Ru-Tethered (*R*, *R*)-TsDpen with DMAB as an efficient Catalytic system for High Enantioselective One-Pot Synthesis of Chiral β-aminol *via* Asymmetric Transfer Hydrogenation

Ashish A. Mishra and Prof. Bhalchandra M. Bhanage*

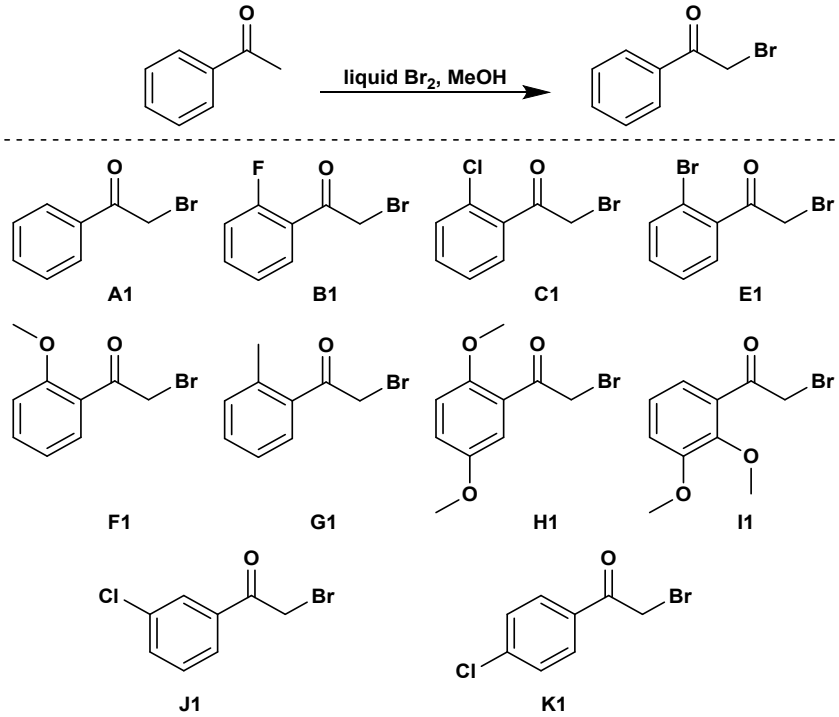
Department of Chemistry, Institute of Chemical Technology,
Nathalal Parekh Marg, Matunga, Mumbai 400019, India;
Fax: (+91)-22-24145614; phone:(+91)-22-3361-1111/2222
E-mail: *bm.bhanage@gmail.com* ; *bm.bhanage@ictmumbai.edu.in*

General material and methods for the synthesis of catalyst:

For the preparation of substituted α-bromoketones various chemicals were used such as: 2-Bromoacetophenone, *n*-hexane (HPLC grade) and IPA (HPLC grade) were procured from Oxford Product Pvt. Ltd. 2'-floroacetophenone, 2'-chloroacetophenone, 2'-bromoacetophenone, 2'-methoxyacetophenone and 2'-methylacetophenone were purchased from Spectrochem. 2',5'-dimethoxyacetophenone, 2',3'-dimethoxyacetophenone, 3'-chloroacetophenone, 4'-chloroacetophenone, $NaHCO_3$ and Ru-Teth-TsDPEN (*R*, *R*) catalyst was purchased from Sigma Aldrich. MeOH, bromine liquid (for synthesis) and DCM were purchased from s d-fine chemicals. Thin Layer Chromatography Silica Gel 60 F_{254} was purchased from Merck Specialities Pvt. Ltd., Silica gel for column chromatography (100-200 mesh) was purchased from SRL, India. NMR spectra were recorded with 500 MHz for ^{1}H NMR and 126 MHz for ^{13}C NMR spectrometer. The chemical shifts are reported in parts per million related to tetramethyl silane as an internal standard and the coupling constant *J* in hertz. ^{1}H NMR spectra are reported relative to residual $CDCl_3$ (d= 7.26 ppm), ^{13}C NMR are reported relative to $CDCl_3$ (d=77.02 ppm). The reaction was monitored by GC and TLC. The products were analysed and confirmed by GC-MS and NMR-Spectroscopy. Enantiomeric excess was determined by HPLC analysis, using chiral column ChiralPAK AD-H and ChiralPAK OJ-H. Optical rotation was measured by Rudolph Research Analytical Autopol VI automatic polarimeter using a 50 mm path-length cell at 589 nm.

Preparation of α-bromoketone:

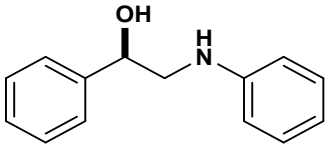
Different substituted α-bromoketones were prepared except A1 by dissolving substituted acetophenone derivatives of 2 mmol in 15 mL of methanol for 30 min. followed by gradual addition of 2-3 mL of liquid bromine in it. Reaction stirred for 5-6 h followed by extraction with ethyl acetate and chilled water, followed by dried of this organic layer over anhydrous Na_2SO_4 further it is filtered and solvent removed under vacuum on rotary evaporator. Final mixture then purified using silica gel chromatography (eluent: *n*-hexane-ethyl acetate, 98-2) to obtain pure substituted α-bromoketones which was then kept under freeze for 12 h as a result most of the compound get solidified and then used in the reaction for chiral synthesis of β-aminol.



Scheme S1: Preparation of α-bromoketones and its derivatives.

Analytical data of *β*-aminol:

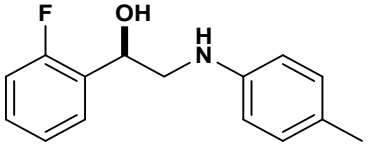
(-)-1-phenyl-2-(phenylamino) ethan-1-ol [D1]



In 15 ml of pressure tube cylinder 1 mmol of 2-bromoacetophenone (A1) and 1 mmol of aniline are taken along with 1 mol% of catalyst Ru-Teth-TsDPEN (*R*, *R*) which was then dissolved in 4 ml of DCM along with the addition of 1 mmol of $NaHCO_3$. After 15 min again 1 mmol of DMAB is added under nitrogen atmosphere and the synthesis of product determined by repeated checking with Thin Layer Chromatography (TLC) further compound is extracted with DCM and water, after this organic layer is dried over anhydrous Na_2SO_4 filtered and solvent removed under vacuum on rotary evaporator. Final mixture then purified using silica gel column chromatography (eluent: *n*-hexane-ethyl acetate, 90-10) to obtain pure (-)-1-phenyl-2-(phenylamino) ethan-1-ol.

Yellow liquid; Yield = 209 mg (98%); (97.95: 2.05 %er, 96% ee); R_f = 0.65 (*n*-hexane: ethyl acetate, 90:10 v/v); $[\alpha]_D^{25}$ = -33.5 (*c* = 1.0 in abs. EtOH)
MS (EI, 70 eV) m/z (%): 213 (M^+15), 182 (100), 107 (100), 77 (85)
^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.45 – 7.37 (m, 4H), 7.36 – 7.31 (m, 1H), 7.24 – 7.16 (m, 2H), 6.76 (t, *J* = 7.3 Hz, 1H), 6.69 (d, *J* = 7.7 Hz, 2H), 4.93 (dd, *J* = 8.3, 3.4 Hz, 1H), 3.44 (dd, *J* = 13.1, 3.4 Hz, 1H), 3.31 (dd, *J* = 13.1, 8.3 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) *δ* 147.86, 142.02, 129.34, 128.63, 128.00, 125.89, 118.13, 113.46, 72.47, 51.79.
HPLC (CHIRALPAK®AD-H elute: *n*-Hexane/*i*-PrOH = 90/10, detector: 210–280 nm, flow rate: 1.0 mL/min); t_{major} = 9.10 min, t_{minor} = 10.94 min.

(-) 1-(2-fluorophenyl)-2-(*p*-tolylamino) ethan-1-ol [D2]

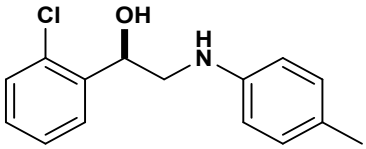


In 15 ml of pressure tube cylinder 1 mmol of 2-bromo-2'-fluoroacetophenone (B1) and 1 mmol of *p*-toluidine are taken along with 1 mol% of catalyst Ru-Teth-TsDPEN (*R*, *R*) which was then dissolved in 4 mL of DCM along with the addition of 1 mmol of $NaHCO_3$. After 15 min again 1 mmol of DMAB is added under nitrogen atmosphere and the synthesis of product determined by repeated checking with Thin Layer Chromatography (TLC) further compound is extracted with DCM and water, after this organic layer is dried over anhydrous Na_2SO_4 filtered and solvent removed under vacuum on rotary evaporator. Final mixture then purified using silica gel column chromatography (eluent: *n*-hexane-ethyl acetate, 90-10) to obtain pure (-)-1-(2-fluorophenyl)-2-(*p*-tolylamino) ethan-1-ol.

Colourless liquid; Yield = 240 mg (98%); (99.6: 0.4 %er, 99% ee); R_f = 0.59 (*n*-hexane: ethyl acetate, 90:10 v/v); $[\alpha]_D^{25}$ = -25.7 (*c* = 1.0 in abs. EtOH)
MS (EI, 70 eV) m/z (%): 245 (M^+15),137 (74), 109 (100), 95 (19)
^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.56 (td, J = 7.4, 1.3 Hz, 1H), 7.33 – 7.26 (m, 1H), 7.19 (td, J = 7.5, 0.9 Hz, 1H), 7.06 (ddd, J = 10.4, 8.3, 1.0 Hz, 1H), 7.03 (dd, J = 12.3, 4.5 Hz, 2H), 6.65 (d, J = 8.4 Hz, 2H), 5.24 (dd, J = 8.8, 3.1 Hz, 1H), 3.52 (dd, J = 13.3, 3.1 Hz, 1H), 3.21 (dd, J = 13.3, 9.0 Hz, 1H), 2.25 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) *δ* 160.75, 158.80, 145.37, 129.84, 129.19, 129.13, 127.53, 127.31, 127.28, 124.42, 124.39, 115.37, 115.20, 113.65, 66.66, 51.02, 20.38.

HPLC (CHIRALCEL®OJ-H elute: *n*-Hexane/*i*-PrOH = 90/10, detector: 210–280 nm, flow rate: 0.7 mL/min); t_{major} = 30.26 min, t_{minor} = 35.38 min.

(-) 1-(2-chlorophenyl)-2-(*p*-tolylamino) ethan-1-ol [D3]



In 15 ml of pressure tube cylinder prepared 1 mmol of 2-bromo-2'-chloroacetophenone (C1) and 1 mmol of *p*-toluidine are taken along with 1 mol% of catalyst Ru-Teth-TsDPEN (*R*, *R*) which was then dissolved in 4 mL of DCM along with the addition of 1 mmol of $NaHCO_3$. After 15 min again 1 mmol of DMAB is added under nitrogen atmosphere and the synthesis of product determined by repeated checking with Thin Layer Chromatography (TLC) further compound is extracted with DCM and water, after this organic layer is dried over anhydrous Na_2SO_4 filtered and solvent removed under vacuum on rotary evaporator. Final mixture then purified using silica gel column chromatography (eluent: *n*-hexane-ethyl acetate, 90-10) to obtain pure (-)-1-(2-chlorophenyl)-2-(*p*-tolylamino) ethan-1-ol.

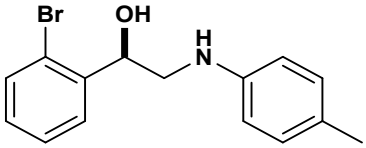
Colourless liquid; Yield = 253 mg (97%); (95.82: 4.18 %er, 92% ee); R_f = 0.57 (*n*-hexane: ethyl acetate, 90:10 v/v); $[\alpha]_D^{25}$ = -37.5 (*c* = 1.0 in abs. EtOH)

MS (EI, 70 eV) m/z (%): 261 (M^+9), 263 (3),120 (100), 91 (14), 65 (9)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 6.5 Hz, 1H), 7.36 (d, *J* = 7.9 Hz, 1H), 7.33 (t, *J* = 7.8 Hz, 1H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.02 (d, *J* = 7.9 Hz, 2H), 6.68 (d, *J* = 8.2 Hz, 2H), 5.32 (dd, *J* = 8.9, 2.7 Hz, 1H), 3.58 (dd, *J* = 13.4, 2.7 Hz, 1H), 3.10 (dd, *J* = 13.4, 9.1 Hz, 1H), 2.25 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.40, 139.40, 129.81, 129.41, 128.78, 127.56, 127.27, 127.19, 113.74, 106.03, 69.05, 50.52, 20.38.

HPLC (CHIRALPAK®AD-H elute: *n*-Hexane/*i*-PrOH = 90/10, detector: 210–280 nm, flow rate: 1.2 mL/min); t_{major} = 16.31 min, t_{minor} = 18.63 min.

(-) 1-(2-bromophenyl)-2-(*p*-tolylamino) ethan-1-ol [D4]



In 15 ml of pressure tube cylinder prepared 1 mmol of 2-bromo-2'-bromoacetophenone (E1) and 1 mmol of *p*-toluidine are taken along with 1 mol% of catalyst Ru-Teth-TsDPEN (*R*, *R*) which was then dissolved in 4 mL of DCM along with the addition of 1 mmol of $NaHCO_3$. After 15 min. again 1 mmol of DMAB is added under nitrogen atmosphere and the synthesis of product determined by repeated checking with Thin Layer Chromatography (TLC) further compound is extracted with DCM and water, after this organic layer is dried over anhydrous Na_2SO_4 filtered and solvent removed under vacuum on rotary evaporator. Final mixture then purified using silica gel column chromatography (eluent: *n*-hexane-ethyl acetate, 90-10) to obtain pure (-)-1-(2-bromophenyl)-2-(*p*-tolylamino) ethan-1-ol.

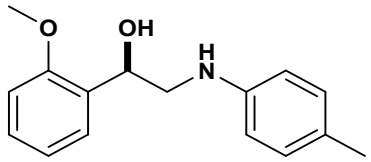
Colourless liquid; Yield = 297 mg (97%); (3.57: 96.43 %er, 93% ee); R_f = 0.50 (*n*-hexane: ethyl acetate, 90:10 v/v); $[\alpha]_D^{25}$ = -27.3 (*c* = 1.0 in abs. EtOH)

MS (EI, 70 eV) m/z (%): 305/307 (M^+24), 185/187 (100), 105 (51), 77 (28)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.55 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.37 (td, *J* = 7.7, 0.7 Hz, 1H), 7.17 (td, *J* = 7.9, 1.7 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 2H), 6.70 (d, *J* = 8.4 Hz, 2H), 5.26 (dd, *J* = 9.1, 3.0 Hz, 1H), 3.58 (dd, *J* = 13.4, 3.0 Hz, 1H), 3.09 (dd, *J* = 13.4, 9.1 Hz, 1H), 2.25 (s,

3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.38, 140.99, 132.69, 129.80, 129.17, 127.80, 127.61, 127.58, 121.81, 113.82, 71.23, 50.58, 20.38.
HPLC (CHIRALCEL®OJ-H elute: *n*-Hexane/*i*-PrOH = 90/10, detector: 210–280 nm, flow rate: 0.7 mL/min); t_{major} = 45.91 min, t_{minor} = 43.27 min.

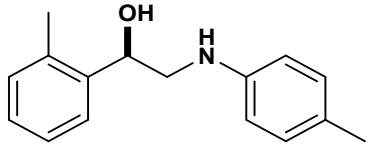
(-) 1-(2-methoxyphenyl)-2-(*p*-tolylamino) ethan-1-ol [D5]



In 15 ml of pressure tube cylinder prepared 1 mmol of 2-bromo-2'-methoxyacetophenone (F1) and 1 mmol of *p*-toluidine are taken along with 1 mol% of catalyst Ru-Teth-TsDPEN (*R*, *R*) which was then dissolved in 4 mL of DCM along with the addition of 1.2 mmol of $NaHCO_3$. After 15 min again 1 mmol of DMAB is added under nitrogen atmosphere and the synthesis of product determined by repeated checking with Thin Layer Chromatography (TLC) further compound is extracted with DCM and water, after this organic layer is dried over anhydrous Na_2SO_4 filtered and solvent removed under vacuum on rotary evaporator. Final mixture then purified using silica gel column chromatography (eluent: *n*-hexane-ethyl acetate, 90-10) to obtain pure (-)-1-(2-methoxyphenyl)-2-(*p*-tolylamino) ethan-1-ol.

Colourless liquid; Yield = 239 mg (93%), (98.95: 1.05 %er, 98% ee); R_f = 0.58 (*n*-hexane: ethyl acetate, 90:10 v/v); $[\alpha]_D^{25}$ = -37.5 (*c* = 1.0 in abs. EtOH)
MS (EI, 70 eV) m/z (%): 257 (M^+30), 241 (64),120 (100), 107 (42), 77 (18)
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.4 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.92 (d, *J* = 8.7 Hz, 2H), 6.61 (d, *J* = 8.4 Hz, 2H), 4.86 (dd, *J* = 8.6, 3.9 Hz, 1H), 3.82 (s, 3H), 3.36 (dd, *J* = 13.0, 4.0 Hz, 1H), 3.27 (dd, *J* = 13.0, 8.6 Hz, 1H), 2.25 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.34, 145.60, 134.18, 129.79, 127.76, 127.16, 113.99, 113.67, 72.05, 67.37, 59.56, 55.31, 52.18, 20.38.
HPLC (CHIRALPAK®AD-H elute: *n*-Hexane/*i*-PrOH = 90/10, detector: 210–280 nm, flow rate: 1.0 mL/min); t_{major} = 19.24 min, t_{minor} = 20.04 min.

(-) 1-(*o*-tolyl)-2-(*p*-tolylamino) ethan-1-ol [D6]

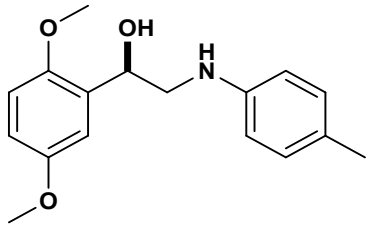


In 15 ml of pressure tube cylinder prepared 1 mmol of 2-bromo-2'-methylacetophenone (G1) and 1 mmol of *p*-toluidine are taken along with 1 mol% of catalyst Ru-Teth-TsDPEN (*R*, *R*) which was then dissolved in 4 mL of DCM along with the addition of 1.2 mmol of $NaHCO_3$. After 15 min again 1 mmol of DMAB is added under nitrogen atmosphere and the synthesis of product determined by repeated checking with Thin Layer Chromatography (TLC) further compound is extracted with DCM and water, after this organic layer is dried over anhydrous Na_2SO_4 filtered and solvent removed under vacuum on rotary evaporator. Final mixture then purified using silica gel column chromatography (eluent: *n*-hexane-ethyl acetate, 90-10) to obtain pure (-)-1-(*o*-tolyl)-2-(*p*-tolylamino) ethan-1-ol.

Colourless liquid; Yield = 219 mg (91%), (96.57: 3.43 %er, 93% ee); R_f = 0.64 (*n*-hexane: ethyl acetate, 90:10 v/v); $[\alpha]_D^{25}$ = -45.3 (*c* = 1.0 in abs. EtOH)
MS (EI, 70 eV) m/z (%): 241 (M^+62), 120 (100), 107 (39), 77 (25)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, J = 6.8 Hz, 1H), 7.26 (t, J = 3.0 Hz, 1H), 7.22 (td, J = 7.3, 1.3 Hz, 1H), 7.17 (d, J = 6.8 Hz, 1H), 7.01 (d, J = 7.9 Hz, 2H), 6.62 (d, J = 8.3 Hz, 2H), 5.15 (dd, J = 9.0, 3.4 Hz, 1H), 3.40 (dd, J = 13.1, 3.4 Hz, 1H), 3.20 (dd, J = 13.1, 9.0 Hz, 1H), 2.38 (s, 3H), 2.25 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.61, 140.07, 134.68, 130.48, 129.82, 127.64, 127.44, 126.41, 125.44, 113.65, 69.11, 51.03, 20.38, 19.13.
HPLC (CHIRALCEL®OJ-H elute: *n*-Hexane/*i*-PrOH = 90/10, detector: 210–280 nm, flow rate: 0.7 mL/min); t_{major} = 31.46 min, t_{minor} = 32.13 min.

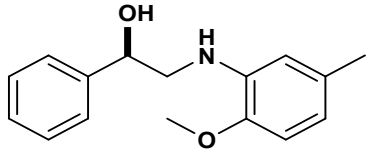
(-) 1-(2,5-dimethoxyphenyl)-2 -(*p*-tolylamino) ethan-1-ol [D7]



In 15 ml of pressure tube cylinder prepared 1 mmol of 2-bromo-2',5'-dimethoxyacetophenone (H1) and 1 mmol of *p*-toluidine are taken along with 1 mol% of catalyst Ru-Teth-TsDPEN (*R*, *R*) which was then dissolved in 4 mL of DCM along with the addition of 1.2 mmol of $NaHCO_3$. After 15 min again 1 mmol of DMAB is added under nitrogen atmosphere and the synthesis of product determined by repeated checking with Thin Layer Chromatography (TLC) further compound is extracted with DCM and water, after this organic layer is dried over anhydrous Na_2SO_4 filtered and solvent removed under vacuum on rotary evaporator. Final mixture then purified using silica gel column chromatography (eluent: *n*-hexane-ethyl acetate, 90-10) to obtain pure (-)-1-(2,5-dimethoxyphenyl)-2 -(*p*-tolylamino) ethan-1-ol.

Colourless liquid; Yield = 273 mg (95%), (98.54: 1.46 %er, 97% ee); R_f = 0.59 (*n*-hexane: ethyl acetate, 90:10 v/v); $[\alpha]_D^{25}$ = -60.0 (*c* = 1.0 in abs. EtOH)
MS (EI, 70 eV) m/z (%): 287 (M^+11), 271 (30),165 (100), 120 (81), 107 (41), 77 (15)
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.01 (dd, J = 7.2, 5.7 Hz, 3H), 6.81 (dt, J = 8.9, 5.9 Hz, 2H), 6.65 (d, J = 8.4 Hz, 2H), 5.11 (dd, J = 8.8, 3.5 Hz, 1H), 3.84 (s, 3H), 3.78 (s, 3H), 3.49 (dd, J = 13.0, 3.5 Hz, 1H), 3.20 (dd, J = 13.0, 8.8 Hz, 1H), 2.25 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 153.89, 150.57, 145.78, 131.07, 129.72, 127.02, 113.55, 112.99, 112.94, 111.45, 68.94, 55.79, 55.76, 50.49, 20.36.
HPLC (CHIRALCEL®OJ-H elute: *n*-Hexane/*i*-PrOH = 90/10, detector: 210–280 nm, flow rate: 0.8 mL/min); t_{major} = 28.03 min, t_{minor} = 31.71 min.

(-) 2-((2-methoxy-5-methylphenyl) amino)-1-phenylethan-1-ol (D8)



In 15 ml of pressure tube cylinder prepared 1 mmol of 2-bromoacetophenone (A1) taken along with 1 mmol of 2-methoxy-5-methylaniline and 1 mol% of catalyst Ru-Teth-TsDPEN (*R*, *R*) which was then dissolved in 4 mL of DCM along with the addition of 1.5 mmol of $NaHCO_3$. After 15 min. 1 mmol of DMAB is added under nitrogen atmosphere and the synthesis of product determined by repeated checking with Thin Layer Chromatography (TLC) further compound is extracted with DCM and water, after this organic layer is dried over anhydrous Na_2SO_4 filtered and solvent removed under vacuum on rotary evaporator. Final mixture then purified using silica-gel column chromatography (eluent: *n*-hexane-ethyl acetate, 90-10) to obtain pure (-)-2-((2-methoxy-5-methylphenyl) amino)-1-phenylethan-1-ol.

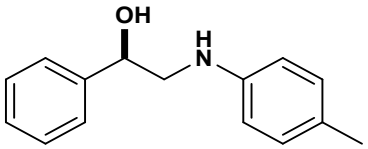
Colourless liquid; Yield = 231 mg (90%), (97.9: 2.3 %er, 95% ee); R_f = 0.59 (*n*-hexane: ethyl acetate, 90:10 v/v); $[\alpha]_D^{25}$ = -63.3 (*c* = 1.0 in abs. EtOH)

MS (EI, 70 eV) m/z (%): 257 (M^+18), 151 (100), 122 (75), 77 (21)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.35 (m, 4H), 7.34 – 7.28 (m, 1H), 6.67 (d, *J* = 8.5 Hz, 1H), 6.50 (s, 2H), 4.93 (dd, *J* = 8.9, 3.4 Hz, 1H), 3.80 (s, 3H), 3.41 (dd, *J* = 13.1, 3.6 Hz, 1H), 3.29 (dd, *J* = 13.1, 8.9 Hz, 1H), 2.25 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.24, 142.11, 137.56, 130.62, 128.54, 127.86, 125.88, 117.37, 111.64, 109.71, 72.53, 55.64, 51.87, 21.12.

HPLC (CHIRALPAK®AD-H elute: *n*-Hexane/*i*-PrOH = 90/10, detector: 210–280 nm, flow rate: 1.0 mL/min); t_{major} = 20.67 min, t_{minor} = 22.31 min.

(-) 1-phenyl-2-(*p*-tolylamino) ethan-1-ol [D9]



In 15 ml of pressure tube cylinder prepared 1 mmol of 2-bromoacetophenone (A1) taken along with 1 mmol of *p*-toluidine and 1 mol% of catalyst Ru-Teth-TsDPEN (*R*, *R*) which was then dissolved in 4 mL of DCM along with the addition of 1 mmol of $NaHCO_3$. After 15 min, 1 mmol of DMAB is added under nitrogen atmosphere and the synthesis of product determined by repeated checking with Thin Layer Chromatography (TLC) further compound is extracted with DCM and water, after this organic layer is dried over anhydrous Na_2SO_4 filtered and solvent removed under vacuum on rotary evaporator. Final mixture then purified using silica-gel column chromatography (eluent: *n*-hexane-ethyl acetate, 90-10) to obtain pure (-)-1-phenyl-2-(*p*-tolylamino) ethan-1-ol.

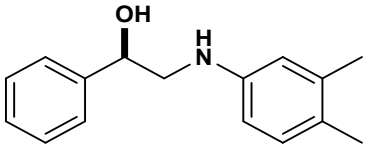
Colourless liquid; Yield = 218 mg (96%), (1.85: 98.15 %er, 96% ee); R_f = 0.59 (*n*-hexane: ethyl acetate, 90:10 v/v); $[\alpha]_D^{25}$ = -45.3 (*c* = 1.0 in abs. EtOH)

MS (EI, 70 eV) m/z (%): 227 (M^+63), 121 (100), 91 (65), 77 (30), 65 (30)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.37 (m, 4H), 7.34 (d, *J* = 6.2 Hz, 1H), 7.02 (d, *J* = 8.1 Hz, 2H), 6.62 (d, *J* = 8.1 Hz, 2H), 4.91 (dd, *J* = 8.7, 3.7 Hz, 1H), 3.41 (dd, *J* = 13.1, 3.7 Hz, 1H), 3.27 (dd, *J* = 13.1, 8.7 Hz, 1H), 2.27 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.55, 142.12, 129.83, 128.60, 127.93, 127.46, 125.90, 113.75, 72.40, 52.26, 20.41.

HPLC (CHIRALCEL®OJ-H elute: *n*-Hexane/*i*-PrOH = 90/10, detector: 210–280 nm, flow rate: 0.5 mL/min); t_{major} = 44.85 min, t_{minor} = 37.21 min.

(-) 2-((3,4-dimethylphenyl) amino)-1-phenylethan-1-ol (D10)



In 15 ml of pressure tube cylinder prepared 1 mmol of 2-bromoacetophenone (A1) taken along with 1 mmol of 3,4-dimethylaniline and 1 mol% of catalyst Ru-Teth-TsDPEN (*R*, *R*) which was then dissolved in 4 mL of DCM along with the addition of 1 mmol of $NaHCO_3$. After 15 min, 1 mmol of DMAB is added under nitrogen atmosphere and the synthesis of product determined by repeated checking with Thin Layer Chromatography (TLC) further compound is extracted with DCM and water, after this organic layer is dried over anhydrous Na_2SO_4 filtered and solvent removed under vacuum on rotary evaporator. Final mixture then purified using silica-gel column chromatography (eluent: *n*-hexane-ethyl acetate, 90-10) to obtain pure (-)-2-((3,4-dimethylphenyl) amino)-1-phenylethan-1-ol.

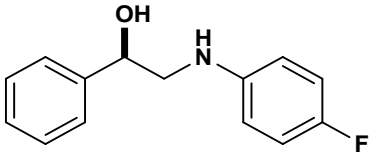
Yellow liquid; Yield = 221 mg (92%), (5.85: 94.15 %er, 88% ee); R_f = 0.56 (*n*-hexane: ethyl acetate, 90:10 v/v); $[\alpha]_D^{25}$ = -63.5 (*c* = 1.0 in abs. EtOH)

MS (EI, 70 eV) m/z (%): 241 (M^+59), 222 (3),134 (100), 105 (26), 77 (35)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 26.1, 5.4 Hz, 5H), 6.97 (d, *J* = 7.9 Hz, 1H), 6.50 (s, 1H), 6.46 (d, *J* = 7.9 Hz, 1H), 4.88 (dd, *J* = 9.1, 3.2 Hz, 1H), 3.38 (dd, *J* = 12.9, 3.2 Hz, 1H), 3.24 (dd, *J* = 12.5, 9.1 Hz, 1H), 2.21 (s, 3H), 2.18 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.96, 142.18, 137.41, 130.35, 128.59, 127.90, 126.29, 125.90, 115.54, 111.06, 72.41, 52.30, 20.03, 18.71.

HPLC (CHIRALPAK®AD-H elute: *n*-Hexane/*i*-PrOH = 90/10, detector: 210–280 nm, flow rate: 1.2 mL/min); t_{major} = 15.57 min, t_{minor} = 12.27 min.

(-) 2-((4-fluorophenyl) amino)-1-phenylethan-1-ol (D11)



In 15 ml of pressure tube cylinder prepared 1 mmol of 2-bromoacetophenone (A1) taken along with 1 mmol of *p*-fluoroaniline and 1 mol% of catalyst Ru-Teth-TsDPEN (*R*, *R*) which was then dissolved in 4 mL of DCM along with the addition of 1 mmol of $NaHCO_3$. After 15 min, 1 mmol of DMAB is added under nitrogen atmosphere and the synthesis of product determined by repeated checking with Thin Layer Chromatography (TLC) further compound is extracted with DCM and water, after this organic layer is dried over anhydrous Na_2SO_4 filtered and solvent removed under vacuum on rotary evaporator. Final mixture then purified using silica-gel column chromatography (eluent: *n*-hexane-ethyl acetate, 90-10) to obtain pure (-)-2-((4-fluorophenyl) amino)-1-phenylethan-1-ol.

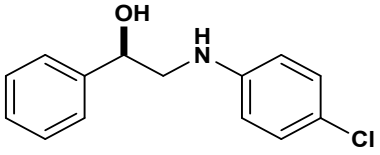
Yellow liquid; Yield = 222 mg (96%), (99.38: 0.62 %er, 99% ee); R_f = 0.68 (*n*-hexane: ethyl acetate, 90:10 v/v); $[\alpha]_D^{25}$ = -58.3 (*c* = 1.0 in abs. EtOH)

MS (EI, 70 eV) m/z (%): 231 (M^+29), 200 (100), 122 (100), 95 (69), 77 (27)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.38 (m, 1H), 7.35 (d, *J* = 4.1 Hz, 3H), 7.32 – 7.26 (m, 1H), 6.85 (dt, *J* = 50.2, 8.7 Hz, 2H), 6.55 (ddd, *J* = 13.4, 9.0, 3.4 Hz, 2H), 4.43 (dd, *J* = 7.2, 4.1 Hz, 1H), 3.93 (dd, *J* = 11.1, 4.1 Hz, 1H), 3.74 (dd, *J* = 11.1, 7.2 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.13, 154.79, 143.49, 143.47, 139.84, 128.85, 128.65, 128.07, 127.69, 126.68, 125.84, 115.84, 115.65, 115.62, 115.43, 114.73, 114.66, 114.41, 114.34, 72.44, 67.33, 60.46, 52.42.

