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Gold-catalyzed glycosidations: unusual cleavage of the interglycosidic bond while studying the armed/disarmed effect of propargyl glycosides

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ABSTRACT

Armed/disarmed effect of propargyl glycosides in the presence of $AuBr_3$ is studied. Observed that oxophilic $AuBr_3$ cleaves interglycosidic bond of an armed disaccharide resulting in the formation of a disaccharide and a 1,6-anhydro sugar. Trisaccharides were obtained after fine tuning the reactivity of the glycosyl donor with different protecting groups.

Oligosaccharides and glycoconjugates are implicated in various intracellular and extracellular molecular recognition events.[1] In this regard, several strategies were developed for the synthesis of oligosaccharides; Fraser-Reid pioneered strategy of armed/disarmed *n*-pentenyl glycosides that exploits differential reactivity of protecting groups is one of the most significant advancements in the annals of oligosaccharide synthesis.[2a,3] Ethers at the *C*-2 position of alkyl glycosides (armed) electronically facilitate the departure of the alkyl-leaving group at the anomeric position favoring the formation of oxocarbenium ion and thus transglycosides are easily formed.[2a,s] Whereas, C-2 esters (disarmed) make the anomeric carbon electron deficient and as a consequence, the alkyl-leaving group at the C-1 position does not depart quickly and hence do not facilitate transglycoside formation.[2a,s]

We have recently identified propargyl glycosides as glycosyl donors in the presence of catalytic amount of Au(III) salts.[4a–c] Subsequently, propargyl 1,2-orthoesters were reported for the 1,2-*trans* selective glycosidation under $AuBr_3/CH_2Cl_2$/rt.[4d] Furthermore, gold-catalyzed activation was found to activate the propargyl moiety of 1,2-orthoesters in the presence of aglycones having propargyl group to obtain propargyl disaccharides.[4e] In all these studies, we observed that alkyl glycosides get disarmed when the protecting group at the C-2 position is an ester and armed to participate in the glycosidation when the protecting group at the C-2 position is a benzyl ether.[4f] In continuation of our efforts on the development of novel strategies for the glycoconjugate synthesis,[4] we got interested in the study of armed/disarmed effects for propargyl glycosides to enable sequential glycosylations.

Initial set of experiments were planned with propargyl 2,3,4,6-tetra-*O*-benzyl α-D-mannopyranoside (**1**) as the armed glycosyl donor and the propargyl 2,3,4-tri-*O*- benzoyl α-D-mannopyranoside (**2**) as the disarmed aglycone mainly due to the prospect of 1,2-*trans* stereoselectivity in the resulting disaccharide.[4a,h] Accordingly, armed glycosyl donor **1** was allowed to react with aglycone **2** in the presence of $AuBr_3$ in CH_3CN at 70 °C for 8 h and obtained the anticipated disaccharide **3a** in 68% (Scheme 1).[4a,5,6a] The disarmed disaccharide was then converted to an armed disaccharide **3b** in two steps involving Zemplén debenzoylation (NaOMe/MeOH/rt) followed by benzylation using NaH and benzyl bromide in DMF. In continuation, the armed disaccharide **3b**[6c] was allowed to react with disarmed aglycone **2** in anticipation of a trisaccharide **5**, resulting in the isolation of two compounds. Purification by conventional silica gel column chromatography enabled us to characterize the major component not as the trisaccharide **5** but surprisingly as **3a**.[5,6b] For instance, only two anomeric protons were noticed at δ 5.26(d, 1H, J = 1.8 Hz), 5.68 (dd, 1H, J = 1.8, 2.9 Hz) in the ^{1}H NMR spectrum instead of three if it were **5**. The ^{13}C NMR spectrum of **3a** revealed that there are two mannose residues with 1,2-*trans* configuration as their anomeric carbons were noticed at δ 96.2 ($^1J_{C-H}$ = 175.5 Hz) and 98.2 ($^1J_{C-H}$ = 170.9 Hz) ppm and the molecular weight was found to be 1075.3889 ($C_{64}H_{60}O_{14}$Na).[5,6b] These observations and matching of the data with that of **3a** previously synthesized led us to assign the structure of the major component (53%) to be propargyl 2,3,4-tri-*O*-benzoyl-6-(2,3,4,6-tetra-*O*-benzyl α-D-mannopyranosyl)-α-D-manno-pyranoside **3a**. The minor component (16%) was identified to be 1,6-anhydro derivative **4**.[4h,5,6e]

