Supporting Information I:

Vinylogous Aldol Products From Chiral Crotylsilanes Obtained By Enantioselective Rh(II) and Cu(I) Carbenoid Si-H Insertion

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Part I: General information:

All reactions were carried out in oven or flame-dried glassware under argon atmosphere. $Rh_2(OAc)_4$ and sample Rh_2(*S*-DOSP)$_4$ were obtained from Strem. Triethylsilane, TMSOBn and dimethylphenylsilane was obtained from Gelest. *p*-Dodecylbenzene sulfonyl chloride was purchased from Wako Chemicals. $(Me_3Si)SiMe_2H$ was prepared by the literature procedure.[1] $(Me_3Si)_2SiMeH$ was prepared using Christoph's method.[2] 2,6-dichloro-4-decylbenzaldehyde was prepared by literature procedure.[3] All other reagents were purchased from Aldrich and used as supplied. CH_2Cl_2 and Et_2O were distilled over calcium hydride and stored over 4 Å molecular seives. THF was distilled over sodium and benzophenone. All other solvents used for chemical transformations were obtained from a dry solvent system (alumina) and used without further drying, unless otherwise noted. Reactions were magnetically stirred and monitored by thin layer chromatography with Sorbent Technologies 0.20 mm silica gel 60 Å plates. Flash chromatography was performed on Sorbent Technologies 32-63 μm 60 Å silica gel. Yields refer to chromatographically and spectroscopically pure compounds, unless otherwise noted. ^{1}H and ^{13}C NMR spectra were taken in $CDCl_3$ at 400 MHz and 75 MHz, respectively. Chemical shifts are reported in parts per million using the solvent internal standard (chloroform, 7.24 and 77.0 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d= doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet, br = broad), coupling constant, integration. Peaks for inseparable minor diasteromers are noted with an asterisk (*). Diastereomeric ratios were determined by ^{1}H NMR (400 MHz) analysis of crude mixtures, operating at signal/noise ratio of 200:1. Infrared resonance spectra were recorded on a Nexus 670 FT-IR spectrometer. Optical rotations were recorded on an Autopol III digital polarimeter at 589 nm and reported as follows: $[\alpha]_D^{20}$(concentration in g/100 mL solvent and solvent). High resolution mass-spectra were obtained on a Waters Q-TOF mass spectrometer at Boston University Chemical Instrumentation Center (CIC).

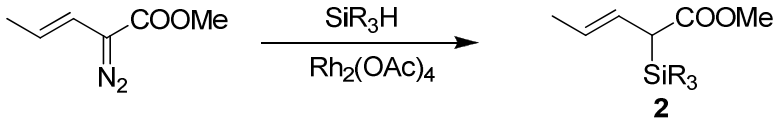
(1) Kumada, M.; Ishikawa, M.; Maeda, S. *J. Organomet. Chem.* **1964**, *2*, 478-484.

(2) (a) Marschner, C. *Eur. J. Inorg. Chem.* **1998**, 221-226. (b) Kayser, C.; Fischer, R.; Baumgartner, J.; Marschner, C. *Organometallics* **2002,** *21,* 1023-1030.

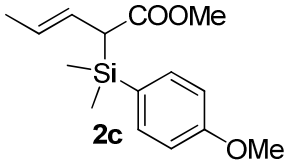
(3) (a) Eapen, K. C.; Dua S. S.; Tamborski, C. *J. Org. Chem.* **1984**, *49*, 478-482. (b) Lulinski, S.; Serwatowski, J. *J. Org. Chem.* **2003**, *68*, 5384-5387.

Part II Experimental procedures:

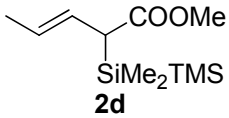
A. Preparation of racemic silane reagent 2



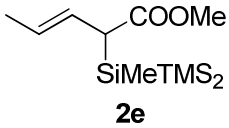
General procedure for the Rh(II) promoted Si-H insertion to vinyl diazo esters: To a stirred solution of silane (2.4 mmol, 1.2 equiv) and $Rh_2(OAc)_4$ (9 mg, 0.02 mmol, 0.01 equiv) in dry DCM (10 mL) was added the diazoester[4] (280 mg, 2 mmol, 1 equiv) in a solution of DCM (10 mL) dropwise at rt. The mixture was stirred at rt for another 20 min, and the solvent was evaporated under vacuum. Chromatography of the crude reaction mixture (gradient evolution using hexane, hexane/ethyl acetate 98:2) gave pure product **2**.



***rac*-(*E*)-Methyl 2-((4-methoxyphenyl)dimethylsilyl)pent-3-enoate (2c)**: Prepared using the general procedure. After chromatography on silica gel (hexane, 2% EtOAc in hexane), the desired product **2c** (384 mg, 69% yield) was isolated as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37(d, *J*=13.2Hz, 2H), 6.88(d, *J*=13.2Hz, 2H), 5.57(m, 1H), 5.20(m, 1H), 3.80(s, 3H), 3.50(s, 3H), 2.98(d, *J*=10.0Hz, 1H), 1.62(d, *J*=6.4Hz, 3H), 0.33(s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.7, 160.7, 135.4, 126.5, 124.9, 124.8, 113.4, 55.0, 51.0, 43.4, 17.9, -4.4, -4.4; IR (thin film) υ_{max} 2954, 1716, 1594, 1278, 1247, 1112, 810 cm^{-1}; HRMS(CI/NH_3) m/z calcd for $C_{15}H_{22}O_3NaSi$ $[M+Na]^+$ 301.1236, found 301.1288.



***rac*-(*E*)-Methyl 2-(1,1,2,2,2-pentamethyldisilyl)pent-3-enoate (2d):** Prepared using the general procedure. After chromatography on silica gel (hexane, 2% EtOAc in hexane), the desired product **2d** (264 mg, 54% yield) was isolated as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.62(m, 1H), 5.27(m, 1H), 3.62(s, 3H), 2.92(d, *J*=10.4Hz, 1H), 1.66(d, *J*=6.4Hz, 3H), 0.07(s, 15H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.0, 125.6, 124.2, 51.1, 41.7, 17.9, -2.1, -5.0, -5.2; IR (thin film) υ_{max} 2951, 2895, 1721, 1434, 1245, 1150, 833 cm^{-1}; HRMS(CI/NH_3) m/z calcd for $C_{11}H_{24}O_2NaSi_2$ $[M+Na]^+$ 267.1213, found 267.1237.



***rac*-(*E*)-Methyl 2-(1,1,1,2,3,3,3-heptamethyltrisilan-2-yl)pent-3-enoate (2e):** Prepared using the general procedure. After chromatography on silica gel (hexane, 2% EtOAc in hexane), the desired product **2e** (302 mg, 50% yield)

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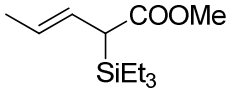
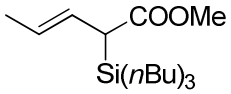
(4) For diazoester preparation, see: Davies, H. M.; Walji, A. M. *Angew. Chem. Int. Ed.* **2005**, *44*, 1733 –1735.

was isolated as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.63(m, 1H), 5.27(m, 1H), 3.61(s, 3H), 3.04(d, *J*=10.4Hz, 1H), 1.65(d, *J*=6.4Hz, 3H), 0.10(s, 21H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.4, 126.8, 123.7, 51.1, 39.3, 17.7, -0.8, -8.7; IR (thin film) υ_{max} 2950, 2893, 1721, 1244, 1151, 833, 779 cm^{-1}; HRMS(CI/NH_3) m/z calcd for $C_{13}H_{30}O_2NaSi_3$ $[M+Na]^+$ 325.1451, found 325.1428.



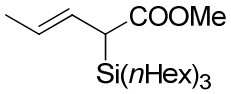
2f

***rac*-(*E*)-Methyl 2-(triethylsilyl)pent-3-enoate (2f):** Prepared using the general procedure. After chromatography on silica gel (hexane, 2% EtOAc in hexane), the desired product **2f** (296 mg, 65% yield) was isolated as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.65(m, 1H), 5.28(m, 1H), 3.62(s, 3H), 2.94(d, *J*=10.4Hz, 1H), 1.66(d, *J*=6.4Hz, 3H), 0.94(m, 9H), 0.58(m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.2, 125.5, 124.1, 51.1, 40.3, 18.0, 7.1, 2.4; IR (thin film) υ_{max} 2952, 2877, 1721, 1433, 1260, 1149, 730 cm^{-1}; HRMS(CI/NH_3) m/z calcd for $C_{12}H_{24}O_2NaSi$ $[M+Na]^+$ 251.1443, found 251.0996.



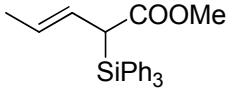
2g

***rac*-(*E*)-Methyl 2-(tributylsilyl)pent-3-enoate (2g):** Prepared using the general procedure. After chromatography on silica gel (hexane, 2% EtOAc in hexane), the desired product **2g** (424 mg, 68% yield) was isolated as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.60(m, 1H), 5.25(m, 1H), 3.60(s, 3H), 2.91(d, *J*=10.4Hz, 1H), 1.65(d, *J*=6.4Hz, 3H), 1.25(m, 12H), 0.85(m, 9H), 0.55(m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.2, 125.6, 124.1, 51.0, 40.8, 26.7, 25.6, 17.9, 13.7, 11.0; IR (thin film) υ_{max} 3900, 3745, 2403, 1700, 776 cm^{-1}; HRMS(CI/NH_3) m/z calcd for $C_{18}H_{36}O_2NaSi$ $[M+Na]^+$ 335.2382, found 335.2419.



2h

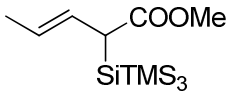
***rac*-(*E*)-Methyl 2-(trihexylsilyl)pent-3-enoate (2h)**: Prepared using the general procedure. After chromatography on silica gel (hexane, 2% EtOAc in hexane), the desired product **2h** (475 mg, 60% yield) was isolated as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.63(m, 1H), 5.27(dt, *J*=15.6, 6.8 Hz, 1H), 3.61(s, 3H), 2.91(d, *J*=10.0Hz, 1H), 1.62(d, *J*=6.8Hz, 3H), 0.35(s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.3, 135.7, 133.9, 129.2, 127.4, 125.0,124.5, 67.0, 43.0, 21.8, 21.5, 17.8, -4.5, -4.7; IR (thin film) υ_{max} 3071, 2977, 1709, 1428, 1249, 1106, 698 cm^{-1}; HRMS(CI/NH_3) m/z calcd for $C_{24}H_{48}O_2NaSi$ $[M+Na]^+$ 419.3321, found 419.2748.



2i

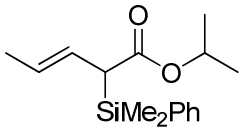
***rac*-(*E*)-Methyl 2-(triphenylsilyl)pent-3-enoate (2i)**: Prepared using the general procedure. After chromatography on silica gel (hexane, 2% EtOAc in hexane), the desired product **2i** (655 mg, 88% yield) was isolated as a white solid. Melting point: 118-120 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58(m, 6H), 7.39(m, 9H), 5.70(m, 1H), 5.33(m, 1H), 3.72(d,

J=10.0Hz, 1H), 3.32(s, 3H), 1.57(d, *J*=6.4Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.6, 136.3, 132.4, 129.8, 127.7, 127.1,124.9, 51.1, 41.9, 18.0; IR (thin film) υ_{max} 3070, 2948, 2913, 1717, 1427, 1107, 695 cm^{-1}; HRMS(CI/NH_3) m/z calcd for $C_{24}H_{24}O_2NaSi$ $[M+Na]^+$ 395.1443, found 395.1489.



2j

***rac*-(*E*)-Methyl 2-(1,1,1,3,3,3-hexamethyl-2-(trimethylsilyl)trisilan-2-yl)pent-3-enoate (2j):** Prepared using the general procedure. After chromatography on silica gel (hexane, 2% EtOAc in hexane), the desired product **2j** (346 mg, 48% yield) was isolated as a white solid. Melting point: 169-171 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.62(m, 1H), 5.27(m, 1H), 3.60(s, 3H), 3.13(d, *J*=10.8Hz, 1H), 1.63(d, *J*=6.4Hz, 3H), 0.18(s, 27H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.0, 128.6, 123.4, 51.3, 36.1, 17.9, 1.4; IR (thin film) υ_{max} 2952, 2896, 1722, 1219, 1059, 772 cm^{-1}; HRMS(CI/NH_3) m/z calcd for $C_{15}H_{36}O_2NaSi_4$ $[M+Na]^+$ 383.1690, found 383.1658.

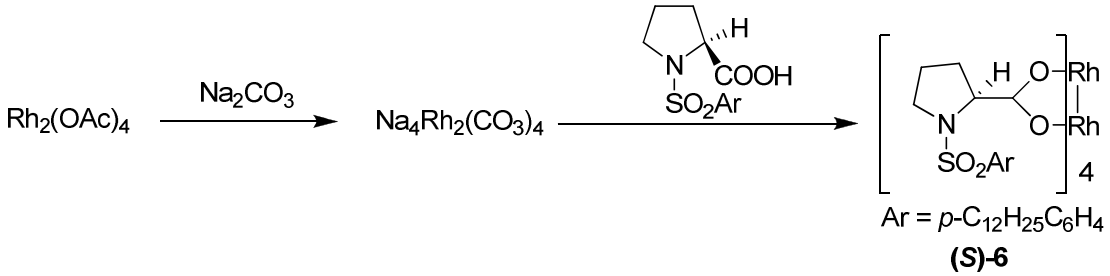


2k

***rac*-(*E*)-Isopropyl 2-(dimethyl(phenyl)silyl)pent-3-enoate (2k):** To a stirred solution of diazoisopropylester (336 mg, 2 mmol, 1 equiv) and dimethylphenylsilane (372 *u*L, 2.4 mmol, 1.2 equiv) in dry CH_2Cl_2 (20 mL) was added at rt $Rh_2(OAc)_4$ (9 mg, 0.02 mmol, 1% equiv). The mixture was stirred at rt for 20 min, and the solvent was evaporated in vacuo. Chromatography of the crude reaction mixture (hexane, hexane/ethyl acetate 98:2) gave pure product **2k** (341 mg, 62% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46(m, 2H), 7.33(m, 3H), 5.58(dd, *J*=16.8, 10.0 Hz, 1H), 5.19(dt, *J*=16.8, 6.4 Hz, 1H), 4.84(m, 1H), 2.96(d, *J*=10.4Hz, 1H), 1.62(d, *J*=6.4Hz, 3H), 1.11(d, *J*=6.4Hz, 3H), 0.98(d, *J*=6.4Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.3, 135.7, 133.9, 129.2, 127.4, 125.0,124.5, 67.0, 43.0, 21.8, 21.5, 17.8, -4.5, -4.7; IR (thin film) υ_{max} 3071, 2977, 1709, 1428, 1249, 1106, 698 cm^{-1}; HRMS(CI/NH_3) m/z calcd for $C_{16}H_{24}O_2NaSi$ $[M+Na]^+$ 299.1443, found 299.1432.

B. Preparation of enantioenriched silane reagent 2

i. Preparation of **(*S*)-6**.



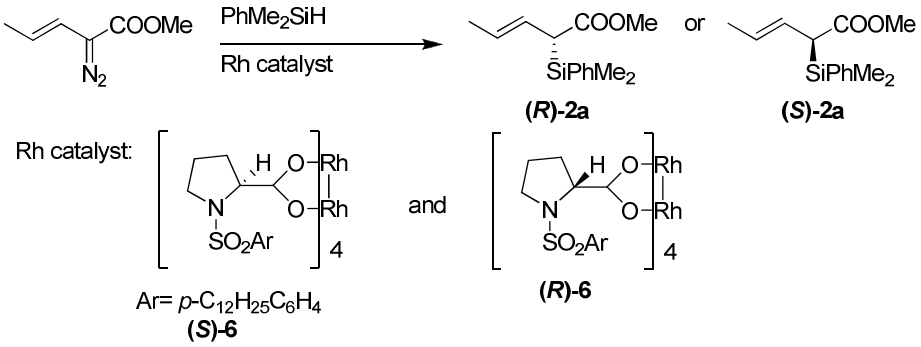
(*S*)-6

To a stirred solution of $Rh_2(OAc)_4$ (250 mg, 0.57 mmol) in H_2O (7 mL) was added at rt Na_2CO_3 (1.48 g 14 mmol). The mixture was stirred at 90 °C for 2 hours, during

which time the catalyst color changed from green to blue. Then, the reaction mixture was cooled in ice and filtered. The blue solid was gradually washed by H_2O (1 mL), MeOH (10 mL), dry ether (10 mL). Vacuum dry afforded $Na_4Rh_2(CO_3)_4$ (294 mg, 96% yield), which was then added in 27 mL H_2O and *p*-dodecylbenzene sulfonyl acid (1.86 g, 4.4 mmol, 8 equiv). The mixture was stirred at 95 °C for 2 hours, during which time the catalyst color change from blue back to green. The reaction was cooled to room temperature and added to 100 mL DCM. The mixture was then washed sequentially with saturated $NaHCO_3$ and brine, dried (Na_2SO_4), and then concentrated *in vacuo*. The crude reaction mixture was purified on silica using ether/petroleum ether (50/50, 60/40, 70/30) to afford product **(*S*)-6** as a green crystal (574 mg, 55% yield). Spectral data was in complete agreement with the literature report, see: Davies, H. M.; Bruzinski, P. R.; Lake, D. H.; Kong N.; Fall M. J. *J. Am. Chem. Soc.* **1996,** *118,* 6897-6907.

ii. Optimization of conditions for preparation of enantioenriched silane ***2a****:*

Table 1*: Preparation of enantioenriched α-dimethylphenyl-(E)-pentenoate*



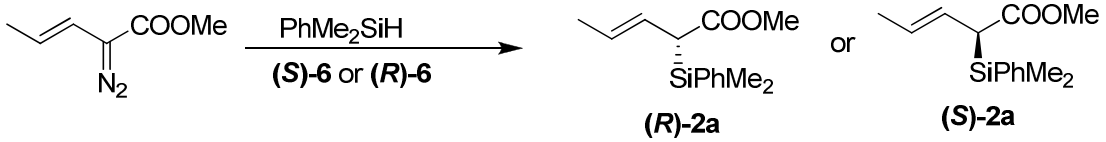
entry	catalyst loading	equiv of silane	yield[a]	ee[b]
1	1%	1.5	65%	48%
2	1%	5	70%	88%
3	2%	5	68%	93%
4	3%	5	72%	95-97%

a) Isolated yields were determined after purification over silica gel.
b) Based on HPLC data (ChiralCel OD 1%IPA) of primary alcohol derived from reduction of the methyl ester with LAH.