HPLC (CHIRALPAK®AD-H elute: *n*-Hexane/*i*-PrOH = 90/10, detector: 210–280 nm, flow rate: 1.0 mL/min); t_{major} = 15.77 min, t_{minor} = 16.45 min.

(-) 2-((4-chlorophenyl) amino)-1-phenylethan-1-ol (D12)

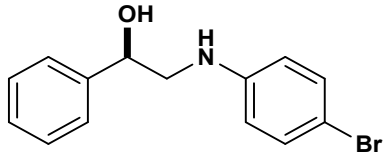


In 15 ml of pressure tube cylinder prepared 1 mmol of 2-bromoacetophenone (A1) taken along with 1 mmol of *p*-chloroaniline and 1 mol% of catalyst Ru-Teth-TsDPEN (*R*, *R*) which was then dissolved in 4 mL of DCM along with the addition of 1 mmol of $NaHCO_3$. After 15 min., 1 mmol of DMAB is added under nitrogen atmosphere and the synthesis of product determined by repeated checking with

Thin Layer Chromatography (TLC) further compound is extracted with DCM and water, after this organic layer is dried over anhydrous Na_2SO_4 filtered and solvent removed under vacuum on rotary evaporator. Final mixture then purified using silica-gel column chromatography (eluent: *n*-hexane-ethyl acetate, 90-10) to obtain pure (-)-2-((4-chlorophenyl) amino)-1-phenylethan-1-ol.

Yellow liquid; Yield = 233 mg (94%), (96.48: 3.52 %er, 93% ee); R_f = 0.69 (*n*-hexane: ethyl acetate, 90:10 v/v); $[\alpha]_D^{25}$ = -56.0 (*c* = 1.0 in abs. EtOH)
MS (EI, 70 eV) m/z (%): 247 (M^+57), 249 (19), 141 (100), 105 (25), 77 (46)
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.37 (m, 4H), 7.36 – 7.30 (m, 1H), 7.13 (dd, *J* = 6.8, 2.1 Hz, 2H), 6.58 (d, *J* = 8.7 Hz, 2H), 4.91 (dd, *J* = 8.2, 3.7 Hz, 1H), 3.38 (dd, *J* = 12.9, 3.7 Hz, 1H), 3.28 (dd, *J* = 12.9, 8.6 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 146.47, 141.84, 129.13, 128.69, 128.15, 125.86, 122.60, 114.48, 72.47, 51.73.
HPLC (CHIRALPAK®AD-H elute: *n*-Hexane/*i*-PrOH = 90/10, detector: 210–280 nm, flow rate: 0.8 mL/min); t_{major} = 27.64 min, t_{minor} = 34.08 min.

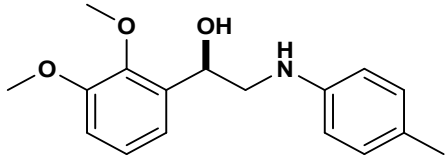
(-) 2-((4-bromophenyl) amino)-1-phenylethan-1-ol (D13)



In 15 ml of pressure tube cylinder prepared 1 mmol of 2-bromoacetophenone (A1) taken along with 1.2 mmol of *p*-bromoaniline and 1 mol% of catalyst Ru-Teth-TsDPEN (*R*, *R*) which was then dissolved in 4 mL of DCM along with the addition of 1.5 mmol of $NaHCO_3$. After 15 min. 1 mmol of DMAB is added under nitrogen atmosphere and the synthesis of product determined by repeated checking with Thin Layer Chromatography (TLC) further compound is extracted with DCM and water, after this organic layer is dried over anhydrous Na_2SO_4 filtered and solvent removed under vacuum on rotary evaporator. Final mixture then purified using silica-gel column chromatography (eluent: *n*-hexane-ethyl acetate, 90-10) to obtain pure (-)-2-((4-bromophenyl) amino)-1-phenylethan-1-ol.

Yellow liquid; Yield = 271 mg (93%), (97.07: 2.93 %er, 94% ee); R_f = 0.69 (*n*-hexane: ethyl acetate, 90:10 v/v); $[\alpha]_D^{25}$ = -54.0 (*c* = 1.0 in abs. EtOH)
MS (EI, 70 eV) m/z (%): 291/293 (M^+26), 184/186 (100), 105 (49), 77 (24)
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 4.0 Hz, 4H), 7.36 – 7.31 (m, 1H), 7.26 (d, *J* = 8.5 Hz, 2H), 6.53 (d, *J* = 8.5 Hz, 2H), 4.89 (dd, *J* = 8.1, 3.6 Hz, 1H), 3.37 (dd, *J* = 12.9, 3.6 Hz, 1H), 3.27 (dd, *J* = 12.9, 8.6 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 146.90, 141.83, 132.00, 128.70, 128.15, 125.86, 114.95, 109.61, 72.44, 51.59.
HPLC (CHIRALPAK®AD-H elute: *n*-Hexane/*i*-PrOH = 90/10, detector: 210–280 nm, flow rate: 1.0 mL/min); t_{major} = 17.50 min, t_{minor} = 29.56 min.

(-) 1-(2,3-dimethoxyphenyl)-2 -(*p*-tolylamino) ethan-1-ol [D14]

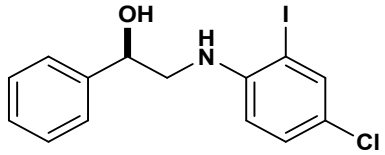


In 15 ml of pressure tube cylinder prepared 1 mmol of 2-bromo-2',3'-dimethoxyacetophenone (I1) taken along with 1.2 mmol of *p*-toluidine and 1 mol% of catalyst Ru-Teth-TsDPEN (*R*, *R*) which was then dissolved in 4 mL of DCM along with the addition of 1.2 mmol of $NaHCO_3$. After 15 min., 1 mmol

of DMAB is added under nitrogen atmosphere and the synthesis of product determined by repeated checking with Thin Layer Chromatography (TLC) further compound is extracted with DCM and water, after this organic layer is dried over anhydrous Na_2SO_4 filtered and solvent removed under vacuum on rotary evaporator. Final mixture then purified using silica-gel column chromatography (eluent: *n*-hexane-ethyl acetate, 90-10) to obtain pure (-)-1-(2,3-dimethoxyphenyl)-2 -(*p*-tolylamino)ethan-1-ol.

Colourless liquid; Yield = 270 mg (94%), (98.57: 1.43 %er, 97% ee); R_f = 0.62 (*n*-hexane: ethyl acetate, 90:10 v/v); $[\alpha]_D^{25}$ = -61.3 (*c* = 1.0 in abs. EtOH)
MS (EI, 70 eV) m/z (%): 287 (M^+18), 271 (34), 165 (100), 120 (75), 77 (15)
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.01 (dd, *J* = 7.2, 5.7 Hz, 3H), 6.81 (dt, *J* = 8.9, 5.9 Hz, 2H), 6.65 (d, *J* = 8.4 Hz, 2H), 5.11 (dd, *J* = 8.8, 3.5 Hz, 1H), 3.84 (s, 3H), 3.78 (s, 3H), 3.49 (dd, *J* = 13.0, 3.5 Hz, 1H), 3.20 (dd, *J* = 13.0, 8.8 Hz, 1H), 2.25 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 13C NMR (126 MHz, cdcl3) δ 153.89, 150.57, 145.78, 131.07, 129.72, 127.02, 113.55, 112.99, 112.94, 111.44, 68.95, 55.79, 55.76, 50.49, 20.36.
HPLC (CHIRALPAK®AD-H elute: *n*-Hexane/*i*-PrOH = 90/10, detector: 210–280 nm, flow rate: 1.0 mL/min); t_{major} = 28.24 min, t_{minor} = 33.80 min.

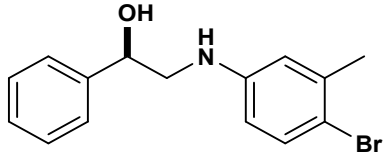
(-) 2-((4-chloro-2-iodophenyl) amino)-1-phenylethan-1-ol (D15)



In 15 ml of pressure tube cylinder prepared 1 mmol of 2-bromoacetophenone (A1) taken along with 1.5 mmol of 4-chloro-2-iodoaniline and 1 mol% of catalyst Ru-Teth-TsDPEN (*R*, *R*) which was then dissolved in 4 mL of DCM along with the addition of 1.5 mmol of $NaHCO_3$. After 15 min., 1 mmol of DMAB is added under nitrogen atmosphere and the synthesis of product determined by repeated checking with Thin Layer Chromatography (TLC) further compound is extracted with DCM and water, after this organic layer is dried over anhydrous Na_2SO_4 filtered and solvent removed under vacuum on rotary evaporator. Final mixture then purified using silica-gel column chromatography (eluent: *n*-hexane-ethyl acetate, 75-25) to obtain pure (-)-2-((4-chloro-2-iodophenyl) amino)-1-phenylethan-1-ol.

Dark Yellow liquid; Yield = 355 mg (95%), (99.34: 0.66 %er, 99% ee); R_f = 0.39 (*n*-hexane: ethyl acetate, 75:25 v/v); $[\alpha]_D^{25}$ = -63.5 (*c* = 1.0 in abs. EtOH)
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 2.3 Hz, 1H), 7.41 – 7.36 (m, 4H), 7.33 (d, *J* = 5.4 Hz, 1H), 7.15 (dd, *J* = 8.2, 1.6 Hz, 1H), 6.50 (d, *J* = 8.7 Hz, 1H), 4.94 (dd, *J* = 7.3, 3.7 Hz, 1H), 3.40 (dd, *J* = 12.3, 3.9 Hz, 1H), 3.32 (dd, *J* = 12.3, 7.3 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.85, 141.55, 138.00, 129.19, 128.74, 128.26, 125.86, 122.44, 111.23, 85.30, 72.36, 51.80.
HPLC (CHIRALPAK®AD-H elute: *n*-Hexane/*i*-PrOH = 90/10, detector: 210–280 nm, flow rate: 1.0 mL/min); t_{major} = 16.27 min, t_{minor} = 20.32 min.

(-) 2-((4-bromo-3-methylphenyl) amino)-1-phenylethan-1-ol (D16)

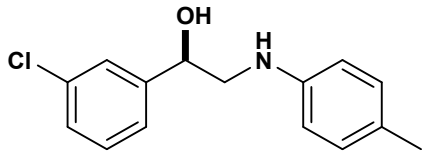


In 15 ml of pressure tube cylinder prepared 1 mmol of 2-bromoacetophenone (A1) taken along with 1.5 mmol of 4-bromo-3-methylaniline and 1 mol% of catalyst Ru-Teth-TsDPEN (*R*, *R*) which was then

dissolved in 4 mL of DCM along with the addition of 1.5 mmol of $NaHCO_3$. After 15 min., 1 mmol of DMAB is added under nitrogen atmosphere and the synthesis of product determined by repeated checking with Thin Layer Chromatography (TLC) further compound is extracted with DCM and water, after this organic layer is dried over anhydrous Na_2SO_4 filtered and solvent removed under vacuum on rotary evaporator. Final mixture then purified using silica-gel column chromatography (eluent: *n*-hexane-ethyl acetate, 90-10) to obtain pure (-)-2-((4-bromo-3-methylphenyl) amino)-1-phenylethan-1-ol.

Yellow liquid; Yield = 279 mg (91%), (92.78: 7.22 %er, 86% ee); R_f = 0.62 (*n*-hexane: ethyl acetate, 90:10 v/v); $[\alpha]_D^{25}$ = -64.0 (*c* = 1.0 in abs. EtOH)
MS (EI, 70 eV) m/z (%): 305/307 (M^+25), 198/200 (100), 122 (81), 77 (11)
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.43 (d, *J* = 6.8 Hz, 1H), 7.29 (d, *J* = 6.8 Hz, 1H), 7.22 (t, *J* = 7.7 Hz, 1H), 7.00 (d, *J* = 8.3 Hz, 2H), 6.59 (d, *J* = 8.3 Hz, 2H), 4.83 (dd, *J* = 8.8, 3.7 Hz, 1H), 3.36 (dd, *J* = 13.2, 3.7 Hz, 1H), 3.19 (dd, *J* = 13.2, 8.8 Hz, 1H), 2.25 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.23, 144.41, 130.92, 130.14, 129.87, 128.96, 127.74, 124.48, 122.73, 113.78, 71.61, 52.24, 20.42.
HPLC (CHIRALCEL®OJ-H elute: *n*-Hexane/*i*-PrOH = 90/10, detector: 210–280 nm, flow rate: 0.8 mL/min); t_{major} = 47.81 min, t_{minor} = 50.21 min.

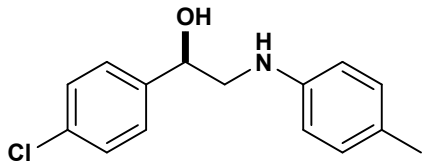
(-) 1-(3-chlorophenyl)-2-(*p*-tolylamino) ethan-1-ol (D17)



In 15 ml of pressure tube cylinder prepared 1 mmol of 2-bromo-3'-chloroacetophenone (J1) taken along with 1.2 mmol of *p*-toluidine and 1 mol% of catalyst Ru-Teth-TsDPEN (*R*, *R*) which was then dissolved in 4 mL of DCM along with the addition of 1.4 mmol of $NaHCO_3$. After 15 min, 1 mmol of DMAB is added under nitrogen atmosphere and the synthesis of product determined by repeated checking with Thin Layer Chromatography (TLC) further compound is extracted with DCM and water, after this organic layer is dried over anhydrous Na_2SO_4 filtered and solvent removed under vacuum on rotary evaporator. Final mixture then purified using silica-gel column chromatography (eluent: *n*-hexane-ethyl acetate, 90-10) to obtain pure (-)-1-(3-chlorophenyl)-2-(*p*-tolylamino)ethan-1-ol.

Yellow liquid; Yield = 246 mg (94%), (9.57: 90.43 %er, 81% ee); R_f = 0.52 (*n*-hexane: ethyl acetate, 90:10 v/v); $[\alpha]_D^{25}$ = -63.3 (*c* = 1.0 in abs. EtOH)
MS (EI, 70 eV) m/z (%): 261 (M^+11), 120 (100), 91 (9), 77 (15)
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.45 (d, *J* = 8.5 Hz, 1H), 7.31 (d, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 7.7 Hz, 1H), 7.02 (d, *J* = 7.9 Hz, 2H), 6.61 (d, *J* = 8.8 Hz, 2H), 4.85 (dd, *J* = 8.6, 3.7 Hz, 1H), 3.38 (dd, *J* = 13.3, 3.7 Hz, 1H), 3.21 (dd, *J* = 13.3, 8.8 Hz, 1H), 2.26 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.27, 144.44, 130.93, 130.14, 129.87, 128.98, 127.74, 124.48, 122.75, 113.80, 71.66, 52.27, 20.40.
HPLC (CHIRALPAK®AD-H elute: *n*-Hexane/*i*-PrOH = 90/10, detector: 210–280 nm, flow rate: 1.0 mL/min); t_{major} = 17.95 min, t_{minor} = 13.15 min.

(-) 1-(4-chlorophenyl)-2-(*p*-tolylamino) ethan-1-ol (D18)



In 15 ml of pressure tube cylinder prepared 1 mmol of 2-bromo-4'-chloroacetophenone (J1) taken along with 1.5 mmol of *p*-toluidine and 1 mol% of catalyst Ru-Teth-TsDPEN (*R*, *R*) which was then dissolved in 4 mL of DCM along with the addition of 1.5 mmol of $NaHCO_3$. After 10 min., 1 mmol of DMAB is added under nitrogen atmosphere and the synthesis of product determined by repeated checking with Thin Layer Chromatography (TLC) further compound is extracted with DCM and water, after this organic layer is dried over anhydrous Na_2SO_4 filtered and solvent removed under vacuum on rotary evaporator. Final mixture then purified using silica-gel column chromatography (eluent: *n*-hexane-ethyl acetate, 90-10) to obtain pure (-)-1-(4-chlorophenyl)-2-(*p*-tolylamino)ethan-1-ol.

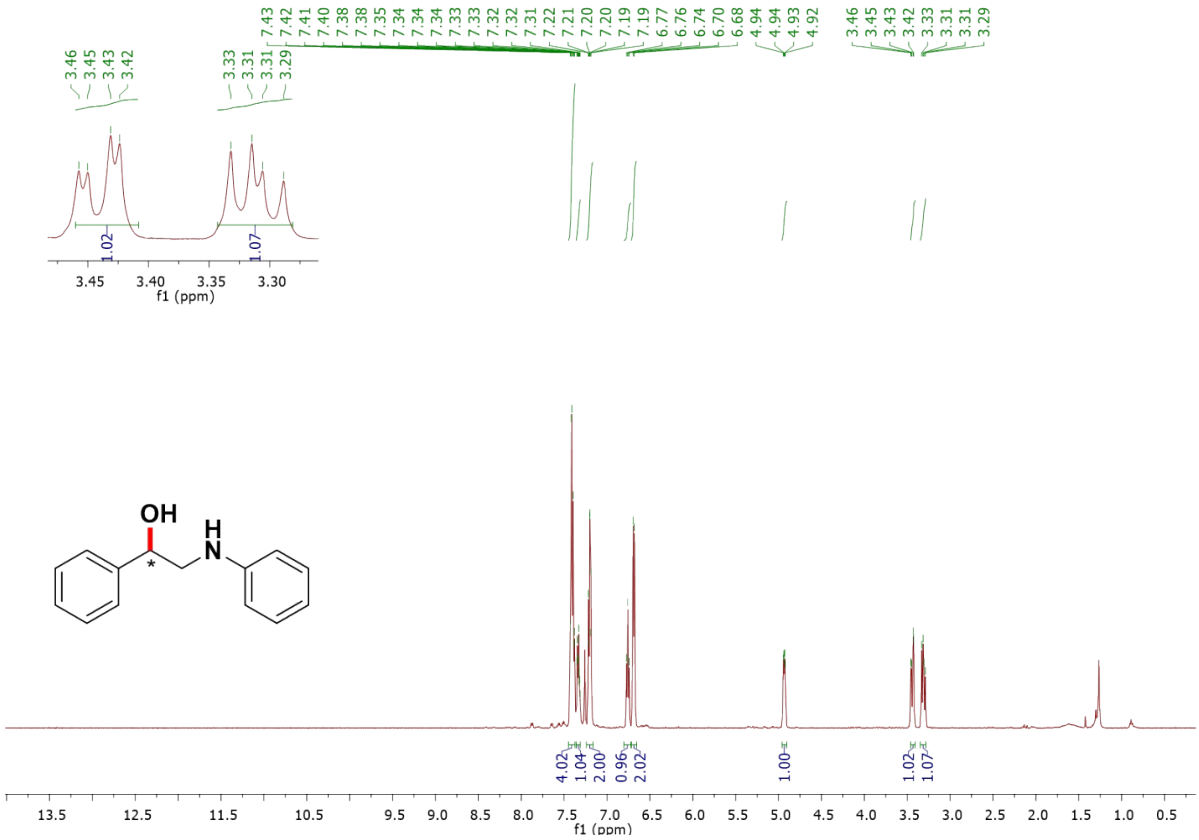
Yellow liquid; Yield = 251 mg (96%), (93.44: 6.56 %er, 87% ee); R_f = 0.52 (*n*-hexane: ethyl acetate, 90:10 v/v); $[\alpha]_D^{25}$ = -56.0 (*c* = 1.0 in abs. EtOH)

MS (EI, 70 eV) m/z (%): 261 (M^+19), 120 (100), 91 (15), 65 (9)

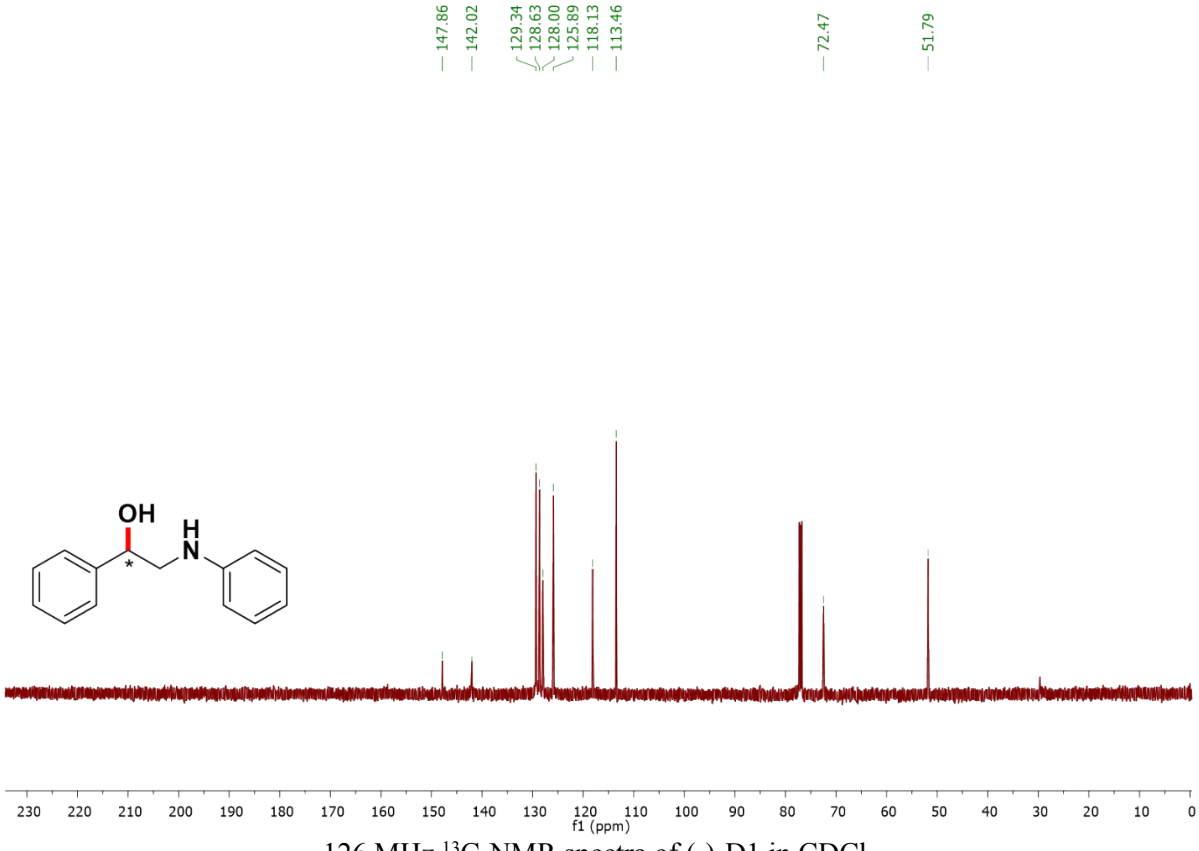
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (s, 4H), 7.00 (d, *J* = 7.9 Hz, 2H), 6.59 (d, *J* = 7.9 Hz, 2H), 4.86 (dd, *J* = 8.5, 3.5 Hz, 1H), 3.35 (dd, *J* = 13.2, 3.5 Hz, 1H), 3.20 (dd, *J* = 13.2, 8.5 Hz, 1H), 2.24 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 145.33, 140.53, 133.59, 129.85, 128.72, 127.71, 127.24, 113.76, 71.72, 52.29, 20.38.

HPLC (CHIRALPAK®AD-H elute: *n*-Hexane/*i*-PrOH = 90/10, detector: 210–280 nm, flow rate: 1.0 mL/min); t_{major} = 15.27 min, t_{minor} = 19.29 min.

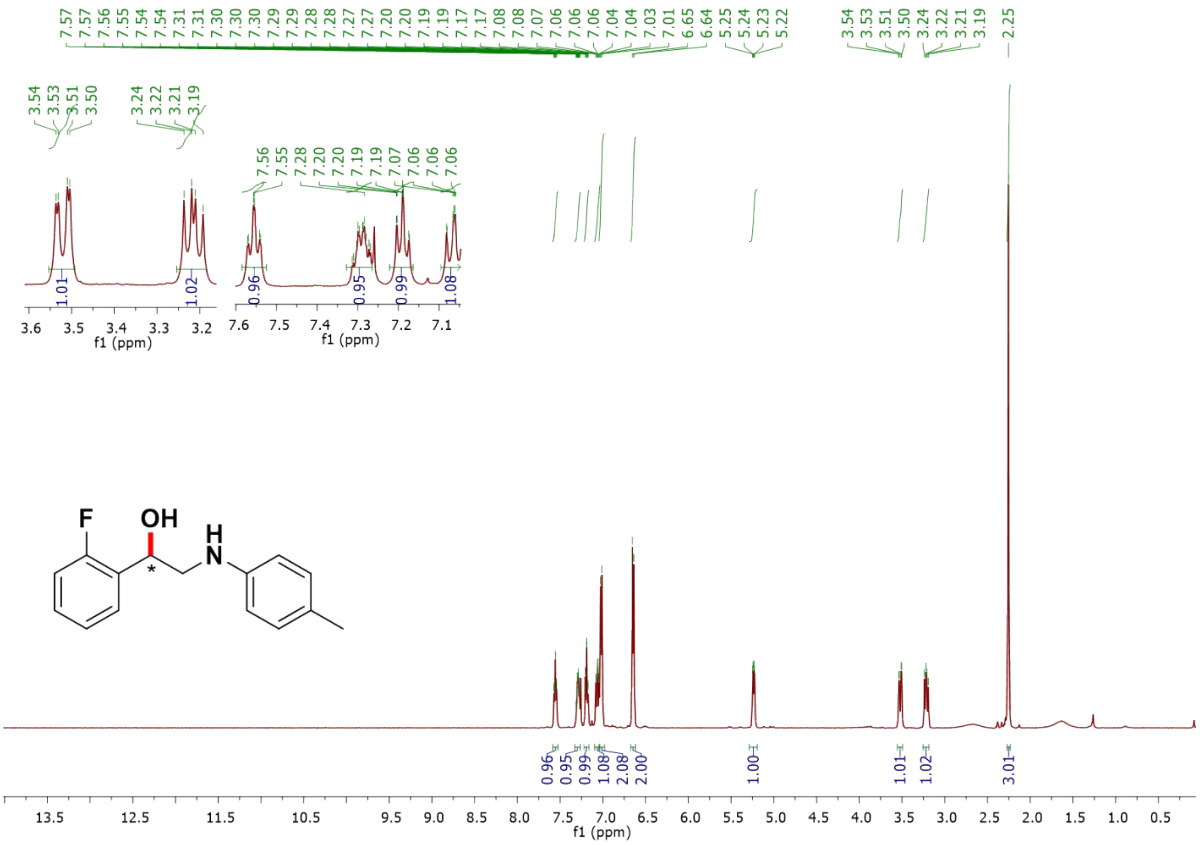
^{1}H & ^{13}C–NMR copy of β-aminol



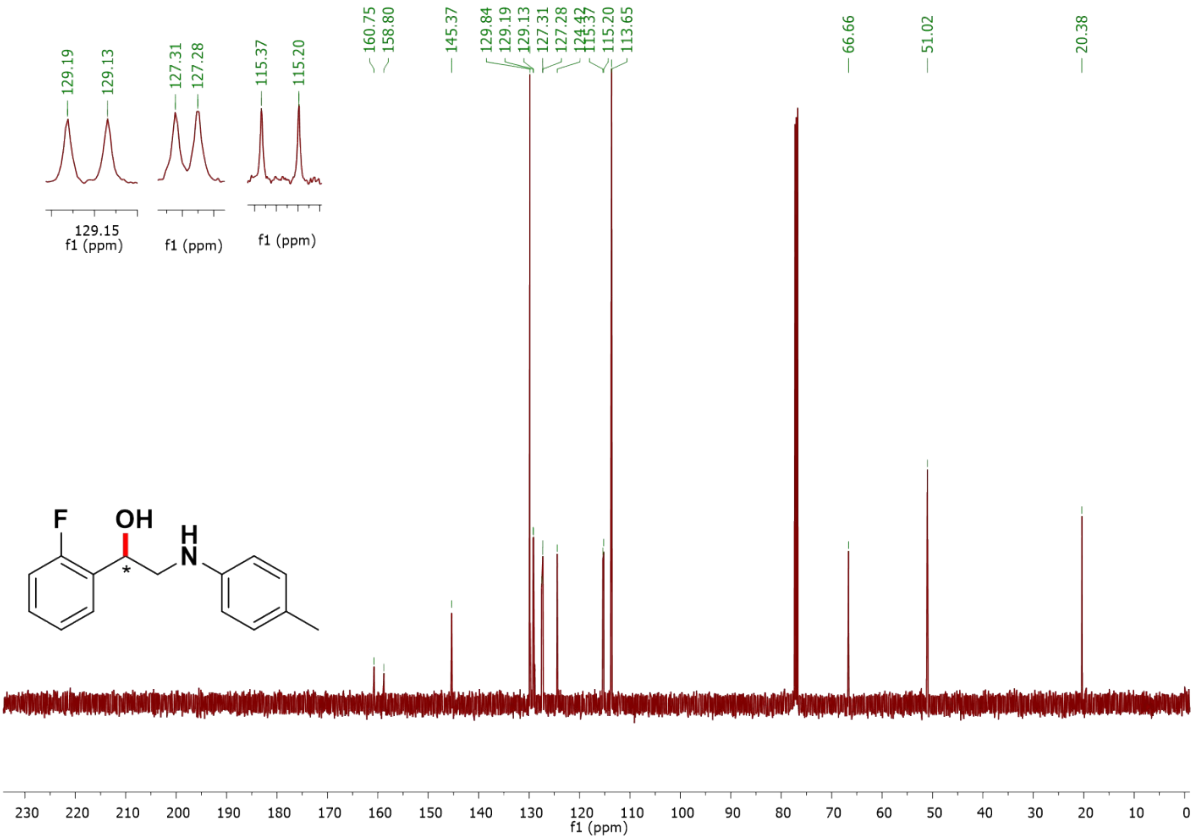
500 MHz ^{1}H-NMR spectra of (-)-D1 in $CDCl_3$