The formation of disaccharide **3a** and the 1,6-anhydro sugar formation can be rationalized by a double activation of the armed glycosyl donor **3b** in the presence of $AuBr_3$ (Fig. 1). Initially, oxophilic $AuBr_3$ cleaved the interglycosidic bond leaving the intermediate oxocarbenium ion (**A**) with the extrusion of propargyl mannoside **B**. Intermediate **A** was then attacked by the disarmed aglycone **2** resulting in disaccharide **3a** whereas the ejected product **B** led to the second oxocarbenium ion **C** which is trapped intramolecularly by the 6-OH group to give 1,6-anhydro derivative **4**. The sequence of events could not be established. Similar reaction on disaccharide

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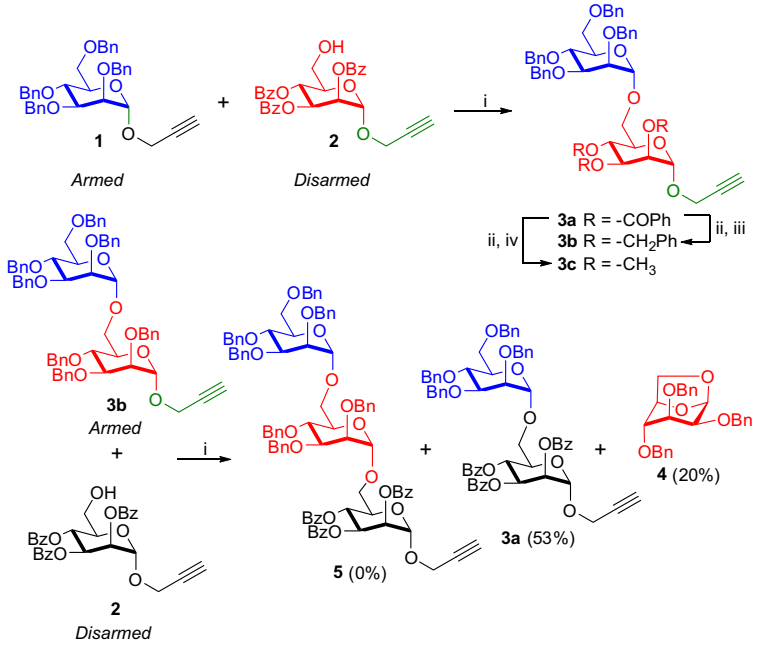


Scheme 1. A study on the armed-disarmed effect of propargyl glycosides. Regents and conditions: (i) $AuBr_3$, CH_3CN, 70 °C, 8 h, 68%; (ii) NaOMe, MeOH, rt,, 0.5 h, 95%; (iii) NaH, DMF, 0 °C to rt, 0.5 h, then BnBr, 0 °C to rt, 4 h, 94%; (iv) KOH, DMSO, 0 °C to rt, 0.5 h then CH_3I, 0 °C to rt, 3 h, 96%.

