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Steric determinants in diastereocontrol during Baylis–Hillman reaction of sugar-derived aldehydes☆

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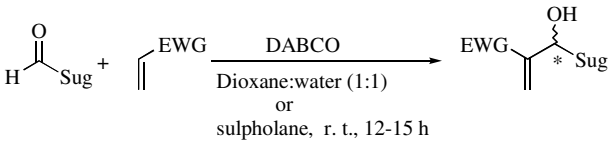
Abstract—Diastereoselective Baylis–Hillman reaction using different sugar-derived aldehydes with various activated olefins afforded chiral multifunctional adducts in good yields. Steric factors that dictate and determine the diastereoselection will be discussed.

1. Introduction

The asymmetric Baylis–Hillman reaction[1] has witnessed a renaissance in recent times due to the efforts of many researchers, particularly due to trend setting contributions made by Drewes et al.,[2] Leahy et al.,[3] and Shi et al.[4a–4d] Our own recent contributions to the Baylis–Hillman reaction[5] led to reports on diastereoselective Baylis–Hillman reaction of sugar-derived aldehydes[6] and chiral 2,3-epoxy aldehydes as electrophiles.[7] However, a thorough study was initiated to understand the factors that govern the stereochemical outcome of the ensuing adducts when sugar-derived aldehydes are electrophiles. Architecturally and structurally different protecting groups/stereochemistries that adorn the periphery of sugar scaffolds were chosen as the means of affecting stereo differentiation (Eq. 1). Toward this goal, initially the known[8] 1,2-*O*-isopropylidene-3-*O*-methoxy-α-D-*xylo*-pentodialdo-1,4-furanose **1** was chosen as the electrophile. Thus, Baylis–Hillman reaction of **1** with ethyl acrylate **a** was carried out in different solvent systems viz. CH_2Cl_2 (no reaction), THF–H_2O (only 48% conversion), and in dioxane–water (1:1)[9] in the presence of 100 mol % of DABCO at room temperature to afford adduct **1a** (73%) in 15 h. Likewise, **1** was reacted with other activated olefins, methyl vinyl ketone **b** and acrylonitrile **c**, to afford adducts **1b** (82%) and **1c** (76%), respectively (Scheme 1 and Table 1), under standardized reaction conditions. Adducts **1a–c** were thoroughly characterized by their spectral data.



(1)

The next task in hand was to extend the scope of this study to other sugar-derived aldehydes. Accordingly, the known aldehydes, 2,3-*O*-isopropylidene-1-*O*-methyl-α-D-*lyxo*-pentodialdo-1,4-furanose[10] **2**, 1,2:3,4-di-*O*-isopropylidene-α-D-*galacto*-hexodialdo-1,5-pyranose[11] **3**, **4**, and **5** when subjected to a Baylis–Hillman reaction with **a**, **b**, and **c** in dioxane–H_2O for 15 h gave adducts **2a–c**, **3a–c**, **4a–c**, and **5a**, respectively, in good yields. Furthermore, when aldehydes 1,2-*O*-isopropylidene-3-*O*-methoxy-α-D-*arabino*-pentodialdo-1,4-furanose[12] **6**, 1,2-*O*-isopropylidene-3-*O*-methoxy-β-L-*arabino*-pentodialdo-1,4-furanose[12] **7**, and 1,2:3,5-di-*O*-isopropylidene-β-L-*sarbo*-1,4-hexa-furanose-1-carboxaldehyde[13] **10** were subjected to a Baylis–Hillman reaction with activated olefins **a** and **c** in sulfolane[14] at room temperature, they afforded adducts **6a–10a** and **6c–10c**, respectively, in yields as specified in Table 1. A change in solvent was sought because of our earlier experience with regards to the less reactive aldehydes that could be made to undergo a Baylis–Hillman reaction in an aprotic polar solvent

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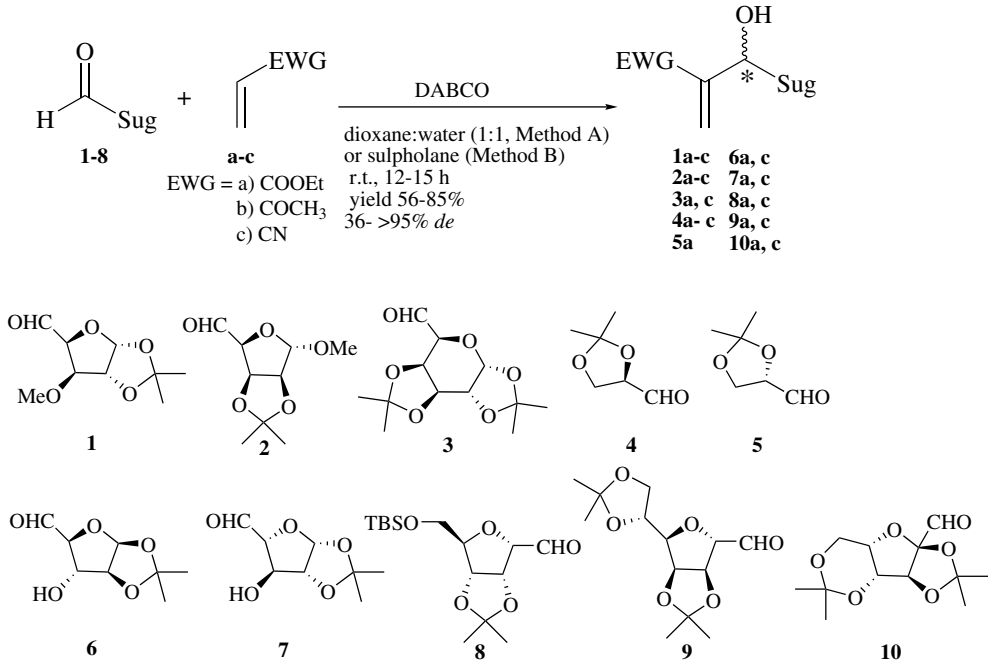


Scheme 1.

Table 1. Baylis–Hillman reaction of sugar-derived aldehydes with activated olefins[a]

S. no.	Chiral aldehyde	Activated olefin	Yield (%)[b]	Method	de (%)[c]
1	**1**	**a**	**1a** (73)	A	36
2	**2**	**a**	**2a** (56)	A	56
3	**3**	**a**	**3a** (65)	A	40
4	**4**	**a**	**4a** (82)	A	80
5	**5**	**a**	**5a** (76)	A	82
6	**6**	**a**	**6a** (70)	B	54
7	**7**	**a**	**7a** (78)	B	60
8	**8**	**a**	**8a** (60)	B	40
9	**9**	**a**	**9a** (85)	B	45
10	**10**	**a**	**10a** (80)	B	>95
11	**1**	**b**	**1b** (82)	A	53
12	**2**	**b**	**2b** (69)	A	60
13	**4**	**b**	**4b** (69)	A	69
14	**1**	**c**	**1c** (76)	A	60
15	**2**	**c**	**2c** (72)	A	72
16	**3**	**c**	**3c** (69)	A	86
17	**4**	**c**	**4c** (77)	A	75
18	**6**	**c**	**6c** (80)	B	76
19	**7**	**c**	**7c** (85)	B	76
20	**8**	**c**	**8c** (65)	B	47
21	**9**	**c**	**9c** (75)	B	80
22	**10**	**c**	**10c** (85)	B	90

[a] Method A: DABCO (1 equiv), olefin (3 equiv), dioxane–water (1:1), rt; Method B: DABCO (1 equiv), olefin (3 equiv), sulfolane, rt.
[b] Isolated yields.
[c] As determined by ^{1}H NMR and/or HPLC analysis (ODS column; UV: 225 nm; 250 nm; 4.6 mm; 30% CH_3CN in potassium buffer; flow rate = 1.0 mL/min).

both by activation of the aldehydes and stabilization of charge–dipole interactions of the zwitterion intermediate. In fact, the formation of adducts was cleaner and faster rates were accomplished when the Baylis–Hillman reaction was conducted in sulfolane as the solvent.

2. Results and discussion

2.1. Determination of des and absolute stereochemistry of the newly created center in adducts

The diastereomeric excess (de) of all adducts (36–>95%) was determined by ^{1}H NMR and/or HPLC. For example, the ^{1}H NMR spectrum of **1a** revealed 36% de determined by the relative integration of H-5 and the olefinic protons. Independently, the ratio was also obtained by HPLC (ODS column; UV: 225 nm; 250 mm × 4.6 mm; 30% CH_3CN in potassium buffer; flow rate = 1 mL/min). Subsequently, the isomeric mixture of **1a** was resolved into pure components by preparative HPLC (semi-preparative ODS column; UV: 225 nm; 250 mm × 25 mm; 30% CH_3CN in potassium buffer; flow rate = 1.0 mL/min). The absolute stereochemistry of the major and minor isomers was unambiguously assigned based on the vicinal coupling constants between the H-4 and H-5[15] protons and extensive NMR studies. The ^{1}H NMR spectrum of major isomer **1a** revealed the characteristic H-5 proton at δ 4.64 as doublet with J = 8.9 Hz (L-*ido* configuration), the same proton in the minor isomer resonated at δ 4.83 as doublet with J = 5.9 Hz (D-*gluco* configuration). Similarly, the major isomer of **2a**, **3a** also showed larger vicinal coupling constant between H-4 and H-5. The diastereomeric excesses for adducts **6a**, **6c**, **7a**, and **7c** were determined from their ^{1}H NMR spectra by the relative integration of the separable protons. For example, one of the olefinic protons for **6a** resonated at δ 5.96 integrating for 0.7H and another at δ 6.01 integrating for 0.3H, while the

