Enantioselective Synthesis of Allylboronates Bearing Tertiary or Quaternary B-Stereogenic Carbon by NHC-Cu-Catalyzed Substitution Reactions

Aikomari Guzman-Martinez and Amir H. Hoveyda*

Department of Chemistry, Merkert Chemistry Center,
Boston College, Chestnut Hill, Massachusetts 02467

SUPPORTING INFORMATION, PART I

List of Contents

General. Infrared (IR) spectra were recorded on a Bruker FTIR Alpha (ATR mode) spectrophotometer, ν_{max} in cm^{-1}. Bands are characterized as broad (br), strong (s), medium (m), and weak (w). ^{1}H NMR spectra were recorded on a Varian Unity INOVA 400 (400 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), and coupling constants (Hz). ^{13}C NMR spectra were recorded on a Varian Unity INOVA 400 (100 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: 77.16 ppm). High resolution mass spectrometry was performed on a JEOL AccuTOF-DART (positive mode) at the Mass Spectrometry Facility, Boston College. Enantiomer ratios were determined by GLC analysis [Alltech Associated Chiraldex CDB/DM column (30m x 0.25 mm), Betadex 120 column (30 m x 0.25 mm), and Alphadex 120 column (30 m x 0.25 mm)] in comparison with authentic racemic materials. The inlet and detector temperatures are set to 250 °C and runs were isothermal of the temperature given using ultra high purity helium as the carrier gas. Other enantiomer ratios were determined by high performance liquid chromatography (HPLC) with a Shimadzu chromatograph [Chiral Technologies Chiralcel OD-H (4.6 x 250 mm)] in comparison with authentic racemic materials. Specific rotations were measured on a Rudolph Research Analytical Autopol IV Polarimeter. Unless otherwise noted, all reactions were carried out with distilled and degassed solvents under an atmosphere of dry N_2 in oven- (135 ºC) or flame-dried glassware with standard dry box or vacuum-line techniques. 1,2-Dimethoxyethane (Aldrich Chemical Co.) was purified by distillation from sodium benzophenone ketal immediately prior to use. Dichloromethane (Fisher Scientific) was purified by being passed through two alumina columns under a positive pressure of dry argon by a modified Innovative Technologies purification system. Tetrahydrofuran (Aldrich Chemical Co.) was purified by distillation from sodium benzophenone ketal immediately prior to use unless otherwise specified. All work-up and purification procedures were carried out with reagent grade solvents (purchased from Doe & Ingalls) under air.

Reagents and Ligands:

Benzoyl Chloride: purchased from Aldrich Chemical Co. and used as received.

Bis(pinacolato)diboron (1): gifted from Frontier Scientific, Inc., dried overnight in vacuo.

***tert*-Butyldimethylsilyl chloride:** purchased from Aldrich Chemical Co. and used as received.

***meta*-Chloroperoxybenzoic acid:** purchased from Aldrich Chemical Co. and used as received.

Copper (II) triflate (98%)**:** purchased from Aldrich Chemical Co. and used as received.

Copper salts (for copper screening)**:** purchased from Strem and used as received.

4-Dimethylaminopyridine: purchased from Aldrich Chemical Co. and used as received.

***N,N*-Dimethylforamide** (99.8%, Acroseal)**:** was purchased from Acros was used as received.

Hydrogen peroxide (35 wt. % solution in water)**:** purchased from Aldrich Chemical Co. and used as received.

Imidazole: was purchased from Aldrich and used as received.

Imidazolinium salt (2): prepared according to previously reported procedures.[1]

Imidazolinium salt (3): prepared according to previously reported procedures.[2]

Imidazolinium salt (4a-b): prepared according to previously reported procedures.[3]

Imidazolinium salt (5a-c): prepared according to previously reported procedures.[4] *(opposite enantiomers to what is shown in publication)*

Imidazolinium salt (6,7): prepared according to previously reported procedures.[5]

Periodic acid: purchased from Aldrich Chemical Co. and used as received.

Pyridine (anhydrous): purchased from Aldrich Chemical Co. and used as received.

Sodium borohydride: purchased from Aldrich Chemical Co. and used as received.

Sodium *tert*-butoxide (98%)**:** purchased from Strem Chemicals Inc. and used as received.

Sodium hydride (60% in mineral oil)**:** purchased from Strem Chemicals Inc. and used as received.

Sodium methoxide (98%)**:** purchased from Strem Chemicals Inc. and used as received.

---

(1) Van Veldhuizen, J. J.; Campbell, J. E. ; Giudici, R. E.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2005**, *127*, 6877–6882.

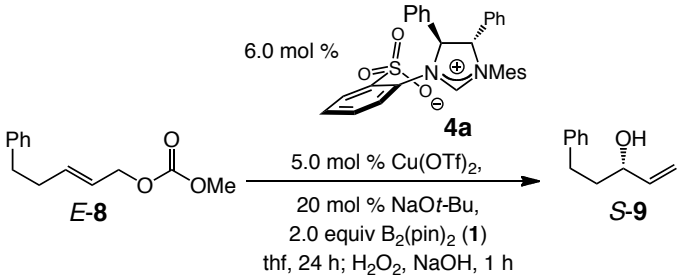
(2) Clavier, H.; Coutable, L.; Toupet, L.; Guillemin, J.-C.; Mauduit, M. *J. Organometallic Chem.* **2005**, *690*, 5237–5254.

(3) Brown, M. K.; May, T. L.; Baxter, C. A.; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2007**, *46*, 1097–1100.

(4) (a) Lee, Y.; Akiyama, K.; Gillingham, D. G.; Brown, M. K.; Hoveyda A. H. *J. Am. Chem. Soc.* **2008***, 130,* 446–447. (b) Akiyama, K.; Gao, F.; Hoveyda, A. H. *Angew. Chem., Int. Ed.* **2010**, *49*, 419–423.

(5) Lee, K.-s.; Hoveyda, A. H. *J. Org. Chem*. **2009**, *74*, 4455–4462.

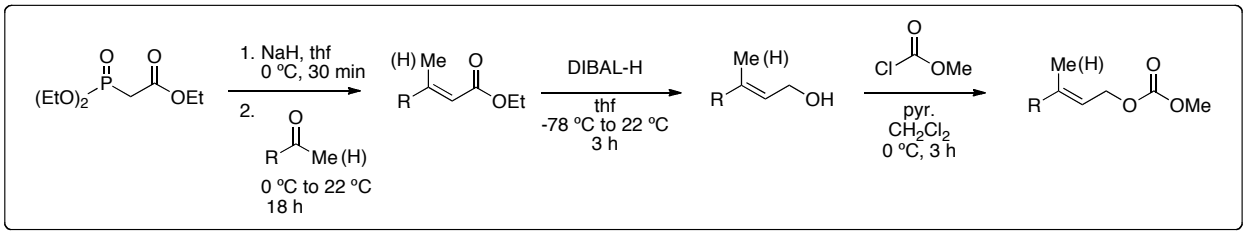
Table 1. Evaluation of Cu Salts[a]



entry	Cu salt	temp (°C)	conv (%)[b]	yield (%)[c]	er[d]
1	CuCl	22	75	70	77:23
2	CuBr	22	41	40	78:22
3	CuI	22	23	21	81:19
4	$(CuOTf)_2$•tol	22	>98	72	72:28
5	CuTC	22	>98	97	76:24
6	CuTC	–30	43	41	80:20
7	CuCN	22	42	38	77:23
8	CuOAc	22	70	54	69:31
9	$CuCl_2$•$2H_2O$	22	35	27	79:21
10	$CuCl_2$	22	83	80	77:23
11	$CuBr_2$	22	11	10	75:25
12	$Cu(OTf)_2$	22	>98	94	83:17
13	$Cu(OTf)_2$	–30	81	76	85:15
14	$Cu(OAc)_2$•H_2O	22	>98	93	81:19
15	$Cu(OAc)_2$•H_2O	–30	46	43	83:17

[a] Reactions were performed under N_2 atm; >98% site selectivity in all cases (e.g., <2% S_N2 product). [b]Values determined by analysis of 400 MHz ^{1}H NMR spectra of unpurified mixtures. [c]Yields of Purified products. [d] By GLC analysis. (see page *S*-14).

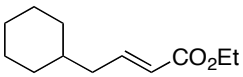
■ ■ **Preparation of Substrates:** Allylic alcohols were synthesized from the corresponding aldehydes or ketones by a two-step Horner-Wadsworth-Emmons olefination[6]/dibal–H reduction[7] sequence. Allylic alcohols were converted to the corresponding allylic carbonates based on well-established methods.[8] Physical attributes of compounds that have not been previously reported are presented below.



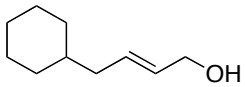
(6) (a) Martyn, D. C.; Hoult, D. A.; Abell, A. D. *Aust. J. Chem.* **2001**, 54, 391–396. (b) Dyker, G.; Grundt, P. *Helv. Chim. Acta* **1999**, *82*, 588–596.

(7) Clive, D. L. J.; Stoffman, E. J. L. *Chem. Comm.* **2007**, *21*, 2151–2153.

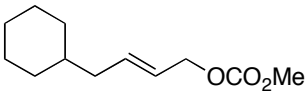
(8) (a) Meyers, A. I.; Tomioka, K.; Ronald, D. M.; Comins, D. *Tetrahedron Lett.* **1978**, *19*, 1375–1378. (b) Hu, T; Corey, E. J. *Org. Lett.*, **2002**, *4*, 2441–2443.



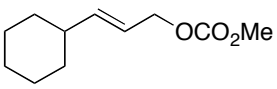
(*E*)-Ethyl 4-cyclohexylbut-2-enoate: IR (neat): 2922 (m), 2851 (w), 1718 (s), 1654 (w), 1448 (w), 1367 (w), 1306 (w), 1264 (m), 1206 (w), 1163 (m), 1132 (w), 1045 (m), 983 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 6.93 (1H, dt, *J* = 15.5, 7.6 Hz), 5.78 (1H, dt, *J* = 15.7, 1.4 Hz), 4.17 (2H, q, *J* = 7.1 Hz), 2.08 (2H, t, *J* = 7.8 Hz), 1.71-1.62 (5H, m), 1.47-1.36 (1H, m), 1.28 (3H, t, *J* = 7.2 Hz), 1.25-1.07 (3H, m), 0.97-0.87 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.7, 148.2, 122.1, 60.1, 40.1, 37.2, 33.1, 26.3, 26.2, 14.3; HRMS (ESI+): Calcd for $C_{12}H_{21}O_2$ $[M+H]^+$: 197.15415, Found: 197.15441.



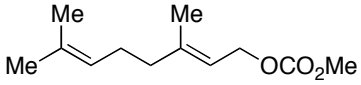
(*E*)-4-Cyclohexylbut-2-en-1-ol: IR (neat): 3312 (br), 2919 (s), 2850 (m), 1670 (w), 1447 (m), 1366 (w), 1262 (w), 1094 (w), 1070 (w), 1046 (w), 999 (m), 968 (s), 889 (w), 843 (w), 665 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.71-5.57 (2H, m), 4.08 (2H, t, *J* = 4.4 Hz), 1.94 (2H, t, *J* = 6.7 Hz), 1.71-1.61 (5H, m), 1.34-1.07 (5H, m), 0.93-0.83 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.0, 129.8, 63.8, 40.2, 37.7, 33.0, 26.5, 26.2; HRMS (ESI+): Calcd for $C_{10}H_{17}$ $[M-OH]^+$: 137.13303, Found: 137.13323.



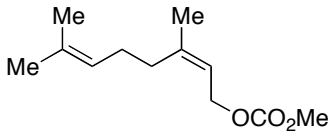
(*E*)-4-Cyclohexylbut-2-en-1-yl methyl carbonate: IR (neat): 2921 (m), 2850 (w), 1746 (s), 1672 (w), 1587 (w), 1443 (m), 1381 (w), 1250 (s), 1114 (w), 972 (m), 941 (s), 899 (w), 844 (w), 791 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.83-5.75 (1H, m), 5.60-5.52 (1H, m), 4.57 (2H, dd, *J* = 6.5, 1.0 Hz), 3.78 (3H, s), 1.95 (2H, t, *J* = 7.0 Hz), 1.70-1.61 (5H, m), 1.35-1.08 (4H, m), 0.92-0.84 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.7, 136.1, 124.1, 68.7, 54.7, 40.2, 37.6, 33.0, 26.5, 26.2; HRMS (ESI+): Calcd for $C_{10}H_{17}$ $[M-OCO_2Me]^+$: 137.13303, Found: 137.13370.



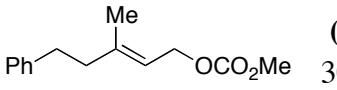
(*E*)-3-Cyclohexylallyl methyl carbonate: IR (neat): 2923 (m), 2851 (w), 1746 (s), 1670 (w), 1442 (m), 1382 (w), 1250 (s), 1116 (w), 1088 (w), 970 (m), 940 (m), 899 (w), 791 (m), 508 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.76 (1H, dd, *J* = 15.6, 6.6 Hz), 5.67-5.49 (1H, m), 4.57 (2H, d, *J* = 6.6 Hz), 3.78 (3H, s), 1.99-197 (1H, m), 1.74-1.62 (5H, m), 1.31-1.02 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.6, 142.9, 120.6, 68.9, 54.6, 40.3, 32.4, 26.0, 25.9; HRMS (ESI+): Calcd for C_9H_{15} $[M-OCO_2Me]^+$: 123.11683, Found: 123.11454.



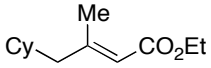
(*E*)-3,7-Dimethylocta-2,6-dien-1-yl methyl carbonate: IR (neat): 2959 (br, w), 2918 (br, w), 2857 (br, w), 1745 (s), 1670 (w), 1588 (w), 1441 (m), 1379 (w), 1340 (w), 1251 (s), 1108 (w), 938 (m), 903 (w), 833 (w), 792 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.40-5.37 (1H, m), 5.09-5.05 (1H, m), 4.65 (2H, dd, *J* = 7.2, 0.6 Hz), 3.77 (3H, s), 2.13-2.02 (4H, m), 1.72 (3H, s), 1.68 (3H, s), 1.59 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.9, 143.2, 131.9, 123.6, 117.7, 64.7, 54.6, 39.5, 26.2, 25.6, 17.5, 16.5; HRMS (ESI+): Calcd for $C_{10}H_{17}$ $[M-OCO_2Me]^+$: 137.13303, Found: 137.13351.



