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Diastereoselective Nucleophilic Addition to Aldehydes with Polar α- and α,β-Substituents

Tessie Borg,[a] Jakob Danielsson,[a] Maziar Mohiti,[a] Per Restorp,[a] and Peter Somfai[a,b,*]

[a] KTH Chemical Science and Engineering, Organic Chemistry, Royal Institute of Technology, S-100 44 Stockholm, Sweden
Fax: (+46)-8-791-2333; e-mail: somfai@kth.se
[b] Institute of Technology, University of Tartu, Nooruse 1, 504 41 Tartu, Estonia

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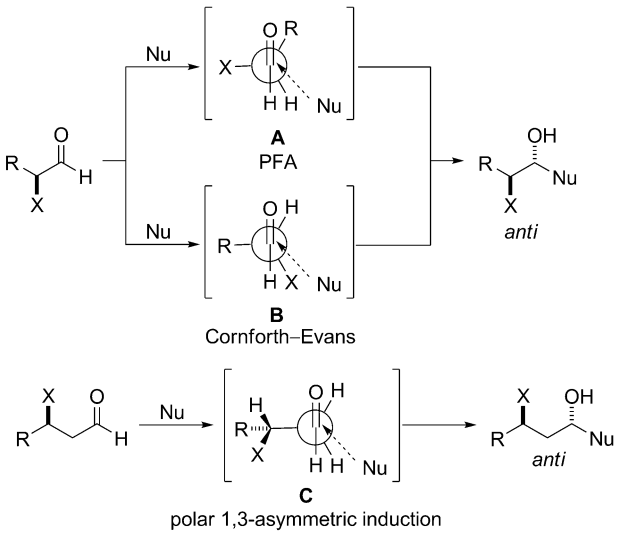
Abstract: The stereoselectivities obtained in Lewis acid-promoted Mukaiyama aldol additions and Sakurai allylations of mono-, and *syn*- and *anti*-disubstituted aldehydes possessing various polar α- and β-substituents under non-chelating conditions are presented. The stereochemical outcome in the nucleophilic addition to α-substituted aldehydes containing an α-benzyloxy, α-fluoro or α-sulfonamide substituent are accurately predicted by current stereoinduction models. In contrast, the selectivitites obtained from addition of sterically demanding nucleophiles to α-chloro-substituted aldehydes cannot be rationalized by the same models and an alternative is discussed. The stereochemichal outcome in the additions to α,β-disubstituted aldehydes is more complex and cannot be predicted using current models.

Keywords: aldol reaction; allylation; diastereoselectivity; induction model

Introduction

Nucleophilic addition to chiral carbonyl compounds is an important tool for stereoselective C–C bond formation,[1] and the aldol reaction is an integral part of the arsenal of reactions for the total synthesis of natural products.[2] In these reactions the addition to the diastereotopic π-faces of a C=O moiety give rise to stereoisomeric products. Thus an integral aspect of these reactions is the ability to predict and control the stereochemical outcome, which is of great importance for the design and synthesis of complex molecules. Consequently, much work has been expended on developing models that accurately predict the π-facial selectivities for this type of reaction.[3] For additions to α-substituted aldehydes under non-chelation controlled conditions the Felkin–Anh model, in which torsional strain and hyperconjugation are important controlling elements and govern the conformation of the transition state, has been used with great success.[4] Application of these criteria to aldehydes having an α-heteroatom substituent results in structure **A** (Scheme 1) having a staggered conformation where the best vicinal acceptor is oriented antiperiplanar to the forming σ-bond. It can be seen that the polar Felkin–Anh (PFA) model predicts the formation of the *anti* product and this is in accord with experimental observations.[5]

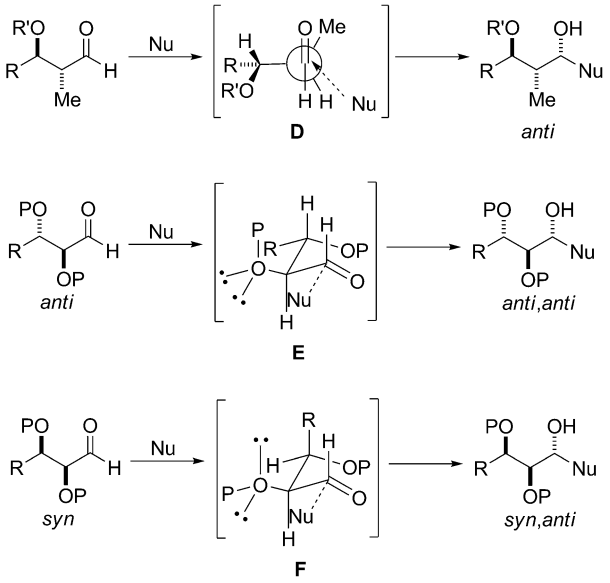


Scheme 1. The polar Felkin–Anh (**A**) and Cornforth–Evans (**B**) models for the addition to α-heteroatom substituted aldehydes, and the polar 1,3-asymmetric induction model (**C**).

Recently the validity of the PFA model was questioned by Evans and co-workers who showed that the stereochemical outcome in the addition of *E* and *Z* boron enolates to α-alkoxy aldehydes was best rationalized by the modified Cornforth model (**B**) (Cornforth–Evans).[6,7] Structure **B** is based on the assumption that, in addition to having a staggered conformation, minimization of dipole interactions is an important transition state control element. Hence, the C–X bond in **B** is almost antiparallel to the carbonyl group. A recent computational study supports the importance of the Cornforth–Evans model in the addition of enol boranes to α-heteroatom-substituted aldehydes having electronegative substituents (X = F, OMe, Cl), while those having less electronegative substituents (X = NMe_2, SMe, PMe_2) favor the PFA reaction manifold.[8]

In contrast, no general models have been advanced for the prediction of the stereochemical outcome in nucleophilic additions to β-substituted aldehydes in the absence of chelation. However, Evans has proposed that for the particular case when the β-substituent is a polar heteroatom moiety (OR, Cl) structure **C**, in which steric and electrostatic effects are minimized, accounts for the observed *anti* selectivity in the $BF_3{\cdot}OEt_2$-mediated addition of enolsilanes to these substrates.[9]

The considerably more complex task of rationalizing the stereochemical outcome in the addition of nucleophiles to α,β-disubstituted aldehydes has been addressed by the Evans group for α-alkyl-β-alkoxy substrates. Superficially, it can be expected that the relative stereochemistry of the major product can be predicted by analyzing the individual directing effects of the α- and β-stereocenters, respectively. In this scenario one stereoisomer of the aldehyde will have a matched combination of the α- and β-stereocenters, which will mutually reinforce the formation of a particular stereoisomeric product, while the other combination will be mismatched. Indeed, Mukaiyama aldol additions to *anti*-α-methyl-β-alkoxy aldehydes, where both stereodirecting elements promote addition to the same diastereotopic C=O π-face, afforded the products in high selectivity, and transition state (TS) conformation **D** was suggested (Scheme 2).[9b] As can be seen in structure **D**, both the α- (Felkin–Anh) and β-stereocenters (polar 1,3-asymmetric induction model) are acting in concert which favors addition to the C=O *Re* face. As expected, addition to the corresponding mismatched *syn* aldehyde proceeded with varying diastereoselectivity. However, in a continuation of this investigation the addition of silyl enol ethers to α,β-bisalkoxy aldehydes was also studied.[10] Based on analysis of the individual stereodirecting contributions from both alkoxy substituents it was predicted that the *syn*-α,β-bisalkoxy diastereomer should be matched, and that nucleophilic addition to this aldehyde should proceed with high selectivity. Experimentally, however, it was found that the Mukaiyama aldol reactions with *anti*-α,β-bisalkoxy aldehydes in most cases exhibited good diastereoselectivities, while the corresponding *syn* isomer displayed lower selectivities. To rationalize the stereochemical outcome both PFA and Cornforth–Evans transition states conformations were analyzed, and by considering the inherent and the developing *syn*-pentane interactions,[1d,11] it was concluded that the Cornforth–Evans model most accurately predicted the observed stereochemical trends. Thus, for the $BF_3{\cdot}OEt_2$-mediated addition of silyl enol ethers to *anti*-α,β-bisalkoxy aldehydes transition state structure **E** was proposed, while the *syn* isomer should react through transition state **F**, which suffers from an unfavorable R↔H interaction. It is evident from these studies that prediction of the stereochemical outcome in the nucleophilic addition to α,β-disubstituted aldehydes is far from trivial and cannot be addressed by simple additive analysis of the participating stereocontrolling elements.



Scheme 2. The merged FA-polar 1,3-asymmetric induction model (**D**) and the Cornforth–Evans transition state structures for addition to an *anti*- and *syn*-α,β-bisalkoxy aldehyde (**E** and **F**).

As parts of an ongoing investigation we have previosly described a diastereoselective aldol addition α-amino-β-silyloxy aldehydes and an unexpected *syn* selectivity in the Mukaiyama aldol addition to α-chloro-substituted aldehydes.[12,13] Herein, we report our full investigation of the nucleophilic addition to α- and α,β-polar substituted aldehydes, including chloro-, fluoro-, alkoxy- and amino-substituted aldehydes.

Results and Discussion

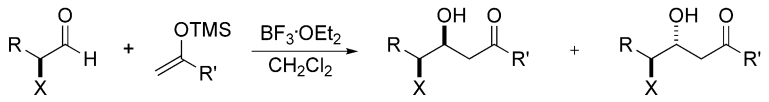
α-Substituted Aldehydes

The initial focus of this study was directed towards the investigation of the facial bias exerted by a polar α-substituent in the Mukaiyama aldol addition. α-Substituted aldehydes **1**–**5**,[14] having varying electronic and steric properties were selected and subjected to the Mukaiyama aldol addition and the results are summarized in Table 1. α-Alkoxy (entries 7–9)[10] and α-fluoro aldehydes (entries 10–12) gave generally poor *anti* selectivity, the trend being that larger nucleophiles gave lower *dr*. For α-chloro aldehydes (entries 1-6) a similar but more pronounced trend was observed. Addition of the hindered pinacolone enol silane (**6a**) to α-chloro aldehydes **1** and **2** gave the *syn* isomer as the major product in good selectivities (entries 1 and 4), which is unanticipated and cannot be predicted by the PFA or the Cornforth–Evans models. A completely opposite trend was observed for the α-sulfonamide **5** (entries 13–15), where an increase in size of the nucleophile led to an enhanced amount of the *anti* isomer, which is expected on the basis of the PFA model.[3a]

In order to begin to decipher the observed results an examination of the operative transition states was needed. The validity of the Cornforth–Evans model for additions to α-chloro-, α-alkoxy- and α-fluoro-substituted aldehydes was supported in a recent theoretical investigation of enol borane additions to α-heteroatom-substituted aldehydes,[8] and for the latter two substrates this has been verified experimentally.[6a,15] It was shown that α-substituted aldehydes reacting *via* the Cornforth–Evans manifold confer a higher diastereoselectivity with boron *Z*(O)-enolates than with the corresponding *E*(O)-enolates due to a destabilizing *syn*-pentane interaction in the *E*(O)-enolate TS. The opposite trend was observed for substrates reacting *via* the PFA TS. In a similar vein α-chloro aldehyde **1** was subjected to boron enolates **22** and **23** (Scheme 3).[12] Addition of *E*(O)-enolate **22**[16] to aldehyde **1** furnished adduct **24b** in modest yield and selectivity, while the use of *Z*(O)-enolate **23**[16] afforded **25b** in excellent yield and selectivity which indicates that also **1** prefers to react through a Cornforth–Evans TS in boron-mediated aldol reactions.

