Diastereomerically Pure 1,2-Diols by Nucleophilic Displacement Reactions of 3-Oxetanols – A Study Directed Towards the Identification of Suitable Nucleophiles and the Elucidation of Possible Side Reactions☆

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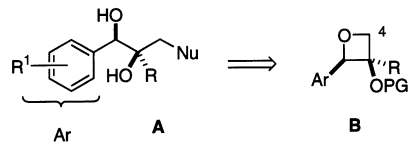
The ring opening of 3-isopropyl-2-phenyl-3-oxetanol (**2a**) by various nucleophiles has been studied. In the presence of BF_3 as a Lewis acid, a clean reaction at the less substituted C-4 position was observed and the corresponding 1,2-diols **6**–**11** and **21**–**23** were isolated in diastereomerically pure form (47–97% yield). Alkyl-, aryl-, alkynyl- and alkenyllithium compounds proved to be suitable carbon nucleophiles. Deprotonated thiols were used as sulfur nucleophiles. An alkoxide derived from benzyl alcohol and an amide derived from benzylamine reacted less readily under these conditions, yielding the 1,2,3-trifunctional compounds **24** (42% yield) and **26** (54% yield). Other 2-phenyl-3-oxetanols such as **2b** and **2c** can also be employed as electrophiles, whereas 2-anisyl derivatives preferentially undergo rearrangement reactions, as exemplified by the conversion of oxetane **16** to the hydroxy ketone **17** (84% yield). The superior behaviour of 3-oxetanols as compared to their silyl derivatives in reactions with nucleophiles became evident from the reaction of 3-silyloxyoxetane **1a** with alkyllithium reagents. A β elimination occurred upon treatment with *n*BuLi, which, after pericyclic ring opening and addition of *n*BuLi, yielded the allylic alcohol **20**.

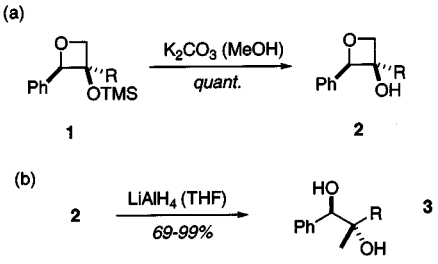
Nucleophilic ring opening of 3-heteroatom-substituted oxetanes gives access to acyclic 1,2-difunctional compounds.[1] 2-Aryl-3-oxetanols and their derivatives (**B**, PG = protective group) should be convertible to 1,2-diols by nucleophilic attack at the less substituted C-4 position (Scheme 1). As the reaction takes place at a non-stereogenic center, the relative configuration of the starting material is expected to be retained. Thus, *cis*-oxetanols of the general structure **B** (PG = H) should yield *syn*-diols of type **A**.

Scheme 1. General strategy for the formation of diastereomerically pure 1,2-diols **A** from 3-oxetanol derivatives **B** by nucleophilic ring opening



Our interest in this type of ring opening arose from the facile synthesis of diastereomerically pure *cis*-2-aryl-3-silyloxyoxetanes by a recently described Paternò–Büchi reaction of trimethylsilyl (TMS) enol ethers and aromatic aldehydes.[2] The preference for the major *cis* diastereoisomer **B** (Scheme 1, PG = TMS) is high (*d.r.* > 90:10) if R is a group bulkier than methyl, and the yield of the product oxetanes varies between 45 and 70% depending on the substitution pattern of R or Ar. In combination with the aforementioned Paternò–Büchi reaction, the ring opening depicted in Scheme 1 appeared to be a useful application of the photochemical "umpolung" of the carbonyl compound, which leads to a 1,2-difunctional bond connection.

Initial attempts to ring-open 3-silyloxyoxetanes by previously described methods[3] were unsuccessful[2b][4]. However, an intramolecular attack of heteroatom nucleophiles was possible and five-, six- and seven-membered heterocycles could be generated by this approach in moderate to excellent yields[5]. In terms of the intermolecular ring-opening, we suspected the silyl protective groups to be responsible for the low reactivity of 3-silyloxyoxetanes such as **1** and their removal was considered in order to generate the potentially more electrophilic 3-oxetanols. Treatment with K_2CO_3 in MeOH resulted in the clean conversion of 2-phenyl-3-silyloxyoxetanes **1** to the corresponding 3-oxetanols **2** [Eq. (a)][4][6].



Indeed, it turned out that the 2-phenyl-3-oxetanols **2** prepared by this means undergo a clean reductive ring fission upon treatment with $LiAlH_4$ in THF[4]. The reactions proceed smoothly at room temperature and yield the diols **3** in

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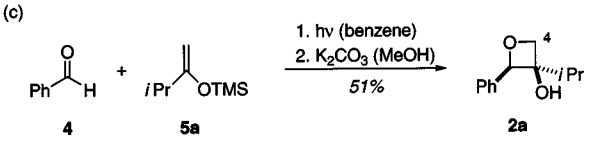
excellent yields [Eq. (b)]. It is assumed that an intramolecular coordination of the aluminium hydride to the 3-oxetanol facilitates the hydride transfer (vide infra).

As an extension of our work on the nucleophilic ring opening, we have now studied the reaction of 3-oxetanols with other nucleophiles. 3-Isopropyl-2-phenyl-3-oxetanol (**2a**) was selected as a test substrate, which was prepared in diastereomerically pure form from benzaldehyde (**4**) and the corresponding silyl enol ether **5a** by the previously described sequence of steps [Eq. (c)].[2b][6]

(c)



4 5a 2a

It was of particular interest to us to determine what type of nucleophiles is best suited for a regioselective attack at the carbon atom C-4 and which factors may influence the regioselectivity. The results of our study are presented herein.

1. Reaction with Carbon Nucleophiles

For the reaction of carbon nucleophiles with 3-oxetanol **2a**, the conditions described by Ganem et al.[7] and by Yamaguchi et al.[8] were particularly appealing. In these procedures the oxygen heterocycle (oxirane or oxetane) is activated by BF_3 and an alkyl-[7] or alkynyllithium[8] reagent is employed as the potential nucleophile. Although this method has been extensively applied to simple mono- or disubstituted oxetanes,[9] it was unclear how the hydroxy group of the 3-oxetanol would interact with the Lewis acid and whether the sterically encumbered oxetanol **2a** would be prone to attack at C-4. It turned out that the reaction can be favourably conducted if the oxetanol is first deprotonated by one equivalent of the organolithium reagent and subsequently treated according to the known protocols. For the deprotonation, any alkyllithium compound (e.g. *n*BuLi) can be used. We were delighted to find that a clean and regioselective reaction occurred with various carbon nucleophiles. The successful reactions according to Eq. (d) are listed in Table 1. In variant A (entries 1−3), the oxetanol was treated with 4 equivalents of commercially available lithium reagents (PhLi, MeLi or *n*BuLi) at 0°C and, after cooling to −78°C, the ring opening was induced by addition of the Lewis acid. Alternatively, the oxetanol anion was first generated by deprotonation with one equivalent of *n*BuLi and was subsequently treated with the nucleophile (3 equivalents) at 0°C and with BF_3 at −78°C (variant B). If the conjugate acid of the nucleophile is acidic, it is possible to prepare the oxetanol anion and the carbanion in one flask by addition of 4 equivalents of *n*BuLi (variant C). The ring-opening was promoted by BF_3 at −78°C, as in the other cases.

The influence of the counterion on the reactivity of the carbon nucleophile was found to be minor. The reaction

(d)

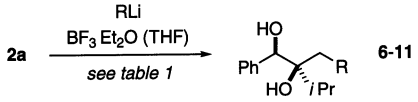


Table 1. Ring opening of oxetanol **2a** with various nucleophiles RLi according to Equation (d)

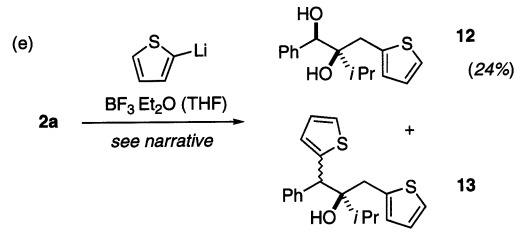
entry	R	variant[a]	time [h][b]	product	yield (%)[c]
1	Ph	A	–	**6**	97
2	Me	A	–	**7**	88
3	*n*Bu	A	–	**8**	70
4	H_2CCH	B	12	**9**	47
5	2-furyl	C	8	**10**	64
6	*t*BuCC	C	12	**11**	72

[a] See text. – [b] In variants B and C the reaction mixture was stirred for the indicated time at room temp. – [c] Yield of isolated product.

with vinylmagnesium bromide ($CH_2CHMgBr$) according to procedure B, for example, resulted in a similar yield (44%) as the reaction with the lithium reagent. Variant A proved to be slightly inferior in this instance (40% yield).

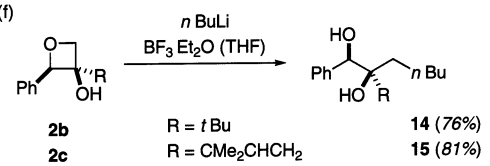
In general, the ring opening proceeded regioselectively at the C-4 position and gave a single substitution product.[10] An exception was observed, however, in the reaction of oxetanol **2a** with heterocyclic anions, e.g. thiophen-2-yllithium according to variant B [Eq. (e)]. Two major products were isolated, one of which was the expected C-4 ring opening product **12**. The other product **13** contained two thiophene rings, as was evident from its NMR spectra. Due to its lability, we were not able to unambiguously elucidate its structure. A disubstitution of oxygen by the heterocycle, i.e. a formal substitution at C-2 and C-4 of oxetane **2a**, appears to be plausible and accounts for the data obtained to date.

(e)



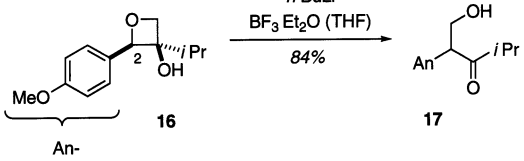
Other 3-oxetanols can also be used as electrophiles in the ring-opening reaction with alkyllithium reagents. Even with bulky substituents in the 3-position, there was no severe deterioration in terms of reaction rate and yield. For example, oxetanols **2b** and **2c**, which are available from the known 2-phenyl-3-silyloxyoxetanes,[2b][2d] reacted with *n*BuLi to yield the corresponding 1,2-diols **14** and **15** [Eq. (f)].

