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TETRAHEDRON: *ASYMMETRY*

# Synthesis of spiro carbon linked deoxy disaccharides†

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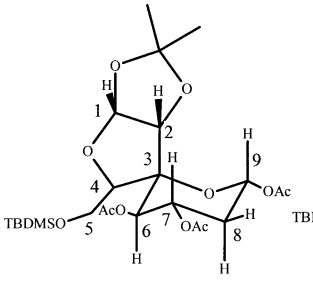
**Abstract**—Synthesis of the isomers of deoxy spiro carbon linked disaccharides has been reported. But-3-yn-1-ol has been utilised as a four carbon conjunctive reagent for the C–C bond formation and was later stereoselectively converted into *cis* and *trans* olefins for further elaboration into the deoxy sugar moiety through *cis* dihydroxylation. © 2002 Elsevier Science Ltd. All rights reserved.

## 1. Introduction

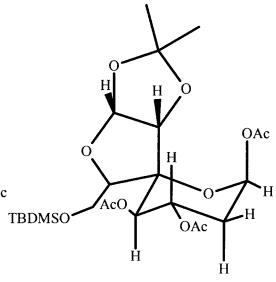
Carbohydrates were earlier recognised as suitable chiral starting materials for the synthesis of a plethora of non-carbohydrate compounds and as chiral auxiliaries.[1,2] Because of their important role in complex biological processes, over the years bioactive glycosubstances have received a great deal of attention in chemical, medical and pharmaceutical research.[3–6] Though several synthesis of glycosyl mimics,[7] such as *C*-glycosides, *C*-saccharides etc., are reported, much work has not been done on the synthesis of spiro *C*-disaccharides, in which the sugars are attached through a 'spiro' carbon atom. Recently we have demonstrated the use of furan for the first synthesis[8] of spiro carbon linked disaccharides. Our continued interest in the use of carbohydrate-derived chiral templates for the synthesis of various bioactive compounds[9] as well as new glycosubstances,[10] prompted us to report the synthesis of the 'spiro' carbon linked deoxy disaccharides **1**, **2**, **3** and **4**. Since the newly constructed sugar moiety is a deoxy sugar, deoxy disaccharides **1**–**4** are named as 'spiro' carbon linked deoxy disaccharides.

## 2. Results and discussion

Our earlier studies in this direction have extensively utilised methodologies for C–C bond formation between an 'enantiopure' precursor and a homologative, manipulable reactant, from which the new sugar is derived 'de novo'. Thus, the retrosynthetic analysis of **1**–**4** (Scheme 1) indicated that the olefinic alcohol **5** could be an appropriate homochiral intermediate for the stereoselective construction of the new sugar, while **5** could be made from propargylic carbinol **6**. Further, the synthesis of **6** could be envisaged from 'enantiopure' ketone **7**, which could be derived from D-xylose.




**1**

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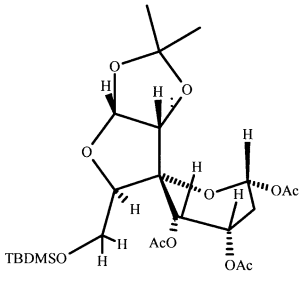
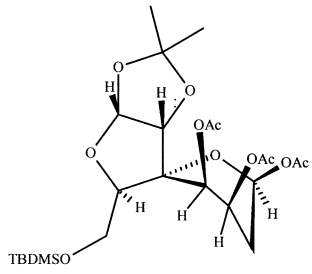



**3**




**4**

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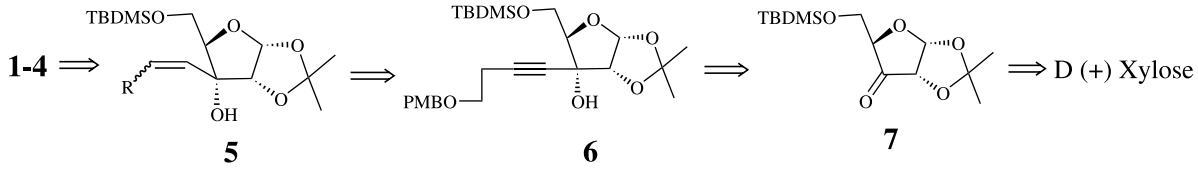



**Scheme 1.**

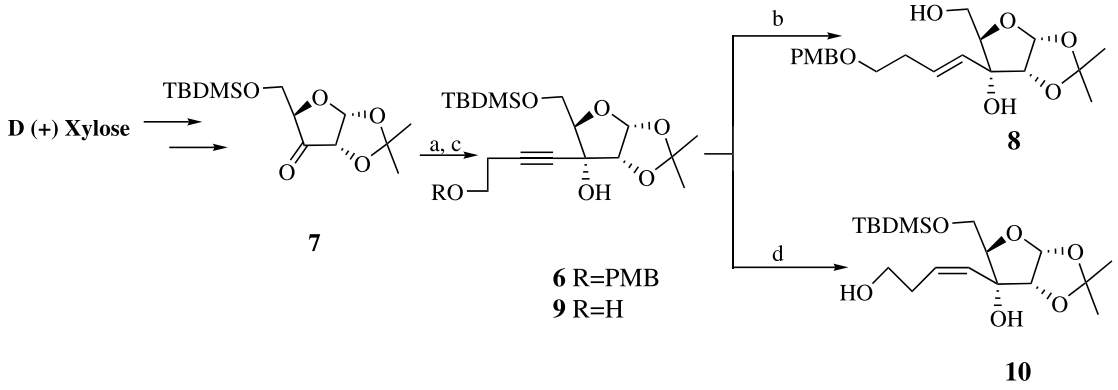
Accordingly, addition of lithium anion generated from **A** to ketone **7** (Scheme 2), afforded the 3-*C*-homopropargyl-D-allose derivative **6** (50%) $[\alpha]_D = +11.8$ (*c* 1.0 $CHCl_3$). Because of steric hindrance of the 1,2-*O*-isopropylidene group, the attack of homopropargyl group is from the β-face to give **6** as an exclusive product. The acetylenic group in **6** was subjected to reduction under two different reaction conditions to obtain stereoselectively both the *cis* and *trans* olefinic compounds. Thus, on reaction with LAH in THF, **6** gave the *trans* olefin **8** (77%), whose $^1H$ NMR spectrum amply indicated the disappearance of the TBDMS group. Similarly, oxidative deprotection of **6** with DDQ in aq. $CH_2Cl_2$ gave alcohol **9** (72%), which on further partial hydrogenation with Lindlar's catalyst afforded **10** (80%) $[\alpha]_D = +5.8$ (*c* 0.38, $CHCl_3$).

Treatment of alcohol **8** with TBDMSCl and imidazole in $CH_2Cl_2$ (Scheme 3) afforded **11** (80%), which on *cis* hydroxylation[11] using $OsO_4$–NMO in acetone–water (3:1) furnished the diols **12a** (70%) and **12b** (23%) in 3:1 ratio. Acetylation with $Ac_2O$ and $Et_3N$ in $CH_2Cl_2$, **12a** gave the diacetate **13a** in 80% yield, while isomer **12b** gave triacetate **13b** in 50% yield. The diacetate **13a** on deprotection of PMB group with DDQ, gave alcohol **14** in 75% yield, $[\alpha]_D = -17.6$ (*c* 1.0 $CHCl_3$). Further oxidation of the primary alcohol **14** with IBX in DMSO gave the lactol **15** (50%) along with enal **16** (20%) as a separable mixture (3:1) of isomers. Lactol **15** on reaction with $Ac_2O$ and $Et_3N$ in $CH_2Cl_2$ gave a separable mixture of anomers **1** (74%) and **2** (4.6%) in 16:1 ratios.

