Asymmetric Allylboration of Acyl Imines Catalyzed by Chiral Diols

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Supporting Information

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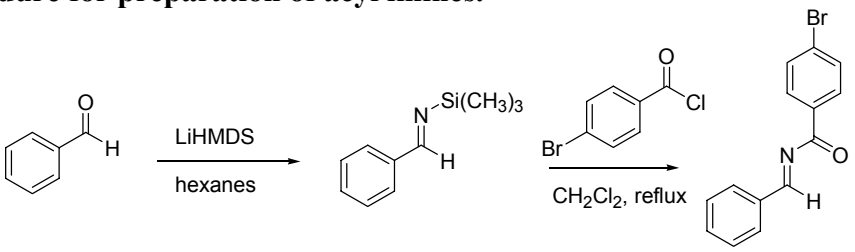
General Information. All ^{1}H NMR, and ^{13}C NMR spectra were recorded using Varian Unity Plus 400 (93.94 kG, ^{1}H 400 MHz) or Varian Gemini 300 (70.5 kG, ^{13}C 75 MHz) spectrometers at ambient temperature in $CDCl_3$. Chemical shifts are reported in parts per million as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant, and integration. Infrared spectra were recorded on a Nicolet Nexus 670 FT-IR ESP spectrophotometer. Optical rotations were recorded on an AUTOPOL III digital polarimeter at 589 nm, and were reported as $[\alpha]_D$ (concentration in grams/100 mL solvent). Analytical thin layer chromatography was performed using EMD 0.25 mm silica gel 60-F plates. Flash column chromatography was performed on Sorbent Technologies 60 Å silica gel. Chiral HPLC analysis was performed using an Agilent 1100 series HPLC with a diode array detector. Chiral columns include Chiralcel®OD (Chiral Technologies Inc., 24cm×4.6mm I.D.), Chiralpak®AD-H (Chiral Technologies Inc., 25cm × 4.6 mm I.D.) and (*R,R*)-Whelk-O 1 (Regis® Technologies Inc., 25cm× 4.6mm I.D.) columns. High-resolution mass spectra were obtained in the Boston University Chemical Instrumentation Center using a Waters Q-TOF mass spectrometer. Low-resolution mass were performed on a MicroMass ZQ 2000 mass spectrometer. Melting points were recorded using a Thomas Hoover capillary melting point apparatus. All reactions were performed under argon, in oven dried glassware with magnetic stirring. (*S*)-BINOL **7e** and (*S*)-3,3'-Br_2-BINOL **7f**, and (*S*)-3,3'-Br_2-H_8-BINOL **7g** were purchased from STREM and used without further purification. (*S*)-3,3'-Ph_2-BINOL **7h** was prepared according to literature procedure.[1] Monomethyl ether **7i** was prepared via reaction of **7h** with CH_3I in the presence of NaH in DMF at room temperature. Kinetic parameters for the asymmetric allylboration reaction were determined by *in situ* monitoring of the formation of homoallylic amide **6a** at 1428.23 cm^{-1} using a ReactIR 4000 system (Mettler Toledo-AutoChem). The ReactIR 4000 system, running software version 3.1, was fitted with a FiberConduit and a 6 mm DiComp Probe. IR spectra, comprised of 64 scans per spectrum, were collected every one minute at a resolution of 8 cm^{-1}. Allyldiisopropoxyborane was prepared according our previous reported procedure.[2]

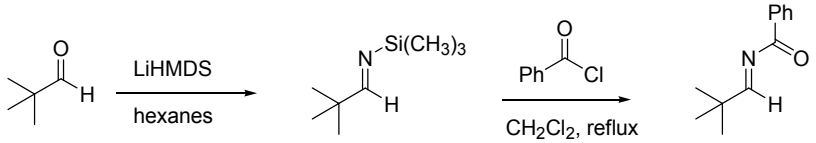
General procedure for preparation of acyl imines.[3]



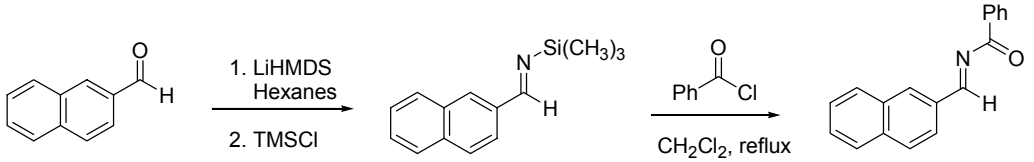
Method A: To a 100 mL flame-dried round bottom flask equipped with stir bar was added 1,1,1,3,3,3-hexamethyldisilazane (16 mL, 75.8 mmol) under Ar and cooled to 0 ˚C. *n*-BuLi (1.6 M in hexanes, 45.2 mL, 72.3 mmol) was added slowly using an air-tight syringe, and the reaction was warmed to room temperature for 15 minutes. The solution was cooled to 0 ˚C and benzaldehyde (7.0 mL, 68.8 mmol) was slowly added. The reaction was warmed to room temperature and stirred for 30 minutes. The hexane was rotavaped and the resulting slurry was

(1) (a) Wipf, P.; Jung, J-K. *J. Org. Chem.* **2000**, *20*, 6319. (b) McDougal, N. T.; Trevellini, W. L.; Rodgen, S. A.; Kliman, L. T.; Schaus, S. E. *Adv. Synth. Catal.* **2004**, *346*, 1231.
(2) Lou, S.; Moquist P. N. ; Schaus S. E. *J. Am. Chem. Soc.* **2006**, *128*, 12660.
(3) (a) Hart, D. J.; Kanai, K-I.; Thomas, D. G.; Y, T-K. *J. Org. Chem*. **1983**, *48*, 289. (b) Vidal, J.; Damaestoy, S.; Guy, L.; Hannachi, J-C.; Aubry, A.; Collet, A. *Chem. Eur. J.* **1997**, *3*, 1691.

distilled *in vacuo* to give silyl imine (bp 55 ˚C, 0.2 mm Hg) as a pale yellow liquid (10.3 g, 84.5% yield). A portion of the silyl imine distillate (4.27 g, 24.1 mmol) was dissolved in CH_2Cl_2 (30 mL) and cooled to 0 ˚C. To the solution 4-bromobenzoyl chloride (5.02 g, 23.0 mmol) was added and the reaction mixture was refluxed for 3 hours. Upon cooling the solvent and TMSCl were removed under reduced pressure to afford the acyl imine as yellow solid (6.5 g, 99% yield). ^{1}H NMR spectra was in agreement with reported data.[4] Imines **8a-8i**, **10a-10l** were prepared using similar procedure.

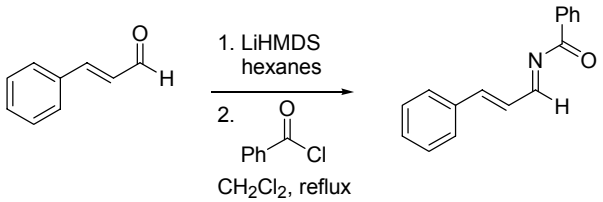


To a 100 mL flame-dried round bottom flask equipped with stir bar was added 1,1,1,3,3,3-hexamethyldisilazane (5.34 mL, 25.3 mmol) under Ar and cooled to 0 ˚C. *n*-BuLi (1.6 M in hexane, 15.1 mL, 24.1 mmol) was added slowly using an air-tight syringe, and the reaction was warmed to room temperature for 15 minutes. The solution was cooled to 0 ˚C and pivaldehyde (2.5 mL, 23.0 mmol) was slowly added. The reaction was warmed to room temperature and stirred for 30 minutes. The hexane was rotovaped and the resulting slurry was distilled *in vacuo* to give silyl imine (bp 65 ˚C, 30 Torr) as clear liquid. The resulting silyl imine (2.82g, 78% yield) was dissolved CH_2Cl_2 (30 mL) and cooled to 0 ˚C. To the solution benzoyl chloride (1.97mL, 17.0 mmol) was added and the reaction was refluxed for 3 hours. Upon cooling the solvent and TMSCl were removed under reduced pressure to afford the acyl imine as clear oil (3.2 g, 99% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 8.0 Hz, 2H), 7.92 (s, 1H), 7.50 (t, *J* = 7.2 Hz, 1H), 7.38 (t, *J* = 8.0 Hz, 2H), 1.15 (s, 9H). **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ 181.2, 175.7, 135.6, 133.5, 130.1, 128.7, 26.4.

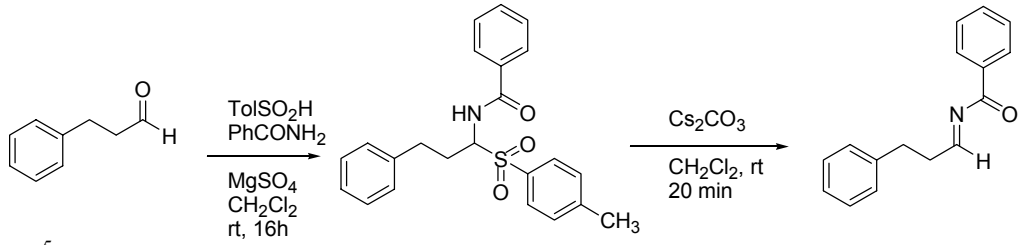


Method B: To a 100 mL flame-dried round bottom flask equipped with stir bar was added 1,1,1,3,3,3-hexamethyldisilazane (4.46 mL, 21.1 mmol) under Ar and cooled to 0 ˚C. *n*-BuLi (1.6 M in hexane, 12.6 mL, 20.2 mmol) was added slowly using an air-tight syringe, and the reaction was warmed to room temperature for 15 minutes. The solution was cooled to 0 ˚C and 2-naphthaldehyde (3.0 g, 19.2 mmol) was slowly added. The reaction was stirred at room temperature for 30 minutes then cooled to 0 ˚C. TMSCl (2.44 mL, 19.2 mmol) was added slowly and the resulting reaction mixture was stirred at room temperature for 2 hours. The precipitate was filtered through a celite bed. The filtrate was concentrated *in vacuo* and diluted with CH_2Cl_2 (30 mL). Benzoyl chloride (2.1 mL, 18.2 mmol) was added and the reaction mixture was refluxed overnight. The solvent and TMSCl were removed under reduced pressure to afford the acyl imine as yellow solid (4.8 g, 96% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.94 (s, 1H), 8.29 (s, 1H), 8.23 (d, *J* = 7.2 Hz, 2H), 8.19 (d, *J* = 8.8 Hz, 1H), 7.95 (t, *J* = 7.8 Hz, 2H), 7.89 (t, *J* = 8.0 Hz, 1H), 7.60 (m, 3H), 7.50 (t, *J* = 8.0 Hz, 2H). **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ 179.6, 163.4, 134.6, 132.6, 132.2, 131.5, 131.0, 128.9, 127.8, 127.6, 127.2, 127.1, 126.6, 125.6, 122.4.

(4) Uraguchi, D.; Sorimachi, K.; Terada, M. *J. Am. Chem. Soc.* **2005**, *127*, 9360.



Method C: To a 100 mL flame-dried round bottom flask equipped with stir bar was added 1,1,1,3,3,3-hexamethyldisilazane (5.53 mL, , 26.2 mmol) under Ar and cooled to 0 ˚C. *n*-BuLi (1.6 M in hexane, 15.6 mL, 25.0 mmol) was added slowly using an air-tight syringe, and the reaction was warmed to room temperature for 15 minutes. The solution was cooled to 0 ˚C and *trans*-cinnamaldehyde (3.0 mL, 23.8 mmol) was added. The reaction was stirred at room temperature for 30 minutes and the hexane was removed *in vacuo*. The resulting slurry was diluted with 30 mL CH_2Cl_2 and benzoyl chloride (2.63mL, 22.6 mmol) was added. The reaction mixture was refluxed for overnight. Upon cooling hexanes (10 mL) was added and the precipitate was filtered through a celite bed. The filtrate was concentrated and the residue was dried under reduced pressure to afford the acyl imine as orange solid (4.5 g, 98% yield). This product was used in the allylboration reaction without further purification. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.48 (d, *J* = 9.2 Hz, 1H), 8.09 (d, *J* = 8.0 Hz, 2H), 7.52-7.31 (m, 4H), 6.98 (dd, *J* = 16, 9.2 Hz, 1H). **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ 180.8, 166.3, 149.9, 134.9, 133.6, 130.8, 130.3, 129.2, 128.6, 128.3, 126.9.

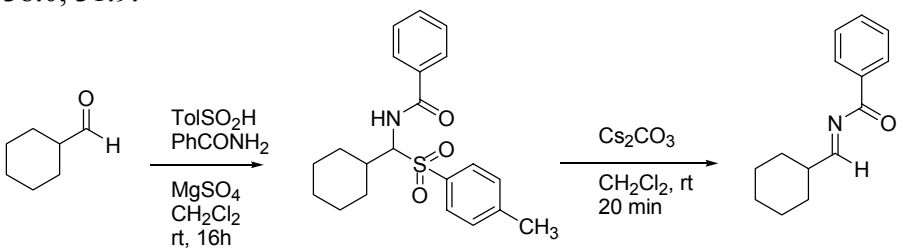


Method D:[5] To a 100 mL round bottom flask equipped with stir bar was added flame dried magnesium sulfate (12 g, 100 mmol), benzamide (1.21 g, 10 mmol), and *p*-toluene sulfinic acid (1.56 g, 10 mmol). CH_2Cl_2 (20 mL) and 3-phenylpropanal (1.31 mL, 10 mmol) were added subsequently and the reaction mixture was stirred at room temperature for 16 h. The solution was diluted with CH_2Cl_2 (20 mL) and filtered through a celite bed. The filtrate was concentrated under reduced pressure to afford the *α*-amido sulfone as white solid (3.9 g , 99% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.71 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 8.0 Hz, 2H), 7.25-7.18 (m, 5H), 7.15 (t, *J* = 6.8 Hz, 2H), 6.95 (d, *J* = 10.0 Hz, 1H), 5.49 (td, *J* = 10.8, 3.2 Hz, 1H), 2.84-2.78 (m, 2H), 2.65 (m, 1H), 2.37 (s, 3H), 2.29(m, 1H).

To a round bottom flask equipped with stir bar was added flame-dried cesium carbonate (1.63 g, 5.0 mmol) and CH_2Cl_2 (20 mL). The solution was vigorously stirred (>800 rpm) and *α*-amido sulfone (393 mg, 1.0 mmol) was added. The reaction mixture was stirred at room temperature for 10 min. The mixture was diluted with hexanes (20 mL), filtered through a celite bed and washed with CH_2Cl_2 (20 mL). The filtrate was concentrated under reduced pressure to afford the acyl imine as yellow oil (230 mg, 96%yield). This acyl imine was used in the allylboration reaction

(5) (a) Song, J.; Wang, Y.; Deng, L. *J. Am. Chem. Soc.* **2006**, *128*, 6048. (b) Trost, B. M.; Jaratjaroonphong, J.; Reutrakul, V. *J. Am. Chem. Soc.* **2006**, *128*, 2778. (c) Mataloni, M.; Petrini, M.; Profeta, R. *Synlett*, **2003**, 1129. (d) Murry, J. A.; Frantz, D. E.; Soheili, A.; Tillyer, R.; Grabowski, E. J. J.; Reider, P. J. *J. Am. Chem. Soc.* **2001**, *123*, 9696-9697.

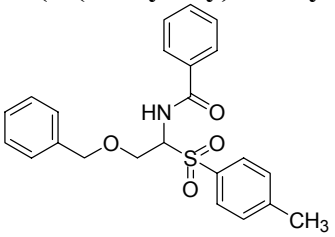
immediately. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.16 (t, *J* = 4.4 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 2H), 7.52 (t, *J* = 8.0 Hz, 1H), 7.39 (t, *J* = 8.4 Hz, 2H), 7.22 (m, 5H), 3.05 (t, *J* = 7.6 Hz, 2H), 2.97 (t, *J* = 7.6 Hz, 2H). **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ 181.0, 168.5, 140.2, 133.6, 130.1, 129.3, 128.8, 128.3, 126.5, 38.0, 31.9.



To a round bottom flask equipped with stir bar was added flame-dried magnesium sulfate (12 g, 100 mmol), benzamide (1.21 g, 10 mmol), and *p*-toluene sulfinic acid (1.56 g, 10 mmol). CH_2Cl_2 (20 mL) and cyclohexanecarboxaldehyde (1.21 mL, 10 mmol) were added subsequently and the reaction mixture was stirred at room temperature for 16 h. The solution was diluted with CH_2Cl_2 (20 mL) and filtered through a celite bed. The filtrate was concentrated under reduced pressure to afford the *α*-amido sulfone as white solid (3.7 g , 99% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.72 (d, J = 8.4 Hz, 2H), 7.61 (d, *J* = 8.0 hz, 2H), 7.53 (t, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 6.59 (d, *J* = 10.4 Hz, 1H), 5.29 (dd, *J* = 10.8, 3.6 Hz, 1H), 2.57 (m, 1H), 2.36 (s, 3H), 2.20 (d, *J* = 24 Hz, 1H), 1.89 (d, *J* = 24 Hz, 1H), 1.79 (t, *J* = 24 Hz, 2H), 1.68 (d, *J* = 24 Hz, 1H), 1.38 (m, 2H), 1.18 (m, 2H).

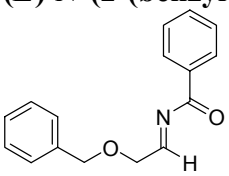
To a round bottom flask equipped with stir bar was added flame-dried cesium carbonate (1.63 g, 5.0 mmol) and CH_2Cl_2 (20 mL). The solution was vigorously stirred (>800 rpm) and *α*-amido sulfone (371 mg, 1.0 mmol) was added. The reaction mixture was stirred at room temperature for 20 min. The solution was diluted with hexanes (20 mL) and filtered through a celite bed and washed with CH_2Cl_2 (20 mL). The filtrate was concentrated under reduced pressure to afford the desired acyl imine as a white solid (210 mg, 95%yield). This imine was used in the allylboration reaction immediately. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 4 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 2H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.42 (t, *J* = 8.0 Hz, 2H), 2.36 (m, 1H), 1.96 (m, 2H), 1.79 (m, 2H), 1.69 (m, 1H), 1.35 (m, 4H), 1.25 (m, 1H). **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ 180.8, 172.6, 133.2, 129.7, 128.3, 44.2, 28.7, 25.8, 25.2.

***N*-(2-(benzyloxy)-1-tosylethyl)benzamide**



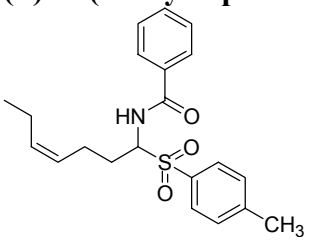
Following method D, this compound was prepared as white solid (1.35 g, 5.0 mmol, 99% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.51 (t, *J* = 8.0 Hz, 1H), 7.39 (t, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.20 (m, 5H), 7.18 (d, *J* = 10.0 Hz, 1H), 5.64 (m, 1H), 4.62 (d, *J* = 11.6 Hz, 1H), 4.56 (d, *J* = 11.6 Hz, 1H), 4.28 (dd, *J* = 10.8, 4.0 Hz, 1H), 3.96 (dd, *J* = 10.8, 4.0 Hz, 1H), 2.37 (s, 3H); **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ 166.7, 145.5, 137.3, 134.7, 133.1, 132.5, 130.1, 129.3, 128.9, 128.7, 128.2, 128.1, 127.4, 73.9, 68.8, 65.9, 21.9.

(*E*)-*N*-(2-(benzyloxy)ethylidene)benzamide (9p)



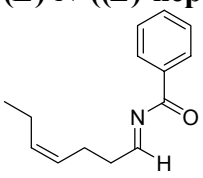
To a round bottom flask equipped with stir bar was added flame-dried cesium carbonate (163 mg, 0.5 mmol) and CH_2Cl_2 (4.0 mL). The mixture was vigorously stirred (>800 rpm) and *α*-amido sulfone (104 mg, 0.25 mmol) was added. The reaction mixture was stirred at room temperature for 30 min. The solution was diluted with hexanes (4.0 mL) and filtered through a celite bed and washed with CH_2Cl_2 (4.0 mL). Toluene (2.5 mL) was added to the filtrate and the solvent was concentrated under reduced pressure to afford the desired imine in a toluene solution which was used in the allylation reaction immediately. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.04 (t, *J* = 2.8 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.47 (t, *J* = 8.0 Hz, 1H), 7.37 (t, *J* = 8.0 Hz, 2H), 7.21 (m, 5H), 4.69 (d, *J* = 1.2 Hz, 1H), 4.67 (d, *J* = 1.2 Hz, 1H), 4.37 (d, *J* = 1.2 Hz, 1H), 4.35 (d, *J* = 1.2 Hz, 1H).

(*Z*)-*N*-(1-tosylhept-4-enyl)benzamide



Following method D, this compound was prepared as white solid (1.35 g, 5.0 mmol, 99% yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.34 (t, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 10.4 Hz, 1H), 5.45 (m, 2H), 5.34 (m, 1H), 2.35 (s, 3H), 2.22-2.07 (m, 4H), 1.92 (m, 2H), 0.89 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ 166.9, 145.3, 134.5, 134.0, 133.2, 132.3, 130.0, 129.3, 128.8, 127.4, 126.5, 69.4, 28.6, 26.7, 25.7, 21.9, 13.9.

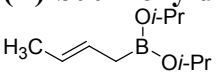
(*E*)-*N*-((*Z*)-hept-4-enylidene)benzamide (9p)



To a round bottom flask equipped with stir bar was added flame-dried cesium carbonate (163 mg, 0.5 mmol) and CH_2Cl_2 (4 mL). The solution was vigorously stirred (>800 rpm) and *α*-amido sulfone (96 mg, 0.25 mmol) was added. The reaction mixture was stirred at room temperature for 30 min. The solution was diluted with hexanes (4 mL) and filtered through a celite bed and washed with CH_2Cl_2 (4 mL). The filtrate was concentrated under reduced pressure at 20 ºC to afford the desired imine as clear oil (51 mg, 96%yield). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.04 (t, *J* = 4.4 Hz, 1H), 7.93 (d, *J* = 8.0 Hz, 2H), 7.47 (t, *J* = 8.0 Hz, 1H), 7.37 (t, *J* = 8.0 Hz, 2H), 5.47 (m, 1H), 5.39 (m, 1H), 2.47 (m, 1H), 2.34 (m, 2H), 1.94 (m, 2H), 0.88 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ 181.0, 169.4, 1333.9, 133.6, 130.1, 128.6, 127.1, 36.5, 28.1, 25.7, 13.9.

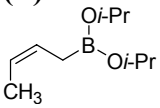
Preparation of crotyldiisopropoxyboranes[6]

(*E*)-but-2-enyldiisopropoxyborane (18a)



To a 250 mL flame-dried three-neck round bottom flask equipped with stir bar and thermometer was added *t*-BuOK (4.65 g, 41.5 mmol) and THF (40 mL) under Ar and cooled to −78 ºC. *trans*-2-Butene (2.50g, 44 mmol), condensed into a flame-dried rubber-stoppered flask at −78 ºC, was added to the mixture via cannula. *n*-BuLi (1.6 M in hexane, 26 mL, 41.5 mmol) was added drop wise over 1 hour using an addition funnel ensuring internal temperature did not rise. Upon completion, the reaction was warmed to an internal temperature of −52 ºC. The reaction was maintained at −52 ºC for 15 minutes, and cooled back to −78 ºC. Triisopropylborate (10.5 mL, 45.6 mmol) was then added drop wise over 0.5 hours by an addition funnel. The reaction mixture was maintained at −78 ºC for 2 hours and followed by a slow addition of HCl (2.0 M in Et_2O, 41.5 mL, 83 mmol,). The solution was stirred for 0.5 hours and warmed to room temperature. Reaction was concentrated under reduced pressure to 25 mL and filtered. The filtrate was concentrated *in vacuo* and filtered again. The remaining oily product was dissolved in toluene and stored as 1.0 M solution at 0 ºC. This solution was used in the crotylboration reaction without any further purification. The analytical sample was obtained by distillation under reduce pressure (90 ºC, 0.1 Torr) and the pure sample was sensitive to moisture. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.43(m, 1H), 5.30 (m, 1H), 4.42-4.27 (m, 2H), 1.61 (br d, *J* = 6.0 Hz, 2H), 1.56 (br d, *J* = 6.0 Hz, 3H), 1.10 (d, *J* = 6.0 Hz, 12H); **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ 129.0, 128.2, 69.1, 24.6, 24.5, 18.1.

(*Z*)-but-2-enyldiisopropoxyborane (18b)

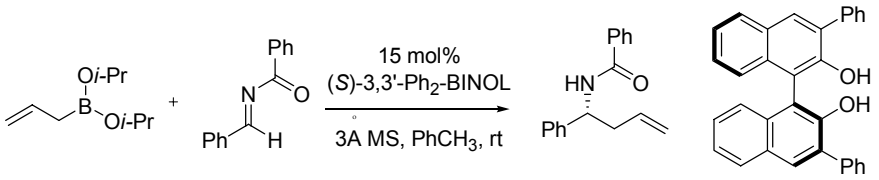


To a 250 mL flame-dried three-neck round bottom flask equipped with stir bar and thermometer was add *t*-BuOK (4.65 g, 41.5 mmol) and THF (40 mL) under Ar and cooled to −78 ºC. *cis*-2-Butene (2.50 g, 44 mmol), condensed into a flame-dried rubber-stoppered flask at −78 ºC, was added to the mixture via cannula. *n*-BuLi (1.6 M in hexane, 26 mL, 41.5 mmol) was added drop wise over 0.5 hours by an addition funnel ensuring internal temperature did not rise. Upon completion, the reaction was warmed to an internal temperature of −25 ºC. The solution was maintained at −25 ºC for 30 minutes, and cooled to -78 ºC. Triisopropylborate (10.5 mL, 45.6 mmol) was then added drop wise over 0.5 hours by an addition funnel. The reaction mixture was maintained at −78 ºC for 2 hours and followed by a slow addition of HCl (2.0 M in Et_2O, 41.5 mL, 83 mmol, 2.0 M solution). The solution was stirred for 0.5 hours and warmed to room temperature. Reaction was concentrated under reduced pressure to 25 mL and filtered. The filtrate was concentrated *in vacuo* and filtered again. The remaining oily product was dissolved in toluene and stored as 1.0 M solution at 0 ºC. This solution was used in the crotylboration reaction without any further purification. The analytical sample was obtained by distillation under reduce pressure (90 ºC, 0.1 Torr) and the pure sample was sensitive to moisture. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.52 (m, 2H), 4.47 (m, 1H), 4.36 (m, 1H), 1.64 (br d, *J* = 7.2 Hz, 2H), 1.58

(6) Roush, W. R.; Ando, K.; Powers, D. B.; Palkowitz, A. D.; Halterman, R. L. *J. Am. Chem. Soc.* **1990**, *112*, 6339

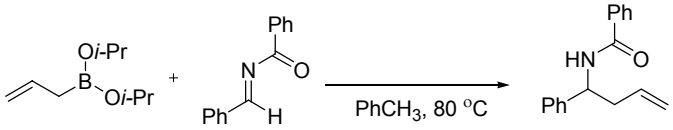
(br d, J = 6.0 Hz, 3H), 1.18 (d, J = 6.0 Hz, 12H); **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ 126.9, 124.8, 68.1, 24.8, 12.7.

General procedure for asymmetric allylboration of acyl imines.



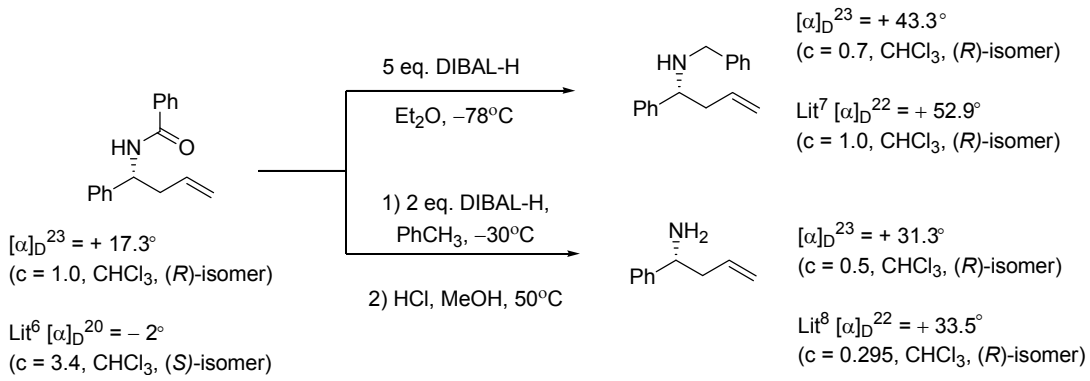
A 50 mL oven-dried round bottom flask was charged with stir bar and flushed with Ar. To the flask was added *N*-benzylidenebenzamide **5** (104 mg, 0.5 mmol), 3Å molecular sieves (500 mg), and (*S*)-3,3'-Ph2-BINOL **7h** (33 mg, 0.05 mol). The flask was fitted with a septum and placed under an atmosphere of Ar. To the flask was added toluene (3.0 mL) and the mixture was stirred at room temperature. Allyldiisopropoxyborane **4** (500 μL, 0.50 mmol, 1.0 M in toluene) was added drop wise and the reaction mixture was stirred at room temperature for 24 hours. The reaction was diluted with ether (10 mL) and water (10 mL). The biphasic mixture was stirred at room temperature for 10 minutes. The organic layer was separated and dried over Na_2SO_4. The organic layer was isolated by filtration and the filtrate was concentrated *in vacuo* at 20 ˚C. The residue was purified by flash chromatography over silica gel (elution with 95:5 – 9:1, hexanes:EtOAc) to afford the homoallylic amide as a white solid (109 mg, 85% yield). The enantiomeric ratio of the product was determined to be 99:1 by chiral HPLC analysis. t_R minor: 5.9 min, t_R major: 9.1 min, [Chiralcel®OD column, 24cm × 4.6 mm I.D., hexanes:IPA 90:10, 1.5 mL/min].

General procedure for preparation of racemic allylboration products.



A 15 × 100 mm oven-dried glass vessel was charged with stir bar and flushed with Ar. To the flask was added *N*-benzylidenebenzamide **5** (26.2 mg, 0.125 mmol) and toluene (0.5 mL). The mixture was stirred under Ar at room temperature and allyldiisopropoxyborane **4** (1.0 M in toluene,125 μL, 0.125 mmol) was added. The reaction mixture was heated to 80 ˚C and stirred for 12 hours. The reaction was diluted with ether (3.0 mL) and water (3.0 mL). The biphasic mixture was stirred at room temperature for 10 minutes. The organic layer was separated and dried over Na_2SO_4. After filtration, the filtrate was concentrated and the residue was purified by flash chromatography over silica gel (elution with 95:5 – 9:1, hexanes:EtOAc) to afford the homoallylic amide as a white solid.

Absolute stereochemical determination of allylboration products.



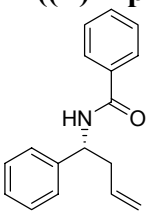
Direct stereochemical determination was assigned to *N*-((*R*)-1-phenylbut-3-enyl)benzamide **9a** by comparison of optical rotation to the known compound $[\alpha]_D^{23} = +17.3^\circ$ (c = 1.0, $CHCl_3$) Lit:[7] $[\alpha]_D^{20} = -2.0^\circ$ (c = 3.4, $CHCl_3$, (*S*)-isomer). In addition, **9a** was reduced by DIBAL-H to the known benzyl-(1-phenyl-but-3-enyl)-amine and optical rotation was in agreement with the (*R*)-isomer $[\alpha]_D^{23} = +43.3^\circ$ (c = 0.7, $CHCl_3$) Lit: $[\alpha]_D^{22} = +52.9^\circ$ (c = 1.0, $CHCl_3$, 93% ee).[8] Furthermore, reduction of amide followed by hydrolysis yielded corresponding homoallylic amine and optical rotation was in agreement literature value. $[\alpha]_D^{23} = +31.3^\circ$ (c = 0.5, $CHCl_3$) Lit: $[\alpha]_D = +33.5^\circ$ (c = 0.295, $CHCl_3$).[9]

Experimental Detail. A 50 mL flame-dried round bottom flask equipped with stir bar and flushed with Ar. *N*-(1-phenylbut-3-enyl)benzamide **9a** (62 mg, 0.25 mmol) was added, dissolved in CH_2Cl_2 (2.0 mL) and cooled to –35 °C. Diisobutylaluminum hydride (5 mL, 0.5 mmol, 0.1 M in toluene) was slowly added in over 10 hours via syringe pump and stirred overnight. The reaction was quenched with MeOH (30 μL) and warmed to room temperature. To the reaction mixture was added NaF (60 mg), KOH(30 mg) and water (30 μL), and the resulting mixture was vigorously stirred for 1 hour. The solution was diluted with chloroform (10 mL) and filtered through a celite bed. The filtrate was dried over anhydrous Na_2SO_3 and concentrated under reduced pressure. The residue was dissolved in MeOH (3.0 mL) and concentrated HCl (0.5 mL) and stirred at 50 °C overnight. The mixture was diluted with chloroform (6.0 mL) and water (6.0 mL) and pH adjusted to 12 with solid KOH. The organic layer was separated and aqueous layer was extracted with chloroform (2 × 10 mL). The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography over silica gel (elution with 98:2 – 9:1 CH_2Cl_2:MeOH) to afford the desired homoallylic amine as a clear oil (31 mg, 82% yield).

(7) Ding, H.; Friestad, G. *Angew Chem. Int. Ed*. **2001,** *40*, 4491.
(8) Fernandes, R.; Yamamoto, Y. *J. Org. Chem*. **2004**, *69*, 735.
(9) Berger, R.; Rabbat, P. M. A.; Leighton, J. L. *J. Am. Chem. Soc.* **2003**, *125*, 9596.

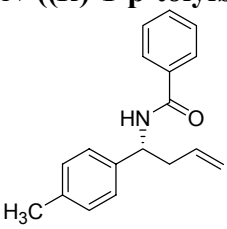
Analytical data for homoallylic acyl amines.

