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The Baylis–Hillman reaction: a strategic tool for the synthesis of higher-carbon sugars☆

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Abstract—The Baylis–Hillman reaction of acyclic sugar-derived aldehydes is invoked as an attractive synthetic strategy for ready access to higher-carbon sugars.

Higher-carbon sugars are carbohydrates containing seven or more consecutive carbon atoms and are frequently encountered as subunits in a number of natural products of biological significance and have found important use as chiral synthons.[1] They often play a major role in cell–cell recognition, consequently, their synthesis has been a challenge in carbohydrate chemistry for more than a century and assumes ever increasing significance.[2] The addition of more carbon atoms to unprotected pentoses and hexoses is often plagued by low yields, poor diastereoselectivity and troublesome isolation of the products.[3] The general method for accessing them involves olefination of the C1 or C5 aldehyde and subsequent cis-dihydroxylation.[4] However, the yield in the Wittig reaction using $Ph_3P{=}CHCO_2Et$ was moderate (30–60%) due to a concomitant intramolecular Michael addition occurring in the products.[5] The Michael addition side reaction is a well-known problem in Wittig reactions on pentofuranoses and on hexopyranoses with methyl or ethyl ester stabilized phosphoranes. As part of our research on the Baylis–Hillman reaction,[6] herein we report a novel Baylis–Hillman reaction based synthetic protocol for ready access of diverse and rare heptanoates and octanoates in their protected form. Towards this endeavour, we examined 2,3-*O*-isopropylidene D-ribose **5** and diacetone D-mannose **13** as starting materials to perform the Baylis–Hillman reaction on their acyclic derivatives for the first time and elaborated the resulting adducts into polyhydroxylated seven- and eight-carbon-containing higher sugars with a terminal ester moiety (compounds **1**–**4** and **9**–**12**).

Initially, 2,3-*O*-isopropylidene D-ribose (**5**) was selected to test the efficacy of the proposed methodology. Thus, **5** was treated with LAH in dry THF to give triol **6** (75%). Triol **6** was treated with 2,2-DMP in the presence of a catalytic amount of PTSA in CH_2Cl_2 to furnish the diacetonide protected primary alcohol **7** (85%). Alcohol **7** was oxidized under Swern conditions and the ensuing aldehyde was subjected to a Baylis–Hillman reaction with ethyl acrylate under standard conditions (DABCO/DMSO/rt) to afford a separable mixture of Baylis–Hillman adducts **8a** and **8b** (6.5:3.5). Following separation of the diastereomers, our next task was to assign the stereochemistry at the newly created stereogenic centres. Earlier, we demonstrated that the Baylis–Hillman reaction of sugar-derived aldehydes gave the *anti*-product as the major diastereomer.[6c,g,k] By analogy, the stereochemistry at the newly created centres of compounds **8a** and **8b** was assigned (Scheme 1). Compound **8a** was identified as the major product where the C3 stereochemistry was assigned as *anti* to C4 ($J_{3,4} = 9.6$ Hz). Likewise, in the minor product **8b** the C3 stereochemistry was assigned *syn* ($J_{3,4} = 3.0$ Hz). Next, these two adducts were independently subjected to ozonolysis followed by reduction with $NaBH_4$ in MeOH at 0 °C

