Pergamon

Tetrahedron 58 (2002) 7545–7552

TETRAHEDRON

Asymmetric epoxidation catalyzed by D-glucose-derived uloses

Tony K. M. Shing* and Gulice Y. C. Leung

Department of Chemistry, The Chinese University of Hong Kong, Shatin, Hong Kong, People's Republic of China

Received 19 February 2002; revised 15 May 2002; accepted 6 June 2002

Abstract—Three ulose catalysts (**1**–**3**) were prepared from D-glucose via an intramolecular nitrile oxide cycloaddition (INOC) as the key step. The enantioselectivity of ulose **2** and **3** in asymmetric epoxidation was poor (up to 26% ee). Ulose **1** afforded good chemical yields (up to 83% yield) and the enantiomeric excess is up to 71% for the formation of (−)-*trans*-stilbene oxide.

1. Introduction

Dioxiranes are versatile epoxidizing agents that can be generated in situ from oxone and a catalytic amount of electrophilic ketones.[1] In recent years, Yang,[2] Shi[3] and other workers[4] have developed elegant chiral ketones and applied them in asymmetric epoxidation, via their corresponding dioxiranes. According to their studies, cyclic C_2-symmetry and fructose-derived ketones can function as catalysts to afford chiral epoxides in high chemical yields and enantiomeric excesses. Our long term interest in employing carbohydrates in asymmetric synthesis has therefore initiated our search for efficient ulose catalysts that can induce chirality with high ee in asymmetric epoxidation. In this paper, we report our results on asymmetric epoxidation catalyzed by D-glucose-derived uloses **1**–**3** (Fig. 1).

2. Results and discussion

D-Glucose was used as the starting material because it is inexpensive and contains a number of stereogenic centers. The syntheses of the ulose catalysts primarily follow the reaction sequence developed earlier by us[5] with some modifications, and are shown in Schemes 1 and 2. The intramolecular nitrile oxide cycloaddition (INOC) was used as the key step to construct the isoxazolidines **10**, **11** and **18**. Hydrogenolysis of the isoxazolidines with Ra-Ni and subsequent protection of the corresponding β-hydroxyketones **12**, **13**, and **19** with TBDMSCl afforded uloses **1**, **2**, and **3**, respectively. The difference between **1** and **2** is that for ulose **2**, a methyl group occupies the α-position relative to the ketone function. This methyl group should impose significant steric hindrance around the ketone group in ulose **2**, thereby affecting the asymmetric induction of the epoxidation. For ulose **3**, the pyranone ring is *trans*-fused to the furanoid ring and the spatial orientation of the exocyclic silyl ether is at the β-face of the pyranone ring.

The relative stereochemistry of ulose **2** was confirmed by an X-ray crystallographic analysis of its acetate derivative **14** (Fig. 2). The structure of ulose **3** was also confirmed by an X-ray crystallographic analysis (Fig. 3).

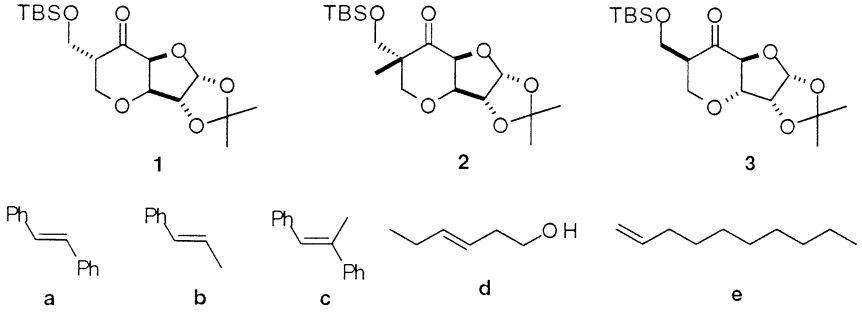
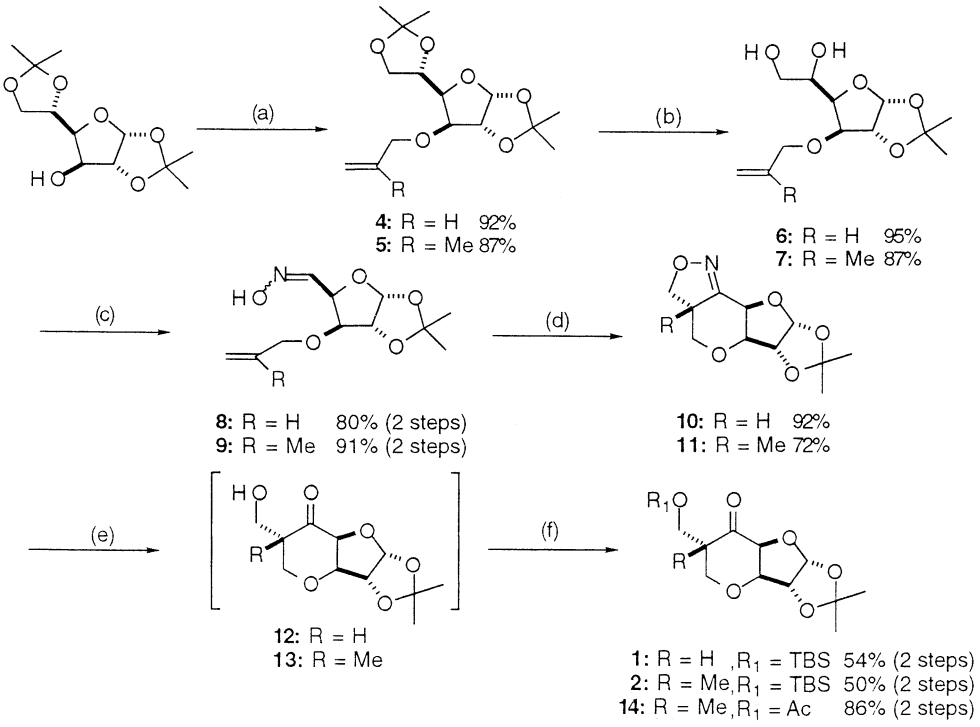


Figure 1. The structures of uloses **1**–**3** and of alkenes **a**–**e**.

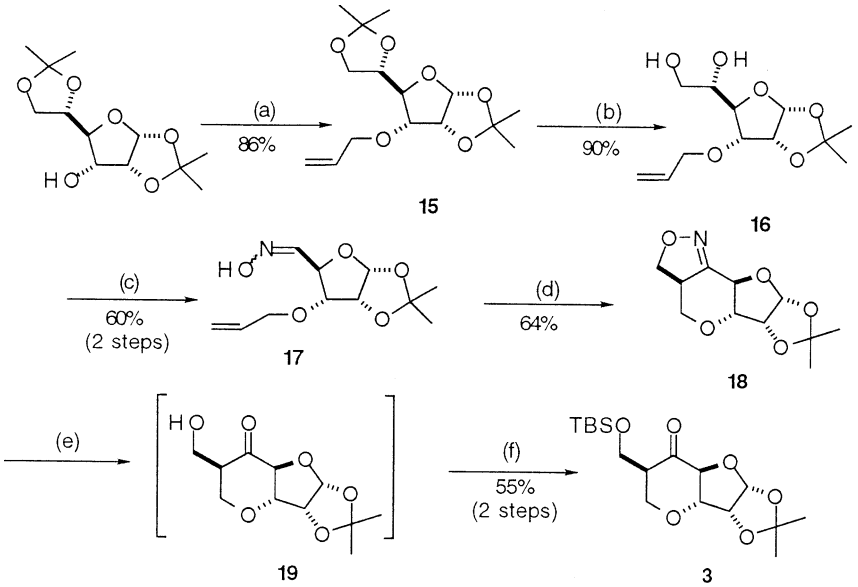
Keywords: asymmetric epoxidation; ulose; D-glucose.
* Corresponding author. Tel.: +852-2609-6367; fax: +852-2603-5057; e-mail: tonyshing@cuhk.edu.hk

0040–4020/02/$ - see front matter
PII: S0040-4020(02)00577-X



Scheme 1. Syntheses of uloses **1**, **2**, and **14**. Key: (a) **4**: (i) NaH, THF; (ii) allyl bromide; **5**: (i) NaH, THF; (ii) 3-bromo-2-methylpropene; (b) 90% AcOH; (c) i) $NaIO_4$-silica gel,[14] CH_2Cl_2; (ii) $NH_2OH{\cdot}HCl$, $NaHCO_3$, EtOH, reflux; (d) 10% NaOCl, CH_2Cl_2, reflux; (e) Ra-Ni, H_2, CH_2Cl_2/MeOH/AcOH (10:5:1, v/v); (f) **1** and **2**: TBDMSCl, imidazole,CH_2Cl_2; **14**: Ac_2O, pyridine.