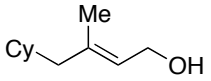
(*Z*)-3,7-Dimethylocta-2,6-dien-1-yl methyl carbonate: IR (neat): 2961 (br, w), 2917 (br, w), 2857 (br, w), 1745 (s), 1670 (w), 1442 (m), 1378 (w), 1347 (w), 1251 (s), 1108 (w), 1043 (w), 937 (m), 904 (w), 830 (w), 792 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.39-5.35 (1H, m), 5.10-5.06 (1H, m), 4.61 (2H, d, *J* = 7.4 Hz), 3.76 (3H, d, *J* = 0.8 Hz), 2.14-2.06 (4H, m), 1.76 (3H, s), 1.67 (3H, s), 1.59 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.8, 143.2, 132.2, 123.5, 118.6, 64.4, 54.6, 32.1, 26.6, 25.6, 23.4, 17.6; HRMS (ESI+): Calcd for $C_{10}H_{17}$ [M-OCO_2Me]$^+$: 137.13303, Found: 137.13260.



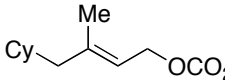
(*E*)-Methyl (3-methyl-5-phenylpent-2-en-1-yl) carbonate IR (neat): 3027 (w), 2954 (br, w), 2857 (w), 1743 (s), 1670 (w), 1602 (w), 1495 (w), 1441 (m), 1382 (w), 1340 (w), 1251 (s), 1115 (w), 1076 (w), 936 (m), 903 (w), 791 (m), 745 (w), 698 (m), 582 (w), 521 (w), 465 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.36-7.25 (2H, m), 7.20-7.16 (3H, m), 5.42-5.37 (1H, m), 4.65 (2H, dd, *J* = 7.2, 0.7 Hz), 3.78 (3H, s), 2.76-2.72 (2H, m), 2.34 (2H, t, *J* = 8.0 Hz), 1.77 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.8, 142.6, 141.7, 128.2, 125.8, 118.2, 64.5, 54.6, 41.3, 34.1, 16.6; HRMS (ESI+): Calcd for $C_{12}H_{15}$ [M-OCO_2Me]$^+$: 159.11738, Found: 159.11714.



(*E*)-Ethyl 4-cyclohexyl-3-methylbut-2-enoate: IR (neat): 2980 (w), 2922 (m), 2850 (w), 1715 (s), 1647 (w), 1448 (w), 1381 (w), 1368 (w), 1323 (w), 1268 (w), 1220 (s), 1146 (s), 1126 (m), 1096 (w), 1073 (m), 983 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.61-5.60 (1H, m), 4.12 (2H, q, *J* = 7.1 Hz), 2.12 (3H, t, *J* = 1.0 Hz), 1.99 (2H, d, *J* = 7.0 Hz), 1.71-1.62 (5H, m), 1.55-1.45 (1H, m), 1.28-1.10 (6H, m), 0.91-0.81 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.7, 158.8, 116.6, 59.4, 49.1, 35.6, 33.2, 26.4, 26.2, 18.7, 14.3; HRMS (ESI+): Calcd for $C_{13}H_{23}O_2$ [M+H]$^+$: 211.16980, Found: 211.16990.

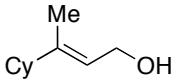


(*E*)-4-Cyclohexyl-3-methylbut-2-en-1-ol: IR (neat): 3313 (br), 2918 (s), 2849 (m), 1667 (w), 1447 (m), 1381 (w), 1268 (w), 1239 (w), 1182 (w), 1093 (w), 1060 (w), 995 (s), 892 (w), 845 (w), 769 (w), 733 (w), 585 (w), 513 (w), 485 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.36 (1H, td, *J* = 6.8, 1.0 Hz), 4.13 (2H, d, *J* = 6.9 Hz), 1.88 (2H, d, *J* = 7.2 Hz), 1.70-1.62 (8H, m), 1.47-1.35 (2H, m), 1.26-1.07 (3H, m), 0.89-0.78 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.4, 124.6, 59.3, 47.8, 35.4, 33.2, 26.5, 26.3, 16.2; HRMS (ESI+): Calcd for $C_{11}H_{21}O$ [M+H]$^+$: 169.15924, Found: 169.15927.

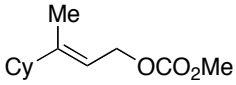


(*E*)-4-Cyclohexyl-3-methylbut-2-en-1-yl methyl carbonate: IR (neat): 2920 (m), 2850 (w), 1745 (s), 1668 (w), 1442 (m), 1382 (w), 1341 (w), 1249 (s), 1112 (w), 1062 (w), 938 (m), 903 (w), 845 (m), 792 (w), 770 (w), 571 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.34-5.30 (1H, m), 4.64 (2H, d, *J* = 7.0 Hz), 3.76 (3H, s), 1.90 (2H, d, *J* = 7.2 Hz), 1.70-1.60 (8H, m), 1.45-1.36 (1H, m), 1.25-1.07 (3H, m), 0.88-0.77 (2H, m); ^{13}C NMR

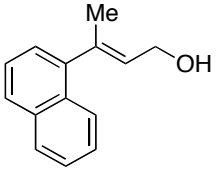
(100 MHz, $CDCl_3$): δ 155.8, 141.9, 118.9, 64.7, 54.6, 47.8, 35.3, 33.2, 26.5, 26.3, 16.4; HRMS (ESI+): Calcd for $C_{11}H_{19}$ $[M\text{-}OCO_2Me]^+$: 151.14868, Found: 151.14823.



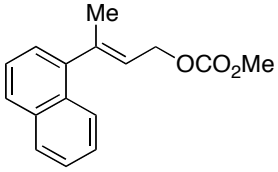
(*E*)-3-Cyclohexylbut-2-en-1-ol: IR (neat): 3309 (br), 2922 (s), 2851 (m), 1662 (w), 1447 (m), 1379 (w), 1261 (w), 1229 (w), 1187 (w), 1078 (w), 995 (s), 891 (w), 858 (w), 840 (w), 806 (w), 761 (w), 618 (w), 528 (w), 435 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.41-5.37 (1H, m), 4.16 (2H, t, *J* = 6.2 Hz), 1.88-1.65 (9H, m), 1.36-1.07 (6H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 121.5, 59.4, 47.1, 31.7, 31.5, 26.6, 26.3, 14.6; HRMS (ESI+): Calcd for $C_{10}H_{17}$ $[M\text{-}OH]^+$: 137.13303, Found: 137.13331.



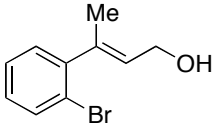
(*E*)-3-Cyclohexylbut-2-en-1-yl methyl carbonate: IR (neat): 3309 (br), 2922 (s), 2851 (m), 1662 (w), 1447 (m), 1379 (w), 1261 (w), 1229 (w), 1187 (w), 1078 (w), 995 (s), 891 (w), 858 (w), 840 (w), 806 (w), 761 (w), 618 (w), 528 (w), 435 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.37-5.33 (1H, m), 4.66 (2H, d, *J* = 7.0 Hz), 3.78 (3H, s), 1.90-1.84 (1H, m), 1.78-1.66 (8H, m), 1.32-1.08 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.9, 148.1, 115.8, 64.9, 54.6, 47.1, 31.5, 26.5, 26.2, 14.9; HRMS(ESI+): Calcd for $C_{10}H_{17}$ $[M\text{-}OCO_2Me]^+$: 137.13248, Found: 137.13385.



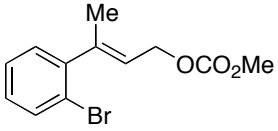
(*E*)-3-(Naphthalen-1-yl)but-2-en-1-ol: IR (neat): 3332 (br, w), 3058 (w), 2976 (w), 2915 (w), 2871 (w), 1661 (w), 1590 (w), 1506 (w), 1438 (w), 1394 (w), 1375 (w), 1337 (w), 1246 (w), 1215 (w), 1181 (w), 1090 (w), 1061 (w), 998 (m), 907 (w), 863 (w), 799 (s), 729 (s), 648 (w), 609 (w), 573 (w), 500 (w), 472 (w), 432 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.97-7.93 (1H, m), 7.88-7.83 (1H, m), 7.76 (1H, d, *J* = 8.4 Hz), 7.49-7.41 (3H, m), 7.29-7.27 (1H, m), 5.78-5.74 (1H, m), 4.46 (2H, d, *J* = 6.7 Hz), 2.15 (3H, d, *J* = 0.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.8, 138.4, 133.7, 130.8, 129.3, 128.3, 127.2, 125.8, 125.6, 125.5, 125.3, 124.7, 59.6, 19.1; HRMS (ESI+): Calcd for $C_{14}H_{13}$ $[M\text{-}OH]^+$: 181.10173, Found: 181.10197.



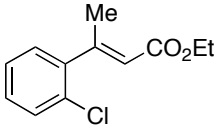
(*E*)-Methyl (3-(naphthalen-1-yl)but-2-en-1-yl) carbonate: IR (neat): 3043 (w), 2956 (w), 2854 (w), 1743 (s), 1659 (w), 1590 (w), 1506 (w), 1441 (m), 1376 (w), 1323 (w), 1251 (s), 1184 (w), 1137 (w), 1108 (w), 1011 (w), 940 (m), 904 (w), 864 (w), 800 (m), 790 (m), 775 (s), 738 (w), 652 (w), 612 (w), 575 (w), 519 (w), 495 (w), 468 (w), 449 (w), 427 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.93-7.89 (1H, m), 7.87-7.83 (1H, m), 7.77 (1H, d, *J* = 8.4 Hz), 7.49-7.40 (3H, m), 7.28-7.25 (1H, m), 5.74-5.70 (1H, m), 4.94 (2H, d, *J* = 6.9 Hz), 3.83 (3H, s), 2.20 (3H, t, *J* = 0.6 Hz),); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.9, 142.4, 141.8, 133.7, 130.7, 128.3, 127.4, 125.9, 125.7, 125.5, 125.3, 124.7, 123.7, 64.6, 54.8, 19.4; HRMS (ESI+): Calcd for $C_{14}H_{13}$ $[M\text{-}OCO2Me]^+$: 181.10173, Found: 181.10128.



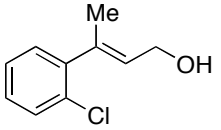
(*E*)-3-(2-Bromophenyl)but-2-en-1-ol: IR (neat): 3299 (br, w), 3053 (w), 2917 (w), 2871 (w), 1661 (w), 1587 (w), 1559 (w), 1466 (w), 1430 (w), 1375 (w), 1284 (w), 1247 (w), 1212 (w), 1111 (w), 1072 (w), 1019 (m), 1000 (m), 942 (w), 751 (s), 726 (m), 659 (w), 604 (w), 561 (w), 549 (w), 446 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.54 (1H, dd, J = 8.0, 1.2 Hz), 7.29-7.24 (1H, m), 7.18-7.10 (2H, m), 5.62-5.58 (1H, m), 4.35 (2H, t, J = 5.7 Hz), 2.02 (3H, d, J = 0.8 Hz), 1.32 (1H, t, J = 5.5 Hz; ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.3, 139.3, 132.7, 129.7, 129.3, 128.3, 127.2, 121.8, 59.4, 17.8; HRMS (ESI+): Calcd for $C_{10}H_{10}Br$ $[M\text{-}OH]^+$: 208.99659, Found: 208.99594.



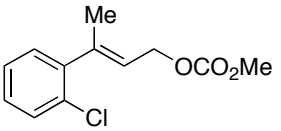
(*E*)-3-(2-Bromophenyl)but-2-en-1-yl methyl carbonate: IR (neat): 2956 (w), 1744 (s), 1662 (w), 1588 (w), 1560 (w), 1467 (w), 1441 (m), 1377 (w), 1330 (w), 1252 (s), 1119 (w), 1024 (w), 943 (s), 905 (w), 851 (w), 791 (m), 753 (s), 727 (w), 659 (w), 559 (w), 456 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.54 (1H, dd, J = 8.0, 1.2 Hz), 7.28-7.24 (1H, m), 7.17-7.10 (2H, m), 5.59-5.54 (1H, m), 4.83 (2H, dd, J = 6.8, 0.8 Hz), 3.81 (3H, s), 2.07-2.06 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.8, 144.9, 142.4, 132.7, 129.6, 128.6, 127.2, 123.8, 121.6, 64.4, 54.8, 18.0; HRMS (ESI+): Calcd for $C_{10}H_{10}Br$ $[M\text{-}OCO_2Me]^+$: 208.99659, Found: 208.99685.



(*E*)-Ethyl 3-(2-chlorophenyl)but-2-enoate: IR (neat): 3057 (w), 2980 (w), 1714 (s), 1642 (w), 1591 (w), 1565 (w), 1471 (w), 1430 (w), 1367 (w), 1341 (w), 1287 (w), 1246 (w), 1172 (s), 1128 (w), 1093 (w), 1041 (m), 945 (w), 878 (w), 758 (m), 676 (w), 592 (w), 569 (w), 545 (w), 456 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.40-7.36 (1H, m), 7.28-7.22 (2H, m), 7.19-7.15 (1H, m), 5.83 (1H, q, J = 1.4 Hz), 4.22 (2H, q, J = 7.2 Hz), 2.49 (3H, d, J = 1.6 Hz), 1.32 (3H, t, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.2, 155.6, 142.7, 131.3, 129.8, 129.0, 128.9, 126.7, 120.5, 59.9, 20.1, 14.2; HRMS (ESI+): Calcd for $C_{12}H_{14}ClO_2$ $[M+H]^+$: 225.06823, Found: 225.06795.

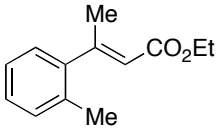


(*E*)-3-(2-Chlorophenyl)but-2-en-1-ol: IR (neat): 3311 (br, w), 3064 (w), 2918 (w), 2871 (w), 1657 (w), 1592 (w), 1564 (w), 1470 (w), 1428 (w), 1376 (w), 1286 (w), 1265 (w), 1248 (w), 1213 (w), 1127 (w), 1112 (w), 1074 (w), 1044 (w), 999 (m), 943 (w), 750 (s), 730 (w), 680 (m), 606 (w), 554 (w), 455 (w), 429 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.36-7.34 (1H, m), 7.22-7.17 (3H, m), 5.65-5.61 (1H, m), 4.35 (2H, t, J = 5.9 Hz), 2.04-2.03 (3H, m), 1.33-1.31 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.4, 137.9, 132.0, 129.8, 129.5, 128.2, 126.7, 59.4, 17.6; HRMS (ESI+): Calcd for $C_{10}H_{15}ClO$ $[M+NH_4]^+$: 200.08422, Found: 200.08377.

