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Gold-catalyzed glycosidations: synthesis of 1,6-anhydro saccharides

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ABSTRACT

Various 1,6-anhydro sugars are synthesized utilizing salient features of gold-catalyzed glycosidations. All the reactions occurred under mild conditions in the presence of 7 mol % of $AuBr_3$ enabling easy synthesis of 1,6-anhydro sugars from corresponding 6-hydroxy propargyl/methyl monosaccharides, disaccharides, and trisaccharides in good yields.

1,6-Anhydro sugars are excellent synthons for the syntheses of medicinally important molecules[1] and materials.[2] They are also known to be precursors for the synthesis of proteoglycans, glycosyl halides,[3a] N- or S-glycosides,[3b–d] and C-glycosides.[3e,f] Stereoregular or hyperbranched glycopolymers are also reported from 1,6-anhydro sugars by cationic ring-opening polymerization.[4] Interesting opportunities for the synthesis of complex molecules and novel glycopolymers prompted the development of methods for the synthesis of this set of sugar derivatives.[5]

1,6-Anhydro sugar derivatives are synthesized either by thermal degradation or alternatively by chemical reactions.[5] Thermal degradation or pyrolysis exploited all the major conventional and non-conventional reaction media as well as the convection sources to get 1,6-anhydro sugars.[5b–f] The major limitation of a thermal degradation process is that they are more suitable to 1,6-anhydro monosaccharides and really tough to limit pyrolysis for 1,6-anhydro oligosaccharides.[5a] However, 1,6-anhydro sugar derivatives by chemical reactions enjoy the control and selective synthesis which are otherwise not easy.[1b] An usual sequence for the chemical synthesis of 1,6-anhydro sugars involves a leaving group at the anomeric position with the 6-hydroxyl group and the remaining hydroxyl groups are protected. Till date, Shoda's direct synthesis of 1,6-anhydro saccharides from unprotected glycopyranosides by the use of 2-chloro-1,3-dimethylimidazolinium chloride is the best.[5a] In summary, most of the reported methods use stoichiometric quantities of reagents, often long reaction times, and tedious isolation procedures. Thus methods that enable the synthesis of 1,6-anhydro sugar derivatives through catalytic means are needed.[1b]

The foregoing discussion encouraged us to ponder upon developing a catalytic route to the synthesis of 1,6-anhydro saccharides taking the cue from recent observations in gold-catalyzed glycosidations. In our laboratory, we have identified propargyl and methyl glycosides as novel glycosyl donors taking advantage of both the Lewis as well as the Brønsted acidity of Au(III) salts.[6] Usually, a glycosylation reaction involves a fully protected glycosyl donor with a leaving group at the anomeric position and a glycosyl acceptor (aglycone) that frequently contains a single hydroxyl moiety and the reaction happens in an intermolecular fashion.[7]

Thus we hypothesized that if the glycosylation is carried out intramolecularly on a sugar substrate containing a 6-OH group (other hydroxyl groups being protected) and a leaving group at the *C*-1 position, the reaction shall proceed to yield 1,6-anhydro sugars. This proposition was further fueled by a recent observation that showed cleavage of the interglycosidic bond and formation of 1,6-anhydro mannoside (**4**) and disaccharide **3** from an armed disaccharide (**1**) and aglycone **2** under gold-catalyzed glycosidation conditions (Scheme 1).[8]

Accordingly, an acetonitrile solution of propargyl 2,3,4-tri-*O*-benzyl mannopyranoside **5a** was heated to 70 °C for 10 h to isolate 1,6-anhydro mannoside **4** in 71% yield after concentration in vacuo followed by filter column chromatographic purification.[9–11] In another reaction, methyl mannopyranoside (**5b**) was also found to give compound **4** in 62% yield when subjected to above delineated reaction conditions (Scheme 2).[10]

Aforementioned results enticed us to evaluate the general applicability of the current protocol for the synthesis of other 1,6-anhydro sugars of monosaccharides, disaccharides, and trisaccharides. 1,6-Anhydro sugar formation was then checked with *gluco*-(**6a**,**6b**) and galacto-(**7a**,**7b**) substrates as well to obtain the corresponding 1,6-anhydro derivatives **8** and **9** in good yields (Table 1).[9] In addition, the suitability of 1,6-anhydro sugar formation has been studied with a panel of disaccharides and trisaccharides. Interesting to note that $AuBr_3$-catalyzed intramolecular reaction occurred on disaccharides (**10a**, **10b**, **11a**, and **11b**) and trisaccharides (**14a**, **14b**, **15a**, and **15b**) resulting in the formation of the corresponding 1,6-anhydro sugar derivatives (**12**, **13**, **16**, and **17**) in good yields.[9] It is pertinent to mention that the inherent acidity in the Au(III)-catalyzed glycosidation showed the domino effect in one-pot. Deprotection of 6-*O*-silyl ether happened first to give the 6-OH compound that got subsequently converted to

