Enantioselective Addition of Boronates to Acyl Imines Catalyzed by Chiral Biphenols

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Supporting Information

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G**eneral 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). 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.) and Chiralpak®AD-H (Chiral Technologies Inc., 25cm × 4.6 mm I.D.). 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. All reactions were performed under argon, in oven dried glassware with magnetic stirring. (*R*)-BINOL and (*S*)-BINOL were purchased from STREM and used without further purification. (*S*)-VAPOL, (*R*)-VAPOL, (*S*)-VANOL and (*R*)-VANOL were purchased from Aldrich and used without further puricification. All other BINOL derivatives were prepared according to known literature procedure.[1] All acyl imines were synthesized according to known literature procedures.[2] Deprotection of chiral amide was done following the procedure of Pratti et. al.[3]

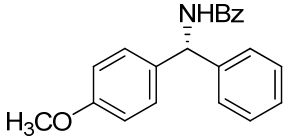
General Procedure for Preparation of Di(n-butyl)-alkenyl- and arylboronates

A 100 mL oven-dried round bottom flask equipped with stir bar was charged with the corresponding boronic acid (2.5 mmol), *n*-butanol (10 mL), chloroform (20 mL) and flame dried $MgSO_4$ (10 g). The reaction was refluxed overnight. The drying agents were filtered off *via* celite bed and the resulting filtrate was treated with 10 mL anhydrous toluene and concentrated under reduced pressure. The residue was placed under high vacuum for 2 h to pull off the remaining butanol. The resulting dibutylboronate was used to prepare the 1.0 M toluene solution without further purification.

General Procedure for Arylboronate Addition to Acyl Imines

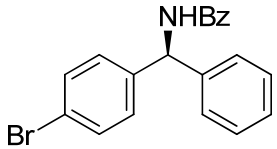
A 15 mL oven-dried round bottom flask was charged with stir bar and flushed with Ar. To the flask was added acyl imine (0.25 mmol), and (*S*)-3,3'-Br_2-BINOL (16.6 mg, 0.0375 mol). The flask was fitted with a septum and placed under an atmosphere of Ar. To the flask was added toluene (2.5 mL) and the mixture was stirred at 0°C. Dibutyl arylboronate (250 μL, 0.25 mmol, 1.0 M in toluene) was added drop wise to the reaction solution. The resulting reaction mixture was stirred at 0°C and allowed to warm to rt for 18h. The reaction mixture was then quenched with water (5.0 mL) and diluted with ethyl acetate (5.0 mL). The biphasic mixture was stirred at room temperature for 10 min. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (2×5.0 mL). The organic layers were combined, dried over Na_2SO_4 and filtered. The filtrate was concentrated *in vacuo* at 25 °C. The resulting residue was subjected to flash chromatography over silica gel to afford the diarylmethyl amide.

(*R*)-*N*-((4-methoxyphenyl)(phenyl)methyl)benzamide ((*R*)-catalyst was used in this case.)



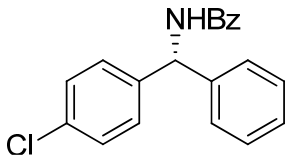
Following the general procedure, the crude mixture was purified by flash column chromatography with elution by 15-30% ethyl acetate in hexanes to afford the product as a white solid. **Yield:** 63 mg, 80%; **er:** 98:2; $[\alpha]_D^{23}$ = +18.8° (c = 1.0, $CHCl_3$); **HPLC Analysis,** t_r minor: 9.88 min., t_r major: 12.1 min., [Chiralcel®OD column, 24cm×4.6 mm I.D., Hexanes:IPA = 85:15, 1.0 mL/min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ7.82 (d, J = 7.2 Hz, 2H), 7.51 (t, J = 7.2 Hz, 1H), 7.44 (t, J = 7.2 Hz, 2H), 7.35-7.28 (m, 5H), 7.21 (d, J = 8.4 Hz, 2H), 6.88 (d, J = 8.4 Hz, 2H), 6.63 (d, J = 7.6 Hz, 1H), 6.40 (d, J = 7.6 Hz, 1H), 3.80 (s, 3H); **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ166.4, 159.0, 141.6, 134.3, 133.6, 131.7, 128.74, 128.70, 128.6, 127.5, 127.3, 127.0, 114.1, 56.9, 55.3; **IR** (thin film, cm^{-1}): 3301, 2925, 1634, 1510, 1488, 1248, 1176, 1030, 696; **HRMS**: calc'd for $(M+Na)^+$ $C_{21}H_{19}NO_2Na$: 340.1313; found: 340.1299.

(*S*)-*N*-((4-bromophenyl)phenyl)methyl)benzamide ((*S*)-catalyst was used in this case)



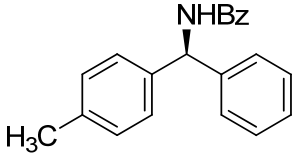
Following the general procedure, the crude mixture was purified by flash column chromatography with elution by 20% ether in hexane to afford the product as a white solid. **Yield:** mg, %; **er:** 98:2; $[\alpha]_D^{23}$ = -10.3° (c =0.1, $CHCl_3$); **HPLC Analysis,** t_r minor: 7.1 min., t_r major: 7.8 min., [Chiralcel®OD column, 24cm×4.6 mm I.D., Hexanes:IPA = 90:10, 1.0 mL/min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.32 (d, *J* = 10.4Hz, 1H) δ 6.56 (d, *J* = 10.4,1H) δ 7.12 (d, *J* = 11.6Hz, 2H) δ 7.26 (m, 4H) δ 7.41 (m, 5H) δ 7.74 (d, *J* = 9.2Hz) **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ 56.9, 121.4, 126.9, 127.5, 127.9, 128.6, 128.9, 129.0, 131.76, 131.79, 133.9, 140.4, 140.8, 166.4. **IR** (thin film, cm^{-1}): 3299, 3015, 2925, 1634, 1529, 1486, 1011, 694. **HRMS**: calc'd for $(M+Na)^+$ $C_{20}H_{16}NONaBr$: 388.0313; found: 388.0319.

(*R*)-*N*-((4-chlorophenyl)phenyl)methyl)benzamide ((*R*)-catalyst was used in this case)



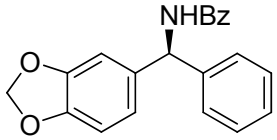
Following the general procedure, the crude mixture was purified by precipitation from toluene with hexanes, gave white solid. **Yield:** 152 mg, 94%; **er:** 98:2; $[\alpha]_D^{23}$ = -20.4° (c = 1.0, $CHCl_3$); **HPLC Analysis**: 14.09 min., t_r minor: 12.1 min., [Chiralcel®OD column, 24cm×4.6 mm I.D., Hexanes:IPA = 90:10, 1.0 mL/min] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.41 (d, *J* = 7.8Hz, 1H) δ 6.62 (d, *J* = 7.8Hz, 1H) δ 7.3 (m, 9H) δ 7.45 (m, 2H) δ 7.53 (m, 1H) δ 7.82 (d, *J* = 8.7, 2H). **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ 56.9, 127.0, 127.5, 127.9, 128.69, 128.76, 128.87, 128.94, 131.8, 133.4, 133.9, 139.9, 140.9, 166.5. **IR** (thin film, cm^{-1}): 1244, 1310, 1488, 1521, 1577, 1631, 2988, 3102, 3294. **HRMS**: calc'd for $(M+Na)^+$ $C_{20}H_{16}NONaCl$: 344.0818; found: 344.0800.

(*S*)-*N*-((4-methylphenyl)phenyl)methyl)benzamide



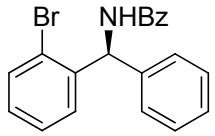
Following the general procedure, the crude mixture was purified by flash column chromatography with elution by 20% ether in hexane to afford the product as a white solid. **Yield:** 28.5 mg, 82%; **er:** 98:2; $[\alpha]_D^{23}$ = -15.6° (c = 0.1, $CHCl_3$); **HPLC Analysis,** t_r minor: 9.6 min., t_r major: 11.1 min., [Chiralcel®OD column, 24cm×4.6 mm I.D., Hexanes:IPA = 90:10, 1.0 mL/min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.34 (s, 3H) δ 6.40 (d, *J* = 7.6Hz, 1H) δ 6.65 (d, *J* = 7.6Hz, 1H) δ 7.15 (m, 4H) δ 7.29 (m, 5H) δ 7.43 (m, 3H) δ 7.80 (d, *J* = 6.8Hz, 2H) **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ 20.5, 57.8, 126.59, 126.96, 127.01, 127.04, 128.18, 128.27, 129.00, 131.2, 133.8, 136.9, 138.1, 141.1, 166.0 **IR** (thin film, cm^{-1}): 696, 1033, 1311, 1488, 1528, 1635, 3059, 3308. **HRMS**: calc'd for $(M+Na)^+$ $C_{21}H_{19}NONa$: 324.1364 found: 324.1327.

(*S*)-*N*-(benzo[d][1,3]dioxol-5-yl(phenyl)methyl)benzamide



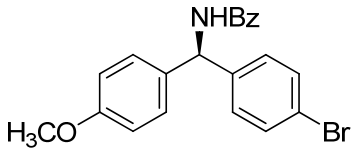
Following the general procedure, the crude mixture was purified by flash column chromatography with elution by 20% ether in hexane to afford the product as a whie solid. **Yield:** 38.1 mg, 91%; **er:** 98:2; $[\alpha]_D^{23}$ = -9.7° (c = 0.05, $CHCl_3$); **HPLC Analysis,** t_r major: 36.5 min., t_r minor: 40.1 min., [Chiralpak®AD column, 24cm×4.6 mm I.D., Hexanes:IPA = 90:10, 1.0 mL/min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.93 (s, 2H) δ 6.33 (d, *J* = 7.6Hz, 1H) δ 6.61 (d, *J* = 7.6Hz, 1H) δ 6.75 (d, *J* = 5.6Hz, 2H) δ 6.761 (s, 1H) δ 7.32 (m, 5H) δ 7.42 (m, 3H) δ 7.80 (d, *J* = 6.8Hz, 2H). **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ 57.2, 101.2, 108.0, 108.4, 120.8, 127.0, 127.3, 127.6, 128.6, 128.8, 131.7, 134.1, 135.4, 141.4, 146.9, 147.9, 166.4. **IR** (thin film, cm^{-1}): 1039, 1247, 1487, 1502, 1529, 1635, 2924, 3061, 3309. **HRMS**: calc'd for $(M+Na)^+$ $C_{21}H_{17}NO_3Na$ 354.1106 found: 354.1087

(*S*)-*N*-((2-Bromophenyl)(phenyl)methyl)benzamide



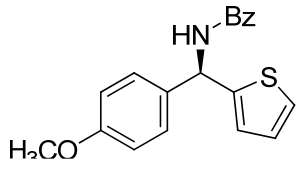
Following the general procedure, the crude mixture was purified by flash column chromatography with elution by 15-30% ethyl acetate in hexanes to afford the product as a white solid. **Yield:** 65 mg, 72%; **er:** 97:3; $[\alpha]_D^{23}$ = -6.8° (c = 1.0, $CHCl_3$); **HPLC Analysis,** t_r major: 13.7 min., t_r minor: 16.2 min., [Chiralcel®OD column, 24cm×4.6 mm I.D., Hexanes:IPA = 85:15, 1.0 mL/min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ7.85 (d, J = 7.2 Hz, 2H), 7.61 (dd, J = 7.6, 1.2 Hz, 1H), 7.53 (t, J = 7.2 Hz, 1H), 7.45 (t, J = 7.2 Hz, 2H), 7.39-7.29 (m, 5H), 7.20-7.18 (m, 2H), 7.11(td, J = 7.6, 2.0 Hz, 1H), 6.77 (d, J = 7.2 Hz, 1H), 6.62 (d, J = 7.2 Hz, 1H); **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ166.3, 140.1, 139.9, 134.0, 133.7, 131.8, 129.3, 129.2, 128.7, 128.6, 127.7, 127.5, 127.1, 123.9, 57.5; **IR** (thin film, cm^{-1}): 3294, 3061, 1636, 1528, 1487, 1286, 1027, 908, 750, 695; **HRMS**: calc'd for $(M+Na)^+$ $C_{20}H_{16}NONaBr$: 388.0313; found: 388.0300.

(*R*)-*N*-((4-bromophenyl)(4-methoxyphenyl)methyl)benzamide



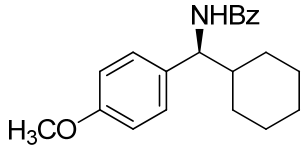
Following the general procedure, the crude mixture was purified by flash column chromatography with elution by 15-30% ethyl acetate in hexanes to afford the product as a white solid. **Yield:** 79 mg, 80%; **er:** 98.5:1.5; $[\alpha]_D^{23}$ = -9° (c = 1.0, $CHCl_3$); **HPLC Analysis,** t_r major: 8.8 min., t_r minor: 10.4 min., [Chiralcel®OD column, 24cm×4.6 mm I.D., Hexanes:IPA = 85:15, 1.5 mL/min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.78 (d, J = 7.2 Hz, 2H), 7.50 (t, J = 7.2 Hz, 1H), 7.42 (t, J = 7.2 Hz, 2H), 7.16 (d, J = 8.8 Hz, 2H), 6.86 (d, J = 8.8 Hz, 2H), 6.80 (d, J = 7.6 Hz, 1H), 6.30 (d, J = 7.6 Hz, 1H), 3.79 (s, 3H); **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ166.6, 159.2, 140.7, 134.0, 133.0, 131.8, 131.7, 129.0, 128.9, 128.6, 127.1, 121.3, 114.2, 56.5, 55.3; **IR** (thin film, cm^{-1}): 3295, 3060, 2932, 2835, 1635, 1511, 1487, 1249, 1176, 1010, 909, 825, 731, 694; **HRMS**: calc'd for $(M+Na)^+$ $C_{21}H_{18}NO_2NaBr$: 418.0419; found: 418.0393.

(*R*)-*N*-((4-methoxyphenyl)(thiophen-2-yl)methyl)benzamide



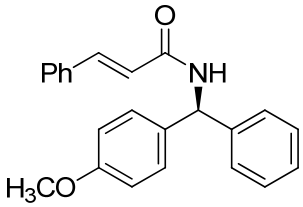
Following the general procedure, the crude mixture was purified by flash column chromatography with elution by 15-30% ethyl acetate in hexanes to afford the product as a white solid. **Yield:** 72.5 mg, 89%; **er:** 96:4; $[\alpha]_D^{23}$ = +5.9° (c = 1.05, $CHCl_3$); **HPLC Analysis,** t_r major: 7.0 min., t_r minor: 7.8 min., [Chiralcel®OD column, 24cm×4.6 mm I.D., Hexanes:IPA = 85:15, 1.0 mL/min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ7.80 (d, J = 7.2 Hz, 2H), 7.50 (t, J = 7.2 Hz, 1H), 7.40 (t, J = 7.2 Hz, 2H), 7.32 (d, J = 7.2 Hz, 2H), 7.24 (dd, J = 5.2, 1.2 Hz, 1H), 6.95 (dd, J = 5.2, 3.6 Hz, 1H), 6.90 (d, J = 7.2 Hz, 2H), 7.89 (m, 2H), 6.59 (d, J = 8.0 Hz, 1H), 3.80 (s, 3H); **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ166.3, 159.2, 146.1, 134.1, 133.3, 131.7, 128.6, 128.4, 127.1, 127.0, 125.8, 125.2, 114.1, 55.3, 52.9; **IR** (thin film, cm^{-1}): 3294, 3065, 2932, 1636, 1511, 1487, 1248, 1177, 1032, 909, 831, 695; **HRMS**: calc'd for $(M+Na)^+$ $C_{19}H_{17}NO_2NaS$: 346.0878; found: 346.0888.

(*S*)-*N*-(cyclohexyl(4-methoxyphenyl)methyl)benzamide



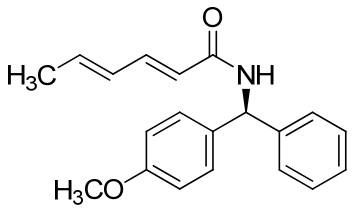
Following the general procedure, the crude mixture was purified by flash column chromatography with elution by 15-30% ethyl acetate in hexanes to afford the product as a white solid. **Yield:** 59 mg, 70%; **er:** 98:2; $[\alpha]_D^{23}$ = +4.7° (c = 1.0, $CHCl_3$); **HPLC Analysis,** t_r major: 1 min., t_r minor: 1 min., [Chiralpak®AD column, 24cm×4.6 mm I.D., Hexanes:IPA = 95:5, 1.0 mL/min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ7.75 (d, J = 8.0 Hz, 2H), 7.50-7.41 (m, 3H), 7.21 (d, J = 8.4 Hz, 2H), 6.86 (d, J = 8.4 Hz, 2H), 6.38 (d, J = 8.0 Hz, 1H), 4.91 (t, J = 8.4 Hz, 1H), 3.78 (s, 3H), 2.01 (m, 2H), 1.78-1.48 (m, 5H), 1.27-1.11 (m, 4H); **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ166.7, 158.6, 134.9, 133.6, 131.4, 128.5, 128.1, 126.9, 123.5, 113.9, 58.3, 55.2, 43.2, 30.2, 29.7, 26.3, 26.1, 25.0; **IR** (thin film,cm^{-1}): 3330, 2926, 1634, 1513, 1250, 1044, 693; **HRMS**: calc'd for $(M+Na)^+$ $C_{21}H_{25}NO_2Na$: 346.1783; found: 346.1779.

(*S*)-*N*-((4-methoxyphenyl)(phenyl)methyl)cinnamamide



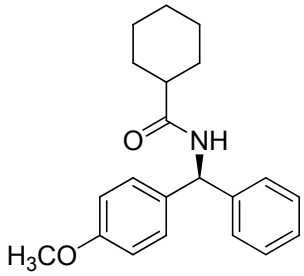
Following the general procedure, the crude mixture was purified by flash column chromatography with elution by 15-30% ethyl acetate in hexanes to afford the product as a white solid. **Yield:** 75 mg, 87%; **er:** 98:2; $[\alpha]_D^{23}$ = -21° (c = 0.5, $CHCl_3$); **HPLC Analysis,** t_r major: 25.6 min., t_r minor: 32.4 min., [Chiralcel®OD column, 24cm×4.6 mm I.D., Hexanes:IPA = 90:10, 1.5 mL/min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ7.64 (d, J = 15.6 Hz, 1H), 7.44 (m, 2H), 7.33 – 7.27 (m, 8H), 7.16 (d, J = 8.8 Hz, 2H), 6.82 (d, J = 8.8 Hz, 2H), 6.64 (d, J = 8.0 Hz, 1H), 6.51 (d, J = 15.6 Hz, 1H), 6.33 (d, J = 8.0 Hz, 1H), 3.76 (s, 3H); **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ165.1, 158.9, 141.7, 141.6, 134.8, 134.7, 129.7, 128.8, 128.6, 127.8, 127.4, 120.5, 114.0, 56.6, 55.3; **IR** (thin film, cm^{-1}): 3269, 3060, 3028, 1654, 1615, 1511, 1352, 1248, 1217, 1176, 1032, 730, 698; **HRMS**: calc'd for $(M+Na)^+$ $C_{23}H_{21}NO_2Na$: 366.1425; found: 366.1493.

(2*E*,4*E*)-*N*-((*S*)-(4-methoxyphenyl)(phenyl)methyl)hexa-2,4-dienamide



Following the general procedure, the crude mixture was purified by flash column chromatography with elution by 15-30% ethyl acetate in hexanes to afford the product as a white solid. **Yield:** 64 mg, 83%; **er:** 98:2; $[\alpha]_D^{23}$ = -25° (c = 0.5, $CHCl_3$); **HPLC Analysis,** t_r major: 7.7 min., t_r minor: 11.3 min., [Chiralcel®OD-H column, 24cm×4.6 mm I.D., Hexanes:IPA = 85:15, 1.0 mL/min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ7.38 (t, J = 7.6 Hz, 2H), 7.34 - 7.28 (m, 4H), 7.22 (d, J = 6.8 Hz, 2H), 6.91 (d, J = 6.8 Hz, 2H), 6.35 (d, J = 8.4 Hz, 1H), 6.25 – 6.16 (m, 3H), 5.88 (d, J = 16 Hz, 1H), 3.84 (s, 3H), 1.90 (d, J = 7.2 Hz, 3H); **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ165.4, 158.8, 141.9, 141.7, 138.2, 138.8, 129.6, 128.7, 128.6, 127.4, 127.3, 121.1, 114.0, 56.4, 55.3, 18.6; **IR** (thin film, cm^{-1}): 3272, 3028, 2932, 1656, 1628, 1611, 1511, 1354, 1249, 1176, 999, 698; **HRMS**: calc'd for $(M+Na)^+$ $C_{20}H_{21}NO_2Na$: 330.1470; found: 330.1485.

(*S*)-*N*-((4-methoxyphenyl)(phenyl)methyl)cyclohexanecarboxamide

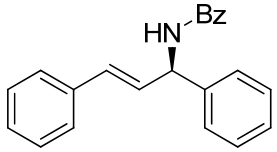


Following the general procedure, the crude mixture was purified by flash column chromatography with elution by 15-30% ethyl acetate in hexanes to afford the product as a white solid. **Yield:** 57 mg, 71%; **er:** 97.5:2.5; $[\alpha]_D^{23}$ = -21.5° (c = 1.0, $CHCl_3$); **HPLC Analysis,** t_r major: 13.4 min., t_r minor: 15.2 min., [Chiralpak®AD-H column, 24cm×4.6 mm I.D., Hexanes:IPA = 90:10, 1.0 mL/min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ7.32 (t, J = 7.2 Hz, 2H), 7.25 (m, 1H), 7.20 (d, J = 7.6 Hz, 2H), 7.11 (d, J = 8.8 Hz, 2H), 6.85 (d, J = 8.8 Hz, 2H), 6.19 (d, J = 7.6 Hz, 1H), 5.93 (d, J = 8.8 Hz, 1H), 3.78 (s, 3H), 2.15 (m, 1H), 1.90 (d, J = 12.4 Hz, 2H), 1.78 (d, J = 12.4 Hz, 2H), 1.67 (m, 1H), 1.48 (m, 2H), 1.25 (m, 3H); **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ175.0, 158.8, 141.9, 134.0, 128.6, 128.5, 127.3, 127.2, 114.0, 55.9, 55.3, 45.4, 29.7, 25.7; **IR** (thin film, cm^{-1}): 3258, 3061, 2928, 2851, 1638, 1512, 1448, 1250, 1216, 1176, 1034, 967, 821, 757; **HRMS**: calc'd for $(M+1)^+$ $C_{21}H_{26}NO_2$: 324.1964; found: 324.1970.

General Procedure for Vinylboronate Addition to Acyl Imines

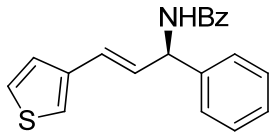
A 15 mL oven-dried round bottom flask was charged with stir bar and flushed with Ar. To the flask was added acyl imine (0.25 mmol), and (*S*)-3,3'-(3,5-$(CH_3)_2$-$C_6H_4)_2$-BINOL (18.6 mg, 0.0375 mol). The flask was fitted with a septum and placed under an atmosphere of Ar. To the flask was added toluene (2.5 mL) and the mixture was stirred at 0°C. (*E*)-dibutyl vinylboronate (250 µL, 0.25 mmol, 1.0 M in toluene) was added drop wise to the reaction solution. The resulting reaction mixture was stirred at 0 °C and allowed to warm to rt over a period of 18h. The reaction mixture was then quenched with water (5.0 mL) and diluted with ether (5.0 mL). The biphasic mixture was stirred at room temperature for 10 min. The organic layer was separated and the aqueous layer was extracted with ether (2×5.0 mL). The organic layers were combined, dried over Na_2SO_4 and filtered. The filtrate was concentrated *in vacuo* at 20 °C. The resulting residue was subjected to flash chromatography over silica gel to afford the allylic amide.

(*R*,*E*)-*N*-(1,3-diphenylallyl)benzamide



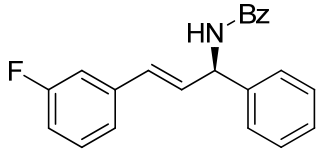
Following the general procedure, the crude mixture was purified by flash column chromatography with elution by 15-30% ethyl acetate in hexanes to afford the product as a white solid. **Yield:** 66.5 mg, 85%; **er:** 97.5:2.5; $[\alpha]_D^{23}$ = 20.4° (c = 1.0, $CHCl_3$); **HPLC Analysis,** t_r major: 15.1 min., t_r minor: 16.7 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 7.83 (d, J = 8.0 Hz, 2H), 7.52 (t, J = 8.0 Hz, 1H), 7.45 (t, J = 8.0 Hz, 2H), 7.43-7.22 (m, 10H), 6.62 (d, J = 16 Hz, 1H), 6.55 (d, J = 7.6 Hz, 1H), 6.44 (dd, J = 16, 6.0 Hz, 1H), 6.02 (t, J = 7.6 Hz, 1H); **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ 166.7, 140.6, 136.3, 134.1, 131.9, 131.8, 128.9, 128.7, 128.6, 128.0, 127.9, 127.2, 127.0, 126.6, 126.1, 55.4; **IR** (thin film, cm^{-1}): 3296, 2925, 1634, 1520, 1491, 1334, 1028, 852, 693; **HRMS**: calc'd for $(M+Na)^+$ $C_{22}H_{19}NONa$: 336.1364; found: 336.1397.

