1,3-DIPOLAR CYCLOADDITIONS OF D-ERYTHROSE- AND D-THREOSE-DERIVED ALKENES WITH NITRONES

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Dedicated to the memory of Professor Otakar Červinka.

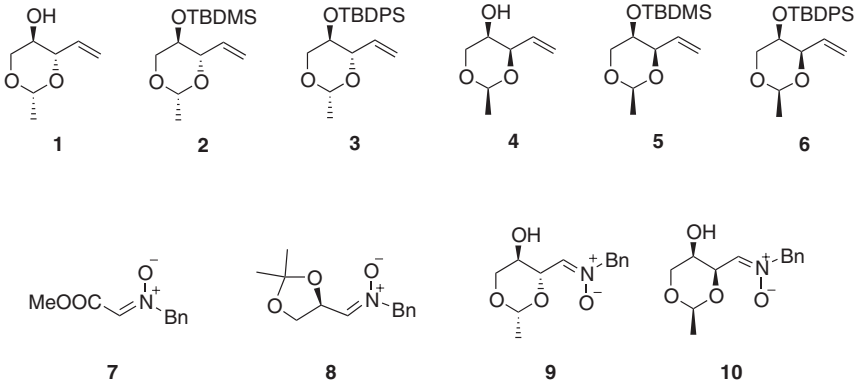
The new chiral terminal alkenes derived from cyclic acetals of D-erythrose **1–3** and D-threose **5**, **6** were prepared. The alkenes **1**, **2** and **5** react with chiral nitrones to afford the corresponding diastereomeric isoxazolidines **19–21**. The stereoselectivity was dependent on the steric hindrance of the nitrone. In all cases the cycloadditions are *endo*-selective. The major products were found to have the C-3/C-4 *erythro*- and C-3/C-3a *cis*-configuration. Its formation can be rationalized by a less hindered *endo*-attack of the (*Z*)-nitrone in an antiperiplanar manner with respect to the largest group of the cyclic acetal.

Keywords: Dipolar cycloadditions; Chiral nitrones; Isoxazolidines; Chiral alkenes; Stereoselectivity; Carbohydrates; Polyols; Wittig reaction.

The nitrone–olefin 1,3-dipolar cycloaddition is a powerful reaction since it can create as many as three new contiguous stereogenic centers in a single step[1]. Based on an evaluation of the nitrone cycloaddition, it was felt that the configuration of these new centers could be influenced if the reaction system was properly designed[2]. Regio- and stereoselective nitrone cycloaddition, followed by reduction of the N–O bond to produce both an amino and a hydroxy function, allows the synthesis of many products of potential interest[3]. Over the years, nitrones have become important building blocks in organic synthesis[1,4]. With the goal of developing a simple route to polyhydroxy derivatives of piperidine[5] *via* an asymmetric 1,3-dipolar cycloaddition, we have recently published the preparation of new

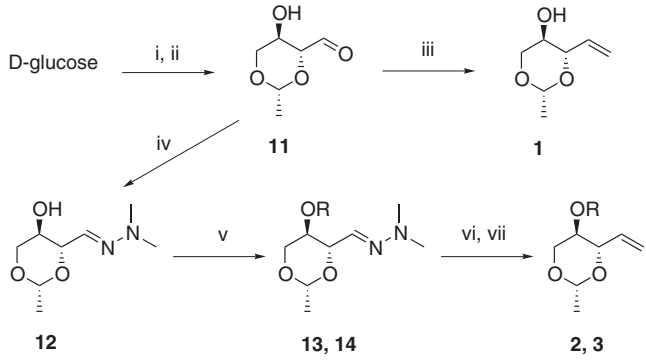
D-erythrose- and D-threose-derived nitrones **9** and **10** and the stereoselectivity of their cycloadditions to styrene and methyl acrylate[6,7].

In this paper we report in detail the preparation of new D-erythrose- and D-threose-derived alkenes **1–3** and **5**, **6** and the stereoselectivity of their cycloaddition to achiral nitrone **7** and chiral saccharide-derived nitrones **8**, **9** and **10** (Scheme 1).



SCHEME 1

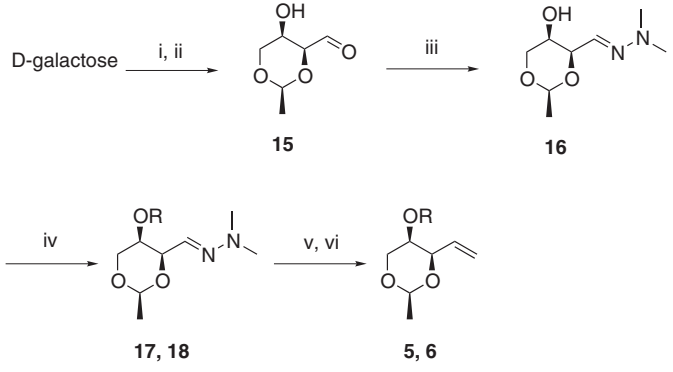
The chiral alkene **1** was prepared in 31% yield by Wittig reaction of 2,4-*O*-ethylidene-D-erythrose (**11**)[8], readily available from D-glucose, with methylenetriphenylphosphorane, generated from methyltriphenylphosphonium bromide and butyllithium (Scheme 2). The chiral alkene **4** could not be prepared by Wittig reaction from the D-threose derivative[8] **15** under the same reaction conditions as for **1**. In this case the reaction proceeded only under the formation of unidentified compounds. Since the directly silylation of alkene **1** was not successful, we have decided to overcome this problem by the preparation of the corresponding hydrazone **12**, with the subsequent silylation, deprotection of the carbonyl group and smooth Wittig reaction. Thus, the key step for the preparation of the D-erythrose- (**2** and **3**) and D-threose-derived alkenes **5** and **6**, consists in the protection of the free hydroxy group on C-3 (Schemes 2 and 3). The alkenes **2** and **3** were synthesized starting from the D-erythrose derivative **11**, which was smoothly transformed *via* intermediate **12** into the corresponding protected hydrazones[9] **13** and **14** in 82 and 76% yield, respectively. The corresponding alkenes **2** and **3** were obtained by degradation of hydrazones **13** and **14** with nitrous acid[10] followed by Wittig reaction in yields of 48 and 58% in two steps (Scheme 2). Analogously, 2,4-*O*-ethylidene-D-threose (**15**), readily available from D-galactose, was converted to the corresponding to D-threose-derived alkenes **5** and **6** (Scheme 3).