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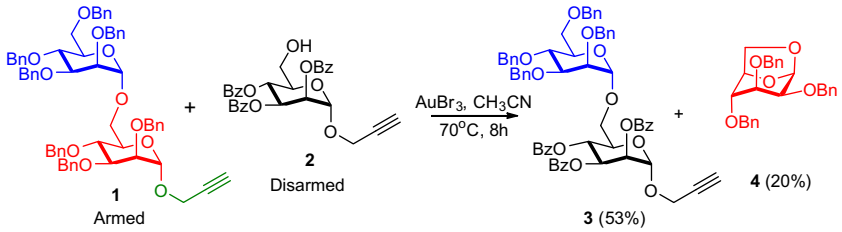
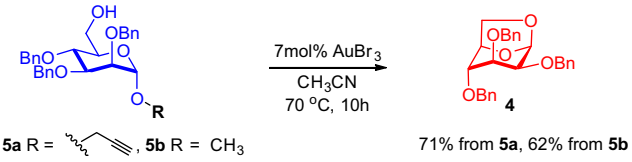


Scheme 1. Cleavage of interglycosidic bond and formation of 1,6-anhydro mannoside.

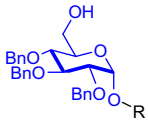
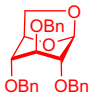
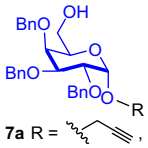
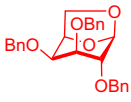
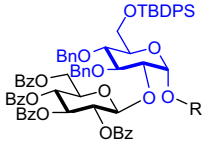
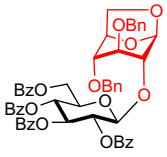
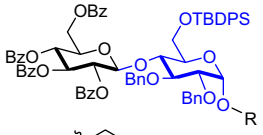
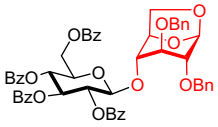
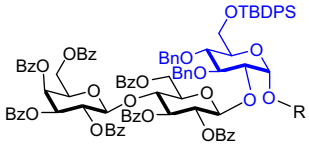
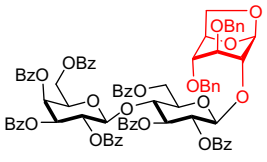
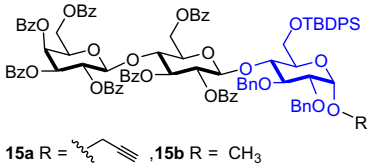
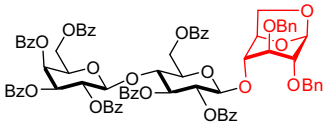


Scheme 2. $AuBr_3$ catalyzed synthesis of 1,6-anhydro mannoside from propargyl and methyl mannopyranosides.

1,6-anhydro sugar via the intramolecular trapping of the oxocarbenium ion generated due to the extrusion of the anomeric alkyl (propargyl/methyl) group by the action of $AuBr_3$.

In conclusion, the synthesis of 1,6-anhydro sugars from the corresponding 6-hydroxy propargyl/methyl glycosides was realized in the presence of a catalytic amount of $AuBr_3$ at 70 °C in acetonitrile. Interestingly, deprotection of 6-*O*-TBDPS ether was observed for the first time in the presence of catalytic quantity of $AuBr_3$ and subsequent intramolecular glycosidation happened in domino

Table 1
Synthesis of 1,6-anhydro saccharides

Substrate	Product	Time, Yield	
		R =	R = CH3
 **6a** R = , **6b** R = CH_3	 **8**	4 h, 75%	24 h, 69%
 **7a** R = , **7b** R = CH_3	 **9**	12 h, 76%	18 h, 65%
 **10a** R = , **10b** R = CH_3	 **12**	18 h, 71%	20 h, 64%
 **11a** R = , **11b** R = CH_3	 **13**	20 h, 72%	24 h, 68%
 **14a** R = , **14b** R = CH_3	 **16**	20 h, 67%	18 h, 64%
 **15a** R = , **15b** R = CH_3	 **17**	10 h, 65%	18 h, 62%

fashion to give 1,6-anhydro sugar derivatives of disaccharides and trisaccharides.

Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.09.004.

References and notes

1. (a) Hattori, K.; Yoshida, T. *Macromolecules* **2009**, *42*, 6044–6049; (b) Kulkarni, S. S.; Lee, J.-C.; Hung, S.-C. *Curr. Org. Chem.* **2004**, *8*, 475–509; (c) Hung, S.-C.; Wang, C.-C.; Chang, S.-W.; Chen, C.-S. *Tetrahedron Lett.* **2001**, *42*, 1321–1324; (d) Hung, S.-C.; Puranik, R.; Chi, F.-C. *Tetrahedron Lett.* **2000**, *41*, 77–80; (e) Takeuchi, M.; Taniguchi, T.; Ogasawara, K. *Tetrahedron Lett.* **2000**, *41*, 2609–2611; (f) Witczak, Z. J. *Pure Appl. Chem.* **1994**, *66*, 2189–2192; (g) Georges, M.; MacKay, D.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1982**, *104*, 1101–1103; (h) Kochetkov, N. K.; Sviridov, A. F.; Ermolenko, M. S. *Tetrahedron Lett.* **1981**, *22*, 4315–4322; (i) Kochetkov, N. K.; Sviridov, A. F.; Ermolenko, M. S. *Tetrahedron Lett.* **1981**, *22*, 4319–4322; (j) Kelly, A. G.; Roberts, J. S. *J. Chem. Soc., Chem. Commun.* **1980**, 228–230; (k) Ogawa, T.; Kawano, T.; Matsui, M. *Carbohydr. Res.* **1977**, *57*, C31–C35.
2. (a) Ruckel, E. R.; Schuerch, C. *J. Am. Chem. Soc.* **1966**, *88*, 2605–2606; (b) Satoh, T.; Imai, T.; Ishihara, H.; Maeda, T.; Kitajyo, Y.; Sakai, Y.; Kaga, H.; Kaneko, N.; Ishii, F.; Kakuchi, T. *Macromolecules* **2005**, *38*, 4202–4210; (c) Ohara, M.; Takagaki, A.; Nishimura, S.; Kohki, E. *Appl. Catal., A Gen.* **2010**, *383*, 149–155.
3. (a) Shimawaki, K.; Fujisawa, Y.; Sato, F.; Fujitani, N.; Kurogochi, M.; Hoshi, H.; Hinou, H.; Nishimura, S. *Angew. Chem., Int. Ed.* **2007**, *46*, 3074–3079; (b) Nambia, S.; Daeuble, J. F.; Doyle, R. J.; Taylor, K. G. *Tetrahedron Lett.* **1989**, *30*, 2179–2182; (c) Arndt, S.; Hsieh-Wilson, L. C. *Org. Lett.* **2003**, 4179–4182; (d) Tanaka, T.; Matsumoto, T.; Noguchi, M.; Kobayashi, A.; Shoda, S.-I. *Chem. Lett.* **2009**, *38*, 458–459; (e) McDevitt, J. P.; Lansbury, P. T., Jr. *J. Am. Chem. Soc.* **1996**, *118*, 3818–3828; (f) Stichler-Bonaparte, J.; Vasella, A. *Helv. Chem. Acta* **2001**, *84*, 2355–2367.
4. (a) Satoh, T.; Imai, T.; Kitajyo, Y.; Kakuchi, T. *Curr. Top. Polym. Res.* **2005**, 195–231; (b) Varma, A. J.; Kennedy, J. F.; Galgali, P. *Carbohydr. Polym.* **2004**, *56*, 429–445; (c) Mori, M.; Kusuno, A.; Satoh, T.; Kaga, H.; Miura, M.; Tsuda, K.; Kakuchi, T. *Polym. Preprints* **2002**, *43*, 547–548.