Given these results it is then not clear why α-chloro-, α-alkoxy- and α-fluoro-substituted aldehydes react with poor Cornforth–Evans, or even anti-Cornforth–Evans, selectivity in the Mukaiyama aldol reaction (Table 1, entries 1–12). It is generally accepted that the reaction proceeds through an open TS,[6a,17] having either *antiperiplanar* or *synclinal* TS conformations, although exceptions are known.[18] To rationalize the stereochemical outcome in the Mukaiyama

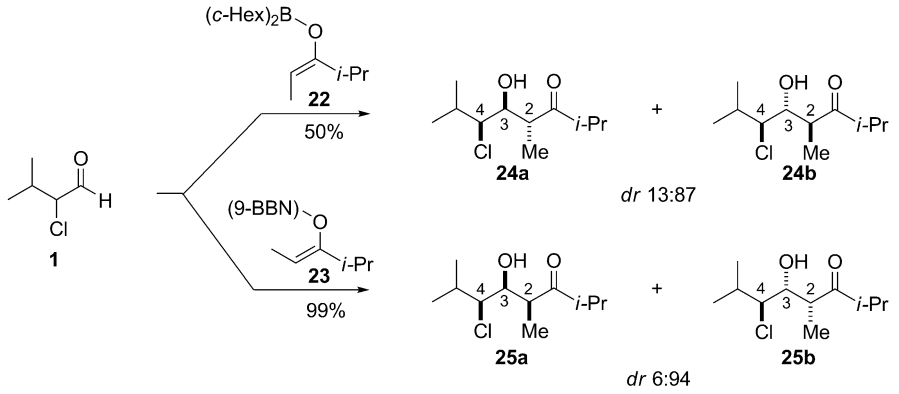
Table 1. Mukaiyama aldol reaction to aldehydes **1**-**5**.[a]



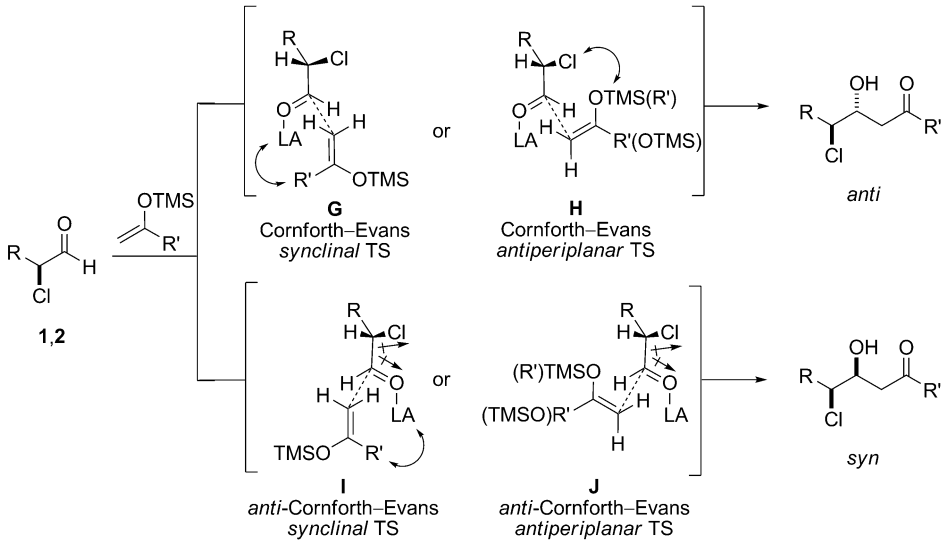
1 – 5 **6a – c** **7 – 21a** (*syn*) **7 – 21b** (*anti*)

Entry	Aldehyde	X	R	**6**	R′	Products[b] (Ratio)	Yield[c] [%]
1	**1**	Cl	*i*-Pr	**a**	*t*-Bu	**7a:7b** (84:16)	99
2	**1**	Cl	*i*-Pr	**b**	*i*-Pr	**8a:8b** (35:65)	92
3	**1**	Cl	*i*-Pr	**c**	Me	**9a:9b** (40:60)	94
4	**2**	Cl	CH_2Ph	**a**	*t*-Bu	**10a:10b** (78:22)	99
5	**2**	Cl	CH_2Ph	**b**	*i*-Pr	**11a:11b** (29:71)	97
6	**2**	Cl	CH_2Ph	**c**	Me	**12a:12b** (40:60)	94
7[d]	**3**	OTBS	*i*-Pr	**a**	*t*-Bu	**13a:13b** (50:50)	66
8[d]	**3**	OTBS	*i*-Pr	**b**	*i*-Pr	**14a:14b** (25:75)	69
9[d]	**3**	OTBS	*i*-Pr	**c**	Me	**15a:15b** (18:82)	66
10	**4**	F	CH_2Ph	**a**	*t*-Bu	**16a:16b** (43:57)	43
11	**4**	F	CH_2Ph	**b**	*i*-Pr	**17a:17b** (27:73)	35
12	**4**	F	CH_2Ph	**c**	Me	**18a:18b** (36:64)	63
13	**5**	NTsBn	*i*-Pr	**a**	*t*-Bu	**19a:19b** (>2:98)	85
14	**5**	NTsBn	*i*-Pr	**b**	*i*-Pr	**20a:20b** (7:93)	94
15	**5**	NTsBn	*i*-Pr	**c**	Me	**21a:21b** (22:78)	60

[a] *Reaction conditions:* To a solution of the aldehyde (1 equiv.) in CH_2Cl_2 at −60 °C was added $BF_3{\cdot}OEt_2$ (3 equiv.) and **6** (2 equiv.) and the mixture was stirred for 18 h.
[b] Diastereomeric ratio was determined by ^1H NMR spectroscopy of the crude reaction mixture.
[c] Isolated yield.
[d] See ref.[10] for experimental details.



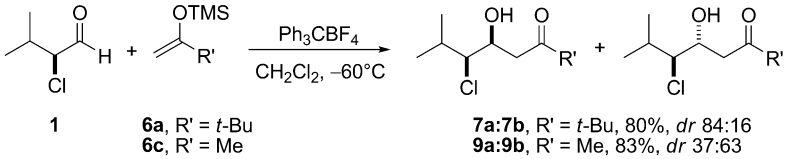
Scheme 3. *E*(O)- and *Z*(O)-boron enolate additions to α-chloro aldehyde **1**.



Scheme 4. Transition state structures in nucleophilic additions to α-chloro aldehydes **1** and **2**.

aldol addition to α-chloro-substituted aldehydes **1** and **2** TS structures **G**–**J** will be considered (Scheme 4). Structures **G** and **H** represent Cornforth–Evans structures in which the enol silane has a *synclinal* or *antiperiplanar* orientation, respectively, whereas structures **I** and **J** are anti-Cornforth–Evans arrangements,[19,20] in which the diastereotopic C=O face is exposed for attack. Also, in structures **I** and **J** the dihedral angle between the carbonyl group and the α-chloro substituent is relatively small, resulting in a destabilizing dipole repulsion.[21] In the *antiperiplanar* TS **H** the major steric interaction is between the enol silane R′-substituent and the α-chloro substituent,[9b,22] while the relevant *synclinal* TSs **G** and **I** are characterized by a destabilizing interaction between the enol silane and the Lewis acid coordinated to the carbonyl oxygen.[9b,17,23]

To differentiate between the *synclinal* and *antiperiplanar* TSs, aldehyde **1** was reacted with enol silanes **6a** (R′ = *t*-Bu) and **6c** (R′ = Me) in the presence of the sterically demanding Lewis acid trityl tetrafluoroborate (Scheme 5).[9b,24] By increasing the size of the



Scheme 5. Mukaiyama aldol addition to aldehyde **1** using trityl tetrafluoroborate.

Lewis acid, the *synclinal* TSs are expected to be destabilized and changing the enol silane R′-substituent from Me (**6c**) to *t*-Bu (**6a**) is expected to further disfavor this reaction pathway. However, when using Ph_3CBF_4 the diastereoselectivity remains unchanged within experimental error (compare with Table 1, entries 1 and 3), suggesting that TS structures **G** and **I** are not relevant in this reaction, and that the *antiperiplanar* arrangements **H** and **J** are operative in the Mukaiyama additions to aldehydes **1** and **2**.

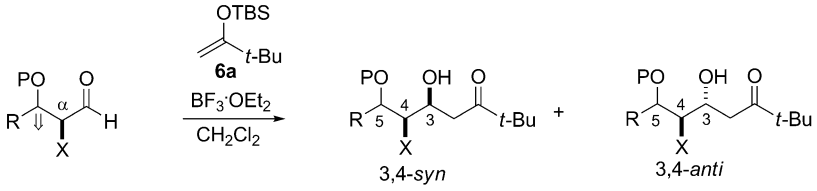
It can then be argued that the $BF_3{\cdot}OEt_2$-mediated addition of pinacolone enolsilane **6a** to aldehydes **1** and **2** will preferentially proceed through **J** in order to avoid steric interactions with the α-chloro substituent present in structure **H** (Table 1, Entries 1 and 4). When decreasing the size of the enol silane R′ moiety the destabilizing steric interactions in **H** will be attenuated, while the unfavorable dipole interaction in TS structure **J** remains unchanged, resulting in an increased formation of the *anti* diastereomer (Table 1, entries 2, 3, 5 and 6). It is also evident that both α-silyloxy aldehyde **3**[10] and α-fluoro aldehyde **4** follows a similar trend in diastereoselectivity when changing the size of the enol silane (Table 1, entries 7–9 and 10–12, respectively), and it is suggested that similar factors as those outlined in Scheme 4 also dictate the outcome for these substrates.[25] The higher *anti* selectivity obtained in the Mukaiyama aldol addition to **3** (X = O) and **4** (X = F) compared to **1** and **2** (X = Cl) could then be rationalized as a manifestation of the increased electronegativity of the α-heteroatom substituent, which should destabilize the TS structure corresponding to **J**, as is observed (Table 1, entries 7–12).

The phenomenon discussed above should be specific for α-heteroatom-substituted aldehydes that preferentially react through Cornforth–Evans TS structures. For aldehydes reacting *via* the PFA manifold, it is well established that smaller nucleophiles generally give lower levels of facial discrimination.[26] Hence, substrates preferring the PFA conformation are expected to show a reversed dependence of the selectivity on the sterics of the enolsilane.[27] Indeed, addition of **6a** and **b** to *N*-Ts-*N*-Bn-protected valinal (**5**) proceed with excellent *anti* selectivity, while the addition of **6c** displayed reduced levels of *anti* selectivity (Table 1, entries 13–15, R = *t*-Bu→Me, *syn*:*anti* > 2:98→22:78).

α,β-Disubstituted Aldehydes

In the continuation of this study additions to aldehydes having both polar α- and β-substituents were examined, the aim being to unravel any trends in the diastereochemical outcomes. Three sets of aldehydes were selected, all containing a β-alkoxy moiety, while the steric and the electronic properties of the α-substituent were varied: α,β-bisalkoxy aldehydes **28**–**31**,

Table 2. Mukaiyama aldol reaction to α,β-disubstituted aldehydes **28**-**37**.[a]



28 – 37 **38a – 47a** **38b – 47b**

Entry	Aldehyde	α,β	X	P	R	Products[b] (Ratio)	Yield[c] [%]
1	**28**	*anti*	OBn	Bn	CH_2CH_2Ph	**38a:38b** (14:86)	99
2	**29**	*anti*	OBn	Bn	*n*-C_6H_{13}	**39a:39b** (16:84)	93
3	**30**	*syn*	OBn	Bn	CH_2CH_2Ph	**40a:40b** (49:51)	90
4	**31**	*syn*	OBn	Bn	*n*-C_6H_{13}	**41a:41b** (45:55)	92
5	**32**	*anti*	NTsBn	TBS	CH_2CH_2Ph	**42a:42b** (> 2:98)	92
6	**33**	*anti*	NTsBn	TBS	*c*-C_6H_{11}	**43a:43b** (> 2:98)	81
7[d]	**34**	*syn*	NTsBn	TBS	CH_2CH_2Ph	**44a:44b** (53:47)	91
8[e]	**35**	*syn*	NTsBn	TBS	*c*-C_6H_{11}	**45a:45b** (56:44)	49
9	**36**	*anti*	Cl	TBS	CH_2CH_2Ph	**46a:46b** (95:5)	99
10	**37**	*syn*	Cl	TBS	CH_2CH_2Ph	**47a:47b** (91:9)	94

[a] *Reaction conditions:* To a solution of the aldehyde (1 equiv.) in CH_2Cl_2 at −60 °C was added $BF_3{\cdot}OEt_2$ (3 equiv.) and **6a** (2 equiv.) and the mixture was stirred for 18 h.
[b] Determined by ^1H NMR spectroscopy of the crude reaction mixture.
[c] Yields are reported for diastereomeric mixtures.
[d] The reaction time was 40 h.
[e] The reaction was run at −40 °C.

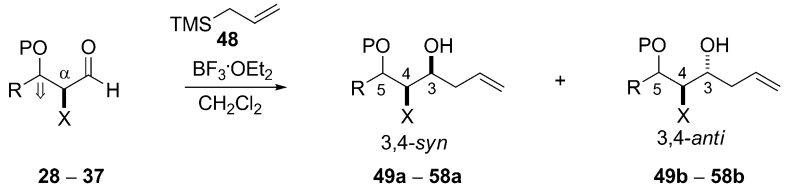
α-amino-β-alkoxy derivatives **32**–**35** and α-chloro-β-silyloxy aldehydes **36** and **37**. These substrates were applied in the Mukaiyama aldol addition with silyl enol ether **6a** and the Sakurai allylation reaction with allyltrimethylsilane (**48**), and the results are detailed below.

