# Practical Synthesis of Four Stereoisomers of 6-(*t*-Butyldiphenylsiloxy)-3,5-dimethyl-1-(triphenylmethoxy)hexane-2,4-diol via Dithiane Coupling with Oxirane

**Mitsuaki Ide, Keiji Tsunashima, and Masaya Nakata***

Department of Applied Chemistry, Faculty of Science and Technology, Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223-8522

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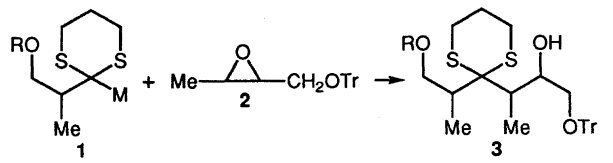
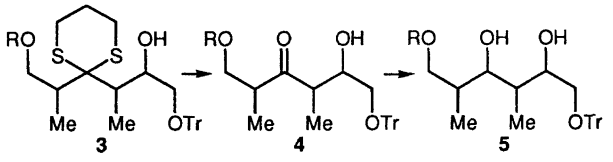
The anion derived from 2-substituted 1,3-dithiane derivative, (*S*)-2-[2-(*t*-butyldiphenylsiloxy)-1-methylethyl]-1,3-dithiane, with *n*-BuLi at room temperature (r.t.) in THF was subjected to coupling with 2,3-disubstituted oxirane, (2*S*, 3*S*)- or (2*S*,3*R*)-2,3-epoxy-1-(triphenylmethoxy)butane, at r.t., giving the coupling products in satisfactory yield. These coupling products were subjected to de-dithioacetalization, and the resulting carbonyl compounds were stereoselectively reduced to afford four stereoisomers of 6-(*t*-butyldiphenylsiloxy)-3,5-dimethyl-1-(triphenylmethoxy)hexane-2,4-diol.

In the preceding article[1] of this issue, we described the effective coupling reactions of 2-substituted 2-metallo-1,3-dithiane derivatives **1** with 2,3-disubstituted oxirane **2** (*trans*-oxirane) at room temperature (r.t.) to afford coupling products **3** in satisfactory yield (Eq. 1). This type of coupling reaction has been considered to be impractical because of the temperature-dependent instability of the dithianide anions and poor electrophilicity of 2,3-disubstituted oxiranes; therefore they have not been used in natural product syntheses. The above-mentioned success described in the preceding article,[1] however, would broaden the synthetic usefulness of 1,3-dithiane chemistry; namely the coupling product **3** would be converted into **5**, which has a sequential array of alternate Me and OH groups, via de-dithioacetalization (**3** to **4**) and reduction (**4** to **5**) (Eq. 2). This array is often found in the framework of natural products which are biogenetically synthesized from the propionate units. In this article we report the demonstration of this strategy.

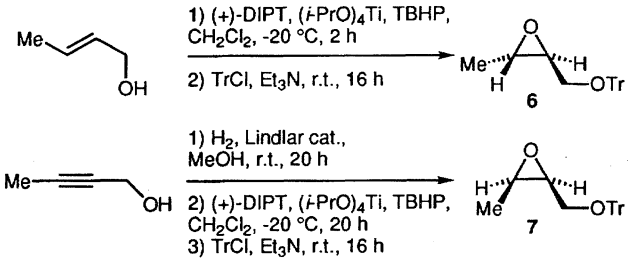



(1)



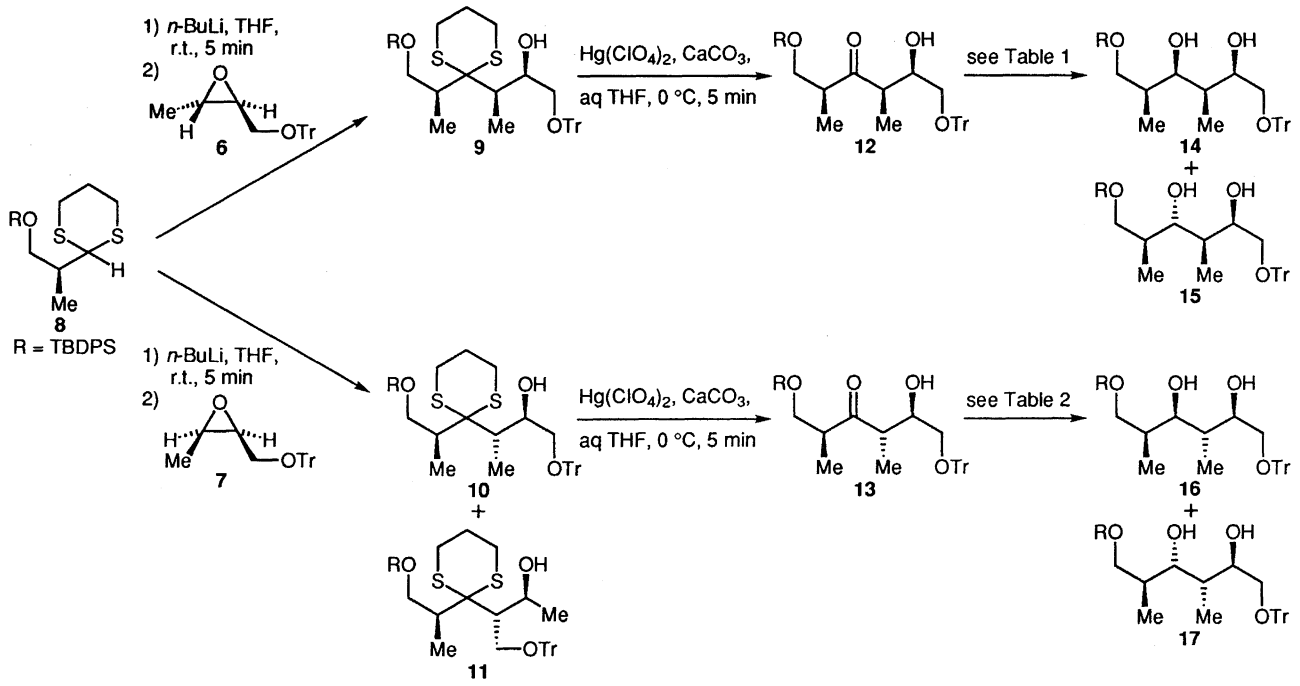

(2)

Both the chiral *trans*- and *cis*-oxiranes, **6** and **7**, were prepared from the corresponding (*E*)- and (*Z*)-2-buten-1-ol by Sharpless asymmetric epoxidation including in situ derivatization[2] (Scheme 1). The treatment of (*E*)-2-buten-1-ol with diisopropyl L-tartrate ((+)-DIPT), titanium(IV) isopropoxide, and *t*-butyl hydroperoxide (TBHP) in $CH_2Cl_2$ followed by in situ derivatization[2] with trityl chloride and triethylamine afforded *trans*-oxirane **6**[3] in 56% yield. The enantiomeric excess of **6** was determined to be 85% by $^1$H NMR analysis of the (*R*)- and (*S*)-$\alpha$-methoxy-$\alpha$-(trifluoromethyl)phenylacetate (MTPA esters)[4] of the corresponding intermediate epoxy alcohol[3,5] of **6** (see Experimental). (*Z*)-2-Buten-1-ol, prepared from 2-butyn-1-ol by hydrogenation[6] with hydrogen and Lindlar catalyst in MeOH, was converted into *cis*-oxirane **7** by the same procedure as described above for the preparation of **6**. The enantiomeric excess of **7** was 80% (see Experimental).



