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Stereoselective synthesis of *C*-phenyl D- and L-*glycero* heptopyranosides☆

Palakodety Radha Krishna,* B. Lavanya and G. V. M. Sharma

D-206/B, Discovery Laboratory, Organic Chemistry Division-III, Indian Institute of Chemical Technology, Hyderabad 500 007, India

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Abstract—D- and L-*glycero*-*C*-Phenyl heptopyranosides **1**, **2** and **3** are synthesized for the first time from (*R*)-glyceraldehyde and L-ascorbic acid derivatives. The main strategy involves intramolecular nucleophilic substitution and double bond functionalisation.

1. Introduction

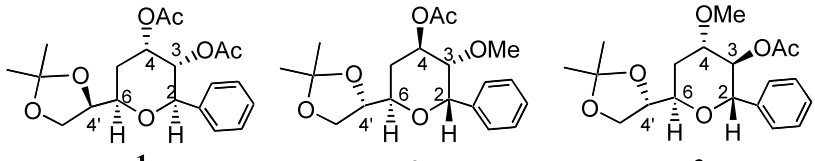
C-Glycosides have been the subject of considerable interest in carbohydrate, enzymatic and metabolic chemistry since *C*-aryl and 2-deoxy-*C*-aryl glycosides are commonly encountered structural features in a variety of natural products[1] and are chiral building blocks for the asymmetric synthesis of natural products. Because of the strong C–C bond at the anomeric center *C*-aryl glycosides are endowed with an ability to withstand enzymatic and acid hydrolysis.[2] Hence, the synthesis of *C*-aryl glycosides has become a challenging subject to organic chemists and several synthetic strategies have resulted.[3–6] Similarly, higher and rare monosaccharides are important structural features of highly functionalised carbohydrates and find applications as intermediates in natural product synthesis.[7] However, to date, there appears to be less attention drawn towards the synthesis of *C*-aryl glycosides of higher and rare sugar homologues. In continuation of our studies on the synthesis of *C*-alkyl,[8,9] and aryl[10] glycosides, *C*-saccharides,[11] spiro-*C*-saccharides,[12] 2-deoxy and rare saccharides[13] and pseudo saccharides,[14] we describe herein a simple and straightforward synthetic approach towards the synthesis of *C*-aryl heptopyranosides **1**, **2** and **3**, starting from 1,2-*O*-isopropylidene-(*R*)-glyceraldehyde and L-ascorbic acid.

2. Results and discussion

2.1. Synthesis of 6-[2′,2′-dimethyl-(4′*R*)-1′,3′-dioxolan-4′-yl]-3-methylcarbonyloxy-2-phenyl-(2*R*,3*S*,4*S*,6*R*)-tetrahydro-2*H*-4-pyranyl acetate 1 from 1,2-*O*-isopropylidine-(*R*)-glyceraldehyde

The envisaged synthesis of **1**, as outlined in Scheme 1, involves the construction of a carbon skeleton **4** with an appropriately positioned leaving group and an internal nucleophile, wherein the phenylsulphonyl group was chosen to act as both a protecting group and a leaving group for the base-induced ring closure. Compound **4** is envisaged from acetylene **5**, which in turn could be formed from **6**, the acetylenic group of which serves both as a handle to extrapolate the carbon chain as well as to introduce the *cis* double bond for further functionalisation.

Accordingly, the known compound[15] 1,2-*O*-isopropylidine-(*R*)-glyceraldehyde **7** on Grignard reaction (Scheme 2) with propargyl bromide in the presence of Zn dust and saturated ammonium chloride in THF gave **6** (68%) with predominant formation of the *anti* isomer.[16]



1 **2** **3**

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* Corresponding author. Fax: 91-40-7160387, 7160757; e-mail: prkgenius@iict.ap.nic.in

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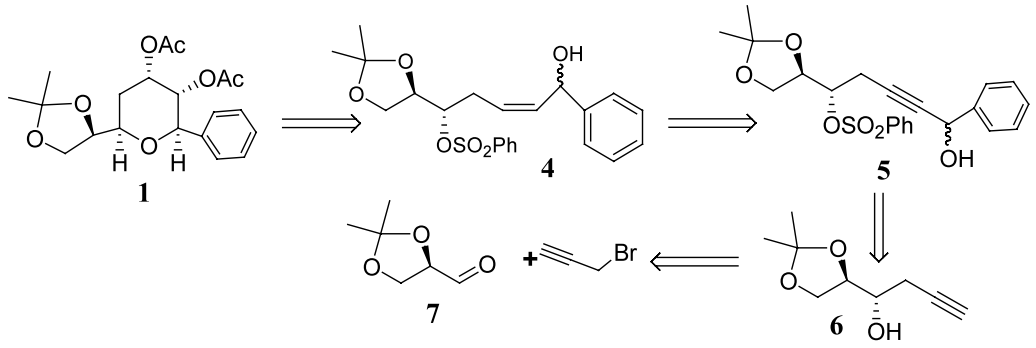
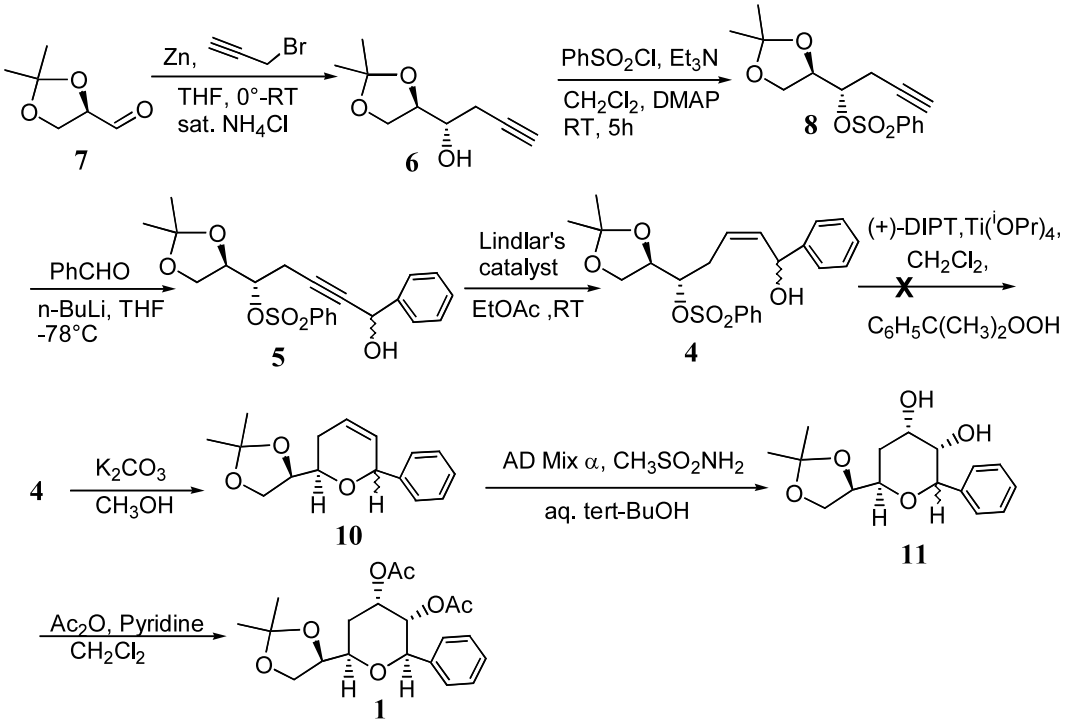


Scheme 1.



