A Stereospecific Access to Allylic Systems Using Rhodium(II)−Vinyl Carbenoid Insertion into Si−H, O−H, and N−H Bonds

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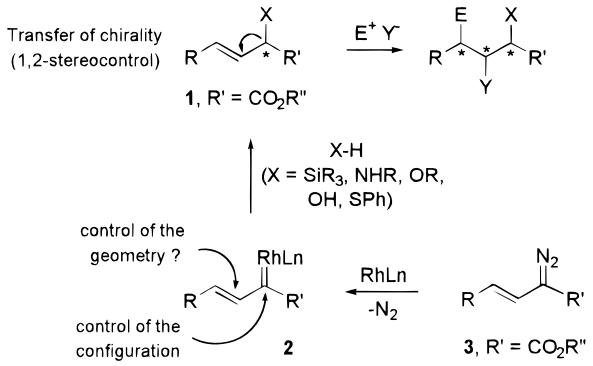
Rhodium-catalyzed decomposition of α-vinyldiazoesters in the presence of silanes, alcohols, ethers, amines, and thiols have been shown to produce the corresponding α-silyl, α-hydroxy, α-alkoxy, α-amino, and α-thioalkoxy esters in generally good yield with a complete retention of the stereochemistry of the double bond of the diazo precursor. An extension of the process in homochiral series has also been devised using either a chiral auxiliary attached to the ester function or achiral α-vinyldiazoesters and Doyle's chiral catalyst $Rh_2(MEPY)_4$. In the former approach, pantolactone as chiral auxiliary gave diastereoselectivities of up to 70%, while the second approach produced the desired allylsilane with ee as high as 72%. On the other hand, $Rh_2(MEPY)_4$-catalyzed insertion into the O−H bond of water led to poor or no enantioselectivity in good agreement with recent literature reports.

Introduction

The stereocontrolled electrophilic functionalization of chiral allylic systems is one of the most powerful ways to generate complex targets having several new stereogenic centers.[1] 1,2-Stereocontrol in acyclic and cyclic allylic systems has been thoroughly studied and the transfer of chirality from the allylic center to proximal prochiral centers is usually efficient (Scheme 1). Several models have been developed over the last 20 years to account for the stereochemical outcome of these electrophilic processes, and it is now possible to predict with confidence the stereochemical outcome of the reaction.[2] However, such a transfer of chirality is only possible providing that both the geometry of the allylic double bond and the absolute configuration of the allylic chiral center have been perfectly set up prior to functionalization. In this context, we recently reported a straightforward entry to (*Z*) and (*E*)-allylsilanes **1** where both the configuration of the double bond and that of the chiral allylic center would be controlled.[3] It was shown that a putative vinylrhodium carbenoid species **2**, generated *in situ* through $Rh_2(OAc)_4$-catalyzed decomposition of stereochemically defined (*E*) or (*Z*)-vinyldiazoesters **3**, inserted into the Si−H bond of a silane *stereospecifically* with retention of the geometry of the starting double bond. We report here that the strategy is of general utility and can be applied to the stereospecific preparation of other allylic systems such as allylic amines, alcohols, and thioethers, through insertion into N−H, O−H, and S−H bonds, respectively. A study on the control of the absolute configuration of the chiral allylic center is also described. Two different routes for controlling the stereochemistry at the allylic center have been devised for this purpose. The first route involves the insertion of a vinyldiazoester where the chirality is located on the ester function. In this case, we have observed that readily available pantolactone (as a chiral auxiliary) is the best choice. In the second approach, we have investigated the use of achiral vinyldiazoesters and optically active rhodium catalysts, such as Doyle's $Rh_2(MEPY)_4$.[4] Encouraging levels of stereocontrol have been observed for the first time in these insertions using chiral catalysts.

Scheme 1



Discussion

Synthesis of (*E*)- and (*Z*)-Vinyldiazoesters. Vinyldiazomethanes have been used in various contexts in the

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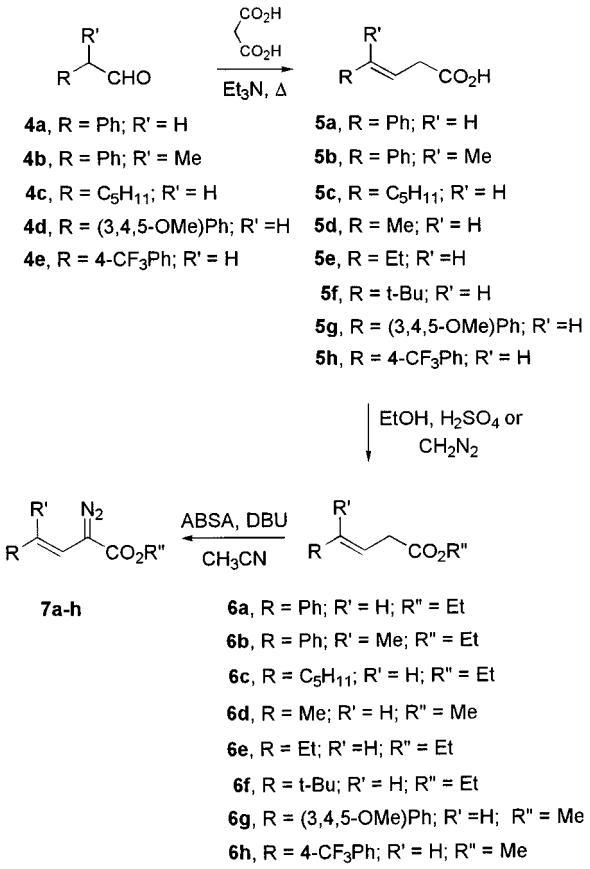
Scheme 2



4a, R = Ph; R' = H
4b, R = Ph; R' = Me
4c, R = C_5H_{11}; R' = H
4d, R = (3,4,5-OMe)Ph; R' =H
4e, R = 4-CF_3Ph; R' = H

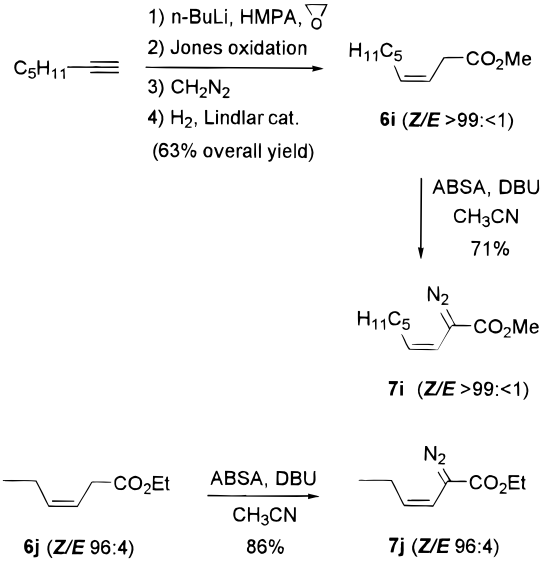
5a, R = Ph; R' = H
5b, R = Ph; R' = Me
5c, R = C_5H_{11}; R' = H
5d, R = Me; R' = H
5e, R = Et; R' =H
5f, R = t-Bu; R' = H
5g, R = (3,4,5-OMe)Ph; R' =H
5h, R = 4-CF_3Ph; R' = H

7a-h

6a, R = Ph; R' = H; R" = Et
6b, R = Ph; R' = Me; R" = Et
6c, R = C_5H_{11}; R' = H; R" = Et
6d, R = Me; R' = H; R" = Me
6e, R = Et; R' =H; R" = Et
6f, R = t-Bu; R' = H; R" = Et
6g, R = (3,4,5-OMe)Ph; R' =H; R" = Me
6h, R = 4-CF_3Ph; R' = H; R" = Me

past,[5] including the synthesis of divinylcyclopropanes and more recently their analogues, *i.e.*, vinyldiazoesters **3** have been introduced by Davies and co-workers[6] in a cyclopropanation−Cope rearrangement sequence to provide an efficient route to seven-membered rings and tropane skeletons. Surprisingly, only one example of insertion of these vinylmetal carbenoids into the O−H bond has been reported before our investigations.[6d] Moreover, while the preparation of (*E*)-vinyldiazoesters is well documented,[6,7] no report concerning the stereocontrol occurring during the diazo-transfer process with

Scheme 3



6i (*Z*/*E* >99:<1)

7i (*Z*/*E* >99:<1)

6j (*Z*/*E* 96:4)

7j (*Z*/*E* 96:4)

analogous *Z*-isomers has so far appeared. The most straightforward access to diazoesters **7** involves the treatment of β,γ-unsaturated esters **6** with a diazo-transfer reagent (mesyl azide[8] (MsN_3) or acetylbenzenesulfonyl azide[9] (ABSA)) in the presence of a base (DBU or NEt_3), according to the Davies procedure (Scheme 2).[6] The uncommon β,γ-unsaturated acids **5a**−**c** and **5f**−**h** prepared using a reported method from aldehydes **4a**−**e**,[10] were esterified and submitted to diazo-transfer reaction to afford esters **7a**−**h** in good overall yield (Scheme 2). ^{1}H NMR and capillary GC showed that this sequence afforded the *E* isomer as the sole product.

We were also pleased to find that (*Z*)-β,γ-unsaturated esters **6i,j** led with complete stereocontrol (within the limits of detection of ^{1}H NMR and capillary GC) to the desired (*Z*)-vinyldiazoesters **7i,j** in excellent overall yield and that no isomerization or migration of the double bond occurred in our conditions.[10b] This represents the first and indeed a general route to this kind of diazo precursor. The ester function in **7i** was easily introduced through the sequence depicted below with the geometry of the olefin being secured during the hydrogenation of the triple bond (Scheme 3).

Stereospecific Synthesis of (*E*) and (*Z*)-Allylsilanes. Our first insertion experiments were carried out by slowly adding styryldiazoester **7a** to a suspension of silane in CH_2Cl_2 and a catalytic amount of $Rh_2(OAc)_4$. The desired allylsilane **8a** was thus formed in 70% yield after evaporation of the solvent, and the ^{1}H NMR of the crude reaction mixture indicated that **8a** was pure enough to be used without further purifications (Scheme 4, Table 1, entry 1). The protocol could be simplified to a large extent by simply mixing the diazoester and the silane in CH_2Cl_2 and then adding a catalytic amount of $Rh_2(OAc)_4$. The deep red coloration of the diazo precursor vanished over a period of 20 min, indicating that the diazo precursor was no longer present in the reaction mixture. Consequently, in contrast to what is usually

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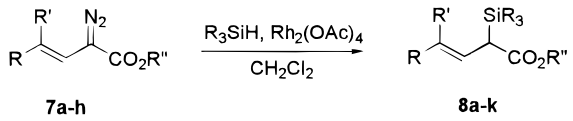
Table 1. Synthesis of Allylsilanes 8a−k (Scheme 4)

entry	7[a]	R_3Si	8[a]	% yield[c]
1	**7a**	$PhMe_2Si$	**8a**	70
2	**7a**	$(Thien)Me_2Si$[b]	**8b**	72
3	**7a**	$(Me_3Si)_3Si$	**8c**	45
4	**7a**	$(i\text{-}PrO)Me_2Si$	**8d**	85
5	**7a**	$(i\text{-}Pr)_2FSi$	**8e**	76
6	**7b**	$PhMe_2Si$	**8f**	80
7	**7b**	$(Thien)Me_2Si$[b]	**8g**	61
8	**7d**	$PhMe_2Si$	**8h**	76
9	**7f**	$PhMe_2Si$	**8i**	87
10	**7a**	$allylMe_2Si$	**8j**	98
11	**7a**	$(BrCH_2)Me_2Si$	**8k**	97

[a] E/Z > 98: < 2. [b] $(Thien)Me_2Si$:(5-methylthienyl)dimethylsilyl. [c] Estimated yield from ^1H NMR after evaporation of the solvent and the excess of silane.

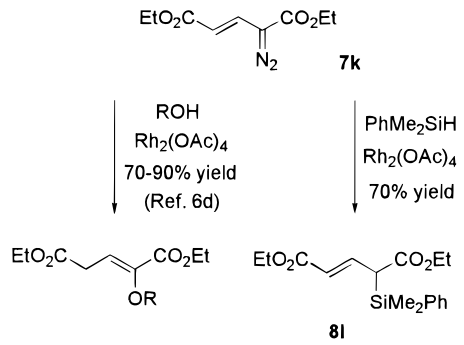
Scheme 4



7a-h **8a-k**

observed with α-alkyldiazoesters,[11] vinyldiazoesters do not seem to dimerize under our reaction conditions, so that the concentration of the diazo precursor in the medium is no longer a problem. Other vinyldiazoesters undergo the insertion process with generally good yields (Table 1). Although the products obtained are generally clean enough to be used as such, distillation of the allylsilane can be performed, and is preferable to chromatography over silica gel which results in extensive desilylation. Different substituents on the silane have been used, demonstrating that the insertion process can accommodate nearly any kind of silicon group. This is of importance from the perspective of the oxidation of the C−Si bond into the corresponding C−OH bond, since Tamao, Kumada, and Fleming[12] in their pioneering studies have clearly shown that an activating group on the silicon is generally required for this oxidation to take place. For instance, alkoxysilane can be introduced by this route via insertion using $(i\text{-}PrO)SiMe_2H$ (entry 4). It is noteworthy that ethyldiazoacetate gave poor yields on reaction with the same silane, indicating again a contrasting reactivity of vinyldiazoesters compared to their alkyl analogues. $(Me_3Si)_3SiH$ also led to the desired silane although in moderate yield (entry 3). This silane is often used as an alternative to Bu_3SnH due to the low bond energy of the Si−H bond. Therefore, it is a good reducing agent, which explains the large amount of ester **6a** formed through reduction of **7a**.[13] The insertion into the unusual $(i\text{-}Pr)_2SiFH$, prepared from the corresponding chlorosilane, gave rise to the unstable α-silylester **8e** in good yield (entry 5). The thiophene−silane reagent also reacts cleanly in the presence of the presumed rhodium−vinylcarbenoid species without competitive sulfur ylide[14] or cyclopropanation reactions[15] (entries 2 and 7). Interestingly, the insertion using an allylsilane (*i.e.* $allylSiMe_2H$, entry 10) produced the desired ester **8j** in excellent yield without a trace of cyclopropanation products. This demonstrates that insertion into the Si−H bond is a more favorable process than cyclopropanation, at least when one has to deal with monosubstituted olefinic silanes. Insertion into the Si−H of (bromomethyl)silane (entry 11) also led to α-silylester **8k** which might be a useful synthon for further radical functionalization.[16]

Scheme 5



8l

Finally, a recent report by Davies et al.[6d] mentioned that the insertion of the vinylrhodium carbenoid generated from **7k** into the O−H bond of water did occur in good yield but was followed by a migration of the allylic double bond to form the corresponding α-hydroxy-α,β-unsaturated ester (Scheme 5). Such a double bond migration was not observed during the insertion into the Si−H bond, since treatment of **7k** with $PhMe_2SiH$ in the presence of $Rh_2(OAc)_4$ produced the expected allylsilane **8l** in 70% yield and not the vinylsilane. **8l** could not be purified due to extensive desilylation, but its structure was unambiguously assigned from its ^1H NMR spectrum.