(f)



Aryl substituents at the 2-position of the 3-oxetanol that stabilize a positive charge facilitate a rearrangement reaction and the desired ring opening is prohibited. The conversion of compound **16** to the β-hydroxyketone **17** illustrates this behaviour [Eq. (g)]. The migratory aptitude of the hydroxymethyl group is apparently higher than that of the isopropyl group. In contrast to this result, we had previously observed a preferential migration of the alkyl vs. the hydroxymethyl group in the acid-catalysed rearrangement of 2-phenyl-3-silyloxyoxetanes.[11] The latter finding can be explained by the required alignment of leaving group and migrating group in these rearrangements, which preferentially proceed via a protonated oxetane and not via a carbenium ion. The alkyl group resides in the puckered conformation of these oxetanes, *anti* to the C−O bond that is cleaved during the rearrangement.[12] The anisyl substituent in compound **16**, however, stabilizes a free carbenium ion and the better migrating ability of the hydroxymethyl group is the decisive factor that leads to formation of compound **17**. Indeed, 2,2-diphenyl-3-oxetanols from which stable carbenium ions are formed at the former C-2 carbon atom exhibit identical behaviour upon treatment with BF_3.[13]

(g)

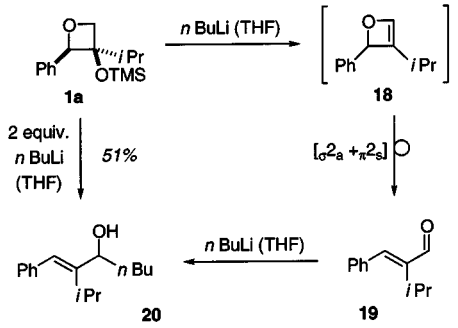


Attempts to induce a ring opening of 3-oxetanols without Lewis acid activation were invariably unsuccessful. Common carbon nucleophiles previously employed for the reaction with the parent oxetane (trimethylene oxide)[14][15][16][17] are not suitable for inducing a ring opening of more complex four-membered oxygen heterocycles.

It remains an open question as to whether the free alkoxide group in the deprotonated oxetanol **2a** intramolecularly assists the delivery of the nucleophile to the C-4 position, or whether it is only the decreased steric bulk of the oxy substituent as compared to the silyloxy group that accounts for the facile ring opening. For the reduction with $LiAlH_4$ [Eq. (b)] there was evidence for a precoordination.[4][18] For example, one indication was the fact that no reaction occurred upon treating several ethers of 3-oxetanols with $LiAlH_4$. Even with small alkoxy groups in the 3-position (e.g. methoxy), there was no ring opening, even under forcing conditions.[19] Similar experiments carried out with the reagent combination RLi/BF_3 led to elimination products. The 3-silyloxyoxetane **1a** employed as starting material for the preparation of oxetanol **2a** reacted with alkyllithium reagents, irrespective of whether BF_3 was added or not. As a product of the reaction with *n*BuLi, the allylic alcohol **20** was isolated (Scheme 2).

The formation of alcohol **20** can be explained by assuming that a 1,2-elimination occurs in oxetane **1a** upon treatment with base. The intermediate oxete **18** is unstable and undergoes a pericyclic rearrangement to the α,β-unsaturated aldehyde **19**, which reacts further with excess

Scheme 2. Possible pathway for the formation of allylic alcohol **20** from 3-silyloxyoxetane **1a**



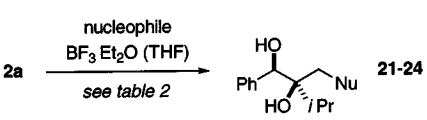
*n*BuLi to yield the final product. Indeed, there is precedence for the ring-opening of oxetes by this pathway.[20] The torque selectivity of the ring opening, which favours the outward rotation of the phenyl substituent,[21][22] is responsible for the exclusive formation of the (*E*)-double bond in aldehyde **19**. The relative configuration was elucidated by NOESY studies performed with alcohol **20**. We have not been able to isolate the intermediate aldehyde **19** by using stoichiometric amounts of the alkyllithium reagent. Other bases failed to induce the desired 1,2-elimination.

In summary, the reaction patterns observed upon treatment of 2-phenyl-3-oxetanols and their TMS-protected derivatives with carbon nucleophiles are completely different. Whereas the latter do not undergo a ring opening to a significant degree but rather follow other reaction pathways, the former were found to be cleaved readily at the C-4 position to yield the desired 1,2-diols.

2. Reaction with Heteroatom Nucleophiles

The reaction of 3-oxetanols with heteroatom nucleophiles should lead to 1,2,3-trifunctional compounds, which are amenable to further derivatization at the primary site $-CH_2Nu$ (Scheme 1). Thiols, alcohols and amines were screened as heteroatom nucleophiles, employing essentially the same protocol as detailed above. Not unexpectedly in view of previous literature accounts,[9g] sulfur nucleophiles reacted most cleanly[23] and the corresponding 3-sulfanyl-1,2-diols **21**−**23** were obtained in excellent yields [Equation (h), Table 2, entries 1−3].

(h)



Variant C was conveniently employed for the transformation as the thiols are sufficiently acidic for an in situ deprotonation. Even the less reactive thiophenolate anion reacted well and no side reactions were observed (entry 3). In the latter case, the commercially available sodium salt of thiophenol was employed and the oxetanol was deprotonated with NaH. Benzyl alcohol proved to be inferior as compared to the sulfur nucleophiles (entry 4). The reaction mix-

Table 2. Ring opening of oxetanol **2a** with various nucleophiles according to Equation (h)

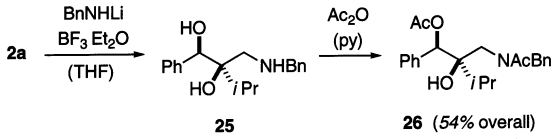
entry	nucleophile	variant[a]	time [h][b]	product	yield (%)[c]
1	BnSLi	C	–	**21**	95
2	EtSLi	C	–	**22**	96
3	PhSNa	B[d]	–	**23**	95
4	BuOLi	C	12	**24**	42

[a] See text. – [b] In variants B and C the reaction mixture was stirred for the indicated time at room temp. – [c] Yield of isolated product. – [d] NaH (1.5 equiv.) was used as the base for the deprotonation of oxetanol **2a**.

ture had to be stirred at room temperature for an extended period of time in order to achieve a satisfactory conversion. Despite the fact that the yield of isolated product **24** was only modest (42%), the reaction proceeded cleanly and 47% of the starting material was recovered.

The high polarity of the amino alcohol **25** derived from benzylamine[24] and 3-oxetanol **2a** (Scheme 3) precluded its isolation by column chromatography on silica gel. The crude reaction mixture obtained from the ring opening of oxetanol **2a** with lithium benzylamide was therefore treated with acetic anhydride in pyridine. A complete diacetylation was achieved and the consecutive product **26** could be isolated in diastereomerically pure form.

Scheme 3. Formation and acylation of the benzylamine ring-opening product **25**



3. Summary and Conclusion

In our studies related to the ring opening of 2-aryl-3-oxetanols we have sought possibilities for transforming the photochemically available diastereomerically pure four-membered heterocycles into other cyclic or acyclic products. It turned out that a regioselective ring fission by nucleophilic attack can be achieved between O and C-4 of the oxetanols if this position is not substituted. Whereas in intramolecular displacement reactions a silyl protective group at the oxetanol oxygen atom did not prohibit the reaction,[5] it became clear in the course of this work that an intermolecular nucleophilic substitution is only possible with 3-oxetanols, e.g. **2a**–**2c**. A broad variety of nucleophiles can be used for this purpose and we successfully employed aryl-, alkyl-, alkenyl- and alkynyllithium reagents in the presence of BF_3 for the transformation of 3-oxetanols to acyclic 1,2-diols (**6**–**11**, **14**, **15**). 1,2,3-Trifunctionality can be achieved by the reaction of 3-oxetanols with heteroatom nucleophiles. 3-Sulfanyl-1,2-diols **21**–**23**, the 3-alkoxy-1,2-diol **24**, and the protected 3-amino-1,2-diol **26** were obtained from our test substrate **2a** by applying conditions similar to those used for carbon nucleophiles. A drawback of the reagent combination nucleophile/BF_3 is its Lewis acidity. Its use is thus limited to 3-oxetanols that do not readily form carbenium ions, otherwise rearrangements and other side reactions can be expected. Nonetheless, in combination with the preceding photocycloaddition, the described ring-opening procedure appears to be a versatile method for generating diastereomerically pure 1,2-diols that are inaccessible or are only accessible with difficulty by other means.

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Experimental Section

General: All reactions involving water-sensitive compounds were carried out in flame-dried glassware with magnetic stirring under Ar. Irradiation experiments were performed in degassed benzene (Merck p.a.) under Ar. – *N,N*-Diisopropylamine and pyridine were distilled from calcium hydride. Common solvents (*tert*-butyl methyl ether, pentane and diethyl ether), acetic anhydride and $BF_3{\cdot}OEt_2$ were distilled prior to use. THF was distilled from K/Na immediately prior to use. All other reagents and solvents were used as received. – Melting points (uncorrected): Reichert hot-stage. – IR: Bruker IFS 88 FT-IR or Nicolet 510M FT-IR. – MS: Varian CH7 (EI). – GC: Hewlett-Packard HP 6890 series GC system, column HP-1 (cross-linked methylsiloxane, 30 m). – ^1H and ^{13}C NMR: Bruker ARX-200, Bruker AC-300, Bruker AM-400, Bruker HMX-500. Chemical shifts are reported relative to tetramethylsilane as internal reference. $CDCl_3$ was used as solvent unless noted otherwise. The multiplicities of the ^{13}C-NMR signals were determined by attached proton test (APT) experiments. – Elemental analysis: Varian Elementar vario EL. – TLC: Merck aluminium sheets (0.2 mm silica gel 60 F_{254}); a pentane (P)/*tert*-butyl methyl ether (E) mixture was used; detection by UV or by colouration with cerium(IV) ammonium molybdate (CAM). – Flash chromatography[25]: Merck silica gel 60 (230–400 mesh) (ca. 50 g for 1 g of material to be separated), eluent given in brackets. – Some of the ketones employed for the preparation of silyl enol ethers were commercially available and were distilled immediately prior to use. The others were obtained by literature procedures.[26]

(1RS,2SR)-2-Benzyl-3-methyl-1-phenylbutane-1,2-diol (**6**). – *Typical Procedure A:* To a stirred solution of 1 mmol of oxetanol **2a**[4] (192 mg) in 10 ml of THF, 4 mmol of phenyllithium (1.8 M in cyclohexane/diethyl ether, 70:30, 2.25 ml) was slowly added at 0°C. After 5 min, the mixture was cooled to −78°C and 3 mmol of $BF_3{\cdot}OEt_2$ (426 mg, 380 μl) was added dropwise by means of a syringe. The reaction was monitored by TLC. After stirring for 1 h at −78°C, the mixture was quenched at this temperature with 1 ml of saturated aq. $NaHCO_3$ solution and was allowed to warm to ambient temperature. The product was extracted with diethyl ether (4 × 20 ml), the combined organic layers were washed with brine (10 ml), dried with $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by flash chromatography (P/E, 9:1) to give 267 mg (97%) of compound **6** as colorless crystals. – R_f = 0.57 (P/E, 7:3). – M.p. 79°C. – IR (KBr): $\tilde{\nu}$ = 3440 cm^{-1} (vs, br., OH), 3360 (vs, br., OH), 3085 (w, $C_{ar}H$), 3065 (w, $C_{ar}H$), 3025 (w, $C_{ar}H$), 2990 (m, $C_{al}H$), 2960 (m, $C_{al}H$), 2920 (m, $C_{al}H$), 2850 (m, $C_{al}H$), 1455 (w, CH_2), 1395 (w, CH_3), 1370 (w, CH_3), 1060 (m, C–O), 735 (m, Ph), 700 (m, Ph). – ^1H NMR: δ = 0.79 (d, ^3J = 6.9 Hz, 3 H, $CHCH_3$), 0.97 (d, ^3J = 6.9 Hz, 3 H, $CHCH_3$), 1.58 [pseudo sept,