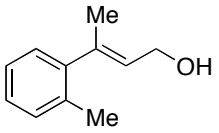


(*E*)-3-(2-Chlorophenyl)but-2-en-1-yl methyl carbonate: IR (neat): 2957 (w), 1744 (s), 1662 (w), 1591 (w), 1565 (w), 1471 (w), 1441 (m), 1378 (w), 1331 (w), 1252 (s), 1128 (w), 1076 (w), 1044 (w), 999 (w), 943

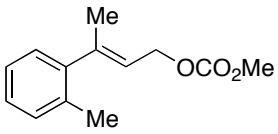
(s), 905 (w), 850 (w), 791 (m), 753 (s), 732 (w), 712 (w), 678 (w), 611 (w), 562 (w), 466 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.36-7.33 (1H, m), 7.22-7.16 (3H, m), 5.62-5.57 (1H, m), 4.83 (2H, dd, *J* = 6.8, 0.8 Hz), 3.81 (3H, s), 2.07-2.08 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.8, 142.9, 141.0, 131.9, 129.7, 129.6, 128.4, 126.7, 123.9, 64.4, 54.8, 17.8; HRMS (ESI+): Calcd for $C_{10}H_{10}Cl$ $[M\text{-}OCO_2Me]^+$: 165.04710, Found: 165.04712.



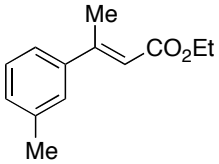
(*E*)-Ethyl 3-(*o*-tolyl)but-2-enoate: IR (neat): 2980 (w), 1712 (s), 1639 (m), 1601 (w), 1485 (w), 1446 (w), 1366 (w), 1338 (w), 1290 (w), 1262 (m), 1197 (w), 1158 (s), 1122 (w), 1095 (w), 1072 (w), 1041 (m), 942 (w), 876 (m), 811 (w), 760 (m), 726 (m), 601 (w), 578 (w), 556 (w), 512 (w), 455 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.22-7.15 (3H, m), 7.08-7.06 (1H, m), 5.76 (1H, q, *J* = 1.4 Hz), 4.22 (2H, q, *J* = 7.2 Hz), 2.44 (3H, d, *J* = 1.4 Hz), 2.29 (3H, s), 1.31 (3H, t, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.5, 158.1, 143.8, 133.7, 130.3, 127.5, 126.9, 125.6, 119.3, 59.7, 20.7, 19.6, 14.2; HRMS (ESI+): Calcd for $C_{13}H_{17}O_2$ $[M+H]^+$: 205.12285, Found: 205.12373.



(*E*)-3-(*o*-Tolyl)but-2-en-1-ol: IR (neat): 3316 (br, w), 3059 (w), 3015 (w), 2920 (w), 2869 (w), 1658 (w), 1486 (w), 1439 (w), 1377 (w), 1306 (w), 1215 (w), 1098 (w), 1064 (w), 996 (s), 940 (w), 852 (w), 801 (w), 756 (s), 727 (s), 613 (w), 565 (w), 517 (w), 451 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.18-7.12 (3H, m), 7.09-7.06 (1H, m), 5.56-5.52 (1H, m), 4.34 (2H, t, *J* = 5.9 Hz), 2.28 (3H, s), 1.98-1.97 (3H, m), 1.30-1.27 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.5, 139.4, 134.4, 130.0, 128.0, 127.9, 126.8, 125.5, 59.4, 19.6, 18.1; HRMS (ESI+): Calcd for $C_{11}H_{13}$ $[M\text{-}OH]^+$: 145.10173, Found: 145.10201.

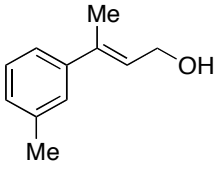


(*E*)-Methyl (3-(*o*-tolyl)but-2-en-1-yl) carbonate: IR (neat): 2956 (w), 1744 (s), 1661 (w), 1588 (w), 1486 (w), 1441 (m), 1377 (w), 1328 (w), 1252 (s), 1113 (w), 1046 (w), 998 (w), 941 (s), 904 (w), 852 (w), 791 (m), 759 (s), 728 (m), 564 (w), 516 (w), 460 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.18-7.12 (3H, m), 7.08-7.05 (1H, m), 5.52-5.47 (1H, m), 4.82 (2H, dd, *J* = 7.0, 0.6 Hz), 3.80 (3H, s), 2.27 (3H, s), 2.02-2.01 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.8, 144.1, 142.9, 134.4, 130.1, 127.8, 127.0, 125.6, 122.4, 64.6, 54.7, 19.6, 18.4; HRMS (ESI+): Calcd for $C_{11}H_{13}$ $[M\text{-}OCO_2Me]^+$: 145.10173, Found: 145.10187.

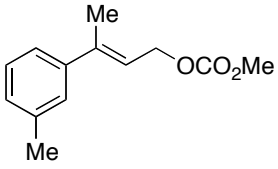


(*E*)-Ethyl-3-(*m*-tolyl)but-2-enoate: IR (neat): 2979 (w), 1710 (s), 1627 (m), 1605 (w), 1584 (w), 1444 (w), 1366 (w), 1340 (w), 1283 (w), 1199 (m), 1155 (s), 1096 (w), 1043 (m), 1000 (w), 870 (w), 786 (m), 747 (w), 696 (w), 581 (w), 449 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.29-7.24 (3H, m), 7.19-7.16 (1H, m), 6.12 (1H, q, *J* = 1.4 Hz), 4.22 (2H, q, *J* = 7.2 Hz), 2.57 (3H, d, *J* = 1.4 Hz), 2.38 (3H, s), 1.32 (3H, t, *J* = 7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.9, 155.7, 142.2, 138.1, 129.7, 128.3,

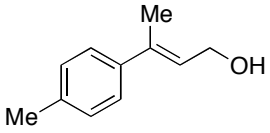
127.0, 123.4, 116.9, 59.8, 21.4, 17.9, 14.3; HRMS (ESI+): Calcd for $C_{13}H_{17}O_2$ $[M+H]^+$: 205.12285, Found: 205.12314.



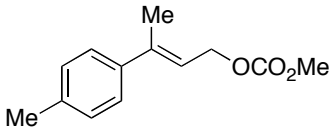
(*E*)-3-(*m*-Tolyl)but-2-en-1-ol: IR (neat): 3318 (br. w), 3028 (w), 2919 (w), 2861 (w), 1646 (w), 1603 (w), 1582 (w), 1486 (w), 1441 (w), 1377 (w), 1282 (w), 1222 (w), 1189 (w), 1171 (w), 1100 (w), 1066 (w), 993 (s), 904 (w), 878 (w), 776 (s), 697 (s), 613 (w), 582 (w), 533 (w), 441 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.23-7.21 (3H, m), 7.10-7.07 (1H, m), 5.99-5.94 (1H, m), 4.36 (2H, t, *J* = 5.9 Hz), 2.36 (3H, s), 2.08-2.07 (3H, m), 1.30 (1H, t, *J* = 5.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.8, 137.8, 137.7, 128.1, 127.9, 126.5, 126.3, 122.8, 59.8, 21.4, 16.0; HRMS (ESI+): Calcd for $C_{11}H_{13}$ $[M-OH]^+$: 145.10173, Found: 145.10243.



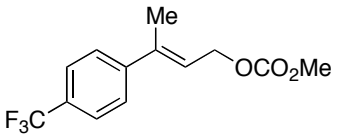
(*E*)-Methyl (3-(*m*-tolyl)but-2-en-1-yl) carbonate: IR (neat): 2956 (w), 1743 (s), 1647 (w), 1603 (w), 1583 (w), 1441 (m), 1376 (w), 1332 (w), 1251 (s), 1173 (w), 1125 (w), 941 (s), 903 (w), 833 (w), 779 (s), 698 (m), 584 (w), 536 (w), 453 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.24-7.19 (3H, m), 7.11-7.09 (1H, m), 5.93-5.88 (1H, m), 4.84 (2H, dd, *J* = 7.0, 0.6 Hz), 3.80 (3H, s), 2.36 (3H, s), 2.12 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.8, 142.4, 141.1, 137.8, 128.3, 128.2, 126.6, 123.0, 120.4, 64.9, 54.7, 21.4, 16.3; HRMS (ESI+): Calcd for $C_{11}H_{13}$ $[M-OCO_2Me]^+$: 145.10173, Found: 145.10203.



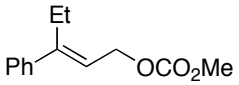
(*E*)-3-(*p*-Tolyl)but-2-en-1-ol: IR (neat): 3316 (br, w), 3085 (w), 3024 (w), 2920 (w), 2864 (w), 1645 (w), 1512 (m), 1441 (w), 1409 (w), 1377 (w), 1312 (w), 1275 (w), 1216 (w), 1189 (w), 1112 (w), 1064 (w), 994 (s), 925 (w), 808 (s), 717 (w), 699 (w), 642 (w), 547 (m), 512 (w), 458 (w), 407 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.33-7.30 (2H, m), 7.16-7.13 (2H, m), 5.98-5.94 (1H, m), 4.36 (2H, t, *J* = 5.9 Hz), 2.35 (3H, s), 2.08-2.07 (3H, m), 1.32-1.29 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.9, 137.6, 137.0, 128.9, 125.6, 59.9, 21.0, 15.9; HRMS (ESI+): Calcd for $C_{11}H_{13}$ $[M-OH]^+$: 145.10173, Found: 145.10189.



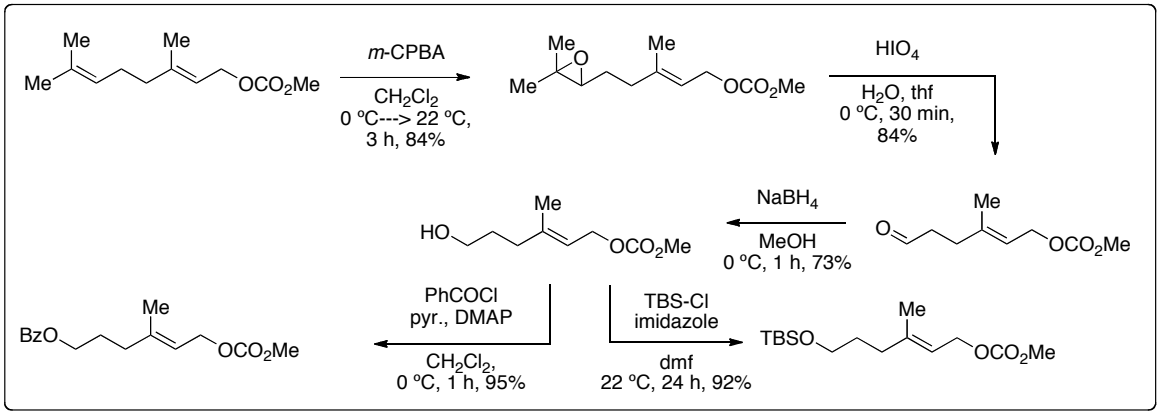
(*E*)-Methyl (3-(*p*-tolyl)but-2-en-1-yl) carbonate: IR (neat): 2956 (w), 1747 (s), 1514 (w), 1443 (m), 1378 (w), 1333 (w), 1261 (s), 1128 (w), 943 (m), 904 (w), 812 (w), 792 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.32-7.29 (2H, m), 7.13 (2H, d, *J* = 8.0 Hz), 5.93-5.88 (1H, m), 4.84 (2H, d, *J* = 7.0 Hz), 3.80 (3H, s), 2.35 (3H, s), 2.11 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.8, 140.9, 139.5, 137.4, 129.0, 125.7, 119.7, 65.0, 54.7, 21.0, 16.2; HRMS (ESI+): Calcd for $C_{13}H_{16}O_3$ $[M]^+$: 220.10994, Found: 220.10914.



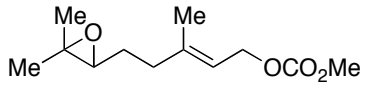
(*E*)-Methyl (3-(4-(trifluoromethyl)phenyl)but-2-en-1-yl) carbonate: IR (neat): 2959 (w), 1746 (s), 1617 (w), 1444 (m), 1412 (w), 1379 (w), 1323 (s), 1257 (s), 1195 (w), 1164 (m), 1113 (s), 1073 (m), 1059 (m), 1014 (m), 944 (m), 906 (w), 829 (m), 791 (m), 727 (w), 631 (w), 604 (m), 540 (w), 509 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.58 (2H, d, J = 8.4 Hz), 7.49 (2H, d, J = 8.4 Hz), 5.99-5.95 (1H, m), 4.86 (2H, d, J = 6.8 Hz), 3.81 (3H, s), 2.14 (3H, d, J = 0.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.8, 145.9, 139.6, 129.7, 129.4, 126.1, 125.5, 125.3, 125.2, 122.7, 64.6, 54.8, 16.2; HRMS (ESI+): Calcd for $C_{11}H_{10}F_3$ [M-OCO_2Me]$^+$: 199.07346, Found: 199.07287.



(*E*)-Methyl (3-phenylpent-2-en-1-yl) carbonate (12): IR (neat): 2967 (w), 2875 (w), 1743 (s), 1644 (w), 1598 (w), 1492 (w), 1442 (m), 1376 (w), 1346 (w), 1306 (w), 1251 (s), 1128 (w), 1065 (w), 1031 (w), 937 (m), 904 (m), 852 (w), 791 (m), 760 (s), 696 (s), 514 (w), 445 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.38-7.27 (5H, m), 5.79 (1H, t, J = 7.0 Hz), 4.85 (2H, d, J = 7.0 Hz), 3.80 (3H, s), 2.59 (2H, q, J = 7.5 Hz), 1.00 (3H, t, J = 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.8, 147.9, 141.4, 128.3, 127.5, 126.5, 120.3, 64.7, 54.7, 23.4, 13.7; HRMS (ESI+): Calcd for $C_{11}H_{13}$ [M-OCO_2Me]$^+$: 145.10173, Found: 145.10203.



