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Synthesis of spiro carbon linked disaccharides from D-glucose, D- and L-arabinose☆

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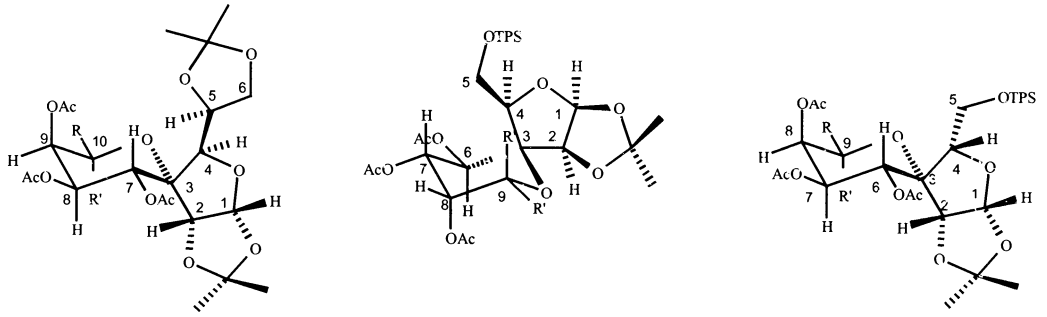
Abstract—The synthesis of new spiro carbon linked disaccharides from D-glucose, D- and L-arabinose is described. In the present study furan is used as a masked sugar synthon, while chirality is transferred from the sugar derived chiral templates.

1. Introduction

Bio-active glycosubstances, over the years, have received great attention in chemical, medicinal and pharmaceutical research.[1–4] As a consequence, the design and implementation of stereoselective strategies for preparing them by using readily available homochiral precursors constituted prominent issue of a number of laboratories[5–9] Among the various means with which a carbohydrate unit can be assembled, methodologies involving carbon-carbon bond formation between an enantiopure 'short' precursor and a homologative manipulable reactant constitute a leading subject in the modern synthetic chemistry panorama.[10,11] This has led to interest in the synthesis of glycosyl mimics such as *C*-glycosides, *C*-saccharides,[12] aza-sugars[13] etc. Notwithstanding these advances, no attempt has ever been made to synthesize spiro-*C*-disaccharides in which the sugars are attached through a 'spiro' carbon atom. Due to the rigidity of the spiro system, these systems should hold the hydroxy substituents in a precisely defined fashion and hence should have potential for specific interactions. Our continued interest on the use of carbohydrate derived chiral templates for the synthesis of new glycosubstances as well as glycosyl mimics,[14–18] prompted the synthesis of the new 'spiro carbon linked disaccharides' (Fig. 1).



1 R = OMe, R' = H
2 R = H, R' = OMe

3 R = H, R' = OMe
4 R = OMe, R' = H

5 R = OMe, R' = H
6 R = H, R' = OMe

Figure 1.

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Keywords: carbohydrates; glycosyl mimics; furan; spiro carbon liked disaccharides.
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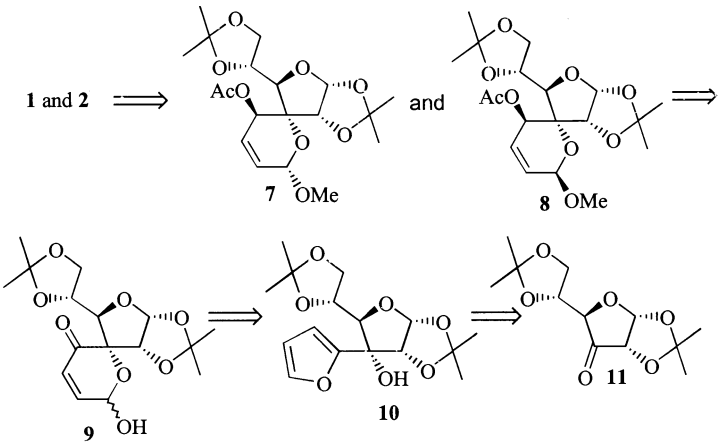


Scheme 1.

2. Results and discussion

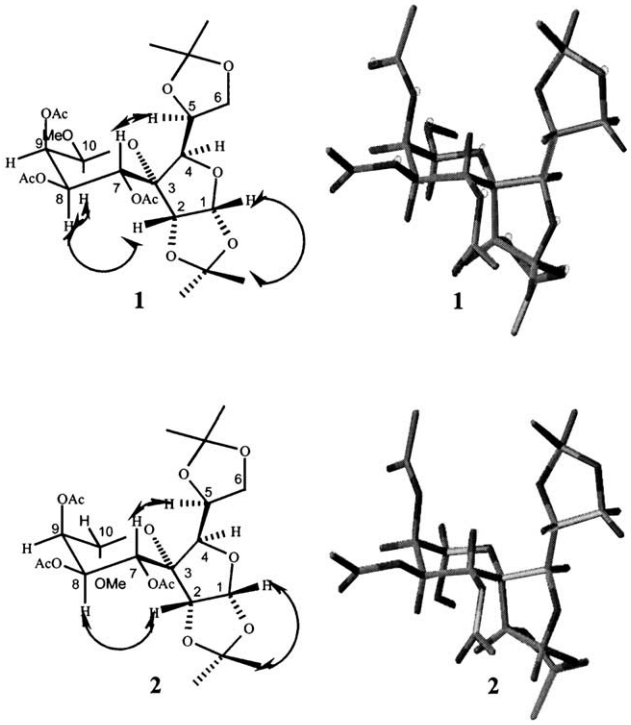
2.1. Synthesis and conformational analysis of spiro carbon linked disaccharides from D-glucose

The construction of spiro disaccharides **1** and **2** was attempted according to the retrosynthetic analysis shown in Scheme 1. Accordingly, allyl acetates **7** and **8** were envisaged as late stage precursors for **1** and **2**, while **7** and **8** in turn would be derived from the enone **9**. Oxidative ring opening of furan in the furyl sugar **10**, which was envisaged from 'diacetone glucose', would easily make the enone **9**. Thus overall, in the present study on synthesis of spiro carbon linked disaccharides **1** and **2**, furan was utilized as a four carbon masked sugar synthon, while the requisite chirality would be defined by chiral building block **11** derived from 'diacetone glucose'.

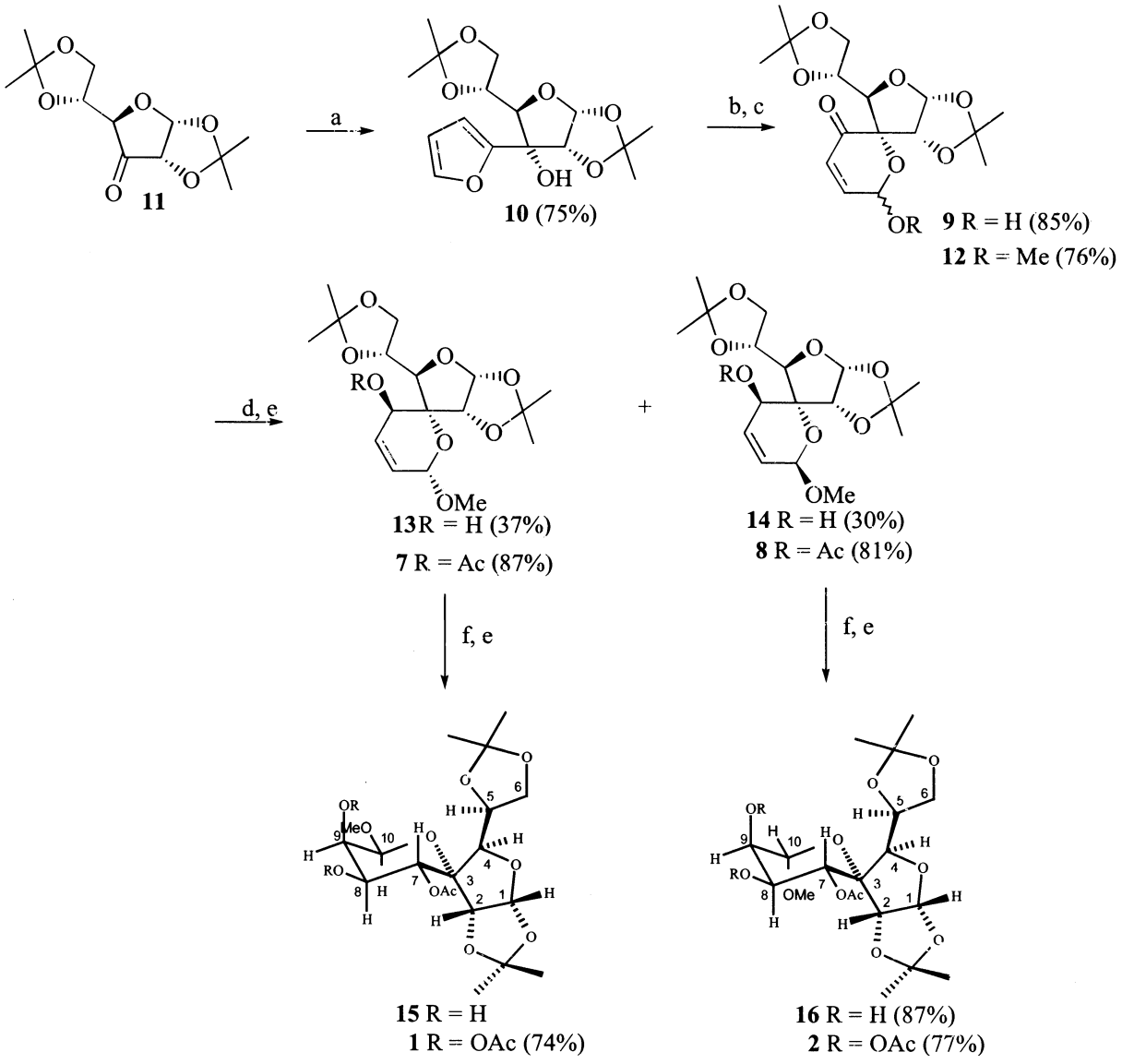
Accordingly, 1,2:5,6-di-*O*-isopropylidine-α-D-glucofurano-3-ulose (**11**) prepared[19,20] from D-glucose was subjected to alkylation (Scheme 2) with 2-furyl lithium[21] in THF at −40°C to afford the 3-*C*-furanyl-D-allose derivative **10**[22] in 75% yield. The stereochemical outcome at the C-3 center is a consequence of steric hindrance of the 1,2-*O*-isopropylidine group on the α-face.[22] Oxidative ring opening[23] of the furan in **10** with NBS in aqueous THF at −5°C gave an anomeric mixture of lactols **9**, which were subsequently converted into an inseparable mixture of the α,β-*O*-methyl pyranosides **12** using Ag_2O–MeI, in 3:2 ratio (76%). Stereoselective reduction of **12** under Luche's[24,25] reaction conditions using $CeCl_3{\cdot}7H_2O$–$NaBH_4$ in methanol and chromatographic purification afforded allylic alcohols **13** and **14** with complete facial selectivity.[26]

Alcohols **13** and **14** were acetylated independently using Ac_2O–Et_3N to give the corresponding acetates **7** (87%) and **8** (81%), respectively. Having made the allylic acetates **7** and **8**, these were submitted to catalytic osmylation[27,28] using OsO_4–NMO in acetone–water (4:1) to afford the diols **15** and **16** respectively with diastereofacial control, i.e. *anti* relative to the –OAc group. A key observation made during the osmylation of allylic acetates **7** and **8** was that the α-anomer **7** underwent osmylation at a very slow rate resulting in trace amounts of the diol **15**, even after 15 days with the majority of the starting material being recovered. On the other hand, osmylation of acetate **8** was completed in 16 h and gave the diol **16** in 87% yield. The diols **15** and **16** were independently subjected to acetylation with Ac_2O–Et_3N to furnish the spiro disaccharides **1** (74%) and **2** (77%), respectively.