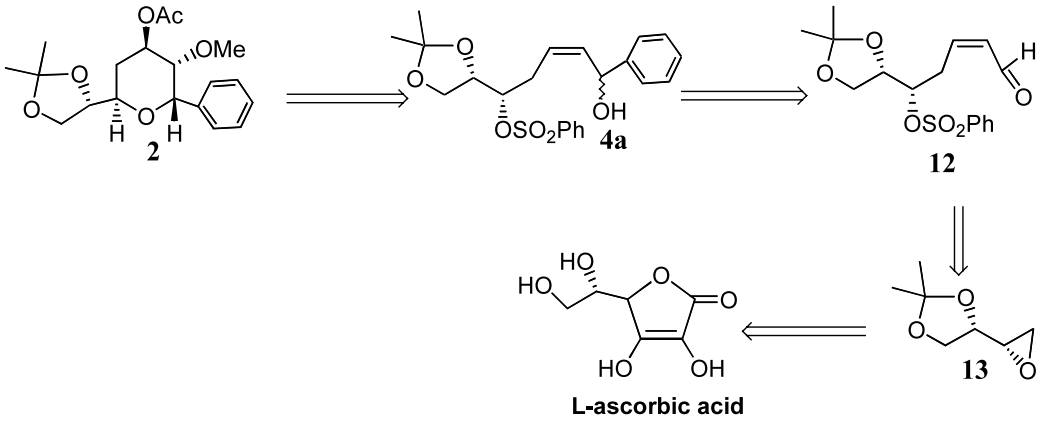
Scheme 2.

Compound **6** thus prepared was treated with benzene sulphonyl chloride in the presence of Et_3N to afford **8** (75%), wherein the sulphonate ester not only acts as a protective group but also serves as a good leaving group. Reaction of **8** with *n*-BuLi and benzaldehyde in THF at −78°C gave carbinol **5** in 70% yield as a diastereomeric mixture. The thus prepared alkyne **5** was subjected to hydrogenation with Lindlar's catalyst (Pd/$BaSO_4$) at room temperature in ethyl acetate to furnish **4** in quantitative yield.

Attempted Sharpless asymmetric epoxidation of alcohol **4** with (+)-DIPT and $Ti(O^iPr)_4$ in the presence of cumene hydroperoxide was found to be very sluggish and **4** was recovered unchanged. Hence, it was planned to effect an intramolecular nucleophilic substitution reaction first to result in dihydropyrans, which could be further functionalised. Accordingly, cyclisation of **4** with K_2CO_3 in methanol furnished dihydropyrans **10** (58%) as an inseparable diastereomeric mixture, which on asymmetric dihydroxylation[17] (AD Mix α, $CH_3SO_2NH_2$, aq. *tert*-BuOH) afforded a mixture of diols **11** in 60% yield. Diol **11** was acetylated without purification using Ac_2O–pyridine to afford **1** in 73% yield, which was unambiguously characterized from its spectroscopic data. For instance, ^1H NMR analysis of **1** amply indicated a *cis* ring junction, wherein H-2 and H-6 resonated at δ 4.4 and δ 3.8, as double doublet and multiplet, respectively.

2.2. Synthesis of 6-[2′,2′-dimethyl-(4′*S*)-1′,3′-dioxolan-4′-yl]-3-methoxy-2-phenyl-(2*S*,3*S*,4*R*,6*R*)-tetrahydro-2*H*-4-pyranyl acetate 2 and 6-[2′,2′-dimethyl-(4′*S*)-1′,3′-dioxolan-4′-yl]-4-methoxy-2-phenyl-(2*S*,3*R*,4*S*,6*R*)-tetrahydro-2*H*-3-pyranyl acetate 3 from L-ascorbic acid

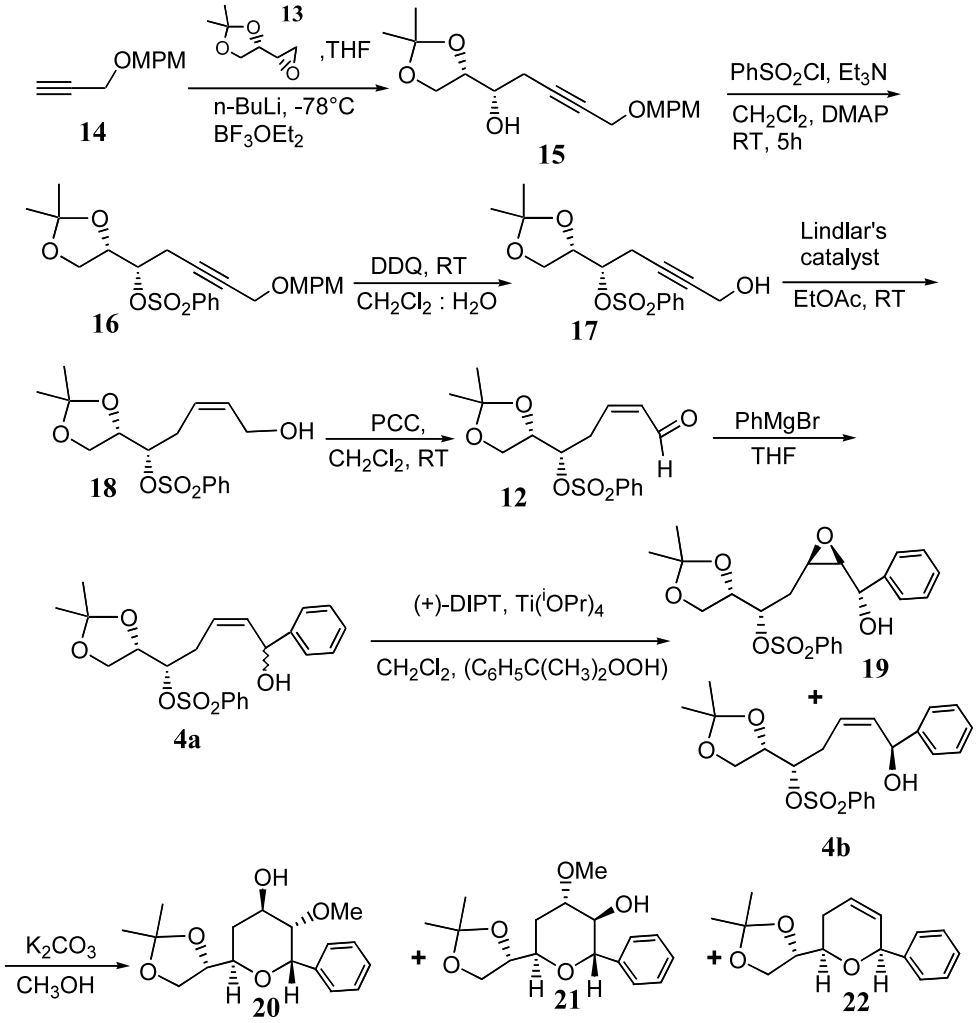
The synthetic approach to the L-*glycero*-α-*C*-phenyl heptopyranosides is outlined in Scheme 3, wherein the epoxide **13** obtained from L-ascorbic acid was envisioned as a good starting material to realize **2**. Thus, **2**



Scheme 3.

could be made from **4a**, which in turn could be obtained on treatment of aldehyde **12** with aryl Grignard, while **12** in turn could be obtained from L-ascorbic acid, through **13**.

