# Mechanism and an Improved Asymmetric Allylboration of Ketones Catalyzed by Chiral Biphenols

David S. Barnett, Philip N. Moquist and Scott E. Schaus*

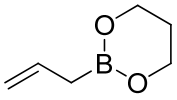
*Department of Chemistry, Center for Chemical Methodology and Library Development at Boston University (CMLD-BU), Life Science and Engineering Building, Boston University 24 Cummington Street, Boston, Massachusetts, 02215*

## Supporting Information

## Table of Contents

**General Information.** All $^{1}H$ NMR, and $^{13}C$ NMR spectra were recorded using Varian Unity Plus 400 (93.94 kG, $^{1}H$ 400 MHz) or Varian Gemini 300 (70.5 kG, $^{13}C$ 75 MHz) spectrometers at ambient temperature in $CDCl_3$. Chemical shifts are reported in parts per million as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant, and integration. Infrared spectra were recorded on a Nicolet Nexus 670 FT-IR ESP spectrophotometer. Optical rotations were recorded on an AUTOPOL III digital polarimeter at 589 nm, and were reported as $[\alpha]_D$ (concentration in grams/100 mL solvent). Analytical thin layer chromatography was performed using EMD 0.25 mm silica gel 60-F plates. Flash column chromatography was performed on Sorbent Technologies 60 Å silica gel. Chiral HPLC analysis was performed using an Agilent 1100 series HPLC or Waters Breeze HPLC System with a diode array detector. Chiral columns include Chiralcel®OD (Chiral Technologies Inc., 25cm×4.6mm I.D.) and Chiralpak®AD-H (Chiral Technologies Inc., 25cm × 4.6 mm I.D.). All reactions were performed under argon with anhydrous solvents in oven dried glassware with magnetic stirring. The 3,3'-$Br_2$-BINOL **1** and allyldiisopropoxyboronate was prepared according to literature procedure.[1] Kinetic parameters for the asymmetric allylboration reaction were determined by *in situ* monitoring of the disappearing of acetophenone **9a** at 1690.67 $cm^{-1}$ using a ReactIR 4000 system (Mettler Toledo-AutoChem). The ReactIR 4000 system, software version 3.1, was fitted with a FiberConduit and a 6 mm DiComp Probe. IR spectra, comprised of 64 scans per spectrum, were collected every one minute at a resolution of 8 $cm^{-1}$. Allylmagnesium bromide, *n*-BuLi, *t*-BuOH, methylborate, and isopropylborate were purchased from Aldrich and used without further purification. KO*t*-Bu was purchased from Acros and used without further purification.

**Preparation of *B*-allyl-1,3,2-dioxaborinane 9**

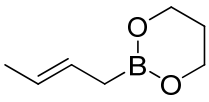


To an oven-dried 500 mL round-bottom flask, charged with a magnetic stir bar and flushed with argon, was added trimethyl borate (10.4 g, 100 mmol) in $Et_2O$ (100 mL) and cooled to –78 °C in a dry ice/acetone bath. A solution of allylmagnesium bromide (14.5 g, 100 mmol, 1.0 M) was added dropwise from an addition funnel over 30 min. The reaction was stirred for 2 h at –78 °C and allowed to warm to room temperature. The reaction was cooled to 0 °C, and 120 mL of an aqueous solution of HCl (3 M) was added slowly through an addition funnel. The biphasic mixture was stirred until all solids were dissolved and an additional 20 min. The mixture was poured into a separatory funnel and the organic layer was removed. The aqueous layer was extracted with $Et_2O$ (3 x 50 mL). The organic layers were combined and dried over $MgSO_4$, filtered, and concentrated to 200 mL in a dry 500 mL round-bottom flask. To the solution was added 1,3-propanediol (7.2 mL, 100 mmol) and 20 g of flame-dried 4Å molecular sieves. The suspension was allowed to stir at room temperature for 16 h. The reaction mixture was filtered through a sintered glass funnel and the molecular sieves were washed with $Et_2O$ (2 x 75 mL). The solvent was removed by rotary evaporator without allowing the water-bath to exceed 25 °C.

(1) (a) P. Wipf, J.K. Jung, *J. Org. Chem.* **2000**, *65*, 6319. (b) N.T. McDougal, W.L. Trevellini, S.A. Rodgen, L.T. Kliman, S.E. Schaus, *Adv. Synth. Catal.* **2004**, *346*, 1231. (c) S. Lou, P.N. Moquist, S.E. Schaus, *J. Am. Chem. Soc.* **2006**, *128*, 12660.

The crude product was then dissolved in 150 mL of pentane to give a cloudy suspension and filtered through a pad of Celite®. The solvent was removed under reduced pressure and the resulting clear liquid was dissolved in 100 mL solution of pentane:$Et_2O$ (2:1) and loaded on a short, pre-equilibrated silica gel column with and flushed with an additional 200 mL of solvent. The solution is concentrated in an oven dried 500 mL round bottom flask, charged with a magnetic stir bar, placed in an ice bath and concentrated to constant weight under high vacuum with stirring to yield *B*-allyl-1,3,2-dioxaborinane (11.4 g, 90% yield) as a colorless liquid. Alternatively, the product can be purified via distillation (40 °C, 4 mmHg) with the receiving flask submerged in a dry ice/acetone bath. The spectral data was in agreement with reported values.[2]

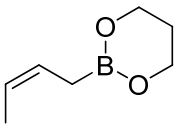
**Preparation of *B*-(*E*)-but-2-enyl-1,3,2-dioxaborinane 11a**[3]




A 500 mL three-neck round bottom flask was charged with a magnetic stir bar and equipped with a thermometer. To the flask was added KO*t*-Bu (100 mL, 100 mmol, 1.0 M in THF). The mixture was flushed with Ar and cooled to −78 ºC. *Trans*-2-butene (5.9 g, 105 mmol), condensed into a rubber-stoppered test tube at −78 ºC, was added via cannula. *n*-BuLi (1.6 M in hexane, 62.5 mL, 100 mmol) was added dropwise over 1 h with an addition funnel to maintain the internal temperature. The reaction mixture was allowed to warm until the internal temperature reached −52 ºC. The solution was maintained at −52 ºC for 15 minutes, and cooled back to −78 ºC. Triisopropyl borate (25.5 mL, 110 mmol) was added dropwise over 30 minutes through an addition funnel. The reaction mixture was maintained at −78 ºC for 3 h and rapidly poured into a 500 mL separation funnel containing 120 mL of 3 N HCl saturated with NaCl. The organic phases were separated, and the aqueous layer was extracted with additional $Et_2O$ (3 × 50 mL). The combined extracts were dried with $MgSO_4$, filtered and concentrated to 200 mL and treated with 1,3-propanediol (7.2 mL, 100 mmol) and flame-dried 4 Å molecular sieves (20 g). The mixture was stirred under Ar for 16 hours at room temperature, filtered through sintered glass funnel and the molecular sieves washed with $Et_2O$ (2x75 ml) and concentrated. The crude product was then dissolved in 100 mL of pentane to give a cloudy solution. If two layers are observed, residual 1,3-propanediol can be removed as the bottom layer of the pentane solution. 50 mL of diethyl ether is added and the solution loaded on a short silica gel column (4.0 x 4.0 cm) pre-equilibrated with pentane:$Et_2O$ (2:1) solution and the column then flushed. The solution is concentrated in an oven dried 500 mL round bottom flask, charged with a magnetic stir bar and concentrated to constant weight under high vacuum with stirring to yield 10.5 g (75 mmol, 75%) *B-(E)-crotyl-1,3,2-dioxaborinane* as a colorless liquid **$^1$H NMR** (400 MHz, $CDCl_3$) δ 5.46 (m, 1H), 5.34 (m, 1H), 3.99 (t, *J* = 5.4, 3H), 1.94 (m, 2H), 1.63 (m, 3H), 1.54 (br d, *J* = 6.8, 2H). **$^{13}$C NMR** (75.0 MHz, $CDCl_3$): δ = 127.2, 124.3, 61.7, 27.3, 18.0.

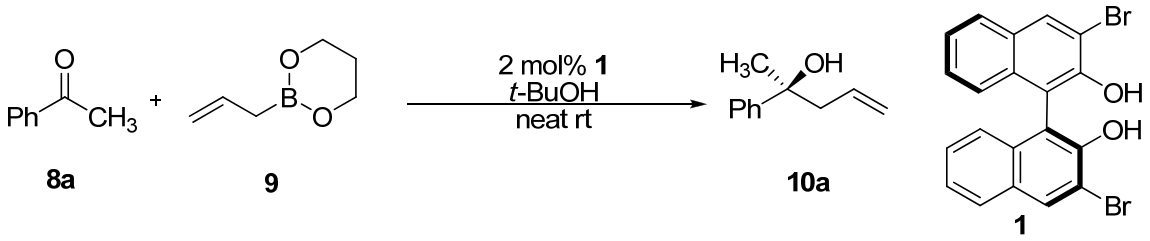
(2) H.C. Brown, U.S. Rachela, P.J. Pellechia, *J. Org. Chem.* **1990**, *55*, 1868.
(3) W.R. Roush, K. Ando, D.B. Powers, A.D. Palkowitz, R.L. Halterman, *J. Am. Chem. Soc.* **1990**, *112*, 6339.

**B-(*Z*)-but-2-enyl-1,3,2-dioxaborinane 11b**



The procedure is identical to the preparation of **11a** with a few modifications. *Cis*-2-butene is used in place of *trans*-2-butene and the reaction is warmed to –25 °C for 30 minutes instead of –52 °C for 15 minutes. *B-(Z)-crotyl-1,3,2-dioxaborinane* was obtained as a colorless liquid with a yield of 11.4 g (81 mmol, 81%). **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 5.47 (m, 2H), 3.99 (t, 4H), 1.94 (m, 2H), 1.60 (br d, *J* = 10.3, 5H); **$^{13}$C NMR** (75.0 MHz, $CDCl_3$) δ = 126.3, 122.7, 61.8, 27.3, 12.4.

**General Procedure for the Asymmetric Allylboration of Ketones.**



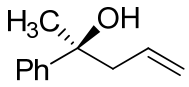

**8a** **9** **10a** **1**

A 10 mL round-bottom flask was charged with stir bar and flushed with Ar. To the flask was added 3,3'-dibromo-1,1'-bi-2-naphthol **1** (8.88 mg, 0.020 mmol), *t*-BuOH (148 mg, 2.00 mmol) and *B*-allyl-1,3,2-dioxaborinane **9** (189 mg, 1.50 mmol). The mixture was stirred at room temperature for 5 min and acetophenone **8a** (117 μL, 1.00 mmol) was added dropwise. The reaction mixture was stirred at room temperature for 24 h, dissolved in hexanes and purified by flash chromatography over silica gel directly (elution with 2% – 5% acetone in hexanes) to afford the homoallylic alcohol **10a** as a white solid.

**General Procedure for preparation of racemic products.**

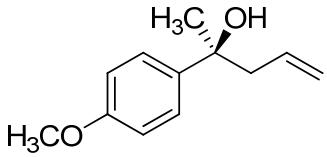
A 10 mL oven-dried glass vessel was charged with stir bar and flushed with Ar. To the flask was added *B*-allyl-1,3,2-dioxaborinane **9** (189 mg, 1.50 mmol) and acetophenone **8a** (117 μL, 1.00 mmol). The mixture was stirred under Ar at 40 °C overnight. The reaction mixture was diluted with hexanes and purified by flash chromatography over silica gel directly (elution with 2% - 5% acetone in hexanes) to afford the racemic homoallylic alcohol **10a** as clear oil.

**(*S*)-(−)-2-phenylpent-4-en-2-ol (10a)**



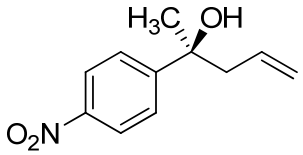
The crude mixture was purified by flash column chromatography with elution by 2% acetone in hexanes. **Yield:** 155mg, 96%; **er:** 99:1; $[\alpha]_D^{23} = -52.4^\circ$ (c = 1.7, $CHCl_3$); Lit[4] : $[\alpha]_D = -48.8^\circ$ (c = 0.84, $CHCl_3$, 82% ee); **HPLC Analysis**, $t_r$ minor: 17.2 min., $t_r$ major: 18.6 min., [Chiralpak®AD-H column, 25cm × 4.6 mm I.D., Hexanes:IPA = 99:1, 0.8 mL/min]; Other spectral data was in agreement with reported data.[4]

**(*S*)-(−)-2-(4-methoxyphenyl)-4-penten-2-ol (10b)**



The crude mixture was purified by flash column chromatography with elution by 2 - 5% acetone in hexanes. **Yield:** 169 mg, 88% ; **er:** 98.8:1.2 $[\alpha]_D^{23} = -64.0^\circ$ (c = 1.2, $CHCl_3$); Lit[6] : $[\alpha]_D^{31} = +43.1^\circ$ (c = 0.57, $CHCl_3$, 79% ee, (+) isomer); **HPLC Analysis,** $t_r$ minor: 21.3 min., $t_r$ major: 22.9 min., [Chiralcel®OD-H column, 25cm × 4.6 mm I.D., Hexanes:IPA = 99:1, 0.8 mL/min]; Other spectral data was in agreement with reported data.[7]

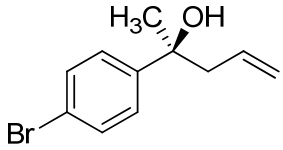
**(*S*)-(−)-2-(4-nitrophenyl)-pent-4-en-2-ol (10c)**



The crude mixture was purified by flash column chromatography with elution by 2 - 5% acetone in hexanes. **Yield:** 193 mg, 93%, **er:** 99:1, $[\alpha]_D^{23} = -58.5°$ (c = 1.78, $CHCl_3$); **HPLC Analysis,** $t_r$ minor: 17.9 min., $t_r$ major: 15.6 min., [Chiralpak®AD-H column, 25cm × 4.6 mm I.D., Hexanes:IPA = 95:5 0.8mL/min]; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 9.0, 2H), 7.61 (d, *J* = 9.0, 2H), 5.58 (m, 1H), 5.13 (m, 2H), 2.60 (m, 2H), 2.22 (s, 1H), 1.57 (s, 3H). **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ = 155.02, 146.71, 132.52, 125.98, 123.41, 120.59, 73.66, 48.24, 29.81. **IR** (thin film, $cm^{-1}$): 3539, 3077, 2978, 2932, 2709, 2454, 1935, 1802, 1640, 1603, 1521, 1348, 1069.

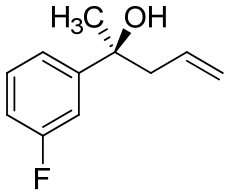
(4) R. Wada, K. Oisaki, M. Kanai, M. Shibasaki, *J. Am. Chem. Soc.* **2004**, *126*, 8910.

**(*S*)-(−)- 2-(4-bromophenyl)-pent-4-en-2-ol (10d)**



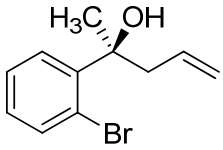

The crude mixture was purified by flash column chromatography with elution by 2 - 5% acetone in hexanes. **Yield:** 234mg, 97%; **er:** 99:1, $[\alpha]^{23}_{D}$ = –53.6° (c = 1.5 , $CHCl_3$); Lit[5] : $[\alpha]^{26}_{D}$ = –44° (c = 1.6 , $CHCl_3$, 98% ee); **HPLC Analysis,** $t_r$ minor: 17.3 min., $t_r$ major: 15.9 min., [Chiralcel®OD column, 25cm × 4.6 mm I.D., Hexanes:IPA = 99:1, 1.0mL/min]; Other spectral data was in agreement with reported data.[6]

**(*S*)-(−)-2-(3-fluorophenyl)-pent-4-en-2-ol (10e)**




The crude mixture was purified by flash column chromatography with elution by 2 - 5% acetone in hexanes. **Yield:** 171 mg, 95% **er:** 98.7:1.3, $[\alpha]^{23}_{D}$ = –54.9° (c = 1.2, $CHCl_3$) **HPLC Analysis**, $t_r$ minor: 18.5 min., $t_r$ major: 19.7 min. [Chiralpak®AD-H column, 25cm × 4.6 mm I.D., Hexanes:IPA = 99:1, 0.8mL/min], **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 7.29 (m, 1H), 7.17 (m, 2H), 6.92 (m, 1H), 5.61 (m, 1H), 5.15 (m, 2H), 2.57 (ddd, *J* = 7.4, 2H), 2.11 (s, 1H), 1.53 (s, 3H). **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ = 164.1, 161.6, 150.5, 133.2, 129.6, 120.4, 119.9, 113.5, 113.3, 112.2, 112.0, 73.4, 48.3, 29.8. **IR** (thin film, $cm^{-1}$): 3438, 3077, 2979, 2931, 1640, 1614, 1589, 1437, 1271.

**(*S*)-(−)-2-(3-bromophenyl)-pent-4-en-2-ol (10f)**

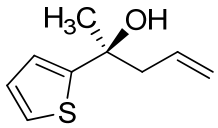



The reaction was run on a 0.5 mmol scale with 17 mg, 7.5 mol% of catalyst **1** and without *t*-BuOH in 1.0 mL of toluene. The crude mixture was purified by flash column chromatography with elution by 2 - 5% acetone in hexanes. **Yield:** 114 mg, 95% **er:** 98.6:1.4, $[\alpha]^{23}_{D}$ = –35.7° (c = 1.34, $CHCl_3$) **HPLC Analysis**, $t_r$ minor: 10.7 min., $t_r$ major: 12.7 min. [Chiralpak®AD-H column, 25cm × 4.6 mm I.D., Hexanes:IPA = 99:1, 1.0mL/min], **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 7.70 (d, *J* = 8.0, 1H), 7.58 (d, *J* = 7.9, 1H), 7.30 (t, *J* = 7.6, 1H), 7.09 (t, *J* = 7.6, 1H), 5.55 (m,

(5) E. Canales, K.G. Prasad, J.A. Soderquist, *J. Am. Chem. Soc.* **2005**, *127*, 11572.

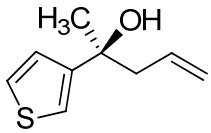
1H), 5.11 (m, 2H), 3.28 (dd, *J* = 6.4, 1H), 2.65 (m, 2H), 1.72 (s, 4H). **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ = 145.0, 135.0, 133.6, 128.5, 128.2, 127.4, 120.0, 119.3, 74.6, 45.1, 27.3. **IR** (thin film, $cm^{-1}$): 3466, 3073, 2976, 2931, 1639, 1592, 1431, 1270, 1016.

**(*S*)-(–)-2-thiophen-2-yl-pent-4-en-2-ol (10g)**



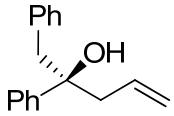

Reaction was run with 18 mg, 4 mol% catalyst **1**. The crude mixture was purified by flash column chromatography with elution by 2 - 5% acetone in hexanes. **Yield:** 155 mg, 92% **er:** 99.6:0.4 **$[\alpha]^{23}_D$** = –40.1° (c = 1.28 , $CHCl_3$); **HPLC Analysis,** $t_r$ minor: 16.9 min., $t_r$ major: 18.9 min., [Chiralcel®OD column, 25cm × 4.6 mm I.D., Hexanes:IPA = 99:1 0.8 mL/min]; Other spectral data was in agreement with reported data.[6]

**(*S*)-(–)-2-thiophen-3-yl-pent-4-en-2-ol (10h)**




Reaction was run with 18 mg, 4 mol% catalyst. The crude mixture was purified by flash column chromatography with elution by 2 - 5% acetone in hexanes. **Yield:** 156 mg, 93% **er:** 99.4:0.6, **$[\alpha]^{23}_D$** = –49.4° (c = 0.99 , $CHCl_3$); Lit[3] : **$[\alpha]^{26}_D$** = –47.1° (c = 1.17 , $CHCl_3$, 94% ee); **HPLC Analysis,** $t_r$ minor: 16.9 min., $t_r$ major: 17.7 min., [Chiralcel®OD column, 25cm × 4.6 mm I.D., Hexanes:IPA = 99:1 0.8 mL/min]; Other spectral data was in agreement with reported data.[5]

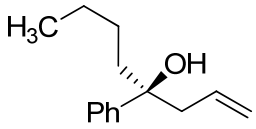
**(*R*)-(+)-1,2-diphenylpent-4-en-2-ol (10i)**




The crude mixture was purified by flash column chromatography with elution by 2 - 5% acetone in hexanes. **Yield:** 234 mg, 98%, **er:** 99.5:0.5 **$[\alpha]^{23}_D$** = +25.3° (c = 1.5 , $CHCl_3$) **HPLC Analysis,** $t_r$ minor: 15.3 min., $t_r$ major: 12.8 min., [Chiralpak®AD-H column, 25cm × 4.6 mm I.D., Hexanes:IPA = 99:1 0.8mL/min], **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 7.36 (m, 4H), 7.22 (m, 4H), 7.00 (m, 2H), 5.65 (ddd, *J* = 7.7, 1H), 5.13 (m, 2H), 3.14 (dd, *J* = 13.4, 2H), 2.87 (dd, *J* = 5.9, 1H), 2.56 (dd, *J* = 8.5, 2H), 2.12 (s, 1H), **$^{13}$C NMR** (75 MHz, $CDCl_3$, δ) 145.6, 136.5, 133.5, 130.8, 128, 127.9, 126.6, 125.6, 119.4, 75.9, 49.3, 46.2. **IR** (thin film, $cm^{-1}$): 3556, 3061, 3028, 2923, 1495, 1446, 1342, 1264, 1032.

