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Asymmetric Induction in the [2,3] Wittig Rearrangement by Chiral Substituents in the Allyl Moiety: 1,3-Asymmetric Induction

Stefan W. Scheuplein, Andreas Kusche, Reinhard Brückner*, and Klaus Harms [+)]

Fachbereich Chemie, Universität Marburg,
Hans-Meerwein-Straße, D-3550 Marburg, F.R.G.

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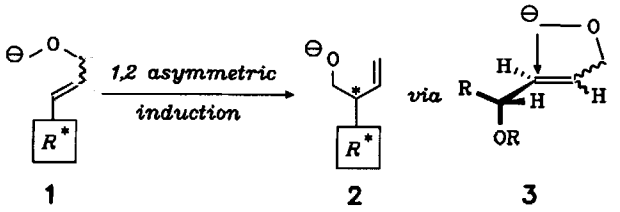
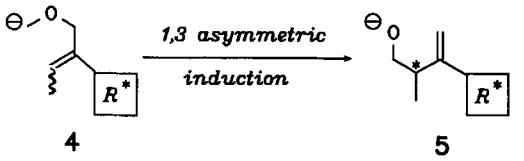
Wittig rearrangement of the type **4**→**5** can exhibit stereocontrol due to asymmetric induction. The Wittig-Still rearrangements of stannylated ethers (*E*)-**10** and (*Z*)-**10** are stereochemically complementary and furnish the homoallylic alcohols *anti*-**11** and *syn*-**11** with high diastereoselectivity (ds = 95:5 and 97:3, respectively). The 1,3-asymmetric induction established in the transformation of ether (*Z*)-**10** can be reversed and combined with a 1,4-asymmetric induction as shown by the stereoselective Wittig rearrangement of allyl propargyl ether **28** (ds = 88:6:5:1). 1,4-Asymmetric induction *alone* was observed neither in the [2,3] Wittig rearrangement of propargyl ether **34** nor in that of (allyloxy)acetate **37**.

In the past few years, the chemistry of [2,3] Wittig rearrangements has continued to be an area of rapid growth[1]. Recent contributions to this increasingly important group of reactions include stereoselective ring contractions by Marshall[2] and Takahashi[3], control of (*E*)/(*Z*) and *syn*/*anti* selectivity by remote substituent effects as explored by Katsuki[4] and Kallmerten[5], Nakai's diastereoselective syntheses of vicinal diols[6], Brocard's stereocontrolled rearrangements of $Cr(CO)_3$ complexes of allyl benzyl ethers[7], and, finally, the use of allyl [(phenylthio)methyl] ethers by Broka[8] and ourselves[9] as novel starting materials for [2,3] Wittig rearrangements.

We became involved in this field while seeking a novel $C_{14}-C_{20}$ building block for the synthesis of the polyol/polyene antibiotic amphotericin B[10]. The purported access offered an incentive to study the stereochemistry of [2,3] Wittig rearrangements of the **1**→**2** class. It turned out that such rearrangements are subject to good to excellent stereocontrol through asymmetric induction[11]. Product configurations were rationalized in terms of transition state **3**. When the new C–C bond forms, **3** allows for optimum delocalization of the charge of the attacking carbanion into the $\pi^*_{C=C}$ orbital *and* the low-lying σ^*_{C-O} orbital at the allylic stereocenter.



Turning our attention to Wittig rearrangements of the type **4**→**5**, we wondered whether they, too, would be subject to stereocontrol through asymmetric induction. In **4**, the chiral inducer is located *at C-2 of the allyl moiety* of the rearranging species. In the previously investigated lithio ethers **1**, the chiral inducer resides *at C-3 of the allyl moiety*[11,12].



We considered stannylated ethers **10** as reasonably accessible precursors of rearrangement substrates which display the novel substitution pattern **4**. (*E*)- and (*Z*)-**10** are equipped with a chiral dioxolane ring. Such a dioxolane had proved to be an efficient inducer of asymmetry in [2,3] Wittig rearrangements of the **1**→**2** class[11a–d].

The synthesis of **10** (Scheme 1) started from hydroxy ester **6**, which may be prepared from ascorbic acid in three steps[13]. Ester **6** was oxidized by pyridinium chlorochromate (PCC) in the presence of molecular sieves[14]. After filtration through a pad of silica gel, the crude keto ester was olefinated with excess ethylidenetriphenylphosphorane. The resulting mixture of α,β-unsaturated esters (*Z*)- and (*E*)-**7** was separated by column chromatography. Isomeric purities were 99.86% for (*Z*)-**7** and 97.8% for (*E*)-**7** by capillary gas chromatography (GLC). (*E*)/(*Z*) assignments for **7** follow from the low-field shift of the vinylic proton 3-H in (*E*)-**7** (δ = 7.05) vs. (*Z*)-**7** (δ = 6.58). The separated esters (*Z*)-**7** and (*E*)-**7** were reduced with DIBAH to allylic alcohols (*E*)-**9** and (*Z*)-**9**, respectively. Etherification of their potassium alcoholates according to Still's procedure[15] with Bu_3Sn-

[+)] To whom inquiries concerning the X-ray structural analysis should be addressed.

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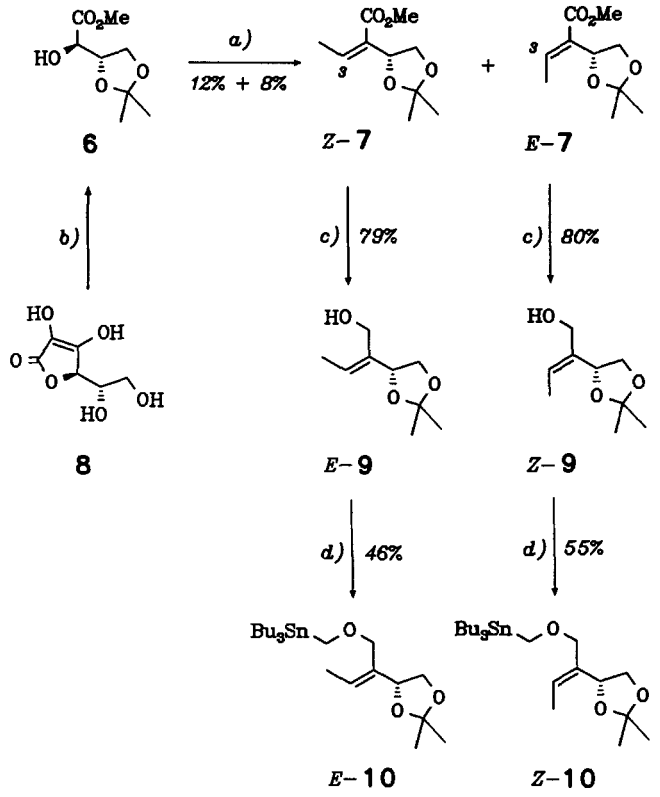
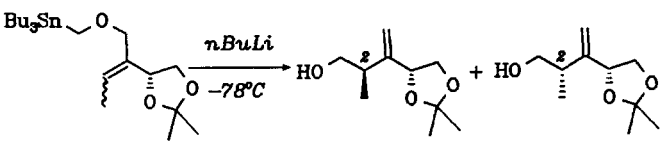
CH_2-I[16] furnished the stannylated ethers (*E*)-**10** and (*Z*)-**10** in moderate yields (46% and 55%, respectively).

Scheme 1



a) PCC, 3 Å molecular sieves; $Ph_3P=CH-Me$. – b) Ref.[13] (3 steps). – c) DIBAH. – d) KH, $I-CH_2-SnBu_3$.

Lithiated ethers, representative of structural type **4**, were obtained from the stannylated ethers (*E*)-**10** and (*Z*)-**10** upon treatment with *n*BuLi (method: Still[15]). By the ensuing [2,3] shift, (*E*)-**10** gave *one* homoallylic alcohol **11**, in 89% yield. The isomeric ether (*Z*)-**10**, upon tin/lithium exchange, led to 70% of a *different* homoallylic alcohol **11**. According to GLC, *both* reactions furnished only 5 rel-% of the epimeric rearrangement product. Based on sterically *pure* starting materials, this result is equivalent to a 95:5 diastereoselectivity in the rearrangement (*E*)-**10** → *anti*-**11** and a 97:3 selectivity for the reaction (*Z*)-**10** → *syn*-**11**. Obviously, 1,3-asymmetric induction *can* be a viable means for achieving stereocontrol in the [2,3] Wittig rearrangement.



10	yield	anti-11		syn-11
E (99.9 : 0.1)	*89%*	*95*	:	*5*
Z (97.8 : 2.2)	*70%*	*5*	:	*95*

The configuration at the newly formed stereocenter C-2 of *syn*-**11** and *anti*-**11** could not be clarified by NMR spectroscopy. Attempts to crystallize the 3,5-dinitrobenzoate of *anti*-**11** or the tris(3,5-dinitrobenzoate) of the triol obtained after hydrolysis of the acetonide met with failure. Therefore, we took recourse to a stereochemically unambiguous, *independent* synthesis of *syn*- and *anti*-**11**. In fact – for the sake of convenience – this structure-proving synthesis headed for the *enantiomers* of the compounds in question (Scheme 2).

