

Extending on C₂-Symmetric Organocatalysts – correlating catalytic activity with molecular architecture in the direct asymmetric aldol reaction

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ELECTRONIC SUPPLEMENTARY INFORMATION

- S2 – General Experimental and Equipment
- S3 – Experimental
- S21 – Determination of reaction outcomes
- S23 – HPLC of chiral products and racemic examples.
- S74 – Evaluation of diprolineamides 1-5: Alternate aldehydes
- S75 – Evaluation of diprolineamides 1-5: Alternate ketones
- S76 – References

General Experimental

All ^1H and ^{13}C NMR spectra were recorded on a Jeol JNM-EX 270 MHz, Jeol JNM-EX 400 MHz or Bruker Avance III 500 MHz as indicated. Samples were dissolved in deuterated chloroform (CDCl_3) or deuterated methanol (CD_3OD) with the residual solvent peak used as an internal reference (CDCl_3 : $\delta_{\text{H}} = 7.26$ ppm; CD_3OD : $\delta_{\text{H}} = 3.31$ ppm). Proton spectra are reported as follows: chemical shift δ (ppm), [integral, multiplicity (s = singlet, br s = broad singlet, d = doublet, dd = doublet of doublets, ddd = doublet of doublets of doublets, t = triplet, dt = doublet of triplets, ddt = doublet of doublets of triplets, tt = triplet of triplets, q = quartet, m = multiplet), coupling constant J (Hz), assignment].

Thin Layer Chromatography (TLC) was performed using aluminium-backed Merck TLC Silica gel 60 F254 plates, and samples were visualised using 254 nm ultraviolet (UV) light, potassium permanganate/potassium carbonate oxidising dip (1:1:100 KMnO_4 : K_2CO_3 : H_2O w/w), or cerium-ammonium-molybdate (CAM) stain (1:2.5:100 Cerium ammonium sulphate dehydrate: Ammonium Molybdate: H_2SO_4 (10% w/w)).

Column Chromatography was performed using silica gel 60 (70-230 mesh). All solvents used were AR grade. Specialist reagents were obtained from Sigma-Aldrich Chemical Company and used without further purification. Petroleum spirits refers to the fraction boiling between 40-60 °C.

Chiral HPLC was performed with a 1200 series Agilent. Separation of stereoisomers was carried out with a Diacel Chiralpak AD-H chiral column (0.46 cm \times 25 cm). Retention times were reported at ambient temp (24 °C) with an injection volume of 20 μL at a flow rate of 1 mL/min. A mobile phase of 10% isopropanol/ 90% hexane was used.

HRMS was found via a 6210 MSD TOF mass spectrometer under the conditions: gas temperature (350 °C), vaporizer (28 °C), capillary voltage (3.0 kV), cone voltage (40 V), nitrogen flow rate (7.0L/min), nebuliser (15 psi). Samples were dissolved in MeOH.

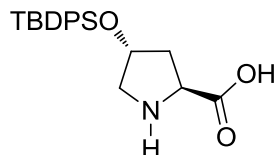
Specific rotation $[\alpha]_{\text{D}}$ was obtained using a JASCO DIPP Digital Polarimeter. Compounds were dissolved in CHCl_3 where indicated. Rotation was measured at $\lambda = 584$ nm and reported with the units $10^{-1} \text{ } ^\circ\text{C cm}^2\text{g}^{-1}$.

ATR-FTIR measurements were conducted using an Alpha FTIR spectrometer (Bruker Optik GmbH, Ettlingen, Germany) equipped with a deuterated triglycine sulfate (DTGS) detector and a single-reflection diamond ATR sampling module (Platinum ATR QuickSnap™). All absorption bands are reported in wavenumbers (cm^{-1}) and signals are reported as weak (w), medium (m), strong (s) and/or broad (br). Background spectra of a clean ATR surface were acquired prior to each sample measurement using the same acquisition parameters

Melting points were found on a Stuart Scientific Melting Point Apparatus SMP3, v. 5 and are uncorrected.

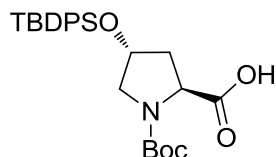
Experimental

trans-4-*tert*butyldiphenylsiloxy-L-proline



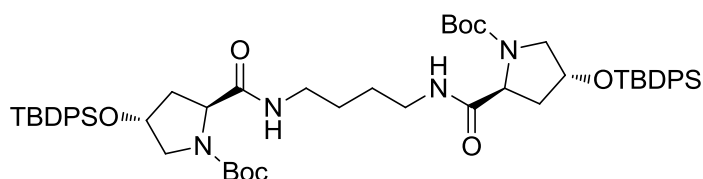
Trans-4-hydroxy-L-proline (1.0 g, 0.763 mmol) was added to acetonitrile (20 mL) and stirred. TBDPS-Cl (6.94 mL, 0.026 mol) was added to the stirring solution and the reaction was cooled to 0 °C. DBU (4.22 mL, 0.028 mol) was subsequently added to the stirring solution and the mixture was allowed to reach room temperature and stirred for 24 hrs. The resulting reaction mixture was then quenched with hexane and the product was extracted into hexane (3 × 30 mL). The combined hexane layers were combined and the solvent was removed *in vacuo*. The resulting oil was redissolved in a methanol (32 mL), THF (18 mL), water (16 mL) and 2M NaOH (24 mL) mixture and allowed to stir for 90 mins at room temperature. The solution was then titrated to a pH of 6 with 2M HCl before removing the organic solvents under reduced pressure. To the resulting water layer a 1:1 ratio of Et₂O was added and the biphasic mixture was allowed to stand for 24h, resulting in crystals forming in the organic phase. The solid was filtered and washed with cold Et₂O to give the silylated intermediate as white crystals (2.71 g, 0.733 mol, 96%). ¹H NMR (400 MHz, CD₃OD) δ 7.67-7.64 (m, 4H, aryl), 7.45-7.42 (m, 6H, aryl), 4.59 (s, *J* = 0.27, 1H, chiral), 4.23 (1H, chiral), 3.30 (dd, *J* = 10.8, 5.4 Hz, 1H, N-CH₂), 3.29 (dt, *J* = 13.5, 2.7 Hz, 1H, N-CH₂), 2.31 (ddt, *J* = 13.5, 7.56, 1.88 Hz, 1H, CH-CH₂-CH), 1.93 (ddd, *J* = 13.5, 9.99, 4.05 Hz, 1H, CH-CH₂-CH), 1.08 (9H, *t*-butyl). Compound was identified by ¹H NMR and was consistent with literature values.¹

trans-N-Boc-4-*tert*butyldiphenylsiloxy-L-proline 7

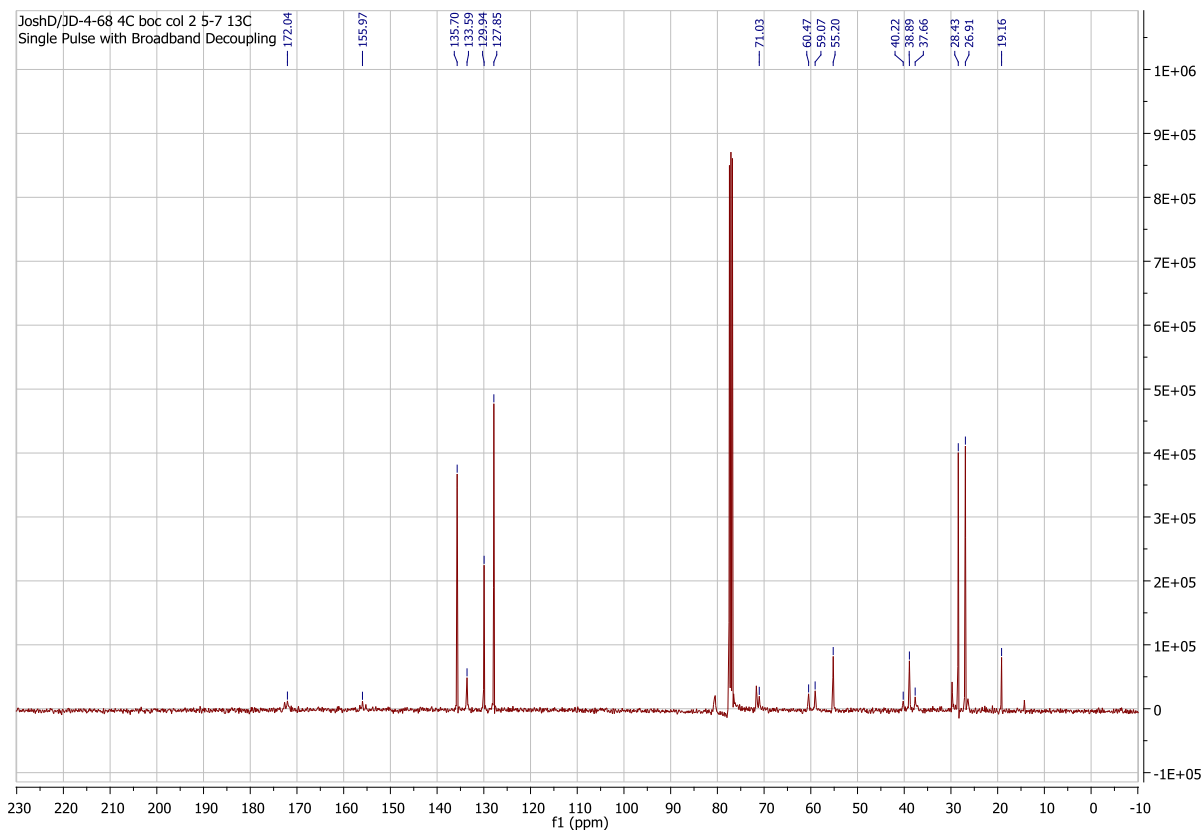


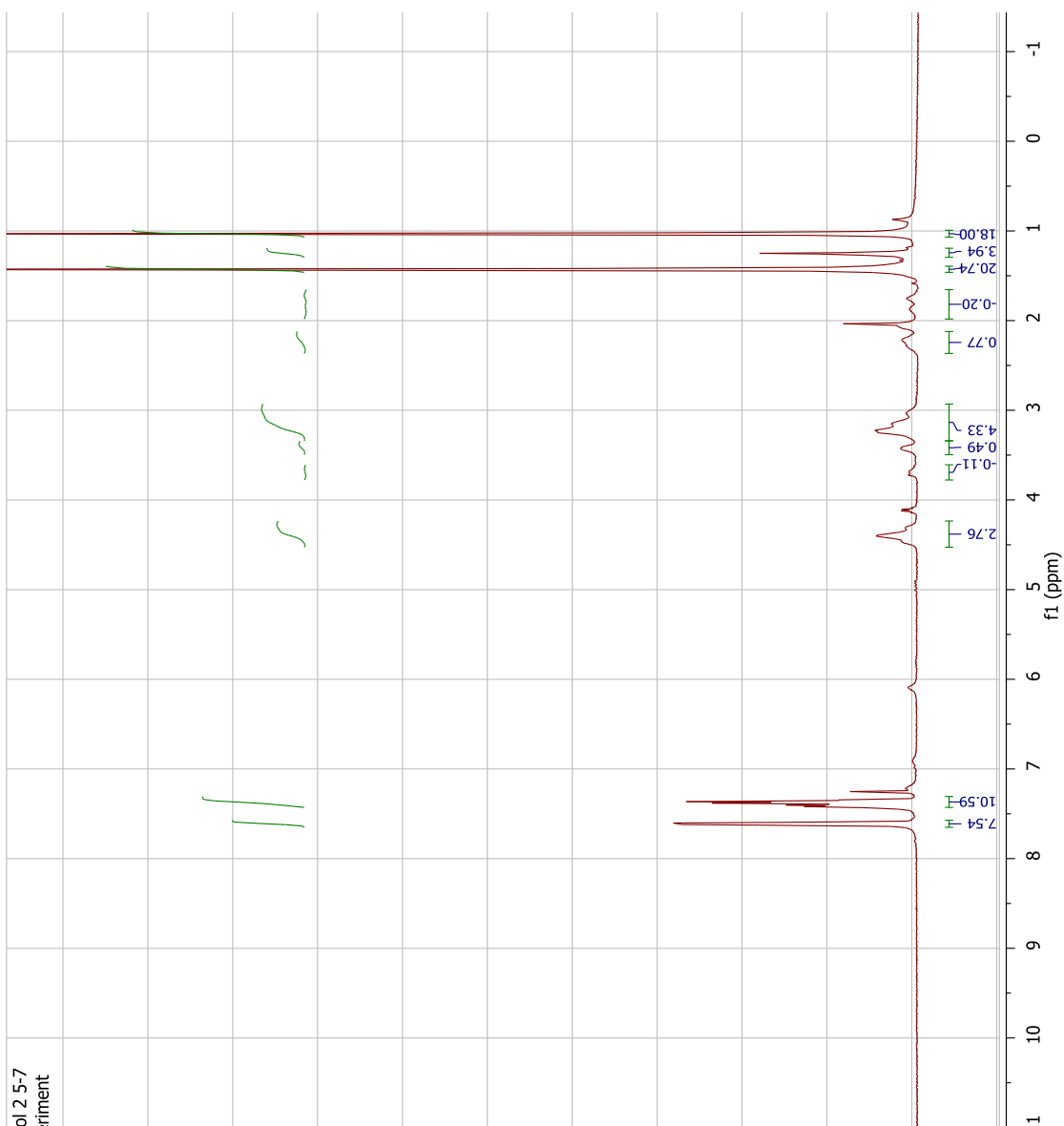
TBDPS-Proline (2.71 g, 0.7337 mmol) was dissolved in a 1:1 ratio of THF/H₂O (20 mL : 20 mL). To this mixture was added NaOH (0.733 g, 0.018 mol) along with Boc₂O (2.08 g, 0.953 mmol) and the solution was stirred for 16 h at room temperature. The resulting solution was then acidified with 2M HCl and extracted into Diethyl Ether (3 × 20 mL). The combined organic phase was dried over MgSO₄ and the solvent was removed *in vacuo* to afford clear viscous oil. The crude mixture was purified *via* flash chromatography (1/4 EtOAc : Pet spirits) to give the pure monomer as a colourless oil (2.82 g, 0.6 mol, 82%). ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.64 (m, 4H, Alkyl), 7.39 (m, 6H, Alkyl), 4.56 (t, *J* = 8 Hz, 1H, Chiral), 4.43 (m, 1H, Chiral), 3.59-3.29 (m, 2H, CH₂-NH), 2.28-2.04 (m, 2H, N-CH₂), 1.47 (m, 9H, *t*-butyl), 1.07 (m, 9H, *t*-butyl). Compound was identified by ¹H NMR and was consistent with literature values.¹

1,4-di(*trans*-*N*-Boc-4-*tert*butyldiphenylsiloxy-L-prolinamide) butane. **8**

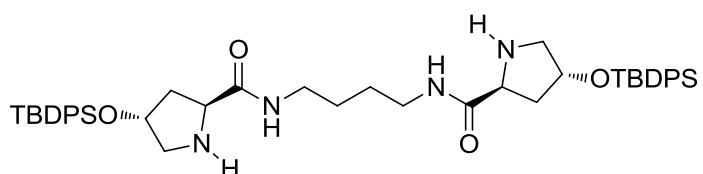


trans-*N*-Boc-4-*tert*butyldiphenylsiloxy-L-proline **7** (0.295 g, 0.623 mmol) was dissolved in DCM (20 mL) and cooled to 0 °C. HOBT (0.02 g, 0.015 mmol) was added to the solution and the mixture was stirred for 5 min. EDCI (0.085 g, 0.074 mmol) was added to the mixture followed by 3 min additional stirring followed by the introduction of 1,4-diaminobutane (0.03 mL, 0.297 mmol) was introduced. The mixture was allowed to reach room temperature and stirred for 16 h. The final reaction mixture was diluted with additional DCM (30 mL) and washed with 10% citric acid (3 × 30 mL), saturated NaHCO₃ (3 × 30 mL) and brine (1 × 30 mL). The resulting organic phase was dried over MgSO₄ and the solvent was removed *in vacuo* to give the crude *N*-Boc protected diprolineamide **8** as a colourless oil. The crude mixture was purified *via* flash chromatography (1/3 EtOAc : Pet spirits → 1/1 EtOAc : Pet spirits) to give the pure dimer as a viscous colourless oil (0.292 g, 0.254 mmol, 85%). R_f = 8/33 (1:1 EtOAc : Pet. Spirits); ¹H NMR (400 MHz, CDCl₃) δ (ppm) = 7.62 (m, 8H, aryl), 7.40 (m, 12H, aryl), 4.40 (br, 4H, chiral), 3.72 (br, 1H, CH₂-NH), 3.43 (br, 1H, CH₂-NH), 3.23 (br, 4H CO-NH-CH₂), 2.22 (br, 2H, CH₁-CH₂), 1.88 – 1.76 (br. m, 2H, CH₁-CH₂), 1.43 (br, 18H, O-*t*-butyl), 1.25 (br, 4H, alkyl), 1.03 (br, 18H, Si-*t*-butyl); ¹³C NMR (400 MHz, CDCl₃) δ (ppm) = 172.04, 155.97, 135.70, 133.59, 129.94, 127.85, 71.03, 60.47, 59.07, 55.20, 40.22, 37.66, 37.66, 37.66, 37.66, 28.43, 26.91, 19.16; [α]_D^{22.2} = -30.8 ° (c = 0.00089, CHCl₃); IR ν_{max} = 2930 (m), 1660 (s), 1105 (s), 700 (s); HRMS calculated for [C₅₆H₇₉N₄O₈Si₂]⁺ M = 991.5431 found 991.53809.



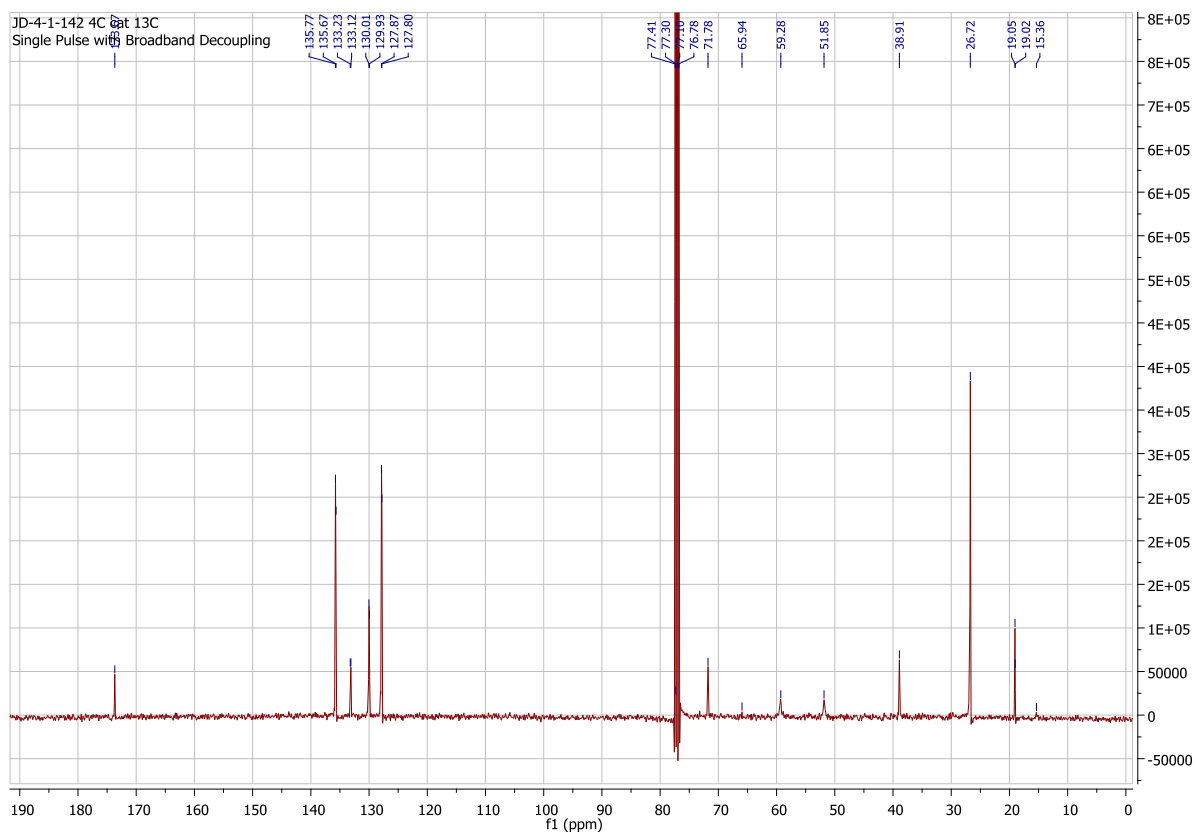


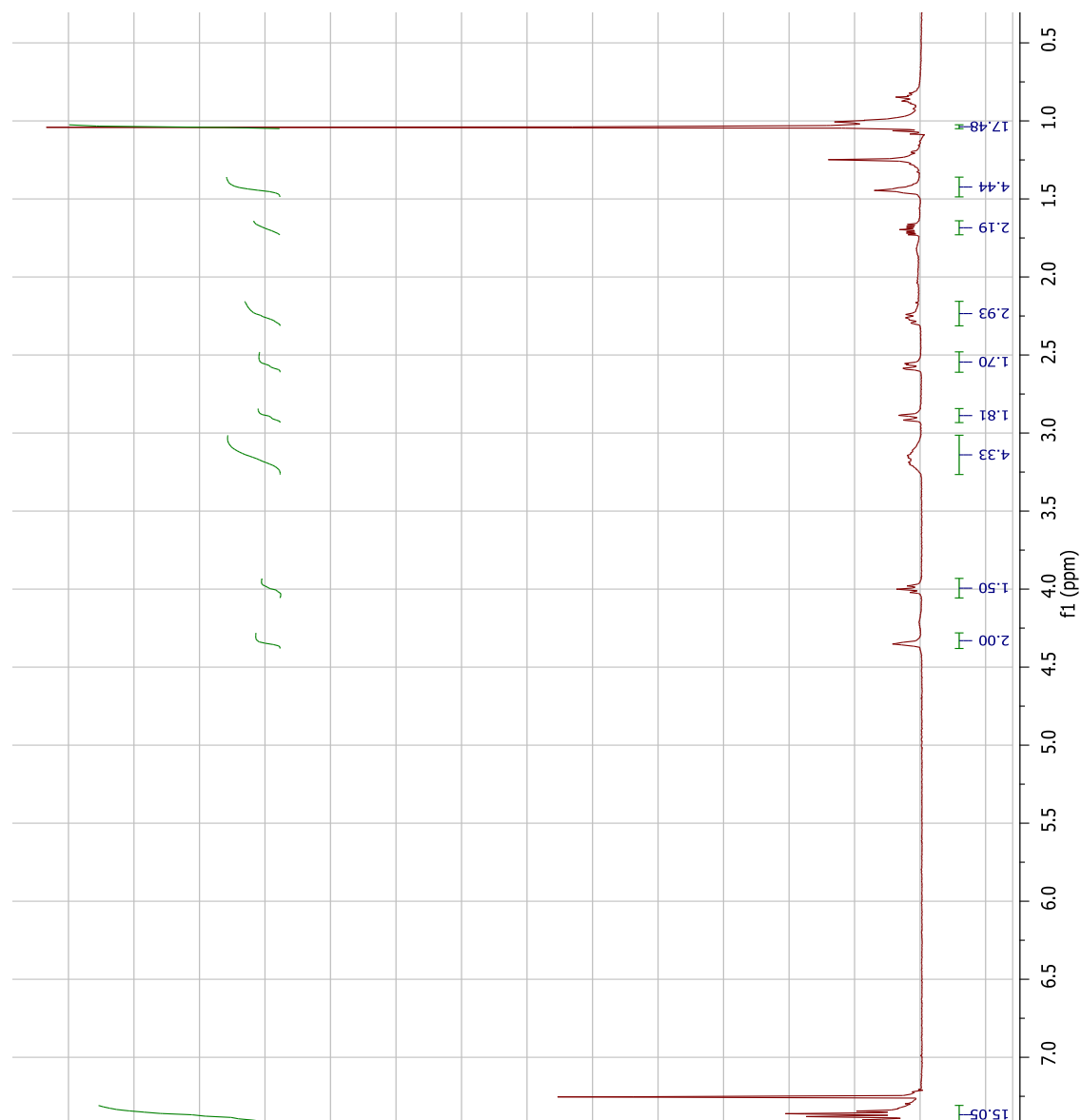
1,4-di(*trans*-4-*tert*butyldiphenylsiloxy-L-prolinamide) butane **1**



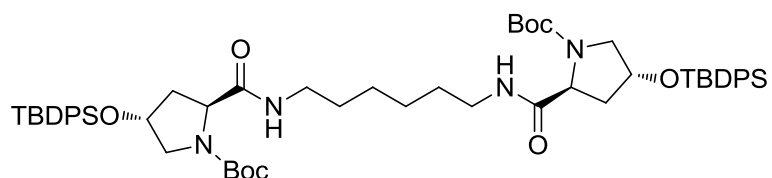
N-Boc protected diproline **8** (0.394 g, 0.398 mmol) was solvated in DCM (18 mL) and stirred. To the stirring solution was added TFA (2 mL) to bring the solution to a 10 vol% concentration of acid/DCM. The solution was

stirred for 6h under an inert atmosphere at room temperature. The final mixture was basified with saturated NaHCO₃ (50 mL) and extracted into DCM (3 × 30 mL). The combined organic phase was then washed with additional NaHCO₃ (3 × 30 mL) and the organic phase was dried over MgSO₄. The solvent was removed in vacuo to give an opaque oil. Residual solvent was azeotroped with Et₂O to give the final organocatalyst **1** as an amorphous pale brown solid (0.309 g, 0.39 mmol, 98%). R_f = 4/33 (1:9 MeOH : EtOAc); Mp = 205.5 – 207 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm) = 7.61 (m, 8H, aryl), 7.36 (m, 12H, aryl), 4.35 (br, 2H, CH₁-O), 4.00 (t, J = 8.4 Hz, 2H, CH₁-N), 3.14 (m, 4H, CO-NH-CH₂), 2.9 (d, J = 12.1 Hz, 2H, CH₂-NH), 2.58 (d, J = 12.1 Hz, 2H, CH₂-NH), 2.26 (m, 2H, CH₁-CH₂), 1.70 (ddd, J = 13.6, 8.4, 4.8 Hz, 2H, CH₁-CH₂), 1.45 (br, 4H, alkyl), 1.04 (br, 18H, *t*-butyl); ¹³C NMR (400 MHz, CDCl₃) δ (ppm) = 173.7, 135.8, 133.2, 129.9, 127.9, 71.8, 65.9, 59.4, 51.9, 38.9, 26.7, 19, 15.4; [α]_D^{23.3} = -37.6 ° (c = 0.0025, CHCl₃); IR ν_{max} = 2925 (m), 1624 (s) 698 (s); HRMS calculated for [C₄₆H₆₃N₄O₈Si₂]⁺ M = 791.4382 found 791.4395.