2, 13: R = TBDMS
3, 14: R = TBDPS

(i) paraldehyde, H_2SO_4, 3 d, r.t.; (ii) $NaIO_4$, H_2O, MeOH, 10 °C, 2 h; (iii) $Ph_3P^+CH_3Br^-$, 3 eq. BuLi, THF, 75 °C; (iv) NH_2NMe_2, $MgSO_4$, MeOH, 3.5 h; (v) R-Cl, imidazole, CH_2Cl_2, 24 h; (vi) $NaNO_2$, AcOH, H_2O, 4 h; (vii) $Ph_3P^+CH_3Br^-$, 2 eq. BuLi, THF, 0 °C - r.t.;

SCHEME 2



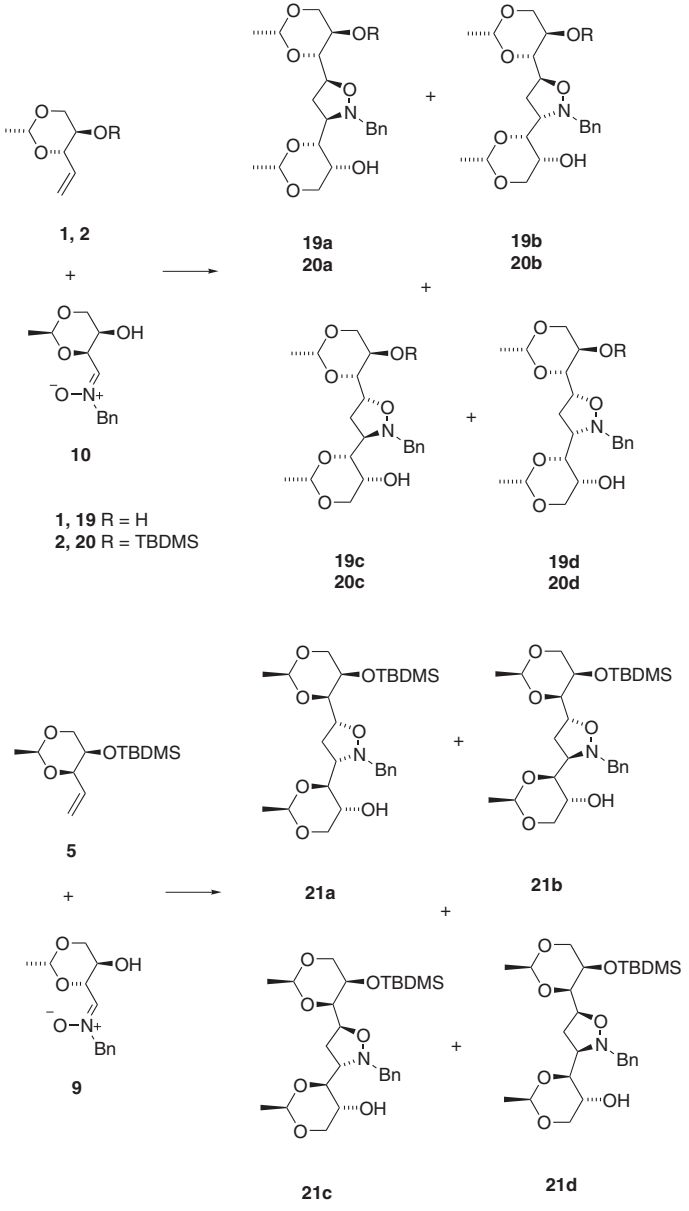
5, 17: R = TBDMS
6, 18: R = TBDPS

(i) paraldehyde, H_2SO_4, 3 d, r.t.; (ii) $NaIO_4$, H_2O, MeOH, 10 °C, 2 h; (iii) NH_2NMe_2, $MgSO_4$, MeOH, 3.5 h; (iv) R-Cl, imidazole, CH_2Cl_2, 24 h; (v) $NaNO_2$, AcOH, H_2O, 4 h; (vi) $Ph_3P^+CH_3Br^-$, 2 eq. BuLi, THF, 0 °C - r.t.

SCHEME 3

The prepared chiral diastereomerically pure terminal alkenes **1**, **2** and **5** were subjected to 1,3-dipolar cycloadditions. Our concern was to study the asymmetric induction from the alkene part with achiral nitrone **7** and double asymmetric induction in cycloaddition with chiral nitrones **8–10**. The

regioselectivity of the cycloaddition was high; indeed 5-substituted isoxazolidines were formed exclusively, 4-substituted isoxazolidines were not detected in crude reaction mixtures by NMR spectra. There are four possible products; *cis*- and *trans*-isomers from *anti*- and *syn*-attack (Scheme 4).



SCHEME 4

The ratio of diastereoisomers was determined from ^{13}C NMR spectra by integration of the peaks of the C-4 signals of the isoxazolidine products.

The cycloadditions were first carried out in boiling toluene with alkene **1**, **2** and **5** and achiral nitrone **7**. The cycloaddition led to an unseparable mixture of four diastereoisomeric isoxazolidines in all cases (Table I, entries 1–3). Therefore, we focused our attention on chiral nitrones with the aim to investigate the double asymmetric induction. The pairs of the alkene–nitrone were chosen as "matched pairs" *e.g.* chiral alkenes **1** and **2** with nitrone **10** and chiral alkene **5** with nitrones **8** and **9** (Scheme 4), since the "mismatched pairs" cycloaddition of alkene **1** with nitrone **9** was less selective and stereoisomers were found in the disappointing ratio of 30:25:25:20.

It is worth mentioning that the chiral D-glyceraldehyde derived nitrone **8** did not react with chiral alkene **5** under various condition (Table I, entries 4 and 5). Only starting alkene **5** was isolated from the reaction mixture. On the other hand, the cycloaddition of the alkenes **1**, **2** and **5** with nitrones **9** and **10** gave only two pairs of diastereoisomers, *erythro* (H-3/H-4′)-*endo* (H-3/H-5)-*erythro* (H-5/H-4′) **19a**, **20a** and **21a** and *threo-exo-erythro* **19b**, **20b** and **21b** (Table I, entries 6, 7 and 8). The other two possible cycloadducts **22c–24c** and **22d–24d** were not detected in the crude reaction mixture by NMR spectra (Scheme 4). The cycloadditions requires very long reaction times and the yields were not very high for the protected alkenes

TABLE I
1,3-Dipolar cycloaddition of chiral terminal alkenes **1**, **2** and **5** to nitrones **7–10**

Entry	Alkene	Nitrone	Reaction conditions	Yield %	Compounds ratio			
					a	b	c	d
1	**1**	**7**	toluene, reflux, 10 h	64	41	26	25	8
2	**2**	**7**	toluene, reflux, 17 h	74	54	32	8	6
3	**5**	**7**	toluene, reflux, 17 h	65	53	27	10	8
4	**5**	**8**	toluene, reflux, 72 h	–	–	–	–	–
5	**5**	**8**	toluene, mw[a], 60 min	–	–	–	–	–
6	**1**	**10**	toluene, reflux, 38 h	74	82	18	–	–
7	**2**	**10**	toluene, reflux, 72 h	45	79	21	–	–
8	**5**	**9**	toluene, reflux, 72 h	41	80	20	–	–

[a] Microwave, 1000 W.

2 and **5** (Table I, entries 7 and 8). The cycloadditions with chiral protected alkene **6** proceded extremely slowly and selectivity was comparable with protected alkene **5**. Purification by flash chromatography allowed the isolation of pure cycloadducts **19a**, **20a**, **21a**, **20b** and **21b** which were identified by spectroscopic analysis, particularly NOE difference experiments. The most important and decisive information obtained from these experiments is the presence or absence of the NOE interaction between the protons H-5/H-3 of the isoxazolidine ring in the corresponding *exo*- and *endo*-cycloadducts. These assignments were subsequently confirmed by X-ray crystallographic analysis in the case of **19a** (Fig. 1).

The analysis of product configuration indicates that isoxazolidines **19a–21a** arise from a cycloaddition which has occurred on the sterically more accessible face of the nitrone, *via* an *endo*-transition state with antiperiplanar relationship of the substituent of the alkene and *N*-benzyl group of the nitrone (Scheme 5). Dipolar cycloaddition of *C*-α-alkoxy-substituted nitrones have been shown to occur preferentially *via* transition states in which the developing carbon–carbon bond avoids steric interaction with the more bulky group. On the other hand, we assume that isoxazolidines **19b–21b** result from an *exo*-attack of the dipolarophile on the (*Z*)-nitrones **9** and **10.** It should be mentioned that there was no thermal interconversion between the prepared adducts in refluxing toluene, thus indicating that the cycloadditions proceeded irreversibly under the reaction conditions to give the kinetically controlled products **19a–21a** and **19b–21b**.