Accordingly, the propargyl ether **14** was treated with *n*-BuLi and epoxide **13**[18] in THF at −78°C to afford **15** in 51% yield (Scheme 4). Alcohol **15** was protected as the sulphonate ester **16** ($PhSO_2Cl$–Et_3N) which on further reaction with DDQ in aq. CH_2Cl_2 (9:1) afforded **17** in 71% yield. Lindlar's reaction of compound **17** in ethyl acetate afforded *cis* olefin **18** (94%), which on further oxidation using PCC in CH_2Cl_2 afforded aldehyde **12** in 83% yield. Aldehyde **12** was subjected to



Scheme 4.

Table 1. Spectroscopic data for compound **2**

Proton	δ (ppm)	Multiplicity	NOE
H-2	4.22	d ($J_{2,3}=2.2$ Hz)	With OMe, H-5(β)
H-3	4.11	dd ($J_{3,2}=2.2$ Hz, $J_{3,4}=4.6$ Hz)	With H-5(β)
H-4	5.30	dt ($J_{4,5}=6.0$ Hz, $J_{4,3}=4.6$ Hz)	With H-5(α), Ph, acetate CH_3
H-5(α)	2.01	ddd ($J_{5\alpha,6}=2.2$ Hz, $J_{5\alpha,5\beta}=13.7$ Hz, $J_{5\alpha,4}=5.6$ Hz)	With H-6
H-5(β)	1.79	ddd ($J_{5\beta,6}=9.7$, $J_{5\alpha,5\beta}=13.7$, $J_{4,5\beta}=5.6$ Hz)	With H-2
H-6	3.99	ddd ($J_{6,4'}=6.0$, $J_{6,5\alpha}=2.6$, $J_{6,5\beta}=9.7$ Hz)	With H-5(α)
H-4′	3.87	m	With acetonide CH_3
H-5′b	3.87	m	No NOE
H-5′a	4.06	m	No NOE

Table 2. Spectroscopic data for compound **3**

Proton	δ (ppm)	Multiplicity	NOE
H-2	4.20	d ($J_{2,3}=4.6$ Hz)	With H-5(β)
H-3	5.25	dd ($J_{3,2}=4.6$ Hz, $J_{3,4}=6.8$ Hz)	With H-5(α)
H-4	4.05	m	With H-5(β)
H-5(α)	2.01	m	With H-6, H-3
H-5(β)	1.78	ddd ($J_{5\beta,6}=9.7$ Hz, $J_{5\alpha,5\beta}=13.7$ Hz, $J_{\beta,4}=5.6$ Hz)	With H-2, H-4
H-6	3.99	ddd ($J_{6,4'}=6.0$ Hz, $J_{6,5\alpha}=2.6$ Hz, $J_{6,5\beta}=9.7$ Hz)	With H-5(α)
H-4′	3.87	m	No NOE
H-5′b	3.87	m	No NOE
H-5′a	4.05	m	No NOE

Grignard reaction with phenylmagnesium bromide in THF to afford a diastereomeric mixture of alcohols **4a** in 86% yield. Kinetic resolution of **4a** under Sharpless asymmetric epoxidation conditions using (+)-DIPT, $Ti(^iOPr)_4$ and cumene hydroperoxide afforded an inseparable mixture of alcohols, i.e. epoxy alcohol **19** and allylic alcohol **4b**. Subsequent reaction of the mixture of **19** and **4b** with K_2CO_3 in refluxing methanol afforded three chromatographically separable products **20** (34%), **21** (12%) and **22** (22%). Regioisomers **20** and **21** were reasoned to have been derived from the epoxy alcohol **19** by cyclisation.

On reaction with Ac_2O in pyridine at room temperature, the *C*-aryl glycosides **20** and **21**, were independently converted into the corresponding acetates **2** and **3** in quantitative yields, respectively (Scheme 5).

The structures of **2** and **3** were unambiguously determined based on their spectroscopic data. The ^{1}H NMR spectrum of compound **2** revealed H-2 resonance at δ 4.22 as a doublet ($J=2.2$ Hz) and H-4 at δ 5.30 as doublet by triplet ($J=4.6$, 6.0 Hz), while the ^{1}H NMR of compound **3** revealed H-2 at δ 4.20 as doublet ($J=4.6$ Hz) and H-4 as multiplet at δ 4.05 respectively supporting the predicted structure. The structures of these two compounds **2** and **3** were further established from the detailed spectral analysis (Fig. 1) using the vicinal couplings (J) as well as the data from the NOESY experiments (Table 1).

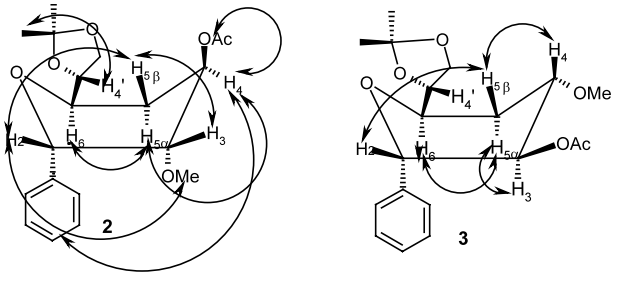
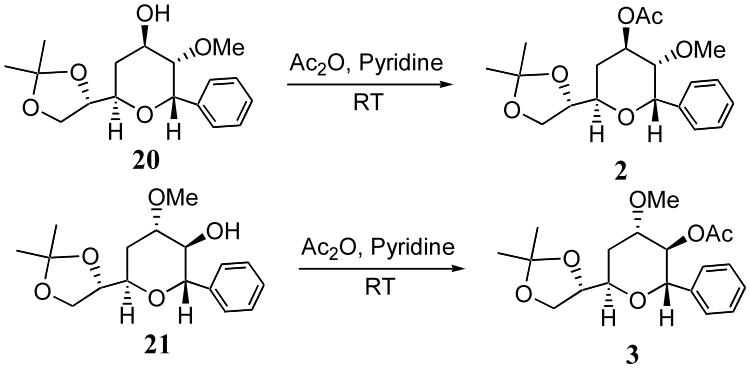


Figure 1.



Scheme 5.

The six-membered pyran ring in **2** adopts the boat conformation (Fig. 1). The assigned structure is supported by NOESY cross peaks between H2-OCH_3, H2–H5(β) and H6–H5(α). It was also observed that there was no NOE between H2–H4 and H2–H6, indicating that both the substituents at C-2 and C-6 are *trans* to each other.

In the ^{1}H NMR spectrum of compound **3** the observed resonance for H-2 at δ 4.22 as doublet and H-4 at δ 4.05 as multiplet, respectively, supported the predicted structure. For compound **3** the six-membered pyran ring is in the boat conformation (Fig. 1). NOESY experiments have shown the cross peaks between H2–H5(β), H4–H5(β), H3–H5(α) and H5(α)–H6, thus confirming the assigned structure (Table 2).

