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Asymmetric Allylation of Methyl Ketones by Using Chiral Phenyl Carbinols

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Dedicated to Professor Hans-Ulrich Reißig on the occasion of his 60th birthday

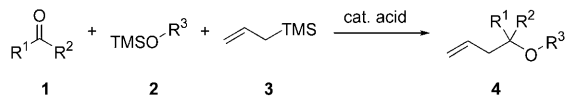
Abstract: Novel chiral auxiliaries for the stereoselective allylation of aliphatic methyl ketones with allyltrimethylsilane and their use in the synthesis of homoallylic ethers are described. In a multicomponent domino process catalyzed by trifluoromethanesulfonic acid, the allyl moiety and the auxiliary are transferred onto the substrate to yield tertiary homoallylic ethers. The most useful auxiliary for a general application turned out to be the trimethylsilyl ether of phenyl benzyl carbinol with an induced diastereoselectivity of 90:10 using ethyl methyl ketone and 94:6 using isopropyl methyl ketone as substrates. The transferred substituted benzyl moiety has good protecting properties in subsequent transformations and can easily be removed under reductive conditions to provide the corresponding homoallylic alcohol. The origin of the high selectivity could be elucidated by identifying the relevant transition states using quantum-chemical calculations. An excellent agreement between calculated and experimentally observed selectivities was obtained assuming an oxocarbenium ion as intermediate.

Keywords: allylation · auxiliary methods · density functional calculations · diastereoselectivity · domino reactions · ketones

Introduction

Allylations of carbonyl compounds are amongst the most frequently used C–C bond-forming reactions and are widely employed in the synthesis of natural products and other biologically active compounds.[1] An excellent allylation method is the multicomponent domino reaction[2] of a carbonyl compound **1** using a trimethyl silyl ether **2** and allyltrimethylsilane (**3**) in the presence of a catalytic amount of an acid to give homoallylic ethers **4** (Scheme 1).[3] Using silyl ethers **2** with one or more stereogenic centers in R^3 as auxiliaries, the reactions can be performed in a stereoselective way. Moreover, the transferred auxiliary can act as a hydroxy protecting group in subsequent transformations.[4]

Based on the natural product norpseudoephedrine (NPED), we have developed auxiliary **6** (NPED auxiliary) with which both aliphatic aldehydes and ketones can be allylated in excellent yields and selectivities.[5] Thus, even the differentiation between a methyl and an ethyl group as in butanone (**5**) is possible to give the tertiary homoallylic ether **7** in 95% yield and in a diastereomeric ratio of 90:10 at −78 °C (Scheme 2). Interestingly, there is a reversal in the induced selectivity of the allylation when going from a ketone to an aldehyde. The origin of the stereoselectivity could be elucidated for both substance classes.[6]



Scheme 1. Multicomponent reaction for the synthesis of homoallylic ethers.

Since the allylation of butanone (**5**) in the presence of the trimethyl silyl ether of 1-phenylethanol (**10a**) yielded the two possible diastereomeric products only in a <2:1 ratio, we initially assumed that the trifluoroacetamide moiety in **6** is essential for high selectivity. While the amide group does indeed directly take part in the stereoselective step of aldehyde allylations via the formation of an intermediate oxazolidinium ion,[6a] our recent theoretical studies on the allylation of butanone with **7** showed that in the case of ketones the amide moiety is simply a spectator substituent.[6b]

Though the NPED auxiliary gave a high selectivity a disadvantage of the trifluoroacetamide moiety in the product is its low stability under basic conditions, which limits the applicability of the transferred NPED group as protecting

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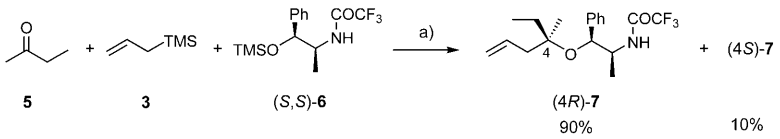


Scheme 2. Auxiliary-mediated stereoselective allylation of butanone. a) 0.2 equiv TfOH, CH_2Cl_2, −78 °C, 2 h, 95 %.

group. Thus, in the course of the total synthesis of natural products there is a need for a removal of the auxiliary in the product and a reprotection of the formed homoallylic alcohol.[7] An additional drawback of the described allylation using the NPED auxiliary is the necessity for the employment of two equivalents of the ketone to obtain yields of > 90 % (see Table 2, entry 1).

On the basis of the aforementioned calculations, we have now developed new auxiliaries of type **10** that give excellent yields and selectivities as obtained with the NPED auxiliary but in addition show excellent protecting group qualities and can be applied using only one equivalent of the ketone. Here we describe their synthesis and their employment for the allylation of butanone (**5**) and methyl ketones **13a–g**. In addition, the origin of stereoselectivity was determined with quantum-chemical methods.

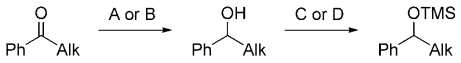
Results and Discussion

Development of the novel auxiliary: As novel auxiliaries for the stereoselective allylation of ketones we developed the phenylcarbinols **10a–10k** and tested them in the allylation of butanone.

The racemic auxiliaries were synthesized by silylation of the corresponding alcohols **9a–9k** using either chlorotrimethylsilane (TMSCl) or trimethylsilyl trifluoromethanesulfonate (TMSOTf) as silylating agents in the presence of triethylamine (Table 1). In those cases where the alcohol was not commercially available, it was obtained by reduction of the corresponding ketone **8** with sodium borohydride or, in the sterically challenging cases, with isopropyl magnesium chloride. Alcohol **9i** was synthesized by addition of phenyl magnesium chloride to diphenylacetaldehyde. Ketone **8g** was provided by reaction of 1-adamantanecarboxylic acid with two equivalents of phenyllithium, and ketone **8k** was obtained by permethylation of deoxybenzoin (**8h**) with methyl iodide in the presence of powdered potassium hydroxide and catalytic amounts of [18]crown-6.[8]

To examine the achievable level of induced selectivity with auxiliaries **10a–10k** we followed the procedure for the allylation of ketones with the NPED-auxiliary **6**, using two equivalents of butanone (**5**), two equivalents of allyltrimethylsilane (**3**) and one equivalent of the racemic silyl ether **10a–10k** in dichloromethane at −78 °C in the presence of 20 mol % trifluoromethanesulfonic acid (TfOH). The reactions with auxiliaries **10e** and **10h** were additionally performed in a 1:1:1 stoichiometric ratio of the substrates. After 15–20 h, the reactions were quenched by addition of triethylamine. The diastereomeric ratio of the products was determined from their ^{13}C NMR spectra and in some cases from their GC at achiral stationary phase; both analytic procedures gave identical results. The stereochemistry of the obtained products was exemplarily clarified for the enantiomerically pure homoallylic ethers **11a** and **11h** that were synthesized using the auxiliaries (*R*)-**10a** and (*R*)-**10h**, respectively. The alcohols that were formed by deprotection of **11a** and **11h** were compared by GC at chiral stationary phase with those that were obtained by cleavage of the NPED residue from the mixture of **7**. The stereochemistry of the remaining homoallylic ethers was assigned by comparison of their ^{13}C NMR spectra.

Table 1. Synthesis of racemic auxiliaries **10a–10k**. A) $NaBH_4$, MeOH, 0.5–2 h (TLC); B) *i*PrMgCl, toluene, 0.5 h; C) TMSCl, NEt_3, CH_2Cl_2, 24 h; D) TMSOTf, NEt_3, CH_2Cl_2, 0.5–1 h (TLC).



8 *rac*-**9** *rac*-**10**

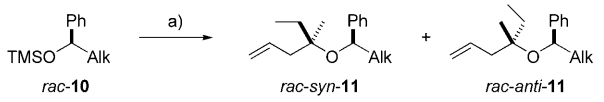
Alk	**8**	Reduction (Yield [%])	**9**	Silylation (Yield [%])	**10**
Me	–	–	**9a**	D (76)	**10a**
Et	–	–	**9b**	C (86)	**10b**
*i*Pr	–	–	**9c**	C (94)	**10c**
*n*Bu	–	–	**9d**	C (96)	**10d**
*t*Bu	–	–	**9e**	D (97)	**10e**
cHex	**8f**	A (97)	**9f**	C (91)	**10f**
adamantyl	**8g**	B	**9g**	D (44)[a]	**10g**
CH_2Ph	**8h**	A (92)	**9h**	D (94)	**10h**
$CHPh_2$	–	–	**9i**	D (96)	**10i**
CPh_3	**8j**	B (76)	**9j**	D (93)	**10j**
CMe_2Ph	**8k**	B (59)[b]	**9k**	D (97)	**10k**

[a] Yield over three steps (1-adamantanecarboxylic acid→**8g**→**9g**→**10g**). [b] Yield over two steps (**8h**→**8k**→**9k**).

The results of the allylation of butanone (**5**) using the different auxiliaries **10a–10k** to give the homoallylic ethers **11a–11k** are displayed in Table 2. Selectivity increases with increasing steric volume of the alkyl group when going from methyl (**10a**) to *tert*-butyl (**10e**). However, a further increase in size as in **10f** and **10g** leads to a decrease in selectivity. Both yield and selectivity are improved when there are one or two phenyl groups in the 1-position of the alkyl chain; on the other hand, no product was obtained when the trityl-auxiliary **10j** was used. Auxiliary **10k**, in which the two hydrogen atoms of the benzyl moiety in **10h** are replaced by methyl groups, leads to an even higher selectivity of 94:6, however at the cost of significantly reduced yield.

Replacing the phenyl moiety in the phenyl-*tert*-butyl auxiliary **10e** by a 2,6-dichlorophenyl group increases the selectivity from 87:13 to 92:8, but with diminished yield. A simi-

Table 2. Yields and selectivities of the allylation of butanone in the presence of the auxiliaries **10a**–**10k**. a) Butanone (**5**), allyltrimethylsilane (**3**), 0.2 equiv TfOH, CH_2Cl_2, −78 °C, 15–20 h.



rac-**10** *rac-syn*-**11** *rac-anti*-**11**

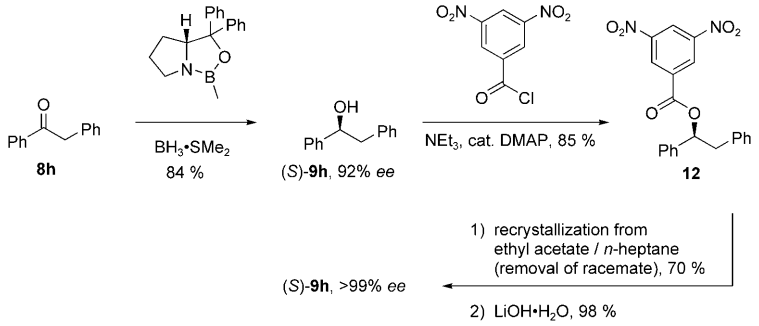
Entry	Alk	Auxiliary	Product	Yield [%][a]	Selectivity *rac-syn*-**11**/ *rac-anti*-**11**
1	NPED-Auxiliary	**6**	**7**	95 (48)	90:10
2	Me	**10a**	**11a**	56	65:35
3	Et	**10b**	**11b**	89	73:27
4	*i*Pr	**10c**	**11c**	88	80:20
5	*n*Bu	**10d**	**11d**	85	70:30
6	*t*Bu	**10e**	**11e**	84 (84)	87:13
7	*c*Hex	**10f**	**11f**	71	78:22
8	adamantyl	**10g**	**11g**	90	82:18
9	CH_2Ph	**10h**	**11h**	95 (93)	90:10
10	$CHPh_2$	**10i**	**11i**	99	91:9
11	CPh_3	**10j**	**11j**	0	–
12	CMe_2Ph	**10k**	**11k**	57	94:6

[a] Yield for butanone/allylsilane/auxiliary 2:2:1 stoichiometry. Values in parentheses: yield for 1:1:1 stoichiometry.

lar increase in selectivity from 90:10 to 92:8 was observed with the 2,6-dichlorophenyl analogue of the auxiliary **10h** which however, led to the corresponding homoallylic ether in 98% yield. Slightly decreased selectivities of 85:15 and 84:16 were obtained using the auxiliaries, where the phenyl group was replaced by a 1-naphthyl and a 3,5-dimethylphenyl group, respectively.

It is important to note that in contrast to the use of the NPED auxiliary **6**, the allylations in the presence of the auxiliaries **10**, as shown for **10e** and **10h**, give nearly the same yields regardless of whether one or two equivalents of ketone were employed. From this observation, we conclude that the necessity of using two equivalents of the ketone is specific only for the NPED-auxiliary **6**. However, so far we do not have an explanation for this unusual behavior.

Among the synthesized and tested auxiliaries of type **10**, the trimethylsilyl ether of the simple phenylbenzylcarbinol (**10h**, PBn auxiliary) is best suited for a general application in the light of its high induced diastereoselectivity and its ready availability as well as atom economy. The corresponding alcohol **9h** is commercially available in both enantiomeric forms with 98% *ee*. It can also be synthesized by CBS reduction[9] of deoxybenzoin (**8h**) in 92% *ee*, and enriched via recrystallization of the nitrobenzoate **12** to >99% *ee* (Scheme 3). The following preparation of the auxiliary **10h** from alcohol **9h** is a simple one-step procedure with almost quantitative yield. The easy accessibility of **10h** compensates for the fact that its chiral information is lost in the final removal of the group after having done its duty as protecting group.



Scheme 3. Synthesis of enantiopure alcohol (*S*)-**9h**.

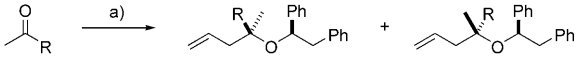
Scope of the allylation with 10h: The large scope of the allylation using the PBn-auxiliary **10h** is demonstrated by the allylation of the methylketones **13a**–**13e** where high yields and selectivities were obtained (Table 3). Thus, for the reaction of isopropyl methyl ketone (**13b**) and cyclohexyl methyl ketone (**13c**) a selectivity of even 94:6 is found. On the other hand, the method is not suitable for the facial selective allylation of sterically very demanding ketones as pinacolone **13g** and aromatic ketones like acetophenone (**13f**). Though for the latter ketone the highest selectivity with 97:3 was observed the yields are too low. Thus, our new procedure complements very well existing methods that work nicely with aromatic ketones,[10] but fail using aliphatic ketones. Moreover, the pronounced variation of reactivity of different ketones offers the possibility of a chemoselective allylation in substrates with several ketone functionalities.

Protecting-group properties of the phenylbenzyl moiety: The usefulness of the PBn moiety as protecting group was investigated for subsequent transformations of the homoallylic ether **14c**. Ozonolysis as well as hydroboration of **14c** gave the aldehyde **15** and the alcohol **16**, respectively, in excellent yields without affecting the PBn group (Scheme 4).

The cleavage of the PBn residue, for example, from **14c** to **17**, can be achieved under Birch conditions[11] (Na/liquid NH_3), or by elementary hydrogen over Pd/C, whereas the latter proceeds under concomitant hydrogenation of the double bond to give **18** (Scheme 5).

Origin of stereoselectivity: In order to rationalize the observed stereoselectivities, we computationally identified the transition states (TSs) of the stereogenic step for the allylations of butanone (**5**) with auxiliaries (*R*)-**10a** (Alk = Me), (*R*)-**10e** (Alk = *t*Bu) and (*R*)-**10h** (Alk = Bn). The proposed reaction mechanism includes the intermediate formation of oxocarbenium ion **19**, which is intercepted by the nucleophile allyltrimethylsilane (**3**), thereby forming the new stereogenic center at C-4 of **11** (Scheme 6).[12,4b]

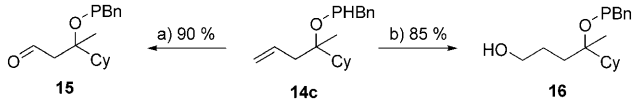
Table 3. Allylation of ketones **5** and **13a–13g** with the phenylbenzyl auxiliary (PBn auxiliary) **10h**. a) TMSO-PBn (**10h**), allyltrimethylsilane (**3**), 0.2 equiv TfOH, CH_2Cl_2, −78 °C, 15–20 h.



