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Reversal of the Facial Diastereoselectivity in the Paternò-Büchi Reaction of Silyl Enol Ethers Carrying a Chiral Substituent in α-Position

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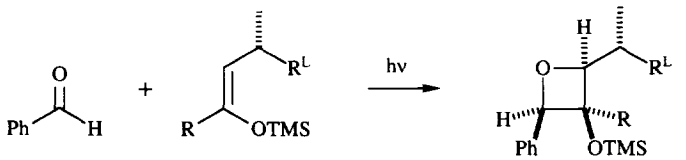
Abstract: The facial diastereoselectivity in the Paternò-Büchi reaction of benzaldehyde and silyl enol ethers **1** which bear a chiral substituent R* in α-position has been studied. Since the regioselectivity and the simple diastereoselectivity of the photocycloaddition is very good only two diastereoisomers are obtained whose ratio reflects the facial diastereoselectivity. With the silyloxy substituted substrates **1a-1c** the selectivity is low (d.r. = <60/40). The benzyloxy substitued silyl enol ether **1d** (R* = CHOB*n*i-Pr), however, exhibits already a significant degree of diastereofacial selection and yields preferentially the oxetane **2d** (d.r. = 67/33). If the benzyloxy substituent in the substrate is replaced by a chlorine atom (R* = CHCl*i*-Pr) the direction of the facial diastereoselecitivity is reverted. Thus, the reaction of silyl enol ether **1e** with benzaldehyde gives preferentially oxetane **3e** (d.r. = 85/15). Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

The problem of acyclic stereoselection has been of central importance to Organic Synthesis during the last decades. A wide array of reactions has been shown to proceed with excellent facial diastereoselectivity if the substrate and the reaction conditions are well tuned.[2] Constant progress concerning the acyclic stereoselection has also been made in the area of photochemical synthesis.[3] In several instances it has been demonstrated that a transformation can be highly stereoselective if the appropriate stereogenic device is properly placed in either one of the substrates. On the contrary, there are still many examples of the very same reaction which lack almost any diastereoselectivity even if the the newly formed bonds are adjacent to a stereogenic center. A point in case is the well known photocycloaddition of a carbonyl compound to an alkene, the so called Paternò-Büchi reaction,[4] whose intermolecular variant appears well suited to study the facial stereoselection on prostereogenic sp^2 carbon atoms.

Perfect stereoselection induced by a concave chiral auxiliary attached to the carbonyl component has been reported for this transformation.[5] Moreover, we have recently shown that silyl enol ethers which carry a chiral substituent in β-position smoothly add to aromatic aldehydes yielding mainly one out of eight possible stereoisomers (scheme 1).[6] The 1,3-allylic strain exerted by the TMSO-group at the double bond was identified as the reason for the observed preference. It acts as a conformational lock for the chiral substituent orienting the hydrogen atom and the double bond synperiplanar to each other. The attack of a photoexcited aldehyde occurs

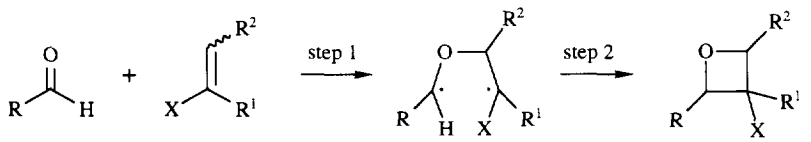
from the side of the small methyl group. The relative configuration within the ring framework is determined by previously encountered selection steps.[7]



R^L = Ph, *t* Bu, OMe, $SiMe_2Ph$ 44-70%

Scheme 1.

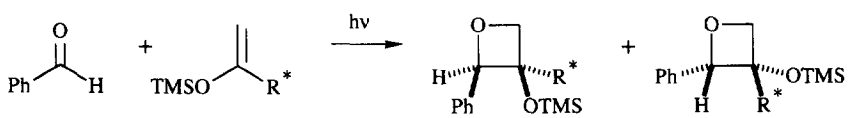
In strong contrast to the above-mentioned successful results any attempts to induce a significant facial diastereoselectivity by a single stereogenic center attached to the carbonyl carbon or to the α-carbon of the alkene have failed so far.[8] Considering a 1,4-biradical as likely intermediate[9] it becomes clear that the stereoselection occurs either in the course of the C–O bond formation (step 1) or at the ring closure step (step 2) (scheme 2).



Scheme 2.

If R^2 = H the ring closure step and the competing retrocleavage (step 2) are the only decisive parameters for the stereoselection. If R^2 and X are connected, i.e. in cyclic alkenes, the C–O-bond formation (step 1) can be of prime importance as pointed out by Schreiber.[8b] The 1,4-relationship of a stereogenic center (R = R*) to this bond has been considered responsible for low stereoselectivities in the Paternò-Büchi reaction of chiral aldehydes and furan.

In the following study chiral silyl enol ethers **1** were used which have no β-substituent. For these substrates the formal recombination of two radical centers determines the facial and the simple diastereoselectivity. From previous results it was to be expected that the phenyl group of the former benzaldehyde and the TMSO group of the silyl enol ether will end up *cis* to each other in the product oxetane.[10] Only two diastereomers **2** and **3** should therefore be formed whose ratio can be directly correlated to the facial diastereoselectivity exerted by the stereogenic center in α-position of the silyl enol ether (scheme 3).

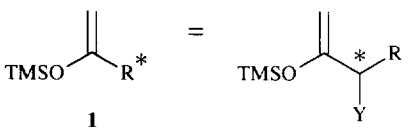


1 **2** **3**

Scheme 3.

RESULTS AND DISCUSSION

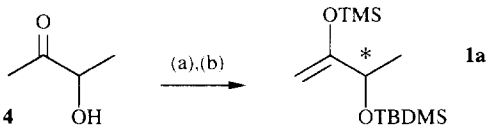
Scope of the Study. The silyl enol ethers employed in this work were to carry a chiral substituent in α-position. Based on experimental and theoretical work concerning the conformational restrictions in chiral radicals (*vide infra)* we considered a polar group at the stereogenic center to be a promising control element. A hydrogen atom and an alkyl or aryl group were chosen as the other substituents. Five different silyl enol ethers **1a**-**1e** (scheme 4) of this type were tested in their photocycloaddition to benzaldehyde.



a	Y = OTBDMS	R = Me
b	Y = OTBDMS	R = Ph
c	Y = OTMS	R = Ph
d	Y = OBn	R = *i* Pr
e	Y = Cl	R = *i* Pr

Scheme 4.

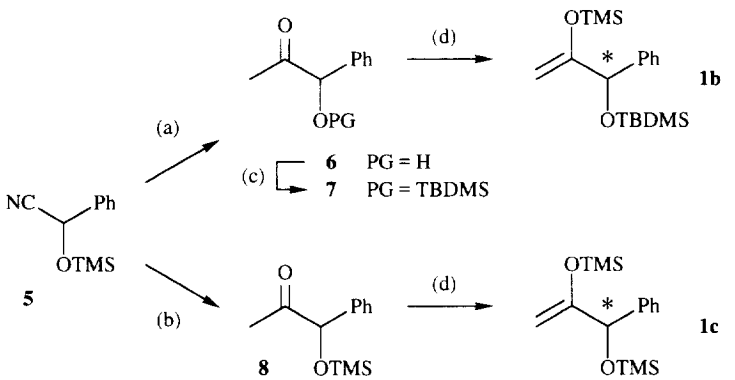
Preparation of Starting Materials. Silyl enol ether **1a** was prepared in a straightforward manner from acetoin **4** by simple protection[11] and conventional silylation of the enolate[12] formed by kinetically controlled deprotonation (scheme 5).



(a) TBDMSCl, im, 25°C (DMF), 80%. (b) LDA, TMSCl, -78°C → 25°C (THF), 84%.

Scheme 5.

The construction of silyl enol ethers **1b** and **1c** commenced with a Grignard addition to the readily available TMS-protected cyanohydrin **5**[13] of benzaldehyde. Depending on the work-up conditions either the alcohol **6**[13] or the silyl ether **8**[13] were obtained. The transformation of ketone **6** to the corresponding silyl enol ether **1b** proceeded smoothly via the TBDMS-protected intermediate **7**.

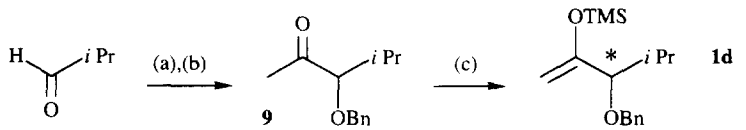


(a) MeMgI, 30°C (Et_2O), H_2O (pH = 1), 22%. (b) MeMgI, 30°C (Et_2O), H_2O (pH = 7), 40%.
(c) TBDMSCl, im, 25°C (DMF), 63%. (d) LDA, TMSCl, -78°C → 25°C (THF), **1b**: 98%, **1c**: 35%.

Scheme 6.

Disappointingly, the formation of silyl enol ether **1c** turned out to be sluggish and the yield was low. Since we were primarily interested in the consecutive reaction of compound **1c** we did not attempt a possible optimization of the reaction conditions (scheme 6).

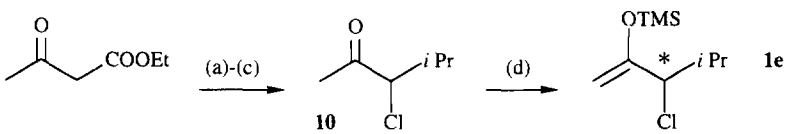
Another Grignard reaction served as an entry for the synthesis of alkene **1d** (scheme 7). The pre-requisite nitrile[14] was obtained from *i*-butyraldehyde by a known procedure and was subsequently converted to ketone **9**. Further transformation by the standard protocol yielded silyl enol ether **1d** without complications.



(a) KCN, BnBr, Et_3NBnCl, 40°C (CH_2Cl_2/H_2O), 53%. (b) MeMgI, -10°C → 40°C (Et_2O), 75%.
(c) LDA, TMSCl, -78°C → 25°C (THF), 94%.