(*R*,*E*)-*N*-(1-phenyl-3-(thiophen-3-yl)allyl)benzamide



Following the general procedure, the crude mixture was purified by flash column chromatography with elution by 15-30% ethyl acetate in hexanes to afford the product as a white solid. **Yield:** 70 mg, 88%; **er:** > 99.5:0.5; $[\alpha]_D^{23}$ = 10° (c = 1.0, $CHCl_3$); **HPLC Analysis,** t_r minor: 18.4 min., t_r major: 20.4 min., [Chiralcel®OD column, 24cm×4.6 mm I.D., Hexanes:IPA = 85:15, 1.0 mL/min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.83 (d, J = 7.2 Hz, 2H), 7.51 (t, J = 7.2 Hz, 1H), 7.45-7.36 (m, 7H), 7.31 (m, 1H), 7.26 (dd, J = 5.2, 3.2 Hz, 1H), 7.20 (d, J = 5.2 Hz, 1H), 7.14 (d, J = 3.2 hz, 1H), 6.66 (d, J = 8.0 hz, 1H), 6.60 (d, J = 16 Hz, 1H), 6.30 (dd, J = 16, 6.4 Hz, 1H), 5.99 (t, J = 6.8 Hz, 1H); **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ166.3, 144.7, 126.2, 134.1, 132.1, 131.8, 128.7, 128.6, 128.0, 127.9, 127.2, 127.1, 126.7, 125.3, 125.2, 51.0; **IR** (thin film, cm^{-1}): 3301, 3058, 3028, 1630, 1536, 1490, 1329, 1095, 961, 770, 700; **HRMS**: calc'd for $(M+Na)^+$ $C_{20}H_{17}NONaS$: 342.0929; found: 342.0953.

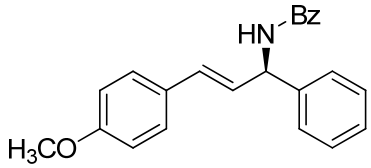
(*R*,*E*)-*N*-(3-(3-fluorophenyl)-1-phenylallyl)benzamide



Following the general procedure, the crude mixture was purified by flash column chromatography with elution by 15-30% ethyl acetate in hexanes to afford the product as a white solid. **Yield:** 68 mg, 82%; **er:** 95.5:4.5; $[\alpha]_D^{23}$ = +29° (c = 1.0, $CHCl_3$); **HPLC Analysis,** t_r major: 13.3 min., t_r minor: 14.6 min., [Chiralcel®OD column, 24cm×4.6 mm

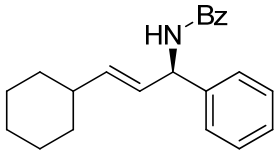
I.D., Hexanes:IPA = 85:15, 1.0 mL/min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.83 (d, J = 8.0 Hz, 2H), 7.52 (t, J = 8.0 Hz, 1H), 7.46-7.37 (m, 6H), 7.33 (m, 1H), 7.26 (m, 1H), 7.13 (d, J = 7.6 Hz, 1H), 7.08 (d, J = 11.2 Hz, 1H), 6.95 (t, J=8.4 Hz, 1H), 6.58 (d, J = 16 Hz, 1H), 6.57 (d, J = 8.0 Hz, 1H), 6.45 (d, J 16, 6.0 Hz, 1H), 6.02 (t, J = 7.2 Hz, 1H); **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ 166.5, 140.4, 134.2, 131.8, 130.5, 130.2, 130.1, 129.9, 129.0, 128.7, 127.9, 127.3, 127.0, 122.6, 122.5, 114.7, 114.5, 113.1, 112.9, 55.1; **IR** (thin film, cm^{-1}): 3300, 3028, 1635, 1581, 1530, 1489, 1215, 1144, 963, 755, 697; **HRMS**: calc'd for $(M+Na)^+$ $C_{22}H_{18}NOFNa$: 354.1270; found: 354.1277.

(*R*,*E*)-*N*-(3-(4-methoxyphenyl)-1-phenylallyl)benzamide



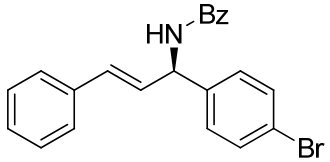
Following the general procedure, the crude mixture was purified by flash column chromatography with elution by 20-50% ethyl acetate in hexanes to afford the product as a white solid. **Yield:** 71 mg, 83%; **er:** 96:4; **$[\alpha]_D^{23}$** = +17.5° (c = 1.0, $CHCl_3$); **HPLC Analysis,** t_r major: 8.3 min., t_r minor: 10.1 min., [Chiralpak®AD column, 24cm×4.6 mm I.D., Hexanes:IPA = 80:20, 1.5 mL/min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.83 (d, J = 7.2 Hz, 2H), 7.53 (t, J = 7.2 Hz, 1H), 7.46–7.38 (m, 6H), 7.32 (d, J = 8.4 Hz, 2H), 7.31 (m, 1H), 3.81 (S, 3H), 6.84 (d, J = 8.4 Hz, 2H), 6.56 (d, J = 16 Hz, 1H), 6.51 (d, J = 7.6 Hz, 1H), 6.30 (dd, J = 16, 6.0 Hz, 1H), 6.01 (t, J = 6.4 Hz, 1H), 3.70 (s, 3H); **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ166.5, 159.4, 141.1, 134.4, 131.6, 131.3, 129.2, 128.8, 128.6, 127.8, 127.7, 127.2, 127.0, 126.5, 114.0, 55.3; **IR** (thin film, cm^{-1}): 3301, 3030, 2835, 1634, 1606, 1510, 1489, 1250, 1175, 1030, 968, 825, 698; **HRMS**: calc'd for $(M+Na)^+$ $C_{23}H_{21}NO_2Na$: 366.1470; found: 366.1502.

(*R*,*E*)-*N*-(3-cyclohexyl-1-phenylallyl)benzamide



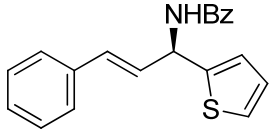
Following the general procedure, excess 2-cyclohexylvinylboronate (3 equiv.) was used. The crude mixture was purified by flash column chromatography with elution by 15-30% ethyl acetate in hexanes to afford the product as a white solid. **Yield:** 59 mg, 75%; **er:** 98:2; **$[\alpha]_D^{23}$** = +8.5° (c = 0.5, $CHCl_3$); **HPLC Analysis,** t_r major: 16.4 min., t_r minor: 18.0 min., [Chiralpak®AD column, 24cm×4.6 mm I.D., Hexanes:IPA = 95:5, 1.0 mL/min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ7.80 (d, J = 8.0 Hz, 2H), 7.50 (t, J = 8.0 Hz, 1H), 7.43 (t, J = 8.0 Hz, 2H), 7.35 (m, 4H), 7.28 (m, 1H), 6.39 (d, J = 8.0 Hz, 1H), 5.80 (dd, J = 8.4, 4.8 Hz, 1H), 5.66 (m, 2H), 2.01 (m, 1H), 1.73 (m, 3H), 1.64 (m, 1H), 1.26 (m, 3H), 1.10 (m, 3H); **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ 166.3, 141.6, 138.9, 134.5, 131.5, 128.7, 128.6, 127.4, 127.1, 127.0, 126.5, 55.0, 40.4, 32.8, 26.1, 26.0; **IR** (thin film, cm^{-1}): 3302, 3061, 3028, 2924, 2850, 1635, 1602, 1579, 1532, 1490, 1448, 1313, 1216, 1028, 969, 756, 697, 667; **HRMS**: calc'd for $(M+Na)^+$ $C_{22}H_{25}NONa$: 342.1834; found: 342.1831.

(*R*,*E*)-*N*-(1-(4-bromophenyl)-3-phenylallyl)benzamide



Following the general procedure, the crude mixture was purified by flash column chromatography with elution by 15-30% ethyl acetate in hexanes to afford the product as a white solid. **Yield:** 80 mg, 82%; **er:** 95.5:4.5; **$[\alpha]_D^{23}$** = -1.7° (c = 1.0, $CHCl_3$); **HPLC Analysis,** t_r major: 17.0 min., t_r minor: 19.4 min., [Chiralpak®AD column, 24cm×4.6 mm I.D., Hexanes:IPA = 85:15, 1.5 mL/min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ7.72 (d, J = 7.6 Hz, 2H), 7.44-7.30 (m, 5H), 7.27-7.16 (m, 7H), 6.69 (d, J = 8.0 Hz, 1H), 6.47 (d, J = 15.6 Hz, 1H), 6.28 (dd, J = 16, 6.4 Hz, 1H), 5.85 (t, J = 7.2 Hz, 1H); **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ 166.6, 139.9, 136.1, 134.0, 132.4, 131.9, 131.8, 128.9, 128.6, 128.1, 127.1, 126.6, 121.6, 54.8; **IR** (thin film, cm^{-1}): 3295, 3026, 1634, 1530, 1486, 1312, 1216, 1072, 1010, 966, 750, 692; **HRMS**: calc'd for $(M+Na)^+$ $C_{22}H_{18}NOBrNa$: 414.0469; found: 414.0488.

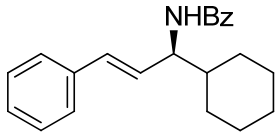
(*R*,*E*)-*N*-(3-phenyl-1-(thiophen-2-yl)allyl)benzamide



Following the general procedure, the crude mixture was purified by flash column chromatography with elution by 15-30% ethyl acetate in hexanes to afford the product as a white solid. **Yield:** 72 mg, 91%; **er:** 95:5; **$[\alpha]_D^{23}$** = +6.7° (c = 1.0, $CHCl_3$); **HPLC Analysis,** t_r minor: 13.6 min., t_r major: 14.8 min., [Chiralpak®AD column, 24cm×4.6 mm I.D., Hexanes:IPA = 85:15, 1.0 mL/min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ7.83 (d, J = 8.0 Hz, 2H), 7.52 (t, J = 8.0 Hz, 1H), 7.44 (t, J = 8.0 Hz, 2H), 7.39 (d, J = 7.2 Hz, 2H), 7.32 (t, J = 7.2 Hz, 2H), 7.26 (m, 3H), 7.08 (d, J = 3.6 Hz, 1H), 7.01 (dd, J = 5.2, 3.6 Hz, 1H), 6.72 (d, J = 15.6 Hz, 1H), 6.65 (d, J = 8.0 Hz, 1H), 6.46 (dd, J = 15.6, 6.4 Hz, 1H), 6.27 (t, J = 7.6 Hz, 1H); **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ166.3, 144.8, 136.2, 134.1, 132.1, 131.8, 128.7, 128.6, 128.0, 127.8, 127.2, 127.1, 126.7, 125.3,

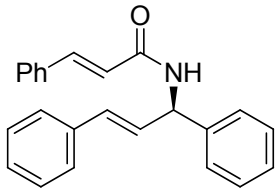
125.2, 51.0; **IR** (thin film, cm^{-1}): 3290, 2359, 1635, 1524, 1488, 1325, 965, 692; **HRMS**: calc'd for $(M+Na)^+$ $C_{20}H_{17}NONaS$: 342.0929; found: 342.0911.

(*S*,*E*)-*N*-(1-cyclohexyl-3-phenylallyl)benzamide



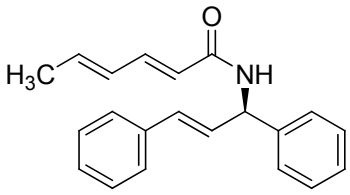
Following the general procedure, three equivalents of acyl imines were used in the styrylboronate addition reaction. The crude mixture was purified by flash column chromatography with elution by 15-30% ethyl acetate in hexanes to afford the product as a white solid. **Yield:** 56 mg, 70%; **er:** 95.5:4.5; $[\alpha]_D^{23}$ = +16° (c = 1.0, $CHCl_3$); **HPLC Analysis,** t_r major: 11.8 min., t_r minor: 14.7 min., [Chiralpak®AD column, 24cm×4.6 mm I.D., Hexanes:IPA = 90:10, 1.0 mL/min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ7.78 (d, J = 8.0 Hz, 2H), 7.52-7.22 (m, 8H), 6.58 (d, J = 16 Hz, 1H), 6.18 (dd, J = 16, 6.0 Hz, 1H), 6.15 (d, J = 6.0 Hz, 1H), 4.70 (dd, J = 6.0, 3.2 Hz, 1H), 1.93-1.62 (m, 7H), 1.35-1.06 (m, 4H); **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ 166.4, 136.2, 134.4, 132.1, 131.3, 128.7, 128.6, 127.9, 127.7, 127.1, 126.5, 51.3, 41.1, 30.1, 29.5, 26.0, 25.9; **IR** (thin film, cm^{-1}): 3327, 2928, 1623, 1576, 1515, 1448, 1347, 1073, 746, 690; **HRMS**: calc'd for $(M+Na)^+$ $C_{22}H_{25}NONa$: 342.1834; found: 342.1873.

***N*-((*R*,*E*)-1,3-diphenylallyl)cinnamamide**



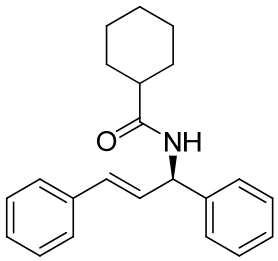
Following the general procedure, the crude mixture was purified by flash column chromatography with elution by 15-30% ethyl acetate in hexanes to afford the product as a white solid. **Yield:** 74 mg, 87%; **er:** 98.5:1.5; $[\alpha]_D^{23}$ = +20.9° (c = 1.0, $CHCl_3$); **HPLC Analysis,** t_r major: 13.1 min., t_r minor: 16.5 min., [Chiralpak®AD-H column, 24cm×4.6 mm I.D., Hexanes:IPA = 85:15, 1.5 mL/min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ7.69 (d, J = 15.6 Hz, 1H), 7.49 (m, 2H), 7.41 – 7.34 (m, 9H), 7.30 (t, J = 8.0 Hz, 2H), 7.24 (m, 2H), 6.59 (d, J = 8.4 Hz, 1H), 6.48 (d, J = 15.6 Hz, 1H), 6.40 (dd, J = 16, 6.0 Hz, 1H), 6.14 (d, J = 8.4 Hz, 1H), 5.97 (t, J = 7.2 Hz, 1H); **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ164.9, 141.8, 140.8, 136.4, 134.7, 131.5, 129.8, 128.9, 128.8, 128.7, 128.6, 127.8, 127.8, 127.3, 126.6, 120.4, 54.9; **IR** (thin film, cm^{-1}): 3266, 3028, 2926, 1653, 1616, 1539, 1448, 1352, 1216, 967, 745, 695; **HRMS**: calc'd for $(M+Na)^+$ $C_{24}H_{21}NONa$: 362.1521; found: 362.1555.

(2*E*,4*E*)-*N*-((*R*,*E*)-1,3-diphenylallyl)hexa-2,4-dienamide



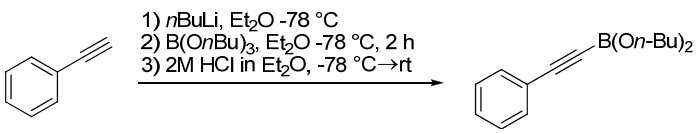
Following the general procedure, the crude mixture was purified by flash column chromatography with elution by 15-30% ethyl acetate in hexanes to afford the product as a white solid. **Yield:** 66 mg, 87%; **er:** 97.5:2.5; $[\alpha]_D^{23}$ = -16.8° (c = 0.5, $CHCl_3$); **HPLC Analysis,** t_r major: 10.4 min., t_r minor: 11.7 min., [Chiralpak®AD-H column, 24cm×4.6 mm I.D., Hexanes:IPA = 85:15, 1.5 mL/min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ7.40-7.20 (m, 10H), 6.58 (d, J = 15.6 Hz, 1H), 6.38 (dd, J = 15.6, 5.6 Hz, 1H), 6.12 (m, 3H), 5.90 (m, 1H), 5.80 (d, J = 14.4 Hz, 2H), 1.82 (d, J = 7.2 Hz, 3H); **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ165.0, 141.7, 140.6, 138.0, 136.1, 131.1, 129.2, 128.5, 128.2, 127.4, 126.9, 126.2, 120.7, 54.4, 18.3; **IR** (thin film, cm^{-1}): 3256, 3023, 2928, 1656, 1642, 1627, 1534, 1353, 1215, 1154, 998, 966, 755; **HRMS**: calc'd for $(M+Na)^+$ $C_{21}H_{21}NONa$: 326.1521; found: 326.1528.

(*R*,*E*)-*N*-(1,3-diphenylallyl)cyclohexanecarboxamide



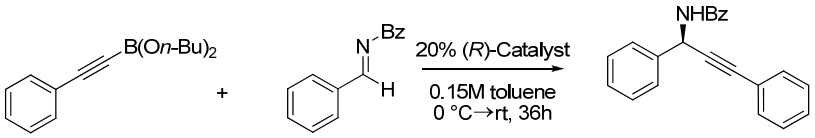
Following the general procedure, the crude mixture was purified by flash column chromatography with elution by 15-30% ethyl acetate in hexanes to afford the product as a white solid. **Yield:** 65 mg, 82%; **er:** 97.5:2.5; $[\alpha]_D^{23}$ = -3.8° (c = 0.5, $CHCl_3$); **HPLC Analysis,** t_r major: 11.9 min., t_r minor: 13.0 min., [Chiralpak®AD column, 24cm×4.6 mm I.D., Hexanes:IPA = 90:10, 1.0 mL/min]; **^{1}H NMR** (400 MHz, $CDCl_3$): δ7.4-7.2 (m, 10H), 6.51 (d, J = 16 Hz, 1H), 6.33 (dd, J = 16, 5.6 Hz, 1H), 5.83 (m, 2H), 2.16 (m, 1H), 1.92 (t, J = 12.8 Hz, 2H), 1.81 (m, 2H), 1.68 (m, 2H), 1.49 (m, 2H), 1.28 (m, 2H); **^{13}C NMR** (75.0 MHz, $CDCl_3$): δ175.0, 141.0, 136.5, 131.3, 129.0, 128.8, 128.6, 127.7, 127.6, 127.1, 126.5, 54.2, 45.6, 29.7, 25.7; **IR** (thin film, cm^{-1}): 3275, 3027, 2928, 2853, 1638, 1533, 1494, 1448, 1212, 1029, 965, 745, 695; **HRMS**: calc'd for $(M)^+$ $C_{22}H_{26}NO$: 320.2014; found: 320.2020.

General Pocedure For Synthesis of Alkynyl Boronates



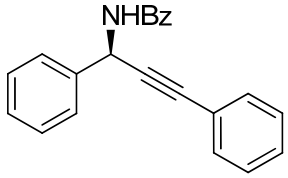
To a flask charged with argon was added 25mL diethyl ether and 1.53g phenyl acetylene (15mmol, 1eq.). Solution was cooled to -78 °C and to it was added 9.4mL *n*BuLi (15mmol, 1.6M in hexane). Solution was allowed to stir at this temp for 20 minutes. To a second flask charged with argon was added 50mL diethyl ether and 4.05mL tri-*n*-butyl borate (15mmol). Solution was cooled to -78 °C and to it was added *via* cannula the solution of lithium-acetylene. Reaction was allowed to stir at this temperature for 2 hours, at which point to it was added 7.5mL anhydrous HCl (2M solution in diethyl ether, 15mmol). Reaction was removed from the dryice-acetone bath and allowed to warm to rt for one hour, after which it was filtered through celite, azeotroped with toluene, concentrated *in vaccu*, and made into a 1M solution in toluene. Other variants were prepared in the same manner.

General Procedure for Alkynylboronate Addition to Acyl Imines



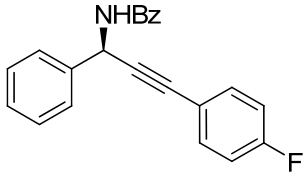
To a flask charged with argon was added appropriate imine SM (0.115mmol, 1 equiv.), 12mg catalyst ((*R*)-3,3'-Diphenyl-Dimethyl-H_8-BINOL 20 mol%), and 1mL toluene. Solution was cooled to 0 °C and to it was then added 115uL boronate (1M solution in toluene, .115mmol, 1 equiv.). Reaction was allowed to stir and warm to rt on its own accord over 36 hours. Reaction was then quenched by the addition of saturated ammonium chloride (5mL). Crude material was then extracted with $CHCl_3$ (2 X 15ml), dried over sodium sulfate, concentrated in vacuum and isolated *via* column chromatography, eluant 20% diethyl ether in hexanes. Reaction gave 35.6 mg desired product (99% yield) with an er of 96:4.

(*R*)-N-(1-phenylnon-2-ynyl)benzamide



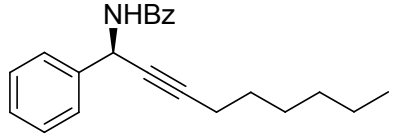
Following the general procedure, the crude mixture was purified by flash column chromatography with elution by 20% ether in hexane to yield the desired propargylic amide as a white solid. **Yield:** 35.6 mg, 99%; **er:** 96:4; $[\alpha]_D^{23}$ = -5.7° (c = 0.08, $CHCl_3$); **HPLC Analysis,** t_r minor: 11.2 min., t_r major: 14.4 min., [Chiralpak®AD-H column, 24cm×4.6 mm I.D., Hexanes:IPA = 90:10, 1.0 mL/min] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.47 (d, *J* = 8.4Hz, 1H), δ 6.63 (d, *J* = 8.4Hz, 1H), δ 7.41 (m, 11H), δ 7.64 (d, *J* = 7.6Hz, 2H), δ 7.81 (d, *J* = 6.8Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 45.6, 85.08, 86.93, 122.4, 127.16, 128.22, 128.34, 128.64, 128.82, 131.86, 133.8, 139.01, 166.18. **IR** (thin film, cm^{-1}): 1330.4, 1451.3, 1489.7, 1526.1, 1579.3, 1601.4, 1636.8, 3030.5, 3291.2. **HRMS**: calc'd for $(M+Na)^+$ 334.1208 found: 334.1228

(*R*)-N-(1-phenylnon-2-ynyl)benzamide



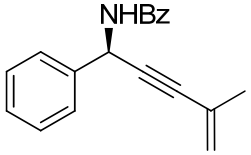
Following the general procedure, the crude mixture was purified by flash column chromatography with elution by 20% ether in hexane to yield the desired propargylic amide as a white solid. **Yield:** 29 mg, 76%; **er:** 93:7; $[\alpha]_D^{23}$ = -25.1° (c = 0.05, $CHCl_3$); **HPLC Analysis,** t_r minor: 12.3 min., t_r major: 15.9 min., [Chiralpak®AD-H column, 24cm×4.6 mm I.D., Hexanes:IPA = 90:10, 1.0 mL/min]. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.40 (d, *J* = 8.4Hz, 1H) δ 6.57 (d, *J* = 8.4Hz, 1H) δ 6.95 (t, *J* = 8.4Hz, 17.2Hz, 2H) δ 7.30 (m, 1H), δ 7.34 (m, 2H) δ 7.45 (m, 5H) δ 7.57 (d, *J* = 7.2Hz, H) δ 7.75 (d, *J* = 7.2Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 29.80, 45.66, 84.07, 86.80, 115.57, 115.87, 127.24, 128.35, 128.73, 128.93, 131.96, 133.81, 133.86, 133.92, 138.97, 166.26. **IR** (thin film, cm^{-1}): 835.3, 1231.5, 1488.9, 1525.7, 1506.7, 1635.9, 3061.5, 3290.2. **HRMS**: calc'd for $(M+Na)^+$ 352.1114 found: 352.1158

(*R*)-N-(1-phenylnon-2-ynyl)benzamide



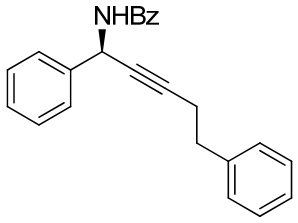
Following the general procedure, the crude mixture was purified by flash column chromatography with elution by 20% ether in hexane to yield the desired propargylic amide as a white solid. **Yield:** 31 mg, 84%; **er:** 92.5:6.5; $[\alpha]_D^{23}$ = -7.4° (c = 0.4, $CHCl_3$); **HPLC Analysis,** t_r minor: 5.2 min., t_r major: 6.2min., [Chiralpak®AD-H column, 24cm×4.6 mm I.D., Hexanes:IPA = 90:10, 1.0 mL/min]. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.87 (t, *J* = 6.8Hz, 3H), δ 1.29 (m, 4H), δ 1.4 (m, 2H), 1.54 (m, 2H), δ 2.25 (t, *J* = 7.2Hz, 2H) δ 6.2 (d, *J* = 8.4Hz, 1H), 6.6 (d, *J* = 8.4Hz, 1H), δ 7.38 (m, 5H), δ 7.45 (m, 1H), δ 7.57 (d, *J* = 7.2Hz, 2H), 7.71 (d, *J* = 7.2Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 14.02, 18.77, 22.51, 28.55, 31.26, 45.27, 85.92, 127.06, 127.92, 128.53, 131.67, 133.92, 139.61, 166.06. **IR** (thin film, cm^{-1}): 1325.1, 1488.4, 1519.1, 1633.8, 2855.7, 2929.3, 3301.1. **HRMS**: calc'd for $(M+Na)^+$ 342.1834 found: 342.1853