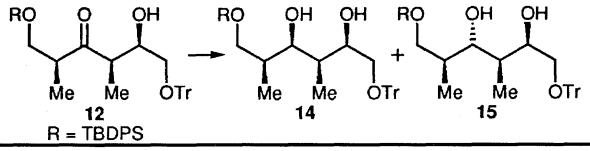

Scheme 1.

The coupling reaction of 2-substituted 1,3-dithiane derivative **8**[1] (nearly 100% ee) with *trans*-oxirane **6** was carried out by the almost same procedure as described in the preceding article;[1] namely, to a stirred solution of **8** (one molar amount) in THF was added at r.t. (20—25 °C) *n*-BuLi (1.2 molar amounts). After 5 min at r.t., *trans*-oxirane **6** (one molar amount) in THF was added and the mixture was stirred at r.t. for 3 h, giving the coupling product **9** in 70% yield as the sole coupling product (Scheme 2). On the other hand, the coupling reaction of **8** with *cis*-oxirane **7** proceeded faster (within 1 h) than the coupling reaction of **8** with **6**, giving the coupling product **10** and its regioisomer **11** in 73 and 8.5%




Scheme 2.

Table 1. Reduction of the Carbonyl Group in **12**




| Entry | Reagents | Solvent | Temp/°C | Time/h | Ratio, **14** : **15**[a] |
|---|---|---|---|---|---|
| 1 | DIBAH | $CH_2Cl_2$ | −78 | 0.5 | 45 : 55 |
| 2 | DIBAH | Ether | −78 | 0.5 | 87 : 13 |
| 3 | DIBAH[b] | THF | −78 | 0.5 | 82 : 18 |
| 4 | DIBAH[b] | THF | −100 | 0.5 | 100 : 0 |
| 5 | $ZnCl_2$, DIBAH[c] | Ether | −78 | 0.5 | 75 : 25 |
| 6 | $Me_4N[BH(OAc)_3]$[d] | AcOH/ MeCN | r.t. | 9 | 5 : 95 |
| 7 | $NaBH_4$, $CeCl_3$ | EtOH | r.t. | 1 | 71 : 29 |

a) Product ratio was based on $^1$H NMR analysis of the crude products after usual workup. All reactions proceeded cleanly without decomposition (checked by TLC). b) Ref. 8. c) Ref. 12. d) Ref. 9.

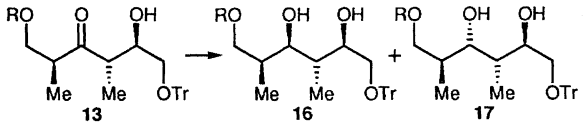
yields, respectively. Each coupling product (**9**, **10**, and **11**) was contaminated with the diastereomer originating from the enantiomer of oxirane **6** or **7**. These diastereomers could not be separated at this stage, were separated in the next stage of de-dithioacetalization.

De-dithioacetalization of **9** was realized by the treatment with $Hg(ClO_4)_2$ in aqueous THF[7] at 0 °C for 5 min to afford ketone **12** and its diastereomer in 73 and 5.9% yields, respectively, after chromatographic separation. By the same procedure, **10** was converted into ketone **13** and its diastereomer in 78 and 8.7% yields, respectively.

Next, we turned our attention to the crucial stereoselective reduction of ketones **12** and **13** in order to obtain the four possible stereoisomers **14**, **15**, **16**, and **17**. Relevant data for the reduction are shown in Tables 1 and 2. In the case of ketone **12**, reduction with diisobutylaluminium hydride (DIBAH) in THF at −100 °C[8] provided **14** in 89% yield as the sole reduction product (Table 1, Entry 4). In contrast, the best selectivity in favor of **15** was obtained by the Evans procedure[9] using tetramethylammonium triacetoxyborohydride in acetonitrile and acetic acid, affording in 91% combined yield a chromatographically separable mixture of **14** and **15** in a ratio of 5 : 95 (Table 1, Entry 6). The same conditions could be applied to reduction of ketone **13**; the ratio of **16** : **17** was 89 : 11 in DIBAH reduction (Table 2, Entry 4) and 0 : 100 in $Me_4N[BH(OAc)_3]$ reduction (Table 2, Entry 6).

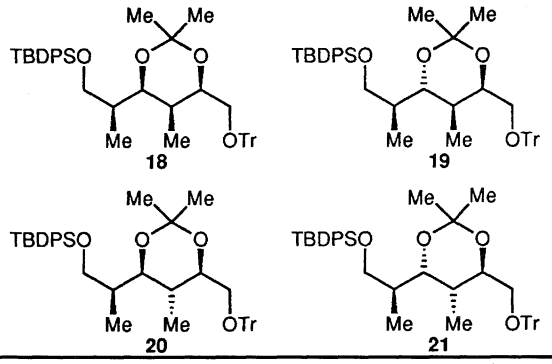
The configurations of these diols (**14**, **15**, **16**, and **17**) were determined by $^{13}$C NMR analysis of their corresponding ace-

Table 2. Reduction of the Carbonyl Group in **13**




| Entry | Reagents | Solvent | Temp/°C | Time/h | Ratio, **16** : **17**[a] |
|---|---|---|---|---|---|
| 1 | DIBAH | $CH_2Cl_2$ | −78 | 0.5 | 71 : 29 |
| 2 | DIBAH | Ether | −100 | 0.5 | 55 : 45 |
| 3 | DIBAH[b] | THF | −78 | 0.5 | 88 : 12 |
| 4 | DIBAH[b] | THF | −100 | 0.5 | 89 : 11 |
| 5 | $ZnCl_2$, DIBAH[c] | Ether | −78 | 0.5 | 70 : 30 |
| 6 | $Me_4N[BH(OAc)_3]$[d] | AcOH/ MeCN | −30 | 8 | 0 : 100 |
| 7 | $NaBH_4$, $CeCl_3$ | EtOH | r.t. | 1 | 18 : 82 |
| 8 | $Bu_3B$, $NaBH_4$ [e] | THF | −78 | 0.5 | 30 : 70 |
| 9 | $NaBH_4$ | MeOH | r.t. | 1 | 52 : 48 |
| 10 | $Zn(BH_4)_2$ [f] | Ether | −78 | 0.5 | 45 : 55 |
| 11 | $LiAlH_4$ | THF | 0 | 0.5 | 51 : 49 |

a) Product ratio was based on $^1$H NMR analysis of the crude products after usual workup. All reactions proceeded cleanly without decomposition (checked by TLC). b) Ref. 8. c) Ref. 12. d) Ref. 9. e) Ref. 13. f) Ref. 14.




| | Methyl carbon | Methyl carbon | Acetal carbon |
|---|---|---|---|
| *syn* 1,3-Diol acetonides[a] | 19.4±0.21 | 30.0±0.15 | 98.1±0.83 |
| **18** | 19.57 | 29.87 | 98.88 |
| **20** | 19.67 | 30.04 | 97.68 |
| *anti* 1,3-Diol acetonides[a] | 24.6±0.76 | 24.6±0.76 | 100.6±0.25 |
| **19** | 23.49 | 25.38 | 100.31 |
| **21** | 23.97 | 25.22 | 100.59 |

Fig. 1. $^{13}$C NMR chemical shifts of the methyl groups and acetal carbon of acetonides **18**, **19**, **20**, and **21**. a) Ref. 11.

tonides (**18**, **19**, **20**, and **21**, respectively) on the basis of the $^{13}$C chemical shift method proposed by Rychnovsky[10] and Evans.[11] The $^{13}$C chemical shifts of the methyl groups and acetal carbon of *syn*-1,3-diol acetonides (**18** and **20**) and *anti*-1,3-diol acetonides (**19** and **21**) are in the proposed range[11] (Fig. 1).