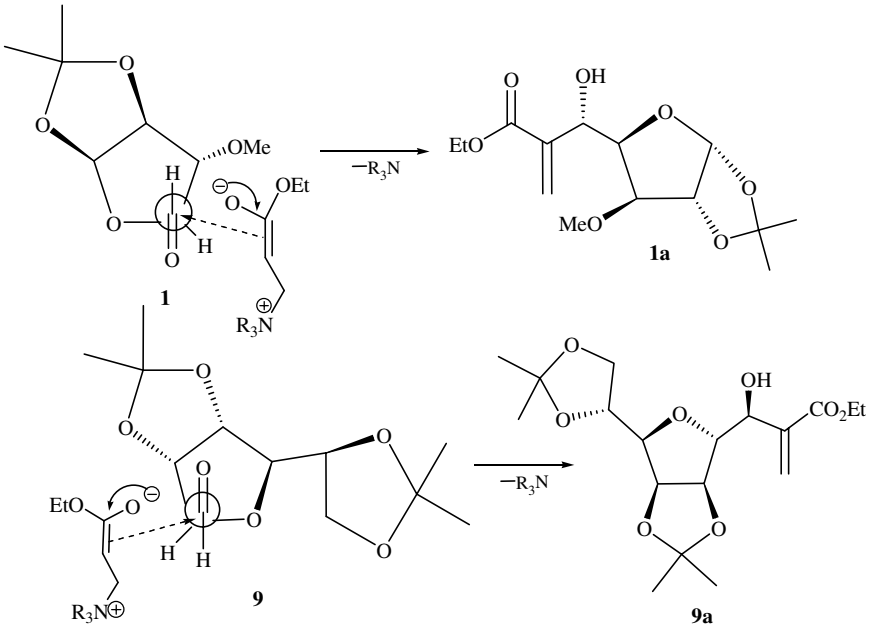
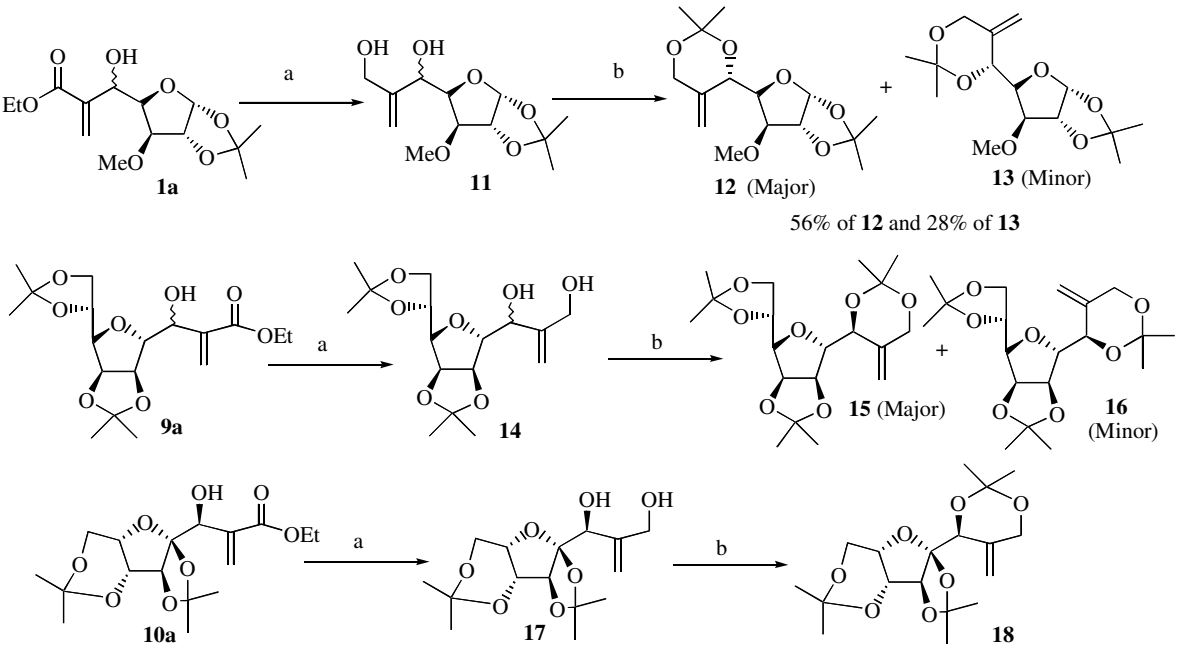


Figure 1. Schematic representation of Felkin–Ahn model.

other olefinic proton appeared at δ 6.35 integrating for 0.7H and at δ 6.40 integrating for 0.3H. The de was thus calculated as 40%. Similarly, **6c** also revealed separable olefinic protons whose integral values gave a de as 71%. The de for **7a** and **7c** was also read from the ^{1}H NMR as 77% and 71%, respectively (see Experimental). The observed stereoselectivity can be explained by the favorable attack of the carbanion from the *si*-face of all the sugar aldehydes (except for aldehyde **7**) leading to the (*S*)-isomer as the major product at the newly created stereocenter according to Felkin–Ahn model[16] by a non-chelation protocol. A similar analogy was adopted for evaluating the diastereomeric excesses for adducts **8a**, **8c**, **9a**, and **9c** (Table 1). Interestingly, adducts **10a** and **10c** showed high des since the ^{1}H NMR spectra were consistent with the presence of a single isomer. Although the diastereomeric excess could not be deduced for the adducts **8** and **9** through their ^{1}H NMR, which revealed the merger of the allylic proton, the diastereoselectivities, as mentioned against each of them in Table 1, were identified from the separable olefinic protons in their ^{1}H NMR for these adducts (Fig. 1).

In order to ascertain the absolute stereochemistry of the diastereomeric adducts of **1a**, the mixture was converted into the corresponding cyclic adducts by a two-step sequence (Scheme 2). Accordingly, the reduction of **1a**



Scheme 2. Reagents and conditions: (a) $AlCl_3/LiAlH_4$, 0 °C, 2 h, 68%; (b) 2,2′-dimethoxypropane, PTSA, 6 h.

with $AlCl_3$–LAH gave the 1,3 diol **11** (68%), which on reaction with 2,2′-dimethoxypropane and PTSA resulted in **12** and **13** in 84% combined yield. It is noteworthy that both isomers **12** and **13** were separated by column chromatography. Furthermore, to assign the stereochemistry at C1′ unambiguously, reduction of adducts **9a** and **10a** under similar reaction conditions resulted in diols **14** (45%) and **17** (32%) on similar lines to **11,** to afford separable **15** (26%) and **16** (16%); and exclusively **18** (46%), respectively.

2.2. 2-D NOESY and energy minimization studies

The minimum energy structures[17] adopt a dihedral angle of about 170° in both compounds (Fig. 2). The coupling of $J = 8.9$ Hz in **12** and 7.8 Hz in **13** indicates the presence of more than one conformer, which is predominantly *trans*. Further evidence for the proposed structure comes from 2D-NOESY experiments. Spectra were acquired with 2×192 free induction decays containing 16 transients with a relaxation delay of 1.5 s and

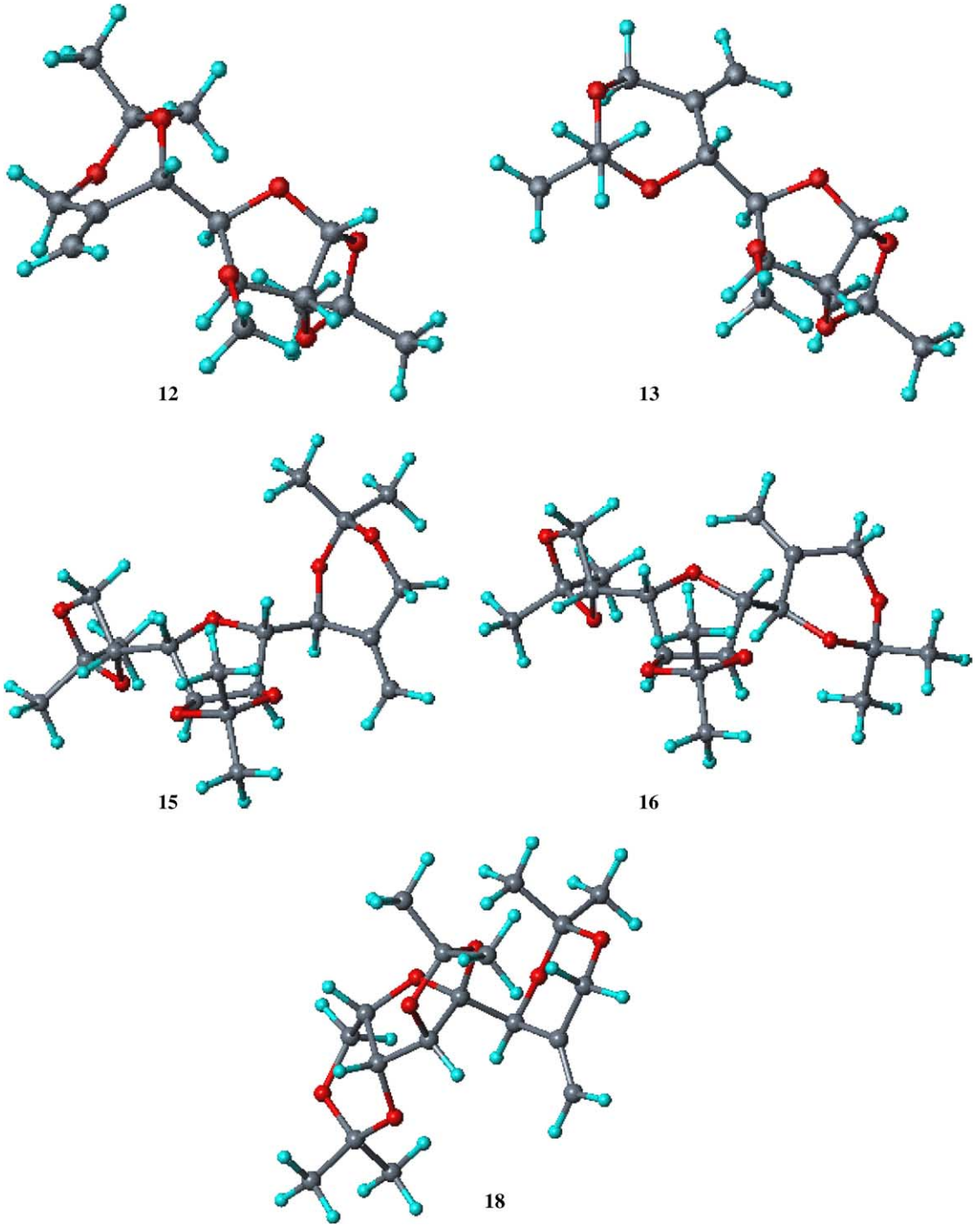


Figure 2. Energy minimized structures.

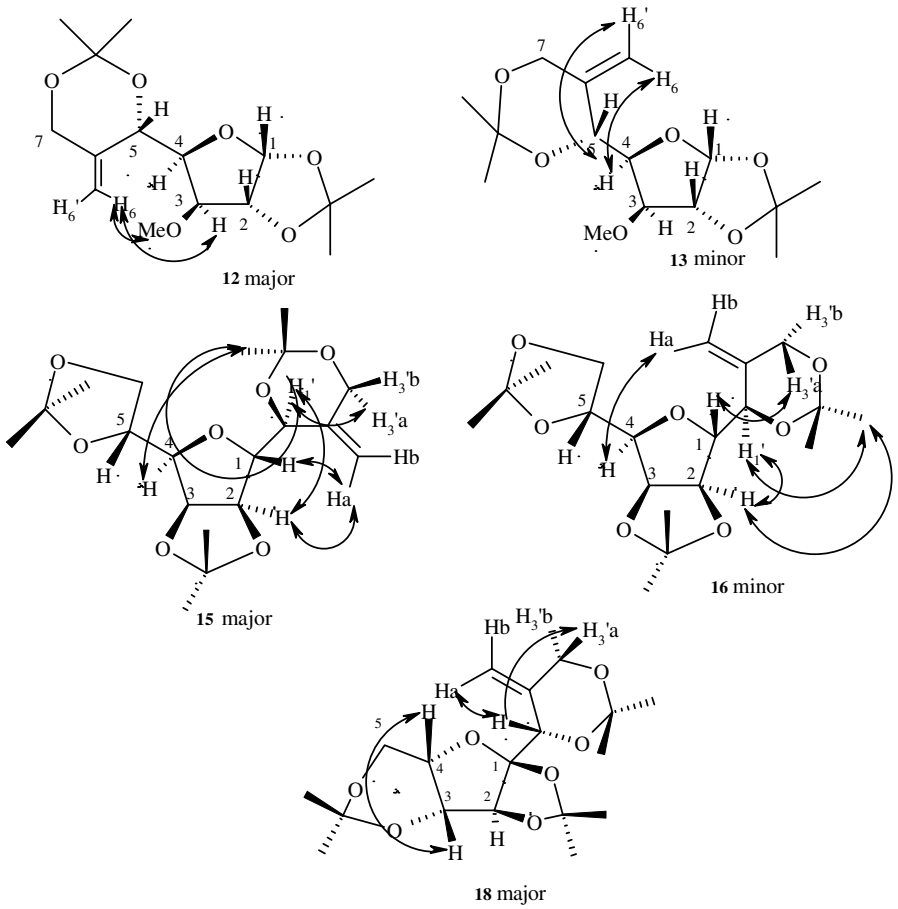


Figure 3. Diagramatic representations of NOEs.

