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Note

Cyclodextrins selectively modified on both rims using an *O*-3-debenzylative post-functionalisation, a consequence of the Sorrento meeting

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ABSTRACT

A de-O-benzylation reaction induced by I_2–Et_3SiH and developed by Iadonisi et al. on mono- and disaccharides was applied to per- or polybenzylated α-cyclodextrins to furnish compounds deprotected at position 3 of all sugar units. This methodology allows the straightforward post-functionalisation of the secondary rim of cyclodextrins already functionalised on their primary rim.

Regioselective access to a specific hydroxyl group is a central chemical challenge in carbohydrate research. Selective protection is a well-established strategy[1] with recent spectacular advances such as one pot access to any free hydroxyl group of a monosaccharide.[2] A reverse approach consists in regioselective deprotection of partially or fully protected sugars.[3] We have contributed to that field uncovering the ability of *iso*-butyl aluminium derivatives to regioselectively debenzylate perbenzylated sugars.[4] Understanding the mechanism of the reaction at the monosaccharide level and its extension to cyclodextrins (CDs)[5] allowed us to build-up on this reaction to introduce one,[5,6] two[7] or three[8] functionalities on the primary rim of CD in a completely regioselective manner. This new ability opened new possibilities in the field of biomaterials[9] and catalysis[10] as presented at the 16th Eurocarb. In addition, the Sorrento meeting[†] also drew our attention to recently published work by Iadonisi et al. dealing with selective debenzylations of poly-O-benzylated mono- and disaccharides using a combination of Et_3SiH and I_2.[11] One feature of this reaction is the absence of 6-O-debenzylation, preferentially leading to O-3 or O-4-debenzylated pyranosides, while the aluminium-based deprotections mainly produce O-2 and O-6-debenzylated products. More specifically, a perbenzylated maltose derivative undergoes a O-3-debenzylation using I_2–Et_3SiH. Returning from the congress, we logically wondered what would be the outcome of this reaction on polybenzylated CDs, expecting a similar regioselectivity.

Perbenzylated CD **1** was hence submitted to the action of Et_3SiH and I_2 (6.6 equiv) for 30 min from −60 to −35 °C and afforded compound **2** in a 58% yield (Scheme 1). Mass spectrometry (ESIMS) indicated the removal of six benzyl groups and ^1H NMR spectroscopy showed a single set of glucosidic signals characteristic of the C_6 symmetrical compound **2**. The cleavage of all benzyl groups at position 3 of the glucose units was further confirmed by COSY NMR experiment displaying cross peak between OH and H-3 (Fig. 1).

Hence, I_2–Et_3SiH gives an efficient access to positions 3 through deprotection of perbenzylated α-CD **1**. Usual access to these hydroxyl groups consists of selective protection of 2- and 6-OHs.[12] If compatible with already primary-rim-functionalised CDs, this methodology could constitute a new post-functionalisation approach in the challenging task of simultaneous and regioselective access to specific hydroxyl groups on both rims of the CD.[13] We therefore wondered if diol CD **3**[5] and monoalcohol CD **4**[8] both obtained through DIBAL-H deprotection of the perbenzylated CD **1** could undergo the deprotection reaction mediated by I_2–Et_3SiH. Similar conditions as those delineated for CD **1** applied on CDs **3** and **4** (6.6 equiv of I_2 and Et_3SiH for 30 min to 1 h at −60 to −35 °C) afforded compounds **5** and **6** in 41% and 46% yields, respectively. The structures of both CDs **5** and **6** were confirmed to be hexa-de-O-benzylated by mass spectrometry (Scheme 2).

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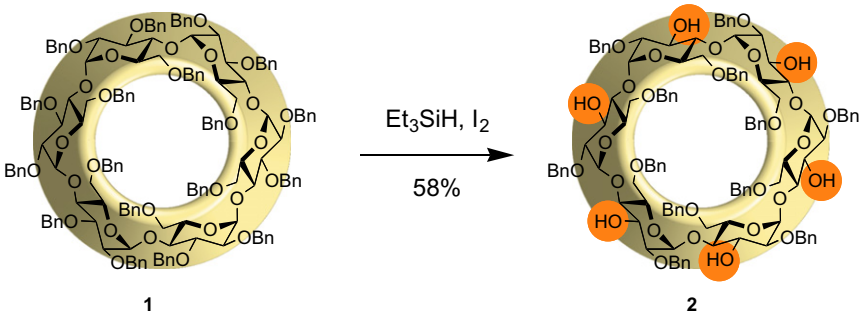


Scheme 1. Hexa-de-O-benzylation of perbenzylated CD **1**.