***N*-((*R*)-1-phenylbut-3-enyl)benzamide (9a)**



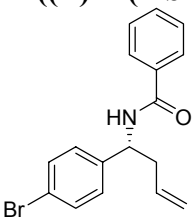
The reaction was run on 0.5 mmol scale and crude mixture was purified by flash column chromatography with elution by 95:5 – 9:1, hexanes:EtOAc. **Yield:** 112 mg**,** 85%; **er:** 99:1; $[\alpha]_D^{23}$ = +17.3° (c = 1.0, $CHCl_3$) Lit: $[\alpha]_D^{20}$ = –2.0° (c = 3.4, $CHCl_3$, (S)-isomer); **mp:** 122-123 °C; **HPLC Analysis**, t_r minor: 5.94 min., t_r major: 9.06 min., [Chiralcel®OD column, 24cm × 4.6 mm I.D., Hexanes:IPA = 90:10, 1.5 mL/min]; All spectra was in agreement with reported data.[7]

***N*-((*R*)-1-p-tolylbut-3-enyl)benzamide (9b)**



The crude mixture was purified by flash column chromatography with elution by 95:5 – 9:1, hexanes:EtOAc. **Yield:** 106 mg**,** 80%; **er:** 98:2; $[\alpha]_D^{23}$ = +14.9° (c = 1.0, $CHCl_3$); **mp:** 121-125 °C; **HPLC Analysis**, t_r minor: 6.49 min., t_r major: 9.91 min., [Chiralcel®OD column, 24cm × 4.6 mm I.D., Hexanes:IPA = 90:10, 1.5 mL/min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.48 (m, 3H) , 7.39 (m, 4H), 6.46 (b, 1H), 5.76 (m, 1H), 5.28 (dd, *J* = 10.5, 6.8 Hz,1H), 5.15 (m, 2H) 2.69 (t, *J* = 6.8 Hz, 2H) 2.41 (s, 3H) **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ 168.1, 134.3, 131.8, 128.9, 128.8, 127.7, 127.2, 126.6, 118.8, 52.9, 40.87, 23.4 **IR** (thin film, cm^{-1}): 3320, 3062, 3027, 2926, 2847, 1643, 1507, 1451, 1358, 1258, 1148 **HRMS**: calc'd for $(M)^+$ $C_{18}H_{19}NO$: 266.1500; found: 266.1489.

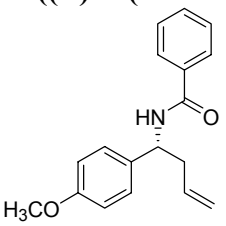
***N*-((*R*)-1-(4-bromophenyl)but-3-enyl)benzamide (9c)**



The crude mixture was purified by flash column chromatography with elution by 95:5 – 85:15, hexanes:EtOAc. **Yield:** 141 mg**,** 86%; **er:** 97.5:2.5; $[\alpha]_D^{23}$ = +12.5° (c = 1.0, $CHCl_3$); **mp:** 125-128 °C; **HPLC Analysis**, t_r major: 6.7 min., t_r minor: 9.1 min., [Chiralcel®OD column, 24cm × 4.6 mm I.D., Hexanes:IPA = 90:10, 1.5 mL/min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.53 – 7.41 (m, 5H), 7.22 (d, *J* = 8.4 Hz, 2H), 6.43 (d, *J* = 7.2 Hz, 1H), 5.75 (m, 1H), 5.25 – 5.15 (m, 3H), 2.65 (t, *J* = 6.8 Hz, 2H); **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ 166.9, 141.0, 134.5, 133.8, 132.0, 131.9, 128.9, 128.4, 127.1, 121.4, 119.1, 52.5, 40.7; **IR** (thin film, cm^{-1}):

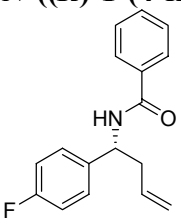
3311, 3065, 2924, 1634, 1527, 1296, 1066, 1007, 920, 817, 696; **HRMS**: calc'd for $(M+1)^+$ $C_{17}H_{17}BrNO$: 330.0494; found: 330.0492.

***N*-((*R*)-1-(4-methoxyphenyl)but-3-enyl)benzamide (9d)**



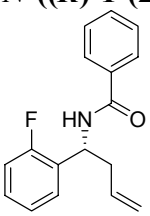
The crude mixture was purified by flash column chromatography with elution by 98:2 – 95:5, hexanes:EtOAc. **Yield:** 120 mg, 85%; **er:** 95:5; $[\alpha]_D^{23}$ = +17.7° (c = 1.0, $CHCl_3$); **mp:** 122-124 °C; **HPLC Analysis,** t_r major: 7.8 min., t_r minor: 9.4 min., [Chiralcel®OD column, 24cm × 4.6 mm I.D., Hexanes:IPA = 90:10 1.5mL/min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.77 (d, J = 8.0 Hz, 1H), 7.49 (m, 1H), 7.42 (m, 2H), 7.28 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.37 (d, *J* = 6.8 Hz, 1H), 5.77 (m, 1H), 5.25 (dd, *J* = 10.4, 6.8 Hz, 1H), 5.13 (m, 2H), 3.80 (s, 3H), 2.68 (m, 2H); **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ 166.4, 155.3, 134.4, 131.7, 128.8, 127.8, 127.1, 118.5, 114.3, 55.5, 52.5, 40.7; **IR** (thin film, cm^{-1}): 3310, 3063, 2948, 2842, 1645, 1521, 1253, 1177, 1032, 925, 824, 706; **HRMS**: calc'd for $(M+1)^+$ $C_{18}H_{20}NO_2$: 282.1494; found: 282.1497.

***N*-((*R*)-1-(4-fluorophenyl)but-3-enyl)benzamide (9e)**



The crude mixture was purified by flash column chromatography with elution by 98:2 – 95:5, hexanes:EtOAc. **Yield:** 124 mg, 92%. **er:** 98:2; $[\alpha]_D^{23}$ = +16.9° (c = 1.0, $CHCl_3$); **mp:** 92-95 °C; **HPLC Analysis,** t_r major: 5.7 min., t_r minor: 7.3 min., [Chiralcel®OD column, 24cm × 4.6 mm I.D., Hexanes:IPA = 90:10 1.5mL/min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.76 (d, *J* = 8.0 Hz, 2H), 7.53 (m, 1H), 7.44 (t, *J* = 8.0 Hz, 2H), 7.32 (m, 2H), 7.04 (t, *J* = 8.4 Hz, 2H), 6.40 (d, *J* = 6.8 Hz, 1H), 5.76 (m, 1H), 5.26 (dd, *J* = 14.4, 6.8 Hz, 1H), 5.22-5.14 (m, 2H), 2.67 (t, *J* = 6.8 Hz, 1H); **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ 163.1, 157.2, 143.1, 133.9, 131.8, 128.8, 128.3, 128.2, 127.1, 119.0, 115.8, 115.6, 52.3, 40.9; **IR** (thin film, cm^{-1}): 3308, 3068, 2925, 1642, 1518, 1226, 1058, 919, 830, 697; **HRMS**: calc'd for $(M+1)^+$ $C_{17}H_{16}FNO$: 270.1294; found: 270.1277.

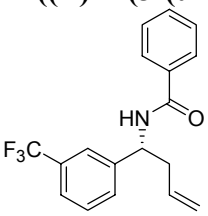
***N*-((*R*)-1-(2-fluorophenyl)but-3-enyl)benzamide (9f)**



The crude mixture was purified by flash column chromatography with elution by 98:2 – 95:5, hexanes:EtOAc. **Yield:** 117 mg, 87% **er:** 95.5:4.5; $[\alpha]_D^{23}$ = +15.8° (c = 1.0, $CHCl_3$); **mp:** 157-161 °C; **HPLC Analysis,** t_r major: 4.7 min., t_r minor: 6.3 min., [Chiralcel®OD column,

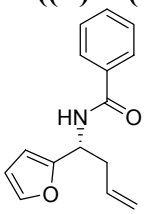
24cm × 4.6 mm I.D., Hexanes:IPA = 90:10 1.5mL/min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.80 (d, *J* = 8.0 Hz, 1H), 7.58 (m, 1H), 7.50 (m, 2H), 7.31 (m, 1H), 7.17 (m, 1H), 7.10 (m, 1H), 6.88 (d, *J* = 6.8 Hz, 1H), 5.75 (m, 1H), 5.13 (m, 2H), 2.70 (dd, *J* = 13.2, 6.8 Hz, 2H); **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ 166.9, 159.3, 134.1, 132.1, 130.3, 129.3, 129.2, 128.8, 127.3, 127.1, 124.5, 118.7, 116.2, 116.0, 50.0, 40.1; **IR** (thin film, cm^{-1}): 3443, 3282, 3058, 1658, 1511, 1286, 1222, 1039, 750; **HRMS**: calc'd for $(M+1)^+$ $C_{17}H_{17}FNO$: 270.1294; found: 270.1259.

***N*-((*R*)-1-(3-(trifluoromethyl)phenyl)but-3-enyl)benzamide (9g)**



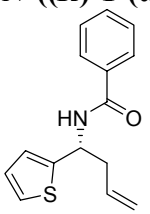
The crude mixture was purified by flash column chromatography with elution by 95:5 – 9:1, hexanes:EtOAc. **Yield:** 143 mg**,** 90%; **er:** 97.5:2.5; **$[\alpha]_D^{23}$** = +19.0° (c = 1.0, $CHCl_3$); **mp:** 64-67 °C; **HPLC Analysis**, t_r major: 4.8 min., t_r minor: 7.3 min., [Chiralcel®OD column, 24cm × 4.6 mm I.D., Hexanes:IPA = 90:10, 1.5 mL/min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.59 (s, 1H), 7.53 (m, 3H), 7.45 (m, 3H), 6.49 (d, *J* = 6.0 Hz, 1H), 5.76 (m, 1H), 5.32 (dd, *J* = 13.2, 6.0 Hz, 1H), 5.25-5.18 (m, 2H), 2.68 (m, 1H); **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ 166.7, 142.8, 134.1, 133.3, 131.8, 129.9, 129.1, 128.7, 126.9, 124.3, 122.9, 119.2, 52.4, 40.6; **IR** (thin film, cm^{-1}): 3301, 3068, 2932, 1643, 1531, 1323, 1166, 919, 802, 701; **HRMS**: calc'd for $(M+1)^+$ $C_{18}H_{17}F_3NO$: 320.1262; found: 320.1254.

***N*-((*R*)-1-(furan-2-yl)but-3-enyl)benzamide (9h)**



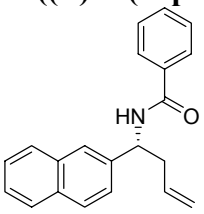
The reaction was run in 0.125 mmol scale and the crude mixture was purified by flash column chromatography with elution by 98:2 – 95:5, hexanes:EtOAc. **Yield:** 25 mg, 83%; **er:** 96:4; **$[\alpha]_D^{23}$** = +75.0° (c = 0.5, $CHCl_3$); **HPLC Analysis,** t_r major: 4.8 min., t_r minor: 5.5 min., [Chiralcel®OD column, 24cm × 4.6 mm I.D., Hexanes:IPA = 90:10 1.5mL/min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.51 (m, 1H), 7.44 (m, 2H), 7.38 (s, 1H), 6.40 (d, *J* = 7.2 Hz, 1H), 6.33 (s, 1H), 6.25 (s, 1H), 5.78 (m, 1H), 5.42 (dd, *J* = 14.4, 7.2 Hz, 1H), 5.18-5.11 (m, 2H), 2.72 (m, 2H); **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ 167.1, 151.1, 142.2, 133.7, 131.8, 129.2, 127.2, 118.8, 110.5, 106.8, 47.2, 38.6; **IR** (thin film, cm^{-1}): 3306, 3072, 2928, 1643, 1531, 1291, 1143, 1004, 921, 703; **HRMS**: calc'd for $(M)^+$ $C_{15}H_{15}NO_2$: 241.1103; found: 241.1035.

***N*-((*R*)-1-(thiophen-2-yl)but-3-enyl)benzamide (9i)**



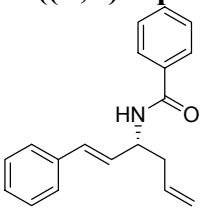
The crude mixture was purified by flash column chromatography with elution by 98:2 – 95:5, hexanes:EtOAc. **Yield:** 105 mg, 82%; **er:** 95:5; $[\alpha]_D^{23}$ = +51.8° (c = 0.5, $CHCl_3$); **mp:** 74-76 °C; **HPLC Analysis,** t_r major: 6.3 min., t_r minor: 9.6 min., [Chiralcel®OD column, 24cm × 4.6 mm I.D., Hexanes:IPA = 90:10 1.5mL/min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.78 (d, *J* = 8.0 Hz, 1H), 7.51 (m, 1H), 7.43 (m, 2H), 7.23 (d, *J* = 5.2 Hz, 1H), 7.03 (m, 1H), 6.97 (dd, *J* = 5.2, 3.6 Hz, 1H), 6.40 (d, *J* = 6.8 Hz, 1H), 5.85 (m, 1H), 5.62 (dd, *J* = 14.8, 6.8 Hz, 1H), 5.19 (m, 2H), 2.78 (dd, *J* = 6.8 Hz, 2H); **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ 164.6, 133.7, 131.8, 128.8, 127.2, 124.7, 119.1, 48.8, 41.0; **IR** (thin film, cm^{-1}): 3305, 3071, 2925, 1648, 1532, 1393, 1294, 1055, 922, 702; **HRMS**: calc'd for $(M+Na)^+$ $C_{15}H_{15}NONaS$: 280.0772; found: 280.0761.

***N*-((*R*)-1-(naphthalen-3-yl)but-3-enyl)benzamide (9j)**



The reaction was run in 0.125 mmol scale and the crude mixture was purified by flash column chromatography with elution by 98:2 – 95:5, hexanes:EtOAc. **Yield:** 33 mg, 88%; **er:** 96:4; $[\alpha]_D^{23}$ = +14.9° (c = 0.8, $CHCl_3$); **mp:** 72-75 °C; **HPLC Analysis,** t_r major: 8.9 min., t_r minor: 15.9 min., [Chiralcel®OD column, 24cm × 4.6 mm I.D., Hexanes:IPA = 90:10 1.5mL/min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.0-7.78 (m, 6H), 7.69-7.42 (m, 6H), 7.29 (m, 1H), 6.55 (m, 1H), 5.83 (m, 1H), 5.47 (m, 1H), 5.27-5.13 (m, 2H), 2.81 (m, 2H); **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ 167.6, 134.8, 134.2, 131.8, 128.9, 128.8, 128.2, 127.9, 127.2, 126.5, 126.2, 125.4, 124.9, 118.8, 53.0, 40.7; **IR** (thin film, cm^{-1}): 3302, 3056, 2972, 2927, 1648, 1521, 1333, 1271, 1128, 1055, 926, 817, 702; **HRMS**: calc'd for $(M)^+$ $C_{21}H_{19}NONa$: 324.1364; found: 324.1393.

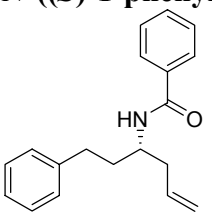
***N*-((*R*,*E*)-1-phenylhexa-1,5-dien-3-yl)benzamide (9k)**



The crude mixture was purified by flash column chromatography with elution by 98:2 – 9:1, hexanes:EtOAc. **Yield:** 111 mg, 82%; **er:** 95.5:4.5; $[\alpha]_D^{23}$ = +26.6° (c = 0.5, $CHCl_3$); **mp:** 97-100 °C; **HPLC Analysis,** t_r minor: 11.8 min., t_r minor: 14.5 min., [Chiralcel®OD column, 24cm × 4.6 mm I.D., Hexanes:IPA = 90:10 1.5mL/min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.8 Hz, 2H), 7.51 (t, *J* = 8.4 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.30 (t, *J* = 8.0 Hz, 2H), 7.25 (m, 1H), 6.59 (d, *J* = 16 Hz, 1H), 6.24 (dd, *J* = 16, 6.0 Hz, 1H), 6.21 (d, *J* = 6.8 Hz, 1H), 5.87 (m, 1H), 5.21 (d, *J* = 16 Hz, 1H), 5.18 (d, *J* = 13.6 Hz, 1H), 4.96

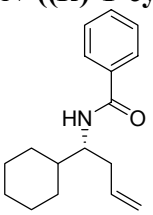
(m, 1H), 2.55 (t, J = 6.4 Hz, 2H); **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ 166.9, 136.8, 134.8, 134.1, 131.7, 131.0, 129.3, 128.8, 127.9, 127.1, 126.7, 118.9, 50.5, 39.7; **IR** (thin film, cm^{-1}): 3303, 3063, 2924, 1638, 1534, 1306, 973, 920, 701; **HRMS**: calc'd for $(M+Na)^+$ $C_{19}H_{19}NONa$: 300.1364; found: 300.1364.

***N*-((*S*)-1-phenylhex-5-en-3-yl)benzamide (9l)**



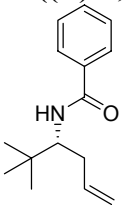
The crude mixture was purified by flash column chromatography with elution by 98:2 – 9:1, hexanes:EtOAc. **Yield:** 115 mg, 83%; **er:** 99.5:0.5; **$[\alpha]_D^{23}$** = +3.2° (c = 1.0, $CHCl_3$); **HPLC Analysis,** t_r major: 8.1 min., t_r minor: 10.0 min., [Chiralcel®OD-H column, 24cm × 4.6 mm I.D., Hexanes:IPA = 90:10 1.5mL/min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.68 (d, J = 8.4 Hz, 2H), 7.49 (t, J = 7.6 Hz, 1H), 7.42 (t, J = 8.0 Hz, 2H), 7.27 (m, 3H), 7.20 (m, 2H), 5.87 (m, 2H), 5.13 (m, 2H), 4.30 (m, 1H), 2.73 (t, J = 8.0 Hz, 2H), 2.39 (m, 2H), 1.95 (m, 1H), 1.87 (m, 1H); **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ 167.2, 141.9, 134.3, 131.6, 128.9, 128.8, 128.7, 128.5, 126.9, 126.2, 118.4, 49.2, 39.5, 36.4, 32.7; **IR** (thin film, cm^{-1}): 3298, 3063, 2923, 1636, 1534, 1489, 1304; **HRMS**: calc'd for $(M+H)^+$ $C_{19}H_{21}NO$: 280.1701; found: 280.1662.

***N*-((*R*)-1-cyclohexylbut-3-enyl)benzamide (9m)**



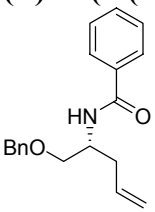
The crude mixture was purified by flash column chromatography with elution by 98:2 – 9:1, hexanes:EtOAc. **Yield:** 102 mg, 80%; **er:** 98:2; **$[\alpha]_D^{23}$** = + 10.5° (c = 0.8, $CHCl_3$); **mp:** 105-107 °C; **HPLC Analysis,** t_r major: 6.2 min., t_r minor: 8.0 min., [Chiralpak®AD-H column, 24cm × 4.6 mm I.D., Hexanes:IPA = 90:10 1.0mL/min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.74 (d, J = 8.0 Hz, 2H), 7.51 (d, J = 7.6 Hz, 1H), 7.43 (d, J = 8.0 Hz, 2H), 5.88 (d, J = 10.4 Hz, 1H), 5.82 (m, 1H), 5.08 (m, 2H), 4.09 (m, 1H), 2.40 (m, 1H), 2.28 (m, 1H), 2.16 (m, 2H), 1.78 (m, 3H), 1.64 (d, J = 12 Hz, 1H), 1.50 (m, 1H), 1.27-1.02 (m, 4H); **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ 167.3, 135.1, 131.4, 128.7, 127.0, 117.8, 53.5, 41.6, 36.6, 29.0, 28.3, 27.2, 26.4; **IR** (thin film, cm^{-1}): 3301, 1917, 1852, 1637, 1532, 1487, 1444, 1283; **HRMS**: calc'd for $(M+H)^+$ $C_{17}H_{23}NO$: 258.1813; found: 258.1868.

***N*-((*R*)-2,2-dimethylhex-5-en-3-yl)benzamide (9n)**



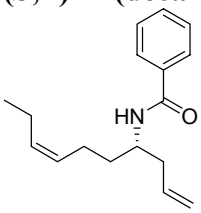
The crude mixture was purified by flash column chromatography with elution by 98:2 – 9:1, hexanes:EtOAc. **Yield:** 94 mg, 81%; **er:** 99.5:0.5; $[\alpha]_D^{23} = -8.4^\circ$ (c = 1.4, $CHCl_3$); **mp:** 151-155 °C; **HPLC Analysis,** t_r minor: 5.24 min., t_r major: 5.72 min., [Chiralpak®AD-H column, 24cm × 4.6 mm I.D., Hexanes:IPA = 90:10 1.0mL/min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.8 Hz, 2H), 7.48 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.2 Hz, 2H), 5.80 (m, 2H), 5.05 (d, *J* = 17.2 Hz, 1H), 5.01 (d, *J* = 10.4 Hz, 1H), 4.11 (ddd, *J* = 10.4, 10.4, 3.2 Hz, 1H), 2.55 (m, 1H), 2.05 (m, 1H), 0.99 (s, 9H); **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ 166.7, 136.1, 131.5, 128.8, 126.9, 117.1, 57.1, 35.4, 35.1, 26.8; **IR** (thin film, cm^{-1}): 3332, 3061, 2960, 1638, 1535, 1356, 1269, 1074, 992, 921, 728; **HRMS**: calc'd for $(M+H)^+$ $C_{15}H_{22}NO$: 232.1701; found: 232.1682.

(*R*)-*N*-(1-(benzyloxy)pent-4-en-2-yl)benzamide (9o)



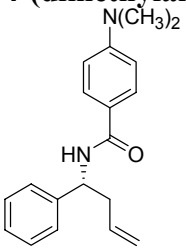
The crude mixture was purified by flash column chromatography with elution by 9:1 – 85:15, hexanes:EtOAc. **Yield:** 124 mg, 84%; **er:** 96.5:3.5; $[\alpha]_D^{23} = +7.2^\circ$ (c = 1.0, $CHCl_3$); **HPLC Analysis,** t_r major: 16.7 min., t_r minor: 18.2 min., [(*R,R*)-Whelk-O 1 (Regis® Technologies Inc., 25cm× 4.6mm I.D., Hexanes:IPA = 90:10 1.0mL/min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.8 Hz, 2H), 7.48 (t, *J* = 7.2 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.49 (t, *J* = 8.4 Hz 1H), 7.41 (t, *J* = 8.4 Hz, 2H), 7.34 (m, 5H), 6.40 (d, *J* = 8.0 Hz, 1H), 5.83 (m, 1H), 5.12 (dd, *J* = 16, 1.2 Hz, 1H), 5.08 (dd, *J* = 12 , 1.2 Hz, 1H), 4.52 (d, *J* = 4.0 Hz, 2H), 4.35 (m, 1H), 3.64 (dd, *J* = 9.6, 3.6 Hz, 1H), 3.57 (dd, *J* = 9.6, 3.6 Hz, 1H), 2.48 (t, *J* = 7.6 Hz, 2H); **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ 167.1, 138.3, 135.0, 134.7, 131.6, 128.87, 128.6, 128.0, 127.9, 127.1, 118.1, 73.5, 70.9, 49.1, 36.5; **IR** (thin film, cm^{-1}): 3342, 3065, 2917, 1737, 1641, 1536, 1487, 1453, 1246, 1112, 914; **HRMS**: calc'd for $(M+H)^+$ $C_{19}H_{22}NO_2$: 296.1651; found: 296.1625.

(*S,Z*)-*N*-(deca-1,7-dien-4-yl)benzamide (9p)



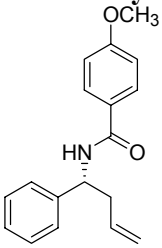
The crude mixture was purified by flash column chromatography with elution by 98:2 – 9:1, hexanes:EtOAc. **Yield:** 94 mg, 82%; **er:** 95.5:4.5; $[\alpha]_D^{23} = +4.3^\circ$ (c = 1.0, $CHCl_3$); **HPLC Analysis,** t_r major: 7.3 min., t_r minor: 9.3 min., [Chiralcel®OD column, 24cm × 4.6 mm I.D., Hexanes:IPA = 93:7 1.0mL/min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.8 Hz, 2H), 7.48 (t, *J* = 8.8 Hz, 1H), 7.41 (t, *J* = 8.8 Hz, 2H), 5.95 (d, *J* = 8.4 Hz, 1H), 5.82 (m, 1H), 5.44 (m, 2H), 5.13 (d, *J* = 16.4 Hz, 1H), 5.11 (d, *J* = 12 Hz, 1H), 4.22 (m, 1H), 2.31 (m, 2H), 2.09 (m, 1H), 1.98 (m, 1H), 1.67 (m, 1H), 1.55 (m, 1H), 0.94 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ 167.1, 134.5, 133.1, 131.5, 128.7, 128.4, 127.0, 118.2, 48.9, 39.3, 34.5, 29.3, 25.8, 14.0; **IR** (thin film, cm^{-1}): 3306, 3065, 2961, 2931, 2243, 1733, 1635, 1579, 1490, 1448, 1311, 1265, 968, 911, 737, 703; **HRMS**: calc'd for $(M+H)^+$ $C_{17}H_{24}NO$: 258.1858; found: 258.1861.

4-(dimethylamino)-*N*-((*R*)-1-phenylbut-3-enyl)benzamide (11e)



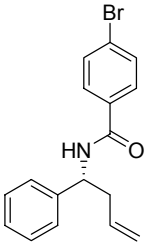
The reaction was run in 0.125 mmol scale and the crude mixture was purified by flash column chromatography with elution by 9:1 – 7:3, hexanes:EtOAc. **Yield:** 28 mg**,** 80%; **er:** 97:3; $[\alpha]_D^{23}$ = –14.1° (c = 1.4, $CHCl_3$); **mp:** 137-141 °C; **HPLC Analysis**, t_r major: 15.4 min., t_r minor: 17.6 min., [Chiralcel®OD column, 24cm × 4.6 mm I.D., Hexanes:IPA = 90:10, 1.5 mL/min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 9.2 Hz, 2H), 7.34 (m, 4H), 7.25 (m, 1H), 6.68 (d, *J* = 9.2 Hz, 2H), 6.28 (d, *J* = 7.6 Hz, 1H), 5.75 (m, 1H), 5.29 (dd, *J* = 16, 6.8 Hz, 1H), 5.18 (d, *J* = 17.2 Hz, 1H), 5.11 (d, *J* = 10 Hz, 1H), 3.02 (s, 6H), 2.68 (t, *J* = 6.8 Hz, 2H). **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ 166.5, 152.4, 142.1, 134.2, 128.5, 128.3, 127.2, 126.4, 118.2, 111.1, 52.4, 40.7, 40.1; **IR** (thin film, cm^{-1}): 3323, 2919, 1609, 1513, 1358, 1296, 1192, 760; **HRMS**: calc'd for $(M+1)^+$ $C_{18}H_{20}NO_2$: 282.1494; found: 282.1490.

4-methoxy-*N*-((*R*)-1-phenylbut-3-enyl)benzamide (11f)



The reaction was run in 0.125 mmol scale and the crude mixture was purified by flash column chromatography with elution by 9:1 – 7:3, hexanes:EtOAc. **Yield:** 28 mg**,** 80%; **er:** 97.5:2.5; $[\alpha]_D^{23}$ = +1.6° (c = 0.5, $CHCl_3$); **mp:** 143-146 °C; **HPLC Analysis**, t_r major: 9.3 min., t_r minor: 13.7 min., [Chiralcel®OD column, 24cm × 4.6 mm I.D., Hexanes:IPA = 90:10, 1.5 mL/min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.8 Hz, 2H), 7.35 (d, *J* = 4.4 Hz, 3H), 7.27 (m, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.35 (d, J = 6.8 Hz, 1H), 5.77 (m, 1H), 5.27 (dd, *J* = 14.4, 6.8 Hz, 1H), 5.15 (m, 2H), 3.85 (s, 3H), 2.68 (t, *J* = 6.8 Hz, 2H); **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ 166.4, 159.9, 152.2, 134.5, 128.9, 127.6, 126.7, 118.6, 114.0, 55.6, 52.8, 40.8; **IR** (thin film, cm^{-1}): 3302, 3068, 2926, 1639, 1535, 1484, 1299, 1006, 918, 841, 750, 695; **HRMS**: calc'd for $(M+1)^+$ $C_{18}H_{19}NO_2$: 282.1449; found: 282.1445.

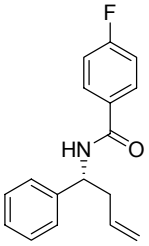
4-bromo-*N*-((*R*)-1-phenylbut-3-enyl)benzamide (11g)



The reaction was run in 0.125 mmol scale and the crude mixture was purified by flash column chromatography with elution by 95:5 – 9:1, hexanes:EtOAc. **Yield:** 34 mg**,** 84%; **er:** 96.5:3.5;

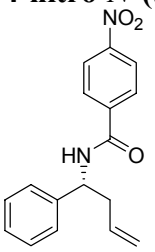
$[\alpha]_D^{23}$ = –2.9° (c = 0.8, $CHCl_3$); **mp:** 107-110 °C; **HPLC Analysis**, t_r major: 6.9 min., t_r minor: 11.4 min., [Chiralcel®OD column, 24cm × 4.6 mm I.D., Hexanes:IPA = 90:10, 1.5 mL/min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 8.8 Hz, 2H), 7.56 (d, *J* = 8.8 Hz, 2H), 7.34 (m, 4H), 7.28 (m, !H), 6.37 (d, *J* = 6.8 Hz, 1H), 5.76 (m, 1H), 5.26 (dd, *J* = 14.4, 6.8 Hz, 1H), 5.18 (dd, *J* = 16.8, 1.6 Hz, 1H), 5.13 (d, *J* = 9.6 Hz, 1H), 2.69 (t, *J* = 6.8 Hz, 2H); **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ 167.1, 143.5, 137.2, 134.1, 132.1, 128.9, 128.7, 127.7, 126.6, 118.8, 53.1, 40.7; **IR** (thin film, cm^{-1}): 3307, 3067, 2929, 1628, 1500, 1253, 1179, 1028, 844, 757; **HRMS**: calc'd for $(M+Na)^+$ $C_{17}H_{16}BrNNaO$: 352.0912; found: 352.0925.

4-fluoro-*N*-((*R*)-1-phenylbut-3-enyl)benzamide (11h)



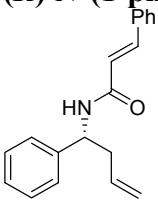
The reaction was run in 0.125 mmol scale and the crude mixture was purified by flash column chromatography with elution by 95:5 – 9:1, hexanes:EtOAc. **Yield:** 34 mg**,** 84%; **er:** 97.5:2.5; **$[\alpha]_D^{23}$** = +16.2° (c = 0.7, $CHCl_3$); **mp:** 120-122 °C; **HPLC Analysis**, t_r major: 6.0 min., t_r minor: 9.5 min., [Chiralcel®OD column, 24cm × 4.6 mm I.D., Hexanes:IPA = 90:10, 1.5 mL/min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.77 (m, 2H), 7.33 (m, 4H), 7.28 (m, 1H), 7.09 (m, 2H), 6.41 (d, *J* = 6.8 Hz, 1H), 5.76 (m, 1H), 5.26 (dd, *J* = 14.8, 6.8 Hz, 1H), 5.18 (d, *J* = 16.2 Hz, 1H), 5.13 (d, *J* = 10 Hz, 1H), 2.69 (t, *J* = 6.8 Hz, 2H); **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ 166.6, 165.8, 141.7, 134.2, 129.4, 128.9, 127.7, 126.6, 118.7, 115.9, 115.7, 53.1, 40.8; **IR** (thin film, cm^{-1}): 3336, 3072, 2923, 1631, 1540, 1499, 1286, 1232, 1157, 853, 752, 692; **HRMS**: calc'd for $(M+1)^+$ $C_{17}H_{17}FNO$: 270.1294; found: 270.1275.

4-nitro-*N*-((*R*)-1-phenylbut-3-enyl)benzamide (11i)



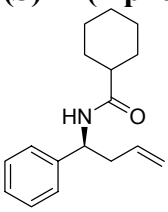
he reaction was run in 0.125 mmol scale and the crude mixture was purified by flash column chromatography with elution by 95:5 – 9:1, hexanes:EtOAc. **Yield:** 34 mg**,** 92%; **er:** 99.5:0.5; **$[\alpha]_D^{23}$** = –1.6° (c = 1.1, $CHCl_3$); **mp:** 105-108 °C; **HPLC Analysis**, t_r major: 23.4 min., t_r minor: 35.4 min., [Chiralcel®OD column, 24cm × 4.6 mm I.D., Hexanes:IPA = 90:10, 1.5 mL/min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.28 (d, *J* = 8.8 Hz, 2H), 7.91 (d, *J* = 8.8 Hz, 2H), 7.36-7.30 (m, 5H), 6.43 (br, 1H), 5.78 (m, 1H), 5.30 (dd, *J* = 13.2, 6.8 Hz, 1H), 5.22-5.14 (m, 2H), 2.72 (t, *J* = 6.8 Hz, 2H); **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ 164.6, 140.9, 140.1, 133.7, 128.8, 128.1, 127.7, 126.4, 123.9, 118.8, 53.1, 40.5; **IR** (thin film, cm^{-1}): 3420, 3303, 3073, 2928, 1645, 1531, 1341, 856, 701; **HRMS**: calc'd for $(M)^+$ $C_{17}H_{16}N_2O_3Na$: 319.1059; found: 319.1075.

(*R*)-*N*-(1-phenylbut-3-enyl)cinnamamide (11k)



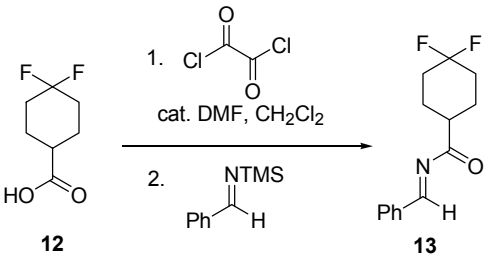
The crude mixture was purified by flash column chromatography with elution by 95:5 – 9:1, hexanes:EtOAc. **Yield:** 113 mg, 82%; **er:** 95:5; $[\alpha]_D^{23} = -8.4^{\circ}$ (c = 1.4, $CHCl_3$); **mp:** 107-109 °C; **HPLC Analysis,** t_r major: 16.3 min., t_r minor: 18.3 min., [Chiralpak®AD-H column, 24cm × 4.6 mm I.D., Hexanes:IPA = 90:10 1.5mL/min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.63 (d, *J* = 16 Hz, 1H), 7.47 (m, 2H), 7.32 (m, 7H), 7.26 (m, 1H), 6.42 (d, *J* = 16 Hz, 1H), 6.01 (d, *J* = 7.6 Hz, 1H), 5.73 (m, 1H), 5.23 (dd, *J* = 14.4, 7.2 Hz, 1H), 5.14 (d, *J* = 16 Hz, 1H), 5.09 (d, *J* = 10.4 Hz, 1H), 2.65 (t, *J* = 7.8 Hz, 2H); **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ 167.2, 141.6, 135.0, 134.2, 129.9, 129.0, 128.9, 128.0, 127.6, 126.7, 120.8, 118.5, 52.9, 40.7; **IR** (thin film, cm^{-1}): 3271, 3062, 1655, 1618, 1543, 1344, 1215, 989, 919, 738; **HRMS**: calc'd for $(M+H)^+$ $C_{19}H_{20}NO$: 278.1545; found: 278.1526.

