Tetrahedron: Asymmetry Vol. 1, No. 11, pp. 801-816, 1990
Printed in Great Britain

0957-4166/90 $3.00+.00
Pergamon Press plc

SYNTHESIS, RESOLUTION AND ABSOLUTE STEREOCHEMICAL ASSIGNMENT OF C1-OXYGENATED ALLYLSILANES AND C3-OXYGENATED VINYLSILANES.‡

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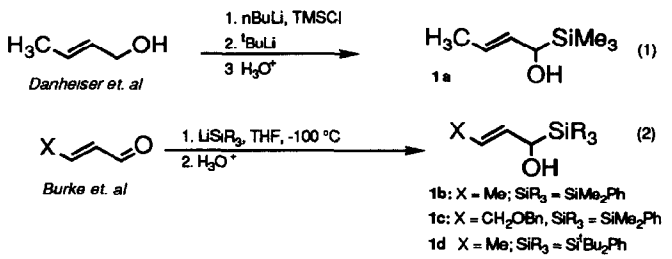
(*Received* 22 *October* 1990)

Abstract: (*R*)-O-acetyl mandelic acid has been utilized for the development of a procedure for resolution and absolute stereochemical assignment of C1-oxygenated E-crotylsilanes **1a-c**. The procedure is enhanced further by an efficient boron trifluoride etherate catalyzed allylic transposition which generates E-vinylsilanes. Subsequent resolution and hydrolysis produced the vinylsilanes **6a, b** and **d** in optically active form. The published method of Trost and cowoarkers has allowed for the assignment of absolute stereochemistry.

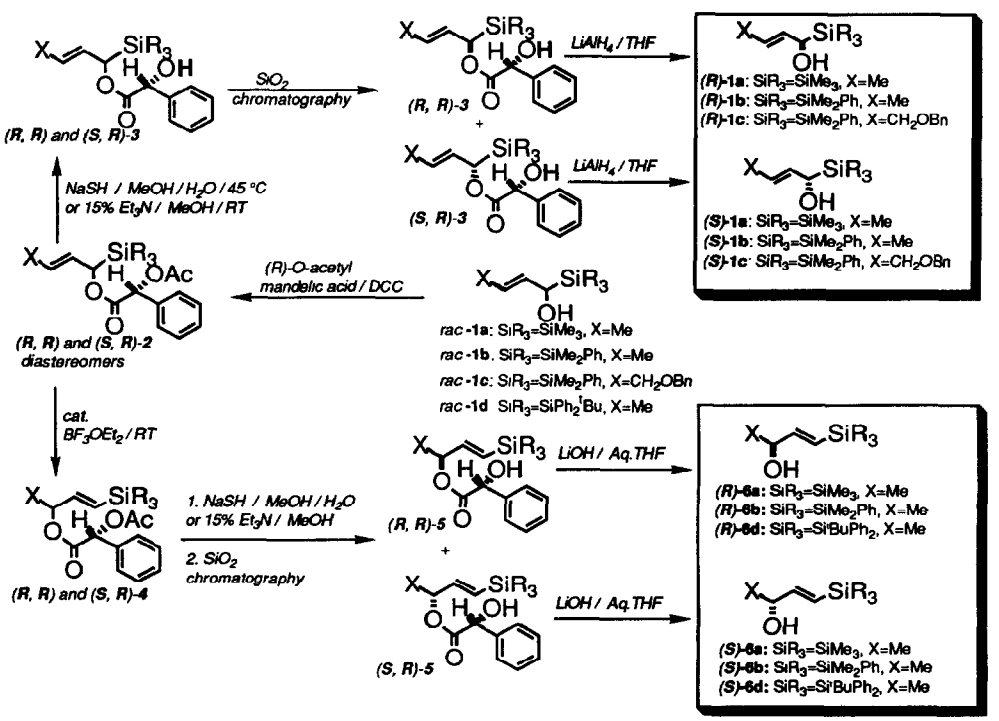
Allyl and vinylsilanes are related classes of organometallic compounds which are widely recognized as valuable reagents in organic chemistry not only for their ability to participate in a large number of synthetically useful reactions.[1,2] We have investigated the potential utility of hetero-substituted allylsilanes (C1-alkoxy allylsilanes) as important synthons in organic chemistry. We and others have documented several aspects of the synthetic utility of chiral hetero-substituted allylsilanes including fluoride ion catalyzed conjugate additions,[3] Lewis acid catalyzed O- and C-glycosidation reactions,[4] π-facial selective osmylation reactions,[5] Claisen rearrangements[6] and Pd (II) and boron trifluoride etherate catalyzed allylic transpositions.[7] These studies have demonstrated that molecules incorporating an allylic silicon functionality are capable of participating in a variety of reactions with useful levels of selectivity. In this article we describe the first general method for the production of C1-oxygenated E-crotylsilanes (*R*)- and (*S*)-**1a-c** with excellent levels of optical purity. A classical resolution employing (*R*)-O-acetyl mandelic acid was necessarily developed because existing procedures describing enzymic[8] and Sharpless kinetic resolution[9] for allylic alcohols were unsuccessful (Scheme 1). The utility of this procedure is further enhanced by the fact that the mandelate esters **2** undergo an efficient, stereospecific, Lewis acid catalyzed allylic transposition giving the E-vinylsilanes. Subsequent resolution and hydrolysis produced the vinylsilanes (*R*)- and (*S*)-**6a, b** and **d** in optically active form.[10]

As illustrated in equations 1 and 2, the racemic silanes **1a-d** were obtained in multigram quantities using previously published procedures.[11,12]



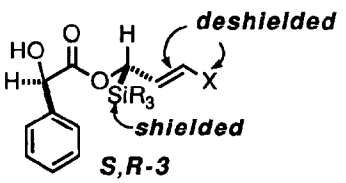
Thus *rac*-**1a** was prepared from E-crotyl alcohol in 90% yield with a reverse-Brook rearrangement.[13] The crotyl dimethylphenylsilyl ether and the C4-benzyloxy derivatives did not undergo the same rearrangement in useful yield. However the 1,2-addition of $LiSiMe_2Ph$ or $LiSiPh_2{}^tBu$[14] to crotonaldehyde gave the desired silanes **1b** and **1d** in yields ranging from 60 to 80% after purification on SiO_2. Similarly, the addition of $LISiMe_2Ph$ to 4-benzyloxy-2-butenal[15] afforded the 1-dimethylphenylsilyl-4-benzyloxy-2-buten-1-ol **1c** in 70 % isolated yield.

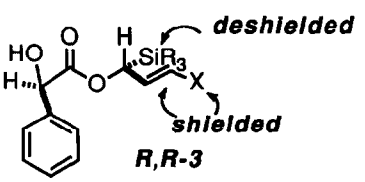
Scheme 1



The use of (*R*)-O-acetyl mandelic acid[16] as our resolving agent we were able to not only resolve but also determine the enantiomeric purity and assign the absolute configuration of the derived silanes **1**. As reported by Trost, *et. al.*[17] and employing the method originally conceived by Dale and Mosher,[18] we have assigned the absolute stereochemistry of the unknown stereocenter in each of the mandelate esters [***(R,R)*-3a-c** and ***(S,R)*-3a-c**] via ^{1}H NMR analysis and chemical shift correlation. The racemic hydroxy silanes were esterified with *(R)*-O-acetyl mandelic acid using dicyclohexylcarbodiimide for carboxylate activation (DCC, 1.0 equiv, cat. DMAP, CH_2Cl_2, RT)[19] giving the ***(R,R)*-** and ***(S,R)*-2a-c** diastereomers in quantitative yield as shown in Scheme I. Because of the nonpolar nature of the esters, chromatographic separation at this stage proved to be difficult and only small quantities could be obtained in diastereomerically pure form. In an effort to impart more polarity to the esters, we attempted the selective hydrolysis of the acetyl group. Fortunately, Whitesell and Reynolds[20] had previously reported the selective thioloysis of an acetyl mandelate ester on a chiral secondary alcohol. Thus, we were able to accomplished the selective removal of the acetate ester in the presence of the mandelate and without damage to the sensitive allylic silane. Treatment with sodium hydrosulfide (excess NaSH, aq. MeOH, 60 °C / 18-24 h) gave the desired hydroxy esters. This method worked quite well on small scale (< 2.0 grams) reactions

