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# Synthesis of *C*-disaccharide analogues of the α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl motif of mycobacterial cell walls via alkynyl intermediates

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**Abstract**—Two *C*-glycosides related to the recurrent α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl structural motif of mycobacterial arabinan have been prepared by routes involving acetylenic intermediates.


Tuberculosis remains one of the major infectious diseases worldwide, responsible for around two million deaths annually, particularly in the developing world.[1] Additionally, the synergism of the disease with HIV and the appearance of multi-drug resistant strains of the causative agent, *Mycobacterium tuberculosis*, raises the prospect that tuberculosis may become prevalent as a disease only curable with great difficulty in developed nations.[2]

In a search for new drug targets, the mycobacterial cell envelope[3] is attractive. Major components of the cell wall are two polysaccharide structures, lipoarabinomannan (LAM) and arabinogalactan (AG), this latter structure being covalently linked to the bacterial peptidoglycan and esterified as the non-reducing termini of the arabinan component with long-chain fatty acids (mycolic acids).

In seeking to block the biosynthesis of AG[4] and/or LAM,[5] the glycosyl transferases responsible for assembly of the arabinan components of both these polymers[6] are appealing targets for inhibitor design, given that the D-arabinose units are exclusively in their furanose form, and the xenobiotic status of the furanose form of D-arabinose. It is known that arabinofuranosyl transfer to the growing arabinan from the sugar donor β-D-arabinofuranosyl-1-monophosphoryldecaprenol is inhibited by one major anti-tuberculosis agent in clinical use, ethambutol.[7]

The most common recurrent structural motif in mycobacterial arabinan is the α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl unit **1**. *C*-Glycosides are close analogues of oligosaccharide structures, which are resistant to chemical and enzymic degradation.[8] We here describe direct routes for the synthesis of two *C*-glycosides **2** and **3** related to motif **1**, by the use of acetylenic intermediates. An alternative route to **2** using a Wittig-based approach had recently been reported,[9] whilst a synthesis of **3** using the Henry reaction as a key step has been claimed.[10]

For the synthesis of **2** (see Scheme 1) the lactone **4**, prepared by oxidation[11] of commercially available tri-*O*-benzyl-D-arabinofuranose, was treated with lithio(trimethylsilyl)ethyne at low temperature to give the lactol **5** (66%). Treatment of this with triethylsilane and $BF_3 \cdot Et_2O$ gave the separable isomers **6α** (60%) and **6β** (13%).[12] That the major isomer **6α** was the expected[13] isomer in which hydride delivery had occurred *cis* to the vicinal benzyloxy group was confirmed by the observation of an NOE interaction between H-1′ and H-3′, which was absent in the spectrum of **6β**, which however showed a strong interaction between H-1′ and H-2′. Desilylation of **6α** gave **7** (97%), which again showed an NOE interaction between H-1′ and H-3′, confirming the stereochemistry of this material. The synthesis could then be completed by an iterative route. Treatment of **7** with *n*-BuLi, followed by addition of lactone **4** gave the

