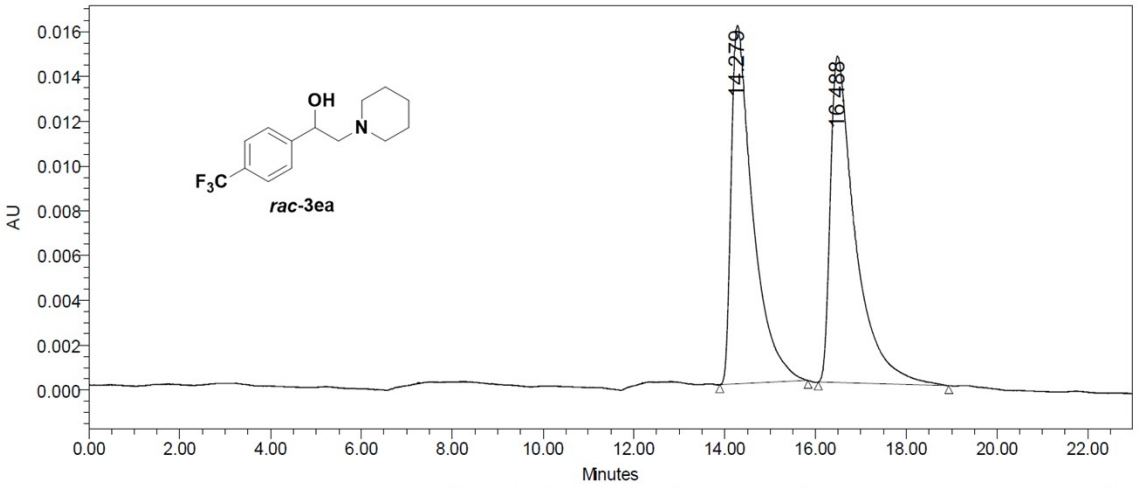
Channel: W2489 ChB; Processed Channel: W2489 ChB 230nm; Result Id: 2223; Processing Method: p

Peak#	Ret. Time	Area	Height	Area %
1	7.017	6955716	444737	49.51
2	8.381	7094371	363801	50.49



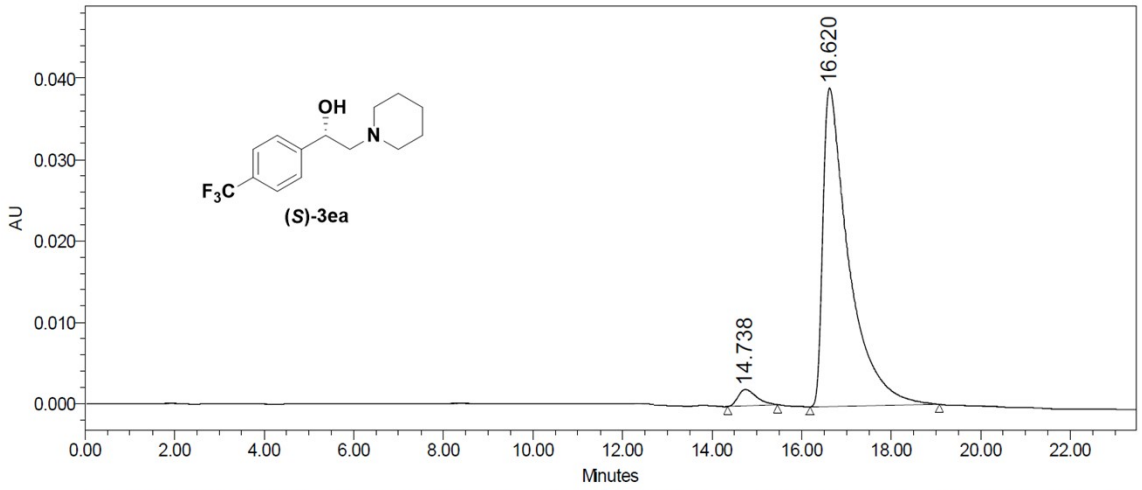
Channel: W2489 ChB; Processed Channel: W2489 ChB 230nm; Result Id: 2221; Processing Method: p

Peak#	Ret. Time	Area	Height	Area %
1	7.302	121210	10030	1.38
2	8.383	8649496	449863	98.62



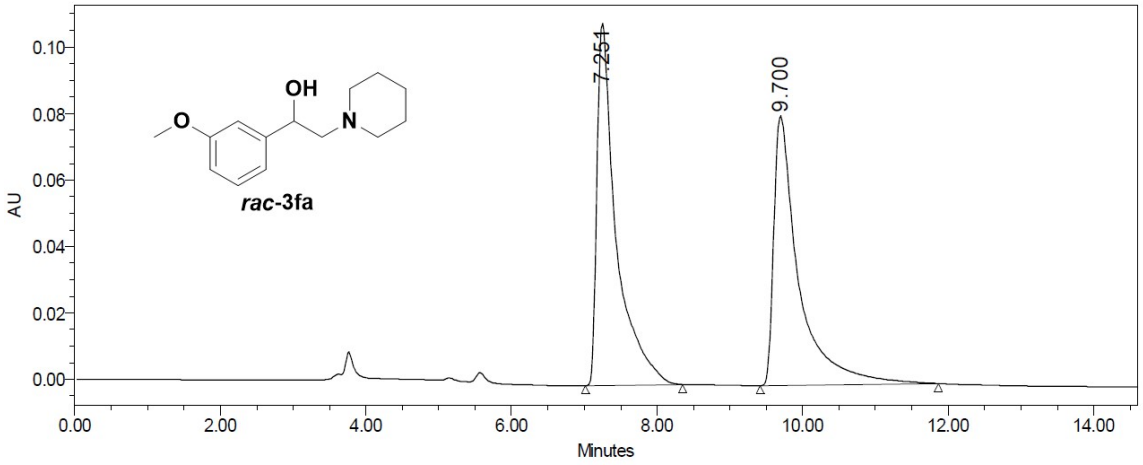
Channel: W2489 ChA; Processed Channel: W2489 ChA 225nm; Result Id: 1570; Processing Method: 5

Peak#	Ret. Time	Area	Height	Area %
1	14.279	534520	16020	49.02
2	16.488	555887	14580	50.98



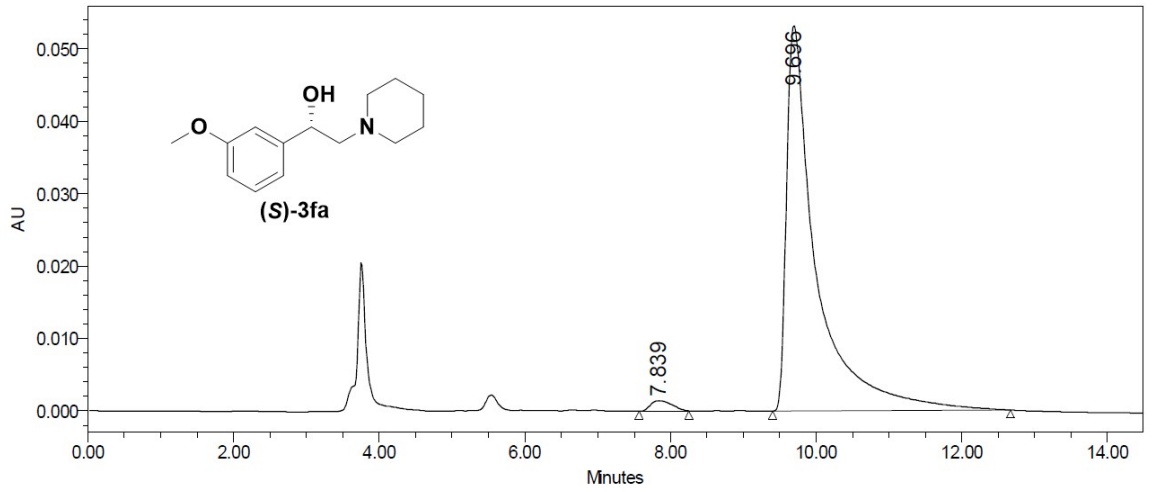
Channel: W2489 ChA; Processed Channel: W2489 ChA 225nm; Result Id: 1579; Processing Method: 6