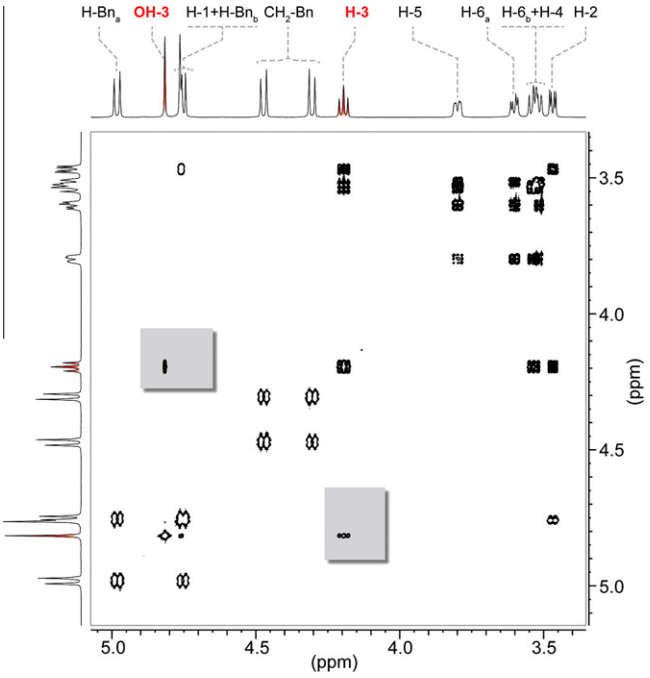


Figure 1. COSY NMR experiment (600 MHz, 300 K) of CD **2** in $CDCl_3$. The grey areas emphasise the cross-correlation between H-3 and OH.

^{1}H NMR spectra of compounds **5** and **6** displayed, respectively three and six sets of glucosidic signals accounting for their corresponding C_2 and C_1 symmetries (Fig. 2). A complete NMR study (COSY, HSQC, HMBC, TOCSY and NOESY) conducted on both **5** and **6** revealed chemical shifts in similar regions as observed for compound **2**. In particular, H-3s are located around 4.2 ppm and the OH-3s are partially overlapping with H-1s and some –CH_2Ph protons in the 4.70–4.85 ppm area (Fig. 2).

The COSY experiments show cross-correlation peaks (3 and 6 for **5** and **6**, respectively) between all H-3 and the OH, H-1 and the CH_2Ph region. By deduction, because in this region the OHs can only correlate with H-3s, we can conclude that the debenzylation reaction occurs on the position 3 of all glucose units, even in the case of already partially deprotected CDs (Fig. 3).

In conclusion, we have shown that the I_2/Et_3SiH O-debenzylation developed by Iadonisi et al.[11] on mono- and disaccharides could be efficiently applied to per- or polybenzylated α-CDs. Furthermore, this methodology allows the straightforward post-functionalisation at the secondary rim on CDs pre-functionalised at their primary rim.