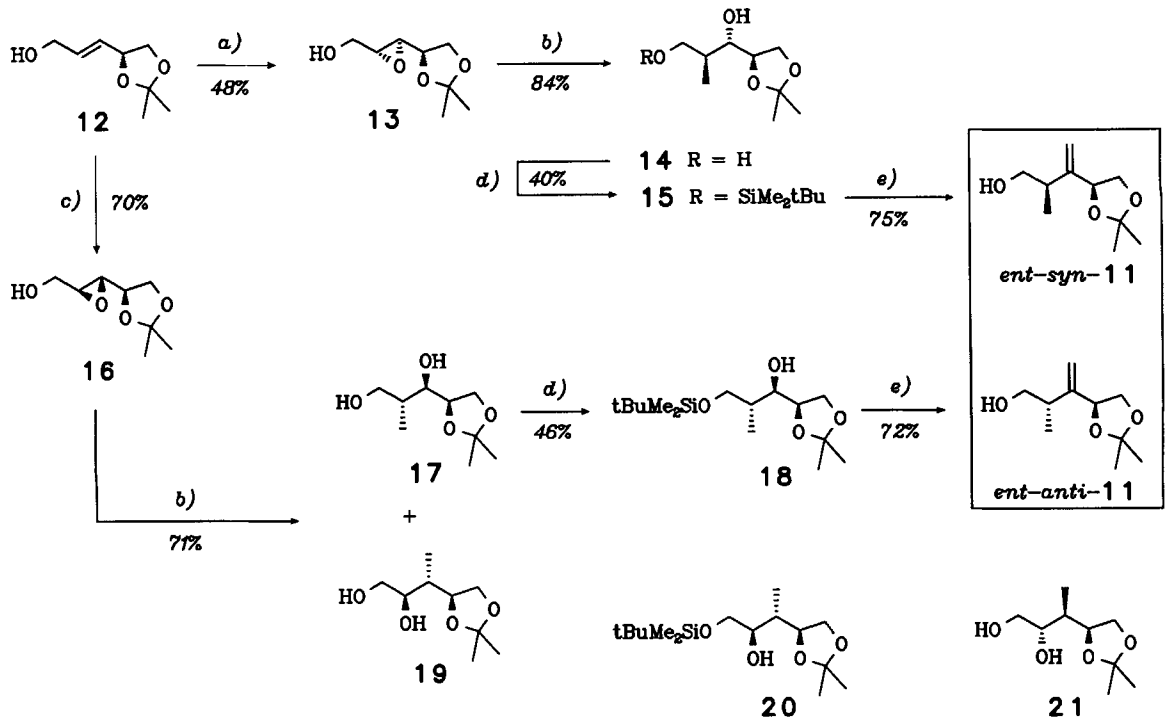
We started from the allylic alcohol **12**, which we had prepared earlier[11d] (cf. ref.[17,18]). By asymmetric Sharpless epoxidation[19], **12** was converted into **13** in the presence of (–)-diethyl tartrate, and into **16** with (+)-diethyl tartrate as auxiliary[18,20]. Each of these epoxy alcohols was ring-opened with Me_2CuLi according to the Kishi aldol methodology[21]. The *anti*-epoxide **13** gave the expected 1,3-diol **14**[20b] essentially regioselectively. The isomeric 1,2-diol **21** was formed only in trace quantities. However, the *syn*-epoxide **16** took up the cuprate with *opposite* but fortunately low regioselectivity, and we obtained a mixture of 64% of the undesired 1,2-diol **19** and 36% of the desired 1,3-diol **17**. While failure in regiocontrol is known in *other* epoxyalcohol/cuprate reactions[21] there was no reference to it in an earlier report of the ring-opening of **16** with Me_2CuLi[20b].

The *mixture* of isomeric diols **17** and **19** was initially monosilylated with *tert*-butyldimethylsilyl chloride (TBDMSCl)[23]. However, the resulting silyl ethers **18** and **20** were even more resistant to chromatographic separation than their diol precursors. Therefore, we continued the correlation with the small fraction of pure 1,3-diol **17** obtainable by flash chromatography[24] from the **17**/**19** mixture. The primary hydroxy group of **17** was protected as its TBDMS ether **18**. The epimeric 1,3-diol **14** (vide supra) was silylated similarly to give **15**. TBDMS ethers **15** and **18** were than submitted to a three-step sequence, each without purification of intermediates: (1) Oxidation of the unprotected secondary OH group with PCC in the presence of molecular sieves[14]; (2) Wittig reaction of the resulting ketone with $Ph_3P=CH_2$; (3) desilylation with Bu_4NF. This provided homoallylic alcohols *ent-syn*-**11** and *ent-anti*-**11**, respectively, of known stereochemistry. *These compounds were indistinguishable by capillary GLC or ^{1}H-NMR spectroscopy from the homoallylic alcohols syn-***11** *and anti-***11** *obtained from the Wittig-Still rearrangements of (Z)- and (E)-***10**, *respectively.*

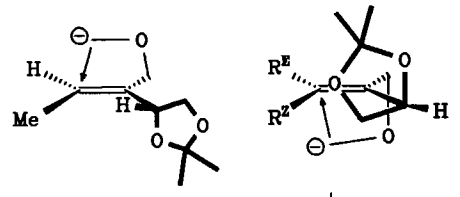
This result was a surprise. By extrapolation from the Houk-like (cf. ref.[25]) transition-state structure **3** – which describes the asymmetric induction in [2,3] Wittig rearrangements of the type **1** → **2** successfully[11] – we had expected transition state **22** for the Wittig-Still rearrangement of allylic ether (*Z*)-**10**. However, the *syn* configuration of the *observed* rearrangement product is clearly at odds with this transition state: The facial selectivity of double-bond attack must be *opposite* to that depicted in **22**!

We do not consider structure **23a** a likely transition state. Because of the (*Z*) configuration of its double bond, **23a** should suffer from severe 1,3-allyl strain[26,27]. Transition state

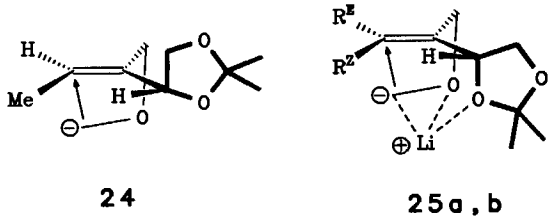
Scheme 2



a) *t*BuOOH, Ti(O*i*Pr)$_4$, (−)-diethyl tartrate. – b) Me_2CuLi. – c) *t*BuOOH, Ti(O*i*Pr)$_4$, (+)-diethyl tartrate. – d) *t*$BuMe_2SiCl$, 4-(dimethylamino)pyridine, NEt_3. – e) PCC, 3 Å molecular sieves; $Ph_3P=CH_2$; Bu_4NF.

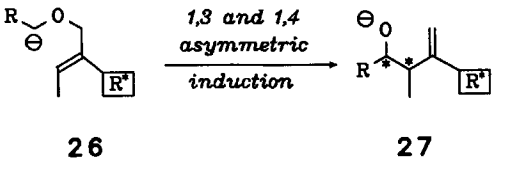


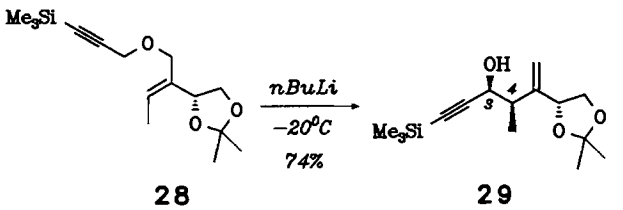
23	R^E	R^Z
a	H	Me
b	Me	H



24 would be devoid of 1,3-allyl strain. However, it is unapt to stabilize the approaching negative charge by overlap with a properly aligned allylic σ^*_{C-O} orbital (which effect is believed to favor the "established" transition state **3**; vide supra). Transition state **25a** as an alternative is also free from 1,3-allyl strain, *plus* it maintains the charge-delocalizing capacity of the expected transitions state **22** to some extent. **25a** differs from **22** in that the carbanion approaches the C=C bond *syn* to the allylic C–O bond instead of *anti*. Why this mode of attack should be preferred is not clear at this stage of our investigations. One possibility might be complexation of the lithium counterion of the metalated ether by the dioxolane: Such chelation *could* entail – as formula **25a** indicates – a *syn*-selective attack on the C=C bond.

The isomeric ether (*E*)-**10** – by analogy to its (*Z*) counterpart – might rearrange by *syn* attack in a chelated transition state **25b**. Alternatively, the *anti* configuration of the preferred rearrangement product might result from an *anti* attack in transition state **23b**.





Having demonstrated the existence of a 1,3-asymmetric induction in [2,3] Wittig rearrangements of the **4** → **5** class,

we sought concomitant 1,3- *and* 1,4-asymmetric inductions in Wittig rearrangements of conjugated anions **26** (→**27**)[28]. Our study case was the (trimethylsilyl)propargyl ether **28**. **28** was obtained from allylic alcohol (*Z*)-**9** by alkylation with propargyl bromide followed by treatment with *n*BuLi/Me_3SiCl (58% yield).

Propargylic ether **28** was lithiated under the conditions of Nakai[29], and we obtained *one* main product **29** in 74% yield, contaminated with 6, 5, and 1 rel-% of its three possible diastereomers. The stereocontrol looked for hence *exists*.

The major rearrangement product **29** crystallized from petroleum ether. Its stereochemistry was elucidated by X-ray crystallography (Figure 1). The (*R*) configuration at C-4 shows that in the Wittig rearrangement of **28** the 1,3-asymmetric induction is *reversed* compared with the asymmetric induction in the Wittig-Still rearrangement (*Z*)-**10** → *syn*-**11**. This means that propargyl ether **28** does not rearrange via transition state **30**. (In **30**, chelation of the accompanying lithium ion would have directed the carbanion towards the C=C bond *syn* with respect to the allylic C–O bond.) Rather, the (*R*) configuration of C-4 agrees with transition state **31**. In **31**, the carbanion approaches the C=C bond *anti* with respect to the allylic C–O bond. This mode of attack could be favored stereoelectronically since it is "Houk-like" (vide supra).

