*J. Braz. Chem. Soc.*, Vol. 11, No. 3, 266-273, 2000.
Printed in Brazil


0103 - 5053 $6.00+0.00

Article

# Synthesis of New Chiral Auxiliares from Carbohydrates for $Et_2AlCl$-Promoted Diels-Alder Reactions

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Os acrilatos 3-*O*-acriloil-4,5-di-*O*-benzoil-1,2-*O*-isopropilideno-β-D-frutopiranose (**6**) e 3-*O*-benzil-5-*O*-acriloil-1,2-*O*-isopropilideno-α-D-xilofuranose (**8**) foram sintetizados em poucas etapas a partir dos respectivos monossacarídeos para utilização como auxiliares quirais em reações de Diels-Alder assimétricas com o ciclopentadieno, sob condições térmicas e promovidas por $Et_2AlCl$. Os resultados indicaram que, embora tenham sido obtidas relações *endo*/*exo* de moderadas a excelentes, foram observadas baixas diastereosseletividades π-faciais para os cicloadutos 3-*O*-[(1'*R*, 4'*R*)-biciclo-[2.2.1]hept-2'-eno-5'-formil]-4,5-di-*O*-benzoil-1,2-*O*-isopropilideno-β-D-frutopiranose (**21a**) e 3-*O*-benzil-5-*O*-[(1'*S*, 4'*S*)-biciclo-[2.2.1]hept-2'-eno-5'-formil]-1,2-*O*-isopropilideno-α-D-xilofuranose (**22b**), indicando que as conformações tipo do "π-stacked" desejadas nos complexos formados entre os acrilatos e o ácido de Lewis não foram estabelecidas.

Acrylates 3-*O*-acryloyl-4,5-di-*O*-benzoyl-1,2-*O*-isopropylidene-β-D-fructopyranose (**6**) and 3-*O*-benzyl-5-*O*-acryloyl-1,2-*O*-isopropylidene-α-D-xylofuranose (**8**) were synthesized in few steps from carbohydrates to construct chiral dienophiles for asymmetric Diels-Alder reaction with cyclopentadiene under thermal and $Et_2AlCl$-promoted conditions. Although from moderate to excellent *endo*/*exo* ratios were obtained, low p-facial diastereoselectivities were observed for the cycloadducts 3-*O*-[(1'*R*, 4'*R*)-bicyclo-[2.2.1]hept-2'-ene-5'-formyl]-4,5-di-*O*-benzoyl-1,2-*O*-isopropylidene-β-D-fructopyranose (**21a**) and 3-*O*-benzyl-5-*O*-[(1'*S*, 4'*S*)-bicyclo-[2.2.1]hept-2'-ene-5'-formyl]-1,2-*O*-isopropylideno-α-D-yilofuranose (**22b**) indicating that π-stacked conformations in the Lewis acid-acrylates complex were not effective.

**Keywords:** asymmetric Diels-Alder reactions, chiral dienophiles, carbohydrates

## Introduction

The utilization of stoichiometric chiral auxiliaries is one of the most flexible and predictable methods by which stereocontrol can be imposed on asymmetric synthesis, specially in the carbon-carbon bond formation[1]. The synthesis of carbohydrate derivatives has been a topic of continuous interest since they are widespread and inexpensive chiral natural products from which several chiral auxiliaries have been built[2].

Our continuing interest has been focused on the synthesis and use of carbohydrate derivatives as auxiliaries in several organic reactions in order to broaden the application of these readily available chiral compounds. Indeed, some time ago we described the utilization of carbohydrate-based chiral auxiliaries in α-alkylation of esters enolates[3] and in Michael and aldol addition reactions[4].

The Diels-Alder reactions have been among the most popular and successful synthetic applications of carbohydrate auxiliaries, particularly when they are attached to the dienophile[2,5]. In fact, among other carbohydrates[6], arabinose[7], ribose[7], sorbitol[8] and galactose[9] have been used to built chiral auxiliaries.

Recently we reported[10] the use of acrylates **1**-**4** (Figure 1) derived from D-galactose, D-allose, D-glucose and D-fructose, respectively, as dienophiles in Lewis acid-catalyzed Diels-Alder reactions in up to 60 % of optical purity. Attempts to improve the π-facial diastereoselectivity in this cycloaddition reaction led us to conceive the new acrylates **5**-**8** by simple elaborations from carbohydrates. These dienophiles were designed in order to favour the establishment of Lewis acid assisted π-stacked conformations[11] A (derived from **6**) and B (derived from **8**) where the carbonyl in their s-*trans* conformations adopt[10] a *syn*-periplanar

relationship to the hydrogens H-3 and H-5, respectively, in order to block one of the face of the acrylates moieties (Figure 2). In chiral auxiliaries derived from carbohydrates this principle was postulated by Shing and coworkers[12] which showed that this interaction controls the stereochemical pathway in Diels-Alder reactions catalyzed by Lewis acids between C (derived from D-arabinose) and cyclopentadiene.

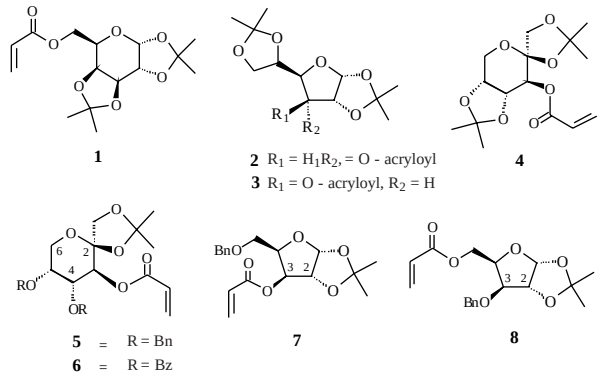



**Figure 1.** Some chiral carbohydrate-acrylates recently used in Diels-Alder reactions.

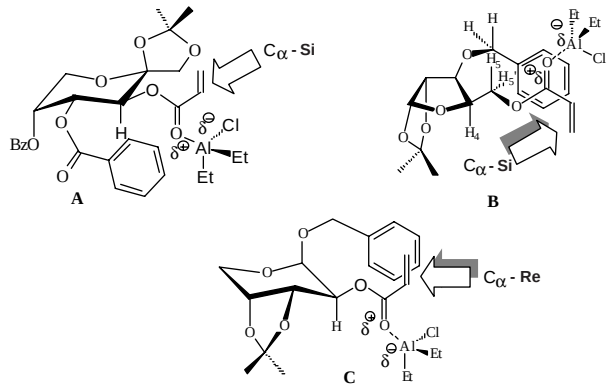
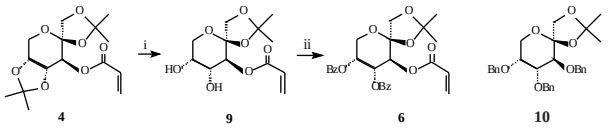