1. Experimental part

1.1. General methods

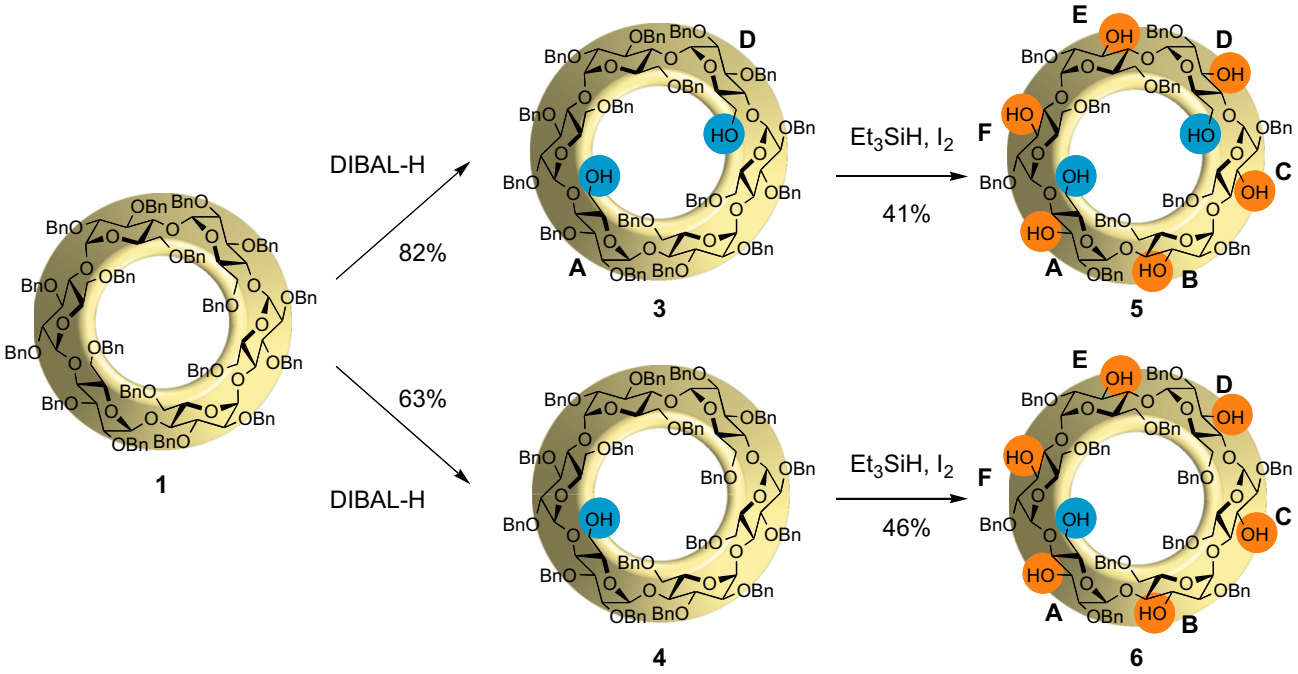
Dichloromethane was freshly distilled from P_2O_5. Iodine and triethylsilane were purchased from commercial sources and used without further purification. HRMS were recorded on a Bruker micrOTOF spectrometer, using Tuning-Mix as reference. Optical rotations were measured on a Perkin–Elmer 341 digital polarimeter with a path length of 1 dm. NMR spectra were recorded on a Bruker Avance II 600 MHz using residual $CHCl_3$ signal as internal reference ($\delta(^1H)$ = 7.26 ppm and $\delta(^{13}C)$ = 77.16 ppm) and concentrations of CD ca. 18 mM. Assignments were aided by COSY, HSQC, NOESY, TOCSY and HMBC experiments.

1.2. Typical procedure (adapted from the procedure by Iadonisi et al.)[11]

In a round-bottomed flask under nitrogen was charged 50 mg of the cyclodextrin derivative and iodine (6.6 equiv.). Then dichloromethane (18 mM I_2) was added and the mixture was stirred at room temperature until complete dissolution of the iodine. The purple solution was then cooled to −60 °C, triethylsilane (6.6 equiv) was added and the reaction was closely followed by TLC while keeping the temperature below −35 °C. Upon completion, the reaction was quenched by adding K_2CO_3 (ca. 50 mg) and the cooling bath was removed. The solution was then diluted with dichloromethane (5 mL) and washed with 5 mL of a 0.1 M solution of aq $Na_2S_2O_3$. The aqueous phase was extracted three times with dichloromethane (3 × 5 mL) and the combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by preparative TLC (cyclohexane–EtOAc 1:1 for the compounds **5** and **6**, 6:4 for **2**) to afford the corresponding O-3-debenzylated product.

1.3. 2$^{A–F}$, 6$^{A–F}$-Dodeca-*O*-benzyl-α-cyclodextrin (2)