Nucleophilic additions of TMS-enol ether **6a** to *anti*-aldehydes **28**, **29** proceeded in good yields and selectivities to afford the corresponding 3,4-*anti* isomers (Table 2, entries 1, 2).[28] In contrast, additions to *syn*-aldehydes **30**, **31** delivered triols **40** and **41** in equally good yields but with poor diastereoselectivities (entries 3 and 4). Similar observations have been made previously and were rationalized by invoking Cornforth–Evans TS structures (e.g., see **E** and **F**, Scheme 2).[10] In this scenario the lower diastereoselectivities obtained for the *syn* isomers **30** and **31** were traced to an unfavorable *syn*-pentane interaction between R and the CHO proton in TS **F**, which is absent in structure **E**.

Mukaiyama aldol additions to α-(*N*-benzyl-*N*-tosylamino)-β-silyloxy aldehydes **32**–**35** follow a similar trend.[13] Thus, addition of **6a** to *anti*-aldehydes **32** and **33** afforded the corresponding 3,4-*anti* adducts **42b** and **43b**, respectively, in excellent yields and diastereoselectivities (Table 2, entries 5 and 6) while aldol additions to *syn*-aldehydes **34** and **35** resulted in lower yields and no appreciable selectivity (entries 7 and 8). Although it would be tempting to speculate that the stereochemical outcome for aldehydes **32**–**35** can be rationalized by applying similar models as for α,β-bisalkoxy aldehydes **28**–**31**,[10] it is assumed that the former aldehydes react through a PFA manifold and,[8] consequently, that the Cornforth–Evans TS structures proposed for **28**–**31** do not apply. Although we can offer no explanation for the stereochemical outcome in additions to aldehydes **32**–**35** it is noted that these results could not have been predicted by simply analyzing the individual contributions from the α- and β-stereocenters, respectively. This point is further highlighted by the π-facial selectivities obtained in the Mukaiyama aldol reactions with α-chloro-β-silyloxy aldehydes **36** and **37** (entries 9 and 10). Additions to both *anti*-**36** and *syn*-**37** afforded the 3,4-*syn* products **46a** and **47a**, respectively, in excellent yield and with high diastereoselectivity. Superficially, it appears as the α-chloro substituent dictates the stereochemical outcome and that the β-substituent only has a minor influence. Once again, this outcome could not have been predicted by applying the conventional induction models. Taken together, the results in Table 2 highlight the increased complexity of predicting the stereochemical outcome in the Mukaiyama aldol addition to α,β-disubstituted aldehydes compared to α-substituted ones.

In order to further investigate the nucleophilic addition to these substrates, Sakurai allylations of aldehydes **28**–**37** were performed. The π-facial selectivities in these additions are presented in Table 3. In general, the stereochemical trends are in line with those obtained in the Mukaiyama aldol reaction. Allylation of aldehyde **28** and **29** proceeded with similar diastereo-

Table 3. Sakurai allylation reaction to α,β-disubstituted aldehydes **28**–**37**.[a]



28 – 37 **49a – 58a** **49b – 58b**

Entry	Aldehyde	α,β	X	P	R	Products (Ratio)[b]	Yield [%][c]
1	**28**	*anti*	OBn	Bn	CH_2CH_2Ph	**49a:49b** (13:87)	95
2	**29**	*anti*	OBn	Bn	*n*-C_6H_{13}	**50a:50b** (16:84)	93
3	**30**	*syn*	OBn	Bn	CH_2CH_2Ph	**51a:51b** (21:79)	83
4	**31**	*syn*	OBn	Bn	*n*-C_6H_{13}	**52a:52b** (33:67)	87
5	**32**	*anti*	NTsBn	TBS	CH_2CH_2Ph	**53a:53b** (13:87)	67
6	**33**	*anti*	NTsBn	TBS	*c*-C_6H_{11}		decomp.[d]
7	**34**	*syn*	NTsBn	TBS	CH_2CH_2Ph	**54a:54b** (45:55)	<5
8	**35**	*syn*	NTsBn	TBS	*c*-C_6H_{11}		decomp.[d]
9	**36**	*anti*	Cl	TBS	CH_2CH_2Ph	**55a:55b** (60:40)	88
10	**37**	*syn*	Cl	TBS	CH_2CH_2Ph	**56a:56b** (59:41)	94

[a] *Reaction conditions:* To a solution of the aldehyde (1 equiv.) in CH_2Cl_2 at −60 °C was added $BF_3{\cdot}OEt_2$ (3 equiv.) and allyltrimethylsilane (2 equiv.) and the mixture was stirred for 18 h.
[b] Isolated yield.
[c] Determined by ^1H NMR spectroscopy of the crude reaction mixture.
[d] No allylation, even at elevated temperature, only decomposition of the aldehyde was observed.

selectivity as in the addition of pinacolone enol silane (**6a**) to these substrates. In contrast, the additions to the corresponding *syn*-aldehydes **30** and **31** proceeded with higher *anti* selectivities.[29] Sakurai allylation of *anti*-α-amino-β-silyloxy aldehyde **32** displayed reduced selectivity compared with the Mukaiyama aldol addition, which would be expected from a PFA-controlled reaction.[26] All attempts to allylate aldehydes **33** and **35**, even at elevated temperatures, were unsuccessful and gave only decomposition products. The diminished diastereoselectivity in the allylations of aldehyde **36** and **37** compared with the Mukaiyama aldol additions (Table 2, entries 11 and 12) should be noted and indicates that the size of the nucleophile influences the selectivity in the addition to these substrates.

Conclusions

In conclusion, it has been shown that the stereochemical outcome in the Mukaiyama aldol addition to α-chloro-substituted aldehydes is sensitive to the size of the silyl enol ether and it is proposed that small nucleophiles preferentially react through Cornforth–Evans TS structures, while sterically more hindered enol silanes preferentially react through anti-Cornforth–Evans TS. A similar relationship between the size of the nucleophile and the stereochemical outcome is also observed for α-alkoxy- and α-fluoro-substituted aldehydes, and it is proposed that similar factors govern the diastereofacial selectivity with this class of substrates. It has also been shown that α-sulfonamide-substituted aldehydes, which preferentially react through a PFA manifold, follow the opposite trend, i.e., an increase in the size of the nucleophile gives higher diastereoselectivity in favor of the *anti* diastereomer. It has also been shown that the stereochemical outcome in the Mukaiyama aldol addition and Sakurai allylation of α,β-bisheteroatom-substituted aldehydes cannot be predicted using current models for rationalizing stereoinduction.

Experimental Section

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ using the residual peak of $CHCl_3$ (^{1}H: $\delta = 7.26$; ^{13}C $\delta = 77.0$). Only the strongest/structurally most important peaks (cm^{-1}), in the IR spectra, are listed. Analytical TLC plates were visualized with UV light and phosphomolybdic acid/cerium sulfate staining reagent. Air- and moisture-sensitive reactions were carried out in flame-dried, septum-capped flasks under an atmospheric pressure of N_2. All liquid reagents were transferred *via* oven-dried syringes. THF and CH_2Cl_2 were dried using a Glass-contour solvent dispersion system.

Mukaiyama Aldol Reaction: Aldehydes 1, 2, 4, 5, 28–37

The experimental procedure for Mukaiyama aldol reaction of aldehyde **1** with enol ether **6a** is representative for all aldehydes **1**, **2**, **6**, **7**, **9**.

(5*S**,6*S**/5*R**,6*S**)-6-Chloro-5-hydroxy-2,2,7-trimethyloctan-3-one (7a, 7b)

To a stirred solution of **1** (19 mg, 156 μmol) in CH_2Cl_2 (1 mL) was added $BF_3{\cdot}OEt_2$ (60 μL, 468 μmol) at −60 °C. After 5 min. was added **6a** (69 μL, 312 μmol) and the resultant solution was stirred at −60 °C for 18 h. The reaction was quenched by addition of H_2O (5 mL) and allowed to reach room temperature. The aqueous phase was extracted with CH_2Cl_2 (3×7 mL), dried ($MgSO_4$) and concentrated under reduced pressure to afford **7a** and **7b** as a colorless oil; yield: 34 mg (99%), *dr* 86:14 (*syn*:*anti*). The diastereomers were separated by flash chromatography (pentane:EtOAc 12:1).

Major isomer **7a**, white solid mp 40–45 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 4.37$ (ddd, $J = 7.5$, 4.5, 2.9 Hz, 1H), 3.68 (dd, $J = 7.6$, 2.9 Hz, 1H), 2.89 (dd, $J = 17.7$, 7.7 Hz, 1H), 2.76 (dd, $J = 17.8$, 4.6 Hz, 1H), 2.68 (s, 1H), 2.14 (qd, $J = 13.4$, 6.7, 6.7, 6.7 Hz, 1H), 1.15 (s, 9H), 1.08 (t, $J = 6.9$, 6.9 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 215.6$, 74.3, 68.0, 44.4, 41.9, 32.4, 26.2, 20.3, 19.9; IR (film): $\nu_{max} = 3491$, 2962, 1701, 737 cm^{-1}; HR-MS (FAB+): $m/z = 221.1303$, calcd. for $C_{11}H_{21}ClO_2$ (M+H): 221.1308.

Minor isomer **7b**, colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 4.05$ (dt, $J = 8.6$, 8.5, 2.4 Hz, 1H), 3.78 (dd, $J = 8.9$, 3.4 Hz, 1H), 3.72–3.55 (br s, 1H), 3.08 (dd, $J = 18.0$, 2.4 Hz, 1H), 2.78 (dd, $J = 18.0$, 8.1 Hz, 1H), 2.41 (m, 1H), 1.18–1.15 (s, 9H), 1.02 (d, $J = 6.8$ Hz, 3H) , 0.97 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 218.3$, 71.3, 69.4, 44.6, 40.0, 29.0, 26.2, 20.7, 15.6; IR (film): $\nu_{max} = 3479$, 2966, 1689, 725 cm^{-1}; HR-MS (FAB+): $m/z = 221.1303$, calcd. for $C_{11}H_{21}ClO_2$ (M+H): 221.1308.

(5*S**,6*S**/5*R**,6*S**)-6-Chloro-5-hydroxy-2,7-dimethyloctan-3-one (8a, 8b)

Prepared from aldehyde **1** and enol silane **6b** as described for **7a** and **7b** to afford **8a** and **8b** as a colorless oil; yield: 112 mg (83%); *dr* 35:65 (*syn*:*anti*). The diastereomers were separated by flash chromatography (pentane:EtOAc 8:1).

Minor isomer **8a**. ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 4.37$ (td, $J = 7.5$, 3.7, 3.7 Hz, 1H), 3.68 (dd, $J = 7.3$, 3.1 Hz, 1H), 2.86 (dd, $J = 17.5$, 7.9 Hz, 1H), 2.71 (dd, $J = 17.5$, 4.4 Hz, 1H), 2.67 (s br, 1H), 2.61 (m, 1H), 2.19–2.08 (m, 1H), 1.11 (d, $J = 7.0$ Hz, 6H), 1.07 (dd, $J = 6.5$, 5.4 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 214.1$, 74.4, 68.0, 45.2, 41.5, 32.3, 20.4, 19.7, 17.99, 17.95; IR (film): $\nu_{max} = 3479$, 2970, 1709, 741 cm^{-1}; HR-MS (FAB+): $m/z = 207.1147$, calcd. for $C_{10}H_{19}ClO_2$ (M+H): 207.1146.

Major isomer **8b**. ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 4.05$ (dt, $J = 8.5$, 8.5, 2.3 Hz, 1H), 3.74 (dd, $J = 8.7$, 3.5 Hz, 1H), 3.51 (s br, 1H), 3.01 (dd, $J = 17.9$, 2.5 Hz, 1H), 2.73 (dd, $J = 18.0$, 8.2 Hz, 1H), 2.61 (m, 1H), 2.42–2.31 (m, 1H), 1.10 (d, $J = 6.9$ Hz, 6H) , 1.00 (d, $J = 6.8$ Hz, 3H), 0.94 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 214.1$, 74.4, 68.0, 45.2, 41.5, 32.3, 20.4, 19.7, 17.99, 17.96; IR (film): $\nu_{max} = 3475$,

2970, 1704, 733 cm^{-1}; HR-MS (FAB+): m/z=207.1149, calcd. for $C_{10}H_{19}ClO_2$ (M+H): 207.1146.

(5*S**,6*S**/5*R**,6*S**)-5-Chloro-4-hydroxy-6-methylheptan-2-one (9a, 9b)

Prepared from aldehyde **1** and enol silane **6c** as described for **7a** and **7b** to afford **9a** and **9b** as a colorless oil; yield: 136 mg (94%); *dr* 40:60 (*syn*:*anti*). The diastereomers were separated by flash chromatography (pentane:EtOAc 6:1).