Scheme 7.

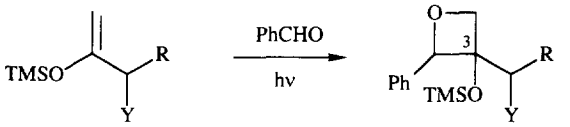
In attempts to synthesize silyl enol ether **1e** from ketone **10**[15] we had to struggle with the anticipated instability of the intermediate enolate (Favorski rearrangement) and the insufficient regioselectivity of the deprotonation step. The latter problem was partially overcome using lithium 2,2,6,6-tetramethylpiperidide (LTMP) as base which resulted in a ratio of 85/15 in favor of the desired regioisomer (scheme 8). The former problem remained unsolved and lowered the yield significantly even while using TMSCl as an *in situ* trapping reagent. Ketone **10** was generated from ethyl acetoacetate by an alkylation, chlorination, decarboxylation sequence.[15]



(a) *i* PrI, NaOH, NBu_4HSO_4, 25°C ($CHCl_3/H_2O$), 74%. (b) $SOCl_2$, 25°C (CH_2Cl_2), 88%.
(c) H_2SO_4, 100°C (H_2O), 53%. (d) LDA, TMSCl, -78°C → 25°C (THF), 36%.

Scheme 8.

Photocycloaddition Experiments. With a representative array of silyl enol ethers in hand we began the irradiation experiments employing benzaldehyde as the carbonyl compound. The reactions were conducted either at -25°C in a liquid-cooled immersion apparatus (radiation source: Original Hanau TQ 150; solvent: *n*-hexane) or at 30°C in an air-cooled chamber reactor (radiation source: Rayonet RPR 3000; solvent: benzene). The photocycloaddition of the silyl substituted substrates **1a-1c** proceeded nicely and yielded the desired oxetanes with perfect regio- and simple diastereoselectivity. As expected only two diastereoisomers (**2a-2c** and **3a-3c**) were formed. In no case, however, did one of the two isomers prevail over the other to a significant extent (Table 1). Due to the low facial diastereoselectivity no attempt was undertaken to elucidate the relative configuration of the products.



1a-1c **2a/3a-2c/3c**

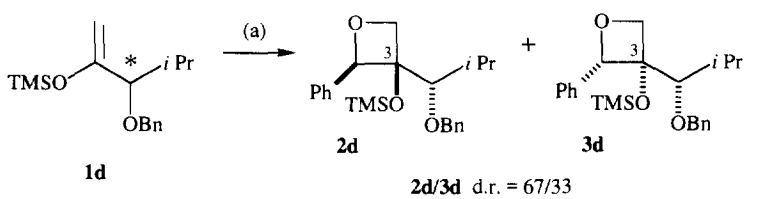
Scheme 9.

Table 1: Facial Diastereoselectivity in the Paternò-Büchi Reaction of Chiral Silyl Enol Ethers (cf. scheme 9)

Alkene	Y	R	Temp. [°C]	Solvent	Products	Yield [%]	d.r.
1a	OTBDMS	Me	-25	*n*-hexane	**2a,3a**	56	57/43
1a	OTBDMS	Me	30	PhH	**2a,3a**	67	55/45
1b	OTBDMS	Ph	-25	*n*-hexane	**2b,3b**	66	51/49
1b	OTBDMS	Ph	30	PhH	**2b,3b**	60	53/47
1c	OTMS	Ph	30	PhH	**2c,3c**	58	51/49

The situation changed when we studied the benzyloxy-substituted silyl enol ether **1d**. At -25°C there was a clear-cut preference for a major oxetane product **2d** (d.r. = 67/33) which could be isolated in diastereomerically pure form (scheme 10). The diastereomeric ratio of the crude product mixture decreased at higher temperature (d.r. = 59/41 at 30°C).

Subsequent degradation (*vide infra*) of compound **2d** proved the stereochemical relationship of the exocyclic stereogenic center and the carbon C(3) within the ring. As the relative configuration of the stereogenic ring carbon atoms is well established by previous work structure **2d** represents the major and **3d** the minor diastereoisomer.



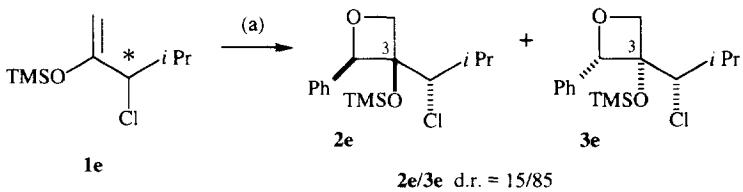
1d **2d** **3d**

2d/3d d.r. = 67/33

(a) PhCHO, hv, -25°C (*n* hexane), 35%.

Scheme 10.

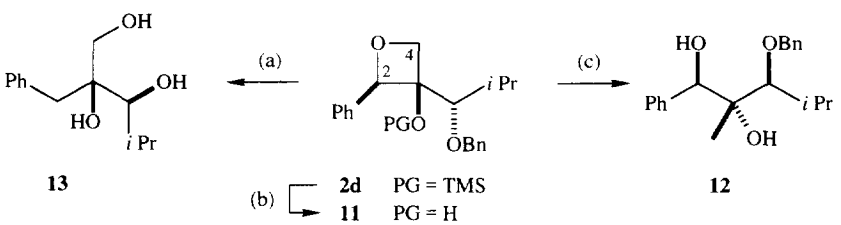
It was a pleasant surprise that the yet unprecedented facial diastereoselectivity encountered with alkene **1d** could seemingly be increased by employing the chloro-substituted olefin **1e**. By irradiation of this substrate at 30°C essentially a single diastereoisomer was isolated which was detected in the crude product mixture together with its epimer in a ratio of 85/15 (scheme 11). The result which we obtained from the structure elucidation was stunning. NOE studies (^{1}H NMR) on a degradation product strongly suggest that the relative configuration of the exocyclic stereogenic center and the oxetane's C(3) in the major product is *opposite* to the one established for oxetane **2d**. In other words, the direction of the facial diastereoselecitivity has been reverted by changing the polar substituent at the stereogenic center from OBn to Cl.



(a) PhCHO, hv, 30°C (PhH), 28%.

Scheme 11.

Proof of Relative Configuration and Ring Opening Experiments. Initially, we intended to prove the relative configuration of the oxetanes by X-ray crystallography. Since the silyloxyoxetanes **2d/3d** and **2e/3e** did not solidify but remained liquid further transformations were required to obtain crystalline material. For oxetane **2d** two standard methods frequently used in our laboratories were applied. The directed reductive ring opening at C(4)[16] of oxetanol **11** occurred readily and yielded the diol **12** which contains three contiguous stereogenic centers two of which were formed in the course of the photocycloaddition. Hydrogenolysis[17] of oxetane **2d** resulted in the anitcipated cleavage between oxygen and the C(2) carbon. The benzyl group was simultaneously removed and triol **13** was isolated in good yield (scheme 12).



(a) H_2, 1 atm, Pd/C, 25°C (MeOH), 69%. (b) K_2CO_3, 25°C (MeOH), 89%. (c) $LiAlH_4$, 25°C (THF), 82%.

Scheme 12.

The latter material gave crystals suited for X-ray crystallography.[18] The structure depicted in figure 1 reveals the (*SR,SR*) relationship of the two remaining stereogenic centers and unambiguously proves the relative configuration of oxetane **2d** (*vide supra*).

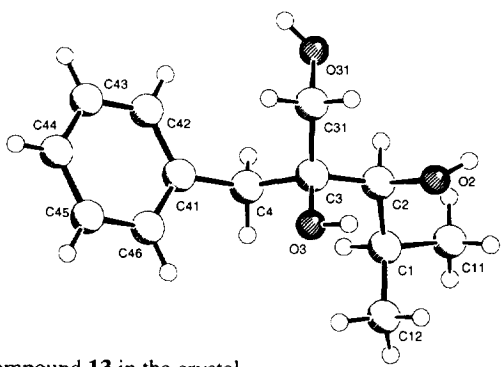
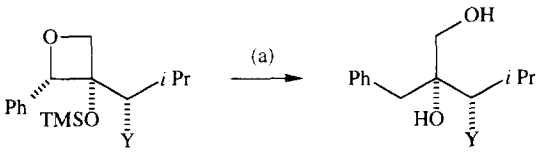


Figure 1. A molecule of compound **13** in the crystal

The hydrogenolysis of the minor diastereoisomer **3d** turned out to be sluggish and resulted in a low yield of triol **14**. The chloro-substituted product **3e** resisted all attempts to receive crystals from a degradation product. A hydrogenolysis was carried out as described above leading to diol **15** which in turn was transformed to various protected derivatives. None of these substances gave material suited for X-ray crystallography (scheme 13).



3d Y = OBn **14** Y = OH (43%)
3e Y = Cl **15** Y = Cl (62%)

(a) H_2, 1 atm, Pd/C, 25°C (MeOH).

Scheme 13.

Therefore we have to rely on NOE studies[19] (^{1}H NMR, 600 MHz) which were conducted on the epoxide **16**. This intriguing spiro compound can be readily generated form the major diastereomeric oxetane **3e** upon treatment with K_2CO_3 in MeOH.

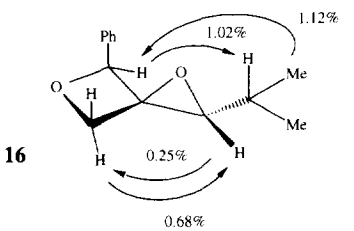
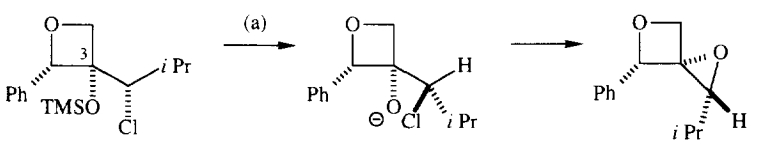


Figure 2. NOE data of epoxide **16**

Its formation can be rationalized by a deprotection of the silyl group in the course of which a tertiary alkoxide **17** is formed (scheme 14). Nucleophilic displacement of the chloride occurs in an S_N2 fashion with inversion at the stereogenic center. The structure depicted in figure 2 consequently points towards the initial relative configuration as already mentioned.