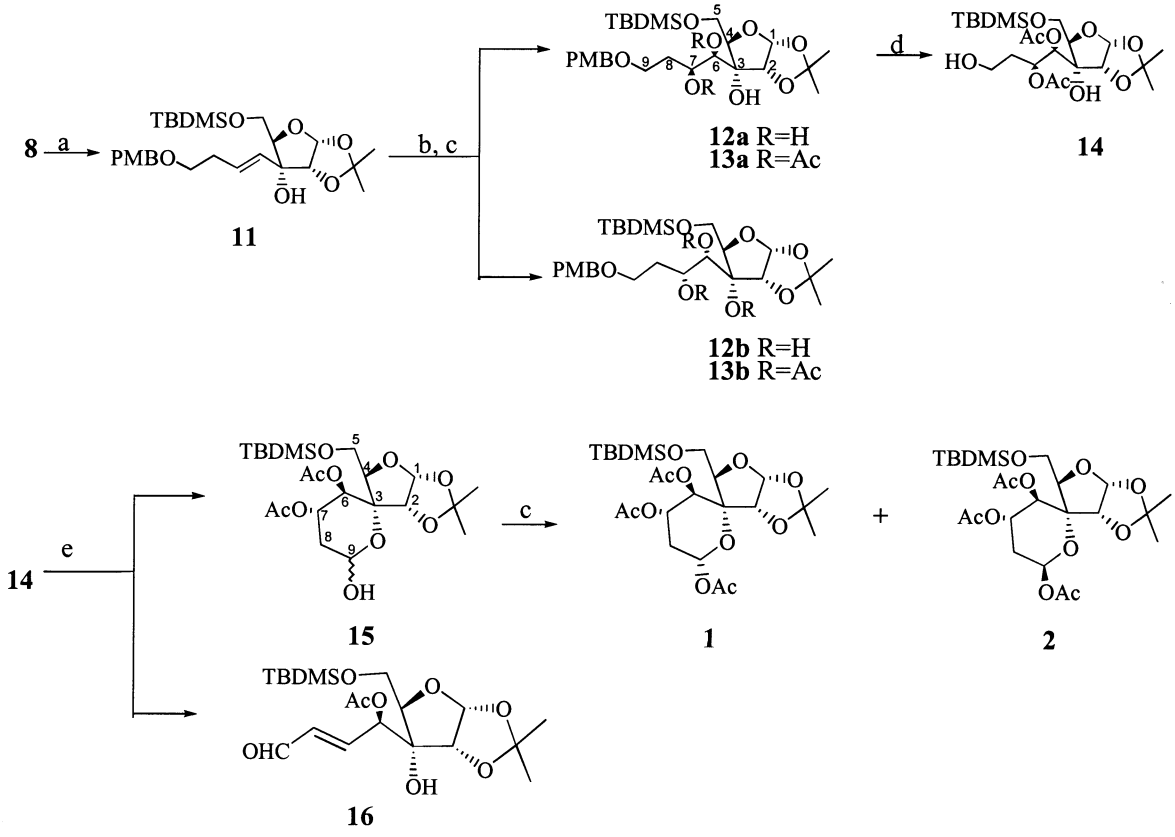
Extensive NMR studies were carried out for the structural characterisation of **1** and **2** (Fig. 1). The six-membered ring in **1** and **2** exists in the energetically favoured chair form with all the bulky acetates in equatorial positions, except at C9 in **2**. This is supported by the vicinal coupling constants ($^3J$) and NOE effects between H7 and H9, H6 and H8a in **1**. The relative orientation of two sugar rings was confirmed by characteristic NOEs, like H2–H7, H2–H9. The presence of NOE between Me (A)–H1 and Me (A)–H2 as well as Me (B)–H4 indicates that the five-membered ring containing cyclic acetal is in equilibrium between two envelope conformations. The sugar ring conformation in **2** is also consistent with the vicinal couplings as the characteristic NOE H6–H8a, supporting a chair form. The cross peak in the NOESY spectrum between H2 and H7 supports the relative orientation of the two sugar rings.

The *cis* olefin **10** (Scheme 4) was subjected to oxidation with IBX in DMSO to afford the lactol **17** (70%), which on acetylation ($Ac_2O$, $Et_3N$) in $CH_2Cl_2$ gave a separable mixture of anomers **18a** (30%) $[\alpha]_D = -12.7$ (*c* 1.5, $CHCl_3$) and **18b** (60%) $[\alpha]_D = +44.2$ (*c* 1.01, $CHCl_3$) (1:2), respectively. *cis*-Hydroxylation ($OsO_4$–NMO) of olefins **18a** and **18b** in acetone–water (3:1) afforded diols **19a** (80%) and **19b** (85%), respectively, with complete diastereoselectivity albeit at a very slow rate with only 60 and 75% conversion even after 20 days. Finally, acetylation ($Ac_2O$, $Et_3N$) of the diols **19a** and **19b** in $CH_2Cl_2$ furnished the spiro saccharides **4** and **3** in 98 and 94%, respectively, whose structures were unambiguously confirmed by spectral analysis.

Unlike **1** and **2**, in spiro saccharides **3** and **4**, the six-membered ring exists in distorted boat configuration since the bulky acetate groups are occupying axial positions. This is evident from the $^3J$ couplings, $J_{8a,9} = 2.9$, $J_{8b,9} = 6.9$, $J_{7,8a} = 6.9$, $J_{7,8b} = 3.9$, $J_{6,7} = 3.4$ Hz for **3** and about 4 Hz vicinal couplings in the six-membered ring for **4**. Further support for this and the relative orientation of the two rings at the spiro carbon comes from the NOE data (Fig. 2). In **3** H6–H8a, H2–H9,




**Scheme 2.** *Reagents and conditions*: (a) HC≡$CCH_2CH_2OPMB$ (**A**), *n*-BuLi, THF; (b) LAH, THF; (c) DDQ, $CH_2Cl_2$:$H_2O$ (19:1); (d) $H_2$, $Pd/CaCO_3$, *n*-hexane, quinoline.




**Scheme 3.** *Reagents and conditions*: (a) TBDMSCl, imidazole, $CH_2Cl_2$; (b) $OsO_4$–NMO, acetone:water (3:1); (c) $Ac_2O$, $Et_3N$, DMAP, $CH_2Cl_2$; (d) DDQ, $CH_2Cl_2$:$H_2O$ (19:1); (e) IBX, DMSO.

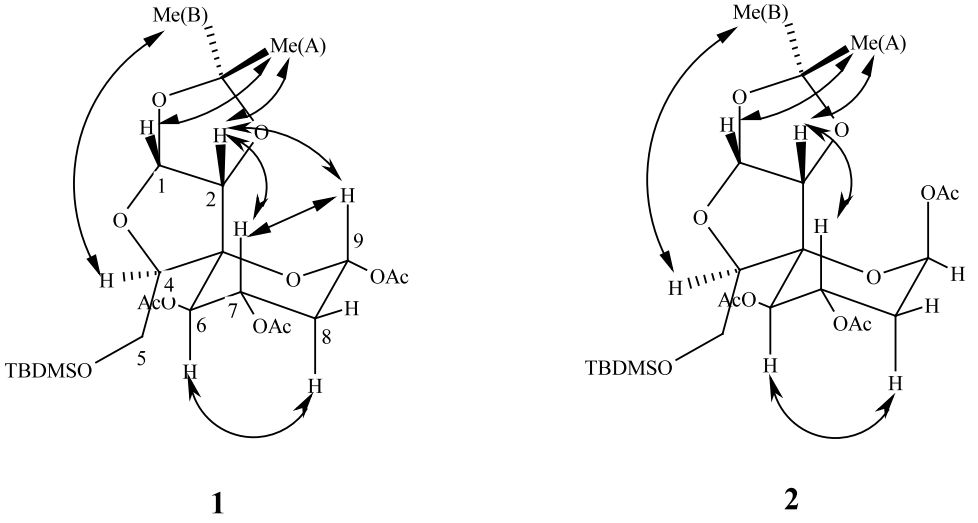
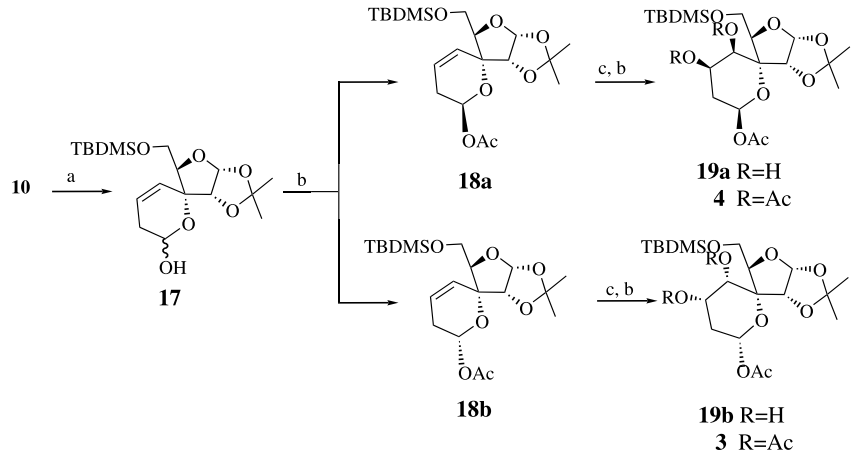



**Figure 1.**

H2–H6, H5–H6, H5′–H6 NOEs are consistent with the proposed structure, whereas in **4** NOE between H4 and H9 supports the structure. The conformation of the five-membered ring with the isopropylidene ring is similar to **1** and **2**.

Thus, in conclusion, a simple, efficient and enantioselective synthesis of the spiro carbon linked deoxy disaccharides **1**, **2**, **3** and **4** has been achieved starting from the chiral ketone **5** and but-3-yn-1-ol. The homopropargyl alcohol is utilised as a four carbon conjunctive reagent for developing stereoselectively into the new sugar moiety, while the stereochemical outcome of the formation of the spiro junction is defined by the 1,2-*O*-isopropylidene group and the chirality being transferred from the sugar synthon during the introduction of the diol system on the *cis* and *trans* olefins to give the new sugar systems in **1**–**4**.




**Scheme 4.** *Reagents and conditions*: (a) IBX, DMSO; (b) $Ac_2O$, $Et_3N$, DMAP, $CH_2Cl_2$; (c) $OsO_4$–NMO, acetone: water (3:1).