(*R*)-N-(4-methyl-1-phenylpent-4-en-2-ynyl)benzamide



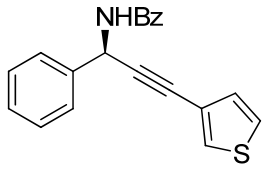
Following the general procedure, the crude mixture was purified by flash column chromatography with elution by 20% ether in hexane to yield the desired propargylic amide as a white solid. **Yield:** 25.1 mg, 80%; **er:** 96:4; $[\alpha]_D^{23}$ = -6.4° (c = 0.05, $CHCl_3$); **HPLC Analysis,** t_r major: 9.09 min., t_r minor: 9.79min., [Chiralpak®AD-H column, 24cm×4.6 mm I.D., Hexanes:IPA = 90:10, 1.0 mL/min]. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.92 (s, 3H), δ 6.36 (d, *J* = 8.8Hz, 1H) δ 6.59 (d, *J* = 8.4Hz, 1H), δ 7.40 (m, 5H) δ 7.50 (m, 1H), δ 7.58 (d, *J* = 9.6Hz, 2H), δ 7.78 (d, *J* = 9.6Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 23.337, 45.41, 85.83, 86.21, 122.69, 127.09, 128.10, 128.58, 128.72, 131.78, 133.81, 139.05, 166.06. **IR** (thin film, cm^{-1}): 1290.4, 1489.1, 1526.4, 1637.2, 2920.3, 3061.8, 3291.2. **HRMS**: calc'd for $(M+Na)^+$ 276.1388 found: 276.1380

(*R*)-N-(1,5-diphenylpent-2-ynyl)benzamide



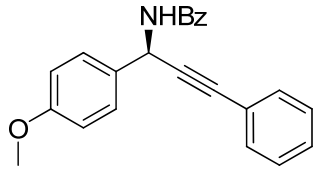
Following the general procedure, the crude mixture was purified by flash column chromatography with elution by 20% ether in hexane to yield the desired propargylic amide as a white solid. **Yield:** 27.5 mg, 71%; **er:** 96.5:3.5; $[\alpha]_D^{23}$ = -18.6° (c = 0.09, $CHCl_3$); **HPLC Analysis,** t_r minor: 18.3 min., t_r major: 19.4 min., [Chiralpak®AD-H column, 24cm×4.6 mm I.D., Hexanes:IPA = 90:10, 1.0 mL/min]. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.59 (t, *J* = 7.2Hz, 14.8Hz, 2H) δ 2.872 (t, *J* = 7.2Hz, 14.8Hz, 2H) δ 6.17 (d, *J* = 8.4Hz, 1H) δ 6.44 (d, *J* = 8.4, 1H) δ 7.29 (m, 8H) δ 7.48 (m, 5H) δ 7.77 (d, *J* = 7.2Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 20.87, 34.77, 45.22, 78.77, 84.89, 126.27, 127.03, 127.063, 127.90, 128.32, 128.51, 128.56, 128.68, 131.67, 133.84, 139.29, 140.43, 166.01. **IR** (thin film, cm^{-1}): 1330.3, 1489.1, 1526.6, 1636.2, 2927.6, 3028.3, 3060.7, 3292.7. **HRMS**: calc'd for $(M+Na)^+$ 362.1521 found: 362.1494

(*R*)-N-(1-phenyl-3-(thiophen-3-yl)prop-2-ynyl)benzamide



Following the general procedure, the crude mixture was purified by flash column chromatography with elution by 20% ether in hexane to yield the desired propargylic amide as a white solid. **Yield:** 26 mg, 72%; **er:** 96:4; $[\alpha]_D^{23}$ = -12.8° (c = 0.08, $CHCl_3$); **HPLC Analysis,** t_r minor: 15.2 min., t_r major: 20.6 min., [Chiralpak®AD-H column, 24cm×4.6 mm I.D., Hexanes:IPA = 90:10, 1.0 mL/min] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.4 (d, *J* = 8.4Hz, 1H), δ 6.58 (d, *J* = 8.4Hz, 1H), δ 7.09 (m, 1H), δ 7.21 (m, 1H), δ 7.27 (s, 1H), δ 7.35 (m, 4H), δ 7.45 (m, 2H), δ 7.57 (d, *J* = 7.6Hz, 2H), δ 7.75 (d, *J* = 6.8Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 45.51, 80.09, 86.46, 125.26, 127.02, 128.06, 128.47, 128.65, 129.20, 129.79, 131.69, 133.65, 138.82, 166.03. **IR** (thin film, cm^{-1}): 782.4, 1051.9, 1327.9, 1488.2, 1524.9, 1636.9, 3060.5, 3106.2, 3285.4. **HRMS**: calc'd for $(M+Na)^+$ 318.0953 found: 318.0948

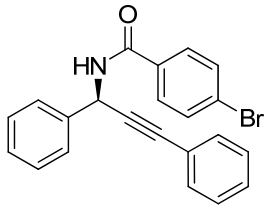
(*R*)-N-(1-(4-methoxyphenyl)-3-phenylprop-2-ynyl)benzamide



Following the general procedure, the crude mixture was purified by flash column chromatography with elution by 20% ether in hexane to yield the desired propargylic amide as a white solid. **Yield:** 38.7 mg, 99%; **er:** 96:4; $[\alpha]_D^{23}$ = -10.9° (c = 0.06,

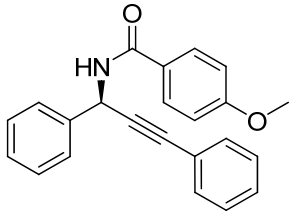
$CHCl_3$); **HPLC Analysis,** t_r minor: 19.9 min., t_r major: 24.6 min., [Chiralpak®AD-H column, 24cm×4.6 mm I.D., Hexanes:IPA = 90:10, 1.0 mL/min. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 3.73 (s, 3H) δ 6.34 (d, *J* = 8.4Hz, 1H) δ 6.59 (d, *J* = 8.4Hz, 1H) δ 6.84 (d, *J* = 9Hz, 2H) δ 7.25 (m, 3H) δ 7.39 (m, 5H) δ 7.50 (d, *J* = 9Hz, 2H) δ 7.74 (d, *J* = 7.2Hz, 2H) **^{13}C NMR** (75 MHz, $CDCl_3$): δ 44.95, 55.20, 84.72, 87.05, 113.95, 126.97, 127.01, 128.19, 128.33, 128.36, 128.41, 128.45, 128.49, 131.68, 131.71, 133.74, 159.34, 165.94. **IR** (thin film, cm^{-1}): 1174.0, 1249.3, 1488.8, 1510.5, 1634.8, 2834.6, 2953.9, 3058.9, 3277.7. **HRMS**: calc'd for $(M+Na)^+$ 364.1313 found: 364.1350

(*R*)-4-bromo-N-(1,3-diphenylprop-2-ynyl)benzamide



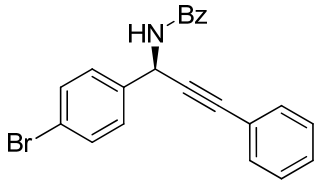
Following the general procedure, the crude mixture was purified by flash column chromatography with elution by 20% ether in hexane to yield the desired propargylic amide as a white solid. **Yield:** 27.5 mg, 70%; **er:** 97:3 **$[\alpha]_D^{23}$** = -10.6° (c = 0.07, $CHCl_3$); **HPLC Analysis,** t_r minor: 6.1 min., t_r major: 13.6 min., [Chiralpak®AD-H column, 24cm×4.6 mm I.D., Hexanes:IPA = 90:10, 1.0 mL/min] **^{1}H NMR** (300 MHz, $CDCl_3$): δ 6.38 (d, *J* = 8.4Hz, 1H) δ 6.60 (d, *J* = 8.4Hz, 1H) δ 7.36 – 7.19 (m, 6H) δ 7.42 (dd, *J* = 2, 6.8Hz, 2H) δ 7.50 (d, *J* = 8.4Hz, 2H) δ 7.55 (d, *J* = 7.2Hz, 2H) δ 7.62 (d, *J* = 8.4Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 45.8, 85.3, 86.7, 122.4, 126.6, 127.2, 128.37, 128.41, 128.74, 128.82, 128.90, 131.90, 131.92, 132.7, 138.9, 165.3. **IR** (thin film, cm^{-1}): 841.7, 1144.3, 1481.4, 1526.3, 1636.1, 2924.2, 3287.0. **HRMS**: calc'd for $(M+Na)^+$ $C_{22}H_{16}BrNONa$ 390.0494 found: 390.0474

(*R*)-N-(1,3-diphenylprop-2-ynyl)-4-methoxybenzamide



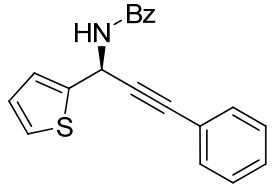
Following the general procedure, the crude mixture was purified by flash column chromatography with elution by 20% ether in hexane to yield the desired propargylic amide as a white solid. **Yield:** 31.5 mg, 80%; **er:** 93:7; **$[\alpha]_D^{23}$** = -7.3° (c =0.9, $CHCl_3$); **HPLC Analysis,** t_r minor: 11.0 min., t_r major: 13.0 min., [Chiralpak®AD-H column, 24cm×4.6 mm I.D., Hexanes:IPA = 85:15, 1.0 mL/min] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 3.82 (s, 3H), δ 6.46 (d, *J* = 8.4Hz, 1H), δ 6.58 (d, *J* = 8.4Hz, 1H), δ 6.91 (d, *J* = 8.8Hz, 2H), δ 7.316 (m, 4H), δ 7.379 (t, *J* = 7.2Hz, 14.8Hz, 2H), δ 7.47 (m, 2H), δ 7.63(d, *J* = 7.2Hz, 2H), δ 7.77 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 45.72, 55.67, 85.19, 87.37, 114.02, 122.70, 126.25, 127.43, 128.38, 128.56, 128.82, 129.01, 129.26, 132.08, 139.43, 162.67, 165.92. **IR** (thin film, cm^{-1}): 1177.3, 1254.9, 1501.0, 1532, 1606.4, 1633.5, 2932.0, 3293.5. **HRMS**: calc'd for $(M+Na)^+$ 364.1313 found: 364.1342

(*R*)-N-(1-(4-bromophenyl)-3-phenylprop-2-ynyl)benzamide



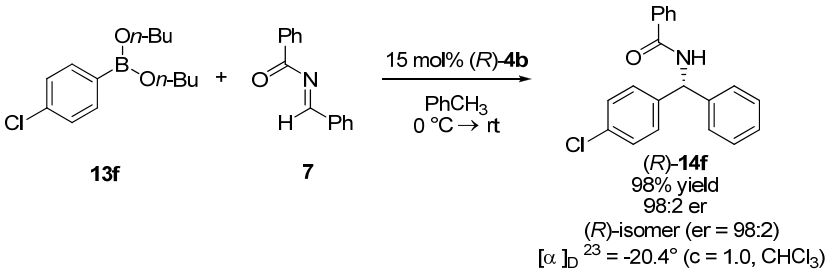
Following the general procedure, the crude mixture was purified by flash column chromatography with elution by 20% ether in hexane to yield the desired propargylic amide as a white solid. **Yield:** 28 mg, 63%; **er:** 93:7; **$[\alpha]_D^{23}$** = -10.6° (c = 0.07, $CHCl_3$); **HPLC Analysis,** t_r minor: 11.1 min., t_r major: 14.3 min., [Chiralpak®AD-H column, 24cm×4.6 mm I.D., Hexanes:IPA = 90:10, 1.0 mL/min] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.41(d, *J* = 8.4Hz, 1H) δ 6.65 (d, *J* = 8.4Hz, 1H) δ 7.33 (m, 3H) δ 7.45 (m, 9H) δ 7.79 (d, *J* = 7.2Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 45.1,85.4, 86.2, 122.0, 122.1, 127.1 ,128.3, 128.6, 128.7, 128.9, 131.8, 131.9, 133.5, 138.2, 166.2. **IR** (thin film, cm^{-1}): 1335.7, 1442.8, 1486.3, 1521.0, 1634.9, 2854.9, 2924.0, 3281.2. **HRMS**: calc'd for $(M+Na)^+$ 412.0313 found: 412.0273

(*S*)-N-(3-phenyl-1-(thiophen-2-yl)prop-2-ynyl)benzamide



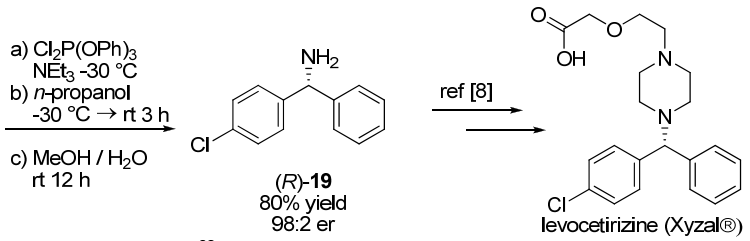
Following the general procedure, the crude mixture was purified by flash column chromatography with elution by 20% ether in hexane to yield the desired propargylic amide as a white solid. **Yield:** 29.1 mg, 80%; **er:** 97:3; **$[\alpha]_D^{23}$** = -13.1° (c = 0.1, $CHCl_3$); **HPLC Analysis,** t_r minor: 12.6 min., t_r major: 13.5 min., [Chiralpak®AD-H column, 24cm×4.6 mm I.D., Hexanes:IPA = 90:10, 1.0 mL/min] **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.64 (d, *J* = 8.4Hz, 1H), δ 6.70 (d, *J* = 8.4Hz, 1H), δ 6.99 (q, *J* = 3.6Hz, 1.6Hz, 1H), δ 7.27 (dd, *J* = 5.2Hz, 1.6Hz, 1H), δ 7.29 (m, 1H), δ 7.33 (m, 3H), δ 7.47 (m, 5H), δ 7.81 (d, *J* = 7.2Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 41.4, 84.3, 86.3, 122.0, 125.6, 126.0, 126.8, 127.1, 128.3, 128.6, 128.7, 131.8, 131.9, 133.5, 142.8, 165.9. **IR** (thin film, cm^{-1}): 1330.9, 1442.4, 1488.2, 1519.3, 1637.6, 2924.9, 3278.7. **HRMS**: calc'd for $(M+Na)^+$ 340.0772 found: 340.0796

Absolute Stereochemistry Determination for Arylboronate Addition and Formal Synthesis of Leveocetirizine



13f **7**

(*R*)-**14f**
98% yield
98:2 er
(*R*)-isomer (er = 98:2)
$[\alpha]_D^{23}$ = -20.4° (c = 1.0, $CHCl_3$)

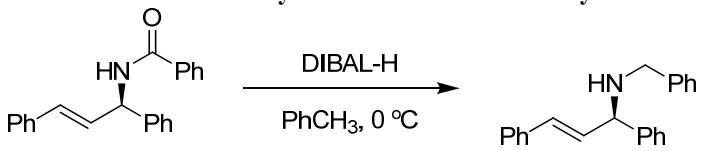


(*R*)-**19**
80% yield
98:2 er
$[\alpha]^{23}_D$ = –8.9° (c = 0.1, EtOH)
Lit[4]: $[\alpha]^{23}_D$ = -9.1° (c 1.1, EtOH)
(*R*)-enantiomer

levocetirizine (Xyzal®)
20

A flame dried 50mL round bottom flask was charged with argon and to it was added 15mL dry $CHCl_3$ and 1.5mL $P(OPh)_3$ (5.75mmol, 3.7 equiv). Solution was cooled to -30 °C and Cl_2 gas was then bubbled through until a bright yellow color appeared. $P(OPh)_3$ was then titrated into the solution at -30 °C until the yellow color disapated to almost colorless (apprx 250uL). To this reaction was then added via cannula a solution of 500mg chiral amide (*R*)-**21** (98:2er, 1.55mmol, 1equiv) in 5mL $CHCl_3$ followed immediately by 1.2mL triethylamine (8.9mmol, 5.7 equiv). Reaction was allowed to stir at this temperature for 3 hours, to it was then added 15 equiv of anhydrous *n*-propanol (35mL). Reaction was then allowed to warm to rt on its own accord over 3 hours. After this time solvent was removed under vacuum and material was taken up in a 1:1 mixture of water and methanol. This heterogeneous mixture was allowed to stir at rt for 12 hours. After stirring, the top portion was decanted, leaving behind the insoluble material. The organic phase was then acidified with 40mL 3M HCl and extracted with ether (2 X 30mL). The aqueous layer was then basified with 50mL 3M NaOH and extracted with ether again (2 X 30mL). The two organic portions were then collected, dried over sodium sulfate, filtered and solvent removed under reduced pressure. Crude material was then put on a column and eluted with 2% to 10 % MeOH in $CHCl_3$ to give the desired free amine in 80% yield (271mg, 1.25mmol). The optical rotation along with other analytical data matched previous reports.[4] HPLC analysis of the free amine was not done as previous reports have shown that re-acylating the amine can be done without racemizing of the chiral center.[4]

Absolute Stereochemistry Determination for Alkenylboronate Addition



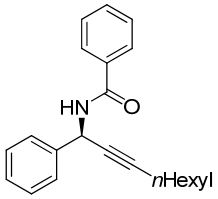
(R)-isomer (97.5:2.5 er)
$[\alpha]^{23}_D$ = +18.8° (C = 1.0, $CHCl_3$)

$[\alpha]^{23}_D$ = –22.8° (C = 1.0, $CHCl_3$)
Lit: $[\alpha]^{20}_D$ = –24.8° (C = 1.4, $CHCl_3$, 98.5:1.5 er)

A 25 mL flame-dried round bottom flask was equipped with stir bar and flushed with Ar. Allylic benzamide (62 mg, 0.20 mmol) was added and dissolved in CH_2Cl_2 (2.0 mL). The solution was cooled to 0 °C. Diisobutylaluminum hydride (1.0 mL, 1.0 mmol, 1 M in toluene) was added drop wise. The reaction was slowly warmed up to room temperature and stirred for 3 h. The reaction mixture was quenched with water (5.0 mL) and extracted with CH_2Cl_2 (5 mL×2). The organic layers were combined, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography over silica gel (elution with 5-20% ethyl acetate in hexanes) to afford the desired homoallylic benzylamine as a waxy compound (54mg, 91% yield) with $[\alpha]_D^{23}$ =-22.8° (c = 0.5, $CHCl_3$). Lit[5]: $[\alpha]_D^{20}$ = -24.8° (c = 1.4, $CHCl_3$, 98.5:1.5 er).

Absolute Stereochemistry Determination for alkynylboronate Addition

Absolute stereochemistry of the propargyl amides was done by comparison of known literature values to observed values. Alkyl substituted propargyl amide has a reported value of $[\alpha]_D^{23}$ = +8.9 (c = 0.9 $CHCl_3$ er = 90:10) for the *S*-enantiomer.[6] Our propargyl amide (Table 3, entry 2) was observed to have a value $[\alpha]_D^{23}$ = -15.3 (c = 0.07 $CHCl_3$ er = 92:8) and was assigned as the (*R*)-enantiomer. This is congruent with our illustrated transition state as our theory for stereochemical outcome shows that the (*R*) catalyst will give the (*R*) enantiomer product.



(*R*) enantiomer: $[\alpha]_D^{23}$ = -15.3 (c = 0.07) $CHCl_3$
(*S*) enantiomer lit[6]: $[\alpha]_D^{23}$ = +8.9 (c = 0.9) $CHCl_3$

Direct Injection MS studies of ligand exchange; Boronate and Diol.

To a flask charged with argon was added 2.5mL toluene-d_8, 250uL vinyl boronate solution (0.25mmol, 1equiv, 1M) in toluene, and 22mg catalyst (0.038mmol, 0.15 equiv). Thirty microlitres of this solution was then dilluted with 500uL acetonitrile and directly injected into our MicroMass ZQ 2000 mass sprectrometer in negative electron spray ionization mode (ES/voltages : capillary 3.01 KV, cone ramped from 10 to 80 V; Temperature: source 130 °C, desolvation 260 °C; gas flow : desolvation 250L/h, cone 50 L/h; pumpflow 150uL/min). The spectrum observed is illustrated below in Figure 1.

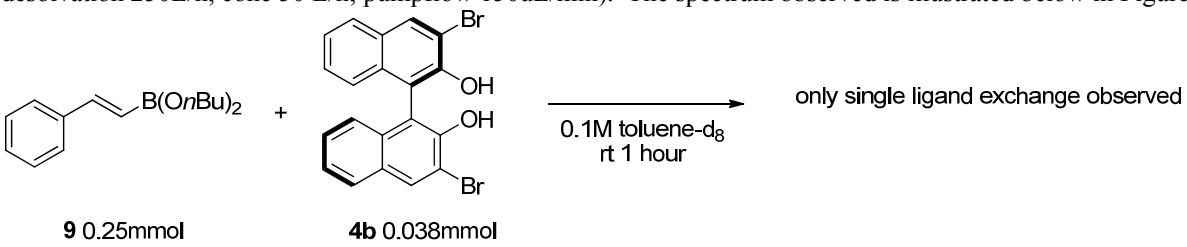
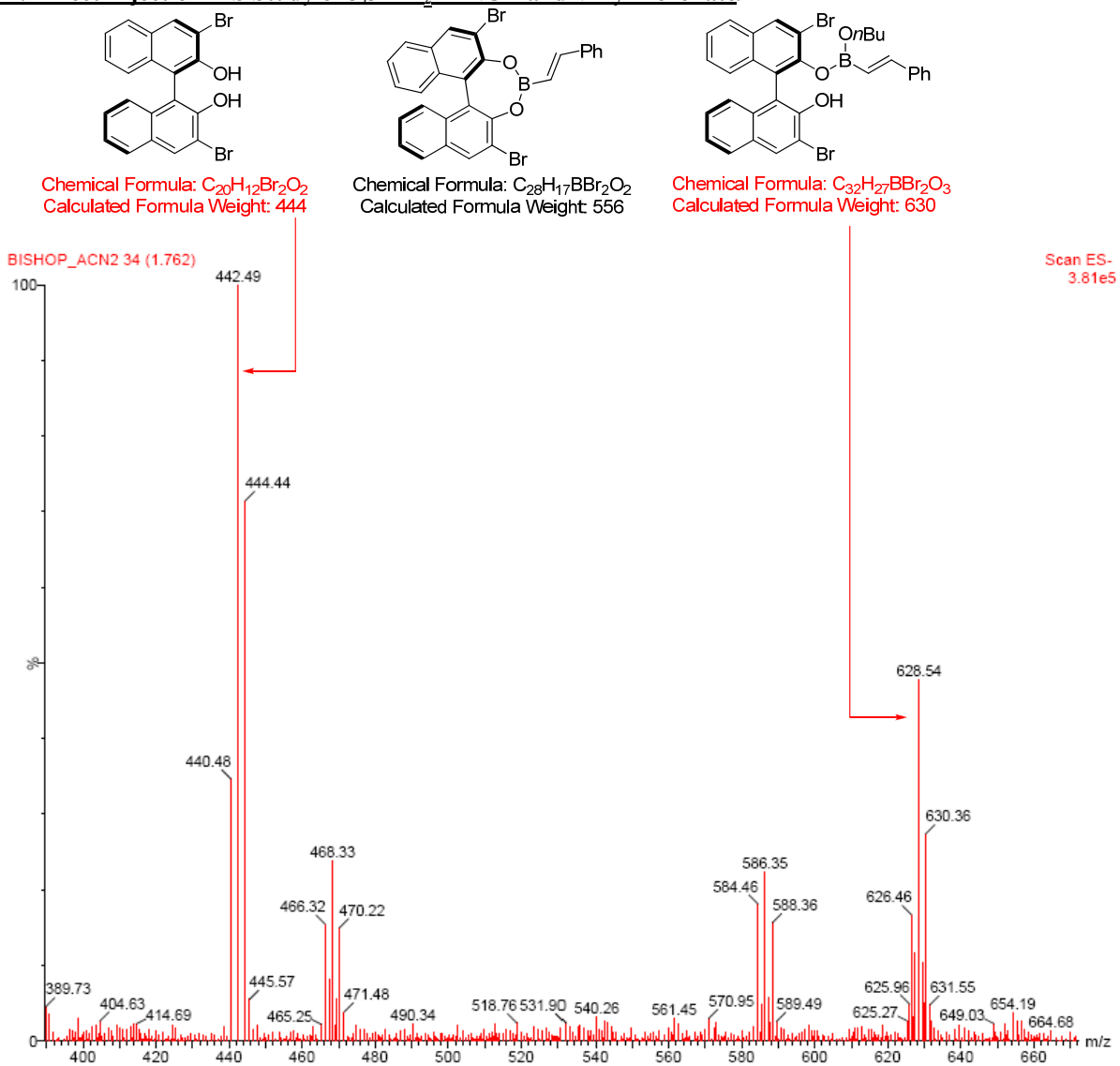
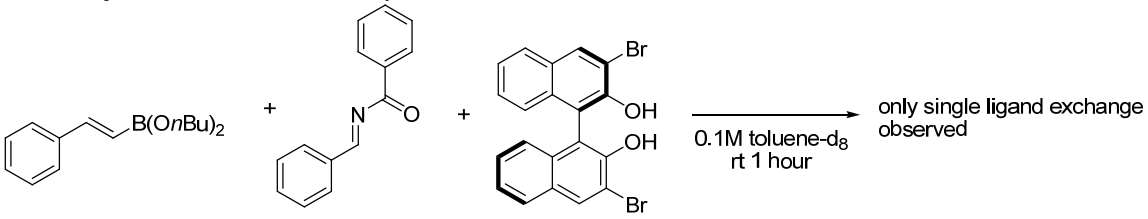


Figure 1. **Direct Injection MS Study of 3,3'-Br_2-BINOL and Vinyl Boronate.**



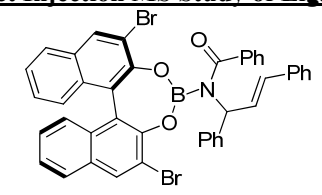
We found that direct injection MS studies are the preferred process for explicating the most likely mechanistic pathway of this addition reaction. Illustrated above in Figure 1 is the spectrum generated from the reaction between a catalytic amount of chiral diol **4b** and 1 equivalent vinyl boronate **9**. The observed results depict a lone acyclic product of the single ligand exchange pathway (Calculated formula weight: **630**, observed: **628.54**). No amount of the cyclic product generated by a dual ligand exchange pathway is observed (Calculated formula weight: **556**). The data generated here, as well as in a previous report,[2] leads us to the conclusion that the single ligand exchange species is the active nucleophile.

