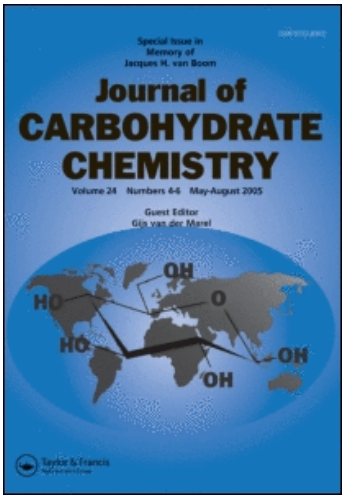

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HIGHLY DIASTEREOSELECTIVE DIELS-ALDER REACTIONS OF ACRYLIC ESTERS INCORPORATED INTO A VARIETY OF HEXOPYRANOSIDES

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HIGHLY DIASTEREOSELECTIVE DIELS-ALDER REACTIONS OF ACRYLIC ESTERS INCORPORATED INTO A VARIETY OF HEXOPYRANOSIDES

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This paper is dedicated to Professor Joachim Thiem with respect and admiration on the occasion of his 60th birthday.

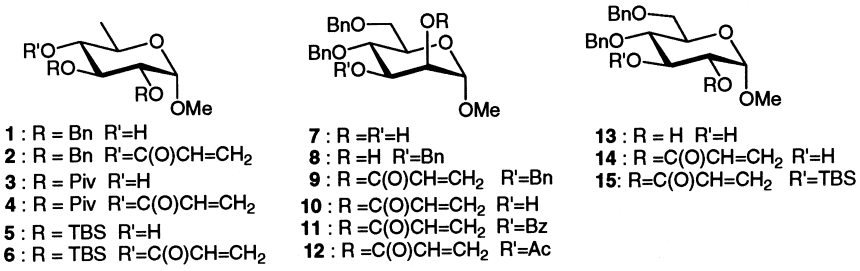
ABSTRACT

The Diels-Alder reactions of a variety of hexopyranosides carrying an acrylic ester with cyclopentadiene were examined. Some acrylic esters provided the cycloaddition products carrying a norbornene carboxylate with a high level of diastereoselectivity. Plausible mechanisms are presented for the cases of a 4-*O*-acryloyl-6-deoxy-α-D-glucopyranosidic and 2-*O*-acryloyl-α-D-glucopyranosidic substrates. By reductive removal of the carbohydrate templates from the adducts, either 2*S* or 2*R*-enriched 5-norbornene-2-methanol were obtained.

INTRODUCTION

The use of chiral auxiliaries prepared from readily available natural products, such as carbohydrates, is one of the promising approaches for asymmetric synthesis of chiral compounds.[1,2] Several carbohydrate derivatives are sources of chiral nonracemic materials, from which synthetically useful auxiliaries have been designed and prepared.[3–6] We have studied extensively the utility of hexopyranose derivatives as chiral templates for stereoselective carbon-carbon bond forming re-

*Corresponding author.

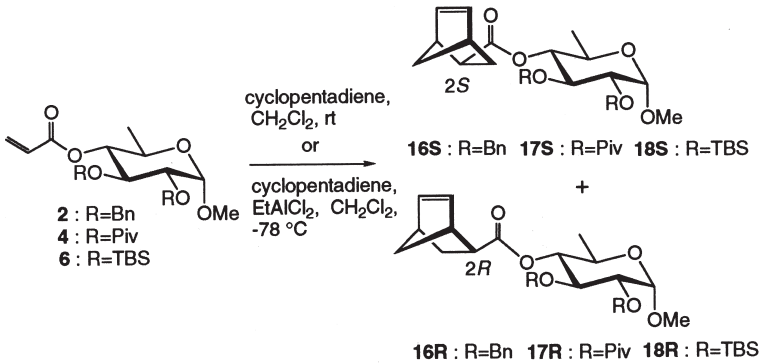


Scheme 1.

actions, and reported the highly stereoselective 1,4-conjugate additions of organocopper reagents[7] or alkyl radicals[8] to a variety of hexopyranose-derived chiral crotonyl esters. In this paper, we report in detail the results on the intermolecular Diels-Alder reactions conducted using chiral acrylic esters incorporated into methyl α-D-gluco- and mannopyranosidic templates.[9,10]

RESULTS AND DISCUSSION

4-*O*-Acrylic ester derivatives of methyl 6-deoxy-α-D-glucopyranoside **2**, **4**, and **6** (Scheme 1) as substrates for the attempted Diels-Alder reaction, were prepared from known 2,3-*O*-alkylated **1**,[7] 2,3-*O*-acylated **3**,[7] or 2,3-*O*-silylated **5**[8] methyl 6-deoxy-α-D-glucopyranosides, respectively, by acryloylation at 4-OH. Acrylic esters incorporated at C-2 of methyl α-D-mannopyranoside **9**, **11**, and **12** (Scheme 1) were prepared from the known 4,6-*O*-benzyl derivative of methyl α-D-mannopyranoside **7**[11] via regioselective benzylation of 3-OH (for **8**) or regioselective acryloylation of 2-OH (for **10**) followed by acryloylation (for **9**) or acylation (for **11** and **12**), respectively. On the other hand, 2-acrylic ester **15** (Scheme 1) was prepared from methyl 4,6-*O*-benzyl-α-D-glucopyranoside **13**,[12] which was in turn prepared from methyl 4,6-*O*-benzylidene-α-D-glucopyranoside in an overall yield



Scheme 2.

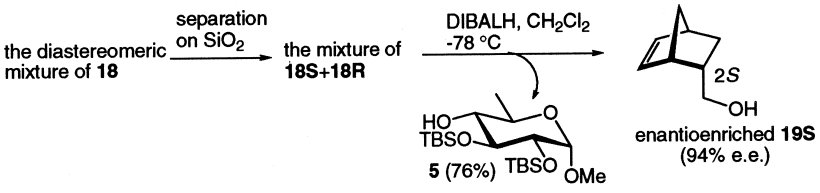
Table 1. Diels-Alder Reaction of the Substrates **2, 4** and **6** Under Thermal Conditions[a]

Entry	Substrate	Yield[b]	*Endo*:*Exo*[c]	*Endo-S*:*R*[c]
1	**2**	96	79:21	71:29
2	**4**	96	89:11	87:13
3	**6**	97	80:20	>95:5

[a] Cyclopentadiene, CH_2Cl_2, rt, 2–5 days. [b]Combined yield of diastereomeric adducts (%). [c]Determined by ^{1}H NMR analysis.

of 62% (four steps), via regioselective acryloylation of 2-OH followed by silylation of 3-OH.

We investigated first the Diels-Alder reactions of the methyl 6-deoxy-α-D-glucopyranosidic substrates **2**, **4**, and **6** with cyclopentadiene (Scheme 2). The results under thermal conditions (conducted at room temperature) are shown in Table 1. In every case, the Diels-Alder reaction proceeded efficiently to provide the adduct as a mixture of diastereomers (*endo-S*, *endo-R*, and *exo* isomers). The ratio of the *endo*/*exo* isomers and the diastereomeric ratio of the two *endo* adducts (**16S**:**16R**, **17S**:**17R**, or **18S**:**18R**) were determined by ^{1}H NMR analysis on the basis of the integration ratio of ring protons on each norbornene part in the diastereomeric mixture. In the case of 2,3-*O*-benzyl derivative **2**, moderate *endo*/*exo* selectivity and moderate diastereoselectivity in the π-facial attack leading to the two *endo*-adducts were observed (entry 1). The reaction of **4** or **6**, which possesses a bulkier substituent (R = Piv or TBS) at C-3, afforded the *endo*-S adduct **17S** or **18S** with improved diastereoselectivity (entries 2 and 3). However, the *endo*/*exo* selectivity was not satisfactorily high in each case. The absolute configuration for the newly formed norbornene ring was determined by comparison with the reported optical signs for both enantiomers of 5-norbornene-2-carboxylic acid and/or 2-methanol,[13–15] prepared by hydrolytic or reductive removal of the carbohydrate templates. In the case of the substrate **6**, the mixture of the *endo* adducts **18S/18R** was obtained after separating the minor *exo* adducts by chromatographic purification on silica gel (Scheme 3). Removal of the carbohydrate templates from this mixture was conducted by reductive cleavage using DIBALH to provide (2*S*) enriched 5-norbornene-2-methanol **19S**. The carbohydrate template **5** was recovered efficiently. The optical rotation of (2*S*)-enriched **19S** was $[\alpha]^{22}_D$ −69° (*c* 0.195,



Scheme 3.