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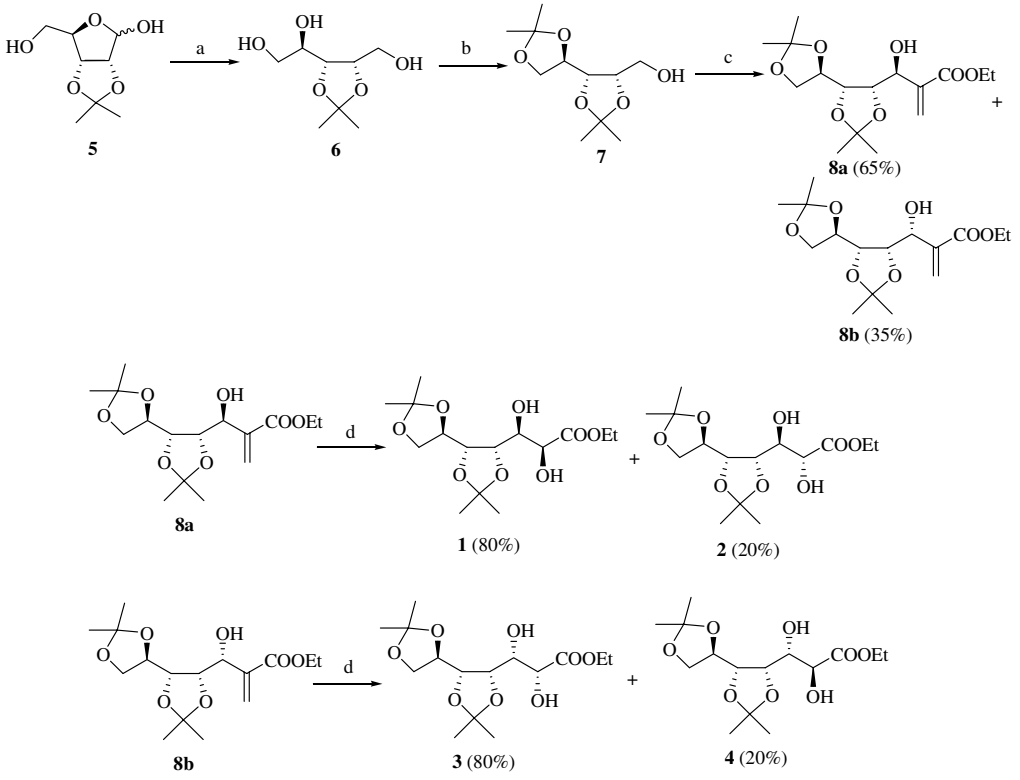


Scheme 1. Reagents and conditions: (a) LAH, THF, 0 °C–rt, 5 h, (75%); (b) 2,2-DMP, PTSA, CH_2Cl_2, 0 °C–rt, 6 h, (85%); (c) (i) $(COCl)_2$, DMSO, Et_3N, −78 °C; (ii) ethyl acrylate, DABCO, DMSO, 0 °C–rt, 36 h, (60% over two steps); (d) (i) O_3, CH_2Cl_2, −78 °C; (ii) $NaBH_4$, MeOH, 0 °C–rt, 0.5 h (65% over two steps).

to afford all four possible diastereomers **1**–**4** (**1**:**2** and **3**:**4** in 8:2 ratios, respectively). To determine the absolute stereochemistry at C2, diastereomers **1**–**4** were converted into their respective cyclic carbonate derivatives **1a**–**4a** (Fig. 1) using triphosgene in the presence of Et_3N in CH_2Cl_2.[7] A comparative NMR study of compounds **1a**–**4a** helped in the unambiguous determination of the absolute stereochemistries at C2 and C3. For example, the ^{1}H NMR spectrum of **1a**, derived from the major adduct **8a**, revealed both the H2 and H3 protons at δ 5.05 as a pair of doublets ($J = 9.4$ Hz) integrating for 2H, while in **2a,** H2 appeared as a doublet at δ 5.03 ($J = 4.1$ Hz) and H3 appeared as a double doublet at δ 4.90 ($J = 2.8$, 4.1 Hz). These ^{1}H NMR values indicated that C2 and C3 in **1** were *syn* and in **2** were *anti*.[8] Thus the absolute stereochemistry at C2 and C3 was unambiguously determined for **1**/**1a** (as depicted in Fig. 1) taking into account that C3 was already assigned for adduct **8a**. Likewise the C2 and C3 stereochemistry for compounds **2**/**2a** was also established based on the above ^{1}H NMR data. Analogously, the ^{1}H NMR spectrum of **3a** showed the H2 proton as a doublet at δ 5.01 ($J = 8.0$ Hz) and H3 as a double doublet at δ 4.80 ($J = 8.0$, 9.2 Hz) indicative of a C2/C3-*syn* relationship, while the ^{1}H NMR spectrum of **4a** revealed H2 as a doublet at δ 4.98 ($J = 4.5$ Hz) and H3 as double doublet at δ 4.95 ($J = 2.2$, 4.5 Hz) being indicative of a C2/C3-*anti* relative arrangement. From these data the absolute configurations of C2 and C3 were assigned for compounds **3**/**3a** and **4**/**4a**. The relative spatial arrangements of the C2–C3 and C2–C4 protons in **3a** and **4a** were examined through 1D-NOESY studies, and the results supported the above conclusions. Thus, it is clear that reduction after ozonolysis afforded the major products as C2/C3-*syn* isomers (**1** and **3**) and the minor products as C2/C3-*anti* isomers (**2** and **4**).