5. (a) Tanaka, T.; Huang, W. C.; Noguchi, M.; Kobyashi, A.; Shoda, S.-I. *Tetrahedron Lett.* **2009**, *50*, 2154–2157; (b) Miura, M.; Kaga, H.; Sakurai, A.; Kakuchi, T.; Takahashi, K. *J. Anal. Appl. Pyrolysis* **2004**, *71*, 187–199; (c) Kawamoto, H.; Hatanaka, W.; Saka, S. *J. Anal. Appl. Pyrolysis* **2003**, *70*, 303–313; (d) Miura, M.; Kaga, H.; Yoshida, T.; Ando, K. *J. Wood Sci.* **2001**, *47*, 502–506; (e) Huang, Y. F.; Kuan, W. H.; Lo, S. L.; Lin, C. F. *Bioresour. Technol.* **2010**, *101*, 1968–1973; (f) Kwon, G.-J.; Kuga, S.; Hori, K.; Ytagai, M.; Ando, K.; Hattori, N. *J. Wood Sci.* **2006**, *52*, 461–465; (g) Byramova, N. E.; Tuzikov, A. B.; Tyrtysh, T. V.; Bovin, N. V. *Russ. J. Bioorg. Chem.* **2007**, *33*, 99–109; (h) Award, L.; Demange, R.; Zhu, Y.-H.; Vogel, P. *Carbohydr. Res.* **2006**, *341*, 1235–1252; (i) Hung, S.-C.; Thopate, S. R.; Chi, F.-C.; Chang, S.-W.; Lee, J.-C.; Wang, C.-C.; Wen, Y.-S. *J. Am. Chem. Soc.* **2001**, *123*, 3153–3154; (j) Boissiere-Junot, N.; Tellier, C.; Rabiller, C. *J. Carbohydr. Chem.* **1998**, *17*, 99–115; (k) Lafont, D.; Boullanger, P.; Banoub, J.; Descotes, G. *Can. J. Chem.* **1990**, *68*, 828–835; (l) Sakairi, N.; Hayashida, M.; Kuzuhara, H. *Carbohydr. Res.* **1989**, *185*, 91–104; (m) Rao, M. V.; Nagarajan, M. *Carbohydr. Res.* **1987**, *162*, 141–144; (n) Fujimaki, I.; Ichikawa, Y.; Kuzuhara, H. *Carbohydr. Res.* **1982**, *101*, 148–151; (o) Černý, M.; Staněk, J. *Adv. Carbohydr. Chem. Biochem.* **1977**, *34*, 23–177; (p) Shafizadeh, F.; Furneaux, R. H.; Stevenson, T. T.; Cochran, T. G. *Carbohydr. Res.* **1978**, *67*, 433–447; (q) Hann, R. M.; Hudson, C. S. *J. Am. Chem. Soc.* **1942**, *64*, 2435–2438.
6. (a) Hotha, S.; Kashyap, S. *J. Am. Chem. Soc.* **2006**, *128*, 9620–9621; (b) Kashyap, S.; Hotha, S. *Tetrahedron Lett.* **2006**, *47*, 2021–2023; (c) Kashyap, S.; Vidadala, S. R.; Hotha, S. *Tetrahedron Lett.* **2007**, *48*, 8960–8962; (d) Sureshkumar, G.; Hotha, S. *Tetrahedron Lett.* **2007**, *48*, 6564–6568; (e) Sureshkumar, G.; Hotha, S. *Chem. Commun.* **2008**, 4282–4284; (f) Vidadala, S. R.; Hotha, S. *Chem. Commun.* **2009**, 4282–4284; (g) Vidadala, S. R.; Thadke, S. A.; Hotha, S. *J. Org. Chem.* **2009**, *74*, 9233–9236.
7. (a) Zhu, X.; Schmidt, R. R. *Angew. Chem., Int. Ed.* **2009**, *48*, 1900–1934; (b) Paulsen, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 155–173; (c) Fraser-Reid, B.; Udodong, U. E.; Wu, Z.; Ottosson, H.; Merritt, J. R.; Rao, C. S.; Roberts, C.; Madsen, R. *Synlett* **1992**, 927–942.
8. Kayastha, A. K.; Hotha, S. *Tetrahedron Lett.* **2010**, *51*, 5269–5272.
9. All products gave satisfactory ^{1}H, ^{13}C, DEPT NMR and MS analysis. See Supplementary data.
10. *General procedure for the synthesis of 1,6-anhydro sugars*: To a solution of 6-hydroxy alkyl glycopyranoside (0.1 mmol) in anhydrous acetonitrile (2 mL) was added 7 mol % of $AuBr_3$ under argon atmosphere at room temperature. The resulting mixture was heated to 70 °C and stirred till the completion of the reaction as judged by TLC analysis (Table 1). The reaction mixture was concentrated in vacuo to obtain a crude residue which was purified by silica gel column chromatography using ethyl acetate–petroleum ether (1:4) as mobile phase.
