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Chain elongation of monosaccharides by sequential cross metathesis and asymmetric dihydroxylation: expeditious approach to higher sugars

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ABSTRACT

Glucose-derived alkenes were homologated via chain elongation to afford higher sugars by the application of cross metathesis with an alkene followed by Sharpless asymmetric dihydroxylation. Heptose, octose, nonose, and decose derivatives were expeditiously prepared by this method.

Carbohydrates play a vital role in living systems. Their profound biological importance has made the synthesis of carbohydrates and their derivatives an important task for synthetic chemists. Although the majority of carbohydrate derivatives are made up of hexose and pentose units, significant effort has been noticed in the area of synthesis of higher sugars because of the biological activity found in some natural products containing sugar units, which have a higher number of carbon atoms than pentoses and hexoses.[1–4] In this context it is imperative that an efficient method for homologation of readily available pentoses or hexoses will enable the synthesis of higher monosaccharides, which will be useful for future research in the area of carbohydrates. The classical Kiliani synthesis has served its purpose, but the use of cyanide makes its application rather restricted. There have been reports of other homologation procedures, which are efficient but require reagents that may not be user friendly.

As examples, Casiraghi reported four-carbon homologation of aldehydo-sugars by using 2-(trimethylsi1oxy)furan.[5] In another approach, two- to three-carbon homologation was demonstrated by Marshall by stereoselective synthesis of higher sugars by the reaction of carbohydrate-derived enals with nonracemic γ-(silyloxy) allylic stannanes followed by substrate-directed hydroxylation.[6,7] Synthesis of higher dialdoses has been achieved by using suitable thiazole-bearing reagents.[8] 2-(Trimethylsilyl)thiazole[8–10] and allyloxymethylmagnesium chloride[11] have been employed for one-carbon homologation. An attractive approach to the homologation process would be the use of a methodology in which the homologating partner has a flexible length, so that the same method would furnish higher sugars of varying sizes. We outline in Scheme 1 an expeditious strategy, which could be utilized to homologate an alkenic sugar derivative **1** to a higher sugar **4** via chain elongation by employing two well-known and remarkably efficacious reactions used in organic synthesis. One of these reactions is cross metathesis, which has been fruitfully used for the coupling of two alkene fragments.[12,13] We envisaged that the application of cross metathesis reaction between two alkene counterparts, one of which is a monosaccharide template **1** and the other is alkene **2** with varying number of carbon atoms and hydroxyl groups, would lead to alkene **3** (Scheme 1). The molecule **3** is a dehydro sugar, and introduction of two hydroxyl groups would transform **3** to its native form **4**. Sharpless asymmetric dihydroxylation procedure has been widely employed to introduce hydroxyl groups on alkenes stereoselectively,[14,15] and application of this reaction to **3** would serve the desired purpose, and make available a higher sugar derivative **4**. The homologation in this case is achieved via the extension of the tail-end of the monosaccharide unit, and the extent

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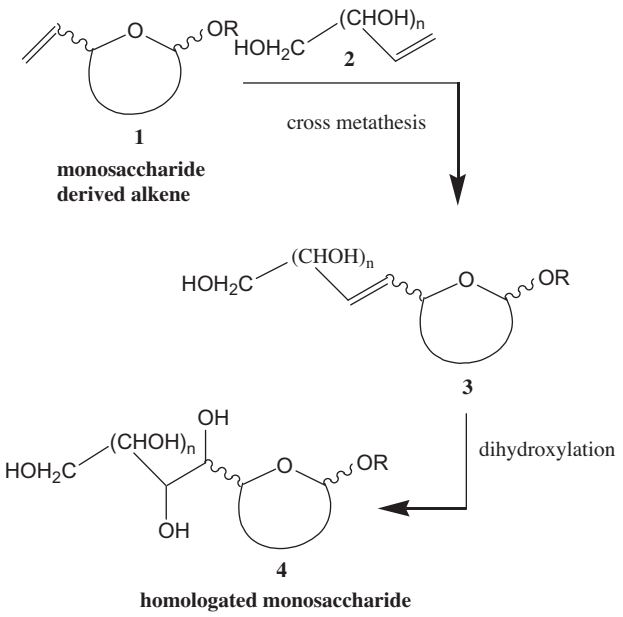
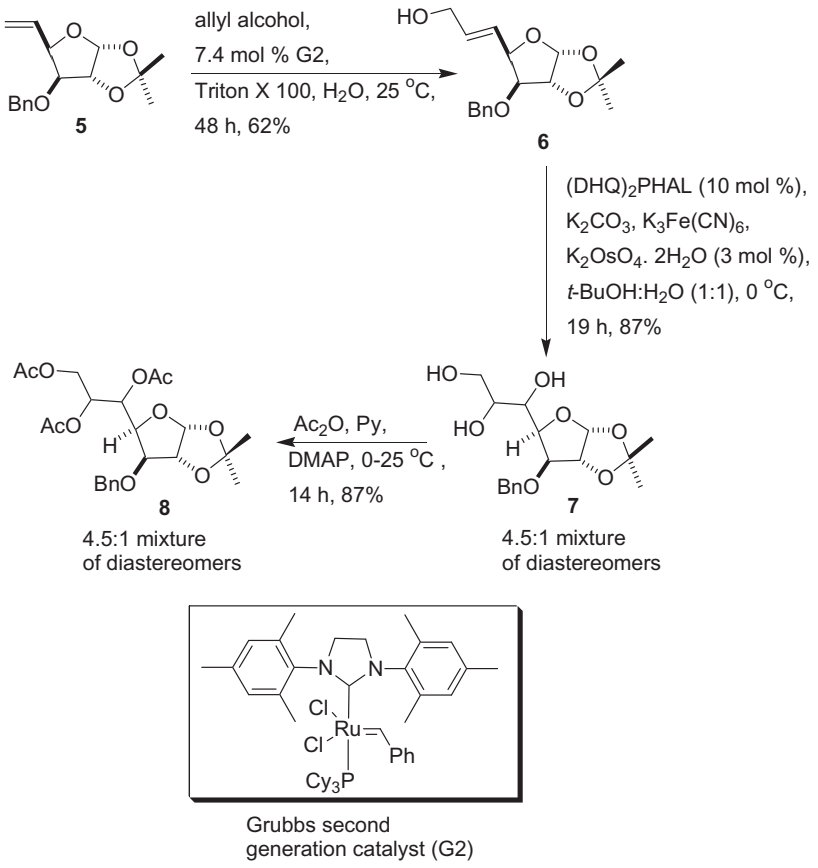