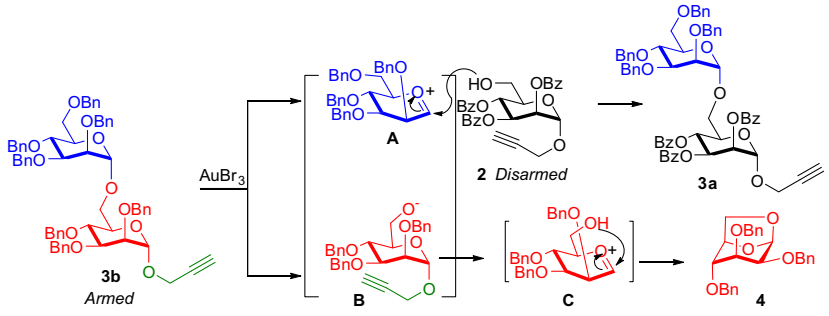
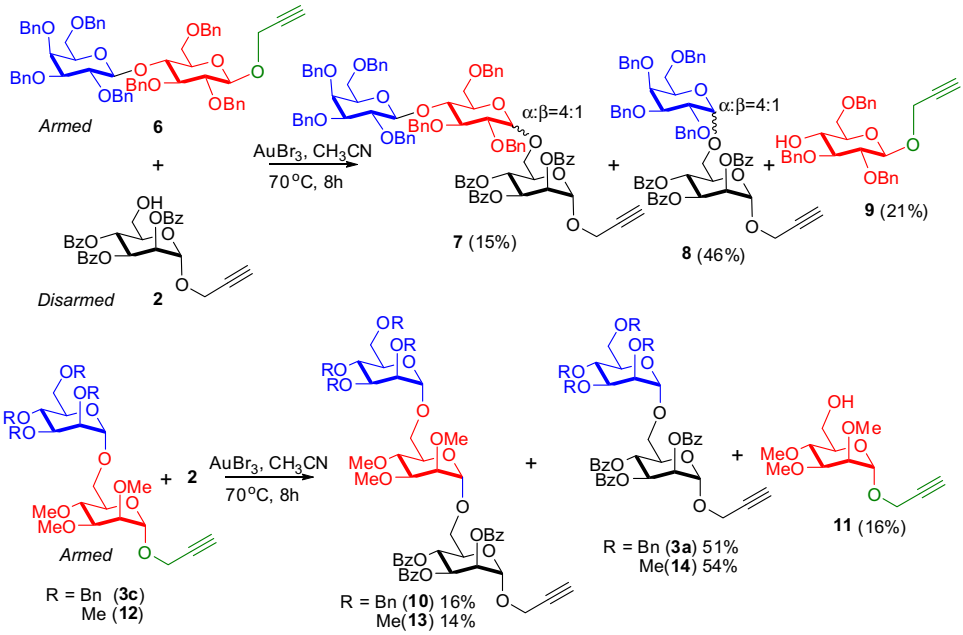


Figure 1. Mechanistic rationale.



Scheme 2. Study of armed/disarmed effect for the trisaccharide synthesis.

6[6f] resulted in the identification of trisaccharide **7**,[6g] disaccharide **8**,[6h] and ejected out monosaccharide **9**[6i] but not the anhydro sugar due to the unfavorable spatial separation (Scheme 2).

Replacement of benzoyl groups of disaccharide **3a** by methyl groups via a two-step procedure gave armed disaccharide **3c**[6d] with less-directing methyl groups on the sugar at the reducing end. $AuBr_3$- catalyzed glycosidation gave us the trisaccharide **10**,[6j] disaccharide **3a**[6b], and propargyl 2,3,4-tri-*O*-methyl mannoside **11**[6k] in 16%, 51%, and 16%, respectively. Similar observations were noticed with the per O-methylated disaccharide **12**[6l] to give the trisaccharide **13**,[6m] disaccharide **14**[6n], and the monosaccharide **11**[6k] (Scheme 2). The foregoing studies led us to understand that the propargyl glycosides are highly dependent on the electronic effect of the protecting groups.

In conclusion, armed/disarmed effects of propargyl glycosides in the presence of catalytic amount of $AuBr_3$ were studied. The cleavage of interglycosidic bond was noticed in the presence of armed-protecting groups due to the double activation and the resulting oxocarbenium ion is attacked by the aglycone giving, respectively, disaccharide and 1,6-anhydro sugar as major and minor products. Fine tuning of protecting groups led to the synthesis of trisaccharides albeit in poor yields. The unusual cleavage of the interglycosidic bond can be circumvented if the glycosidations were conducted at room temperature. Efforts in this direction are currently underway and results will be reported in future. Application of these results for the synthesis of significant carbohydrate epitopes is currently underway.

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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.2010.07.157.