The ^{1}H and 2D-NOESY experiments unambiguously determined the structures of both the disaccharides **1** and **2**, and further confirmations were made from other spectral data like mass and HRMS analysis. Compound **1** has shown characteristic nOe cross-peak between H8 and H10, while in compound **2**, no nOe was observed between H8 and H10 indicating epimeric nature of stereocentre at C10. Presence



nOe and energy minimized structures of compounds 1 and 2



Scheme 2. *Reagents*: (a) Furan, *n*-BuLi, THF, −40°C; (b) NBS, THF–H_2O (4:1), −5°C; (c) Ag_2O, MeI, CH_2Cl_2, RT; (d) $CeCl_3{\cdot}7H_2O$, $NaBH_4$, MeOH, 0°C; (e) Ac_2O, Et_3N, CH_2Cl_2, (f) OsO_4, NMO, acetone–water (4:1).

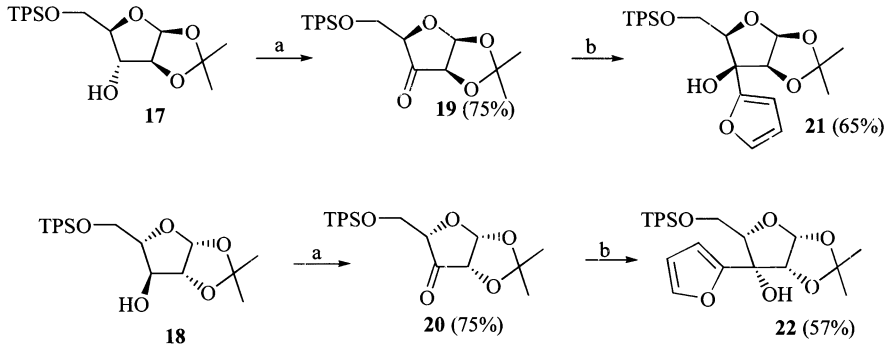
of nOe cross peaks between H1-Me (A) and H2-Me (A) implies an envelope conformation for the isopropylidine group. Relative orientation of both the sugar rings is confirmed by the nOe cross peaks between H8 and H2 and H7 and H5. The NMR data is in agreement with the energy minimized structures obtained by using SYBYL program.

2.2. Synthesis and conformational analysis of enantiomeric spiro carbon linked disaccharides from D- and L-arabinoses

In the preceding discussion, a new methodology was described for the synthesis of spiro carbon linked disaccharides, a new class of glycosubstances. Having developed a methodology for the synthesis of new class of disaccharides from D-glucose, it was next aimed at extension of the same study for the synthesis of enantiomeric spiro carbon linked disaccharides **3** and **4** from D-arabinose, **5** and **6** from L-arabinose. As described earlier, the 1,2-*O*-isopropylidine group of furanoses play a crucial role in dictating the stereochemical outcome at the spiro centre as evidenced by complete facially selective attack of the furyl lithium on the prochiral ketonic functionality. Thus, the study on D- and L-arabinose should result in the enantiomeric spiro carbon linked disaccharides.

Accordingly, compounds **17** and **18** (Scheme 3) on treatment with PDC and Ac_2O in CH_2Cl_2 at reflux temperature gave ketones **19** and **20**, respectively, in 75% yield, which on C-alkylation with furan and *n*-BuLi in THF at −40°C furnished 3-*C*-furanyl derivatives **21** (65%) and **22** (57%), respectively.

Compound **21** (Scheme 4) was subjected to oxidative ring opening with NBS in aqueous THF at −5°C to afford the lactols **23** (85%), which on treatment with Ag_2O and MeI in CH_2Cl_2 gave a chromatographically separable mixture of

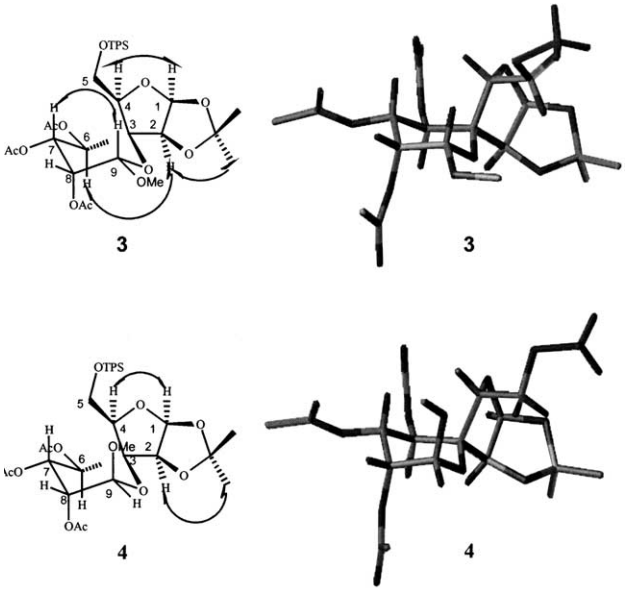


Scheme 3. *Reagents*: (a) PDC, Ac_2O, CH_2Cl_2, reflux; (b) Furan, *n*-BuLi, THF, −40°C.

pyranosides **24** and **25**. Similarly, **22** on reaction with NBS gave **26** (85%), which on methylation gave **27** (62%) as an inseparable mixture.

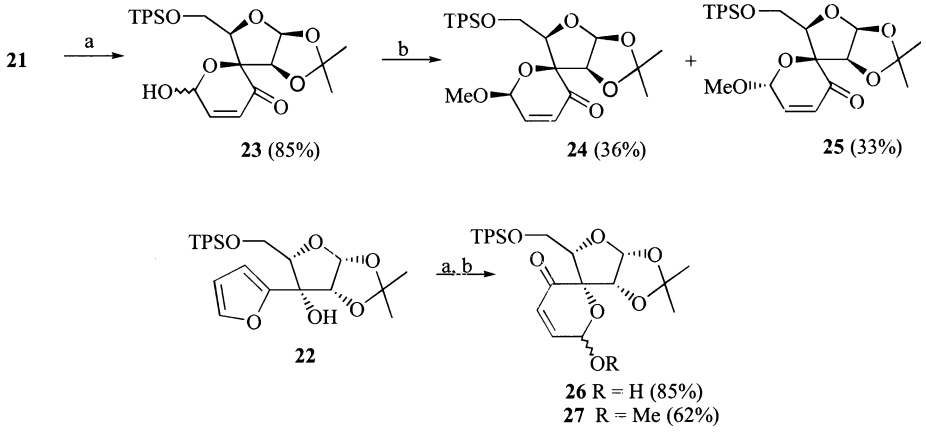
Stereoselective reduction of enones **24** and **25** (Scheme 5) using $CeCl_3{\cdot}7H_2O$–$NaBH_4$ in MeOH afforded **28** (80%) and **31** (76%), which on acetylation (Ac_2O and Et_3N) afforded the acetates **29** (70%) and **32** (87%), respectively. Acetates **29** and **32** were subjected to osmylation (OsO_4–NMO) in acetone–water (4:1) for one week to give the diols **30** (60%) and **33** (33%). Finally, acetylation of **30** and **33** with Ac_2O and Et_3N in CH_2Cl_2 afforded the spiro carbon linked disaccharides **3** (65%) and **4** (72%), respectively.

The structures of these disaccharides were unambiguously assigned from their spectral analysis and NOESY experiments. nOe between H7 and H9 supports their diaxial disposition in compound **3**, whereas in compound **4** no nOe was observed between H7 and H9, indicating that C9 center is epimeric. These observations in combination with the other couplings in the six membered rings suggest a chair conformation for hexose. The relative orientation of the sugar rings is confirmed, by the nOe cross peaks between H2 and H6 in compounds **3** and **4** along with the nOe between H4 and H9 in compound **3**. The structures obtained from the diagnostic data derived from the measurements of interproton coupling constants and detection of specific

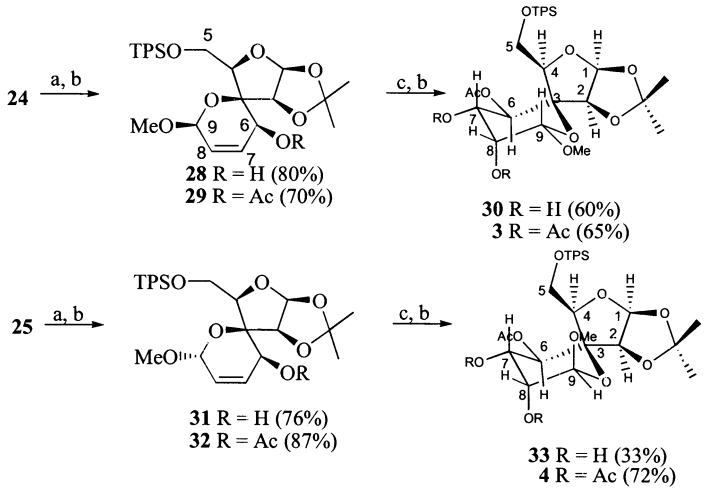


nOe and energy minimised structures of compounds 3 and 4

(Phenyls and acetate protons are removed after minimization for better view)



Scheme 4. *Reagents*: (a) NBS, THF–H_2O (4:1), −5°C; (b) Ag_2O, MeI, CH_2Cl_2, RT.

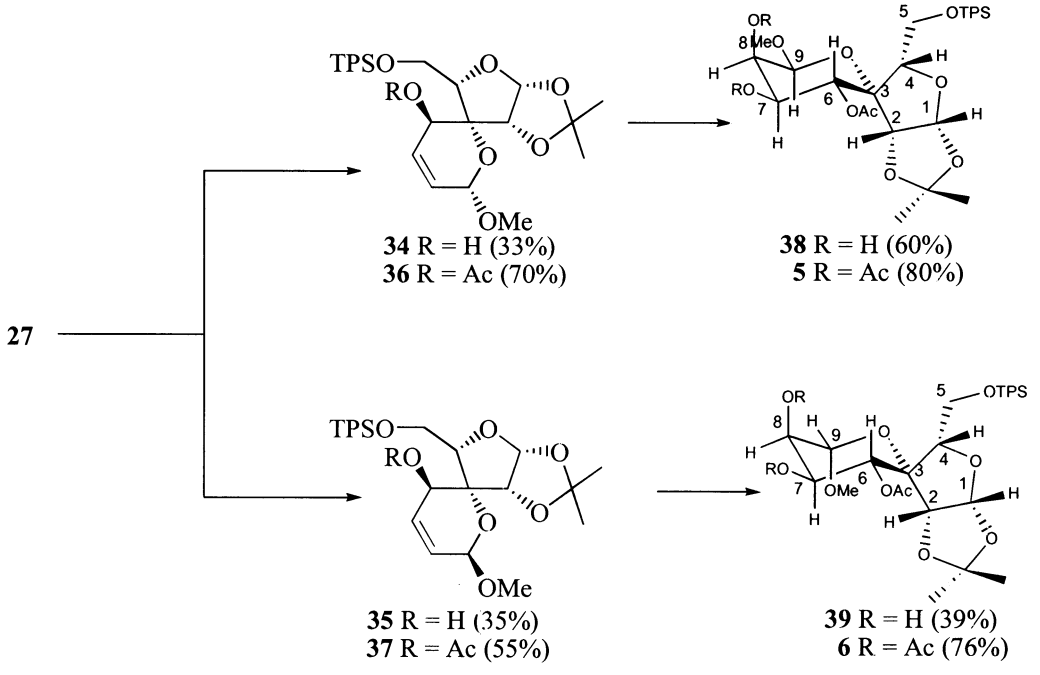


Scheme 5. *Reagents*: (a) $CeCl_3{\cdot}7H_2O$, $NaBH_4$, MeOH, 0°C; (b) Ac_2O, Et_3N, CH_2Cl_2; (c) OsO_4, NMO, acetone–water (4:1).

nOe's were further supported by molecular modeling calculations using SYBYL program.