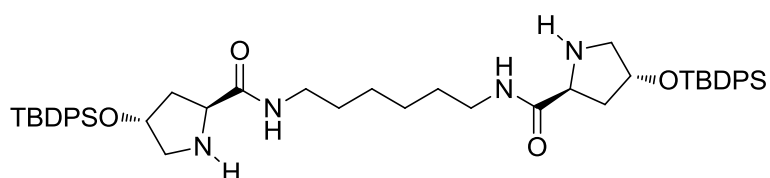
1,6-di(trans-N-Boc-4-tertbutyldiphenylsiloxy-L-prolinamide) hexane 9



Trans-N-Boc-4-tertbutyldiphenylsiloxy-L-proline **7** (0.714 g, 1.52 mmol) was dissolved in DCM (20 mL) and cooled to 0 °C. HOBt (0.042 g, 0.36 mmol) was added to the solution and the mixture was stirred for 5 min. EDCI (0.218 g, 1.41 mmol) was added to the mixture followed by 3 min additional stirring followed by the introduction of 1,6-diaminohexane (0.084 g, 0.72 mmol) was introduced. The mixture was allowed to reach room temperature

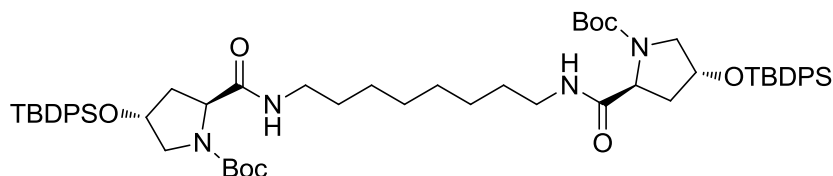
and stirred for 16 h. The final reaction mixture was diluted with additional DCM (30 mL) and washed with 10% citric acid (3 × 30 mL), saturated NaHCO₃ (3 × 30 mL) and brine (1 × 30 mL). The resulting organic phase was dried over MgSO₄ and the solvent was removed *in vacuo* to give the crude *N*-Boc protected diprolinamide **8**. The crude mixture was purified *via* flash chromatography (1/3 EtOAc : Pet spirits) to give the pure dimer as a white amorphous solid (0.484 g, 0.475 mmol, 66%). ¹H NMR (270 MHz, CDCl₃) δ (ppm) = 7.59 – 7.25 (m, 20H aryl), 4.39 (m, 4H, chiral H), 3.69 – 3.42 (m, 4H, CH-CH₂-CH), 3.17 (br s, 4 H, CO-NH-CH₂), 2.39 – 1.97 (br m, 4H, N-CH₂), 1.43 (s, 18H, *N*-*t*-butyl), 1.40 (br, 4H, alkyl), 1.24 (br, 4H, alkyl), 1.02 (s, 18H, Si-*t*-butyl). The compound was confirmed by correlation to published ¹H NMR spectra.^{2,3}

1,6-di(*trans*-4-*tert*butyldiphenylsiloxy-L-prolinamide) hexane **2**



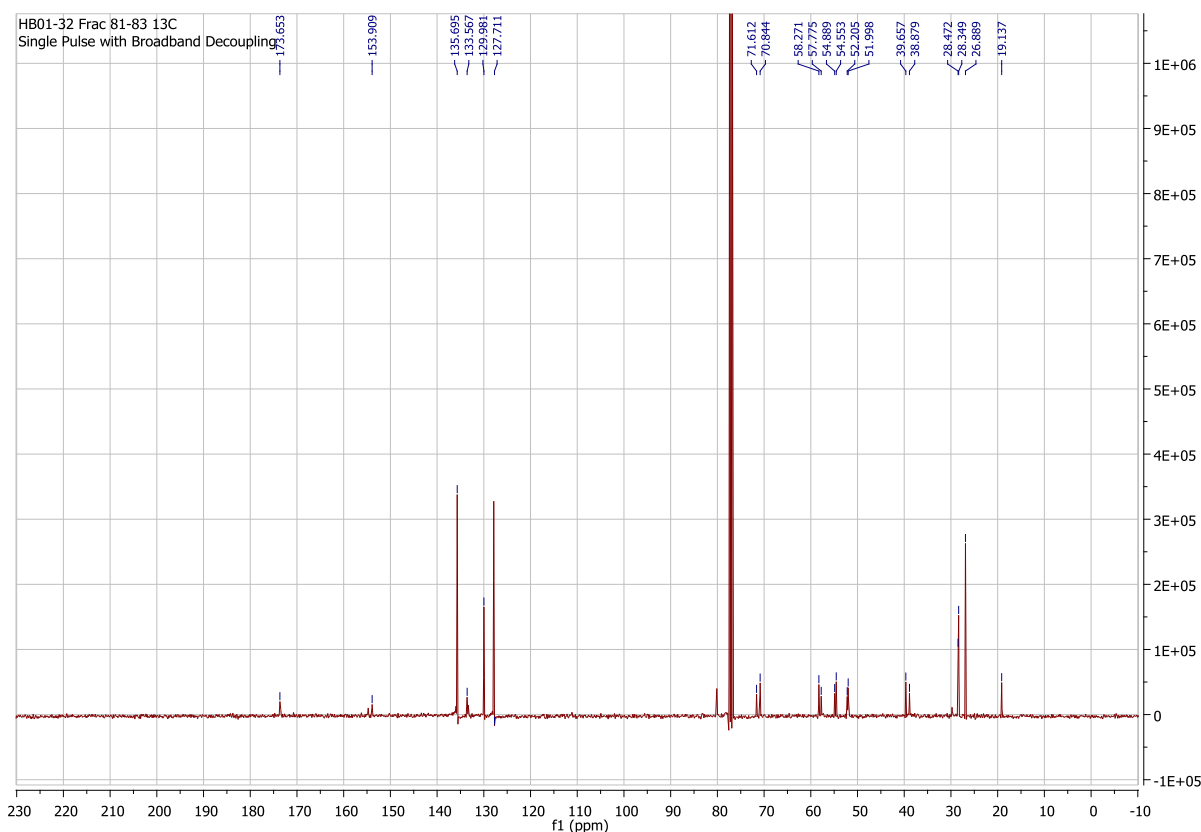
N-Boc protected diprolinamide **9** (0.318 g, 0.312 mmol) was solvated in DCM (18 mL) and stirred. To the stirring solution was added TFA (2 mL) to bring the solution to a 10 vol% concentration of acid/DCM. The solution was stirred for 6h under an inert atmosphere at room temperature. The final mixture was basified with saturated NaHCO₃ (50 mL) and extracted into DCM (3 × 30 mL). The combined organic phase was then washed with additional NaHCO₃ (3 × 30 mL) and the organic phase was dried over MgSO₄. The solvent was removed *in vacuo* to give an opaque oil. Residual solvent was azeotroped with Et₂O to give the final organocatalyst **1** as an amorphous pale brown solid (0.252 g, 0.31 mmol, 99%). ¹H NMR (270 MHz, CDCl₃) δ (ppm) = 7.608 (br m, 8H, aryl), 7.38 (br m, 12H, aryl), 4.35 (br, 2H, CH₁-O), 3.99 (t, *J* = 8.4 Hz, CH₁-N), 3.14 (tt, *J* = 19.2, 6.88, Hz, 4H, CH₂-N), 2.89 (d, *J* = 12.1 Hz, 2H, N-CH₂-CH), 2.56 (dd, *J* = 4.45, 7.7 Hz, 2H, CH₂-NH), 2.24 (m, 2H, CH₁-CH₂), 1.7 (ddd, *J* = 13.2, 8.8, 4.8 Hz, 2H, CH₁-CH₂), 1.41 (m, 4H, alkyl), 1.27 (m, 4H, alkyl), 1.03 (br s, 18H, *t*-butyl). The compound was confirmed by correlation to published ¹H NMR spectra.^{2,3}

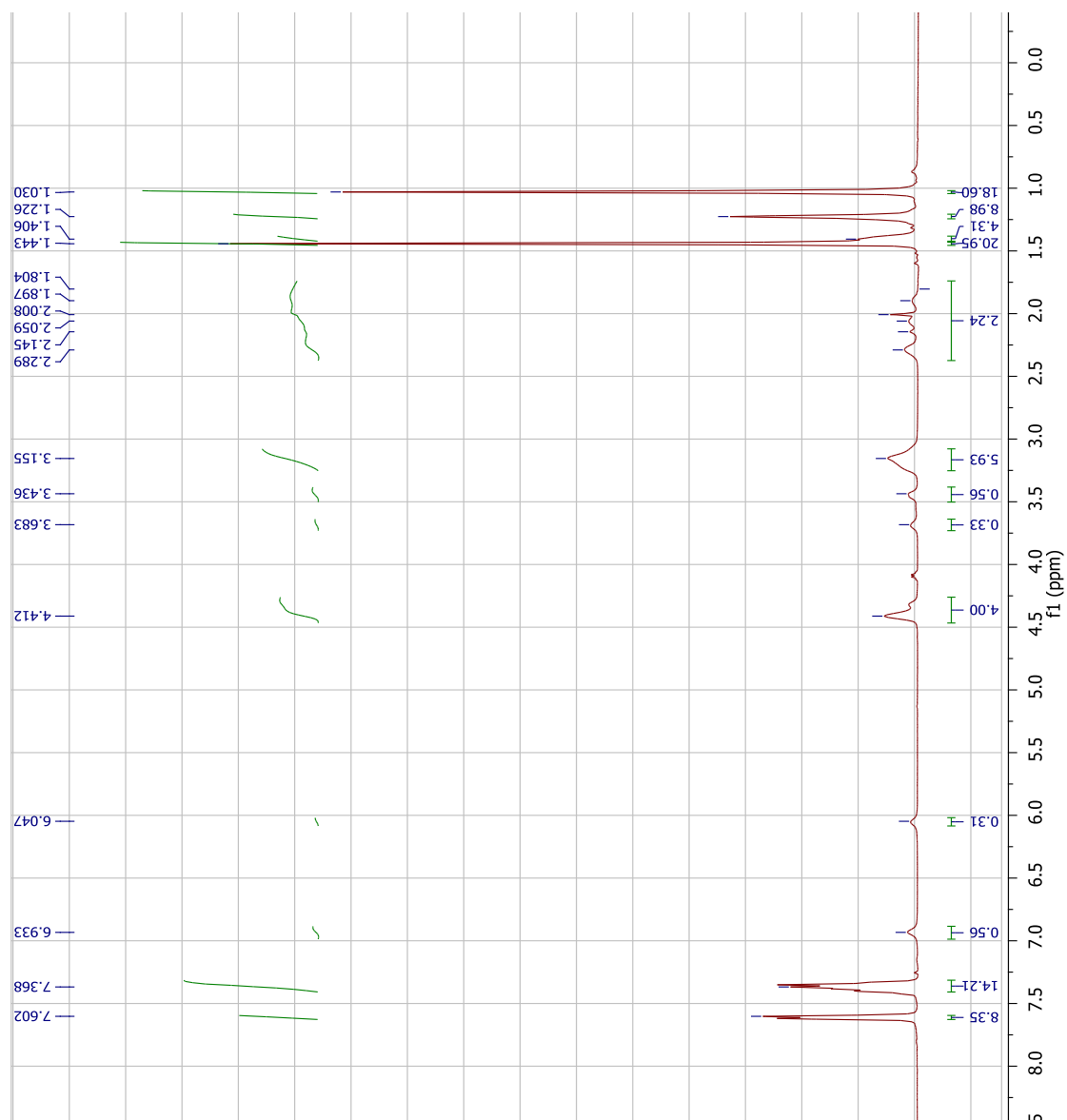
1,8-di(*trans*-*N*-Boc-4-*tert*butyldiphenylsiloxy-L-prolinamide) octane **10**



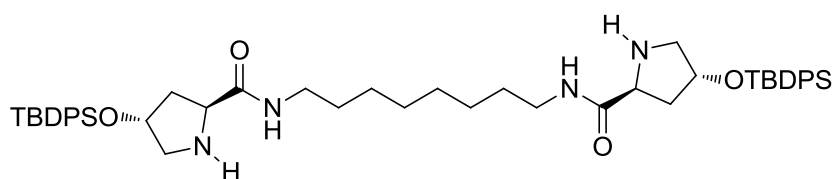
Trans-*N*-Boc-4-*tert*butyldiphenylsiloxy-L-proline **7** (0.565 g, 0.120 mmol) was dissolved in DCM (15 mL) and cooled to 0 °C. HOBt (0.030 g, 0.022 mmol) was added to the solution and the mixture was stirred for 5 min. EDCI (0.241 g, 0.125 mmol) was added to the mixture followed by 3 min additional stirring followed by the introduction of 1,8-diaminooctane (0.082 g, 0.057 mmol). The mixture was allowed to reach room temperature and stirred for 16 h. The final reaction mixture was diluted with additional DCM (30 mL) and washed with 2M HCl

(2 × 30 mL), saturated NaHCO₃ (2 × 30 mL) and brine (2 × 30 mL). The resulting organic phase was dried over MgSO₄ and the solvent removed *in vacuo* to give the crude *N*-Boc protected diprolinamide as a colourless oil. The crude mixture was purified *via* flash chromatography (1/9 EtOAc : Pet spirits) to give the pure dimer **10** as a viscous colourless oil (0.507 g, 0.0544 mmol, 45%). R_f = 11/31 (1/3 EtOAc : Pet. Spirits); ¹H NMR (270 MHz, CDCl₃) δ (ppm) = 7.69-7.36 (m, 20H, aryl), 4.52-4.36 (m, 4H, chiral H), 3.67-3.65 (m, 4H, CH-CH₂-CH), 3.52-3.37 (m, 4H, CH₂-NH), 2.29-1.79 (m, 4H, N-CH₂), 1.57 (s, 4H, Alkyl), 1.43 (s, 18H, O-*t*-butyl), 1.24 (s, 8H, Alkyl), 1.03 (s, 18H, Si-*t*-butyl); ¹³C NMR (400 MHz, CDCl₃) δ (ppm) = 173.7, 153.9, 135.7, 133.6, 123.0, 127.7, 71.6, 70.8, 58.3, 57.8, 54.9, 54.6, 52.2, 52.0, 39.7, 38.9, 28.5, 28.4, 26.9, 19.4; [α]_D^{21.2} = -89.2 ° (c = 0.001, CHCl₃); IR ν_{max} = 2928 (s), 1664 (s), 1162 (s); 702 (s); HRMS calculated for [C₆₀H₈₇N₄O₈Si₂]⁺ M = 1047.6057 found 1047.6185.

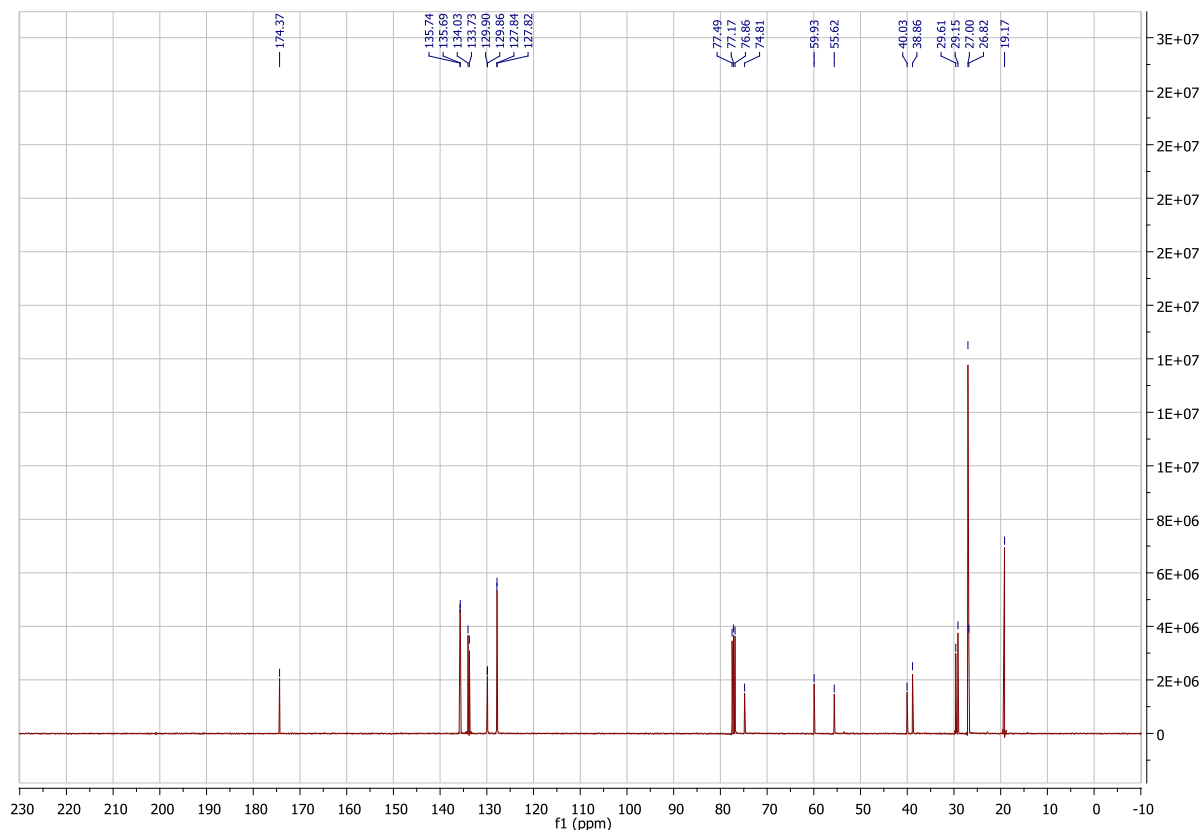


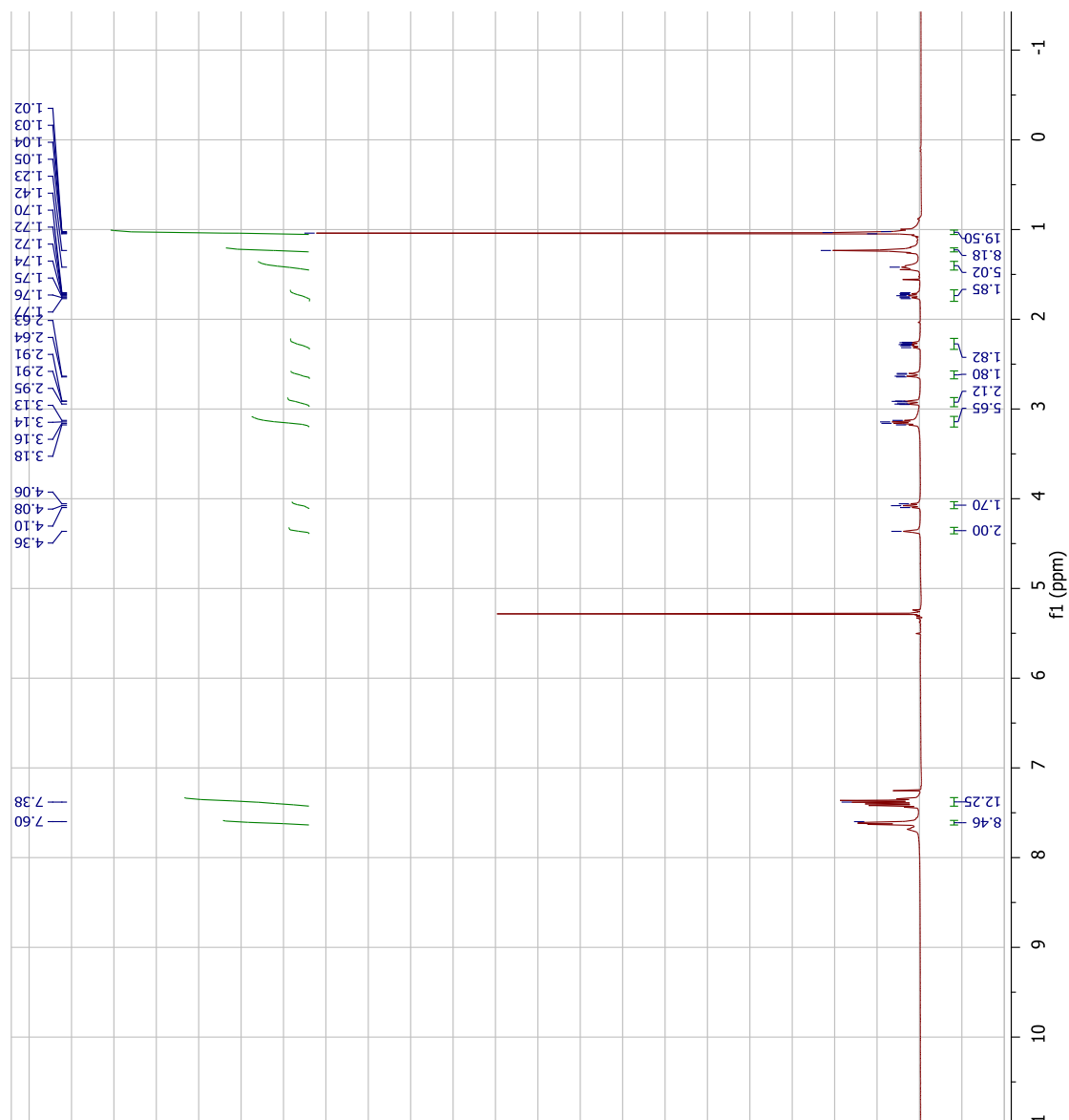


1,8-di(*trans*-*N*-Boc-4-*tert*butyldiphenylsiloxy-*L*-prolinamide) octane **3**

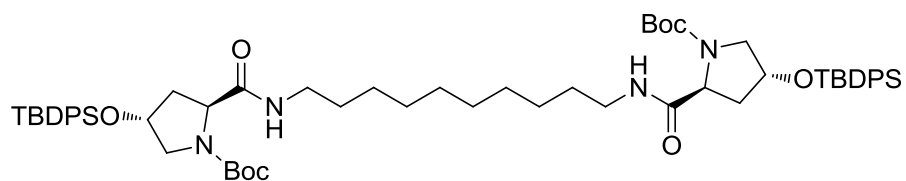


N-Boc protected diprolineamide **10** was solvated in DCM (18 mL) and stirred. To the stirring solution TFA (2 mL) was added to bring the solution to a 10 vol% concentration of acid/DCM. The solution was stirred for 7 h under an inert atmosphere at room temperature. The final mixture was basified with saturated NaHCO₃ (50 mL) and extracted into DCM (3 × 30 mL). The combined organic phase was then washed with additional NaHCO₃ (3 × 30 mL) and the organic phase was dried over MgSO₄. The solvent was removed *in vacuo* to give an opaque oil. Residual solvent was azeotroped with Et₂O to give the final organocatalyst **3** as pale brown oil (0.248 g, 0.029 mmol, 54%). *R*_f = 0.5; ¹H NMR (400 MHz, CDCl₃) δ (ppm) = 7.6 (m, 8H, aryl), 7.38 (m, 12H, aryl), 4.36 (br, 2H, Chiral), 4.08 (t, *J* = 8 Hz, 2H, chiral), 3.15 (q, *J* = 4 Hz, 4H, CH₂-NH), 2.95-2.91 (dt, *J* = 12, 1.6 Hz, NH-CH₂-CH), 2.62 (dd, *J* = 12, 3.2 Hz, 2H, NH-CH₂-CH), 2.29 (m, 2H, CH-CH₂-CH), 1.74 (ddd, *J* = 13.2, 8.4, 4.4 Hz, 2H, CH-CH₂-CH), 1.42 (m, 8H, Alkyl), 1.23 (m, 4H, Alkyl), 1.04 (m, 18H, *t*-butyl); ¹³C NMR (400 MHz, CDCl₃) δ (ppm) 174.37, 135.74, 135.69, 134.03, 133.73, 129.90, 129.86, 127.84, 127.82, 77.49, 77.17, 76.86, 74.81, 59.93, 55.62, 40.03, 38.86, 29.61, 29.15, 27.00, 26.82, 19.17; [α]_D^{22.5} = -16.0 ° (c = 0.001, CHCl₃); IR ν_{max} = 2929 (s), 1657 (s), 702 (s); HRMS calculated for [C₅₀H₇₁O₄Si₂]⁺ M = 847.5008 found 847.5016.



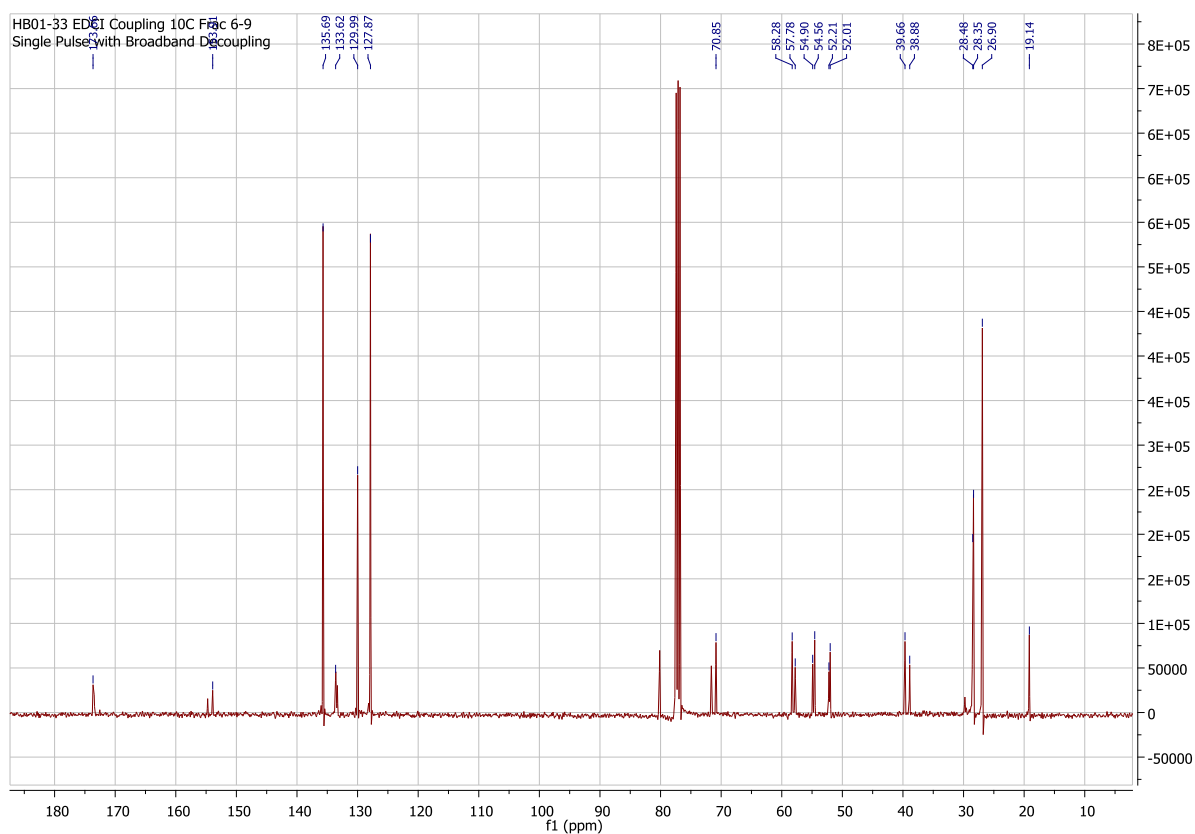


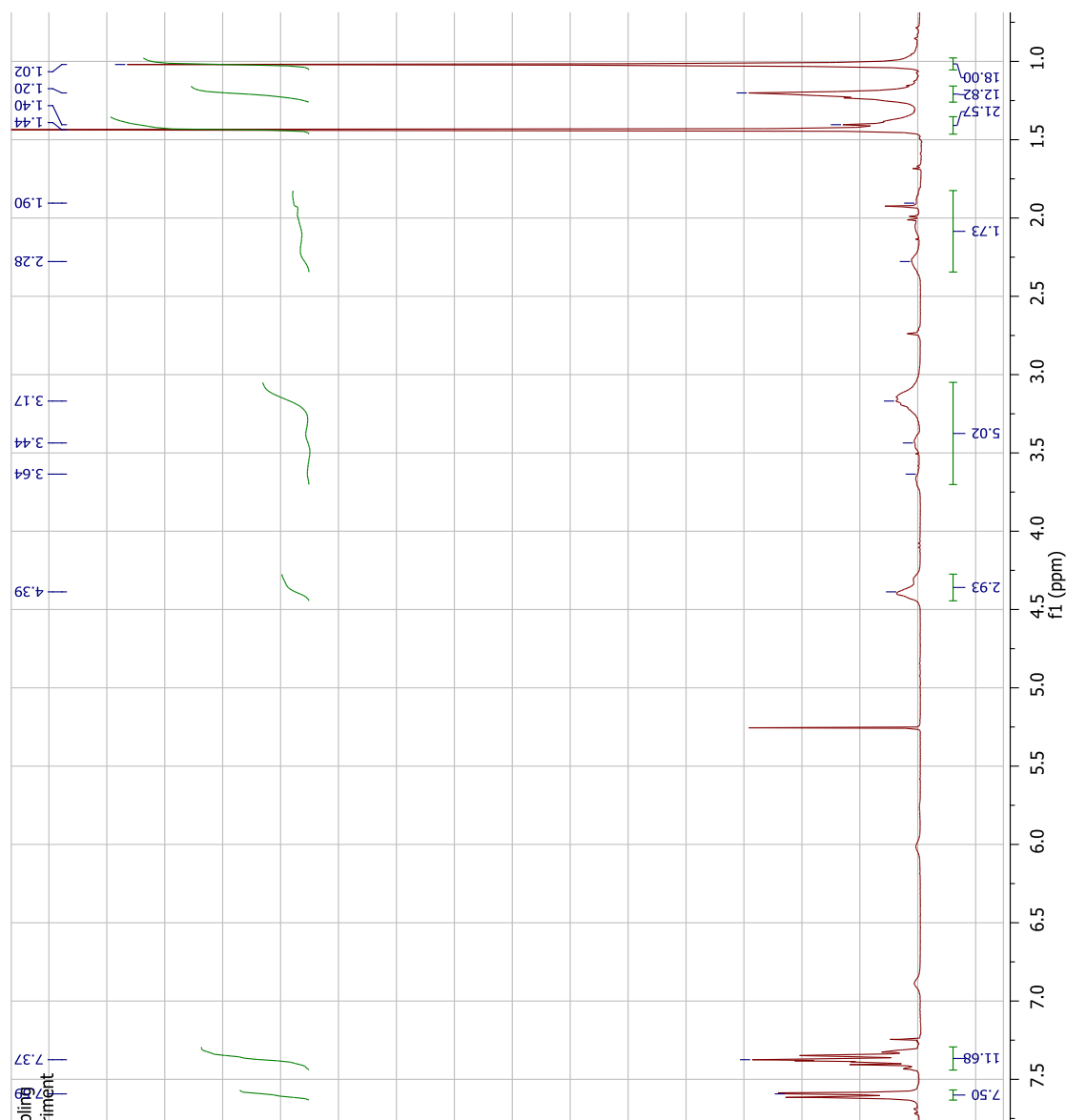
1,10-di(trans-N-Boc-4-tertbutyldiphenylsiloxy-L-prolinamide) decane 11



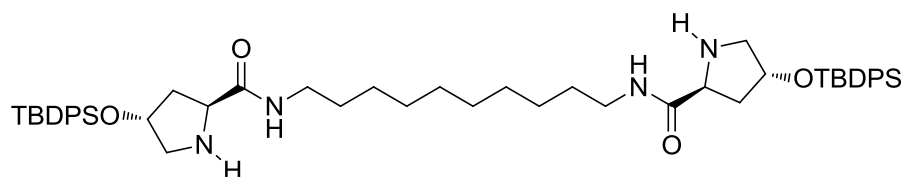
trans-N-Boc-4-tertbutyldiphenylsiloxy-L-proline **7** (0.296 g, 0.063 mmol) was dissolved in DCM (15 mL) and cooled to 0 °C. HOBt (0.016 g, 0.012 mmol) was added to the solution and the mixture was stirred for 5 min.