Table 2. Diels-Alder Reaction of the Substrates **2**, and **4** in the Presence of $EtAlCl_2$[a]

Entry	Substrate	Yield[b]	*Endo*:*Exo*[c]	*Endo-S*:*R*[c]
1	**2**	63	>95:5	ca. 1:1
2	**4**	79	>95:5	10:90
3	**6**	NR[d]	—	—

[a] $EtAlCl_2$ (2 eq), cyclopentadiene, CH_2Cl_2, −78°C, 15 min. [b]Combined yield of diastereomeric adducts (%). [c]Determined by ^1H NMR analysis. [d]Reaction did not take place.

EtOH), and that of enantiopure (2*S*)-*endo*-5-norbornene-2-methanol is $[\alpha]_D$ −76.6° (95% EtOH). Therefore, the absolute stereochemistry of **19S** was established. Benzoylation of the (2*S*) enriched **19S** and HPLC analysis (serial connection of Chiralcel OD+OD—H; hexane:EtOH = 300:1) of the resulting benzoate verified that the enantiomeric ratio (2*S* :2*R*) of **19** was 97:3.

The results of the Diels-Alder reactions of **2** and **4** conducted in the presence of $EtAlCl_2$ (2 molar equivalents) as Lewis acid are summarized in Table 2. The Diels-Alder reactions proceeded at −78 °C efficiently to provide a mixture of the *endo* adducts **16S/16R** or **17S/17R** predominantly although the combined yield of two *endo* adducts was moderate in each case (entries 1 and 2). In the case of **4**, highly diastereoselective formation of the *endo* adduct **17R** was observed. Interestingly, the p-facial selectivity in the Lewis acid mediated *endo* mode Diels-Alder

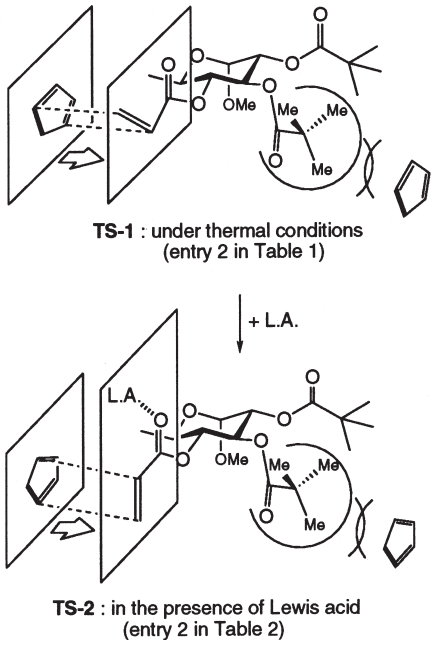
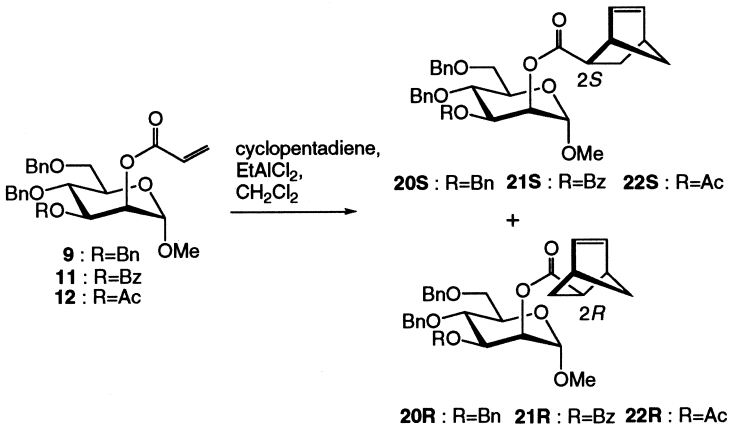


Figure 1. Plausible transition states of Diels-Alder reactions for substrate 4.



Scheme 4.

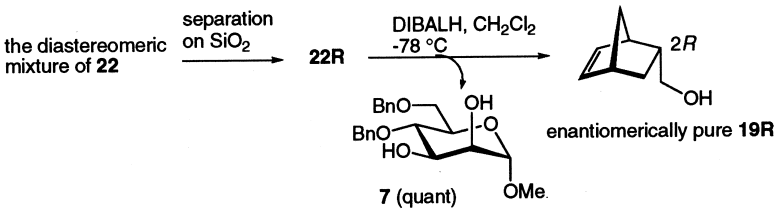
reaction of **4** was opposite to that observed under the thermal conditions (entry 2 in Table 1 vs. entry 2 in Table 2). We propose a plausible transition state mechanism to interpret this reverse p-facial selectivity observed using the substrate **4** under the thermal or the Lewis acid mediated conditions (Figure 1). In the case of the thermal conditions, the dienophile part is apt to exist in an *s-cis, syn* conformation (**TS-1**). Then cyclopentadiene approaches from the less hindered side by reason of avoiding the steric hindrance expected by the presence of a substituent at C-3 such as a pivaloyloxy group in the case of **4**. Consequently, the *endo-S* adduct **17S** was obtained predominantly. By comparison, in the presence of $EtAlCl_2$, the dienophile part is likely to change to *s-trans, syn* conformation as a result of Lewis acid coordination to the acryloyl carbonyl.[16,17] Cyclopentadiene can then favorably approach the dienophile part from the less hindered side (**TS-2**). As a result, the *endo-R* adduct **17R** was obtained predominantly under the latter conditions.

Next we investigated the Diels-Alder reactions of the α-D-mannopyranosidic substrates **9**, **11**, and **12** with cyclopentadiene (Scheme 4). The Diels-Alder reactions of these substrates under thermal conditions proceeded with no significant π-facial selectivities (d.r. of two *endo* adducts was *ca.* 1 : 1 in every case). In contrast, the Diels-Alder reactions in the presence of Lewis acid proceeded stereoselectively, especially in the cases of **11** and **12**. The results are summarized in Table 3.

Table 3. Diels-Alder Reaction of the Substrates **9**, **11**, and **12** in the Presence of $EtAlCl_2$[a]

Entry	Substrate	Yield[b]	*Endo*:*Exo*[c]	*Endo-S*:*R*[c]
1	**9**	83	>95:5	33:67
2	**11**	84	>95:5	9:91
3	**12**	98	>95:5	11:89

[a] $EtAlCl_2$ (2 eq), cyclopentadiene, CH_2Cl_2, −78°C, 15 min. [b]Combined yield of diastereomeric adducts (%). [c]Determined by ^1H NMR analysis.



Scheme 5.

The Diels-Alder reaction proceeded at −78 °C to provide a mixture of two *endo* adducts **20S/20R**-**22S/22R** with high *endo/exo* selectivity. Also, the substrates **11** and **12** possessing an acyloxy substituent at C-3 provided the respective *endo*-R adducts **21R** and **22R** with remarkably high diastereoselectivity (entry 1 vs. entries 2 and 3). As shown in Scheme 5, the diastereomerically homogeneous *endo-R* adduct **22R** was separated from other adducts by chromatographic separation on silica gel. After reductive cleavage of the carbohydrate template, enantiomerically pure (2*R*)-*endo*-5-norbornene-2-methanol **19R** was obtained. The carbohydrate template **7** was recovered quantitatively.

We investigated the influence of the stoichiometry of Lewis acid on the Diels-Alder reaction using **4** or **11** as the substrate. The results are summarized in Table 4. Independent of the amount of $EtAlCl_2$, high *endo*/*exo* selectivities were observed in every case. Despite the low yield of the reaction, the substrate **4** provided **17R** with high π-facial selectivity using 1 equiv of $EtAlCl_2$.

Finally, we conducted the Diels-Alder reaction of another glucopyranose derivative **15**, which was more accessible than the 6-deoxyglucopyranosidic substrates **2**, **4**, and **6** (Scheme 6). As shown in Table 5, the Diels-Alder reaction under thermal conditions provided the *endo-R* adduct **23R** preferentially although the *endo*/*exo* selectivity was moderate. On the other hand, the Lewis acid promoted Diels-Alder reaction proceeded smoothly at −78 °C to provide the *endo-S* adduct **23S** with high *endo*/*exo* and π-facial selectivities. As shown in Figure 2, this stereochemical reversal of the π-facial selectivity can be interpreted using the analogous transition state argument described for the case of **4**. The conformational

Table 4. Influence of $EtAlCl_2$ Stoichiometry[a]

Entry	Substrate	$EtAlCl_2$ (eq.)	Yield[b] (%)	*Endo*:*exo*[c]	*Endo-S*:*R*[c]
1	**4**	1	*ca.* 30	>95:5	12:88
2	**4**	2	79	>95:5	10:90
3	**4**	4	85	>95:5	8:92
4	**11**	1	83	>95:5	17:83
5	**11**	2	85	>95:5	9:91
6	**11**	4	84	>95:5	10:90

[a] $EtAlCl_2$, cyclopentadiene, CH_2Cl_2, −78°C, 15 min. [b] Combined yield of diastereomeric adducts (%). [c] Determined by ^1H NMR analysis.