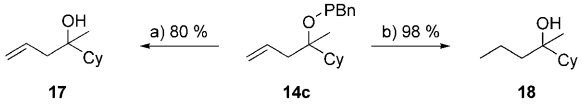
13 *rac-syn*-**14** *rac-anti*-**14**

Entry	Ketone	R	Product	Yield [%][a]	Selectivity *syn*-**14**/*anti*-**14**	$[\alpha]_D^{20}$ [°][b]
1	**5**	Et	**11h**	93	90:10	+27.8[c]
2	**13a**	*n*Pent	**14a**	93	88:12	−19.7[d]
3	**13b**	*i*Pr	**14b**	91	96:4	
4	**13c**	*c*Hex	**14c**	89	96:4	−15.5[d]
5	**13d**	CH_2Ph	**14d**	86	91:9	
6	**13e**	$(CH_2)_2Ph$	**14e**	76	86:14	−17.2[d]
7	**13f**	Ph	**14f**	9	97:3	
8	**13g**	*t*Bu	**14g**	8	72:28	

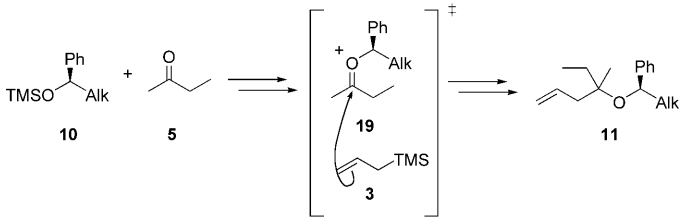
[a] Yield for ketone/allylsilane/auxiliary ratio 1:1:1. [b] Optical rotation of the mixture of diastereomers. [c] Reaction with (*R*)-**10h** (*ee* 98%). [d] Reaction with (*S*)-**10h** (*ee* >99%).



Scheme 4. Investigation of the protecting group quality of the PBn group in ozonolysis and hydroboration reactions of **14c**. a) 1) O_3, 2) PPh_3, CH_2Cl_2, −78 °C; b) 1) 9-BBN, 2) H_2O_2, NaOH, THF, RT.



Scheme 5. Cleavage of the PBn protecting group under Birch-conditions and with elementary hydrogen. a) Na/NH_3 (l), −78 °C; b) H_2, Pd/C, MeOH, RT.



Scheme 6. Stereogenic step of the allylation of butanone with phenylalkyl auxiliaries.

By analyzing all possible TS structures (48 for the allylation with **10a** or **10e**, 144 for the allylation with **10h**, see Supporting Information) we found that in each case, the selectivities can be explained solely with TSs **A1**, **A2**, **B1** and **B2** in which **19** has the *E* configuration and where the double bonds of **19** and **3** adopt an antiperiplanar orientation (Figure 1).[13] TSs **A1** and **B1** differ from TSs **A2** and **B2** in the respective position of the CH_2TMS group. In **A**-TSs, the *Si* face of **19** is attacked, leading to the *syn*-configured product (4*R*,1′*R*)-**11**, while the attack to the *Re* face of **19** in **B**-TSs gives rise to the *anti*-isomer (4*S*,1′*R*)-**11**.

In the relevant TS for the reaction with the PBn auxiliary **10h**, oxocarbenium ion **19h** adopts one of the conformations **19h-1** or **19h-2** that are displayed in Figure 2.

Table 4 lists the TS energies and the calculated selectivities. In each case, the stereochemistry of the main product is correctly predicted and furthermore, the trend of increasing selectivity in the series **10a**, **10e** and **10h** is properly reproduced. In the case of the PBn-auxiliary **10h**, the computationally calculated and experimentally determined selectivities match perfectly.

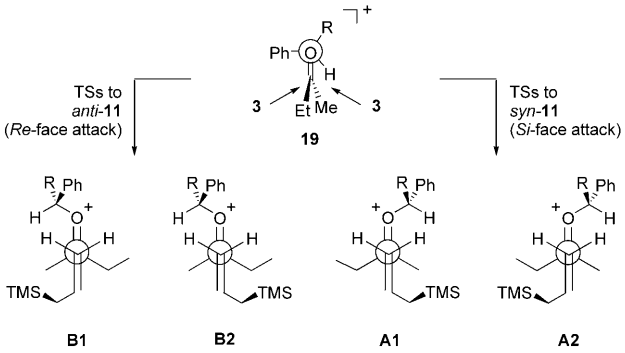


Figure 1. TSs **A1**, **A2**, **B1** and **B2**. R = Me, *t*Bu, CH_2Ph.

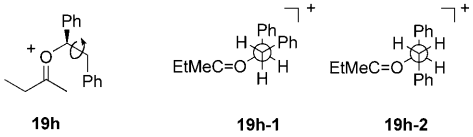


Figure 2. Conformations of **19h** in relevant TSs.

In all relevant TSs, the phenyl group in **19** is fixed in orthogonal position to the C=O$^+$ bond by a stereoelectronic effect (Figure 1). Since the attack to the *Re* face of **19** in **B**-TSs leads to a steric repulsion between **3** and the phenyl group, their energies are in general above those for the **A**-TSs, and the reaction is predicted to give the *syn* isomer preferentially.

Small alkyl substituents such as methyl in the case of **10a** that should lead to better selectivities because of less steric bulk for the **A**-TSs do however give lower selectivities. On the contrary, selectivity increases with the size of the alkyl moiety up to Alk = *t*Bu in **10e** but only then decreases with further increase in alkyl size. The calculations show that this

Table 4. Relative TS energies $\Delta\Delta G$ for the stereogenic step of the allylation of butanone with auxiliaries **10a**, **10e** and **10h**, and the therefrom calculated selectivities.

System	TS[a]	Product	$\Delta\Delta G$ [kJ mol^{-1}]	Selectivity *syn*-**11**/*anti*-**11** calcd	exptl
19a + **3** (Alk = Me)	**A1**	*syn*-**11a**	2.4	72:28	65:35
	A2	*syn*-**11a**	0.0		
	B1	*anti*-**11a**	1.5		
	B2	*anti*-**11a**	4.4		
19e + **3** (Alk = *t*Bu)	**A1**	*syn*-**11e**	4.5	79:21	87:13
	A2	*syn*-**11e**	0.0		
	B1	*anti*-**11e**	4.3		
	B2	*anti*-**11e**	2.5		
19h + **3** (Alk = CH_2Ph)	**A1-1**	*syn*-**11h**	1.6	91:9	90:10
	A1-2	*syn*-**11h**	1.8		
	A2-1	*syn*-**11h**	3.8		
	A2-2	*syn*-**11h**	0.0		
	B1-1	*anti*-**11h**	6.3		
	B1-2	*anti*-**11h**	6.0		
	B2-1	*anti*-**11h**	4.1		
	B2-2	*anti*-**11h**	5.1		

[a] The suffix **-1** and **-2** for the TSs of the system **19h** + **3** denotes the conformation of **19h** according to Figure 2.

observation cannot be traced back to TSs with *Z*-configured **19** that might potentially be easier accessible with smaller alkyl groups. We therefore assume that the **A**-TSs are stabilized by a van der Waals interaction between the alkyl group and the attacking silane **3** which increases with alkyl group size. At a certain size, steric repulsion counterbalances this effect and as a result, selectivity drops. Benzyl-substituted auxiliaries such as **10h** exhibit excellent selectivities because the van der Waals stabilization with **3** is possible without leading to unfavorable steric interactions (Figure 3).

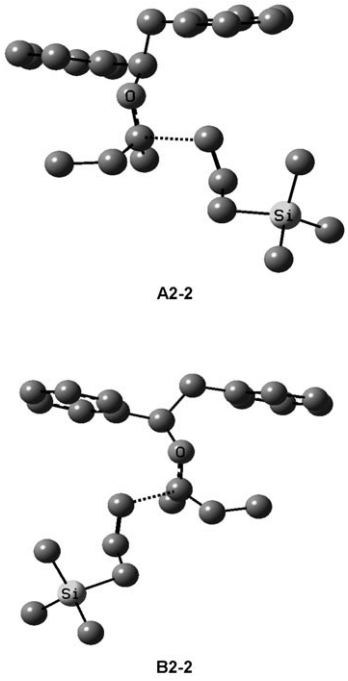


Figure 3. TS structures **A2-2** and **B2-2** for the allylation of **19h**. Hydrogen atoms are omitted for clarity.

Conclusion

Based on the results of our previous theoretical studies, we developed a new simple phenyl benzyl carbinol-based auxiliary, which is easily accessible in both enantiomeric forms and exhibits high selectivity in aliphatic methyl ketone allylations. In addition, the transferred moiety is a good protecting group and is readily cleaved under standard conditions. The origin of stereoselectivity was elucidated by quantum-chemical calculations of the relevant transition states. Excellent agreement between experimentally observed and computationally predicted selectivity was found.

Experimental Section

General methods: All reactions were performed under argon in flame-dried flasks. Solvents were used from commercial sources and stored over molecular sieves. All reagents obtained from commercial sources were used without further purification. Thin-layer chromatography (TLC) was performed on precoated silica gel SIL G/UV$_{254}$ plates (Macherey-Nagel) and silica gel 60 (0.032–0.063 mm, Merck) was used for column chromatography. Vanillin in methanolic sulfuric acid was used as staining reagents for TLC. UV spectra were taken with a Perkin-Elmer Lambda 2 spectrometer. IR spectra were recorded as KBr pellets or as films between NaCl plates with a Bruker IFS 25 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded with Mercury-200, VXR-200, Unity-300, Inova-500, Unity Inova-600 (Varian) or AMX 300 (Bruker) spectrometer. Chemical shifts are reported in ppm with tetramethylsilane (TMS) as internal standard. Multiplicities of ^{13}C NMR peaks were determined with the APT pulse sequence. Mass spectra were measured with a Finnigan MAT 95, TSQ 7000 or LCQ instrument. High resolution mass spectra (ESI-HRMS) were recorded with a Apex IV (Bruker Daltronik).

General procedure A for the reduction of ketones with $NaBH_4$: $NaBH_4$ (1.2 equiv) was added carefully to a stirred 0.3 M solution of the ketone (1 equiv) in MeOH at 0 °C. Stirring was continued for 0.5–2 h, the solvent removed under reduced pressure and the residue dissolved in Et_2O (0.3 M). The solution was washed with a saturated solution of NH_4Cl (3 mL mmol^{-1} ketone), water (3 mL mmol^{-1} ketone) and brine (3 mL mmol^{-1} ketone), and dried over Na_2SO_4. After evaporation of the solvent the crude product was purified by column chromatography on silica gel.

General procedure B for the reduction of ketones with *i*PrMgCl: To a stirred solution of isopropyl magnesium chloride (2 M solution in Et_2O, 2 equiv) in toluene (2 mL mmol^{-1} ketone), was added slowly at room temperature a 1 M solution of the ketone (1 equiv) in toluene. Stirring was continued for 0.5 h, the reaction mixture then cooled to 0 °C and crushed ice added until gas formation ceased. The formed precipitate was dissolved by adding a 2 N aqueous solution of HCl and the aqueous layer was extracted with CH_2Cl_2 (2 × 2 mL mmmol^{-1} ketone). The combined organic layers were dried over Na_2SO_4. After evaporation of the solvent, the crude product was purified by column chromatography on silica gel.

General procedure C for the silylation of alcohols with TMSCl: To a stirred 0.2 M solution of the alcohol (1 equiv) in CH_2Cl_2 and NEt_3 (2.5 equiv), TMSCl (1.2 equiv) was added dropwise at 0 °C. After stirring for 24 h at room temperature, a saturated solution of NH_4Cl was added, the layers separated and the aqueous layer extracted with CH_2Cl_2 (3 × 3 mL mmol^{-1} ketone). The combined organic layers were washed with brine and dried over Na_2SO_4. After evaporation of the solvent the crude product was purified by column chromatography on silica gel or by distillation.

General procedure D for the silylation of alcohols with TMSOTf: To a stirred 0.2 M solution of the alcohol (1 equiv) in CH_2Cl_2 and NEt_3 (5 equiv) was added dropwise TMSOTf (2.5 equiv) at 0 °C. After stirring for 0.5–2 h at room temperature, a saturated solution of NH_4Cl was added. The layers were separated and the aqueous layer extracted with CH_2Cl_2 (3×3 mL mmol^{-1} ketone). The combined organic layers were washed with brine and dried over Na_2SO_4. After evaporation of the solvent the crude product was purified by column chromatography on silica gel or by distillation.

(*R*)-Trimethyl-(1-phenylethoxy)silane (10a): According to general procedure D, (*R*)-1-phenylethanol (**9a**) (3.00 g, 24.5 mmol, 1.00 equiv) was reacted with NEt_3 (12.4 g, 17.0 mL, 123 mmol, 5.02 equiv) and TMSOTf (13.1 g, 10.7 mL, 59.0 mmol, 2.41 equiv) in CH_2Cl_2 (100 mL). Distillation of the crude product at reduced pressure afforded the title compound (3.71 g, 19.1 mmol, 76 %) as colorless liquid. B.p. 44 °C (2.0 mbar); $[\alpha]_D^{20}=+57.7°$ ($c=1$, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=0.07$ (s, 9H, TMS), 1.43 (d, $J=6.4$ Hz, 3H, 2-H), 4.85 (q, $J=6.4$ Hz, 1H, 1-H), 7.18–7.36 ppm (m, 5H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=0.08$ (TMS), 26.85 (C-2), 70.58 (C-1), 125.34, 126.82, 128.12, 146.44 ppm (Ph); IR (film): $\tilde{\nu}=$ 2959, 1493, 1450, 1370, 1251, 1207, 1098, 1034, 959, 841, 756, 699 cm^{-1}; UV (MeOH): λ_{max} (lg ε) = 204.5 (4.0075), 246.5 (2.9203), 251.5 (2.9309), 257.0 (2.9298), 263.5 (2.8745), 288.5 nm (2.9607); HRMS (ESI): *m*/*z*: calcd for $C_{11}H_{18}NaOSi$: 217.10191; found 217.10204 $[M+Na]^+$.

Trimethyl-(1-phenylpropoxy)silane (10b): According to general procedure C, *rac*-1-phenylpropanol (**9b**) (3.27 g, 24.0 mmol, 1.00 equiv) was reacted with NEt_3 (6.13 g, 8.40 mL, 60.6 mmol, 2.52 equiv) and TMSCl (3.17 g, 3.70 mL, 29.1 mmol, 1.21 equiv) in CH_2Cl_2 (105 mL). Distillation of the crude product at reduced pressure afforded the title compound (4.32 g, 20.7 mmol 86 %) as colorless liquid. B.p. 49–50 °C (1.5 mbar); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta=0.00$ (s, 9H, TMS), 0.84 (t, $J=7.4$ Hz, 3H, 3-H), 1.53–1.77 (m, 2H, 2-H$^{\alpha}$, 2-H$^{\beta}$), 4.50 (t, $J=6.4$ Hz, 1H, 1-H), 7.12–7.32 ppm (m, 5H, Ph); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta=0.09$ (TMS), 10.34 (C-3), 33.44 (C-2), 76.36 (C-1), 125.88, 126.81, 127.98, 145.40 ppm (Ph); HRMS (ESI): *m*/*z*: calcd for $C_{12}H_{20}NaOSi$: 231.11756; found 231.11765 $[M+Na]^+$.