With the ulose catalysts in hand, we began our study on the concentration effect of ulose **1** in CH_3CN. The results are summarized in Table 1. Ulose catalyst **1** showed moderate catalytic activities (63% yield using 10 mol% catalyst) and chiral induction (65% ee). The 1:10 ratio of catalyst to substrate exhibited the similar results as 1:1 ratio of catalyst to substrate, hinting at 10 mol% as the optimum concentration for the epoxidation. The optical rotation values of the recovered catalysts were in close agreement to that of the enantiopure **1** ($[\alpha]_D^{20}=+37.4$, *c* 0.8, $CHCl_3$), thereby indicating that epimerization did not occur during the epoxidation, which would otherwise have affected the enantioselectivity of the epoxidation. Having realised the optimum concentration of catalyst as 10 mol%, we went



Scheme 2. Synthesis of ulose **3**. Key: (a) (i) NaH, THF; (ii) allyl bromide; (b) 90% AcOH; (c) (i) $NaIO_4$-silica gel,[14] CH_2Cl_2; (ii) $NH_2OH{\cdot}HCl$, $NaHCO_3$, EtOH, reflux; (d) 10% NaOCl, CH_2Cl_2, reflux; (e) Ra-Ni, H_2, CH_2Cl_2/MeOH/AcOH (10:5:1, v/v); (f) TBDMSCl, imidazole, CH_2Cl_2.

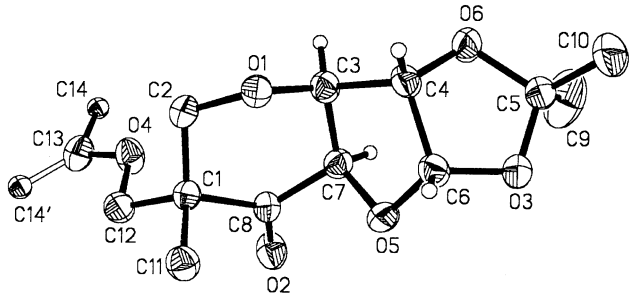


Figure 2. Molecular structure of ulose **14** (CCDC no. 183919). Thermal ellipsoids are drawn at 20% probability level.

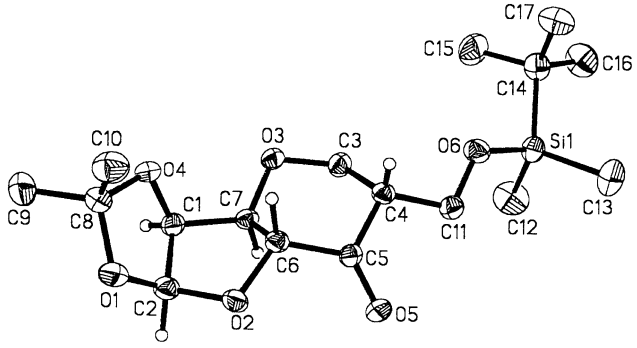


Figure 3. Molecular structure of ulose **3** (CCDC no. 183918). Thermal ellipsoids are drawn at 20% probability level.

Table 1. Concentration effect of ulose **1** in catalyzing in situ epoxidation of *trans*-stilbene in CH_3CN

Entry[a]	Mol% of **1**	Yield (%)[b]	ee (%)[c]	$[\alpha]_D^{20}$ of recovered catalyst[d]
1	10	63	65	+37.1, *c* 0.3, $CHCl_3$
2	50	66	64	+36.8, *c* 1.7, $CHCl_3$
3	100	64	66	+37.3, *c* 3.5, $CHCl_3$

[a] *Reaction conditions*: rt, 0.1 mmol of *trans*-stilbene at pH 7 for 2.5 h (entry 1); 1 h (entry 2); 0.5 h (entry 3).
[b] Isolated yield from column chromatography.
[c] Enantiomeric excess (ee) was determined by ^{1}H NMR with shift reagent Eu(hfc)$_3$.
[d] Catalyst was recovered from column chromatography.

on to study the asymmetric epoxidation of alkenes **a**–**e** using uloses **1**–**3** at this concentration (Fig. 1). The results are summarized in Table 2. Uloses **1** and **3** afforded better chemical yields (43–80% yields) than ulose **2** (26% yield at best) and all the ulose catalysts were recovered without decomposition. This shows that ulose **2** is not an efficient catalyst. Ulose **1** displayed better enantioselectivity than uloses **2** and **3** (Table 2, entries 1, 4, 7 and 13). The best ee was 65% for *trans*-stilbene oxide (Table 2, entry 1), but poor ee's were obtained for other alkenes (Table 2, entries 4, 7, 10 and 13).

Examination of molecular models can provide better understanding to the stereochemical outcome of the dioxirane epoxidation and suggest explanation for the poor enantioselectivity results of other alkenes. The epoxidation of

Table 2. Asymmetric epoxidation catalyzed by uloses **1**–**3** in CH_3CN

Entry[a]	Catalysts	Substrates	Yield (%)[b]	ee (%)[c]	Configuration [d]
1	**1**	**a**	63	65	(−)-(*S*,*S*)[7]
2	**2**	**a**	23	11	(−)-(*S*,*S*)[7]
3	**3**	**a**	66	26	(−)-(*S*,*S*)[7]
4	**1**	**b**	78	28	(+)-(*R*,*R*)[8]
5	**2**	**b**	16	4	(+)-(*R*,*R*)[8]
6	**3**	**b**	80	7	(+)-(*R*,*R*)[8]
7	**1**	**c**	80	45	(−)-(*S*,*S*)[9]
8	**2**	**c**	14	4	(−)-(*S*,*S*)[9]
9	**3**	**c**	81	40	(−)-(*S*,*S*)[9]
10	**1**	**d**	66	11	(−)-(*S*,*S*)[10]
11	**2**	**d**	26	4	(−)-(*S*,*S*)[10]
12	**3**	**d**	60	5	(−)-(*S*,*S*)[10]
13	**1**	**e**	61	10	(−)-(*S*)[11]
14	**2**	**e**	14	5	(−)-(*S*)[11]
15	**3**	**e**	43	3	(−)-(*S*)[11]

[a] All reactions were carried out at room temperature with substrate (0.1 mmol), ketone (0.01 mmol) at pH 7 for 2.5 h.
[b] Isolated yield.
[c] Enantioselectivity was determined by ^{1}H NMR analysis of the epoxide products directly with shift reagent Eu(hfc)$_3$.
[d] The absolute configurations were determined by comparing the measured optical rotations with the reported ones.

trans-stilbene catalyzed by ulose **1** is used as an example (Fig. 4). The well-established spiro transition state[6] is used to explain the predominant formation of the (*S*,*S*)-stilbene oxide. Fig. 4 shows all the possible transition states (TS) and the corresponding stereochemistry of the stilbene oxides. TS-**3** and TS-**4** experience steric interaction between the phenyl group in alkene and the silyl blocking group or the furanose ring of ulose **1**, respectively. Therefore, (*R*,*R*)-stilbene oxide was not favored to form. In contrast, TS-**1** and TS-**2** have no such interaction, (*S*,*S*)-stilbene oxide becomes the dominant product. Similar results are obtianed for alkene **c**. For alkenes **b**, **d** and **e**, the steric effects for TS-**3** and TS-**4** are reduced and hence the formation of (*R*,*R*)-epoxide increased, leading to poor enantioselectivity. The poor ee results (3–40% ee) for ulose catalysts **2** and **3** indicate that the silyl blocking groups and the furanose ring could not impose sufficient steric interaction to induce chirality with high ee's (Fig. 4).