Minor isomer **9a**. ^{1}H NMR ($CDCl_3$, 500 MHz): δ=4.36 (m, 1H), 3.67 (dd, J=7.1, 3.4 Hz, 1H), 2.85 (dd, J=17.3, 8.2 Hz, 1H), 2.67 (dd, J=17.3, 4.1 Hz, 1H), 2.62 (s br, 1H), 2.21 (s, 3H), 2.13 (qd, J=13.5, 6.7, 6.7, 6.7 Hz, 1H), 1.07 (dd, J=6.7, 3.4 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ= 207.9, 74.3, 68.0, 48.4, 32.2, 30.9, 20.4, 19.5; IR (film): ν_{max}= 3456, 2966, 1712, 737 cm^{-1}; HR-MS (FAB+): m/z= 201.0653, calcd. for $C_8H_{15}ClNaO_2$ (M+Na): 201.0653.

Major isomer **9b**: ^{1}H NMR ($CDCl_3$, 400 MHz): δ=4.10 (dt, J=8.6, 8.6, 2.5 Hz, 1H), 3.75 (dd, J=8.6, 3.7 Hz, 1H), 3.36 (s br, 1H), 3.01 (dd, J=18.0, 2.4 Hz, 1H), 2.72 (dd, J= 18.0, 8.5 Hz, 1H), 2.35 (dtd, J=13.4, 6.7, 6.7, 3.7 Hz, 1H), 2.21 (s, 3H), 1.01 (d, J=6.8 Hz, 3H), 0.96 (d, J=6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ=210.1, 71.3, 68.9, 46.7, 30.9, 29.0, 20.6, 15.8; IR (film): ν_{max}=3448, 2966, 1708, 733 cm^{-1}; HR-MS (FAB+): m/z=201.0651, calcd. for $C_8H_{15}ClNaO_2$ (M+Na): 201.0653.

(5*S**,6*S**/5*R**,6*S**)-6-Chloro-5-hydroxy-2,2-dimethyl-7-phenylheptan-3-one (10a, 10b)

Prepared from aldehyde **2** as described for **7a** and **7b** to afford **10a** and **10b** as a colorless oil; yield: 575 mg (99%); *dr* 78:22 (*syn*:*anti*). The diastereomers were separated by flash chromatography (heptane:EtOAc 5:1→3:1).

Major isomer **10a**. ^{1}H NMR ($CDCl_3$, 500 MHz): δ=7.30 (m, 5H), 4.22 (ddd, J=8.3, 3.9, 2.2 Hz, 1H), 4.16 (ddd, J= 8.6, 6.6, 2.2 Hz, 1H), 3.32 (dd, J=14.0, 6.6 Hz, 1H), 3.12 (dd, J=14.0, 8.2 Hz, 1H), 3.03 (s br, 1H), 2.92 (dd, J=17.9, 8.3 Hz, 1H), 2.81 (dd, J=17.9, 4.0 Hz, 1H), 1.16 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ=216.0, 137.6, 129.3, 128.5, 126.8, 68.2, 66.8, 44.4, 41.0, 40.8, 26.2; IR (film): ν_{max}=3479, 2970, 1701, 702 cm^{-1}; HR-MS (FAB+): m/z=269.1304, calcd. for $C_{15}H_{21}ClO_2$ (M+H): 269.1303.

Minor isomer **10b**. ^{1}H NMR ($CDCl_3$, 500 MHz): δ=7.37–7.22 (m, 5H), 4.12 (ddd, J=8.6, 7.2, 3.9 Hz, 1H), 4.07 (t, J= 7.5, 7.5 Hz, 1H), 3.69 (s br, 1H), 3.37 (dd, J=14.4, 3.8 Hz, 1H), 3.03–2.93 (m, 2H), 2.85 (dd, J=18.0, 8.0 Hz, 1H), 1.17 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ=217.5, 137.3, 129.6, 128.3, 126.8, 70.8, 65.5, 44.6, 40.1, 39.2, 26.2; IR (film): ν_{max}= 2475, 2970, 1701, 702 cm^{-1}; HR-MS (FAB+): m/z= 269.1305, calcd for $C_{15}H_{21}ClO_2$ (M+H): 269.1303.

(5*S**,6*S**/5*R**,6*S**)-6-Chloro-5-hydroxy-2-methyl-7-phenylheptan-3-one (11a, 11b)

Prepared from aldehyde **2** and enol silane **6b** as described for **7a** and **7b** to afford **11a** and **11b** as a colorless oil; yield: 163 mg (97%); *dr* 29:71 (*syn*:*anti*). The diastereomers were separated by flash chromatography (heptane:EtOAc 5:1).

Minor isomer **11a**: ^{1}H NMR ($CDCl_3$, 500 MHz): δ=7.36–7.30 (m, 2H), 7.29–7.24 (m, 3H), 4.22 (ddd, J=8.5, 3.8, 2.4 Hz, 1H), 4.13 (ddd, J=6.7, 8.1, 2.4 Hz, 1H), 3.31 (dd, J=14.0, 6.7 Hz, 1H), 3.10 (dd, J=14.0, 8.1 Hz, 1H), 2.90 (dd, J=17.8, 8.5, Hz, 1H), 2.75 (dd, J=17.8, 3.8 Hz, 1H), 2.61 (hept, J=6.9 Hz, 1H), 1.12 (d, J=6.9 Hz, 3H), 1.11 (d, J=6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ=214.6, 137.6, 129.3, 128.5, 126.9, 68.1, 66.8, 44.3, 41.5, 40.8, 17.96, 17.95; IR (film): ν_{max}=3467, 2970, 1705, 702 cm^{-1}; HR-MS (FAB+): m/z=255.1147, calcd. for $C_{14}H_{19}ClO_2$ (M+H): 255.1146.

Major isomer **11b**: ^{1}H NMR ($CDCl_3$, 500 MHz): δ=7.34–7.28 (m, 2H), 7.27–7.22 (m, 3H), 4.12–4.05 (m, 2H), 3.59 (br s, 1H), 3.34 (dd, J=14.4, 3.3 Hz, 1H), 2.99–2.91 (m, 2H), 2.82 (dd, J=17.8, 7.9 Hz, 1H), 2.62 (hept, J=6.9 Hz, 1H), 1.12 (d, J=6.9 Hz, 3H), 1.11 (d, J=6.9 Hz, 3H).; ^{13}C NMR ($CDCl_3$, 125 MHz): δ=214.6, 137.6, 129.3, 128.5, 126.9, 68.1, 66.8, 44.3, 41.5, 40.8, 17.96, 17.95; IR (film): ν_{max}=3479, 2970, 1709, 1466, 1045 cm^{-1}; HR-MS (FAB+): m/z= 255.1145, calcd. for $C_{14}H_{19}ClO_2$ (M+H): 255.1146.

(5*S**,6*S**/5*R**,6*S**)-6-Chloro-5-hydroxy-2,2-dimethyl-7-phenylheptan-3-one (12a, 12b)

Prepared from aldehyde **2** and enol silane **6c** as described for **7a** and **7b** to afford **12a** and **12b** as a colorless oil; yield: 354 mg (51%); *dr* 66:34 (*syn*:*anti*). The following ratios were used: aldehyde 2 equiv., BF_3·OEt_2 2 equiv., enol silane 1 equiv. The diastereomers were separated by preparative HPLC (hexanes 99.5%, 2-propanol 0.5%).

Minor isomer **12a**. ^{1}H NMR ($CDCl_3$, 500 MHz): δ=7.35–7.30 (m, 2H), 7.28–7.24 (m, 3H), 4.24–4.19 (ddd, J=8.7, 3.6, 2.3 Hz, 1H), 4.11 (ddd, J=8.0, 6.8, 2.3 Hz, 1H), 3.29 (dd, J=14.0, 6.8 Hz, 1H), 3.09 (dd, J=14.0, 8.0 Hz, 1H), 2.90 (dd, J=17.8, 8.7 Hz, 1H), 2.71 (dd, J=17.8, 3.6 Hz, 1H), 2.19 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ=208.4, 137.5, 129.3, 128.6, 126.9, 67.9, 66.8, 47.6, 40.8, 30.7; IR (film): ν_{max}=3448, 2912, 1712, 702 cm^{-1}; HR-MS (FAB+): m/z= 227.0833, calcd. for $C_{12}H_{15}ClO_2$ (M+H): 227.0833.

Major isomer **12b**. ^{1}H NMR ($CDCl_3$, 500 MHz): δ=7.35–7.30 (m, 2H), 7.28–7.24 (m, 3H), 4.14–4.08 (m, 2H), 3.42 (br s, 1H), 3.32 (dd, J=14.4, 3.3 Hz, 1H), 2.98–2.92 (m, 2H), 2.81 (dd, J=17.9, 8.1 Hz, 1H), 2.22 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ=209.4, 137.2, 129.5, 128.4, 126.9, 70.4, 65.5, 45.9, 40.1, 30.9; IR (film): ν_{max}=3440, 2931, 1701, 1408, 698 cm^{-1}; HR-MS (FAB+): m/z=227.0834, calcd. for $C_{12}H_{15}ClO_2$ (M+H): 227.0833.

(5*S**,6*S**/5*R**,6*S**)-6-Fluoro-5-hydroxy-2,2-dimethyl-7-phenylheptan-3-one (16a, 16b)

Prepared from aldehyde **4** as described for **7a** and **7b** to afford **16a** and **16b** as a colorless oil; yield: 55.0 mg (43%), *dr* 43:57 (*syn*:*anti*).

Minor isomer **16a**. ^{1}H NMR ($CDCl_3$, 500 MHz): δ=7.27–7.16 (m, 5H), 4.51 (dddd, J=47.0, 7.9, 5.9, 2.3 Hz, 1H), 4.01 (ddddd, J=16.2, 4.8, 3.1, 3.1, 3.0 Hz, 1H), 3.07 (d, J= 4.8 Hz, 1H), 3.09–2.95 (m, 2H), 2.81 (dd, J=17.9, 9.0 Hz, 1H), 2.66 (dd, J=17.9, 3.3 Hz, 1H), 1.08 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ=216.6, 136.9 (d, J=6.4 Hz), 129.4, 128.6, 126.7, 95.6 (d, J=177.1 Hz), 67.8 (d, J=20.0 Hz), 39.2 (d, J=3.6 Hz), 37.1 (d, J=22.2 Hz), 26.3; IR (film): ν_{max}= 3437, 2924, 1701, 1369, 1169 cm^{-1}; HR-MS (FAB+): m/z= 253.1597, calcd. for $C_{15}H_{21}FO_2$ (M+H): 253.1598.

Major isomer **16b**. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.35–7.22 (m, 5H), 4.56 (dddd, J = 47.9, 7.5, 7.5, 3.3 Hz, 1H), 4.04–3.97 (m, 1H), 3.55 (d, J = 4.3 Hz, 1H), 3.15 (ddd, J = 32.9, 14.7, 3.3 Hz, 1H), 2.95 (ddd, J = 23.0, 14.8, 7.9 Hz, 1H), 2.88 (ddd, J = 18.0, 2.2, 2.2 Hz, 1H), 2.71 (dd, J = 18.0, 8.6 Hz, 1H), 1.15 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 217.7, 136.9 (d, J = 1.6 Hz), 129.6, 128.4, 126.6, 94.9 (d, J = 174.0 Hz), 68.8 (d, J = 24.9 Hz), 44.6, 38.4 (d, J = 3.6 Hz), 37.7 (d, J = 20.4 Hz), 26.2; IR (neat): ν_{max} = 3475, 2966, 1701, 1365, 1061 cm^{-1}; HR-MS (FAB+): m/z = 253.1591, calcd. for $C_{15}H_{21}FO_2$ (M+H): 253.1598.

(5*S**,6*S**/5*R**,6*S**)-6-Fluoro-5-hydroxy-2-methyl-7-phenylheptan-3-one (17a, 17b)

Prepared from aldehyde **4** and enol silane **6b** as described for **7a** and **7b** to afford **17a** and **17b** as a colorless oil; yield: 63.0 mg (35%); *dr* 27:73 (*syn*:*anti*).

Minor isomer **17a**. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.22 (m, 5H), 4.57 (dddd, J = 46.4, 8.0, 5.9, 2.5 Hz, 1H), 4.16–4.04 (m, 1H), 3.13–3.00 (m, 3H), 2.86 (dd, J = 17.7, 9.0 Hz, 1H), 2.69 (dd, J = 17.7, 3.4 Hz, 1H), 2.61 (hept, J = 6.9 Hz, 1H), 1.12 (d, J = 6.9 Hz, 3H), 1.11 (d, J = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 215.0, 136.8 (d, J = 6.3 Hz), 129.4, 128.6, 126.7, 95.6 (d, J = 177.0 Hz), 67.7 (d, J = 20.1 Hz), 42.5 (d, J = 3.5 Hz), 41.6, 37.0 (d, J = 22.2 Hz), 18.0, 17.9; IR (neat): ν_{max} = 3341, 1709, 1643 cm^{-1}; HR-MS (FAB+): m/z = 239.1439, calcd. for $C_{14}H_{19}FO_2$ (M+H): 239.1442.

