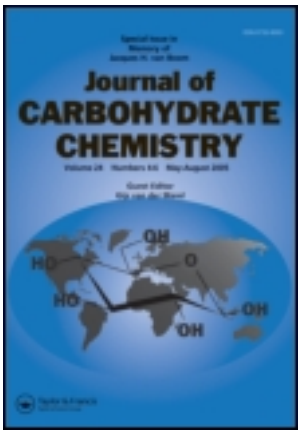

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Transformation of Terminal Diols of Cyclic and Acyclic Saccharides to Epoxides and Alkenes by Reaction with Triphenylphosphine, Imidazole and Iodine

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TRANSFORMATION OF TERMINAL DIOLS OF CYCLIC AND ACYCLIC SACCHARIDES TO EPOXIDES AND ALKENES BY REACTION WITH TRIPHENYLPHOSPHINE, IMIDAZOLE AND IODINE

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ABSTRACT

Reaction of various terminal diols **1,4,6,8-12**, derived from cyclic and acyclic monosaccharides, with 2 mol equivalents each of TPP-imidazole-I_2 between -8 °C and 15 °C in THF afforded the corresponding epoxides **2,5,7,13-17**, respectively, with 4 mol equivalents each of TPP-imidazole-I_2 in toluene at reflux temperature the starting diols afforded the corresponding alkenes **3,18-24**, respectively.

INTRODUCTION

Terminal epoxides and alkenes derived from cyclic and acyclic saccharides have been used as building blocks for the total synthesis of natural products[1] such as prostaglandins,[2] pentenomycin,[3] allethrin,[4] karalicin,[5] (-)nonactic acid,[6] goniofufurone,[7] kaumasyne[8] and Hagen's gland lactones.[9] For example, 5,6-anhydro-3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucofuranose[10] served as a chiral synthon for the synthesis of

karalicin.[5] Recently we have shown that vinyl (hydroxy)furans[11] are useful synthons for the construction of tetrahydrofurofuran containing natural products.

Synthesis of terminal epoxides and alkenes have been earlier achieved starting from easily available terminal diols bearing a primary and a secondary alcohol. The most commonly used practical method for preparing epoxides involved regioselective tosylation of the primary alcohol followed by treatment with base.[12] Mack et al. have described use of the Mitsunobu reagent, diethyl azodicarboxylate-triphenylphosphine (DEAD-TPP), for quantitative preparation of epoxides.[13] Rokach et al. have recently described a new methodology where bis-*O,O'*-dithiocarbonate of the terminal diol was converted to epoxide by sequential reactions with MeI, DIBAL-H and NaOMe.[14]

Terminal alkenes of cyclic and acyclic saccharides have been prepared from the dimesylate of a terminal diol by reaction with NaI in acetone.[15] They have also been prepared by transforming vicinal diols either to the corresponding bis-*O,O'*-dithiocarbonates followed by reaction with tributyltin hydride,[16] or to 1-dimethylamino(methylene) acetals and decomposition with iodomethane.[17] Garegg and Samuelsson have reported use of TPP-imidazole-I_2 for the conversion of vicinal secondary alcohols to alkenes,[18] a method that was also successfully applied to conversion of inositol derivatives[19] to the corresponding alkenes.

RESULTS AND DISCUSSION

We herein report a general method for preparation of cyclic and acyclic saccharide epoxides and alkenes from terminal diols by use of TPP-imidazole-I_2 reagent system developed first by Garegg et al., to prepare iodohydrins[20] and alkenes from diols. Variation of temperature, solvent and mole equivalents of reagents has been studied to produce either epoxide or alkene from diols.

Reaction of 1,2-*O*-isopropylidene-α-D-glucofuranose (**1**)[21] with TPP-imidazole-I_2 (2 moles each/mol diol) at room temperature in THF for 4 h resulted in the isolation of the corresponding epoxide **2** and alkene **3** in equal amounts (by ^{1}H NMR). After optimisation of the reaction conditions, the best conditions established required the reaction of **1** with TPP-imidazole-I_2 (2 moles each/mol diol) in THF between -8 °C and 15 °C to obtain epoxide **2** in high yield. Formation of alkene **3** was not observed. This method was successfully applied for the conversion of diol **4**[22] to the corresponding epoxide **5**. Formation of the epoxide was evident from the appearence of epoxy protons (3H) between δ 2.74-3.35. Generality of the reaction was extended to diol **6** derived from mannose, to give the corresponding diastereomeric mixture of epoxide **7** in good yield. This reaction

was also applied to acyclic saccharide diol **8**[23] and aryl ether diols **9-12** to obtain the corresponding epoxides **13-17**, respectively, in good yield (Table).

Attention was then turned to transformation of terminal diols to alkenes by variation of molar ratio of the reagents TPP-imidazole-I_2, solvent and temperature. The best reaction condition established required reaction of one mole of triol **1** with 4 moles each of TPP, imidazole, I_2 in toluene at reflux temperature for 4 h to give exclusively the alkene **3** in good yield after work up.[18] Use of 4.5 moles each of TPP, imidazole, I_2 did not affect the yield of alkenes. Formation of alkene was evident from the ^{1}H NMR spectrum from the appearance of olefinic protons (3H) between δ 5.20-6.15. Practical utility of the method was demonstrated by conversion of diverse diols **4,6,8-12** to the corresponding alkenes **18-24**, respectively, in good yield.