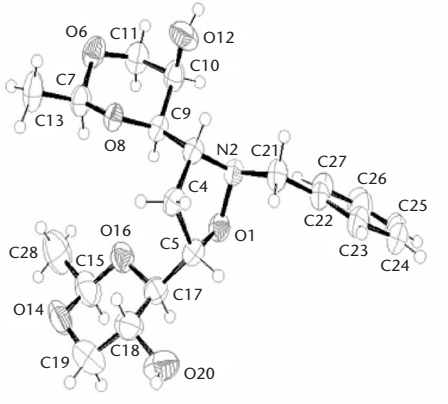
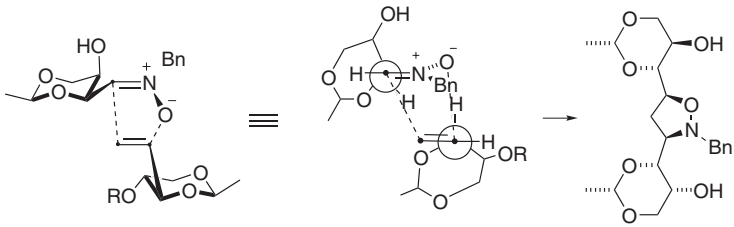
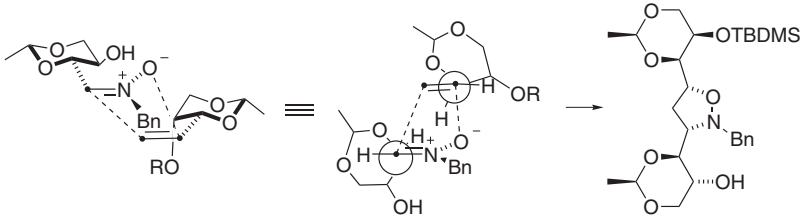


FIG. 1
X-Ray analysis (ORTEP drawing) of **19a**



D-*erythro* alkene with D-*threo* nitrone **19a**



D-*erythro* nitrone with D-*threo* alkene **21a**

SCHEME 5

In conclusion, the new chiral terminal alkenes derived from cyclic acetals of D-erythrose **1–3** and D-threose **5**, **6** were prepared. The 1,3-dipolar cycloaddition with achiral and chiral nitrones afforded the corresponding diastereomeric isoxazolidines **19–21**. The stereoselectivity of the cycloaddition was dependent on the steric hindrance of the nitrone. In all cases the cycloadditions are *endo*-selective. The major products were found to have the C-3/C-4 *erythro*- and C-3/C-3a *cis*-configuration. Its formation can be rationalized by a less hindered *endo*-attack of the (*Z*)-nitrone in an antiperiplanar manner with respect to the largest group of the cyclic acetal.

EXPERIMENTAL

All starting materials and reagents are commercially available (Fluka, Merck or Avocado) and were used without further purification. Solvents were dried before use. Thin-layer chromatography (TLC, on aluminium plates coated with silica $60F_{254}$, 0.25 mm thickness, Merck) was used for monitoring reactions; eluents are given in the text. For column chromatography, the flash chromatography technique was employed using silica 60 (0.040–0.063 mm, Merck). Melting points (m.p.) were determined on a Kofler hot plate apparatus and are uncorrected. Elemental analyses were performed by the microanalysis service of the Department of Analytical Chemistry, Slovak University of Technology, Bratislava.

The ^{1}H and ^{13}C NMR spectra of deuterochloroform solutions were obtained using Varian VXR 300 (300 MHz) instrument, tetramethylsilane being the internal reference. Chemical shifts are given in ppm (δ-scale), coupling constants (*J*) in Hz. Optical rotations

were measured on an IBZ Messtechnik Polar-LμP polarimeter and $[\alpha]_D$ values are given in 10^{-1} deg cm^2 g^{-1}.

1,2-Dideoxy-3,5-*O*-ethylidene-D-*erythro*-pent-1-enitol (**1**)

To a stirred solution of methyltriphenylphosphonium bromide (12.3 g, 34.2 mmol) in THF (50 ml) at room temperature was added 15% butyllithium in hexane (22 ml, 52.0 mmol) over a period of 5 min. The resulting mixture was stirred at room temperature for 15 min and then was added 2,4-*O*-ethylidene-D-erythrose (**11**; 2.5 g, 17.18 mmol) in THF (40 ml). This mixture was stirred at reflux (65 °C) for 3 h, then was added water (100 ml) and extracted with Et_2O (3 × 40 ml). The organic layers were combined, dried and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel (16 × 2 cm) using EtOAc/hexanes (15:85) to give product **1** (769 mg, 31%) as yellow oil with $[\alpha]_D^{25}$ –23.5 (*c* 1.0, EtOAc). TLC: R_F 0.39 in EtOAc/hexanes (50:50). ^{1}H NMR: 5.91 ddd, 1 H, $J_{1trans,2}$ = 17.3, $J_{1cis,2}$ = 10.5, $J_{2,3}$ = 6.8 (H-2); 5.31–5.48 m, 2 H (H-1); 4.73 q, 1 H, *J* = 5.1 (C**H**CH$_3$); 4.10–4.18 m, 1 H (H-4); 3.80 dd, 1 H, $J_{3,4}$ = 8.6, $J_{2,3}$ = 6.8 (H-3); 3.34–3.54 m, 2 H (H-5); 2.20 br s, 1 H (OH); 1.35 d, 3 H, *J* = 5.1 (CHC**H**$_3$). ^{13}C NMR: 134.78 (C-2), 119.26 (C-1), 98.82 (**C**HCH$_3$), 82.90 (C-3), 70.40 (C-5), 65.09 (C-4), 20.52 (CH**C**H$_3$).

2,4-*O*-Ethylidene-D-erythrose *N*,*N*-Dimethylhydrazone[9] (**12**)

A solution of 2,4-*O*-ethylidene-D-erythrose (**11**; 3.0 g, 20.5 mmol), *N*,*N*-dimethylhydrazine (1.2 g, 20.6 mmol), $MgSO_4$ (6.8 g, 56.5 mmol) and a catalytic amount of 2-pyridone (100 mg) in methanol was stirred at room temperature for 3.5 h, then was filtered through a pad of Celite and the filtrate was evaporated. The crude product was purified by crystallization from Et_2O to give product **12** (3.3 g, 85%) as colorless solid with m.p. 99–100 °C (Et_2O), $[\alpha]_D^{25}$ –4.7 (*c* 1.6, $CHCl_3$), ref.[9] m.p. 97–98 °C, $[\alpha]_D^{18}$ –7.0 (*c* 1.6, $CHCl_3$). TLC: R_F 0.16 in EtOAc/hexanes (50:50). For $C_8H_{16}N_2O_3$ (188.2) calculated: 51.05% C, 8.57% H, 14.88% N; found: 51.35% C, 8.69% H, 14.7% N. IR (KBr): 3434, 3002, 2988, 2961, 2938, 2911, 2867, 2795, 2681, 2649, 1591 (C=N), 1468, 1447, 1404. ^{1}H NMR: 6.49 d, 1 H, $J_{1,2}$ = 4.4 (H-1); 4.74 q, 1 H, $J_{5,6}$ = 5.1 (C**H**CH$_3$); 4.12 dd, 1 H, $J_{4A,4B}$ = 10.3, $J_{3,4A}$ = 5.1 (H-4$_A$); 3.96 dd, 1 H, $J_{2,3}$ = 8.8, $J_{1,2}$ = 4.4 (H-2); 3.75 ddd, 1 H, $J_{3,4A}$ = 10.3, $J_{2,3}$ = 8.8, $J_{3,4B}$ = 5.1 (H-3); 3.71 br s, 1 H (OH); 3.43 dd, 1 H, $J_{4A,4B}$ = 10.3, $J_{3,4B}$ = 10.3 (H-4$_B$); 2.82 s, 2 × 3 H (N(CH$_3$)$_2$); 1.33 d, 3 H, $J_{5,6}$ = 5.1 (CHC**H**$_3$). ^{13}C NMR: 132.7 (C-1), 98.5 (**C**HCH$_3$), 80.2 (C-2), 69.6 (C-4), 64.3 (C-3), 42.1 (N(CH$_3$)$_2$), 20.1 (CH**C**H$_3$).