Trimethyl-(2-methyl-1-phenylpropoxy)silane (10c): According to general procedure C, *rac*-1-phenyl-2-methylpropanol (**9c**) (3.03 g, 20.2 mmol, 1.00 equiv) was reacted with NEt_3 (5.11 g, 7.00 mL, 50.5 mmol, 2.50 equiv) and TMSCl (2.61 g, 3.05 mL, 24.0 mmol, 1.19 equiv) in CH_2Cl_2 (90 mL). Distillation of the crude product at reduced pressure afforded the title compound (4.17 g, 18.7 mmol, 94 %) as colorless liquid. B.p. 54–55 °C (1.5 mbar); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta=0.00$ (s, 9H, TMS), 0.76 (d, $J=6.9$ Hz, 3H, 3a-H), 0.91 (d, $J=6.6$ Hz, 3H, 3b-H), 1.85 (dqq, $J=6.6$, 6.6, 6.9 Hz, 1H, 2-H), 4.28 (d, $J=6.6$ Hz, 1H, 1-H), 7.15–7.35 ppm (m, 5H, Ph); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta=0.06$ (TMS), 18.12 (C-3a), 19.21 (C-3b), 36.29 (C-2), 80.37 (C-1), 126.66, 126.74, 127.70, 144.44 ppm (C-Ph); HRMS (ESI): *m*/*z*: calcd for $C_{13}H_{22}NaOSi$: 245.13321; found 245.13331 $[M+Na]^+$.

Trimethyl-(1-phenylpentoxy)silane (10d): According to general procedure C, *rac*-1-phenylpentanol (**9d**) (3.94 g, 24.0 mmol, 1.00 equiv) was reacted with NEt_3 (6.13 g, 8.40 mL, 60.6 mmol, 2.52 equiv) and TMSCl (3.17 g, 3.70 mL, 29.1 mmol, 1.21 equiv) in CH_2Cl_2 (105 mL). Distillation of the crude product at reduced pressure afforded the title compound (5.44 g, 23.0 mmol, 96 %) as colorless liquid. B.p. 66–67 °C (1.0 mbar); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta=-0.02$ (s, 9H, TMS), 0.83 (t, $J=6.9$ Hz, 3H, 5-H), 1.10–1.45 (m, 4H, 3-H, 4-H), 1.45–1.77 (m, 2H, 2-H), 4.55 (dd, $J=7.7$, 5.4 Hz, 1H, 1-H), 7.12–7.33 ppm (m, 5H, Ph); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta=0.10$ (TMS), 14.05 (C-5), 22.57 (C-4), 28.11 (C-3), 40.47 (C-2), 75.02 (C-1), 125.82, 126.80, 128.01, 145.72 ppm (Ph); HRMS (ESI): *m*/*z*: calcd for $C_{14}H_{24}NaOSi$: 259.14886; found 259.14910 $[M+Na]^+$.

Trimethyl-(2,2-dimethyl-1-phenylpropoxy)silane (10e): According to general procedure D, *rac*-1-phenyl-2,2-dimethylpropanol (**9e**) (5.12 g, 31.2 mmol, 1.00 equiv) was reacted with NEt_3 (15.5 g, 21.2 mL, 153 mmol, 4.90 equiv) and TMSOTf (16.8 g, 13.7 mL, 75.5 mmol, 2.42 equiv) in CH_2Cl_2 (150 mL). Distillation of the crude product at reduced pressure afforded the title compound (7.14 g, 30.2 mmol, 97 %) as colorless liquid. B.p. 52–54 °C (1.0 mbar); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta=0.00$ (s, 9H, TMS), 0.89 (s, 9H, 3-H), 4.30 (s, 1H, 1-H), 7.20–7.35 ppm (m, 5H, Ph); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta=-0.02$ (TMS), 26.00 (C-3), 36.02 (C-2), 82.67 (C-1), 126.64, 127.03, 127.91, 142.81 ppm (Ph); HRMS (ESI): *m*/*z*: calcd for $C_{14}H_{24}NaOSi$: 259.14886; found 259.14902 $[M+Na]^+$.

Cyclohexylphenylmethanol (9f): According to general procedure A, cyclohexyl phenyl ketone (**8f**) (3.00 g, 15.9 mmol, 1.00 equiv) was reacted with sodium borohydride (720 mg, 19.2 mmol, 1.21 equiv) in methanol (50 mL). Purification by column chromatography afforded the title compound (2.93 g, 15.4 mmol, 97 %) as colorless oil. $R_f=0.44$ (hexanes/ethyl acetate 4:1); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=0.80$–2.02 (m, 12H, *c*-Hex, OH), 4.34 (d, $J=7.2$ Hz, 1H, 1-H), 7.20–7.37 ppm (m, 5H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=25.97$ (C-3′), 26.06 (C-5′), 26.39 (C-4′), 28.80 (C-6′), 29.26 (C-2′), 44.91 (C-1′), 79.37 (C-1), 126.61, 127.38, 128.16, 143.57 ppm (Ph).

(Cyclohexylphenylmethoxy)trimethylsilane (10f): According to general procedure C, *rac*-cyclohexylphenylmethanol (**9f**) (2.85 g, 14.9 mmol, 1.00 equiv) was reacted with NEt_3 (3.94 g, 5.40 mL, 39.0 mmol, 2.62 equiv) and TMSCl (1.97 g, 2.30 mL, 18.1 mmol, 1.21 equiv) in CH_2Cl_2 (70 mL). Distillation of the crude product at reduced pressure afforded the title compound (3.55 g, 13.5 mmol, 91 %) as yellow liquid. B.p. 78 °C (0.2 mbar); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=-0.04$ (s, 9H, TMS), 0.80–2.05 (m, 11H, *c*-Hex), 4.23 (d, $J=7.0$ Hz, 1H, 1-H), 7.16–7.36 ppm (m, 5H, Ph); minor conformer (distinguishable signals): $\delta=0.14$ (s, 9H, TMS), 4.35 ppm (d, $J=7.3$ Hz, 1H, 1-H). (major/minor conformer 80:20); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=0.07$ (TMS), 26.07 (C-3′), 26.18 (C-5′), 26.52 (C-4′), 28.88 (C-6′), 29.26 (C-2′), 45.84 (C-1′), 79.84 (C-1), 126.75, 127.71, 128.18, 144.34 ppm (Ph); minor conformer (distinguishable signals): $\delta=1.32$ (TMS), 25.99 (C-3′), 26.40 (C-5′), 28.81 (C-4′), 29.29 (C-6′), 44.94 (C-1′), 79.39 (C-1), 126.62, 127.41 ppm (Ph); IR (film): $\tilde{\nu}=$ 3028, 2925, 2853, 1451, 1250, 1058, 1028, 964, 928, 903, 841, 748, 700 cm^{-1}; UV (CH_3CN): λ_{max} (lg ε) = 206.5 (3.9129), 209.0 (3.9145), 252.0 (2.2678), 258.0 (2.3347), 264.0 nm (2.2009); HRMS (EI): *m*/*z*: calcd for $C_{16}H_{26}OSi$: 262.1753; found 262.1750 $[M]^+$.

[(1′-Adamantyl)phenylmethoxy]trimethylsilane (10g): 1) Phenyllithium (20.6 mL of a 2 M solution in dibutyl ether, 41.2 mmol, 2.00 equiv) was added to a solution of adamantane 1-carboxylic acid (3.71 g, 20.6 mmol, 1.00 equiv) in Et_2O (200 mL) at 0 °C. After stirring for 1 h at room temperature, the reaction mixture was poured into a saturated solution of ammonium chloride (200 mL), and the forming precipitate was dissolved by addition of 2 M HCl solution (100 mL). The aqueous layer was extracted with Et_2O (2×100 mL). The combined organic layers were dried over sodium sulfate and the solvent was evaporated. The obtained yellow oil (**8g**) (3.60 g) was used for the next step without further purification.

2) According to general procedure B, crude **8g** was reacted with isopropyl magnesium chloride (20.6 mL of a 2 M solution in Et_2O, 41.2 mmol, 2.0 equiv) in toluene (50 mL), which afforded a yellow solid (**9g**) (3.88 g) that was used for the next step without further purification.

3) According to general procedure D, crude **9g** was reacted with NEt_3 (8.25 g, 11.3 mL, 81.5 mmol, 3.96 equiv) and TMSOTf (8.94 g, 7.30 mL, 40.2 mmol, 1.95 equiv) in CH_2Cl_2 (70 mL). Purification by column chromatography afforded the title compound (2.82 g, 8.97 mmol, 44 % over three steps) as colorless oil. $R_f=0.60$ (hexanes/ethyl acetate 10:1); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=-0.07$ (s, 9H, TMS), 1.35–1.67 (m, 12H, 2′-H, 4′-H), 1.90 (m, 3H, 3′-H), 4.05 (s, 1H, 1-H), 7.14–7.30 ppm (m, 5H, Ph); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=0.00$ (TMS), 28.43 (C-3′), 37.17 (C-4′), 37.42 (C-1′), 38.23 (C-2′), 83.27 (C-1), 126.58, 126.92, 128.06, 141.82 ppm (Ph); IR (KBr): $\tilde{\nu}=3026$, 2847, 1450, 1360, 1249, 1058, 944, 927, 841, 700, 614, 512 cm^{-1}; UV (CH_3CN): λ_{max} (lg ε) = 191.5 (4.6263), 206.0 (3.9328), 209.5 (3.9272), 252.5 (2.2529), 258.0 nm (2.3216); HRMS (EI): *m*/*z*: calcd for $C_{20}H_{30}OSi$: 314.2066; found 314.2065 $[M]^+$.

(*S*)-1,2-Diphenylethanol (9h) (92 % *ee*): To a solution of deoxybenzoin (**8h**) (1.0 g, 5.1 mmol, 1.0 equiv) and (*R*)-*Me*CBS reagent (1.0 mL of an 1 M solution in toluene, 1 mmol, 20 mol %) in CH_2Cl_2 (5 mL), $BH_3{\cdot}SMe_2$ (3.0 mL of a 2 M solution in toluene, 6.0 mmol, 1.2 equiv) was slowly added dropwise at −35 °C over 6 h. The reaction was quenched by addition of MeOH (3 mL). After warming to room temperature the solution was washed with a half-saturated solution of NH_4Cl and the aqueous layer was extracted with CH_2Cl_2 (3×15 mL). The combined organic layers were washed with a saturated solution of NH_4Cl and dried over

Na_2SO_4. Purification by column chromatography afforded the title compound (600 mg, 4.3 mmol, 84%, 92% *ee*) as colorless solid. $R_f = 0.20$ (hexanes/ethyl acetate 20:1); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.99$ (d, $J = 2.7$ Hz, 1H, OH), 3.00 (dd, $J = 13.5$, 8.2 Hz, 1H, 2-H_a), 3.07 (dd, $J = 13.5$, 5.1 Hz, 1H, 2-H_b), 4.92 (m, 1H, 1-H), 7.18–7.40 ppm (m, 10H, 10× Ph-H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 46.1$ (C-2), 75.3 (C-1), 125.9 (2× C-Ph), 126.6 (C-Ph), 127.6 (C-Ph), 128.4 (2×C-Ph), 128.5 (2×C-Ph), 129.5 (2×C-Ph), 138.0 (C-Ph), 143.8 ppm (C-Ph); MS (EI, 70 eV): *m/z* (%): 77 (24) $[Ph]^+$, 91 (29) $[Bn]^+$, 92 (100) $[Bn+H]^+$, 107 (74) $[M-Bn]^+$, 180 (23) $[M-H_2O]^+$, 198 (3) $[M]^+$; HPLC (Chiralpak IA, *n*-hexane/*i*PrOH 99:1, flow: 0.8 mL min^{-1}, load: 1 mg mL^{-1}, injection volume: 10 µL, $\lambda = 210$): $t_R = 33$ min (*R* enantiomer), 37 min (*S* enantiomer); HRMS (EI): *m/z*: calcd for $C_{14}H_{14}O$: 198.1045; found 198.1040 $[M]^+$.

(*S*)-1′,2′-Diphenylethyl-3,5-dinitrobenzoate (12): To a stirred suspension of (*S*)-1,2-diphenylethanol (**9h**, 92% *ee*) (570 mg, 2.87 mmol, 1.0 equiv), 3,5-dinitrobenzoyl chloride (820 mg, 3.56 mmol, 1.2 equiv) and DMAP (35 mg, 0.29 mmol, 10 mol%) in CH_2Cl_2 (15 mL) was added dropwise at 0°C triethylamine (0.65 mL, 4.6 mmol, 1.6 equiv). After stirring for 2 h CH_2Cl_2 (200 mL) was added. The obtained solution was washed with 1 M HCl (50 mL) and the aqueous layer was extracted with CH_2Cl_2 (3× 80 mL). The combined organic layers were washed with a saturated solution of NH_4Cl and dried over Na_2SO_4. After purification of the crude product by column chromatography (pentane/CH_2Cl_2 2:1→CH_2Cl_2), the obtained 3,5-dinitrobenzoate (966 mg, 2.46 mmol, 85%) was recrystallized from ethyl acetate/heptane. The racemate was first obtained first as colorless, rectangular crystals. The following recrystallizations yielded the title compound (680 mg, 1.73 mmol, 60% from **9h**) as thick, colorless needles. $R_f = 0.38$ (*n*-pentane/CH_2Cl_2 1:2); $[\alpha]_D^{20} = -21.0°$ ($c = 0.1$, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.27$ (dd, $J = 14.0$, 5.7 Hz, 1H, 2′-H_a), 3.40 (dd, $J = 14.0$, 8.4 Hz, 1H, 2′-H_b), 6.22 (dd, $J = 8.4$, 5.7 Hz, 1H, 1′-H), 7.15–7.42 ppm (m, 10H, 10×Ph-H), 9.07 (d, $J = 2.1$ Hz, 2H, 2-H, 6-H), 9.18 ppm (t, $J = 2.1$ Hz, 1H, 4-H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 42.8$ (C-2′), 79.6 (C-1′), 122.3 (C-Ph), 126.7 (2×C-Ph), 127.0 (C-Ph), 128.5 (2× C-Ph), 128.7 (2×C-Ph), 129.3 (2×C-Ph), 129.3 (C-2, C-6), 129.4 (C-3, C-5), 134.0 (C-Ph), 136.3 (C-1), 138.7 (C-Ph), 148.6 (C-4), 161.6 ppm (C=O); MS (DCI, 200 eV): *m/z* (%): 198 (100), 216 (55), 410 (16) $[M+NH_4]^+$.

(*S*)-1,2-Diphenylethanol (9h) (>99% *ee*): To a solution of the 3,5-dinitrobenzoate (**12**; 290 mg, 0.74 mmol, 1.0 equiv) in CH_2Cl_2 (2 mL) was added a solution of LiOH·H_2O (47 mg, 1.1 mmol, 1.5 equiv) in MeOH (10 mL) and H_2O (0.5 mL) at 0°C. After stirring at room temperature for 0.5 h, saturated NH_4Cl solution (3 mL) was added and the aqueous layer was extracted with CH_2Cl_2 (3×20 mL). The combined organic layers were washed with brine and dried over Na_2SO_4. Purification by column chromatography afforded the title compound (144 mg, 0.73 mmol, 98%, >99% *ee*) as colorless solid. $[\alpha]_D^{20} = +50.3°$ ($c = 1$, EtOH).

(*S*)-(1,2-Diphenylethoxy)trimethylsilane (10h) (>99% *ee*): According to general procedure D, (*S*)-1,2-diphenylethanol (**9h**) (590 mg, 3.0 mmol, 1.0 equiv) was reacted with NEt_3 (2.1 mL, 15 mmol, 5.0 equiv) and TMSOTf (1.4 mL, 7.5 mmol, 2.5 equiv) in CH_2Cl_2 (20 mL). Purification by column chromatography afforded the title compound (756 mg, 2.8 mmol, 93%) as colorless oil. $R_f = 0.70$ (hexanes/ethyl acetate 15:1); $[\alpha]_D^{20} = -27.0°$ ($c = 1$, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.00$ (s, 9H, TMS), 3.07 (d, $J = 6.5$ Hz, 2H, 2-H), 4.92 (t, $J = 6.5$ Hz, 1H, 1-H), 7.28–7.49 ppm (m, 10H, 2×Ph); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = -0.28$ (TMS), 47.52 (C-2), 76.40 (C-1), 125.82, 126.08, 126.99, 127.95, 128.03, 129.79, 139.04, 144.91 ppm (2×Ph); IR (film): $\tilde{\nu} = 3029$, 2956, 1495, 1454, 1251, 1092, 943, 841, 758, 698 cm^{-1}; UV (CH_3CN): λ_{max} (lg ε) = 194.0 (4.8064), 252.5 (2.5678), 258.0 (2.645), 264.0 nm (2.5313); HRMS (ESI): *m/z*: calcd for $C_{17}H_{22}NaOSi$: 293.13321; found 293.13343 $[M+Na]^+$.