Direct Injection MS studies of vinyl boronate addition reaction.

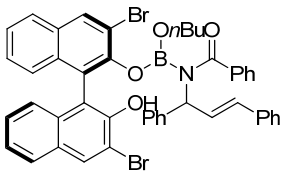


To the same reaction vessel described above was then added 52mg imine (0.25mmol, 1 equiv) and was allowed to stir at rt 1 hour. Thirty microlitres of this solution was then dilluted with 500uL acetonitrile. 150uL of this solution was then directly injected into our MicroMass ZQ 2000 mass sprectrometer in positive electron spray ionization mode (ES/voltages : capillary 3.01 KV, cone ramped from 10 to 80 V; Temperature: source 130 °C, desolvation 260 °C; gas flow : desolvation 250L/h, cone 50 L/h; pumpflow 150uL/min). The spectrum observed is illustrated below in Figure 2.

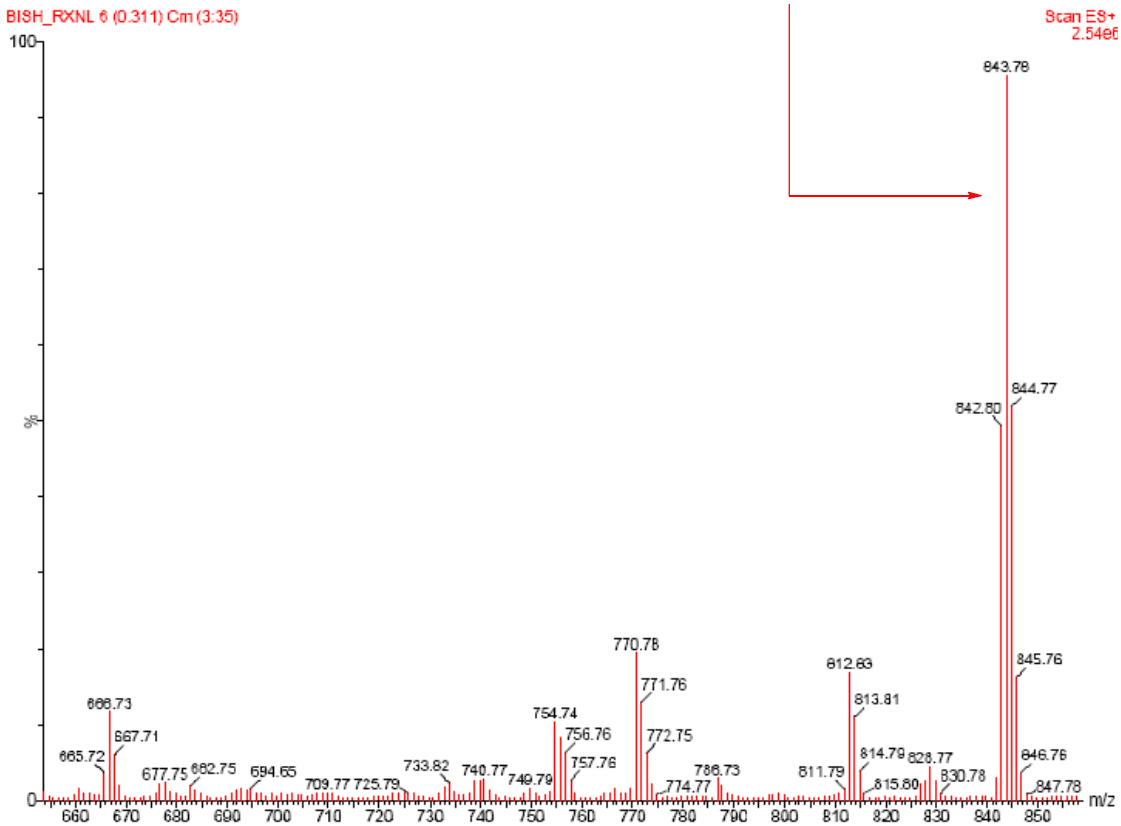
Figure 2. **Direct Injection MS Study of Ligand Exchange/Vinyl Boronate Addition Process.**



Chemical Formula: $C_{42}H_{28}BBr_2NO_3$
Calculated Formula Weight: 767



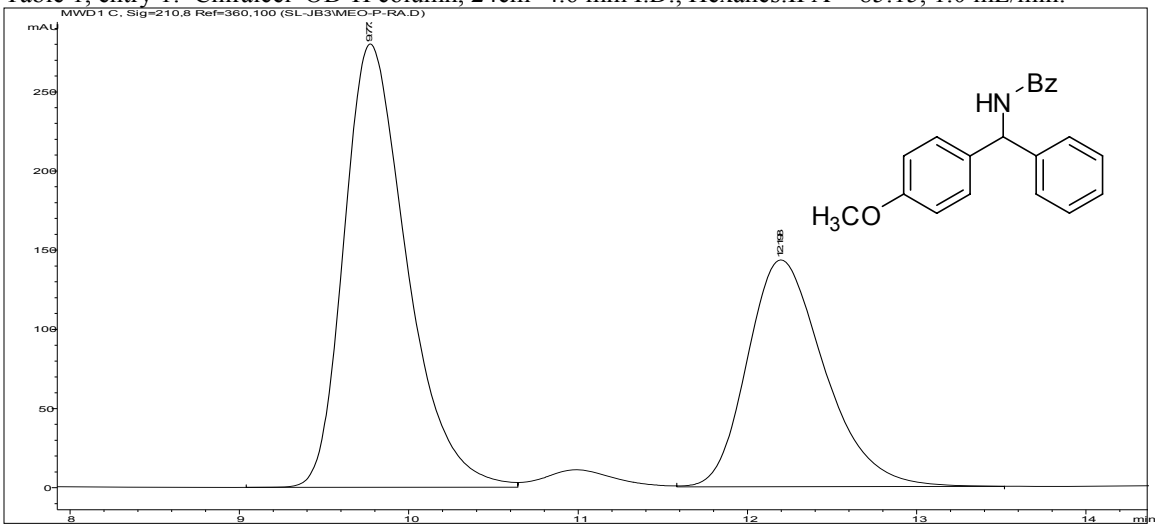
Chemical Formula: $C_{46}H_{38}BBr_2NO_4$
Calculated Formula Weight: 841



Further evidence to support our hypothesis is produced when performing the same ESI-MS analysis on the reaction mixture. Illustrated in Figure 2 above is the spectrum of a solution consisting of vinyl boronate **9**, chiral diol **4b** and imine **7**. The resting state of the catalytic cycle as the sinlge ligand exchange species **21** is observed (Calculated formula weight: **841**, observed: **843.79**). Again, no cyclic dual ligand exchange species is detected (Calculated formula weight: **767**). This result also strengthens our hypothesis that the boron is activated by the nitrogen of the imine before the addition occurs. Activation of boron in this manner is not a novel concept as Corey[7] has shown this type of reactivity in the past. These results lead us to believe that the active catalytic species is the single ligand exchange intermediate.

HPLC Analysis of Chiral Aryl Amide Products

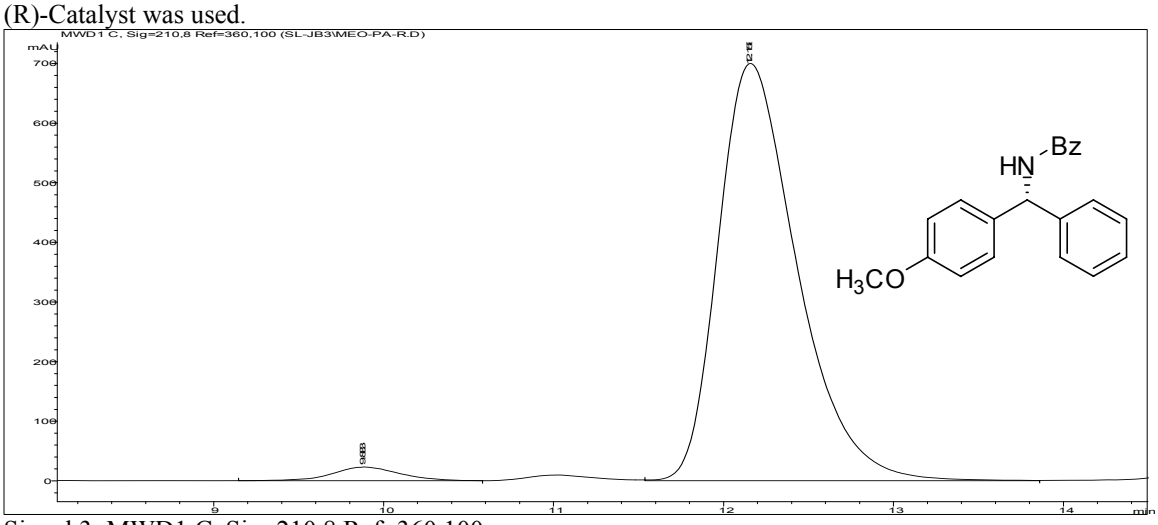
Table 1, entry 1: Chiralcel®OD-H column, 24cm×4.6 mm I.D., Hexanes:IPA = 85:15, 1.0 mL/min.



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

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.773	VV	0.3944	7208.23828	279.91806	61.3750
2	12.198	VB	0.4856	4536.34570	143.19022	38.6250
Totals :				1.17446e4	423.10828	

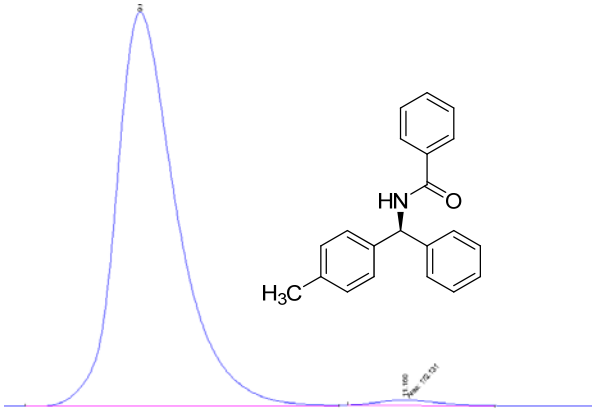
(R)-Catalyst was used.



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

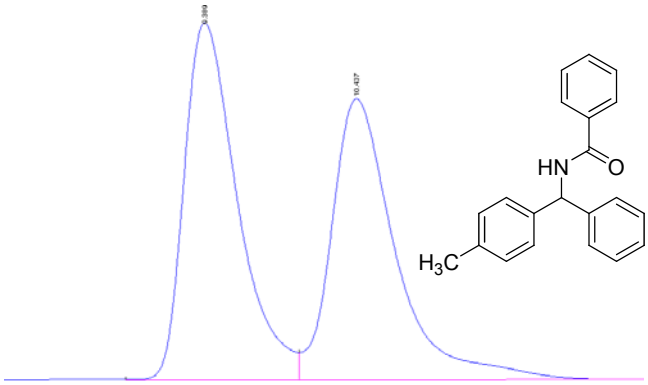
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.883	BV	0.4167	623.95898	22.70119	2.6905
2	12.158	VB	0.4941	2.25671e4	700.02368	97.3095
Totals :				2.31910e4	722.72487	

Table 1, Entry 2



4-ch3 aryl add
cat add to parent imine
10% ipa hexane
chiral cel od col

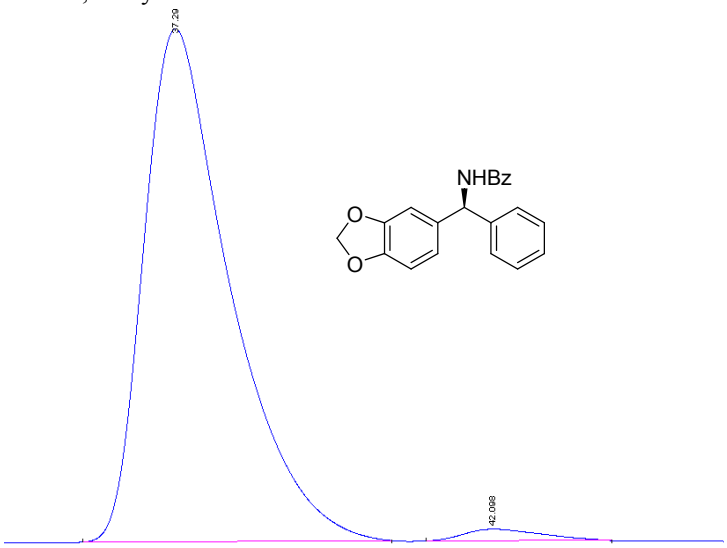
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.614	VV	0.3711	1.10702e4	446.78793	98.4689
2	11.160	MM	0.4451	172.13052	6.44548	1.5311



4-CH3 aryl add rac
10% ipa in hexane
chiral cel od col

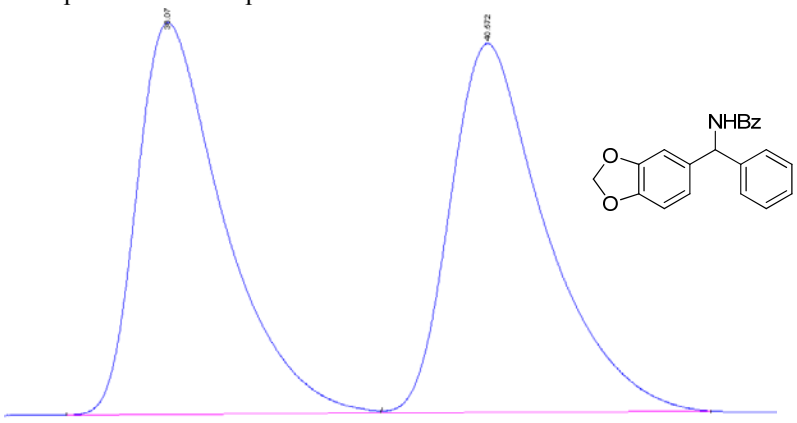
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.389	VV	0.3922	1.84146e4	720.45837	51.3739
2	10.437	VB	0.4547	1.74297e4	566.86792	48.6261

Table 1, Entry 3



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	37.299	BB	1.3193	7093.71484	78.12447	97.9144
2	42.098	BB	0.9857	151.09909	1.79577	2.0856

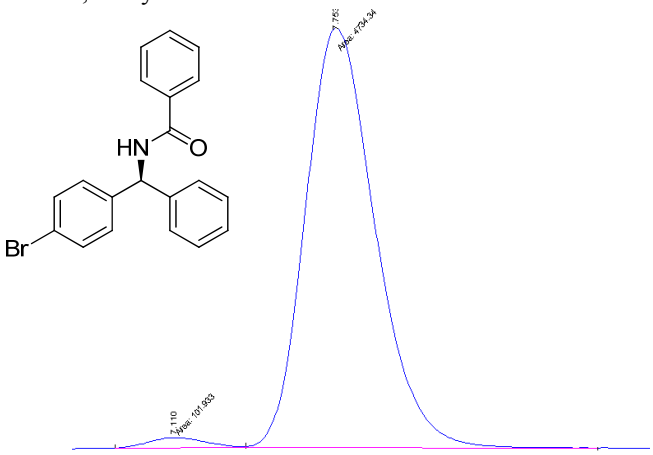
dioxle aryl boronate addition
parent imine S Br2 BINOL cat
10% ipa hexane chiral pak adh col



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.077	VB	1.2336	7284.78320	85.53969	49.1152
2	40.572	BB	1.2828	7547.24023	80.57362	50.8848

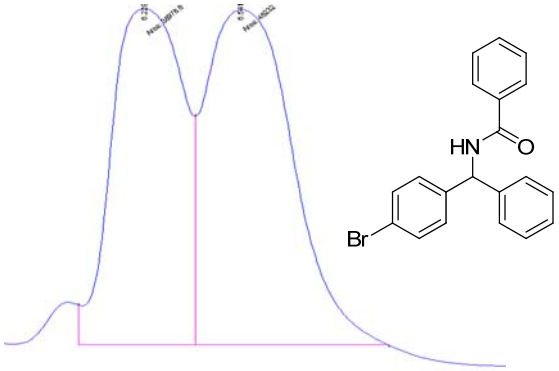
dioxle aryl boronate add
parent imine RAC addition
10% ipa in hexane chiral pak adh col

Table 1, Entry 4



4-br aryl cat add to parent imine
chiral cel OD col
10% ipa in hexane

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.110	MM	0.2674	101.93267	6.35386	2.1077
2	7.753	MM	0.3206	4734.33887	246.10439	97.8923

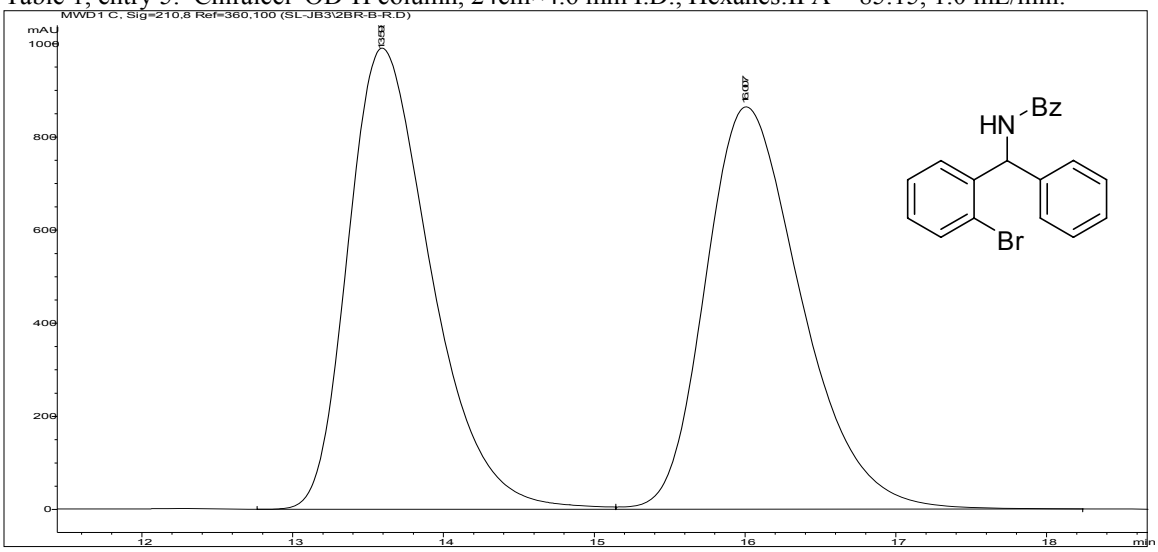


4-br rac add to parent imine

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.228	FM	0.2697	3.89786e4	2408.66577	45.7439
2	6.541	FM	0.3209	4.62320e4	2401.33447	54.2561

12% ipa in hexane
chiralcel OD col

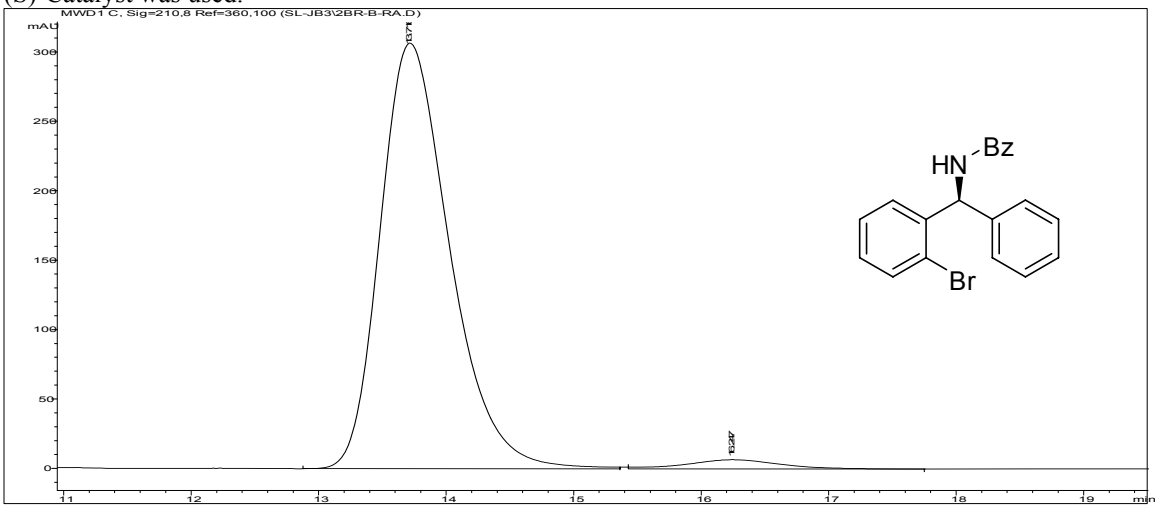
Table 1, entry 5: Chiralcel®OD-H column, 24cm×4.6 mm I.D., Hexanes:IPA = 85:15, 1.0 mL/min.



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

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.593	VV	0.5862	3.78613e4	990.02405	49.7854
2	16.007	VB	0.6839	3.81878e4	863.66937	50.2146
Totals :				7.60491e4	1853.69342	

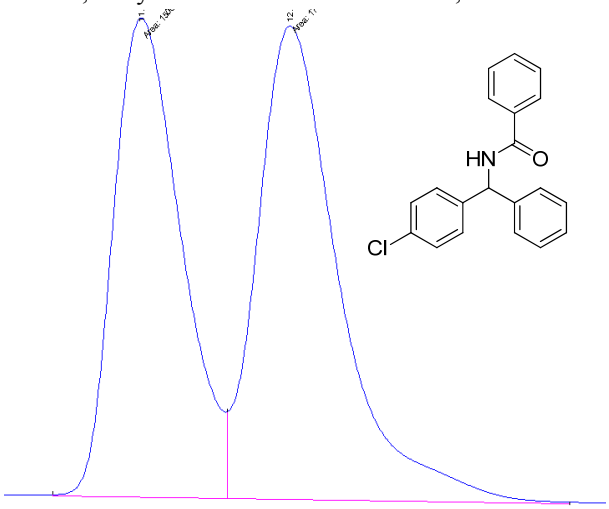
(S)-Catalyst was used.



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

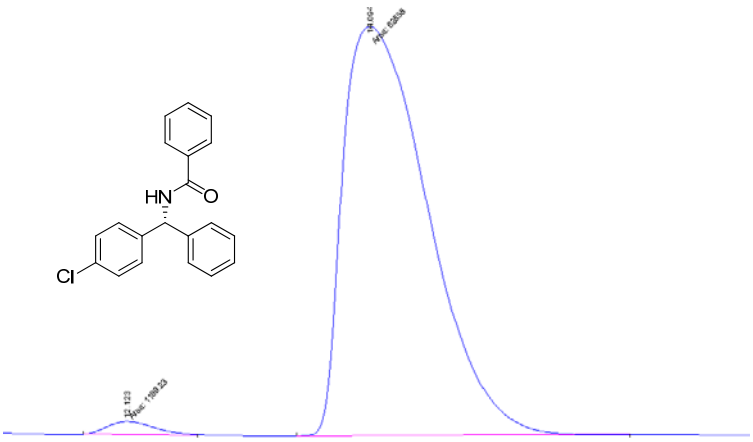
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.716	PB	0.5847	1.16349e4	306.58441	97.1262
2	16.247	BP	0.6575	344.25525	6.67687	2.8738
Totals :				1.19791e4	313.26128	

Table 1, entry 6: Chiralcel®OD-H column, 24cm×4.6 mm I.D., Hexanes:IPA = 85:15, 1.5 mL/min.