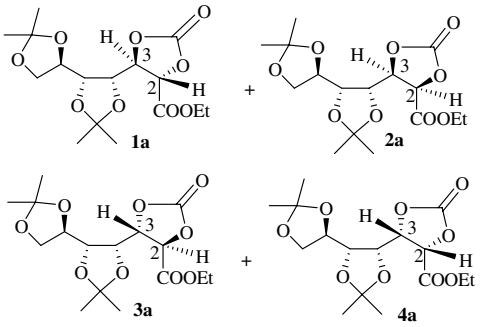
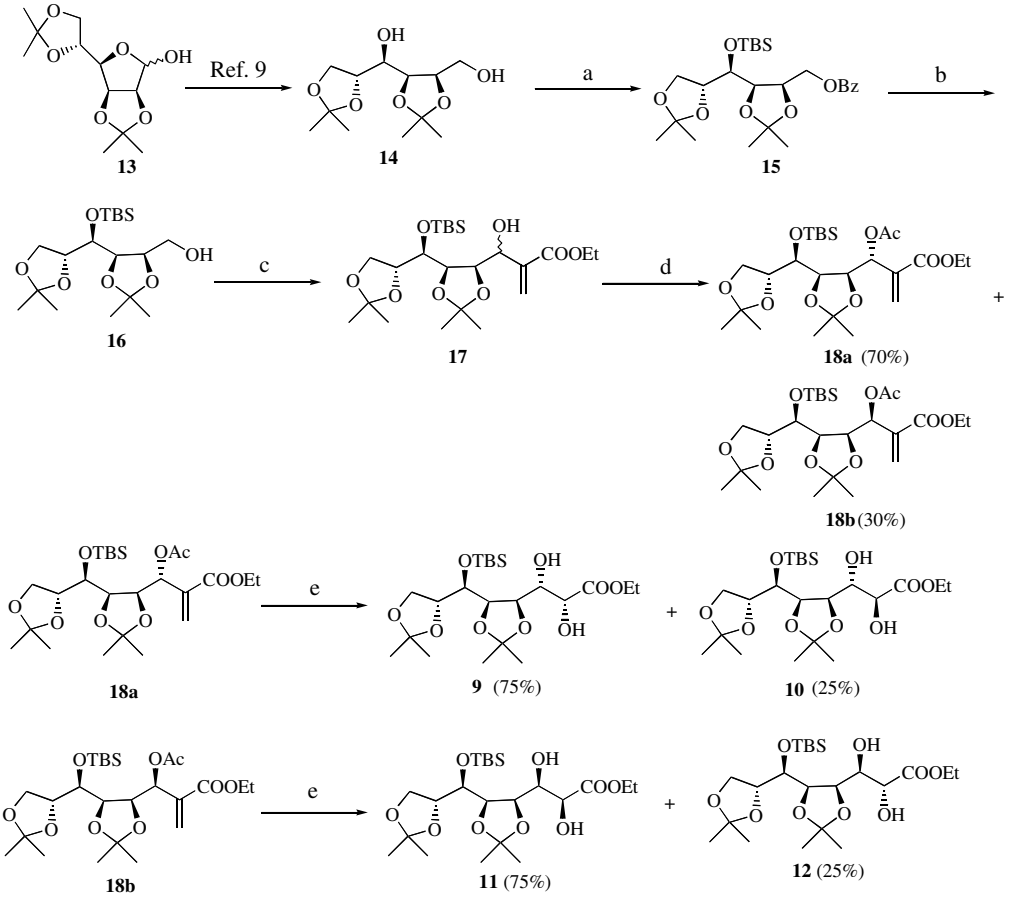