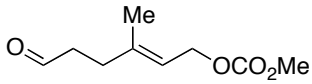
Preparation of ether-containing substrates: Allylic carbonate **12** was converted to the corresponding ether-containing allylic carbonates based on previously established methods.[9]



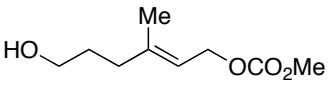
(*E*)-5-(3,3-Dimethyloxiran-2-yl)-3-methylpent-2-en-1-yl methyl carbonate: *m*-Chloroperbenzoic acid (1.7 g, 10 mmol) was added to a solution of (*E*)-3,7-dimethylocta-2,6-dien-1-yl methyl carbonate (2.1 g, 10 mmol) in CH_2Cl_2 (70 mL) at 0 ºC. The mixture was allowed to warm to 22 ºC and stir for 4 hours. Calcium hydroxide (2.8 g, 37 mmol) was added and the reaction was allowed to stir for 40 min. The reaction was filtered, eluting with Et_2O, and

(9) Tago, K; Arai, M.; Kogen, H. *J. Chem. Soc., Perkin Trans. 1* **2000**, 2073–2078.

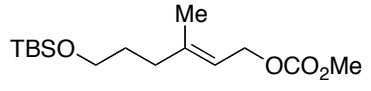
concentrated in vacuo to provide a yellow oil. The resulting residue was purified by silica gel column chromatography (gradient 10% to 12% Et_2O in hexanes) to afford the desired compound as clear oil (1.9 g, 8.4 mmol, 84%). IR (neat): 2959 (br, w), 1744 (s), 1670 (w), 1442 (m), 1378 (w), 1340 (w), 1252 (s), 1121 (w), 1049 (m), 936 (m), 903 (w), 874 (w), 792 (m), 737 (w), 679 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.44-5.40 (1H, m), 4.66 (2H, d, *J* = 7.2 Hz), 3.77 (3H, s), 2.70 (1H, t, *J* = 6.4 Hz), 2.27-2.11 (2H, m), 1.74 (3H, s), 1.69-1.63 (2H, m), 1.30 (3H, s), 1.26 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.8, 142.2, 118.3, 65.8, 64.5, 63.8, 58.3, 54.6, 36.1, 27.0, 24.8, 18.7, 16.5, 15.2; HRMS (ESI+): Calcd for $C_{12}H_{24}NO_4$ $[M+NH_4]^+$: 246.1705, Found: 246.1711.



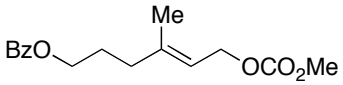
(*E*)-Methyl (3-methyl-6-oxohex-2-en-1-yl) carbonate: A solution of $HIO_4•2H_2O$ (1.9 g, 8.5 mmol) in water (8 mL) was slowly added to a solution of the epoxide (1.8 g, 7.7 mmol) in THF (13 mL) at 0 ºC. The reaction was allowed to stir for 30 min. Brine (15 mL) was added to the reaction and the solution was extracted with Et_2O (10 mL x 3). The combined organic layers were washed with a saturated solution of $NaHCO_3$ (15 mL x 2), and brine (15 mL x 2). The organic layer was separated, dried over Na_2SO_4, filtered, and concentrated in vaccuo. The resulting residue was purified by silica gel chromatography (10%→30% Et_2O in hexanes) to provide the product as clear oil (1.2 g, 6.44 mmol, 84%). IR (neat): 2958 (br, w), 2857 (br, w), 2724 (w), 1742 (s), 1721 (m), 1672 (w), 1442 (m), 1386 (w), 1340 (w), 1251 (s), 1120 (w), 1065 (w), 933 (m), 904 (w), 791 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 9.76 (1H, t, *J* = 1.6 Hz), 5.40-5.36 (1H, m), 4.64 (2H, dd, *J* = 7.2, 0.8 Hz), 3.77 (3H, s), 2.59-2.55 (2H, m), 2.37 (2H, t, *J* = 7.4 Hz), 1.73 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.5, 155.7, 141.0, 118.7, 64.3, 62.4, 54.7, 41.6, 31.3, 16.6; HRMS (ESI+): Calcd for $C_9H_{18}NO_4$ $[M+NH_4]^+$: 204.1236, Found: 204.1245.



(*E*)-6-Hydroxy-3-methylhex-2-en-1-yl methyl carbonate: Sodium Borohydrate (0.19 g, 5.4 mmol) was added to a solution of aldehyde (1.0 g, 5.4 mmol) in methanol (60 mL) at 0 ºC. The mixture was allowed to stir for one hour at 0 ºC. Acetone (10 mL) and water (30 mL) were added and the reaction was allowed to warm to 22 ºC and washed with Et_2O (30 mL x 3). The combined organic layers were combined and washed with HCl (0.1 M aqueous solution, 25 mL x 2) and brine (25 mL x 2). The organic layer was separated, dried over Na_2SO_4, filtered, and concentrated under vacuo. The product was purified by silica gel chromatography with Et_2O/hexanes (1:1), to provide the product as clear oil (0.73 g, 3.9 mmol, 73%). IR (neat): 2942 (br), 2870 (br), 1743 (s), 1670 (w), 1442 (m), 1382 (w), 1339 (w), 1252 (s), 1120 (w), 1058 (m), 1006 (w), 932 (m), 904 (w), 792 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.42-5.38 (1H, m), 4.65 (2H, d, *J* = 7.2 Hz), 3.77 (3H, s), 3.65-3.61 (2H, m), 2.12 (2H, t, *J* = 7.8 Hz), 1.73 (3H, s), 1.71-1.66 (2H, m), 1.36 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.8, 142.8, 118.0, 64.6, 62.4, 54.7, 35.7, 30.4, 16.4; HRMS (ESI+): Calcd for $C_9H_{20}NO_4$ $[M+NH_4]^+$: 206.1392, Found: 206.1396.



(*E*)-6-((*tert*-Butyldimethylsilyl)oxy)-3-methylhex-2-en-1-yl methyl carbonate: *t*-Butyldimethylsilyl chloride (280 mg, 1.80 mmol) was added to a solution of the alcohol (300 mg, 1.60 mmol) and imidazole (440 mg, 6.40 mmol) in DMF (20 mL) at 22 ºC. The mixture was allowed to stir for 24 h. Water (20 mL) was added and washed with Et_2O (20 mL x 3). The combined organic layers were washed with water (25 mL x 2) and brine (25 mL x 2), dried over Na_2SO_4, filtered, and concentrated under vacuo. The product was purified by silica gel column chromatography (5% Et_2O in hexanes) to provide the product as clear yellow oil (445 mg, 1.47 mmol, 92%). IR (neat): 2953 (w), 2930 (w), 2890 (w), 2857 (w), 1747 (s), 1671 (w), 1442 (m), 1385 (w), 1361 (w), 1338 (w), 1252 (s), 1096 (m), 1006 (w), 939 (m), 904 (w), 833 (m), 792 (w), 774 (m), 714 (w), 662 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.42-5.38 (1H, m), 4.65 (2H, dd, *J* = 7.2, 0.6 Hz), 3.77 (3H, s), 3.59 (2H, t, *J* = 6.5 Hz), 2.08 (2H, t, *J* = 7.8 Hz), 1.72 (3H, s), 1.67-1.60 (2H, m), 0.90 (9H, s), 0.04 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.9, 143.1, 117.7, 64.7, 62.6, 54.6, 35.7, 30.7, 25.9, 18.3, 16.5, -5.3; HRMS (ESI+): Calcd for $C_{15}H_{34}NO_4Si$ $[M+NH_4]^+$: 320.2257, Found: 320.2249.

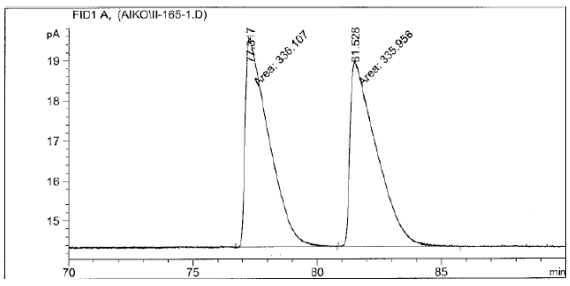


(*E*)-6-((Methoxycarbonyl)oxy)-4-methylhex-4-en-1-yl benzoate: Benzoyl chloride (170 µL, 1.50 mmol) was added to a solution of alcohol (200 mg, 1.10 mmol), pyridine (450 µL, 5.50 mmol), and *N*,*N*-dimethylaminopyridine (8.0 mg, 70.0 µmol) in CH_2Cl_2 (3 mL) at 0 ºC. The mixture was allowed to stir for 1 hour at 0 ºC. Water (10 mL) was added and the solution was allowed to warm to 22 ºC, and washed with Et_2O (10 mL x 3). The combined organic layers were washed with brine (15 mL x 2), dried over Na_2SO_4, filtered, and concentrated under vacuo. The residue was purified by silica gel chromatography (6%→12% Et_2O in hexanes) to provide the product as clear yellow oil (310 mg, 1.06 mmol, 95%). IR (neat): 2956 (b), 1744 (s), 1716 (s), 1602 (w), 1584 (w), 1442 (m), 1383 (w), 1338 (w), 1314 (w), 1251 (s), 1175 (w), 1111 (m), 1070 (w), 1026 (w), 935 (m), 904 (w), 852 (w), 792 (w), 710 (s) 688 (w), 675 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.05-8.02 (2H, m), 7.58-7.53 (1H, m), 7.46-7.42 (2H, m), 5.46-5.41 (1H, m), 4.65 (2H, dd, *J* = 7.0, 0.6 Hz), 4.31 (2H, t, *J* = 6.5 Hz), 3.77 (3H, s), 2.21 (2H, t, *J* = 8.2, 6.8 Hz), 1.95-1.88 (2H, m), 1.76 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.5, 155.8, 142.0, 132.9, 130.3, 129.5, 128.3, 118.5, 64.5, 64.3, 54.7, 35.8, 26.6, 16.4; HRMS (ESI+): Calcd for $C_{16}H_{24}NO_5$ $[M+NH_4]^+$: 310.1655, Found: 310.1659.

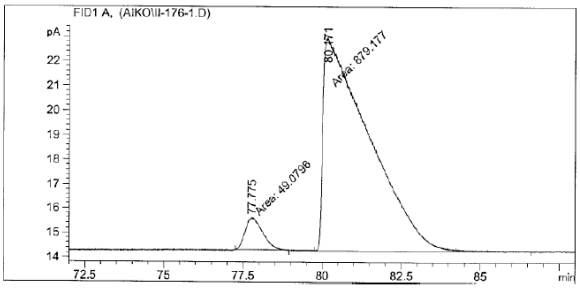
Representative experimental procedure for enantioselective Cu-catalyzed substitution reaction of (*E*)-methyl(3-methyl-5-phenylpent-2-en-1-yl)carbonate with bis(pinacolato) diboron: (*R*)-3-Methyl-5-phenylpent-1-en-3-ol: In an N_2-filled glove-box, an oven-dried vial (4 mL, 17 x 38 mm) with magnetic stir bar was charged with imidazolinium salt **4a** (6.0 mg, 0.012 mmol, 6.0 mol %), $Cu(OTf)_2$ (3.7 mg, 0.010 mmol, 5.0 mol %), NaOMe (8.8 mg, 0.16 mmol, 80 mol %) and DME (1.0 mL) under a N_2 atmosphere. The vessel was sealed with a cap (phenolic open top cap with red PTFE/white silicone) and the green solution was allowed to stir for 30

min. The color of the solution was then clear blue. Bis(pinacolato)diboron (102 mg, 0.400 mmol, 2.0 equiv) was added to the solution. The color of the solution immediately turned dark brown. The vial was resealed with a cap (phenolic open top cap with red PTFE/white silicone). After 30 min, (*E*)-methyl(3-methyl-5-phenylpent-2-en-1-yl)carbonate (46.9 mg, 0.200 mmol, 1.0 equiv) was added neat by syringe. After 24 h, the solution was quenched by passing through a short plug of celite and silica gel and washed with (reagent grade) thf (3 x 2 mL). The filtrate was allowed to cool to at 0 °C (ice bath) and H_2O_2 (217 μL, 2.23 mmol) and 2 N NaOH (0.500 mL, 1.00 mmol) were added. The resulting solution was allowed to stir for 1 hour. After this time, the mixture was diluted with water (3 mL), washed with Et_2O (3 x 1 mL) and filtered through a plug of $MgSO_4$ and silica gel. The filtrate was concentrated in vacuo to provide colorless oil, which was purified by silica gel chromatography (5%→15% Et_2O in hexanes) to afford the allylic alcohol, (*R*)-3-methyl-5-phenylpent-1-en-3-ol, as colorless oil (33.8 mg, 0.192 mmol, 96% yield).

(*R*)-5-Phenylpent-1-en-3-ol (*R*-**9**)**:** This product isolated as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31–7.36 (m, 2H), 7.22-7.17 (m, 2H), 5.95–5.87 (1H, ddd, J = 16.6, 10.4, 6.1 Hz), 5.28–5.23 (1H, m), 5.16-5.13 (1H, m), 4.13 (1H, q, J = 6.5 Hz), 2.75–2.66 (2H, m), 1.89–1.83 (2H, m), 1.58(1H, s). Optical rotation: $[\alpha]_D^{20}$ –5.8 (*c* 1.0, $CHCl_3$) for a sample with 95:5 er. The spectroscopic data match those reported previously.[10] Enantiomeric purity was determined by GLC analysis in comparison with authentic racemic material (95:5 er shown below; CDB/DM, 15 psi, 100 ºC; the GC trace was taken with the *R* enantiomer of product prepared by using the *R* enantiomer of ligand).



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	77.317	MM	1.0740	336.10703	5.21579	50.01107
2	81.528	MM	1.1994	335.95828	4.66827	49.98893



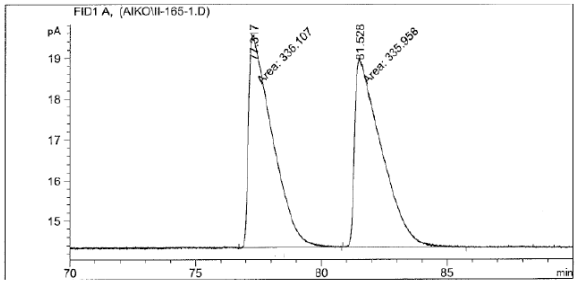
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	77.775	MM	0.6297	49.07956	1.29895	5.28728
2	80.171	MM	1.6815	879.17749	8.71434	94.71272

Retention time	Area	Area %	Retention time	Area	Area %
77.317	336.13703	50.01107	77.775	49.07956	5.28723
81.528	335.95828	49.98893	80.171	879.17749	94.71272

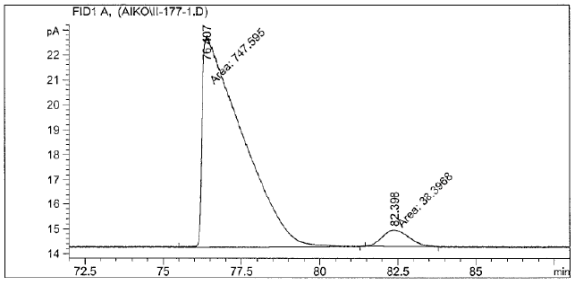
■ **Proof of Stereochemistry:** Literature value ($[\alpha]_D^{21}$ +4.96 is assigned for the (*S*) enantiomer[10a] and ($[\alpha]_D^{21}$ –5.8 (c 1.3, $CHCl_3$) is assigned for the (*R*) enantiomer.[10b]

(10) (a) Discordia, R. P.; Dittmer, D. C. *J. Org. Chem.* **1990**, *55*, 1414–1415. (b) Sato, I.; Asakura, N.; Iwashita, T. *Tetrahedron: Asym.* **2007**, *18*, 2638–2642.