Scheme 1. Chain elongation of monosaccharide by cross metathesis and asymmetric dihydroxylation.

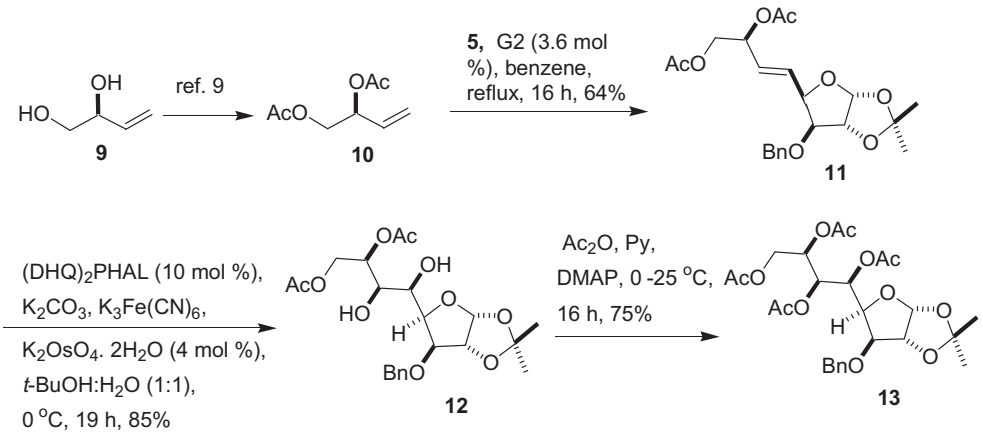
of homologation is determined by the value of *n*. We demonstrate herein the application of this strategy by the synthesis of seven- to ten-membered protected monosaccharide derivatives from alkene **5**.

Alkene **5** obtained from D-glucose according to known protocol[16] was subjected to cross metathesis with allyl alcohol in the presence of Grubbs second generation catalyst and Triton X-100 in water following a recently developed procedure (Scheme 2).[17] The product obtained in 62% yield was identified to be *E*-alkene **6** as evident from the vicinal *J* value of 15.9 Hz for one of the alkene protons in the ^{1}H NMR spectrum taken in C_6D_6. The cross metathesis could also be achieved by using non-aqueous medium, although the yields were poorer. The next step involved the introduction of hydroxyl groups on the alkene moiety, which was accomplished by employing the efficient and operationally simple Sharpless asymmetric dihydroxylation procedure. As a random choice the chiral ligand $(DHQ)_2PHAL$ was used for this purpose.[14,15] Dihydroxylation of **6** using K_2OsO_4 as the osmium source and the aforementioned ligand resulted in the formation of diol **7** in 87% yield as a 4.5:1 diastereomeric mixture as evident from its ^{1}H NMR spectrum (Scheme 2). The individual components of the mixture could not be separated, and instead, the mixture was acetylated for characterization to give again an inseparable 4.5:1 diastereomeric mixture of heptose acetate **8**. The introduction of two hydroxyl groups in the hydroxylation reaction was evident from the mass spectrum as well as the ^{1}H NMR spectrum of **8** exhibiting singlets due the corresponding acetates.