To improve the catalytic features of ulose catalyst **1**, the solvent effect and the catalyst concentration effect were investigated. The results are summarized in Tables 3 and 4. Among the solvents tested (Table 3), the mixture of acetonitrile and diglyme in a ratio of 3:2 (v/v) (entry 9) was found to be the solvent of choice for better reactivity and selectivity. In addition, the results in Table 4 show that 5–10 mol% was the optimum catalyst concentration (entries 4 and 5). Using the fine-tuned reaction conditions, the asymmetric epoxidation using ulose **1** was further studied and the results are summarized in Table 5. The chemical yields and enantioselectivity were improved slightly (up to 20% yield and up to 10% ee increase).

In conclusion, ulose **1** gave good reactivity towards the epoxidation (63–80%) but the enantioselectivity was poor for various alkenes. The poor stereochemical communication between the catalyst **1** and substrates caused us to design new ulose catalysts for asymmetric epoxidation. The research in this direction is in progress.

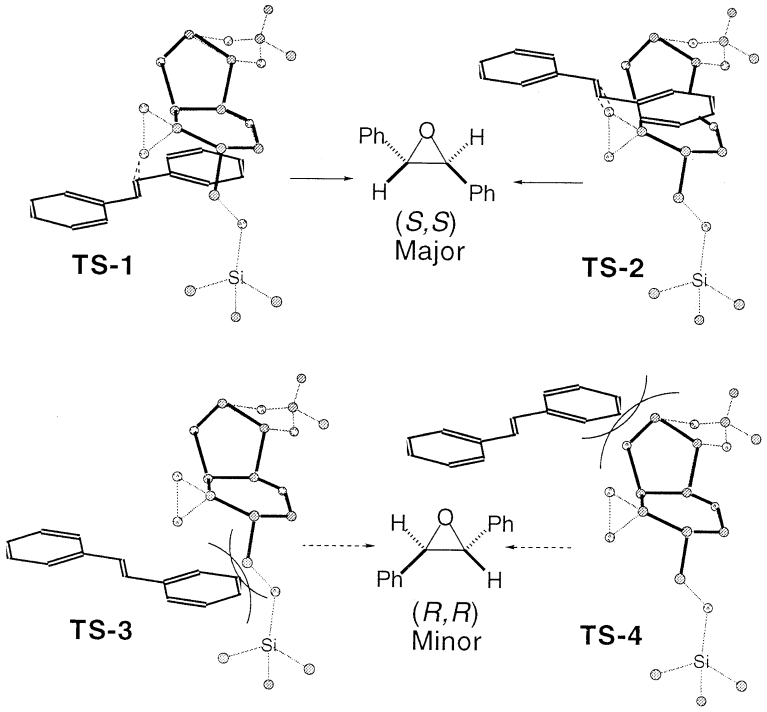


Figure 4. The spiro transition states for *trans*-stilbene epoxidation catalyzed by ulose **1**.

Table 3. Solvent effect on asymmetric epoxidation of *trans*-stilbene catalyzed by ulose **1**

Entry[a]	Solvent	Yield (%)[b]	ee (%)[c]	Configuration [d]
1	CH_3CN	63	65	(−)-(*S*,*S*)
2[e]	CH_3CN	23	0	–
3	CH_3CN/DME (4:1, v/v)	80	51	(−)-(*S*,*S*)
4	CH_3CN/DME (3:2, v/v)	82	60	(−)-(*S*,*S*)
5	CH_3CN/DME (2:3, v/v)	69	41	(−)-(*S*,*S*)
6	CH_3CN/DME (1:4, v/v)	20	25	(−)-(*S*,*S*)
7	DME	0	–	–
8	CH_3CN/Diglyme (4:1, v/v)	86	58	(−)-(*S*,*S*)
9	CH_3CN/Diglyme (3:2, v/v)	80	71	(−)-(*S*,*S*)
10	CH_3CN/Diglyme (2:3, v/v)	84	66	(−)-(*S*,*S*)
11	CH_3CN/Diglyme (1:4, v/v)	69	62	(−)-(*S*,*S*)
12	Diglyme	47	65	(−)-(*S*,*S*)
13	Diglyme/DME (4:1, v/v)	68	66	(−)-(*S*,*S*)
14	Diglyme/DME (3:2, v/v)	44	61	(−)-(*S*,*S*)
15	Diglyme/DME (2:3, v/v)	17	63	(−)-(*S*,*S*)
16	Diglyme/DME (1:4, v/v)	0	–	–

[a] All reactions were carried out at room temperature with substrate (0.1 mmol), ketone (0.01 mmol) at pH 7 for 2.5 h.
[b] Isolated yield.
[c] Enantioselectivity was determined by chiral HPLC (Chiralcel OD); eluant: (9:1 hexane/IPA, v/v); retention time: 5.7 and 8.6 min.
[d] The absolute configurations were determined by comparing the measured optical rotations with the reported ones.[7]
[e] Reaction was carried out without catalyst for 24 h.

3. Experimental

Melting points were measured with a Reichert apparatus in Celsius degrees and are uncorrected. NMR spectra were measured with a Bruker DPX300 NMR spectrometer at 300.13 MHz (^1H) or at 75.47 MHz (^{13}C) in $CDCl_3$, unless stated otherwise. Elemental analyses were carried out by MEDAC Ltd, Department of Chemistry, Brunel University, Uxbridge, UK. All reactions were monitored by analytical thin-layer chromatography (TLC) on Merck aluminum-precoated plates of silica gel 60 F_{254} with detection by spraying with 5% (w/v) dodecamolybdophosphoric acid in ethanol and subsequent heating. E. Merck silica gel 60 (230–400 mesh) was used for flash chromatography. All reagents and solvents were general reagent grade unless otherwise stated. Other reagents were purchased from commercial suppliers and were used without purification.

3.1. General in situ epoxidation procedure at pH 7–7.5

To a stirred solution of substrate (0.1 mmol), ketone (0.01 mmol) and *n*-Bu_4NHSO_4 (0.5 mg) in solvent (5 mL) and aqueous solution (1 mL, 4×10^{-4} M aqueous EDTA) were added dropwise a solution of oxone (1 mmol) in

Table 4. Catalyst concentration effect for asymmetric epoxidation of *trans*-stilbene catalyzed by ulose **1** in CH_3CN/diglyme (3:2)

Entry[a]	Mol%	Yield (%)[b]	ee (%)[c]	Configuration [d]
1	100	82	72	(−)-(*S*,*S*)
2	50	79	69	(−)-(*S*,*S*)
3	25	81	71	(−)-(*S*,*S*)
4	10	80	71	(−)-(*S*,*S*)
5	5	76	66	(−)-(*S*,*S*)
6	2	76	64	(−)-(*S*,*S*)
7	1	41	57	(−)-(*S*,*S*)

[a] All reactions were carried out at room temperature with substrate (0.1 mmol), ketone at pH 7 for 2.5 h.
[b] Isolated yield.
[c] Enantioselectivity was determined by chiral HPLC (Chiralcel OD) eluent: (9:1 hexane/IPA, v/v); retention time: 5.7 and 8.6 min.
[d] The absolute configurations were determined by comparing the measured optical rotations with the reported ones.[7]