^3J = 6.9 Hz, 1 H, C*H*(CH_3)$_2$], 1.97 (br. s, 1 H, OH), 2.39 (br. s, 1 H, OH), 2.97 (d, ^2J = 13.9 Hz, 1 H, PhCH*H*), 3.07 (d, ^2J = 13.9 Hz, 1 H, PhC*H*H), 4.84 (s, 1 H, PhC*H*), 7.26−7.39 (m, 8 H, arom. H), 7.42−7.46 (m, 2 H, arom. H). − ^{13}C NMR: δ = 17.3 (q, CH*C*H$_3$), 17.4 (q, CH*C*H$_3$), 33.9 [d, *C*H(CH_3)$_2$], 39.7 (t, Ph*C*H$_2$), 78.2 [s, PhCH(OH)*C*OH], 78.3 (d, Ph*C*H), 126.5 (d, C_{ar}H), 127.9 (d, C_{ar}H), 128.1 (d, C_{ar}H), 128.4 (d, C_{ar}H), 130.7 (d, C_{ar}H), 138.1 (s, C_{ar}), 140.8 (s, C_{ar}). − MS (70 eV); *m/z* (%): 179 (7) [M^+ − C_7H_7], 108 (18) [$C_7H_7O^+$], 107 (18) [$C_7H_6O^+$], 91 (100) [$C_7H_7^+$], 77 (13) [$C_6H_5^+$], 65 (7) [$C_5H_5^+$], 43 (80) [$C_3H_7^+$]. − $C_{18}H_{22}O_2$ (270.37): calcd. C 79.96, H 8.20; found C 79.71, H 8.13.

(1RS,2SR)-2-Ethyl-3-methyl-1-phenylbutane-1,2-diol (**7**): As described in typical procedure A, the ring opening of oxetanol **2a** was carried out on a 1-mmol scale using 4 mmol of methyllithium (1.6 M in diethyl ether, 2.5 ml). After stirring for 5 min at −78°C, the mixture was quenched at this temperature. The residue was purified by flash chromatography (P/E, 9:1) to give 183 mg (88%) of compound **7** as colorless crystals. − R_f = 0.46 (P/E, 7:3). − M.p. 92°C. − IR (KBr): $\tilde{\nu}$ = 3450 cm^{-1} (vs, br., OH), 3340 (vs, br., OH), 3095 (w, C_{ar}H), 3060 (w, C_{ar}H), 3025 (w, C_{ar}H), 2965 (m, C_{al}H), 2945 (m, C_{al}H), 1090 (m, C−O), 1040 (m, C−O), 740 (m, Ph), 700 (m, Ph). − ^{1}H NMR: δ = 0.84 (d, ^3J = 6.9 Hz, 3 H, CHC*H*$_3$), 0.98 (d, ^3J = 6.9 Hz, 3 H, CHC*H*$_3$), 1.02 (t, ^3J = 7.6 Hz, 3 H, CH$_2$C*H*$_3$), 1.52−1.72 (m, 2 H, C*H*$_2$CH$_3$), 1.82 [pseudo sept, ^3J = 6.9 Hz, 1 H, C*H*(CH_3)$_2$], 4.79 (s, 1 H, PhC*H*), 7.29−7.37 (m, 3 H, arom. H), 7.43−7.46 (m, 2 H, arom. H). − ^{13}C NMR: δ = 8.6 (q, CH$_2$*C*H$_3$), 17.4 (q, CH*C*H$_3$), 17.4 (q, CH*C*H$_3$), 26.6 (t, *C*H$_2$CH$_3$), 32.4 [d, *C*H(CH_3)$_2$], 77.5 [s, PhCH(OH)*C*OH], 77.9 (d, Ph*C*H), 127.7 (d, C_{ar}H), 127.8 (d, C_{ar}H), 128.1 (d, C_{ar}H), 141.4 (s, C_{ar}). − MS (70 eV); *m/z* (%): 208 (0.1) [M^+], 108 (64) [$C_7H_7O^+$], 107 (19) [$C_7H_6O^+$], 101 (100) [$C_6H_{13}O^+$], 91 (18) [$C_7H_7^+$], 77 (10) [$C_6H_5^+$], 43 (19) [$C_3H_7^+$]. − $C_{13}H_{20}O_2$ (208.30): calcd. C 74.96, H 9.68; found C 74.89, H 10.01.

(1RS,2SR)-2-Isopropyl-1-phenylheptane-1,2-diol (**8**): As described in typical procedure A, the ring opening of oxetanol **2a** was carried out on a 1-mmol scale using 4 mmol of *n*-butyllithium (1.6 M in hexane, 2.5 ml). After stirring for 5 min at −78°C, the mixture was quenched at this temperature. The residue was purified by flash chromatography (P/E, 95:5) to give 175 mg (70%) of compound **8** as colourless crystals. R_f = 0.29 (P/E, 9:1). − M.p. 87−89°C. − IR (KBr): $\tilde{\nu}$ = 3455 cm^{-1} (vs, br., OH), 3315 (vs, br., OH), 3085 (w, C_{ar}H), 3065 (w, C_{ar}H), 3025 (w, C_{ar}H), 2960 (m, C_{al}H), 2930 (m, C_{al}H), 2870 (m, C_{al}H), 1455 (w, CH_2), 1375 (w, CH), 1270 (w, OH), 1150 (m, C−O), 1060 (m, C−O), 750 (m, Ph), 705 (m, Ph). − ^{1}H NMR: δ = 0.83 (d, ^3J = 7.0 Hz, 3 H, CHC*H*$_3$), 0.90 (t, ^3J = 6.9 Hz, 3 H, CH$_2$C*H*$_3$), 0.97 (d, ^3J = 7.0 Hz, 3 H, CHC*H*$_3$), 1.15−1.68 (m, 8 H, C*H*$_2$C*H*$_2$C*H*$_2$C*H*$_2$CH$_3$), 1.81 [sept, ^3J = 7.0 Hz, 1 H, C*H*(CH_3)$_2$], 2.19 (s, 1 H, OH), 4.78 (s, 1 H, PhC*H*), 7.28−7.47 (m, 5 H, arom. H). − ^{13}C NMR: δ = 14.1 (q, CH$_2$*C*H$_3$), 17.4 (q, CH*C*H$_3$), 17.5 (q, CH*C*H$_3$), 22.6 (t, CH$_2$CH$_2$-CH$_2$*C*H$_2$CH$_3$), 23.7 (t, CH$_2$CH$_2$*C*H$_2$CH$_2$CH$_3$), 32.6 [d, *C*H(CH_3)$_2$], 32.9 (t, CH$_2$*C*H$_2$CH$_2$CH$_2$CH$_3$), 34.3 (t, *C*H$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 77.6 [s, PhCH(OH)*C*OH], 78.0 (d, Ph*C*H), 127.7 (d, C_{ar}H), 127.8 (d, C_{ar}H), 128.1 (d, C_{ar}H), 141.4 (s, C_{ar}). − MS (70 eV); *m/z* (%): 250 (0.7) [M^+], 143 (100), 108 (58) [$C_7H_7O^+$], 91 (25) [$C_7H_7^+$], 77 (14) [$C_6H_5^+$], 57 (43) [$C_4H_9^+$], 43 (34) [$C_3H_7^+$]. − $C_{16}H_{26}O_2$ (250.38): calcd. C 76.75, H 10.47; found C 76.53, H 10.36.

(1RS,2SR)-2-Isopropyl-1-phenylpent-4-ene-1,2-diol (**9**). − *Typical Procedure B:* To a stirred solution of 1 mmol of oxetanol **2a** (192 mg) in 5 ml of THF, 1 mmol of *n*-butyllithium (1.6 M in hexane, 630 μl) was slowly added at 0°C. A solution of vinyllithium, prepared[27] from 3 mmol of vinyl bromide (320 mg, 210 μl) and 6 mmol of *tert*-butyllithium (1.7 M in pentane, 3.5 ml) in 10 ml of Trapp mixture (THF/diethyl ether/pentane, 4:1:1)[28] at −100°C, was added to the solution of deprotonated oxetanol at 0°C. After 5 min, the mixture was cooled to −78°C and 3 mmol of BF_3·OEt_2 (425 mg, 380 μl) was added dropwise by means of a syringe. The reaction was monitored by TLC. After 30 min, the mixture was slowly allowed to warm to ambient temperature and was then stirred for 12 h. Quenching and work-up were carried out as described in typical procedure A. The residue was purified by flash chromatography (P/E, 92:8) to give 103 mg (47%) of compound **9** as colourless crystals. − R_f = 0.62 (P/E, 1:1). − M.p. 98°C. − IR (KBr): $\tilde{\nu}$ = 3430 cm^{-1} (vs, br., OH), 3295 (vs, br., OH), 3070 (w, C_{ar}H), 3025 (w, C_{ar}H), 3000 (w, C_{ar}H), 2975 (m, C_{al}H), 2930 (m, C_{al}H), 2900 (m, C_{al}H), 905 (s, C=C), 755 (m, Ph), 700 (m, Ph). − ^{1}H NMR: δ = 0.83 (d, ^3J = 7.0 Hz, 3 H, CHC*H*$_3$), 0.97 (d, ^3J = 6.8 Hz, 3 H, CHC*H*$_3$), 1.72 [pseudo sept, ^3J = 6.9 Hz, 1 H, C*H*(CH_3)$_2$], 2.11 (s, 1 H, COH), 2.37 (d, ^3J = 4.3 Hz, 1 H, PhCHO*H*), 2.41−2.47 (m, 2 H, C*H*$_2$CH=CH$_2$), 4.76 (d, ^3J = 4.3 Hz, 1 H, PhC*H*), 5.13−5.14 (m, 1 H, CH=C*H*H), 5.17−5.20 (m, 1 H, CH=CH*H*), 5.99−6.13 (m, 1 H, C*H*=CH$_2$), 7.26−7.37 (m, 3 H, arom. H), 7.42−7.46 (m, 2 H, arom. H). − ^{13}C NMR: δ = 17.3 (q, CH*C*H$_3$), 17.4 (q, CH*C*H$_3$), 33.2 [d, *C*H(CH_3)$_2$], 38.6 (t, *C*H$_2$CH=CH$_2$), 77.5 [s, PhCH(OH)*C*OH], 78.1 (d, Ph*C*H), 118.2 (t, CH=*C*H$_2$), 127.8 (d, C_{ar}H), 127.9 (d, C_{ar}H), 128.1 (d, C_{ar}H), 135.1 (d, *C*H=CH$_2$), 140.9 (s, C_{ar}). − MS (70 eV); *m/z* (%): 220 (0.3) [M^+], 179 (3) [M^+ − C_3H_7], 108 (48) [$C_7H_7O^+$], 91 (21) [$C_7H_7^+$], 43 (74) [$C_3H_7^+$]. − $C_{14}H_{20}O_2$ (220.31): calcd. C 76.33, H 9.15; found C 75.93, H 9.50.