Peak#	Ret. Time	Area	Height	Area %
1	14.738	58089	2012	3.55
2	16.620	1578808	39152	96.45



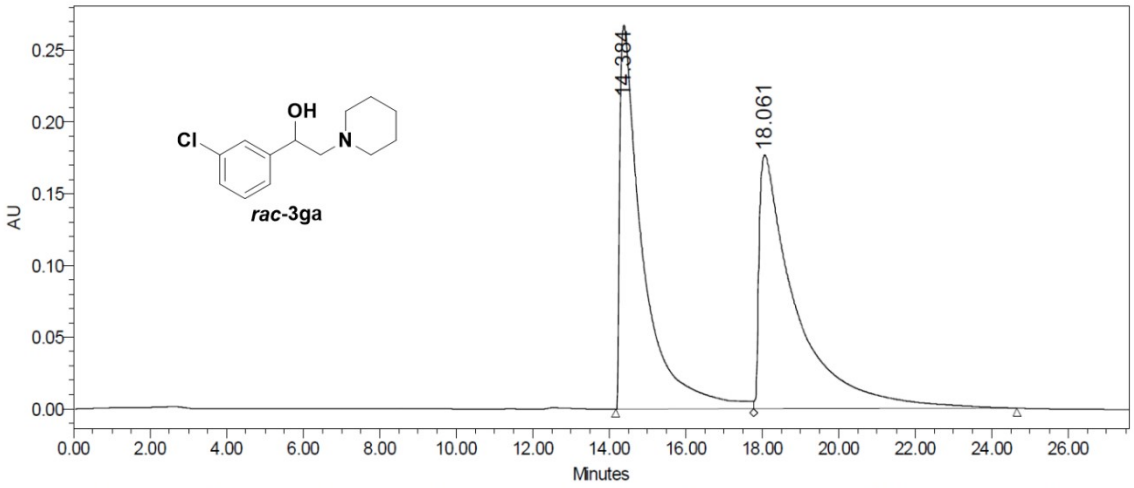
Channel: W2489 ChB; Processed Channel: W2489 ChB 230nm; Result Id: 2340; Processing Method: mOMe

Peak#	Ret. Time	Area	Height	Area %
1	7.251	2002810	108961	50.85
2	9.700	1935530	81159	49.15

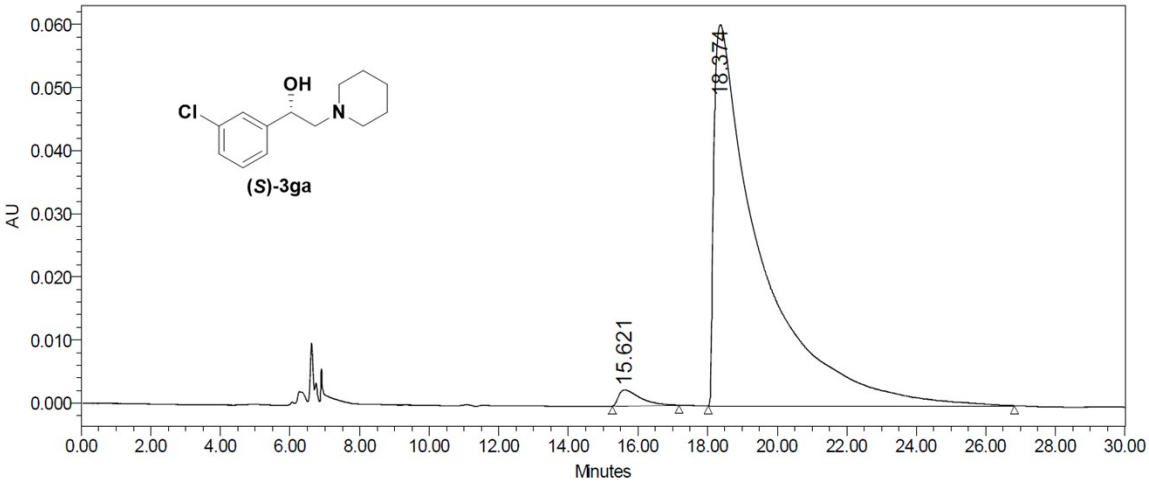


Channel: W2489 ChB; Processed Channel: W2489 ChB 230nm; Result Id: 2342; Processing Method: S

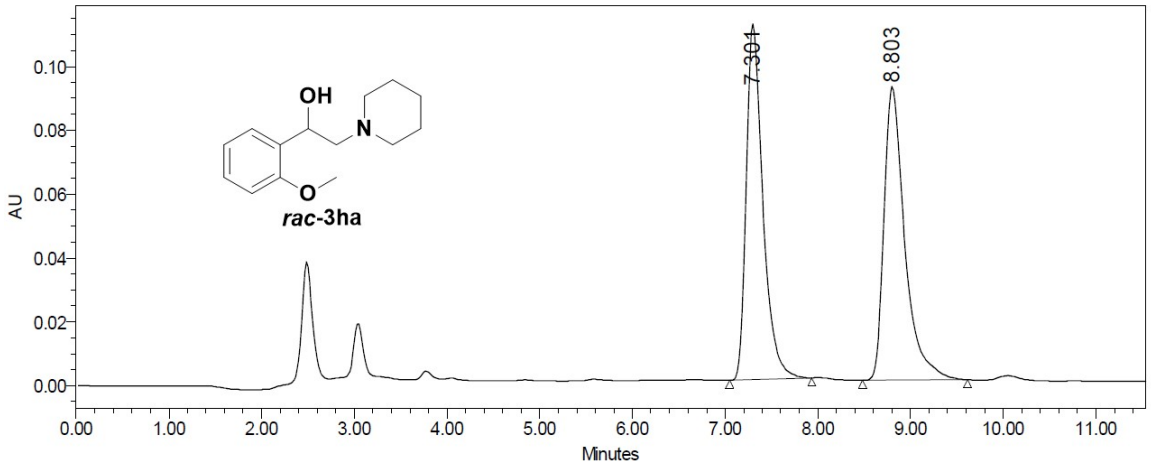
Peak#	Ret. Time	Area	Height	Area %
1	7.839	28831	1432	1.87
2	9.696	1512761	53290	98.13