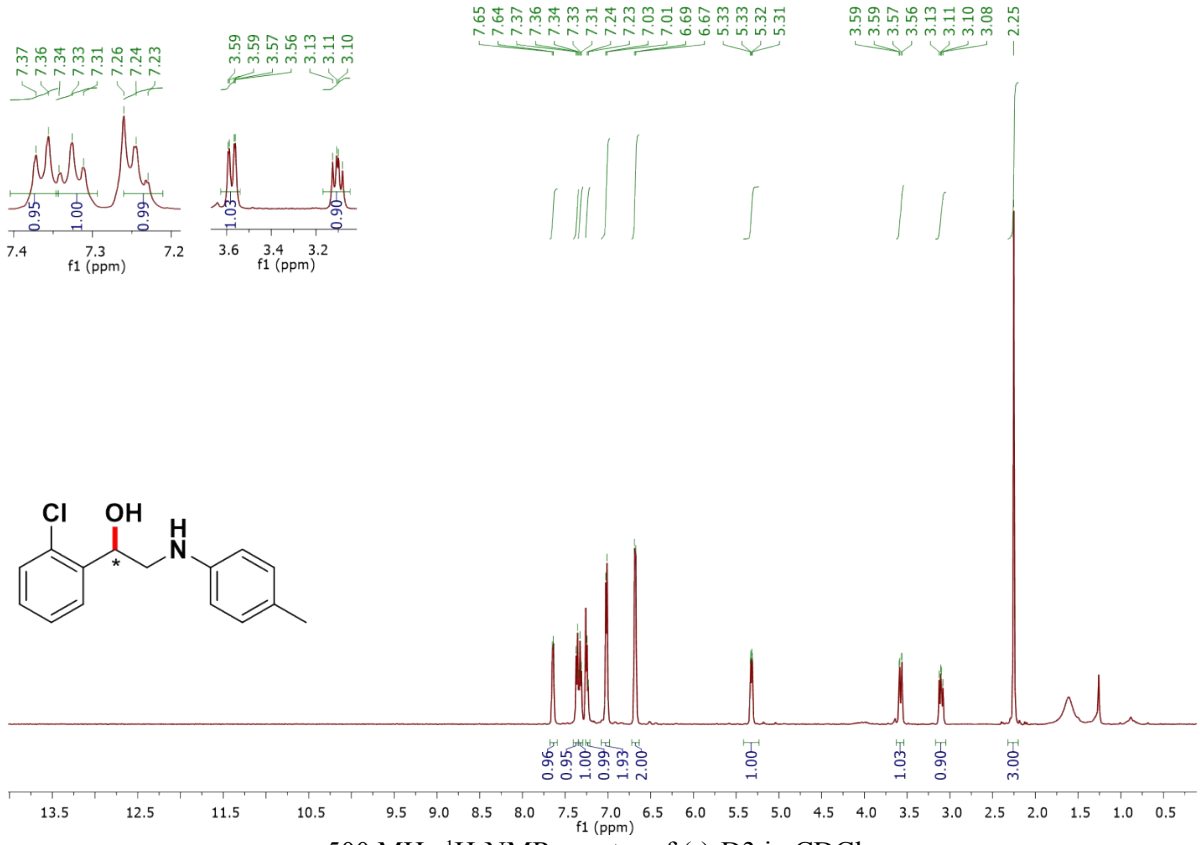
126 MHz ^{13}C-NMR spectra of (-)-D1 in $CDCl_3$



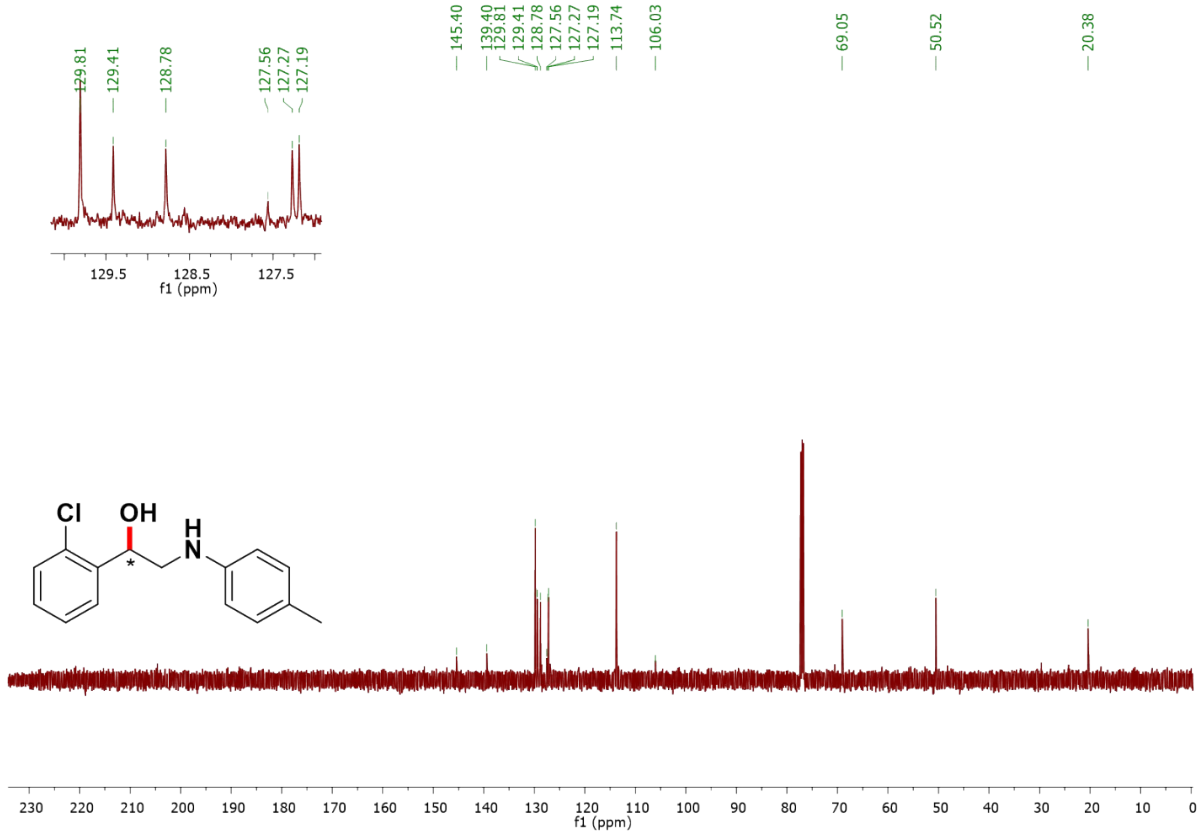
500 MHz ^{1}H-NMR spectra of (-)-D2 in $CDCl_3$



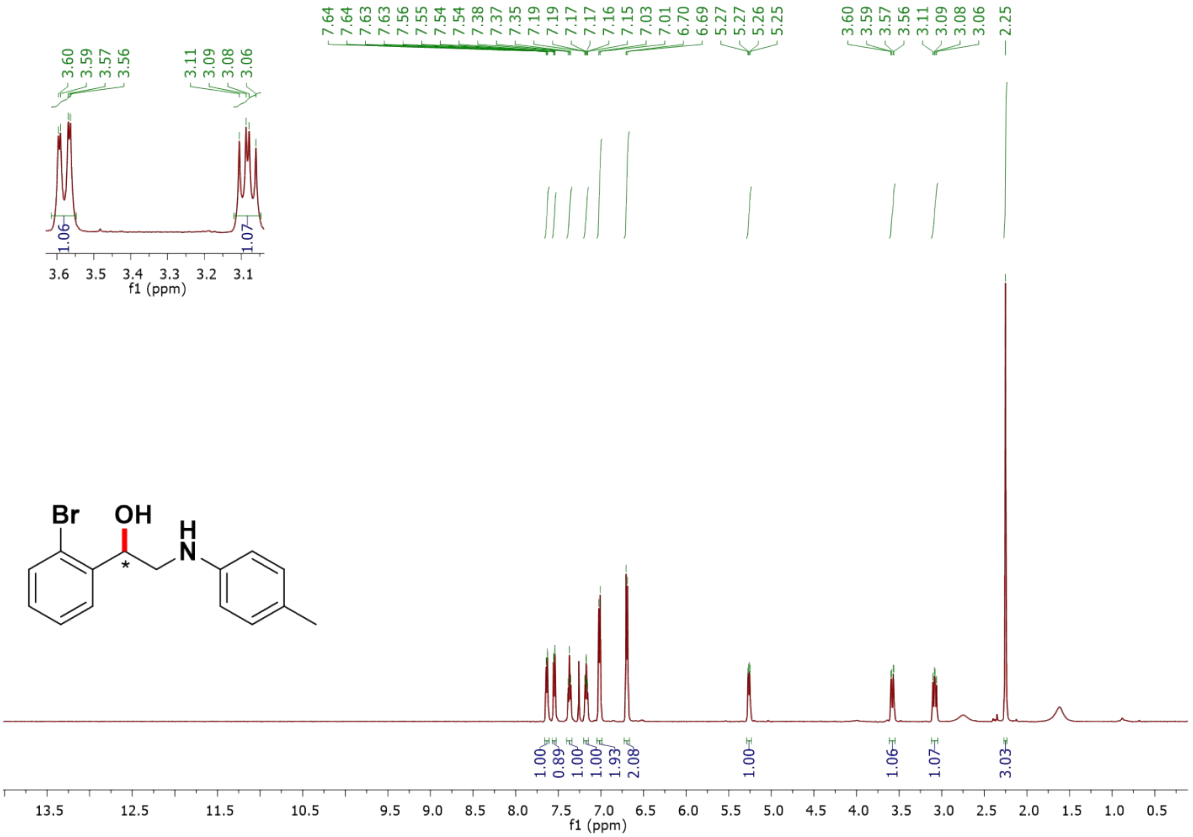
126 MHz ^{13}C-NMR spectra of (-)-D2 in $CDCl_3$



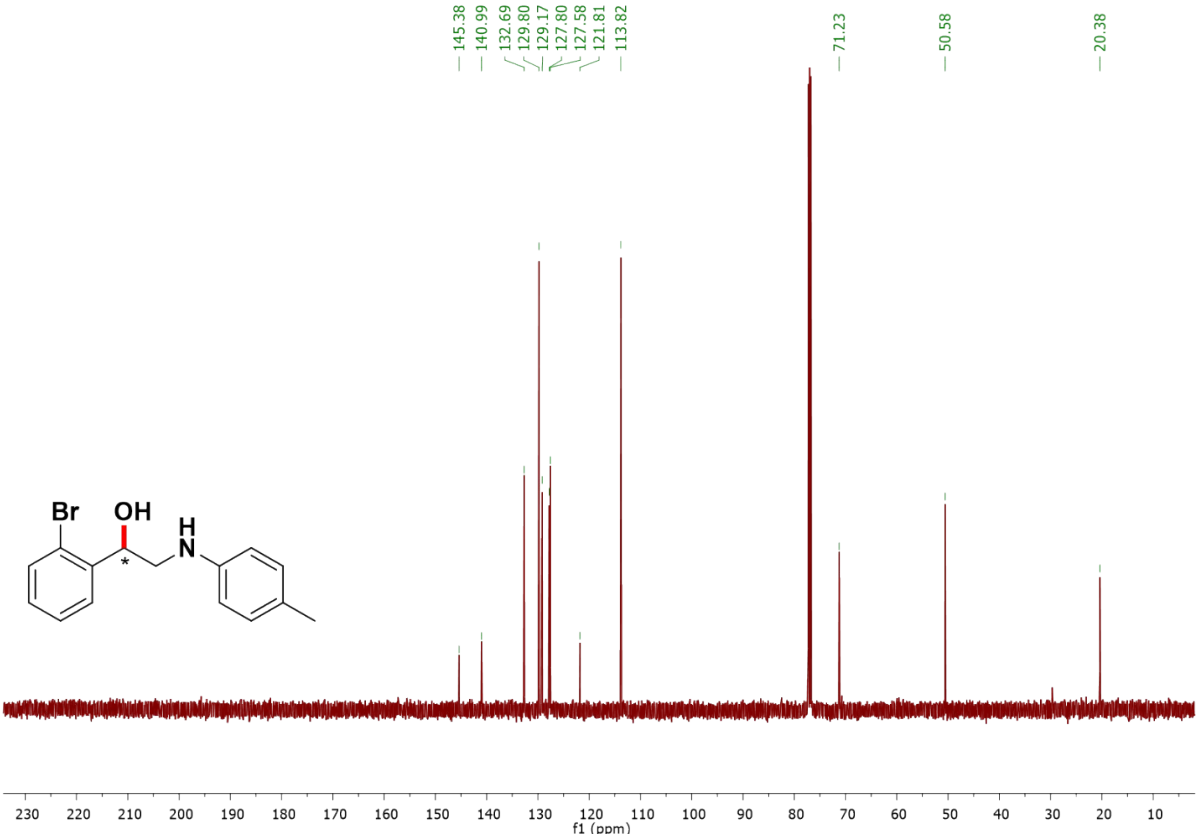
500 MHz ^{1}H-NMR spectra of (-)-D3 in $CDCl_3$



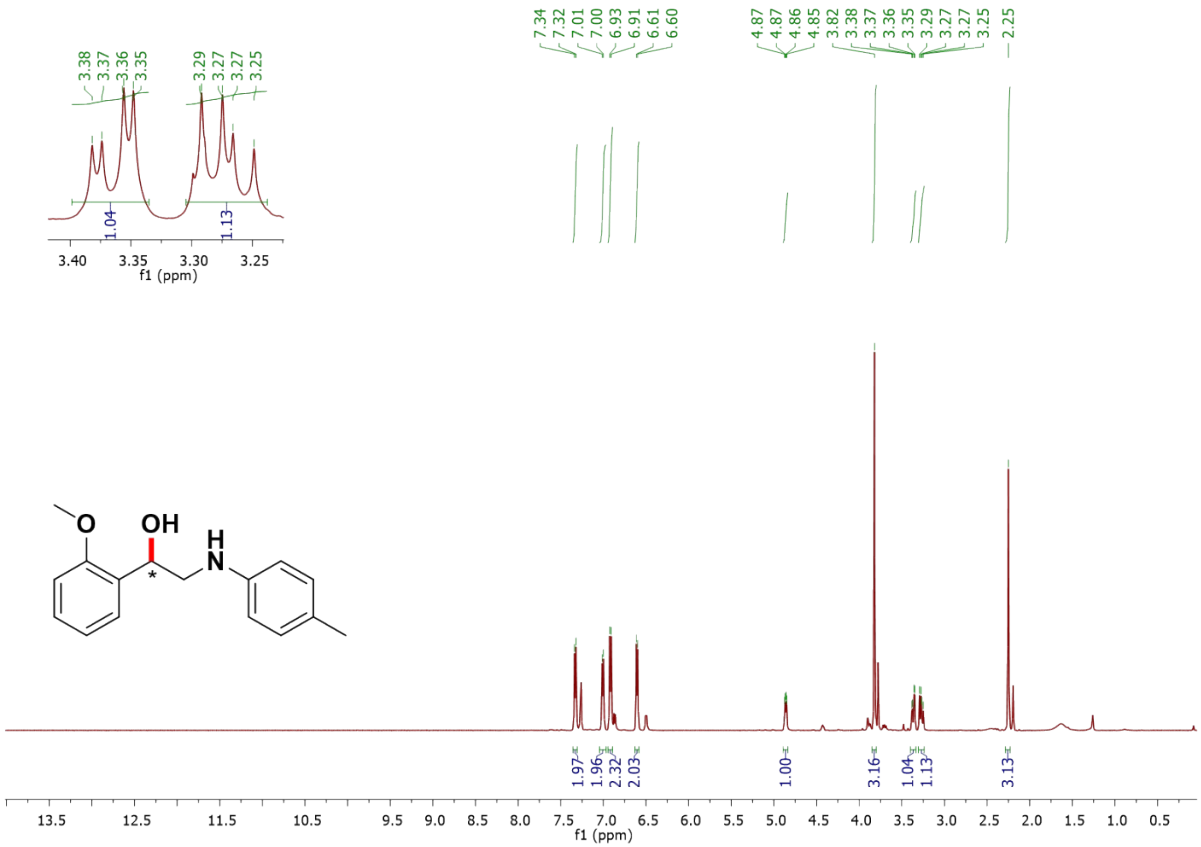
126 MHz ^{13}C-NMR spectra of (-)-D3 in $CDCl_3$



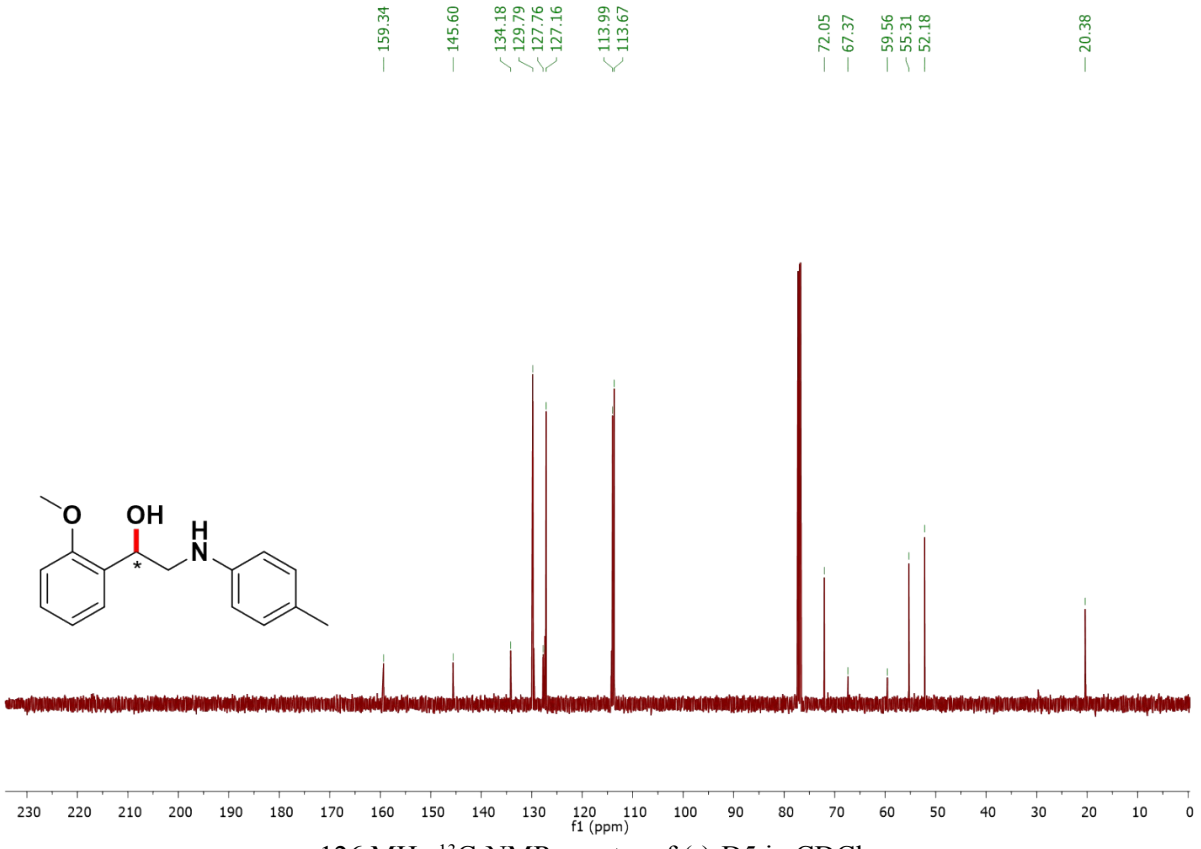
500 MHz ^{1}H-NMR spectra of (-)-D4 in $CDCl_3$



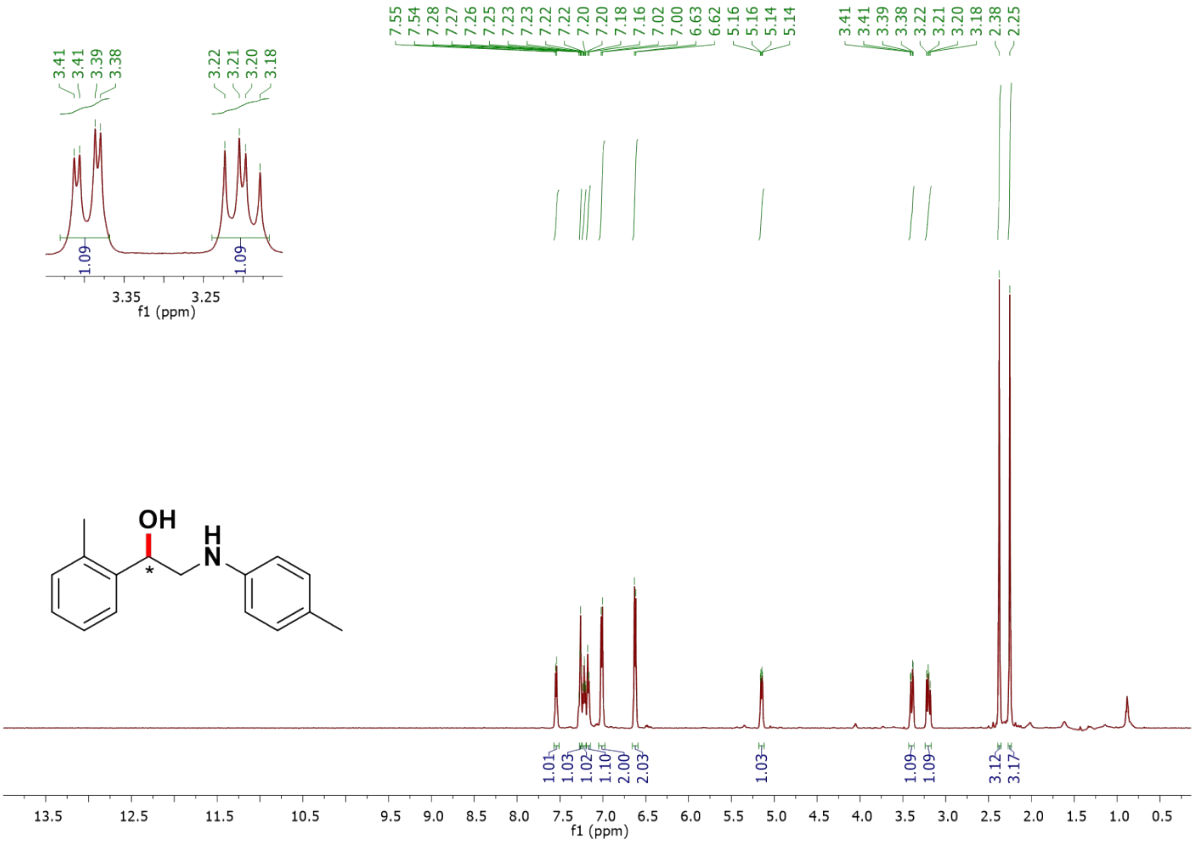
126 MHz ^{13}C-NMR spectra of (-)-D4 in $CDCl_3$



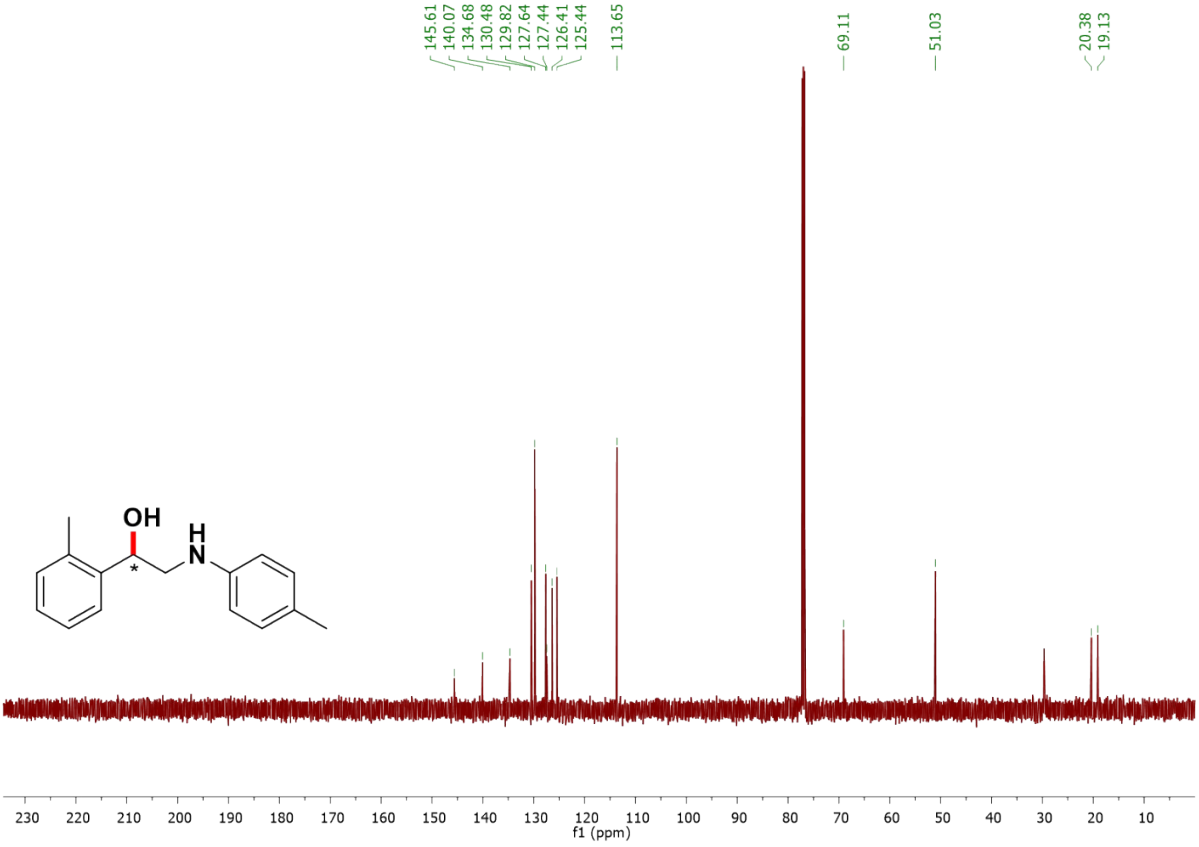
500 MHz ^{1}H-NMR spectra of (-)-D5 in $CDCl_3$



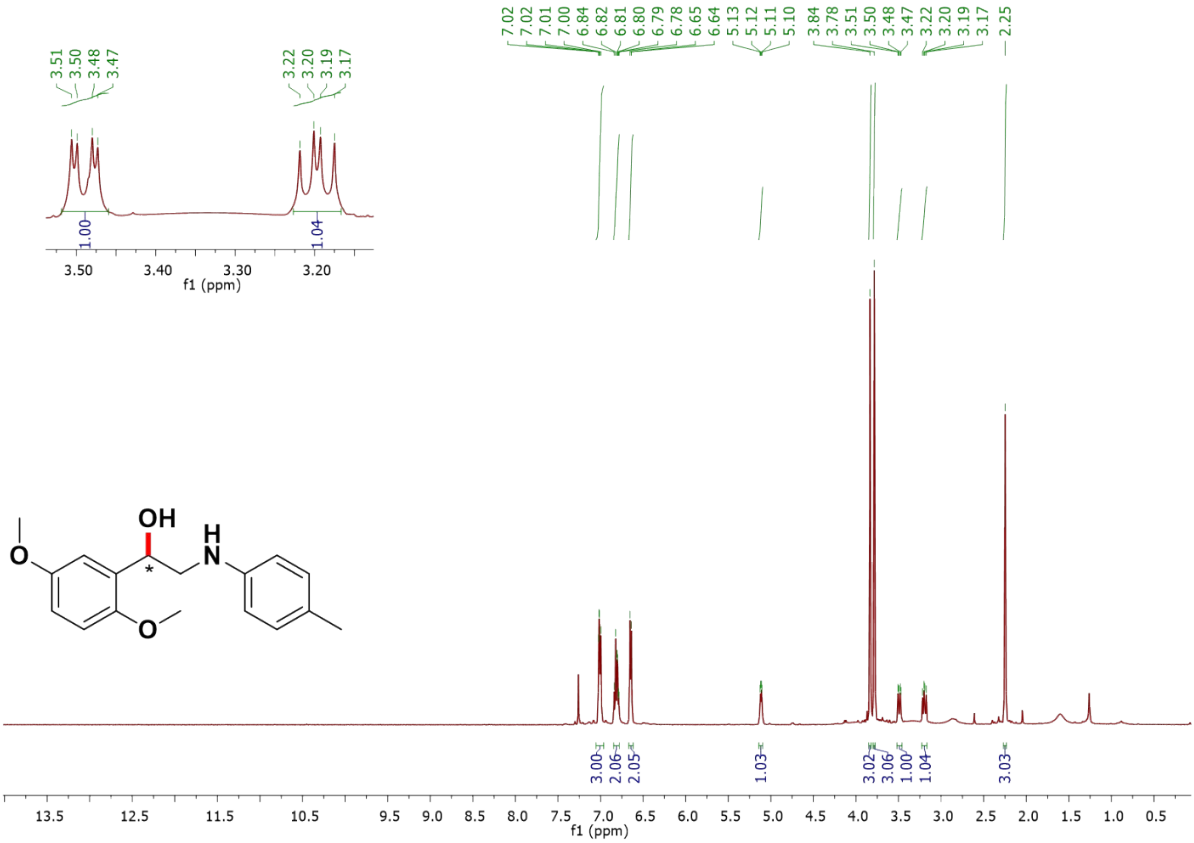
126 MHz ^{13}C-NMR spectra of (-)-D5 in $CDCl_3$



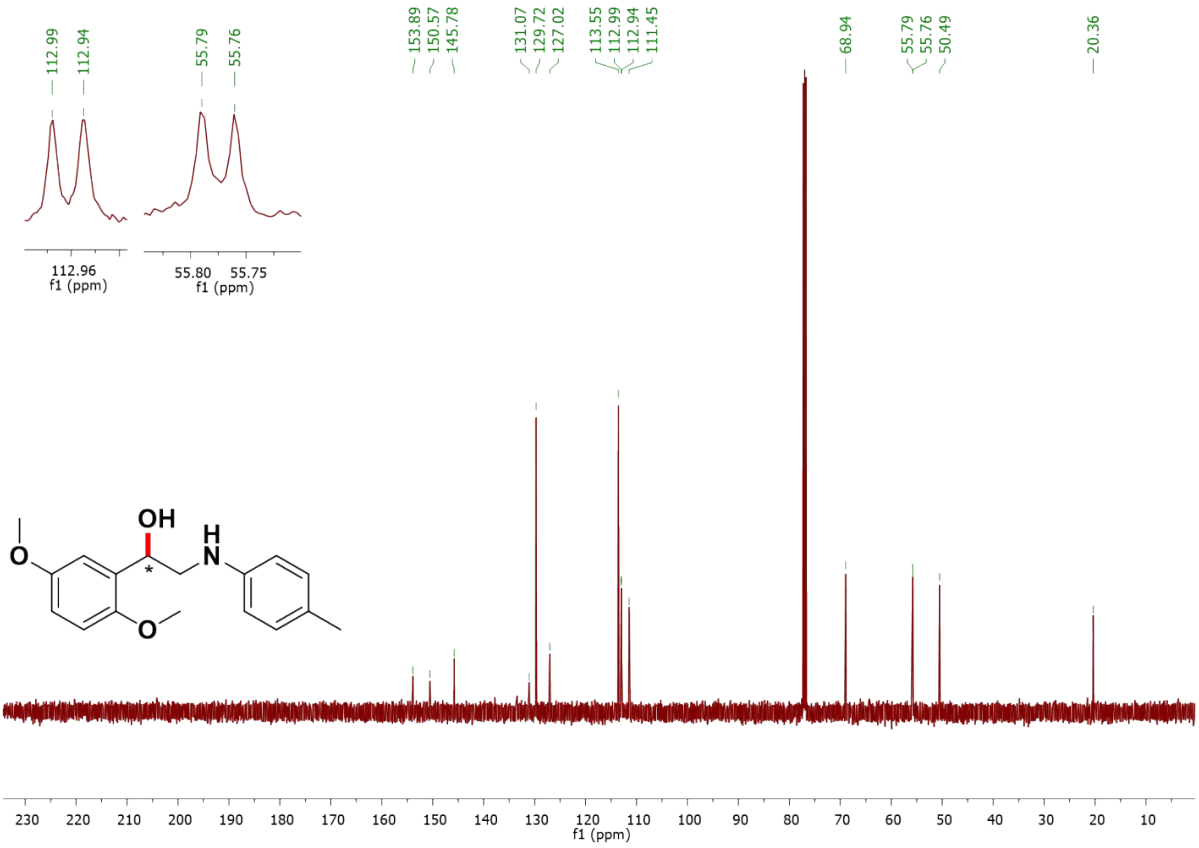
500 MHz ^{1}H-NMR spectra of (-)-D6 in $CDCl_3$