Excess dimethylphenyl silane was crucial to obtain product with high ee (Table 1, entry 1 and 2). The enantiomeric excesses were measured on the reduced alcohols by HPLC (ChiralCel OD, 1% IPA), assuming that no racemization had occurred during the reduction of the ester function. Further investigation revealed that higher catalyst loading afforded silane reagents with higher ee up to 97% (entry 3 and 4). This silane reagent could be purified by chromatography and stored at 4 °C for one month without evidence of decomposition.

iii. Procedure for preparation of enantioenriched silanes **(*R*)-2a and (*S*)-2a** *using*

$Rh_2(DOSP)_4$:



(R)-2a **(S)-2a**

(*R*,*E*) and (*S*,*E*)-Methyl 2-(dimethyl(phenyl)silyl)pent-3-enoate ((*R*)-2a and (*S*)-2a): To a stir solution of Rh_2(*S*-DOSP)$_4$ (190 mg, 0.1 mmol, 0.02 equiv) in pentane (5 mL, molecular sieves dried overnight before using) was added dimethylphenylsilane (3.88 mL, 25 mmol, 5 equiv). The mixture was cooled to -78 °C, and diazo ester (700 mg, 5 mmol, 1 equiv) in pentane (5 mL) was added dropwise over a period of 10 min. The mixture was stirred at -75 °C for 24 hours and concentrated *in vacuo*. Chromatography on silica gel (hexane, hexane/ethyl acetate 98:2) afforded **(*R*)-2a** (843 mg, 68% yield) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45(m, 2H), 7.34(m, 3H), 5.56(dd, *J*=15.6, 10.0 Hz, 1H), 5.19(dt, *J*=15.6, 6.8 Hz, 1H), 3.49(s, 3H), 3.00(d, *J*=10.0Hz, 1H), 1.62(d, *J*=6.8Hz, 3H), 0.35(s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.5, 135.7, 133.9, 129.4, 127.6, 124.9,124.7, 51.0, 43.2, 17.9, -4.6, -4.6; $[\alpha]_D^{20}$ +37.5 (c = 2.2, CH_2Cl_2); IR (thin film) υ_{max} 3071, 2951, 1717, 1428, 1250, 1149, 698 cm^{-1}; HRMS(CI/NH_3) m/z calcd for $C_{14}H_{20}O_2NaSi$ $[M+Na]^+$ 271.1130, found 271.1162. Using the racemic versions of **2a**, the baseline separation by HPLC could not be achieved. To check the product's % ee, **(*R*)-2a** was reduced to the primary alcohol using LAH in diethyl ether, and HPLC (ChiralCel OD, 1% IPA/Hexane, 1 mL/min, t_R 15.5 min, t_S 11.6 min) showed 93% ee. Catalyst Rh_2(*R*-DOSP)$_4$ afforded product **(*S*)-2a** with the same yield and ee. **(*S*)-2a**: $[\alpha]_D^{20}$ -22.3 (c = 0.7, CH_2Cl_2).

Waters

Project Name: Jie
Reported by User: Panek_Labs

Breeze

SAMPLE INFORMATION

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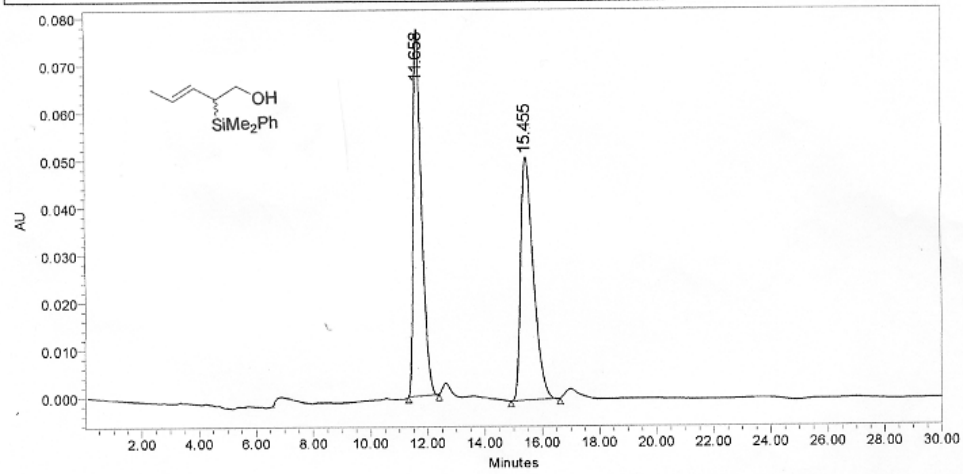
Vial:	10	Acq. Method:	01% IPA
Injection #:	1	Date Processed:	11/7/2007 3:37:07 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	30.00 Minutes	Sample Set Name:	racemic sioh again



	RT (min)	Area (µV*sec)	% Area	Height (µV)	% Height
1	11.658	1559080	49.74	77440	60.22
2	15.455	1575115	50.26	51153	39.78

Waters

Project Name: Jie
Reported by User: Panek_Labs

Breeze

SAMPLE INFORMATION

Sample Name:	fromdiol	Acquired By:	Panek_Labs
Sample Type:	Unknown	Date Acquired:	4/1/2008 3:53:31 PM
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Injection #:	1	Date Processed:	4/1/2008 5:04:37 PM
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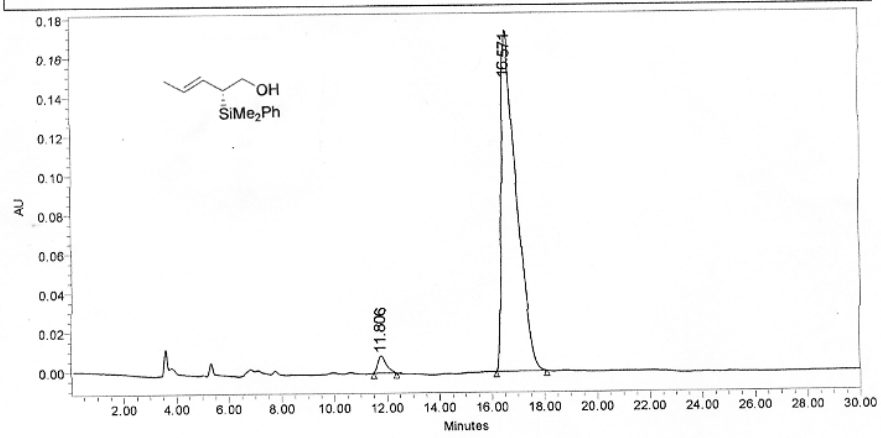
Run Time:	30.00 Minutes	Sample Set Name:	silanefromdiol



	RT (min)	Area (µV*sec)	% Area	Height (µV)	% Height
1	11.806	189595	2.70	8703	4.76
2	16.571	6821795	97.30	174058	95.24

Project Name: JasonWu
Reported by User: System

Breeze

SAMPLE INFORMATION

Sample Name:	econo	Acquired By:	System
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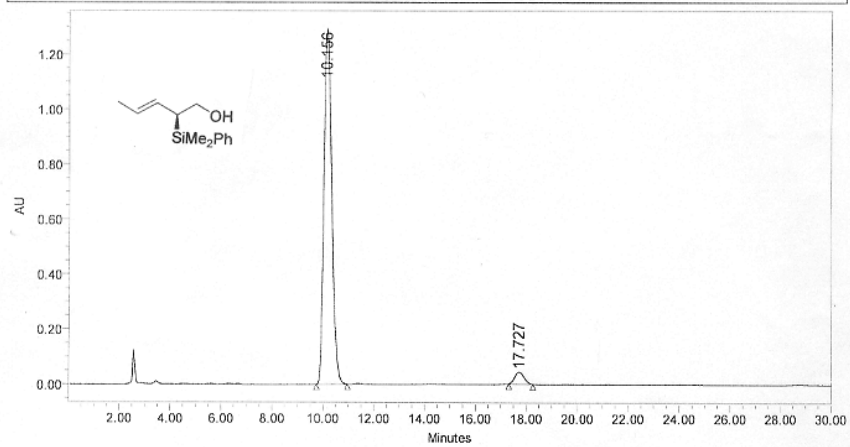
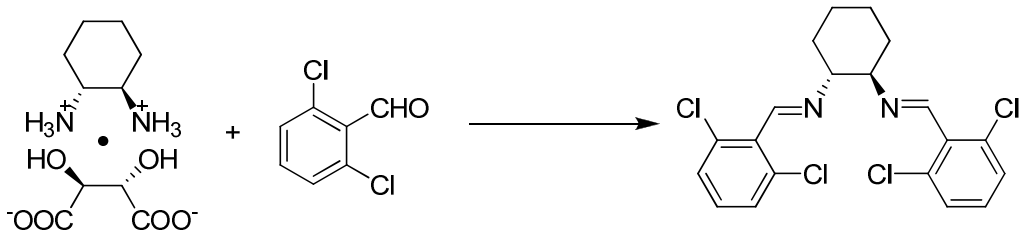
Injection #:	1	Date Processed:	6/2/2008 1:59:43 PM
Injection Volume:	10.00 ul	Channel Name:	2487Channel 2
Run Time:	30.00 Minutes	Sample Set Name:	econo

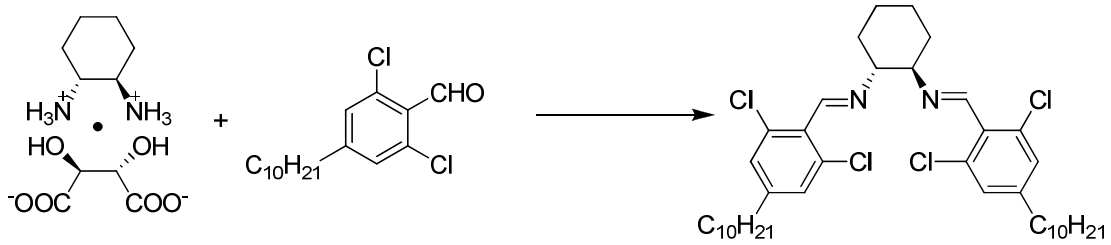


	RT (min)	Area (µV*sec)	% Area	Height (µV)	% Height
1	10.156	27652303	96.29	1293629	96.79
2	17.727	1066745	3.71	42857	3.21

iv. Procedure for preparation of diimine ligand:



(1*R*,2*R*,N^1*E*,N^2*E*)-N^1,N^2-*bis*(2,6-Dichlorobenzylidene)cyclohexane-1,2-diamine: (*R*, *R*)-1,2-diammoniumcyclohexane mono-(+)-tartrate salt[5] (2.97 g, 11.2 mmol, 1 equiv) was added to a 200 mL round bottom flask equipped with a stir bar, followed by adding K_2CO_3 (3.12 g, 22.5 mmol, 2 equiv) and distilled water (15 mL). The mixture was stirred for 30 min, and EtOH (60 mL) was added. Then a solution of 2,6-dichlorobenzaldehyde (3.92 g, 22.5 mmol, 2 equiv) in EtOH (25 mL) was added dropwise. The flask was equipped with a reflux condenser and the resulting mixture was refluxed for 2 hours before being diluted by water (20 mL). The resulting mixture was cooled to ice bath for 1 hour. The product was collected by vacuum filtration and washed with EtOH (2 x 10 mL). The crude solid was redissolved in DCM (50 mL) and washed with water (2 x 30 mL). After drying over $MgSO_4$, the solvent was removed to afford product as a white solid (4.2 g, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45(s, 2H), 7.26(d, *J*=2.0 Hz, 2H), 7.13(m, 4H), 3.58(m, 2H), 1.87(m, 6H), 1.49(m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.6, 134.8, 132.9, 129.9, 128.6, 74.9, 32.9, 24.2; $[\alpha]_D^{20}$ +18.3 (c = 1.6, CH_2Cl_2); IR (thin film) υ_{max} 2930, 2859, 1646, 1430, 772 cm^{-1}; HRMS(CI/NH_3) m/z calcd for $C_{20}H_{19}Cl_4N_2$ $[M+H]^+$ 427.0302, found 427.0313.

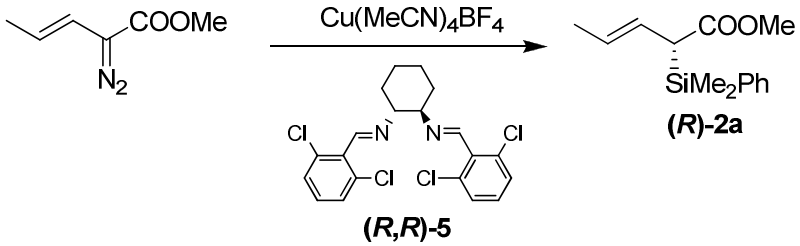


(1*R*,2*R*,N^1*E*,N^2*E*)-N^1,N^2-*bis*(2,6-Dichloro-4-decylbenzylidene)cyclohexane-1,2-dia mine: (*R*, *R*)-1,2-diammoniumcyclohexane mono-(+)-tartrate salt (265 mg, 1 mmol, 1 equiv) was added to a 20 mL round bottom flask equipped with a stir bar, followed by adding K_2CO_3 (279 mg, 2 mmol, 2equiv) and distilled water (1.3 mL). The mixture was stirred for 30 min, and EtOH (5.5 mL) was added. Then a solution of 2,6-dichloro-4-decylbenzaldehyde (628 mg, 2 mmol, 2 equiv) in EtOH (2.2 mL) was added dropwise. The flask was equipped with a reflux condenser and the resulting mixture was refluxed for 2 hours before being diluted by water (1.5 mL). The mixture was cooled to ice bath for 1 hour. The product was collected by vacuum filtration and washed with EtOH (2 x 1 mL). The crude solid was redissolved in DCM (5 mL) and washed with water (2 x 3 mL). After drying over $MgSO_4$, the solvent was removed to

(5) For tartrate salt preparation, see: Larrow J. F.; Jacobsen, E. N. *J. Org. Chem.* **1994**, *59*, 1939-1942.

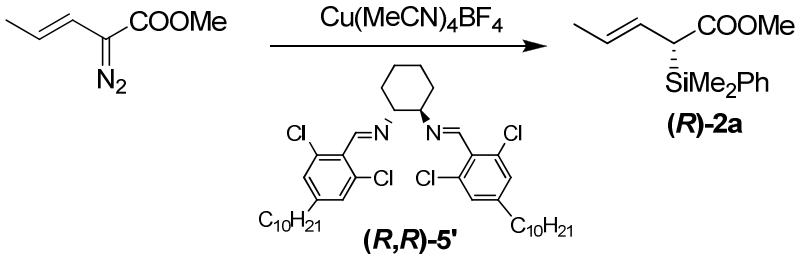
afford product as a white solid (560 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42(s, 2H), 7.06(s, 4H), 3.54(m, 2H), 2.50(t, *J*=12.5 Hz, 4H), 1.85(m, 6H), 1.53(m, 6H), 1.23(m, 28H), 0.87(t, *J*=10.5 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.6, 145.7, 134.5, 130.1, 128.6, 74.9, 35.1, 32.9, 31.9, 30.7, 29.6, 29.5, 29.4, 29.3, 29.0, 24.3, 22.7, 14.1; $[\alpha]_D^{20}$ +29.2 (c = 0.7, CH_2Cl_2); IR (thin film) υ_{max} 2926, 2855, 1647, 1465 cm^{-1}; HRMS(CI/NH_3) m/z calcd for $C_{40}H_{59}Cl_4N_2$ $[M+H]^+$ 707.3432, found 707.3414.

v. Procedure for preparation of enantioenriched silanes ***2a*** *using Cu(I) complexe*:



(*R*,*R*)-5

To a round-bottom flask charged with a stir bar was added $[Cu(CH_3CN)_4](BF_4)$ (157 mg, 0.5 mmol, 0.05 equiv) and the dichlorodiimine ligand (300 mg, 0.7 mmol, 0.07 equiv). The mixture was dissolved in benzene (25 mL), and the resulting heterogeneous yellow solution was allowed to stir at room temperature for 30 min to form diimine copper complex **(*R*,*R*)-5**. To this mixture was added via syringe dimethylphenylsilane (7.76 mL, 50 mmol, 5 equiv), which was then cooled to 0 °C. To the cooled reaction mixture was slowly added a solution of diazo ester (1.4 g, 10 mmol, 1 equiv) in benzene (25 mL) in one hour by syringe pump. The mixture was allowed to stir at 0 °C for another 12 hours before flushed through a thin pad of silica gel to remove the catalyst. The resulting solution was then concentrated under vacuum. The crude product was purified by silica chromatography, hexane eluant recovered dimethylphenylsilane, using 1% ethyl acetate/hexanes as eluant afforded **(*R*)-2a** as a yellow oli (1.25 g, 5.01 mmol, 50% yield). To check its % ee, **(*R*)-2a** was reduced to the primary alcohol by LAH in diethyl ether, and HPLC (ChiralCel OD, 1% IPA/Hexane, 1 mL/min, t_R 15.5 min, t_S 11.6 min) showed 72% ee.

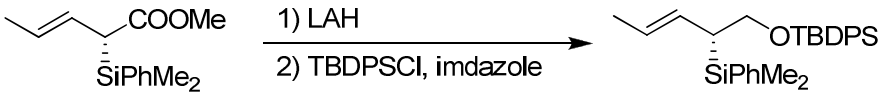


(*R*,*R*)-5'

To a round-bottom flask charged with a stir bar was added $[Cu(CH_3CN)_4](BF_4)$ (157 mg, 0.5 mmol, 0.05 equiv) and the decyldichloro diimine ligand (534 mg, 0.7 mmol, 0.07 equiv). The mixture was dissolved in benzene (25 mL), and the resulting homogeneous yellow solution was allowed to stir at room temperature for 30 min to form diimine copper complex **(*R*,*R*)-5'**. To this solution was added via syringe

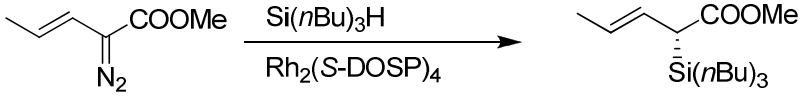
dimethylphenylsilane (7.76 mL, 50 mmol, 5 equiv), which was then cooled to 0 °C. To the cooled reaction mixture was slowly added a solution of diazo ester (1.4 g, 10 mmol, 1 equiv) in benzene (25 mL) in one hour by syringe pump. The solution was allowed to stir at 0 °C for another 12 hours before flushed through a thin pad of silica gel to remove the catalyst. The resulting solution was then concentrated under vacuum. The crude product was purified by silica chromatography, hexane eluant recovered dimethylphenylsilane, using 1% ethyl acetate/hexanes as eluant afforded **(*R*)-2a** as a yellow oli (1.3 g, 5.21 mmol, 52% yield). To check its % ee, **(*R*)-2a** was reduced to the primary alcohol by LAH in diethyl ether, and HPLC (ChiralCel OD, 1% IPA/Hexane, 1 mL/min, t_R 15.5 min, t_S 11.6 min) showed 78% ee.