**Figure 2.** Possible π-stacked conformations for acrylates **6** and **8**.

## Results and Discussion

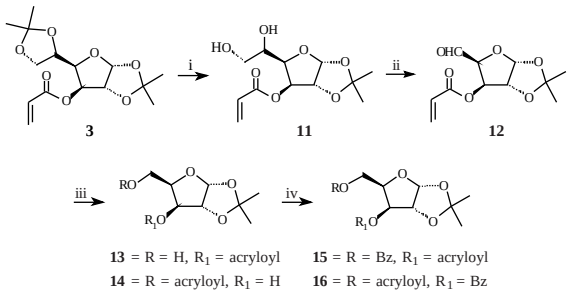
Compound **4** already prepared from D-fructose[10] was employed to synthesize the new acrylate **6** (Scheme 1). The selective hydrolysis[13] of the isopropylidene group at C-4 and C-5 led to diol **9** in good yields. Since benzylation (NaH, cat. n-$Bu_4NI$, THF, 0°C to r.t. then BnBr, THF, 50°C)[13] of the hydroxyl groups occurred with removal of the acrylate moiety at C-3 producing compound **10** in 33 % yield, this approach did not allow to reach acrylate **5**. However, diol **9** was converted into acrylate **6** upon treatment with benzoic acid in the presence of DCC-DMAP,[14] since the reaction using benzoyl chloride in pyridine led to products from acid-catalyzed polymerization of **9**, due to pyridinium chloride formation in the reaction media.




i)MeOH, aq. HOAc, 50 °C, 17 h, 70 %; ii) $PhCO_2H$, DCC, DMAP, $CH_2Cl_2$, 4 days, 87 %.

**Scheme 1.** Synthesis of new chiral acrylate **6**.

Ester **3** already obtained from D-glucose[10] was employed in an attempt to prepare acrylate **7** (Scheme 3). Hydrolysis[13] with selective removal of the isopropylidene group at C-4 and C-5 produced diol **11** in excellent yields. Subsequent cleavage with sodium periodate[15] led to the aldehyde **12**.



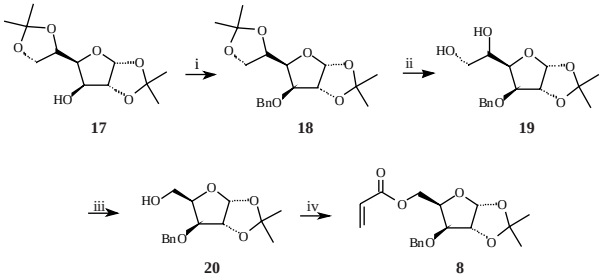

i) MeOH, aq. HOAc, 50 °C, 17 h, 98 %; ii) aq. $NaIO_4$, $SiO_2$, $CH_2Cl_2$, r.t., 1 h, 95 %; iii) TBAC, 2N HCl, MeOH, r.t., 66 %, **13**:**14** = 1:1; iv) benzoic acid, DCC, DMAP, $CH_2Cl_2$, r.t., 4 days, 71 %, **15**:**16** = 1:1.

**Scheme 2**. Preparation of an equimolecular mixture of **15** and **16**.

Since the reactions of aldehyde **12** with both $NaBH_4$ / MeOH and $NaBH_3CN$ / EtOH led to a complex mixture of products from acryloyl cleavage and degradation of the carbohydrate moiety, the reduction of the aldehyde group was conducted under mild conditions. However, the reaction with tetrabutylammonium cyanoborohydride (TBAC) in acidic media[16] produced an equimolecular mixture of isomers **13** and **14**, the ratio being determined by $^1H$ NMR from the relative intensities of the signals due to the methyl groups of **13** (1.54 and 1.33 ppm) and of **14** (1.51 and 1.22 ppm). Attempts to convert this mixture into isomer **14**, which could be used to reach acrylate **8**, by migration of the acrylate moiety from C-3 to C-5 was carried out by treatment with silica gel in dichloromethane at room temperature for a month.[17] Under these conditions and even for a longer time, the mixture **13**:**14** = 1:1 was converted mainly into **14** in a ratio **13**:**14** = 1:3.

Since these isomers showed to be difficult to separate by chromatrography, the equimolecular mixture of **13** and **14** was esterified with benzoic acid in the presence of DCC-DMAP[14] leading to a mixture of compounds **15** and **16**. As these isomers also showed to be difficult to be separated in silica gel, this approach did not allow to prepare acrylate **7**.

The synthesis of acrylate **8** was accomplished in four steps from commercially available diacetone glucose **17** (Scheme 3). After standard benzylation reaction[13] giving **18** in almost quantitative yield, this compound underwent a selective deprotection of the hydroxyl groups at C-5 and C-6 leading to **19**. Diol cleavage followed by reduction produced **20** which upon esterification gave **8** in 59 % overall yield[13].




i) NaH, cat. n-$Bu_4I$, THF, 0 °C to r.t. then benzyl bromide, THF, r.t. to 50 °C, 99 %; ii) MeOH, 50 % aqueous HOAc, 50 °C, 17 h, 93 %; iii) $NaIO_4$, aqueous EtOH, r.t., 3 h then $NaBH_4$, $CH_2Cl_2$, aqueous EtOH, 0 °C to r.t., 12 h, 92 %; iv) acrylic acid, DCC, DMAP, $CH_2Cl_2$, r.t., 4 days, 70 %.

**Scheme 3.** Synthesis of new acrylate **8**.

Thermal[18] and $Et_2AlCl$-promoted[19] Diels-Alder reactions of dienophiles **6** and **8** were carried out by using freshly distilled cyclopentadiene in dry $CH_2Cl_2$ following typical procedures described in the literature (Table 1).