(*S*)-5-Phenylpent-1-en-3-ol (*S*-9): prepared from ***Z*-8**. Optical rotation: $[\alpha]_D^{20}$ +5.8 (*c* 1.0, $CHCl_3$) for a sample with 95:5 er.Enantiomeric purity was determined by GLC analysis in comparison with authentic racemic material (95:5 er shown below; CDB/DM, 15 psi, 100 ºC; the chiral GC trace was taken with the *S* enantiomer of product prepared by using the *R* enantiomer of ligand).



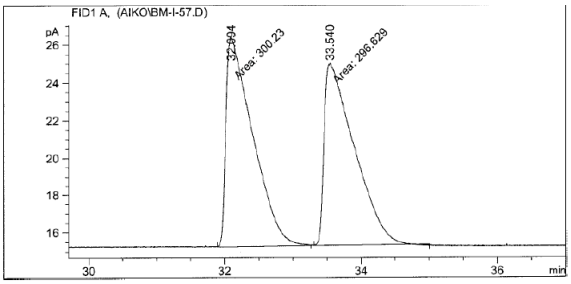
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	77.317	MM	1.0740	336.10703	5.21579	50.01107
2	81.528	MM	1.1994	335.95828	4.66827	49.98893



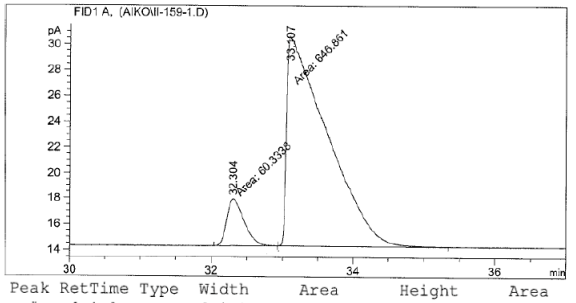
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	76.407	MM	1.4627	747.59467	8.51872	95.11486
2	82.398	MM	0.9494	38.39680	6.74083e-1	4.88514

Retention time	Area	Area %	Retention time	Area	Area %
77.317	336.13703	50.01107	76.407	747.59467	95.11486
81.528	335.95828	49.98893	82.398	38.39680	4.88514

(*R*)-1-Cyclohexylbut-3-en-2-ol (10): IR (neat): 3332 (b), 3077 (w), 2920 (s), 2851 (m), 1644 (w), 1447 (w), 1425 (w), 1321 (w), 1262 (w), 1201 (m), 1148 (w), 1103 (w), 1080 (w), 1060 (w), 1043 (w), 1016 (w), 989 (m), 964 (w), 917 (m), 896 (w), 878 (w), 825 (w), 687 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.86 (1H, ddd, *J* = 17.2, 10.4, 6.26 Hz), 5.22 (1H, dt, *J* = 17.2, 1.4 Hz), 5.08 (1H, dt, *J* = 10.4, 1.4 Hz), 4.20 (1H, q, *J* = 6.5 Hz), 1.81-1.62 (5H, m), 1.48-1.10 (7H, m), 0.99-0.86 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.8, 114.3, 70.8, 44.9, 33.9, 33.8, 33.1, 26.5, 26.3, 26.2; HRMS (ESI+): Calcd for $C_{10}H_{22}NO$ $[M+NH_4]^+$: 172.17014, Found: 172.17043. $[\alpha]_D^{20}$ +5.4 (*c* = 1.0, $CHCl_3$) for an enantiomerically enriched sample of 91.5:8.5 er. Enantiomeric purity was determined by GLC analysis in comparison with authentic racemic material (91.5:8.5 er shown; CDB/DM column, 15 psi, 100 ºC; the chiral GC trace was taken with the *R* enantiomer of product prepared by using the *R* enantiomer of ligand).



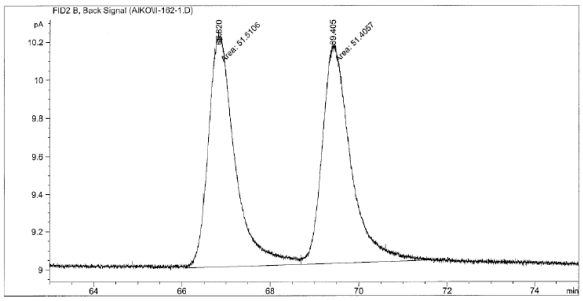
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	32.094	MM	0.4454	300.23016	11.23326	50.30166
2	33.540	MM	0.5098	296.62924	9.69704	49.69834



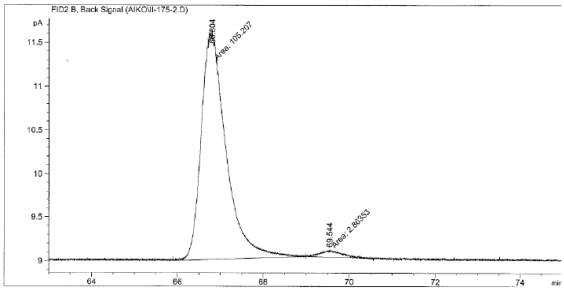
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	32.304	MM	0.2755	60.33381	3.65018	8.53142
2	33.107	MM	0.6602	646.86133	16.33092	91.46858

Retention time	Area	Area %	Retention time	Area	Area %
32.094	300.23016	50.30166	32.304	60.33381	8.53142
33.540	296.62924	49.69834	33.107	646.86133	91.46858

(*S*)-1-Cyclohexylprop-2-en-1-ol (11): IR (neat): 3353 (br, m), 3076 (w), 2921 (s), 2851 (m), 1644 (w), 1449 (m), 1424 (w), 1307 (w), 1260 (w), 1232 (w), 1213 (w), 1184 (w), 1145 (w), 1094 (w), 1081 (w), 1051 (w), 1017 (m), 990 (m), 973 (m), 918 (s), 891 (m), 862 (w), 840 (w), 779 (w), 728 (w), 690 (w), 617 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.86 (1H, ddd, *J* = 17.2, 10.4, 6.6 Hz), 5.21 (1H, dt, *J* = 17.2, 1.4 Hz), 5.14 (1H, dt, *J* = 10.4, 1.2 Hz), 3.85 (1H, t, *J* = 6.4 Hz), 1.80-1.62 (5H, m), 1.48-1.36 (2H, m), 1.29-0.95 (5H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.8, 115.5, 77.8, 43.5, 28.7, 28.2, 26.5, 26.13, 26.06; HRMS (ESI+): Calcd for $C_9H_{20}NO$ $[M+NH_4]^+$: 158.15449, Found: 158.15489. $[\alpha]_D^{20}$ +13.4 (*c* = 1.00, $CHCl_3$) for an enantiomerically enriched sample of 97:3 er. Enantiomeric purity was determined by GLC analysis in comparison with authentic racemic material (97:3 er shown; α-dex column, 15 psi, 70 ºC; the GC trace was taken with the *S*-enantiomer of product prepared by using the *R* enantiomer of ligand).



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	66.820	MF	0.6919	51.51059	1.24073	50.05094
2	69.405	FM	0.7323	51.40574	1.16999	49.94906



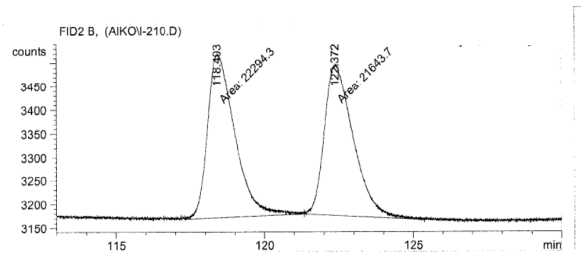
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	66.804	MM	0.6689	105.20673	2.62145	97.35030
2	69.544	MM	0.5391	2.86353	8.85204e-2	2.64970

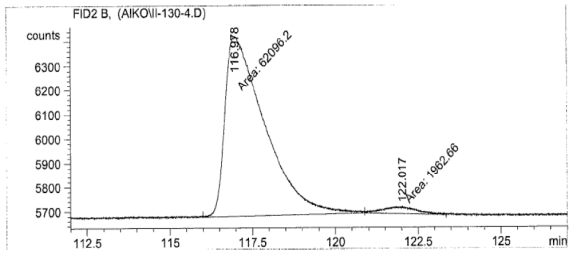
Retention time	Area	Area %	Retention time	Area	Area %
66.820	51.51059	50.05094	66.804	105.20673	97.35030
69.405	51.40574	49.94906	69.544	2.86353	2.64970

(–)-Linalool (Table 2, entry 1 and 2): ^1H NMR (400 MHz, $CDCl_3$): δ 5.91 (1H, dd, *J* = 17.4, 10.8 Hz), 5.22 (1H, dd, *J* = 17.4, 1.4 Hz), 5.14-5.10 (1H, m), 5.06 (1H, dd, *J* = 10.8, 1.2 Hz), 2.10-1.95 (2H, m), 1.68 (3H, d, *J* = 1.2 Hz), 1.60–1.53 (6H, m), 1.28 (1H, s); HRMS (ESI+): Calcd for $C_{10}H_{22}NO$ $[M+NH_4]^+$: 172.17014, Found: 172.17095. $[\alpha]_D^{20}$ –17.2 (*c* 1.00, $CHCl_3$) for a sample with 97:3 er. The spectroscopic data match those reported previously.[11] Enantiomeric purity was determined by GLC analysis in comparison with authentic racemic material (97:3 er shown below; *β*-dex column, 15 psi, 70 ºC).

(11) (a) Ohloff, G.; Klein, E. *Tetrahedron* **1962**, *18*, 37-42. (b) Schneider, J. S.; Yoshihara, K.; Nakanishi, K. *J. Chem. Soc., Chem. Comm.* **1983**, *7*, 352–353. (c) Reich, H. J.; Yelm, K. E. *J. Org. Chem.* **1991**, *56*, 5672–5679.

■ **Proof of Stereochemistry:** Value reported previously ($[\alpha]_D^{20}$ –19.4, c 8.15, $CHCl_3$) is assigned for the (*R*)-(–)-Linalool.[11]



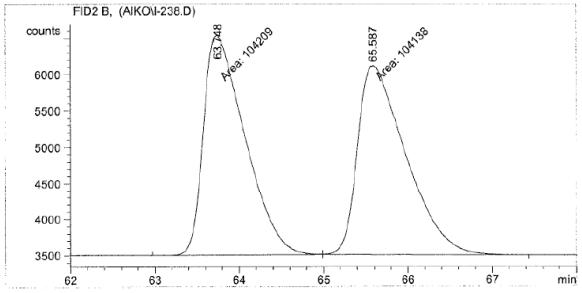


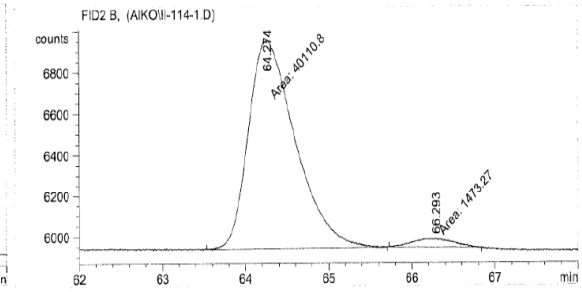
Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	118.403	MM	1.0584	2.22943e4	351.07968	50.74035
2	122.372	MM	1.1158	2.16437e4	323.30225	49.25965

Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	116.978	MM	1.3938	6.20962e4	742.51752	96.93616
2	122.017	MM	1.0476	1962.65979	31.22404	3.06384

Retention time	Area	Area %	Retention time	Area	Area %
118.403	22294.3	50.74035	116.978	62096.2	96.93616
122.372	21643.7	49.25965	122.017	1962.66	3.06384

(*R*)-3-Methyl-5-phenylpent-1-en-3-ol, (Table 2, entry 3): IR (neat): 3409 (br, w), 3085 (w), 3062 (w), 3026 (w), 2971 (w), 2930 (w), 2864 (w), 1643 (w), 1603 (w), 1497 (w), 1454 (w), 1411 (w), 1370 (w), 1266 (w), 1216 (w), 1155 (w), 1105 (w), 1069 (w), 1030 (w), 996 (w), 917 (m), 828 (w), 756 (w), 730 (m), 697 (s), 620 (w), 558 (w), 503 (w), 425 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.30-7.25 (2H, m), 7.20-7.16 (3H, m), 5.98 (1H, dd, *J* = 17.4, 10.8 Hz), 5.27 (1H, dd, *J* = 17.2, 1.2 Hz), 5.12 (1H, dd, *J* = 10.8, 1.2 Hz), 2.722.60 (2H, m), 1.92-1.78 (2H, m), 1.45 (1H, bs), 1.35 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.8, 142.3, 128.4, 128.3, 125.7, 112.0, 73.2, 44.0, 30.3, 28.0; HRMS (ESI+): Calcd for $C_{12}H_{20}NO$ $[M+NH_4]^+$: 194.15449, Found: 194.15449. $[\alpha]_D^{20}$ –25.0 (*c* = 1.00, $CHCl_3$) for an enantiomerically enriched sample of 96.5:3.5 er. Enantiomeric purity was determined by GLC analysis in comparison with authentic racemic material (96.5:3.5 er shown; *β*-dex column, 15 psi, 120 ºC).



