Claisen Rearrangements of Enantiomerically Pure C3-(Acyloxy)-(*E*)-vinylsilanes†

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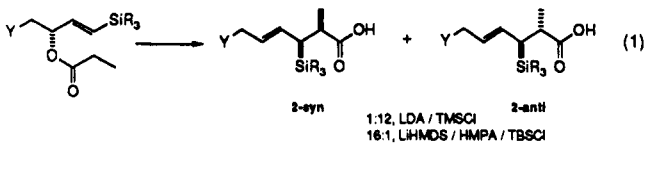
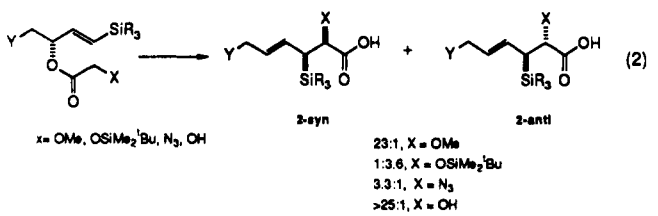
The Ireland ester Claisen rearrangement of chiral (*R*)- and (*S*)-C3-(acyloxy)-(*E*)-vinylsilanes gives access to a wide range of α-chiral-β-silyl-(*E*)-hexenoic acids with useful levels of diastereoselectivity for both the 2,3-syn and 2,3-anti diastereomers as illustrated in eqs 1 and 2. The vicinal diastereoselectivities for simple propionate esters *rac*-**1b**, (*S*)-**1e**, and (*R*)-**1g** can be varied from 1:12 to 16:1 (syn:anti) depending on reaction conditions. The employment of appropriately protected glycolate esters yields Claisen products with diastereoselectivities ranging from 23:1 (syn:anti), resulting from chelation control of enolate geometry, to 1:3.6 (syn:anti) via the use of a nonchelating, silicon-protecting group. The reaction of α-azido acetate (*R*)-**1i** is the first example of a Claisen rearrangement involving an α-azido ester and results in a new approach toward the asymmetric synthesis of α-amino acids. The assignment of relative stereochemistry based on the vicinal coupling constant data has been well documented.

Introduction

Among the many possible synthetic methodologies available for acyclic diastereoselection and the construction of vicinal stereocenters, the Claisen rearrangement is one of the most predictable and widely used among synthetic organic chemists.[2] Well-documented studies elucidating the effects of solvent,[3] additives,[4] and appropriate protecting groups[5] have culminated in an extensive database of information describing both the conditions and transition state rationale for the formation of syn and anti diastereomers.[6,7] Our research in the area of new reaction methodology for stereoselective bond forming processes has focused on the development of chiral, heterosubstituted allylsilanes as useful organometallic reagents.[8] Recently we have shown that the magnitude of π-facial selectivity in catalytic osmylation reactions of oxygen-substituted allylsilanes is dramatically influenced by the type of allylic substituents.[9] In an effort both to further these studies and to develop a de novo synthesis of simple hexoses we required a route to highly functionalized α-chiral-β-silyl-substituted hexenoic acids. In this paper we report our use of the Ireland ester Claisen methodology to transform chiral C3-oxygenated (*E*)-vinylsilanes[10] into the desired α-chiral-β-silylhexenoic acids illustrated for the *R* isomer in eqs 1 and 2.



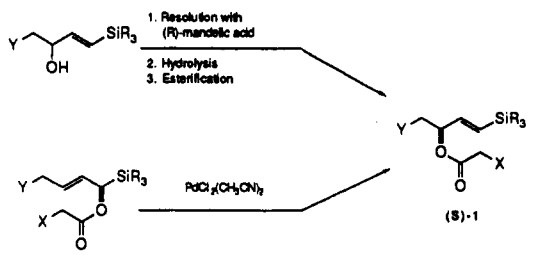
(1)



(2)

The inherent flexibility of the Claisen strategy combined with three features present in the starting materials make these reactions particularly useful for the synthesis of optically pure allylic silanes: (1) the utilization of the

Scheme I. Preparation of Optically Pure (*E*)-Vinylsilanes



enantiomerically pure esters of C3-oxygenated (*E*)-vinylsilanes *with β-heteroatom substitution* allow for the formation of enantiomerically pure α-alkoxy-substituted β-silylhexenoic acids; (2) the process is tolerant of different size silicon groups including the dimethylphenylsilane group which allows for further functionalization of the

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(2) Hill, R. K. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1984; Vol. 3, p 503.

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(4) Uchiyama, H.; Kawano, M.; Katsuki, T.; Yamaguchi, M. *Chem. Lett.* **1987**, 351.

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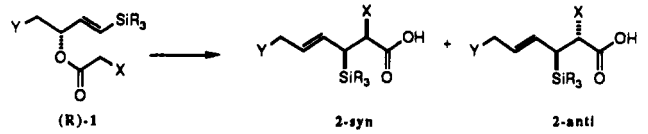
0022-3263/91/1956-3431$02.50/0

Table I. Claisen Rearrangements of Chiral (*R*)-(*E*)-Vinylsilanes



		vinylsilane				α-chiral-β-silylalkenoic acid	
entry	compd	SiR_3	X	Y	method[a]	ratio *syn*-2/*anti*-2[b]	product (yield, %)[c]
1	*rac*-1a	$SiMe_3$	H	H	D	–	**2a** (55)
2	*rac*-1b	$SiMe_3$	CH_3	H	A	1:12	**2b** (70)
3	*rac*-1b				C	16:1	**2b** (65)
4	*rac*-1b				D	2.4:1	**2b** (50)
5	*rac*-1c	$SiMe_3$	OCH_3	H	A	23:1	**2c** (95)
6	*rac*-1c				B	22:1	**2c** (90)
7	(*R*)-1f	$SiMe_2Ph$	OCH_3	H	A	23:1	**2f** (81)
8	(*R*)-1f				B	23:1	**2f** (68)
9	(*R*)-1f				D	9:1	**2f** (50)
10	(*R*)-1h	$SiMe_2Ph$	OH	H	A	>25:1[d]	**2h** (65)
11	(*R*)-1i	$SiMe_2Ph$	N_3	H	D	3.3:1	**2i** (70)
12	(*R*)-1j	$SiMe_2Ph$	$OSiPh_2{}^tBu$	H	A	1.6:1	**2j** (71)
13	(*R*)-1j				C	10:1	**2j** (69)

[a] Procedure A: Addition of substrate to LDA (1.7 equiv), THF, −78 °C, with TMSCl (10.8 eqiv) and pyridine (11.9 equiv), −78 °C to 0 °C. Procedure B: LHMDS (1.8 equiv), THF, −78 °C, then TMSCl (2 equiv), −78 °C to rt. Procedure C: LHMDS (2.0 equiv), THF, −78 °C, then TBSCl (2 equiv) and HMPA, −78 °C to rt and reflux. Hydrolysis of TBS ester with 10% HCl in THF, rt. Procedure D: TBSOTf (1.5 equiv), Et_3N (2.0 equiv), CH_2Cl_2, −78 °C to rt and reflux. Hydrolysis of TBS ester with 10% HCl in THF, rt. [b] Ratios were determined by integration of the C2 methine proton in the ^1H NMR spectrum (93.94 kG). [c] Isolated yield after chromatography on SiO_2. [d] The other diastereomer was not detected by ^1H NMR.

β-position of the Claisen product via oxidative replacement[11,12] or protiodesilylation;[13] (3) stereochemical imperfections arising (from a loss of selectivity in the enolization process) in the Claisen reaction can, in many cases, be corrected via chromatographic separation of the syn and anti diastereomers. In these compounds in which the sp^3-hybridized carbon of the allylic ester is chirotopic and the termini of the allylic and derived silyl ketene groups are unsymmetrically substituted, the Claisen rearrangement destroys the original asymmetric center while simultaneously generating two new ones in a vicinal relationship. When a single stereoisomer is used, the stereogenic character of that atom is preserved and optical activity is retained. Thus, taking advantage of earlier reports reflecting the solvent dependency[3] of the Claisen rearrangement as it affects the diastereoselectivity of the reaction, as well as exploiting the use of heterosubstituted (*E*)-vinylsilanes with the appropriate heteroatom protecting groups, we have applied this methodology for the preparation of a wide range of 2,3-syn and 2,3-anti α,β-functionalized hexenoic acids containing a configurationally pure (*E*)-crotylsilane.

Results and Discussion

As we have recently described, the optically active vinylsilanes (*R*)-1 and (*S*)-1 may be obtained by one of two methods as shown in Scheme I. Suprafacial Pd(II)-catalyzed allylic transposition of enantiomerically pure C1-(acyloxy)-(*E*)-crotylsilanes[14,15] results in the formation of the required (*E*)-vinylsilanes in good yield with complete preservation of chirality.[16] Alternatively one may resolve the racemic vinylsilanes via their mandelic acid ester derivatives,[14] hydrolyze, and re-esterify with the desired anhydride or carboxylic acid.