Major isomer **17b**. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.26–7.15 (m, 5H), 4.56–4.48 (m, 1H), 3.96 (q, J = 7.0 Hz, 1H), 3.41 (s, 1H), 3.06 (ddd, J = 33.1, 14.8, 3.3 Hz, 1H), 2.88 (ddd, J = 22.9, 14.7, 8.0 Hz, 1H), 2.77 (dt, J = 17.9, 2.3 Hz, 1H), 2.62 (dd, J = 17.9, 8.6 Hz, 1H), 2.53 (hept, J = 7.0 Hz, 1H), 1.04 (d, J = 2.7 Hz, 3H), 1.03 (d, J = 2.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 216.0, 136.8 (d, J = 1.6 Hz), 129.5, 128.4, 126.6, 94.9 (d, J = 174.2 Hz), 68.6 (d, J = 24.8 Hz), 41.7 (d, J = 3.6 Hz), 41.6, 37.6 (d, J = 20.4 Hz), 17.9, 17.9; IR (neat): ν_{max} = 3340, 2966, 1709, 1462, 1107 cm^{-1}; HR-MS (FAB+): m/z = 239.1440, calcd. for $C_{14}H_{19}FO_2$ (M+H): 239.1442.

(5*S**,6*S**/5*R**,6*S**)-5-Fluoro-4-hydroxy-6-phenylhexan-2-one (18a, 18b)

Prepared from aldehyde **4** and enol silane **6c** as described for **7a** and **7b** to afford **18a** and **18b** as a colorless oil; yield: 112 mg (63%); *dr* 36:64 (*syn*:*anti*).

Minor isomer **18a**. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.22 (m, 5H), 4.56 (dddd , J = 46.7, 8.0, 5.8, 2.6 Hz, 1H), 4.10 (dddd, J = 24.6, 9.1, 2.8, 2.8 Hz, 1H), 3.01 (m, 2H), 2.97 (br s, 1H), 2.86 (dd, J = 17.7, 9.1 Hz, 1H), 2.67 (dd, J = 17.7, 3.3 Hz, 1H), 2.20 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 209.6, 136.72 (d, J = 1.7 Hz), 129.5, 128.5, 126.7, 94.9 (d, J = 174.2 Hz), 68.4 (d, J = 24.9 Hz), 45.0 (d, J = 3.7 Hz), 37.6 (d, J = 20.5 Hz), 30.9; IR (neat): ν_{max} = 3371, 1709, 1107 cm^{-1}; HR-MS (FAB+): m/z = 211.1127, calcd. for $C_{12}H_{15}FO_2$ (M+H): 211.1129.

Major isomer **18b**. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.34–7.23 (m, 5H), 4.56 (dddd, J = 47.8, 8.0, 7.5, 3.3 Hz, 1H), 4.10–4.02 (m, 1H), 3.30 (d, J = 4.5 Hz, 1H), 3.12 (ddd, J = 33.0, 14.8, 3.3 Hz, 1H), 2.95 (ddd, J = 22.9, 14.7, 8.0 Hz, 1H), 2.85 (unresolved ddd, J = 18.0 Hz, 1H), 2.68 (dd, J = 18.0, 8.8 Hz, 1H), 2.20 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 209.7, 136.71 (d, J = 1.7 Hz), 129.5, 128.5, 126.7, 94.9 (d, J = 174.2 Hz), 68.4 (d, J = 24.9 Hz), 45.0 (d, J = 3.6 Hz), 37.6 (d, J = 20.4 Hz), 30.9; IR (neat): ν_{max} = 3371, 1709, 1107 cm^{-1}; HR-MS (FAB+): m/z = 211.1127, calcd. for $C_{12}H_{15}FO_2$ (M+H): 211.1129.

(5*R**,6*S**)-6-(*N*-Benzyl-*N*-tosylamino)-5-hydroxy-2,2,7-trimethyloctan-3-one (19b)[12]

Prepared from aldehyde **5** as described for **7a** and **7b** to afford **19b** as a colorless oil; yield: 90 mg (85%); *dr* > 2:98 (*syn*:*anti*).

Major isomer **19b**. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.68 (d, J = 8.2 Hz, 2H), 7.46 (d, J = 7.0 Hz, 2H), 7.35–7.21 (m, 5H), 4.61 (d, J = 15.4 Hz, 1H), 4.36 (d, J = 15.4 Hz, 1H), 4.01 (m, 1H), 3.43 (m, 1H), 3.26 (d, J = 2.2 Hz, 1H), 2.53 (m, 2H), 2.42 (s, 3H), 1.91 (m, 1H), 1.04 (s, 9H), 0.74 (d, J = 6.8 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 217.5, 143.2, 138.2, 137.6, 129.6, 129.1, 128.4, 127.7, 127.3, 69.2, 44.2, 41.7, 29.3, 26.3, 22.3, 21.5, 20.2; IR (neat): ν_{max} = 3400, 2970, 1690, 1160 cm^{-1}; HR-MS (FAB+): m/z = 446.2359, calcd. for $C_{25}H_{35}NO_4S$ (M+H): 446.2365.

(5R*,6S*)-6-(*N*-Benzyl-*N*-tosylamino)-5-hydroxy-2,7-dimethyloctan-3-one (20a, 20b)

Prepared from aldehyde **5** and enol silane **6b** as described for **7a** and **7b** to afford **20a** and **20b** as a colorless oil; yield: 140 mg (94%); *dr* 7:93 (*syn*:*anti*). The diastereomers were separated by flash chromatography (heptane:EtOAc 6:1).

Major isomer **20b**. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.69 (d, J = 8.2 HZ, 2H), 7.48 (d, J = 7.2 Hz, 2H), 7.34–7.24 (m, 5H), 4.63 (d, J = 15.4 Hz, 1H), 4.33 (d, J = 15.4 Hz, 1H), 3.99 (unresolved m, 1H), 3.43 (unresolved m, 1H), 3.27 (br s, J = 2.1 Hz, 1H), 2.55–2.35 (m, 6H), 1.96–1.77 (unresolved m, 1H), 1.03 (d, J = 6.8 Hz, 3H), 1.01 (d, J = 6.9 Hz, 3H), 0.97 (d, J = 6.9 Hz, 3H), 0.73 (d, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 215.8, 143.2, 138.0, 137.5, 129.5, 129.0, 128.3, 127.6, 127.2, 69.12, 67.0 (br), 48.9 (br), 44.9, 41.0, 29.2, 22.2, 21.4, 20.0, 17.9, 17.8; IR (film): ν_{max} = 3521(br), 2970, 1705, 1335, 1157 cm^{-1}; HR-MS (FAB+): m/z = 432.2205, calcd. for $C_{24}H_{33}NO_4S$ (M+H): 432.2203.

(4*R**,5*S**)-5-(*N*-Benzyl-*N*-tosylamino)-4-hydroxy-6-methylheptan-2-one (21a, 21b)

Prepared from aldehyde **5** and enol silane **6c** as described for **7a** and **7b** to afford **21a** and **21b** as a colorless oil; yield: 47.3 mg (60%); *dr* 22:78 (*syn*:*anti*). The following ratios were used: aldehyde 2 equiv., $BF_3{\cdot}OEt_2$ 2 equiv., enol silane 1 equiv. The diastereomers were separated by flash chromatography (heptane:EtOAc 8:1→4:1).

Major isomer **21b**. ^{1}H NMR ($CDCl_3$, 400 MHz, 55 °C): δ = 7.70 (d, J = 8.1 Hz, 2H), 7.46 (d, J = 7.0 Hz, 2H), 7.36–7.24 (m, 5H), 4.64 (d, J = 15.5 Hz, 1H), 4.32 (d, J = 15.5 Hz, 1H), 4.04 (unresolved m, 1H), 3.44 (dd, J = 6.2, 6.2 Hz 1H), 3.09 (br s, 1H), 2.63–2.46 (m, 2H), 2.44 (s, 3H), 2.01 (s, 3H), 1.99–1.87 (m, 1H), 1.04 (d, J = 6.7 Hz, 3H), 0.75 (d, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, 45 °C): δ = 209.6, 143.3, 138.4, 137.6, 129.6, 129.2, 128.5, 127.8, 127.4, 69.5, 67.2 (br), 49.3 (br), 48.0, 30.3, 29.4, 22.3, 21.4, 20.0; IR (film):

ν_{max} = 3618 (br), 2962, 1709, 1334, 1157 cm^{-1}; HR-MS (FAB+): *m/z* = 404.1890, calcd. for $C_{22}H_{29}NO_4S$ (M+H): 404.1890.

(5*S**,6*S**/5*R**,6*S**)-6-Chloro-5-hydroxy-2,2,7-trimethyloctan-3-one (7a, 7b)

To a solution of Ph_3CBF_4 (657 mg, 1.99 mmol) in CH_2Cl_2 (17 mL) at −60 °C was added **1** (80 mg, 0.66 mmol) and the solution stirred for 15 min followed by addition of **6a** (229 mg, 1.33 mmol). The resultant mixture stirred for 18 h and then quenched by addition of H_2O (17 mL) and allowed to reach room temperature. The aqueous phase was extracted with CH_2Cl_2 (3×10 mL), dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by flash chromatography (pentane:EtOAc 12:1) to afford **7a** and **7b** as a colorless oil; yield: 117 mg (80%); *dr* 84:16 (*syn*:*anti*). See above for characterization details.

(5*S**,6*S**/5*R**,6*S**)-5-Chloro-4-hydroxy-6-methylheptan-2-one (9a, 9b)

Prepared from aldehyde **1** and enol silane **6c** as described for **7a** and **7b**. The mixture was purified by flash chromatography (pentane:EtOAc 6:1) to afford **9a** and **9b** as colorless oils; yield: 99 mg (83%); *dr* 37:63 (*syn*:*anti*). See above for characterization details.

Mukaiyama Aldol Reaction: Aldehydes 28–37

The experimental procedure for Mukaiyama aldol reaction of aldehyde **28** is representative for all aldehydes **28**–**37**.

(6*S**,7*R**)-6,7-Bis(benzyloxy)-5-hydroxy-2,2-dimethyl-9-phenylnonan-3-one (38a, 38b)

To a stirred solution of **28** (27.3 mg, 72.9 μmol) in CH_2Cl_2 (1 mL) was added $BF_3{\cdot}OEt_2$ (28 μL, 219 μmol) at −60 °C. After 5 min. was added **6a** (32 μL, 146 μmol) and the resultant solution was stirred at −60 °C for 18 h. The reaction was quenched by addition of H_2O (5 mL) and allowed to reach room temperature. The aqueous phase was extracted with CH_2Cl_2 (3×7 mL), dried ($MgSO_4$) and concentrated under reduced pressure to afford **38a** and **38b** as a colorless oil; yield: 34.5 mg (99%); *dr* 86:14 (*syn*:*anti*).

Major isomer **38b**. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28 (m, 15H), 4.82 (d, *J* = 11.7 Hz, 1H), 4.69 (d, *J* = 8.1 Hz, 1H), 4.66 (d, *J* = 7.9 Hz, 1H), 4.55 (d, *J* = 11.5 Hz, 1H), 4.12 (ddt, *J* = 6.2, 3.5, 2.4 Hz, 1H), 3.79 (td, *J* = 8.0, 3.4 Hz, 1H), 3.67 (dd, *J* = 6.4, 3.4 Hz, 1H), 3.39 (d, *J* = 3.7 Hz, 1H), 2.93 (dd, *J* = 18.1, 2.3 Hz, 1H), 2.86 (m, 1H), 2.67 (ddd, *J* = 13.8, 10.1, 6.4 Hz, 1H), 2.57 (dd, *J* = 18.2, 9.2 Hz, 1H), 2.06 (m, 1H), 1.94 (m, 1H), 1.08 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 218.3, 142.4, 138.5, 128.48, 128.44, 128.42, 128.37, 128.1, 128.0, 127.72, 127.68, 125, 81.5, 79.1, 73.7, 71.9, 68.2, 44.4, 39.5, 31.9, 31.7, 26.3; IR (film): ν_{max} = 3485 (br), 1703, 1454, 1073 cm^{-1}; HR-MS (FAB+): *m/z* = 475.2838, calcd. for $C_{31}H_{38}O_4$ (M+H): 475.2848.

(6*S**,7*R**)-6,7-Bis(benzyloxy)-5-hydroxy-2,2-dimethyltridecan-3-one (39b, 39b)

Prepared from aldehyde **29** as described for **38** to afford **39a** and **39b** as a colorless oil; yield: 92 mg (93%); *dr* 84:16 (*syn*:*anti*).