(1RS,2SR)-2-(Furan-2-ylmethyl)-3-methyl-1-phenylbutane-1,2-diol (**10**). − *Typical Procedure C:* To a stirred solution of 1 mmol of oxetanol **2a** (192 mg) and 3 mmol of furan (204 mg, 220 μl) in 10 ml of THF, 4 mmol of *n*-butyllithium (1.8 M in hexane, 2.2 ml) was slowly added at 0°C. After 5 min, the mixture was cooled to −78°C and 3 mmol of BF_3·OEt_2 (425 mg, 380 μl) was added dropwise by means of a syringe. The reaction was monitored by TLC. After 10 min, the mixture was allowed to warm to ambient temperature and was then stirred for 8 h. Quenching and work-up were carried out as described in typical procedure A. The residue was purified by flash chromatography (P/E, 9:1) to give 167 mg (64%) of compound **10** as colourless crystals. The compound was not stable and a correct combustion analysis could not be obtained. − R_f = 0.12 (P/E, 9:1). − M.p. 77°C − IR (KBr): $\tilde{\nu}$ = 3440 cm^{-1} (vs, br., OH), 3390 (vs, br., OH), 3085 (w, C_{ar}H), 3060 (w, C_{ar}H), 3030 (w, C_{ar}H), 2970 (m, C_{al}H), 2950 (m, C_{al}H), 2912 (m, C_{al}H), 2885 (m, C_{al}H), 1595 (m, C=C_{furan}), 1495 (m, C=C_{furan}), 1260 (w, C−O), 1060 (m, C−O), 1015 (m, C=C), 750 (m, Ph), 700 (m, Ph). − ^{1}H NMR: δ = 0.76 (d, ^3J = 6.9 Hz, 3 H, CHC*H*$_3$), 0.91 (d, ^3J = 6.9 Hz, 3 H, CHC*H*$_3$), 1.64 [sept, ^3J = 6.9 Hz, 1 H, C*H*(CH_3)$_2$], 2.51 (d, ^3J = 3.8 Hz, 1 H, PhCHO*H*), 2.58 [s, 1 H, PhCH(OH)CO*H*], 3.00 (d, ^2J = 15.3 Hz, 1 H, C*H*H), 3.07 (d, ^2J = 15.3 Hz, 1 H, CH*H*), 4.80 (d, ^3J = 3.8 Hz, 1 H, PhC*H*), 6.17 (dd, ^3J = 3.1 Hz, ^4J = 0.9 Hz, 1 H, furan H), 6.35 (dd, ^3J = 3.1 Hz, ^3J = 1.9 Hz, 1 H, furan H), 7.29−7.37 (m, 3 H, arom. H), 7.38 (dd, ^3J = 1.9 Hz, ^4J = 0.9 Hz, 1 H, furan H), 7.46−7.49 (m, 2 H, arom. H). − ^{13}C NMR: δ = 17.0 (q, CH*C*H$_3$), 17.2 (q, CH*C*H$_3$), 32.2 (t, CH_2), 33.4 [d, *C*H(CH_3)$_2$], 77.5 (d, Ph*C*H), 78.0 [s, PhCH(OH)*C*OH], 108.3 (d, C_{fu}H), 110.7 (d, C_{fu}H), 127.8 (d, C_{ar}H), 128.0 (d, C_{ar}H), 128.1 (d, C_{ar}H), 140.6 (s, C_{ar}), 141.4 (d, C_{fu}H), 152.5 (s, C_{fu}). − MS (70 eV); *m/z* (%): 260 (1.4) [M^+], 179 (11) [M^+ − C_5H_5O], 161 (64) [M^+ − C_5H_5O − H_2O], 107 (32) [$C_7H_7O^+$], 91 (54) [$C_7H_7^+$], 81 (100) [$C_5H_5O^+$], 71 (84) [$C_4H_7O^+$], 43 (95) [$C_3H_7^+$]. − $C_{16}H_{20}O_3$ (260.33); exact mass: calcd. 260.1412; found 260.1413.

(1RS,2SR)-2-Isopropyl-6,6-dimethyl-1-phenylhept-4-yne-1,2-diol (**11**): As described in typical procedure C, the ring opening of oxetanol **2a** was carried out on a 1-mmol scale using 3 mmol of 3,3-dimethylbutyne (250 mg, 390 µl). The mixture was stirred for 12 h at ambient temperature. The residue was purified by flash chromatography (P/E, 9:1) to give 199 mg (72%) of compound **11** as colourless crystals. − R_f = 0.62 (P/E, 7:3). − M.p. 72°C. − IR (KBr): $\tilde{\nu}$ = 3410 cm^{-1} (vs, br., OH), 3085 (w, $C_{ar}H$), 3060 (w, $C_{ar}H$), 3025 (w, $C_{ar}H$), 2970 (m, $C_{al}H$), 2900 (m, $C_{al}H$), 1455 (w, CH_2), 1360 [w, $C(CH_3)_3$], 750 (m, Ph), 705 (m, Ph). − ^{1}H NMR: δ = 0.85 (d, ^3J = 6.9 Hz, 3 H, CHCH_3), 1.00 (d, ^3J = 6.9 Hz, 3 H, CHCH_3), 1.23 [s, 9 H, C(CH_3)$_3$], 1.86 [sept, ^3J = 6.9 Hz, 1 H, CH(CH$_3$)$_2$], 2.43 (d, ^2J = 16.8 Hz, 1 H, CHHC≡C), 2.44 (s, 1 H, OH), 2.53 (d, ^2J = 16.8 Hz, 1 H, CHHC≡C), 3.09 (s, 1 H, OH), 4.87 (s, 1 H, PhCH), 7.26−7.37 (m, 3 H, arom. H), 7.45−7.48 (m, 2 H, arom. H). − ^{13}C NMR: δ = 17.2 (q, CHCH$_3$), 17.6 (q, CHCH$_3$), 24.2 (t, CH$_2$C≡C), 27.6 [s, C(CH$_3$)$_3$], 31.1 [q, C(CH$_3$)$_3$], 32.7 [d, CH(CH$_3$)$_2$], 75.0 (s), 76.7 (s), 78.0 (d, PhCH), 93.7 (s, C≡C), 127.8 (d, $C_{ar}H$), 127.8 (d, $C_{ar}H$), 128.1 (d, $C_{ar}H$), 140.3 (s, C_{ar}). − MS (70 eV); *m/z* (%): 274 (0.1) [M^+], 179 (17) [$M^+ - C_6H_5 - H_2O$], 108 (24) [$C_7H_7O^+$], 91 (17) [$C_7H_7^+$], 77 (9) [$C_6H_5^+$], 57 (22) [$C_4H_9^+$], 43 (91) [$C_3H_7^+$]. − $C_{18}H_{26}O_2$ (274.40): calcd. C 78.79, H 9.55; found C 78.78, H 9.45.

(1RS,2SR)-3-Methyl-1-phenyl-2-(thiophen-2-ylmethyl)butane-1,2-diol (**12**): As described in typical procedure B, the ring opening of oxetanol **2a** was carried out on a 1-mmol scale using 3 mmol of thiophen-2-yllithium, prepared at 0°C from 3 mmol of thiophene (240 mg, 250 µl) and 3 mmol of *n*-butyllithium (1.5 M in hexane, 2.0 ml) in 5 ml of THF. The mixture was stirred for 12 h at ambient temperature. The residue was purified by flash chromatography (P/E, 99:1 → 6:4) to give 69 mg (24%) of compound **12** as colourless crystals. The compound was not stable and a correct combustion analysis could not be obtained. − R_f = 0.58 (P/E, 7:3). − M.p. 55°C. − IR (KBr): $\tilde{\nu}$ = 3510 cm^{-1} (s, OH), 3415 (s, br., OH), 3085 (w, $C_{ar}H$), 3070 (w, $C_{ar}H$), 3025 (w, $C_{ar}H$), 2995 (m, $C_{al}H$), 2970 (m, $C_{al}H$), 2930 (m, $C_{al}H$), 1455 (w, C=C), 1380 (w, C=C), 1050 (m, C−O), 1015 (m, C−O), 740 (m, Ph), 700 (vs, Ph). − ^{1}H NMR: δ = 0.79 (d, ^3J = 7.0 Hz, 3 H, CHCH_3), 0.96 (d, ^3J = 6.8 Hz, 3 H, CHCH_3), 1.69 [pseudo sept, ^3J = 6.9 Hz, 1 H, CH(CH$_3$)$_2$], 3.18 (d, ^3J = 15.0 Hz, 1 H, CHH), 3.29 (d, ^3J = 15.0 Hz, 1 H, CHH), 5.48 (s, 1 H, PhCH), 6.90−7.01 (m, 2 H, arom. H), 7.15−7.19 (m, 1 H, arom. H), 7.26−7.36 (m, 5 H, arom. H). − ^{13}C NMR: δ = 17.3 (q, CHCH$_3$), 17.5 (q, CHCH$_3$), 33.4 [d, CH(CH$_3$)$_2$], 34.3 (t, CH_2), 77.5 [s, PhCH(OH)COH], 77.7 (d, PhCH), 124.9 (d, $C_{ar}H$), 126.7 (d, $C_{ar}H$), 127.7 (d, $C_{ar}H$), 128.0 (d, $C_{ar}H$), 128.2 (d, $C_{ar}H$), 139.8 (s, C_{ar}), 140.6 (s, C_{ar}). − MS (70 eV); *m/z* (%): 276 (0.4) [M^+], 215 (0.5) [$M^+ - C_3H_7 - H_2O$], 179 (18) [$M^+ - C_5H_5S$], 161 (32) [$M^+ - C_5H_5S - H_2O$], 107 (22) [$C_7H_7O^+$], 97 (100) [$C_5H_5S^+$], 91 (26) [$C_7H_7^+$], 71 (67) [$C_4H_7O^+$], 43 (50) [$C_3H_7^+$]. − $C_{16}H_{20}O_2S$ (276.39); exact mass: calcd. 276.1184; found 276.1181.