*vi. Procedure for preparation of enantioenriched silanes **2b**, **2g**, **2i***:



(*R*)-2a **(*R*)-2b**

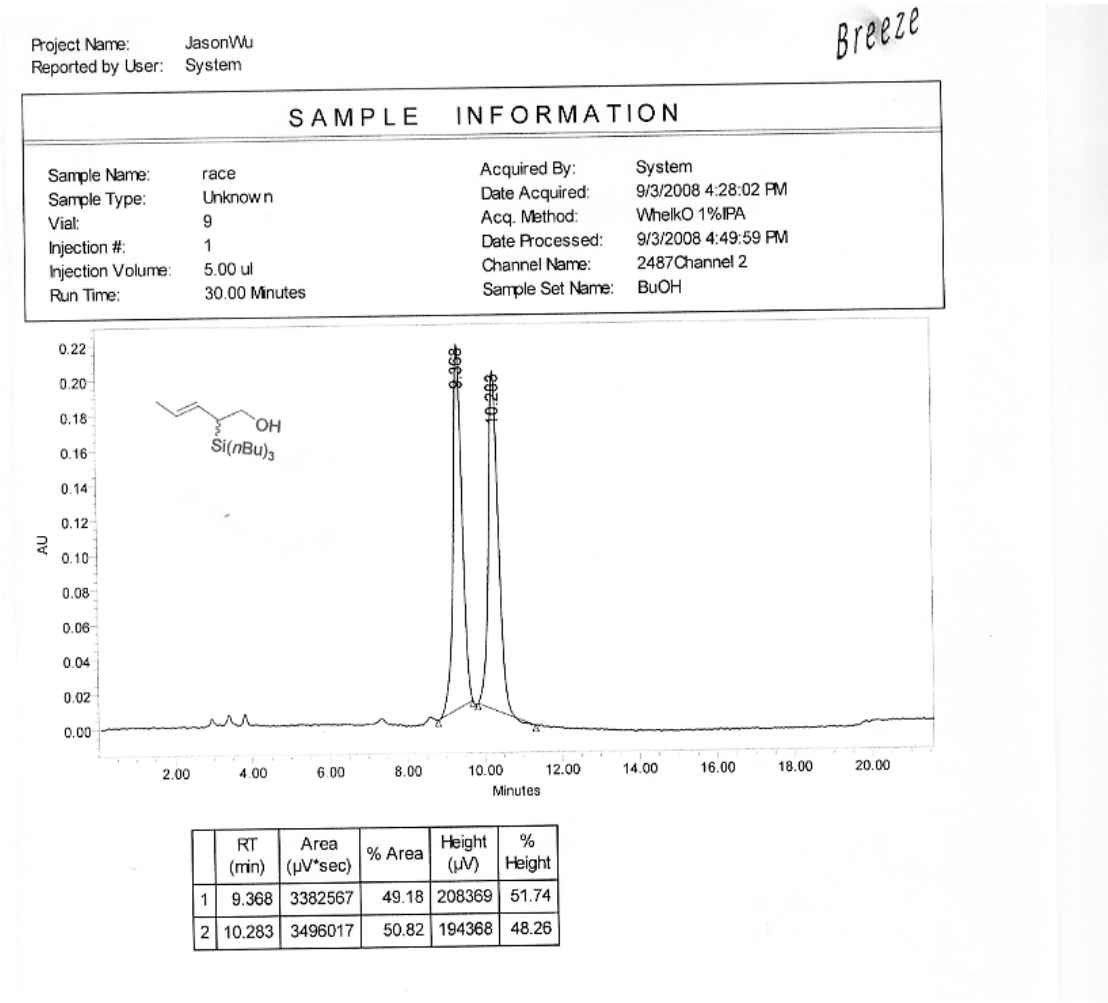
(*R,E*)-1-((1-(*tert*-Butyldiphenylsilyloxy)pent-3-en-2-yl)dimethylsilyl)benzene ((*R*)-2b): To a solution of **(*R*)-2a** (1.24 g, 5 mmol, 1 equiv) in ether (50 mL) was added LAH (570 mg, 15 mmol, 3 equiv) at 0 °C. The mixture was continue stirred at 0 °C for 2 hours, and quenched by water carefully. The mixture then was filtered and organic layer was concentrated *in vacuo*. The residue was added in DMF (10 mL), TBDPSCl (1.64 g, 6 mmol, 1.2 equiv) and imidazole (1.02 g, 15 mmol, 3 equiv). The resultant solution was stirred at rt for 12 hours, followed by adding water (20 mL) and extracting with hexane (3 x 20 mL). The organic layer was combined and concentrated under reduced pressure. Purification of the crude product by chromatography on silica gel afforded **(*R*)-2b** (2.08 g, 91% yield over two steps) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57(m, 4H), 7.39(m, 4H), 7.31(m, 7H), 5.32(dd, *J*=15.2, 9.2 Hz, 1H), 5.22(dt, *J*=15.2, 6.0 Hz, 1H), 3.71(m, 2H), 1.95(m, 1H), 1.62(d, *J*=6.0Hz, 3H), 0.97(s, 9H), 0.22(s, 3H), 0.20(s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.9, 135.7, 135.6, 134.0, 133.9, 129.7, 129.4, 129.3, 128.8, 127.6, 127.5, 124.4, 64.8, 36.9, 26.9, 19.2, 18.2, -3.6, -4.2; $[\alpha]_D^{20}$ -6.0 (c = 1.9, CH_2Cl_2); IR (thin film) υ_{max} 3069, 3014, 2959, 2856, 1427, 1110, 1064, 811, 698 cm^{-1}; HRMS(CI/NH_3) m/z calcd for $C_{29}H_{38}ONaSi_2$ $[M+Na]^+$ 481.2359, found 481.2385.



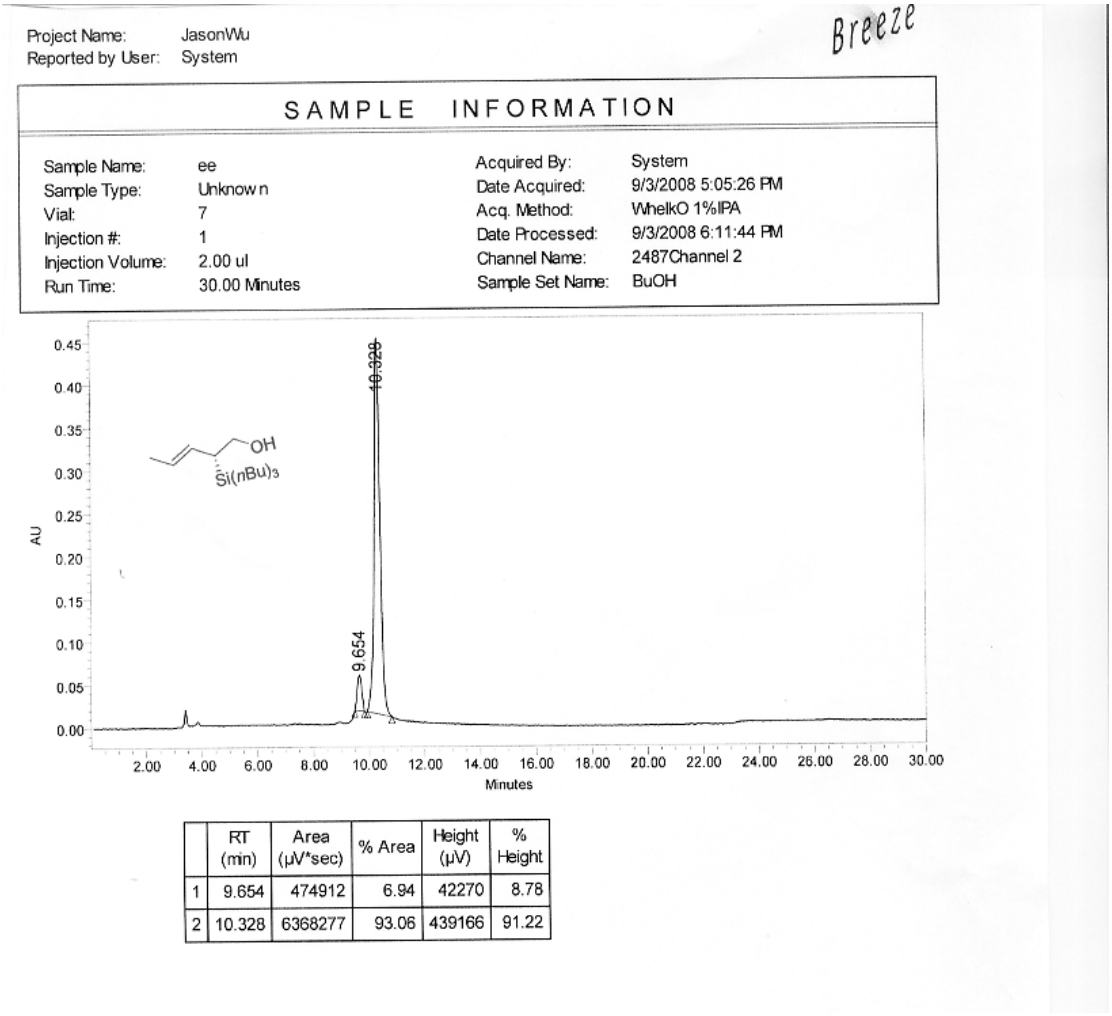
(*R*)-2g

(*R,E*)-Methyl 2-(tributylsilyl)pent-3-enoate ((*R*)-2g): To a stir solution of Rh_2(*S*-DOSP)$_4$ (190 mg, 0.1 mmol, 0.02 equiv) in pentane (5 mL) was added tributylsilane (6.48 mL, 25 mmol, 5 equiv). The mixture was cooled to -78 °C, and diazo ester (700 mg, 5 mmol, 1 equiv) pentane solution (5 mL) was added dropwise.

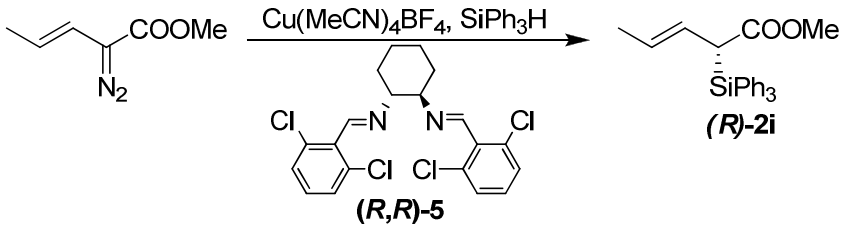
The mixture was stirred at -75 °C for 24 hours and concentrated in vacuo. Chromatography on silica gel (hexane, hexane/ethyl acetate 98:2) afforded **(*R*)-2g** (748 mg, 48% yield) as a light yellow oil. $[\alpha]_D^{20}$ +13.4 (c = 1.2, CH_2Cl_2). To check its % ee, **(*R*)-2g** was reduced to the primary alcohol by LAH in diethyl ether, and HPLC (WhelkO, 1% IPA/Hexane, 1 mL/min, t_R 10.3 min, t_S 9.6 min) showed 86% ee.



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	9.368	3382567	49.18	208369	51.74
2	10.283	3496017	50.82	194368	48.26

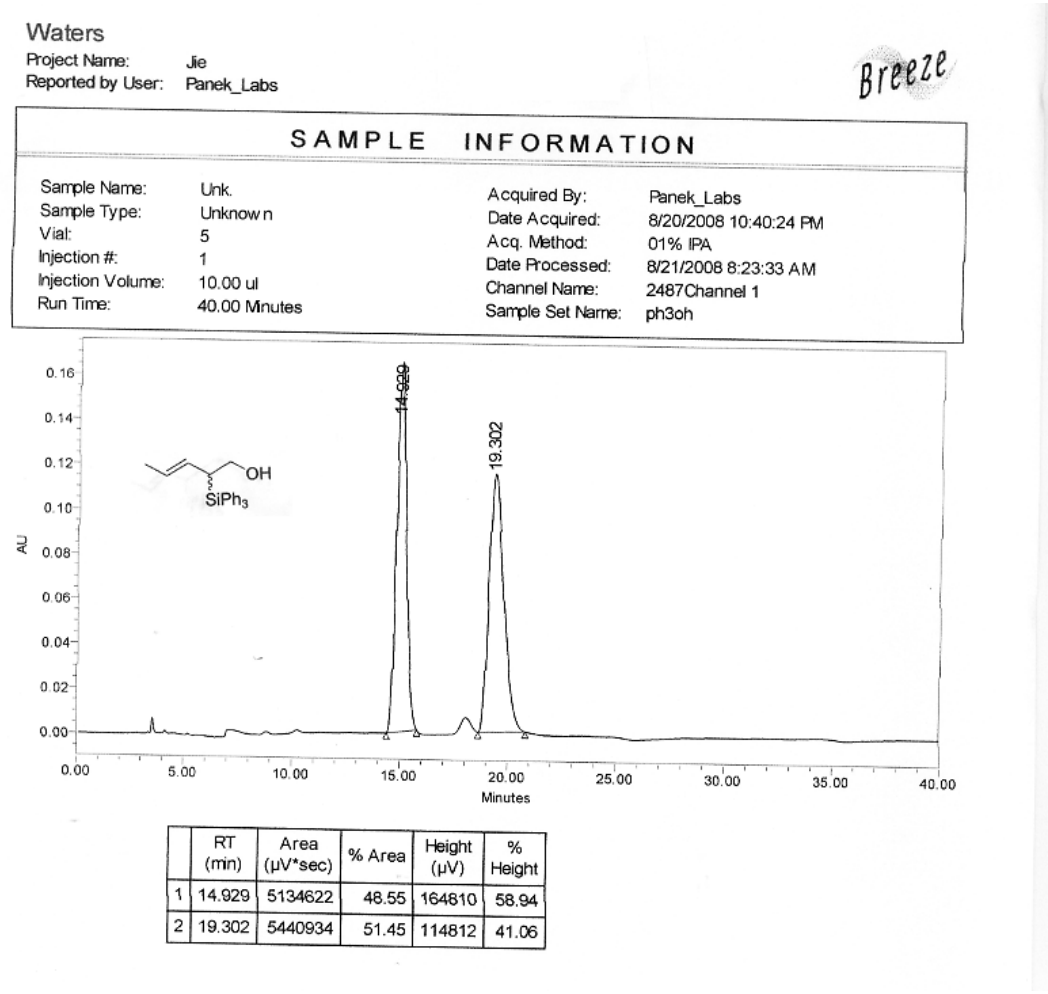


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	9.654	474912	6.94	42270	8.78
2	10.328	6368277	93.06	439166	91.22

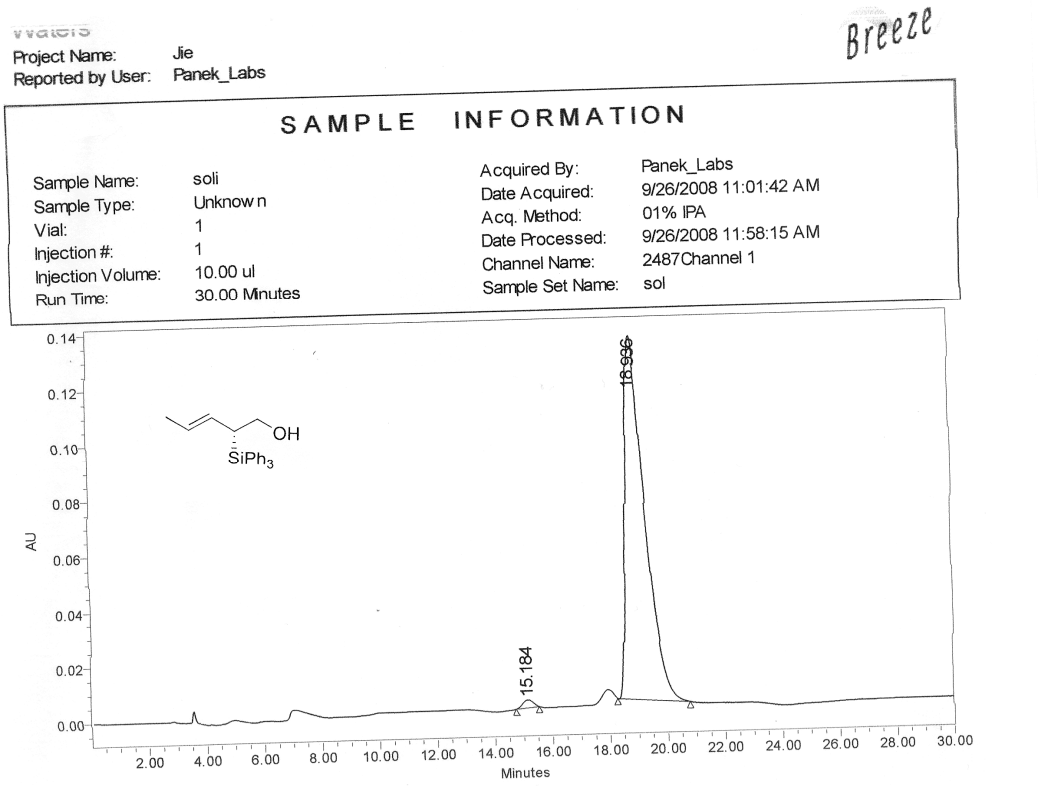


(*R*,*E*)-Methyl 2-(triphenylsilyl)pent-3-enoate ((*R*)-2i): To a round-bottom flask charged with a stir bar was added $[Cu(CH_3CN)_4](BF_4)$ (471 mg, 1.5 mmol, 0.15 equiv) and the dichlorodiimine ligand (852 mg, 2 mmol, 0.2 equiv). The mixture was dissolved in benzene (20 mL), and the resulting heterogeneous yellow solution was allowed to stir at room temperature for 30 min to form the diimine copper complex **(*R*,*R*)-5**. To this mixture was added via syringe triphenylsilane (75 g, 200 mmol, 20 equiv) benzene (20 mL) solution followed by cooling to 0 °C. To the cooled reaction mixture was slowly added a solution of diazo ester (1.4 g, 10 mmol, 1 equiv) in benzene (10 mL) in 10 hours by syringe pump. The resulting mixture was allowed to stir at 0 °C for another 24 hours before flushed through a thin pad of silica gel to remove the the catalyst. The resulting solution was then concentrated under vacuum. The crude product was purified by silica chromatography. Hexane eluant recovered

triphenylsilane and 2% ethyl acetate/hexanes as eluant afforded **(*R*)-2i** as a white crystal (1.52 g, 40.7 mmol, 41% yield). To check its % ee, **(*R*)-2i** was reduced to the primary alcohol by LAH in diethyl ether, and HPLC (chiral OD, 1% IPA/Hexane, t_R 19.7 min, t_S 15.4 min) showed 70% ee. The racemate crystallized selectively, and the first recrystallization utilizing petroleum ether left mother liquor more enantioenriched (85% ee); the second recrystallization using petroleum ether afforded the enantioenriched crystal product (97% ee, 890 mg, 25% overall yield). $[\alpha]_D^{20}$ +15.3 (c = 1.8, CH_2Cl_2).