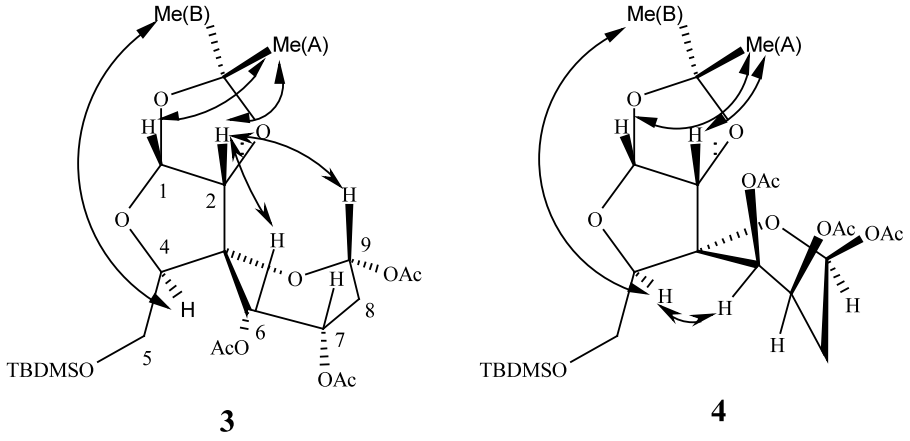



**Figure 2.**

## 3. Experimental

### 3.1. 5-*tert*-Butyldimethylsilyloxymethyl-6-[4-(4-methoxybenzyloxy)-1-butynyl]-2,2-dimethyl-(3a*R*,5*R*,6R,6a*R*)-perhydrofuro[2,3-*d*][1,3]dioxol-6-ol, 6

To a stirred solution of 1-(*p*-methoxybenzyl-but-3-yn-1-ol (1.13 g, 5.95 mmol) in dry THF (10 mL), was added *n*-BuLi (4.57 mL, 5.95 mmol, 1.3 molar solution in hexane) dropwise at −78°C. After 30 min, a solution of ketone **7** (1.5 g, 4.96 mmol) in dry THF (10 mL) was added dropwise at the same temperature and the reaction mixture warmed to room temperature over a period of 1 h. The reaction mixture was treated with saturated aqueous $NH_4Cl$ solution (10 mL), diluted with water (20 mL) and extracted with ethyl acetate (2×50 mL). The organic layer was washed with water (20 mL), brine (10 mL), dried ($Na_2SO_4$) and concentrated to the crude, which was purified by column chromatography (silica gel, 1:12 ethyl acetate–petroleum ether) to afford **6** as a syrup (1.4 g, 50%). $[\alpha]_D = +11.8$ (*c* 1.0, $CHCl_3$); IR (neat): 750, 850, 1000, 1060, 1100, 1260, 1350, 1480, 1600, 2240, 2840, 2900, 3400 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 200 MHz): $\delta$ 0.06 (s, 6H, 2 Si $CH_3$), 0.88 (s, 9H, $C(CH_3)_3$), 1.35, 1.56 (2s, 6H, 2 $CH_3$), 2.49 (t, 2H, *J* 7.5 Hz, H-8, 8′), 2.92 (br. s, 1H, OH), 3.5 (t, 2H, *J* 7.5 Hz, H-9, 9′), 3.78–3.80 (m, 4H, H-5′, $OCH_3$), 3.80–3.95 (m, 2H, H-4, 5), 4.42 (d, 1H, $J_{1,2}$ 3.8 Hz, H-2),4.46 (AB q, 2H, $OCH_2$), 5.74 (d, 1H $J_{1,2}$ 3.8 Hz, H-1), 6.83 (d, 2H, *J* 8.4 Hz, Ar-H), 7.2 (d, 2H, *J* 8.4 Hz, Ar-H); $^{13}C$ NMR ($CDCl_3$, 50 MHz): $\delta$ −5.51, −5.32, 18.27, 20.15, 25.87 (3C), 26.65, 29.66, 55.25, 63.03, 67.76, 72.62, 75.58, 77.74, 81.18, 84.14, 85.72, 104.23, 113.34, 113.85 (2C), 113.95, 129.06, 130.0, 159.06; FABMS (*m*/*z*, %): 515 ($M^+$+23, 6), 492 ($M^+$, 3), 491 ($M^+$−1, 7), 121 (100), 73 (33). Anal. calcd for $C_{26}H_{40}O_7Si$ (492): C, 63.38; H, 8.18. Found: C, 63.29; H, 8.12%.

### 3.2. 5-Hydroxymethyl-6-[4-(4-methoxybenzyloxy)-(*E*)-1-butenyl]-2,2-dimethyl-3a*R*,5*R*,6*R*,6a*R*)-perhydrofuro[2,3-*d*][1,3]dioxol-6-ol, 8

To a cooled (0°C) suspension of $LiAlH_4$ (0.084 g, 2.23 mmol) in dry THF (10 mL), was added a solution of **6** (0.5 g, 1.01 mmol) in dry THF (5 mL) dropwise at the same temperature and stirred for 12 h at room temperature. The reaction mixture was quenched with saturated aqueous $Na_2SO_4$ solution (10 mL), diluted with ethyl acetate (20 mL), filtered through Celite and washed with ethyl acetate (2×10 mL). The combined organic layers were dried ($Na_2SO_4$), ethyl acetate evaporated and the obtained residue was purified by column chromatography (silica gel, 1:3 ethyl acetate–petroleum

ether) to afford **8** as a syrup (0.30 g, 77%). $[\alpha]_D = +20.2$ ($c$ 1.0, $CHCl_3$); IR (neat): 750, 1000, 1050, 1280, 1400, 1500, 1600, 2850, 2900, 3400 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 200 MHz): $\delta$ 1.34, 1.57 (2s, 6H, 2 $CH_3$), 2.33 (m, 2H, H-8 8′), 2.88, 2.96 (2s, 2H, 2 OH), 3.45 (t, 2H, $J$ 6.4 Hz, H-9, 9′), 3.60 (d, 2H, $J$ 5.5 Hz, H-5, 5′), 3.78 (s, 3H, $OCH_3$), 3.89 (t, 1H, $J$ 5.5 Hz, H-4), 4.15 (d, 1H, $J_{1,2}$ 4.1 Hz, H-2), 4.51 (s, 2H, $OCH_2$), 5.42 (br. d, 1H, $J_{6,7}$ 16.0 Hz, H-6), 5.78 (d, 1H, $J_{1,2}$ 4.1, Hz, H-1), 5.99 (dt, 1H, $J$ 16.1, 5.9 Hz, H-7), 6.84 (d, 2H, $J$ 9.2 Hz, Ar-H), 7.20 (d, 2H, $J$ 9.2 Hz, Ar-H); FABMS ($m/z$, %): 403 ($M^+$+23, 12), 341 (25), 147 (40), 73 (100), 55 (38). Anal. calcd for $C_{20}H_{28}O_7$ (380): C, 63.14; H, 7.42. Found: C, 63.09; H, 7.31%.

### 3.3. 4-[6-Hydroxy-5-*tert*-butyldimethylsilyloxymethyl-2,2-dimethyl-(3a*R*,5*R*,6*R*,6a*R*)perhydrofuro[2,3-*d*]-[1,3]dioxol-6-yl]-3-butyn-1-ol, 9

To a stirred solution of **6** (1.590 g, 3.23 mmol) in dichloromethane–water (20 mL, 19:1) was added DDQ (0.88 g, 3.87 mmol) at 0°C and the reaction mixture stirred for 1 h at room temperature. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution (5 mL) and extracted with dichloromethane (2×50 mL). The combined organic layers were washed with water (10 mL), brine (10 mL), dried ($Na_2SO_4$), concentrated and the residue was purified by column chromatography (silica gel, 3:7 ethyl acetate–petroleum ether) to afford alcohol **9** as a gummy syrup (0.865 g, 72%). $[\alpha]_D = +11.65$ ($c$ 3.54, $CHCl_3$); IR (neat): 750, 850, 1025, 1100, 1250, 1350, 1480, 1600, 2250, 2880, 2950, 3450 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 200 MHz): $\delta$ 0.12 (s, 6H, 2 Si $CH_3$), 0.94 (s, 9H, $C(CH_3)_3$), 1.39, 1.60 (2s, 6H, 2 $CH_3$), 2.51 (t, 2H, $J$ 7.2 Hz, H-8, 8′), 3.15 (br. s, 2H, OH), 3.74 (t, 2H, $J$ 7.2 Hz, H-9, 9′), 3.94 (m, 3H, H-4, 5, 5′), 4.51 (d, 1H, $J_{1,2}$ 4.8 Hz, H-2), 5.81 (d, 1H, $J_{1,2}$ 4.8 Hz, H-1); FABMS ($m/z$, %): 395 ($M^+$+23, 10), 297 (64), 165 (100), 149 (75). Anal. calcd for $C_{18}H_{32}O_6Si$ (372): C, 58.03; H, 8.66. Found: C, 57.99; H, 8.49%.