1,2,2-Triphenylethane-1-ol (9i): A solution of phenyl magnesium chloride (7.60 mL of a 2 M solution in THF, 15.2 mmol, 1.49 equiv) was diluted with dry THF (20 mL) and cooled to 0°C. Diphenylacetaldehyde (2.00 g, 10.2 mmol, 1.00 equiv) was added and the reaction mixture was stirred at room temperature for 1 h. The reaction was stopped by the addition of saturated ammonium chloride solution (10 mL). Water was added (60 mL), and the mixture was extracted with CH_2Cl_2 (3×30 mL). The combined organic layers were dried over sodium sulfate and the solvent was evaporated. Purification by column chromatography afforded the title compound (1.91 g, 6.96 mmol, 68%) as colorless solid. $R_f = 0.22$ (hexanes/Et_2O 5:1); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.15$ (d, $J = 2.9$ Hz, 1H, OH), 4.25 (d, $J = 8.8$ Hz, 1H, 2-H), 5.40 (dd, $J = 8.8$, 2.9 Hz, 1H, 1-H), 7.02–7.46 ppm (m, 15H, 3×Ph); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 60.27$ (C-2), 76.78 (C-1), 126.34, 126.85, 126.91, 127.52, 128.00, 128.19, 128.56, 128.72, 128.92, 140.88, 141.52, 142.21 ppm (3×Ph); IR (KBr): $\tilde{\nu} = 3425$, 2894, 1598, 1492, 1451, 1032, 743, 698, 600 cm^{-1}; UV (CH_3CN): λ_{max} (lg ε) = 194.5 (4.8923), 523.5 (2.8007), 258.5 nm (2.8527); HRMS (EI): *m/z*: calcd for $C_{20}H_{18}O$: 274.1358; found 274.1358 $[M]^+$.

(1,2,2-Triphenyl-1-ethoxy)trimethylsilane (10i): According to general procedure D, *rac*-1,2,2-triphenyl-ethane-1-ol (**9i**) (1.50 g, 5.47 mmol, 1.00 equiv) was reacted with NEt_3 (2.99 g, 4.10 mL, 29.6 mmol, 5.41 equiv) and TMSOTf (3.19 g, 2.60 mL, 14.3 mmol, 2.62 equiv) in CH_2Cl_2 (30 mL). Purification by column chromatography afforded the title compound (1.82 g, 5.25 mmol, 96%) as slightly yellowish oil. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = -0.14$ (s, 9H, TMS), 4.22 (d, $J = 7.9$ Hz, 1H, 2-H), 5.29 (d, $J = 7.9$ Hz, 1H, 1-H), 6.94–7.45 ppm (m, 15H, 3×Ph); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = -0.10$ (TMS), 60.77 (C-2), 78.37 (C-1), 126.06, 126.10, 126.92, 127.61, 127.85, 127.99, 128.92, 129.41, 141.82, 142.08, 143.48 ppm (3×Ph); IR (film): $\tilde{\nu} = 3028$, 2957, 1494, 1452, 1251, 1069, 922, 893, 841, 748, 698 cm^{-1}; UV (CH_3CN): λ_{max} (lg ε) = 194.5 (4.8449), 253.5 (2.8899), 258.5 nm (2.9355); HRMS (ESI): *m/z*: calcd for $C_{23}H_{26}NaOSi$: 369.16451; found 369.16450 $[M+Na]^+$.

1,2,2,2-Tetraphenylethanol (9j): According to general procedure B, triphenylacetophenone (**8j**) (2.00 g, 5.74 mmol, 1.00 equiv) was reacted with isopropyl magnesium chloride (5.70 mL of a 2 M solution in Et_2O, 11.4 mmol, 1.99 equiv) in toluene (15 mL). Purification by column chromatography afforded the title compound (1.52 g, 4.34 mmol, 76%) as colorless oil. $R_f = 0.13$ (hexanes/ethyl acetate 20:1); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.18$ (brs, 1H, OH), 6.32 (s, 1H, 1-H), 6.75–7.40 ppm (m, 20H, 4×Ph); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 64.49$ (C-2), 76.73 (C-1), 126.32, 127.04, 127.37, 127.49, 129.03, 130.81, 140.81, 143.78 ppm (4×Ph).

(1,2,2,2-Tetraphenylethoxy)trimethylsilane (10j): According to general procedure D, 1,2,2,2-tetraphenylethanol (1.20 g, 3.42 mmol, 1.00 equiv) was reacted with NEt_3 (1.75 g, 2.40 mL, 17.3 mmol, 5.06 equiv) and TMSOTf (1.90 g, 1.55 mL, 8.54 mmol, 2.50 equiv) in CH_2Cl_2 (15 mL). Purification by column chromatography afforded the title compound (1.34 g, 3.17 mmol, 93%) as colorless solid. $R_f = 0.67$ (hexane/ethyl acetate 10:1); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = -0.14$ (s, 9H, TMS), 6.04 (s, 1H, 1-H), 6.67–7.23 ppm (m, 20H, 4×Ph); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 0.30$ (TMS), 64.27 (C-2), 79.27 (C-1), 125.85, 126.77, 126.89, 127.27, 130.14, 131.20, 141.45, 144.71 ppm (4×Ph); HRMS (EI): *m/z*: calcd for $C_{29}H_{30}OSi$: 422.2066; found 422.2066 $[M]^+$.

1,2-Diphenyl-2-methylpropane-1-ol (9k) 1) In a round-bottom flask equipped with a reflux condenser, a suspension of 2-phenylacetophenone (**8h**) (4.00 g, 20.4 mmol, 1.00 equiv), powdered KOH (techn. 85%, 5.40 g, 82.5 mmol, 4.04 equiv) and [18]crown-6 (10 mg, 37.8 µmol, 0.002 equiv) in toluene (8 mL) was heated to 70°C. Methyl iodide (8.80 g, 62.0 mmol, 3.03 equiv) was added and the reaction was stirred at 70°C for 3 h. Again, methyl iodide was added (8.80 g, 62.0 mmol, 3.03 equiv) and the reaction was stirred at 70°C for 15 h. After cooling to room temperature, water was added (30 mL), the layers were separated and the aqueous layer was extracted with Et_2O (2×30 mL). The combined organic phases were evaporated in vacuo to afford a yellow oil (**8k**) (4.40 g), which was used for the next step without further purification.

2) According to general procedure B, crude **8k** was reacted with isopropyl magnesium chloride (19.6 mL of a 2 M solution in Et_2O, 39.2 mmol, 1.92 equiv) in toluene (60 mL). Purification by column chromatography afforded the title compound (2.74 g, 12.1 mmol, 59% over two steps) as colorless solid. $R_f = 0.29$ (hexanes/ethyl acetate 10:1); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.28$ (s, 3H, 3a-H), 1.32 (s, 3H, 3b-H), 1.77 (brs, 1H, OH), 4.76 (s, 1H, 1-H), 7.10–7.43 ppm (m, 10H, 2×Ph); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 22.40$ (C-3a), 25.72 (C-3b), 43.15 (C-2), 82.01 (C-1), 126.28, 126.95, 127.30, 127.76, 128.09, 140.79, 146.28 ppm (2×Ph); IR (film): $\tilde{\nu} = 3454$, 2971, 1601, 1452, 1387, 1042, 771, 723, 700 cm^{-1}; UV (CH_3CN): λ_{max} (lg ε) = 192.5 (4.7093), 194.5 (4.7124), 252.0 (2.5737), 257.5 (2.6452), 264.0 nm (3.5178). MS (EI, 70 eV): *m/z* (%): 226.3 (1) $[M]^+$,

209.2 (1) $[M-OH]^+$, 149.2 (5) $[M-Ph]^+$, 120.2 (100) $[M-2Me-Ph]^+$, 119.2 (55) $[PhCMe_2]^+$, 107.1 (50) $[PhCHOH]^+$.

(1,2-Diphenyl-2-methyl-1-propoxy)trimethylsilane (10k): According to general procedure D, *rac*-1,2-diphenyl-2-methylpropane-1-ol (**9k**) (2.23 g, 9.85 mmol, 1.00 equiv) was reacted with NEt_3 (5.33 g, 7.30 mL, 52.7 mmol, 5.35 equiv) and TMSOTf (5.76 g, 4.70 mL, 25.9 mmol, 2.63 equiv) in CH_2Cl_2 (65 mL). Purification by column chromatography afforded the title compound (2.85 g, 9.54 mmol, 97%) as slightly yellowish liquid. $R_f=0.71$ (hexanes/Et_2O 10:1); ^1H NMR (300 MHz, $CDCl_3$): $\delta=-0.19$ (s, 9H, TMS), 1.22 (s, 3H, 3a-H), 1.30 (s, 3H, 3b-H), 4.59 (s, 1H, 1-H), 6.92–7.31 ppm (m, 10H, 2×Ph); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=-0.32$ (TMS), 23.74 (C-3a), 24.49 (C-3b), 43.36 (C-2), 82.73 (C-1), 125.65, 126.69, 126.73, 126.81, 127.32, 127.40, 127.89, 142.05, 147.22 ppm (2×Ph); IR (film): $\tilde{\nu}=2959$, 1699, 1603, 1497, 1452, 1384, 1363, 1251, 1068, 1031, 884, 842, 771, 699 cm^{-1}; UV (CH_3CN): λ_{max} (lg ε) = 194.0 (4.7434), 252.0 (2.5429), 258.0 (2.6196), 264.0 nm (2.4921); HRMS (ESI): *m/z*: calcd for $C_{19}H_{26}NaOSi$: 321.16451; found 321.16464 $[M+Na]^+$.

General procedure E for the allylation of methyl ketones: To a stirred 0.2 M solution of the auxiliary (1 equiv) and the ketone (1 or 2 equiv) in CH_2Cl_2 was added at −78 °C allyltrimethylsilane (1 or 2 equiv) and trifluoromethanesulfonic acid (TfOH) (20 mol%) and stirring was continued for 12 h at the same temperature. The reaction was quenched by adding NEt_3 (1.5 equiv) and the solvent was evaporated in vacuo. The residue was taken up in THF to give a 0.2 M solution, which was treated with TBAF·3H_2O (1.2 equiv) to deprotect unreacted auxiliary. The solution was stirred at room temperature for 2 h, filtered through Celite, which was washed with Et_2O (3×3 mL $mmol^{-1}$ ketone). After evaporation of the solvent, the crude product was purified by column chromatography on silica gel.

4-Methyl-4-(1′-phenyl-1′-ethoxy)hex-1-ene (11a): According to general procedure E, (*R*)-trimethyl-(1-phenylethoxy)silane (**10a**) (3.11 g, 16.0 mmol, 1.00 equiv) was reacted with butanone (**5**) (1.15 g, 16.0 mmol, 1.00 equiv), allyltrimethylsilane (**3**) (1.83 g, 16.0 mmol, 1.00 equiv) and TfOH (496 mg, 290 µL, 3.30 mmol, 0.21 equiv) in CH_2Cl_2 (80 mL). Purification by column chromatography afforded the title compound (1.96 g, 8.98 mmol, 56%) as colorless oil. $[\alpha]_D^{20}=+39.5°$ ($c=1$, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): (4*R*,1′*R*)-**11a**: $\delta=0.84$ (t, $J=7.4$ Hz, 3H, 6-H), 1.02 (s, 3H, 4-CH_3), 1.39 (d, $J=6.5$ Hz, 3H, 2′-H), 1.42–1.67 (m, 2H, 5-H), 2.22 (dd, $J=14.2$, 7.3 Hz, 1H, 3-H^α), 2.35 (dd, $J=14.2$, 7.3 Hz, 1H, 3-H^β), 4.69 (q, $J=6.4$ Hz, 1H, 1′-H), 4.95–5.15 (m, 2H, 1-H), 5.70–5.95 (m, 1H, 2-H), 7.18–7.40 ppm (m, 5H, Ph); (4*S*,1′*R*)-**11a** (distinguishable signals): $\delta=0.89$ (t, $J=7.4$ Hz, 3H, 6-H), 1.03 (s, 3H, 4-CH_3), 1.47 (d, $J=6.8$ Hz, 3H, 2′-H), 2.15–2.31 ppm (m, 2H, 3-H^α, 3-H^β); ^{13}C NMR (125 MHz, $CDCl_3$): (4*R*,1′*R*)-**11a**: $\delta=8.15$ (C-6), 23.18 (4-CH_3), 26.69 (C-2′), 31.60 (C-5), 43.33 (C-3), 69.46 (C-1′), 78.12 (C-4), 116.90 (C-1), 125.60, 126.47, 128.05, 147.59 (Ph), 134.94 ppm (C-2); (4*S*,1′*R*)-**11a** (distinguishable signals): $\delta=8.07$ (C-6), 23.57 (4-CH_3), 26.89 (C-2′), 31.07 (C-5), 43.34 (C-3), 69.39 (C-1′), 78.08 (C-4), 126.17, 128.19, 128.41, 147.58 (Ph), 134.97 ppm (C-2); IR (film): $\tilde{\nu}=1639$, 1451, 1375, 1084, 1030, 912, 760, 700 cm^{-1}; UV (CH_3CN): λ_{max} (lg ε) = 247.5 (2.2569), 252.0 (2.3391), 257.5 (2.3852), 263.0 nm (2.2477); HRMS (ESI): *m/z*: calcd for $C_{15}H_{22}NaO$: 241.15629; found 241.15639 $[M+Na]^+$.

4-Methyl-4-(1′-phenyl-1′-propoxy)hex-1-ene (11b): According to general procedure E, *rac*-trimethyl-(1-phenylpropoxy)silane (**10b**) (1.04 g, 5.00 mmol, 1.00 equiv) was reacted with butanone (**5**) (720 mg, 10.0 mmol, 2.00 equiv), allyltrimethylsilane (**3**) (1.14 g, 10.0 mmol, 2.00 equiv) and TfOH (151 mg, 88.0 µL, 1.00 mmol, 0.20 equiv) in CH_2Cl_2 (25 mL). Aqueous workup and evaporation of the solvent afforded 1.45 g crude product. 1.04 g of the crude product was reacted with TBAF·3H_2O (0.5 g) in CH_2Cl_2 (3 mL). Purification by column chromatography afforded the title compound (737 mg, 3.17 mmol, corresponds to 89%) as colorless oil. $R_f=0.70$ (hexanes/Et_2O 50:1); ^1H NMR (600 MHz, $CDCl_3$): (4,1′)-*syn*-**11b**: $\delta=0.74$ (t, $J=7.2$ Hz, 3H, 6-H), 0.80 (t, $J=7.2$ Hz, 3H, 3′-H), 0.94 (s, 4-CH_3), 1.27–1.49 (s, 2H, 5-H), 1.54–1.60 (m, 1H, 2′-H^α), 1.65–1.72 (m, 1H, 2′-H^β), 2.07–2.38 (m, 2H, 3-H), 4.34 (dd, $J=6.5$, 6.5 Hz, 1H, 1′-H), 4.86–5.06 (m, 2H, 1-H), 5.82 (dddd, $J=18.0$, 9.1, 7.4, 7.4 Hz, 1H, 2-H), 7.10–7.33 ppm (m, 5H, Ph); (4,1′)-*anti*-**11b** (distinguishable signals): $\delta=0.75$ (t, $J=7.3$ Hz, 3H, 6-H), 0.84 (t, $J=7.4$ Hz, 3H, 3′-H), 0.96 (s, 3H, 4-CH_3), 1.49–1.56 (m, 1H, 2′-H^α), 1.56–1.62 (m, 1H, 2′-H^β), 4.35 (dd, $J=6.5$, 6.5 Hz, 1H, 1′-H), 5.72 ppm (dddd, $J=17.0$, 10.3, 7.3, 7.3 Hz, 1H, 2-H); ^{13}C NMR (75 MHz, $CDCl_3$): *(4,1′)-syn-**11b***: $\delta=$ 8.16 (C-6), 10.32 (C-3′), 23.27 (4-CH_3), 31.93 (C-5), 32.88 (C-2′), 43.43 (C-3), 75.02 (C-1′), 78.00 (C-4), 116.82 (C-1), 126.41, 126.50, 127.86, 146.32 (Ph), 135.14 ppm (C-2); (4,1′)-*anti*-**11b** (distinguishable signals): $\delta=8.12$ (C-6), 10.29 (C-3′), 23.49 (4-CH_3), 31.35 (C-5), 43.67 (C-3), 74.96 (C-1′), 77.96 (C-4), 116.74 (C-1), 127.75, 127.88, 128.16, 146.28 ppm (Ph); IR (film): $\tilde{\nu}=3076$, 2969, 1639, 1493, 1453, 1377, 1052, 912, 755, 701 cm^{-1}; UV (CH_3CN): λ_{max} (lg ε) = 192.0 (4.5631), 252.5 (2.2807), 258.0 (2.3445), 264.0 nm (2.2306); HRMS (ESI): *m/z*: calcd for $C_{16}H_{24}NaO$: 255.17194; found 255.17204 $[M+Na]^+$.