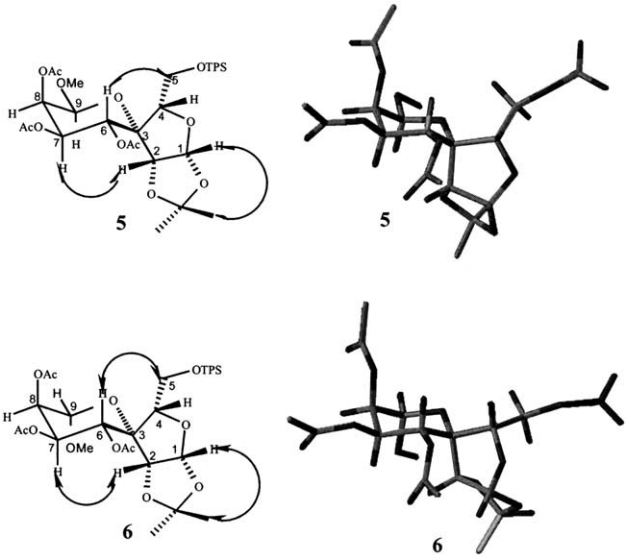
Similarly, the inseparable mixture of **27** (Scheme 6) was subjected to reduction with $CeCl_3{\cdot}7H_2O$–$NaBH_4$ to afford the alcohols **34** and **35**, which were chromatographically separable. Acetylation of **34** and **35** and osmylation of the resultant acetates **36** and **37** gave diols **38** (60%) and **39** (39%), respectively. Finally diols **38** and **39** on acetylation afforded the spiro carbon linked disaccharides **5** (80%) and **6** (76%).

The structures of **5** and **6** were assigned from ^1H NMR and other spectral data such as 2D-NOESY spectra. Large vicinal coupling between H6 and H7 of 8.5 Hz and nOe cross peak between H7 and H9 support their their diaxial disposition in compound **5** and one large vicinal coupling $J_{6,7}$ of 10.8 Hz was observed in compound **6**. These observations in combination with the other couplings in the six membered ring suggest a chair conformation for hexose. The relative orientation of the sugar rings is confirmed by the nOe cross peaks between H7 and H2 and H6 and H5′. The structures obtained from the diagnostic data derived from the measurements of interproton coupling constants and detection of specific nOe's were further supported by molecular modeling calculations using



Scheme 6. *Reagents*: (a) $CeCl_3{\cdot}7H_2O$, $NaBH_4$, MeOH, 0°C; (b) Ac_2O, Et_3N, CH_2Cl_2; (c) OsO_4, NMO, acetone–water (4:1).

SYBYL program. The ^{1}H NMR and optical rotation data clearly indicate that the spiro disaccharides derived from D- and L-arabinose were enantiomeric.



nOe and energy minimised structures of compounds 5 and 6
(Phenyls and acetate protons are removed after minimization for better view)

3. Conclusion

Thus, in conclusion the first synthesis of spiro carbon linked disaccharides as a new class of glycosubstances has been achieved by using a 3-keto sugar resulting in the spiro carbon center on sugar templates. The presence of the 1,2-*O*-isopropylidine group on the α- and β-faces determines the entry of the furan moiety on nucleophilic addition, thereby determining the course of spiro carbon linked disaccharide generation. Overall, the chirality is induced from the sugar template, while D- and L-arabinose gave access to a new class of enantiomeric spiro carbon linked disaccharides. The methodology developed in the present study would be of immense utility in the synthesis of new glycosubstances and the thus made new disaccharides might find potential use biologically.

4. Experimental

4.1. General

All moisture sensitive reactions were performed under nitrogen atmosphere using flame-dried glassware. Solvents were dried over standard drying agents and freshly distilled prior to use. NMR spectra were recorded on Varian Gemini FT-200 MHz, Unity-400 MHz (21°C) and Inova-500 MHz (30°C) spectrometers, with 7–10 mM solutions in appropriate solvents using TMS as internal standard. ^{13}C NMR spectra were recorded with complete proton decoupling. The assignments were carried out with the help of two-dimensional Double Quantum Filtered Correlation Spectroscopy (DQFCOSY) and Nuclear Overhauser Effect Spectroscopy (NOESY) experiments. All the experiments were carried out in the phase sensitive mode using the procedure of States et al.[29] The spectra were acquired with 2×192 free induction decays (FID) containing 8–16 transients with the relaxation decay of 1.5 s. The NOESY were performed with mixing time of 0.5 s. The two dimensional data were processed with gaussian apodization in both the dimensions.

All molecular mechanical calculations were carried out using SYBYL 6.8 program on a silicon graphics O_2 workstation. The Tripos force field with default parameters was used through out the simulations. Minimization's were done first with Steepest Decent, followed by Conjugate Gradient methods for a maximum of 1000 iterations or RMS deviation of 0.005 kcal mol^{-1}, whichever was earlier. The energy minimized molecules were then subjected to MOPAC. The new geometrical structures thus obtained were again minimized using the above mentioned energy minimization protocol.

Optical rotations were measured with a JASCO DIP-370 instrument, and $[\alpha]_D$-values are in units of 10^{-1} deg cm^2 g^{-1}. IR spectra were taken with a Perkin–Elmer 1310 spectrometer. Mass spectra were recorded on CEC-21-11013 or Finnigan Mat 1210 double focussing mass spectrometers operating at a direct inlet system and FABMS and HRMS were measured using VG AUTOSPEC mass spectrometers at 5 or 7 K resolution using perfluorokerosene as an internal reference. Nomenclature mentioned in this section was adopted from ACD/Name Version 1.0 β, Advanced Chemistry Development Inc., Toronto, Canada. Organic solutions were dried over anhydrous Na_2SO_4 and concentrated below 40°C in vacuo.

4.1.1. 5-(2,2-Dimethyl-(4*R*)-1,3-dioxolan-4-yl)-6-(2-furyl)-2,2-dimethyl-(3a*R*,5*R*,6*R*,6a*R*)-perhydrofuro-[2,3-*d*][1,3]-dioxol-6-ol (10). To a stirred solution of furan (1.48 mL, 20.3 mmol) in dry THF (15 mL), *n*-BuLi (13.5 mL, 20.3 mmol, 1.5 M solution in hexane) was added dropwise at −40°C. After 1 h, ketone **11** (3.5 g, 13.56 mmol) in dry THF (8 mL) was added dropwise at the same temperature over 10 min and the reaction mixture warmed slowly to room temperature over a period of 30 min. The reaction mixture was treated with saturated aqueous NH_4Cl solution (20 mL), diluted with water (40 mL) and extracted with ether (3×50 mL). The ethereal solution was washed with water (40 mL), brine (35 mL), dried (Na_2SO_4) and concentrated to the crude. The residue was purified by column chromatography (*Si*-gel, 60–120 mesh, 6% EtOAc–hexane) to afford *5-(2,2-dimethyl-(4R)-1,3-dioxolan-4-yl)-6-(2-furyl)-2,2-dimethyl-(3aR,5R,6R,6aR)-perhydrofuro-[2,3-d][1,3]dioxol-6-ol* (**10**, 3.3 g, 75%) as a colorless syrup. $[\alpha]_D^{27}$=+21.6 (*c* 0.72, $CHCl_3$); δ_H (200 MHz, $CDCl_3$), 7.38 (1H, br s, H-10), 6.38 (2H, br s, H-8,9), 5.95 (1H, d, $J_{1,2}$=4.0 Hz, H-1), 4.52 (1H, d, $J_{1,2}$=5.0 Hz, H-2), 4.05 (1H, d, $J_{4,5}$=5.8 Hz, H-4), 3.80–3.72 (1H, m, H-5), 3.70–3.60 (1H, m, H-6′), 3.50–3.40 (1H, m, H-6), 3.05 (1H, br s, O*H*), 1.22, 1.38, 1.60 (12H, 3s, CH_3); δ_C (50 MHz, $CDCl_3$), 152.4, 142.2, 113.1, 110.5, 109.0, 107.4, 104.6, 82.6, 82.2, 79.0, 74.0, 65.4, 26.7, 26.6 (2C), 25.1; *m/z*: 311 (EIMS, M^+-15), 196, 110; HRMS: (EIMS, M^+-15), found 311.1129. $C_{15}H_{19}O_7$ requires 311.1131.

4.1.2. 5-(2,2-Dimethyl-(4*R*)-1,3-dioxolan-4-yl)-6′-methoxy-2,2-dimethyl-(3a*R*,5*R*,6′*R*,6a*R*)spiro[perhydrofuro-[2,3-*d*][1,3]-dioxole-6,2′-(6′*H*-pyran)]-3′-one (12). A solution of **10** (2.0 g, 6.13 mmol) in THF–water (10 mL, 4:1) was cooled to −5°C and NBS (1.09 g, 6.13 mmol) added in portions. After 5 min, the reaction mixture was neutralized with saturated $NaHCO_3$ solution (5 mL), diluted with water (20 mL) and extracted with ethylacetate (3×30 mL). The combined organic layers were washed with water (2×30 mL), brine (30 mL), dried (Na_2SO_4) and concentrated to afford the lactols **9** (1.78 g, 85%) as a syrup.

A solution of the above lactols **9** (1.5 g, 4.38 mmol) in CH_2Cl_2 (10 mL) was treated with MeI (0.62 mL, 8.77 mmol) in the presence of Ag_2O (1.0 g, 4.38 mmol) for 12 h. The reaction mixture was filtered through celite and washed with CH_2Cl_2 (3×50 mL). The organic layer was evaporated and the crude purified by column chromatography (*Si*-gel, 10% EtOAc–hexane) to afford an anomeric mixture of O-methyl glycosides *5-(2,2-dimethyl-(4R)-1,3-dioxolan-4-yl)-6′-methoxy-2,2-dimethyl-(3aR,5R,6′R,6aR)-spiro[perhydrofuro-[2,3-d][1,3]-dioxole-6,2′-(6′H-pyran)]-3′-one* (**12**, 1.18 g, 76%) as a syrup in 3:2 ratio. δ_H (200 MHz, $CDCl_3$), 6.86–6.15 (2H, m, H-8,9), 5.81 (1H, d, $J_{1,2}$=4.0 Hz, H-1), 5.45 (0.4H, d, $J_{9,10}$=2.7 Hz, H-10), 5.20 (0.6H, d, $J_{9,10}$=4.5 Hz, H-10), 4.38 (1H, d, $J_{1,2}$=4.0 Hz, H-2), 4.16–4.05 (1H, m, H-5), 4.00–3.80 (3H, m, H-4,6,6′), 3.58, 3.54 (3H, 2s, OCH_3), 1.60, 1.40, 1.30, 1.20 (12H, 4s, CH_3), IR (neat): 2930, 2885, 1694, 1052 cm^{-1}; *m/z*: 341 (EIMS, M^+-15); HRMS: M^+-15, found 341.1246. $C_{16}H_{21}O_8$ requires 341.1236.

4.1.3. Reduction of enones 12. To a solution of **12** (0.3 g, 0.84 mmol) in methanol (6 mL), was added $CeCl_3{\cdot}7H_2O$ (0.47 g, 1.26 mmol) and stirred at room temperature for 10 min. The reaction mixture was cooled to 0°C, treated with $NaBH_4$ (0.046 g, 1.26 mmol) in portions over a period of 5 min. and methanol was removed under vacuum. The reaction mixture was quenched with ice-cold water (10 mL) and extracted with ethylacetate (3×25 mL). The organic layer was washed with water (2×25 mL), brine (30 mL), dried (Na_2SO_4) and concentrated to the crude. The crude containing a mixture of anomers **13** and **14** was separated by column chromatography (*Si*-gel, 15% EtOAc–hexane).

First eluted was *5-(2,2-dimethyl-(4R)-1,3-dioxolan-4-yl)-6′-methoxy-2,2-dimethyl-(3′R,3aR,5R,6′R, 6′S,6aR)-spiro[-perhydrofuro[2,3-d][1,3]dioxole-6,2′-(3′H,6′H-pyran)]-3′-ol* (**13**; 0.11 g, 37%) as a syrup, $[\alpha]_D^{27}$=+63.9 (*c* 1.1, $CHCl_3$); δ_H (200 MHz, $CDCl_3$), 6.18 (1H, dd, $J_{8,9}$=7.8 Hz, $J_{7,8}$=7.0 Hz, H-8), 5.90 (1H, dd, $J_{8,9}$=7.8 Hz, $J_{9,10}$=2.0 Hz, H-9), 5.60 (1H, d, $J_{1,2}$=4.4 Hz, H-1), 4.96 (1H, d, $J_{9,10}$= 2.0 Hz, H-10), 4.65 (1H, dd, $J_{7,OH}$=8.5 Hz, $J_{7,8}$=7.0 Hz, H-7), 4.23 (1H, d, $J_{1,2}$=4.4 Hz, H-2), 4.15–4.05 (2H, m, H-4,6′), 3.98–3.89 (1H, m, H-6), 3.70–3.53 (1H, m, H-5), 3.45 (3H, s, 3H, OCH_3), 2.67 (1H, br d, OH), 1.60, 1.47, 1.32, 1.30 (12H, 4s, CH_3); *m/z*: (EIMS, M^+-15), 343.