4-cl rac addition to parent imine
15% ipa in hexane
chiral cel OD col

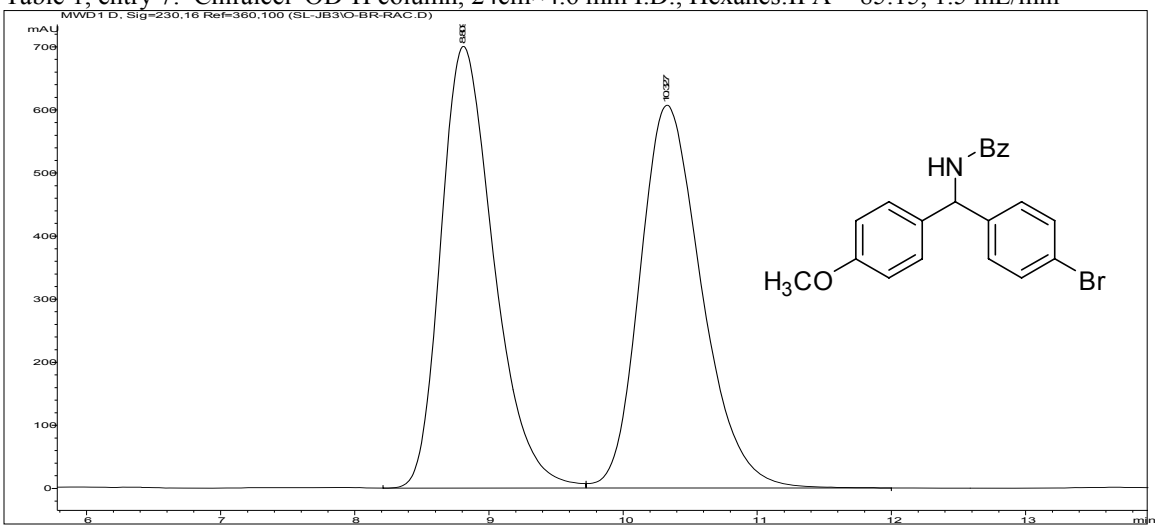
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.929	MF	0.5383	1.50853e4	467.07596	45.6863
2	12.947	FM	0.6478	1.79340e4	461.38361	54.3137



4-Cl aryl add
parent imine cat add
10% ipa in hexane
chiral cel OD col

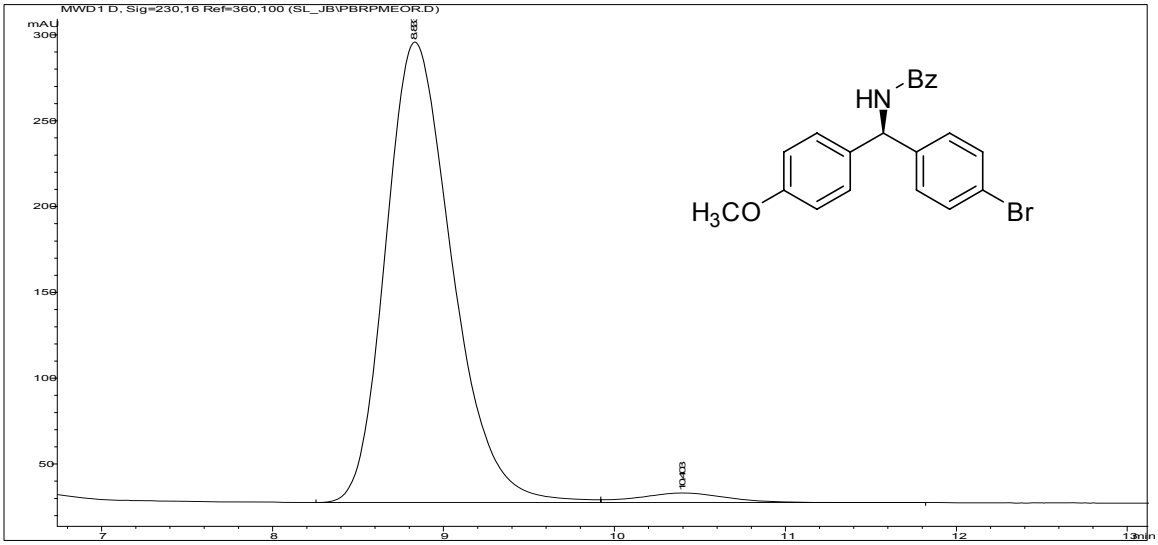
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.123	MM	0.4541	1169.22522	42.91714	1.8261
2	14.094	MM	0.8000	6.28580e4	1309.59607	98.1739

Table 1, entry 7: Chiralcel®OD-H column, 24cm×4.6 mm I.D., Hexanes:IPA = 85:15, 1.5 mL/min



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

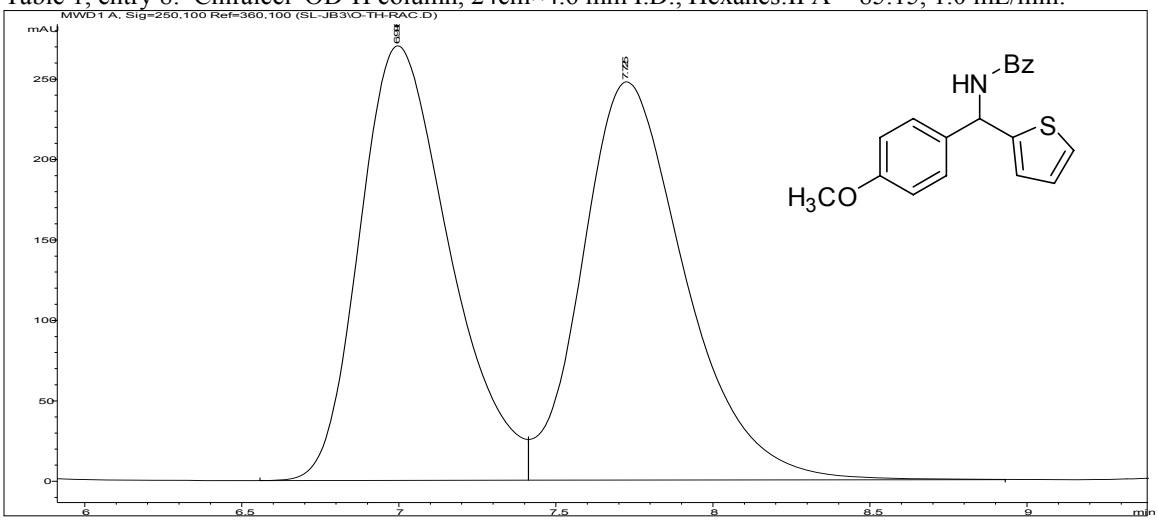
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.809	VV	0.4199	1.92040e4	700.25598	49.7700
2	10.327	VB	0.4906	1.93815e4	606.84607	50.2300
Totals :				3.85854e4	1307.10205	



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

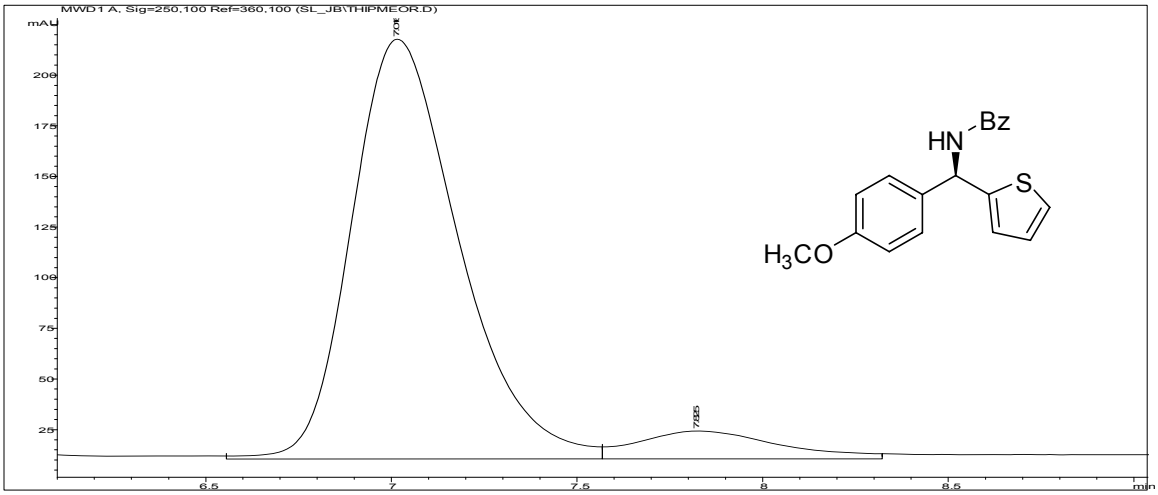
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.833	PB	0.4167	7237.32129	268.33923	98.4428
2	10.413	MM	0.4512	114.48315	4.22922	1.5572
Totals :				7351.80444	272.56845	

Table 1, entry 8: Chiralcel®OD-H column, 24cm×4.6 mm I.D., Hexanes:IPA = 85:15, 1.0 mL/min.



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

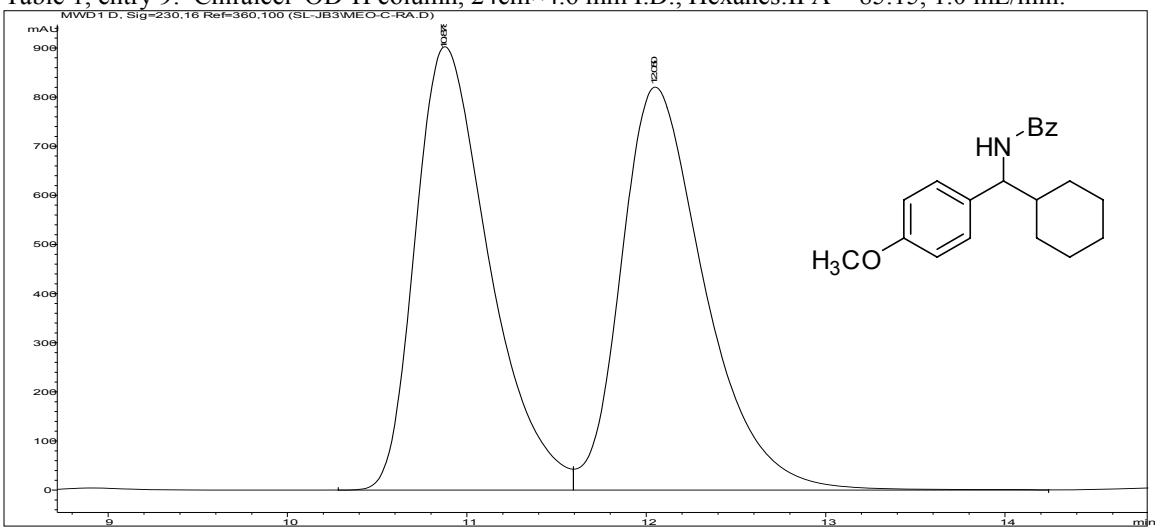
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.996	BV	0.3072	5398.97461	270.13000	48.8780
2	7.725	VB	0.3482	5646.83691	247.52339	51.1220
Totals :				1.10458e4	517.65340	



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

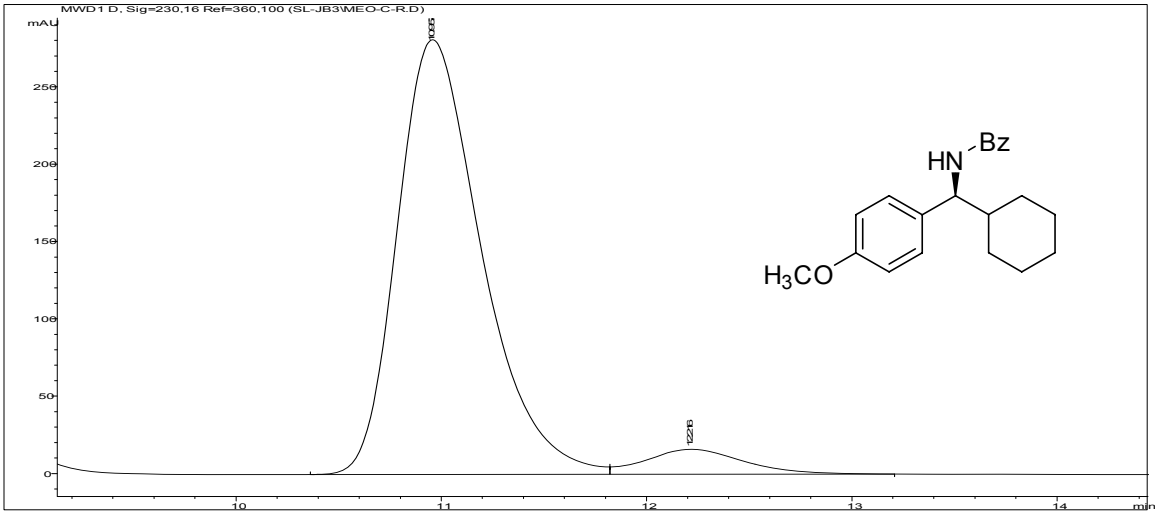
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.016	VV	0.3070	4174.81299	207.25307	96.0564
2	7.829	MM	0.3133	171.39931	9.11857	3.9436
Totals :				4346.21230	216.37164	

Table 1, entry 9: Chiralcel®OD-H column, 24cm×4.6 mm I.D., Hexanes:IPA = 85:15, 1.0 mL/min.



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

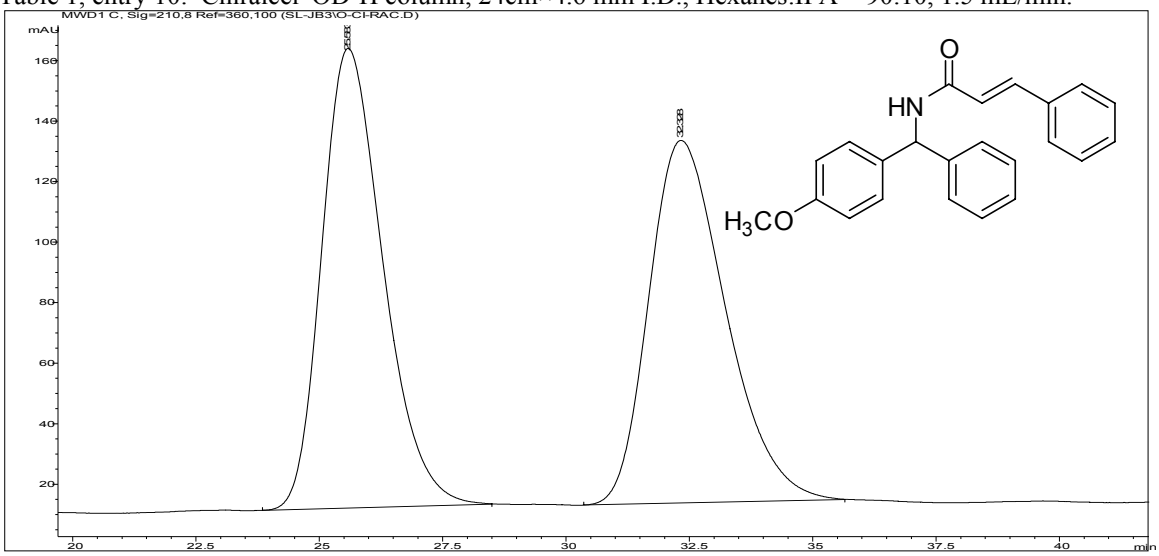
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.878	BV	0.4355	2.57990e4	902.45428	49.2695
2	12.050	VB	0.4939	2.65641e4	820.14801	50.7305
Totals :				5.23631e4	1722.60229	



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

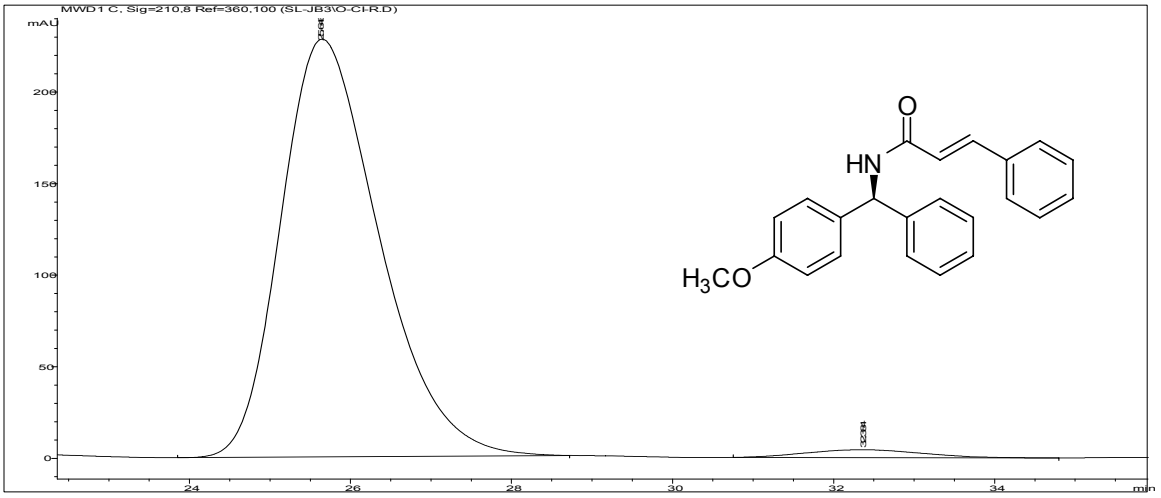
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.957	BV	0.4367	8014.79199	281.07831	95.6440
2	12.222	MM	0.4610	365.02673	13.19595	4.3560
Totals :				8379.81873	294.27426	

Table 1, entry 10: Chiralcel®OD-H column, 24cm×4.6 mm I.D., Hexanes:IPA = 90:10, 1.5 mL/min.



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

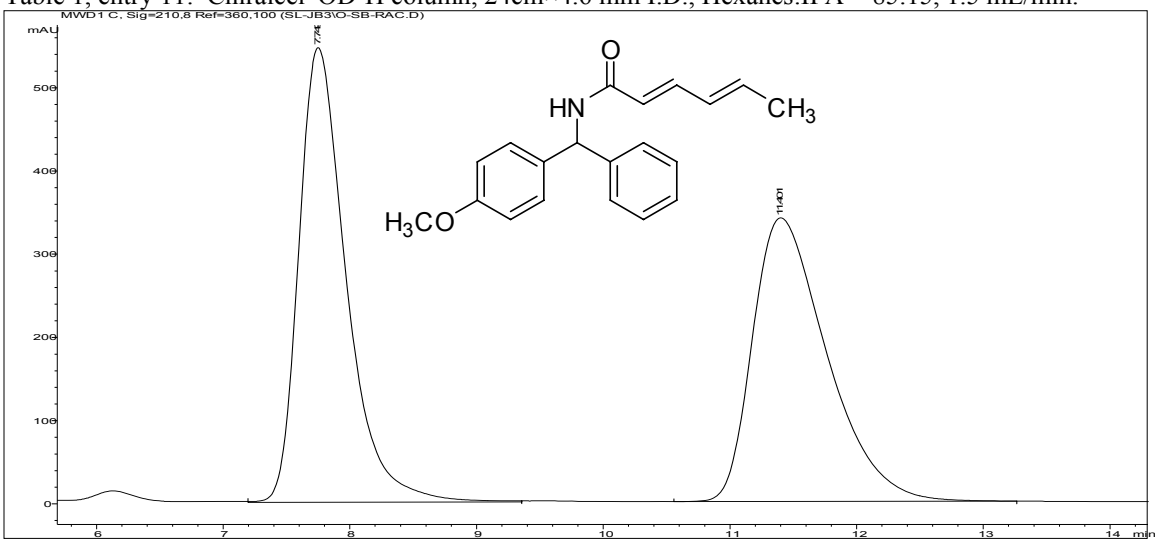
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.583	BB	1.2802	1.30977e4	151.87277	50.2433
2	32.328	BB	1.5927	1.29709e4	119.84405	49.7567
Totals :				2.60687e4	271.71682	



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

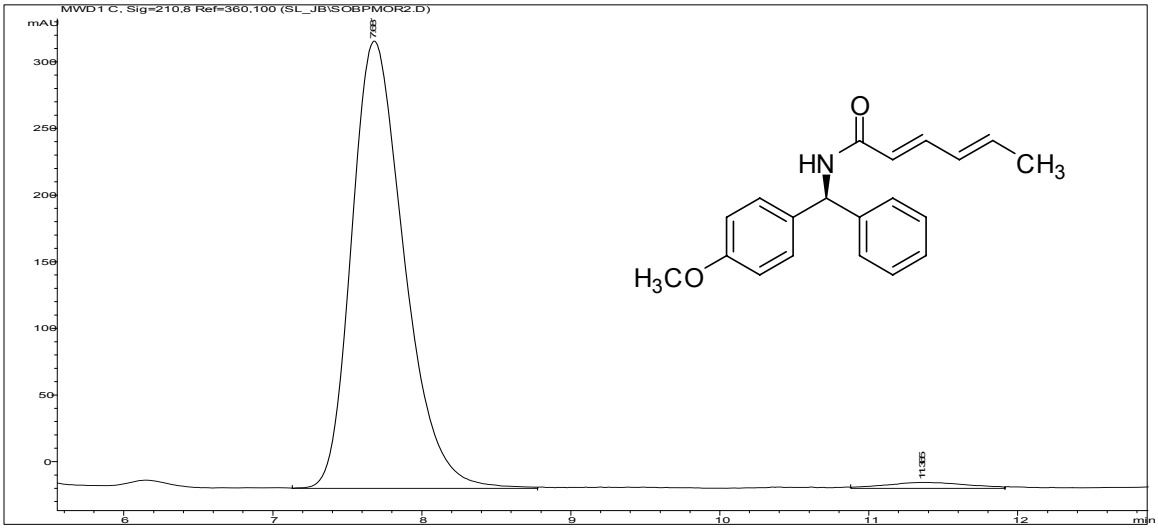
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.646	PB	1.2791	1.93826e4	228.15237	97.7582
2	32.384	BP	1.2023	444.48978	4.34208	2.2418
Totals :				1.98271e4	232.49445	

Table 1, entry 11: Chiralcel®OD-H column, 24cm×4.6 mm I.D., Hexanes:IPA = 85:15, 1.5 mL/min.



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

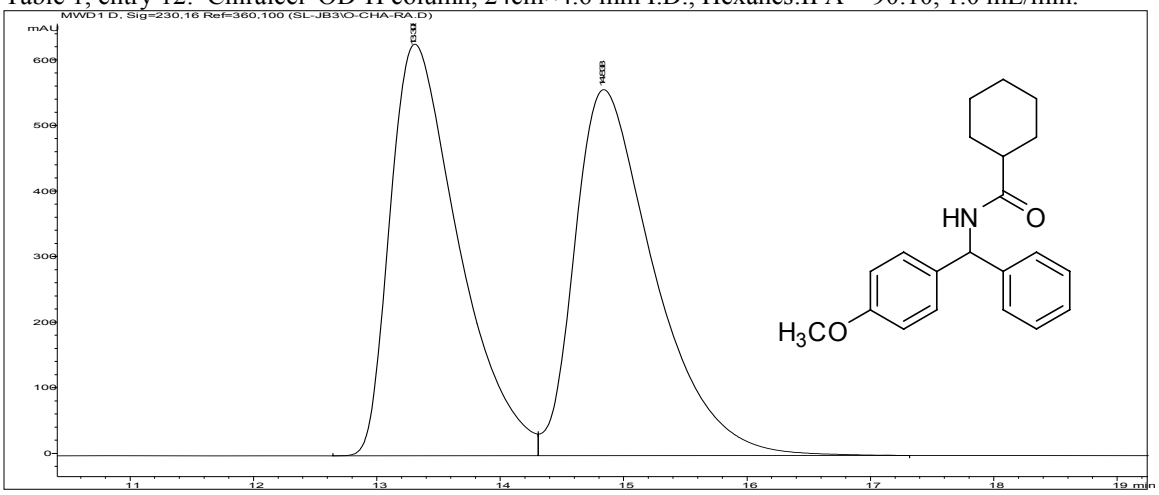
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.749	VB	0.3951	1.41936e4	546.32623	50.5788
2	11.401	PB	0.6248	1.38688e4	340.78531	49.4212
Totals :				2.80625e4	887.11154	



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

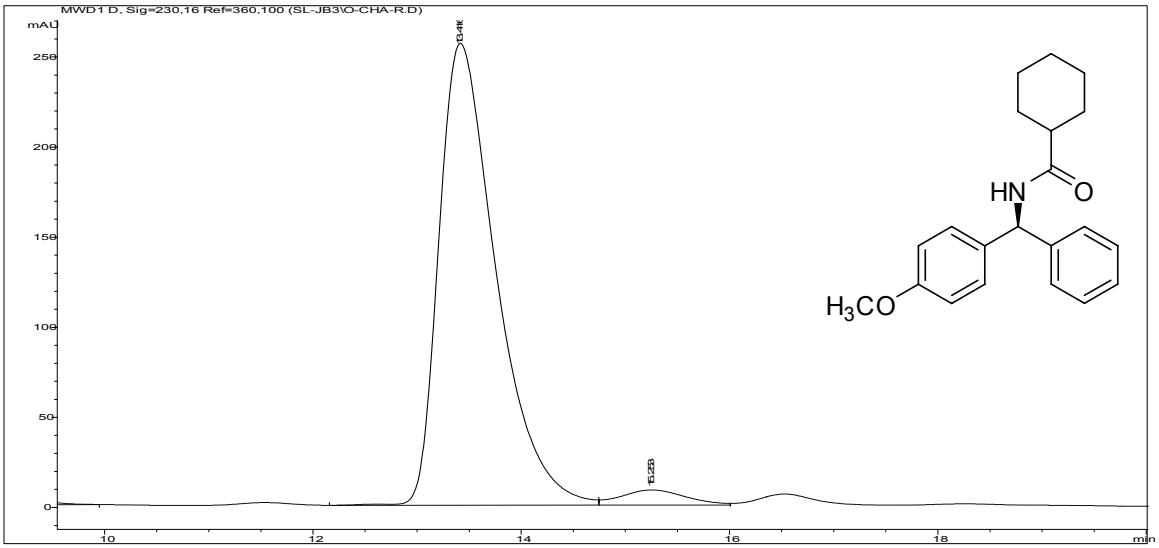
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.681	VV	0.3781	8232.26465	335.75433	97.8844
2	11.365	VV	0.4561	177.92862	4.61168	2.1156
Totals :				8410.19327	340.36601	

Table 1, entry 12: Chiralcel®OD-H column, 24cm×4.6 mm I.D., Hexanes:IPA = 90:10, 1.0 mL/min.