2,4-*O*-Ethylidene-D-threose *N*,*N*-Dimethylhydrazone (**16**)

Title compound was prepared from **15** according to the procedure described for **9**. The crude product was purified by column chromatography on silica gel using EtOAc/hexanes (35:65) to give compound **16** (79%) as colorless solid with m.p. 59–61 °C (EtOAc/petroleum ether), $[\alpha]_D^{25}$ –95.0 (*c* 1.1, $CHCl_3$). TLC: R_F 0.18 in EtOAc/hexanes (50:50). For $C_8H_{16}N_2O_3$ (188.2) calculated: 51.05% C, 8.57% H, 14.88% N; found: 51.10% C, 8.92% H, 14.86% N. IR ($CHCl_3$): 3600 (OH), 3460 (OH), 2860, 2820, 2815, 1610 (C=N), 1485, 1470, 1460, 1420, 1400. ^{1}H NMR: 6.62 d, 1 H, $J_{1,2}$ = 5.1 (H-1); 4.84 q, 1 H, $J_{5,6}$ = 5.1 (C**H**CH$_3$); 4.30 dd, 1 H, $J_{1,2}$ = 5.1, $J_{2,3}$ = 0.6 (H-2); 4.12 dd, 1 H, $J_{4A,4B}$ = 12.0, $J_{3,4A}$ = 0.9 (H-4$_A$); 3.88 dd, 1 H, $J_{4A,4B}$ = 12.0, $J_{3,4B}$ = 0.6 (H-4$_B$); 3.67 br s, 1 H (H-3); 3.40 br s (OH); 2.86 s, 2 × 3 H (N(CH$_3$)$_2$); 1.40 d, 3 H,

$J_{5,6}$ = 5.1 (CHC**H**$_3$). ^{13}C NMR: 131.2 (C-1), 99.5 (**C**HCH$_3$), 78.9 (C-2), 71.6 (C-4), 64.4 (C-3), 42.4 (N(CH$_3$)$_2$), 21.0 (CH**C**H$_3$).

3-*O*-*tert*-(Butyldimethylsilyl)-2,4-*O*-ethylidene-D-erythrose *N*,*N*-Dimethylhydrazone (**13**)

To the solution of hydrazone **12** (2.1 g, 11.2 mmol) and imidazole (1.8 g, 26.4 mmol) in CH_2Cl_2 (10 ml) *tert*-butyldimethylsilyl chloride (1.8 g, 11.9 mmol) was added. The resulting mixture was stirred at room temperature for 24 h, then was poured into water and extracted with CH_2Cl_2 (3 × 20 ml). The organic layers were combined, dried and concentrated under reduced pressure. The crude product was purified by column chromatography over silica gel (16 × 2 cm) using EtOAc/hexanes (30:70) to give compound **13** (3.1 g, 97%) as colorless oil, $[\alpha]_D^{25}$ –33.1 (*c* 1.0, $CHCl_3$). TLC: R_F 0.54 in EtOAc/hexanes (70:30). IR (KBr): 2955, 2930, 2886, 2859, 1605 (C=N), 1472, 1464. ^{1}H NMR: 6.34 d, 1 H, $J_{1,2}$ = 6.6 (H-1); 4.71 q, 1 H, J = 5.1 (C**H**CH$_3$); 4.06 dd, 1 H, $J_{4A,4B}$ = 10.8, $J_{3,4A}$ = 5.2 (H-4$_A$); 3.92 dd, 1 H, $J_{2,3}$ = 9.0, $J_{1,2}$ = 6.6 (H-2); 3.67 ddd, $J_{3,4A}$ = 9.9, $J_{2,3}$ = 9.0, $J_{3,4B}$ = 5.2 (H-3); 3.39 dd, 1 H, $J_{4A,4B}$ = 10.8, $J_{3,4B}$ = 9.9 (H-4$_B$); 2.81 s, 2 × 3 H (N(CH$_3$)$_2$); 1.31 d, 3 H, $J_{5,6}$ = 5.1 (CHC**H**$_3$); 0.80 s, 9 H (SiC(CH$_3$)$_3$); 0.00 and –0.03 2 × s, 2 × 3 H (Si(CH$_3$)$_2$). ^{13}C NMR: 130.4 (C-1), 98.4 (**C**HCH$_3$), 82.3 (C-2), 71.2 (C-4), 64.9 (C-3), 42.2 (N(CH$_3$)$_2$), 25.6 (SiC(**C**H$_3$)$_3$), 20.5 (CH**C**H$_3$), 17.8 (Si**C**(CH$_3$)$_3$), –4.5 and –4.8 (Si(CH$_3$)$_2$).

3-*O*-(*tert*-Butyldimethylsilyl)-2,4-*O*-ethylidene-D-threose *N*,*N*-Dimethylhydrazone (**17**)

Title compound was prepared from compound **16** according to the procedure described for compound **13**. The crude product was purified by column chromatography on silica gel using EtOAc/hexanes (30:70) to give **17** (96%) as colorless oil, $[\alpha]_D^{25}$ –13.4 (*c* 1.0, $CHCl_3$). TLC: R_F 0.43 in EtOAc/hexanes (70:30). IR (KBr): 2955, 2930, 2886, 2859, 1605, 1472, 1464. ^{1}H NMR: 6.62 d, 1 H, $J_{1,2}$ = 6.2 (H-1); 4.79 q, 1 H, J = 5.1 (C**H**CH$_3$); 4.26 dd, 1 H, $J_{2,3}$ = 1.8, $J_{1,2}$ = 6.2 (H-2); 3.98 and 3.83 2 × dd, 2 × 1 H, $J_{4A,4B}$ = 12.3, $J_{3,4A,B}$ = 1.6 (H-4$_A$); 3.61 ddd, $J_{3,4A}$ = $J_{3,4B}$ = 1.6, $J_{2,3}$ = 1.8 (H-3); 2.81 s, 2 × 3 H (N(CH$_3$)$_2$); 1.37 d, 3 H, $J_{5,6}$ = 5.1 (CHC**H**$_3$); 0.91 s, 9 H (SiC(CH$_3$)$_3$); 0.07 and –0.02 2 × s, 2 × 3 H (Si(CH$_3$)$_2$). ^{13}C NMR: 133.4 (C-1), 98.8 (**C**HCH$_3$), 80.3 (C-2), 71.8 (C-4), 66.9 (C-3), 42.5 (N(CH$_3$)$_2$), 25.8 (SiC(**C**H$_3$)$_3$), 21.0 (CH**C**H$_3$), 18.2 (Si**C**(CH$_3$)$_3$), –4.5 and –4.7 (Si(CH$_3$)$_2$).