We next tackled the critical question of the stereoselectivity of the insertion process. (*E*)- and (*Z*)-vinyldiazoesters **7c−e** and **7i,j** were thus submitted to the same reaction conditions as those described above. Examination of the crude reaction mixture in both cases unambiguously revealed that the insertion process is *stereospecific* leading to (*Z*)- and (*E*)-allylsilanes **8m−p** in good yields, *with retention of the geometry of the double bond* (Scheme 6). The retention of the stereochemistry supports the hypothesis of a concerted mechanism for the insertion into the Si−H bond,[17] similar to the one proposed by Doyle for metal−carbenoid insertion into the C−H bond.[18] A stepwise organometallic process would probably involve isomerization or migration of the double bond, leading to a conjugated ester through *i.e.* oxidative addition onto the Si−H bond and formation of an hydrido−rhodium complex.[11e,19]

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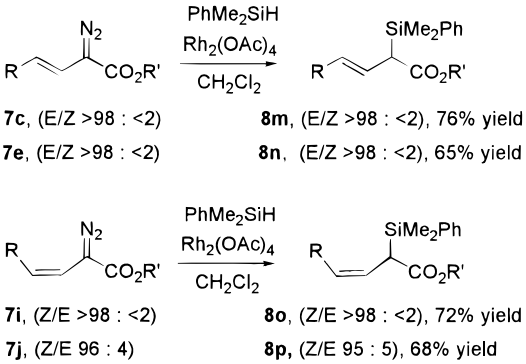
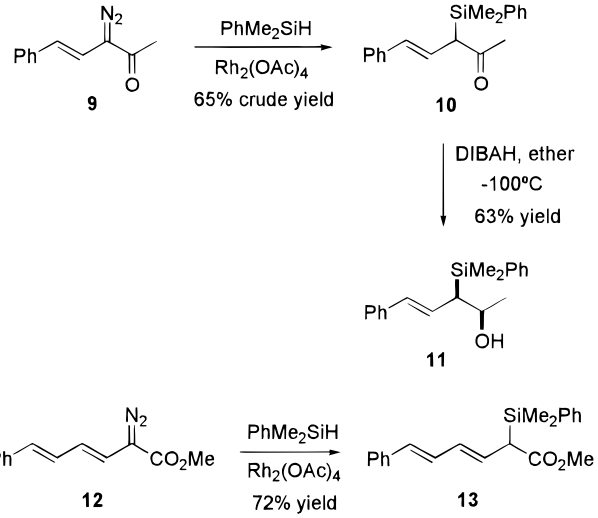
Scheme 6



Scheme 7



We also extended our methodology to the synthesis of allylsilane ketone **10** and dienylsilane **13** which were obtained in 65% and 72% yield, respectively, from the corresponding diazo precursors **9**[6k] and **12**[6k] (Scheme 7). Again, it is important to note that the α-silylketone was obtained pure enough to be used without further purifications since it was found very sensitive to chromatography and distillation.[11a,20] The α-silylketone was thus directly reduced using DIBAH to afford the more stable *syn*-*β*-hydroxysilane **11** in reasonable yield as a single diastereoisomer.

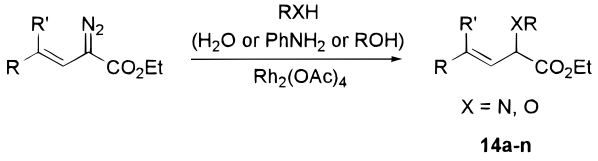
Insertion of Rhodium−Vinyl Carbenoids into N−H, O−H, and S−H Bonds. The decomposition of α-diazoesters catalyzed by metal complexes in the presence of an amine or an alcohol is known to produce, through insertion into the N−H and O−H bond, respectively, the corresponding α-amino and α-hydroxy esters.[21,22] Surprisingly, however, the application of this methodology to the stereoselective synthesis of allylic amines and alcohols has never been reported. We therefore extended our methodology to the insertion into O−H and N−H bonds and showed that similarly to the insertion into the Si−H bond, the process is *stereospecific* leading to (*Z*)- and (*E*)-allylic amines, alcohols, and ethers in good yields (Scheme 8, Table 2).

Table 2. Insertion of Rhodium−Vinyl Carbenoid into N−H and O−H Bonds (Scheme 8)

entry	7[a]	cond[b]	RX	14[a]	%yield[c]
1	**7a**	A	HO	**14a**	77
2	**7b**	A	HO	**14b**	54
3	**7c**	A	HO	**14c**	53
4	**7g**	A	HO	**14d**	63
5	**7h**	A	HO	**14e**	32
6	**7i**	A	HO	**14f**	50
7	**7a**	B	EtO	**14g**	75
8	**7c**	B	MeO	**14h**	65
9	**7i**	B	MeO	**14i**	65
10	**7a**	C	RO	**14j**	52
11	**7a**	D	PhO	**14k**	40
12	**7a**	E	PhNH	**14l**	68
13	**7c**	E	PhNH	**14m**	62
14	**7i**	E	PhNH	**14n**	70

[a] *E*/*Z* or *Z*/*E* ratio >98:<2. [b] Conditions: A, wet ether, 1 h, rt, B, ROH (solvent), 15 min, rt; C, ROH:CF_3CH_2OH (10 equiv), benzene, 5 min, reflux; D, PhOH (5 equiv), benzene, 1 h, reflux; E, $PhNH_2$ (5 equiv), benzene, 10 min, reflux. [c] Isolated yield after purification by chromatography.

Scheme 8



The reactions were performed starting from vinyldiazoesters **7a**−**i** under conditions which differ slightly from those described for the insertion into the Si−H bond. Insertion into the O−H bond of H_2O was best carried out in wet ether at room temperature (entries 1−6), affording the expected allylic alcohols in 32−77% yield. With EtOH and MeOH, the insertion occurred at room temperature when the reagent is also the solvent (entries 7−9). Such conditions are not convenient for the less nucleophilic CF_3CH_2OH or PhOH, so in these cases, the reaction was best performed in benzene under reflux, producing the ethers in moderate yields (40−50%) (entries 10 and 11). More interestingly, the (*E*)-ester **7c** and (*Z*)-ester **7i**, gave rise to the corresponding (*E*)- and (*Z*)-allylic alcohols **14c** and **14f** in good yields (entries 3 and 6), *stereospecifically with retention of the geometry of the double bond*. Similar behavior was observed during insertion into the O−H bond of alcohols (entries 8 and 9). The contrasting yields summarized in entries 4 and

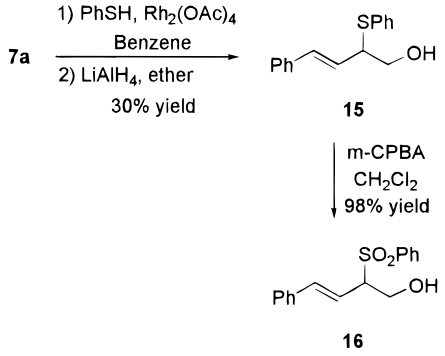
(19) (a) Hill, J. E.; Nile, T. A. *J. Organomet. Chem.* **1977**, *137*, 293. (b) Brockmann, M.; Dieck, T. H.; Klaus, J. *J. Organomet. Chem.* **1986**, *301*, 209. (c) Lappert, M. F.; Maskell, R. K. *J. Organomet. Chem.* **1984**, *264*, 217. (d) Bergens, S. H.; Noheda, P.; Whelan, J.; Bosnich, B. *J. Am. Chem. Soc.* **1992**, *114*, 2128. (e) Brown, J. M.; Lloyd-Jones, G. C. *J. Am. Chem. Soc.* **1994**, *116*, 866. (f) Hiyama, T.; Kusumoto, T. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; p 763. (g) Tamao, K.; Nakagawa, Y.; Ito, Y. *Organometallics* **1993**, *12*, 2297. (h) Horn, K. A. *Chem. Rev.* **1995**, *95*, 1317.

(20) The α-silylketone might undergo Brook rearrangement, although we have not isolated the corresponding silyl enol ether. The parent vinylketone is sometimes present in small amount as a byproduct and could be formed either through desilylation of **10** or hydrolysis of a silyl enol ether.

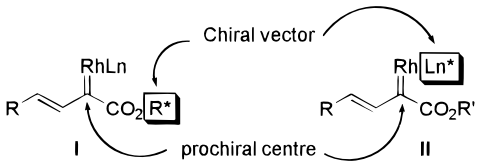
(21) For metallo-carbene insertion into N−H bonds: see: (a) Paulissen, R.; Hayez, E.; Hubert, A. J.; Teyssié, P. *Tetrahedron Lett.* **1974**, 607. (b) Nicoud, J.-F.; Kagan, H. *Tetrahedron Lett.* **1971**, 2065. O−H bonds: (a) Cox, G. C.; Miller, D. J.; Moody, C. J.; Sie, E.-R.H.B.; Kulagowski, J. J. *Tetrahedron* **1994**, *50*, 3195. (c) Haigh, D. *Tetrahedron* **1994**, *50*, 3177. (c) Aller, E.; Cox, G. G.; Miller, D. J.; Moody, C. J. *Tetrahedron Lett.* **1994**, *35*, 5949. (d) Landais, Y.; Planchenault, D. *Synlett* **1995**, 1191. (e) Cox, G. G.; Moody, C. J.; Austin, D. J.; Padwa, A. *Tetrahedron* **1993**, *49*, 5109.

(22) (a) Demonceau, A.; Hubert, A. J.; Noels, A. F. In *Metal Promoted Selectivity in Organic Synthesis*; Noels, A. F., Graziani, M., Hubert, A. J., Eds.; Kluwer Academic Publ.: Dordrecht, Netherlands, 1991; p 237. (b) Paulissen, R.; Reimlinger, H.; Hayez, E.; Hubert, A. J.; Teyssié, P. *Tetrahedron Lett.* **1973**, 2233. (c) Petiniot, N.; Anciaux, A. J.; Noels, A. F.; Hubert, A. J.; Teyssié, P. *Tetrahedron Lett.* **1978**, 1239. (d) Noels, A. F.; Demonceau, A.; Petiniot, N.; Hubert, A. J.; Teyssié, P. *Tetrahedron* **1982**, *38*, 2733.

Scheme 9



Scheme 10



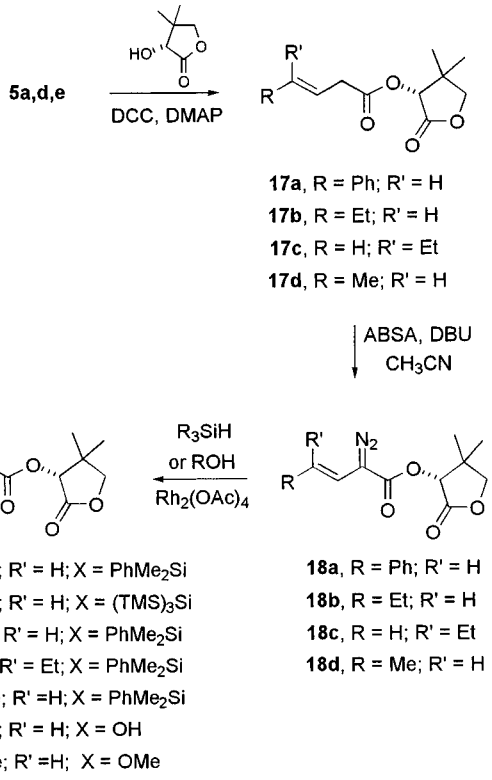
5 suggests that the reaction is also sensitive to electronic effects, with electron-withdrawing substituents on the diazo precursor probably slowing down the insertion process. Electron-withdrawing groups on the alcohol chain (CF_3) similarly led to a lower yield of the corresponding allylic ether (entry 10). This is a trend which we have already noticed during our recent studies on Si−H bond insertion.[17] The mechanism of the insertion of metal−carbenoid species into O−H bonds is not known with certainty, but the above observations fit well with the hypothesis of a nucleophilic attack of the alcohol onto the electrophilic carbenoid center.[23]

Insertion into the N−H bond of aniline was found to go to completion after only 10 min in benzene under reflux, leading to α-aminoesters in good yield. As observed for the Si−H and O−H bonds, the insertion process occurs *stereospecifically with retention of the double bond geometry* (Table 2, entries 13 and 14), thus giving a straightforward access to unusual α-aminoesters having a vinyl group on the chiral center.

Insertion into the S−H bond was also investigated with less success,[24] giving modest yields of the corresponding α-phenylthio ester (Scheme 9) along with a byproduct which we have not been able to purify. The phenylthio allylic derivative was isolated as the alcohol **15** after reduction of the ester function. The presence of the double bond onto which thiophenol can readily add might be at the origin of this disappointingly low yield. Finally, the thioether **15** can be oxidized, affording the expected allylsulfone **16** in nearly quantitative yield. Such a synthon could be particularly useful as a precursor of allylstannes or for the generation of functionalized polyanions.[25]

Asymmetric Access to Allylic Systems. Having a straightforward method for controlling the stereochemistry of the allylsilane double bond, we were next concerned with the control of the stereochemistry at the allylic center. Two different procedures were envisaged, starting either from a diazoester having a chiral auxiliary attached to the ester function (*i.e.* **I**, Scheme 10) or from a prochiral racemic vinyldiazoester with a chiral catalyst (*i.e.* **II**). The second approach has recently been investigated in O−H insertion reactions and led to very disappointing results.[26] However, this is an attractive possibility since the insertion process is virtually absent without catalyst and hence is likely to occur within the rhodium complex framework, thereby forcing both protagonists (the carbenoid species and the X−H bond) to meet in a chiral environment. High levels of enantioselectivity during these investigations would therefore strongly support the hypothesis that the rhodium catalyst and its ligands are intimately bound to the carbenoid center during the insertion.