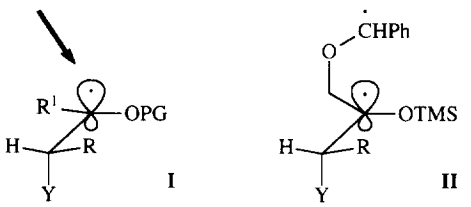
3e **17** **16**

(a) K_2CO_3, 25°C (MeOH), 66%.

Scheme 14.

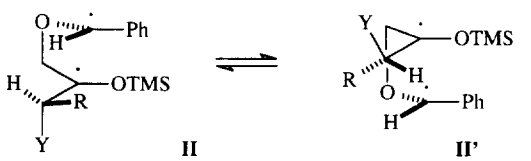
It is unfortunate that we were not able to isolate a sufficient quantity of the minor diastereoisomeric oxetane **2e** in order to make the diastereomer of compound **16** available. However, the observed NOE signals are unambiguous proof for the relative configuration in epoxide **16**, i.e. for the *cis*-relationship of the *i*-propyl group and the carbon atom C(2) of the oxetane and for the *cis*-relationship of the carbon atom C(4) and the hydrogen atom.

Discussion. In various abstraction and addition reactions of radicals **I** (scheme 15) which carry an α-silyloxy or an α-acyloxy group (Y) and which bear a stereogenic center in α-position good facial diastereoselectivity has been recorded.[20] The observations have led to the formulation of two general rules for radical chemistry which are analogous to the Felkin-Anh and the Cram model for conventional carbonyl addition reactions.[21] Accordingly, the best electron accepting substituent Y adopts a synperiplanar position to the radical's SOMO and an attack at the nucleophilic radical occurs antiperiplanar to this substituent Y at an angle of roughly 105° relative to the plane defined by the three substituents on the radical center. Indeed, ESR measurements reveal a preference for this confirmation in the ground state and suggest a certain degree of s-character for the SOMO. In the early transition state of these radical reactions the conformational situation is considered to resemble the one in the ground state.



Scheme 15.

It is tempting to project this situation to the described Paternò-Büchi reactions. If one does so the arrangement **II** for a 1,4-biradical can be identified as most favorable. The heteroatom adopts the position synperiplanar to the SOMO and the bulky substituents R and CH_2OCHPh are oriented in an antiperiplanar fashion. However, the mechanistic scheme is more complex. The intermediate biradical is a triplet species and has to undergo an intersystem crossing (ISC) before oxetane formation can occur. In addition, a competition between retrocleavage and ring closure may intervene in the process of facial diastereoselection. In the restricted environment of the biradical the angle under which the two radical centers approach each other plays an important role. Assuming that the attacking angle is less than 90° the conformation **II** depicted above leads to a severe interaction between R and the hydrogen atom on the former carbonyl carbon. In this case the retrocleavage may be predominant and even if conformation **II'** is less populated it may still lead to the major diastereoisomer (scheme 16).



Scheme 16.

Based on the experimental data the configuration of the major diastereomeric oxetane **2d** can be traced back to conformation **II** depicted in scheme 16 whereas the major product **3e** results from a preferred arrangement **II'**. As can be seen from the above discussion some factors which may contribute to the selection are difficult to address. The role of possible preferred ISC geometries which have been successfully applied to explain the simple diastereoselectivity of some Paternò-Büchi reactions remains obscure.[22] Even if the angle of approach

acts as a selectivity determining device the reason why the angles are different is not obvious. Only a combination of theoretical methods and further practical work may lead to a conclusive proposal.

EXPERIMENTAL

General. All reactions involving water sensitive chemicals were carried out in flame-dried glassware with magnetic stirring under Ar. Chemicals and solvents for this kind of reactions were distilled from an appropriate drying agent. Irradiation experiments were performed in degassed solvents under Ar. Common solvents (cyclohexane, ethyl acetate, pentane, ether) used for chromatography were distilled prior to use. All other reagents and solvents were used as received. - Melting points: Reichert hot bench (uncorrected). - IR: Perkin Elmer 1605 FT or Perkin Elmer 298. - MS: Varian Saturn II ion trap instrument (GC/MS), Finnigan MAT 8230 (GC/MS) or Finnigan MAT 312. - ^{1}H and ^{13}C NMR: Varian U-600 unity, Bruker AM-400, Bruker AM-360 or Bruker WM-300. Chemical shifts are reported relative to tetramethylsilane as an internal reference. $CDCl_3$ was used as solvent unless noted otherwise. The multiplicities of the ^{13}C NMR signals were determined with DEPT puls sequences. - Elemental analyses: Perkin Elmer 240. - TLC: glass-backed plates (Merck 0.25 mm silica gel 60-F); eluent given in brackets, a cyclohexane (CH) / ethyl acetate (EA) mixture was used unless stated otherwise; detection by UV or by coloration with ceric ammonium molybdate (CAM). - Flash chromatography[23] (FC): Merck silica gel 60 (230-400 mesh) (50 g for 1 g of material to be separated). - Column chromatography (CC): Merck silica gel 60 (70-230 mesh) or Woelm aluminum oxide neutral (activity II).

1-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]-1-phenyl-2-propanone (7). To a solution of 22 mmol hydroxyketone **6**[13] (3.1 g) in 25 ml DMF 30 mmol TBDMSCl (4.5 g) and 80 mmol imidazole (5.5 g) were added. The mixture was stirred for 3 d at room temperature and subsequently hydrolyzed with a sat. $NaHCO_3$ solution (50 ml). The organic layer was separated and the aqueous layer was extracted with ether (3 x 15 ml). The combined organic layers were washed with brine (30 ml), dried over $MgSO_4$ and filtered. After removal of the solvent *in vacuo* the residue was purified by chromatography (FC, CH/EA = 98/2). Yield: 3.59 g (63%). - R_f = 0.46 (90/10). - IR (film): $\tilde{\nu}$ = 3005 cm^{-1} (w), 2955 (s), 2840 (sh), 1710 (s), 1250 (m), 860 (sh), 830 (vs), 770 (s), 690 (m). - ^{1}H NMR (300 MHz): δ = 0.00 (s, 3 H, $SiCH_3$), 0.09 (s, 3 H, $SiCH_3$), 0.95 [s, 9 H, $SiC(CH_3)_3$], 2.10 (s, 3 H, CH_3), 5.04 (s, 1 H, CH), 7.33-7.41 (m, 5 H, arom. H). - ^{13}C NMR (75.5 MHz): δ = -5.2 (q, $SiCH_3$), -5.0 (q, $SiCH_3$), 18.2 [s, $SiC(CH_3)_3$], 23.8 (q, CH_3), 25.7 [q, $SiC(CH_3)_3$], 81.2 (d, CH), 125.8 (d, $C_{ar}H$), 128.0 (d, $C_{ar}H$), 128.4 (d, $C_{ar}H$), 138.6 (s, C_{ar}), 208.8 (s, CO). - MS (EI), *m/z* (%): 249 (5) [M$^+$ - Me], 221 (55) [M$^+$ - MeCO], 207 (50) [M$^+$ - *t*-Bu], 163 (10), 149 (10), 73 (100) [$SiMe_3^+$], 59 (10). - $C_{15}H_{24}O_2Si$ (264.4): Calc. C 68.13, H 9.15; found. C 67.91, H 9.18.

3-Benzyloxy-4-methyl-2-pentanone (9). A solution of 0.10 mol 2-benzyloxy-3-methyl-butyronitrile[14] (18.9 g) in 50 ml of ether was added at -10°C to 40 ml of a 4.0 M solution of MeMgI in ether (0.16 mol) within 10 min. After stirring at this temperature for another 15 min the mixture was refluxed for 2 h. It was subsequently hydrolyzed with an ice cold 2 N HCl solution (200 ml) and the organic layer was separated. The aqueous layer was extracted with ether (2 x 50 ml). The combined organic layers were washed with a sat. $NaHCO_3$-solution (50 ml) and with brine (100 ml). After drying over $MgSO_4$ and filtration the solvent was removed *in vacuo* and

the residual oil was distilled. Yield: 15.4 g (75%). - b.p.: 78°C (0.6 mbar). - R_f = 0.34 (90/10). - IR (film): $\tilde{\nu}$ = 3020 cm^{-1} (w), 2950 (m), 2850 (sh), 1700 (s), 730 (m), 690 (m). - ^1H NMR (300 MHz): δ = 0.90 (d, 3 H, ^3J = 6.8 Hz, CHCH_3), 0.98 (d, 3 H, ^3J = 6.8 Hz, CHCH_3), 2.00 (dsept, 1 H, ^3J = 6.8 Hz, ^3J = 6.8 Hz, CHMe$_2$), 2.15 (s, 3 H, CH_3CO), 3.43 (d, 1 H, ^3J = 6.8 Hz, CHO), 4.38 (d, 1 H, ^2J = 11.9 Hz, CHHPh), 4.59 (d, 1 H, ^2J = 11.9 Hz, CHHPh), 7.30-7.39 (m, 5 H, arom. H). - ^{13}C NMR (75.5 MHz): δ = 18.1 (q, CHCH$_3$), 18.6 (q, CHCH$_3$), 25.8 (q, CH$_3$CO), 30.9 (d, CHMe$_2$), 72.8 (t, CH$_2$Ph), 90.5 (d, CHO), 127.8 (d, C$_{ar}$H), 128.4 (d, C$_{ar}$H), 137.6 (s, C$_{ar}$), 211.5 (s, CO). - MS (EI), *m/z* (%): 163 (15) [M$^+$ - *i*-Pr], 91 (100) [$C_7H_7^+$], 65 (12), 43 (22) [$C_3H_7^+$]. - $C_{13}H_{18}O_2$ (206.3). Calc. C 75.69, H 8.79; found C 75.49, H 8.76.