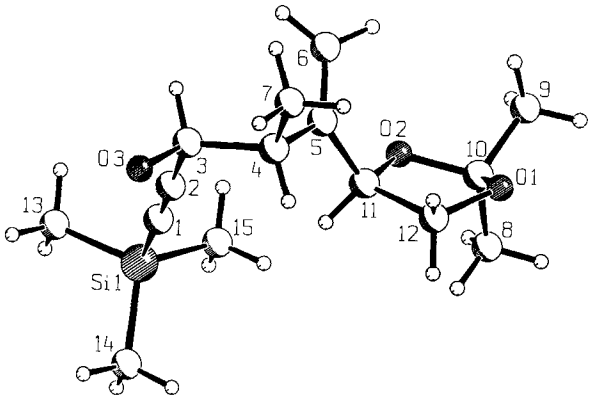
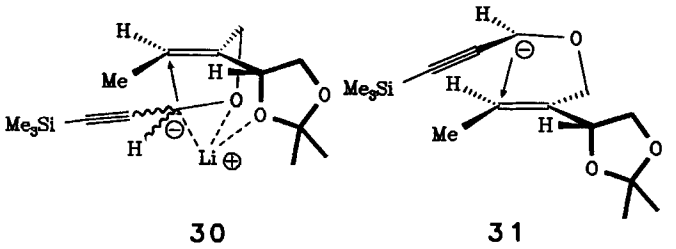
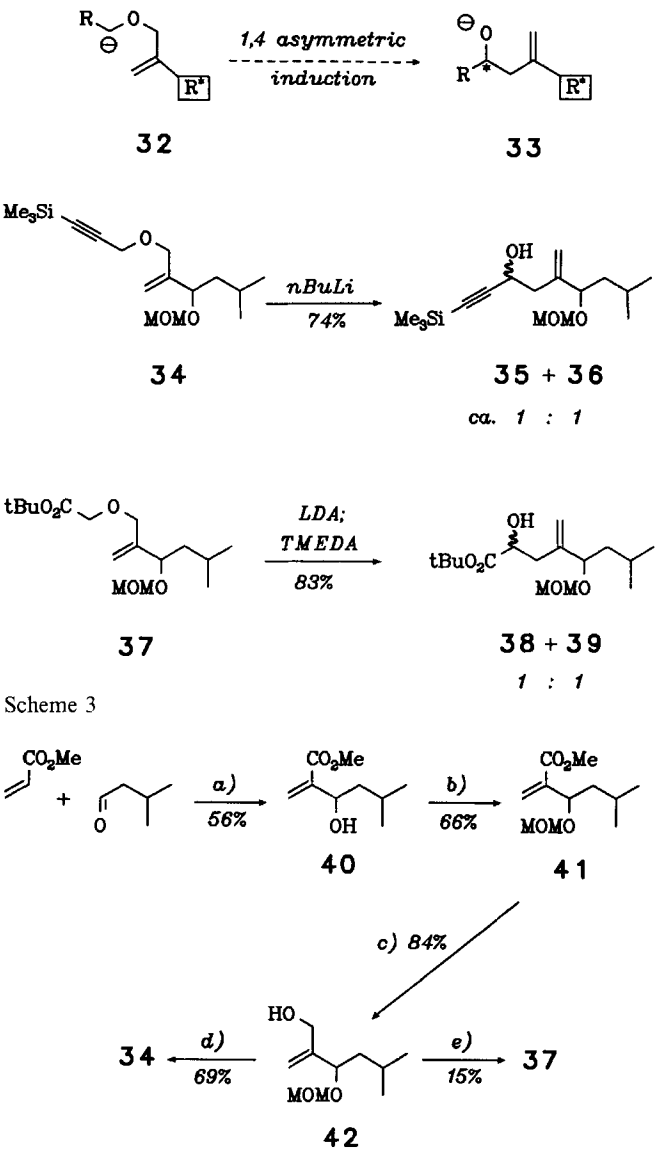


Figure 1. SCHAKAL plot of the solid-state structure of homoallylic alcohol **29**[30]



Why should a stereoelectronic effect dominate the transition state of the [2,3] rearrangement of lithio propargyl ether **28**, while chelation of the counterion is believed to control the transition-state geometry of analogous Wittig-Still rearrangements? Perhaps, lithio-**28** is dissociated into a metal cation and a resonance-stabilized propargyl anion in the transition state. Since the rearranging species would then be a *naked* anion, chelation should not intervene. The intermediates of the corresponding Wittig-Still rearrangements, by contrast, are *prim*-alkyl lithium compounds. As such, they should be covalent rather than ionic, which would leave the metal close enough to effect chelation control in the ensuing rearrangement step.

The (*S*) configuration at C-3 of the major rearrangement product **29** requires that the propargyl group in transition state **31** be on the concave face of the envelope conformation of the C=C–C–O–C$^{\ominus}$ subunit. The *same* orientational preference of the propargyl moiety was inferred from the stereochemistry of the [2,3] Wittig rearrangement of lithiated (*trans*-crotyloxy)(trimethylsilyl)propyne[29].



Scheme 3

a) DABCO (method: ref.[31]). – b) $MeOCH_2OMe$, *p*-TsOH, LiBr (method: ref.[32]). – c) DIBAH. – d) 3-Bromopropyne, KOH, $BzlNEt_3Cl$; *n*BuLi, Me_3SiCl (method: ref.[29]). – e) Sodium methylsulfinylmethide, $ClCH_2-CO_2^{\ominus}Na^{\oplus}$; *t*BuOH, DCC, 4-(dimethylamino)pyridine.

Finally, we tried to extend the stereocontrol observed in [2,3] Wittig rearrangement of type **26** → **27** – i.e. 1,4- *plus* 1,3-asymmetric induction – to rearrangements like **32** → **33**, i.e. 1,4-asymmetric induction *only*. To this end, we synthesized (trimethylsilyl)propargyl ether **34** and *tert*-butyl(allyloxy) acetate **37** as racemates, using standard methods (Scheme 3). Both compounds are equipped with allylic MOMO groups, a functionality which had caused a particularly high 1,2-asymmetric induction in [2,3] Wittig rearrangements of the type **1** → **2**[11c]. However, when the lithiated propargyl ether **34** or the lithium enolate of ester **37** underwent Wittig rearrangements, *no stereoselectivity whatever* was found: *syn/anti* diastereomers **35/36** (from **34**) and **38/39** (from **37**) resulted as 1:1 mixtures. So far, therefore, stereocontrol through asymmetric induction in [2,3] Wittig rearrangements of ethers of type **32** remains an elusive goal.

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Experimental

^{1}H NMR: Bruker AC 300; TMS as internal standard in $CDCl_3$; integrals in accord with assignments; coupling constants J in Hz. – GLC: Sichromat 3 (Siemens). – MS: MAT CH7A, MAT 711. – All reactions were performed in oven-dried (100°C) glassware under dry nitrogen. – Compounds were purified by flash chromatography[24] on Merck silica gel 60 (particle size 0.040–0.063 mm, 230–400 mesh ASTM). – Yields refer to analytically pure samples.

Methyl (2E)-2-[(4R)-2,2-Dimethyl-1,3-dioxolan-4-yl]-2-butenoate [(*E*)-**7**] *and Methyl (2Z)-2-[(4R)-2,2-Dimethyl-1,3-dioxolan-4-yl]-2-butenoate* [(*Z*)-**7**]: Methyl (2*R*)-2-[(4*R*)-2,3-dimethyl-1,3-dioxolan-4-yl]-2-hydroxyacetate[13] (**6**) {10.2 g, 53.4 mmol; $[\alpha]_D^{20}$ = +16.2 (*c* = 3.7, CH_2Cl_2); ref.[13] $[\alpha]_D^{25}$ = +18.39 (*c* = 1.0442, $CHCl_3$)} in CH_2Cl_2 (20 ml), pyridinium chlorochromate[30] (47.0 g, 0.20 mol, 4.0 equiv.), and freshly activated powdered 3 Å molecular sieves[14] (100 g) were stirred at room temp. for 3.5 h. After dilution with ether (200 ml), column chromatography (SiO_2, ether) furnished crude *methyl 2-[(4'S)-2,2-dimethyl-1,3-dioxolan-4-yl]-2-oxoacetate* (9.50 g). 9.00 g of this material in DME (60 ml) was added at −30°C to a solution prepared from ethyltriphenylphosphonium bromide (41 g, 110 mmol, ≥ 2.3 equiv.) in DME (150 ml) and *n*BuLi (1.50 mol/l in hexane, 67 ml, 100 mmol, ≥ 2.1 equiv.). After 60 min, the mixture was allowed to warm to room temp., where DME (50 ml) was added. After another 2 h, the reaction was quenched by addition of satd. aqueous NH_4Cl (500 ml). Extraction with ether and removal of $Ph_3P{=}O$ by crystallization at 5°C (after dilution with petroleum ether) followed. Flash chromatography [petroleum ether/ether (30:1)], followed by column chromatography [SiO_2, petroleum ether/ether (3:1)] gave (*Z*)-**7** [1.20 g, 12% from **6**; isomeric purity (by GLC) 99.9%] and (*E*)-**7** [0.80 g, 8% from **6**; isomeric purity (by GLC) 97.8%]. – No correct combustion analyses could be obtained from these compounds.

(*E*)-**7**: $[\alpha]_D^{19}$ = −29.6 (*c* = 4.1, CH_2Cl_2). – ^{1}H NMR: δ = 1.41 and 1.51 [2 s, 2'-$(CH_3)_2$], 2.02 (d, $J_{4,3}$ = 7.4, 4-H_3), 3.74 (s, OCH_3), 3.86 (dd, $J_{5'\text{-}H^{1},4'}$ = 8.3, J_{gem} = 7.8, 5'-H^1), 4.18 (dd, J_{gem} = 7.7, $J_{5'\text{-}H^{2},4'}$ = 6.8, 5'-H^2), 5.12 (dd, $J_{4',5'\text{-}H^{1}}$ = 8.4, $J_{4',5'\text{-}H^{2}}$ = 6.8, 4'-H), 7.05 (q, $J_{3,4}$ = 7.4, 3-H).

(*Z*)-**7**: $[\alpha]_D^{20}$ = −47.3 (*c* = 3.9, CH_2Cl_2). – ^{1}H NMR: δ = 1.42 and 1.45 [2 s, 2'-$(CH_3)_2$], 2.07 (d, $J_{4,3}$ = 7.4, 4-H_3), 3.62 (br. dd, $J_{gem} \approx J_{5'\text{-}H^{1},4'} \approx$ 7.5, 5'-H^1), 3.76 (s, OCH_3), 4.29 (dd, J_{gem} = 8.1, $J_{5'\text{-}H^{2},4'}$ = 6.6, 5'-H^2), 4.81 (m_c, 4'-H), 6.58 (br. q, $J_{3,4}$ = 7.3, 3-H).