mixing time of 0.4 s. For major isomer **12**, distinctive NOE cross peaks between H3–H6 and OMe–H6 support the assigned structure with the absolute stereochemistry at C-5 being determined as (*S*) (Fig. 3). Conversely, for minor isomer **13**, NOE cross peaks between H4 and H5, support the structure with absolute stereochemistry at C-5 as (*R*). Similarly, since aldehydes **1**–**3** and **6** are obtained from D-sugars and the Baylis–Hillman reaction was conducted at the C-5 site adjacent to C-4, their respective major adducts exhibited larger vicinal coupling constants (*J*), it could be concluded that the new stereocenter is defined as (*S*) (*threo* relationship between C-4 and C-5) for all aldehydes derived from D-sugars **1**–**3** and **6**. The opposite is true when the aldehyde is derived from the L-sugar. More explicitly, aldehyde **7**, an L-sugar-derived aldehyde, is the enantiomer of **6** and the newly created stereocenter of the major isomer can be assigned as (*R*) by correlation. The $[\alpha]_D$ values corroborate the prediction. For instance, **6a** exhibited $[\alpha]_D = -14.40$ (*c* 0.1, $CHCl_3$); while **7a** has $[\alpha]_D = +14.4$ (*c* 0.1, $CHCl_3$); also **6c** $[\alpha]_D = +18.4$ (*c* 0.25, $CHCl_3$); **7c** $[\alpha]_D = -19.4$ (*c* 0.4, $CHCl_3$); these values unambiguously prove their assigned structures. Likewise, the adducts obtained from glyceraldehydes bear the values **4a** $[\alpha]_D = -6.4$ (*c* 1.0, $CHCl_3$); **5a** $[\alpha]_D = +6.4$ (*c* 1.0, $CHCl_3$), which demonstrate their enantiomeric nature. The NOE cross peaks between H1′–H3a′ and H1′–H2 in major isomer **15** indicate the near *anti* relationship ($J = 6.5$ Hz) between H1 and H1′. The NOE cross peak H1–Ha′ also supports the assigned structure with an (*S*)-absolute configuration at C-1′. Similarly, the NOE cross peaks between H1′–H3a′ and H2–H1′ in minor isomer **16** confirms a near *anti* relationship between H1′ and Ha′ ($J = 6.9$ Hz) with an (*R*)-configuration at C1′. The presence of NOE cross peaks between H1–Ha and H1′–H3a in **18** ascertains the structure with an (*R*)-configuration at the newly created stereocenter.[18] However, the newly created stereogenic center in the major isomers for adducts **8a** and **8c** was assigned as (*S*) based on analogy (Felkin–Ahn model).

It can be deduced that steric factors dictate the facial selection of the aldehyde during the 'aldol' reaction. The more steric crowding at the aldehyde (**8**–**10**) site, the more the selectivity becomes increasingly in favor of one isomer.

3. Conclusion

In conclusion, a DABCO catalyzed Baylis–Hillman reaction of sugar-derived aldehydes was successfully conducted in dioxane–water (1:1) at ambient temperature. The yields and rate of reaction were slightly improved upon when the solvent was changed to

sulfolane. Diastereomeric excesses of the order of 36–>95% were achieved for the adducts. For the first time, enantiomeric sugar-derived aldehydes in the form of (*R*)- and (*S*)-2,3-isopropylidene glyceraldehydes, D- and L-arabinose were performed and the ensuing adducts were enantiomeric (major) to each other.

The isopropylidene groups and their stereochemical disposition played a decisive role in diastereoselection to enhance the des, as observed in the case of L-sorbose, D-ribose-1-carboxaldehyde and D-mannose-1-carboxaldehyde.

4. Experimental

4.1. General

Solvents were dried over standard drying agents and freshly distilled prior to use. ^{1}H NMR (200, 300, and 500 MHz) and ^{13}C NMR (50 and 75 MHz) spectra were measured with a Varian Gemini FT-200 MHz spectrometer, Bruker Avance 300 MHz, and Varian Inova 500 MHz with tetramethylsilane as internal standard for solutions in deuteriochloroform. *J* values are given in hertz. IR spectra were recorded on Perkin–Elmer IR-683 spectrophotometer with NaCl optics. Optical rotations were measured with a JASCO DIP 300 digital polarimeter at 25 °C. Mass spectra were recorded on a CEC-21-11013 or Fannigan Mat 1210 double focusing mass spectrometers operating at a direct inlet system. Organic solutions were dried over anhydrous Na_2SO_4 and concentrated below 40 °C in vacuo.

4.2. General experimental procedure (Method A)

To an aldehyde (1 mmol) in dioxane–H_2O [(1:1), 5 mL], DABCO (1 mmol) and ethyl acrylate (3 mmol) were added and the reaction mixture stirred for 15 h at room temperature. After complete conversion of the aldehyde, the reaction mixture was partitioned between ethyl acetate (3×15 mL) and water (1×25 mL) and the collected organic layers were washed with brine (25 mL), dried over Na_2SO_4, and concentrated under reduced pressure to give a residue, which was purified by chromatography (silica gel 60–120 mesh, EtOAc–hexane, 1.5:8.5–2:8) to afford adducts **1a**–**c**, **2a**–**c**, **3a**, **3c**, **4a**–**c**, and **5a** in 56–82% yield.

4.3. General experimental procedure (Method B)

To an aldehyde (1 mmol) in sulfolane (5 mL), DABCO (1 mmol), and ethyl acrylate (3 mmol) were added and the reaction mixture stirred for 12–15 h at room temperature. After complete conversion of the aldehyde, the reaction mixture was partitioned between ether (3×15 mL) and water (1×25 mL) and the collected organic layers were washed with brine (25 mL), dried over Na_2SO_4, and concentrated under reduced pressure to give a residue, which was purified by chromatography (silica gel 60–120 mesh, EtOAc–hexane, 1.5:8.5–3:7) to afford adducts **6a**–**10a** and **6c**–**10c** in 60–85% yield.

4.4. Ethyl 2-hydroxy[6-methoxy-2,2-dimethyl-(3a*R*,5*R*,6*S*,6a*R*)-perhydrofuro[2,3-*d*][1,3]dioxol-5-yl]methylacrylate 1a

1,2-*O*-Isopropylidene-3-*O*-methyl-α-D-*xylo*-pentodialdo-1,4-furanose **1** (0.20 g, 1 mmol) in dioxane–water [(1:1), 5 mL] was treated with ethyl acrylate **a** (0.33 mL, 3 mmol) in the presence of DABCO (0.11 g, 1 mmol) at room temperature for 15 h. Then, the reaction mixture was diluted with water (15 mL) and extracted with ethyl acetate (3×15 mL). The combined organic layers were washed with brine (25 mL), dried over Na_2SO_4, and concentrated under reduced pressure to give a residue, which was purified by chromatography (silica gel 60–120 mesh, hexane–EtOAc, 8.5:1.5–8:2) to afford adduct **1a** (0.22 g, 74%) as a colorless syrup with 36% de as determined by chiral HPLC analysis. HPLC (column: ODS, 30% CH_3CN in potassium buffer, flow rate: 1 mL/min, t_r(minor) = 7.0 min, t_r(major) = 7.7 min); $[\alpha]_D = -22.4$ (*c* 0.7, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$, TMS): δ 6.37 (s, 0.32H, olefinic), 6.33 (s, 0.68H, olefinic), 6.08 (s, 0.32H, olefinic), 5.92 (s, 0.68H, olefinic), 5.83 (d, 1H, $J = 3.9$ Hz, H-1), 4.81 (br s, 0.32H, H-5), 4.62 (br s, 0.68H, H-5), 4.54 (d, 1H, $J = 3.9$ Hz, H-2), 4.32–4.18 (m, 3H, H-4, CH_2), 3.82 (br s, 1H, H-3), 3.45 (s, 3H, OMe), 1.42 (s, 3H, CH_3), 1.38–1.24 (m, 6H, $2 \times CH_3$); IR (neat) ν 3410, 1748, 1680 cm^{-1}; FABMS: *m*/*z* 303 (M^++1); Anal. Calcd for $C_{14}H_{22}O_7$: C, 55.62; H, 7.33. Found: C, 55.67; H, 7.29.

4.5. Ethyl 2-(*S*)-hydroxy[6-methoxy-2,2-dimethyl-(3a*R*,5*R*,6*S*,6a*R*)-perhydrofuro[2,3-*d*][1,3]dioxol-5-yl]methylacrylate (*S*)-1a

Compound **1a** was resolved into pure entities by preparative HPLC (semi-preparative ODS column; UV: 225 nm; 250 mm × 25 mm; 30% CH_3CN in potassium buffer; flow rate = 1.0 mL/min), the first eluted was minor (t_r = 7.0 min) ethyl 2-(*R*)-hydroxy[6-methoxy-2,2-dimethyl-(3a*R*,5*R*,6*S*,6a*R*)-perhydrofuro[2,3-*d*][1,3]dioxol-5-yl]-methylacrylate (*R*)-**1a** and the second eluted was major (t_r = 7.7 min) (*S*)-**1a**. (*R*)-**1a**: $[\alpha]_D = -28.8$ (*c* 1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 6.79 (s, 1H, olefinic), 6.08 (s, 1H, olefinic), 5.95 (d, 1H, $J = 3.9$ Hz, H-1), 4.83 (d, 1H, $J = 5.9$ Hz, H-5), 4.58 (d, 1H, $J = 3.9$ Hz, H-2), 4.40 (dd, 1H, $J = 3.0$, 5.9 Hz, H-4), 4.28 (q, 2H, $J = 7.4$ Hz, –OCH_2–), 3.83 (d, 1H, $J = 3.0$ Hz, H-3), 3.48 (s, 3H, –OMe), 1.48 (s, 3H, CH_3), 1.30–1.39 (m, 6H, $2 \times CH_3$); FABMS: *m*/*z* 303 (M^++1); Anal. Calcd for $C_{14}H_{22}O_7$: C, 55.62; H, 7.33. Found: C, 55.68; H, 7.29. (*S*)-**1a**: $[\alpha]_D = -47.4$ (*c* 0.8, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$, TMS): δ 6.38 (s, 1H, olefinic), 5.96 (s, 1H, olefinic), 5.85 (d, 1H, $J = 3.7$ Hz, H-1), 4.64 (d, 1H, $J = 8.9$ Hz, H-5), 4.54 (d, 1H, $J = 3.7$ Hz, H-2), 4.20–4.36 (m, 3H, H-4, –OCH_2–), 3.82 (d, 1H, $J = 3.0$ Hz, H-3), 3.50 (s, 3H, –OMe), 1.46 (s, 3H, CH_3), 1.26–1.42 (m, 6H, $2 \times CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$, TMS), δ 166.73, 140.06, 127.81, 112.25, 105.46, 86.35, 82.02, 80.32, 70.03, 61.25, 58.28, 30.00, 27.21, 14.49; FABMS: *m*/*z* 303 (M^++1); Anal. Calcd for $C_{14}H_{22}O_7$: C, 55.62; H, 7.33. Found: C, 55.51; H, 7.28.