Major isomer **39b**. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.32 (m, 10H), 4.79 (d, *J* = 11.6 Hz, 1H), 4.67 (d, *J* = 11.6 Hz, 1H), 4.62 (d, *J* = 11.5 Hz, 1H), 4.55 (d, *J* = 11.5 Hz, 1H), 4.13 (ddt, *J* = 6.0, 3.6, 2.3 Hz, 1H), 3.72 (m, 1H), 3.62 (dd, *J* = 6.2, 3.5 Hz, 1H), 3.43 (d, *J* = 3.7 Hz, 1H), 2.92 (dd, *J* = 18.1, 2.3 Hz, 1H), 2.58 (dd, *J* = 18.2, 9.2 Hz, 1H), 1.69 (m, 1H), 1.59 (m, 1H), 1.48 (m, 1H), 1.30 (m, 7H), 1.07 (s, 9H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 218.4, 138.6, 138.5, 128.36, 128.32, 128.1, 127.8, 127.6, 127.5, 81.7, 79.7, 73.6, 71.9, 68.2, 44.3, 39.4, 31.8, 29.9, 29.4, 26.2, 25.6, 22.6, 14.1; IR (film): ν_{max} = 3492(br), 1696, 1455, 1089 cm^{-1}; HR-MS (FAB+): *m/z* = 461.3222, calcd. for $C_{29}H_{42}O_4$ (M+Li): 461.3238.

(6*R**,7*R**)-6,7-Bis(benzyloxy)-5-hydroxy-2,2-dimethyl-9-phenylnonan-3-one (40a, 40b)

Prepared from aldehyde **30** as described for **38** to afford **40a** and **40b** as a colorless oil; yield: 32 mg (90%); *dr* 51:49 (*syn*:*anti*).

Mixture of isomers. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26 (m, 15H_{maj}, 15H_{min}), 4.79 (AB-d, *J* = 11.7 Hz, 1H_{maj}), 4.72–4.54 (m, 3H_{maj}, 4H_{min}), 4.28 (m, 1H_{min}), 4.18 (qd, *J* = 5.0, 3.7 Hz, 1H_{maj}), 3.76 (ddd, *J* = 8.1, 6.3, 3.9 Hz, 1H_{maj}), 3.60 (m, 2H_{min}), 3.51 (d, *J* = 3.46 Hz, 1H_{min}), 3.44 (dd, *J* = 6.3, 3.6 Hz, 1H_{maj}), 2.87 (d, *J* = 5.2 Hz, 1H_{maj}), 2.85–2.51 (m, 3H_{maj}, 4H_{min}), 2.44 (dd, *J* = 17.9, 3.8 Hz, 1H_{maj}), 2.09–1.96 (m, 1H_{maj}, 2H_{min}), 1.88 (m, 1H_{maj}), 1.07 (s, 9H_{min}), 1.04 (s, 9H_{maj}); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 216.8, 216.2, 142.1, 141.8, 138.5, 138.1, 138.2, 138.0, 128.46, 128.47, 128.40, 128.38, 128.36, 128.35, 128.2, 128.1, 128.21, 127.9, 127.8, 127.7, 125.3, 125.77, 81.5, 80.6, 79.1 78.5, 74.4, 73.7, 73.0, 72.5, 68.5, 67.4, 44.3, 44.2, 40.5, 39.6, 32.7, 31.9, 31.8, 31.7, 26.22, 26.18; IR (film): ν_{max} = 3489 (br), 1703, 1454, 1070 cm^{-1}; HR-MS (FAB+): *m/z* = 475.2838, calcd. for $C_{31}H_{38}O_4$ (M+H): 475.2848.

(6*R**,7*R**)-6,7-Bis(benzyloxy)-5-hydroxy-2,2-dimethyltridecan-3-one (41a, 41b)

Prepared from aldehyde **31** as described for **38** to afford **41a** and **41b** as a colorless oil; yield: 49 mg (92%); *dr* 55:45 (*syn*:*anti*).

Minor isomer **41a**. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30 (m, 10H), 4.67 (d, *J* = 11.8 Hz, 4H), 4.29 (dq, *J* = 6.2, 3.1 Hz, 1H), 3.59 (dt, *J* = 6.4, 3.9 Hz, 1H), 3.54 (dd, *J* = 5.8, 3.8 Hz, 1H), 3.50 (d, *J* = 3.5 Hz, 1H), 2.82 (dd, *J* = 17.7, 2.8 Hz, 1H), 2.63 (dd, *J* = 17.7, 8.9 Hz, 1H), 1.66 (m, 2H), 1.29 (m, 8H), 1.08 (s, 9H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 217.0, 138.3, 138.2, 128.4, 128.3, 128.2, 127.8, 128.2, 127.7, 80.9, 79.5, 73.8, 72.5, 68.6, 44.3, 39.7, 31.8, 30.2, ,29.4, 26.2, 25.9, 22.6, 14.1.

Major isomer **41b**. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30 (m, 10H), 4.83 (d, *J* = 11.7 Hz, 1H), 4.63 (m, 3H), 4.16 (m, 1H), 3.73 (ddd, *J* = 7.8, 6.4, 4.2 Hz, 1H), 3.39 (dd, *J* = 6.3, 3.5 Hz, 1H), 2.88 (d, *J* = 5.1 Hz, 1H), 2.73 (dd, *J* = 17.9, 8.5 Hz, 1H), 2.45 (dd, *J* = 17.9, 3.7 Hz, 1H), 1.66 (m, 2H),

1.29 (m, 8H), 1.08 (s, 9H), 0.88 (t, $J=6.9$ Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=216.3$, 138.7, 138.43, 128.43, 128.3, 128.0, 127.8, 127.6, 81.9, 80.1, 74.5, 73.1, 67.5, 44.2, 40.6, 31.8, 31.0, 29.5, 26.2, 25.5, 22.6, 14.1; IR (film): $\nu_{max}=348$ 0(br), 1703, 1455, 1072 cm^{-1}; HR-MS (FAB+): *m/z* = 455.3154, calcd. for $C_{29}H_{42}O_4$ (M+H): 455.3156.

N-Benzyl-*N*-{(1*R**,2*R**)-1-[(*S**)-1-(*tert*-butyl)-dimethylsilanyloxy-3-phenylpropyl]-2-hydroxy-5,5-dimethyl-4-oxohexyl}-4-methylbenzenesulfonamide (42b)

Prepared from aldehyde **32** as described for **38a** and **38b** to afford **42b** as a colorless oil; yield: 141 mg (92%); *dr* > 2:98 (*syn*:*anti*). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.75$ (d, $J=8.0$ Hz, 2H), 7.51 (d, $J=6.8$ Hz, 2H), 7.37–7.18 (m, 10H), 4.81 (d, $J=15.2$ Hz, 1H), 4.40 (d, $J=15.2$ Hz, 1H), 4.24 (m, 1H), 4.07 (m, 1H), 3.91 (m, 1H), 3.64 (d, $J=2.3$ Hz, 1H), 2.88 (dt, $J=13.0$, 4.6 Hz, 1H), 2.69 (m, 1H), 2.61 (dt, $J=13.0$, 4.6 Hz, 1H), 2.45 (s, 3H), 2.21 (d, $J=18.0$ Hz, 1H), 2.00 (m, 1H), 1.63 (m, 1H), 1.03 (s, 9H), 0.92 (s, 3H), 0.02 (s, 3H), −0.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=$ 215.6, 143.5, 142.6, 138.0, 137.7, 129.8, 129.0, 128.6, 128.5, 128.3, 127.7, 127.3, 125.6, 72.4, 68.9, 44.0, 41.6, 35.8, 28.8, 26.0, 21.4, 18.1, −4.3, −4.4; IR (film): $\nu_{max}=2960$, 1690, 1160 cm^{-1}; HR-MS (FAB+): *m/z* = 652.3484, calcd. for $C_{37}H_{53}NO_5SSi$ (M+H): 652.3492.

N-Benzyl-*N*-{(1*R**,2*R**)-1-[(*S**)-1-(*tert*-butyl)-dimethylsilanyloxy-3-cyclohexyl-ethyl]-2-hydroxy-5,5-dimethyl-4-oxohexyl}-4-methylbenzenesulfonamide (43b)

Prepared from aldehyde **33** as described for **38a** and **38b** to afford **43b** as a colorless oil; yield: 29 mg (81%); *dr* > 2:98 (*syn*:*anti*). ^{1}H NMR (500 MHz, d8-PhMe, 90 °C): $\delta=7.61$ (d, $J=8.2$ Hz, 2H), 7.41 (d, $J=7.4$ Hz, 2H), 7.13–6.82 (m, 5H), 4.68 (d, $J=15.4$ Hz, 1H), 4.50 (m, 1H), 4.34 (d, $J=15.4$, 1H), 4.04–3.90 (m, 2H), 3.47 (s, 3H), 2.71 (dd, $J=17.0$, 9.6 Hz, 1H), 2.27 (d, $J=17.0$ Hz, 1H), 1.99–0.94 (m, 29H), 0.17 (s, 3H), −0.02 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6): $\delta=213.8$, 137.9, 134.8, 130.4, 129.1, 128.6, 127.8, 127.6, 75.6, 67.9, 62.7, 43.8, 43.2, 30.1, 27.0, 26.3, 24.5, 21.4, 19.1, −1.7, −4.5; IR (film): $\nu_{max}=3450$, 2970, 1690, 1340, 1160 cm^{-1}; HR-MS (FAB+): *m/z* = 630.3643, calcd. for $C_{35}H_{55}NO_5SSi$ (M+H): 630.3648.

N-Benzyl-*N*-{(1*S**,2*S**/1*S**,2*R**)-1-[(*S**)-1-(*tert*-butyl)-dimethylsilanyloxy-3-phenylpropyl]-2-hydroxy-5,5-dimethyl-4-oxohexyl}-4-methylbenzenesulfonamide (44a, 44b)

Prepared from aldehyde **34** as described for **38a** and **38b** to afford **44a** and **44b** as a colorless oil; yield: 45 mg (91%); *dr* 53:47 (*syn*:*anti*). The diastereomers were separated by flash chromatography (pentane:EtOAc 20:1).

Major isomer **44a**. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.49$–7.02 (m, 14H), 4.72 (d, $J=16.0$ Hz, 1H), 4.62 (d, $J=16.0$ Hz, 1H), 4.30 (m, 1H), 4.11 (dd, $J=8.9$, 2.5 Hz, 1H), 3.94 (dt, $J=6.1$, 2.5 Hz, 1H), 2.97 (d, $J=4.5$ Hz, 1H), 2.82 (dd, $J=18.0$, 2.0 Hz, 1H), 2.57 (m, 3H), 2.43 (s, 3H), 1.96 (m, 1H), 1.62 (m, 1H), 1.11 (s, 9H), 0.82 (s, 9H), 0.08 (s, 3H), 0.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=216.3$, 142.6, 141.5, 138.3, 137.8, 128.8, 128.7, 128.5, 128.3, 128.0, 127.9, 127.0, 125.9, 74.1, 65.3, 64.2, 49.7, 44.3, 41.2, 35.7, 32.3, 26.2, 25.9, 21.4, 18.0, −4.4, −4.5; IR (film): $\nu_{max}=2960$, 1700, 1160 cm^{-1}; HR-MS (FAB+): *m/z* = 652.3503, calcd. for $C_{37}H_{53}NO_5SSi$ (M+H): 652.3492.

Minor isomer **44b**. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.43$ (m, 2H), 7.32–7.18 (m, 8H), 7.07 (d, $J=7.0$ Hz, 2H), 6.91 (d, $J=8.1$ Hz, 2H), 4.79 (d, $J=14.5$ Hz, 1H), 4.61 (d, $J=14.5$ Hz, 1H), 4.43 (dt, $J=6.3$, 2.3 Hz, 1H), 4.27 (m, 1H), 3.97 (dd, $J=10.2$, 2.3 Hz, 1H), 3.59 (d, $J=3.2$ Hz, 1H), 2.87 (d, $J=18.5$ Hz, 1H), 2.73–2.51 (m, 3H), 2.24 (s, 3H), 2.22 (m, 2H), 1.10 (s, 9H), 0.87 (s, 9H), 0.14 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=218.6$, 142.8, 141.6, 138.3, 137.3, 129.8, 129.0, 128.4, 128.3, 128.0, 127.5, 127.3, 125, 72.4, 65.1, 63.5, 49.9, 44.3, 40.9, 36.7, 32.7, 26.4, 26.2, 21.4, 18.3, −4.2, −5.2; IR (film): $\nu_{max}=2960$, 1690, 1160 cm^{-1}; HR-MS (FAB+): *m/z* = 674.3324, calcd for $C_{37}H_{53}NO_5SSi$ (M+Na): 674.3311.

N-Benzyl-*N*-{(1*S**,2*S**/1*S**,2*R**)-1-[(*S**)-1-(*tert*-butyl)-dimethylsilanyloxy-3-cyclohexylmethyl]-2-hydroxy-5,5-dimethyl-4-oxohexyl}-4-methylbenzene-sulfonamide (45a, 45b)

Prepared from aldehyde **35** as described for **38a** and **38b** to afford **45a** and **45b** as a colorless oil; yield: 34 mg (49%); *dr* 56:44 (*syn*:*anti*). The diastereomers were separated by preparative HPLC (hexane:*i*-PrOH 99:1).