(2E)-2-[(4R)-2,2-Dimethyl-1,3-dioxolan-4-yl]-2-buten-1-ol [(*E*)-**9**] (0.753 g, 79%) was prepared from (*Z*)-**7** (1.10 g, 5.49 mmol) as described for the transformation (*E*)-**7** → (*Z*)-**9**. – $[\alpha]_D^{20}$ = −58.4 (*c* = 6.4, CH_2Cl_2). – ^{1}H NMR: δ = 1.39 and 1.48 [2 s, 2'-$(CH_3)_2$], 1.76 (d, $J_{4,3}$ = 6.9, 4-H_3), 2.17 (dd, $J_{OH,1\text{-}H^{2}}$ = 7.8, $J_{OH,1\text{-}H^{1}}$ = 3.9, OH), 3.73 (dd, $J_{gem} = J_{5'\text{-}H^{1},4'}$ = 8.1, 5'-H^1), 4.08 (dd, J_{gem} = 8.4, $J_{5'\text{-}H^{2},4'}$ = 6.5, 5'-H^2), AB signal (δ_A = 4.19, δ_B = 4.27, $J_{A,B}$ = 11.9, in addition split by $J_{A,OH}$ = 3.9, $J_{B,OH}$ = 7.7, 1-H_2), 4.62 (dd, both J_{vic} = 7.3, 4'-H), 5.75 (q, $J_{3,4}$ = 7.0, 3-H). – MS: *m/z*(M^+ − CH_3) = 157.0883 (calcd. for $C_9H_{16}O_3$ − CH_3: 157.0865).

(2Z)-2-[(4R)-2,2-Dimethyl-1,3-dioxolan-4-yl]-2-buten-1-ol [(*Z*)-**9**]: At −78°C, DIBAH (1.0 mol/l in hexane, 17.0 ml, 17.0 mmol, 4.5 equiv.) was added to (*E*)-**7** (0.750 g, 3.75 mmol) in THF (40 ml). During 4 h, the temp. was increased to −30°C. Excess reagent was destroyed by addition of H_2O (5 ml) at −78°C. Extractive workup (0.1 M NaOH/ether) and flash chromatography [petroleum ether/diethyl ether (1:1)] yielded (*Z*)-**9** as a yellowish oil (0.516 g, 80%). – $[\alpha]_D^{21}$ = −40.8 (*c* = 6.2, CH_2Cl_2). – ^{1}H NMR: δ = 1.42 and 1.49 [2 s, 2'-$(CH_3)_2$], 1.68 (d, $J_{4,3}$ = 7.0, 4-H_3), 2.48 (dd, $J_{OH,1\text{-}H^{1}}$ = 9.0, $J_{OH,1\text{-}H^{2}}$ = 3.5, OH), 3.64 (dd, $J_{gem} = J_{5'\text{-}H^{1},4'}$ = 8.3, 5'-H^1), 3.98 (dd, J_{gem} = 12.3, $J_{1\text{-}H^{1},OH}$ = 9.1, 1-H^1), 4.12 (dd, J_{gem} = 8.2, $J_{5'\text{-}H^{2},4'}$ = 6.5, 5'-H^2), 4.25 (very br. d, J_{gem} = 12.3, 1-H^2), 5.09 (dd, $J_{4',5'\text{-}H^{1}} = J_{4',5'\text{-}H^{2}}$ = 7.4, 4'-H), 5.74 (q, $J_{3,4}$ = 6.9, 3-H). – MS: *m/z*(M^+ − CH_3) = 157.0878 (calcd. for $C_9H_{16}O_3$ − CH_3: 157.0865).

(2E)-2-[(4R)-2,2-Dimethyl-1,3-dioxolan-4-yl]-1-[(tributylstannyl)methoxy]-2-butene [(*E*)-**10**] (0.505 g, 46%) was prepared from (*E*)-**9** (0.400 g, 2.32 mmol) as described for the transformation of (*Z*)-**9** to (*Z*)-**10**. – $[\alpha]_D^{18}$ = −18.9 (*c* = 3.1, CH_2Cl_2). – ^{1}H NMR: δ = 0.89 (m_c, 3 4'''-H_3 and 3 1'''-H_2), 1.30 (tq, both $J \approx$ 7, 3 3'''-H_2), 1.40 and 1.45 [2 s, 2'-$(CH_3)_2$], 1.46–1.56 (m, 3 2'''-H_2), 1.73 (d, $J_{4,3}$ = 6.9, 4-H_3), 3.62–3.71 (m, 5'-H^1, 1''-H_2), AB signal (δ_A = 3.89, δ_B = 3.94, $J_{A,B}$ = 11.0, 1-H_2), 4.06 (dd, J_{gem} = 8.2, $J_{5'\text{-}H^{2},4'}$ = 6.3, 5'-H^2), 4.50 (very br. dd, both $J_{vic} \approx$ 7.2, 4'-H), 5.89 (q, $J_{3,4}$ = 7.1, 3-H).

$C_{22}H_{44}O_3Sn$ (475.3) Calcd. C 55.60 H 9.33
Found C 55.65 H 9.14

(2Z)-2-[(4R)-2,2-Dimethyl-1,3-dioxolan-4-yl]-1-[(tributylstannyl)methoxy]-2-butene [(*Z*)-**10**]: At 0°C, tributyl(iodomethyl)stannane[15,16] (0.430 g, 1.00 mmol, 1.3 equiv.) and (*Z*)-**9** (0.130 g, 0.755 mmol) in THF (3 ml) were added to KH (0.100 g, 2.49 mmol, 3.3 equiv.) in THF (2 ml). After 4 h, satd. aqueous NH_4Cl (5 ml) was added. Extraction with ether followed by flash chromatography [petroleum ether/ether (50:1 → 5:1)] gave the title compound (0.194 g, 55%). – $[\alpha]_D^{18}$ = −16.3 (*c* = 2.5, CH_2Cl_2). – ^{1}H NMR: δ = 0.90 (m_c, 3 4'''-H_3 and 3 1'''-H_2), 1.29 (tq, both J = 7.0, 3 3'''-H_3), 1.41 and 1.45 [2 s, 2'-$(CH_3)_2$], 1.46–1.56 (m, 3 2'''-H_2), 1.74 (d, $J_{4,3}$ = 6.5, 4-H_3), AB signal (δ_A = 3.64, δ_B = 3.69, $J_{A,B}$ = 10.3, 1''-H_2), AB signal (δ_A = 3.71, δ_B = 4.02, $J_{A,B} \approx$ 11.5, 1-H_2), 3.76 (dd, $J_{5'\text{-}H^{1},4'}$ = 8.6, J_{gem} = 8.2, 5'-H^1), 4.01 (m_c, 5'-H^2), 4.95 (dd, $J_{4',5'\text{-}H^{1}}$ = 8.6, $J_{4',5'\text{-}H^{2}}$ = 6.3, 4'-H), 5.75 (qd, $J_{3,4}$ = 7.0, $J_{3,4'}$ = 1.0, 3-H).

$C_{22}H_{44}O_3Sn$ (475.3) Calcd. C 55.60 H 9.33
Found C 55.78 H 9.28

(2S)-3-[(4R)-2,2-Dimethyl-1,3-dioxolan-4-yl]-2-methyl-3-buten-1-ol (*syn*-**11**): At −78°C, *n*BuLi (1.5 M in hexane, 0.32 ml, 0.48 mmol, 1.8 equiv.) was added to (*Z*)-**10** (0.130 g, 0.274 mmol) in THF (3 ml). Extractive workup after 2 h (satd. aqueous NH_4Cl/ether; *syn*:*anti*-**11** = 95.0:5.0 in the crude product according to GLC) and flash chromatography [petroleum ether/ether (1:1)] gave *syn*-**11** as an oil (0.035 g, 70%). – $[\alpha]_D$ not measured due to the

small quantity of available material. – ^{1}H NMR: δ = 1.08 (d, $J_{2\text{-Me},2}$ = 7.1, 2-CH_3), 1.40 and 1.48 [2 s, 2′-$(CH_3)_2$], 2.29 (dd, $J_{OH,1\text{-}H^1}$ = 6.7, $J_{OH,1\text{-}H^2}$ = 4.8, OH), 2.46 (m_c, 2-H), 3.47–3.63 (m, 1-H_2), 3.65 (dd, J_{gem} = $J_{5'\text{-}H^1,4'}$ = 8.0, 5′-H^1), 4.12 (dd, J_{gem} = 8.2, $J_{5'\text{-}H^2,4'}$ = 6.6, 5′-H^2), 4.59 (dd, both $J_{vic} \approx$ 7.2, 4′-H), 5.09 (s, 4-H^1), 5.29 (s, 4-H^2). – MS: $m/z(M^+ - CH_3)$ = 171.1020 (calcd. for $C_9H_{15}O_3 - CH_3$: 171.1021); m/z of the corresponding ^{13}C satellite 172.1041 (calcd. for $^{12}C_8{}^{13}C_1H_{15}O_3$: 172.1055).

(2R)-3-[(4R)-2,2-Dimethyl-1,3-dioxolan-4-yl]-2-methyl-3-buten-1-ol (*anti*-**11**) (0.159 g, 89%) was obtained from (*E*)-**10** (0.456 g, 0.959 mmol) by the procedure described for the preparation of *syn*-**11** from (*Z*)-**10**. The crude product contained a 95.1:4.9 ratio of *anti*- and *syn*-**11** (GLC). – $[\alpha]_D^{19}$ = –25 (*c* = 1.6, CH_2Cl_2). – ^{1}H NMR: δ = 1.11 (d, $J_{2\text{-Me},2}$ = 7.0, 2-CH_3), 1.41 and 1.46 [2 s, 2′-$(CH_3)_2$], 1.66 (t, $J_{OH,1}$ = 6.1, OH), 2.36 (tq, $J_{2,1}$ = $J_{2,2\text{-Me}}$ = 6.7, 2-H), 3.58 (t, $J_{1,OH}$ = 6.1, 1-H_2), 3.66 (dd, J_{gem} = $J_{5'\text{-}H^1,4'}$ = 7.9, 5′-H^1), 4.15 (dd, J_{gem} = 8.0, $J_{5'\text{-}H^2,4'}$ = 6.6, 5′-H^2), 4.56 (br. dd, both $J_{vic} \approx$ 7.2, 4′-H), 5.03 (s, 4-H^1), 5.33 (s, 4-H^2).

