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Stereoselective Preparation of 2-Silylated 1,3-Diols and the Regioselectivity of their Peterson Olefination

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Abstract: The reduction of the carbonyl group of α-silylated aldols with complex hydrides was shown to proceed with high stereoselectivity. The center of chirality in the α-position to the ketone, at the C-atom where the silicon group is attached, usually dominated the stereochemical control of the reaction. The presence of the β-hydroxy functionality, however, also seems to be necessary for a high degree of selectivity. Peterson olefination of 2-silylated 1,3-diols afforded stereoselectively (*E*)-configured allylic alcohols as the major products. With KH as the base, the reaction proceeds predominantly in a *syn*-fashion, preferring to eliminate a *syn*- rather than an *anti*-configured β-hydroxysilane unit. Under 'silico-nucleophilic' conditions (OH^- or F^-), an *anti*-configured β-hydroxysilane moiety can also be eliminated in an *anti*-fashion. This reaction is strongly preferred over the corresponding *syn*-elimination, but is still less prominent than a competitive *syn*-elimination of a *syn*-configured β-hydroxysilane unit.

Keywords: Aldols, Reduction, Regioselection, Stereoselection

INTRODUCTION

The diastereoselective addition of nucleophiles to the carbonyl group of 'α-chiral' or 'β-chiral' ketones has been investigated thoroughly, and the type of diastereoselectivity is usually predicted with good reliability. For instance, Cram's or Felkin-Ahn's rules, based on an 'open-chain model', suggest that the addition of nucleophiles, *e.g.*, a Grignard reagent, to the carbonyl group of 'α-chiral' ketones **1** would preferentially form alcohols **2a** rather than the isomeric compounds **2b** (Scheme 1). If a heteroatom is attached to the stereogenic center of **1**, the selectivity can be — according to Cram's 'chelate model' — predictably opposite (see, *e.g.*,[2]). In the case of 'β-chiral' ketones, the influence of the remote stereogenic center on the π-face selectivity of a nucleophilic attack at the carbonyl group is usually low[3], except for compounds that have a heteroatom attached to the center of chirality. In these cases, 'chelate-controlled' reactions occur, which give rise to addition products with high stereoselectivities[4-7]. For instance, the stereogenic center of a β-hydroxy ketone of the type **3** efficiently controls the stereochemical outcome of reduction reactions. It has been shown that the π-face selectivity of hydride reductions, which form compounds of the type **4**, is not only high but that the *syn*- versus *anti*-selectivity can be influenced by the choice of the reaction conditions.

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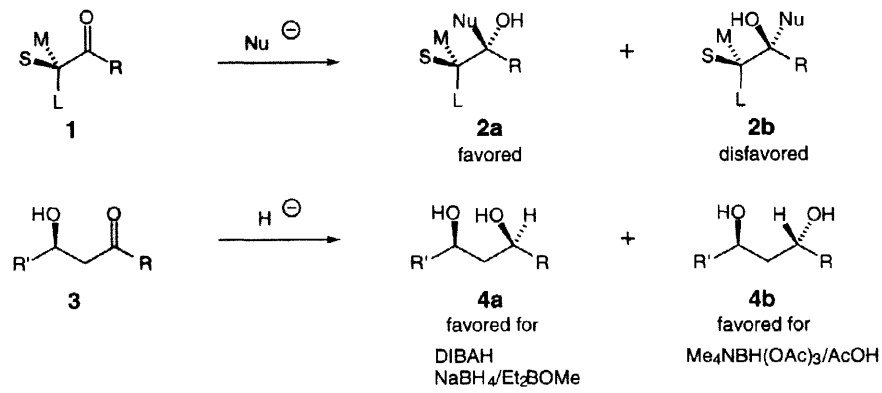
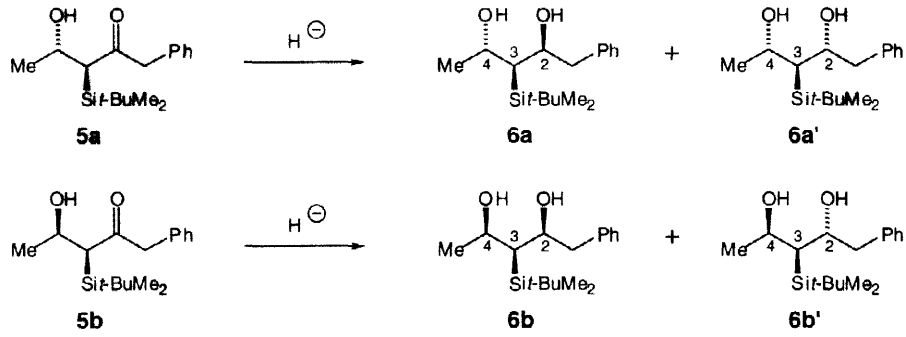


Scheme 1

Having stereoselective access to the α-silylated β-hydroxy ketones **5a** and **5b** by a novel reaction cascade[8] and knowing the rather strong stereodirecting effect of a silicon group that is attached in the α-position to a carbonyl group[9], we wanted to study the competitive and/or collaborative effects of the two stereogenic units in compounds of the type **5** on the stereochemical outcome of the carbonyl reduction. The 1,3-dihydroxy-2-silylated reduction products of the type **6** (Scheme 2), which were expected to be formed from **5a** and **5b**, possess two β-hydroxysilane sub-units. These compounds were regarded as suitable substrates for the study of the influence of steric factors on the rate of the Peterson olefination[10].



The reactions were performed with racemates; the structures reflect the relative configurations only.

Scheme 2

Results and Discussion

1. Reduction of α-Silylated β-Hydroxy Ketones. The α-silylated β-hydroxy ketones **5a** and **5b**[8] were reduced under several conditions with boro- and aluminum hydrides to yield the 2-silylated 1,3-diols **6a/6a'** and **6b/6b'** (Scheme 2), respectively. The results of these experiments are summarized in Table 1. It is readily recognized from the data that the stereochemical course of the reductions was almost uniform throughout the investigation.

All but one of the transformations — including the reaction in which the usually barely selective $LiAlH_4$ was employed as the reducing agent — afforded highly selectively the same type of product, namely compounds **6a** and **6b**, which are *syn*-configured with respect to the newly formed stereogenic C(2)-atom and

the center of chirality at the C(3)-atom. The relative configurations of the compounds **6a** and **6b** were ascertained from the single-crystal X-ray structures of their bis-(3,5-dinitrobenzoate) derivatives **7a** and **7b**, respectively (Figure 1). Only the reaction of **5b** with $Me_4NBH(OAc)_3$/AcOH followed a different stereochemical course. The '*anti*'-compound **6b'** was formed as the major product, although with poor stereoselectivity. However, the result merely reflects in a more pronounced fashion the competitive stereodirecting effects of the two stereogenic units in **5b**; effects that are also observed in the other transformations. The stereoselectivities of the reductions of **5b** are notably lower than those for the reductions of **5a**. This indicates a mismatched situation for the two stereogenic units, where, in most cases, the influence of the center of chirality at C(3) dominates the overall control of the stereochemical course of the reactions.