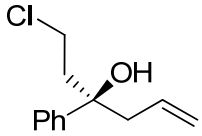
(6) P. Gomes, C. Gosmini, J. Perichon, *Synthesis*, **2003**, 12, 1909.

**(*S*)-(–)-4-phenyloct-1-en-4-ol (10j)**



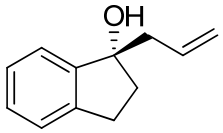

The crude mixture was purified by flash column chromatography with elution by 2 - 5% acetone in hexanes. **Yield:** 190 mg, 93%, **er:** 99:1 $[\alpha]^{23}_{D}$ = –53.0 (c = 1.65, $CHCl_3$) **HPLC Analysis,** $t_r$ minor: 10.7 min., $t_r$ major: 11.7 min., [Chiralpak®AD-H column, 25cm × 4.6 mm I.D., Hexanes:IPA = 99:1 0.8mL/min], **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 7.36 (m, 4H), 7.24 (m, 1H), 5.57 (m, 1H), 5.12 (m, 2H), 2.61 (ddd, 2H), 2.03 (s, 1H), 1.81 (m, 2H), 1.27 (m, 4H), 0.84 (t, 3H). **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ = 146.1, 133.6, 128.0, 126.4, 125.3, 119.6, 75.8, 47.4, 42.5, 25.6, 23.0, 14.0. **IR** (thin film, $cm^{-1}$): 3560, 3477, 3069, 3027, 2928, 2871, 1638, 1494, 1446, 1379, 1032.

**(*R*)-(–)-1-chloro-3-phenylhex-5-en-3-ol (10k)**




Reaction was run with 18 mg, 4 mol% catalyst. The crude mixture was purified by flash column chromatography with elution by 2 - 5% acetone in hexanes. **Yield:** 200 mg, 95%, **er:** 99.5:0.5 $[\alpha]^{23}_{D}$ = −44.9° (c = 1.1, $CHCl_3$) **HPLC Analysis,** $t_r$ minor: 30.3 min., $t_r$ major: 31.4 min., [Chiralpak®AD-H column, 25cm × 4.6 mm I.D., Hexanes:IPA = 99:1 0.4mL/min], **$^1$H NMR** (400 MHz, $CDCl_3$) δ = 7.29 (m, 4H), 7.19 (m, 1H), 5.46 (ddd, 1H), 5.10 (m, 2H), 3.50 (m, 1H), 3.14 (m, 1H), 2.67 (m, 1H), 2.44 (m, 1H), 2.24 (m, 2H), 2.14 (s, 1H). **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ = 144.3, 132.5, 128.4, 128.3, 128.3, 126.9, 126.9, 125.0, 124.9, 124.9, 124.8, 120.6, 120.5, 105.0, 75.2, 47.8, 45.5, 40.1. **IR** (thin film, $cm^{-1}$): 3555, 3472, 3076, 3027, 2929, 1638, 1494, 1446, 1337, 1060.

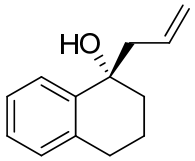
**(*S*)-(–)-1-allyl-2,3-dihydro-1H-inden-1-ol (10l)**




The crude mixture was purified by flash column chromatography with elution by 2 - 5% acetone in hexanes. **Yield:** 166 mg**,** 95%; **er:** 98:2; $[\alpha]_D^{23}$ = – 9.1° (c = 1.0, $CHCl_3$); Lit[7] : $[\alpha]_D^{31}$ = + 6.2° (c = 0.25, $CHCl_3$, 91%ee, (+)-isomer); **HPLC Analysis**, $t_r$ major: 19.2 min., $t_r$ minor: 25.0 min., [Chiralcel®OD column, 25cm × 4.6 mm I.D., Hexanes:IPA = 98:2, 1.0 mL/min]; Other spectral data was in agreement with reported data.[5]

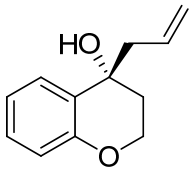
(7) M. Wadamoto, H. Yamamoto, *J. Am. Chem. Soc.* **2005**, *127*, 14556.

**(*S*)-(−)-1-allyl-1,2,3,4-tetrahydronaphthalen-1-ol (10m)**



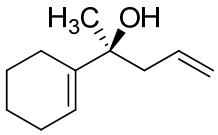

Reaction was run with 18 mg, 4 mol%, catalyst. The crude mixture was purified by flash column chromatography with elution by 2-5% acetone in hexanes. **Yield:** 183 mg**,** 97% **er:** 99:1 $[\alpha]_D^{23}$ = – 42.2° (c = 1.1, $CHCl_3$); Lit[5] : $[\alpha]_D^{31}$ = –28.5° (c = 1.17, $CHCl_3$, 84%ee); **HPLC Analysis**, $t_r$ minor: 18.3 min., $t_r$ major: 20.2 min., [Chiralcel®OD column, 25cm × 4.6 mm I.D., Hexanes:IPA = 99:1, 0.8 mL/min]; Other spectral data was in agreement with reported data.[8]

**(*S*)-(–)-4-allyl-3,4-dihydro-2H-chromen-4-ol (10n)**




The crude mixture was purified by flash column chromatography with elution by 2-5% acetone in hexanes. **Yield:** 181 mg**,** 95% **er:** 99:1; $[\alpha]_D^{23}$ = –14.5° (c = 1.2, $CHCl_3$); Lit[5] : $[\alpha]_D^{28}$ = –15.8° (c = 0.71, $CHCl_3$, 92%ee); **HPLC Analysis**, $t_r$ minor: 20.3 min., $t_r$ major: 25.8 min., [Chiralcel®OD column, 25cm × 4.6 mm I.D., Hexanes:IPA = 99:1, 0.8 mL/min]; Other spectral data was in agreement with reported data.[5]

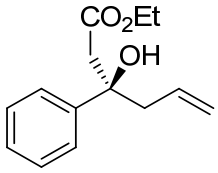
**(*S*)-(–)-2-Cyclohexenylpent-4-en-2-ol (10o)**




Reaction was run with 18 mg, 4 mol%, catalyst. The crude mixture was purified by flash column chromatography with elution by 2 - 5% acetone in hexanes. **Yield:** 160 mg, 96% $[\alpha]^{23}_D$ = –55.3 (c = 1.68, $CHCl_3$), The purified product was acetylated prior to HPLC analysis to form a UV-active species, **er:** 98:2 **HPLC Analysis,** $t_r$ minor: 22.8 min., $t_r$ major: 25.1 min., [Chiralpak-®AD-H column, 25cm × 4.6 mm I.D., Hexanes:IPA = 99:1 1.0mL/min] Other spectral data was in agreement with reported data.[6]

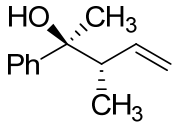
(8) S. Casolari, D. D'Addario, E. Tagliavine, *Org. Lett.* **1999**, *1*, 1061.

**(*S*)-(+)-ethyl 3-hydroxy-3-(2-oxo-2-phenylethyl)hex-5-enoate (10p)**



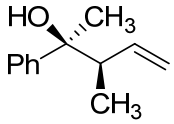

The crude mixture was purified by flash column chromatography with elution by 2 - 5% acetone in hexanes. **Yield:** 230 mg**,** 98% **er:** 99:1; $[\alpha]_D^{23}$ = 17.2° (c 1.45, $CHCl_3$) **HPLC Analysis**, $t_r$ minor: 14.0 min., $t_r$ major: 13.0 min., [Chiralcel®AD-H column, 25 cm × 4.6 mm I.D., Hexanes:IPA = 99:1, 0.8 mL/min]; **$^1$H NMR** (400 MHz, $CDCl_3$, δ) δ = 7.41 (d, *J* = 7.4, 2H), 7.33 (t, *J* = 7.7, 2H), 7.24 (m, 1H), 5.69 (ddd, *J* = 7.2, 11.0, 17.1, 1H), 5.04 (m, 2H), 4.37 (s, 1H), 4.02 (q, *J* = 7.1, 2H), 2.90 (dd, *J* = 15.9, 57.9, 2H), 2.54 (ddd, *J*=7.2, 13.9, 21.7, 2H), 1.10 (t, *J* = 7.1, 3H), **$^{13}$C NMR** (75 MHz, $CDCl_3$, δ) 172.6, 145.3, 133.1, 128.2, 125.1, 118.5, 74.6, 60.7, 47.8, 44.4, 14.1. **IR** (thin film, $cm^{-1}$): 3496, 3075, 2981, 2936, 1713, 1640, 1373, 1337, 1198, 1025.

**(2*S*, 3*S*)-3-methyl-2-phenylpent-4-en-2-ol (12a)**




The crude mixture was purified by flash column chromatography with elution by 2 - 5% ethyl acetate in hexanes. **Yield:** 169 mg**,** 96% **er:** 99:1, **dr:** 97:3, $[\alpha]_D^{23}$ = – 67.8° (c = 0.2, $CHCl_3$); Lit[4] : $[\alpha]_D$ = – 72.8° (c = 1.05, $CHCl_3$, 85% ee); **HPLC Analysis**, $t_r$ minor: 16.3 min., $t_r$ major: 22.8 min., [Chiralpak®OD column, 25cm × 4.6 mm I.D., Hexanes:IPA = 99.5:0.5, 0.8 mL/min]; Other spectral data was in agreement with reported data.[4]

**(2*S*,3*R*)-3-methyl-2-phenylpent-4-en-2-ol (12b)**




The crude mixture was purified by flash column chromatography with elution by 2 - 5% ethyl acetate in hexanes. **Yield:** 166 mg**,** 94% **er:** 97:3, **dr:** 98:2, $[\alpha]_D^{23}$ = + 6.1° (c = 1.5, $CHCl_3$); Lit[4] : $[\alpha]_D^{22}$ = + 4.4° (c = 1.09, $CHCl_3$, 83% ee); **HPLC Analysis**, $t_r$ minor: 16.0 min., $t_r$ major: 19.4 min., [Chiralpak®OD column, 25 cm × 4.6 mm I.D., Hexanes:IPA = 99.5:0.5, 0.8 mL/min]; Other sepctral data was in agreement with reported data.[4]

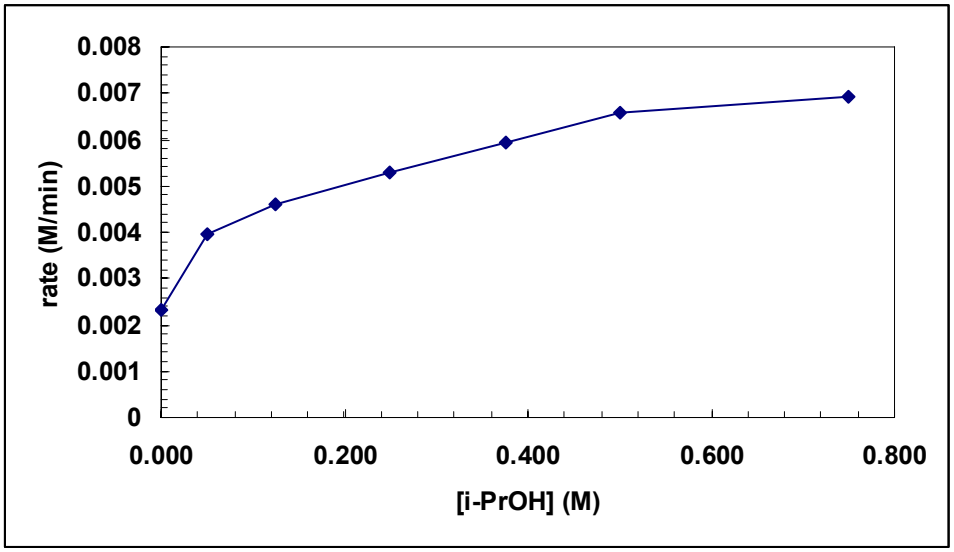
**Kinetic Experiments**

**Determination of the kinetic order in isopropanol using the ReactIR.** To a 20 mL vial equipped with a stir bar, was added (*S*)-3,3'-$Br_2$-BINOL **1** (33 mg, 0.075 mmol, 10 mol% catalyst loading), $PhCH_3$ (1.5 mL) and *i*-PrOH (variable). To the suspension was added allyldiisopropoxyboronate **2** (1.5 mL, 1.50 mmol, 1.0 M solution in $PhCH_3$) and stirred for 5 min until the solution was clear. Acetophenone **8a** (90 μL, 0.75 mmol) was added to the solution and the vial was sealed with a septum and equipped with the DiComp ReactIR 4000 Probe. The solution was stirred at room temperature for 150 min and the carbonyl stretch of acetophenone **8a** was monitored at 1690.67 $cm^{-1}$ by ReactIR in real time. Reactions were run for an additional 12.5 h, purified by silica gel chromatography, and run on chiral HPLC to determine enantiomeric ratio.

***Table S1***. Effect of *i*-PrOH concentration on the initial rate of the allylboration reaction.

| $[i\text{-PrOH}]_{initial}$ (M) | $k_{obs}$ ($Mmin^{-1}$) |
|---|---|
| 0.000 | 0.002307185 |
| 0.050 | 0.003955175 |
| 0.125 | 0.00461437 |
| 0.250 | 0.005273566 |
| 0.375 | 0.005932762 |
| 0.500 | 0.006591958 |
| 0.750 | 0.006921556 |

***Figure S1***. Rate of the reaction versus [*i*-PrOH] in the allylboration of acetophenone.

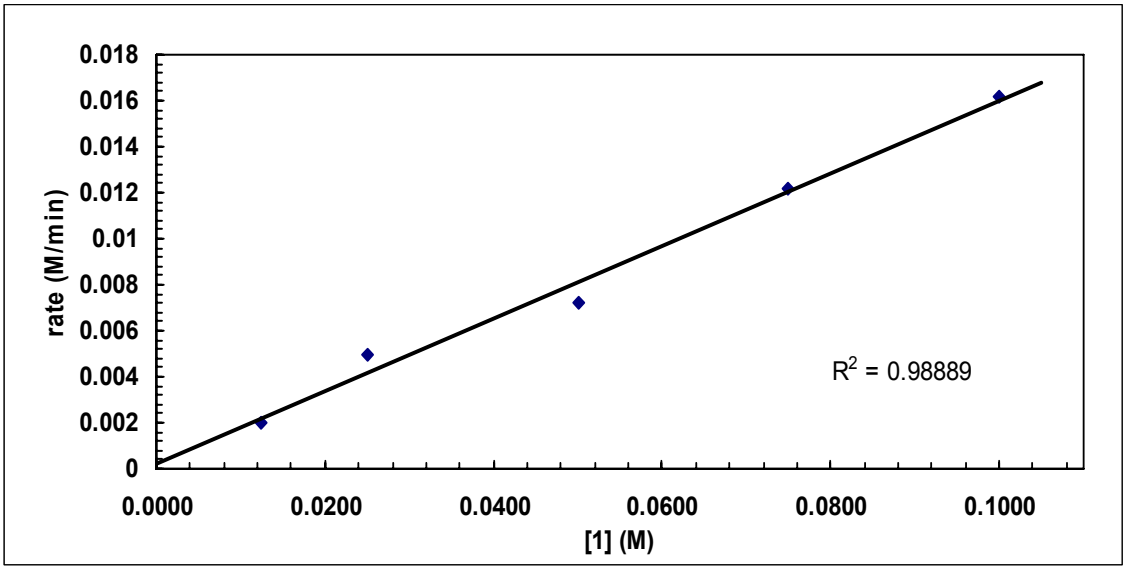


**Determination of the order in catalyst 1 using the ReactIR.** To a 20 mL vial equipped with a stir bar, was added (*S*)-3,3'-$Br_2$-BINOL **1** (variable), $PhCH_3$ (1.5 mL) and *i*-PrOH (86 μL, 0.113 mmol). To the suspension was added allyldiisopropoxyboronate **2** (1.5 mL, 1.50 mmol, 1.0 M solution in $PhCH_3$) and stirred for 5 min until the solution was clear. Acetophenone **8a** (90 μL, 0.75 mmol) was added to the solution and the vial was sealed with a septum and equipped with the DiComp ReactIR 4000 Probe. The solution was stirred at room temperature for 150 min and the carbonyl stretch of acetophenone **8a** was monitored at 1690.67 $cm^{-1}$ by ReactIR in real time.

***Table S2***. Effect of catalyst **1** concentration on the initial rate of the allylboration reaction.

| $[\mathbf{1}]_{initial}$ (M) | $k_{obs}$ ($Mmin^{-1}$) |
|---|---|
| 0.0125 | 0.001977587 |
| 0.0250 | 0.004943968 |
| 0.0500 | 0.007251154 |
| 0.0750 | 0.012195122 |
| 0.1000 | 0.016150297 |

***Figure S2***. First-order in catalyst in allylboration of acetophenone.

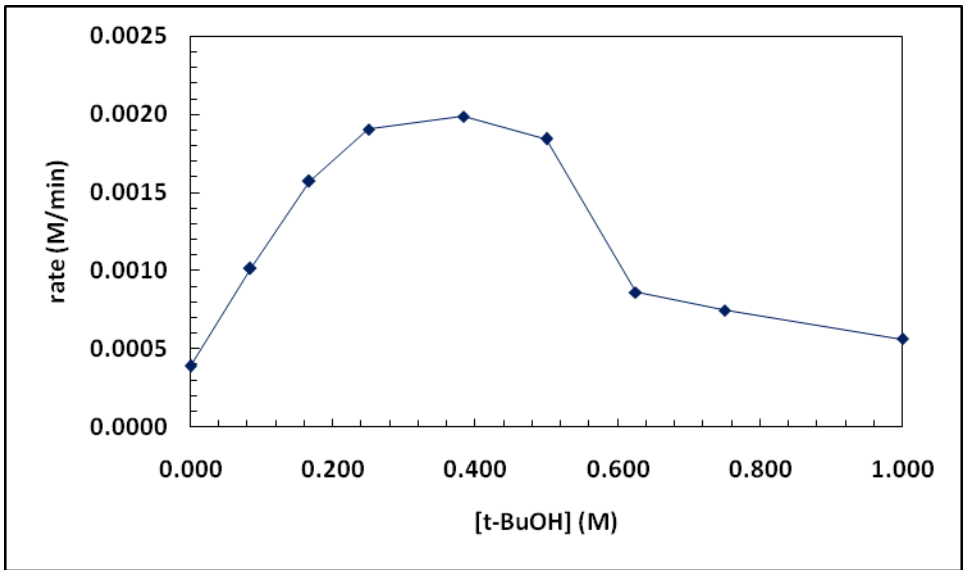


**Determination of the kinetic order in *t*-BuOH using the ReactIR.** To a 20 mL vial equipped with a stir bar, was added (*S*)-3,3'-$Br_2$-BINOL **1** (67 mg, 0.15 mmol, 15 mol% catalyst loading), $PhCH_3$ (3.0 mL) and *t*-BuOH (variable). To the suspension was added *B*-allyl-1,3,2-dioxaborinane **9** (189 mg, 1.5 mmol) and stirred for 5 min until the solution was clear. Acetophenone **8a** (117 μL, 1.0 mmol) was added to the solution and the vial was sealed with a septum and equipped with the DiComp ReactIR 4000 Probe. The solution was stirred at room temperature for 15 h and the carbonyl stretch of acetophenone **8a** was monitored at 1690.67 $cm^{-1}$ by ReactIR in real time.