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

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.308	BV	0.5866	2.42548e4	627.93634	49.1644
2	14.838	VB	0.6761	2.50793e4	558.24994	50.8356
Totals :				4.93341e4	1186.18628	

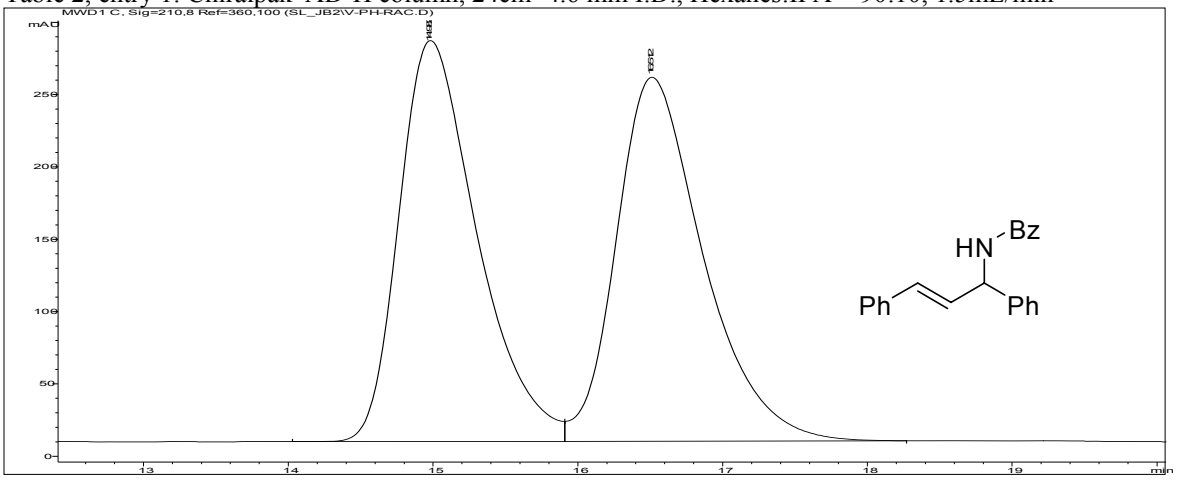


Signal 4: MWD1 D, Sig=230,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.416	MM	0.6282	9650.19043	256.01608	97.6828
2	15.262	MM	0.5872	228.91667	6.49718	2.3172
Totals :				9879.10710	262.51326	

HPLC Analysis of Chiral Vinyl Amide Products

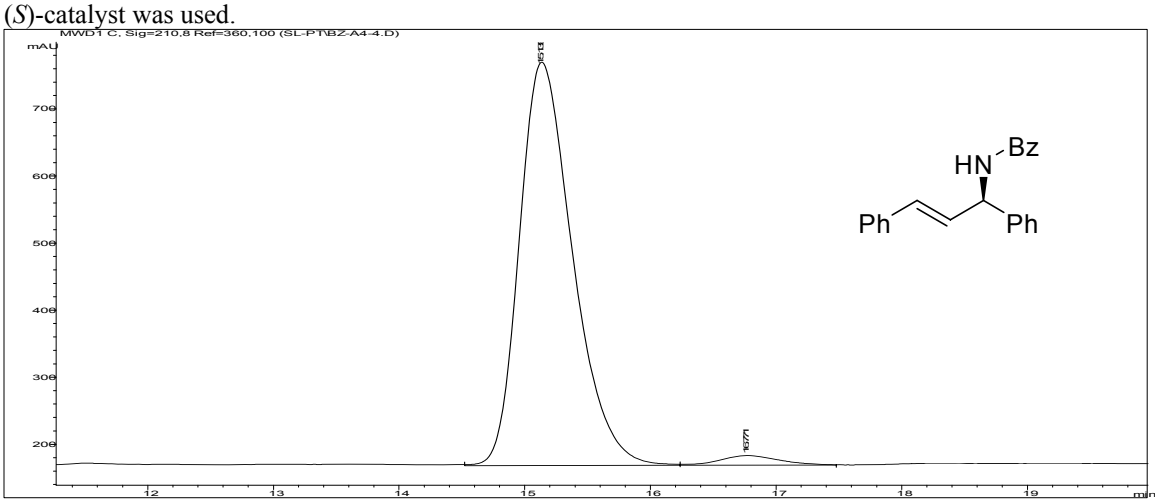
Table 2, entry 1: Chiralpak® AD-H column, 24cm×4.6 mm I.D., Hexanes:IPA = 90:10, 1.5mL/min



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

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.982	VV	0.5703	1.03674e4	277.19812	49.6757
2	16.512	VB	0.6311	1.05028e4	251.55400	50.3243
Totals :				2.08703e4	528.75212	

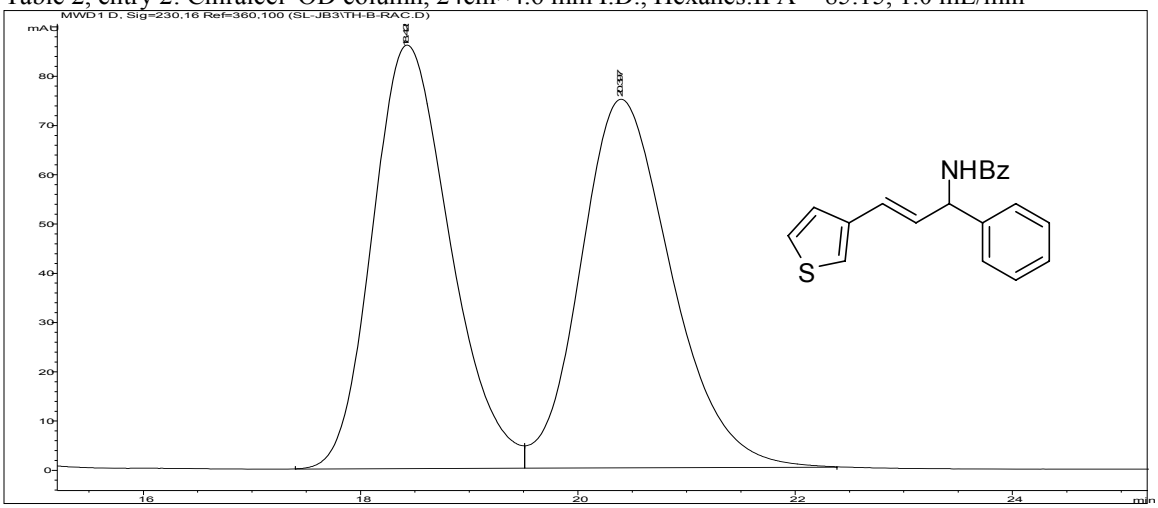
(*S*)-catalyst was used.



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

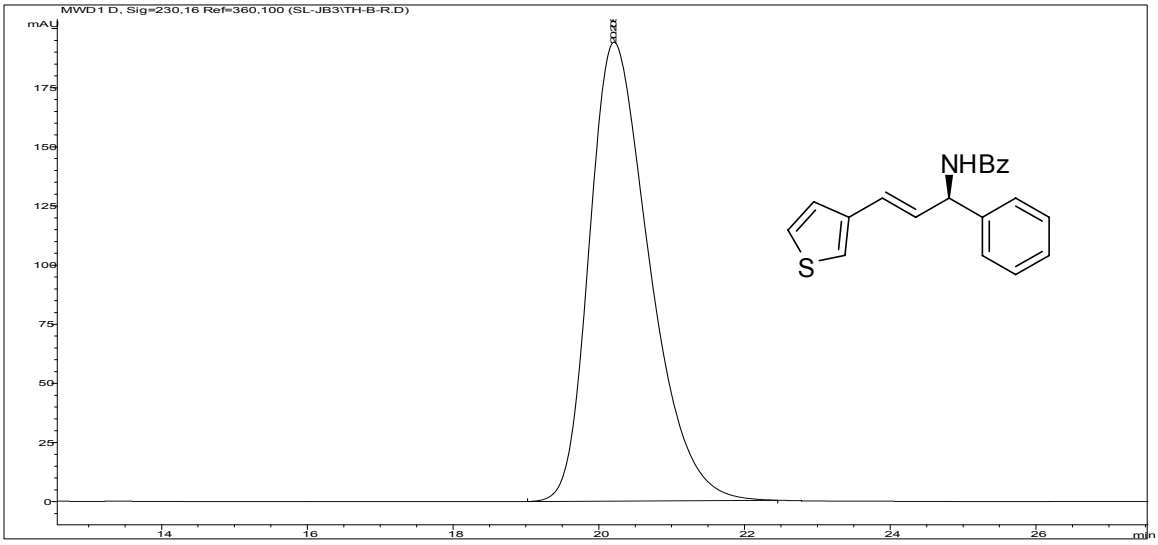
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.135	VV	0.4493	1.76922e4	601.30450	97.5654
2	16.771	VV	0.4447	460.08896	14.17573	2.4346
Totals :				1.81523e4	615.48023	

Table 2, entry 2: Chiralcel®OD column, 24cm×4.6 mm I.D., Hexanes:IPA = 85:15, 1.0 mL/min



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

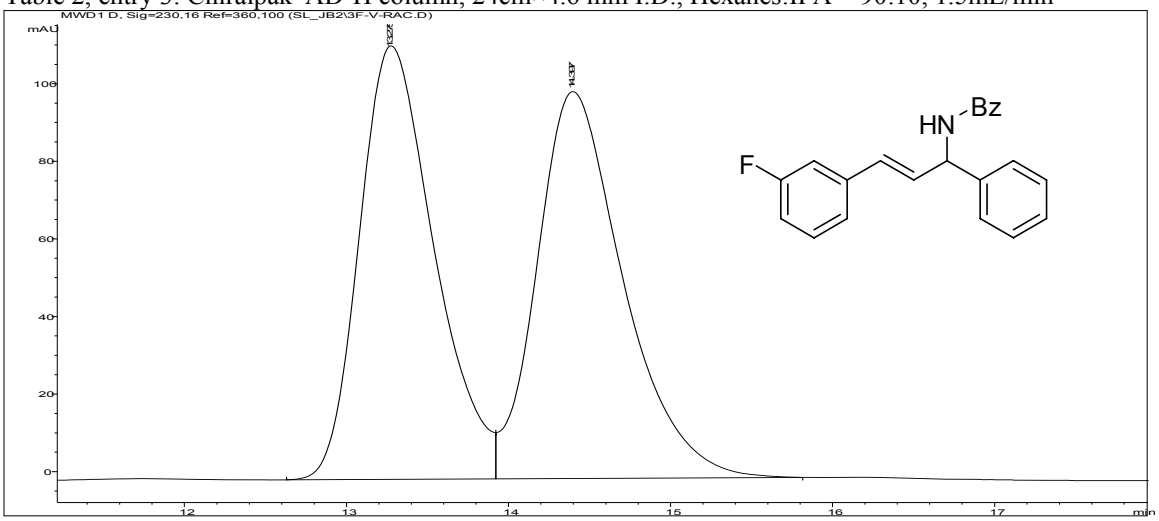
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.428	BV	0.7695	4273.20557	86.02419	49.5806
2	20.397	VB	0.8912	4345.49707	74.86439	50.4194
Totals :				8618.70264	160.88857	



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

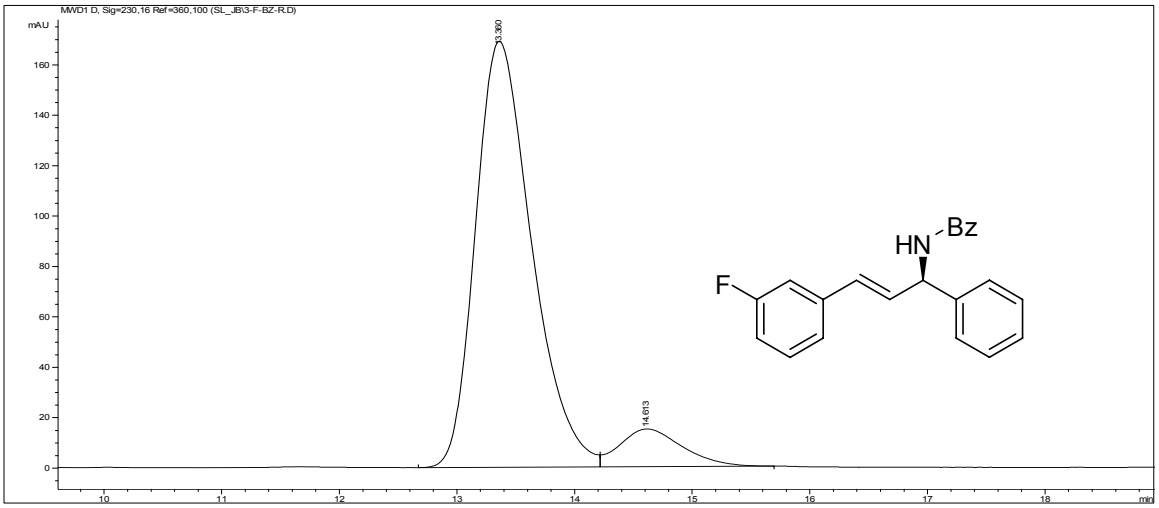
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.208	BB	0.8713	1.10978e4	194.03604	100.0000
Totals :				1.10978e4	194.03604	

Table 2, entry 3: Chiralpak®AD-H column, 24cm×4.6 mm I.D., Hexanes:IPA = 90:10, 1.5mL/min



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

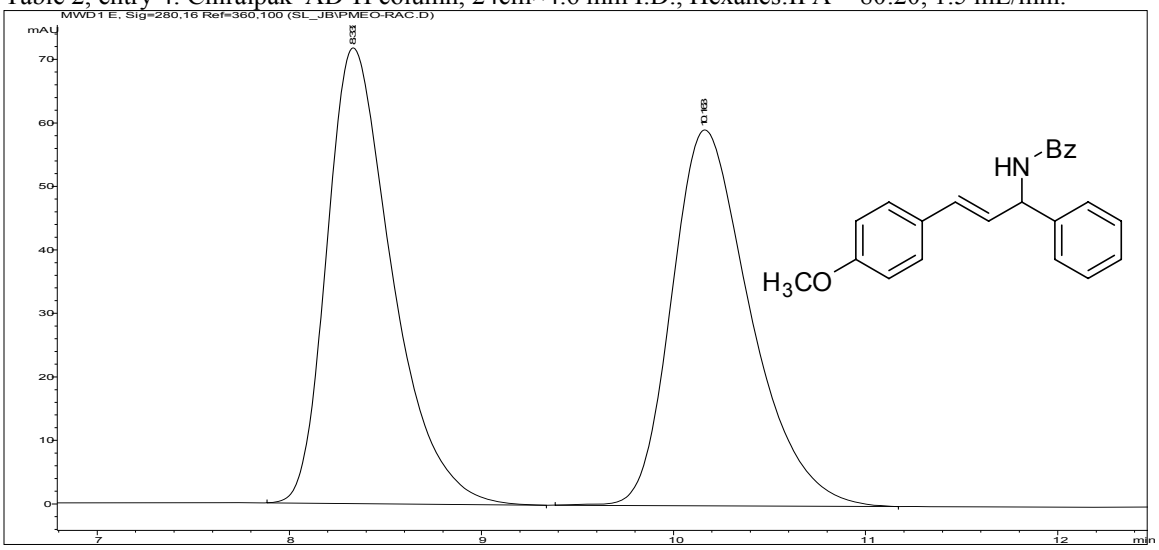
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.275	BV	0.4922	3585.25977	111.77981	49.2559
2	14.397	VB	0.5598	3693.58423	99.78970	50.7441
Totals :				7278.84399	211.56951	



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

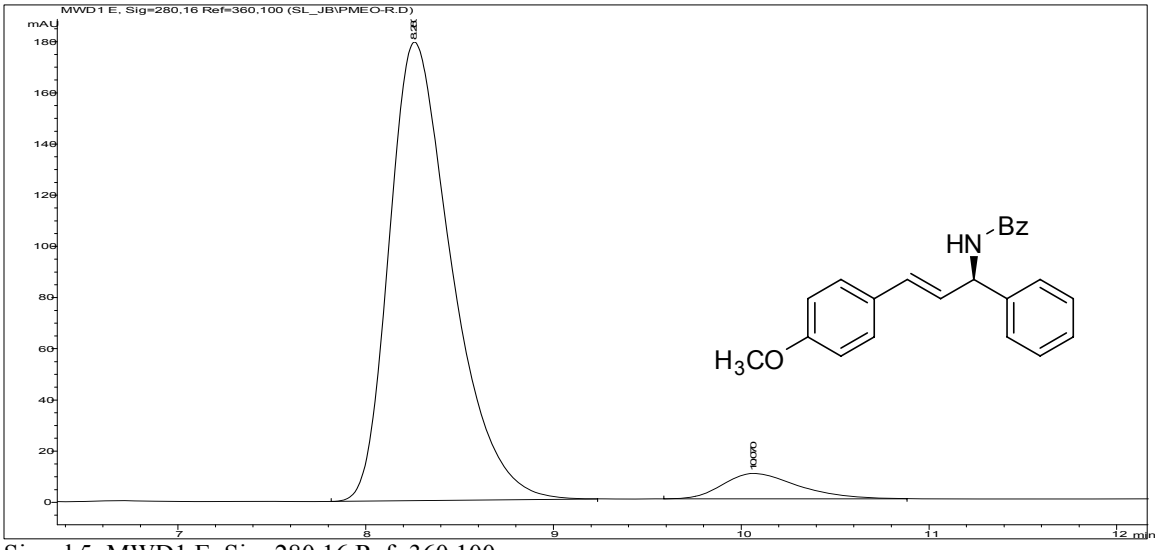
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.360	PV	0.5066	5600.18848	169.02145	95.4606
2	14.618	MM	0.4370	266.30118	10.15634	4.5394
Totals :				5866.48965	179.17779	

Table 2, entry 4: Chiralpak®AD-H column, 24cm×4.6 mm I.D., Hexanes:IPA = 80:20, 1.5 mL/min.



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

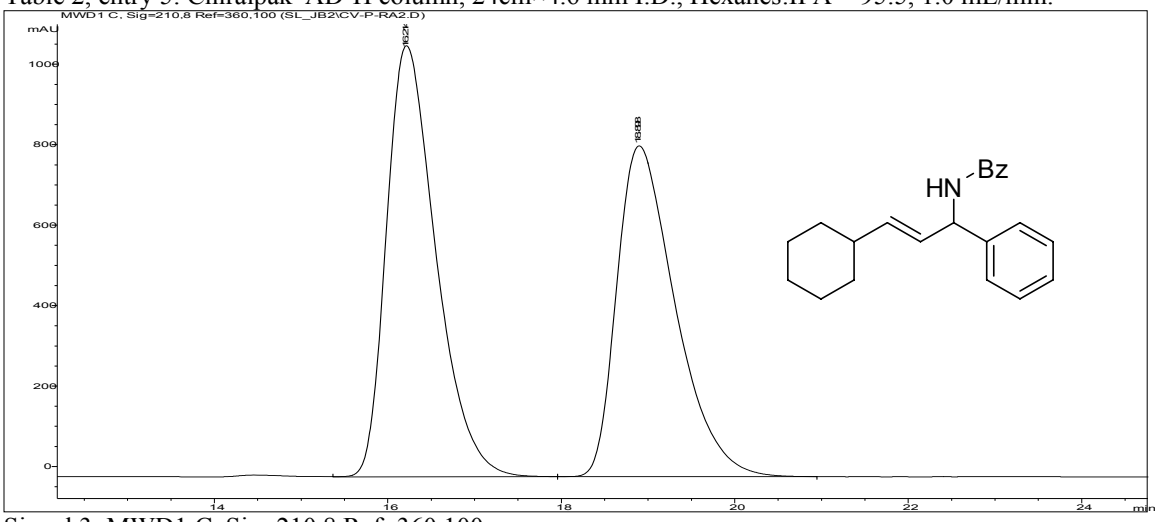
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.333	BP	0.3576	1696.33398	71.79662	50.2006
2	10.163	BB	0.4336	1682.77795	59.20156	49.7994
Totals :				3379.11194	130.99819	



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

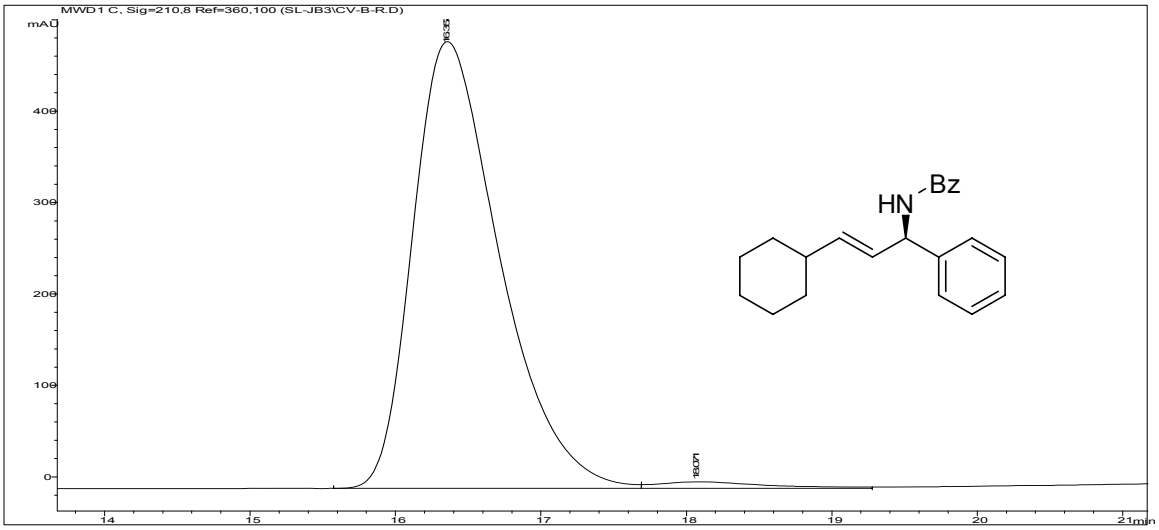
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.260	PB	0.3504	4153.03906	179.19017	96.1980
2	10.070	MM	0.3529	164.14087	7.75224	3.8020
Totals :				4317.17993	186.94242	

Table 2, entry 5: Chiralpak®AD-H column, 24cm×4.6 mm I.D., Hexanes:IPA = 95:5, 1.0 mL/min.



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

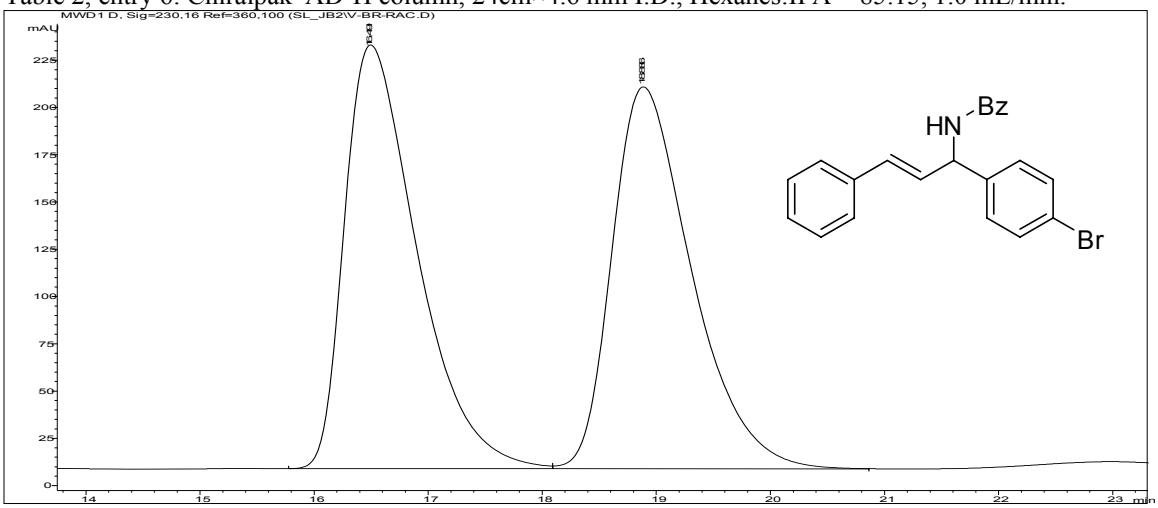
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.214	VV	0.6058	4.24050e4	1071.41309	52.4795
2	18.898	VB	0.7128	3.83980e4	822.31238	47.5205
Totals :				8.08031e4	1893.72546	



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

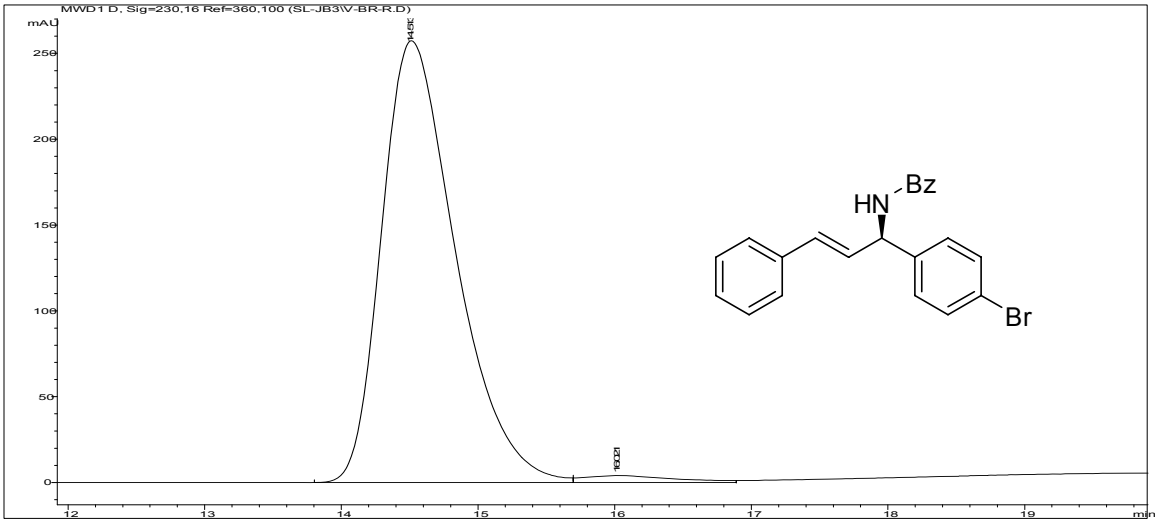
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.357	BV	0.6298	2.02679e4	488.71332	98.2131
2	18.071	VV	0.6824	368.76419	7.14209	1.7869
Totals :				2.06366e4	495.85541	

Table 2, entry 6: Chiralpak®AD-H column, 24cm×4.6 mm I.D., Hexanes:IPA = 85:15, 1.0 mL/min.