Garegg et al.,[18a] having developed this reagent system consisting of TPP-imidazole-I_2, proposed a mechanism involving formation of reagent complex (**I**) followed by reaction with a diol to afford the alkene via the iodophenylphosphonium ion intermediate (**II**) (Pathway A, Scheme). We found, use of 2 moles each of TPP-imidazole-I_2, instead of 4 mole equivalents, between -8 °C and 15 °C in a polar solvent such as tetrahydrofuran resulted in the formation of an epoxide (Pathway B, Scheme). Formation of epoxide from a terminal diol could be visualised via iodohydrin intermediate (**III**) formed by reaction of the reagent complex (**I**) with diol followed by base catalysed elimination.

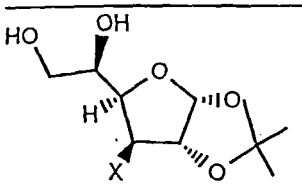
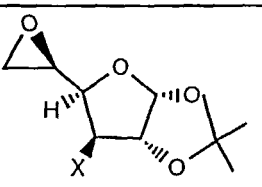
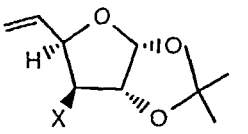
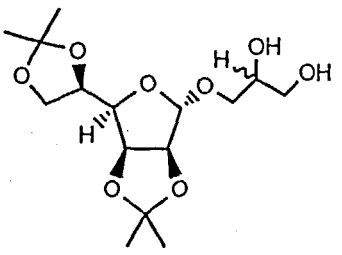
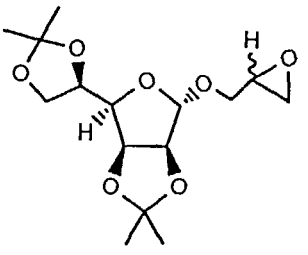
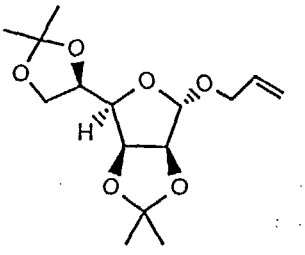
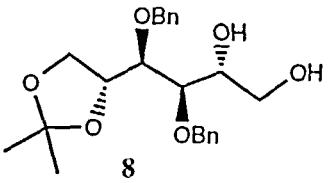
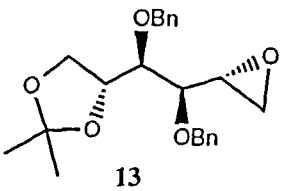
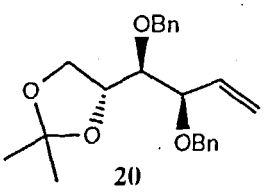
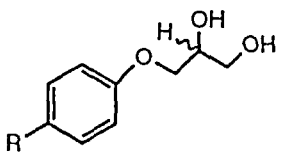
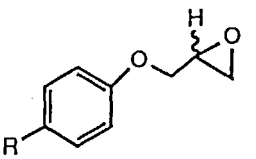
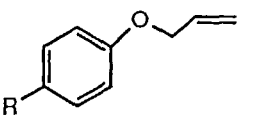
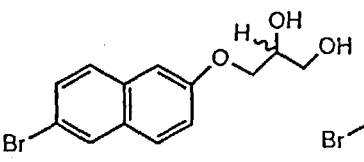
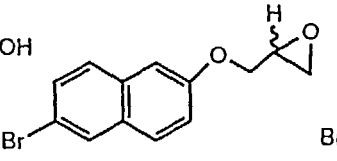
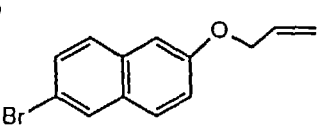
CONCLUSION

Transformation of each mole of diol to epoxide was best performed by use of 2 mole each of TPP-imidazole-I_2 in THF between -8 °C and 15 °C, whereas use of 4 moles each of the same reagent in toluene at reflux temperature afforded alkenes.