Peak#	Ret. Time	Area	Height	Area %
1	14.384	11334190	267615	49.02
2	18.061	11789244	177001	50.98

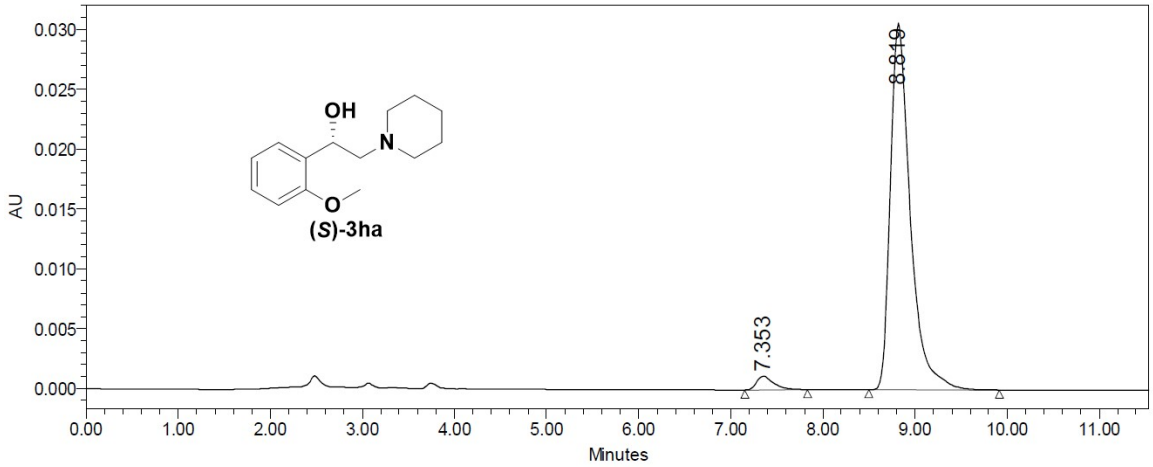


Peak#	Ret. Time	Area	Height	Area %
1	15.621	109311	2537	1.93
2	18.374	5558894	60411	98.07



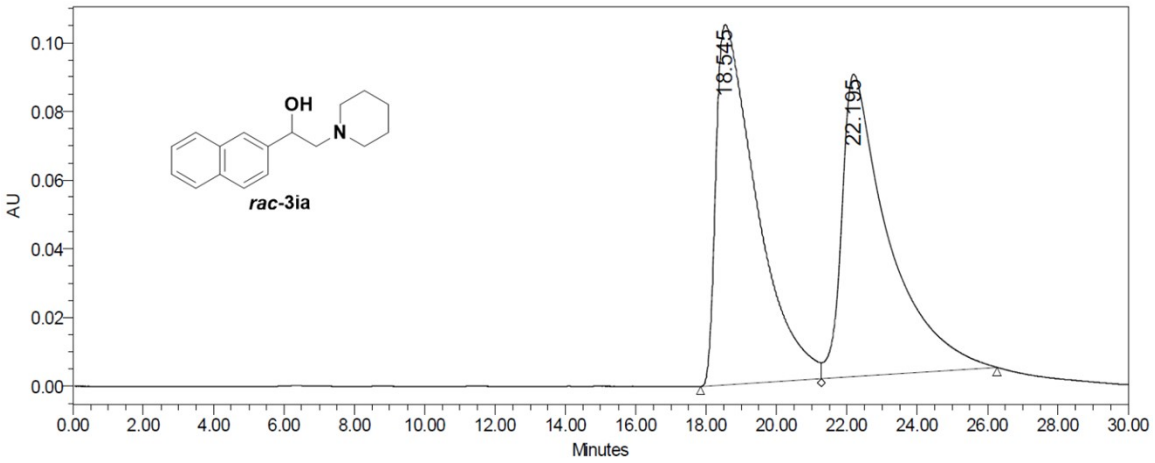
Channel: W2489 ChA; Processed Channel: W2489 ChA 225nm; Result Id: 2596; Processing Method: oOMe

Peak#	Ret. Time	Area	Height	Area %
1	7.301	1395487	111291	49.31
2	8.803	1434297	92033	50.69



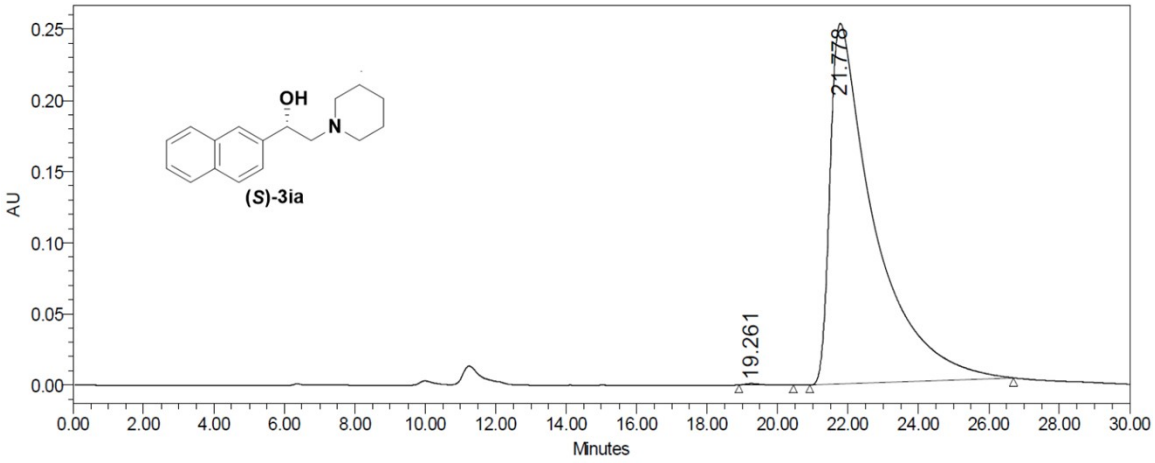
Channel: W2489 ChB; Processed Channel: W2489 ChB 225nm; Result Id: 2598; Processing Method: oOMe

Peak#	Ret. Time	Area	Height	Area %
1	7.353	14798	1157	3.12
2	8.819	459321	30614	96.88



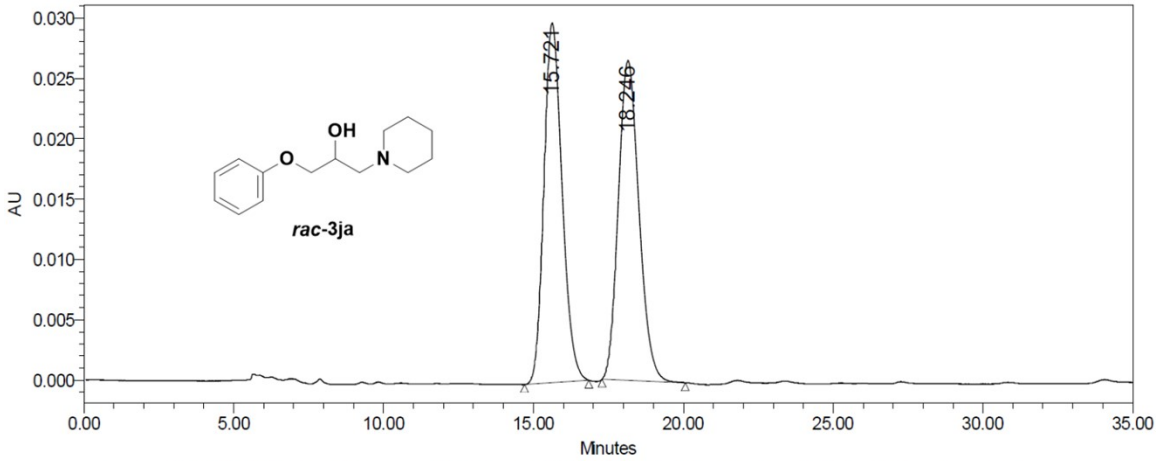
Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 1395; Processing Method: Default