Table 1. *Reduction of α-Silylated Aldols* **5a** *and* **5b**

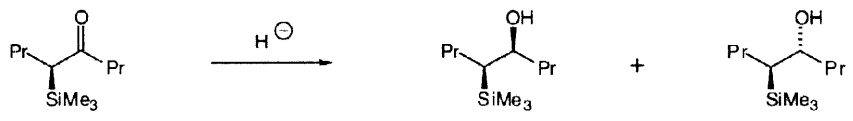
Starting Material	Conditions	Products		
No		No	Ratio	Yield [%]
5a	DIBAH	**6a/6a'**	97:3	89
	$NaBH_4/Et_2BOMe$	**6a/6a'**	98:2	87
	$LiAlH_4$	**6a/6a'**	97:3	89
	$Me_4NBH(OAc)_3$/AcOH	**6a/6a'**	97:3	74
5b	DIBAH	**6b/6b'**	99:1	75
	$NaBH_4/Et_2BOMe$	**6b/6b'**	100:0	14[a])
	$LiAlH_4$	**6b/6b'**	94:6	71[b])
	$Me_4NBH(OAc)_3$/AcOH	**6b/6b'**	29:71	31[c])

[a]) Two additional fractions from flash chromatography were collected. They might consist of boron complexes; however, we have not been able to assign definite structures.

[b]) Compound **10** (12%) was also isolated.

[c]) The reaction was incomplete after 2 d (41% of **5b** was recovered), and additional products were formed, presumably boron complexes.

The π-face selectivity of the reductions of the ketones **5a** and **5b** to the '*syn*-configured' alcohols **6a** and **6b** corresponds with that predicted by Cram's 'open-chain model' for α-chiral carbonyl compounds. The degree of selectivity, however, seems to be rather astonishing for an 'open-chain controlled' process, and the fact that the stereochemical result of the transformations is broadly independent of the reducing agents and of the reaction conditions seems also surprising. At least for the reduction of α-silylated ketone **8**, where additional chiral elements and functionality are absent, it was found that the stereoselectivity varied strongly with the reaction conditions (Scheme 3). The *syn*-product **9** was obtained only in high excess when the reaction was performed with DIBAH in pentane at −120 °C; several other conditions led to mixtures of **9/9'** with less pronounced differentiation[9]. Therefore, the involvement of cyclic intermediary structures, as proposed for the reductions of α-non-substituted aldols, also appears to be rather likely for the reactions of the compounds **5a** and **5b**.



8 **9** **9'**

Scheme 3

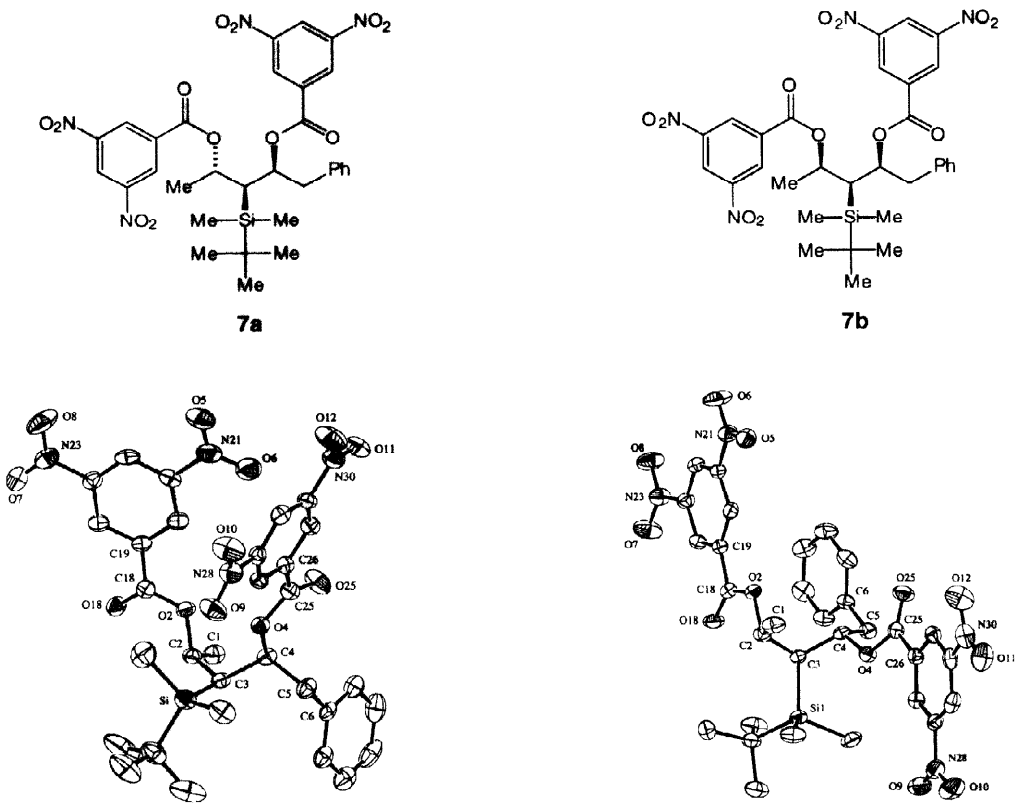


Figure 1. ORTEP plots[33] of the molecular structures of **7a** (50% probability ellipsoids) and one of the two independent molecules of **7b** ((A), 30% probability ellipsoids). The other molecule of **7b** (B) has an almost identical conformation. H-atoms omitted for clarity.

The two types of cyclic transition structures **A** and **B** that were proposed for 'chelate-controlled' reductions[4-6] and for 'intramolecular hydride transfer' reactions[7], respectively, would in fact nicely account for the preferred formation of the diols **6a** and **6b** as well (Figure 2). The location of the bulky silyl group, expected to strongly favor a *pseudo*-equatorial position in the six-membered transition structures, should determine the overall folding of the substrates. Consequently, the configuration of the center of chirality located at the carbinol C-atom has negligible importance for the stereochemical control of the reaction. In transient structures of the type **A**, regardless of the positioning of the Me group, the attack of a nucleophile would be compelled to occur at the unhindered π-face of the carbonyl functionality, remote from the silicon group. In structures of the type **B**, where conformation **B1** should be favored over conformation **B2** due to a smaller 1,3-diaxial interaction, the same π-face of the ketone should be offered to the hydride source.

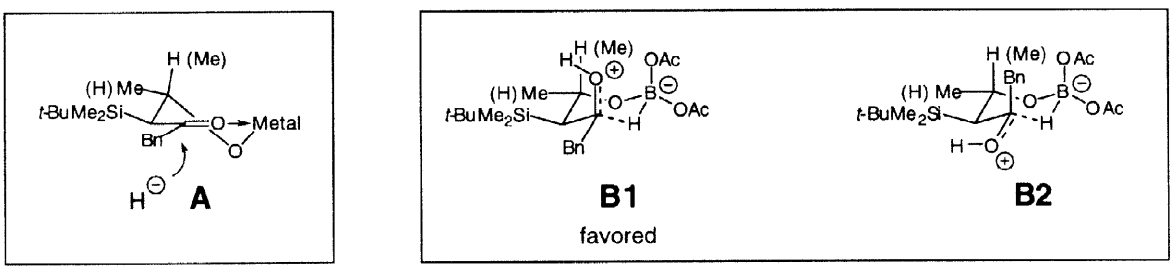
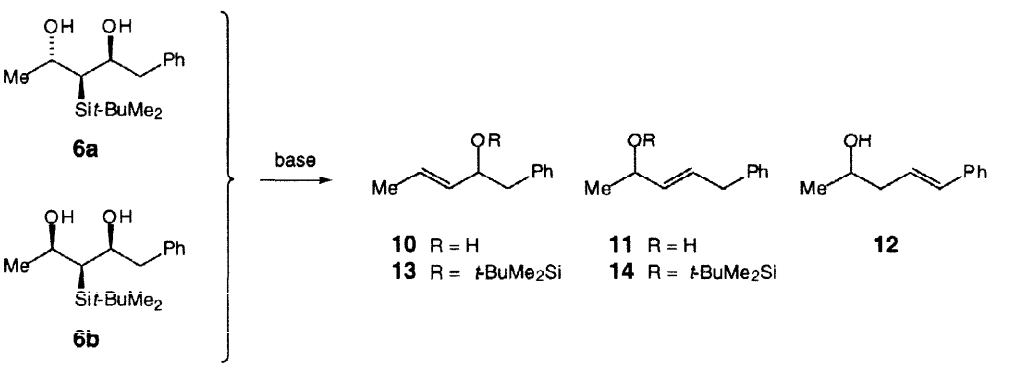


Figure 2. Proposed cyclic transition structures for the 'chelate-controlled' intermolecular reduction (**A**) or the intramolecular hydride transfer (**B1/B2**) for α-silylated aldols.