4-Methyl-4-(2′-methyl-1′-phenyl-1′-propoxy)hex-1-ene (11c): According to general procedure D, *rac*-trimethyl-(2-methyl-1-phenylpropoxy)silane **10c** (1.11 g, 5.00 mmol, 1.00 equiv) was reacted with butanone (**5**) (720 mg, 10.0 mmol, 2.00 equiv), allyltrimethylsilane (**3**) (1.14 g, 10.0 mmol, 2.00 equiv) and TfOH (151 mg, 88.0 µL, 1.00 mmol, 0.20 equiv) in CH_2Cl_2 (25 mL). Aqueous workup and evaporation of the solvent afforded 1.32 g of the crude product. 781 mg of the crude product were reacted with TBAF·3H_2O (1.1 g) in Et_2O (12 mL). Purification by column chromatography afforded the title compound (640 mg, 2.60 mmol, corresponds to 88%) as colorless oil. $R_f=0.65$ (hexanes/Et_2O 50:1); ^1H NMR (300 MHz, $CDCl_3$): (4,1′)-*syn*-**11c**: $\delta=0.71$ (d, $J=6.8$ Hz, 3H, 3′a-H), 0.74 (t, $J=7.5$ Hz, 3H, 6-H), 0.90 (d, $J=6.8$ Hz, 3H, 3′b-H), 0.91 (s, 3H, 4-CH_3), 1.33 (dq, $J=3.5$, 7.5 Hz, 2H, 5-H), 1.79 (dqq, $J=6.5$, 6.8, 6.8 Hz, 1H, 2′-H), 2.25 (d, $J=7.4$ Hz, 2H, 3-H), 4.14 (d, $J=6.5$ Hz, 1H, 1′-H), 4.96–5.09 (m, 2H, 1-H), 5.84 (dddd, $J=17.7$, 9.4, 7.4, 7.4 Hz, 1H, 2-H), 7.15–7.29 ppm (m, 5H, Ph); (4,1′)-*anti*-**11c** (distinguishable signals): $\delta=0.86$ (t, $J=7.4$ Hz, 3H, 6-H), 0.94 (s, 3H, 4-CH_3), 1.49 (dq, $J=$ 3.5, 7.4 Hz, 2H, 5-H), 2.04 (d, $J=7.4$ Hz, 2H, 3-H), 4.83–4.96 (m, 2H, 1-H), 5.71 ppm (dddd, $J=16.4$, 10.4, 7.5, 7.5 Hz, 1H, 2-H); ^{13}C NMR (75 MHz, $CDCl_3$): (4,1′)-*syn*-**11c**: $\delta=8.21$ (C-6), 18.93 (C-3′b), 19.14 (C-3′a), 23.20 (4-CH_3), 32.23 (C-5), 35.84 (C-2′), 43.36 (C-3), 77.83 (C-4), 78.73 (C-1′), 116.77 (C-1), 126.42, 127.27, 127.49, 145.07 (Ph), 135.29 ppm (C-2); (4,1′)-*anti*-**11c** (distinguishable signals): $\delta=8.26$ (C-6), 19.12 (C-3′a), 31.52 (C-5), 43.96 (C-3), 77.79 (C-4), 78.67 (C-1′), 116.60 (C-1), 126.44, 127.52, 145.00 ppm (Ph); IR (film): $\tilde{\nu}=3076$, 2969, 1639, 1492, 1376, 1052, 912, 746, 702 cm^{-1}; UV (CH_3CN): λ_{max} (lg ε) = 191.5 (4.6181), 248.0 (2.1612), 252.5 (2.2506), 258.5 (2.2983), 264.5 nm (2.1421); HRMS (ESI): *m/z*: calcd for $C_{17}H_{26}NaO$: 269.18759; found 269.18772 $[M+Na]^+$.

4-Methyl-4-(1′-phenyl-1′-pentoxy)hex-1-ene (11d): According to general procedure E, *rac*-trimethyl-(1-phenylpentoxy)silane (**10d**) (1.18 g, 5.00 mmol, 1.00 equiv) was reacted with butanone (**5**) (720 mg, 10.0 mmol, 2.00 equiv), allyltrimethylsilane (**3**) (1.14 g, 10.0 mmol, 2.00 equiv) and TfOH (151 mg, 88.0 µL, 1.00 mmol, 0.20 equiv) in CH_2Cl_2 (25 mL). Aqueous workup and evaporation of the solvent afforded the crude product (1.35 g). The crude product (1.01 g) was reacted with TBAF·3H_2O (0.5 g) in CH_2Cl_2 (3 mL). Purification by column chromatography afforded the title compound (826 mg, 3.17 mmol, corresponds to 89%) as colorless oil. $R_f=0.49$ (hexanes/Et_2O 50:1); ^1H NMR (600 MHz, $CDCl_3$): (4,1′)-*syn*-**11d**: $\delta=0.75$ (t, $J=7.3$ Hz, 3H, 6-H), 0.83 (t, $J=7.3$ Hz, 3H, 5′-H), 0.93 (s, 3H, 4-CH_3), 1.06–1.76 (m, 8H, 4′-H, 3′-H, 2′-H, 5-H), 2.05–2.39 (m, 2H, 3-H), 4.41 (t, $J=6.4$ Hz, 1H, 1′-H), 4.83–5.08 (m, 2H, 1-H), 5.81 (dddd, $J=17.8$, 9.5, 7.3, 7.3 Hz, 1H, 2-H), 7.10–7.37 ppm (m, 5H, Ph); (4,1′)-*anti*-**11d** (distinguishable signals): $\delta=$ 0.81 (t, $J=7.6$ Hz, 3H, 6-H), 0.84 (t, $J=7.4$ Hz, 3H, 5′-H), 0.96 (s, 3H, 4-CH_3), 4.40 (t, $J=6.4$ Hz, 1H, 1′-H), 5.71 ppm (dddd, $J=17.1$, 10.2, 7.3, 7.3 Hz, 1H, 2-H); ^{13}C NMR (75 MHz, $CDCl_3$): (4,1′)-*syn*-**11d**: $\delta=8.15$ (C-6), 14.02 (C-5′), 22.72 (C-4′), 23.30 (4-CH_3), 28.03 (C-3′), 31.93 (C-5), 39.92 (C-2′), 43.44 (C-3), 73.86 (C-1′), 78.05 (C-4), 116.83 (C-1), 126.35, 126.49, 127.90, 146.66 (Ph), 135.12 ppm (C-2); (4,1′)-*anti*-**11d** (distinguishable signals): $\delta=23.53$ (4-CH_3), 28.01 (C-3′), 31.35 (C-5), 39.94 (C-2′), 43.68 (C-3), 73.79 (C-1′), 78.01 (C-4), 116.74 (C-1), 127.67, 12.91, 128.17, 146.63 ppm (Ph); IR (film): $\tilde{\nu}=3075$, 2934, 1639, 1454, 1376, 1053, 913, 758, 701 cm^{-1}; UV (CH_3CN): λ_{max} (lg ε) = 191.5 (4.6481), 252.5 (2.6051), 258.0 nm (2.5905); HRMS (ESI): *m/z*: calcd for $C_{18}H_{28}NaO$: 283.20324; found 283.20331 $[M+Na]^+$.

4-Methyl-4-(2′,2′-dimethyl-1′-phenyl-1′-propoxy)hex-1-ene (11e): According to general procedure E, *rac*-trimethyl-(2,2-dimethyl-1-phenylpropoxy)silane (**10e**) (500 mg, 2.11 mmol, 1.00 equiv) was reacted with butanone (**5**) (152 mg, 2.11 mmol, 1.00 equiv), allyltrimethylsilane (**3**) (241 mg, 2.11 mmol, 1.00 equiv) and TfOH (65.0 mg, 38.0 μL, 0.43 mmol, 0.20 equiv) in CH_2Cl_2 (10 mL). The crude product was reacted with TBAF·3 H_2O (333 mg, 1.10 mmol) in CH_2Cl_2 (3 mL). Purification by column chromatography afforded the title compound (458 mg, 1.76 mmol, 84%) as colorless oil. R_f = 0.40 (hexanes 100%); ^{1}H NMR (600 MHz, $CDCl_3$): (4,1′)-*syn*-**11e**: δ = 0.77 (t, J = 7.5 Hz, 3H, 6-H), 0.84 (s, 9H, 3′-H), 0.85 (s, 3H, 4-CH_3), 1.21–1.33 (m, 2H, 5-H), 2.24 (dd, J = 13.6, 7.4 Hz, 1H, 3-H$^{\alpha}$), 2.30 (dd, J = 13.6, 7.4 Hz, 1H, 3-H$^{\beta}$), 4.11 (s, 1H, 1′-H), 4.98–5.05 (m, 2H, 1-H), 5.85 (dddd, J = 16.7, 10.4, 7.4, 7.4 Hz, 1H, 2-H), 7.14–7.31 ppm (m, 5H, Ph); (4,1′)-*anti*-**11e** (distinguishable signals): δ = 0.88 (t, J = 7.5 Hz, 3H, 6-H), 0.90 (s, 3H, 4-CH_3), 1.45–1.53 (m, 2H, 5-H), 1.96 (d, J = 7.3 Hz, 2H, 3-H), 4.85–4.94 (m, 2H, 1-H), 5.70 ppm (dddd, J = 17.2, 10.2, 7.3, 7.3 Hz, 1H, 2-H); ^{13}C NMR (75 MHz, $CDCl_3$): (4,1′)-*syn*-**11e**: δ = 8.41 (C-6), 22.96 (4-CH_3), 26.69 (C-3′), 32.72 (C-5), 35.81 (C-2′), 43.18 (C-3), 77.76 (C-4), 80.93 (C-1′), 116.74 (C-1), 126.32, 126.35, 128.35, 143.92 (Ph), 135.46 ppm (C-2); (4,1′)-*anti*-**11e** (distinguishable signals): δ = 8.43 (C-6), 22.77 (4-CH_3), 31.65 (C-5), 43.35 (C-3), 77.73 (C-4), 80.87 (C-1′), 116.52 (C-1), 135.50 ppm (C-2); IR (film): $\tilde{\nu}$ = 3076, 2973, 1639, 1481, 1453, 1375, 1199, 1144, 1088, 1058, 1030, 912, 733, 704 cm^{-1}; UV (CH_3CN): λ_{max} (lg ε) = 191.5 (4.6489), 253.0 (2.1985), 258.5 (2.2787), 264.5 nm (2.1355); HRMS (ESI): m/z: calcd for $C_{18}H_{28}NaO$: 283.20324; found 283.20347 [M+Na]$^+$.

4-Methyl-4-(1′-cyclohexyl-1′-phenylmethoxy)hex-1-ene (11f): According to general procedure E, *rac*-(cyclohexylphenylmethoxy)trimethylsilane (**10f**) (393 mg, 1.50 mmol, 1.00 equiv) was reacted with butanone (**5**) (216 mg, 3.00 mmol, 2.00 equiv), allyltrimethylsilane (**3**) (343 mg, 3.00 mmol, 2.00 equiv) and TfOH (44.5 mg, 26.0 μL, 0.30 mmol, 0.20 equiv) in CH_2Cl_2 (8 mL). Aqueous workup and evaporation of the solvent afforded the crude product (395 mg). The crude product (164 mg) was reacted with TBAF·3 H_2O (0.2 g) in CH_2Cl_2 (3 mL). Purification by column chromatography afforded the title compound (127 mg, 0.44 mmol, corresponds to 71%) as colorless oil. R_f = 0.66 (hexanes/Et_2O 50:1); ^{1}H NMR (600 MHz, $CDCl_3$): (4,1′)-*syn*-**11f**: δ = 0.80 (t, J = 7.5 Hz, 3H, 6-H), 0.96 (s, 3H, 4-CH_3), 1.06–2.08 (m, 11H, *c*-Hex), 2.30 (d, J = 7.3 Hz, 2H, 3-H), 4.20 (d, J = 7.1 Hz, 1′ H), 5.05–5.12 (m, 2H, 1-H), 5.89 (dddd, J = 16.7, 10.8, 7.3, 7.3 Hz, 1H, 2-H), 7.04–7.47 ppm (m, 5H, Ph); (4,1′)-*anti*-**11f** (distinguishable signals): δ = 0.92 (t, J = 7.4 Hz, 3H, 6-H), 1.00 (s, 3H, 4-CH_3), 2.10 (d, J = 7.4 Hz, 2H, 3-H), 4.95–5.00 (m, 2H, 1-H), 5.76 ppm (dddd, J = 16.7, 10.3, 7.4, 7.4 Hz, 1H, 2-H); ^{13}C NMR (75 MHz, $CDCl_3$): (4,1′)-*syn*-**11f**: δ = 8.20 (C-6), 23.25 (4-CH_3), 26.32 (C-3″), 26.60 (C-5″), 29.49 (C-4″), 29.69 (C-2″), 29.71 (C-6″), 32.24 (C-5), 43.43 (C-3), 45.50 (C-1″), 77.88 (C-4), 78.38 (C-1′), 116.77 (C-1), 126.40, 127.30, 127.52, 145.29 ppm (Ph); (4,1′)-*anti*-**11f** (distinguishable signals): δ = 26.49 (C-5″), 26.53 (C-3″), 29.46 (C-4″), 31.57 (C-5), 43.98 (C-3), 45.53 (C-1″), 77.85 (C-4), 78.32 (C-1′), 116.58 (C-1), 125.78, 126.43, 127.55, 145.23 ppm (Ph); IR (film): $\tilde{\nu}$ = 3075, 2925, 2852, 1639, 1451, 1375, 1147, 1052, 912, 759, 702 cm^{-1}; UV (CH_3CN): λ_{max} (lg ε) = 192.0 (4.6359), 248.0 (2.3179), 253.0 (2.4011), 258.5 (2.4392), 264.5 nm (2.3274); HRMS (ESI): m/z: calcd for $C_{20}H_{30}NaO$: 309.21889; found 309.21900 [M+Na]$^+$.

