Highly Diastereo- and Enantioselective Synthesis of Protected *anti*-1,3-Diols

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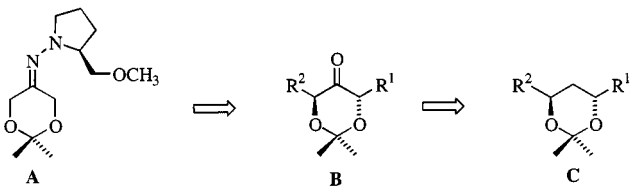
An efficient asymmetric synthesis of protected *anti*-1,3-diols **5** (*de* ≥ 98%, *ee* = 92–98%) from 2,2-dimethyl-1,3-dioxan-5-one SAMP hydrazone **1** is described. The key steps are the diastereo- and enantioselective α,α′-bisalkylation followed by reduction of the ketones **2** and a variant of the Barton–McCombie deoxygenation. The new method allows the synthesis of acetonide-protected *anti*-1,3-diols with a broad range of substituents in good overall yields (31–69%).

Introduction

The development of highly stereoselective syntheses of 1,3-polyol chains has received considerable attention in recent years due mainly to the growing interest in polyene macrolides as challenging synthetic targets with desirable pharmacological features[1]. Accordingly, much effort has been devoted to the synthesis of *syn*- and *anti*-1,3-diols as key precursors of the extended 1,3-polyol structural elements of polyene macrolides. Early work has mainly been based on the enantioselective reduction of β-ketoesters and 1,3-diketones, the diastereoselective reduction of β-hydroxyketones and the Sharpless epoxidation of allylic alcohols and subsequent epoxide opening[2]. In 1990, Evans et al. reported the synthesis of differentiated *anti*-1,3-diols by samarium-catalysed intramolecular Tishchenko reduction of β-ketoesters[3]. In 1991, Rychnovsky et al. developed a flexible access to *syn*- and *anti*-1,3-diols based on epoxide opening of 1,2:4,5-diepoxypentane[4]. The latter have also reported efficient access to *syn*-1,3-diols based on the alkylation and reductive decyanation of 4-cyano-2,2-dimethyl-1,3-dioxanes[5]. In addition, the Lewis acid-catalysed addition of dialkylzinc reagents and allylic and propargylic organometallics to 4-acetoxy-1,3-dioxanes gives *anti*-1,3-diols in high yields[6]. The efficiency of these protocols has been demonstrated in the remarkable total syntheses of several members of the polyene-polyol macrolides[7]. An elegant approach by Harada and Oku towards enantiomerically pure *anti*-1,3-diols which has been extended to *anti*-1,3-polyols, relies on the deracemization of *syn*-1,3-diols[8]. Brückner et al. introduced butyrolactones which can be transformed to *syn*-diols and -polyols and the usefulness of this approach was demonstrated in the total syntheses of *Tolypothrix* pentamethyl ethers[9]. Recently, Brückner et al. developed a β-epoxyketone building block, that can be transformed to either *syn*- or *anti*-1,3-diols depending on the epoxide opening and reduction sequence. The substitution pattern of these 1,3-diols allows a subsequent transformation after protecting-group manipulations[10].

In this paper we would like to report on the synthesis of *anti*-1,3-diols based on the highly diastereo- and enantioselective α,α′-bisalkylation of 2,2-dimethyl-1,3-dioxan-5-one SAMP-hydrazone **A,** which we first reported in 1991[11]. It has been demonstrated that these alkylations occur with diastereo- and enantioselectivities of *de, ee* ≥ 98% to afford, after cleavage of the auxiliary, 4,6-disubstituted 2,2-dimethyl-1,3-dioxan-5-ones **B** with the 4,6-substituents in *trans* relationship. We envisaged that reduction of the carbonyl group and subsequent deoxygenation of the hydroxy functionality would provide a highly stereoselective method for the synthesis of *anti*-1,3-diols **C** bearing a broad range of substituents.



Results and Discussion

As a model system for the reduction and deoxygenation sequence we chose 4-benzyloxymethyl-2,2-dimethyl-1,3-dioxan-5-one [(*S*)-**2a**], which was readily available from the dioxanone SAMP hydrazone (*S*)-**1** according to our literature procedure in gram quantities and with high enantiomeric excess (Scheme 1). Thus, metalation of (*S*)-**1** with *tert*-butyllithium, alkylation of the lithio aza-enolate with benzyloxymethyl chloride (BomCl) and removal of the auxiliary with oxalic acid[12a,b] yielded (*S*)-**2a** in 84% yield and *ee* = 94% as shown by GC analysis with a chiral stationary phase. The reduction of the carbonyl group proceeded smoothly with sodium borohydride in methanol to yield a diastereomeric mixture (*trans*:*cis* = 70:30) of the corresponding alcohol (*S*,*R*/*S*)-**3a** in 98% yield. Taking into

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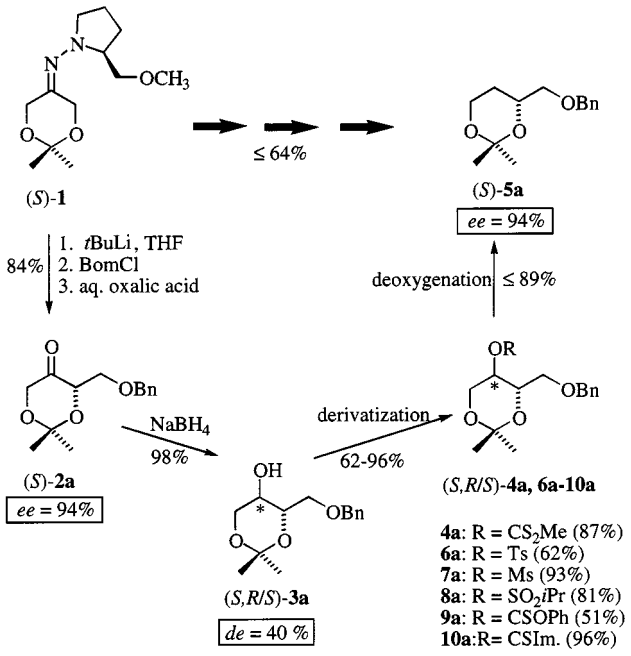
account the ease of this reaction and the removal of the newly generated stereogenic center in the final step, experiments towards higher diastereoselectivities with sterically more demanding reducing agents were not conducted. The diastereomeric alcohols (*S*,*R*/*S*)-**3a** were then converted to several derivatives as suitable substrates for hydride displacements or radical-chain deoxygenation protocols. Firstly, we explored hydride displacements since it was desirable to avoid the use of the toxic tri-*n*-butyltin hydrides commonly employed in the Barton−McCombie deoxygenation reaction[13]. Brown et al. introduced lithium triethylborohydride (superhydride®) as a powerful reducing agent capable of reducing tertiary toluenesulfonates to the corresponding alkanes in boiling THF[14]. Lithium aluminium hydride in diethyl ether also converts toluenesulfonates to alkanes[15]. The alcohol (*S*,*R*)-**3a** was converted to the corresponding toluenesulfonate (*S*,*R*)-**6a** in 62% yield by reaction with *p*-toluenesulfonyl chloride and triethylamine in dichloromethane, but subsequent experiments revealed that the hydride displacements with superhydride® in boiling THF were unsatisfactory, yielding a mixture of the desired product (*S*)-**5a** in 25% yield and alcohol (*S*,*R*)-**3a** in 42% yield. Conversion of the diastereomeric alcohols (*S*,*R*/*S*)-**3a** to the methanesulfonate (*S*,*R*/*S*)-**7a** and to the isopropyl sulfonate (*S*,*R*/*S*)-**8a** proceeded in high yields of 93% and 81%, respectively. A higher reactivity of methyl sulfonates and isopropyl sulfonates towards carbon−oxygen bond scission is reported in the literature[16]. Unfortunately, the dioxane (*S*)-**5a** was not obtained on use of superhydride® or samarium(II) iodide[17] as reducing agents because of decomposition under the reaction conditions.

Scheme 1. Optimization of the reduction and deoxygenation sequence of (*S*)-**2a**



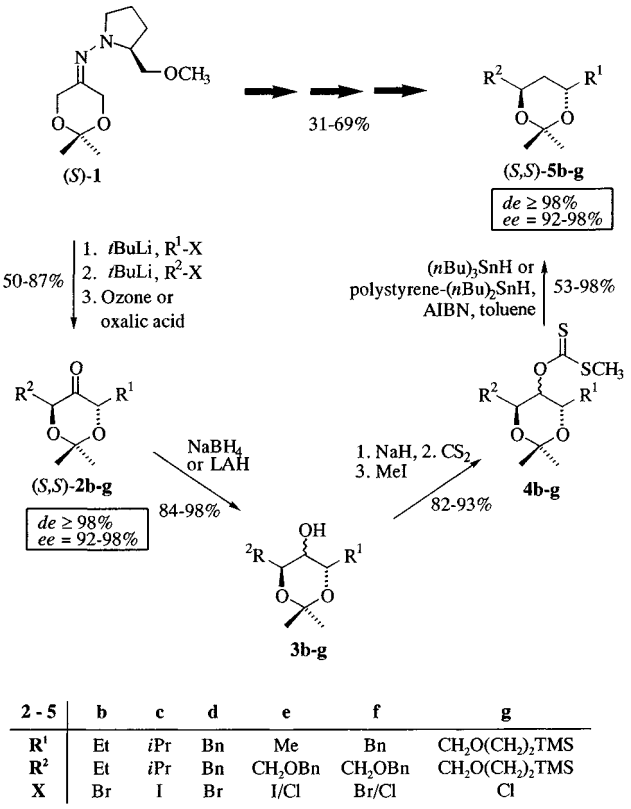
We then turned our attention to radical deoxygenation processes[13] and accordingly converted the alcohol (*S*,*R*/*S*)-**3a** into the xanthate (*S*,*R*/*S*)-**4a** in 87% yield, the phenoxythiocarbonate (*S*,*R*/*S*)-9**a** in 51% yield and the *N*,*N*′-thiocarbodiimide (*S*,*R*/*S*)-**10a** in 96% yield. The deoxygenation of (*S*,*R*/*S*)-**10a** according to Rasmussen et al.[18] with tri-*n*-butyltin hydride in refluxing toluene gave (*S*)-**5a** in modest 49% yield. The Barton−McCombie deoxygenation of the xanthate (*S*,*R*/*S*)-**4a** furnished dioxane (*S*)-**5a** consistently in 89% yield[17]. In contrast to reports which describe difficulties to remove tin by-products and recommend specific workup procedures[19], evaporation of the solvent and column chromatography effectively removed tin by-products to yield microanalytically pure (*S*)-**5a**. Fu′s novel protocol for the deoxygenation of phenoxythiocarbonates catalytic in tri-*n*-butyltin hydride[20] was attempted for the deoxygenation of both (*S*,*R*/*S*)-**4a** and (*S*,*R*/*S*)-**9a** but the reaction suffered from extended reaction times (>36 h) and incomplete conversions to yield the dioxane in 31% yield. Recently, Barton et al. reported a selective deoxygenation procedure, which relies on phosphane−boranes as reducing agents under radical conditions[21]. When employed, the deoxygenation of the xanthate (*S*,*R*/*S*)-**4a** yielded only 5% of the dioxane (*S*)-**5a** and 80% recovered starting material.

Gratifyingly, the repeated use of stoichiometric amounts of tin reagents can be avoided by using the polymer-supported organotin hydride introduced by Neumann et al., which was successfully employed in our deoxygenations[22]. After completed reactions, the polymer is removed from the reaction mixture by filtration and is recyclable. With two variants of the Barton−McCombie reaction in hand, we were able to synthesize several C_2-symmetrical and unsymmetrical acetonide-protected *anti*-1,3-diols from (*S*)-**1** in 31−69% overall yield with diastereo- and enantiomeric excesses of *de* ≥ 98 and *ee* = 92−98% (Scheme 2, Table 1).

The α,α′-bisalkylation of (*S*)-**1** with unfunctionalized and α-oxygen-containing alkyl halides yielded the crude hydrazones. Cleavage of the auxiliary with either ozone or with aqueous oxalic acid furnished the dioxanones (*S*,*S*)-**2** in overall yields of 50−87% and with excellent diastereo- and enantiomeric excesses of *de* ≥ 98 and *ee* = 92−98%. Reduction to the alcohols (*S*,*R*/*S*,*S*)-**3** with either sodium borohydride or lithium aluminium hydride and subsequent reaction of the corresponding sodium alkoxides with carbon disulphide and iodomethane gave the xanthates (*S*,*R*/*S*,*S*)-**4** in 82−93% yield (two steps). The deoxygenation afforded the acetonide-protected *anti*-1,3-diols (*S*,*S*)-**5** in 75−98% yield, with the exception of (*S*,*S*)-**5b**, which could be obtained in only modest yield of 53% probably due to the volatility of the product.

In order to demonstrate the possibility for transformation into building blocks for polyol-chain construction, we employed α-oxygen-containing electrophiles, such as benzyloxymethyl chloride (BomCl), i.e. (*S*,*S*)-**5a,e** and **f**. Subsequent debenzylation by hydrogenolysis and conversion of the corresponding alcohol into the iodide allow the synthesis of *anti*-1,3-diol building blocks[23]. The α,α′-bisalkylation with benzyloxymethyl chloride failed due to the acidity of the benzylic protons which interfere the clean lithiation of the monoalkylated hydrazone. This problem was

Scheme 2. Diastereo- and enantioselective synthesis of *anti*-1,3-diols (*S,S*)-**5** by α,α′-bisalkylation of SAMP hydrazone (*S*)-**1** and subsequent deoxygenation



2 - 5	b	c	d	e	f	g
R^1	Et	*i*Pr	Bn	Me	Bn	$CH_2O(CH_2)_2TMS$
R^2	Et	*i*Pr	Bn	CH_2OBn	CH_2OBn	$CH_2O(CH_2)_2TMS$
X	Br	I	Br	I/Cl	Br/Cl	Cl

overcome by using 2-(trimethylsilyl)ethoxymethyl chloride (SemCl) as electrophile to furnish the C_2-symmetric *anti*-1,3-diol (*S,S*)-**5g**.