An important aspect of the Ireland study was the finding that the configuration of the enolate can be controlled by proper choice of reaction conditions and solvent.[3] In particular it was found that with hindered lithium amide bases and simple propionate esters, varying the enolate configuration and hence the product outcome is easily achieved. The generation of the kinetic enolate in THF–hexanes produces an (*E*)-silyl ketene acetal which rearranges to give the anti diastereomer as the major product while generation of the thermodynamic enolate with 23% hexamethylphosphoramide (HMPA) in THF (v/v) gives rise to the (*Z*)-silyl ketene acetal and hence produces the syn product.[3] In the case of heteroatom-substituted esters, chelation controls selective enolization and ultimately the diastereoselective outcome of the sigmatropic reaction.[17] Changes in solvents or reaction conditions do not dramatically change the outcome of chelation controlled Claisen reactions.[4] Under normal Ireland ester Claisen

(11) Unfortunately, known reaction conditions for the oxidative removal of dimethylphenylsilicon result in a Peterson olefination on these substrates (see ref 17e and Ager, D. J. *Synthesis* **1984**, 384). In order to effectively remove an *allylic* silane and replace with oxygen, the silicon must first contain an oxygen or nitrogen substituent (see ref 12b,c). Attempts to prepare alkoxy-substituted crotylsilanes and transform them into alkoxy-substituted β-silylhexenoic acids are currently in progress.

(12) For procedures used to affect the oxidative replacement of silicon see: (a) Fleming, I.; Sanderson, P. E. J. *Tetrahedron Lett.* **1987**, *28*, 4229. (b) Fleming, I.; Henning, R.; Plant, H. *J. Chem. Soc., Chem. Commun.* **1984**, 29. (c) Tamao, K.; Kakui, T.; Akita, M.; Iwahara, T.; Kanatani, R.; Yoshida, J.; Kumada, M. *Tetrahedron* **1983**, *39*, 983.

(13) For examples of protiodesilylation on α- and β-hydroxy silanes see: Hudrlik, P. F.; Hudrlik, A. M.; Kulkarni, A. K. *J. Am. Chem. Soc.* **1982**, *104*, 6809.

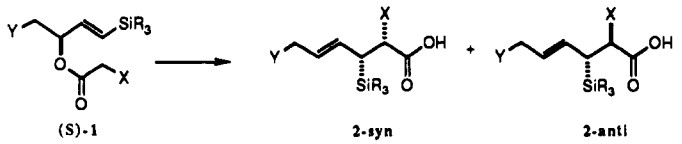
(14) For the preparation and resolution of C1-oxygenated crotylsilanes and C3-oxygenated vinylsilanes, see: Panek, J. S.; Sparks, M. A. *Tetrahedron Asymmetry* **1990**, *1*, 801.

(15) Ireland has performed Claisen rearrangements on optically pure (*tert*-butyldimethylsilyl)crotylsilanes, see: Ireland, R. E.; Varney, M. D. *J. Am. Chem. Soc.* **1984**, *106*, 3668.

(16) The procedure for the prearation of these compounds using an allylic transposition of C1-oxygenated crotylsilanes has been previously reported: Panek, J. S.; Sparks, M. A. *J. Org. Chem.* **1990**, *55*, 5564.

(17) Examples of Claisen rearrangements of chelated glycolate derivatives: (a) Burke, S. D.; Fobare, W. F.; Pacofsky, G. J. *J. Org. Chem.* **1983**, *48*, 5221. (b) Sato, T.; Tajima, K.; Fujisawa, T. *Tetrahedron Lett.* **1983**, *24*, 729. (c) Fujisawa, T.; Tajima, K.; Sato, T. *Chem. Lett.* **1984**, 1669. (d) Gould, T. J.; Balastera, M.; Wittmann, M. D.; Gary, J. A.; Rossano, L. T.; Kallmertan, J. *J. Org. Chem.* **1987**, *52*, 3889. (e) Claisen rearrangement on racemic glycolic esters of (*E*)-vinylsilanes, see: Sato, T.; Tsunekawa, H.; Kohama, H.; Fujisawa, T. *Chem. Lett.* **1986**, 1556.

Table II. Claisen Rearrangements of Chiral (*S*)-(*E*)-Vinylsilanes



		vinylsilane				α-chiral-β-silylalkenoic acid	
entry	compd	SiR_3	X	Y	method[a]	ratio *syn*-2/*anti*-2[b]	product (yield, %)[c]
1	(*S*)-1d	$SiMe_2Ph$	H	H	D	-	2d (50)
2	(*S*)-1e	$SiMe_2Ph$	CH_3	H	A	1:12	2e (81)
3	(*S*)-1e				C	16:1	2e (69)
4	(*S*)-1g	$SiMe_2Ph$	CH_3	OBn	A	1:5	2g (65)
5	*rac*-1k	$SiMe_2Ph$	$OSiMe_2{}^tBu$	H	A	1:2.2	2k (65)
6	*rac*-1k	$SiMe_2Ph$	$OSiMe_2{}^tBu$	H	C	1:3.6	2k (75)
7	(*S*)-1l	$SiPh_2{}^tBu$	OCH_3	H	A	22:1	2l (55)
8	(*S*)-1l				B	23:1	2l (51)
9	(*S*)-1l				D	3.7:1	2l (50)
10	*rac*-1m	$SiPh_2{}^tBu$	$OSiPh_2{}^tBu$	H	B	1:2.6	2m (59)

[a] Procedure A: Addition of substrate to LDA (1.7 equiv), THF, -78 °C, with TMSCl (10.8 equiv) and pyridine (11.9 equiv), -78 °C to 0 °C. Procedure B: LHMDS (1.8 equiv), THF, -78 °C, then TMSCl (2 equiv), -78 °C to rt. Procedure C: LHMDS (1.8 equiv), THF, -78 °C, then TBSCl (2 equiv) and HMPA, -78 °C to rt and reflux. Hydrolysis of TBS ester with 10% HCl in THF, rt. Procedure D: TBSOTf (1.5 equiv), Et_3N (2.0 equiv), CH_2Cl_2, -78 °C to rt and reflux. Hydrolysis of TBS ester with 10% HCl in THF, rt. [b] Ratios were determined by integration of the C2 methine proton in the ^1H NMR spectrum (93.94 kG). [c] Isolated yield after chromatography on SiO_2.

conditions, the chelated, thermodynamic enolate is trapped by the trialkylsilane as shown in Scheme II, resulting in excellent diastereoselection in favor of the 2,3-syn products. We have found, however, that by using the large, nonchelating *tert*-butyldimethylsilyl protecting group[5] in combination lithium hexamethyldisilylamide (LHMDS) and the addition of HMPA allows for formation of the kinetic (*E*)-silyl ketene acetal and ultimately the 2,3-*anti*-α-(silyloxy)-β-silylhexenoic acid.

Ratios and yields of a number of Claisen reactions using the described reaction conditions and a series of related vinylsilanes are illustrated in Tables I and II. The acetate esters (**1a** and **1d**) would not undergo the desired rearrangement in useful yield under standard Ireland ester Claisen conditions; however, the addition of triethylamine and *tert*-butyldimethylsilyl trifluoromethanesulfonate (TBSOTf) at -78 °C in CH_2Cl_2 followed by warming to room temperature and gentle refluxing (procedure D) did afford the β-silyl acids (**2a** and **2d**) in good yield. The propionate derivatives *rac*-**1b**, (*S*)-**1e**, and (*S*)-**1g**, entries 2–4 in Table I and entries 2–4 in Table II, gave the corresponding syn and anti hexenoic acid derivatives with excellent levels of diastereoselectivity.[18] Addition of the vinyltrimethylsilyl propionate ester (*rac*-**1b**) to a THF solution of lithium diisopropylamide and trimethylsilyl chloride/pyridine allowed for ketene acetal formation (procedure A).[19] Warming to room temperature resulted in a 70% yield of 2-methyl-3-(trimethylsilyl)hex-4-enoic acids (**1b**) in a 1:12 syn:anti ratio. Formation of the syn diastereomer was made possible by addition of the same propionate ester to a THF solution of LHMDS at -78 °C (procedure C). The addition of TBSCl in HMPA, warming to room temperature, and refluxing (67 °C) resulted in the formation of the corresponding *tert*-butyldimethylsilyl hexenoate. Hydrolysis of the silyl ester in a 10% HCl/THF solution gave the desired 2-methyl-3-(trimethylsilyl)hex-4-enoic acid in a syn:anti ratio of 16:1 (50% chemical yield).

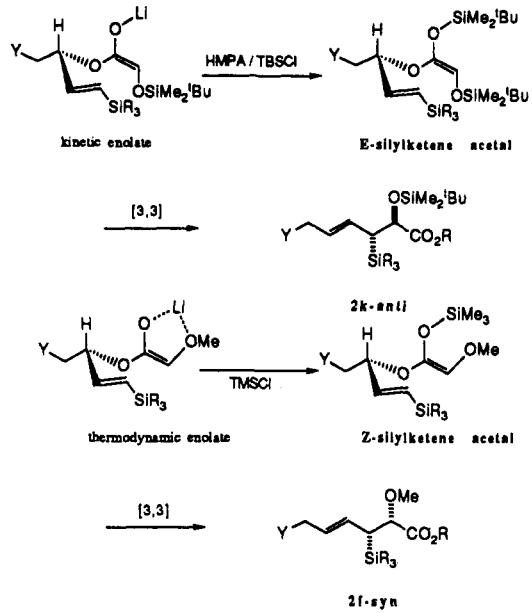
For vinylsilanes bearing α-methoxy- and α-hydroxy-substituted esters, the (*Z*)-enolate was easily obtained through chelation.[17] The vinylsilanes *rac*-**1c**, (*R*)-**1f**, and *rac*-**1l** were subjected to standard Claisen conditions[19] (1.7 equiv of LHMDS or LDA, TMSCl, -78 °C to rt, H_3O^+, procedure A or B) to afford predominantly the *syn*-2-methoxy-3-silyl-4-hexenoic acids (**2c,f,l**) with excellent levels of diastereoselectivity and good yields (see Table I, entries 5–8, and Table II, entries 7 and 8). Using triethylamine and TBSOTf (procedure D) as agents for silyl ketene acetal formation and subsequent rearrangement afforded the desired hexenoic acids in good yield albeit diminished diastereoselectivity (see Table I, entries 9 and 11, and Table II, entry 9).