Peak#	Ret. Time	Area	Height	Area %
1	18.545	8422235	104832	50.91
2	22.195	8122607	88026	49.09



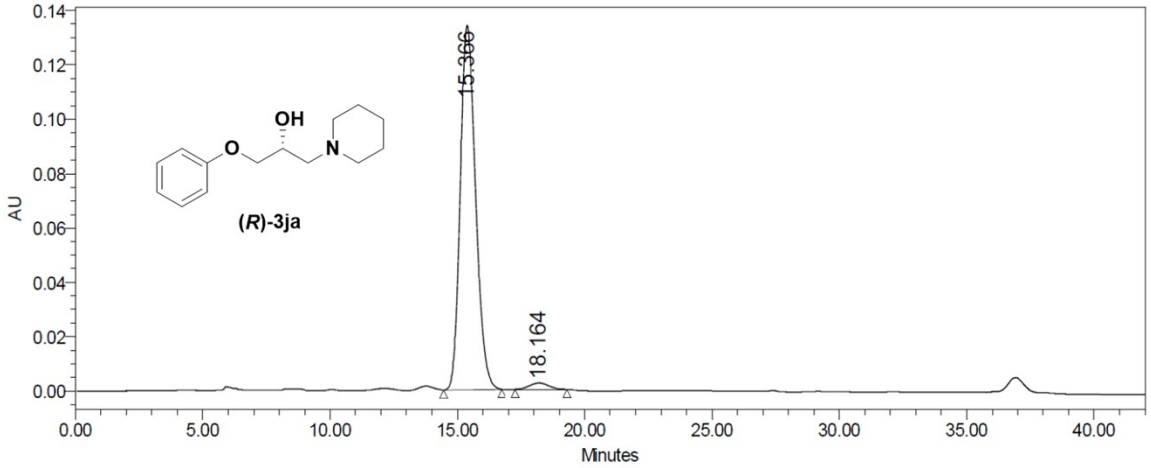
Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 1397; Processing Method: Default

Peak#	Ret. Time	Area	Height	Area %
1	19.261	30121	966	0.14
2	21.778	22057560	253394	99.86



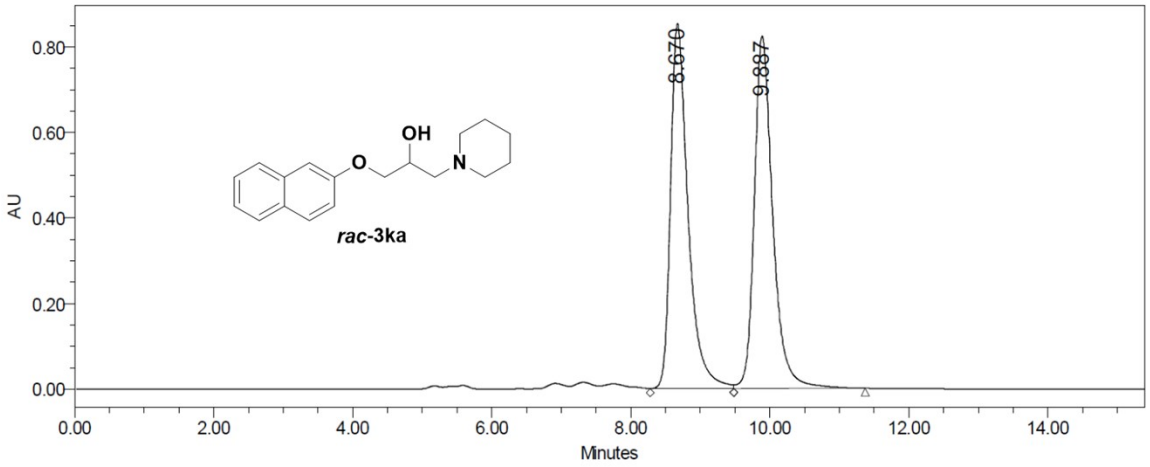
Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 4514; Processing Method: RAC

Peak#	Ret. Time	Area	Height	Area %
1	15.721	1263437	29794	50.07
2	18.246	1259821	26480	49.93



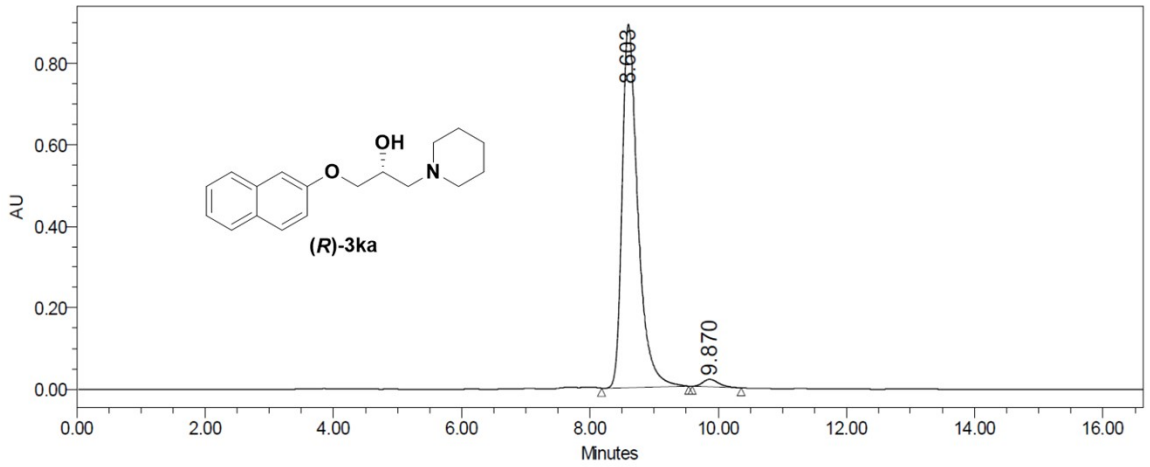
Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 4528; Processing Method:

Peak#	Ret. Time	Area	Height	Area %
1	15.366	5608020	134089	97.79
2	18.164	126979	2402	2.21