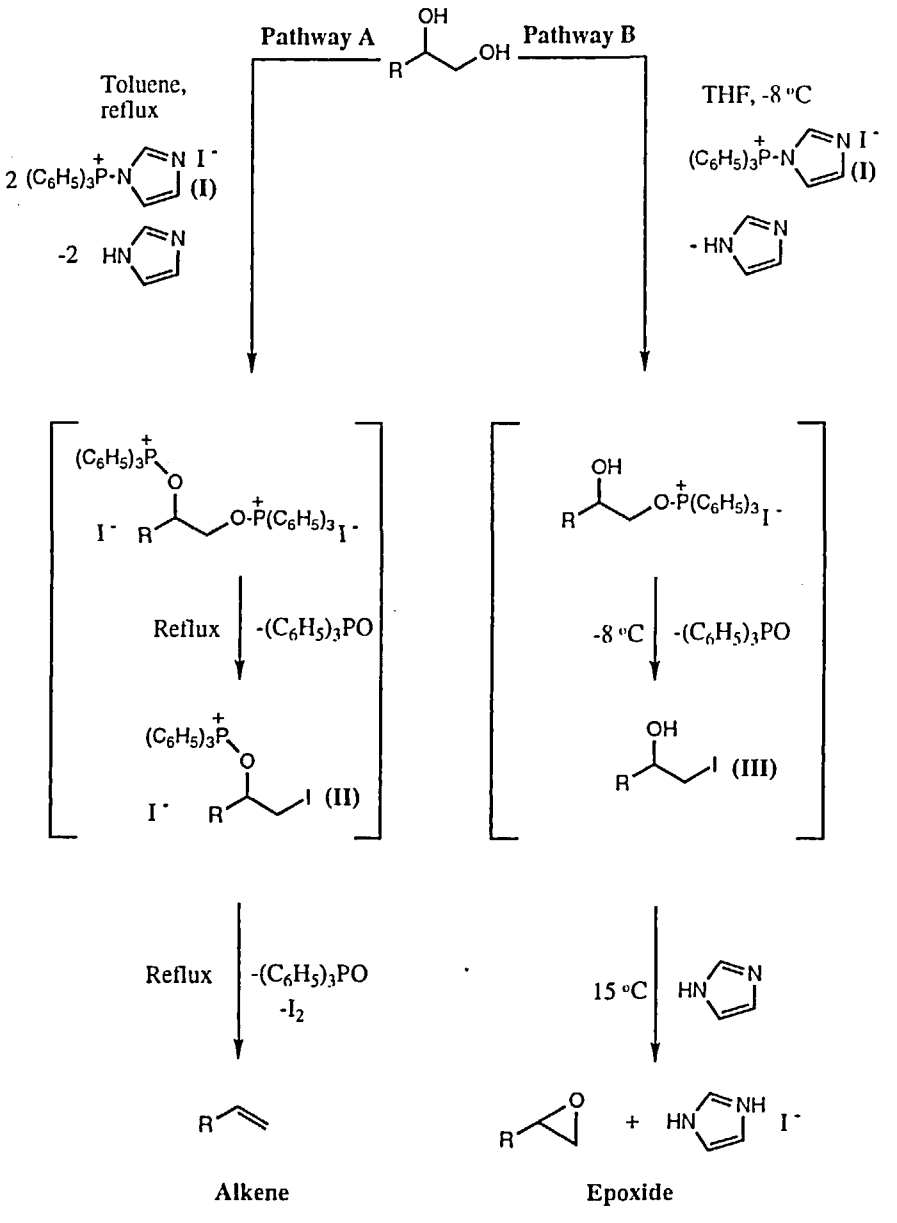
EXPERIMENTAL

5,6-Anhydro-1,2-*O*-isopropylidene-α-D-glucofuranose (2)[24]. To a solution of 1,2-*O*-isopropylidene-α-D-glucofuranose (**1**) (5.0 g, 22.7 mmol) in THF (250 mL) was added imidazole (3.10 g, 45.4 mmol) and triphenylphosphine (11.9 g, 45.4 mmol), and the mixture was stirred at room temperature until a clear solution was obtained. The solution was cooled to -8 °C in an ice salt mixture, and iodine (11.5 g, 45.4 mmol) was added in small lots while the temperature of the reaction was maintained at -8 °C. The reaction mixture was then warmed to 15 °C gradually during 30 min and stirred for 3 h. It was then cooled to -8 °C and 5% aqueous sodium hydroxide solution (50 mL) was added dropwise maintaining temperature at 0 °C. Solvent was evaporated from the reaction

Table

Diol	Epoxide from Reagent system A	Ene from Reagent system B
		
1 X = OH 4 X = H	2 X = OH 5 X = H	3 X = OH 18 X = H
		
6	7	19
		
8	13	20
		
9 R = NO_2 10 R = $CMe_2CH_2CH_3$ 11 R = $COCH_3$	14 R = NO_2 15 R = $CMe_2CH_2CH_3$ 16 R = $COCH_3$	21 R = NO_2 22 R = $CMe_2CH_2CH_3$ 23 R = $COCH_3$
		
12	17	24

Reagent System A = TPP-Imidazole-I_2, -8 °C to 15 °C in THF
Reagent System B = TPP-Imidazole-I_2, reflux in toluene



Scheme

mixture under vacuum without heating to give a residue that was extracted into ethyl acetate (3x250 mL). The organic phase was separated, washed with satd. sodium thiosulphate solution (2x100 mL), water (2x100 mL), dried (Na_2SO_4) and concentrated to yield a white residue containing epoxide together with triphenylphosphine oxide. This residue was dissolved in diethyl ether (300 mL) and triturated with hexane (200 mL) to give a residue, containing epoxide and a trace amount of triphenylphosphine oxide, which was chromatographed (60-120 mesh, hexane:EtOAc) yielding the title compound **2** (3.7 g, 80%) as a crystalline solid: mp 131-132 °C [lit.[24] mp 133.5 °C]; $[\alpha]_D$ -24.40° (*c* 4.0, H_2O) {lit[24]. $[\alpha]_D$ -26.5° (*c* 4.0, water)}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.35, 1.50 (2s, 6H, 2xCH_3), 2.80-3.10 (m, 3H, H-6,6' and OH), 3.4-3.5 (m, 1H, H-5), 4.08 (dd, 1H, $J_{3,4}$=2.4 Hz; $J_{4,5}$=3.1 Hz, H-4), 4.25 (d, 1H, $J_{3,4}$=2.4 Hz, H-3), 4.51 (d, 1H, $J_{1,2}$=3.9 Hz, H-2), 5.99 (d, 1H, $J_{1,2}$=3.9 Hz, H-1).

Anal. Calcd for $C_9H_{14}O_5$: C, 53.46; H, 6.98. Found: C, 53.56; H, 7.08.