3-*O*-(*tert*-Butyldiphenylsilyl)-2,4-*O*-ethylidene-D-erythrose *N*,*N*-Dimethylhydrazone (**14**)

Title compound was prepared from hydrazone **12** and *tert*-butyldiphenylsilyl chloride according to the procedure described for compound **13**. The crude product was purified by column chromatography over silica gel using EtOAc/hexanes (10:90) to give product **14** (89%) as colorless solid with m.p. 40–43 °C (EtOAc/hexanes), $[\alpha]_D^{25}$ +52.4 (*c* 1.0, $CHCl_3$). TLC: R_F 0.47 in EtOAc/hexanes (30:70). For $C_8H_{16}N_2O_3$ (426.6) calculated: 67.57% C, 8.03% H, 6.57% N; found: 67.39% C, 8.10% H, 6.46% N. ^{1}H NMR: 7.71, 7.58 and 7.36 3 × m, 10 H (C$_6$H$_5$); 6.14 d, 1 H, $J_{1,2}$ = 6.8 (H-1); 4.69 q, 1 H, J = 4.7 (C**H**CH$_3$); 4.08 dd, 1 H, $J_{2,3}$ = 8.5, $J_{1,2}$ = 6.8 (H-2); 3.83 dd, 1 H, $J_{4A,4B}$ = 10.7, $J_{3,4A}$ = 5.1 (H-4$_A$); 3.73 m, 1 H (H-3); 3.44 dd, 1 H, $J_{4A,4B}$ = 10.7, $J_{3,4B}$ = 9.4 (H-4$_B$); 2.73 s, 2 × 3 H (N(CH$_3$)$_2$); 1.24 d, 3 H, $J_{5,6}$ = 5.1 (CHC**H**$_3$); 0.99 s, 9 H (SiC(CH$_3$)$_3$). ^{13}C NMR: 135.9, 135.8 (C$_6$H$_5$, q), 134.8 (C-1), 133.1, 129.9, 129.7, 129.6, 127.6, 127.5 (C$_6$H$_5$), 98.6 (**C**HCH$_3$), 82.4 (C-2), 71.1 (C-4), 65.7 (C-3), 42.2 (N(CH$_3$)$_2$), 26.6 (SiC(**C**H$_3$)$_3$), 20.5 (CH**C**H$_3$), 19.2 (Si**C**(CH$_3$)$_3$).

3-(*O*-*tert*-Butyldiphenylsilyl)-2,4-*O*-ethylidene-D-threose *N*,*N*-Dimethylhydrazone (**18**)

Title compound was prepared from hydrazone **16** and *tert*-butyldiphenylsilyl chloride according to the procedure described for compound **13**. The crude product was purified by column chromatography on silica gel using EtOAc/hexanes (15:85) to give compound **18** (85%) as colorless oil with $[\alpha]_D^{25}$ +56.7 (*c* 1.5, $CHCl_3$). TLC: R_F 0.42 in EtOAc/hexanes (30:70). ^{1}H NMR: 7.71, 7.64, 7.35 3 × m, 10 H (C_6H_5); 6.75 d, 1 H, $J_{1,2}$ = 6.0 (H-1); 4.76 q, 1 H, *J* = 4.6 (C**H**CH_3); 4.22 dd, 1 H, $J_{2,3}$ = 1.3, $J_{1,2}$ = 6.0 (H-2); 3.70 m, 1 H (H-3); 3.68 and 3.48 2 × dd, 2 × 1 H, $J_{4A,4B}$ =12.4, $J_{3,4A}$ = 1.7, $J_{3,4B}$ = 0.9 (H-$4_{A,B}$); 2.76 s, 2 × 3 H ($N(CH_3)_2$); 1.41 d, 3 H, $J_{5,6}$ = 4.6 (CH**C**H_3); 1.07 s, 9 H ($SiC(CH_3)_3$). ^{13}C NMR: 135.9, 135.8 (C_6H_5, q), 132.5 (C-1), 133.1, 129.9, 129.7, 129.6, 127.6, 127.5 (C_6H_5), 98.8 (**C**HCH_3), 80.6 (C-2), 70.8 (C-4), 68.1 (C-3), 42.4 ($N(CH_3)_2$), 29.9 (SiC(**C**$H_3)_3$), 21.2 (CH**C**H_3), 19.6 (Si**C**$(CH_3)_3$).

4-(*O*-*tert*-Butyldimethylsilyl)-1,2-dideoxy-3,5-*O*-ethylidene-D-*erythro*-pent-1-enitol (**2**)

Hydrazone **13** (1.5 g, 4.8 mmol) was dissolved in acetic acid (25 ml) containing water (4 ml). Sodium nitrite (3.3 g, 48 mmol) was added in small portions to stirred solution at room temperature during 3 h. This mixture was stirred for 1 h and then concentrated. The residue was partioned between $CHCl_3$ (50 ml) and water (50 ml). The aqueous layer was thoroughly extracted with $CHCl_3$ (3 × 15 ml) and the combined organic layers were washed with water (30 ml) and aqueous $NaHCO_3$ solution (50%, 30 ml), dried and concentrated to afford the crude aldehyde. To a stirred solution of methyltriphenylphosphonium bromide (3.5 g, 9.8 mmol) in THF (10 ml) at 0–5 °C was added 15% butyllithium in hexanes (4.8 ml, 9.8 mmol) over a period of 5 min. The resulting mixture was stirred at 0–5 °C for 15 min and then the crude aldehyde was added in THF (10 ml). This mixture was stirred at room temperature for 5 h, then was added water (30 ml) and extracted with Et_2O (3 × 20 ml). The organic layers were combined, dried and concentrated under reduced pressure. The crude product was purified by column chromatography over silica gel (30 × 2 cm) using EtOAc/hexanes (4:96) to give compound **2** (614 mg, 48%) as colorless oil with $[\alpha]_D^{20}$ –35.3 (*c* 1.9, $CHCl_3$). TLC: R_F 0.48 in EtOAc/hexanes (10:90). For $C_{13}H_{26}O_3Si$ (258.4) calculated: 60.42% C, 10.14% H; found: 60.61% C, 10.08% H. IR (KBr): 2957, 2930, 2886, 2857, 1472, 1463, 1403, 1256, 1113, 1006, 906, 871. ^{1}H NMR: 5.86 ddd, 1 H, $J_{1trans,2}$ = 16.7, $J_{1cis,2}$ = 10.6, $J_{2,3}$ = 6.2 (H-2); 5.33 and 5.21 2 × m, 2 × 1 H (H-1); 4.68 q, 1 H, *J* = 5.0 (C**H**CH_3); 3.76 dd, 1 H, $J_{3,4}$ = 8.6, $J_{2,3}$ = 6.2 (H-3); 3.43 m, 1 H (H-4); 3.35 m, 2 H (H-5); 1.31 d, 3 H, *J* = 5.0 (CHC**H**$_3$); 0.82 s, 9 H ($SiC(CH_3)_3$); 0.00 and –0.04 2 × s, 2 × 3 H ($Si(CH_3)_2$). ^{13}C NMR: 135.5 (C-2), 118.1 (C-1), 98.9 (**C**HCH_3), 82.9 (C-3), 71.2 (C-5), 66.9 (C-4), 26.0 (SiC(**C**$H_3)_3$), 20.9 (CH**C**H_3), 18.5 (Si**C**$(CH_3)_3$), –4.2 and –4.0 ($Si(CH_3)_2$).