3. Conclusion

The present protocol describes a simple and flexible approach for the synthesis of *C*-aryl heptopyranosides with rare stereochemistries, which are otherwise inaccessible from natural sources. Thus, the present strategy adopted resulted in the first synthesis of new *C*-aryl heptopyrasnosides **1**, **2** and **3**.

4. Experimental

4.1. Synthesis of 6-[2′,2′-dimethyl-(4′*R*)-1′,3′-dioxolan-4-yl]-3-methylcarbonyloxy-2-phenyl-(2*R*,3*S*,4*S*,6*R*)-tetrahydro-2*H*-4-pyranyl acetate, 1

4.1.1. 1-[2′,2′-Dimethyl-(4′*R*)-1′,3′-dioxolan-4′-yl]-(1*S*)-3-butyn-1-ol, 6. To a cooled (0°C) and stirred mixture of **7** (5.0 g, 38.4 mmol), Zn dust (4.99 g, 76.9 mmol) and propargyl bromide (9.1 g, 76.9 mmol) in THF (60 mL) was added a saturated aq. solution of NH_4Cl (15 mL) dropwise over a period of 30 min and the mixture was stirred for 12 h at ambient temperature. It was filtered and the precipitate was thoroughly washed with chloroform (3×25 mL). The aqueous layer was separated and treated with 5% cold HCl (10 mL) to dissolve the suspended turbid material. The clear solution was extracted with $CHCl_3$ (2×20 mL) and the combined organic layers were washed successively with 10% aq. $NaHCO_3$ (30 mL), brine (25 mL), dried ($NaSO_4$) and concentrated to furnish crude alcohol, which was purified by flash chromatography (silica gel, 60–120 mesh, EtOAc:hexane, 1:9) to afford 1-[2′,2′-dimethyl-(4′*R*)-1′,3′-dioxolan-4′-yl]-(1*S*)-3-butyn-1-ol **6** as a thick syrup (4.42 g, 68%). $[\alpha]_D$ +3.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ 4.20–3.90 (m, 3H, H-5′, 4′), 3.75–3.65 (m, 1H, H-1), 2.50 (m, 2H, H-2), 2.00 (m, 1H, H-4), 1.40, 1.39 (2s, 6H, -CH_3); IR (neat): 3320 cm^{-1}; EIMS (*m*/*z*): 170 (M^+). Anal. calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29; found: C, 63.58; H, 8.0%.

4.1.2. 2,2-Dimethyl-4-[1′-phenylsulfonyloxy-(1′*S*)-3′-butynyl]-(4*R*)-1,3-dioxolane, 8. A solution of compound **6** (4.0 g, 23.5 mmol), benzene sulphonyl chloride (4.8 g, 27 mmol) and Et_3N (3.5 g, 35.3 mmol) in CH_2Cl_2 (40 mL) containing DMAP (catalytic) at 0°C was stirred for 5 h. It was treated with saturated aq. $NaHCO_3$ solution (10 mL) for 30 min, diluted with CH_2Cl_2 (50 mL) and the organic layer was separated. Organic layer was washed with water (10 mL), brine (10 mL) and dried (Na_2SO_4). Evaporation of solvent and purification of residue by column chromatography (silica gel, 60–120 mesh, EtOAc:hexane, 1:9) afforded 2,2-dimethyl-4-[1′-phenylsulfonyloxy-(1′*S*)-3′-butynyl]-(4*R*)-1,3-dioxolane **8** as a semi-solid (5.5 g, 75% yield). $[\alpha]_D^{25}$ +9.4 (*c* 1.2, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.0–7.9 (d, 2H, *J*=4.7 Hz, Ar-H), 7.6 (m, 3H, Ar-H), 4.5 (q, 1H, *J*=4.7 Hz, H-1′), 4.24 (q, 1H, *J*=4.7 Hz, H-4), 4.0 (dd, 1H, *J*=4.7, 5.7 Hz, H-5a), 3.82 (dd, 1H, *J*=4.7, 2.3 Hz, H-5b), 2.6 (br.s, 2H, H-2′), 1.9 (br.s, 1H, H-4′), 1.4–1.2 (br.s, 6H, -CH_3); IR (neat): 1360, 3320 cm^{-1}; EIMS (*m*/*z*): 310 (M^+), 311 (M^++1). Anal. calcd for $C_{15}H_{18}O_5S$: C, 58.05; H, 5.85; S, 10.33; found: C, 58.18; H, 5.60; S, 10.0%.

4.1.3. 4-[5′-Hydroxy-5′-phenyl-(5′*R*/*S*)-1′-phenylsulfonyloxy-(1′*S*)-3′-pentynyl]-2,2-dimethyl-(4*R*)-1,3-dioxolane, 5. To a stirred solution of compound **8** (1.5 g, 4.8 mmol) in dry THF (10 mL) at −78°C was added *n*-BuLi (0.5 mL, 7.2 mmol; 1.5N hexane solution) dropwise. After 30 min a solution of freshly distilled benzaldehyde (0.62 g, 5.8 mmol) in THF (5 mL) was added and the mixture stirred at the same temperature for further 2 h. The reaction mixture was allowed to attain room temperature, diluted with sat. aq. NH_4Cl solution (30 mL) and extracted with ethyl acetate (2×30 mL). Organic layer was washed with brine (5 mL), dried (Na_2SO_4), evaporated and the residue purified by column chromatography (silica gel, 60–120 mesh, EtOAc:hexane, 3:10) to afford 4-[5′-hydroxy-5′-phenyl-(5′*R*/*S*)-1′-phenylsulfonyloxy-(1′S)-3′-pentynyl]-2,2-dimethyl-(4*R*)-1,3-dioxolane **5** as a colorless syrup (1.4 g, 70%). $[\alpha]_D^{25}$ +17.0 (*c* 0.9, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.90–7.80 (m, 2H, Ar-H), 7.6–7.4 (m, 5H, Ar-H), 7.3–7.2 (m, 3H, Ar-H), 5.3 (br.s, 1H, H-5′), 4.6 (q, 1H, *J*=5.2 Hz, H-1′), 4.2–3.9 (m, 2H, H-4, 5a), 3.8–3.6 (dd, 1H, *J*=5.2, 2.6 Hz, H-5b), 2.55 (br.d, 2H, *J*=2.6 Hz, H-2′), 1.3–1.2 (br.s, 6H, -CH_3); IR (neat): 1360, 2140 cm^{-1}; FABMS (*m*/*z*): 416 (M^+), 330, 275. Anal. calcd for $C_{22}H_{24}O_6S$: C, 63.45; H, 5.81; S, 7.70; found: C, 63.48; H, 5.2; S, 7.0%.