Table I Proton NMR Data and Optical Rotations for Mandelate Esters 3





entry	allylsilane			[α]$_D^{24}$	vinyl CH$_n$ (ppm)[a]	δ SiR$_3$ (ppm)[a,b]	Yield(%)[c]
		SiR$_3$	X				
1	*(R,R)*-3a	SiMe$_3$	Me	-54.17 (C 1.27, CHCl$_3$)	1.50	Si**Me$_3$** = 0.3	45
2	*(S,R)*-3a	SiMe$_3$	Me	-109.33 (C 1.04, CHCl$_3$)	1.71	Si**Me$_3$** = -0.25	40
3	*(R,R)*-3b	SiMe$_2$Ph	Me	-29.34 (C 1.52, CHCl$_3$)	1.48	Si**Me$_2$**Ph = 0.32	45
4	*(S,R)*-3b	SiMe$_2$Ph	Me	-65.21 (C 1.69, CHCl$_3$)	1.68	Si**Me$_2$**Ph = 0.06	43
5	*(R,R)*-3c	SiMe$_2$Ph	CH$_2$OBn	-17.68 (C 1.16, CHCl$_3$)	3.90	Si**Me$_2$**Ph = 0.37	44[d]
6	*(S,R)*-3c	SiMe$_2$Ph	CH$_2$OBn	-48.65 (C 0.74, CHCl$_3$)	4.10	Si**Me$_2$**Ph = 0.16, 0.17	40[d]

(a) All compounds were purified by chromatography on SiO_2 and exhibited the expected ^{1}H,^{13}C NMR and mass spectral characteristics. (b) This resonance is for the methyl groups or the tert-butyl group of the TMS, DMPS or the TBDPS moieties respectively. (c) Based on an optimum yield of 50% for each diastereomer after thiolysis and resolution. (d) Resolved as O-acetyl mandelate esters.

and gave satisfactory yields of the desired hydroxy esters. However, on larger scales (> 10 grams) the thiolysis was too slow (2 - 5 days for completion) to be of practical value. Efforts to increase the rate of hydrolysis by running the reaction at slightly higher temperatures (>80 °C) resulted in

hydrolysis of the mandelate ester. The problem was conveniently solved by using a tertiary amine in anhydrous methanol. Treatment of the mandelate ester with 15% triethylamine in absolute methanol (v/v) at room temperature for 18 h gave the hydroxy acids in excellent yield. In terms of reproducibility and operational simplicity we recommend the later method since the rate of acetate cleavage is faster, the reaction temperature does not have to be carefully controlled and hydrolysis of the mandelate ester is not a factor under these conditions. The mandelate esters ***(R,R)*-3a** and ***(S,R)*-3a** of 1-trimethylsilyl-2-buten-1-ol (**1a**) were resolved by medium pressure chromatography (SiO_2, hexanes with 0 - 4% ethyl acetate). Similarly the other crotyl silanes (**1b** and **1c**) have been resolved and the pertinent proton NMR data and optical rotations for their respective mandelate esters are listed in Table I. Unfortunately, the chromatographic conditions employed did not separate the tert-butyldiphenylsilyl derivative *rac*-**1d**.

The substituents shielded by the mandelate phenyl ring exhibit a $\Delta\delta$ of 0.12 to 0.21 ppm upfield from the unshielded substituents of the other diastereomer. For example, note the δ of the vinyl methyl in Table I, entries 1, 3, and 5 *vs* 2, 4, and 6. Lithium aluminum hydride reduction of the mandelate esters provided the desired alcohols in optically pure form (Table II).

Table II Lithium Aluminum Hydride Reduction of *(R,R)* - and *(S,R)* - 3

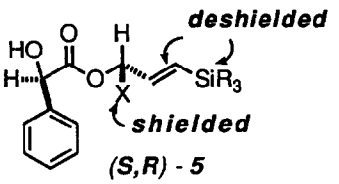
entry	silane	yield(%)[a]	$[\alpha]_D^{24}$	entry	silane	yield(%)[b]	$[\alpha]_D^{24}$
1	*(R)*-1a	70	35.48 (C 1.15, $CHCl_3$)	4	*(S)*-1a	62	-39.2 (C 1.19, $CHCl_3$)
2	*(R)*-1b	71	31.69 (C 1.04, $CHCl_3$)	5	*(S)*-1b	92	-28.32 (C1.28, $CHCl_3$)
3	*(R)*-1c	80	10.68 (C 2.64, $CHCl_3$)	6	*(S)*-1c	80	-11.69 (C0.65, $CHCl_3$)

(a) All compounds were purified by chromatography on SiO_2 and exhibited the expected ^1H, ^{13}C NMR and mass spectral characteristics.

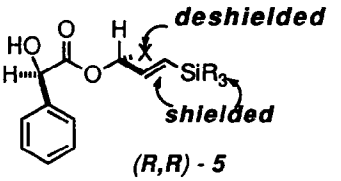
Treatment of a diastereomeric mixture of O-acetyl mandelate esters **2** with $BF_3{\cdot}OEt_2$ (0.1 equiv) in CH_2Cl_2 induced an allylic transposition resulting in the stereospecific formation of the desired E-vinylsilanes **4**, as a mixture of diastereomers in excellent yield (Scheme I). Treatment of the *(1R)*-1-(1-trimethylsilyl-2-butene) (2*R*)-O-acetyl mandelate ester ***(R,R)*-2a** with $BF_3{\cdot}OEt_2$ produced a 1.2:1 (*SR*:*RR*) mixture of E-vinylsilanes indicating a lack of preservation of chirality in this reaction. The vinylsilanes were selectively hydrolyzed to the hydroxy mandelate esters ***(R,R)*-5** and ***(S,R)*-5** and separated via flash chromatography.[21] The yields and optical rotations of the E-vinylsilane mandelate esters ***(R,R)*** and ***(S,R)*-5a, b** and **d** are listed in Table III. Assignment of the absolute stereochemistry of the vinyl silanes was based on the premise described previously. The same trends are observed with $\Delta\delta$ ranging from 0.07 to 0.11 ppm.

Each mandelate ester was subjected to lithium hydroxide hydrolysis [LiOH, 3 equiv, THF/H_2O (5:1)] followed by standard extractive isolation (H_2O, Et_2O) to afford the crude vinylsilane.

Table III Proton NMR Data and Optical Rotations for Mandelate Esters 5



(S,R) - 5



(R,R) - 5

	vinyl silane			vinyl SiR_3			
entry		SiR_3	X	$[\alpha]_D^{24}$	(ppm)[a]	δ SiR_3 (ppm)[a,b]	Yield (%)[c]
1	*(R,R)*- 5a	$SiMe_3$	Me	-66.57 (C 0.73, $CHCl_3$)	1.32	$SiMe_3$ = -0.05	45
2	*(S,R)* -5a	$SiMe_3$	Me	-84.37 (C 0.48, $CHCl_3$)	1.17	$SiMe_3$ = 0.08	40
3	*(R,R)*- 5b	$SiMe_2Ph$	Me	-49.01 (C 1.14, $CHCl_3$)	1.34	$SiMe_2Ph$ = 0.22	48
4	*(S,R)*- 5b	$SiMe_2Ph$	Me	-51.36 (C 1.19, $CHCl_3$)	1.18	$SiMe_2Ph$ = 0.35	45
5	*(R,R)*- 5d	Si^tBuPh_2	Me	-25.00 (C 0.80, $CHCl_3$)	1.35	Si^tBuPh_2= 0.98	47
6	*(S,R)*- 5d	Si^tBuPh_2	Me	-34.21 (C 1.26 ,$CHCl_3$)	1.24	Si^tBuPh_2= 1.07	48

(a) This resonance is for the methyl groups or the tert-butyl group of the TMS, DMPS or the TBDPS moieties respectively. (b) All compounds were purified by chromatography on SiO_2 and exhibited the expected ^1H, ^{13}C NMR and mass spectral characteristics. (c) Based on an optimum yield of 50% for each diastereomer after thiolysis and resolution.

Purification by flash chromatography[21] resulted in good to excellent yields of the desired vinylsilanes in optically pure form. Yields and rotations for the 1-trialkylsilyl-1-buten-3-ols (**6a, b** and **d**) are presented below in Table IV. In this instance the derivatizing agent was recycled by acidification of the aqueous layer (pH 2) and extraction with ethyl acetate. This procedure afforded the *(R)*-mandelic acid in 80% yield (optical purity > 98%).