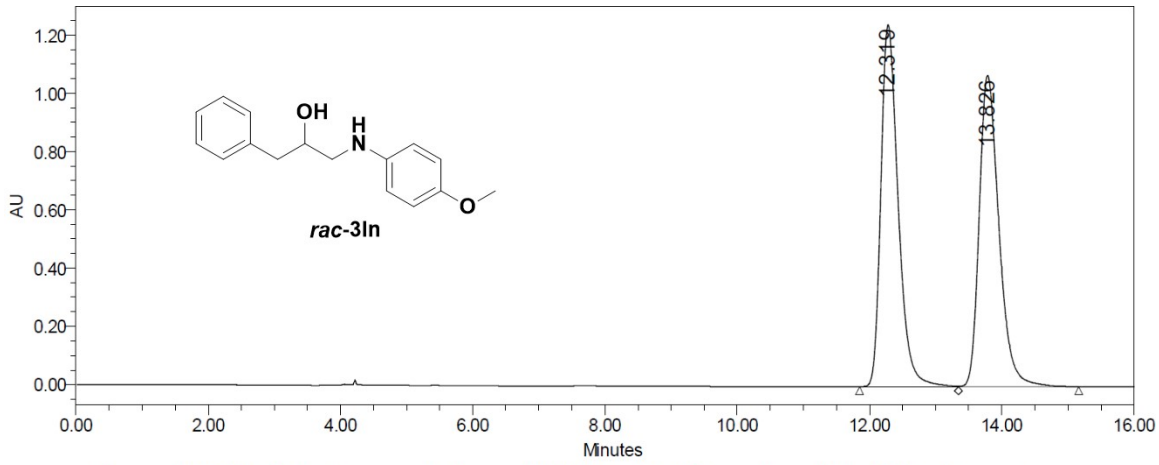
Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 4504; Processing Method: NeO

Peak#	Ret. Time	Area	Height	Area %
1	8.670	14862713	853755	49.47
2	9.887	15178537	824254	50.53



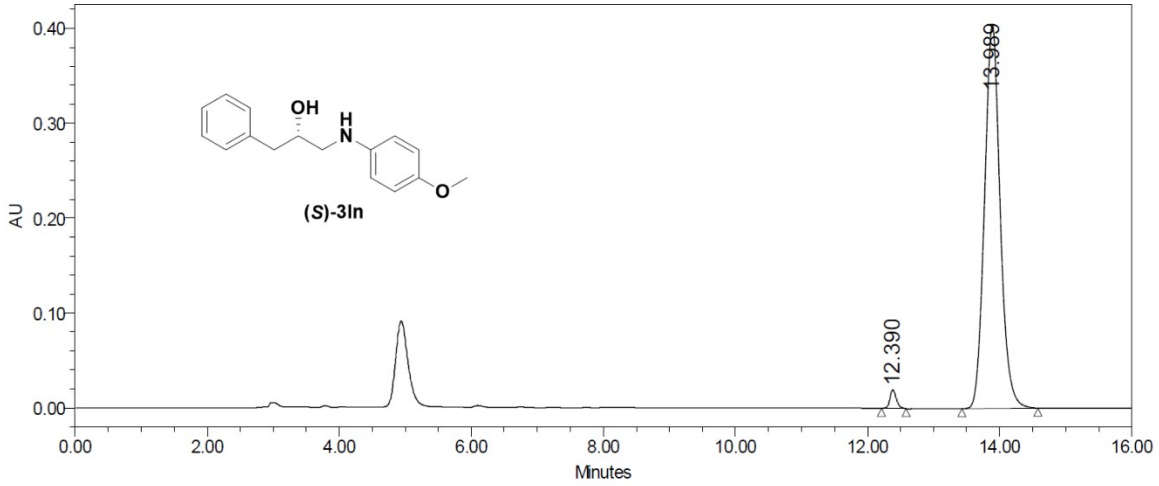
Channel: W2489 ChA; Processed Channel: W2489 ChA 254nm; Result Id: 4502; Processing Method:

Peak#	Ret. Time	Area	Height	Area %
1	8.603	15131180	891127	97.96
2	9.870	315225	18117	2.04



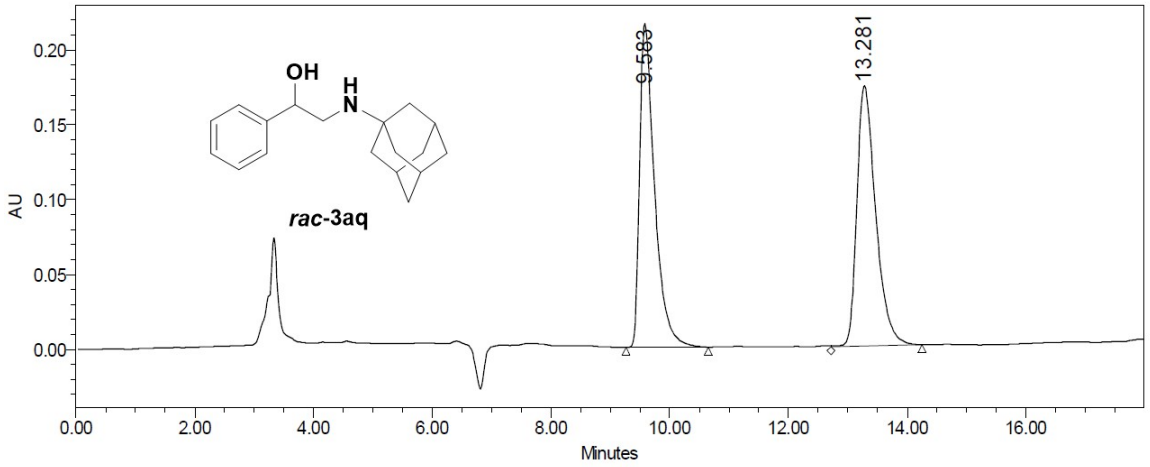
Channel: W2489 ChA; Processed Channel: W2489 ChA 230nm; Result Id: 1528; Processing Method: rac

Peak#	Ret. Time	Area	Height	Area %
1	12.319	22559634	1242041	50.48
2	13.826	22128797	1067949	49.52



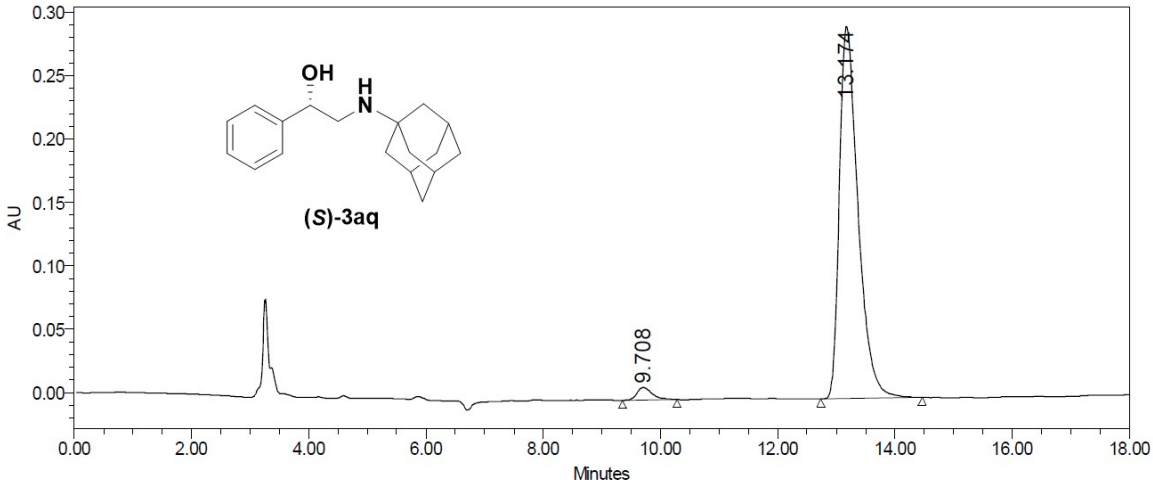
Channel: W2489 ChA; Processed Channel: W2489 ChA 230nm; Result Id: 1533; Processing Method: S