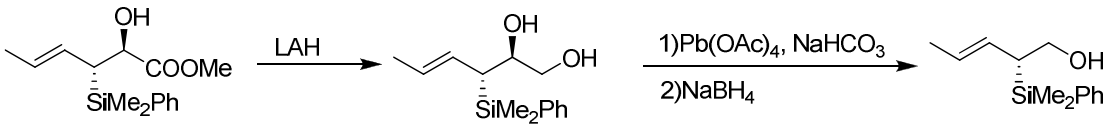


	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	14.929	5134622	48.55	164810	58.94
2	19.302	5440934	51.45	114812	41.06



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	15.184	70956	1.14	2814	2.10
2	18.936	6140112	98.86	131355	97.90

*vii. Assignment of absolute stereochemistry of enantioenriched silanes **2**:*



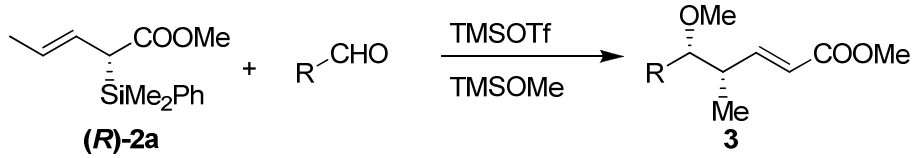
7 **8** **9**

The absolute stereochemistry of **(*R*)-2a** and **(*S*)-2a** was assigned by comparison with silylalcohol **9**, which was made from the known hydroxyl-silane **7** by a straightforward three-step reaction sequence.[6] **2a** derived from Rh_2(*S*-DOSP)$_4$ **(*S*)-6** catalyzed carbenoid Si-H insertion reaction, was reduced to the primary alcohol using LAH, which had the same retention time as **9** in the HPLC analysis. Thus, the absolute configuration of **2a** resulted from **(*S*)-6** was assigned as *R*. Following the same route, the major product derived from **(*R,R*)-5** diimine and $Cu(MeCN)_4BF_4$ complex catalyzed Si-H insertion reaction with $SiMe_2PhH$ was also assigned as **(*R*)-2a**. The absolute stereochemistry of **(*R*)-2g** and **(*R*)-2i** are tentatively assigned on the assumption the asymmetric induction paralles that for the formation of **(*R*)-2a**.

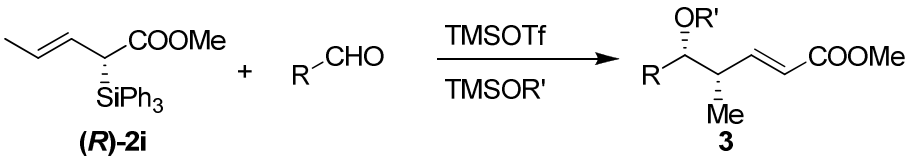
(6) (a) For synthesis compound **7**, see: Panek J. S.; Yang, M.; Solomon, J. S. *J. Org.Chem.* **1993**, *58*, 1003-1010. (b) For diol cleavage step, see:Chauret, D. C.; Chong J. M.; Ye Q. *Tetrahedron Asymmetry* **1999**, *10*, 3601-3614.

C. Synthesis of homoallylic ethers 3 bearing an α,β-unsaturated ester subunit

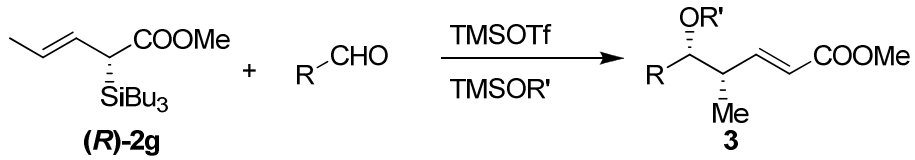
i. Experimental procedures and product characterization



Condition C1 for crotylation utilizing silane **(*R*)-2a***:* To a 10mL round-bottom flask equipped with a stirbar were added aldehyde (0.4 mmol, 1 equiv), **(*R*)-2a** (109 mg, 0.44 mmol, 1.1 equiv) and 5-10 mg 4 Å molecular sieves. The flask was capped with a rubber septum, and the reaction was placed under an atmosphere of argon. Anhydrous DCM (2 mL) was added to the flask, followed by slowly adding TMSOMe (60 μL, 0.44 mmol, 1.1 equiv). The solution was cooled to -78 °C. TMSOTf (72 μL, 0.4 mmol, 1 equiv) was added dropwise, and resulting mixture was stirred at -70 °C for 24 to 48 hours. The reaction was quenched with saturated sodium bicarbonate, and slowly warmed to room temperature. The mixture was extracted with ether (3 x 5 mL), and the combined organic layers were dried over $MgSO_4$, filtered and concentrated. Purification over silica gel (98:2 hexanes/ ethyl acetate) afforded the crotylation product **3**.

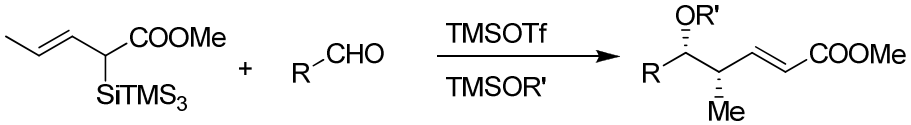


Condition C2 for crotylation utilizing silane **(*R*)-2i***:* To a 10 mL round-bottom flask equipped with a stirbar were added aldehyde (0.4 mmol, 1 equiv), **(*R*)-2i** (164 mg, 0.44 mmol, 1.1 equiv) and 5-10 mg 4 Å molecular sieves. The flask was capped with a rubber septum, and the reaction was placed under an atmosphere of argon. Anhydrous DCM (2 mL) was added to the flask, followed by slowly adding TMSOMe (60 μL, 0.44 mmol, 1.1 equiv). The solution was cooled to -78 °C. TMSOTf (72 μL, 0.4 mmol, 1 equiv) was added dropwise, and resulting mixture was stirred at -60 °C for 72 hours. The reaction was quenched with saturated sodium bicarbonate, and warmed to room temperature. The mixture was extracted with ether (3 x 5 mL), and the combined organic layers were dried over $MgSO_4$, filtered and concentrated. Purification over silica gel (98:2 hexanes/ ethyl acetate) afforded the crotylation product **3**.



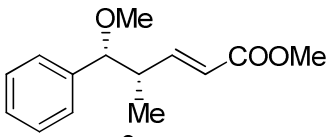
Condition C3 for crotylation utilizing silane **(*R*)-2g***:* To a 10 mL round-bottom flask equipped with a stirbar were added aldehyde (0.4 mmol, 1 equiv), **(*R*)-2g** (137 mg, 0.44 mmol, 1.1 equiv) and 5-10 mg 4 Å molecular sieves. The flask was capped with a rubber septum, and the reaction was placed under an atmosphere of argon.

Anhydrous DCM (1 mL) was added to the flask, followed by slowly adding TMSOMe (60 μL, 0.44 mmol, 1.1 equiv). The solution was cooled to -78 °C. TMSOTf (72 μL, 0.4 mmol, 1 equiv) was added dropwise, and resulting mixture was stirred at -60 °C for 72 hours. The reaction was quenched with saturated sodium bicarbonate, and warmed to room temperature. The mixture was extracted with ether (3 x 5 mL), and the combined organic layers were dried over $MgSO_4$, filtered and concentrated. Purification over silica gel (98:2 hexanes/ ethyl acetate) afforded the crotylation product **3**.



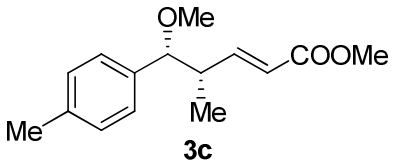
***rac*-2j** **rac-syn-3**

Condition C4 for crotylation utilizing silane ***rac*-2j***:* To a 10 mL round-bottom flask equipped with a stirbar were added aldehyde (0.4 mmol, 1 equiv), ***rac*-2j** (158 mg, 0.44 mmol, 1.1 equiv). The flask was capped with a rubber septum, and the reaction was placed under an atmosphere of argon. Anhydrous DCM (0.8 mL) was added to the flask, followed by slowly adding TMSOMe (60 μL, 0.44 mmol, 1.1 equiv). The solution was cooled to -78 °C. TMSOTf (72 μL, 0.4 mmol, 1 equiv) was added dropwise, and resulting mixture was stirred at -70 °C for 48 hours and warmed up to -50 °C for 24 hours. The reaction was quenched with saturated sodium bicarbonate, and warmed to room temperature. The mixture was extracted with ether (3 x 5 mL), and the combined organic layers were dried over $MgSO_4$, filtered and concentrated. Purification over silica gel (98:2 hexanes/ ethyl acetate) afforded the racemic *syn* crotylation product **3**.



3a

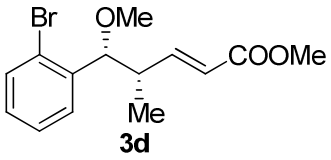
(4*S*,5*R*,*E*)-Methyl 5-methoxy-4-methyl-5-phenylpent-2-enoate (3a): Following *Condition C2*. Chromatography on silica gel (98:2 hexanes/ ethyl acetate) afforded product **3a** (74 mg, 79% yield) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27(m, 5H), 7.06(dd)*, 6.88(dd, *J*=15.6, 7.2 Hz, 1H), 5.82(d)*, 5.68(d, *J*=15.2Hz, 1H), 4.05(d, *J*=6.0Hz, 1H), 3.93(d)*, 3.71(s)*, 3.67(s, 3H), 3.20(s, 3H), 3.15(s)*, 2.65(m, 1H), 1.04(d, *J*=6.8Hz, 3H), 0.85(d)*; ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.0, 151.6*, 150.8, 139.4, 128.3*, 128.2, 127.9*, 127.7, 127.3*, 127.2, 120.9,87.5*, 86.6, 57.0, 52.4, 43.2, 16.1*, 14.7; $[\alpha]_D^{20}$ +19.2 (c = 1.4, CH_2Cl_2); IR (thin film) υ_{max}2928, 1723, 1436, 1274, 1174 cm^{-1}; HRMS(CI/NH_3) m/z calcd for $C_{14}H_{18}O_3Na$ $[M+Na]^+$ 257.1154, found 257.1164.



3c

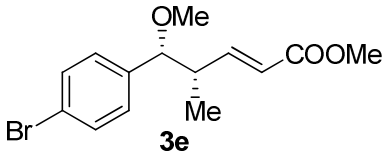
(4*S*,5*R*,*E*)-Methyl 5-methoxy-4-methyl-5-p-tolylpent-2-enoate (3c): Following *Condition C2,* reaction run under -50 °C instead of -60 °C. Chromatography on silica gel (98:2 hexanes/ ethyl acetate) afforded product **3c** (74 mg,

75% yield) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10(m, 4H), 6.89(dd, *J*=15.6, 7.6 Hz, 1H), 5.70(d, *J*=15.6Hz, 1H), 4.01(d, *J*=6.4Hz, 1H), 3.67(s, 3H), 3.18(s, 3H), 2.69(m, 1H), 2.33(s, 3H), 1.03(d, *J*=6.4Hz, 3H); ^{13}C NMR (75MHz, $CDCl_3$) δ 167.1, 151.0, 137.4, 136.3, 128.9, 127.2, 120.7, 86.5, 56.9, 51.4, 43.2, 21.1, 14.8; $[\alpha]_D^{20}$ +19.0 (c = 0.5, CH_2Cl_2); IR (thin film) υ_{max}2948, 1724, 1273, 1174, 1086, 814 cm^{-1}; HRMS(CI/NH_3) m/z calcd for $C_{15}H_{20}O_3Na$ $[M+Na]^+$ 271.1310, found 271.1384.



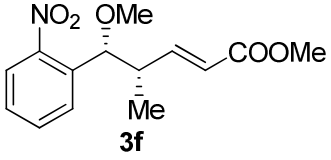
3d

(4*S*,5*R*,*E*)-Methyl 5-(2-bromophenyl)-5-methoxy-4-methylpent-2-enoate (3d): Following *Condition C1*. Chromatography on silica gel (98:2 hexanes/ ethyl acetate) afforded product **3d** (101 mg, 81% yield) as a white solid. Melting point: 60-62 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50(d, *J*=7.6Hz, 1H), 7.30(m, 2H), 7.10(t, *J*=8.0Hz, 1H), 7.04(dd, *J*=15.6, 7.2 Hz, 1H), 5.80(d, *J*=15.2Hz, 1H), 4.57(d, *J*=4.4Hz, 1H), 3.69(s, 3H), 3.19(s, 3H), 2.69(m, 1H), 0.98(d, *J*=6.8Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.0, 151.3, 138.7, 132.8, 129.0, 128.4, 127.3, 123.5, 120.7, 84.1, 57.4, 51.4, 41.5, 12.9; $[\alpha]_D^{20}$ +29.2 (c = 1.0, CH_2Cl_2); IR (thin film) υ_{max}2935, 2826, 1721, 1435, 1272, 1175, 1108, 1024, 757 cm^{-1}; HRMS(CI/NH_3) m/z calcd for $C_{14}H_{18}O_3Br$ $[M+H]^+$ 313.0439, found 313.0499.



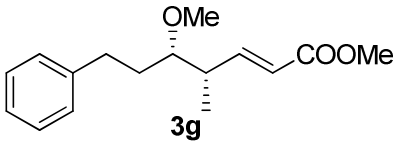
3e

(4*S*,5*R*,*E*)-Methyl 5-(4-bromophenyl)-5-methoxy-4-methylpent-2-enoate (3e): Following *Condition C2*. Chromatography on silica gel (98:2 hexanes/ ethyl acetate) afforded product **3e** (84 mg, 67% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44(d, *J*=8.0Hz, 2H), 7.07(d, *J*=8.0Hz, 2H), 6.84(dd, *J*=16.0, 7.6 Hz, 1H), 5.68(d, *J*=16.0Hz, 1H), 4.00(d, *J*=6.4Hz, 1H), 3.68(s, 3H), 3.19(s, 3H), 2.63(m, 1H), 1.03(d, *J*=6.8Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.9, 150.2, 138.5, 131.4,128.9, 121.6, 121.2, 86.0, 57.1, 51.5, 43.0, 14.7; $[\alpha]_D^{20}$ +3.4 (c = 1.3, CH_2Cl_2); IR (thin film) υ_{max}2953, 1723, 1485, 1251, 1071, 843 cm^{-1}; HRMS(CI/NH_3) m/z calcd for $C_{14}H_{18}O_3Br$ $[M+H]^+$ 313.0439, found 313.0431.



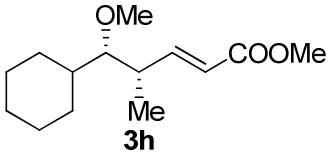
3f

(4*S*,5*R*,*E*)-Methyl 5-methoxy-4-methyl-5-(2-nitrophenyl)pent-2-enoate (3f): Following *Condition C1*. Chromatography on silica gel (90:10 hexanes/ ethyl acetate) afforded product **3f** (79 mg, 81% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96(d, *J*=8.0Hz, 1H), 7.64(m, 2H), 7.44(t, *J*=6.0Hz, 1H), 7.00(dd, *J*=16.0, 7.6 Hz, 1H), 5.78(d, *J*=16.0Hz, 1H), 4.87(d, *J*=4.4Hz, 1H), 3.69(s, 3H), 3.19(s, 3H), 2.72(m, 1H), 1.02(d, *J*=6.8Hz, 3H); ^{13}C NMR (75MHz, $CDCl_3$) δ 167.0, 150.7, 135.9, 133.2, 128.8, 128.4, 124.7, 121.2, 80.9, 57.7, 51.8, 42.4, 13.2; $[\alpha]_D^{20}$ +26.1 (c = 0.8, CH_2Cl_2); IR (thin film) υ_{max}2948, 2829, 1723, 1527, 1343, 1276, 1111, 724 cm^{-1}; HRMS(CI/NH_3) m/z calcd for $C_{14}H_{17}NNaO_5$ $[M+Na]^+$ 302.1004, found 302.1002.



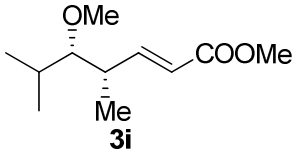
3g

(4*S*,5*S*,*E*)-Methyl 5-methoxy-4-methyl-7-phenylhept-2-enoate (3g): Following *Condition C3.* Chromatography on silica gel (98:2 hexanes/ ethyl acetate) afforded product **3g** (59 mg, 57% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27(m, 2H), 7.18(m, 3H), 6.99(dd, *J*=16.0, 7.6 Hz, 1H), 5.81 (d, *J*=16.0Hz, 1H), 3.71(s, 3H), 3.38(s, 3H), 3.10(m, 1H), 2.77(m, 1H), 2.58(m, 2H), 1.72(m, 2H), 1.04(d, *J*=6.8Hz, 3H); ^{13}C NMR (75MHz, $CDCl_3$) δ 167.0, 150.9, 142.0, 128.4, 128.4, 128.0, 120.8, 83.5, 57.7, 51.4, 39.0, 32.9, 31.9, 14.7; $[\alpha]_D^{20}$ -48.0 (c = 0.3, CH_2Cl_2); IR (thin film) υ_{max}2948, 1721, 1435, 1272, 1174, 1092, 700 cm^{-1}; HRMS(CI/NH_3) m/z calcd for $C_{16}H_{22}O_3Na$ $[M+H]^+$ 285.1467, found 285.1549.



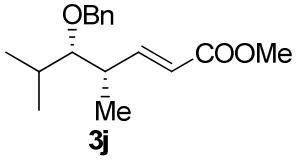
3h

(4*S*,5*S*,*E*)-Methyl 5-cyclohexyl-5-methoxy-4-methylpent-2-enoate (3h): Following *Condition C3*. Chromatography on silica gel (98:2 hexanes/ ethyl acetate) afforded product **3h** (58 mg, 61% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97(dd, *J*=16.0, 8.4Hz, 1H), 5.81 (d, *J*=16.0Hz, 1H), 3.71(s, 3H), 3.37(s, 3H), 3.10(m, 1H), 2.77(t, *J*=5.6Hz, 1H), 2.54(m, 1H), 1.61(m, 5H), 1.38(m, 1H), 1.10(m, 5H), 1.05(d, *J*=6.8Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.2, 152.8, 120.0, 89.3, 61.5, 51.5, 41.1, 39.0, 30.3, 27.9, 26.4, 26.3, 26.1, 14.1; $[\alpha]_D^{20}$ -39.0 (c = 0.3, CH_2Cl_2); IR (thin film) υ_{max}2925, 2852, 1924, 1666, 1435, 1270, 1173, 1106, 987 cm^{-1}; HRMS(CI/NH_3) m/z calcd for $C_{14}H_{24}O_3Na$ $[M+Na]^+$ 263.1623, found 263.1700.



3i

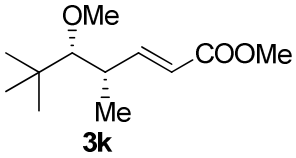
(4*S*,5*S*,*E*)-Methyl 5-methoxy-4,6-dimethylhept-2-enoate (3i): Following *Condition C3.* Chromatography on silica gel (98:2 hexanes/ ethyl acetate) afforded product **3i** (33 mg, 41% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94(dd, *J*=16.0, 8.0Hz, 1H), 5.82 (d, *J*=16.0Hz, 1H), 3.71(s, 3H), 3.40(s, 3H), 2.76(t, *J*=5.6Hz, 1H), 2.53(m, 1H), 1.73(m, 1H), 1.06(d, *J*=6.8Hz, 3H), 0.90(d, *J*=7.2Hz, 3H), 0.88(d, *J*=7.2Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.2, 152.5, 120.0, 89.9, 61.5, 51.5, 39.8, 31.2, 20.1, 17.2, 14.5; $[\alpha]_D^{20}$ +10.2 (c = 1.1, CH_2Cl_2); IR (thin film) υ_{max}2962, 2875, 1724, 1273, 1092, 989 cm^{-1}; HRMS(CI/NH_3) m/z calcd for $C_{14}H_{18}O_3Br$ $[M+Na]^+$ 223.1310, found 223.1283.