Scheme 11



The choice of pantolactone as a chiral auxiliary was dictated by prior results in our group and the pioneering work of Davies and co-workers[6h] who demonstrated that excellent diastereoselectivities could be attained using this chiral auxiliary during cyclopropanation reactions. Such high levels of stereoselectivity is attributed to a favored coordination of the electrophilic carbenoid center with the carbonyl group of pantolactone. A stabilization and a rigidification of the transition state would then lead to higher diastereofacial differentiation. We report here that pantolactone is also an efficient chiral auxiliary for rhodium−carbenoid insertion reactions even if our diastereoselectivities do not compete with those reported by Davies for cyclopropanations.

The diazo precursors **18a**−**d** were prepared in 40−55% overall yield, by condensation of acids **5a,d,e** and commercial hex-3-enoic acid with pantolactone in the presence of DCC and DMAP, followed by the diazo transfer process (Scheme 11). Using this esterification protocol,

(23) (a) Miller, D. J.; Moody, C. J. *Tetrahedron* **1995**, *51*, 10811. (b) Aller, E.; Brown, D. S.; Cox, G. G.; Miller, D. J.; Moody, C. J. *J. Org. Chem.* **1995**, *60*, 4449.

(24) (a) Moyer, M. P.; Feldman, P. L.; Rapoport, H. *J. Org. Chem.* **1985**, *50*, 5223. (b) Brunner, H.; Wutz, K.; Doyle, M. P. *Monatsh. Chem.* **1990**, *121*, 755.

(25) Simpkins, N. S. *Sulfones in Organic Synthesis*; Pergamon: Oxford, 1993.

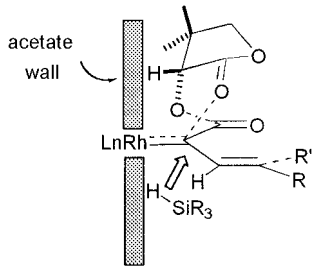
(26) Ferris, L.; Haigh, D.; Moody, C. J. *Tetrahedron Lett.* **1996**, *37*, 107.

Table 3. Synthesis of Allylsilanes, Allylic Alcohols, and Ethers 19a−g (Scheme 11)

entry	diazo[a]	product[a]	de[c]	%yield[d]
1	**18a**	**19a**	32	70
2	**18a**	**19b**	34	55
3	**18b**[b]	**19c**[b]	50	67
4	**18c**	**19d**	70	75
5	**18d**	**19e**	44	65
6	**18a**	**19f**	50	75
7	**18a**	**19g**	5	75

[a] *E*/*Z* or *Z*/*E* ratio >98:<2. [b] *E*/*Z* ratio 96:4. [c] de was estimated from ^{1}H NMR of the crude reaction mixture. [d] Isolated yield after flash chromatography.

Scheme 12

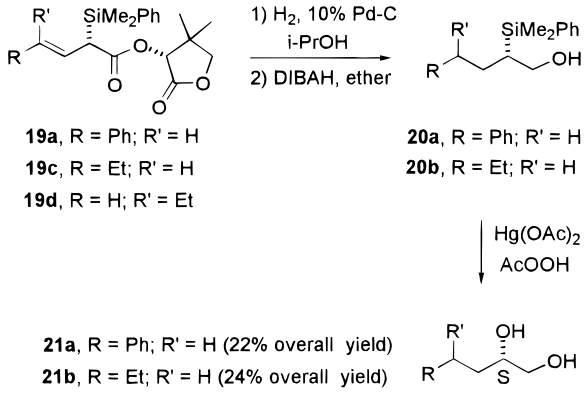


the geometry of the olefin was thus left unchanged in contrast to the condensation of the chiral auxiliary with the acyl chloride derivative which leads to partial isomerization of the double bond.[27] **18a−d** were then treated as above ($PhMe_2SiH$ or $(Me_3Si)_3SiH$) to afford the corresponding allylsilanes **19a−e** in good yields and with diastereoselectivities as high as 70% (Scheme 11, Table 3).

As the mechanism of the insertion is not known with certainty, it is premature to give a definitive rationalization of our stereoselectivities. However, model reactions using menthol as chiral auxiliary gave much lower diastereoselectivities than pantolactone, hence we assume that electronic and not just steric effects are involved during the insertion process. Stabilization of the transition state through coordination of the carbenoid center with the carbonyl of the pantolactone might be invoked (*vide supra*), with the vinylrhodium carbenoid probably in a *s-trans-s-trans* conformation and the silane approaching on the opposite face relative to the pantolactone (Scheme 12). Both methyl groups on the chiral auxiliary then occupy a position where the steric interactions between them and the "rhodium-acetate-wall" are minimized.[6h] It should be emphasized that (*Z*)-olefins led to slightly higher diastereoselectivities than (*E*)-olefins (compare entries 3 and 4). We also observed that changing from $PhMe_2SiH$ (entry 1) to $(Me_3Si)_3SiH$ (entry 2) did not alter the diastereoselectivity, indicating that the size of the silane had little influence. This is in good agreement with our previous observations made during a study of insertions in the alkyl series.[28] We attribute the low sensitivity of rhodium carbenoids toward structural changes and steric effects to the occurrence of an early transition state, a hypothesis which has been consistently put forward in carbene transfer processes.[17,29]

The absolute configuration of the allylsilanes **19a−d** was determined by a three-step sequence: the hydrogenation of the double bond of **19a**, **19c**, and **19d**, followed by reduction of the ester group, gave the β-hydroxysilanes

Scheme 13



20a,b.[30] Oxidative cleavage of the C−Si bond, with retention of configuration,[12] finally afforded the desired diols **21a,b**.[31] In contrast to what we observed previously with menthol or analogues,[28] the reduction of the ester function occurred with partial epimerization at the allylic center. Nevertheless, we were able to demonstrate unambiguously that the allylsilanes **19a−d** all possessed the *S* absolute configuration irrespective of the geometry of the diazo precursor (Scheme 13).

Similarly, **18a** and **18d** were submitted to the $Rh_2(OAc)_4$ decomposition in the presence of H_2O and MeOH, to afford the corresponding esters **19f** and **19g** as a diastereoisomeric mixture (Scheme 11, Table 3, entries 6 and 7). With **19f**, we have been able to separate both diastereoisomers using flash chromatography (**19fa** and **19fb**). Surprisingly, as the diastereoselectivity of the insertion into the O−H bond of H_2O was on the same order of magnitude as that observed for insertion into the Si−H bond, the diastereoselectivity of the insertion process into the O−H bond of MeOH was very low. This is in good agreement with the recent investigations of Moody et al. on the insertion of menthyl-derived diazoesters into MeOH.[32] As for the Si−H insertion process, the mechanism is presently unknown, and a rationalization of our stereoselectivity is therefore compromised. Moreover, comparison between insertion in H_2O and MeOH could be misleading if one looks at the difference in reaction conditions. Water is used as a reagent, but methanol is also the solvent for the reaction. The conversion of ester **19f** into the corresponding methyl ester **22** as depicted in Scheme 14 allowed us to assign the *S* absolute configuration for the major isomer **19fa**. Consequently, insertion into Si−H and O−H bonds occurs with the same topicity, and it is likely that the coordination proposed for the former (Scheme 12) is also operative for the latter. Again, higher diastereoselectivities were found with pantolactone as a chiral auxiliary compared to menthol, but, as mentioned previously with

(27) A 30−50% isomerization of the double bond was observed under these conditions with the (*Z*)-hex-3-enoic acid.

(28) Landais, Y.; Planchenault, D. *Tetrahedron* **1997**, in press.

(29) (a) Wee, A. G. H.; Liu, B. *Tetrahedron Lett.* **1996**, *37*, 145. (b) Müller, P.; Fernandez, D. *Helv. Chim. Acta* **1995**, *78*, 947. (c) Doyle, M. P.; Griffin, J. H.; Bagheri, V.; Dorow, R. L. *Organometallics* **1984**, *3*, 53. (d) Doyle, M. P.; Wang, L. C.; Loh, K.-L. *Tetrahedron Lett.* **1984**, *25*, 4087. Recent studies in our group on the mechanism of the Si−H insertion corroborate the hypothesis of a mechanism involving an early transition state with the development of partial positive charge on the silicon center.[17]

(30) Hydrogenation of the double bond of **19c** and **19d** led to products with the same configuration, indicating that the topicity of the insertion reaction was identical for (*E*) and (*Z*)-diazo precursors.

(31) (a) Jeong, K.-S.; Sjö, P.; Sharpless, K. B. *Tetrahedron Lett.* **1992**, *33*, 3833. (b) Regeling, H.; Chittenden, G. J. F. *Carbohydr. Res.* **1991**, *216*, 79. (c) Corey, E. J.; Link, J. O. *Tetrahedron Lett.* **1992**, *33*, 3431.

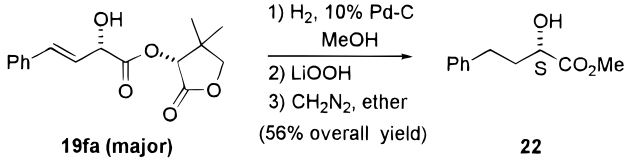
(32) Cox, G. G.; Haigh, D.; Hindley, R. M.; Miller, D. J.; Moody, C. J. *Tetrahedron Lett.* **1994**, *35*, 3139.

Table 4. $Rh_2(5S\text{-MEPY})_4$-Catalyzed Insertion into Si−H and O−H Bonds (Scheme 15)

entry	diazo	product	ee[a]	%yield
1	**7a**	**23a**	72	30[b]
2	**7b**	**23b**	52	32[b]
3	**7a**	**14a**	8	59[c]

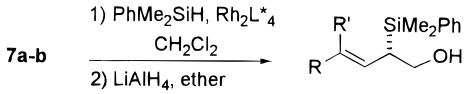
[a] Measured from the ^{1}H NMR of the corresponding Mosher's esters and by capillary GC. [b] Isolated overall yield (two steps) after flash chromatography. [c] Isolated yield of the α-hydroxy ester **14a** after flash chromatography.

Scheme 14



19fa (major) **22**

Scheme 15



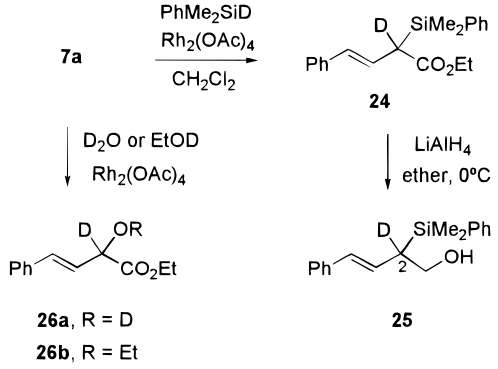
23a, R = Ph; R' = H
23b, R = Ph; R' = Me

the α-silylesters **19a** and **19c,d**, while the removal of pantolactone in **19fa** occurred in good yield it was also accompanied by partial epimerization.

As shown above, the pantolactone can lead to useful diastereoselectivities, indeed the best which have been so far reported in such insertion reactions, but the epimerization during the DIBAH reduction and the loss of pantolactone (only in the silicon series) somewhat limit the utility of this approach. Several attempts to overcome this problem have not so far been successful. For instance, pig liver esterase treatment of the ester **19a** led exclusively to desilylation and more surprisingly without further hydrolysis of the ester function of the desilylated product.[33]

We thus turned our attention to the use of chiral rhodium catalysts (model **II**, Scheme 10). Asymmetric insertions were carried out using Doyle's $Rh_2(5S\text{-MEPY})_4$[4] and $Rh_2(MEOX)_4$[34] under the conditions described previously for $Rh_2(OAc)_4$ (Scheme 15, Table 4). The resulting α-silylesters were directly submitted to reduction using $LiAlH_4$ in ether affording the corresponding alcohols **23a,b**[35] in modest overall yields (Scheme 15). The enantiomeric excesses were then measured either on the crude alcohols (GC or HPLC) or from the ^{1}H NMR of the Mosher's esters of the alcohols, assuming that no racemization had occurred during the reduction of the ester function. This was unambiguously demonstrated through reduction of α-deutero-α-silylester **24** which gave the desired deutero-alcohol **25** in 64% yield (from **7a**) with no incorporation of hydrogen at C-2 (Scheme 16). **24** was prepared by insertion of the rhodium−vinyl carbenoid

Scheme 16



26a, R = D
26b, R = Et

25

generated from **7a**, into the Si−D bond of $PhMe_2SiD$. The insertion process was found to occur with virtually complete incorporation of deuterium (limit of detection of ^{1}H NMR). This route thus offers an easy entry to deuterium labeled allylsilanes which would be difficult to prepare using other known methods. Similarly, insertion into the O−D bond of D_2O and EtOD gave the desired α-deutero-α-alkoxy esters **26a,b** in 54% and 62% yield, respectively, with complete incorporation of deuterium (Scheme 16).

The insertion into the Si−H bond was found to give reasonable enantioselectivity[36,37] with $Rh_2(5S\text{-MEPY})_4$ (Table 4, entries 1 and 2) . On the opposite and in good agreement with literature reports,[26] nearly no selectivity was observed on insertion of **7a** into the O−H bond of H_2O (entry 3). This suggests that insertion of metal−carbenoid species into polar (O−H and N−H) and nonpolar bonds (C−H and Si−H) involves intermediates of different nature. The metal and its chiral ligands might be partially dissociated from the carbenoid center in the former case, and on the opposite might be more intimately bound to the reactive carbenoid center in the second case hence contributing more efficiently to the stereocontrol. The good level of enantioselectivity reached with Si−H insertion represents a useful alternative to the nonselective O−H bond insertion since the silicon group can be regarded as an OH equivalent.[12] Finally, we also tested $Rh_2(MEOX)_4$ and found this catalyst to be poorly reactive, leading to no enantioselectivity at all. It must be emphasized though that both $Rh_2(5S\text{-MEPY})_4$ and $Rh_2(MEOX)_4$ are much less reactive than $Rh_2(OAc)_4$ and therefore require much longer reaction times. Nonetheless, these few examples demonstrate that this strategy is of interest and will certainly deserve much more attention in the future. The search for a more reactive and more selective catalyst is therefore needed to further enhance the value of this methodology. Work along these lines is now in progress in our group.