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5. All products gave satisfactory ^1H, ^{13}C, DEPT NMR and HRMS (MALDI-TOF) analysis. See Supplementary data.
6. (a) *General procedure for glycosylations using propargyl glycosides as glycosyl donor:* To a solution of glycosyl donor (0.1 mmol) and aglycone (0.12 mmol) in anhydrous acetonitrile (5 mL) was added a solution of 5 mol% of $AuBr_3$ in anhydrous acetonitrile (2 mL) 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. The reaction mixture was concentrated in vacuo to obtain a crude residue which was purified by conventional silica gel column chromatography using ethyl acetate/petroleum ether (ratio?) as mobile phase.
(b) *Compound characterization data for disarmed disaccharide* **3a***:* $[\alpha]_D^{25} = -23.3°$($CHCl_3$, *c* 1.0); ^1H NMR (200.13 MHz, $CDCl_3$): δ 2.50 (t, 1H, *J* = 2.4 Hz), 3.53–3.78 (m, 4H), 3.84 (dd, 1H, *J* = 3.3, 9.2 Hz), 3.88–4.05 (m, 2H), 4.22 (m, 1H), 4.31 (d, 2H, *J* = 2.4 Hz), 4.37 (d, 2H, *J* = 4.5 Hz), 4.43 (s, 2H) 4.49 (ABq, 2H, *J* = 12.3 Hz), 4.63 (s, 2H), 4.86 (d, 1H, *J* = 10.9 Hz), 4.96 (d, 1H, *J* = 1.8 Hz), 5.26 (d, 1H, *J* = 1.8 Hz), 5.68 (dd, 1H, *J* = 1.8, 2.9 Hz), 5.89 (m, 2H), 7.10–7.56 (m, 29H), 7.75–8.11 (m, 6H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 55.1, 66.6, 67.1, 69.0, 69.7, 69.8, 70.4, 71.8, 71.9, 72.5, 73.2, 74.7, 74.8, 74.9, 75.7, 78.1, 80.1, 96.2, 98.2, 127.3–128.9, 133.1, 133.3, 133.5, 138.3, 138.4, 138.5, 138.6, 165.3, 165.4, 165.4; HRMS (MALDI-TOF) calcd for $C_{64}H_{60}O_{14}Na$, 1075.3881; found, 1075.3889.
(c) *Compound characterization data for armed disaccharide* **3b***:* $[\alpha]_D^{25} = +31.4°$($CHCl_3$, *c* 1.0); ^1H NMR (200.13 MHz, $CDCl_3$): δ 2.37 (t, 1H, *J* = 2.4 Hz), 3.58–4.07 (m, 12H), 4.10 (dd, 2H, *J* = 0.7, 2.4 Hz), 4.42–4.71 (m, 8H), 4.61 (s, 2H), 4.68 (s, 2H), 4.87 (d, 2H, *J* = 10.8 Hz), 4.99 (d, 1H, *J* = 1.6 Hz), 5.11 (d, 1H, *J* = 1.6 Hz), 7.10–7.45 (m, 35H); ^{13}C NMR (100.61 MHz, $CDCl_3$): δ 54.1, 65.9, 69.1, 71.5, 71.8, 72.0, 72.1, 72.4, 72.9, 73.2, 74.4, 74.6, 74.7, 74.7, 74.9, 74.9, 75.0, 78.8, 79.3, 80.0, 96.5, 98.1, 127.3–128.4, 138.1, 138.4(×4), 138.6, 138.7; Mol. HRMS (MALDI-TOF) calcd for $C_{64}H_{66}O_{11}Na$, 1033.4503; found, 1033.4510.