Peak#	Ret. Time	Area	Height	Area %
1	12.390	132598	19556	1.95
2	13.989	6653439	404421	98.05



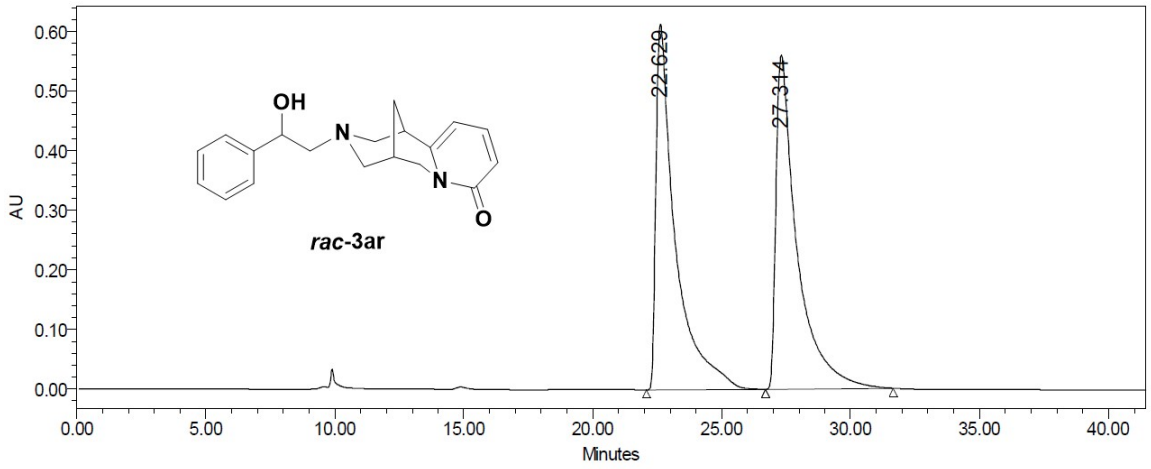
Channel: W2489 ChA; Processed Channel: W2489 ChA 210nm; Result Id: 3244; Processing Method: RAC

Peak#	Ret. Time	Area	Height	Area %
1	9.583	3784345	216176	49.75
2	13.281	3822330	173665	50.25



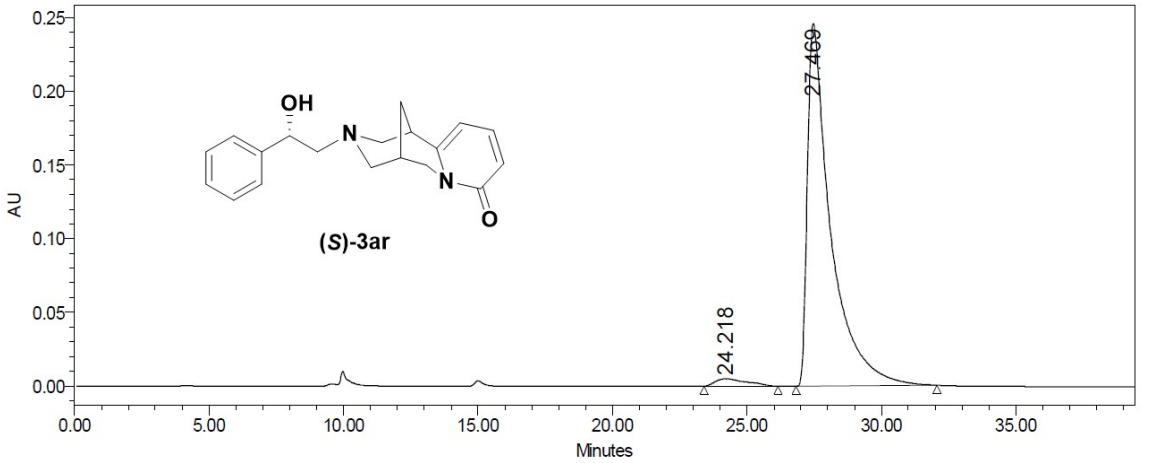
Channel: W2489 ChA; Processed Channel: W2489 ChA 210nm; Result Id: 3246; Processing Method: S

Peak#	Ret. Time	Area	Height	Area %
1	9.708	180844	10078	2.71
2	13.174	6489498	294124	97.29



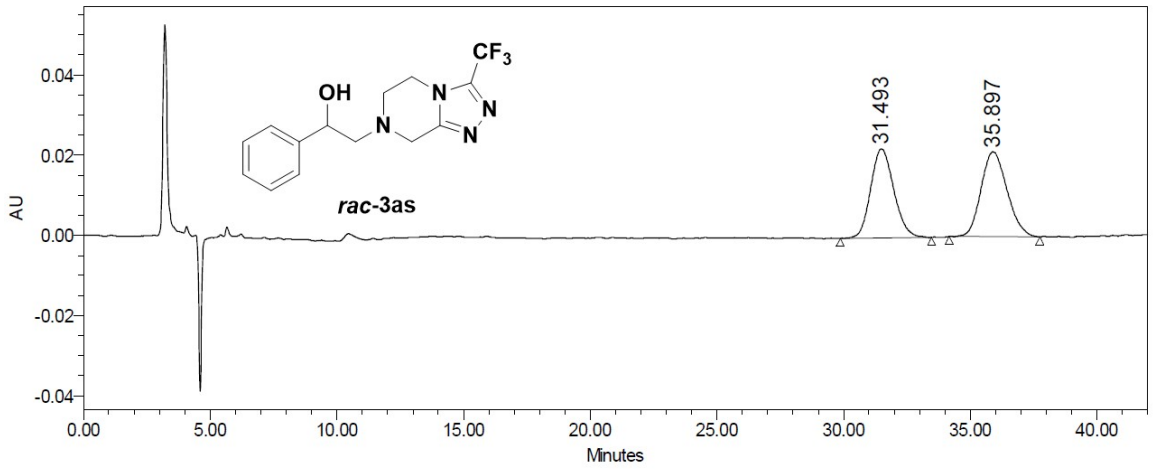
Channel: W2489 ChB; Processed Channel: W2489 ChB 230nm; Result Id: 2867; Processing Method: LYS

Peak#	Ret. Time	Area	Height	Area %
1	22.629	31919457	612776	50.13
2	27.314	31755926	560076	49.87