$C_{10}H_{13}O_3$ (186.3) Calcd. C 64.50 H 9.74
Found C 64.25 H 10.04

(2R)-3-[(4S)-2,2-Dimethyl-1,3-dioxolan-4-yl]-2-methyl-3-buten-1-ol (*ent-syn*-**11**) (22 mg, 75%) was obtained from **15** (50 mg, 0.16 mmol) by the three-step sequence described for the transformation of **18** into *ent-anti*-**11**. The ^{1}H-NMR spectra of *ent-syn*-**11** and *syn*-**11** were identical. *ent-syn*-**11** cochromatographed with *syn*-**11** on capillary GLC; *ent-syn*-**11** migrated faster during gas chromatography than coinjected samples of *ent-anti*-**11** and *anti*-**11**.

(2S)-3-[(4S)-2,2-Dimethyl-1,3-dioxolan-4-yl]-2-methyl-3-buten-1-ol (*ent-anti*-**11**): **18** (26.8 mg, 0.088 mmol), PCC[33] (190 mg, 0.880 mmol, 10 equiv.), and powdered 3 Å molecular sieves[14] (activated at 300°C) were stirred at room temp. in CH_2Cl_2 (3 ml) for 1 h. The mixture was diluted with ether (50 ml) and filtered through a pad of silica gel. Evaporation of the solvent under reduced pressure gave the crude silyl ketone. It was dissolved in DME (1.5 ml) and added at –30°C to an ylid solution prepared from methyltriphenylphosphonium bromide (314 mg, 0.880 mmol, 10 equiv.) in DME (2 ml) and MeLi (1.6 M in ether; 0.50 ml, 0.80 mmol, 9.1 equiv.). After 5 min, the cooling bath was removed for 90 min. Satd. aqueous NH_4Cl (1 ml), ether (250 ml), and $MgSO_4$ were added. After drying was complete, the mixture was filtered and evaporated. The resulting olefin was stirred with Bu_4NF (1.0 M in THF; 3.80 ml, 3.80 mmol). NH_4Cl/ether/$MgSO_4$ workup as before and flash chromatography [petroleum ether/ether (1:1 → 1:2)] gave the final product (11.7 mg, 72% for the three steps). – The ^{1}H-NMR spectrum of *syn-anti*-**11** was identical with that of *anti*-**11**. *ent-anti*-**11** cochromatographed with *anti*-**11** on capillary GLC. In the gas chromatograph *ent-anti*-**11** migrated more slowly than coinjected samples of *ent-syn*-**11** and *syn*-**11**.

{(2R,3S)-3-[(4R)-2,2-Dimethyl-1,3-dioxolan-4-yl]oxiran-2-yl}methanol (**13**) (0.796 g, 48%) was obtained from **12** (1.50 g, 9.48 mmol) by Sharpless oxidation in the presence of (–)-diethyl tartrate as described for the reaction of **12** → **16**. – $[\alpha]_D^{20}$ = 29 (*c* = 3.2, CH_2Cl_2). – ^{1}H NMR: δ = 1.37 and 1.45 [2 s, 2″-$(CH_3)_2$], 1.74 (dd, $J_{OH,1\text{-}H^1}$ = 7.5, $J_{OH,1\text{-}H^2}$ = 5.5, OH), 3.08–3.14 (m, 2′-H, 3′-H), 3.69 (ddd, J_{gem} = 12.7, $J_{1\text{-}H^1,OH}$ = 7.5, $J_{1\text{-}H^1,2'}$ = 3.9, 1-H^1), 3.88–4.02 (m, 1-H^2, 5″-H_2), 4.10–4.17 (m, 4″-H).

$C_8H_{14}O_4$ (174.2) Calcd. C 55.16 H 8.10
Found C 54.97 H 7.85

(1S,2S)-1-[(4R)-2,2-Dimethyl-1,3-dioxolan-4-yl]-2-methyl-1,3-propanediol (**14**) (0.184 g, 84%) was prepared from **13** (0.200 g, 1.15 mmol) by the procedure outlined for the conversion of **16** into **17**/**19**. – $[\alpha]_D^{20}$ = 29 (*c* = 2.7, CH_2Cl_2). – ^{1}H NMR: δ = 0.95 (d, *J* = 7.0, 2-CH_3), 1.38 and 1.44 [2 s, 2′-$(CH_3)_2$], 1.75 (m_c, 2-H), 2.73 (d, $J_{OH,1}$ = 3.1, 1-OH), 2.82 (dd, $J_{OH,3\text{-}H^1}$ = 7.1, $J_{OH,3\text{-}H^2}$ = 4.3, 3-OH), 3.66–3.79 (m, 1-H, 3-H_2), AB signal (δ_A = 3.96, δ_B = 4.03, $J_{A,B}$ = 8.1, in addition split by $J_{A,4'}$ = 7.7, $J_{B,4'}$ = 6.4, 5′-H_2), 4.22 (ddd, $J_{4',5'\text{-}A}$ = 7.3, $J_{4',5'\text{-}B}$ = 6.4, $J_{4',1}$ = 4.4, 4′-H).

$C_9H_{18}O_4$ (190.2) Calcd. C 56.82 H 9.54
Found C 56.54 H 9.26

After elution of the main product, careful chromatography allowed the isolation of trace amounts of the isomeric 1,2-diol *(2S,3R)-3-[(4S)-2,2-Dimethyl-1,3-dioxolan-4-yl]-1,2-butanediol* (**21**). – ^{1}H NMR: δ = 0.92 (d, *J* = 7.0, 4-H_3), 1.36 and 1.44 [2 s, 2′-$(CH_3)_2$], 1.96 (qdd, $J_{3,4}$ = $J_{3,2}$ = 7.1, $J_{3,4'}$ = 4.3, 3-H), 2.32 (very br. s, OH), 3.33 (br. s, OH), 3.48–3.79 (m, 1-H_2, 2-H, 5′-H^1), 4.05 (dd, J_{gem} = 8.3, $J_{5'\text{-}H^2,4'}$ = 6.6, 5′-H^2), 4.34 (ddd, $J_{4',5'\text{-}H^1}$ = $J_{4',5'\text{-}H^2}$ = 7.1, $J_{4',3}$ = 4.3, 4′-H).

(1S,2S)-3-[(tert-Butyldimethylsilyl)oxy]-1-[(4R)-2,2-dimethyl-1,3-dioxolan-4-yl]-2-methyl-1-propanol (**15**) (51.5 mg, 40%) was obtained by silylation of **14** (82 mg, 0.43 mmol) as described for the conversion of **17** → **18**. – $[\alpha]_D^{24}$ = 6.6 (*c* = 1.9, CH_2Cl_2). – ^{1}H NMR: δ = 0.08 [Si$(CH_3)_2$], 0.90 [s, C$(CH_3)_3$], 1.08 (d, *J* = 7.2, 2-CH_3), 1.37 and 1.40 [2 s, 2′-$(CH_3)_2$], 1.85 (m_c, 2-H), 3.51–3.58 (m, 2H), 3.64 (dd, J_a = 10.1, J_b = 4.0, 1H), 3.94–4.03 and 4.06–4.15 (2 m, 2H each).

$C_{15}H_{32}O_4Si$ (304.5) Calcd. C 59.17 H 10.59
Found C 59.65 H 10.60

{(2S,3R)-3-[(4R)-2,2-Dimethyl-1,3-dioxolan-4-yl]oxiran-2-yl}methanol (**16**): (+)-Diethyl tartrate (1.36 ml, 7.95 mmol, 1.1 equiv.) in CH_2Cl_2 (10 ml) was added at –30°C to a solution of $Ti(OiPr)_4$ (2.24 ml, 7.6 mmol, 1.05 equiv.) in CH_2Cl_2 under stirring. After 15 min, **12** (1.14 g, 7.23 mmol) in CH_2Cl_2 (20 ml) was added dropwise, followed by *t*BuOOH (3 M in isooctane; 5.20 ml, 15.6 mmol, 2.2 equiv.). The reaction was allowed to proceed at –20°C for 1 d and was then quenched with satd. aqueous Na_2SO_3 and satd. aqueous Na_2SO_4 (10 ml of each). The resulting mixture was extracted several times with ether (total 1.5 l). The combined extracts were washed with 50% KOH (30 ml) and brine (20 ml). Flash chromatography [petroleum ether/ether (1:7)] gave **16** (0.882 g, 70%). – $[\alpha]_D^{20}$ = –26 (*c* = 2.1, CH_2Cl_2). – ^{1}H NMR: δ = 1.37 and 1.43 [2 s, 2″-$(CH_3)_2$], 1.79 (dd, $J_{OH,1\text{-}H^1}$ = 7.7, $J_{OH,1\text{-}H^2}$ = 5.3, OH), 3.11 (dd, $J_{3',4''}$ = 4.7, $J_{3',2'}$ = 2.3, 3′-H), 3.16 (ddd, $J_{2',1\text{-}H^1}$ = 3.7, $J_{2',3'}$ = $J_{2',1\text{-}H^2}$ = 2.3, 2′-H), 3.68 (ddd, J_{gem} = 12.8, $J_{1\text{-}H^1,OH}$ = 7.7, $J_{1\text{-}H^1,2'}$ = 3.8, 1-H^1), 3.82–3.90 (m, 5″-H^1), 3.96 (ddd, J_{gem} = 12.8, $J_{1\text{-}H^2,OH}$ = 5.1, $J_{1\text{-}H^2,2'}$ = 2.4, 1-H^2), 4.06–4.15 (m, 4″-H, 5″-H^2).

$C_8H_{14}O_4$ (174.2) Calcd. C 55.16 H 8.10
Found C 55.01 H 8.03

(1R,2R)-1-[(4R)-2,2-Dimethyl-1,3-dioxolan-4-yl]-2-methyl-1,3-propanediol (**17**) *and (2R,3S)-3-[(4S)-2,2-Dimethyl-1,3-dioxolan-4-yl]-1,2-butanediol* (**19**): At –23°C, MeLi [1.6 M in ether, "low halide" (Janssen); 11.4 ml, 18.2 mmol, 20 equiv.] was added dropwise to a stirred suspension of CuI (1.73 g, 9.10 mmol, 10 equiv.) in ether (20 ml). When the yellow color had disappeared, the solution was cooled to –40°C. **16** (0.158 g, 0.91 mmol) in ether (5 ml) was added, and stirring was continued for 4 h between –30 and –25°C. Quenching with concd. NH_3 and satd. aqueous NH_4Cl (3 ml each), extraction with ether (3 × 250 ml), and flash chromatography (ether) furnished **19**/**17** as a 64:36 mixture (0.124 g, 71%), from which essentially pure **17** could be separated in the early fractions (0.037 g, 21%).