In order to reverse the diastereoselectivity of the glycolate ester derivatives, the *tert*-butyldiphenylsilyl and *tert*-butyldimethylsilyl groups were employed as potential nonchelating, protecting groups.[5] Surprisingly, reaction of the (*tert*-butyldiphenylsilyl)oxy acetate [(*R*)-**1j**] under the conditions prescribed by procedure A or B resulted in poor diastereoselectivity for the anti diastereomer (see Table I, entry 12). Upon addition of HMPA and TBSCl as the enolate trapping agent (procedure C), the selectivities were enhanced to 10:1 *in favor of the syn diastereomer* (Table I, entry 13). In order to confirm our stereochemical assignments, the *tert*-butyldiphenylsilyl ethers were converted into the corresponding α-hydroxy-β-(dimethylphenylsilyl)hexenoic acids (i.e. *syn*-**2j** and *anti*-**2j**

(18) All ratios were measured by ^1H NMR from the crude reaction mixture. The signal to noise ratio was measured to be >200:1 for these measurements (400 MHz, 93.94 kG).

(19) As the reader may know there are several experimental variants of the original Ireland ester Claisen methodology using LDA. We have experimented with preparing LDA, adding a large excess of trimethylsilyl chloride/pyridine in THF to the LDA at -78 °C (see ref 5a), and *then* adding the substrate for ketene acetal formation and subsequent rearrangement. For the substrates in this study, we have found this method to be the most reliable both in terms of reproducibility and yield. Alternate methods include adding the amide base to a THF solution of substrate at -78 °C followed by TMSCl or adding a THF solution of the substrate to the amide base at -78 °C and then TMSCl. Employing either of these two methods, the best results in terms of both yield and selectivity were obtained when the enolization process (time between reaction of the substrate with base and addition of the trapping agent) was kept at a minimum (ca. 2–4 min); see ref 17d. For instance, enolization of compound **1f** with LDA for 4 min followed by trapping with TMSCl at -78 °C and warming to room temperature resulted in a 22:1 syn:anti ratio in 90% chemical yield. Addition of TMSCl after 1 h on an identical reaction gave a 10:1 syn:anti ratio with an average chemical yield of 65%. Longer enolization times result in a significant amount of hydrolyzed starting material whereas virtually none is present in a crude ^1H NMR where enolization is held under 5 min.

Scheme II. Glycolate Ester Claisen Rearrangements



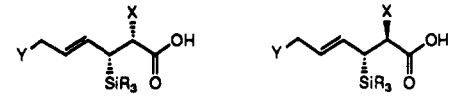
were converted into *syn*-**2h** and *anti*-**2h**) by treatment with *n*-Bu_4NF in THF. An examination of coupling constants and chemical shift values and comparison of these values to those recorded by Fujisawa and co-workers[17e] for the analogous α-hydroxy-β-(trimethylsilyl)hexenoic acid confirms that the Claisen rearrangement of the *tert*-butyldiphenylsilyl ether (**1j**) favors the formation of the syn diastereomer by as much as 10:1. Changing the silyl protecting group to *tert*-butyldimethylsilyl (**1k**) did result in diastereoselection for the anti diastereomer in a modest ratio of 1:2.2 (syn:anti) using LDA (procedure A). Upon treatment with LHMDS/TBSCl/HMPA (procedure C) the ratio was enhanced slightly to 1:3.6 (syn:anti). Similar to the dimethylphenylsilyl derivative (**2j**) above, the stereochemistry of the *tert*-butyldimethylsilyl ethers (**2k**) were confirmed by converting them to the α-hydroxy-β-silylhexenoic acids (**2h**).

Of particular significance is the Claisen rearrangement of an α-azido acetate (Table I, entry 11). Despite the modest selectivity[20] for the 2,3-syn diastereomer, this case is to our knowledge, the first example of a Claisen rearrangement involving an α-azido group and represents a new approach toward the asymmetric synthesis of α-amino acids as well as α-amino-β-hydroxy acids, should the properly substituted silicon group ($R_2R'Si$) be used.[11,12]

Assignment of Stereochemistry. The assignment of relative stereochemistry for the α-chiral-β-silylhexenoic acids is based upon the three-bond coupling constant values ($^3J_{2,3}$) as shown in Table III. In most cases the vicinal coupling constants for the 2,3-syn diastereomer (zigzag conformation as shown) are larger than those of the 2,3-anti counterpart.[21] It is interesting to note that in the case of the three 2-methoxy-3-silylhexenoic acids, a clear trend appears when the size of the silyl group increases from $SiMe_3$ < $SiMe_2Ph$ < $SiPh_2{}^tBu$. As the silicon group becomes larger, the coupling constant for the 2,3-syn diastereomer *increases* (7.57, 8.00, and 9.80 Hz) while the coupling values of the 2,3-anti diastereomers *decrease* (3.17, 3.10, and 2.40 Hz). In every case save one, where the α-position of the hexenoic acid is heteroatom-substituted, the chemical shift of the C-2 proton of the anti diastereomer appears at a lower field (Δδ of 0.04 to 0.27 Hz) than that of the corresponding syn diastereomer. The single case where both the chemical shift and $^3J_{2,3}$ are the opposite of what we expect to find is α-((*tert*-butyldiphenylsilyl)oxy)-β-(dimethylphenylsilyl)hexenoic acid (**2j**) (see Table III, entry 10); hence the need to convert these compounds to their α-hydroxy-β-silylhexenoic acid counterparts (**2h**) as described above (see Table III, entry 7). For the α-((*tert*-butyldimethylsilyl)oxy)-β-(dimethylphenylsilyl)hexenoic acid (**2k**) the chemical shifts followed the expected trend however the coupling constants are identical (Table III, entry 9). In the cases where there is a methyl group at the C-2 position, it is the C-2 proton of the anti diastereomer that is found at higher field (Table III, entries 1–3).[22]

In summary, the Ireland ester Claisen rearrangement of enantiomerically pure (*E*)-vinylsilanes (*R*)-**1** and (*S*)-**1** has proven to be an efficient approach for the synthesis of optically active γ,δ-unsaturated hexenoic acid derivatives of structural type **2**. Exploiting the flexibility of the Claisen rearrangement, both the 2,3-syn and 2,3-anti hexenoic acids are available in good yields with high levels of diastereoselection. In addition, it appears that in the case of glycolic acid derivatives "chelation control" may be attenuated by choosing the appropriate protecting group for the glycolate oxygen. The assignment of relative stereochemistry has been based on three bond coupling

Table III. $^3J_{2,3}$ and Chemical Shift Values for C2-Substituted Claisen Products



2-syn 2-anti

entry	compd	SiR_3	X	Y	$^3J_{2,3}$, Hz (δ ppm)[a]
1	**2b**	$SiMe_3$	Me	H	$J_{2,3syn}$ = 7.20 (2.61) $J_{2,3anti}$ = 6.40 (2.59)
2	**2d**	$SiMe_2Ph$	Me	H	$J_{2,3syn}$ = 7.20 (2.61) $J_{2,3anti}$ = 6.40 (2.56)
3	**2g**	$SiMe_2Ph$	Me	OBn	$J_{2,3syn}$ = 7.20 (2.68) $J_{2,3anti}$ = 6.40 (2.63)
4	**2c**	$SiMe_3$	OMe	H	$J_{2,3syn}$ = 7.57 (3.80) $J_{2,3anti}$ = 3.17 (3.93)
5	**2f**	$SiMe_2Ph$	OMe	H	$J_{2,3syn}$ = 8.00 (3.62) $J_{2,3anti}$ = 3.10 (3.66)
6	**2l**	$SiPh_2{}^tBu$	OMe	H	$J_{2,3syn}$ = 9.80 (3.41) $J_{2,3anti}$ = 2.40 (3.68)
7	**2h**	$SiMe_2Ph$	OH	H	$J_{2,3syn}$ = 4.80 (4.26) $J_{2,3anti}$ = 2.80 (4.28)
8	**2i**	$SiMe_2Ph$	N_3	H	$J_{2,3syn}$ = 7.81 (3.74) $J_{2,3anti}$ = 4.64 (3.88)
9	**2k**	$SiMe_2Ph$	$OSiMe_2{}^tBu$	H	$J_{2,3syn}$ = 3.20 (4.28) $J_{2,3anti}$ = 3.20 (4.34)
10	**2j**	$SiMe_2Ph$	$OSiPh_2{}^tBu$	H	$J_{2,3syn}$ = 3.17 (4.28) $J_{2,3anti}$ = 5.86 (4.24)
11	**2m**	$SiPh_2{}^tBu$	$OSiPh_2{}^tBu$	H	$J_{2,3syn}$ = 4.40 (4.30) $J_{2,3anti}$ = 3.20 (3.20)

[a] All ^1H NMR data was recorded on a Varian XL-400 (93.94 kG) at S/N > 200:1.

(20) Other Claisen conditions were attempted to affect this reaction including the conditions described in procedures A–C. A large excess of lithium amide base (5–10 equiv) did appear to generate the red enolate; however, upon warming and subsequent workup, only starting material and hydrolyzed ester were detected by crude ^1H NMR. For an example of the enolization and trapping of α-azido ketones, see: Takeuchi, H.; Yanagida, S.; Ozaki, T.; Hagiwara, S.; Eguchi, S. *J. Org. Chem.* **1989**, *54*, 431.