Table IV Lithium Hydroxide Hydrolysis of Vinyl Silanes *(R,R)*- and *(S,R)*-6

entry	silane	yield(%)[a]	$[\alpha]_D^{24}$	entry	silane	yield(%)[a]	$[\alpha]_D^{24}$
1	*(R)*-6a	61	2.48 (C 1.13, $CHCl_3$)	4	*(S)*-6a	65	-2.36 (C 1.02, $CHCl_3$)
2	*(R)*-6b	90	-1.65 (C 1.64, $CHCl_3$)	5	*(S)*-6b	80	1.94 (C 1.65, $CHCl_3$)
3	*(R)*-6d	95	-1.10 (C 1.01, $CHCl_3$)	6	*(S)*-6d	95	1.27 (C 1.02, $CHCl_3$)

(a) All compounds were purified by chromatography on SiO_2 and exhibited the expected ^1H, ^{13}C NMR and mass spectral characteristics.

In conclusion, utilization of *(R)*-mandelic acid has allowed for the resolution, evaluation of optical purity, and absolute stereochemical assignment of a series of C1-oxygenated E-crotylsilanes and C3-oxygenated vinylsilanes. The availability of these silanes in their optically pure form should prove useful to those interested in applying these versatile reagents towards the synthesis of complex molecules and natural products. Further development of these reagents, as well as their application towards the synthesis of carbohydrate based natural products is underway in our laboratory.

Acknowledgments. This work has been financially supported by the National Institutes of Health (CA47249). M.A.S. gratefully acknowledges support in the form of a fellowship from the Organic Division of the American Chemical Society through Merck Sharpe and Dohme (1989-1990). We are grateful to Mr. Pier F. Cirillo for performing the triethylamine promoted selective acetate cleavage of the mandelate esters and to Ms. Heather L. Nimmons and Mr. Michael Creech for performing mass spectral measurements. We also thank Dr. Han-Li Sun for valuable technical assistance.

Experimental Section

General Methods. Unless otherwise noted commercial reagents were purchased and used without further purification. Diethyl ether (Et_2O) and tetrahydrofuran (THF) were distilled from sodium benzophenone ketyl under nitrogen just prior to use. Methylene chloride (CH_2Cl_2) was distilled from CaH_2 under nitrogen atmosphere immediately before use. Prior to use methanol was distilled from magnesium methoxide. All extraction and chromatographic solvents: acetone, ethyl acetate (EtOAc), petroleum ether (PE), and chloroform ($CHCl_3$) were distilled prior to use. Boron trifluoride etherate ($BF_3{\cdot}OEt_2$) was distilled prior to use. All ^1H (400 MHz) and ^{13}C NMR (100 MHz) spectra were obtained on a Varian XL400 (93.94 kG) at ambient temperature in deuterochloroform ($CDCl_3$). IR spectra (IR) were obtained on a Perkin Elmer 1310 infrared spectrometer. All mass spectral (low resolution/ chemical ionization and high resolution/ chemical ionization) measurements were obtained on a Finnegan MAT-90 high resolution mass spectrometer. Rotations were recorded in $CHCl_3$ on a Rudolph Research Autopol III polarimeter. TLC plates used for determining reaction progress were plastic sheets precoated with SiO_2 60 F_{254} as purchased from E. Merck, Darmstadt. Flash chromatography[21] was performed on E. Merck silica gel 230-400 mesh. Medium pressure chromatography was performed on 230-400 mesh silica gel with an apparatus consisting of a Gilson 4 channel peristaltic pump (max flow rate 15 mL/min) and a Gilson FC 203 fraction collector. Glass columns (Ace Glass Inc) used for medium pressure ranged in size from 25mm x 500mm to 50 mm x 600 mm.

General Experimental Procedure for the Esterification of *rac*-C1-Oxygenated Allylic Silanes 1a-d , Depicted for 1b.[11, 12] A solution of ***rac*-1b** (10g, 48.54 mmol) in 200 mL methylene chloride (0.24 **M**) at 0 °C under nitrogen atmosphere was treated with (*R*)-O-acetyl mandelic acid[16] (1.1equiv, 53.4 mmol, 10.25g) and cat. DMAP (ca. 100 mg). To the stirred solution was then added dicyclohexylcarbodiimide[19] (DCC, 1.1 equiv, 10.8g, 53.4 mmol). Immediately after addition of DCC a white suspension of urea precipitated out of solution. The solution was allowed to warm to room temperature over 6 h before filtering the suspension of urea through a pad of celite in a sintered glass funnel. The solvent of the filtrate was removed *in vacuo* to produce a crude yellow oil. The crude material was purified by flash chromatography on SiO_2 (100% petroleum ether - 20% ethyl acetate in petroleum ether gradient elution) to afford 18.40g (1*R*)-1-(1-dimethylphenylsilyl-2-butene) (2*R*)-2-O-acetyl-2-phenylacetate, **(*RR*)-2b** and (1*S*)-1-(1-

dimethylphenylsilyl-2-butene) (2*R*)-2-O-acetyl-2-phenylacetate, **(*SR*)-2b** as a mixture of diastereomers (quantitive yield).

Experimental Procedure for the Selective Acetate Thiolysis of Mandelate Esters (*RR*) and (*SR*) 2a-2d, depicted for 2b.[20] To a 1L round bottom flask equipped with a reflux condenser and magnetic stirring bar was added a solution of **2b** (19.35g, 50.92 mmol) in MeOH (100 mL, 0.51 **M**) The reaction was placed under a nitrogen atmosphere, treated with 200 mL of a 0.62 **M** solution of NaHS (124 mmol, 3:2 MeOH:H_2O solution) and warmed to 60 °C. Over 2 days the reaction was treated with alternating 0.62 **M** NaHS (100 mL portions) and MeOH (enough to keep the solution clear, ~50 mL portions) until the starting material was consumed as evidenced by TLC. When the reaction was complete (approx. 48 h) the solution was cooled to room temperature and diluted with H_2O (500 mL) and extracted with methylene chloride (2 x 250 mL). The organic phase was dried with $MgSO_4$, filtered and the solvent removed *in vacuo* to afford 18g of a crude yellow oil. The crude material was put through a plug of SiO_2 (10% ethyl acetate in petroleum ether eluant) to afford 13.77g of (1*R*)-1-(1-trimethylsilyl-2-butene) (2*R*)-2-hydroxy-2-phenyl-acetate, (1*R*)-1-(1-dimethylphenylsilyl-2-butene) (2*R*)-2-hydroxy-2-phenylacetate, **(*RR*)-3b** and (1*S*)-1-(1-dimethylphenylsilyl-2-butene) (2*R*)-2-hydroxy-2-phenylacetate, **(*SR*)-3b** as a clean mixture of diastereomers (80%, 17.21g theoretical).

Experimental Procedure for the Selective Acetate Cleavage of Mandelate Esters (*RR*) and (*SR*) 2a-2d Using Triethylamine, Depicted for 2a. To a 1L round bottom flask equipped with a magnetic stir bar was added a solution of **1b** (12.64 g, 39.50 mmol), in 350 mL of a 15 % (v/v) triethylamine in methanol (0.11 **M**). The reaction mixture was left to stir at ambient temperature for 14 h. The solvent was then removed *in vacuo* to yield 10.45g (95.2 %, 10.97g theoretical) of crude (1*R*)-1-(1-trimethylsilyl-2-butene) (2*R*)-2-hydroxy-2-phenyl-acetate, **(*RR*)-3a** and (1*S*)-1-(1-trimethylsilyl-2-butene) (2*R*)-2-hydroxy-2-phenylacetate, **(SR)-3a** without contamination of the allylic alcohol resulting from hydrolysis of the mandelate ester functionality as evidenced by ^1H NMR.