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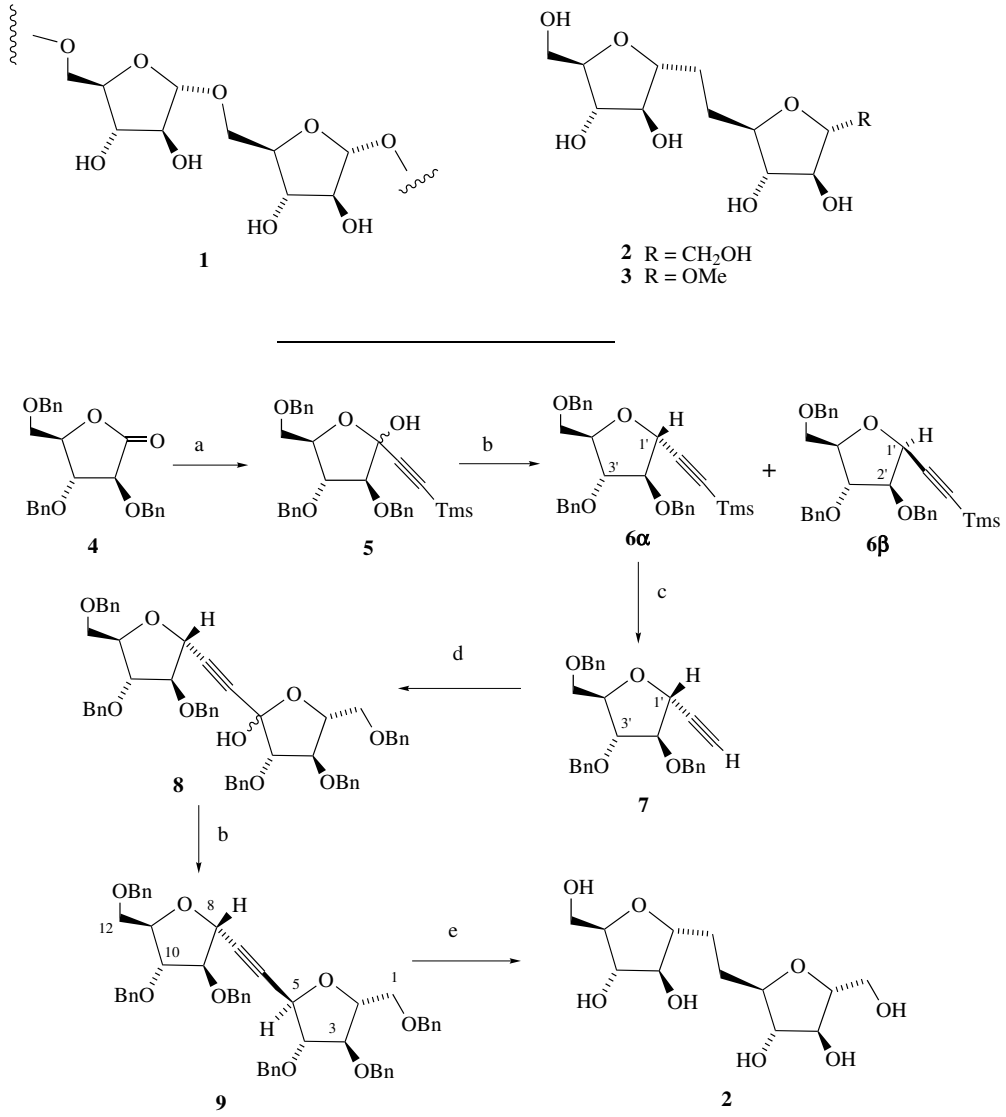
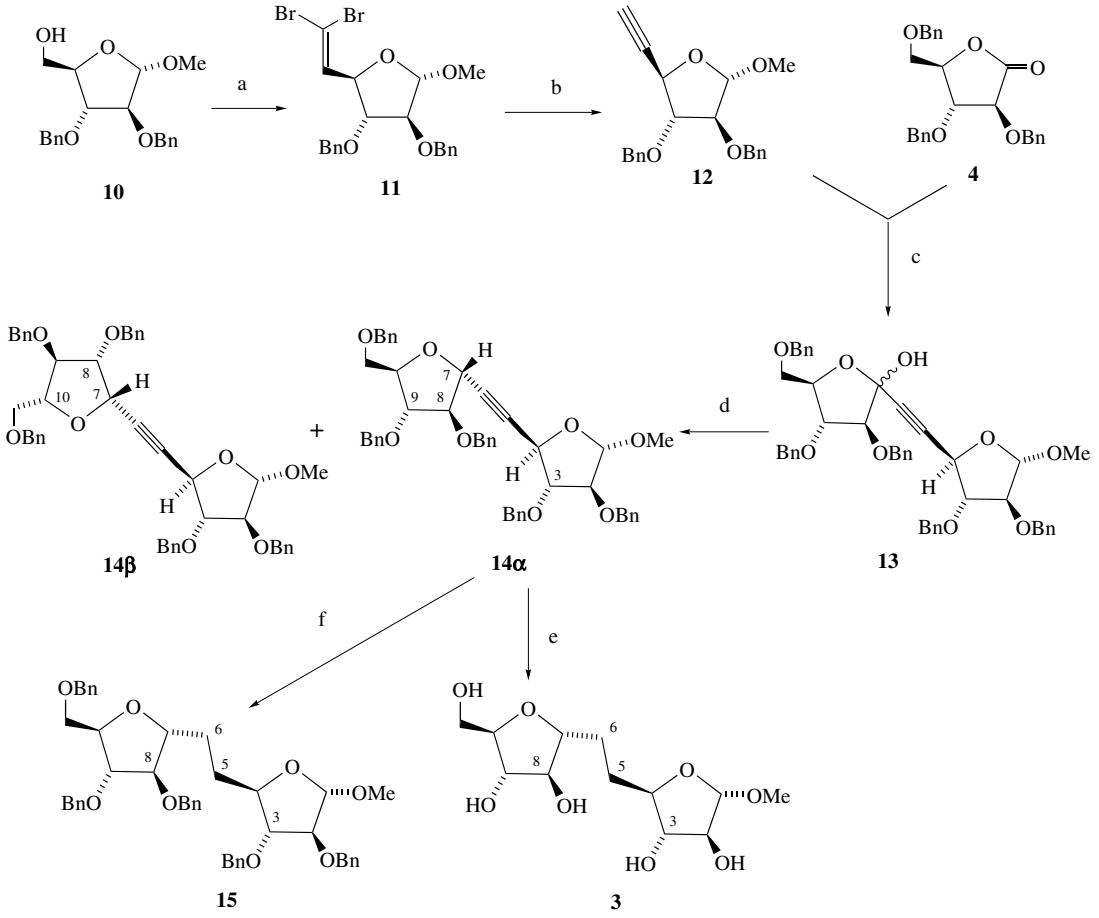