Second eluted was *5-(2,2-dimethyl-(4R)-1,3-dioxolan-4-yl)-6′-methoxy-2,2-dimethyl-(3′R,3aR,5R,6′R, 6′R,6aR)-spiro-[perhydrofuro[2,3-d][1,3]dioxole-6,2′-(3′H,6′H-pyran)]-3′-ol* (**14**; 0.09 g, 30%) as a colorless solid, mp: 143°C; $[\alpha]_D^{27}$=+59.1 (*c* 0.61, $CHCl_3$); Analysis found: C 56.81, H 7.19. $C_{17}H_{26}O_8$ requires C 56.98, H 7.26%; δ_H (200 MHz, $CDCl_3$), 6.20 (1H, dd, $J_{8,9}$=12.5 Hz, $J_{7,8}$=7.0 Hz, H-8), 5.85 (1H, br d, $J_{8,9}$=12.5 Hz, H-9), 5.68 (1H, d, $J_{1,2}$=4.4 Hz, H-1), 5.32 (1H, br s, H-10), 4.65 (1H, dd, $J_{7,8}$=7.0 Hz, $J_{7,OH}$=8.5 Hz, H-7), 4.18 (1H, d, $J_{1,2}$=4.4 Hz, H-2), 4.10–3.90 (3H, m, H-4,6,6′), 3.70–3.55 (1H, m, H-5), 3.48 (3H, s, OCH_3), 3.0 (1H, br d, OH), 1.60,1.40, 1.30, 1.29 (12H, 4s, CH_3); IR (neat): 3440, 2942, 2895, 1100 cm^{-1}; *m/z*: (EIMS, M^+-15), 343.

4.1.4. 5-(2,2-Dimethyl-(4*R*)-1,3-dioxolan-4-yl)-6′-methoxy-2,2-dimethyl-(3′*R*,3a*R*,5*R*,6′*R*,6′*S*,6a*R*)-spiro[perhydrofuro[2,3-*d*][1,3]dioxole-6,2′-(3′*H*,6′*H*-pyran)]-3-yl acetate (7). A solution of **13** (0.07 g, 0.19 mmol) and Et_3N (0.05 mL, 0.38 mmol) in CH_2Cl_2 (5 mL) was treated with Ac_2O (0.04 mL, 0.39 mmol) in presence catalytic DMAP at 0°C. After stirring for 1hr, it was neutralized with saturated aqueous $NaHCO_3$ solution and extracted with CH_2Cl_2 (2×10 mL). Combined organic layers were washed with water (20 mL), dried (Na_2SO_4) and concentrated to the crude, which on purification by column chromatography (*Si*-gel, 10% EtOAc–hexane) gave *5-(2,2-dimethyl-(4R)-1,3-dioxolan-4-yl)-6′-methoxy-2,2-dimethyl-(3′R,3aR,5R, 6′R,6′S,6aR)-spiro[perhydrofuro[2,3-d][1,3]dioxole-6,2′-(3′H,6′H-pyran)]-3-yl acetate* (**7**, 0.068 g, 87%) as a syrup. Analysis found: C 56.82; H 6.93. $C_{19}H_{28}O_9$ requires C 56.99; H 7.05%; IR (neat, cm^{-1}): 2930, 2885, 1710, 1050; $[\alpha]_D^{27}$=+133.5 (*c* 1.3, $CHCl_3$); δ_H (200 MHz, $CDCl_3$), 6.15 (1H, dd, $J_{7,8}$=5.4 Hz, $J_{8,9}$=1.7 Hz, H-8), 6.00 (1H, d, $J_{8,9}$=1.7 Hz, H-9), 5.60 (1H, d, $J_{1,2}$=4.2 Hz, H-1), 5.05 (1H, s, H-10), 4.74 (1H, d, $J_{7,8}$=5.4 Hz, H-7), 4.36 (1H, q, J'=10.8 Hz, H-5), 4.29 (1H, d, $J_{1,2}$=4.2 Hz, H-2), 4.15 (1H, d, $J_{4,5}$=5.7 Hz, H-4), 3.82–4.0 (2H, m, H-6,6′), 3.45 (3H, s, OCH_3), 2.10 (3H, s, CH_3), 1.60, 1.45, 1.31, 1.29 (12H, 4s, CH_3), δ_c (50 MHz, $CDCl_3$), 169.7, 130.9, 124.0, 112.5, 109.3, 102.7, 84.9, 82.1, 81.2, 80.7, 73.6, 67.0, 64.4, 55.4, 26.78, 26. 7 (2C), 25.4, 20.9; *m/z*: (EIMS, M^+-15), 385.

4.1.5. 5-(2,2-Dimethyl-(4*R*)-1,3-dioxolan-4-yl)-6′-methoxy-2,2-dimethyl-(3′*R*,3a*R*,5*R*,6′*R*,6′*R*,6a*R*)-spiro[perhydrofuro[2,3-*d*][1,3]dioxole-6,2′-(3′*H*,6′*H*-pyran)]-3-yl acetate (8). A solution of **14** (0.07 g, 0.19 mmol) and Et_3N (0.05 mL, 0.38 mmol) in CH_2Cl_2 (5 mL) was treated with Ac_2O (0.04 mL, 0.39 mmol) in presence catalytic DMAP at 0°C and worked up as described for **7** to afford *5-(2,2-dimethyl-(4R)-1,3-dioxolan-4-yl)-6′-methoxy-2,2-dimethyl-(3′R,3aR,5R,6′R,6′R,6aR)-spiro [perhydrofuro[2,3-d][1,3]-dioxole-6,2′-(3′H,6′H-pyran)]-3-yl acetate* (**8**, 0.063 g, 81%) as a syrup. Analysis found: C 56.80; H 6.87. $C_{19}H_{28}O_9$ requires C 56.99; H 7.05%; $[\alpha]_D^{27}$=+13.7 (*c* 1.5, $CHCl_3$); δ_H (200 MHz, $CDCl_3$), 6.16, 6.10 (1H, 2d, $J_{7,8}$=5.4 Hz, $J_{8,9}$=1.6 Hz, H-8), 5.98, 5.90, (1H, 2d, $J_{9,10}$=1.8 Hz, $J_{8,9}$=1.6 Hz, H-9), 5.69 (1H, d, $J_{1,2}$=4.5 Hz, H-1), 5.32 (1H, d, $J_{9,10}$=1.8 Hz, H-10), 4.74 (1H, d, $J_{7,8}$=5.4 Hz, H-7), 4.58–4.50 (1H, m, H-5), 4.25 (1H, d, $J_{1,2}$=4.5 Hz, H-2), 4.06–3.83 (3H, m, H-4,6,6′), 3.50 (3H, s, OCH_3), 2.10 (3H, s, CH_3), 1.30, 1.40, 1.60 (12H, 3s, CH_3); *m/z*: (EIMS, M^+-15), 385.

4.1.6. 5-(2,2-Dimethyl-(4*R*)-1,3-dioxolan-6′-methoxy-2,2-dimethyl-(3′*R*,3a*R*,4′*R*,5*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)]-3-yl acetate (1). To a stirred solution of **7** (0.041 g,

0.10 mmol) in acetone–water (5 mL, 4:1), were added sequentially NMO (0.023 g, 0.20 mmol) and OsO_4 (2 drops, 1.0 M solution in toluene) at room temperature. After 15 days, the reaction mixture was quenched with aqueous $NaHSO_3$ solution and acetone was evaporated on rotary evaporator. The reaction mixture was diluted with water (20 mL) and extracted with ethylacetate (2×15 mL). The organic layer was washed with water (15 mL), brine (20 mL), dried (Na_2SO_4) and concentrated to the crude, which on purification by column chromatography (*Si*-gel, 60–120 mesh, 60% EtOAc–hexane) furnished **15** (5 mg) as a syrup.

The above diol **15** (5 mg, 0.01 mmol) in CH_2Cl_2 (5 mL) was treated with Et_3N (2 drops) and Ac_2O (2 drops) and worked up as described for **7** to afford *5-(2,2-dimethyl-(4R)-1,3-dioxolan-6′-methoxy-2,2-dimethyl-(3′R,3aR,4′R,5R,5′R,6′S,6′S,6aR)-spiro[perhydrofuro[2,3-d][1,3]dioxole-6,2′-(3′H,4′H,5′H,6′H-pyran)]-3-yl acetate* (**1**, 4 mg, 74%) as a syrup. $[\alpha]_D^{27}=-8.0$ (*c* 0.25, $CHCl_3$); δ_H (200 MHz, $CDCl_3$), 5.75 (1H, d, $J_{1,2}=4.05$ Hz, H-1), 5.40 (1H, dd, $J_{8,9}=5.3$ Hz, $J_{7,8}=1.9$ Hz, H-8), 5.09 (1H, dd, $J_{8,9}=5.3$ Hz, $J_{9,10}=3.7$ Hz, H-9), 5.02 (1H, d, $J_{9,10}=3.7$ Hz, H-10), 4.85 (1H, d, $J_{7,8}=1.9$ Hz, H-7), 4.50 (1H, d, $J_{1,2}=4.05$ Hz, H-2), 4.48–4.36 (1H, m, H-5), 4.15 (1H, d, $J_{4,5}=4.5$ Hz, H-4), 3.95–3.80 (2H, m, H-6,6′), 3.55 (3H, s, OCH_3), 2.18, 2.12, 2.02 (9H, 3s, OAc), 1.60, 1.45, 1.35, 1.25 (12H, 4s, CH_3); *m/z*: (FABMS), 519 (M^++1), 503 (M^+−15).

4.1.7. 5-(2,2-Dimethyl-(4*R*)-1,3-dioxolan-4-yl)-6′-methoxy-2,2-dimethyl-3′,4′-di(methylcarbonyl-oxy)-(3′*R*, 3a*R*,4′*R*,5*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)]-5-yl acetate (2). To a stirred solution of **8** (0.041 g, 0.14 mmol) in acetone–water (5 mL, 4:1) were added sequentially NMO (0.032 g, 0.27 mmol) and OsO_4 (2 drops) at room temperature. After 16 h (monitered by TLC), it was worked up as described for **15** to afford **16** (0.038 g, 87%) as a syrup.

The above diol **16** (0.03 g, 0.07 mmol) in CH_2Cl_2 was treated with Et_3N (0.024 mL, 0.17 mmol) and Ac_2O (0.01 mL, 0.1 mmol) and worked up as described for **7** to afford *5-(2,2-dimethyl-(4R)-1,3-dioxolan-4-yl)-6′-methoxy-2,2-dimethyl-3′,4′-di(methylcarbonyl-oxy)(3′R,3aR,4′R,5R,5′R,6′S,6′R,6aR)-spiro[perhydrofuro[2,3-d][1,3]dioxole-6,2′-(3′H,4′H,5′H,6′H-pyran)]-5-yl acetate* (**2**, 0.027 g, 77%) as a colorless solid. Mp 117–119°C; $[\alpha]_D^{27}=+27.9$ (*c* 0.91, $CHCl_3$); δ_H (200 MHz, $CDCl_3$), 5.61 (1H, d, $J_{1,2}=4.5$ Hz, H-1), 5.48 (1H, dd, $J_{7,8}=5.4$ Hz, $J_{8,9}=4.5$ Hz, H-8), 5.16 (1H, dd, $J_{9,10}=9.1$ Hz, $J_{8,9}=4.5$ Hz, H-9), 5.10 (1H, d, $J_{9,10}=9.1$ Hz, H-10), 4.86 (1H, d, $J_{7,8}=5.4$ Hz, H-7), 4.80 (1H, d, $J_{1,2}=4.5$ Hz, H-2), 4.70–4.59 (1H, m, H-5), 4.20 (1H, d, $J_{4,5}=4.5$ Hz, H-4), 4.19–3.80 (2H, m, H-6,6′), 3.55 (3H, s, OCH_3), 2.19, 2.12, 2.10 (9H, 3s, $OCOCH_3$), 1.62, 1.49, 1.39 (1×6H, 2×3H, 3s, CH_3); δ_C (50 MHz, $CDCl_3$), 169.6 (2C), 168.9, 112.9 (2C), 108.8, 102.9, 98.1, 82.8, 82.2, 73.5, 69.2, 68.8, 66.9, 65.8, 56.6, 29.6, 26.7 (2C), 26.4, 25.5, 20.7 (2C); *m/z*: 519 (FABMS, M^++1), 503 (M−15); HRMSFAB: found 503.1763. $C_{22}H_{31}O_{13}$ (M^+−15) requires 503.1765.