EDCI (0.127 g, 0.066 mmol) was added to the mixture followed by 3 min additional stirring followed by the introduction of 1,10-diaminodecane (0.051 g, 0.030 mmol). The mixture was allowed to reach room temperature and stirred for 16 h. The final reaction mixture was diluted with additional DCM (30 mL) and washed with 2M HCl (2 × 30 mL), saturated NaHCO₃ (2 × 30 mL) and brine (2 × 30 mL). The resulting organic phase was dried over MgSO₄ and the solvent removed *in vacuo* to give the crude *N*-Boc protected diprolineamide as a colourless oil. The crude mixture was purified *via* flash chromatography (1/4 EtOAc : Pet spirits) to give the pure dimer **11** as a viscous colourless oil (0.246 g, 0.023 mmol, 36%). R_f = 18/31 (1/3 EtOAc : Pet. Spirits); ¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.59 (m, 8H, aryl), 7.37 (m, 12H, aryl), 4.39 (s, 4H, chiral), 3.64 – 3.44 (m, 4H, NH-CH₂-CH), 3.17 (br, 4H, alkyl), 2.60 (dd, 2H, *J* = 12, 4, CH₂NH), 2.28 (m, 2H, CH-CH₂-CH), 1.73 (m, 2H, CH-CH₂-CH), 1.43 (m, 4H, alkyl), 1.28 – 1.9 (m, 4H, CH-CH₂-CH), 1.44 (br, 18H, O-*t*-butyl), 1.4 (br, 4H, alkyl), 1.2 (br, 12H, alkyl), 1.02 (s, 18H, Si-*t*-butyl); ¹³C NMR (400MHz, CDCl₃) δ (ppm) = 173.66, 153.91, 135.69, 133.62, 129.99, 127.87, 70.85, 58.28, 57.78, 54.90, 54.56, 52.21, 52.01, 39.66, 38.88, 28.48, 28.35, 26.90, 19.14; [α]_D^{23.6} = -29.4 ° (c = 0.001, CHCl₃); IR ν_{max} = 2929 (s), 1700 (s), 1162 (s), 702 (s); HRMS calculated for [C₆₂H₉₁N₄O₈Si₂⁺] M = 1075.6370 found 1047.6435.



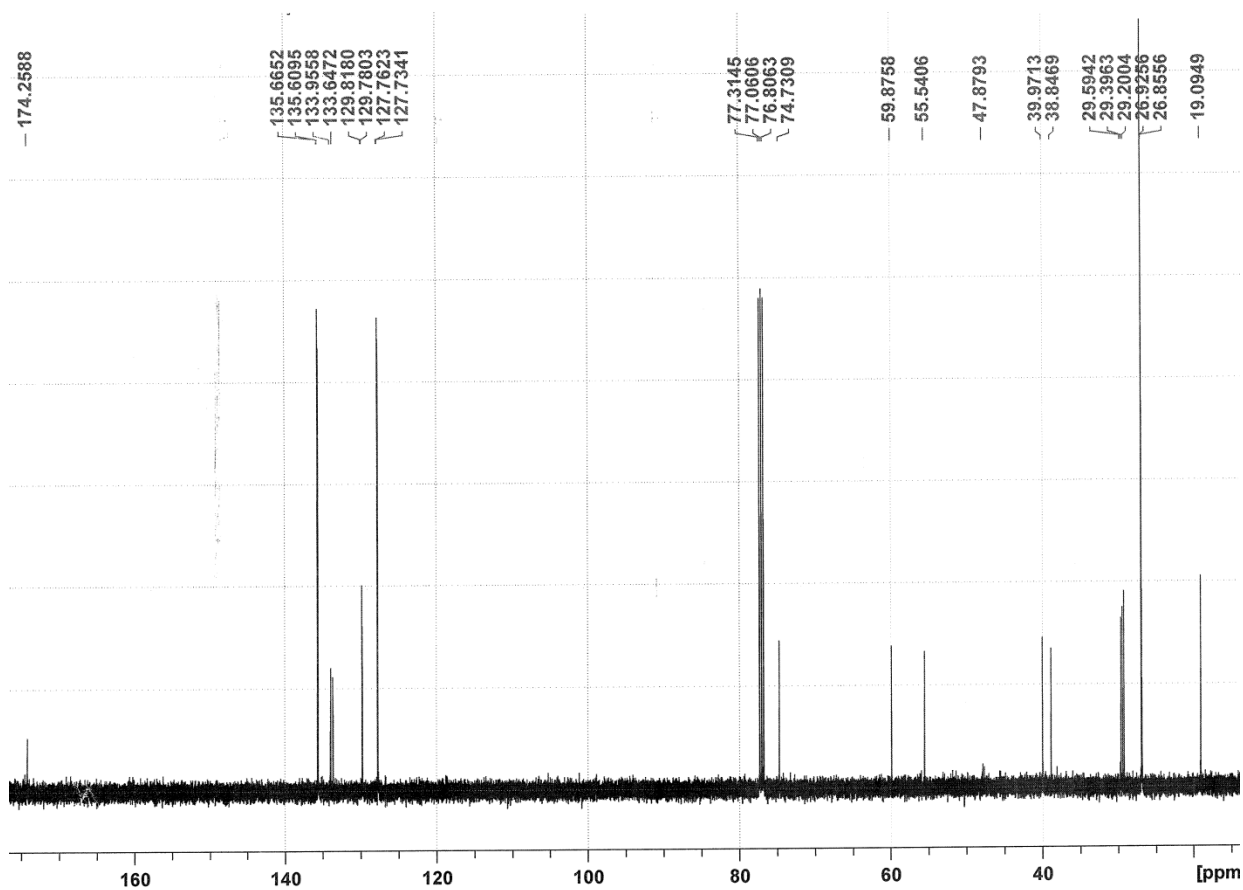


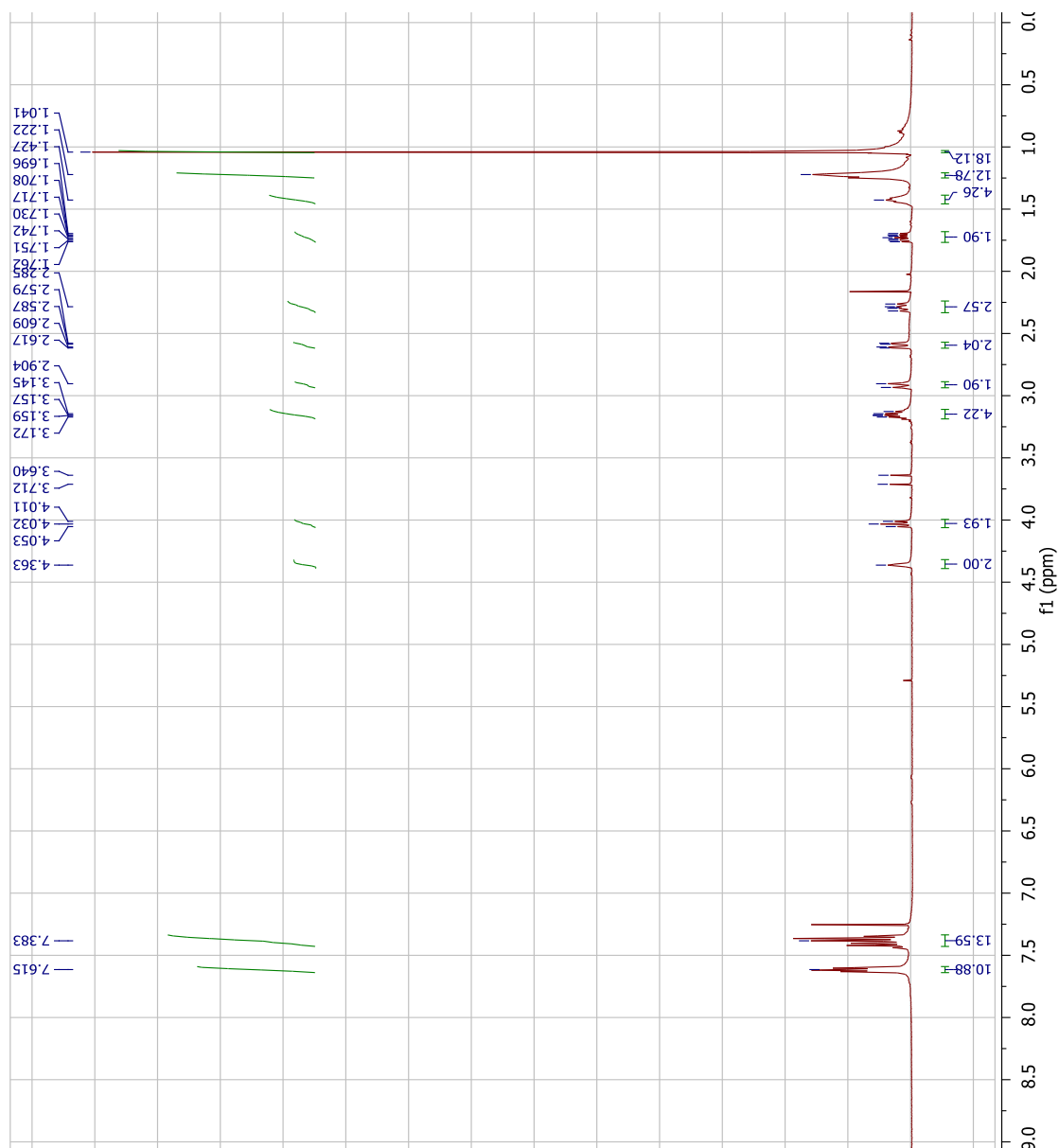
1,10-di(*trans*-4-*tert*butyldiphenylsiloxy-L-prolinamide) decane **4**



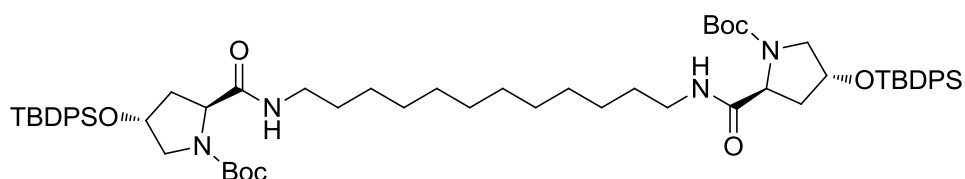
N-Boc protected diprolinamide **11** was solvated in DCM (18 mL) and stirred. To the stirring solution TFA (2 mL) was added to bring the solution to a 10 vol% concentration of acid/DCM. The solution was stirred for 6 h under an inert atmosphere at room temperature. The final mixture was basified with saturated NaHCO₃ (50 mL) and extracted into DCM (3 × 30 mL). The combined organic phase was then washed with additional NaHCO₃ (3 × 30 mL) and the organic phase was dried over MgSO₄. The solvent was removed *in vacuo* to give an opaque oil. Residual solvent was azeotroped with Et₂O to give the final organocatalyst **4** as pale brown oil (0.136 g, 0.015 mmol, 66%). *R*_f = 0.63 (1:9 MeOH/EtOAc); ¹H NMR (400 MHz, CDCl₃) δ (ppm) = 7.62 (m, 8H, aryl), 2.38 (m, 12H, aryl), 4.36 (s, 2H, chiral), 4.03 (t, 2H, *J* = 8.4 Hz, chiral), 3.15 (m, 4H, CO-NH-CH₂), 2.92 (d, 2H, *J* = 12 Hz, NH-CH₂-CH), 2.60 (9dd, 2H, *J* = 12, 3.2 Hz, NH-CH₂-CH), 2.32 – 2.26 (m, 2H, CH-CH₂-CH), 1.73 (ddd, 2H, *J* = 12.8, 8, 4.4 Hz, CH-CH₂-CH), 4.13 (br. m, 4H, alkyl), 1.22 (br. s, 12H, alkyl), 1.04 (s, 18H, *t*-butyl); ¹³C NMR

(500MHz, CDCl₃) δ (ppm) = 174.3, 135.7, 134.0, 133.6, 129.8, 121.8, 59.9, 55.5, 47.9, 40.0, 38.8, 29.6, 29.4, 29.2, 26.9, 26.85, 19.0; [α]_D^{24.1} = -49.4 ° (c = 0.001, CHCl₃); IR ν_{max} = 2928 (s), 1662 (s), 702 (s); HRMS calculated for [C₅₂H₇₅N₄O₄Si₂⁺] M = 875.5321 found 875.5337.

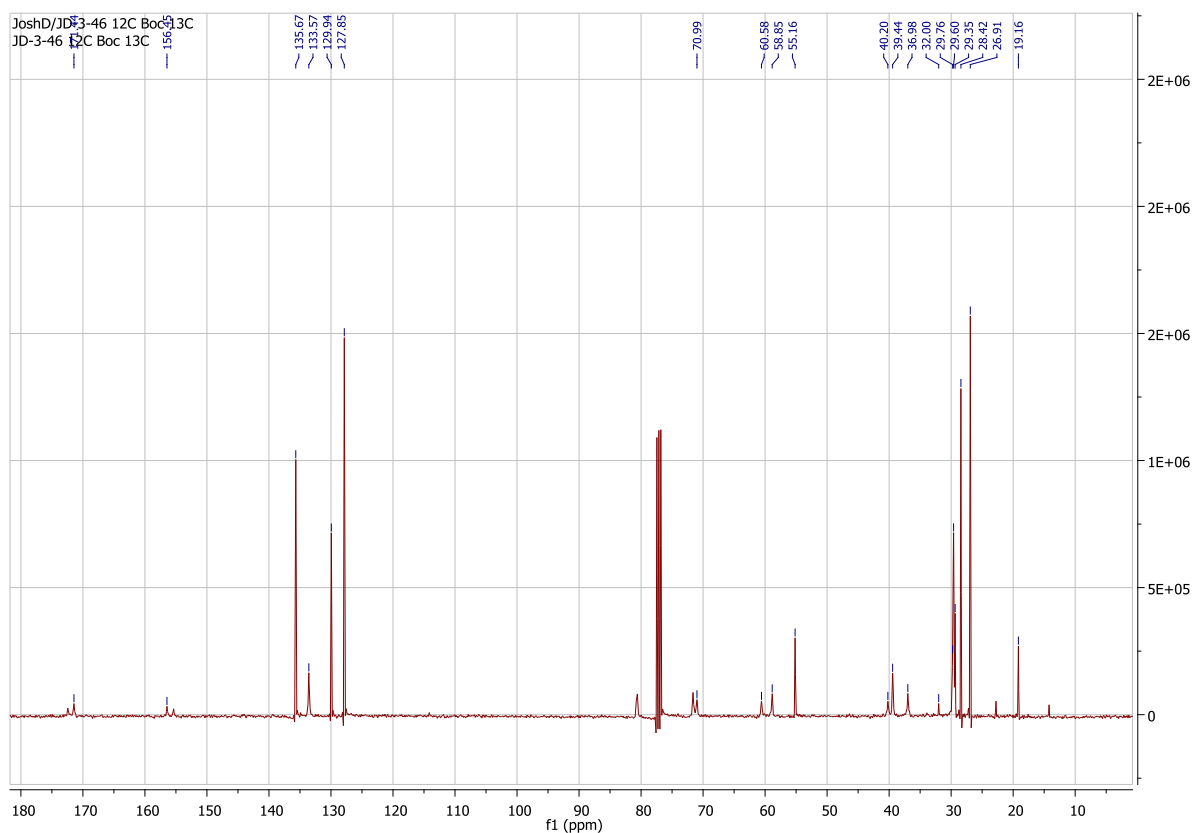


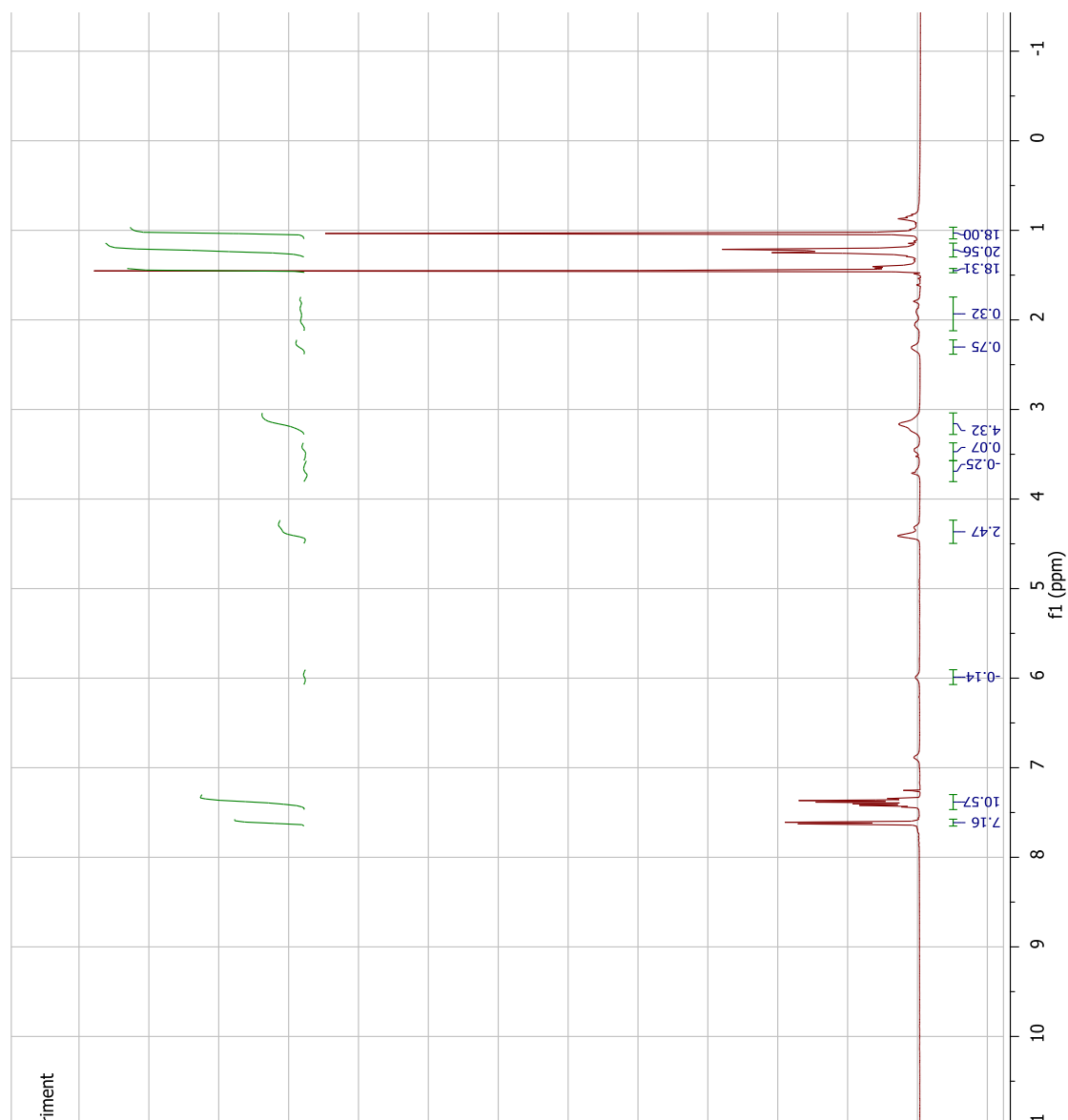


1,12-di(*trans*-*N*-Boc-4-*tert*butyldiphenylsiloxy-*L*-prolinamide) dodecane **12**

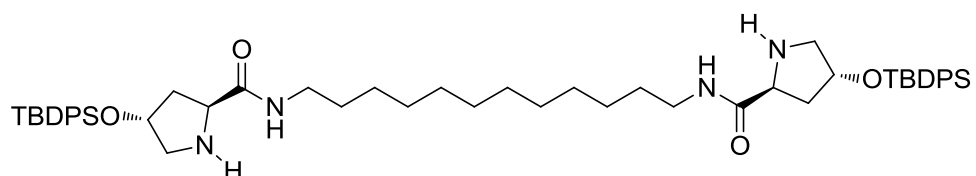


trans-*N*-Boc-4-*tert*butyldiphenylsiloxy-*L*-proline **7** (0.3 g, 0.64 mmol) was dissolved in DCM (25 mL) and cooled to 0 °C. HOBT (0.021 g, 0.152 mmol) was added to the solution and the mixture was stirred for 5 min. EDCI (0.077 g, 0.67 mmol) was added to the mixture followed by 3 min additional stirring followed by the introduction of 1,12-diaminododecane (0.061 g, 0.305 mmol) was introduced. The mixture was allowed to reach room temperature and stirred for 16 h. The final reaction mixture was diluted with additional DCM (30 mL) and washed with 10% citric acid (3 × 30 mL), saturated NaHCO₃ (3 × 30 mL) and brine (1 × 30 mL). The resulting organic phase was dried over MgSO₄ and the solvent was removed *in vacuo* to give crude *N*-Boc protected diprolinamide as colourless oil. The crude compound was purified *via* flash chromatography (1/3 EtOAc : Pet spirits) to give the pure dimer **12** as a viscous colourless oil (0.14 g, 0.127 mmol, 42%). *R*_f = 1/3 (1:1 EtOAc : Pet. Spirits); ¹H NMR (400 MHz, CDCl₃) δ (ppm) = 7.62 (m, 8H, aryl), 7.38 (m, 12H aryl), 4.41 – 4.32 (br. m, 4H, chiral H), 3.71 (br, 2H, NH-CH₂), 3.44 (br, 2H, NH-CH₂), 3.16 (4H, NH-CH₂), 2.31 (br, 2H, CH-CH₂-CH), 2.06 – 1.94 (br. m, 2H, CH-CH₂-CH), 1.42 (br, 18H, O-*t*-butyl), 1.25 (br, 20H, alkyl), 1.04 (br, 18H, Si-*t*-butyl); ¹³C NMR (400 MHz, CDCl₃) δ (ppm) = 171.44, 156.45, 135.67, 133.57, 129.94, 127.85, 70.99, 60.58, 58.85, 55.16, 40.20, 39.44, 36.98, 32.00, 29.76, 29.60, 29.35, 28.42, 26.91, 19.16.; [α]_D^{24.6} = -46.7 ° (c = 0.00033, CHCl₃); IR ν_{max} = 2927 (s), 11656 (s), 700 (s); HRMS calculated for [C₆₄H₉₅N₄O₈Si₂⁺] M = 1103.6683 found 1103.69985.