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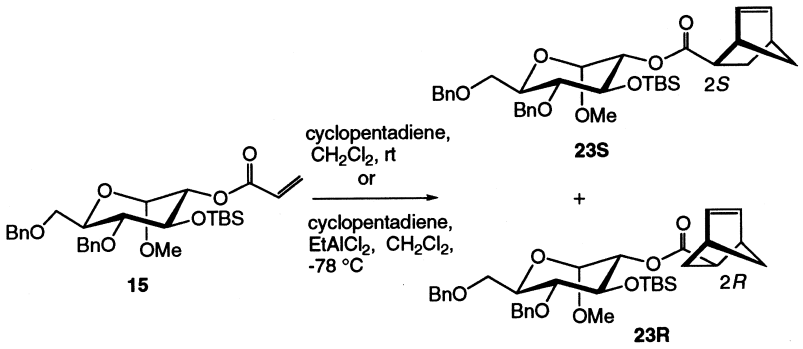


Scheme 6.

Table 5. Diels-Alder Reaction of the Gluco-Type Substrate **15**

Entry	$EtAlCl_2$ (eq.)	Time/temp.	Yield[a]	*Endo*:*exo*[b]	*Endo-S*:*R*[b]
1	—	2 days/rt	96	74:26	9:91
2	2	1 h/−78°C	97	94:6	92:8

[a] Combined yield of diastereomeric adducts (%). [b] Determined by ^{1}H NMR analysis.

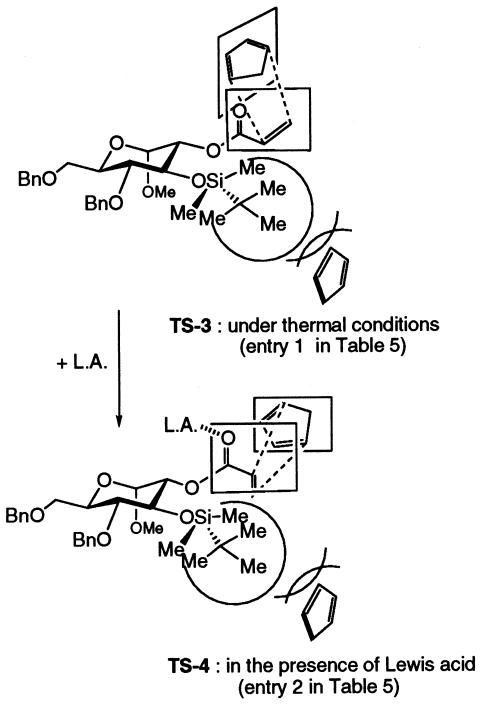
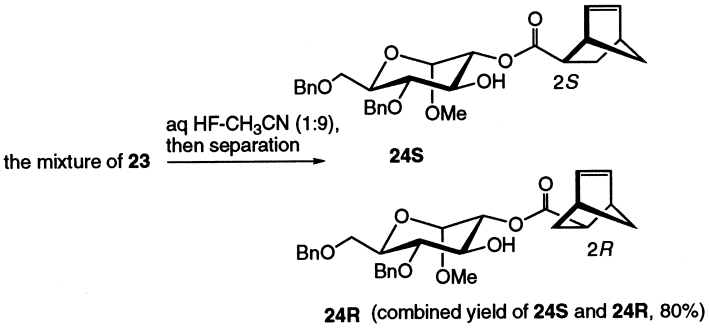


Figure 2. Plausible transition states of Diels-Alder reactions for substrate 15.



Scheme 7.

change of the acryloyl ester part in the presence of $EtAlCl_2$ is responsible for the reversal of the π-facial selectivity (**TS-3** vs **TS-4**). As shown in Scheme 7, the mixture of the *endo*-adducts **24S/24R** was readily obtained by separation of the exo-isomers from the mixture of the adducts **23** after desilylation of the 2-*O*-TBS group.

In summary, we have found a novel diastereoselective Diels-Alder reaction realized on the carbohydrate templates. The present work provides a practical method to prepare optically active chiral norbornene derivatives. In some cases, the predominant *endo* adducts can be readily separated from the other diastereomers. Removal of the carbohydrate templates from the *endo*-adducts provides enantiomerically enriched or pure (2*S*) or (2*R*)-*endo*-5-norbornene-2-methanol.

EXPERIMENTAL

General Methods. Specific rotations were measured in a 10 mm cell by a JASCO DIP-370 instrument. IR spectra were recorded by a JASCO FT-IR-200 spectrometer. ^1H (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded by a JEOL JNM-LA 300FT NMR spectrometer in $CDCl_3$ solution with tetramethylsilane as an internal standard. High-resolution mass spectra (HRMS) were measured by a JEOL JMS-GC MATE spectrometer (EI, 70 eV). Thin-layer chromatography (TLC) was performed on Merck Kieselgel 60 F_{254} plates. Crude reaction mixtures and extractive materials were purified by chromatography on silica gel 60K070 (Katayama Chemical) or Wakogel C-300 (Wako Chemicals). Unless otherwise described, reactions were carried out at room temperature. Combined organic extracts were dried over anhydrous Na_2SO_4. Solvents were removed from the reaction mixture or combined organic extracts by concentration under reduced pressure using an evaporator at a bath temperature of 30–40 °C.

The Preparation of the Substrates 2, 4, 6 and 9. To a cooled (−18 °C) stirred solution of **1**[7] (644 mg, 1.56 mmol) in CH_2Cl_2 (15 mL) were added acryloyl chloride (0.26 mL, 3.2 mmol) and triethylamine (0.88 mL, 6.3 mmol). The mixture

was stirred for 20 min and quenched with saturated aqueous $NaHCO_3$, diluted with $CHCl_3$ (100 mL) and then washed with saturated aqueous $NaHCO_3$ (50 mL × 3). The organic layer was dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc:hexane, 1:7) to give 566 mg (76%) of **2**. Analogously, the substrates **4**, **6**, and **9** were prepared from **3**[7] (75%), **5**[8] (98%), and **8**[11] (53%), respectively.

Methyl 4-*O*-acryloyl-2,3-di-*O*-benzyl-6-deoxy-α-D-glucopyranoside (2). Compound **2** was obtained as a colorless oil : TLC, R_f 0.37 (EtOAc:hexane, 1:3); $[\alpha]_D^{28.0}$ +28.7° (*c* 0.66, $CHCl_3$); IR (neat) 3100−2800, 1735, 1635 cm^{-1}; ^1H NMR δ 1.13 (d, *J* = 6.1 Hz, 3H, 6-CH_3), 3.39 (s, 3H, OMe), 3.58 (dd, *J* = 3.7, 9.5 Hz, 1H, H-2), 3.79 (dq, *J* = 9.6, 6.1 Hz, 1H, H-5), 3.91 (t, *J* = 9.4 Hz, 1H, H-3), 4.54 (d, *J* = 3.6 Hz, 1H, H-1), 4.63, 4.84 (ABq, *J* = 11.2 Hz, 2H, C*H*$_2$—Ph), 4.65, 4.80 (ABq, *J* = 12.0 Hz, 2H, C*H*$_2$—Ph), 4.83 (t, *J* = 9.6 Hz, 1H, H-4), 5.84 (dd, *J* = 1.5, 10.4 Hz, 1H, COCH═C*H*H), 6.05 (dd, *J* = 10.4, 17.3 Hz, 1H, COC*H*═CHH), 6.40 (dd, *J* = 1.5, 17.3 Hz, 1H, COCH═CH*H*), 7.24–7.35 (m, 10H, Ph × 2); ^{13}C NMR δ 17.32, 55.29, 65.34, 73.46, 75.27, 75.39, 78.94, 79.86, 98.17, 127.48, 127.93 × 4, 128.11, 128.14, 128.27 × 2, 128.45 × 2, 131.28, 138.06, 138.47, 165.15. HRMS: Calcd for $C_{24}H_{28}O_6$ $(M)^+$*m/z*: 412.1886. Found: 412.1883.