3-Methyl-1-phenyl-1-(thiophen-2-yl)-2-(thiophen-2-ylmethyl)butan-2-ol (**13**): Yield: 203 mg (76%) of diastereomerically pure compound **13** as a colourless solid. The compound was not stable and a correct combustion analysis could not be obtained. − R_f = 0.69 (P/E, 9:1). − IR (KBr): $\tilde{\nu}$ = 3455 cm^{-1} (s, br., OH), 3105 (w, $C_{ar}H$), 3085 (w, $C_{ar}H$), 3065 (w, $C_{ar}H$), 3030 (m, $C_{al}H$), 2975 (m, $C_{al}H$), 2960 (m, $C_{al}H$), 2930 (m, $C_{al}H$), 2875 (m, $C_{al}H$), 1525 (s, C=$C_{thiophene}$), 1425 (s, C=$C_{thiophene}$), 1240 (m, C−O), 1020 (s, C−O), 725 (m, arom.), 695 (s, arom.). − ^{1}H NMR: δ = 0.66 (d, ^3J = 6.8 Hz, 3 H, CHCH_3), 0.90 (d, ^3J = 6.8 Hz, 3 H, CHCH_3), 1.90 [sept, ^3J = 6.8 Hz, 1 H, CH(CH$_3$)$_2$], 3.19 (d, ^2J = 15.3 Hz, 1 H, CHH), 3.50 (d, ^2J = 15.3 Hz, 1 H, CHH), 5.43 (s, 1 H, PhCH), 6.93 (dd, ^3J = 5.2 Hz, ^3J = 3.3 Hz, 1 H, thiophene H), 6.99 (d, ^3J = 3.3 Hz, 1 H, thiophene H), 7.17 (dd, ^3J = 5.2 Hz, ^4J = 1.1 Hz, 1 H, thiophene H), 7.23 (dd, ^3J = 4.4 Hz, ^3J = 3.3 Hz, 1 H, thiophene H), 7.28−7.34 (m, 5 H, arom. H), 7.68 (dd, ^3J = 4.4 Hz, ^4J = 1.1 Hz, 1 H, thiophene H), 7.73 (dd, ^3J = 3.3 Hz, ^4J = 1.1 Hz, 1 H, thiophene H). − ^{13}C NMR: δ = 17.6 (q, CHCH$_3$), 17.7 (q, CHCH$_3$), 32.9 [d, CH(CH$_3$)$_2$], 35.6 (PhCH$_2$), 84.0 (d, PhCH), 89.1 (s, COH), 125.4 (d, $C_{ar}H$), 126.8 (d, $C_{ar}H$), 127.8 (d, $C_{ar}H$), 127.9 (d, $C_{ar}H$), 128.1 (d, $C_{ar}H$), 128.3 (d, $C_{ar}H$), 132.6 (d, $C_{ar}H$), 137.5 (d, $C_{ar}H$), 138.1 (s, C_{ar}), 138.1 (s, C_{ar}). − MS (70 eV); *m/z* (%): 271 (100) [$M^+ - C_3H_3S$], 229 (30) [$C_{14}H_{13}OS^+$], 173 (10) [$C_{11}H_9S^+$], 105 (12) [$C_8H_8^+$], 97 (25) [$C_5H_5S^+$], 91 (21) [$C_7H_7^+$], 43 (19) [$C_3H_7^+$].

(1RS,2SR)-2-tert-Butyl-1-phenylheptane-1,2-diol (**14**): As described in typical procedure A, the ring opening of oxetanol **2b**[4] was carried out on a 0.5-mmol scale using 2 mmol of *n*-butyllithium (1.5 M in hexane, 1.35 ml). After stirring for 1 h at −78°C, the mixture was quenched at this temperature. The residue was purified by flash chromatography (P/E, 98:2 → 9:1) to give 100 mg (76%) of compound **14** as a colourless oil. − R_f = 0.46 (P/E, 9:1). − IR (film): $\tilde{\nu}$ = 3580 cm^{-1} (s, OH), 3435 (s, br., OH), 3080 (w, $C_{ar}H$), 3060 (w, $C_{ar}H$), 3030 (w, $C_{ar}H$), 2960 (m, $C_{al}H$), 2870 (m, $C_{al}H$), 1450 (m, CH), 1395 [m, $C(CH_3)_3$], 1360 [m, $C(CH_3)_3$], 1090 (m, C−O), 1045 (s, C−O), 725 (s, arom.), 700 (s, arom.). − ^{1}H NMR: δ = 0.83 (t, ^3J = 6.5 Hz, 3 H, CH_2CH_3), 1.01 [s, 9 H, C(CH_3)$_3$], 1.12−1.30 (m, 6 H, $CH_2CH_2CH_2CH_2CH_3$), 1.51 (s, 1 H, COH), 1.66−1.80 (m, 2 H, $CH_2CH_2CH_2CH_2CH_3$), 2.09 (d, ^3J = 3.4 Hz, 1 H, PhCHOH), 4.92 (d, ^3J = 3.4 Hz, 1 H, PhCH), 7.30−7.47 (m, 5 H, arom. H). − ^{13}C NMR: δ = 14.0 (q, CH_2CH_3), 22.5 (t, $CH_2CH_2CH_2CH_2CH_3$), 24.5 (t, $CH_2CH_2CH_2CH_2CH_3$), 26.6 [q, C(CH$_3$)$_3$], 31.3 (t, $CH_2CH_2CH_2CH_2CH_3$), 32.7 (t, $CH_2CH_2CH_2CH_2CH_3$), 39.0 [s, C(CH$_3$)$_3$], 77.0 (d, PhCH), 78.2 [s, PhCH(OH)COH], 127.6 (d, $C_{ar}H$), 127.7 (d, $C_{ar}H$), 127.9 (d, $C_{ar}H$), 142.3 (s, C_{ar}). − MS (70 eV); *m/z* (%): 246 (10) [$M^+ - H_2O$], 207 (15) [$M^+ - C_4H_9$], 189 (30) [$M^+ - C_4H_9 - H_2O$], 157 (30) [$M^+ - C_7H_7O$], 107 (70) [$C_7H_7O^+$], 91 (90) [$C_7H_7^+$], 71 (55) [$C_5H_{11}^+$], 57 (100) [$C_4H_9^+$]. − $C_{17}H_{28}O_2$ (264.41): calcd. C 77.22, H 10.67; found C 77.15, H 10.74.

(1RS,2SR)-3,3-Dimethyl-2-pentyl-1-phenylpent-4-ene-1,2-diol (**15**): As described in typical procedure A, the ring opening of oxetanol **2c**[4] was carried out on a 1-mmol scale using 4 mmol of *n*-butyllithium (1.5 M in hexane, 2.7 ml). After stirring for 15 min at −78°C, the mixture was quenched at this temperature. The residue was purified by flash chromatography (P/E, 95:5) to give 225 mg (81%) of compound **15** as a colourless oil. − R_f = 0.23 (P/E, 95:5). − IR (film): $\tilde{\nu}$ = 3555 cm^{-1} (s, OH), 3460 (s, br., OH), 3085 (m, $C_{ar}H$), 3060 (m, $C_{ar}H$), 3030 (m, $C_{ar}H$), 2960 (vs, $C_{al}H$), 2930 (vs, $C_{al}H$), 2870 (vs, $C_{al}H$), 1635 (w, C=C), 1455 (s, OH), 1380 (s, OH), 1040 (s, C−O), 1025 (s, C−O), 960 (s, C=C), 725 (m, Ph), 705 (vs, Ph). − ^{1}H NMR: δ = 0.79 (t, ^3J = 6.6 Hz, 3 H, CH_2CH_3), 1.05−1.22 (m, 6 H, $CH_2CH_2CH_2CH_3$), 1.11 (s, 3 H, CH_3), 1.18 (s, 3 H, CH_3), 1.56 [s, 1 H, PhCH(OH)COH], 1.64−1.77 (m, 2 H, $CH_2CH_2CH_2CH_2CH_3$), 2.33 (s, 1 H, PhCHOH), 4.88 (s, 1 H, PhCH), 5.08 (dd, ^3J_Z = 10.8 Hz, ^2J = 1.5 Hz, 1 H, CH=CHH), 5.11 (dd, ^3J_E = 17.5 Hz, ^2J = 1.5 Hz, 1 H, CH=CHH), 6.23 (dd, ^3J_Z = 10.8 Hz, ^3J_E = 17.5 Hz, 1 H, CH=CHH), 7.25−7.36 (m, 3 H, arom. H), 7.40−7.45 (m, 2 H, arom. H). − ^{13}C NMR: δ = 13.9 (q, CH_2CH_3), 22.3 (q, CH_3), 22.4 (t, $CH_2CH_2CH_2CH_2CH_3$), 23.5 (q, CH_3), 24.2 (t, $CH_2CH_2CH_2CH_2CH_3$), 30.8 (t, $CH_2CH_2CH_2CH_2CH_3$), 32.5 (t, $CH_2CH_2CH_2CH_2CH_3$), 45.2 [s, C(CH$_3$)$_2$], 77.0 (d, PhCH), 77.7 [s, PhCH(OH)COH], 112.5 (t, CH=CH_2), 127.5 (d, $C_{ar}H$), 127.6 (d, $C_{ar}H$), 127.8 (d, $C_{ar}H$), 141.3 (s, C_{ar}), 146.6 (d, CH=CH$_2$). − MS (70 eV); *m/z* (%): 207 (1) [$M^+ - C_5H_9$], 189 (23) [$M^+ - C_5H_9 - H_2O$], 169 (17) [$M^+ - C_7H_7O$],

107 (17) [$C_7H_7O^+$], 99 (100) [$C_6H_{11}O^+$], 91 (52) [$C_7H_7^+$], 71 (43) [$C_5H_{11}^+$], 69 (15) [$C_5H_9^+$], 43 (61) [$C_3H_7^+$]. − $C_{18}H_{28}O_2$ (276.42): calcd. C 78.21, H 10.21; found C 77.93, H 10.13.

(2RS,3RS)-3-Isopropyl-2-(4-methoxyphenyl)oxetan-3-ol (**16**): As described in the literature,[2b] the oxetane formation was carried out on a 9-mmol scale starting using 18 mmol (2.85 g) of 3-methyl-2-[(trimethylsilyl)oxy]but-1-ene and 9 mmol (1.23 g) of anisaldehyde. After 2 h, an additional 12 mmol (1.90 g) of the silyl enol ether was added. Irradiation was stopped after 20 h and the crude product (*d.r.* 92:8) was desilylated as described previously.[4] The resulting yellow residue was purified by flash chromatography (P/E, 9:1 → 7:3) to give 793 mg (40%) of compound **16** as a waxy, colourless solid. − R_f = 0.57 (P/E, 7:3). − IR (KBr): $\tilde{\nu}$ = 3375 cm^{-1} (s, br., OH), 2960 (s, $C_{al}H$), 2935 (s, $C_{al}H$), 1250 (vs, O−CH_3), 1035 (m, C−O), 975 (m, C−O), 810 (m, arom.). − ^1H NMR: δ = 0.97 (d, ^3J = 7.0 Hz, 3 H, CHCH_3), 0.99 (d, ^3J = 6.6 Hz, 3 H, CHCH_3), 1.58 (s, 1 H, O*H*), 2.24 [pseudo sept, ^3J = 6.8 Hz, 1 H, C*H*(CH_3)$_2$], 3.82 (s, 3 H, OCH_3), 4.46 (d, ^2J = 7.0 Hz, 1 H, OC*H*H), 4.67 (d, ^2J = 7.0 Hz, 1 H, OCH*H*), 5.55 (s, 1 H, ArC*H*), 6.96 (d, ^3J = 8.8 Hz, 2 H, arom. H), 7.34 (d, ^3J = 8.8 Hz, 2 H, arom. H). − ^{13}C NMR: δ = 15.4 (q, CH*C*H_3), 15.8 (q, CH*C*H_3), 35.2 [d, *C*H(CH_3)$_2$], 55.3 (q, OCH_3), 78.4 (s, COH), 81.6 (t, OCH_2), 90.8 (d, Ar*C*H), 114.2 (d, $C_{ar}H$), 127.8 (d, $C_{ar}H$), 129.0 (s, C_{ar}), 159.7 (s, C_{ar}). − MS (70 eV); *m/z* (%): 192 (6) [M^+ − H_2CO], 137 (100) [$C_8H_8O_2$ + H^+], 121 (18) [$C_7H_5O_2^+$], 86 (7) [$C_5H_{10}O^+$]. − $C_{13}H_{18}O_3$ (222.28): calcd. C 70.24, H 8.16; found C 70.45, H 7.91.