***Table S3***. Effect of *i*-PrOH concentration on the initial rate of the allylboration reaction.

| [tBuOH] (M) | $k_{obs}$ ($Mmin^{-1}$) |
|---|---|
| 0.000 | 0.00038893 |
| 0.083 | 0.00101187 |
| 0.167 | 0.00157218 |
| 0.250 | 0.00190508 |
| 0.383 | 0.00198418 |
| 0.500 | 0.00184245 |
| 0.625 | 0.00086025 |
| 0.750 | 0.00074489 |
| 1.000 | 0.00056361 |

***Figure S3***. Rate of the reaction versus [*t*-BuOH] in the allylboration of acetophenone.

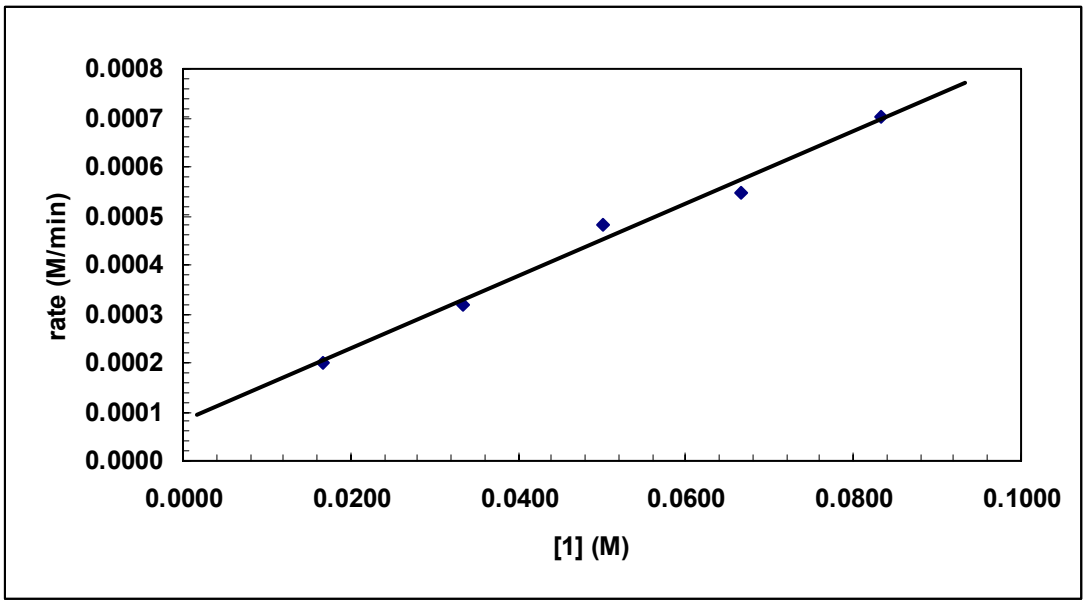


**Determination of the order in catalyst 1 using the ReactIR.** To a 20 mL vial equipped with a stir bar, was added (*S*)-3,3'-$Br_2$-BINOL **1** (variable), $PhCH_3$ (3 mL) and *t*-BuOH (191 μL, 2.0 mmol). To the suspension was added *B*-allyl-1,3,2-dioxaborinane **9** (189 mg, 1.5 mmol) and stirred for 5 min until the solution was clear. Acetophenone **8a** (117 μL, 1.0 mmol) was added to the solution and the vial was sealed with a septum and equipped with the DiComp ReactIR 4000 Probe. The solution was stirred at room temperature for 15 h and the carbonyl stretch of acetophenone **8a** was monitored at 1690.67 $cm^{-1}$ by ReactIR in real time.

***Table S4.*** Effect of catalyst **1** concentration on the initial rate of the allylboration reaction using allyldioxaborinane **8**.

| $[\mathbf{1}]_{initial}$ (M) | $k_{obs}$ ($Mmin^{-1}$) |
|---|---|
| 0.0167 | 0.000201384 |
| 0.0333 | 0.000316744 |
| 0.0500 | 0.000481213 |
| 0.0667 | 0.000547132 |
| 0.0833 | 0.000702044 |
| 0.1000 | 0.000731707 |

***Figure S4***. First order in catalyst in allylboration of acetophenone using allyldioxaborinane **9**.



**Direct-Inject Mass Spectrometry Experiments.**

**Mass Spectrometry of Reaction with Allyldiisopropoxyboronate 2.**

To a dry vial was added catalyst **1** (11 mg, 0.025 mmol), *i*-PrOH (29 μL, 0.10 mmol). A mixed solvent system of $CH_3CN$ (0.5 mL) and $PhCH_3$ (0.125 mL) was added under Ar. The solution was charged with allyldiisopropoxyboronate **2** (375 μL, 0.375 mmol, 1.0 M solution in $PhCH_3$) then acetophenone **8a**. The reaction was allowed to stir for 2 h at room temperature. An aliquot (30 μL) was taken into a 1 mL syringe and diluted with $CH_3CN$ (0.5 mL) and $PhCH_3$ (0.5 mL). The solution was injected into MicroMass ZQ 2000 mass spectrometer via syringe pump (150 mL/min) with negative electron spray ionization mode (ESI–, ES/voltages: capillary 3.01 KV, cone 60 V; Temperature: source 130 °C, desolvation 260 °C; Gas flow: desolvation 250 L/h, one 50 L/h; Pump flow: 60 μL/min). The mass of 3,3'-$Br_2$-BINOL **1**, the allyldiisopropoxyboronate **2**, and the acyclic boronate **3** with complexed $CH_3CN$ was observed. The remainder of the reaction was run to completion and purified according to the aforementioned procedure. The yield and er were 68% and 97:3, respectively, indicating the presence of $CH_3CN$ does not negatively affect the reaction.

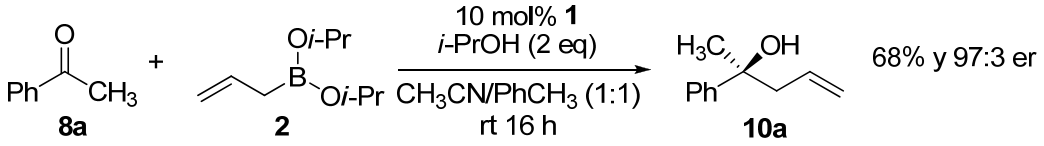
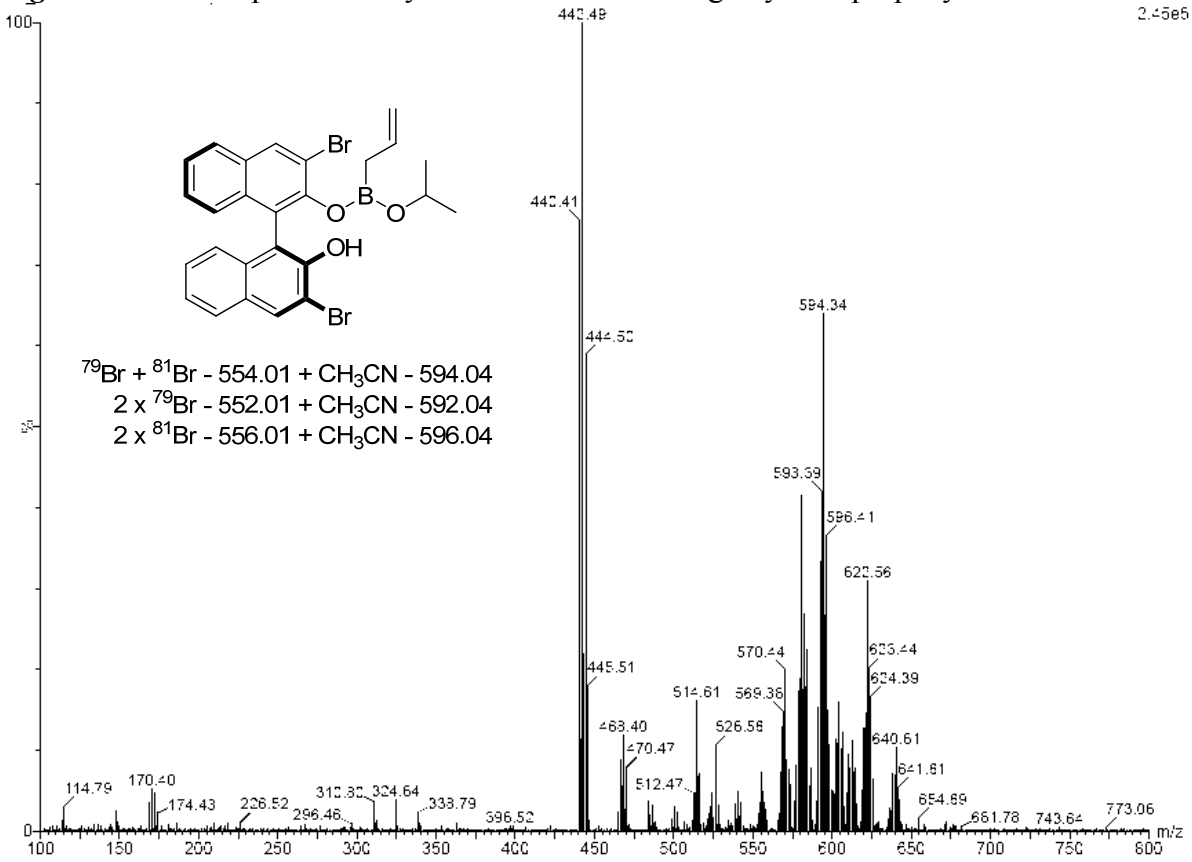



***Figure S5.*** Mass Spectra of allylboration reaction using allyldiisopropoxyboronate



**Mass Spectrometry of Reaction with *B*-allyl-1,3,2-dioxaborinane 9.**

To a dry vial was added catalyst **1** (22 mg, 0.05 mmol), *t*-BuOH (191 μL, 2.0 mmol) and *B*-allyl-1,3,2-dioxaborinane **9** (189 mg, 1.5 mmol) under Ar. The reaction was allowed to stir for 5 minutes and acetophenone **8a** (117 μL, 1.00 mmol) was added dropwise. The reaction was allowed to stir for 2 h at room temperature. An aliquot (30 μL) was taken into a 1 mLsyringe and diluted with $CH_3CN$ (1.0 mL). The solution was injected into MicroMass ZQ 2000 mass spectrometer via syringe pump (150 mL/min) with negative electron spray ionization mode (ESI–, ES/voltages: capillary 3.01 KV, cone 60 V; Temperature: source 130 °C, desolvation 260 °C; Gas flow: desolvation 250 L/h, one 50 L/h; Pump flow: 60 μL/min). The mass of 3,3'-$Br_2$-BINOL **1** and the acyclic boronate was observed. The remainder of the reaction was run to completion and purified according to the aforementioned procedure. The yield and er were 98% and 99:1.

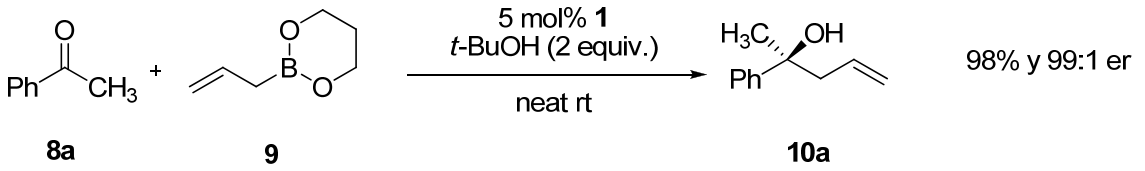
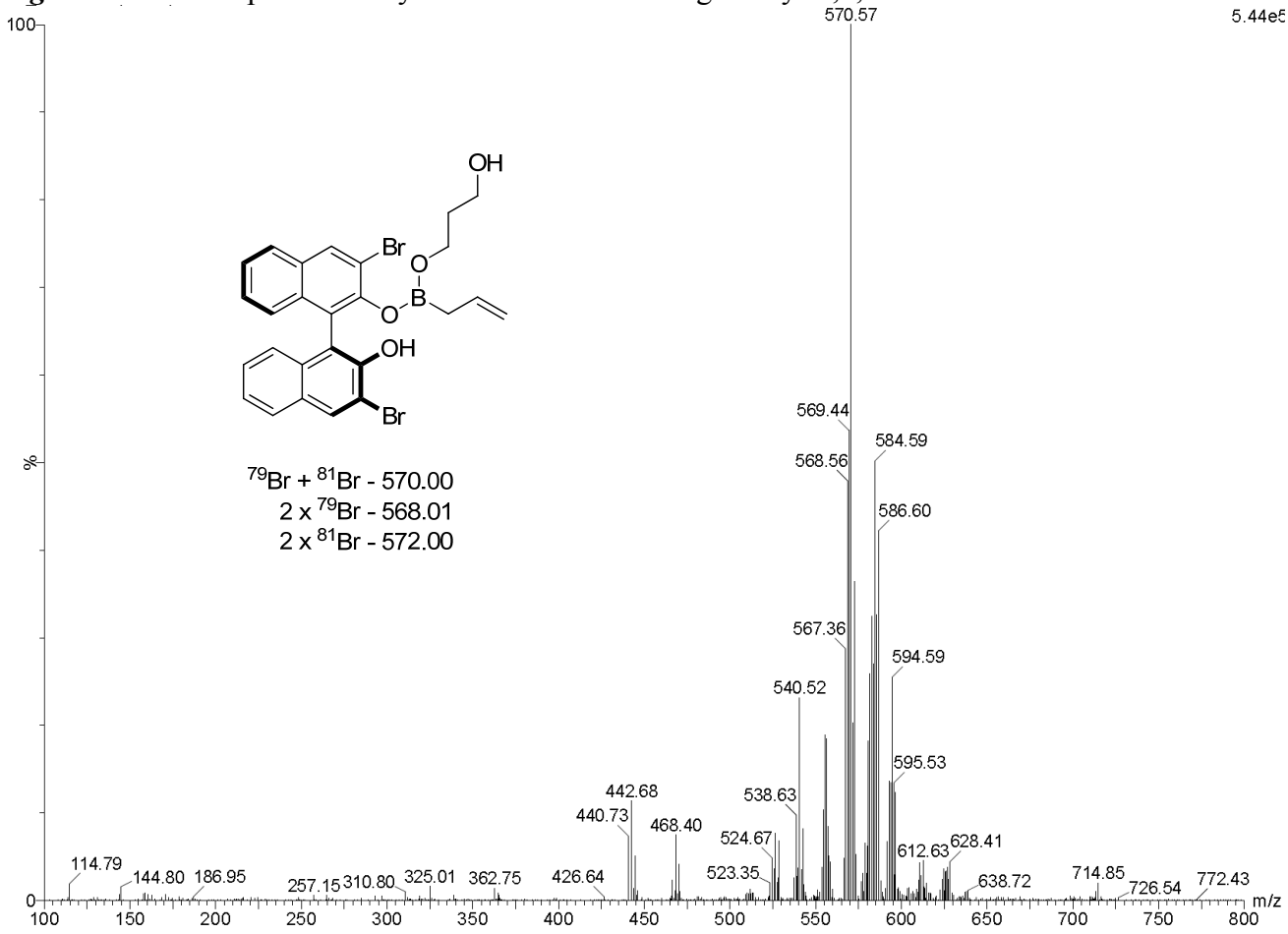


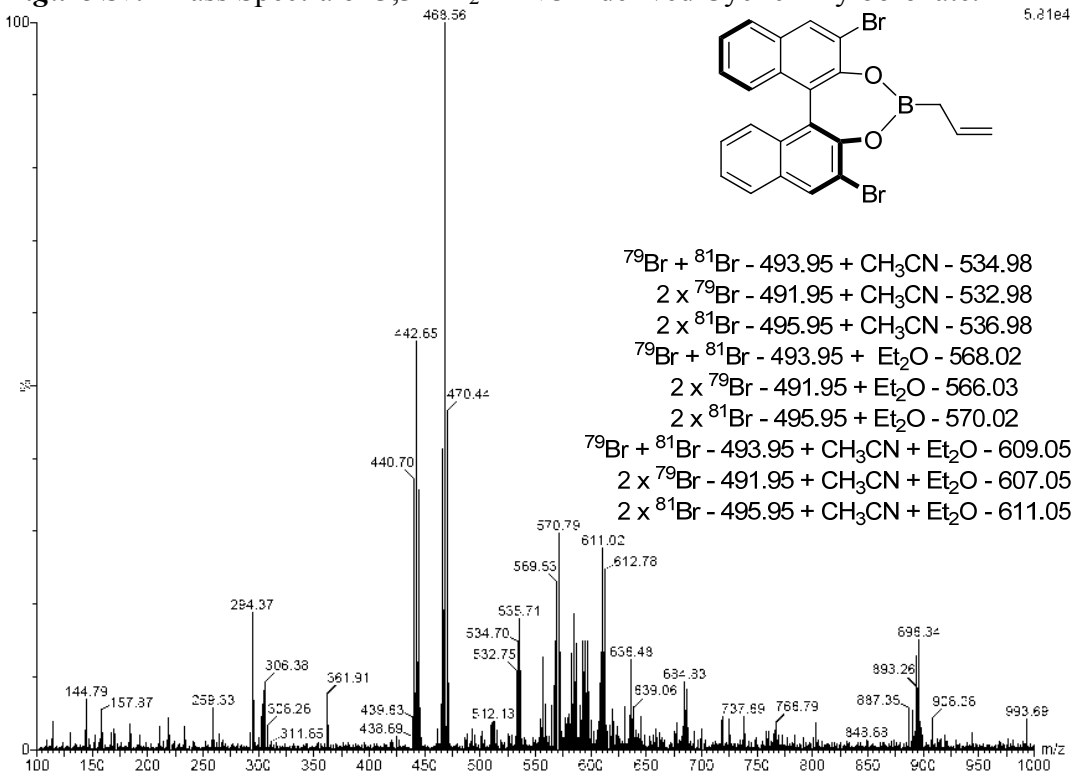

***Figure S6.*** Mass Spectra of allylboration reaction using *B*-allyl-1,3,2-dioxaborinane



**Mass Spectrometry of 3,3'-$Br_2$-BINOL-derived Cyclic Allylboronate.**

A solution of 3,3'-$Br_2$-BINOL-derived cyclic allylboronate in dry $Et_2O$ was prepared according to literature.[9] An aliquot (30 μL) was taken into a 1 mL syringe and diluted with $CH_3CN$ (0.5 mL) and $PhCH_3$ (0.5 mL). The solution was injected into MicroMass ZQ 2000 mass spectrometer via syringe pump (150 uL/min) with negative electron spray ionization mode (ESI−, ES/voltages: capillary 3.01 KV, cone 60 V; Temperature: source 130 °C, desolvation 260 °C; Gas flow: desolvation 250 L/h, one 50 L/h; Pump flow: 60 μL/min). The mass of cyclic boronate with solvents $CH_3CN$ (535), $Et_2O$ (570), and $CH_3CN$ + $Et_2O$ (611) were observed. These peaks were not observed in the catalytic reaction. The mass of 3,3'-$Br_2$-BINOL **1** (442 + 468) was also observed.

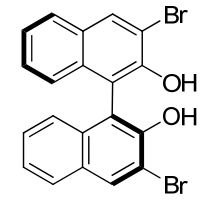
***Figure S7.*** Mass Spectra of 3,3'-$Br_2$-BINOL-derived Cyclic Allylboronate.