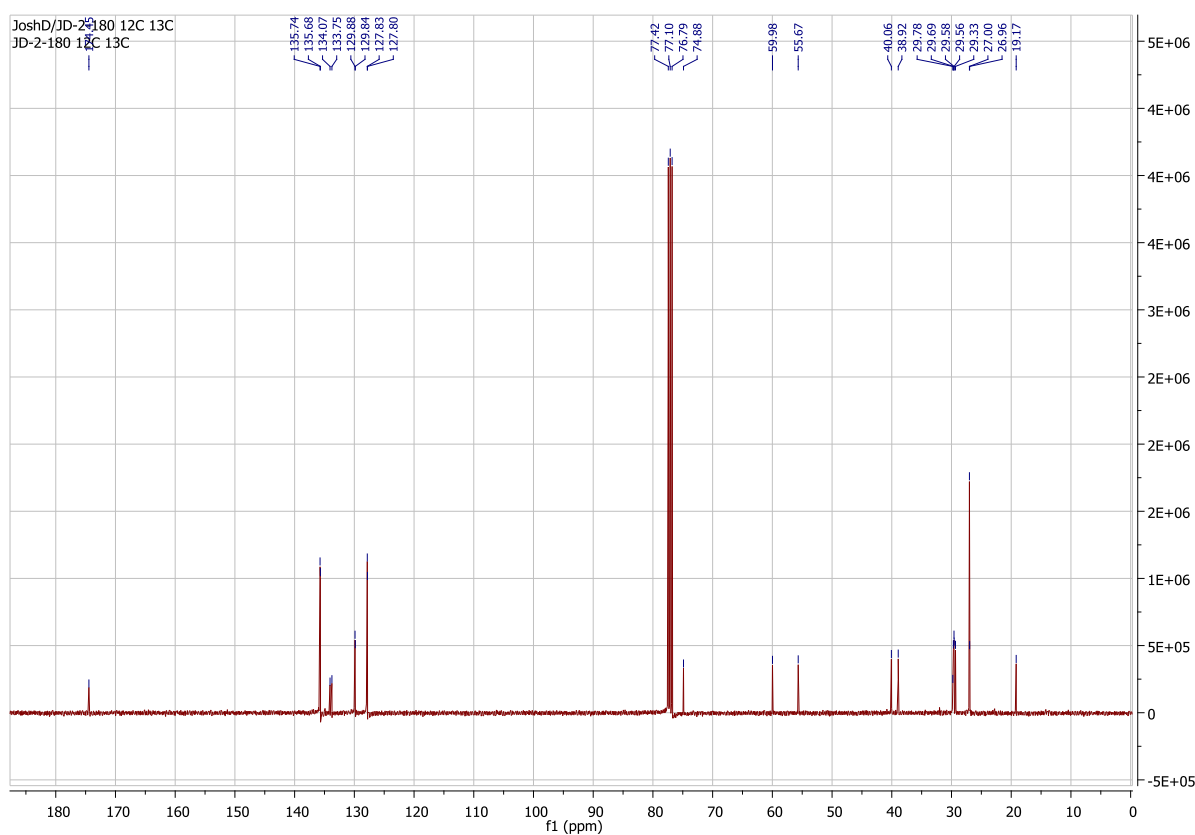


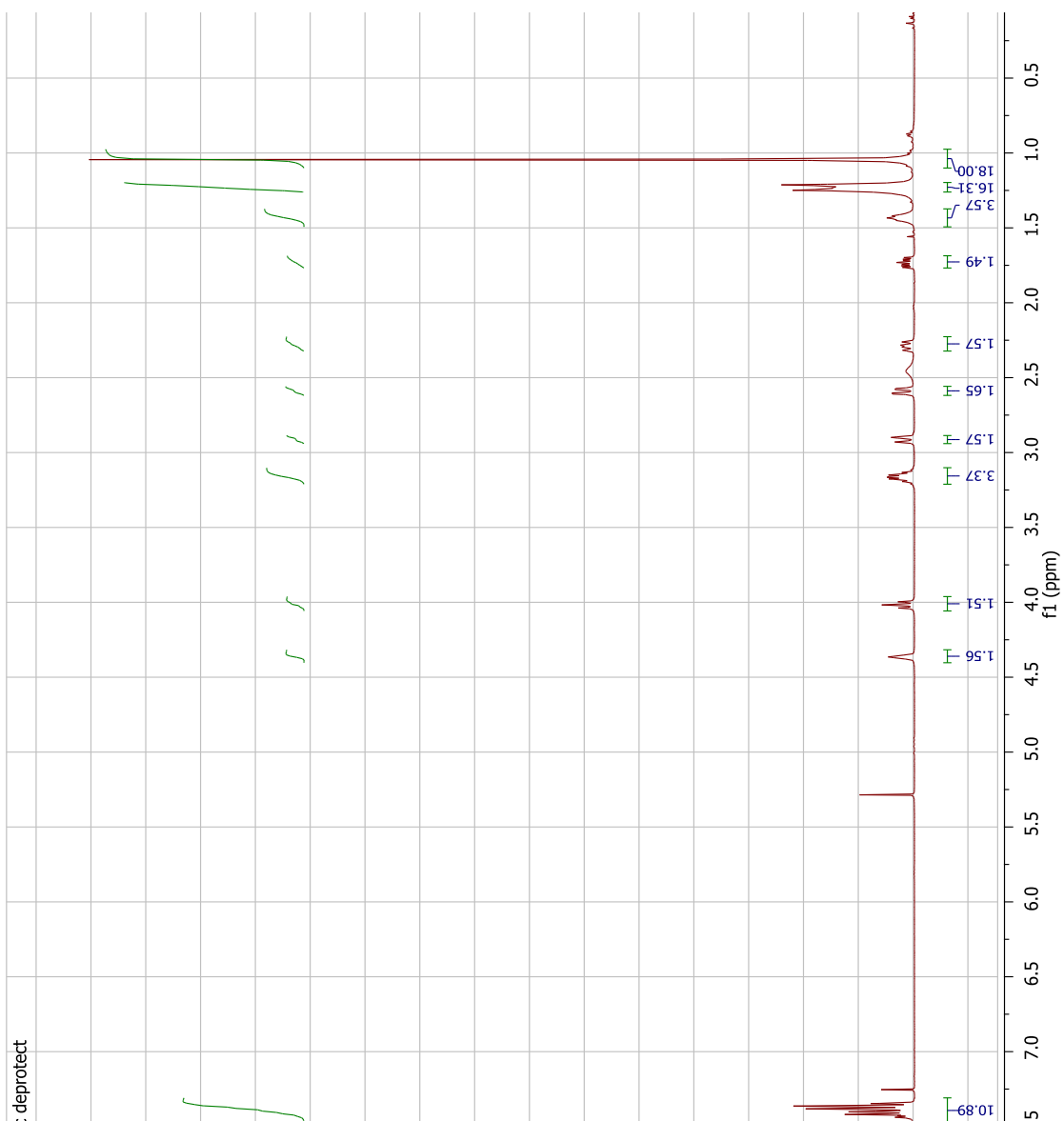
1,12-di(*trans*-4-*tert*butyldiphenylsiloxy-L-prolinamide) dodecane **5**



N-Boc protected diprolineamide **12** (0.16 g, 0.0145 mmol) was dissolved in (18 mL) and stirred. To the stirring solution was added TFA (2 mL) to bring the solution to a 10 vol% concentration of acid/DCM. The solution was

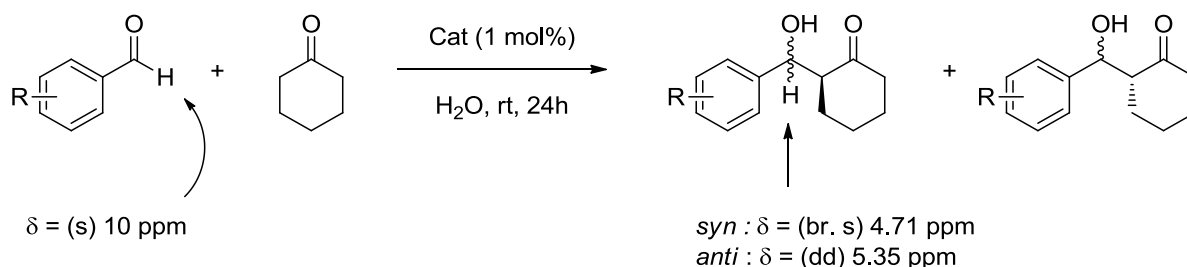
stirred for 6h under an inert atmosphere at room temperature. The final mixture was basified with saturated NaHCO₃ (50 mL) and extracted into DCM (3 × 30 mL). The combined organic phase was then washed with additional NaHCO₃ (3 × 30 mL) and the organic phase was dried over MgSO₄. The solvent was removed in vacuo to give a pale yellow oil. Residual solvent was azeotroped with Et₂O to give the final organocatalyst **5** as a viscous pale yellow oil (0.13 g, 0.144 mmol, 99%). R_f = 20/33 (1:9 MeOH : EtOAc); ¹H NMR (270 MHz, CDCl₃) δ (ppm) = 7.59 (br m, 8H, aryl), 7.38 (m, 12H, aryl), 4.36 (br, 1H, CH₁-O), 4.09 (t, J = 8.4 Hz, 1H, CH₁-N), 3.14 (m, 4H, NH-CH₂), 2.94 (d, 2H J = 11.9 Hz, CH₂-NH), 2.65 (dd, 2H, J = 11.9, 3.32 Hz, CH₂-NH), 2.27 (m, 2H, CH-CH₂-CH), 1.76 (ddd, 2H, J = 13.2, 8, 4.4 Hz, CH-CH₂-CH), 1.41 (br, 4H, alkyl), 1.21 (br, 16H, alkyl), 1.03 (br, 18H, *t*-butyl); ¹³C NMR (400 MHz, CDCl₃) δ (ppm) = 173.9, 135.7, 133.9, 133.6, 129.1, 127.8, 74.6, 65.9, 59.8, 55.5, 39.7, 39.03, 29.78, 29.62, 29.52, 29.247, 26.7, 19.1, 15.4; [α]_D^{24.3} = -12.8 °(0.00113, CHCl₃); IR ν_{max} = 2927 (s), 1658 (s), 1105 (s), 700 (s); HRMS calculated for [C₅₄H₇₉N₄O₈Si₂⁺] M = 903.5634 found 903.56196.



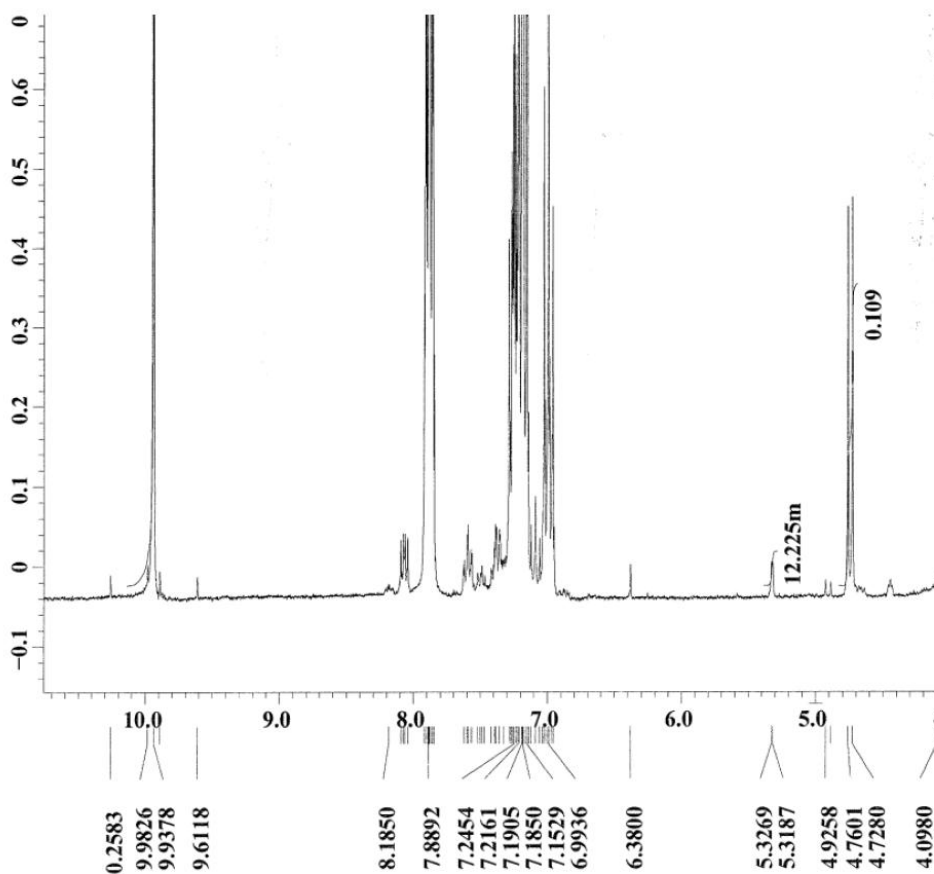


Determination of Reaction Outcomes: Conversion and dr

The conversion of the initial aldehyde into the target compound was determined by the integration of key peaks within the ^1H NMR spectra. The diastereomeric ratio was determined by integration of the chiral proton peaks for both the *syn* and the *anti* diastereomers.



The key ^1H NMR peaks that are integrated are determined from reported examples and lie in uncluttered regions of the NMR spectra.



Determination of Reaction Outcomes: Enantiomeric Excess.

Enantiomeric excess was determined by chiral HPLC, integrating the peak area of each enantiomer from the major diastereomer. The elution times were compared to racemic examples synthesised through one of two methods.

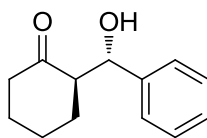
Representative Syntheses for Aldol Product Racemates (Benzaldehyde)

Procedure A: A stirred solution of water (15 mL) was charged with 10M NaOH (1 mL). Ketone (0.28 mL, 2.7 mol, 5 equiv.) was added and the solution was stirred for 1 min. To the mixture was added aryl aldehyde (0.6 mL, 0.54 mmol, 1 equiv.) and the solution was stirred for 3 h. The mixture was extracted into CHCl₃ (3×20 mL) and the combined organic phase was dried with MgSO₄. The racemic mixture was isolated via flash chromatography (1/3 EtOAc/Petroleum spirits).

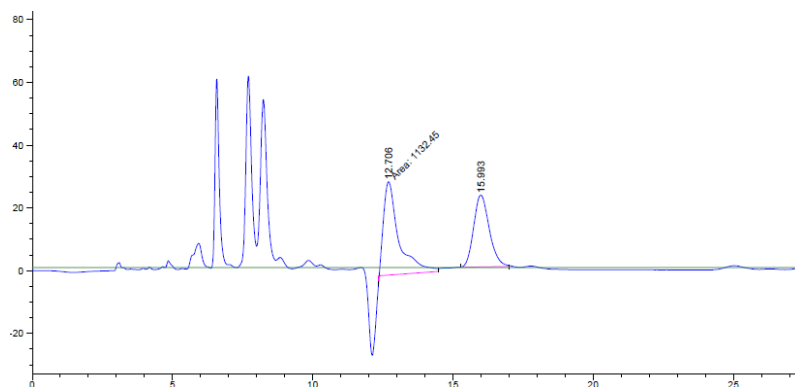
Procedure B: Pyrrolidine (0.44 mL, 0.53 mmol, 1 equiv.) was added to a stirred solution of CHCl₃. To the stirred mixture was added ketone (0.223 mL, 2.65 mmol, 5 equiv.) and aldehyde (80 mg, 0.53 mmol, 1 equiv.). Benzoic acid (20 mg, 0.16 mmol, 0.3 equiv.) was added to the mixture and the reaction was stirred at room temperature for 16 h. The reaction mixture was taken up in additional CHCl₃ and washed with 2M HCl (2×20 mL). The organic phase was dried with MgSO₄. The racemic mixture was analysed by chiral HPLC without purification.

Structures of racemates were confirmed through correlation to reported ¹H NMR spectra.⁴

2-[Hydroxy-(phenyl)-methyl]-cyclohexanone



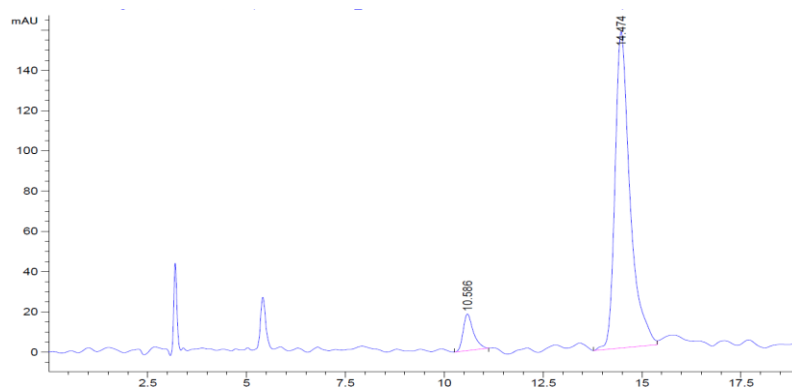
Racemate



Signal 1: DAD1 C, Sig=278,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.706	MM	0.6344	1132.45313	29.75147	56.0912
2	15.993	BB	0.5977	886.49481	22.89845	43.9088
Totals :				2018.94794	52.64992	

Table 1, Entry 1, Catalyst 1 (1 mol%)



Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.586	BB	0.2678	326.59290	18.16563	7.2672
2	14.474	BV	0.3932	4167.46631	157.22237	92.7328
Totals :				4494.05920	175.38800	

2-[Hydroxy-(phenyl)-methyl]-cyclohexanone

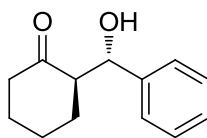
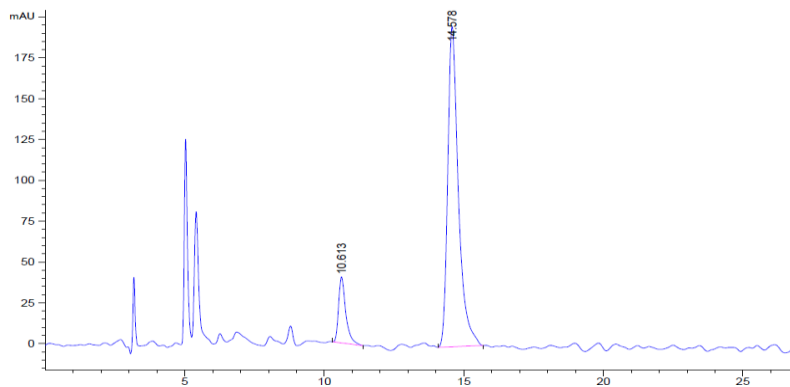


Table 1, Entry 2, Catalyst 2 (1 mol%)

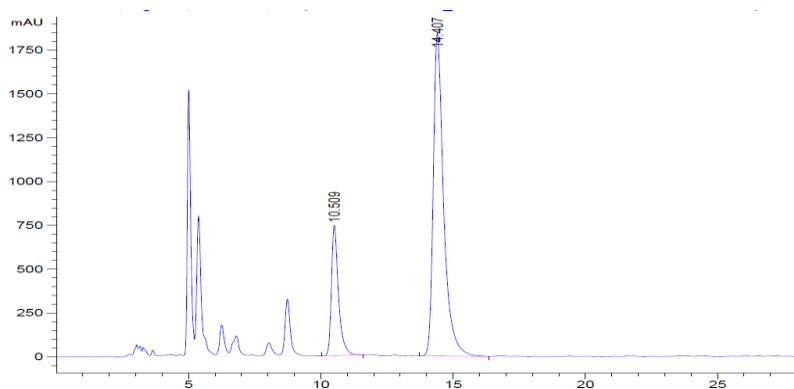


Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.613	BB	0.2673	725.07477	40.42458	12.2043
2	14.578	BB	0.3965	5216.06299	195.99823	87.7957

Totals : 5941.13776 236.42281

Table 1, Entry 3, Catalyst 3 (1 mol%)



Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.509	BB	0.2731	1.37054e4	743.31232	21.4271
2	14.407	BB	0.4044	5.02574e4	1841.45679	78.5729

Totals : 6.39628e4 2584.76910

2-[Hydroxy-(phenyl)-methyl]-cyclohexanone

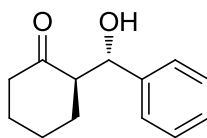
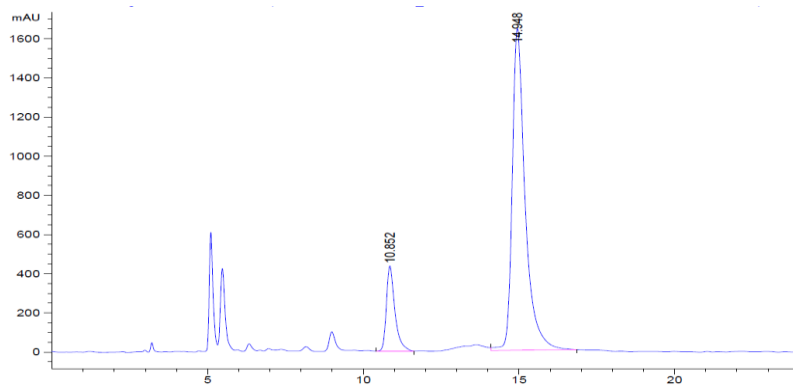


Table 1, Entry 4, Catalyst 4 (1 mol%)

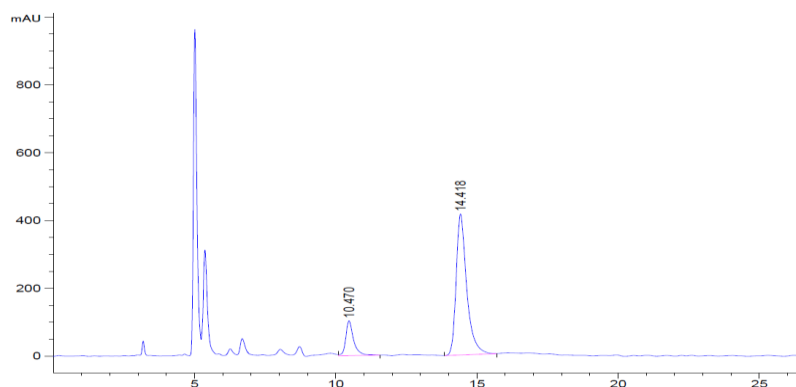


Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.852	BV	0.2839	8273.09766	434.87924	14.8339
2	14.948	VB	0.4253	4.74986e4	1643.03223	85.1661

Totals : 5.57717e4 2077.91147

Table 1, Entry 5, Catalyst 5 (1 mol%)



Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.470	VB	0.2831	1980.74329	102.65174	15.4854
2	14.418	BB	0.3874	1.08103e4	415.67197	84.5146

Totals : 1.27910e4 518.32371

2-[Hydroxy-(phenyl)-methyl]-cyclohexanone

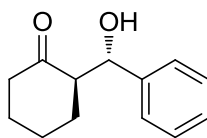
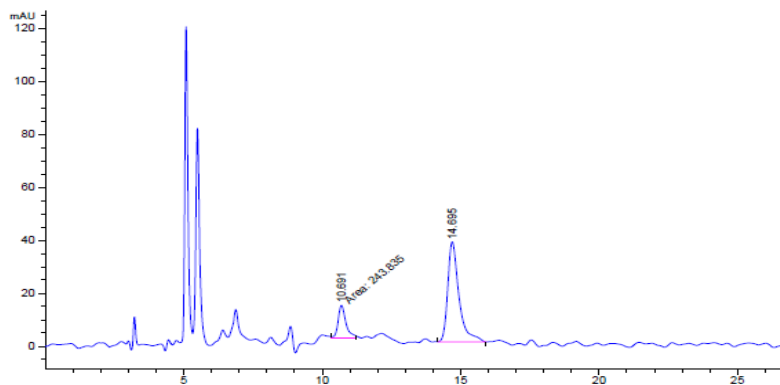


Table 3, Entry 1, Catalyst 3 (neat)

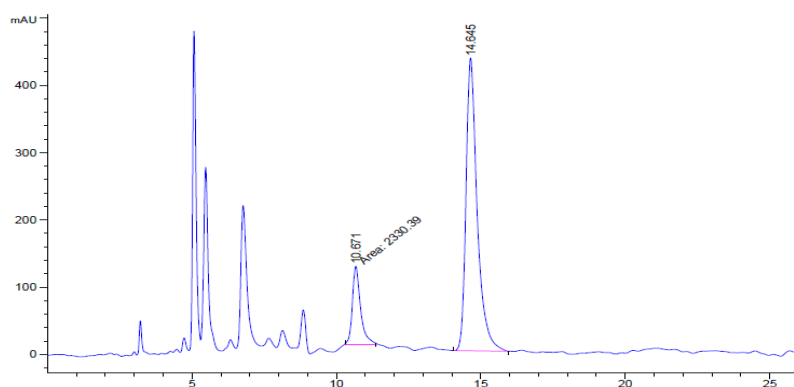


Signal 1: DAD1 H, Sig=250,100 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.691	MM	0.3293	243.83472	12.34279	18.6483
2	14.695	BB	0.4169	1063.71057	37.73480	81.3517

Totals : 1307.54529 50.07759

Table 3, Entry 2, Catalyst 16 (neat)



Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.671	MM	0.3326	2330.39014	116.76873	16.5788
2	14.645	BB	0.4004	1.17260e4	435.06998	83.4212

Totals : 1.40564e4 551.83871

2-[Hydroxy-(phenyl)-methyl]-cyclohexanone

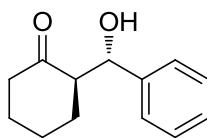
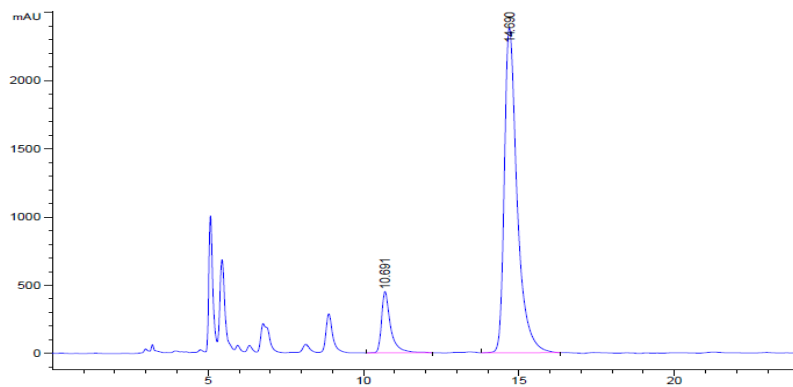


Table 3, Entry 3, Catalyst 16

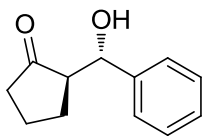


Signal 1: DAD1 B, Sig=210,4 Ref=360,100

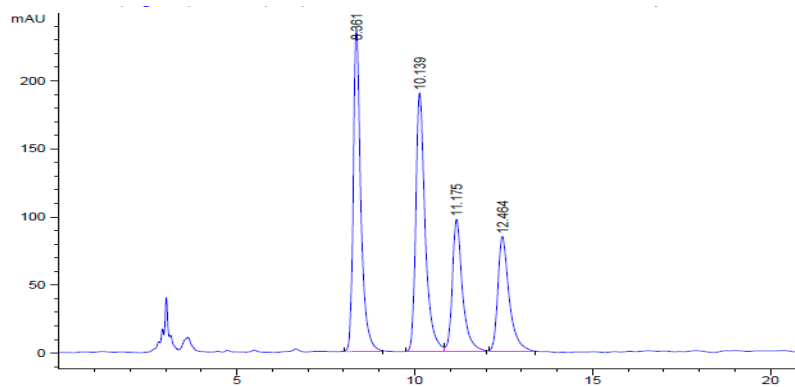
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.691	BB	0.2957	9078.38086	449.28537	11.7558
2	14.690	VB	0.4278	6.81466e4	2382.12891	88.2442

Totals : 7.72250e4 2831.41428

2-[Hydroxy-(phenyl)-methyl]-cyclopentanone



Racemate

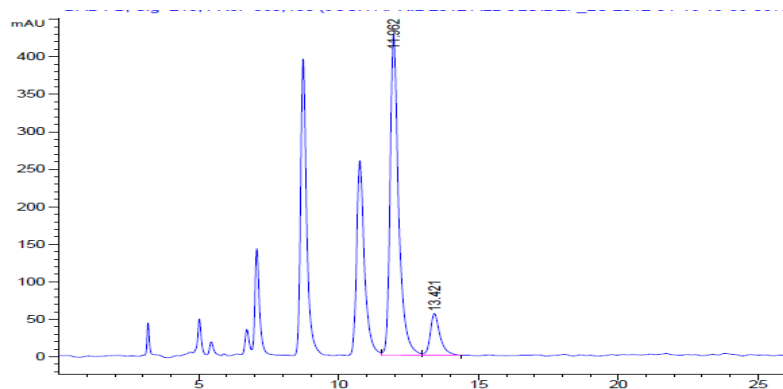


Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.361	BB	0.2203	3495.37964	236.61053	32.4870
2	10.139	BV	0.2711	3470.04028	189.97961	32.2515
3	11.175	VB	0.2924	1917.81604	97.10879	17.8247
4	12.464	BB	0.3287	1876.06555	84.61137	17.4367

Totals : 1.07593e4 608.31031

Table 2, Entry 1, Catalyst 1



Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.962	VV	0.3136	9076.65723	427.73917	87.1707
2	13.421	VB	0.3559	1335.85474	55.68472	12.8293

Totals : 1.04125e4 483.42389

2-[Hydroxy-(phenyl)-methyl]-cyclopentanone

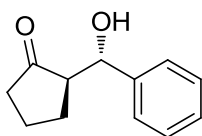
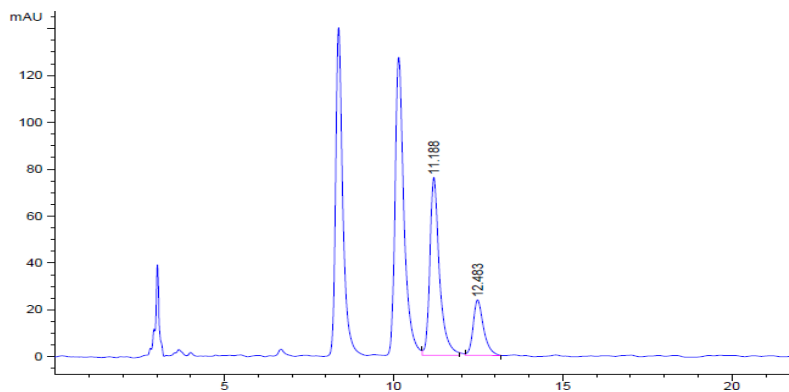


Table 2, Entry 1, Catalyst 2

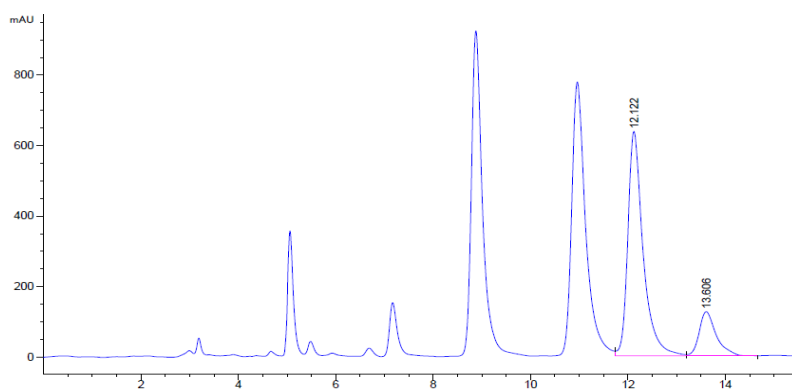


Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.188	VB	0.2919	1496.58984	75.93364	74.6640
2	12.483	BB	0.3215	507.84387	23.74301	25.3360

Totals : 2004.43372 99.67665

Table 2, Entry 1, Catalyst 3



Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.122	VV	0.3223	1.38806e4	636.76221	82.0942
2	13.606	VB	0.3598	3027.53003	125.34208	17.9058