(21) Doyle, M. P.; Bagheri, V.; Harn, N. K. *Tetrahedron Lett.* **1988**, *29*, 5119 and ref 8.

(22) A method for assinging the relative stereochemistry of vicinal stereocenters in carbinols, with a wide range of functional groups (including silicon), has been published: Hildebrandt, H.; Brinkmann, H.; Hoffmann, R. W. *Chem. Ber.* **1990**, *123*, 869.

constant data and a broad base of existing experimental data which delineate the stereochemical outcome of a variety Claisen rearrangement reaction conditions. However, as we have demonstrated, this method of stereochemical assignment should be used with caution. In particular the debated electronic and steric properties of silicon[5g-i] can give rise to experimental results which may lead to misinterpretation. Studies designed to elucidate the effect of silicon on π face-selective addition reactions to these substrates, as well as their further application toward the synthesis of simple hexoses, are currently being carried out in these laboratories and will be reported in due course.

Experimental Section[23]

(E)-1-(Trimethylsilyl)-1-buten-3-ol Propanoate (1b). To a solution of (E)-1-(trimethylsilyl)-2-buten-1-ol propanoate[14,16] (1.26 g, 6.77 mmol) in 50 mL of dry CH_2Cl_2 was added $BF_3{\cdot}OEt_2$ (0.05 equiv, 0.32 mmol, 38.7 μL). The solution was stirred at ambient temperature for 1 h, diluted with saturated aqueous $NaHCO_3$ (20 mL), and extracted with CH_2Cl_2 (2 × 20 mL). The organic phase was dried ($MgSO_4$) and filtered, and the solvent removed in vacuo to afford a crude yellow oil. Purification on SiO_2 (100% petroleum ether–20% ethyl acetate in petroleum ether gradient elution) gave **1b** as a clear oil (1.10 g, 87%): ^1H NMR (400 MHz, $CDCl_3$) δ 5.90 (dd, 1 H, J = 4.8, 18.8 Hz), 5.74 (d, 1 H, J = 18.8 Hz), 5.25 (m, 1 H), 2.25 (q, 2 H, J = 7.6 Hz), 1.20 (d, 3 H, J = 6.6 Hz), 1.06 (t, 3 H, J = 7.6 Hz), –0.02 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 144.8, 130.22, 71.9, 27.7, 19.7, 9.1, –1.5 (3 C); IR (neat) ν_{max} 2950, 1740, 1460, 1370, 1250, 1190 cm^{-1}; CIMS (NH_3) m/e (relative intensity) 218 (M + NH_4^+, 57), 181 (29), 144 (40), 127 (52), 90 (100); CIHRMS (NH_3) m/e M 200.1229 ($C_{10}H_{20}O_2Si$ requires 200.1223).

(E)-(3S)-1-(Dimethylphenylsilyl)-1-buten-3-ol Propanoate (1e). A solution of (E)-(3S)-1-(dimethylphenylsilyl)-1-buten-3-ol[14] (595.8 mg, 2.90 mmol) in 15 mL of dry CH_2Cl_2 was cooled to 0 °C and treated with catalytic DMAP followed by pyridine (1.2 equiv, 3.48 mmol, 281.5 μL) and then propionyl chloride (1.2 equiv, 3.48 mmol, 291.1 μL). Over 12 h the solution was allowed to warm to ambient temperature at which time the reaction mixture was diluted with an 5% aqueous HCl solution (10 mL) and then extracted with CH_2Cl_2 (2 × 20 mL). The organic phase was dried ($MgSO_4$), filtered, and dried in vacuo to give a crude oil. Purification on SiO_2 (100% petroleum ether–20% ethyl acetate in petroleum ether gradient elution) afforded **1e** as a clear oil (684 mg, 90%): ^1H NMR (400 MHz, $CDCl_3$) δ 7.53–7.26 (m, 5 H), 6.10 (dd, 1 H, J = 4.8, 18.8 Hz), 5.40 (m, 1 H), 2.35 (q, 2 H, J = 7.6 Hz), 1.32 (d, 3 H, J = 6.6 Hz), 1.61 (t, 3 H, J = 7.6 Hz), 0.36 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 146.7, 138.3, 133.8, 129.1, 127.9, 127.8 (2 C), 71.9, 27.8, 19.8, 9.2, –2.7 (2C); IR (neat) ν_{max} 3040, 2980, 1730, 1620, 1425, 1365 cm^{-1}; CIMS (NH_3) m/e (relative intensity) 280 (M + NH_4^+, 100), 206 (21), 189 (44), 135 (23), 131 (78); CIHRMS (NH_3) m/e M 262.1387 ($C_{15}H_{22}O_2Si$ requires 262.1389); S-Ent $[\alpha]^{23}_D$ –39.18 (c 1.59, $CHCl_3$).

(E)-(3R)-1-(Dimethylphenylsilyl)-1-buten-3-ol Hydroxyacetate (1h). To a solution of (R)-**1j** (580 mg, 1.16 mmol) in 10 mL of dry THF at 0 °C was added n-Bu_4NF (0.9 equiv, 1.04 mmol, 1.04 mL, 1.0 M solution in THF). The reaction was allowed to stir for 30 min and then diluted with 5% aqueous HCl (10 mL). The solution was extracted with Et_2O (2 × 20 mL) and dried ($MgSO_4$), and the solvent was removed in vacuo to produce a crude orange oil. Purification of SiO_2 (100% petroleum ether–30% ethyl acetate in petroleum ether gradient elution) produced (R)-**1h** as a clear, viscous oil (378 mg, 90%): ^1H NMR (400 MHz, $CDCl_3$) δ 7.55–7.38 (m, 5 H), 6.01 (dd, 1 H, J = 4.3, 19.0 Hz), 6.03 (d, 1 H, J = 19.0 Hz), 5.51 (m, 1 H), 4.20 (s, 2 H), 2.79 (broad s, OH), 11.39 (d, 3 H, J = 6.5 Hz), 0.40 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 145.5, 137.9, 133.7, 129.2, 129.0, 127.8, 73.7, 60.7, 19.8, –2.8 (2 C); IR (neat) ν_{max} 3430, 2950, 1730, 1420, 1210, 1100 cm^{-1}; CIMS (NH_3) m/e (relative intensity) 382 (M + NH_4^+, 57), 206 (11), 189 (100), 145 (59), 131 (55); CIHRMS (NH_3) m/e M + NH_4^+ 282.1536 ($C_{14}H_{24}O_3SiN$ requires 282.1526); R-Ent $[\alpha]^{23}_D$ +27.40 (c 4.00, $CHCl_3$).

(E)-1-(Dimethylphenylsilyl)-1-buten-3-ol ((tert-Butyldiphenylsilyl)oxy)acetate (1j). To a solution of 1-(dimethylphenylsilyl)-1-buten-3-ol[14] (1.0 g, 4.85 mmol) and ((tert-butyldiphenylsilyl)oxy)acetic acid[24] (1.1 equiv, 5.4 mmol, 854 mg) in 30 mL of dry CH_2Cl_2 at ambient temperature was added catalytic DMAP (ca. 20 mg) and then dicyclohexylcarbodiimide[25] (1.1 equiv, 5.4 mmol, 1.12 g). A white precipitate of urea immediately formed. The reaction was allowed to stir for 4 h before the solution was filtered through a sintered-glass funnel to remove the precipitated urea. Removal of the solvent in vacuo followed by chromatography on SiO_2 (100% petroleum ether–10% ethyl acetate in petroleum ether gradient elution) afforded 400 mg of starting alcohol and **1i** as a clear oil (1.21 g, 83% based on recovered starting material): ^1H NMR (400 MHz, $CDCl_3$) δ 7.71–7.33 (m, 15 H), 6.02 (dd, 1 H, J = 4.3, 18.8 Hz), 5.93 (d, 1 H, J = 18.8 Hz), 5.41 (m, 1 H), 4.26 (s, 2 H), 1.28 (d, 3 H, J = 6.5 Hz), 1.10 (s, 9 H), 0.35 (s, 3 H), 0.34 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 146.1, 135.6, 133.8, 132.8, 129.8, 129.0, 128.5, 127.8, 127.7, 72.6, 62.4, 34.9, 26.7, 19.7, –2.7 (2 C); IR (neat) ν_{max} 3060, 2920, 2850, 1760, 1450, 1130 cm^{-1}; CIMS (NH_3) m/e (relative intensity) 520 (M + NH_4^+, 100), 425 (36), 145 (26), 131 (30); CIHRMS (NH_3) m/e M 502.2377 ($C_{30}H_{38}O_3Si_2$ requires 502.2360).

(E)-1-(Dimethylphenylsilyl)-1-buten-3-ol ((tert-butyldimethylsilyl)oxy)acetate (1k) was prepared as described for compound **1j** using ((tert-butyldimethylsilyl)oxy)acetic acid[5a] as the acid source to afford **1k** in 80% (293 mg) isolated yield: ^1H NMR (400 MHz, $CDCl_3$) δ 7.52–7.26 (m, 5 H), 6.10 (dd, 1 H, J = 4.56, 18.78 Hz), 6.01 (d, 1 H, J = 18.78 Hz), 5.44 (m, 1 H), 4.26 (s, 2 H), 1.33 (d, 3 H, J = 6.54 Hz), 0.93 (s, 9 H), 0.35 (s, 2 × 3 H), 0.12 (s, 3 H), 0.11 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 146.1, 133.7, 129.0, 128.8, 128.7, 127.8, 127.7, 72.7, 61.9, 25.7, 25.6, 19.7, –2.7 (2 C), –5.4 (2 C); IR (neat) ν_{max} 3040, 2920, 2850, 1760, 1450, 1130 cm^{-1}; CIMS (NH_3) m/e (relative intensity) 396 (M + NH_4^+, 100), 378 (20), 263 (15); CIHRMS (NH_3) m/e M 378.2050 ($C_{20}H_{34}O_3Si_2$ requires 378.2046).