The known enantiomerically pure alkene **10**[18,19] was used as the cross metathesis partner in order to achieve two-carbon chain elongation according to Scheme 3. Reaction between **10** and alkene **5** using Grubbs second generation catalyst in refluxing benzene led to *E*-alkene **11** in 64% yield. Unlike the previously mentioned cross metathesis reaction the use of aqueous medium containing Triton X-100 gave poorer yields in this and the reactions described later. Dihydroxylation of **11** gave a single carbohydrate derivative **12**.



Scheme 2. Homologation of hexose **5** to heptose **8**.

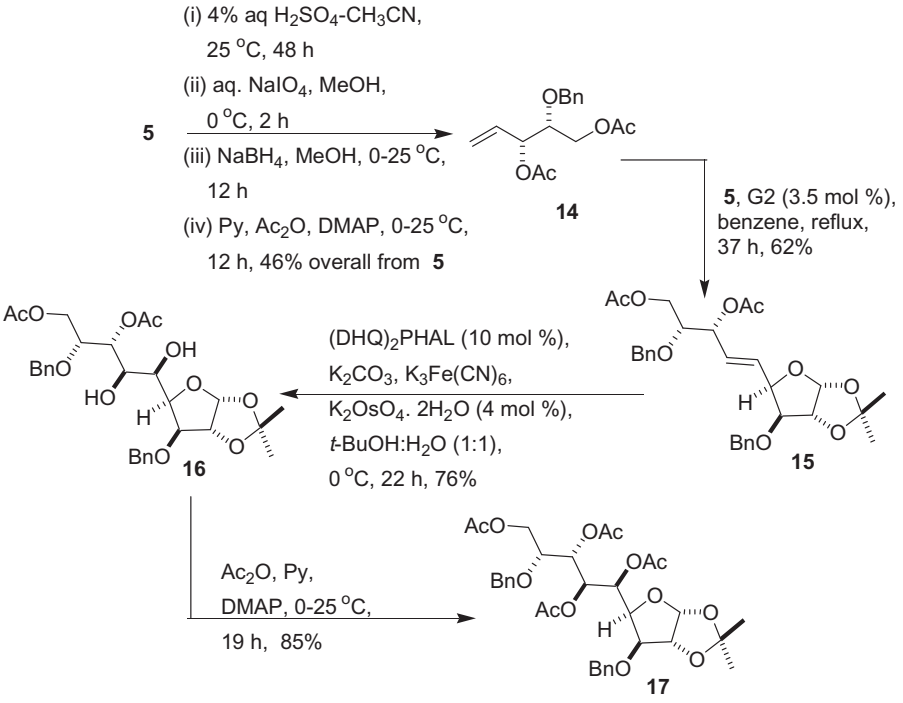


Scheme 3. Homologation of hexose **5** to octose **13**.

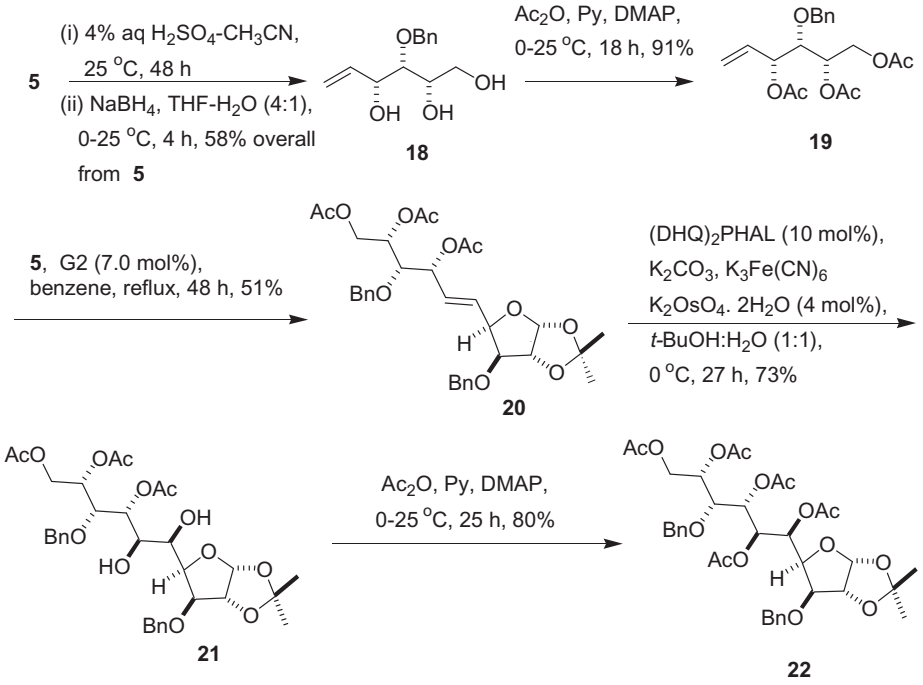
The mass spectrum of **12** was consistent with the introduction of two hydroxyl groups. The assignment of stereochemistry to the newly formed diol in **12** proved problematic due to the overlapping nature of the ^{1}H NMR signals of the relevant protons. The direct assignment of stereochemistry by X-ray crystallographic method was also precluded by our inability to obtain solid derivatives of the diols suitable for this purpose. This is why we had to take recourse to the mnemonic device formulated by Sharpless for predicting the stereochemistry of the diol formed in the dihydroxylation reaction using DHQ,[14,15] and the indicated stereochemistry of **12** was tentatively assigned on the basis of this rule.[20] Diol **12** was characterized as acetate **13**, which represents a protected octose.