5,6-Dideoxy-1,2-*O*-isopropylidene-α-D-*xylo*-hexo-5-enofuranose (3). A solution of **1** (10.0 g, 45 mmol), triphenylphosphine (TPP) (47.6 g, 180 mmol) and imidazole (12.3 g, 180 mmol) in toluene (400 mL) was stirred and warmed to 50 °C. Iodine (46.1 g, 180 mmol) was added to the above reaction mixture in small lots during 40 min with the temperature of the reactants being maintained between 58-62 °C. The reaction mixture was heated to reflux for 4 h, cooled to room temperature and solvent removed on a rotary evaporator to produce a dark brown syrup (141.2 g). The syrup was dissolved in ethyl acetate (300 mL), iodine was added (30 g), the mixture was stirred at room temperature for 15 min and 5% aqueous sodium hydroxide solution (450 mL) was then added. The organic phase was separated and aqueous phase was extracted with ethyl acetate (2x50 mL). The combined organic phases were washed with water (3x250 mL), 20% aqueous $Na_2S_2O_3$ (2x250 mL) and water (2x100 mL). The organic phase was separated, concentrated to a brown residue (94.3 g) and triturated with diethyl ether (300 mL) to give a solid which was filtered. The filtrate was concentrated to about 200 mL and cooled to 0 °C yielding a solid that was filtered off. The filtrate was concentrated to a thick syrup (19.4 g) which was then extracted into a mixture of hexane-diethyl ether (100 mL, 1:1) three times to leave an insoluble syrupy residue containing the title compound **3** (12.1 g) which was pure enough for further chemical reactions. Crude **3** was purified further by filtering on a bed of silica gel (60-120 mesh, hexane:EtOAc, 4:1) to afford **3** (6.76 g, 80%) as a colourless solid: mp 61-65 °C [lit.[21] mp 64-65 °C]; $[\alpha]_D$ -51.5° (*c* 1.1, $CHCl_3$), {lit.[21] $[\alpha]_D$ -52.1° (*c* 2.27, $CHCl_3$)}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.25, 1.47

(2s, 6H, 2xCH_3), 4.0 (d, 1H, $J_{3,4}$=2.8 Hz, H-3), 4.50 (d, 1H, $J_{1,2}$=4.0 Hz, H-2), 4.6-4.7 (m, 1H, H-4), 5.38 (d, 1H, $J_{5,6cis}$=11.0 Hz, H-6), 5.5 (d, 1H, $J_{5,6trans}$=18.0 Hz, H-6'), 5.7-5.96 (m, 2H, H-1,5).

Anal. Calcd for $C_9H_{14}O_4$: C, 58.05; H, 7.58. Found: C, 58.14; H, 7.67.

5,6-Anhydro-3-deoxy-1,2-*O*-isopropylidene-α-D-*ribo*-hexofuranose (5). Compound **5** was prepared from 3-deoxy-1,2-*O*-isopropylidene-α-D-glucofuranose (**4**) (0.5 g, 2.45 mmol), I_2 (1.24 g, 4.9 mmol), TPP (1.25 g, 4.9 mmol), and imidazole (0.32 g, 4.9 mmol) in THF (20 mL) for 4 h as described for compound **2**: (0.37 g, 82%) as a colorless syrup; $[\alpha]_D$ -14.9° (*c* 1.0, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.3, 1.49 (2s, 6H, 2xCH_3), 2.7 (ddd, 1H, $J_{3,3'gem}$=15.2 Hz, $J_{2,3}$=4.5 Hz, $J_{3,4}$=4.8 Hz, H-3), 2.08 (ddd, 1H, $J_{2,3}$=4.5 Hz, $J_{3',4}$=11.8 Hz, H-3'), 2.57 (dd, 1H, $J_{6,6'}$=2.3 Hz, $J_{5,6}$=5.0 Hz, H-6), 2.80 (dd, 1H, $J_{5,6'}$=4.6 Hz, H-6'), 3.08 (ddd, 1H, $J_{4,5}$=4.4 Hz, $J_{5,6}$=5.0 Hz, $J_{5,6'}$=4.6 Hz, H-5), 4.12 (ddd, 1H, $J_{3,4}$=4.8 Hz, $J_{3',4}$=11.8 Hz, $J_{4,5}$=4.4 Hz, H-4), 4.70 (dt, 1H, $J_{1,2}$=3.8 Hz, $J_{2,3}$=$J_{2,3'}$=4.5 Hz, H-2), 5.81 (d, 1H, $J_{1,2}$=3.8 Hz, H-1).

Anal. Calcd for $C_9H_{14}O_4$: C, 58.05; H, 7.58. Found: C, 58.14; H, 7.69.

A mixture of 2,3:5,6-di-*O*-isopropylidene-1-*O*-[2'(*R/S*)-3'-dihydroxypropyl]-α-D-mannofuranoside (6). To a solution of 2,3:5,6-di-*O*-isopropylidene-1-*O*-(prop-2-enyl)-α-D-mannofuranoside (**19**)[25] (1.5 g, 5.0 mmol) in acetone:water (20 mL, 4:1) was added OsO_4 (0.0025 g, 0.01 mmol) and *N*-methylmorpholine-*N*-oxide monohydrate (1.35 g, 10 mmol) at room temperature and the reaction mixture stirred for 28 h. After completion of the reaction, acetone was removed on a rotary evaporator, satd. aqueous $NaHCO_3$ (5 mL) was added to the residue and the mixture stirred for an additional 30 min. The reaction mixture was diluted with water (50 mL), extracted into ethyl acetate (2x100 mL), the organic phase separated, dried (Na_2SO_4) and concentrated to give a syrupy residue which was filtered on a bed of silica gel (60-120 mesh, hexane:EtOAc, 1:1) yielding the title compound **6** (1.55 g, 93%) as a syrup: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.32, 1.40, 1.49 (3s, 12H, 4xCH_3), 2.2 (br.s, 1H, OH), 3.49-4.12 (m, 7H, H-1',1",2,3',3",5,6a,6b), 4.36 (dd, 1H, J=4.6, 6.8 Hz, H-4), 4.6 (d, 1H, J=5.4 Hz, H-3), 4.76 (dd, 1H, J=3.1, 5.4 Hz, H-2), 5.0 (d, 1H, J=3.2 Hz, H-1).