4.1.4. 4-[5′-Hydroxy-5′-phenyl-1′-phenylsulfonyloxy-(1′*S*,5′*R*/*S*,3′*Z*)-3′pentenyl]-2,2-dimethyl-4(*R*)-1,3-dioxolane, 4. A solution of compound **5** (1.2 g, 2.8 mmol) in ethyl acetate (50 mL) was treated with Lindlar's catalyst (cat.) in the presence of quinoline (two drops) and subjected to hydrogenation for 4 h. The reaction mixture was filtered, solvent evaporated and residue purified by column chromatography (silica gel, 60–120 mesh, EtOAc:hexane, 3:10) to afford 4-[5′-hydroxy-5′-phenyl-1′-phenylsulfonyloxy-(1′*S*,5′*R*/*S*,3′*Z*)-3′pentenyl]-2,2-dimethyl-4(*R*)-1,3-dioxolane **4** as a colorless liquid (1.1 g, 91%). $[\alpha]_D^{25}$ +17.7 (*c* 1.1, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.95 (d, 2H, *J*=2.9 Hz, Ar-H), 7.50

(m, 5H, Ar-H), 7.20 (m, 3H, Ar-H), 5.8–5.70 (dd, 1H, $J=1.17$ Hz, H-4′), 5.70–5.6 (m, 1H, H-3′), 5.10 (m, 1H, H-5′), 4.70–4.60 (m, 1H, H-1′), 4.2 (m, 1H, H-4), 3.9 (m, 1H, H-5a), 3.8 (m, 1H, H-5b), 2.50–2.42 (m, 1H, H-2′a), 2.40–2.38 (m, 1H, H-2′b), 1.38–1.22 (s, 6H, $-CH_3$); ^{13}C NMR (50 MHz, $CDCl_3$): δ 171.60, 129.84, 128.98 (3C), 128.20 (2C), 127.03, 77.64, 72.50 (3C), 70.91 (2C), 31.28, 25.41, 22.15 (3C), 22.08 (3C); IR (neat): 728, 1360 cm^{-1}; FABMS (m/z): 418 (M^+), 332, 277. Anal. calcd for $C_{22}H_{26}O_6S$: C, 63.14; H, 6.26; S, 7.66; found: C, 63.18; H, 6.32; S, 7.56%.

4.1.5. (2*R*)-2-[2′,2′-Dimethyl-(4′*R*)-1′,3′-dioxolan-4′-yl)-6-(*R*/*S*)-6-phenyl-3,6-dihydro-2*H*-pyran, 10. A solution of compound **4** (0.5 g, 1.2 mmol) in methanol (10 mL) was treated with K_2CO_3 (0.16 g, 1.2 mmol) and heated under reflux for 4 h. Methanol was evaporated and the residue extracted with ethyl acetate (50 mL). The organic layer was washed with water (5 mL), brine (5 mL), dried (Na_2SO_4), concentrated and the residue purified by column chromatography (silica gel, 60–120 mesh, EtOAc:hexane, 3:20) to afford **10** as a syrup (0.18 g, 58%). $[\alpha]_D^{25}$ +7.5 (*c* 0.8, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ 7.4–7.2 (m, 5H, Ar-H), 6.1 (t, 1H, $J=5.26$ Hz, H-4), 5.7 (dd, 1H, $J=15.7$, 5.26 Hz, H-5), 5.6 (m, 2H, H-6), 4.5 (m, 1H, H-2), 4.0 (m, 2H, H-5′), 3.6 (dt, 1H, $J=5.26$, 1.32 Hz, H-4′), 1.8–1.9 (br.s, 2H, H-4), 1.35 (br.s, 6H, CH_3); FABMS (m/z): 260 (M^+). Anal. calcd for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74; found: C, 73.85; H, 8.0%.

4.1.6. 6-[2′,2′-Dimethyl-(4′*R*)-1′,3′-dioxolan-4′-yl]-3-methylcarbonyloxy-2-phenyl-(2*R*,3*S*,4*S*,6*R*)-tetrahydro-2*H*-4-pyranyl acetate, 1. A solution of AD Mix α (0.54 g, 0.69 mmol) in water:*tert*-BuOH (5 mL, 1:2) was treated with $CH_3SO_2NH_2$ (0.065 g, 0.69 mmol) and cooled to 0°C. A solution of dihydropyran **10** (0.18 g, 0.69 mmol) in *tert*-BuOH (2 mL) was added to the reaction mixture all at once and the heterogeneous slurry stirred for 24 h. Solid Na_2SO_4 (10 mg) was added and the reaction mixture allowed to warm to room temperature. After 30 min the reaction mixture was extracted with ethyl acetate (3×10 mL), washed with brine (2×10 mL) and dried (Na_2SO_4). The organic layer was evaporated under reduced pressure and the residue purified by column chromatography (silica gel, 60–120 mesh, ethyl acetate:pet. ether, 1:2) to afford **11** as a thick syrup (0.36 g, 60%) as an inseparable mixture. $[\alpha]_D^{25}$ +7.5 (*c* 0.8, $CHCl_3$).

A solution of the above crude diol **11** (0.1 g, 0.34 mmol) in pyridine (0.50 mL) containing DMAP (catalytic) was treated with Ac_2O (0.068 mL, 0.68 mmol) at 0°C and stirred for 1 h at room temperature. The reaction mixture was diluted with a saturated aq. $NaHCO_3$ solution (15 mL) and extracted with CH_2Cl_2 (2×10 mL). The combined organic layers were washed with a saturated aq. $CuSO_4$ solution (10 mL), water (10 mL), brine (15 mL) and dried (Na_2SO_4). The solvent was evaporated under reduced pressure and the residue was purified by column chromatography (silica gel, 60–120 mesh, EtOAc:hexane, 1:4) to afford 6-[2′,2′-dimethyl-(4′*R*)-1′,3′-dioxolan-4′-yl]-3-methylcarbonyloxy-2-phenyl (2*R*,3*S*,4*S*,6*R*)-tetrahydro-2*H*-4-pyranyl acetate **1** as a syrup (0.088 g, 70%). $[\alpha]_D^{25}$ +7.5 (*c* 0.8, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ 7.4–7.2 (m, 5H, Ar-H), 5.9 (d, 1H, $J=9.6$ Hz, H-4), 4.9 (q, 1H, $J=3.84$ Hz, H-3), 4.4 (dd, 1H, $J=6.2$, 3.84 Hz, H-2), 4.2 (m, 2H, H-4′, 5′a), 3.8 (m, 1H, H-6), 3.64 (m, 1H, H-5′b), 2.1 (s, 3H, OAc), 2.0 (s, 3H, OAc), 1.79 (m, 1H, H-5a), 1.6 (m, 1H, H-5b), 1.40, 1.35 (br.s, 6H, CH_3); FABMS (m/z): 378 (M^+), 319, 260. Anal. calcd for $C_{20}H_{26}O_7$: C, 63.48; H, 6.92; found: C, 63.54; H, 7.0%.