(E)-(3S)-1-(tert-Butyldiphenylsilyl)-1-buten-3-ol Methoxyacetate (1l). Prepared from (S)-1-(tert-butyldiphenylsilyl)-1-buten-3-ol[14] as described for compound **1j**) with methoxyacetic acid as the acid source to afford **1l** as a clear oil in 92% (350 mg) isolated yield: ^1H NMR (400 MHz, $CDCl_3$) δ 7.59–7.34 (m, 10 H), 6.30 (d, 1 H, J = 18.74 Hz), 6.03 (dd, 1 H, J = 5.31, 18.74 Hz), 5.53 (m, 1 H), 4.04 (s, 2 H), 3.46 (s, 3 H), 1.37 (d, 3 H, 6.66 Hz), 1.08 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 149.6, 136.1, 134.0, 129.2, 127.6, 124.5, 73.1, 69.9, 59.3, 27.6(3C), 19.9, 18.1; IR (neat) ν_{max} 3060, 2920, 2850, 1750, 1620, 1425 cm^{-1}; CIMS

(23) All reactions were run in oven-dried glassware, sealed with a rubber septa and stirred with a magnetic stirring bar under N_2. Unless otherwise noted commercial reagents were purchased and used without further purification. *tert*-Butyldimethylsilyl trifluoromethanesulfonate (TBSOTf) and $BF_3{\cdot}OEt_2$ were distilled from flame-dried glassware prior to use. Triethylamine (Et_3N) and hexamethyl phosphoramide (HMPA) were distilled from CaH_2. Diisopropylamine was distilled from NaOH. Trimethylsilyl chloride was distilled from quinoline just prior to use. Diethyl ether (Et_2O) and tetrahydrofuran (THF) were distilled from sodium benzophenone ketyl under nitrogen just prior to use. CH_2Cl_2 was distilled from CaH_2 under N_2 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 $CHCl_3$ were distilled prior to use. 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 (Still, W. C.; Khan, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923) was performed on E. Merck silica gel 230–400 mesh.

(24) Silylation of *cis*-2-butene-1,4-diol with *tert*-butyldiphenylsilyl chloride (imidazole, DMF, rt) followed by ozonolysis (O_3, CH_2Cl_2, –78 °C) and reductive workup (dimethyl sulfide, –78 °C to rt) afforded the (silyloxy)acetaldehyde which when subjected to Masamune's oxidation procedure [cf. Abiko, A.; Roberts, J. C.; Takemasa, T.; Masamune, S. *Tetrahedron Lett.* **1986**, *27*, 4537] afforded the desired ((tert-butyldiphenylsilyl)oxy)acetic acid in 60% overall yield after purification on SiO_2 (3 steps).

(25) Hydrolysis of the resulting ester followed by reesterification with (R)-O-acetylmandelic acid indicates that racimization during DCC coupling is negligible. For a study of racimization during coupling procedures see: Trost, B. M.; Belletire, J. L.; Godleski, S.; McDougal, P. G.; Balkovek, J. M.; Baldwin, J. J.; Christy, M. E.; Ponticello, G. S.; Varga, S.; Springer, J. P. *J. Org. Chem.* **1986**, *51*, 2370.

(NH_3) m/e (relative intensity) 400 ($M + NH_4^+$, 100), 325 (44), 293 (21), 251 (27); CIHRMS (NH_3) m/e $M + NH_4^+$ 400.2334 ($C_{23}H_{34}O_3SiN$ requires 400.2308); S-Ent $[\alpha]^{23}_D$ -21.95 (c 1.44, $CHCl_3$).

(*E*)-1-(*tert*-Butyldiphenylsilyl)-1-buten-3-ol ((*tert*-Butyldiphenylsilyl)oxy)acetate (1m). Prepared from 1-(*tert*-butyldiphenylsilyl)-1-buten-3-ol[14] as described for compound 1j (80% yield after purification on SiO_2): ^1H NMR (400 MHz, $CDCl_3$) δ 7.59–7.32 (m, 20 H), 6.38 (d, 1 H, J = 18.69 Hz), 6.05 (dd, 1 H, J = 5.42, 18.69 Hz), 5.45 (m, 1 H), 4.27 (s, 2 H), 1.31 (d, 3 H, J = 6.59 Hz), 1.08 (s, 9 H), 1.07 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 136.13, 135.5, 134.1, 129.8, 129.1, 127.7, 127.6, 127.5, 124.0, 72.8, 62.4, 27.6 (3 C), 26.6 (3 C), 19.9, 19.5, 18.1; IR (neat) ν_{max} 3040, 2920, 2850, 1750, 1425, 1110 cm^{-1}; CIMS (NH_3) m/e (relative intensity) 624 ($M + NH_4^+$, 100), 549 (55), 199 (24), 135 (32); CIHRMS (NH_3) m/e $M + NH_4^+$ 624.3327 ($C_{38}H_{50}O_3SiN$ requires 624.3329).

Representative Procedures for the Claisen Rearrangements of Vinylsilanes 1a–l. Procedure A,[5a] as described for **2f.** To a solution of diisopropylamine (12.22 mmol, 1.71 mL) in 23 mL of freshly distilled THF at 0 °C was added n-BuLi (11.51 mmol, 5.75 mL, 2.0 M in hexanes). The solution was stirred at 0 °C for 30 min before cooling to -78 °C and adding a solution of TMSCl (10.8 equiv, 77.65 mmol, 9.85 mL) and pyridine (11.9 equiv, 85.56 mmol, 6.92 mL) in 17 mL of dry THF. After 5 min a solution of (*E*)-1-(dimethylphenylsilyl)-1-buten-3-ol 2-methoxyacetate[16] (**1f**) (2.0 g, 7.19 mmol, in 47.9 mL of dry THF) was added. The solution was stirred at -78 °C for 5 min before warming to 0 °C for 1 h. The solution was then diluted with 10% aqueous HCl (50 mL). The solution was extracted with EtOAc (2 × 50 mL) and dried ($MgSO_4$), and the solvent was removed in vacuo to afford a crude yellow oil. Purification on SiO_2 (100% petroleum ether–80% ethyl acetate in petroleum ether gradient elution) afforded **2f** as a clear oil (1.68 g, 84%) in a syn:anti ratio of 20:1 as determined by ^1H NMR analysis.[18]

Procedure B, as described for **2c.** To a solution of freshly distilled hexamethyldisilazane (4.22 mmol, 890 μL) in 8.44 mL of freshly distilled THF at 0 °C was added n-BuLi (4.17 mmol, 4.17 mL, 1.0 M in hexanes). After 30 min at 0 °C the solution was added to a THF solution of **1c**[16] (500 mg, 2.32 mmol) in 9.3 mL of dry THF at -78 °C. The yellow solution was allowed to stir for 1 h at -78 °C before the addition of TMSCl (3 equiv, 883 μL, 6.96 mmol). The solution was allowed to warm to room temperature over 14 h before being diluted with 10% aqueous HCl (50 mL). The solution was extracted with EtOAc (2 × 50 mL) and dried ($MgSO_4$), and the solvent was removed in vacuo to afford a crude yellow oil. Purification on SiO_2 (100% petroleum ether–80% ethyl acetate in petroleum ether gradient elution) afforded **2c** as a clear oil (452 mg, 90.0%) in a syn:anti ratio of 22:1 as determined by ^1H NMR analysis.[18]

Procedure C, as described for *syn*-**2e.** To a solution of freshly distilled hexamethyldisilazane (1.53 mmol, 322 μL) in 3 mL of freshly distilled THF at 0 °C was added n-BuLi (1.53 mmol, 1.53 mL, 1.0 M in hexanes). The solution was stirred at 0 °C for 30 min before adding the LHMDS to a solution of **1e** (200 mg, 0.76 mmol, in 5.06 mL of dry THF) at -78 °C. After 10 min the yellow solution was treated with TBSCl (1.53 mmol, 229.5 mg) in 1 mL of HMPA. The solution was allowed to warm to room temperature over 5 h and then refluxed for 2 h before before being diluted with 10% aqueous HCl (50 mL). The solution was extracted with EtOAc (2 × 50 mL), dried ($MgSO_4$), and filtered and the solvent removed in vacuo to afford a crude yellow oil. The crude oil was redissolved in 10 mL of THF and then treated with 2 mL of 10% aqueous HCl at room temperature and allowed to stir for 2 h. Further dilution with 5% aqueous HCl (10 mL) and extraction with EtOAc (2 × 20 mL) followed by drying ($MgSO_4$), filtration, and removal of solvent in vacuo resulted in isolation of a crude orange oil. Purification on SiO_2 (100% petroleum ether–80% ethyl acetate in petroleum ether gradient elution) afforded **2e** as a clear oil (150 mg, 75%) in a syn:anti ratio of 16:1 as determined by ^1H NMR analysis.[18]

Procedure D, as described for **2d.** A solution of **1d**[16] (804 mg, 3.24mmol) in 10.0 mL of dry CH_2Cl_2 was cooled to -78 °C and treated with Et_3N (2.0 equiv, 6.48 mmol, 916 μL) followed by TBSOTf (2.0 equiv, 6.48 mmol, 1.49 mL). The solution was allowed to warm to room temperature over 14 h and then brought to reflux for 1 h before diluting with 10% aqueous HCl (50 mL). The solution was extracted with EtOAc (2 × 50 mL) and dried ($MgSO_4$), and the solvent was removed in vacuo to afford a crude yellow oil. The crude oil was redissolved in 10 mL of THF and then treated with 2 mL of 10% aqueous HCl at room temperature and allowed to stir for 2 h. Further dilution with 5% aqueous HCl (10 mL) and extraction with EtOAc (2 × 20 mL) followed by drying ($MgSO_4$), filtration, and removal of solvent in vacuo resulted in the isolation of a crude orange oil. Purification on SiO_2 (100% petroleum ether–80% ethyl acetate in petroleum ether gradient elution) afforded **2d** as a clear oil (418.5 mg, 52%).