4.6. 3-Hydroxy[6-methoxy-2,2-dimethyl-(3a*R*,5*R*,6*S*,6a*R*)-perhydrofuro[2,3-*d*]dioxol-5-yl]-methyl-3-buten-2-one 1b

1,2-*O*-Isopropylidene-3-*O*-methyl-α-D-*xylo*-pentodialdo-1,4-furanose **1** (0.20 g, 1 mmol) in dioxane–water [(1:1), 5 mL] was treated with MVK **b** (0.25 mL, 3 mmol) in the presence of DABCO (0.11 g, 1 mmol) at room temperature for 15 h. The reaction mixture was worked up and purified as described for **1a** to give **1b** (0.223 g, 82%) as a pale yellow syrup with 53% de as determined by chiral HPLC analysis. HPLC (column: ODS, 30% CH_3CN in potassium buffer, flow rate: 1 mL/min, t_r(minor) = 6.8 min, t_r(major) = 7.5 min); $[\alpha]_D = -41.5$ (*c* 2.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 6.32 (s, 0.24H, olefinic), 6.28 (s, 0.24H, olefinic), 6.22 (s, 0.76H, olefinic), 6.09 (s, 0.76H, olefinic), 5.82 (d, 1H, J = 3.8 Hz, H-1), 4.60–4.48 (m, 2H, H-2, H-5), 4.25–4.17 (m, 1H, H-4), 3.81 (d, 1H, J = 3.6 Hz, H-3), 3.49 (s, 3H, OMe), 2.40 (s, 3H, CH_3), 1.46 (s, 3H, CH_3), 1.30 (s, 3H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$, TMS): δ 200.90, 147.11, 128.01, 111.70, 105.01, 86.47, 84.23, 81.49, 80.18, 69.54, 57.95, 26.75, 26.33; IR (neat) ν 3431, 1762, 1664 cm^{-1}; FABMS: *m*/*z* 273 (M^++1). Anal. Calcd for $C_{13}H_{20}O_6$: C, 57.34; H, 7.40. Found: C, 57.26; H, 7.41.

4.7. 2-Hydroxy[6-methoxy-2,2-dimethyl-(3a*R*,5*R*,6*S*,6a*R*)-perhydrofuro[2,3-*d*][1,3]-dioxol-5-yl]-methylacryloyl cyanide 1c

1,2-*O*-Isopropylidene-3-*O*-methyl-α-D-*xylo*-pentodialdo-1,4-furanose **1** (0.20 g, 1 mmol) in dioxane–water [(1:1), 5 mL] was treated with acrylonitrile **c** (0.20 mL, 3 mmol) in the presence of DABCO (0.11 g, 1 mmol) at room temperature for 15 h. The reaction mixture was worked up and purified as described for **1a** to give **1c** (0.193 g, 76%) as a yellow oil with 60% de as determined by chiral HPLC analysis. HPLC (column: ODS, 30% CH_3CN in potassium buffer, flow rate: 1 mL/min, t_r(minor) = 11.0 min, t_r(major) = 11.9 min); $[\alpha]_D = -40.9$ (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 6.06 (br s, 2H, olefinic), 5.96 (d, 1H, J = 4.0 Hz, H-1), 4.58 (br s, 2H, H-2, H-5), 4.22–4.18 (m, 1H, H-4), 3.96 (d, 1H, J = 3.2 Hz, H-3), 3.44 (s, 3H, OMe), 3.28 (d, 1H, J = 4.8 Hz, OH), 1.52 (s, 3H, CH_3), 1.34 (s, 3H, CH_3); IR (neat) ν 3431, 2228, 1759 cm^{-1}; FABMS: *m*/*z* 256 (M^++1); Anal. Calcd for $C_{12}H_{17}NO_5$: C, 56.46; H, 6.71; N, 5.81. Found: C, 56.41; H, 6.68; N, 5.80.

4.8. Ethyl 2-hydroxy[6-methoxy-2,2-dimethyl-(3a*S*,4*R*,6a*S*)-perhydrofuro[3,4-*d*][1,3]-dioxol-4-yl]methylacrylate 2a

2,3-*O*-Isopropylidene-1-*O*-methyl-α-D-*lyxo*-pentodialdo-1,4-furanose **2** (0.20 g, 1 mmol) in dioxane–water [(1:1), 5 mL] was treated with ethyl acrylate **a** (0.33 mL, 3 mmol) in the presence of DABCO (0.11 g, 1 mmol) at room temperature for 15 h. The reaction mixture was worked up and purified as described for **1a** to give **2a** (0.168 g, 56%) as a colorless syrup with 56% de as determined by chiral HPLC analysis. HPLC (column: ODS, 30% CH_3CN in potassium buffer, flow rate: 1 mL/min, t_r(minor) = 4.9 min, t_r(major) = 6.4 min); $[\alpha]_D = +58.6$ (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 6.37 (s, 0.22H, olefinic), 6.32 (s, 0.78H, olefinic), 6.10 (s, 0.22H, olefinic), 5.96 (s, 0.78H, olefinic), 4.86 (s, 1H, H-1), 4.80–4.78 (m, 2H, H-4, H-5), 4.53 (d, 1H, J = 5.2 Hz, H-2), 4.25 (q, 2H, J = 7.4 Hz, CH_2), 4.08 (dd, 1H, J = 3.8, 6.1 Hz, H-3), 3.40 (d, 1H, J = 6.2 Hz, OH), 3.26 (s, 3H, OMe), 1.52 (s, 3H, CH_3), 1.38–1.30 (m, 6H, $2 \times CH_3$); ^{13}C NMR (50 MHz, $CDCl_3$, TMS): δ 166.50, 139.69, 127.26, 112.81, 107.17, 84.94, 80.14, 79.41, 70.05, 60.93, 54.56, 26.04, 24.68, 14.14; IR (neat) ν 3396, 1728, 1665 cm^{-1}; FABMS: *m*/*z* 303 (M^++1); Anal. Calcd for $C_{14}H_{22}O_7$: C, 55.62; H, 7.33. Found: C, 55.57; H, 7.31.

4.9. 3-Hydroxy[6-methoxy-2,2-dimethyl-(3a*S*,4*R*,6a*S*)-perhydrofuro[3,4-*d*][1,3]dioxol-4-yl]methyl-3-buten-2-one 2b

2,3-*O*-Isopropylidene-1-*O*-methyl-α-D-*lyxo*-pentodialdo-1,4-furanose **2** (0.20 g, 1 mmol) in dioxane–water [(1:1), 5 mL] was treated with MVK **b** (0.25 mL, 3 mmol) in the presence of DABCO (0.11 g, 1 mmol) at room temperature for 15 h. The reaction mixture was worked up and purified as described for **1a** to furnish **2b** (0.188 g, 69%) as a pale yellow syrup with 60% de as determined by chiral HPLC analysis. HPLC (column: ODS, 30% CH_3CN in potassium buffer, flow rate: 1 mL/min, t_r(minor) = 8.6 min, t_r(major) = 9.8 min); $[\alpha]_D = +52.0$ (*c* 0.7, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 6.29 (s, 0.2H, olefinic), 6.20 (s, 0.2H, olefinic), 6.15 (s, 0.8H, olefinic), 6.08 (s, 0.8H, olefinic), 4.80 (s, 1H, H-1), 4.75–4.68 (m, 2H, H-4, H-5), 4.45 (d, 1H, J = 5.8 Hz, H-2), 4.0–3.95 (m, 1H, H-3), 3.42 (d, 1H, J = 5.6 Hz, OH), 3.22 (s, 3H, OMe), 2.36 (s, 3H, CH_3), 1.48 (s, 3H, CH_3), 1.27 (s, 3H, CH_3); IR (neat) ν 3445, 1735, 1680 cm^{-1}; FABMS: *m*/*z* 273 (M^++1); Anal. Calcd for $C_{13}H_{20}O_6$: C, 57.34; H, 7.40. Found: C, 57.24; H, 7.39.

4.10. 1-Hydroxy[6-methoxy-2,2-dimethyl-(3a*S*,4*R*,6a*S*)-perhydrofuro[3,4-*d*][1,3]dioxol-4-yl]methylvinyl cyanide 2c

2,3-*O*-Isopropylidene-1-*O*-methyl-α-D-*lyxo*-pentodialdo-1,4-furanose **2** (0.20 g, 1 mmol) in dioxane–water [(1:1), 5 mL] was treated with acrylonitrile **c** (0.20 mL, 3 mmol) in the presence of DABCO (0.11 g, 1 mmol) at room temperature for 15 h. The reaction mixture was worked up and purified as described for **1a** to afford **2c** (0.182 g, 72%) as a colorless syrup with 72% de as determined by chiral HPLC analysis.

HPLC (column: ODS, 30% CH_3CN in potassium buffer, flow rate: 1 mL/min, t_r(minor) = 7.9 min, t_r(major) = 8.8 min); $[\alpha]_D = +82.7$ (*c* 0.9, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$, TMS): δ 6.13 (s, 1H, olefinic), 6.08 (s, 1H, olefinic), 4.87 (s, 1H, H-1), 4.83–4.79 (m, 1H, H-4), 4.56–4.43 (m, 2H, H-2, H-5), 3.98 (dd, 1H, J = 3.9, 7.9 Hz, H-3), 3.30 (s, 3H, OMe), 3.17 (br s, 1H, OH), 1.48 (s, 3H, CH_3), 1.34 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 132.26, 123.78, 116.76, 113.21, 107.14, 84.85, 79.91, 79.42, 70.97,

54.75, 25.79, 24.49; IR (neat) ν 3426, 2235, 1718 cm^{-1}; FABMS: m/z 256 (M^++1). Anal. Calcd for $C_{12}H_{17}NO_5$: C, 56.46; H, 6.71; N, 5.49. Found: C, 56.51; H, 6.68; N, 5.47.