Major isomer **45a**. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.51$–7.12 (m, 9H), 4.72 (d, $J=16.2$ Hz, 1H), 4.56 (d, $J=16.2$ Hz, 1H), 4.34 (m, 1H), 3.98 (dd, $J=9.4$, 3.0, 1H), 3.75 (t, $J=3.5$, 1H), 3.10 (d, $J=17.3$, 1H), 2.90 (d, $J=4.6$ Hz, 1H), 2.51 (dd, $J=17.3$, 9.0 Hz, 1H), 2.37 (s, 3H), 1.57–0.79 (m, 29H), 0.16 (s, 3H), 0.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=$ 216.7, 142.6, 138.7, 137.7, 128.9, 128.7, 128.1, 127.9, 127.1, 79.7, 77.3, 65.2, 49.8, 44.3, 42.1, 39.7, 31.8, 28.6, 26.3, 26.2, 26.09, 26.05, 21.4, 18.5, −3.3, −4.7; IR (film): $\nu_{max}=3490$, 1700, 1340, 1100 cm^{-1}; HR-MS (FAB+): *m/z* = 630.3651, calcd. for $C_{35}H_{55}NO_5SSi$ (M+H): 630.3648.

Minor isomer **45b**. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.31$–7.01 (m, 9H), 4.82 (d, $J=14.5$ Hz, 1H), 4.48 (d, $J=14.5$ Hz, 1H), 4.33 (m, 1H), 4.13 (m, 2H), 3.36 (s, 1H), 2.91 (m, 1H), 2.69 (m, 1H), 2.33 (s, 3H) 1.99–0.80 (m, 29H), 0.21 (s, 3H), 0.13 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$); $\delta=218.6$, 142.6, 138.5, 136.8, 129.7, 128.9, 127.9, 127.5, 127.3, 109.0, 64.9, 62.1, 50.3, 44.4, 41.2, 39.8, 31.1, 29.7, 29.4, 26.9, 26.4, 26.3, 26.0, 21.3, 18.7, −3.5, −4.5; IR (film): $\nu_{max}=3500$, 1690, 1100 cm^{-1}; HR-MS (FAB+): *m/z* = 630.3648, calcd. for $C_{35}H_{55}NO_5SSi$ (M+H): 630.3648.

(5*S**,6*S**,7*R**)-6-Chloro-5-yloxy-(*tert*-butyl)-dimethylsilane-7-hydroxy-2,2-dimethyl-9-phenyl-nonan-3-one (46a)

Prepared from aldehyde **36** as described for **38** to afford **46a** as a colorless oil; yield: 16 mg (99%); *dr* 95:5 (*syn*:*anti*).

Major isomer **46a.** ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=7.13$ (m, 5H), 4.56 (ddt, $J=6.3$, 2.7, 1.2 Hz, 1H), 4.04 (dd, $J=11.0$, 5.4 Hz, 1H), 3.90 (dd, $J=5.5$. 1.2 Hz, 1H), 3.40 (d, $J=2.8$ Hz, 1H), 2.76 (dd, $J=6.2$, 5.7 Hz, 2H), 2.66 (ddd, $J=13.5$, 11.3, 5.1 Hz, 1H), 2.55 (ddd, $J=13.5$, 11.1, 6.0 Hz, 1H),

1.95 (m, 2H), 1.05 (s, 9H), 0.81 (s, 9H), 0.14 (d, $J=20.9$ Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=215.3$, 141.5, 129.3, 128.4, 128.3, 125.9, 74.8, 65.7, 65.4, 44.3, 41.4, 36.7, 30.3, 26.2, 25.8, 18.0, −4.5, −4.7; IR (film): $\nu_{max}=3436$ (br), 1702, 1644, 1255, 1095, 837, 777 cm^{-1}; HR-MS (FAB+): $m/z=427.2428$, calcd for $C_{23}H_{39}ClO_3Si$ (M+H): 427.2430.

(5*S**,6*S**,7*R**)-6-Chloro-5-yloxy-(*tert*-butyl)-dimethylsilane-7-hydroxy-2,2-dimethyl-9-phenylnonan-3-one (47a)

Prepared from aldehyde **37** as described for **38** to afford **47a** as a colorless oil; yield: 24 mg (94%); *dr* 91:9 (*syn*:*anti*).

Major isomer **47a**. ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta=7.25$ (m, 5H), 4.41 (m, 1H), 4.01 (dd, $J=4.7$, 2.7 Hz, 1H), 3.14 (d, $J=4.1$ Hz, 1H), 2.85 (m, 2H), 2.67 (m, 2H), 2.14 (s, 1H), 1.91 (m, 1H), 1.16 (s, 9H), 0.93 (s, 9H), 0.12 (d, $J=2.6$ Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta=215.2$, 141.5, 128.5, 128.3, 126.0, 74.8, 68.2, 68.1, 44.4, 41.4, 35.7, 31.2, 26.4, 26.2, 25.8, 18.1, −4.1, −4.4; IR (film): $\nu_{max}=3488$, 1703, 1255, 1095, 1072, 837, 778 cm^{-1}; HR-MS (FAB+): $m/z=427.2431$, calcd for $C_{23}H_{39}ClO_3Si$ (M+H): 427.2430.

Boron Enolate Addition to Aldehyde 1: (4*R*,5*S*/4*S*,5*R*)-6-Chloro-5-hydroxy-2,4,7-trimethyloctan-3-one (24a, 24b)

To a stirred solution of 2-methyl-3-pentanone (41 mL, 332 mmol) in Et_2O (0.6 mL) was added $(c\text{-Hex})_2BCl$ (349 mL, 1M in hexane) and Et_3N (51 mL, 365 mmol) at 0°C. The solution turned white and was stirred for 1 h before it was cooled down to −78°C and **1** (40 mg, 332 mmol) dissolved in Et_2O (0.4 mL) was added dropwise. The resultant mixture was stirred at −78°C for 2 h, allowed to warm up to 0°C and after 10 min. quenched by sequential addition of phosphate buffer pH 7 (1.5 mL), MeOH (1.5 mL) and H_2O_2 (1.5 mL). The mixture was stirred for additional 30 min at room temperature and diluted with buffer (5 mL) and CH_2Cl_2 (5 mL). The aqueous phase was extracted (CH_2Cl_2, 3×5 mL), the combined organic phases were washed (1:1 NaS_2O_3, 20 wt%, aqueous and $NaHCO_3$, saturated, aqueous), dried (Na_2SO_4) and concentrated to afford **24a** and **24b** as a colorless oil; yield: 30 mg (50%); *dr* 13:87 (*syn*:*anti*). The diastereomers were separated by flash chromatography (pentane:EtOAc 16:1).

Minor isomer **24a**. ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta=3.67$ (dd, $J=8.6$, 1.7 Hz, 1H), 4.03 (d, $J=7.9$, 1H), 3.06 (m, 1H), 2.74 (sept, $J=6.9$ Hz, 1H), 2.11 (m, 1H), 1.08 (m, 9H), 1.01 (m, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta=218.1$, 73.1, 71.8, 48.6, 41.1, 32.7, 20.8, 20.1, 18.0, 17.9, 13.9; HRMS (FAB+): $m/z=221.1302$, calcd. for $C_{11}H_{21}ClO_2$ (M+H): 221.1303.

Major isomer **24b**. ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta=3.99$ (s, 1H), 3.64 (dd, $J=10.1$, 2.3 Hz, 1H), 3.52 (d, $J=10.2$ Hz, 1H), 3.46 (dq, $J=7.4$, 2.8 Hz, 1H), 2.77 (sept, $J=6.9$ Hz, 1H), 2.54 (dsept, $J=6.7$, 2.32 Hz, 1H), 1.32 (d, $J=7.35$ Hz, 3H), 1.14 (d, $J=7.0$ Hz, 3H), 1.10 (d, $J=6.82$ Hz, 3H), 1.01 (d, $J=6.85$ Hz, 3H), 0.92 (d, $J=6.58$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta=223.1$, 76.3, 70.8, 43.3, 40.9, 28.8, 20.9, 18.1, 17.6, 15.7, 14.5; IR (film): $\nu_{max}=3413$ (br), 1641, 1065, 1025, 742 cm^{-1}; HR-MS (FAB+): $m/z=221.1302$, calcd for $C_{11}H_{21}ClO_2$ (M+H): 221.1303.

(4*R**,5*R**,6*S**)-6-Chloro-5-hydroxy-2,4,7-trimethyl-octan-3-one (25b)

To 2-methyl-3-pentanone (41 mL, 332 mmol) in Et_2O (0.6 mL) at 0°C was added 9-BBNOTf (730 mL, 0.5M in hexane) and DIPEA (69 mL, 398 mmol). The solution turned yellow and was allowed to reach room temperature and stirred for 1 h before it was cooled down to −78°C and **1** (40 mg, 332 mmol) dissolved in Et_2O (0.7 mL) was added dropwise. The resultant mixture was stirred at −78°C for 2 h, allowed to warm up to 0°C and after 10 min. quenched by sequential addition of phosphate buffer pH 7 (1.5 mL), MeOH (1.5 mL) and H_2O_2 (1.5 mL). The mixture was stirred for additional 30 min at room temperature, then diluted with buffer (5 mL) and CH_2Cl_2 (5 mL). The aqueous phase was extracted (CH_2Cl_2, 3×5 mL), the combined organic phases were washed (1:1 NaS_2O_3, 20 wt%, aqueous and $NaHCO_3$ saturated, aqueous), dried (Na_2SO_4) and concentrated. The residue was purified by flash chromatography (pentane:EtOAc 16:1) to afford **25b** as a colorless oil; yield: 61 mg (99%); *dr* 94:6 (*syn*:*anti*).

Major isomer **25b**. ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta=3.93$ (td, $J=10.1$, 1.7, 1.7 Hz, 1H), 3.77 (dd, $J=10.1$, 2.2 Hz, 1H), 3.61 (d, $J=1.9$ Hz, 1H), 3.35 (dq, $J=7.3$, 7.3, 7.3, 1.5 Hz, 1H), 2.82 (sept., $J=6.9$, 6.9, 6.9, 6.9, 6.9, 6.9 Hz, 1H), 2.46 (dtd, $J=13.4$, 6.7, 6.7, 2.2 Hz, 1H), 1.38–1.10 (m, 9H), 1.04 (d, $J=6.8$ Hz, 3H), 0.94 (d, $J=6.6$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta=221.3$, 71.1, 67.8, 43.9, 40.0, 28.1, 20.9, 18.7, 17.8, 14.5, 8.6; IR (film): $\nu_{max}=3451$ (br), 1681, 1090, 1017, 735 cm^{-1}; HR-MS (FAB+): $m/z=221.1301$, calcd for $C_{11}H_{21}ClO_2$ (M+H): 221.1303.

Sakurai Allylation Reaction of Aldehydes 28–37

The experimental procedure for Sakurai allylation of aldehyde **28** is representative for all aldehydes **28–37**.

(5*S**,6*R**)-5,6-Bis(benzyloxy)-8-phenyloct-1-en-4-ol (49a, 49b)

To a stirred solution of **28** (22.2 mg, 59.3 μmol) in CH_2Cl_2 (1 mL) was added $BF_3{\cdot}OEt_2$ (23 μL, 178 μmol) at −60°C. After 5 min. was added allyl trimethylsilane (19 μL, 119 μmol) and the resultant solution was stirred at −60°C for 18 h. The reaction was quenched by addition of H_2O (5 mL) and allowed to reach room temperature. The aqueous phase was extracted with CH_2Cl_2 (3×2.5 mL), dried ($MgSO_4$) and concentrated under reduced pressure. Flash chromatography (pentane:EtOAc 8:1) of the residue gave **49a** and **49b** as colorless oil; yield: 23.4 mg (95%); *dr* 87:13 (*syn*:*anti*).

Major isomer **49b**. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=7.27$ (m, 15H), 5.82 (m, 1H), 5.13 (m, 2H), 4.77 (d, $J=11.4$ Hz, 1H), 4.65 (dd, $J=11.4$, 8.5 Hz, 2H), 4.56 (d, $J=11.5$ Hz, 1H), 3.79 (m, 2H), 3.57 (dd, $J=6.6$, 3.6 Hz, 1H), 2.86 (m, 1H), 2.67 (m, 1H), 2.52 (m, 1H), 2.24 (m, 2H), 2.10 (ttd, $J=11.6$, 9.0, 4.5 Hz, 1H), 1.99 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=142.2$, 138.4, 138.3, 135.0, 128.43, 128.41, 128.36, 128.3, 127.95, 127.89, 127.70, 127.67, 125.7, 118.1, 81.9, 79.5, 73.63, 72.0, 71.0, 38.0, 32.2, 31.8; IR (film): $\nu_{max}=3428$ (br), 1640, 1454, 1095, 1071, 916 cm^{-1}; HR-MS (FAB+): $m/z=417.2423$, calcd. for $C_{28}H_{32}O_3$ (M+H): 417.2424.