11. (a) Compound characterization data for compound **4**: $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0) −16.6; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 3.47(t, 1H, *J* = 1.8 Hz), 3.58(dd, 1H, *J* = 1.8, 5.4 Hz), 3.73(dd, 1H, *J* = 6.0, 7.1 Hz), 3.81(qd, 1H, *J* = 1.6, 3.1, 5.0 Hz), 4.25(dd, 1H, *J* = 0.9, 7.1 Hz), 4.43–4.57(m, 5H), 4.52(ABq, 2H, *J* = 12.4 Hz), 5.46(s, 1H), 7.20–7.38(m, 15H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 65.0, 71.3, 71.4, 73.4, 74.1, 74.4, 74.5, 76.5, 100.1, 127.7–128.5, 137.6, 137.9, 137.9; HRMS (MALDI-TOF) Calcd for $C_{27}H_{28}O_5Na$: 455.1834; Found, 455.1830.
(b) Compound characterization data for compound **8**: $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.0) −26.0; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 3.34(d, 2H, *J* = 1.7 Hz), 3.58(quintet, 1H, *J* = 2.4, 3.6 Hz), 3.67(dd, 1H, *J* = 5.9, 7.2 Hz), 5.91(dd, 1H, *J* = 0.8, 7.2 Hz), 4.41(ABq, 2H, *J* = 12.5 Hz), 4.48–4.63(m, 5H), 5.46(s, 1H), 7.21–7.35(m, 15H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 65.3, 71.1, 71.7, 71.9, 74.2, 75.8, 75.9, 76.6, 100.5, 127.5–128.4, 137.7, 137.8, 137.8; HRMS (MALDI-TOF) Calcd for $C_{27}H_{28}O_5Na$, 455.1834; Found, 455.1840.
(c) Compound characterization data for compound **9**: $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.2) −34.9; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 3.52(t, 1H, *J* = 1.7 Hz), 3.62(t, 1H, *J* = 6.0 Hz), 3.77–3.92(m, 2H), 4.35–4.66(m, 8H), 5.36(t, 1H, *J* = 1.7 Hz), 7.22–7.37(m, 15H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 64.3, 71.1, 72.1, 72.7, 73.0, 73.1, 74.1, 76.3, 100.2, 127.6–128.5, 137.5, 137.9, 138.2; HRMS (MALDI-TOF) Calcd for $C_{27}H_{28}O_5Na$, 455.1834; Found, 455.1836.
(d) Compound characterization data for compound **12**: $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.1) +16.2; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ 3.07(s, 1H), 3.42(s, 1H), 3.49(dd, 1H, *J* = 5.9, 7.3 Hz), 3.77(dd, 1H, *J* = 0.8, 7.3 Hz), 3.88(m, 1H), 4.31–4.57(m, 7H), 4.62(ABq, 2H, *J* = 12.4 Hz), 5.21(s, 1H), 5.38(dd, 1H, *J* = 8.0, 9.6 Hz), 5.58(t, 1H, *J* = 9.8 Hz), 5.75(t, 1H, *J* = 9.8 Hz), 7.20–7.76(m, 22H), 7.77–8.09(m, 8H); ^{13}C NMR (100.61 MHz, $CDCl_3$): δ 62.8, 64.8, 69.5, 71.2, 71.4, 72.2, 72.2, 72.5, 74.2, 75.2, 75.7, 76.0, 99.8, 100.2, 127.6–129.9, 133.2, 133.3, 133.3, 133.5, 137.7, 137.9, 164.9, 165.2, 165.7, 166.0; HRMS (MALDI-TOF) Calcd for $C_{54}H_{48}O_{14}Na$, 943.2942; Found, 943.2949.