3j

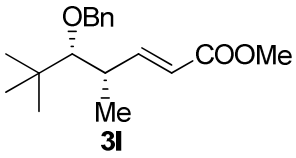
(4*S*,5*S*,*E*)-Methyl 5-(benzyloxy)-4,6-dimethylhept-2-enoate (3j): Following Condition *C3.* Chromatography on silica gel (98:2 hexanes/ ethyl acetate) afforded product **3j** (70 mg, 63% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26(m, 5H), 6.98(dd, *J*=15.6, 8.0Hz, 1H), 5.83(d, *J*=15.6Hz, 1H), 4.53(s, 2H), 3.71(s, 3H), 3.07(t, *J*=5.6Hz, 1H), 2.62(m, 1H), 1.80(m, 1H), 1.10(d, *J*=6.8Hz, 3H), 0.93(m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.2, 152.6, 138.6 , 128.3 , 127.6 , 127.5 , 120.1 ,

87.8 , 75.2 , 51.5 , 39.8 , 31.3 , 20.3 , 17.5 , 14.7; $[\alpha]_D^{20}$ +9.4 (c = 0.4, CH_2Cl_2); IR (thin film) υ_{max}2963 , 1723 , 1656 , 1275 , 1176 , 1066 cm^{-1}; HRMS(CI/NH_3) m/z calcd for $C_{17}H_{24}O_3Na$ $[M+Na]^+$ 299.1623, found 199.1671.



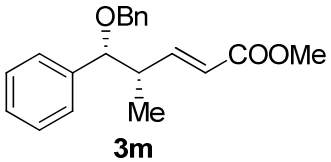
3k

(4*S*,5*R*,*E*)-Methyl 5-methoxy-4,6,6-trimethylhept-2-enoate (3k): Following *Condition C3.* Chromatography on silica gel (98:2 hexanes/ ethyl acetate) afforded product **3k** (33 mg, 39% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02(dd, *J*=15.6, 8.0Hz, 1H), 5.75 (d, *J*=15.6Hz, 1H), 3.70(s, 3H), 3.37(s, 3H), 2.73(d, *J*=4.4Hz, 1H), 2.61(m, 1H), 1.08(d, *J*=6.8Hz, 3H), 0.89(s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.4, 155.3, 118.7, 91.8, 61.6, 51.5, 38.3, 37.0, 26.8, 15.1; $[\alpha]_D^{20}$ +3.7 (c = 0.4, CH_2Cl_2); IR(thin film) υ_{max}2948 , 2844 , 1725 , 1647 , 1458 , 1110 cm^{-1}; HRMS(CI/NH_3) m/z calcd for $C_{12}H_{22}O_3Na$ $[M+Na]^+$ 237.1467, found 237.1474.



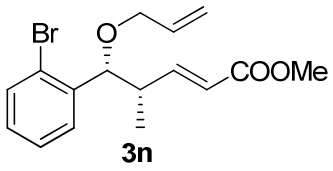
3l

(4*S*,5*R*,*E*)-Methyl 5-(benzyloxy)-4,6,6-trimethylhept-2-enoate (3l): Following *Condition C3.* Chromatography on silica gel (98:2 hexanes/ ethyl acetate) afforded product **3l** (91 mg, 79% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27(m, 5H), 7.07(dd, *J*=20.8, 10.4Hz, 1H), 5.82(d, *J*=20.8Hz, 1H), 4.56(d, *J*=15.6Hz, 1H), 4.45(d, *J*=15.6Hz, 1H), 3.72(s, 3H), 3.05(d, *J*=4.8Hz, 1H), 2.69(m, 1H), 1.13(d, *J*=9.2Hz, 3H), 0.94(s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.3, 155.4, 138.7, 128.2, 127.4, 127.4, 118.8, 89.4, 74.9, 51.5, 38.1, 37.1, 26.9, 15.1; $[\alpha]_D^{20}$ +12.2 (c = 0.4, CH_2Cl_2); IR (thin film) υ_{max}2953, 2870, 1722, 1271, 1173, 1069, 734, 697 cm^{-1}; HRMS(CI/NH_3) m/z calcd for $C_{18}H_{26}O_3Na$ $[M+Na]^+$ 313.1780, found 313.1857.



3m

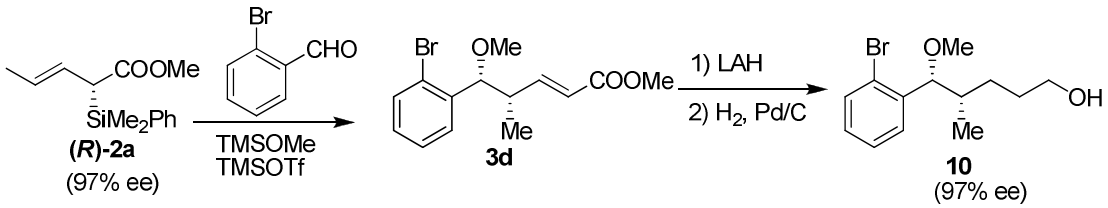
(4*S*,5*R*,*E*)-Methyl 5-(benzyloxy)-4-methyl-5-phenylpent-2-enoate (3m): Following *Condition C2,* using TMSOBn (80 mg, 0.44 mmol, 1.1 equiv) instead of TMSOMe (60 μL, 0.44 mmol, 1.1 equiv); reaction run under -80 °C instead -70 °C for 24 hours. Chromatography on silica gel (98:2 hexanes/ ethyl acetate) afforded product **3m** (84 mg, 68% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30(m, 10H), 6.88(dd, *J*=15.6, 7.6 Hz, 1H), 5.67(d, *J*=15.6Hz, 1H), 4.47(d, *J*=12.0Hz, 1H), 4.25(s, 1H), 4.22(d, *J*=4.8Hz, 1H), 3.67(s, 3H), 2.71(m, 1H), 1.10(d, *J*=6.8Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.0, 150.8, 139.6, 138.2, 128.3, 127.8, 127.7, 127.6, 127.5, 127.4, 120.9, 84.0, 70.5, 51.4, 43.4, 15.0; $[\alpha]_D^{20}$ +7.0 (c = 0.8, CH_2Cl_2); IR (thin film) υ_{max}3029, 2949, 2869, 1720, 1453, 1273, 1174, 1066, 699 cm^{-1}; HRMS(CI/NH_3) m/z calcd for $C_{20}H_{22}O_3Na$ $[M+Na]^+$ 333.1467, found 333.149.



3n

(4*S*,5*R*,*E*)-Methyl 5-(allyloxy)-5-(2-bromophenyl)-4-methylpent-2-enoate (3n): Following *Condition C2*. Chromatography on silica gel (98:2 hexanes/ ethyl acetate) afforded product **3n** (101 mg, 75% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50(m, 1H), 7.40(m, 1H), 7.31(m, 1H), 7.12(m, 1H), 7.04(dd, *J*=15.6, 8.0Hz, 1H), 5.87(m, 1H), 5.79(d, *J*=15.6, 1H), 5.26(m, 1H), 5.14(m, 1H), 4.74(d, *J*=4.4Hz, 1H), 3.87(m,1H), 3.74(m, 1H), 3.71(s, 3H), 2.71(m, 1H), 1.03(d, *J*=6.4Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.1, 151.2, 139.1, 134.4, 132.8, 129.0, 128.6, 127.4, 123.4, 120.8, 117.0, 81.5, 70.1, 51.4, 41.7, 13.2; $[\alpha]_D^{20}$ +10.2 (c = 1.6, CH_2Cl_2); IR (thin film) υ_{max}3853, 1734, 1653, 1540, 1506 cm^{-1}; HRMS(CI/NH_3) m/z calcd for $C_{16}H_{20}BrO_3$ $[M+H]^+$ 339.0596, found 339.0610.

*ii. Ee analysis of product **3***



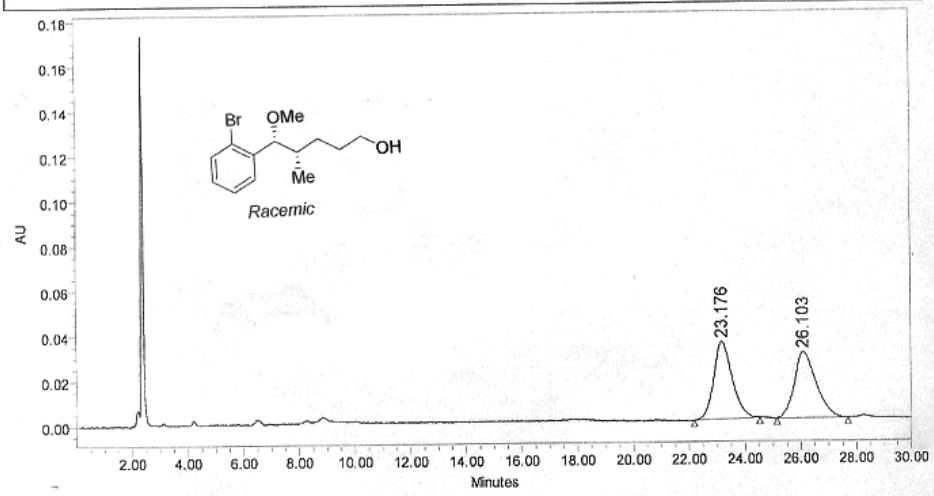
Representablely, *syn*-homo allylic ether **3d** was prepared by three-component crotylation using 97% ee silane **(*R*)-2a**. Since its racemic version cannot achieve baseline separation on HPLC, it was converted to primary alcohol product **10** with LAH reduction followed by hydrogenation. Compound **10** was run on HPLC using a ChiralCel AD column, isocratic 1% isopropanol/hexanes at a flow rate of 1 mL/min. It was found that the product had 97% ee. (See attached HPLC traces for racemic and enantioenriched product **10**).

Project Name: JasonWu
Reported by User: System

Breeze

SAMPLE INFORMATION

Sample Name:	Unk.	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	6/7/2008 12:50:30 PM
Vial:	1	Acq. Method:	ChiralPak AD 1%IPA
Injection #:	1	Date Processed:	6/7/2008 2:19:59 PM
Injection Volume:	10.00 ul	Channel Name:	2487Channel 2
Run Time:	30.00 Minutes	Sample Set Name:	AD



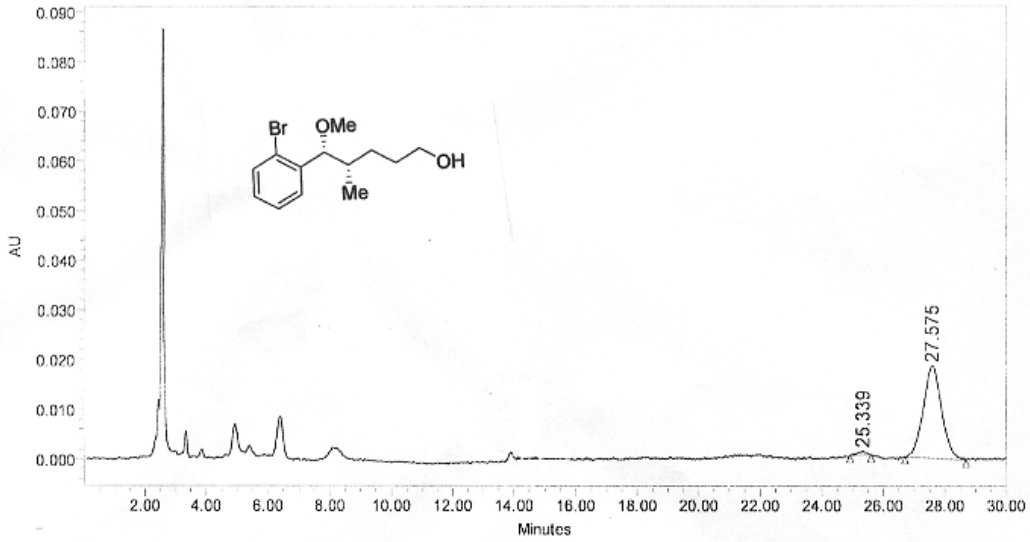
	RT (min)	Area (µV*sec)	% Area	Height (µV)	% Height
1	23.176	1599716	49.86	34738	54.05
2	26.103	1608969	50.14	29534	45.95

Project Name: JasonWu
Reported by User: System

Breeze

SAMPLE INFORMATION

Sample Name:	Br	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	6/10/2008 11:10:05 AM
Vial:	5	Acq. Method:	ChiralPak AD 1%IPA
Injection #:	1	Date Processed:	6/10/2008 12:03:12 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 2
Run Time:	30.00 Minutes	Sample Set Name:	Br_enan



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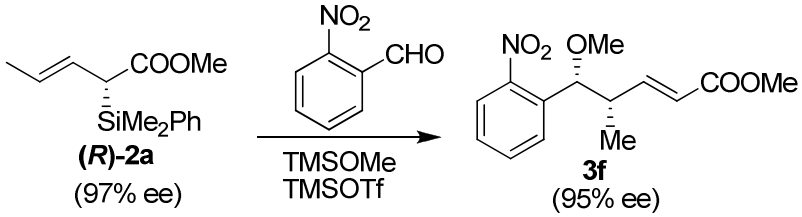
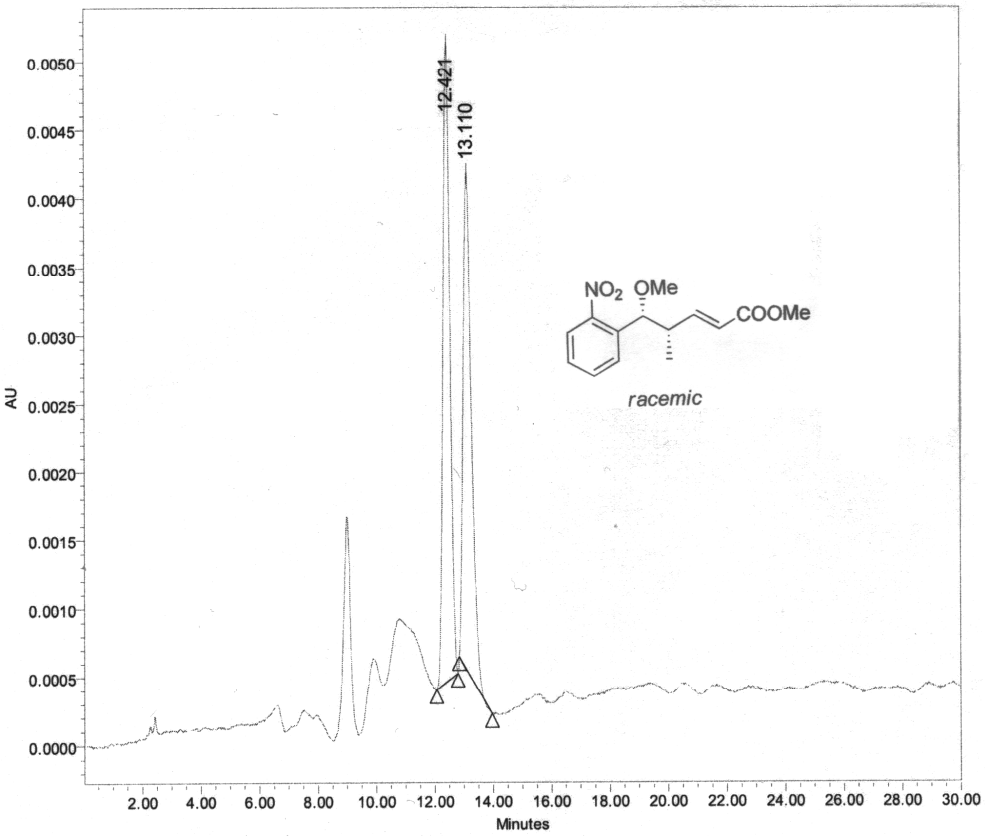
2	27.575	767120	98.28	18479	96.12



Syn-homo allylic ether **3f**, which was prepared by three-component crotylation using 97% ee silane **(*R*)-2a**, was run on HPLC using a ChiralCel AD column, isocratic 0.5% isopropanol/hexanes at a flow rate of 1 mL/min. It was found that product had 95% ee. (See attached HPLC traces for racemic and enantioenriched product **3f**).