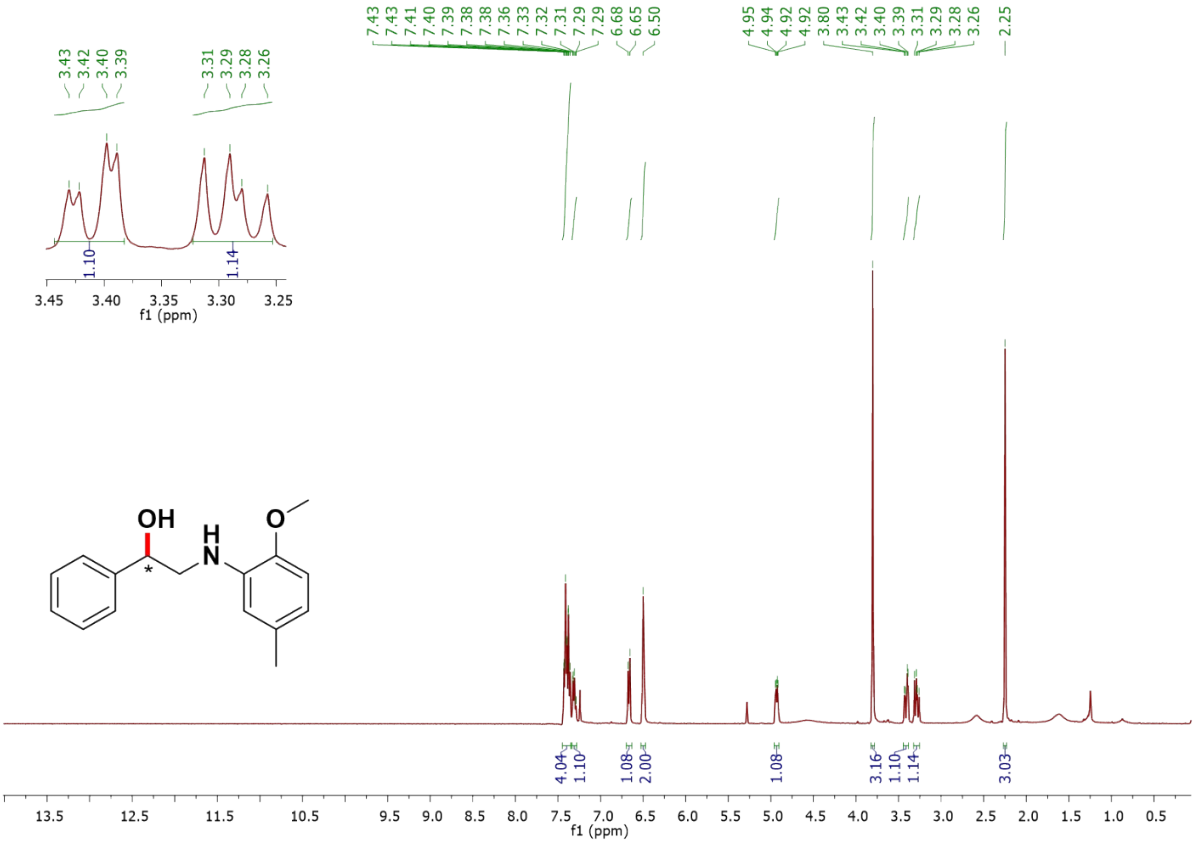
126 MHz ^{13}C-NMR spectra of (-)-D6 in $CDCl_3$



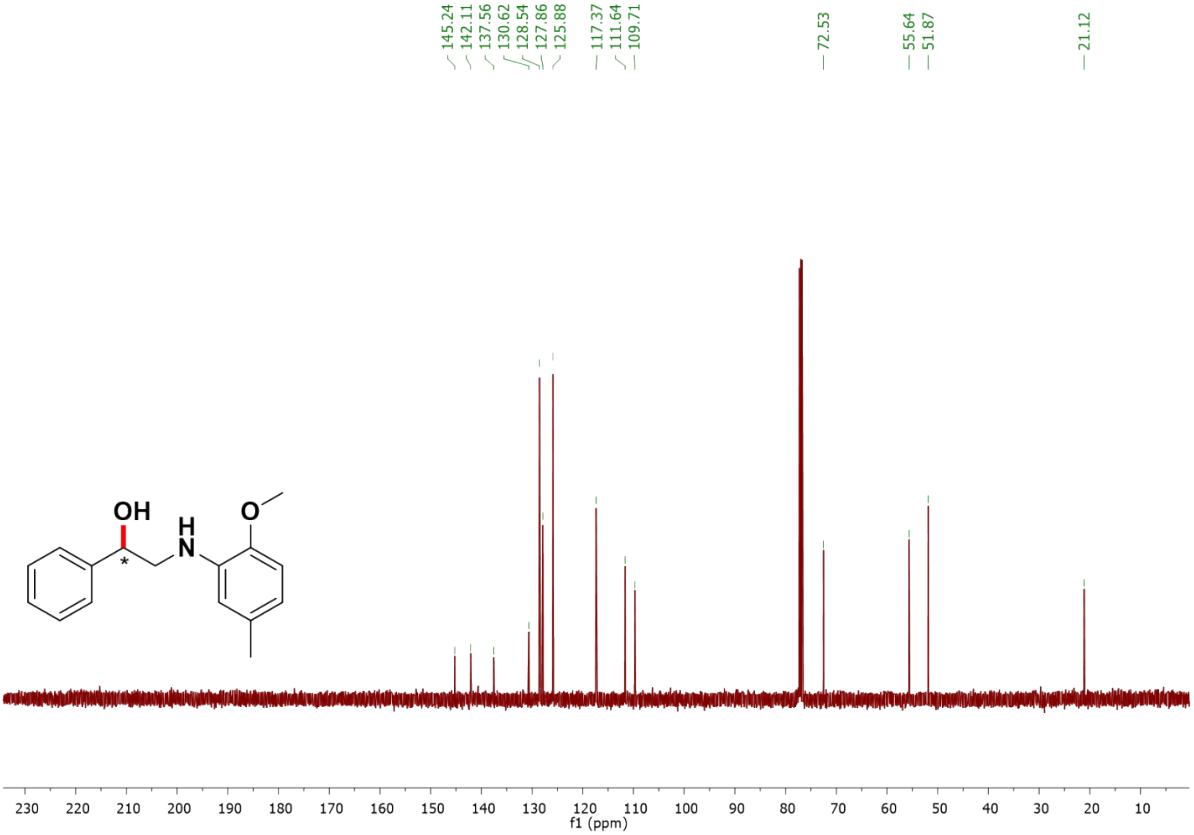
500 MHz ^{1}H-NMR spectra of (-)-D7 in $CDCl_3$



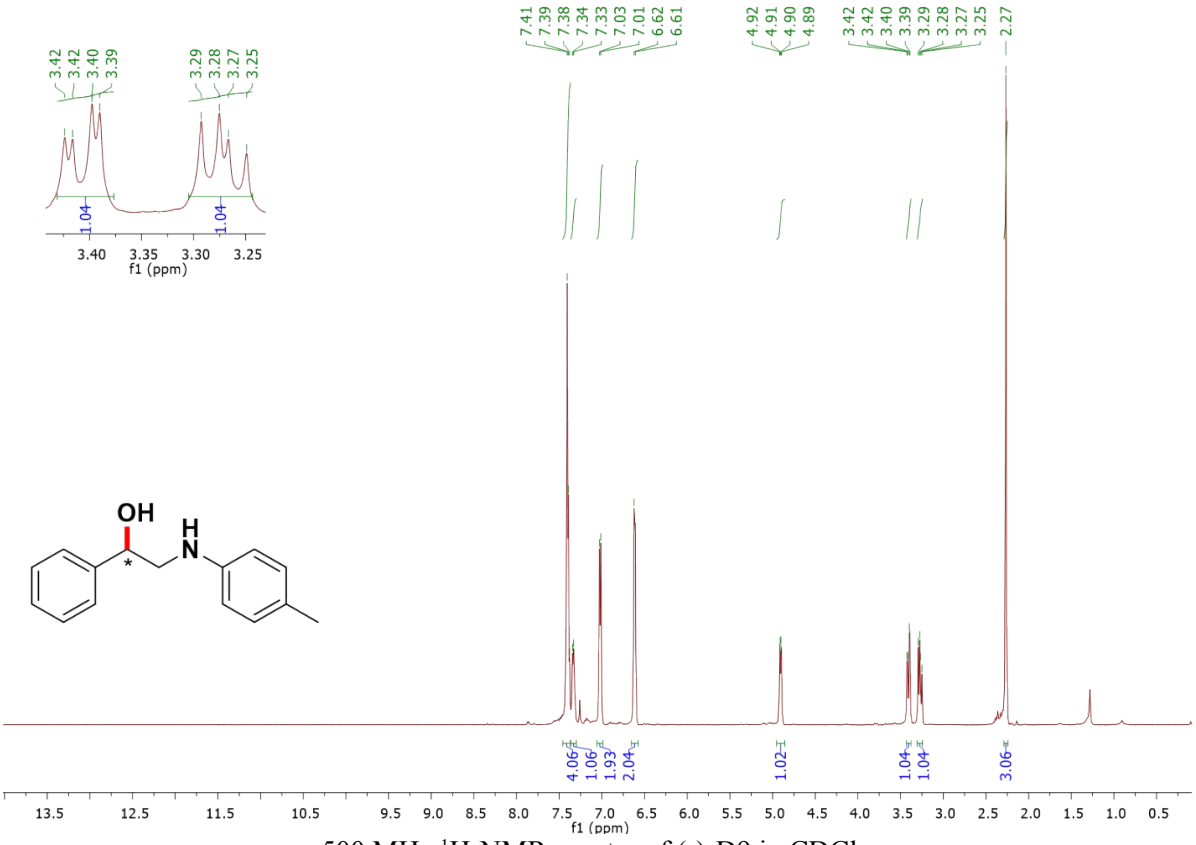
126 MHz ^{13}C-NMR spectra of (-)-D7 in $CDCl_3$



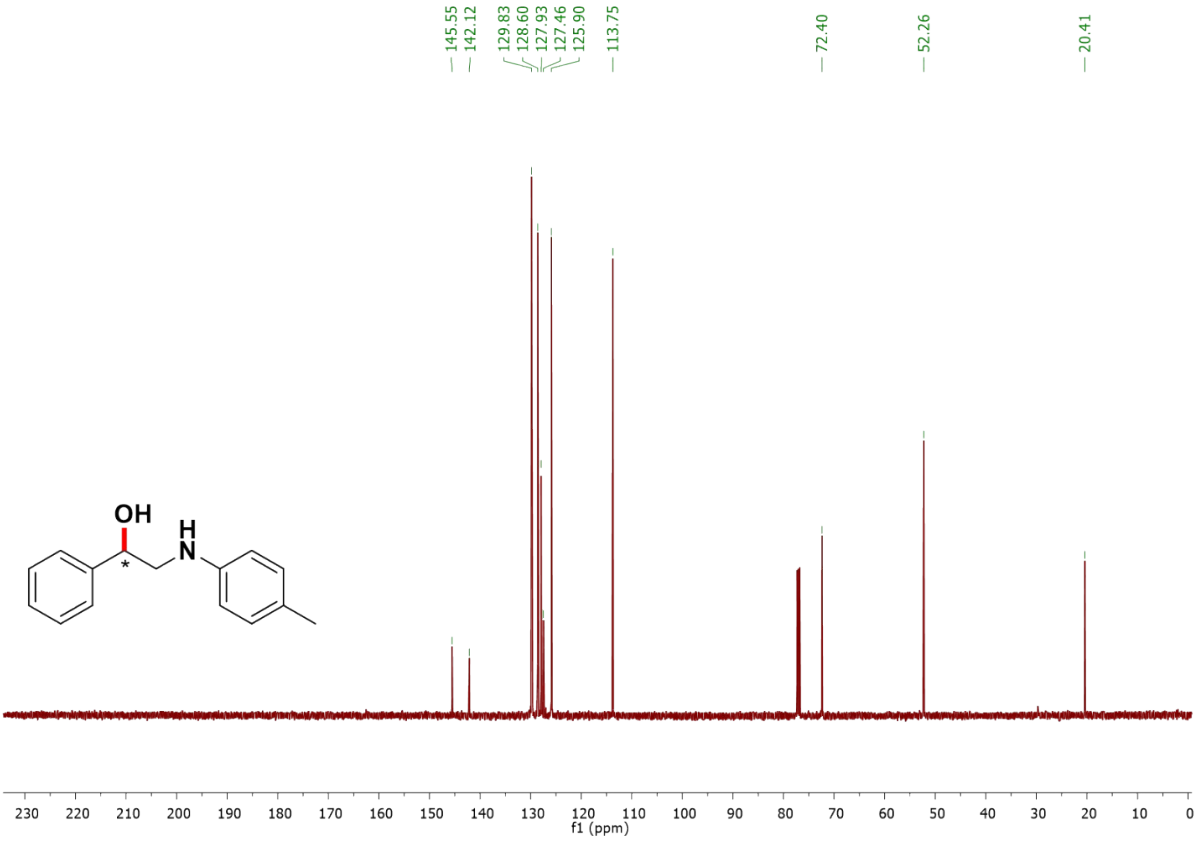
500 MHz ^{1}H-NMR spectra of (-)-D8 in $CDCl_3$



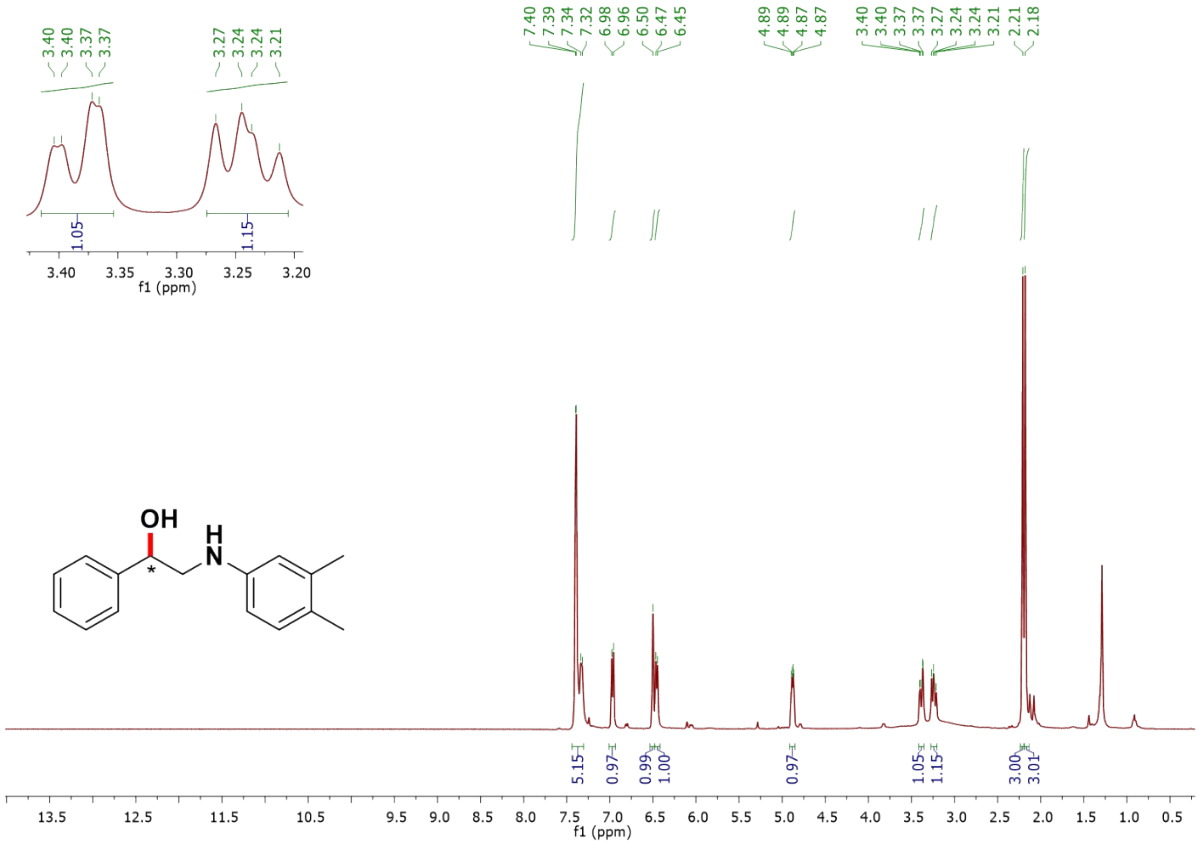
126 MHz ^{13}C-NMR spectra of (-)-D8 in $CDCl_3$



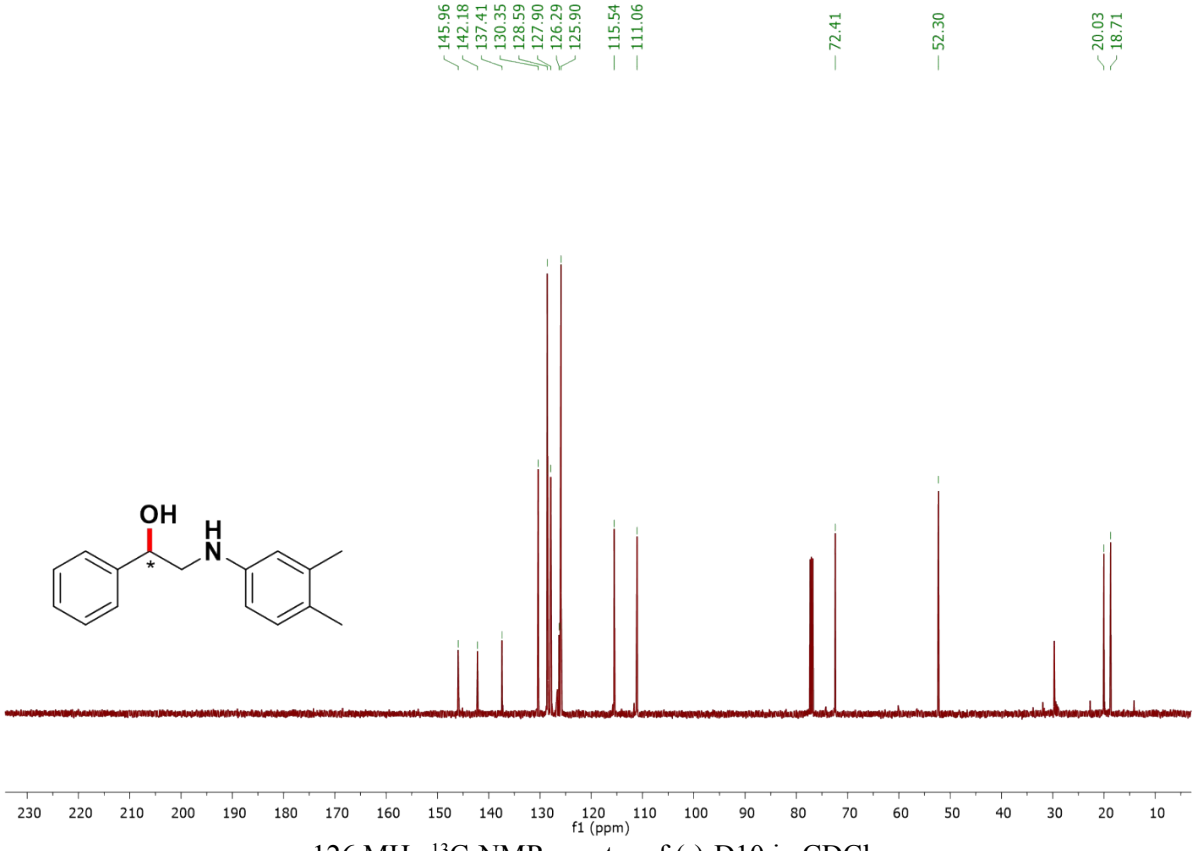
500 MHz ^{1}H-NMR spectra of (-)-D9 in $CDCl_3$



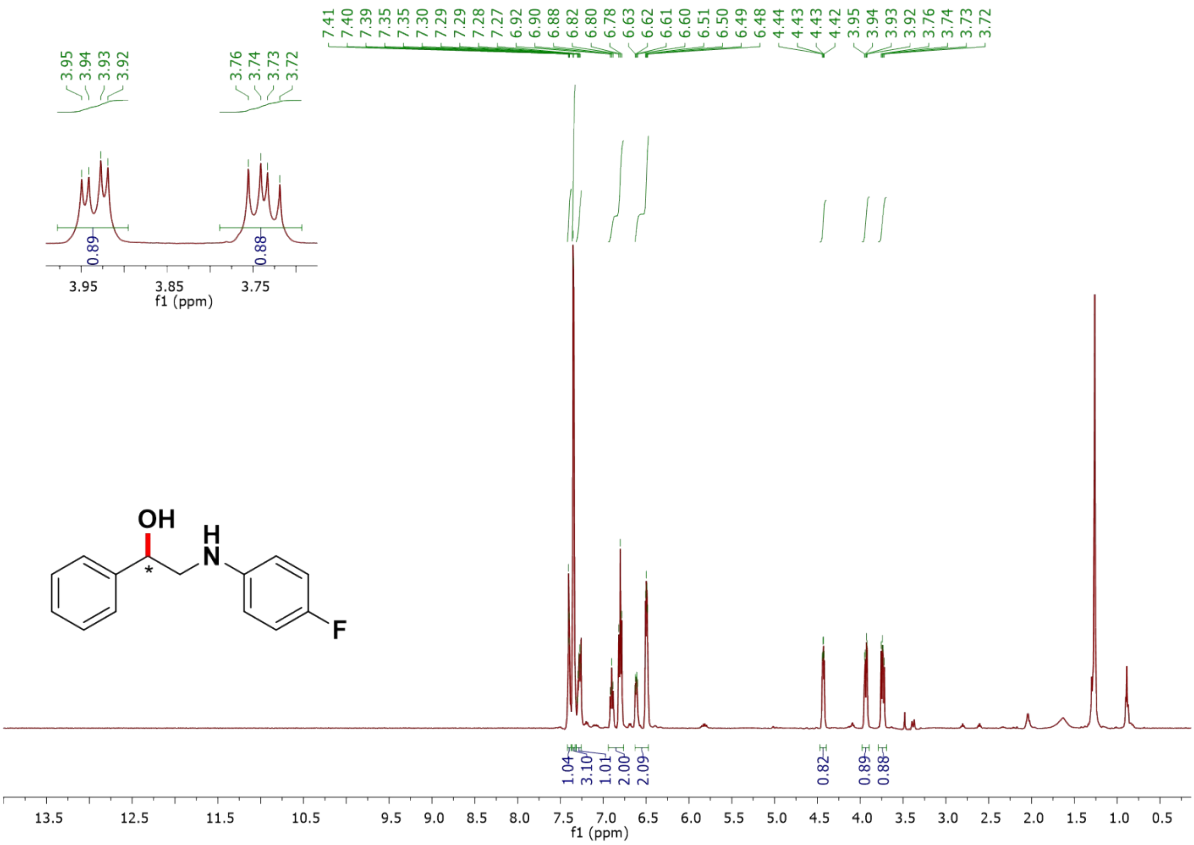
126 MHz ^{13}C-NMR spectra of (-)-D9 in $CDCl_3$



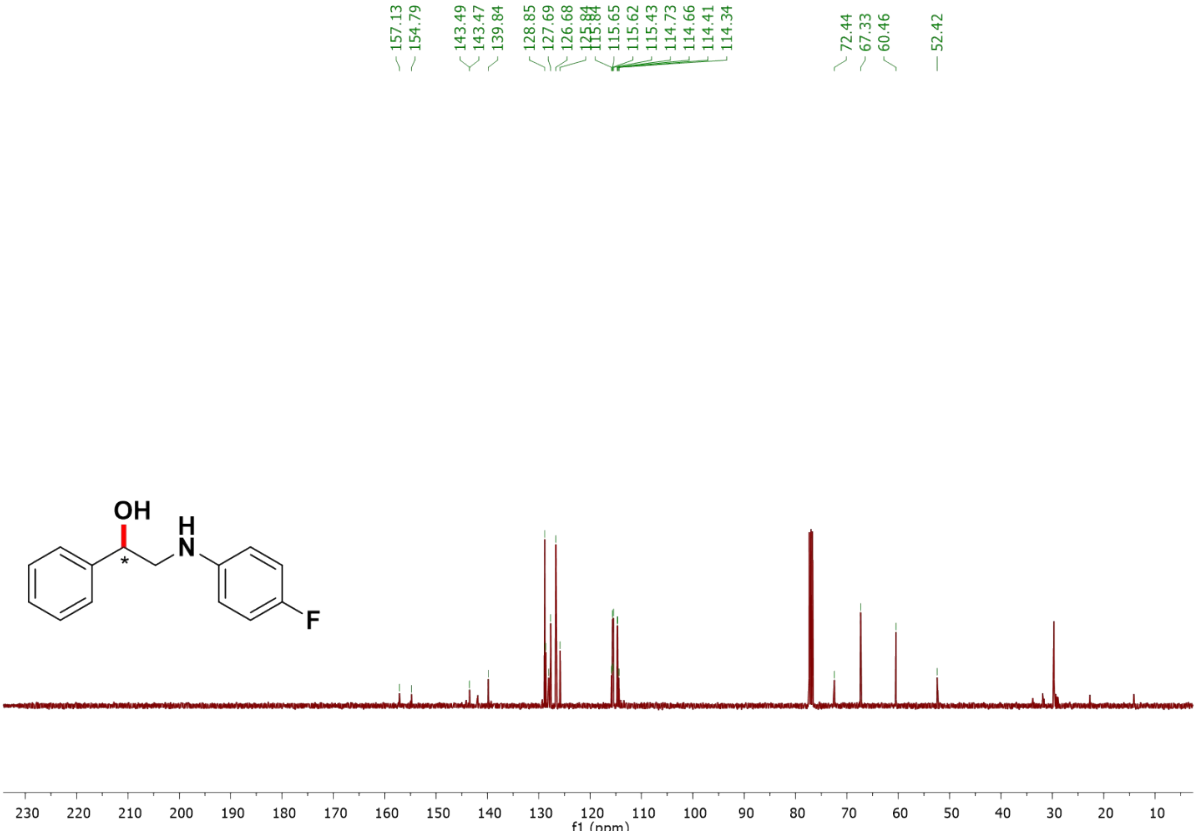
500 MHz ^{1}H-NMR spectra of (-)-D10 in $CDCl_3$



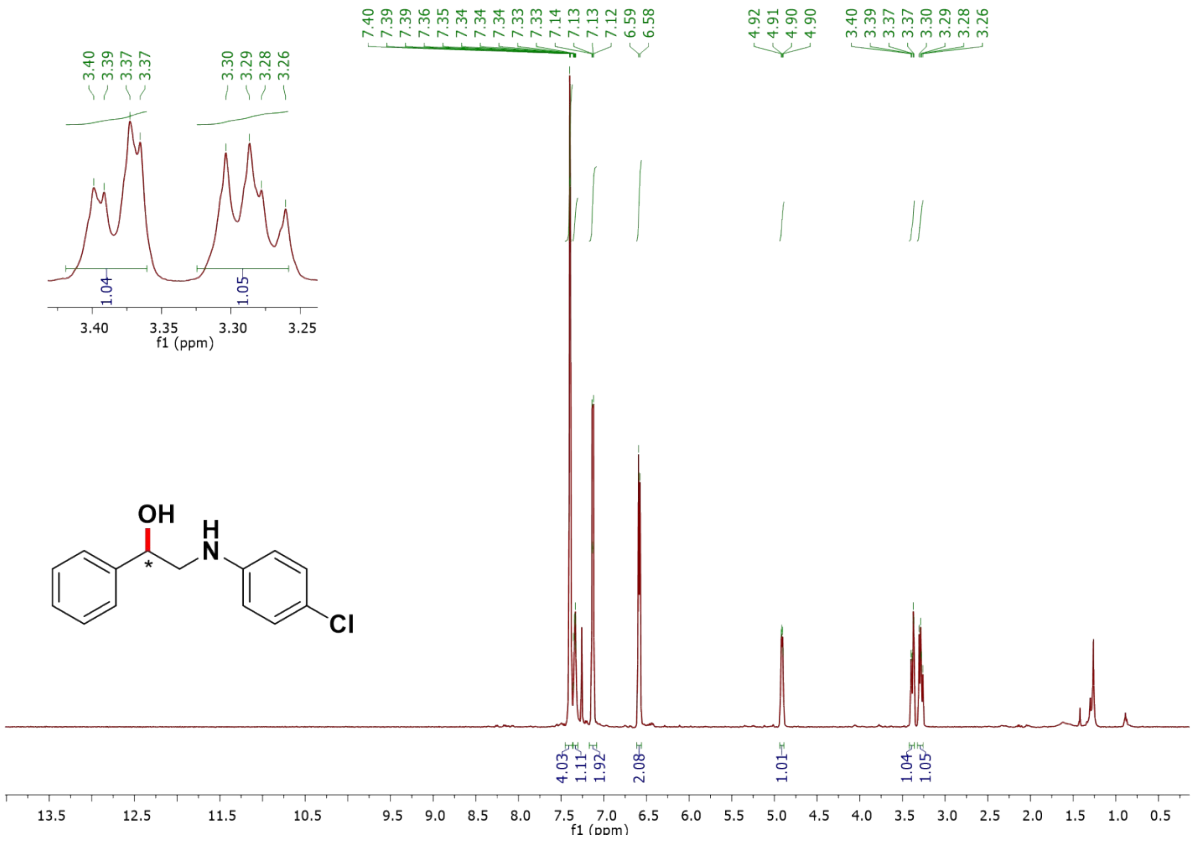
126 MHz ^{13}C-NMR spectra of (-)-D10 in $CDCl_3$



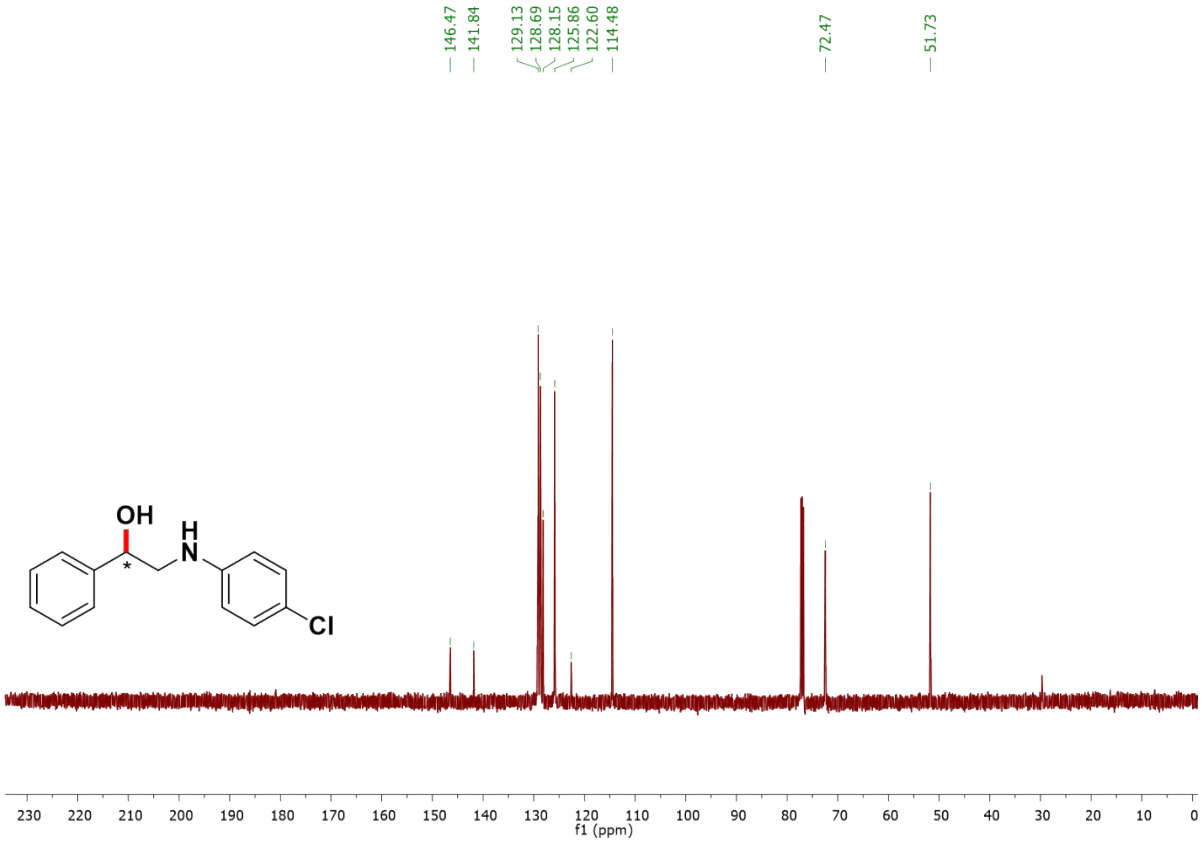
500 MHz ^{1}H-NMR spectra of (-)-D11 in $CDCl_3$