(*S*)-*N*-(1-phenylbut-3-enyl)cyclohexanecarboxamide (11l) [(*R*)-**7h** was used as catalyst]



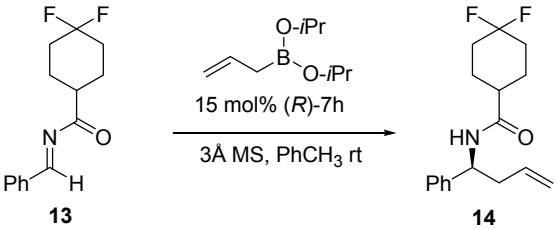
The crude mixture was purified by flash chromatography with elution by 95:5 – 9:1, hexanes:EtOAc. **Yield:** 238 mg, 83% **er:** 95:5; $[\alpha]_D^{23} = -35.0^{\circ}$ (c =0.5, $CHCl_3$); **mp:** 108-110 °C; **HPLC Analysis,** t_r major: 7.7 min., t_r minor: 5.7 min., [Chiralcel®AD column, 24cm × 4.6 mm I.D., Hexanes:IPA = 90:10 1.5mL/min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.33-7.21 (m, 5H), 5.88 (d, *J* = 8 Hz, 1H), 5.67 (m, 1H), 5.07 (m, 3H), 2.43 (m, 2H), 2.06 (m, 1H), 1.80 (m, 4H), 1.42 (t, *J* = 12.4 Hz, 2H), 1.26 (m, 4H) **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ 175.5, 142.2, 134.4, 128.8, 127.4, 126.6, 118.3, 52.0, 45.8, 40.8, 30.0, 29.9, 25.9 **IR** (thin film, cm^{-1}): 3269, 3066, 2928, 2852, 1640, 1549, 1459, 1448, 1336, 1271, 1220, 915, 701 **HRMS**: calc'd for $(M+1)^+$ $C_{17}H_{23}NO$: 258.1858; found: 258.1862.

Procedure for the Synthesis of Maraviroc[10]
4,4-Difluoro-cyclohexanecarboxylic acid benzylideneamide (13)



A 100 mL flame-dried round bottom flask under Ar was charged with a stir bar and 4,4-difluoro-cyclohexanecarboxylic acid (2.0 g, 12.2 mmol) **12**.[11] The flask was charged with dry CH_2Cl_2 (12.2 mL) and 3 drops of dry DMF. Reaction was cooled to 0°C and under vigorous stirring oxalyl chloride (1.34 mL, 15.8 mmol) was carefully added. After evolution of gas was complete the reaction was warmed to room temperature and stirred an additional 30 min. Solvent and excess oxalyl chloride was removed *in vacuo* to give orange oil. The crude oil was distilled under reduced pressure to afford the acid chloride as a clear oil (1.9 g, 85% yield, bp 80-85, 10 Torr). In a new flame-dried flask under Ar charged with a stir bar and freshly distilled benzylidene-trimethylsilanylamine[12] (1.94g, 10.9 mmol) was added dry CH_2Cl_2 (10.9 mL) and cooled to 0°C. A solution of the acid chloride (1.99 g, 10.9 mmol, 2.0 M in CH_2Cl_2) was slowly added via air-tight syringe. Upon completion of addition the reaction was refluxed at 55°C for 3 hours. The reaction was cooled to ambient temperature and the solvent was removed *in vacuo* to give the acyl imine **13** as yellow oil which slowly crystallized to a white solid over 48 hours. **Yield:** 2.08 g, 76% **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.42 (b, 1H), 7.84 (d, *J* = 7.2 Hz, 2H), 7.53 (t, *J* = 5.2 Hz, 1H), 7.46 (t, *J* = 7.2 Hz, 2H), 2.65 (m, 1H), 2.18-2.06 (m, 4H), 1.94-1.72 (m, 4H) **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ 174.7, 138.5, 133.4, 129.2, 129.1, 126.5, 126.2, 12.0, 43.9, 43.0, 32.9, 25.9, 25.1

4,4-Difluoro-cyclohexanecarboxylic acid (1-phenyl-but-3-enyl)-amide (14)



A 50 mL flame-dried round bottom flask was charged with stir bar and flushed with Ar. To the flask was added **14** (31 mg, 0.125 mmol), 3Å molecular sieves (120 mg), (*R*)-3,3'-Ph_2-BINOL (8 mg, 0.02 mol) and toluene (3 mL). The mixture was stirred under Ar at room temperature and allyldiisopropoxyborane (1.0 M in toluene, 125 μL, 0.125 mmol) was slowly added. The reaction

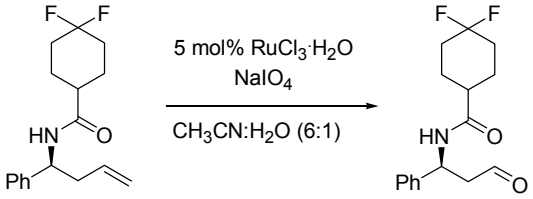
(10) Dorr, P.; Westby, M.; Dobbs, S.; Griffin, P.; Irvine, B.; Macartney,M.; Mori, J.; Rickett, G.; Smith-Burchnell, C.; Napier, C.; Webster,R.; Armour, D.; Price, D.; Stammen, B.; Wood, A.; Perros, M. *Antimicrob. Agents Chemother.* **2005**, *49*, 4721-4732.

(11) Price, D.; Gayton, S.; Selby, M. D.; Ahman, J.; Haycock-Lewandowski, S.; Stammen, B. L.; Warren, A. *Tetrahedron Lett.* **2005**, *46*, 5005-5007.

(12) See Method A.

mixture was stirred at room temperature for 24 hours and diluted with ether (2 mL) and water (2.0 mL). The biphasic mixture was stirred at room temperature for 10 minutes. The organic layer was separated and dried over Na_2SO_4. The organic layer was isolated by filtration and the filtrate was concentrated *in vacuo* at 20 ˚C. The residue was purified directly by flash chromatography over silica gel (elution with 95:5 – 8:2, hexanes:EtOAc) to afford the homoallylic amide **14** as a white solid. **Yield:** 27 mg, 75% **er:** 95.5:4.5 ; $[\alpha]_D^{23}$ = +17.3˚ (c =0.4, $CHCl_3$); **mp:** 109-110 ˚C; **HPLC Analysis,** t_r major: 12.5 min., t_r minor: 6.8 min., [Chiralcel®OD column, 24cm × 4.6 mm I.D., Hexanes:IPA = 90:10, 1.5mL/min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.24 (t, *J* = 1.6 Hz, 2H), 7.26 (m, 3H), 5.72 (d, *J* = 7.6 Hz, 1H), 5.59 (m, 1H), 5.01 (m, 3H), 2.47 (m, 1H), 2.09 (m, 3H), 1.88-1.60 (m, 6H). **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ 173.4, 141.8, 134.2, 128.9, 127.7, 126.5, 125.3, 122.9, 120.5, 118.6, 52.3, 42.0, 40.8, 33.0, 26.2, 25.4. **IR** (thin film, cm^{-1}): 3295, 3065, 2941, 1642, 1542, 1496, 1373, 1110, 963; **HRMS**: calc'd for $(M+1)^+$ $C_{17}H_{21}F_2NO$: 316.1489; found 316.1488.

4,4-Difluoro-cyclohexanecarboxylic acid (3-oxo-1-phenyl-propyl)-amide (15)[13]

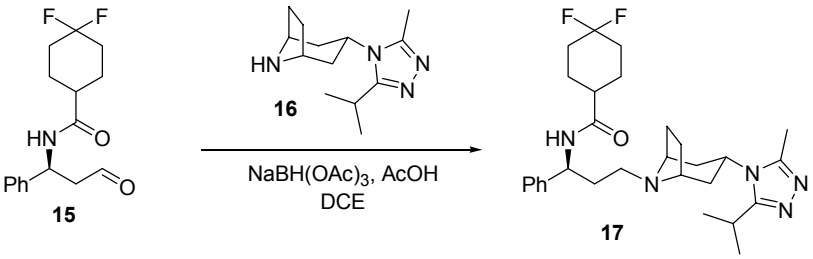


14 **15**

To an oven-dried round bottom flask was charged homoallylic amide **14** (50 mg, 0.170 mmol under N_2 and dissolved in acetonitrile (3 mL). A solution of $RuCl_3 \cdot H_2O$ (2 mg, 0.0085 mmol) in water (0.5 mL) was added at room temperature. Under vigorous stirring sodium periodate is added in one portion. Reaction was stirred for 3 hours and monitored by TLC. After consumption of starting material the reaction was quenched with a saturated aqueous solution of $Na_2S_2O_3$ (2 mL). The phases were separated and the aqueous layer was extracted with EtOAc (3 ×5 mL. The organic layers were combined and dried over Na_2SO_4. Silica gel flash chromatography (elution with 9:1 – 1:1, hexanes:EtOAc) afforded the aldehyde **15** as a white solid. **Yield:** 34 mg, 68% $[\alpha]_D^{23}$ = –8.2˚ (c = 1.0, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.71 (s, 1H), 7.36 (m, , 2H), 7.27 (m, 3H), 6.17 (d, *J* = 8 Hz, 1H), 5.50 (q, *J* = 6.9 Hz, 1H), 2.95 (qd, 1H), 2.09 (m, 3H), 1.89-1.61 (m, 6H) **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ 173.6, 148.1, 140.5, 133.2, 129.3, 128.3, 126.6, 122.8, 55.8, 49.1, 48.6, 33.3, 33.0, 32.7, 26.0 **IR** (thin film, cm^{-1}): 3302, 3087, 2941, 1723, 1647, 1589, 1496, 1373, 1263, 1109, 963, 848; **HRMS**: calc'd for $(M+1)^+$ $C_{16}H_{19}F_2NO_2$: 296.1; found: 296.2

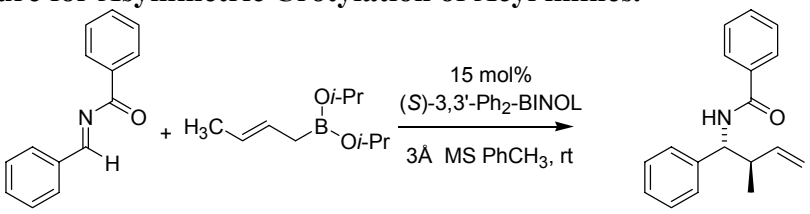
(13) Yang, D.; Zhang, C. *J. Org. Chem.* **2001**, *66*, 4814-4818.

Maravircoc. 4,4-Difluoro-cyclohexanecarboxylic acid {3-[3-(3-isopropyl-5-methyl-[1,2,4]triazol-4-yl)-8-aza-bicyclo[3.2.1]oct-8-yl]-1-phenyl-propyl}-amide (17)



To a flame-dried reaction vial equipped with stir under Ar was added aldehyde **15** (9 mg, 0.03 mmol), tropane **16**[1,14] (8 mg, 0.03 mmol) and dry 1,2-dichloroethane (0.5 mL). Acetic acid (2 μL, 0.03 mmol) was added via syringe and the solution stirred for 15 min at room temperature. In one portion, sodium triacetoxyborohydride (12 mg, 0.05 mmol) was added followed by the evolution of H_2 gas. The reaction was stirred for 12 hrs and monitored by TLC until consumption of the aldehyde was complete. The reaction was quenched with saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2 (2 × 5 mL) and the combined organic layers were purified by flash chromatography over silica gel (elution with 9:1 CH_2Cl_2:MeOH). The product **17** was obtained as a sticky white solid. **Yield:** 15 mg, 88% $[\alpha]_D^{23} = -16.8^{\circ}$ (c = 0.4, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.36 (m, 2H), 7.23 (m, 3H), 6.55 (b, 1H), 5.15 (d, *J* = 6.6 Hz, 1H), 4.27 (m, 1H), 3.33 (m, 1H), 2.85 (m, 1H), 2.48 (s, 3H), 2.28 (m, 2H), 2.20-1.64 (m, 19H), 1.39 (d, *J* = 6.8 Hz, 6H); **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ 172.4,158.0, 149.6, 140.8, 127.8, 127.5, 126.5, 125.4, 123.9, 121.6, 119.2, 57.9, 57.0, 46.7, 46.0, 41.8, 34.0, 31.7, 31.5, 30.6, 28.7, 25.7, 24.8, 24.3, 21.6, 20.6, 13.1, 12.1 **IR** (thin film, cm^{-1}): 3288, 3030, 2960, 1736, 1664, 1534, 1451, 1372, 1260, 1108, 1031, 964; **HRMS**: calc'd for $(M+1)^+$ $C_{29}H_{41}F_2N_5O$: 514.3357; found: 514.3409.

General Procedure for Asymmetric Crotylation of Acyl imines.

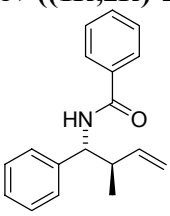


To a 15 × 100 mm oven-dried glass vessel equipped with stir bar was added (*E*)-*N*-benzylidenebenzamide (26.2 mg, 0.125 mmol), 3Å molecular sieves (125 mg), (*S*)-3,3'-Ph_2-BINOL (8.3 mg, 0.019 mmol) and dissolved in toluene (1.125 mL) under Ar. The mixture was stirred for 5 minutes at room temperature, charged with (*E*)-crotyldiisopropoxyborane (1.0 M in toluene, 125 μL, 0.125 mmol) and stirred for 24 hours. The mixture was diluted with Et_2O (1mL) and water (1.5 mL) and stirred for 10 minutes at room temperature. The organic layer was separated and dried over Na_2SO_4. The organic layer was separated by filtration and the filtrate was concentrated *in vacuo* at 20 ˚C. The residue was purified by flash chromatography

(14) (a) Armour, D. R.; de Groot, M. J. ; Price, D. A.; Stammen, B. L. C.; Wood, A.; Perros, M. Burt, C; *Chem. Biol. Drug. Des.* **2006**, *67*, 305–308. (b) Lewin, A. H.; Sun, G.; Fudala, L.; Navarro, H.; Zhou, L.-M.; Popik, P.; Faynsteyn, A.; Skolnick, P. *J. Med. Chem.* **1998,** *41,* 988-995. (c) Price, D. A.; Gayton, S.; Selby, M. D.; Ahman, J. Haycock-Lewandowski, S. *Synlett*, **2005**, *7*, 1133-1134.

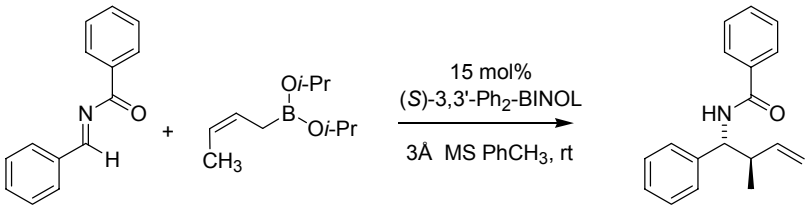
over silica gel (elution with 98:5 – 9:1, hexanes:EtOAc) to afford the homoallylic amide as a white solid.

***N*-((1*R*,2*R*)-2-methyl-1-phenylbut-3-enyl)benzamide 19**



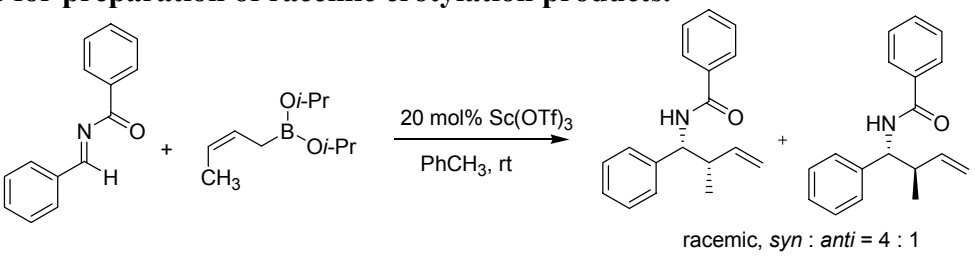
The reaction was run with (*E*)-crotyldiisopropoxyborane on 0.125 mmol scale and crude mixture was purified by flash column chromatography over silica gel (elution with 98:5 – 9:1, hexanes:EtOAc) to afford the homoallyic amide. **IR** (thin film, cm^{-1}): **Yield:** 28 mg**,** 85%; **er:** 98.5:1.5; $[\alpha]_D^{23}$ = +13.3° (c = 1.0, $CHCl_3$); **mp:** 120-121 °C; **HPLC Analysis**, t_r minor: 12.64 min., t_r major: 15.33 min., [Chiralcel®OD column, 24cm × 4.6 mm I.D., Hexanes:IPA = 95:5, 1.0 mL/min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 7.5 Hz,2H), 7.50 (t, *J* = 6.5 Hz,1H), 7.44 (d, *J* = 7.5 Hz, 2H), 7.33 (m, 5H), 6.45 (d, *J* = 8.0 Hz, 1H), 5.83 (m, 1H), 5.18 (m, 2H), 5.03 (t, *J* = 7.5 Hz,1H), 2.75 (m, 1H), 1.05 (d, *J* = 6.5 Hz, 3H) **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ 166.9, 141.5, 140.1, 134.9, 131.7, 129.0, 128.7, 127.5, 127.0, 116.6, 57.8, 43.8, 17.4 **IR** (thin film, cm^{-1}): 3272, 3003, 2857, 1636, 1557, 1509, 1488, 1373, 1239, 1111, 1019 **HRMS**: calc'd for $(M+1)^+$ $C_{18}H_{20}NO$ 266.1427; found 266.1448.

***N*-((1*R*,2*R*)-2-Methyl-1-phenyl-but-3-enyl)-benzamide 19**



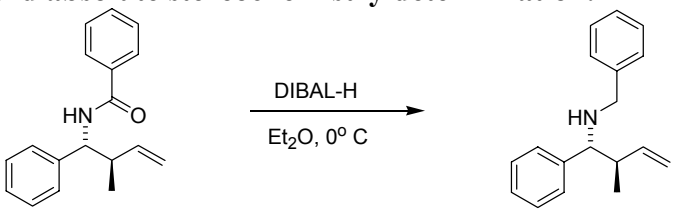
The reaction was run with (*Z*)-crotyldiisopropoxyborane on 0.125 mmol scale and crude mixture was purified by flash column chromatography over silica gel (elution with 98:2 – 9:1, hexanes:EtOAc) to afford the homoallyic amide. **Yield:** 21 mg**,** 64%; **er:** 94:6; $[\alpha]_D^{23}$ = +9.6° (c = 1.0, $CHCl_3$); **HPLC Analysis**, t_r minor: 21.5 min., t_r major: 29.1 min., [Chiralcel®OD column, 24cm × 4.6 mm I.D., Hexanes:IPA = 98:2, 1.5 mL/min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.75 (d, *J*=7.5 Hz,2H), 7.50 (t, *J*=6.5 Hz,1H), 7.44 (d, *J*=7.5 Hz, 2H), 7.33 (m, 5H), 6.45 (d, *J*=8 Hz, 1H), 5.83 (m, 1H), 5.18 (m, 2H), 5.03 (t, *J*=7.5 Hz,1H), 2.75 (m, 1H), 1.05 (d, *J*=6.5 Hz, 3H) **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ 166.9, 141.5, 140.1, 134.9, 131.7, 129.0, 128.7, 127.5, 127.0, 116.6, 57.8, 43.8, 17.4 **IR** (thin film, cm^{-1}): 3272, 3003, 2857, 1636, 1557, 1509, 1488, 1373, 1239, 1111, 1019.

Procedure for preparation of racemic crotylation products.

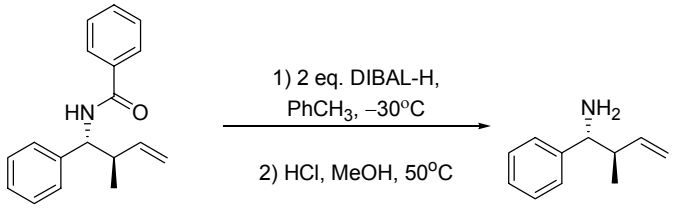


A 15 × 100 mm oven dried glass vessel was charged with stir bar and flushed with Ar. (*E*)-*N*-benzylidenebenzamide (26.2 mg, 0.125 mmol) was added and dissolved in toluene (1.125 mL). Scandium triflate (12.3 mg, 0.025 mmol) and (*Z*)-crotyldiisopropoxyborane (125 μL, 0.125 mmol, 1.0 M in toluene) were added subsequently into the reaction mixture and stirred for 24 hours. The mixture was diluted with ether (1 mL) and water (1.5 mL) and stirred for 10 minutes at room temperature. The organic layer was separated and dried over Na_2SO_4. The organic layer was separated by filtration, and the filtrate was concentrated *in vacuo* and the residue was purified by flash chromatography over silica gel (elution with 98:2 – 9:1, hexanes:EtOAc) to afford the homoallylic amide as a white solid.

Diastereoselectivity and absolute stereochemistry determination.



A 15 × 100 mm oven dried glass vessel was charged with stir bar and flushed with Ar. *N*-(2-methyl-1-phenyl-but-3-enyl)-benzamide **19** (33.1 mg, 0.125 mmol) was added and dissolved in Et_2O (1.0 mL) and cooled to 0 °C. Diisobutylaluminum hydride (0.375 mL, 0.375 mmol 1.0 M in hexanes) was slowly added via syringe. Reaction was warmed to room temperature and stirred for 2 hours. Reaction was quenched with saturated sodium bicarbonate and the organic layer extracted. Concentration under reduced pressure afforded the product in 94% yield. ^{1}H NMR spectra was in agreement with the *anti* product previously described literature[15].



A 15 × 100 mm oven-dried glass vessel was charged with stir bar and flushed with Ar. *N*-(2-methyl-1-phenyl-but-3-enyl)-benzamide **19** (33.1 mg, 0.125 mmol) was added and dissolved in toluene (1 mL) and cooled to –35 °C. Diisobutylaluminum hydride (2.5 mL, 0.25 mmol, 0.1 M in toluene) was slowly added in 5 hour via syringe pump and stirred overnight. The reaction was quenched with MeOH (15 μL) and warmed to room temperature. To the reaction mixture was added NaF (30 mg), KOH (15 mg) and water (15 μL) and stirred vigorously for 1 hour. The solution was diluted with chloroform (5 mL) and filtered through a celite bed. The filtrate was

(15) Fujita, K.; Yorimitsu, H.; Shinokubo, H., Oshima, K. *J. Org. Chem*. **2004**, *69*. 3302

dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was dissolved in MeOH (1.0 mL) and concentrated HCl (0.3 mL) was added. The reaction mixture was stirred at 50 °C overnight. The mixture was diluted with chloroform (3.0 mL) and water (3.0 mL) and pH was adjusted to 12 with solid KOH. The organic layer was separated and aqueous layer was extracted with chloroform (5 mL). The combined organic layers was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography over silica gel (elution with 98:2 – 9:1, CH_2Cl_2:MeOH) to afford the desired (1*R*,2*R*)-2-methyl-1-phenylbut-3-en-1-amine as clear oil in 81% yield. The spectroscopic data was is agreement with previously reported data.[10,15] $[\alpha]_D^{23} = -86^\circ$ (c = 0.4, $CHCl_3$). Lit.[16] $[\alpha]_D^{22} = +76^\circ$ (c = 0.92, $CHCl_3$, (1*S*,2*S*)-isomer).

(16) Ramachandran, P. V.; Burghardt, T. E.; Bland-Berry, L. *J. Org. Chem.* **2005**, *70*, 7911.

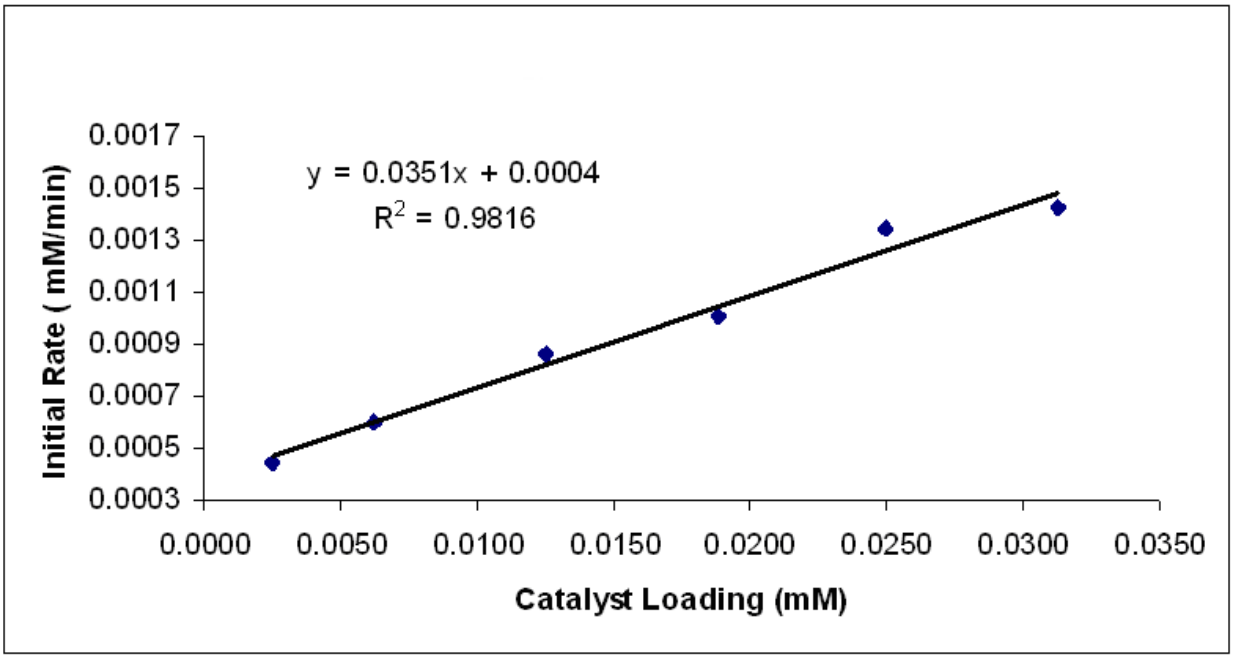
Kinetic Experiment

General experimental to determine catalyst order. A 5 mL vial equipped with stir bar was fitted with a rubber septum to the DiComp ReactIR 4000 Probe. The vial was charged toluene (2.0 mL) and the background spectrum was recorded. (*E*)-*N*-benzylidenebenzamide **5** (55mg .25 mmol) was charged into the flask and stirred for 5 minutes. 3,3'-Ph_2-BINOL **7h** (16.5 mg, .038 mmol, 15 mol% catalyst loading) was charged and stirred for 1 minute followed by addition of pure diisopropylallylborane (50 µL, 0.25 mmol). The reaction mixture was stirred at room temperature for 150 minutes and the product peak at 1482.23 cm^{-1} was monitored by ReactIR at real time.

Table. Molarity and k_{obs}

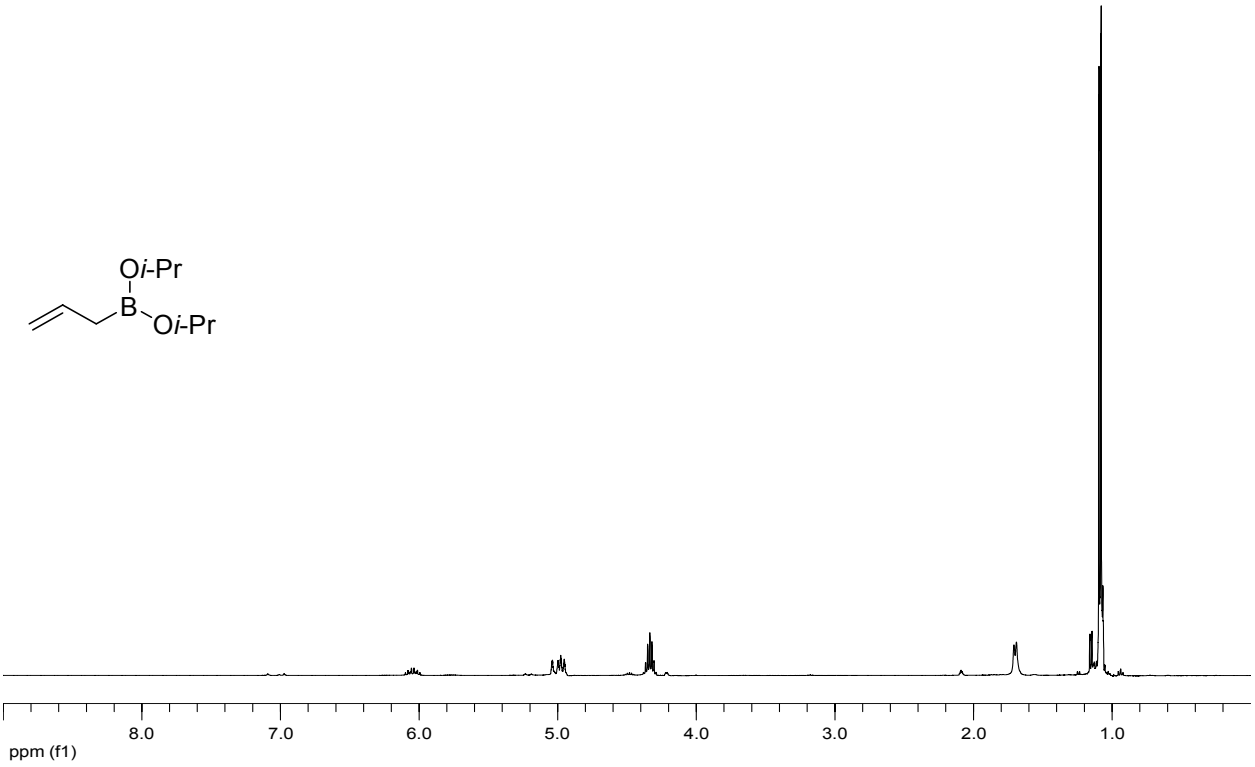
Molarity (M)	k_{obs} (mM/min)
0.02	0.0004
0.05	0.0006
0.10	0.0009
0.15	0.0010
0.20	0.0013
0.25	0.0014

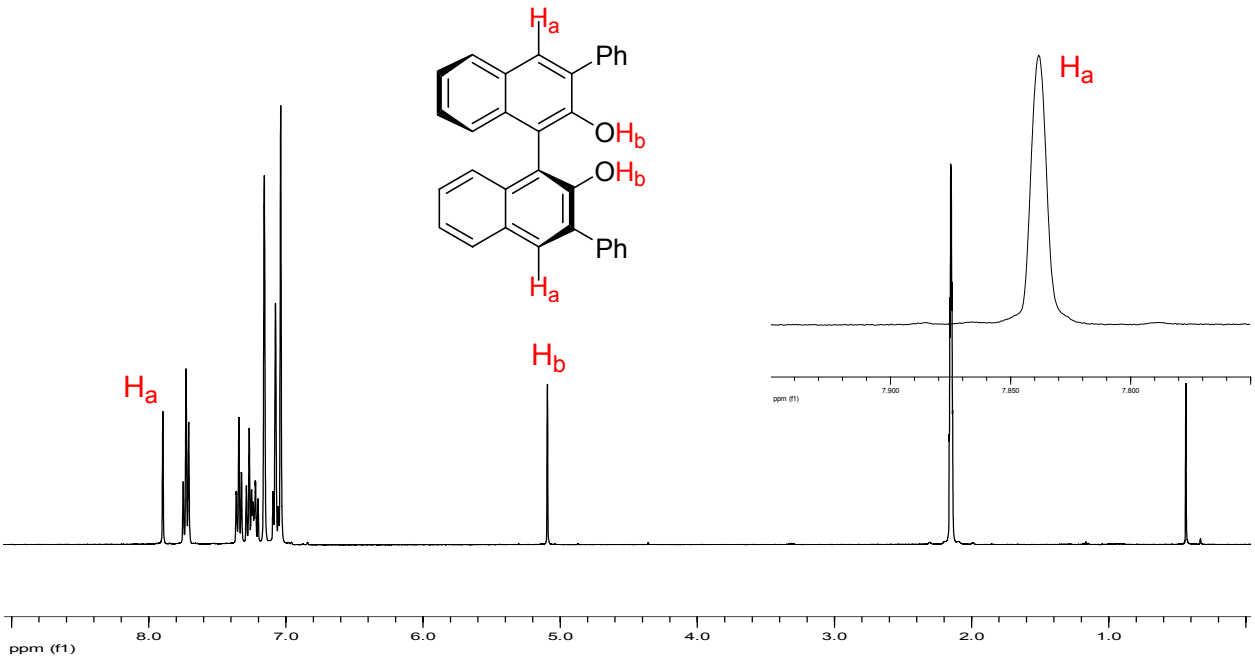
Figure. First-order catalyst in allylboration of imine

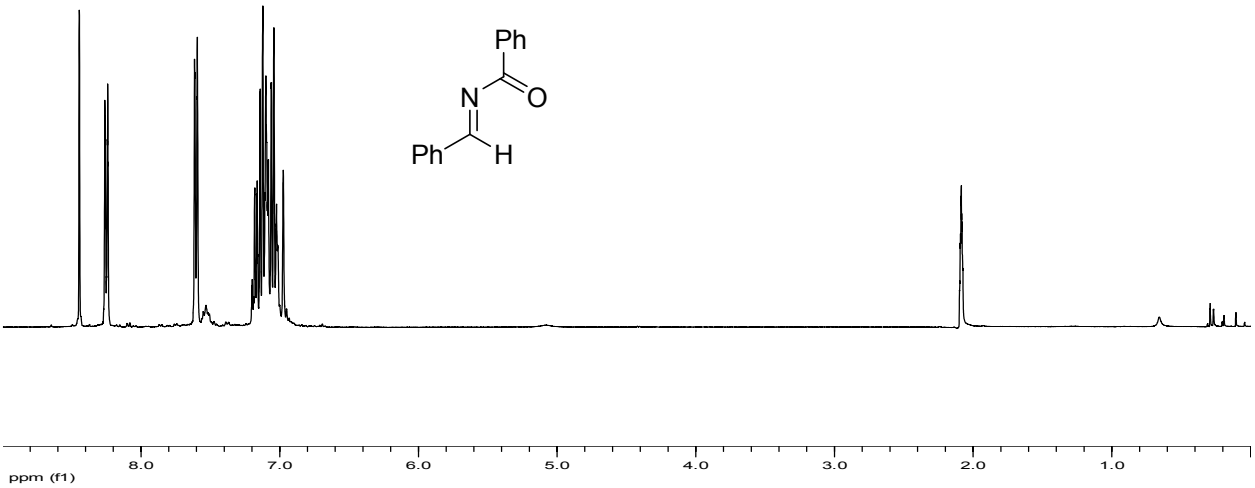


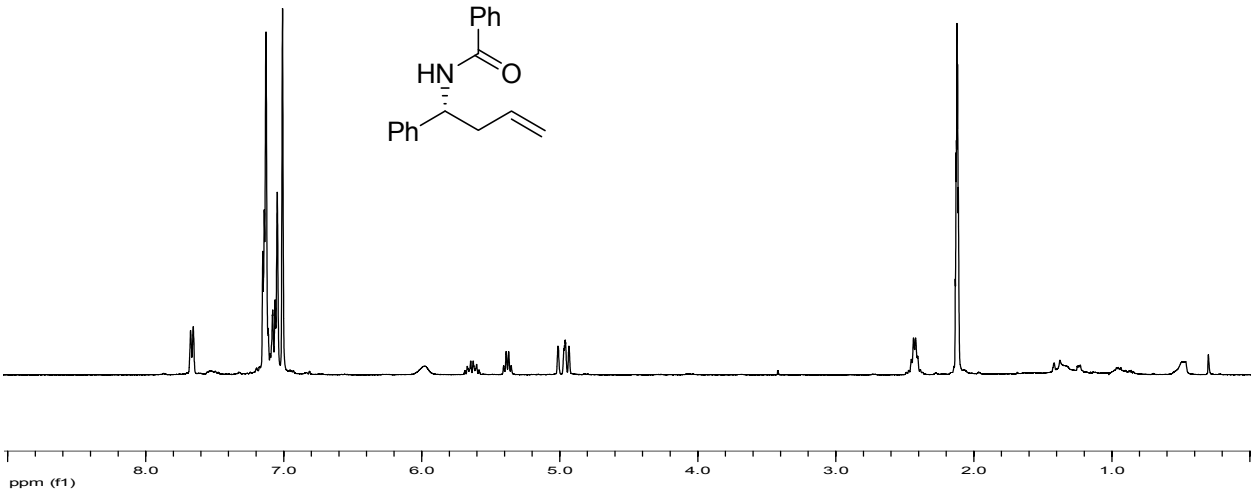
NMR Samples:

To an NMR tube purged with Ar was added a pure sample of allyldiisopropoxyborane **4** and $CD_3C_6D_5$ (1.0 mL). The ^{1}H-NMR spectra was taken at room temperature. Three singlet peaks (7.10 ppm, 7.02 ppm, 6.98 ppm, 2.09 ppm) were reference peaks of $CD_3C_6D_5$. The impurity in allyldiisopropoxyborane was allylboronic acid due to hydrolysis.