4-(*O*-*tert*-Butyldimethylsilyl)-1,2-dideoxy-3,5-*O*-ethylidene-D-*threo*-pent-1-enitol (**5**)

Title compound was prepared from compound **17** according to the procedure described for compound **2**. The crude product was purified by column chromatography over silica gel using EtOAc/hexanes (2:98) to give compound **5** (46%) as colorless oil with $[\alpha]_D^{20}$ –30.7 (*c* 1.9, $CHCl_3$). TLC: R_F 0.50 in EtOAc/hexanes (10:90). For $C_{13}H_{26}O_3Si$ (258.4) calculated: 60.42% C, 10.14% H; found: 60.58% C, 10.10% H. IR (KBr): 2955, 2929, 2885, 2856, 1473, 1463, 1403, 1256, 1183, 1113, 1110, 1006, 935, 906, 876, 837. ^{1}H NMR: 5.86 ddd, 1 H, $J_{1trans,2}$ = 17.3, $J_{1cis,2}$ = 10.5, $J_{2,3}$ = 6.7 (H-2); 5.22 and 5.10 2 × m, 2 × 1 H (H-1); 4.69 q, 1 H, *J* = 5.0 (C**H**CH_3); 4.04 dd, 1 H, $J_{3,4}$ = 1.7, $J_{2,3}$ = 6.7 (H-3); 3.91 and 3.73 2 × dd, 2 × 1 H,

$J_{4,5A} = J_{4,5B}$ = 1.6, $J_{5A,5B}$ = 12.0 (H-$4_{A,B}$); 3.42 dd, 1 H, $J_{3,4}$ = 1.7, $J_{4,5A} = J_{4,5B}$ = 1.6 (H-4); 1.29 d, 3 H, J = 5.0 (CHC**H**$_3$); 0.84 s, 9 H (SiC(CH$_3$)$_3$); 0.00 and –0.03 2 × s, 2 × 3 H (Si(CH$_3$)$_2$). ^{13}C NMR: 136.1 (C-2), 117.3 (C-1), 99.0 (**C**HCH$_3$), 81.3 (C-3), 72.2 (C-5), 67.4 (C-4), 26.2 (SiC(**C**H$_3$)$_3$), 21.8 (CH**C**H$_3$), 18.6 (Si**C**(CH$_3$)$_3$), –3.9 and –4.1 (Si(CH$_3$)$_2$).

4-(*O*-*tert*-Butyldiphenylsilyl)-1,2-dideoxy-3,5-*O*-ethylidene-D-*erythro*-pent-1-enitol (**3**)

Title compound was prepared from compound **14** according to the procedure described for compound **2**. The crude product was purified by column chromatography on silica gel using EtOAc/hexanes (5:95) to give compound **3** (58%) as colorless oil with $[\alpha]_D^{20}$ –3.3 (*c* 0.3, CHCl$_3$). TLC: R_F 0.58 in EtOAc/hexanes (10:90). ^{1}H NMR: 7.65 and 7.62 2 × m, 10 H (C$_6$H$_5$); 5.86 ddd, 1 H, $J_{1trans,2}$ = 17.1, $J_{1cis,2}$ = 10.3, $J_{2,3}$ = 6.2 (H-2); 5.39 and 5.21 2 × m, 2 × 1 H (H-1); 4.68 q, 1 H, J = 5.1 (C**H**CH$_3$); 3.92 m, 1 H (H-3); 3.75 dd, 1 H, $J_{4,5A}$ = 5.1, $J_{5A,5B}$ = 10.7 (H-5_A); 3.59 ddd, 1 H, $J_{4,5A}$ = 5.1, $J_{4,5B}$ = 9.8, $J_{4,3}$ = 9.0 (H-4); 3.38 dd, 1 H, $J_{5A,5B}$ = 10.7, $J_{4,5B}$ = 9.8 (H-5_B); 1.26 d, 3 H, J = 5.1 (CHC**H**$_3$); 1.04 s, 9 H (SiC(CH$_3$)$_3$). ^{13}C NMR: 136.0, 135.8 (C$_6$H$_5$, q), 133.9, 132.9, 130.0, 129.9, 127.7 (C$_6$H$_5$), 135.2 (C-2), 118.4 (C-1), 98.5 (**C**HCH$_3$), 82.7 (C-3), 71.1 (C-5), 67.3 (C-4), 26.9 (SiC(**C**H$_3$)$_3$), 20.5 (CH**C**H$_3$), 19.3 (Si**C**(CH$_3$)$_3$).

4-(*O*-*tert*-Butyldiphenylsilyl)-1,2-dideoxy-3,5-*O*-ethylidene-D-*threo*-pent-1-enitol (**6**)

Title compound was prepared from compound **18** according to the procedure described for compound **2**. The crude product was purified by column chromatography on silica gel using EtOAc/hexanes (2:98) to give product **6** (48%) as colorless oil with $[\alpha]_D^{20}$ –21.4 (*c* 0.35, CHCl$_3$). TLC: R_F 0.60 in EtOAc/hexanes (10:90). ^{1}H NMR: 7.81, 7.69 and 7.36 3 × m, 10 H (C$_6$H$_5$); 6.06 ddd, 1 H, $J_{1trans,2}$ = 17.5, $J_{1cis,2}$ = 10.7, $J_{2,3}$ = 6.8 (H-2); 5.27 and 5.10 2 × m, 2 × 1 H (H-1); 4.74 q, 1 H, J = 5.1 (C**H**CH$_3$); 4.06 dd, 1 H, $J_{3,4}$ = 1.3, $J_{2,3}$ = 6.8 (H-3); 3.71 dd, 1 H, $J_{4,5A}$ = 1.3, $J_{5A,5B}$ = 12.4 (H-4_A); 3.56 dd, 1 H, $J_{3,4} = J_{4,5A} = J_{4,5B}$ = 1.3 (H-4); 3.49 dd, 1 H, $J_{4,5B}$ = 1.3, $J_{5A,5B}$ = 12.4 (H-4_B); 1.43 d, 3 H, J = 5.1 (CHC**H**$_3$); 1.09 s, 9 H (SiC(CH$_3$)$_3$). ^{13}C NMR: 136.1 (C-2), 135.9, 134.1 (C$_6$H$_5$, q), 133.4, 129.6, 129.5, 127.5, 127.4 (C$_6$H$_5$), 116.9 (C-1), 98.6 (**C**HCH$_3$), 80.9 (C-3), 70.8 (C-5), 67.9 (C-4), 26.9 (SiC(**C**H$_3$)$_3$), 21.1 (CH**C**H$_3$), 19.6 (Si**C**(CH$_3$)$_3$).

General Procedure for Cycloaddition

To a stirred solution of an alkene (1.0 mmol) in toluene (10 ml) was added a nitrone (3 mmol) in three portions after 10 h each and the solution was heated at reflux (110 °C) for several hours. The resulting mixture was evaporated under reduced pressure.