3-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]-2-[(trimethylsilyl)oxy]-1-butene (1a). At 0°C 7.5 ml of a 1.7 M solution of n-BuLi (13 mmol) in hexane was added slowly to a solution of 13.0 mmol diisopropylamine (1.31 g, 1.81 ml) in 60 ml of THF. After stirring for 10 min at 0°C the LDA solution was cooled to -78°C and 16.0 mmol chlorotrimethylsilane (1.74 g, 2.02 ml) was slowly added followed by 13 mmol of TBDMS-protected acetoin[11] (2.6 g). After another 30 min the mixture was warmed to room temperature and the solvent was removed *in vacuo*. The residue was filtered and the filter was washed thoroughly with pentane. The solvent was removed and the procedure (filtration, washing, solvent removal) was repeated until a clear solution resulted. This solution was further purified by distillation in a Kugelrohr apparatus. Yield: 1.97 g (84%). - b.p.: 140°C (18 mbar). - R_f = 0.60 (90/10) - IR (film): $\tilde{\nu}$ = 2950 cm^{-1} (m), 2850 (m), 1630 (m), 1250 (s), 1020 (m). - ^1H NMR (300 MHz): δ = 0.06 [s, 6 H, Si(CH$_3$)$_2$], 0.21 [s, 9 H, Si(CH$_3$)$_3$], 0.91 [s, 9 H, SiC(CH$_3$)$_3$], 1.24 (d, 3 H, ^3J = 6.0 Hz, CHCH_3), 4.01 (q, 1 H, ^3J = 6.0 Hz, CHCH$_3$), 4.08 (d, 1 H, ^2J = 1.0 Hz, CHH), 4.41 (d, 1 H, ^2J = 1.0 Hz, CHH). - ^{13}C NMR (75.5 MHz): δ = -5.1 (q, SiCH$_3$), -4.9 (q, SiCH$_3$), 0.1 [q, Si(CH$_3$)$_3$], 18.2 (s, SiCMe$_3$), 22.4 (q, CHCH$_3$), 25.8 [q, SiC(CH$_3$)$_3$], 69.6 (d, CH), 87.7 (t, CH$_2$), 161.9 (s, CCH$_2$). - MS (EI), *m/z* (%): 259 (25) [M$^+$ - Me], 217 (42) [M$^+$ - *t*-Bu], 185 (5) [M$^+$ - OSiMe$_3$], 147 (100) [Me$_3$SiOSiMe$_2^+$], 73 (38) [SiMe$_3^+$], 45 (20). - $C_{13}H_{30}O_2Si_2$ (274.6): Calc. C 56.87, H 11.01; found C 56 92, H 11.03.

1-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]-1-phenyl-2-[(trimethylsilyl)oxy]-2-propene (1b). As described above the silyl enol ether formation was carried out on a 12.0 mmol-scale with ketone **7** (3.24 g). After usual work-up (*vide infra*) and solvent removal the product proved to be sufficiently pure according to GLC analysis and was used without further purification. Yield: 3.96 g (98%). - R_f = 0.80 (90/10). - IR (film): $\tilde{\nu}$ = 3020 cm^{-1} (w), 2940 (s), 2840 (m), 1630 (m), 1250 (s), 840 (vs), 770 (m), 690 (w). - ^1H NMR (300 MHz): δ = -0.06 (s, 3 H, SiCH$_3$), 0.01 [s, 9 H, Si(CH$_3$)$_3$], 0.07 (s, 3 H, SiCH$_3$), 0.90 [s, 9 H, SiC(CH$_3$)$_3$], 4.13 (d, 1 H, ^2J = 0.8 Hz, CHH), 4.59 (d, 1 H, ^2J = 0.8 Hz, CHH), 4.87 (s, 1 H, CH), 7.24-7.37 (m, 5 H, arom. H). - ^{13}C NMR (75.5 MHz): δ = -5.5 (q, SiCH$_3$), -5.5. (q, SiCH$_3$), -0.2 [q, Si(CH$_3$)$_3$], 18.3 (s, SiCMe$_3$), 25.8 [q, SiC(CH$_3$)$_3$], 75.9 (d, CH), 88.7 (t, CH$_2$), 126.9 (d, C$_{ar}$H), 127.2 (d, C$_{ar}$H), 127.7 (d, C$_{ar}$H), 142.7 (s, C$_{ar}$), 160.4 (s, CCH$_2$). - MS (EI), *m/z* (%): 279 (42) [M$^+$ - *t*-Bu], 147 (100) [Me$_3$SiOSiMe$_2^+$], 115 (10), 73 (43) [M$^+$ - SiMe$_3$], 57 (8), 45 (13). - $C_{18}H_{32}O_2Si_2$ (336.6): Calc. C 64.23, H 9.58; found C 64.38, H 9.64.

1,2-Bis[(trimethylsilyl)oxy]-1-phenyl-2-propene (1c). As described above the silyl enol ether formation was carried out on a 7.0 mmol-scale with ketone **8**[13] (1.56 g). After usual work-up (*vide infra*) and solvent removal the residue was purified by chromatography (CC, alumina, CH/EE = 98/2) and subsequent distillation in a Kugelrohr apparatus. Yield: 719 mg (35%). - b.p.: 115°C (0.07 mbar). - R_f = 0.39 (90/10). - IR (film): $\tilde{\nu}$ = 3020 cm^{-1} (w), 2950 (s), 2890 (sh), 1630 (s), 1250 (s), 1100 (s), 830 (s), 750 (m). - ^1H NMR (300 MHz): δ =

-0.09 [s, 9 H, $Si(CH_3)_3$], -0.04 [s, 9 H, $Si(CH)_3)_3$], 4.03 (d, 1 H, ^2J = 1.0 Hz, C*H*H), 4.42 (d, 1 H, ^2J = 1.0 Hz, CH*H*), 4.77 (s, 1 H, CH), 7.12-7.23 (m, 5 H, arom. H). - ^{13}C NMR (75.5 MHz): δ = -0.1 [q, $Si(CH_3)_3$], 0.0 [q, $Si(CH_3)_3$], 75.8 (d, CH), 89.5 (t, CH_2), 127.0 (d, $C_{ar}H$), 127.2 (d, $C_{ar}H$), 127.8 (d, $C_{ar}H$), 142.4 (s, C_{ar}), 160.1 (s, *C*CH_2). - MS (EI), *m/z* (%): 294 (20) [M^+], 205 (15) [M^+ - $OSiMe_3$], 179 (70) [M^+ - $H_2CCOSiMe_3$], 147 (35) [$Me_3SiOSiMe_2^+$], 115 (10), 73 (100) [$SiMe_3^+$], 45 (28). - $C_{15}H_{26}O_2Si_2$ (294.5): Calc. C 61.17, H 8.90; found C 60.88, H 8.93.

3-Benzyloxy-4-methyl-2-[(trimethylsilyl)oxy]-1-pentene (1d). As described above the silyl enol ether formation was carried out on a 40 mmol-scale with ketone **9** (8.25 g). In this case the ketone addition preceded the addition of TMSCl. After usual work-up (*vide infra*) and solvent removal the residue was purified by chromatography (FC, CH/EE = 99/1). Yield: 10.5 g (94%). - R_f = 0.61 (90/10). - IR (film): $\tilde{\nu}$ = 3015 cm^{-1} (w), 2960 (s), 2870 (sh), 1660 (m), 1250 (s), 850 (s), 740 (m), 700 (m). - ^1H NMR (300 MHz): δ = 0.26 [s, 9 H, $Si(CH_3)_3$], 0.90 (d, 3 H, ^3J = 6.8 Hz, CHCH_3), 0.97 (d, 3 H, ^3J = 6.8 Hz, CHCH_3), 1.94 (oct, 1 H, ^3J = 6.8 Hz, ^3J = 6.8 Hz, C*H*Me_2), 3.25 (d, 1 H, ^3J = 6.8 Hz, CHO), 4.28 (d, 1 H, ^2J = 1.1 Hz, CC*H*H), 4.30 (d, 1 H, ^{2} = 1.1 Hz, CCH*H*), 4.35 (d, 1 H, ^2J = 12.0 Hz, C*H*HPh), 4.67 (d, 1 H, ^2J = 12.0 Hz, C*H*HPh), 7.26-7.38 (m, 5 H, arom. H). - ^{13}C NMR (75.5 MHz): δ = 0.1 [q, $Si(CH_3)_3$], 18.2 (q, CH*C*H_3), 19.2 (q, CH*C*H_3), 30.1 [d, *C*$H(CH_3)_2$], 70.6 (t, *C*H_2Ph), 86.3 (d, CHO), 91.8 (t, *C*CH_2), 127.2 (d, $C_{ar}H$), 127.7 (d, $C_{ar}H$), 128.1 (d, $C_{ar}H$), 138.9 (s, C_{ar}), 156.1 (s, *C*CH_2). - MS (EI), *m/z* (%): 172 (55) [M^+ - C_7H_7O], 157 (100) [M^+ - PhCHO - Me], 145 (20), 91 (100) [$C_7H_7^+$], 73 (54) [$SiMe_3^+$], 65 (15). - $C_{16}H_{26}O_2Si$ (278.5): Calc. C 69.01, H 9.41; found C 68.74, H 9.55.