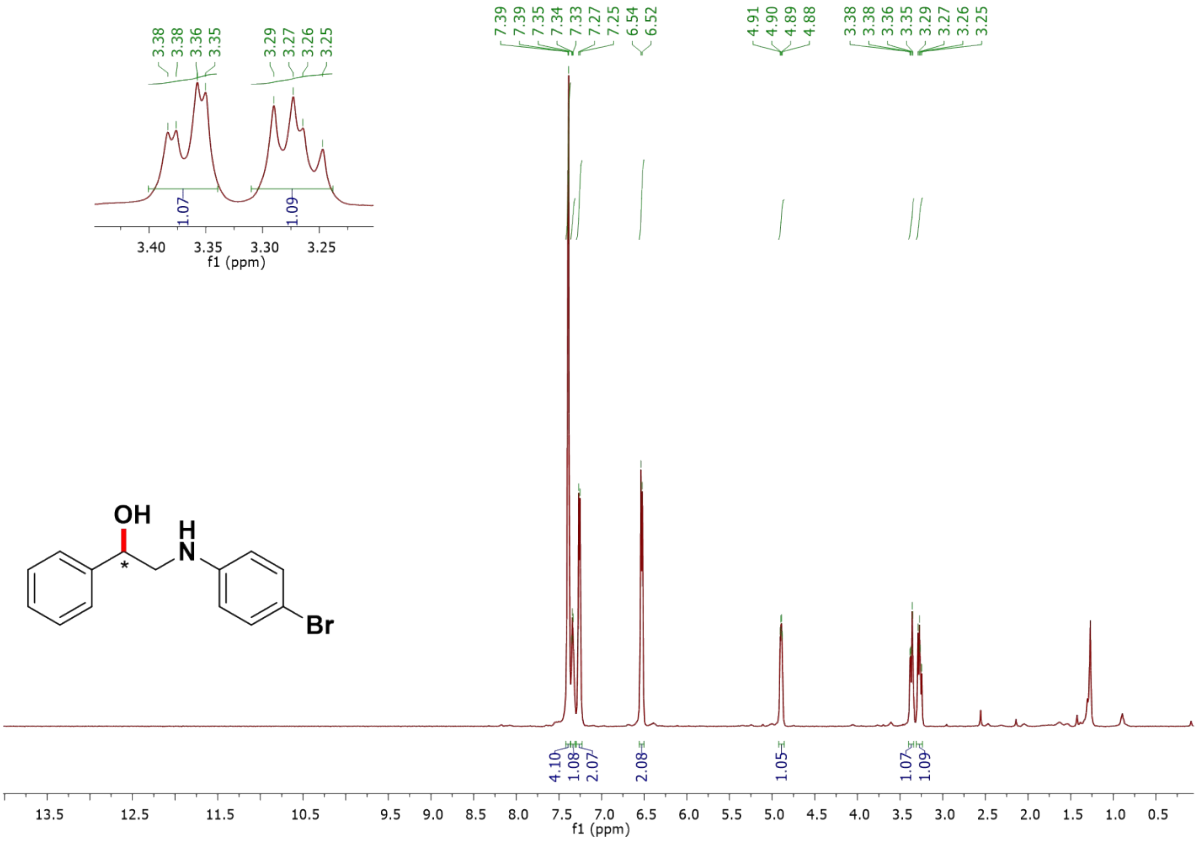
126 MHz ^{13}C-NMR spectra of (-)-D11 in $CDCl_3$



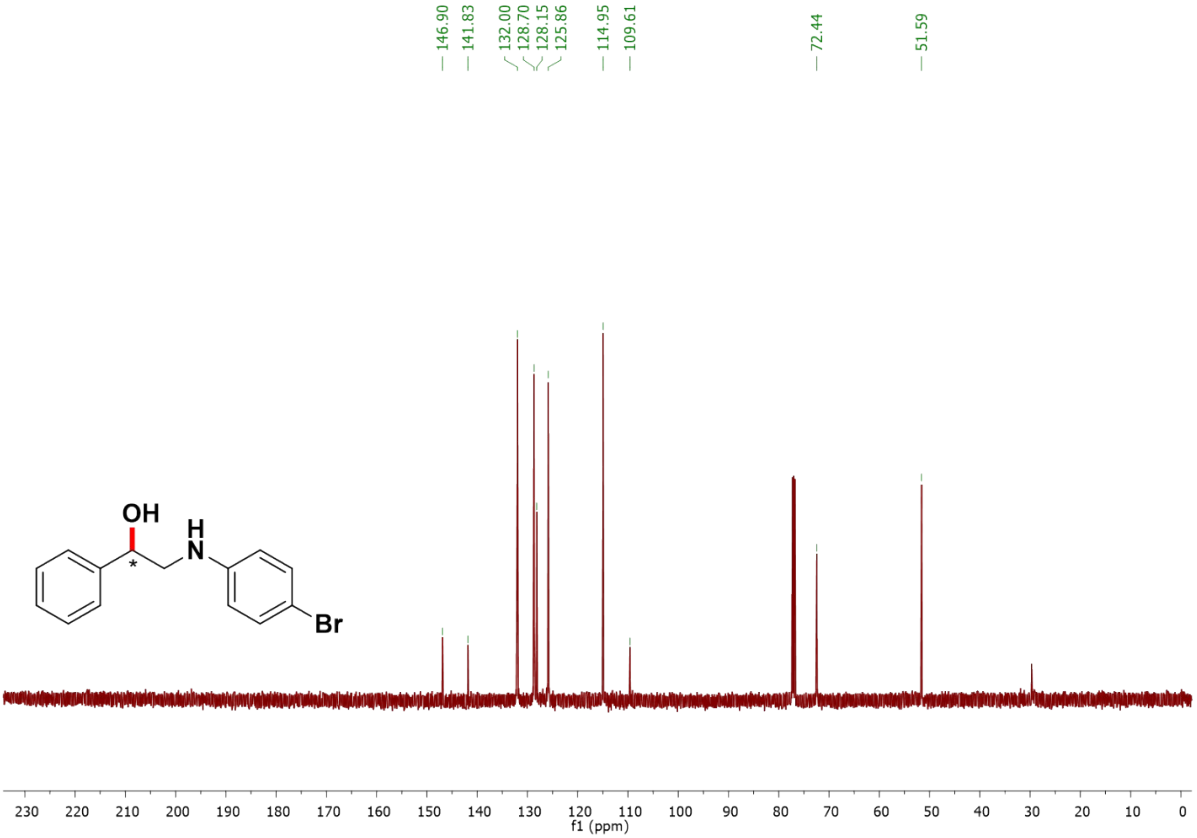
500 MHz ^{1}H-NMR spectra of (-)-D12 in $CDCl_3$



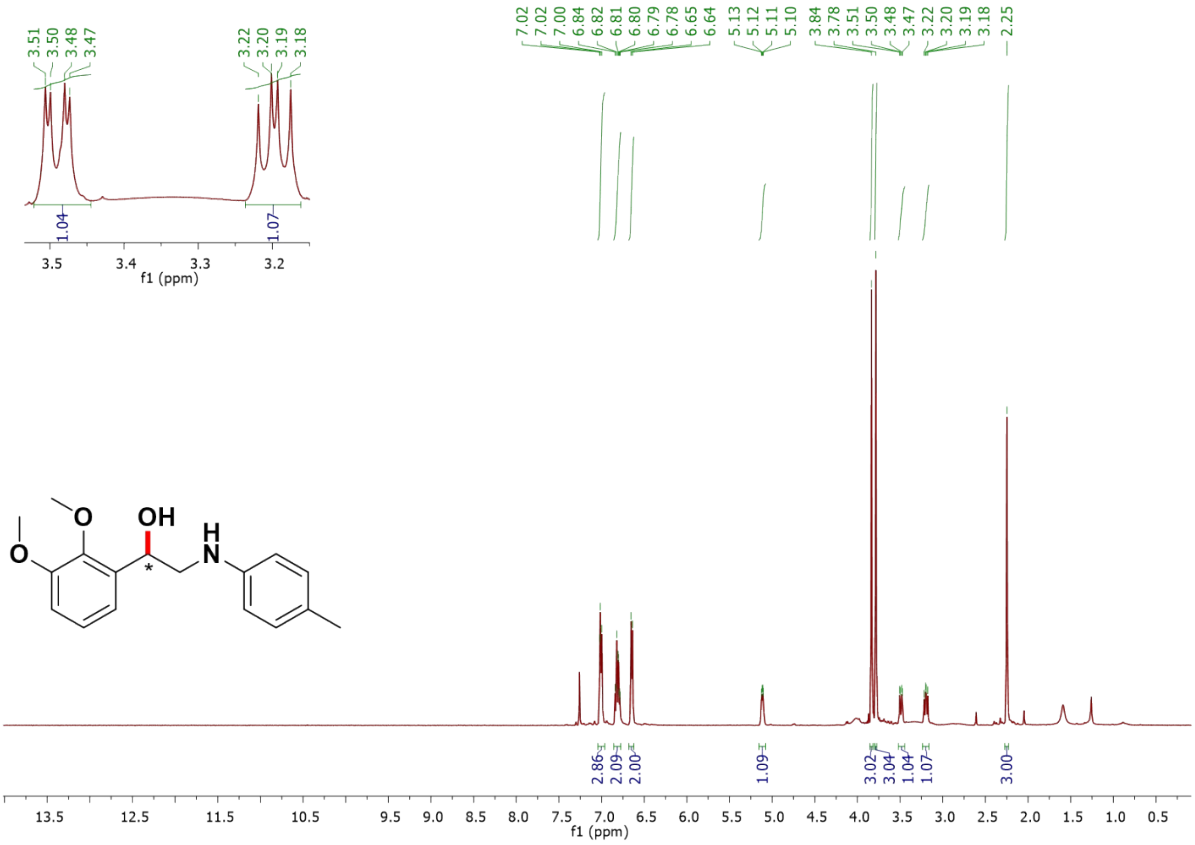
126 MHz ^{13}C-NMR spectra of (-)-D12 in $CDCl_3$



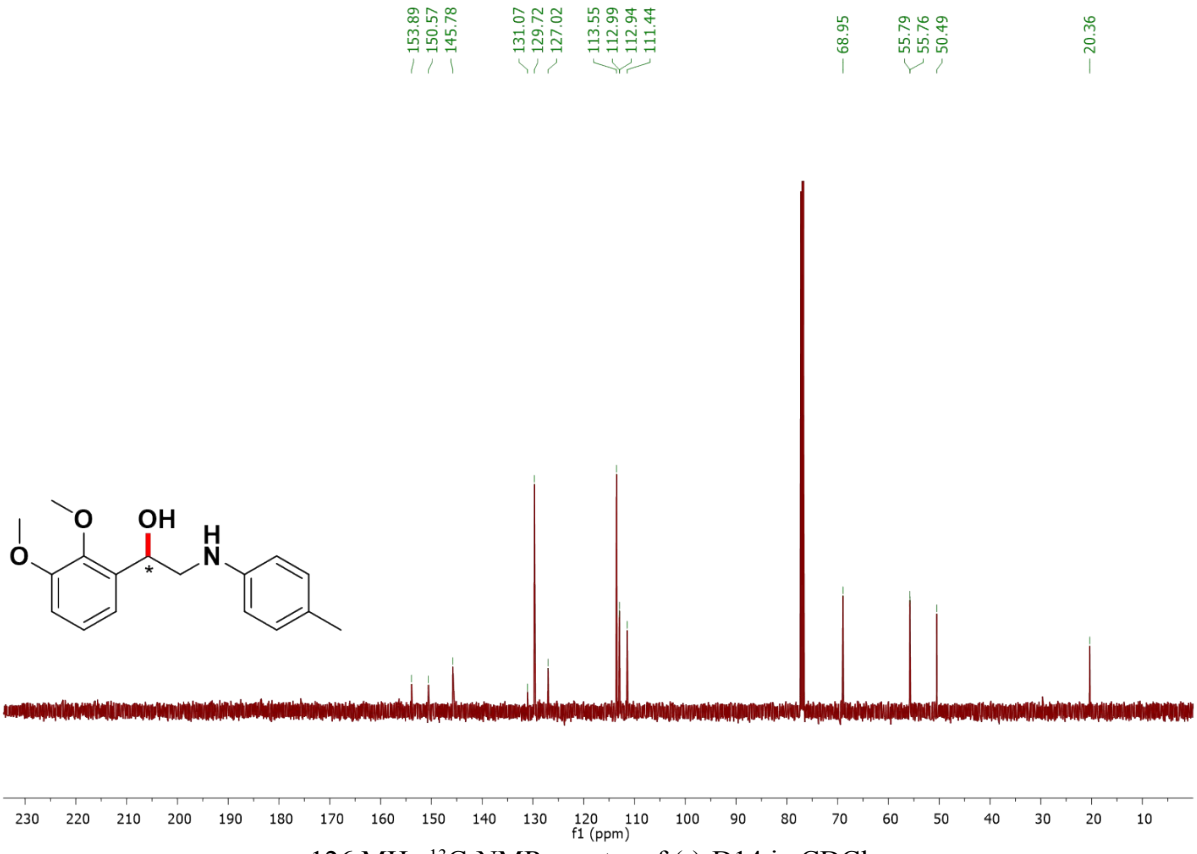
500 MHz ^{1}H-NMR spectra of (-)-D13 in $CDCl_3$



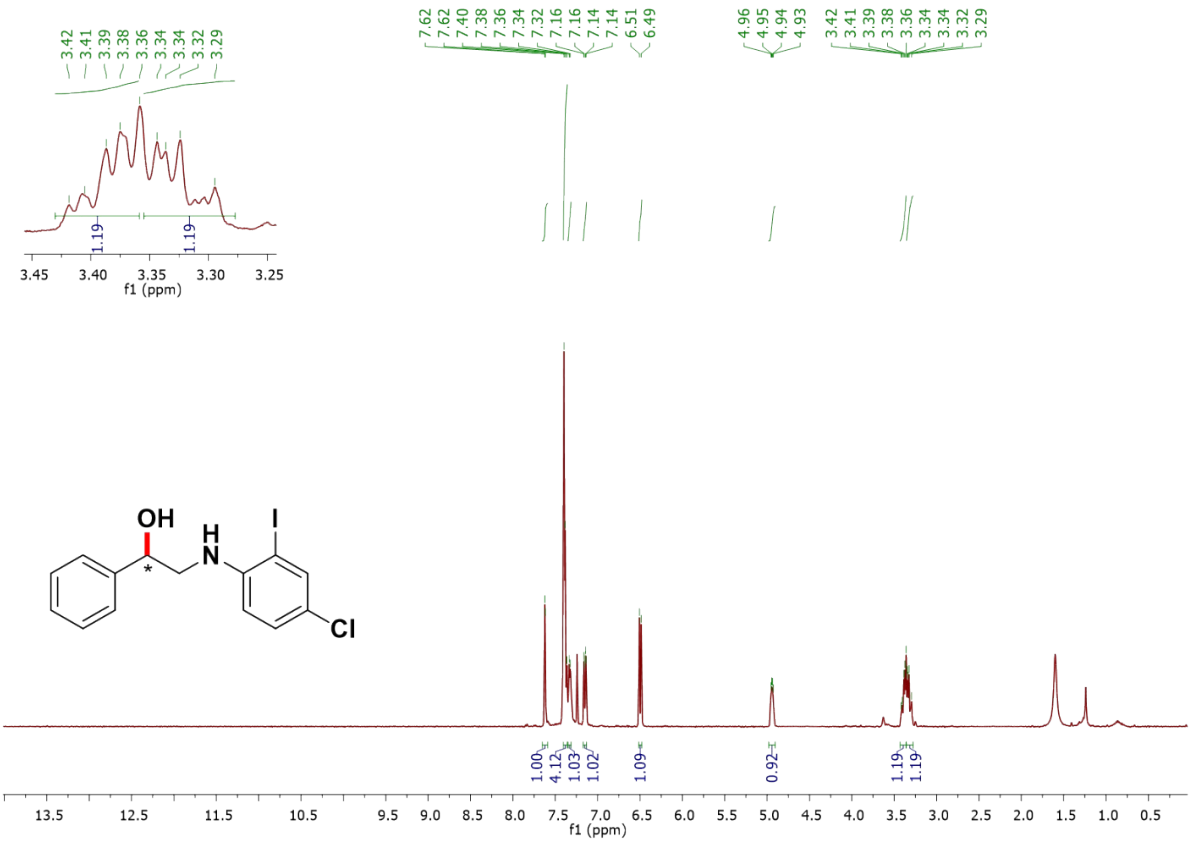
126 MHz ^{13}C-NMR spectra of (-)-D13 in $CDCl_3$



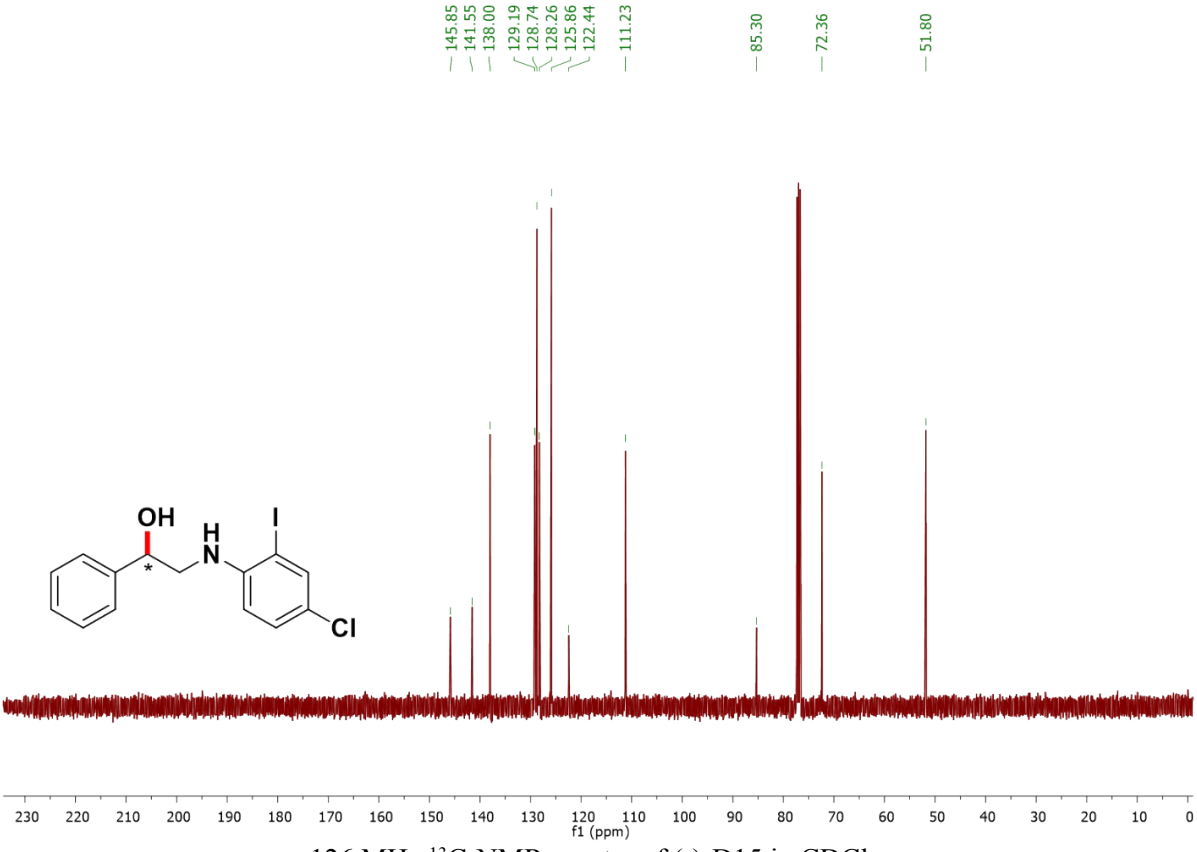
500 MHz ^{1}H-NMR spectra of (-)-D14 in $CDCl_3$



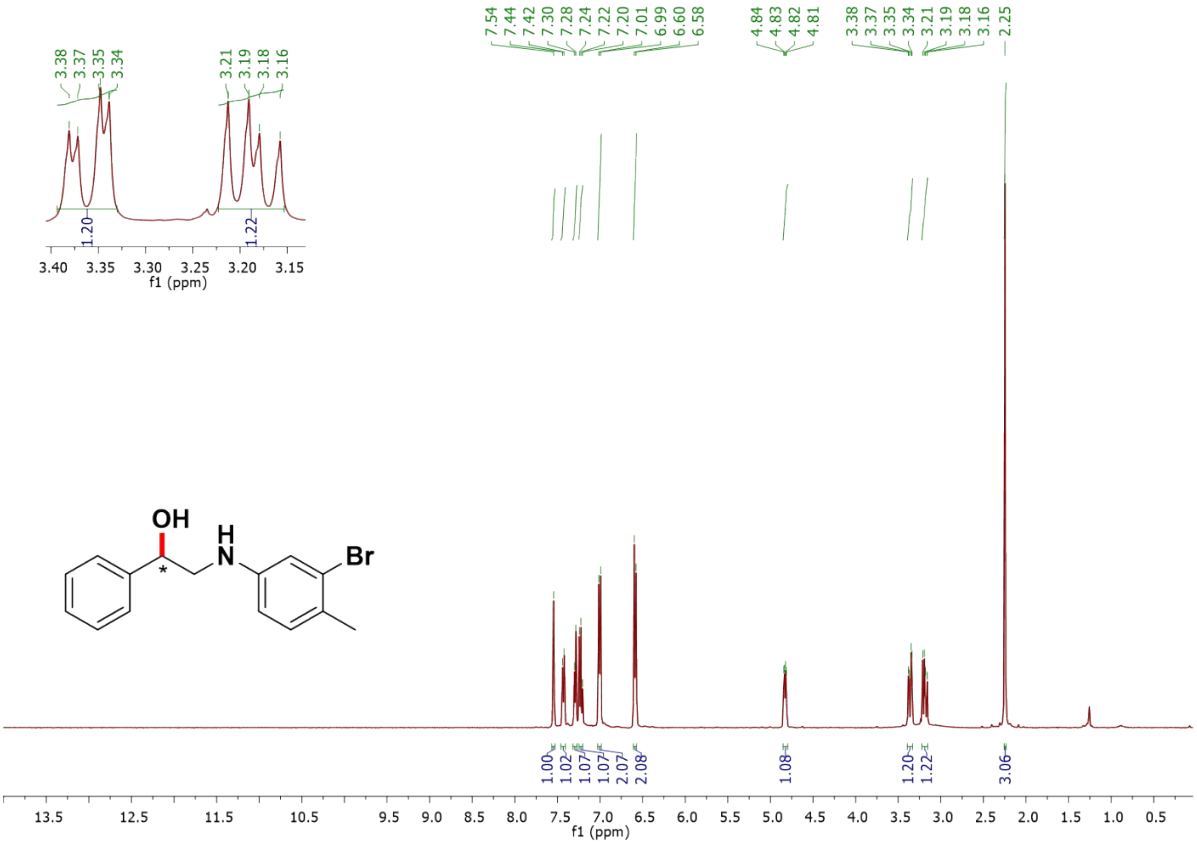
126 MHz ^{13}C-NMR spectra of (-)-D14 in $CDCl_3$



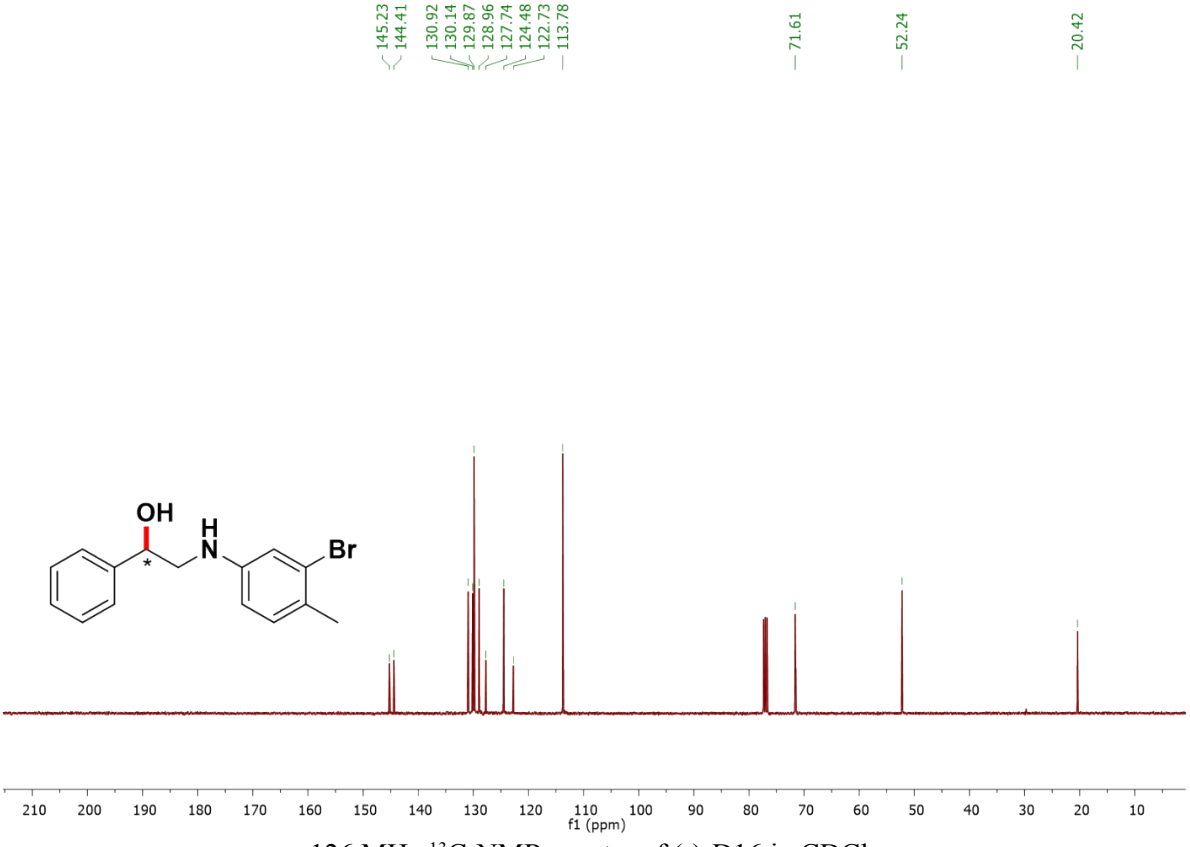
500 MHz ^{1}H-NMR spectra of (-)-D15 in $CDCl_3$



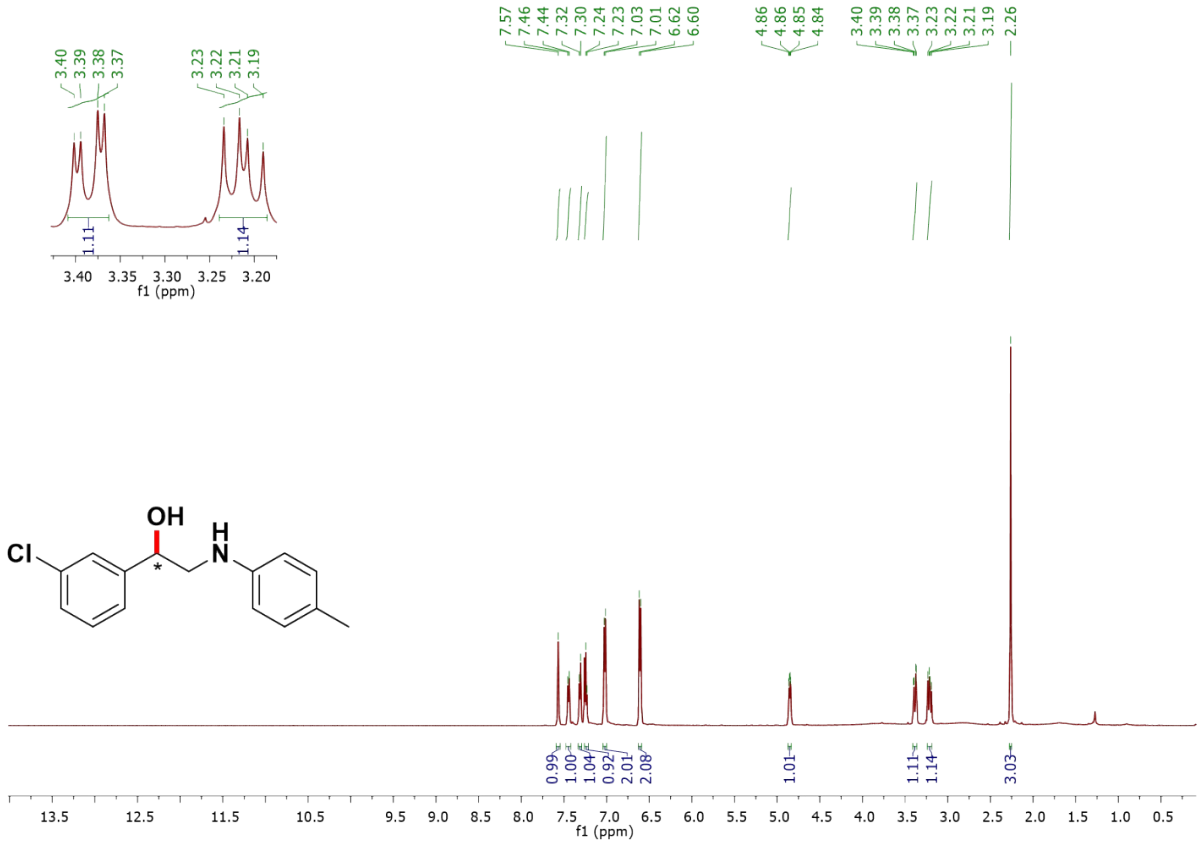
126 MHz ^{13}C-NMR spectra of (-)-D15 in $CDCl_3$