While the experiments conducted under thermal conditions (entries 1 and 3) led, as expected,[10] to mixtures of the adducts (*R*)-**21a, b** and (*S*)-**22a, b** in moderate *endo*/*exo* ratio and without control of the stereochemistry at C-2', the reactions performed in the presence of 1.2 equivalents of $Et_2AlCl$ (entries 2 and 4) allowed to reach these cycloadducts, which were not separated, in moderate to excellent *endo*/*exo* ratios but with low π-facial diastereoselectivities.

Based on the model proposed by Shing[12] it was expected an attack from the Cα-Si face in the Lewis acid promoted Diels-Alder reaction of dienophile **8** in consequence of a more effective π-stacking since the groups are more close related. However, the result (entry 4) showed that enatiomer (S)-**22b** was obtained from the attack by the Cα-Re face indicating a transition state without π-stacking preference. Other Lewis acid having two coordination centers like $TiCl_4$ were used, but due to low stability of the carbohydrate moiety, there was decomposition even at low temperature. Although acrylate **6** leads to (R)-**21a** by the attack from its Cα-Si face, also in this case the low selectivity suggests that π-stacking interactions were not effective.

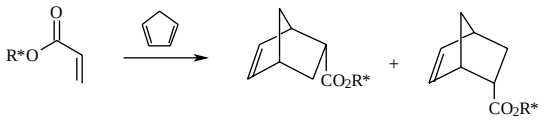
Both *endo*/*exo* ratios and *R*/*S* selectivities were determined from the relative intensities of the signals attributed to hydrogens H-5' and H-6' in the $^1H$ NMR spectra at 200 MHz of crude mixtures of the *endo* and *exo* adducts (*R*)-**21a**, **b** and (*S*)-**22a**, **b.** These assignments were performed based on previous reports[7,10] for Diels-Alder reactions of chiral acrylates and cyclopentadiene, but the spectral analyses did not allow neither to determine the absolute configuration of the major *exo* isomer nor the *R*/*S* ratios between them (Table 2).

While the *endo*/*exo* ratio for the mixture (*R*)-**21a** / (*S*)-**22a** = 6 / 4 was obtained from the signals of H-5' and H-6' of (R)-**21a** and (S)-**22a** (entries 1 and 2) and the multiplet attributed to H-5' and H-6' of the *exo* isomer **23a** (entry 3), the relative intensities of the signals of H-6' furnished the *R*/*S* selectivities between these isomeric adducts.

## Conclusions

This work shows the syntheses of two new acrylates **6** and **8** in few steps from D-fructose and D-glucose, respectively. Compounds **6** and **8** are complementary in the sense of the $Et_2AlCl$-promoted Diels-Alder reaction with cyclopentadiene, affording the cycloadducts (*R*)-**21a** and (*S*)-**22b**, respectively. Although these dienophiles led to high *endo*/*exo* ratios, they failed to control the stereochemistry at C-2' of the cycloadducts (20 % d.e.) and these results indicated that π-stacked conformations in the Lewis acid-acrylates complex were not effective.

**Table 1.** Stereoselectivities in Diels-Alder reactions from acrylates **6** and **8**.

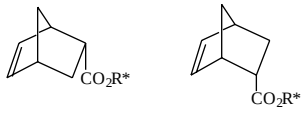



**6 or 8** ***(R)*-21a,b** ***(S)*-22a,b**

| Entry | Acrylate | Lewis acid | T (°C) | Yield (%) | Adduct (*Endo*/ *Exo*)[a] | **21**:**22** [a] |
|---|---|---|---|---|---|---|
| 1 | **6** | ——- | 0 | 99 | **a** (74:26) | 1:1 |
| 2 | **6** | $Et_2AlCl$ | -78 | 64 | **a** (78:22) | 6:4 |
| 3 | **8** | ——- | 0 | 85 | **b** (80:20) | 1:1 |
| 4 | **8** | $Et_2AlCl$ | -78 | 50 | **b** (96: 4) | 4:6 |

[a] Ratios determined by $^1H$ NMR from the signals in positions 5' and 6'.

**Table 2.** Assignments for H-5' and H-6' in $^1$H NMR at 200 MHz.




*(R)*-**21a** *(S)*-**22a** **23a**

| Entry | Adduct | H-5' | H-6' |
|---|---|---|---|
| 1 | (*R*)-**21a** | 5.97 (dd) | 5.80 (dd) |
| 2 | (*S*)-**22a** | 5.88 (dd) | 5.51(dd) |
| 3 | **23a** | 6.09-6.00 (m) | 6.09-6.00 (m) |

## Experimental

*General Procedures.*

Melting point was determined with a Thomas-Hoover apparatus and is uncorrected. Optical rotations were recorded with a Acatec polarimeter. Column chromatography was performed on silica gel 230-400 mesh (Merck). TLC was carried out on precoated silica gel plates (0.2mm) F-254 (Merck). Infrared spectra were recorded with a Nicolet Magna-750 spectrophotometer. High Resolution Electron Impact Mass Spectra (HREIMS) and Low Resolution Electron Impact Mass Spectra (LREIMS) were measured on a V.G. Auto Spec. Q spectrometer. NMR spectra were recorded with a Varian Gemini (200 MHz) and a Varian VXR (300 MHz) for solutions in $CDCl_3$. The structures of the substances were confirmed by NMR and HRMS.

*General procedure for the preparation of 3-O-acryloyl-1,2-O-isopropylidene-β-D-fructopyranose (***9***), 3-O-acryloyl-1,2-O-isopropylidene-α-D-glucofuranose (***11***) and 3-O-benzyl-1,2-O-isopropylidene-α-D-glucofuranose (***19***).*

A solution of **4** or **3** or **18** (3.8 mmol) in 10 mL of the mixture methanol:acetic acid:water (1:1:1) was stirred for 17 h at 50°C. The solvent was removed under reduced pressure and the crude residue chromatographed on a silica gel column eluted with 20 % ethyl acetate in n-hexane.