4.11. Ethyl 2-hydroxy[2,2,7,7-tetramethyl-(3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-perhydrodi[1,3]dioxolo-[5,4-*b*:5,4-*d*]pyran-5-yl]-methylacrylate 3a

1,2:3,4-Di-*O*-isopropylidene-α-D-*galacto*-hexodialdo-1,5-pyranose **3** (0.26 g, 1 mmol) in dioxane–water [(1:1), 5 mL] was treated with ethyl acrylate **a** (0.33 mL, 3 mmol) in the presence of DABCO (0.11 g, 1 mmol) at room temperature for 15 h. The reaction mixture was worked up and purified as described for **1a** to give **3a** (0.234 g, 65%) as a colorless syrup with 40% de as determined by chiral HPLC analysis. HPLC (column: ODS, 20% CH_3CN in potassium buffer, flow rate: 0.6 mL/min, t_r(major) = 67.2 min, t_r(minor) = 80.9 min); $[\alpha]_D = -47.9$ (c 1.0, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$, TMS): δ 6.40 (s, 0.3H, olefinic), 6.37 (s, 0.7H, olefinic), 6.04 (s, 0.3H, olefinic), 5.98 (s, 0.7H, olefinic), 5.58 (d, 0.3H, J = 5.0 Hz, H-1), 5.44 (d, 0.7H, J = 5.0 Hz, H-1), 4.59–4.33 (m, 3H, H-2, H-4, H-6), 4.21–4.12 (m, 3H, H-3, CH_2), 3.98 (dd, 1H, J = 3.2, 7.9 Hz, H-5), 3.17 (br s, 1H, OH), 1.52–1.42 (m, 6H, $2\times CH_3$), 1.38–1.22 (m, 9H, $3\times CH_3$); FABMS: m/z 359 (M^++1); Anal. Calcd for $C_{17}H_{26}O_8$: C, 56.97; H, 7.31. Found: C, 56.87; H, 7.31.

4.12. 3-Hydroxy[2,2,7,7-tetramethyl-(3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-perhydrodi[1,3]dioxolo[5,4-*b*:5,4-*d*]pyran-5-yl]methyl-3-buten-2-one 3b

1,2:3,4-Di-*O*-isopropylidene-α-D-*galacto*-hexodialdo-1,5-pyranose **3** (0.26 g, 1 mmol) in dioxane–water [(1:1), 5 mL] was treated with MVK **b** (0.25 mL, 3 mmol) in the presence of DABCO (0.11 g, 1 mmol) at room temperature for 15 h. The reaction mixture was worked up and purified as described for **1a** to give **3b** (0.282 g, 86%) as a pale yellow syrup with 80% de as determined by ^1H NMR.

$[\alpha]_D = -62.3$ (c 0.5, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$, TMS): δ 6.30 (s, 0.1H, olefinic), 6.24 (s, 0.1H, olefinic), 6.16 (s, 0.9H, olefinic), 6.08 (s, 0.9H, olefinic), 5.50 (d, 0.1H, J = 4.9 Hz, H-1), 5.42 (d, 0.9H, J = 4.9 Hz, H-1), 4.58 (dd, 1H, J = 2.6, 8.0 Hz, H-4), 4.48–4.42 (m, 2H, H-3, H-6), 4.23 (dd, 1H, J = 2.6, 4.9 Hz, H-2), 3.89 (dd, 1H, J = 2.6, 7.8 Hz, H-5), 3.42 (d, 1H, J = 4.8 Hz, OH), 2.38 (s, 3H, CH_3), 1.42 (s, 3H, CH_3), 1.38 (s, 3H, CH_3),1.31 (s, 3H, CH_3), 1.26 (s, 3H, CH_3); FABMS: m/z 329 (M^++1); Anal. Calcd for $C_{16}H_{24}O_7$: C, 58.53; H, 7.37. Found: C, 58.45; H, 7.36.

4.13. 1-Hydroxy[2,2,7,7-tetramethyl-(3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-perhydrodi[1,3]dioxolo[5,4-*b*:5,4-*d*]pyran-5-yl]methylvinyl cyanide 3c

1,2:3,4-Di-*O*-isopropylidene-α-D-*galacto*-hexodialdo-1,5-pyranose **3** (0.26 g, 1 mmol) in dioxane–water [(1:1), 5 mL] was treated with acrylonitrile **c** (0.20 mL, 3 mmol) in the presence of DABCO (0.11 g, 1 mmol) at room temperature for 15 h. The reaction mixture was worked up and purified as described for **1a** to give **3c** (0.215 g, 69%) as a colorless syrup with 86% de as determined by chiral HPLC analysis. HPLC (column: ODS, 30% CH_3CN in potassium buffer, flow rate: 0.4 mL/min, t_r(minor) = 13.9 min, t_r(major) = 16.0 min); $[\alpha]_D = -36.0$ (c 0.5, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$, TMS): δ 6.20 (s, 1H, olefinic), 6.13 (s, 1H, olefinic), 5.56 (d, 1H, J = 4.8 Hz, H-1), 4.61 (dd, 1H, J = 2.8, 5.2 Hz, H-4), 4.45 (d, 1H, J = 4.8 Hz, H-2), 4.34–4.27 (m, 2H, H-3, H-6), 3.85 (dd, 1H, J = 2.6, 8.0 Hz, H-5), 3.46 (br s, 1H, –OH), 1.58 (s, 3H, CH_3), 1.47 (s, 3H, CH_3), 1.32 (s, 6H, $2\times CH_3$); FABMS: m/z 312 (M^++1); Anal. Calcd for $C_{15}H_{21}NO_6$: C, 57.87; H, 6.80; N, 4.50. Found: C, 57.64; H, 6.79; N, 4.49.

4.14. Ethyl 2-[2,2-dimethyl-(4*R*)-1,3-dioxolan-4-yl(hydroxy)-methyl]acrylate 4a

2,3-*O*-Isopropylidene-(*R*)-glyceraldehyde **4** (0.13 g, 1 mmol) in dioxane–water [(1:1), 5 mL] was treated with ethyl acrylate **a** (0.33 mL, 3 mmol) in the presence of DABCO (0.11 g, 1 mmol) at room temperature for 15 h. The reaction mixture was worked up and purified as described for **1a** to give **4a** (0.191 g, 82%) as a colorless syrup with 80% de as determined by chiral HPLC analysis. HPLC (column: chiralcel OD, 0.5:9.5 ^{i}PrOH–*n*-hexane, flow rate: 1 mL/min, t_r(major) = 22.5 min, t_r(minor) = 23.6 min); $[\alpha]_D = -6.4$ (c 1.0, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$, TMS): δ 6.38 (s, 0.1H, olefinic), 6.36 (s, 0.9H, olefinic), 5.99 (s, 1H, olefinic), 4.50 (dd, 1H, J = 4.5, 10.4 Hz, allylic), 4.38–4.23 (m, 3H, H-2, CH_2), 3.91 (d, 2H, J = 7.5 Hz, H-3), 2.94 (d, 1H, J = 4.5 Hz, OH), 1.45 (s, 3H, CH_3), 1.38–1.32 (m, 6H, $2\times CH_3$); IR (neat) ν 3395, 1750, 1668 cm^{-1}; EIMS: m/z 215 (M^+-15); Anal. Calcd for $C_{11}H_{18}O_5$: C, 57.38; H, 7.88. Found: C, 57.48; H, 7.87.

4.15. 3-[2,2-Dimethyl-(4*R*)-1,3-dioxolan-4-yl(hydroxy)-methyl]-3-buten-2-one 4b

2,3-*O*-Isopropylidene-(*R*)-glyceraldehyde **4** (0.26 g, 1 mmol) in dioxane–water [(1:1), 5 mL] was treated with MVK **b** (0.25 mL, 3 mmol) in the presence of DABCO (0.11 g, 1 mmol) at room temperature for 15 h. The reaction mixture was worked up and purified as described for **1a** to give **4b** (0.138 g, 69%) as a pale yellow syrup. $[\alpha]_D = +3.2$ (c 1.0, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$, TMS): δ 6.21 (d, 2H, J = 5.3 Hz, olefinic), 4.50 (dd, 1H, J = 4.4, 10.1 Hz, allylic), 4.27 (q, 1H, J = 5.7 Hz, H-2), 3.86 (d, 2H, J = 7.5 Hz, H-3), 3.02 (d, 1H, J = 4.6 Hz, OH), 2.40 (s, 3H, CH_3), 1.44 (s, 3H, CH_3), 1.36 (s, 3H, CH_3); IR (neat) ν 3419, 1735, 1634 cm^{-1}; EIMS: m/z 186 (M^+-14); Anal. Calcd for $C_{10}H_{16}O_4$: C, 59.99; H, 8.05. Found: C, 59.85; H, 8.06.

4.16. 1-[2,2-Dimethyl-(4*R*)-1,3-dioxolan-4-yl(hydroxy)-methyl]vinyl cyanide 4c

1,2-*O*-Isopropylidene-(*R*)-glyceraldehyde **4** (0.13 g, 1 mmol) in dioxane–water [(1:1), 5 mL] was treated with acrylonitrile **c** (0.20 mL, 3 mmol) in the presence of DABCO (0.11 g, 1 mmol) at room temperature for

15 h. The reaction mixture was worked up and purified as described for **1a** to afford **4c** (0.141 g, 77%) as a colorless syrup with 75% de as determined by chiral HPLC analysis. HPLC (column: ODS, 30% CH_3CN in potassium buffer, flow rate: 1 mL/min, t_r(minor) = 36.1 min, t_r(major) = 53.4 min); $[\alpha]_D = -3.1$ (*c* 0.6, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$, TMS): δ 6.18 (d, 1H, *J* = 5.8 Hz, olefinic), 6.12 (d, 1H, *J* = 5.8 Hz, olefinic), 4.42 (dd, 1H, *J* = 4.5, 9.8 Hz, allylic), 4.16 (q, 1H, *J* = 6.1 Hz, H-2, CH_2), 3.92 (d, 2H, *J* = 7.4 Hz, H-3), 2.62 (d, 1H, *J* = 5.2 Hz, OH), 1.45 (s, 3H, CH_3), 1.39 (s, 3H, CH_3); IR (neat) ν 3389, 2230, 1652 cm^{-1}; EIMS: *m*/*z* 184 (M^++1); Anal. Calcd for $C_9H_{13}NO_3$: C, 59.00; H, 7.15; N, 7.65. Found: C, 59.05; H, 7.16; N, 7.64.

4.17. Ethyl 2-[2,2-dimethyl-(4*S*)-1,3-dioxolan-4-yl(hydroxy)methyl]acrylate 5a

1,2-*O*-Isopropylidene-(*S*)-glyceraldehyde **5** (0.13 g, 1 mmol) in dioxane–water [(1:1), 5 mL] was treated with ethyl acrylate **a** (0.33 mL, 3 mmol) in the presence of DABCO (0.11 g, 1 mmol) at room temperature for 15 h. The reaction mixture was worked up and purified as described for **1a** to furnish **5a** (0.220 g, 76%) as a colorless syrup. $[\alpha]_D = +6.2$ (*c* 1.0, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$, TMS): δ 6.36 (s, 1H, olefinic), 5.94 (s, 1H, olefinic), 4.41 (br d, 1H, *J* = 10.1 Hz, allylic), 4.34–4.19 (m, 3H, H-2, CH_2), 3.83 (d, 2H, *J* = 7.5 Hz, H-3), 2.89 (br s, 1H, OH), 1.42 (s, 3H, CH_3), 1.38–1.34 (m, 6H, $2 \times CH_3$); EIMS: *m*/*z* 215 (M^+-15); Anal. Calcd for $C_{11}H_8O_5$: C, 57.38; H, 7.88. Found: C, 57.24; H, 7.87.