Since each enantiomer of 1,3-dithiane derivative **8** and oxirane **6** or **7** is readily prepared, it is apparent that other 12 stereoisomers are available by the present method. These compounds or their acetonides possess different protecting groups on their primary hydroxy groups; therefore, it would be possible to independently elongate a carbon chain toward the two directions. Moreover, the present method would be applied to structurally more complex substrates, and hence would broaden the synthetic usefulness of 1,3-dithiane chemistry.

## Experimental

The melting points were determined on a micro hot-stage Yanaco MP-S3 and were uncorrected. Optical rotations were measured on JASCO DIP-360 photoelectric polarimeters in chloroform, unless otherwise noted. IR spectra were recorded on a JASCO FT IR-200 spectrometer (neat, 25 °C) and $^1$H NMR spectra were on a JEOL GSX270 or a JEOL LAMBDA300 spectrometer in $CDCl_3$ at 25 °C using TMS as an internal standard, unless otherwise noted. Mass spectra (EI) were recorded on a JEOL GCmate mass spectrometer.

Silica-gel TLC and column chromatography were performed on a Merck TLC 60F-254 and a Fuji-Davison BW-820MH, respectively. Air- and/or moisture-sensitive reactions were carried out under an atmosphere of argon with oven-dried glassware. In general, the organic solvents were purified and dried by appropriate procedures, and evaporation and concentration were carried out under reduced pressure below 30 °C, unless otherwise noted.

**(2*S*,3*S*)-2,3-Epoxy-1-(triphenylmethoxy)butane (6).**[3] To a suspension of 3A molecular sieves powder (720 mg) in dry $CH_2Cl_2$ (9.0 ml) were added at −20 °C (+)-DIPT (58.5 mg, 0.250 mmol), (*E*)-2-buten-1-ol (300 mg, 4.16 mmol), and titanium(IV) isopropoxide (0.0614 ml, 0.208 mmol). After 15 min, 3.87 M (1 M = 1 mol $dm^{-3}$) TBHP in 2,2,4-trimethylpentane (2.15 ml, 8.32 mmol) was added and the mixture was stirred at −20 °C for 2 h. Trimethyl phosphite (0.491 ml, 4.16 mmol) was added and the mixture was gradually warmed to 0 °C during 1 h. A small portion of this solution of (2*S*,3*S*)-2,3-epoxy-1-butanol (ca. 0.13 ml, ca. 0.058 mmol) was drawn off for the MTPA ester formation (vide infra). Triethylamine (0.696 ml, 4.99 mmol) and TrCl (1.55 g, 5.55 mmol) were added and the mixture was stirred at r.t. for 16 h. The mixture was filtered with Celite and the filter cake was washed with hexane; the combined filtrate and washings were concentrated. The residue was dissolved in ethyl acetate and washed with 10% aqueous tartaric acid, saturated aqueous $NaHCO_3$, saturated aqueous NaCl, dried, and concentrated. The residue was chromatographed on silica gel (150 g) with 25 : 1 hexane–ethyl acetate to afford **6** (772 mg, 56%) as colorless crystals; $R_f$ = 0.48 (10 : 1 hexane–ethyl acetate); mp 122—124 °C (not recrystallized); IR (neat) 3060, 3020, 3000, 1490, 1450, 1220, 1080, 1060, 1030, 1000, 900, 870, 760, and 700 $cm^{-1}$; $^1$H NMR (270 MHz) $\delta$ = 1.30 (3H, d, $J$ = 5.0 Hz), 2.86—2.94 (2H, m), 3.14 (1H, dd, $J$ = 10.2, 5.2 Hz), 3.28 (1H, dd, $J$ = 10.2, 3.0 Hz), 7.18—7.35 (9H, m), and 7.43—7.48 (6H, m); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ = 17.42, 52.26, 58.17, 64.30, 86.61, 126.99, 127.80, 128.62, and 143.82. Found: C, 83.59; H, 6.57%. Calcd for $C_{23}H_{22}O_2$: C, 83.61; H, 6.71%.

**(*S*)-α-Methoxy-α-(trifluoromethyl)phenylacetate of (2*S*,3*S*)-2,3-Epoxy-1-butanol.** The above-mentioned solution of (2*S*,3*S*)-2,3-epoxy-1-butanol (ca. 0.063 ml, ca. 0.029 mmol) was diluted with dry $CH_2Cl_2$ (0.50 ml) and to this were added at 0 °C triethylamine (0.0202 ml, 0.145 mmol), 4-dimethylaminopyridine (DMAP) (3.5 mg, 0.0290 mmol), and (*S*)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride (0.0065 ml, 0.035 mmol). After 0.5 h at r.t., water was added and the mixture was extracted with hexane. The extracts were washed with saturated aqueous NaCl, dried, and concentrated. The residue was chromatographed on silica gel (1 g) with 3 : 1 hexane–ethyl acetate to afford MTPA ester (ca. 6.5 mg) as a colorless syrup: $R_f$ = 0.40 (3 : 1 hexane–ethyl acetate); $^1$H NMR (270 MHz, $C_6D_6$) $\delta$ = 0.82 (3H, d, $J$ = 5.0 Hz), 2.30—2.40 (2H, m), 3.42 (3H, s), 3.77 (1H, dd, $J$ = 12.0, 6.4 Hz), 4.03 (1H, dd, $J$ = 12.0, 3.8 Hz), 7.00—7.15 (3H, m), and 7.68 (2H, d, $J$ = 7.2 Hz). In addition, there are two distinct peaks at $\delta$ = 3.64 (1H, dd, $J$ = 12.0, 6.4 Hz) and 4.20 (1H, dd, $J$ = 12.0, 3.8 Hz), showing the %ee is 85.

**(*R*)-α-Methoxy-α-(trifluoromethyl)phenylacetate of (2*S*,3*S*)-2,3-Epoxy-1-butanol.** This was prepared from (2*S*,3*S*)-2,3-epoxy-1-butanol and (*R*)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride as described above: $R_f$ = 0.40 (3 : 1 hexane–ethyl acetate); $^1$H NMR (270 MHz, $C_6D_6$) $\delta$ = 0.82 (3H, d, $J$ = 5.0 Hz), 2.35—2.45 (2H, m), 3.42 (3H, s), 3.64 (1H, dd, $J$ = 12.0, 6.4 Hz), 4.20 (1H, dd, $J$ = 12.0, 3.8 Hz), 7.00—7.15 (3H, m), and 7.68 (2H, d, $J$ = 7.2 Hz). In addition, there are two distinct peaks at $\delta$ = 3.77 (1H, dd, $J$ = 12.0, 6.4 Hz) and 4.03 (1H, dd, $J$ = 12.0, 3.8 Hz), showing the %ee is 85.