Table 5. Asymmetric epoxidation catalyzed by ulose **1** in CH_3CN/diglyme (3:2)

Entry[a]	Substrates	Yield (%)[b]	ee (%)[c]	Configuration [d]
1	**a**	80	71	(−)-(*S*,*S*)[7]
2	**b**	77	29	(+)-(*R*,*R*)[8]
3	**c**	83	47	(−)-(*S*,*S*)[9]
4	**d**	80	22	(−)-(*S*,*S*)[10]
5	**e**	63	23	(−)-(*S*)[11]

[a] All reactions were carried out at room temperature with substrate (0.1 mmol), ketone (0.01 mmol), oxone (1 mmol) at pH 7 for 2.5 h.
[b] Isolated yield.
[c] Enantioselectivity was determined by ^{1}H NMR analysis of the epoxide products directly with shift reagent Eu(hfc)$_3$.
[d] The absolute configurations were determined by comparing the measured optical rotations with the reported ones.

aqueous EDTA (3 mL, 4×10^{-4} M) and a solution of $NaHCO_3$ (3.1 mmol) in H_2O (3 mL) concomitantly via two dropping funnels. The pH of the mixture was maintained at about 7–7.5 over a period of 2.5 h. The reaction mixture was then poured into water (10 mL), extracted with $CHCl_3$ (3×10 mL), dried with anhydrous magnesium sulfate, and filtered. The filtrate was concentrated under reduced pressure to give a residue that was purified by flash column chromatography to give the epoxide. Enantioselectivity was determined by ^{1}H NMR analysis of the epoxide directly with shift reagent Eu(hfc)$_3$ at the NMR signal 3.8–4.1 ppm.

3.1.1. 3-*O*-Allyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (4).[12] Sodium hydride (60%, 0.70 g, 17.4 mmol) was suspended in dry THF (5 mL) under nitrogen at 0°C. A solution of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose[13] (3.00 g, 11.6 mmol) in THF (30 mL) was added dropwise using a dropping funnel and the mixture was stirred for 1/2 h at rt. Allyl bromide (2.2 mL, 24 mmol) was added slowly at 0°C. The mixture was heated under reflux for 6 h. Saturated NH_4Cl was added very slowly at 0°C and the solution was extracted with $CHCl_3$ (3×50 mL), dried over anhydrous $MgSO_4$, and filtered. The filtrate was concentrated to give a yellow syrup. The crude syrup was purified by flash chromatography to allyl ether **4** as a yellow syrup (3.20 g, 92%): $[\alpha]_D^{23}=-25$ (*c* 1.1, $CHCl_3$) (optical rotation was not reported previously)[12] R_f 0.57 (Et_2O/hexane, 1:1); ν_{max}($CHCl_3$) 1470 (C=C) cm^{-1}; ^{1}H NMR δ 5.88 (1H, d, *J*=3.9 Hz); 5.97–5.81 (1H, m), 5.30 (1H, dt, *J*=17.3, 1.5 Hz), 5.19 (1H, dt, *J*=10.4, 1.4 Hz), 4.53 (1H, d, *J*=3.7 Hz), 4.30 (1H, q, *J*=4.3 Hz), 4.14–3.92 (6H, m), 1.48, 1.43, 1.35 and 1.30 (4×Me, s); MS (EI) *m*/*z* 285 (M^+-Me, 40.6).

3.1.2. 3-*O*-(2′-Methyl-2′-propenyl)-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (5). Sodium hydride (60%, 0.22 g, 5.7 mmol) was suspended in dry THF (5 mL) under nitrogen at 0°C. A solution of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose[13] (1.00 g, 3.8 mmol) in THF (20 mL) was added dropwise using a dropping funnel and the mixture was stirred for 1/2 h at rt. 3-Bromo-2-methylpropene (0.74 mL, 8 mmol) was added slowly at 0°C. The mixture was heated under reflux for 6 h. Saturated NH_4Cl was added very slowly at 0°C and the solution was extracted with $CHCl_3$ (3×50 mL), dried over anhydrous $MgSO_4$, and filtered. The filtrate was concentrated to give compound **5** as a yellow syrup that was used in the next stage without purification (1.04 g, 87%): R_f 0.45 (Et_2O/hexane, 1:4); ^{1}H NMR δ 5.82 (1H, d, *J*=3.6 Hz), 4.93 (1H, s), 4.85 (1H, s), 4.48 (1H, d, *J*=3.6 Hz), 4.27 (1H, q, *J*=6 Hz), 4.07–3.87 (6H, m), 1.69, 1.43, 1.36, 1.28 and 1.25 (5×Me, s); ^{13}C NMR δ 141.4, 112.7, 111.5, 108.8, 105.1, 82.3, 81.1, 80.9, 73.9, 72.2, 67.2, 26.7, 26.6, 26.1, 25.2, 19.2; MS (FAB) *m*/*z* 315 (M^++H, 36), 299 (100), 257 (31).

3.1.3. 3-*O*-Allyl-1,2-*O*-isopropylidene-α-D-glucofuranose (6).[5] Diacetonide **4** (1.00 g, 3.3 mmol) was dissolved in 90% aqueous acetic acid (30 mL) and the resulting solution was stirred for 24 h at rt. The solution was concentrated to give a crude syrup which was flash chromatographed on silica gel (Et_2O/hexane, 3:1) to yield diol **6** (0.83 g, 95%) as a pale yellow syrup: R_f 0.48 (Et_2O/hexane, 3:1); $[\alpha]_D^{23}=-45$ (*c* 1, $CHCl_3$) (lit.,[5] $[\alpha]_D^{23}=-46$ (*c* 1.6, $CHCl_3$)); ν_{max}($CHCl_3$) 3425 (OH) cm^{-1}; ^{1}H NMR δ 5.87 (1H, d, *J*=3.8 Hz), 5.92–5.79 (1H, m), 5.28 (1H, dd, *J*=17.4, 1.1 Hz), 5.18 (1H, dd, *J*=10.3, 10 Hz), 4.51 (1H, d, *J*=3.8 Hz), 4.16–3.91 (5H, m), 3.71 (2H, qd, *J*=11.5, 3.2 Hz), 1.45, 1.27 (2×Me, s), MS (EI) *m*/*z* 245 (M^+-Me, 6.7).

3.1.4. 3-*O*-(2′-Methyl-2′-propenyl)-1,2-*O*-isopropylidene-α-D-glucofuranose (7). Selective deprotection of the terminal acetonide in **5** (2.00 g, 6.3 mmol) in a similar manner as in the preparation of diol **6** gave diol **7** (1.50 g, 87%) as a colorless syrup: R_f 0.52 (EtOAc/hexane, 2:1); $[\alpha]_D^{23}=-5.9$ (*c* 1.0, $CHCl_3$); ν_{max}($CHCl_3$) 3410 (OH) cm^{-1}; ^{1}H NMR δ 5.87 (1H, d, *J*=3.6 Hz), 4.96 (1H, s), 4.88 (1H, s), 4.54 (1H, d, *J*=3.9 Hz), 4.10–3.91 (5H, m), 3.79 (1H, dd, *J*=11.4, 3.3 Hz), 3.68 (1H, dd, *J*=11.4, 5.4 Hz), 3.09 (2H, s), 1.72, 1.45, 1.28 (3×Me, s); ^{13}C NMR δ 141.3, 112.8, 111.6, 104.9, 81.9, 81.8, 79.8, 74.0, 69.0, 64.2, 26.6, 26.1, 19.5; MS (FAB) *m*/*z* 275 (M^++H, 77), 217 (100), 199 (37). Anal. calcd for $C_{13}H_{22}O_6$: C, 56.92; H, 8.08. Found: C, 56.81; H, 7.95.