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

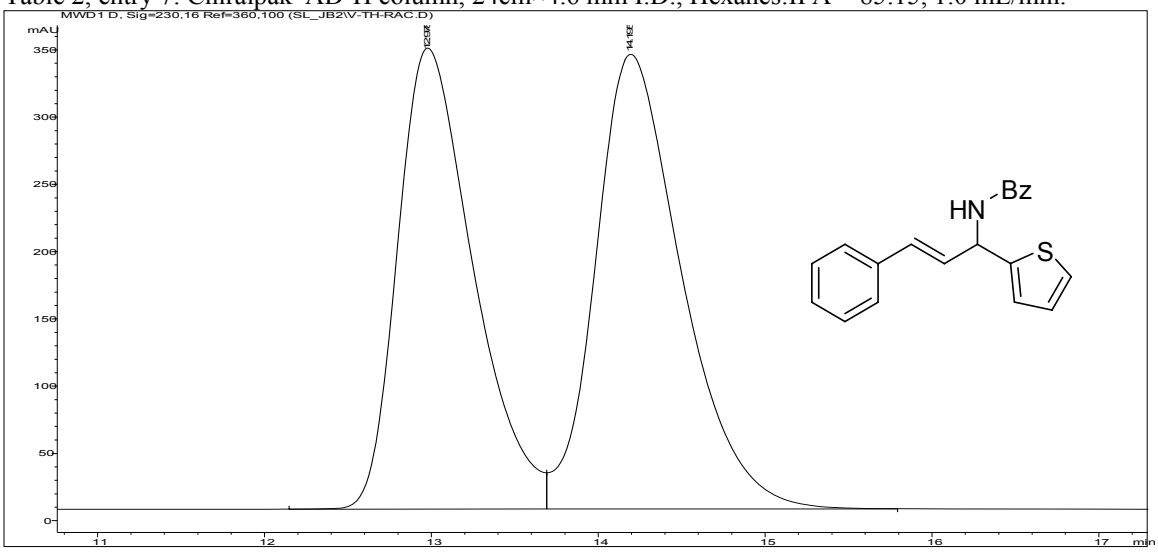
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.495	PV	0.6727	9888.23340	224.12767	50.2628
2	18.886	VB	0.7412	9784.83008	201.96854	49.7372
Totals :				1.96731e4	426.09621	



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

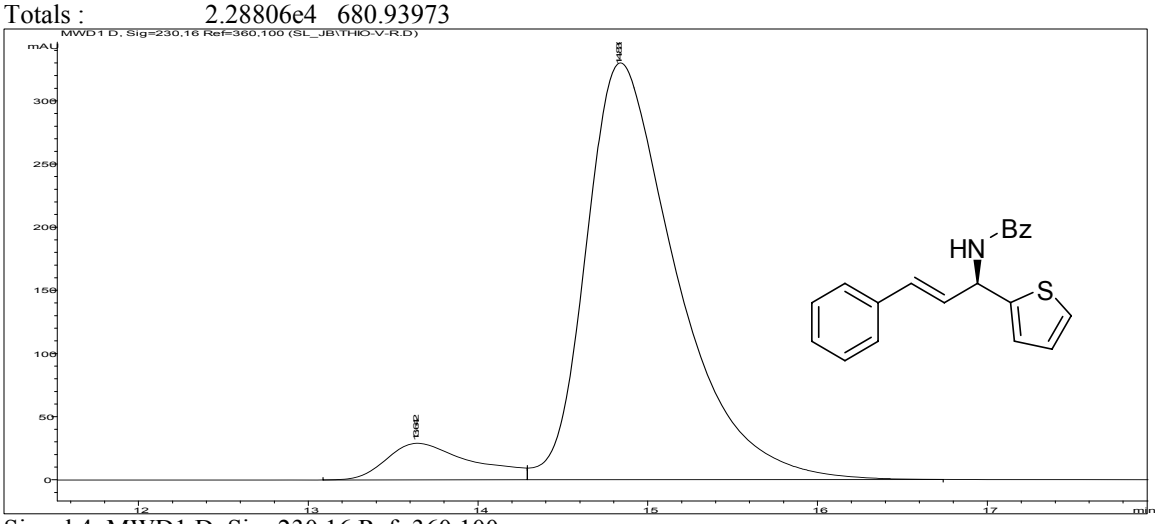
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.037	PB	0.6738	3553.24243	80.37569	95.3726
2	19.436	MM	0.3706	172.40155	7.75419	4.6274
Totals :				3725.64398	88.12988	

Table 2, entry 7: Chiralpak®AD-H column, 24cm×4.6 mm I.D., Hexanes:IPA = 85:15, 1.0 mL/min.



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

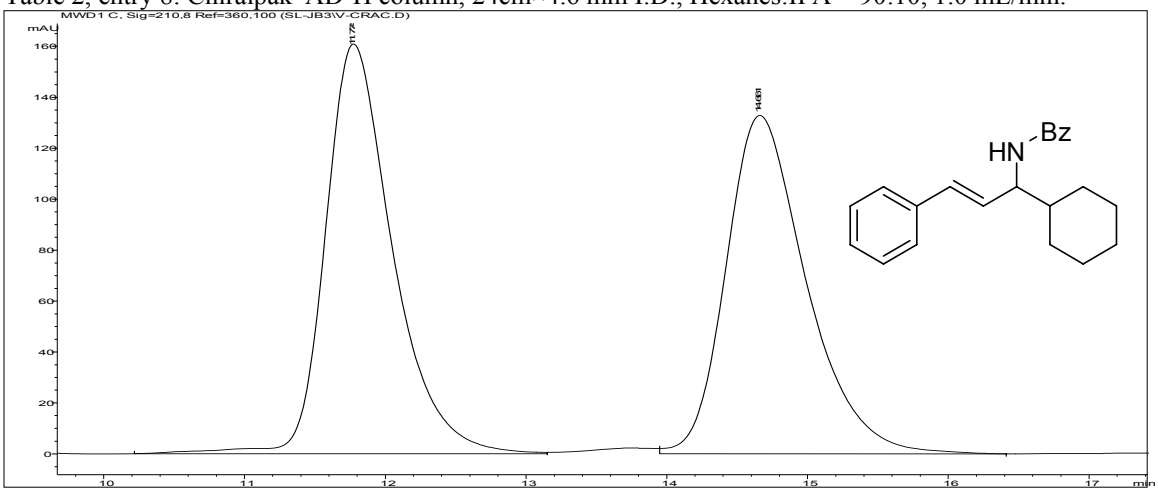
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.978	BV	0.4808	1.07755e4	342.76849	47.0947
2	14.195	VB	0.5396	1.21050e4	338.17123	52.9053
Totals :				2.28806e4	680.93973	



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

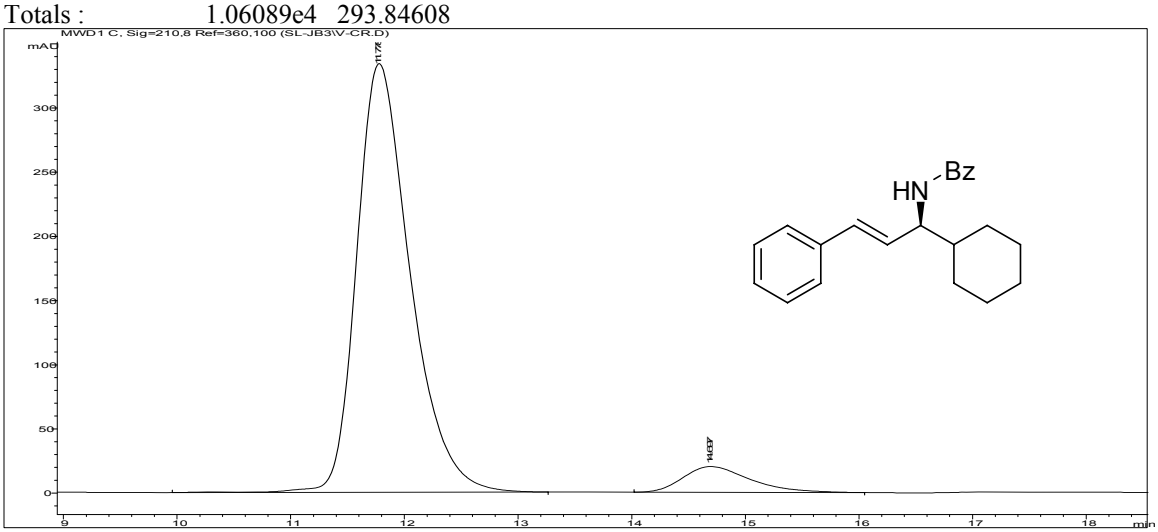
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.642	MM	0.4411	622.37897	23.51438	4.9802
2	14.839	MM	0.6064	1.18746e4	326.36249	95.0198
Totals :				1.24970e4	349.87687	

Table 2, entry 8: Chiralpak®AD-H column, 24cm×4.6 mm I.D., Hexanes:IPA = 90:10, 1.0 mL/min.



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

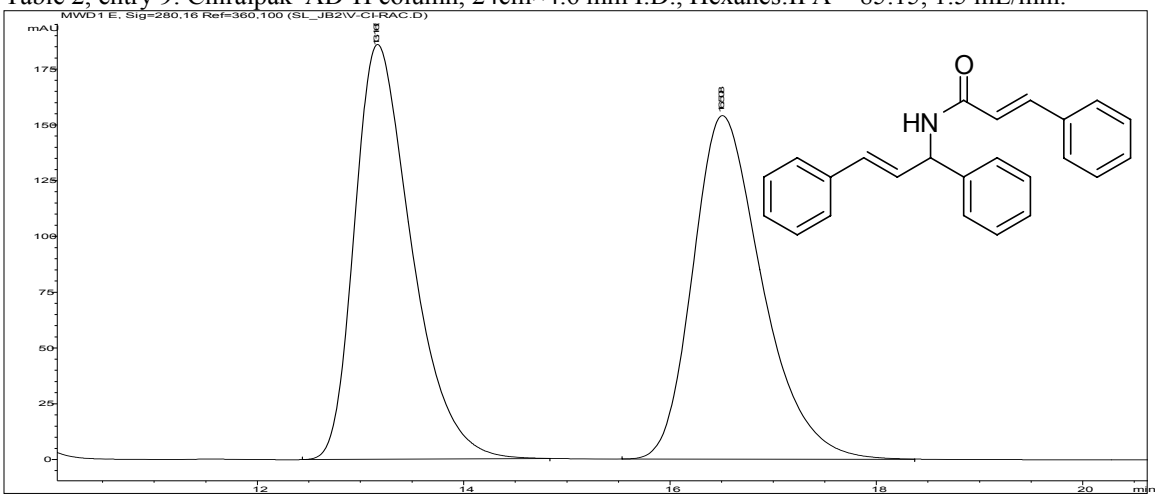
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.774	BB	0.4993	5343.25977	160.95232	50.3658
2	14.661	VB	0.5943	5265.65381	132.89377	49.6342
Totals :				1.06089e4	293.84608	



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

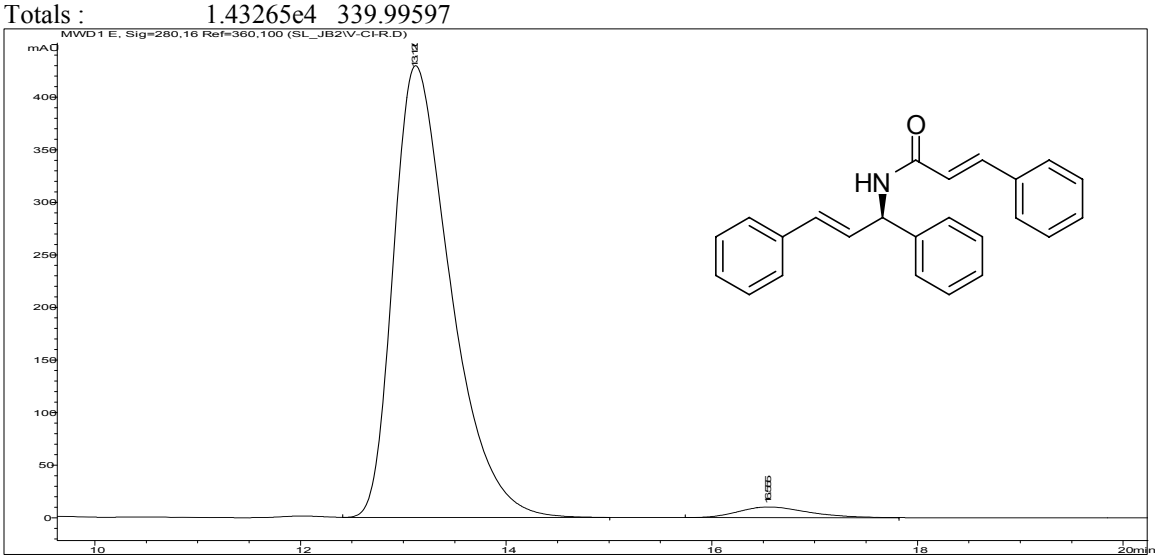
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.778	PP	0.4947	1.08989e4	333.98276	95.4995
2	14.705	MM	0.5366	513.61957	15.95436	4.5005
Totals :				1.14125e4	349.93711	

Table 2, entry 9: Chiralpak®AD-H column, 24cm×4.6 mm I.D., Hexanes:IPA = 85:15, 1.5 mL/min.



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

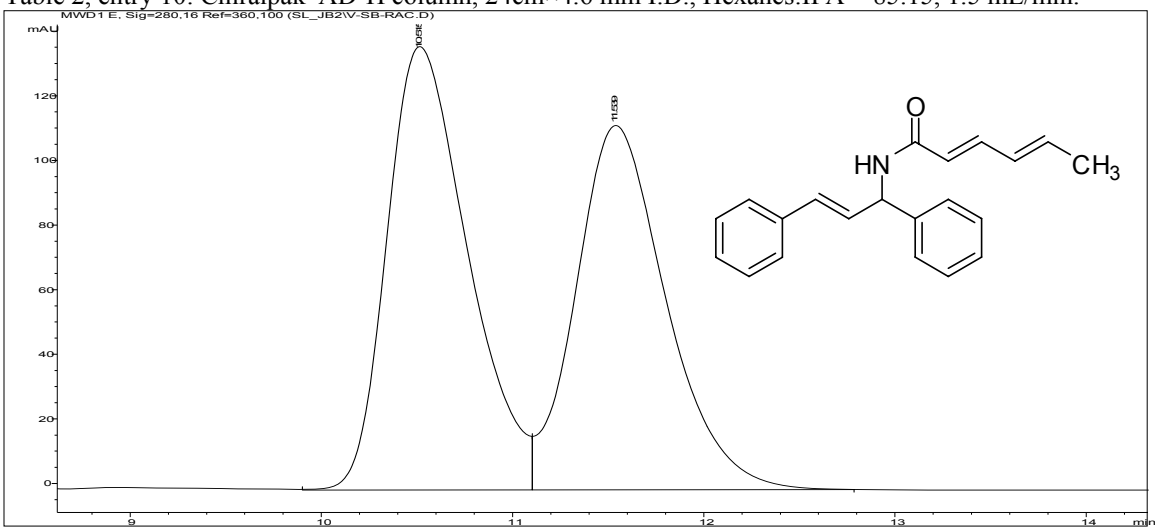
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.165	BB	0.5823	7147.42920	185.98766	49.8895
2	16.508	BB	0.7078	7179.10254	154.00832	50.1105
Totals :				1.43265e4	339.99597	



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

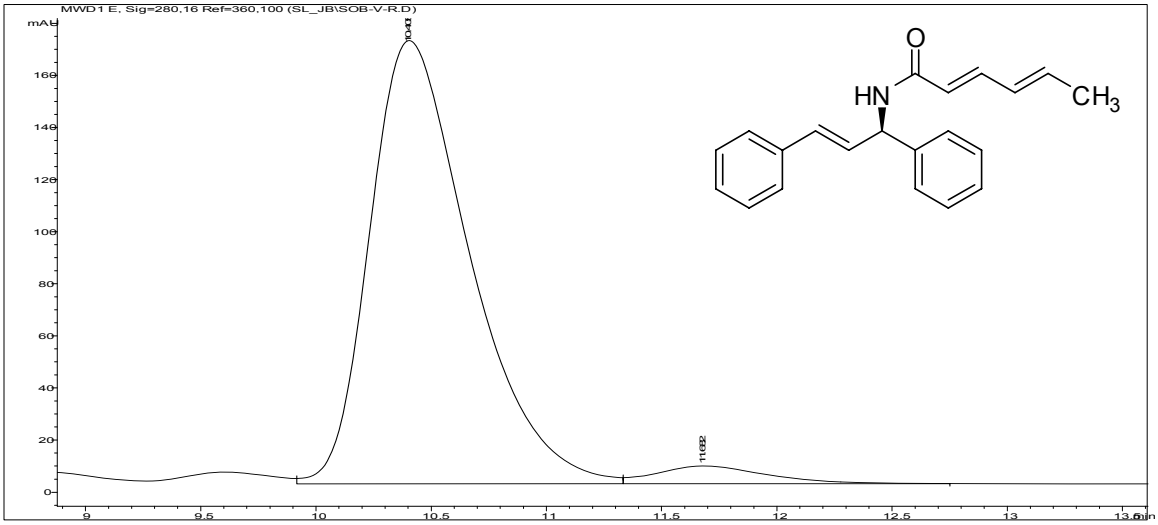
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.120	VB	0.5897	1.66416e4	429.84842	98.5705
2	16.555	MM	0.5440	241.33760	7.39349	1.4295
Totals :				1.68829e4	437.24191	

Table 2, entry 10: Chiralpak®AD-H column, 24cm×4.6 mm I.D., Hexanes:IPA = 85:15, 1.5 mL/min.



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

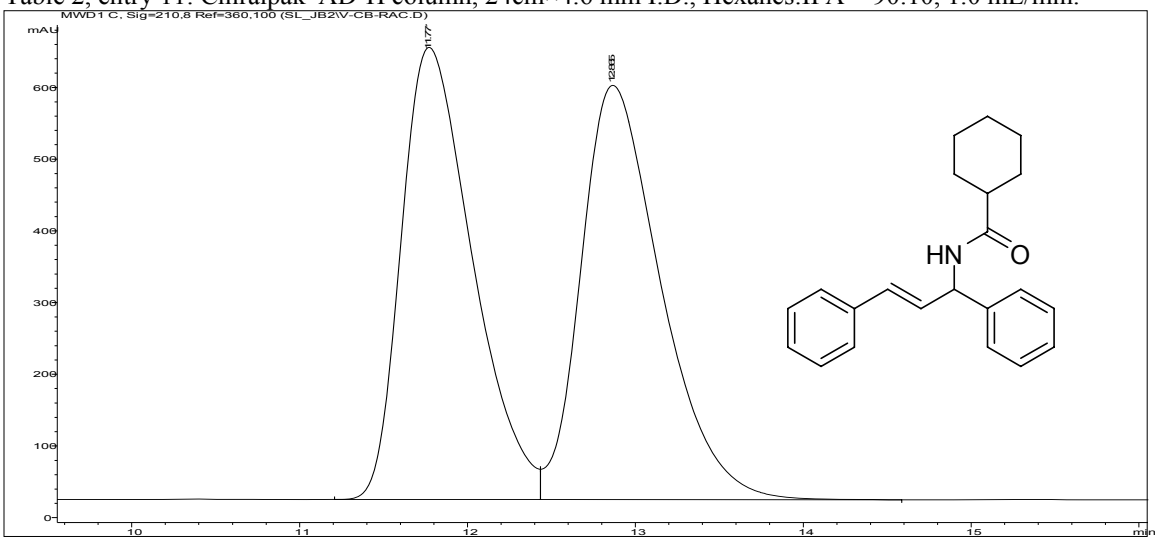
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.515	VV	0.4511	4035.35938	137.22482	52.1316
2	11.539	VB	0.4993	3705.35937	112.76820	47.8684
Totals :				7740.71875	249.99302	



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

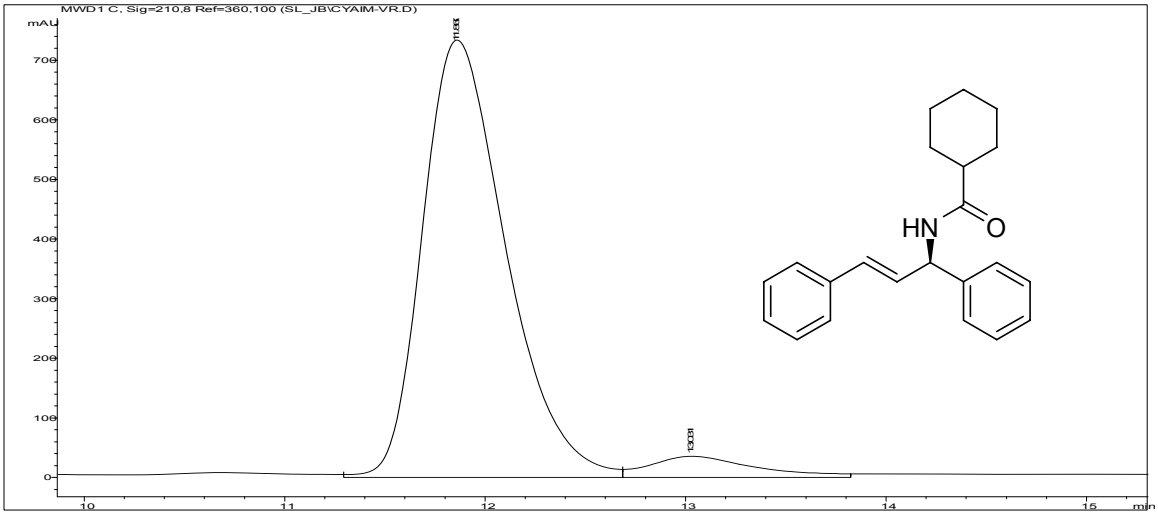
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.405	VV	0.4601	5138.36768	170.23669	97.4833
2	11.684	MM	0.4292	132.65646	5.15075	2.5167
Totals :				5271.02414	175.38745	

Table 2, entry 11: Chiralpak®AD-H column, 24cm×4.6 mm I.D., Hexanes:IPA = 90:10, 1.0 mL/min.