3-Chloro-4-methyl-2-[(trimethylsilyl)oxy]-1-pentene (1e). As described above the silyl enol ether formation was carried out on a 2.80 mmol-scale with ketone **10**[15] (1.35 g) employing lithium tetramethylpiperidide (LTMP) as base. In this case the ketone addition preceded the addition of TMSCl. After usual work-up (*vide infra*) and solvent removal the residue was purified by chromatography (FC, Et_2O/pentane = 15/85). Yield: 206 mg (36%).- R_f = 0.67 (90/10). - IR (film): $\tilde{\nu}$ = 2940 cm^{-1} (s, $C_{al}H$), 2850 (sh, $C_{ar}H$), 1620 (s, C=C), 1240 (s, $SiMe_3$), 830 (vs, $SiMe_3$). - ^1H NMR (300 MHz): δ = 0.05 [s, 9 H, $Si(CH_3)_3$], 0.99 (d, ^3J = 6.7 Hz, 3 H, CH_3), 1.02 (d, ^3J = 6.7. 3 H, CH_3), 2.26 (oct, ^3J = 6.7 Hz, ^3J = 6.7 Hz, 1 H,C*H*Me_2), 2.28 (s, 2 H, CH_2), 3.98 (d, ^3J = 6.7 Hz, 1 H, CHCl). - ^{13}C NMR (75.5 MHz): δ = 1.8 [q, $Si(CH_3)_3$], 19.8 (q, CH_3), 19.8 (q, CH_3), 31.7 (d, *C*HMe_2), 71.2 (d, CHCl), 91.9 (t, CH_2), 203.5 (s, *C*CH_2). - MS (EI, 70 eV), *m/z* (%): 191 (26) [M^+ - Me], 171 (21) [M^+ - Cl], 164 (95) [M^+ - $MeCHCH_2$], 149 (48) [164 - Me], 81 (30) [M^+ - $SiMe_3$ - HCl], 73 (100) [$SiMe_3^+$]. - $C_9H_{19}ClOSi$ (206.8): Calc. C 52.28, H 9.26; found: C 52.60, H 9.30.

General procedure (A) for the Irradiation at Low Temperature. A Duran glass jacket (ca. 50 ml volume) directly attached to a liquid cooled immersion lamp (Orginal Hanau TQ 150) and equipped with a septum-capped joint was charged with 20 ml of *n*-hexane and 4.0 mmol of silyl enol ether. The mixture was stirred by a continuous Ar stream which was introduced through a bent gas inlet on the bottom of the glass jacket. After cooling to -25 °C irradiation was started and 2.0 mmol of benzaldehyde (212 mg, 202 µl) dissolved in 10 ml of *n*-hexane was slowly added via a syringe (within ca. 1.5 h). The reaction was subsequently monitored by TLC. After complete consumption of benzaldehyde the mixture was filtered and the solvent was evaporated from the filtrate *in vacuo*. Further work-up was carried out as outlined in procedure B.

General Procedure (B) for the Irradiation at Room Temperature. A quartz tube was charged with 1.50 mmol of benzaldehyde (159 mg, 150 µl), 3.0 mmol of silyl enol ether and 10 ml of benzene. The sample was irradiated at 300 nm (RPR 3000 Å) in a merry-go-round unit. The reaction was monitored by TLC. After complete consumption of benzaldehyde irradiation was stopped. The solvent was evaporated *in vacuo* and the residue was analyzed by ^{1}H-NMR spectroscopy to determine the diastereo- and regioselectivity. Purification was carried out by flash chromatography with the solvent mixture indicated below.

3-[1-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]ethyl]-2-phenyl-3-[(trimethylsilyl)oxy]oxetane (2a,3a). Purification by chromatography (FC, CH/EA = 95/5). The diastereoisomers were not fully separable. Total yield according to procedure A: 420 mg (56%). - d.r. = 58/42. Total yield according to procedure B: 382 mg (67%). - d.r. = 55/45. - R_f = 0.51 (90/10). - IR (film): $\tilde{\nu}$ = 3020 cm^{-1} (w), 2940 (s), 2840 (sh), 1250 (s), 980 (m), 830 (vs), 770 (m), 690 (m). - $C_{20}H_{36}O_3Si_2$ (380.7): Calc. C 63.10, H 9.53; found C 62.90, H 9.68.

Major diastereoisomer: ^{1}H NMR (300 MHz): δ = -0.12 [s, 9 H, Si(CH$_3$)$_3$], 0.16 [s, 6 H, Si(CH$_3$)$_2$], 0.99 [s, 9 H, SiC(CH$_3$)$_3$], 1.16 (d, 3H, ^3J = 6.0 Hz, CHC*H*$_3$), 3.85 (q, 1 H, ^3J = 6.0 Hz, C*H*Me), 4.59 (d, 1 H, ^2J = 6.4 Hz, C*H*H), 4.79 (d, 1 H, ^2J = 6.4 Hz, CH*H*), 5.80 (s, 1 H, CHO), 7.25-7.36 (m, 5 H, arom. H). - ^{13}C NMR (75.5 MHz,): δ = -4.3 (q, SiCH$_3$), -3.9 (q, SiCH$_3$), 1.5 [q, Si(CH$_3$)$_3$], 17.4 (q, CH*C*H$_3$), 18.0 (s, Si*C*Me$_3$), 25.8 [q, SiC(*C*H$_3$)$_3$], 70.9 (d, *C*HMe), 78.0 (t, *C*H$_2$), 80.8 (s, *C*OTMS), 90.0 (d, CHO), 126.2 (d, C$_{ar}$H), 127.2 (d, C$_{ar}$H), 127.7 (d, C$_{ar}$H), 138.9 (s, C$_{ar}$). - MS (EI), *m/z* (%): 293 (10) [M$^+$ - H$_2$CO - *t*-Bu], 217 (45) [M$^+$ - PhCHO - *t*-Bu], 147 (100) [SiMe$_3$OSiMe$_2^+$], 129 (10), 115 (6) [SiMe$_2$*t*-Bu$^+$], 73 (54) [SiMe$_3^+$].

Minor diastereoisomer: ^{1}H NMR (300 MHz): δ = -0.16 [s, 9 H, Si(CH$_3$)$_3$], 0.15 [s, 6 H, Si(CH$_3$)$_2$], 0.94 [s, 9 H, SiC(CH$_3$)$_3$], 1.19 (d, 3H, ^3J = 6.0 Hz, CHC*H*$_3$) 4.27 (q, 1 H, ^3J = 6.0 Hz, C*H*Me), 4.61 (d, 1 H, ^2J = 6.4 Hz, C*H*H), 4.71 (d, 1 H, ^2J = 6.4 Hz, CH*H*), 5.39 (s, 1 H, CHO), 7.25-7.36 (m, 5 H, arom. H). - ^{13}C NMR (75.5 MHz): δ = -4.8 (q, SiCH$_3$), -4.4 (q, SiCH$_3$), 1.5 [q, Si(CH$_3$)$_3$], 16.9 (q, CH*C*H$_3$), 18.1 (s, Si*C*Me$_3$), 26.0 [q, SiC(*C*H$_3$)$_3$], 73.3 (d, *C*HMe), 79.3 (t, *C*H$_2$), 80.4 (s, *C*OTMS), 88.0 (d, CHO), 126.8 (d, C$_{ar}$H), 127.0 (d, C$_{ar}$H), 127.5 (d, C$_{ar}$H), 138.5 (s, C$_{ar}$). - MS (EI), *m/z* (%): 293 (10) [M$^+$ - H$_2$CO - *t*-Bu], 217 (45) [M$^+$ - PhCHO - *t*-Bu], 147 (100) [SiMe$_3$OSiMe$_2^+$], 129 (10), 115 (6) [SiMe$_2$*t*-Bu$^+$], 73 (54) [SiMe$_3^+$].

3-[[(1,1-Dimethylethyl)dimethylsilyl]oxy]phenylmethyl-2-phenyl-3-[(trimethylsilyl)oxy]oxetane (2b,3b). Purification by chromatography (FC, CH/EA = 98/2). The diastereoisomers were fully separable. Total yield according to procedure A: 585 mg (66%). - d.r. = 53/47. Total yield according to procedure B: 400 mg (60%). - d.r. = 55/45.

Major diastereoisomer: R_f = 0.60 (90/10), R_f = 0.22 (98/2) - IR (film): $\tilde{\nu}$ = 3010 cm^{-1} (w), 2940 (s), 2840 (m), 1245 (s), 1000 (m), 830 (vs), 770 (m), 690 (m). - ^{1}H NMR (300 MHz): δ = -0.38 [s, 9 H, Si(CH$_3$)$_3$], -0.16 (s, 3 H, SiCH$_3$), -0.11 (s, 3 H, SiCH$_3$), 0.98 [s, 9 H, SiC(CH$_3$)$_3$], 4.58 (d, 1 H, ^2J = 6.8 Hz, C*H*H), 4.84 (d, 1 H, ^2J = 6.8 Hz, CH*H*), 4.86 (s, 1 H, C*H*OTBDMS), 5.90 (s, 1 H, CHO), 6.98-7.43 (m, 10 H, arom. H). - ^{13}C NMR (75.5 MHz): δ = -5.1 (q, SiCH$_3$), -4.4 (q, SiCH$_3$), 0.9 [q, Si(CH$_3$)$_3$], 18.2 (s, Si*C*Me$_3$), 25.9 [q, SiC(*C*H$_3$)$_3$], 77.9 (t, CH$_2$), 77.9 (d, *C*HOTBDMS), 80.1 (s, *C*OTMS), 88.6 (d, CHO), 125.7 (d, C$_{ar}$H), 126.5 (d, C$_{ar}$H), 127.4 (d, C$_{ar}$H), 127.6 (d, C$_{ar}$H), 128.0 (d, C$_{ar}$H), 128.1 (d, C$_{ar}$H), 138.5 (s, C$_{ar}$), 140.1 (s, C$_{ar}$). - MS (EI), *m/z* (%): 355 (10) [M$^+$ - H$_2$CO - *t*-Bu], 279 (45) [M$^+$ - PhCHO - *t*-Bu], 221 (19) [M$^+$ - CHPhOTBDMS], 191 (21), 147 (100) [SiMe$_3$OSiMe$_2^+$], 115 (8) [SiMe$_2$*t*-Bu$^+$], 73 (60) [SiMe$_3^+$]. - $C_{25}H_{38}O_3Si_2$ (442.7): Calc: C 67.82, H 8.65; found: C 67.88, H 8.78.