**(2*S*,3*R*)-2,3-Epoxy-1-(triphenylmethoxy)butane (7).** To a suspension of 3A molecular sieves powder (720 mg) in dry $CH_2Cl_2$ (9.0 ml) were added at −20 °C (+)-DIPT (78.0 mg, 0.333 mmol), (*Z*)-2-buten-1-ol[6] (400 mg, 5.55 mmol), and titanium(IV) isopropoxide (0.0819 ml, 0.278 mmol). After 15 min, 3.87 M TBHP in 2,2,4-trimethylpentane (2.87 ml, 11.1 mmol) was added and the mixture was stirred at −20 °C for 20 h. Trimethyl phosphite (0.655 ml, 5.55 mmol) was added and the mixture was gradually warmed to 0 °C during 1 h. A small portion of this solution of (2*S*,3*R*)-2,3-epoxy-1-butanol (ca. 0.094 ml, ca. 0.058 mmol) was drawn off for the MTPA ester formation (vide infra). Triethylamine (0.928 ml, 6.66 mmol) and TrCl (1.55 g, 5.55 mmol) were added and the mixture was stirred at r.t. for 16 h. The mixture was filtered with Celite and the filter cake was washed with hexane; the combined filtrate and washings were concentrated. The residue was dissolved in ethyl acetate and washed with 10% aqueous tartaric acid, saturated aqueous $NaHCO_3$, saturated aqueous NaCl, dried, and concentrated. The residue was chromatographed on silica gel (200 g) with 25 : 1 hexane–ethyl acetate to afford **7** (965 mg, 53%) as colorless crystals: $R_f$ = 0.44 (10 : 1 hexane–ethyl acetate); mp 72—74 °C (not recrystallized); IR (neat) 3060, 3020, 3000, 1490, 1450, 1220, 1090, 1070, 1030, 980, 900, 760, 750, and 700 $cm^{-1}$; $^1$H NMR (270 MHz) $\delta$ = 1.12 (3H, d, $J$ = 5.4 Hz), 3.03—3.20 (3H, m), 3.25—3.37 (1H, m), 7.20—7.35 and 7.44—7.50 (total 15H, m); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ = 13.32, 52.05, 55.25, 62.00, 86.75, 127.02, 127.81, 128.59, and 143.77. Found: C, 83.62; H, 6.68%. Calcd for $C_{23}H_{22}O_2$: C, 83.61; H, 6.71%.

**(*S*)-α-Methoxy-α-(trifluoromethyl)phenylacetate of (2*S*,3*R*)-2,3-Epoxy-1-butanol.** The above-mentioned solution of (2*S*,3*R*)-2,3-epoxy-1-butanol (ca. 0.047 ml, ca. 0.029 mmol) was diluted with dry $CH_2Cl_2$ (0.50 ml) and to this were added at 0 °C triethylamine (0.0202 ml, 0.145 mmol), DMAP (3.5 mg, 0.0290 mmol), and (*S*)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride (0.0065 ml, 0.035 mmol). After 0.5 h at r.t., water was added and the mixture was extracted with hexane. The extracts were washed with saturated aqueous NaCl, dried, and concentrated. The residue was chromatographed on silica gel (1 g) with 3 : 1 hexane–ethyl acetate to afford MTPA ester (ca. 5.9 mg) as a colorless syrup: $R_f$ = 0.59 (3 : 1 hexane–ethyl acetate); $^1$H NMR (270 MHz, $C_6D_6$) $\delta$ = 0.79 (3H, d, $J$ = 5.0 Hz), 2.50 (1H, dq, $J$ = 5.0, 4.0 Hz), 2.68 (1H, ddd, $J$ = 7.0, 4.0, 4.0 Hz), 3.42 (3H, s), 3.94 (1H, dd, $J$ = 12.0, 4.0 Hz), 4.06 (1H, dd, $J$ = 12.0, 7.0 Hz), 7.00—7.15 (3H, m), and 7.68 (2H, d, $J$ = 7.0 Hz). In addition, there is a distinct peak at $\delta$ = 2.75 (1H, ddd, $J$ = 7.0, 4.0, 4.0 Hz), showing the %ee is 80.

**(*R*)-α-Methoxy-α-(trifluoromethyl)phenylacetate of (2*S*,3*R*)-2,3-Epoxy-1-butanol.** This was prepared from (2*S*,3*R*)-2,3-epoxy-1-butanol and (*R*)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride as described above: $R_f$ = 0.59 (3 : 1 hexane–ethyl acetate); $^1$H NMR (270 MHz, $C_6D_6$) $\delta$ = 0.79 (3H, d, $J$ = 5.0 Hz), 2.50 (1H, dq, $J$ = 5.0, 4.0 Hz), 2.75 (1H, ddd, $J$ = 7.0, 4.0, 4.0 Hz), 3.42 (3H, s), 3.89 (1H, dd, $J$ = 12.0, 4.0 Hz), 4.01 (1H, dd, $J$ = 12.0, 7.0 Hz), 7.00—7.15 (3H, m), and 7.68 (2H, d, $J$ = 7.0 Hz). In addition, there is a distinct peak at $\delta$ = 2.68 (1H, ddd, $J$ = 7.0, 4.0, 4.0 Hz), showing the %ee is 80.

**(2*R*,3*R*)-3-{2-[(*S*)-2-(*t*-Butyldiphenylsiloxy)-1-methylethyl]-1,3-dithian-2-yl}-1-(triphenylmethoxy)-2-butanol (9).** To a stirred solution of **8** (510 mg, 1.22 mmol) in dry THF (5.0 ml) was added at r.t. 3.02 M *n*-BuLi in hexane (0.486 ml, 1.47 mmol). After 5 min at r.t., a solution of **6** (404 mg, 1.22 mmol) in dry THF (2.0 ml) was added. A red color once faded away, but soon returned. After 3 h at r.t., saturated aqueous $NH_4Cl$ was added and the mixture was extracted with ethyl acetate. The extracts were washed

with saturated aqueous NaCl, dried, and concentrated. The residue was chromatographed on silica gel (50 g) with 20 : 1 hexane–ethyl acetate to afford **9** (640 mg, 70%) as colorless crystals: $R_f = 0.36$ (10 : 1 hexane–ethyl acetate); mp 46—48 °C (not recrystallized); IR (neat) 3480, 2960, 2930, 2900, 2860, 1490, 1470, 1450, 1430, 1220, 1110, 1070, 1030, 820, 760, and 700 $cm^{-1}$; $^1H$ NMR (270 MHz) $\delta = 0.75$ (3H, d, $J = 7.0$ Hz), 1.06 (9H, s), 1.34 (3H, d, $J = 7.0$ Hz), 1.70—1.95 (2H, m), 2.13 (1H, q, $J = 7.8$ Hz), 2.40—2.85 (6H, m), 2.87 (1H, dd, $J = 9.0$, 7.0 Hz), 3.18 (1H, dd, $J = 9.0$, 6.0 Hz), 3.68 (1H, dd, $J = 8.8$, 8.8 Hz), 4.22 (1H, dd, $J = 8.8$, 3.0 Hz), 4.73 (1H, br m), and 7.17—7.76 (25H, m). In addition, there are two distinct peaks at $\delta = 0.85$ (3H, d, $J = 7.0$ Hz) and 4.29 (1H, dd, $J = 8.8$, 3.0 Hz), showing the diastereomer ratio is 12.3 : 1. Found: C, 73.75; H, 7.55%. Calcd for $C_{46}H_{54}O_3SiS_2$: C, 73.95; H, 7.28%.