Totals : 1.69081e4 762.10429

2-[Hydroxy-(phenyl)-methyl]-cyclopentanone

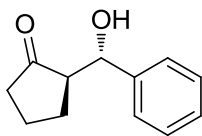
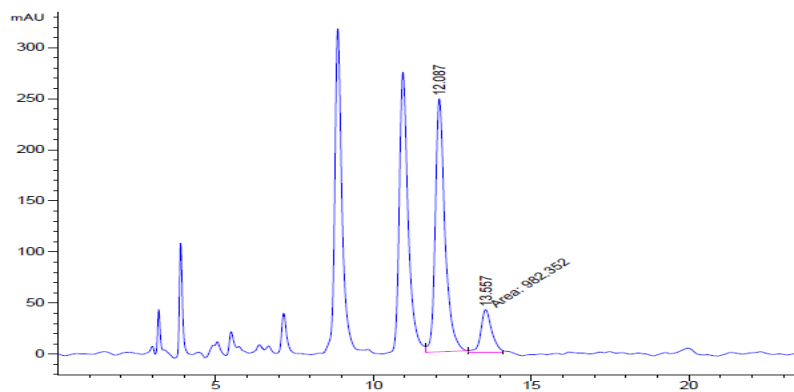


Table 2, Entry 1, Catalyst 4

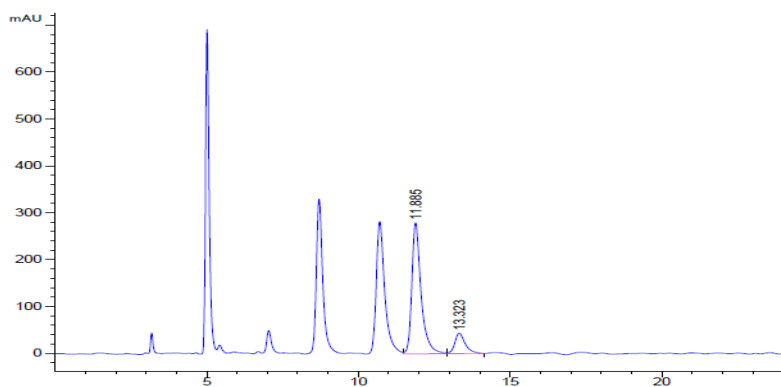


Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.087	VB	0.3154	5300.89697	247.97881	84.3655
2	13.557	MM	0.3943	982.35150	41.52491	15.6345

Totals : 6283.24847 289.50372

Table 1, Entry 1, Catalyst 5



Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.885	VV	0.3143	5959.23193	280.05145	85.0133
2	13.323	VB	0.3571	1050.53479	43.60067	14.9867

Totals : 7009.76672 323.65212

2-[Hydroxy-(phenyl)-methyl]-cyclopentanone

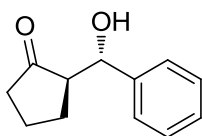
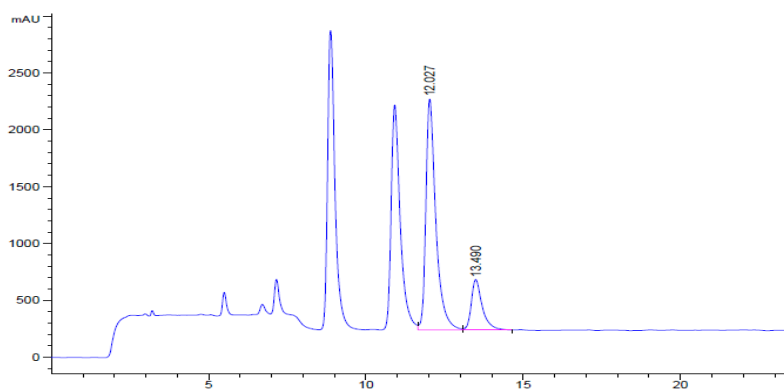


Table 3, Entry 6, Catalyst 16

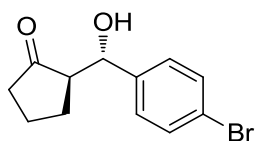


Signal 1: DAD1 B, Sig=210,4 Ref=360,100

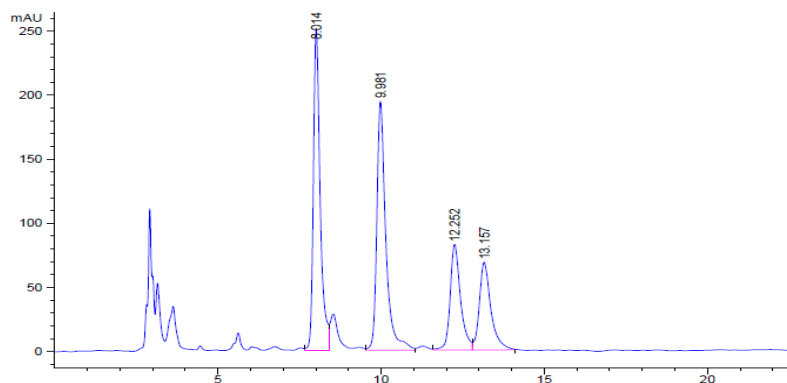
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.027	VV	0.3272	4.47521e4	2030.26294	80.6483
2	13.490	VB	0.3562	1.07383e4	443.96396	19.3517

Totals : 5.54904e4 2474.22690

2-[Hydroxy-(4-bromo-phenyl)-methyl]-cyclopentanone



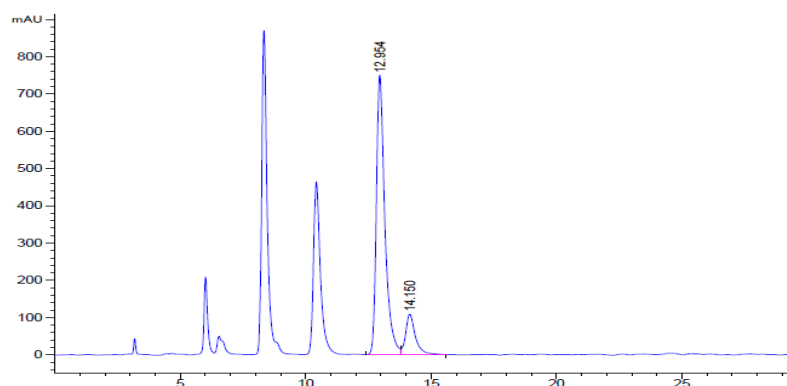
Racemate



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.014	VV	0.2168	3635.32544	251.24251	33.4384
2	9.981	VB	0.2835	3721.97803	194.30759	34.2355
3	12.252	VV	0.3287	1830.25940	82.53169	16.8351
4	13.157	VB	0.3628	1684.13660	68.50395	15.4910

Totals : 1.08717e4 596.58574

Table 2, Entry 2, Catalyst 1



Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.954	BV	0.3481	1.76408e4	750.73376	85.7326
2	14.150	VB	0.3947	2935.73901	108.85099	14.2674

Totals : 2.05765e4 859.58475

2-[Hydroxy-(4-bromo-phenyl)-methyl]-cyclopentanone

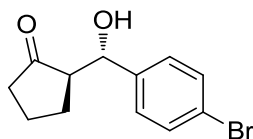
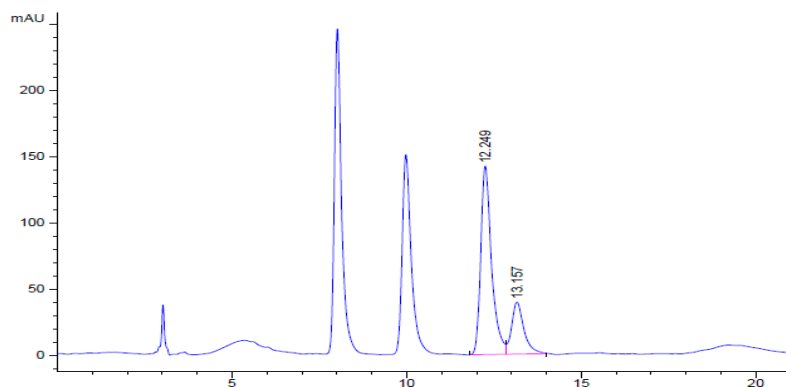


Table 2, Entry 2, Catalyst 2

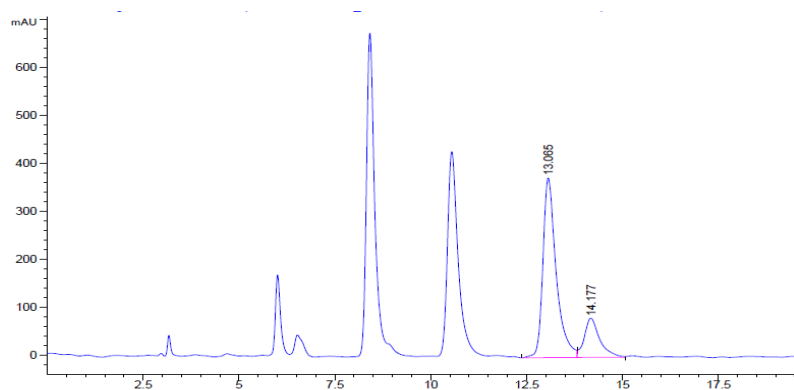


Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.249	BV	0.3212	3066.74878	142.41505	76.0788
2	13.157	VB	0.3614	964.26501	39.41864	23.9212

Totals : 4031.01379 181.83369

Table 2, Entry 2, Catalyst 3



Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.065	BV	0.3551	9039.16797	375.16849	79.7610
2	14.177	VV	0.4077	2293.65186	82.15737	20.2390

Totals : 1.13328e4 457.32586

2-[Hydroxy-(4-bromo-phenyl)-methyl]-cyclopentanone

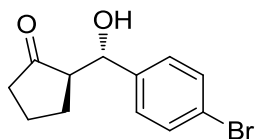
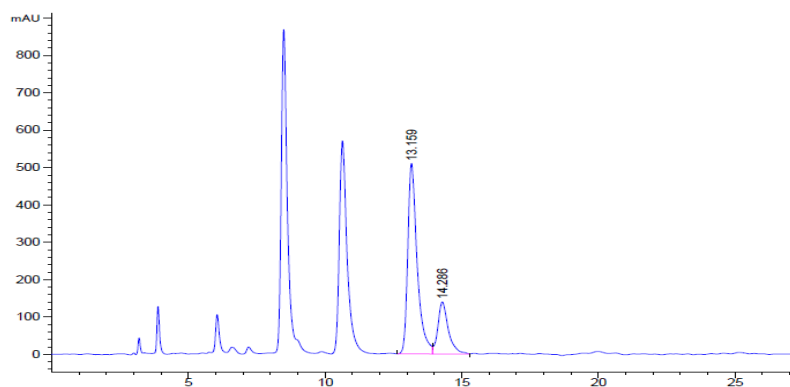


Table 2, Entry 2, Catalyst 4

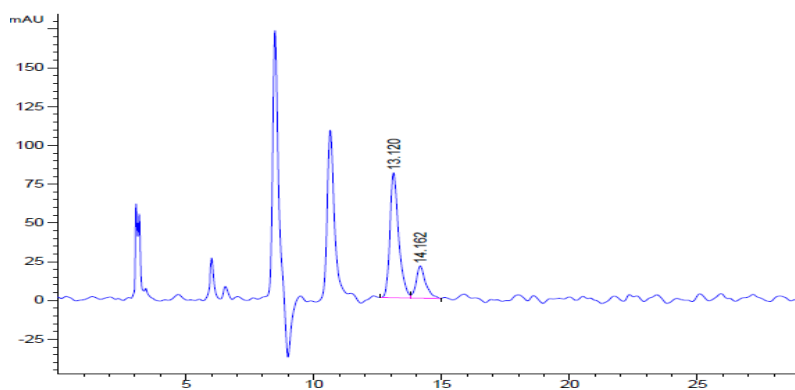


Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.159	BV	0.3551	1.22047e4	510.23578	76.5758
2	14.286	VV	0.3939	3733.36450	139.65157	23.4242

Totals : 1.59380e4 649.88734

Table 2, Entry 2, Catalyst 5

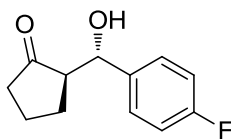


Signal 1: DAD1 B, Sig=210,4 Ref=360,100

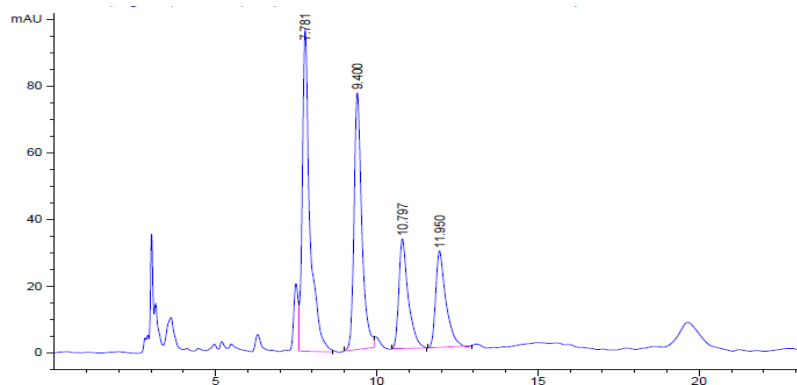
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.120	BV	0.3521	1906.72095	80.57981	78.2213
2	14.162	VB	0.3765	530.87738	20.74697	21.7787

Totals : 2437.59833 101.32678

2-[Hydroxy-(4-fluoro-phenyl)-methyl]-cyclopentanone



Racemate

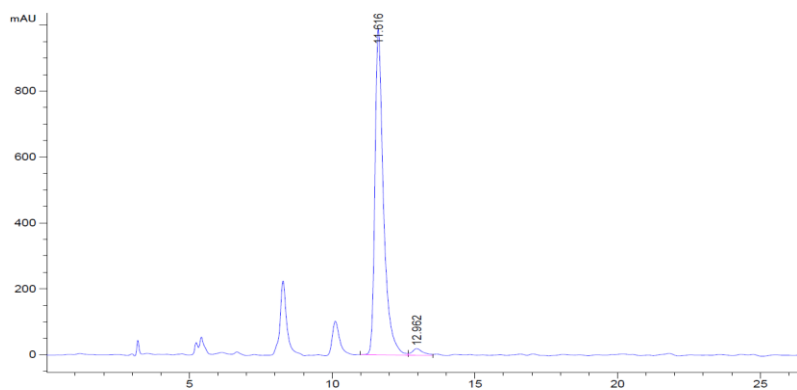


Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.781	VB	0.2343	1574.88477	96.54327	37.7562
2	9.400	BB	0.2507	1298.56799	77.00474	31.1318
3	10.797	BB	0.2939	664.95892	32.89122	15.9417
4	11.950	BB	0.3191	632.78021	28.94192	15.1702

Totals : 4171.19189 235.38115

Table 2, Entry 3, Catalyst 1



Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.616	BV	0.3068	2.05460e4	987.40698	97.4475
2	12.962	VV	0.3775	538.16736	20.41842	2.5525

Totals : 2.10842e4 1007.82541

2-[Hydroxy-(4-fluoro-phenyl)-methyl]-cyclopentanone

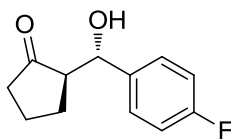
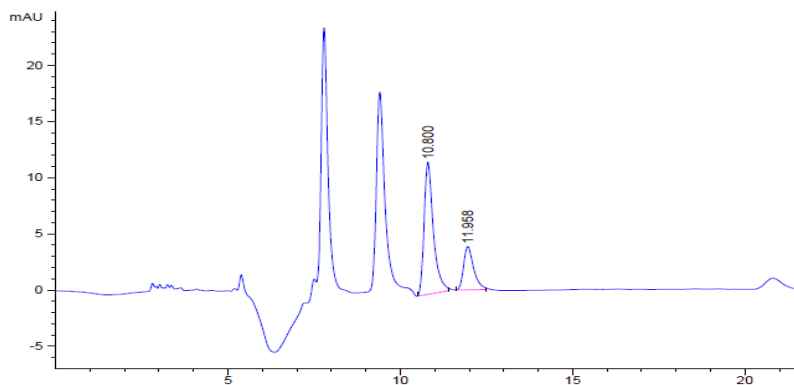


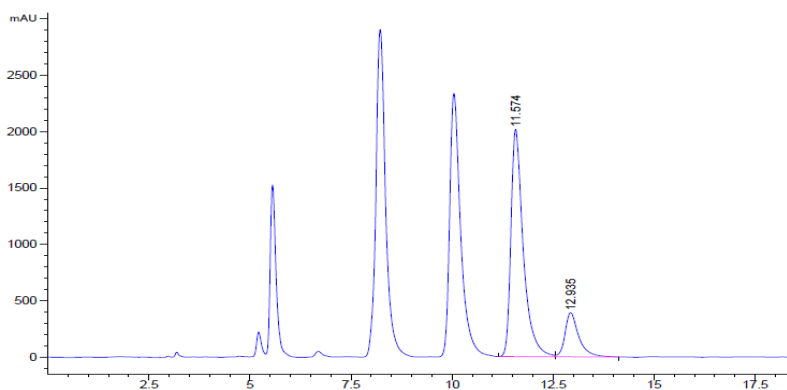
Table 2, Entry 3, Catalyst 2



Signal 1: DAD1 A, Sig=256,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.800	BB	0.2783	220.50552	11.78294	73.8500
2	11.958	BB	0.3018	78.08017	3.86323	26.1500
Totals :				298.58569	15.64617	

Table 2, Entry 3, Catalyst 3



Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.574	BV	0.3157	4.27724e4	2014.84033	82.3265
2	12.935	VB	0.3457	9182.21094	391.39844	17.6735
Totals :				5.19546e4	2406.23877	

2-[Hydroxy-(4-fluoro-phenyl)-methyl]-cyclopentanone

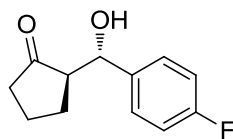
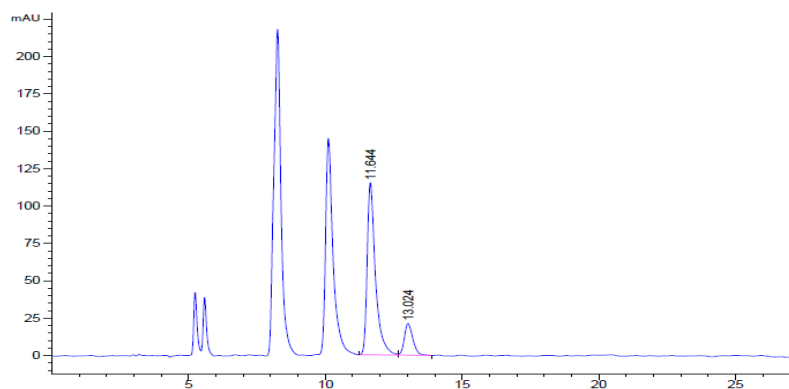


Table 2, Entry 3, Catalyst 4

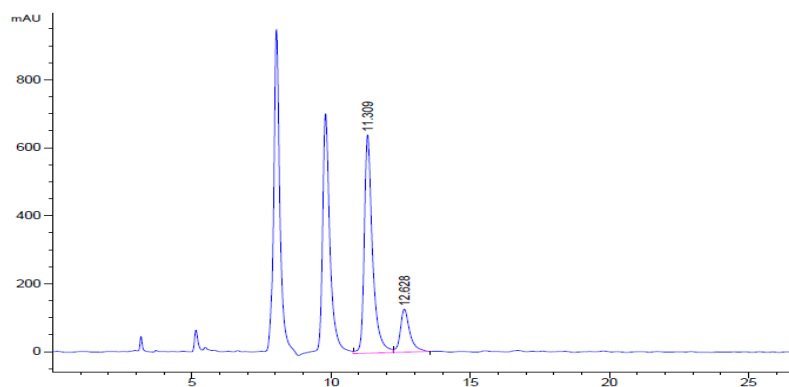


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.644	BV	0.3091	2418.94678	115.12611	84.1014
2	13.024	VB	0.3276	457.28101	21.20150	15.8986

Totals : 2876.22778 136.32761

Table 2, Entry 3, Catalyst 5



Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.309	VV	0.3055	1.33005e4	642.58447	81.6356
2	12.628	VB	0.3472	2992.01196	126.82888	18.3644

Totals : 1.62925e4 769.41335

2-[Hydroxy-(4-fluoro-phenyl)-methyl]-cyclopentanone

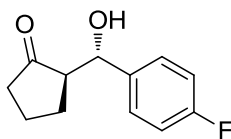
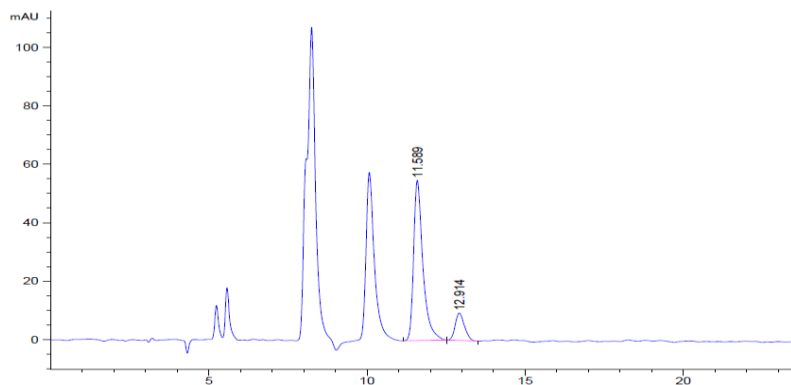


Table 3, Entry 8, Catalyst 16

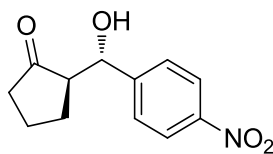


Signal 1: DAD1 C, Sig=260,4 Ref=360,100

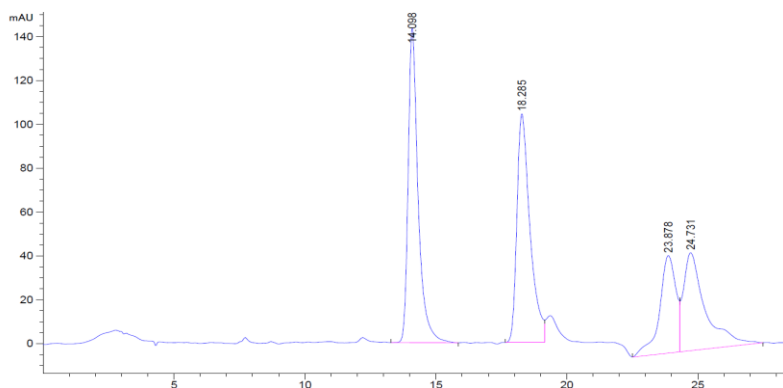
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.589	BB	0.3039	1118.12842	54.84337	85.4568
2	12.914	BB	0.3084	190.28459	9.38982	14.5432

Totals : 1308.41301 64.23319

2-[Hydroxy-(4-nitro-phenyl)-methyl]-cyclopentanone



Racemate

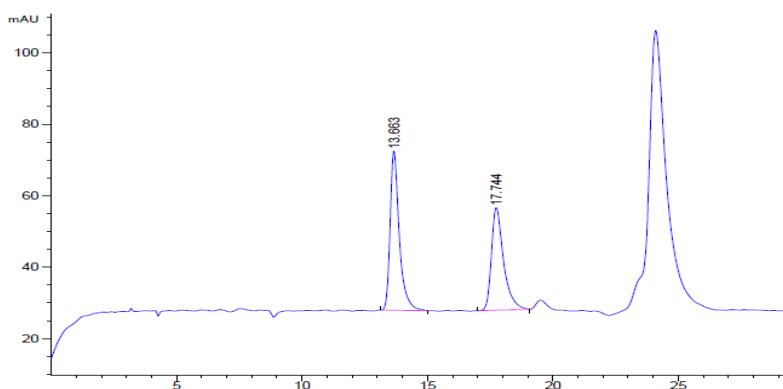


Signal 1: DAD1 C, Sig=260,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.098	BB	0.3928	3792.53906	143.28381	31.7199
2	18.285	BV	0.5170	3617.49316	104.19711	30.2559
3	23.878	BV	0.6522	1946.36365	44.51057	16.2789
4	24.731	VB	0.8171	2599.93848	44.66543	21.7453

Totals : 1.19563e4 336.65693

Table 2, Entry 4, Catalyst 1



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.663	BB	0.3788	1134.67493	44.59967	53.9982
2	17.744	BB	0.5009	966.64355	28.70624	46.0018

Totals : 2101.31848 73.30591

2-[Hydroxy-(4-nitro-phenyl)-methyl]-cyclopentanone

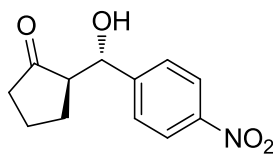
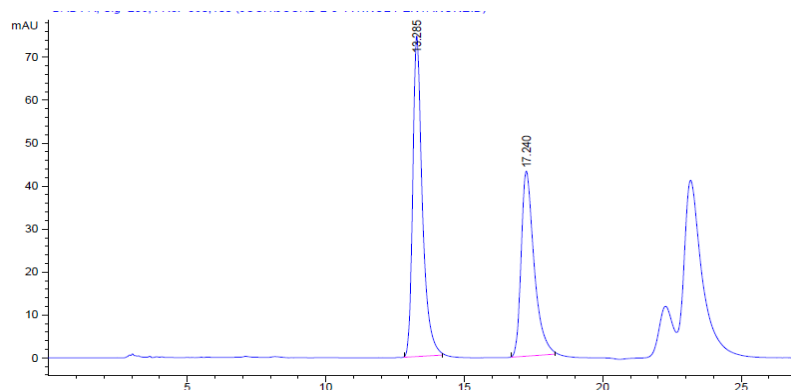


Table 2, Entry 4, Catalyst 2

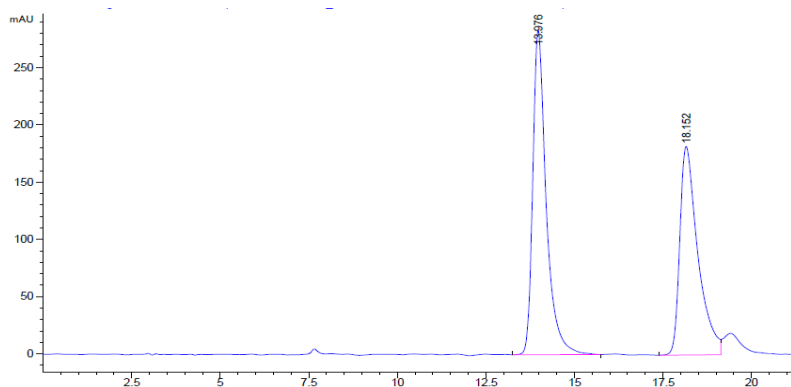


Signal 1: DAD1 A, Sig=256,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.285	BB	0.3600	1804.30042	74.63374	56.3304
2	17.240	BB	0.4847	1398.76416	43.08734	43.6696

Totals : 3203.06458 117.72108

Table 2, Entry 4, Catalyst 3



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.976	BB	0.3920	7480.90332	283.38196	53.7163
2	18.152	BV	0.5209	6445.79834	182.14673	46.2837

Totals : 1.39267e4 465.52869

2-[Hydroxy-(4-nitro-phenyl)-methyl]-cyclopentanone

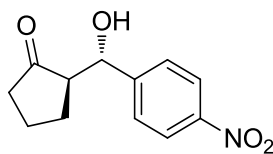
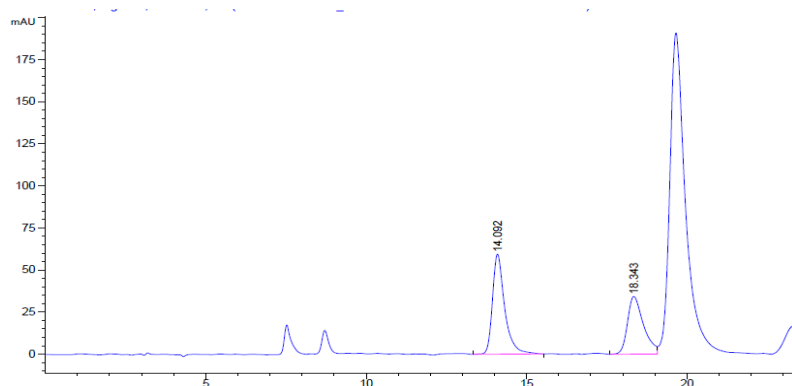


