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A general strategy for the synthesis of 3,6-branched gluco-oligosaccharides: facile synthesis of the phytoalexin elicitor oligosaccharides

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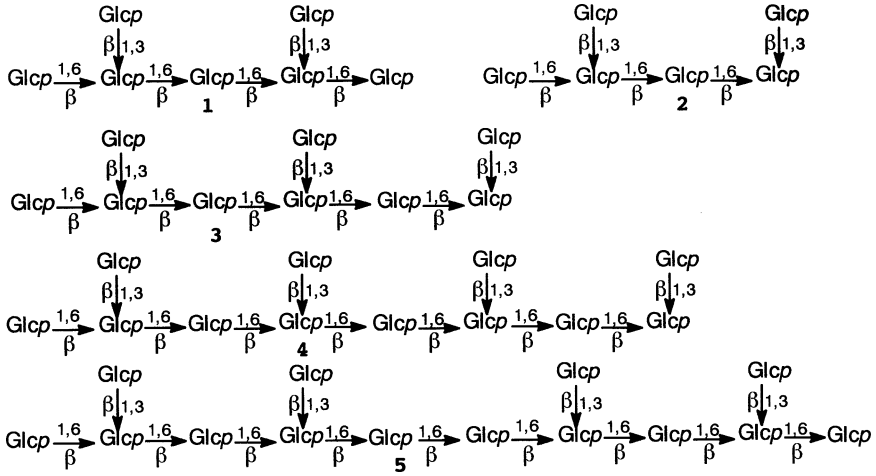
Abstract—A general method for the synthesis of 3,6-branched gluco-oligosaccharides has been developed. As a typical example of the method, the synthesis of the glucohexatose phytoalexin elicitor on a large scale was achieved via coupling of a trisaccharide donor with a trisaccharide acceptor. The donor and acceptor were prepared easily from 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose, 2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranosyl trichloroacetimidate, and 6-*O*-acetyl-2,3,4-tri-*O*-benzoyl-α-D-glucopyranosyl trichloroacetimidate in a regio- and stereoselective manner. Higher oligosaccharides of the elicitor including the hepta-, nona-, dodeca- and tetradecasaccharides have also been readily synthesized by this strategy.

A central problem in carbohydrate chemistry is how to prepare oligosaccharides efficiently and simply. During the last decades, much effort has been paid to oligosaccharide synthesis. However, up to now, there are no general applicable methods or strategies for oligosaccharide synthesis, and consequently the preparation of oligosaccharides is time consuming compared with the synthesis of other biopolymers such as peptides and nucleic acids. Generally speaking, the production of a complex oligosaccharide on an industrial scale is very difficult, if not impossible, so far. We always ask the question as to which method is the most suitable in carbohydrate synthesis. Maybe, owing to this structural complexity, the preparation of oligosaccharides will never achieve the same levels as the preparation of peptides and nucleic acids, but we can create relatively general procedures which are effective for certain types of oligosaccharides.