**(2*R*,3*S*)-3-{2-[(*S*)-2-(*t*-Butyldiphenylsiloxy)-1-methylethyl]-1,3-dithian-2-yl}-1-(triphenylmethoxy)-2-butanol (10) and (2*S*,3*S*)-3-{2-[(*S*)-2-(*t*-Butyldiphenylsiloxy)-1-methylethyl]-1,3-dithian-2-yl}-4-(triphenylmethoxy)-2-butanol (11).** To a stirred solution of **8** (1.07 g, 2.57 mmol) in dry THF (10 ml) was added at r.t. 3.02 M *n*-BuLi in hexane (1.02 ml, 3.08 mmol). After 5 min at r.t., a solution of **7** (848 mg, 2.57 mmol) in dry THF (4.0 ml) was added. A red color once faded away, but soon returned. After 1 h at r.t., saturated aqueous $NH_4Cl$ was added and the mixture was extracted with ethyl acetate. The extracts were washed with saturated aqueous NaCl, dried, and concentrated. The residue was chromatographed on silica gel (100 g) with 20 : 1 hexane–ethyl acetate to afford **10** (1.41 g, 73%) and **11** (164 mg, 8.5%) as colorless crystals.

**10:** $R_f = 0.30$ (10 : 1 hexane–ethyl acetate); mp 36—37 °C (not recrystallized); IR (neat) 3400, 3000, 2950, 2930, 2890, 2860, 1490, 1470, 1450, 1430, 1220, 1110, 1080, 1030, 820, 760, and 700 $cm^{-1}$; $^1H$ NMR (270 MHz) $\delta = 0.88$ (3H, d, $J = 7.0$ Hz), 1.05 (9H, s), 1.24 (3H, d, $J = 7.0$ Hz), 1.75—1.87 (2H, m), 2.35—2.70 (5H, m), 2.85—2.95 (1H, m), 2.98 (1H, dd, $J = 9.8$, 6.0 Hz), 3.52 (1H, dd, $J = 9.8$, 2.4 Hz), 3.67 (1H, dd, $J = 9.5$, 9.5 Hz), 3.65—3.80 (1H, br), 4.10—4.25 (1H, m), 4.26 (1H, dd, $J = 9.5$, 2.8 Hz), and 7.17—7.70 (25H, m). In addition, there is a distinct peak at $\delta = 0.72$ (3H, d, $J = 7.0$ Hz), showing the diastereomer ratio is 9 : 1. Found: C, 73.75; H, 7.48%. Calcd for $C_{46}H_{54}O_3SiS_2$: C, 73.95; H, 7.28%.

**11:** $R_f = 0.16$ (10 : 1 hexane–ethyl acetate); mp 57—58 °C (not recrystallized); IR (neat) 3520, 3400, 3000, 2960, 2930, 2900, 2860, 1490, 1470, 1450, 1430, 1220, 1110, 1080, 1060, 1030, 820, 760, and 700 $cm^{-1}$; $^1H$ NMR (270 MHz) $\delta = 1.03$ (9H, s), 1.10 (3H, d, $J = 7.0$ Hz), 1.27 (3H, d, $J = 7.0$ Hz), 1.65—1.80 (2H, m), 2.15—2.30 (1H, m), 2.40—2.70 (5H, m), 3.14 (1H, dd, $J = 9.0$, 9.0 Hz), 3.43 (1H, dd, $J = 9.0$, 9.0 Hz), 3.75 (1H, dd, $J = 9.2$, 2.2 Hz), 3.78 (1H, d, $J = 8.0$ Hz), 3.87 (1H, dd, $J = 9.2$, 2.5 Hz), 4.00—4.15 (1H, br m), and 7.17—7.65 (25H, m). In addition, there are two distinct peaks at $\delta = 3.29$ (1H, dd, $J = 9.0$, 9.0 Hz) and 3.55 (1H, dd, $J = 9.0$, 9.0 Hz), showing the diastereomer ratio is 9 : 1. Found: C, 73.85; H, 7.66%. Calcd for $C_{46}H_{54}O_3SiS_2$: C, 73.95; H, 7.28%.

**(2*S*,4*R*,5*R*)-1-(*t*-Butyldiphenylsiloxy)-5-hydroxy-2,4-dimethyl-6-(triphenylmethoxy)hexan-3-one (12) and Its Diastereomer.** To a stirred solution of **9** (638 mg, 0.854 mmol) in 10 : 1 THF–$H_2O$ (11 ml) were added at 0 °C $CaCO_3$ (854 mg, 8.53 mmol) and Hg$(ClO_4)_2 \cdot 3H_2O$ (1.16 g, 2.56 mmol). After 5 min at 0 °C, saturated aqueous $NaHCO_3$ was added and the mixture was filtered with Celite. The filter cake was washed with ethyl acetate and the combined filtrate and washings were separated. The aqueous layer was extracted with ethyl acetate and the combined organic layers were washed with saturated aqueous NaCl, dried, and concentrated. The residue was chromatographed on silica gel (100 g) with 20 : 1 hexane–ethyl acetate to afford **12** (409 mg, 73%) and its diastereomer (33.2 mg, 5.9%) as colorless syrups.

**12:** $R_f = 0.44$ (8 : 1 hexane–ethyl acetate); $[\alpha]_D^{27}$ +25.0, $[\alpha]_{435}^{27}$ +54.3 (*c* 0.90); IR (neat) 3520, 3060, 3020, 2960, 2930, 2880, 2860, 1700, 1490, 1470, 1450, 1430, 1220, 1110, 1090, 1080, 1030, 1000, 820, 760, and 700 $cm^{-1}$; $^1H$ NMR (270 MHz) $\delta = 0.97$ (3H, d, $J = 7.0$ Hz), 0.98 (3H, d, $J = 7.0$ Hz), 1.03 (9H, s), 2.88—3.10 (4H, m), 3.26 (1H, dd, $J = 9.2$, 6.8 Hz), 3.57 (1H, dd, $J = 10.0$, 5.8 Hz), 3.82 (1H, dd, $J = 10.0$, 8.2 Hz), 4.26—4.35 (1H, m), 7.17—7.47 and 7.60—7.68 (total 25H, m); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta = 9.11$, 13.50, 19.08, 26.78, 47.13, 47.74, 64.50, 66.41, 69.45, 86.67, 127.01, 127.73, 127.81, 128.57, 129.77, 132.98, 133.13, 135.50, 135.54, 143.82, and 217.88. Found: C, 78.85; H, 7.62%. Calcd for $C_{46}H_{48}O_4Si$: C, 78.62; H, 7.36%.

**Diastereomer of 12:** $R_f = 0.38$ (8 : 1 hexane–ethyl acetate); $[\alpha]_D^{27}$ +10.1, $[\alpha]_{435}^{27}$ +23.4 (*c* 1.01); IR (neat) 3480, 3060, 3020, 2960, 2930, 2860, 1710, 1490, 1470, 1450, 1430, 1220, 1110, 1090, 1030, 1000, 820, 760, and 700 $cm^{-1}$; $^1H$ NMR (270 MHz) $\delta = 0.87$ (3H, d, $J = 7.0$ Hz), 1.01 (9H, s), 1.03 (3H, d, $J = 7.0$ Hz), 2.76 (1H, br), 2.90—3.05 (2H, m), 3.09 (1H, dd, $J = 9.4$, 5.8 Hz), 3.19 (1H, dd, $J = 9.4$, 6.2 Hz), 3.54 (1H, dd, $J = 10.0$, 5.0 Hz), 3.82 (1H, dd, $J = 10.0$, 8.0 Hz), 4.09 (1H, br m), 7.19—7.46 and 7.60—7.67 (total 25H, m); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta = 9.92$, 13.19, 19.08, 26.71, 47.49, 47.70, 64.70, 65.86, 70.57, 86.77, 127.11, 127.68, 127.86, 128.59, 129.69, 133.08, 133.29, 135.51, 135.56, 143.70, and 217.02. Found: *m/z* 656.3312. Calcd for $C_{43}H_{48}O_4Si$: $M^+$, 656.3322.