Resolution Procedure for the Separation of Mandelate Esters (*RR*) and (*SR*) 3a-c, Depicted for 3a. These separations are best accomplished by medium pressure chromatography, however they may be done, albeit tediously, via flash chromatography. A 1:1 mixture of **(*RR*)-3a** and **(*SR*)-3a** (10g dissolved in ~5 mL methylene chloride) was added via syringe to the top of a previously packed (100% petroleum ether), glass, medium pressure chromatography column (50 mm x 600 mm). The sample was carefully eluted with a 2-5% ethyl acetate in petroleum ether gradient system to afford 34 % **(*SR*)-3a** (less polar diastereomer) and then 40 % **(*RR*)-3a** (more polar diastereomer). Arbitrary fractions had to be checked by ^1H NMR for purity as these two diastereomers elute too closely to discern purity either via a UV detector or TLC.

Experimental Procedure for the $LiAlH_4$ Reduction of Optically Pure Mandelate Esters (*RR*) and (*SR*) 3a-b, Depicted for (*SR*)-3b. To an oven dried 50 mL round bottom flask equipped with a magnetic stir bar and rubber septa was added **(*SR*)-3b** (791.4 mg, 2.34 mmol). The flask was filled with 15.6 mL dry THF (0.15 **M**), cooled to 0 °C and treated with $LiAlH_4$ (1.0 equiv, 2.34 mmol, 87.75 mg). The solution was allowed to stir under a nitrogen atmosphere for 1 h before adding MeOH (1 mL) and allowing the reaction to warm to room temperature. The suspension of Al salts was dissolved by diluting with a saturated aqueous solution of Na/K tartrate (1x15 mL). The desired alcohol was extracted with ethyl acetate (2x10 mL), the solvent dried with $MgSO_4$ and filtered. The solvent was removed *in vacuo* to provide the crude product as a clear oil. The crude oil was purified on SiO_2 (100% petroleum ether - 10% ethyl acetate in petroleum ether gradient) to afford 398.4 mg of (1*R*)-1-dimethylphenylsilyl-2-buten-1-ol **(*R*)-1b** (82%, 486.16 mg theoretical).

Experimental Procedure for the $BF_3{\cdot}OEt_2$ Catalyzed Allylic Transposition of Mandelate Esters (*RR*) and (*SR*) 2a, b, d, Depicted for 2b. To an oven dried 500 mL round bottom flask equipped with a magnetic stirr bar and a rubber septa was added **(*RR*)-2b** and **(*SR*)-2b** as a mixture of diastereomers (10g, 26.3 mmol). The mandelic esters were dissolved in 200 mL dry methylene chloride (0.13 **M**) placed under a nitrogen atmosphere and treated with freshly distilled $BF_3{\cdot}OEt_2$ (0.1 equiv, 319 µL, 2.63 mmol). The solution was stirred for 2h at ambient temperature. The reaction was then diluted with saturated aqueous $NaHCO_3$ (1 x 100 mL) and extracted with methylene chloride (2 x 100 mL). The organic phase was dried with $MgSO_4$ and filtered. The solvent was removed under reduced pressure to afford a crude yellow oil. Purification on SiO_2 (100% petroleum ether-20% ethyl acetate in petroleum ether) afforded 9.90g of (1*R*)-3-(1-dimethylphenylsilyl-1-butene) (2*R*)-2-O-acetyl-2-phenylacetate, **(*RR*)-4b** and (1*S*)-3-(1-dimethylphenylsilyl-1-butene) (2*R*)-2-O-acetyl-2-phenylacetate, **(*SR*)-4b** as a mixture of diastereomers (99%, 10.0g theoretical).

Experimental Procedure for the Selective Acetate Thiolysis of Mandelate Esters (*RR*) and (*RS*) 4a, b, d.[20] See experimental for selective acetate thiolysis of mandelate esters **(*RR*)** and **(*SR*) 2a-2d** above.

Experimental Procedure for the Selective Acetate Hydrolysis of Mandelate Esters (*RR*) and (*SR*) 4a, b, d. See experimental for selective acetate hydrolysis of mandelate esters **(*RR*)** and **(*SR*) 2a-2d** above.

Resolution Procedure for the Separation of Mandelate Esters (*RR*) and (*SR*) 5a, b, d, depicted for 5d. All 2-hydroxy-2-phenylacetate esters of the vinyl silanes are separable via flash chromatography,[21] for example: a sample of **5d** (3g ester absorbed onto 5g SiO_2) was added to the top of a previously packed flash column (25mm x 300mm, 63.35g SiO_2, 100% petroleum ether). The esters were carefully eluted (100% petroleum ether - 10% ethyl acetate in petroleum

ether gradient system) to afford 1.2g **(*SR*)-5d** (40%, R_f 0.34, 10% ethyl acetate in petroleum ether) and 1.3g **(*RR*)-5d** (43%, R_f 0.24, 10% ethyl acetate in petroleum ether). A total of 0.5g (17%) material was recovered unresolved.

Experimental Procedure for the Lithium Hydroxide Hydrolysis of Optically Pure Mandelate Esters (*RR*) and (*SR*) 5a, b, d, Depicted for 5b. To a stirred solution of **(*RR*)-5b** (2.0g, 5.92 mmol) in a solution of THF-H_2O (5:1, 30mL total, 0.2 **M**) was added $LiOH{\cdot}H_2O$ (2.0 equiv, 497.3 mg, 11.84 mmol). The solution was allowed to stir 4h before diluting with H_2O (1x15 mL) and extracted with diethyl ether (2 x 20 mL). The organic phase was dried with $MgSO_4$ and filtered. The solvent was removed under reduced pressure to give the crude product as a clear oil. The alcohol was purified on SiO_2 (100% petroleum ether- 10% ethyl acetate in petroleum ether gradient) to afford 1.0g (3*R*)-1-dimethylphenylsilyl-1-buten-3-ol **(6b)** as a clear, yellow oil (82%, 1.22g theoretical). The remaining aqueous layer was then acidified to pH 2 (10% HCl) and extracted with ethyl acetate (1x 50 mL). The organic phase was dried with MgSO4, filtered, and the solvent removed *in vacuo* to afford an 80% recovery of (*R*)-mandelic acid in >98% optical purity.

1-trimethylsilyl-2-buten-1-ol (1a), 90% yield, see ref 11(a): ^1H NMR (400 MHz, $CDCl_3$) δ 5.58 (ddd, 1H, J = 1.36, 6.68, 14.61 Hz), 5.48 (ddq, 1H, J = 1.36, 6.27, 14.61 Hz), 3.88 (dd, 1H, J = 1.36, 6.68 Hz), 1.70 (d, 3H, J = 6.27 Hz), 0.03 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.3, 122.1, 68.2, 17.8, -4.3 (3C); IR (neat) υ_{max} 3400, 2960, 2860, 1250, 970, 840 cm^{-1}; ***R*-Ent** $[\alpha]_D^{23}$ +35.48 (C 1.15, $CHCl_3$) , ***S*-Ent** $[\alpha]_D^{23}$ -39.2 (C 1.19, $CHCl_3$); R_f 0.63 (eluant 10% EtOAc in petroleum ether).

1-dimethylphenylsilyl-2-buten-1-ol (1b), 70% yield, see ref 12 and 14: ^1H NMR (400 MHz, $CDCl_3$) δ 7.62-7.39 (m, 5H), 5.63 (ddd, J = 1.38, 6.62, 15.88 Hz), 5,25 (ddq, 1H, J = 1.38, 6.19, 15.88 Hz), 4.14 (dd, 1H, J = 1.38, 6.62 Hz), 1.74 (d, 3H, J = 6.19 Hz), 0.38 (s, 3H), 0.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.4, 134.1, 131.7, 129.2, 127.7, 122.7, 67.6, 17.8, -5.6, -6.1; IR (neat) υ_{max} 3420, 3075, 3020, 2960, 1430, 1250, 1110, 970, 840 cm^{-1}; CIMS (ammonia), m/e (relative intensity) 224 ($M+NH_4$, 66), 206 (100), 189 (43), 152 (44), 135 (21), 91 (33); CIHRMS (ammonia), m/e M, 206.1114 ($C_{12}H_{18}OSi$ requires 206.1127); ***R*-Ent** $[\alpha]_D^{23}$ +31.23 (C 1.62, $CHCl_3$) , ***S*-Ent** $[\alpha]_D^{23}$ -28.32 (C 1.30, $CHCl_3$); R_f 0.46 (eluant 10% EtOAc in petroleum ether).