(e) Compound characterization data for compound **13**: $[\alpha]_D^{25}$ ($CHCl_3$, *c* 0.9) −13.4; ^{1}H NMR (500.13 MHz, $CDCl_3$): δ 3.27(s, 1H), 3.55(dd, 1H, *J* = 6.2, 7.2 Hz), 3.65(s, 1H), 3.80(s, 1H), 3.84(d, 1H, *J* = 7.3 Hz), 4.10(m, 1H), 4.41(ABq, 2H, *J* = 12.0 Hz), 4.42(ABq, 2H, *J* = 12.3 Hz), 4.43(dd, 1H, *J* = 5.3, 12.2 Hz), 4.56(dd, 1H, *J* = 3.0, 12.1 Hz), 4.63(d, 1H, *J* = 5.8 Hz), 5.25(d, 1H, *J* = 5.8.1 Hz), 5.37(s, 1H), 5.56(dd, 1H, *J* = 8.1, 9.8 Hz), 5.66(t, 1H, *J* = 9.8 Hz), 5.99(t, 1H, *J* = 9.6 Hz), 7.15–7.56(m, 22H), 7.80–8.05(m, 8H); ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 63.0, 65.4, 69.6, 71.2, 72.0, 72.1, 72.4, 73.0, 74.2, 75.3, 77.0, 77.7, 99.7, 100.5, 127.5–129.9, 133.2, 133.2, 133.3, 133.5, 137.6, 137.8, 165.0, 165.2, 165.8, 166.1; HRMS(MALDI-TOF) Calcd for $C_{54}H_{48}O_{14}Na$, 943.2942; Found, 943.2950.
(f) Compound characterization data for compound **16**: $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.3) +47.4; ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 3.05(s, 1H), 3.33(m, 1H), 3.38(s, 1H), 3.49(t, 1H, *J* = 6.3 Hz), 3.65–3.98(m, 5H), 4.14(t, 1H, *J* = 9.7 Hz), 4.15(d, 1H, *J* = 8.1 Hz), 4.44(ABq, 2H, *J* = 12.2 Hz), 4.38–4.64(m, 5H), 4.71(m, 1H), 4.86(d, 1H, *J* = 7.8 Hz), 5.22(s, 1H), 5.31(dd, 1H, *J* = 8.1, 9.9 Hz), 5.44(dd, 1H, *J* = 3.3, 10.3 Hz), 5.64(t, 1H, *J* = 9.4 Hz), 5.78(m, 1H), 7.05–8.15(m, 45H); ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 61.0, 61.9, 64.6, 67.4, 69.9, 70.9, 71.2, 71.3, 71.6, 72.3, 72.5, 72.8, 73.8, 74.9, 75.0, 75.7, 76.2, 99.7, 100.2, 101.0, 127.6–130.0, 133.1, 133.2, 133.3, 133.4, 133.5, 133.6, 133.6, 137.6, 137.9, 164.7, 165.0, 165.2, 165.3, 165.4, 165.6, 165.7; HRMS(MALDI-TOF) Calcd for $C_{81}H_{70}O_{22}Na$, 1417.4256; Found, 1417.4251.
(g) Compound characterization data for compound **17**: $[\alpha]_D^{25}$ ($CHCl_3$, *c* 1.2) +28.2; ^{1}H NMR (500.13 MHz, $CDCl_3$): δ 3.23(s, 1H), 3.54(dd, 1H, *J* = 6.1, 7.1 Hz), 3.58(td, 1H, *J* = 3.3, 6.1, 10.3 Hz), 3.63(dd, 1H, *J* = 6.7, 11.4 Hz), 3.66(m, 1H), 3.72(dd, 1H, *J* = 6.7, 11.3 Hz), 3.76–3.94(m, 2H), 4.18–4.63(m, 9H), 4.89(ABq, 2H, *J* = 7.7 Hz), 5.34(d, 1H, *J* = 1.1 Hz), 5.35(dd, 1H, *J* = 3.5, 10.6 Hz), 5.49(dd, 1H, *J* = 8.1, 10.2 Hz), 5.69–5.77(m, 3H), 7.05–8.08(m, 45H); ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 61.1, 62.2, 65.3, 67.5, 69.9, 71.0, 71.4, 71.8, 71.8, 71.9, 73.0, 73.1, 74.3, 75.0, 75.8, 76.0, 78.7, 100.4, 100.5, 101.0, 127.4–130.0, 133.1, 133.2, 133.3, 133.4, 133.4, 133.4, 133.5, 137.6, 139.9, 164.7, 165.0, 165.2, 165.4, 165.4, 165.6, 165.8; HRMS(MALDI-TOF) Calcd for $C_{81}H_{70}O_{22}Na$, 1417.4256; Found, 1417.4251.