Analysis of the ^{1}H- and ^{13}C-NMR data of the acetonides, according to Rychnovsky's criteria[24], revealed that the reduction-deoxygenation sequence did not lead to any detectable epimerization of the stereocenters. The quaternary acetonide carbon atoms of all dioxanes (*S,S*)-**5** show ^{13}C-NMR resonances around δ = 100.5. In addition, the shift differences of the diastereotopic methyl groups in 2-position of unsymmetrically alkylated dioxanes are insignificant in both ^{1}H- and ^{13}C-NMR spectra, which also proved the 4,6-*anti*-relationship.

Conclusion

In summary, an efficient asymmetric synthesis of protected *anti*-1,3-diols starting from commercially available 2,2-dimethyl-1,3-dioxan-5-one has been developed, which could be extended to the synthesis of *anti*-1,3-polyol building blocks. The key steps are the diastereo- and enantioselective α,α′-bisalkylation of the corresponding SAMP hydrazone with subsequent Barton−McCombie deoxygenation, which can be carried out with either tri-*n*-butyltin hydride or a polymer-supported organotin hydride reagent. The chiral auxiliary as well as the organotin polymer can be recycled. Because a great variety of electrophilic α-substitutions by the SAMP hydrazone method can be carried out, the 4,6-substitution pattern is virtually unrestricted depending only on the nature of the introduced electrophiles. Furthermore, the variety of substituents could be extended by employing our recently reported *anti*-aldol addition[25] and Michael addition[26] protocols.

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Experimental Section

All solvents were dried and purified prior to use. − Column chromatography: Merck silica gel 60, 0.040−0.063 mm (230−400 mesh). − Optical rotation values: Perkin−Elmer P 241 (254 nm); solvents Merck Uvasol quality. − IR: Perkin−Elmer FT/IR 1750. − NMR: Varian VXR 300 and Gemini 300, TMS as internal standard. − MS: Finnigan MAT 212 and Finnigan SSQ 7000 (70 eV). − Microanalyses: Elementar vario EL. − THF was dried by distillation from potassium/benzophenone under Ar. Diethyl ether, benzene and toluene were dried by distillation from sodium/benzophenone under Ar. 2,2-Dimethyl-1,3-dioxan-5-one was prepared according to the procedure described by Hoppe et al.[27]. − 2,2-Dimethyl-1,3-dioxan-5-one SAMP hydrazone was prepared according to our published procedure[12a]. Benzyloxymethyl chloride was prepared according to the literature procedure[28]. Polystyrene−di-*n*-butyltin hydride was a gift from the late Prof. *W. P. Neumann*, University of Dortmund. All other reagents were purchased and used as received.

Table 1. Diastereo- and enantioselective synthesis of *anti*-1,3-diols (*S,S*)-**5** by α,α′-bisalkylation of SAMP hydrazone (*S*)-**1**

2−5	R^1	R^2	yield [%]	yield [%]	yield [%]	yield [%]	*de*[a]/*ee*[b]
			1→2	**2→3**	**3→4**	**4→5**	(*S,S*)-**2,5**
a	CH_2OBn	H	84	98	87	89	−/94
b	Et	Et	73	89	91	53	98/98
c	*i*Pr	*i*Pr	50	84	82	89	98/98
d	Bn	Bn	65	96	89	75	98/98
e	Me	CH_2OBn	62	95	90	78	98/95
f	Bn	CH_2OBn	87	94	93	91	98/98
g	$CH_2O(CH_2)_2TMS$	$CH_2O(CH_2)_2TMS$	61	95	88	98	98/92

[a] Diastereomeric excesses were determined by ^{1}H- and ^{13}C-NMR spectroscopy. − [b] Enantiomeric excesses were determined by GC on chiral stationary phases.

General Procedure (GP1) for the α,α′-Alkylation of 2,2-Dimethyl-1,3-Dioxan-5-one SAMP Hydrazone [(*S*)-**1**]: 3.0 g (12.4 mmol, 1.0 equiv.) of (*S*)-**1** was dissolved in 50 ml of dry THF and cooled to −78°C under Ar. 8.5 ml of *t*BuLi (1.6 N in pentane, 13.6 mmol, 1.1 equiv.) was added. After stirring for 2 h at −78°C, the solution was cooled to −105°C and the electrophile (1.1 equiv.) was added dropwise. The solution was stirred at this temperature for 3 h and then allowed to reach room temperature overnight. 5 ml of aqueous pH7 buffer solution and 200 ml of Et_2O were added. The organic phase was washed with water and brine, dried with $MgSO_4$ and the solvent was removed under reduced pressure. The crude monoalkylated hydrazone thus obtained was again subjected to this procedure to yield the crude α,α′-alkylated 2,2-dimethyl-1,3-dioxan-5-one SAMP hydrazone.

General Procedures for the Cleavage of the Auxiliary (GP2 and GP3). − GP2: Ozonolytic Cleavage (**2b−e**, **g**): The crude product hydrazone was dissolved in CH_2Cl_2 (50 ml) and cooled to −78°C under Ar. Ozone was bubbled through the solution for 30 min until TLC indicated complete conversion of the starting material. The solution was purged with Ar and allowed to reach room temperature. Purification by column chromatography as indicated below afforded the ketones (*S*,*S*)-**2**.

GP3: Hydrolysis, Mediated by Oxalic Acid[12b] (**2a**,**f**): The crude alkylated hydrazone dissolved in Et_2O (2 ml/mmol) was vigorously stirred at room temperature with a sat. aqueous solution of oxalic acid (1.5 ml/mmol) until TLC control indicated complete conversion of starting material. The aqueous layer was separated, extracted with ether and the combined organic extracts were washed with water, brine, dried with $MgSO_4$ and concentrated under reduced pressure to give the alkylated ketones (*S*,*S*)-**2**. The auxiliary can be recovered following our literature procedure.[12b]

(4S)-4-(Benzyloxy)methyl-2,2-dimethyl-1,3-dioxan-5-one [(*S*)-**2a**]: According to GP1, 8.88 g (36.4 mmol) of (*S*)-**1** was α-alkylated with 36.4 mmol of *t*BuLi and 6.20 g (40.0 mmol) of BomCl to yield the crude hydrazone in quantitative (13.1 g) yield. The crude monoalkylated hydrazone (9.30 g, 25.6 mmol) dissolved in ether (60 ml) was then cleaved according to GP3 with a sat. aqueous solution of oxalic acid (40 ml) for 3 h (TLC control). The residue was taken up again in hexane (250 ml) the formed foamy residue was removed by filtration, the solvent was evaporated to give (S)-**2a** as a colourless oil. − Yield: 5.54 g; 84%. − $[\alpha]_D^{30} = -158.7$ (c = 0 1.0, $CHCl_3$). − Ref.[12a]: $[\alpha]_D^{25} = -92$ (neat). − The spectroscopic data were in accordance with previously published data[12a].

(4S,6S)-4,6-Diethyl-2,2-dimethyl-1,3-dioxan-5-one [(*S*,*S*)-**2b**]: According to GP1 using ethyl bromide (1.47 g, 13.6 mmol, 1.1 equiv.) as electrophile and subsequent cleavage following GP2 (*S*,*S*)-**2b** was obtained as a colourless oil. − Yield: 1.68 g; 73%. − $[\alpha]_D^{23} = -315.2$ (c = 0.9, $CHCl_3$). − Ref.[11]: $[\alpha]_D^{23} = -297.1$ (neat). − The spectroscopic data were in accordance with previously published data[11].

(4S,6S)-4,6-Diisopropyl-2,2-dimethyl-1,3-dioxan-5-one [(*S*,*S*)-**2c**]: According to GP1 using isopropyl iodide (1.4 ml, 13.6 mmol, 1.1 equiv.) as electrophile and subsequent cleavage following GP2 (*S*,*S*)-**2c** was obtained as a colourless oil. − Yield: 1.33 g; 50%. − $[\alpha]_D^{23} = -287.5$ (c = 0.98, $CHCl_3$). − Ref.[11]: $[\alpha]_D^{23} = -265.6$ (neat). − The spectroscopic data were in accordance with previously published data[11].

(4S,6S)-4,6-Dibenzyl-2,2-dimethyl-1,3-dioxan-5-one [(*S*,*S*)-**2d**]: According to GP1 1.21 g (5.0 mmol) of (*S*)-**1** was lithiated with 5.5 mmol of *t*BuLi and treated with 1.17 g (5.5 mmol) of benzyl bromide as electrophile and after subsequent cleavage following GP2 (*S*,*S*)-**2d** was obtained as a colourless solid. − Yield: 1.0 g; 65%. − M.p. 54°C. − $[\alpha]_D^{23} = -218.9$ (c = 0.95, $CHCl_3$). − The spectroscopic data were in accordance with previously published data[11].

(4*S*,6*S*)-*4-(Benzyloxy)methyl-2,2,6-trimethyl-1,3-dioxan-5-one* [(*S*,*S*)-**2e**]: According to GP1, 2.42 g (10.0 mmol) of (*S*)-**1** was lithiated with 11.0 mmol of *t*BuLi and treated with iodomethane (1.57 ml, 11.0 mmol, 1.1 equiv.). After workup, the crude hydrazone was lithiated with 11.0 mmol of *t*BuLi and treated with BomCl (1.69 g, 11.0 mmol, 1.1 equiv.) as electrophile. Subsequent cleavage following GP2 gave (*S*,*S*)-**2e** as a colourless oil. − Yield: 1.78 g; 62%. − $[\alpha]_D^{23} = -193.85°$ (neat). − The spectroscopic data were in accordance with previously published data[11].

(4S,6S)-4-Benzyl-6-[(benzyloxy)methyl]-2,2-dimethyl-1,3-dioxan-5-one [(*S*,*S*)-**2f**]: According to GP1, 4.86 g (20.0 mmol) of (*S*)-**1** was lithiated with 22.0 mmol of *t*BuLi and treated with 4.1 g (20.0 mmol) of benzyl bromide. After workup, the crude hydrazone was lithiated with 22 mmol of *t*BuLi and treated with 3.70 g (24.0 mmol) of BomCl to yield the crude α,α′-alkylated hydrazone, which was dissolved in 100 ml of ether and was vigorously stirred at room temperature with a sat. aqueous solution of oxalic acid (54 ml) for 12 h (TLC control). The aqueous layer was separated, extracted with ether and the organic extracts were combined, washed with water and brine, and dried with $MgSO_4$, and concentrated under reduced pressure to give (*S*,*S*)-**2f** as a brown oil. Column chromatography (SiO_2, pentane/Et_2O: 10:1) provided pure (*S*,*S*)-**2f** as a colourless oil. − Yield: 5.9 g; 87%. − $[\alpha]_D^{25} = -167.8$ (c = 2.9, $CHCl_3$). − IR (film): $\tilde{\nu}$ = 3088 cm^{-1} (m), 3063 (m), 3030 (m), 2987 (m), 2936 (m), 2868 (m), 1746 (vs), 1497 (s), 1454 (m), 1376 (m), 1225 (m), 1172 (m), 1101 (vs), 1028 (m), 744 (s) 699 (m). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.35 (s, 3 H, CH_3), 1.43 (s, 3 H, CH_3), 2.76 (dd, J = 14.8 Hz, J = 9.0 Hz, 1 H, CHC*H*HPh), 3.22 (dd, J = 14.8 Hz, J = 3.4 Hz, 1 H, CHCH*H*Ph), 3.76 (dd, J = 11.0 Hz, J = 6.0 Hz, 1 H, CHC*H*HOBn), 3.85 (dd, J = 11.0 Hz, J = 3.0 Hz, 1 H, CHCH*H*OBn), 4.39 (m, 1 H, C*H*CH_2Ph) 4.43 (m, 1 H, C*H*CH_2OBn), 4.55 (s, 2 H, OCH_2Ph), 7.20−7.33 (m, 10 H, aromatic H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.9 (2 × CH_3), 34.4 (CH_2Ph), 68.2 (CH_2OBn), 73.6 (OCH_2Ph), 75.0 (*C*HCH_2Ph), 75.2 (*C*HCH_2OBn), 101.4 [*C*$(CH_3)_2$], 126.3, 127.7, 128.2, 128.4, 129.2, 129.3, 137.7, 137.9 (aromatic C), 208.3 (C=O). − MS (EI, 70 eV); *m/z* (%): 340 (M^+, 1), 249 ($M^+ - C_7H_7$, 6), 191 (6), 162 (21), 160 (8), 134 (19), 119 (7), 104 (43), 91 (100), 77 (8), 59 (5). − $C_{21}H_{24}O_4$ (340.42): calcd. C 74.09, H 7.11; found C 73.78, H 7.33.

(4S,6S)-2,2-Dimethyl-4,6-bis{[2-(1,1,1-trimethylsilyl)ethoxy]methyl}-1,3-dioxan-5-one [(*S*,*S*)-**2g**]: According to GP1, 970 mg (4.00 mmol) of (*S*)-**1** was lithiated with 4.4 mmol of *t*BuLi and treated with 800 mg (4.80 mmol) of 2-(trimethylsilyl)ethoxymethyl chloride (SemCl). After workup, the procedure was repeated and the crude hydrazone was oxidatively cleaved following GP2 to yield (*S*,*S*)-**2g** as a colourless oil. − Yield: 940 mg; 61%. − $[\alpha]_D^{25} = -67.5$ (c = 6.35, $CHCl_3$). − IR (film): $\tilde{\nu}$ = 2988 cm^{-1} (m), 2953 (vs), 2886, (vs), 2865 (vs), 1749 (vs), 1459 (m), 1407 (m), 1375 (vs), 1326 (m), 1249 (vs) 1221 (vs), 1197 (s), 1109 (vs), 1062 (vs), 1010 (m), 861 (vs), 839 (vs). − ^{1}H NMR: (300 MHz, $CDCl_3$): δ = 0.1 (s, 18 H, $SiCH_3$), 0.90 (t-like, J = 8.1 Hz, J = 7.7 Hz, 4 H, CH_2Si), 1.48 [s, 6 H, C(CH_3)$_2$], 3.56 (t-like, 4 H, J = 8.1 Hz, J = 7.7 Hz, CH_2OCH_2CH), 3.62 (dd, J = 11.1, J = 6.0 Hz, 2 H, OCH_2CH), 3.78 (dd, J = 11.1 Hz, J = 2.4 Hz, 2 H, OCH_2CH), 4.38 (dd, J = 5.7 Hz, J = 2.4 Hz, 2 H, C*H*CH_2O). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = −1.1 (Si*C*H_3), 17.9 (*C*H_2Si), 24.0 [C(*C*H_3)$_2$], 67.9 (CH_2O), 68.8 (CH_2O), 74.8 (*C*HCH_2O), 101.3 [*C*$(CH_3)_2$], 206.9 (CO). − MS (CI, isobutane); *m/z* (%): 391 (M^++1, 20), 365 (10),

363 (100), 335 (19), 317 (18), 305 (15), 278 (16), 277 (78), 247 (18), 245 (40), 217 (13), 187 (31), 117 (38), 101 (29), 73 (11). − $C_{18}H_{38}O_5Si_2$ (390.67): calcd. C 55.34, H 9.80; found C 54.91 H 9.51.