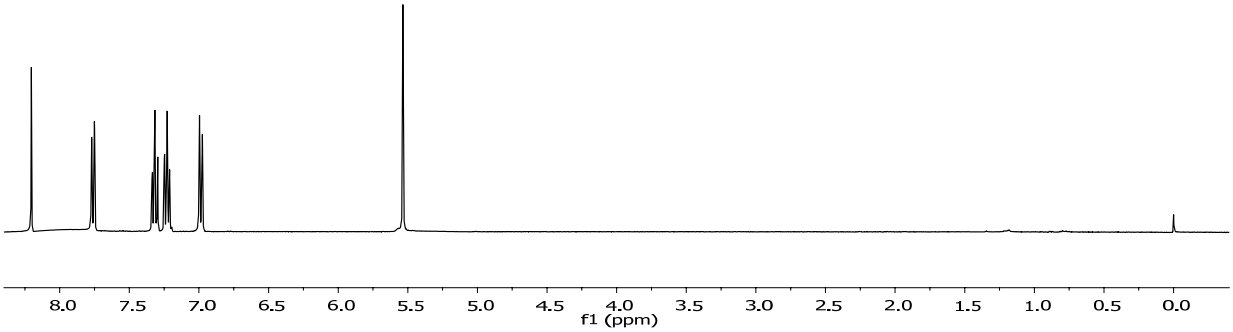

(9) T.R. Wu, L. Shen, J.M. Chong, *Org. Lett.* **2004**, *6*, 2701.

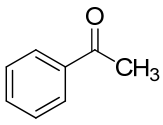
## NMR Experiments

To a NMR tube purged with Ar was added pure sample and deuterated solvent (0.75 mL) was added.

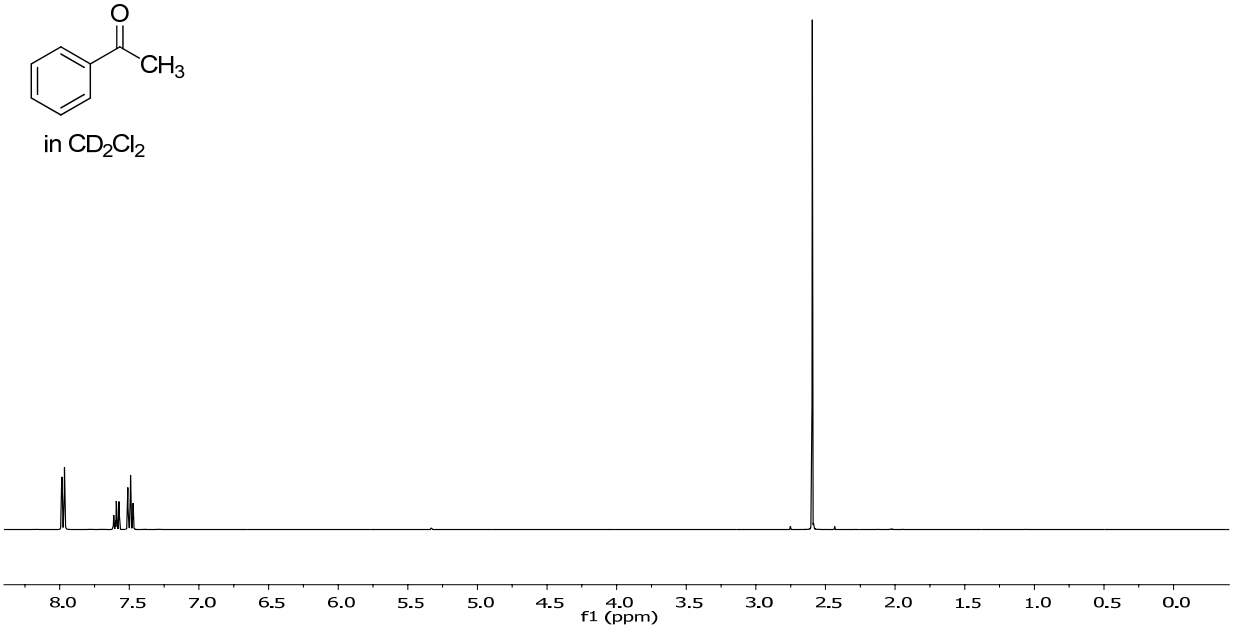


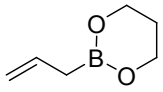

(*S*)-3,3'-$Br_2$-BINOL
in $CD_2Cl_2$



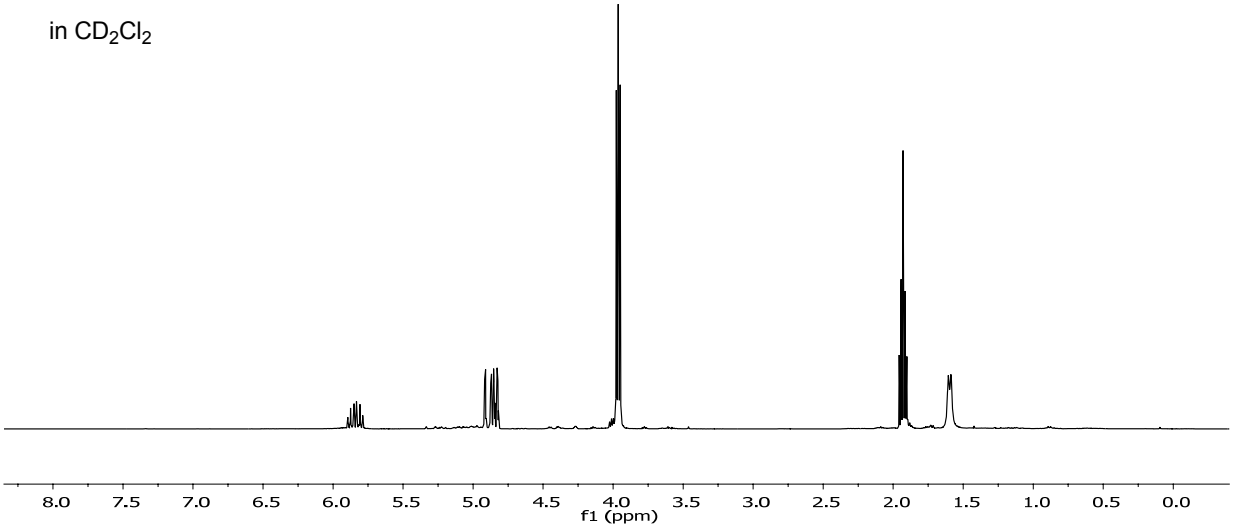



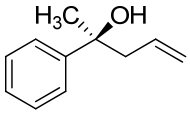

in $CD_2Cl_2$



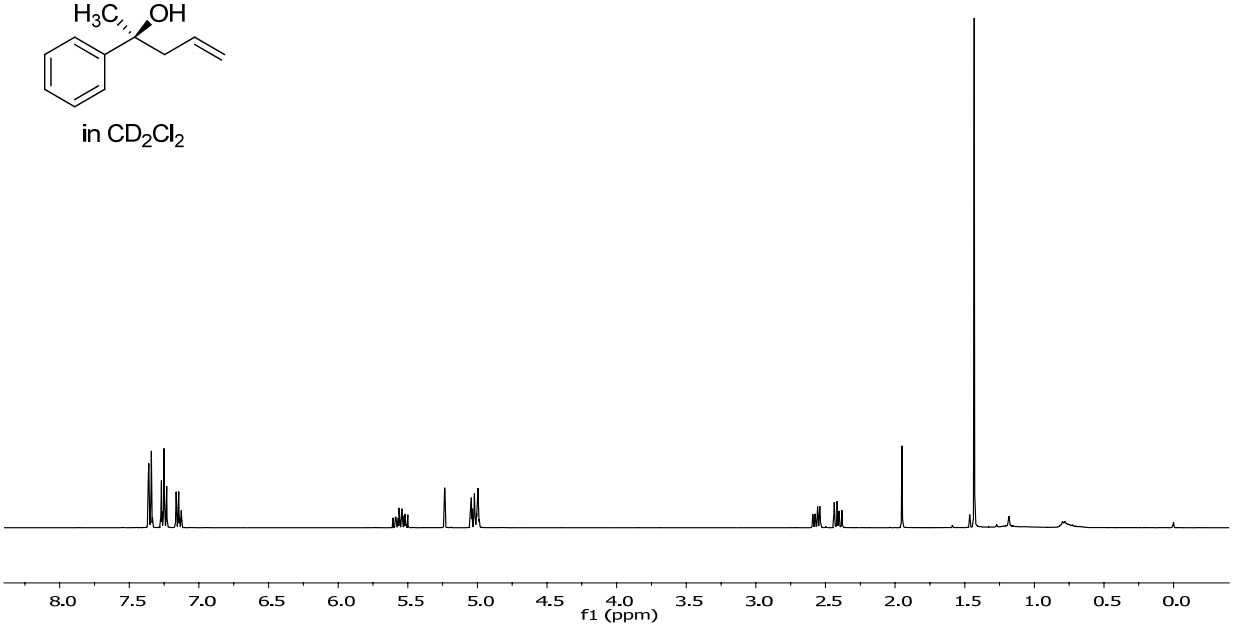



in $CD_2Cl_2$



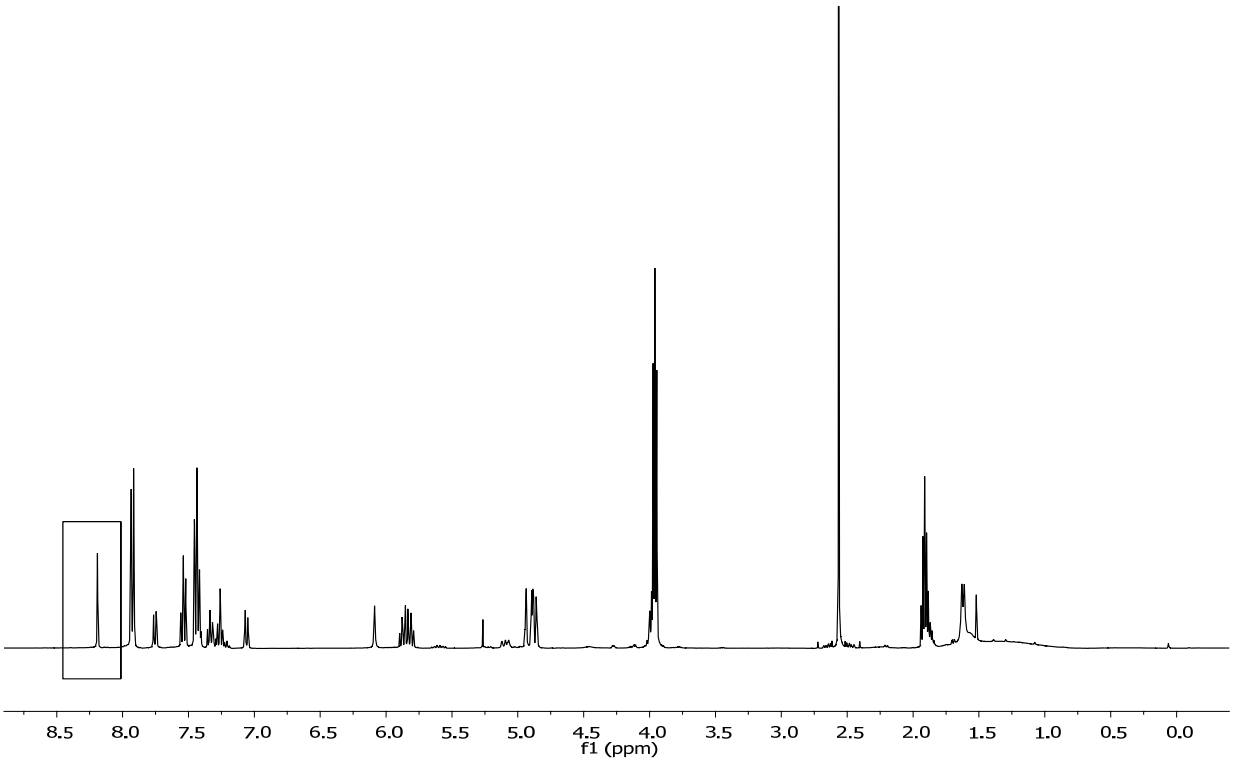

in $CD_2Cl_2$

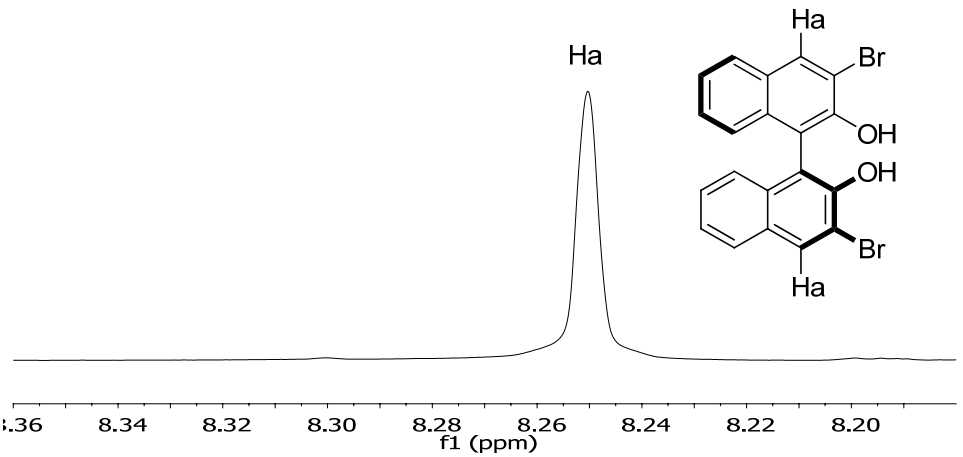


**NMR monitoring**

To a NMR tube under Ar was added 3,3'-$Br_2$-BINOL **1** (22 mg, 0.05 mmol), $CD_2Cl_2$ (0.75 mL) and *B*-allyl-1,3,2-dioxaborinane **9** (32 mg, 0.25 mmol). Next, acetophenone **8a** (30μL, 0.25 mmol) was added and a $^1$H-NMR was taken at room temperature. The reaction was monitored over the period of 24 hours under Ar. The diastereotopic peak at 8.32 ppm was assigned as Hb of **1** according the reported chemical shift of BINOL boronate.[10]

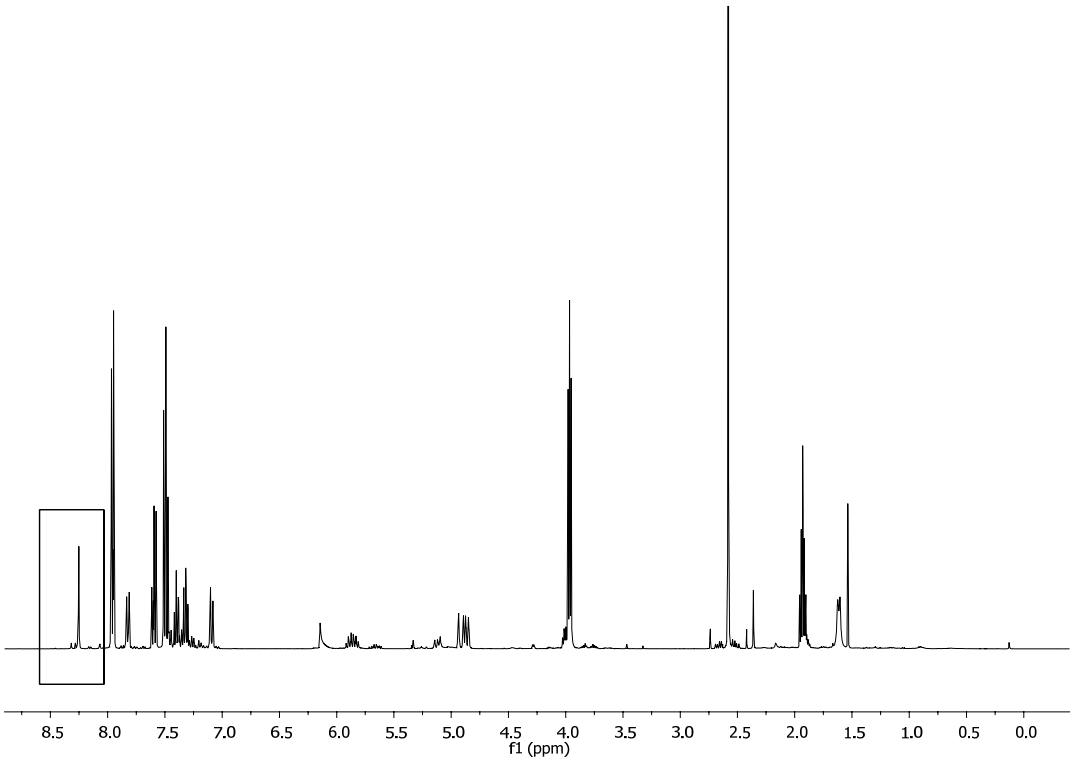
**5 Minutes**

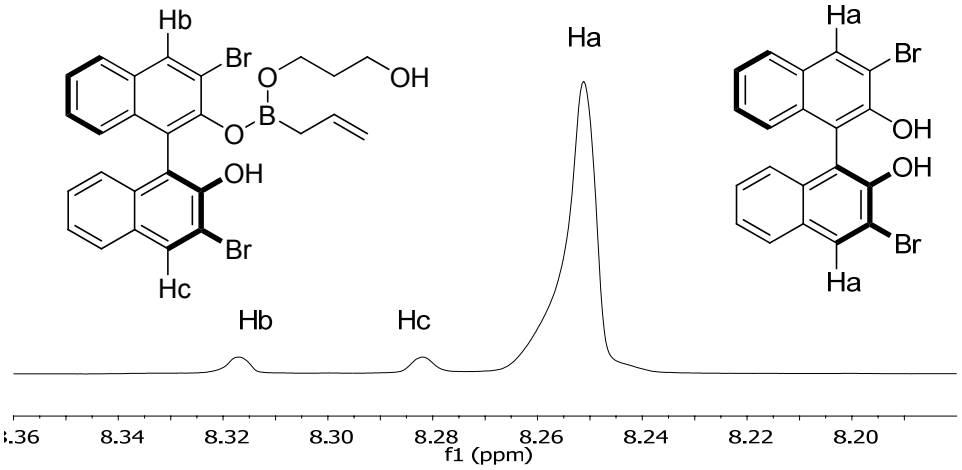


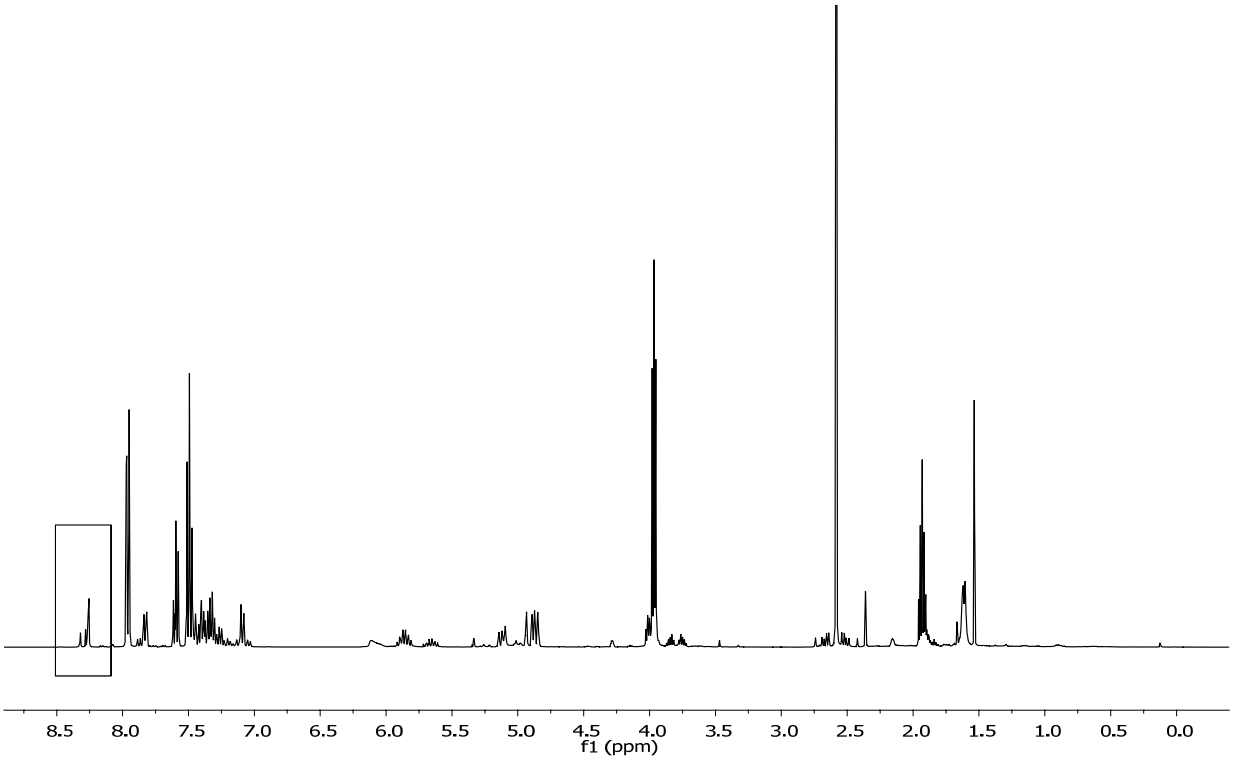

(10) S. Thormeier, B. Carboni, D.E. Kaufmann, *Journal of Organometallic Chemistry* **2002**, *657*, 136.