(*RS*)*-1-Hydroxy-2-(4-methoxyphenyl)-4-methylpentan-3-one* (**17**): As described in typical procedure A, the ring opening of oxetane **16** was carried out on a 1-mmol scale using 2.2 mmol of *n*-butyllithium (1.5 M in hexane, 1.5 ml) and 1 mmol of BF3·OEt2. After stirring for 10 min at −78°C, the mixture was quenched at this temperature. The residue was purified by flash chromatography (P/E, 7:3) to give 186 mg (84%) of compound **17** as a colourless oil. − R_f = 0.31 (P/E, 1:1). − IR (film): $\tilde{\nu}$ = 3435 cm^{-1} (s, br., OH), 3065 (w, $C_{ar}H$), 3035 (w, $C_{ar}H$), 2970 (s, $C_{al}H$), 2935 (s, $C_{al}H$), 2875 (s, $C_{al}H$), 2835 (m, OCH_3), 1705 (vs, C=O), 1255 (vs, O−CH_3), 1040 (vs, C−O), 835 (m, arom.). − ^1H NMR: δ = 0.94 (d, ^3J = 6.7 Hz, 3 H, CHCH_3), 1.10 (d, ^3J = 7.1 Hz, 3 H, CHCH_3), 2.22 (s, 1 H, O*H*), 2.64 [pseudo sept, ^3J = 6.9 Hz, 1 H, C*H*(CH_3)$_2$], 3.66 (dd, ^3J = 10.6 Hz, ^3J = 4.3 Hz, 1 H, ArC*H*CH_2), 3.79 (s, 3 H, OCH_3), 4.02 (dd, ^2J = 8.7 Hz, ^3J = 4.3 Hz, 1 H, ArCHC*H*H), 4.10 (dd, ^2J = 8.7 Hz, ^3J = 10.6 Hz, 1 H, ArCHCH*H*), 6.87 (d, ^3J = 8.6 Hz, 2 H, arom. H), 7.11 (d, ^3J = 8.6 Hz, 2 H, arom. H). − ^{13}C NMR: δ = 17.9 (q, CH*C*H_3), 19.0 (q, CH*C*H_3), 39.8 [d, *C*H(CH_3)$_2$], 55.2 (q, OCH_3), 58.2 (d, Ar*C*H), 64.4 (t, *C*H_2OH), 114.5 (d, $C_{ar}H$), 127.4 (s, C_{ar}), 129.7 (d, $C_{ar}H$), 159.2 (d, $C_{ar}H$), 215.2 (s, CO). − MS (70 eV); *m/z* (%): 222 (4) [M^+], 151 (75) [M^+ − COCH(CH_3)$_2$], 134 (100) [$C_9H_{10}O^+$], 121 (56) [$C_8H_9O^+$], 91 (30) [$C_7H_7^+$], 71 (13) [$COCH(CH_3)_2^+$], 43 (50) [$C_3H_7^+$]. − $C_{13}H_{18}O_3$ (222.28): calcd. C 70.24, H 8.16; found C 70.06, H 7.98.

(*RS*)-(*E*)*-2-Isopropyl-1-phenylhept-1-en-3-ol* (**20**): To a stirred solution of 1 mmol of oxetane **1a**[2b] (264 mg, *d.r.* 88:12) in 10 ml of THF, 2.2 mmol of *n*-butyllithium (1.5 M in hexane, 1.5 ml) was slowly added at −90°C. The reaction was monitored by TLC. The mixture was stirred for 1 h at −90°C. Quenching and work-up were carried out as described in typical procedure A. The residue was purified by flash chromatography (P/E, 9:1) to give 118 mg (51%) of compound **20** as a colourless oil. − R_f = 0.30 (P/E, 9:1). − IR (film): $\tilde{\nu}$ = 3385 cm^{-1} (s, br., OH), 3080 (w, $C_{ar}H$), 3055 (w, $C_{ar}H$), 3025 (w, $C_{ar}H$), 2960 (s, $C_{al}H$), 2930 (s, $C_{al}H$), 2870 (s, $C_{al}H$), 1380 [m, CH(CH_3)$_2$], 1365 [m, CH(CH_3)$_2$], 1025 (m, C=C), 700 (m, arom.). − ^1H NMR: δ = 0.94 (t, ^3J = 7.1 Hz, 3 H, CH_2CH_3), 1.02 (d, ^3J = 7.0 Hz, 3 H, CHCH_3), 1.12 (d, ^3J = 6.9 Hz, 3 H, CHCH_3), 1.33−1.42 (m, 3 H, O*H*, $CH_2CH_2CH_2CH_3$), 1.47−1.52 (m, 2 H, $CH_2CH_2CH_2CH_3$), 1.66−1.71 (m, 2 H, $CH_2CH_2CH_2CH_3$), 3.10 [pseudo t, ^3J = 7.0 Hz, 1 H, C*H*(CH_3)$_2$], 4.27 [dd, ^3J = 7.2 Hz, ^3J = 5.5 Hz, 1 H, C*H*(OH)CH_2], 6.64 (s, 1 H, PhC*H*), 7.20−7.28 (m, 3 H, arom. H), 7.40−7.46 (m, 2 H, arom. H). − ^{13}C NMR: δ = 14.1 (q, CH_2CH_3), 21.4 (q, CH*C*H_3), 21.7 (q, CH*C*H_3), 22.7 (t, $CH_2CH_2CH_2CH_3$), 28.4 [d, *C*H(CH_3)$_2$], 28.6 (t, $CH_2CH_2CH_2CH_3$), 38.1 (t, $CH_2CH_2CH_2CH_3$), 70.1 (d, CHOH), 124.3 (d, Ph*C*H), 126.3 (d, $C_{ar}H$), 128.1 (d, $C_{ar}H$), 128.7 (d, $C_{ar}H$), 137.9 (s, C_{ar}), 151.7 (s, PhCH=*C*). − MS (70 eV); *m/z* (%): 232 (10) [M^+], 214 (13) [M^+ − H_2O], 189 (20) [M^+ − C_3H_7], 171 (28) [M^+ − H_2O − C_3H_7], 129 (100), 91 (36) [$C_7H_7^+$], 77 (12) [$C_6H_5^+$], 43 (35) [$C_3H_7^+$]. − $C_{16}H_{24}O$ (232.36): calcd. C 82.70, H 10.41; found C 82.60, H 10.24.

(1RS,2SR)-2-(Benzylsulfanylmethyl)-3-methyl-1-phenylbutane-1,2-diol (**21**): As described in typical procedure C, the ring opening of oxetanol **2a** was carried out on a 1-mmol scale using 3 mmol of benzylthiol (370 mg, 350 µl). After stirring for 10 min at −78°C, the mixture was quenched at this temperature. The residue was purified by flash chromatography (P/E, 95:5) to give 300 mg (95%) of compound **21** as colourless crystals. − R_f = 0.46 (P/E, 7:3). − M.p. 61°C. − IR (KBr): $\tilde{\nu}$ = 3460 cm^{-1} (vs, br., OH), 3380 (vs, br., OH), 3085 (w, $C_{ar}H$), 3065 (w, $C_{ar}H$), 3035 (w, $C_{ar}H$), 2985 (m, $C_{al}H$), 2960 (m, $C_{al}H$), 2925 (m, $C_{al}H$), 1455 (w, CH_2), 1390 (w, CH), 1065 (w, C−O), 770 (m, Ph), 705 (m, Ph). − ^1H NMR: δ = 0.75 (d, ^3J = 6.9 Hz, 3 H, CHCH_3), 0.91 (d, ^3J = 6.9 Hz, 3 H, CHCH_3), 1.76 [pseudo sept, ^3J = 6.9 Hz, 1 H, C*H*(CH_3)$_2$], 2.70 (d, ^2J = 13.8 Hz, 1 H, C*H*HSCH_2Ph), 2.73 (d, ^3J = 5.5 Hz, 1 H, PhCHO*H*), 2.82 (d, ^2J = 13.8 Hz, 1 H, CH*H*SCH_2Ph), 2.85 [s, 1 H, PhCH(OH)CO*H*], 3.67 (s, 2 H, PhCH_2), 4.69 (d, ^3J = 5.5 Hz, 1 H, PhC*H*), 7.23−7.40 (m, 10 H, arom. H). − ^{13}C NMR: δ = 17.2 (q, CH*C*H_3), 17.3 (q, CH*C*H_3), 33.1 [d, *C*H(CH_3)$_2$], 36.2 (t, *C*H_2SCH_2Ph), 38.6 (t, Ph*C*H_2), 76.7 [s, PhCH(OH)*C*OH], 77.8 (d, Ph*C*H), 127.2 (d, $C_{ar}H$), 127.8 (d, $C_{ar}H$), 127.8 (d, $C_{ar}H$), 128.1 (d, $C_{ar}H$), 128.6 (d, $C_{ar}H$), 129.0 (d, $C_{ar}H$), 138.0 (s, C_{ar}), 140.5 (s, C_{ar}). − MS (70 eV); *m/z* (%): 123 (6) [SCH_2Ph^+], 107 (8) [$C_7H_6O^+$], 91 (100) [$C_7H_7^+$], 77 (9) [$C_6H_5^+$], 65 (6) [$C_5H_5^+$], 51 (3) [$C_4H_3^+$], 43 (13) [$C_3H_7^+$]. − $C_{19}H_{24}O_2S$ (316.46): calcd. C 72.11, H 7.64; found C 71.88, H 7.45.

(1RS,2SR)-2-(Ethylsulfanylmethyl)-3-methyl-1-phenylbutane-1,2-diol (**22**): As described in typical procedure C, the ring opening of oxetanol **2a** was carried out on a 1-mmol scale using 3 mmol of ethanethiol (187 mg, 220 µl). After stirring for 10 min at −78°C, the mixture was quenched at this temperature. The residue was purified by flash chromatography (P/E, 95:5) to give 243 mg (96%) of compound **22** as a colourless oil. − R_f = 0.57 (P/E, 7:3). − IR (film): $\tilde{\nu}$ = 3435 cm^{-1} (s, br., OH), 3085 (w, $C_{ar}H$), 3065 (w, $C_{ar}H$), 3030 (w, $C_{ar}H$), 2965 (m, $C_{al}H$), 2930 (m, $C_{al}H$), 2875 (m, $C_{al}H$), 1455 (m, CH_2), 1385 (m, CH), 1055 (m, C−O), 755 (s, Ph), 700 (s, Ph). − ^1H NMR: δ = 0.81 (d, ^3J = 7.0 Hz, 3 H, CHCH_3), 0.97 (d, ^3J = 7.0 Hz, 3 H, CHCH_3), 1.23 (t, ^3J = 7.3 Hz, 3 H, SCH_2CH_3), 1.81 [sept, ^3J = 7.0 Hz, 1 H, C*H*(CH_3)$_2$], 2.50 (q, ^3J = 7.3 Hz, 2 H, SCH_2CH_3), 2.7−3.2 (br. s, 2 H, 2 OH), 2.75 (d, ^2J = 13.5 Hz, 1 H, C*H*HSCH_2CH$_3$), 2.94 (d, ^2J = 13.5 Hz, 1 H, CH*H*SCH_2CH$_3$), 4.71 (s, 1 H, PhC*H*), 7.26−7.36 (m, 3 H, arom. H), 7.44−7.47 (m, 2 H, arom. H). − ^{13}C NMR: δ = 14.8 (q, CH_2CH_3), 17.3 (q, CH*C*H_3), 17.4 (q, CH*C*H_3), 28.8 (t, S*C*H_2CH$_3$), 33.0 [d, *C*H(CH_3)$_2$], 37.1 (t, *C*H_2SCH_2CH$_3$), 76.4 [s, PhCH(OH)*C*OH], 77.9 (d, Ph*C*H), 127.8 (d, $C_{ar}H$), 127.8 (d, $C_{ar}H$), 128.1 (d, $C_{ar}H$), 140.6 (s, C_{ar}). − MS (70 eV); *m/z* (%): 254 (1) [M^+], 147 (66) [M^+ − C_7H_7O], 107 (23) [$C_7H_7O^+$], 91 (20)

$[C_7H_7^+]$, 75 (100) $[C_3H_7S^+]$, 43 (18) $[C_3H_7^+]$. – $C_{14}H_{22}O_2S$ (254.39): calcd. C 66.10, H 8.72; found C 66.27, H 8.66.