4.2. Synthesis of 6-[2′,2′-dimethyl-(4′*S*)-1′,3′-dioxolan-4′-yl]-3-methoxy-2-phenyl-(2*S*,3*S*,4*R*,6*R*)-tetrahydro-2*H*-4-pyranyl acetate, 2 and 6-[2′,2′-dimethyl-(4′*S*)-1′,3′-dioxolan-4′-yl]-4-methoxy-2-phenyl-(2*S*,3*R*,4*S*,6*R*)-tetrahydro-2*H*-3-pyranyl acetate, 3

4.2.1. 1-[2′,2′-Dimethyl-(4′*S*)-1′,3′-dioxolan-4′-yl]-5-(4-methoxybenzyloxy)-(1*S*)-3-pentyn-1-ol, 15. A stirred solution of 1-(4-methoxybenzyloxy) propyne **14** (3.6 g, 20.4 mmol) in dry THF (30 mL) at −78°C under a nitrogen atmosphere was sequentially treated with *n*-BuLi (15 mL, 216 mmol, 1.6N hexane solution), BF_3Et_2O (2.95 mL, 20.7 mmol), followed by the addition 2,2-dimethyl-4-[(2*S*)-oxiran-2yl]-(4*S*)-1,3-dioxalane **13** (2.3 g, 15.9 mmol) in THF (20 mL) at an interval of 10 min. After 6 h the reaction mixture was treated with a sat. $NaHCO_3$ solution (15 mL) at −78°C followed by the addition of saturated aqueous NH_4Cl solution (10 mL) and stirred for 30 min. The reaction mixture was diluted with ethyl acetate (100 mL) and washed with sat $NaHCO_3$ (15 mL). Combined organic extracts were washed successively with saturated NH_4Cl (50 mL), brine (50 mL) and dried (Na_2SO_4). Evaporation of solvent under reduced pressure and purification of residue by column chromatography (silica gel 60–120 mesh, EtOAc:hexane, 3:17) gave 1-[2′,2′-dimethyl-(4′*S*)-1′,3′-dioxolan-4′-yl]-5-(4-methoxybenzyloxy)-(1*S*)-3-pentyn-1-ol, **15** as a yellow syrup (3.3 g, 51%). $[\alpha]_D^{25}$: −1.8 (*c* 1.0, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ 7.5 (d, 2H, $J=7.5$ Hz, Ar-H), 6.85 (d, 2H, $J=7.5$ Hz, Ar-H), 4.50 (.s, 2H, $-OCH_2$), 4.2–4.0 (m, 5H, H-4′, 5, 5′), 3.8–3.6 (m, 1H, H-1), 3.6 (s, 3H, $-OCH_3$), 2.5–2.4 (m, 2H, H-2), 1.5–1.4 (br.s, 3H, $-CH_3$), 1.4–1.3 (br.s, 3H, $-CH_3$); FABMS (m/z): 320 (M^+). Anal. calcd for $C_{18}H_{24}O_5$: C, 67.5; H, 7.5; found: C, 67.6; H, 7.7%.

4.2.2. 4-[5′-(4-Methoxybenzyloxy)-1′-phenylsulfonyloxy-(1′*S*)-3′-pentynyl]-2,2-dimethyl-(4*S*)-1,3-dioxolane, 16. To a solution of **15** (1.4 g, 4.3 mmol) in CH_2Cl_2 (20 mL) Et_3N (0.66 mL, 6.5 mmol) was added and cooled to 0°C. After 5 min benzenesulphonyl chloride (1.15 mL, 6.5 mmol), was added the reaction mixture was stirred at room temperature for 6 h. The reaction mixture was diluted with water (20 mL) and extracted with CH_2Cl_2 (3×50 mL). The combined organic extracts were washed with brine (20 mL), dried (Na_2SO_4) and concentrated in vacuum to a syrup, which was purified

by column chromatography (silica gel, EtOAc:hexane, 3:22) to afford 4-[5′-(4-methoxybenzyloxy)-1′-phenylsulfonyloxy - (1′*S*) - 3′ - pentynyl] - 2,2 - dimethyl - (4*S*) - 1,3-dioxolane, **16** as a syrup (1.6 g, 80%). $[\alpha]_D^{25}$: −0.55 (*c* 1.8, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ 7.95 (d, 2H, $J=6.9$ Hz, Ar-H), 7.7 (m, 3H, Ar-H), 7.25 (d, 2H, $J=7.5$ Hz, Ar-H), 6.85 (d, 2H, $J=7.5$ Hz, Ar-H), 4.55 (q, 1H, $J=5.1$ Hz, H-1′), 4.50 (s, 2H, -OCH_2), 4.25–4.02 (m, 3H, H-4, 5), 4.02–3.92 (m, 2H, H-5′), 3.80 (s, 3H, -OCH_3), 2.80 (dd, 1H, $J=15.3$ Hz, H-2′a), 2.60 (dd, 1H, $J=6.1$ Hz, H-2′b), 1.3–1.2 (br.s, 6H, CH_3); FABMS (*m*/*z*): 460 (M^+), 323, 319. Anal. calcd for $C_{24}H_{28}O_7S$: C, 62.5; H, 6.1; S, 6.9; found: C, 62.6; H, 6.0; S, 6.8%.

4.2.3. 4-[5′-Hydroxy-1′-phenylsulfonyloxy-(1′*S*)-3′-pentynyl]-2,2-dimethyl-(4*S*)-1,3-dioxolane, 17. DDQ (0.59 g, 2.62 mmol) was added to a stirred solution of **16** (1.2 g, 2.6 mmol) in aq. CH_2Cl_2 (15 mL; 1:9) and stirred at room temperature for 2 h. The reaction mixture was diluted with water (10 mL) and extracted with CH_2Cl_2 (3×10 mL), organic layer was dried (Na_2SO_4), evaporated under reduced pressure and purified the residue by column chromatography (silica gel 60–120 mesh, EtOAc:hexane, 3:22) to afford 4-[5′-hydroxy-1′-phenylsulfonyloxy - (1′*S*) - 3′ - pentynyl] - 2,2 - dimethyl - (4*S*) - 1,3-dioxolane, **17** as a syrup (0.63 g, 71%). $[\alpha]_D^{25}$: −1.0 (*c* 1.1, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ 7.9 (d, 2H, $J=5$Hz, Ar-H), 7.7 (m, 1H, Ar-H), 7.6 (m, 2H, Ar-H), 4.6 (m, 1H, H-1′), 4.4 (m, 1H, H-5a), 4.2 (m, 2H, H-5b, 4), 4.0 (m, 1H, H-5′a), 3.8 (m, 1H, H-5′b), 2.8 (dd, 1H, $J=10.0$, 5.0 Hz, H-2′a), 2.58 (dd, 1H, $J=5.0$, 10.0 Hz, H-2′b), 1.3–1.2 (br.s, 6H, CH_3); EIMS (*m*/*z*): 341 (M^++ 1), 340 (M^+). Anal. calcd for $C_{16}H_{20}O_6S$: C, 56.4; H, 5.9; S, 9.4; found: C, 56.5; H, 6.0; S, 9.3%.

4.2.4. 4-[5′-Hydroxy-1′-phenylsulfonyloxy-(1′*S*,3′*Z*)-3′-pentenyl]-2,2-dimethyl-(4*S*)-1,3-dioxolane, 18. To a solution of **17** (0.60 g, 1.76 mmol) in ethyl acetate (10 mL), quinoline (0.01 mL) and Lindlar catalyst (0.01 g) were added and stirred at room temperature under hydrogen atmosphere for 6 h. Work up of the reaction mixture as described for **4** purification by column chromatography (silica gel, EtOAc:hexane, 3:22) furnished 4-[5′-hydroxy-1′-phenylsulfonyloxy-(1′*S*,3′*Z*)-3′-pentenyl]-2,2-dimethyl-(4*S*)-1,3-dioxolane, **18** as a syrup (0.56 g, 94%). $[\alpha]_D^{25}$: −1.7 (*c* 1.8, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ 8.0–7.9 (d, 2H, $J=5.5$ Hz, Ar-H), 7.7–7.5 (m, 3H, Ar-H), 5.82–5.75 (m, 1H, H-4′), 5.45–5.28 (m, 1H, H-3′), 4.62–4.45 (m, 1H, H-1′), 4.25–3.84 (m, 4H, H-5′a, H-4, H-5), 3.82–3.78 (m, 1H, H-5′b), 2.65–2.28 (m, 2H, H-2′), 1.25–1.20 (br.s, 6H, CH_3); FABMS (*m*/*z*): 342 (M^+), 332, 277. Anal. calcd for $C_{16}H_{22}O_6S$: C, 56.1; H, 6.4; S, 9.3; found: C, 56.2; H, 6.2; S, 9.4%.