$C_9H_{18}O_4$ (190.2) Calcd. C 56.82 H 9.54
Found C 56.79 H 9.46

17: ^{1}H NMR: δ = 0.98 (d, J = 7.0, 2-CH_3), 1.39 and 1.46 [2 s, 2′-$(CH_3)_2$], 1.83 (qddd, $J_{2,Me} = J_a = J_b$ = 6.7, J_c = 4.2, 2-H), 2.55 (d, $J_{OH,1}$ = 6.6, 1-OH), 2.81 (dd, $J_{OH,3\text{-}H^1}$ = 6.8, $J_{OH,3\text{-}H^2}$ = 5.0, 3-OH), 3.47 (m_c, 3-H^1*), 3.69 (m_c, 1-H*, 3-H^2), 3.84 (dd, J_{gem} = 8.1, $J_{5'\text{-}H^1,4'}$ = 6.8, 5′-H^1), 4.06 (dd, J_{gem} = 8.1, $J_{5'\text{-}H^2,4'}$ = 6.6, 5′-H^2), 4.25 (ddd, $J_{4',5'\text{-}H^1} = J_{4',5'\text{-}H^2}$ = 6.7, $J_{4',1}$ = 4.1, 4′-H); * assignments interchangeable.

19: ^{1}H NMR: δ = 0.83 (d, J = 6.9, 4-H_3), 1.40 and 1.43 [2 s, 2′-$(CH_3)_2$], 1.74–1.87 (m, 3-H, superimposed by signals of **17**), 2.46 (t, $J_{OH,1}$ = 6.4, 1-OH), 3.43–4.18 (m, 6H, superimposed by signals of **17**), 4.15 (dd, J_a = 8.1, J_b = 5.9, 1 H).

(1R,2R)-3-[(tert-Butyldimethylsilyl)oxy]-1-[(4R)-2,2-dimethyl-1,3-dioxolan-4-yl]-2-methyl-1-propanol (**18**): **17** (27 mg, 0.19 mmol), tBuMe$_2$SiCl (32 mg, 0.21 mmol, 1.1 equiv.), 4-dimethylaminopyridine (1 mg, 0.008 mmol, 0.04 equiv.), NEt_3 (0.04 ml, 0.31 mmol, 1.6 equiv.), and CH_2Cl_2 (1.30 ml) were stirred at room temp. After 24 h, NEt_3 was added (0.50 ml, 3.9 mmol, 14 equiv.), and stirring was continued for 5 h. Removal of the solvent and flash chromatography [petroleum ether/ether (10:1)] gave **18** (27 mg, 46%). – ^{1}H NMR: δ = 0.07 [s, Si$(CH_3)_2$], 0.90 [s, C$(CH_3)_3$], 0.98 (d, J = 7.0, 2-CH_3), 1.38 and 1.44 [2 s, 2′-$(CH_3)_2$], 1.80 (m_c, 2-H), 3.11 (d, $J_{OH,1}$ = 5.7, OH), 3.45 (br. ddd, all $J \approx$ 5, 1-H), AB signal (δ_A = 3.67, δ_B = 3.74, $J_{A,B}$ = 10.0, additionally split by $J_{A,2}$ = 6.0, $J_{B,2}$ = 4.5, 3-H_2), 3.85 (dd, $J_{gem} = J_{5'\text{-}H^1,4'}$ = 7.6, 5′-H^1), 4.02 (dd, J_{gem} = 8.0, $J_{5'\text{-}H^2,4'}$ = 6.6, 5′-H^2), 4.25 (ddd, $J_{4',5'\text{-}H^1} = J_{4',5'\text{-}H^2}$ = 6.9, $J_{4',1}$ = 4.4, 4′-H).

$C_{15}H_{32}O_4Si$ (304.5) Calcd. C 59.17 H 10.59
Found C 59.33 H 10.65

(2R,3S)-1-[(tert-Butyldimethylsilyl)oxy]-3-[(4S)-2,2-dimethyl-1,3-dioxolan-4-yl]-2-butanol (**20**) was obtained – along with **18** – when a mixture of **17** and **19** (69.5 mg, 0.37 mmol) was silylated as described for the preparation of **18** from **17** (yield of the mixture: 91.4 mg, 82%). Pure **20** (25.6 mg, 23%) could be separated from this mixture by flash chromatography. – ^{1}H NMR: δ = 0.08 [s, Si$(CH_3)_2$], 0.87 (d, J = 7.0, 4-H_3), 0.91 [s, C$(CH_3)_3$], 1.36 and 1.41 [2 s, 2′-$(CH_3)_2$], 1.94 (qdd, $J_{3,4} = J_{3,2} = J_{3,4'}$ = 7.0, 3-H), 3.03 (d, J = 2.8, OH), 3.54–3.74 (m, 1-H_2, 2-H, 5′-H^1), 4.05 (dd, J_{gem} = 8.0, $J_{5'\text{-}H^2,4'}$ = 6.1, 5′-H^2), 4.17 (ddd, $J_{4',5'\text{-}H^1} = J_{4',3}$ = 7.7, $J_{4',5'\text{-}H^2}$ = 6.2, 4′-H).

(2Z)-2-[(4R)-2,2-Dimethyl-1,3-dioxolan-4-yl]-1-{[3-(trimethylsilyl)-2-propyn-1-yl]oxy}-2-butene (**28**): (*Z*)-**9** (0.115 g, 0.668 mmol), propargyl bromide (0.24 g, 2.0 mmol, 3.0 equiv.), benzyltriethylammonium chloride (0.100 g, 0.370 mmol, 0.55 equiv.), and 50% KOH (3 ml) were agitated violently for 110 min. Extractive workup (ether/H_2O) and filtration through a pad of silica gel [petroleum ether/ether (2:1)] gave crude *(2Z)-2-[(4R)-2,2-dimethyl-1,3-dioxolan-4-yl]-1-[(2-propyn-1-yl)oxy]-2-butene*, which was dissolved in THF (4 ml). nBuLi (1.50 M in hexane, 0.400 ml, 0.600 mmol, ⩾0.90 equiv.) was added at −78 °C, followed, 4 h later, by Me_3SiCl (0.12 ml, 0.95 mmol, ⩾1.4 equiv.). After 2 h at room temp., conversion was incomplete according to TLC, so the mixture was cooled to −78 °C again, and more nBuLi and Me_3SiCl were added (half as much as before). The reaction was warmed to room temp. slowly, quenched with NEt_3 (0.75 ml) and satd. aqueous NH_4Cl, and extracted with ether. Flash chromatography [petroleum ether/ether (10:1)] led to **28** (0.110 g, 58% over 2 steps) and a small amount of *(2Z)-2-[(4R)-2,2-dimethyl-1,3-dioxolan-4-yl]-1-[(2-propyn-1-yl)oxy]-2-butene*.

(2Z)-2-[(4R)-2,2-Dimethyl-1,3-dioxolan-4-yl]-1-[(2-propyn-1-yl)oxy]-2-butene: $[\alpha]_D^{20}$ = −49 (*c* = 1.0, CH_2Cl_2). – ^{1}H NMR: δ = 1.42 and 1.46 [2 s, 2′-$(CH_3)_2$], 1.75 (d, $J_{4,3}$ = 7.0, 4-H_3), 2.43 (t, $^4J_{3'',1''}$ = 2.4, 3″-H), 3.77 (dd, $J_{gem} = J_{5'\text{-}H^1,4'}$ = 8.5, 5′-H^1), br. AB signal (δ_A = 3.96, δ_B = 4.19, $J_{A,B}$ = 11.3, 1-H_2), 4.05 (dd, J_{gem} = 8.2, $J_{5'\text{-}H^2,4'}$ = 6.3, 5′-H^2), 4.13 (m_c, 1″-H_2), 4.98 (dd, $J_{4',5'\text{-}H^1}$ = 8.5, $J_{4',5'\text{-}H^2}$ = 6.6, 4′-H), 5.85 (br. qd, $J_{3,4}$ = 7.0, $J_{allylic}$ = 0.8, 3-H).

$C_{12}H_{18}O_3$ (210.3) Calcd. C 68.55 H 8.63
Found C 68.31 H 8.79

28: $[\alpha]_D^{19}$ = −44.1 (*c* = 3.9, CH_2Cl_2). – ^{1}H NMR: δ = 0.18 [s, Si$(CH_3)_3$], 1.42 and 1.46 [2 s, 2′-$(CH_3)_2$], 1.75 (d, $J_{4,3}$ = 7.1, 4-H_3), 3.79 (dd, $J_{gem} = J_{5'\text{-}H^1,4'}$ = 8.5, 5′-H^1), br. AB signal (δ_A = 3.94, δ_B = 4.18, $J_{A,B}$ = 11.4, 1-H_2), AB signal (δ_A = 4.11, δ_B = 4.14, $J_{A,B}$ = 15.9, 1″-H_2), 4.04 (dd, J_{gem} = 8.2, $J_{5'\text{-}H^2,4'}$ = 6.3, 5′-H^2), 4.97 (dd, $J_{4',5'\text{-}H^1}$ = 7.8, $J_{4',5'\text{-}H^2}$ = 6.2, 4′-H), 5.84 (br. qd, $J_{3,4}$ = 7.0, $J_{allylic}$ = 1.0, 3-H).