**Scheme 1.** Reagents and conditions: (a) TMS–acetylene, *n*-BuLi, THF, −78 °C; (b) $BF_3{\cdot}Et_2O$, $Et_3SiH$, DCM, −78 °C; (c) $K_2CO_3$, MeOH; (d) BuLi, THF, −78 °C, then **4**; (e) $Pd(OH)_2/C$, $H_2$ (1 atm), MeOH–EtOAc (5:1).

hemiacetal **8** (85%), which on reduction with $Et_3SiH$ and $BF_3{\cdot}Et_2O$ gave the disubstituted alkyne **9** (83%) as the major product. The stereochemistry of **9** was clear from its NMR spectra,[14] which indicated $C_2$ symmetry, and the observation of NOEs between H-5/8 and both H3/10 and (weakly) H-1/12. Reduction–hydrogenolysis of **9** then gave the *C*-disaccharide **2**[15] in near-quantitative yield.

For the synthesis of the methyl glycoside **3** (see Scheme 2), methyl 2,3-di-*O*-benzyl-α-D-arabinofuranoside (**10**)[16] was prepared by modifications of the original route.[17] Swern oxidation of **10**, followed by treatment of the aldehyde with $CBr_4$–$Ph_3P$ gave the dibromoalkene **11** (73% overall), which on treatment with *n*-BuLi gave alkyne **12** (75%).[18] Reaction of the lithio-derivative of **12** with lactone **4** gave hemiacetal **13** (87%), which on treatment with $Et_3SiH$ and $BF_3{\cdot}Et_2O$ gave **14α** (66%) and **14β** (20%),[19] separable by chromatography. The stereochemistry of the major product **14α** was indicated by an NOE between H-7 and H-9; by comparison, the minor product **14β** showed an NOE between H-7 and H-10. Additionally, the signal for C-8 in **14β** was significantly shielded ($\delta$ 83.4) as compared with the equivalent signal for **14α** ($\delta$ 88.8), a correlation, which was also found for alkynes **6α** and **6β**,[12] and for **7** and its β-isomer. Both **14α** and **14β** showed C-3 in the region of $\delta$ 88. For **14α**, the signals for H-8 ($\delta$ 4.23), and to a smaller extent, H-10 ($\delta$ 4.25), were also deshielded by the anisotropic effect of the alkyne as compared with the equivalent signals for **14β** ($\delta$ 4.00 and 4.06, respectively). It should also be noted that alkyne **9** showed signals for positions 4/9 at $\delta_C$ 88.8 and $\delta_H$ 4.23.