### 3.4. 4-[6-Hydroxy-5-*tert*-butyldimethylsilyloxymethyl-2,2-dimethyl-(3a*R*,5*R*,6*R*,6a*R*)-perhydrofuro[2,3-*d*]-[1,3]dioxol-6-yl]-(*Z*)-3-buten-1-ol, 10

To a stirred solution of alcohol **9** (0.300 g, 0.806 mmol) in hexane (5 mL) were added Pd–$CaCO_3$ (0.010 g) followed by quinoline (0.010 g, 0.0806 mmol) and stirred for 4 h at room temperature. The reaction mixture was filtered and washed with ethyl acetate (2×20 mL). The combined organic extracts were washed with brine (10 mL), dried ($Na_2SO_4$), evaporated and the residue purified by column chromatography (silica gel, 1:7 ethyl acetate–petroleum ether) to afford **10** as a solid (0.240 g, 80%). Mp = 80–85°C; $[\alpha]_D = +5.8$ ($c$ 0.385, $CHCl_3$); IR (KBR): 720, 750, 820, 900, 1050, 1180, 1240, 1280, 1400, 1450, 1600, 2800, 2840, 2920, 3200, 3390 $cm^{-1}$ $^1H$ NMR ($CDCl_3$, 200 MHz): $\delta$ 0.08 (s, 6H, 2 Si $CH_3$), 0.89 (s, 9H, $C(CH_3)_3$), 1.35, 1.60 (2s, 6H, 2 $CH_3$), 2.23 (br. s, 1H, OH), 2.43–2.84 (m, 2H, H-8, 8′), 3.24 (br. s, 1H, OH), 3.55–3.94 (m, 5H, H-4, 5, 5′, 9, 9′), 4.25 (d, 1H, $J_{1,2}$ 4.8 Hz, H-2), 5.40 (br. d, 1H, $J_{6,7}$ 10.6 Hz, H-6), 5.60–5.75 (m, 1H, H-7), 5.75 (d, 1H, $J_{1,2}$ 4.8 Hz, H-1); $^{13}C$ NMR ($CDCl_3$, 50 MHz): $\delta$ −5.42, −5.24, 18.28, 25.87 (3C), 26.56, 26.64, 31.67, 61.25, 62.09, 80.42, 83.24, 84.27, 103.84, 112.89, 127.77, 132.01; FABMS ($m/z$, %): 397 ($M^+$+23, 18), 199 (12), 89 (26), 73 (100). Anal. calcd for $C_{18}H_{34}O_6Si$ (374): C, 57.72; H, 9.15. Found: C, 57.64; H, 9.09%.

### 3.5. 5-*tert*-Butyldimethylsilyloxymethyl-6-[4-(4-methoxybenzyloxy)-(*E*)-1-butenyl]-2,2-dimethyl-(3a*R*,5*R*,6*R*,6a*R*)-perhydrofuro[2,3-*d*][1,3]dioxol-6-ol, 11

To a stirred solution of **8** (0.3 g, 0.789 mmol) and imidazole (0.107 g, 1.57 mmol) in dichloromethane (5 mL) was added TBDMSCl (0.118g, 0.789 mmol) in portions at 0°C. After 12 h it was diluted with water (20 mL) and extracted with dichloromethane (2×20 mL). The combined organic layers were washed with water (20 mL), brine (10 mL), dried ($Na_2SO_4$) and concentrated. The crude was purified by column chromatography (silica gel, 1:20 ethyl acetate–petroleum ether) to afford **11** as a syrup (0.312 g, 80%). $[\alpha]_D = +17.55$ ($c$ 1.0, $CHCl_3$); IR (neat): 800, 1050, 1100, 1250, 1500, 1625, 1700, 2850, 2950, 3400 $cm^{-1}$ $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 0.08, 1.10 (2s, 6H, 2 Si $CH_3$), 0.88, 0.92 (2s, 9H, $C(CH_3)_3$), 1.34, 1.56 (2s, 6H, 2 $CH_3$), 2.36 (m, 2H, H-8, 8′), 3.47 (t, 2H, $J$ 6.7 Hz, H-9, 9′), 3.55–3.68 (m, 2H, H-5, 5′), 3.77 (s, 3H, $OCH_3$), 3.90 (t, 1H, $J$ 4.8 Hz, H-4), 4.14 (d, 1H, $J_{1,2}$ 5.7 Hz, H-2), 4.46 (s, 2H, -$CH_2$), 5.40 (br. d, 1H, $J_{6,7}$ 16.2 Hz, H-6), 5.71 (d, 1H, $J_{1,2}$ 5.7 Hz, H-1), 5.85–5.95 (dt, 1H, $J$ 8.6, 16.2 Hz, H-7), 6.82 (d, 2H, $J$ 8.5 Hz, Ar-H), 7.20 (d, 2H, $J$ 8.6 Hz, Ar-H); $^{13}C$ NMR ($CDCl_3$, 50 MHz): $\delta$ −5.57, −5.41, 18.10, 25.75 (2C), 26.44 (2C), 29.49, 32.75, 55.06, 62.20, 64.44, 69.12, 72.37, 79.22, 82.80, 83.73, 103.76, 112.55, 113.66 (2C), 127.98, 128.34, 129.02, 130.34, 159.06; FABMS ($m/z$, %): 517 ($M^+$+23, 21), 493 ($M^+$−1, 8), 403 (24), 121 (100), 69 (44). Anal. calcd for $C_{26}H_{42}O_7Si$ (494): C, 63.13; H, 8.56. Found: C, 63.01; H, 8.42%.

### 3.6. Hydroxylation of 11

To a stirred solution of **11** (0.2 g, 0.404 mmol) in acetone–water (10 mL, 3:1) were added sequentially $N$-methyl morpholine $N$-oxide (0.093 g, 0.808 mmol) and $OsO_4$ (four drops) at room temperature. After completion of reaction (2 days, monitored by TLC), reaction mixture was quenched by saturated aqueous $NaHSO_3$ solution (3 mL) and acetone evaporated on rotary evaporator. The reaction mixture was diluted with water (15 mL) and extracted with ethyl acetate (2×15 mL). The combined organic layers were washed with water (10 mL), brine (10 mL), dried ($Na_2SO_4$), concentrated and purified by column chromatography (silica gel, 1:5 ethyl acetate–petroleum ether) to afford **12a** (0.150 g, 70%) and **12b** (0.050 g, 23%) as syrups in 3:1 ratio.

First eluted was **1-[6-hydroxy-5-*tert*-butyldimethylsilyloxymethyl-2,2-dimethyl-(3a*R*,5*R*,6*R*,6a*R*)-perhydrofuro-[2,3-*d*][1,3]dioxol-6-yl]-4-(4-methoxybenzyloxy)-(1*R*,2*S*)-butane-1,2-diol**, **12a**: $[\alpha]_D = +15.9$ ($c$ 1.0, $CHCl_3$); IR (neat): 750, 850, 1020, 1100, 1260, 1320, 1440, 1600,

2840, 2920, 3400, 3520 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 200 MHz): $\delta$ 0.10 (s, 6H, 2 Si $CH_3$), 0.90 (s, 9H, $C(CH_3)_3$), 1.37, 1.54 (2s, 6H, 2 $CH_3$), 1.65–1.84 (m, 1H, H-8), 1.88–2.12 (m, 1H, H-8′), 2.96 (s, 1H, OH), 3.54–3.70 (m, 2H, H-9, 9′), 3.70–3.81 (m, 5H, H-5, 5′, $OCH_3$), 3.88 (d, 1H, $J_{6,7}$ 10.3 Hz, H-6), 3.95–4.08 (m, 1H, H-7), 4.11–4.30 (m, 1H, H-4), 4.44 (s, 2H, $OCH_2$-), 5.11 (d, 1H, $J_{1,2}$ 3.8 Hz, H-2), 5.78 (d, 1H, $J_{1,2}$ 3.8 Hz, H-1), 6.82 (d, 2H, $J$ 10.3 Hz, Ar-H), 7.22 (d, 2H, $J$ 10.3 Hz, Ar-H); FABMS ($m/z$, %): 551 ($M^+$+23, 68), 493 (7), 121 (100), 69 (19), 57 (33).

Second eluted was **1-[6-hydroxy-5-*tert*-butyldimethylsilyloxymethyl - 2,2 - dimethyl - (3a*R*,5*R*,6*R*,6a*R*) - perhydrofuro[2,3-*d*][1,3]dioxol-6-yl]-4-(4-methoxybenzyloxy)-(1*S*,2*R*)-butane-1,2-diol**, **12b**: $[\alpha]_D$ = +10.35 (*c* 1.0, $CHCl_3$); IR (neat): 720, 840, 1040, 1100, 1250, 1350, 1400, 1600, 2800, 2900, 3400, 3520 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 200 MHz): $\delta$ 0.06 (s, 6H, 2 Si $CH_3$), 0.86 (s, 9H, $C(CH_3)_3$), 1.34, 1.56 (2s, 6H, 2 $CH_3$), 1.94–2.16 (m, 2H, H-8, 8′), 3.44 (br. s, 1H, H-5), 3.5-3.61 (m, 3H, H-5′, 9, 9′), 3.78 (s, 3H, $OCH_3$), 3.81 (dd, 1H, $J_{6,7}$ 4.1, $J_{7,8}$ 11.3 Hz, H-7), 3.97 (d, 1H, $J_{6,7}$ 4.1 Hz, H-6), 4.14 (dd, 1H, $J_{4,5}$ 4.1 Hz, $J_{4,5'}$ 10.3 Hz, H-4), 4.42 (s, 2H, $OCH_2$-), 4.45 (d, 1H, $J_{1,2}$ 5.1 Hz, H-2), 5.74 (d, 1H, $J_{1,2}$ 5.1 Hz, H-1), 6.82 (d, 2H, $J$ 8.2 Hz, Ar-H), 7.20 (d, 2H, $J$ 8.2 Hz, Ar-H); FABMS ($m/z$, %): 551 ($M^+$+23, 62), 459 (15), 121 (100), 73 (52), 69 (44), 57 (74).