(33) (a) Azerad, R. *Bull. Soc. Chim. Fr.* **1995**, *132*, 17. (b) Wong, C.-H.; Whitesides, G. M. *Enzymes in Synthetic Organic Chemistry*; Pergamon: Oxford, 1994.

(34) Doyle, M. P.; Eismont, M. Y.; Protopopova, M. N.; Kwan, M. M. Y. *Tetrahedron* **1994**, *50*, 1665.

(35) The absolute configuration of alcohol **23a** was determined as follows: hydrogenation of the double bond and oxidation of the C−Si bond of **23a** afforded the known diol **21a** possessing the *S* configuration.[31c] **23b** was assumed to possess the same absolute configuration as **23a**.

(36) A preliminary account of these results has been presented: *Chiral 2 symposium*, (03-29-1995), Gwatt (Switzerland).

(37) For other asymmetric routes to α-silylcarbonyl compounds, see: (a) Enders, D.; Nakai, S. *Helv. Chim. Acta* **1990**, *73*, 1833. (b) Enders, D.; Nakai, S. *Chem. Ber.* **1991**, *24*, 219. (c) Bhushan, V.; Lohray, B. B.; Enders, D. *Tetrahedron Lett.* **1993**, *34*, 5067. (d) Gilloir, F.; Malacria, M. *Tetrahedron Lett.* **1992**, *33*, 3859. (e) Le Bideau, F.; Gilloir, F.; Nilsson, Y.; Aubert, C.; Malacria, M. *Tetrahedron Lett.* **1995**, *36*, 1641. (f) Paquette, L. A.; Maynard, J. D.; Ra, C. S.; Hoppe, M. *J. Org. Chem.* **1989**, *54*, 1408. (g) Paquette, L. A.; Gilday, J. P.; Ra, C. S.; Hoppe, M. *J. Org. Chem.* **1988**, *53*, 704. (h) Gilday, J. P.; Gallucci, J. C.; Paquette, L. A. *J. Org. Chem.* **1989**, *54*, 1399. (i) Le Bideau, F.; Aubert, C.; Malacria, M. *Tetrahedron: Asym.* **1995**, *6*, 697. (j) Le Bideau, F.; Gilloir, F.; Nilsson, Y.; Aubert, C.; Malacria, M. *Tetrahedron* **1996**, *52*, 7487. (k) Enders, E.; Lohray, B. B.; Burkamp, F.; Bhushan, V.; Hett, R. *Liebigs. Ann. Chem.* **1996**, 189.

Conclusion

We have demonstrated here that the extension of our methodology to the rhodium−vinyl carbenoid insertion into O−H, N−H, and S−H bonds provides an easy and stereospecific access to chiral α-hydroxy, α-alkoxy, α-amino, and α-thioalkoxy allylic systems. The development of an asymmetric approach to the synthesis of these allylic synthons has been carried out using either a chiral auxiliary such as pantolactone attached to the ester function or, more attractively, using chiral catalysts such as Doyle's Rh_2(5*S*-MEPY)$_4$. In the latter approach, enantioselectivities up to 72% were obtained, which to our knowledge is the best selectivity attained so far in such insertions.[38] Finally, it is worth underlining the large difference in enantioselectivities obtained with substrate **7a** upon insertion into Si−H and O−H bonds with the same chiral catalyst (Table 4). This obviously calls for a distinct mechanism for insertion into polar O−H and N−H bonds and nonpolar Si−H and C−H bonds.[17,18,23] Although this appears conceivable, studies reported to date along with the results herein are not sufficient yet for one to draw definitive conclusions.

Experimental Section

Elemental analyses were performed by the I. Beetz laboratory, W-8640 Kronach (Germany). CH_2Cl_2 was distilled from CaH_2. THF and ether were distilled from sodium and benzophenone. **4d,e** were prepared according to a reported procedure.[39] **5d,e** are commercially available (Fluka). Combustion analysis of allylsilanes **8c,e,j,k,l,o** have not been provided due to their relative instability. Analysis and spectroscopic data of corresponding alcohols are available as Supporting Information.

General Procedure for the Preparation of the *β,γ*-Unsaturated Esters 6. A solution of aldehyde **4** (0.17 mmol), malonic acid (0.19 mmol), and triethylamine (29 mL) was refluxed 1 h then cooled to rt. The solution was extracted with ether, and the combined extracts were washed with a 1 M HCl solution and then treated wth 5% NaOH. The aqueous layer was washed with ether and then acidified with 1 M HCl (pH 1). The solution was extracted with ether, the combined extracts were washed with a saturated solution of NaCl and dried over $MgSO_4$, and the solvent was evaporated in vacuo. The resulting acid **5** was then dissolved in EtOH (100 mL), and one drop of concentrated H_2SO_4 was added. The solution was refluxed for 3 h. After cooling at 0 °C, the mixture was treated with a saturated solution of $NaHCO_3$ and extracted with ether. The combined extracts were washed with brine and dried ($MgSO_4$), and the solvent was evaporated in vacuo. Chromatography of the residue (petroleum ether/ethyl acetate 98:2) gave **6** as a colorless oil.

Ethyl (*E*)-non-3-enoate (6c) (76%): ^{1}H NMR δ 5.62−5.44 (2H, m), 4.13 (2H, q, J = 7.1 Hz), 3.01 (2H, d, J = 5.4 Hz), 2.06−1.98 (2H, m), 1.43−1.18 (6H, m), 1.27 (3H, t, J = 7.1 Hz), 0.88 (3H, t, J = 6.8 Hz); IR (film) 2970, 2940, 2870, 1740, 1460, 1250, 1160, 970 cm^{-1}. Anal. Calcd for $C_{11}H_{20}O_2$: C 71.70, H 10.94. Found: C 71.55, H, 10.77.

Methyl (*Z*)-Non-3-enoate (6i). To a stirred solution of heptyne (5 g, 52 mmol) in HMPA (25 mL) was added dropwise, at 0 °C, a 1.6 M solution of n-BuLi in hexane (31.2 mL, 6.55 mmol). The solution was stirred at rt for 15 min and at 50 °C for 30 min. Oxirane (3.82 mL, 78 mmol) was then added at −50 °C, and the mixture was allowed to warm to rt over 1 h and then heated at 50 °C for 2 h. The solution was treated with water at 0 °C and then extracted with ether. The combined extracts were washed with brine and dried over $MgSO_4$, and the solvents were evaporated in vacuo. Distillation (70 °C, 0.15 mbar) gave hept-3-ynol (6.3 g, 82%) as a colorless oil. To a stirred solution of the preceding alcohol (1.27 g, 9 mmol) in freshly distilled acetone (25 mL) was added dropwise at −5 °C, over a period of 30 min, a solution of the Jones reagent (5.05 mL, 13.6 mmol). After the addition was complete, the mixture was stirred at rt for 3 h and then treated with water. The solution was extracted with ether, and the combined extracts were dried over $MgSO_4$ and evaporated in vacuo to afford hept-3-ynoic acid (1.07 g, 77%) used in the next step without further purification. To a stirred solution of hept-3-ynoic acid (1 g, 6.48 mmol) in dry ether (10 mL) was added dropwise, at 0 °C, an ethereal solution of diazomethane until no starting material could be detected by TLC. The solvent was evaporated in vacuo to give methyl hept-3-ynoate (1.1 g, 100%) used in the next step without further purification. The preceding ester (1 g, 5.94 mmol), Lindlar catalyst (100 mg), and quinoline (two drops) in dry hexane (10 mL) were stirred under an hydrogen atmosphere at rt for 4 h. After filtration of the catalyst through Celite, evaporation of the solvent in vacuo, and flash chromatography of the residue (petroleum ether/ethyl acetate 9:1), **6i** was obtained as a colorless oil (1.04 g, 100%) (63% overall yield from heptyne): ^{1}H NMR δ 5.65−5.46 (2H, m), 3.68 (3H, s), 3.10 (2H, d, J = 5.8 Hz), 2.07−1.98 (2H, m), 1.43−1.22 (6H, m), 0.88 (3H, t, J = 6.7 Hz); IR (film) 3030, 2960, 1740, 1430, 1260, 1200, 1020 cm^{-1}; MS m/z (%): 169 ($M^+ - 1$, 59), 133 (41), 112 (43), 97 (98), 83 (96), 71 (100). Anal. Calcd for $C_{10}H_{18}O_2$: C 70.55, H 10.66. Found: C 70.45, H 10.52.

General Procedure for the Preparation of the α-Diazo-*β,γ*-unsaturated Esters 7.[6k] To a stirred solution of **6** (21 mmol) and ABSA (31.5 mmol) in acetonitrile (80 mL) was added dropwise at 0 °C DBU (31.5 mmol). The reaction mixture was stirred at rt for 30 min and then treated with a saturated solution of NH_4Cl. The solution was extracted with ether, and the combined extracts were washed with a saturated solution of NaCl and dried over $MgSO_4$. Evaporation of the solvent in vacuo and chromatography of the residue (petroleum ether/ethyl acetate 6:4) gave **7** as an orange-red oil.

Ethyl (*E*)-2-diazonon-3-enoate (7c) (72%): ^{1}H NMR δ 5.73 (1H, dt, J = 1.4 and 15.9 Hz), 5.31 (1H, dt, J = 7.0 and 15.9 Hz), 4.26 (2H, q, J = 7.1 Hz), 2.16 (2H, ddt, J = 1.4, 7.0 and 7.0 Hz), 1.30 (3H, t, J = 7.1 Hz), 1.46−1.18 (6H, m), 0.89 (3H, t, J = 6.8 Hz); IR ($CHCl_3$) 3020, 2960, 2100, 1700, 1470, 1380, 1320, 1110, 960 cm^{-1}; MS m/z (%): 211 ($M^+ + 1$, 54), 210 (M^+, 27), 193 (20), 181 (31), 168 (52), 165 (54), 154 (100), 135 (20), 121 (23), 108 (71), 79 (43). Anal. Calcd for $C_{11}H_{18}O_2N_2$: C 62.83, H 8.63, N 13.32. Found: C 63.00, H 8.53, N 13.14.

Methyl (*Z*)-2-diazonon-3-enoate (7i) (71%): ^{1}H NMR δ 5.62−5.45 (2H, m), 3.80 (3H, s), 2.08−1.98 (2H, m), 1.47−1.21 (6H, m), 0.89 (3H, t, J = 6.5 Hz); IR (film) 2970, 2930, 2870, 2100, 1710, 1440, 1300, 1200, 1120, 1020 cm^{-1}; MS m/z (%): 196 (M^+, 5), 169 (100), 168 (29), 131 (44), 111 (44), 97 (63), 81 (88), 71 (40). Anal. Calcd for $C_{10}H_{16}O_2N_2$: C 61.20, H 8.22, N 14.27. Found: C 61.17, H 8.25, N 14.27.

General Procedure for the Preparation of Allylsilanes 8. To a stirred solution of diazoester **7** (2.3 mmol) and dimethylphenylsilane (4.6 mmol) in dry CH_2Cl_2 (20 mL) was added at rt $Rh_2(OAc)_4$ (0.01 mmol). The mixture was stirred at rt for 20 min, and the solvent was evaporated in vacuo. Kugelrohr distillation of the residue gave **8** as a colorless oil.

Ethyl (*E*)-2-(dimethylphenylsilyl)-4-phenylbut-3-enoate (8a) (70%): ^{1}H NMR δ 7.53−7.19 (10H, m), 6.40 (1H, dd, J = 10.0 and 16.0 Hz), 6.12 (1H, d, J = 16.0 Hz), 4.03 (1H, dq, J = 7.1 and 10.1 Hz), 3.99 (1H, dq, J = 7.1 and 10.1 Hz), 3.24 (1H, d, J = 10.0 Hz), 1.11 (3H, t, J = 7.1 Hz), 0.44 (6H, s); IR ($CHCl_3$) 3000, 1700, 1650, 1600, 1380, 1300, 1260, 1160, 1130, 980, 830 cm^{-1}; MS m/z (%): 324 (M^+, 24), 145 (17), 144 (100), 135 (73), 116 (33), 115 (50), 105 (16), 91 (20), 75 (18). Anal. Calcd for $C_{20}H_{24}O_2Si$: C 74.03, H 7.45, Si 8.66. Found: C 73.97, H 7.32, Si 8.75.

(38) While this work was submitted, an article on asymmetric Si−H insertion of phenyldiazoacetate appeared, reporting enantioselectivities of up to 50%, see: Buck, R. T.; Doyle, M. P.; Drysdale, M. J.; Ferris, L.; Forbes, D. C.; Haigh, D.; Moody, C. J.; Pearson, N. D.; Zhou, Q.-L. *Tetrahedron Lett.* **1996**, *37*, 7631.

(39) Rosowsky, A.; Mota, C. E.; Wright, J. E.; Freisheim, J.-H.; Heusner, J. J.; McCormak, J. J.; Queener, S. F. *J. Med. Chem.* **1993**, *36*, 3103.

Ethyl (*E*)-2-(dimethyl(5-methylthien-2-yl)silyl)-4-phenylbut-3-enoate (8b): ^{1}H NMR δ 7.34−7.18 (5H, m), 7.09 (1H, d, J = 3.4 Hz), 6.86−6.84 (1H, m), 6.42 (1H, dd, J = 10.0 and 16.0 Hz), 6.20 (1H, d, J = 16.0 Hz), 4.12 (1H, dq, J = 7.1 and 10.1 Hz), 4.06 (1H, dq, J = 7.1 and 10.1 Hz), 3.23 (1H, d, J = 10.0 Hz), 2.54 (3H, d, J = 0.6 Hz), 1.20 (3H, t, J = 7.1 Hz), 0.44 (3H, s), 0.43 (3H, s); IR (film) 2970, 2920, 1710, 1640, 1600, 1440, 1370, 1250, 1000, 960, 750, 700 cm^{-1}; MS m/z (%): 362 ($M^+ + NH_4^+$, 6), 344 (8), 264 (41), 247 (100), 218 (10), 155 (11), 144 (23), 91 (27), 74 (16). Anal. Calcd for $C_{19}H_{24}O_2$SiS: C 66.24, H 7.02, Si 8.15, S 9.31. Found: C 66.40, H 6.99, Si 8.11, S 9.26.