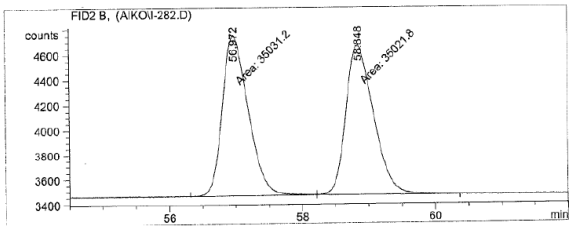


Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	63.748	MM	0.5715	1.04209e5	3039.13135	50.01686
2	65.587	MM	0.6639	1.04138e5	2614.46558	49.98314

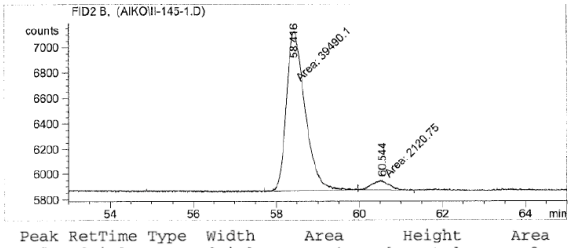
Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	64.274	MM	0.6563	4.01108e4	1018.62891	96.45714
2	66.293	MM	0.5271	1473.26636	46.58758	3.54286

Retention time	Area	Area %	Retention time	Area	Area %
63.748	104209	50.01686	64.274	40110.8	96.45714
65.587	104138	49.98314	66.293	1473.26636	3.54286

(*R*)-6-((*tert*-Butyldimethylsilyl)oxy)-3-methylhex-1-en-3-ol, (Table 2, entry 4): IR (neat): 3413 (br, w), 2953 (w), 2929 (w), 2857 (w), 1645 (w), 1472 (w), 1462 (w), 1409 (w), 1388 (w), 1362 (w), 1254 (m), 1095 (s), 1004 (w), 938 (w), 918 (m), 832 (s), 773 (s), 712 (w), 682 (w), 661 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.89 (1H, dd, *J* = 17.2, 10.6 Hz), 5.23 (1H, dd, *J* = 17.2, 1.4 Hz), 5.04 (1H, dd, *J* = 10.8, 1.6 Hz), 3.69-3.59 (2H, m), 2.72 (1H, br s), 1.68-1.55 (4H, m), 1.27 (3H, s), 0.90 (9H, s), 0.06 (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.3, 111.7, 72.6, 63.8, 39.5, 28.2, 27.3, 25.9, 18.3, -5.40; HRMS (ESI+): Calcd for $C_{13}H_{27}OSi$ [M-OH]: 227.1831, Found: 227.1829. $[\alpha]_D^{20}$ –3.2 (*c* = 1.00, $CHCl_3$) for an enantiomerically enriched sample of 95:5 er. Enantiomeric purity was determined by GLC analysis in comparison with authentic racemic material (95:5 er shown; β-dex column, 15 psi, 110 ºC).



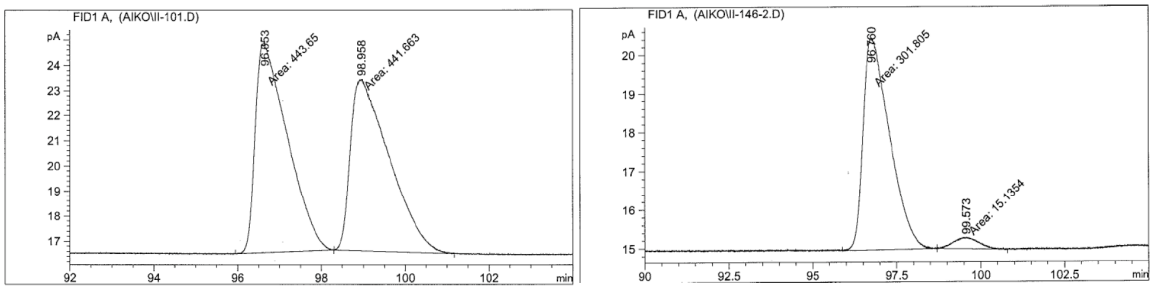
Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	56.972	MM	0.4516	3.50312e4	1292.86169	50.00670
2	58.848	MM	0.4833	3.50218e4	1207.67468	49.99330



Peak #	RetTime [min]	Type	Width [min]	Area counts*s	Height [counts]	Area %
1	58.416	MM	0.5230	3.94901e4	1258.56445	94.90338
2	60.544	MM	0.4485	2120.74707	78.80415	5.09662

Retention time	Area	Area %	Retention time	Area	Area %
56.792	35031.2	50.00670	58.416	39490.1	94.90338
58.848	35021.8	49.99330	60.544	2120.75	5.09662

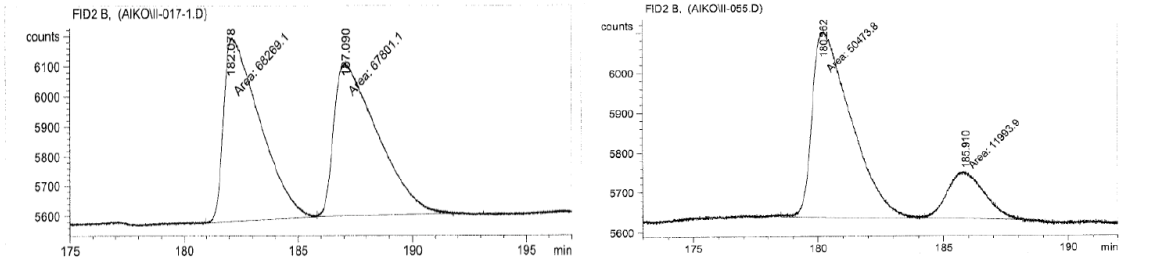
(*R*)-4-Hydroxy-4-methylhex-5-en-1-yl benzoate (Table 2, entry 5): IR (neat): 3494 (b, w), 3064 (w), 2965 (w), 1716 (m), 1703 (m), 1602 (w), 1584 (w), 1452 (w), 1315 (w), 1272 (s), 1176 (w), 1111 (m), 1070 (w), 1026 (w), 995 (w), 920 (m), 852 (w), 709 (s), 687 (m), 675 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.06-8.03 (2H, m), 7.58-7.54 (1H, m), 7.46-7.42 (2H, m), 5.93 (1H, dd, *J* = 17.4, 10.8 Hz), 5.24 (1H, dd, *J* = 17.4, 1.2 Hz), 5.09 (1H, dd, *J* = 10.8, 1.2 Hz), 4.33 (2H, t, *J* = 6.6 Hz), 1.87-1.79 (2H, m), 1.71-1.65 (2H, m), 1.44-1.43 (1H, m), 1.32 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 144.7, 132.8, 130.3, 129.5, 128.3, 112.1, 72.9, 65.2, 38.4, 28.0, 23.5; HRMS (ESI+): Calcd for $C_{14}H_{22}NO_3$ $[M+NH_4]^+$: 252.15997, Found: 252.16059. $[\alpha]_D^{20}$ -8.6 (*c* = 1.00, $CHCl_3$) for an enantiomerically enriched sample of 95:5 er. Enantiomeric purity was determined by GLC analysis in comparison with authentic racemic material (95:5 er shown; CDB/DM column, 15 psi, 140 ºC).




```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]       %
----|-------|----|-------|----------|----------|--------|
   1  96.653 MM   0.8860  443.64960   8.34536 50.11223
   2  98.958 MM   1.0781  441.66251   6.82754 49.88777

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [pA*s]      [pA]       %
----|-------|----|-------|----------|----------|--------|
   1  96.760 MM   0.9168  301.80536   5.48679 95.22453
   2  99.573 MM   0.8524   15.13542 2.95941e-1  4.77547
```

Retention time	Area	Area %	Retention time	Area	Area %
96.653	443.64960	50.11223	96.760	301.80536	95.22453
98.958	441.66251	49.88777	99.573	15.13542	4.77547

(*R*)-1-Cyclohexyl-2-methylbut-3-en-2-ol (Table 2, entry 6): IR (neat): 3423 (b, m), 3085 (w), 2919 (s), 2850 (m), 1642 (w), 1448 (m), 1411 (w), 1369 (w), 1283 (w), 1259 (w), 1228 (w), 1102 (w), 995 (w), 975 (m), 916 (s), 892 (w), 845 (w), 744 (w), 690 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.93 (1H, dd, J = 17.6, 10.8 Hz), 5.20 (1H, dd, J = 17.2, 1.2 Hz), 5.02 (1H, dd, J = 10.4, 1.2 Hz), 1.77-1.73 (2H, m), 1.67-1.57 (3H, m), 1.45-1.36 (4H, m), 1.27-1.07 (6H, m), 1.01-0.88 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.7, 111.0, 73.8, 49.8, 35.11, 35.07, 33.7, 28.7, 26.4, 26.3, 26.2; HRMS (ESI+): Calcd for $C_{11}H_{19}$ [M-OH]: 151.14868, Found: 151.14920. $[\alpha]_D^{20}$ -25.0 (c = 1.00, $CHCl_3$) for an enantiomerically enriched sample of 81:19 er. Enantiomeric purity was determined by GLC analysis in comparison with authentic racemic material (81:19 er shown; β-dex column, 15 psi, 80 ºC).

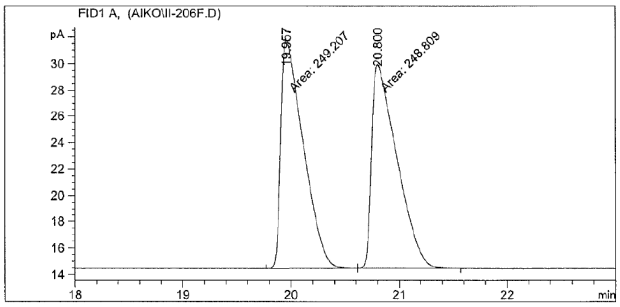


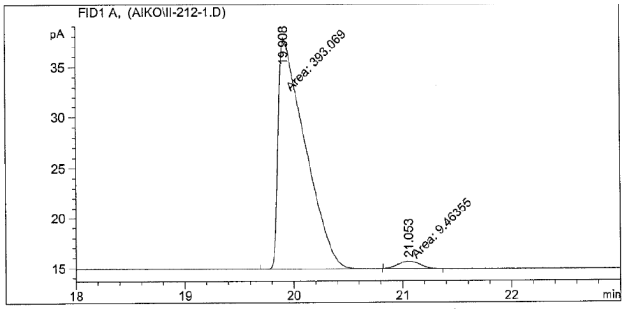

```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min] counts*s     [counts]     %
----|-------|----|-------|----------|----------|--------|
   1 182.078 MM   1.8493 6.82691e4   615.27551 50.17194
   2 187.090 MM   2.1757 6.78011e4   519.39020 49.82806

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min] counts*s     [counts]     %
----|-------|----|-------|----------|----------|--------|
   1 180.262 MM   1.7802 5.04738e4   472.55536 80.79984
   2 185.910 MM   1.6534 1.19939e4   120.90170 19.20016
```

Retention time	Area	Area %	Retention time	Area	Area %
182.078	68269.1	50.17194	180.262	472.55536	80.79984
187.090	67801.1	49.82806	185.910	120.90170	19.20016

(*S*)-2-Cyclohexylbut-3-en-2-ol (Table 2, entry 7): IR (neat): 3436 (b, m), 3085 (w), 2923 (s), 2852 (m), 1642 (w), 1450 (m), 1411 (w), 1369 (w), 1291 (w), 1244 (w), 1194 (w), 1157 (w), 1130 (w), 1090 (w), 1015 (w), 996 (m), 917 (s), 892 (m), 848 (w), 809 (w), 761 (w), 744 (w), 696 (w) cm-

[1]; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.91 (1H, dd, *J* = 17.4, 10.8 Hz), 5.18 (1H, dd, *J* = 17.2, 1.4 Hz), 5.06 (1H, dd, *J* = 10.8, 1.5 Hz), 1.82-1.75 (4H, m), 1.68-1.63 (1H, m), 1.43-0.92 (10H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.4, 111.9, 75.3, 48.0, 27.4, 27.0, 26.6, 26.5, 26.4, 25.1; HRMS (ESI+): Calcd for $C_{10}H_{17}[M\text{-}OH]^+$: 137.13303, Found: 137.13258. $[\alpha]_D^{20}$ –13.6 (*c* = 1.00, $CHCl_3$) for an enantiomerically enriched sample of 98:2 er. Enantiomeric purity was determined by GLC analysis in comparison with authentic racemic material (98:2 er shown; CDB/DM column, 15 psi, 100 ºC).





Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	19.957	MM	0.2388	249.20706	17.39065	50.03999
2	20.800	MM	0.2677	248.80875	15.49159	49.96001

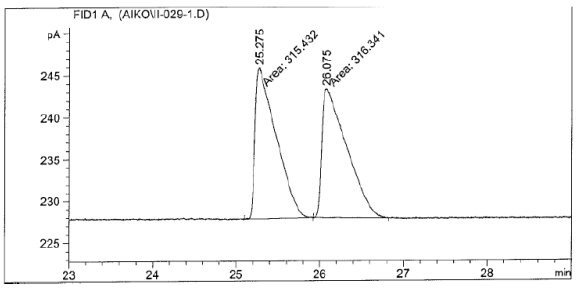
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	19.908	MM	0.2844	393.06921	23.03469	97.64900
2	21.053	MM	0.2189	9.46355	7.20685e-1	2.35100

Retention time	Area	Area %	Retention time	Area	Area %
19.957	249.20706	50.03999	19.908	472.55536	97.64900
20.800	248.80875	49.96001	21.053	120.90170	2.35100

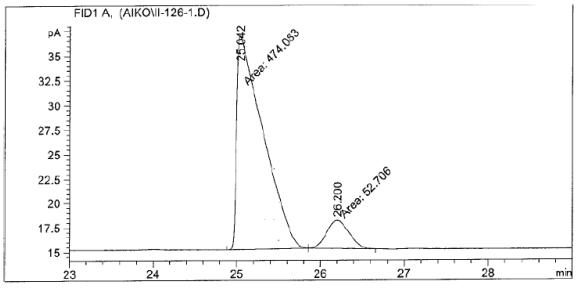
(*S*)-2-Phenylbut-3-en-2-ol (Table 3, entry 1): IR (neat): 3411 (b), 3086 (w), 3059 (w), 3026 (w), 2979 (w), 2927 (w), 1645 (w), 1601 (w), 1492 (w), 1446 (w), 1367 (w), 1218 (w), 1177 (w), 1123 (w), 1064 (w), 1027 (w), 993 (w), 921 (m), 874 (w), 765 (m), 715 (w), 699 (s) 591 (w), 539 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49-7.46 (2H, m), 7.37-7.32 (2H, m), 7.28-7.23 (1H, m,), 6.18 (1H, dd, *J* = 17.2, 10.8 Hz), 5.30 (1H, dd, *J* = 17.2, 1.2 Hz), 5.15 (1H, dd, *J* = 10.8, 1.2 Hz), 1.89 (1H, br. s), 1.66 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.4, 144.8, 128.2, 127.0, 125.1, 112.3, 74.7, 29.3; HRMS (ESI+): Calcd for $C_{10}H_{11}$ [M-OH]: 131.0861, Found: 131.0854. All spectral data matched the published values.[12] $[\alpha]_D^{20}$ –23.3 (*c* = 1.00, $CHCl_3$) for an enantiomerically enriched sample of 90:10 er. Enantiomeric purity was determined by GLC analysis in comparison with authentic racemic material (90:10 er shown; CDB/DM column, 15 psi, 100 ºC).