$C_{15}H_{26}O_3Si$ (282.5) Calcd. C 63.79 H 9.28
Found C 63.57 H 9.36

(3S,4R)-5-[(4R)-2,2-Dimethyl-1,3-dioxolan-4-yl]-4-methyl-1-(trimethylsilyl)-5-hexen-1-yn-3-ol (**29**): At −78 °C, nBuLi (1.50 M in hexane; 0.300 ml, 0.450 mmol, 1.3 equiv.) was added to **28** (0.100 g, 0.354 mmol) in THF (3 ml). The reaction was kept at −78 °C for 5.5 h and at −20 °C for 20 h. Extractive workup (ether/H_2O) and flash chromatography [petroleum ether/ether (5:1)] gave a major fraction (0.069 g) consisting of a 89.4:5.5:5.1 mixture of **28**, minor isomer **A** and minor isomer **B** (according to integrals of the olefinic signals in the 400-MHz ^{1}H-NMR spectrum), plus a minor fraction (0.004 g) with a 60.7:8.7:6.8:23.8 mixture of **29**, minor isomer **A**, minor isomer **B**, and minor isomer **C**. Total yield: 0.073 g (74%) of **29**, minor isomer **A**, minor isomer **B**, and minor isomer **C** in a 87.9:5.6:5.2:1.3 ratio. – The major isomer crystallized from petroleum ether at −20 °C; it was X-rayed and subsequently identified by its 400-MHz ^{1}H-NMR spectrum and by GLC. – ^{1}H NMR: δ = 0.17 [s, Si$(CH_3)_3$], 1.22 (d, $J_{4\text{-}Me,4}$ = 7.0, 4-CH_3), 1.40 and 1.46 [2 s, 2′-$(CH_3)_2$], 2.19 (d, $J_{OH,3}$ = 5.8, OH), 2.42 (dq, $J_{4,3} = J_{4,4\text{-}Me}$ = 6.4, 4-H), 3.76 (dd, $J_{gem} = J_{5'\text{-}H^1,4'}$ = 7.8, 5′-H^1), 4.15 (dd, $J_{gem} = J_{5'\text{-}H^2,4'} \approx$ 7.5, 5′-H^2), 4.35 (dd, $J_{3,4} = J_{3,OH}$ = 5.7, 3-H), 4.60 (dd, both J_{vic} = 6.9, 4′-H), 5.18 (s, 6-H^1), 5.37 (s, 6-H^2). – ^{13}C NMR: δ = −0.20 [Si$(CH_3)_3$], 16.53 (4-CH_3), 25.63 and 26.44 [2′-$(CH_3)_2$], 42.11 (C-4), 66.36 (C-3), 69.08 (C-5′), 78.57 (C-4′), 90.59 (C-1*), 105.36 (C-2*), 109.39 (C-2′), 113.06 (C-6), 147.81 (C-5); * assignments interchangeable. – Olefinic resonances of the minor isomers: **A**: δ = 5.30 and 5.35; **B**: δ = 5.16 and 5.26; **C**: δ = 5.11 and 5.36 (superimposed by signals of **29**). – MS: m/z($M^+ - CH_3$) = 267.1440 (calcd. for $C_{15}H_{26}O_3Si - CH_3$: 267.1417; m/z of the corresponding ^{13}C satellite 268.1444 (calcd. for $^{12}C_{13}{}^{13}C_1H_{23}O_3Si$: 268.1450).

3-(Methoxymethoxy)-5-methyl-2-{[3-(trimethylsilyl)-2-propyn-1-yl]oxymethyl}-1-hexene (**34**) (0.394 g, 78% for the 2 steps) was prepared from **42** (0.318 g, 1.69 mmol) as described for the conversion of (*Z*)-**9** → **28**. – ^{1}H NMR: δ = 0.18 [s, Si$(CH_3)_3$], 0.93 and 0.94 (2 d, J = 6.6, 6-H_3, 5-CH_3), 1.30–1.40 and 1.53–1.63 (2 m, 4-H_2), 1.77 (br. ddsept, all $J \approx$ 6.8, 5-H), 3.38 (s, OCH_3), AB signal (δ_A = 4.02, δ_B = 4.08, $J_{A,B}$ = 13.2, 1′-H_2), 4.156 and 4.161 (AB signal whose less intense peaks do not emerge from the spectral noise; 1″-H_2), 4.16–4.22 (m, 3-H), 4.49 and 4.65 (2 d, J = 6.8, OCH_2O), 5.19 (br. s, 1-H^1), 5.25 (br. d, J_{gem} = 1.5, 1-H^2).

$C_{16}H_{30}O_3Si$ (298.5) Calcd. C 64.38 H 10.13
Found C 64.00 H 9.88

rel-(3S,6R)-6-(Methoxymethoxy)-8-methyl-5-methylene-1-(trimethylsilyl)-1-nonyn-3-ol (*syn*-**35**) *and rel-(3S,6S)-6-(Methoxymethoxy)-8-methyl-5-methylene-1-(trimethylsilyl)-1-nonyn-3-ol* (*anti*-**36**): The [2,3] Wittig rearrangement of **34** (0.391 g, 1.31 mmol) was performed as described for the reaction of **28** → **29**. We isolated 0.150 g of pure **35**, 0.120 g of pure **36**, and a **35**/**36** mixture (0.019 g); total yield 74%.

35: ^{1}H NMR: δ = 0.15 [s, Si(CH$_3$)$_3$], 0.92 and 0.94 (2 d, J = 6.3, 8-CH$_3$, 9-H$_3$), 1.36–1.72 (m, 7-H$_2$, 8-H), AB signal (δ_A = 2.36, δ_B = 2.60, $J_{A,B}$ = 14.6, in addition split by $J_{A,3}$ = 4.4, $J_{A,=CH}$ = 1.0, $J_{B,3}$ = 6.0, 4-H$_2$), 3.39 (s, OCH$_3$), 3.87 (d, $J_{OH,3}$ = 8.7, OH), 4.17 (dd, $J_{6,7\text{-}H^1}$ = 7.9, $J_{6,7\text{-}H^2}$ = 6.2, 6-H), 4.50 and 4.77 (2 d, J = 6.9, OCH$_2$O), superimposes in part 4.48–4.57 (m, 3-H), 5.11 (br. s, =CH^1H^2), 5.18 (br. d, J_{gem} = 1.7, =CH$^1H^2$).

C$_{16}$H$_{30}$O$_3$Si (298.5) Calcd. C 64.38 H 10.13
Found C 64.48 H 10.10

36: ^{1}H NMR: δ = 0.17 [s, Si(CH$_3$)$_3$], 0.92 and 0.93 (2 d, J = 6.6, 8-CH$_3$, 9-H$_3$), 1.30–1.75 (m, 7-H$_2$, 8-H), AB signal (δ_A = 2.42, δ_B = 2.51, $J_{A,B}$ = 14.5, in addition split by $J_{A,3} \approx 5$, $J_{A,=CH} \approx 1$, $J_{B,3} \approx 7$, $J_{B,=CH} \approx 1$, 4-H$_2$), 3.07 (d, $J_{OH,3}$ = 4.6, OH), 3.38 (s, OCH$_3$), 4.10 ($J_{6,7\text{-}H^1}$ = 8.3, $J_{6,7\text{-}H^2}$ = 5.7, 6-H), 4.51 and 4.68 (2 d, J = 6.9, OCH$_2$O), superimposes 4.51 (!) (m$_c$, 3-H), 5.13 (br. d, J = 1.2, =CH^1H^2), 5.16 (br. s, =CH$^1H^2$).

C$_{16}$H$_{30}$O$_3$Si (298.5) Calcd. C 64.38 H 10.13
Found C 64.85 H 10.13

tert-Butyl [3-(Methoxymethoxy)-5-methyl-2-methylenehexyloxy]acetate (**37**): **42** (0.533 g, 2.83 mmol) in DMSO (5 ml) and sodium chloroacetate (0.466 g, 4.00 mmol) were added to sodium methylsulfinylmethide (0.5 M in DMSO; 10 ml). After 1 h, the mixture was diluted with H$_2$O (40 ml), washed with CH$_2$Cl$_2$ (3 × 40 ml), acidified with satd. aqueous citric acid, extracted with CH$_2$Cl$_2$ (4 × 35 ml), and dried (MgSO$_4$). The solution was concentrated to a volume of 10 ml. It was stirred with *t*BuOH (0.26 g, 3.5 mmol, ≥1.2 equiv.), dicyclohexylcarbodiimide (0.72 g, 3.5 mmol, ≥1.2 equiv.), and 4-(dimethylamino)pyridine (0.064 g, 0.53 mmol, ≥0.19 equiv.) for 30 min. Extraction with satd. aqueous NH$_4$Cl/CH$_2$Cl$_2$ followed by flash chromatography [petroleum ether/ether (8:1 → 6.5:1)] gave **37** (0.132 g, 15%). – ^{1}H NMR: δ = 0.91 and 0.94 (2 d, J = 6.6, 6″-H$_3$, 5″-CH$_3$), 1.48 [s, C(CH$_3$)$_3$], superimposes 1.3–1.8 (4″-H$_2$, 5″-H), 3.38 (s, OCH$_3$), sharp AB signal (δ_A = 3.96, δ_B = 3.98, $J_{A,B}$ = 16.2, 1′-H$_2$), br. AB signal (δ_A = 4.03, δ_B = 4.10, $J_{A,B}$ = 13.3, 1″-H$_2$), 4.49 and 4.65 (2 d, J = 6.7 and 6.8, resp., OCH$_2$O), 5.19 (br. s, =CH^1H^2), 5.29 (dt, J_{gem} = ^4J = 1.6, =CH$^1H^2$).