(d) *Compound characterization data for compound* **3c***:* $[\alpha]_D^{25} = +56.6°$($CHCl_3$, *c* 1.0); ^1H NMR (200.13 MHz, $CDCl_3$): δ 2.42 (t, 1H, *J* = 2.4 Hz), 3.44, 3.46, 3.48 (3s, 9H), 3.46 (m, 2H), 3.55 (td, 1H, *J* = 2.4, 11.5 Hz), 3.63–4.02 (m, 9H), 4.14 (t, 2H, *J* = 2.4 Hz), 4.60 (ABq, 2H, *J* = 12.0 Hz), 4.61 (s, 2H), 4.70 (ABq, 2H, *J* = 10.9 Hz), 4.73 (s, 2H), 5.02 (d, 1H, *J* = 1.5 Hz), 5.09 (d, 1H, *J* = 1.3 Hz), 7.04–7.45 (m, 20H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 54.1, 57.9, 58.9, 60.8, 65.8, 69.2, 71.7, 71.8, 71.8, 72.3, 73.2, 74.7, 74.8, 74.9, 74.9, 75.9, 76.8, 78.7, 79.7, 81.1, 95.2, 98.0, 127.3-128.3, 138.3, 138.4, 138.5, 138.6; HRMS (MALDI-TOF) calcd for $C_{46}H_{54}O_{11}Na$, 805.3564; found, 805.3560.
(e) *Compound characterization data for 1,6-anhydro sugar* **4***:* $[\alpha]_D^{25} = -16.6°$($CHCl_3$, *c* 1.0); ^1H 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.
(f) *Compound characterization data for disaccharide* **6***:* $[\alpha]_D^{25} = +5.3°$($CHCl_3$, *c* 1.0); ^1H NMR (200.13 MHz, $CDCl_3$): δ 2.44 (t, 1H, *J* = 2.4 Hz), 3.25–4.05 (m, 12H), 4.28 (ABq, 2H, *J* = 11.8 Hz), 4.40 (m, 3H), 4.48–4.65 (m, 3H), 4.62–4.83 (m, 7H), 4.97 (ABq, 2H, *J* = 9.1 Hz), 4.98 (ABq, 1H, *J* = 12.8 Hz), 7.10–7.42 (m, 35H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 55.8, 68.0, 68.1, 72.5, 72.9, 73.0, 73.3, 73.5, 74.7, 74.8, 74.9, 75.1, 75.2, 75.4, 77.2, 79.0, 79.9, 81.4, 82.4, 82.8, 101.3, 102.7, 127.0-128.4, 138.0, 138.2, 138.5, 138.6, 138.7, 139.0, 139.1; HRMS (MALDI-TOF) calcd for $C_{64}H_{66}O_{11}Na$, 1033.4503; found, 1033.4509.
(g) *Compound characterization data for compound* **7***:* Overall α/β = 9:1; Data for the major isomer: $[\alpha]_D^{25} = -5.9°$($CHCl_3$, *c* 1.0); ^1H NMR (500.13 MHz, $CDCl_3$): δ 2.52 (t, 1H, *J* = 2.4 Hz), 3.43–3.78 (m, 10H), 3.83–3.98 (m, 4H), 4.02 (dd, 1H, *J* = 3.7, 9.8 Hz), 4.16 (t, 1H, *J* = 6.7 Hz), 4.29–5.00 (m, 17H), 5.29 (m, 1H), 5.74 (dd, 1H, *J* = 1.8, 3.1 Hz), 5.88 (m, 1H), 5.96 (t, 1H, *J* = 10.2 Hz), 7.10–7.55 (m, 44H), 7.78–8.14 (m, 6H); ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 54.9, 66.7, 67.1, 68.9, 69.2, 69.6, 70.1, 70.2, 70.2, 70.3, 70.8, 72.8, 72.9, 73.3, 73.5, 73.6, 74.6, 74.7, 75.2, 75.8, 76.6, 78.2, 78.7, 79.7, 81.3, 91.9, 96.1, 97.3, 127.4–130.1, 133.1, 133.4, 133.5, 137.9, 138.0, 138.2, 138.3, 138.5, 138.6, 138.9, 165.4, 165.4, 165.6; HRMS (MALDI-TOF) calcd for $C_{91}H_{88}O_{19}Na$, 1508.5851; found, 1508.5855.
(h) *Compound characterization data for compound* **8***:* Overall α/β = 3:1; Data for the major isomer: $[\alpha]_D^{25} = -19.2°$($CHCl_3$, *c* 1.0); ^1H NMR (200.13 MHz, $CDCl_3$): δ 2.31–2.48 (m, 1H), 3.36–5.12 (m, 21H), 5.26 (m, 1H), 5.72 (m, 1H), 5.81–5.98 (m, 1H), 7.09–7.63 (m, 29H), 7.76–8.12 (m, 6H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 54.7, 66.9, 67.1, 68.6, 69.1, 70.1, 70.1, 70.2, 72.9, 73.0, 73.1, 74.7, 75.0, 75.8, 77.2,