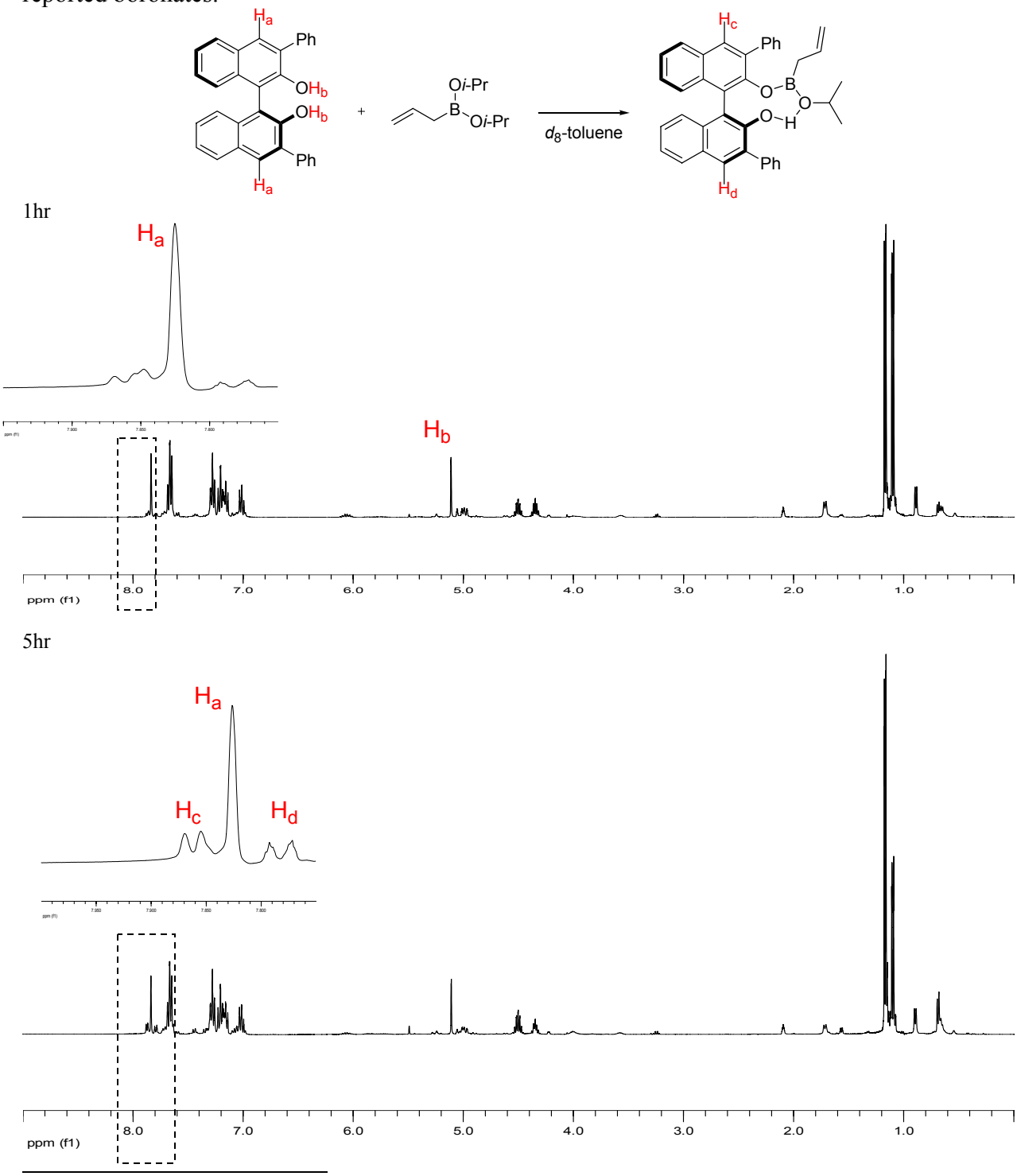



Ph
N
O
Ph
H
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)


Ph
HN
O
Ph
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)

^{1}H-NMR of mixing (*S*)-3,3'-Ph$_2$-BINOL 7h and allyldiisopropoxyborane 4:

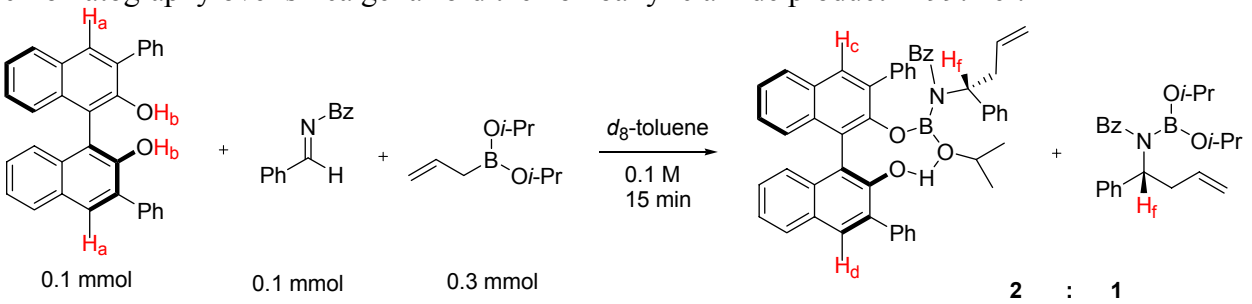
To an NMR tube was added allyldiisopropoxyborane **4** (40 uL, 0.10 mmol) and $CD_3C_6D_5$ under Ar. (*S*)-3,3'-Ph$_2$-BINOL **7h** (6.8 mg, 0.015 mmol) was added subsequently. The solution was left under Ar at room temperature for 20 hours. ^{1}H-NMR spectra was taken at room temperature. Peak at 7.84 ppm was assigned as H_a. Peaks H_b and H_c were assigned based on previously reported boronates.[17]

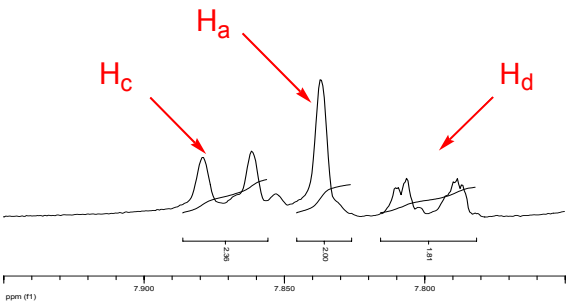


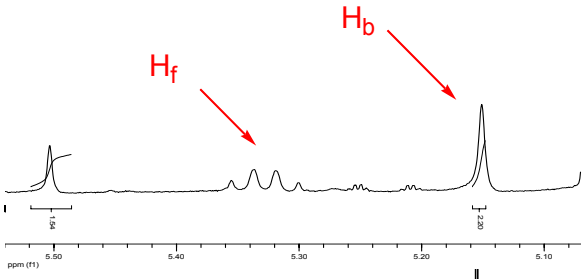
(17) Thormeier, S.; Carboni, B.; Kaufmann, D. E. *Journal of Organometallic Chemistry* **2002**, *657*, 136.

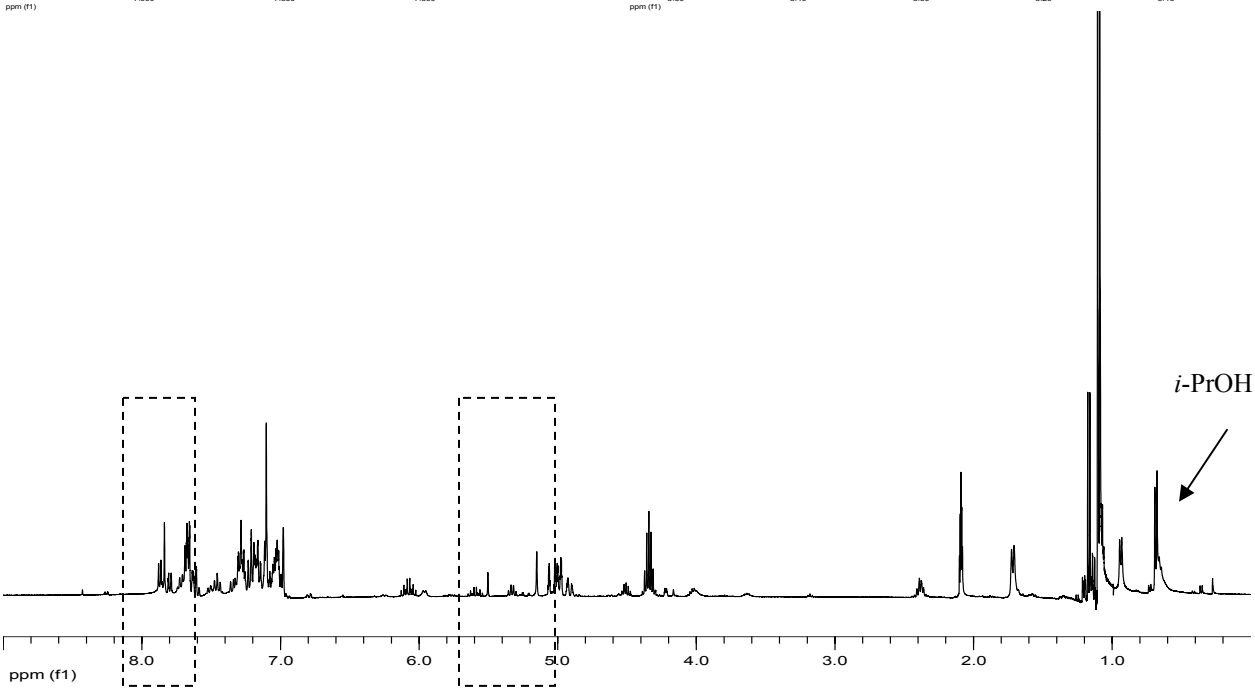
^{1}H-NMR experiment to monitor the reaction using stoichiometric amount of (*S*)-3,3'-Ph$_2$-BINOL 7h:

In a dry vial was added acyl imine **5** (20 mg, 0.10 mmol) and (*S*)-3,3'-Ph$_2$-BINOL **7h** (44mg, 0.10 mmol) and dissolved in $CD_3C_6D_5$ (5.0 mL) under Ar. The solution was charged with allyldiisopropoxyborane **4** (75 uL, 0.30 mmol) and transferred to a dry NMR tube. The reaction was monitored by ^{1}H-NMR at room temperature. The acyl imine and allyldiisopropyoxyborane were completely consumed after 15 min. In the resulting mixture, 65% of the product was assigned to the (*S*)-3,3'-Ph$_2$-BINOL associated complex. This solution was quenched with water followed by the general workup procedure. The crude mixture was subjected flash chromatography over silica gel afford the homoallylic amide product in 99:1 er.

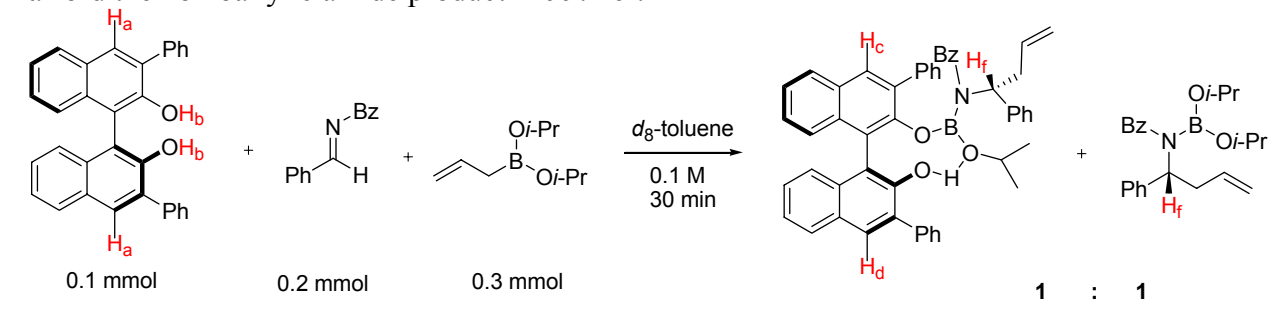


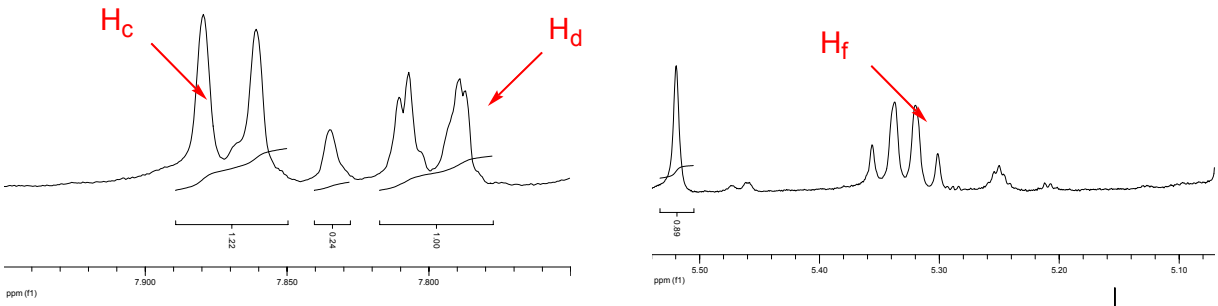


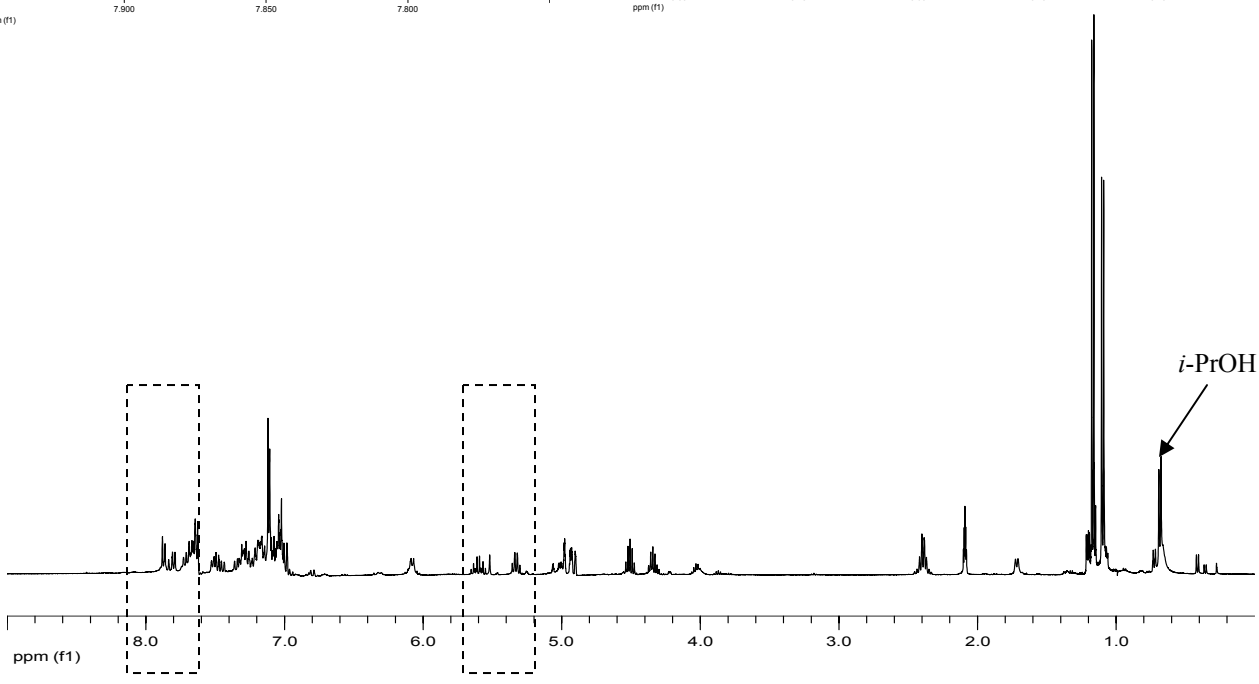




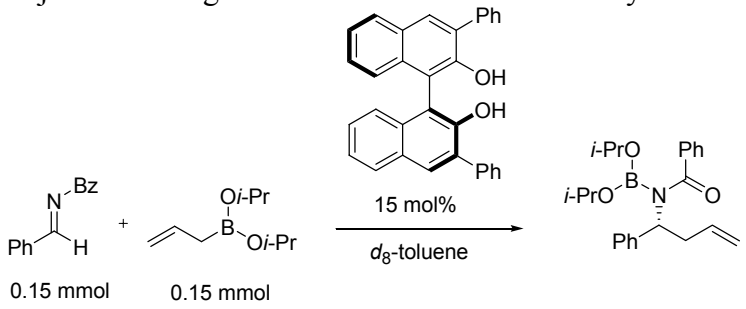
In a dry vial was added acyl imine **5** (40 mg, 0.20 mmol) and (*S*)-3,3'-Ph_2-BINOL **7h** (44mg, 0.10 mmol) and dissolved in $CD_3C_6D_5$ (5.0 mL) under Ar. The solution was charged with allyldiisopropoxyborane **4** (75 uL, 0.30 mmol) and transferred to a dry NMR tube. The reaction was monitored by ^{1}H-NMR at room temperature. The acyl imine and allyldiisopropyoxyborane were completely consumed after 30 min. In the resulting mixture, 50% of the product was assigned to the (*S*)-3,3'-Ph_2-BINOL associated complex. This solution was quenched with water followed by general workup procedure. The crude mixture was subject to silica gel column to afford the homoallylic amide product in 99:1 er.



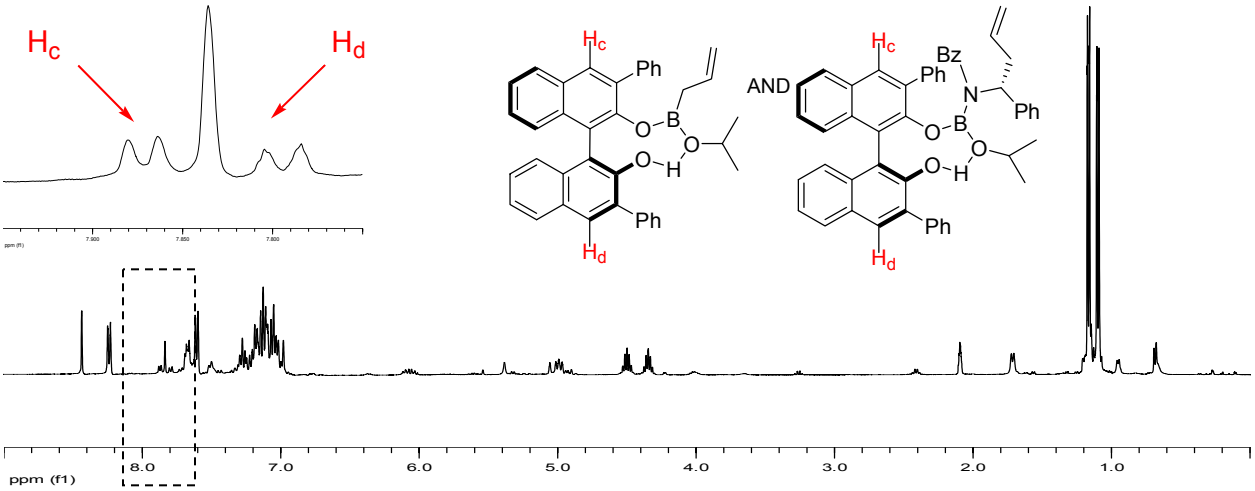




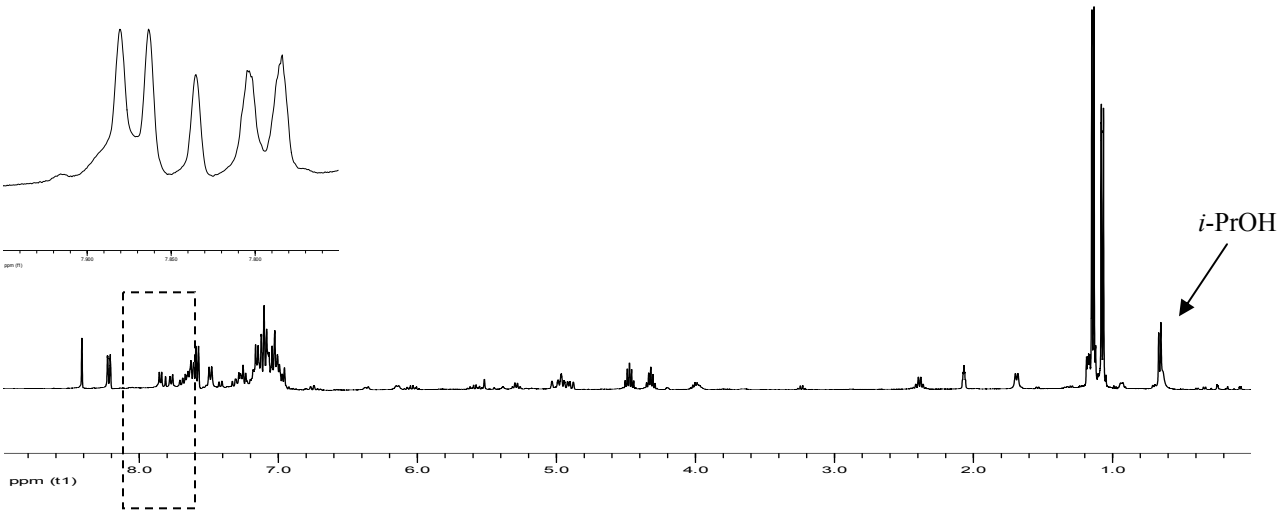
Standard ^{1}H-NMR experiment to monitor the reaction under catalytic condition:
In a dry vial the acyl imine **5** (31mg, 0.15 mmol) and (*S*)-3,3'-Ph_2-BINOL **7h** (10mg, 0.022 mmol) was dissolved in $CD_3C_6D_5$ (1.0 mL) under Ar. The solution was transferred to a dry NMR tube under Ar and charged with allyldiisopropoxyborane **4** (40 uL, 0.15 mmol). Solution was monitored by ^{1}H-NMR at room temperature for 20 h until all starting materials were consumed. This solution was quenched with water followed by general workup procedure. The crude mixture was subject to silica gel column to afford the homoallylic amide product in 99:1 er.



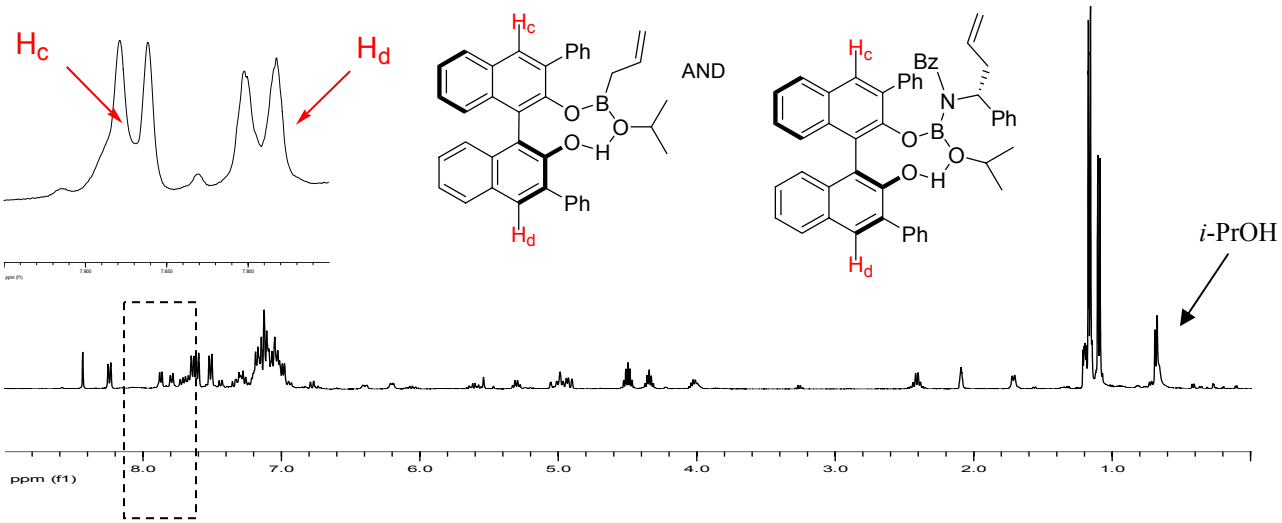
1 min



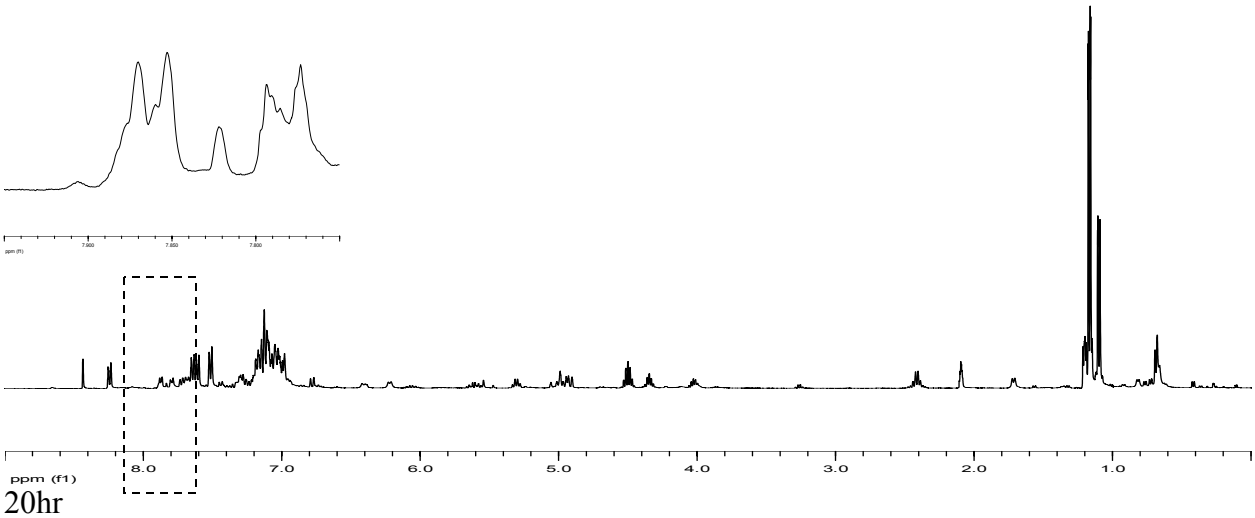
5 min



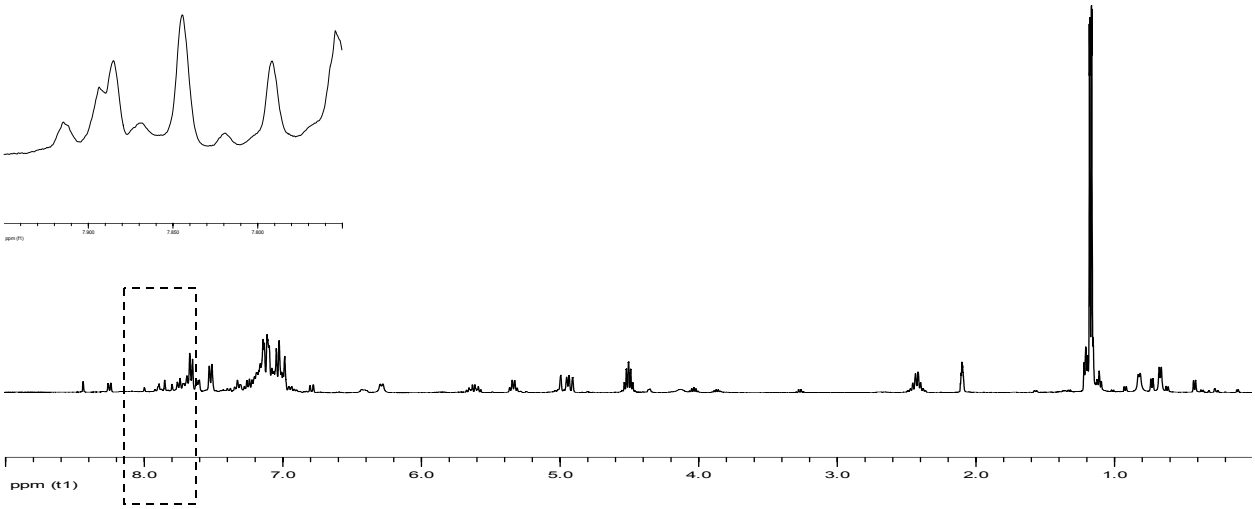
30 min



2 hr

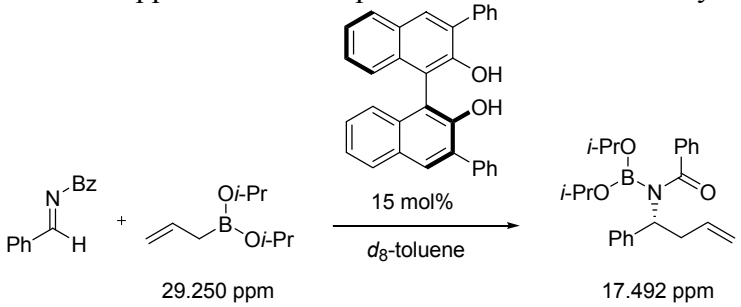


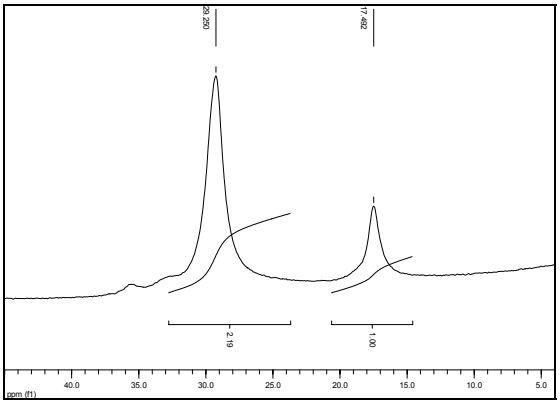
20hr



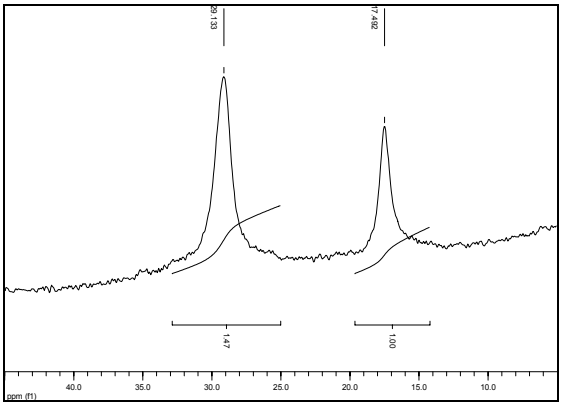
Standard ^{11}B-NMR experiment:

In a dry vial the acyl imine **5** (16mg, 0.075 mmol) and (*S*)-3,3'-Ph_2-BINOL **7h** (5mg, 0.011 mmol) was dissolved in $CD_3C_6D_5$ (1.0 mL) under Ar. The solution was transferred to a dry NMR tube under Ar and charged with allyldiisopropoxyborane **4** (20 uL, 0.075 mmol). Solution was monitored by ^{11}B-NMR at room temperature for 48 hours. Disappearance of allyldiisopropoxyborane and appearance of the product was simultaneously monitored.