Compound **9** was obtained as a white solid in 70 % yield. m.p. 120°C; IR (KBr) 3300, 2980, 2930, 1720, 1630, 1450, 1400, 1380, 1290, 1255, 1180, 1165, 1080, 1060, 1035, 960, 890, 875, 855, 800 and 770 cm$^{-1}$; $^1$H NMR (200 MHz, $CD_3OD$) δ 1.37 (s, 3H, $CH_3$), 1.46 (s, 3H, $CH_3$), 3.71 and 4.00 (2 x dd, J = 12.6 and J = 1.9 Hz, 2H, H-6), 3.84 and 3.92 (2 x d, J = 9.1 Hz, 2H, H-1); 3.89-3.99 (m, 2H, H-4 and H-5), 5.28 (d, J= 10.2 Hz, 1H, H-3), 5.95 (dd, J = 2.0 and J = 10.9 Hz, 1H, H-3'), 6.20 (dd, J = 10.9 and J = 17.7 Hz, 1H, H-2'), 6.47 (dd, J = 2.0 and J = 17.7 Hz, 1H, H-3') ppm; $^{13}$C NMR ($CD_3OD$, DEPT) δ 26.8 ($CH_3$), 27.2 ($CH_3$), 66.2 (C-6), 70.6 (C-4), 71.2 (C-3), 71.4 (C-5), 73.2 (C-1), 106.4 (C-2), 113.3 (C-7), 129.7 (C-2'), 132.5 (C-3'), 167.9 (C-1') ppm; LREIMS m/z (relative intensity): 259 ($M^+$-15, 3), 59 (25), 55 (100); HREIMS calcd for $C_{11}H_{15}O_7$ ($M^+$ - 15): 259.081778. Found: 259.082434.

Compound **11** was obtained as a colorless oil in a 98 % yield. $[\alpha]_D^{25}$ - 41° (c 2, $CHCl_3$); IR (neat) 3434, 2980, 2930, 1736, 1620, 1400, 1381, 1290, 1250, 1180, 1150, 1075, 1060, 1010, 910, 880, 840 and 800 cm$^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$) δ 1.33 (s, 3H, $CH_3$), 1.54 (s, 3H, $CH_3$), 1.95 (b, OH), 3.26 (b, OH), 3.60-3.95 (m, 3H, H-5 and H-6), 4.24 (dd, J =3.0 and J = 9.3 Hz, 1H, H-4), 4.63 (d, J = 3.7 Hz, 1H, H-2), 5.37 (d, J = 3.0 Hz, 1H, H-3), 5.95 (d, J = 3.6 Hz, 1H, H-1), 5.98 (dd, J = 1.5 and 10.9 Hz, 1H, H-3'), 6.18 (dd, J = 10.9 and J = 17.1 Hz, 1H, H-2'), 6.53 (dd, J = 1.5 and J = 17.1 Hz,1H, H-3') ppm; $^{13}$C NMR ($CDCl_3$, DEPT) δ 26.0 ($CH_3$), 26.4 ($CH_3$), 63.9 (C-6), 68.1 (C-5), 76.5 (C-3), 79.0 (C-2), 82.9 (C-4), 104.7 (C-1), 112.2 (C-7), 127.2 (C-2'), 132.6 (C-3'), 165.6 (C-1') ppm; LREIMS m/z (relative intensity): 259 ($M^+$ - 15, 100), 213 (95), 185 (82), 155 (100), 145 (34), 143 (32), 139 (35), 127 (88), 113 (99), 100 (32), 85 (95), 73 (63); HREIMS calcd for $C_{11}H_{15}O_7$ ($M^+$ - 15): 259.081778. Found: (259.080983).

Compound **19** was obtained as a colorless oil in a 93 % yield. IR (neat) 3460, 3072, 3039, 2987, 2934, 2893, 1500, 1460, 1387, 1257, 1219, 1164, 1098, 1018, 858, 743 and 696 cm$^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$) δ 1.32 (s, 3H, $CH_3$), 1.49 (s, 3H, $CH_3$), 2.10-2.40 (bs, 2H, 2 OH), 3.68 (dd, J = 15.5 and J = 5.5 Hz, 1H, H-6), 3.82 (dd, J = 15.5 and J = 3.3 Hz, 1H, H-6), 3.95-4.20 (m, 3H, H-3, H-4 and H-5), 4.55 and 4.73 (2 x d, J = 12.2 Hz, 2H, H-7), 4.63 (d, J = 4.4 Hz, 1H, H-2), 5.93 (d, J = 4.4 Hz, 1H, H-1), 7.20-7.50 (m, 5H, Ph) ppm; $^{13}$C NMR ($CDCl_3$, DEPT) δ 26.0 ($CH_3$), 26.5 ($CH_3$), 64.1 (C-6), 69.0 (C-5), 72.0 (C-8), 79.7 (C-3), 81.8 (C-2), 82.0 (C-4), 104.9 (C-1), 111.6 (C-7), 127.7 (C-10), 128.0 (C-12), 128.5 (C-11), 131.1 (C-9) ppm; LREIMS m/z (relative intensity): 295 ($M^+$ - 15, 2), 91 (100).

*3-O-acryloyl-4,5-di-O-benzoyl-1,2-O-isopropylidene-β-D-fructopyranose (***6***).*

A mixture of benzoic acid (1.22 g; 10 mmol), **9** (1.37 g; 5 mmol), DCC (2.06 g; 10 mmol) and DMAP (0.122 g, 1 mmol) in dry $CH_2Cl_2$ (100 mL) was stirred for 4 days at room temperature. The reaction mixture was filtered to remove N,N-dicyclohexylurea and the residue was washed with ether. The organic phase was washed with water (3 x 100 mL), 5% aqueous HOAc (3 x 100 mL), again with water (3 x 100 mL) and dried over anhydrous $Na_2SO_4$. The solvent was removed under reduced pressure and the crude residue chromatographed on a silica gel column eluted with 10 % ethyl acetate in n-hexane to give **6** (2.1 g; 87 %) as a colorless oil. IR (neat) 3068, 3035, 2940, 2894, 1728, 1636, 1606, 1456, 1411, 1372, 1293, 1176, 1091, 1072, 975, 905, 808, 761 and 721 cm$^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$) δ 1.43 (s, 3H, $CH_3$), 1.53 (s, 3H, $CH_3$), 4.00 and 4.10 (2 x d, J = 9.2 Hz, 2H, H-1), 4.01 and 4.29 (2 x dd, J = 1.8 and J = 13.4 Hz, 2H, H-6), 5.65-5.85 (m, 3H, H-3, H-4