The latter postulation, however, seems to be in disagreement with the result that was obtained from the reaction of compound **5b** with $Me_4NBH(OAc)_3$/AcOH: the model would predict the selective formation of **6b**, but **6b'** was identified as the major component of the product mixture! We think that the preferred formation of **6b'** can be attributed to a process not involving a cyclic intermediary structure. It is known from the literature that the reduction of ketones with $Me_4NBH(OAc)_3$/AcOH is only reasonably rapid when the hydride transfer can proceed intramolecularly[7,11]. Since the reaction of **5b** with this reducing system is very slow, much slower than the corresponding reaction of **5a**, which notably proceeds with the expected stereoselectivity, we must assume an intermolecular hydride transfer. The stereoselectivity of the reduction can then be explained by applying Cram's rule for non-chelating 'α-chiral' ketones and assuming that the OH-bearing group becomes the large group due to complexation of the oxygen with boron.

Independently of the exact rationalization of the selectivities that are obtained in the majority of the investigated reductions, we can conclude for the reactions of compounds of the type **5** with complex metal hydrides that the stereocontrolling effect of the center of chirality in the α-position to the carbonyl group is dominant over the effect of the stereogenic center in the β-position to the ketone. The effect of the 'α-chirality' is dominant to such an extent that it controls almost solely the stereochemical course of the reactions; the 'β-chirality' — at least in compounds **5** with the rather small terminal Me group — merely reduces or enhances the degree of selectivity. It appears, however, that the presence of the β-hydroxy functionality is important for the high levels of selectivity that were observed. This structural feature seems to amplify the stereochemical influence of the dominant chiral element. Thus, the introduction of a stereodirecting silicon group in the α-position to the carbonyl functionality of β-hydroxyketones might be a suitable way to enhance the efficiency of stereoselection in addition reactions to the carbonyl group of aldols.

2. Peterson Olefination of 2-Silylated 1,3-Diols. The 2-silylated 1,3-diols **6a** and **6b** were treated with Lewis acids, bases, and fluoride ions to effect removal of the silicon group. While the reactions with acids only resulted in decomposition of the products, the treatment of **6a** and **6b** with bases and fluoride ions usually afforded mixtures of the Peterson olefination products **10** and **11** and of products **12**, **13**, and **14**[18] (Scheme 4). The homoallylic alcohol **12** was most probably formed by base-catalyzed isomerization of alcohol **11**; compounds **13** and **14** presumably arose by 'substitutive' Peterson olefination (a combination of a homo-Brook rearrangement and Peterson elimination[19]). The compositions of the product mixtures, which depend upon the starting material and the conditions used, are summarized in Table 2.



Scheme 4

Table 2. *Treatment of 2-Silylated 1,3-Diols* **6a** *and* **6b** *with Base*

Starting Material	Conditions	Products (rel. Amounts)					Yield [%]
No		**10**	**11**	**12**	**13**	**14**	
6a	KH/THF	—	80	20	—	—	76
6b	KH/THF	36	56	8	—	—	81
6a	NaOH/DMSO/H_2O	18	61	9	12	—	93
6b	NaOH/DMSO/H_2O	34	55	3	4	4	92
6a	TBAF/THF	8	92	—	—	—	95
6b	TBAF/THF	27	73	—	—	—	92

Of central interest are the molar ratios of compound **10** to compounds (**11**+**12**), which reflect the regioselectivity of the Peterson olefination. The results obtained with the *anti,syn*-configured diol **6a** give the clearest picture about the reaction paths that are followed. Under classical basic Peterson olefination conditions, upon treatment of **6a** with KH[10], highly regio- and stereoselective elimination took place to give the (*E*)-configured allylic alcohol **11**, which subsequently led to **12**. This reaction can readily be explained. It is known from the literature that the Peterson elimination follows a *syn*-mechanism when performed under basic conditions[9]. Thus, the formation of the products **11** and the (*Z*)-configured isomer of **10** would be the expected result for the transformation. The exclusive formation of **11** and **12**, which reflects the complete regioselectivity of the Peterson elimination of 2-silylated 1,3-diols of the type **6a** to the 'right side' of the molecule, shows, however, that the two possible transition structures for *syn*-elimination of a silanol unit must be markedly different energetically. It is conceivable, by regarding the pair of projections **C1**/**C2**, that conformation **C1** and a transition state related to it should in fact be favored over **C2** (Figure 3): an *eclipsing* interaction comparable to that of R^2 and Me found in **C2** is missing in **C1**.

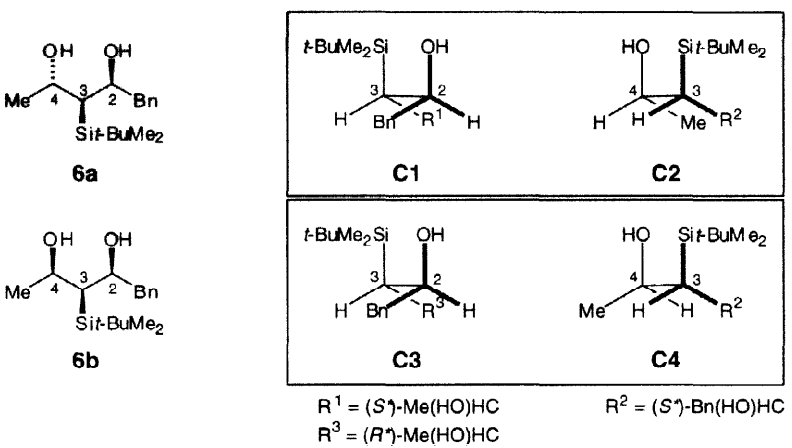


Figure 3. Comparison of the relevant conformations **C1**/**C2** and **C3**/**C4** for the *syn*-elimination of *t*-$BuMe_2SiOH$ from compound **6a** or **6b**, respectively.

Analogously to the reaction of **6a**, the reaction of **6b** with KH can be understood: *syn*-elimination should *a priori* deliver the two observed products **10** and **11**, and the low regioselectivity of the reaction is readily explained by the two conformations **C3** and **C4** (Figure 3), which are structurally — and thus also energetically — rather closely related to each other. The trifling excess of **11** that is found for the reaction of **6b** shows that

the elimination towards the sterically more demanding side of **6b** (*via* a transition structure related to **C3**) is slightly preferred.

The reactions of **6a** and **6b** with NaOH/DMSO/H_2O or with TBAF/THF follow a slightly different course. Again, the elimination products **10** and **11** were formed, and with NaOH as the base, the isomerization product **12** and silyl ethers **13** and **14** also arose[22]. The regioselectivities of the Peterson olefinations are almost unchanged for compound **6b** but are strongly affected for compound **6a**. With **6b**, the olefination seems to proceed largely by a course similar to that in the reaction with KH as the base. With **6a**, however, the formation of (*E*)-configured allylic alcohol **10** demonstrates that the respective Peterson elimination occurs in an *anti*-fashion. This *anti*-elimination is apparently made possible by the 'silico-nucleophilic' conditions, which allow a direct attack of the nucleophile at the silicon center. The *anti*-elimination is evidently favored over the corresponding *syn*-elimination of the silyl group at C(3) and OH at C(4) — none of the (*Z*)-configured isomer of **10** was found — but it is still less prominent than the *syn*-elimination towards the 'right-side' of the molecule, which delivers the allylic alcohol **11**, the major product of the reaction.