3.1.5. 3-*O*-Allyl-1,2-*O*-isopropylidene-α-D-arabino-pentodialdo-1,4-furanose oxime (8).[5] To a vigorously stirred suspension of silica gel supported $NaIO_4$ reagent[14] (2.00 g) in CH_2Cl_2 (5 mL) in a 25 mL round bottom flask was added a solution of the diol **7** (310 mg, 1.2 mmol) in CH_2Cl_2 (5 mL). The reaction was monitored by TLC until

disappearance of the starting material (about 30 min). The mixture was filtered through a sintered glass funnel, and the silica gel was thoroughly washed with $CHCl_3$ (3×10 mL). Removal of solvent from the filtrate afforded the crude aldehyde that was used in the next stage without purification. $NH_4OH{\cdot}HCl$, (153 mg, 2.20 mmol) and then $NaHCO_3$ (185 mg, 2.20 mmol) were added to a solution of the aldehyde (251 mg, 1.10 mmol) in ethanol (25 mL). The reaction mixture was heated under reflux for 1.5 h. The cooled mixture was concentrated under reduced pressure and the residue subjected to silica gel filtration with eluant (EtOAc/hexane, 1:1) to afford colorless needles **8** (recrystallization from hexane/ether) as a mixture of *Z*/*E* isomer (2:1 respectively, determined by ^{1}H NMR) (247 mg, 80%): R_f 0.47 (EtOAc/hexane, 1:1); mp 89–91°C; $[\alpha]_D^{23}=-45$ (*c* 1, $CHCl_3$) (lit.,[5] mp 90–91°C; $[\alpha]_D^{23}=-46$ (*c* 1.6, $CHCl_3$)); ^{1}H NMR δ 7.50 (0.3H, d, *J*=7.4 Hz), 6.86 (0.6H, d, *J*=4.0 Hz), 5.92 (1H, d, *J*=3.6 Hz), 5.82–5.68 (1H, m), 5.25–5.09 (3H, m), 4.54 (1H, dd, *J*=5.2, 3.7 Hz), 4.00–3.91 (3H, m), 1.44 (3H, s), 1.26 (3H, s); MS (EI) *m*/*z* 257 (M^+, 2.3).

3.1.6. 3-*O*-(2′-Methyl-2′-propenyl)-1,2-*O*-isopropylidene-α-D-arabino-pentodialdo-1,4-furanose oxime (9). Conversion of the diol **7** (1.46 g, 5.33 mmol) in a similar manner as in the preparation of oxime **8** gave oxime **9** (1.25 g, 91%) as colorless needles (recrystallization from hexane/ether) as a mixture of *Z*/*E* isomer (1:1 respectively, determined by ^{1}H NMR): R_f 0.55 (EtOAc/hexane, 1:1); mp 80–82°C; $[\alpha]_D^{23}=-147.6$ (*c* 1.3, $CHCl_3$); $\nu_{max}(CHCl_3)$ 3375 (OH) cm^{-1}; ^{1}H NMR δ 7.51 (0.53H, d, *J*=7.5 Hz), 6.96 (0.5H, d, *J*=3.9 Hz), 5.99 (1H, t, *J*=3.6 Hz), 5.24 (0.5H, t, *J*=3.6 Hz), 4.95 (1H, s), 4.92 (1H, d, *J*=7.2 Hz), 4.76 (0.5H, dd, *J*=7.5, 3.3 Hz), 4.61 (1H, t, *J*=4.2 Hz), 4.31 (0.5H, d, *J*=3.3 Hz), 4.02–3.87 (2.4H, m), 1.71 (3H, s), 1.52 (3H, s), 1.34 (3H, s); ^{13}C NMR δ 149.7, 147.9, 141.2, 140.9, 113.3, 112.1, 112.0, 105.3, 104.8, 83.2, 82.7, 82.4, 82.1, 77.8, 75.5, 74.3, 74.1, 26.8, 26.2, 19.3; MS (FAB) *m*/*z* 258 (M^++H, 100), 242 (17), 200 (42). Anal. calcd for $C_{12}H_{19}O_5N$: C, 56.02; H, 7.44; N, 5.44. Found: C, 56.10; H, 7.52; N, 5.44.

3.1.7. Isoxazoline 10.[5] To a solution of oxime **8** (128 mg, 0.53 mmol) in CH_2Cl_2 (50 mL), was added 10% aqueous NaOCl (3.30 mL, 5.5 mmol) and the resulting solution was heated under reflux for 10 h. The cooled solution was extracted with CH_2Cl_2 (3×20 mL). The combined organic extracts were dried over anhydrous $MgSO_4$, and filtered. The filtrate was concentrated under reduced pressure and the crude residue was purified by flash chromatography (hexane/Et_2O, 2:1) to afford the isoxazoline **10** as a white solid (124 mg, 92%). Recrystallization from hexane/acetone gave colorless prisms: R_f 0.35 (hexane/Et_2O, 2:1); mp 125–126°C; $[\alpha]_D^{23}=+17$ (*c* 0.7, $CHCl_3$) (lit.,[5] mp 124.5–125°C; $[\alpha]_D^{23}=+17$ (*c* 1.0, $CHCl_3$)); ^{1}H NMR δ 5.99 (1H, d, *J*=3.6 Hz), 4.99 (1H, d, *J*=1.7 Hz), 4.59 (1H, d, *J*=3.6 Hz), 4.53 (1H, dd, *J*=10.8, 8.7 Hz), 4.21 (1H, dd, *J*=10.8, 6.3 Hz), 4.00 (1H, d, *J*=1.7 Hz), 3.87 (1H, t, *J*=9.0 Hz), 3.72–3.59 (1H, m), 3.31 (1H, t, *J*=10.8 Hz), 1.54 (3H, s), 1.21 (3H, s); MS (EI) *m*/*z* 255 (M^+, 0.7).

3.1.8. Isoxazoline 11. Conversion of oxime **9** (149 mg, 0.58 mmol) in a similar manner as in the preparation of isoxazoline **10** gave isoxazoline **11** (107 mg, 72%) as a white solid. Recrystallization from hexane/EtOAc gave white prisms: R_f 0.47 (hexane/EtOAc, 1:1); mp 104–106°C; $[\alpha]_D^{23}=+61.8$ (*c* 2.8, $CHCl_3$); ^{1}H NMR δ 5.96 (1H, d, *J*=3.6 Hz), 4.91 (1H, d, *J*=2.1 Hz), 4.60 (1H, d, *J*=3.3 Hz), 4.18 (1H, d, *J*=8.4 Hz), 3.95 (1H, d, *J*=1.8 Hz), 3.92 (1H, d, *J*=10.8 Hz), 3.89 (1H, d, *J*=8.4 Hz), 3.41 (1H, d, *J*=10.8 Hz), 1.50 (3H, s), 1.40 (3H, s), 1.32 (3H, s); MS (FAB) *m*/*z* 256 (M^++H, 100), 240 (15), 198 (11). Anal. calcd for $C_{12}H_{17}O_5N$: C, 56.46; H, 6.71; N, 5.48. Found: C, 56.54; H, 6.75; N, 5.42.