4.1.8. 5-*t*-Butyldiphenylsilyloxymethyl-6-(2-furyl)-2,2-dimethyl-(3a*S*,5*R*,6*S*,6a*S*)-perhydrofuro-[2,3-*d*][1,3]-dioxol-6-ol (21). To a solution of **17** (3.0 g, 7.0 mmol) in CH_2Cl_2 (50 mL), were added PDC (5.27 g, 14.0 mmol), Ac_2O (catalytic) and heated at reflux temperature for 3 h. Reaction mixture was evaporated and the residue dissolved in ether. Ethereal solution was filtered through silica gel, washed with ether and the combined ethereal layers were concentrated below 25°C to afford **19** (2.24 g, 75%) as a syrup.

To a stirred solution of furan (0.52 mL, 7.74 mmol) in dry THF (10 mL), *n*-BuLi (5.16 mL, 7.74 mmol, 1.5 M solution in hexane) was added dropwise at −40°C. After 1 h, ketone **19** (2.2 g, 5.16 mmol) in dry THF (6 mL) was added dropwise at the same temperature over 10 min and the reaction mixture was worked up as described for **10** and purified by column chromatography (*Si*-gel, 60-–120 mesh, 3% ethylacetate in hexane) to afford *5-t-butyldiphenylsilyloxymethyl-6-(2-furyl)-2,2-dimethyl-(3aS,5R,6S,6aS)-perhydrofuro-[2,3-d][1,3]dioxol-6-ol* (**21**, 1.65 g, 65%) as a syrup. $[\alpha]_D^{27}=-20.6$ (*c* 1.32, $CHCl_3$); δ_H (200 MHz, $CDCl_3$), 7.80–7.60 (5H, m, Ph), 7.46–7.25 (6H, m, H-8, Ph), 6.32 (2H, br s, H-6,7), 5.80 (1H, d, $J_{1,2}=4.0$ Hz, H-1), 4.70 (1H, d, $J_{1,2}=4.0$ Hz, H-2), 4.25 (1H, t, $J=4.8$ Hz, H-4), 4.07 (1H, dd, $J_{5,5'}=11.0$ Hz, $J_{4,5}=4.8$ Hz, H-5′), 3.92 (1H, dd, $J_{5,5'}=11.0$ Hz, $J_{4,5}=4.8$ Hz, H-5), 3.50 (1H, br s. *OH*), 1.60, 1.45 (6H, 2s, CH_3), 1.10, 1.02 (9H, 2s, CH_3); δ_C NMR (50 MHz, $CDCl_3$), 142.4, 135.65, 135.6 (2C), 134.7, 129.6 (3C), 127.6 (4C), 115.4, 110.3, 106.5, 104.6, 85.2, 84.4, 75.9, 62.7, 27.3, 27.2, 26.7 (3C), 26.5 (2C), 19.1; *m/z*: (FABMS), 517 (M^++23), 437, 419; HRMS found: 517.2021. $C_{28}H_{34}O_6NaSi$ (M^++23) requires 517.2022.

4.1.9. Ring opening of 21. A solution of **21** (1.4 g, 2.82 mmol) in THF–water (10 mL, 4:1) was cooled to −5°C and NBS (0.5 g, 2.82 mmol) added in portions. After 5 min, the reaction mixture was worked up as described for **9** and concentrated to afford a mixture of the lactols **23** (1.22 g) in 85% yield.

A mixture of the above lactols **23** (1.22 g, 2.39 mmol) in CH_2Cl_2 (10 mL) was treated with MeI (0.34 mL, 4.78 mmol) in the presence of Ag_2O (0.55 g, 2.39 mmol) for 12 h. The reaction mixture was worked up as described for **12** and purified by column chromatography (*Si*-gel, 60–120 mesh, 7% EtOAc–hexane).

First eluted was: *5-t-butyldiphenylsilyloxymethyl-6′-methoxy-2,2-dimethyl-(3aS,5R,6′S,6′S,6aS)-spiro[perhydrofuro-[2,3-d][1,3]dioxole-6,2′-(3′H,6′H-pyran)]-3′-one* (**24**, 0.45 g, 36%) as a syrup, $[\alpha]_D^{27}=-35.35$ (*c* 1.68, $CHCl_3$); δ_H (200 MHz, $CDCl_3$) 7.80–7.60 (4H, m, Ph), 7.50–7.30 (6H, m, Ph), 6.88 (1H, dd, $J_{7,8}=11.5$ Hz, $J_{8,9}=1.4$ Hz, H-8), 6.18 (1H, d, $J_{7,8}=11.5$ Hz, H-7), 5.90 (1H, br s, H-9), 5.78 (1H, d, $J_{1,2}=4.3$ Hz, H-1), 4.62 (1H, d, $J_{1,2}=4.3$ Hz, H-2), 4.45 (1H, dd, $J_{4,5}=3.8$ Hz, $J_{4,5'}=3.7$ Hz, H-4), 3.78 (1H, dd, $J_{4,5'}=3.7$ Hz, $J_{5,5'}=10.4$ Hz, H-5′), 3.72 (1H, dd, $J_{4,5}=3.8$ Hz, $J_{5,5'}=10.4$ Hz, H-5), 3.56 (3H, s, OCH_3), 1.41, 1.32, 1.03, 1.0 (15H, 4s, CH_3), IR (neat, cm^{-1}): 2925, 2885, 1690, 1060; *m/z*: (FABMS), 547 (M^++23), 467, 435; HRMS found: 523.2128. $C_{29}H_{35}O_7Si$ (M^+−1) requires 523.2152.

Second eluted was: *5-t-butyldiphenylsilyloxymethyl-6′-methoxy-2,2-dimethyl-(3aS,5R,6′R,6′S,6aS)-spiro [perhydrofuro[2,3-d][1,3]dioxole-6,2′-(3′H,6′H-pyran)]-3′-one* (**25**,

0.41 g, 33%) as a syrup, $[\alpha]_D^{27}=-16.66$ (*c* 1.2, $CHCl_3$); δ_H (200 MHz, $CDCl_3$) 7.80–7.60 (4H, m, Ph), 7.50–7.30 (6H, m, Ph), 6.82 (1H, dd, $J_{7,8}$=12.2 Hz, $J_{8,9}$=3.4 Hz, H-8), 6.16 (1H, d, $J_{7,8}$=12.2 Hz, H-7), 5.72 (1H, d, $J_{1,2}$=4.0 Hz, H-1), 5.12 (1H, d, $J_{8,9}$=3.4 Hz, H-9), 4.45 (1H, d, $J_{1,2}$=4.0 Hz, H-2), 4.19 (1H, dd, $J_{4,5}$=5.2 Hz, $J_{4,5'}$=5.3 Hz, H-4), 3.90–3.70 (2H, m, H-5,5′), 3.47 (3H, s, OCH_3), 1.40, 1.25, 1.02, 1.0 (15H, 4s, CH_3); *m/z*: (FABMS), 547 (M^++23), 467, 435. HRMS found: 523.2143. $C_{29}H_{35}O_7Si$ (M^+−1) requires 523.2152.

4.1.10. 5-*t*-Butyldiphenylsilyloxymethyl-6′-methoxy-2,2-dimethyl-(3′*S*,3*aS*,5*R*,6′*S*,6′*S*,6*aS*)-spiro[perhydrofuro-[2,3-*d*][1,3]dioxole-6,2′-(3′*H*,6′*H*-pyran)]-3′-ol (28). To a solution of **24** (0.3 g, 0.57 mmol) in methanol (5 mL), $CeCl_3{\cdot}7H_2O$ (0.21 g, 0.57 mmol) and $NaBH_4$ (21 mg, 0.57 mmol) were added sequentially at 0°C and worked up as described for **13** to afford *5-t-butyldiphenylsilyloxymethyl-6′-methoxy-2,2-dimethyl(3′S,3aS,5R,6′S,6′S,6aS)-spiro[perhydrofuro[2,3-d][1,3]dioxole-6,2′-(3′H,6′H-pyran)]-3′-ol* (**28**, 0.24 g, 80%) as a syrup. $[\alpha]_D^{27}=-19.8$ (*c* 1.0, $CHCl_3$); IR (neat, cm^{-1}): 3445, 2942, 2880, 1050; δ_H (200 MHz, $CDCl_3$) 7.80–7.60 (4H, m, Ph), 7.48–7.30 (6H, m, Ph), 5.90 (1H, br s, H-8), 5.75–5.88 (1H, m, H-7), 5.69 (1H, d, $J_{1,2}$=4.4 Hz, H-1), 5.32 (1H, br s, H-9), 4.54 (1H, d, $J_{1,2}$=4.4 Hz, H-2), 4.26 (1H, brs, H-6), 4.20–3.95 (3H, m, H-4,5,5′), 3.25 (3H, s, OCH_3), 1.40, 1.25, 1.20, 1.06 (15H, 4s, CH_3); *m/z*: (FABMS), 549 (M^++23), 469, 437; HRMS found: 526.2384. $C_{29}H_{38}O_7Si$ requires 526.2387.

4.1.11. 5-*t*-Butyldiphenylsilyloxymethyl-6′-methoxy-2,2-dimethyl-(3′*S*,3*aS*,5*R*,6′*R*,6′*S*,6*aS*)-spiro[perhydrofuro-[2,3-*d*][1,3]dioxole-6,2′-(3′*H*,6′*H*-pyran)]-3′-ol (31). To a stirred solution of **25** (0.32 g, 0.61 mmol) in methanol (5 mL), $CeCl_3{\cdot}7H_2O$ (0.22 g, 0.61 mmol) and $NaBH_4$ (23 mg, 0.61 mmol) were added sequentially at 0°C and worked up as described for **13** to afford *5-t-butyldiphenylsilyloxymethyl-6′-methoxy-2,2-dimethyl-(3′S,3aS,5R,6′R,6′S,6aS)-spiro[perhydrofuro[2,3-d][1,3]dioxole-6,2′-(3′H,6′H-pyran)]-3′-ol* (**31**, 0.24 g, 76%) as a syrup. $[\alpha]_D^{27}=+5.53$ (*c* 1.3, $CHCl_3$); δ_H (200 MHz, $CDCl_3$) 7.85–7.50 (4H, m, Ph), 7.50–7.30 (6H, m, Ph), 6.02–5.83 (2H, m, H-7, 8), 5.73 (1H, d, $J_{1,2}$=4.0 Hz, H-1), 4.90 (1H, br s, H-9), 4.60 (1H, d, $J_{1,2}$=4.0 Hz, H-2), 4.27 (1H, br s, H-6), 4.20–3.98 (3H, m, H-4,5,5′), 3.35 (3H, s, OCH_3), 1.40, 1.32, 1.31, 1.10 (15H, 4s, CH_3); *m/z*: (FABMS), 549 (M^++23), 437. Analysis found: C 65.97; H 7.14. $C_{29}H_{38}O_7Si$ requires C 66.13; H 7.27.