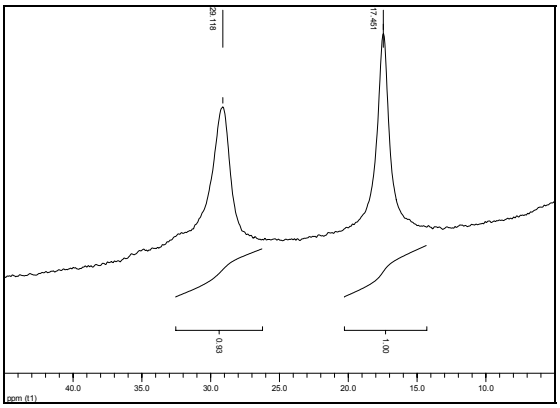




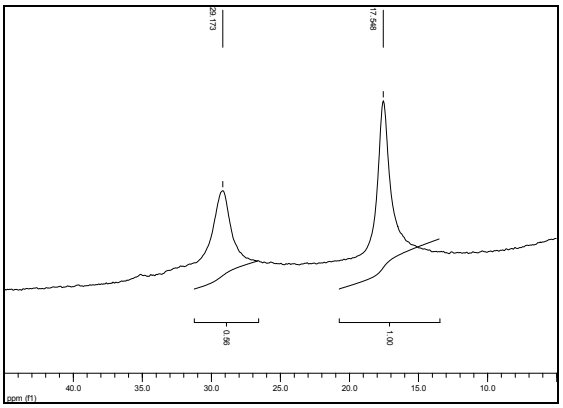
15 min



8 hr



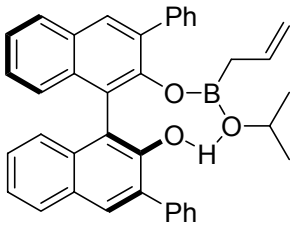
16 h



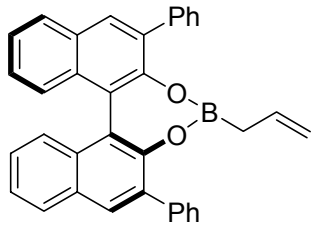
24 h

Mass spectra

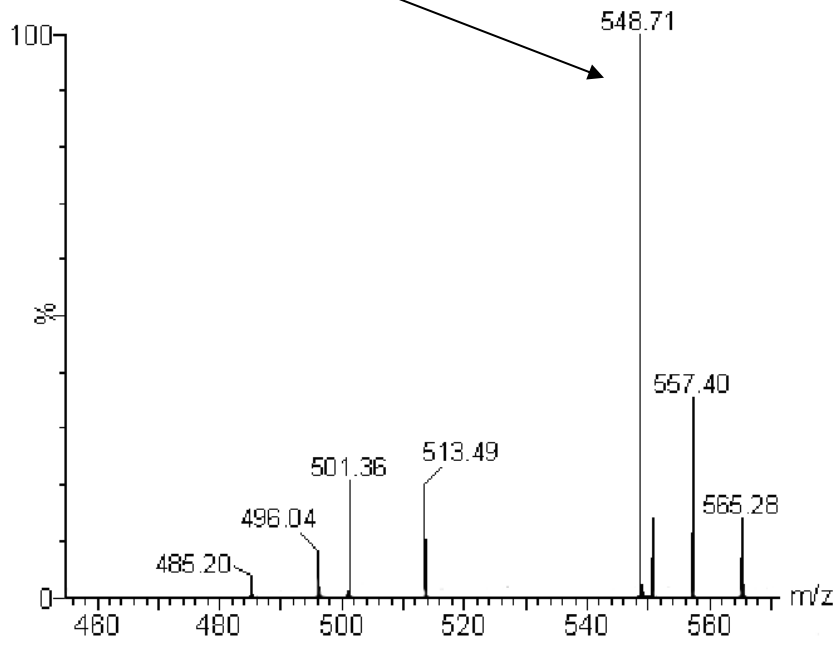
To a dry vial was added allyldiisopropoxyborane **4** (40 uL, 0.10 mmol) and $CD_3C_6D_5$ (0.5 mL) under Ar. (*S*)-3,3'-Ph_2-BINOL **7h** (6.8 mg, 0.015 mmol) was added. The solution was stirred under Ar at room temperature for 4 hours. This solution (0.1 mL) was directly infused into MicroMass ZQ 2000 mass spectrometer with positive electronspray ionization mode (ESI+, ES/voltages: capillary 3.01 KV, cone 24 V; Temperature: source 130 ˚C, desolvation 260 ˚C; Gas flow: desolvation 250 L/h, Cone 50 L/h; Pump flow: 60 μL/min). The mass of BINOL-boronate complex having one isopropoxy ligand was observed.



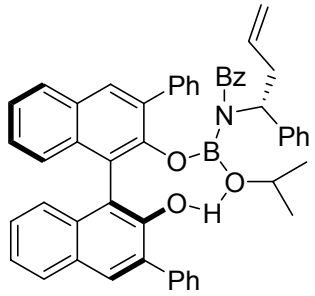
Chemical Formula: $C_{38}H_{33}BO_3$
Exact Mass: 548.2523



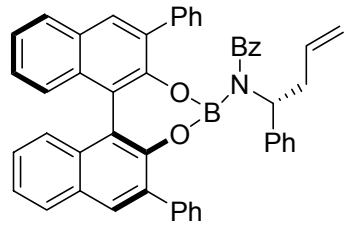
Chemical Formula: $C_{35}H_{25}BO_2$
Exact Mass: 488.1948



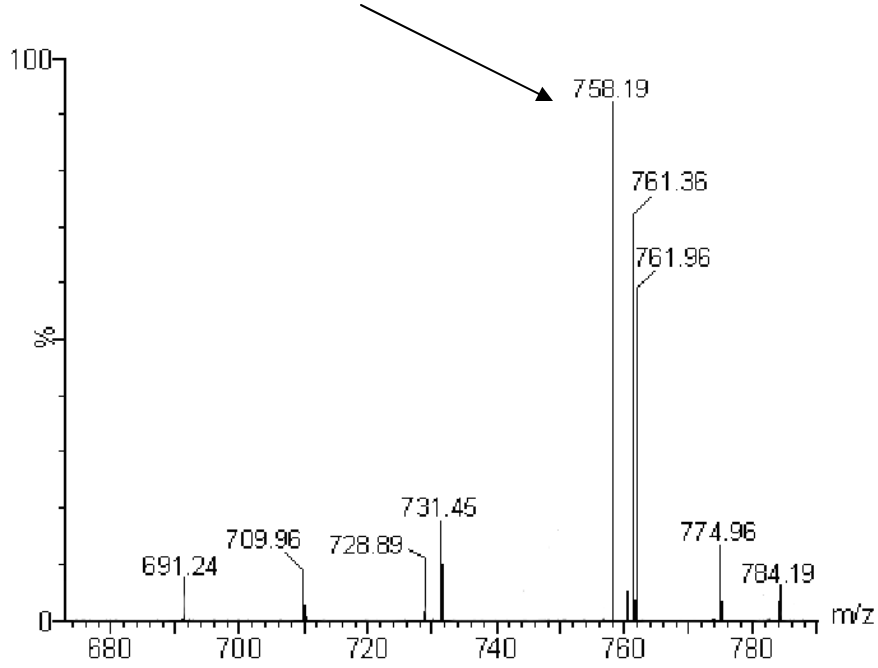
To a dry vial were added the acyl imine **5** (40 mg, 0.20 mmol), (*S*)-3,3'-Ph_2-BINOL **7h** (44mg, 0.10 mmol) and $CD_3C_6D_5$ (5.0 mL) under Ar. The solution was charged with allyldiisopropoxyborane **4** (46 uL, 0.20 mmol). After 15 min, the solution (0.1 mL) was infused into MicroMass ZQ 2000 mass spectrometer with positive electron spray ionization mode (ESI+, ES/voltages: capillary 3.01 KV, cone 24 V; Temperature: source 130 ˚C, desolvation 260 ˚C; Gas flow: desolvation 250 L/h, Cone 50 L/h; Pump flow: 60 μL/min). The mass of homoallylic amide product having one isopropoxy ligand was observed.



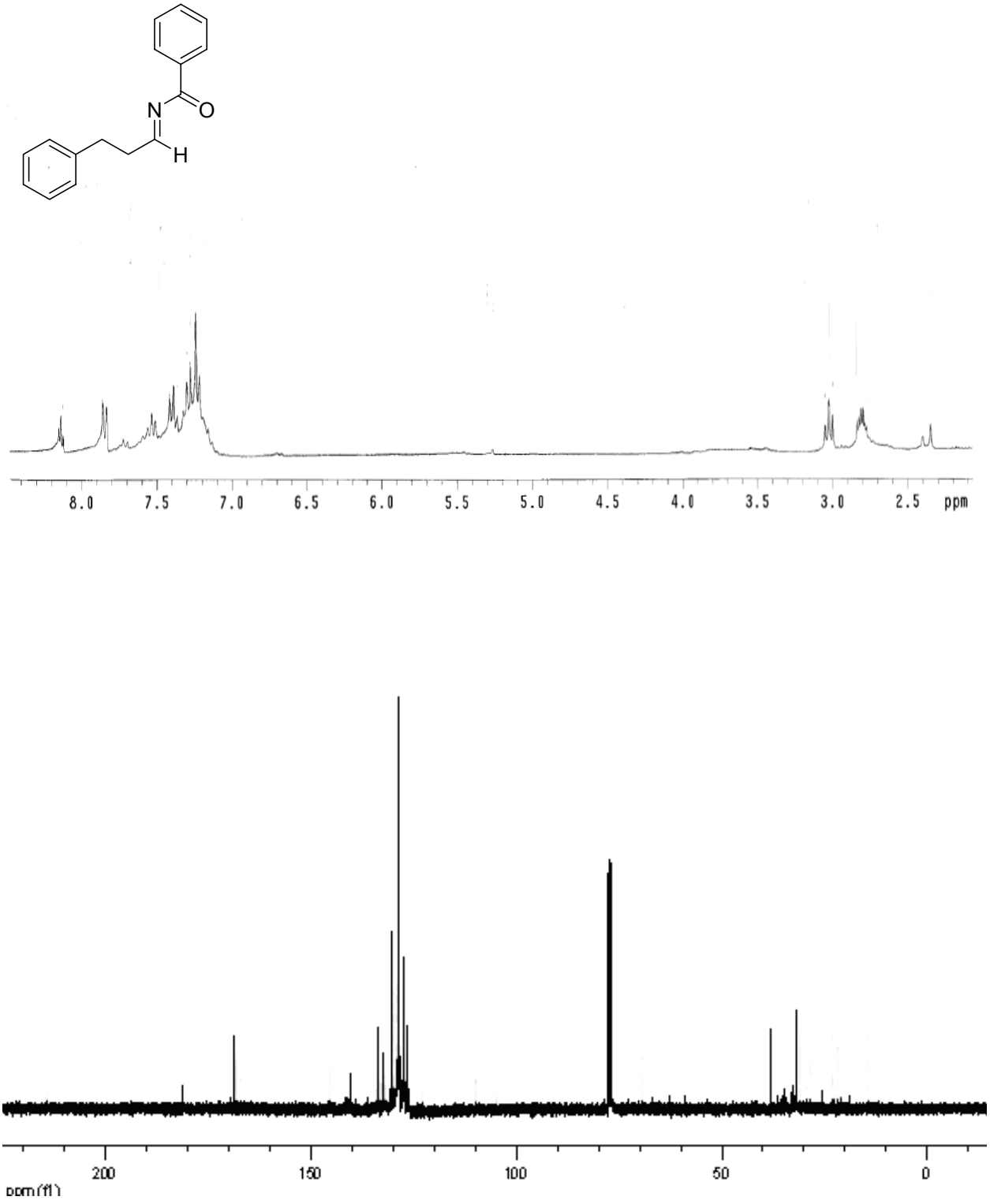
Chemical Formula: $C_{52}H_{44}BNO_4$
Caculated Mass: 757.34

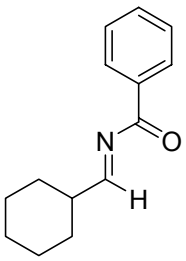


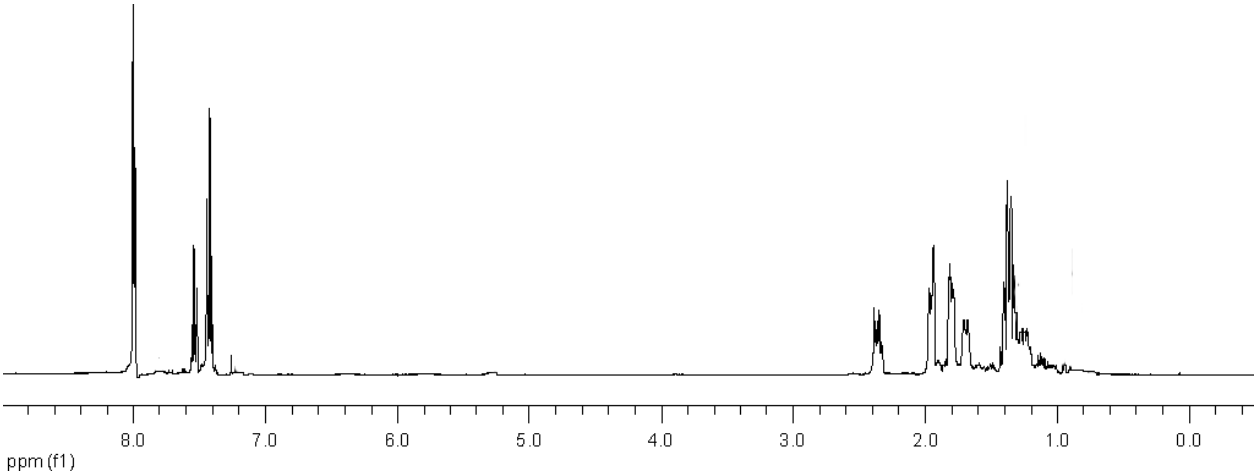
Chemical Formula: $C_{49}H_{36}BNO_3$
Calculated Mass: 697.28

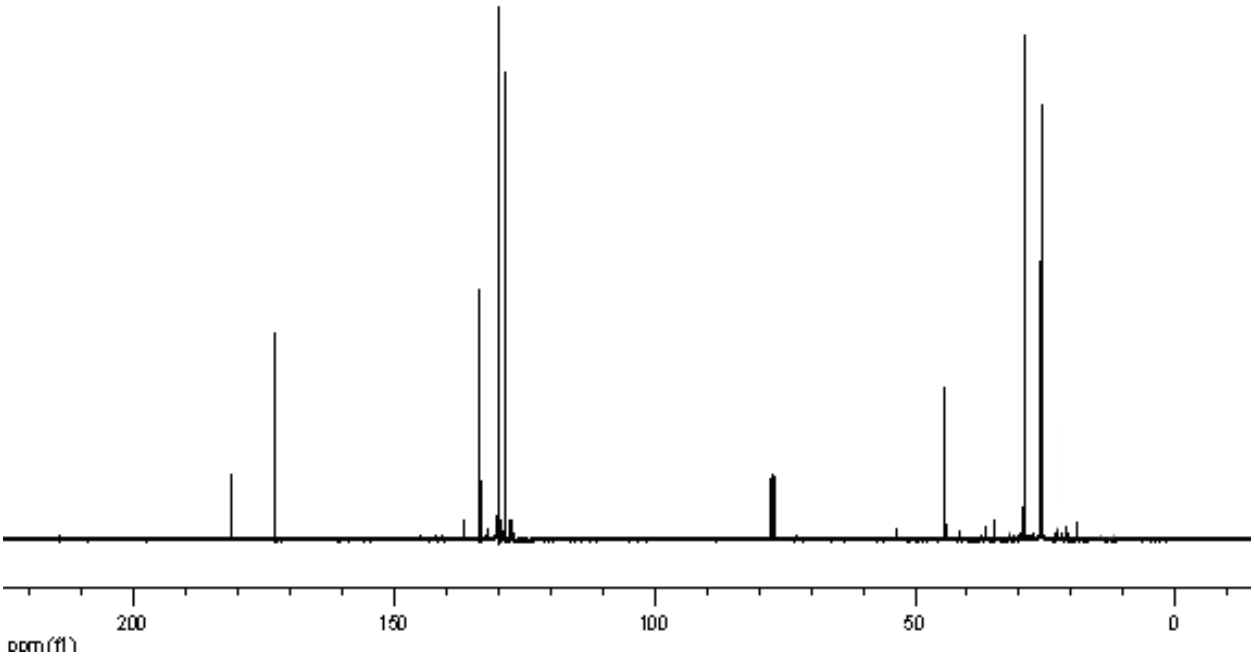


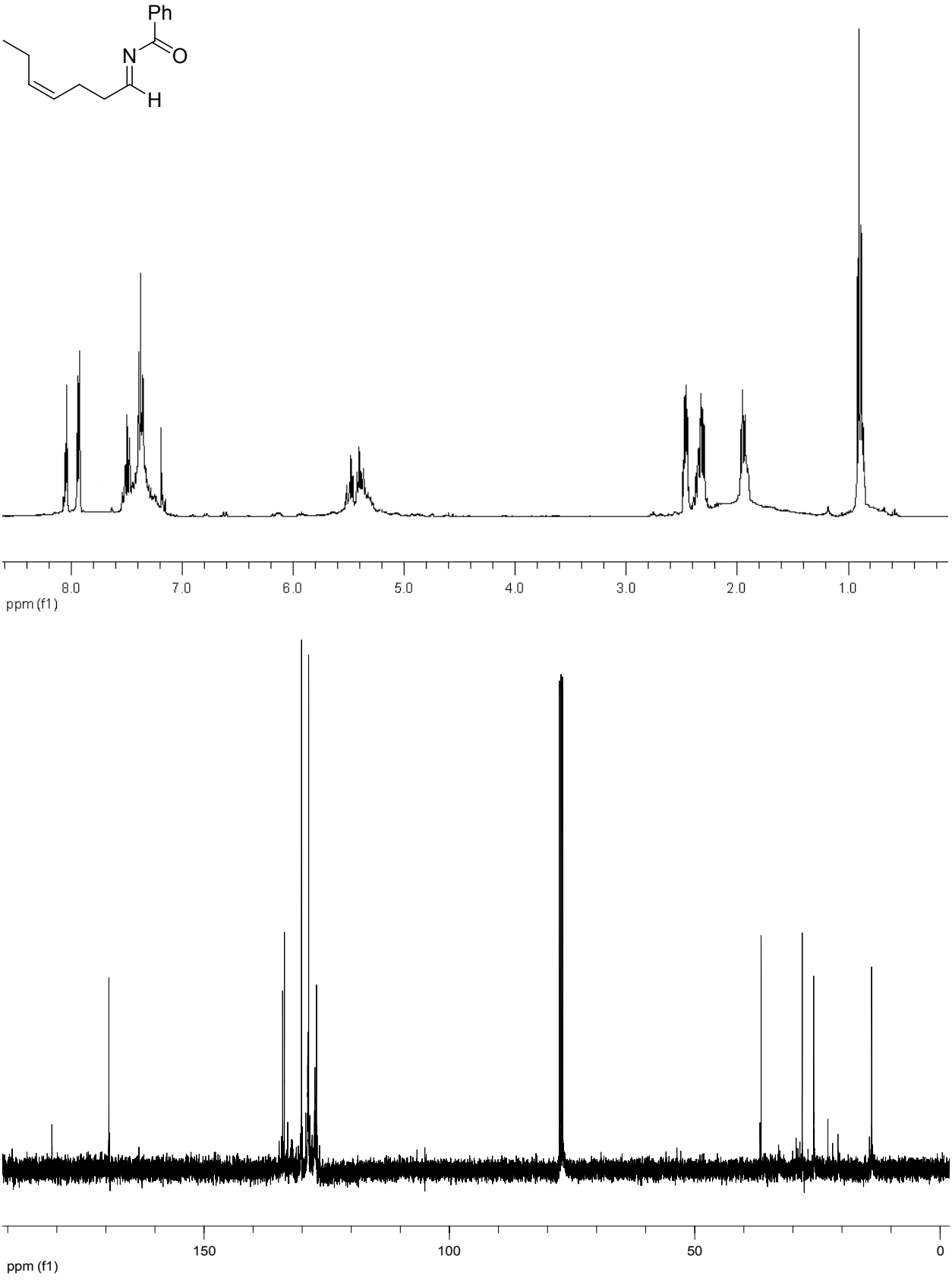
NMR Spectra of Aliphatic Imines



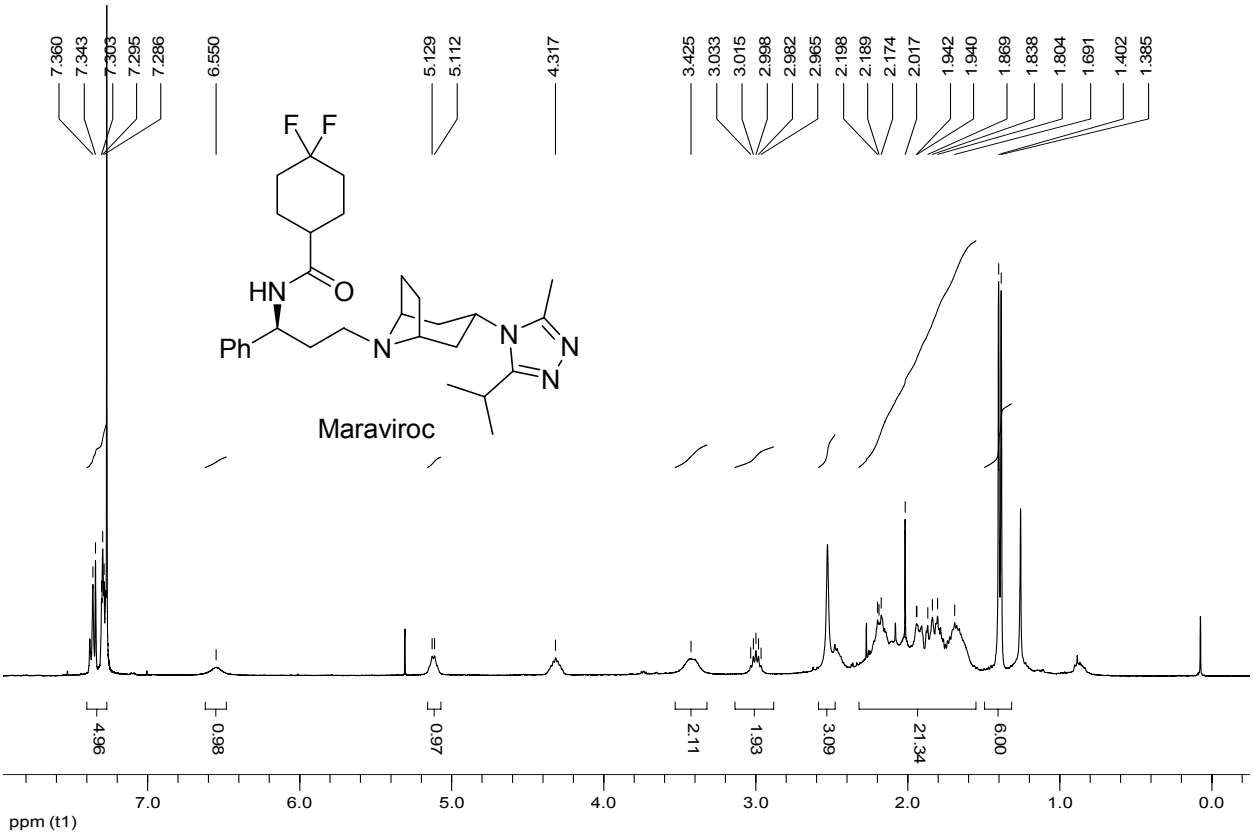

N
O
H


8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


200
150
100
50
0
ppm (f1)


Ph
N
O
H
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)
150
100
50
0
ppm (f1)

Maraviroc


7.360
7.343
7.303
7.295
7.286
6.550
5.129
5.112
4.317
3.425
3.033
3.015
2.998
2.982
2.965
2.198
2.189
2.174
2.017
1.942
1.940
1.869
1.838
1.804
1.691
1.402
1.385
F F
HN
O
Ph
N
N
N
N
Maraviroc
4.96
0.98
0.97
2.11
1.93
3.09
21.34
6.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

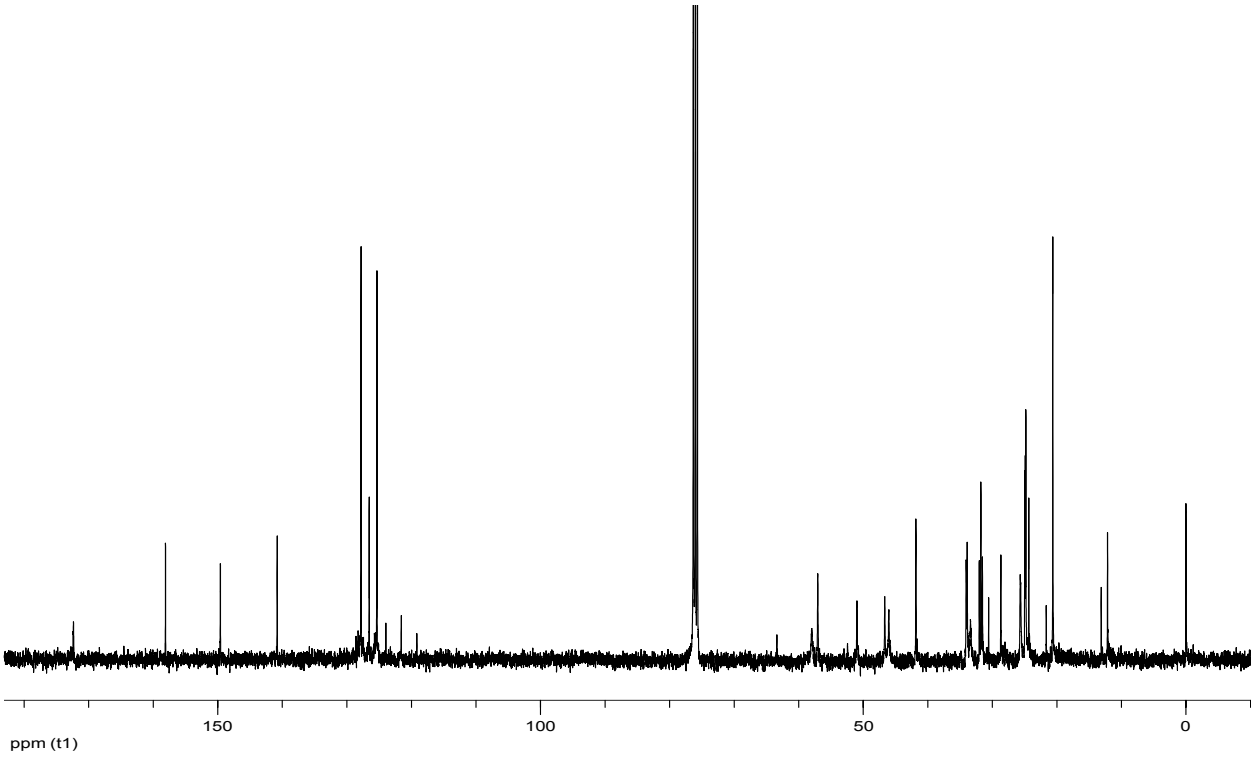
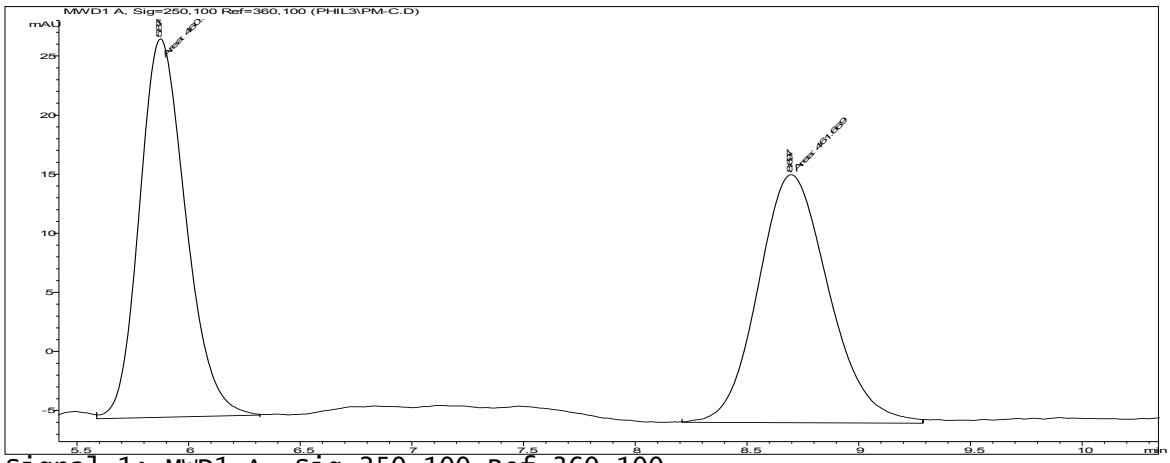
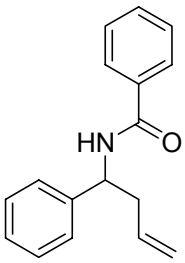

150
100
50
0
ppm (t1)

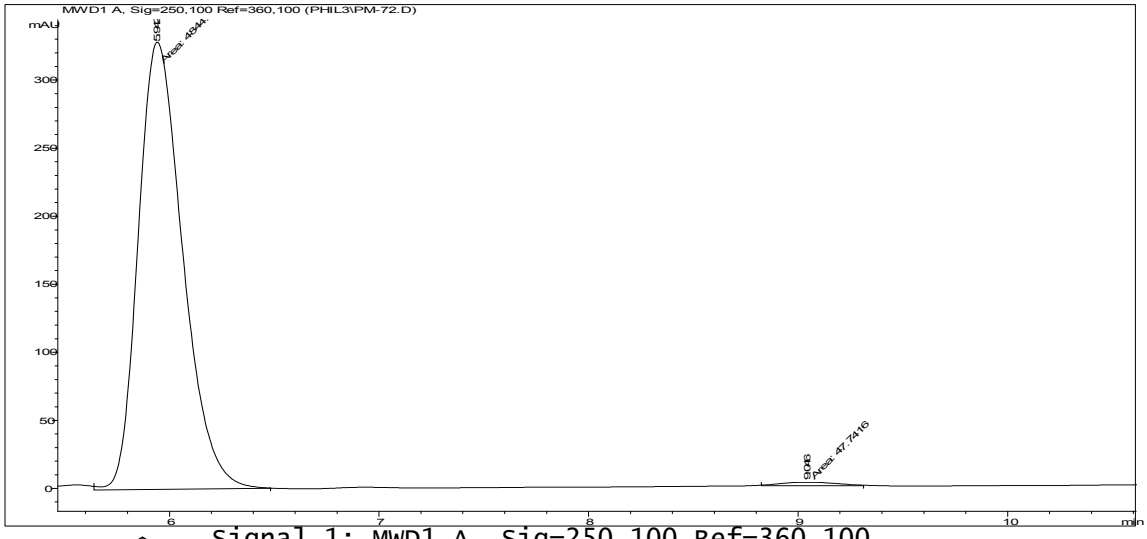
Table 3, entry 1: 9a Chiralcel®OD Column, Hexane:IPA = 90:10, 1.5 mL/min, 250 nm



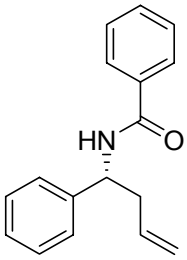
Signal 1: MWD1 A, Sig=250,100 Ref=360,100



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.874	MM	0.2398	460.98135	32.04158	49.9628
2	8.697	MM	0.3667	461.66864	20.98511	50.0372
Totals :				922.64999	53.02669	

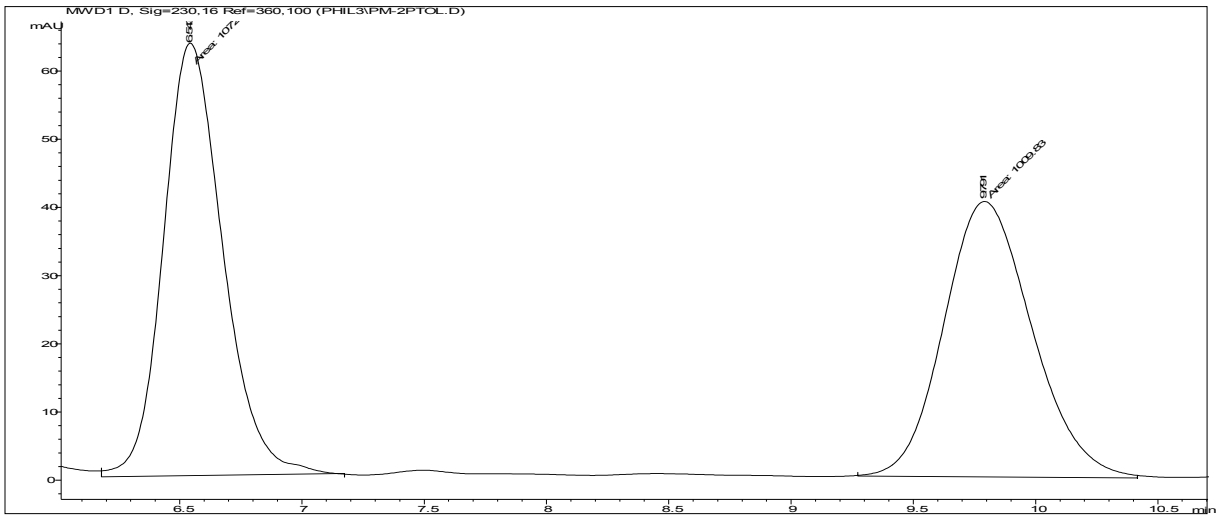


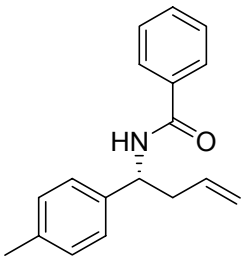
Signal 1: MWD1 A, Sig=250,100 Ref=360,100



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.942	MM	0.2455	4844.96533	328.87216	99.0242
2	9.046	MM	0.3072	47.74155	2.59021	0.9758
Totals :				4892.70688	331.46237	

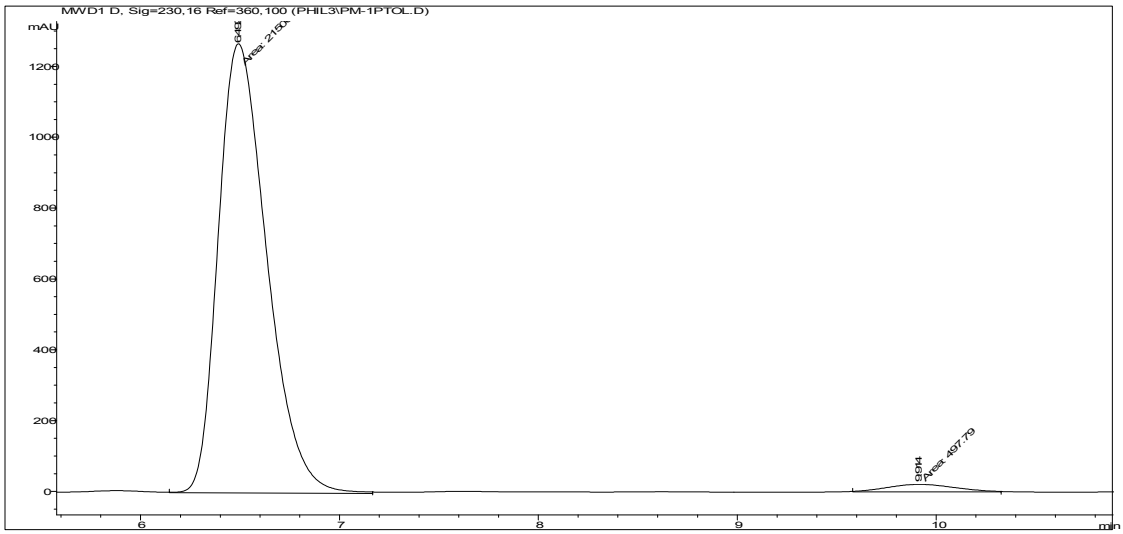
Table 3, entry 2, 9b: Chiralcel®OD Column, Hexane:IPA = 90:10, 1.5 mL/min, 230 nm