### 3.7. 1-[6-Hydroxy-5-*tert*-butyldimethylsilyloxymethyl-2,2-dimethyl-(3a*R*,5*R*,6*S*,6a*R*)-perhydrofuro[2,3-*d*][1,3]dioxol-6-yl]-4-(4-methoxybenzyloxy)-2-methylcarbonyloxy-(1*R*,2*S*)-butyl acetate, 13a

A solution of the diol **12a** (0.140 g, 0.265 mmol) and triethylamine (0.18 mL, 1.325 mmol), in dichloromethane (5 mL) was treated with acetic anhydride (0.05 mL, 0.53 mmol) in presence of catalytic DMAP at 0°C. After 1 h, the mixture was neutralised with saturated aqueous $NaHCO_3$ solution (5 mL) and extracted with dichloromethane (2×10 mL). Combined organic layers were washed with water (10 mL), brine (10 mL), dried ($Na_2SO_4$), concentrated and the residue was purified by column chromatography (silica gel, 1:12 ethyl acetate–petroleum ether) to afford **13a** as a syrup (0.13 g, 80%). $[\alpha]_D$ = −14.2 (*c* 1.0, $CHCl_3$); IR (neat): 720, 840, 1020, 1150, 1240, 1340, 1450, 1750, 2850, 2920, 3400 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 200 MHz): $\delta$ 0.08 (2s, 6H, 2 Si $CH_3$), 0.90 (s, 9H, $C(CH_3)_3$), 1.39, 1.57 (2s, 6H, 2 $CH_3$), 1.65–1.93 (m, 2H, H-8, 8′), 2.10, 2.80 (2s, 6H, 2 OAc), 2.88 (s, 1H, OH), 3.31–3.49 (m, 2H, H-5, 5′), 3.60 (t, 2H, $J$ 8.7 Hz, H-9, 9′), 3.79 (s, 3H, $OCH_3$), 3.97 (t, 1H, $J$ 7.8 Hz, H-4), 4.37 (s, 2H, $OCH_2$-) 4.81 (d, 1H, $J_{1,2}$ 4.6 Hz, H-2), 5.15 (d, 1H, $J_{6,7}$ 3.6 Hz, H-6), 5.44–5.58 (m, 1H, H-7), 5.72 (d, 1H, $J_{1,2}$ 4.6 Hz, H-1), 6.83 (d, 2H, $J$ 8.2 Hz, Ar-H), 7.21 (d, 2H, $J$ 8.2 Hz, Ar-H); $^{13}C$ NMR ($CDCl_3$, 50 MHz): $\delta$ −5.59, −5.43, 18.11, 20.56, 20.76, 25.56, 25.77 (2C), 26.39, 26.50, 29.51, 32.22, 55.08, 61.52, 66.00, 69.59, 71.65, 72.51, 76.38, 78.75, 80.07, 84.33, 105.03, 112.32, 113.65, 129.17, 130.34, 159.09, 169.20, 169.83; FABMS ($m/z$, %): 582 ($M^+$+1−$OCH_3$, 16), 241 (32), 176 (37), 165 (46), 154 (100). Anal. calcd for $C_{30}H_{48}O_{11}Si$ (612): C, 58.80; H, 7.90. Found: C, 58.78; H, 7.79%.

### 3.8. 1-[5-Hydroxymethyl-2,2-dimethyl-6-methylcarbonyloxy-(3a*R*,5*R*,6*S*,6a*R*)-perhydrofuro[2,3-*d*][1,3]dioxol-6-yl]-4-(4-methoxybenzyloxy)-2-methylcarbonyloxy-(1*S*,2*R*)-butyl acetate, 13b

A solution of the diol **12b** (0.150 g, 0.284 mmol) and triethylamine (0.2 mL, 1.42 mmol), in dichloromethane (5 mL) was treated with acetic anhydride (0.08 mL, 0.85 mmol) in the presence of catalytic DMAP at 0°C. After 1 h, worked up as described for **13a**, purified by column chromatography (silica gel, 1:19 ethyl acetate–petroleum ether) to afford **13b** (0.08 g) in 50% yield as a syrup. $[\alpha]_D$ = +41.4 (*c* 1.0, $CHCl_3$); IR (neat): 750, 820, 1040, 1090, 1200, 1240, 1350, 1450, 1740, 2800, 2900 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 200 MHz): $\delta$ 0.07, 0.10 (2s, 6H, 2 Si $CH_3$), 0.90 (s, 9H, $C(CH_3)_3$), 1.29, 1.46 (2s, 6H, 2 $CH_3$), 1.52–1.90 (m, 2H, H-8, 8′), 2.04, 2.05, 2.10 (3s, 9H, 3 OAc), 3.36 (t, 2H, $J$ 5.5 Hz, H-9, 9′), 3.78 (s, 3H, $OCH_3$), 3.93–4.20 (m, 3H, H-4, 5, 5′), 4.34 (s, 2H, $OCH_2$-), 4.98 (d, 1H, $J_{1,2}$ 4.5 Hz, H-2), 5.19–5.34 (m, 1H, H-7), 5.50–5.60 (m, 1H, H-6), 5.72 (d, 1H, $J_{1,2}$ 4.5 Hz, H-1), 6.82 (d, 2H, $J$ 9.4 Hz, Ar-H), 7.20 (d, 2H, $J$ 9.4 Hz, Ar-H).

### 3.9. 4-Hydroxy-1-[6-5-*tert*-butyldimethylsilyloxymethyl-2,2-dimethyl-(3a*R*,5*R*,6S,6a*R*)-perhydrofuro[2,3-*d*][1,3]dioxol-6-yl]-2-methylcarbonyloxy-(1*R*,2*S*)-butyl acetate, 14

To a stirred solution of **13a** (0.110 g, 0.179 mmol) in dichloromethane-water (5 mL, 19:1), was added DDQ (0.049 g, 0.215 mmol), reaction mixture stirred for 1 h. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution (5 mL) and extracted with dichloromethane (2×20 mL). The combined organic layers were washed with water (10 mL), brine (10 mL), dried ($Na_2SO_4$), concentrated and the residue was purified by column chromatography (silica gel, 1:5 ethyl acetate–petroleum ether) to afford **14** as a syrup (0.066 g, 75%). $[\alpha]_D$ = −17.6 (*c* 1.0, $CHCl_3$); IR (neat): 720, 850, 1020, 1100, 1240, 1340, 1750, 2850, 2920, 3400, 3520 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 200 MHz): $\delta$ 0.09 (s, 6H, 2 Si $CH_3$), 0.91 (s, 9H, $C(CH_3)_3$), 1.39, 1.58 (2s, 6H, 2 $CH_3$), 1.70–1.89 (m, 2H, H-8, 8′), 2.11, 2.14 (2s, 6H, 3 OAc), 2.90 (s, 1H, OH), 3.45 (ddd, 1H, $J_{8,9}$ 4.3, $J_{8',9}$ 10.0, $J_{9,9'}$ 11.0 Hz, H-9), 3.66 (dt, 1H, $J_{8,9'}$ 4.8, $J_{8',9'}$ 4.8, $J_{9,9'}$ 11.0 Hz, H-9′), 3.80 (d, 2H, $J_{4,5}$ 5.3 Hz, H-5, 5′), 3.91 (t, 1H, $J$ 5.3 Hz, H-4), 4.87 (d, 1H, $J_{1,2}$ 4.0 Hz, H-2), 5.22 (d, 1H, $J_{6,7}$ 3.3 Hz, H-6), 5.64 (dt, 1H, $J_{6,7}$ 3.3, $J_{7,8}$ 3.3, $J_{7,8'}$ 9.6 Hz, H-7), 5.72 (d, 1H, $J_{1,2}$ 4.0 Hz, H-1); FABMS ($m/z$, %): 515 ($M^+$+23, 28), 147 (34), 117 (100), 107 (38), 95 (56), 89 (96). Anal. calcd for $C_{22}H_{40}O_{10}Si$ (492): C, 53.64; H, 8.18. Found: C, 53.57; H, 8.07%.

### 3.10. Conversion of 14 to 1 and 2

A stirred solution of **14** (0.040 g, 0.08 mmol) in DMSO (3 mL) was treated with iodoxy benzoic acid (IBX, 0.027 g, 0.097 mmol) at room temperature for 1 h. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution (5 mL) and extracted with ethyl

acetate (2×10 mL). The combined organic layers were washed with water (10 mL), brine (10 mL), dried ($Na_2SO_4$), concentrated and the residue was purified by column chromatography (silica gel, 1:5 ethyl acetate–petroleum ether) to afford separable mixture of **15** (0.020 g, 50%) and **16** (0.007 g, 20%) as a syrup.