23 mg (58%); $[\alpha]_D^{24}$ +27.8 (*c* 1, $CHCl_3$); R_f = 0.71 (cyclohexane–EtOAc 6:4); ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.42–7.39 (m, 12H, 12 × *Ph*^{ortho}-CH_2-O-2), 7.38–7.35 (m, 12H, 12 × *Ph*^{meta}-CH_2-O-2), 7.34–7.30 (m, 6H, 6 × *Ph*^{para}-CH_2-O-2), 7.24–7.20 (m, 18H, 12 × *Ph*^{meta}-CH_2-O-6, 6 × *Ph*^{para}-CH_2-O-6), 7.19–7.15 (m, 12H, 12 × *Ph*^{ortho}-O-6), 4.98 (d, $J_{Ph\text{-}CHH}$ = 12.1 Hz, 6H, 6 × Ph-C*H*$_2$-O-2), 4.82 (s, 6H, 6 × CH-3-O*H*), 4.78–4.73 (m, 12H, 6 × H-1, 6 × Ph-C*H*$_2$-O-2), 4.47 (d, $J_{Ph\text{-}CHH}$ = 12.0 Hz, 6H, 6 × Ph-C*H*$_2$-O-6), 4.30 (d, $J_{Ph\text{-}CHH}$ = 12.0 Hz, 6H, 6 × Ph-C*H*$_2$-O-6), 4.20 (t, $J_{2,3}$ = $J_{3,4}$ = 9.1 Hz, 6H, 6 × H-3), 3.82–3.77 (m, 6H, 6 × H-5), 3.60 (dd, 6H, $J_{6a\text{-}6b}$ = 10.8 Hz, $J_{5,6a}$ = 4.0 Hz, 6 × H-6a), 3.56–3.50 (m, 12H, 6 × H-4, 6 × H-6b), 3.47 (dd, $J_{2,3}$ = 9.7 Hz, $J_{1,2}$ = 3.4 Hz, 6H, 6 × H-2); ^{13}C NMR ($CDCl_3$, 151 MHz): δ 138.05 (6 × C-Ar^{ipso}-O-6), 137.78 (6 × C-Ar^{ipso}-O-2), 128.89 (12 × C-Ar^{ortho}-O-2), 128.59 (12 × C-Ar^{meta}-O-



Scheme 2. Hexa-de-O-benzylation of diol and monol CDs **3** and **4**.

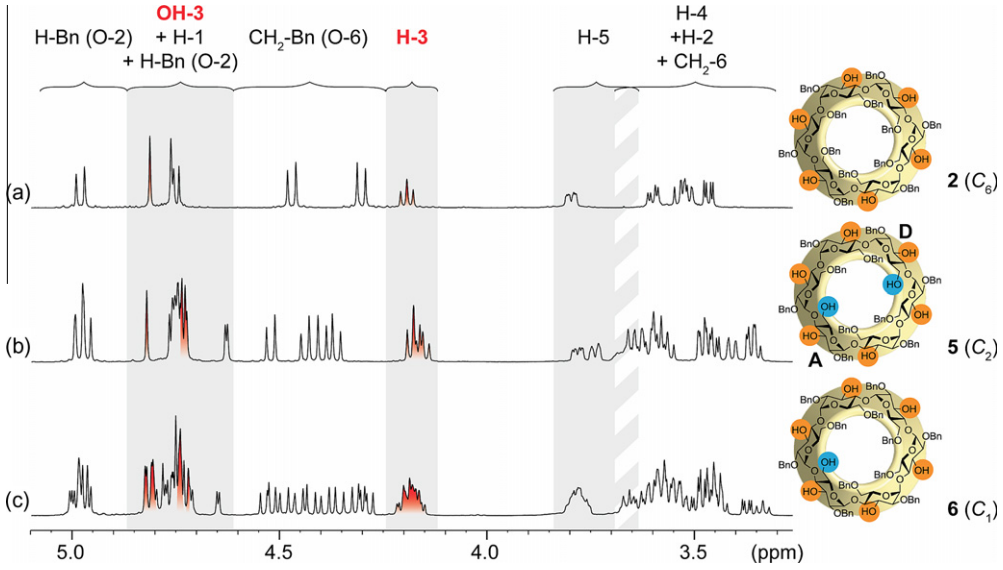


Figure 2. ^{1}H NMR spectra (600 MHz, 300 K) of CDs **2** (a), **5** (b) and **6** (c) in $CDCl_3$. Alternative grey and white zones indicate specific chemical shift regions for selected protons.