4.1.12. 5-*t*-Butyldiphenylsilyloxymethyl-6′-methoxy-2,2-dimethyl-(3′*S*,3*aS*,5*R*,6′*S*,6′*S*,6*aS*)-spiro[perhydrofuro-[2,3-*d*][1,3]dioxole-6,2′-(3′*H*,6′*H*-pyran)]-3-yl acetate (29). A solution of **28** (0.2 g, 0.38 mmol) and Et_3N (0.13 mL, 0.95 mmol) in CH_2Cl_2 (5 mL) was treated with Ac_2O (0.06 mL, 0.57 mmol) in presence of catalytic DMAP at 0°C and worked up as described for **7** to afford *5-t-butyldiphenylsilyloxymethyl-6′-methoxy-2,2-dimethyl-(3′S,3aS,5R,6′S,6′S,6aS)-spiro[perhydrofuro[2,3-d][1,3]dioxole-6,2′-(3′H,6′H-pyran)]-3-yl acetate* (**29**, 0.15 g, 70%) as a syrup. $[\alpha]_D^{27}=+0.27$ (*c* 1.44, $CHCl_3$); IR (neat, cm^{-1}): 2940, 2885, 1720, 1060; δ_H (200 MHz, $CDCl_3$) 7.80–7.60 (4H, m, Ph); 7.45–7.30 (6H, m, Ph), 5.95–5.75 (2H, m, H-7,8), 5.69 (1H, d, $J_{1,2}$=3.9 Hz, H-1), 5.55 (1H, d, $J_{6,7}$=3.2 Hz, H-6), 5.40 (1H, br s, H-9), 4.55 (1H, d, $J_{1,2}$=3.9 Hz, H-2), 4.14–4.0 (2H, m, H-4,5′), 3.95–3.85 (1H, m, H-5), 3.23 (3H, s, OCH_3), 2.12 (3H, s, $COCH_3$), 1.40, 1.32, 1.26, 1.05 (15H, 4s, CH_3); δ_C (50 MHz, $CDCl_3$) 169.6, 135.7 (2C), 135.6 (2C), 129.4 (2C), 128.9 (2C), 127.5 (4C), 113.7, 105.5, 95.5, 84.9, 82.5, 81.4, 69.1, 63.0, 54.1, 26.8 (5C), 26.7 (2C), 20.9, 19.1; *m/z*: (FABMS), 591 (M^++23); HRMSFAB found: 568.6484. $C_{31}H_{40}O_8Si$ (M^+) requires 568.6517.

4.1.13. 5-*t*-Butyldiphenylsilyloxymethyl-6′-methoxy-2,2-dimethyl-(3′*S*,3*aS*,5*R*,6′*S*,6′*R*,6*aS*)-spiro[perhydrofuro-[2,3-*d*][1,3]dioxole-6,2′-(3′*H*,6′*H*-pyran)]-3-yl acetate (32). A solution of **31** (0.2 g, 0.35 mmol) and Et_3N (0.12 mL, 0.88 mmol) in CH_2Cl_2 (5 mL) was treated with Ac_2O (0.06 mL, 0.57 mmol) in presence of catalytic DMAP at 0°C and worked up as described for **7** to afford *5-t-butyldiphenylsilyloxymethyl-6′-methoxy-2,2-dimethyl-(3′S,3aS,5R,6′S,6′R,6aS)-spiro[perhydrofuro[2,3-d][1,3]dioxole-6,2′-(3′H,6′H-pyran)]-3-yl acetate* (**32**, 0.18 g, 87%) as a syrup. $[\alpha]_D^{27}=+8.08$ (*c* 0.94, $CHCl_3$); δ_H (200 MHz, $CDCl_3$) 7.80–7.60 (4H, m, Ph), 7.45–7.30 (6H, m, Ph), 5.90–5.75 (2H, m, H-7,8), 5.65 (1H, d, $J_{1,2}$=4.1 Hz, H-1), 5.55 (1H, d, $J_{6,7}$=2.5 Hz, H-6), 4.89 (1H, br s, H-9), 4.42 (1H, d, $J_{1,2}$=4.1 Hz, H-2), 4.22–4.10 (2H, m, H-4,5′), 3.92–3.80 (1H, m, H-5), 3.24 (3H, s, OCH_3), 2.13 (3H, s, $COCH_3$), 1.26, 1.25, 1.05 (15H, 3s, CH_3); δ_C (50 MHz, $CDCl_3$) 169.8, 135.7 (3C), 129.4 (2C), 128.0, 127.8, 127.57 (3C), 111.9, 105.8, 94.7, 87.9, 79.9, 78.6, 70.9, 64.2, 56.0, 29.7, 26.8 (4C), 26.4 (2C), 26. 0 (2C), 21.0, 19.2; *m/z*: (FABMS), 591 (M^++23). HRMSFAB found: 568.6495. $C_{31}H_{40}O_8Si$ (M^+) requires 568.6517.

4.1.14. 5-*t*-Butyldiphenylsilyloxymethyl-4′,5′-dihydroxy-6′-methoxy-2,2-dimethyl-(3′*S*,3*aS*,4′*S*,5*R*,5′*S*,6′*S*,6′*R*,6*aS*)-spiro[perhydrofuro[2,3-*d*][1,3]dioxole-6,2′-(3′*H*,4′,5′*H*,6′*H*-pyran)]-3-yl acetate (30). To a stirred solution of **29** (0.15 g, 0.26 mmol) in acetone–water (5 mL, 4:1) were added sequentially NMO (31 mg, 0.26 mmol) and OsO_4 (2 drops) at room temperature. After completion of reaction (1 week, monitered by TLC), the reaction mixture was worked up as described for **15** and purified by column chromatography (*Si*-gel, 60–120 mesh, 30% EtOAc–hexane) to afford *5-t-butyldi-phenylsilyloxymethyl-4′,5′-dihydroxy-6′-methoxy-2,2-dimethyl-(3′S,3aS,4′S,5R,5′S,6′S,6′R,6aS)-spiro[perhydrofuro[2,3-d][1,3]dioxole-6,2′-(3′H,4′H,5′H,6′H-pyran)]-3-yl acetate* (**30**, 0.095 g, 60%) as a syrup. Analysis found: C 61.59; H 6.91. $C_{31}H_{42}O_{10}Si$ requires C 61.77; H 7.02%; $[\alpha]_D^{27}=-14.6$ (*c* 0.5, $CHCl_3$); δ_H (200 MHz, $CDCl_3$) 7.76–7.65 (5H, m, Ph), 7.42–7.30 (5H, m, Ph), 5.60 (1H, d, $J_{1,2}$=4.0 Hz, H-1), 5.39 (1H, br d, $J_{6,7}$=9.6 Hz, H-6), 4.53 (1H, br s, H-9), 4.46 (1H, d, $J_{1,2}$=4.0 Hz, H-2), 4.31–4.10 (2H, m, H-7,8), 4.0–3.85 (3H, m, H-4,5,5′), 3.45 (3H, s, OCH_3), 2.15 (3H, s, $COCH_3$), 1.25, 1.20, 1.04 (15H, 3s, CH_3); *m/z*: (FABMS), 625 (M^++23), 551, 545.

4.1.15. 5-*t*-Butyldiphenylsilyloxymethyl-4′,5′-dihydroxy-6′-methoxy-2,2-dimethyl-(3′*S*,3*aS*,4′*S*,5*R*,5′*S*,6′*R*,6′*R*,6*aS*)-spiro[perhydrofuro[2,3-*d*][1,3]dioxole-6,2′-(3′*H*,4′*H*,5′*H*,6′*H*-pyran)]-3-yl acetate (33). To a stirred solution of **32** (0.1 g, 0.17 mmol) in acetone–water (5 mL, 4:1) were added sequentially NMO (21 mg, 0.17 mmol) and

OsO_4 (2 drops) at room temperature. After completion of reaction (1 week, monitered by TLC), the reaction mixture was worked up as described for **15** and purified by column chromatography (*Si*-gel, 60–120 mesh, 30% EtOAc–hexane) to afford *5-t-butyldi- phenylsilyloxymethyl-4′,5′-dihydroxy-6′-methoxy-2,2-dimethyl-(3′S,3aS,4′S,5R, 5′S,6′R,6′R,6aS)-spiro[perhydrofuro[2,3-d][1,3]dioxole-6,2′-(3′H,4′H,5′H,6′H-pyran)]-3-yl acetate* (**33**, 0.035 g, 33%) as a syrup. Analysis found: C 61.62; H 6.87. $C_{31}H_{42}O_{10}Si$ requires C 61.77; H 7.02%; $[\alpha]_D^{27}=+7.5$ (*c* 0.64, $CHCl_3$); δ_H (200 MHz, $CDCl_3$) 7.80–7.60 (5H, m, Ph), 7.51–7.30 (5H, m, Ph), 5.52 (1H, d, $J_{1,2}=4.0$ Hz, H-1), 5.48 (1H, d, $J_{6,7}=4.7$ Hz, H-6), 4.98 (1H, d, $J_{8,9}=7.3$ Hz, H-9), 4.85 (1H, d, $J_{1,2}=4.0$ Hz, H-2), 4.05–3.95 (2H, m, H-7,8), 3.90–3.70 (2H, m, H-4,5′), 3.52 (3H, s, OCH_3), 3.50–3.40 (1H, m, H-5), 2.19 (3H, s, $COCH_3$), 1.48, 1.40, 1.04 (15H, 3s, CH_3); *m/z*: (FABMS), 625 (M^++23), 551, 545.

4.1.16. 5-*t*-Butyldiphenylsilyloxymethyl-6′-methoxy-2,2-dimethyl-3′,4′-di(methylcarbonyloxy)-(3′*S*,3*aS*,4′*S*,5*R*, 5′*S*,6′*S*,6′*R*,6*aS*)-spiro[perhydrofuro[2,3-*d*][1,3]dioxole-6,2′-(3′*H*,4′*H*,5′*H*,6′*H*-pyran)]-5-yl acetate (3). A solution of the diol **30** (0.03 g, 0.05 mmol) in CH_2Cl_2 (5 mL) was treated with Et_3N (0.017 mL, 0.12 mmol) and Ac_2O (0.01 mL, 0.1 mmol) and worked up as described for **7** to afford *5-t-butyldiphenylsilyloxymethyl-6′-methoxy-2,2-dimethyl-3′,4′-di(methylcarbonyloxy) (3′S,3aS,4′S,5R,5′S, 6′S,6′R,6aS)-spiro[perhydrofuro[2,3-d][1,3]dioxole-6,2′-(3′H,4′H,5′H,6′H-pyran)]-5-yl acetate* (**3**, 0.022 g, 65%) as a syrup. $[\alpha]_D^{27}=+21.14$ (*c* 1.05, $CHCl_3$); IR (neat, cm^{-1}): 2930, 2885, 1700, 1725, 1050; δ_H (400 MHz, $CDCl_3$) 7.76–7.65 (5H, m, Ph), 7.42–7.30 (5H, m, Ph), 5.61–5.52 (2H, m, H-1,6), 5.40 (1H, dd, $J_{7,8}=3.4$ Hz, $J_{8,9}=2.9$ Hz, H-8), 5.19 (1H, t, $J=3.4$ Hz, H-7), 4.63 (1H, d, $J_{8,9}=2.9$ Hz, H-9), 4.58 (1H, d, $J_{1,2}=4.1$ Hz, H-2), 4.30–4.10 (2H, m, H-4,5′), 3.73 (1H, dd, $J_{5,5'}=11.2$ Hz, $J_{4,5}=5.6$ Hz, H-5), 3.42 (3H, s, OCH_3), 2.15, 2.10, 2.01 (9H, 3s, $COCH_3$), 1.28, 1.20, 1.05 (15H, 3s, CH_3); *m/z*: (FABMS), 709 (M^++23); HRMSFAB found: 709.2644. $C_{35}H_{46}O_{12}NaSi$ (M^++23) requires 709.2656.