Methyl 4-*O*-acryloyl-6-deoxy-2,3-di-*O*-pivaloyl-α-D-glucopyranoside (4). Compound **4** was obtained as colorless crystals: mp 71.0–73.0 °C; TLC, R_f 0.75 (EtOAc:hexane, 1:4); $[\alpha]_D^{25.0}$ +124° (*c* 1.59, $CHCl_3$); IR (neat) 3100−2800, 1740, 1635 cm^{-1}; ^1H NMR δ 1.08, 1.17 (2s, 18H, OPiv × 2), 1.20 (d, *J* = 6.3 Hz, 3H, 6-CH_3), 3.39 (s, 3H, OMe), 3.93 (dq, *J* = 10.0, 6.3 Hz, 1H, H-5), 4.82 (dd, *J* = 3.8, 10.0 Hz, 1H, H-2), 4.90 (d, *J* = 3.8 Hz, 1H, H-1), 4.94 (t, *J* = 10.0 Hz, 1H, H-3), 5.56 (t, *J* = 10.0 Hz, 1H, H-4), 5.87 (dd, *J* = 1.2, 10.5 Hz, 1H, COCH═C*H*H), 6.05 (dd, *J* = 10.2, 17.2 Hz, 1H, COC*H*═CHH), 6.40 (dd, *J* = 1.2 Hz, 17.2 Hz, 1H, COCH═CH*H*); ^{13}C NMR δ 17.11, 26.88 × 3, 26.91 × 3, 38.57, 38.62, 55.40, 65.04, 69.17, 71.24, 73.56, 96.62, 127.58, 132.01, 164.79, 177.01, 177.61. HRMS: Calcd for $C_{19}H_{29}O_7$ (M—OCH_3)$^+$*m/z*: 369.1913. Found: 369.1903.

Methyl 4-*O*-acryloyl-2,3-di-*O*-*t*-butyldimethylsilyl-6-deoxy-α-D-glucopyranoside (6). Compound **6** was obtained as colorless crystals: mp 88.0–90.0 °C: TLC, R_f 0.64 (EtOAc:hexane, 1:8); $[\alpha]_D^{26.0}$ +70.0° (*c* 1.82, $CHCl_3$); IR (neat) 3100−2800, 1730, 1635 cm^{-1}; ^1H NMR δ 0.00, 0.07, 0.10, 0.10 (4s, 12H, (t-Bu)(*CH*$_3$)$_2$Si × 2), 0.80, 0.92 (2s, 18H, (*t-Bu*)(CH$_3$)$_2$Si × 2), 1.11 (d, *J* = 6.6 Hz, 3H, 6-CH_3), 3.37 (s, 3H, OMe), 3.67 (dd, *J* = 3.7, 9.1 Hz, 1H, H-2), 3.73–3.79 (m, 1H, H-5), 3.94 (t, *J* = 9.1 Hz, 1H, H-3), 4.62 (d, *J* = 3.7 Hz, 1H, H-1), 4.75 (t, *J* = 9.1 Hz, 1H, H-4), 5.86 (dd, *J* = 1.7, 10.4 Hz, 1H, COCH═C*H*H), 6.13 (dd, *J* = 10.4, 17.4 Hz, 1H, COC*H*═CHH), 6.43 (dd, *J* = 1.7, 17.4 Hz, 1H, COCH═CH*H*); ^{13}C NMR δ −4.56, −4.43, −3.44, −3.03, 17.53, 17.76, 18.37, 25.79 × 3, 26.12 × 3, 55.02, 65.44, 71.80, 74.37, 76.52, 100.19, 128.49, 131.45, 165.30. HRMS: Calcd for $C_{21}H_{41}O_5Si_2$ (M—OCH_3)$^+$*m/z*: 429.2493. Found: 429.2483.

Methyl 2-*O*-acryloyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (9). Compound **9** was obtained as a colorless oil: TLC, R_f 0.58 (EtOAc:hexane, 1:2); $[\alpha]_D^{25.0}$ + 15.2° (*c* 0.525, $CHCl_3$); IR (neat) 3100−2800, 1730 cm^{-1}; ^1H NMR δ 3.37 (s, 3H, OMe), 3.71–3.84 (m, 3H, H-5, 6, 6′), 3.91 (t, *J* = 9.3 Hz, 1H, H-4), 4.01 (dd, *J* = 3.4, 9.3 Hz, 1H, H-3), 4.48, 4.68 (ABq, *J* = 11.0 Hz, 2H, C*H*$_2$-Ph), 4.52, 4.72 (ABq, *J* = 12.5 Hz, 2H, C*H*$_2$-Ph), 4.52, 4.85 (ABq, *J* = 10.7 Hz, 2H, C*H*$_2$-Ph), 4.77 (d, *J* = 1.9 Hz, 1H, H-1), 5.45 (dd, *J* = 1.9 Hz, 3.4 Hz, 1H, H-2), 5.86 (dd, *J* = 1.5, 10.4 Hz, 1H, COCH═C*H*H), 6.21 (dd, *J* = 10.4, 17.3 Hz, 1H, COC*H*═CHH), 6.47 (dd, *J* = 1.5, 17.3 Hz, 1H, COCH═CH*H*), 7.14–7.37 (m, 15H, Ph × 3); ^{13}C NMR δ 54.96, 68.63, 68.91, 71.26, 71.62, 73.41, 74.27, 75.14, 78.14, 98.73, 127.55, 127.60, 127.67, 127.71 × 2, 127.86 × 2, 128.03 × 2, 128.18, 128.29 × 4, 128.34 × 2, 131.63, 137.93, 138.24, 138.37, 165.45. HRMS: Calcd for $C_{30}H_{31}O_6$ (M—OCH_3)$^+$ *m/z*: 487.2121. Found: 487.2119.

Methyl 2-*O*-acryloyl-4,6-di-*O*-benzyl-α-D-mannopyranoside (10). To a cooled (0 °C) stirred solution of **7**[11] (1.48 g, 3.96 mmol) in THF (30 mL) was added NaH (60% in mineral oil, 361 mg, 9.03 mmol). After the mixture was stirred for 1 h at 0 °C, $HgCl_2$ (1.08 g, 3.96 mmol) was added. The mixture was stirred at 0 °C for 1 h and acryloyl chloride (0.66 mL, 7.90 mmol) was added. After being stirred at 0 °C for 1.5 h, the mixture was quenched with water and several drops of AcOH, diluted with EtOAc (200 mL), and washed with saturated aqueous $NaHCO_3$ (100 mL × 2). The organic layer was dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc:hexane, 1:5 to 1:1) to give 1.47 g (87%) of **10** as a colorless oil and 0.147 g (9%) of the 3-*O*-acryloyl derivative. Compound **10** as a colorless oil: TLC, R_f 0.74 (EtOAc:toluene, 1:1); $[\alpha]_D^{25.0}$ +31.1° (*c* 0.90, $CHCl_3$); IR (neat) 3460, 3100−2800, 1725 cm^{-1}; ^1H NMR δ 1.95 (b, 1H, OH), 3.37 (s, 3H, OMe), 3.72–3.85 (m, 4H, H-4, 5, 6, 6′), 4.16 (dd, *J* = 3.6, 8.6 Hz, 1H, H-3), 4.54, 4.71(ABq, *J* = 12.0 Hz, 2H, C*H*$_2$-Ph), 4.57, 4.77 (ABq, *J* = 10.5 Hz, 2H, C*H*$_2$-Ph), 4.77 (d, *J* = 1.7 Hz, 1H, H-1), 5.17 (dd, *J* = 1.7, 3.6 Hz, 1H, H-2), 5.88 (dd, *J* = 1.5, 10.5 Hz, 1H, COCH═C*H*H), 6.19 (dd, *J* = 10.5, 17.3 Hz, 1H, COC*H*═CHH), 6.45 (dd, *J* = 1.5, 17.3 Hz, 1H, COCH═CH*H*), 7.22–7.36 (m, 10H, Ph × 2); ^{13}C NMR δ 55.04, 68.87, 70.44, 71.01, 72.54, 73.51, 74.83, 75.86, 98.47, 127.62, 127.76 × 2, 127.81, 127.85 × 2, 127.94, 128.32 × 2, 128.44 × 2, 131.84, 138.16, 138.21, 165.85. HRMS: Calcd for $C_{24}H_{28}O_7$ (M)$^+$ *m/z*: 428.1815. Found: 428.1839.