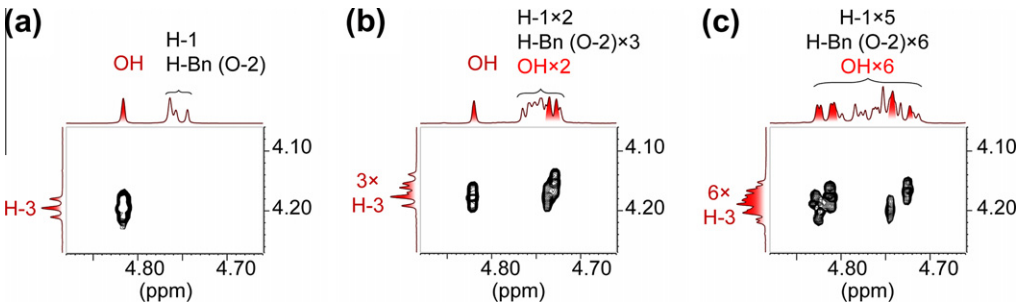


Figure 3. COSY NMR experiments (600 MHz, 300 K) of CD **2** (a), **5** (b) and **6** (c) in $CDCl_3$ displaying 1, 3 and 6 cross-correlations between H-3s and OHs, respectively.

2), 128.44 (12 × C-Ar^{meta}-O-6), 128.18 (6 × C-Ar^{para}-O-2), 127.95 (12 × C-Ar^{ortho}-O-6), 127.76 (6 × C-Ar^{para}-O-6), 101.77 (6 × C-1), 83.52 (6 × C-4), 78.01 (6 × C-2), 74.27 (6 × C-3), 73.94 (6 × Ph-*C*H$_2$-O-2), 73.62 (6 × Ph-*C*H$_2$-O-6), 70.46 (6 × C-5), 68.89 (6 × C-6). HRMS [$C_{120}H_{132}O_{30}$+Na]$^+$: calcd 2075.8696, found 2075.8756.

1.4. 2$^{A–F}$, 6^{B}, 6^{C}, 6^{E}, 6^{F}-Deca-*O*-benzyl-α-cyclodextrin (5)

16 mg (41%); $[\alpha]_D^{24}$ +31.4 (*c* 1, $CHCl_3$); R_f = 0.44 (cyclohexane–EtOAc 1:1); ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.46–7.17 (m, 50H, 50 × H-Ar), 5.00–4.94 (m, 6H, 6 × Ph-C*H*$_2$-O-2$^{A–F}$), 4.82 (s, 2H, 2 × CH-3^{C,F}-O*H*), 4.78–4.71 (m, 14H, 4 × H-1^{B,C,E,F}, 4 × CH-3^{A,B,D,E}-O*H*, 6 × Ph-C*H*$_2$-O$^{A–F}$-2), 4.63 (d, $J_{1,2}$ = 3.3 Hz, 2H, 2 × H-1^{A,D}), 4.52 (d, $J_{Ph\text{-}CHH}$ = 12.2 Hz, 2H, 2 × Ph-C*H*$_2$-O-6^{B,E}), 4.44 (d, $J_{Ph\text{-}CHH}$ = 11.7 Hz, 2H, 2 × Ph-C*H*$_2$-O-6^{C,F}), 4.40 (d, $J_{Ph\text{-}CHH}$ = 12.2 Hz, 2H, 2 × Ph-C*H*$_2$-O-6^{B,E}), 4.36 (d, $J_{Ph\text{-}CHH}$ = 11.7 Hz, 2H, 2 × Ph-C*H*$_2$-O-6^{C,F}), 4.18 (t, $J_{2,3}$ = $J_{3,4}$ = 9.0 Hz, 4H, 4 × H-3^{B,C,E,F}), 4.16 (t, $J_{2,3}$ = $J_{3,4}$ = 9.2 Hz, 2H, 2 × H-3^{A,D}), 3.80–3.76 (m, 2H, 2 × H-5^{C,F}), 3.76–3.72 (m, 2H, 2 × H-5^{B,E}), 3.70–3.54 (m, 14H, 2 × H-4^{B,E}, 2 × H-5^{A,D}, 8 × H-6^{A,C,D,F}, 2 × H-6^{B,E}), 3.50–3.43 (m, 6H, 4 × H-2^{B,C,E,F}, 2 × H-4^{C,F}), 3.41 (m, 2H, 2 × H-6^{B,E}), 3.38–3.33 (m, 4H, 2 × H-2^{A,D}, 2 × H-4^{A,D}), 1.50 (br s, 2H, 2 × CH$_2$-6^{A,D}-O*H*) ppm; ^{13}C NMR ($CDCl_3$, 151 MHz): δ 138.01, 137.94, 137.76, 137.75 (10 × C-Ar^{ipso}), 128.93, 128.89, 128.83, 128.61, 128.47, 128.45, 128.26, 128.20, 128.18, 127.95, 127.90, 127.80 (50 × C-Ar^{ortho,meta,para}), 101.82, 101.80 (4 × C-1^{B,C,E,F}), 101.34 (2 × C-1^{A,D}), 83.71, 83.68 (4 × C-4^{A,C,D,F}), 83.12 (2 × C-4^{B,E}), 78.10 (2 × C-2^{A,D}), 77.98 (2 × C-2^{B,E}), 77.71 (2 × C-2^{C,F}), 74.28, 74.24 (4 × C-3^{B,C,E,F}), 74.00, 73.95, 73.92 (2 × C-3^{A,D}, 6 × Ph-*C*H$_2$-O-2^{A-F}), 73.81 (2 × Ph-*C*H$_2$-O-6^{B,E}), 73.72 (2 × Ph-*C*H$_2$-O-6^{C,F}), 71.24 (2 × C-5^{A,D}), 70.61 (2 × C-5^{C,F}), 70.35 (2 × C-5^{B,E}), 69.24 (2 × C-6^{C,F}), 68.35 (2 × C-6^{B,E}), 61.93 (2 × C-6^{A,D}) ppm; HRMS [$C_{106}H_{120}O_{30}$+Na]$^+$: calcd 1895.7757, found 1895.7800.