4.1.17. 5-*t*-Butyldiphenylsilyloxymethyl-6′-methoxy-2,2-dimethyl-3′,4′-di(methylcarbonyloxy)-(3′*S*,3*aS*,4′*S*,5*R*, 5′*S*,6′*R*,6′*R*,6*aS*)-spiro[perhydrofuro[2,3-*d*][1,3]dioxole-6,2′-(3′*H*,4′*H*,5′*H*,6′*H*-pyran)]-5-yl acetate (4). A solution of the diol **33** (30 mg, 0.05 mmol) in CH_2Cl_2 (5 mL) was treated with Et_3N (0.017 mL, 0.12 mmol) and Ac_2O (0.01 mL, 0.1 mmol) and worked up as described for **7** to afford *5-t-butyldiphenylsilyloxymethyl-6′-methoxy-2,2-dimethyl-3′,4′-di(methylcarbonyloxy)-(3′S,3aS,4′S,5R,5′S, 6′R,6′R,6aS)-spiro[perhydrofuro[2,3-d][1,3]dioxole-6,2′-(3′H,4′H,5′H,6′H-pyran)]-5-yl acetate* (**4**, 24 mg, 72%) as a syrup. $[\alpha]_D^{27}=-29.2$ (*c* 0.9, $CHCl_3$); δ_H (500 MHz, $CDCl_3$) 7.65–7.76 (5H, m, Ph), 7.30–7.42 (5H, m, Ph), 5.69 (1H, dd, $J_{8,9}=3.3$ Hz, $J_{7,8}=3.1$ Hz, H-8), 5.60 (1H, d, $J_{1,2}=4.0$ Hz, H-1), 5.23 (1H, d, $J_{8,9}=3.3$ Hz, H-9), 5.18 (1H, d, $J_{6,7}=8.5$ Hz, H-6), 4.99 (1H, d, $J_{1,2}=4.0$ Hz, H-2), 4.88 (1H, dd, $J_{6,7}=8.5$ Hz, $J_{7,8}=3.1$ Hz, H-7), 4.04 (1H, dd, $J_{5,5'}=10.1$ Hz, $J_{4,5}=6.05$ Hz, H-5), 3.85 (1H, dd, $J_{4,5}=6.0$ Hz, $J_{4,5'}=10.1$ Hz, H-4), 3.80 (1H, t, $J=10.1$ $J_{5,5'}=10.1$ Hz, H-5′), 3.44 (3H, s, OCH_3), 2.19, 2.05, 2.02 (9H, 3s, CH_3), 1.49, 1.40 (6H, 2s, CH_3), 1.20, 1.02 (9H, 2s, CH_3), *m/z*: (FABMS), 709 (M^++23); HRMSFAB found: 709.2652. $C_{35}H_{46}O_{12}NaSi$ (M^++23) requires 709.2656.

4.1.18. 5-*t*-Butyldiphenylsilyloxymethyl-6-(2-furyl)-2,2-dimethyl-(3a*R*,5*S*,6*R*,6a*R*)-perhydrofuro[2,3-*d*][1,3]-dioxol-6-ol (22). To a solution of **18** (3.0 g, 7.0 mmol) in CH_2Cl_2 was added PDC (5.2 g, 14.0 mmol), Ac_2O (catalytic) and heated at reflux temperature for 3 h. Usual work up as described for **19** gave **20** (2.23 g, 75%) as a syrup.

To a stirred solution of furan (0.52 mL, 7.74 mmol) in dry THF (10 mL), *n*-BuLi (5.16 mL, 7.74 mmol, 1.5 M solution in hexane) was added dropwise at −40°C. After 1 h, ketone **20** (2.2 g, 5.16 mmol) in dry THF (6 mL) was added dropwise at the same temperature over 10 min and the reaction mixture was worked up as described for **10** and purified by column chromatography (*Si*-gel, 60–120 mesh, 3% ethylacetate in hexane) to afford *5-t-butyldiphenylsilyloxymethyl-6-(2-furyl)-2,2-dimethyl-(3aR,5S,6R,6aR)-perhydrofuro-[2,3-d][1,3]dioxol-6-ol* (**22**, 1.45 g, 57%) as a syrup. $[\alpha]_D^{27}=-3.4$ (*c* 1.8, $CHCl_3$); δ_H (200 MHz, $CDCl_3$) 7.80–7.60 (5H, m, Ph), 7.41–7.25 (6H, m, H-8, Ph), 6.32 (2H, br s, H-6,7), 5.79 (1H, d, $J_{1,2}=3.9$ Hz, H-1), 4.68 (1H, d, $J_{1,2}=3.9$ Hz, H-2), 4.28–4.01 (2H, m, H-4,5′), 3.89 (1H, dd, $J_{4,5}=5.5$ Hz, $J_{5,5'}=11.0$ Hz, H-5), 3.50 (1H, br s. OH), 1.51, 1.32 (6H, 2s, CH_3), 1.01, 0.09 (9H, 2s, CH_3); δ_C (50 MHz, $CDCl_3$) 142.0, 135.6 (2C), 135.5 (2C), 134.7 (2C), 129.5 (2C), 127.6 (4C), 110.3, 106.4, 104.5, 85.1, 84.4, 62.7, 41.5, 27.2, 27.1, 26.7 (2C), 26.5 (2C), 23.2, 19.0; *m/z*: (FABMS), 517 (M^++23), 437, 419; HRMS found: 517.2016. $C_{28}H_{34}O_6NaSi$ (M^++23) requires 517.2022.

4.1.19. 5-*t*-Butyldiphenylsilyloxymethyl-6′-methoxy-2,2-dimethyl-(3a*R*,5*S*,6′*R*,6a*R*)-spiro[perhydrofuro[2,3-*d*]-[1,3]dioxole-6,2′-(3′*H*,6′*H*-pyran)]-3′-one (27). A solution of **22** (1.4 g, 2.83 mmol) in THF–water (10 mL, 4:1) was cooled to −5°C and NBS (0.5 g, 2.83 mmol) was added in portions. After 5 min, the reaction mixture was worked up as described for **9** to afford the lactols **26** (1.22 g, 85%, 3:2) as a syrup.

A mixture of the above lactols **26** (1.22 g, 2.39 mmol) in CH_2Cl_2 (10 mL) was treated with MeI (0.34 mL, 4.78 mmol) in the presence of Ag_2O (0.55 g, 2.39 mmol) for 12 h. The reaction mixture was worked up as described for **10** to afford an anomeric mixture of *O*-methyl glycosides *5-t-butyldiphenylsilyloxymethyl-6′-methoxy-2,2-dimethyl-(3aR,5S,6′R,6aR)-spiro[perhydrofuro[2,3-d][1,3]di -oxole-6,2′-(3′H,6′H-pyran)]-3′-one* (**27**, 0.77 g, 62%) as a syrup. Trace of the β-anomer was separated by column chromatography. β-anomer: δ_H (200 MHz, $CDCl_3$) 7.80–7.60 (5H, m, Ph), 7.50–7.32 (5H, m, Ph), 6.16 (1H, dd, $J_{7,8}=9.3$ Hz, H-8), 6.05 (1H, dd, $J_{7,8}=9.3$ Hz, H-7), 5.85 (1H, s, H-9), 5.72 (1H, d, $J_{1,2}=4.2$ Hz, H-1), 4.60 (1H, d, $J_{1,2}=4.2$ Hz, H-2), 4.40 (1H, dd, $J_{4,5}=5.3$ Hz, $J_{4,5'}=10.5$ Hz, H-4), 4.10 (1H, t, $J=10.5$ Hz, H-5′), 3.82–3.70 (1H, m, H-5), 3.52 (3H, s, OCH_3), 1.60, 1.42, 1.27, 1.0 (15H, 4s, CH_3); *m/z*: (FABMS), 547 (M^++23), 467, 435; HRMS found: 523.2149. $C_{29}H_{35}O_7Si$ (M^+−1) requires 523.2152.

4.1.20. Reduction of enone 27. To a solution of **27** (0.6 g, 1.14 mmol) in methanol (5 mL), $CeCl_3{\cdot}7H_2O$ (0.42 g, 1.14 mmol) and $NaBH_4$ (42 mg, 1.14 mmol) were added sequentially and it was worked up as described for **7** and purified by column chromatography (*Si*-gel, 60–120 mesh, 10% EtOAc–hexane).

First eluted was: *3′-t-butyldiphenylsilyloxy-6′-methoxy-2,2-dimethyl-(3′R,3aR,5S,6′S,6′R,6aR)-spiro [perhydrofuro[2,3-d][1,3]dioxole-6,2′-(3′H,6′H-pyran)]-5-ylmethanol* (**34**, 0.20 g, 33%), $[\alpha]_D^{27}=-19.8$ (*c* 1.0, $CHCl_3$); δ_H (200 MHz, $CDCl_3$) 7.70–7.55 (5H, m, Ph), 7.35–7.22 (5H, m, Ph), 5.82 (1H, dd, $J_{7,8}$=7.2 Hz, H-8), 5.66 (1H, dd, $J_{7,8}$=7.2 Hz, H-7), 5.60 (1H, d, $J_{1,2}$=3.8 Hz, H-1), 5.29 (1H, br s, H-9), 4.49 (1H, d, $J_{1,2}$=3.8 Hz, H-2), 4.20 (1H, br s, H-6), 4.12–3.82 (3H, m, H-4,5,5′), 3.18 (3H, s, OCH_3), 1.30, 1.23, 1.20, 1.0 (15H, 4s, CH_3), *m/z*: (FABMS), 549 (M^++23), 469, 437; HRMS found: 526.2383. $C_{29}H_{38}O_7Si$ requires 526.2386.

Second eluted was: *3′-t-butyldiphenylsilyloxy-6′-methoxy-2,2-dimethyl-(3′R,3aR,5S,6′R,6′R,6aR)-spiro[perhydrofuro[2,3-d][1,3]dioxole-6,2′-(3′H,6′H-pyran)]-5-ylmethanol* (**35**, 0.21 g, 35%) as a syrup, Analysis found: C 65.97; H 7.03. $C_{29}H_{38}O_7Si$ requires C 66.13; H 7.27%; $[\alpha]_D^{27}=+0.42$ (*c* 0.6, $CHCl_3$); δ_H (200 MHz, $CDCl_3$) 7.80–7.67 (5H, m, Ph), 7.45–7.30 (5H, m, Ph), 5.99 (1H, dd, $J_{7,8}$=7.8 Hz, H-8), 5.82 (1H, dd, $J_{7,8}$=7.8 Hz, $J_{6,7}$=4.6 Hz, H-7), 5.70 (1H, d, $J_{1,2}$=4.2 Hz, H-1), 4.89 (1H, br s, H-9), 4.53 (1H, d, $J_{1,2}$=4.2 Hz, H-2), 4.20 (1H, d, $J_{6,7}$=4.6 Hz, H-6), 4.16–3.90 (3H, m, H-4,5,5′), 3.29 (3H, s, OCH_3), 1.28, 1.24, 1.21, 1.05 (15H, 4s, CH_3); *m/z*: (FABMS), 549 (M^++23), 469, 437.

4.1.21. 5-*t*-Butyldiphenylsilyloxymethyl-6′-methoxy-2,2-dimethyl-(3′*R*,3a*R*,5*S*,6′*R*,6′*S*,6a*R*)spiro[perhydrofuro-[2,3-*d*][1,3]dioxole-6,2′-(3′*H*,6′*H*-pyran)]-3-yl acetate (36). A solution of **34** (0.2 g, 0.38 mmol) and Et_3N (0.13 mL, 0.95 mmol) in CH_2Cl_2 (5 mL) was treated with Ac_2O (0.06 mL, 0.57 mmol) in presence of catalytic DMAP at 0°C and worked up as described for **7** afforded *5-t-butyldiphenylsilyloxymethyl-6′-methoxy-2,2-dimethyl-(3′R,3aR,5S,6′R,6′S,6aR)-spiro[perhydrofuro[2,3-d][1,3]dioxole-6,2′-(3′H,6′H-pyran)]-3-yl acetate* (**36**, 0.15 g, 70%) as a syrup. Analysis found: C 65.32; H 6.87. $C_{31}H_{40}O_8Si$ requires C 65.47; H 7.09%; $[\alpha]_D^{27}=+35.5$ (*c* 0.25, $CHCl_3$); δ_H (200 MHz, $CDCl_3$) 7.75–7.60 (5H, m, Ph), 7.42–7.30 (5H, m, Ph), 5.93–5.88 (2H, m, H-7,8), 5.80 (1H, d, $J_{1,2}$=4.1 Hz, H-1), 5.58 (1H, d, $J_{6,7}$=2.2 Hz, H-6), 5.42 (1H, br s, H-9), 4.53 (1H, d, $J_{1,2}$=4.1 Hz, H-2), 4.12–4.0 (2H, m, H-4,5′), 3.94–3.87 (1H, m, H-5), 3.21 (3H, s, OCH_3), 2.12 (3H, s, $COCH_3$), 1.40, 1.39, 1.22, 1.02 (15H, 4s, CH_3); δ_C (50 MHz, $CDCl_3$) 169.5, 135.7 (2C), 135.6 (2C), 133.5, 129.4 (2C), 128.9 (2C), 127.5 (3C), 113.7, 105.5, 95.5, 84.9, 82.5, 81.4, 69.1, 63.0, 54.1, 29.3, 26.8 (4C), 26.7 (2C), 20.9, 19.1; *m/z*: (FABMS), 591 (M^++23).