Ethyl (*E*)-2-(Tris(trimethylsilyl)silyl)-4-phenylbut-3-enoate (8c): ^{1}H NMR δ 7.48−7.16 (5H, m), 6.46 (1H, dd, J = 10.6 and 15.9 Hz), 6.25 (1H, d, J = 15.9 Hz), 4.42−4.06 (2H, m), 3.38 (1H, d, J = 10.6 Hz), 1.28 (3H, t, J = 6.9 Hz), 0.234 (9H, s), 0.232 (9H, s), 0.206 (9H, s); IR (film) 3061, 2950, 1717, 1640, 1600, 1500, 1400, 1367, 1250, 840, 750 cm^{-1}; MS m/z (%): 437 (M^+, 1), 363 (44), 317 (15), 219 (23), 173 (19), 115 (27), 73 (100).

Ethyl (*E*)-2-(dimethyl(isopropyloxy)silyl)-4-phenylbut-3-enoate (8d): ^{1}H NMR δ 7.38−7.17 (5H, m), 6.48 (1H, dd, J = 9.7 and 16.0 Hz), 6.31 (1H, d, J = 16.0 Hz), 4.20 (1H, dq, J = 7.1 and 10.1 Hz), 4.15 (1H, dq, J = 7.1 and 10.1 Hz), 4.08 (1H, sept, J = 6.1 Hz), 3.20 (1H, d, J = 9.7 Hz), 1.30 (3H, t, J = 7.1 Hz), 1.17 (6H, d, J = 6.1 Hz), 0.26 (3H, s), 0.25 (3H, s); IR (film) 2980, 2950, 1710, 1640, 1590, 1440, 1370, 1250, 1140, 1030, 970, 750 cm^{-1}; MS m/z (%): 307 ($M^+ + 1$, 100), 261 (45), 247 (68), 219 (19). Anal. Calcd for $C_{17}H_{26}O_3$Si: C 66.62, H 8.55. Found: C 66.72, H 8.46.

Ethyl (*E*)-2-(fluorodiisopropylsilyl)-4-phenylbut-3-enoate (8e): ^{1}H NMR δ 7.40−7.22 (5H, m), 6.47 (1H, dd, J = 9.8 and 16 Hz), 6.39 (1H, dd, J = 1.7 and 16 Hz), 4.19 (2H, q, J = 7.2 Hz), 3.48 (1H, d, J = 9.8 Hz), 1.38−1.24 (2H, m), 1.30 (3H, t, J = 7.2 Hz), 1.16−1.10 (12H, m); IR (film) 3082, 2950, 1721, 1642, 1600, 1496, 1464, 1253, 1147, 883, 835 cm^{-1}; MS m/z (%): 338 (4), 322 (M^+, 4), 251 (3), 144 (100), 115 (68), 93 (18).

Ethyl (*E*)-2-(allyldimethylsilyl)-4-phenylbut-3-enoate (8j): ^{1}H NMR δ 7.38−7.23 (5H, m), 6.47 (1H, dd, J = 10.2 and 16 Hz), 6.28 (1H, d, J = 16 Hz), 5.86−5.74 (1H, m), 4.97−4.91 (2H, m), 4.19 (1H, q, J = 7.2 Hz), 4.18 (1H, q, J = 7.2 Hz), 3.16 (1H, d, J = 9.8 Hz), 1.68 (2H, d, J = 8.1 Hz), 1.30 (3H, t, J = 7.2 Hz), 0.15 (3H, s), 0.14 (3H, s); IR (film) 3079, 2977, 1717, 1629, 1597, 1251, 968, 740 cm^{-1}; MS m/z (%): 273 ($M^+ - 1$, 1), 247 (44), 219 (11), 159 (7), 144 (100), 129 (7), 115 (62), 103 (29), 91 (9).

Ethyl (*E*)-2-((bromomethyl)dimethylsilyl)-4-phenylbut-3-enoate (8k): ^{1}H NMR δ 7.38−7.23 (5H, m), 6.44 (1H, dd, J = 9.8 and 16 Hz), 6.34 (1H, d, J = 16 Hz), 4.19 (2H, q, J = 7.2 Hz), 3.29 (1H, d, J = 9.8 Hz), 2.57 (2H, s), 1.30 (3H, t, J = 7.2 Hz), 0.29 (3H, s), 0.27 (3H, s); IR (film) 3059, 2979, 1718, 1640, 1600, 1250, 900, 700 cm^{-1}; MS m/z (%): 342 ($M^+ + 1$, 11), 341 (M^+, 6), 247 (3), 190 (3), 144 (87), 115 (100), 91 (10).

Diethyl (*E*)-2-(dimethylphenylsilyl)pent-3-ene-1,5-dioate (8l): ^{1}H NMR δ 7.60−7.34 (5H, m), 7.18 (1H, dd, J = 10.3 and 15.7 Hz), 5.60 (1H, dd, J = 0.61 and 15.7 Hz), 4.18 (4H, q, J = 7.1 Hz), 3.29 (1H, d, J = 10.3 Hz), 1.28 (6H, t, J = 7.1 Hz), 0.45 (6H, s); IR (film) 3070, 2979, 1720, 1606, 1250, 881, 700 cm^{-1}; MS m/z (%): 321 ($M^+ + 1$, 14), 320 (6), 259 (40), 235 (46), 219 (9), 165 (8), 135 (100), 114 (21).

Ethyl (*E*)-2-(dimethylphenylsilyl)non-3-enoate (8m): ^{1}H NMR δ 7.51−7.47 (2H, m), 7.39−7.32 (3H, m), 5.59 (1H, ddt, J = 1.3, 10.0 and 15.4 Hz), 5.20 (1H, dt, J = 7.0 and 15.3 Hz), 4.01 (1H, dq, J = 7.1 and 10.7 Hz), 3.93 (1H, dq, J = 7.1 and 10.8 Hz), 3.02 (1H, d, J = 10.0 Hz), 2.01−1.93 (2H, m), 1.40−1.16 (6H, m), 1.08 (3H, t, J = 7.1 Hz), 0.88 (3H, t, J = 6.8 Hz), 0.38 (6H, s); IR ($CHCl_3$) 2970, 2870, 1720, 1600, 1470, 1380, 1260, 1180, 1100, 820 cm^{-1}; MS m/z (%): 318 (M^+, 37), 273 (13), 261 (26), 241 (30), 155 (17), 135 (100), 95 (15), 81 (52). Anal. Calcd for $C_{19}H_{30}O_2$Si: C 71.64, H 9.49, Si 8.82. Found: C 71.91, H 9.41, Si 8.54.

Ethyl (*E*)-2-(dimethylphenylsilyl)hex-3-enoate (8n): ^{1}H NMR δ 7.51−7.47 (2H, m), 7.39−7.31 (3H, m), 5.59 (1H, dd, J = 10.0 and 15.4 Hz), 5.23 (1H, dt, J = 6.4 and 15.4 Hz), 4.01 (1H, dq, J = 7.1 and 10.9 Hz), 3.94 (1H, dq, J = 7.1 and 10.9 Hz), 3.01 (1H, d, J = 10.0 Hz), 2.05−1.94 (2H, m), 1.08 (3H, t, J = 7.1 Hz), 0.92 (3H, t, J = 7.4 Hz), 0.38 (6H, s); IR ($CHCl_3$) 2960, 1710, 1460, 1430, 1370, 1250, 1160, 1120, 910, 840, 820 cm^{-1}; MS m/z (%): 276 (M^+, 31), 199 (32), 194 (18), 135 (79), 129 (24), 123 (22), 96 (100), 95 (23), 91 (20), 81 (72), 76 (23). Anal. Calcd for $C_{16}H_{24}O_2$Si: C 69.52, H 8.75, Si 10.16. Found: C 69.56, H 8.73, Si 10.07.

Methyl (*Z*)-2-(dimethylphenylsilyl)non-3-enoate (8o): ^{1}H NMR δ 7.53−7.48 (2H, m), 7.40−7.32 (3H, m), 5.61 (1H, ddt, J = 1.8, 11.3 and 11.3 Hz), 5.32 (1H, ddt, J = 0.9, 8.7 and 11.3 Hz), 3.53 (3H, s), 3.38 (1H, dd, J = 0.9 and 11.0 Hz), 1.88−1.55 (2H, m), 1.38−1.08 (6H, m), 0.85 (3H, t, J = 6.6 Hz), 0.40 (3H, s), 0.39 (3H, s); IR ($CHCl_3$) 3020, 2960, 2870, 1720, 1640, 1430, 1400, 1300, 1255, 1155, 1060, 820 cm^{-1}; MS m/z (%): 305 ($M^+ + 1$, 6), 228 (16), 227 (100), 170 (3), 135 (4), 91 (3), 89 (5), 74 (5). Anal. Calcd for $C_{18}H_{28}O_2$Si: C 71.00, H 9.27, Si 9.22. Found: C 71.15, H 9.14, Si 9.04.

Ethyl (*Z*)-2-(dimethylphenylsilyl)hex-3-enoate (8p): ^{1}H NMR δ 7.53−7.49 (2H, m), 7.39−7.31 (3H, m), 5.60 (1H, ddt, J = 1.5, 11.0 and 11.0 Hz), 5.30 (1H, dt, J = 7.0 and 11.0 Hz), 4.01−3.91 (2H, m), 3.36 (1H, d, J = 11.0 Hz), 1.91−1.82 (1H, m), 1.71−1.62 (1H, m), 1.10 (3H, t, J = 7.1 Hz), 0.81 (3H, t, J = 7.5 Hz), 0.40 (6H, s); IR ($CHCl_3$) 2970, 2940, 2870, 1700, 1460, 1370, 1260, 1120, 1080, 840 cm^{-1}; MS m/z (%): 276 (M^+, 16), 231 (10), 199 (14), 135 (64), 105 (13), 96 (100), 81 (29). Anal. Calcd for $C_{16}H_{24}O_2$Si: C 69.52, H 8.75, Si 10.16. Found: C 69.51, H 8.69, Si 10.08.

(*E*)-5-Phenyl-3-(dimethylphenylsilyl)pent-4-en-2-one (10). To a stirred solution of $Rh_2(OAc)_4$ (5 mg, 0.01 mmol) and dimethylphenylsilane (0.5 mL, 3.22 mmol) in dry CH_2Cl_2 (2 mL) was added using a syringe pump (0.3 mmol/h) a solution of **9**[6k] (0.3 g, 1.61 mmol) in dry CH_2Cl_2 (4 mL) at rt. When the addition was complete, the solvent was evaporated in vacuo to afford **10** (crude yield: 65%) which was used in the next step without further purification. ^{1}H NMR δ 7.67−7.20 (10H, m), 6.53 (1H, ddd, J = 1.5, 10.1 and 16 Hz), 6.17 (1H, d, J = 16 Hz), 3.65 (1H, d, J = 10.1 Hz), 2.48 (3H, s), 0.46 (3H, s), 0.45 (3H, s); IR (film) 3069, 2959, 1719, 1592, 1450, 1252, 881, 833 cm^{-1}; MS m/z (%): 294 (M^+, 68), 267 (64), 233 (52), 205 (25), 135 (100), 105 (67), 91 (51).

(2*R,3*R**)-(*E*)-5-Phenyl-3-(dimethylphenylsilyl)pent-4-enol (11).** To a solution of **10** (193 mg, 0.65 mmol) in dry THF (10 mL) was added dropwise, at −100 °C, a 1 M solution of DIBAH in toluene (1.31 mL, 1.31 mmol). The mixture was stirred at −100 °C for 2 h and then treated with a 1 M solution of HCl. The aqueous layer was extracted with ether, the combined extracts were washed with 1 M HCl and brine and dried over $MgSO_4$, and the solvents were evaporated in vacuo. Chromatography of the residue (petroleum ether/ethyl acetate/NEt_3 98:1.5:0.5) gave *syn* alcohol **11** (122 mg, 63%) as a colorless oil: ^{1}H NMR δ 7.61−7.55 (2H, m), 7.42−7.19 (8H, m), 6.32 (1H, d, J = 15.7 Hz), 6.12 (1H, dd, J = 10.5 and 15.7 Hz), 4.0 (1H, dq, J = 6.4 and 6.4 Hz), 2.22 (1H, dd, J = 6.6 and 10.5 Hz), 1.50 (1H, s), 1.21 (3H, d, J = 6.3 Hz), 0.41 (3H, s), 0.40 (3H, s); ^{13}C NMR δ 137.9, 134.1, 130.8, 129.2, 128.5, 127.9, 127.5, 126.8, 125.9, 69.0, 44.5, 23.2, −2.9, −3.6; IR (film) 3430, 3070, 2970, 1600, 1490, 1250, 1120, 840, 820, 740 cm^{-1}; MS m/z (%): 145 (11), 144 (69), 135 (40), 129 (100), 115 (11), 105 (7), 91 (13). Anal. Calcd for $C_{19}H_{24}$OSi: C 76.97, H 8.16, Si 9.47. Found: C 77.00, H 8.29, Si 9.65.

Methyl (3*E*,5*E*)-2-Diazo-6-phenylhexa-3,5-dienoate (12). Prepared according to reference 6k. ^{1}H NMR δ 7.42−7.22 (5H, m), 6.89 (1H, ddd, J = 1.0, 8.5 and 15.6 Hz), 6.48 (1H, d, J = 15.6 Hz), 6.51−6.08 (2H, m), 3.85 (3H, s); IR ($CHCl_3$) 3010, 2950, 2100, 1700, 1600, 1420, 1370, 1310, 980 cm^{-1}; MS m/z (%): 228 (M^+, 43), 227 (43), 195 (61), 157 (62), 141 (90), 128 (73), 115 (100), 91 (98), 77 (35), 73 (77). Anal. Calcd for $C_{13}H_{12}O_2N_2$: C 68.41, H 5.30, N 12.27. Found: C 68.47, H 5.21, N 12.22.