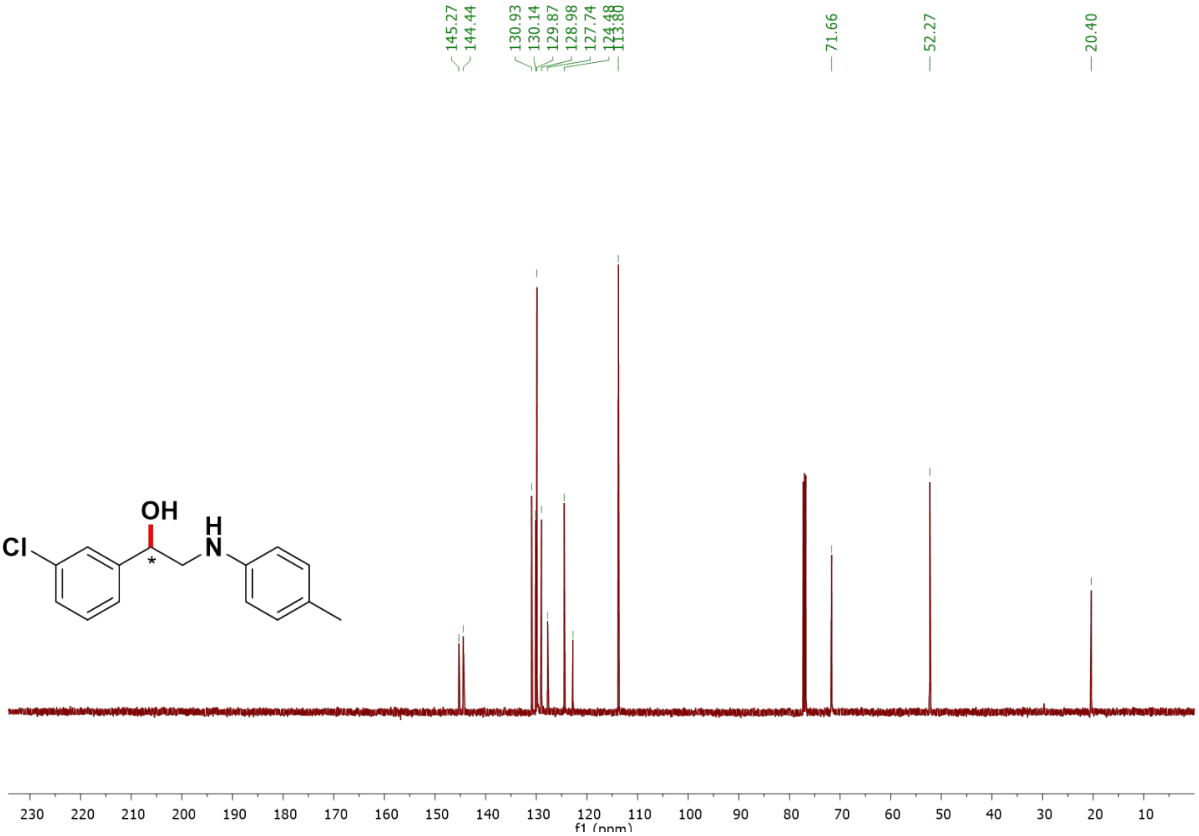
500 MHz ^{1}H-NMR spectra of (-)-D16 in $CDCl_3$



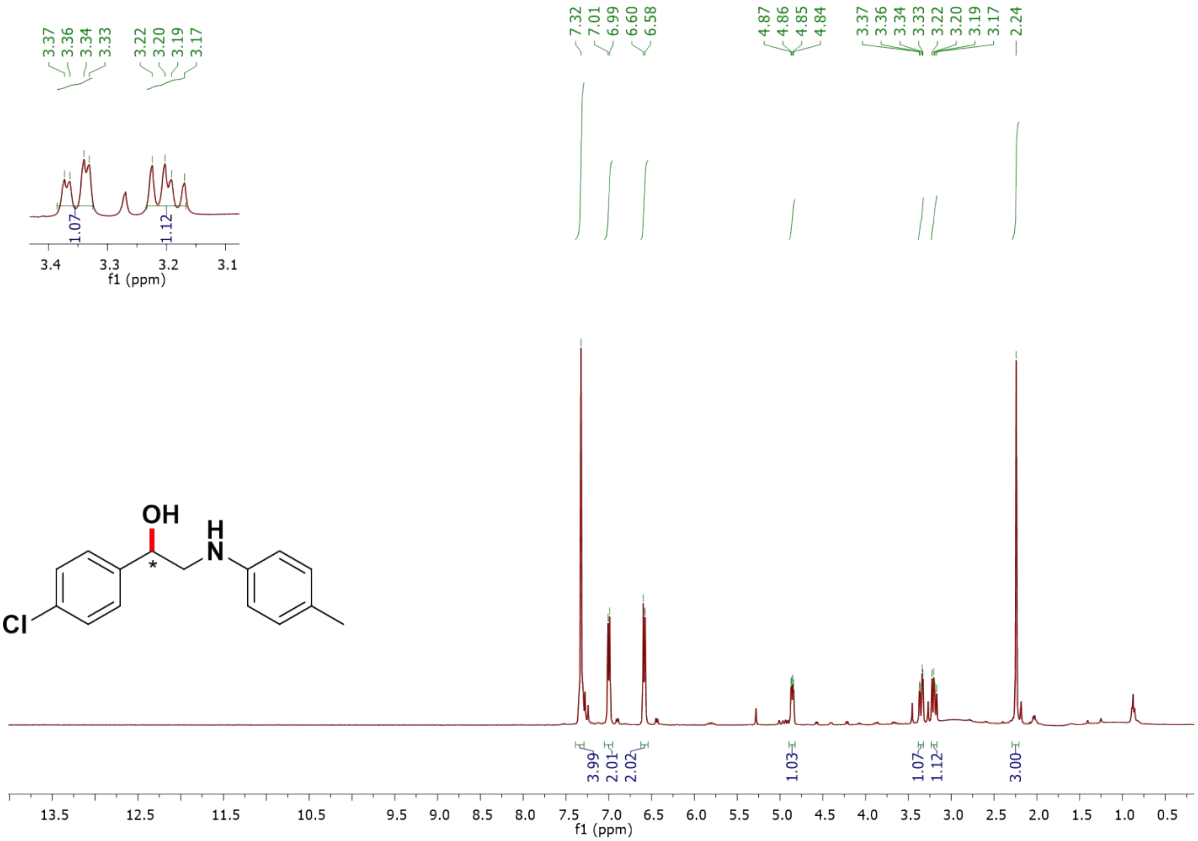
126 MHz ^{13}C-NMR spectra of (-)-D16 in $CDCl_3$



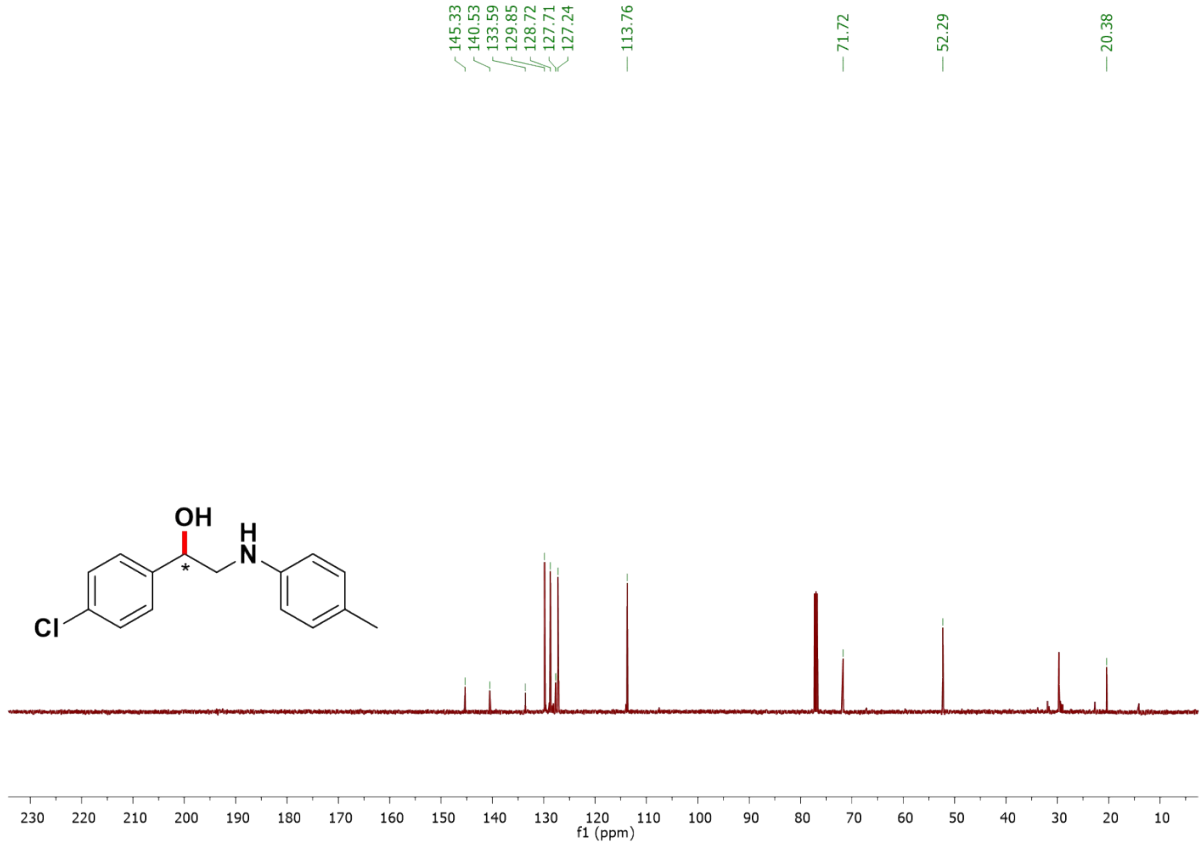
500 MHz ^{1}H-NMR spectra of (-)-D17 in $CDCl_3$



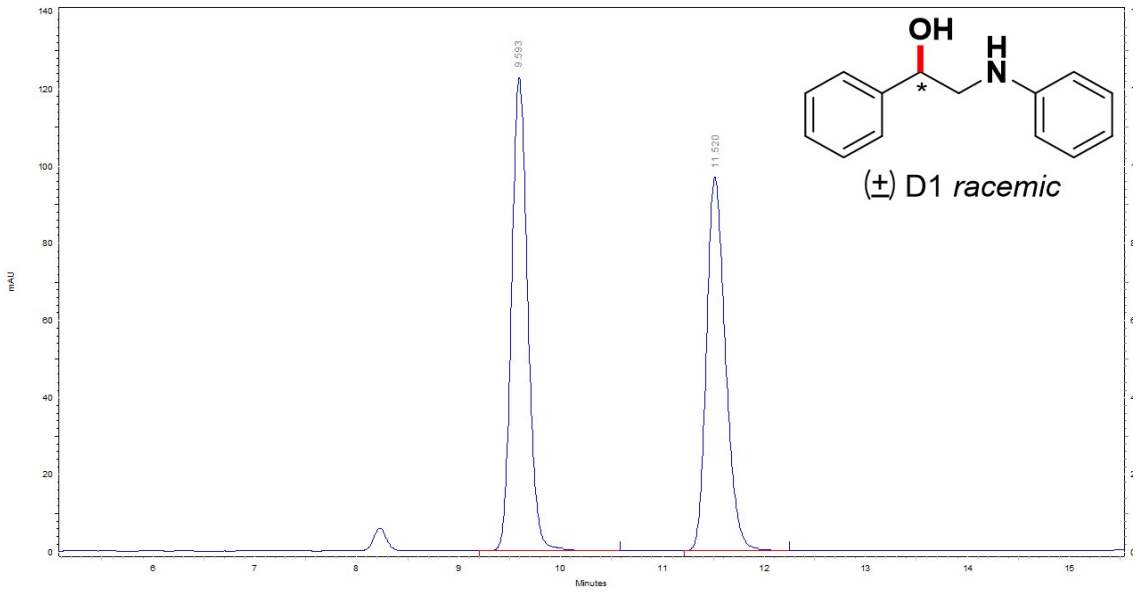
126 MHz ^{13}C-NMR spectra of (-)-D17 in $CDCl_3$



500 MHz ^{1}H-NMR spectra of (-)-D18 in $CDCl_3$



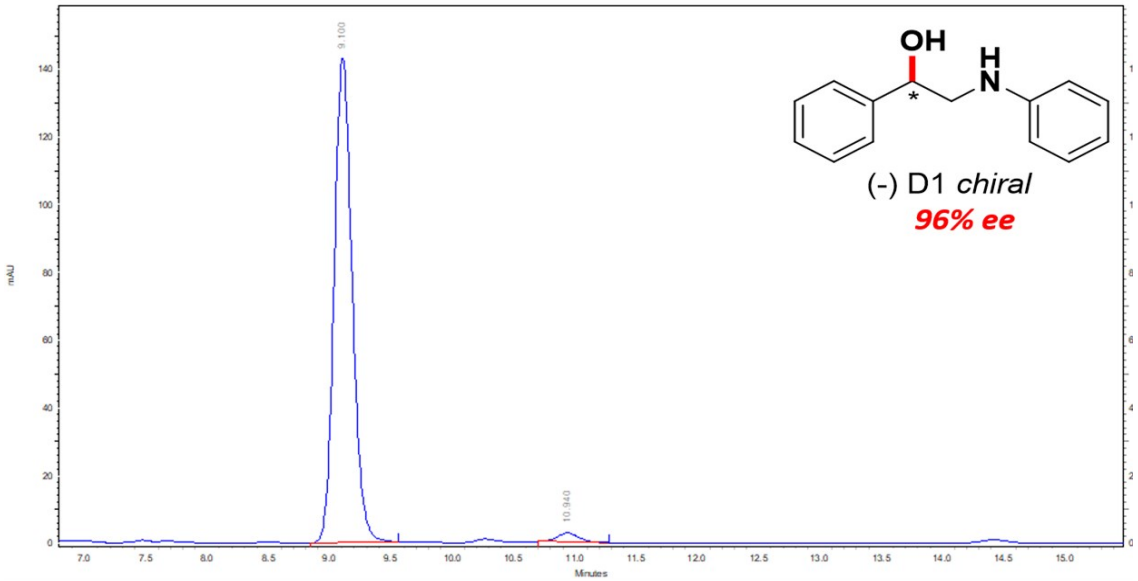
126 MHz ^{13}C-NMR spectra of (-)-D18 in $CDCl_3$



DAD: Signal A, 250 nm/Bw:4 nm Results

Retention Time	Area	Area %	Height	Height %
9.593	2845240	51.98	257191	55.89
11.520	2628939	48.02	203004	44.11

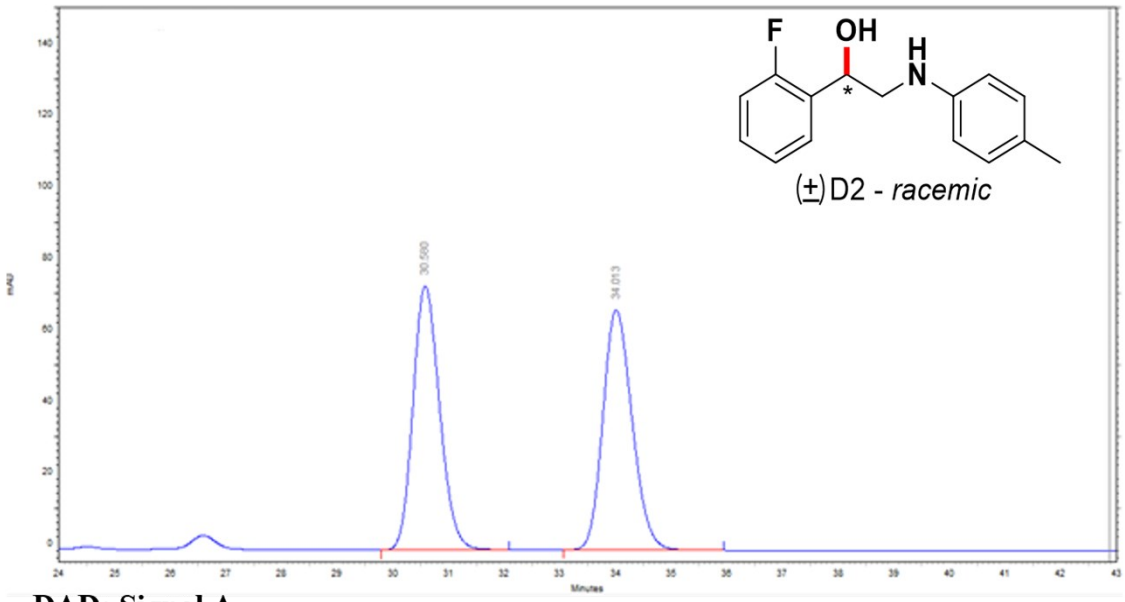
Totals	5474179	100.00	460195	100.00



DAD: Signal A, 250 nm/Bw:4 nm Results

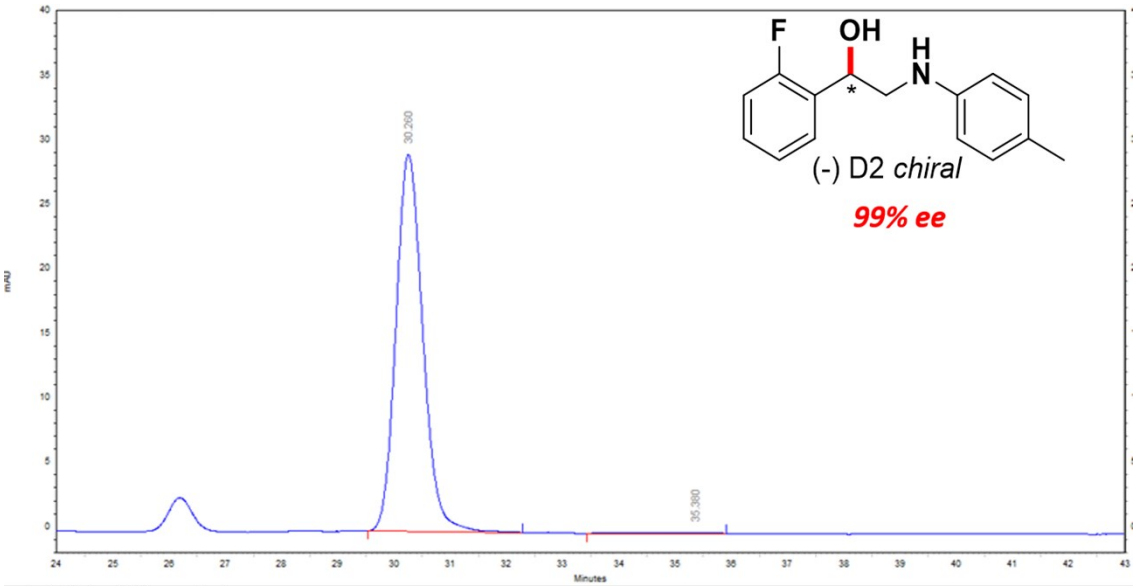
Retention Time	Area	Area %	Height	Height %
9.100	3055549	97.95	300139	98.23
10.940	63834	2.05	5396	1.77

Totals	3119383	100.00	305535	100.00



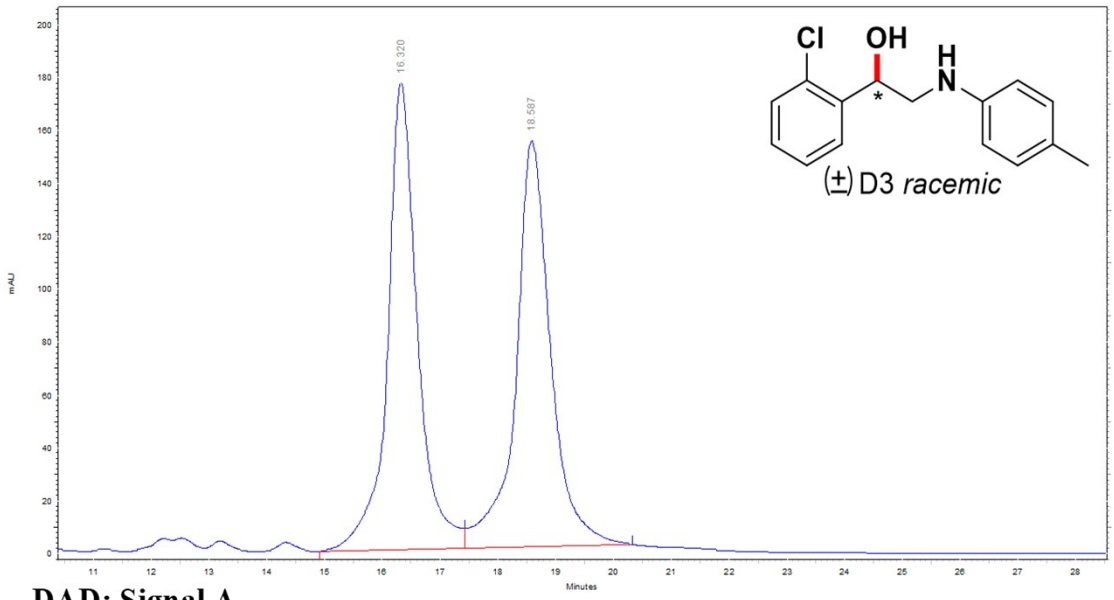
DAD: Signal A, 250 nm/Bw:4 nm Results

Retention Time	Area	Area %	Height	Height %
30.580	5145595	50.01	154935	52.38
34.013	5142916	49.99	140852	47.62
Totals	10288511	100.00	295787	100.00



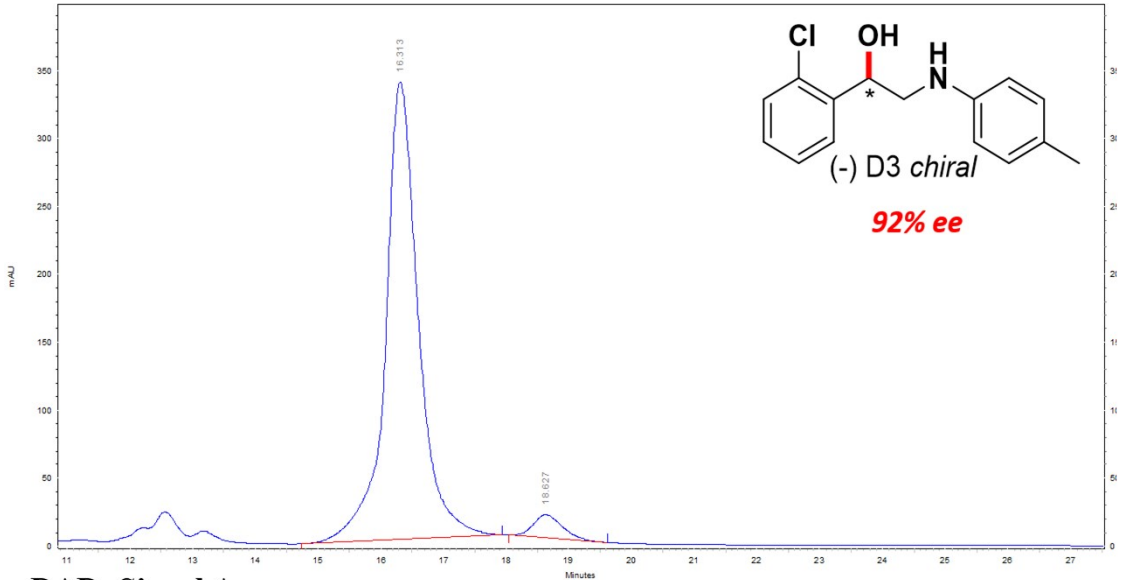
DAD: Signal A, 250 nm/Bw:4 nm Results

Retention Time	Area	Area %	Height	Height %
30.260	2038837	99.59	61287	99.86
35.380	8350	0.41	88	0.14
Totals	2047187	100.00	61375	100.00



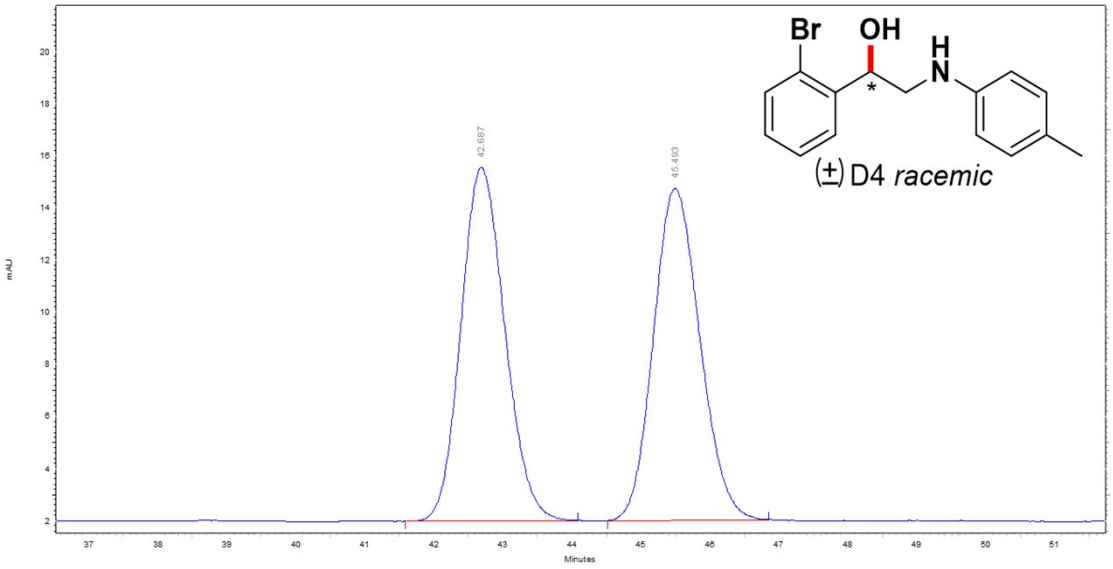
DAD: Signal A, 220 nm/Bw:4 nm Results

Retention Time	Area	Area %	Height	Height %
16.320	13286028	49.59	369551	53.47
18.587	13504194	50.41	321576	46.53
Totals	26790222	100.00	691127	100.00



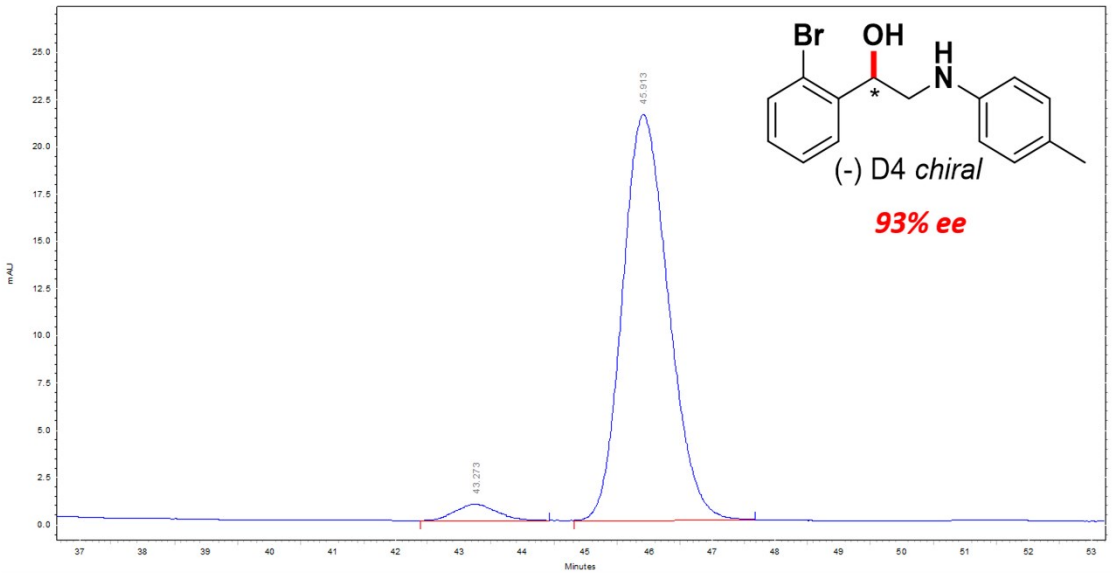
DAD: Signal A, 220 nm/Bw:4 nm Results

Retention Time	Area	Area %	Height	Height %
16.313	25712512	95.82	704936	95.31
18.627	1120374	4.18	34700	4.69
Totals	26832886	100.00	739636	100.00



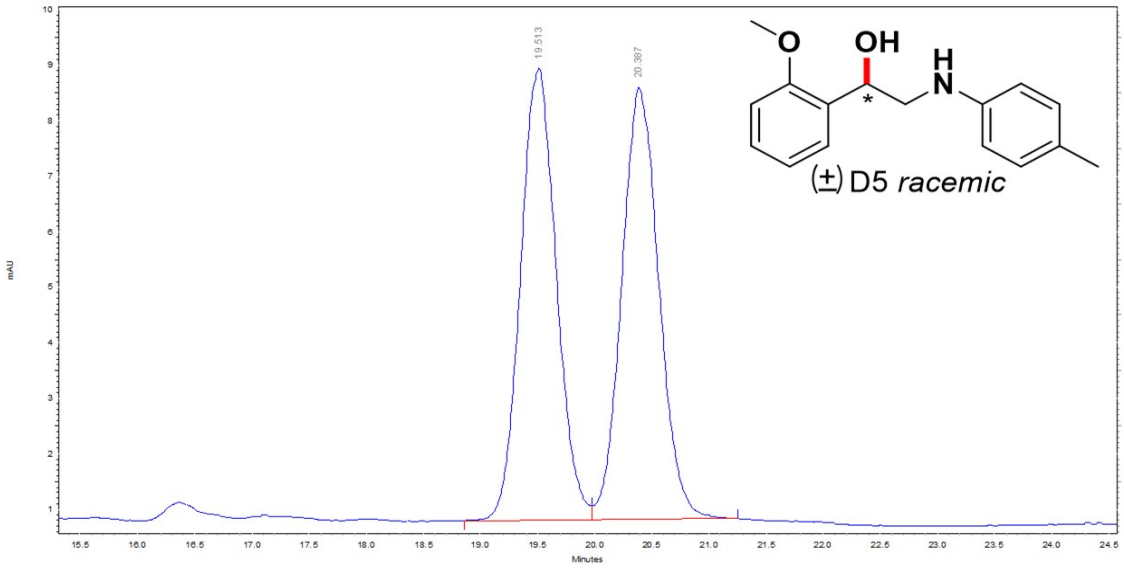
DAD: Signal A, 250 nm/Bw:4 nm Results

Retention Time	Area	Area %	Height	Height %
42.687	1254912	50.22	28390	51.57
45.493	1244116	49.78	26657	48.43
Totals	2499028	100.00	55047	100.00



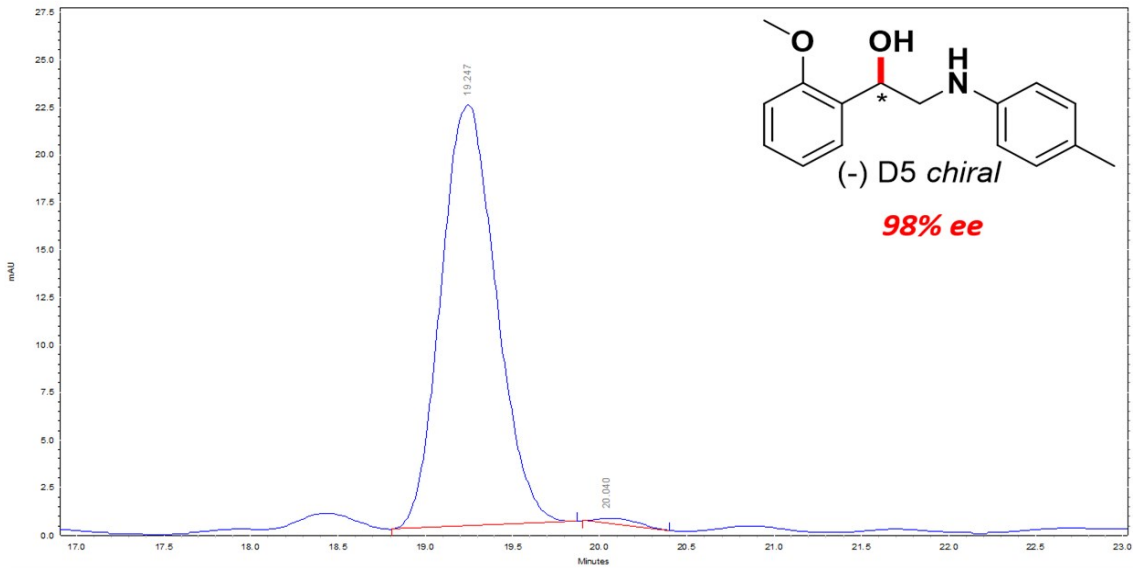
DAD: Signal A, 250 nm/Bw:4 nm Results

Retention Time	Area	Area %	Height	Height %
43.273	83929	3.57	1784	3.81
45.913	2265145	96.43	45015	96.19
Totals	2349074	100.00	46799	100.00