Minor diastereoisomer: R_f = 0.60 (90/10), R_f = 0.19 (98/2) - IR (film): $\tilde{\nu}$ = 3010 cm^{-1} (w), 2940 (s), 2840 (m), 1245 (s), 1000 (m), 830 (vs), 770 (m), 690 (m). - ^1H NMR (300 MHz): δ = -0.37 [s, 9 H, $Si(CH_3)_3$], -0.15 (s, 3 H, $SiCH_3$), -0.09 (s, 3 H, $SiCH_3$), 0.92 [s, 9 H, $SiC(CH_3)_3$], 4.57 (d, 1 H, ^2J = 6.8 Hz, C*H*H), 4.90 (s, 1 H, C*H*OTBDMS), 4.99 (d, 1 H, ^2J = 6.8 Hz, CH*H*), 5.75 (s, 1 H, CHO), 6.96-7.41 (m, 10 H, arom. H). - ^{13}C NMR (75.5 MHz): δ = -4.9 (q, $SiCH_3$), -4.4 (q, $SiCH_3$), 1.1 [q, $Si(CH_3)_3$], 18.2 (s, $SiCMe_3$), 25.8 [q, $SiC(CH_3)_3$], 77.4 (t, CH_2), 77.7 (d, *C*HOTBDMS), 80.7 (s, *C*OTMS), 89.0 (d, CHO), 125.4 (d, $C_{ar}H$), 126.7 (d, $C_{ar}H$), 127.5 (d, $C_{ar}H$), 127.8 (d, $C_{ar}H$), 128.4 (d, $C_{ar}H$), 138.3 (s, C_{ar}), 140.0 (s, C_{ar}). - MS (EI), *m/z* (%): 355 (10) [M^+ - H_2CO - *t*-Bu], 279 (45) [M^+ - PhCHO - *t*-Bu], 221 (19) [M^+ - CHPhOTBDMS], 191 (21), 147 (100) [$SiMe_3OSiMe_2^+$], 115 (8) [$SiMe_2$t-Bu$^+$], 73 (60) [$SiMe_3^+$]. - $C_{25}H_{38}O_3Si_2$ (442.7): Calc. C 67.82, H 8.65; found C 67.60, H 8.60.

3-[(Trimethylsilyl)oxy]phenylmethyl-2-phenyl-3-[(trimethylsilyl)oxy]oxetane (2c,3c). Purification by chromatography (FC, CH/EA = 99/1). The diastereoisomers were not fully separable. Total yield according to procedure B: 345 mg (59%). - d.r. = 51/49. - R_f = 0.46 (90/10). - IR (film): $\tilde{\nu}$ = 3060 cm^{-1} (w), 3020 (w), 2950 (s), 2880 (sh), 1250 (s), 1200 (s), 850 (vs), 750 (m), 700 (m). - $C_{22}H_{32}O_3Si_2$ (400.6): Calc. C 65.96, H 8.05; found C 66.16, H 8.23.

Major diastereoisomer: ^1H NMR (300 MHz): δ = -0.27 [s, 9 H, $Si(CH_3)_3$], 0.05 [s, 9 H, $Si(CH_3)_3$], 4.63 (d, 1 H, ^2J = 6.6 Hz, C*H*H), 4.86 (d, 1 H, ^2J = 6.6 Hz, CH*H*), 4.98 (s, 1 H, C*H*OTMS) 5.63 (s, 1 H, CHO), 6.88-7.42 (m, 10 H, arom. H). - ^{13}C NMR (75.5 MHz): δ = 0.1 [q, $Si(CH_3)_3$], 1.2 [q, $Si(CH_3)_3$], 77.2 (d, *C*HOTMS), 78.9 (s, *C*OTMS), 79.1 (t, CH_2), 89.1 (d, CHO), 125.5 (d, $C_{ar}H$), 125.8 (d, $C_{ar}H$), 126.7 (d, $C_{ar}H$), 127.8 (d, $C_{ar}H$), 128.5 (d, $C_{ar}H$), 138.1 (s, C_{ar}), 139.8 (s, C_{ar}). - MS (EI), *m/z* (%): 294 (25) [M^+ - PhCHO], 204 (21), 179 (75) [$CHPhOSiMe_3^+$], 147 (20) [$SiMe_3OSiMe_2^+$], 105 (12), 73 (100) [$SiMe_3^+$], 45 (26).

Minor diastereoisomer: ^1H NMR (300 MHz): δ = -0.37 [s, 9 H, $Si(CH_3)_3$], 0.11 [s, 9 H, $Si(CH_3)_3$], 4.59 (d, 1 H, ^2J = 6.8 Hz, C*H*H), 4.85 (d, 1 H, ^2J = 6.8 Hz, CH*H*), 4.90 (s, 1 H, C*H*OTMS), 5.83 (s, 1 H, CHO), 6.88-7.42 (m, 10 H, arom. H). - ^{13}C NMR (75.5 MHz): δ = 0.2 [q, $Si(CH_3)_3$], 1.0 [q, $Si(CH_3)_3$], 77.2 (s, *C*OTMS)), 77.9 (t, CH_2), 78.2 (d, *C*HOTMS), 89.1 (d, CHO), 125.8 (d, $C_{ar}H$), 126.7 (d, $C_{ar}H$), 127.5 (d, $C_{ar}H$), 127.6 (d, $C_{ar}H$), 127.7 (d, $C_{ar}H$), 127.9 (d, $C_{ar}H$), 138.5 (s, C_{ar}), 140.1 (s, C_{ar}). - MS (EI), *m/z* (%): 294 (25) [M^+ - PhCHO], 204 (21), 179 (75) [$CHPhOSiMe_3^+$],147 (20) [$SiMe_3OSiMe_2^+$], 105 (12), 73 (100) [$SiMe_3^+$], 45 (26).

3-[1-(Benzyloxy)-2-methylpropyl]-2-phenyl-3-[(trimethylsilyl)oxy]oxetane (2d,3d). Purification by chromatography (FC, CH/EA = 98/2). The diastereoisomers were fully separable. Total yield according to procedure A: 240 mg (31%). - d.r. = 67/33. Total yield according to procedure B: 174 mg (30%). - d.r. = 59/41.

Major diastereoisomer 2d: R_f = 0.39 (90/10). - IR (film): $\tilde{\nu}$ = 3020 cm^{-1} (w), 2980 (s), 2890 (sh), 1260 (s), 1020 (m), 980 (m), 840 (vs), 750 (m), 690 (m). - ^1H NMR (300 MHz): δ = -0.17 [s, 9 H, $Si(CH_3)_3$], 1.01 (d, 3H, ^3J = 6.8 Hz, $CHCH_3$), 1.12 (d, 3 H, ^3J = 6.8 Hz, $CHCH_3$), 2.16 (dsept, 1H, ^3J = 6.8 Hz, ^3J = 3.8 Hz, C*H*Me_2), 3.65 (d, 1 H, ^3J = 3.8 Hz, C*H*CHMe_2), 4.61 (d, 1 H, ^2J = 6.8 Hz, C*H*H), 4.75 (d, 1 H, ^2J = 11.3 Hz, C*H*HPh), 4.84 (d, 1 H, ^2J = 11.3 Hz, CH*H*Ph), 4.86 (d, 1 H, ^2J = 6.8 Hz, CH*H*), 5.65 (s, 1 H, CHO), 7.23-7.42 (m, 10 H, arom. H). - ^{13}C NMR (75.5 MHz): δ = 1.7 [q, $Si(CH_3)_3$], 17.7 (q, $CHCH_3$), 22.1 (q, $CHCH_3$), 29.6 (d, 1 H, *C*HMe_2), 75.8 (t, *C*H_2Ph), 79.3 (t, CH_2), 81.6 (s, *C*OTMS), 87.7 (d, *C*HCHMe_2), 90.0 (d, CHO), 126.4 (d, $C_{ar}H$), 127.2 (d, $C_{ar}H$), 127.4 (d, $C_{ar}H$), 127.5 (d, $C_{ar}H$), 127.8 (d, $C_{ar}H$), 128.3 (d, $C_{ar}H$), 138.3 (s, C_{ar}),

138.6 (s, C_{ar}). - MS (EI), *m/z* (%): 172 (10), 157 (55) [M^+ - 2 PhCHO - Me], 91 (100) [$C_7H_7^+$], 73 (31) [$SiMe_3^+$], 65 (10), 45 (10). - $C_{23}H_{32}O_3Si$ (384.6): Calc. C 71.83, H 8.39; found C 70.45, H 8.22.

Minor diastereoisomer ***3d****:* R_f = 0.36 (90/10). - IR (film): $\tilde{\nu}$ = 3020 cm^{-1} (w), 2980 (s), 2890 (sh), 1260 (s), 1020 (m), 980 (m), 840 (vs), 750 (m), 690 (m). - ^1H NMR (300 MHz) δ = -0.09 [s, 9 H, $Si(CH_3)_3$], 0.99 (q, 3H, ^3J = 7.2 Hz, $CHCH_3$), 1.06 (q, 3 H, ^3J = 7.2 Hz, $CHCH_3$), 2.11 (dsept, 1 H, ^3J = 7.2 Hz, ^3J = 5.3 Hz, $CHMe_2$), 3.40 (d, 1 H, ^3J = 5.3 Hz, $CHCHMe_2$), 4.65 (d, 1 H, ^2J = 7.2 Hz, CHH), 4.75 (d, 1 H, ^2J = 12.0 Hz, CHHPh), 4.78 (d, 1 H, ^2J = 7.2 Hz, CHH), 4.85 (d, 1 H, ^2J = 12.0 Hz, CHHPh), 5.93 (s, 1 H, CHO) 7.22-7.47 (m, 10 H, arom. H). - ^{13}C NMR (75.5 MHz): δ = 1.8 [q, $Si(CH_3)_3$], 18.5 (q, $CHCH_3$), 21.6 (q, $CHCH_3$), 29.4 (d,1 H, $CHMe_2$), 75.2 (t, CH_2Ph), 79.6 (t, CH_2), 81.4 (s, COTMS), 87.5 (d, $CHCHMe_2$), 89.4 (d, CHO), 125.4 (d, $C_{ar}H$), 127.3 (d, $C_{ar}H$), 127.4 (d, $C_{ar}H$), 127.6 (d, $C_{ar}H$), 127.8 (d, $C_{ar}H$), 128.4 (d, $C_{ar}H$), 138.4 (s, C_{ar}), 138.5 (s, C_{ar}).- MS (EI), *m/z* (%): 172 (10), 157 (55) [M^+ - 2 PhCHO - Me], 91 (100) [$C_7H_7^+$], 73 (31) [$SiMe_3^+$], 65 (10), 45 (10). - $C_{23}H_{32}O_3Si$ (384.6): Calc. C 71.83, H 8.39; found C 70.36, H 8.02.