General Procedures for the Reduction of the Alkylated Dioxanones (*S*,*S*)-**2**

Lithium Aluminium Hydride Reduction (GP4): (*S*,*S*)-**2b**−**e** (5.00 mmol) dissolved in dry ether (10.0 ml) was added dropwise to a stirred suspension of LAH (95.0 mg, 2.50 mmol, 0.5 equiv.) in dry ether (12.5 ml) at 0°C under Ar. The reaction mixture was allowed to reach room temperature (TLC control) and was then again cooled to 0°C. Water (10 ml) was added and the reaction mixture was extracted with ether (3 × 50 ml). The combined organic layers were washed with saturated aqueous $NaHCO_3$ and brine, dried (Na_2SO_4) and concentrated under reduced pressure. Purification by column chromatography (SiO_2, petroleum ether/Et_2O 3:1) gave the corresponding alcohol (*S*,*S*/*R*,*S*)-**3**.

Sodium Borohydride Reduction of (*S*,*S*)-**3** (GP5): (*S*,*S*)-**2a, f, g** was dissolved in MeOH and cooled to −78°C. Then $NaBH_4$ (2.0 equiv.) was added, the mixture was allowed to reach room temperature and stirred for 2 h subsequently. The solvent was removed under reduced pressure and the residue was taken up in CH_2Cl_2 and treated with water. The organic phase was washed with pH-7 buffer and brine, and was dried over $MgSO_4$. The solvent was removed under reduced pressure to yield the alcohol (*S*,*S*/*R*,*S*)-**3**.

(4S,5R/S)-4-(Benzyloxy)methyl-2,2-dimethyl-1,3-dioxan-5-ol [(*S*,*R*/*S*)-**3a**]: According to GP5, 2.45 g (9.8 mmol) of ketone (*S*)-**2a** was dissolved in 100 ml of MeOH and reduced with 0.74 g (19.6 mmol) of $NaBH_4$ to yield (*S*,*R*/*S*)-**3a** (*trans*/*cis* = 70:30) as a colourless oil. An analytical sample was obtained by column chromatography (SiO_2, pentane/Et_2O 1:1). − Yield: 2.40 g; 98%. − (*S*/*R*)-**3a** (*trans*-isomer): $[\alpha]_D^{23}$ = +23.6 (*c* = 0.9, $CHCl_3$). − IR (film): $\tilde{\nu}$ = 3600−3250 cm^{-1} (br), 3064 (m), 3031 (m), 2993 (s), 2940 (m), 2923 (m), 2874 (m), 1497 (s), 1454 (s), 1382 (s), 1310 (m), 1276 (s), 1225 (s), 1200 (s), 1170 (s), 1144 (s), 1128 (s), 1101 (s), 1029 (s), 1019 (s), 976 (s), 959 (s), 948 (s), 906 (s), 849 (s), 747 (s). − ^{1}H NMR (300 MHz, C_6D_6): δ = 1.15 (s, 3 H, CH_3), 1.38 (s, 3 H, CH_3), 2.80 (br s, 1 H, OH), 3.24 (d, *J* = 10.2 Hz, 1 H, C*H*OH), 3.50−3.74 (m, 4 H, CH_2OBn, CH_2CHOH), 3.87 (m, 1 H, C*H*CH_2OBn), 4.38 (s, 2 H, OCH_2Ph), 7.06−7.31 (m, 5 H, aromatic H). − ^{13}C NMR (75 MHz, C_6D_6): δ = 18.4 (CH_3), 29.8 (CH_3), 63.9 (*C*HOH), 65.9 (CH_2OBn), 70.5 (*C*H_2CHOH), 71.7 (*C*HCH_2OBn), 73.6 (OCH_2Ph), 98.9 [*C*(CH_3)$_2$], 127.9, 128.6, 128.7, 139.0 (aromatic C). − (*S*/*S*)-**3a** (*cis*-isomer): ^{1}H NMR (300 MHz, C_6D_6): δ = 1.28 (s, 3 H, CH_3), 1.44 (s, 3 H, CH_3), 2.72 (s, 1 H, OH), 3.34−3.74 (m, 5 H, C*H*O H, CH_2OBn, CH_2CHOH), 3.92 (m, 1 H, C*H*CH_2OBn), 4.29 (d, *J* = 2.5 Hz, 2 H, OCH_2Ph), 7.06−7.31 (m, 5 H, aromatic H). − ^{13}C NMR (75 MHz, C_6D_6): δ = 19.2 (CH_3), 28.9 (CH_3), 64.6 (CH_2OBn), 66.2 (*C*HOH), 72.4 (*C*H_2CHOH), 73.1 (*C*HCH_2OBn), 73.8 (OCH_2Ph), 98.7 [*C*(CH_3)$_2$], 128.0, 128.6, 128.7, 138.5 (aromatic C). − MS (EI, 70eV); *m*/*z* (%): 252 (M^+, 4), 237 (28), 195 (10), 194 (49), 193 (12), 181 (6), 180 (8), 177 (7), 176 (50), 133 (32), 107 (25), 91 (100), 59 (85). − $C_{14}H_{20}O_4$ (252.27): calcd. C 66.66, H 7.99; found C 66.64, H 8.24.

(4S,6S)-4,6-Diethyl-2,2-dimethyl-1,3-dioxan-5-ol [(*S*,*S*)-**3b**]: According to GP4, (*S*,*S*)-**3b** was obtained as a colourless oil. Yield: 0.84 g; 89%. − $[\alpha]_D^{23}$ = +11.8 (*c* = 1.2, $CHCl_3$). − IR (film): $\tilde{\nu}$ = 3435 cm^{-1} (s), 3000−2800 (s), 1462 (s), 1438 (s), 1272 (s), 1225 (s), 1180 (s), 1159 (s), 1125 (s), 1103 (s), 1064 (s), 1041 (s), 1031 (s), 982 (s), 937 (m), 907 (s), 885 (s), 849 (s), 818 (m), 801 (m), 772 (s). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.96 (t, *J* = 7.1 Hz, 3 H, CH_2CH_3), 1.03 (t, *J* = 7.1 Hz, 3 H, CH_2CH_3), 1.33 (s, 3 H, CCH_3), 1.37 (s, 3 H, CCH_3), 1.56 (quin, *J* = 7.5 Hz, 2 H, C$H_2$$CH_3$), 1.65−1.80 (m, 2 H, C$H_2$$CH_3$), 2.13 (s, 1 H, OH), 3.35 (ddd, *J* = 8.5 Hz, *J* = 6.4 Hz, *J* = 4.8 Hz, 1 H, C*H*$CH_2$$CH_3$), 3.46 (m, 1 H, C*H*OH), 3.66 (td, *J* = 7.1 Hz, *J* = 3.4 Hz, 1 H, C*H*$CH_2$$CH_3$). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 10.1 (CH_3), 10.2 (CH_3), 22.0 (CH_2), 24.1 (C*C*H_3), 24.7 (C*C*H_3), 26.7 (CH_2), 72.5 (*C*H$CH_2$$CH_3$), 74.3 (*C*H$CH_2$$CH_3$), 76.7 (CHOH), 100.7 [*C*(CH_3)$_2$]. − MS (70 eV, EI); *m*/*z* (%): 189 (1, M^++1), 130 (48), 113 (5), 73 (13), 72 (100), 71 (10), 60 (6), 59 (98), 58 (8), 57 (90), 55 (7), 54 (8), 43 (58), 41 (16), 39 (8). − $C_{10}H_{20}O_3$ (188.27): calcd. C 63.80, H 10.71; found C 63.84, H 11.07.

(4S,6S)-4,6-Diisopropyl-2,2-dimethyl-1,3-dioxan-5-ol [(*S*,*S*)-**3c**]: According to GP4, (*S*,*S*)-**3c** was obtained as a clear colourless oil. − Yield: 0.91 g; 84%. − $[\alpha]_D^{23}$ = +29.9 (*c* = 1.0, $CHCl_3$). − IR ($CHCl_3$): $\tilde{\nu}$ = 3457 cm^{-1} (s), 3040−2800 (s), 1471 (s), 1379 (s) 1307 (m), 1276 (m), 1227 (s) 1189 (s), 1171 (s), 1152 (s), 1123 (s), 1090 (s), 1048 (s), 1008 (s), 965 (m), 944 (w), 925 (w), 901 (s), 873 (m), 857 (m), 802 (w), 758 (s). − ^{1}H NMR (300 MHz, C_6D_6): δ = 0.90 (d, *J* = 6.7 Hz, 3 H, CHCH_3), 1.01 (d, *J* = 6.7 Hz, 3 H, CHCH_3), 1.02 (d, *J* = 6.7 Hz, 3 H, CHCH_3), 1.04 (d, *J* = 6.4 Hz, 3 H, CHCH_3), 1.27 (s, 3 H, CCH_3), 1.33 (s, 3 H, CCH_3), 1.83 [sept, *J* = 6.7 Hz, 1 H, C*H*(CH_3)$_2$], 1.86 (s, br, 1 H, OH), 2.00 [sept, *J* = 6.7 Hz, *J* = 3.7 Hz, 1 H, C*H*(CH_3)$_2$], 3.10−3.20 [m, 2 H, C*H*CH(CH_3)$_2$], 3.60−3.69 (m, 1 H, C*H*OH). − ^{13}C NMR (75 MHz, C_6D_6): δ = 18.2 (CH*C*H_3), 18.4 (CH*C*H_3), 18.7 (CH*C*H_3), 19.9 (CH*C*H_3), 23.7(C*C*H_3), 24.9 (C*C*H_3), 27.4 [*C*H(CH_3)$_2$], 31.6 [*C*H(CH_3)$_2$], 71.8 [*C*HCH(CH_3)$_2$], 77.5 [CH*C*H(CH_3)$_2$], 80.6 (CHOH), 100.7 [(*C*(CH_3)$_2$]. − MS (70 eV, EI); *m*/*z* (%): 201 (2, M^+ − CH_3), 144 (12), 87 (7), 86 (95), 85 (6), 72 (5), 71 (100), 69 (6), 68 (32), 59 (60), 58 (5), 57 (7), 55 (7), 43 (14), 43 (20), 41 (19), 39 (7). − $C_{12}H_{24}O_3$ (216.3): calcd. C 66.64, H 11.18; found C 66.40, H 11.39.

(4S,6S)-4,6-Dibenzyl-2,2-dimethyl-1,3-dioxan-5-ol [(*S*,*S*)-**3d**]: According to GP4, (*S*,*S*)-**3d** was obtained as a colourless solid. − Yield: 1.36 g; 96%. − $[\alpha]_D^{23}$ = +9.0 (*c* = 1.0, $CHCl_3$). − M.p. 76°C. − IR (KBr): $\tilde{\nu}$ = 3340 cm^{-1} (br), 3100−3020 (m), 3000−2800 (s), 1605 (m), 1498 (s), 1452 (s), 2419 (m), 1380 (s), 1360 (m), 1280 (m), 1255 (m), 1225 (s), 1208 (s), 1160 (m), 1128 (s), 1100 (m), 1078 (s), 1068 (s), 1020 (s), 940 (m), 918 (m), 904 (m), 824 (s), 760 (m), 745 (m). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.24 (s, 3 H, CH_3), 1.29 (s, 3 H, CH_3), 1.74 (d, *J* = 7.7 Hz, 1 H, OH), 2.85 (dd, *J* = 14 Hz, *J* = 5.5 Hz, 1 H, C*H*HPh), 2.86 (d, *J* = 7.1 Hz, 2 H, CH_2Ph), 2.90 (dd, *J* = 14 Hz, *J* = 5.5 Hz, 1 H, CH*H*Ph), 3.55 (m, 1 H, C*H*OH), 3.76 (td, *J* = 7.7 Hz, *J* = 5.7 Hz, 1 H, CHOBn), 4.06 (td, *J* = 7.1 Hz, *J* = 3.4 Hz, 1 H, CHOBn), 7.16−7.31 (m, 10 H, aromatic H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.1 (CH_3), 24.6 (CH_3), 35.4 (*C*H_2Bn), 39.8 (*C*H_2Bn), 71.7 (*C*HOH), 73.5 (*C*HCH_2OBn), 76.0 (*C*HCH_2OBn), 101.0 [*C*(CH_3)$_2$], 126.2, 126.3, 128.2, 128.3, 129.1, 129.2, 138.2, 138.4 (aromatic C). − $C_{20}H_{24}O_3$ (312.41): calcd. C 76.89, H 7.74; found C 76.75, H 7.82.