Anal. Calcd for $C_{15}H_{26}O_8$: C, 53.88; H, 7.84. Found: C, 53.95; H, 7.91.

A mixture of 2,3:5,6-di-*O*-isopropylidene-1-*O*-[2'(*R/S*)-3'-anhydropropyl]-α-D-mannofuranoside (7). Compound **7** was prepared from 2,3:5,6-di-*O*-isopropylidene-1-*O*-(2',3'-dihydroxypropyl)-α-D-mannofuranoside (**6**) (0.5 g, 1.45 mmol), I_2 (0.76 g, 2.9 mmol), TPP (0.73 g, 2.9 mmol) and imidazole (0.19 g, 2.9 mmol) in THF (20 mL) as described for compound **2**: (0.39 g, 84%) as a syrup; $[\alpha]_D$ -16.1° (*c*

1.0, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$) δ 1.31, 1.39, 1.52, 1.54 (4s, 12H, 4xCH_3), 2.50-2.65 (m, 1H, H-3'), 2.70-2.75 (m, 1H, H-3"), 3.0-3.2 (m, 1H, H-2'), 3.3-4.2 (m, 5H, H-1',1",5,6a,6b), 4.3-4.45 (m, 1H, H-4), 4.62 (dd, 1H, $J_{2,3}$=2.4 Hz, $J_{3,4}$=4.2 Hz, H-3), 4.78 (dd, 1H, $J_{2,3}$=2.4 Hz, H-2), 4.99 (d, 1H, $J_{1,2}$=4.4 Hz, H-1).

Anal. Calcd for $C_{15}H_{24}O_7$: C, 56.95; H, 7.65. Found: C, 57.04; H, 7.75.

A mixture of 3-[4-(1',1"-dimethylpropyl)phenoxy]-1,2-propanediol (10). Compound **10** was prepared from 1-allyloxy-4-(1',1"-dimethylpropyl)benzene (**22**)[26] (0.8 g, 3.9 mmol) in acetone:water (15 mL, 4:1), OsO_4 (0.0019 g, 0.007 mmol) and *N*-methylmorpholine-*N*-oxide monohydrate (1.06 g, 7.8 mmol) at room temperature for 24 h as described for the compound **6**: (0.86 g, 95%) as a thick syrup; ^1H NMR (200 MHz, $CDCl_3$) δ 1.20 (t, 3H, J=7.6 Hz, CH_2-CH_3), 1.3 (s, 6H, CMe_2), 1.62 (q, 2H, J=7.6 Hz, CH_2CH$_3$), 2.6 (br.s, OH), 3.65-4.16 (m, 5H, H-1',1",2',3',3"), 6.82 (d, 2H, J=8.4 Hz, H_{Ar}), 7.19 (d, 2H, J=8.4 Hz, H_{Ar}).

Anal. Calcd for $C_{14}H_{22}O_3$: C, 70.56; H, 9.30. Found: C, 70.69; H, 9.38.

A mixture of 1-[4-(2,3-dihydroxypropoxy)phenyl]-1-ethanone (11). Compound **11** was prepared from 1-(4-allyloxyphenyl)-1-ethanone (**23**)[27] (1.0 g, 5.7 mmol) in acetone:water (20 mL, 4:1) using OsO_4 (0.0028 g, 0.011 mmol) and *N*-methylmorpholine-*N*-oxide monohydrate (1.53 g, 11.4 mmol) at room temperature for 24 h as described for the compound **6**: (1.14 g, 96%) as a crystalline solid; mp 93-94 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 2.58 (s, 3H, $COCH_3$), 3.1 (br.s, 1H, OH), 3.6-4.2 (m, 5H, H-1',1",2',3',3"), 6.95 (d, 2H, J=8.0 Hz, H_{Ar}), 7.9 (d, 2H, J=8.0 Hz, H_{Ar}).

Anal. Calcd for $C_{11}H_{14}O_4$: C, 62.85; H, 6.71. Found: C, 62.88; H, 6.75.

A mixture of 3-(6-bromo-2-naphthyloxy)-1,2-propanediol (12). To a solution of 6-bromo-2-napthalenol (0.7 g, 3.1 mmol), K_2CO_3 (1.3 g, 9.4 mmol) in acetone (25 mL) was added allyl bromide (0.49 g, 4.0 mmol). The reaction mixture was refluxed for 6 h, solvent was removed under reduced pressure and water (50 mL) was added to the residue which was then extracted into diethyl ether (75 mL). Combined ethereal layers were washed with water, dried (Na_2SO_4) and concentrated to a syrupy residue which was filtered on a bed of silica gel (60-120 mesh, hexane:EtOAc, 7:1) affording 2-allyloxy-6-bromonaphthalene (**24**) (0.78 g, 95%) as a syrup. Compound **24** (0.5 g, 1.9 mmol) was reacted with OsO_4 (0.0009 g, 0.003 mmol) and *N*-methylmorpholine-*N*-oxide monohydrate (0.51 g, 3.8 mmol) in acetone:water (10 mL, 4:1) at room temperature for 26 h as described for compound **6** producing the title compound **12** (0.54 g, 96%) as a crystalline solid: mp 132-134 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 3.65-3.90 (m, 2H, H-1',1"), 4.02-4.29 (m, 3H, H-2',3',3"), 7.06-7.98 (m, 6H, H_{Ar}).