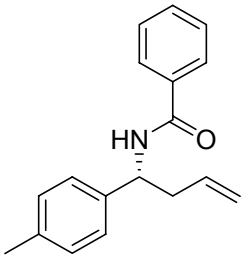




Signal 4: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.543	MM	0.2817	1072.62244	63.45734	51.5076
2	9.791	MM	0.4168	1009.83295	40.37722	48.4924
Totals :				2082.45538	103.83456	

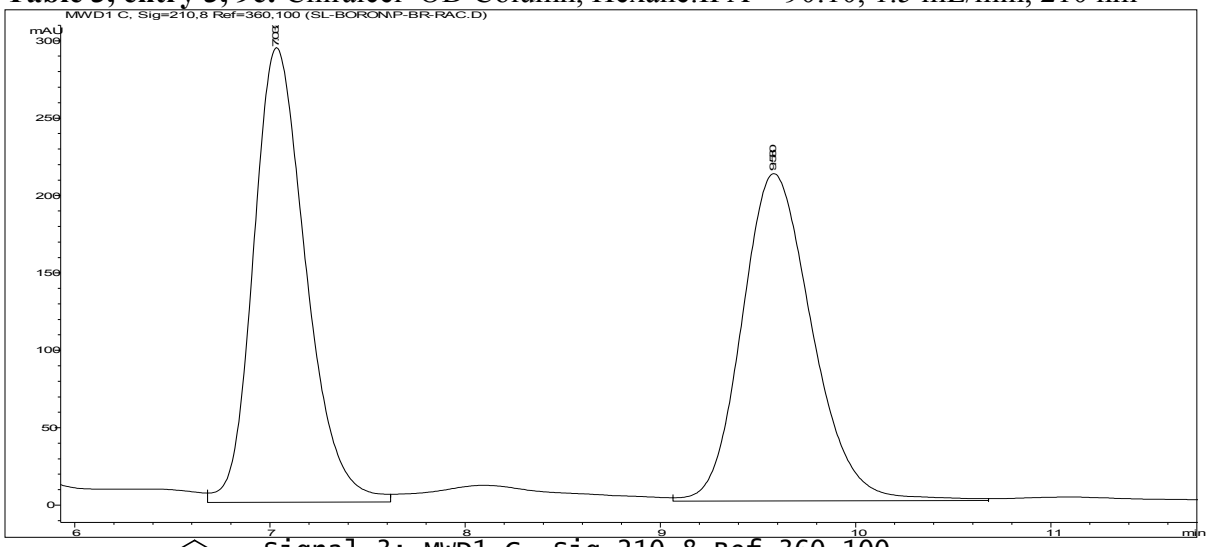


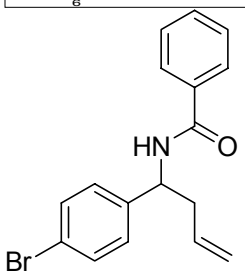


Signal 4: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.492	MM	0.2824	2.15001e4	1269.01355	97.7371
2	9.914	MM	0.3944	497.79001	21.03384	2.2629
Totals :				2.19979e4	1290.04739	

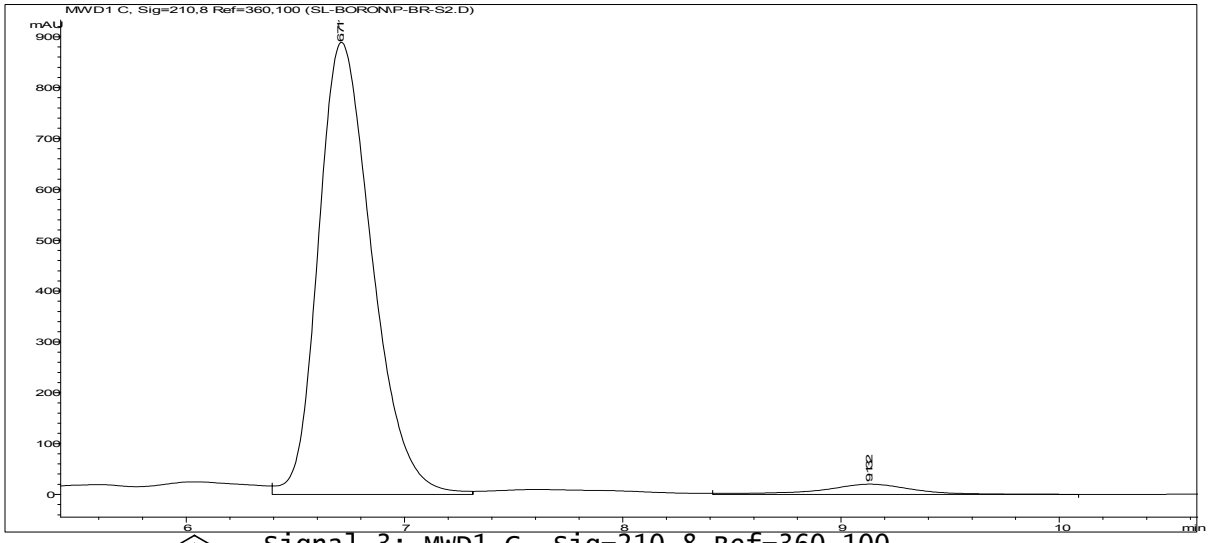
Table 3, entry 3, 9c: Chiralcel®OD Column, Hexane:IPA = 90:10, 1.5 mL/min, 210 nm

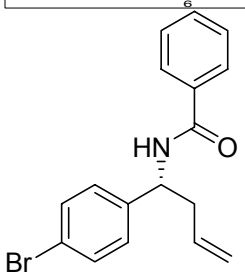




Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.033	VV	0.2893	5467.69482	293.55197	50.8933
2	9.580	VB	0.3870	5275.75000	211.50700	49.1067
Totals :				1.07434e4	505.05898	

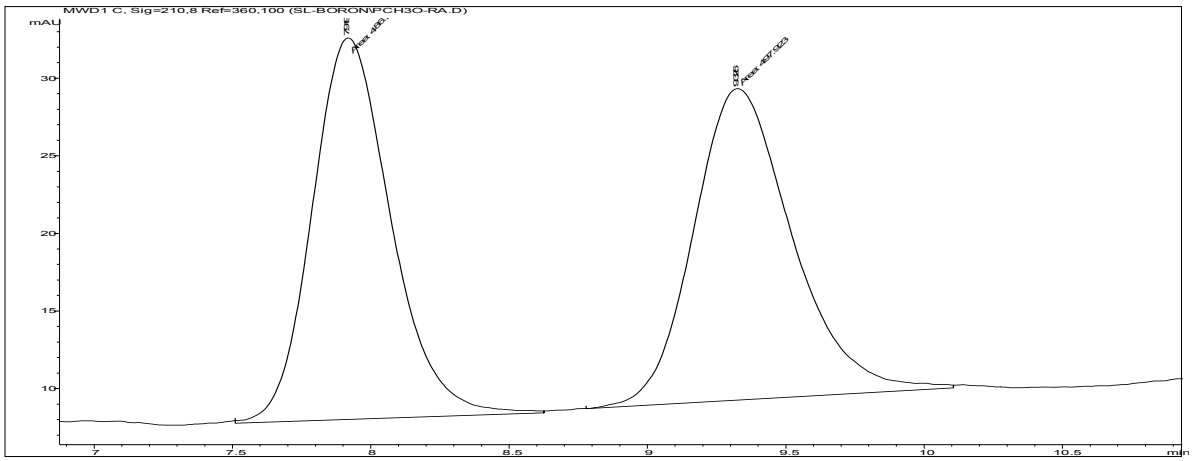


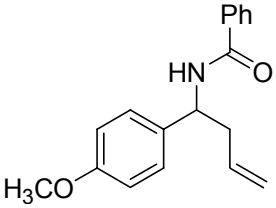


Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.711	MM	0.2817	1.48848e4	880.75336	97.5460
2	9.141	MM	0.3555	374.46323	17.55733	2.4540
Totals :				1.52592e4	898.31069	

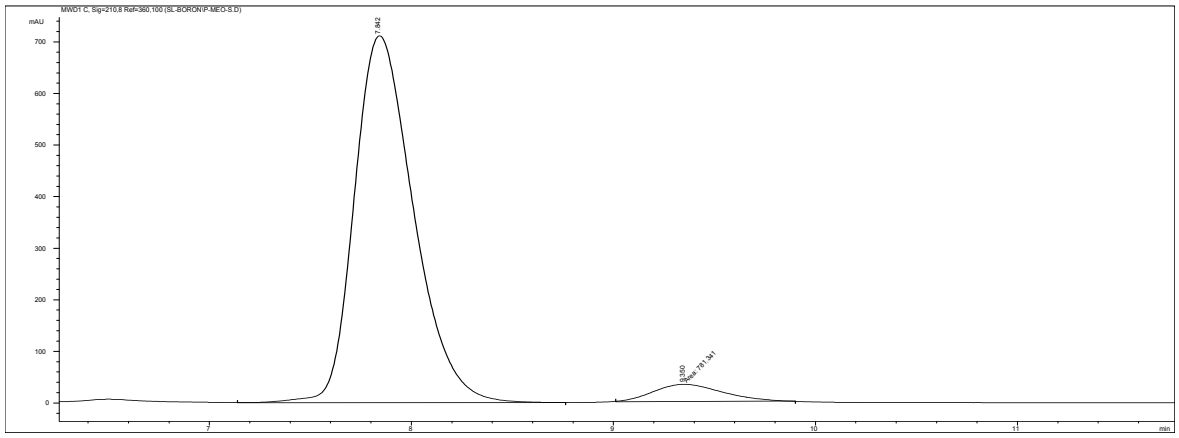
Table 3, entry 4, 9d: Chiralcel®OD Column, Hexane:IPA = 90:10, 1.5 mL/min, 210 nm

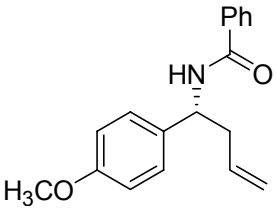




Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.919	MM	0.3299	486.70691	24.59229	49.4304
2	9.326	MM	0.4134	497.92310	20.07438	50.5696
Totals :				984.63000	44.66667	

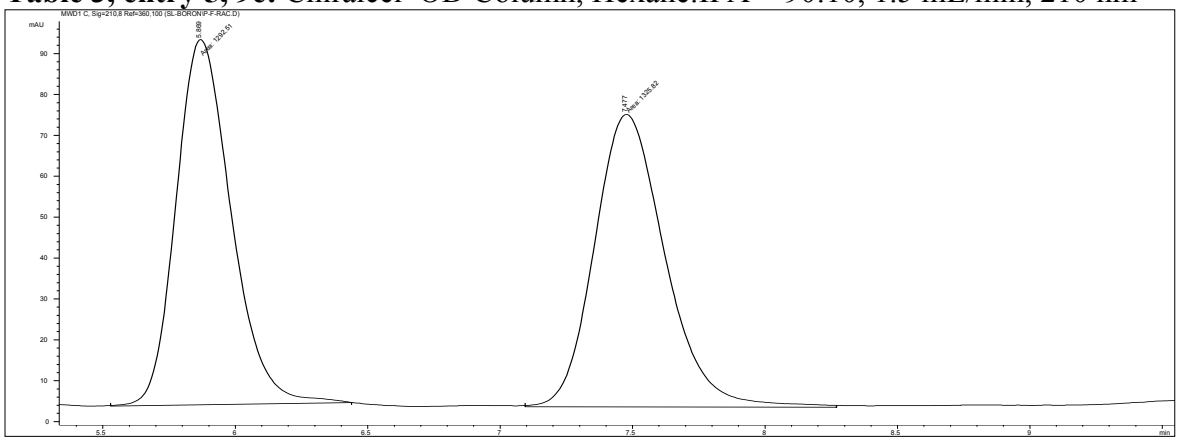


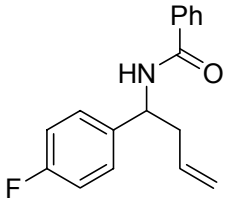


Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.842	VV	0.3137	1.44910e4	711.34308	94.8840
2	9.350	MM	0.3931	781.34064	33.12932	5.1160
Totals :				1.52724e4	744.47240	

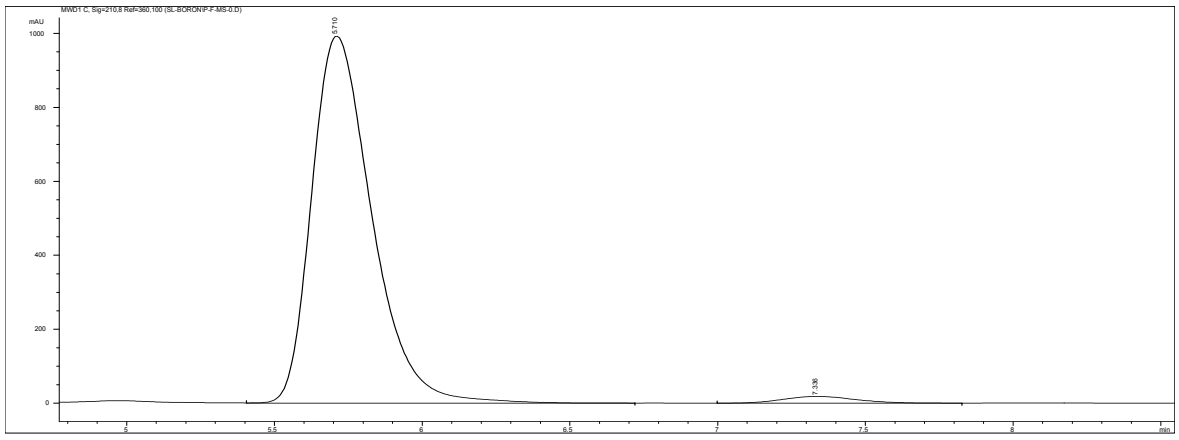
Table 3, entry 5, 9e: Chiralcel®OD Column, Hexane:IPA = 90:10, 1.5 mL/min, 210 nm

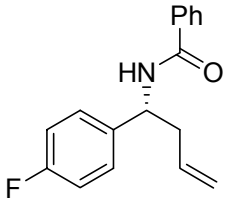




Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.869	MM	0.2412	1292.50537	89.32421	49.3638
2	7.477	MM	0.3089	1325.81873	71.52424	50.6362
Totals :				2618.32410	160.84845	

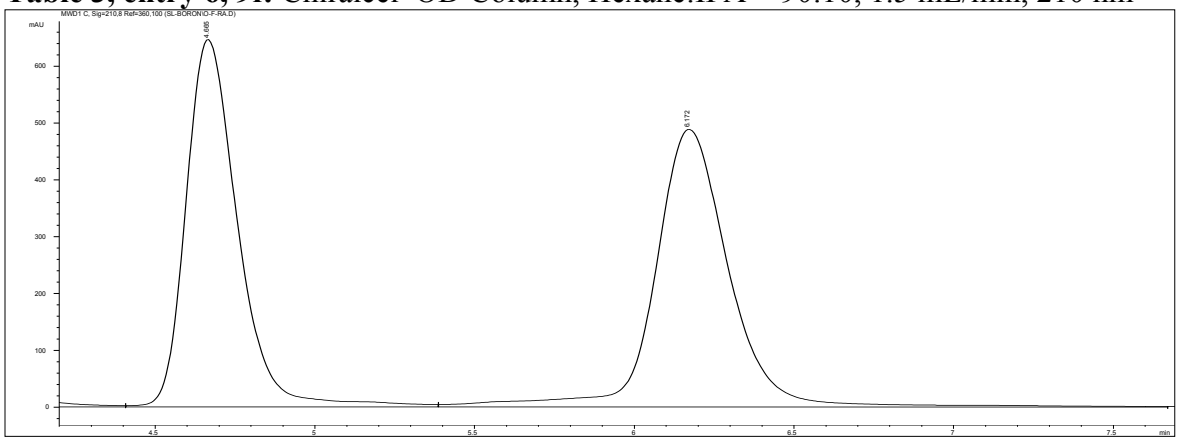


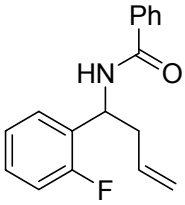


Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.710	VB	0.2172	1.40494e4	992.48022	97.8511
2	7.336	VP	0.2645	308.53735	18.13293	2.1489
Totals :				1.43579e4	1010.61316	

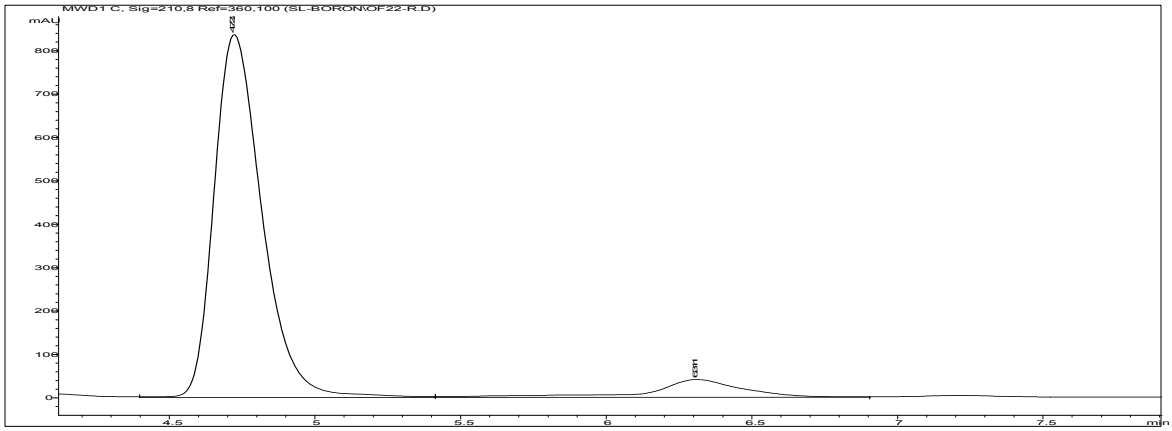
Table 3, entry 6, 9f: Chiralcel®OD Column, Hexane:IPA = 90:10, 1.5 mL/min, 210 nm

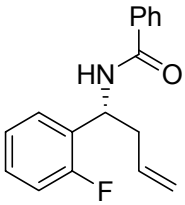




Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.665	MM	0.1790	6887.73730	641.48547	49.7373
2	6.172	MM	0.2428	6960.50195	477.70819	50.2627
Totals :				1.38482e4	1119.19366	

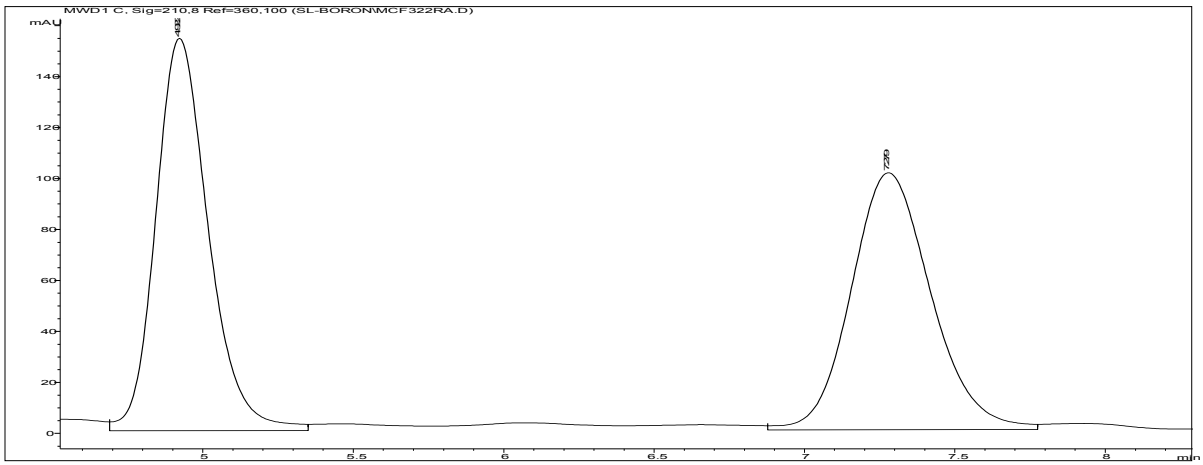


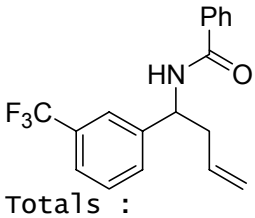


Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.722	VV	0.1753	9565.36133	836.96912	95.5123
2	6.311	MM	0.2272	449.43320	32.96613	4.4877
Totals :				1.00148e4	869.93524	

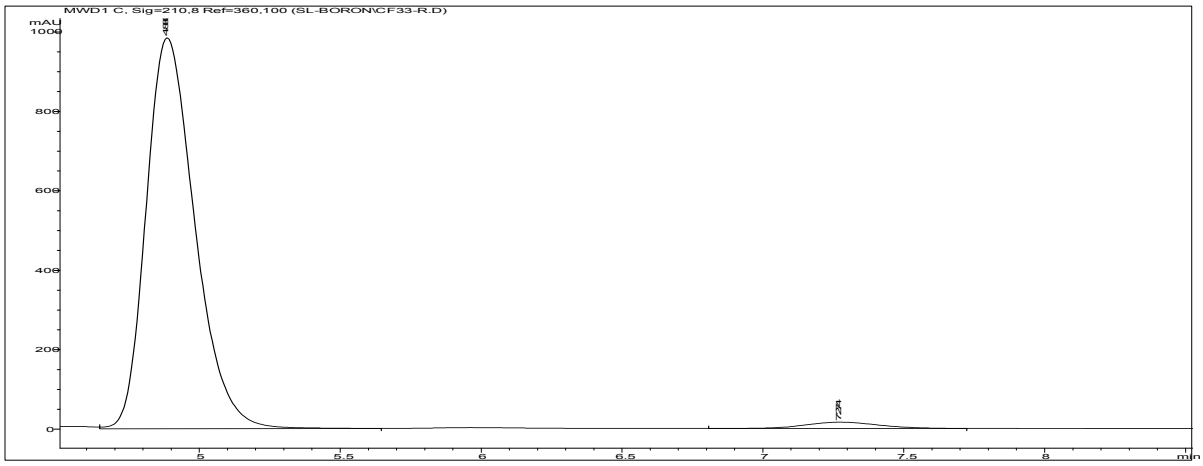
Table 3, entry 7, 9g: Chiralcel®OD Column, Hexane:IPA = 90:10, 1.5 mL/min, 210 nm

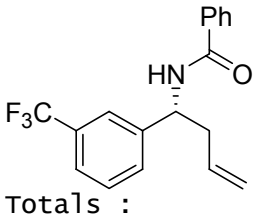




Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.922	VV	0.1859	1874.17468	154.05171	50.2262
2	7.279	VV	0.2849	1857.29565	100.83331	49.7738
Totals :				3731.47034	254.88502	

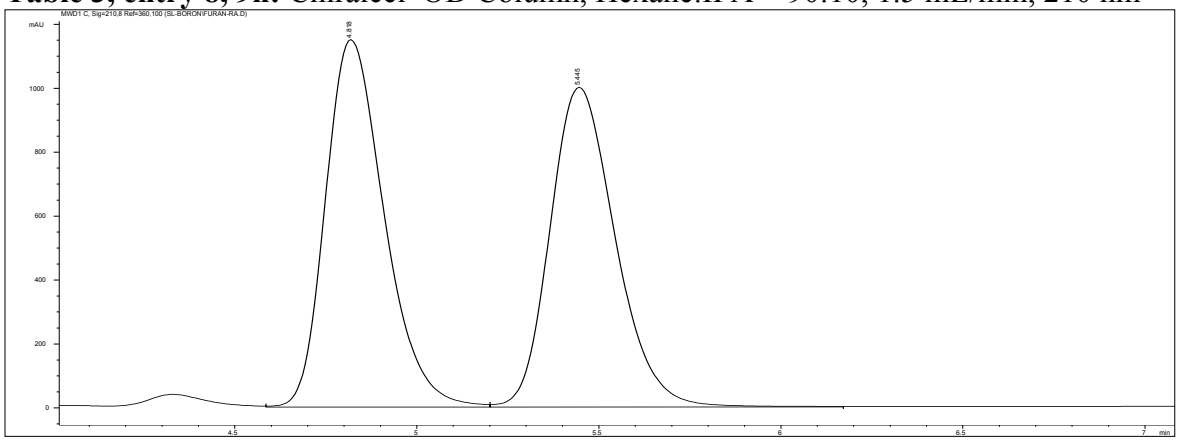


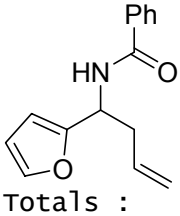


Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.886	VB	0.1863	1.18352e4	984.28387	97.5079
2	7.274	VV	0.2841	302.48611	16.03446	2.4921
Totals :				1.21377e4	1000.31833	

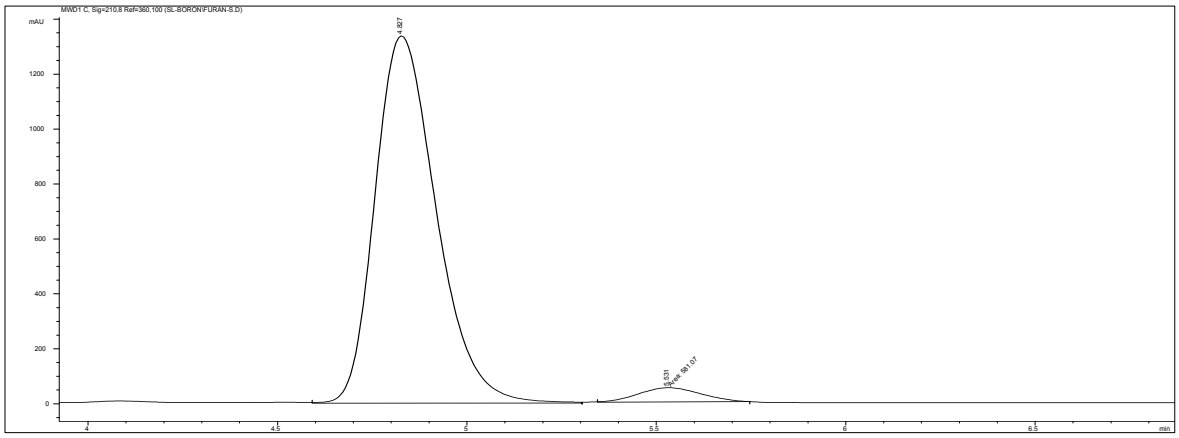
Table 3, entry 8, 9h: Chiralcel®OD Column, Hexane:IPA = 90:10, 1.5 mL/min, 210 nm

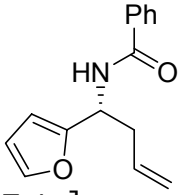




Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.818	VV	0.1729	1.29056e4	1149.97949	50.8263
2	5.445	VB	0.1936	1.24860e4	1000.35681	49.1737
Totals :				2.53916e4	2150.33630	

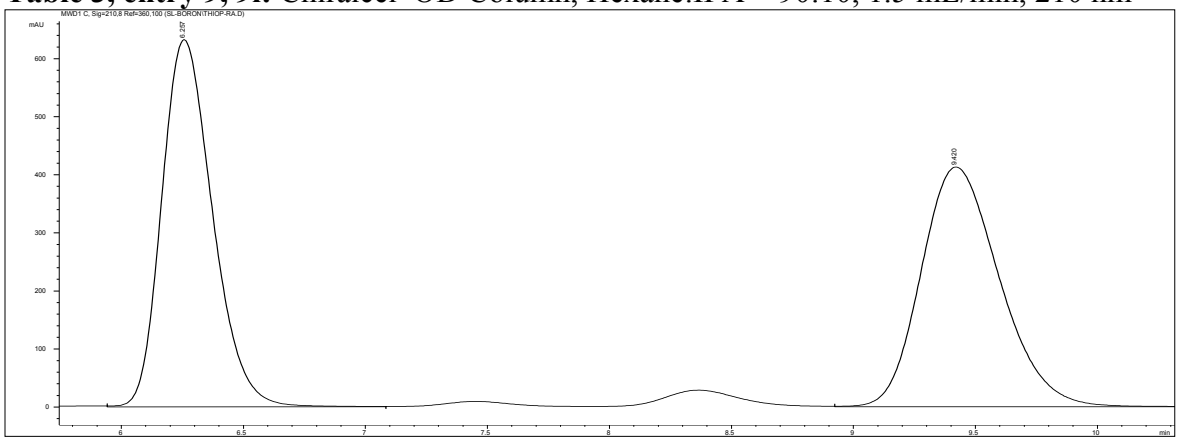


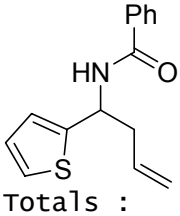


Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.827	VV	0.1748	1.49942e4	1336.92786	96.2693
2	5.531	MM	0.1891	581.06952	51.20559	3.7307
Totals :				1.55753e4	1388.13345	

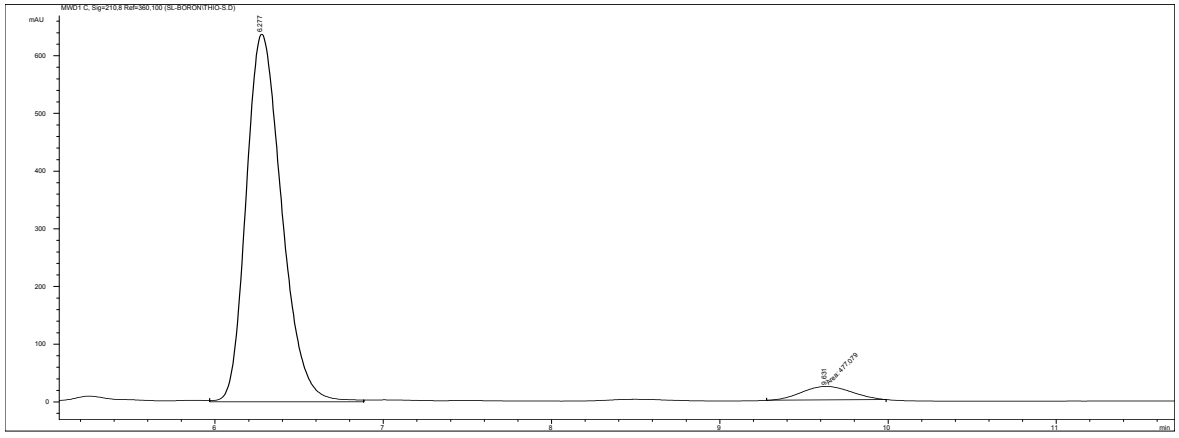
Table 3, entry 9, 9i: Chiralcel®OD Column, Hexane:IPA = 90:10, 1.5 mL/min, 210 nm

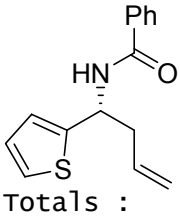




Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.257	VB	0.2246	9138.05762	632.39270	49.8643
2	9.420	VB	0.3498	9187.80469	412.66037	50.1357
Totals :				1.83259e4	1045.05307	

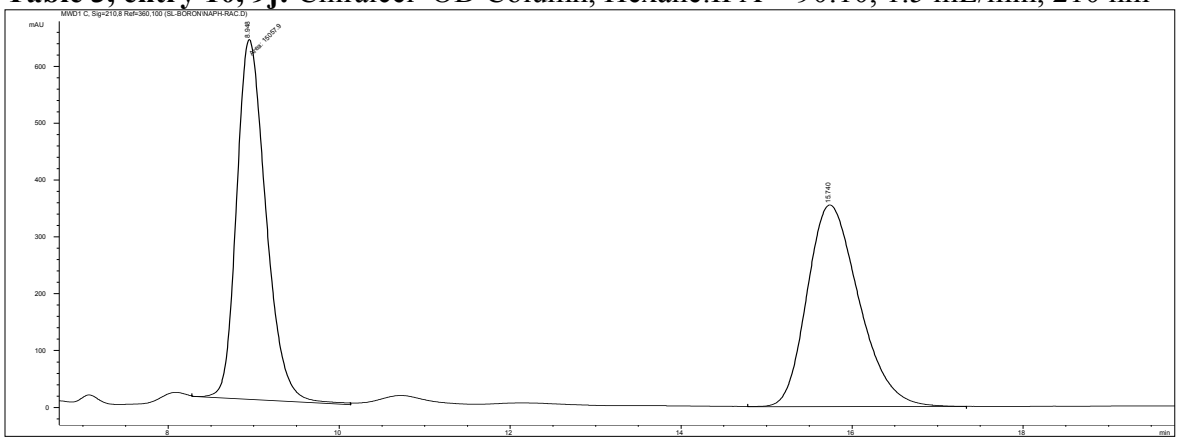


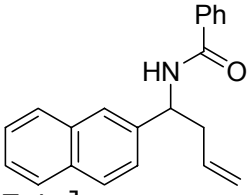


Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.277	VV	0.2294	9359.82520	637.17743	95.1501
2	9.631	MM	0.3395	477.07889	23.41896	4.8499
Totals :				9836.90408	660.59639	

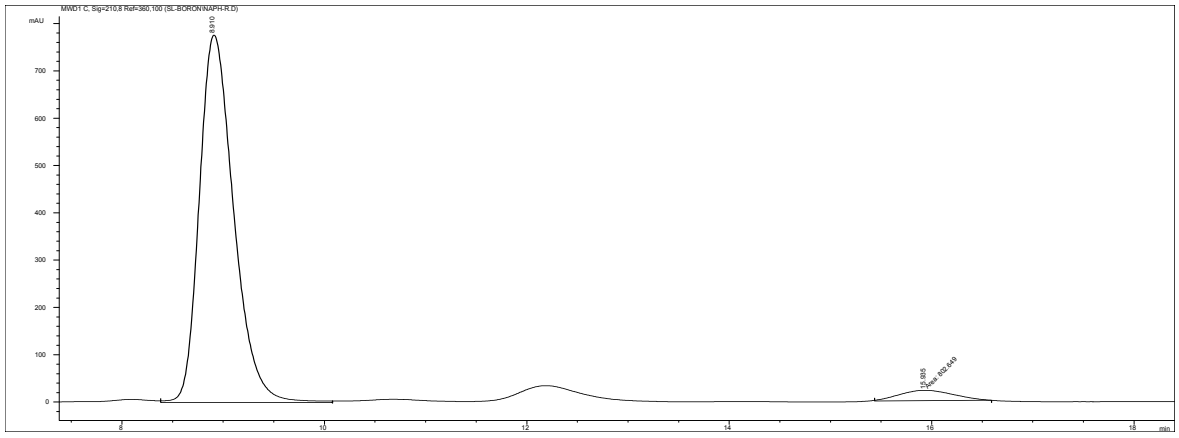
Table 3, entry 10, 9j: Chiralcel®OD Column, Hexane:IPA = 90:10, 1.5 mL/min, 210 nm