Boston University
Project Name: JasonWu
Reported by User: System

Breeze



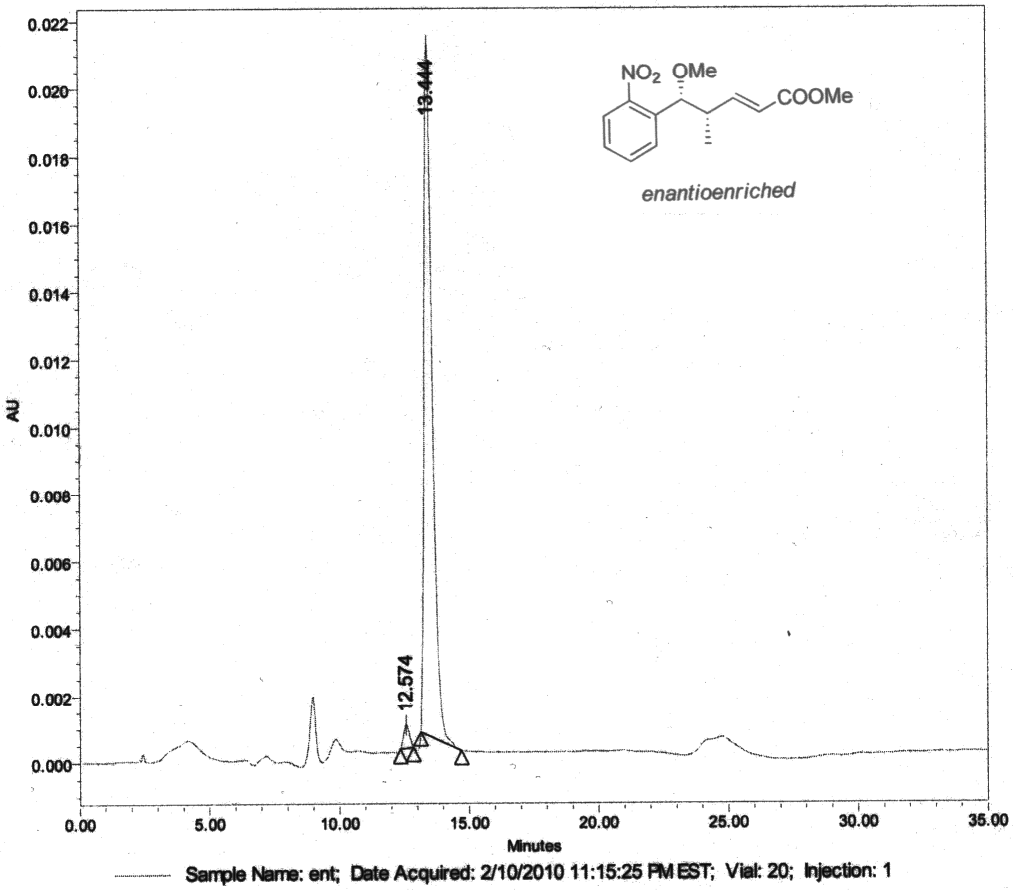
Sample Name: raceNO2; Date Acquired: 2/12/2010 11:01:34 AM EST; Vial: 20; Injection: 1

Peak Summary with Statistics
Peak Name:

	Sample Name	Vial	Inj.	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	raceNO2	20	1	12.421	77606	51.84	4675
2	raceNO2	20	1	13.110	72091	48.16	3637

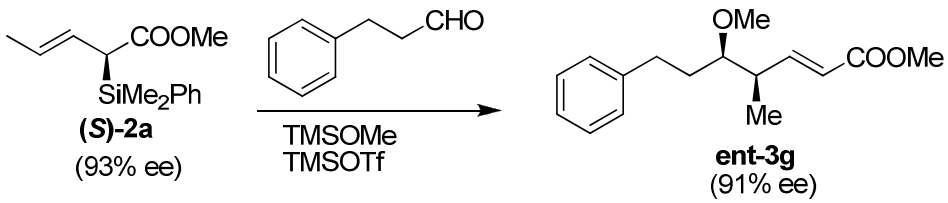
Boston University
Project Name: JasonWu
Reported by User: System

Breeze



Peak Summary with Statistics
Peak Name:

	Sample Name	Vial	Inj.	RT (min)	Area (µV*sec)	% Area	Height (µV)
1	ent	20	1	12.574	10874	2.37	692
2	ent	20	1	13.444	447482	97.63	20516



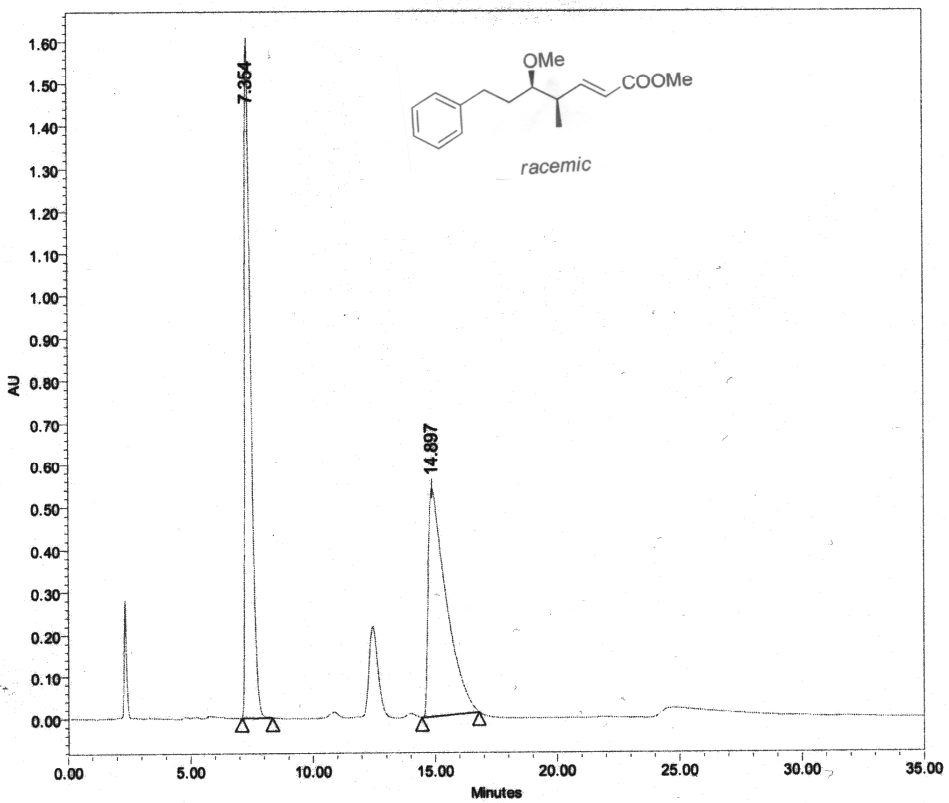
Syn-homo allylic ether **ent-3g**, which was prepared by three-component crotylation using 93% ee silane **(*S*)-2a**, was run on HPLC using a WhelkO column, isocratic 1% isopropanol/hexanes at a flow rate of 1 mL/min. It was found that product had 91% ee. (See attached HPLC traces for racemic and enantioenriched product **ent-3g**).

Boston University

Project Name: JasonWu

Reported by User: System

Breeze

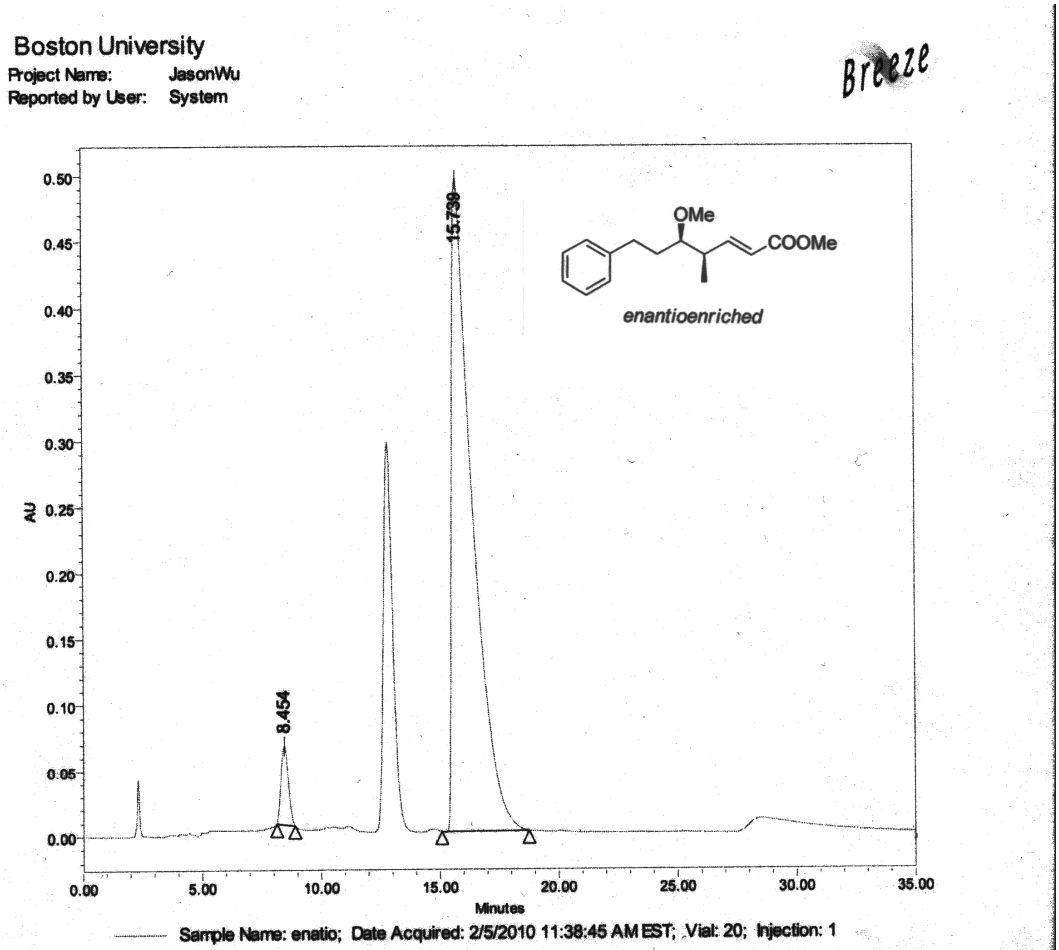


Sample Name: race; Date Acquired: 2/5/2010 12:14:54 PM EST; Vial: 19; Injection: 1

Peak Summary with Statistics

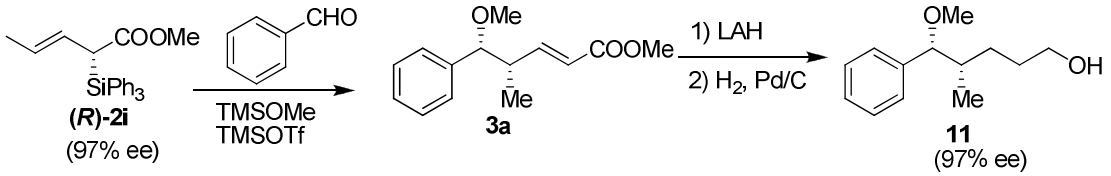
Peak Name:

	Sample Name	Vial	Inj.	RT (min)	Area (µV*sec)	% Area	Height (µV)
1	race	19	1	7.354	27113362	49.34	1589463
2	race	19	1	14.897	27840754	50.66	539082



Peak Summary with Statistics
Peak Name:

	Sample Name	Vial	Inj.	RT (min)	Area (µV*sec)	% Area	Height (µV)
1	enatio	20	1	8.454	1284422	4.14	60542
2	enatio	20	1	15.739	29751206	95.86	494026



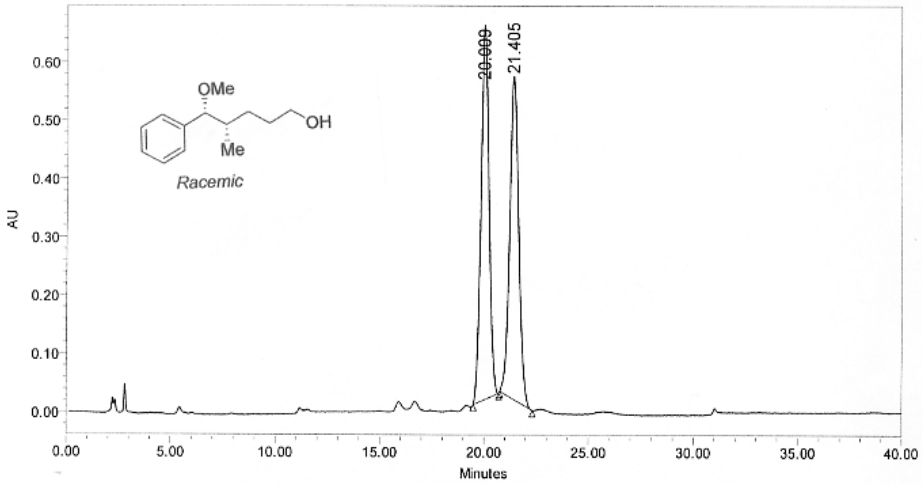
Syn-homo allylic ether **3a**, which was prepared by three-component crotylation using 97% ee silane **(*R*)-2i**, was converted to primary alcohol product **11** with LAH reduction followed by hydrogenation. Compound **11** was run on HPLC using a ChiralPak AD column, isocratic 1% isopropanol/hexanes at a flow rate of 1 mL/min. It was found that product has 97% ee. (See attached HPLC traces for racemic and enantioenriched product **11**).

Project Name: JasonWu
Reported by User: System

Breeze

SAMPLE INFORMATION

Sample Name:	race	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	9/19/2008 10:55:27 AM
Vial:	1	Acq. Method:	ChiralPak AD 1%IPA
Injection #:	1	Date Processed:	9/19/2008 1:58:20 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 2
Run Time:	40.00 Minutes	Sample Set Name:	priOH



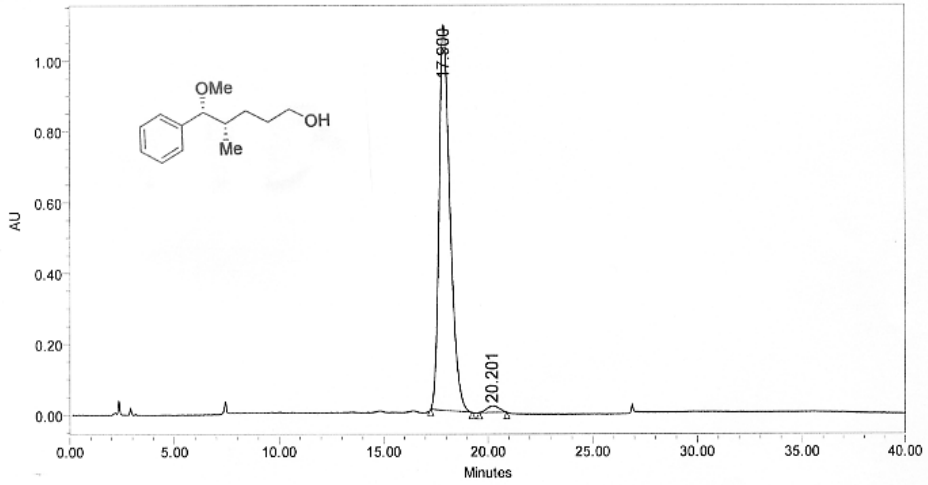
	RT (min)	Area (µV*sec)	% Area	Height (µV)	% Height
1	20.009	17027134	50.72	642021	53.69
2	21.405	16540961	49.28	553669	46.31

Project Name: JasonWu
Reported by User: System

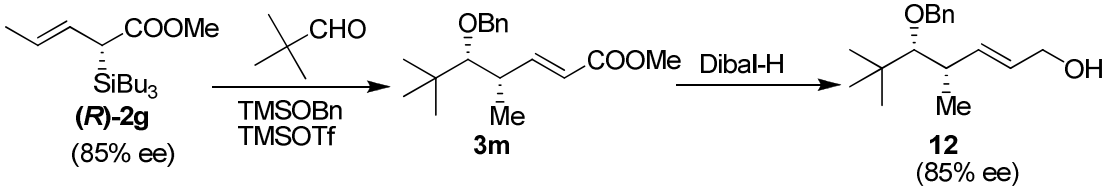
Breeze

SAMPLE INFORMATION

Sample Name:	ee	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	9/18/2008 3:43:30 PM
Vial:	7	Acq. Method:	ChiralPak AD 1%IPA
Injection #:	1	Date Processed:	9/18/2008 6:24:25 PM
Injection Volume:	5.00 ul	Channel Name:	2487Channel 2
Run Time:	40.00 Minutes	Sample Set Name:	primaryOH



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	17.900	39734027	98.21	1089261	98.40
2	20.201	722235	1.79	17703	1.60



Syn-homo allylic ether **3m**, which was prepared by three-component crotylation using 86% ee silane **(*R*)-2g**, was converted to allylic alcohol product **12**. Compound **12** was run on HPLC using a ChiralPak AD column, isocratic 1% isopropanol/hexanes at a flow rate of 1 mL/min. It was found that product had 86% ee. (See attached HPLC traces for racemic and enantioenriched product **12**).

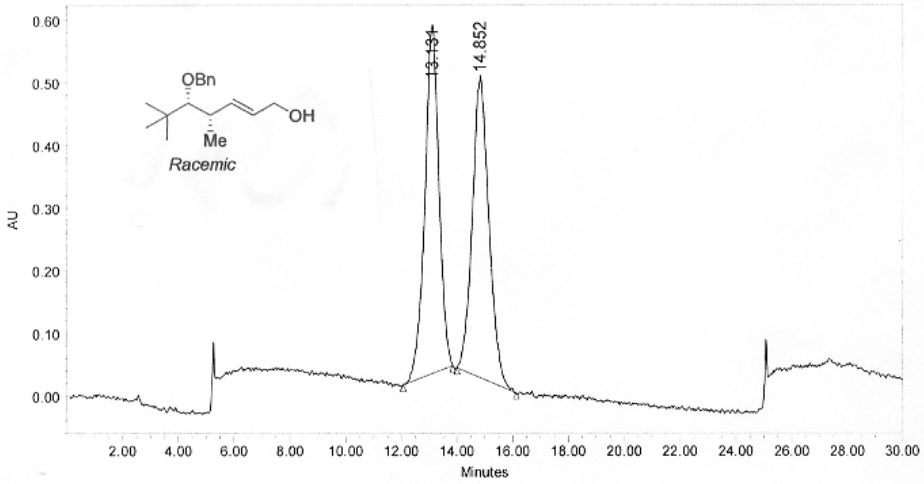
Project Name: JasonWu
Reported by User: System

Breeze

SAMPLE INFORMATION

Sample Name:	Unk.	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	11/10/2008 4:15:49 PM
Vial:	1	Acq. Method:	ChiralPak AD 1%IPA
Injection #:	1	Date Processed:	11/10/2008 6:18:56 PM
Injection Volume:	2.00 ul	Channel Name:	2487Channel 2
Run Time:	30.00 Minutes	Sample Set Name:	race_OH_AD

214 nm



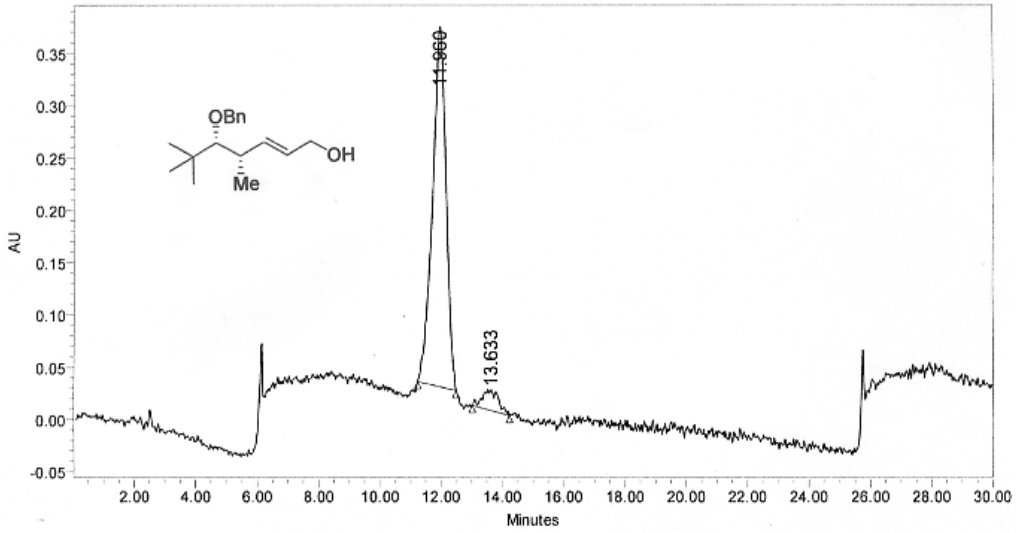
	RT (min)	Area (µV*sec)	% Area	Height (µV)	% Height
1	13.131	19554058	49.59	556704	53.57
2	14.852	19876702	50.41	482524	46.43

Project Name: JasonWu
Reported by User: System

Breeze

SAMPLE INFORMATION

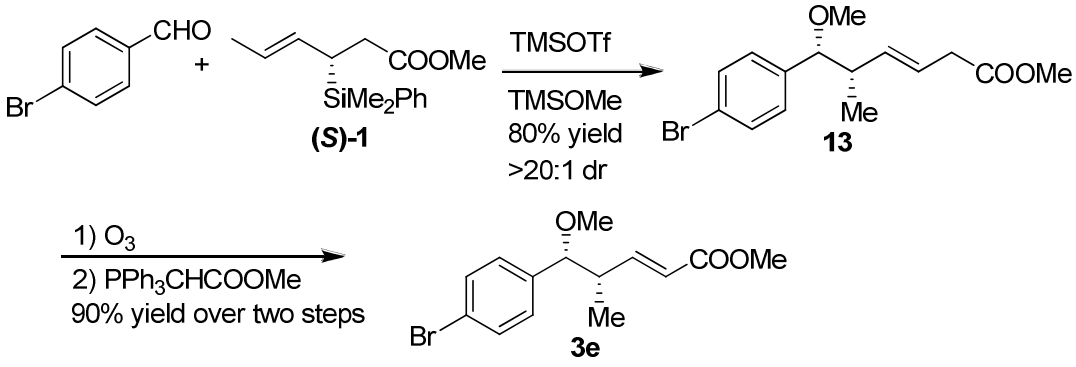
Sample Name:	tert	Acquired By:	System
Sample Type:	Unknown	Date Acquired:	11/29/2008 12:29:41 PM
Vial:	1	Acq. Method:	ChiralPak AD 1%IPA
Injection #:	1	Date Processed:	11/29/2008 2:50:55 PM
Injection Volume:	2.00 ul	Channel Name:	2487Channel 2
Run Time:	30.00 Minutes	Sample Set Name:	tertOBn



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	11.960	10523765	93.54	343907	94.53
2	13.633	727322	6.46	19898	5.47

iii. Assignment of absolute and relative stereochemistry of crotylation product:

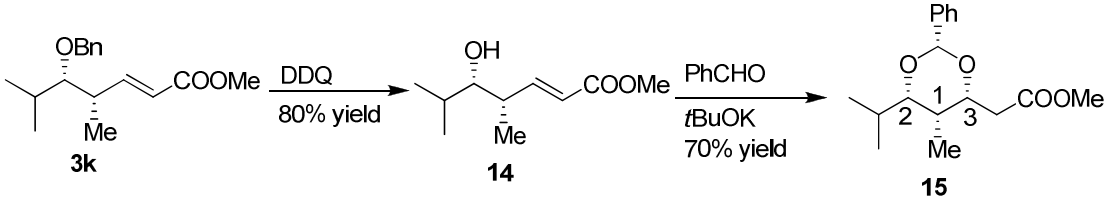
1) Confirmed absolute stereochemistry by utilizing known method to synthesize crotylation product **3e**.