Figure 1. Cyclic carbonates of heptonoates **1**–**4**.

Similarly, diol **14** obtained from diacetone D-mannose[9] (**13**, Scheme 2) was protected as its benzoate ester (benzoyl chloride/Et_3N/CH_2Cl_2) and the secondary hydroxyl group as its TBS ether with TBSOTf, 2,6-lutidine in CH_2Cl_2 to afford **15** (80% over two steps). Compound **15**, on methanolysis with excess K_2CO_3 in MeOH gave primary alcohol **16** (95%). Alcohol **16** on oxidation under Swern conditions followed by Baylis–Hillman reaction with ethyl acrylate under standard conditions (DABCO/DMSO/rt) yielded the corresponding adduct



Scheme 2. Reagents and conditions: (a) (i) benzoyl chloride, Et_3N, CH_2Cl_2, 0 °C–rt, 8 h. (ii) TBSOTf, 2,6-lutidine, CH_2Cl_2, 0 °C–rt, 3 h, (80% over two steps); (b) K_2CO_3, MeOH, 0 °C–rt, 2 h, (95%); (c) (i) $(COCl)_2$, DMSO, Et_3N, CH_2Cl_2, −78 °C; (ii) ethyl acrylate, DABCO, DMSO, 0 °C–rt, 24 h, (65%); (d) Ac_2O, Et_3N, CH_2Cl_2, 0 °C–rt, (95%); (e) O_3, CH_2Cl_2, −78 °C, 0.5 h, (ii) $NaBH_4$, MeOH, 0 °C, (70% over two steps).

17 in 65% yield as a mixture of inseparable diastereomers. The mixture was acetylated ($Ac_2O/Et_3N/CH_2Cl_2$) to afford the separable diastereomers **18a** as the major (70%) and **18b** as the minor (30%) products, respectively. Based on our previous results[6c,g,k] and on ^1H NMR spectral analysis of adducts **18a** and **18b**, wherein H3 (allylic proton) appeared at δ 5.77 ($J = 5.9$ Hz) in **18a** and at δ 5.78 ($J = 2.3$ Hz) in **18b**, the stereochemistry of the allylic hydroxyl group was tentatively assigned as depicted (Scheme 2). Later, both the major (**18a**) and minor (**18b**) acetate derivatives were independently subjected to ozonolysis followed by reduction with $NaBH_4$ in MeOH. As expected two sets of diastereomers **9**–**12** were formed. However, during this reaction, the acetate group was cleaved and the products were obtained as diols. Due to the overlap of the diagnostic H2 and H3 protons in all the ^1H NMR spectra of diols **9**–**12**, the stereochemistry was established from their corresponding carbonate derivatives. Thus, diols **9** and **10** obtained from major isomeric adduct **18a**, when independently treated with triphosgene in the presence of Et_3N in CH_2Cl_2, afforded cyclic carbonates **9a** and **10a** (Fig. 2) while **18b** gave **11a** and **12a**. ^1H NMR analysis of **9a** revealed the H2 proton as a doublet at δ 5.01 ($J = 8.2$ Hz) and H3 as a double doublet at δ 4.7 ($J = 8.2$, 9.5 Hz). Similarly, the ^1H NMR spectrum of **10a** revealed H2 as a doublet at δ 4.95 ($J = 4.0$ Hz) and H3 as a double