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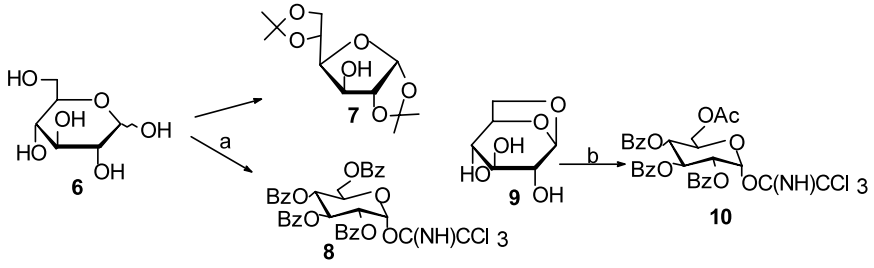
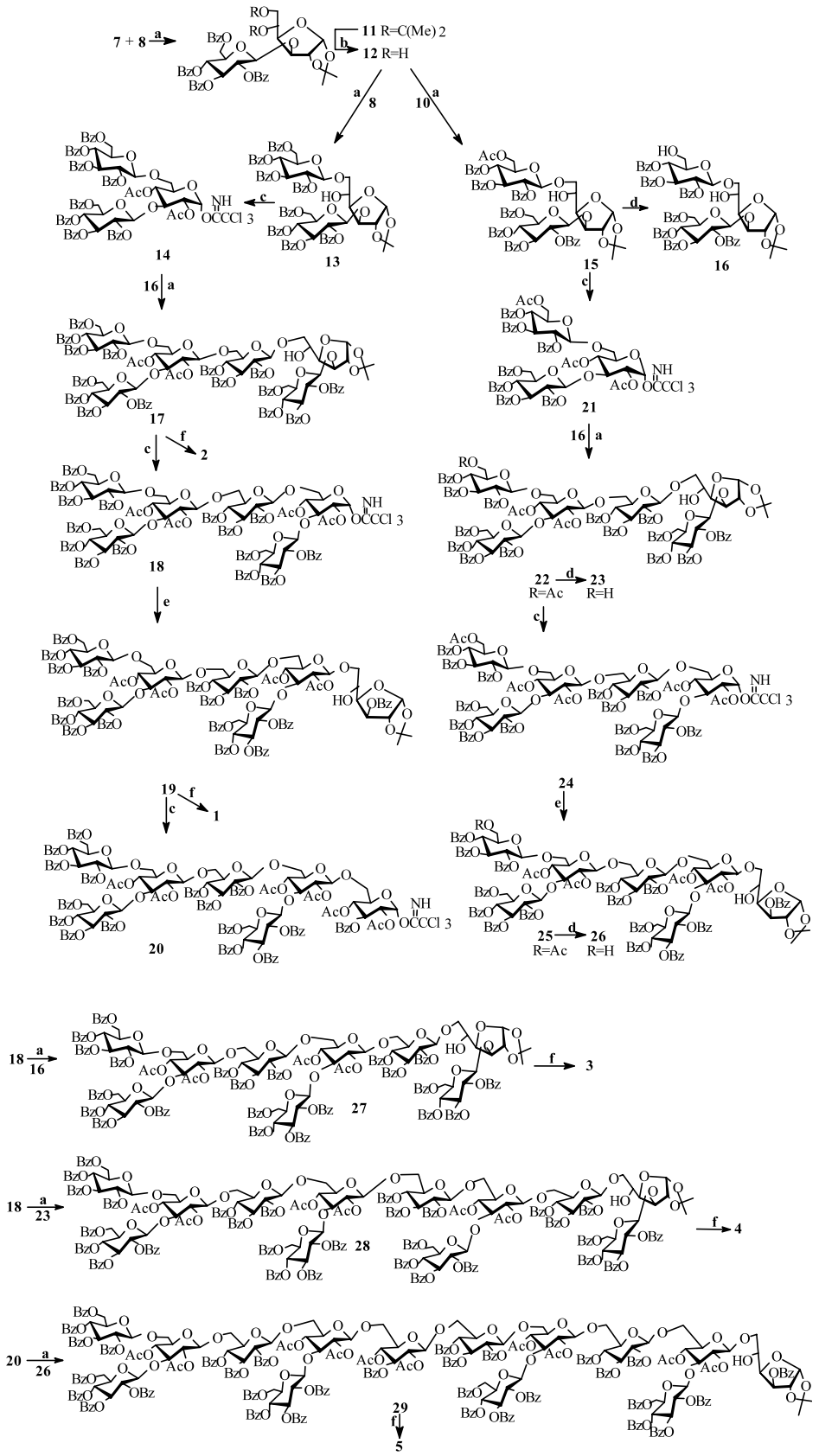
3,6-Branched gluco-oligosaccharides are a common structural characteristic of many biologically active polysaccharides such as the phytoalexin elicitor β-glucan and antitumor polysaccharides from schizophyllan, sceroglucan, and lentinan.[1] The β-(1→3)-branched β-(1→6)-linked glucose oligomers isolated from mycelial walls of the fungus *Phytophthora megasperma* f. sp. *Glycinea* can induce the formation of phytoalexins in soybean.[2] The most active heptasaccharide **1** is effective in very low doses, approximately 0.1 pmol per cotyledon.[3] Biological assays of several oligosaccharides revealed that D-glucohexatose **2** is the minimum structural element required for high elicitor activity.[4] It should be noted that, although much of this work was done with soybean cotyledons, it was established that the glucan elicitor also elicited the synthesis of different phytoalexins in a wide range of other plant species.[5] These important discoveries stimulated the interest of scientists. Since their isolation and identification, the glucan elicitors have been prepared by different groups,[6] and various methods and strategies have been used including very elegant solid-phase strategies.[6k,l] However, most of the reported procedures are only suitable for the preparation of samples for the investigation of structure–bioactivity relationships. Production of these molecules on a large scale, which is very important from the point of view of both carbohydrate chemistry and its practical application, has been hampered by the expensive reagents and complex operations involved in the synthesis. Seeberger has made phytoalexin elicitor oligosaccharides in a completely automated fashion on the solid-phase, but the key disaccharide glycosyl donors used in his synthesis were made in solution phase via a complex procedure.[6l] Here we would like to disclose the preparation of phytoalexin–elicitor oligoglucosaccharides using our strategy developed for the synthesis of 3,6-branched gluco-oligosaccharides.[7] With this new method, glucohexatose **2** was produced on a large scale using cheap materials through simple operations. Meanwhile, higher oligosaccharides of the elicitor including the hepta-, nona-, dodeca- and tetradecasaccharides **1**, **3**, **4** and **5**, respectively, have been synthesized readily.