(*E*)-(3*S)-3-(Trimethylsilyl)-4(*E*)-hexenoic acid (2a, Table I):** ^1H NMR (400 MHz, $CDCl_3$) δ 5.30 (m, 2 H), 2.41 (dd, 1 H, J = 4.4, 15.2 Hz), 2.31 (dd, 1 H, J = 10.8, 15.2 Hz), 1.94 (m, 1 H), 1.64 (d, 3 H, J = 3.9 Hz), -0.02 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.3, 129.9, 123.4, 34.3, 28.9, 18.1, -3.4(3C); IR (neat) ν_{max} 3500–2500 (b), 1700, 1410, 1250, 860, 840 cm^{-1}; CIMS (NH_3) m/e (relative intensity) 204 ($M + NH_4^+$, 63), 187 (34), 171 (15), 90 (100), 73 (50); CIHRMS (NH_3) m/e $M + NH_4^+$ 204.1415 ($C_9H_{22}O_2SiN$ requires 204.1419).

(*E*)-(2*R,3*R**)-2-Methyl-3-(trimethylsilyl)-4(*E*)-hexenoic acid (*anti*-2b, Table I):** ^1H NMR (400 MHz, $CDCl_3$) δ 5.33 (m, 2 H), 2.65 (m, 1 H), 1.68 (m, 1 H), 1.67 (d, 3 H, J = 4.5 Hz), 1.20 (d, 3 H, J = 6.9 Hz), 0.04 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.9, 128.9, 125.1, 40.5, 37.5, 17.9, 17.2, -1.9 (3 C); IR (neat) ν_{max} 3500–2500 (b), 1700, 1450, 1400, 1250, 850 cm^{-1}; CIMS (NH_3) m/e (relative intensity) 218 ($M + NH_4^+$, 100), 201 (89), 185 (27), 90 (35); CIHRMS (NH_3) m/e M^+ 200.1234 ($C_{10}H_{20}O_2Si$ requires 200.1233).

(*E*)-(2*S,3*R**)-2-Methyl-3-(trimethylsilyl)-4(*E*)-hexenoic acid (*syn*-2b, Table I):** ^1H NMR (400 MHz, $CDCl_3$) δ 5.35 (dq, 1 H, J = 6.10, 15.0 Hz), 5.27 (dd, 1 H, J = 10.4, 15.0 Hz), 2.61 (m, 1 H), 1.91 (dd, 1 H, J = 6.7, 10.4 Hz), 1.67 (d, 3 H, J = 5.1 Hz), 1.16 (d, 3 H, J = 7.0 Hz), 0.02 (s, 9 H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 183.3, 127.5, 125.7, 39.8, 36.2, 18.1, 15.3, -2.3 (3 C); IR (neat) ν_{max} 3500–2500 (b), 1700, 1450, 1400, 1250, 860 cm^{-1}; CIMS (NH_3) m/e (relative intensity) 218 ($M + NH_4^+$, 24), 201 (M^+, 48), 185 (38); CIHRMS (NH_3) m/e M^+ 201.1313 ($C_{10}H_{21}O_2Si$ requires 201.1311).

(*E*)-(2*R,3*R**)-2-Methoxy-3-(trimethylsilyl)-4-hexenoic acid (*syn*-2c, Table I):** ^1H NMR (400 MHz, $CDCl_3$) δ 5.35 (m, 2 H), 3.80 (d, 1 H, J = 7.6 Hz), 3.39 (s, 3 H), 2.06 (dd, 1 H, J = 7.6, 10.0 Hz), 1.65 (d, 3 H, J = 6.0 Hz), 0.04 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 126.6, 125.9, 82.6, 57.9, 37.7, 18.0, -1.9 (3 C); IR (neat) ν_{max} 3500–2500 (b), 1720, 1450, 1250, 1200, 1130, 910 cm^{-1}; CIMS (NH_3) m/e (relative intensity) 234 ($M + NH_4^+$, 69), 185 (100), 168 (96), 94 (41); CIHRMS (NH_3) m/e $M + NH_4^+$ 234.1529 ($C_{10}H_{24}O_3SiN$ requires 234.1525).

(*E*)-(2*S,3*R**)-2-Methoxy-3-(trimethylsilyl)-4-hexenoic acid (*anti*-2c, Table I):** ^1H NMR (400 MHz, $CDCl_3$) δ 5.37 (m, 2 H), 3.93 (d, 1 H, J = 3.2 Hz), 3.40 (s, 3 H), 1.94 (dd, 1 H, J = 3.2, 10.3 Hz), 1.63 (d, 3 H, J = 6.2 Hz), 0.04 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.8, 126.3, 125.6, 81.5, 58.4, 37.9, 18.0, -2.43 (3 C).

(*E*)-(3*S*)-3-(Dimethylphenylsilyl)-4-hexenoic acid (2d, Table II): ^1H NMR (400 MHz, $CDCl_3$) δ 7.54–7.37 (m, 5 H), 5.34 (m, 2 H), 2.41 (dd, 1 H, J = 4.3, 15.4 Hz), 2.33 (dd, 1 H, J = 10.9, 15.4 Hz), 2.23 (m, 1 H), 1.68 (d, 3 H, J = 4.5 Hz), 0.33 (s, 6 H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 179.9, 136.7, 133.9, 129.5, 129.3, 127.8, 124.1, 34.3, 28.5, 18.2, -4.5, -5.5; IR (neat) ν_{max} 3010–2450 (b), 1700, 1420, 1200, 750 cm^{-1}; CIMS (NH_3) m/e (relative intensity) 266 ($M + NH_4^+$, 100), 226 (22), 188 (30), 171 (92), 135 (24); CIHRMS (NH_3) m/e $M + NH_4^+$ 266.1522 ($C_{14}H_{24}O_2SiN$ requires 266.1577).

(*E*)-(2*S*,3*R*)-2-Methyl-3-(dimethylphenylsilyl)-4-hexenoic acid (*anti*-2e, Table II): ^1H NMR (400 MHz, $CDCl_3$) δ 7.53–7.27 (m, 5 H), 5.32 (m, 2 H), 2.59 (dq, 1 H, J = 6.4, 7.0 Hz), 2.21 (dd, 1 H, J = 6.4, 10.0 Hz), 1.70 (d, 3 H, J = 5.1 Hz), 1.12 (d, 3 H, J = 7.0 Hz), 0.37 (s, 3 H), 0.34 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.9, 137.4, 134.1, 134.0, 129.1, 127.6, 126.9, 126.4, 39.7, 35.8, 18.2, 15.2, -3.5, -3.9; IR (neat) ν_{max} 3100–2500 (b), 1700, 1420, 1250, 1100, 835 cm^{-1}; CIMS (NH_3) m/e (relative intensity) 280 ($M + NH_4^+$, 78), 202 (29), 185 (100), 169 (30); CIHRMS (NH_3) m/e $M + NH_4^+$ 280.1731 ($C_{15}H_{26}O_2SiN$ requires 280.1732).

(*E*)-(2*R*,3*R*)-2-Methyl-3-(dimethylphenylsilyl)-4-hexenoic acid (*syn*-2e, Table II): ^1H NMR (400 MHz, $CDCl_3$) δ 7.53–7.27

(m, 5 H), 5.35 (m, 2 H), 2.59 (dq, 1 H, J = 6.8, 7.2 Hz), 1.94 (dd, 1 H, J = 7.2, 9.4 Hz), 1.67 (d, 3 H, J = 6.0 Hz), 1.08 (d, 3 H, J = 6.8 Hz), 0.35 (s, 3 H), 0.32 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.2, 138.1, 133.9, 128.9, 128.5, 127.5, 125.7, 40.4, 37.0, 18.0, 17.4, −2.9, −4.1; IR (neat) ν_{max} 3500–2500 (b), 1700, 1420, 1250, 1110, 840 cm^{-1}; CIMS (NH_3) m/e (relative intensity) 280 (M + NH_4^+, 47), 184 (65), 169 (100), 135 (70); CIHRMS (NH_3) m/e M + NH_4^+ 280.1736 ($C_{15}H_{26}O_2SiN$ requires 280.1732).

(*E*)-(2*R*,3*R*)-2-Methoxy-3-(dimethylphenylsilyl)-4-hexenoic acid (*syn*-2f, Table I): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51–7.31 (m, 5 H), 5.23 (m, 2 H), 3.63 (d, 1 H, J = 8.2 Hz), 3.25 (s, 3 H), 2.36 (m, 1 H), 1.60 (d, 3 H, J = 4.8 Hz), 0.37 (s, 3 H), 0.32 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.1, 137.3, 134.2, 129.0, 127.6, 126.4, 126.2, 82.5, 57.9, 37.7, 18.1, −2.9, −3.2; IR (neat) ν_{max} 3500–2600 (b), 1720, 1420, 1250, 1110, 840, 730 cm^{-1}; CIMS (NH_3) m/e (relative intensity) 296 (M + NH_4^+, 33), 168 (42), 134 (12); CIHRMS (NH_3) m/e M + NH_4^+ 296.1681 ($C_{15}H_{26}O_3SiN$ requires 296.1681).