78.1, 78.7, 95.8, 97.9, 127.3–130.0, 133.1, 133.4, 133.4, 138.0, 138.6, 138.7, 138.9, 165.4, 165.4, 165.8; HRMS (MALDI-TOF) calcd for $C_{64}H_{60}O_{14}Na$, 1075.3881; found, 1075.3889.

(i) *Compound characterization data for compound* **9**: $[\alpha]_D^{25} = -11.0°$($CHCl_3$, *c* 1.0); ^1H NMR (200.13 MHz, $CDCl_3$): δ 2.47 (t, 1H, *J* = 2.4 Hz), 2.51 (br s, 1H), 3.38–3.82 (m, 6H), 4.43 (t, 2H, *J* = 2.4 Hz), 4.58 (d, 2H, *J* = 1.8 Hz), 4.63–4.76 (m, 3H), 4.90-5.03 (m, 2H), 7.23–7.44 (m, 15H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 56.0, 70.0, 71.2, 73.7, 74.1, 74.7, 75.0, 75.3, 78.9, 81.4, 83.9, 101.5, 127.5–128.6, 137.9, 138.3, 138.6; HRMS (MALDI-TOF) calcd for $C_{30}H_{32}O_6Na$, 511.2097; found, 511.2090.

(j) Compound characterization data for **10**: $[\alpha]_D^{25} = -11.1°$($CHCl_3$, *c* 1.0); ^1H NMR (200.13 MHz, $CDCl_3$): δ 2.50 (t, 1H, *J* = 2.4 Hz), 3.30, 3.36, 3.46 (3s, 9H), 3.45 (m, 4H), 3.58–4.09 (m, 10H), 4.24 (m, 1H), 4.35 (d, 2H, *J* = 2.4 Hz), 4.43–4.71 (m, 7H), 4.86 (dd, 2H, *J* = 4.8, 6.2 Hz), 4.99 (d, 1H, *J* = 1.7 Hz), 5.26 (d, 1H, *J* = 1.7 Hz), 5.67 (dd, 1H, *J* = 1.7, 3.2 Hz), 5.86 (dd, 1H, *J* = 3.2, 10.2 Hz), 6.03 (t, 1H, *J* = 10.2 Hz), 7.09–7.66 (m, 29H), 7.75–8.17 (m, 6H); ^{13}C NMR (125.76 MHz, $CDCl_3$): δ 55.4, 57.4, 58.7, 60.7, 65.6, 66.1, 67.3, 69.3, 69.9, 69.9, 70.5, 71.6, 71.7, 71.8, 72.3, 73.3, 74.8, 75.0, 75.0, 75.6, 75.8, 76.7, 78.2, 79.9, 81.2, 96.6 ($^1J_{C-H}$ = 170.5 Hz), 97.1 ($^1J_{C-H}$ = 169.7), 98.1 ($^1J_{C-H}$ = 174.2), 127.3–130.2, 133.1, 133.4, 133.6, 138.5, 138.5, 138.7, 138.7, 165.3, 165.4, 165.4; HRMS (MALDI-TOF) calcd for $C_{73}H_{76}O_{19}Na$, 1279.4879; found, 1279.4870.

(k) *Compound characterization data for* **11**: $[\alpha]_D^{25} = +75.5°$($CHCl_3$, *c* 1.0); ^1H NMR (200.13 MHz, $CDCl_3$): δ 2.18 (br s, 1H), 2.47 (t, 1H, *J* = 2.4 Hz), 3.50, 3.51, 3.55 (3s, 9H), 3.52 (m, 3H), 3.62 (m, 1H), 3.71–3.90 (m, 2H), 4.23 (d, 2H, *J* = 2.4 Hz), 5.09 (d, 1H, *J* = 1.7 Hz); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 54.3, 57.7, 59.1, 60.8, 62.1, 72.4, 74.9, 76.3, 76.9, 78.6, 80.9, 95.6 HRMS (MALDI-TOF) calcd for $C_{12}H_{20}O_6Na$, 283.1158; found, 283.1164.