Anal. Calcd for $C_{13}H_{13}O_3Br$: C, 52.55; H, 4.41. Found: C, 52.645; H, 4.48.

5,6-Anhydro-3,4-di-*O*-benzyl-1,2-*O*-isopropylidene-D-mannitol (13). Compound **13** was prepared from 3,4-di-*O*-benzyl-1,2-*O*-isopropylidene-D-mannitol (**8**) (0.7 g, 1.7 mmol), I_2 (0.88 g, 3.4 mmol), TPP (0.91 g, 3.4 mmol), and imidazole (0.23 g, 3.4 mmol) in THF (20 mL) for 4 h as described for compound **2**: (0.54 g, 82%) as a thick syrup; $[\alpha]_D$ 23.3° (*c* 0.75, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$) δ 1.38, 1.42 (2s, 6H, 2xCH_3), 2.62 (dd, 1H, $J_{6,6'}$=4.6 Hz, $J_{5,6'}$=2.3 Hz, H-6'), 2.80 (dd, 1H, $J_{6,6'}$=4.6 Hz, $J_{5,6}$=4.4 Hz, H-6), 3.10 (ddd, 1H, $J_{4,5}$=1.7 Hz, $J_{5,6}$=4.4 Hz, $J_{5,6'}$=2.3 Hz, H-5), 3.35 (dd, 1H, $J_{3,4}$=4.5 Hz, $J_{4,5}$=1.7 Hz, H-4), 3.80 (dd, 1H, $J_{2,3}$=4.8 Hz, $J_{3,4}$=4.5 Hz, H-3), 3.85-4.40 (m, 3H, H-1,1',2), 4.63 (dd, 2H, J=11.5 Hz, OCH_2Ph), 4.78 (s, 2H, OCH_2Ph), 7.30-7.40 (m, 10H, H_{Ar}).

Anal. Calcd for $C_{23}H_{28}O_5$: C, 71.85; H, 7.34. Found: C, 71.92; H, 7.39.

A mixture of 4-nitrophenyl 2-oxiranylmethyl ether (14). Compound **14** was prepared from 3-(4-nitrophenoxy)-1,2-propanediol (**9**)[28] (0.2 g, 1.0 mmol), I_2 (0.5 g, 2.0 mmol), TPP (0.54 g, 2.0 mmol), and imidazole (0.13 g, 2.0 mmol) for 3 h as described for compound **2**: (0.16 g, 89%) as a syrup; ^1H NMR (200 MHz, $CDCl_3$) δ 2.75 (dd, 1H, $J_{3,3'}$=9.0 Hz, $J_{2,3}$=3.8 Hz, H-3), 2.92 (dd, 1H, $J_{3,3'}$=9.0 Hz, $J_{2,3'}$=4.0 Hz, H-3'), 3.30-3.45 (m, 1H, H-2), 3.98 (dd, 1H, $J_{1,1'}$=14.0 Hz, $J_{1,2}$=5.6 Hz, H-1), 4.36 (dd, 1H, $J_{1,1'}$=14.0 Hz, $J_{1',2}$=2.4 Hz, H-1'), 6.95 (d, 2H, J=9.5 Hz, H_{Ar}), 8.2 (d, 2H, J=9.5 Hz, H_{Ar}).

Anal. Calcd for $C_9H_9O_4N$: C, 55.39; H, 4.65. Found: C, 55.48; H, 4.74.

A mixture of 2-oxiranylmethyl 4-(1',1''-dimethylpropyl)phenyl ether (15). Compound **15** was prepared from 3-[4-(1',1''-dimethylpropyl)phenoxy]-1,2-propanediol (**10**) (0.25 g, 1.05 mmol), I_2 (0.5 g, 2.1 mmol), TPP (0.55 g, 2.1 mmol), and imidazole (0.14 g, 2.1 mmol) in THF (10 mL) for 4 h as described for compound **2**: (0.196 g, 85%) as a syrup; ^1H NMR (200 MHz, $CDCl_3$) δ 0.64 (t, 1H, J=6.8 Hz, CH_2CH_3), 1.25 (s, 6H, CMe_2), 1.6 (q, 2H, J=6.8 Hz, CH_2CH_3), 2.7 (dd, 1H, $J_{3,3'}$=6.5 Hz, $J_{2,3}$=3.9 Hz, H-3), 2.87 (dd, 1H, $J_{3,3'}$=5.0 Hz, $J_{2,3'}$=5.0 Hz, H-3'), 3.25-3.35 (m, 1H, H-2), 3.98 (dd, 1H, $J_{1,1'}$=14.0 Hz, $J_{1,2}$=4.9 Hz, H-1), 4.12 (dd, 1H, $J_{1,1'}$=14.0 Hz, $J_{1',2}$=3.6 Hz, H-1'), 6.8 (d, 2H, J=9.0 Hz, H_{Ar}), 7.2 (d, 2H, J=9.0 Hz, H_{Ar}).