Methyl (3*E*,5*E*)-6-phenyl-2-(dimethylphenylsilyl)hexa-3,5-dienoate (13): ^{1}H NMR δ 7.52−7.17 (10H, m), 6.81−6.71 (1H, m), 6.38 (1H, d, J = 15.6 Hz), 6.01−5.97 (2H, m), 3.55 (3H, s), 3.22−3.19 (1H, m), 0.44 (3H, s), 0.43 (3H, s); IR ($CHCl_3$) 2950, 1710, 1630, 1490, 1440, 1360, 1260, 920 cm^{-1}; MS m/z (%): 354 ($M^+ + NH_4^+$, 13), 337 ($M^+ + 1$, 41), 305 (37), 259

(100), 231 (24), 227 (13), 152 (13), 135 (29). Anal. Calcd for $C_{21}H_{24}O_2Si$: C 74.96, H 7.19, Si 8.35. Found: C 74.97, H 7.25, Si 8.38.

General Procedure for the Preparation of Allylic Alcohols 14a−f. $Rh_2(OAc)_4$ (0.01 mmol) was added at rt to a solution of **7** (6.94 mmol) in moist ether (50 mL). The mixture was stirred at rt for 6 h, and the solvent was evaporated in vacuo. Chromatography of the residue (petroleum ether/ethyl acetate 9:1) gave **14** as a pale yellow oil.

Ethyl (*E*)-2-hydroxy-4-phenylbut-3-enoate (14a): ^{1}H NMR δ 7.43−7.23 (5H, m), 6.83 (1H, dd, J = 1.6 and 15.9 Hz), 6.26 (1H, dd, J = 5.6 and 15.9 Hz), 4.84 (1H, ddd, J = 1.6, 5.6 and 5.6 Hz), 4.33 (1H, dq, J = 7.1 and 10.8 Hz), 4.26 (1H, dq, J = 7.1 and 10.8 Hz), 3.13 (1H, d, J = 5.6 Hz), 1.33 (3H, t, J = 7.1 Hz); IR ($CHCl_3$) 3550, 3000, 1730, 1600, 1450, 1370, 1260, 1100, 1080, 1020, 860 cm^{-1}; MS m/z (%): 206 (M^+, 8), 189 (6), 188 (6), 134 (10), 133 (100), 115 (22), 103 (16), 77 (12). Anal. Calcd for $C_{12}H_{14}O_3$: C 69.89, H 6.84. Found: C 69.96, H 6.94.

Ethyl (*E*)-2-hydroxynon-3-enoate (14c): ^{1}H NMR δ 5.89 (1H, ddt, J = 1.4, 6.8 and 15.3 Hz), 5.50 (1H, ddt, J = 1.5, 4.6 and 15.3 Hz), 4.58 (1H, d, J = 4.6 Hz), 4.26 (2H, q, J = 7.2 Hz), 2.92 (1H, s), 2.11−2.02 (2H, m), 1.42−1.27 (6H, m), 1.30 (3H, t, J = 7.2 Hz), 0.88 (3H, t, J = 6.7 Hz); IR (film) 3211, 3182, 2957, 1742, 1376, 1112 cm^{-1}; MS m/z (%): 200 (M^+, 3), 183 (7), 135 (8), 125 (27), 109 (17), 99 (100), 83 (33). Anal. Calcd for $C_{11}H_{20}O_3$: C 65.95, H 10.07. Found: C 66.05, H 10.02.

Methyl (*Z*)-2-hydroxynon-3-enoate (14f): ^{1}H NMR δ 5.72 (1H, ddt, J = 1.2, 7.5 and 10.7 Hz), 5.35 (1H, ddt, J = 1.6, 8.9 and 10.7 Hz), 4.94 (1H, d, J = 8.9 Hz), 3.79 (3H, s), 2.23−2.16 (2H, m), 1.46−1.22 (6H, m), 0.90 (3H, t, J = 6.8 Hz); IR (film) 3448, 2955, 1740, 1379, 1084 cm^{-1}; MS m/z (%): 186 (M^+, 9), 153 (3), 125 (100), 109 (46), 99 (23), 81 (34). Anal. Calcd for $C_{10}H_{18}O_3$: C 64.49, H 9.74. Found: C 64.42, H 9.70.

General Procedure for the Preparation of Allylic Methoxy and Ethoxy Ethers 14g−i. $Rh_2(OAc)_4$ (0.01 mmol) was added at rt to a solution of **7** (0.97 mmol) in ethanol or methanol (3 mL). The mixture was stirred at rt for 15 min, and the solvent was evaporated in vacuo. Chromatography of the residue (petroleum ether/ethyl acetate 95:5) gave **14** as a pale yellow oil.

Ethyl (*E*)-2-ethoxy-4-phenylbut-3-enoate (14g): ^{1}H NMR δ 7.42−7.26 (5H, m), 6.78 (1H, d, J = 15.7 Hz), 6.24 (1H, dd, J = 6.9 and 15.7 Hz), 4.52 (1H, dd, J = 1.2 and 6.8 Hz), 4.25 (2H, q, J = 7.1 Hz), 3.64 (1H, dq, J = 7.1 and 10.1 Hz), 3.59 (1H, dq, J = 7.1 and 10.1 Hz), 1.31 (6H, t, J = 7.1 Hz); IR (film) 2980, 1740, 1440, 1250, 1180, 1030, 970 cm^{-1}; MS m/z (%): 253 (100), 252 ($M^+ + NH_4^+$, 97), 207 (34), 206 (50), 190 (39), 189 (77), 161 (51). Anal. Calcd for $C_{14}H_{18}O_3$: C 71.77, H 7.74. Found: C 71.91, H 7.76.

Ethyl (*E*)-2-methoxynon-3-enoate (14h): ^{1}H NMR δ 5.89 (1H, dt, J = 6.8 and 15.4 Hz), 5.46 (1H, ddt, J = 1.3, 7.3 and 15.4 Hz), 4.23 (2H, q, J = 7.2 Hz), 4.19 (1H, d, J = 7.3 Hz), 3.37 (3H, s), 2.11−2.03 (2H, m), 1.46−1.24 (6H, m), 0.88 (3H, t, J = 6.8 Hz); IR (film) 2956, 1734, 1368, 1187 cm^{-1}; MS m/z (%): 214 (M^+, 3), 213 ($M^+ - 1$, 7), 183 (9), 159 (2), 141 (100), 125 (5), 109 (24), 85 (11). Anal. Calcd for $C_{12}H_{22}O_3$: C 67.24, H 10.35. Found: C 67.29, H 10.32.

Methyl (*Z*)-2-methoxynon-3-enoate (14i): ^{1}H NMR δ 5.79 (1H, ddt, J = 0.9, 7.5 and 10.8 Hz), 5.38 (1H, ddt, J = 1.6, 9.1 and 10.8 Hz), 4.59 (1H, dd, J = 0.9 and 8.9 Hz), 3.76 (3H, s), 3.37 (3H, s), 2.28−2.14 (2H, m), 1.47−1.20 (6H, m), 0.90 (3H, t, J = 6.7 Hz); IR (film) 2955, 1758, 1636, 1377, 1165, 1109, 733 cm^{-1}; MS m/z (%): 186 (M^+, 9), 168 (5), 125 (100), 109 (46), 99 (23), 81 (34). Anal. Calcd for $C_{11}H_{20}O_3$: C 65.97, H 10.07. Found: C 65.97, H 9.98.

Ethyl (*E*)-2-(2,2,2-Trifluoroethoxy)-4-phenylbut-3-enoate (14j). $Rh_2(OAc)_4$ (5 mg, 0.01 mmol) was added at rt to a solution of **7a** (199 mg, 0.92 mmol) and 2,2,2-trifluoroethanol (0.66 mL, 9.2 mmol) in dry benzene (5 mL), and the mixture was then refluxed for 10 min. After evaporation of the solvent in vacuo, chromatography of the residue (petroleum ether/ethyl acetate 95:5) gave **14j** as a pale yellow oil (135 mg, 52%): ^{1}H NMR δ 7.45−7.28 (5H, m), 6.81 (1H, dd, J = 0.8 and 16.0), 6.22 (1H, dd, J = 6.9 and 16.0 Hz), 4.71 (1H, dd, J = 0.9 and 6.8 Hz), 4.27 (2H, q, J = 7.1 Hz), 4.04 (1H, dq, J = 8.6 and 12.4 Hz), 3.92 (1H, dq, J = 8.6 and 12.5 Hz), 1.32 (3H, t, J = 7.1 Hz); IR (film) 2990, 2940, 1740, 1600, 1450, 1280, 1170, 1030, 970, 700 cm^{-1}; MS m/z (%): 288 (M^+, 3), 259 (2), 215 (100), 169 (6), 131 (37), 115 (58), 91 (28), 77 (18). Anal. Calcd for $C_{14}H_{15}O_3F_3$: C 58.33, H 5.24. Found: C 58.36, H 5.37.

Ethyl (*E*)-2-Phenoxy-4-phenylbut-3-enoate (14k). To a solution of phenol (220 mg, 2.33 mmol) and $Rh_2(OAc)_4$ (5 mg, 0.01 mmol) in dry benzene (4 mL) under reflux was added slowly, over a period of 2 h (syringe pump), a solution of **7a** (110 mg, 0.5 mmol) in dry benzene (1 mL). After evaporation of the solvent in vacuo, chromatography of the residue (petroleum ether/ethyl acetate 95:5) gave **14k** as a pale yellow oil (58 mg, 40%): ^{1}H NMR δ 7.50−7.28 (7H, m), 7.07−6.96 (3H, m), 6.92 (1H, d, J = 16.0 Hz), 6.40 (1H, dd, J = 6.3 and 16.0 Hz), 5.31 (1H, dd, J = 1.3 and 6.3 Hz), 4.29 (1H, dq, J = 7.1 and 10.1 Hz), 4.25 (1H, dq, J = 7.1 and 10.1 Hz), 1.28 (3H, t, J = 7.1 Hz); IR (film) 3040, 2990, 1750, 1600, 1490, 1370, 1240, 970, 700 cm^{-1}, MS m/z (%): 283 ($M^+ + 1$, 15), 282 (M^+, 12), 189 (33), 143 (14), 115 (100), 94 (13). Anal. Calcd for $C_{18}H_{18}O_3$: C 76.57, H 6.43. Found: C 76.47, H 6.23.

General Procedure for the Preparation of Allylic Amine 14l−n. $Rh_2(OAc)_4$ (0.01 mmol) was added at rt to a solution of diazoester **7** (0.46 mmol) and aniline (2.3 mmol) in dry benzene (5 mL), and the mixture was refluxed for 10 min. After evaporation of the solvent in vacuo, chromatography of the residue (petroleum ether/ethyl acetate 95:5) gave the allylic amines **14l−n** as a pale yellow oil.

Ethyl (*E*)-2-(*N*-phenylamino)non-3-enoate (14m): ^{1}H NMR δ 7.18 (2H, dd, J = 7.4 and 8.5 Hz), 6.74 (1H, t, J = 7.4 Hz), 6.63 (2H, d, J = 8.6 Hz), 5.88 (1H, dt, J = 6.8 and 15.7 Hz), 5.52 (1H, dd, J = 5.7 and 15.7 Hz), 4.53−4.50 (1H, m), 4.23 (2H, q, J = 7.2 Hz), 2.10−2.02 (2H, m), 1.43−1.21 (6H, m), 1.29 (3H, t, J = 7.2 Hz), 0.88 (3H, t, J = 6.6 Hz); IR (film) 2956, 1734, 1368, 1187 cm^{-1}; MS m/z (%): 276 ($M^+ + 1$, 18), 275 (M^+, 22), 202 (100), 144 (10), 132 (28), 117 (12), 93 (11). Anal. Calcd for $C_{17}H_{25}NO_2$: C 74.13, H 9.16, N 5.09. Found: C 74.25, H 9.07, N 5.15.

Methyl (*Z*)-2-(*N*-phenylamino)non-3-enoate (14n): ^{1}H NMR δ 7.18 (2H, dd, J = 7.4 and 8.6 Hz), 6.75 (1H, t, J = 7.4 Hz), 6.61 (2H, d, J = 8.6 Hz), 5.73 (1H, ddt, J = 1.2, 7.5 and 10.7 Hz), 5.31 (1H, ddt, J = 1.7, 8.8 and 10.7 Hz), 4.84 (1H, d, J = 8.7 Hz), 3.75 (3H, s), 2.33−2.24 (2H, m), 1.56−1.31 (6H, m), 0.92 (3H, t, J = 6.6 Hz); IR (film) 3409, 3082, 2954, 1738, 1644, 1600, 1500, 1176 cm^{-1}; MS m/z (%): 261 (M^+, 18), 202 (100), 144 (11), 132 (22), 117 (12), 93 (71). Anal. Calcd for $C_{16}H_{23}NO_2$: C 73.53, H 8.87, N 5.36. Found: C 73.52, H 8.81, N 5.16.

(*E*)-4-Phenyl-2-(phenylthio)but-3-enol (15). $Rh_2(OAc)_4$ (5 mg, 0.01 mmol) was added at rt to a solution of **7a** (848 mg, 3.92 mmol) and thiophenol (0.8 mL, 7.84 mmol) in dry CH_2Cl_2 (50 mL). The mixture was stirred at rt for 40 min and then treated with a saturated solution of Na_2CO_3. The aqueous layer was extracted with CH_2Cl_2, the combined extracts were washed with a saturated solution of Na_2CO_3 and brine and drived over $MgSO_4$, and the solvent was evaporated in vacuo. To the residual oil in dry ether (50 mL) was added dropwise, at 0 °C, a 1 M solution of $LiAlH_4$ in ether (3.92 mL, 3.92 mmol). The mixture was stirred at rt for 15 h and then treated with a 1 M HCl. The aqueous layer was extracted with ether, the combined extracts were washed with brine and dried over $MgSO_4$, and the solvent was evaporated in vacuo. Flash chromatography of the residue (petroleum ether/ethyl acetate 9.1) gave **15** as a pale yellow oil (0.3 g, 30%): ^{1}H NMR δ 7.50−7.45 (2H, m), 7.36−7.20 (8H, m), 6.47 (1H, d, J = 15.8 Hz), 6.15 (1H, dd, J = 8.5 and 15.8 Hz), 3.97−3.89 (1H, m), 3.81 (1H, dd, J = 3.5 and 9.1 Hz), 3.75 (1H, dd, J = 4.7 and 9.1 Hz); IR (film) 3400, 3060, 2870, 1580, 1480, 1380, 1180, 970, 700 cm^{-1}; MS m/z (%): 258 ($M^+ + 2$, 2), 256 (M^+, 1), 147 (64), 129 (100), 117 (22), 115 (33), 110 (28), 109 (17), 91 (77). Anal. Calcd for $C_{16}H_{16}OS$: C 74.96, H 6.29, S 12.51. Found: C 74.81, H 6.23, S 12.60.