■ **Proof of Stereochemistry:** Literature value ($[\alpha]_D^{20}$ –28.3, c 2.1, acetone) is assigned for the (*S*) enantiomer with 98:2 er.[12]

(12) (a) Ruano, J. L. G.; Rodriguez-Fernández, M. M.; Maestro, M. C. *Tetrahedron* **2004**, *60*, 5701–5710. (b) Stymiest, J. L.; Bagutski1, V.; French, R. M.; Aggarwal, V. K. *Nature* **2008**, *456*, 778–783.



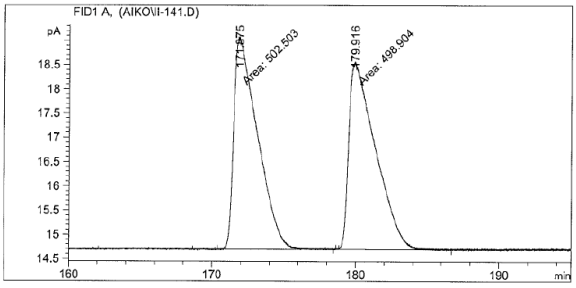
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	25.275	MM	0.2916	315.43250	18.03122	49.92807
2	26.075	MM	0.3422	316.34131	15.40611	50.07193



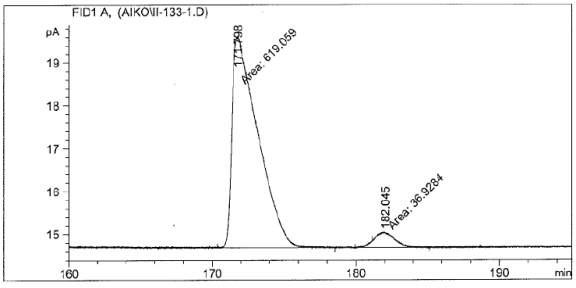
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	25.042	MM	0.3635	474.08286	21.73487	89.99486
2	26.200	MM	0.3060	52.70595	2.87089	10.00514

Retention time	Area	Area %	Retention time	Area	Area %
25.275	315.43250	49.92807	25.042	474.08286	89.99486
26.075	316.34131	50.07193	26.200	52.70595	10.00514

(*S*)-2-(Naphthalen-1-yl)but-3-en-2-ol (Table 3, entry 2): IR (neat): 3413 (b, w), 3086 (w), 3048 (w), 2975 (w), 2930 (w), 1598 (w), 1509 (w), 1453 (w), 1408 (w), 1395 (w), 1367 (w), 1265 (w), 1233 (w), 1162 (w), 1096 (m), 1068 (w), 1015 (w), 991 (m), 921 (m), 882 (w), 862 (w), 802 (m), 775 (s), 737 (w), 704 (w), 666 (w) 612 (w), 572 (w), 546 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.52-8.50 (1H, m), 7.87-7.85 (1H, m), 7.80 (1H, d, *J* = 8.2 Hz), 7.70 (1H, dd, *J* = 7.2, 1.0 Hz), 7.48-7.42 (3H, m), 6.40 (1H, dd, *J* = 17.4, 10.6 Hz), 5.28 (1H, d, *J* = 17.4 Hz), 5.22 (1H, d, *J* = 10.6 Hz), 2.09 (1H, br. s), 1.90 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.3, 141.3, 134.7, 130.7, 128.8, 128.8, 127.4, 125.2, 125.1, 124.8, 123.6, 113.7, 75.7, 29.8; HRMS (ESI+): Calcd for $C_{14}H_{13}$ [M-OH]: 181.1017, Found: 181.1016. All spectral data matched the published values (racemic compound).[13] $[\alpha]_D^{20}$ –16.6 (*c* = 1.00, $CHCl_3$) for an enantiomerically enriched sample of 94.4:5.6 er. Enantiomeric purity was determined by GLC analysis in comparison with authentic racemic material (94.4:5.6 er shown; CDB/DM column, 15 psi, 120 ºC).



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	171.875	MM	1.9002	502.50287	4.40741	50.17968
2	179.916	MM	2.1432	498.90421	3.87977	49.82032



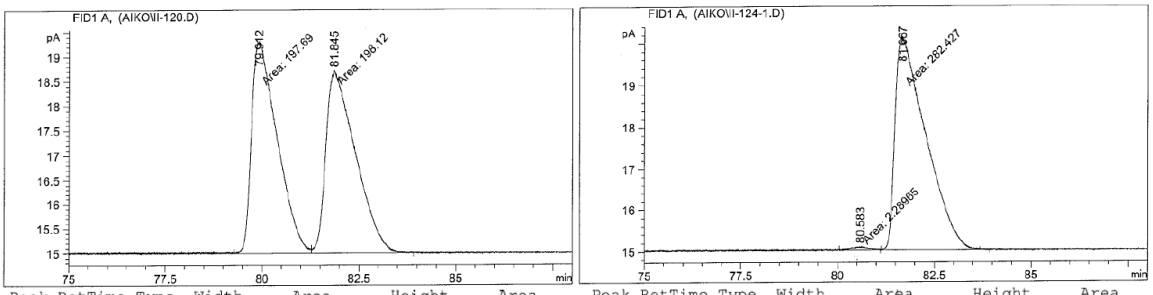
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	171.798	MM	2.0774	619.05872	4.96665	94.37055
2	182.045	MM	1.6708	36.92845	3.68371e-1	5.62945

Retention time	Area	Area %	Retention time	Area	Area %
171.875	502.50287	50.17968	171.798	619.05872	94.37055

(13) Roversi, E.; Vogel, P. *Helv. Chim. Acta* **2002**, *85*, 761–771.

179.916	498.90421	49.82032	182.045	36.92845	5.62945

(*S*)-2-(2-Bromophenyl)but-3-en-2-ol (Table 3, entry 3): IR (neat): 3441 (b, w), 3062 (w), 2978 (w), 2927 (w), 2850 (w), 1588 (w), 1563 (w), 1463 (w), 1428 (w), 1408 (w), 1370 (w), 1328 (w), 1268 (w), 1233 (w), 1206 (w), 1164 (w), 1130 (w), 1074 (w), 1044 (w), 1017 (m), 988 (w), 921 (m), 872 (w), 755 (s), 729 (m), 683 (w), 650 (w), 596 (w), 553 (w), 457 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.69 (1H, dd, *J* = 8.0, 1.8 Hz), 7.58 (1H, dd, *J* = 7.8, 1.4 Hz), 7.32 (1H, dt, *J* = 7.6, 1.4 Hz), 7.13 (1H, dt, *J* = 7.6, 1.8 Hz), 6.31 (1H, dd, *J* = 17.6, 10.4 Hz), 5.21 (1H, d, *J* = 0.8 Hz), 5.17 (1H, dd, *J* = 5.3, 0.8 Hz), 2.93 (1H, s), 1.80 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.2, 143.8, 134.9, 128.8, 127.9, 127.4, 121.3, 114.2, 75.5, 27.9; HRMS (ESI+): Calcd for $C_{10}H_{15}BrNO[M+NH_4]^+$: 244.03370, Found: 244.03358. $[\alpha]_D^{20}$ –19.2 (*c* = 1.00, $CHCl_3$) for an enantiomerically enriched sample of 99:1 er. Enantiomeric purity was determined by GLC analysis in comparison with authentic racemic material (99:1 er shown; CDB/DM column, 15 psi, 100 ºC).

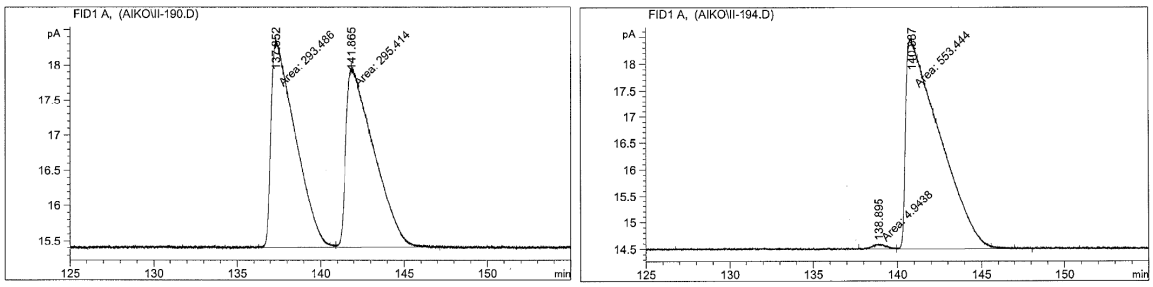


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	79.912	MF	0.7600	197.69003	4.33537	49.94566
2	81.845	FM	0.8862	198.12021	3.72622	50.05434

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	80.583	MM	0.4488	2.28965	8.50251e-2	0.80419
2	81.667	MM	0.9178	282.42691	5.12854	99.19581

Retention time	Area	Area %	Retention time	Area	Area %
79.912	197.69003	49.94566	80.583	2.28965	0.80419
81.845	198.12021	50.05434	81.667	282.42691	99.19581

(*S*)-2-(2-Chlorophenyl)but-3-en-2-ol (Table 3, entry 4): IR (neat): 3566 (w), 3426 (b, w), 3063 (w), 2979 (w), 2931 (w), 1638 (w), 1592 (w), 1567 (w), 1467 (w), 1432 (w), 1409 (w), 1370 (w), 1329 (w), 1271 (w), 1162 (w), 1134 (w), 1097 (w), 1035 (m), 989 (w), 921 (m), 874 (w), 755 (s), 738 (m), 731 (m), 689 (w), 660 (w), 596 (w), 555 (w), 466 (w), 418 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.68 (1H, dd, *J* = 7.6, 1.8 Hz), 7.36 (1H, dd, *J* = 7.6, 1.5 Hz), 7.30-7.20 (2H, m), 6.31 (1H, dd, *J* = 17.2, 10.7 Hz), 5.22-5.16 (2H, m), 2.81 (1H, s), 1.78 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.6, 142.8, 131.9, 131.2, 128.6, 127.5, 126.9, 113.7, 75.0, 27.7; HRMS (ESI+): Calcd for $C_{10}H_{10}Cl[M+H-H_2O]^+$: 165.04710, Found: 165.04647. $[\alpha]_D^{20}$ –23.4 (*c* = 1.00, $CHCl_3$) for an enantiomerically enriched sample of 99:1 er. Enantiomeric purity was determined by GLC analysis in comparison with authentic racemic material (99:1 er shown; CDB/DM column, 15 psi, 80 ºC).

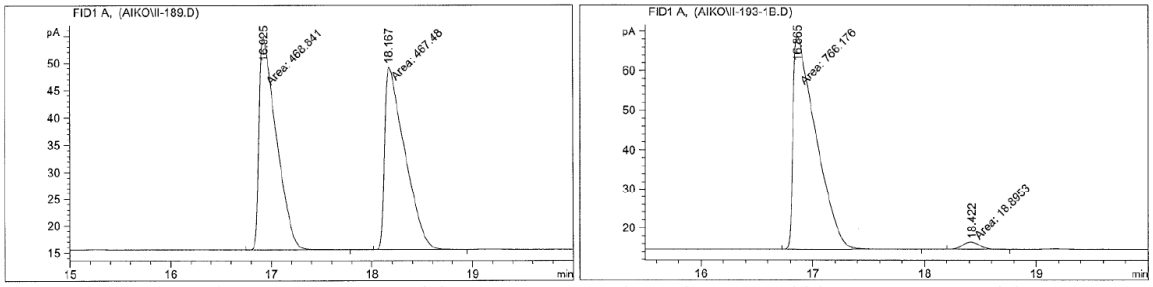


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	137.352	MF	1.6454	293.48584	2.97279	49.83628
2	141.865	FM	1.8744	295.41409	2.62681	50.16372

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	138.895	MF	0.8626	4.94380	9.55228e-2	0.88537
2	140.887	FM	2.3169	553.44440	3.98127	99.11463

Retention time	Area	Area %	Retention time	Area	Area %
137.352	293.43584	49.83628	138.895	4.94380	0.88537
141.865	295.41409	50.16372	140.887	553.44440	99.11463

(*S*)-2-(*o*-Tolyl)but-3-en-2-ol (Table 4, entry 5): IR (neat): 3397 (b, w), 3063 (w), 3015 (w), 2976 (w), 2930 (w), 1639 (w), 1602 (w), 1486 (w), 1455 (w), 1407 (w), 1367 (w), 1290 (w), 1213 (w), 1164 (w), 1129 (w), 1099 (m), 1049 (m), 993 (w), 917 (s), 876 (w), 794 (w), 760 (s), 728 (s), 702 (w), 676 (w), 614 (w), 558 (w), 462 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.54-7.50 (1H, m), 7.19-7.14 (3H, m), 6.18 (1H, dd, *J* = 17.4, 10.6 Hz), 5.20-5.13 (2H, m), 2.46 (3H, s), 1.80 (1H, s), 1.72 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.4, 143.3, 136.4, 132.3, 127.3, 125.7, 125.5, 112.9, 75.5, 29.0, 21.9; HRMS (ESI+): Calcd for $C_{11}H_{13}[M+H-H_2O]^+$: 145.10173, Found: 145.10113. $[\alpha]_D^{20}$ –19.8 (*c* = 1.00, $CHCl_3$) for an enantiomerically enriched sample of 98:2 er. Enantiomeric purity was determined by GLC analysis in comparison with authentic racemic material (98:2 er shown; CDB/DM column, 15 psi, 120 ºC).