4.2.5. 4-[5′-Hydroxy-5′-phenyl-1′-phenylsulfonyloxy-(1′*S*,5′*R*/*S*,3′*Z*)-3′pentenyl]-2,2-dimethyl-(4*S*)-1,3-dioxolane, 4a. To a stirred suspension of pyridinium chlorochromate (PCC; 0.47 g, 2.21 mmol) in CH_2Cl_2 (5 mL), a solution of alcohol **18** (0.50 g, 1.46 mmol) in CH_2Cl_2 (5 mL) was added and the mixture was stirred for 1 h. The reaction mixture was diluted with ether (45 mL), decanted and washed repeatedly with ether. The combined ethereal layers were filtered over a bed of Celite to afford crude 4-[4′-formyl-1′-phenylsulfonyloxy-(1′*S*,3′*Z*)-3′-butenyl]-2,2-dimethyl-(4*S*)-1,3-dioxolane, **12** (0.41 g, 83%), which was used in the next reaction without purification.

To a freshly prepared solution of phenyl magnesium bromide [prepared from bromobenzene (0.56 g, 3.5 mmol) and magnesium (0.085 g, 3.5 mmol) in THF (10 mL)], aldehyde **12** (0.40 g, 1.2 mmol) in THF (20 mL) was added dropwise at 0°C and stirred at room temperature for 3 h. The reaction mixture was quenched with a sat. aq. NH_4Cl (5 mL) solution and extracted with ethyl acetate (3×25 mL). The organic layer was washed with water (10 mL), brine (10 mL), dried (Na_2SO_4) and evaporated. The crude product was purified by column chromatography (silica gel 60–120 mesh, EtOAc: hexane, 1:4) to afford 4-[5′-hydroxy-5′-phenyl-1′-phenylsulfonyloxy - (1′*S*,5′*R*/*S*,3′*Z*) - 3′pentenyl] - 2,2-dimethyl-(4*S*)-1,3-dioxolane, **4a**, as a syrup (0.42 g, 86%). $[\alpha]_D^{25}$: −14.8 (*c* 0.8, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ 7.9 (d, 2H, $J=1.3$ Hz, Ar-H), 7.6 (m, 5H, Ar-H), 7.3 (m, 3H, Ar-H), 5.8–5.7 (dd, 1H, $J=1.3$, 2.6 Hz, H-4′), 5.65 (m, 1H, H-3′), 5.1 (t, 1H, $J=1.3$ Hz, H-5′), 4.6 (m, 1H, H-1′), 4.2 (m, 1H, H-4), 3.9 (m, 1H, H-5a), 3.8 (m, 1H, H-5b), 2.5 (m, 1H, H-2′a), 2.39 (m, 1H, H-2′b), 1.28–1.22 (s, 6H, CH_3); EIMS (*m*/*z*): 418 (M^+), 332, 277. Anal. calcd for $C_{22}H_{26}O_6S$: C, 63.1; H, 6.2; S, 7.6; found: C, 63.0; H, 6.3; S, 7.8%.

4.2.6. Sharpless kinetic resolution of 4a to give 19 and 4b. Anhydrous CH_2Cl_2 (2 mL) was cooled to −20°C under N_2, Ti(^{i}OPr)$_4$ (0.29 mL, 1.06 mmol) and (+)-DIPT (0.29 mL, 1.12 mmol) were sequentially added and stirred for 5–10 min. A solution of alcohol **4a** (0.4 g, 0.95 mmol) in CH_2Cl_2 (5 mL) followed by cummene hydroperoxide (0.16 mL, 0.5 mmol) was added to the reaction mixture. The resulting mixture was stored at −10°C for 2 days. The cold reaction mixture was allowed to warm to 0°C and quenched with 10% aq. NaOH solution saturated with NaCl (8 mL) stirred vigorously for 1 h. The reaction mixture was filtered through Celite and extracted with ethyl acetate (2×25 mL). The organic layer was washed with brine (10 mL), dried (Na_2SO_4) evaporated under reduced pressure and purified by column chromatography (silica gel 60–120 mesh, EtOAc:hexane, 1:4) to afford a mixture of 4-[2′(3″ - hydroxy - (3″*S*) - (phenyl)methyl - (1′*R*,2′*R*) - 2′-(oxiranyl] - 1‴ - phenylsulfonyloxy - (1‴*S*) - ethyl) - 2,2-dimethyl-(4*S*)-1,3-dioxolane **19** and 4-[5′-hydroxy-5′-phenyl-1′-phenylsulfonyloxy-(1′*S*,3′*Z*)-3′-pentenyl]-2,2-dimethyl-(4*S*)-1,3-dioxolane **4b** as a syrup (0.42 g, 86%). $[\alpha]_D^{25}$: −2.7 (*c* 0.5, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ 7.9 (br.t, 2H, $J=1.3$ Hz, Ar-H), 7.6 (m, 3H, Ar-H), 7.3 (br.s, 5H, Ar-H), 5.75 (dd, 0.5H, $J=1.3$, 2.6 Hz, H-3′), 5.65 (m, 0.5H, H-4′), 5.1 (t, 1H, $J=1.3$ Hz, H-5′), 4.6 (m, 1H, H-1′), 4.2 (m, 1H, H-4), 3.9 (m, 1H, H-5a), 3.8 (m, 1H, H-5b), 3.12–2.93 (m, 1H, epoxy protons), 2.5 (m, 1H, H-2′a), 2.39 (m, 1H, H-2′b), 1.28–1.22 (s, 6H, CH_3).

4.2.7. Cyclisation of the mixture 19 and 4b. A solution of the mixture of **19**+**4b** (0.5 g, 1.2 mmol) in methanol (10 mL) was treated with K_2CO_3 (0.16 g, 1.2 mmol) and heated under reflux for 4 h. Work up of the reaction as reported for 10 gave the residue, which was purified by column chromatography (silica gel, 100–200 mesh, EtOAc:hexane, 3:20). First eluted was 2-[2′,2′-dimethyl-(4′S)-1′,3′-dioxolan-4′-yl]-6-phenyl-(2*R*,6*S*)-3,6-dihydro-2*H*-pyran **22** as a syrup (0.033 g, 22%). $[\alpha]_D^{25}$ −17.8 (*c* 0.8, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.4–7.2 (m, 5H, Ar-H), 5.8–5.9 (dt, 1H, $J=2.6$ Hz, H-4), 5.7–5.6 (dd, 1H, $J=5.2$, 2.6 Hz, H-5), 5.2 (m, 1H, H-6), 4.5 (m, 1H, H-2), 4.1 (m, 2H, H-5′), 3.59 (dt, 1H, $J=5.2$ Hz, H-4′), 1.9 (m, 2H, H-3), 1.4–1.35 (br.s, 6H, CH_3). EIMS (*m*/*z*): 260 (M^+). Anal. calcd for $C_{16}H_{20}O_3$: C, 73.8; H, 7.7; found: C, 73.6; H, 7.8%.