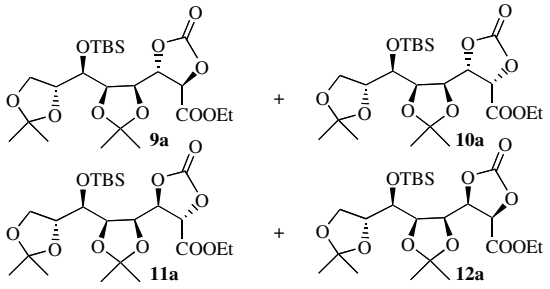


Figure 2. Cyclic carbonates of octanoates **9**–**12**.

doublet at δ 4.89 ($J = 4.0$, 5.1 Hz). These results for **9a** and **10a** were very similar to those of **3a** and **4a**, which suggests that **9a** is C2/C3-*syn* and **10a** is C2/C3-*anti*. Likewise, the minor Baylis–Hillman adduct **18b**, following ozonolysis-reduction, furnished two products **11** and **12** whose structures were determined using the above analogy. Based on carbohydrate nomenclature,[10] compound **1** was named as the D-*glycero*-D-*altro* heptose derivative and compound **9** as the D-*erythro*-L-*altro* octose derivative. On closer inspection of compounds **2**–**4** and **10**–**12**, it was apparent that in general, the D-ribose derivative furnished the D-series while the D-mannose derivative gave the L-series. Thus, heptanoates

1–**4** and octanoates **9**–**12** were synthesized and their structures assigned.[11]

In summary, we have reported a novel synthetic protocol for the construction of higher-carbon sugars through the elaboration of Baylis–Hillman adducts of acyclic sugar-derived aldehydes. This protocol should prove useful to access other members of this class of compounds. These products should find wide use in the synthesis of bio-conjugates.