(4S,5R/S,6S)-4-Benzyloxymethyl-2,2,6-trimethyl-1,3-dioxan-5-ol [(*S*,*R*/*S*,*S*)-**3e**]: According to GP4, 1.50 g (5.70 mmol) of (*S*,*S*)-**2e** was reduced to yield (*S*,*R*/*S*,*S*)-**3e** (*de* = 13%) after column chromatography (SiO_2, pentane/Et_2O 1:1) as a colourless oil. − Yield: 1.44 g; 95%. Employing our published procedure,[30] 266 mg (1.00 mmol) of (*S*,*S*)-**2e** was reduced with *L*-selectride® in toluene at −78°C to yield 190 mg (68%) of (4*S*,5*R*,6*S*)-**3e** after column chromatography (SiO_2, Et_2O/pentane 1:1) as a colourless oil. − (4*S*,5*R*,6*S*)-**3e**: $[\alpha]_D^{25}$ = +15.3 (*c* = 1.5, $CHCl_3$). − IR (film): $\tilde{\nu}$ = 3440 cm^{-1} (br), 3100−3020 (w), 3000−2780 (s), 1452 (m), 1380 (s), 1225 (s) 1180 (s), 1150 (m), 1120 (s), 1100 (s), 1070 (s), 1045 (s),

1028 (m), 995 (s), 950 (m), 822 (m), 735 (m). − ^{1}H NMR: (300 MHz, $CDCl_3$): δ = 1.18 (d, *J* = 6.7 Hz, 3 H, CHC*H*$_3$), 1.34 (s, 3 H, CH_3), 1.38 (s, 3 H, CH_3), 2.40 (d, *J* = 7.1 Hz,1 H, O*H*), 3.56−3.74 (m, 4 H, C*H*O H, C*H*C*H*$_2$OBn), 3.99 (qd, 1 H, *J* = 6.7 Hz, *J* = 3.7 Hz, C*H*CH$_3$), 4.58 (s, 2 H, OC*H*$_2$Ph), 7.31 (s, 5 H, aromatic H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.5 (CH*C*H$_3$), 24.1 (CH_3), 24.6 (CH_3), 66.9 (*C*HOH), 70.9 (CH_2OBn), 71.8 (*C*HCH$_3$), 73.4 (O*C*H$_2$Ph), 73.8 (*C*HCH$_2$OBn), 100.8 [*C*(CH$_3$)$_2$], 127.6, 127.7, 128.3, 137.9 (aromatic C). − MS (EI, 70 eV); *m/z* (%): 266 (M^+, 1), 251 (7), 147 (5), 107 (6), 101 (6), 91 (100), 65 (7), 59 (42), 45 (6). − $C_{15}H_{22}O_4$ (266.34): calcd. C 67.64, H 8.33; found C 67.65, H 8.29.

(4S,5R/S,6S)-4-Benzyl-6-[(benzyloxy)methyl]-2,2-dimethyl-1,3-dioxan-5-ol [(*S,R/S,S*)-**3f**]: Following GP5, 490 mg (1.43 mmol) of (*S,S*)-**2f** was reduced with 106 mg (2.80 mmol) of $NaBH_4$ to yield the diastereomeric mixture (*S,R/S,S*)-**3f** (d.r. = 72:28) as a colourless oil. An analytical sample was obtained by column chromatography (SiO_2, pentane/Et_2O 1:1). − Yield: 480 mg; 94%. − IR ($CHCl_3$): $\tilde{\nu}$ = 3421 cm^{-1} (m), 3086 (m), 3062 (m), 3028 (m), 2987 (m), 2934 (m), 2915 (s), 2837 (m), 1604 (m), 1496 (s), 1454 (vs), 1380 (vs), 1226 (vs), 1233 (vs), 1169 (vs), 1102 (s), 1083 (vs), 1028 (vs), 910 (m), 752 (s). − ^{1}H NMR (300 MHz, $CDCl_3$) (*S,R,S*)-**3f** : δ = 1.26 (s, 3 H, CH_3), 1.41 (s, 3 H, CH_3), 2.09 (d, *J* = 8.2 Hz, 1 H, O*H*), 2.85 (dt, *J* = 7.0 Hz, *J* = 2.5 Hz, 2 H, CHC*H*$_2$Ph), 3.54−3.80 (m, 4 H, C*H*CH$_2$Ph, CHC*H*$_2$OBn, C*H*OH), 4.05 (m, 1 H, C*H*CH$_2$OBn), 4.56 (s, 2 H, OC*H*$_2$Ph), 7.26−7.36 (m, 10 H, aromatic H). − ^{13}C NMR (75 MHz, $CDCl_3$) (*S,R,S*)-**3f**: δ = 24.1 (CH_3), 24.5 (CH_3), 35.2 (*C*H$_2$Ph), 70.9 (CH_2OBn), 71.2 (*C*HOH), 71.8 (*C*HCH$_2$Ph), 73.3 (O*C*H$_2$Ph), 74.1 (*C*HCH$_2$OBn), 101.2 [*C*(CH$_3$)$_2$], 126.2, 127.7, 128.2, 128.4, 129.2, 129.3, 137.9, 138.4 (aromatic C). − MS (CI, isobutane); *m/z* (%): 343 (M^++1, 100), 285 (71), 267 (16), 249 (17), 193 (6), 177 (3). − $C_{21}H_{26}O_4$ (342.43): calcd. C 73.66, H 7.65; found C 73.94, H 7.86.

(4S,6S)-2,2-Dimethyl-4,6-bis{[2-(1,1,1-trimethylsilyl)ethoxy]-methyl}-1,3-dioxan-5-ol [(*S,S*)-**3g**]: 280 mg (0.71 mmol) of (*S,S*)-**2g** was reduced following GP5 with 53 mg (1.42 mmol) of $NaBH_4$ to yield (*S,S*)-**3g** as a colourless solid. − Yield: 271 mg; 95%. − $[\alpha]_D^{25}$ = −45.0 (*c* = 1.2, $CHCl_3$). − M.p. 71°C. − IR (KBr): $\tilde{\nu}$ = 3429 cm^{-1}(s), 2988 (m), 2954 (vs), 2928 (s), 2900, (s), 2864 (s), 1637 (w), 1482 (w), 1459 (m), 1432 (m), 1379 (s), 1343 (m), 1326 (m), 1285 (m), 1249 (vs), 1222 (vs), 1177 (s), 1110 (vs), 1062 (vs), 1046 (vs), 1000 (m), 939 (s), 863 (vs), 836 (vs). − ^{1}H NMR: (300 MHz, $CDCl_3$): δ = 0.1 (s, 18 H, SiCH$_3$), 0.96 (m, 4 H, CH_2Si), 1.35 [s, 3 H, C(C*H*$_3$)$_2$], 1.42 [s, 3 H, C(C*H*$_3$)$_2$], 2.72 (d, *J* = 4.7 Hz, 1 H, OH), 3.55−3.75 (m, 9 H, C*H*$_2$OC*H*$_2$, C*H*OH), 3.86 (m, 1 H, C*H*CH$_2$O), 4.01 (m, 1 H, C*H*CH$_2$O). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = −1.4 (Si*C*H$_3$), 18.0 (*C*H$_2$Si), 18.2 (*C*H$_2$Si), 24.1 [C(*C*H$_3$)$_2$], 24.6 [C(*C*H$_3$)$_2$], 68.8 (CH_2O), 68.9 (CH_2O), 69.0 (CH_2O), 69.4 (CHOH), 70.9 (CH_2O), 71.0 (*C*HCH$_2$O), 73.1 (*C*HCH$_2$O), 101.1 [*C*(CH$_3$)$_2$]. − MS (EI, 70eV); *m/z* (%): 392 (M^+, 1), 377 (M^+ − 15, 4), 291 (1), 245 (2), 189 (6), 146 (11), 143 (6), 133 (3), 131 (36), 116 (17), 101 (23), 75 (19), 73 (100), 59 (13), 57 (7), 45 (6). − $C_{18}H_{40}O_5Si_2$ (392.68): calcd. C 55.06, H 10.27; found C 54.56 H 10.56.

(4S/5R)-4-(Benzyloxy)methyl-2,2-dimethyl-1,3-dioxan-5-yl p-Toluenesulfonate [(*S/R*)-**6a**]: To a solution of 460 mg (1.80 mmol) of (*S,R/S*)-**2a** (*trans/cis* = 70:30) in 20 ml of CH_2Cl_2 were added 363 mg (3.60 mmol) of NEt_3 and a catalytic amount of DMAP. The mixture was cooled to 0°C and 446 mg (2.3 mmol) of TsCl dissolved in 1 ml of CH_2Cl_2 was added dropwise. The resulting mixture was stirred at 0°C for 30 min at room temperature for 20 h, then 181 mg (1.8 mmol) of NEt_3 and 223 mg (1.2 mmol) of TsCl were added, and the mixture was stirred again for 24 h. 20 ml of CH_2Cl_2 and 5 ml of a sat. aqueous NH_4Cl solution were added. The organic layer was washed with a sat. aqueous NH_4Cl solution, water and brine, and was dried with $MgSO_4$. Column chromatography (SiO_2: pentane/Et_2O 3:1) yielded pure (*S/R*)-**6a** as a colourless oil {(*S/S*)-**6a** (*cis*-isomer) was not isolated}. − Yield: 459 mg; 62%. − $[\alpha]_D^{25}$ = −35.2 (*c* = 1.15, $CHCl_3$). − IR (film): $\tilde{\nu}$ = 3089 cm^{-1} (m), 3064 (m), 3031 (m), 2993 (s), 2940 (m), 2923 (m), 2874 (m), 1598 (s), 1225 (vs), 1191 (vs), 1179 (vs), 1099 (vs), 1063 (vs), 1028 (s), 1019 (s), 988 (vs), 959 (vs), 914 (vs), 844 (s), 816 (vs), 737 (vs). − ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.34 (s, 3 H, CH_3), 1.42 (s, 3 H, CH_3), 2.35 (s, 3 H, C*H*$_3$Ph), 3.32 (dd, *J* = 10.9 Hz, *J* = 4.9 Hz 1 H, C*H*HOBn), 3.41 (dd, *J* = 10.9 Hz, *J* = 2.1 Hz, 1 H, CH*H*OBn), 3.69 (dd, *J* = 12.2 Hz, *J* = 6.7 Hz, 1 H, C*H*HCHOTs), 3.88 (ddd, *J* = 9.7 Hz, *J* = 5.2 Hz, *J* = 2.1 Hz, 1 H, CHOTsC*H*) 3.93 (dd, *J* = 12.2 Hz, *J* = 5.19 Hz, 1 H, CH*H*CHOTs), 4.37 (s, 2 H, OC*H*$_2$Ph), 4.52 (m, 1 H, C*H*OTs), 7.20−7.33 (m, 7 H, aromatic H) 7.72 (m, 2 H, aromatic H). − ^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.2 (CH_3), 21.5 (Ph*C*H$_3$), 26.9 (CH_3), 62.0 (CH_2OBn), 68.6 (*C*H$_2$CHOTs), 70.3 (CHOTs*C*H), 72.5 (CHOTs), 73.1 (O*C*H$_2$Ph), 99.5 [*C*(CH$_3$)$_2$], 127.3, 127.4, 127.8, 128.2, 129.9, 132.9, 137.9, 145.1 (aromatic C). − MS (EI, 70 eV); *m/z* (%): 406 (M^+, 1), 391 (M^+ − 15, 2), 227 (17), 176 (30), 159 (3), 155 (28), 133 (20), 107 (12), 105 (11), 91 (100), 65 (11). − $C_{21}H_{26}O_6S$ (406.49): calcd. C 62.05, H 6.45; found C 62.40, H 6.67.

(4S,5R/S)-4-(Benzyloxy)methyl-2,2-dimethyl-1,3-dioxan-5-yl Methanesulfonate [(*S,R/S*)-**7a**]: To a solution of 290 mg (1.15 mmol) of (*S,R/S*)-**2a** (*trans/cis* = 70:30) in 12 ml of CH_2Cl_2 were added 303 mg (3.0 mmol) of NEt_3 and a catalytic amount of DMAP. The mixture was cooled to 0°C and 229 mg (1.6 mmol) of $MeSO_2Cl$ dissolved in 1 ml of CH_2Cl_2 was added dropwise. The resulting mixture was stirred for 30 min at 0°C and for 90 min at room temperature until TLC indicated complete conversion of the starting material. 20 ml of CH_2Cl_2 and 5 ml of a sat. aqueous NH_4Cl solution were added. The organic layer was washed with a sat. aqueous NH_4Cl solution, water and brine, and was dried with $MgSO_4$. Column chromatography (SiO_2: pentane/Et_2O 3:1) yielded (*S,R/S*)-**7a** (*trans/cis* = 70:30) as an oil. Yield: 352 mg; 93%. − IR (film): $\tilde{\nu}$ = 3089 cm^{-1} (m), 3064 (m), 2992 (m), 2938 (m), 2875 (m), 1496 (m), 1454 (m), 1419 (m), 1361 (vs), 1274 (m), 1225 (s), 1202 (s), 1178 (vs), 1129 (vs), 1099 (s), 1063 (m), 1027 (m), 998 (m), 957 (vs), 912 (vs), 847 (s).− ^{1}H NMR (300 MHz, $CDCl_3$) (*S,R*)-**7a**: δ = 1.40 (s, 3 H, CH_3), 1.46 (s, 3 H, CH_3), 2.89 (s, 3 H, SO_2CH_3), 3.65−3.75 (m, 2 H, CH_2OBn), 3.80−3.96 (m, 2 H, C*H*$_2$CHOMs), 4.05−4.20 (m, 1 H, CHOMsC*H*), 4.39−4.81 (m, 3 H, C*H*OMs, OC*H*$_2$Ph), 7.22−7.38 (m, 5 H, aromatic H); (*S,S*)-**7a**: δ = 1.42 (s, 3 H, CH_3), 1.45 (s, 3 H, CH_3), 3.01 (s, 3 H, SO_2CH_3), 3.55−3.75 (m, 2 H, CH_2OBn), 3.80−3.96 (m, 2 H, C*H*$_2$CHOMs), 4.05−4.19 (m, 1 H, CHOMsC*H*), 4.49−4.81 (m, 3 H, C*H*OMs, OC*H*$_2$Ph), 7.22−7.38 (m, 5 H, aromatic H). − ^{13}C NMR (75 MHz, $CDCl_3$) (*S,R*)-**7a**: δ = 20.3 (CH_3), 26.9 (CH_3), 37.8 (SO_2CH_3), 62.4 (CH_2OBn), 68.8 (*C*H$_2$CHOMs), 70.4 (CHOMs*C*H), 72.6 (CHOMs), 73.7 (O*C*H$_2$Ph), 99.8 [*C*(CH$_3$)$_2$], 127.8, 127.9, 128.4, 137.8 (aromatic C); (*S,S*)-**7a**: δ = 18.0 (CH_3), 28.8 (CH_3), 38.6 (SO_2CH_3), 63.0 (CH_2OBn), 68.4 (*C*H$_2$CHOMs), 69.0 (CHOMs*C*H), 72.0 (CHOMs), 73.6 (O*C*H$_2$Ph), 99.0 [*C*(CH$_3$)$_2$], 127.2, 128.0, 128.5, 137.6 (aromatic C). − MS (CI, isobutane); *m/z* (%): 331 (M^++1, 100), 330 (M^+, 3), 273 (16), 180 (8), 177 (4), 149 (3), 107 (6). − $C_{15}H_{22}O_6S$ (330.40): calcd. C 54.53, H 6.71; found C 54.40, H 6.72.