(*E*)-4-Phenyl-2-(phenylsulfonyl)but-3-enol (16). To a solution of **15** (0.2 g, 0.78 mmol) in CH_2Cl_2 (5 mL) was added dropwise, at 0 °C, a 70% solution of m-CPBA (423 mg, 1.72

mmol), in CH_2Cl_2 (5 mL). The mixture was stirred at rt for 1 h and then treated with a saturated solution of $NaHCO_3$. The aqueous layer was extracted with CH_2Cl_2, the combined extracts were washed successively with a 5% solution of NaOH and a 1 M solution of HCl, brine and then dried over $MgSO_4$, and the solvent was evaporated in vacuo. Chromatography of the residue (CH_2Cl_2/MeOH 98:2) afforded **16** as a pale yellow oil (0.22 g, 98%): ^{1}H NMR δ 7.88−7.24 (10H, m), 6.34 (1H, d, J = 15.9 Hz), 6.0 (1H, dd, J = 9.3 and 15.9 Hz), 4.27 (1H, dd, J = 7.2 and 12.4 Hz), 4.07 (1H, dd, J = 4.1 and 12.4 Hz), 3.98−3.89 (1H, m); IR (film) 3500, 3060, 2930, 1580, 1450, 1300, 1150, 970 cm^{-1}; MS m/z (%): 147 (62), 130 (31), 129 (100), 117 (27), 115 (20), 91 (58), 77 (20). Anal. Calcd for $C_{16}H_{16}O_3S$: C 66.64, H 5.59, S 11.12. Found: C 66.50, H 5.60, S 11.02.

General Procedure for the Preparation of the Pantolactone β,γ-Unsaturated Esters 17. A solution of **5** (15 mmol), pantolactone (15.8 mmol), DCC (16.5 mmol), and (dimethylamino)pyridine (0.04 mmol) in dry CH_2Cl_2 (80 mL) was stirred at rt for 30 min and then filtered, and the solvent was evaporated in vacuo. Chromatography of the residue (petroleum ether/ethyl acetate 9:1) gave **17** as a colorless oil.

17b (80%): ^{1}H NMR δ 5.73−5.47 (2H, m), 5.37 (1H, s), 4.06 (1H, d, J = 9.0 Hz), 4.02 (1H, d, J = 9.0 Hz), 3.18 (2H, d, J = 6.2 Hz), 2.12−2.01 (2H, m), 1.20 (3H, s), 1.11 (3H, s), 0.99 (3H, t, J = 7.5 Hz); IR ($CHCl_3$) 2970, 1800, 1740, 1460, 1300, 1240, 1020, 970 cm^{-1}; MS m/z (%): 227 (M^+ + 1, 5), 226 (M^+, 2), 131 (21), 113 (17), 99 (23), 97 (35), 96 (100), 83 (26), 81 (29), 71 (21); $[\alpha]^{25}_D$: +3.8 (c 1.26, $CHCl_3$). Anal. Calcd for $C_{12}H_{18}O_4$: C 63.70, H 8.02. Found: C 63.85, H 7.92.

17c (83%): ^{1}H NMR δ 5.68−5.48 (2H, m), 5.37 (1H, s), 4.06 (1H, d, J = 9.0 Hz), 4.02 (1H, d, J = 9.0 Hz), 3.25 (2H, d, J = 7.3 Hz), 2.14−2.02 (2H, m), 1.20 (3H, s), 1.11 (3H, s), 0.99 (3H, t, J = 7.5 Hz); IR ($CHCl_3$) 3570, 3040, 2950, 2870, 1800, 1760, 1635, 1440, 1310, 1250, 1030 cm^{-1}; MS m/z (%): 226 (M^+, 2), 131 (17), 113 (18), 99 (23), 97 (37), 96 (100), 83 (31), 71 (38); $[\alpha]^{25}_D$: +1.9 (c 1.38, $CHCl_3$). Anal. Calcd for $C_{12}H_{18}O_4$: C 63.70, H 8.02. Found: C, 63.68, H 7.89.

18b. Prepared according to the general procedure reported for esters **7** (71%): ^{1}H NMR δ 5.72 (1H, dt, J = 1.4 and 15.7 Hz), 5.47 (1H, s), 5.43 (1H, dt, J = 7.4 and 15.7 Hz), 4.08 (1H, d, J = 9.0 Hz), 4.04 (1H, d, J = 9.0 Hz), 2.20 (2H, ddt, J = 1.4, 7.4 and 7.4 Hz), 1.23 (3H, s), 1.11 (3H, s), 1.04 (3H, t, J = 7.4 Hz); IR ($CHCl_3$) 3550, 2950, 2870, 2100, 1800, 1720, 1660, 1480, 1380, 1280, 1010 cm^{-1}; MS m/z (%): 224 (4), 170 (10), 169 (48), 168 (18), 109 (17), 105 (15), 97 (59), 95 (50), 85 (56), 83 (100), 81 (55), 77 (22), 71 (75); $[\alpha]^{25}_D$: −0.4 (c 1.23, $CHCl_3$). Anal. Calcd for $C_{12}H_{16}O_4N_2$: C 57.13, H 6.39. Found: C 57.60, H 6.60.

18c (64%): ^{1}H NMR δ 5.64−5.54 (2H, m), 5.46 (1H, s), 4.08 (1H, d, J = 9.2 Hz), 4.04 (1H, d, J = 9.2 Hz), 2.18−2.04 (2H, m), 1.24 (3H, s), 1.12 (3H, s), 1.05 (3H, t, J = 7.5 Hz); IR ($CHCl_3$) 2950, 2100, 1800, 1710, 1650, 1460, 1370, 1270, 1020, 950 cm^{-1}; MS m/z (%): 253 (M^+ + 1, 24), 252 (M^+, 16), 124 (10), 123 (100), 113 (11), 97 (39), 83 (56); $[\alpha]^{25}_D$: + 1.1 (c 1.39, $CHCl_3$). Anal. Calcd for $C_{12}H_{16}O_4N_2$: C 57.13, H 6.39. Found: C 57.29, H 6.44.

19a. Prepared according to the general procedure reported for esters **8** (67%) (two diastereoisomers): ^{1}H NMR δ 7.57−7.20 (10H, m), 6.36 (2H, d, J = 9.9 and 16.0 Hz), 6.16 (1H, d, J = 16.0 Hz), 6.11 (1H, d, J = 16.0 Hz), 5.35 (2H, s), 4.01 (2H, s), 3.98 (2H, s), 3.40 (1H, d, J = 9.9 Hz), 3.38 (1H, d, J = 9.9 Hz), 1.15 (3H, s), 1.05 (3H, s), 1.03 (3H, s), 0.93 (3H, s), 0.54 (6H, s), 0.52 (6H, s); IR (film) 3060, 2950, 1790, 1640, 1600, 1460, 1370, 1250, 1000, 700 cm^{-1}; MS m/z (T): 275 (2), 145 (25), 144 (100), 135 (7), 117 (42), 115 (34), 91 (11).

19b (two diastereoisomers): ^{1}H NMR δ 7.53−7.22 (10H, m), 6.49 (1H, dd, J = 10 and 16 Hz), 6.4 (1H, dd, J = 10 and 16 Hz), 6.32 (1H, d, J = 16 Hz), 6.29 (1H, d, J = 16 Hz), 5.40 (2H, s), 4.04−4.00 (4H, m), 3.22 (1H, d, J = 10 Hz), 3.21 (1H, d, J = 10 Hz), 1.20 (3H, s), 1.16 (3H, s), 1.13 (3H, s), 1.06 (3H, s), 0.24−0.11 (54H, m); IR (film) 3063, 2959, 1794, 1732, 1248, 848, 754 cm^{-1}; MS m/z (%): 520 (M^+, 0.2), 415 (3), 281 (46), 207 (33), 174 (14), 144 (56), 117 (41), 73 (100).

19c (two diastereoisomers): ^{1}H NMR δ 7.57−7.49 (4H, m), 7.42−7.33 (6H, m), 5.56 (2H, ddt, J = 1.4, 10.0 and 15.5 Hz), 5.31 (2H, s), 5.22 (2H, dt, J = 6.4 and 15.5 Hz), 3.99 (2H, s), 3.96 (2H, s), 3.17 (1H, d, J = 10.0 Hz), 3.14 (1H, d, J = 10.0 Hz), 2.04−1.93 (4H, m), 1.13 (3H, s), 1.02 (3H, s), 0.99 (3H, s), 0.91 (6H, t, J = 7.4 Hz), 0.89 (3H, s), 0.47 (6H, s), 0.45 (6H, s); IR ($CHCl_3$) 2970, 1790, 1720, 1460, 1300, 1290, 1120, 1020, 840 cm^{-1}; MS m/z (%): 360 (M^+, 41), 283 (3), 231 (6), 187 (14), 135 (56), 105 (9), 96 (100), 81 (47). Anal. Calcd for $C_{20}H_{28}O_4Si$: C 66.63, H 7.83, Si 7.79. Found: C 66.40, H 7.47, Si 7.94.

19d (two diastereoisomers): ^{1}H NMR δ 7.58−7.50 (4H, m), 7.42−7.31 (6H, m), 5.59 (2H, ddt, J = 1.6, 11.0 and 11.0 Hz), 5.34 (2H, dt, J = 6.8 and 11.0 Hz), 5.31 (2H, s), 3.99 (2H, s), 3.97 (2H, s), 3.50 (1H, d, J = 11.0 Hz), 3.48 (1H, d, J = 11.0 Hz), 1.98−1.77 (2H, m), 1.70−1.52 (2H, m), 1.14 (3H, s), 1.06 (3H, s), 1.0 (3H, s), 0.93 (3H, s), 0.80 (6H, t, J = 7.5 Hz), 0.49 (6H, s), 0.47 (6H, s); IR ($CHCl_3$) 2970, 1790, 1460, 1430, 1370, 1300, 1260, 1140, 1000, 910 cm^{-1}; MS m/z (%): 360 (M^+, 41), 187 (11), 155 (11), 135 (52), 105 (8), 96 (100), 81 (46). Anal. Calcd for $C_{20}H_{28}O_4Si$: C 66.63, H 7.83, Si 7.79. Found: C 66.54, H 7.84, Si 7.74.

19e (two diastereoisomers): ^{1}H NMR δ 7.57−7.50 (4H, m), 7.42−7.31 (6H, m), 5.64−5.53 (2H, m), 5.31−5.16 (2H m), 5.30 (2H, s), 3.98 (2H, s), 3.96 (2H, s), 3.18 (1H, d, J = 10.1 Hz), 3.15 (1H, d, J = 10.0 Hz), 1.67−1.62 (6H, m), 1.12 (3H, s), 1.01 (3H, s), 0.99 (3H, s), 0.88 (3H, s), 0.47 (6H, s), 0.45 (6H, s); IR ($CHCl_3$) 2975, 1780, 1720, 1460, 1340, 1290, 1250, 1120, 960, 840 cm^{-1}; MS m/z (%): 346 (M^+, 7), 187 (3), 135 (19), 105 (5), 83 (17), 82 (100). Anal. Calcd for $C_{19}H_{26}O_4Si$: C 65.86, H 7.56, Si 8.11. Found: C 65.92, H 7.56, Si 8.26.

19f. $Rh_2(OAc)_4$ (5 mg, 0.01 mmol) was added at rt to a solution of **18a** (1.45 g, 4.82 mmol) in moist ether (40 mL). The mixture was stirred at rt for 4 h, and the solvent was evaporated in vacuo. Chromatography of the residue (CH_2Cl_2/MeOH 99.5:0.5) gave (2*S*)-alcohol **19fa** as a pale yellow oil (0.79 g, 56%): ^{1}H NMR δ 7.44−7.23 (5H, m), 6.89 (1H, d, J = 16.0 Hz), 6.34 (1H, ddd, J = 0.6, 5.4 and 16.0 Hz), 5.43 (1H, s), 5.02−5.0 (1H, m), 4.09 (1H, d, J = 9.1 Hz), 4.04 (1H, d, J = 9.1 Hz), 3.21 (1H, s), 1.24 (3H, s), 1.14 (3H, s); IR ($CHCl_3$) 3550, 3020, 2970, 1790, 1600, 1465, 1370, 1160, 1080, 1020, 970 cm^{-1}; MS m/z (%): 290 (M^+, 2), 144 (17), 134 (14), 133 (100), 131 (31), 115 (32), 114 (14), 104 (18), 99 (22), 91 (17), 77 (11); $[\alpha]^{25}_D$: +0.6 (c 1.45, $CHCl_3$). Anal. Calcd for $C_{16}H_{18}O_5$: C 66.20, H 6.25. Found: C 66.15, H 6.33. (2*R*)-alcohol **19fb** (0.27 g, 19%): ^{1}H NMR δ 7.42−7.27 (5H, m), 6.88 (1H, dd, J = 1.6 and 15.9 Hz), 6.27 (1H, dd, J = 6.0 and 15.9 Hz), 5.46 (1H, s), 5.08−5.06 (1H, m), 4.08 (1H, d, J = 9.1 Hz), 4.04 (1H, d, J = 9.1 Hz), 3.18 (1H, s), 1.19 (3H, s), 1.09 (3H, s); IR ($CHCl_3$) 3550, 3020, 2920, 1790, 1600, 1460, 1050, 1020, 880, 850 cm^{-1}; MS m/z (%): 290 (M^+, 3), 144 (8), 134 (10), 133 (100), 131 (18), 115 (22), 114 (12), 105 (13), 99 (24), 91 (10); $[\alpha]^{25}_D$: +5.1 (c 1.07, $CHCl_3$). Anal. Calcd for $C_{16}H_{18}O_5$: C 66.20, H 6.25. Found: C 66.25, H 6.17.