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References and notes

1. (a) Secrist, J. A., III; Barnes, K. D.; Wu, S.-R. In *Trends in Synthetic Carbohydrate Chemistry*; Horton, D., Hawkins, L. D., McGarvey, G. J., Eds.; ACS Symposium Series 386; American Chemical Society: Washington, DC, 1989; p 93; (b) Danishefsky, S. J.; DeNinno, M. P. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 15–23; (c) Lundt, I. *Top. Curr. Chem.* **1997**, *187*, 117; (d) Casiraghi, G.; Zanardi, F.; Rassu, G.; Spanu, P. *Chem. Rev.* **1995**, *95*, 1677–1716; (e) Fleet, G. W. J. In *Antibiotics and Antiviral Compounds—Chemical Synthesis and Modification*; Krohn, K., Kirst, H. A., Maag, H., Eds.; VCH: Weinheim, 1993; p 333; (f) Hanessian, S. Total Synthesis of Natural Products: The 'Chiron' Approach; Pergamon Press: Oxford, 1983.
2. Györgydeák, Z.; Pelyvás, I. F. *Monosaccharide Sugars–Chemical Synthesis by Chain Elongation*. In *Degradation and Epimerization*; Academic Press: San Diego, 1998.
3. (a) Dromowicz, M.; Köll, P. *Carbohydr. Res.* **1998**, *308*, 169; (b) Bell, A. A.; Nash, R. J.; Fleet, G. W. J. *Tetrahedron: Asymmetry* **1996**, *7*, 595–606; (c) Lundt, I.; Madsen, R. *Synthesis* **1995**, 787; (d) Sato, K.-I.; Miyata, T.; Tanai, I.; Yonezawa, Y. *Chem. Lett.* **1994**, 129–132.
4. Kochetkov, N. K.; Dmitriev, B. A. *Tetrahedron* **1965**, *21*, 803–815.
5. (a) Mootoo, D. R.; Fraser-Reid, B. *J. Org. Chem.* **1987**, *52*, 4511–4517; (b) Mootoo, D. R.; Fraser-Reid, B. *J. Org. Chem.* **1989**, *54*, 5548–5550.
6. (a) Radha Krishna, P.; Kannan, V.; Ilangovan, A.; Sharma, G. V. M. *Tetrahedron: Asymmetry* **2001**, *12*, 829–837; (b) Radha Krishna, P.; Raja Sekhar, E.; Kannan, V. *Tetrahedron Lett.* **2003**, *44*, 4973–4975; (c) Radha Krishna, P.; Kannan, V.; Sharma, G. V. M.; Ramana Rao, M. H. V. *Synlett* **2003**, 888–890; (d) Radha Krishna, P.; Kannan, V.; Sharma, G. V. M. *Synth. Commun.* **2004**, *34*, 55–64; (e) Radha Krishna, P.; Raja Sekhar, E.; Kannan, V. *Synthesis* **2004**, 857–860; (f) Radha Krishna, P.; Kannan, V.; Narasimha Reddy, P. V. *Adv. Synth. Catal.* **2004**, *346*, 603–606; (g) Radha Krishna, P.; Narsingam, M.; Kannan, V. *Tetrahedron Lett.* **2004**, *45*, 4773–4775; (h) Radha Krishna, P.; Krishnarao, Lopinti; Kannan, V. *Tetrahedron Lett.* **2004**, *45*, 7847–7850; (i) Radha Krishna, P.; Rachna Sachwani; Kannan, V. *Chem. Commun.* **2004**, 2580–2581; (j) Radha Krishna, P.; Kannan, V.; Sharma, G. V. M. *J. Org. Chem.* **2004**, *69*, 6467–6469; (k) Radha Krishna, P.; Manjuvani, A.; Kannan, V. *Tetrahedron: Asymmetry* **2005**, *16*, 2691–2703.
7. Kang, S.-K.; Jeon, J.-Ho.; Nam, K.-S.; Park, C.-H.; Lee, H.-W. *Synth. Commun.* **1994**, *24*, 305–312.
8. (a) Rama Rao, A. V.; Murali Dhar, T. G.; Chakraborty, T. K.; Gurjar, M. K. *Tetrahedron Lett.* **1988**, *29*, 2069–2072; (b) Contelles, J. M.; de Opazo, E.; Arroyo, N. *Tetrahedron* **2001**, *57*, 4729–4739.
9. Bird, J. W.; Jones, J. K. N. *Can. J. Chem.* **1963**, *41*, 1877–1881.
10. McNaught, A. D. *Pure Appl. Chem.* **1996**, *68*, 1919–2008.