In conclusion it can be stated that the Peterson olefination proceeds only with *syn,anti*-configured 2-silylated 1,3-diols (compounds of the type **6a**) with high stereo- and regioselectivity. The regioselectivity of the reaction with *syn,syn*-configured compounds of the type **6b** is low, as expected, and synthetically not useful.

Experimental Part

General. Unless otherwise stated: Manipulations involving air- and H_2O-sensitive reagents were carried out in oven-dried glass equipment under an Ar atmosphere. For reactions, Et_2O and THF were freshly distilled over Na with benzophenone ketyl as the indicator; pentane, CH_3CN, pyridine, and MeOH were dried according to standard procedures. All other org. solvents were distilled prior to use. The starting materials were purchased from commercial sources and used as received. Soln. for workup procedures were prepared in deionized H_2O. Workup implies: dilution with sat. aq. NH_4Cl soln., extraction with Et_2O, washing with brine until pH = 7, and drying of the extracts with $MgSO_4$ prior to evaporation of the solvents *in vacuo*. Flash chromatography (FC) was performed on Merck silica gel 60 (40–63 μm). Melting points (M.p.) were measured with a Mettler FP5/FP52. Infrared spectra (IR) were taken as neat liquid films between NaCl plates on a Perkin-Elmer 297 or 781, data in cm^{-1}. ^1H NMR in $CDCl_3$: Bruker AC-300 (300 MHz), ARX-300 (300 MHz), or AMX-600 (600 MHz), δ in ppm relative to $CHCl_3$ (δ_H = 7.26), J in Hz. ^{13}C NMR in $CDCl_3$: Bruker ARX-300 (75.5 MHz), δ in ppm relative to $CDCl_3$ (δ_C = 77.0), multiplicities from DEPT-135 and DEPT-90 experiments. Some spectra (uncorr.) are not corrected to chemical shifts relative to the solvent due to overlapping signals. Chemical ionization mass spectra (CI-MS) were taken on a Finnigan MAT 90 with NH_3 as the reactant gas, data in *m/z* (rel%).

1. Reduction Reactions (Summarized in Table 1).

1.1. *(2*R*, 3*R*, 4*R*)-3-[(*tert*-Butyl)dimethylsilyl]-1-phenyl-2,4-pentanediol* (**6a**) and *(2*R*, 3*S*, 4*S*)-3-[(*tert*-Butyl)dimethylsilyl]-1-phenyl-2,4-pentanediol* (**6a'**). Reduction with DIBAH: Diisobutyl aluminum hydride (DIBAH, 0.43 ml of a 1.5M soln. in toluene, 0.65 mmol) was added dropwise along the wall of the flask to a soln. of (*R**,*R**)-3-[(*tert*-butyl)dimethylsilyl]-4-hydroxy-1-phenylpentan-2-one (**5a**[8], 61.9 mg, 0.21

mmol) in pentane (2.5 ml) at –120 °C. The soln. was kept at –120 °C for 2.5 h and allowed to warm to –80 °C over a period of 25 min. Workup and FC (gradient: hexane/ Et_2O 4:1 to 3:1) afforded **6a'** (first eluate, 1.8 mg, 0.006 mmol, 3%) and **6a** (second eluate, 53.1 mg, 0.18 mmol, 86%).

Reduction with $NaBH_4/Et_2BOMe$: Et_2BOMe (0.06 ml, 0.45 mmol) and, after 1 h, $NaBH_4$ (*ca.* 100 mg, *ca.* 2.6 mmol) were added to a soln. of **5a** (66.0 mg, 0.23 mmol) in THF/MeOH 4:1 (2.25 ml) at –40 °C. After 28 h at –40 °C, workup and repeated coevaporation of the crude product with MeOH/AcOH[6] followed by FC (gradient: hexane/AcOEt 6:1 to 5:1) afforded **6a'** (1.3 mg, 0.004 mmol, 2%) and **6a** (56.8 mg, 0.19 mmol, 85%).

Reduction with $LiAlH_4$: A soln. of **5a** (41.1 mg, 0.14 mmol) in Et_2O (2 ml) was added dropwise along the wall of the flask to a suspension of $LiAlH_4$ (48 mg, 1.26 mmol) in Et_2O (4 ml) at –80 °C. The soln. was allowed to warm to –50 °C over a period of 1 h and stirred for another 2 h. Workup and FC (gradient: hexane/ Et_2O 4:1 to 3:1) afforded **6a'** (1.2 mg, 0.004 mmol, 3%) and **6a** (35.6 mg, 0.12 mmol, 86%).

Reduction with $Me_4NBH(OAc)_3$: A soln. of **5a** (43.1 mg, 0.15 mmol) in MeCN (2 ml) was added to a soln. of $Me_4NBH(OAc)_3$ (300 mg, 1.14 mmol) in AcOH/MeCN (1:1, 2 ml) at 0 °C. The soln. was warmed to 23 °C and stirred for an additional 48 h. Workup and FC (gradient: hexane/AcOEt 7:1 to 6:1 to 5:1) afforded recovered **5a** (6.2 mg, 14%), **6a'** (0.7 mg, 0.002 mmol, 2%), and **6a** (31.1 mg, 0.11 mmol, 72%).

Data of **6a**: Colorless oil. IR: 3350*s* (br.), 3080*w*, 3060*m*, 3020*m*, 2950*s*, 2920*s*, 2875*s*, 2850*s*, 2730*w*, 2700*w*, 1940*w*, 1870*w*, 1800*w*, 1600*w*, 1580*w*, 1490*m*, 1460*m*, 1450*m*, 1410*s*, 1385*m*, 1370*m*, 1360*s*, 1310*m*, 1250*s*, 1185*w*, 1160*m*, 1110*s*, 1085*m*, 1030*s*, 1005*m*, 975*w*, 935*m*, 905*w*, 890*w*, 825*s*, 805*m*, 770*m*, 750*m*, 700*s*, 680*m*, 665*m*. ^{1}H NMR (uncorr.): 7.20–7.02 (*m*, 5 arom. H); 4.27 (*ddd*, J = 9.2, 5.0, 0.9, $PhCH_2CH$); 4.12 (*qd*, J = 6.2, 3.5, $MeCH$); 2.82, 2.57 (*AB* of *ABX*, J_{AB} = 13.6, J_{AX} = 9.2, J_{BX} = 5.0, $PhCH_2$); 2.42 (br. *s*, 2 OH); 1.04 (*d*, J = 6.2, *Me*CH, SiCH (*m*, hidden underneath the *d*)); 0.74 (*s*, *t*-Bu); 0.13, 0.00 (2*s*, Me_2Si). ^{13}C NMR: 139.1 (*s*, arom. C); 129.3, 128.6 (2*d*, 2×2 arom. C); 126.5 (*d*, arom. C); 73.2 (*d*, $PhCH_2CH$); 69.0 (*d*, *MeCH*); 42.7 (*t*, $PhCH_2$); 36.6 (*d*, SiCH); 27.2 (*q*, Me_3C); 24.5 (*q*, *Me*CH); 17.5 (*s*, Me_3C); –3.1, –4.8 (2*q*, Me_2Si). CI-MS: 162 (27, $[M+NH_4-t\text{-}BuMe_2SiOH-H_2O]^+$), 145 (100, $[M+H-t\text{-}BuMe_2SiOH-H_2O]^+$).