(4S,5R/S)-4-(Benzyloxy)methyl-2,2-dimethyl-1,3-dioxan-5-yl 2-Propanesulfonate [(*S,R/S*)-**8a**]: To a solution of 252 mg (1.0 mmol) of (*S,R/S*)-**2a** (*trans/cis* = 70:30) in 10 ml of Et_2O were added 303

mg (3.0 mmol) of NEt_3 and a catalytic amount of DMAP. The mixture was cooled to 0°C and 213 mg (1.5 mmol) of isopropylsulfonyl chloride dissolved in 1 ml of Et_2O was added dropwise. The resulting mixture was stirred for 30 min at 0°C and for 20 h at room temperature. 10 ml of Et_2O and 5 ml of a sat. aqueous NH_4Cl solution were added. The organic layer was washed with a sat. aqueous NH_4Cl solution, water and brine, and was dried with $MgSO_4$. Column chromatography (SiO_2: pentane/Et_2O 10:1 to 1:1) yielded 230 mg of (*S,R*)-**8a** and 60 mg of (*S,S*)-**8a** as a colourless oil. − Combined yield: 290 mg; 81%. − (*S,R*)-**8a**: IR (film): $\tilde{\nu}$ = 3089 cm^{-1}, 3064 (m), 3031 (m), 2992 (s), 2941 (m), 2876 (m), 1497 (m), 1454 (vs), 1374 (vs), 1350 (vs), 1273 (s), 1225 (vs), 1203 (vs), 1179 (vs), 1158 (vs), 1099 (vs), 1064 (vs), 987 (vs). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.31, [d, *J* = 6.6 Hz, 3 H, $CH(CH_3)_2$], 1.35 [d, *J* = 6.9 Hz, 3 H, $CH(CH_3)_2$], 1.40 (s, 3 H, CH_3), 1.47 (s, 3 H, CH_3), 3.18 [qq, *J* = 6.9 Hz, *J* = 6.6 Hz 1 H, $CH(CH_3)_2$], 3.65 (m, 2 H, CH_2OBn), 3.86 (dd, *J* = 12.3 Hz, *J* = 6.3 Hz, 1 H, $CHCHOSO_2$), 3.95 (m, 1 H, SO_2CH), 4.11 (dd, *J* = 12.3 Hz, *J* = 5.2 Hz, 1 H, $CHCHOSO_2$), 4.59 (s, 2 H, OCH_2Ph), 4.73 (ddd, *J* = 8.6 Hz, *J* = 6.3 Hz, *J* = 5.2 Hz, 1 H, $CHOSO_2$), 7.29−7.36 (m, 5 H, aromatic H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 16.5, 16.6 [$CH(CH_3)_2$], 20.6 (CH_3), 26.8 (CH_3), 52.6 (SO_2CH), 62.0 (CH_2OBn), 69.2 (CH_2CHOSO_2), 70.6 ($CHCH_2OBn$), 71.8 ($CHOSO_2$), 73.6 (OCH_2Ph), 99.9 [$C(CH_3)_2$], 127.7, 127.9, 128.4, 137.9 (aromatic C). − MS (EI, 70 eV); *m/z* (%): 358 (M^+, 1), 343 (M^+ − 15, 3), 237 (3), 179 (11), 176 (34), 136 (34), 133 (37), 107 (21), 105 (11), 92 (14), 91 (100), 59 (27). − $C_{17}H_{26}O_6S$ (358.45): calcd. C 56.96, H 7.31; found C 56.78, H 7.37.

(4S,5R/S)-4-(Benzyloxy)methyl-2,2-dimethyl-1,3-dioxan-5-yl Phenoxymethanethioate [(*S,R/S*)-**9a**]: According to Robins et al.,[29] to a solution of 252 mg (1.0 mmol) of (*S,R/S*)-**2a** (*trans*/*cis* = 70:30) in 10 ml of CH_2Cl_2 were added 373 mg (3.7 mmol) of NEt_3 and a catalytic amount of DMAP. The mixture was cooled to 0°C and 226 mg (1.2 mmol) of phenoxythiocarbonyl chloride dissolved in 1 ml of CH_2Cl_2 was added dropwise. The resulting mixture was stirred for 30 min at 0°C and for 12 h at room temperature . The organic layer was washed with an aqueous 1 N HCl solution, sat. aqueous $NaHCO_3$ solution, water, brine, and was dried with $MgSO_4$. Column chromatography (SiO_2: pentane/Et_2O 5:1) yielded 139 mg of (*S,R*)-**9a** and 60 mg of (*S,S*)-**9a** as yellow oils. Combined yield: 199 mg; 51%. − IR (film): $\tilde{\nu}$ = 3061 cm^{-1} (m), 3028 (m), 2989 (s), 2935 (m), 2870 (m), 1475 (vs), 1441 (vs), 1418 (vs), 1382 (vs), 1357 (s), 1303 (m), 1269 (vs), 1217 (vs), 1167 (vs), 1142 (vs), 1098 (vs), 1053 (vs), 1022 (vs), 1001 (vs), 1098 (vs), 1053 (vs), 1022 (vs), 1001 (vs), 981 (m). − ^{1}H NMR (300 MHz, $CDCl_3$) (*S,R*)-**9a**: δ = 1.38 (s, 3 H, CH_3), 1.39 (s, 3 H, CH_3), 3.48 (m, 2 H, CH_2OBn), 3.71 (dd, *J* = 12.4 Hz, *J* = 5.4 Hz, 1 H, $CHCHOCS$), 3.88 (m, 1 H, $CHCH_2OBn$), 4.21 (dd, *J* = 12.4 Hz, *J* = 5.0 Hz, 1 H, $CHCHOCS$), 4.47 (d, *J* = 12.4 Hz, 1 H, $OCHPh$), 4.60 (d, *J* = 12.0 Hz, 1 H, $OCHPh$), 5.53 (ddd, *J* = 9.1 Hz, *J* = 5.4 Hz, *J* = 5.0 Hz, 1 H, $CHOCSOPh$), 7.28−7.49 (m, 10 H, aromatic H). − ^{13}C NMR (75 MHz, $CDCl_3$) (*S,R*)-**9a**: δ = 21.3 (CH_3), 26.2 (CH_3), 61.3 (CH_2OBn), 69.8 (CH_2CHOCS), 73.7 (OCH_2Ph), 76.2 ($CHOCSOPh$), 99.8 ($C(CH_3)_2$), 127.7, 127.8, 128.4, 129.0, 129.2, 130.2, 135.1, 138.0 (aromatic C), 212.0 ($CSOPh$). − MS (EI, 70 eV); *m/z* (%): 388 (M^+, 0.1), 225 (30), 116 (100), 108 (17), 91 (14), 88 (93), 86 (9), 77 (24), 65 (16), 59 (73). − $C_{21}H_{24}O_5S$ (388.48): calcd. C 64.93, H 6.23; found: it was not possible to obtain a correct combustion analysis.

(4S,5R/S)-4-(Benzyloxy)methyl-2,2-dimethyl-1,3-dioxan-5-yl 1H-1-Imidazolecarbothioate [(*S,R/S*)-**10a**]: Following Rasmussen's procedure,[18] 1.06 g (6.0 mmol) of *N,N′*-thiocarbonyldiimidazole was added to 756 mg (3.0 mmol) of (*S,R/S*)-**2a** in 15 ml of THF and the mixture was heated to reflux for 24 h. Column chromatography (SiO_2, Et_2O) yielded 729 mg of (*S/R*)-**10a** as a colourless solid and 312 mg of (*S/S*)-**10a** as a colourless oil. − Combined yield: 1.04 g; 96%. − (*S/R*)-**10a** (*trans*-isomer): M.p. 78°C. − $[\alpha]_D^{25}$ = −72.0 (*c* = 1.05, CH_3COCH_3). − IR (KBr) : $\tilde{\nu}$ = 3088 cm^{-1} (w), 3063 (w), 3029 (w), 2991 (m), 2939 (m), 2917 (m), 2869 (m), 1531 (m), 1495 (m), 1464 (m), 1391 (vs), 1323 (vs), 1285 (vs), 1244 (vs), 1233 (vs), 1104 (vs), 1082 (s), 981 (m), 936 (m). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.43 (s, 3 H, CH_3), 1.50 (s, 3 H, CH_3), 3.61 (d, *J* = 4.4, 2 H, CH_2OBn), 3.85 (dd, *J* = 12.4 Hz, *J* = 5.0 Hz, 1 H, $CHCHOCS$), 4.16 (m, 2 H, $CHCHOCS$, $CHCH_2OBn$), 4.48 (d, *J* = 12.1 Hz, 1 H, $OCHPh$), 4.58 (d, *J* = 12.1 Hz, 1 H, $OCHPh$), 5.61 (m, 1 H, $CHOCS$), 6.99 (s, 1 H, imidazole H), 7.19−7.27 (m, 5 H, aromatic H), 7.50 (s, 1 H, imidazole H), 8.22 (s, 1 H, imidazole H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.5 (CH_3), 26.0 (CH_3), 61.2 (CH_2OBn), 69.3 (CH_2CHOCS), 69.6 ($CHCH_2OBn$), 73.5 (OCH_2Ph), 76.7 ($CHOCS$), 100.3 [$C(CH_3)_2$], 117.8 (imidazole C), 127.7, 127.8, 128.3 (aromatic C), 130.9, 136.7, 137.5 (imidazole C), 182.9 (OCS). − MS (CI, isobutane); *m/z* (%): 363 (M^+ + 1, 100), 362 (M^+, 3), 305 (24), 235 (6), 179 (6), 125 (4)69 (34). − $C_{18}H_{22}N_2O_4S$ (362.45): calcd. C 59.64, H 6.12, N 7.73; found C 59.72, H 6.15, N 7.47. − (*S/S*)-**10a** (*cis*-isomer): $[\alpha]_D^{25}$ = +74.4 (*c* = 1.0, CH_3COCH_3). − IR (film): $\tilde{\nu}$ = 3150 cm^{-1} (m), 3139 (m), 3028 (w), 2993 (m), 2937 (m), 2884 (s), 2815 (m), 1540 (m), 1508 (m), 1468 (s), 1468 (s), 1393 (vs), 1336 (vs), 1306 (vs), 1296 (vs), 1285 (vs), 1244 (vs), 1233 (vs), 1104 (vs), 1082 (s), 981 (m), 936 (m). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.42 (s, 3 H, CH_3), 1.50 (s, 3 H, CH_3), 3.49 (m, 2 H, CH_2OBn), 4.12 (d, *J* = 13.5 Hz, 1 H, $OCHPh$), 4.19 (d, *J* = 13.5 Hz, 1 H, $OCHPh$), 4.34 (d, *J* = 12.0 Hz, 1 H, $CHCHOCS$), 4.36 (m, 1 H, $CHCH_2OBn$), 4.57 (d, *J* = 12.0 Hz, 1 H, $CHCHOCS$), 5.45 (br. s, 1 H, $CHOCS$), 7.02 (s, 1 H, imidazole H), 7.16−7.24 (m, 5 H, aromatic H), 7.57 (s, 1 H, imidazole H), 8.29 (s, 1 H, imidazole H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.6 (CH_3), 29.1 (CH_3), 61.4 (CH_2OBn), 67.6 (CH_2CHOCS), 69.0 ($CHCH_2OBn$), 73.4 (OCH_2Ph), 73.8 ($CHOCS$), 98.9 [$C(CH_3)_2$], 117.8 (imidazole C), 127.8, 127.9, 128.3 (aromatic C), 130.8, 136.8, 137.2 (imidazole C), 183.3 (OCS). − MS (EI, 70 eV); *m/z* (%): 347 (M^+ − 15, 2), 329 (1), 219 (2), 129 (6), 113 (10), 107 (13), 91 (100), 70 (11), 58 (18), 57 (11). − $C_{18}H_{22}N_2O_4S$ (362.45): calcd. C 59.64, H 6.12, N 7.73 found C 59.64, H 6.15, N 7.55.

General Procedure for the Preparation of Xanthates (*S,R/S,S*)-**4** (GP6): To a solution of (*S,R/S,S*)-**3** (4.00 mmol) in dry THF (15 ml) under Ar were added imidazole (cat.) and a 60% suspension of NaH in mineral oil (0.32 g, 8.00 mmol, 2.0 equiv.) at 0°C. After 30 minutes, CS_2 (1.8 ml, 30.0 mmol, 7.5 equiv.) was added dropwise. Stirring was continued for additional 30 min and iodomethane (0.3 ml, 4.40 mmol, 1.1 equiv.) was added. The mixture was stirred at room temperature overnight. The suspension was hydrolysed with water and extracted with Et_2O. The combined organic layers were washed with sat. aqueous NH_4Cl solution (30 ml) and brine (30 ml), dried (Na_2SO_4) and concentrated under reduced pressure. Purification by column chromatography as indicated afforded the xanthates (*S,R/S,S*)-**4**.