4.18. 1-[6-Methoxy-2,2-dimethyl-(3a*R*,5*R*,6*S*,6a*R*)-perhydrofuro[2,3-*d*][1,3]dioxol-5-yl]-2-methylene-1,3-propanediol 11

To a cooled solution of $LiAlH_4$ (0.038 g, 0.99 mmol) in dry ether was added a solution of $AlCl_3$ (0.044 g, 0.33 mmol) in ether and stirred for 15 min. Then, a solution of **1a** (0.2 g, 0.66 mmol) in dry ether was added and stirred at 0 °C for 2 h. After completion of reaction, the reaction mixture was quenched with satd Na_2SO_4 solution at 0 °C, filtered through a pad of Celite and extracted with ethyl acetate. The filtrate was concentrated under reduced pressure to obtain a residue, which was purified by chromatography (silica gel 60–120 mesh, EtOAc–hexane, 6:4) to afford diol **11** (0.117 g, 68%) as a colorless syrup. $[\alpha]_D = -45.5$ (*c* 0.8, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$, TMS): δ 5.85 (d, 1H, $J_{1,2}$ = 3.9 Hz, H-1), 5.24 (d, 2H, *J* = 6.3 Hz, olefinic), 4.56 (d, 1H, *J* = 3.9 Hz, H-2), 4.46 (d, 1H, *J* = 7.8 Hz, H-5), 4.25 (d, 1H, *J* = 3.1 Hz, H-4), 4.17 (dd, 2H, *J* = 3.1, 8.6 Hz, CH_2), 3.85 (d, 1H, *J* = 3.1 Hz, H-3), 3.47 (s, 3H, OMe), 3.04 (br s, 1H, OH), 1.51 (s, 3H, CH_3), 1.36 (s, 3H, CH_3).

4.19. 5-[2,2-Dimethyl-5-methylene-(4*S*)-1,3-dioxan-4-yl]-2,2-dimethyl-(3a*R*,5*R*,6*S*,6a*R*)-perhydrofuro-[2,3-*d*][1,3]-dioxol-6-yl methyl ethers 12 and 13

To a stirred solution of diol **11** (0.1 g, 0.384 mmol) in DMP (2 mL), PTSA (catalytic) was added and allowed to stir at room temperature for 6 h. Then, the reaction mixture was quenched with Et_3N, after which ethyl acetate was added and washed with water (1×15 mL). The collected organic layer was dried over Na_2SO_4, concentrated, and the residue obtained was purified by chromatography (silica gel 60–120 mesh, EtOAc–hexane, 1:9) to afford **12** (0.065 g, 56%) and 5-[2,2-dimethyl-5-methylene-(4*R*)-1,3-dioxan-4-yl]-2,2-dimethyl-(3a*R*,6*S*,6a*R*)-perhydrofuro[2,3-*d*][1,3]dioxol-6-yl methyl ether **13** (0.032 g, 28%) as a colorless syrups.

Compound **12**: $[\alpha]_D = -52.3$ (*c* 0.8, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$, TMS): 5.94 (d, 1H, $J_{1,2}$ = 3.9 Hz, H-1), 5.28 (s, 1H, olefinic), 4.99 (s, 1H, olefinic), 4.58 (d, 1H, $J_{4,5}$ = 8.9 Hz, H-5), 4.53 (d, 1H, *J* = 3.9 Hz, H-2), 4.37 (d, 1H, *J* = 13.2 Hz, –CH), 4.25 (d, 1H, *J* = 13.2 Hz, $-CH_2$), 4.23 (dd, 1H, *J* = 2.9, 8.9 Hz, H-4), 3.61 (d, 1H, *J* = 2.9 Hz, H-3), 3.44 (s, 3H, –OMe), 1.48 (s, 6H, $2 \times CH_3$), 1.39 (s, 3H, CH_3), 1.32 (s, 3H, CH_3); FABMS: *m*/*z* 301 (M^++1); Anal. Calcd for $C_{15}H_{24}O_6$: C, 59.99; H, 8.05. Found: C, 59.82; H, 8.06.

Compound **13**: $[\alpha]_D = +22.0$ (*c* 0.6, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$, TMS): 5.99 (d, 1H, *J* = 3.9 Hz, H-1), 5.0 (s, 1H, olefinic), 4.96 (s, 1H, olefinic), 4.71 (d, 1H, *J* = 7.8 Hz, H-5), 4.60 (d, 1H, *J* = 3.9 Hz, H-2), 4.43 (dd, 1H, *J* = 3.9, 7.8 Hz, H-4), 4.36 (d, 1H, *J* = 13.2 Hz, $-CH_2$), 4.21 (d, 1H, *J* = 13.2 Hz, $-CH_2$), 3.78 (d, 1H, *J* = 3.9 Hz, H-3), 3.38 (s, 3H, –OMe), 1.52 (s, 3H, CH_3), 1.46 (s, 6H, $2 \times CH_3$), 1.34 (s, 3H, CH_3); FABMS: *m*/*z* 301 (M^++1); Anal. Calcd for $C_{15}H_{24}O_6$: C, 59.99; H, 8.05. Found: C, 59.93; H, 8.12.

4.20. Ethyl-2-hydroxy[6-hydroxy-2,2-dimethyl-(3a*S*,5*R*,6*R*,6a*S*)-perhydrofuro[2,3-*d*][1,3]-dioxol-5-yl]methylacrylate 6a

6-Hydroxy-2,2-dimethyl-(3a*S*,5*S*,6*R*,6a*S*)-perhydrofuro-[2,3-*d*][1,3]dioxole-5-carbaldehyde **6** (0.20 g, 1.062 mmol) in sulfolane (5 mL) was treated with ethyl acrylate **a** (0.34 mL, 3.18 mmol) in the presence of DABCO (0.118 g, 1.062 mmol) at room temperature for 15 h. Then, the reaction mixture was diluted with water (15 mL) and extracted with ether (3×15 mL). The combined organic layers were washed with brine (25 mL), dried over Na_2SO_4, and concentrated under reduced pressure to give a residue, which was purified by chromatography (silica gel 60–120 mesh, hexane–EtOAc, 3:17) to afford adduct **6a** (0.215 g, 70%) as a colorless liquid with 54% de.

$[\alpha]_D = -14.4$ (*c* 0.1, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ 6.40 (s, 0.23H, olefinic), 6.35 (s, 0.77H, olefinic), 6.01 (s, 0.23H, olefinic), 5.96 (s, 0.77H, olefinic), 5.85 (d, *J* = 4.4 Hz, H-1), 4.53 (br d, 2H, *J* = 5.0 Hz, allylic, H-2), 4.35 (d, 1H, *J* = 3.1 Hz, H-4), 4.24 (q, 2H, *J* = 7.5, 14.4 Hz, CH_2), 4.07 (dd, 1H, *J* = 3.76, 7.5 Hz, H-3), 1.55 (s, 3H, CH_3), 1.20–1.40 (m, 6H, $2 \times CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 132.77, 113.74, 88.41, 75.24, 71.69, 29.67, 27.00, 26.00; IR (neat): 3461, 2925, 2500, 1217, 1065 cm^{-1}; FABMS: *m*/*z* (%) = 289 (10) (M+1), 259 (10), 231 (14), 191 (10),

155(100); Anal. Calcd for $C_{13}H_{20}O_7$: C, 54.16; H, 6.99. Found: C, 54.14; H, 6.95.

4.21. 1-Hydroxy[6-hydroxy-2,2-dimethyl-(3a*S*,5*R*,6*R*,6a*S*)-perhydrofuro[2,3-*d*][1,3]dioxol-5-yl]methylvinyl cyanide 6c

6-Hydroxy-2,2-dimethyl-(3a*S*,5*S*,6*R*,6a*S*)-perhydrofuro-[2,3-*d*][1,3]dioxole-5-carbaldehyde (0.20 g, 1.062 mmol) in sulfolane (5 mL) was treated with acrylonitrile **b** (0.20 mL, 3.18 mmol) in the presence of DABCO (0.118 g, 1 mmol) at room temperature for 15 h. The reaction mixture was worked up and purified as described for **6a** to give **6c** (0.204 g, 80%) as a colorless oil with 76% de. $[\alpha]_D = +18.4$ (*c* 0.25, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 6.20 (s, 0.12H, olefinic), 6.15 (s, 0.88H, olefinic), 6.13 (s, 0.12H, olefinic), 6.10 (s, 0.88H, olefinic), 5.88 (s, 1H, H-1), 4.54 (d, 1H, $J = 3.7$ Hz, H-2), 4.46 (d, 1H, $J = 6.0$ Hz, allylic), 4.38 (d, 1H, $J = 3.0$ Hz, H-4), 4.10 (dd, 1H, $J = 3.0$ Hz, $J = 6.0$ Hz, H-3), 1.54 (s, 3H, CH_3), 1.30 (s, 3H, CH_3); IR (neat): 3480, 2951, 1714, 1633, 1300 cm^{-1}; FABMS: *m*/*z* (%) = 241 (20) (M+1), 147 (10), 105 (12), 95 (21), 81(30), 67 (36), 57 (100); Anal. Calcd for $C_{11}H_{15}NO_5$: C, 54.77; H, 6.27; N, 5.81. Found: C, 54.75; H, 6.25; N, 5.80.

4.22. Ethyl 2-hydroxy[6-hydroxy-2,2-dimethyl-(3a*R*,5*S*,6*S*,6a*R*)-perhydrofuro[2,3-*d*][1,3]dioxol-5-yl]methylacrylate 7a

6-Hydroxy-2,2-dimethyl-(3a*R*,5*R*,6*S*,6a*R*)-perhydrofuro-[2,3-*d*][1,3]dioxole-5-carbaldehyde **7** (0.20 g, 1.062 mmol) in sulfolane (5 mL) was treated with ethyl acrylate **a** (0.34 mL, 3.18 mmol) in the presence of DABCO (0.118 g, 1.062 mmol) at room temperature for 15 h. The reaction mixture was worked up and purified as described for **6a** to give **7a** (0.24 g, 78%) as a yellow liquid with 60% de. $[\alpha]_D = +14.40$ (*c* 0.1, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ 6.40 (s, 0.20H, olefinic), 6.35 (s, 0.80H, olefinic), 6.01 (s, 0.20H, olefinic), 5.96 (s, 0.8H, olefinic), 5.85 (d, 1H, $J = 4.4$ Hz, H-1), 4.53 (d, 2H, $J = 5.0$ Hz, H-2, allylic), 4.35 (d, 1H, $J = 3.1$ Hz, H-4), 4.24 (q, 2H, $J = 7.5$Hz, CH_2), 4.07 (dd, 1H, $J = 3.7$, 7.5 Hz, H-3), 1.55 (s, 3H, CH_3), 1.40–1.20 (m, 6H, $2 \times CH_3$); IR (neat): 3461, 2925, 2500, 1217, 1065 cm^{-1}; FABMS: *m*/*z* (%) = 289 (10, M+1), 259 (10), 231 (14), 191 (10), 155 (100); Anal. Calcd for $C_{13}H_{20}O_7$: C, 54.16; H, 6.99. Found: C, 54.14; H, 6.95.