Table 2, Entry 4, Catalyst 4

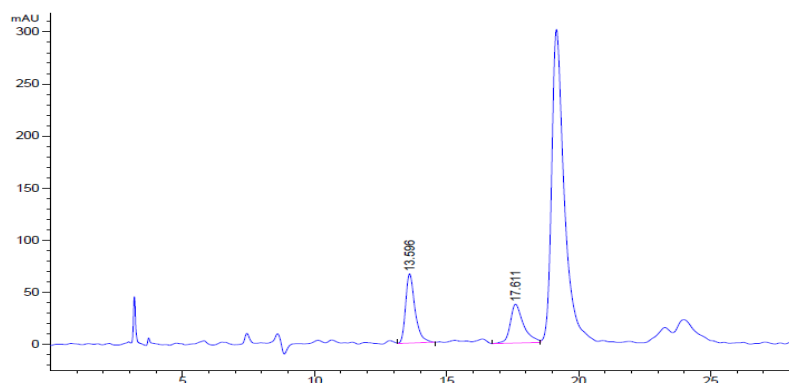


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.092	BB	0.3949	1573.83228	59.44992	57.0028
2	18.343	BV	0.5179	1187.13977	34.29309	42.9972

Totals : 2760.97205 93.74301

Table 2, Entry 4, Catalyst 5



Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.596	VB	0.3729	1648.11609	66.54864	55.8640
2	17.611	BV	0.5068	1302.11353	37.34649	44.1360

Totals : 2950.22961 103.89512

2-[Hydroxy-(4-nitro-phenyl)-methyl]-cyclopentanone

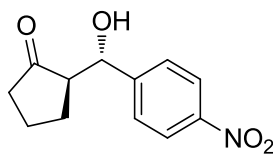
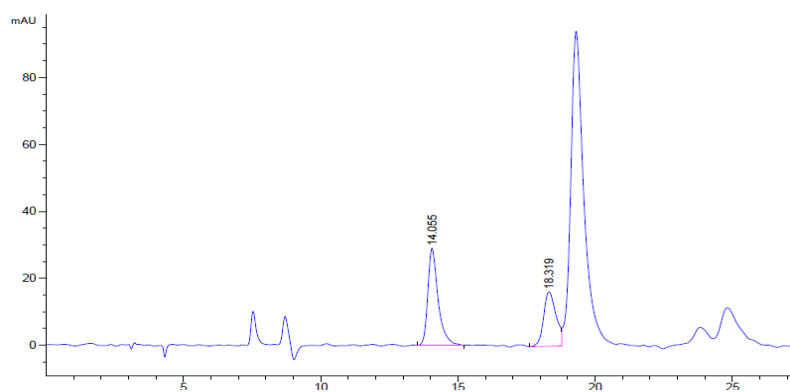


Table 3, Entry 7, Catalyst 16

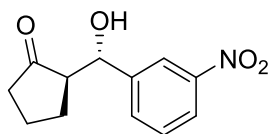


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

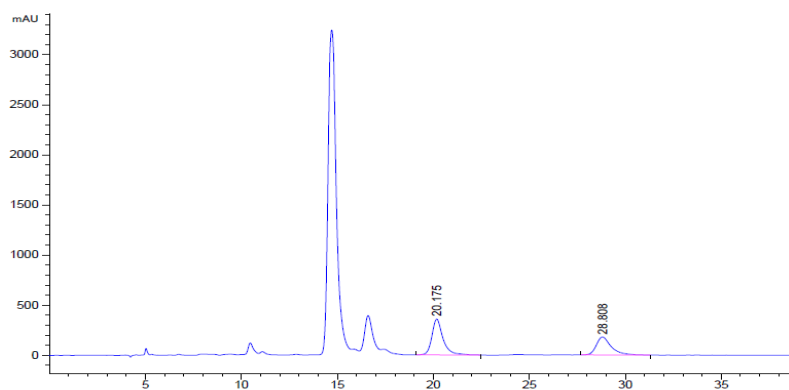
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.055	BB	0.3887	757.66418	29.01055	59.6933
2	18.319	BV	0.4729	511.59760	16.26625	40.3067

Totals : 1269.26178 45.27680

2-[Hydroxy-(3-nitro-phenyl)]-cyclopentanone



Racemate

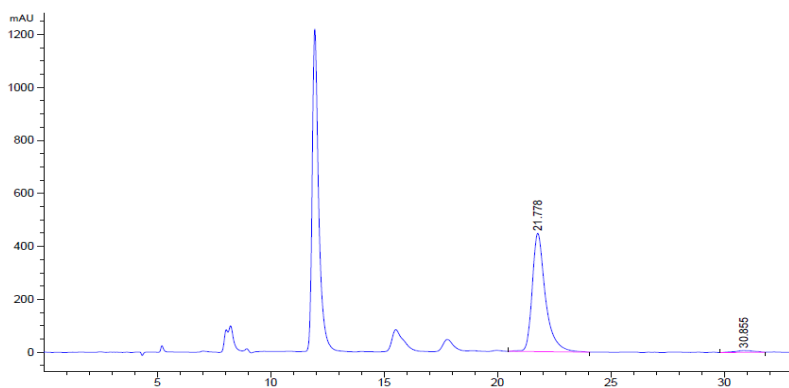


Signal 1: DAD1 C, Sig=260,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.175	BB	0.5923	1.43957e4	358.61813	59.8745
2	28.808	BB	0.7969	9647.44629	179.53302	40.1255

Totals : 2.40432e4 538.15115

Table 2, Entry 5, Catalyst 1



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.778	BB	0.6034	1.81388e4	446.98816	97.8948
2	30.855	BB	0.8734	390.06393	6.63934	2.1052

Totals : 1.85289e4 453.62749

2-[Hydroxy-(3-nitro-phenyl)]-cyclopentanone

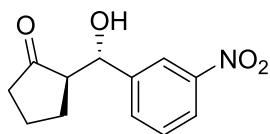
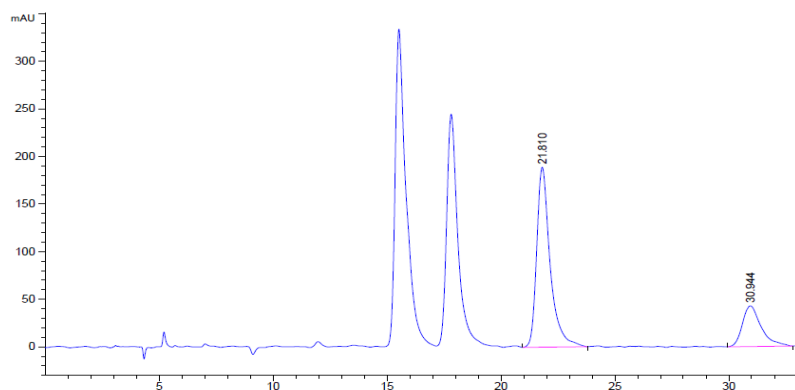


Table 2, Entry 5, Catalyst 2

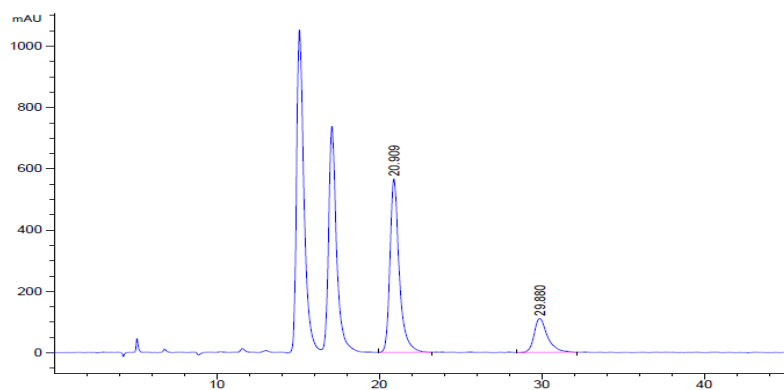


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.810	BB	0.6098	7745.41357	189.13760	75.9866
2	30.944	BB	0.8477	2447.71143	42.77121	24.0134

Totals : 1.01931e4 231.90882

Table 2, Entry 5, Catalyst 3



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.909	BB	0.5931	2.24732e4	566.13184	77.9149
2	29.880	BB	0.8589	6370.04297	111.10529	22.0851

Totals : 2.88432e4 677.23712

2-[Hydroxy-(3-nitro-phenyl)]-cyclopentanone

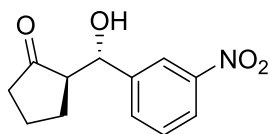
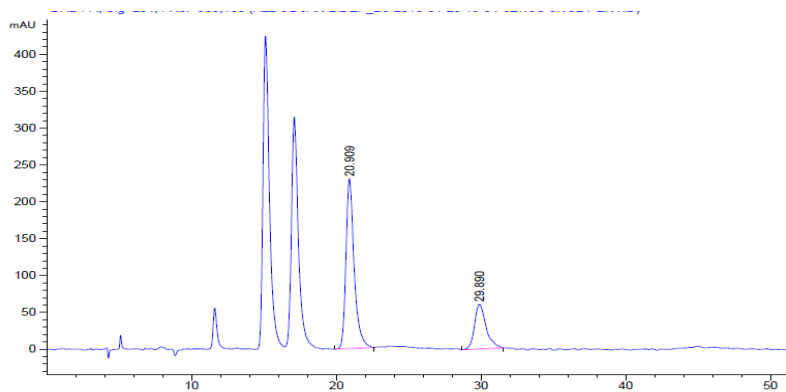


Table 2, Entry 5, Catalyst 4

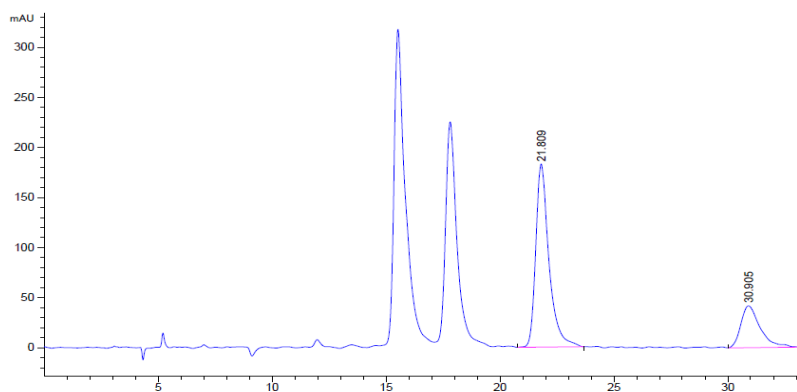


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.909	BB	0.5895	9061.52930	230.05556	72.8977
2	29.890	BB	0.8459	3368.94238	60.66157	27.1023

Totals : 1.24305e4 290.71713

Table 2, Entry 5, Catalyst 5

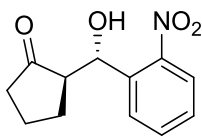


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

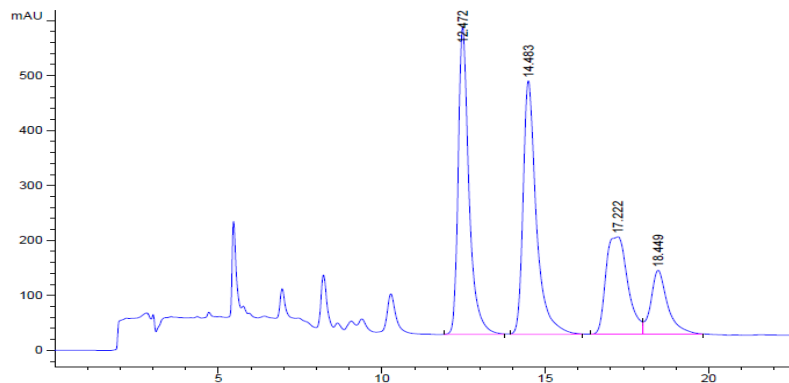
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.809	BB	0.5983	7370.71191	182.84116	75.0064
2	30.905	BB	0.8908	2456.06299	41.83992	24.9936

Totals : 9826.77490 224.68108

2-[Hydroxy-(2-nitro-phenyl)]-cyclopentanone



Racemate

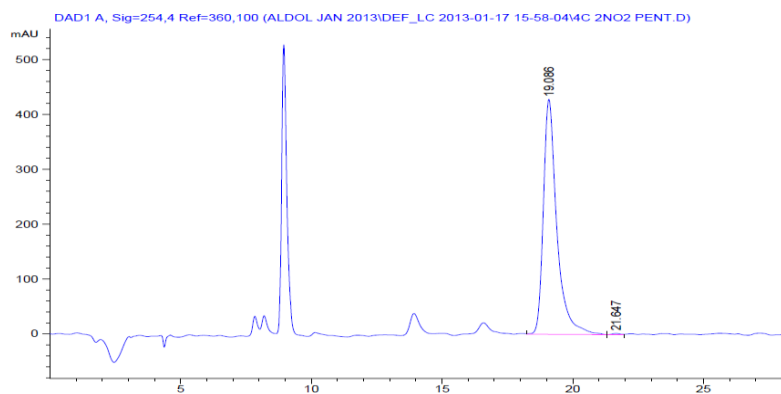


Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.472	BB	0.3413	1.28337e4	560.20288	33.6211
2	14.483	BB	0.4162	1.29737e4	461.24097	33.9878
3	17.222	BV	0.6228	8226.79688	177.48163	21.5521
4	18.449	VB	0.5213	4137.42920	116.21823	10.8390

Totals : 3.81716e4 1315.14371

Table 2, Entry 6, Catalyst 1



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.086	VB	0.5339	1.53521e4	428.61487	99.7455
2	21.647	BV	0.2806	39.16740	2.10967	0.2545

Totals : 1.53913e4 430.72454

2-[Hydroxy-(2-nitro-phenyl)]-cyclopentanone

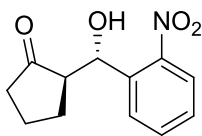
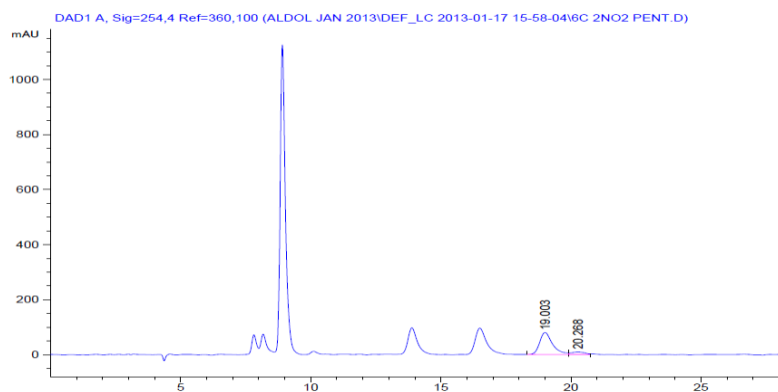


Table 2, Entry 6, Catalyst 2

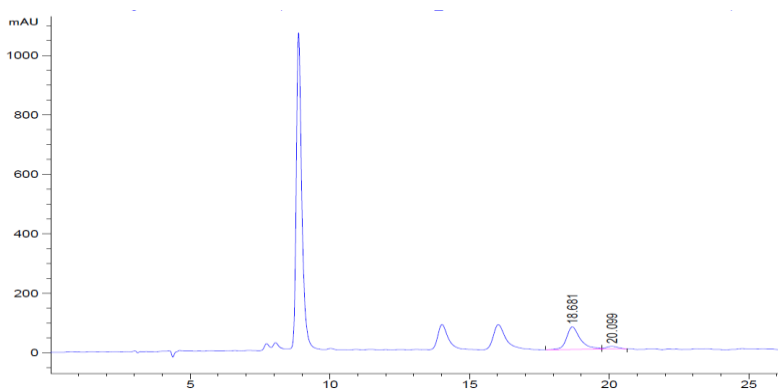


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.003	BV	0.5143	2766.39233	80.21597	88.6703
2	20.268	VV	0.5494	353.47192	10.17341	11.3297

Totals : 3119.86426 90.38937

Table 2, Entry 6, Catalyst 3



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.681	BV	0.5020	2588.49976	75.87394	90.9397
2	20.099	VB	0.4483	257.89047	8.94585	9.0603

Totals : 2846.39023 84.81979

2-[Hydroxy-(2-nitro-phenyl)]-cyclopentanone

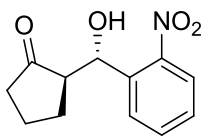
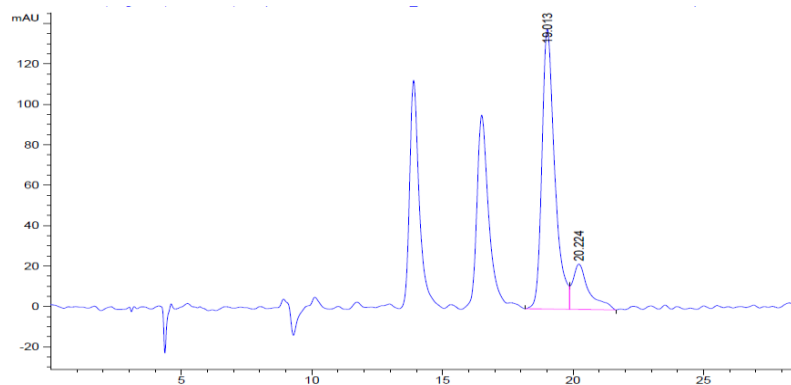


Table 2, Entry 6, Catalyst 4

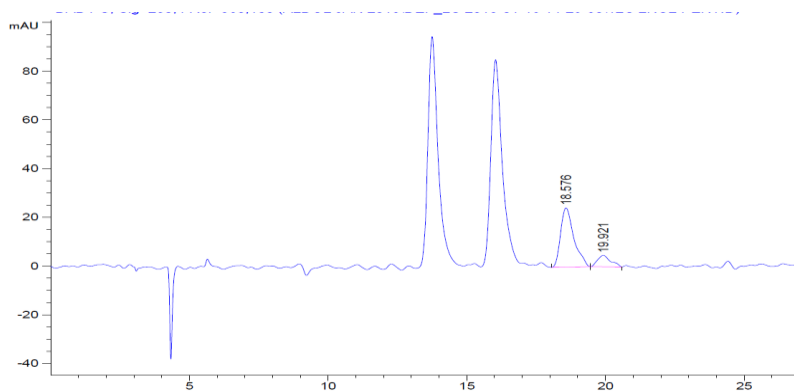


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.013	BV	0.5107	4737.32568	138.61998	82.8496
2	20.224	VB	0.6179	980.65588	22.43907	17.1504

Totals : 5717.98157 161.05905

Table 2, Entry 6, Catalyst 5

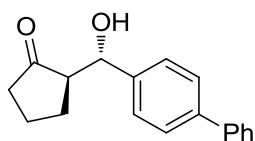


Signal 1: DAD1 G, Sig=280,4 Ref=360,100

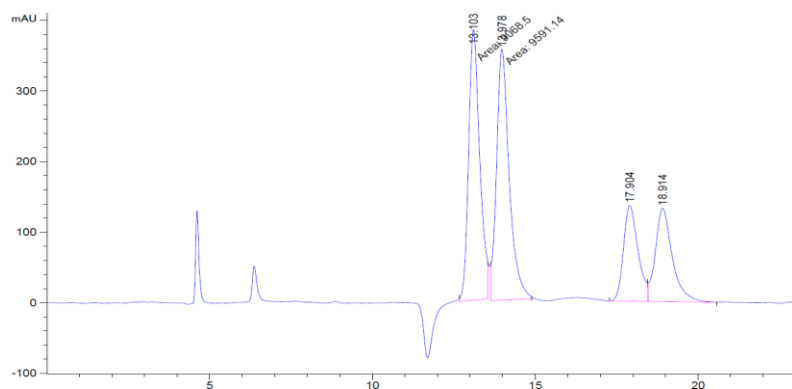
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.576	BB	0.5046	808.86017	24.28157	84.1417
2	19.921	BB	0.4737	152.44731	4.65918	15.8583

Totals : 961.30748 28.94075

2-[Hydroxy-(biphenyl)-methyl]-cyclopentanone



Racemate

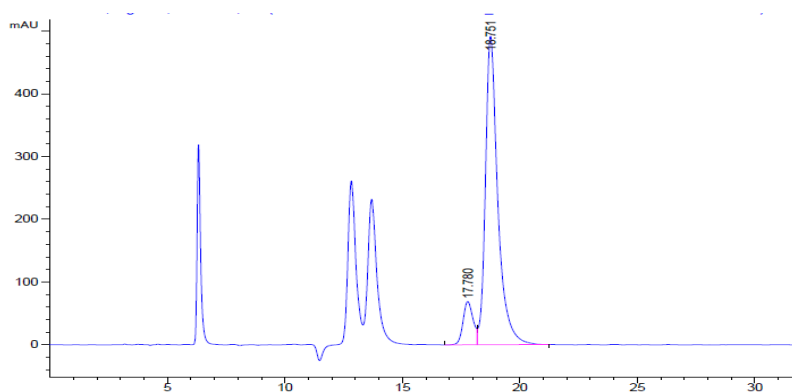


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.103	MM	0.3941	9068.50000	383.53708	32.7777
2	13.978	MM	0.4499	9591.14453	355.28961	34.6668
3	17.904	BV	0.4700	4208.43164	135.63654	15.2112
4	18.914	VB	0.5372	4798.58545	132.29437	17.3443

Totals : 2.76667e4 1006.75760

Table 2, Entry 7, Catalyst 1



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.780	BV	0.4514	2052.36597	68.91732	10.2152
2	18.751	VB	0.5417	1.80388e4	492.11285	89.7848

Totals : 2.00912e4 561.03017

2-[Hydroxy-(biphenyl)-methyl]-cyclopentanone

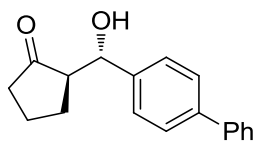
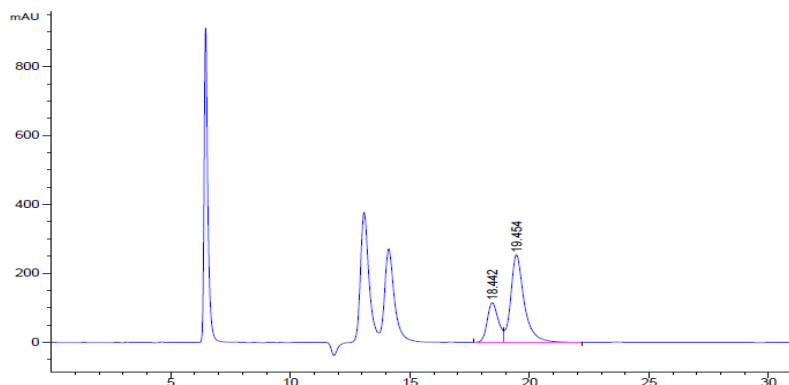


Table 2, Entry 7, Catalyst 2

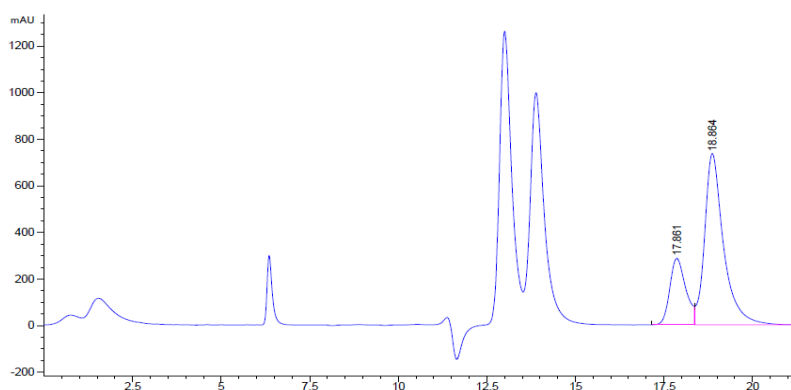


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.442	BV	0.4925	3714.95728	114.49740	27.3624
2	19.454	VB	0.5716	9861.89258	253.65324	72.6376

Totals : 1.35768e4 368.15064

Table 2, Entry 7, Catalyst 3



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.861	BV	0.4728	8931.35156	285.63715	24.6233
2	18.864	VB	0.5459	2.73406e4	735.07385	75.3767

Totals : 3.62720e4 1020.71100

2-[Hydroxy-(biphenyl)-methyl]-cyclopentanone

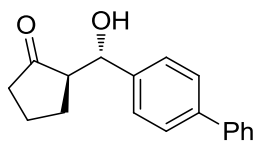
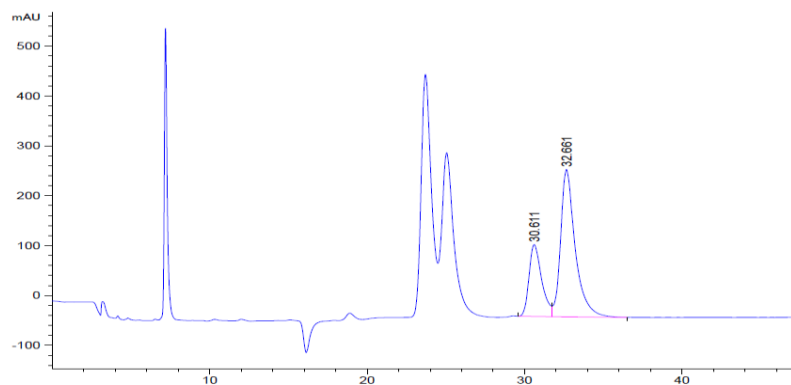


Table 2, Entry 7, Catalyst 4

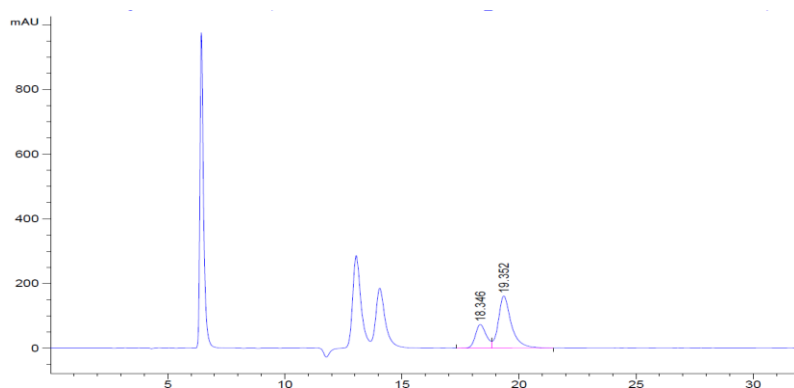


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	30.611	BV	0.8416	8044.42188	144.02803	29.6980
2	32.661	VB	0.9527	1.90430e4	295.16159	70.3020

Totals : 2.70875e4 439.18962

Table 2, Entry 7, Catalyst 5

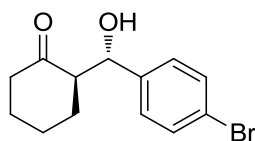


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

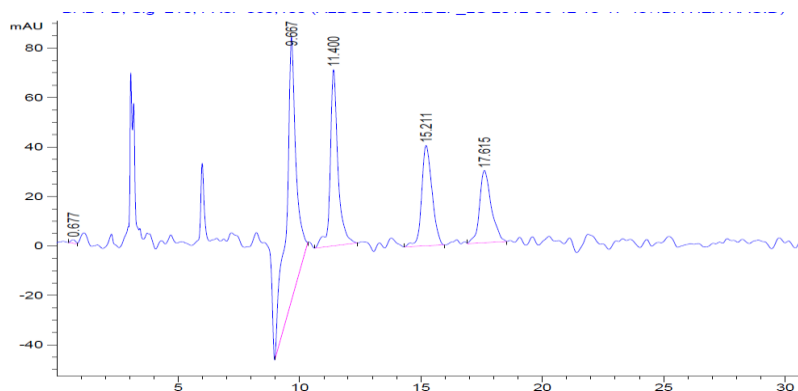
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.346	BV	0.4843	2347.13037	73.15690	27.5070
2	19.352	VB	0.5658	6185.71680	161.16283	72.4930