(*E*)-(2*S*,3*R*)-2-Methoxy-3-(dimethylphenylsilyl)-4-hexenoic acid (*anti*-2f, Table I): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.33 (m, 5 H), 5.30 (m, 2 H), 3.66 (d, 1 H, J = 2.8 Hz), 3.26 (s, 3 H), 2.20 (m, 1 H), 1.62 (d, 3 H, J = 4.8 Hz), 0.35 (s, 3 H), 0.28 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.2, 134.0, 129.1, 129.0, 127.7, 127.2, 125.1, 81.3, 58.4, 37.8, 18.1, −4.4 (2 C).

(*E*)-(2*S*,3*S*)- and (*E*)-(2*S*,3*R*)-2-Methyl-3-(dimethylphenylsilyl)-6-(benzyloxy)-4-hexenoic acid (*syn*- and *anti*-2g, Table II) (a mixture of diastereomers 5:1 2*S*,3*S*:2*S*,3*R*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54–7.27 (m, 20 H), 5.70 (m, 1 H), 5.51 (m, 3 H), 4.45 (s, 2 × 2 H), 3.99 (m, 2 × 2 H), 2.61 (m, 2 × 1 H), 2.30 (dd, 1 H, J = 6.6, 9.9 Hz, anti isomer), 2.10 (dd, 1 H, J = 7.2, 9.8 Hz, syn isomer), 1.12 (d, 2 × 3 H, J = 7.0 Hz), 0.39 (s, 3 H), 0.38 (s, 3 H), 0.37 (s, 3 H), 0.35 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.4, 138.4, 136.8, 134.1, 133.9, 132.7, 131.0, 129.3, 128.4, 127.8, 127.7, 127.5, 127.1, 71.1, 70.6, 39.5, 36.0, 15.4, −3.5, −3.8; IR (neat) ν_{max} 3500–2500 (b), 1700, 1250, 1110, 840 cm^{-1}; CIMS (NH_3) m/e (relative intensity) 386 (M + NH_4^+, 100), 368 (20), 326 (10), 191 (23), 90 (45); CIHRMS (NH_3) m/e M + NH_4^+ 386.2149 ($C_{22}H_{32}O_3SiN$ requires 386.2151).

(*E*)-(2*R*,3*S*)-2-Hydroxy-3-(dimethylphenylsilyl)-4-hexenoic acid (*syn*-2h, Table I): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.26 (m, 5 H), 5.37 (m, 2 H), 4.26 (dd, 1 H, J = 6.8, 4.8 Hz), 2.68 (d, 1 H, J = 6.8 Hz, OH), 2.28 (dd, 1 H, J = 4.8, 9.8 Hz), 1.69 (d, 3 H, J = 5.2 Hz), 0.34 (s, 3 H), 0.32 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.7, 137.5, 134.2, 129.1, 127.6, 127.3, 126.5, 72.3, 51.9, 39.7, 18.1, −3.3, −3.7; IR ($CHCl_3$) ν_{max} 3500–2500 (b), 1700, 1250, 1120, 830 cm^{-1}; CIMS (NH_3) m/e (relative intensity) 278 (M + NH_4^+, 17), 264 (100), 201 (13); CIHRMS (NH_3) m/e M + NH_4^+ 278.1215 ($C_{14}H_{20}O_3SiN$ requires 278.1212).

(*E*)-(2*R*,3*S*)-2-Hydroxy-3-(dimethylphenylsilyl)-4-hexenoic Acid (*anti*-2h, Table I). To a mixture of *anti*-2j and *syn*-2j (60 mg, 0.12 mmol, 2:1 anti:syn) in THF (2 mL) at 0 °C was added *n*-Bu_4NF (0.5 equiv, 1.0 M in THF, 0.06 mmol, 60 μL). The solution was allowed to stir for 1 h before diluting with 10% HCl 910 mL). The reaction mixture was extracted with ethyl acetate (2 × 10 mL), dried over $MgSO_4$, and filtered. The solvent was removed in vacuo to afford 2:1 *anti*-2h:*syn*-2h as a clear oil (30 mg crude product, 95%). Purification of this compound on SiO_2 has resulted in decomposition, hence further manipulations are carried out on the crude acid. *anti*-2h: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75–7.33 (m, 5 H), 5.39 (m, 2 H), 4.28 (d, 1 H, J = 2.8 Hz), 2.17 (dd, 1 H, J = 2.8, 9.8 Hz), 1.65 (d, 3 H, J = 5.2 Hz), 0.37 (s, 3 H), 0.36 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.7, 137.4, 134.22, 134.1, 129.2, 127.7, 127.6, 127.5, 124.4, 71.5, 37.8, 18.3, −3.7, −4.1; IR ($CHCl_3$) ν_{max} 3500–2500 (b), 1700, 1250, 1120, 830 cm^{-1}.

(*E*)-(2*R*,3*R*)-2-Azido-3-(dimethylphenylsilyl)-4-hexenoic acid (*syn*-2i, Table I): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.27 (m, 5 H), 5.39 (dq, 1 H, J = 6.3, 15.4 Hz), 5.26 (dd, 1 H, J = 10.0, 15.4 Hz), 3.75 (d, 1 H, J = 8.0 Hz), 2.33 (dd, 1 H, J = 8.0, 10.0 Hz), 1.66 (d, 3 H, J = 6.3 Hz), 0.40 (s, 3 H), 0.38 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.4, 134.2, 133.9, 129.3, 127.9, 127.7, 125.8, 125.6, 63.3, 36.1, 18.1, −3.5, −4.1; IR (neat) ν_{max} 3500–2500 (b), 2100, 1700, 1420, 1250, 1110 cm^{-1}; CIMS (NH_3) m/e (relative intensity) 307 (M + NH_4^+, 100), 218 (31), 169 (117), 152 (117); CIHRMS (NH_3) m/e M + NH_4^+ 307.1597 ($C_{14}H_{23}O_2SiN_4$ requires 307.1590).

(*E*)-(2*S*,3*R*)-2-Azido-3-(dimethylphenylsilyl)-4-hexenoic acid (*anti*-2i, Table I): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57–7.28 (m, 5 H), 5.40 (m, 2 H), 3.88 (d, 1 H, J = 4.6 Hz), 2.29 (dd, 1 H, J = 4.6, 9.3 Hz), 1.68 (d, 3 H, J = 5.4 Hz), 0.43 (s, 3 H), 0.33 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.8, 136.3, 129.5, 128.2, 127.8, 127.7, 124.6, 63.4, 36.2, 18.2, −3.8, −4.8.

(*E*)-(2*R*,3*R*)- and -(2*S*,3*R*)-2-((*tert*-butyldiphenylsilyl)-oxy)-3-(dimethylphenylsilyl)-4-hexenoic acid (*syn*- and *anti*-2j, Table I) (a mixture of diastereomers 10:1 2*R*,3*R*:2*S*,3*R*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.20 (m, 30 H), 5.05 (m, 4 H), 4.28 (d, 1 H, J = 3.2 Hz, CHOSi, 2*S*,3*R*), 4.24 (d, 1 H, J = 5.9 Hz, CHOSi, 2*R*,3*R*), 2.05 (dd, 1 H, J = 5.7, 10.5 Hz, CHSi, 2*R*,3*R*), 1.67 (dd, 1 H, J = 3.2, 10.2 Hz, CHSi, 2*S*,3*R*), 1.55 (d, 3 H, J = 6.2 Hz, $CHCH_3$, 2*S*,3*R*), 1.44 (d, 3 H, J = 6.0 Hz, $CHCH_3$, 2*R*,3*R*), 0.97 (s, 9 H, Si^{t}Bu, 2*S*,3*R*), 0.95 (s, 9 H, Si^{t}Bu, 2*R*,3*R*), 0.21 (s, 3 H, SiMe, 2*R*,3*R*), 0.15 (s, 3 H, SiMe, 2*R*,3*R*), 0.03 (s, 3 H, SiMe, 2*S*,3*R*), 0.02 (s, 3 H, SiMe, 2*S*,3*R*), ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 172.9, 137.5, 135.9, 135.6, 134.1, 133.9, 133.5, 132.9, 132.4, 131.9, 131.7, 130.3, 129.8, 129.7, 128.9, 128.7, 128.3, 128.0, 127.9, 1227.8, 127.7, 127.6, 127.5, 127.4, 127.3, 126.8, 124.8, 74.33, 74.2, 40.1, 39.4, 27.0, 26.9, 19.3, 19.2, 18.1, 18.0, −3.5, −3.7, −4.2, −4.4; IR ($CHCl_3$) ν_{max} 3360, 3040, 2920, 2840, 1760, 1710, 1100 cm^{-1}; CIMS (NH_3) m/e (relative intensity) 520 (M + NH_4^+, 6), 408 (19), 346 (26), 282 (96), 274 (100), 268 (45); CIHRMS (NH_3) m/e M + NH_4^+ 520.2734 ($C_{30}H_{42}O_3Si_2N$ requires 502.2703).