Data of **6a'**: Colorless oil. IR: 3360*m* (br.), 3085*w*, 3060*m*, 3025*m*, 2955*s*, 2925*s*, 2880*s*, 2855*s*, 1940*w*, 1870*w*, 1800*w*, 1740*w*, 1670*w*, 1600*w*, 1490*m*, 1460*m*, 1450*m*, 1405*m*, 1385*m*, 1360*m*, 1250*s*, 1185*m*, 1155*m*, 1120*s*, 1075*s*, 1030*s*, 1000*m*, 965*m*, 940*m*, 900*m*, 835*s*, 810*m*, 775*s*, 745*s*, 700*s*. ^{1}H NMR: 7.35–7.16 (*m*, 5 arom. H); 4.32–4.22 (*m*, $MeCHCHCH$); 3.17, 2.93 (*AB* of *ABX*, J_{AB} = 13.4, J_{AX} = 9.9, J_{BX} = 3.9, $PhCH_2$); 1.51 (*d*, J = 6.5, *Me*CH); 1.18 (*dd*, J = 3.9, 2.2, SiCH); 0.89 (*s*, *t*-Bu); 0.11, 0.09 (2*s*, Me_2Si). ^{13}C NMR: 139.2 (*s*, arom. C); 129.3, 128.8 (2*d*, 2×2 arom. C); 126.6 (*d*, arom. C); 75.1 (*d*, $PhCH_2CH$); 69.4 (*d*, MeCH); 46.7 (*t*, $PhCH_2$); 35.2 (*d*, SiCH); 27.2 (*q*, Me_3C); 26.6 (*q*, *Me*CH); 17.5 (*s*, Me_3C); –5.67, –5.73 (2*q*, Me_2Si). CI-MS: 295 (1, $[M+H]^+$), 294 (4, $[M+NH_4-H_2O]^+$), 259 (5, $[M+H-2H_2O]^+$), 236 (13), 185 (25), 162 (78, $[M+NH_4-t\text{-}BuMe_2SiOH-H_2O]^+$), 145 (100, $[M+H-t\text{-}BuMe_2SiOH-H_2O]^+$).

1.2. *(2R*, 3R*, 4S*)-3-[(*tert*-Butyl)dimethylsilyl]-1-phenyl-2,4-pentanediol* (**6b**) and *(2R*, 3S*, 4R*)-3-[(*tert*-Butyl)dimethylsilyl]-1-phenyl-2,4-pentanediol* (**6b'**). Reduction with DIBAH: DIBAH (1.40 ml of a

1.5M soln. in toluene, 2.1 mmol) was added dropwise along the wall of the flask to a soln. of (*R**,*S**)-3-[(*tert*-butyl)dimethylsilyl]-4-hydroxy-1-phenylpentan-2-one (**5b**[8], 122.3 mg, 0.42 mmol) in CH_2Cl_2 (3 ml) and pentane (2 ml) at –95 °C. The soln. was kept at –95 °C for 1 h, allowed to warm to –80 °C over a period of 20 min, and stirred for another 4.5 h. Workup and FC (gradient: hexane/AcOEt 6:1 to 5:1) afforded **6b'** (first eluate, 0.4 mg, 0.0014 mmol, <1%) and **6b** (second eluate, 92.0 mg, 0.31 mmol, 75%).

Reduction with $NaBH_4/Et_2BOMe$: Et_2BOMe (0.046 ml, 0.35 mmol) and, after 1 h, $NaBH_4$ (*ca.* 100 mg, *ca.* 2.6 mmol) were added to a soln. of **5b** (51.4 mg, 0.18 mmol) in THF/MeOH 4:1 (2 ml) –40 °C. After 28 h at –40 °C, workup and repeated coevaporation of the crude product with MeOH/AcOH[6] followed by FC (gradient: hexane/AcOEt 6:1 to 5:1) afforded **6b** (7.1 mg, 0.024 mmol, 14%).

Reduction with $LiAlH_4$: A soln. of **5b** (51.8 mg, 0.18 mmol) in Et_2O (2 ml) was added dropwise along the wall of the flask to a suspension of $LiAlH_4$ (45 mg, 1.19 mmol) in Et_2O (4 ml) at –80 °C. The soln. was allowed to warm to –50 °C over a period of 1 h and stirred for another 2 h. Workup and FC (gradient: hexane/AcOEt 6:1 to 5:1) afforded **6b'** (2.1 mg, 0.007 mmol, 4%) and **6b** (34.9 mg, 0.12 mmol, 67%).

Reduction with $Me_4NBH(OAc)_3$: A soln. of **5b** (48.4 mg, 0.17 mmol) in MeCN (2 ml) was added to a soln. of $Me_4NBH(OAc)_3$ (372 mg, 1.41 mmol) in AcOH/MeCN (1:1, 2.4 ml) at 0 °C. The soln. was warmed to 23 °C and stirred for an additional 48 h. Workup and FC (gradient: hexane/AcOEt 7:1 to 6:1 to 5:1) afforded recovered **5b** (19.7 mg, 41%), **6b'** (10.6 mg, 0.036 mmol, 22%), and **6b** (4.2 mg, 0.014 mmol, 9%).

Data of **6b**: Amorphous crystalline solid. M.p.: 105–106.3 °C (hexane/AcOEt). IR (KBr): 3340*s* (br.), 3080*w*, 3030*m*, 3000*m*, 2950*s*, 2930*s*, 2880*s*, 2850*s*, 2710*w*, 1600*w*, 1495*m*, 1470*s*, 1455*m*, 1415*m*, 1390*w*, 1380*m*, 1360*m*, 1350*m*, 1325*w*, 1290*w*, 1250*s*, 1215*w*, 1195*w*, 1175*w*, 1125*s*, 1025*s*, 1070*s*, 1030*m*, 1005*s*, 965*m*, 935*w*, 910*w*, 870*m*, 835*s*, 825*s*, 800*s*, 765*s*, 740*s*, 700*s*, 685*m*, 665*m*. ^{1}H NMR (uncorr.): 7.19–7.05 (*m*, 5 arom. H); 4.18 (*qd*, *J* = 6.6, 2.9, MeC*H*); 4.11 (*ddd*, *J* = 9.7, 4.0, 2.9, $PhCH_2CH$); 2.77, 2.71 (*AB* of *ABX*, J_{AB} = 13.6, J_{AX} = 9.7, J_{BX} = 4.0, $PhCH_2$); 1.70 (br. *s*, 2 OH); 1.39 (*t*, *J* = 2.9, SiCH); 1.19 (*d*, *J* = 6.6, *Me*CH); 0.79 (*s*, *t*-Bu); 0.10, 0.00 (2*s*, Me_2Si). ^{13}C NMR: 139.3 (*s*, arom. C); 129.3, 128.7 (2*d*, 2×2 arom. C); 126.6 (*d*, arom. C); 74.0 (*d*, $PhCH_2CH$); 69.5 (*d*, MeCH); 44.1 (*t*, $PhCH_2$); 39.4 (*d*, SiCH); 27.4 (*q*, Me_3C); 23.1 (*q*, *Me*CH); 17.5 (*s*, Me_3C); –3.1, –3.6 (2*q*, Me_2Si). CI-MS: 162 (30, $[M+NH_4-t\text{-}BuMe_2SiOH-H_2O]^+$), 145 (100, $[M+H-t\text{-}BuMe_2SiOH-H_2O]^+$).