Totals : 8532.84717 234.31973

2-[Hydroxy-(4-bromo-phenyl)-methyl]-cyclohexanone



Racemate

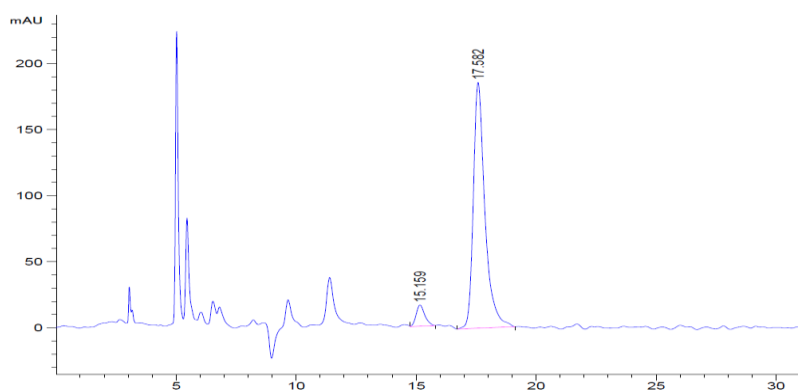


Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	0.677	BV	0.2188	18.99023	1.41325	0.2802
2	9.667	BB	0.3809	2985.45020	106.55878	44.0564
3	11.400	BB	0.3249	1582.24487	71.29802	23.3492
4	15.211	BB	0.4610	1208.03052	40.61239	17.8270
5	17.615	VB	0.5060	981.71234	29.22028	14.4872

Totals : 6776.42816 249.10273

Table 2, Entry 8, Catalyst 1



Signal 1: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.159	VB	0.3803	402.20715	16.05486	6.0526
2	17.582	BB	0.4995	6243.01123	186.05635	93.9474

Totals : 6645.21838 202.11121

2-[Hydroxy-(4-bromo-phenyl)-methyl]-cyclohexanone

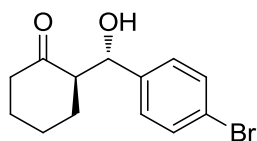
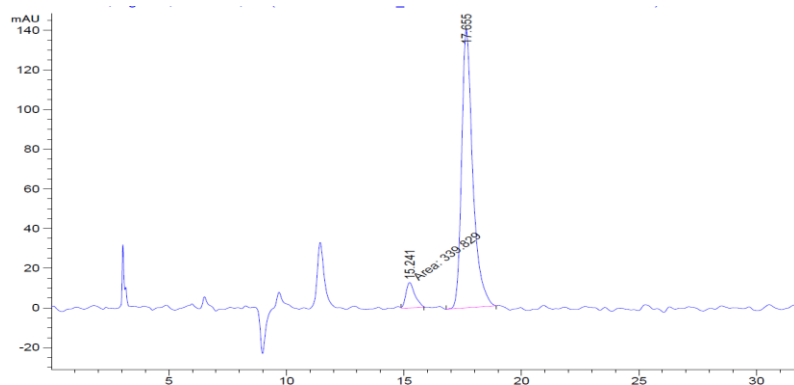


Table 2, Entry 8, Catalyst 2

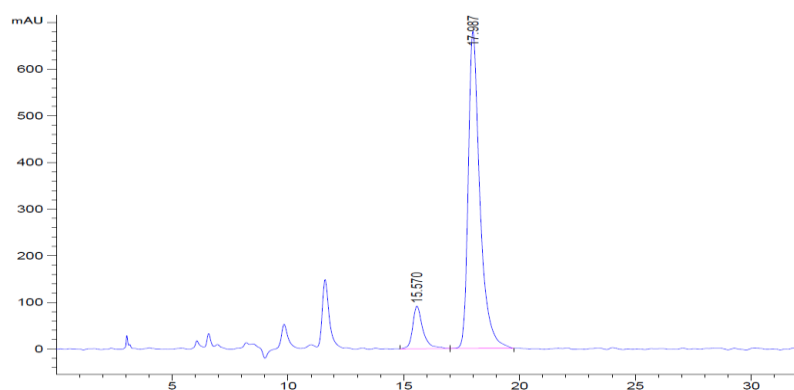


Signal 1: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.241	MM	0.4413	339.82904	12.83379	6.8395
2	17.655	BB	0.4927	4628.80664	140.37726	93.1605

Totals : 4968.63568 153.21105

Table 2, Entry 8, Catalyst 3



Signal 1: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.570	BB	0.4513	2785.76172	91.47964	10.4978
2	17.987	BB	0.5194	2.37509e4	680.21094	89.5022

Totals : 2.65367e4 771.69058

2-[Hydroxy-(4-bromo-phenyl)-methyl]-cyclohexanone

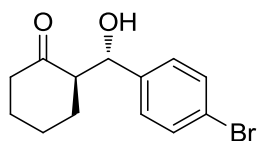
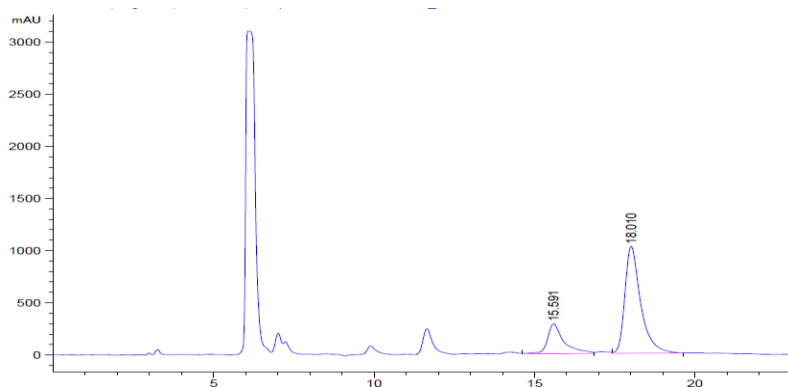


Table 2, Entry 8, Catalyst 4

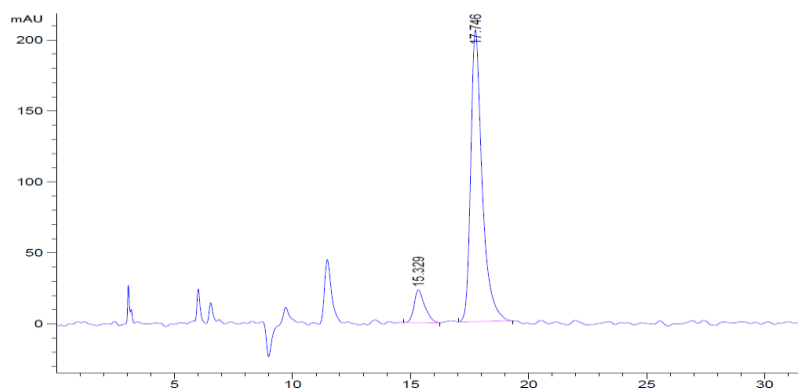


Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.591	VV	0.5057	1.01240e4	285.47794	22.4365
2	18.010	VB	0.5083	3.49988e4	1025.06433	77.5635

Totals : 4.51228e4 1310.54227

Table 2, Entry 8, Catalyst 5

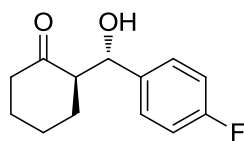


Signal 1: DAD1 D, Sig=230,4 Ref=360,100

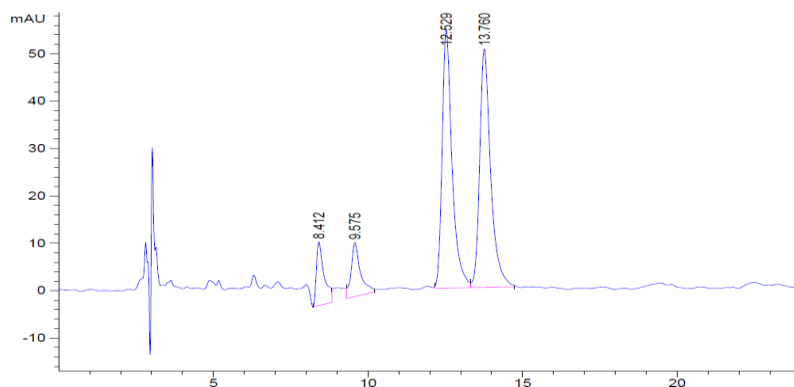
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.329	BB	0.4578	717.78943	23.01823	9.4042
2	17.746	BB	0.4982	6914.86963	205.68797	90.5958

Totals : 7632.65906 228.70620

2-[Hydroxy-(4-fluoro-phenyl)-methyl]-cyclohexanone



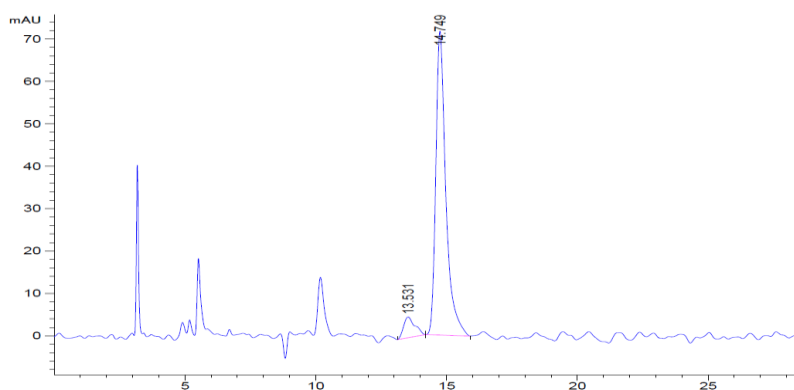
Racemate



Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.412	VB	0.2505	233.07262	13.42521	7.9207
2	9.575	BB	0.3017	239.56458	11.37315	8.1413
3	12.529	BV	0.3286	1220.61682	54.63713	41.4810
4	13.760	VB	0.3695	1249.33508	50.33954	42.4570

Table 2, Entry 9, Catalyst 1



Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.531	BB	0.4352	146.62860	4.89894	7.1240
2	14.749	BB	0.3950	1911.59973	71.70232	92.8760

Totals : 2058.22833 76.60126

2-[Hydroxy-(4-fluoro-phenyl)-methyl]-cyclohexanone

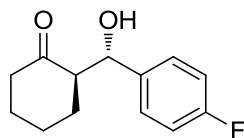
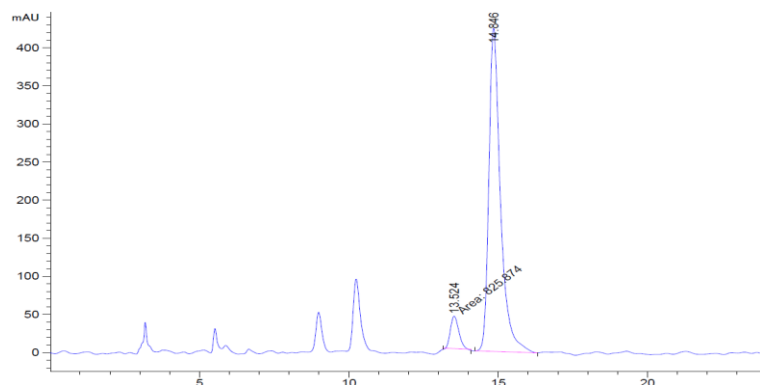


Table 2, Entry 9, Catalyst 2

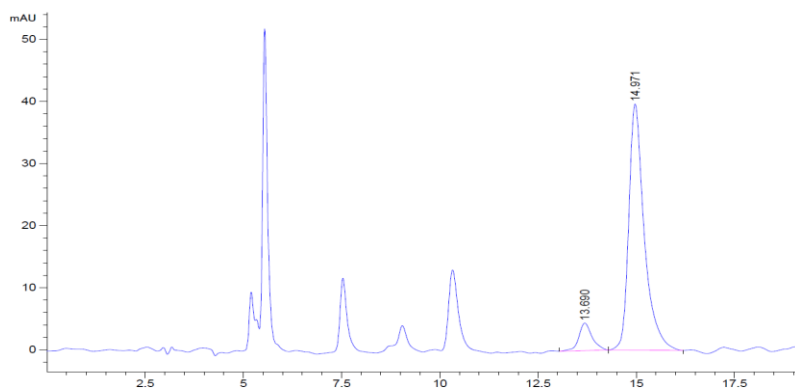


Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.524	MM	0.3238	825.87372	42.50507	6.7311
2	14.846	BB	0.4009	1.14436e4	423.98584	93.2689

Totals : 1.22694e4 466.49091

Table 2, Entry 9, Catalyst 3



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.690	BB	0.3497	103.81554	4.42519	8.7101
2	14.971	BB	0.4062	1088.08960	39.64024	91.2899

Totals : 1191.90514 44.06544

2-[Hydroxy-(4-fluoro-phenyl)-methyl]-cyclohexanone

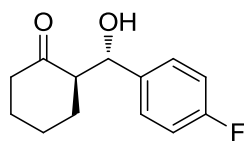
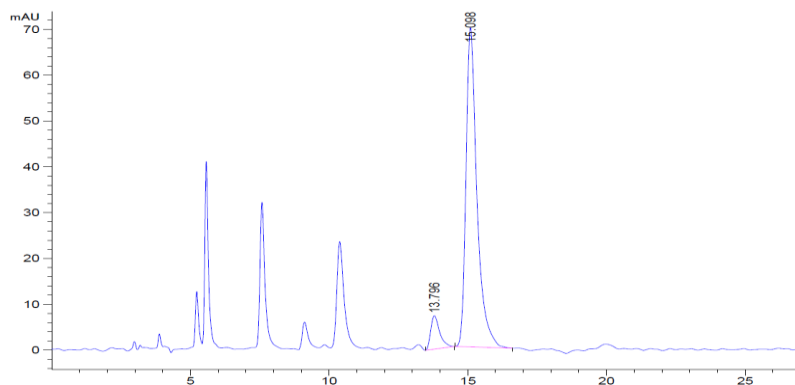


Table 2, Entry 9, Catalyst 4

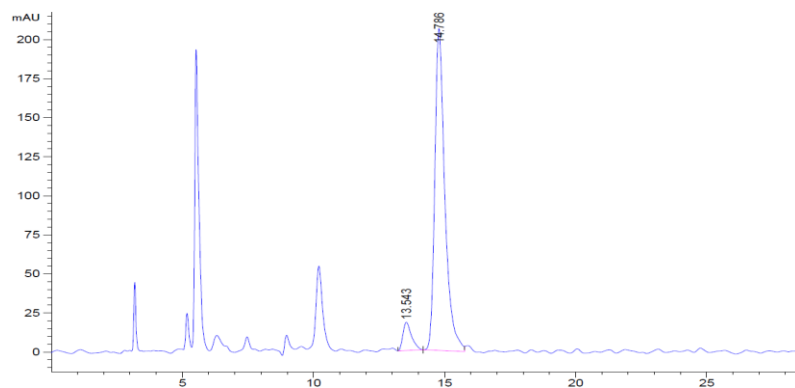


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.796	BB	0.3408	164.35617	7.29572	7.9173
2	15.098	BB	0.4082	1911.56091	69.65408	92.0827

Totals : 2075.91708 76.94980

Table 2, Entry 9, Catalyst 5



Signal 1: DAD1 B, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.543	BB	0.3411	411.32962	18.10303	6.9534
2	14.786	BV	0.3976	5504.14941	206.10719	93.0466

Totals : 5915.47903 224.21022

2-[Hydroxy-(4-fluoro-phenyl)-methyl]-cyclohexanone

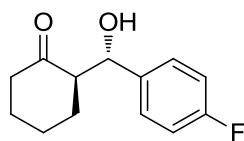
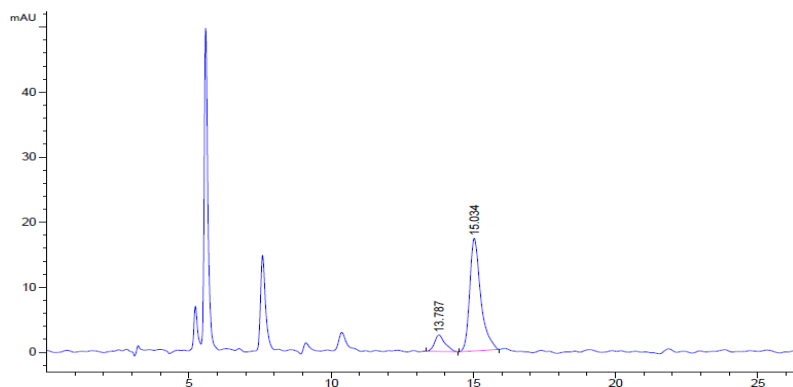


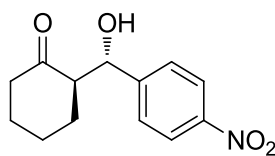
Table 3, Entry 5, Catalyst 16



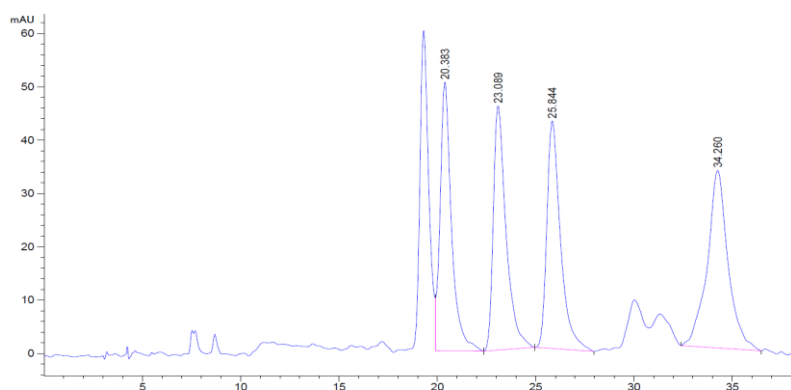
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.787	BB	0.3665	64.43161	2.53550	12.0913
2	15.034	BB	0.4038	468.44385	17.30833	87.9087
Totals :				532.87546	19.84383	

2-[Hydroxy-(4-nitro-phenyl)-methyl]-cyclohexanone



Racemate

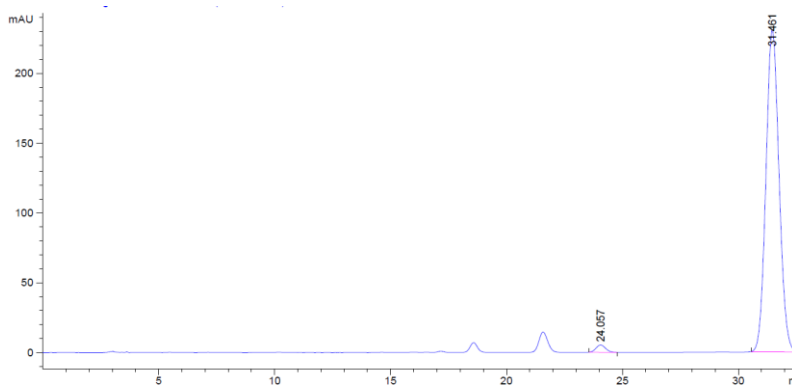


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.383	VB	0.5924	2038.33252	50.34125	23.6846
2	23.089	BB	0.6707	2065.04346	45.74075	23.9950
3	25.844	BB	0.7174	2059.34912	42.64633	23.9288
4	34.260	BB	1.0390	2443.42090	33.26344	28.3916

Totals : 8606.14600 171.99176

Table 2, Entry 10, Catalyst 1



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.057	BB	0.4382	150.81140	5.26504	1.6356
2	31.461	BB	0.6101	9069.78125	231.00755	98.3644

Totals : 9220.59265 236.27259

2-[Hydroxy-(4-nitro-phenyl)-methyl]-cyclohexanone

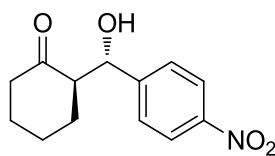
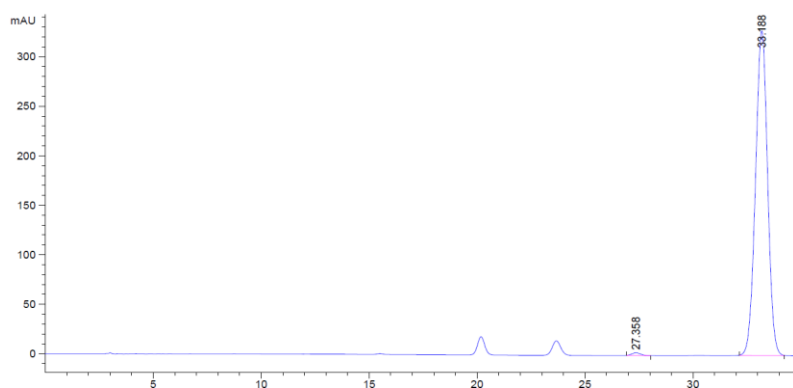


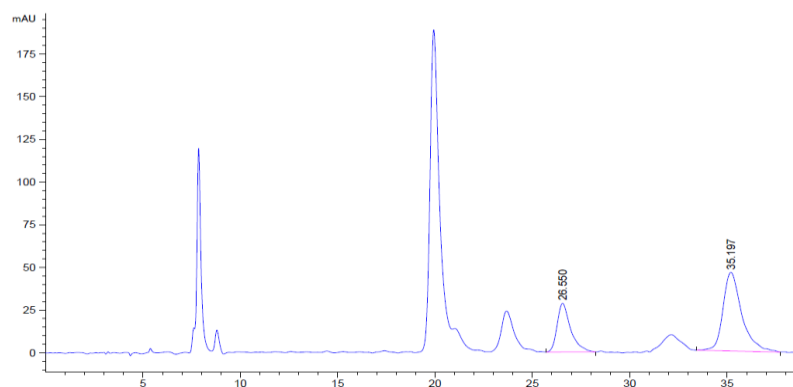
Table 2, Entry 10, Catalyst 2



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.358	BB	0.4265	77.65517	2.72491	0.6048
2	33.188	BB	0.6060	1.27614e4	327.92426	99.3952

Totals : 1.28390e4 330.64916

Table 2, Entry 10, Catalyst 3



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.550	BB	0.7195	1371.31873	28.49310	30.7020
2	35.197	BB	1.0366	3095.22925	46.02365	69.2980

Totals : 4466.54797 74.51674

2-[Hydroxy-(4-nitro-phenyl)-methyl]-cyclohexanone

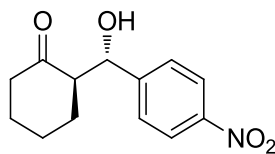
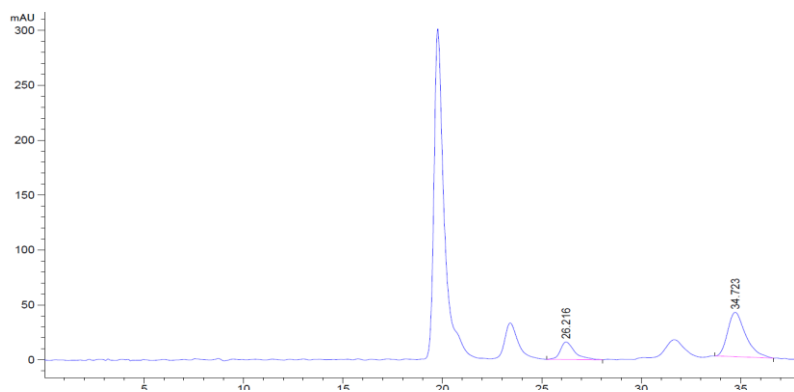


Table 2, Entry 10, Catalyst 4

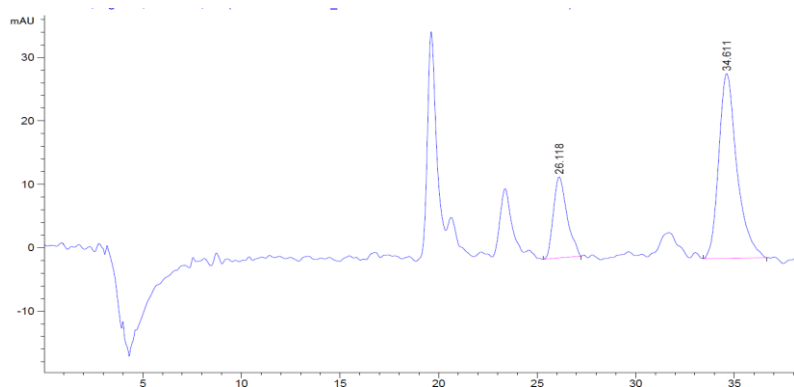


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.216	BB	0.7673	804.63885	15.98302	24.0521
2	34.723	BB	0.9396	2540.75708	40.40771	75.9479

Totals : 3345.39594 56.39073

Table 2, Entry 10, Catalyst 5



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.118	BB	0.7301	613.33429	12.77630	24.6328
2	34.611	BB	0.9767	1876.57397	29.08643	75.3672

Totals : 2489.90826 41.86273

2-[Hydroxy-(4-nitro-phenyl)-methyl]-cyclohexanone

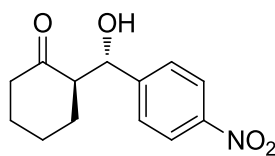
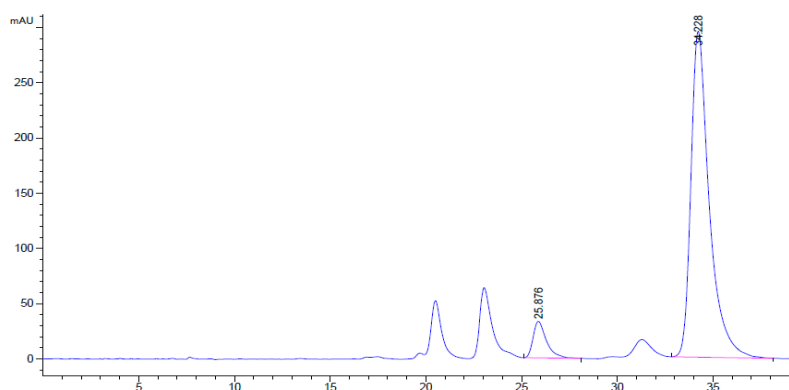


Table 3, Entry 4, Catalyst 16

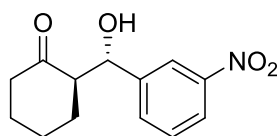


Signal 1: DAD1 C, Sig=260,4 Ref=360,100

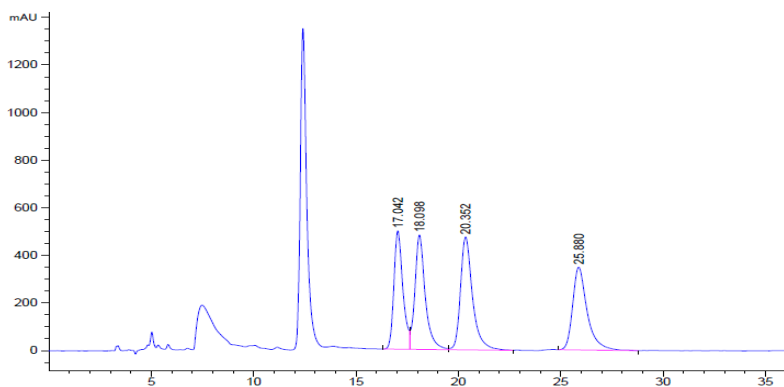
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.876	BB	0.7171	1591.80237	32.98138	7.4970
2	34.228	BB	0.9909	1.96408e4	294.95438	92.5030

Totals : 2.12326e4 327.93575

2-[Hydroxy-(3-nitro-phenyl)]-cyclohexanone



Racemate

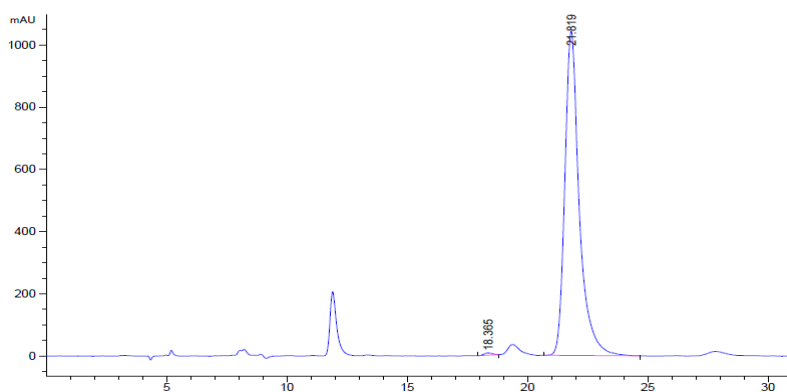


Signal 1: DAD1 C, Sig=260,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.042	BV	0.4582	1.51797e4	497.18906	22.1490
2	18.098	VV	0.5206	1.69213e4	480.75165	24.6903
3	20.352	VB	0.6144	1.93592e4	474.14063	28.2475
4	25.880	BB	0.7314	1.70740e4	347.39310	24.9132

Totals : 6.85343e4 1799.47443

Table 2, Entry 11, Catalyst 1



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.365	BB	0.3984	169.05835	6.93454	0.3870
2	21.819	BB	0.6205	4.35138e4	1043.45776	99.6130