4-Methyl-4-[1′-(1″-adamantyl)-1′-phenylmethoxy]hex-1-ene (11g): According to general procedure E, *rac*-[(1′-adamantyl)phenylmethoxy]trimethylsilane (**10g**) (472 mg, 1.50 mmol, 1.00 equiv) was reacted with butanone (**5**) (216 mg, 3.00 mmol, 2.00 equiv), allyltrimethylsilane (**3**) (343 mg, 3.00 mmol, 2.00 equiv) and TfOH (44.5 mg, 26.0 μL, 0.30 mmol, 0.20 equiv) in CH_2Cl_2 (8 mL). Aqueous workup and evaporation of the solvent afforded 559 mg crude product. 299 mg of the crude product was reacted with TBAF·3 H_2O (0.3 g) in CH_2Cl_2 (3 mL). Purification by column chromatography afforded the title compound (245 mg, 0.72 mmol, corresponds to 90%) as colorless oil. R_f = 0.70 (hexanes/Et_2O 50:1); ^{1}H NMR (300 MHz, $CDCl_3$): (4,1′)-*syn*-**11g**: δ = 0.76 (t, J = 7.5 Hz, 3H, 6-H), 0.82 (s, 3H, 4-CH_3), 1.25 (q, J = 7.5 Hz, 1H, 5-H$^{\alpha}$), 1.26 (q, J = 7.5 Hz, 1H, 5-H$^{\beta}$), 1.33–1.68 (m, 12H, 2″-H, 4″-H), 2.18–2.34 (m, 2H, 3-H), 3.92 (s, 1H, 1′-H), 4.97–5.08 (m, 2H, 1-H), 5.85 (dddd, J = 16.1, 10.6, 7.6, 7.6 Hz, 1H, 2-H), 6.80–7.60 ppm (m, 5H, Ph); (4,1′)-*anti*-**11g** (distinguishable signals): δ = 0.86 (t, J = 7.5 Hz, 3H, 6-H), 0.88 (s, 3H, 4-CH_3), 1.92–1.98 (m, 2H, 3-H), 4.82–4.95 (m, 2H, 1-H), 5.73 ppm (dddd, J = 16.6, 10.4, 7.4, 7.4 Hz, 1H, 2-H); ^{13}C NMR (75 MHz, $CDCl_3$): (4,1′)-*syn*-**11g**: δ = 8.42 (C-6), 22.99 (4-CH_3), 28.51 (C-3″), 32.72 (C-5), 37.18 (C-4″), 37.28 (C-1″), 38.82 (C-2″), 43.21 (C-3), 77.61 (C-1′), 81.69 (C-4), 116.72 (C-1), 126.28, 127.03, 128.62, 142.91 ppm (Ph); (4,1′)-*anti*-**11g** (distinguishable signals): δ = 135.50 (C-2), 8.48 (C-6), 22.79 (4-CH_3), 31.69 (C-5), 44.35 (C-3), 81.63 (C-4), 116.48 (C-1), 126.32, 126.61, 128.42 ppm (Ph). IR (film): $\tilde{\nu}$ = 2904, 2848, 1639, 1451, 1375, 1086, 1053, 911, 704 cm^{-1}; UV (CH_3CN): λ_{max} (lg ε) = 191.5 (4.7137), 247.5 (2.5908), 253.0 (2.6033), 258.5 (2.6124), 265.0 nm (2.5071); HRMS (ESI): m/z: calcd for $C_{24}H_{34}NaO$: 361.25019; found 361.25012 [M+Na]$^+$.

4-Methyl-4-(1,2-diphenylethoxy)hex-1-ene (11h): According to general procedure E, *rac*-(1,2-diphenylethoxy)-trimethylsilane (**10h**) (270 mg, 1.00 mmol, 1.00 equiv) was reacted with butanone (**5**) (72.2 mg, 1.00 mmol, 1.00 equiv), allyltrimethylsilane (**3**) (114 mg, 1.00 mmol, 1.00 equiv) and TfOH (30.1 mg, 18.0 μL, 0.21 mmol, 0.21 equiv) in CH_2Cl_2 (4 mL). Aqueous workup and evaporation of the solvent afforded the crude product (309 mg). The crude product (260 mg) was reacted with TBAF·3 H_2O (0.3 g) in CH_2Cl_2 (4 mL). Purification by column chromatography afforded the title compound (231 mg, 0.78 mmol, corresponds to 93%) as colorless oil. R_f = 0.64 (hexanes/Et_2O 5:1); $[\alpha]_D^{20}$ = +27.8° (c = 1, $CHCl_3$, when using (*R*)-**10h**); ^{1}H NMR (300 MHz, $CDCl_3$): (4,1′)-*syn*-**11g**: δ = 0.72 (t, J = 7.4 Hz, 3H, 6-H), 0.79 (s, 3H, 4-CH_3), 1.34 (q, J = 7.3 Hz, 1H, 5-H$^{\alpha}$), 1.35 (q, J = 7.6 Hz, 1H, 5-H$^{\beta}$), 2.01 (d, J = 7.2 Hz, 2H, 3-H), 2.82 (dd, J = 13.1, 5.8 Hz, 1H, 2′-H$^{\alpha}$), 2.96 (dd, J = 13.1, 7.5 Hz, 1H, 2′-H$^{\beta}$), 4.62 (dd, J = 7.5, 5.8 Hz, 1H, 1′-H), 4.90–5.00 (m, 2H, 1-H), 5.67 (dddd, J = 16.2, 11.2, 7.2, 7.2 Hz, 1H, 2-H), 6.97–7.36 ppm (m, 10H, 2×Ph); (4,1′)-*anti*-**11g** (distinguishable signals): δ = 0.73 (t, J = 7.4 Hz, 3H, 6-H), 5.66 ppm (dddd, J = 17.3, 10.2, 7.2, 7.2 Hz, 1H, 2-H); ^{13}C NMR (125 MHz, $CDCl_3$): (4,1′)-*syn*-**11g**: δ = 8.11 (C-6), 23.02 (4-CH_3), 31.90 (C-5), 43.05 (C-3), 47.03 (C-2′), 75.44 (C-1′), 78.30 (C-4), 116.68 (C-1), 125.98, 126.38, 126.67, 127.80, 127.86, 130.01, 138.89, 145.79 (2×Ph), 135.07 ppm (C-2); (4,1′)-*anti*-**11g** (distinguishable signals): 7.97 (C-6), 23.14 (4-CH_3), 31.20 (C-5), 43.58 (C-3), 47.07 (C-2′), 75.40 (C-1′), 78.26 (C-4), 116.68 (C-1), 135.04 (C-2), 127.88, 145.76 ppm (Ph); IR (film): $\tilde{\nu}$ = 3028, 2969, 1639, 1495, 1454, 1377, 1060, 912, 758, 699 cm^{-1}; UV (CH_3CN): λ_{max} (lg ε) = 253.0 (2.551), 258.5 (2.6297), 264.0 nm (2.5119); HRMS (ESI): m/z: calcd for $C_{21}H_{26}NaO$: 317.18759; found 317.18789 [M+Na]$^+$.

4-Methyl-4-(1,2,2-triphenylethoxy)hex-1-ene (11i): According to general procedure E, *rac*-(1,2,2-triphenyl-1-ethoxy)trimethylsilane (**10i**) (693 mg, 2.00 mmol, 1.00 equiv) was reacted with butanone (**5**) (288 mg, 4.00 mmol, 2.00 equiv), allyltrimethylsilane (**3**) (456 mg, 4.00 mmol, 2.00 equiv) and TfOH (61.6 mg, 36.0 μL, 0.41 mmol, 0.20 equiv) in CH_2Cl_2 (8 mL). Aqueous workup and evaporation of the solvent afforded the crude product (797 mg). The crude product (722 mg) was reacted with TBAF·3 H_2O (0.5 g) in CH_2Cl_2 (3 mL). Purification by column chromatography afforded the title compound (671 mg, 1.81 mmol, corresponds to 99%) as colorless oil. R_f = 0.63 (hexanes/Et_2O 5:1); ^{1}H NMR (300 MHz, $CDCl_3$): (4,1′)-*syn*-**11i**: δ = 0.75 (t, J = 7.3 Hz, 3H, 6-H), 0.87 (s, 3H, 4-CH_3), 1.27–1.47 (m, 2H, 5-H), 2.03 (dd, J = 13.9, 7.2 Hz, 1H, 3-H$^{\alpha}$), 2.18 (dd, J = 13.9, 7.4 Hz, 1H, 3-H$^{\beta}$), 4.31 (d, J = 7.8 Hz, 1H, 2′-H), 4.93–5.08 (m, 2H, 1-H), 5.26 (d, J = 7.8 Hz, 1H, 1′-H), 5.60 (dddd, J = 18.0, 9.3, 7.4, 7.2 Hz, 1H, 2-H), 7.17–7.79 ppm (m, 15H, 3×Ph); (4,1′)-*anti*-**11i** (distinguishable signals): δ = 4.36 (d, J = 8.0 Hz, 1H, 2′-H), 5.27 (d, J = 8.0 Hz, 1H, 1′-H), 5.49 ppm (dddd, J = 16.6, 10.4, 7.4, 7.4 Hz, 1H, 2-H); ^{13}C NMR (125 MHz, $CDCl_3$): (4,1′)-*syn*-**11i**: δ = 8.08 (C-6), 22.93 (4-CH_3), 32.29 (C-5), 42.91 (C-3), 61.15 (C-2′), 77.89 (C-1′), 78.61 (C-4), 116.42 (C-1), 126.01, 126.15, 126.58, 127.43, 127.46, 127.82, 127.90, 129.16, 129.74, 141.82, 141.98, 144.48 (3×Ph), 135.19 ppm (C-2); (4,1′)-*anti*-**11i** (distinguishable signals): δ = 7.87 (C-6), 22.77 (4-CH_3), 31.36 (C-5), 44.06 (C-3), 60.77 (C-2′), 77.86 (C-1′), 78.55 (C-4), 116.49 (C-1), 126.06, 126.10, 126.61, 126.92, 127.61, 127.85, 127.98, 128.91, 129.41, 141.84, 144.44 (3×Ph), 135.14 ppm (C-2); IR (film): $\tilde{\nu}$ = 3028, 2971, 2935, 1600, 1494, 1452, 1376, 913, 754, 699 cm^{-1}; UV (CH_3CN): λ_{max} (lg ε) = 194.5 (4.901), 220.5 (4.2386), 254.5 (2.7928), 259.5 nm (2.8514); HRMS (ESI): m/z: calcd for $C_{27}H_{30}NaO$: 393.21889; found 393.21907 [M+Na]$^+$.

4-Methyl-4-(1,2-diphenyl-2-methyl-1-propoxy)hex-1-ene (11k): According to general procedure E, *rac*-(1,2-diphenyl-2-methyl-1-propoxy)trimethylsilane (**10k**) (299 mg, 1.00 mmol, 1.00 equiv) was reacted with butanone (**5**) (144 mg, 2.00 mmol, 2.00 equiv), allyltrimethylsilane (**3**) (228 mg, 2.00 mmol, 2.00 equiv) and TfOH (30.8 mg, 18.0 μL, 0.21 mmol, 0.21 equiv) in CH_2Cl_2 (4 mL). Aqueous workup and evaporation of the solvent afforded the crude product (331 mg). The crude product (231 mg) was reacted with TBAF·$3H_2O$ (0.3 g) in CH_2Cl_2 (3 mL). Purification by column chromatography afforded the title compound (127 mg, 0.39 mmol, corresponds to 57%) as colorless oil. R_f = 0.72 (hexanes/Et_2O 5:1); ^{1}H NMR (300 MHz, $CDCl_3$): (4,1′)-*syn*-**11k**: δ = 0.66 (s, 3H, 4-CH_3), 0.70 (t, J = 7.4 Hz, 3H, 6-H), 1.18 (q, J = 7.4 Hz, 2H, 5-H), 1.21 (s, 3H, 3a′-H), 1.32 (s, 3H, 3b′-H), 1.93 (dd, J = 13.6, 7.0 Hz, 1H, 3-H$^{\alpha}$), 2.10 (dd, J = 13.6, 7.6 Hz, 1H, 3-H$^{\beta}$), 4.43 (s, 1H, 1′-H), 4.89–5.00 (m, 2H, 1-H), 5.70 (dddd, J = 16.0, 11.2, 7.6, 7.0 Hz, H, 2-H), 6.88–7.40 ppm (m, 10H, 2×Ph); (4,1′)-*anti*-**11k** (distinguishable signals): δ = 0.68 (s, 3H, 4-CH_3), 0.77 (t, J = 7.4 Hz, 3H, 6-H), 1.25 (s, 3H, 3a′-H), 1.34 (s, 3H, 3b′-H), 4.78–4.89 (m, 2H, 1-H), 5.64 ppm (dddd, J = 16.9, 10.3, 7.3, 7.3 Hz, 1H, 2-H); ^{13}C NMR (125 MHz, $CDCl_3$): (4,1′)-*syn*-**11k**: δ = 8.38 (C-6), 22.93 (4-CH_3), 24.28 (C-3a′), 25.42 (C-3b′), 32.52 (C-5), 42.91 (C-3), 43.17 (C-2′), 78.12 (C-4), 81.40 (C-1′), 116.60 (C-1), 125.64, 126.40, 126.68, 127.28, 127.57, 128.42, 143.07, 147.49 (2×Ph), 135.35 ppm (C-2); (4,1′)-*anti*-**11k** (distinguishable signals): δ = 8.30 (C-6), 22.77 (4-CH_3), 24.35 (C-3a′), 26.91 (C-3b′), 31.47 (C-5), 44.09 (C-3), 78.09 (C-4), 81.33 (C-1′), 116.53 (C-1), 126.44, 127.37 ppm (C-Ph); IR (film): $\tilde{\nu}$ = 2971, 1639, 1453, 1382, 1056, 912, 772, 700 cm^{-1}; UV (CH_3CN): λ_{max} (lg ε) = 194.0 (4.7922), 253.0 (2.5924), 258.5 (2.6501), 264.0 nm (2.5191); HRMS (ESI): m/z: calcd for $C_{23}H_{30}NaO$: 345.21889; found 345.21885 $[M+Na]^+$.

4-(1,2-Diphenylethoxy)-4-methylnon-1-ene (14a): According to general procedure E, (*S*)-(1,2-diphenyl-ethoxy)trimethylsilane (**10h**) (76 mg, 0.29 mmol, 1.0 equiv), 2-heptanone (**13a**) (42 μL, 0.29 mmol 1.0 equiv) and allyltrimethylsilane (**3**) (50 μL, 0.29 mmol, 1.0 equiv) was reacted with TfOH (6 μL, 0.06 mmol, 20 mol%) in CH_2Cl_2 (2 mL). Purification by column chromatography afforded the title compound (82 mg, 0.24 mmol, 85% [with 1.0 mmol *rac*-**10h**: 93%]) as colorless oil. R_f = 0.32 (pentane/Et_2O 100:1); $[\alpha]_D^{20}$ = −19.7° (c = 1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.82 (s, 3H, 4-CH_3), 0.85 (t, J = 7.0 Hz, 3H, 9-H_3), 0.94–1.36 (m, 8H, 5-H_2, 6-H_2, 7-H_2, 8-H_2), 2.09 (d, J = 7.2 Hz, 2H, 3-H_2), 2.85 (dd, J = 13.3, 5.8 Hz, 1H, 2′-H_a), 3.01 (dd, J = 13.3, 7.6 Hz, 1H, 2′-H_b), 4.63 (dd, J = 7.6, 5.8 Hz, 1H, 1′-H), 4.97 (br d, J = 16 Hz, 1H, 1-H_a), 4.98 (br d, J = 11 Hz, 1H, 1-H_b), 5.68 (ddt, J = 16, 11, 7.2 Hz, 1H, 2-H), 7.10 (dd, J = 7.8, 1.8 Hz, 2H, 2×Ph-H), 7.16–7.31 ppm (m, 8H, 8×Ph-H); ^{13}C NMR (125 MHz, $CDCl_3$): (4,1′)-*syn*-**14a**: δ = 14.02 (C-9), 22.58 (C-8), 23.20 (C-7), 23.66 (4-CH_3), 32.29 (C-6), 39.31 (C-5), 43.49 (C-3), 47.01 (C-2′), 75.51 (C-1′), 78.11 (C-4), 116.69 (C-1), 125.97 (C-Ph), 126.43 (2×C-Ph), 126.68 (C-Ph), 127.80 (2×C-Ph), 127.85 (2×C-Ph), 130.00 (2×C-Ph), 135.10 (C-2), 138.91 (C_{quart}-Ph), 145.71 ppm (C_{quart}-Ph); (4,1′)-*anti*-**14a** (distinguishable signals): δ = 14.07 (C-9), 23.13 (C-7), 23.61 (4-CH_3), 32.40 (C-6), 38.67 (C-5), 44.21 (C-3), 47.09 (C-2′), 75.47 (C-1′), 78.09 (C-4), 126.39 (2×C-Ph), 127.88 (2×C-Ph), 138.95 (C_{quart}-Ph), 145.76 ppm (C_{quart}-Ph); IR (film): $\tilde{\nu}$ = 3064, 3028, 2933, 2860, 1639, 1603, 1495, 1454, 1376, 1315, 1146, 1057, 998, 912, 757, 699 cm^{-1}; UV (CH_3CN): λ_{max} (lg ε) = 253.0 (2.4705), 258.5 (2.5577), 264.0 nm (2.4238); MS (DCI, 200 eV): m/z (%): 139 (27), 156 (100), 173 (19), 198 (13), 216 (7), 336 (16), 354 (65) $[M+NH_4]^+$.