4.23. 1-Hydroxy[6-hydroxy-2,2-dimethyl-(3a*R*,5*S*,6*S*,6a*R*)-perhydrofuro[2,3-*d*][1,3]dioxol-5-yl]methylvinyl cyanide 7c

6-Hydroxy-2,2-dimethyl-(3a*R*,5*R*,6*S*,6a*R*)-perhydrofuro-[2,3-*d*][1,3]dioxole-5-carbaldehyde **7** (0.20 g, 1.062 mmol) in sulfolane (5 mL) was treated with acrylonitrile **c** (0.20 mL, 3.18 mmol) in the presence of DABCO (0.118 g, 1 mmol) at room temperature for 15 h. The reaction mixture was worked up and purified as described for **6a** to give **7c** (0.218 g, 85%) as a yellow liquid with 76% de. $[\alpha]_D = -19.4$ (*c* 0.25, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz): δ 6.20 (s, 0.12H, olefinic), 6.15 (s, 0.88H, olefinic), 6.10 (s, 1H, olefinic), 5.88 (d, $J = 3.7$ Hz, H-1), 4.54 (d, 1H, $J = 3.7$ Hz, H-2), 4.46 (d, 1H, $J = 6.0$ Hz, allylic), 4.38 (d, 1H, $J = 3.0$ Hz, H-4), 4.10 (dd, 1H, $J = 3.0$, 6.0 Hz, H-3), 1.54 (s, 3H, CH_3), 1.30 (s, 3H, CH_3); IR (neat): 3480, 2951, 1714, 1633, 1300 cm^{-1}; FABMS: *m*/*z* (%) = 241 (20) (M+1), 147 (10), 105 (12), 95 (21), 81(30), 67 (36), 57 (100); Anal. Calcd for $C_{11}H_{15}NO_5$: C, 54.75; H, 6.27; N, 5.81. Found: C, 54.79; H, 6.25; N, 5.80.

4.24. Ethyl-2-hydroxy[6-*O*-*tert*-butyldimethylsilyl-methyl-2,2-dimethyl-(3a*R*,5*S*,6*S*,6a*R*)-perhydrofuro-[2,3-*d*]-[1,3]dioxol-5-yl]methylacrylate 8a

6-*O*-*tert*-Butyldimethylsilyl-methyl-2,2-dimethyl-(3a*R*,4*S*,6*R*,6a*R*)-perhydrofuro-[3,4-*d*][1,3]dioxole-4-carbaldehyde **8** (0.20 g, 0.632 mmol) in sulfolane (5 mL) was treated with ethyl acrylate **a** (0.20 mL, 1.896 mmol) in the presence of DABCO (0.070 g, 0.632 mmol) at room temperature for 15 h. The reaction mixture was worked up and purified as described for **6a** to give **8a** (0.16 g, 60%) as a colorless syrup with 40% de.

Yellow liquid; $[\alpha]_D = -27.8$ (*c* 0.15, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): 6.15 (s, 1H, olefinic), 6.11 (s, 1H, olefinic), 4.76–4.72 (m, 1H, allylic), 4.64 (d, 0.3H, $J = 3.76$ Hz, H-1), 4.60 (d, 0.7H, $J = 3.76$ Hz, H-1), 4.54 (d, 0.7H, $J = 5.3$ Hz, H-2), 4.50 (d, 0.3H, $J = 3.1$ Hz, H-2), 4.47–4.40 (m, 1H, H-4), 4.34 (br t, 1H, $J = 2.5$ Hz, H-3), 4.14–4.20 (m, 0.6H, H-5′), 4.14–4.00 (m, 1.4H, H-5), 3.96 (br t, 0.3H, $J = 3.14$ Hz, OTBS–CH), 3.88 (br t, 0.7H, $J = 3.3$ Hz, OTBS–CH), 3.80 (br d, 0.7H, $J = 1.2$ Hz, OTBS–CH), 3.74 (br d, 0.3H, $J = 1.9$ Hz, OTBS–CH), 1.53 (s, 3H, CH_3), 1.30 (s, 3H, CH_3), 0.95 (s, 9H, $3 \times CH_3$), 0.15 (s, 6H, $2 \times CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 165.87; 127.00, 113.00, 97.40, 84.68, 83.22, 82.52, 82.97, 70.66, 64.86, 60.79, 29.68, 26.33, 25.82, 24.83, 14.14, −5.58; IR (neat): 3486, 2985, 2300, 1710, 1302 cm^{-1}; FABMS: *m*/*z* (%) = 418 (2) (M+2), 370 (22), 347 (12), 312 (40), 287(9), 259 (22), 236 (18), 201 (21), 117 (11), 89 (29), 73 (100). Anal. Calcd for $C_{20}H_{36}O_7Si$: C, 57.66; H, 8.71. Found: C, 57.64; H, 8.69.

4.25. 1-Hydroxy [6-*O*-*tert*-butyldimethylsilyl-methyl-2,2-dimethyl-(3a*S*,4*R*,6*R*,6a*R*)-perhydrofuro-[3,4-*d*][1,3]dioxol-4-yl]methylvinyl cyanide 8c

6-*O*-*tert*-Butyldimethylsilyl-methyl-2,2-dimethyl-(3a*R*,4*S*,6*R*,6a*R*)-perhydrofuro-[3,4-*d*][1,3]dioxole-4-carbaldehyde **8** (0.20 g, 0.632 mmol) in sulfolane (5 mL) was treated with acrylonitrile **c** (0.12 mL, 1.896 mmol) in the presence of DABCO (0.070 g, 0.632 mmol) at room temperature for 15 h. The reaction mixture was worked up and purified as described for **6a** to give **8c** (0.152 g, 65%) as a yellow oil with 47% de. $[\alpha]_D = -26.0$ (*c* 0.1, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 6.35 (s, 0.27H, olefinic), 6.30 (s, 0.73H, olefinic), 6.05 (s, 0.27H, olefinic), 5.90 (s, 0.73H, olefinic), 4.85–4.75

(m, 2H, H-1, allylic), 4.30–4.15 (m, 3H, H-3, H-2, H-4), 3.75–3.65 (m, 2H, OTBS–CH_2), 3.50 (br s, 0.27H, OH), 3.45 (br s, 0.73H, OH), 1.55 (s, 3H, CH_3), 1.35 (s, 3H, CH_3), 0.90 (s, 9H, $3\times CH_3$), 0.10 (s, 6H, $2\times CH_3$); IR (neat): 3448, 2984, 1710, 1603, 1302 cm^{-1}; FABMS: *m/z* (%) = 370 (M^++1); Anal. Calcd for $C_{18}H_{31}NO_5Si$: C, 58.51; H, 8.46; N, 3.79. Found: C, 58.49; H, 8.44; N, 3.78.

4.26. Ethyl 2-[6-[2,2-dimethyl-(4*R*)-1,3-dioxolan-4-yl]-2,2-dimethyl-(3a*R*,4*R*,6*R*,6a*S*)-perhydrofuro[3,4-*d*]-[1,3]dioxol-4-yl(hydroxy)methyl]acrylate 9a

6-[2,2-Dimethyl-(4*R*)-1,3-dioxolan-4-yl]-2,2-dimethyl-(3a*S*,4*R*,6*R*,6a*S*)-perhydrofuro[3,4-*d*][1,3]dioxole-4-carbaldehyde **9** (0.20 g, 0.74 mmol) in sulfolane (5 mL) was treated with ethyl acrylate **a** (0.24 mL, 2.22 mmol) in the presence of DABCO (0.082 g, 0.740 mmol) at room temperature for 15 h. The reaction mixture was worked up and purified as described for **6a** to give **9a** (0.234 g, 85%) as a colorless syrup with 45% de. $[\alpha]_D$ = +1.1 (*c* 2.85, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.37 (s, 0.28H, olefinic), 6.29 (s, 0.72H, olefinic), 5.90 (s, 0.28H, olefinic), 5.80 (s, 0.72H, olefinic), 4.75–4.65 (m, 2H, allylic, H-4), 4.48–4.32 (m, 1H, H-5), 4.40 (d, 0.35H, *J* = 6.2 Hz, H-2), 4.30–4.10 (m, 3H, H-2, CH_2), 4.00–3.58 (m, 4H, H-6, H-6′, H-1, H-3), 2.52 (d, 1H, *J* = 4.4 Hz, OH), 1.47 (s, 3H, CH_3), 1.40 (s, 3H, CH_3), 1.36–1.30 (m, 9H, $3\times CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 166.48, 139.00, 126.41, 113.00, 97.43, 86.37, 82.12, 81.15, 71.32, 66.72, 60.99, 51.06, 26.81, 26.22, 25.16, 24.77, 22.69, 14.14; IR (neat): 3486, 2984, 1711, 1316, 1302 cm^{-1}; FABMS: *m/z* (%) = 371 (9) (M+1), 307 (12), 289 (10), 273 (8), 257(7), 166 (8), 154 (100); Anal. Calcd for $C_{18}H_{28}O_8$: C, 58.05; H, 7.58. Found: C, 58.02; H, 7.55.

4.27. 1-[6-[2,2-Dimethyl-(4*R*)-1,3-dioxolan-4-yl]-2,2-dimethyl-(3a*R*,4*R*,6*R*,6a*S*)-perhydrofuro[3,4-*d*][1,3]dioxol-4-yl(hydroxy)methyl]vinyl cyanide 9c

6-[2,2-Dimethyl-(4*R*)-1,3-dioxolan-4-yl]-2,2-dimethyl-(3a*S*,4*R*,6*R*,6a*S*)-perhydrofuro[3,4-*d*][1,3]dioxole-4-carbaldehyde **9** (0.20 g, 0.74 mmol) in sulfolane (5 mL) was treated with acrylonitrile **c** (0.14 mL, 2.22 mmol) in the presence of DABCO (0.082 g, 0.74 mmol) at room temperature for 15 h. The reaction mixture was worked up and purified as described for **6a** to give **9c** (0.18 g, 75%) as a yellow oil with 80% de. $[\alpha]_D$ = −3.15 (*c* 0.95, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.18 (s, 0.10H, olefinic), 6.12 (s, 0.90H, olefinic), 6.08 (s, 0.10H, olefinic), 6.05 (s, 0.90H, olefinic), 4.85–4.72 (m, 2H, allylic, H-4), 4.56 (d, 1H, *J* = 4.5 Hz, H-5), 4.30 (dd, 1H, *J* = 6.8, 13.6 Hz, H-5), 4.10–3.92 (m, 4H, H-6, H-6′, H-1, H-3), 1.50 (s, 3H, CH_3), 1.40 (s, 3H, CH_3), 1.34 (s, 6H, $2\times CH_3$); IR (neat): 3448, 2985, 2250, 1550, 1301 cm^{-1}; FABMS: *m/z* (%) = 324 (18, M+1), 199 (10), 154 (10), 121 (10), 95 (32), 81 (44), 57 (100). Anal. Calcd for $C_{16}H_{23}NO_6$: C, 59.06; H, 7.13; N, 4.31. Found: C, 59.03; H, 7.10; N, 4.30.