Catalytic hydrogenation of **14α** gave the *C*-disaccharide **3** in quantitative yield. The data for **3**[20] was similar to, but significantly different from, that noted in the previous report[10] on the synthesis of this compound. However, in the $^1H$ NMR data of **3**, NOEs were observed between the multiplet for H-5/6 and both H-8 and H-3, in support of its stereostructure. Given these discrepancies, **14α** was subjected to diimide reduction to give




**Scheme 2.** Reagents and conditions: (a) i. DMSO, $(COCl)_2$, DCM, −78 °C, then $Et_3N$; ii. $CBr_4$, $Ph_3P$, DCM, 0 °C; (b) *n*-BuLi, THF, −78 to 0 °C; (c) *n*-BuLi, THF, −78 °C, then **4**; (d) $BF_3{\cdot}Et_2O$, $Et_3SiH$, DCM, −78 °C; (e) $Pd(OH)_2/C$, $H_2$ (1 atm), MeOH; (f) dipotassium azodicarboxylate, MeOH–pyridine, then HOAc.

the saturated compound **15**[21] (83%), which had also been reported by the previous workers.[10] This compound, as prepared here, had spectroscopic data in full agreement with its structure, but at considerable variance from the data reported earlier.[10] In the $^1H$ NMR data of **15**, NOEs were again observed between H-5/6 and both H-8 and H-3. We thus must question the previous report on the synthesis of **3**, and suggest that our work constitutes the first definitive synthesis of this compound.

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12. Selected data: **6α**: $[\alpha]_D$ +43.4 (*c* 1.0, $CHCl_3$); $\delta_H$ (400 MHz, $CDCl_3$): 0.20 (9H, s, $SiMe_3$), 3.58 (1H, dd, *J* 10.6, 4.9, H-5′a), 3.63 (1H, dd, *J* 10.6, 4.3, H-5′b), 4.04 (1H, dd, *J* 5.8, 3.5, H-3′), 4.20–4.27 (2H, m, H-2′, H-4′), 4.49–4.60 (5H,

m, OC$H_2$Ph), 4.68 (1H, d, $J$ 11.6, OC$H_2$Ph), 4.70 (1H, d, $J$ 4.2, H-1′), 7.20–7.40 (15H, m, Ph); $\delta_C$ (100 MHz, $CDCl_3$): −0.2 ($SiMe_3$), 69.7 (C-5′), 72.05, 72.1 (2 × O$CH_2$Ph), 72.3 (C-1′), 73.4 (O$CH_2$Ph), 81.2 (C-4′), 84.2 (C-3′), 88.8 (C-2′), 91.8, 102.8 (alkyne), 127.6–128.4 (Ph), 137.4, 137.9. 138.1 (Ph, q). Compound **6β**: $[\alpha]_D$ −39.8 (*c* 1.3, $CHCl_3$); $\delta_H$ (400 MHz, $CDCl_3$): 0.10 (9H, s, $SiMe_3$), 3.59 (1H, dd, $J$ 10.0, 6.6, H-5′a), 3.69 (1H, dd, $J$ 10.0, 5.9, H-5′b), 3.93 (1H, dd, $J_{3',4'}$ 3.7, $J_{3',2'}$ 1.9, H-3′), 3.98 (1H, dd, $J_{2',1'}$ 4.1, $J_{2',3'}$ 1.8, H-2′), 4.02 (1H, ddd, $J$ 6.6, 6.0, 3.7, H-4′), 4.40–4.62 (5H, m, OC$H_2$Ph), 4.68 (1H, d, $J$ 4.1, H-1′), 4.69 (1H, d, $J$ 12.4, OC$H_2$Ph), 7.20–7.40 (15H, m, Ph); $\delta_C$ (100 MHz, $CDCl_3$): −0.3 ($SiMe_3$), 70.3 (C-5′), 71.66 (O$CH_2$Ph), 71.7 (C-1′), 72.0, 73.3 (2 × O$CH_2$Ph), 82.3 (C-4′), 83.3 (C-2′), 84.6 (C-3′), 93.0, 100.1 (alkyne), 127.6–128.4 (Ph), 137.6, 137.9, 138.2 (Ph, q).