and H-5), 5.80 (dd, J = 2.0 and J = 10.0 Hz, 1H, H-3'), 6.05 (dd, J = 10.0 and J = 17.0 Hz, 1H, H-2'), 6.40 (dd, J = 2.0 and J = 17.0 Hz, 1H, H-3'), 7.23-7.63 (m, 6H, Ph), 7.80-7.88 (m, 2H, Ph), 8.00-8.08 (m, 2H, Ph) ppm; $^{13}$C NMR ($CDCl_3$, DEPT) δ 25.9 ($CH_3$), 26.3 ($CH_3$), 62.3 (C-6), 67.0 (C-4), 69.9 (C-3), 70.0 (C-5), 71.8 (C-1), 104.5 (C-2), 112.3 (C-7), 127.2 (C-2'), 128.2, 128.4, 128.9, 129.4, 129.5, 129.7 and 133.1 (Ph), 132,3 (C-3'), 165.3, 165.4 and 165.6 (C=O) ppm; LREIMS m/z (relative intensity): 467 ($M^+$ - 15, 4), 105 (100), 86 (29), 84 (47), 83 (39).

*3-O-acryloyl-4(S)-formyl-1,2-O-isoprolylidene-β-L-treofuranose (***12***).*

To a mixture of silica gel (2 g) in $CH_2Cl_2$ (16 mL) was added dropwise 15% aq. $NaIO_4$ (2 mL) and to this suspension was added a solution of **11** (0.274 g; 1 mmol) in $CH_2Cl_2$ (2 mL). The mixture was stirred for 1 h, filtered and the solvent was removed under reduced pressure. The resulting yellow oil was purified by column chromatography on silica gel (20 % ethyl acetate in n-hexane as the eluant) to give **11** as a yellowish oil (0.23 g; 95 %). IR (neat) 3473, 2971, 2932, 2850, 1734, 1635, 1618, 1412, 1380, 1189, 1168, 1079, 1024, 860 and 812 $cm^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$) 1.34 (s, 3H, $CH_3$), 1.53 (s, 3H, $CH_3$), 4.64 (d, J = 3.9 Hz, 1H, H-2), 4.77 (dd, J = 3.9 and J = 1.1 Hz, 1H, H-4), 5.59 (d, J = 3.9 Hz, 1H, H-3), 5.90 (dd, J = 10.5 and J = 1.4 Hz, 1H, H-3'), 6.06 (dd, J = 17.1 and J = 10.5 Hz, 1H, H-2'), 6.11 (d, J = 3.9 Hz, 1H, H-1), 6.42 (dd, J = 17.1 and J = 1.4 Hz, 1H, H-3'), 9.67 (s, 1H, CHO) ppm; $^{13}$C NMR ($CDCl_3$, DEPT) δ 26.1 ($CH_3$), 26.7 ($CH_3$), 77.1 (C-3), 82.9 (C-2), 83.3 (C-4), 105.5 (C-1), 112.9 (C-6), 126.7 (C-2'), 132.8 (C-3'), 164.3 (C-1'), 196.7 (CHO) ppm; LREIMS m/z (relative intensity): 227 ($M^+$ - 15, 18), 213 (24), 155 (44), 86 (29), 84 (45), 55 (100).

*3-O-acryloyl-1,2-O-isopropylidene-α-D-xylofuranose (***13***) and 5-O-acryloyl-1,2-O-isopropylidene-α-D-xylofuranose (***14***).*

To a stirred mixture of **12** (0.242 g; 1 mmol), tetrabutylammonium cyanoborohydride (TBAC, 0.556 g; 2 mmol) and methyl orange (5 mg) in methyl alcohol (2 mL) was added dropwise a 2N methanolic HCl solution until the mixture becomes red. The solvent was removed under reduced pressure and water (10 mL) was added. The aqueous layer was extracted with $CH_2Cl_2$ (3 X 15 mL), dried over anhydrous $Na_2SO_4$ and the solvent removed under reduced pressure. The residue was purified by column chromatography on silica gel (20 % ethyl acetate in n-hexane as the eluant) giving the mixture of **13** and **14** (0.161 g; 66 %) as a colorless oil. IR (neat) 3478, 2989, 2938, 1729, 1635, 1410, 1370, 1263, 1190, 1075, 1018, 887, 861 and 811 $cm^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$) δ 1.30 (s, 3H, $CH_3$), 1.50 (s, 3H, $CH_3$ of **14**), 1.54 (s, 3H, $CH_3$ of **13**), 1.80 (b, OH), 3.21 (b, OH), 3.62 (dd, J = 11.9 and J = 6.3 Hz, 1H, H-5 of **13**), 3.82 (dd, J = 11.9 and J = 6.0 Hz, 1H, H-5 of **13**), 4.08-4.70 (m, 7H, H-2, H-4, H-3 of **14** and H-5 of **14**), 5.29 (d, J = 3.0 Hz, 1H, H-3 of **13**), 5.91 (dd, J = 6.8 and 1.2 Hz, 1H, H-3' of **14**), 5.94 (dd, J = 10.5 and 1.5 Hz, 1H, H-3' of **13**), 5.95 (d, J = 6.0 Hz, 1H, H-1 of **13**), 5.96 (d, J = 2.4 Hz, 1H, H-1 of **14**), 6.14 (dd, J = 11.3 and J = 6.8 Hz, 1H, H-2' of **14**), 6.15 (dd, J = 17.5 and 10.5 Hz, 1H, H-2' of **13**), 6.47 (dd, J = 11.2 and J = 1.2 Hz, 1H, H-3' of **14**), 6.49 (dd, J = 17.0 and J = 2.0 Hz, 1H, H-3' of **13**) ppm; $^{13}$C NMR ($CDCl_3$, DEPT) δ 26.0 ($CH_3$), 26.4 ($CH_3$ of **13**), 26.6 ($CH_3$ of **14**), 59.5 (C-5 of **13**), 61.3 (C-5 of **14**), 74.3 (C-3 of **14**), 76.3 (C-3 of **13**), 78.2 (C-2 of **14**), 79.5 (C-2 of **13**), 83.3 (C-4 of **13**), 84.9 (C-4 of **14**), 104.4 (C-1 of **13**), 104.6 (C-1 of **14**), 111.6 (C-6 of **14**), 112.1 (C-6 of **14**), 127.0 (C-2' of **13**), 127.5 (C-2' of **14**), 131.9 (C-3' of **13**), 132.6 (C-3' of **14**), 165.4 (C-1' of **13**), 166.6 (C-1' of **14**) ppm; LREIMS m/z (relative intensity): 229 ($M^+$ - 15, 50), 155 (20), 115 (23), 85 (21), 59 (39), 55 (100).