(4S,5R/S)4-(Benzyloxy)methyl-2,2-dimethyl-1,3-dioxan-5-yl (Methylsulfanyl)methanethioate [(*S,R/S*)-**4a**]: According to GP6, 504 mg (2.0 mmol) of (*S,R/S*)-**3a** was sequentially treated with 62 mg (2.6 mmol) of NaH, 532 mg (7.0 mmol) of CS_2 and 400 mg (2.8 mmol) of MeI. Column chromatography (SiO_2, pentane/Et_2O 4:1) yielded (*S,R/S*)-**4a** as colourless oil. The diastereomers were separated by column chromatography (SiO_2, pentane/Et_2O 20:1). − Combined yield: 675 mg; 87%. − (*S/R*)-**4a** (*trans*-isomer): $[\alpha]_D^{25}$ = −177.6 (*c* = 3.0, $CHCl_3$). − IR (film): $\tilde{\nu}$ = 3088 cm^{-1}

(w), 3063 (w), 3031 (w), 2990 (m), 2937 (m), 2919 (m), 2867 (m), 1496 (m), 1478 (m), 1383 (s), 1373 (s), 1319 (m), 1271 (m), 1211 (vs), 1168 (vs), 1103 (vs), 1070 (vs), 1007 (m) 950 (vs), 849 (vs). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.41 (s, 3 H, CH_3), 1.49 (s, 3 H, CH_3), 2.50(s, 3 H, SCH_3), 3.58 (m, 2 H, CH_2OBn), 3.78 (dd, *J* = 12.4 Hz, *J* = 5.7 Hz, 1 H, C*H*HCHOCS), 4.15 (m, 2 H, CH*H*CHOCS, C*H*CH_2OBn), 4.53 (d, *J* = 12.4 Hz, 1 H, OC*H*HPh), 4.61 (d, *J* = 12.4 Hz, 1 H, OCH*H*Ph), 5.61 (dt, *J* = 9.1 Hz, *J* = 5.4 Hz, 1 H, C*H*OCS), 7.26−7.34 (m, 5 H, aromatic H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.2 (SCH_3), 21.2 (CH_3), 26.4 (CH_3), 61.4 (CH_2OBn), 69.5 (*C*H_2CHOCS), 70.1 (*C*HCH_2OBn), 73.4 (OCH_2Ph), 75.7 (*C*HOCS), 99.9 [*C*$(CH_3)_2$], 127.6, 127.7, 128.3, 137.9 (aromatic C), 215.2 (O*C*SSCH_3). − MS (CI, isobutane); *m/z* (%): 399 (M^++57, 2), 343 (M^++1, 8), 287 (13), 285 (100), 253 (9), 235 (19), 177 (18), 161 (6), 147 (7), 128 (6). − $C_{16}H_{22}O_4S_2$ (342.48): calcd. C 56.11, H 6.47; found C 55.76, H 6.51. − (*S*/*S*)-**4a** (*cis*-isomer): $[\alpha]_D^{25}$ = +64.3 (*c* = 1.15, $CHCl_3$). − IR (film): $\tilde{\nu}$ = 3087 cm^{-1} (w), 3063 (w), 2991 (vs), 2939 (s), 2919 (vs), 2869 (vs), 1496 (m), 1454 (vs), 1427 (s), 1383 (vs), 1275 (vs), 1197 (vs), 1175 (vs), 1073 (vs),950 (vs), 849 (vs). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.44 (s, 3 H, CH_3), 1.48 (s, 3 H, CH_3), 2.52 (s, 3 H, SCH_3), 3.53 (d, *J* = 6.7 Hz, 2 H, CH_2OBn), 4.10 (m, 2 H, C*H*HCHOCS, C*H*CH_2OBn), 4.32 (dt, *J* = 6.4 Hz, *J* = 1.8 Hz, 1 H, CH*H*CHOCS), 4.44 (d, *J* = 12.0 Hz, 1 H, OC*H*HPh) 4.56 (d, *J* = 12.0 Hz, 1 H, OCH*H*Ph), 5.56 (dd-like, *J* = 4.0 Hz, *J* = 1.8 Hz, 1 H, C*H*OCS), 7.24−7.36 (m, 5 H, aromatic H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.9 (SCH_3), 19.0 (CH_3), 29.1 (CH_3), 62.1 (CH_2OBn), 68.7 (*C*H_2CHOCS), 69.6 (*C*HCH_2OBn), 73.8 (OCH_2Ph), 74.1 (*C*HOCS), 98.9 (*C*$(CH_3)_2$), 127.9, 128.0, 128.5, 137.8 (aromatic C), 215.4 (O*C*SSCH_3). − MS (CI, isobutane); *m/z* (%): 343 (M^++1, 19), 287 (10), 285 (100), 235 (6), 234 (5), 195 (4). − $C_{16}H_{22}O_4S_2$ (342.48): calcd. C 56.11, H 6.47; found C 56.52, H 6.33.

(4S,6S)-4,6-Diethyl-2,2-dimethyl-1,3-dioxan-5-yl (Methylsulfanyl)methanethioate [(*S*,*S*)-**4b**]: Following GP6, (*S*,*S*)-**4b** was isolated as a yellow oil. − Yield: 975 mg; 91%. − $[\alpha]_D^{23}$ = −51.5 (*c* = 0.96, $CHCl_3$). − IR (film): $\tilde{\nu}$ = 3000−2800 cm^{-1} (s, br) 1461 (m), 1425 (w), 1380 (s), 1319 (w), 1212 (s), 1179 (s), 1158 (s), 1147 (s), 1126 (m), 1058 (s), 1024 (m), 997 (m), 982 (s). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.93 (t, *J* = 7.4 Hz, 3 H, CH_2CH_3), 0.95 (t, *J* = 7.4 Hz, 3 H, CH_2CH_3), 1.35 (s, 3 H, CCH_3), 1.42 (s, 3 H, CCH_3), 1.50 (quin, *J* = 7.4 Hz, 2 H, CH_2), 1.55−1.77 (m, 2 H, CH_2), 2.58 (s, 3 H, SCH_3), 3.67 (ddd, *J* = 8.4 Hz, *J* = 7.1 Hz, *J* = 4.4 Hz, 1 H, C*H*CH_2CH_3), 3.85 (td, *J* = 7.1 Hz, *J* = 3.7 Hz, 1 H, C*H*CH_2CH_3), 5.88 (dd, *J* = 6.7 Hz, *J* = 3.7 Hz, 1 H, C*H*OCSSCH_3). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 9.7 (CH_2CH_3), 10.2 (CH_2CH_3), 19.1 (SCH_3), 22.1 (CH_2), 23.9 (CCH_3), 24.4 (CCH_3), 26.10 (CH_2), 71.9 (*C*HCH_2CH_3), 72.1 (*C*HCH_2CH_3), 84.2 (*C*HOCSSCH_3), 100.9 [*C*$(CH_3)_2$], 216.7 (*C*SSCH_3). − MS (EI, 70 eV); *m/z* (%): 263 (0.5) [$M^+ - CH_3$], 171 (5), 170 (42), 141 (10), 134 (9), 113 (28), 112 (96), 102 (5), 95 (5), 93 (9), 91 (94), 86 (10), 84 (8), 83 (100). − $C_{12}H_{22}O_3S_2$ (278.43): calcd. C 51.76, H 7.96; found C 51.89, H 7.98.

(4S,6S)-(4,6-Diisopropyl-2,2-dimethyl-1,3-dioxan-5-yl (Methylsulfanyl)methanethioate [(*S*,*S*)-**4c**]: Following GP6, (*S*,*S*)-**4c** was isolated as a yellow oil. − Yield: 1.0 g; 82%. − $[\alpha]_D^{23}$ = −19.9 (*c* = 1.0, $CHCl_3$).− IR (film): $\tilde{\nu}$ = 3000−2800 cm^{-1} (s), 1470 (m), 1425 (m), 1379 (s), 1318 (w), 1213 (s), 1173 (s), 1152 (s), 1122 (s), 1059 (s), 1025 (s), 1003 (s), 980 (s), 965 (m), 930 (m), 903 (m), 872 (m), 806 (w), 758 (w), 725 (w). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (d, *J* = 6.9 Hz, 3 H, CHCH_3), 0.96 (d, *J* = 6.9 Hz, 6 H, CHCH_3), 0.97 (d, 3 H, *J* = 6.6 Hz, CHCH_3), 1.32 (s, 3 H, CCH_3), 1.40 (s, 3 H, CCH_3), 1.82 (septd, *J* = 6.6 Hz, *J* = 9.4 Hz, 1 H, C*H*CH_3), 1.98 (septd, *J* = 6.0 Hz, *J* = 3.0 Hz, 1 H, C*H*CH_3), 2.57 (s, 3 H, SCH_3), 3.43 [dd *J* = 9.3 Hz, *J* = 3.0 Hz, 1 H, C*H*$CH(CH_3)_2$], 3.53 [dd, *J* = 6.0 Hz, *J* = 3.0 Hz, 1 H, C*H*$CH(CH_3)_2$], 6.01 (dd, *J* = 6.3 Hz, *J* = 3.0 Hz, 1 H, C*H*OCSSCH_3). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.8 (CH*C*H_3), 18.8 (CH*C*H_3), 19.1 (SCH_3), 19.4 (CH*C*H_3), 19.5 (CH*C*H_3), 23.6 (C*C*H_3), 24.5 (C*C*H_3), 27.4 (*C*HCH_3), 29.8 (*C*HCH_3), 75.8 [*C*H$CH(CH_3)_2$], 76.0 [*C*H$CH(CH_3)_2$], 81.9 (*C*HOCSSCH_3), 100.8 [*C*$(CH_3)_2$], 216.2 (*C*SSCH_3). − MS (EI, 70 eV); *m/z* (%): 199 (1.6), 198 (10), 155 (33), 141 (6), 140 (22), 100 (6), 98 (8), 97 (100), 91 (48), 85 (8), 71 (38), 69 (26) 67 (6), 59 (18), 57 (9), 55 (11), 53 (5), 43 (45), 43 (27), 41 (36), 39 (11). − $C_{14}H_{26}O_3S_2$ (306.46): calcd. C 54.86, H 8.55; found C 54.99, H 8.44.

(4S,6S)-4,6-Dibenzyl-2,2-dimethyl-1,3-dioxan-5-yl (Methylsulfanyl)methanethioate [(*S*,*S*)-**4d**]: Following GP6, (*S*,*S*)-**4d** was isolated as a yellow oil. − Yield: 1.05 g; 89%. − $[\alpha]_D^{23}$ = −38.0 (*c* = 0.67, $CHCl_3$). − IR (film): $\tilde{\nu}$ = 3090−3030 cm^{-1} (m), 3000−2800 (s), 2000−1650 (w, br), 1605 (w), 1585 (w), 1496 (s), 1455 (s), 1426 (m), 1381 (s), 1319 (w), 1210 (s), 1163 (s), 1122 (s), 1063 (s), 1000 (s), 966 (m), 942 (m), 905 (m), 875 (w), 859 (w), 824 (m), 749 (s). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.18 (s, 3 H, CCH_3), 1.31 (s, 3 H, CCH_3), 2.56 (s, 3 H, SCH_3), 2.74−2.79 (m, 2 H, CH_2), 2.89 (dd, *J* = 14.1 Hz, *J* = 8.1 Hz, 1 H, C*H*H), 2.99 (dd, *J* = 14.4 Hz, *J* = 3.7 Hz, 1 H, CH*H*), 4.02−4.18 (m, 2 H, C*H*Bn), 5.88 (dd, *J* = 6.4 Hz, *J* = 3.7 Hz, 1 H, C*H*OCSSCH_3), 7.11−7.26 (m, 10 H, aromatic H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.2 (SCH_3), 23.9 (C*C*H_3), 24.7 (C*C*H_3), 35.4 (CH_2), 39.2 (CH_2), 71.1 (CHBn), 71.9 (CHBn), 83.5 (*C*HOCSSCH_3), 101.1 [*C*$(CH_3)_2$], 126.2, 126.3, 128.1, 128.2, 129.0, 129.4, 137.6, 137.8 (aromatic C), 216.4 (*C*S). − MS (EI, 70 eV); *m/z* (%): 387 (0.2), 236 (14), 204 (11), 145 (100), 118 (5), 117 (14), 115 (6), 105 (9), 92 (6), 91 (68), 75 (8), 43 (9), 39 (5). − $C_{22}H_{26}O_3S_2$ (402.58): calcd. C 65.64, H 6.51; found C 65.67, H 6.74.