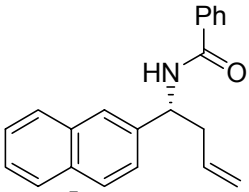




Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.948	MM	0.3965	1.50579e4	632.92438	50.2528
2	15.740	VV	0.6524	1.49064e4	354.61392	49.7472
Totals :				2.99643e4	987.53830	

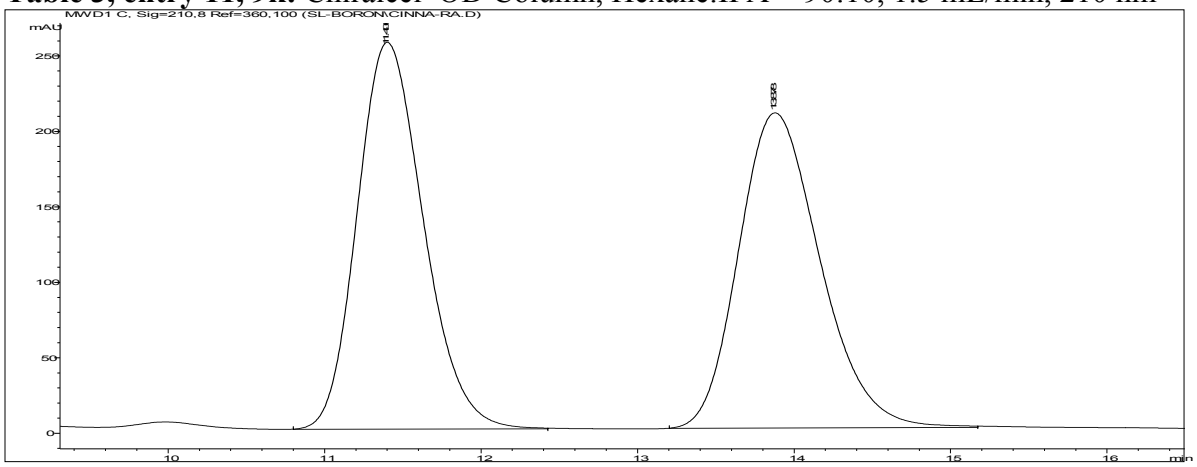


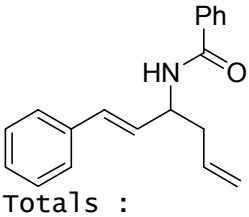


Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.910	VB	0.3628	1.82864e4	776.43866	95.7952
2	15.935	MM	0.6140	802.64948	21.78878	4.2048
Totals :				1.90891e4	798.22744	

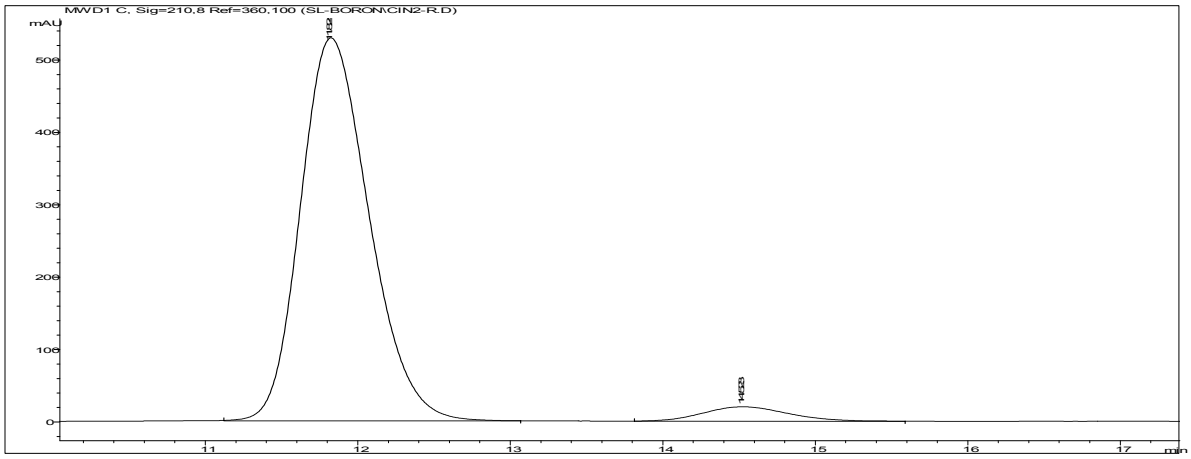
Table 3, entry 11, 9k: Chiralcel®OD Column, Hexane:IPA = 90:10, 1.5 mL/min, 210 nm

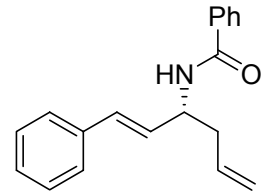




Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.400	BB	0.4593	7543.50537	256.37012	49.9571
2	13.878	BB	0.5621	7556.45703	208.87456	50.0429
Totals :			1.51000e4	465.24467		

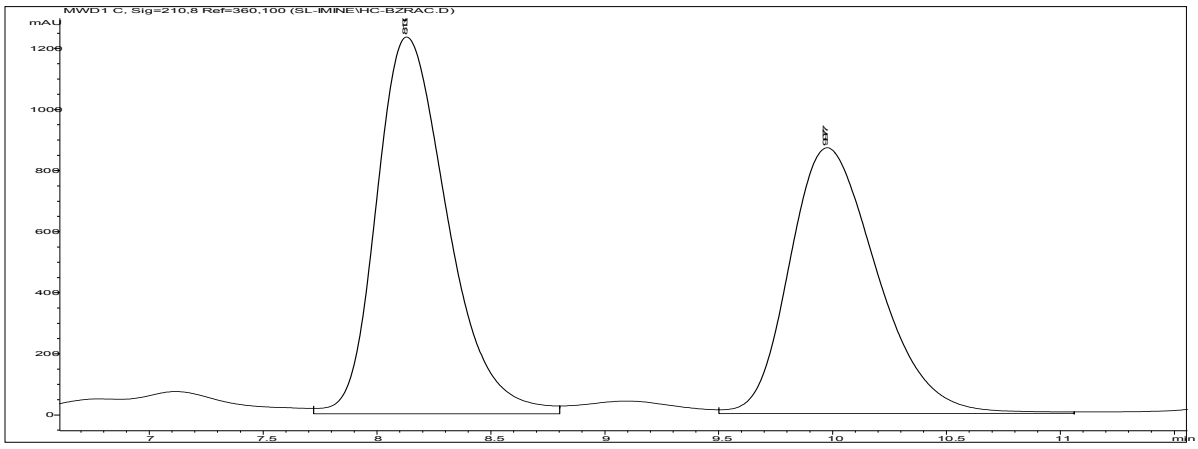


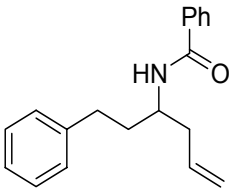


Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.824	BB	0.4849	1.65499e4	529.06519	95.5603
2	14.523	PB	0.5954	768.89362	19.87295	4.4397
Totals :			1.73188e4	548.93814		

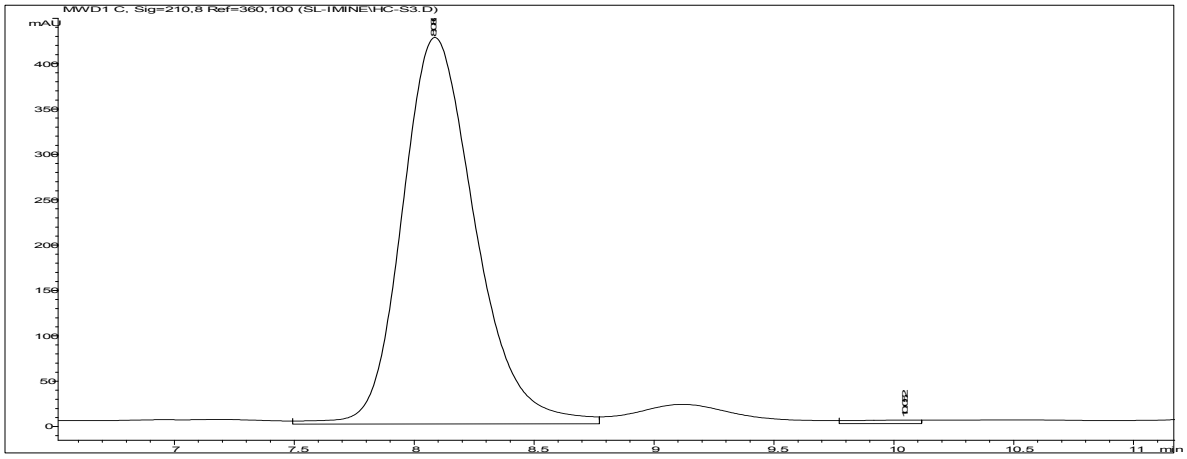
Table 3, entry 12, 9l: Chiralcel®OD Column, Hexane:IPA = 90:10, 1.5 mL/min, 210 nm

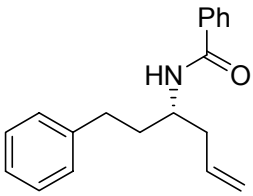




Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.130	MM	0.3403	2.43939e4	1194.61963	51.1832
2	9.977	VV	0.4158	2.32661e4	870.45038	48.8168
Totals :				4.76600e4	2065.07001	

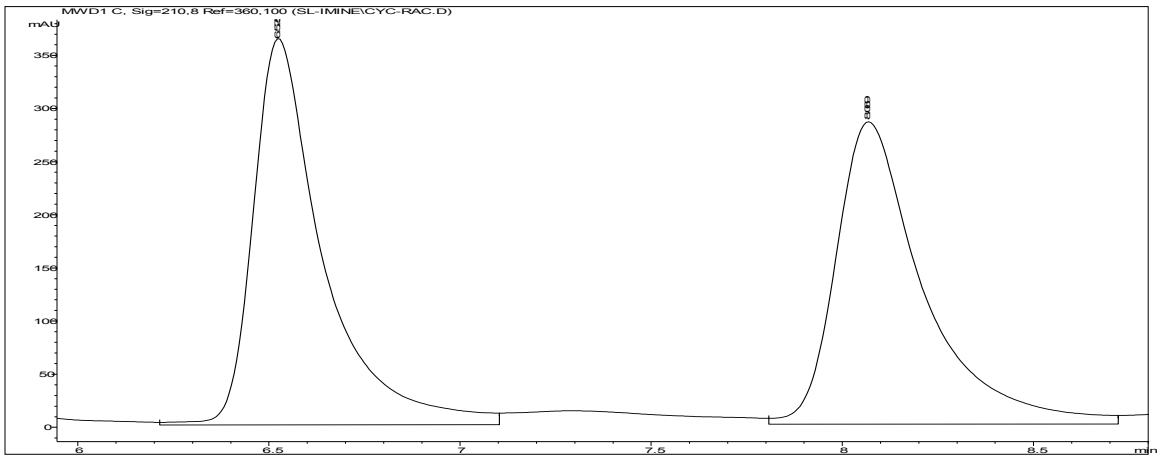


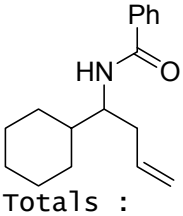


Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.086	VV	0.3269	9018.47266	426.07907	99.1914
2	10.052	VV	0.2338	73.51500	3.83194	0.8086
Totals :				9091.98766	429.91101	

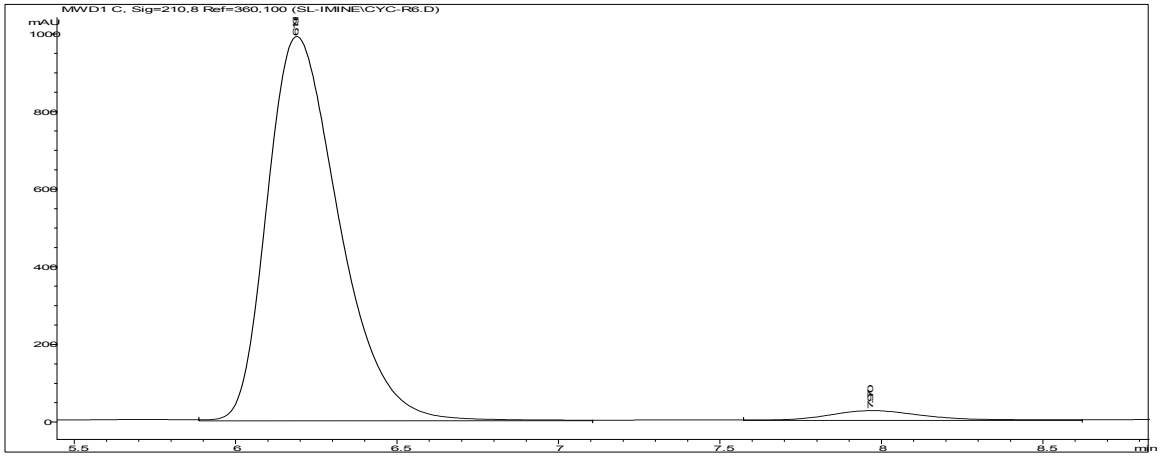
Table 3, entry 13, 9m: Chiralpak®AD-H Column, Hexane:IPA = 90:10, 1.0 mL/min, 210 nm

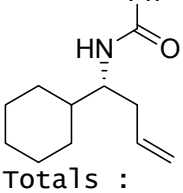




Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.525	VV	0.1865	4628.27344	363.57437	50.4718
2	8.069	VV	0.2341	4541.74854	284.74835	49.5282
Totals :				9170.02197	648.32272	

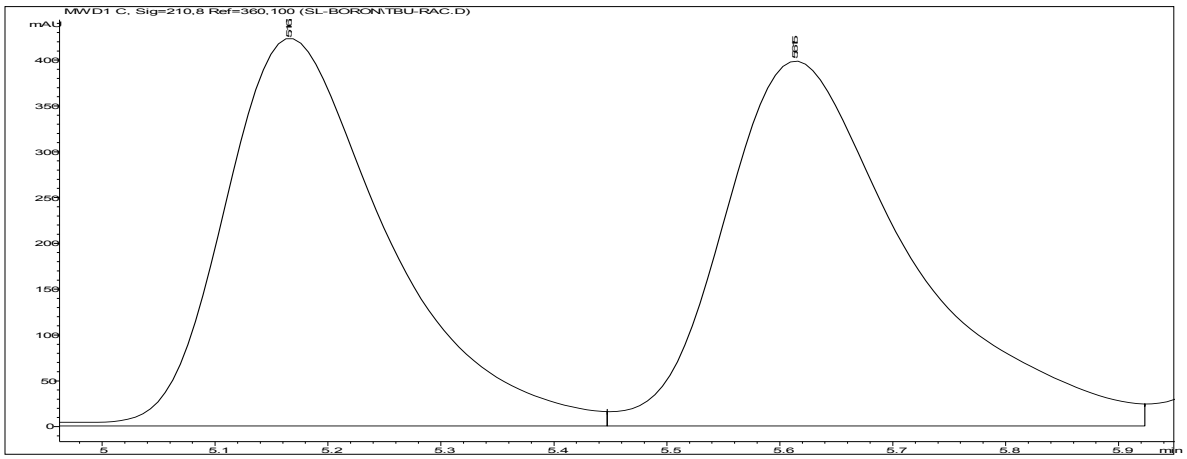


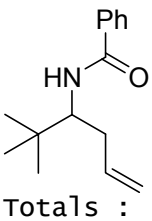


Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.190	VB	0.2385	1.53226e4	990.24982	98.0187
2	7.970	MM	0.2562	309.72220	20.14779	1.9813
Totals :				1.56323e4	1010.39761	

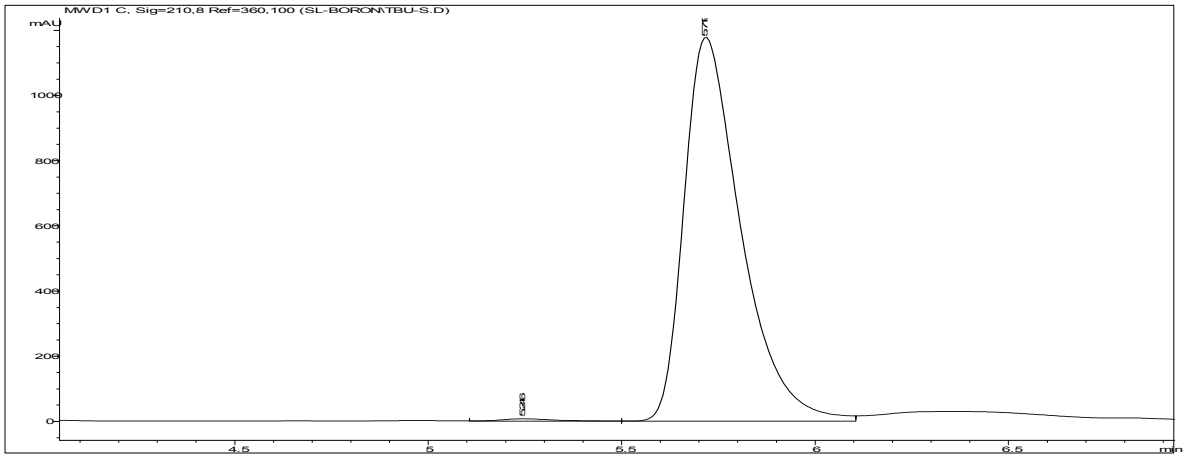
Table 3, entry 14, 9n: Chiralpak®AD-H Column, Hexane:IPA = 90:10, 1.0 mL/min, 210 nm

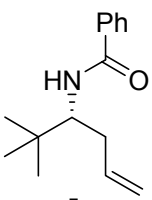




Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.167	VV	0.1496	4252.20557	421.85791	48.2876
2	5.615	VV	0.1695	4553.79346	397.94125	51.7124
Totals :				8805.99902	819.79916	

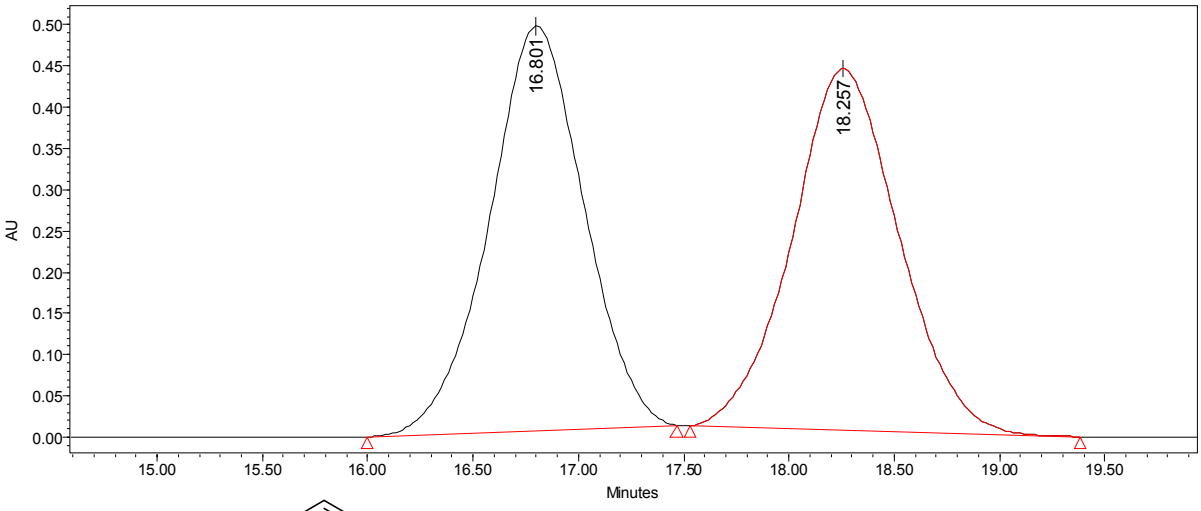


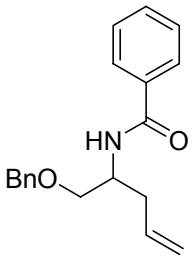


Signal 3: MWD1 C, Sig=210,8 Ref=360,100

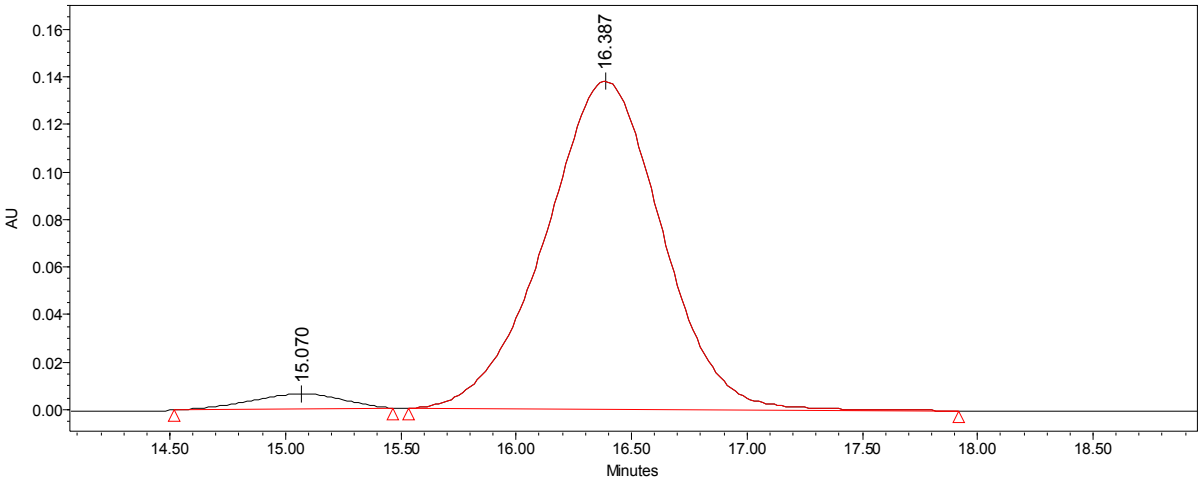
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.246	VV	0.1558	81.01602	7.63209	0.6673
2	5.719	VV	0.1555	1.20596e4	1177.41174	99.3327
Totals :				1.21406e4	1185.04383	

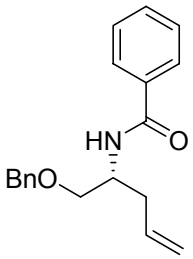
Table 1, entry 15, 9o: Whelk-O Column, Hexane:IPA = 90:10, 1.0 mL/min, 210 nm





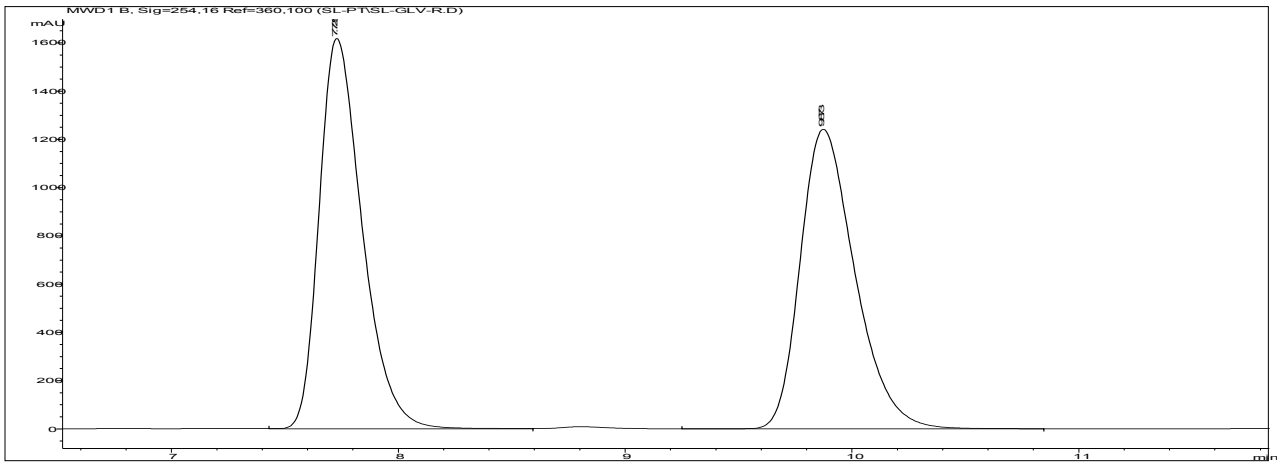
	Retention Time	Area	% Area
1	16.772	118659504	48.31
2	18.272	126978155	51.69

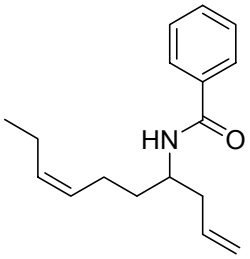




	Retention Time	Area	% Area
1	15.070	177464	3.54
2	16.387	4838350	96.46

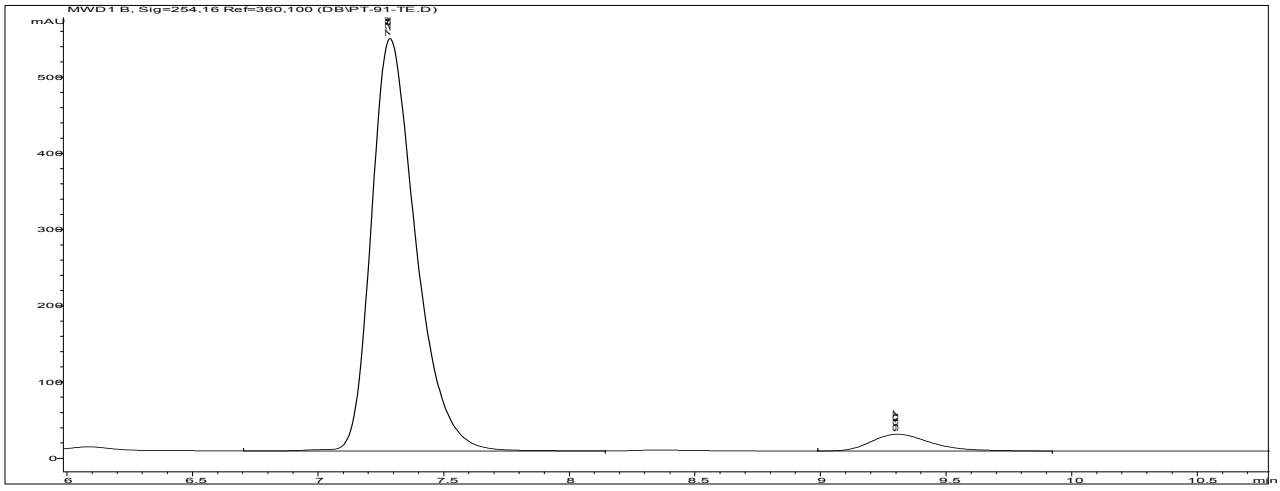
Table 1, entry 16, 9p: Chiralcel®OD Column, Hexane:IPA = 93:7, 1.0 mL/min, 254 nm

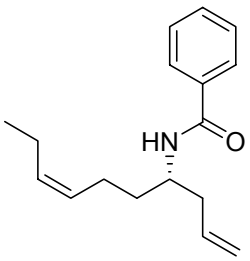




Signal 2: MWD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.729	VV	0.2019	2.13518e4	1619.07935	50.6710
2	9.873	VB	0.2573	2.07862e4	1241.97949	49.3290
Totals :				4.21380e4	2861.05884	

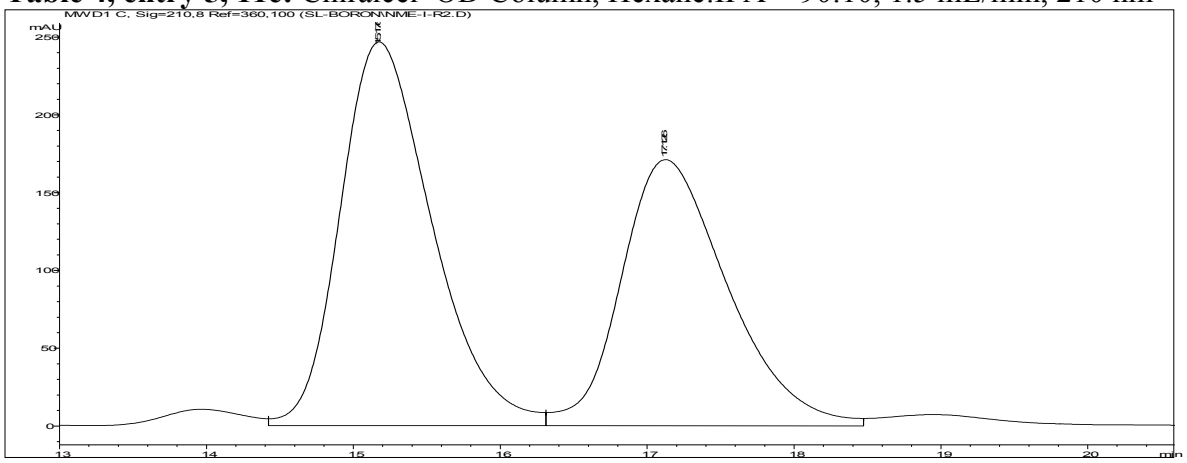


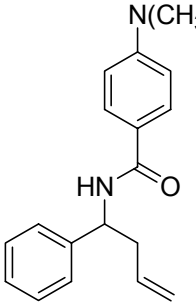


Signal 2: MWD1 B, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.286	BB	0.1875	6663.55762	541.82336	95.6928
2	9.307	MM	0.2394	299.93033	20.87802	4.3072
Totals :				6963.48795	562.70138	

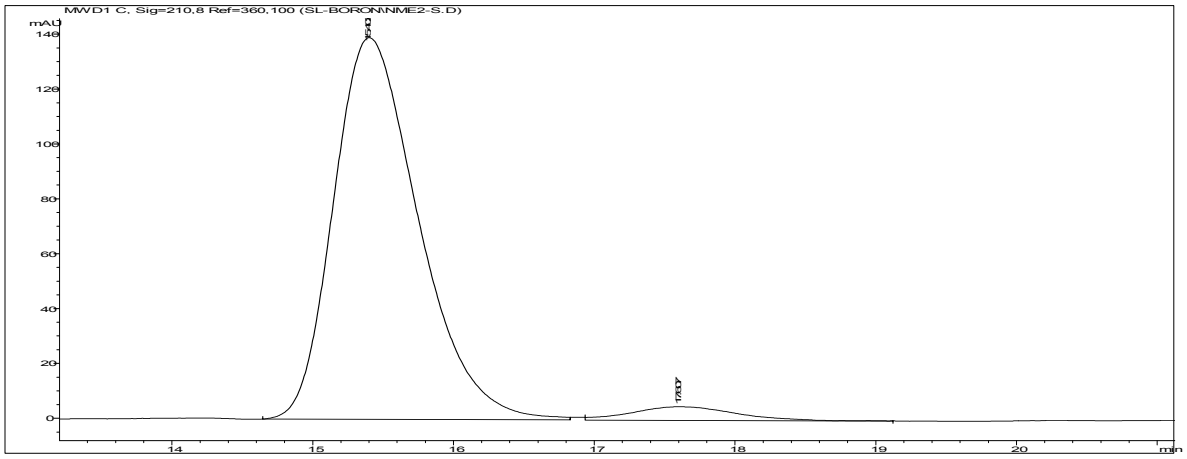
Table 4, entry 5, 11e: Chiralcel®OD Column, Hexane:IPA = 90:10, 1.5 mL/min, 210 nm

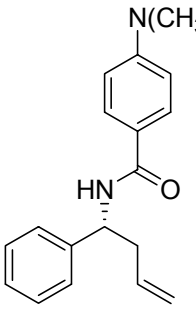




Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.175	MM	0.6510	9025.19531	231.05045	50.9743
2	17.128	MM	0.8693	8680.18750	166.42128	49.0257
Totals :				1.77054e4	397.47173	

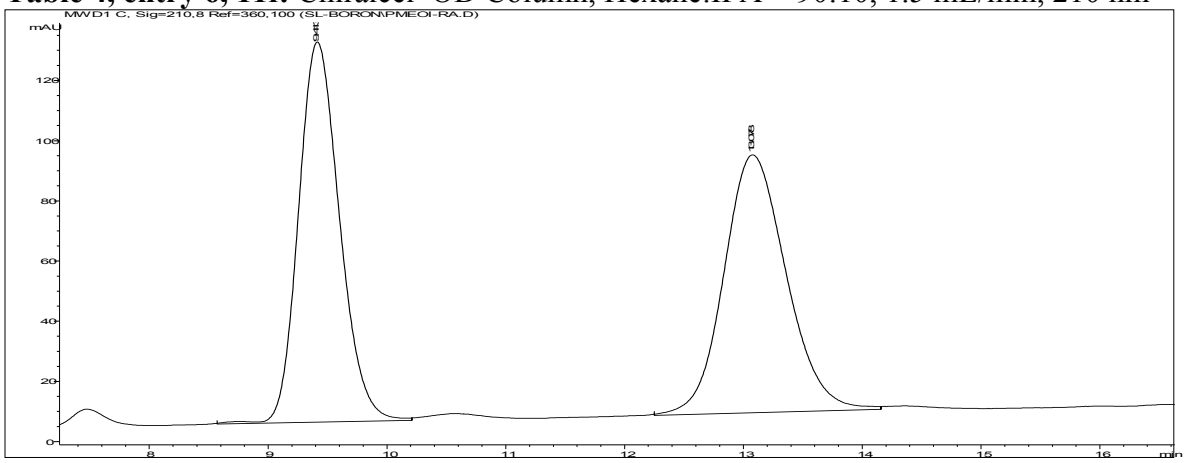


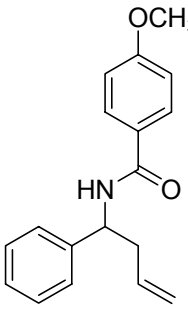


Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.402	PB	0.6493	5832.73828	139.07399	97.0419
2	17.616	MM	0.7079	177.79588	4.18622	2.9581
Totals :				6010.53416	143.26021	