11. *Spectral data of selected compounds:* Compound **8a**: White syrup; $[\alpha]_D^{25}$ +13.8 (*c* 1.5, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$); δ 6.30 (s, 1H), 5.86 (s, 1H), 4.62 (d, 1H, $J = 9.6$ Hz), 4.26–4.18 (m, 2H), 4.11–3.99 (m, 3H), 3.96–3.90 (m, 2H), 2.89 (d, 1H, $J = 9.4$ Hz), 1.43–1.40 (m, 15H). ^{13}C NMR (100 MHz, $CDCl_3$); δ 166.1, 140.3, 125.9, 109.7, 81.4, 77.4, 76.9, 69.2, 67.5, 60.7, 27.1, 26.8, 26.5, 26.4, 25.2, 14.0. IR (thin film) 3473, 2987, 2934, 1716, 1631, 1376 cm^{-1}; ESIMS; 331 $(M^+ + 1)$ 353 $(M+Na)^+$. Anal. Calcd for $C_{16}H_{26}O_7$: C, 58.17; H, 7.93. Found: C, 58.19; H, 7.88. Compound **8b**: White syrup; $[\alpha]_D^{25}$ +63.3 (*c* 1.5, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$); δ 6.26 (s, 1H), 5.91 (s, 1H), 4.55 (dd, 1H, $J = 3.0$, 6.0 Hz), 4.22 (q, 2H, $J = 7.55$ Hz), 4.14–4.06 (m, 1H), 4.01–3.87 (m, 2H), 3.79 (dd, 1H, $J = 6.7$, 8.3 Hz), 3.45 (d, 1H, $J = 3.0$ Hz), 1.38–1.30 (m, 15H). ^{13}C NMR (100 MHz, $CDCl_3$); δ 166.2, 139.4, 126.2, 109.9, 82.2, 79.5, 75.7, 68.2, 67.6, 60.6, 58.3, 28.3, 26.8, 26.1, 25.1, 14.0. IR (thin film) 3477, 2929, 2910, 1730, 1216, 1067 cm^{-1}; ESIMS; 331 $(M^+ + 1)$ 353 $(M+Na)^+$. Anal. Calcd for $C_{16}H_{26}O_7$: C, 58.17; H, 7.93. Found: C, 58.21; H, 7.90. Compound **1a**: White syrup; $[\alpha]_D^{25}$ +45.7 (*c* 0.25, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$); δ 5.13–5.00 (2d, 2H, $J = 9.4$ Hz each), 4.37–4.20 (m, 2H), 4.15–4.09 (m, 2H), 4.03–3.91 (m, 3H), 1.41–1.25 (m, 15H). ^{13}C NMR (100 MHz, $CDCl_3$); δ 165.7, 152.3, 110.8, 109.9, 77.6, 77.2, 75.6, 73.9, 67.9, 62.1, 27.2, 26.9, 26.2, 25.3, 14.1. IR (thin film) 2986, 2931, 1800, 1760, 1376, cm^{-1}; ESIMS; 361 $(M^+ + 1)$ 378 $(M+NH_4)^+$. Anal. Calcd for $C_{16}H_{24}O_9$: C, 53.33; H, 6.71. Found: C, 53.00; H, 6.80. Compound **3a**: White syrup; $[\alpha]_D^{25}$ +9.3 (*c* 0.5, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$); δ 5.03 (d, 1H, $J = 8.0$ Hz), 4.79 (dd, 1H, $J = 8.0$, 9.2 Hz), 4.34–4.23 (m, 3H), 4.10–4.01 (m, 2H), 4.00–3.88 (m, 2H), 1.42–1.25 (m, 15H). ^{13}C NMR (100 MHz, $CDCl_3$); δ 165.3, 155.2, 111.4, 110.0, 79.8, 77.1, 74.9, 66.6, 62.4, 31.9, 26.6, 27.4, 26.5, 25.1, 22.6, 13.9. IR (thin film) 2975, 2923, 1825, 1756, 1392, cm^{-1}; ESIMS; 361 $(M^+ + 1)$ 378 $(M+NH_4)^+$. Anal. Calcd for $C_{16}H_{24}O_9$: C, 53.33; H, 6.71. Found: C, 53.36; H, 6.68. Compound **4a**: White syrup; $[\alpha]_D^{25}$ +23.2 (*c* 0.2, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$); δ 4.94 (d, 1H, $J =$ 4.5 Hz), 4.86 (dd, 1H, $J = 2.2$, 4.5 Hz), 4.36–4.25 (m, 3H), 4.18–3.89 (m, 3H), 3.63 (t, 1H, $J = 7.9$ Hz), 1.43–1.25 (m, 15H). ^{13}C NMR (100 MHz, $CDCl_3$); δ 165.8, 153.2, 110.2, 109.9, 80.2, 77.5, 76.9, 66.9, 61.9, 31.2, 26.0, 27.8, 26.7, 25.0, 22.1, 14.1. IR (thin film) 2960, 2955, 1830, 1745, 1380, cm^{-1} ESIMS; 361 $(M^+ + 1)$ 378 $(M+NH_4)^+$. Anal. Calcd for $C_{16}H_{24}O_9$: C, 53.33; H, 6.71. Found: C, 53.30; H, 6.70. Compound **18a**: Yellowish syrup; $[\alpha]_D^{25}$ −23.6 (*c* 1.5, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$); δ 6.40 (s, 1H), 5.88 (s, 1H), 5.77 (d, 1H, $J = 5.9$ Hz), 4.33–4.08 (m, 4H), 3.97–3.77 (m, 3H), 3.73 (dd, 1H, $J = 2.9$, 5.1 Hz), 2.08 (s, 3H), 1.42–1.25 (m, 15H), 0.90 (s, 9H), 0.11 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$); δ 169.1, 165.0, 137.5, 128.1, 110.0, 108.4, 79.9, 72.6, 71.4, 66.1, 61.1, 31.8, 29.6, 29.3, 27.2, 27.1, 26.4, 26.0, 24.9, 22.6, 20.9, 18.3, 14.0. IR (thin film) 2984, 2929, 1752, 1723, 1465, 1220 cm^{-1}; ESIMS; 517 $(M^+ + 1)$, 534 $(M+NH_4)^+$, 539 $(M+Na)^+$. Anal. Calcd for $C_{25}H_{44}O_9Si$: C, 58.11; H, 8.58; Si, 5.44. Found: C, 58.18; H, 8.59; Si, 5.42. Compound **18b**: Yellowish syrup; $[\alpha]_D^{25}$ +21.0 (*c* 1.5, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$); δ