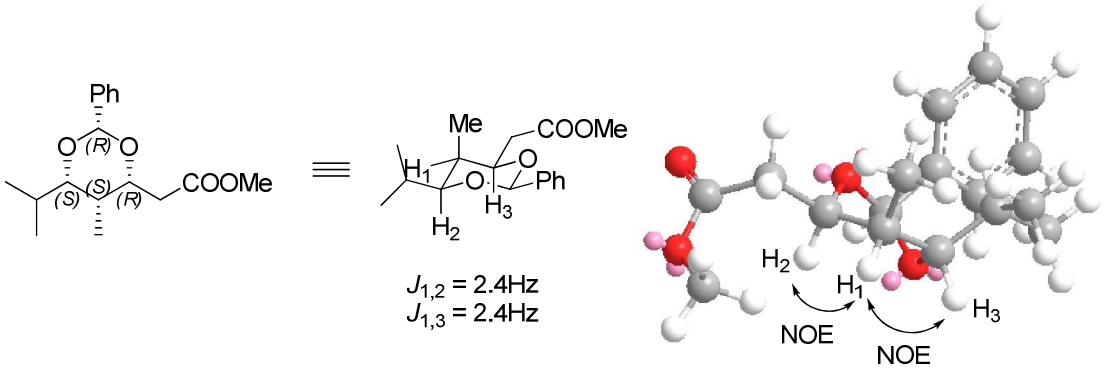
The absolute stereochemistry of **3e** was assigned by conversion of homoallylic ether

13[7] to *α,β*-unsaturate ester **3e**. **3e** obtained by this three-step procedure exhibited the same optical rotation data with **3e** derived from silane **(*R*)-2i**.

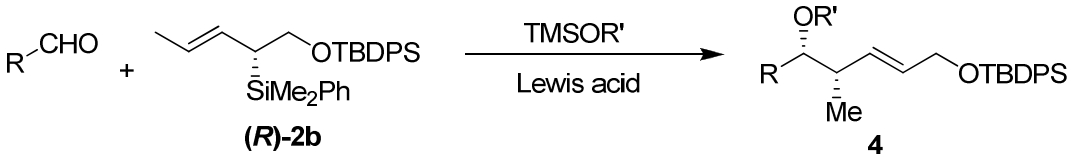
2) Confirmed relative stereochemistry by generating benzylidine-protected *syn*-dihydroxyester **15**.



Crotylation product **3k** was converted to the benzylidine-protected dihydroxyester **15** using condition reported by Evans.[8] Three-bond coupling constants and NOE measurements supported the *syn* diastereomer configuration. Benzylidine acetal **15** was isolated as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (m, 2H), 7.33 (m, 3H), 5.53 (s, 1H), 4.35 (ddd, *J* = 8.0, 5.6, 2.4Hz, 1H), 3.69 (s, 3H), 3.35 (dd, *J* = 10.0, 2.4Hz, 1H), 2.72 (dd, *J* = 15.6, 8.0Hz, 1H), 2.48 (dd, *J* = 15.6, 5.6Hz, 1H), 1.83 (m, 1H), 1.70 (qt, *J* = 6.8, 2.4Hz, 1H), 1.03 (d, *J* = 6.4Hz, 3H), 0.94 (d, *J* = 6.8Hz, 3H), 0.84 (d, *J* = 6.8Hz, 3H).



D. Synthesis of homoallylic ethers 4 bearing an allylic ether subunit



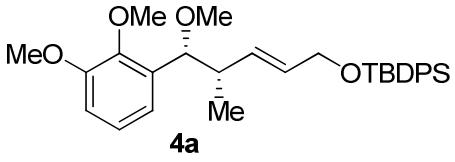
i. Reaction procedure and product characterization

Condition D1: To a 10 mL round-bottom flask equipped with a stirbar were added aromatic aldehyde (0.4 mmol, 1 equiv), **(*R*)-2b** (201 mg, 0.44 mmol, 1.1 equiv) and

(7) Panek, J. S.; Yang, M.; Feng, X. *J. Org. Chem.* **1992**, *57*, 5790-5792.
(8) Evans, D. A.; Gauchet-Prunet, J. A. *J. Org. Chem.* **1993**, *58*, 2446-2453.

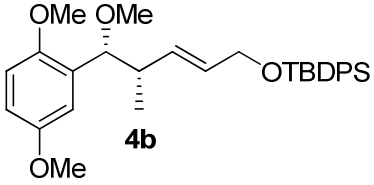
5-10 mg 4 Å molecular sieves. The flask was capped with a rubber septum and the reaction was placed under an Ar atmosphere. Anhydrous DCM (2 mL) was added to the flask, followed by slowly adding TMSOMe (60 μL, 0.44 mmol, 1.1 equiv). The solution was cooled to -78 °C. TMSOTf (72 μL, 0.4 mmol, 1 equiv) was added dropwise, and resulting mixture was stirred at -78 °C for 24 to 48 hours. The reaction was diluted with saturated sodium bicarbonate, and warmed to room temperature. The mixture was extracted with ether (3 x 5 mL), and the combined organic layers were dried over $MgSO_4$, filtered and concentrated. Purification over silica gel (98:2 hexanes/ ethyl acetate) afforded the crotylation product **4**.

Condition D2: To a 10 mL round-bottom flask equipped with a stirbar were added aliphatic aldehyde (0.4 mmol, 1 equiv), **(*R*)-2b** (201 mg, 0.44 mmol, 1.1 equiv) and 5-10 mg 4 Å molecular sieves. The flask was capped with a rubber septum and the reaction was placed under an Ar atmosphere. Anhydrous DCM (2 mL) was added, followed by slowly adding TMSOMe (189 μL, 1.32 mmol, 3.3 equiv). The solution was cooled to -78 °C. $BF_3.OEt_2$ (102 μL, 0.8 mmol, 2 equiv) was added dropwise, and resulting mixture was stirred at -40 °C for 24 to 48 hours. The reaction was diluted with saturated sodium bicarbonate, and warmed to room temperature. The mixture was extracted with ether (3 x 5 mL), and the combined organic layers were dried over $MgSO_4$, filtered and concentrated. Purification over silica gel (98:2 hexanes/ ethyl acetate) afforded the crotylation product **4**.



4a

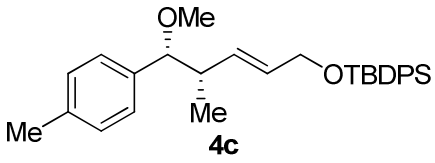
***tert*-Butyl((4*S*,5*R*,*E*)-5-(2,3-dimethoxyphenyl)-5-methoxy-4-methylpent-2-enyloxy)diphenylsilane (4a):** Following procedure *D1*, using TMSOTf (14.4 μL, 0.08 mmol, 0.2 equiv) instead of (72 μL, 0.4 mmol, 1 equiv). Chromatography on silica gel (95:5 hexanes/ ethyl acetate) afforded product **4a** (185 mg, 92% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63(m, 4H), 7.37(m, 6H), 7.04(dd, *J*=8.0, 8.0Hz, 1H), 6.91(dd, *J*=8.0, 1.6 Hz, 1H), 6.80(dd, *J*=8.0, 1.6 Hz, 1H), 5.62(dd, *J*=16.8, 7.6 Hz, 1H), 5.47(dt, *J*=16.8, 4.8Hz, 1H), 4.43(d, *J*=6.4Hz, 1H), 4.09(d, *J*=4.8Hz, 2H), 3.84(s, 3H), 3.80(s, 3H), 2.95(s, 3H), 2.56(m, 1H), 1.05(d, *J*=6.8Hz, 3H), 1.01(s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.3, 147.4, 135.5, 134.3, 133.9, 133.2, 129.5, 128.6, 127.5, 123.7, 119.5, 111.0, 81.1, 64.5, 60.6, 57.0, 55.6, 42.1, 26.8, 19.2, 15.5; $[\alpha]_D^{20}$ +16.9 (c = 2.8, CH_2Cl_2); IR (thin film) υ_{max} 2959, 2931, 2894, 2857, 1587, 1479, 1428, 1264, 1111, 1009, 702 cm^{-1}; HRMS(CI/NH_3) m/z calcd for $C_{31}H_{40}O_4NaSi$ $[M+Na]^+$ 527.2594, found 527.2579.



4b

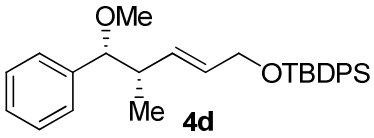
***tert*-Butyl((4*S*,5*R*,*E*)-5-(2,5-dimethoxyphenyl)-5-methoxy-4-methylpent-2-enyloxy)diphenylsilane (4b):** Following procedure *D1*, using TMSOTf (14.4 μL, 0.08 mmol, 0.2 equiv) instead of (72 μL, 0.4 mmol, 1

equiv). Chromatography on silica gel (95:5 hexanes/ ethyl acetate) afforded product **4b** (183 mg, 91% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63(m, 4H), 7.35(m, 6H), 6.88(d, *J*=2.4Hz, 1H), 6.74(m, 2H), 5.66(dd, *J*=15.6, 7.6 Hz, 1H), 5.44(dt, *J*=15.6, 5.2 Hz, 1H), 4.45(d, *J*=5.6 Hz, 1H), 4.09(d, *J*=5.2Hz, 2H), 3.74(s, 3H), 3.71(s, 3H), 3.20(s, 3H), 2.50(m, 1H), 1.01(s, 9H), 0.98(d, *J*=6.8Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.6, 151.7, 135.5, 133.9, 133.5, 130.2, 129.5, 128.3, 127.5, 113.1, 112.5, 111.3, 80.9, 64.6, 57.2, 55.8, 55.6, 41.8, 26.8, 19.2, 15.1; $[\alpha]_D^{20}$ +2.2 (c = 2.3, CH_2Cl_2); IR (thin film) υ_{max} 2932, 2857, 1496, 1216, 1111, 702 cm^{-1}; HRMS(CI/NH_3) m/z calcd for $C_{31}H_{40}O_4NaSi$ $[M+Na]^+$ 527.2594, found 527.2585.



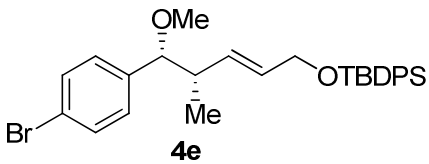
4c

***tert*-Butyl((4*S*,5*R*,*E*)-5-methoxy-4-methyl-5-p-tolylpent-2-enyloxy)diphenylsilane (4c):** Following procedure *D1*. Chromatography on silica gel (98:2 hexanes/ ethyl acetate) afforded product **4c** (144 mg, 79% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63(m, 4H), 7.36(m, 6H), 7.10(s, 4H), 5.54(dd, *J*=14.0, 6.4 Hz, 1H), 5.41(dt, *J*=14.0, 4.8 Hz, 1H), 4.07(d, *J*=4.8Hz, 2H), 3.87(d, *J*=6.8Hz, 1H), 3.19(s, 3H), 2.50(m, 1H), 2.32(s, 3H), 1.04(d, *J*=8.0Hz, 3H), 1.01(s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.3, 136.8, 135.5, 133.9, 132.6, 129.5, 128.7, 128.6, 127.5, 127.3, 87.9, 64.4, 56.8, 42.8, 26.8, 21.1, 19.1, 15.9; $[\alpha]_D^{20}$ +8.5 (c = 1.0, CH_2Cl_2); IR (thin film) υ_{max} 3071, 3050, 2959, 2930, 2857, 2246, 1428, 1106, 907, 815, 730, 699 cm^{-1}; HRMS(CI/NH_3) m/z calcd for $C_{30}H_{38}O_2NaSi$ $[M+Na]^+$ 481.2539, found 481.2586.



4d

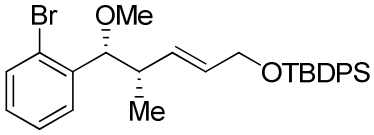
***tert*-Butyl((4*S*,5*R*,*E*)-5-methoxy-4-methyl-5-phenylpent-2-enyloxy)diphenylsilane (4d):** Following procedure *D1*. Chromatography on silica gel (98:2 hexanes/ ethyl acetate) afforded product **4d** (136 mg, 77% yield) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64(m, 4H), 7.30(m, 11H), 5.55(dd, *J*=15.2, 7.2 Hz, 1H), 5.41(dt, *J*=15.2, 4.8 Hz, 1H), 4.06(d, *J*=4.8Hz, 2H), 3.91(d, *J*=6.4Hz, 1H), 3.19(s, 3H), 2.50(dq, *J*=13.6, 6.8 Hz, 1H), 1.03(d, *J*=6.8Hz, 3H), 1.00(s, 9H); ^{13}C NMR (75MHz, $CDCl_3$) δ 140.5, 135.5, 133.9, 132.4, 129.5, 128.4, 128.0, 127.6, 127.5, 127.3, 88.0, 64.4, 57.0, 42.9, 26.8, 19.2, 15.9; $[\alpha]_D^{20}$ +8.5 (c = 1.1, CH_2Cl_2); IR (thin film) υ_{max} 3032 , 2930 , 2856, 1427, 1220, 1056, 700 cm^{-1}; HRMS(CI/NH_3) m/z calcd for $C_{29}H_{36}O_2NaSi$ $[M+Na]^+$ 467.2382, found 467.2385.



4e

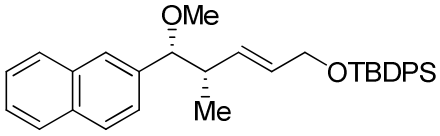
((4*S*,5*R*,*E*)-5-(4-Bromophenyl)-5-methoxy-4-methylpent-2-enyloxy)(*tert*-butyl)diphenylsilane (4e): Following procedure *D1*. Chromatography on silica gel (98:2 hexanes/ ethyl acetate) afforded product **4e** (115 mg, 55% yield) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ

7.61(m, 4H), 7.37(m, 8H), 7.07(m, 2H) 5.51(dd, *J*=15.2, 7.2 Hz, 1H), 5.41(dt, *J*=15.2, 4.4Hz, 1H), 4.06(d, *J*=6.0Hz, 2H), 3.85(d, *J*=6.8Hz, 1H), 3.17(s, 3H), 2.46(m, 1H), 1.02(d, *J*=6.8Hz, 3H), 1.00(s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.6, 135.5, 133.8, 133.8, 131.7, 131.1, 129.5, 129.2, 127.6, 121.1, 87.4, 64.2, 57.0, 42.8, 26.8, 19.2, 16.0; $[\alpha]_D^{20}$ +4.9 (c = 1.7, CH_2Cl_2); IR (thin film) υ_{max} 3070, 2959, 2930, 2892, 2856, 1590, 1485, 1427, 1110, 1070, 1010, 971, 821, 701 cm^{-1}; HRMS(CI/NH_3) m/z calcd for $C_{29}H_{35}O_2NaSiBr$ $[M+Na]^+$ 545.1487, found 545.1474.



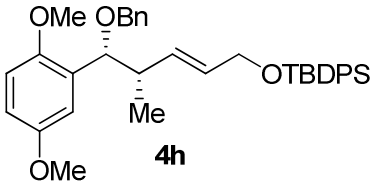
4f

((4*S*,5*R*,*E*)-5-(2-Bromophenyl)-5-methoxy-4-methyl pent-2-enyloxy)(*tert*-butyl)diphenylsilane (4f): Following procedure *D1*. Chromatography on silica gel (98:2 hexanes/ ethyl acetate) afforded product **4f** (121 mg, 58% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64(m, 4H), 7.49(dd, *J*=8, 1.2 Hz, 1H), 7.37(m, 8H), 7.09(m, 1H), 5.69(dd, *J*=15.6, 7.6 Hz, 1H), 5.49(dt, *J*=15.6, 5.2 Hz, 1H), 4.47(d, *J*=5.6Hz, 1H), 4.10(d, *J*=4.8Hz, 2H), 3.19(s, 3H), 2.53(m, 1H), 1.01(m,12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.0, 135.6, 133.9, 132.7, 132.6, 129.5, 129.0, 128.6, 128.5, 127.6, 127.3, 124.0, 85.5, 64.4, 57.3, 41.9, 26.8, 19.2, 14.7; $[\alpha]_D^{20}$ +8.8 (c = 0.8, CH_2Cl_2); IR (thin film) υ_{max}3071, 2959, 2930, 2893, 2856, 1463, 1427, 1105, 970, 700 cm^{-1}; HRMS(CI/NH_3) m/z calcd for $C_{29}H_{35}O_2NaSiBr$ $[M+Na]^+$ 545.1487, found 545.1463.