4.28. Ethyl-2-hydroxy[6-methoxy-5-methoxymethyl-2,2-dimethyl-(3a*S*,5*R*,6*R*,6a*S*)-perhydrofuro[2,3-*d*][1,3]-dioxol-3-yl]methylacrylate 10a

6-Methoxy-5-methoxymethyl-2,2-dimethyl-(3a*R*,5*R*,6*R*,6a*S*)-perhydrofuro[2,3-*d*][1,3]dioxole-3a-carbaldehyde **10** (0.20 g, 0.774 mmol) in sulfolane (5 mL) was treated with ethyl acrylate **a** (0.25 mL, 2.32 mmol) in the presence of DABCO (0.086 g, 0.774 mmol) at room temperature for 15 h. The reaction mixture was worked up and purified as described for **6a** to give **10a** (0.222 g, 80%) as a yellow syrup with 100% de. $[\alpha]_D$ = +0.9 (*c* 0.85, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.33 (s, 1H, olefinic), 5.96 (s, 1H, olefinic), 4.54 (s, 1H, allylic), 4.26 (s, 1H, H-2), 4.22 (q, 2H, CH_2), 4.08–3.92 (m, 4H, H-3, H-4, H-5), 1.43 (s, 6H, $2\times CH_3$), 1.37 (s, 3H, CH_3), 1.33 (m, 6H, $2\times CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 166.87, 137.94, 128.00, 115.50, 112.70, 97.40, 86.65, 84.37, 73.08, 72.71, 72.15, 61.23, 59.31, 28.36, 27.27, 26.08, 17.93, 12.70; IR (neat): 3486, 2990, 1718, 1630, 1378 cm^{-1}; FABMS: *m/z* (%) = 359 (41, M+1), 301 (12), 243 (10), 229 (11), 195 (21), 171 (30), 154 (100), 120 (19), 107 (32), 77 (33); Anal. Calcd for $C_{17}H_{26}O_8$: C, 56.97; H, 7.31. Found: C, 55.95; H, 7.29.

4.29. 1-Hydroxy[6-methoxy-5-methoxymethyl-2,2-dimethyl-(3a*S*,5*R*,6*R*,6a*S*)-perhydrofuro[2,3-*d*][1,3]dioxol-3-yl]methylvinyl cyanide 10c

6-Methoxy-5-methoxymethyl-2,2-dimethyl-(3a*R*,5*R*,6*R*,6a*S*)-perhydrofuro[2,3-*d*][1,3]dioxole-3a-carbaldehyde **10** (0.20 g, 0.774 mmol) in sulfolane (5 mL) was treated with acrylonitrile **c** (0.15 mL, 2.32 mmol) in the presence of DABCO (0.086 g, 0.774 mmol) at room temperature for 15 h. The reaction mixture was worked up and purified as described for **6a** to give **10c** (0.205 g, 85%) as a yellow syrup with 90% de.

$[\alpha]_D$ = +1.1 (*c* 1.5, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.15 ($2\times$s, olefinic), 4.80 (br s, 2H, allylic, H-2), 4.32 (d, 1H, *J* = 2.1 Hz, H-4), 4.12 (d, 1H, *J* = 1.42 Hz, H-3), 4.04 (br s, 2H, H-5), 3.24 (s, 1H, OH), 1.49 (s, 3H, CH_3), 1.44 (s, 3H, CH_3), 1.40 (br s, 6H, $2\times CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$, TMS): δ 133.39, 123.46, 113.83, 97.90, 86.98, 84.34, 77.56, 76.33, 72.53, 71.82, 60.63, 29.24, 27.32, 26.85, 8.13; IR (neat): 3487, 2990, 1455, 1375, 1198 cm^{-1}; FABMS: *m/z* (%) = 312 (32, M+1), 296 (12), 286 (10), 254 (8), 196 (8), 166 (9), 154 (100); Anal. Calcd for: $C_{15}H_{21}NO_6$: C, 57.87; H, 6.80; N, 4.50. Found: C, 57.75; H, 6.79; N, 4.49.

4.30. 1-[6-[2,2-Dimethyl-(4*R*)-1,3-dioxolan-4-yl]-2,2-dimethyl-(3a*R*,4*R*,6*R*,6a*S*)-perhydrofuro[3,4-*d*][1,3]dioxol-4-yl]-2-methylene-1,3-propanediol 14

To a cooled solution of $LiAlH_4$ (0.030 g, 0.810 mmol) in dry THF was added a solution of $AlCl_3$ (0.035 g, 0.27 mmol) in dry THF and stirred for 15 min. Then, a solution of **9a** (0.2 g, 0.54 mmol) in dry THF was added and stirred at 0 °C for 2 h. After the completion of reaction, the reaction mixture was quenched with satd Na_2SO_4 solution at 0 °C, filtered through a pad of Celite

and with ethyl acetate. The filtrate was concentrated under reduced pressure to obtain a residue, which was purified by chromatography (silica gel 60–120 mesh, EtOAc–hexane, 3:7) to afford diol **14** (0.100 g, 45%) as a white solid. $[\alpha]_D = +19.8$ (*c* 0.45, $CHCl_3$). ^{1}HNMR ($CDCl_3$, 200 MHz): δ 5.24 (s, 1.6H, olefinic), 5.13 (s, 0.4H, olefinic), 4.86–4.92 (m, 1H, allylic), 4.68–4.78 (m, 1H, H-2), 4.18–4.36 (m, 3H, H-4, H-1, H-5), 3.94–4.18 (m, 5H, CH_2, H-6, H-6′), 1.48 (s, 3H, CH_3), 1.40 (s, 3H, CH_3), 1.34 (br s, 6H, $2 \times CH_3$).

4.31. 2-Methylene-1-[2,3,4-trimethoxy-5-methoxymethyl-(2*R*,3*S*,4*R*,5*R*)-dihydro-2-furan-yl]-1,3-propanediol 17

To a cooled solution of $LiAlH_4$ (0.031 g, 0.837 mmol) in dry THF was added a solution of $AlCl_3$ (0.037 g, 0.279 mmol) in dry THF and stirred for 15 min. Then, a solution of **10a** (0.2 g, 0.558 mmol) in dry THF was added and stirred at 0 °C for 2 h. After the completion of reaction, the reaction mixture was quenched with satd Na_2SO_4 solution at 0 °C, filtered through a pad of Celite and with ethyl acetate. The filtrate was concentrated under reduced pressure to obtain a residue, which was purified by chromatography (silica gel 60–120 mesh, EtOAc–hexane, 3:7) to afford diol **17** (0.100 g, 32%) as a white solid. $[\alpha]_D = +29.0$ (*c* 0.30, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$, TMS): δ 5.22 (s, 2H, olefinic), 4.50–4.60 (m, 2H, allylic, H-2), 4.20–4.45 (m, 2H, H-3, H-4), 3.90–4.15 (m, 4H, CH_2, H-5), 1.40 (s, 12H, $4 \times CH_3$).

4.32. 4-[2,2-Dimethyl-(4*R*)-1,3-dioxolan-4-yl]-6-[2,2-dimethyl-5-methylene-(4*R*)-1,3-dioxan-4yl]-2,2-dimethyl-(3a*R*,4*R*,6*R*,6a*S*)-perhydrofuro[3,4-*d*][1,3]dioxol-4-yl]-2-methylene-1,3-propanediol 15 and 16

To a stirred solution of diol **14** (0.1 g, 0.304 mmol) in DMP (2 mL), PTSA (catalytic) was added and allowed to stir at room temperature for 6 h. Then, the reaction mixture was quenched with Et_3N and ethyl acetate was added and washed with water (1×15 mL). The collected organic layer was dried (Na_2SO_4), concentrated, and the residue obtained was purified by chromatography (silica gel 60–120 mesh, EtOAc–hexane, 1:3) to afford **15** (0.028 g, 26%) and **16** (0.015 g, 16%) as a colorless syrup.

Compound **15**. $[\alpha]_D = +11.45$ (*c* 0.55, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 200 MHz): δ 4.96 (d, 2H, $J = 5.09$ Hz, olefinic), 4.85 (d, 1H, $J = 6.5$ Hz, allylic), 4.77–4.65 (m, 1H, H-5), 4.52 (br s, 1H, H-2), 4.30–4.18 (m, 4H, H-1, H-6, H-6′, H-4), 4.12–3.95 (m, 3H, H-3, CH_2), 1.50 (s, 3H, CH_3), 1.46 (s, 3H, CH_3), 1.38 (br s, 9H, $3 \times CH_3$); IR (neat): 3445, 1718, 1456, 1374, 1207, 1161, 1077 cm^{-1}; FABMS: *m*/*z* (%) = 357 (M^++1); Anal. Calcd for $C_{19}H_{30}O_7$: C, 16.60; H, 8.16. Found: C, 16.59; H, 8.15.

Compound **16**. $[\alpha]_D = -5.3$ (*c* 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 200 MHz): δ 4.97 (d, 2H, $J = 5.09$ Hz, olefinic); 4.88 (d, 1H, $J =$ **6.9** Hz, allylic), 4.80–4.69 (m, 1H, H-5), 1.41 (br s, 9H, $3 \times CH_3$), 4.56 (br s, 1H, H-2), 4.31–4.19 (m, 4H, H-4, H-6, H-6′, H-4), 4.14–3.96 (m, 3H, H-3, CH_2), 1.52 (s, 3H, CH_3), 1.49 (s, 3H, CH_3); IR (neat): 3445, 1718, 1456, 1374, 1207, 1161, 1077 cm^{-1}; FABMS: *m*/*z* (%) = 357 (M^++1); Anal. Calcd for $C_{19}H_{30}O_7$: C, 16.60; H, 8.16. Found: C, 16.59; H, 8.15.

4.33. 2,2-Dimethyl-5-methylene-4-[2,3,4-trimethoxy-5-methoxymethyl-(2*R*,3*S*,4*R*,5*S*)-tetrahydro-2-furanyl]-(4*R*)-1,3-dioxane 18

To a stirred solution of diol **17** (0.1 g, 0.316 mmol) in DMP (2 mL), PTSA (catalytic) was added and allowed to stir at room temperature for 6 h. Then, the reaction mixture was quenched with Et_3N, then ethyl acetate was added, and washed with water (1×15 mL). The collected organic layer was dried over Na_2SO_4, concentrated, and the residue obtained was purified by chromatography (silica gel 60–120 mesh, EtOAc–hexane, 1:3) to afford **18** (0.050 g, 46%) as a colorless syrup. $[\alpha]_D = -18.0$ (*c* 0.8, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$, TMS): δ 5.30 (s, 1H, olefinic), 5.10 (s, 1H, olefinic), 4.40–4.32 (m, 2H, allylic, H-2), 4.25 (br d, 1H, $J = 12.6$ Hz, H-4), 4.20 (s, 1H, H-3), 4.15–4.05 (m, 4H, CH_2, H-5), 1.30 (s, 12H, $4 \times CH_3$), 1.25 (s, 12H, $4 \times CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 140.08, 115.32, 114.7, 112.6, 111.05, 99.5, 97.21, 84.99, 72.93, 71.75, 65.3, 60.42, 29.68, 29.13, 27.76, 27.3, 26.4, 22.32, 17.7; IR (neat): 3443, 1723, 1456, 1377, 1210, 1161, 1072 cm^{-1}; FABMS: *m*/*z* (%) = 344 (8, M^+), 299 (10), 183 (10), 154 (14), 136 (16), 109 (30), 95 (50), 81 (58), 69 (80), 55 (100); Anal. Calcd for $C_{18}H_{28}O_7$: C, 60.66; H, 7.92. Found: C, 60.65; H, 7.90.

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