Methyl 2-*O*-acryloyl-3-*O*-benzoyl-4,6-di-*O*-benzyl-α-D-mannopyranoside (11). To a cooled (0 °C) stirred solution of **10** (70.2 mg, 0.164 mmol) in pyridine (2 mL) was added benzoyl chloride (0.05 mL, 0.4 mmol). The mixture was stirred for 13 h, diluted with EtOAc (20 mL), and washed with saturated aqueous $NaHCO_3$ (10 mL × 5). The organic layer was dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc:hexane, 1:5) to provide 72.5 mg (83%) of **11** as a colorless oil: TLC, R_f 0.51 (EtOAc:hexane, 1:2); $[\alpha]_D^{25.0}$ −8.0° (*c* 2.01, $CHCl_3$); IR (neat) 3200−2800, 1730, 1640, 1620, 1600 cm^{-1}; ^1H NMR δ 3.42 (s, 3H, OMe), 3.75 (dd, *J* = 1.7, 10.7 Hz, 1H, H-6),

3.85–3.96 (m, 2H, H-5, 6′), 4.19 (t, J = 9.8 Hz, 1H, H-4), 4.50, 4.63 (ABq, J = 10.7 Hz, 2H, CH_2-Ph), 4.55, 4.74 (ABq, J = 11.9 Hz, 2H, CH_2-Ph), 4.82 (d, J = 2.0 Hz, 1H, H-1), 5.45 (dd, J = 2.0, 3.4 Hz, 1H, H-2), 5.66 (dd, J = 3.4, 9.8 Hz 1H, H-3), 5.87 (dd, J = 1.5, 10.4 Hz, 1H, COCH═C*H*H), 6.20 (dd, J = 10.4, 17.3 Hz, 1H, COC*H*═CHH), 6.42 (dd, J = 1.5, 17.3 Hz, 1H, COCH═CH*H*), 7.03–7.60 (m, 15H, Ph × 3); ^{13}C NMR δ 55.12, 68.61, 70.37, 71.23, 72.36, 73.12, 73.55, 74.85, 98.53, 127.65 × 2, 127.80 × 2, 127.83 × 2, 127.86, 128.22 × 4, 128.32 × 3, 129.61 × 2, 131.83, 133.06, 137.67, 138.11, 165.02, 165.30. HRMS: Calcd for $C_{31}H_{32}O_8$ $(M)^+$ *m/z*: 532.2097. Found: 532.2082.

Methyl 3-*O*-acetyl-2-*O*-acryloyl-4,6-di-*O*-benzyl-α-D-mannopyranoside (12). To a solution of **10** (117 mg, 0.27 mmol) in pyridine (2 mL) was added acetic anhydride (1 mL). The mixture was stirred for 11 h and the solvent was removed by concentration in vacuo. The residue was purified by column chromatography on silica gel (EtOAc:hexane, 1:5) to provide 114 mg (89%) of **12** as a colorless oil : TLC, R_f 0.53 (EtOAc:hexane, 1:2); $[\alpha]_D^{26.0}$ +31.8° (*c* 1.46, $CHCl_3$); IR (neat) 3100−2800, 1740 cm^{-1}; ^{1}H NMR δ 1.95 (s, 3H, OAc), 3.39 (s, 3H, OMe), 3.70–3.76 (m, 1H, H-6), 3.81–3.87 (m, 2H, H-5, 6′), 4.02 (t, J = 9.5 Hz, 1H, H-4), 4.50, 4.63 (ABq, J = 11.2 Hz, 2H, CH_2-Ph), 4.53, 4.73 (ABq, J = 12.0 Hz, 2H, CH_2-Ph), 4.75 (d, J = 1.7 Hz, 1H, H-1), 5.33 (dd, J = 1.7, 3.4 Hz, 1H, H-2), 5.37 (dd, J = 3.4, 9.5 Hz, 1H, H-3), 5.89 (dd, J = 1.0, 10.4 Hz, 1H, COCH═C*H*H), 6.19 (dd, J = 10.4, 17.3 Hz, 1H, COC*H*═CHH), 6.46 (dd, J = 1.0, 17.3 Hz, 1H, COCH═CH*H*), 7.15–7.39 (m, 10H, −Ph × 2); ^{13}C NMR δ 20.81, 55.02, 68.53, 70.04, 71.19, 71.88, 72.92, 73.45, 74.71, 98.48, 127.48 × 2, 127.60, 127.63, 127.75 × 2, 127.86, 128.29 × 4, 131.76, 138.00, 138.09, 165.09, 169.84. HRMS: Calcd for $C_{26}H_{30}O_8$ $(M)^+$ *m/z*: 470.1941. Found: 470.1944.

Methyl 2-*O*-acryloyl-4,6-di-*O*-benzyl-α-D-glucopyranoside (14). As described for the preparation of **10**, 802 mg (2.14 mmol) of **13**[12] was treated with NaH (60% in mineral oil, 202 mg, 5.06 mmol), $HgCl_2$ (581 mg, 2.14 mmol), and acryloyl chloride (0.36 mL, 4.3 mmol) to give 810 mg (88%) of **14** after chromatographic purification on silica gel. Compound **14** as a colorless oil: TLC, R_f 0.32 (EtOAc:hexane, 1:2); $[\alpha]_D^{26.0}$ +100.8° (*c* 1.70, $CHCl_3$); IR (neat) 3100−2800, 1725 cm^{-1}; ^{1}H NMR δ 2.28 (br, 1H, OH), 3.36 (s, 3H, OMe), 3.60–3.81 (m, 4H, H-4, 5, 6, 6′), 4.13 (t. J = 10.0 Hz, 1H, H-3), 4.54, 4.67 (ABq, J = 11.9 Hz, 2H, CH_2-Ph), 4.57, 4.77 (ABq, J = 11.2 Hz, 2H, CH_2-Ph), 4.82 (dd, J = 3.8, 10.0 Hz, 1H, H-2), 4.97 (d, J = 3.8 Hz, 1H, H-1), 5.88 (dd, J = 1.5, 10.4 Hz, 1H, COCH═C*H*H), 6.20 (dd, J = 10.4, 17.3 Hz, 1H, COC*H*═CHH), 6.28 (dd, J = 1.5, 17.3 Hz, 1H, COCH═CH*H*), 7.21–7.36 (m, 10H, −Ph × 2); ^{13}C NMR δ 55.15, 68.35, 69.81, 71.98, 73.51, 73.63, 74.73, 77.90, 96.87, 127.71 × 2, 127.91 × 5, 128.37 × 2, 128.47 × 2, 132.02, 137.83, 138.11, 165.89. HRMS: Calcd for $C_{23}H_{25}O_6$ $(M—OCH_3)^+$ *m/z*: 397.1651. Found: 397.1655.

Methyl 2-*O*-acryloyl-4,6-di-*O*-benzyl-3-*O*-*t*-butyldimethylsilyl-α-D-glucopyranoside (15). To a cooled (0 °C) stirred solution of **14** (113 mg, 0.26

mmol) in pyridine (3 mL) was added TBSOTf (0.07 mL, 0.30 mmol). The mixture was stirred for 2 h, diluted with EtOAc (20 mL), and washed with saturated aqueous $NaHCO_3$ (10 mL × 3). The organic layer was dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc:hexane, 1:10) to give 129 mg (90%) of **15** as a colorless oil : TLC, R_f 0.63 (EtOAc:hexane, 1:3); $[\alpha]_D^{20.5}$ +107° (*c* 3.41, $CHCl_3$); IR (neat) 3100−2800, 1730, 1635 cm^{-1}; ^1H NMR δ 0.04, 0.07 (2s, 6H, (*t*-Bu)*Me*$_2$Si), 0.85 (s, 9H, *(t-Bu)*Me$_2$Si), 3.34 (s, 3H, OMe), 3.45–3.81 (m, 4H, H-4, 5, 6, 6′), 4.14 (t, *J* = 9.2 Hz, 1H, H-3), 4.50, 4.82 (ABq, *J* = 11.2 Hz, 2H, C*H*$_2$-Ph), 4.54, 4.60 (ABq, *J* = 12.2 Hz, 2H, C*H*$_2$-Ph), 4.84 (dd, *J* = 3.7, 9.2 Hz, 1H, H-2), 4.91 (d, *J* = 3.7 Hz, 1H, H-1), 5.86 (dd, *J* = 1.5, 10.2 Hz, 1H, COCH═C*H*H), 6.20 (dd, *J* = 10.2, 17.3 Hz, 1H, COC*H*═CHH), 6.48 (dd, *J* = 1.5, 17.3 Hz, 1H, COCH═CH*H*), 7.18–7.34 (m, 10H, Ph × 2); ^{13}C NMR δ −4.21, −4.13, 17.88, 25.74 × 3, 54.99, 68.58, 70.12, 72.03, 73.45, 74.10, 74.80, 78.92, 97.02, 127.29 × 2, 127.39, 127.60, 127.75 × 2, 128.06, 128.21 × 2, 128.31 × 2, 131.65, 137.86, 138.18, 165.60. HRMS: Calcd for $C_{29}H_{39}O_6Si$ $(M—OCH_3)^+$ *m/z*: 511.2516. Found: 511.2515.