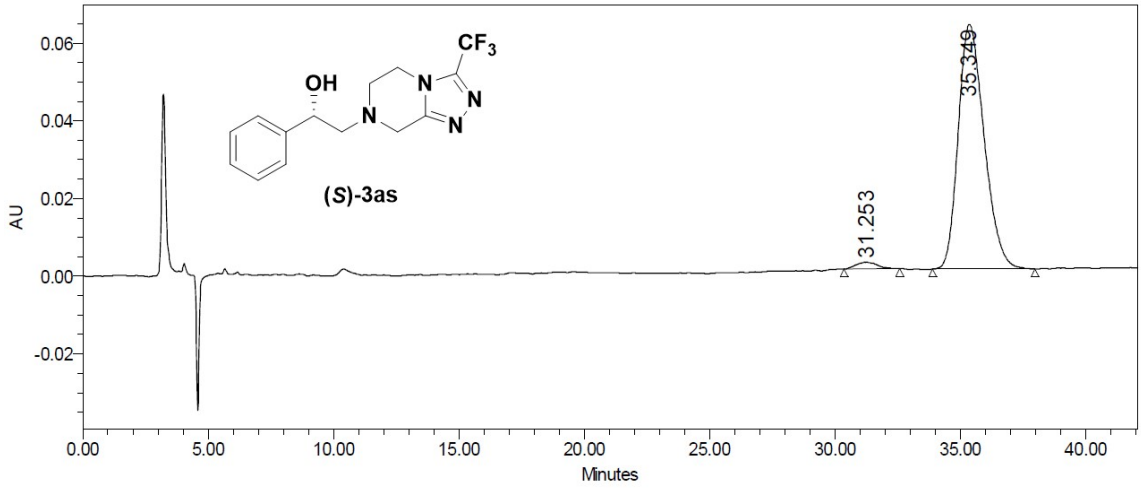
Channel: W2489 ChB; Processed Channel: W2489 ChB 230nm; Result Id: 2869; Processing Method: LYS

Peak#	Ret. Time	Area	Height	Area %
1	24.218	418674	5093	2.74
2	27.469	14841521	246152	97.26



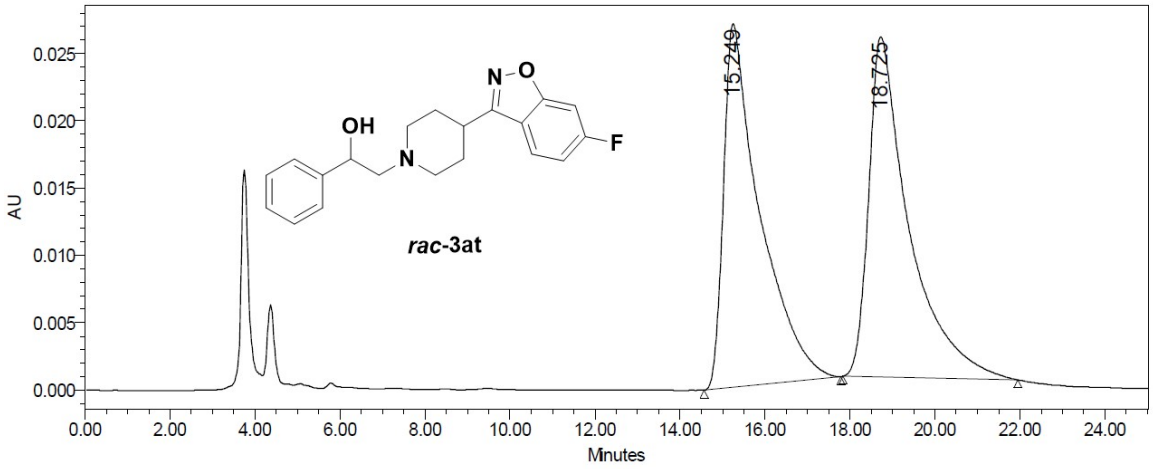
Channel: W2489 ChA; Processed Channel: W2489 ChA 220nm; Result Id: 3299; Processing Method: RAC

Peak#	Ret. Time	Area	Height	Area %
1	31.493	1409802	22206	48.14
2	35.897	1518622	21167	51.86



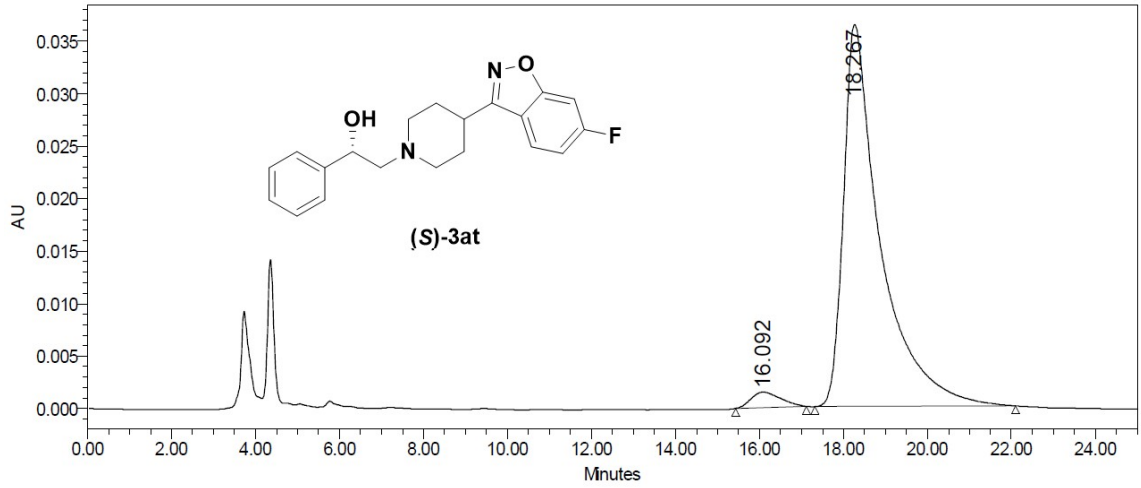
Channel: W2489 ChA; Processed Channel: W2489 ChA 220nm; Result Id: 3297; Processing Method: S

Peak#	Ret. Time	Area	Height	Area %
1	31.253	103546	1714	2.24
2	35.349	4526713	62995	97.76



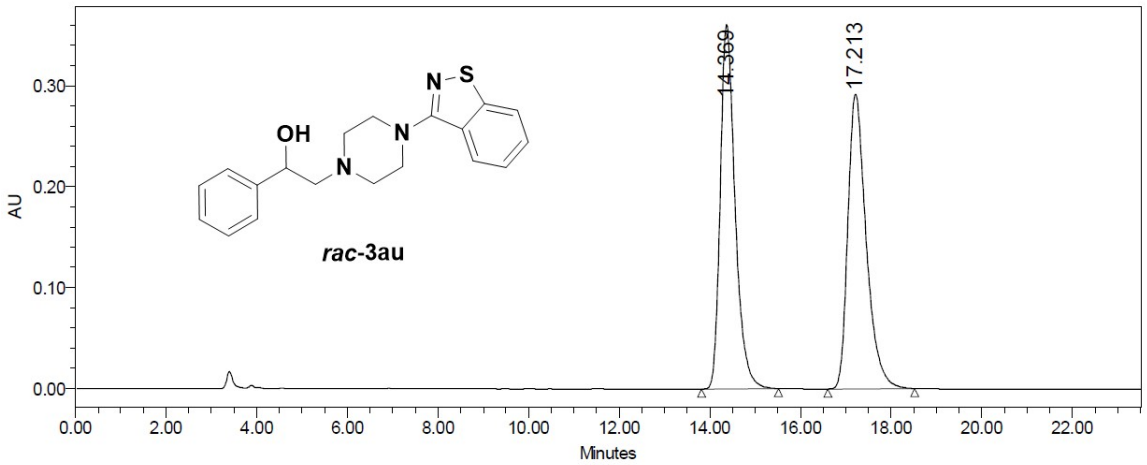
Channel: W2489 ChB; Processed Channel: W2489 ChB 225nm; Result Id: 2650; Processing Method: LPT