In our synthesis, 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose **7**, 2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranosyl trichloroacetimidate **8** and 6-*O*-acetyl-2,3,4-tri-*O*-benzoyl-α-D-glucopyranosyl trichloroacetimidate **10** were the starting materials and the trisaccharides **13** and **15** were the key intermediates. Compound **8** was prepared as fine crystals via benzoylation of D-glucose followed by 1-*O*-debenzoylation with ammonia in THF–CH_3OH and trichloroacetimidation (Scheme 1). Compound **10** was prepared as crystals from the benzoylation of 1,6-anhydro-β-D-glucopyranose **9** (levoglucosan), a cheap material obtained from pyrolysis of cellulose,[8] followed by acetolysis, 1-*O*-deacetylation and trichloroacetimidation. Compound **7** is a commercially available material. The coupling of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose **7** with perbenzoyl glucosyl trichloroacetimidate **8** in the presence of TMSOTf (0.01 equiv.) as the catalyst, followed by selective 5,6-*O*-deacetonation afforded β-(1→3)-linked disaccharide **12** as crystals in high yield (76% over the two steps) (Scheme 2). Condensation of **12** with either **8** or **10**, catalyzed by TMSOTf, regio- and stereoselectively gave the key intermediates: the 3,6-branched trisaccharides **13** and **15**, respectively, in excellent yields (87%). Removal of the 1,2-*O*-isopropylidene group of **13** in 80% HOAc followed by acetylation with acetic anhydride in pyridine, selective 1-*O*-deacetylation with ammonia in THF–CH_3OH, and subsequent treatment with trichloroacetonitrile in the presence of K_2CO_3 afforded the desired trisaccharide glycosyl donor **14** in good yield (71% over the four steps). Selective 6-*O*-deacetylation of **15** in CH_2Cl_2–CH_3OH containing 0.3% HCl gave the trisaccharide acceptor **16** in high yield (90%). Coupling of **16** with **14** using TMSOTf as the catalyst regio- and stereoselectively afforded the blocked hexasaccharide **17** in high yield (84%). De-isopropylidenation of **17** in 80% HOAc, followed by deacetylation in an ammonia-saturated solution in 1:1 CH_2Cl_2–CH_3OH, furnished the free hexasaccharide **2** as an amorphous white solid in 92% yield (over the two steps).[9]

Using the same procedure as for the preparation of the trisaccharide glycosyl donor **14**, the hexasaccharide glycosyl donor **18** was obtained from **17**. Coupling **18** with 3-*O*-benzoyl-1,2-*O*-isopropylidene-α-D-glucofuranose and **16** afforded the blocked heptasaccharide **19** and



Scheme 1. *Reagents and conditions*: (a) i. PhCOCl (6.3 equiv.), pyridine (6.6 equiv.) and toluene, 70°C, 8 h; ii. 3:1 (v/v) THF–CH_3OH, 1.5N NH_3, rt, 12 h; iii. CH_2Cl_2, CCl_3CN (1.1 equiv.), K_2CO_3 (2.0 equiv.), rt, 12 h, 56% (over three steps). (b) i. PhCOCl (3.3 equiv.), pyridine (3.5 equiv.) and toluene, 70°C, 8 h; ii. 1:1:1:0.1 (v/v) CH_2Cl_2–Ac_2O–AcOH–H_2SO_4, rt, 20 h; iii. 3:1 (v/v) THF–CH_3OH, 1.5N NH_3, rt, 3 h; iv. CH_2Cl_2 (solvent), CCl_3CN (1.1 equiv.), K_2CO_3 (2.0 equiv.), rt, 12 h, 54% (over four steps).