(4S,5R/S,6S)-(4-Benzyloxy)methyl-2,2,6-trimethyl-1,3-dioxan-5-yl (Methylsulfanyl)methanethioate [(*S*,*R*/*S*,*S*)-**4e**]: Following GP6, (*S*,*R*/*S*,*S*)-**4e** was isolated as a yellow oil. − Yield: 1.27 g; 90%. The two diastereomers were separated by column chromatography (SiO_2, petroleum ether/Et_2O 10:1). (*S*,*R*,*S*)-**4e**: $[\alpha]_D^{23}$ = −37.1 (*c* = 1.0, $CHCl_3$). − IR (CH_2Cl_2): $\tilde{\nu}$ = 3090−3030 cm^{-1} (w), 3000−2800 (s), 2000−1650 (w), 1586 (w), 1496 (w), 1454 (s), 1424 (m), 1381 (s), 1319 (m), 1208 (s), 1183 (s), 1138 (s), 1100 (s), 1056 (s), 998 (s), 970 (s), 937 (m), 903 (m), 873 (w), 833 (m), 737 (s), 699 (s). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.15 (d, *J* = 6.9 Hz, 3 H, CHCH_3), 1.39 (s, 3 H, CCH_3), 1.45 (s, 3 H, CCH_3), 2.55 (s, 3 H, SCH_3), 3.61 (dd, *J* = 10.7 Hz, *J* = 4.9 Hz, 1 H, C*H*HOBn), 3.64 (dd, *J* = 10.7 Hz, *J* = 3.3 Hz, 1 H, CH*H*OBn), 3.97 (ddd, *J* = 7.1 Hz, *J* = 4.9 Hz, *J* = 3.6 Hz, 1 H, C*H*CH_2OBn), 4.18 (qd, *J* = 6.6 Hz, *J* = 3.8 Hz, 1 H, C*H*CH_3), 4.57 (s, 2 H, CH_2Ph), 6.02 (dd, *J* = 7.1 Hz, *J* = 3.6 Hz, 1 H, C*H*OCSSCH_3), 7.23−7.35 (m, 5 H, ArH). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.9 (CH*C*H_3), 19.1 (SCH_3), 24.0 (C*C*H_3), 24.7 (C*C*H_3), 66.4 (*C*HCH_3), 70.1 (*C*H_2Ph), 70.6 (*C*HCH_2OBn), 73.6 (*C*H_2OBn), 81.1 (*C*HOCSSCH_3), 101.1 [*C*$(CH_3)_2$], 127.6, 127.7, 128.3, 138.0 (aromatic C), 216.6 (*C*SSCH_3). − (*S*,*S*,*S*)-**4e**: $[\alpha]_D^{23}$ = −5.0 (*c* = 1.0, $CHCl_3$). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.33 (d, *J* = 6.7 Hz, 3 H, CHCH_3), 1.39 (s, 3 H, CCH_3), 1.44 (s, 3 H, CCH_3), 2.54 (s, 3 H, SCH_3), 3.55 (dd, *J* = 10.1 Hz, *J* = 5.7 Hz, 1 H, C*H*HOBn), 3.58 (dd, *J* = 10.4 Hz, *J* = 6.4 Hz, 1 H, CH*H*OBn), 3.92 (quin, *J* = 6.4 Hz, 1 H, C*H*CH_3), 4.28 (ddd, *J* = 6.4 Hz, *J* = 6.0 Hz, *J* = 3.7 Hz, 1 H, C*H*CH_2OBn), 4.46 (d, *J* = 12.1 Hz, 1 H, C*H*HPh), 4.54 (d, *J* = 11.8 Hz, 1 H, CH*H*Ph), 5.83 (dd, *J* = 6.1 Hz, *J* = 3.4 Hz, 1 H, C*H*OCSSCH_3), 7.22−7.36 (m, 5 H, Ph). − ^{13}C NMR (75 MHz,

$CDCl_3$): δ = 19.3 (SCH_3), 19.4 ($CHCH_3$), 24.3 (CCH_3), 25.1 (CCH_3), 67.7 ($CHCH_3$), 68.1 (CH_2Ph), 69.1 ($CHCH_2OBn$), 73.7 (CH_2OBn), 83.8 ($CHOCSSCH_3$), 101.1 [$C(CH_3)_2$], 127.7, 127.9, 128.4, 138.0 (aromatic C), 216.2 ($CSSCH_3$). − MS (EI, 70 eV); *m/z* (%): 340.9 (1, $M^+ - CH_3$), 142 (36), 107 (5), 92 (9), 91 (100), 85 (9), 84 (74), 69 (21), 59 (6), 43 (17), 41 (5). − $C_{17}H_{24}O_4S_2$ (356.50): calcd. C 57.28, H 6.79; found C 57.39, H 6.98.

(4S,5R/S,6S)-4-Benzyl-6-[(benzyloxy)methyl]-2,2-dimethyl-1,3-dioxan-5-yl (Methylsulfanyl)methanethioate [(*S,R/S,S*)-**4f**]: According to GP6, 480 mg (1.40 mmol) of (*S,R/S,S*)-**3f** (*d.r.* = 72:28) in 10 ml of THF was treated sequentially with 68 mg (2.80 mmol) of NaH, 744 mg (9.8 mmol) of CS_2 and 400 mg (2.8 mmol) of MeI. Column chromatography (SiO_2, pentane/Et_2O 15:1) yielded 405 mg of (*S,R,S*)-**4f** and 156 mg of (*S,S,S*)-**4f** as colourless oils. Combined yield: 561 mg; 93%. − (*S,R,S*)-**4f**: $[\alpha]_D^{25}$ = −52.7 (*c* = 1.0, CH_3COCH_3). − IR (film): $\tilde{\nu}$ = 3088 cm^{-1} (m), 3063 (w), 3030 (m), 2988 (m), 2936 (m), 2919 (m), 2862 (m), 1496 (m), 1479 (m), 1454 (s), 1425 (s), 1381 (s), 1208 (vs), 1161 (s), 1126 (vs), 1061 (vs), 1009 (s), 910 (m), 831 (m), 739 (s). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.23 (s, 3 H, CH_3), 1.44 (s, 3 H, CH_3), 2.58 (s, 3 H, SCH_3), 2.80 (m, *J* = 8.7 Hz, 2 H, $CHCH_2Ph$), 3.67 (m, 2 H, CH_2OBn), 3.98 (m, 1 H, CHBn), 4.25 (m, 1 H, $CHCH_2OBn$), 4.53 (m, 1 H, $OCHHPh$), 4.58 (d, *J* = 12.1 Hz, 1 H, $OCHHPh$), 6.02 (dd, *J* = 6.4 Hz, *J* = 3.4 Hz, 1 H, CHOCS), 7.18−7.32 (m, 10 H, aromatic H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.2 (SCH_3), 23.9 (CH_3), 24.8 (CH_3), 35.4 (CH_2Ph), 70.3 (CH_2OBn), 71.3 (CHBn), 71.4 ($CHCH_2OBn$), 73.6 (OCH_2Ph), 80.5 (CHOCS), 101.2 [$C(CH_3)_2$], 126.3, 127.5, 127.7, 128.2, 128.3, 129.1, 137.8, 138.0 (aromatic C), 216.3 ($OCSSCH_3$). − MS (CI, isobutane); *m/z* (%): 432 (M^++1, 54), 376 (20), 375 (100), 343 (13), 325 (25), 325 (25), 285 (17), 267 (46), 251 (15), 249 (14), 233 (33), 179 (16), 107 (11), 91 (13). − $C_{23}H_{28}O_4S_2$ (432.47): calcd. C 63.86, H 6.52; found C 63.66, H 6.68. − (*S,S,S*)-**4f**: $[\alpha]_D^{25}$ = +7.4 (*c* = 1.0, CH_3COCH_3). − IR (film): $\tilde{\nu}$ = 3087 cm^{-1} (w), 3063 (m), 3030 (m), 2988 (m), 2936 (m), 2919 (s), 2868 (m), 1496 (s), 1454 (m), 1382 (s), 1210 (vs), 1139 (s), 1104 (s), 1066 (vs), 945 (m), 834 (m), 737 (m), 699 (vs). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.32 (s, 3 H, CH_3), 1.37 (s, 3 H, CH_3), 2.52 (s, 3 H, SCH_3), 2.89 (dd, *J* = 8.7 Hz, 1 H, $CHCHHPh$), 3.03 (dd, *J* = 14.4 Hz, *J* = 3.8 Hz, 1 H, $CHCHHPh$), 3.56 (m, 2 H, CH_2OBn), 4.06 (m, 1 H, CHBn), 4.21 (m, 1 H, $CHCH_2OBn$), 4.48 (d, *J* = 11.7 Hz, 1 H, $OCHHPh$), 4.52 (d, *J* = 11.8 Hz, 1 H, $OCHHPh$), 5.99 (dd, *J* = 6.5 Hz, *J* = 3.8 Hz, 1 H, CHOCS), 7.19−7.30 (m, 10 H, aromatic H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.2 (SCH_3), 23.8 (CH_3), 24.8 (CH_3), 39.0 (CH_2Ph), 68.1 (CH_2OBn), 69.5 (CHBn), 71.8 ($CHCH_2OBn$), 73.5 (OCH_2Ph), 82.3 (CHOCS), 101.2 [$C(CH_3)_2$], 126.3, 127.6, 127.7, 128.1, 128.3, 129.3, 137.7, 137.9 (aromatic C), 216.1 ($OCSSCH_3$). − MS (CI, isobutane); *m/z* (%): 432 (M^++1, 17), 417 ($M^+ - 15$, 3), 375 (100), 343 (18), 327 (9), 325 (21), 285 (22), 269 (13), 267 (44), 251 (17), 249 (16), 237 (18), 233 (15), 219 (7), 203 (7), 193 (8), 179 (30), 160 (20), 146 (11), 107 (23), 91 (26), 75 (30). − $C_{23}H_{28}O_4S_2$ (432.60): calcd. C 63.86, H 6.52; found C 63.80, H 6.50.

(4S,6S)-2,2-Dimethyl-4,6-bis[2-(1,1,1-trimethylsilyl)ethoxymethyl]-1,3-dioxan-5-yl (Methylsulfanyl)methanethioate [(*S,S*)-**4g**]: According to GP6, 388 mg (1.0 mmol) of (*S,S*)-**3g** was treated sequentially with 58 mg (2.8 mmol) of NaH, 266 mg (3.50 mmol) of CS_2 and 284 mg (2.0 mmol) of MeI. Column chromatography (SiO_2, pentane/Et_2O 30:1→4:1) yielded (*S,S*)-**4g** as a pale yellow oil. − Yield: 430 mg; 88%. − $[\alpha]_D^{25}$ = −3.5 (*c* = 1.0, CH_3OCH_3). − IR (film): $\tilde{\nu}$ = 2989 cm^{-1} (m), 2952 (m), 2917 (m), 2864 (m), 1456 (m), 1424 (m), 1380 (s), 1244 (vs), 1209 (vs), 1171 (m), 1118 (s), 1059 (vs), 966 (m), 860 (vs), 838 (vs). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.01 (s, 18 H, $SiCH_3$), 0.94 (m, 4 H, CH_2Si), 1.41 [s, 3 H, $C(CH_3)_2$], 1.47 [s, 3 H, $C(CH_3)_2$], 2.58 (s, 3 H, SCH_3), 3.41−3.64 (m, 8 H, CH_2OCH_2), 3.93 (td, *J* = 6.4 Hz, *J* = 3.0 Hz, 1 H, $CHCH_2O$), 4.19 (m, 1 H, $CHCH_2O$), 6.09(dd, *J* = 6.7 Hz, *J* = 3.7 Hz, 1 H, CHOCS). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = −1.2, −1.3 ($SiCH_3$), 18.1 (CH_2Si), 19.2 (SCH_3), 23.9 [$C(CH_3)_2$] 24.8 [$C(CH_3)_2$], 67.8 (CH_2O), 68.1 (CH_2O), 68.9 (CH_2O), 69.7 ($CHCH_2O$), 70.2 (CH_2O), 71.2 ($CHCH_2O$), 79.7 (CHOCS), 101.3 [$C(CH_3)_2$], 216.1 ($CSSCH_3$)− MS (CI, isobutane); *m/z* (%): 483 (M^++1, 100), 455 (28), 291 (1), 425 (9), 397 (15), 383 (7), 369 (14), 349 (11), 335 (12), 291 (14), 279 (24), 263 (23), 247 (118), 191 (16), 189 (30), 173 (20) 131 (14), 117 (19), 101 (28). − $C_{20}H_{42}O_5S_2Si_2$ (482.85): calcd. C 49.75, H 8.77; found C 49.68 H 8.76.

***General Procedures for the Preparation of Dioxanes* (*S,S*)-5**:

Deoxygenation Employing Polymer-Supported Tin Hydride[22] (GP7): To a solution of (*S,R/S,S*)-**5** (3 mmol) in benzene under Ar was added polystyrene-di-*n*-butyltin hydride (15 g, 1.3 mmol SnH/g of polymer). The suspension was purged with Ar for 10 min and a catalytic amount of AIBN was added. The suspension was heated to reflux until TLC control indicated complete conversion of the starting material (20 h). After filtration and removal of the solvent under reduced pressure, the crude product was purified by column chromatography as indicated below.

Barton−McCombie Deoxygenation Employing Tri-n-butyltin Hydride (GP8): Tri-*n*-butyltin hydride (1.5 equiv.) was dissolved in toluene in a Schlenk flask. The solution was purged with Ar for 10 min and was then heated to reflux. The xanthate (*S,R/S,S*)-**5** (1.0 equiv.) dissolved in 10 ml of toluene was added dropwise by canula over a period of 3 h. During the addition a sat. solution of AIBN in toluene was added dropwise by canula (ca. 0.1 equiv.) and the solution was stirred under reflux overnight. After conversion of the starting material had been indicated by TLC the solvent was removed under reduced pressure and directly subjected to chromatographic purification as indicated.

(4S)-4-(Benzyloxy)methyl-2,2-dimethyl-1,3-dioxane [(*S*)-**5a**]: According to GP8, 1.71 g (5.0 mmol) of (*S,S/R*)-**4a** was deoxygenated employing 2.2 g of tri-*n*-butyltin hydride in 200 ml of toluene. Column chromatography (SiO_2, pentane/Et_2O 5:1) gave (*S*)-**5a** as a colourless oil. − Yield: 1.05 g; 89%. − $[\alpha]_D^{25}$ = +7.9 (*c* = 1.7, $CHCl_3$). − IR (film): $\tilde{\nu}$ = 3088 cm^{-1} (w), 3063 (w), 2992 (s), 2940 (s), 2919 (s), 2866 (s), 1515 (w), 1497 (m), 1454 (s), 1381 (vs), 1370 (vs), 1314 (m), 1272 (s), 1239 (m), 1199 (vs), 1170 (vs), 1104 (vs), 1052 (s), 970 (m), 739 (m). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.41 (s, 3 H, CH_3), 1.48 (s, 3 H, CH_3), 1.44-1.52 (m, 1 H, $HCCHHCH$) 1.57−1.74 (m, 1 H, $HCCHHCH$), 3.37 (dd, *J* = 9.8 Hz, *J* = 4.9 Hz, 1 H, $CHHOBn$), 3.50 (dd, *J* = 9.8 Hz, *J* = 5.7 Hz, 1 H, $CHHOBn$), 3.84 (ddd, *J* = 12.0 Hz, *J* = 5.4 Hz, *J* = 2.0 Hz, 1 H, $CHHCH_2CH$), 3.98 (td, *J* = 12.0 Hz, *J* = 2.7 Hz, 1 H, $CHHCH_2CH$), 4.13 (m, 1 H, $CHCH_2OBn$), 4.55 (d, *J* = 12.2 Hz, 1 H, $OCHHPh$), 4.61 (d, *J* = 12.2 Hz, 1 H, $OCHHPh$), 7.27 (m, 5 H, aromatic H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.2 (CH_3), 29.9 (CH_3), 28.1 ($HCCH_2CH$), 59.6 (CH_2), 68.4 ($CHCH_2OBn$), 73.5 (CH_2), 73.7 (OCH_2Ph), 98.4 [$C(CH_3)_2$], 127.7, 127.8, 128.4, 138.3 (aromatic C). − MS (CI, isobutane); *m/z* (%): 237 (M^++1, 25), 236 (M^++1, 1), 181 (10), 179 (100), 178 (4), 107 (5) (91). − $C_{14}H_{20}O_3$ (236.31): calcd. C 71.16, H 8.53; found C 70.96, H 8.58.