First eluted was **3-formyl-1-[6-hydroxy 5-*tert*-butyldimethylsilyloxymethyl-2,2-dimethyl-(3a*R*,5*R*,6*R*,6a*R*)-perhydrofuro[2,3-*d*][1,3]dioxol-6-yl]-(1*R*,2*E*)-2-propenyl acetate**, **16**: $[\alpha]_D = 17.51$ (*c* 1.0, $CHCl_3$); IR (neat): 720, 800, 1050, 1120, 1240, 1290, 1300, 1500, 1600, 1750, 1800, 3390, 3400 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 200 MHz): $\delta$ 0.06, 0.08 (2s, 6H, 2 Si $CH_3$), 0.90 (s, 9H, $C(CH_3)_3$), 1.38, 1.58 (2s, 6H, 2 $CH_3$), 2.10 (s, 3H, OAc), 2.95 (s, 1H, OH), 3.74 (d, 2H, $J_{4,5}$ 6.5 Hz, H-5, 5′), 3.97 (t, 1H, *J* 6.5 Hz, H-4), 4.29 (d, 1H, $J_{1,2}$ 4.3 Hz, H-2), 5.74 (d, 1H, $J_{1,2}$ 4.3 Hz, H-1), 5.80 (d, 1H, $J_{6,7}$ 7.6 Hz, H-6), 6.10 (dd, 1H, $J_{7,8}$ 16.2 $J_{8,9}$ 7.6 Hz, H-8), 7.00 (dd, 1H, $J_{6,7}$ 7.6, $J_{7,8}$ 16.2 Hz, H-7) 9.58 (d, 1H, $J_{8,9}$ 7.6 Hz, H-9).

Second eluted was **6′-hydroxy- 5-*tert*-butyldimethylsilyloxymethyl-2,2-dimethyl-3′-methylcarbonyloxy-(3′*S*,3a*R*,4′*R*,5*R*,6′*S*,6a*R*)-spiro[perhydrofuro[2,3-*d*][1,3]-dioxole-6,2′-(3′*H*,4′*H*,5′*H*,6′*H*-pyran)]-4-yl acetate**, **15**: IR (neat): 680, 750, 800, 1020, 1080, 1220, 1340, 1750, 3390, 3460 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 200 MHz):$\delta$ 0.09 (s, 6H, 2 Si $CH_3$), 0.9 (s, 9H, $C(CH_3)_3$), 1.38, 1.58 (2s, 6H, 2 $CH_3$), 1.65–1.84 (m, 1H, H-8′), 2.04 (s, 6H, 3 OAc), 2.19–2.4 (m, 1H, H-8), 3.26 (br. d, 1H, OH), 3.67–3.82 (m, 2H, H-5, 5′), 4.02 (dd, 1H, $J_{4,5}$ 8.6, $J_{4,5'}$ 3.8 Hz, H-4), 4.82 (d, 1H, $J_{1,2}$ 3.8 Hz, H-2), 5.06 (br. d, 1H, $J_{6,7}$ 10.3 Hz, H-6), 5.39 (br. d, 1H, H-9), 5.44–5.62 (m, 1H, H-7), 5.67 (d, 1H, $J_{1,2}$ 3.8 Hz, H-1); $^{13}C$ NMR ($CDCl_3$, 50 MHz): $\delta$ −5.48, −5.29, 18.31, 20.20, 25.90, 26.69, 55.29, 63.05, 67.82, 72.67, 75.66, 77.21, 77.78, 81.19, 84.19, 104.29, 113.39, 113.89, 129.28, 130.08, 159.34, 170.88; FABMS (*m*/*z*, %): 513 ($M^+$+23, 5), 313 (36), 191 (55), 171 (62), 159 (81) 154 (100).

The above mixture of lactols **15** (0.100 g, 0.204 mmol) and triethylamine (0.07 mL, 0.510 mmol), in dichloromethane (10 mL) was treated with acetic anhydride (0.02 mL, 0.204 mmol) in presence of catalytic DMAP at 0°C. After 1 h, it was worked up as described for **13** and the residue was purified by column chromatography (silica gel, 1:20 ethyl acetate–petroleum ether) to afford a separable mixture of **1** (0.080 g, 74%) and **2** (0.005 g, 4.6%) in a 16:1 ratio as syrup.

First eluted was **5-*tert*-butyldimethylsilyloxymethyl-2,2-dimethyl-3′,4′-di(methylcarbonyloxy)-(3′*S*,3a*R*,4′*R*,5*R*,6′*S*,6′*R*,6a*R*)-spiro[perhydrofuro[2,3-*d*][1,3]dioxole-6,2′-(3′*H*,4′*H*,5′*H*,6′*H*-pyran)]-6-yl acetate**, **2**: $[\alpha]_D = -6.1$ (*c* 0.25, $CHCl_3$); IR (neat): 820, 1100, 1240, 1300, 1350, 1750, 2850, 2900 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 500 MHz): $\delta$ 0.07, 0.08 (2s, 6H, 2 Si $CH_3$), 0.89 (s, 9H, $C(CH_3)$), 1.38 (s, 3H, $CH_3$(A)), 1.57 (s, 3H, $CH_3$(B)), 1.73 (dt, 1H, $J_{8a,9}$ 2.8, $J_{7,8a}$ 11.9, $J_{8a,8e}$ 11.9 Hz, H-8a), 2.01, 2.02 (2s, 9H, 3 OAc), 2.27 (ddd, 1H, $J_{7,8e}$ 5.2, $J_{8e,9}$ 0.9 Hz, H-8e), 3.76 (dd, 1H, $J_{4,5'}$ 4.3, $J_{5,5'}$ 11.4 Hz, H-5′), 3.83 (dd, 1H, $J_{4,5}$ 7.6, $J_{5,5'}$ 11.4 Hz, H-5), 4.09 (dd, 1H, $J_{4,5}$ 7.6, $J_{4,5'}$ 4.3 Hz, H-4), 4.83 (d, 1H, $J_{1,2}$ 3.8 Hz, H-2), 5.10 (d, 1H, $J_{6,7}$ 9.5 Hz, H-6), 5.40 (br. d, 1H, $J_{8a,9}$ 2.8, $J_{8e,9}$ 0.9 Hz, H-9), 5.56 (ddd, 1H, $J_{6,7}$ 9.5, $J_{7,8a}$ 11.9, $J_{7,8e}$ 5.2 Hz, H-7), 5.70 (d, 1H, $J_{1,2}$ 3.8 Hz, H-1); FABMS (*m*/*z*, %): 552 ($M^+$+23−3, 01), 325 (9), 281 (25), 207 (45), 173 (42), 165 (59), 153 (100). Anal. calcd for $C_{24}H_{40}O_{11}Si$ (532): C, 54.12; H, 7.57. Found: C, 54.09; H, 7.46%.

Second eluted was **5-*tert*-butyldimethylsilyloxymethyl-2,2-dimethyl-3′,4′-di(methyl carbonyloxy)-(3′*S*,3a*R*,4′*R*,5*R*,6′*S*,6′*S*,6a*R*) - spiro[perhydrofuro[2,3 - *d*][1,3]dioxole-6,2′-(3′*H*,4′*H*,5′*H*,6′*H*-pyran)]-6-yl acetate**, **1**: mp = 120–125°C; $[\alpha]_D = 18.71$ (*c* 1.3, $CHCl_3$); IR (KBR): 840, 1050, 1240, 1300, 1360, 1740, 2840, 2920 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 500 MHz): $\delta$ 0.06, 0.07 (2s, 6H, 2 $SiCH_3$), 0.90 (s, 9H, $C(CH_3)_3$), 1.38 (s, 3H, $CH_3$(A)), 1.56 (s, 3H, $CH_3$(B)), 1.78 (ddd, 1H, $J_{7,8a}$ 11.5, $J_{8a,9}$ 10.1, $J_{8a,8e}$ 12.0 Hz, H-8a), 2.01, 2.02, 2.10 (3s, 9H, 3 OAc), 2.37 (ddd, 1H, $J_{7,8e}$ 5.3, $J_{8e,9}$ 2.4 Hz, H-8e), 2.78 (m, 2H, H-5,5′), 4.16 (t, 1H, $J_{4,5}$ 6.2, $J_{4,5'}$ 6.2 Hz, H-4), 4.70 (d, 1H, $J_{1,2}$ 3.9 Hz, H-2), 5.12 (d, 1H, $J_{6,7}$ 9.6 Hz, H-6), 5.24 (ddd, 1H, $J_{6,7}$ 9.6, $J_{7,8a}$ 11.5, $J_{7,8e}$ 5.3 Hz, H-7), 5.77 (d, 1H, $J_{1,2}$ 3.9 Hz H-1), 6.02 (dd, 1H, $J_{8a,9}$ 10.1, $J_{8e,9}$ 2.4 Hz, H-9), $^{13}C$ NMR ($CDCl_3$, 50 MHz): $\delta$ −5.41, −5.25, 18.31, 20.76, 20.90, 25.89, 26.61, 26.85, 29.30, 29.66, 34.94, 61.41, 68.78, 69.25, 76.18, 78.45, 81.19, 81.96, 89.42, 105.77, 113.02, 168.24, 169.04, 170.10. FABMS (*m*/*z*, %): 555 ($M^+$+23, 51), 295 (52), 255 (67), 185 (91), 163 (99), 153 (100), 147 (69). HRMS: calcd for $C_{24}H_{40}O_{11}NaSi$: 555.223761. Observed: 555.225681.