Totals : 4.36828e4 1050.39230

2-[Hydroxy-(3-nitro-phenyl)]-cyclohexanone

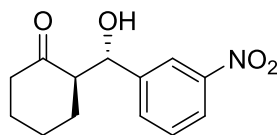
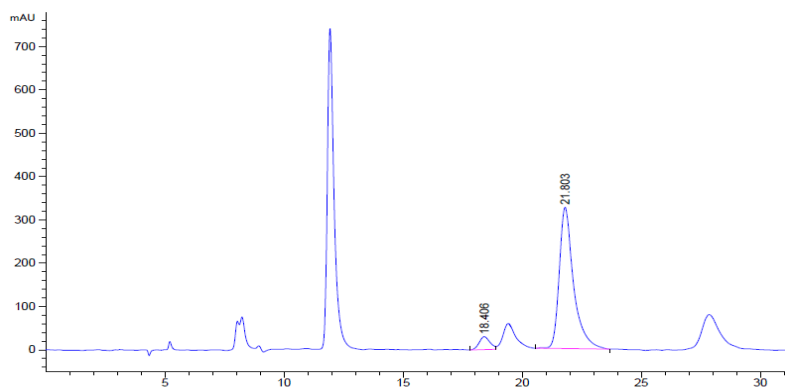


Table 2, Entry 11, Catalyst 2

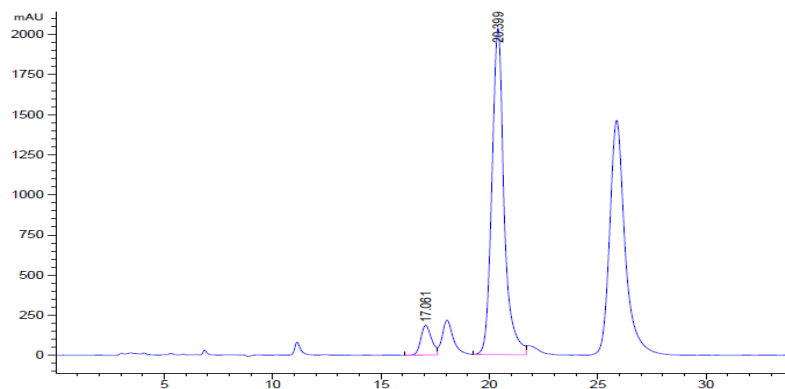


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.406	BV	0.4781	940.22955	29.79788	6.4589
2	21.803	BB	0.6172	1.36170e4	326.10489	93.5411

Totals : 1.45572e4 355.90277

Table 2, Entry 11, Catalyst 3



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.061	BV	0.5182	6309.92969	185.82240	7.3616
2	20.399	BV	0.5875	7.94043e4	2033.93445	92.6384

Totals : 8.57143e4 2219.75685

2-[Hydroxy-(3-nitro-phenyl)]-cyclohexanone

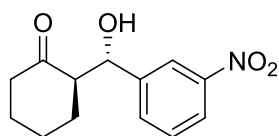
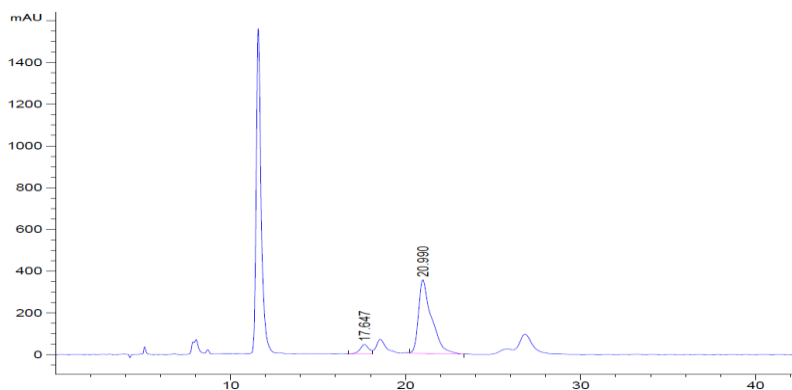


Table 2, Entry 11, Catalyst 4

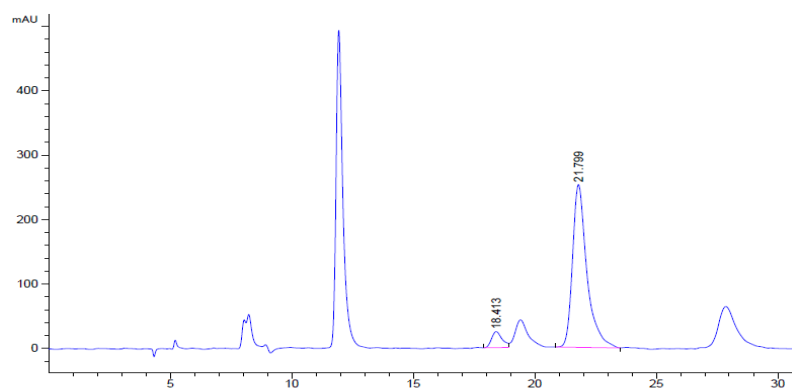


Signal 1: DAD1 C, Sig=260,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.647	BV	0.4999	1522.50171	44.63845	7.7328
2	20.990	VB	0.7222	1.81665e4	353.13251	92.2672

Totals : 1.96890e4 397.77096

Table 2, Entry 11, Catalyst 5

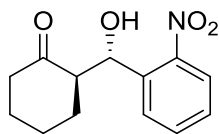


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

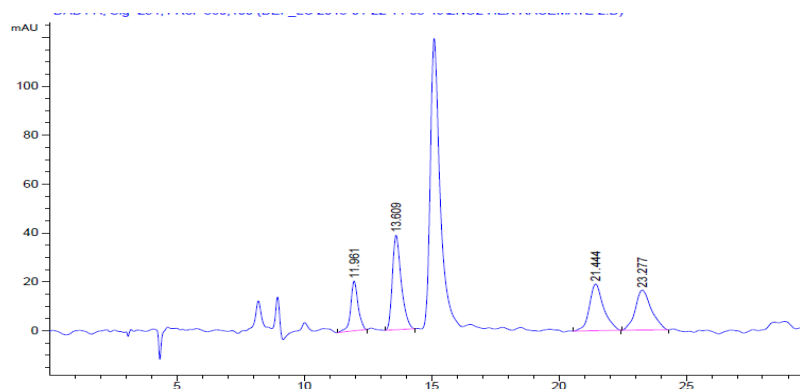
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.413	BV	0.4547	750.13171	24.81470	6.7444
2	21.799	BB	0.6110	1.03721e4	252.64702	93.2556

Totals : 1.11222e4 277.46172

2-[Hydroxy-(2-nitro-phenyl)-methyl]-cyclohexanone



Racemate

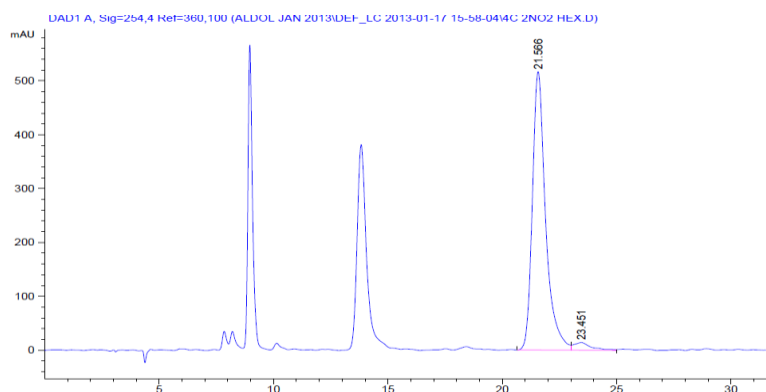


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.961	BB	0.2972	411.35648	20.40641	14.6775
2	13.609	BB	0.3616	933.15485	38.66509	33.2956
3	21.444	BB	0.5713	739.95465	19.12959	26.4021
4	23.277	BB	0.6492	718.16852	16.39021	25.6248

Totals : 2802.63449 94.59130

Table 2, Entry 12, Catalyst 1



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.566	BV	0.6013	2.07832e4	516.65967	96.4329
2	23.451	VV	0.7305	768.77460	14.22613	3.5671

Totals : 2.15520e4 530.88580

2-[Hydroxy-(2-nitro-phenyl)-methyl]-cyclohexanone

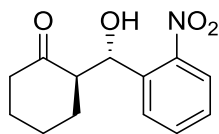


Table 2, Entry 12, Catalyst 2

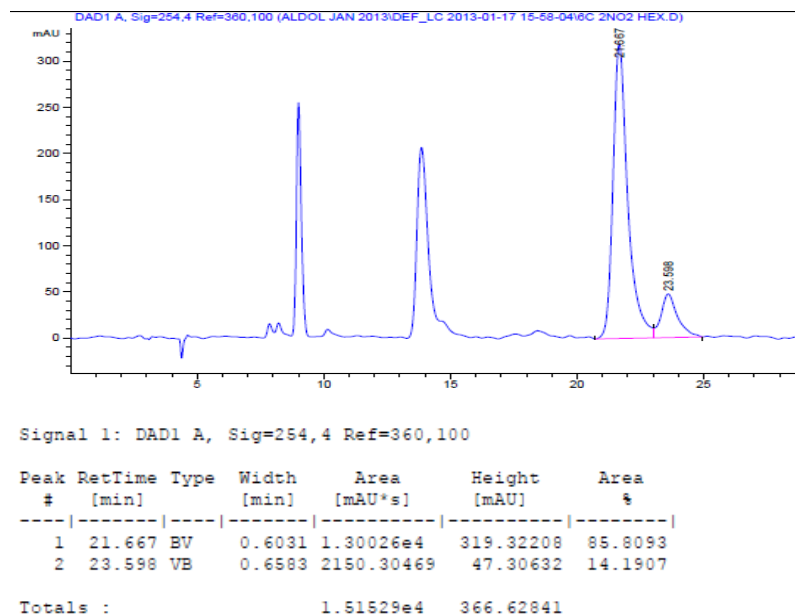
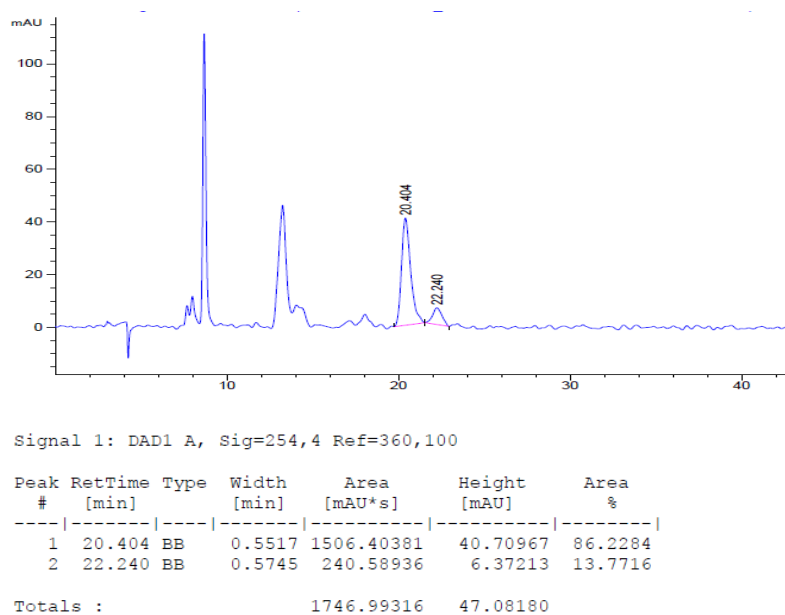


Table 2, Entry 12, Catalyst 3



2-[Hydroxy-(2-nitro-phenyl)-methyl]-cyclohexanone

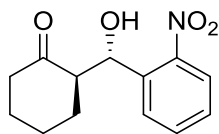
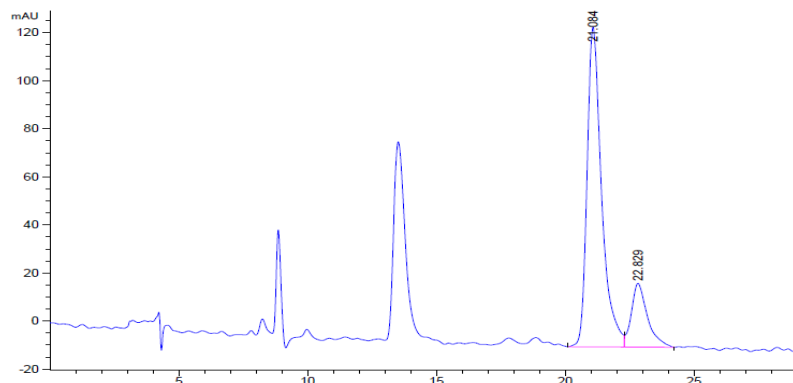


Table 2, Entry 12, Catalyst 4

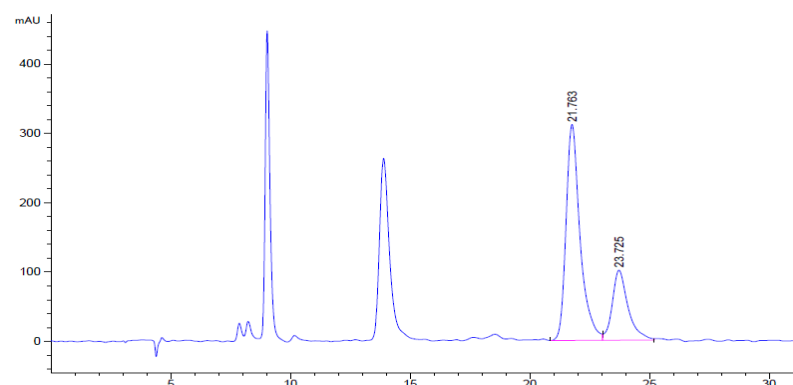


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.084	BV	0.5854	5216.42627	133.06281	81.9128
2	22.829	VB	0.6352	1151.83899	26.49606	18.0872

Totals : 6368.26526 159.55886

Table 2, Entry 12, Catalyst 5

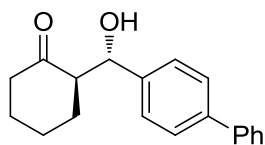


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

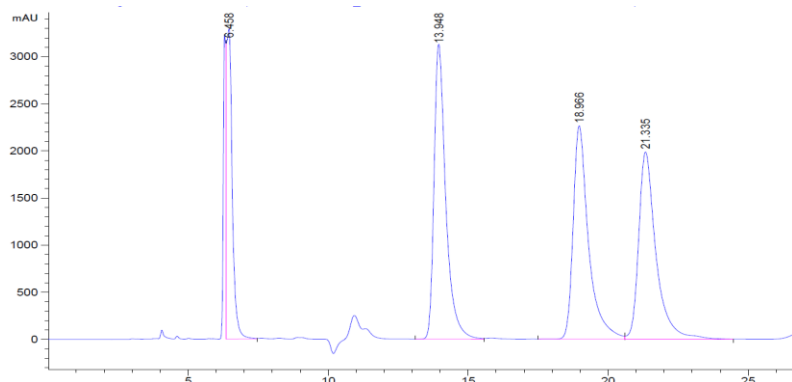
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.763	BV	0.6084	1.27194e4	311.51456	73.2370
2	23.725	VV	0.6807	4648.04541	101.04308	26.7630

Totals : 1.73674e4 412.55763

2-[Hydroxy-(biphenyl)-methyl]-cyclohexanone



Racemate

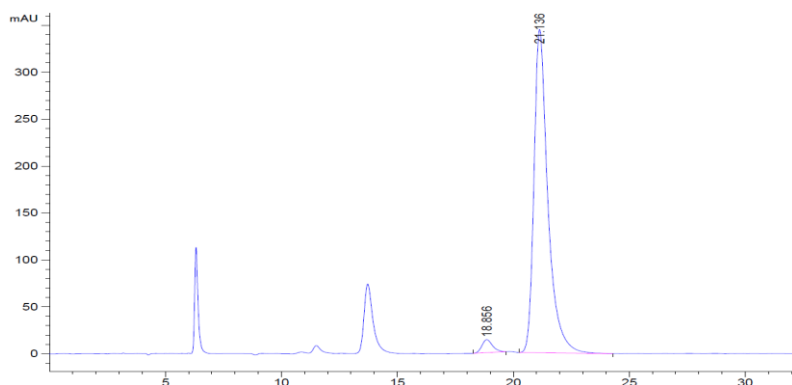


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.458	VV	0.2028	4.76873e4	3295.32642	15.3845
2	13.948	BV	0.4335	9.10662e4	3129.83057	29.3791
3	18.966	BV	0.5596	8.60778e4	2263.71265	27.7698
4	21.335	VB	0.6343	8.51379e4	1985.50842	27.4666

Totals : 3.09969e5 1.06744e4

Table 2, Entry 13, Catalyst 1



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.856	BB	0.4890	440.74829	13.85961	2.9750
2	21.136	BB	0.6226	1.43742e4	344.62250	97.0250

Totals : 1.48150e4 358.48211

2-[Hydroxy-(biphenyl)-methyl]-cyclohexanone

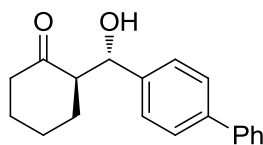
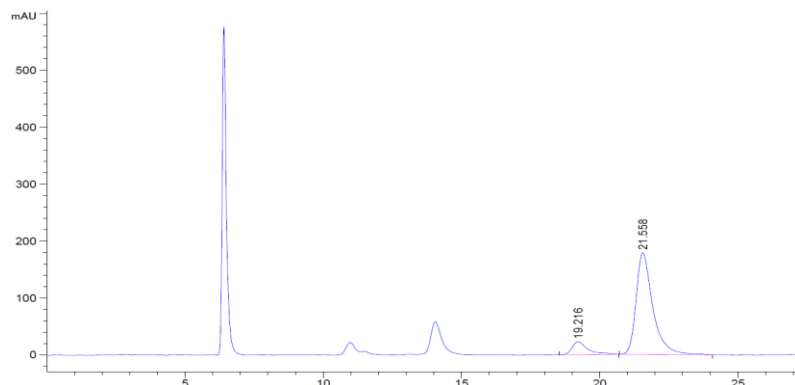


Table 2, Entry 13, Catalyst 2

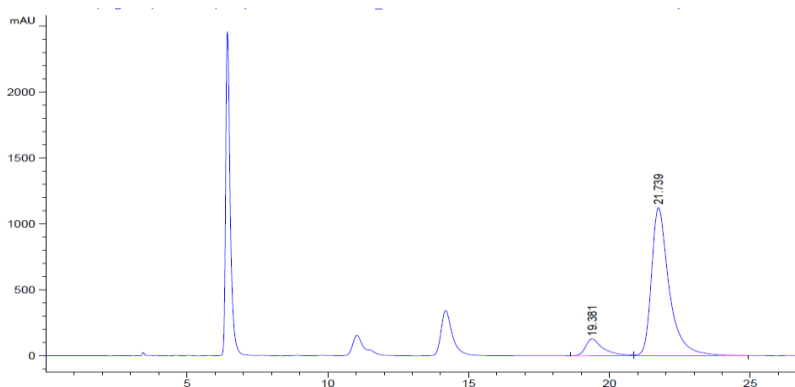


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.216	BB	0.5768	906.49841	22.85207	10.7745
2	21.558	BB	0.6243	7506.87402	178.62817	89.2255

Totals : 8413.37244 201.48024

Table 2, Entry 13, Catalyst 3



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.381	BV	0.6214	5540.06445	128.91678	10.1401
2	21.739	VB	0.6452	4.90952e4	1124.92932	89.8599

Totals : 5.46353e4 1253.84610

2-[Hydroxy-(biphenyl)-methyl]-cyclohexanone

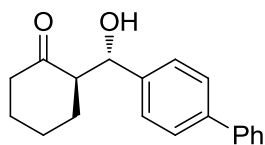
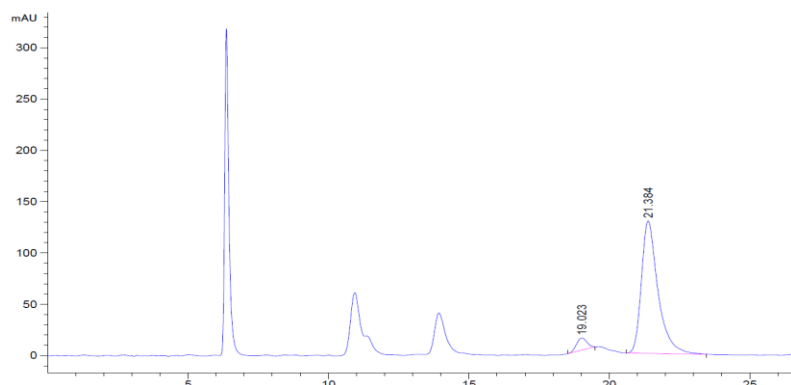


Table 2, Entry 13, Catalyst 4

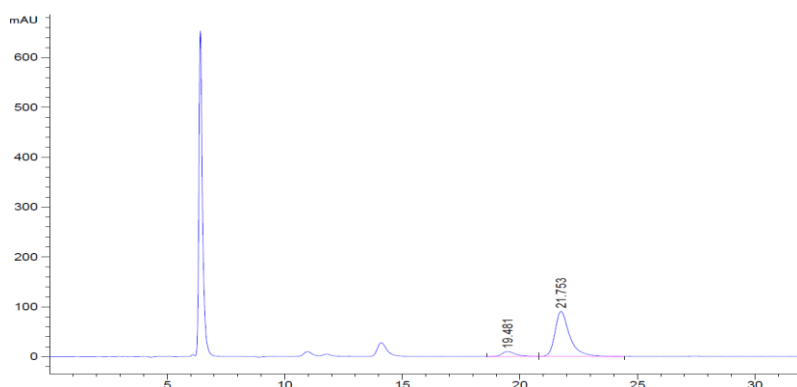


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.023	BB	0.4058	305.20236	11.87754	5.4608
2	21.384	BB	0.6096	5283.76855	129.06317	94.5392

Totals : 5588.97092 140.94071

Table 2, Entry 13, Catalyst 5

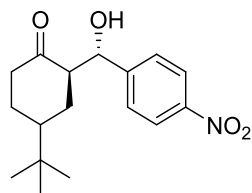


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

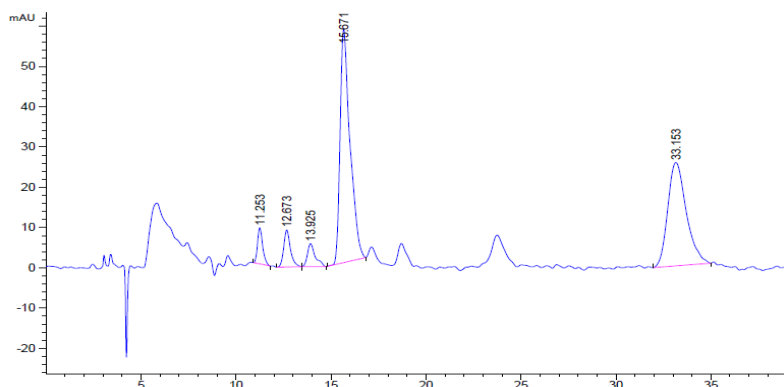
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.481	BB	0.6091	413.47549	10.02655	9.5607
2	21.753	BB	0.6450	3911.26953	90.35899	90.4393

Totals : 4324.74503 100.38555

2-[Hydroxy-(3-benzyloxy-phenyl)]-4-tert-butyl-cyclohexanone



Racemate

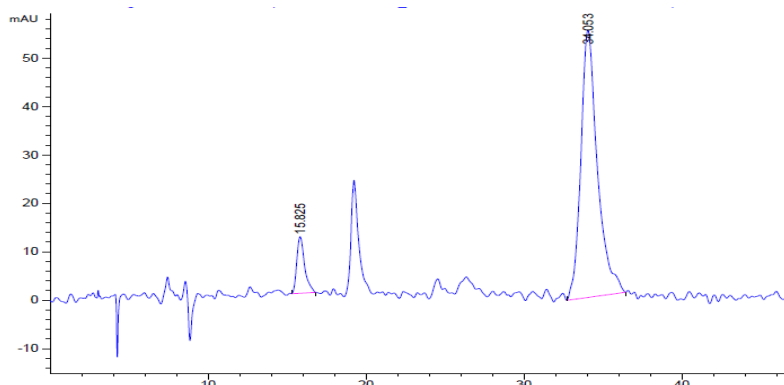


Signal 1: DAD1 F, Sig=273,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.253	BB	0.2874	168.63976	8.96678	3.8248
2	12.673	BB	0.3644	225.69682	9.19358	5.1189
3	13.925	BB	0.4192	162.36644	5.68507	3.6826
4	15.671	BB	0.5253	2106.50537	58.05650	47.7767
5	33.153	BB	1.0182	1745.85144	25.64532	39.5969

Totals : 4409.05983 107.54725

Table 5, Entry 4, Catalyst 1

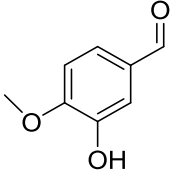
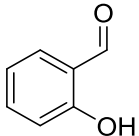
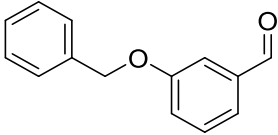
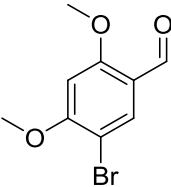
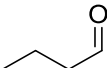


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.825	BB	0.5270	403.42197	11.67810	9.0940
2	34.053	BB	1.0658	4032.69409	55.23366	90.9060

Totals : 4436.11606 66.91176

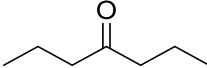
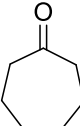
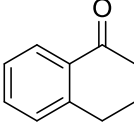
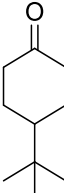
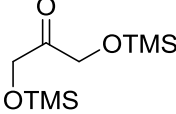
Table 4: Evaluation of diprolinamides 1-5 - Alternate aldehydes

Entry	Aldehyde	Conv (%) ^a	dr <i>syn/anti</i> ^a	ee ^b
1		nr	-	-
2		14	47/53	N.D.
3		trace	-	-
4		nr	-	-
5		nr	-	-

[a] Determined by integration of key signals in the ¹H NMR spectrum.

[b] Determined by Chiral HPLC, Chiralpak AD-H, 1mL/min, IPA/Hexane, 1:9.

Table 5: Evaluation of diprolinamides 1-5 - Alternate ketones

Entry	Ketone	Conv (%) ^a	dr <i>syn/anti</i> ^a	ee ^b
1		<1%	-	-
2		7%	41	N.D.
3		<1%	-	-
4 ⁵		34%	85	82
5				

[a] Determined by integration of key signals in the ¹H NMR spectrum.

[b] Determined by Chiral HPLC, Chiralpak AD-H, 1mL/min, IPA/Hexane, 1:9.

References

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- 2 Delaney JP, Henderson LC. Investigating Ionic Effects Applied to Water Based Organocatalysed Aldol Reactions. *International Journal of Molecular Sciences* 2011; 12: 9083-9094.
- 3 Delaney JP, Henderson LC. Direct Asymmetric Aldol Reactions in Water Catalysed by a Highly Active C2-Symmetrical Bisprolinamide Organocatalyst. *Advanced Synthesis & Catalysis* 2012; 354: 197-204.
4. (a) Kanemitsu T, Umehara A, Miyazaki M, Nagata K, Itoh T. *European Journal of Organic Chemistry* 2011; 2011: 993-997. (b) Li S, Wu C, Long X, Fu X, Chen G, Liu Z. Simple proline derivatives as recoverable catalysts for the large-scale stoichiometric aldol reactions. *Catalysis Science & Technology* 2012; 2: 1068-1071. (c) Hayashi K, Kogiso H, Sano S, Nagao Y. Variable Stereoselectivity in the Imine Aldol Reactions Employing MgBr₂ and Et₃N. *Synlett* 1996; 1996: 1203-1205; (d) Gruttadauria M, Bivona LA, Lo Meo P, Riela S, Noto R. *European Journal of Organic Chemistry* 2012; 2012: 2635-2642.
- 5 Clegg W, Harrington RW, North M, Pizzato F, Villuendas P. Cyclic carbonates as sustainable solvents for proline-catalysed aldol reactions. *Tetrahedron: Asymmetry* 2010; 21: 1262-1271.