Scheme 2. *Reagents and conditions*: (a) TMSOTf (0.01 equiv.), 4 Å MS, CH_2Cl_2, rt, 2–4 h (76% for **11**, 87% for **13**, 87% for **15**, 84% for **17**, 83% for **22**, 78% for **27**, 74% for **28**, 68% for **29**). (b) 90% HOAc, 40°C, 20 h, 100%. (c) i. 80% HOAc, reflux, 4 h; ii. Ac_2O–pyridine, rt, 10 h; iii. THF–CH_3OH, 1.5N NH_3, rt, 2–3 h; iv. CH_2Cl_2, CCl_3CN (2.0 equiv.), K_2CO_3 (2.0 equiv.), rt, 12 h, 71% for **14**, 72% for **18**, 70% for **20**, 74% for **21**, 70% for **24** (over four steps). (d) 0.3% HCl in CH_2Cl_2–CH_3OH, rt, 20 h, 90% for **16**, 80% for **23**, 76% for **26**. (e) 3-*O*-Benzoyl-1,2-*O*-isopropylidene-α-D-glucofuranose (1.2 equiv.), TMSOTf (0.01 equiv.), 4 Å MS, CH_2Cl_2, rt, 2 h, 86% for **19**, 85% for **25**. (f) i. 80% HOAc, reflux, 4 h; ii. CH_2Cl_2–CH_3OH saturated with ammonia, rt, 36 h, 92% for **2**, 90% for **1**, 88% for **3**, 84% for **4**, 76% for **5**.

nonasaccharide **27**, respectively, deprotection of which gave the corresponding compounds **1** and **3**. Utilizing the same procedure used for the preparation of **18**, the heptasaccharide glycosyl donor **20** was obtained from **19**. Similarly, the 6-*O*-acetyl hexasaccharide **22** and heptasaccharide **25** were obtained from **21** and **24**. Selective 6-*O*-deacetylation of **22** and **25** gave the hexasaccharide glycosyl acceptor **23** and heptasaccharide glycosyl acceptor **26**, respectively. Coupling of **18** with **23** gave the dodecasaccharide **28**, while condensation of **20** with **26** afforded the tetradecasaccharide **29**. Compounds **4** and **5** were obtained by deprotection of **28** and **29**, respectively.

In all of the syntheses, the reactions were carried out smoothly in high yields and in large scale. Several intermediates were not separated, but were used directly in further reactions thereby simplifying the procedures substantially. Preparation of the hexasaccharide **2** on a 100 g scale has been accomplished in our laboratory.

In summary, a general strategy for the preparation of 3,6-branched gluco-oligosaccharides has been developed. The strategy presented here also provides a route to the synthesis of β-(1→6) branched β-(1→3)-linked gluco-oligosaccharides which exist in many antitumor polysaccharides such as schizophyllan, sceroglucan and lentinan. The construction and bioassays of β-(1→6) branched β-(1→3)-linked gluco-oligosaccharides are in progress.