19g. $Rh_2(OAc)_4$ (5 mg, 0.01 mmol) was added at rt to a solution of **18a** (105 mg, 0.35 mmol) in methanol (10 mL). The mixture was stirred at rt for 40 min, and the solvent was evaporated in vacuo. Chromatography of the residue (petroleum ether/ethyl acetate 9:1) gave **19g** as an unseparable diastereoisomeric mixture (80 mg, 75%) (two diastereoisomers): ^{1}H NMR δ 7.48−7.23 (10H, m), 6.85 (2H, d, J = 16.0 Hz), 6.28 (1H dd, J = 6.6 and 16.0 Hz), 6.22 (1H, dd, J = 7.0 and 16.0 Hz), 5.46 (1H, s), 5.43 (1H, s), 4.62 (1H, dd, J = 1.3 and 7.1 Hz), 4.58 (1H, dd, J = 1.4 and 6.5 Hz), 4.12−3.95 (4H, m), 3.51 (3H, s), 3.50 (3H, s), 1.23 (3H, s), 1.17 (3H, s), 1.14 (3H, s), 1.07 (3H, s); IR ($CHCl_3$) 2970, 2920, 1800, 1760, 1660, 1470, 1400, 1370, 1300, 1160, 1080, 970, 910 cm^{-1}; MS m/z (%): 322 ($M^+ + NH_4^+$, 98), 305 (M^+ + 1, 7), 274 (21), 273 (100), 147 (14), 115 (7). Anal. Calcd for $C_{17}H_{20}O_5$: C 67.09, H 6.62. Found: C 66.93, H 6.58.

4-Phenyl-2-(dimethylphenylsilyl)butanol (20a). A suspension of 10% palladium on charcoal (137 mg) in 2-propanol (10 mL) was stirred under an hydrogen atmosphere for 30 min, and then a solution of **19a** (0.45 g, 1.25 mmol) in 2-propanol (10 mL) was added slowly. The mixture was stirred at rt for 4 h and then filtered, and the solvent was evaporated in vacuo to give a colorless oil (0.39 g, 87%) which was used in the next step without further purification. To a solution of the resulting oil (0.39 g, 0.95 mmol) in dry ether (25 mL) was added dropwise

at −78 °C a 1 M solution of DIBAH in toluene (1.9 mL, 1.9 mmol). The reaction mixture was stirred at −78 °C for 1 h and then treated with a saturated solution of NH_4Cl, and the organic layer was decanted. The aqueous layer was extracted with ether, the combined extracts were washed with a saturated solution of NH_4Cl and dried over $MgSO_4$, and the solvent was evaporated in vacuo. Chromatography of the residue (petroleum ether/ethyl acetate/NEt_3 90:9.5:0.5) gave **20a** as a colorless oil (165 mg, 61 %): ^{1}H NMR δ 7.57−7.50 (2H, m), 7.41−7.35 (3H, m), 7.32−7.10 (5H, m), 3.88 (1H, dd, J = 4.5 and 10.7 Hz), 3.74 (1H, dd, J = 6.8 and 10.7 Hz), 2.74 (1H, ddd, J = 7.6, 9.2 and 13.6 Hz), 2.56 (1H, ddd, J = 6.9, 9.5 and 13.5 Hz), 1.85−1.75 (2H, m), 1.38 (1H, broad s), 1.20−1.11 (1H, m), 0.36 (3H, s), 0.35 (3H, s); IR ($CHCl_3$) 3630, 3010, 2950, 1250, 1110, 1080 cm^{-1}; MS m/z (%): 271 (10), 137 (65), 136 (19), 135 (84), 132 (33), 105 (13), 104 (33), 91 (100), 75 (16). Anal. Calcd for $C_{18}H_{24}OSi$: C 76.00, H 8.50, Si 9.87. Found: C 75.96, H 8.45, Si 9.81.

2-(Dimethylphenylsilyl)hexanol (20b). Prepared according to the procedure reported for **20a**: ^{1}H NMR δ 7.56−7.50 (2H, m), 7.39−7.34 (3H, m), 3.79 (1H, dd, J = 4.5 and 10.8 Hz), 3.68 (1H, dd, J = 6.8 and 10.8 Hz), 1.50−1.03 (7H, m), 0.85 (3H, t, J = 6.9 Hz), 0.33 (6H, s); IR ($CHCl_3$) 3620, 2960, 2870, 1415, 1250, 1110, 1020, 840 cm^{-1}; MS m/z (%): 169 (10), 137 (100), 135 (21), 97 (10), 83 (13), 71 (14), 69 (12), 57 (23), 55 (21). Anal. Calcd for $C_{14}H_{24}OSi$: C 71.12, H 10.23, Si 11.88. Found: C 71.18, H 10.24, Si 11.74.

4-Phenylbutane-1,2-diol (21a).[31a] To a solution of **20a** (53 mg, 0.19 mmol) in acetic anhydride (0.1 mL) and peracetic acid (32% in acetic acid) (0.6 mL) was added, at 0 °C, $Hg(OAc)_2$ (89 mg, 0.28 mmol). The reaction mixture was stirred at rt for 3 h, and the solvent was evaporated in vacuo. Chromatography of the residue (CH_2Cl_2/MeOH 99:1) afforded **21a** as a colorless oil (13 mg, 42 %).

Hexane-1,2-diol (21b).[31b] Prepared according to the procedure reported for **21a**.

Methyl (2*S*)-Hydroxy-4-phenylbutanoate (22).[31c] A suspension of 10% palladium on charcoal (20 mg) in methanol (10 mL) was stirred under an hydrogen atmosphere for 30 min, and then a solution of alcohol **19fa** (0.41 g, 1.41 mmol) in methanol (10 mL) was added slowly. The reaction mixture was stirred at rt for 3 h and then filtered, and the solvent was evaporated in vacuo to give a colorless oil (0.33 g, 80%) which was used in the next step without further purification. To a solution of the resulting ester (0.24 g, 0.82 mmol) in THF (23 mL) was added dropwise at 0 °C a solution of LiOOH (prepared from LiOH (36 mg, 0.86 mmol), 30% H_2O_2 (0.42 mL), and water (5.8 mL)). The reaction mixture was stirred at 0 °C for 1 h, and then a solution of $NaHSO_3$ (0.85 g, 8.2 mmol) in water (9.3 mL) was added slowly. The mixture was stirred at 0 °C for 15 min, diluted with a 1 M solution of $Na_2S_2O_5$, and extracted with CH_2Cl_2. The combined extracts were dried over $MgSO_4$, and the solvent was evaporated in vacuo. The resulting acid was dissolved in dry ether (10 mL), and an ethereal solution of diazomethane was added until no starting material could be detected by TLC. After evaporation of the solvent in vacuo, chromatography of the residue (petroleum ether/ethyl acetate 5:1) afforded pantolactone (92 mg, 86%) and ester **22** (75 mg, 70%) as a colorless oil (56% overall yield from **19fa**).

General Procedure for the Preparation of Allylsilanes 23a,b Using Rh_2(5*S*-MEPY)$_4$. To a stirred solution of **7a** (or **7b**) (0.5 mmol) and dimethylphenylsilane (1 mmol) in dry CH_2Cl_2 (5 mL) was added at rt $Rh_2(MEPY)_4$ (cat.). The mixture was stirred at rt for 48 h, and then the solvent was evaporated in vacuo to afford the crude optically active allylsilane **8a** (or **8f**) which was used in the next step without further purification. To a solution of **8a** (or **8f**) (0.61 mmol) in dry ether (5 mL) was added dropwise at 0 °C a 1 M solution of $LiAlH_4$ in ether (0.34 mmol). The reaction mixture was stirred at 0 °C for 30 min and then treated with 1 M HCl. The aqueous layer was extracted with ether, the combined extracts were washed with brine and dried over $MgSO_4$, and the solvent was evaporated in vacuo. Chromatography of the residue (petroleum ether/ethyl acetate/NEt_3 95:4.5:0.5) gave **23a,b** as a pale yellow oil.

(*E*)-4-Phenyl-2-(dimethylphenylsilyl)but-3-enol (23a): ^{1}H NMR δ 7.92−7.17 (10H, m), 6.37 (1H, dd, J = 0.6 and 15.8 Hz), 6.10 (1H, dd, J = 9.7 and 15.8 Hz), 3.80−3.76 (2H, m), 2.31 (1H, dt, J = 4.6 and 9.7 Hz), 0.36 (6H, s); IR ($CHCl_3$) 3200, 2990, 2960, 1640, 1600, 1440, 1250, 1120, 970 cm^{-1}; MS m/z (%): 144 (5), 137 (18), 135 (28), 131 (13), 130 (100), 129 (32), 115 (21), 91 (16). Anal. Calcd for $C_{21}H_{24}O_2Si$: C 76.54, H 7.85, Si 9.94. Found: C 76.65, H 7.93, Si 9.93.

(*E*)-4-Phenyl-2-(dimethylphenylsilyl)pent-3-enol (23b): ^{1}H NMR δ 7.55−7.51 (2H, m), 7.46−7.21 (8H, m), 5.66 (1H, dq, J = 1.2 and 11.2 Hz), 3.90−3.80 (1H, m), 3.71 (1H, dd, J = 10.4 and 10.4 Hz), 2.56 (1H, dd, J = 4.2, 10.4 and 11.2 Hz), 1.92 (3H, d, J = 1.3 Hz), 0.38 (3H, s), 0.36 (3H, s); IR ($CHCl_3$) 3580, 3150, 3000, 2960, 2870, 1600, 1500, 1460, 1120, 1100, 1040, 820 cm^{-1}; MS m/z (%): 201 (4), 152 (5), 145 (20), 144 (92), 143 (15), 137 (57), 135 (62), 129 (100), 91 (11). Anal. Calcd for $C_{19}H_{24}OSi$: C 76.97, H 8.16, Si 9.47. Found: C 77.02, H 8.13, Si 9.32.

Ethyl (*E*)-2-Deuterio-2-(dimethylphenylsilyl)-4-phenylbut-3-enoate (24). Prepared according to the general procedure described for **8**: ^{1}H NMR δ 7.53−7.17 (10H, m), 6.40 (1H, d, J = 16.0 Hz), 6.12 (1H, d, J = 16.0 Hz), 4.06 (1H, dq, J = 7.1 and 10.1 Hz), 3.98 (1H, dq, J = 7.1 and 10.1 Hz), 1.12 (3H, t, J = 7.1 Hz), 0.45 (6H, s); IR (film) 3030, 2970, 1720, 1650, 1610, 1460, 1240, 1130, 980, 920, 830 cm^{-1}; MS m/z (%): 343 ($M^+ + NH_4^+$, 5), 326 ($M^+ + 1$, 5), 325 (M^+, 3), 249 (20), 248 (100), 220 (8), 192 (16), 145 (8), 135 (12). Anal. Calcd for $C_{20}H_{25}O_2Si$: C 73.80, H 7.74, Si 8.63. Found: C 73.71, H 7.70, Si 8.56.

25. Prepared according to the procedure described for **23a,b**: ^{1}H NMR δ 7.54−7.20 (5H, m), 6.37 (1H, d, J = 15.9 Hz), 6.10 (1H, d, J = 15.9 Hz), 3.84−3.73 (2H, m), 0.37 (6H, s); IR (film) 3392, 3069, 2956, 1636, 1599, 1427, 1250, 1112, 833, 736 cm^{-1}; MS m/z (%): 281 ($M^+ - 1$, 0.2), 266 (2), 135 (55), 131 (100), 116 (22), 91 (14). Anal. Calcd for $C_{18}H_{21}$-DOSi: C 76.27, H 8.18, Si 9.91. Found: C 76.40, H 8.07, Si 10.08.

Ethyl (*E*)-2-Deuterio-2-deuteroxy-4-phenylbut-3-enoate (26a). Prepared according to the procedure described for **14a**−**f**: ^{1}H NMR δ 7.42−7.24 (5H, m), 6.82 (1H, d, J = 15.9 Hz), 6.26 (1H, d, J = 15.9 Hz), 4.33 (1H, dq, J = 7.1 and 10.8 Hz), 4.27 (1H, dq, J = 7.1 and 10.8 Hz), 1.33 (3H, t, J = 7.1 Hz); IR (CH_2Cl_2) 3470, 3030, 2990, 1730, 1600, 1580, 1250, 1210, 1160, 1020, 970, 740, 700 cm^{-1}; MS m/z (%): 225 ($M^+ + NH_3$, 5), 207 (4), 190 (18), 144 (5), 135 (28), 134 (100), 116 (29), 106 (10). Anal. Calcd for $C_{12}H_{12}O_3D_2$: C 69.21, H 7.74. Found: C 69.28, H 6.95.

Ethyl (*E*)-2-Deuterio-2-ethoxy-4-phenylbut-3-enoate (26b). Prepared according to the procedure described for **14g**−**i**: ^{1}H NMR δ 7.42−7.24 (5H, m), 6.78 (1H, d, J = 16.0 Hz), 6.24 (1H, d, J = 16.0 Hz), 4.26 (1H, q, J = 7.1 Hz), 4.25 (1H, q, J = 7.1 Hz), 3.64 (1H, dq, J = 7.1 and 10.1 Hz), 3.59 (1H, dq, J = 7.0 and 10.1 Hz), 1.31 (6H, t, J = 7.0 Hz); IR (film) 2980, 1740, 1600, 1580, 1450, 1180, 1120, 1100, 970, 910, 700 cm^{-1}; MS m/z (%): 253 ($M^+ + NH_4$, 19), 236 ($M^+ + 1$, 4), 235 (M^+, 2), 207 (12), 206 (50), 190 (73), 162 (100), 134 (32), 116 (34). Anal. Calcd for $C_{14}H_{17}O_3D$: C 71.46, H 8.14. Found: C 71.56, H 7.61.

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Supporting Information Available: Spectroscopic data for compounds **6a,b**, **6d**−**h**, **6j**, **7a,b**, **7d**−**h**, **7j**, diisopropylfluorosilane, **8f**−**i**, alcohols derived from **8e**, **8j**, **8k**, **8o**, **14b**, **14d,e**, **14l**, **17a**, **17d**, **18a**, **18d**, **21a,b**, and **22** (6 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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