(4S,6S)-4,6-Diethyl-2,2-dimethyl-1,3-dioxane [(*S,S*)-**5b**]: According to GP7, (*S,S*)-**5b** was obtained as a colourless oil after purification by column chromatography (SiO_2; pentane/Et_2O 15:1). Yield: 0.27 g; 53%. − $[\alpha]_D^{23}$ = +51.9 (*c* = 1.0, $CHCl_3$). − IR ($CHCl_3$): $\tilde{\nu}$ = 3000−2800 cm^{-1} (s), 1464 (s), 1379 (s), 1367 (s), 1281 (s), 1227 (s), 1181 (s), 1143 (s), 1049 (s), 1020 (s), 989 (s), 981 (s), 955 (m), 940 (m), 887 (s). − ^{1}H NMR (300 MHz, $CDCl_3$): δ =

0.91 (t, J = 7.4 Hz, 6 H, CH_2CH_3), 1.35 [s, 6 H, $C(CH_3)_2$], 1.39−1.61 (m, 6 H, CH_2CH_3, $CHCH_2CH$), 3.68 (qd, J = 7.4 Hz, J = 6.0 Hz, 2 H, $CHCH_2CH_3$). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 9.8 (2 × CH_2CH_3), 24.8 [$C(CH_3)_2$], 28.9 (2 × CH_2CH_3), 38.2 ($CHCH_2CH$), 68.1 (2 × $CHCH_2CH_3$), 100.1 [$C(CH_3)_2$]. − MS (EI, 70 eV,); *m/z* (%): 157 (17), 97 (67), 85 (13), 69 (7), 59 (100), 57 (15), 56 (16), 55 (72), 43 (45), 41 (14), 39 (6). − $C_{10}H_{20}O_2$ (172.27): calcd. C 69.72, H 11.70; found C 70.20, H 11.97.

(4S,6S)-4,6-Diisopropyl-2,2-dimethyl-1,3-dioxane [(*S,S*)-**5c**]: According to GP7, (*S,S*)-**5c** was obtained as a colourless oil after purification by column chromatography (SiO_2; petroleum ether/Et_2O 15:1). Yield: 0.53 g; 89%. − $[\alpha]_D^{23}$ = +65.3 (*c* = 1.0, $CHCl_3$). − IR ($CHCl_3$): $\tilde{\nu}$ = 3000−2800 cm^{-1} (s), 1470 (s), 1378 (s), 1317 (w), 1303 (w), 1226 (s), 1184 (s), 1170 (s), 1145 (s), 1127 (m), 1107 (w), 1072 (s), 1057 (s), 1013 (s), 973 (w), 927 (w), 909 (w), 861 (m), 798 (w), 760 (s). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.79 (d, J = 6.6 Hz, 6 H, $CHCH_3$), 0.85 (d, J = 6.6 Hz, 6 H, $CHCH_3$), 1.25 [s, 6 H, $C(CH_3)_2$], 1.47−1.60 [m, 4 H, CH_2, $CH(CH_3)_2$], 3.22−3.38 [m, 2 H, $CHCH(CH_3)_2$]. − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.2 ($CHCH_3$), 19.4 ($CHCH_3$), 24.9 [$C(CH_3)_2$], 33.6 [$CH(CH_3)_2$], 34.9 (CH_2), 72.5 [$CHCH(CH_3)_2$], 100.7 [$C(CH_3)_2$]. − MS (EI, 70 eV); *m/z* (%): 185 (8), 154 (5), 149 (5), 125 (9), 111 (5), 109 (5), 99 (13), 97 (8), 95 (8), 91 (9), 85 (10), 84 (5), 83 (15), 82 (6), 81 (19), 79 (5), 77 (6), 75 (9), 73 (5), 71 (17), 70 (25), 69 (69), 67 (10), 61 (9), 60 (10), 59 (27), 58 (8), 57 (34), 56 (9), 55 (31), 53 (6), 51 (5), 45 (26), 44 (14), 43 (100), 42 (8), 41 (39), 39 (18). − $C_{12}H_{24}O_2$ (200.30): calcd. C 71.96, H 12.08; found C 71.75, H 12.12.

(4S,6S)-(+)-4,6-Dibenzyl-2,2dimethyl-1,3-dioxane [(*S,S*)-**5d**]: According to GP7, (*S,S*)-**5d** was obtained as a colourless oil after purification by column chromatography (SiO_2; petroleum ether/Et_2O 30:1). − Yield: 0.44 g; 75%. − $[\alpha]_D^{23}$ = +47.64 (*c* = 1.0, $CHCl_3$). − IR (film): $\tilde{\nu}$ = 3090−3030 cm^{-1} (m), 3000−2800 (s), 2000−1650 (w), 1604 (m), 1585 (w), 1497 (s), 1454 (s), 1379 (s), 1363 (s), 1224 (s), 1166 (s), 1114 (s), 1088 (s), 1042 (s), 1017 (s), 990 (s), 943 (s), 927 (m), 904 (s), 873 (w), 852 (m), 817 (m) 748 (s), 700 (s). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.9 (s, 3 H, CCH_3), 0.92 (s, 3 H, CCH_3), 1.25−1.38 (m, 2 H, $CHCH_2CH$), 2.64 (dd, J = 13.9 Hz, J = 6.1 Hz, 2 H, $CHHPh$), 2.87 (dd, J = 13.9 Hz, J = 7.1 Hz, 2 H, $CHHPh$), 4.08 (m, 2 H, $CHBn$), 7.12−7.30 (m, 10 H, aromatic H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.9 [$C(CH_3)_2$], 36.6 ($CHCH_2CH$), 41.0 (CH_2Ph), 66.5 (CHBn), 100.4 [$C(CH_3)_2$], 125.1, 127.1, 128.1, 137.3 (aromatic C). − MS (EI, 70 eV); *m/z* (%): 205 (12), 148 (8), 147 (83), 130 (5), 129 (36), 119 (10), 118 (14), 117 (49), 115 (6), 92 (9), 91 (100), 65 (10), 59 (25). − $C_{20}H_{24}O_2$ (296.41): calcd. C 81.04, H 8.16; found C 80.70, H 8.23.

(4R,6S)-4-Benzyloxy-2,2,6-trimethyl-1,3-dioxane [(*S,S*)-**5e**]: According to GP7, (*S,S*)-**5e** was obtained as a colourless oil after purification by column chromatography (SiO_2; petroleum ether/Et_2O 10:1). − Yield: 0.39 g; 78%. − $[\alpha]_D^{23}$ = +48.7 (*c* = 1.0, $CHCl_3$). − IR ($CHCl_3$): $\tilde{\nu}$ = 3090−3030 cm^{-1} (m), 3000−2800 (s, br), 2000−1650 (w), 1604 (w), 1587 (w), 1497 (s), 1454 (s), 1380 (s), 1324 (m), 1226 (s), 1181 (s), 1144 (s), 1115 (s), 1043 (s), 1028 (s), 1011 (s), 955 (s), 907 (m), 863 (w), 839 (m), 822 (m), 754 (s), 698 (s). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.19 (d, J = 6.3 Hz, 3 H, $CHCH_3$), 1.38 (s, 3 H, CCH_3), 1.40 (s, 3 H, CCH_3), 1.51 (ddd, J = 12.6 Hz, J = 9.3 Hz, J = 6.3 Hz, 1 H, $CHCHHCH$), 1.69 (ddd, J = 12.9 Hz, J = 9.1 Hz, J = 5.8 Hz, 1 H, $CHCHHCH$), 3.43 (dd, J = 10.4 Hz, J = 4.1 Hz, 1 H, $CHHOBn$), 3.50 (dd, ^{J} = 10.4 Hz, J = 6.3 Hz, 1 H, $CHHOBn$), 3.96 (quin.d, J = 9.3 Hz, J = 6.1 Hz, 1 H, $CHCH_3$), 4.06 (tdd, J = 9.3 Hz, J = 6.3 Hz, J = 4.1 Hz, 1 H, $CHCH_2OBn$), 4.55 (d, J = 12.4 Hz, 1 H, $CHHPh$), 4.62 (d, J = 12.1 Hz, 1 H, $CHHPh$), 7.24−7.35 (m, 5 H, aromatic H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.3 ($CHCH_3$), 25.6 (CCH_3), 25.7 (CCH_3), 36.7 ($CHCH_2CH$), 63.3 ($CHCH_3$), 66.8 ($CHCH_2OBn$), 73.3 (CH_2Ph), 73.9 (CH_2OBn), 100.8 [$C(CH_3)_2$], 128.2, 128.3, 128.9, 138.9 (aromatic C). − MS (EI, 70 eV); *m/z* (%): 235 (10, $M^+ - CH_3$), 192 (15), 174 (6), 129 (27), 106 (15), 105 (10), 92 (21), 91 (100), 85 (7), 77 (5), 71 (13), 65 (6), 59 (59), 43 (28), 41 (10), 39 (7). − $C_{15}H_{22}O_3$ (250.31): calcd. C 71.98, H 8.86; found C 72.36, H 9.14.

(4S,6S)-4-Benzyl-6-[(benzyloxy)methyl]-2,2-dimethyl-1,3-dioxane [(*S,S*)-**5f**]: According to GP8, 550 mg (1.30 mmol) of (*S,R/S,S*)-**4f** was deoxygenated yielding (*S,S*)-**5f** after chromatographic purification (SiO_2, pentane/Et_2O 5:1) as a colourless oil. − Yield: 385 mg; 91%. − $[\alpha]_D^{25}$ = +38.8 (*c* = 1.25, $CHCl_3$). − IR (film): $\tilde{\nu}$ = 3086 cm^{-1} (m), 3062 (m), 3082 (m), 2992 (s), 2986 (s), 2935 (s), 2860 (s), 1604 (m), 1496 (s), 1454 (s), 1396 (vs), 1225 (vs), 1166 (vs), 1116 (vs), 1028 (s), 1003 (m), 750 (s). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.32 (s, 3 H, CH_3), 1.39 (s, 3 H, CH_3), 1.50−1.67 (m, 2 H, $HCCHHCH$), 2.66 (dd, J = 13.8 Hz, J = 6.4 Hz, 1 H, $CHHPh$), 2.89 (dd, J = 13.8 Hz, J = 7.0 Hz, 1 H, $CHHPh$), 3.34−3.48 (m, 2 H, $CHBn$,$CHCH_2OBn$), 4.05 (m, 2 H, CH_2OBn), 4.45 (d, J = 12.4 Hz, 1 H, $OCHHPh$), 4.57 (d, J = 12.2 Hz, 1 H, $OCHHPh$), 7.27 (m, 10 H, aromatic H). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.9 (2 × CH_3), 34.2 ($HCCH_2CH$), 42.0 (CH_2Ph), 66.3 (CH), 67.2 (CH), 71.6 (CH_2OBn), 73.2 (OCH_2Ph), 100.4 [$C(CH_3)_2$], 126.2, 127.5, 127.6, 128.2, 128.3, 129.2, 138.2, 138.3 (aromatic C). − MS (CI, isobutane); *m/z* (%): 327 (M^++1, 78), 307 (4), 270 (20), 269 (100), 251 (29), 235 (13), 233 (35), 177 (9), 166 (10), 107 (5). − $C_{21}H_{26}O_3$ (326.43): calcd. C 77.27, H 8.03; found C 77.58, H 8.32.

(4S,6S)-2,2-Dimethyl-4,6-bis[2-(1,1,1-trimethylsilyl)ethoxymethyl]-1,3-dioxane [(*S,S*)-**5g**]: According to GP8, 330 mg (0.68 mmol) of (*S,S*)-**4g** was deoxygenated with 290 mg (1.00 mmol) of tri-*n*-butyltin hydride in 100 ml of toluene to yield (*S,S*)-**5g** as a colourless oil after column chromatography (SiO_2, pentane/Et_2O 8:1). − Yield: 250 mg; 98%. − $[\alpha]_D^{25}$ = +6.1 (*c* = 1.0, CH_3COCH_3). − IR (film): $\tilde{\nu}$ = 2988 cm^{-1} (s), 2952 (s), 2917 (s), 2896 (s), 2859 (s), 1456 (m), 1413 (m), 1379 (s), 1249 (vs), 1225 (vs), 1174 (s), 1117 (vs), 1043 (m), 1010 (m), 954 (m), 860 (vs), 838 (vs). − ^{1}H NMR: (300 MHz, $CDCl_3$): δ = −0.03 (s, 18 H, $SiCH_3$), 0.89 (t, J = 7.7 Hz, 4 H, CH_2Si), 1.39 [s, 6 H, $C(CH_3)_2$], 1.63 (t, J = 7.7 Hz, 2 H, $CHCH_2CH$), 3.28 (dd, J = 10.1 Hz, J = 4.4 Hz, 2 H, $CHCHHO$), 3.42 (dd, J = 10.1 Hz, J = 6.0 Hz, 2 H, $CHCHHO$) 3.47 (t, J = 7.7 Hz, 4 H, OCH_2CH_2Si), 4.08 (m, 2 H, $CHCH_2O$). − ^{13}C NMR (75 MHz, $CDCl_3$): δ = −0.3 ($SiCH_3$), 19.2 (CH_2Si), 26.0 [$C(CH_3)_2$], 32.8 ($CHCH_2CH$), 67.4 ($CHCH_2O$), 69.5 ($CHCH_2OCH_2$), 74.5 ($CHCH_2OCH_2$), 101.0 [$C(CH_3)_2$]. − MS (EI, 70 eV); *m/z* (%): 361 (3), 217 (3), 159 (9), 147 (4), 129 (6), 116 (7), 101 (45), 75 (11), 73 (100), 59 (100). − $C_{18}H_{40}O_4Si_2$ (376.47): calcd. C 57.42, H 10.70; found C 57.36 H 10.21.

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