In this work alkene **5** was used as the carbohydrate derivative undergoing homologation. The same alkene was also advantageously used as a convenient source for some of the other alkene partners required for cross metathesis. For the purpose of three-carbon chain elongation of **5**, alkene **14** was prepared from **5** as shown in Scheme 4. Following a known methodology,[21] **5** was deprotected with aq H_2SO_4, followed by cleavage with $NaIO_4$ giving an aldehyde, and subsequent $NaBH_4$ reduction and acetylation led to the formation of alkene **14** in 46% overall yield. Cross metathesis between **5** and **14** in the presence of Grubbs second generation catalyst in refluxing benzene gave rise to *E*-alkene **15** in 62% yield. Dihydroxylation of **15** led to the formation of the protected nonose **16**, which was characterized as the corresponding acetate **17**.

Four-carbon chain elongation of **5** required the conversion of **5** to the enantiomerically pure triol **18** as outlined in Scheme 5. Deprotection of **5** with aq H_2SO_4 followed by $NaBH_4$ reduction and subsequent acetylation afforded alkene triacetate **19** in 55% overall yield. Cross metathesis between **5** and **19** in the presence of Grubbs second generation catalyst gave rise to *E*-alkene **20** in



Scheme 4. Homologation of hexose **5** to nonose **17**.

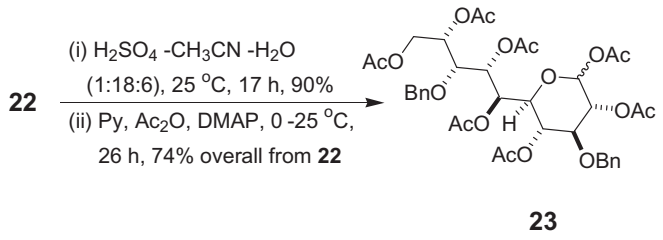


Scheme 5. Homologation of hexose **5** to decose **22**.

51% yield. Dihydroxylation of **20** gave a single carbohydrate derivative **21** in 73% yield. Acetylation of **21** gave rise to **22**, which is a protected form of a decose.

Monosaccharides higher than pentoses occur predominantly in the pyranose form. The homologated monosaccharide molecules described above were synthesized as protected furanosides. In order to demonstrate their conversion to the corresponding pyranosides, the C_{10} carbohydrate derivative **22** was subjected to removal of 1,2-isopropylidene group by treatment with aq H_2SO_4, during which acetates were also hydrolyzed. The resulting mixture was acetylated to furnish the pyranose derivative **23** as a 1:1 inseparable anomeric mixture of acetates (Scheme 6). The structure of **23** was secured by NMR and high resolution mass spectroscopic techniques. The occurrence of two single proton doublets at δ 6.32 (J = 3.6 Hz) and δ 5.54 (J = 8.4 Hz) in the ^{1}H NMR spectrum as well as peaks at 89.4 and 91.9 in the ^{13}C NMR spectrum due to the α- and β-anomeric protons and carbon atoms was consistent with the pyranose structure.[22]

In conclusion, the above work revealed an expeditious strategy for versatile homologation of monosaccharides. The scope of the methodology can be appreciated from the fact that the method employs two efficient reactions viz. alkene cross metathesis and dihydroxylation of an alkene. Both reactions are general, and in principle, elongation can be effected from any site containing an alkene residue, not necessarily the tail-end. Moreover, variation in the sizes of the two alkene partners will enable the synthesis of carbohydrate molecules including oligosaccharides of any desired length. Work in this direction will be reported in due course. We believe that the approach described in this work will be potentially useful as a general method for synthesizing a variety of carbohydrate derivatives.



Scheme 6. Conversion of decofuranose **22** to decopyranose **23**.

Acknowledgments

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Supplementary data

Supplementary data (^{1}H and ^{13}C NMR spectra of **6**, **8**, **11**,**13**, **15**, **17**, **20**, **22** and **23**) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.10.024.