3.1.9. β-*tert*-Butyldimethylsilyloxy-ulose 1. To a solution of isoxazoline **10** (150 mg, 0.5 mmol) containing 3 mol% equivalent of acetic acid in CH_2Cl_2/methanol/water (10 mL, 10:5:1) was added a catalytic amount (10 mg) of Raney-Ni. The system was evacuated and purged three times with H_2 using a 3-way stopcock with a H_2 balloon. The mixture was then stirred vigorously under H_2 (balloon) at 25°C for 3 h. CH_2Cl_2 (20 mL) was added, and the solution was then dried over anhydrous $MgSO_4$, and filtered. The filtrate was concentrated under reduced pressure to give β-hydroxy-ulose **12** that was used in the next stage without purification. To a solution of the hydroxy-ulose **12** in dry CH_2Cl_2 (10 mL), were added imidazole (68 mg, 1.0 mmol), TBDMSCl (90 mg, 0.6 mmol), and a catalytic amount (5 mg) of DMAP. The mixture was stirred at rt for 12 h and then was poured into saturated NH_4Cl (10 mL). The aqueous phase was extracted with CH_2Cl_2 (3×10 mL) and the combined organic extracts were washed with brine (10 mL), dried ($MgSO_4$), and filtered. Concentration of the filtrate followed by flash chromatography (Et_2O/hexane, 1:4) gave a white solid which was recrystallized from EtOAc/hexane to give ulose **1** (97 mg, 54%) as white crystals: R_f 0.50 (Et_2O/hexane, 1:1); mp 76–77°C; $[\alpha]_D^{23}=+37.4$ (*c* 0.8, $CHCl_3$); $\nu_{max}(CHCl_3)$ 1716 (C=O) cm^{-1}; ^{1}H NMR δ 6.04 (1H, d, *J*=3 Hz), 4.62 (1H, d, *J*=3.6 Hz), 4.40 (1H, dd, *J*=11.1, 6.3 Hz), 4.27 (1H, d, *J*=2.0 Hz), 4.21 (1H, d, *J*=2.0 Hz),3.93 (1H, dd, *J*=11.4, 4.1 Hz), 3.66 (1H, dd, *J*=11.1, 8.2 Hz), 3.48 (1H, t, *J*=11.4 Hz), 3.19 (1H, m), 1.49 (3H, s), 1.31 (3H, s), 0.86 (9H, s), 0.04 (6H, s); ^{13}C NMR δ 203.9, 113.4, 107.1, 84.8, 84.4, 81.3, 70.9, 59.1, 49.8, 27.4, 26.9, 26.4, −4.8, −4.9; MS (FAB) *m*/*z* 382 (M^++Na, 2), 359 (M^++H, 81), 301 (100), 243 (45). Anal. calcd for $C_{17}H_{30}O_6Si$: C, 56.95; H, 8.43. Found: C, 56.90; H, 8.60.

3.1.10. β-*tert*-Butyldimethylsilyloxy-ulose 2. Conversion of isoxazoline **11** (210 mg, 0.82 mmol) in a similar manner as in the preparation of ulose **1** gave ulose **2** (152 mg, 50%) as a syrup: R_f 0.50 (Et_2O/hexane, 1:2); $[\alpha]_D^{23}=-14.9$ (*c* 8.3, $CHCl_3$); $\nu_{max}(CHCl_3)$ 1715 (C=O) cm^{-1}; ^{1}H NMR δ 5.99 (1H, d, *J*=3.6 Hz), 4.65 (1H, d, *J*=3.6 Hz), 4.29 (1H, d, *J*=2.7 Hz), 4.22 (1H, d, *J*=3.0 Hz), 3.84–3.80 (3H, m), 3.39 (1H, d, *J*=9.9 Hz), 1.57 (3H, s), 1.49 (3H, s), 1.22 (3H, s), 0.85 (9H, s), 0.02 (6H, d, *J*=2.4 Hz); ^{13}C NMR δ 205.1, 112.6, 105.7, 84.3, 83.2, 79.5, 73.3, 65.2, 50.2, 26.9, 26.4, 25.8, 19.6, 18.1, −5.7; MS (FAB) *m*/*z* 373 (M^++H, 47), 357 (29), 315 (100). Anal. calcd for $C_{18}H_{32}O_6Si$: C, 58.03; H, 8.66. Found: C, 58.34; H, 8.98.

3.1.11. β-Acetoxy-ulose 14. To a solution of isoxazoline **11** (68 mg, 0.27 mmol) in CH_2Cl_2/methanol/AcOH (10 mL,

10:5:1) was added a catalytic amount (10 mg) of Raney-Ni. The system was evacuated and purged three times with H_2 using a 3-way stopcock with a H_2 balloon. The mixture was then stirred vigorously under H_2 (balloon) at 25°C for 3 h. CH_2Cl_2 (20 mL) was added, and the solution was then dried over anhydrous $MgSO_4$ and filtered. The filtrate was concentrated under reduced pressure to give β-hydroxy-ulose **13** that was used in the next stage without purification. To a solution of β-hydroxy-ulose **13** in dry CH_2Cl_2 (5 mL), acetic anhydride (Ac_2O) (43 μL, 0.46 mmol), pyridine (1 mL), and a catalytic amount (5 mg) of DMAP were added. The reaction mixture was stirred at rt and then quenched with saturated NH_4Cl (10 mL). The aqueous phase was extracted with CH_2Cl_2 (3×30 mL) and the combined organic extracts were washed with brine (2×5 mL), dried ($MgSO_4$), and filtered. Concentration of the filtrate followed by flash column chromatography (hexane/Et_2O, 2:1) yielded the β-acetoxy-ulose **14** (69 mg, 86% from **11**) as white crystals: R_f 0.52 (Et_2O/hexane, 1:1); mp 112–113°C; $[\alpha]_D^{23}=-3.4$ (*c* 8.4, $CHCl_3$); $\nu_{max}(CHCl_3)$ 1718 (C=O) cm^{-1}; ^1H NMR δ 5.99 (1H, d, *J*=3.6 Hz), 4.64 (1H, d, *J*=3.3 Hz), 4.29 (1H, d, *J*=1.8 Hz), 4.27 (1H, d, *J*=7.2 Hz), 4.21 (1H, d, *J*=2.4 Hz), 3.91 (1H, d, *J*=11.4 Hz), 3.79 (1H, d, *J*=12.0 Hz), 3.70 (1H, d, *J*=12 Hz), 2.00 (3H, s), 1.46 (3H, s), 1.26 (6H, s); ^{13}C NMR δ 202.8, 170.4, 112.6, 105.7, 83.9, 83.3, 79.3, 72.6, 65.2, 48.3, 26.7, 26.3, 20.6, 19.6; MS (FAB) *m/z* 301 (M^++H, 86), 285 (41), 243 (69), 182 (100). Anal. calcd for $C_{14}H_{20}O_7$: C, 55.99; H, 6.71. Found: C, 55.91; H, 6.73.

3.1.12. 3-*O*-Allyl-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (15). Sodium hydride (60%, 0.25 g, 6.3 mmol) was suspended in dry THF (5 mL) under nitrogen at 0°C. A solution of 1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose[15] (1.10 g, 4.2 mmol) in THF (10 mL) was added dropwise using a dropping funnel and the mixture was stirred for 1/2 h at rt. Allyl bromide (0.55 mL, 6 mmol) was added slowly at 0°C. The mixture was heated under reflux for 6 h. Saturated NH_4Cl solution was added very slowly at 0°C and the solution was extracted with chloroform (3×50 mL), dried over anhydrous $MgSO_4$, and filtered. The filtrate was concentrated to give a yellow syrup which was flash chromatographed to yield allyl ether **15** as a syrup (1.10 g, 86%): R_f 0.45 (Et_2O/hexane, 1:1); $[\alpha]_D^{23}=+96$ (*c* 1.1, $CHCl_3$; $\nu_{max}(CHCl_3)$ 1456 (C=C) cm^{-1}; ^1H NMR δ 6.05–5.90 (1H, m), 5.78 (1H, d, *J*=3.7 Hz); 5.28 (1H, dq, *J*=27.5, 1.6 Hz), 5.24 (1H, dq, *J*=10.4, 1.6 Hz), 4.63 (1H, t, *J*=4.1 Hz), 4.40 (1H, dt, *J*=7.1, 3.0 Hz), 4.23 (1H, ddq, *J*=12.6, 5.9, 1.2 Hz), 4.14–4.01 (4H, m), 3.90 (1H, dd, *J*=8.7, 4.4 Hz), 1.59, 1.46, 1.38 and 1.36 (4×Me, s); MS (EI) *m/z* 285 (M^+−Me, 30.2). Anal. calcd for $C_{15}H_{24}O_6$: C, 59.98; H, 8.05. Found: C, 60.09; H, 8.27.