4-(1,2-Diphenylethoxy)-4,5-dimethylhex-1-ene (14b): According to general procedure E, *rac*-(1,2-diphenyl-ethoxy)-trimethylsilane (**10h**) (270 mg, 1.0 mmol, 1.0 equiv), 3-methyl-2-butanone (**13b**) (110 μL, 1.0 mmol 1.0 equiv) and allyltrimethylsilane (**3**) (160 μL, 1.0 mmol, 1.0 equiv) was reacted with TfOH (18 μL, 0.2 mmol, 20 mol%) in CH_2Cl_2 (4 mL). Purification by column chromatography afforded the title compound (265 mg, 0.91 mmol, 91%) as colorless oil. R_f = 0.35 (hexanes/ethyl acetate 100:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.77 (s, 3H, 4-CH_3), 0.84 (d, J = 6.8 Hz, 3H, 1×CH(CH_3)$_2$), 0.95 (d, J = 6.8 Hz, 3H, 1×CH(CH_3)$_2$), 1.75 (sep, J = 6.8 Hz, 1H, CH(CH_3)$_2$), 2.13 (m, 2H, 3-H_2), 2.88 (dd, J = 13.1, 6.0 Hz, 1H, 2′-H_a), 3.03 (dd, J = 13.1, 7.3 Hz, 1H, 2′-H_b), 4.68 (dd, J = 7.3, 6.0 Hz, 1H, 1′-H), 4.99 (br d, J = 11 Hz, 1H, 1-H_a), 5.00 (br d, J = 16 Hz, 1H, 1-H_b), 5.66 (ddt, J = 16, 11, 7.2 Hz, 1H, 2-H), 7.08 (dd, J = 7.8, 1.8 Hz, 2H, 2×Ph-H), 7.16–7.33 ppm (m, 8H, 8×Ph-H); ^{13}C NMR (125 MHz, $CDCl_3$): *syn*-**14b**: δ = 17.18 (1×CH(CH_3)$_2$), 17.25 (1×CH(CH_3)$_2$), 20.89 (4-CH_3), 35.07 (CH(CH_3)$_2$), 40.49 (C-3), 47.00 (C-2′), 75.44 (C-1′), 80.09 (C-4), 116.51 (C-1), 125.98 (C-Ph), 126.49 (2×C-Ph), 126.64 (C-Ph), 127.80 (2×C-Ph), 127.81 (2×C-Ph), 130.04 (2×C-Ph), 135.00 (C-2), 138.75 (C_{quart}-Ph), 145.83 ppm (C_{quart}-Ph); *anti*-**14b** (distinguishable signals): δ = 17.21 (2×CH(CH_3)$_2$), 20.29 (4-CH_3), 34.97 (CH(CH_3)$_2$), 41.90 (C-3), 47.13 (C-2′), 79.97 (C-4), 126.69 (C-Ph), 127.87 ppm (2×C-Ph); IR (film): $\tilde{\nu}$ = 3064, 3028, 2974, 1638, 1603, 1495, 1453, 1375, 1146, 1059, 912, 758, 700 cm^{-1}; UV (CH_3CN): λ_{max} (lg ε) = 248.0 (2.4154), 253.0 (2.5463), 258.5 (2.6275), 264.0 nm (2.5123); MS (DCI, 200 eV): m/z (%): 111 (42), 128 (100), 145 (27), 198 (27), 216 (18), 308 (14), 326 (35) $[M+NH_4]^+$.

4-(1,2-Diphenylethoxy)-4-cyclohexylpent-1-ene (14c): According to general procedure E, *rac*-(1,2-diphenylethoxy)trimethylsilane (**10h**) (1.35 g, 5.0 mmol, 1.0 equiv), cyclohexyl methyl ketone (**13c**) (0.69 mL, 5.0 mmol 1.0 equiv) and allyltrimethylsilane (**3**) (0.8 mL, 5.0 mmol, 1.0 equiv) was reacted with TfOH (90 μL, 1.0 mmol, 20 mol%) in CH_2Cl_2 (20 mL). Purification by column chromatography afforded the title compound (1.56 g, 4.45 mmol, 89%) as colorless oil. R_f = 0.39 (hexanes/ethyl acetate 100:1); $[\alpha]_D^{20}$ = − 15.5° (c = 1, $CHCl_3$, when (*S*)-**10h** was used); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.75 (s, 3H, 5-H_3), 0.92–1.41 (m, 6H, 6×Cy-H), 1.54–1.92 (m, 5H, 5×Cy-H), 2.09 (br dd, J = 14.2, 7.0 Hz, 1H, 3-H_a), 2.13 (br dd, J = 14.2, 7.0 Hz, 1H, 3-H_b), 2.84 (dd, J = 13.2, 6.0 Hz, 1H, 2′-H_a), 3.01 (dd, J = 13.2, 7.2 Hz, 1H, 2′-H_b), 4.64 (t, J = 6.6 Hz, 1H, 1′-H), 4.91–5.01 (m, 2H, 1-H_2), 5.55–5.72 (m, 1H, 2-H), 7.05 (dd, J = 7.8, 1.8 Hz, 2H, 2×Ph-H), 7.16–7.27 ppm (m, 8H, 8×Ph-H); ^{13}C NMR (125 MHz, $CDCl_3$): *syn*-**14c**: δ = 21.51 (C-5), 26.68 (1×C-Cy), 26.72 (1×C-Cy), 26.92 (1×C-Cy), 27.02 (1×C-Cy), 27.19 (1×C-Cy), 40.45 (C-3), 45.51 (1×C-Cy), 46.94 (C-2′), 75.42 (C-1′), 79.92 (C-4), 116.42 (C-1), 125.94 (C-Ph), 126.51 (2×C-Ph), 126.60 (C-Ph), 127.78 (4×C-Ph), 130.00 (2×C-Ph), 135.05 (C-2), 138.76 (C_{quart}-Ph), 145.79 ppm (C_{quart}-Ph); *anti*-**14c** (distinguishable signals): δ = 20.74 (C-5), 26.97 (1×C-Cy), 27.08 (1×C-Cy), 45.44 (1×C-Cy), 47.12 (C-2′), 79.86 (C-4), 126.47 (2×C-Ph), 127.84 ppm (4×C-Ph); IR (film): $\tilde{\nu}$ = 3064, 3028, 2926, 2852, 1638, 1603, 1495, 1453, 1377, 1150, 1059, 911, 758, 699 cm^{-1}; UV (CH_3CN): λ_{max} (lg ε) = 253.0 (2.5624), 258.5 (2.6376), 264.5 nm (2.5246); MS (DCI, 200 eV): m/z (%): 151 (55), 168 (100), 198 (13), 216 (24), 348 (20), 366 (100) $[M+NH_4]^+$.

4-(1,2-Diphenylethoxy)-4-methyl-5-phenylpent-1-ene (14d): According to general procedure E, *rac*-(1,2-diphenyl-ethoxy)-trimethylsilane (**10h**) (270 mg, 1.0 mmol, 1.0 equiv), phenyl acetone (**13d**) (130 μL, 1.0 mmol 1.0 equiv) and allyltrimethylsilane (**3**; 160 μL, 1.0 mmol, 1.0 equiv) was reacted with TfOH 18 μL, 0.2 mmol, 20 mol%) in CH_2Cl_2 (4 mL). Purification by column chromatography afforded the title compound (317 mg, 0.89 mmol, 89%) as colorless oil. R_f = 0.36 (pentane/Et_2O 100:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (s, 3H, 4-CH_3), 2.14 (dd, J = 14.2, 6.9 Hz, 1H, 3-H_a), 2.23 (dd, J = 14.2, 7.4 Hz, 1H, 3-H_b), 2.74 (d, J = 13.1 Hz, 1H, 5-H_a), 2.84 (d, J = 13.1 Hz, 1H, 5-H_b), 2.97 (dd, J = 13.1, 5.4 Hz, 1H, 2′-H_a), 3.09 (dd, J = 13.1, 7.8 Hz, 1H, 2′-H_b), 4.83 (dd, J = 7.8, 5.4 Hz, 1H, 1′-H), 5.10 (br d, J = 17 Hz, 1H, 1-H_a), 5.16 (br d, J = 10 Hz, 1H, 1-H_b), 5.88 (ddt, J = 17, 10, 7.2 Hz, 1H, 2-H), 7.18 (br dd, J = 7.8, 2.0 Hz, 2H, 2×Ph-H), 7.22–7.43 ppm (m, 13H, 13×Ph-H); ^{13}C NMR (125 MHz, $CDCl_3$): *syn*-**14d**: δ = 23.31 (4-CH_3), 42.83 (C-3), 46.51 (C-5), 46.97 (C-2′), 75.65 (C-1′), 78.23 (C-4), 117.22 (C-1), 125.90 (C-Ph), 125.99 (C-Ph), 126.19 (2×C-Ph), 126.62 (C-Ph), 127.54 (2×C-Ph), 127.77 (2×C-Ph), 127.83 (2×C-Ph), 130.04 (2×C-Ph), 130.98 (2×C-Ph), 134.90 (C-2), 138.21 (C_{quart}-Ph), 138.72 (C_{quart}-Ph), 145.63 ppm (C_{quart}-Ph); *anti*-**14d** (distinguishable signals): δ = 22.47 (4-CH_3), 44.11 (C-3), 45.92 (C-5), 47.03 (C-2′), 75.75 (C-1′), 78.29 (C-4), 117.27 (C-1), 125.92 (C-Ph), 126.06 (C-Ph), 126.25 (2×C-Ph), 126.72 (C-Ph), 127.62 (2×C-Ph), 127.93 (2×C-Ph), 128.02 (2×C-Ph), 129.99 (2×C-Ph), 130.95 (2×C-Ph), 134.85 (C-2), 138.30 (C_{quart}-Ph), 138.75 (C_{quart}-Ph), 145.58 ppm (C_{quart}-Ph); IR (film): $\tilde{\nu}$ = 3062, 3028, 2975, 2919, 1638, 1603, 1494, 1453, 1377, 1265, 1150, 1060, 913, 757, 699 cm^{-1}; UV (CH_3CN): λ_{max} (lg ε) = 252.5 (2.8026), 258.5 (2.8601), 264.0 nm (2.7500); MS (DCI, 200 eV): m/z (%): 176 (18), 194 (16), 198 (11), 339 (13), 356 (20), 374 (100) $[M+NH_4]^+$.

4-(1,2-Diphenylethoxy)-4-methyl-6-phenylhex-1-ene (14e): According to general procedure E, (*S*)-(1,2-diphenyl-ethoxy)-trimethylsilane (**10h**) (118 mg, 0.43 mmol, 1.0 equiv), benzyl acetone (**13e**) (66 μL, 0.43 mmol 1.0 equiv) and allyltrimethylsilane (**3**; 75 μL, 0.43 mmol, 1.0 equiv) was

reacted with TfOH (8 μL, 0.09 mmol, 20 mol %) in CH_2Cl_2 (3 mL). Purification by column chromatography afforded the title compound (116 mg, 0.31 mmol, 72 % [with 1.0 mmol *rac*-**10h**: 76 %]) as colorless oil. R_f = 0.30 (pentane/Et_2O 100:1); $[\alpha]_D^{20} = -17.2°$ (c = 1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (s, 3H, 4-CH_3), 1.56–1.67 (m, 2H, 5-H_2), 2.13 (dd, J = 13.7, 7.4 Hz, 1H, 3-H_a), 2.18 (dd, J = 13.7, 7.4 Hz, 1H, 3-H_b), 2.39–2.69 (m, 2H, 6-H_2), 2.88 (dd, J = 13.2, 5.6 Hz, 1H, 2′-H_a), 3.01 (dd, J = 13.2, 7.8 Hz, 1H, 2′-H_b), 4.68 (dd, J = 7.8, 5.6 Hz, 1H, 1′-H), 4.97–5.06 (m, 2H, 1-H_2), 5.69 (ddt, J = 17.6, 9.5, 7.4 Hz, 1H, 2-H), 6.96 (br d, J = 7.8 Hz, 2H, 2 × Ph-H), 7.10–7.35 ppm (m, 13H, 13 × Ph-H); ^{13}C NMR (125 MHz, $CDCl_3$): (4,1′)-*syn*-**14e**: δ = 23.74 (4-CH_3), 29.93 (C-6), 41.58 (C-5), 43.48 (C-3), 47.07 (C-2′), 75.61 (C-1′), 77.75 (C-4), 117.17 (C-1), 125.45 (C-Ph), 126.06 (C-Ph), 126.47 (2 × C-Ph), 126.87 (C-Ph), 127.85 (2 × C-Ph), 128.03 (2 × C-Ph), 128.15 (2 × C-Ph), 128.25 (2 × C-Ph), 130.03 (2 × C-Ph), 134.70 (C-2), 138.81 (C_{quart}-Ph), 142.96 (C_{quart}-Ph), 145.54 ppm (C_{quart}-Ph); (4,1′)-*anti*-**14e** (distinguishable signals): δ = 23.54 (4-CH_3), 29.83 (C-6), 40.87 (C-5), 44.26 (C-3), 47.14 (C-2′), 77.78 (C-4), 125.50 (C-Ph), 126.39 (C-Ph), 126.84 (C-Ph), 128.00 (2 × C-Ph), 128.20 (2 × C-Ph), 138.86 (C_{quart}-Ph), 142.99 (C_{quart}-Ph), 145.59 ppm (C_{quart}-Ph); IR (film): $\tilde{\nu}$ = 3063, 3027, 2933, 1639, 1603, 1495, 1454, 1377, 1152, 1060, 914, 758, 699 cm^{-1}; UV (CH_3CN): λ_{max} (lg ε) = 253.0 (2.7377), 258.5 (2.8189), 263.5 (2.7129), 267.5 nm (2.6378); MS (DCI, 200 eV): m/z (%): 190 (100), 198 (26), 353 (21), 370 (25), 388 (72) $[M+NH_4]^+$.