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19. Alkene **10** was prepared from diol (*S*)-**9** (Aldrich catalog no. 19159) by acetylation with acetic anhydride and pyridine.
20. In order to apply the mnemonic, the disubstituted alkene was positioned according to the manner specified in the mnemonic device, and the $(DHQ)_2$PHAL-osmium reagent was made to approach the alkene from the bottom face. The indicated stereochemistry of **12**, **18,** and **21** were all assigned in this manner.
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22. *Spectral data* **6**: colorless viscous liquid, $[\alpha]_D^{25}$ −43.2 (*c* 0.18, $CHCl_3$); IR (neat): 3440, 1688, 1455, 1377, 1215, 1163, 1078, 1020, 739, 699 cm^{-1}; ^1H NMR (300 MHz, C_6D_6): δ 1.24 (s, 3H), 1.57 (s, 3H), 3.86 (d, 1H, *J* = 1.8 Hz), 3.91 (d, 2H, *J* = 4.2 Hz), 4.30 (d, 1H, *J* = 12.0 Hz), 4.42 (d, 1H, *J* = 12.0 Hz), 4.52 (d, 1H, *J* = 3.3 Hz), 4.86 (br d, 1H, *J* = 5.1 Hz), 5.87 (td, 1H, *J* = 4.2, 15.9 Hz), 6.06–6.16 (m, 2H), 7.18–7.34 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.2 (CH_3), 26.7 (CH_3), 62.8 (CH_2), 72.1 (CH_2), 80.6 (CH), 82.9 (CH), 83.3 (CH), 104.7 (CH), 111.6 (C), 124.8 (CH), 127.7 (2 × CH), 127.9 (CH), 128.4 (2 × CH), 134.3 (CH), 137.4 (C); HRMS (ESI, positive ion) Calcd for $C_{17}H_{22}O_5Na$, *m/z* 329.1365. Found 329.1347.Compound **8**: colorless oil, $[\alpha]_D^{25}$ −47.9 (*c* 0.22, $CHCl_3$); IR (neat): 1748, 1373, 1218, 1103, 1076, 1028 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$; 4.5:1 diastereomeric mixture; only peaks due to the major isomer are shown): δ 1.31 (s, 3H), 1.46 (s, 3H), 1.96 (s, 3H), 2.02 (s, 3H), 2.07 (s, 3H), 3.88 (d, 1H, *J* = 2.7 Hz), 4.01 (dd, 1H, *J* = 6.9, 11.7 Hz), 4.25 (dd, 1H, *J* = 3.0, 8.7 Hz), 4.33 (dd, 1H, *J* = 5.1, 11.7 Hz), 4.44 (d, 1H, *J* = 11.7 Hz), 4.56–4.60 (m, 2H), 5.42 (m, 1H), 5.49 (dd, 1H, *J* = 3.0, 9.0 Hz), 5.87 (d, 1H, *J* = 3.6 Hz), 7.30–7.35 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.5 (CH_3), 20.60 (CH_3), 20.64 (CH_3), 26.3 (CH_3), 26.7 (CH_3), 62.3 (CH_2), 67.8 (CH), 70.1 (CH), 71.9 (CH_2), 77.6 (CH), 80.4 (CH), 81.3 (CH), 105.0 (CH), 111.8 (C), 128.1 (CH), 128.3 (2 × CH), 128.4 (2 × CH), 136.7 (C), 169.1 (C), 169.6 (C), 170.5 (C); HRMS (ESI, positive ion) Calcd for $C_{23}H_{30}O_{10}Na$, *m/z* 489.1737. Found 489.1718. Compound **11:** sticky liquid, $[\alpha]_D^{25}$ −11.7 (*c* 0.24, $CHCl_3$); IR (neat): 1735, 1380, 1227, 1163, 1081, 1028, 976, 880 cm^{-1}; ^1H NMR (300 MHz, C_6D_6): δ 1.23 (s, 3H), 1.54 (s, 3H), 1.72 (s, 3H), 1.75 (s, 3H), 3.80 (d, 1H, *J* = 3.0 Hz), 4.04 (dd, 1H, *J* = 6.9, 11.7 Hz), 4.29 (two doublets merged, 2 × 1H, *J* = 12.0 Hz), 4.40 (d, 