(1RS,2SR)-3-Methyl-1-phenyl-2-(phenylsulfanylmethyl)butane-1,2-diol (**23**): As described in typical procedure B, the ring opening of oxetanol **2a** was carried out on a 1-mmol scale using 3 mmol of sodium thiophenolate (400 mg), with sodium hydride (1.5 mmol, 36 mg) as the base. After stirring for 10 min at −78°C, the mixture was quenched at this temperature. The residue was purified by flash chromatography (P/E, 95:5) to give 287 mg (95%) of compound **23** as colourless crystals. – R_f = 0.57 (P/E, 7:3). – M.p. 75°C. – IR (KBr): $\tilde{\nu}$ = 3480 cm^{-1} (s, br., OH), 3385 (s, br., OH), 3075 (w, $C_{ar}H$), 2995 (m, $C_{al}H$), 2975 (m, $C_{al}H$), 2950 (m, $C_{al}H$), 1480 (m, CH_2), 1455 (m, CH), 1390 (m, CH), 1065 (m, C−O), 995 (s, C−O), 735 (s, Ph), 705 (s, Ph). – ^{1}H NMR: δ = 0.85 (d, ^3J = 6.9 Hz, 3 H, CHCH_3), 1.01 (d, ^3J = 6.9 Hz, 3 H, CHCH_3), 1.90 [sept, ^3J = 6.9 Hz, 1 H, CH(CH_3)$_2$], 2.62 (br. s, 1 H, OH), 2.87 (br. s, 1 H, OH), 3.21 (d, ^2J = 13.4 Hz, 1 H, CHHSPh), 3.37 (d, ^2J = 13.4 Hz, 1 H, CHHSPh), 4.83 (s, 1 H, PhCH), 7.18−7.38 (m, 8 H, arom. H), 7.45−7.48 (m, 2 H, arom. H). – ^{13}C NMR: δ = 17.4 (q, CHCH_3), 17.5 (q, CHCH_3), 33.1 [d, CH(CH_3)$_2$], 40.3 (t, CH_2SPh), 76.9 [s, PhCH(OH)COH], 77.7 (d, PhCH), 126.4 (d, $C_{ar}H$), 127.9 (d, $C_{ar}H$), 128.0 (d, $C_{ar}H$), 128.2 (d, $C_{ar}H$), 129.0 (d, $C_{ar}H$), 129.7 (d, $C_{ar}H$), 137.4 (s, C_{ar}), 140.4 (s, C_{ar}). – MS (70 eV); *m/z* (%): 302 (0.3) [M^+], 195 (41) [M^+ − C_7H_7O], 123 (100) [M^+ − CH_2SPh], 107 (14) [$C_7H_7O^+$], 91 (8) [$C_7H_7^+$], 77 (9) [$C_6H_5^+$], 43 (16) [$C_3H_7^+$]. – $C_{18}H_{22}O_2S$ (302.43): calcd. C 71.48, H 7.33; found C 71.35, H 7.25.

(1RS,2RS)-2-(Benzyloxymethyl)-3-methyl-1-phenylbutane-1,2-diol (**24**): As described in typical procedure C, the ring opening of oxetanol **2a** was carried out on a 1-mmol scale using 3 mmol of benzyl alcohol (325 mg, 310 µl). The mixture was stirred for 12 h at ambient temperature. Excess benzyl alcohol was removed from the crude product by distillation in a Kugelrohr apparatus. Further purification was carried out by flash chromatography (P/E, 9:1) to give 126 mg (42%) of compound **24** as colourless crystals and 90 mg (47%) of recovered starting material **2a**. – R_f = 0.43 (P/E, 7:3). – M.p. 70°C. – IR (KBr): $\tilde{\nu}$ = 3430 cm^{-1} (vs, br., OH), 3300 (vs, br., OH), 3085 (w, $C_{ar}H$), 3060 (w, $C_{ar}H$), 3030 (w, $C_{ar}H$), 2985 (m, $C_{al}H$), 2960 (m, $C_{al}H$), 2940 (m, $C_{al}H$), 2875 (m, $C_{al}H$), 1390 (w, CH), 1090 (s, C−O), 1020 (s, C−O), 755 (m, Ph), 705 (m, Ph). – ^{1}H NMR: δ = 0.82 (d, ^3J = 7.0 Hz, 3 H, CHCH_3), 0.98 (d, ^3J = 7.0 Hz, 3 H, CHCH_3), 1.82 [sept, ^3J = 7.0 Hz, 1 H, CH(CH_3)$_2$], 2.66 (br. s, 1 H, OH), 3.52 (d, ^2J = 9.2 Hz, 1 H, CHHOCH$_2$Ph), 3.68 (d, ^2J = 9.2 Hz, 1 H, CHHOCH$_2$Ph), 3.82 (br. s, 1 H, OH), 4.54 (d, ^2J = 11.8 Hz, 1 H, PhCHH), 4.60 (d, ^2J = 11.8 Hz, 1 H, PhCHH), 4.88 (s, 1 H, PhCH), 7.25−7.43 (m, 10 H, arom. H). – ^{13}C NMR: δ = 16.9 (q, CHCH_3), 17.1 (q, CHCH_3), 31.3 [d, CH(CH_3)$_2$], 72.8 (t, CH_2OCH$_2$Ph), 74.0 (t, CH$_2$OCH_2Ph), 76.1 [s, PhCH(OH)COH], 77.7 (d, PhCH), 127.7 (d, $C_{ar}H$), 127.9 (d, $C_{ar}H$), 128.0 (d, $C_{ar}H$), 128.0 (d, $C_{ar}H$), 128.1 (d, $C_{ar}H$), 128.6 (d, $C_{ar}H$), 137.2 (s, C_{ar}), 140.1 (s, C_{ar}). – MS (70 eV); *m/z* (%): 193 (8) [M^+ − OCH_2Ph], 107 (14) [OCH_2Ph^+], 91 (100) [$C_7H_7^+$], 77 (4) [$C_6H_5^+$], 65 (3) [$C_5H_5^+$], 43 (5) [$C_3H_7^+$]. – $C_{19}H_{24}O_3$ (300.39): calcd. C 75.97, H 8.05; found C 75.74, H 8.01.

(1RS,2RS)-2-{[(Acetyl)(benzyl)amino]methyl}-2-hydroxy-3-methyl-1-phenylbutyl Acetate (**26**): As described in typical procedure C, the ring opening of oxetanol **2a** was carried out on a 1-mmol scale using 3 mmol of benzylamine (320 mg, 330 µl). After 30 min, the mixture was quenched at −78°C with 1 ml of saturated aq. $NaHCO_3$ solution and was then allowed to warm to ambient temperature. It was diluted with 20 ml of diethyl ether and 10 ml of 1 N HCl. The organic layer was washed with a further 10 ml of 1 N HCl. The combined aqueous layers were neutralized with conc. ammonia and extracted with diethyl ether (4 × 20 ml). Further work-up was carried out as described in typical procedure A. The crude product was purified by a short-column flash chromatography, then dissolved in 20 mmol (1.6 ml) of pyridine and 20 mmol (1.9 ml) of acetic anhydride, and a catalytic amount of DMAP was added. The resulting mixture was stirred for 24 h at ambient temperature. After acidic work-up, the residue was purified by flash chromatography (P/E, 9:1 → 8:2) to give 207 mg (54%) of compound **26** as colourless crystals. – R_f = 0.43 (P/E, 3:7). – M.p. 95°C. – IR (KBr): $\tilde{\nu}$ = 3515 cm^{-1} (s, OH), 3090 (w, $C_{ar}H$), 3060 (w, $C_{ar}H$), 3030 (w, $C_{ar}H$), 2960 (m, $C_{al}H$), 2880 (m, $C_{al}H$), 1725 (vs, OC=O), 1650 (vs, NC=O), 1370 (s, OCOCH_3), 1250 (s, C−O), 735 (s, Ph), 700 (s, Ph). – ^{1}H NMR: δ = 0.92 (d, ^3J = 6.8 Hz, 3 H, CHCH_3), 1.01 (d, ^3J = 7.0 Hz, 3 H, CHCH_3), 1.78 [pseudo sept, ^3J = 6.9 Hz, 1 H, CH(CH_3)$_2$], 1.89 (s, 3 H, COCH_3), 2.12 (s, 3 H, COCH_3), 3.58 [d, ^2J = 14.7 Hz, 1 H, CHHN(COCH$_3$)CH$_2$Ph], 3.70 [d, ^2J = 14.7 Hz, 1 H, CHHN(COCH$_3$)CH$_2$Ph], 4.50 (d, ^2J = 17.3 Hz, 1 H, PhCHH), 4.63 (d, ^2J = 17.3 Hz, 1 H, PhCHH), 5.40 (br. s, OH), 5.90 (s, 1 H, PhCH), 7.11 (d, 2 H, ^3J = 7.0 Hz, arom. H), 7.26−7.39 (m, 6 H, arom. H), 7.49 (d, 2 H, ^3J = 7.0 Hz, arom. H). – ^{13}C NMR: δ = 16.7 (q, CHCH_3), 17.5 (q, CHCH_3), 21.3 (q, COCH_3), 21.5 (q, COCH_3), 34.2 [d, CH(CH_3)$_2$], 52.9 [t, CH_2N(COCH$_3$)CH$_2$Ph], 55.3 (t, PhCH_2), 76.9 (d, PhCH), 77.8 (s, COH), 125.9 (d, $C_{ar}H$), 127.7 (d, $C_{ar}H$), 127.8 (d, $C_{ar}H$), 128.0 (d, $C_{ar}H$), 129.2 (d, $C_{ar}H$), 136.2 (s, C_{ar}), 137.5 (s, C_{ar}), 169.5 (s, C=O), 175.0 (s, C=O). – MS (70 eV); *m/z* (%): 340 (0.8) [M^+ − $COCH_3$], 324 (0.6) [M^+ − $OCOCH_3$], 234 (35) [$C_{14}H_{20}NO_2^+$], 163 (53) [$C_{10}H_{13}NO^+$], 120 (46) [$C_8H_{10}N^+$], 91 (100) [$C_7H_7^+$], 72 (53) [$C_4H_8O^+$], 43 (27) [$C_3H_7^+$]. – $C_{23}H_{29}NO_4$ (383.48): calcd. C 72.04, H 7.62, N 3.65; found C 71.92, H 7.63, N 3.50.