**(2*S*,4*S*,5*R*)-1-(*t*-Butyldiphenylsiloxy)-5-hydroxy-2,4-dimethyl-6-(triphenylmethoxy)hexan-3-one (13) and Its Diastereomer.** To a stirred solution of **10** (998 mg, 1.34 mmol) in 10 : 1 THF–$H_2O$ (22 ml) were added at 0 °C $CaCO_3$ (1.34 g, 13.4 mmol) and Hg$(ClO_4)_2 \cdot 3H_2O$ (1.82 g, 4.01 mmol). After 5 min at 0 °C, saturated aqueous $NaHCO_3$ was added and the mixture was filtered with Celite. The filter cake was washed with ethyl acetate and the combined filtrate and washings were separated. The aqueous layer was extracted with ethyl acetate and the combined organic layers were washed with saturated aqueous NaCl, dried, and concentrated. The residue was chromatographed on silica gel (150 g) with 20 : 1 hexane–ethyl acetate to afford **13** (686 mg, 78%) and its diastereomer (76.2 mg, 8.7%) as colorless syrups.

**13:** $R_f = 0.38$ (8 : 1 hexane–ethyl acetate); $[\alpha]_D^{27}$ +17.9, $[\alpha]_{435}^{27}$ +36.7 (*c* 1.21); IR (neat) 3480, 3070, 3020, 2960, 2930, 2860, 1710, 1490, 1470, 1450, 1430, 1220, 1110, 1090, 1080, 1030, 1000, 820, 760, and 700 $cm^{-1}$; $^1H$ NMR (270 MHz) $\delta = 0.88$ (3H, d, $J = 7.0$ Hz), 1.01 (9H, s), 1.02 (3H, d, $J = 7.0$ Hz), 2.85—2.98 (1H, m), 3.00—3.12 (2H, m), 3.15 (2H, d, $J = 5.5$ Hz), 3.54 (1H, dd, $J = 10.0$, 5.0 Hz), 3.83 (1H, dd, $J = 10.0$, 7.8 Hz), 3.84—3.93 (1H, m), 7.20—7.47 and 7.61—7.67 (total 25H, m); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta = 12.76$, 13.19, 19.08, 26.71, 47.37, 48.94, 65.50, 65.57, 73.15, 86.74, 127.07, 127.65, 127.85, 128.57, 129.67, 133.13, 133.32, 135.51, 135.58, 143.72, and 217.53. Found: C, 78.42; H, 7.60%. Calcd for $C_{46}H_{48}O_4Si$: C, 78.62; H, 7.36%.

**Diastereomer of 13:** $R_f = 0.45$ (8 : 1 hexane–ethyl acetate); $[\alpha]_D^{27}$ +5.5, $[\alpha]_{435}^{27}$ +16.6 (*c* 0.96); IR (neat) 3460, 3070, 3020, 2960, 2930, 2860, 1700, 1490, 1470, 1450, 1430, 1220, 1110, 1090, 1030, 1000, 820, 760, and 700 $cm^{-1}$; $^1H$ NMR (270 MHz) $\delta = 0.90$ (3H, d, $J = 7.0$ Hz), 1.03 (3H, d, $J = 7.0$ Hz), 1.04 (9H, s), 2.85—3.00 (3H, m), 3.04 (1H, dd, $J = 10.0$, 5.9 Hz), 3.28 (1H, dd, $J = 10.0$, 3.5 Hz), 3.57 (1H, dd, $J = 10.0$, 6.0 Hz), 3.80—3.90 (1H, m), 3.85 (1H, dd, $J = 10.0$, 6.2 Hz), 7.17—7.50 and 7.61—7.69 (total 25H, m); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta = 13.26$, 13.36, 19.13, 26.80, 47.87, 48.39, 65.42, 65.73, 73.02, 86.64, 127.02, 127.68,

127.81, 128.59, 129.67, 133.23, 133.27, 135.56, 135.59, 143.82, and 217.28. Found: C, 78.42; H, 7.92%. Calcd for $C_{46}H_{48}O_4Si$: C, 78.62; H, 7.36%.

**(2*R*,3*S*,4*R*,5*S*)-6-(*t*-Butyldiphenylsiloxy)-3,5-dimethyl-1-(triphenylmethoxy)hexane-2,4-diol (14).** To a stirred solution of **12** (120 mg, 0.183 mmol) in dry THF (3.0 ml) was added at −100 °C 1.01 M DIBAH in toluene (0.904 ml, 0.913 mmol). After 0.5 h at −100 °C, the reaction mixture was warmed to 0 °C and to this were added successively 10 M aqueous NaOH, saturated aqueous potassium sodium tartrate, and saturated aqueous $NaHCO_3$. The mixture was extracted with ethyl acetate and the extracts were washed with saturated aqueous NaCl, dried, and concentrated. The residue was chromatographed on silica gel (30 g) with 30 : 1 benzene–ethyl acetate to afford **14** (106 mg, 88%) as a colorless syrup: $R_f$ = 0.40 (20 : 1 benzene–ethyl acetate); $[\alpha]_D^{27}$ −0.83, $[\alpha]_{435}^{27}$ −0.84 (*c* 0.96); IR (neat) 3440, 3070, 2960, 2930, 2860, 1490, 1470, 1460, 1450, 1430, 1220, 1110, 1070, 760, and 700 $cm^{-1}$; $^1H$ NMR (270 MHz) $\delta$ = 0.73 (3H, d, *J* = 7.0 Hz), 1.03 (9H, s), 1.04 (3H, d, *J* = 7.0 Hz), 1.65—1.85 (2H, m), 2.66 (1H, br s), 3.05 (1H, dd, *J* = 10.0, 4.0 Hz), 3.10 (1H, br d, *J* = 2.0 Hz), 3.20 (1H, dd, *J* = 10.0, 8.0 Hz), 3.57 (2H, d, *J* = 4.0 Hz), 3.73—3.80 (1H, br m), 3.93—4.01 (1H, br m), 7.18—7.45 and 7.59—7.65 (total 25H, m); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ = 6.58, 12.86, 19.18, 26.83, 36.68, 37.85, 65.95, 67.41, 74.66, 77.92, 86.75, 127.09, 127.67, 127.85, 128.59, 129.67, 133.19, 133.29, 135.51, 135.61, and 143.77. Found: C, 77.94; H, 7.80%. Calcd for $C_{43}H_{50}O_4Si$: C, 78.38; H, 7.65%.