(3R,5S)-2-Benzyl-3-[(2S,4R,5R)-5-hydroxy-2-methyl-1,3-dioxan-4-yl]-5-[(2R,4S,5R)-5-hydroxy-2-methyl-1,3-dioxan-4-yl]isoxazolidine (**19a**). A crude mixture of diastereoisomers obtained in ratio 82:18 was purified by column chromatography on silica gel eluting with EtOAc/hexanes to give the major product **19a** (74%) as a colorless crystals with m.p. 155–156 °C (EtOAc/hexanes), $[\alpha]_D^{25}$ +27.8 (*c* 1.0, CHCl$_3$). TLC: R_F 0.37 in EtOAc/hexanes (40:60). For C$_{20}$H$_{29}$NO$_7$ (395.5) calculated: 60.75% C, 7.39% H, 3.54% N; found: 60.60% C, 7.42% H, 3.49% N. IR (KBr): 3456, 2991, 2937, 2864, 1454, 1411, 1371, 1225, 1121, 1082, 979, 821. ^{1}H NMR: 7.32 m, 5 H (C$_6$H$_5$); 4.69 and 4.64 2 × q, 2 × 1 H, J = 5.1, 5.0 (H-2′, H-2″); 4.47 ddd, 1 H, $J_{4B,5}$ = 6.4, $J_{4A,5}$ = 8.4, $J_{4'',5}$ = 5.4 (H-5); 4.07 dd, 1 H, $J_{6A'',6B''}$ = 10.8, $J_{6A'',5''}$ = 5.3 (H-6_A″); 4.03 dd, 1 H, $J_{6A',6B'}$ = 12.1, $J_{6A',5'}$ = 2.1 (H-6_A′); 4.00 and 3.95 2 × d, 2 × 1 H, J = 13.1 (C**H**$_2$C$_6$H$_5$); 3.77 m, 2 H (H-5″, H-6_B′); 3.52 m, 3 H (H-3, H-4′, H-5′); 3.39 dd, 1 H, $J_{4'',5}$ =

5.4, $J_{4'',5''}$ = 9.1 (H-4''); 3.32 dd, 1 H, $J_{6A'',6B''}$ = 10.8, $J_{6B'',5''}$ = 10.0 (H-6_B''); 2.90 br s, 1 H (OH); 2.57 ddd, 1 H, $J_{4A,5}$ = 8.4, $J_{3',4A}$ = 8.3, $J_{4A,4B}$ = 13.0 (H-4_A); 2.37 ddd, 1 H, $J_{4B,5}$ = 6.4, $J_{3,4B}$ = 4.4, $J_{4A,4B}$ = 13.0 (H-4_B); 1.35 and 1.30 2 × d, 2 × 3 H, J = 5.1, 5.0 (CH_3). ^{13}C NMR: 130.1 (C_6H_5, q), 129.6, 129.8, 129.1, 128.9, 128.8 (C_6H_5), 100.1, 98.9 (C-2', C-2''), 80.8 (C-4''), 79.5 (C-4'), 78.5 (C-5), 72.2 (C-6'), 70.5 (C-6''), 65.2 (C-5'), 64.8 (C-3), 63.9 (C-5''), 61.6 (**C**$H_2C_6H_5$), 32.6 (C-4), 21.3, 20.9 (2 × CH_3).

(3R,5S)-2-Benzyl-5-{(2R,4S,5R)-5-[(tert-butyldimethylsilyl)oxy]-2-methyl-1,3-dioxan-4-yl}-3-(2S,4R,5R)-5-hydroxy-2-methyl-1,3-dioxan-4-yl)isoxazolidine (**20a**) and *(3R,5R)-2-benzyl-5-{(2R,4S,5R)-5-[(tert-butyldimethylsilyl)oxy]-2-methyl-1,3-dioxan-4-yl}-3-(2S,4R,5R)-5-hydroxy-2-methyl-1,3-dioxan-4-yl)isoxazolidine* (**20b**). The crude reaction mixture of diastereoisomers in ratio 82:18 was purified by column chromatography on silica gel eluting with EtOAc/hexanes to give the starting alkene **2** (19%) as first fraction, the minor product **20b** (10%) as a colorless oil and the major product **20a** (35%) in the third fraction as a colorless oil.

Data for **20a**: $[\alpha]_D^{25}$ –8.8 (*c* 1.2, $CHCl_3$). TLC: R_F 0.48 in EtOAc/hexanes (20:80). IR (film): 3456, 2991, 2929, 2856, 1451, 1410, 1389, 1225, 1159, 1082, 956, 979, 821. ^{1}H NMR: 7.47 and 7.34 2 × m, 5 H (C_6H_5); 4.79 and 4.78 2 × q, 2 × 1 H, J = 5.0 (H-2', H-2''); 4.44 m, 1 H (H-5); 4.21 and 4.14 2 × d, 2 × 1 H, J = 13.2 (C**H**$_2C_6H_5$); 4.15 dd, 1 H, $J_{6A',6B'}$ = 11.8, $J_{6A',5'}$ = 1.7 (H-6_A'); 4.07 dd, 1 H, $J_{6A'',6B''}$ = 10.7, $J_{6A'',5''}$ = 5.3 (H-6_A''); 3.88 m, 1 H (H-5'); 3.85 dd, 1 H, $J_{6A',6B'}$ = 11.8, $J_{6B',5'}$ = 1.3 (H-6_B'); 3.81 ddd, 1 H, $J_{6A'',5''}$ = 5.3, $J_{6B'',5''}$ = 8.8, $J_{4'',5''}$ = 10.0 (H-5''); 3.61 m, 2 H, H-3 (H-4'); 3.76 br s, 1 H (OH); 3.39 dd, 1 H, $J_{4'',5''}$ = 10.0, $J_{4'',5}$ = 10.6 (H-4''); 3.33 dd, 1 H, $J_{6A'',6B''}$ = 10.7, $J_{6B'',5''}$ = 8.8 (H-6_B''); 2.60 and 2.34 2 × m, 2 × 1 H (H-$4_{A,B}$); 1.47 and 1.43 2 × d, 2 × 3 H, J = 5.0 (2 × CH_3); 0.87 s, 9 H ($C(CH_3)_3$); 0.00 and –0.03 2 × s, 2 × 3 H ($Si(CH_3)_2$). ^{13}C NMR: 138.1 (C_6H_5, q), 129.6, 128.1, 127.0 (C_6H_5), 99.7, 99.0 (C-2', C-2''), 80.4 (C-4''), 78.6 (C-4'), 75.5 (C-5), 71.9 (C-6'), 71.4 (C-6''), 65.5 (C-3), 63.3, 63.0 (C-5', C-5''), 62.5 (**C**$H_2C_6H_5$), 30.2 (C-4), 25.6 (**C**$(CH_3)_3$), 20.9, 20.6 (2 × CH_3), 17.8 (**C**$(CH_3)_3$), –4.9 and –5.2 ($Si(CH_3)_2$).