### 3.11. Conversion of 10 to 18a and 18b

To a solution of alcohol **10** (0.200 g, 0.534 mmol) in DMSO (5 mL) was added IBX (0.180 g, 0.641 mmol), and stirred for 5 h at room temperature. It was worked up as described for **15**, purified by column chromatography (silica gel, 1:9 ethyl acetate–petroleum ether) to afford **5-*tert*-butyldimethylsilyloxymethyl-2,2-dimethyl-(3a*R*,5*R*,6′*R*,6a*R*) - piro[perhydrofuro[2,3 - *d*][1,3]dioxole-6,2′-(5′*H*,6′*H*-pyran)]-6′-ol**, **17** as a solid (0.14 g, 70%). Mp = 120–125°C; $[\alpha]_D = +8.6$ (*c* 0.75, $CHCl_3$); IR (KBR): 680, 750, 820, 1050, 1080, 1250, 1350, 1450, 1600, 1700, 3390, 3450 $cm^{-1}$ $^1H$ NMR ($CDCl_3$, 200 MHz): $\delta$ 0.08 (s, 6H, 2 $SiCH_3$), 0.80 (s, 9H, $C(CH_3)_3$), 1.30, 1.36 (2s, 6H, 2 $CH_3$), 2.05–2.52 (m, 2H, H-8, 8′), 3.18 (br. s, 1H, OH), 3.61–3.87 (m, 2H, H-5, 5′), 3.96–4.16 (m, 1H, H-4), 4.40 (d, 1H, $J_{1,2}$ 4.6 Hz, H-2), 5.51 (d, 1H, $J_{8,9}$ 4.6 Hz, H-9), 5.58 (br. d, 1H, $J_{6,7}$ 11.5 Hz, H-6), 5.73–5.81 (m, 1H, H-1), 5.81–5.96 (m, 1H, H-7); FABMS (*m*/*z*, %): 395 ($M^+$+23, 10), 297 (58), 215 (60), 69 (66), 55 (100).

A mixture of the lactols **17** (0.120 g, 0.322 mmol) and triethylamine (0.134 mL, 0.966 mmol), in dichloromethane (5 mL) was treated with acetic anhydride (0.03 mL, 0.322 mmol) in the presence of catalytic DMAP at 0°C. After 1 h, it was worked up as described for **13** and the residue purified by column chromatography (silica gel, 1:14 ethyl acetate–petroleum ether) to afford a separable anomeric mixture of acetates **18a** (0.040 g, 30%) and **18b** (0.080 g, 60%) in a 1:2 ratio.

First eluted was **5-*tert*-butyldimethylsilyloxymethyl-2,2-dimethyl-(3a*R*,5*R*,6′*R*,6′*R*,6a*R*)-spiro[perhydrofuro[2,3-*d*][1,3]dioxole-6,2′-(5′*H*,6′*H*-pyran)]-6-yl acetate**, **18a**: mp = 100–105°C; $[\alpha]_D = -12.7$ (*c* 1.5, $CHCl_3$); IR (KBR): 700, 820, 880, 1080, 1100, 1240, 1350, 1760, 2800, 2840, 2920 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 200 MHz): $\delta$ 0.05 (s, 6H, 2 Si $CH_3$), 0.87 (s, 9H, $C(CH_3)_3$), 1.31, 1.56 (2s, 6H, 2 $CH_3$), 2.04 (s, 3H, OAc), 2.06–2.20 (m, 1H, H-8′), 2.48–2.67 (m, 1H, H-8), 3.58–3.73 (m, 2H, H-5, 5′), 4.10 (t, 1H, *J* 4.6 Hz, H-4), 4.25 (d, 1H, $J_{1,2}$ 3.7 Hz, H-2), 5.64 (br. d, 1H, $J_{6,7}$ 11.5 Hz, H-6), 5.74 (d, 1H, $J_{1,2}$ 3.7 Hz, H-1), 5.83–5.96 (m, 1H, H-7), 6.36 (t, 1H, *J* 4.6 Hz, H-9); $^{13}C$ NMR ($CDCl_3$, 50 MHz): $\delta$ −5.45, −5.30, 18.21, 21.20, 25.80 (2C), 26.51, 26.68, 28.24, 29.58, 61.89, 78.66, 81.06, 83.69, 88.98, 103.85, 112.49, 122.67, 124.01, 169.28; FABMS (*m*/*z*, %): 415 ($M^+$+1, 10), 281 (78), 221 (100), 207 (98). Anal. calcd for $C_{20}H_{34}O_7Si$ (414): C, 57.94; H, 8.27. Found: C, 57.88; H, 8.17%.

Second eluted was **5-*tert*-butyldimethylsilyloxymethyl-2,2-dimethyl-(3a*R*,5*R*,6′*S*,6′*R*,6a*R*)-spiro[perhydrofuro-[2,3-*d*][1,3]dioxole-6,2′-(5′*H*,6′*H*-pyran)]-6-yl acetate**, **18b**: mp = 95–97°C; $[\alpha]_D = 44.20$ (*c* 1.01, $CHCl_3$); IR (KBR): 780, 820, 1020, 1100, 1250,1340, 1440, 1730, 2850, 2920, 2960 $cm^{-1}$ $^1H$ NMR ($CDCl_3$, 200 MHz): $\delta$ 0.09 (s, 6H, 2 Si $CH_3$), 0.91 (s, 9H, $C(CH_3)_3$), 1.36, 1.60 (2s, 6H, 2 $CH_3$), 2.12 (s, 3H, OAc), 2.25–2.50 (m, 2H, H-8, 8′), 3.63 (dd, 1H, $J_{5,5'}$ 11.4, $J_{4,5'}$ 7.1 Hz, H-5′), 3.85 (dd, 1H, $J_{5,5'}$ 11.4, $J_{4,5}$ 2.4 Hz, H-5), 4.13 (dd, 1H, $J_{4,5'}$ 9.5, $J_{4,5}$ 2.4 Hz, H-4), 4.28 (d, 1H, $J_{1,2}$ 4.3 Hz, H-2), 5.66 (br. d, 1H, $J_{6,7}$ 9.5 Hz, H-6), 5.74 (d, 1H, $J_{1,2}$ 4.3 Hz, H-1), 5.90 (dt, 1H, $J_{7,8}$ 4.8, $J_{7,8'}$ 4.8, $J_{6,7}$ 9.5 Hz, H-7), 6.15 (dd, 1H, $J_{8,9}$ 4.2, $J_{8',9}$ 5.1 Hz, H-9); $^{13}C$ NMR ($CDCl_3$, 50 MHz): $\delta$ −5.31, −5.16, 14.05, 18.29, 21.25, 25.89, 26.44, 26.79, 29.28, 29.51, 29.66, 61.93, 81.83, 83.17, 90.49, 103.58, 113.28, 123.79, 125.29, 169.07; FABMS (*m*/*z*, %): 415 ($M^+$+1, 10), 281 (78), 221 (100), 207 (98). Anal. calcd for $C_{20}H_{34}O_7Si$ (414): C, 57.94; H, 8.27. Found: C, 57.85; H, 8.19%.

### 3.12. 3′,4′-Dihydroxy-5-*tert*-butyldimethylsilyloxymethyl-2,2-dimethyl-(3′*S*,3a*R*,4′*S*,5*R*,6′*R*,6′*R*,6a*R*)-spiro[perhydrofuro[2,3-*d*][1,3]dioxole-6,2′-(3′*H*,4′*H*,5′*H*,6′*H*-pyran)]-6-yl acetate, 19a

To a stirred solution of olefin **18a** (0.080 g, 0.193 mmol) in acetone–water (5 mL, 3:1) were added sequentially *N*-methyl morpholine *N*-oxide (0.045 g, 0.386 mmol) and $OsO_4$ (two drops) at room temperature. After 20 days, it was worked up described for **12** and purified by column chromatography (silica gel, 1:3.3 ethyl acetate–petroleum ether) to afford diol **19a** as a solid (0.043 g, 80%). The conversion of the reaction was 60% and starting material 0.030 g recovered. Mp = 125–130°C; $[\alpha]_D = -22.3$ (*c* 1.5, $CHCl_3$); IR (KBR): 680, 1020, 1150, 1220, 1350, 1420, 1680, 2840, 2900, 3380 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 200 MHz): $\delta$ 0.10 (s, 6H, 2 Si $CH_3$), 0.82 (s, 9H, $C(CH_3)_3$), 1.30, 1.48 (2s, 6H, 2 $CH_3$), 2.02 (s, 3H, 1 OAc), 2.06–2.15 (m, 2H, H-8, 8′), 3.52 (d, 1H, $J_{6,7}$ 5.1 Hz, H-6), 3.75–4.06 (m, 3H, H-5, 5′, 7), 4.24 (dd, 1H, $J_{4,5}$ 5.1, $J_{4,5'}$ 8.2 Hz, H-4), 5.32 (d, 1H, $J_{1,2}$ 4.1 Hz, H-2), 5.71 (d, 1H, $J_{1,2}$ 4.1 Hz, H-1), 6.10 (d, 1H, $J_{8,9}$ 5.1 Hz, H-9); FABMS (*m*/*z*, %): 471 ($M^+$+23, 5), 401 (74), 281 (67), 221 (75), 207 (100).