Data of **6b'**: Pale yellow oil. IR: 3350*s* (br.), 3080*w*, 3060*w*, 3025*m*, 2950*s*, 2925*s*, 2880*s*, 2850*s*, 2705*w*, 2240*w*, 1940*w*, 1870*w*, 1800*w*, 1600*w*, 1490*m*, 1465*s*, 1455*s*, 1410*m*, 1385*m*, 1370*m*, 1360*m*, 1315*m*, 1250*s*, 1185*m*, 1160*m*, 1110*m*, 1085*m*, 1030*s*, 1005*m*, 970*m*, 935*m*, 910*m*, 825*s*, 810*s*, 775*s*, 735*s*, 700*s*. ^{1}H NMR (uncorr.): 7.17–6.99 (*m*, 5 arom. H); 4.27 (*ddd*, *J* = 9.2, 4.9, 1.1, $PhCH_2CH$); 4.12 (*qd*, *J* = 6.2, 3.6, MeC*H*); 2.83, 2.57 (*AB* of *ABX*, J_{AB} = 13.6, J_{AX} = 9.2, J_{BX} = 4.9, $PhCH_2$); 2.30 (br. *s*, 2 OH); 1.04 (*d*, *J* = 6.2, *Me*CH, SiCH (*m*, hidden underneath the *d*)); 0.74 (*s*, *t*-Bu); 0.13, 0.00 (2*s*, Me_2Si). ^{13}C NMR: 139.1 (*s*, arom. C); 129.3, 128.6 (2*d*, 2×2 arom. C); 126.5 (*d*, arom. C); 73.2 (*d*, $PhCH_2CH$); 69.0 (*d*, MeCH); 42.7 (*t*, $PhCH_2$); 36.6 (*d*, SiCH); 27.2 (*q*, Me_3C); 24.4 (*q*, *Me*CH); 17.5 (*s*, Me_3C); –3.1, –4.8 (2*q*, Me_2Si). CI-MS: 312 (7, $[M+NH_4]^+$), 294 (9, $[M+NH_4-H_2O]^+$), 259 (5, $[M+H-2H_2O]^+$), 178 (46), 162 (81, $[M+NH_4-t\text{-}BuMe_2SiOH-H_2O]^+$), 145 (100, $[M+H-t\text{-}BuMe_2SiOH-H_2O]^+$).

2. Preparation of Crystalline Derivatives 7a and 7b and Determination of Relative

Configurations by X-Ray Crystallography.

2.1. *(2R*, 3R*, 4R*)-3-[(*tert.*-Butyl)dimethylsilyl]-1-phenylpent-2,4-diyl bis-3,5-Dinitrobenzoate* (**7a**). To a soln. of **6a** (30.2 mg, 0.103 mmol) in pyridine (1.5 ml) at 23 °C was added 3,5-dinitrobenzoyl chloride (144 mg, 0.63 mmol), and the soln. was warmed to 40 °C for 30 min. Workup (extraction with CH_2Cl_2) and FC (gradient: CH_2Cl_2/hexane 1:1 to 2:1) afforded **7a** (69.3 mg, 0.102 mmol, 99%) as pale yellow crystals. M.p. 161.1–165.2 °C (hexane/CH_2Cl_2 2:1). IR (KBr): 3100*m*, 3025*w*, 2985*m*, 2975*m*, 2925*m*, 2880*m*, 2850*m*, 1865*w*, 1735*s*, 1720*s*, 1645*w*, 1630*s*, 1600*m*, 1585*w*, 1565*m*, 1540*s*, 1505*m*, 1495*m*, 1460*s*, 1445*m*, 1405*w*, 1345*s*, 1285*s*, 1275*s*, 1205*w*, 1165*s*, 1120*s*, 1105*m*, 1075*s*, 1025*s*, 1005*m*, 995*m*, 920*s*, 905*s*, 880*m*, 800*w*, 830*m*, 825*s*, 805*s*, 770*m*, 760*m*, 740*s*, 720*s*, 705*s*. ^{1}H NMR: 9.20, 9.13 (2*t*, *J* = 2.2, 2 arom. H); 9.09, 8.99 (2*d*, *J* = 2.1, 4 arom. H); 7.34–7.19 (*m*, 5 arom. H); 6.10–6.05 (symm. *m*, $PhCH_2CH$); 5.69 (*qd*, *J* = 6.3, 2.8, MeC*H*); 3.36, 3.08 (*AB* of *ABX*, J_{AB} = 13.6, J_{AX} = 8.1, J_{BX} = 6.5, $PhCH_2$); 1.86 (*dd*, *J* = 2.8, 1.9, SiCH); 1.36 (*d*, *J* = 6.3, *Me*CH); 1.06 (*s*, *t*-Bu); 0.47, 0.10 (2*s*, Me_2Si). ^{13}C NMR: 162.1, 161.9 (2*s*, 2 CO); 148.7 (*s*, 4 NO_2C); 136.6 (*s*, arom. C); 133.9, 133.7 (2*s*, 2 OC(O)*C*); 129.23, 129.16, 129.1, 128.9, (4*d*, 4×2 arom. C); 127.3 (*d*, arom. C); 122.4 (*d*, 2 arom. C); 78.7, 74.3 (2*d*, MeCHCHCH); 41.5 (*t*, $PhCH_2$); 33.5 (*d*, SiCH); 27.3 (*q*, Me_3C); 21.0 (*q*, *Me*CH); 17.6 (*s*, Me_3C); –3.4, –5.0 (2*q*, Me_2Si). CI-MS: 700 (39, $[M+NH_4]^+$), 259 (100, [*M*+H–2 dinitrobenzoic acid]$^+$), 162 (23), 132 (83). Anal. calc. for $C_{31}H_{34}N_4O_{12}Si$ (682.715): C 54.54, H 5.02; found: C 54.24, H 5.23.

2.2. *(2R*, 3R*, 4S*)-3-[(*tert.*-Butyl)dimethylsilyl]-1-phenylpent-2,4-diyl bis-3,5-Dinitrobenzoate* (**7b**). To a soln. of **6b** (29.0 mg, 0.099 mmol) in pyridine (2 ml) was added 3,5-dinitrobenzoyl chloride (140 mg, 0.61 mmol) at 0 °C, and the soln. was warmed to 50 °C for 20 min. Workup (extraction with CH_2Cl_2) and FC (hexane/AcOEt 7:1, then CH_2Cl_2) afforded **7b** (66.8 mg, 0.098 mmol, 99%) as pale yellow crystals. M.p.: 173.4–175.8 °C ($CHCl_3$/EtOH/CH_2Cl_2 2:2:1). IR (KBr): 3110*m*, 3020*w*, 2975*m*, 2965*m*, 2880*m*, 2835*m*, 1865*w*, 1825*w*, 1730*s*, 1710*s*, 1630*s*, 1600*w*, 1550*s*, 1505*w*, 1495*w*, 1470*m*, 1465*m*, 1455*m*, 1415*w*, 1390*m*, 1345*s*, 1285*s*, 1270*s*, 1175*s*, 1160*s*, 1125*s*, 1100*s*, 1075*s*, 1025*m*, 1000*w*, 950*s*, 920*m*, 895*w*, 865*m*, 830*s*, 825*s*, 805*s*, 775*m*, 750*m*, 730*s*, 720*s*, 705*s*. ^{1}H NMR: 9.27 (*t*, *J* = 2.1, arom. H); 9.20–9.17 (*m*, 3 arom. H); 8.84 (*d*, *J* = 2.2, 2 arom. H); 7.19 (*d*, *J* = 7.1, 2 arom. H); 6.95 (*t*, *J* = 7.7, 2 arom. H); 6.70 (*t*, *J* = 7.5, arom. H); 5.89–5.84 (symm. *m*, $PhCH_2CH$); 5.57 (*qd*, *J* = 6.6, 2.6, MeC*H*); 3.12, 2.87 (*AB* of *ABX*, J_{AB} = 13.1, J_{AX} = 5.0, J_{BX} = 9.0, $PhCH_2$); 2.23 (br. *d*, *J* = 2.1, SiCH); 1.39 (*d*, *J* = 6.6, *Me*CH); 1.16 (*s*, *t*-Bu); 0.55, 0.34 (2*s*, Me_2Si). ^{13}C NMR: 161.9, 161.4 (2*s*, 2 CO); 148.8, 148.4 (2*s*, 2×2 NO_2C); 136.5 (*s*, arom. C); 133.8, 133.6 (2*s*, 2 OC(O)*C*); 129.3, 129.2, 129.1, 128.5 (4*d*, 4×2 arom. C); 126.4, 122.5, 122.1 (3*d*, 3 arom. C); 79.1, 75.1 (2*d*, MeCHCHCH); 41.6 (*t*, $PhCH_2$); 33.0 (*d*, SiCH); 27.0 (*q*, Me_3C); 18.2 (*q*, *Me*CH); 17.8 (*s*, Me_3C); –2.9, –3.7 (2*q*, Me_2Si). CI-MS: 700 (57, $[M+NH_4]^+$), 517 (76), 276 (35), 259 (100, [*M*+H–2 dinitrobenzoic acid]$^+$), 162 (28), 145 (11), 132 (62). Anal. calc. for $C_{31}H_{34}N_4O_{12}Si$ (682.715): C 54.54, H 5.02; found: C 54.37, H 4.83.