☆ Dedicated to Professor *Reinhard W. Hoffmann* on the occasion of his 65th birthday.

[1] Review: T. Bach, *Liebigs Ann.* **1997**, 1627−1634.

[2] [2a] T. Bach, *Tetrahedron Lett.* **1991**, *32*, 7037−7038. – [2b] T. Bach, K. Jödicke, *Chem. Ber.* **1993**, *126*, 2457−2466. – [2c] T. Bach, *Tetrahedron Lett.* **1994**, *35*, 5845−5848. – [2d] T. Bach, *Liebigs Ann.* **1995**, 855−866. – [2e] T. Bach, K. Jödicke, K. Kather, R. Fröhlich, *J. Am. Chem. Soc.* **1997**, *119*, 2437−2445.

[3] Reviews: [3a] S. Searles in *The Chemistry of Heterocyclic Compounds* (Ed.: A. Weissberger), Wiley-Interscience, New York **1964**, vol. 19-2, pp. 983−1068. – [3b] S. Searles in *Comprehensive Heterocyclic Chemistry* (Ed.: A. R. Katritzky), Pergamon Press, Oxford **1984**, vol. 7, pp. 363−402.

[4] T. Bach, K. Kather, *J. Org. Chem.* **1996**, *61*, 3900−3901.

[5] [5a] T. Bach, K. Kather, *J. Org. Chem.* **1996**, *61*, 7642−7643. – [5b] T. Bach, K. Kather, O. Krämer, *J. Org. Chem.* **1998**, *63*, 1910−1918.

[6] T. Bach, K. Kather, *J. Prakt. Chem.* **1996**, *338*, 750−753.

[7] M. J. Eis, J. E. Wrobel, B. Ganem, *J. Am. Chem. Soc.* **1984**, *106*, 3693−3694.

[8] [8a] M. Yamaguchi, Y. Nobayashi, I. Hirao, *Tetrahedron Lett.* **1983**, *24*, 5121−5122. – [8b] M. Yamaguchi, Y. Nobayashi, I. Hirao, *Tetrahedron* **1984**, *40*, 4261−4266.

[9] [9a] M. Yamaguchi, K. Shibato, I. Hirao, *Tetrahedron Lett.* **1984**, *25*, 1159−1162. – [9b] J. P. Gillet, R. Sauvêtre, J. F. Normant, *Synthesis* **1986**, 355−360. – [9c] H. Tanaka, M. Fukui, K. Haraguchi, M. Masaki, T. Miyasaka, *Tetrahedron Lett.* **1989**, *30*, 2567−2570. – [9d] Y.-P. Yen, S.-G. Lin, M.-F. Suen, *Synth. Commun.* **1992**, *22*, 1567−1581. – [9e] B. Mudryk, T. Cohen, *J. Am. Chem. Soc.* **1993**, *115*, 3855−3865. – [9f] T. Imai, S. Nishida, T. Tsuji, *J. Chem. Soc., Chem. Commun.* **1994**, 2353−2354. – [9g] H. Xianming, R. M. Kellogg, *Tetrahedron: Asymmetry* **1995**, *6*, 1399−1408. – [9h] M. Mizuno, M. Kanai, A Iida, K. Tomioka, *Tetrahedron: Asymmetry* **1996**, *7*, 2483−2484.

[10] Proof for the relative configuration of diols **6**−**11** was obtained from the known configuration of oxetanol **2a** (see ref.[2b]). In addition, diol **6** was transformed to its cyclic carbonate whose relative configuration was determined by NOESY studies (cf.

F. Eilers, planned Ph.D. thesis, Universität Marburg, **1998**). Related ring-opening reactions at the C-4 position are known not to interfere with the relative configuration at the stereogenic centers (see ref.[4]).

[11] [11a] T. Bach, K. Kather, *Tetrahedron* **1994**, *50*, 12319−12328. − [11b] See also: J. Kagan, J. T. Przybytek, *Tetrahedron* **1973**, *29*, 1163−1167.

[12] S. Kotila, A. Jäntti, S. Penttinen, T. Bach, *Acta Crystallogr., Sect. C* **1996**, *C52*, 1722−1725.

[13] N. Shimizu, S. Yamaoka, Y. Tsuno, *Bull. Chem. Soc. Jpn.* **1983**, *56*, 3853−3854.

[14] Organolithium reagents: [14a] S. Searles, *J. Am. Chem. Soc.* **1951**, *73*, 124−125. − [14b] J. F. Ansell, B. Gadsby, *J. Chem. Soc.* **1958**, 3388−3397. − [14c] L. L. Darko, J. G. Cannon, *J. Org. Chem.* **1967**, *32*, 2352−2354. − [14d] D. Hoppe, *Angew. Chem.* **1974**, *86*, 878−893; *Angew. Chem. Int. Ed. Engl.* **1974**, *13*, 789−803. − [14e] N. J. Foulger, B. J. Wakefield, *J. Chem. Soc., Perkin Trans. 1* **1974**, 871−875. − [14f] D. Seebach, E. J. Corey, *J. Org. Chem.* **1975**, *40*, 231−237. − [14g] P. F. Hudrlik, C.-N. Wan, *J. Org. Chem.* **1975**, *40*, 2963−2965. − [14h] A. Maercker, M. Passlack, *Chem. Ber.* **1983**, *116*, 710−723. − [14i] A. Maercker, R. Stötzel, *Chem. Ber.* **1987**, *120*, 1695−1706. − [14j] C. S. Shiner, T. Tsunoda, B. A. Goodman, S. Ingham, S.-h. Lee, P. E. Vorndam, *J. Am. Chem. Soc.* **1989**, *111*, 1381−1392. − [14k] R. Grigg, F. Heaney, J. Markandu, S. Surendrakumar, M. Thornton-Pett, W. J. Warnock, *Tetrahedron* **1991**, *47*, 4007−4030. − [14l] J. Fuchs, G. Szeimies, *Chem. Ber.* **1992**, *125*, 2517−2522.

[15] Organomagnesium reagents: [15a] C. G. Derrick, D. W. Bissell, *J. Am. Chem. Soc.* **1916**, *38*, 2478−2486. − [15b] W. Steudel, H. Gilman, *J. Am. Chem. Soc.* **1960**, *82*, 6129−6132. − [15c] F. B. Slezak, J. P. Stallings, D. H. Wagner, J. H. Wotiz, *J. Org. Chem.* **1961**, *26*, 3137−3140. − [15d] L. R. Kray, M. G. Reinecke, *J. Org. Chem.* **1967**, *32*, 225−227. − [15e] E. N. Marvell, D. Sturmer, R. S. Knutson, *J. Org. Chem.* **1968**, *33*, 2991−2993. − [15f] R. D. Rieke, M. S. Sell, H. Xiong, *J. Org. Chem.* **1995**, *60*, 5143−5149.

[16] Organoaluminium reagents: [16a] D. B. Miller, *J. Organomet. Chem.* **1968**, *14*, 253−259. − [16b] A. Alexakis, D. Jachiet, *Tetrahedron* **1989**, *45*, 6197−6202.

[17] Organocopper reagents: [17a] J. Millon, G. Linstrumelle, *Tetrahedron Lett.* **1976**, 1095−1098. − [17b] R. Rossi, A. Carpita, L. Gaudenzi, M. G. Quirici, *Gazz. Chim. Ital.* **1980**, *110*, 237−246. − [17c] A. Alexakis, D. Jachiet, J. F. Normant, *Tetrahedron* **1986**, *42*, 5607−5619.

[18] [18a] T. Bach, C. Lange, *Tetrahedron Lett.* **1996**, *37*, 4363−4364. − [18b] T. Bach, F. Eilers, K. Kather, *Liebigs Ann.* **1997**, 1529−1536.

[19] K. Kather, Ph.D. Thesis, Universität Münster, **1996**.

[20] [20a] L. E. Friedrich, J. D. Bower, *J. Am. Chem. Soc.* **1973**, *95*, 6869−6870. − [20b] J. Koo, G. B. Schuster, *J. Am. Chem. Soc.* **1977**, *99*, 5403−5408. − [20c] P. C. Martino, P. B. Shelvin, *J. Am. Chem. Soc.* **1980**, *102*, 5429−5430. − [20d] L. E. Friedrich, P. Y.-S. Lam, *J. Org. Chem.* **1981**, *46*, 306−311.

[21] Cyclobutenes: [21a] W. Kirmse, N. G. Rondan, K. N. Houk, *J. Am. Chem. Soc.* **1984**, *106*, 7989−7991. − [21b] N. G. Rondan, K. N. Houk, *J. Am. Chem. Soc.* **1985**, *107*, 2099−2111. − [21c] E. Piers, Y.-F. Lu, *J. Org. Chem.* **1989**, *54*, 2267−2268. − [21d] E. Piers, K. A. Ellis, *Tetrahedron Lett.* **1993**, *34*, 1875−1878.

[22] β-Lactone enolates: J. Mulzer, T. Kerkmann, *J. Am. Chem. Soc.* **1980**, *102*, 3620−3622.

[23] Intermolecular ring opening of oxetanes with sulfur nucleophiles: [23a] S. Searles, *J. Am. Chem. Soc.* **1951**, *73*, 4515−4517. − [23b] R. L. Whistler, T. J. Luttenegger, R. M. Powell, *J. Org. Chem.* **1968**, *33*, 396−398. − [23c] G. Godziela, T. Tonker, M. R. DuBois, *Organometallics* **1989**, *8*, 2220−2224.

[24] Intermolecular ring-opening of oxetanes with nitrogen nucleophiles: [24a] S. Searles, V. P. Gregory, *J. Am. Chem. Soc.* **1954**, *76*, 2789−2790. − [24b] M. Chini, P. Crotti, L. Favero, F. Macchia, *Tetrahedron Lett.* **1994**, *35*, 761−764. − [24c] P. Crotti, L. Favero, F. Macchia, M. Pineschi, *Tetrahedron Lett.* **1994**, *35*, 7089−7092. − [24d] M. Meguro, N. Asao, Y. Yamamoto, *J. Chem. Soc., Perkin Trans. 1* **1994**, 2597−2601.

[25] W. C. Still, M. Kahn, A. Mitra, *J. Org. Chem.* **1978**, *43*, 2923−2925.

[26] I. Mori, K. Ishihara, C. H. Heathcock, *J. Org. Chem.* **1990**, *55*, 1114−1117.

[27] H. Neumann, D. Seebach, *Chem. Ber.* **1978**, *111*, 2785−2812.

[28] G. Köbrich, H. Trapp, *Chem. Ber.* **1966**, *99*, 680−688.

[98203]