Acknowledgements

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9. All new compounds gave satisfactory elemental analysis results. Selected physical data for some key compounds are as follows, for **12**: mp 121–123°C; $[\alpha]_D$ +34 (*c* 2.5, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 8.11–7.28 (m, 20H, 4 Ph*H*), 5.94 (dd, 1H, *J*=9.7 Hz, H-3′), 5.72 (dd, 1H, *J*=9.7 Hz, H-4′), 5.54 (dd, 1H, *J*=7.9, 9.7 Hz, H-2′), 5.53 (d, 1H, *J*=3.6 Hz, H-1), 5.03 (d, 1H, *J*=7.9 Hz, H-1′), 4.84 (dd, 1H, *J*=3.6, 11.9 Hz, H-6a′), 4.42 (dd, 1H, *J*=4.3, 11.9 Hz, H-6b′), 4.41 (d, 1H, *J*=2.6, H-3), 4.24–4.23 (m, 2H, H-2, 5′), 4.16 (dd, 1H, *J*=2.6, 8.8 Hz, H-4), 4.02 (m, 1H, H-5), 3.83 (dd, 1H, *J*=3.2, 11.4 Hz, H-6a), 3.67 (dd, 1H, *J*=6.0, 11.4 Hz, H-6b), 1.44, 1.09 (2s, $C(CH_3)_2$). Anal. calcd for $C_{43}H_{42}O_{15}$: C, 64.66; H, 5.30. Found: C, 64.79; H, 5.25. For **13**: $[\alpha]_D$+25.3 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 8.06–7.28 (m, 40H, 8 Ph*H*), 5.88 (dd, 1H, *J*=9.7 Hz, H-3), 5.87 (dd, 1H, *J*=9.7 Hz, H-3), 5.69 (dd, 1H, *J*=9.7 Hz, H-4), 5.64 (dd, 1H, *J*=9.7 Hz, H-4), 5.53 (dd, 1H, *J*=7.9, 9.7 Hz, H-2), 5.43 (dd, 1H, *J*=7.9, 9.7 Hz, H-2), 5.41 (d, 1H, *J*=3.5 Hz, H-1), 4.96 (d, 1H, *J*=7.9 Hz, H-1), 4.93 (d, 1H, *J*=7.9 Hz, H-1), 4.68 (dd, 1H, *J*=3.4, 12.3 Hz, H-6), 4.48 (dd, 1H, *J*=4.9, 12.2 Hz, H-6), 4.67 (dd, 1H, *J*=3.4, 12.2 Hz, H-6), 4.35 (dd, 1H, *J*=4.9, 12.2 Hz, H-6), 4.34–3.65 (m, 8H), 1.26, 1.03 (2s, 6H, $(CCH_3)_2$). Anal. calcd for $C_{77}H_{68}O_{24}$: C, 67.15; H, 4.98. Found: C, 67.29; H, 5.02. For **14**: $[\alpha]_D$ +23.3 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H, CN*H*CCl_3), 8.07–7.19 (m, 40H, 8 Ph*H*), 6.19 (d, 1H, *J*=3.6), 5.91 (dd, 1H, *J*=9.6 Hz), 5.85 (dd, 1H, *J*=9.6 Hz), 5.62 (dd, 1H, *J*=9.6 Hz), 5.61 (dd, 1H, *J*=9.6 Hz), 5.46 (dd, 1H, *J*=7.9, 9.6 Hz), 5.42 (dd, 1H, *J*=7.9, 9.6 Hz), 4.97 (d, 1H, *J*=7.9 Hz), 4.96 (d, 1H, *J*=7.9 Hz), 4.85 (dd, 1H, *J*=9.5 Hz), 4.67–4.59 (m, 3H), 4.50–4.37 (m, 2H), 4.19–4.02 (m, 4H), 3.91 (dd, 1H), 3.69 (dd, 1H), 1.94, 1.78 (2s, 6H, 2 CH_3CO). Anal. calcd for $C_{80}H_{68}Cl_3NO_{26}$: C, 61.37; H, 4.38. Found: C, 61.53; H, 4.41. For **15**: $[\alpha]_D$+18.6 (*c* 1.1, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ

8.05–7.26 (m, 35H), 5.87 (dd, 1H, $J=9.6$ Hz), 5.84 (dd, 1H, $J=9.6$ Hz), 5.65 (dd, 1H, $J=9.6$ Hz), 5.59 (dd, 1H, $J=9.6$ Hz), 5.51 (dd, 1H, $J=7.9$, 9.6 Hz), 5.43 (dd, 1H, $J=7.9$, 9.6 Hz), 5.42 (d, 1H, $J=3.6$ Hz), 4.96 (d, 1H, $J=9.6$ Hz), 4.93 (d, 1H, $J=9.6$ Hz), 4.71–3.79 (m, 12H), 2.05 (s, 3H, CH_3CO), 1.33, 1.05 (2 s, 6H, (CCH_3)$_2$). Anal. calcd for $C_{72}H_{66}O_{24}$: C, 65.75; H, 5.06. Found: C, 66.00; H, 5.03. For **16**: $[\alpha]_D$+22.6 (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05–7.26 (m, 35H), 5.91 (dd, 1H, $J=9.8$ Hz), 5.90 (dd, 1H, $J=9.8$ Hz), 5.73 (dd, 1H, $J=9.8$ Hz), 5.56 (dd, 1H, $J=9.8$ Hz), 5.54–5.42 (m, 3H), 4.99 (d, 1H, $J=7.9$ Hz), 4.95 (d, 1H, $J=7.9$ Hz), 4.75–3.77 (m, 12H), 1.33, 1.05 (2 s, 6H, (CCH_3)$_2$). Anal. calcd for $C_{70}H_{64}O_{23}$: C, 66.03; H, 5.07. Found: C, 66.24; H, 5.10. For **17**: $[\alpha]_D$+26.6 (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04–7.18 (m, 75H), 6.13, 5.88, 5.83, 5.74 (4dd, $J=9.5$ Hz, 4H), 5.69, 5.65, 5.62, 5.57 (4dd, $J=9.5$ Hz, 4H), 5.50, 5.48, 5.44, 5.34 (4dd, $J=7.9$, 9.5 Hz, 4H), 5.45 (d, 1H), 5.07, 4.94, 4.83, 4.80,4.51 (5d, 5H), 1.95, 1.87 (2s, 6H, 2 CH_3CO), 1.33, 1.08 (2s, 6H, C(CH_3)$_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.4, 168.2 (2CH_3CO), 112.2 (C(CH$_3$)$_2$), 105.0, 101.5, 101.1, 101.0, 100.9, 100.2 (6 C-1), 82.9, 82.5 (2 C-3), 26.6, 25.9 (C(CH$_3$)$_2$), 20.85, 20.51 (2 CH$_3$CO). Anal. calcd for $C_{148}H_{130}O_{48}$: C, 66.41; H, 4.90. Found: C, 66.51; H, 4.86. For **2**: $[\alpha]_D$ −39.1 (c 0.2, H_2O); ^{13}C NMR (100 MHz, D_2O): δ 102.6, 102.5, 102.4, 102.4, 102.3, 102.3 (6C-1), 84.0, 83.9 (2C-3); ESMS for $C_{26}H_{62}O_{31}$ (990.86): 989.7 [M−1]$^+$. For **18**: $[\alpha]_D$ +33.1 (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H, CNHCCl$_3$), 7.90–7.26 (m, 75H, 15PhH), 6.24 (d, 1H, $J=3.5$), 6.06, 5.92, 5.88, 5.71, 5.70, 5.69, 5.68, 5.47, 5.46, 5.45, 5.39, 5.37 (12 dd, 4H), 5.01, 4.97, 4.88, 4.75 4.53(5 d, $J=7.9$ Hz, 5H), 1.97, 1.96, 1.85, 1.77 (4s, 12H, 4CH_3CO). Anal. calcd for $C_{151}H_{130}Cl_3NO_{50}$: C, 63.30; H, 4.57. Found: C, 63.21; H, 4.61. For **19**: $[\alpha]_D$+34.3 (c 1.0, $CHCl_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.58, 169.29 168.23, 168.15 (4CH$_3C$O), 165.95, 165.94, 165.94, 165.76, 165.72, 165.60, 165.55,165.50, 165.28, 165.25, 165.10, 165.07, 165.04, 165.01, 165.00, 164.93 (16 PhCO), 112.05 (C(CH$_3$), 105.04, 101.23, 101.05, 100.96, 100.95, 100.58, 100.38 (7C-1), 83.38, 82.20 (2C-3), 26.57, 26.11 (C(CH$_3$)$_2$), 20.78, 20.60, 20.50, 20.42 (4CH$_3$CO). Anal. calcd for $C_{165}H_{148}O_{56}$: C, 65.47; H, 4.93. Found: C, 65.31; H, 4.86. For **1**: $[\alpha]_D$ −25.0 (c 