4.1.22. 5-*t*-Butyldiphenylsilyloxymethyl-6′-methoxy-2,2-dimethyl-(3′*R*,3a*R*,5*S*,6′*R*,6′*R*,6a*R*)-spiro[perhydrofuro-[2,3-*d*][1,3]dioxole-6,2′-(3′*H*,6′*H*-pyran)]-3-yl acetate (37). A solution of **35** (0.2 g, 0.38 mmol) and Et_3N (0.13 mL, 0.95 mmol) in CH_2Cl_2 (5 mL) was treated with Ac_2O (0.06 mL, 0.57 mmol) in presence of catalytic DMAP at 0°C and worked up as described for **8** to afford *5-t-butyldiphenylsilyloxymethyl-6′-methoxy-2,2-dimethyl-(3′R,3aR,5S,6′R,6′R,6aR)-spiro-[perhydrofuro[2,3-d][1,3]dioxole-6,2′-(3′H,6′H-pyran)]-3-yl acetate* (**37**, 0.11 g, 55%) as a syrup. Analysis found: C 65.37; H 6.91. $C_{31}H_{40}O_8Si$ requires C 65.47; H 7.09; $[\alpha]_D^{27}=-18.5$ (*c* 1.5, $CHCl_3$); δ_H (200 MHz, $CDCl_3$) 7.76–7.60 (5H, m, Ph), 7.45–7.30 (5H, m, Ph), 5.88–5.70 (2H, m, H-7,8), 5.60 (1H, d, $J_{1,2}$=4.0 Hz, H-1), 5.52 (1H, d, $J_{6,7}$=2.5 Hz, H-6), 4.89 (1H, s, H-9), 4.40 (1H, d, $J_{1,2}$=4.0 Hz, H-2), 4.22–4.09 (2H, m, H-4,5′), 3.92–3.80 (1H, m, H-5), 3.21 (3H, s, OCH_3), 2.12 (3H, s, $COCH_3$), 1.24, 1.20 (6H, 2s, 6H, CH_3), 1.02 (9H, s, CH_3), ^{13}C NMR (50 MHz, $CDCl_3$): 169.7, 135.6 (3C), 135.4, 129.3 (2C), 128.0, 127.8 (2C), 127.4 (3C), 111.8, 105.7, 94.7, 87.8, 79.8, 78.5, 70.9, 64.2, 56.0, 29.6, 26.8 (4C), 26.3, 26.0, 20.9, 19.1; FABMS: 591 (M^++23).

4.1.23. 5-*t*-Butyldiphenylsilyloxymethyl-4′,5′-dihydroxy-6′-methoxy-2,2-dimethyl-(3′*R*,3a*S*,4′*R*,5*S*,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)]-3-yl acetate (38). To a stirred solution of **36** (0.15 g, 0.26 mmol) in acetone–water (5 mL, 4:1) were added sequentially NMO (31 mg, 0.26 mmol) and OsO_4 (2 drops) at room temperature. After completion of reaction (1 week, monitored by TLC), the reaction mixture was worked up as described for **15** and purified by column chromatography (*Si*-gel, 60–120 mesh, 30% EtOAc–hexane) to afford *5-t-butyldiphenylsilyloxymethyl-4′,5′-dihydroxy-6′-methoxy-2,2-dimethyl-(3′R,3aS,4′R,5S,5′R,6′S,6′S,6aR)-spiro[perhydrofuro[2,3-d][1,3]dioxole-6,2′-(3′H,4′H,5′H,6′H-pyran)]-3-yl acetate* (**38**, 0.095 g, 60%) as a syrup. Analysis found: C 61.56; H 6.82. $C_{31}H_{42}O_{10}Si$ requires C 61.77; H 7.02%; $[\alpha]_D^{27}=+18.5$ (*c* 1.3, $CHCl_3$); δ_H (200 MHz, $CDCl_3$) 7.80–7.65 (5H, m, Ph), 7.46–7.30 (5H, m, Ph), 5.60 (1H, d, $J_{1,2}$=3.8 Hz, H-1), 5.20 (1H, d, $J_{6,7}$=4.7 Hz, H-6), 4.95 (1H, d, $J_{1,2}$=3.8 Hz, H-2), 4.90 (1H, d, $J_{8,9}$=7.2 Hz, H-9), 4.40 (1H, t, *J*=4.4 Hz, H-4), 4.05–3.95 (2H, m, H-7,8), 3.90–3.80 (1H, m, H-5′), 3.80–3.68 (1H, m, H-5), 3.50 (3H, s, OCH_3), 2.15 (3H, s, $COCH_3$), 1.41, 1.25, 1.02 (15H, 3s, CH_3); FABMS: 625 (M^++23).

4.1.24. 5-*t*-Butyldiphenylsilyloxymethyl-4′,5′-dihydroxy-6′-methoxy-2,2-dimethyl-(3′*R*,3a*R*,4′*R*,5*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)]-3-yl acetate (39). To a stirred solution of **37** (0.1 g, 0.17 mmol) in acetone–water (5 mL, 4:1) were added sequentially NMO (21 mg, 0.17 mmol) and OsO_4 (2 drops) at room temperature. After completion of reaction (1 week, monitered by TLC), the reaction mixture was worked up as described for **15** and purified by column chromatography (*Si*-gel, 60–120 mesh, 30% EtOAc–hexane) to afford *5-t-butyldiphenylsilyloxymethyl-4′,5′-dihydroxy-6′-methoxy-2,2-dimethyl-(3′R,3aR,4′R,5S,5′R,6′R,6′S,6aR)-spiro[perhydrofuro[2,3-d]-[1,3]dioxole-6,2′-(3′H,4′H,5′H,6′H-pyran)]-3-yl acetate* (**39**, 0.035 g, 39%) as a syrup. Analysis found: C 61.52; H 6.88. $C_{31}H_{42}O_{10}Si$ requires C 61.77; H 7.02%; $[\alpha]_D^{27}=-15.7$ (*c* 2.2, $CHCl_3$); δ_H (200 MHz, $CDCl_3$) 7.76–7.65 (5H, m, Ph), 7.42–7.30 (5H, m, Ph), 5.60 (1H, d, $J_{1,2}$=4.0 Hz, H-1), 5.39 (1H, br d, $J_{6,7}$=9.6 Hz, H-6), 4.53 (1H, br s, H-9), 4.46 (1H, d, $J_{1,2}$= 4.0 Hz, H-2), 4.31–4.10 (2H, m, H-7,8), 4.0–3.85 (3H, m, H-4,5,5′), 3.35 (3H, s, OCH_3), 2.15 (3H, s, $COCH_3$), 1.25, 1.20, 1.05 (15H, 3s, CH_3), FABMS: 625 (M^++23).

4.1.25. 5-*t*-Butyldiphenylsilyloxymethyl-6′-methoxy-2,2-dimethyl-3′,4′-di(methylcarbonyloxy)-(3′*R*,3a*R*,4′*R*,5*S*,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)]-5-yl acetate (5). A solution of the diol **38** (30 mg, 0.05 mmol) in CH_2Cl_2 (5 mL) was

treated with Et_3N (0.017 mL, 0.12 mmol) and Ac_2O (0.01 mL, 0.1 mmol) and worked up as described for **7** to afford *5-t-butyl diphenylsilyloxymethyl-6′-methoxy-2,2-dimethyl-3′,4′-di(methylcarbonyloxy)-(3′R,3aR,4′R,5S,5′R, 6′S,6′S,6aR)-spiro[perhydrofuro[2,3-d][1,3]dioxole-6,2′-(3′H,4′H,5′H,6′H-pyran)]-5-yl acetate* (**5**, 27 mg, 80%) as a syrup. $[\alpha]_D^{27}=+32.2$ (*c* 0.7, $CHCl_3$); δ_H (500 MHz, $CDCl_3$) 7.76–7.65 (5H, m, Ph), 7.42–7.30 (5H, m, Ph), 5.69 (1H, t, J=3.1 Hz, H-8), 5.60 (1H, d, $J_{1,2}$=4.0 Hz, H-1), 5.22 (1H, d, $J_{8,9}$=3.1 Hz, H-9), 5.18 (1H, d, $J_{6,7}$=8.5 Hz, H-6), 4.99 (1H, d, $J_{1,2}$=4.0 Hz, H-2), 4.88 (1H, dd, $J_{6,7}$=8.46 Hz, $J_{7,8}$=3.1 Hz, H-7), 4.04 (1H, dd, $J_{4,5'}$=10.16 Hz, $J_{4,5}$=6.05 Hz, H-4), 3.84–3.78 (2H, m, H-5,5′), 3.44 (3H, s, OCH_3), 2.19, 2.05, 2.02 (9H, 3s, CH_3), 1.49, 1.40 (6H, 2s, CH_3), 1.20, 1.02 (9H, 2s, CH_3); FABMS: 709 (M^++23). HRMSFAB found: 709.2655. $C_{35}H_{46}O_{12}NaSi$ requires 709.2656.

4.1.26. 5-*t*-Butyldiphenylsilyloxymethyl-6′-methoxy-2,2-dimethyl-3′,4′-di(methylcarbonyloxy)-(3′*R*,3a*R*,4′*R*,5*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)]-5-yl acetate (6). A solution of the diol **39** (30 mg, 0.05 mmol) in CH_2Cl_2 (5 mL) was treated with Et_3N (0.017 mL, 0.12 mmol) and Ac_2O (0.01 mL, 0.1 mmol) and worked up as described for **7** to afford *5-t-butyl diphenylsilyloxymethyl-6′-methoxy-2,2-dimethyl-3′,4′-di(methylcarbonyloxy)-(3′R,3aR,4′R,5S,5′R, 6′R,6′S,6aR)-spiro[perhydrofuro[2,3-d][1,3]dioxole-6,2′-(3′H,4′H,5′H,6′H-pyran)]-5-yl acetate* (**6**, 25 mg, 76%) as a syrup. $[\alpha]_D^{27}=-20.7$ (*c* 0.75, $CHCl_3$); δ_H (500 MHz, $CDCl_3$) 7.76–7.65 (5H, m, Ph), 7.42–7.30 (5H, m, Ph), 5.62 (1H, d, $J_{6,7}$=10.8 Hz, H-6), 5.59 (1H, d, $J_{1,2}$=3.7 Hz, H-1), 5.45 (1H, dd, $J_{7,8}$=3.2 Hz, $J_{6,7}$=10.8 Hz, H-7), 5.22 (1H, dd, $J_{7,8}$=3.2 Hz, $J_{8,9}$=1.9 Hz, H-8), 4.64 (1H, d, $J_{8,9}$=1.9 Hz, H-9), 4.61 (1H, d, 1H, $J_{1,2}$=3.7 Hz, H-2), 4.30–4.10 (2H, m, H-4,5′), 3.73 (1H, dd, $J_{5,5}$=11.2 Hz, $J_{4,5}$=5.6 Hz, H-5), 3.42 (3H, s, OCH_3), 2.15, 2.10, 2.01 (9H, 3s, $COCH_3$), 1.28, 1.20, 1.05 (15H, 3s, CH_3); FABMS: 709 (M^++23). HRMSFAB found: 709.2679. $C_{35}H_{46}O_{12}NaSi$ (M^++23) requires 709.2656.

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