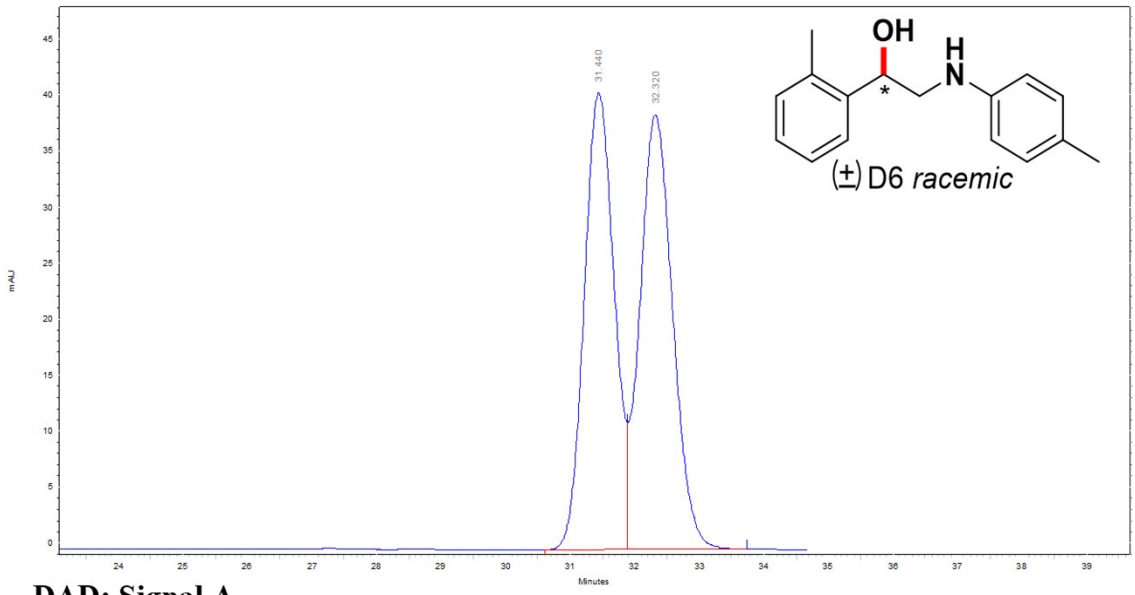
DAD: Signal A,
250 nm/Bw:4
nm Results

Retention Time	Area	Area %	Height	Height %
19.513	371979	50.22	17080	51.15
20.387	368660	49.78	16314	48.85
Totals	740639	100.00	33394	100.00



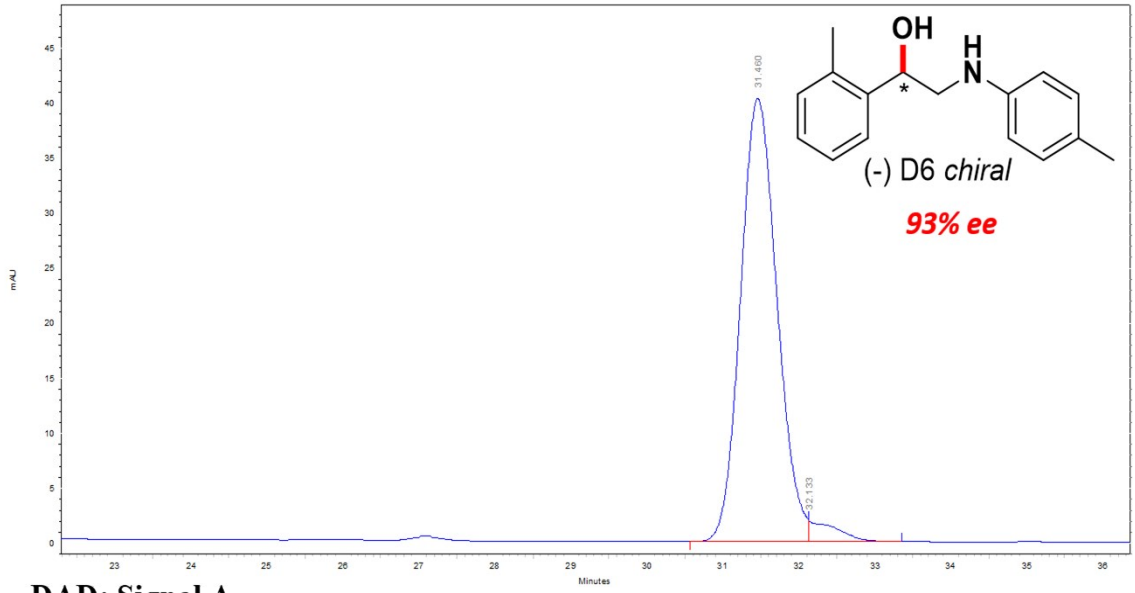
DAD: Signal A,
250 nm/Bw:4
nm Results

Retention Time	Area	Area %	Height	Height %
19.247	1019526	98.95	46412	98.82
20.040	10809	1.05	556	1.18
Totals	1030335	100.00	46968	100.00



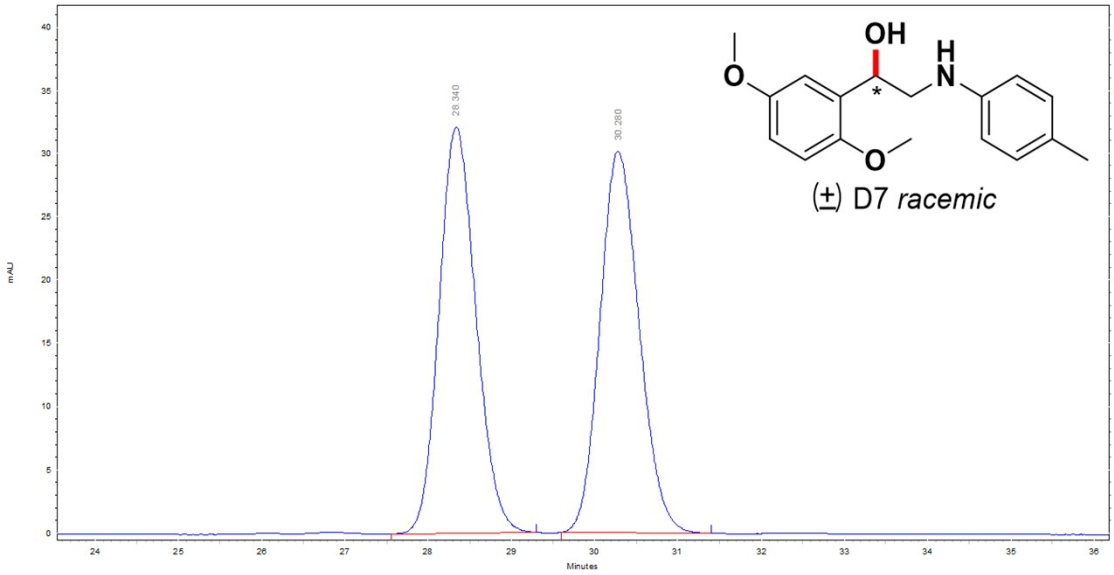
DAD: Signal A, 250 nm/Bw:4 nm Results

Retention Time	Area	Area %	Height	Height %
31.440	2756949	49.02	85485	51.25
32.320	2867372	50.98	81308	48.75
Totals	5624321	100.00	166793	100.00



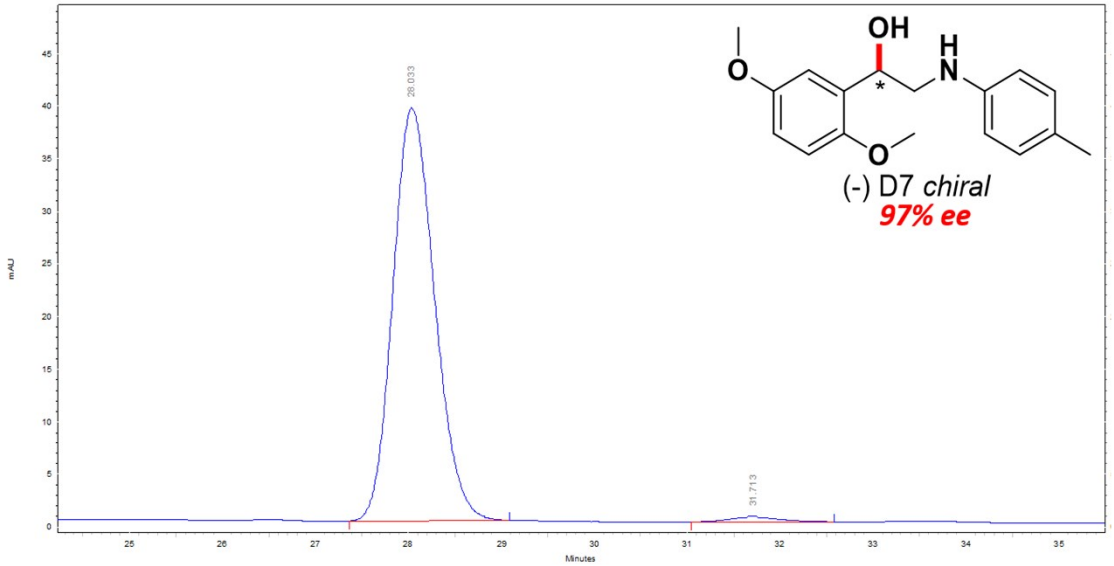
DAD: Signal A, 250 nm/Bw:4 nm Results

Retention Time	Area	Area %	Height	Height %
31.460	2807772	96.57	84439	95.47
32.133	99638	3.43	4005	4.53
Totals	2907410	100.00	88444	100.00



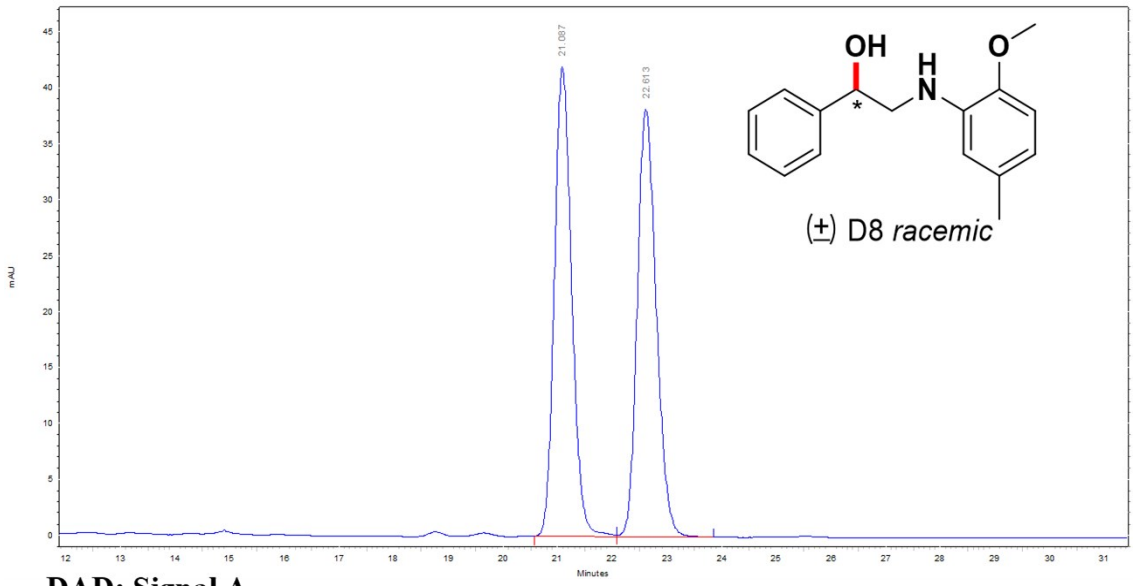
DAD: Signal A,
250 nm/Bw:4
nm Results

Retention Time	Area	Area %	Height	Height %
28.340	2075294	50.06	67307	51.56
30.280	2070247	49.94	63239	48.44
Totals	4145541	100.00	130546	100.00



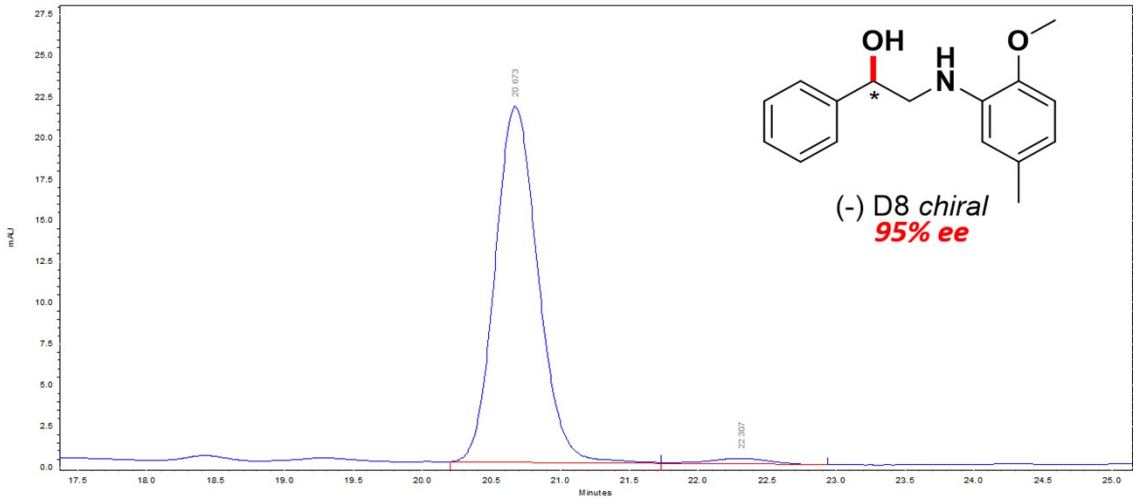
DAD: Signal A,
250 nm/Bw:4
nm Results

Retention Time	Area	Area %	Height	Height %
28.033	2564876	98.54	82231	98.79
31.713	38080	1.46	1005	1.21
Totals	2602956	100.00	83236	100.00



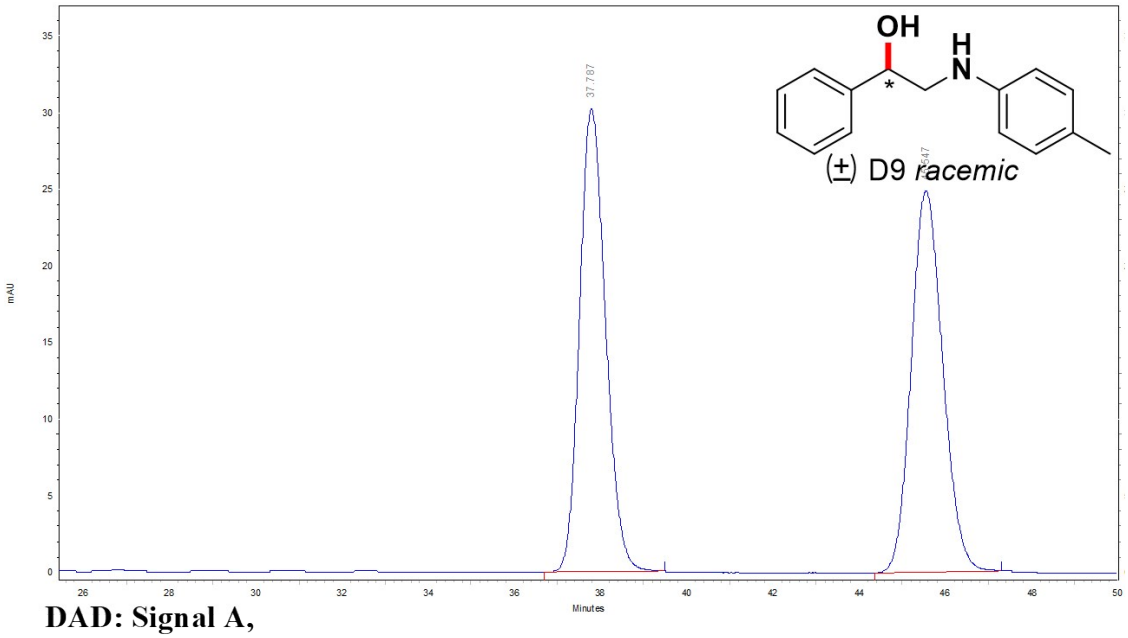
DAD: Signal A, 250 nm/Bw:4 nm Results

Retention Time	Area	Area %	Height	Height %
21.087	1929473	49.88	87840	52.31
22.613	1938827	50.12	80067	47.69
Totals	3868300	100.00	167907	100.00



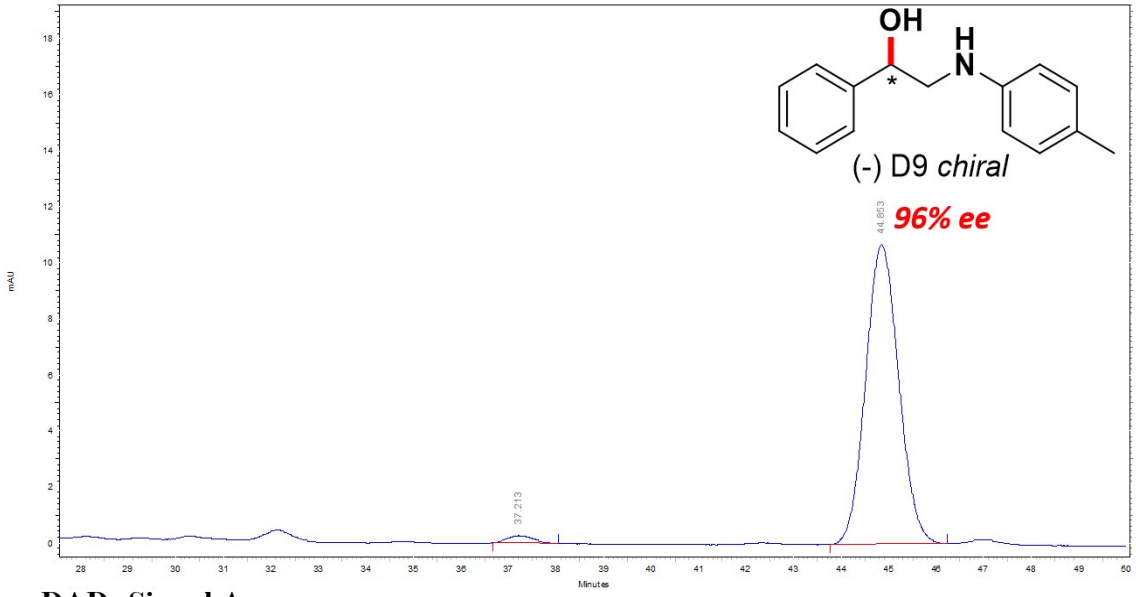
DAD: Signal A, 250 nm/Bw:4 nm Results

Retention Time	Area	Area %	Height	Height %
20.673	980216	97.71	45324	98.40
22.307	22942	2.29	739	1.60
Totals	1003158	100.00	46063	100.00



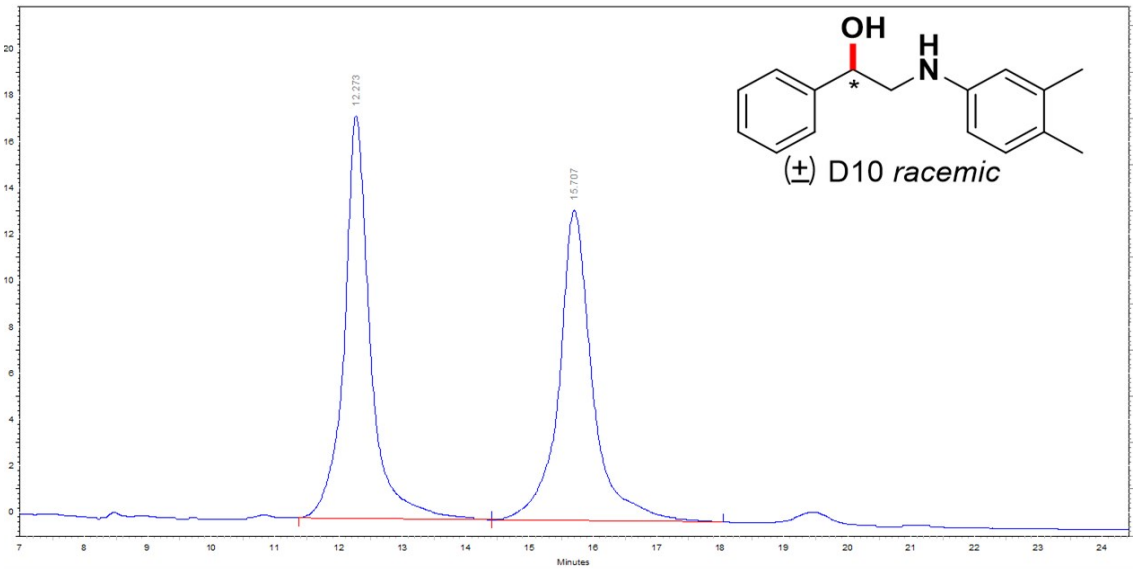
DAD: Signal A, 254 nm/Bw:4 nm Results

Retention Time	Area	Area %	Height	Height %
37.787	2657715	50.08	63392	54.85
45.547	2649749	49.92	52171	45.15
Totals	5307464	100.00	115563	100.00



DAD: Signal A, 254 nm/Bw:4 nm Results

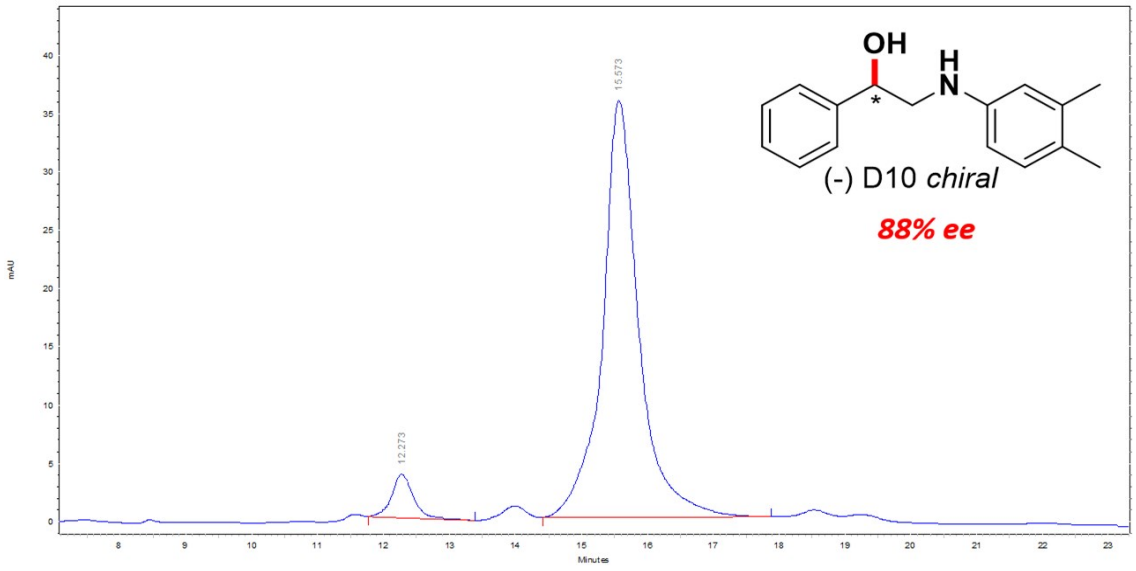
Retention Time	Area	Area %	Height	Height %
37.213	20483	1.85	545	2.38
44.853	1086630	98.15	22397	97.62
Totals	1107113	100.00	22942	100.00



DAD: Signal A,
250 nm/Bw:4
nm Results

Retention Time	Area	Area %	Height	Height %
12.273	1046447	50.21	36403	56.48
15.707	1037812	49.79	28049	43.52

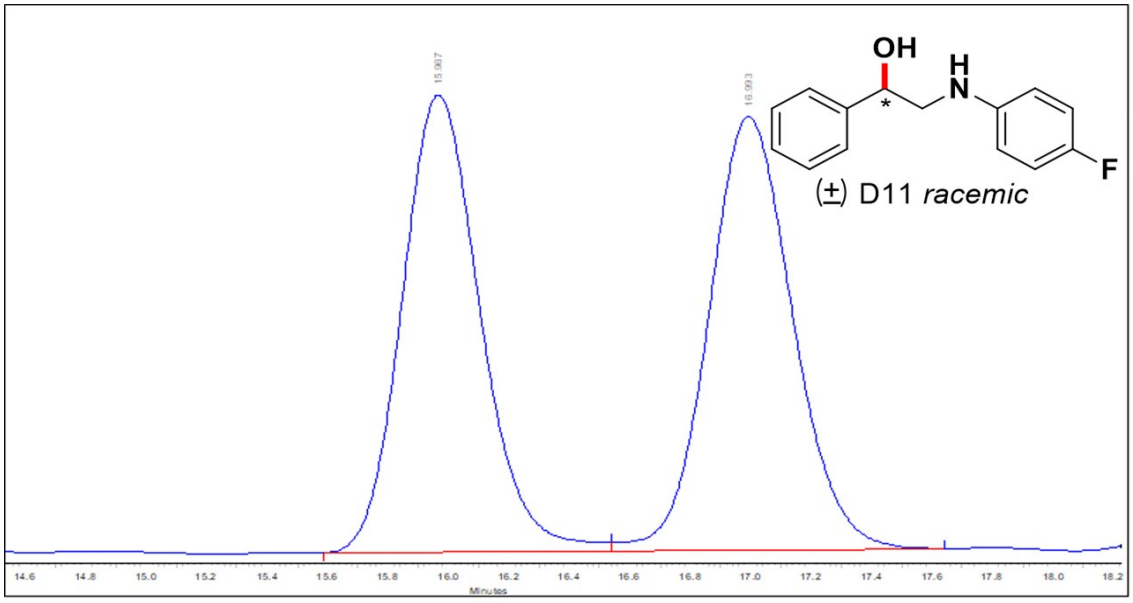
Totals	2084259	100.00	64452	100.00



DAD: Signal A,
250 nm/Bw:4
nm Results

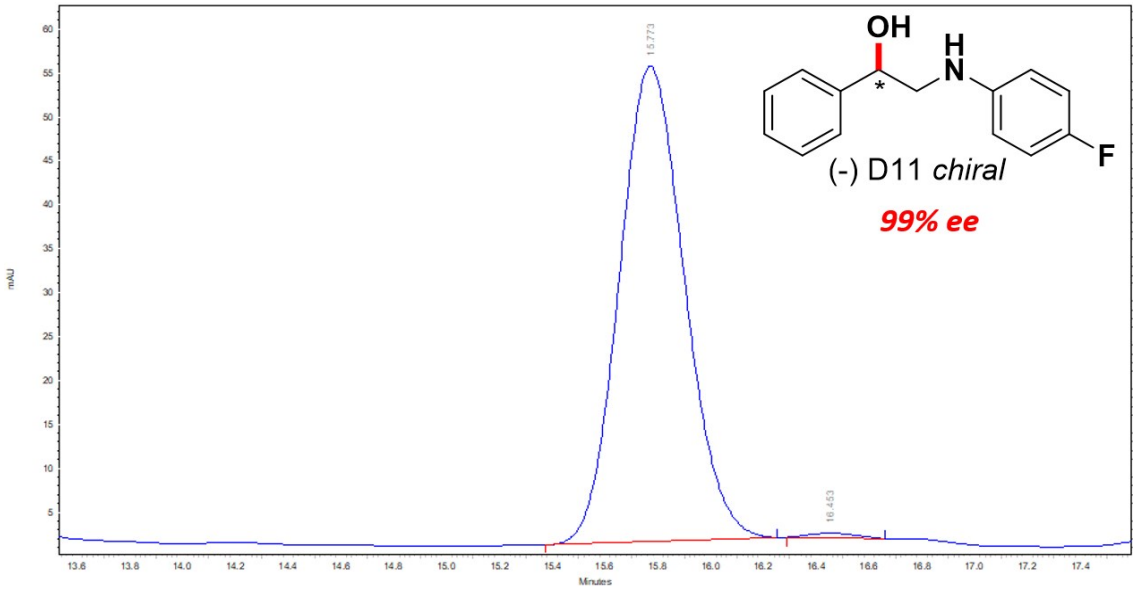
Retention Time	Area	Area %	Height	Height %
12.273	178879	5.85	7756	9.38
15.573	2880578	94.15	74970	90.62

Totals	3059457	100.00	82726	100.00



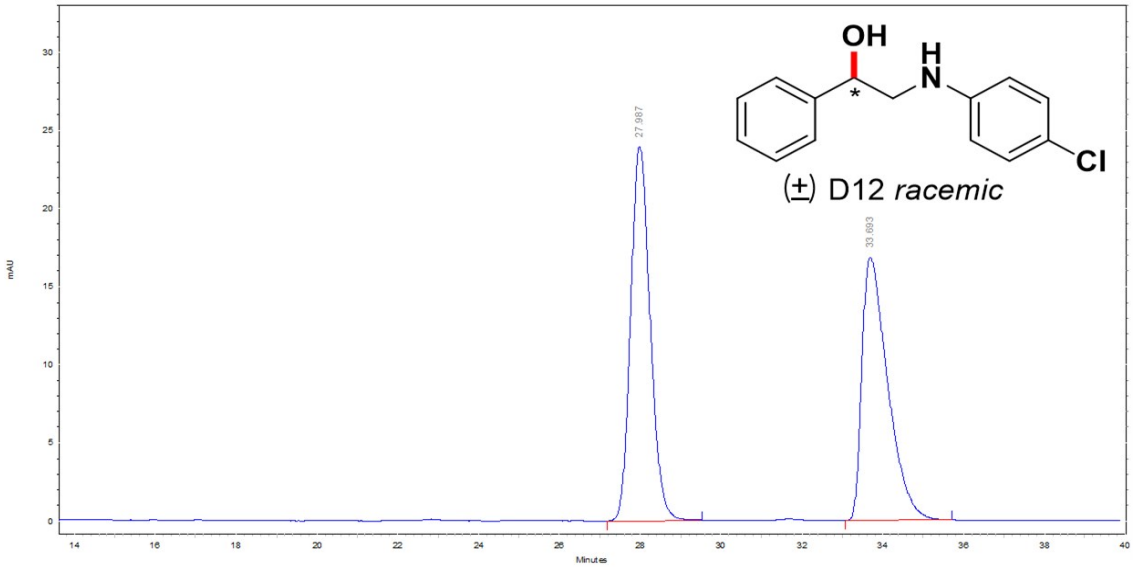
DAD: Signal A, 250 nm/Bw:4 nm Results

Retention Time	Area	Area %	Height	Height %
15.967	1656199	49.47	92350	51.33
16.993	1691991	50.53	87559	48.67
Totals	3348190	100.00	179909	100.00