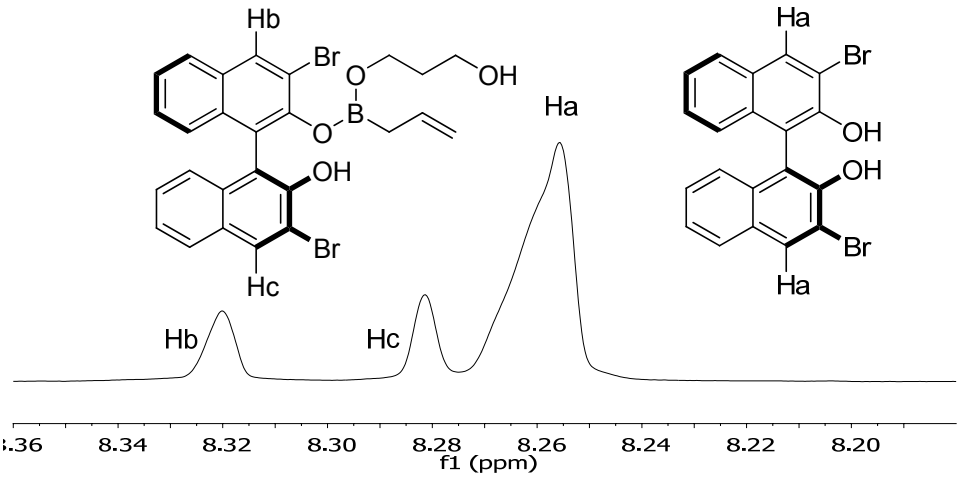
## 7 Hours


8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

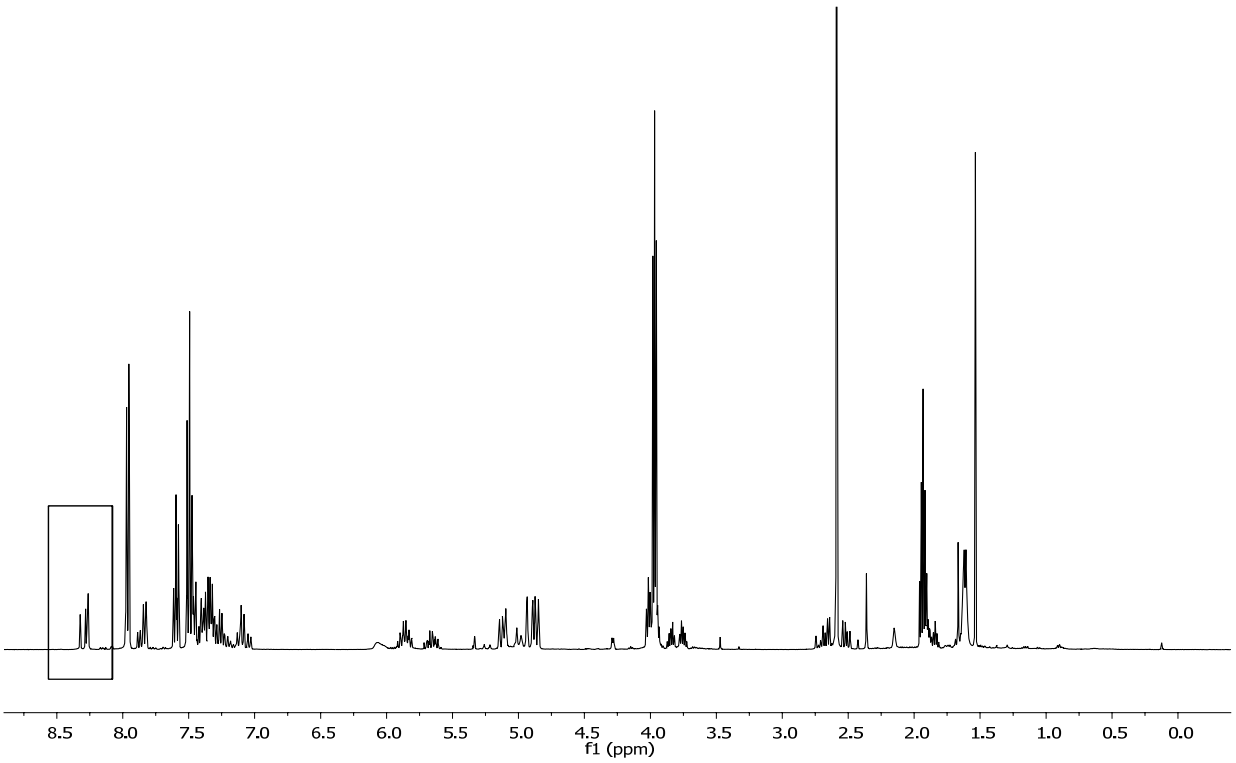

Hb
Br
O
OH
B
O
OH
Br
Hc
Ha
Br
OH
OH
Br
Ha
Hb
Hc
8.36
8.34
8.32
8.30
8.28
8.26
8.24
8.22
8.20
f1 (ppm)

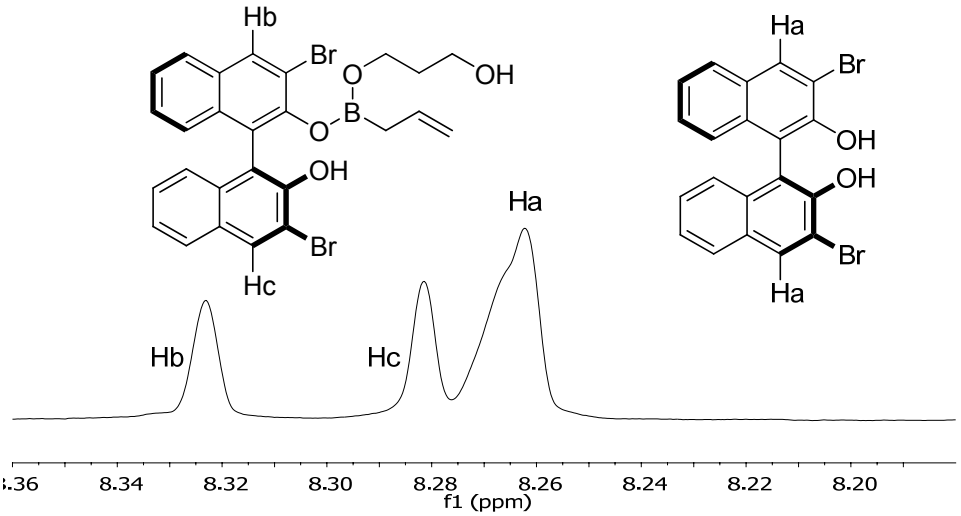
## 16 Hours


8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


Hb
Br
O
OH
B
O
OH
Br
Hc
Ha
Br
OH
OH
Br
Ha
Hb
Hc
8.36
8.34
8.32
8.30
8.28
8.26
8.24
8.22
8.20
f1 (ppm)

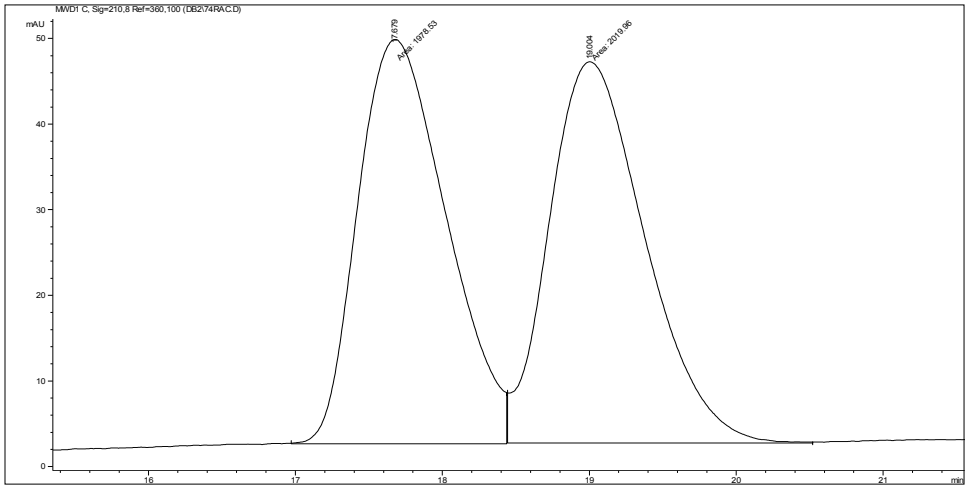
## 24 Hours


8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

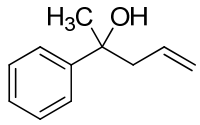

Hb
Br
O
OH
B
O
OH
Br
Hc
Ha
Br
OH
OH
Br
Ha
Hb
Hc
8.36
8.34
8.32
8.30
8.28
8.26
8.24
8.22
8.20
f1 (ppm)

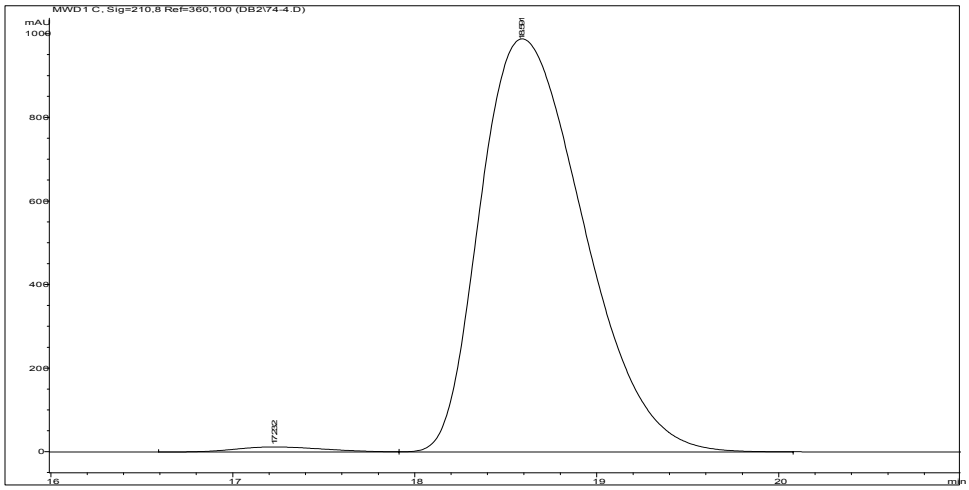
## HPLC Traces

**10a:** Chiralpak®AD-H Column, Hexane:IPA = 99:1, 0.8 mL/min, 210 nm

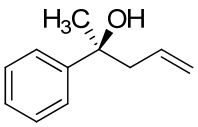



| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 17.679 | MM | 0.6978 | 1978.52942 | 47.25594 | 49.4820 |
| 2 | 19.004 | MM | 0.7558 | 2019.95581 | 44.54107 | 50.5180 |
| Totals : | | | | 3998.48523 | 91.79701 | |

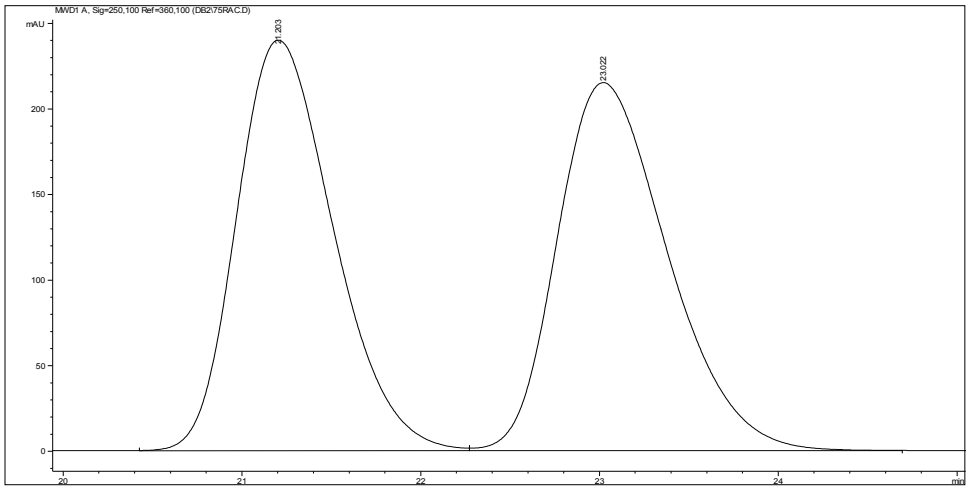


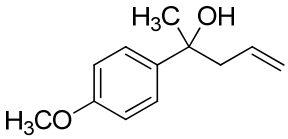

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 17.232 | PV | 0.5384 | 402.81442 | 11.91569 | 1.0216 |
| 2 | 18.591 | VB | 0.6287 | 3.90282e4 | 988.31262 | 98.9784 |
| Totals : | | | | 3.94311e4 | 1000.22831 | |

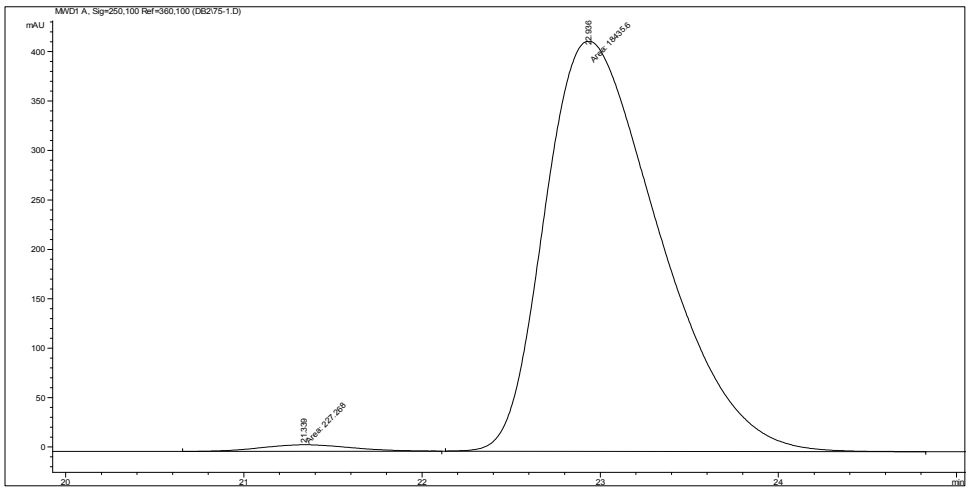


**10b:** Chiralcel®OD Column, Hexane:IPA = 99:1, 0.8 mL/min, 250 nm

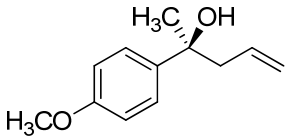



| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 21.203 | BV | 0.5830 | 9026.63574 | 239.87703 | 49.4484 |
| 2 | 23.022 | VB | 0.6686 | 9228.03809 | 215.05219 | 50.5516 |
| Totals : | | | | 1.82547e4 | 454.92921 | |

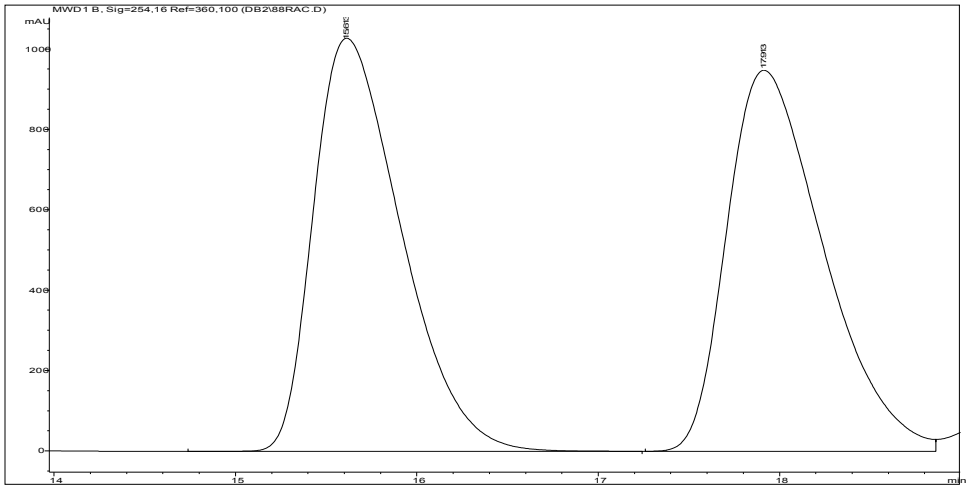


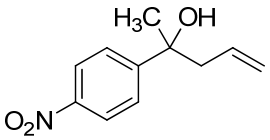

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 21.339 | MM | 0.5767 | 226.26285 | 6.53891 | 1.2125 |
| 2 | 22.936 | MM | 0.7402 | 1.84344e4 | 415.09146 | 98.7875 |
| Totals : | | | | 1.86607e4 | 421.63037 | |

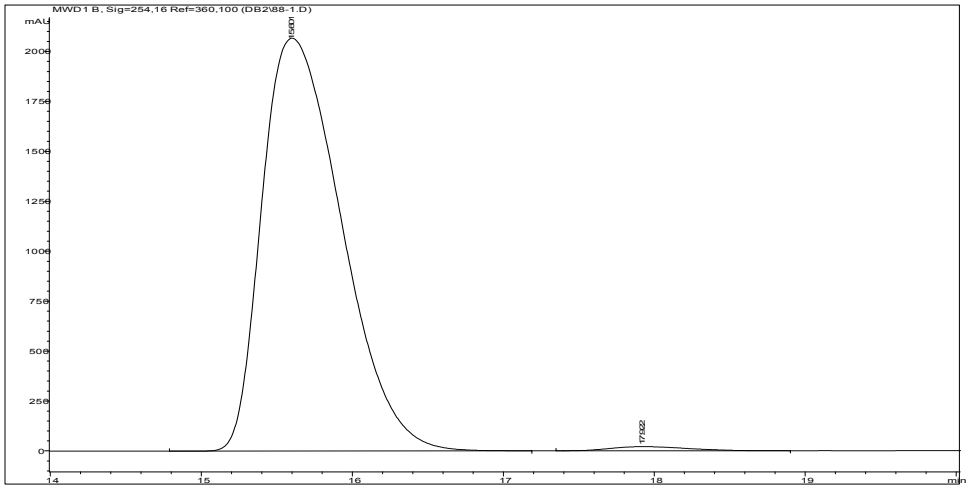


**10c:** Chiralpak® AD-H Column, Hexane:IPA = 95:5, 0.8 mL/min, 254 nm

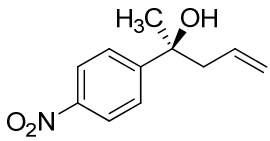



| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 15.613 | VB | 0.5239 | 3.45299e4 | 1027.96338 | 49.6345 |
| 2 | 17.913 | BV | 0.5772 | 3.50385e4 | 948.03406 | 50.3655 |
| Totals : | | | | 6.95685e4 | 1975.99744 | |