C$_{16}$H$_{30}$O$_5$ (302.4) Calcd. C 63.55 H 10.00
Found C 63.45 H 9.72

tert-Butyl [rel-(2S,5R)-2-Hydroxy-5-(methoxymethoxy)-7-methyl-4-methylene]octanoate (*syn*-**38**) *and tert-Butyl [rel-(2S,5S)-2-Hydroxy-5-(methoxymethoxy)-7-methyl-4-methylene]octanoate* (*anti*-**39**): At –78°C, **37** (0.222 g, 0.735 mmol) in THF (4 ml) was added during 15 min to a solution of LDA prepared from diisopropylamine (0.16 ml, 1.1 mmol, 1.6 equiv.) and *n*BuLi (1.50 M in hexane; 0.66 ml, 0.99 mmol, 1.3 equiv.) in THF (6 ml). After 30 min *N,N,N′,N′*-tetramethylethylenediamine (0.60 ml, 4.0 mmol, 5.5 equiv.) was added. After an additonal 20 min, the reaction was allowed to warm to –20°C, where it was kept for another 2.3 h. Extractive workup with satd. aqueous NH$_4$Cl (20 ml)/ether (5 × 20 ml) and flash chromatography [petroleum ether/ether (5:2)] furnished the title compounds as a 1:1 mixture (0.183 g, 83%). – ^{1}H NMR: δ = 0.92, 0.93, 0.94, 0.94 (!) (4 d, obscuring each other in part, all $J \approx 6.5$, 2 7′-CH$_3$), 1.47 and 1.49 [2 s, 2 C(CH$_3$)$_3$], 1.30–1.80 (m, 2 6′-H$_2$, 7′-H), 2.27–2.65 (m, 2 3′-H$_2$), 3.20 (d, $J_{OH,2'}$ = 5.4, 1 OH), 3.38 and 3.39 (2 s, 2 OCH$_3$), 3.78 (d, $J_{OH,2'}$ = 8.3, 1 OH), 4.10–4.28 (m, 2 2′-H, 2 5′-H), 4.49 and 4.68 (2 d, J = 6.9, 1 OCH$_2$O), 4.52 and 4.66 (2 d, J = 7.1, 1 OCH$_2$O), 5.07–5.16 (m, 2 =CH$_2$).

C$_{16}$H$_{30}$O$_5$ (302.4) Calcd. C 63.55 H 10.00
Found C 63.76 H 9.91

Methyl [3-(Methoxymethoxy)-5-methyl-2-methylene]hexanoate (**41**): Isovaleraldehyde (4.31 g, 50.0 mmol), methyl acrylate (4.30 g, 50.0 mmol), and DABCO (1.12 g, 10.0 mmol, 0.2 equiv.) were allowed to react at room temp. for 5 d. Diethyl ether (100 ml) was added. The mixture was extracted with cold (0°C) dil. (1:3) HCl (2 × 30 ml) and satd. aqueous NaCl (2 × 30 ml). Removal of the solvent at 15 Torr gave 5.22 g (<61%) of crude *methyl [3-hydroxy-5-methyl-2-methylene]hexanoate* (**40**). 0.678 g of this material was purified by flash chromatography [petroleum ether/ether (5:1 → 3:1)] to give 0.635 g of **40** [C$_9$H$_{16}$O$_3$ (172.2); calcd. C 62.77, H 9.36; found C 62.76, H 9.43]. Crude **40** (2.18 g, 12.6 mmol), LiBr (0.224 g, 2.58 mmol, 0.2 equiv.), *p*-TsOH hydrate (0.244 g, 1.28 mmol, 0.1 equiv.), and DME (20 ml) were stirred at room temp. for 19 h, and NEt$_3$ (1 ml) was then added. Evaporation of the solvent under reduced pressure and flash chromatography [petroleum ether/ether (10:1)] furnished **41** (1.80 g, 66%). – ^{1}H NMR: δ = 0.93 and 0.98 (2 d, J = 6.7 and 6.6, resp., 5′-CH$_3$, 6′-H$_3$), 1.36–1.60 (m, 4-H$_2$), 1.76–1.90 (m, 5-H), 3.39 (s, CH$_2$OCH_3), 3.77 (s, CO$_2$CH$_3$), AB signal (δ_A = 4.54, δ_B = 4.59, $J_{A,B}$ = 6.8, OCH$_2$O), superimposes in part 4.57 (m$_c$, 3-H), 5.85 (m$_c$, =CH^1H^2), 6.29 (d, J_{gem} = 1.4, =CH$^1H^2$).

C$_{14}$H$_{20}$O$_4$ (216.3) Calcd. C 61.09 H 9.32
Found C 61.27 H 9.39

3-(Methoxymethoxy)-5-methyl-2-methylene-1-hexanol (**42**): At –78°C, DIBAH (1.0 M in hexane, 17.0 ml, 17.0 mmol, 2.0 equiv.) was added to **41** (1.80 g, 8.30 mmol) in THF (10 ml). After 1 h, the reaction was warmed to 0°C, cooled again to –78°C 20 min later, quenched with methanol (5 ml), and extracted with NaOH (1 M, 25 ml), 50% KOH (5 ml), and ether (50 ml + 30 ml). Flash chromatography (petroleum ether/ether) gave **42** (1.22 g, 87%). – ^{1}H NMR: δ = 0.93 and 0.94 (2 d, J = 6.5, 5-CH$_3$, 6-H$_3$), 1.32–1.44 (m, 4-H^1), 1.58–1.79 (m, 4-H^2, 5-H), 2.01 (br. t, $J_{OH,1} \approx 5.6$, OH), 3.38 (s, OCH$_3$), 4.07–4.27 (m, 1-H$_2$, 3-H), 4.52 and 4.69 (2 d, J_{gem} = 6.8, OCH$_2$O), 5.12 (br. s, =CH^1H^2), 5.23 (dt, J_{gem} = ^4J = 1.4, =CH$^1H^2$).

C$_{10}$H$_{20}$O$_3$ (188.3) Calcd. C 63.80 H 10.71
Found C 63.89 H 10.64

Table 1. Coordinates and equivalent isotropic temperature factors for **29** [U(cq.) = 1/3 $\sum_{ij}$ ($U_{ij} \cdot a_i^* \cdot a_j^* \cdot a_i \cdot a_j$)]

Atom	x/a	y/b	z/c	U(eq.)
Si1	0.1059(2)	0.05480(0)	0.6656(1)	0.0911(6)
O1	-0.3546(4)	-0.4146(4)	0.8561(3)	0.080(2)
O2	-0.2054(5)	-0.3539(4)	0.7345(3)	0.093(2)
O3	0.4685(4)	-0.1560(4)	1.0717(3)	0.084(1)
C1	0.2034(7)	-0.0501(6)	0.7967(5)	0.080(3)
C2	0.2679(6)	-0.1246(6)	0.8747(5)	0.068(2)
C3	0.3471(6)	-0.2215(5)	0.9719(4)	0.071(2)
C4	0.1990(6)	-0.2963(5)	1.0039(4)	0.069(2)
C5	0.0733(6)	-0.3625(6)	0.8947(5)	0.072(2)
C6	0.1200(7)	-0.4663(6)	0.8458(6)	0.119(3)
C7	0.2837(7)	-0.3959(5)	1.1024(4)	0.102(2)
C8	-0.5061(8)	-0.2849(6)	0.6836(5)	0.132(3)
C9	-0.4254(7)	-0.5244(6)	0.6706(5)	0.117(3)
C10	-0.3755(7)	-0.3936(6)	0.7355(5)	0.074(2)
C11	-0.1063(6)	-0.2986(5)	0.8470(4)	0.068(2)
C12	-0.2244(6)	-0.3223(6)	0.9247(4)	0.084(2)
C13	0.265(1)	0.087(1)	0.5952(7)	0.36(1)
C14	0.043(1)	0.2089(7)	0.7086(7)	0.288(8)
C15	-0.074(1)	-0.030(1)	0.5705(7)	0.399(8)

Crystal Data for **29**: C$_{15}$H$_{26}$SiO, M_r = 282.46, monoclinic, space group $P2_1$ (No. 4), a = 196.3(1), b = 1001.4(1), c = 1201.1(2) pm, β = 109.220(6)°, V = 904.4(2) · 10^6 pm^3, Z = 2, $D_{calcd.}$ = 1.037 gcm^{-3}, μ(Cu-K_α) = 11.5 cm^{-1}, F(000) = 308 e. – Enraf-Nonius CAD4 diffractometer, Cu-K_α radiation, graphite monochromator. 3678 measured reflections, 1812 unique reflections (R_{int} = 0.0191), 1701 observed reflections [$F_o \geq 5\sigma(F_o)$]. Solution with direct

methods[34], full-matrix least-squares refinement[35], all non-hydrogen atoms anisotropic, hydrogen atoms on calculated positions with a common isotropic temperature factor. The hydroxy hydrogen atom has not been located. Unusual high anisotropic temperature factors indicate a disorder of the $Si(CH_3)_3$ group. All calculations have been performed with a Micro-VAX II[30,36,37]. Coordinates and equivalent isotropic temperature factors for **29** are listed in Table 1.

CAS Registry Numbers

6: 92973-40-5 / (*Z*)-**7**: 124317-78-8 / (*E*)-**7**: 124317-79-9 / (*E*)-**9**: 124317-80-2 / (*Z*)-**9**: 124317-81-3 / (*E*)-**10**: 124317-82-4 / (*Z*)-**10**: 124317-83-5 / *syn*-**11**: 124317-84-6 / *anti*-**11**: 124340-01-8 / *ent-syn*-**11**: 124317-85-7 / *ent-anti*-**11**: 124317-86-8 / **12**: 79060-23-4 / **13**: 80532-36-1 / **14**: 100895-79-2 / **15**: 124317-87-9 / **16**: 80581-19-7 / **17**: 100895-80-5 / **18**: 124377-63-5 / **18** (silyl ketone): 124317-88-0 / **18** ($C=CH_2$ rather than CH—OH): 124317-89-1 / **19**: 124377-64-6 / **20**: 124317-90-4 / **28**: 124317-91-5 / **28** ($HC\equiv C$ rather than $TMS-C\equiv C$): 124317-92-6 / **29**: 124317-93-7 / **29** (minor isomer **A**): 124377-65-7 / **29** (minor isomer **B**): 124377-66-8 / **29** (minor isomer **C**): 124377-67-9 / **34**: 124317-94-8 / **35**: 124317-95-9 / **36**: 124317-96-0 / **37**: 124317-97-1 / **38**: 124317-98-2 / **39**: 124317-99-3 / **40**: 101186-03-2 / **41**: 124318-00-9 / **42**: 124318-01-0 / methyl 2-[(4′*S*)-2-(2,2-dimcthyl-1,3-dioxolan-4-yl)]-2-oxoacetate: 124318-02-1 / ethyltriphenylphosphonium bromide: 1530-32-1 / isovaleraldehyde: 590-86-3 / methyl acrylate: 96-33-3 / methyltriphenylphosphonium bromide: 1779-49-3 / propargyl bromide: 106-96-7 / sodium chloroacetate: 3926-62-3 / tributyl(iodomethyl)stannane: 66222-29-5

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