Second eluted was 6-[2′,2′-dimethyl-(4′*S*)-1′,3′-dioxolan-4′-yl]-3-methoxy-2-phenyl-(2*S*,3*S*,4*R*,6*R*)-tetrahydro-2*H*-4-pyranol, **20** as a syrup (0.06 g, 34%). $[\alpha]_D^{25}$ −18.7 (*c* 1.2, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.4–7.2 (m, 5H, Ar-H), 4.3 (m, 1H, H-4), 4.1 (d, 1H, $J=3.1$ Hz, H-2), 3.95 (m, 2H, H-3,5′a), 3.85 (dt, 1H, $J=4.7$ Hz, H-6), 3.75 (m, 2H, H-4′,5′b), 3.25 (s, 3H, OCH_3), 2.1 (m, 2H, H-5), 1.38, 1.36 (2s, 6H, CH_3). Anal. calcd for $C_{17}H_{25}O_5$: C, 66.0; H, 8.1; found: C, 66.1; H, 8.0%.

Third eluted was 6-[2′,2′-dimethyl-(4′*S*)-1′,3′-dioxolan-4′-yl]-4-methoxy-2-phenyl-(2*S*,3*R*,4*S*,6*R*)-tetrahydro-2*H*-3-pyranol **21** as a syrup (0.021 g, 12%). $[\alpha]_D^{25}$ +2.66 (*c* 1.2, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.4–7.2 (m, 5H, Ar-H), 4.3 (m, 1H, H-4), 4.2 (dd, 1H, $J=4.4$, 6.6 Hz, H-3), 4.1 (d, 1H, $J=4.4$ Hz, H-2), 4.0 (m, 1H, H-6), 3.9 (m, 2H, H-4′, 5′a), 3.6 (dd, 1H, $J=4.4$, 2.2 Hz, H-5′b), 3.25 (s, 3H, OCH_3), 2.2 (ddd, 1H, $J=6.7$, 4.4, 2.2 Hz, H-5α), 1.8 (m, 1H, H-5β), 1.3, 1.2 (2s, 6H, CH_3).

4.2.8. 6-[2′,2′-Dimethyl-(4′*S*)-1′,3′-dioxolan-4′-yl]-3-methoxy-2-phenyl-(2*S*,3*S*,4*R*,6*R*)-tetrahydro-2*H*-4-pyranyl acetate, 2. A solution of **20** (0.1 g, 0.32 mmol) in pyridine (0.5 mL) containing DMAP (catalytic) was treated with Ac_2O (0.03 mL, 0.32 mmol) at 0°C and stirred for 1 h at room temperature. The reaction mixture was worked up as described for **1** and purified by column chromatography (silica gel, 100–200 mesh, EtOAc:hexane, 1:4) to afford 6-[2′,2′-dimethyl-(4′*S*)-1′,3′-dioxolan-4′-yl]-3-methoxy-2-phenyl-(2*S*,3*S*,4*R*,6*R*)-tetrahydro-2*H*-4-pyranyl acetate, **2** as a thick syrup (0.10 g, 92%). $[\alpha]_D^{25}$ −20.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.4–7.2 (m, 5H, Ar-H), 5.3 (dt, 1H, $J_{4,3}=4.6$, $J_{4,5}=6.0$ Hz, H-4), 4.22 (d, 1H, $J_{2,3}=2.2$ Hz, H-2), 4.11 (dd, 1H, $J_{3,2}=2.2$, $J_{3,4}=4.6$ Hz, H-3), 4.06 (m, 1H, H-5′a), 3.99 (ddd, 1H, $J_{6,4'}=6.0$, $J_{6,5\alpha}=2.6$, $J_{6,5\beta}=9.7$ Hz, H-6), 3.87 (m, 2H, H-4′,5′b), 3.25 (s, 3H, OCH_3), 2.01 (ddd, 1H, $J_{5\alpha,6}=2.2$, $J_{5\alpha,5\beta}=13.7$, $J_{5\alpha,4}=5.6$ Hz, H-5α), 1.98 (s, 3H, OAc), 1.79 (ddd, 1H, $J_{5\beta,6}=9.7$, $J_{5\alpha,5\beta}=13.7$, $J_{5\beta,4}=5.6$ Hz, H-5β), 1.38, 1.34 (2s, 6H, CH_3). ^{13}C NMR (50 Hz, $CDCl_3$): δ 21.26, 25.46, 28.68, 29.77, 35.86, 57.34, 67.59, 75.51, 76.83, 79.87, 84.01, 87.54, 127.71, 128.32. FABMS (*m*/*z*): 350 (M^+). Anal. calcd for $C_{19}H_{26}O_6$: C, 65.13; H, 7.48; found: C, 65.11; H, 7.44%.

4.2.9. 6-[2′,2′-Dimethyl-(4′*S*)-1′,3′-dioxolan-4′-yl]-4-methoxy-2-phenyl-(2*S*,3*R*,4*S*,6*R*)-tetrahydro-2*H*-3-pyranyl acetate, 3. A solution of **22** (0.10 g, 0.32 mmol) in pyridine (0.5 mL) containing DMAP (catalytic) was treated with Ac_2O (0.03 mL, 0.32 mmol) at 0°C and stirred for 1 h at room temperature. Work up of the reaction as described for **1** and purification by column chromatography (silica gel, 100–200 mesh, EtOAc:hexane, 1:4) gave 6-[2′,2′-dimethyl-(4′*S*)-1′,3′-dioxolan-4′-yl]-4-methoxy-2-phenyl-(2*S*,3*R*,4*S*,6*R*)-tetrahydro-2*H*-3-pyranyl acetate, **3** as a syrup (0.10 g, 92%). $[\alpha]_D^{25}$ −6.4 (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.4–7.2 (m, 5H, Ar-H), 5.25 (dd, 1H, $J_{3,2}=4.6$, $J_{3,4}=6.8$ Hz, H-3), 4.2 (d, 1H, $J_{2,3}=4.6$ Hz, H-2), 4.05 (m, 2H, H-4,5′a), 3.99 (ddd, 1H, $J_{6,4'}=6.0$, $J_{6,5\alpha}=2.6$, $J_{6,5\beta}=9.7$ Hz, H-6), 3.87 (m, 2H, H-4′,5′b), 3.25 (s, 3H, OCH_3), 2.01 (m, 1H, H-5α), 1.98 (s, 3H, OAc), 1.78 (ddd, 1H, $J_{5\beta,6}=9.7$, $J_{5\alpha,5\beta}=13.7$, $J_{5\beta,4}=5.6$ Hz, H-5β), 1.4, 1.38 (2s, 6H, CH_3). FABMS (*m*/*z*): 350 (M^+).

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