3.1.13. 3-*O*-Allyl-1,2-*O*-isopropylidene-α-D-allofuranose (16). Diacetonide **15** (3.00 g, 10 mmol) was dissolved in 90% aqueous acetic acid (30 mL) and the resulting solution was stirred for 24 h at rt. The mixture was concentrated in vacuo, giving a yellow syrup that was flash chromatographed on silica gel (Et_2O/hexane, 3:1) to yield the diol **16** (2.30 g, 90%) as a pale yellow syrup: R_f 0.29 (Et_2O/hexane, 3:1); $[\alpha]_D^{23}=+108$ (*c* 0.1, $CHCl_3$); $\nu_{max}(CHCl_3)$ 3420 (OH) cm^{-1}; ^1H NMR δ 6.03–5.87 (1H, m), 5.27 (1H, d, *J*=3.7 Hz), 5.33 (1H, dd, *J*=22.4, 1.4 Hz), 5.27 (1H, dd, *J*=16.3, 1.4 Hz), 4.64 (1H, t, *J*=4.0 Hz), 4.25 (1H, ddt, *J*=12.3, 4.5, 1.0 Hz), 4.10–4.01 (3H, m), 3.92 (1H, dd, *J*=8.6, 4.2 Hz), 3.94–3.89 (2H, m), 1.58, 1.36 (2×Me, s); MS (EI) *m/z* 245 (M^+−Me, 16.2). Anal. calcd for $C_{12}H_{20}O_6$: C, 55.37; H, 7.74. Found: C, 55.17; H, 7.66.

3.1.14. 3-*O*-Allyl-1,2-*O*-isopropylidene-α-D-xylo-pentodialdo-1,4-furanose oxime (17). To a vigorously stirred suspension of silica gel supported $NaIO_4$ reagent[14] (2.70 g) in CH_2Cl_2 (5 mL) in a 25 mL round bottom flask was added a solution of the diol **16** (2.19 g, 8.4 mmol) in CH_2Cl_2 (5 mL). The reaction was monitored by TLC until disappearance of the starting material (about 30 min). The mixture was filtered through a sintered glass funnel, and the silica gel was thoroughly washed with $CHCl_3$ (3×10 mL). Removal of solvent from the filtrate afforded the aldehyde that was used in the next stage without purification. NH_4OH·HCl, (1.72 g, 24 mmol) and then $NaHCO_3$ (3.11 g, 29 mmol) were added to a solution of aldehyde in ethanol (25 mL). The reaction mixture was heated under reflux for 1.5 h. The solvent was removed under reduced pressure and the residue subjected to silica gel filtration with eluant (EtOAc/hexane, 1:2) to afford colorless needles **17** (recrystallization from hexane/ether) as a mixture of *Z*/*E* isomer (10:1 respectively, determined by ^1H NMR) (1.25 g, 60% from **16**): R_f 0.45 (EtOAc/hexane, 1:1); mp 117–119°C; $[\alpha]_D^{23}=-108$ (*c* 0.1, $CHCl_3$); ^1H NMR δ 7.32 (0.9H, d, *J*=6.6 Hz), 7.2 (0.2H, s), 6.68 (0.1H, d, *J*=6.7 Hz), 5.92–5.77 (1H, m), 5.73 (1H, d, *J*=3.6 Hz), 5.23 (1H, d, *J*=11.6 Hz), 5.18 (1H, d, *J*=10.4 Hz), 4.58 (1H, t, *J*=3.9 Hz), 4.51 (1H, dd, *J*=9.0, 6.6 Hz), 4.15–4.00 (1H, m), 3.70 (1H, dd, *J*=9.0, 4.3 Hz), 1.55 (3H, s), 1.30 (3H, s); MS (EI) *m/z* 228 (M^+−Me, 3.2). Anal. calcd for $C_{11}H_{17}O_5N$: C, 54.31; H, 7.04; N, 5.76. Found: C, 54.10; H, 6.93; N, 5.70.

3.1.15. Isoxazoline 18. To a solution of oxime **17** (194 mg, 0.75 mmol) in CH_2Cl_2 (30 mL), 10% NaOCl (3.3 mL, 5.5 mmol) was added and left to heat under reflux for 10 h. The product was extracted with CH_2Cl_2 (3×20 mL). The combined organic extracts were dried over anhydrous $MgSO_4$, and filtered. The solvent was removed from the filtrate under reduced pressure. The crude residue was purified by flash chromatography (hexane/EtOAc, 1:1) to afford the isoxazoline **18** as a syrup (115 mg, 64%): R_f 0.32 (hexane/EtOAc, 1:1); $[\alpha]_D^{23}=+61$ (*c* 1.0, $CHCl_3$); ^1H NMR δ 5.87 (1H, d, *J*=2.9 Hz), 4.71 (1H, t, *J*=3.3 Hz), 4.49 (2H, dd, *J*=17.5, 9.8 Hz), 4.40 (1H, dd, *J*=9.6, 5.8 Hz), 3.77 (1H, dd, *J*=18.0, 6.9 Hz), 3.40 (1H, dd, *J*=17.2, 6.8 Hz), 3.54–3.38 (2H, m), 3.17 (1H, ddd, *J*=9.8, 3.9, 1.0 Hz), 1.55 (3H, s), 1.32 (3H, s); MS (EI) *m/z* 241 (M^+, 2.2). Anal. calcd for $C_{11}H_{15}O_5N$: C, 54.77; H, 6.27; N, 5.81. Found: C, 54.48; H, 6.36; N, 5.74.

3.1.16. β-*tert*-Butyldimethylsilyloxy-ulose 3. To a solution of the isoxazoline **18** (130 mg, 0.54 mmol) in CH_2Cl_2/methanol/AcOH (10 mL, 10:5:1) was added a catalytic amount (10 mg) of Raney-Ni. The system was evacuated and purged three times with the H_2 using a 3-way stopcock with a H_2 balloon. The mixture was then stirred vigorously under H_2 (balloon) at 25°C for 3 h. CH_2Cl_2 (20 mL) was added, and the solution was then dried over anhydrous $MgSO_4$ and filtered. The filtrate was concentrated under

reduced pressure to give β-hydroxy-ulose **19** that was used in the next stage without purification. To a solution of the β-hydroxy-ulose **19** in dry CH_2Cl_2 (30 mL), were added imidazole (140 mg, 2.0 mmol), TBDMSCl (150 mg, 1.0 mmol) and a catalytic amount (10 mg) of DMAP. The mixture was stirred at rt for 12 h and then was poured into saturated NH_4Cl (10 mL). The aqueous phase was extracted with CH_2Cl_2 (3×10 mL) and the combined organic extracts were washed with brine (10 mL), dried ($MgSO_4$), and filtered. Concentration of the filtrate followed by flash chromatography (Et_2O/hexane, 3:7) gave a white solid which was recrystallized from EtOAc/hexane to give the ulose the **3** (106 mg, 55% from **18**) as white crystals: R_f 0.42 (Et_2O/hexane, 1:1); mp 108–109°C; $[\alpha]_D^{23}=-71.4$ (*c* 1.4, $CHCl_3$); ν_{max} $CHCl_3$) 1732 (C=O) cm^{-1}; ^1H NMR δ 5.84 (1H, d, *J*=3.3 Hz), 4.77 (1H, t, *J*=3.6 Hz), 4.59 (1H, dd, *J*=11.1, 7.2 Hz), 4.53 (1H, dd, *J*=10.5, 1.5 Hz), 3.99 (1H, dd, *J*=10.8, 4.2 Hz), 3.73 (1H, dd, *J*=11.1, 8.4 Hz), 3.63 (1H, t, *J*=11.1 Hz), 3.48 (1H, dd, *J*=10.2, 3.9 Hz), 2.91–2.87 (1H, m), 1.60 (3H, s), 1.37 (3H, s), 0.84 (9H, s), 0.03 (6H, s); ^{13}C NMR δ 201.4, 114.3, 104.9, 83.7, 79.1, 76.6, 74.0, 58.3, 50.8, 26.3, 26.0, 25.7, 18.0, −5.6; MS (FAB) *m/z* 358 (M^++H, 1), 301 (95), 243 (100). Anal. calcd for $C_{17}H_{30}O_6Si$: C, 56.95; H, 8.43. Found: C, 57.05; H, 8.08.