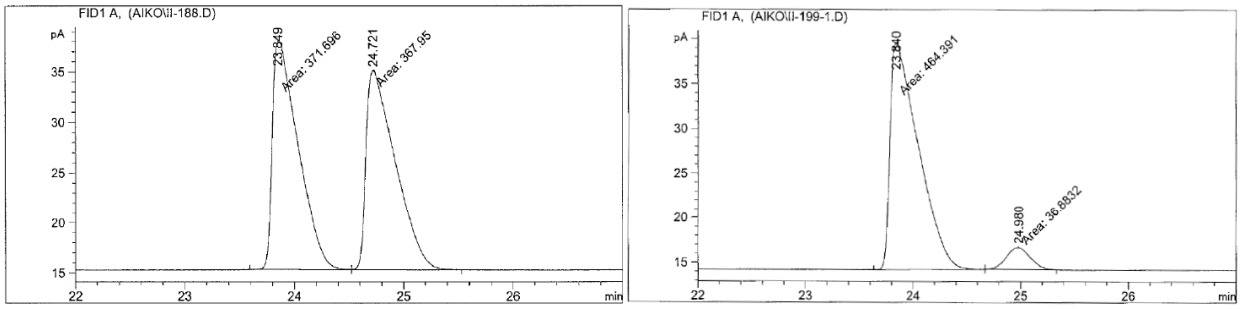
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	16.925	MM	0.1978	468.84094	39.50091	50.07267
2	18.167	MM	0.2312	467.48010	33.69860	49.92733

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	16.865	MM	0.2352	766.17639	54.28933	97.59317
2	18.422	MM	0.1721	18.89531	1.82994	2.40683

Retention time	Area	Area %	Retention time	Area	Area %
16.925	468.84094	50.07267	16.865	766.17639	97.59317
18.167	467.48010	49.92733	18.422	18.89531	2.40683

(*S*)-2-(*m*-Tolyl)but-3-en-2-ol (Table 3, entry 6): IR (neat): 3407 (br), 3087 (w), 2979 (w), 2925 (w), 2862 (w), 1640 (w), 1607 (w), 1588 (w), 1487 (w), 1451 (w), 1411 (w), 1367 (w), 1249 (w), 1170 (w), 1122 (w), 1092 (w), 1070 (w), 993 (m), 920 (s), 820 (w), 785 (s), 700 (s), 680 (w), 616

(w), 529 (w), 475 (w), 448 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.30-7.21 (3H, m), 7.09-7.06 (1H, m), 6.17 (1H, dd, *J* = 17.2, 10.6 Hz), 5.31 (1H, dd, *J* = 17.2, 1.2 Hz), 5.14 (1H, dd, *J* = 10.8, 1.2 Hz), 2.36 (3H, s), 1.86 (1H, s), 1.65 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.4, 144.9, 137.8, 128.1, 127.7, 125.8, 122.2, 112.2, 74.7, 29.3, 21.6; HRMS (ESI+): Calcd for $C_{11}H_{13}[M+H-H_2O]^+$: 145.10173, Found: 145.10185. $[\alpha]_D^{20}$ –13.7 (*c* = 1.00, $CHCl_3$) for an enantiomerically enriched sample of 93:7 er. Enantiomeric purity was determined by GLC analysis in comparison with authentic racemic material (93:7 er shown; CDB/DM column, 15 psi, 110 ºC).

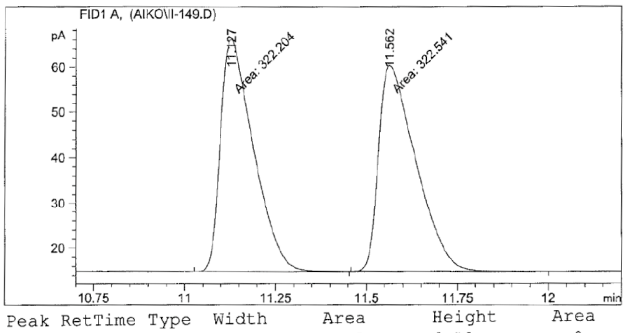


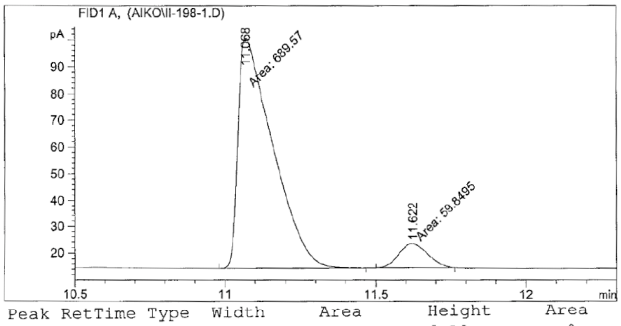
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	23.849	MF	0.2703	371.69626	22.92090	50.25326
2	24.721	FM	0.3093	367.94977	19.82698	49.74674

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	23.840	MM	0.3049	464.39145	25.38482	92.64212
2	24.980	MM	0.2491	36.88320	2.46790	7.35788

Retention time	Area	Area %	Retention time	Area	Area %
23.849	371.69626	50.25326	23.840	464.39145	92.64212
24.721	367.94977	49.74674	24.980	36.88320	7.35788

(*S*)-2-(*p*-Tolyl)but-3-en-2-ol (Table 4, entry 7): IR (neat): 3397 (b, w), 3087 (w), 2978 (w), 2924 (w), 2870 (w), 1641 (w), 1511 (w), 1450 (w), 1410 (w), 1367 (w), 1225 (w), 1183 (w), 1126 (w), 1105 (w), 1067 (w), 1019 (w), 993 (w), 918 (s), 875 (w), 816 (s), 725 (w), 701 (w), 655 (w), 579 (w), 536 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.38-7.35 (2H, m), 7.18-7.15 (2H, m), 6.17 (1H, dd, *J* = 17.2, 10.7 Hz), 5.30 (1H, dd, *J* = 17.2, 1.1 Hz), 5.14 (1H, dd, *J* = 10.8, 1.1 Hz), 2.56 (3H, s), 1.91 (1H, s), 1.65 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.0, 143.5, 136.6, 128.9, 125.1, 112.1, 74.6, 29.3, 20.9; HRMS (ESI+): Calcd for $C_{11}H_{13}[M+H-H_2O]^+$: 145.10173, Found: 145.10243. $[\alpha]_D^{20}$ –17.4 (*c* = 1.00, $CHCl_3$) for an enantiomerically enriched sample of 92:8 er. Enantiomeric purity was determined by GLC analysis in comparison with authentic racemic material (92:8 er shown; CDB/DM column, 15 psi, 130 ºC).



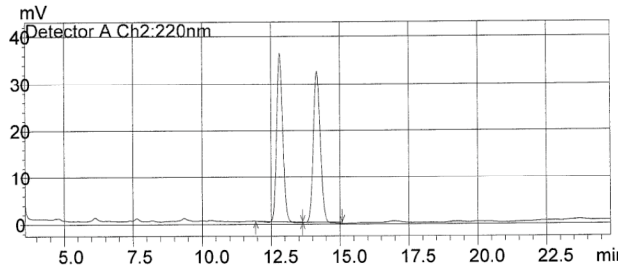


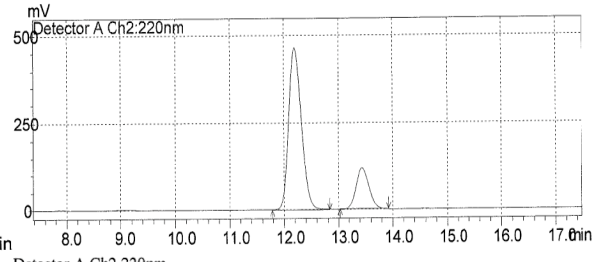
Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	11.127	MM	0.1051	322.20389	51.08350	49.97386
2	11.562	MM	0.1184	322.54102	45.42129	50.02614

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	11.068	MM	0.1334	689.57037	86.13609	92.01389
2	11.622	MM	0.1109	59.84953	8.99823	7.98611

Retention time	Area	Area %	Retention time	Area	Area %
11.127	322.20389	49.97386	11.068	689.57037	92.01389
11.562	322.54102	50.02614	11.622	59.84953	7.98611

(*S*)-3-Phenylpent-1-en-3-ol (13): IR (neat): 3455 (b, w), 3086 (w), 3060 (w), 3027 (w), 2969 (w), 2934 (w), 2879 (w), 1638 (w), 1601 (w), 1492 (w), 1447 (w), 1410 (w), 1377 (w), 1348 (w), 1262 (w), 1167 (w), 1101 (w), 1059 (w), 1030 (w), 975 (w), 917 (m), 905 (m), 787 (w), 759 (s), 698 (s), 614 (w), 557 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.46-7.42 (2H, m), 7.37-7.32 (2H, m), 7.27-7.22 (1H, m,), 6.19 (1H, dd, *J* = 17.2, 10.7 Hz), 5.30 (1H, dd, *J* = 17.2, 1.2 Hz), 5.17 (1H, dd, *J* = 10.6, 1.1 Hz), 2.02-1.86 (2H, m), 1.79 (11H, s), 0.85 (3H, t, *J* = 7.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.4, 144.1, 128.1, 126.8, 125.4, 112.7, 77.1, 34.6, 7.86; HRMS (ESI+): Calcd for $C_{11}H_{13}$ [M-OH]: 145.10173, Found: 145.10191. $[\alpha]_D^{20}$ –16.4 (*c* = 1.00, $CHCl_3$) for an enantiomerically enriched sample of 80:20 er. Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (80:20 er shown; Chiracel HPLC column OD(H)).





Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.815	559073	35980	50.365	52.704
2	14.162	550968	32288	49.635	47.296
Total		1110041	68268	100.000	100.000

Detector A Ch2 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.188	7652904	467243	80.348	80.009
2	13.435	1871820	116748	19.652	19.991
Total		9524724	583990	100.000	100.000

Retention time	Area	Area %	Retention time	Area	Area %
12.815	559073	50.365	12.188	7652904	80.348
14.162	550968	49.635	13.435	187120	19.652

Representative experimental procedure for enantioselective Cu-catalyzed substitution reaction of (*E*)-3-Cyclohexylbut-2-en-1-yl methyl carbonate with bis(pinacolato) diboron: (*R*)-2-(2-Cyclohexylbut-3-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (14): In an N_2-filled glovebox, an oven-dried vial (4 mL, 17 x 38 mm) with magnetic stir bar was charged with imidazolinium salt **4a** (6.0 mg, 0.012 mmol, 6.0 mol %), $Cu(OTf)_2$ (3.7 mg, 0.010 mmol, 5.0 mol %), NaOMe (8.8 mg, 0.16 mmol, 80 mol %) and DME (1.0 mL) under N_2 atmosphere. The mixture was sealed with a cap (phenolic open top cap with red PTFE/white silicone) and allowed to stir for 30 min. The color of the solution was clear blue. Bis(pinacolato)diboron (102 mg, 0.400 mmol, 2.0 equiv) was added to the solution. The color of the solution immediately turned dark brown. The vial was resealed with a cap (phenolic open top cap with red PTFE/white silicone). After 30 min the vial removed from the glove box and was allowed to cool to -30 ºC (cryocool), and stir for 10 min, and (*E*)-3-cyclohexylbut-2-en-1-yl methyl carbonate (42.5 mg, 0.200 mmol, 1.0 equiv) was added neat by syringe. The reaction was allowed to stir 24 h at -30 ºC. The solution was quenched by the addition of THF (reagent grade), was allowed to warm to 22 ºC, and passed through a short plug of celite and silica gel, eluting with Et_2O (3 x 2 mL). The filtrate was concentrated in vacuo to provide dark brown oil, which was purified by silica gel chromatography (0% →1% Et_2O in hexanes) to afford the allylic boronate, (*R*)-2-(2-cyclohexylbut-3-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**15**), as a colorless oil (30.8 mg, 0.200 mmol, >98% yield). IR (neat): 3081 (w), 2977 (w), 2923 (m), 2852 (w), 1626 (w), 1449 (w), 1410 (w), 1371 (w), 1341 (m), 1308 (s), 1271 (w), 1245 (w), 1232 (w), 1193 (w), 1165 (w), 1143 (s), 1110 (m), 1087 (m), 1037 (w), 1004 (w), 966 (w), 898 (m), 886 (w), 852 (m), 808 (w), 772 (w), 722 (w), 671 (w), 662 (w), 579 (w), 520 (w), 445 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.90 (1H, dd, *J* = 17.4, 10.8 Hz), 4.98 (1H, dd, *J* = 10.8, 1.6 Hz), 4.89 (1H, dd, *J* = 17.6, 1.6 Hz), 1.73-1.51 (5H, m), 1.30-0.94 (21H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.9, 111.5, 83.0, 44.2, 30.3, 29.8, 27.6, 27.1, 27.0, 26.8, 24.7, 24.5, 14.3; HRMS (ESI+): Calcd for $C_{16}H_{30}BO_2$[M+H]: 265.23388, Found: 265.23501. $[\alpha]_D^{20}$ –12.6 (*c* = 1.00, $CHCl_3$) for an enantiomerically enriched sample of 98:2 er (enatiomeric purity was comfirmed after oxidation to the alcohol (*S*)-2-cyclohexylbut-3-en-2-ol, page S-21).

(*R*)-2-(2-(2-Bromophenyl)but-3-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (15): IR (neat): 2976 (m), 2929 (w), 1466 (m), 1370 (m), 1315 (s), 1264 (m), 1141 (s), 1125 (s), 1082 (m), 1020 (m), 965 (m), 907 (m), 876 (m), 847 (m), 752 (m), 727 (m), 660 (m), 643 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.53 (1H, dd, *J* = 8.0, 1.2 Hz), 7.30−7.24 (2H, m), 7.05 (1H, ddd, *J* = 8.0, 6.4, 2.4 Hz), 6.26 (1H, dd, *J* = 17.6, 10.8 Hz), 5.21 (1H, dd, *J* = 10.4, 1.2 Hz), 5.03 (1H, dd, *J* = 17.2, 0.8 Hz), 1.40 (3H, s), 1.19 (6H, s), 1.18 (6H, s); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 145.9, 142.7, 133.2, 129.3, 127.6, 127.4, 125.0, 113.8, 83.6, 30.3, 24.8, 24.7, 20.6; HRMS (ESI+): Calcd for $C_{16}H_{23}BBrO_2$ [M+H]: 337.09745, Found: 337.09691. $[\alpha]_D^{20}$ –41.3 (*c* = 1.00, $CHCl_3$) for an enantiomerically enriched sample of 99:1 er (enatiomeric purity was comfirmed after oxidation to the alcohol (*S*)-2-(2-bromophenyl)but-3-en-2-ol, page S-23).