Data for compound **20b**: $[\alpha]_D^{25}$ 3.3 (*c* 1.5, $CHCl_3$). TLC: R_F 0.45 in EtOAc/hexanes (20:80). IR (film): 3456, 3299, 2929, 2856, 1451, 1410, 1389, 1225, 1159, 1082, 956, 979, 821. ^{1}H NMR: 7.21 m, 5 H (C_6H_5); 4.60 m, 3 H, H-2', H-2'' (H-5); 3.96 dd, 1 H, $J_{6A',6B'}$ = 11.8, $J_{6A',5'}$ = 1.8 (H-6_A'); 3.93 dd, 1 H, $J_{6A'',6B''}$ = 10.3, $J_{6A'',5''}$ = 4.9 (H-6_A''); 3.90 and 3.73 2 × d, 2 × 1 H, J = 12.3 (C**H**$_2C_6H_5$); 3.73 m, 1 H (H-5'); 3.68 dd, 1 H, $J_{6A',6B'}$ = 11.8, $J_{6B',5'}$ = 1.3 (H-6_B'); 3.55 m, 3 H (H-3, H-4', H-4''); 3.39 m, 1 H (H-5''); 3.28 dd, 1 H, $J_{6A'',6B''}$ = 10.3, $J_{6B'',5''}$ = 10.0 (H-6_B''); 2.50 ddd, 1 H, $J_{3,4A}$ = 2.0, $J_{4A,5}$ = 6.4, $J_{4A,4B}$ = 12.6 (H-4_A); 2.33 br s, 1 H (OH); 2.28 ddd, 1 H, $J_{3,4B}$ = 9.4, $J_{4B,5}$ = 8.0, $J_{4A,4B}$ = 12.6 (H-4_B); 1.28 and 1.22 2 × d, 2 × 3 H, J = 5.0 (2 × CH_3); 0.83 s, 9 H ($C(CH_3)_3$); 0.00 and –0.01 2 × s, 2 × 3 H ($Si(CH_3)_2$). ^{13}C NMR: 137.5 (C_6H_5, q), 129.6, 128.7, 128.9, 127.9 (C_6H_5), 100.1, 98.7 (C-2', C-2''), 79.5, 79.2 (C-4', C-4''), 76.1 (C-5), 73.4 (C-6'), 71.6 (C-6''), 64.8 (C-5''), 64.1 (C-3), 63.7 (C-5''), 60.8 (**C**$H_2C_6H_5$), 27.7 (C-4), 26.0 (**C**$(CH_3)_3$), 21.3, 20.9 (2 × CH_3), 18.2 (**C**$(CH_3)_3$), –3.8 and –4.6 ($Si(CH_3)_2$).

(3S,5R)-2-Benzyl-5-{(2S,4R,5R)-5-[(tert-butyldimethylsilyl)oxy]-2-methyl-1,3-dioxan-4-yl}-3-(2R,4S,5R)-5-hydroxy-2-methyl-1,3-dioxan-4-yl)isoxazolidine (**21a**) and *(3S,5S)-2-benzyl-5-{(2S,4R,5R)-5-[(tert-butyldimethylsilyl)oxy]-2-methyl-1,3-dioxan-4-yl}-3-(2R,4S,5R)-5-hydroxy-2-methyl-1,3-dioxan-4-yl)isoxazolidine* (**21b**). The crude reaction mixture was purified by column chromatography on silica gel eluting with EtOAc/hexanes to give the starting alkene **5** (20%) as first fraction, the minor product **21b** (9%) as a colorless oil and the major product **21a** (32%) in the third fraction as a colorless oil.

Data for compound **21a**: $[\alpha]_D^{25}$ –14.0 (*c* 1.2, $CHCl_3$). TLC: R_F 0.45 in EtOAc/hexanes (20:80). IR (film): 3448, 2991, 2930, 2857, 1463, 1410, 1389, 1225, 1159, 1082, 956, 979,

821. ^{1}H NMR: 7.23 m, 5 H (C_6H_5); 5.30 br s, 1 H (OH); 4.70 and 4.51 2 × q, 2 × 1 H, J = 5.0 (H-2′, H-2″); 4.45 m, 1 H (H-5); 4.01 and 3.66 2 × d, 2 × 1 H, J = 11.7 (C**H**$_2$C$_6$H$_5$); 3.93 dd, 1 H, $J_{6A',6B'}$ = 10.4, $J_{6A',5'}$ = 4.3 (H-6$_A$′); 3.90 dd, 1 H, $J_{6A'',6B''}$ = 12.3, $J_{6A'',5''}$ = 1.7 (H-6$_A$″); 3.69 dd, 1 H, $J_{6A'',6B''}$ = 12.3, $J_{6B'',5''}$ = 1.9 (H-6$_B$″); 3.53 m, 2 H (H-4″, H-5″); 3.18 m, 4 H (H-3, H-4′, H-5′, H-6$_B$′); 2.45 m, 2 H (H-4$_{A,B}$); 1.27, 1.18 2 × d, 2 × 3 H, J = 5.0 (2 × CH_3); 0.86 s, 9 H (C(C**H**$_3$)$_3$); 0.00 and –0.09 2 × s, 2 × 3 H (Si(C**H**$_3$)$_2$). ^{13}C NMR: 135.6 (C_6H_5, q), 129.7, 129.2, 128.5, 127.9 (C_6H_5), 99.5, 99.2 (C-2′, C-2″), 80.5 (C-4″), 79.6 (C-4′), 78.0 (C-5), 71.9 (C-6′), 70.3 (C-6″), 67.9, 66.6 (C-3, C-5′), 64.9 (C-5″), 60.9 (**C**H$_2$C$_6$H$_5$), 31.4 (C-4), 26.3 (**C**(CH$_3$)$_3$), 21.4, 20.9 (2 × CH_3), 18.6 (**C**(CH$_3$)$_3$), –4.0 and –4.4 (Si(CH$_3$)$_2$).

Data for compound **21b**: $[\alpha]_D^{25}$ +53.4 (*c* 1.3, $CHCl_3$).TLC: R_F 0.48 in EtOAc/hexanes (20:80). IR (film): 3363, 2991, 2929, 2855, 1597, 1451, 1408, 1367, 1253, 1159, 1104, 1052, 1002, 956, 979, 821. ^{1}H NMR: 7.44 m, 5 H (C_6H_5); 4.88 and 4.78 2 × q, 2 × 1 H, J = 5.0 (H-2′, H-2″); 4.78 br s, 1 H (OH); 4.31 m, 1 H (H-5); 4.27 dd, 1 H, $J_{6A',6B'}$ = 10.8, $J_{6A',5'}$ = 5.3 (H-6$_A$′); 4.23 and 4.05 2 × d, 2 × 1 H, J = 13.2 (C**H**$_2$C$_6$H$_5$); 4.08 dd, 1 H, $J_{6A'',6B''}$ = 12.2, $J_{6A'',5''}$ = 1.7 (H-6$_A$″); 3.98 m, 1 H (H-5″); 3.90 dd, 1 H, $J_{6A'',6B''}$ = 12.2, $J_{6B'',5''}$ = 1.5 (H-6$_B$″); 3.69 dd, 1 H, $J_{4'',5''}$ = 1.6, $J_{5,5''}$ = 7.5 (H-4″); 3.61 m, 3 H (H-3, H-4′, H-5′); 3.51 dd, 1 H, $J_{6A',6B'}$ = 10.8, $J_{6B',5'}$ = 9.9 (H-6$_B$′); 2.75 ddd, 1 H, $J_{3,4A}$ = 4.5, $J_{4A,5}$ = 7.4, $J_{4A,4B}$ = 11.8 (H-4$_A$); 2.50 m, 1 H (H-4$_B$); 1.47 and 1.43 2 × d, 2 × 3 H, J = 5.0 (CH_3); 0.86 s, 9 H (C(C**H**$_3$)$_3$); 0.07 and –0.14 2 × s, 2 × 3 H (Si(C**H**$_3$)$_2$). ^{13}C NMR: 136.8 (C_6H_5, q), 128.8, 128.1, 126.3 (C_6H_5), 99.5, 99.3 (C-2′, C-2″), 81.4 (C-4″), 79.3 (C-4′), 77.0 (C-5), 72.2 (C-6″), 70.4 (C-6′), 68.1, 64.5 (C-3, C-5′), 63.0 (**C**H$_2$C$_6$H$_5$), 62.5 (C-5″), 33.3 (C-4), 26.2 (**C**(CH$_3$)$_3$), 21.4, 20.9 (2 × CH_3), 18.5 (**C**(CH$_3$)$_3$), –4.5 and –4.7 (Si(CH$_3$)$_2$).

X-Ray Diffraction Study

CCDC 199965 (for **19a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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