1-dimethylphenylsilyl-4-benzyloxy-2-buten-1-ol (1c), 60% yield, see ref. 12 and 14: ^1H NMR (400 MHz, $CDCl_3$) δ 7.59-7.26 (m, 10H), 5.90 (dd, 1H, J = 5.56, 15.46 Hz), 5.67 (dt, 1H, J = 6.15, 15.46 Hz), 4.45 (s, 2H), 4.24 (m, 1H), 4.03 (dd, 2H, J = 1.14, 6.15 Hz), 0.38 (s, 3H), 0.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.8, 138.4, 135.9, 125.2, 134.2, 123.9, 129.5, 129.3, 128.4, 128.3, 127.9, 127.8, 127.7, 127.6, 122.7, 71.7, 70.5, 67.4, -5.6, -5.9; IR (neat) υ_{max} 3440, 3060, 2950, 2890, 1430, 1250, 1110, 1060, 830, 790 cm^{-1}; CIMS (ammonia), m/e (relative intensity) 330 ($M+NH_4$, 100), 210 (59), 52 (24); CIHRMS (ammonia), m/e $M+NH_4$, 330.1903 ($C_{19}H_{28}O_2SiN$

requires 330.1889); ***R***-Ent $[\alpha]_D^{23}$ +10.68 (C 2.64, $CHCl_3$), ***S***-Ent $[\alpha]_D^{23}$ -11.69 (C 0.65, $CHCl_3$); R_f 0.37 (eluant 20% EtOAc in petroleum ether).

1-^{t}butlydiphenylsilyl-2-buten-1-ol (1d), 71% yield, see ref 12 and 14: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71-7.27 (m, 10H), 5.69 (ddd, 1H, J = 1.54, 6.80, 15.19 Hz), 5.41 (dq, 1H, J = 6.40, 15.19 Hz), 4.69 (d, 1H, J = 6.80 Hz), 1.63 (d, 3H, J = 6.40 Hz), 1.16 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.5, 136.4, 134.7, 132.1, 129.6, 129.3, 129.2, 127.6, 127.5, 127.4, 124.3, 66.5, 26.5(3C), 18.6, 17.7; IR (neat) υ_{max} 3420, 3020, 2930, 2860, 1430, 1220, 1110, 750, 700 cm^{-1}; CIMS (ammonia), m/e (relative intensity) 328 ($M+NH_4$, 100), 310 (m, 39), 274 (62), 196 (14); CIHRMS (ammonia), m/e $M+NH_4$, 328.2065 ($C_{20}H_{30}ONSi$ requires 328.2096); R_f 0.56 (eluant 10% EtOAc in petroleum ether).

1-trimethylsilyl-1-buten-3-ol (6a), 65% yield from 5a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.29 (dd, 1H, J = 5.08, 18.64 Hz), 6.03 (dd, 1H, J = 1.22, 18.64 Hz), 4.45 (m, 1H), 1.45 (d, 3H, J = 6.46 Hz), 0.28 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 127.8, 70.2, 22.8, -1.4 (3C); IR (neat) υ_{max} 3340, 2960, 1250, 1130, 870, 840 cm^{-1}; ***R***-Ent $[\alpha]_D^{23}$ +2.36 (C 1.02, $CHCl_3$), ***S***-Ent $[\alpha]_D^{23}$ -2.48 (C 1.13, $CHCl_3$); R_f 0.63 (eluant 10% EtOAc in petroleum ether).

1-dimethylphenylsilyl-1-buten-3-ol (6b), 90% yield from 5b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.28 (m, 5H), 6.22 (dd, 1H, J = 4.92, 18.69 Hz), 5.99 (dd, 1H, J = 1.32, 18.69 Hz), 4.34 (m, 1H), 1.30 (d, 3H, J = 6.48 Hz), 0.38 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.3, 133.8, 133.7, 128.9, 128.5, 127.7, 127.6, 126.6, 125.9, 70.4, 22.8, -2.7(2C); IR (neat) υ_{max} 3380, 3080, 2960, 1730, 1620, 1430, 1250, 1110, 860 cm^{-1}; CIMS (ammonia), m/e (relative intensity) 224 ($M+NH_4$, 100), 206 (M, 44); CIHRMS (ammonia), m/e $M+NH_4$, 224.1416 ($C_{12}H_{22}OSiN$ requires 224.1470); ***R***-Ent $[\alpha]_D^{23}$ -1.65 (C 1.64, $CHCl_3$), ***S***-Ent $[\alpha]_D^{23}$ +1.94 (C 1.65, $CHCl_3$); R_f 0.46 (eluant 10% EtOAc in petroleum ether).

1-^{t}butyldiphenylsilyl-1-buten-3-ol (6c), 95% yield from 5c: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.27 (m, 10H), 6.28 (dd, 1H, J = 1.30, 18.75), 6.14 (dd, 1H, J = 4.64, 18.75 Hz), 4.40 (m, 1H), 1.29 (d, 3H, J = 6.48 Hz), 1.09 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 136.2, 134.5, 129.2, 127.6, 121.0, 70.5, 27.7(3C), 23.1, 18.2; IR (neat) υ_{max} 3340, 3070, 3050, 2960, 2920, 2860, 1520, 1460, 1110, 910, 740, 700 cm^{-1}; CIMS (ammonia), m/e (relative intensity) 328 ($M+NH_4$, 100); CIHRMS (ammonia), m/e $M+NH_4$, 328.2075 ($C_9H_{17}O_2Si$ requires 328.2096); ***R***-Ent $[\alpha]_D^{23}$ -1.10 (C 1.01, $CHCl_3$), ***S***-Ent $[\alpha]_D^{23}$ +1.27 (C 1.02, $CHCl_3$); R_f 0.56 (eluant 10% EtOAc in petroleum ether).

(1*R*)-1-(1-trimethylsilyl-2-butene) (2*R*)-2-O-acetyl-2-phenyl-acetate, (*RR*)-2a and (1*S*)-1-(1-trimethylsilyl-2-butene) (2*R*)-2-O-acetyl-2-phenyl-acetate, (*SR*)-2a reported as a mixture of diastereomers, 90% yield from 1a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.38 (m, 10H), 6.00 (s, 1H), 5.99 (s, 1H), 5.50 (dd, 1H, J = 6.17, 12.14 Hz), 5.47 (dq, 1H, J = 6.01, 12.14 Hz), 5.30 (dd, 1H, J = 6.15, 8.80 Hz), 5.10 (dq, 1H, J = 6.40, 8.80 Hz), 5.13 (d, 2x1H, J = 6.17 Hz), 2.21

(S, 2x3H), 1.70 (d, 3H, J = 6.01 Hz), 1.54 (d, 3H, J = 6.40 Hz), 0.03(s, 9H), -0.2 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 170.0, 168.5(2C), 134.3, 133.9, 128.9, 128.6, 128.5, 127.5, 126.5, 126.4, 126.3, 125.2, 124.4, 74.7, 74.5, 71.8, 71.5, 53.4, 20.6, 17.9, 17.7, -4.1(3C), -4.4(3C); IR (neat) υ_{max} 3020, 2960, 2920, 1740, 1370, 1230, 1060, 970, 840, 740 cm^{-1}; CIMS (ammonia), m/e (relative intensity) 338 ($M+NH_4$, 100), 224 (12), 131 (11), 90(21); CIHRMS (ammonia), m/e $M+NH_4$, 338.1791 ($C_{17}H_{28}O_4SiN$ requires 338.1788); R_f 0.53 (both diastereomers, eluant 10% EtOAc in petroleum ether).