Anal. Calcd for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15. Found: C, 76.42; H, 9.24.

A mixture of 1-[4-(2-oxiranylmethoxy)phenyl]-1-ethanone (16). Compound **16** was prepared from 1-[4-(2,3-dihydroxypropoxy)phenyl]-1-ethanone (**11**) (0.4 g, 1.9 mmol), I_2 (0.90 g, 3.8 mmol), TPP (0.99 g, 3.8 mmol), and imidazole (0.26 g, 3.8 mmol) in THF (10 mL) for 5 h as described for compound **2**: (0.32 g, 90%) as a

syrup; IR : max 1683 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 2.52 (s, 3H, CH_3), 2.72 (dd, 1H, $J_{3,3'}$=8.0 Hz, $J_{2,3}$=3.4 Hz, H-3), 2.9 (dd, 1H, $J_{3,3'}$=8.0 Hz, $J_{2,3'}$=4.2 Hz, H-3'), 3.25-3.40 (m, 1H, H-2), 4.0 (dd, 1H, $J_{1,1'}$=13.8 Hz, $J_{1,2}$=7.0 Hz, H-1), 4.28 (dd, 1H, $J_{1,1'}$=13.8 Hz, $J_{1',2}$=3.8 Hz, H-1'), 6.90 (d, 2H, J=9.0 Hz, H_{Ar}), 7.9 (d, 2H, J=9.0 Hz, H_{Ar}).

Anal. Calcd for $C_{11}H_{12}O_3$: C, 68.74; H, 6.29. Found: C, 68.81; H, 6.38.

A mixture of 2-(6-bromo-2-napthyloxymethyl)oxirane (17). Compound **17** was prepared from 3-(6-bromo-2-naphthyloxy)-1,2-propanediol (**12**) (0.4 g, 1.30 mmol), I_2 (0.68 g, 2.6 mmol), TPP (0.70 g, 2.6 mmol), and imidazole (0.18 g, 2.6 mmol) in THF (10 mL) for 4 h as described for compound **2**: (0.33 g, 90%) as a white crystalline solid; mp 86-88 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 2.7 (dd, 1H, $J_{3,3'gem}$=9.0 Hz, $J_{2,3}$=2.5 Hz, H-3), 2.88 (dd, 1H, $J_{3,3'gem}$=9.0 Hz, $J_{2,3'}$=3.5 Hz, H-3'), 3.25-3.40 (m, 1H, H-2), 4.0 (dd, 1H, $J_{1,1'gem}$=14.0 Hz, $J_{1,2}$=6.0 Hz, H-1), 4.22 (dd, 1H, $J_{1,1'gem}$=14.0 Hz, $J_{1',2}$=3.0 Hz, H-1'), 6.90-7.90 (m, 6H, H_{Ar}).

Anal. Calcd for $C_{13}H_{11}O_2Br$: C, 55.94; H, 3.97. Found: C, 56.02; H, 4.05.

3,5,6-Trideoxy-1,2-*O*-isopropylidene-α-D-*ribo*-hex-5-enofuranoside (18). Compound **18** was prepared from diol **4** (0.6 g, 2.9 mmol), I_2 (2.94 g, 11.6 mmol), TPP (3.0 g, 11.6 mmol), and imidazole (0.78 g, 11.6 mmol) in toluene (35 mL) for 3 h as described for compound **3**: (0.43 g, 87%) as a colorless oil; $[\alpha]_D$ -7.8° (*c* 0.8, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$) δ 1.35, 1.55 (2s, 6H, 2xCH_3), 1.5-1.75 (m, 1H, H-3), 2.2 (dd, 1H, $J_{3,3'}$=14.0 Hz, $J_{2,3'}$=4.5 Hz, H-3'), 4.45-4.70 (m, 1H, H-4), 4.72 (dd, 1H, $J_{1,2}$=3.5 Hz, $J_{2,3'}$=4.5 Hz, H-2), 5.2 (d, 1H, $J_{5,6cis}$=10.5 Hz, H-6), 5.34 (d, 1H, $J_{5,6trans}$=18.0 Hz, H-6'), 5.70-5.95 (m, 2H, H-1,5).

Anal. Calcd for $C_9H_{14}O_3$: C, 58.14; H, 7.69. Found: C, 58.36; H, 7.78.

2,3:5,6-Di-*O*-isopropylidene-1-*O*-(prop-2-enyl)-α-D-manno-furanoside (19). Compound **19** was prepared from diol **6** (0.5 g, 1.5 mmol), I_2 (1.52 g, 6.0 mmol), TPP (1.56 g, 6.0 mmol), and imidazole (0.40 g, 6.0 mmol) in toluene (20 mL) for 4 h as described for compound **3**: (0.37 g, 84%) as a syrup; $[\alpha]_D$ + 46.2 (*c* 0.9, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$) δ 1.32, 1.38, 1.45, 1.48 (4s, 12H, 4xCH_3), 3.80-4.20 (m, 5H, H-5,6,6' and OCH_2CH=CH_2), 4.35-4.50 (m, 1H, H-4), 4.65 (d, 1H, $J_{2,3}$=6.0 Hz, H-2), 4.78-4.90 (m, 1H, H-3), 5.05 (s, 1H, H-1), 5.18-5.4 (m, 2H,-OCH_2-CH=CH_2), 5.50-6.05 (m, 1H, OCH_2-CH=CH_2).