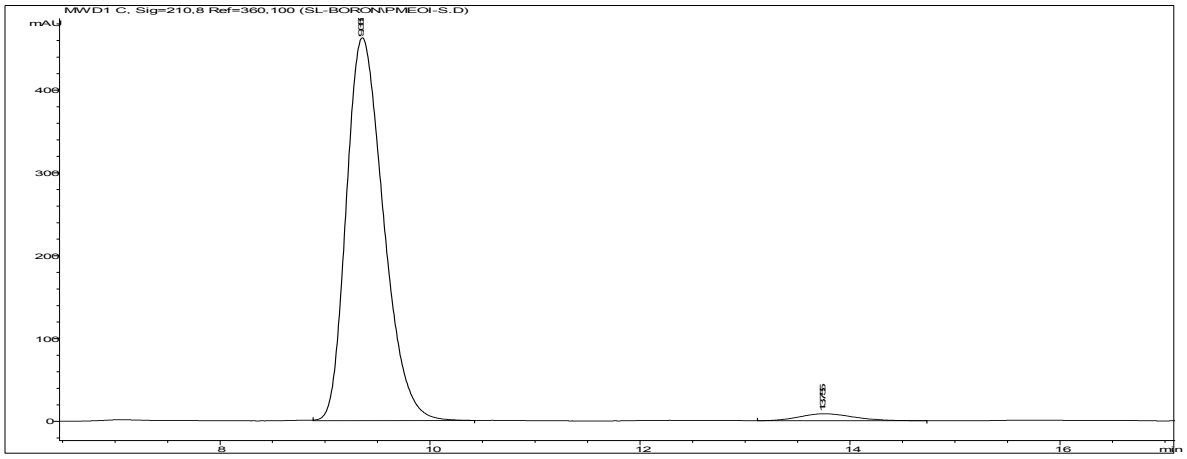
Table 4, entry 6, 11f: Chiralcel®OD Column, Hexane:IPA = 90:10, 1.5 mL/min, 210 nm

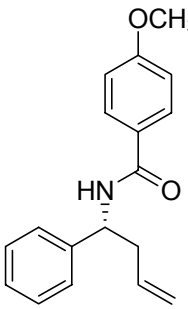




Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.413	BB	0.3727	3041.27539	126.38237	49.3494
2	13.078	BB	0.5690	3121.46973	85.69199	50.6506
Totals :				6162.74512	212.07436	

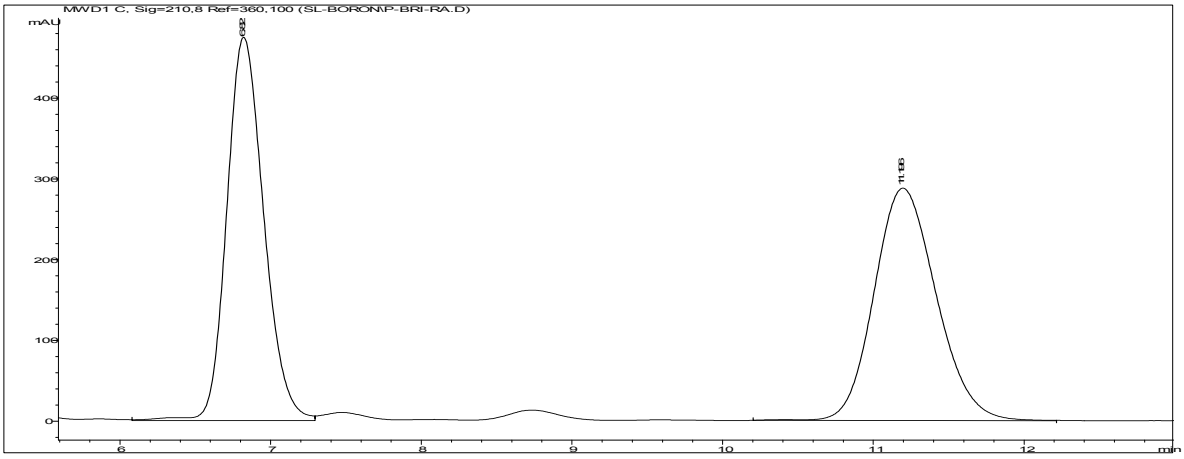


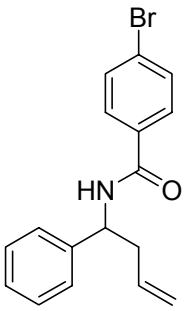


Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.355	BB	0.3864	1.13482e4	462.30347	97.4545
2	13.755	PB	0.5316	296.41287	8.40224	2.5455
Totals :				1.16446e4	470.70571	

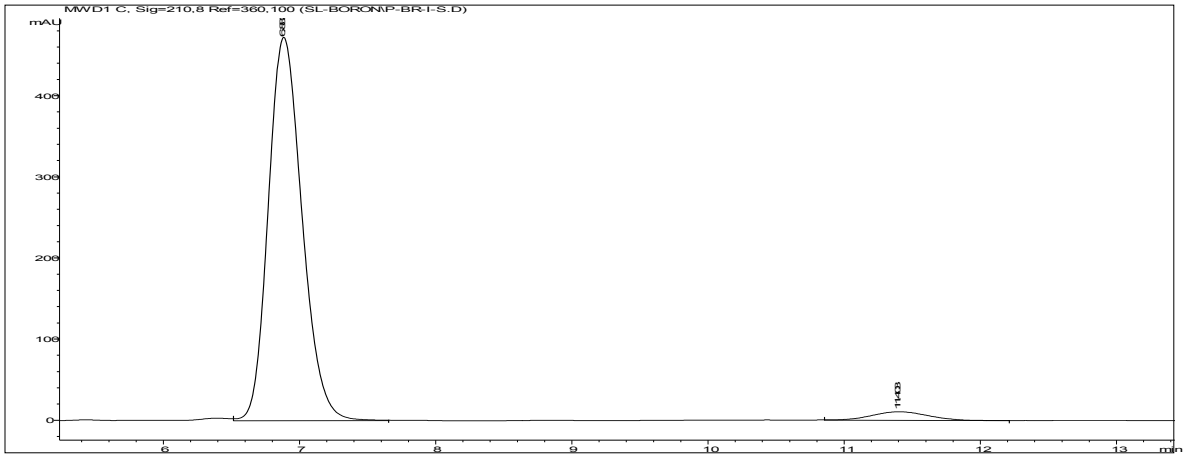
Table 4, entry 7, 11g: Chiralcel®OD Column, Hexane:IPA = 90:10, 1.5 mL/min, 210 nm

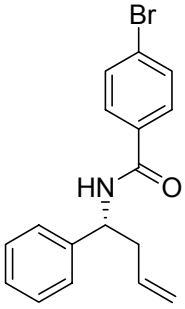




Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.821	VV	0.2633	8104.41797	474.46976	49.6084
2	11.196	BB	0.4460	8232.35840	287.59470	50.3916
Totals :				1.63368e4	762.06445	

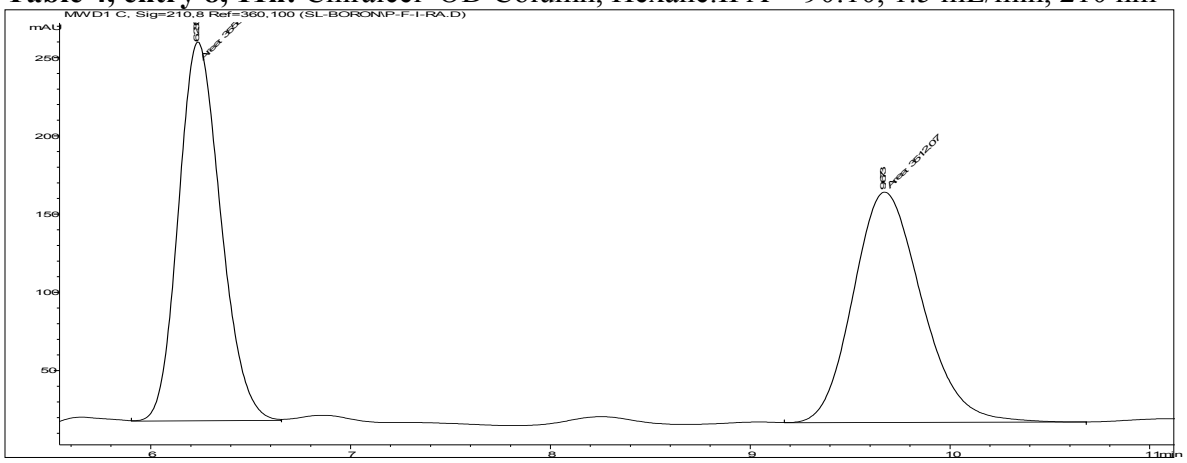


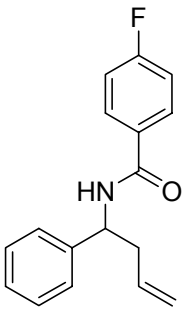


Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.883	VB	0.2682	8107.33740	472.40405	96.4968
2	11.403	BP	0.4471	294.32919	10.49914	3.5032
Totals :				8401.66660	482.90319	

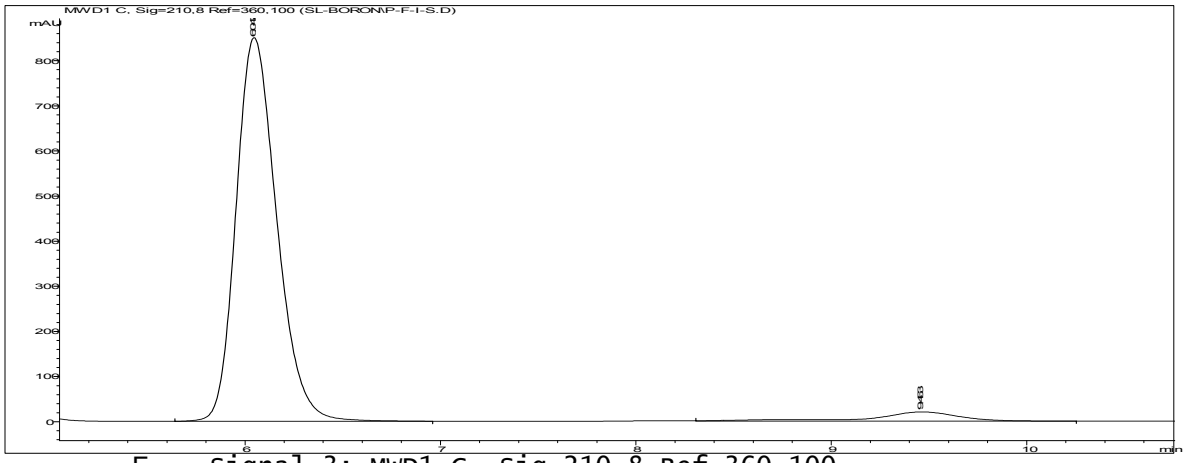
Table 4, entry 8, 11h: Chiralcel®OD Column, Hexane:IPA = 90:10, 1.5 mL/min, 210 nm

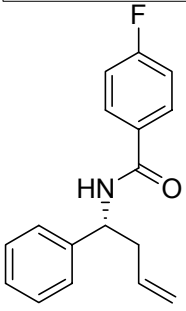




Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.235	MM	0.2447	3558.54980	242.36360	50.3287
2	9.673	MM	0.3975	3512.07056	147.26648	49.6713
Totals :				7070.62036	389.63008	

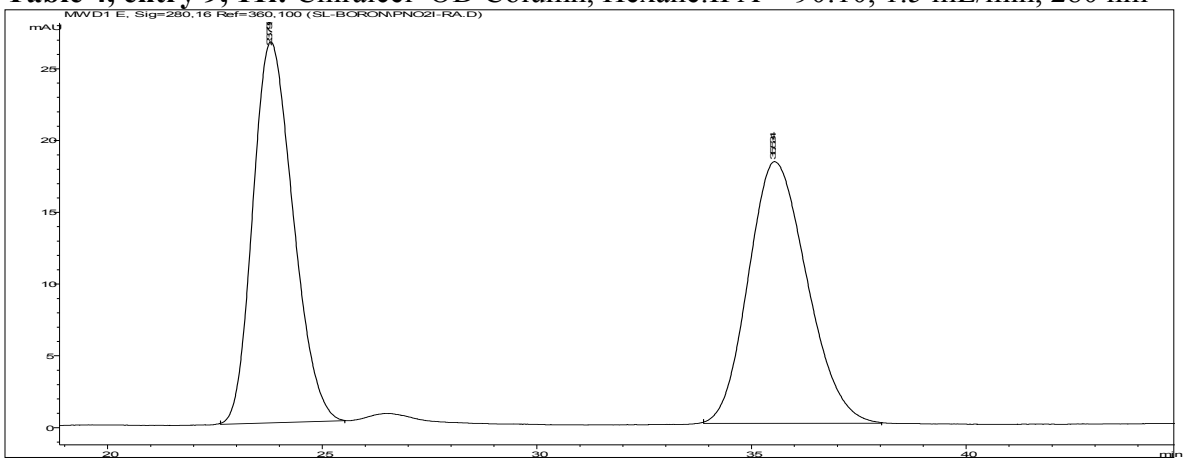


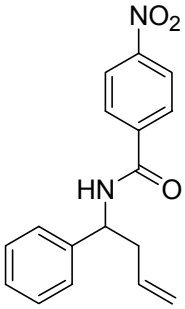


Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.047	BB	0.2248	1.22970e4	849.98114	97.3474
2	9.462	MM	0.3338	335.07645	16.73082	2.6526
Totals :				1.26321e4	866.71196	

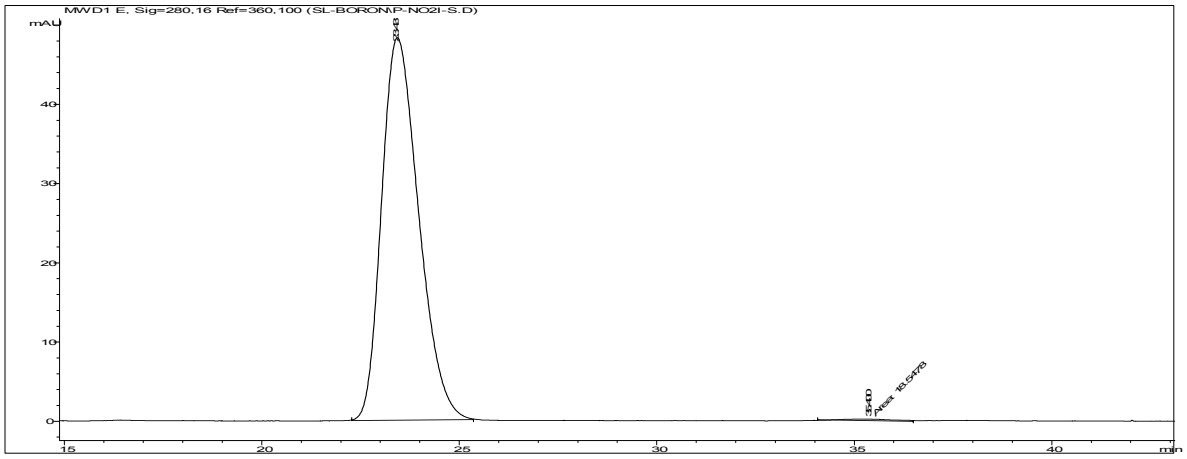
Table 4, entry 9, 11i: Chiralcel®OD Column, Hexane:IPA = 90:10, 1.5 mL/min, 280 nm

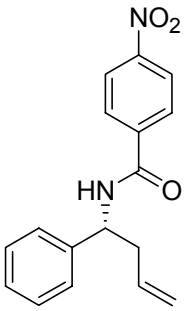




Signal 5: MWD1 E, Sig=280,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.799	BB	0.9715	1727.40979	26.53513	49.9640
2	35.534	BB	1.3090	1729.89868	18.23099	50.0360
Totals :				3457.30847	44.76612	

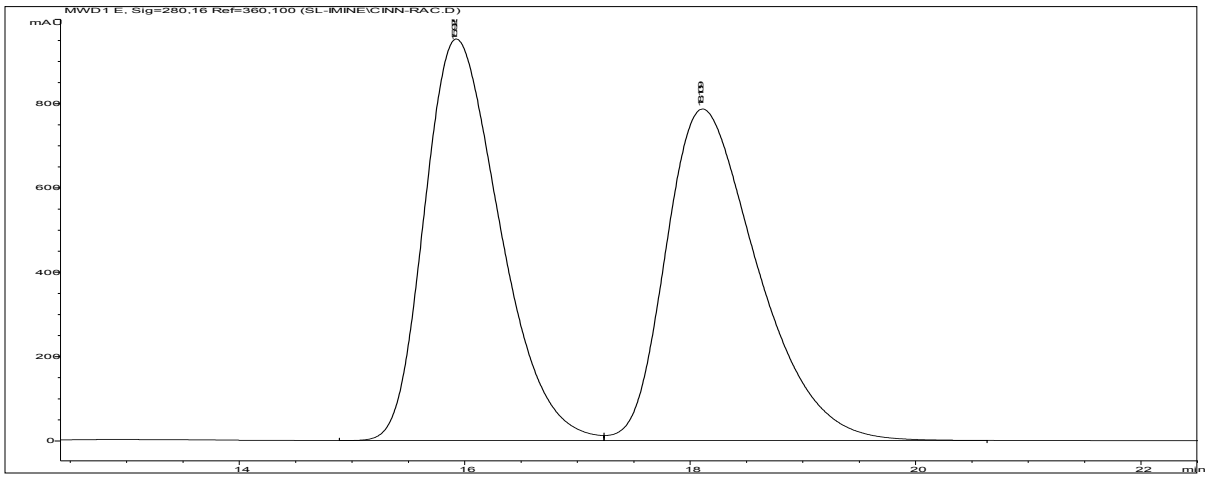


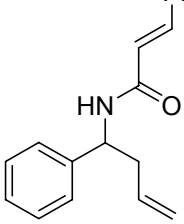


Signal 5: MWD1 E, Sig=280,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.431	MM	1.0986	3192.77124	48.43779	99.4224
2	35.400	MM	1.4983	18.54776	2.06324e-1	0.5776
Totals :				3211.31900	48.64411	

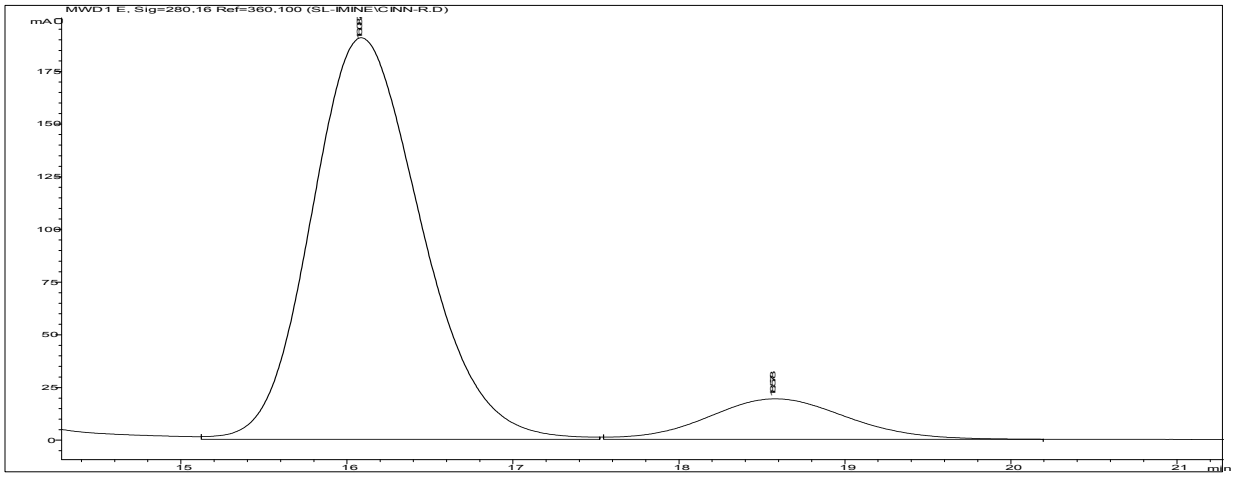
Table 4, entry 11, 11k: Chiralcel®OD Column, Hexane:IPA = 90:10, 1.5 mL/min, 280 nm

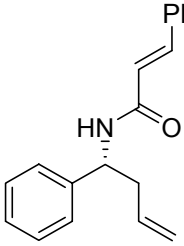




Signal 5: MWD1 E, Sig=280,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.925	VV	0.7265	4.42925e4	952.51953	49.9294
2	18.109	VB	0.8691	4.44176e4	786.24426	50.0706
Totals :				8.87101e4	1738.76379	

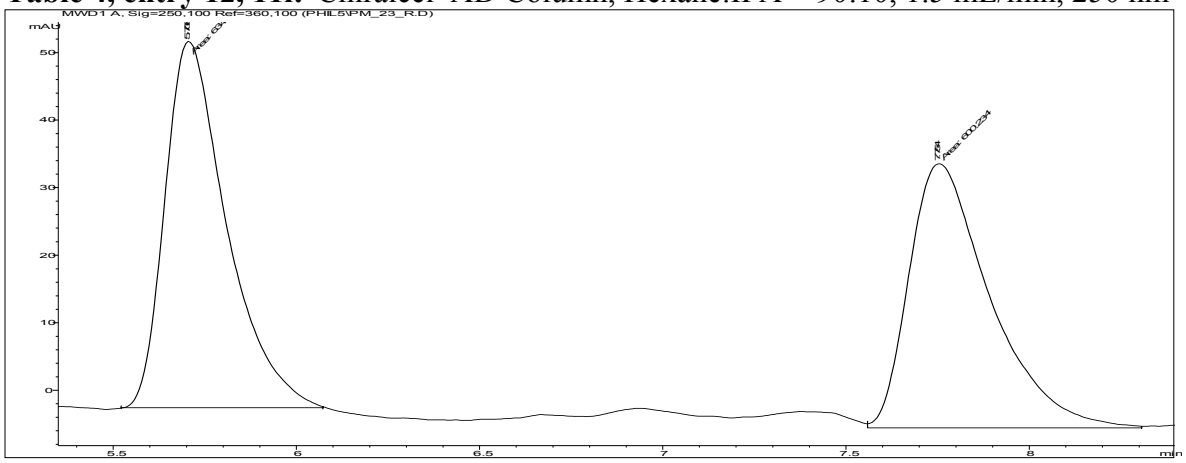


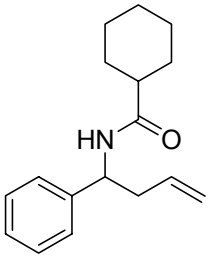


Signal 5: MWD1 E, Sig=280,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.087	BB	0.7177	8750.56445	190.56987	94.8152
2	18.578	MM	0.6510	478.50510	12.25049	5.1848
Totals :				9229.06955	202.82036	

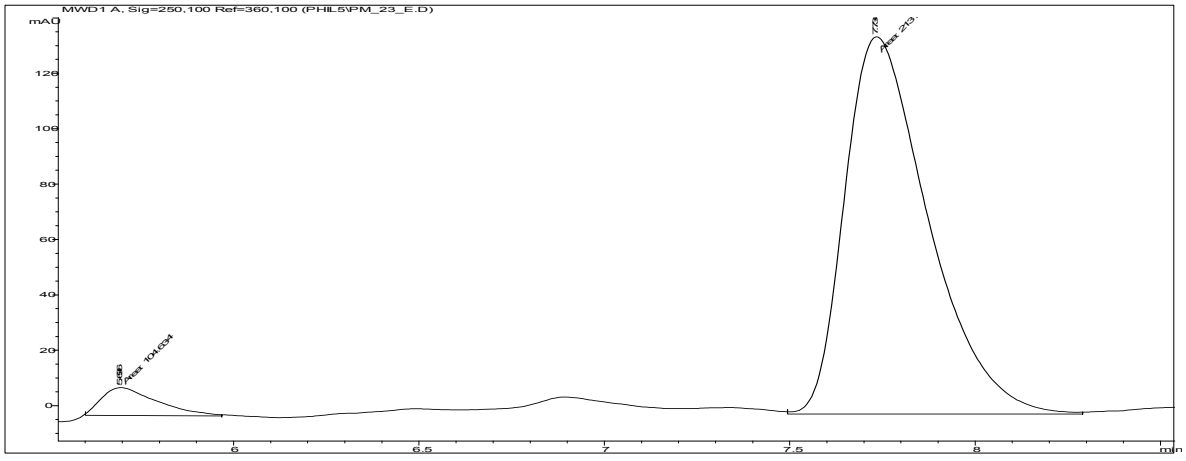
Table 4, entry 12, 11l: Chiralcel®AD Column, Hexane:IPA = 90:10, 1.5 mL/min, 250 nm

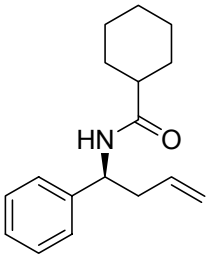




Signal 1: MWD1 A, Sig=250,100 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.706	MM	0.1947	634.17957	54.28231	51.3750
2	7.754	MM	0.2556	600.23358	39.14606	48.6250
Totals :				1234.41315	93.42837	

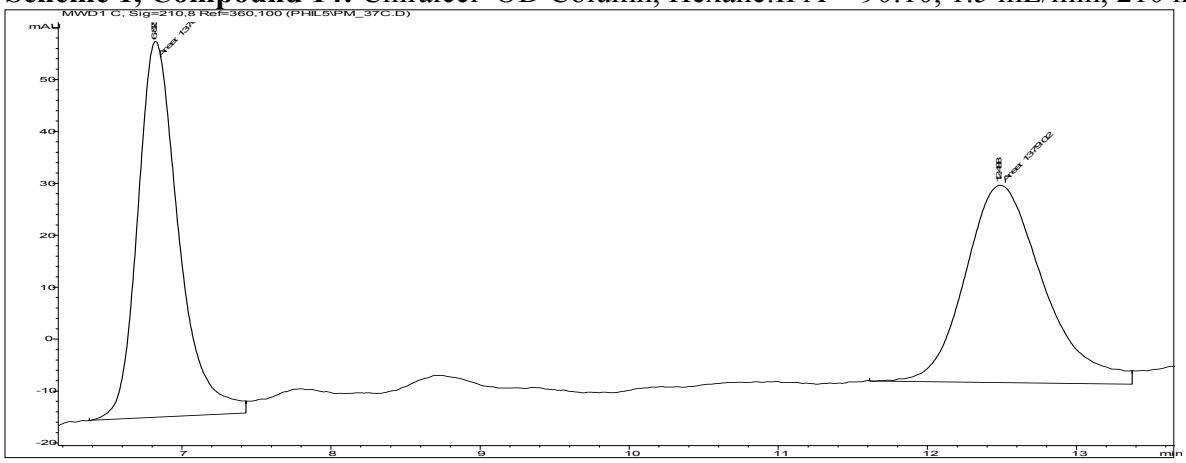


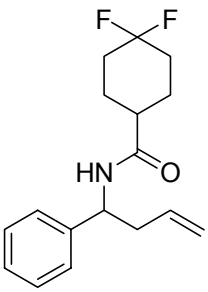


Signal 1: MWD1 A, Sig=250,100 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.696	MM	0.1737	104.63435	10.04069	4.6798
2	7.734	MM	0.2607	2131.21753	136.25139	95.3202
Totals :				2235.85188	146.29208	

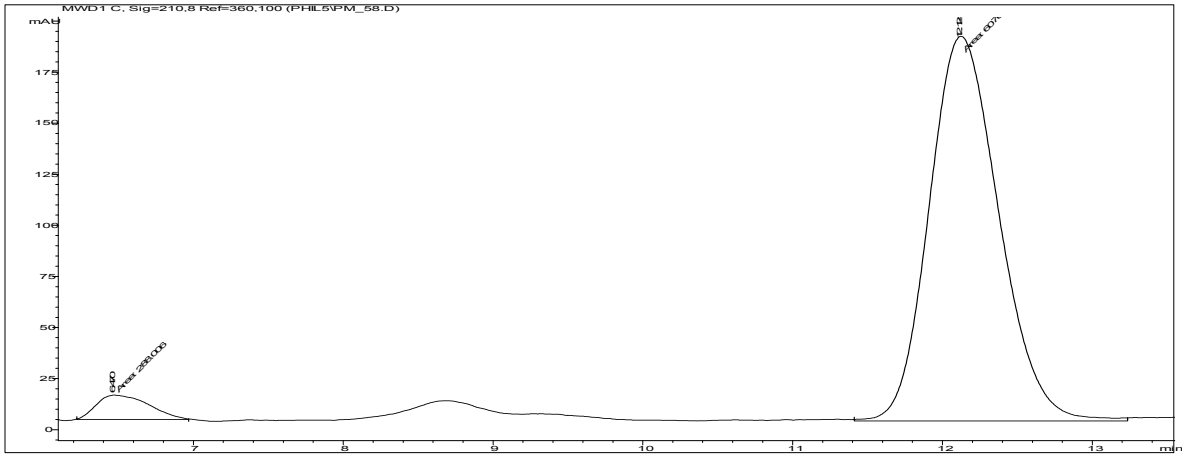
Scheme 1, Compound 14: Chiralcel®OD Column, Hexane:IPA = 90:10, 1.5 mL/min, 210 nm

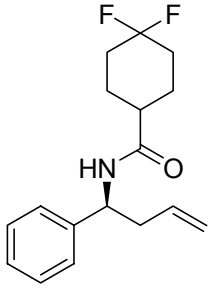




Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.823	MM	0.3166	1376.05200	72.44801	49.9461
2	12.488	MM	0.6051	1379.02100	37.98329	50.0539
Totals :				2755.07300	110.43130	

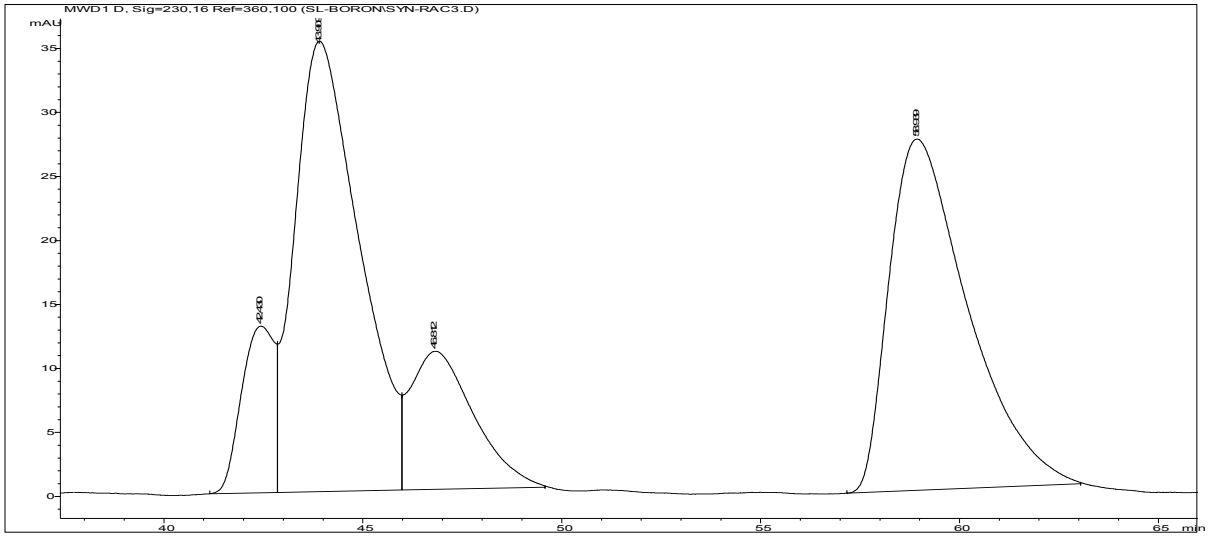


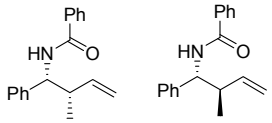


Signal 3: MWD1 C, Sig=210,8 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.470	MM	0.4032	288.00626	11.90623	4.5251
2	12.124	MM	0.5378	6076.65088	188.31277	95.4749
Totals :				6364.65714	200.21901	

Scheme 2, Compound 19: Chiralcel®OD Column, Hexane:IPA = 99:1, 1.5 mL/min, 230 nm

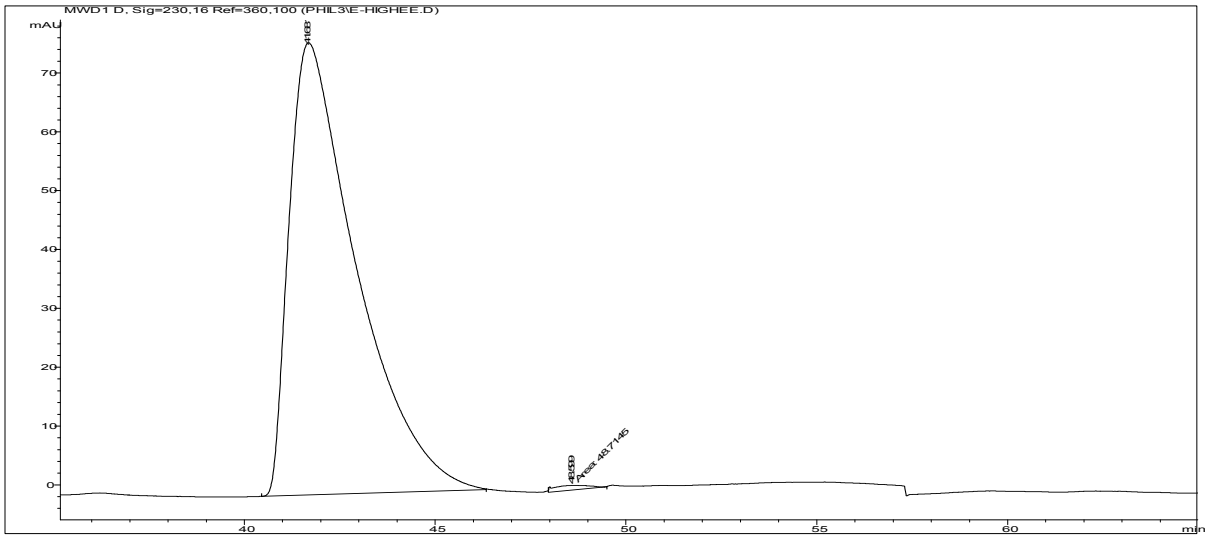


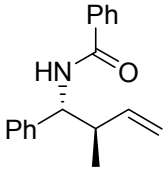


racemic, syn : anti = 4 : 1

Signal 4: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	42.430	MF	1.0882	861.21063	13.18984	8.5737
2	43.909	MF	1.8889	4014.67285	35.42271	39.9676
3	46.812	FM	1.8248	1219.63477	11.13960	12.1419
4	58.939	MM	2.3774	3949.30029	27.68599	39.3168
Totals :				1.00448e4	87.43814	





Signal 4: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	41.681	PB	1.6843	9424.14355	76.86837	99.4857
2	48.599	MM	1.0670	48.71445	7.60893e-1	0.5143
Totals :				9472.85801	77.62926	