(1*R*)-1-(1-trimethylsilyl-2-butene) (2*R*)-2-hydroxy-2-phenyl-acetate (*RR*)-3a (45% yield after resolution) and (1*S*)-1-(1-trimethylsilyl-2-butene) (2*R*)-2-hydroxy-2-phenylacetate (*SR*)-3a (40% yield after resolution): ^1H NMR, **(*RR*)-3a** diastereomer (400 MHz, $CDCl_3$) δ 7.44-7.28 (m, 5H), 5.29 (ddq, 1H, J = 1.30, 6.93, 14.04 Hz), 5.18 (d, 1H, J = 5.56 Hz), 5.12 (dd, 1H, J = 6.93, 14.04 Hz), 4.96 (m, 1H), 3.53 (d, 1H, J = 5.56 Hz, OH), 1.51 (dd, 3H, J = 1.30, 6.50 Hz), 0.03 (s, 9H); ^{13}C NMR, **(*RR*)-3a** diastereomer (100 MHz, $CDCl_3$) δ 173.5(2C), 138.4, 128.3, 128.2, 126.5, 126.1, 124.5, 72.9, 72.2, 17.7, -4.1(3C); ^1H NMR, **(*SR*)-3a** diastereomer (400 MHz, $CDCl_3$) δ 7.43-7.27 (m, 5H), 5.50 (m, 2H), 5.16 (m, 2H), 3.61 (d, 1H, J = 5.19 Hz, OH), 1.71 (d, 3H, J = 6.04 Hz), -0.24 (s, 9H); ^{13}C NMR, **(*SR*)-3a** diastereomer (100 MHz, $CDCl_3$) δ 176.1, 172.9, 138.3, 131.8, 128.6, 128.4, 128.3, 128.2, 74.6, 72.8, 19.4, -1.5(3C); IR (neat) υ_{max} 3480, 3030, 2960, 1720, 1450, 1250, 1180, 1070, 970, 850, 735 cm^{-1}; CIMS (ammonia), m/e (relative intensity) 296 ($M+NH_4$,100), 242 (17), 224 (17), 118 (14), 90 (42); CIHRMS (ammonia), m/e $M+NH_4$, 296.1673 ($C_{15}H_{26}O_3SiN$ requires 296.1681); ***RR*-Diast.** $[\alpha]_D^{23}$ -58.09 (C 1.05, $CHCl_3$), ***SR*-Diast.** $[\alpha]_D^{23}$ -109.56 (C 1.27, $CHCl_3$); R_f 0.35 (both diastereomers, eluant 10% EtOAc in petroleum ether).

(1*R*)-1-(1-dimethylphenylsilyl-2-butene) (2*R*)-2-O-acetyl-2-phenylacetate (*RR*)-2b and (1*S*)-1-(1-dimethylphenylsilyl-2-butene) (2*R*)-2-O-acetyl-2-phenylacetate (*SR*)-2b reported as a mixture of diastereomers, 95% yield from 1b: ^1H NMR (400 MHz, $CDCl_3$) δ 7.56-7.28 (m, 20 H), 6.00 (s, 1H), 5.97 (s, 1H), 5.52-5.23 (m, 7H), 5.08 (m, 1H), 2.20 (s, 3H), 2.19 (s, 3H), 1.66 (d, 3H, J = 6.24 Hz), 1.51 (d, 3H, J = 6.48 Hz), 0.33 (s, 6H), 0.12 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1 (2C), 168.5 (2C), 135.3, 135.0, 134.3, 134.1, 134.0, 132.9, 129.5, 129.4, 129.2, 129.1, 128.7, 128.6, 127.8, 127.7, 127.6, 126.3, 126.1, 125.9, 125.1, 74.7, 74.6, 71.3, 71.0, 20.8, 20.7, 17.9, 17.8, -5.5(2C), -5.7, -5.8; IR (neat) υ_{max} 3080, 2990, 1760, 1385, 1240, 1190, 1070, 850, 830, 750 cm^{-1}; CIMS (ammonia), m/e (relative intensity) 400 ($M+NH_4$, 100), 152 (10), 131 (12); CIHRMS (ammonia), m/e $M+NH_4$, 400.1941 ($C_{22}H_{30}O_4SiN$ requires 400.1944); R_f 0.45 (both diastereomers, eluant 10% EtOAc in petroleum ether).

(1*R*)-1-(1-dimethylphenylsilyl-2-butene) (2*R*)-2-hydroxy-2-phenylacetate (*RR*)-3b (45% yield after resolution) and (1*S*)-1-(1-dimethylphenylsilyl-2-butene) (2*R*)-2-hydroxy-2-phenylacetate (*SR*)-3b (43% yield after resolution): ^1H NMR **(*RR*)-3b** diastereomer (400 MHz, $CDCl_3$) δ 7.64-7.27 (m, 10H), 5.32-5.31 (d, 1H, J = 6.88 Hz), 5.22 (dd, 1H, J = 6.88, 15.56 Hz), 5.12 (s, 1H), 4.93 (m, 1H), 3.50 (s, 1H, OH), 1.48 (d, 3H, J = 6.65 Hz), 0.33 (s,

6H); ^{13}C NMR (***RR***)-**3b** diastereomer (100 MHz, $CDCl_3$) δ 173.4(2C), 138.2, 134.0, 132.9, 129.6, 128.4, 128.3, 127.8, 127.7, 126.6, 125.9, 73.0, 71.7, 17.7, -5.4, -5.7; ^1H NMR (***SR***)-**3b** diastereomer (400 MHz, $CDCl_3$) δ 7.41-7.26 (m, 10H), 5.51 (m, 1H), 5.37 (m, 2H), 5.16 (s, 1H), 3.60 (s, 1H, OH), 1.67 (d, 3H, J = 6.18 Hz), 0.06 (s, 6H); ^{13}C NMR (***SR***)-**3b** diastereomer (100 MHz, $CDCl_3$) δ 172.9, 172.8, 145.3, 144.9, 133.8, 133.7, 128.5, 128.3, 127.8, 127.7, 126.7, 126.4, 73.7, 72.9, 10.7, -2.8, -2.9; IR (neat) υ_{max} 3500, 3020, 2950, 1730, 1430, 1250, 1115, 1065, 835, 700 cm^{-1}; CIMS (ammonia), m/e (relative intensity) 358 ($M+NH_4$, 100), 226 (16), 209 (17), 152 (33), 131 (89), 118 (31); CIHRMS (ammonia), m/e $M+NH_4$, 358.1840 ($C_{20}H_{28}O_3SiN$ requires 358.1838); ***RR***-Diast. $[\alpha]_D^{23}$ -29.34 (C 1.52, $CHCl_3$), ***SR***-Diast. $[\alpha]_D^{23}$ -65.21 (C 1.69, $CHCl_3$); R_f 0.30 (***SR*** diastereomer), 0.25 (***RR*** diastereomer, eluant 10% EtOAc in petroleum ether).

(1*R*)-1-(1-dimethylphenylsilyl-4-benzyloxy-2-butene) (2*R*)-2-O-acetyl-2-phenylacetate (*RR*)-2c (44% yield after resolution) and (1*S*)-1-(1-dimethylphenylsilyl-4-benzyloxy-2-butene) (2*R*)-2-O-acetyl-2-phenylacetate (*SR*)-2c (40% yield aafter resolution): ^1H NMR (***RR***)-**2c** diastereomer (400 MHz, $CDCl_3$) δ 7.53-7.25 (m, 15H), 5.98 (s, 1H), 5.55 (dd, 1H, J = 5.75, 15.58 Hz), 5.43 (dd, 1H, J = 1.17, 4.69 Hz), 5.07 (ddt, 1H, J = 1.17, 5.91, 15.58 Hz), 4.61 (s, 2H), 3.80 (d, 2H, J = 5.91 Hz), 2.21 (s, 3H), 0.37 (s, 6H); ^{13}C NMR (***RR***)-**2c** diastereomer (100 MHz, $CDCl_3$) δ 170.3, 168.5, 138.1, 134.7, 134.1, 133.9, 129.7, 129.2, 129.1, 128.9, 128.8, 128.7, 128.3, 127.9, 127.8, 127.7, 127.6, 127.5, 124.5, 74.7, 71.0, 70.3, 69.7, 20.7, -5.4, -5.7; ^1H NMR (***SR***)-**2c** diastereomer (400 MHz, $CDCl_3$) δ 7.49-7.28 (m, 15H), 6.04 (s, 1H), 5.70 (dd, 1H, J = 5.67, 15.63 Hz), 5.63 (dt, 1H, J = 5.67, 15.63 Hz), 5.45 (d, 1H, J = 5.67 Hz), 4.43 (s, 2H), 3.99 (d, 2H, J = 5.67 Hz), 2.20 (s, 3H), 0.17 (s, 3H), 0.16 (s, 3H); ^{13}C NMR (***SR***)-**2c** diastereomer (100 MHz, $CDCl_3$) δ 170.4, 168.6, 138.1, 134.6, 133.9, 132.9, 129.6, 129.3, 129.2, 128.8, 128.7, 128.5, 128.3, 127.8, 127.7, 127.6, 127.0, 124.9, 74.6, 71.3, 70.6, 69.8, 20.6, -5.7, -5.8; IR (neat) υ_{max} 3060, 3020, 2955, 1735, 1700, 1430, 1250, 1120, 1070, 835, 790 cm^{-1}; CIMS (ammonia), m/e (relative intensity) 506 ($M+NH_4$, 100), 346 (10), 302 (17); CIHRMS (ammonia), m/e $M+NH_4$, 506.2329 ($C_{29}H_{36}O_5SiN$ requires 506.2363); ***RR***-Diast. $[\alpha]_D^{23}$ -17.68 (C 1.20, $CHCl_3$), ***SR***-Diast. $[\alpha]_D^{23}$ -48.65 (C 0.74, $CHCl_3$); R_f 0.57 (***RR*** diastereomer), 0.50 (***SR*** diastereomer, eluant 20% EtOAc in petroleum ether).