### 3.13. 3′,4′-Dihydroxy5-*t*-butyldimethylsilyloxyymethyl-2,2-dimethyl(3′*R*,3a*R*,4′*R*,5*R*,6′*S*,6′*R*,6a*R*)-spiro[perhydrofuro[2,3-*d*][1,3]dioxole-6,2′-(3′*H*,4′*H*,5′*H*,6′*H*-pyran)]-6-yl acetate, 19b

To a stirred solution of olefin **18b** (0.160 g, 0.386 mmol) in acetone–water (10 mL, 3:1) were added sequentially *N*-methyl morpholine *N*-oxide (0.090 g, 0.772 mmol) and $OsO_4$ (four drops) at room temperature. After 20 days, it was worked up as described for **12** and purified by column chromatography (silica gel, 1:3 ethyl acetate–petroleum ether) to afford diol **19b** as a solid (0.110 g, 85%). The conversion of reaction was after 20 days 75% only and 0.040 g of starting material was recovered. Mp = 165–170°C; $[\alpha]_D = 71.60$ (*c* 0.55, $CHCl_3$); IR (KBR): 720, 840, 1020, 1100, 1200, 1250, 1320, 1400, 1720, 2800, 2920, 3400, 3520 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 200 MHz): $\delta$ 0.08 (s, 6H, 2 Si $CH_3$), 0.92 (s, 9H, $C(CH_3)_3$), 1.40, 1.51 (2s, 6H, 2 $CH_3$), 1.92 (ddd, 1H, $J_{7,8}$ 5.0, $J_{8,9}$ 10.2, $J_{8,8'}$ 15.2 Hz, H-8) 2.11 (s, 3H, 1 OAc), 2.28 (dt, 1H, $J_{7,8'}$ 3.8, $J_{8',9}$ 3.8, $J_{8,8'}$ 15.2 Hz, H-8′), 3.65 (d, 1H, $J_{6,7}$ 5.1 Hz, H-6), 3.88–4.01 (m, 2H, H-5′, 7), 4.10 (dd, 1H, $J_{4,5}$ 4.6, $J_{5,5'}$ 15.2 Hz, H-5), 4.32 (dd, 1H, $J_{4,5}$ 4.6, $J_{4,5'}$ 8.1 Hz, H-4), 5.39 (d, 1H, $J_{1,2}$ 5.1 Hz, H-2), 5.78 (d, 1H, $J_{1,2}$ 5.1 Hz, H-1), 6.26 (dd, 1H, $J_{8,9}$ 10.2, $J_{8',9}$ 3.8 Hz, H-9); $^{13}C$ NMR ($CDCl_3$, 50 MHz): $\delta$ −5.44, −5.34, 25.92, 27.00 (7C), 29.79, 35.67, 59.71, 68.10, 68.31, 78.80, 81.73, 89.92, 96.25, 105.13; FABMS (*m*/*z*, %): 471 ($M^+$+23, 100), 391 (44), 331 (70), 181 (72), 171 (74).

### 3.14. 5-*tert*-Butyldimethylsilyloxymethyl-2,2-dimethyl-3′,4′-di(methylcarbonyloxy)-(3′*R*,3a*R*,4′*R*,5*R*,6′*S*,6′*S*,6a*R*)-spiro[perhydrofuro[2,3-*d*][1,3]dioxole-6,2′-(3′*H*,4′*H*,5′*H*,6′*H*-pyran)]-6-yl acetate, 3

A mixture of the diol **19b** (0.090 g, 0.200 mmol) and triethylamine (0.166 mL, 1.200 mmol), in dichloromethane (5 mL) was treated with acetic anhydride (0.037 mL, 0.400 mmol) in the presence of catalytic DMAP at 0°C. After 1 h, it was worked up as described for **13** and the residue was purified by column chromatography (silica gel, 1:20 ethyl acetate–petroleum ether) to afford **3** (0.100 g) in 94% yield as a gummy syrup. $[\alpha]_D = 40.69$ (*c* 1.15, $CHCl_3$); IR (neat): 750, 840, 1000, 1050, 1090, 1210, 1240, 1350, 1440, 1460, 1750, 2800, 2900 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 500 MHz): $\delta$ 0.06, 0.07(2s, 6H, 2 $SiCH_3$), 0.90 (s, 9H, $C(CH_3)_3$), 1.36 (1S, 3H, $CH_3$(A)), 1.54 (s, 3H, $CH_3$(B)), 1.95 (ddd, 1H, $J_{7,8b}$ 3.9, $J_{8b,9}$ 6.9, $J_{8a,8b}$ 13.7 Hz, H-8b), (2s, 9H, 3 OAc), 2.23 (ddd, 1H, $J_{7,8a}$ 6.9, $J_{8a,9}$ 2.9, $J_{8a,8b}$ 13.7 Hz, H-8a), 3.79 (dd, 1H, $J_{4,5'}$ 4.4, $J_{5,5'}$11.3 Hz, H-5′), 3.89 (dd, 1H, $J_{4,5}$ 4.9, $J_{5,5'}$ 11.3 Hz, H-5), 4.26 (t, 1H, $J_{4,5}$ 4.9, $J_{4,5'}$ 4.4 Hz, H-4), 4.87 (d, 1H, $J_{1,2}$ 4.4 Hz, H-2), 5.32 (d, 1H, $J_{6,7}$ 3.4 Hz, H-6), 5.46 (dt, 1H, $J_{6,7}$ 3.4, $J_{7,8a}$ 6.9, $J_{7,8b}$ 3.9 Hz H-7), 5.79 (d, 1H, $J_{1,2}$ 4.4 Hz, H-1), 6.32 (dd, 1H, $J_{8a,9}$ 2.9, $J_{8b,9}$ 6.9 Hz, H-9); $^{13}C$ NMR ($CDCl_3$, 50 MHz): $\delta$ −5.53, −5.43, 18.21, 20.64, 20.88, 21.07, 25.81(2C), 26.79, 27.29, 29.62, 32.10, 61.58, 66.58, 66.68, 80.68, 82.58, 83.04, 89.91, 104.98, 113.34, 168.42, 169.22, 169.57; FABMS (*m*/*z*, %): 555 ($M^+$+23, 6), 415 (52), 255 (65), 185 (82), 163 (78), 147 (100). Anal. calcd for $C_{24}H_{40}O_{11}Si$ (532): C, 54.12; H, 7.57. Found: C, 54.09; H, 7.49%.

### 3.15. 5-*tert*-Butyldimethylsilyloxymethyl-2,2-dimethyl-3′,4′-di(methylcarbonyloxy)-(3′*S*,3a*R*,4′*S*,5*R*,6′*R*,6′*S*,6a*R*)-spiro[perhydrofuro[2,3-*d*][1,3]dioxole-6,2′-(3′*H*,4′*H*,5′*H*,6′*H*-pyran)]-6-yl acetate, 4

A mixture of diol **19a** (0.030 g, 0.066 mmol) and triethylamine (0.055 mL, 0.396 mmol), in dichloromethane (5 mL) was treated with acetic anhydride (0.012 mL, 0.132 mmol) in the presence of catalytic DMAP at 0°C. After 1 h, it was worked up as described for **13** and the residue was purified by column chromatography (silica gel, 1:20 ethyl acetate–petroleum ether) to afford **4** (0.035 g) in 98% yield as a solid. Mp = 120–125°C; $[\alpha]_D = -25.95$ (*c* 1.2, $CHCl_3$); IR (KBR): 720, 820, 1020, 1150, 1210, 1350, 1440, 1480, 1780, 2820, 2900 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 500 MHz): $\delta$ 0.06, 0.07 (2s, 6H, 2 $SiCH_3$), 0.88 (s, 9H, $C(CH_3)_3$), 1.36 (s, 3H, $CH_3$ (A)), 1.54 (s, 3H, $CH_3$(B)), 2.06, 2.07, 2.12 (3s, 9H, 3 OAc), 2.10 (m, 1H, 8b), 2.21 (ddd, 1H, $J_{7,8a}$ 4.3, $J_{8a,9}$ 2.4, $J_{8a,8b}$ 14.8 Hz, H-8a), 3.69 (dd, 1H, $J_{4,5b}$ 5.3, $J_{5a,5b}$ 11.0 Hz, H-5b), 3.77 (dd, 1H, $J_{4,5a}$ 6.2, $J_{5a,5b}$ 11.0 Hz, H-5a), 4.19 (t, 1H, $J_{4,5a}$ 6.2, $J_{4,5b}$ 5.3 Hz, H-4), 5.04 (d, 1H, $J_{6,7}$ 3.8 Hz, H-6), 5.21 (d, 1H, $J_{1,2}$ 3.8 Hz, H-2), 5.36 (ddd, 1H, $J_{6,7}$ 3.8, $J_{7,8a}$ 4.3, $J_{7,8b}$ 3.9 Hz, H-7), 5.73 (d, 1H, $J_{1,2}$ 3.8 Hz, H-1), 6.18 (dd, 1H, $J_{8a,9}$ 2.4, $J_{8b,9}$ 4.3 Hz, H-9); $^{13}C$ NMR ($CDCl_3$, 50 MHz): $\delta$ −5.68, −5.54, 18.10, 20.55, 20.85, 21.15, 25.69, 26.73, 26.84, 29.48, 30.84, 31.72, 61.16, 65.83, 65.96, 79.91, 80.96, 81.57, 88.03, 104.85, 111.95, 168.82(2C), 169.58. FABMS (*m*/*z*, %): 555 ($M^+$+23, 30), 517 (9), 415 (68), 255 (50), 185 (30), 136 (40), 117 (100). HRMS: calcd for $C_{23}H_{37}O_{11}Si$: 517.210516. Observed: 517.209264.

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