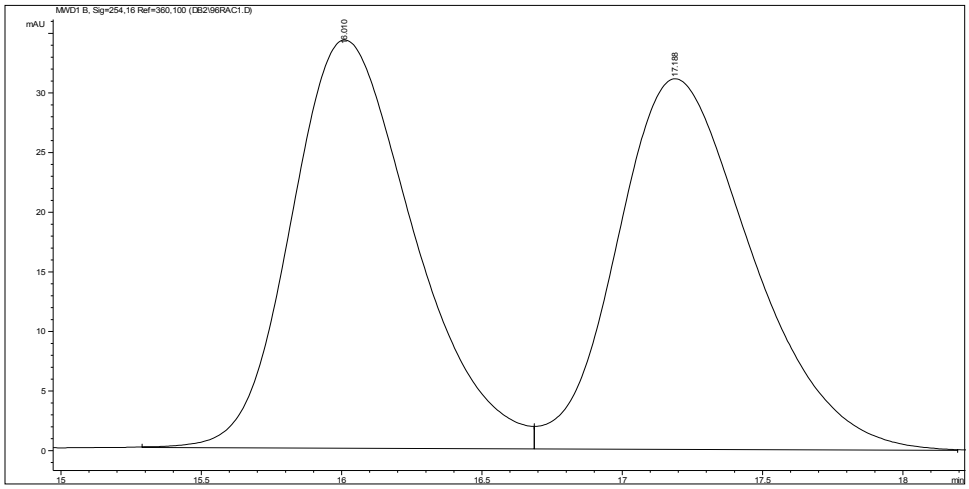


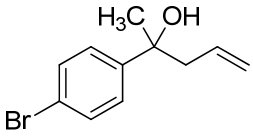

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 15.601 | BB | 0.5853 | 7.57016e4 | 2067.04858 | 99.0374 |
| 2 | 17.922 | BB | 0.5416 | 735.75769 | 20.85498 | 0.9626 |
| Totals : | | | | 7.64374e4 | 2087.90357 | |

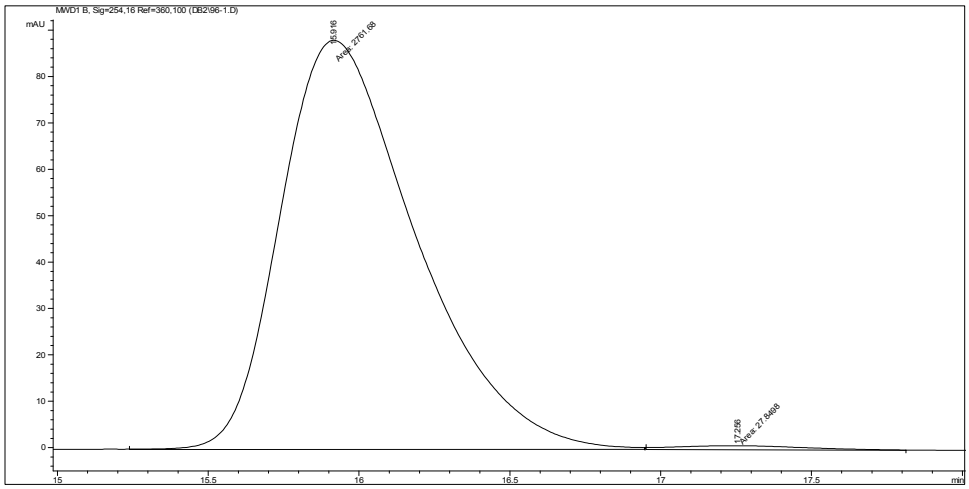


**10d:** Chiralcel®OD Column, Hexane:IPA = 99:1, 0.8 mL/min, 254nm

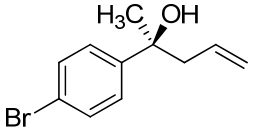



| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 16.010 | BV | 0.4720 | 1038.90027 | 34.24190 | 50.0791 |
| 2 | 17.188 | VB | 0.5068 | 1035.61816 | 31.07288 | 49.9209 |
| Totals : | | | | 2074.51843 | 65.31478 | |

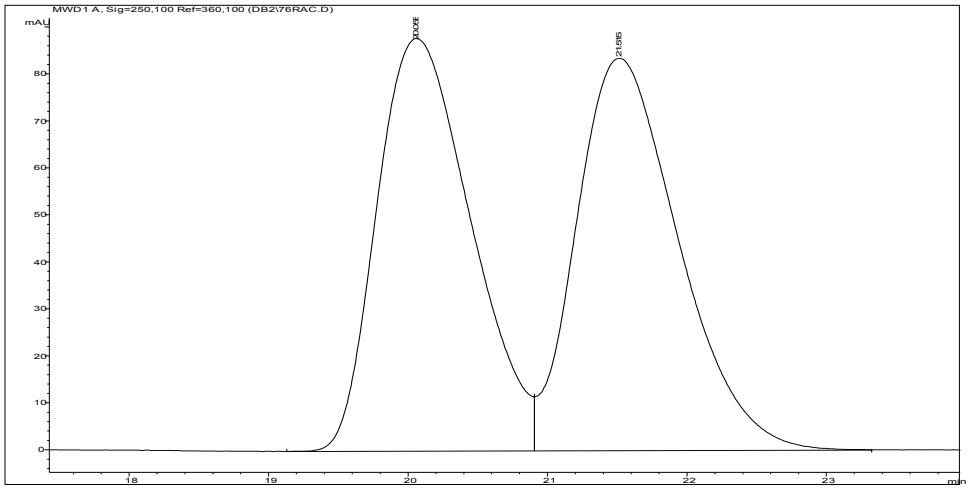


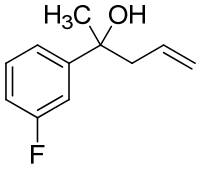

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 15.916 | MM | 0.5220 | 2761.67822 | 88.18259 | 99.0016 |
| 2 | 17.256 | MM | 0.5175 | 27.84975 | 8.96930e-1 | 0.9984 |
| Totals : | | | | 2789.52797 | 89.07952 | |

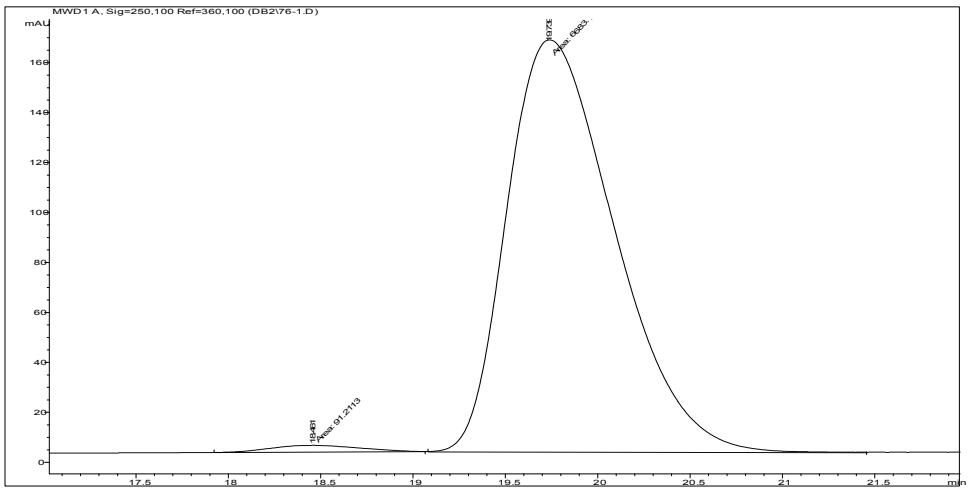


**10e:** Chiralpak® AD-H Column, Hexane:IPA = 99:1, 0.8 mL/min, 250nm

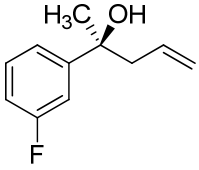



| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 20.058 | VV | 0.7238 | 4109.59766 | 87.84654 | 49.1620 |
| 2 | 21.515 | VB | 0.7818 | 4249.69580 | 83.50000 | 50.8380 |
| Totals : | | | | 8359.29346 | 171.34654 | |

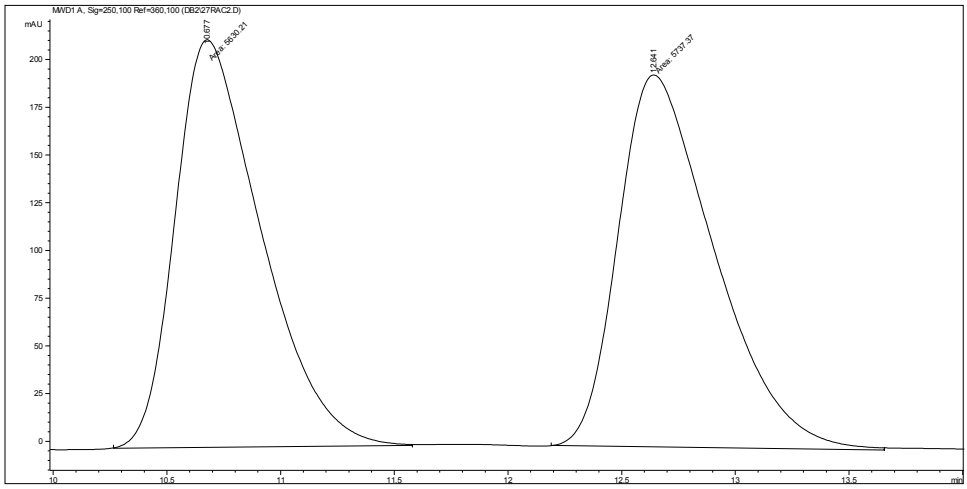


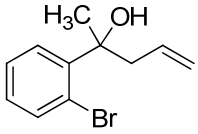

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 18.461 | MM | 0.5641 | 91.21134 | 2.69474 | 1.3464 |
| 2 | 19.739 | MM | 0.6750 | 6683.18848 | 165.01295 | 98.6536 |
| Totals : | | | | 6774.39982 | 167.70770 | |

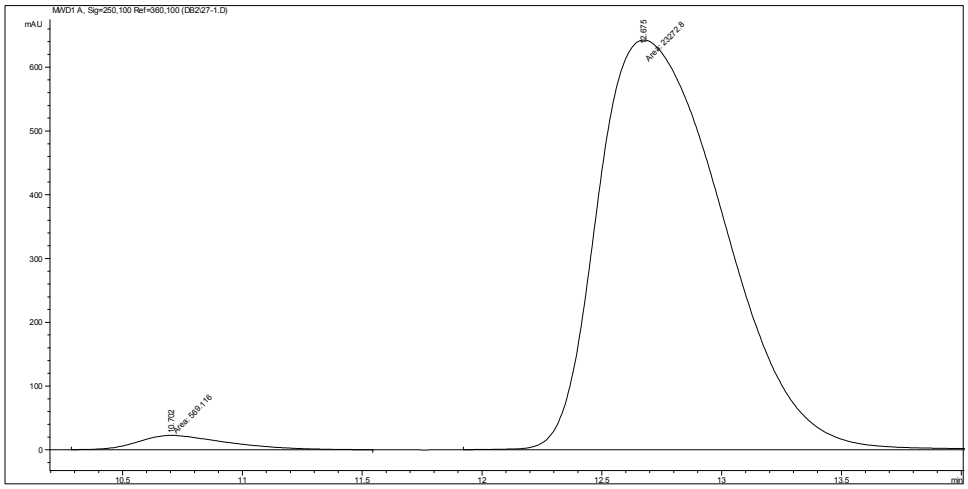


**10f:** Chiralpak®AD-H Column, Hexane:IPA = 99:1, 0.8 mL/min, 250nm

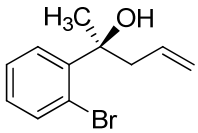



| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 10.677 | MM | 0.4393 | 5630.20703 | 213.61557 | 49.5287 |
| 2 | 12.641 | MM | 0.4910 | 5737.36719 | 194.75995 | 50.4713 |
| Totals : | | | | 1.13676e4 | 408.37552 | |

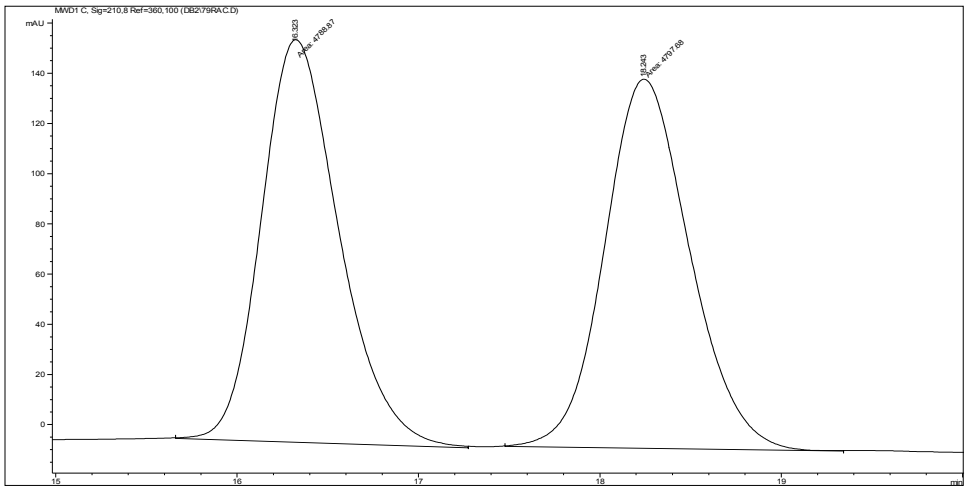


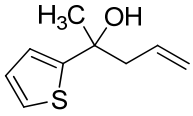

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 10.702 | MM | 0.4249 | 569.11554 | 22.32156 | 2.3870 |
| 2 | 12.675 | MM | 0.6039 | 2.32728e4 | 642.30402 | 97.6130 |
| Totals : | | | | 2.38419e4 | 664.62558 | |

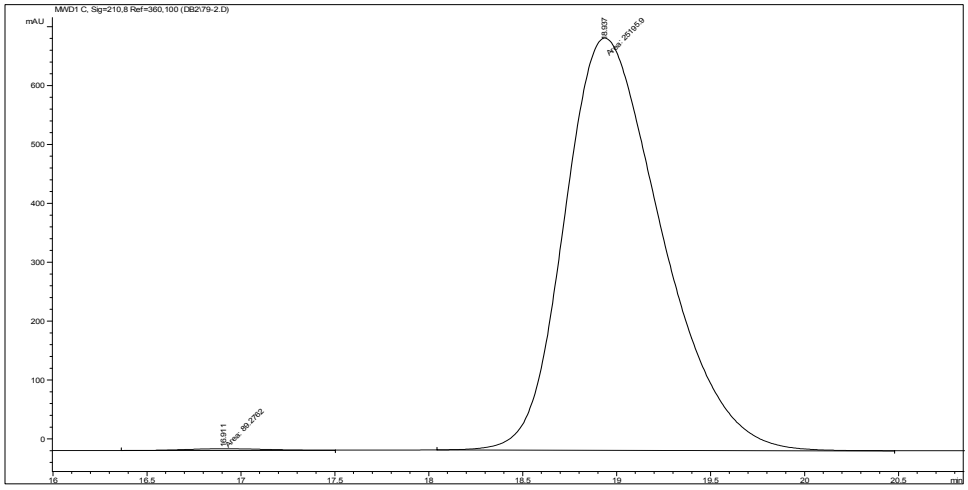


**10g:** Chiralcel®OD, Hexane:IPA = 99:1, 0.8 mL/min, 210nm

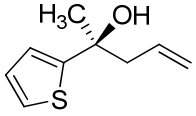



| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 16.323 | MM | 0.4974 | 4788.86865 | 160.47307 | 49.9541 |
| 2 | 18.243 | MM | 0.5436 | 4797.67529 | 147.09807 | 50.0459 |
| Totals : | | | | 9586.54395 | 307.57114 | |

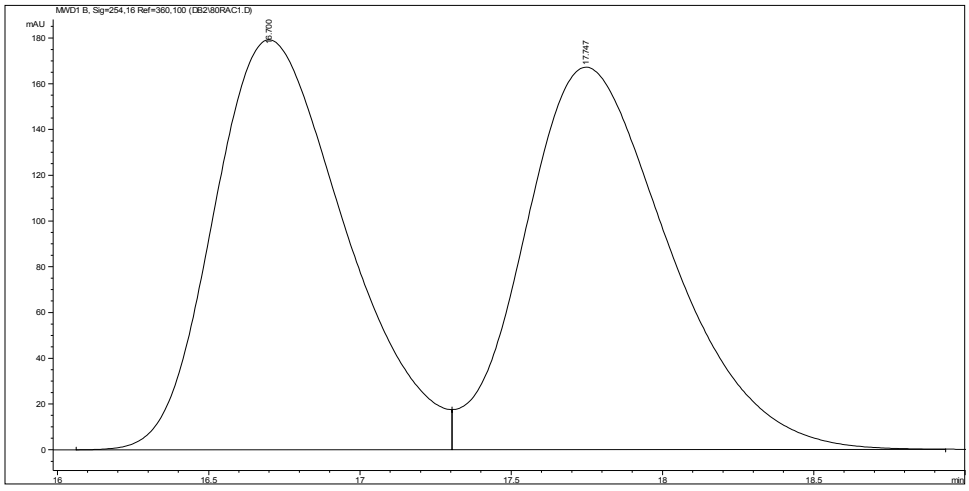


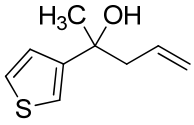

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 16.911 | MM | 0.5178 | 89.27619 | 2.87346 | 0.3531 |
| 2 | 18.937 | MM | 0.5999 | 2.51959e4 | 699.97058 | 99.6469 |
| Totals : | | | | 2.52852e4 | 702.84404 | |

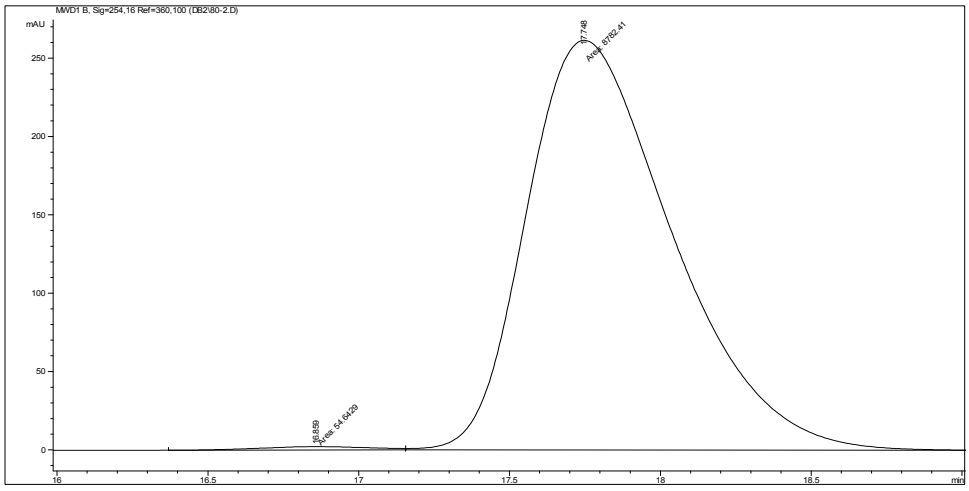


**10h:** Chiralcel®OD, Hexane:IPA = 99:1, 0.8 mL/min, 254nm

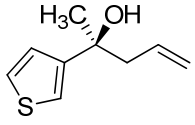



| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 16.700 | BV | 0.4635 | 5429.77441 | 179.18797 | 49.3801 |
| 2 | 17.747 | VB | 0.5125 | 5566.10938 | 167.15427 | 50.6199 |
| Totals : | | | | 1.09959e4 | 346.34224 | |