Acknowledgements

This research was supported by the CUHK Direct Grant.

References

1. (a) Curci, R.; Florentino, M.; Serio, M. R. *J. Chem. Soc., Chem. Commun.* **1984**, 155. (b) Curci, R.; D'Accolti, L.; Fiorentino, M.; Rosa, A. *Tetrahedron Lett.* **1995**, *36*, 5831. (c) Brown, D. S.; Marples, B. A.; Smith, P.; Walton, L. *Tetrahedron* **1995**, *51*, 3587. (d) Song, C. E.; Kim, Y. H.; Lee, K. C.; Lee, S. G.; Jin, B. W. *Tetrahedron: Asymmetry* **1997**, *8*, 2921. (e) Adam, W.; Zhao, C.-G. *Tetrahedron: Asymmetry* **1997**, *8*, 3995. (f) Denmark, S. E.; Wu, Z.; Crudden, C. M.; Matsuhashi, H. *J. Org. Chem.* **1997**, *62*, 8288. (g) Bergbreiter, D. E. *Chemtracts: Org. Chem.* **1997**, *10*, 661. (h) Armstrong, A.; Hayter, B. R. *Chem. Commun.* **1998**, 621. (i) Dakin, L. A.; Panek, J. S. *Chemtracts: Org. Chem.* **1998**, *11*, 531. (j) Adam, W.; Saha-Moller, C. R.; Zhao, C.-G. *Tetrahedron: Asymmetry* **1999**, *10*, 2749.
2. (a) Yang, D.; Yip, Y. C.; Tang, M. W.; Wong, M. K.; Zheng, J. H.; Cheung, K. K. *J. Am. Chem. Soc.* **1996**, *118*, 491. (b) Yang, D.; Wang, X. C.; Wong, M.-K.; Yip, Y. C.; Tang, M.-W. *J. Am. Chem. Soc.* **1996**, *118*, 11311. (c) Yang, D.; Wong, M. K.; Yip, Y. C.; Wang, X. C.; Tang, M. W.; Zheng, J. H.; Cheung, K. K. *J. Am. Chem. Soc.* **1998**, *120*, 5943. (d) Yang, D.; Yip, Y. C.; Chen, J.; Cheung, K. K. *J. Am. Chem. Soc.* **1998**, *120*, 7659.
3. (a) Tu, Y.; Wang, Z. X.; Shi, Y. *J. Am. Chem. Soc.* **1996**, *118*, 9806. (b) Wang, Z. X.; Tu, Y.; Frohn, M.; Shi, Y. *J. Org. Chem.* **1997**, *62*, 2328. (c) Wang, Z. X.; Shi, Y. *J. Org. Chem.* **1997**, *62*, 8622. (d) Wang, Z. X.; Tu, Y.; Frohn, M.; Zhang, J. R.; Shi, Y. *J. Am. Chem. Soc.* **1997**, *119*, 11224. (e) Frohn, M.; Dalkiewicz, M.; Tu, Y.; Wang, Z. X.; Shi, Y. *J. Org. Chem.* **1998**, *63*, 2948. (f) Wang, Z. X.; Shi, Y. *J. Org. Chem.* **1998**, *63*, 3099. (g) Cao, G. A.; Wang, Z. X.; Tu, Y.; Shi, Y. *Tetrahedron Lett.* **1998**, *39*, 4425. (h) Zhu, Y.; Tu, Y.; Shi, Y. *Tetrahedron Lett.* **1998**, *39*, 7819. (i) Tu, Y.; Wang, Z. X.; Frohn, M.; He, M.; Yu, H.; Tang, Y.; Shi, Y. *J. Org. Chem.* **1998**, *63*, 8475. (j) Wang, Z. X.; Miller, S. M.; Anderson, O. P.; Shi, Y. *J. Org. Chem.* **1999**, *64*, 6443. (k) Wang, Z. X.; Cao, G. A.; Shi, Y. *J. Org. Chem.* **1999**, *64*, 7646. (l) Warren, J. D.; Shi, Y. *J. Org. Chem.* **1999**, *64*, 7675. (m) Tian, H.; She, X.; Shi, Y. *Org. Lett.* **2001**, *3*, 715. (n) Tian, H.; She, X.; Xu, J.; Shi, Y. *Org. Lett.* **2001**, *3*, 1929.
4. (a) Solladie-Cavallo, A.; Bouerat, L. *Org. Lett.* **2000**, *2*, 3531. (b) Armstrong, A.; Hayter, B. R.; Moss, W. O.; Reeves, J. R.; Wailes, J. S. *Tetrahedron: Asymmetry* **2000**, *11*, 2057. (c) Armstrong, A.; Hayter, B. R. *Tetrahedron* **1999**, *55*, 11119. (d) Carnell, A. J.; Johnstone, R. A. W.; Parsy, C. C.; Sanderson, W. R. *Tetrahedron Lett.* **1999**, *40*, 8029. (e) Wang, Z.-X.; Miller, S. M.; Anderson, O. P.; Shi, Y. *J. Org. Chem.* **1999**, *64*, 6443. (f) Adam, W.; Saha-Moller, C. R.; Zhao, C.-G. *Tetrahedron: Asymmetry* **1999**, *10*, 2749.
5. Shing, T. K. M.; Fung, W. C.; Wong, C. H. *J. Chem. Soc., Chem. Commun.* **1994**, 449.
6. (a) Baumstark, A. L.; McCloskey, C. J. *Tetrahedron Lett.* **1987**, *28*, 3311. (b) Baumstark, A. L.; Vasquez, P. C. *J. Org. Chem.* **1988**, *53*, 3437. (c) Baumstark, A. L.; Harden, D. B. *J. Org. Chem.* **1993**, *58*, 7615.
7. Chang, H.-T.; Sharpless, K. B. *J. Org. Chem.* **1996**, *61*, 6456.
8. Witkop, B.; Foltz, C. M. *J. Am. Chem. Soc.* **1957**, *79*, 197.
9. Brandes, B. D.; Jacobsen, E. N. *J. Org. Chem.* **1994**, *59*, 4378.
10. Rossiter, B. E.; Sharpless, K. B. *J. Org. Chem.* **1984**, *49*, 3707.
11. Chattopadhyay, S.; Mamdapur, V. R.; Chadha, M. S. *Tetrahedron* **1990**, *46*, 3667.
12. Hoiness, D. E.; Wades, C. P.; Rowland, S. P. *Can. J. Chem.* **1968**, *46*, 667.
13. Schmidt, O. T. *Meth. Carbohydr. Chem.* **1962**, *2*, 319.
14. Shing, T. K. M.; Zhong, Y. L. *J. Org. Chem.* **1997**, *62*, 2622.
15. Baker, D. C.; Hortor, D.; Tindall, C. G. *Carbohydr. Res.* **1972**, *24*, 192.