0.1, H_2O); ^{13}C NMR (100 MHz, D_2O): δ 102.7, 102.6, 102.6, 102.4, 102.4, 102.1, 102.1 (7 C-1); ESMS for $C_{42}H_{72}O_{36}$ (1153.01): 1152.00 [M−1]$^+$. For **27**: $[\alpha]_D$+29.6 (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.98, 1.97, 1.91, 1.85 (4s, 12H, 4CH_3CO), 1.36, 1.09 (2s, 6H, (CCH_3)$_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.83, 169.56, 168.34, 168.22 (4 CH$_3C$O), 112.25 (C(CH$_3$)$_2$), 105.12, 101.59, 101.31, 101.17, 101.10, 101.06, 101.05, 100.40, 100.39 (9 C-1), 83.0, 82.57, 79.45 (3 C-3), 26.72, 25.99 (C(CH$_3$)$_2$), 20.89, 20.85, 20.60, 20.55 (4CH$_3$CO). Anal. calcd for $C_{219}H_{192}O_{72}$: C, 66.16; H, 4.87. Found: C, 66.34; H, 4.70. For **3**: $[\alpha]_D$ −20.1 (c 0.1, H_2O); ^{13}C NMR (100 MHz, D_2O): δ 102.9, 102.8, 102.8, 102.6, 102.5, 102.5, 102.0, 102.0, 101.9 (9 C-1); ESMS for $C_{54}H_{92}O_{46}$ (1477.29): 1476.2 [M−1]$^+$. For **28**: $[\alpha]_D$+20.6 (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.03, 2.01, 2.00, 1.93, 1.92, 1.90 (6s, 18H, 6CH_3CO), 1.37, 1.11 (2s, 6H, 2 CCH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.60, 169.37, 169.12, 168.91, 189.19, 167.92 (6 CH$_3C$O), 112.30 (C(CH$_3$)$_2$), 104.60, 101.66, 101.04, 100.86, 100.84, 100.68, 100.57, 100.56, 100.47, 100.28, 99.89, 99.85 (12 C-1), 82.54, 81.52, 81.20, 80.15 (4 C-3), 26.22, 25.52 (C(CH$_3$)$_2$), 20.52, 20.45, 20.40, 20.32, 20.16, 20.13 (6 CH$_3$CO). Anal. calcd for $C_{290}H_{254}O_{96}$: C, 66.03; H, 4.85. Found: C, 65.96; H, 4.91. For **4**: $[\alpha]_D$ −16.1 (c 0.1, H_2O); ^{13}C NMR (100 MHz, D_2O): δ 102.8, 102.8, 102.7, 102.5, 102.5, 102.3, 102.3, 102.2, 102.2, 101.8, 101.8, 101.8 (12 C-1); ESMS for $C_{72}H_{122}O_{61}$ (1963.72): 1962.6 [M−1]$^+$. For **29**: $[\alpha]_D$+13.3 (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.98, 1.94, 1.91, 1.87, 1.86, 1.85, 1.82, 1.79. 1.78, 1.77 (10 s, 30H, 10CH_3CO), 1.36, 1.09 (2s, 6H, (CCH_3)$_2$); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.68, 169.61, 169.40, 169.37, 169.12, 169.00, 168.88, 168.54, 189.08, 167.99 (10CH$_3C$O), 112.24 (C(CH$_3$)$_2$), 105.20, 101.74, 101.31, 101.11, 100.89, 100.87, 100.78, 100.77, 100.62, 100.57, 100.45, 100.45, 99.91, 99.79 (14 C-1), 83.26, 82.99, 81.78, 81.48 (4C-3), 26.37, 25.65 (C(CH$_3$)$_2$), 20.68, 20.61, 20.49, 20.46, 20.39, 20.36, 20.20, 20.19, 20.14, 20.11 (10CH$_3$CO). Anal. calcd for $C_{324}H_{290}O_{112}$: C, 65.12; H, 4.89. Found: C, 65.31; H, 4.74. For **5**: $[\alpha]_D$ −11.4 (c 0.1, MeOH); ^{13}C NMR (100 MHz, D_2O): δ 102.9, 102.8, 102.7, 102.7, 102.6, 102.6, 102.5, 102.4, 102.3, 102.3, 102.3, 101.9, 101.7, 101.7 (14 C-1); ESMS for $C_{84}H_{142}O_{71}$ (2288.00): 2286.9 [M−1]$^+$.