*3-O-acryloyl-5-O-benzoyl-1,2-O-isopropylidene-α-D-xylofuranose (***15***) and 3-O-benzoyl-5-O-acryloyl-1,2-O-isopropylidene-a-D-xylofuranose (***16***).*

A suspension of benzoic acid (1.22 g; 10 mmol), a 1:1 mixture **13** and **14** (2.508 g; 11 mmol), DCC (2.27 g; 11 mmol) and DMAP (0.122 g, 1 mmol) in dry $CH_2Cl_2$ (100 mL) was stirred for 4 days at room temperature. The reaction mixture was filtrated to remove N,N-dicyclohexylurea and the residue was washed with ether. The organic phase was washed with water (3 x 100 mL), 5% aqueous HOAc (3 x 100 mL), again with water (3 x 100 mL) and dried over anhydrous $Na_2SO_4$. The solvent was removed under reduced pressure and the crude residue chromatographed on a silica gel column eluted with 10 % ethyl acetate in n-hexane to give a 1:1 mixture of **15** and **16** (2.59 g; 71 %) as a colorless oil. IR (neat) 3071, 3032, 2990, 2938, 1728, 1634, 1602, 1452, 1381, 1269, 1187, 1072, 1024, 829 and 809 $cm^{-1}$; $^1$H NMR (200 MHz, $CDCl_3$) d 1.30 (s, 3H, $CH_3$ of **16**), 1.34 (s, 3H, $CH_3$ of **15**), 1.56 (s, 3H, $CH_3$ of **15**), 1.57 (s, 3H, $CH_3$ of **16**), 4.35-4.75 (m, 4H, H-2, H-4 and H-5), 5.53 (d, J = 3.0 Hz, 1H, H-3 of **16**), 5.44 (d, J = 3.0 Hz, 1H, H-3 of **15**), 5.88 (dd, J = 10.0 and J = 2.0 Hz, 1H, H-3' of **15**), 5.91(dd, J = 10.5 and J = 1.5 Hz, 1H, H-3' of **16**), 6.01 (d, J = 4.0 Hz, 1H, H-1 of **15**), 6.04 (d, J = 4.0 Hz, 1H, H-1 of **16**), 6.10 (dd, J = 17.5 and J = 11.0 Hz, 1H, H-2' of **16**), 6.13 (dd, J = 17.0 and J = 10.0 Hz, 1H, H-2' of **15**), 6.42 (dd, J = 17.5 and J = 1.5 Hz, 1H, H-3' of **16**), 6.47 (dd, J = 17.0 and J = 2.0 Hz, 1H, H-3' of **15**), 7.39-7.66 (m, 3H, Ph), 7.98-8.08 (m,2H, Ph) ppm; $^{13}$C NMR ($CDCl_3$, DEPT) δ 26.0 ($CH_3$), 26.4 ($CH_3$), 61.4 (C-5 of **15**), 61.5 (C-5 of **16**), 76.0 (C-3 of **15**), 76.4 (C-3 of **16**), 76.6 (C-2 of **15**), 76.7 (C-2 of **16**), 83.1(C-4), 104.8 (C-1), 112.1 (C-6), 127.0 (C-2' of **15**),

127.5 (C-2' of **16**), 128.3, 129.3 and 129.5 (Ph), 131.3 (C-3' of **15**), 132.2 (C-3' of **16**), 132.9 (Ph), 133.4 (Ph), 164.4 (PhC=O of **15**), 164.9 (PhC=O of **16**), 165.4 (C-1' of **15**), 165.8 (C-1' of **15**) ppm; LREIMS m/z (relative intensity): 333 ($M^+$ - 15, 26), 283 (19), 105 (77), 55 (100).

*3-O-benzyl-1,2:5,6-di-O-isopropylidene-α-D-glucofuranose (**18**).*

To a solution of **17** (1.8g, 6,9 mmol) in dry THF (8 mL) at 0°C was added dropwise a suspension of NaH (60% oil dispersion, 0.306 g, 7.65 mmol) and tetrabutylammonium iodide (0.02 g, 0.054 mmol) in dry THF (5 mL). The mixture was warmed up to room temperature for the addition of benzyl bromide (0.9 mL, 7.6 mmol) and stirred at 50 °C for two hours. After the addition of MeOH (2 mL) the mixture was stirred at the same temperature for additional two hours, cooled, filtered and concentrated under reduced pressure. The resulting oil was diluted with $CH_2Cl_2$ (10 mL), washed with water (2 x 3 mL), dried over $Na_2SO_4$ and the solvent evaporated in a rotatory evaporator, furnishing a crude product that was purified on a silica gel column eluted with 10 % ethyl acetate in n-hexane to give **18** (2.4 g; 99 %) as a colorless oil. IR (neat): 3072, 3039, 2987, 2935, 2893, 1500, 1450, 1380, 1257, 1219, 1170, 1077, 1028, 891, 850, 741 and 700 $cm^{-1}$; $^1H$ NMR (200 MHz, $CDCl_3$) d 1.32 (s, 3H, $CH_3$), 1.39 (s, 3H, $CH_3$), 1.46 (s, 3H, $CH_3$), 1.52 (s, 3H, $CH_3$), 3.98-4.21 (m, 4H, H-3, H-4 and H-6), 4.40 (dt, J = 7.8 and J = 5.9 Hz, 1H, H-5), 4.61 (d, J = 3.7 Hz, 1H, H-2), 4.68 (d, J = 2.6 Hz, 2H, H-7), 5.93 (d, J = 3.7 Hz, 1H, H-1), 7.25-7.45 (m, 5H, Ph) ppm; $^{13}C$ NMR ($CDCl_3$, DEPT) δ 26.0 ($CH_3$), 26.8 ($CH_3$), 27.3 ($CH_3$), 27.4 ($CH_3$), 67.9 (C-6), 72.9 (C-9), 73.0 (C-5), 81.8 (C-3), 82.2 (C-2), 83.2 (C-4), 105.8 (C-1), 109.5 (C-8), 112.3 (C-7), 128.2, 128.3, 128.9 and 138.1(Ph); LREIMS m/z (relative intensity): 335 ($M^+$ - 15, 6), 101 (27), 91 (100).