6.35 (s, 1H), 5.85 (s, 1H), 5.78 (d, 1H, $J = 2.3$ Hz), 4.28–4.17 (m, 3H), 4.08 (t, 1H, $J = 4.5$ Hz), 3.97–3.76 (m, 4H), 2.12 (s, 3H), 1.39–1.25 (m, 15H), 0.90 (s, 9H), 0.11 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$); δ 169.3, 165.1, 137.4, 127.2, 109.9, 108.7, 78.9, 77.5, 72.9, 70.2, 66.2, 61.1, 29.8, 27.4, 26.9, 26.5, 26.0, 25.1, 22.8, 21.0, 18.5, 14.2. IR (thin film) 2972, 2936, 1758, 1742, 1470, 1155 cm^{-1}; ESIMS; 517 $(M^+ + 1)$, 534 $(M + NH_4)^+$, 539 $(M + Na)^+$. Anal. Calcd for $C_{25}H_{44}O_9Si$: C, 58.11; H, 8.58; Si, 5.44. Found: C, 58.09; H, 8.60; Si, 5.45. Compound **9a**: White syrup; $[\alpha]_D^{25}$ −11.1 (c 0.5, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$); δ 5.06 (d, 1H $J = 8.2$ Hz), 4.69 (dd, 1H, $J = 8.2$, 9.5 Hz), 4.31–4.19 (m, 3H), 4.12–4.06 (m, 2H), 3.96 (dd, 1H, $J = 6.2$, 8.2 Hz), 3.89–3.80 (m, 2H), 1.40–1.31 (m, 15H), 0.90 (s, 9H), 0.11 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$); δ 165.1, 152.0, 110.6, 108.8, 82.5, 78.3, 76.8, 75.2, 72.5, 72.1, 66.4, 62.3, 27.4, 26.8, 26.6, 26.1, 25.2, 18.5, 14.0. IR (thin film) 2986, 2931, 1826, 1755, 1376, 1214 cm^{-1}; ESIMS; 505 $(M^+ + 1)$, 522 $(M + NH_4)^+$. Anal. Calcd for $C_{23}H_{40}O_{10}Si$: C, 54.74; H, 7.99; Si, 5.57. Found: C, 54.70; H, 8.00; Si, 5.55.