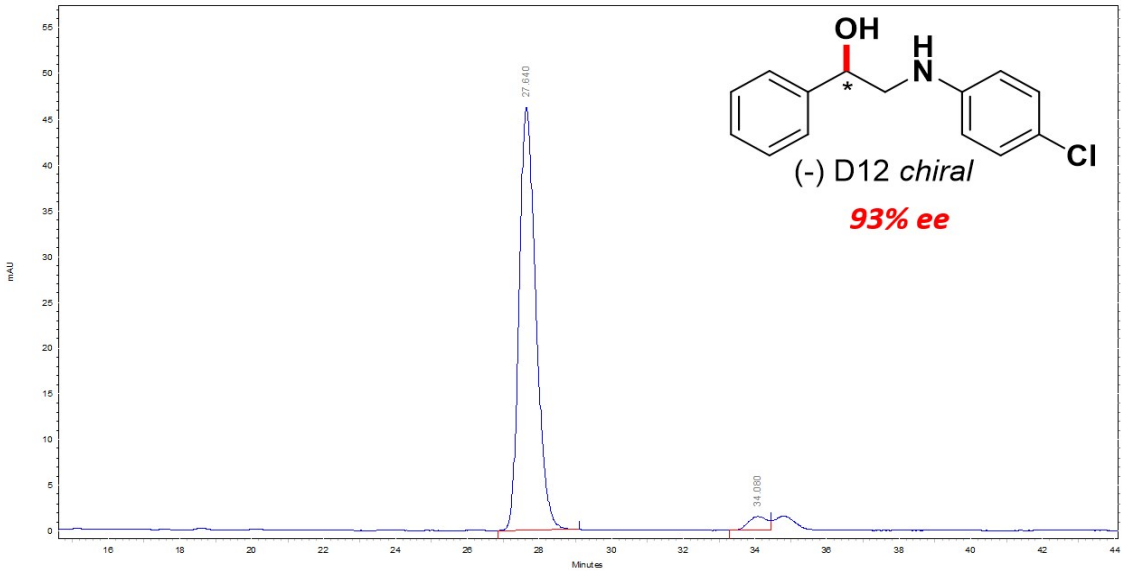
DAD: Signal A, 254 nm/Bw:4 nm Results

Retention Time	Area	Area %	Height	Height %
15.773	1943142	99.38	113456	99.15
16.453	12128	0.62	969	0.85
Totals	1955270	100.00	114425	100.00



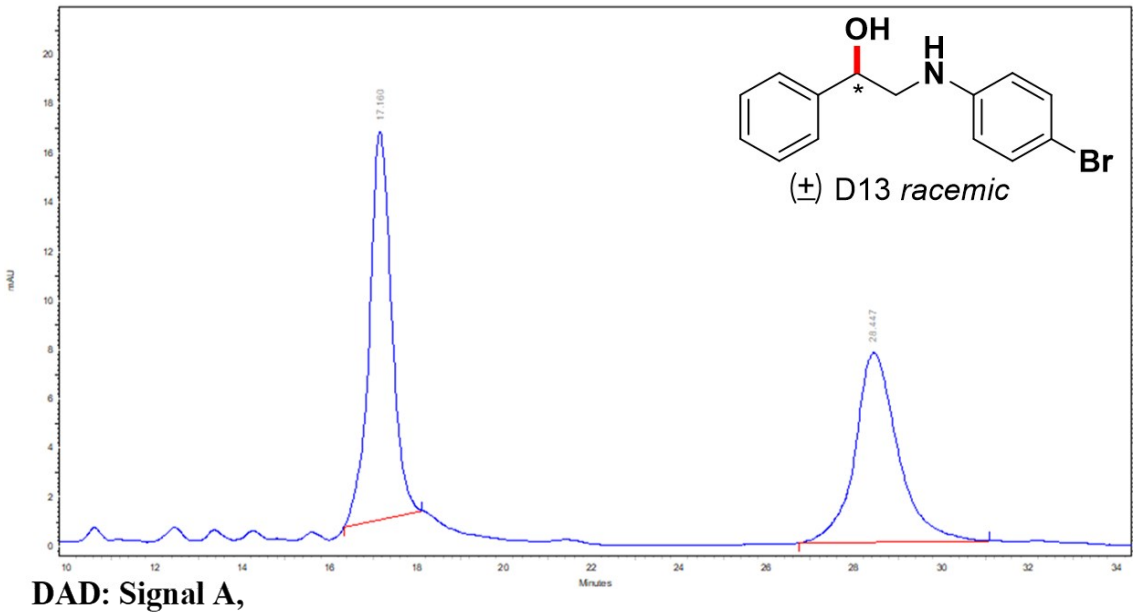
DAD: Signal A, 250 nm/Bw:4 nm Results

Retention Time	Area	Area %	Height	Height %
27.987	1682268	51.74	50204	58.68
33.693	1569201	48.26	35346	41.32
Totals	3251469	100.00	85550	100.00



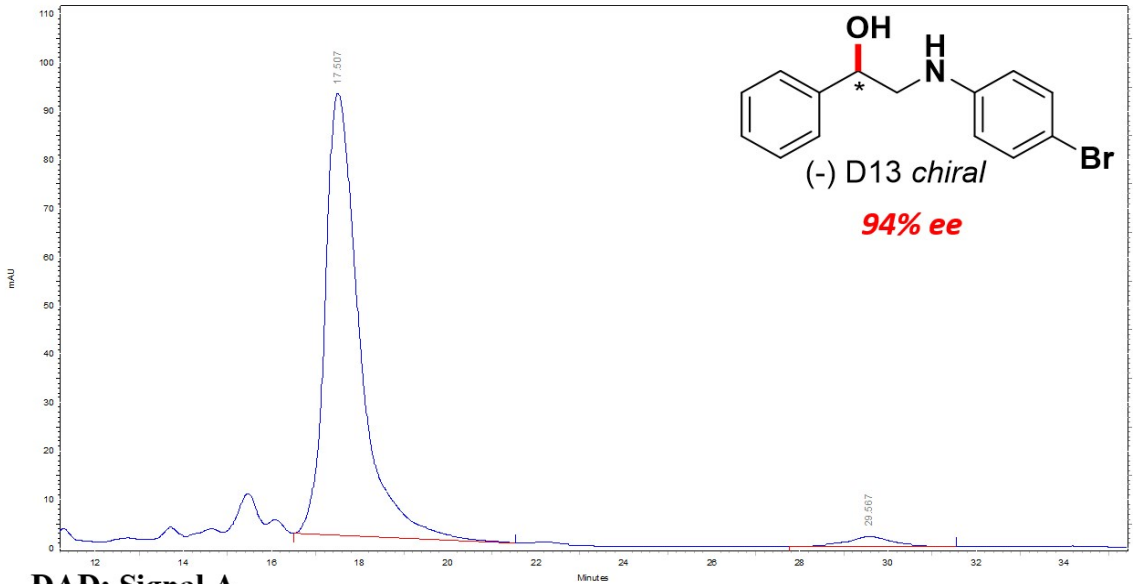
DAD: Signal A, 250 nm/Bw:4 nm Results

Retention Time	Area	Area %	Height	Height %
27.640	3140680	96.48	97032	96.89
34.080	114584	3.52	3116	3.11
Totals	3255264	100.00	100148	100.00



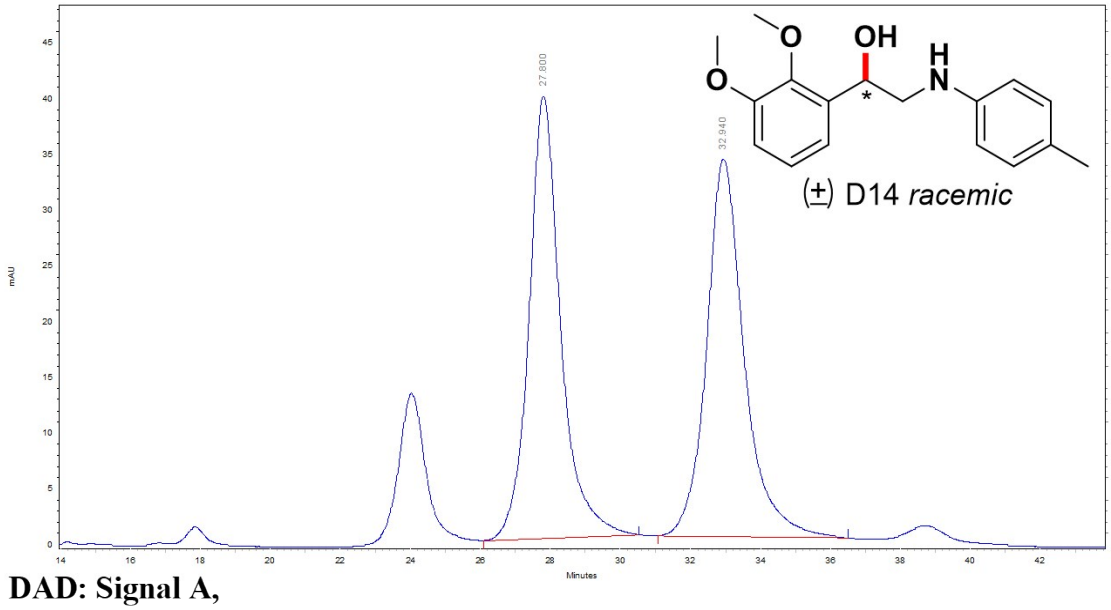
DAD: Signal A, 250 nm/Bw:4 nm Results

Retention Time	Area	Area %	Height	Height %
17.160	1164037	51.34	33106	67.22
28.447	1103119	48.66	16143	32.78
Totals	2267156	100.00	49249	100.00



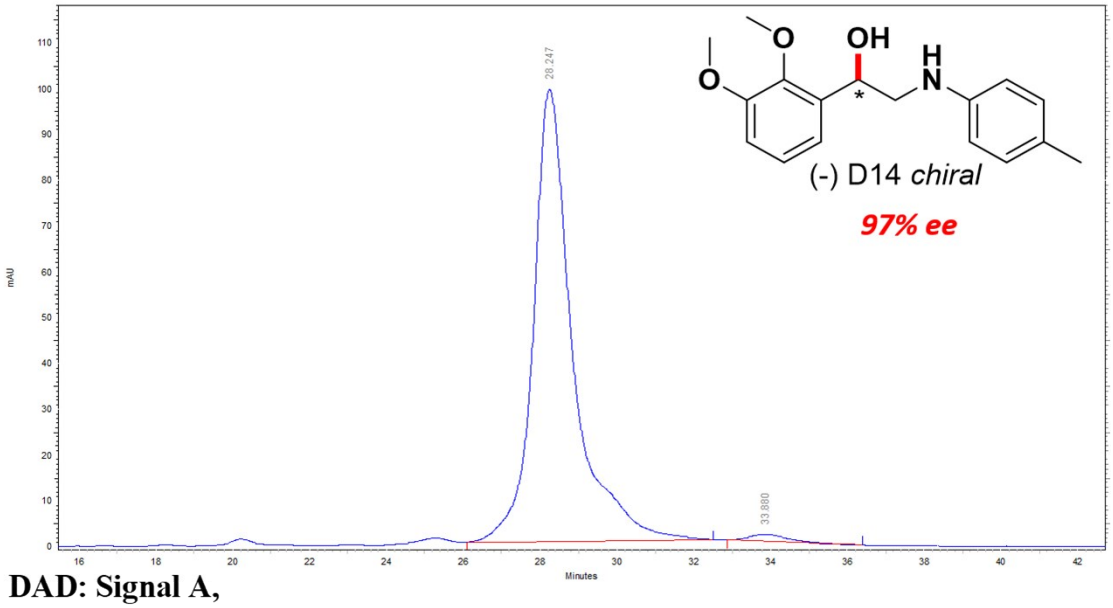
DAD: Signal A, 250 nm/Bw:4 nm Results

Retention Time	Area	Area %	Height	Height %
17.507	10394650	97.07	191070	97.73
29.567	313878	2.93	4432	2.27
Totals	10708528	100.00	195502	100.00



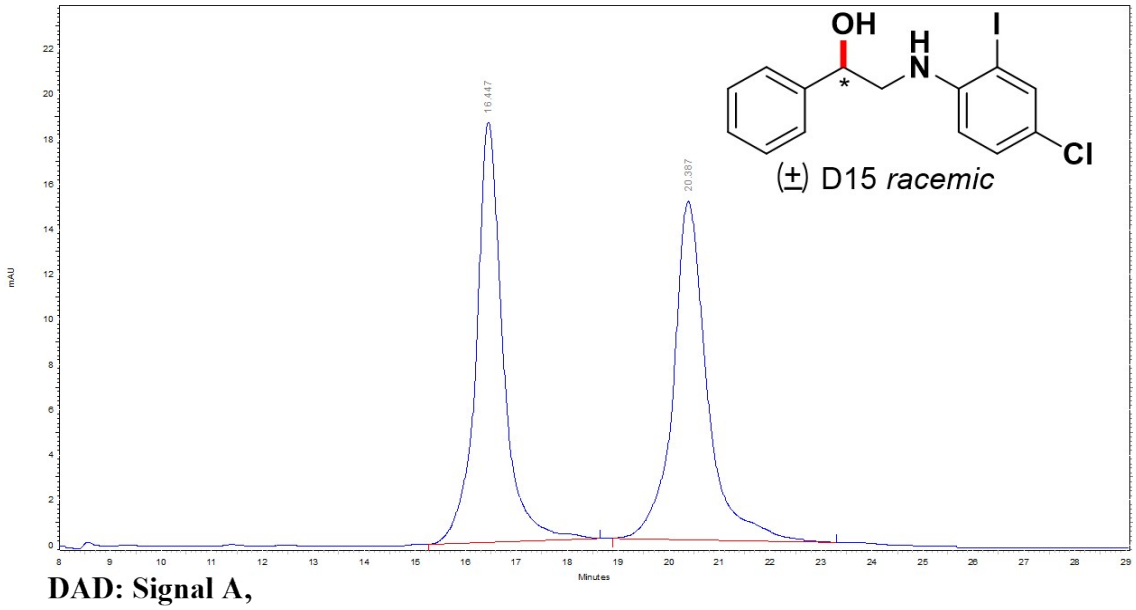
DAD: Signal A, 250 nm/Bw:4 nm Results

Retention Time	Area	Area %	Height	Height %
27.800	5239156	49.57	83133	53.94
32.940	5329656	50.43	71002	46.06
Totals	10568812	100.00	154135	100.00



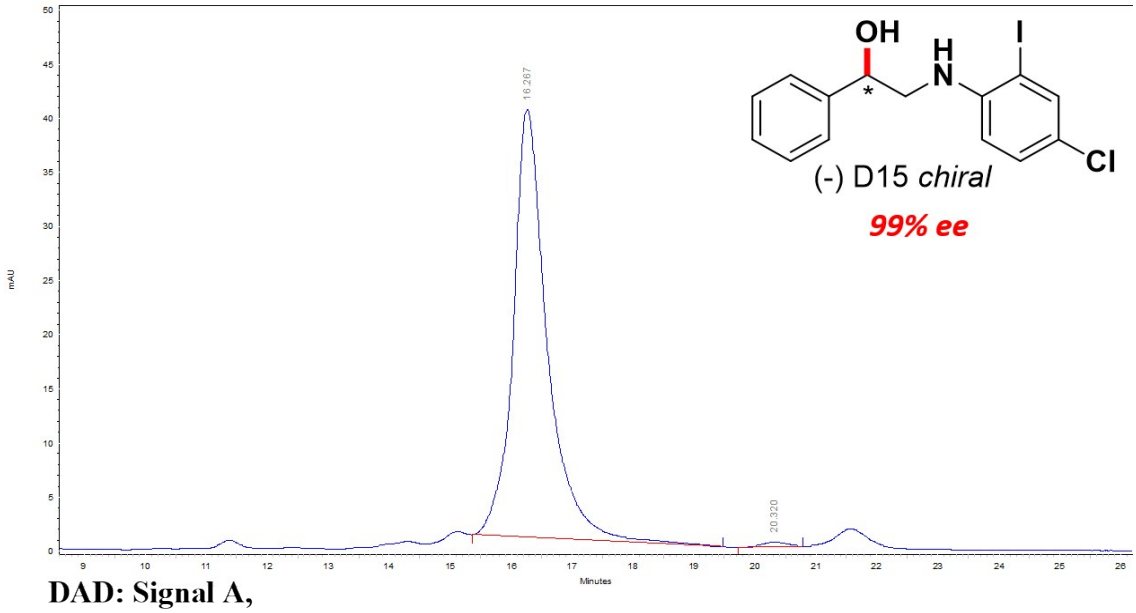
DAD: Signal A, 250 nm/Bw:4 nm Results

Retention Time	Area	Area %	Height	Height %
28.247	14794673	98.57	207046	98.50
33.880	213935	1.43	3145	1.50
Totals	15008608	100.00	210191	100.00



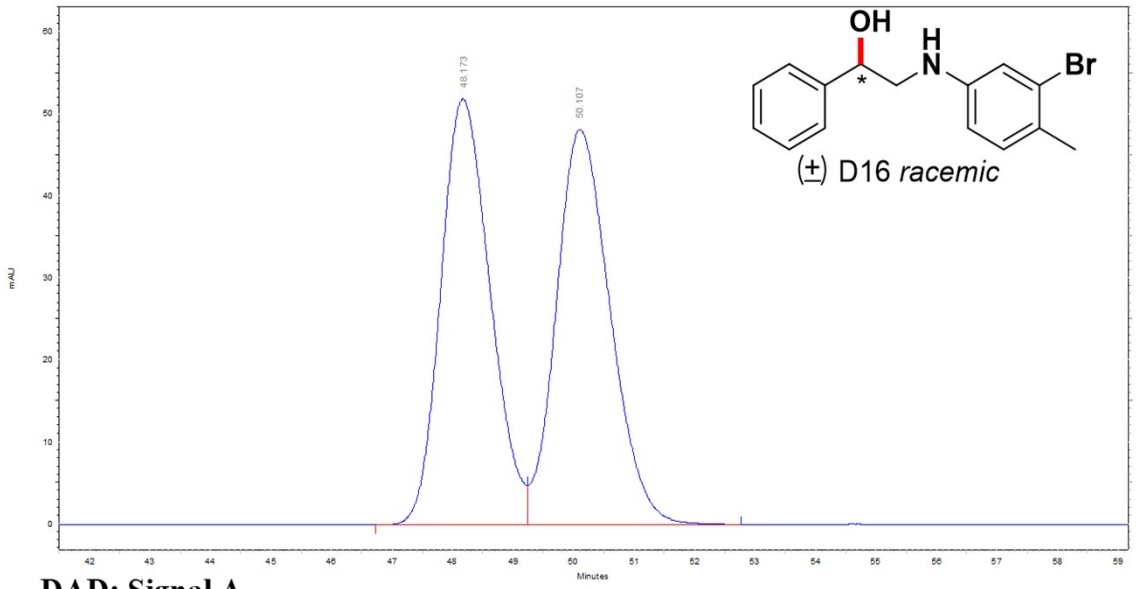
DAD: Signal A, 250 nm/Bw:4 nm Results

Retention Time	Area	Area %	Height	Height %
16.447	1442884	49.48	39009	55.35
20.387	1473100	50.52	31465	44.65
Totals	2915984	100.00	70474	100.00



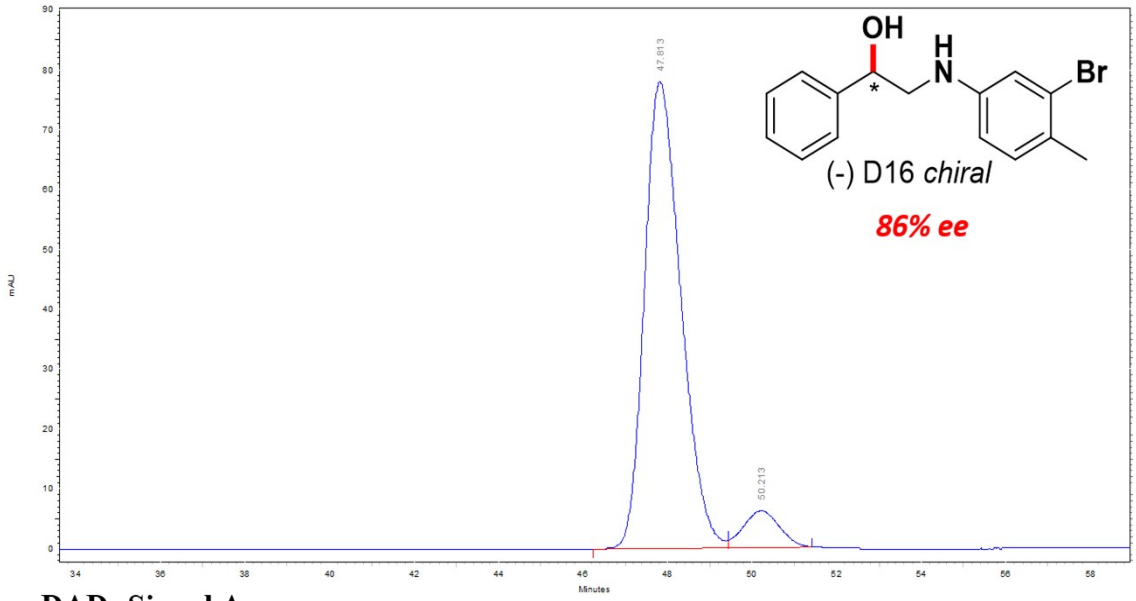
DAD: Signal A, 250 nm/Bw:4 nm Results

Retention Time	Area	Area %	Height	Height %
16.267	3241812	99.34	83022	99.04
20.320	21664	0.66	802	0.96
Totals	3263476	100.00	83824	100.00



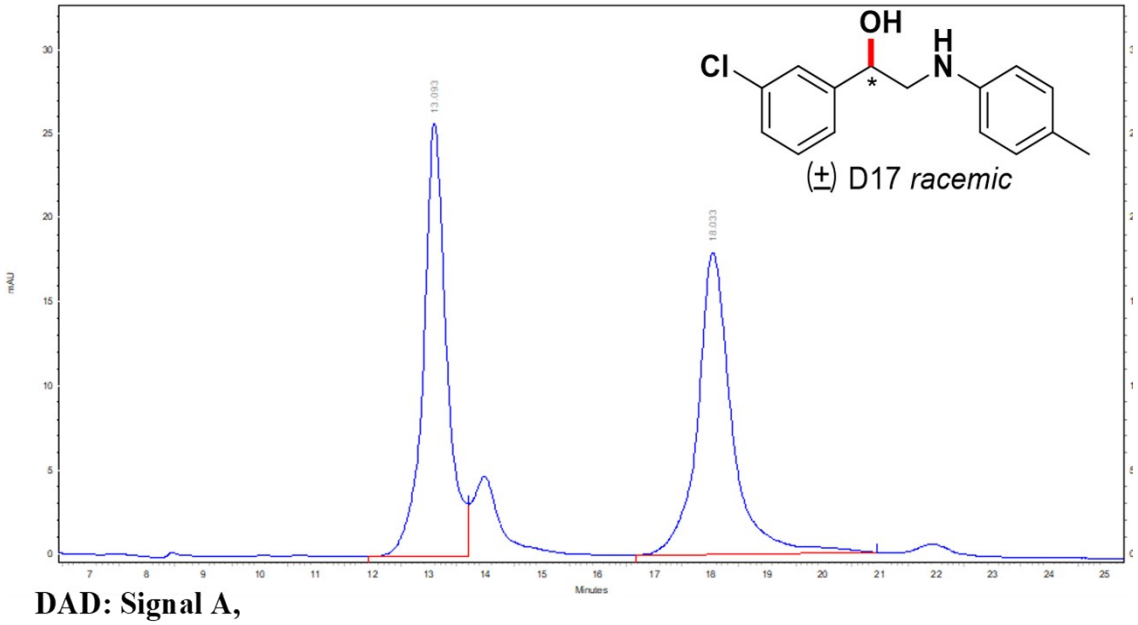
DAD: Signal A, 250 nm/Bw:4 nm Results

Retention Time	Area	Area %	Height	Height %
48.173	6177198	49.55	108971	51.87
50.107	6289613	50.45	101123	48.13
Totals	12466811	100.00	210094	100.00



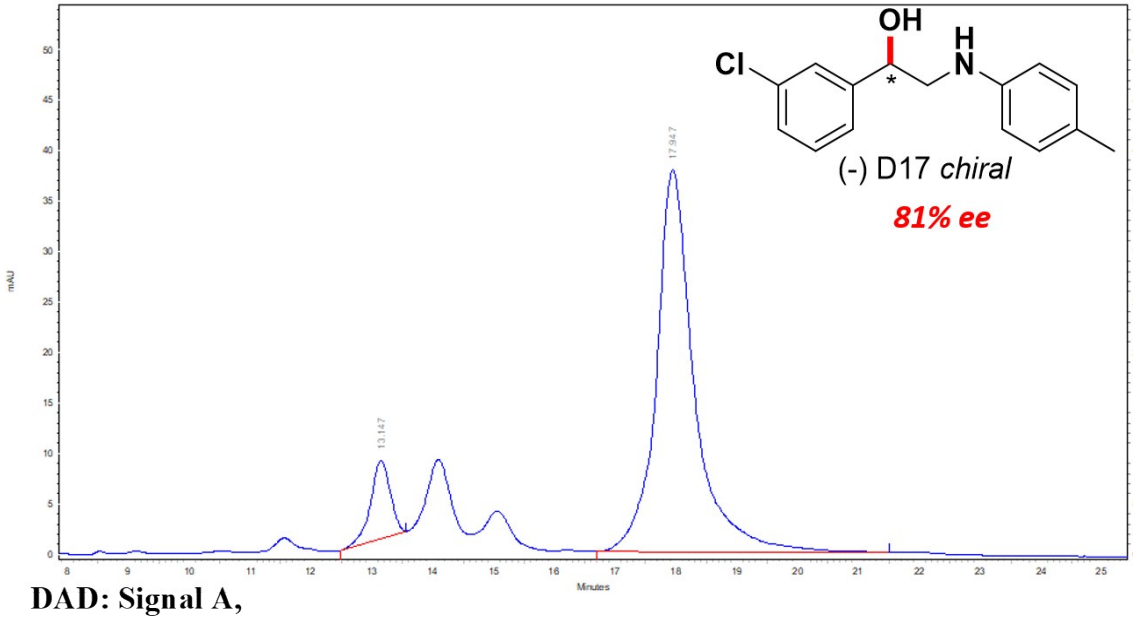
DAD: Signal A, 250 nm/Bw:4 nm Results

Retention Time	Area	Area %	Height	Height %
47.813	9777871	92.78	163448	92.72
50.213	760436	7.22	12830	7.28
Totals	10538307	100.00	176278	100.00



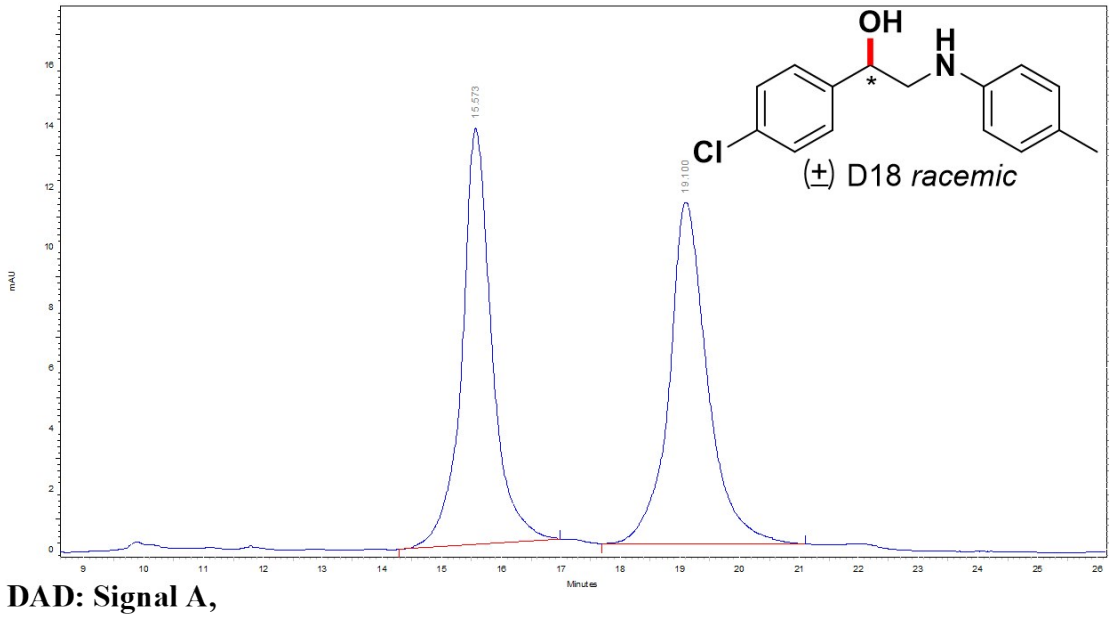
DAD: Signal A, 250 nm/Bw:4 nm Results

Retention Time	Area	Area %	Height	Height %
13.093	1545510	49.19	54090	58.91
18.033	1596266	50.81	37723	41.09
Totals	3141776	100.00	91813	100.00



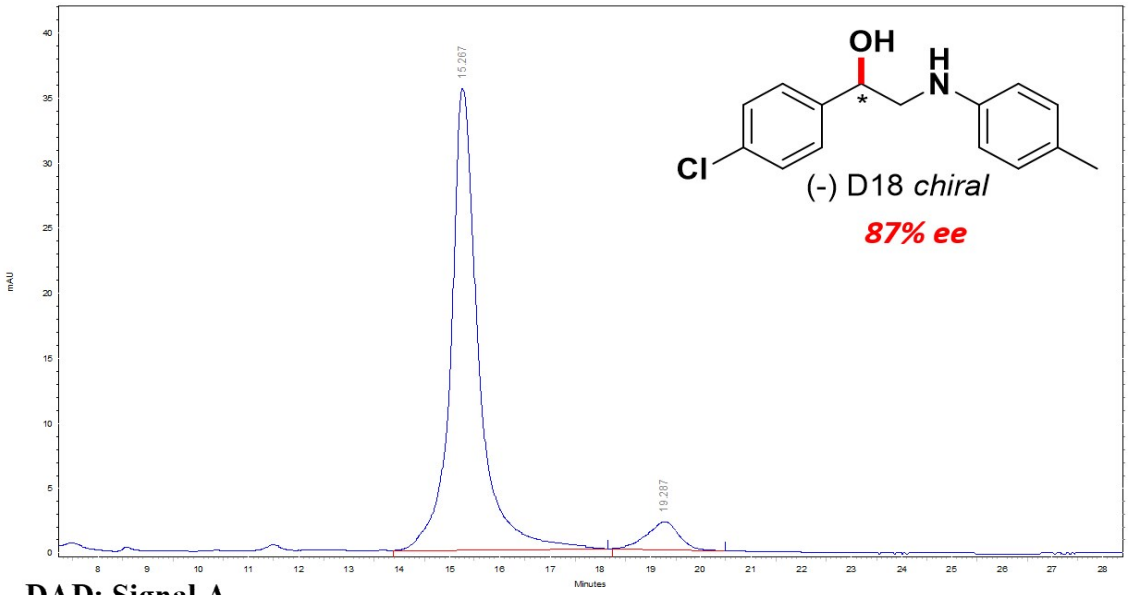
DAD: Signal A, 250 nm/Bw:4 nm Results

Retention Time	Area	Area %	Height	Height %
13.147	365846	9.57	16214	16.98
17.947	3458402	90.43	79282	83.02
Totals	3824248	100.00	95496	100.00



DAD: Signal A, 250 nm/Bw:4 nm Results

Retention Time	Area	Area %	Height	Height %
15.573	1007016	48.48	28820	54.88
19.100	1070236	51.52	23699	45.12
Totals	2077252	100.00	52519	100.00



DAD: Signal A, 250 nm/Bw:4 nm Results

Retention Time	Area	Area %	Height	Height %
15.267	2849634	93.44	74424	94.24
19.287	200162	6.56	4545	5.76
Totals	3049796	100.00	78969	100.00