Typical Experimental Procedures for the Diels-Alder Reaction. Thermal conditions (entry 1 in Table 1). To a stirred solution of **2** (80.3 mg, 0.195 mmol) in CH_2Cl_2 (2 mL) was added cyclopentadiene (0.2 mL) at −18 °C. The mixture was stirred for 2 days and the solvent was removed by concentration in vacuo. The residue was purified by column chromatography (EtOAc:hexane, 1:9) to give 90.7 mg (96%) of **16** as a diastereomeric mixture. The ratio of the mixture was determined by ^1H NMR (300 MHz) analysis. Analogously, compounds **4**, **6**, and **15** were subjected to the Diels-Alder reaction with cyclopentadiene to give the adducts **17** (2 days, 96%; entry 2 in Table 1), **18** (5 days, 97%; entry 3 in Table 1), and **23** (2 days, 96%; entry 1 in Table 5), respectively, after chromatographic purification on silica gel.

Lewis Acid Promoted Conditions (entry 1 in Table 2). The following reaction was carried out under an argon atmosphere. To a cooled (−78 °C) stirred solution of **2** (60.6 mg, 0.147 mmol) in CH_2Cl_2 (1 mL) was added 1.0 M solution of $EtAlCl_2$ in hexane (0.31 mL, 0.31 mmol). The mixture was stirred at −78 °C for 30 min and cyclopentadiene (0.10 mL) was added. After being stirred at −78 °C for 15 min, the mixture was quenched with 1 M aqueous HCl and allowed to warm to room temperature. The mixture was diluted with EtOAc (20 mL) and washed with 1 M aqueous HCl (10 mL × 2). The organic layer was dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc:hexane, 1:9) to give 33.9 mg (63%) of **16** as a diastereomeric mixture. The ratio of the mixture was determined by ^1H NMR (300 MHz) analysis. Analogously, compounds **4**, **9**, **11**, **12**, and **15** were subjected to the Diels-Alder reaction with cyclopentadiene in the presence of $EtAlCl_2$ to give the adducts **17** (at −78 °C for 10 min, 79%; entry 2 in Table 2), **20** (at −78 °C for 15 min, 83%; entry 1 in Table 3), **21** (at −78 °C for 10 min, 84%; entry 2 in Table 3), **22** (at −78 °C for 15 min, 98%; entry 3 in Table 3), and **23** (at −78 °C for 1 hr, 97%; entry 2 in Table 5), respectively, after chromatographic purification on silica gel.

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Methyl 2,3-di-*O*-benzyl-4-*O*-(bicyclo[2.2.1]hept-5-ene-2-carbonyl)-6-deoxy-α-D-glucopyranoside (16) obtained under thermal conditions (entry 1 in Table 1). Compound **16** (*endo* :*exo* = 79:21, *endo-S*:*R* = 71:29) was obtained as a colorless oil : TLC, R_f 0.57 (EtOAc:hexane, 1: 3); IR (neat) 3100−2800, 1740 cm^{-1}; ^1H NMR δ 1.04–1.14 (m, 3H, CH_3-6), 1.21–1.47 (m, 3H, H-3, 7, 7′ of the norbornene), 1.81–1.90 (m, 1H, H-3′ of the norbornene), 2.06–2.10 (m, 1H × 2/9, H-2 of the *exo* norbornene), 2.70 (dt, *J* = 3.9, 9.3 Hz, 1H × 5/9, H-2 of the *endo* 2*S* norbornene), 2.80–2.87 (m, 1H × 2/9, H-2 of the *endo* 2*R* norbornene, and 1H × 7/9, H-4 of the *endo* norbornenes and 1H × 2/9, H-1 of the *exo* norbornene), 2.95 (br, 1H × 2/9, H-4 of the *exo* norbornene), 3.11 (br, 1H × 5/9, H-1 of the *endo* 2*S* norbornene), 3.15 (br, 1H × 2/9, H-1 of the *endo* 2*R* norbornene), 3.38–3.39 (m, 3H, OMe), 3.53–3.61 (m, 1H, H-2), 3.70–3.81 (m, 1H, H-5), 3.84–3.94 (m, 1H, H-3), 4.52–4.55 (m, 1H, H-1), 4.59–4.94 (m, 5H, H-4, CH_2—Ph × 2), 5.83–5.88 (m, 1H × 7/9, H-6 of the *endo* norbornene), 6.06–6.16 (m, 1H, H-5 of the norbornene, and 1H × 2/9, H-6 of the *exo* norbornene), 7.25–7.35 (m, 10H, Ph × 2); ^{13}C NMR for the **16S** δ17.44, 29.20, 42.41, 43.33, 45.53, 49.45, 49.71, 55.29, 65.39, 73.41, 74.78, 75.21, 79.22, 79.78, 98.12, 127.42 × 2, 127.70, 127.91, 128.11 × 2, 128.24 × 2, 128.42 × 2, 132.07, 138.00 × 2, 173.64. HRMS: Calcd for $C_{28}H_{31}O_5$ $(M—OCH_3)^+$ *m/z*: 447.2172. Found: 447.2176.

Methyl 4-*O*-(bicyclo[2.2.1]hept-5-ene-2-carbonyl)-6-deoxy-2,3-di-*O*-pivaloyl-α-D-glucopyranoside (17) obtained under Lewis acid promoted conditions (entry 2 in Table 2). Compound **17** (*endo*:*exo* =>95:5, *endo-S*:*R* = 10:90) was obtained as a colorless oil : TLC, R_f 0.65 (EtOAc:hexane, 1:4); IR (neat) 3100−2800, 1740 cm^{-1}; ^1H NMR δ 1.12, 1.16 (2s, 18H, OPiv × 2), 1.10–1.45 (m, 6H, H-3, 7, 7′ of the norbornene, and CH_3-6 of the *endo* adducts), 1.85 (ddd, *J* = 4.1, 8.3, 16.1 Hz, 1H × 1/10, H-3′ of the *endo* 2*S* norbornene), 1.97 (ddd, *J* = 3.7, 9.8, 12.0 Hz, 1H × 9/10, H-3′ of the *endo* 2*R* norbornene), 2.86–2.92 (m, 2H, H-2, 4 of the norbornene), 3.15 (br, 1H, H-1 of the norbornene), 3.37 (s, 3H × 9/10, OMe of the *endo* 2*R* adduct), 3.39 (s, 3H × 1/10, OMe of the *endo* 2*S* adduct), 3.86 (dq, *J* = 12.4, 6.1 Hz, 1H, H-5), 4.77 (dd, *J* = 3.7, 9.8 Hz, 1H, H-2), 4.81 (t, *J* = 9.8 Hz, 1H, H-3), 4.87 (d, *J* = 3.7 Hz, 1H, H-1), 5.49 (t, *J* = 9.8 Hz, 1H, H-4), 5.87 (dd, *J* = 2.7, 5.7 Hz, 1H × 1/10, H-6 of the *endo* 2*S* norbornene), 5.97 (dd, *J* = 2.9, 5.6 Hz, 1H × 9/10, H-6 of the *endo* 2*R* norbornene), 6.14 (dd, *J* = 2.9, 5.6 Hz, 1H × 9/10, H-5 of the *endo* 2*R* norbornene), 6.20 (dd, *J* = 2.5, 5.7 Hz, 1H × 1/10, H-5 of the *endo* 2*S* norbornene); ^{13}C NMR for **17R** δ 17.25, 26.94 × 3, 27.08 × 3, 29.07, 38.69 × 2, 42.46, 43.08, 45.66, 49.84, 55.47, 65.02, 69.55, 71.32, 73.27, 96.61, 131.83, 138.18, 173.48, 177.18, 177.74. HRMS: Calcd for $C_{25}H_{38}O_8$ $(M)^+$ *m/z*: 466.2566. Found: 466.2573.