4-(1,2-Diphenylethoxy)-4-phenyl-pent-1-ene (14f): According to general procedure E, *rac*-(1,2-diphenyl-ethoxy)-trimethylsilane (**10h**) (270 mg, 1.0 mmol, 1.0 equiv), acetophenone (**13f**) (120 μL, 1.0 mmol 1.0 equiv) and allyltrimethylsilane (**3**) (160 μL, 1.0 mmol, 1.0 equiv) was reacted with TfOH (18 μL, 0.2 mmol, 20 mol %) in CH_2Cl_2 (4 mL). Purification by column chromatography afforded the title compound (32 mg, 0.09 mmol, 9 %) as colorless oil. R_f = 0.19 (pentane/Et_2O 100:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.50 (s, 3H, 5-H_3), 2.65 (d, J = 7.2 Hz,2H, 3-H_2), 3.03 (dd, J = 13.2, 6.7 Hz, 1H, 2′-H_a), 3.11 (dd, J = 13.2, 6.6 Hz, 1H, 2′-H_b), 4.58 (t, J = 6.6 Hz, 1H, 1′-H), 5.04 (br d, J = 10.4 Hz, 1H, 1-H_a), 5.05 (br d, J = 17.0 Hz, 1H, 1-H_b), 5.61 (ddt, J = 17.0, 10.4, 7.2 Hz, 1H, 2-H), 7.08 (br dd, J = 7.5, 1.8 Hz, 2H, 2 × Ph-H), 7.16 (br dd, J = 7.5, 1.8 Hz, 2H, 2 × Ph-H), 7.24–7.44 ppm (2 × m, 11H, 11 × Ph-H); ^{13}C NMR (125 MHz, $CDCl_3$): *syn*-**14f**: δ = 24.75 (C-5), 46.38 (C-2′), 46.41 (C-3), 76.87 (C-1′), 79.64 (C-4), 117.15 (C-1), 125.98 (C-Ph), 126.61 (C-Ph), 126.65 (2 × C-Ph), 126.68 (2 × C-Ph), 126.70 (C-Ph), 127.51 (2 × C-Ph), 127.64 (2 × C-Ph), 127.80 (2 × C-Ph), 129.95 (2 × C-Ph), 134.57 (C-2), 138.41 (C_{quart}-Ph), 144.41 (C_{quart}-Ph), 144.71 ppm (C_{quart}-Ph); *anti*-**14f** (distinguishable signals): δ = 46.60 (C-3/C-2′), 117.34 (C-1), 125.92 (2 × C-Ph), 126.40 (C-Ph), 126.54 (2 × C-Ph), 126.80 (C-Ph), 127.44 (2 × C-Ph), 127.86 (2 × C-Ph), 130.03 (2 × C-Ph), 134.42 ppm (C-2); IR (film): $\tilde{\nu}$ = 3062, 3028, 2978, 2926, 1639, 1603, 1495, 1453, 1375, 1288, 1152, 1071, 914, 759, 699 cm^{-1}; UV (CH_3CN): λ_{max} (lg ε) = 252.5 (2.7523), 258.0 (2.8252), 264.0 nm (2.7265); MS (DCI, 200 eV): m/z (%): 145 (100), 162 (19), 360 (59) $[M+NH_4]^+$.

4-(1,2-Diphenylethoxy)-4,5,5-trimethyl-hex-1-ene (14g): According to general procedure E, *rac*-(1,2-diphenyl-ethoxy)-trimethylsilane (**10h**) (270 mg, 1.0 mmol, 1.0 equiv), 3,3-dimethyl-2-butanone (**13g**) (130 μL, 1.0 mmol 1.0 equiv) and allyltrimethylsilane (**3**) (160 μL, 1.0 mmol, 1.0 equiv) was reacted with TfOH (18 μL, 0.2 mmol, 20 mol %) in CH_2Cl_2 (4 mL). Purification by column chromatography afforded the title compound (25 mg, 0.08 mmol, 8 %) as colorless oil. R_f = 0.50 (pentane/Et_2O 100:1); ^{1}H NMR (300 MHz, $CDCl_3$): *syn*-**14g**: δ = 0.80 (s, 3H, 4-CH_3), 0.93 (s, 9H, C(CH_3)$_3$), 2.10 (br dd, J = 15.0, 7.5 Hz, 1H, 3-H_a), 2.17 (br dd, J = 15.0, 7.3 Hz, 1H, 3-H_b), 2.81 (dd, J = 13.2, 5.8 Hz, 1H, 2′-H_a), 2.98 (dd, J = 13.2, 7.3 Hz, 1H, 2′-H_b), 4.74 (dd, J = 7.3, 5.8 Hz, 1H, 1′-H), 4.89–5.02 (m, 2H, 1-H_2), 5.80 (ddt, J = 16.8, 10.5, 7.4 Hz, 1H, 2-H), 7.00–7.31 ppm (m, 10H, 10 × Ph-H); *anti*-**14g** (distinguishable signals): δ = 2.43 (m, 2H, 3-H_2), 5.67 ppm (ddt, J = 17.2, 10.0, 7.2 Hz, 1H, 2-H); ^{13}C NMR (75 MHz, $CDCl_3$): *syn*-**14g**: δ = 18.90 (4-CH_3), 26.10 (C(CH_3)$_3$), 39.19 (*C*(CH_3)$_3$), 40.56 (C-3), 47.08 (C-2′), 76.10 (C-1′), 81.85 (C-4), 115.98 (C-1), 125.97 (C-Ph), 126.48 (2 × C-Ph), 126.52 (C-Ph), 127.75 (2 × C-Ph), 127.77 (2 × C-Ph), 130.11 (2 × C-Ph), 137.11 (C-2), 138.82 (C_{quart}-Ph), 146.10 ppm (C_{quart}-Ph); *anti*-**14g** (distinguishable signals): δ = 39.82 (*C*(CH_3)$_3$), 42.77 (C-3), 47.69 (C-2′), 116.19 (C-1), 125.79 (C-Ph), 126.09 (2 × C-Ph), 128.03 (2 × C-Ph), 128.15 (2 × C-Ph), 129.17 (2 × C-Ph), 136.77 (C-2), 140.42 (C_{quart}-Ph), 144.40 ppm (C_{quart}-Ph); IR (film): $\tilde{\nu}$ = 3063, 3028, 2957, 1637, 1603, 1495, 1454, 1376, 1362, 1150, 1104, 1063, 912, 758, 699 cm^{-1}; UV (CH_3CN): λ_{max} (lg ε) = 252.5 (2.8771), 258.5 (2.9180), 264.0 (2.8588), 268.0 nm (2.8095); MS (DCI, 200 eV): m/z (%): 125 (20), 142 (100), 159 (19), 198 (3), 216 (5), 322 (1), 340 (5) $[M+NH_4]^+$.

3-Cyclohexyl-3-(1,2-diphenylethoxy)butanal (15): In a 100 mL-flask, a solution of *rac*-**14c** (520 mg, 1.5 mmol, 1.0 equiv) in CH_2Cl_2 (50 mL) was purged with nitrogen, and then ozone was bubbled through the solution at −78 °C until the mixture remained pale blue (≈5 min). To remove excess ozone, the solution was purged with nitrogen. After complete discoloring, triphenylphosphine (547 mg, 2.1 mmol, 1.4 equiv) was added to the solution at −78 °C and then the solution was stirred at −78 °C to room temperature for 8 h. After evaporation of the solvent, the crude product was purified by column chromatography on silica gel (pentane/Et_2O 20:1). The title compound (470 mg, 1.3 mmol, 90 %) was obtained as a colorless oil. R_f = 0.20 (pentane/Et_2O 20:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (s, 3H, 4-H_3), 0.77–1.38 (m, 6H, 6 × Cy-H), 1.56 (br d, J = 8.5, 3 Hz, 2H, 2 × Cy-H), 1.75 (br t, J = 10 Hz, 1H, Cy-H), 2.87 (dd, J = 13.3, 5.2 Hz, 1H, 2-H_a), 2.96 (dd, J = 13.3, 8.4 Hz, 1H, 2-H_b), 4.66 (dd, J = 8.4, 5.2 Hz, 1H, 1′-H), 7.13 ppm (br dd, J = 7.8, 1.8 Hz, 2H, 2 × Ph-H), 7.17–7.33 (m, 8H, 8 × Ph-H), 9.30 (t, J = 3.0 Hz, 1H, 1-H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 22.0 (C-4), 26.3 (C-Cy), 26.4 (C-Cy), 26.7 (C-Cy), 27.3 (C-Cy), 27.5 (C-Cy), 46.6 (C-2), 46.7 (C-Cy), 2′ (C-2′), 76.3 (C-1′), 80.0 (C-3), 126.3 (C-Ph), 126.4 (2 × C-Ph), 127.0 (C-Ph), 128.1 (2 × C-Ph), 128.1 (2 × C-Ph), 129.8 (2 × C-Ph), 138.6 (C_{quart}-Ph), 145.1 (C_{quart}-Ph), 203.6 ppm (C-1); MS (ESI): m/z = 373.4 $[M+Na]^+$.

4-Cyclohexyl-4-(1,2-diphenylethoxy)pentan-1-ol (16): To a stirred solution of *rac*-**14c** (350 mg, 1.0 mmol, 1 equiv) in THF (5 mL), 9-BBN (5 mL of a 0.5 M solution in THF, 3.0 mmol, 3 equiv) was added dropwise at 0 °C. After stirring for 10 h at room temperature, H_2O_2 (1.5 mL of a 30 % solution, 15 mmol, 15 equiv) and NaOH (1.5 mL of a 3 N solution, 4.5 mmol, 4.5 equiv) were added at 0 °C. The solution was stirred for another 12 h and then half of solvent was removed under reduced pressure. CH_2Cl_2 (10 mL) and a saturated solution of NH_4Cl (10 mL) were added and the aqueous layer was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic layers were washed with brine and dried over Na_2SO_4. Purification by column chromatography afforded the title compound (312 mg, 0.85 mmol, 85 %) as colorless oil. R_f = 0.12 (CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.71 (s, 3H, 5-H_3), 0.80–1.35 and 1.38–1.87 (2 × m, 15H, 15 × Cy-H, 2-H_2, 3-H_2), 2.80 (dd, J = 13.2, 5.7 Hz, 1H, 2′-H_a), 2.94 (dd, J = 13.2, 7.7 Hz, 1H, 2′-H_b), 3.33 (dd, J = 11.5, 6 Hz, 1H, 1-H_a), 3.38 (dd, J = 11.5, 6 Hz, 1H, 1-H_b), 4.57 (dd, J = 7.7, 5.7 Hz, 1H, 1′-H), 7.07 (br dd, J = 7.8, 1.8 Hz, 2H, 2 × Ph-H), 7.14–7.25 ppm (m, 8H, 8 × Ph-H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.5 (C-5), 26.3 (C-Cy), 26.7 (C-Cy), 27.0 (C-Cy), 27.2 (C-Cy), 27.5 (C-Cy), 31.6 (C-3), 34.7 (C-2), 45.1 (C-Cy), 47.0 (C-2′), 63.4 (C-1), 75.6 (C-1′), 80.4 (C-4), 125.9 (C-Ph), 126.5 (2 × C-Ph), 126.7 (C-Ph), 127.9 (2 × C-Ph), 127.9 (2 × C-Ph), 130.1 (2 × C-Ph), 139.3 (C_{quart}-Ph), 145.9 ppm (C_{quart}-Ph); MS (DCI, 200 eV): m/z (%): 367 (7) $[M+H]^+$, 384 (26) $[M+NH_4]^+$.

(*R*)-2-Cyclohexyl-pent-4-en-2-ol (17): A solution of (4*R*,1′*S*)-**14c** (80 mg, 0.23 mmol, 1.0 equiv) in dry Et_2O (1 mL) was added to liquid ammonia (30 mL) at −78 °C. Sodium (≈24 mg, 1.0 mmol, 4.3 equiv) was added in small portions until the mixture remained deep blue. After stirring for 1 h, the reaction was quenched by addition of MeOH (2 mL). The solution was allowed to warm to room temperature over 2–3 h. To the solution Et_2O (50 mL) and a half saturated solution of NH_4Cl (25 mL) was added and the aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were washed with brine and dried over Na_2SO_4. After purification by column chromatography on silica gel (pentane/Et_2O 20:1) the title compound (28 mg, 0.17 mmol, 75 %) [using 0.29 mmol *rac*-**14c** as substrate: 80 % yield]) was obtained as a colorless oil. R_f = 0.10 (pentane/Et_2O 20:1); $[\alpha]_D^{20} = -1.8°$ (c = 1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.80–1.47 (m, 6H, 6 × Cy-H), 1.10 (s, 3H, 1-H_3), 1.57–1.93 (m, 5H, 5 × Cy-H), 2.20 (br dd, J = 13.8, 7.5 Hz, 1H, 3-H_a), 2.27 (br dd, J = 13.8, 7.5 Hz, 1H, 3-H_b), 5.07–5.19 (m, 2H, 5-H_2), 5.89 ppm (ddt, J = 17, 10, 7.5 Hz, 1H, 4-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.7 (C-1), 26.5 (C-Cy), 26.7 (C-Cy), 26.7 (C-Cy), 26.8 (C-Cy), 27.6 (C-Cy), 44.2 (C-3), 47.4 (C-Cy), 73.9 (C-2), 118.6 (C-5), 134.1 ppm (C-4); MS (DCI, 200 eV): m/z

(%): 168 (18) $[M-H_2O+NH_4]^+$, 186 (100) $[M+NH_4]^+$, 203 (18) $[M+NH_3+NH_4]^+$, 336 (23) $[2\times M-H_2O+NH_4]^+$, 354 (19) $[2\times M+NH_4]^+$.

2-Cyclohexyl-pentan-2-ol (18): A solution of *rac*-**14c** (351 mg, 1.01 mmol, 1.0 equiv) in MeOH (5 mL) was hydrogenated using 10% palladium on charcoal (11 mg, 10 μmol, 1 mol%) as catalyst under a hydrogen atmosphere (balloon) at room temperature. After stirring the solution for 18 h, the mixture was filtered and the residue was washed with CH_2Cl_2 (3× 20 mL). The combined organic layers were evaporated under reduced pressure (600 mbar, 40 °C). The crude product was purified by column chromatography on silica gel (pentane/Et_2O 20:1) to obtain the title compound (165 mg, 0.99 mmol, 98%) as colorless oil. $R_f=0.21$ (pentane/Et_2O 20:1); ^1H NMR (300 MHz, $CDCl_3$): $\delta=0.89$ (t, $J=6.8$ Hz, 3H, 5-H_3), 1.05 (s, 3H, 1-H_3), 1.15 (s, 1H, OH), 0.92–1.44 and 1.58–1.84 ppm (2×m, 15H, 11×Cy-H, 2-H_2, 3-H_2); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=15.0$ (C-5), 16.7 (C-4), 24.2 (C-1), 26.8 (C-Cy), 27.0 (C-Cy), 27.1 (C-Cy), 27.1 (C-Cy), 27.8 (C-Cy), 42.3 (C-3), 47.5 (C-Cy), 74.7 ppm (C-2); MS (DCI, 200 eV): *m/z* (%): 170 (100) $[M-H_2O+NH_4]^+$, 188 (9) $[M+NH_4]^+$.

Computational details: All calculations were performed with the Gaussian 03 program package.[14] TS geometries and energies for the stereogenic step were calculated at the B3LYP/6-31+G(d)/PCM/UAKS level of theory[15] with CH_2Cl_2 as solvent at $T=195$ K. Our previous theoretical studies on related systems showed that the effect of the solvent need to be included already for the geometry optimization. The nature of the TSs was validated by inspection of the eigenvalues of the Hessian matrices obtained by frequency calculation at the same level of theory. Employing transition-state theory, we calculated the relative rate constants k_{rel} for every TS. Addition of the rate constants k_{rel} of all TSs leading to each of the possible stereoisomers gave overall rate constants the ratio of which corresponds to the predicted ratio of product isomers. In this respect, only TSs with a relative energy to the lowest-energy TS ($\Delta\Delta G$) of not more than 6 kJ mol^{-1} (in the following, termed "relevant TSs") will contribute to product formation with more than 2% in the limiting case of only one lower-energy TS. In each of the three studied systems, there are more than only one lower-energy TSs; consequently, higher-energy TSs can be neglected without any loss of accuracy.

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[13] This limitation neglects TSs that contribute to 25% of product formation in the case of **8a** and to 5% product formation in the case of **8h**. The calculated selectivities change only slightly: For **8a**, considering all relevant TSs leads to a predicted selectivity of 70:30 (in contrast to 72:28 when considering only TSs **A1**, **A2**, **B1** and **B2**). In the case of **8h**, a selectivity of 90:10 is predicted (instead of 91:9) when all relevant TSs are included. For details, see Supporting Information.
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