2.3. *Crystal Structure Determination of* **7a** *and* **7b**.[23] All measurements were conducted on a Rigaku AFC5R diffractometer fitted to a 12kW rotating anode generator. The intensities of three standard reflections, which were measured after every 150 reflections, remained stable throughout each data collection. The intensities were corrected for Lorentz and polarization effects, but not for absorption. The structures were solved by

Table 3. *Crystallographic Data for* **7a** *and* **7b**

			7a	**7b**
Crystallized from			CH_2Cl_2/hexane	EtOH/$CHCl_3$/CH_2Cl_2
Empirical formula			$C_{31}H_{34}N_4O_{12}Si$	$C_{31}H_{34}N_4O_{12}Si$
Formula weight			682.71	682.71
Crystal color, habit			colorless, prism	colorless, prism
Crystal dimensions [mm]			0.15 × 0.30 × 0.42	0.30 × 0.40 × 0.45
Diffractometer			Rigaku AFC5R	Rigaku AFC5R
Radiation, wavelength [Å]			MoK_α, 0.71069	MoK_α, 0.71069
Crystal temp. [K]			173 (1)	273 (1)
Crystal system			triclinic	monoclinic
Space group			$P\bar{1}$	$P2_1/c$
Z			2	8
Reflections for cell determination			25	25
2θ range for cell determination [°]			34–38	36–40
Unit cell parameters	a	[Å]	12.397 (2)	21.499 (3)
	b	[Å]	13.886 (3)	11.817 (3)
	c	[Å]	11.416 (1)	26.737 (6)
	α	[°]	111.587 (9)	90
	β	[°]	92.55 (1)	94.86 (2)
	γ	[°]	69.02 (1)	90
	V	[Å^3]	1697.5 (5)	6768 (2)
F(000)			716	2864
D_x [g cm^{-3}]			1.336	1.340
μ (MoK_α) [mm^{-1}]			0.136	0.137
Scan type			$\omega/2\theta$	ω
$2\theta_{(max)}$ [°]			40	50
Total reflections measured			3356	12884
Symmetry-independent reflections			3164	11893
Reflections used [$I>2\sigma(I)$]			2645	6513
Parameters refined			434	865
R			0.0358	0.0559
wR			0.0362	0.0506
Goodness of fit s			2.237	1.933
Secondary extinction coefficient			5.1 (9) × 10^{-7}	—
Final Δ_{max}/σ			0.0002	0.0003
$\Delta\rho$ (max; min) [e Å^{-3}]			0.18; –0.17	0.25; –0.23
$\sigma(d_{(C-C)})$ [Å]			0.004–0.005	0.005–0.01

direct methods using SHELXS86[24], which revealed the positions of all non-hydrogen atoms. There are two independent molecules with similar conformations in the asymmetric unit of the structure of **7b**, and their atomic coordinates were tested carefully with the MISSYM[25,26] routine of the program PLATON[27] for a relationship from a higher symmetry space group, but none could be found. The non-H-atoms were refined anisotropically. All H-atoms were fixed in geometrically calculated positions with a C-H distance of 0.95 Å, and they were assigned a fixed isotropic displacement parameter with a value equal to 1.2 U_{eq} of the parent C-atom. Refinements of the structures were carried out on F using full-matrix least-squares procedures which minimized the function $\Sigma w(|F_o|-|F_c|)^2$, where $1/w = [\sigma^2(F_o)+(0.005F_o)^2]$. The data collection and refinement parameters for each compound are listed in Table 3. Neutral atom scattering factors for non-H-atoms were taken from[28] and the scattering factors for H-atoms from[29]. Anomalous dispersion effects were included in F_c[30] the values for f' and f'' were taken from[31]. All calculations were performed using the TEXSAN[32] crystallographic software package, and the figures were produced with ORTEPII[33].

Specific Remarks. Due to icing problems during the data collection with racemic **7a**, the data for which 2Θ>40 °C was found to be unreliable and was discarded. Nevertheless, the structure is clearly defined without any ambiguity revealing the (2*R**,3*R**,4*R**)-configuration for **7a**. The reflection/parameter ratio, however, is relatively low.

The crystal of racemic **7b** was fairly weakly diffracting and is possibly also twinned. There was evidence for a second lattice of reflections, but it was still possible to obtain a consistent set of reflections for the determination of the unit cell parameters and the measurement of the data. It is not known if there are any effects due to the overlap of twinned reflections, although the absence of large discrepancies in any of the values of F_o–F_c suggests that such effects are minimal. The enlarged anisotropic displacement parameters for the -NO_2 groups in both molecules, and for the benzyl ring of molecule B might be an indication of slight inaccuracies in the data or they might result from dynamic motion or slight static disorder within the structure. The structure of racemic **7b** reveals for both symmetry-independent molecules in the asymmetric unit the (2*R**,3*R**,4*S**)-configuration.

3. Olefination Reactions (Summarized in Table 2).

3.1. *Reactions with Starting Material* **6a**: With KH: KH (20% suspension in silicon oil, *ca.* 150 mg, *ca.* 0.7 mmol) was added to a stirred soln. of **6a** (52.7 mg, 0.18 mmol) in THF (4 ml) at 23 °C. Workup after 2 h and FC (hexane/Et_2O 3:1) afforded **11** (17.7 mg, 0.11 mmol, 61%) and **12** (4.4 mg, 0.027 mmol, 15%).

With NaOH/DMSO/H_2O: NaOH (6 mg, 0.16 mmol, powdered) was added to a soln. of **6a** (94.3 mg, 0.32 mmol) in DMSO/H_2O 19:1 (5 ml) at 23 °C, and the soln. was stirred for 24 h. Workup and FC (hexane/Et_2O 3:1) afforded **10** (8.9 mg, 0.055 mmol, 17%), **11** (29.5 mg, 0.18 mmol, 57%), **12** (4.0 mg, 0.025 mmol, 8%), and **13** (10.0 mg, 0.04 mmol, 11%).