*3-O-benzyl-1,2-O-isopropylidene-α-D-xylofuranose (**20**).*

To a solution of **19** (1.5 g, 4.8 mmol) in 10 % aqueous ethanol (35 mL) under vigorous stirring was added portionwise $NaIO_4$ (1.5 g; 7 mmol). After three hours, the reaction was quenched by adding $CH_2Cl_2$ (10 mL) and filtration of the solids. To the cooled (0°C) organic phase was added dropwise a suspension of $NaBH_4$ (0.360 g, 9.5 mmol) in 20 % aqueous ethanol (13 mL). The mixture was stirred overnight at room temperature and quenched by the addition of excess ammonium chloride and 10 % aqueous sodium thiosulfate (40 mL). The product was extracted with $CH_2Cl_2$ (3 x 20 mL), dried over $Na_2SO_4$ and the solvent removed under reduced pressure to give **20** (1.25 g: 92 %) as a colorless oil. IR (neat): 3500, 3072, 3039, 2987, 2934, 2893, 1497, 1455, 1377, 1170, 1076, 1017, 891, 863, 740, 699 and 606 $cm^{-1}$; $^1H$ NMR (200 MHz, $CDCl_3$) δ 1.30 (s, 3H, $CH_3$), 1.45 (s, 3H, $CH_3$), 2.00-2.50 (bs, 1H, OH), 3.82 and 3.93 (2 x dd, J = 5.8 and J = 11.7 Hz, 2H, H-5), 3.98 (d, J = 3.9 Hz, 1H, H-3), 4.26 (dt, J = 3.9 and J = 5.8 Hz, 1H, H-4), 4.47 and 4.69 (2 x d, J = 11.7 Hz, 2H, H-6), 4.62 (d, J = 3.9 Hz, 1H, H-2), 5.96 (d. J = 3.9 Hz, 1H, H-1), 7.20-7.45 (m, 5H, Ph) ppm; $^{13}C$ NMR ($CDCl_3$, DEPT) δ 26.0 ($CH_3$), 26.5 ($CH_3$), 60.5 (C-5), 71.6 (C-7), 80.1 (C-3), 82.1 (C-2), 82.2 (C-4), 104.7 (C-1), 111.5 (C-6), 127.4, 127.8, 128.3 and 136.9 (Ph) ppm; LREIMS m/z (relative intensity): 265 ($M^+$ - 15, 4), 249 ($M^+$-31, 2), 91 (100).

*3-O-benzyl-5-O-acryloyl-1,2-O-isopropylidene-α-D-xylofuranose (**8**).*

A suspension of acrylic acid (0.56 g; 10 mmol), **20** (2.80 g; 10 mmol), DCC (2.27 g; 11 mmol) and DMAP (0.122 g, 1 mmol) in dry $CH_2Cl_2$ (100 mL) was stirred for 4 days at room temperature. The reaction mixture was filtered to remove N,N-dicyclohexylurea and the residue was washed with ether. The organic phase was washed with water (3 x 100 mL), 5% aqueous HOAc (3 x 100 mL), again with water (3 x 100 mL) and dried over anhydrous $Na_2SO_4$. The solvent was removed under reduced pressure and the crude residue chromatographed on a silica gel column eluted with 10 % ethyl acetate in n-hexane to give **8** (2.34 g; 70 %) as a colorless oil. $[\alpha]_D^{25}$ -85° (c 2, $CHCl_3$); IR (neat): 3072, 3039, 2993, 2940, 2875, 1729, 1636, 1499, 1454, 1411, 1377, 1195, 1163, 1076, 1015, 891, 857, 812, 741 and 701 $cm^{-1}$; $^1H$ NMR (200 MHz, $CDCl_3$) δ 1.30 (s, 3H, $CH_3$), 1.45 (s, 3H, $CH_3$), 3.95 (bs, 1H, H-3), 4.25-4.48 (m, 3H, H-4, H-5), 4.47 and 4.67 (2 x d, J = 12.1 Hz, 2H, H-6), 4.61 (d, J = 3.7 Hz, 1H, H-2), 5.80 (dd, J = 1.6 and J = 10.0 Hz, 1H, H-3'), 5.95 (d, J = 3.6 Hz, 1H, H-1), 6.10 (dd, J = 10.0 and J = 17.2 Hz, 1H, H-2'), 6.39 (dd, J = 1.6 and J = 17.2 Hz, 1H, H-3'), 7.20- 7.40 (m, 5H, Ph) ppm; $^{13}C$ NMR ($CDCl_3$, DEPT) δ 26.0 ($CH_3$), 26.6 ($CH_3$), 62.1 (C-5), 71.6 (C-7), 77.8 (C-2), 81.3 (C-3), 81.8 (C-4), 105.0 (C-1), 111.6 (C-6), 127.5 (Ph), 127.8 (C-2'), 128.3 and 136.9 (Ph), 130.9 (C-3'), 165.6 (C-1'); LREIMS m/z (relative intensity): 334 ($M^+$, 5), 333 ($M^+$- 1, 26), 139 (21), 105 (100), 91 (88), 77 (21), 55 (38).

*General Procedure for the Diels-Alder Reactions of Acrylates* **6** *and* **8**.

A typical catalyzed asymmetric Diels-Alder reaction was conducted as follows: To a -78°C cooled solution of the acrylates **6** or **8** (0.5 mmol) in dry $CH_2Cl_2$ (10 mL) under a nitrogen atmosphere was added dropwise 1M $Et_2AlCl$ in hexanes (0.6 mL; 0.6 mmol) and the mixture was stirred for 45 minutes. Freshly distilled cyclopentadiene (0.4 mL; 5 mmol) was added dropwise and the mixture was stirred for 2 hours and allowed to reach room temperature. The reaction was quenched with $CaCO_3$ (0.2 g), stirred for additional 15 minutes and dried over $Na_2SO_4$. Solvent removal in vacuum was followed

by column chromatography on silica gel (20 % AcOEt in n-hexane as the eluant) to afford the mixtures of cycloadducts (*R*)-**21a, b** and (*S*)-**22a, b** along with the respective minor *exo* adducts **23a, b**.