1H, *J* = 12.0 Hz), 4.47 (d, 1H, *J* = 3.6 Hz), 4.77 (dd, 1H, *J* = 3.0, 6.6 Hz), 5.72–5.82 (m, 2H), 6.01 (d, 1H, *J* = 3.6 Hz), 6.16 (dd, 1H, *J* = 6.6, 14.4 Hz), 7.20–7.37 (m, 5H, merged with solvent); ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.7 (CH_3), 21.0 (CH_3), 26.2 (CH_3), 26.7 (CH_3), 64.8 (CH_2), 71.2 (CH), 72.1 (CH_2), 80.1 (CH), 82.8 (CH), 82.9 (CH), 104.8 (CH), 111.6 (C), 127.6 (2 × CH), 127.9 (CH), 128.2 (CH), 128.4 (2 × CH), 128.9 (CH), 137.3 (C), 169.9 (C), 170.6 (C); HRMS (ESI, positive ion) Calcd for $C_{22}H_{28}O_8Na$ *m/z* 443.1682. Found 443.1634. Compound **13:** colorless oil, $[\alpha]_D^{25}$ −44.5 (*c* 0.32, $CHCl_3$); IR (neat): 1750, 1373, 1218, 1075, 858 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 1.30 (s, 3H), 1.47 (s, 3H), 2.00 (s, 6H), 2.02 (s, 3H), 2.08 (s, 3H), 3.87 (d, 1H, *J* = 3.0 Hz), 4.09 (dd, 1H, *J* = 6.0, 12.0 Hz), 4.20 (dd, 1H, *J* = 3.6, 8.4 Hz), 4.35 (dd, 1H, *J* = 4.2, 12.0 Hz), 4.46 (d, 1H, *J* = 11.4 Hz), 4.56 (d, 1H, *J* = 3.6 Hz), 4.57 (d, 1H, *J* = 12.0 Hz), 5.26–5.28 (m, 1H), 5.47 (dd, 1H, *J* = 3.0, 8.4 Hz), 5.50 (dd, 1H, *J* = 3.0, 6.6 Hz), 5.86 (d, 1H, *J* = 3.6 Hz), 7.29–7.36 (m, 5H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 20.5 (CH_3), 20.70 (CH_3), 20.74 (CH_3), 20.8 (CH_3), 26.3 (CH_3), 26.8 (CH_3), 62.1 (CH_2), 67.6 (CH), 69.8 (CH), 69.9 (CH), 72.0 (CH_2), 78.3 (CH), 80.8 (CH), 81.3 (CH), 105.0 (CH), 111.9 (C), 128.1 (CH), 128.4 (2 × CH), 128.5 (2 × CH), 136.8 (C), 169.37 (C), 169.44 (C), 170.0 (C), 170.6 (C); HRMS (ESI, positive ion) Calcd for $C_{26}H_{34}O_{12}Na$ *m/z* 561.1948. Found 561.1943. Compound **15:** reddish brown viscous liquid, $[\alpha]_D^{25}$ +1.6 (*c* 0.19, $CHCl_3$); IR (neat): 1741, 1455, 1373, 1230, 1078, 1025, 741, 699 cm^{-1}; ^1H NMR (600 MHz, C_6D_6): δ 1.12 (s, 3H), 1.43 (s, 3H), 1.62 (s, 3H), 1.63 (s, 3H), 3.64 (dd, 1H, *J* = 5.4, 9.6 Hz), 3.73 (d, 1H, *J* = 3.6 Hz), 4.05 (dd, 1H, *J* = 6.0, 11.4 Hz), 4.25 (d, 1H, *J* = 12.0 Hz), 4.31 (d, 1H, *J* = 12.0 Hz), 4.38 (d, 1H, *J* = 4.2 Hz), 4.39 (dd, 1H, *J* = 4.2, 13.2 Hz), 4.44 (d, 1H, *J* = 12.0 Hz), 4.51 (d, 1H, *J* = 12.0 Hz), 4.71 (dd, 1H, *J* = 3.0, 6.6 Hz), 5.75 (dd, 1H, *J* = 5.4, 6.0 Hz), 5.89–5.93 (m, 2H), 6.09 (dd, 1H, *J* = 6.0, 15.6 Hz), 7.06–7.11 (m, 2H), 7.14–7.16 (m, 2H), 7.22 (t, 2H, *J* = 7.8 Hz), 7.26–7.29 (m, 4H): ^{13}C NMR (150 MHz, $CDCl_3$): δ 20.8 (CH_3), 20.9 (CH_3), 26.2 (CH_3), 26.8 (CH_3), 63.2 (CH_2), 72.0 (CH_2), 72.3 (CH), 73.0 (CH_2), 77.5 (CH), 80.3 (CH), 82.9 (CH), 83.3 (CH), 104.8 (CH), 111.6 (C), 127.5 (2 × CH), 127.81 (CH), 127.84 (CH), 128.0 (2 × CH), 128.2 (CH), 128.3 (CH), 128.36 (2 × CH), 128.4 (2 × CH), 137.5 (C), 137.8 (C), 169.8 (C), 170.7 (C); HRMS (ESI, positive ion) Calcd for $C_{30}H_{36}O_9Na$, *m/z* 563.2257. Found, 563.2227. Compound **17:** colorless viscous liquid, $[\alpha]_D^{25}$ −15.7 (*c* 0.21, $CHCl_3$); IR (neat): 1748, 1372, 1220, 1076, 1035, 748 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 1.29 (s, 3H), 1.45 (s, 3H), 2.00 (s, 3H), 2.01 (s, 3H), 2.02 (s, 3H), 2.06 (s, 3H), 3.81 (dd, 1H, *J* = 4.2, 9.6 Hz), 3.83 (d, 1H, *J* = 3.0 Hz), 4.13–4.16 (m, 2H), 4.19 (dd, 1H, *J* = 4.8, 11.4 Hz), 4.47 (d, 1H, *J* = 11.4 Hz), 4.53 (d, 1H, *J* = 12.0 Hz), 4.55 (d, 1H, *J* = 4.2 Hz), 4.59 (d, 1H, *J* = 11.4 Hz), 4.63 (d, 1H, *J* = 11.4 Hz), 5.22 (dd, 1H, *J* = 4.2, 8.4 Hz), 5.60 (dd, 1H, *J* = 1.8, 7.8 Hz), 5.67 (dd, 1H, *J* = 1.8, 7.8 Hz), 5.84 (d, 1H, *J* = 3.6 Hz), 7.25–7.36 (m, 10H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 20.77 (2 × CH_3), 20.87 (CH_3), 20.94 (CH_3), 26.2 (CH_3), 26.7 (CH_3), 63.4 (CH_2), 67.4 (CH), 69.4 (CH), 69.6 (CH), 72.1 (CH_2), 73.2 (CH_2), 75.2 (CH), 78.2 (CH), 80.9 (CH), 81.3 (CH), 104.9 (CH), 111.7 (C), 127.6 (CH), 128.0 (3 × CH), 128.2 (2 × CH), 128.3 (2 × CH), 128.4 (2 × CH), 137.0 (C), 138.0 (C), 169.39 (C), 169.42 (C), 170.1 (C), 170.7 (C); HRMS (ESI, positive ion) Calcd for $C_{34}H_{42}O_{13}Na$ *m/z* 681.2523. Found, 681.2534. Compound **20:** reddish brown viscous material, $[\alpha]_D^{25}$ −14.9 (*c* 0.16, $CHCl_3$); IR (neat): 1744, 1454, 1373, 1226, 1077, 741, 699 cm^{-1}; ^1H NMR (600 MHz, C_6D_6): δ 1.11 (s, 3H), 1.41 (s, 3H), 1.59 (s, 3H), 1.63 (s, 3H), 1.73 (s, 3H), 3.69 (dd, 1H, *J* = 4.2, 5.4 Hz), 3.75 (d, 1H, *J* = 3.0 Hz), 4.21 (dd, 1H, *J* = 6.6, 11.4 Hz), 4.27 (d, 1H, *J* = 12.0 Hz), 4.31 (d, 1H, *J* = 12.0 Hz), 4.36 (d, 1H, *J* = 4.2 Hz), 4.42–4.45 (m, 2H), 4.55 (d, 1H, *J* = 12.0 Hz), 4.76 (dd, 1H, *J* = 3.0, 6.6 Hz), 5.57 (m, 1H), 5.83 (t, 1H, *J* = 6.0 Hz), 5.88 (d, 1H, *J* = 4.2 Hz), 6.03 (dd, 1H, *J* = 6.0, 15.6 Hz), 6.12 (dd, 1H, *J* = 6.6, 15.6 Hz), 7.05 (t, 1H, *J* = 7.2 Hz), 7.10 (t, 1H, *J* = 7.2 Hz), 7.13 (t, 2H, *J* = 7.8 Hz), 7.23 (t, 2H, *J* = 7.8 Hz), 7.27 (m, 4H); ^{13}C NMR: δ 20.6 (CH_3), 20.8 (2 × CH_3), 26.1 (CH_3), 26.7 (CH_3), 62.2 (CH_2), 70.0 (CH), 71.9 (CH_2), 72.2 (CH), 74.4 (CH_2), 77.6 (CH), 80.2 (CH), 82.8 (CH), 83.2 (CH), 104.8 (CH), 111.6 (C), 127.3, 127.7, 127.9, 128.0, 128.1, 128.3 and 128.4 (12 × CH), 137.3 (C), 137.5 (C), 169.6 (C), 170.0 (C), 170.3 (C); HRMS (ESI, positive ion) Calcd for $C_{33}H_{40}O_{11}Na$ *m/z* 635.2468. Found, 635.2457. Compound **22:** yellow viscous material, $[\alpha]_D^{25}$ −30.2 (*c* 0.52, $CHCl_3$); IR (neat): 1747, 1641, 1372, 1222, 1076, 1040, 756 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ 1.30 (s, 3H), 1.45 (s, 3H), 1.97 (s, 3H), 1.98 (s, 3H), 1.99 (s, 3H), 2.00 (s, 3H), 2.06 (s, 3H), 3.84 (d, 1H, *J* = 3.0 Hz), 4.00 (dd, 1H, *J* = 4.8, 6.6 Hz), 4.17 (dd, 1H, *J* = 7.2, 12.0 Hz), 4.19 (dd, 1H, *J* = 3.0, 8.4 Hz), 4.33 (dd, 1H, *J* = 4.2, 12.0 Hz), 4.45 (d, 1H, *J* = 11.4 Hz), 4.53 (d, 1H, *J* = 11.4 Hz), 4.56 (d, 1H, *J* = 3.6 Hz), 4.62 (d, 1H, *J* = 12.0 Hz), 4.71 (d, 1H, *J* = 11.4 Hz), 5.22 (dt, 1H, *J* = 4.8, 6.6 Hz), 5.32 (t, 1H, *J* = 6.0 Hz), 5.52 (dd, 1H, *J* = 1.8, 6.0 Hz), 5.58 (dd, 1H, *J* = 1.8, 8.4 Hz), 5.83 (d, 1H, *J* = 3.6 Hz), 7.29–7.35 (m, 10H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 20.6 (CH_3), 20.68 (CH_3), 20.74 (CH_3), 20.9 (CH_3), 21.0 (CH_3), 26.3 (CH_3), 26.7 (CH_3), 62.0 (CH_2), 67.1 (CH), 69.9 (CH), 70.36 (CH), 70.41 (CH), 72.1 (CH_2), 74.5 (CH_2), 75.2 (CH), 77.8 (CH), 80.5 (CH), 81.3 (CH), 104.9 (CH), 111.8 (C), 127.6, 127.8, 128.1, 128.3 and 128.5 (10 × CH), 136.8 (C), 137.9 (C), 169.3 (C), 169.7 (C), 169.9 (C), 170.3 (C), 170.4 (C); HRMS (ESI, positive ion) *m/z* Calcd for $C_{37}H_{46}O_{15}Na$, 753.2734; found, 753.2709. Compound **23:** colorless oil, $[\alpha]_D^{25}$ +2.7 (*c* 0.7, $CHCl_3$); IR (neat): 1749, 1457, 1371, 1221, 1044, 749 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, 1:1 mixture of anomers): δ 1.91 (s, 3H), 1.93 (s, 3H), 1.97 (s, 3H), 1.98 (s, 3H), 1.99 (s, 3H), 2.00 (s, 3H), 2.02 (s, 3H), 2.03 (s, 3H), 2.05 (s, 3H), 2.08 (s, 3H), 2.09 (s, 3H), 2.10 (s, 3H), 2.11 (s, 3H), 2.13 (s, 3H), 3.71 (t, 1H, *J* = 9.0 Hz), 3.78 (dd, 1H, *J* = 2.4, 7.2 Hz), 3.80 (dd, 1H, *J* = 1.8, 10.2 Hz), 3.83 (br d, 1H, *J* = 6.0 Hz), 3.89 (t, 1H, *J* = 9.6 Hz), 3.99 (dd, 1H, *J* = 6.6, 12.0 Hz), 4.08 (dd, 1H, *J* = 6.0, 12.6 Hz), 4.15 (d, 1H, *J* = 10.2 Hz), 4.32 (dd, 1H, *J* = 3.6, 12.0 Hz), 4.38 (dd, 1H, *J* = 3.0, 12.0 Hz), 4.55–4.72 (m, 8H), 5.03–5.07 (m, 2H), 5.11 (t, 1H, *J* = 9.6 Hz), 5.17–5.22 (m, 4H), 5.26 (br s, 2H), 5.40 (dd, 1H, *J* = 2.4, 7.8 Hz), 5.54 (d, 1H, *J* = 8.4 Hz), 6.32 (d, 1H, *J* = 3.6 Hz), 7.21–7.35 (m, 20H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 20.6, 20.68, 20.7, 20.74, 20.78, 20.8, 20.9 and 21.0 (14 × CH_3), 62.6 (CH_2), 62.7 (CH_2), 66.6 (CH), 67.5 (CH), 67.6 (CH), 67.8 (CH), 68.8 (CH), 69.5 (CH), 70.5 (CH), 70.8 (CH), 70.9 (CH), 71.4 (CH), 71.5 (CH), 73.0 (CH), 74.2 (CH_2), 74.4 (CH_2), 74.6 (CH_2), 74.8 (CH_2), 75.5 (CH), 75.8 (CH), 77.3 (CH), 80.3 (CH), 89.4 (CH), 91.9 (CH), 127.5, 127.6, 127.69, 127.73, 127.9, 128.0, 128.3, 128.4, 128.45 and 128.5 (20 × CH), 137.4 (C), 137.7 (C), 137.8 (C), 138.0 (C), 168.6, 168.9, 169.1, 169.2, 169.4, 169.5, 169.6, 170.1, 170.18, 170.24, 170.4 and 170.5 (14 × C); HRMS (ESI, positive ion) Calcd for $C_{38}H_{46}O_{17}$ Na *m/z* 797.2633. Found 797.2650.