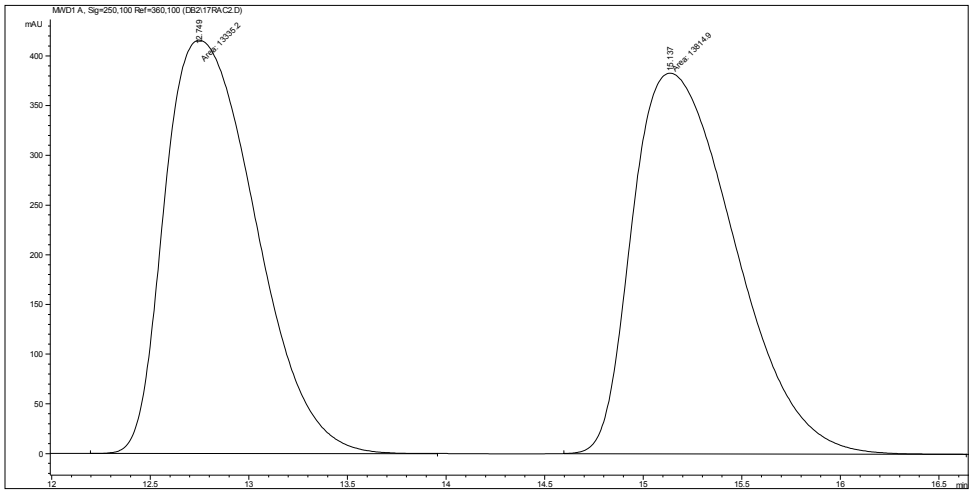


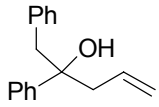

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 16.859 | MM | 0.4306 | 54.64287 | 2.11510 | 0.6183 |
| 2 | 17.748 | MM | 0.5598 | 8782.41406 | 261.46100 | 99.3817 |
| Totals : | | | | 8837.05693 | 263.57609 | |

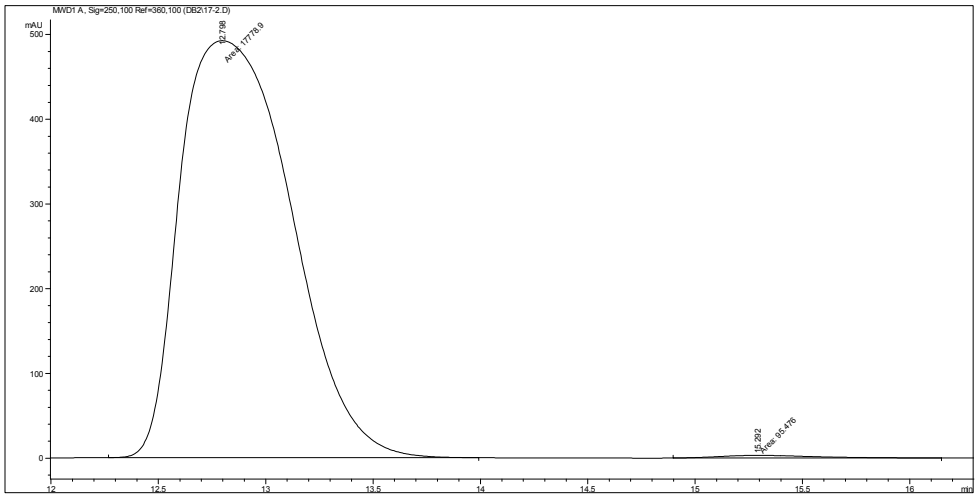


**10i:** Chiralpak®AD-H Column, Hexane:IPA = 99:1, 0.8 mL/min, 250nm

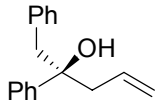



| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 12.749 | MM | 0.5343 | 1.33352e4 | 415.93607 | 49.1167 |
| 2 | 15.137 | MM | 0.6011 | 1.38149e4 | 383.01852 | 50.8833 |
| Totals : | | | | 2.71501e4 | 798.95459 | |

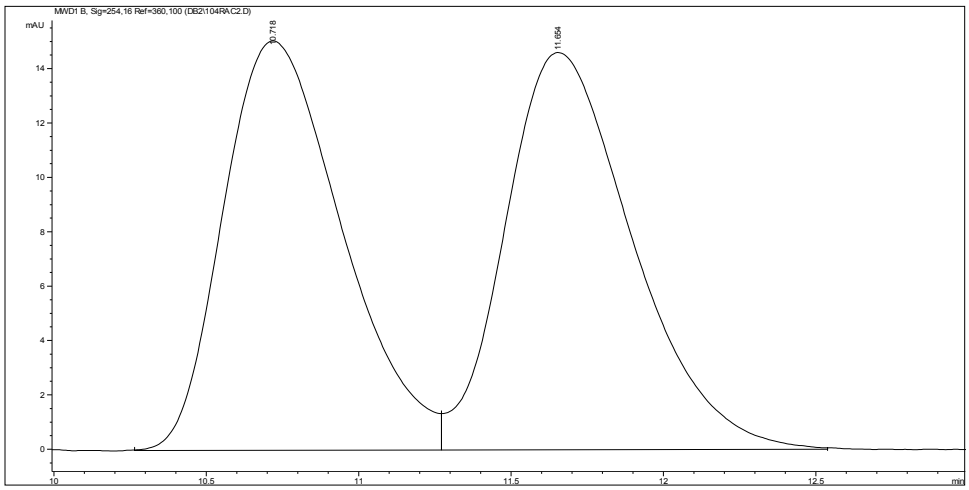


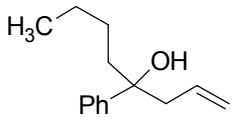

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 12.798 | MM | 0.6018 | 1.77789e4 | 492.40289 | 99.4659 |
| 2 | 15.292 | MM | 0.5120 | 95.47602 | 3.10764 | 0.5341 |
| Totals : | | | | 1.78744e4 | 495.51054 | |

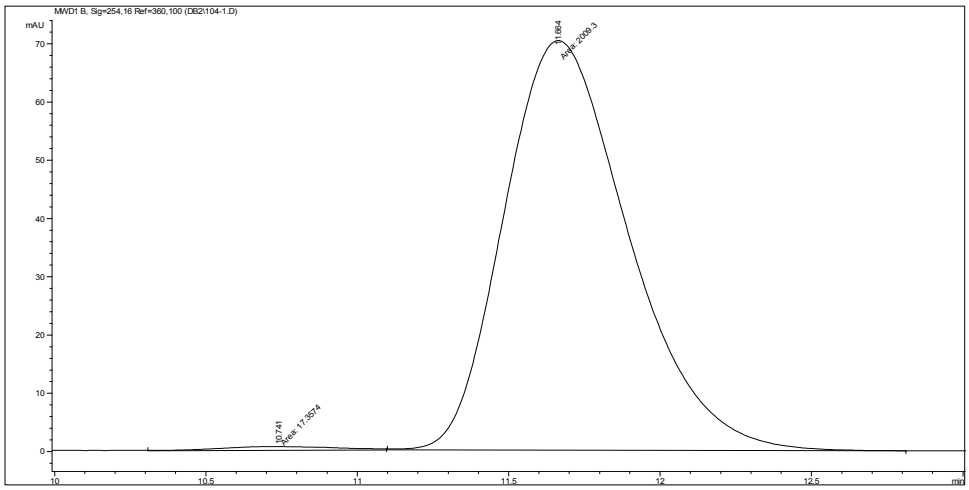


**10j:** Chiralpak® AD-H Column, Hexane:IPA = 99:1, 0.8 mL/min, 254nm

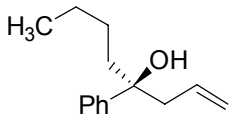



| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 10.718 | BV | 0.4199 | 407.77258 | 15.05834 | 49.0761 |
| 2 | 11.654 | VB | 0.4320 | 423.12546 | 14.60659 | 50.9239 |
| Totals : | | | | 830.89804 | 29.66493 | |

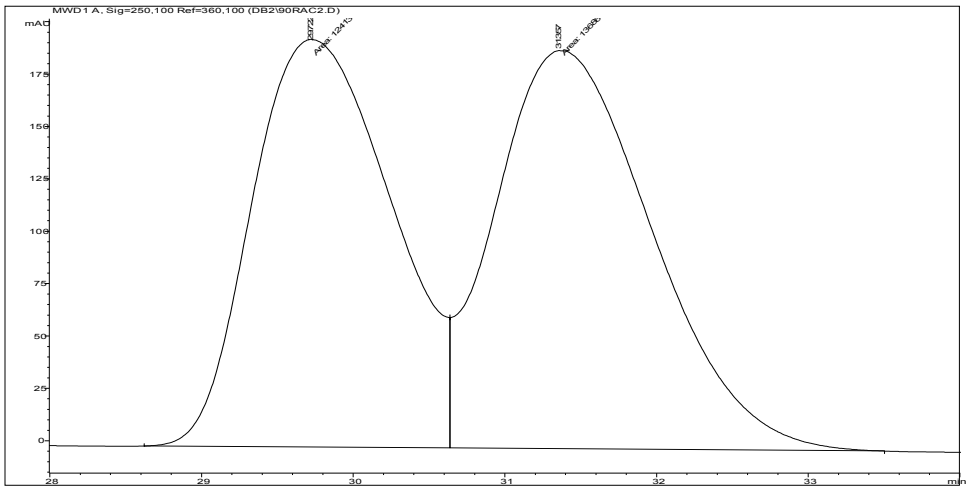


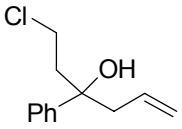

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 10.741 | MM | 0.4471 | 17.35737 | 6.47024e-1 | 0.8565 |
| 2 | 11.664 | MM | 0.4761 | 2009.29932 | 70.33856 | 99.1435 |
| Totals : | | | | 2026.65669 | 70.98559 | |

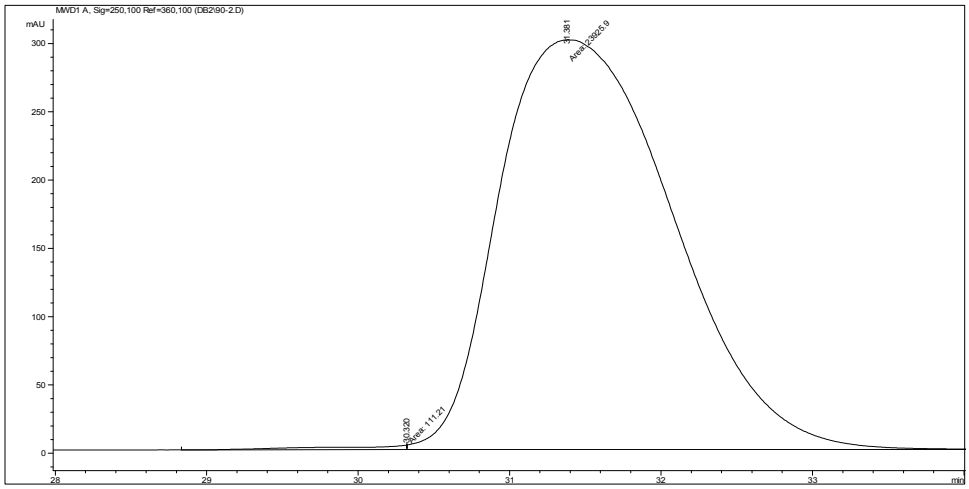


**10k:** Chiralpak®AD-H Column, Hexane:IPA = 99:1, 0.4 mL/min, 250nm

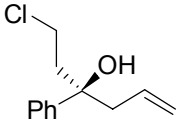



| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 29.722 | MF | 1.0752 | 1.24761e4 | 193.38486 | 49.2659 |
| 2 | 31.357 | FM | 1.1493 | 1.28479e4 | 186.32133 | 50.7341 |
| Totals : | | | | 2.53240e4 | 379.70619 | |

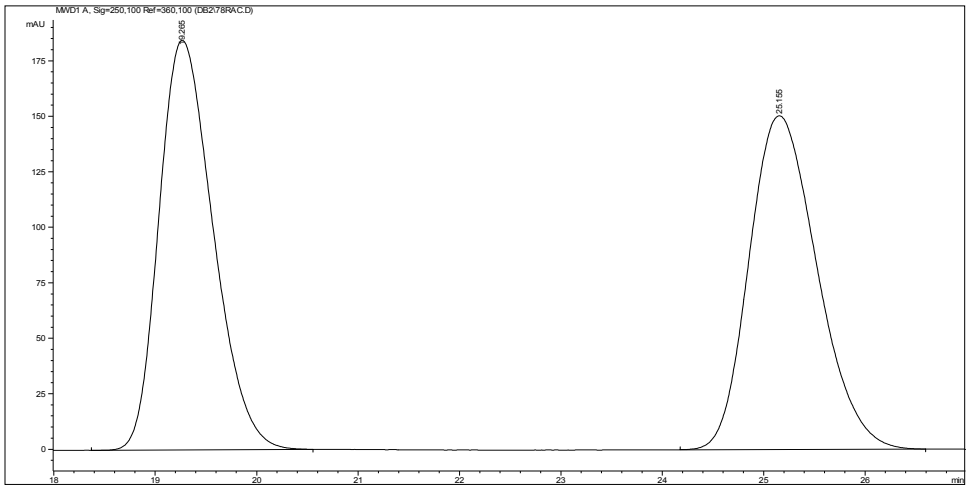


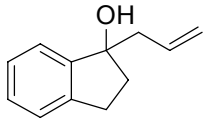

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 30.320 | MM | 0.5499 | 111.20968 | 3.37083 | 0.4627 |
| 2 | 31.381 | MM | 1.3290 | 2.39259e4 | 300.05157 | 99.5373 |
| Totals : | | | | 2.40371e4 | 303.42240 | |

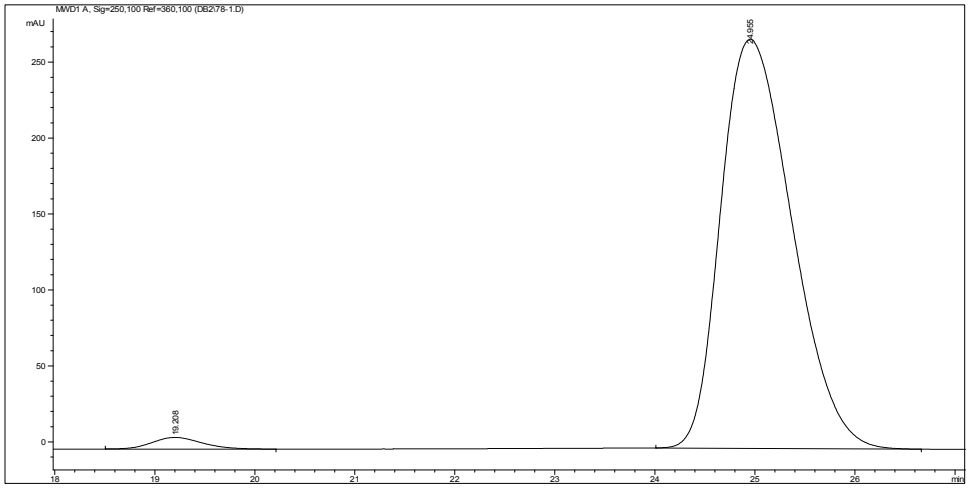


**10l:** Chiralpak®OD Column, Hexane:IPA = 99:1, 0.8 mL/min, 250nm

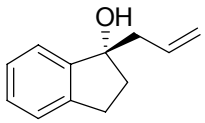



| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 19.265 | VB | 0.5604 | 6838.38428 | 184.52217 | 49.4163 |
| 2 | 25.155 | BB | 0.6952 | 6999.92285 | 150.35075 | 50.5837 |
| Totals : | | | | 1.38383e4 | 334.87292 | |

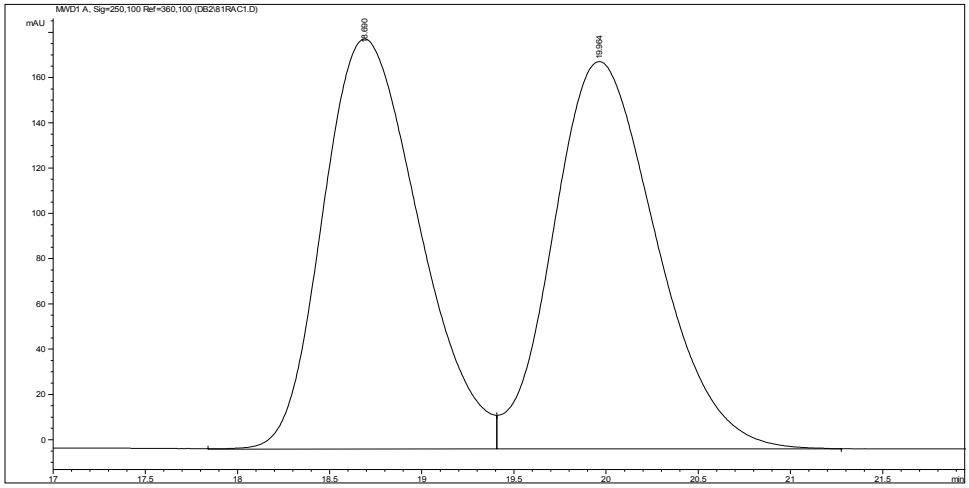


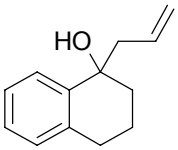

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 19.208 | BB | 0.4687 | 267.53940 | 7.67380 | 1.9689 |
| 2 | 24.955 | BB | 0.7569 | 1.33204e4 | 269.36179 | 98.0311 |
| Totals : | | | | 1.35879e4 | 277.03558 | |

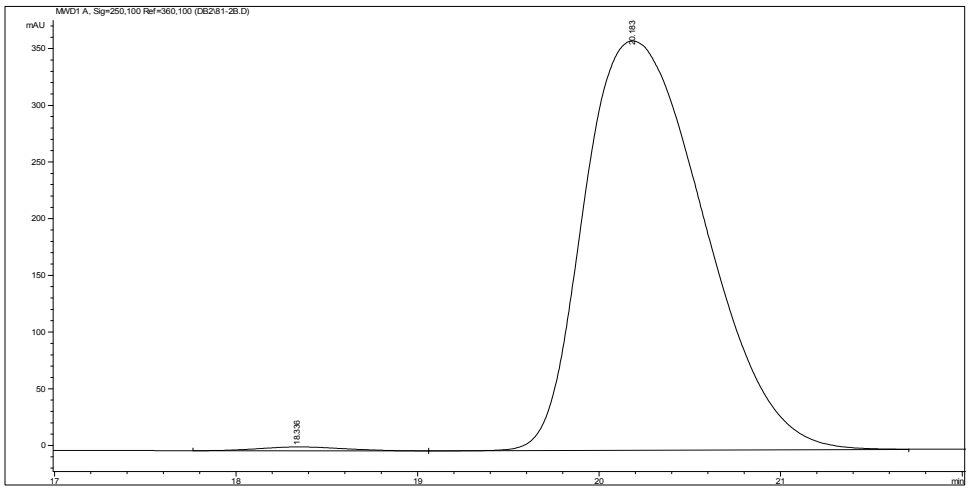


**10m:** Chiralpak®OD Column, Hexane:IPA = 99:1, 0.8 mL/min, 250nm

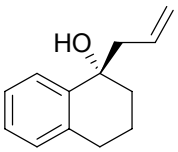



| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 18.690 | VV | 0.5693 | 6575.35693 | 181.23114 | 49.6674 |
| 2 | 19.964 | VB | 0.5963 | 6663.41846 | 171.12703 | 50.3326 |
| Totals : | | | | 1.32388e4 | 352.35817 | |