(5*R**,6*S**)-5,6-Bis(benzyloxy)dodec-1-en-4-ol (50a, 50b)

Prepared from aldehyde **29** as described for **49** to afford **50a** and **50b** as a colorless oil; yield: 118 mg (93%); *dr* 84:16 (*syn*:*anti*).

Major isomer **50b**: ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.45$–7.29 (m, 10H), 5.95 (m, 1H), 5.23–5.13 (m, 2H), 4.78 (d, $J =$ 11.4 Hz, 1H), 4.70–4.54 (m, 3H), 3.85 (d, $J = 8.2$ Hz, 1H), 3.80–3.73 (m, 1H), 3.54 (dd, $J = 6.6$, 3.8 Hz, 1H), 2.65–2.55 (m, 1H), 2.38 (d, $J = 7.9$ Hz, 1H), 2.28 (dd, $J = 14.2$, 8.3 Hz, 1H), 1.82–1.69 (m, 2H), 1.58–1.46 (m, 1H), 1.44–1.25 (m, 7H), 0.93 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 138.4$, 135.2, 127.92, 127.88, 127.7, 127.6, 118.0, 82.2, 80.4, 73.6, 72.1, 71.3, 38.0, 31.8, 30.5, 29.5, 25.5, 22.6, 14.1; IR (film): $\nu_{max} = 3473$ (br), 1640, 1455, 1069, 914 cm^{-1}; HR-MS (FAB+): $m/z = 397.2742$, calcd. for $C_{26}H_{36}O_3$ (M+H): 397.2737.

(5*R**,6*R**)-5,6-Bis(benzyloxy)-8-phenyloct-1-en-4-ol (51a, 52b)

Prepared from aldehyde **30** as described for **49** to afford **51a** and **51b** as a colorless oil; yield: 5 mg (83%); *dr* 79:21 (*syn*:*anti*).

Mixture of isomers. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.32$–7.09 (m, 15H_{maj}, 15H_{min}), 5.89 (dddd, $J = 23.1$, 11.1, 7.7, 6.4 Hz, 1H_{min}), 5.78 (tdd, $J = 17.3$, 10.3, 7.1 Hz, 1H_{maj}), 5.12 (m, 2H_{min}), 5.05 (m, 2H_{maj}), 4.74 (AB-d, $J = 11.2$ Hz, 1H_{maj}), 4.64–4.43 (m, 3H_{maj}, 4H_{min}), 3.92 (ddd, $J = 11.1$, 7.7, 3.5 Hz, 1H_{min}), 3.77 (ddd, $J = 13.6$, 6.7, 3.2 Hz, 1H_{maj}), 3.69–3.61 (m, 1H_{maj}, 1H_{min}), 3.51–3.42 (m, 1H_{maj}, 2H_{min}), 2.84–2.73 (m, 1H_{maj}, 1H_{min}), 2.59 (m, 1H_{maj}, 1H_{min}), 2.67–2.52 (m, 1H_{maj}, 1H_{min}), 2.44 (dddd, $J = 14.3$, 6.3, 3.6, 1.6 Hz, 1H_{min}), 2.30 (dd, $J = 13.6$, 6.9 Hz, 2H_{maj}), 2.37–2.17 (m, 2H_{min}), 2.11–1.85 (m, 2H_{maj}, 2H_{min}); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 142.0$, 141.7, 138.4, 138.1, 137.9, 137.5, 135.1, 134.8, 128.51, 128.46, 128.49, 128.44, 128.41, 128.38, 128.33, 128.1, 128.0, 127.9, 127.8, 127.7, 125.9, 125, 117.5, 117.2, 81.0, 78.8, 78.6, 78.4, 74.4, 73.0, 72.9, 72.4, 70.7, 70.2, 39.3, 38.1, 32.5, 31.95, 31.86, 31.0; IR (film): $\nu_{max} = 3452$ (br), 1640, 1454, 1067, 915 cm^{-1}; HR-MS (FAB+): $m/z = 417.2424$, calcd. for $C_{28}H_{32}O_3$ (M+H): 417.2430.

(5*R**,6*R**)-5,6-Bis(benzyloxy)dodec-1-en-4-ol (52a, 52b)

Prepared from aldehyde **31** as described for **49** to afford **52a** and **52b** as a colorless oil; yield: 122 mg (87%); *dr* 67:33 (*syn*:*anti*).

Mixture of isomers. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.38$–7.22 (m, 10H_{maj}, 10H_{min}), 5.95–5.86 (m, 1H_{min}), 5.85–5.76 (m, 1H_{maj}), 5.14–5.03 (m, 2H_{maj}, 2H_{min}), 4.81 (AB-d, $J = 11.3$, 1H_{maj}), 4.67–4.51 (m, 3H_{maj}, 4H_{min}), 3.92 (m, 1H_{min}), 3.75 (m, 1H_{maj}), 3.63 (m, 1H_{maj}, 1H_{min}), 3.43 (dd, $J = 7.3$, 3.9 Hz, 1H_{min}), 3.40 (dd, $J = 6.0$, 3.2 Hz, 1H_{maj}), 3.30 (d, $J = 3.4$ Hz, 1H_{min}), 2.44 (m, 1H_{min}), 2.35–2.20 (m, 2H_{maj}, 2H_{min}), 1.75–1.49 (m, 2H_{maj}, 1H_{min}), 1.47–1.36 (m, 1H_{maj}, 1H_{min}), 1.35–1.16 (m, 7H_{maj}, 7H_{min}), 0.88 (m, 3H_{maj}, 3H_{min}); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 138.6$, 138.3, 135.2, 134.9, 128.44, 128.42, 128.3, 128.2, 128.02, 128.00, 127.98, 127.9, 127.8, 127.6, 117.4, 81.6, 79.9, 79.5, 79.1, 74.6, 73.2, 72.9, 72.4, 70.6, 70.5, 39.2, 38.2, 31.8, 31.7, 30.8, 29.4, 29.3, 26.0, 25.6, 22.6, 14.1; IR (film): $\nu_{max} = 3451$ (br), 1640, 1455, 1069, 915 cm^{-1}; HR-MS (FAB+): $m/z = 397.2737$, calcd. for $C_{26}H_{36}O_3$ (M+H): 397.2737.

(3*R**,4*S**,5*S**)-4-*N*-Benzyl-*N*-tosylamino-1-phenyloct-7-ene-3-yloxy-(*tert*-butyl)dimethylsilane-5-ol (53a, 53b)

Prepared from aldehyde **32** as described for **49** to afford **53a** and **53b** as a colorless oil; yield: 37 mg (67%); *dr* 87:13 (*syn*:*anti*).

Major isomer **53b**. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.70$ (d, $J = 8.2$, 2H), 7.38 (d, $J = 7.3$, 2H), 7.24 (m, 10H), 5.61 (tdd, $J = 17.0$, 10.1, 6.9 Hz, 1H), 5.02 (dd, $J = 10.3$, 1.1 Hz, 1H), 4.93 (dd, $J = 17.1$, 1.4 Hz, 1H), 4.73 (d, $J = 15.6$ Hz, 1H), 4.39 (d, $J = 15.6$ Hz, 1H), 4.01 (br s, 1H), 3.89 (br s, 1H), 3.68 (br s, 1H), 3.09 (br s, 1H), 2.75 (dt, $J = 12.8$, 4.6, 1H), 2.56 (dt, $J = 12.9$, 4.1 Hz, 1H), 2.43 (s, 3H), 2.10 (m, 2H), 1.93 (m, 1H), 1.63 (m, 1H), 0.88 (s, 9H), −0.00 (s, 3H), −0.01 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 143.6$, 142.1, 137.8, 135.1, 129.7, 128.5, 128.5, 128.3, 127.6, 127.4, 125.7, 117.0, 73.3, 72.6, 40.1, 36.0, 28.8, 25.9, 21.4, 18.0, −3.8, −4.6; IR (film): $\nu_{max} = 3478$ (br), 1341, 1160, 836, 778 cm^{-1}; HR-MS (FAB+): $m/z = 616.2887$, calcd. for $C_{34}H_{47}NO_4SSi$ (M+Na): 616.2893.

(3*R**,4*S**,5*S**)-4-Chloro-1-phenyloct-7-ene-3-yloxy-[(*tert*-butyl)dimethylsilane]-5-ol (55a, 55b)

Prepared from aldehyde **36** as described for **49** to afford **55a** and **55b** as a colorless oil: yield: 12 mg (88%); *dr* 40:60 (*syn*:*anti*).

Mixture of isomers. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.25$ (m, 1H), 5.88 (dddd, $J = 16.8$, 10.3, 7.9, 6.3 Hz, 1H_{min}), 5.78 (m, 1H_{maj}), 5.22–5.12 (m, 2H_{maj}, 2H_{min}), 4.17–4.10 (m, 2H_{maj}, 1H_{min}), 3.97–3.91 (m, 2H_{maj}, 1H_{min}), 2.85 (d, $J = 5.0$ Hz, 1H_{maj}), 2.76 (ddd, $J = 13.4$, 11.6, 5.5 Hz, 1H_{min}), 2.66 (m, 2H_{maj}), 2.58 (m, 1H_{min}), 2.49–2.40 (m, 1H_{maj}, 1H_{min}), 2.35–2.27 (m, 1H_{maj}, 1H_{min}), 2.14–2.05 (m, 1H_{maj}, 1H_{min}), 1.98–1.87 (m, 1H_{maj}, 1H_{min}), 0.94 (s, 9H_{min}), 0.93 (s, 9H_{maj}), 0.16–0.12 (m, 6H_{maj}, 1H_{min}); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta =$ 141.8, 141.5, 133.9, 133.8, 129.3, 128.5, 128.4, 128.3, 128.2, 126.0, 125.9, 118.6, 118.2, 74.5, 74.0, 71.5, 68.9, 66.8, 65.7, 39.3, 37.7, 36.5, 35.9, 30.6, 30.4, 25.8, 18.1, 18.0, −4.2, −4.4, −4.5, −4.7; IR (film): $\nu_{max} = 3449$ (br), 1645, 1457, 1257, 1083, 919, 837, 777 cm^{-1}; HR-MS (FAB+): $m/z = 369.2013$, calcd. for $C_{20}H_{33}ClO_2Si$ (M+H): 369.2011.

(3*R**,4*S**,5*S**)-4-Chloro-1-phenyloct-7-ene-3-yloxy-[(*tert*-butyl)dimethylsilane]-5-ol (56a, 56b)

Prepared from aldehyde **37** as described for **49** to afford **56a** and **56b** as a colorless oil: yield: 21 mg (95%); *dr* 59:41 (*syn*:*anti*).

Mixture of isomers. ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 7.23$–7.16 (m, 5H_{maj}, 5H_{min}), 5.90 (dddd, $J = 16.6$, 10.3, 8.1, 6.2 Hz, 1H_{maj}), 5.79 (tdd, $J = 17.2$, 10.2, 7.1 Hz, 1H_{min}), 5.21–5.17 (m, 2H_{maj}, 2H_{min}), 4.15 (ddd, $J = 7.7$, 4.5, 3.0 Hz, 1H_{maj}), 4.03–3.91 (m, 1H_{maj}, 3H_{min}), 3.78 (dd, $J = 9.2$, 2.9 Hz, 1H_{maj}), 3.27 (d, $J = 2.6$ Hz, 1H_{min}), 2.76 (ddd, $J = 13.5$, 11.4, 5.3 Hz, 1H_{maj}), 2.70–2.55 (m, 2H_{maj}, 2H_{min}), 2.48 (d, $J = 5.3$ Hz, 1H_{min}), 2.40–2.27 (m, 1H_{maj}, 1H_{min}), 2.25–2.11 (m, 1H_{maj}, 1H_{min}), 1.91 (m, 2H), 0.93 (s, 9H_{maj}), 0.92 (s, 9H_{min}), 0.14 (d,

$J = 6.9$ Hz, $6H_{maj}$), 0.11 (d, $J = 4.9$ Hz, $6H_{min}$); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 141.4$, 133.8, 133.7, 128.5, 128.3, 126.0, 118.5, 118.4, 74.5, 74.2, 71.3, 70.8, 68.0, 63.5, 39.5, 38.8, 35.5, 34.1, 32.4, 31.5, 25.82, 25.79, 18.1, 18.0, −4.0, −4.4, −4.5; IR (film): $\nu_{max} = 3471$ (br), 1602, 1462, 1256, 1090, 997, 837, 777 cm^{-1}; HR-MS (FAB+): $m/z = 369.2009$, calcd. for $C_{20}H_{33}ClO_2Si$ (M+H): 369.2011.

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