With TBAF: TBAF (1.39 ml of a 1M soln. in THF, 1.39 mmol) was added to a soln. of **6a** (68.3 mg, 0.23 mmol) in THF (2 ml) at 23 °C, and the soln. was stirred for 2 h. Workup and FC (hexane/Et_2O 3:1) afforded **10** (3.1 mg, 0.019 mmol, 8%) and **11** (32.9 mg, 0.20 mmol, 87%).

3.2. *Reactions with Starting Material* **6b**: With KH: KH (20% suspension in silicon oil, *ca.* 240 mg, *ca.* 1.1 mmol) was added to a soln. of **6b** (86.0 mg, 0.29 mmol) in THF (6.5 ml) at 23 °C, and the soln. was stirred for 50 min. Workup and FC (hexane/Et_2O 3:1) afforded **10** (13.9 mg, 0.09 mmol, 29%), **11** (21.3 mg,

0.13 mmol, 45%), and **12** (3.2 mg, 0.020 mmol, 7%).

With NaOH/DMSO/H_2O: NaOH (4.6 mg, 0.11 mmol, powdered) was added to a soln. of **6b** (67.4 mg, 0.23 mmol) in DMSO/H_2O 19:1 (5 ml) at 23 °C, and the soln. was stirred for 22 h. Workup and FC (hexane/Et_2O 3:1) afforded **10** (11.5 mg, 0.07 mmol, 31%), **11** (18.4 mg, 0.11 mmol, 50%), **12** (1.0 mg, 0.006 mmol, 3%), and **13/14** (as a 1:1 mixture, 5.0 mg, 0.018 mmol, 8%).

With TBAF: TBAF (1.37 ml of a 1M soln. in THF, 1.37 mmol) was added to a soln. of **6b** (67.4 mg, 0.23 mmol) in THF (2 ml) at 23 °C, and the soln. was stirred for 2 h. Workup and FC (hexane/Et_2O 3:1) afforded **10** (9.2 mg, 0.057 mmol, 25%) and **11** (25.0 mg, 0.15 mmol, 67%).

3.3. *(E)-1-Phenylpent-3-en-2-ol* (**10**). Spectroscopic data complementary to[12,13]. IR: 3370*s* (br.), 3080*w*, 3060*m*, 3025*s*, 3000*m*, 2960*m*, 2935*s*, 2915*s*, 2880*m*, 2850*m*, 2725*w*, 1945*w*, 1870*w*, 1800*w*, 1750*w*, 1670*w*, 1600*w*, 1580*w*, 1490*s*, 1450*s*, 1375*m*, 1310*m*, 1265*w*, 1205*w*, 1180*w*, 1155*w*, 1115*m*, 1085*m*, 1030*s*, 1000*m*, 965*s*, 940*m*, 905*w*, 855*w*, 825*w*, 785*w*, 745*s*, 700*s*. ^{1}H NMR (uncorr.): 7.24–7.11 (*m*, 5 arom. H); 5.59 (*dqd*, *J* = 15.3, 6.2, 0.7, MeC*H*); 5.46 (*ddq*, *J* = 15.3, 6.5, 1.3, MeCH=C*H*); 4.22–4.16 (symm. *m*, C*H*(OH)); 2.75, 2.67 (*AB* of *ABX*, J_{AB} = 13.5, J_{AX} = 5.1, J_{BX} = 7.9, PhCH_2); 1.60 (*dd*, *J* = 6.2, 0.7, Me). ^{13}C NMR: 138.0 (*s*, arom. C); 133.2 (*d*, MeCH=*C*H); 129.5, 128.4 (2*d*, 2×2 arom. C); 127.0 (*d*, arom. C); 126.4 (*d*, Me*C*H); 73.5 (*d*, CH(OH)); 44.1 (*t*); 17.6 (*q*). CI-MS: 324 (6, [2*M*+NH_4–H_2O]$^+$), 180 (18, [*M*+NH_4]$^+$), 162 (100, [*M*+NH_4–H_2O]$^+$), 145 (12, [*M*+H–H_2O]$^+$).

3.4. *(E)-5-Phenylpent-3-en-2-ol* (**11**). IR, ^{1}H NMR in accordance with[14,15]; complementary to the literature: ^{13}C NMR: 140.1 (*s*, arom. C); 135.5 (*d*, MeCH*C*H); 129.3 (*d*, arom.C); 128.5, 128.4 (2*d*, 2×2 arom. C); 126.1 (*d*, PhCH_2*C*H); 68.6 (*d*, CH(OH)); 38.5 (*t*); 23.3 (*q*).

3.5. *(E)-5-Phenylpent-4-en-2-ol* (**12**). IR, ^{1}H NMR, and ^{13}C NMR in accordance with[16,17]; complementary to the literature: CI-MS: 180 (100, [*M*+NH_4]$^+$), 162 (22, [*M*+NH_4–H_2O]$^+$), 145 (8, [*M*+H–H_2O]$^+$).

3.6. *1-Benzylbut-2-enyl (*tert*-Butyl)dimethylsilyl Ether* (**13**). Pale yellow oil. IR: 3080*w*, 3060*w*, 3025*m*, 2995*w*, 2950*s*, 2925*s*, 2880*m*, 2850*s*, 2730*w*, 2705*w*, 1940*w*, 1865*w*, 1800*w*, 1740*w*, 1670*w*, 1600*w*, 1490*m*, 1470*m*, 1460*m*, 1450*m*, 1405*w*, 1390*m*, 1375*m*, 1360*m*, 1300*w*, 1255*s*, 1210*w*, 1185*w*, 1120*m*, 1090*s*, 1075*s*, 1060*s*, 1030*m*, 1000*m*, 990*m*, 965*s*, 945*s*, 900*m*, 880*m*, 835*s*, 810*m*, 775*s*, 745*m*, 700*s*. ^{1}H NMR: 7.28–7.15 (*m*, 5 arom. H); 5.58–5.43 (*m*, CH=CH); 4.23–4.17 (symm. *m*, SiOCH); 2.73 (*d*, *J* = 6.5, PhCH_2); 1.67–1.64 (*d*-like *m*, *Me*CH); 0.81 (*s*, *t*-Bu); –0.12, –0.22 (2*s*, Me_2Si). ^{13}C NMR: 139.1 (*s*, arom. C); 134.3 (*d*, MeCH=*C*H); 129.9, 127.9 (2*d*, 2×2 arom. C); 125.9 (*d*, arom. C); 125.0 (*d*, Me*C*H); 74.9 (*d*, SiOCH); 45.4 (*t*, Ph*C*H_2); 25.9 (*q*, *Me*$_3$C); 18.2 (*s*, Me_3*C*); 17.5 (*q*, *Me*CH); –4.6, –5.2 (2*q*, Me_2Si). CI-MS: 294 (3, [*M*+NH_4]$^+$), 206 (11), 185 (20), 164 (11), 162 (75, [*M*+NH_4–*t*-BuMe_2SiOH–H_2O]$^+$), 145 (100, [*M*+H–*t*-BuMe_2SiOH–H_2O]$^+$).

3.7. *(*tert*-Butyl)dimethylsilyl 1-Methyl-4-phenylbut-2-enyl Ether* (**14**). ^{1}H NMR (characteristic signals from mixture **13/14**): 5.56–5.33 (*m*, CH=CH); 4.61–4.54 (symm. *m*, SiOCH); 2.78, 2.68 (*AB* of *ABX*, J_{AB} = 13.1, J_{AX} = 7.4, J_{BX} = 5.6, PhCH_2); 0.81 (*s*, *t*-Bu); –0.13, –0.16 (2*s*, Me_2Si).

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REFERENCES AND NOTES

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