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

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.771	PV	0.4516	1.85687e4	630.54828	49.3201
2	12.865	VB	0.5053	1.90806e4	577.78467	50.6799
Totals :				3.76493e4	1208.33295	

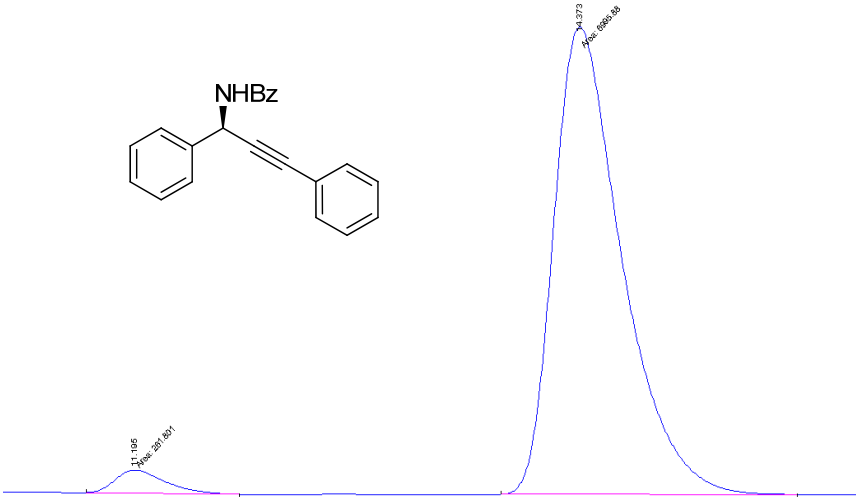


Signal 3: MWD1 C, Sig=210,8 Ref=360,100

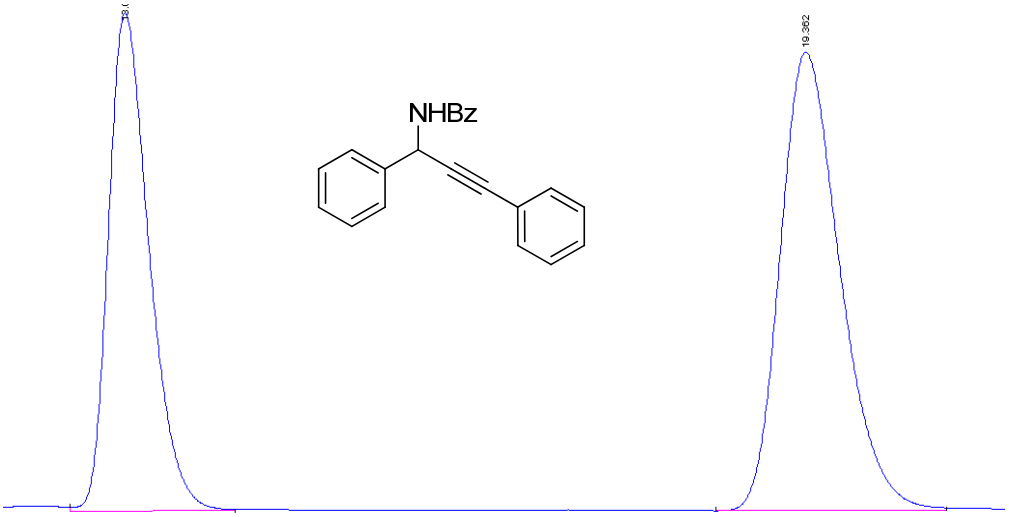
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.860	MM	0.4719	2.06098e4	727.91095	97.3456
2	13.031	MM	0.3994	561.97772	23.45109	2.6544
Totals :				2.11718e4	751.36204	

HPLC Analysis of Chiral Propargyl Amide Products

Table 3. Entry 1 : Chiralpak®AD-H column, 24cm×4.6 mm I.D., Hexanes:IPA = 90:10, 1.5mL/min (*R*) catalyst was used

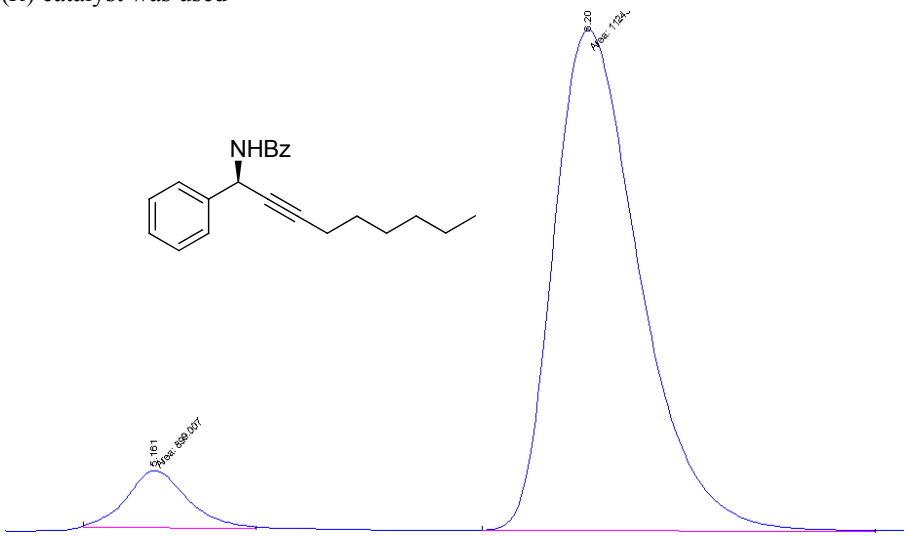


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.195	MM	0.4216	261.80148	10.35062	3.6072
2	14.373	MM	0.5658	6995.87988	206.06712	96.3928

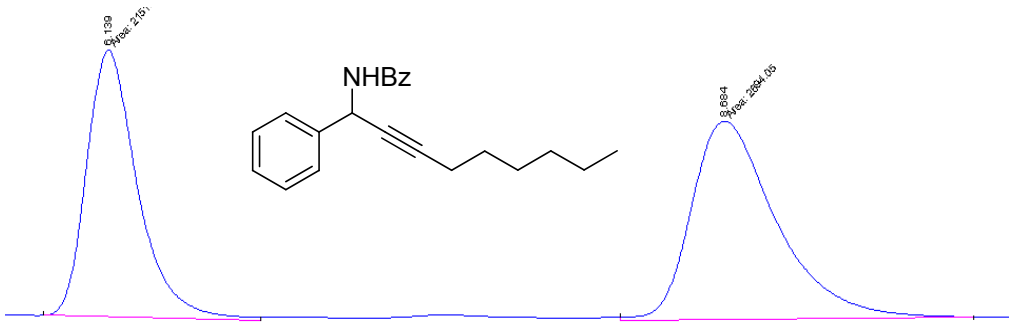


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.036	VV	0.4085	4320.11572	163.35086	42.5697
2	19.362	VV	0.5883	5828.20898	150.32806	57.4303

Table 3. Entry 2. : Chiralpak®AD-H column, 24cm×4.6 mm I.D., Hexanes:IPA = 90:10, 1.5mL/min
(*R*) catalyst was used

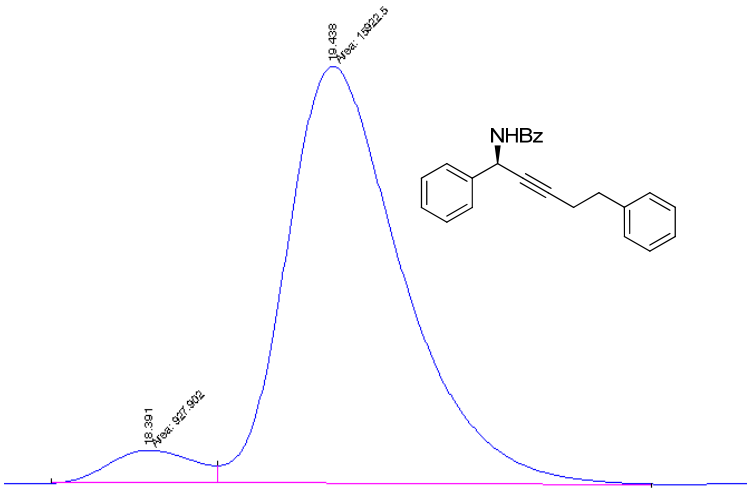


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.161	MM	0.1694	899.00665	88.44326	7.4041
2	6.208	MM	0.2419	1.12430e4	774.61090	92.5959

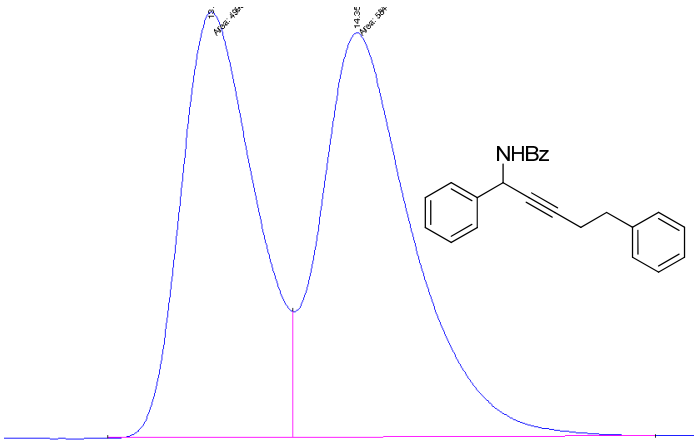


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.139	MM	0.2438	2151.16528	147.07983	44.3977
2	8.684	MM	0.4100	2694.04736	109.50130	55.6023

Table 3. Entry 3. : Chiralpak®AD-H column, 24cm×4.6 mm I.D., Hexanes:IPA = 90:10, 1.5mL/min
(*R*) catalyst was used

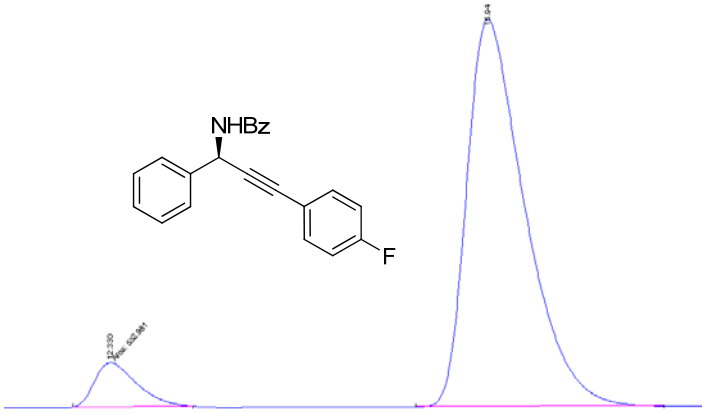


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.389	MM	0.4634	61.09267	2.19745	3.3945
2	19.438	MM	0.7375	1738.64209	39.28995	96.6055

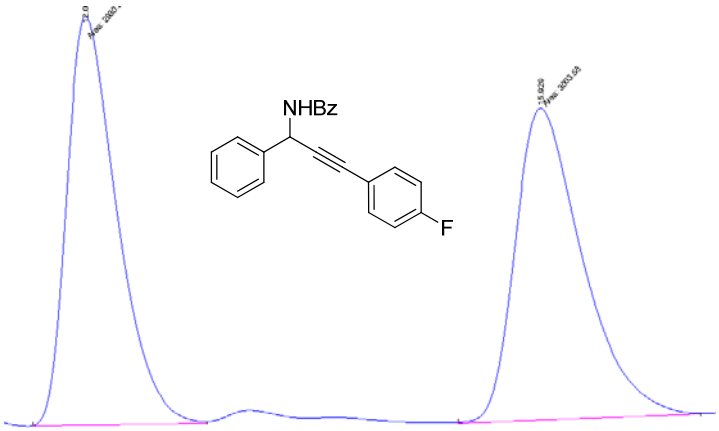


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.561	VV	0.4369	5162.37842	178.76657	46.4911
2	14.354	VB	0.5157	5941.64355	169.17618	53.5089

Table 3. Entry 4. : Chiralpak®AD-H column, 24cm×4.6 mm I.D., Hexanes:IPA = 90:10, 1.5mL/min
(*R*) catalyst was used

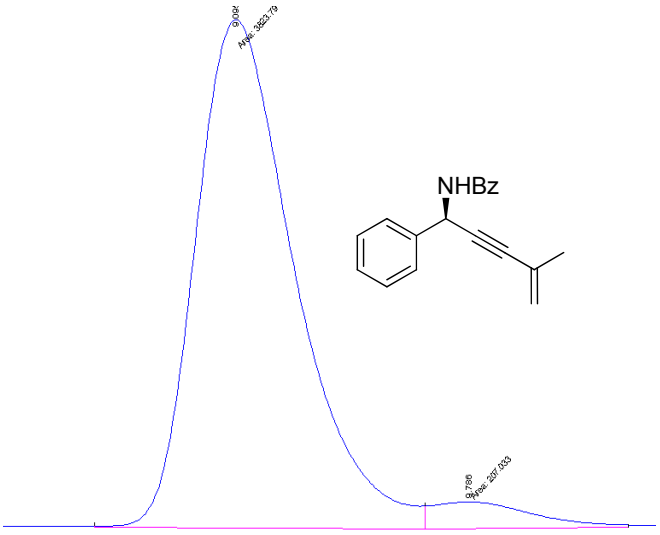


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.330	MM	0.4625	552.98102	19.92714	7.5689
2	15.944	PB	0.5704	6752.95557	174.93858	92.4311

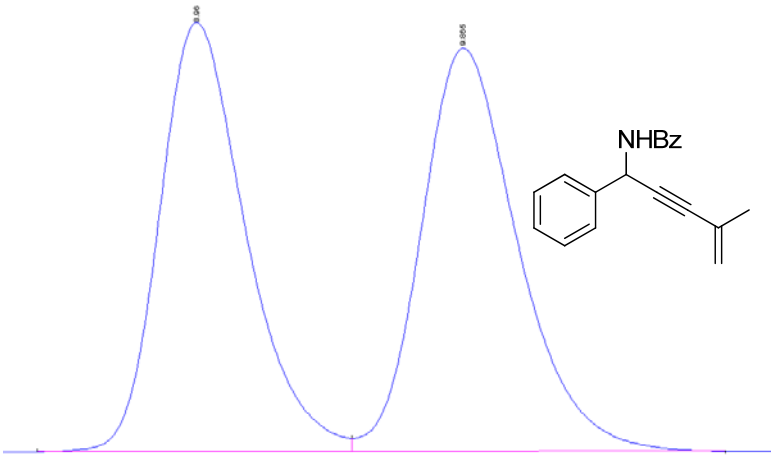


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.079	MM	0.4923	2930.01099	99.19130	49.3800
2	15.929	MM	0.6614	3003.58276	75.68545	50.6200

Table 3. Entry 5. : Chiralpak®AD-H column, 24cm×4.6 mm I.D., Hexanes:IPA = 90:10, 1.5mL/min
(*R*) catalyst was used

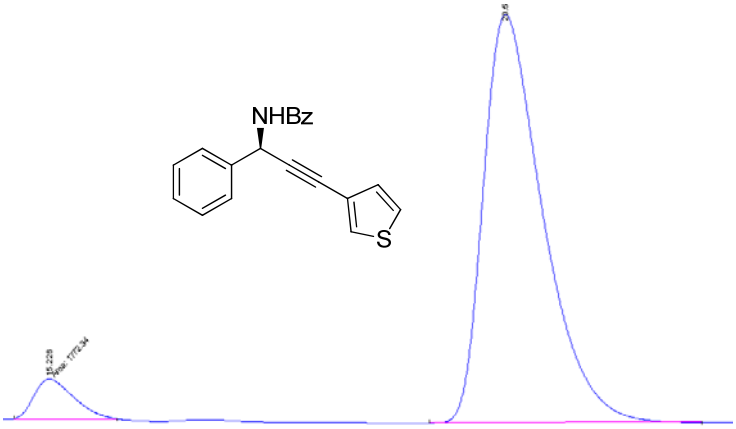


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.095	MM	0.3404	3823.79004	187.19911	94.8638
2	9.786	MM	0.3427	207.03310	10.06764	5.1362

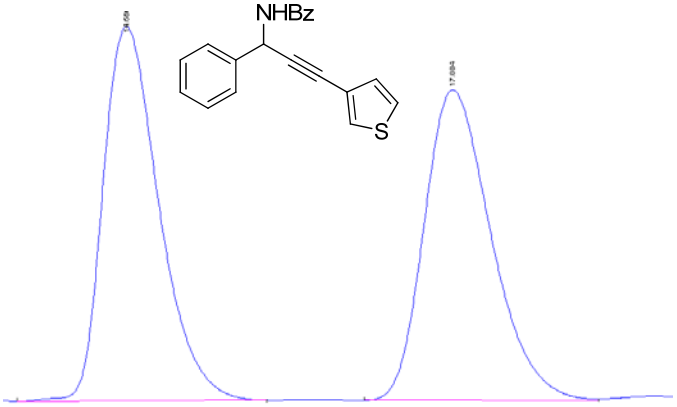


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.966	BV	0.3071	1759.43347	87.29553	48.7458
2	9.865	VB	0.3433	1849.97168	81.96229	51.2542

Table 3. Entry 6. : Chiralpak®AD-H column, 24cm×4.6 mm I.D., Hexanes:IPA = 90:10, 1.5mL/min (*R*) catalyst was used

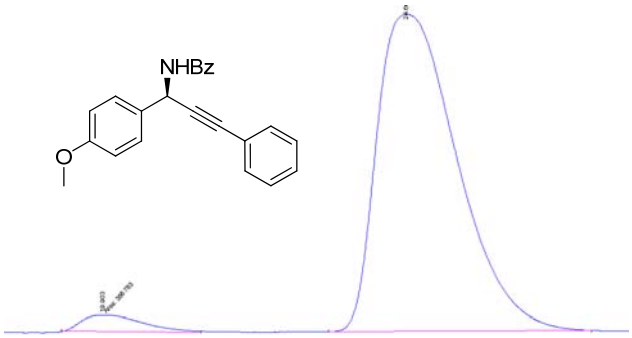


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.226	MM	0.5430	1772.34412	54.39542	6.1875
2	20.575	PB	0.7316	2.68714e4	554.26508	93.8125

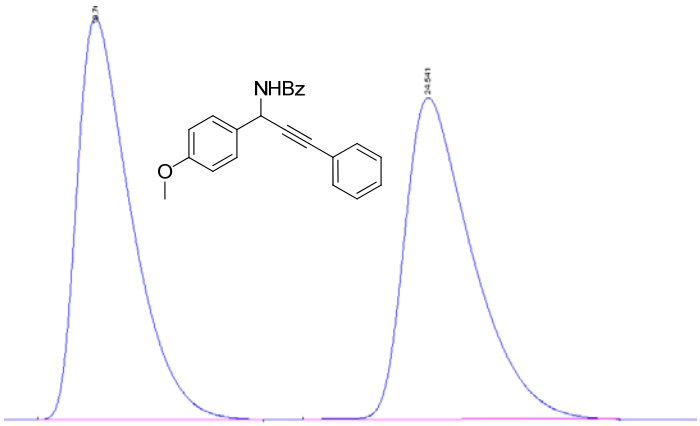


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.560	VB	0.6138	6539.17334	165.20605	50.0483
2	17.884	PB	0.7347	6526.55615	137.26483	49.9517

Table 3. Entry 7. : Chiralpak®AD-H column, 24cm×4.6 mm I.D., Hexanes:IPA = 90:10, 1.5mL/min
(*R*) catalyst was used

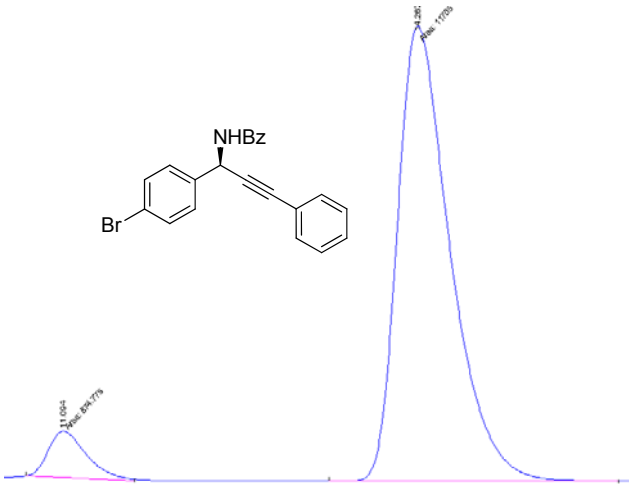


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.903	MM	1.1154	368.76337	5.51027	3.9129
2	24.600	BB	1.3114	9055.55176	104.87513	96.0871

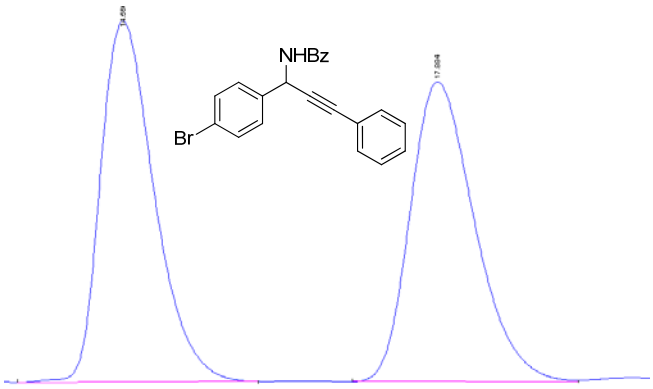


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.760	BB	0.7970	1.20932e4	223.59499	49.9431
2	24.541	BB	0.9938	1.21208e4	179.05164	50.0569

Table 3. Entry 8 : Chiralpak®AD-H column, 24cm×4.6 mm I.D., Hexanes:IPA = 90:10, 1.5mL/min
(*R*) catalyst was used

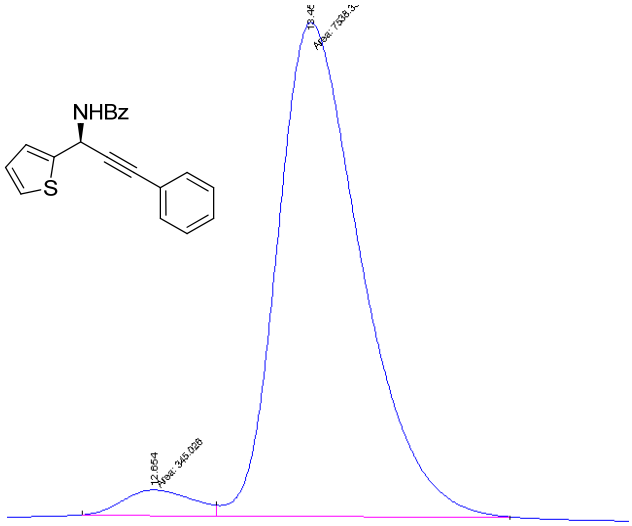


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.094	MM	0.4005	874.77490	36.40479	6.9538
2	14.267	MM	0.5498	1.17050e4	354.85269	93.0462

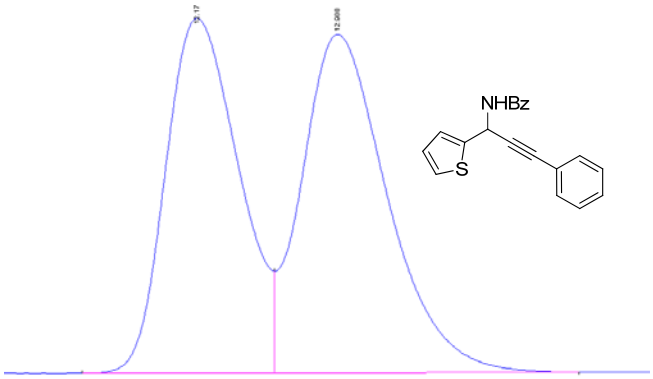


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.560	VB	0.6138	6539.17334	165.20605	50.0483
2	17.884	PB	0.7347	6526.55615	137.26483	49.9517

Table 3. Entry 9. : Chiralpak®AD-H column, 24cm×4.6 mm I.D., Hexanes:IPA = 90:10, 1.5mL/min
(*R*) catalyst was used

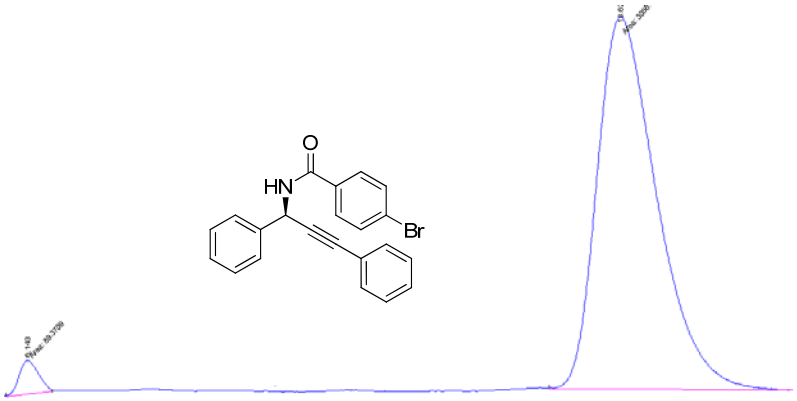


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.654	MF	0.4236	345.02615	13.57430	4.3766
2	13.456	FM	0.4969	7538.33447	252.83704	95.6234

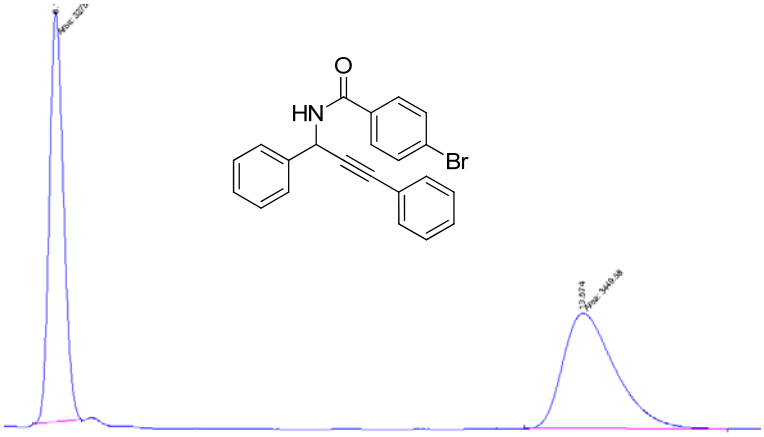


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.178	BV	0.4568	4301.15674	146.38029	47.1997
2	12.988	VB	0.5200	4811.52686	139.63887	52.8003

Table 3. Entry 10: Chiralpak®AD-H column, 24cm×4.6 mm I.D., Hexanes:IPA = 90:10, 1.5mL/min
(*R*) catalyst was used

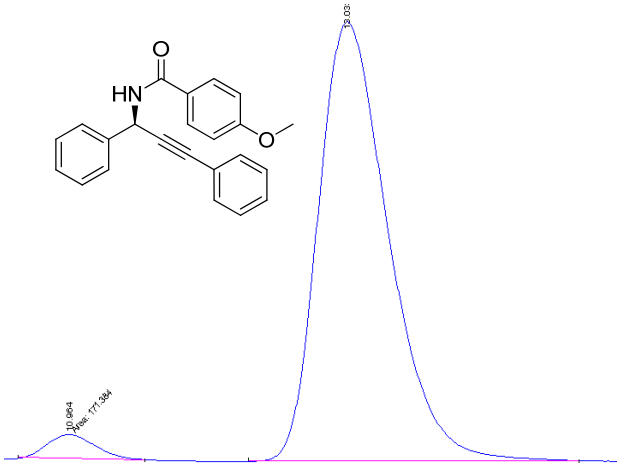


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.143	MM	0.2780	89.37092	5.35837	2.8406
2	13.624	MM	0.8583	3056.79736	59.35861	97.1594

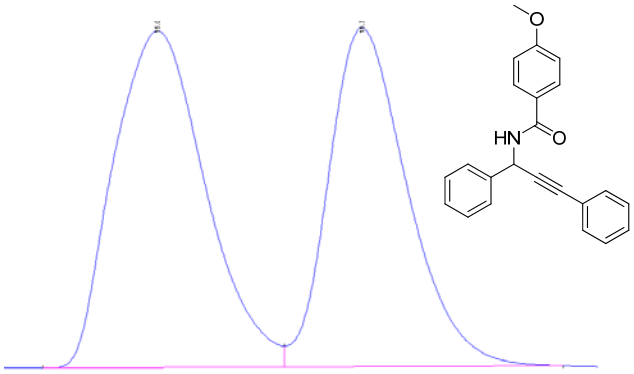


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.172	MM	0.2333	3275.68286	233.99246	48.7071
2	13.674	MM	0.8713	3449.58179	65.98219	51.2929

Table 3. Entry 11. : Chiralpak®AD-H column, 24cm×4.6 mm I.D., Hexanes:IPA = 90:10, 1.5mL/min
(*R*) catalyst was used



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.964	MM	0.4178	171.38419	6.83652	3.6190
2	13.033	BB	0.5498	4564.22998	125.65913	96.3810



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.044	BV	0.8263	6051.69971	115.69158	53.5886
2	16.722	VB	0.6832	5241.18164	116.42956	46.4114

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