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14. Selected data for **9**: $\delta_H$ (400 MHz, $CDCl_3$): 3.59 (2H, dd, $J_{gem}$ 10.6, $J_{1a,2}/J_{12a,11}$ 5.0, H-1a/12a), 3.70 (2H, dd, $J_{gem}$ 10.6, $J_{1b,2}/J_{12b,11}$ 4.4, H-1b/12b), 4.03 (2H, dd, $J_{3,2}/J_{10,11}$ 5.6, $J_{3,4}/J_{10,9}$ 2.9, H-3/10), 4.23 (2H, t, $J_{4,3}/J_{9,10} \sim J_{4,5}/J_{9,8} \sim 3.2$, H-4/9), 4.26 (2H, dt, $J_{2,3}/J_{11,10}$ 5.6, $J_{2,1a}/J_{11,12a} \sim J_{2,1b}/J_{11,12b} \sim 4.9$, H-2/11), 4.48 (2H, d, $J$ 11.7, O$CH_2$Ph), 4.49 (2H, d, $J$ 12.1, O$CH_2$Ph), 4.53 (2H, d, $J$ 12.1, O$CH_2$Ph), 4.54 (2H, s, O$CH_2$Ph), 4.56 (2H, s, O$CH_2$Ph), 4.61 (2H, d, $J$ 11.7, O$CH_2$Ph), 4.78 (2H, d, $J$ 3.2, H-5/8), 7.23–7.36 (30H, m, Ph); $\delta_C$ (100 MHz, $CDCl_3$): 69.7 (C-1/12), 72.0 (O$CH_2$Ph), 72.1 (O$CH_2$Ph), 72.2 (C-5/8), 73.4 (O$CH_2$Ph), 81.5 (C-2/11), 84.20 (C-3/10), 84.24 (C-6/7), 88.8 (C-4/9), 127.5–128.40 (Ph), 137.38, 137.81, 138.05 (Ph, q); *m/z* (ES) 848.4150 $[(M+NH_4)^+$; $C_{54}H_{58}NO_8$ requires 848.41].
15. Selected data for **2**: $\delta_H$ (400 MHz, $D_2O$): 1.78 (4H, m, H-6/7), 3.69 (2H, dd, $J_{gem}$ 12.3, $J_{1a,2}/J_{12a,11}$ 5.9, H-1a/12a), 3.75 (2H, dd, $J_{gem}$ 12.3, $J_{1b,2}/J_{12b,11}$ 3.5, H-1b/12b), 3.83–3.90 (2H, br m, H-5/8), 3.89 (2H, td, $J_{2,3}/J_{11,10} \sim J_{2,1a}/J_{11,12a} \sim 6.2$, $J_{2,1b}/J_{11,12b}$ 3.5, H-2/11), 3.93 (2 × 1H, t, $J_{4,5}/J_{9,8} \sim J_{2,3}/J_{9,10} \sim 6.2$, H-4/9), 4.03 (2H, t, $J_{3,2}/J_{10,11} \sim J_{3,4}/J_{10,9}$ 6.2, H-3/10); $\delta_C$ (100 MHz, $D_2O$): 28.68 (C-6/7), 61.65 (C-1/12), 77.24 (C-3/10), 80.67 (C-4/9), 82.20 (C-5/8), 82.55 (C-2/11); *m/z* (ES) 295.1387 $[(M+H)^+$; $C_{12}H_{23}O_8$ requires 295.1387].
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18. Selected data for **12**: $[\alpha]_D$ +60.8 (*c* 1.085, DCM); $\delta_H$ (200 MHz, $CDCl_3$): 2.62 (1H, d, $J$ 2.1, H-6), 3.40 (3H, s, $OCH_3$), 3.98 (1H, dd, $J_{2,3}$ 3.3, $J_{2,1}$ 1.2, H-2), 4.15 (1H, dd, $J_{3,4}$ 6.6, $J_{3,2}$ 3.3, H-3), 4.48 (1H, d, $J$ 11.6, Bn), 4.55 (1H, d, $J$ 11.6, Bn), 4.60 (1H, d, $J$ 11.6, Bn), 4.65 (1H, dd, $J_{4,3}$ 6.6, $J_{4,6}$ 2.1, H-4), 4.71 (1H, d, $J$ 11.6, Bn), 4.96 (1H, d, $J$ 1.2, H-1), 7.25–7.45 (10H, m, Ph); $\delta_C$ (50 MHz, $CDCl_3$): 55.2 ($OCH_3$), 70.6 (C-6), 72.0 (O$CH_2$Ph), 72.5 (O$CH_2$Ph), 75.1 (C-5), 80.7 (CH), 87.8 (CH), 87.9 (CH), 107.2 (C-1), 127.8, 128.4 (Ph), 137.29 (Ph, q); *m/z* (ES) 356.1847 $[(M+NH_4)^+$; $C_{21}H_{26}NO_4$ requires 356.1856].
19. Selected data: **14α**: $\delta_H$ (400 MHz, $CDCl_3$): 3.37 (3H, s, $OCH_3$), 3.59 (1H, dd, $J_{gem}$ 10.6, $J_{11a,10}$ 5.0, H-11a), 3.63 (1H, dd, $J_{gem}$ 10.6, $J_{11b,10}$ 5.0, H-11b), 3.94 (1H, dd, $J_{2,3}$ 3.5, $J_{2,1}$ = 1.5, H-2), 4.02 (1H, dd, $J_{9,10}$ 5.9, $J_{9,8}$ 3.2, H-9), 4.09 (1H, ddd, $J_{3,4}$ 7.1, $J_{3,2}$ 3.5, $J_{3,1}$ 0.6, H-3), 4.23 (1H, t, $J_{8,7} \sim J_{8,9} \sim 3.2$, H-8), 4.25 (1H, t, $J_{10,9} \sim J_{10,11} \sim 5.0$, H-10), 4.44–4.65 (10H, m, Bn), 4.67 (1H, dd, $J_{4,3}$ 7.1, $J_{4,7}$ 1.5, H-4), 4.80 (1H, dd, $J_{7,8}$ 3.5, $J_{7,4}$ 1.5, H-7), 4.92 (1H, dd, $J_{1,2}$ 1.5, $J_{1,3}$ 0.5, H-1), 7.22–7.36 (25H, m, Ph); $\delta_C$ (100 MHz, $CDCl_3$): 55.2 ($OCH_3$), 69.7 (C-11), 70.8 (C-4), 72.0, 72.1 (O$CH_2$Ph), 72.2 (C-7), 72.6, 73.4 (O$CH_2$Ph), 81.6 (C-10), 83.8 (alkyne), 84.2 (C-9), 84.4 (alkyne), 87.9 (C-3), 88.2 (C-2), 88.8 (C-8), 107.2 (C-1), 127.6–128.5 (Ph), 137.35, 137.43, 137.47, 137.8, 138.1 (Ph, q); *m/z* (ES) 758.3693 $[(M+NH_4)^+$; $C_{47}H_{52}NO_8$ requires 758.3687]. Compound **14β**: $\delta_H$ (400 MHz, $CDCl_3$): 3.36 (3H, s, $OCH_3$), 3.59 (1H, dd, $J_{gem}$ 10.0, $J_{11a,10}$ 6.8, H-11a), 3.68 (1H, dd, $J_{gem}$ 10.0, $J_{11b,10}$ 5.9, H-11b), 3.93–3.96 (2H, m, H-2 and H-9), 4.00 (1H, dd, $J_{8,7}$ 4.1, $J_{8,9}$ 2.1, H-8), 4.06 (1H, dt, $J_{10,11a} \sim J_{10,11b} \sim 6.2$, $J_{10,9}$ 3.8, H-10), 4.12 (1H, ddd, $J_{3,4}$ 6.8, $J_{3,2}$ 3.5, $J_{3,1}$ 0.6, H-3), 4.44–4.68 (10H, m, Bn), 4.71 (1H, dd, $J_{4,3}$ 6.8, $J_{4,7}$ 1.5, H-4), 4.76 (1H, dd, $J_{7,8}$ 4.1, $J_{7,4}$ 1.5, H-7), 4.91 (1H, dd, $J_{1,2}$ 1.5, $J_{2,3}$ 0.6, H-1), 