(1*R*)-1-(1-^{t}butyldiphenylsilyl-2-butene) (2*R*)-2-O-acetyl-2-phenylacetate, (*RR*)-2d and (1*S*)-1-(1-^{t}butyldiphenylsilyl-2-butene) (2*R*)-2-O-acetyl-2-phenylacetate, (*SR*)-2d reported as a mixture of diastereomers, 93% yield from 1d: ^1H NMR (400 MHz, $CDCl_3$) δ 7.75-7.23 (m, 30H), 5.97 (s, 1H), 5.96 (s, 1H), 5.84 (m. 2H), 5.45 (m, 2H), 5.22 (ddd, 1H, J = 1.59, 7.24, 15.32 Hz), 4.93 (dq, 1H, J = 6.47, 15.32 Hz), 2.18 (s, 3H), 2.13 (s, 3H), 1.55 (d, 3H, J = 5.71 Hz), 1.36 (d, 3H, J = 7.24 Hz), 1.12 (s, 9H), 0.91 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1(2C), 168.5(2C), 136.2, 136.2, 136.1, 134.8, 132.1, 129.6, 129.5, 129.4, 129.3, 1229.0, 128.6, 127.9, 127.7, 127.6, 127.5, 127.4, 127.0, 126.7, 126.2, 74.8, 74.7, 69.3, 69.2, 28.1, 27.9, 26.5, 20.7, 18.5, 18.2, 17.9, 17.7; IR (neat) υ_{max} 3020, 2925, 2860, 1740, 1460, 1370, 1210, 1110, 1055, 970, 750 cm^{-1}; CIMS (ammonia), m/e (relative intensity) 504 ($M+NH_4$, 100), 450 (11), 428 (11); CIHRMS (ammonia), m/e

M+NH_4, 504.2569 ($C_{30}H_{38}O_4SiN$ requires 504.2570); R_f 0.56 (both diastereomers, eluant 10% EtOAc in petroleum ether).

(3*R*)-3-(1-trimethylsilyl-1-butene) (2*R*)-2-O-acetyl-2-phenyl-acetate, (*RR*)-4a and (3*S*)-3-(1-trimethylsilyl-1-butene) (2*R*)-2-O-acetyl-2-phenyl-acetate, (*SR*)-4a reported as a mixture of diastereomers, 95% yield from 2a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.37 (m, 10H), 5.97 (dd, 1H, J = 4.64, 18.91 Hz), 5.94 (s, 1H), 5.93 (s, 1H), 5.84 (d, 1H, J = 18.91 Hz), 5.76 (dd, 1H, J = 4.64, 18.57 Hz), 5.45 (dd, 1H, J = 0.84, 18.57 Hz), 5.36 (m, 2x1H), 2.20 (s, 2x3H), 1.31 (d, 3H, J = 6.59 Hz), 1.17 (d, 3H, J = 6.60 Hz), 0.06 (s, 6H), -0.05 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 170.1, 168.0, 167.9, 143.6, 143.4, 133.8, 131.2, 130.5, 129.1, 129.0, 128.6, 128.5, 127.7, 127.5, 74.5(2C), 73.6, 73.2, 20.6(2C), 19.6, 19.2, -1.5(3C), -1.6(3C); IR (neat) υ_{max} 3060, 3040, 2960, 1740, 1620, 1500, 1450, 1370, 1230, 1050, 870, 840 cm^{-1}; CIMS (ammonia), m/e (relative intensity) 338 (M+NH_4, 100), 267 (18), 224 (30), 207, (18), 143 (18), 117 (34), 90 (20); CIHRMS (ammonia), m/e M+NH_4, 338.1787 ($C_{17}H_{28}O_4SiN$ requires 338.1787); R_f 0.57 (both diastereomers, eluant 10% EtOAc in petroleum ether).

(3*R*)-3-(1-trimethylsilyl-1-butene) (2*R*)-2-hydroxy-2-phenyl-acetate (*RR*)-5a (45% yield after resolution) and (3*S*)-3-(1-trimethylsilyl-1-butene) (2*R*)-2-hydroxy-2-phenyl-acetate (*SR*)-5a (40% after resolution): ^{1}H NMR **(*RR*)-5a** diastereomer (400 MHz, $CDCl_3$) δ 7.43-7.32 (m, 5H), 5.76 (dd, 1H, J = 4.64, 18.38 Hz), 5.38 (m, 1H), 5.37 (d, 1H, J = 18.38 Hz), 5.18 (s, 1H), 1.32 (d, 3H, J = 6.47 Hz), -0.05 (s, 9H); ^{13}C NMR **(*RR*)-5a** diastereomer (100 MHz, $CDCl_3$) δ 172.8, 143.4, 138.4, 131.7, 128.4, 128.3, 128.2, 126.5, 126.4, 74.5, 72.8, 19.3, -1.5(3C); ^{1}H NMR **(*SR*)-5a** diastereomer (400 MHz, $CDCl_3$) δ 7.45-7.32 (m, 5H), 5.97 (dd, 1H, J = 5.02, 18.82 Hz), 5.86 (d, 1H, J = 18.82 Hz), 5.39 (m, 1H), 5.19 (s, 1H), 1.18 (d, 3H, J = 6.65 Hz), 0.08 (s, 9H); ^{13}C NMR **(*SR*)-5a** diastereomer (100 MHz, $CDCl_3$) δ 172.9, 143.2, 138.5, 130.5, 128.4, 128.3, 126.6, 73.6, 72.9, 19.7, -1.7(3C); IR (neat) υ_{max} 3480, 3040, 2960, 1730, 1450, 1250, 1180, 1095, 1070, 870, 840 cm^{-1}; CIMS (ammonia), m/e (relative intensity) 296 (M+NH_4, 100), 281 (24), 224 (40), 207 (37), 127 (14), 118 (11); CIHRMS (ammonia) m/e, M+NH_4, 296.1660 ($C_{15}H_{26}O_3SiN$ requires 296.1681); ***RR*-Diast.** $[\alpha]_D^{23}$ -66.57 (C 0.73, $CHCl_3$), ***SR*-Diast.** $[\alpha]_D^{23}$ -84.37 (C 0.48, $CHCl_3$); R_f 0.38 (***SR*** diastereomer), 0.28 (***RR*** diastereomer, eluant 10% EtOAc in petroleum ether).

(3*R*)-3-(1-dimethylphenylsilyl-1-butene) (2*R*)-2-O-acetyl-2-phenylacetate, (*RR*)-4b and (3*S*)-3-(1-dimethylphenylsilyl-1-butene) (2*R*)-2-O-acetyl-2-phenylacetate, (*SR*)-4b reported as a mixture of diastereomers, 90% yield from 2b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.25 (m, 20H), 6.10 (dd, 1H, J = 4.15, 18.85 Hz), 6.00 (d, 1H, J = 18.85 Hz), 5.95 (s, 1H), 5,94 (s, 1H), 5.86 (dd, 1H, J = 4.64, 18.80 Hz), 5.75 (d, 1H, J = 18.80 Hz), 5.41 (m, 2x1H), 2.20 (s, 2x3H), 1.32 (d, 3H, J = 6.59 Hz), 1.19 (d, 3H, J = 6.59 Hz), 0.34 (s, 6H), 0.23 (s, 3H), 0.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 170.1, 168.0, 167.9, 145.4, 145.3, 137.9, 134.1, 133.8, 133.7, 129.1, 129.0, 128.9, 128.6, 128.5, 128.1, 127.7, 127.6, 127.5, 127.4, 74.6, 74.5, 74.4, 73.5, 73.1, 20.7(2C), 19.6, 19.3, -2.7, -2.81, -2.85, -2.9; IR (neat) υ_{max} 3040, 2950, 1740, 1370, 1230, 1210, 1060, 830,

840 cm^{-1}; CIMS (ammonia), m/e (relative intensity) 400 ($M+NH_4$, 100), 338 (61), 296 (54); CIHRMS (ammonia) m/e, $M+NH_4$, 400.1939 ($C_{22}H_{30}O_4SiN$ requires 400.1944); R_f 0.40 (***SR***, diastereomer), 0.35 (***RR*** diastereomer, eluant 10% EtOAc in petroleum ether).