3-(2-Chloro-3-methylpropyl)-2-phenyl-3-oxetane (2e,3e). Purification by chromatography (FC, CH/EA = 200/1). The diastereoisomers were separable, but only the major diastereoisomers was fully characterized. d.r. = 85/15. Yield of major diastereoisomer according to procedure B: 135 mg (28%).

Major diastereoisomer ***3e****:* R_f = 0.44 (90/10). - IR (film): $\tilde{\nu}$ = 3040 cm^{-1} (w, $C_{ar}H$), 3000 (w, $C_{ar}H$), 2940 (vs, $C_{al}H$), 2910 (sh, $C_{al}H$), 2850 (s, $C_{al}H$), 1240 (s, $SiMe_3$), 980 (m, COC), 830 (s, $SiMe_3$), 745 (m, Ph), 690 (s, Ph). - ^1H NMR (300 MHz): δ = -0.17 [s, 9 H, $Si(CH_3)_3$], 1.08 (d, ^3J = 6.7 Hz, $CHCH_3$), 1.13 (d, ^3J = 6.7 Hz, $CHCH_3$), 2.37 (dsept, ^3J = 6.7 Hz, ^3J = 3.3 Hz, 1 H, $CHMe_2$), 4.41 (d, ^3J = 3.3 Hz, 1 H, CHCl), 4.67 (d, ^2J = 7.0 Hz, 1 H, CHH), 4.76 (d, ^2J = 7.0 Hz, 1 H, CHH), 5.56 (s, CHO), 7.25-7.45 (m, 5 H, arom. H). - ^{13}C NMR (75.5 MHz,): δ = 1.6 [q, 9 H, $Si(CH_3)_3$], 17.9 (q, $CHCH_3$), 22.6 (q, $CHCH_3$), 30.1 (d, $CHMe_2$), 74.5 (d, CHCl), 80.8 (t, CH_2), 81.3 (s, COTMS), 90.2 (d, CHO), 126.1 (d, $C_{ar}H$), 127.4 (d, $C_{ar}H$), 128.0 (d, $C_{ar}H$), 137.7 (s, C_{ar}). - MS (EI), *m/z* (%): 166 (35), 164 (100) [M^+ - PhCHO - *i*-Pr], 149 (35), 118 (36), 93 (30), 73 (90) [$SiMe_3^+$]. - $C_{16}H_{25}ClO_2Si$ (HRMS): Calc. 330.1656; found 330.1656.

Minor diastereoisomer ***2e****:* ^1H NMR (300 MHz): δ = -0.16 [s, 9 H, $Si(CH_3)_3$], 1.02 (d, ^3J = 6.9 Hz, $CHCH_3$), 1.13 (d, ^3J = 6.4 Hz, $CHCH_3$), 2.15-2.19 (m, 1 H, $CHMe_2$), 4.13 (d, ^3J = 5.5 Hz, 1 H, CHCl), 4.72 (d, ^2J = 7.4 Hz, 1 H, CHH), 4.77 (d, ^2J = 7.4 Hz, 1 H, CHH), 5.85 (s, CHO), 7.28-7.50 (m, 5 H, arom. H).

3-(2-Benzyloxy-3-methylpropyl)-2-phenyl-3-oxetanol (11). To 10 ml of a saturated solution of K_2CO_3 in MeOH 0.26 mmol (101 mg) oxetane **2d** was added. The mixture was stirred for 16 h at ambient temperature. The solvent was removed *in vacuo* and the residue was partitioned between water (10 ml) and ether (20 ml). The aqueous layer was subsequently extracted with ether (3 x 10 ml). The combined organic layers were washed with brine (50 ml), dried over $MgSO_4$ and filtered. After removal of the solvent *in vacuo* the residue was purified by chromatography (FC, CH/EA = 95/5). Yield: 72 mg (89%). - m.p.: 88°C. - R_f = 0.46 (75/25). - IR (KBr): $\tilde{\nu}$ = 3320 cm^{-1} (vs, OH), 3040 (w, $C_{ar}H$), 3000 (w, $C_{ar}H$), 2940 (s, $C_{al}H$), 2880 (sh, $C_{al}H$), 1150 (s, OH), 980 (s, COC), 740 (s, Ph), 690 (vs, Ph). - ^1H NMR (300 MHz,): δ = 0.92 (d, ^3J = 7.0 Hz, $CHCH_3$), 1.10 (d, ^3J = 7.0 Hz, $CHCH_3$), 1.55 (s, 1 H, OH), 2.19 (dsept, ^3J = 7.0 Hz, ^3J = 2.9 Hz, 1 H, $CHMe_2$), 3.48 (d, ^3J = 2.9 Hz, 1 H, COBn), 4.42 (d, ^2J = 6.9 Hz, 1 H, CHH), 4.71 (d, ^2J = 11.4 Hz, 1 H, CHHPh), 4.82 (d, ^2J = 11.4 Hz, 1 H, CHHPh), 5.01 (d, ^2J = 6.9 Hz, 1 H, CHH), 5.78 (s, CHO), 7.25-7.45 (m, 5 H, arom. H). - ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 17.0 (q, $CHCH_3$), 20.9 (q, $CHCH_3$), 29.4 (d, $CHMe_2$), 74.7 (t, CH_2), 79.0 (s, COH), 80.5 (t,

CH_2Ph), 88.8 (d, CHO), 126.6 (d, $C_{ar}H$), 127.6 (d, $C_{ar}H$), 127.8 (d, $C_{ar}H$), 128.5 (d, $C_{ar}H$), 128.6 (d, $C_{ar}H$), 136.6 (s, C_{ar}), 138.2 (s, C_{ar}). - MS (EI), *m/z* (%): 163 (5) [*i*-PrCHOBn$^+$], 91 (100) [$C_7H_7^+$]. - $C_{20}H_{24}O_3$ (312.4): Calc. C 76.89, H 7.74; found C 76.81, H 7.67.

3-Benzyloxy-2,4-dimethyl-1-phenyl-1,2-pentanediol (12). To a suspension of 3.0 mmol $LiAlH_4$ (114 mg) in 2 ml THF a solution of 1.0 mmol oxetanol **11** (312 mg) in 5 ml THF was slowly added at 0°C. After complete addition the mixture was stirred for another hour at 0°C and subsequently allowed to reach room temperature. Stirring was continued until the reaction was complete according to TLC (96 h). Work-up was carried out according to the standard protocol[24]. The product was purified by chromatography (FC, CH/EA = 92/8). Yield: 255 mg (82%). - m.p.: 91-92°C. - R_f = 0.50 (70/30). - IR (KBr): $\tilde{\nu}$ = 3350 cm^{-1} (vs, OH), 3005 (w, $C_{ar}H$), 2970 (m, $C_{al}H$), 2930 (sh, C_{al}), 2850 (m, C_{al}), 1100 (m, CHOH), 1050 (s, COC), 740 (m, Ph), 685 (s, Ph). - ^{1}H NMR (300 MHz): δ = 1.12 (d, ^3J = 6.9 Hz, 3 H, CHCH_3), 1.14 (d, ^3J = 6.9 Hz, 3 H, CHCH_3), 1.20 (s, 3 H, CH_3), 2.13 (dsept, ^3J = 6.9 Hz, ^3J = 2.4 Hz, 1 H, C*H*Me$_2$), 3.36 (d, ^3J = 2.4 Hz, 1 H, C*H*OH), 4.46 (d, ^2J = 11.0 Hz, 1 H, C*H*HPh), 4.75 (d, ^2J = 11.0 Hz, 1 H, CH*H*Ph), 4.78 (s, 1 H, C*H*PhOH), 7.26-7.43 (m, 5 H, arom. H). - ^{13}C NMR (75.5 MHz): δ = 17.6 (q, CHCH_3), 18.9 (q, CHCH_3), 24.3 (q, CH_3), 28.9 (d, *C*HMe$_2$), 75.3 (t, *C*H_2Ph), 76.6 (s, COH), 79.2 (d, *C*HOBn), 89.3 (d, *C*HPhOH), 127.6 (d, $C_{ar}H$), 127.8 (d, $C_{ar}H$), 128.0 (d, $C_{ar}H$), 128.2 (d, $C_{ar}H$), 128.5 (d, $C_{ar}H$), 138.2 (s, C_{ar}), 140.2 (s, C_{ar}). - MS (EI), *m/z* (%): 207 (14) [M$^+$ - OBn], 133 (17), 108 (12), 91 (100) [$C_7H_7^+$], 79 (8), 43 (9) [CHMe$_2^+$]. - $C_{20}H_{26}O_3$ (314.4): Calc. C 76.40, H 8.33; found C 76.36, H 8.46.