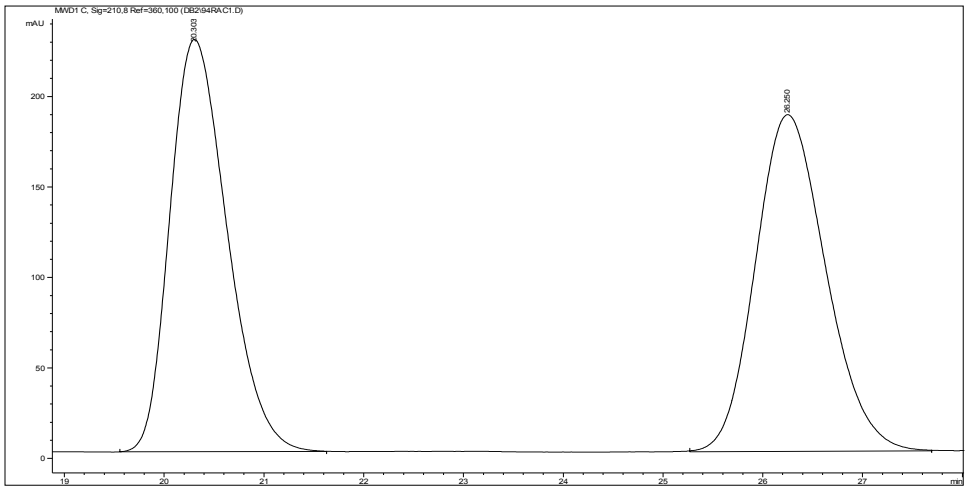


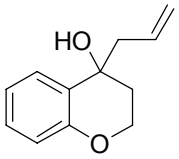

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 18.336 | PP | 0.3912 | 108.91599 | 3.36888 | 0.6542 |
| 2 | 20.183 | VB | 0.7063 | 1.65390e4 | 361.13638 | 99.3458 |
| Totals : | | | | 1.66479e4 | 364.50526 | |

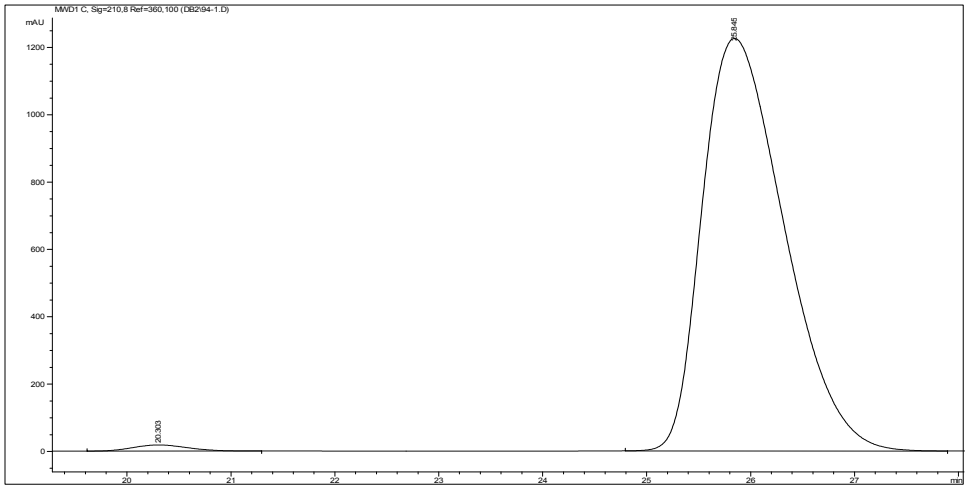


**10n:** Chiralpak®OD Column, Hexane:IPA = 99:1, 0.8 mL/min, 210nm

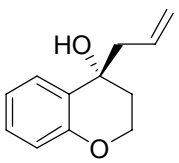



| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 20.303 | BB | 0.6248 | 9074.43359 | 227.76233 | 49.8860 |
| 2 | 26.250 | BB | 0.7637 | 9115.92090 | 186.04440 | 50.1140 |
| Totals : | | | | 1.81904e4 | 413.80673 | |

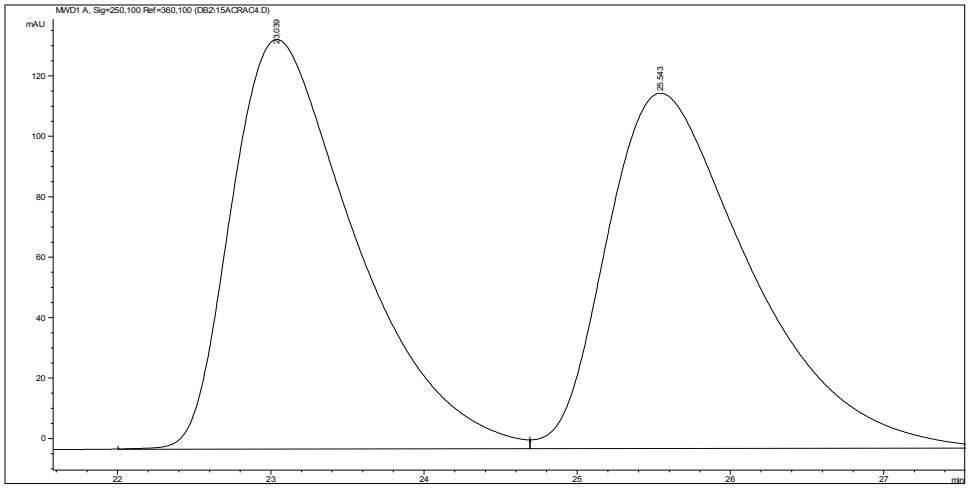


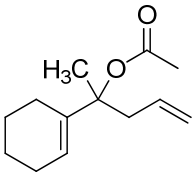

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 20.303 | BB | 0.5733 | 678.29822 | 18.26407 | 1.0006 |
| 2 | 25.845 | BB | 0.8709 | 6.71106e4 | 1225.48621 | 98.9994 |
| Totals : | | | | 6.77889e4 | 1243.75027 | |

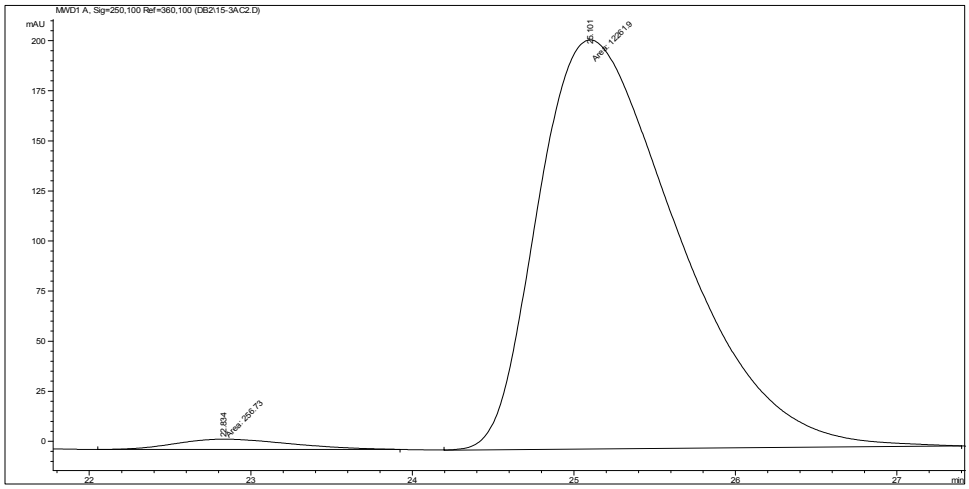


**10o:** Chiralpak®AD-H Column, Hexane:IPA = 99:1, 1.0 mL/min, 250nm

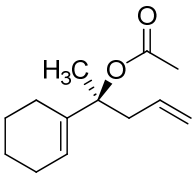



| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 23.039 | BV | 0.8488 | 7652.02832 | 135.51636 | 49.9836 |
| 2 | 25.543 | VB | 0.9878 | 7657.03467 | 117.57721 | 50.0164 |
| Totals : | | | | 1.53091e4 | 253.09357 | |

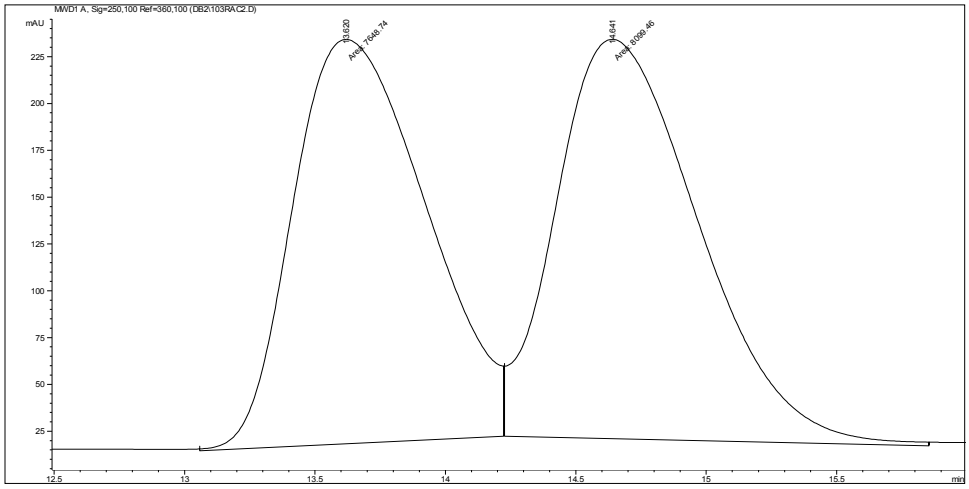


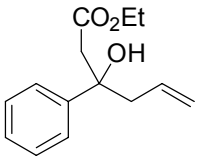

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 22.834 | MM | 0.8291 | 256.72968 | 5.16051 | 2.0140 |
| 2 | 25.101 | MM | 1.0166 | 1.24908e4 | 204.77568 | 97.9860 |
| Totals : | | | | 1.27475e4 | 209.93619 | |

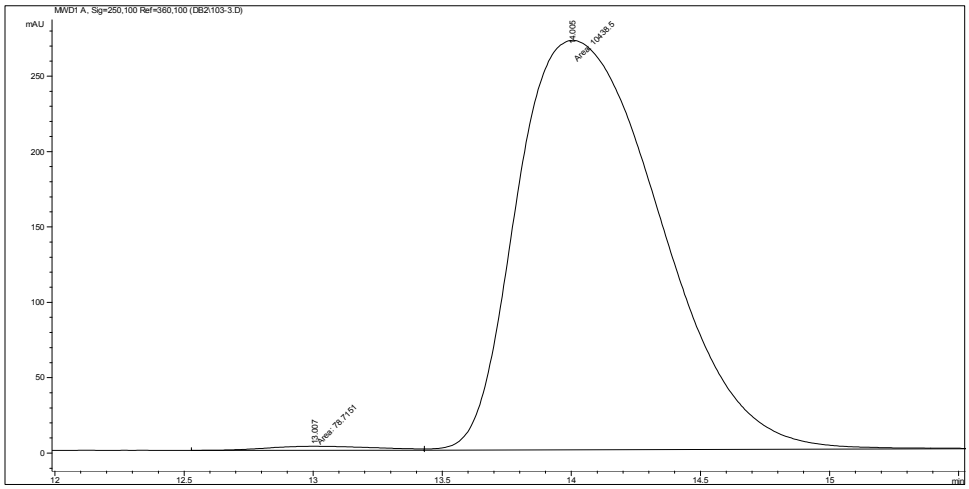


**10p:** Chiralpak®AD-H Column, Hexane:IPA = 99:1, 0.8 mL/min, 250nm

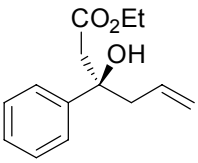



| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 13.620 | MM | 0.5903 | 7648.73584 | 215.96608 | 48.5690 |
| 2 | 14.641 | MM | 0.6332 | 8099.46289 | 213.19003 | 51.4310 |
| Totals : | | | | 1.57482e4 | 429.15611 | |

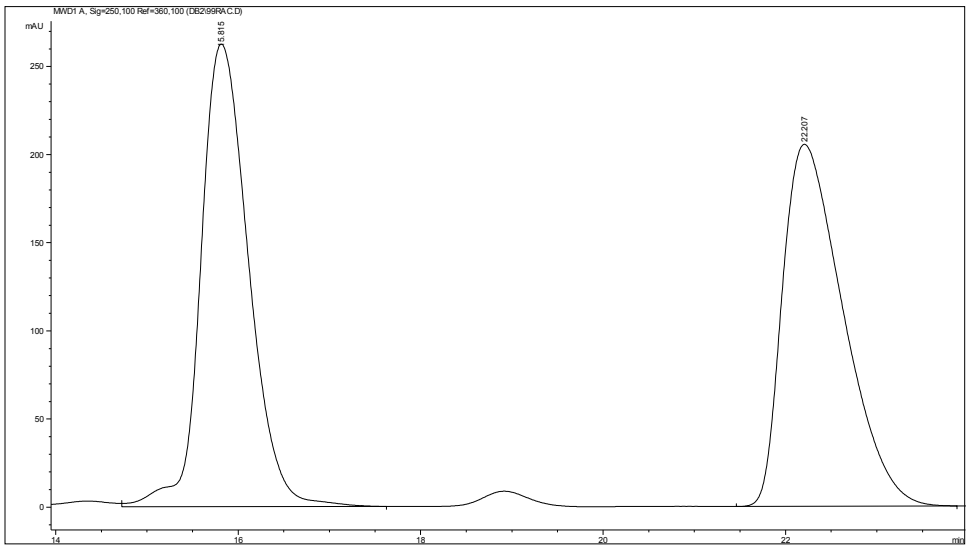


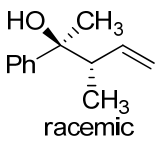

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 13.007 | MM | 0.4946 | 78.71515 | 2.65245 | 0.7484 |
| 2 | 14.005 | MM | 0.6405 | 1.04385e4 | 271.63736 | 99.2516 |
| Totals : | | | | 1.05172e4 | 274.28981 | |



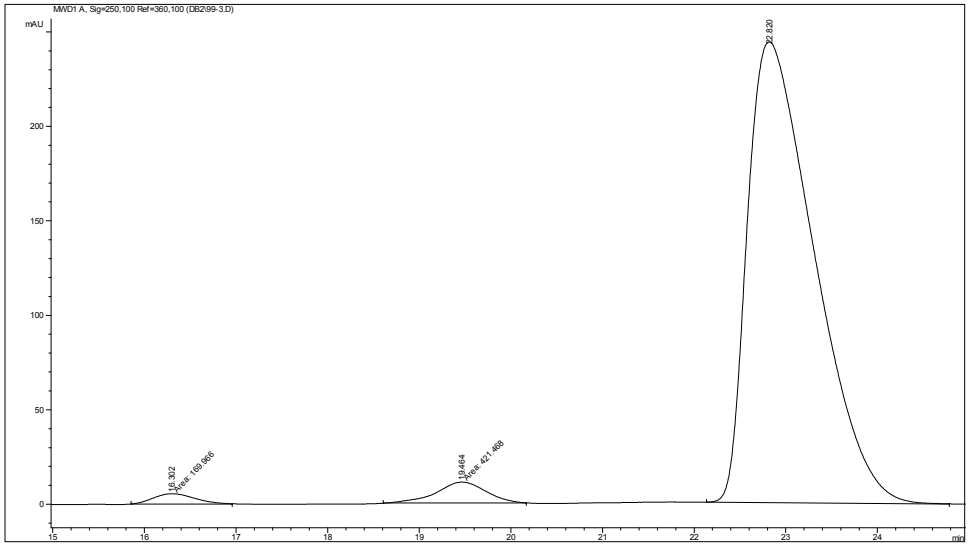
**12a:** Chiralpak®OD Column, Hexane:IPA = 99.5:0.5, 0.8 mL/min, 250 nm



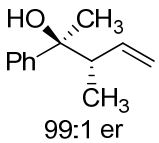

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 15.815 | VB | 0.5640 | 9535.73145 | 262.38782 | 50.1427 |
| 2 | 22.207 | PB | 0.6924 | 9481.43750 | 205.43855 | 49.8573 |
| Totals : | | | | 1.90172e4 | 467.82637 | |



racemic

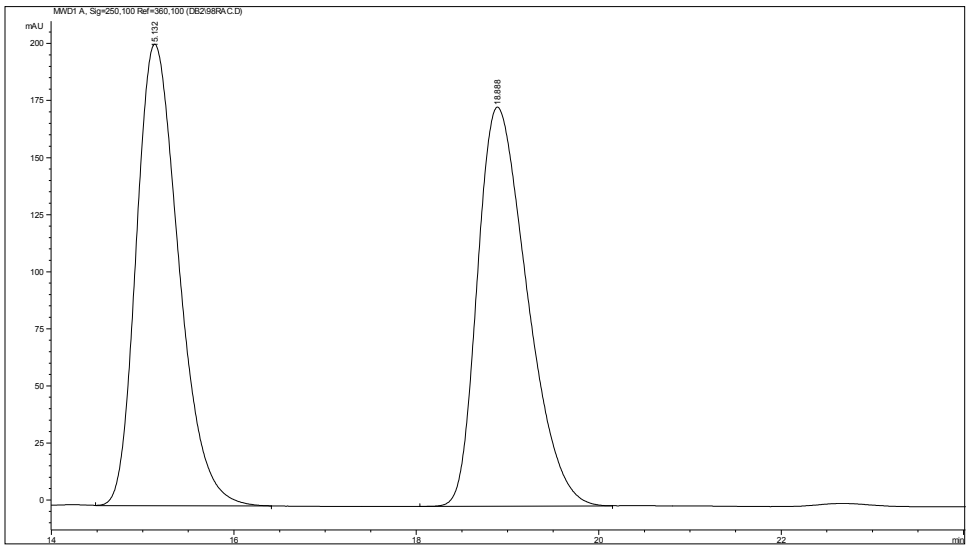



| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 16.302 | MM | 0.5181 | 169.96648 | 5.46769 | 1.3161 |
| 2 | 19.464 | MM | 0.6320 | 421.46799 | 11.11425 | 3.2635 |
| 3 | 22.820 | BB | 0.6955 | 1.23233e4 | 243.86955 | 95.4205 |
| Totals : | | | | 1.29147e4 | 260.45149 | |

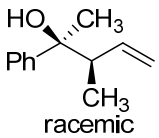


99:1 er
97:3 dr

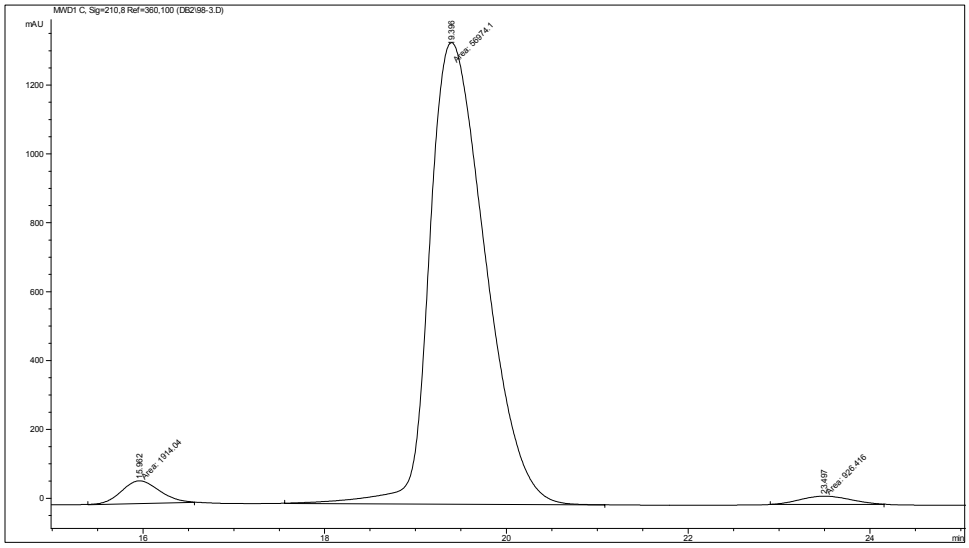
**12b:** Chiralpak®OD Column, Hexane:IPA = 99.5:0.5, 0.8 mL/min, 250 nm



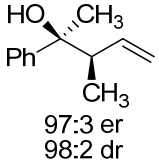

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 15.132 | VB | 0.5069 | 6533.34424 | 202.24631 | 49.7848 |
| 2 | 18.888 | PB | 0.5817 | 6589.83789 | 174.84607 | 50.2152 |
| Totals : | | | | 1.31232e4 | 377.09238 | |



racemic




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 15.966 | MM | 0.4883 | 376.77859 | 12.86080 | 3.2731 |
| 2 | 19.398 | MM | 0.7203 | 1.09423e4 | 253.19804 | 95.0569 |
| 3 | 23.495 | MM | 0.6606 | 192.23553 | 4.84996 | 1.6700 |
| Totals : | | | | 1.15113e4 | 270.90880 | |



97:3 er
98:2 dr