7.21–7.36 (25H, m, Ph); $\delta_C$ (100 MHz, $CDCl_3$): 55.1 ($OCH_3$), 70.4 (C-11), 71.0 (C-4), 71.4 (C-7), 71.7, 72.1, 72.3, 72.4, 73.3 (O$CH_2$Ph), 82.1 (alkyne), 82.3 (C-10), 83.4 (C-8), 84.3 (C-9), 84.8 (alkyne), 87.6 (C-3), 88.1 (C-2), 107.2 (C-1), 127.6–128.4 (Ph), 137.44, 137.45, 137.6, 137.7, 138.1 (C).
20. Selected data for **3**: $\delta_H$ (400 MHz, $D_2O$): 1.76–1.85 (4H, m, H-5, H-6), 3.42 (3H, s, $OCH_3$), 3.70 (1H, dd, $J_{gem}$ 12.3, $J_{11a,10}$ 5.8, H-11a), 3.77 (1H, dd, $J_{gem}$ 12.3, $J_{11b,10}$ 3.4, H-11b), 3.84 (1H, ddd, $J_{3,4}$ 6.0, $J_{3,2}$ 3.3, $J_{3,1}$ 0.4, H-3), 3.86–3.90 (1H, m, H-7), 3.89–3.93 (1H, m, H-10), 3.94 (1H, dd, $J_{8,7}$ 6.7, $J_{8,9}$ 5.7, H-8), 3.40–4.01 (1H, m, H-4), 4.04 (1H, dd, $J_{9,10}$ 6.5, $J_{9,8}$ 5.8, H-9), 4.05 (1H, dd, $J_{2,3}$ 3.3, $J_{2,1}$ 1.6, H-2), 4.91 (1H, dd, $J_{1,2}$ 1.6, $J_{1,3}$ 0.4, H-1); $\delta_C$ (100 MHz, $D_2O$) 28.8 ($CH_2$), 28.9 ($CH_2$), 55.2 ($OCH_3$), 61.7 (C-11), 77.3 (C-9), 80.4 (C-3), 80.7 (C-8), 81.5 (C-2), 82.1 (C-7), 82.6 (C-10), 83.5 (C-4), 108.4 (C-1); *m/z* (ES) 312.1658 $[(M+NH_4)^+$; $C_{12}H_{26}NO_8$ requires 312.1653].
21. Selected data for **15**: $\delta_H$ (400 MHz, $CDCl_3$): 1.62–1.89 (4H, m, H-5, H-6), 3.35 (3H, s, OMe), 3.52 (1H, dd, $J_{gem}$ 10, $J_{11a,10}$ 5.9, H-11a), 3.59 (1H, dd, $J_{gem}$ 10, $J_{11b,10}$ 5.6, H-11b), 3.63 (1H, dd, $J_{3,4}$ 6.8, $J_{3,2}$ 2.9, H-3), 3.81 (1H, dd, $J$ 4.1, 2.6, H-8), 3.93 (1H, dd, $J_{2,3}$ 2.9, $J_{2,1}$ 0.9, H-2), 3.98–4.03 (3H, m, H-7, H-9, H-4), 4.19 (1H, dt, $J_{10,11a} \sim J_{10,11b} \sim 5.3$, $J_{10,9}$ 4.1, H-10), 4.45–4.60 (10H, m, 5 × O$CH_2$Ph), 4.88 (1H, s, H-1), 7.22–7.38 (25H, m, Ph); $\delta_C$ (100 MHz, $CDCl_3$): $\delta$ 29.39 ($CH_2$), 29.45 ($CH_2$), 54.6 ($OCH_3$), 70.3 (C-11), 71.7, 71.8 (O$CH_2$Ph), 72.0, 72.2, 73.3 (O$CH_2$Ph), 80.5 (C-4), 81.2 (C-10), 82.1 (C-9), 85.4 (C-7), 87.2 (C-3), 87.8 (C-8), 88.6 (C-2), 106.7 (C-1), 127.6–128.42 (Ph), 137.6, 137.8, 137.91, 137.94, 138.2 (Ph, q); *m/z* (ES) 762.4002 $[(M+NH_4)^+$; $C_{47}H_{56}NO_8$ requires 762.4000].