(*E*)-(2*S,3*R**)- and -(2*R**,3*R**)-2-((*tert*-butyldimethylsilyl)oxy)-3-(dimethylphenylsilyl)-4-hexenoic acid (*anti*- and *syn*-2k, Table II)** (reported as a mixture of racemic diastereomers 1:3.6 anti:syn): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.27 (m, 10 H), 5.48 (m, 1 H), 5.26 (m, 3 H), 4.34 (d, 1 H, J = 3.2 Hz, CHOSi, anti), 4.28 (d, 1 H, J = 3.2 Hz, CHOSi, syn), 2.17 (m, 2 H, CHSi, syn and anti), 1.66 (d, 3 H, J = 6.0 Hz, $CHCH_3$, syn), 1.65 (d, 3 H, J = 6.5 Hz, $CHCH_3$, anti), 0.91 (s, 9 H, Si^{t}Bu, anti), 0.88 (s, 9 H, Si^{t}Bu, syn), 0.39 (s, 3 H, Si*Me*^{t}Bu), 0.38 (s, 3 H, Si*Me*^{t}Bu), 0.33 (s, 3 H, Si*Me*^{t}Bu), 0.29 (s, 3 H, Si*Me*^{t}Bu), 0.02 (s, 3 H, Si*Me*Ph), 0.01 (s, 3 H, Si*Me*Ph), 0.01 (s, 3 H, Si*Me*Ph), −0.05 (s, 3 H, Si*Me*Ph); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.5 (2 C), 137.4, 134.2, 134.0, 129.0, 128.9, 127.8, 127.6, 127.5, 127.1, 126.7, 125.5, 74.4, 72.9, 57.0, 40.0, 39.0, 25.8, 25.7, 18.2, 18.1, −3.1, −3.2, −3.4, −3.7, −4.2, −4.5, −4.8, −5.1; IR ($CHCl_3$) ν_{max} 3100, 3020, 2900, 1760, 1420, 1360 cm^{-1}; CIMS (NH_3) m/e (relative intensity) 396 (M + NH_4^+, 100), 378 (35); CIHRMS (NH_3) m/e M 378.2045 ($C_{20}H_{34}O_3Si_2$ requires 378.2046).

(*E*)-(2*R*,3*R*)-2-Methoxy-3-(*tert*-butyldiphenylsilyl)-4-hexenoic acid (2l, Table II): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68–7.26 (m, 10 H), 5.42 (m, 2 H), 33.43 (d, 1 H, J = 9.8 Hz), 2.85 (s, 3 H), 2.82 (m, 1 H), 1.60 (d, 3 H, J = 5.6 Hz), 1.07 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.5, 137.0, 136.4, 136.3, 134.5, 133.9, 128.8, 128.7, 127.8, 127.4, 127.3, 127.1, 126.9, 82.7, 57.4, 37.1, 28.4, 19.1, 17.9; IR ($CHCl_3$) ν_{max} 3500–2500 (b), 1710, 1420, 1100, 920 cm^{-1}; CIMS (NH_3) m/e (relative intensity) 400 (M + NH_4^+, 64), 328 (37), 307 (77), 274 (69), 152 (60); CIHRMS (NH_3) m/e M + NH_4^+ 400.2307 ($C_{23}H_{34}O_3SiN$ requires 400.2307).

(*E*)-(2*S,3*R**)-2-((*tert*-Butyldiphenylsilyl)oxy)-3-(*tert*-butyldiphenylsilyl)-4-hexenoic acid (*anti*-2m, Table II)**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66–7.20 (m, 15 H), 5.47 (m, 2 H), 4.51 (d, 1 H, J = 3.2 Hz), 2.60 (m, 1 H), 1.74 (d, 3 H, J = 4.7 Hz), 1.06 (s, 9 H), 0.86 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 136.8, 136.7, 136.1, 135.9, 135.7, 133.9, 133.6, 132.9, 130.1, 129.4, 129.1, 128.6, 127.9, 127.8, 127.6, 126.9, 126.8, 73.7, 37.5, 28.6 (3 C), 26.9 (3 C), 19.4, 18.9, 18.3; IR (neat) ν_{max} 3380, 3000, 2920, 2840, 1760, 1720 cm^{-1}; CIMS (NH_3) m/e (relative intensity) 624 (M + NH_4^+, 25), 549 (39), 471 (76), 293 (88), 273 (50), 253 (45), 199 (100); CIHRMS (NH_3) m/e M + NH_4^+ 624.3324 ($C_{38}H_{50}O_3SiN$ requires 624.3329).

(*E*)-(2*R,3*R**)-2-((*tert*-Butyldiphenylsilyl)oxy)-3-(*tert*-butyldiphenylsilyl)-4-hexenoic acid (*syn*-2m, Table II)**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79–7.12 (m, 15 H), 5.73 (m, 1 H), 5.48 (m, 1 H), 4.49 (d, 1 H, J = 4.2 Hz), 2.75 (dd, 1 H, J = 4.2, 8.6 Hz), 1.67 (d, 3 H, J = 6.3 Hz), 1.03 (s, 9 H), 0.83 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.2, 137.0, 136.8, 136.2, 136.0, 135.9, 133.7, 130.2, 132.9, 129.2, 128.7, 127.9, 127.8, 127.5, 127.4, 126.8, 126.2, 74.3, 36.8, 28.4 (3 C), 27.1 (3 C), 19.5, 19.2, 18.3.

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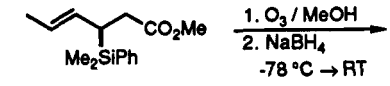
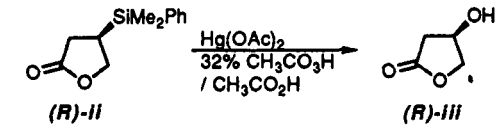
Note Added in Proof. The absolute stereochemistry of the Claisen products was confirmed by the independent synthesis of the hydroxy lactone (*R*)-iii, of known absolute configuration. As illustrated in the scheme below, the (*R*)-(*E*)-crotylsilane (82% enantiomeric purity) was converted to (*R*)-(+)-3-(dimethylphenylsilyl)butyrolactone, ii. Replacement of the silicon group with a hydroxyl was accomplished using the method of Fleming [cf. refs 12a and 12b] and, as expected, occurred with complete retention of configuration to produce (*R*)-(+)-3-hydroxybutyrolactone, iii, 50% yield from (*R*)-i, [lit: $[\alpha]^{23}_D$ +77.0 (*c* 2.0, EtOH), cf. Mori, K.; Takigawa, T.; Matsuo, T. *Tetrahedron* **1979**, *35*, 933]. The discrepancy in rotation values is simply a result of enantiomeric purity of the starting (*R*)-(*E*)-crotylsilane.



(*R*)-*i*

$[\alpha]_D^{23}$ +9.82 (c 1.68, $CHCl_3$)



(*R*)-*ii* (*R*)-*iii*

$[\alpha]_D^{23}$ +8.18 (c 0.22, EtOH) $[\alpha]_D^{23}$ +63.2 (c 1.72, EtOH)

Supplementary Material Available: ^{13}C and ^1H NMR spectra for compounds **1b,e,g,h,j-m**, **2a**, *syn*-**2b**, *anti*-**2b**, **2c,d**, *syn*-**2e**, *anti*-**2e**, and **2f-m** (47 pages). Ordering information is given on any current masthead page.

Evidence of the Rotamerism of the 1,3-Diphosphapropenes

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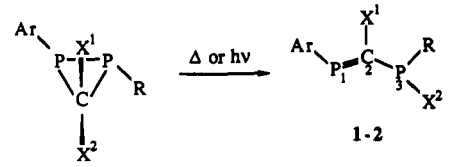
Many stereochemical problems arise from the 1,3-diphosphapropenes obtained by the ring opening of functionalized diphosphiranes. In particular, the structures of **1a** and **2a** show two different conformations. On the one hand, theoretical studies indicate these two conformers are close in energy and are separated by low rotation barrier (5 and 12 kJ·mol^{-1}). In the more stable conformer (gauche conformation), the angle between the tricoordinated phosphorus lone pair and the P–C bond, θ, is 114°, whereas the second minimum corresponds to the syn conformation (θ = 0°). On the other hand, the ^{31}P NMR experiments that we have performed to verify the existence of the two rotamers I and II give experimental barrier of the irreversible transformation **1b**(I) → **1b**(II) as 104 kJ·mol^{-1}.

Introduction

Recently, some of us have characterized new 1,3-diphosphapropenes obtained by photochemical or thermal ring opening of functionalized diphosphiranes[1,2] (Scheme I). The structural analysis by X-ray diffraction indicates that these molecules have the same trans configuration with different conformations. The diphosphapropene **1a** obtained by photochemical ring opening of the symmetrical diphosphirane (R = Ar, $X_1 = X_2$ = Cl) exists in the gauche conformation I, in which the lone pair of the tricoordinated phosphorus P_3 is roughly orthogonal to the σ-plane of the P=C double bond (θ = 100°).[1] The diphosphapropene **2a** produced by thermal ring opening of the unsymmetrical diphosphirane (R = Tsi, $X_1 = X_2$ = Cl) exhibits a syn conformation II in which the two phosphorus lone pairs are approximately in the σ-plane (θ = 12°)[2] (Figure 1).

The main difference in the ^{31}P NMR parameters, in particular the significant enhancement of the $^2J_{PP}$ coupling constant in the II conformation, can be explained by the difference in orientation of the respective phosphorus lone pairs. The existence of these two different conformations for the diphosphapropenes could indicate a possible rotamerism in these models. To our knowledge, this general phenomenon observed especially for unsaturated propenes[3] derivatives, amidines,[4] and ethenylphosphines[5] has not been observed for 1,3-diphosphapropenes.

Scheme I



1-2 **Reaction I**

We have undertaken a theoretical study of the internal rotation process of the phosphino group around the P–C bond and tried to obtain experimental evidence for the interconversion between the two conformers of series **1**.

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