Methyl 4-*O*-(bicyclo[2.2.1]hept-5-ene-2-carbonyl)-2,3-di-*O*-*t*-butyldimethylsilyl-6-deoxy-α-D-glucopyranoside (18) obtained under thermal conditions (entry 3 in Table 1). Compound **18** (**18S**:**18R** =>95:5) was obtained as white solids:TLC, R_f 0.69 for *endo*-isomers (EtOAc:hexane, 1:8); IR (neat) 3000−2800, 1750 cm^{-1}; ^1H NMR for the *endo* 2*S* adduct δ 0.09 (s, 6H, (*t*-Bu)Me_2Si), 0.10 (s, 6H, (*t*-Bu)Me_2Si), 0.82, 0.92 (2s, 18H, (*t-Bu*)Me_2Si), 1.09

(d, J = 6.3 Hz, 3H, 6-CH_3), 1.29–1.32 (m, 1H, H-7 of the norbornene), 1.39–1.45 (m, 2H, H-3, 7′ of the norbornene), 1.89 (ddd, J = 4.1, 9.6, 12.9 Hz, 1H, H-3′ of the norbornene), 2.92 (br, 1H, H-1 of the norbornene), 2.96 (dt, J = 3.9, 9.6 Hz, 1H, H-2 of the norbornene), 3.19 (br, 1H, H-4 of the norbornene), 3.38 (s, 3H, OMe), 3.65 (dd, J = 3.7, 9.1 Hz, 1H, H-2), 3.37–3.75 (m, 1H, H-5), 3.91 (t, J = 9.1 Hz, 1H, H-3), 4.61 (d, J = 3.7 Hz, 1H, H-1), 4.62 (t, J = 9.1 Hz, 1H, H-4), 5.85 (dd, J = 2.7, 5.6 Hz, 1H, H-6 of the norbornene), 6.25 (dd, J = 3.2, 5.6 Hz, 1H, H-5 of the norbornene); ^{13}C NMR for **18S** δ−4.52, −4.43, −3.41, −2.88, 17.73, 17.81, 18.27, 25.84 × 3, 26.12 × 3, 29.49, 42.52, 43.51, 46.01, 50.17, 55.01, 65.50, 71.87, 74.35, 76.24, 100.13, 131.60, 138.21, 173.82. HRMS: Calcd for $C_{26}H_{47}O_5Si_2$ (M—OCH_3)$^+$ *m/z*: 495.2962. Found: 495.2962.

Methyl 3,4,6-tri-*O*-benzyl-2-*O*-(bicyclo[2.2.1]hept-5-ene-2-carbonyl)-α-D-manno-pyranoside (20) obtained under Lewis acid promoted conditions (entry 1 in Table 3). Compound **20** (*endo*:*exo* =>95:5, *endo-S*:*R* = 33:67) was obtained as a colorless oil: TLC, R_f 0.57 (EtOAc:hexane, 1:2); IR (neat) 3100−2800, 1740 cm^{-1}; ^{1}H NMR δ 1.25 (m, 1H, H-7 of the norbornene), 1.37–1.49 (m, 2H, H-3, 7′ of the norbornene), 1.84–1.96 (m, 1H, H-3′ of the norbornene), 2.88 (br, 1H, H-4 of the norbornene), 3.00–3.09 (m, 1H, H-2 of the norbornene), 3.22 (br, 1H × 1/3, H-1 of the *endo* 2*S* norbornene), 3.25 (br, 1H × 2/3, H-1 of the *endo* 2*R* norbornene), 3.35 (s, 3H, OMe), 3.70–3.98 (m, 5H, H-3, 4, 5, 6, 6′), 4.45–4.90 (m, 7H, H-1, C*H*$_2$-Ph × 3), 5.27 (dd, J = 2.0, 2.9 Hz, 1H × 1/3, H-2 of the *endo* 2*S* adduct), 5.35 (dd, J = 2.0, 2.9 Hz, 1H × 2/3, H-2 of the *endo* 2*R* adduct), 5.90 (dd, J = 2.7, 5.6 Hz, 1H × 2/3, H-6 of the *endo* 2*R* norbornene), 6.00 (dd, J = 2.9, 5.5 Hz, 1H × 1/3, H-6 of the *endo* 2*S* norbornene), 6.04 (dd, J = 2.9, 5.6 Hz, 1H × 2/3, H-5 of the *endo* 2*R* norbornene), 6.12 (dd, J = 2.9, 5.5 Hz, 1H × 1/3, H-5 of the *endo* 2*S* norbornene), 7.16–7.39 (m, 15H, Ph × 3); ^{13}C NMR for **20R** δ28.95, 42.46, 43.26, 46.03, 49.50, 54.89, 67.94, 68.96, 71.36, 71.44, 73.36, 74.20, 75.16, 78.30, 98.93, 127.52 × 2, 127.63 × 3, 127.99 × 2, 128.13 × 2, 128.21 × 2, 128.29 × 4, 132.93, 137.26, 138.00, 138.31, 138.41, 173.91. HRMS: Calcd for $C_{35}H_{37}O_6$ (M—OCH_3)$^+$ *m/z*: 553.2590. Found: 553.2579.

Methyl 3-*O*-benzoyl-4,6-di-*O*-benzyl-2-*O*-(bicyclo[2.2.1]hept-5-ene-2-carbonyl)-α-D-mannopyranoside (21) obtained under Lewis acid promoted conditions (entry 2 in Table 3). Compound **21** (*endo*:*exo* =>95:5, *endo-S*:*R* = 9:91) was obtained as a colorless oil: TLC, R_f 0.66 (EtOAc:hexane, 1:2); IR (neat) 3100−2800, 1730, 1600 cm^{-1}; ^{1}H NMR for **21R** δ1.26–1.44 (m, 3H, H-3, 7, 7′ of the norbornene), 1.88 (ddd, J = 3.7, 9.3, 11.9 Hz, 1H, H-3 of the norbornene), 2.87 (br, 1H, H-4 of the norbornene), 3.01 (dt, J = 3.9, 9.3 Hz, 1H, H-2 of the norbornene), 3.26 (br, 1H, H-1 of the norbornene), 3.41 (s, 3H, OMe), 3.77 (dd, J = 2.0, 13.9 Hz, 1H, H-6), 3.85–3.94 (m, 2H, H-5, 6′), 4.23 (t, J = 9.8 Hz, 1H, H-4), 4.54, 4.66 (ABq, J = 10.7 Hz, 2H, C*H*$_2$-Ph), 4.56, 4.76 (ABq, J = 11.9 Hz, 2H, C*H*$_2$-Ph), 4.74 (d, J = 2.0 Hz, 1H, H-1), 5.30 (dd, J = 2.0, 3.3 Hz, 1H, H-2), 5.62 (dd, J = 3.3, 9.8 Hz 1H, H-3), 5.82 (dd, J = 2.7, 5.8 Hz, 1H, H-6 of the nor-

bornene), 6.07 (dd, J = 3.2, 5.8 Hz, 1H, H-5 of the norbornene), 7.06–7.58 (m, 15H, Ph × 3); ^{13}C NMR for **21R** δ29.03, 42.41, 43.31, 45.71, 49.66, 55.07, 68.63, 70.04, 71.36, 72.56, 73.07, 73.40, 74.85, 76.59, 98.58, 127.53, 127.68 × 3, 127.88 × 2, 128.26 × 2, 128.29 × 4, 129.64 × 2, 132.35, 133.06, 137.63, 137.77, 138.18, 165.38, 173.51. HRMS: Calcd for $C_{36}H_{38}O_8$ (M^+) *m/z*: 598.2567. Found: 598.2573.