**(2*R*,3*S*,4*S*,5*S*)-6-(*t*-Butyldiphenylsiloxy)-3,5-dimethyl-1-(triphenylmethoxy)hexane-2,4-diol (15).** To a stirred solution of $Me_4N[BH(OAc)_3]$ (41.3 mg, 0.157 mmol) in 1 : 1 MeCN–AcOH (0.60 ml) was added at r.t. a solution of **12** (20.6 mg, 0.0314 mmol) in 1 : 1 MeCN–AcOH (0.20 ml). After 9 h at r.t., the reaction mixture was cooled to 0 °C and to this were added successively 10 M aqueous NaOH, saturated aqueous potassium sodium tartrate, and saturated aqueous $NaHCO_3$. The mixture was extracted with ethyl acetate and the extracts were washed with saturated aqueous NaCl, dried, and concentrated. The residue was chromatographed on silica gel (5 g) with 30 : 1 benzene–ethyl acetate to afford **14** (ca. 1 mg) and **15** (18.6 mg, 90%) as colorless syrups:

**15**: $R_f$ = 0.25 (20 : 1 benzene–ethyl acetate); $[\alpha]_D^{26}$ +25.8, $[\alpha]_{435}^{26}$ +55.3 (*c* 1.03); IR (neat) 3440, 3060, 2960, 2930, 2880, 2860, 1490, 1470, 1460, 1450, 1430, 1220, 1110, 1070, 760, and 700 $cm^{-1}$; $^1H$ NMR (270 MHz) $\delta$ = 0.82 (3H, d, *J* = 7.0 Hz), 0.88 (3H, d, *J* = 7.0 Hz), 1.05 (9H, s), 1.95—2.06 (1H, m), 2.06—2.20 (1H, m), 2.98 (1H, dd, *J* = 9.0, 7.0 Hz), 3.30 (1H, dd, *J* = 9.0, 6.0 Hz), 3.63—3.72 (2H, m), 3.81 (1H, dd, *J* = 10.0, 4.2 Hz), 3.86 (1H, s), 4.30 (1H, br t, *J* = 6.4 Hz), 4.74 (1H, br s), 7.17—7.50 and 7.65—7.71 (total 25H, m); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ = 10.69, 13.14, 18.98, 26.75, 35.09, 37.22, 64.74, 70.07, 70.21, 82.97, 86.49, 126.92, 127.75, 127.85, 127.90, 128.64, 129.97, 132.29, 132.45, 135.54, and 144.05. Found: *m/z* 658.3463. Calcd for $C_{43}H_{50}O_4Si$: $M^+$, 658.3478.

**(2*R*,3*R*,4*R*,5*S*)-6-(*t*-Butyldiphenylsiloxy)-3,5-dimethyl-1-(triphenylmethoxy)hexane-2,4-diol (16).** To a stirred solution of **13** (125 mg, 0.190 mmol) in dry THF (3.0 ml) was added at −100 °C 1.01 M DIBAH in toluene (0.942 ml, 0.951 mmol). After 0.5 h at −100 °C, the reaction mixture was warmed to 0 °C and to this were added successively 10 M aqueous NaOH, saturated aqueous potassium sodium tartrate, and saturated aqueous $NaHCO_3$. The mixture was extracted with ethyl acetate and the extracts were washed with saturated aqueous NaCl, dried, and concentrated. The residue was chromatographed on silica gel (50 g) with 1 : 1 : 1 : 0.05 benzene–$CHCl_3$–hexane–ethyl acetate to afford **17** (13.7 mg, 11%) and **16** (111 mg, 89%) as colorless syrups:

**16**: $R_f$ = 0.40 (20 : 1 benzene–ethyl acetate); $[\alpha]_D^{26}$ −7.7, $[\alpha]_{435}^{26}$ −16.1 (*c* 1.08); IR (neat) 3440, 3080, 3010, 2960, 2930, 2860, 1490, 1470, 1460, 1450, 1430, 1220, 1110, 1080, 1010, 760, 740, and 700 $cm^{-1}$; $^1H$ NMR (270 MHz) $\delta$ = 0.57 (3H, d, *J* = 7.0 Hz), 0.91 (3H, d, *J* = 7.0 Hz), 1.05 (9H, s), 1.68—1.90 (2H, m), 3.07 (1H, dd, *J* = 9.7, 6.0 Hz), 3.38 (1H, dd, *J* = 9.7, 3.0 Hz), 3.66—3.95 (6H, m), 7.19—7.52 and 7.62—7.70 (total 25H, m); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ = 8.91, 12.45, 19.16, 26.84, 36.48, 38.36, 66.08, 68.74, 75.85, 77.56, 86.62, 126.97, 127.70, 127.80, 128.67, 129.72, 129.75, 133.06, 133.26, 135.53, 135.64, and 143.98. Found: *m/z* 658.3467. Calcd for $C_{43}H_{50}O_4Si$: $M^+$, 658.3478.

**(2*R*,3*R*,4*S*,5*S*)-6-(*t*-Butyldiphenylsiloxy)-3,5-dimethyl-1-(triphenylmethoxy)hexane-2,4-diol (17).** To a stirred solution of $Me_4N[BH(OAc)_3]$ (40.0 mg, 0.152 mmol) in 1 : 1 MeCN–AcOH (0.60 ml) was added at −30 °C a solution of **13** (20.0 mg, 0.0304 mmol) in 1 : 1 MeCN–AcOH (0.20 ml). After 8 h at −30 °C, the reaction mixture was warmed to 0 °C and to this were added successively 10 M aqueous NaOH, saturated aqueous potassium sodium tartrate, and saturated aqueous $NaHCO_3$. The mixture was extracted with ethyl acetate and the extracts were washed with saturated aqueous NaCl, dried, and concentrated. The residue was chromatographed on silica gel (5 g) with 30 : 1 benzene–ethyl acetate to afford **17** (19.4 mg, 97%) as a colorless syrup: $R_f$ = 0.44 (20 : 1 benzene–ethyl acetate); $[\alpha]_D^{26}$ +12.3, $[\alpha]_{435}^{26}$ +22.5 (*c* 0.93); IR (neat) 3460, 3070, 2960, 2930, 2860, 1490, 1470, 1460, 1450, 1430, 1220, 1110, 1070, 1010, 760, 750, and 700 $cm^{-1}$; $^1H$ NMR (270 MHz) $\delta$ = 0.62 (3H, d, *J* = 7.0 Hz), 0.96 (3H, d, *J* = 7.0 Hz), 1.03 (9H, s), 1.80—1.95 (2H, m), 3.22 (1H, dd, *J* = 9.2, 6.2 Hz), 3.30 (1H, dd, *J* = 9.2, 6.6 Hz), 3.43 (1H, d, *J* = 6.4 Hz), 3.58 (1H, dd, *J* = 10.2, 8.4 Hz), 3.68 (1H, dd, *J* = 10.2, 4.0 Hz), 3.75—3.93 (2H, m), 4.14 (1H, s), 7.20—7.50 and 7.62—7.69 (total 25H, m); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ = 9.59, 12.62, 19.00, 26.75, 35.45, 37.14, 65.62, 70.35, 74.32, 75.98, 86.44, 126.97, 127.76, 128.62, 129.89, 132.58, 132.67, 135.53, and 143.98. Found: C, 78.12; H, 7.93%. Calcd for $C_{43}H_{50}O_4Si$: C, 78.38; H, 7.65%.