(l) *Compound characterization data for compound* **12**: $[\alpha]_D^{25} = +106.9°$($CHCl_3$, *c* 1.0); ^1H NMR (200.13 MHz, $CDCl_3$): δ 2.46 (t, 1H, *J* = 2.4 Hz), 3.4, 3.5, 3.5, 3.5, 3.5, 3.5, 3.5 (7s, 21H), 3.42 (m, 1H), 3.50–3.72 (m, 10H), 3.92 (dd, 1H, *J* = 3.7, 11.5 Hz), 4.22 (t, 2H, *J* = 2.4 Hz), 5.07 (d, 1H, *J* = 1.5 Hz), 5.09 (d, 1H, *J* = 1.8 Hz); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 54.2, 57.6, 57.6, 58.7, 58.8, 59.1, 60.6, 60.8, 65.8, 71.2, 71.6, 71.9, 74.8, 75.7, 76.3, 76.8, 76.8, 78.6, 81.1, 81.1, 95.3, 97.0; HRMS (MALDI-TOF) calcd for $C_{22}H_{38}O_{11}Na$, 501.2312; found, 501.2318.

(m) *Compound characterization data for compound* **13**: $[\alpha]_D^{25} = -7.1°$($CHCl_3$, *c* 1.0); ^1H NMR (200.13 MHz, $CDCl_3$): δ 2.57 (t, 1H, *J* = 2.3 Hz), 3.34, 3.37, 3.38, 3.38, 3.44, 3.49, 3.52 (7s, 21H), 3.38–3.59 (m, 8H), 3.69 (m, 3H), 3.78 (dd, 1H, *J* = 3.3, 4.8 Hz), 3.9 (dd, 1H, *J* = 3.5, 11.1 Hz), 4.14–4.36 (m, 2H), 4.40 (d, 2H, *J* = 2.3 Hz), 4.92 (d, 1H, *J* = 1.3 Hz), 4.94 (d, 1H, *J* = 1.3 Hz), 5.29 (d, 1H, *J* = 1.5 Hz), 5.69 (dd, 1H, *J* = 1.8, 3.2 Hz), 5.88 (dd, 1H, *J* = 3.2, 10.1 Hz), 6.02 (t, 1H, *J* = 9.9 Hz), 7.20–7.71 (m, 9H), 7.75–8.18 (m, 6H); ^{13}C NMR (100.61 MHz, $CDCl_3$): δ 55.3, 57.4, 57.6, 58.6, 58.6, 59.1, 60.6, 60.8, 65.6, 66.1, 67.3, 69.9, 69.9, 70.5, 71.1, 71.5, 71.6, 75.6, 75.7, 76.3, 76.6, 77.2, 78.1, 81.2, 81.2, 96.5, 96.9, 96.9, 128.2–130.0, 133.2, 133.5, 133.6, 165.3, 165.4, 165.4; HRMS (MALDI-TOF) calcd for $C_{49}H_{60}O_{19}Na$, 975.3627; found, 975.3631.

(n) *Compound characterization data for compound* **14**: $[\alpha]_D^{25} = -144.3°$($CHCl_3$, *c* 1.0); ^1H NMR (200.13 MHz, $CDCl_3$): δ 2.56 (t, 1H, *J* = 2.4 Hz), 3.21, 3.36, 3.36, 3.50 (4s, 12H), 3.18–3.59 (m, 6H), 3.71 (dd, 1H, *J* = 3.7, 11.1 Hz), 3.96 (dd, 1H, *J* = 3.8, 11.1 Hz), 4.29 (td, 1H, *J* = 3.6, 7.3, 9.8 Hz), 4.40 (d, 2H, *J* = 2.4 Hz), 4.94 (s, 1H), 5.31 (d, 1H, *J* = 1.5 Hz), 5.69 (dd, 1H, *J* = 1.8, 3.1 Hz), 5.87 (dd, 1H, *J* = 3.3, 10.1 Hz), 6.02 (t, 1H, *J* = 9.9 Hz), 7.21–7.68 (m, 9H), 7.79–8.14 (m, 6H); ^{13}C NMR (50.32 MHz, $CDCl_3$): δ 55.3, 57.5, 58.8, 58.9, 60.6, 66.1, 67.2, 69.8, 69.9, 70.4, 71.2, 71.3, 75.6, 76.2, 76.7, 78.1, 80.9, 96.4, 97.0, 128.2–129.9, 133.1, 133.3, 133.6, 165.3, 165.4, 165.4; HRMS (MALDI-TOF) calcd for $C_{40}H_{44}O_{14}Na$, 771.2629; found, 771.2620.