(3*R*)-3-(1-dimethylphenylsilyl-1-butene) (2*R*)-2-hydroxy-2-phenylacetate (*RR*)-5b (48 % yield after resolution) and (3*S*)-3-(1-dimethylphenylsilyl-1-butene) (2*R*)-2-hydroxy-2-phenylacetate (*SR*)-5b (45% yield after resolution): ^1H NMR **(*RR*)-5b** diastereomer (400 MHz, $CDCl_3$) δ 7.42-7.30 (m, 10H), 5.84 (dd, 1H, J = 4.57, 18.61 Hz), 5.83 (d, 1H, J = 18.61 Hz), 5.43 (m, 1H, m), 5.19 (s, 1H), 1.34 (d, 3H, J = 6.65 Hz), 0.23 (s, 3H), 0.22 (s, 3H); ^{13}C NMR **(*RR*)-5b** diastereomer (100 MHz, $CDCl_3$) δ 172.9, 144.9, 138.4, 133.8, 133.7, 128.9, 128.5, 128.4, 128.3, 127.7, 127.6, 126.6, 73.6, 72.9, 19.8, -2.8, -2.9; ^1H NMR **(*SR*)-5b** diastereomer (400 MHz, $CDCl_3$) δ 7.52-7.28 (m, 10H), 6.04 (dd, 1H, J = 5.09, 18.72 Hz), 5.99 (d, 1H, J = 18.72 Hz), 5.43 (m, 1H), 5.19 (s, 1H), 1.18 (d, 3H, J = 6.44 Hz), 0.36 (s, 6H); ^{13}C NMR **(*SR*)-5b** diastereomer (100 MHz, $CDCl_3$) δ 172.8, 145.3, 138.4, 137.9, 133.8, 133.7, 129.4, 129.1, 128.5, 128.3, 127.8, 127.7, 126.4, 74.4, 72.9, 19.4, -2.8(2C); IR (neat) υ_{max} 3480, 3060, 2950, 1730, 1250, 1110, 840, 730, 700 cm^{-1}; CIMS (ammonia), m/e (relative intensity), 358 ($M+NH_4$, 100), 296 (61), 224 (48), 206 (20), ; CIHRMS (ammonia) m/e, $M+NH_4$, 358.1840 ($C_{20}H_{24}O_3SiN$ requires 358.1838); ***RR***-Diast. $[\alpha]_D^{23}$ -49.01 (C 1.16, $CHCl_3$), ***SR***-Diast. $[\alpha]_D^{23}$ -51.36 (C 1.10, $CHCl_3$); R_f 0.65 (***SR*** diastereomer), 0.54 (***RR*** diastereomer, eluant 20% EtOAc in petroleum ether).

(3*R*)-3-(1-^{t}butyldiphenylsilyl-1-butene) (2*R*)-2-O-acetyl-2-phenylacetate, (*RR*)-4d and (3*S*)-3-(1-^{t}butyldiphenylsilyl-1-butene) (2*R*)-2-O-acetyl-2-phenylacetate, (*SR*)-4d reported as a mixture of diastereomers, 97% yield from 2d: ^1H NMR (400 MHz, $CDCl_3$) δ 7.76-7.31 (m, 30H), 6.30 (d, 1H, J = 18.79 Hz), 6.01 (dd, 1H, J = 4.95, 18.79 Hz), 5.99 (s, 1H), 5.98 (s, 1H), 5.95 (d, 1H, J = 18.82 Hz), 5.84 (dd, 1H, J = 4.67, 18.82 Hz), 5.45 (m, 2x1H), 2.22 (s, 3H), 2.21 (s, 3H), 1.34 (d, 3H, J = 6.54 Hz), 1.23 (d, 3H, J = 6.51 Hz), 1.09 (s, 9H), 1.07 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 168.2, 148.9, 148.1, 136.2, 136.1, 135.2, 134.8, 134.0, 129.6, 129.2, 129.1, 128.8, 128.7, 127.7, 127.6, 127.5, 124.5, 123.8, 74.8, 73.9, 73.5, 27.6(3C), 20.8, 20.7, 19.9, 19.6, 19.0; IR (neat) υ_{max} 3060, 2960, 1750, 1430, 1310, 1250, 1190, 1120, 840, 830, 740 cm^{-1}; CIMS (ammonia), m/e (relative intensity) 504 ($M+NH_4$, 100), 358 (10); CIHRMS (ammonia) m/e, $M+NH_4$, 504.2568 ($C_{30}H_{38}O_4SiN$ requires 504.2570); R_f 0.54 (***SR*** diastereomer), 0.46 (***RR*** diastereomer, eluant 10% EtOAc in petroleum ether).

(3*R*)-3-(1-^{t}butyldiphenylsilyl-1-butene) (2*R*)-2-hydroxy-2-phenylacetate (*RR*)-5d (47% yield after resolution) and (3*S*)-3-(1-^{t}butyldiphenylsilyl-1-butene) (2*R*)-2-hydroxy-2-phenylacetate (*SR*)-5d (48% after resolution): ^1H NMR **(*RR*)-5d** diastereomer (400 MHz, $CDCl_3$) δ 7.64-7.33 (m, 15H), 5.92 (d, 1H, J = 18.99 Hz), 5.82 (dd, 1H, J = 4.34, 18.99 Hz), 5.50 (m, 1H), 5.25 (s, 1H), 1.37 (d, 3H, J = 6.64 Hz), 0.98 (s, 9H); ^{13}C NMR **(*RR*)-5d** diastereomer (100 MHz, $CDCl_3$) δ 173.0, 148.5, 138.4, 136.1, 133.9, 129.2, 128.6, 128.4, 127.7, 127.6, 126.5, 123.9, 74.1, 72.9, 27.6(3C), 20.0, 18.0; ^1H NMR **(*SR*)-5d** diastereomer (400 MHz,

$CDCl_3$) δ 7.61-7.32 (m, 15H), 6.32 (dd, 1H, J = 1.29, 18.72 Hz), 6.04 (dd, 1H, J = 5.32, 18.72 Hz), 5.49 (m, 1H), 5.22 (d, 1H, J = 6.10 Hz), 3.49 (d, 1H, J = 6.04 Hz, OH), 1.23 (d, 3H, J = 6.58 Hz), 1.10 (s, 9H); ^{13}C NMR (***SR***)-**5d** diastereomer (100 MHz, $CDCl_3$) δ 172.8, 148.9, 138.4, 136.2, 133.9, 129.3, 128.6, 128.4, 127.7, 126.4, 125.2, 74.7, 73.0, 27.7(3C), 19.7, 18.2; IR (neat) υ_{max} 3500, 3060, 2930, 2860, 1730, 1620, 1450, 1250, 1180, 1100, 730, 700 cm^{-1}; CIMS (ammonia), m/e (relative intensity) 462 ($M+NH_4$, 100), 328 (38), 293 (64), 270 (47), 253 (45), 198 (22), 130 (20); CIHRMS (ammonia) m/e, $M+NH_4$, 462.2454 ($C_{28}H_{36}O_3SiN$ requires 462.2464); ***RR***-Diast. $[\alpha]_D^{23}$ -25.00 (C 0.80, $CHCl_3$), ***SR***-Diast. $[\alpha]_D^{23}$ -34.21 (C 1.26, $CHCl_3$); R_f 0.34 (***SR*** diastereomer), 0.24 (***RR*** diastereomer, eluant 10% EtOAc in petroleum ether).

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‡ Presented at the 199th National Meeting of the American Chemical Society, April 24, 1990, Boston, MA.

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