Anal. Calcd for $C_{15}H_{24}O_6$: C, 59.98; H, 8.05. Found: C, 60.07; H, 8.14.

5,6-Dideoxy-3,4-di-*O*-benzyl-1,2-*O*-isopropylidene-D-manno hexitol (20). Compound **20** was prepared from the diol **8** (0.6 g, 1.5 mmol), I_2 (1.52 g, 6.0

mmol), TPP (1.57 g, 6.0 mmol), and imidazole (0.40 g, 6.0 mmol) in toluene (20 mL) for 3 h as described for the compound **3**: (0.49 g, 89%) as a colorless oil: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.3, 1.4 (2s, 6H, 2xCH_3), 3.75 (dd, 1H, $J_{1,2}$=3.6, $J_{1,1'}$=12.0 Hz, H-1), 3.78-4.05 (m, 2H, H-1',2), 4.15-4.30 (m, 1H, H-3), 4.55 (d, 1H, J=12.0 Hz, OCH_2Ph), 4.60-4.90 (m, 4H, H-4 and OCH_2Ph), 5.28 (d, 1H, $J_{5,6}$=10.5 Hz, H-6), 5.39 (d, 1H, $J_{5,6'}$=14.0 Hz, H-6'), 5.75-6.0 (m, 1H, H-5), 7.15-7.45 (m, 10H, H_{Ar}).

Anal. Calcd for $C_{23}H_{28}O_4$: C,74.97; H, 7.66. Found: C, 74.95; H, 7.69.

1-Allyloxy-4-nitrobenzene (21). Compound **21** was prepared from diol **9** (0.2 g, 1.0 mmol), I_2 (0.95 g, 4.0 mmol), TPP (0.98 g, 4.0 mmol), and imidazole (0.25 g, 4.0 mmol) in toluene for 4 h as described for compound **3**: (0.14 g, 89%) as a syrup; ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.52-4.75 (m, 2H, OCH_2), 5.35 (d, 1H, J_{cis}=10.5 Hz, -CH=CH_2), 5.45 (d, 1H, J_{trans}=15.5 Hz, -CH=CH_2), 5.90-6.20 (m, 1H, -CH=CH_2), 6.70 (d, 2H, J=10.0 Hz, H_{Ar}), 8.2 (d, 2H, J=10.0 Hz, H_{Ar}).

Anal. Calcd for $C_9H_9NO_3$: C, 60.33; H, 5.06. Found: C, 60.47; H, 5.21.

1-Allyloxy-4-(1',1"-dimethylpropyl)benzene (22). Compound **22** was prepared from diol **10** (0.25 g, 1.0 mmol), I_2 (0.50 g, 4.0 mmol), TPP (1.18 g, 4.0 mmol), and imidazole (0.3 g, 4.0 mmol) in toluene (10 mL) for 4 h as described for compound **3**: (0.196 g, 85%) as a syrup; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.67 (t, 3H, J=6.8 Hz, CH_2CH_3), 1.27 (s, 6H, CMe_2), 1.62 (q, 2H, J=6.8 Hz, CH_2CH_3), 4.40-4.60 (m, 2H, OCH_2), 5.24 (d, 1H, J_{cis}=10.5 Hz, -CH=CH_2), 5.40 (d, 1H, J_{trans}=18.0 Hz, -CH=CH_2), 5.90-6.15 (m, 1H, -CH=CH_2), 6.8 (d, 2H, J=9.0 Hz, H_{Ar}), 7.15 (d, 2H, J=9.0 Hz, H_{Ar}).

Anal. Calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.41; H, 9.92.

1-(4-Allyloxyphenyl)-1-ethanone (23). Compound **23** was prepared from diol **11** (0.59 g, 2.8 mmol), I_2 (2.85 g, 11.2 mmol), TPP (2.93 g, 11.2 mmol), and imidazole (0.76 g, 11.2 mmol) in toluene (20 mL) for 3 h as described for compound **3**: (0.44 g, 89%) as a colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.55 (s, 3H, $COCH_3$), 4.55-4.65 (m, 2H, OCH_2), 5.32 (d, 1H, J_{cis}=9.0 Hz, -CH=CH_2), 5.42 (d, 1H, J_{trans}=16.0 Hz, -CH=CH_2), 5.92-6.20 (m, 1H, -CH=CH_2), 6.90 (d, 2H, J=9.0 Hz, H_{Ar}), 7.9 (d, 2H, J=9.0 Hz, H_{Ar}).

Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 75.07; H, 6.95.

2-Allyloxy-6-bromonapthalene (24). Compound **24** was prepared from diol **12** (0.6 g, 2.0 mmol), I_2 (2.05 g, 8.0 mmol), TPP (2.12 g, 8.0 mmol), and imidazole (0.55 g, 8.0 mmol) in toluene (20 mL) for 3 h as described for compound **3**: (0.49 g, 87%) as a colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.55-4.75 (m, 2H, OCH_2), 5.35

(d, 1H, J_{cis}=10.0 Hz, -CH=CH_2), 5.50 (d, 1H, J_{trans}=17.1 Hz, -CH=CH_2), 6.00-6.24 (m, 1H, -CH=CH$_2$), 7.0-8.0 (m, 6H, H_{Ar}).

Anal. Calcd for $C_{13}H_{11}BrO$: C, 59.34; H, 4.21. Found: C, 59.47; H, 4.32.

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