1.5. 2$^{A–F}$, 6$^{B–F}$-Undeca-*O*-benzyl-α-cyclodextrin (6)

18 mg (46%); $[\alpha]_D^{24}$ +25.5 (*c* 1, $CHCl_3$); R_f = 0.63 (cyclohexane–EtOAc 1:1); ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.45–7.14 (m, 55H, 55 × H-Ar), 5.02–4.95 (m, 6H, 6 × Ph-C*H*$_2$-O-2$^{A–F}$), 4.84–4.70 (m, 17H, 5 × H-1$^{B–F}$, 6 × CH-3$^{A–F}$-O*H*, 6 × Ph-C*H*$_2$-O-2$^{A–F}$), 4.65 (d, $J_{1,2}$ = 3.4 Hz, 1H, H-1^{A}), 4.56–4.27 (m, 10H, 10 × Ph-C*H*$_2$-O-6$^{B–F}$), 4.23–4.14 (m, 6H, 6 × H-3$^{A–F}$), 3.82–3.74 (m, 5H, 5 × H-5$^{B–F}$), 3.69–3.42 (m, 23H, 5 × H-2$^{B–F}$, 5 × H-4$^{B–F}$, H-5^{A}, 12 × H-6$^{A–F}$), 3.38 (dd, $J_{2,3}$ = 9.7 Hz, $J_{1,2}$ = 3.3 Hz, 1H, H-2^{A}), 3.34 (t, $J_{3,4}$ = $J_{4,5}$ = 9.0 Hz, 1H, H-4^{A}), 1.50 (br s, 1H, CH$_2$-6^{A}-O*H*) ppm; ^{13}C NMR ($CDCl_3$, 151 MHz): δ 138.03, 137.96, 137.78, 137.75 (11 × C-Ar^{ipso}), 128.94, 128.90, 128.88, 128.87, 128.83, 128.62, 128.60, 128.48, 128.45, 128.44, 128.42, 128.40, 128.24, 128.23, 128.19, 128.18, 128.00, 127.97, 127.92, 127.80, 127.75 (55 x C-Ar^{ortho,meta,para}), 101.82, 101.79, 101.74, 101.73 (5 × C-1$^{B–F}$), 101.36 (C-1^{A}), 83.83 (C-4^{A}), 83.68, 83.51, 83.49, 83.39, 83.22 (5 × C-4$^{B–F}$), 78.11 (C-2^{A}), 77.99, 77.74 (5 × C-2$^{B–F}$), 74.28, 74.24, 73.99, 74.01, 73.94, 73.91, 73.73, 73.69, 73.64, 73.59 (6 × C-3$^{A–F}$, 6 × Ph-*C*H$_2$-O-2$^{A–F}$, 5 × Ph-CH$_2$-O-6$^{B–F}$), 71.29 (C-5^{A}), 70.67, 70.41, 70.37 (5 × C-5$^{B–F}$), 69.29, 68.82, 68.78, 68.42 (5 × C-6$^{B–F}$), 62.03 (C-6^{A}) ppm; HRMS [$C_{113}H_{126}O_{30}$+Na]$^+$: calcd 1985.8226, found 1985.8309.

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