(2SR,3SR)-2-Benzyl-4-methyl-1,2,3-pentanetriol (13). Oxetane **2d** (0.39 mmol, 150 mg) was dissolved in 5 ml of methanol and 0.03 mmol of the catalyst Pd/C [10% w/w] (30 mg) was added to the solution. The hydrogenolysis was carried out in a conventional hydrogenation apparatus at ambient temperature and atmospheric pressure. The progression of the reaction was indicated by the volume of consumed hydrogen and was further monitored by TLC. Upon complete transformation (6 h) the mixture was filtered and the solvent removed *in vacuo*. The residue was purified by chromatography (FC, CH/EE = 75/25). Yield: 60 mg (69%). - m.p.: 65°C. - R_f = 0.22 (60/40). - IR (KBr): $\tilde{\nu}$ = 3350 cm^{-1} (vs, OH), 3005 (w, $C_{ar}H$), 2940 (s, $C_{al}H$), 2900 (sh, C_{al}), 2850 (sh, C_{al}), 750 (m, Ph), 695 (s, Ph). - ^{1}H NMR (300 MHz): δ = 1.06 (d, ^3J = 6.9 Hz, 3 H, CHCH_3), 1.07 (d, ^3J = 6.9 Hz, 3 H, CHCH_3), 2.13 (dsept, ^3J = 6.9 Hz, ^3J = 2.9 Hz, 1 H, C*H*Me$_2$), 2.68 (d, ^2J = 13.6 Hz, 1 H, C*H*HPh), 2.99 (d, ^2J = 13.6 Hz, 1 H, CH*H*Ph), 3.51 (s, 2 H, *C*H_2OH), 3.52 (d, ^3J = 2.9 Hz, 1 H, C*H*OH), 7.24-7.33 (m, 5 H, arom. H). - ^{13}C NMR (75.5 MHz): δ = 16.2 (q, CHCH_3), 21.7 (q, CHCH_3), 28.8 (d, *C*HMe$_2$), 40.3 (t, *C*H_2Ph), 67.3 (t, CH_2OH), 76.6 (s, COH), 78.6 (d, CHOH), 126.7 (d, $C_{ar}H$), 128.4 (d, $C_{ar}H$), 130.3 (d, $C_{ar}H$), 136.5 (s, C_{ar}). - MS (EI), *m/z* (%): 193 (10), 151 (18), 133 (80) [M$^+$ - Bn], 105 (30), 91 (100) [$C_7H_7^+$], 73 (34), 43 (34) [CHMe$_2^+$]. - $C_{13}H_{20}O_3$ (224.3): Calc. C 69.61, H 8.99; found C 69.64, H 8.89.

(2RS,3SR)-2-Benzyl-4-methyl-1,2,3-pentanetriol (14). The diastereomeric oxetane **3d** was hydrogenolytically cleaved as described above. Yield: 38 mg (43%). - m.p.: 79°C. - R_f = 0.22 (60/40).- IR (KBr): $\tilde{\nu}$ = 3350 cm^{-1} (vs, OH), 3005 (w, $C_{ar}H$), 2940 (s, $C_{al}H$), 2900 (s, $C_{al}H$), 2850 (sh, $C_{al}H$), 760 (m, Ph), 695 (s, Ph). - ^{1}H NMR (300 MHz): δ = 1.01 (d, ^3J = 6.7 Hz, 3 H, CHCH_3), 1.03 (d, ^3J = 6.7 Hz, 3 H, CHCH_3), 2.13 (dsept, ^3J = 6.7 Hz, ^3J = 3.0 Hz, 1 H, C*H*Me$_2$), 2.82 (d, ^2J = 13.7 Hz, 1 H, C*H*HPh), 2.93 (d, ^2J = 13.7 Hz, 1 H, CH*H*Ph), 3.40 (d, ^3J = 3.0 Hz, 1 H, C*H*OH), 3.51 (d, ^2J = 11.2 Hz, 1 H, C*H*HOH), 3.73 (d, ^2J = 11.2 Hz, 1 H, CH*H*OH), 7.21-7.34 (m, 5 H, arom. H) - ^{13}C NMR (75.5 MHz): δ = 16.5 (q, CHCH_3), 22.3 (q, CHCH_3),

28.7 (d, *C*HMe$_2$), 40.6 (t, *C*H$_2$Ph), 65.8 (t, CH$_2$OH), 76.5 (s, COH), 79.0 (d, CHOH), 126.6 (d, C$_{ar}$H), 128.3 (d, C$_{ar}$H), 130.4 (d, C$_{ar}$H), 136.4 (s, C$_{ar}$). - MS (EI), *m/z* (%): 133 (38) [M$^+$ - Bn], 91 (100) [C$_7$H$_7^+$], 73 (22), 43 (38) [CHMe$_2^+$]. - C$_{13}$H$_{20}$O$_3$ (224.3): Calc. C 69.61, H 8.99; found C 69.47, H 9.21.

(2RS,3SR)-2-Benzyl-3-chloro-4-methyl-1,2-pentanediol (15). The hydrogenolysis was carried out on a 0.33 mol scale (170 mg oxetane **3e**) as described for compound **2d**. Purification by chromatography (CH/EE = 75/25) yielded 50 mg product (62%). - R_f = 0.34 (75/25). - IR (KBr): $\tilde{\nu}$ = 3400 cm^{-1} (vs, OH), 3040 (w, C$_{ar}$H), 3020 (w, C$_{ar}$H), 2940 (s, C$_{al}$H), 2850 (sh, C$_{al}$), 740 (m, Ph), 690 (s, Ph). - ^{1}H NMR (300 MHz): δ = 1.21 (d, ^3J = 6.7 Hz, 3 H, CHC*H*$_3$), 1.27 (d, ^3J = 6.7 Hz, 3 H, CHC*H*$_3$), 2.59 (dsept, ^3J = 6.7 Hz, ^3J = 2.1 Hz, 1 H, C*H*Me$_2$), 2.96 (d, ^2J = 13.6 Hz, 1 H, C*H*HPh), 3.22 (d, ^2J = 13.6 Hz, 1 H, CH*H*Ph), 3.55 (d, ^2J = 11.0 Hz, 1 H, C*H*HOH), 3.68 (d, ^2J = 11.0 Hz, 1 H, CH*H*OH), 4.35 (d, ^3J = 2.1 Hz, 1 H, C*H*Cl), 7.35-7.47 (m, 5 H, arom. H). - ^{13}C NMR (75.5 MHz): δ = 17.1 (q, CH*C*H$_3$), 22.8 (q, CH*C*H$_3$), 29.3 (d, *C*HMe$_2$), 39.9 (t, *C*H$_2$Ph), 64.6 (t, CH$_2$OH), 74.5 (d, CHCl), 76.7 (s, COH), 126.8 (d, C$_{ar}$H), 128.3 (d, C$_{ar}$H), 130.5 (d, C$_{ar}$H), 136.3 (s, C$_{ar}$). - MS (EI), *m/z* (%): 151 (18) [M$^+$ - Bn], 133 (30) [M$^+$ - Bn - H$_2$O], 91 (100) [C$_7$H$_7^+$], 85 (35), 77 (10) [C$_6$H$_5^+$], 57 (45), 43 (22) [CHMe$_2^+$]. - C$_{13}$H$_{20}$O$_3$ (242.7): Calc. C 64.32, H 7.89; found C 64.43, H 7.64.

2-(1-Methylethyl)-4-phenyl-1,5-dioxa-spiro[2.3]hexane (16). To 20 ml of a saturated solution of K$_2$CO$_3$ in MeOH 0.47 mmol (146 mg) oxetane **3e** was added. The mixture was stirred for 20 h at ambient temperature. The solvent was removed *in vacuo* and the residue was partitioned between water (20 ml) and ether (40 ml). The aqueous layer was subsequently extracted with ether (3 x 20 ml). The combined organic layers were washed with brine (100 ml), dried over MgSO$_4$ and filtered. After removal of the solvent *in vacuo* the residue was purified by chromatography (FC, CH/EA = 99/1). Yield: 65 mg (66%). - m.p.: 57°C. - R_f = 0.44 (90/10). - IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1} (w, C$_{ar}$H), 3000 (w, C$_{ar}$H), 2940 (vs, C$_{al}$H), 2850 (vs, C$_{al}$H), 980 (m, COC), 850 (m, COC), 740 (s, Ph), 685 (s, Ph). - ^{1}H NMR (300 MHz): δ = 0.97 (d, ^3J = 6.4 Hz, CHC*H*$_3$), 1.09 (d, ^3J = 6.5 Hz, CHC*H*$_3$), 1.19 (dsept, ^3J = 8.6 Hz, ^3J = 6.4 Hz, 1 H, C*H*Me$_2$), 2.71 (d, ^3J = 8.6 Hz, 1 H, C*H*CHMe$_2$), 4.98 (d, ^2J = 7.9 Hz, 1 H, C*H*H), 5.01 (d, ^2J = 7.9 Hz, 1 H, CH*H*), 5.85 (s, C*H*Ph), 7.30-7.40 (m, 5 H, arom. H). - ^{13}C NMR (75.5 MHz): δ = 18.4 (q, CH*C*H$_3$), 19.6 (q, CH*C*H$_3$), 29.3 (d, *C*HMe$_2$), 64.8 (d, *C*HCHMe$_2$), 65.9 (s, *C*CHPh), 77.4 (t, CH$_2$), 88.7 (d, *C*HPh), 127.2 (d, C$_{ar}$H), 128.5 (d, C$_{ar}$H), 128.6 (d, C$_{ar}$H), 137.4 (s, C$_{ar}$). - MS (EI), *m/z* (%): 203 (33) [M$^+$ - H], 133 (85) [M$^+$ - *i*-Pr - CO], 104 (100) [C$_8$H$_8^+$], 89 (48), 77 (52) [C$_6$H$_5^+$], 56 (90) [CHCH*i*-Pr$^+$], 55 (53) [M$^+$ - PhCHO - *i*-Pr]. - C$_{13}$H$_{16}$O$_2$ (204.267): Calc. C 76.44, H 7.90; found C 76.34, H 7.73.

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