Peak#	Ret. Time	Area	Height	Area %
1	15.249	1597226	26996	49.06
2	18.725	1658719	25279	50.94



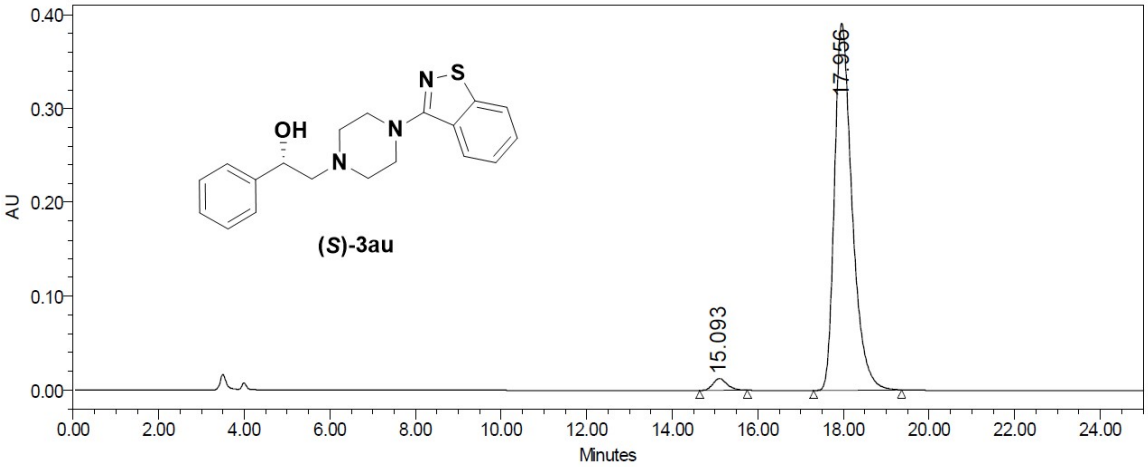
Channel: W2489 ChB; Processed Channel: W2489 ChB 225nm; Result Id: 2662; Processing Method: S

Peak#	Ret. Time	Area	Height	Area %
1	16.092	71779	1472	3.15
2	18.267	2210084	36392	96.85



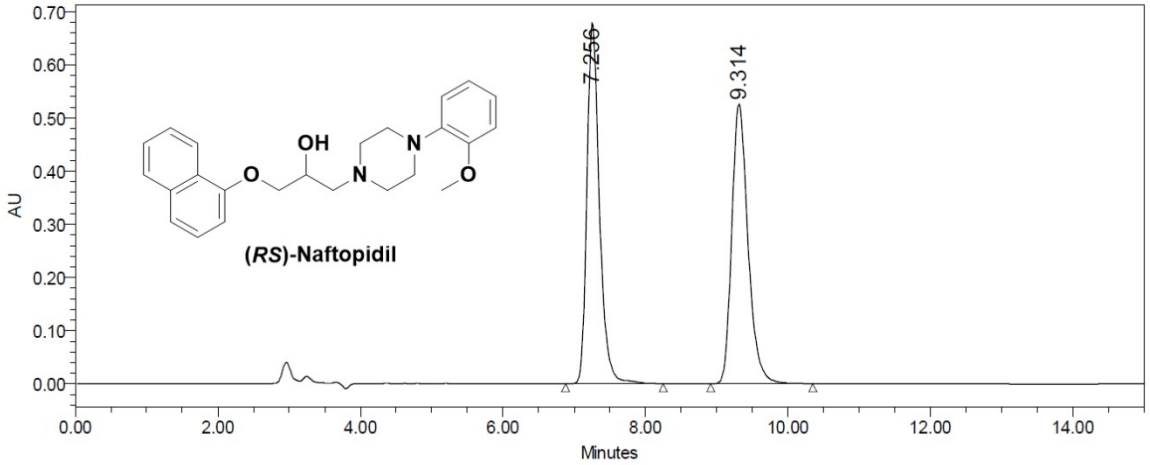
Channel: W2489 ChA; Processed Channel: W2489 ChA 225nm; Result Id: 2676; Processing Method: PLBL

Peak#	Ret. Time	Area	Height	Area %
1	14.369	8210161	360719	50.02
2	17.213	8202298	291957	49.98



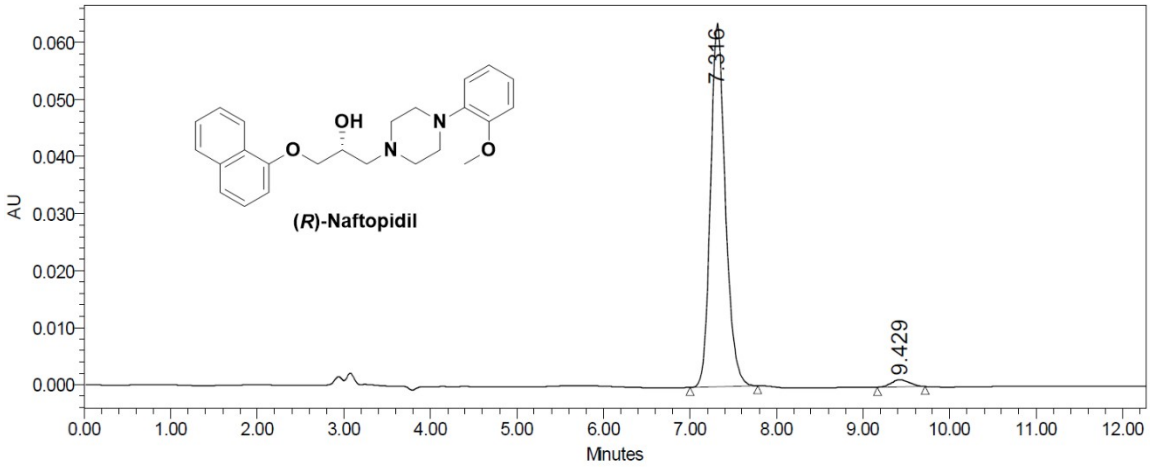
Channel: W2489 ChA; Processed Channel: W2489 ChA 225nm; Result Id: 2696; Processing Method: PLBL

Peak#	Ret. Time	Area	Height	Area %
1	15.093	288216	12538	2.51
2	17.956	11200389	390856	97.49



Channel: W2489 ChB; Processed Channel: W2489 ChB 230nm; Result Id: 3341; Processing Method: RAC

	Ret. Time	Area	Height	Area %
1	7.256	8341007	680775	50.12
2	9.314	8302349	526633	49.88



Channel: W2489 ChB; Processed Channel: W2489 ChB 230nm; Result Id: 3381; Processing Method:

Peak#	Ret. Time	Area	Height	Area %
1	7.316	767526	63676	97.69
2	9.429	18185	1253	2.31