Methyl 3-*O*-acetyl-4,6-di-*O*-benzyl-2-*O*-(bicyclo[2.2.1]hept-5-ene-2-carbonyl)-α-D-mannopyranoside (22) obtained under Lewis acid promoted conditions (entry 3 in Table 3). Diastereomerically homogenous **22R** was obtained as a colorless oil by chromatographic separation of the Diels-Alder adducts on silica gel: TLC, R_f 0.58 (EtOAc:hexane, 1:2); $[\alpha]_D^{21.5}$ +68.1° (*c* 1.96, $CHCl_3$); IR (neat) 3100−2800, 1750 cm^{-1}; ^{1}H NMR δ 1.24–1.46 (m, 3H, H-3, 7, 7′ of the norbornene), 1.84–1.93 (m, 1H, H-3′ of the norbornene), 1.91 (s, 3H, OAc), 2.92 (br, 1H, H-4 of the norbornene), 3.02 (dt, J = 3.8, 9.0 Hz, 1H, H-2 of the norbornene), 3.27 (br, 1H, H-1 of the norbornene), 3.38 (s, 3H, OMe), 3.72–3.89 (m, 3H, H-5, 6, 6′), 4.06 (t, J = 9.8 Hz, 1H, H-4), 4.53, 4.61 (ABq, J = 11.2 Hz, 2H, CH_2-Ph), 4.54, 4.76 (ABq, J = 11.9 Hz, 2H, CH_2-Ph), 4.67 (d, J = 1.9 Hz, 1H, H-1), 5.21 (dd, J = 1.9, 3.3 Hz, 1H, H-2), 5.30 (dd, J = 3.3, 9.8 Hz, 1H, H-3), 5.97 (dd, J = 2.7, 5.6 Hz, 1H, H-6 of the norbornene), 6.18 (dd, J = 2.9, 5.6 Hz, 1H, H-5 of the norbornene), 7.16–7.42 (m, 10H, Ph × 2); ^{13}C NMR δ 20.91, 28.69, 42.44, 43.20, 45.93, 49.64, 55.02, 68.56, 69.48, 71.32, 72.02, 72.81, 73.43, 74.68, 98.68, 127.58 × 2, 127.67 × 2, 127.71 × 2, 128.27 × 2, 128.34 × 2, 132.30, 137.68, 137.98, 138.18, 169.74, 173.49. HRMS: Calcd for $C_{31}H_{36}O_8$ $(M)^+$*m/z*: 536.2410. Found: 536.2412.

Methyl 4,6-*O*-benzyl-2-*O*-(bicyclo[2.2.1]hept-5-ene-2-carbonyl)-3-*O*-*t*-butyldimethylsilyl-α-D-glucopyranoside (23) obtained under Lewis acid promoted conditions (entry 2 in Table 5). Compound **23** (*endo*:*exo* = 94:6, *endo-S*:*R* = 92:8) was obtained as a colorless oil: TLC, R_f 0.66 (EtOAc:hexane, 1:3); IR (neat) 3100−2800, 1730 cm^{-1}; ^{1}H NMR for **23S** δ0.04, 0.11 (2s, 6H, (t-Bu)Me_2Si), 0.89 (s, 9H, (*t-Bu*)Me_2Si), 1.25–1.29 (m, 1H, H-7 of the norbornene), 1.36–1.51 (m, 2H, H-3, 7′ of the norbornene), 2.01 (ddd, J = 3.7, 9.7, 11.5 Hz, 1H, H-3′ of the norbornene), 2.90 (br, 1H, H-4 of the norbornene), 3.00 (dt, J = 3.9, 9.7 Hz, 1H, H-2 of the norbornene), 3.23 (br, 1H, H-1 of the norbornene), 3.28 (s, 3H, OMe), 3.52 (t, J = 9.4 Hz, 1H, H-4), 3.60–3.74 (m, 3H, H-5, 6, 6′), 4.06 (t, J = 9.4 Hz, 1H, H-3), 4.49, 4.59 (ABq, J = 12.0 Hz, 2H, CH_2-Ph), 4.53, 4.80 (ABq, J = 11.2 Hz, 2H, CH_2-Ph), 4.60 (dd, J = 3.7, 9.4 Hz, 1H, H-2), 4.81 (d, J = 3.7 Hz, 1H, H-1), 6.03 (dd, J = 2.7, 5.5 Hz, 1H, H-6 of the norbornene), 6.18 (dd, J = 2.9, 5.5 Hz, 1H, H-5 of the norbornene), 7.17–7.31 (m, 10H, Ph × 2); ^{13}C NMR **23S** δ −4.20, −4.05, 17.98, 25.86 × 3, 30.53, 42.44, 43.72, 45.22, 49.25, 55.25, 68.66, 70.11, 71.98, 73.45, 74.34, 74.73, 78.91, 96.94, 127.25 × 2, 127.35, 127.60, 127.75 × 2, 128.21 × 2, 128.32 × 2, 133.32, 137.22, 137.95, 138.29, 174.45. HRMS: Calcd for $C_{34}H_{45}O_6Si$ $(M{=}{=}OCH_3)^+$*m/z*: 577.2985. Found: 577.2962.

Methyl 4,6-di-*O*-benzyl-2-*O*-(bicyclo[2.2.1]hept-5-ene-2-carbonyl)-α-D-glucopyranoside (24). Compound **23** obtained under thermal conditions (**23R:23S:**the *exo*-isomers = 10 : 1 : 4 by ^{1}H NMR analysis, 54.6 mg, 0.090 mmol) was dissolved in 47% aqueous HF—CH_3CN (1:9, 2.0 mL). The solution was stirred for 4 days and neutralized with saturated aqueous $NaHCO_3$. The mixture was diluted with EtOAc (20 mL) and washed with saturated aqueous $NaHCO_3$ (10 mL × 4). The organic layer was dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc:hexane, 1:4) to give 35.6 mg (80%) of the mixture of adducts **24R** and **24S** and 9.7 mg (20%) of the *exo* adducts. The mixture of **24R** and **24S** (10 : 1) was obtained as a colorless oil: TLC, R_f 0.35 (EtOAc:hexane, 1 : 2); IR (neat) 3500 (br), 3100−2800, 1730 cm^{-1}; ^{1}H NMR for **24R** δ1.26–1.28 (m, 1H, H-7 of the norbornene), 1.41–1.47 (m, 2H, H-3, 7′ of the norbornene), 1.86–1.94 (m, 1H, H-3′ of the norbornene), 2.91 (br, 1H, H-4 of the norbornene), 3.00–3.07 (m, 1H, H-2 of the norbornene), 3.25 (br, 1H, H-1 of the norbornene), 3.36 (s, 3H, OMe), 3.59 (t, J = 9.5 Hz, 1H, H-4), 3.66–3.77 (m, 3H, H-5, 6, 6′), 4.09 (t, J = 9.5 Hz, 1H, H-3), 4.52, 4.66 (ABq, J = 12.2 Hz, 2H, CH_2-Ph), 4.57, 4.77 (ABq, J = 11.3 Hz, 2H, CH_2-Ph), 4.68 (dd, J = 3.7, 9.5 Hz, 1H, H-2), 4.88 (d, J = 3.7 Hz, 1H, H-1), 5.91 (dd, J = 2.7, 5.8 Hz, 1H, H-6 of the norbornene), 6.20 (dd, J = 2.9, 5.8 Hz, 1H, H-5 of the norbornene), 7.21–7.37 (m, 10H, Ph × 2); ^{13}C NMR for **24R** δ29.11, 42.57, 43.13, 45.93, 49.58, 55.11, 68.41, 69.78, 72.02, 73.53 × 2, 74.65, 77.82, 96.84, 127.71, 127.83, 127.90 × 4, 128.37 × 2, 128.47 × 2, 132.14, 137.90 × 2, 138.23, 174.42. HRMS: Calcd for $C_{29}H_{34}O_7(M)^+$ *m/z*: 494.2305. Found: 494.2302.

A Typical Procedure for Removal of the Carbohydrate Templates. The following reaction was carried out under an argon atmosphere. To a cooled (−78 °C) stirred solution of the mixture of **18S** and **18R** (>95:5, 170 mg, 0.323 mmol) in CH_2Cl_2 (4 mL) was added DIBALH (1.0 M solution in toluene, 1.0 mL, 1.0 mmol). The mixture was stirred at −78 °C for 1 h and quenched with 1 M aqueous HCl. This was diluted with 1 M aqueous HCl (20 mL) and extracted with CH_2Cl_2 (20 mL × 3). The combined organic layers were dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc:hexane, 1:8, 1:5 then 1:2) to give 36.3 mg (91%) of enantioenriched **19S** and 99.1 mg (76%) of **5**. For HPLC analysis, thus obtained enantioenriched **19S** was benzoylated as follows. To a solution of **19S** (2.7 mg, 0.02 mmol) in pyridine (1 mL) was added benzoyl chloride (6 μL, 0.05 mmol). The solution was stirred for 7 h and diluted with EtOAc (10 mL), washed with saturated aqueous $NaHCO_3$ (5 mL × 3). The organic layer was dried and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc:hexane, 1:5) to give 4.5 mg (98%) of bicyclo[2.2.1]hept-5-ene-2-methyl benzoate as a colorless oil.

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