*3-O-[(1'R,4'R)-bicyclo-[2.2.1]hept-2'-ene-5'-formyl]-4,5-di-O-benzoyl-1,2-O-isopropyl-idene-β-D-fructopyranose (R)*-**21a** *and (S)*-**22a (*endo* + *exo*)** was obtained as a pale yellow oil in a 64 % yield. IR (neat): 3063, 2988, 2942, 2882, 1731, 1600, 1453, 1374, 1282, 1180, 1072, 1030, 974, 909, 885, 760 and 712 $cm^{-1}$; $^1H$ NMR (200MHz, $CDCl_3$) δ 1.10-1.60 (m, 8H, H-3'and H-7' of **21a** + **22a** and 2 $CH_3$), 1.68 (bs, 1H, H-7' of **23a**), 1.70-1.94 (m, 1H, H-3'), 2.16 (m, 1H, H-2' of **23a**), 2.70-2.98 (m, 3H, H-4' of **23a**, H-2' of **21a** + **22a** and H-1'), 3.04 (bs, 1H, H-4' of **22a**), 3.19 (bs, 1H, H-4' of **21a**), 3.90-4.35 (m, 4H, H-1 and H-6), 5.51 (dd, 1H, J = 3.0 and J = 6.0 Hz, H-6' of **22a**), 5.60-5.77 (m, 3H, H-3, H-4 and H-5), 5.80 (dd, 1H, J = 3.0 and J = 6.0 Hz, H-6' of **21a**), 5.88 (dd, 1H, J = 3.0 and J = 6.0 Hz, H-5' of **22a**), 5.97 (dd, 1H, J = 3.0 and J = 6.0 Hz, H-5' of **21a**), 6.00-6.09 (m, 2H, H-5' and H-6' of **23a**), 7.25-7.65 (m, Ph), 7.80-7.95 (m, Ph), 8.00-8.10 (m, Ph) ppm; $^{13}C$ NMR ($CDCl_3$, DEPT) δ 25.8, 25.9, 26.0 and 26.2 ($CH_3$), 28.6, 29.2, 29.4 and 30.0 (C-3'), 41.99, 42.13, 42.85 and 42.97 (C-1' and C-4' of **21a** + **22a**), 45.04 and 45.37 (C-2' of **21a** + **22a**), 49.33 (C-7'), 62.2 and 62.3 (C-6), 66.5 and 66.7 (C-4), 69.7 and 69.9 (C-3 and C-5), 71.7 and 71.8 (C-1), 104.4 and 104.5 (C-2), 112.0 (C-7), 128.1, 128.2, 128.9, 129.4 and 129.5 (Ph), 131.8 and 132.1 (C-6' of **21a** + **22a**), 133.0 (Ph), 135.1 and 135.2 (C-6' of **23a**), 137.3 and 137.7 (C-5), 165.1, 165.2 and 165.5 (benzoyl C=O), 174.0 and 174.1 (acryloyl C=O of **21a** + **22a**), 176.0 and 176.2 (acryloyl C=O of **23a**); LREIMS m/z (relative intensity): 548 ($M^+$, 3), 533 ($M^+$ - 15, 5), 490 425 (20), 121 (33), 105 (100), 83 (43), 84 (68), 97 (16), 66 (15), 55 (21).

*3-O-benzyl-5-O-[(1'R,4'R)-bicyclo-[2.2.1]hept-2'-ene-5'-formyl]-1,2-O-isopropylidene-α-D-xylofuranose (R)*-**21b** *and (S)*-**22b (*endo* + *exo*)** was obtained as a colorless oil in a 50 % yield. IR (neat): 3072, 3030, 2979, 2940, 2870, 1732, 1497, 1455, 1374, 1213, 1166, 1076, 1022, 891, 859, 738, 712 and 699 $cm^{-1}$; $^1H$ NMR (200MHz, $CDCl_3$) d 1.20-1.60 (m, 9H, H-3', H-7' of **21b** + **22b** and 2 $CH_3$), 1.70 (bs, 1H, H-7' of **23b**), 1.80-2.00 (m, 1H, H-3'), 2.19-2.30 (m, 1H, H-2' of **23b**), 2.85-3.05 (m, 3H, H-1', H-2' of **21b** + **22b** and H-4' of **23b**), 3.14-3.26 (m, 1H, H-4' of **21b** + **22b**), 3.93-4.01 (m, 1H, H-3), 4.18-4.74 (m, 6H, H-2, H-4, H-5 and H-6), 5.92 (dd, 1H, J = 3.0 and J = 6.0 Hz, H-6' of **22b**), 5.96-6.00 (m, 2H, H-6' of **21b** and H-1), 6.05-6.14 (m, 2H, H-5' and H-6' of **23b**), 6.14-6.22 (m, 1H, H-5' of **21b** + **22b**), 7.20-7.50 (m, Ph) ppm; $^{13}C$ NMR ($CDCl_3$, DEPT) d 26.1 ($CH_3$), 26.6 ($CH_3$), 29.0, 29.1, 30.1 and 30.2 (C-3'), 42.3, 42.7, 42.9 and 43.0 (C-1' and C-4' of **21b** + **22b**), 45.5 and 45.6 (C-2' of **21b** + **22b**), 46.1 and 46.5 (C-2' of **23b**), 49.3 and 49.4 (C-7'), 61.6, 61.8 and 62.0 (C-5), 71.7 (C-7), 77.8 and 77.9 (C-2), 81.3, 81.4, 81.5 and 81.7 (C-3 and C-4), 105.0 (C-1), 111.5 (C-6), 127.4, 127.5, 127.8, 127.9 and 128.3 (Ph), 132.0 and 132.1 (C-6' of **21b** + **22b**), 135.4 and 135.5 (C-6' of **23b**), 137.0 (Ph), 137.5 and 137.6 (C-5' of **21b** + **22b**), 137.8 and 137.9 (C-5' of **23b**), 174.2-176.4 (C=O); LREIMS m/z (relative intensity): 385 ($M^+$ - 15, 1), 91 (100), 66 (15).

## Acknowledgments

To INT (Instituto Nacional de Tecnologia) and to PADCT-CNPq for the financial support, as well as to Prof. Dr. Antônio Jorge R. da Silva (NPPN) for NMR and Mass spectra. V.F.F., S.P. and P.R.R.C. are grateful to CNPq for individual research fellowships.

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*Received: September 23, 1999*