**(4*R*,5*S*,6*R*)-4-[(*S*)-2-(*t*-Butyldiphenylsiloxy)-1-methylethyl]-2,2,5-trimethyl-6-(triphenylmethoxymethyl)-1,3-dioxane (18).** To a stirred solution of **14** (54.2 mg, 0.0823 mmol) in dry $CH_2Cl_2$ (2.0 ml) were added at r.t. 2,2-dimethoxypropane (0.0506 ml, 0.412 mmol) and pyridinium *p*-toluenesulfonate (PPTS) (1.0 mg, 0.0040 mmol). After 1 h at r.t., saturated aqueous $NaHCO_3$ was added and the mixture was extracted with ethyl acetate. The extracts were washed with saturated aqueous NaCl, dried, and concentrated. The residue was chromatographed on silica gel (20 g) with 30 : 1 hexane–ethyl acetate to afford **18** (41.5 mg, 72%) as a colorless syrup: $R_f$ = 0.78 (20 : 1 benzene–ethyl acetate); $^1H$ NMR (270 MHz) $\delta$ = 0.55 (3H, d, *J* = 7.0 Hz), 1.06 (3H, d, *J* = 7.0 Hz), 1.08 (9H, s), 1.36 (3H, s), 1.44 (3H, s), 1.55—1.65 (1H, m), 1.65—1.80 (1H, m), 2.87 (1H, dd, *J* = 9.4, 7.0 Hz), 3.25 (1H, dd, *J* = 9.4, 5.9 Hz), 3.49—3.60 (2H, m), 3.75 (1H, dd, *J* = 9.8, 2.0 Hz), 4.05 (1H, ddd, *J* = 7.0, 5.9, 5.9 Hz), 7.17—7.48 and 7.61—7.68 (total 25H, m); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ = 5.16, 14.43, 19.33, 19.57, 26.89, 29.87, 31.25, 36.65, 64.30, 64.86, 72.59, 75.40, 86.39, 98.88, 126.88, 127.65, 127.73, 128.69, 129.61, 133.62, 135.53, 135.59, and 144.08.

**(4*S*,5*S*,6*R*)-4-[(*S*)-2-(*t*-Butyldiphenylsiloxy)-1-methylethyl]-2,2,5-trimethyl-6-(triphenylmethoxymethyl)-1,3-dioxane (19).** To a stirred solution of **15** (82.2 mg, 0.125 mmol) in dry $CH_2Cl_2$ (2.0 ml) were added at r.t. 2,2-dimethoxypropane (0.0767 ml, 0.624 mmol) and PPTS (1.6 mg, 0.0064 mmol). After 1 h at r.t., saturated aqueous $NaHCO_3$ was added and the mixture was extracted with ethyl acetate. The extracts were washed with saturated aqueous

NaCl, dried, and concentrated. The residue was chromatographed on silica gel (20 g) with 30 : 1 hexane–ethyl acetate to afford **19** (65.3 mg, 75%) as a colorless syrup: $R_f = 0.87$ (20 : 1 benzene–ethyl acetate); $^1$H NMR (270 MHz) $\delta = 0.68$ (3H, d, $J = 7.0$ Hz), 0.98 (3H, d, $J = 7.0$ Hz), 1.04 (9H, s), 1.28 (3H, s), 1.33 (3H, s), 1.75—1.90 (2H, m), 2.87 (1H, dd, $J = 9.8$, 6.0 Hz), 3.29 (1H, dd, $J = 9.8$, 6.4 Hz), 3.30 (1H, dd, $J = 7.2$, 6.0 Hz), 3.63 (1H, dd, $J = 10.0$, 6.0 Hz), 3.68 (1H, dd, $J = 10.0$, 5.4 Hz), 3.87—3.95 (1H, m), 7.17—7.49 and 7.65—7.70 (total 25H, m); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta = 12.43$, 13.72, 19.24, 23.49, 25.38, 26.83, 35.05, 39.92, 63.49, 65.11, 68.45, 75.78, 86.41, 100.31, 126.86, 127.55, 127.73, 128.65, 129.49, 133.90, 135.59, and 144.23.

**(4*R*,5*R*,6*R*)-4-[(*S*)-2-(*t*-Butyldiphenylsiloxy)-1-methylethyl]-2,2,5-trimethyl-6-(triphenylmethoxymethyl)-1,3-dioxane (20).** To a stirred solution of **16** (60.3 mg, 0.0915 mmol) in dry $CH_2Cl_2$ (2.0 ml) were added at r.t. 2,2-dimethoxypropane (0.0563 ml, 0.458 mmol) and PPTS (1.2 mg, 0.0048 mmol). After 1 h at r.t., saturated aqueous $NaHCO_3$ was added and the mixture was extracted with ethyl acetate. The extracts were washed with saturated aqueous NaCl, dried, and concentrated. The residue was chromatographed on silica gel (20 g) with 30 : 1 hexane–ethyl acetate to afford **20** (61.1 mg, 96%) as a colorless syrup: $R_f = 0.85$ (20 : 1 benzene–ethyl acetate); $^1$H NMR (270 MHz) $\delta = 0.60$ (3H, d, $J = 7.0$ Hz), 0.75 (3H, d, $J = 7.0$ Hz), 1.04 (9H, s), 1.42 (3H, s), 1.43 (3H, s), 1.63—1.80 (1H, m), 1.85—2.00 (1H, m), 3.12 (1H, dd, $J = 10.1$, 5.0 Hz), 3.19 (1H, dd, $J = 10.1$, 2.8 Hz), 3.44 (1H, dd, $J = 9.5$, 5.8 Hz), 3.68 (2H, dd, $J = 9.5$, 9.5 Hz), 3.60—3.68 (1H, m), 3.86 (1H, dd, $J = 10.5$, 1.9 Hz), 7.17—7.55 and 7.63—7.70 (total 25H, m); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta = 9.03$, 11.73, 19.21, 19.67, 26.84, 30.04, 31.65, 36.06, 65.52, 65.98, 71.98, 74.53, 86.26, 97.68, 126.81, 126.89, 127.53, 127.57, 127.68, 127.75, 128.72, 128.80, 129.47, 129.51, 134.05, 135.56, and 144.36.

**(4*S*,5*R*,6*R*)-4-[(*S*)-2-(*t*-Butyldiphenylsiloxy)-1-methylethyl]-2,2,5-trimethyl-6-(triphenylmethoxymethyl)-1,3-dioxane (21).** To a stirred solution of **17** (82.1 mg, 0.125 mmol) in dry $CH_2Cl_2$ (3.0 ml) were added at r.t. 2,2-dimethoxypropane (0.0765 ml, 0.622 mmol) and PPTS (1.6 mg, 0.0064 mmol). After 1 h at r.t., saturated aqueous $NaHCO_3$ was added and the mixture was extracted with ethyl acetate. The extracts were washed with saturated aqueous NaCl, dried, and concentrated. The residue was chromatographed on silica gel (20 g) with 30 : 1 hexane–ethyl acetate to afford **21** (64.6 mg, 74%) as a colorless syrup: $R_f = 0.82$ (20 : 1 benzene–ethyl acetate); $^1$H NMR (270 MHz) $\delta = 0.78$ (3H, d, $J = 7.0$ Hz), 0.87 (3H, d, $J = 7.0$ Hz), 1.05 (9H, s), 1.27 (3H, s), 1.36 (3H, s), 1.50—1.75 (2H, m), 3.05 (1H, dd, $J = 10.0$, 4.0 Hz), 3.30 (1H, dd, $J = 10.0$, 7.0 Hz), 3.48 (1H, ddd, $J = 7.0$, 7.0, 4.0 Hz), 3.63 (1H, dd, $J = 10.0$, 2.8 Hz), 3.67 (1H, dd, $J = 10.0$, 3.4 Hz), 3.73 (1H, dd, $J = 10.0$, 5.0 Hz), 7.20—7.53 and 7.62—7.69 (total 25H, m); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta = 11.97$, 13.03, 19.36, 23.97, 25.22, 26.99, 34.53, 35.42, 64.98, 66.36, 69.22, 74.96, 86.54, 100.59, 126.89, 127.48, 127.73, 128.78, 129.43, 133.87, 134.01, 135.69, 135.77, and 144.21.

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