4g

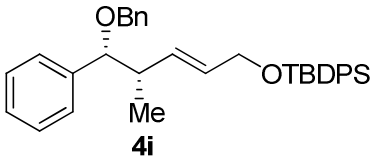
***tert*-Butyl((4*S*,5*R*,*E*)-5-methoxy-4-methyl-5-(naphthalen-2-yl)pent-2-enyloxy)diphenylsilane (4g):** Following general procedure *D1*. Chromatography on silica gel (98:2 hexanes/ ethyl acetate) afforded product **4g** (144 mg, 73% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69(m, 8H), 7.35(m, 9H), 5.58(dd, *J*=15.6, 7.2 Hz, 1H), 5.42(dt, *J*=15.6, 4.8 Hz, 1H), 4.06(d, *J*=6.8Hz, 1H), 4.03(m, 2H), 3.23(s, 3H), 2.62(dq, *J*=13.2, 6.4 Hz, 1H), 1.09(d, *J*=6.8Hz, 3H), 0.94,(s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.1, 135.6, 133.8, 133.0, 132.3, 129.5, 128.9, 127.9, 127.8, 127.7, 127.6, 127.5, 126.7, 125.9, 125.6, 125.3, 88.2, 64.3, 57.1, 42.8, 26.8, 19.1, 16.1; $[\alpha]_D^{20}$ +21.0 (c = 0.7, CH_2Cl_2); IR (thin film) υ_{max} 3051, 2959, 2930, 2856, 1697, 1428, 1111, 702 cm^{-1}; HRMS(CI/NH_3) m/z calcd for $C_{33}H_{38}O_2NaSi$ $[M+Na]^+$ 517.2539, found 517.2527.



4h

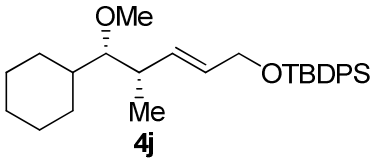
((4*S*,5*R*,*E*)-5-(Benzyloxy)-5-(2,5-dimethoxyphenyl)-4-methylpent-2-enyloxy)(*tert*-butyl)diphenylsilane (4h): Following procedure *D1*, using TMSOBn (80 mg, 0.44 mmol, 1.1 equiv) instead of TMSOMe (60 μL, 0.44 mmol, 1.1 equiv); TMSOTf (14.4 μL, 0.08 mmol, 0.2 equiv) instead of TMSOTf (72 μL, 0.4 mmol, 1 equiv). Chromatography on silica gel (95:5 hexanes/ ethyl acetate) afforded product **4h** (201 mg, 87% yield) as a colorless oil. ^{1}H NMR (400 MHz,

$CDCl_3$) δ 7.63(m, 4H), 7.30(m, 11H), 6.99(s, 1H), 6.76(m, 2H), 5.67(dd, *J*=15.2, 7.6 Hz, 1H), 5.44(dt, *J*=15.2, 5.2 Hz, 1H), 4.68(d, *J*=6.0Hz, 1H), 4.43(d, *J*=12.0Hz, 1H), 4.24(d, *J*=12.0Hz, 1H), 4.07(d, *J*=5.2Hz, 2H), 3.74(s, 3H), 3.71(s, 3H), 2.55(dq, *J*=13.6, 6.8 Hz, 1H), 1.05(d, *J*=6.8Hz, 3H), 1.01,(s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.7, 151.7, 138.9, 135.5, 133.9, 133.4, 130.6, 129.5, 128.3, 128.2, 127.6, 127.5, 127.2, 113.2, 112.8, 111.4, 78.6, 70.9, 64.6, 55.9, 55.7, 42.1, 26.8, 19.2, 15.5; $[\alpha]_D^{20}$ +17.7 (c = 1.7, CH_2Cl_2); IR (thin film) υ_{max} 3069, 2956, 2931, 2857, 1497, 1216, 1112, 1050, 702 cm^{-1}; HRMS(CI/NH_3) m/z calcd for $C_{37}H_{45}O_4Si$ $[M+H]^+$ 581.3087, found 581.3710.



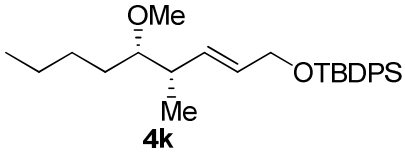
4i

((4*S*,5*R*,*E*)-5-(Benzyloxy)-4-methyl-5-phenylpent-2-enyloxy)(*tert*-butyl)diphenylsilane (4i): Following procedure *D1*, using TMSOBn (80 mg, 0.44 mmol, 1.1 equiv) instead of TMSOMe (60 μL, 0.44 mmol, 1.1 equiv). Chromatography on silica gel (98:2 hexanes/ ethyl acetate) afforded product **4i** (106 mg, 51% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62(m, 4H), 7.30(m, 16H), 5.55(dd, *J*=15.6, 7.2 Hz, 1H), 5.41(dt, *J*=15.6, 4.8 Hz, 1H), 4.46(d, *J*=12Hz, 1H), 4.23(d, *J*=12Hz, 1H), 4.10(d, *J*=6.8Hz, 1H), 4.05(d, *J*=4.4Hz, *2*H), 2.57(m, 1H), 1.10(d, *J*=6.8Hz, 3H), 1.00,(s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.7 , 138.7 , 135.6 , 135.5 , 133.8 , 132.3 , 129.5 , 128.9 , 128.2 , 128.0 , 127.6 , 127.6 , 127.5 , 127.4 , 127.3; $[\alpha]_D^{20}$ +6.6 (c = 1.1, CH_2Cl_2); IR (thin film) υ_{max} 3029, 2930, 2856, 1453, 1427, 1111, 737, 699 cm^{-1}; HRMS(CI/NH_3) m/z calcd for $C_{35}H_{40}NaO_2Si$ $[M+Na]^+$ 543.2695, found 543.2673.



4j

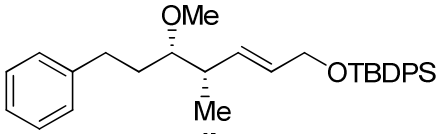
***tert*-Butyl((4*S*,5*S*,*E*)-5-cyclohexyl-5-methoxy-4-methylpent-2-enyloxy)diphenylsilane (4j):** Following procedure *D2*. Chromatography on silica gel (98:2 hexanes/ ethyl acetate) afforded product **4j** (137 mg, 76% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68(m, 4H), 7.38(m, 6H), 5.65(dd, *J*=15.6, 8.0 Hz, 1H), 5.54(dt, *J*=15.6, 4.8 Hz, 1H), 4.17(d, *J*=4.8Hz, 2H), 3.39(s, 3H), 2.66(dd, *J*=6, 5.6Hz, 1H), 2.38(m, 1H), 1.80(m, 1H), 1.57(m, 6H), 1.16(m, 4H), 1.05(s, 9H), 1.00(d, *J*=6.4Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.5, 134.6, 133.9, 129.6, 127.9, 127.6, 90.4, 64.6, 61.5, 41.0, 38.8, 30.6, 27.6, 26.8, 26.6, 26.3, 19.2, 15.4; $[\alpha]_D^{20}$ -11.5 (c = 0.5, CH_2Cl_2); IR (thin film) υ_{max} 3071, 2927, 2853, 1428, 1109, 701 cm^{-1}; HRMS(CI/NH_3) m/z calcd for $C_{29}H_{42}O_2NaSi$ $[M+Na]^+$ 473.2852, found 473.2900.



4k

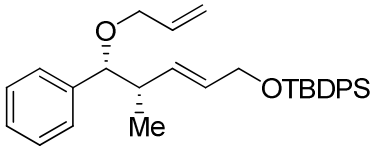
***tert*-Butyl((4*S*,5*S*,*E*)-5-methoxy-4-methylnon-2-enyloxy)diphenylsilane (4k):** Following procedure *D2*. Chromatography on silica gel (98:2 hexanes/ ethyl

acetate) afforded product **4k** (155 mg, 61% yield) as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66(m, 4H), 7.38(m, 6H), 5.61(dd, *J*=15.2, 7.2 Hz, 1H), 5.52(dt, *J*=15.2, 4.8 Hz, 1H), 4.15(d, *J*=4.4Hz, 2H), 3.32(s, 3H), 2.92(m, 1H), 2.36(m, 1H), 1.31(m, 7H), 1.03(s, 9H), 0.99(d, *J*=6.8Hz, 3H), 0.87(t, *J*=7.2Hz, 4H), 1.00(d, *J*=6.4Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.6, 133.9, 133.5, 129.5, 128.5, 127.6, 88.2, 64.7, 57.6, 39.3, 30.7, 27.7, 26.8, 22.9, 19.2, 15.8, 14.1; $[\alpha]_D^{20}$ -11.1 (c = 0.8, CH_2Cl_2); IR (thin film) υ_{max} 3071, 2957, 2930, 2857, 1589, 1462, 1628, 1105, 971, 822, 700, 612 cm^{-1}; HRMS(CI/NH_3) m/z calcd for $C_{27}H_{40}O_2NaSi$ $[M+Na]^+$ 447.2695, found 447.2711.



4l

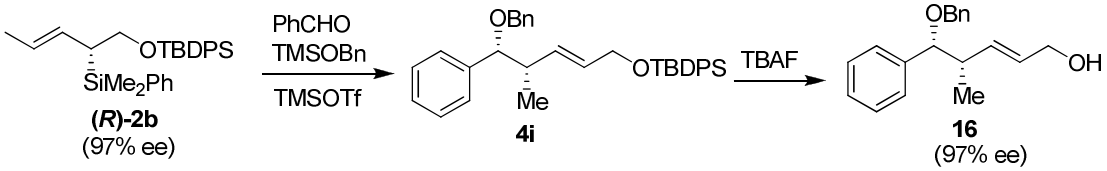
***tert*-Butyl((4*S*,5*S*,*E*)-5-methoxy-4-methyl-7-phenylhept-2-enyloxy)diphenylsilane (4l):** Following procedure *D2*. Chromatography on silica gel (98:2 hexanes/ ethyl acetate) afforded product **4l** (88 mg, 47% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65(m, 4H), 7.36(m, 6H), 7.26(m, 2H), 7.15(m, 3H), 5.62(dd, *J*=15.6, 7.2 Hz, 1H), 5.56(dt, *J*=15.2, 4.4 Hz, 1H), 4.16(d, *J*=4.0Hz, 2H), 3.36(s, 3H), 2.99(m, 1H), 2.76(m, 1H), 2.58(m, 1H), 2.43(m, 1H), 1.73(m, 2H), 1.02(s, 9H), 1.01(d, *J*=6.0Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.6, 135.5, 133.9, 132.9, 129.5, 128.9, 128.4, 128.3, 127.6, 125.7, 84.4, 64.6, 57.5, 39.1, 32.9, 31.7, 26.8, 19.2, 16.1; $[\alpha]_D^{20}$ -11.7 (c = 0.4, CH_2Cl_2); IR (thin film) υ_{max} 3071, 2957, 2930, 2857, 2340, 1728, 1462, 1111, 701 cm^{-1}; HRMS(CI/NH_3) m/z calcd for $C_{31}H_{40}O_2NaSi$ $[M+Na]^+$ 495.2695, found 495.2668.



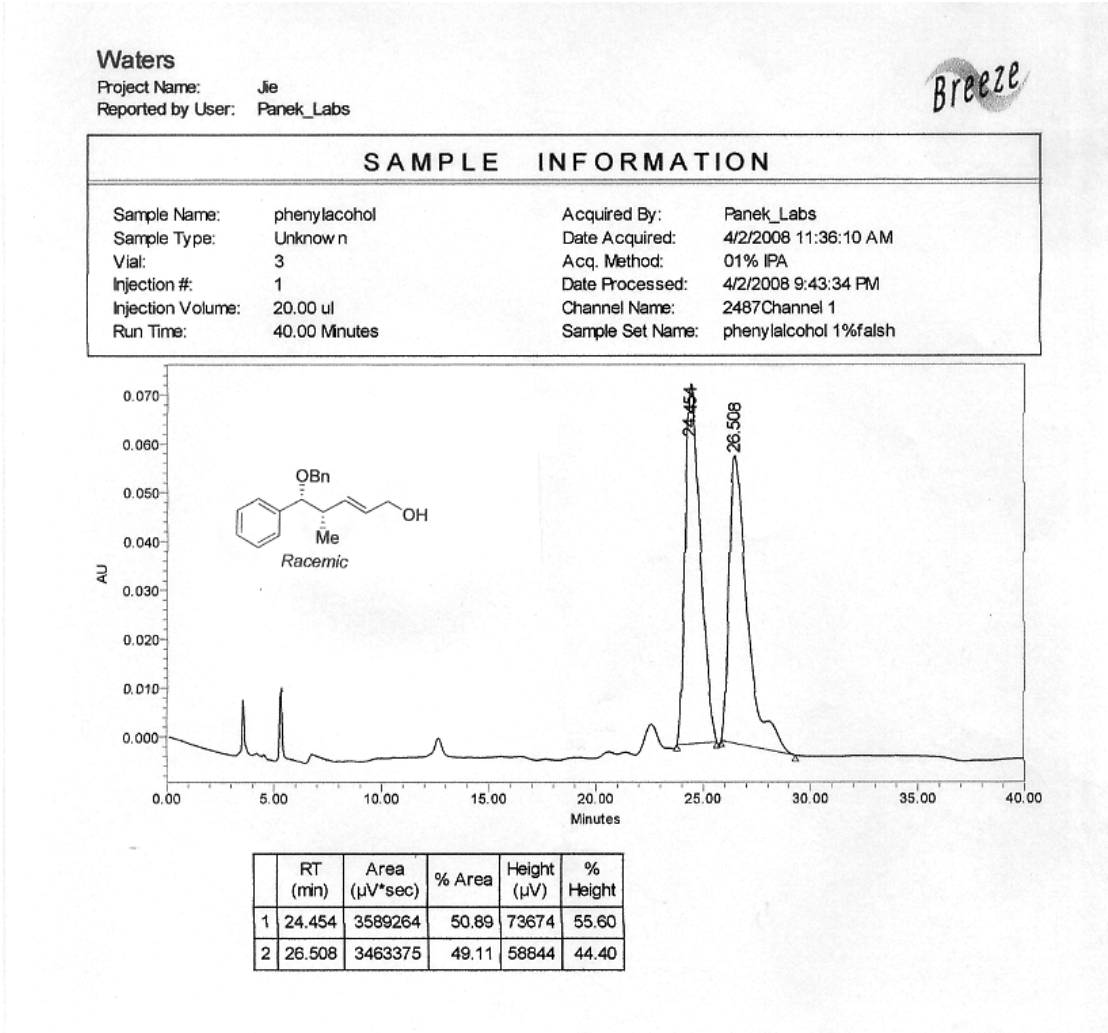
4m

((4*S*,5*R*,*E*)-5-(Allyloxy)-4-methyl-5-phenylpent-2-enyloxy)(*tert*-butyl)diphenylsilane (4m): Following procedure *D1*, using allyloxytrimethylsilane (84 *μ*L, 0.48 mmol, 1.2 equiv) instead of TMSOMe (60 *μ*L, 0.44 mmol, 1.1 equiv). Chromatography on silica gel (95:5 hexanes/ ethyl acetate) afforded product **4m** (135 mg, 72% yield) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62(m, 4H), 7.39(m, 6H), 7.27(m, 5H), 5.88(m, 1H), 5.58(dd, *J*=15.2, 7.2Hz, 1H), 5.42(dt, *J*=15.2, 4.8Hz, 1H), 5.24(dd, *J*=17.6, 1.2Hz, 1H), 5.12(dd, *J*=17.6, 1.6Hz, 1H), 4.08(m, 3H), 3.09(dd, *J*=12.8, 5.2Hz, 1H), 3.73(dd, *J*=13.2, 6.0Hz, 1H), 2.54(m, 1H), 1.08(d, *J*=6.4Hz, 3H), 1.01(s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.8, 135.5, 135.1, 133.8, 132.4, 129.5, 128.8, 128.0, 127.6, 127.5, 127.3, 116.4, 85.3, 69.6, 64.3, 43.0, 26.8, 19.2, 15.9; $[\alpha]_D^{20}$ +10.1 (c = 1.1, CH_2Cl_2); IR (thin film) υ_{max} 3071, 2956, 2930, 2857, 1428, 1112, 701 cm^{-1}; HRMS(CI/NH_3) m/z calcd for $C_{31}H_{39}O_2Si$ $[M+H]^+$ 471.2719, found 471.2725.

*ii. ee analysis of product **4***



The racemic product **4** derived from racemic **2b** cannot achieve baseline separation on HPLC. Thus, **4** was converted to primary alcohol by removal of the silyl group with TBAF. **4i**, which was prepared by three-component crotylation with silane **(*R*)-2b**, was converted to primary alcohol product **16**. Compound **16** was run on HPLC using a ChiralCel OD column, isocratic 1% isopropanol/hexanes at a flow rate of 1 mL/min. It was found that product has >96% ee. (See attached HPLC traces for racemic and enantioenriched product **16**.)



	RT (min)	Area (μV*sec)	% Area	Height (μV)	% Height
1	24.454	3589264	50.89	73674	55.60
2	26.508	3463375	49.11	58844	44.40

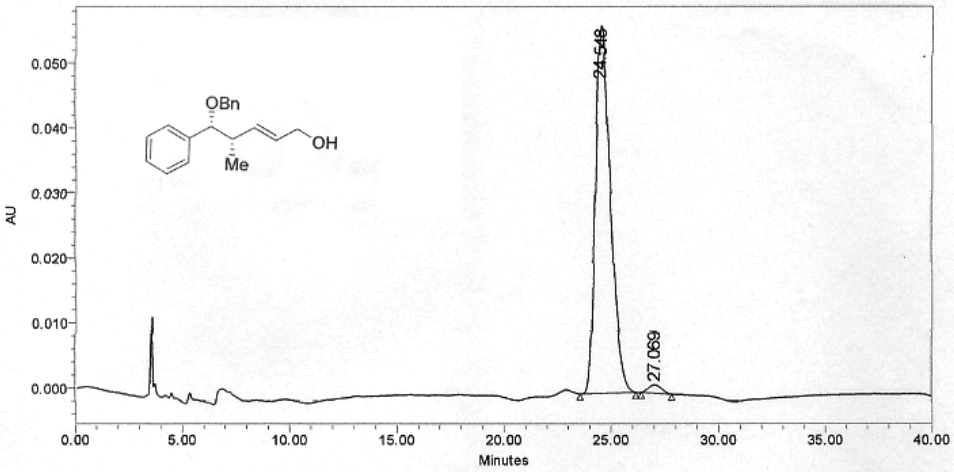
Waters

Project Name: Jie
Reported by User: Panek_Labs

Breeze

SAMPLE INFORMATION

Sample Name:	primaryalcohl	Acquired By:	Panek_Labs
Sample Type:	Unknown	Date Acquired:	4/8/2008 1:54:17 PM
Vial:	5	Acq. Method:	01% IPA
Injection #:	1	Date Processed:	4/8/2008 3:33:32 PM
Injection Volume:	20.00 ul	Channel Name:	2487Channel 1
Run Time:	40.00 Minutes	Sample Set Name:	from diol silane p



	RT (min)	Area (µV*sec)	% Area	Height (µV)	% Height
1	24.548	2757071	98.06	56534	97.77
2	27.069	54444	1.94	1292	2.23