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Note

The tris(4-*tert*-butylphenyl)methyl group: a bulky substituant for effective regioselective difunctionalisation of cyclomaltohexaose

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Abstract

Methodology based on the use of the "supertrityl" group ($= -C(p\text{-}Bu^t\text{-}C_6H_4)_3$) allows convenient difunctionalisation of cyclomaltohexaose. The **AD** regioisomer was obtained in an overall yield of 30%. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: α-Cyclodextrin; Cyclomaltohexaose functionalisation; Tris(4-*tert*-butylphenyl)methyl

The regioselective multifunctionalisation of the cyclomalto-oligosaccharides (cyclodextrins, CDs) has attracted much attention in recent years [1] owing to the fact that their ability to give inclusion complexes with a range of guest molecules in aqueous solution can be combined with many other useful properties such as catalysis [2,3] and molecular recognition [4,5]. Pure di- and trisubstituted regioisomers of α-CD have been produced from linear di- and trisaccharides using chemoenzymatic cyclisations [6–8]. Alternatively, by capping the primary hydroxyl face of the CDs with tailor-made disulfonated bridging molecules, Tabushi et al. [9,10] prepared all possible difunctionalised regioisomers of β-CD in a very selective manner. However, overall yields did not exceed 15%. Attempts to achieve the required selectivity with less synthetically demanding groups such as naphtylsulphonyl [11–13], tosyl [14,15], mesitylsulfonyl [16], azido [17], *tert*-butyldimethtylsilyl [18] and trityl [19] were made with only limited success except for the preparation of tri- and tetratritylated derivatives of α-CD which could be isolated in about 20% yield after flash chromatography [20,21].

In this communication, we show how the bulkiness of the easily accessible tris(4-*tert*-butylphenyl)methyl group [22] can be exploited to discriminate between primary hydroxyl groups and allows the preparation of gram-scale quantities of disubstituted α-CD derivatives from native α-CD. For simplification, we propose to name this bulky group "supertrityl".

Tris(4-*tert*-butylphenyl)methyl chloride (**1**) was obtained by reaction of methyl 4-*tert*-butylbenzoate

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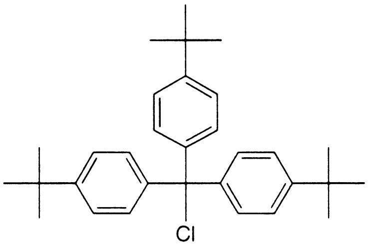
with the Grignard reagent derived from 4-bromo-*tert*-butylbenzene followed by chlorination of the resulting carbinol with acetylchloride according to a previously described procedure [22].



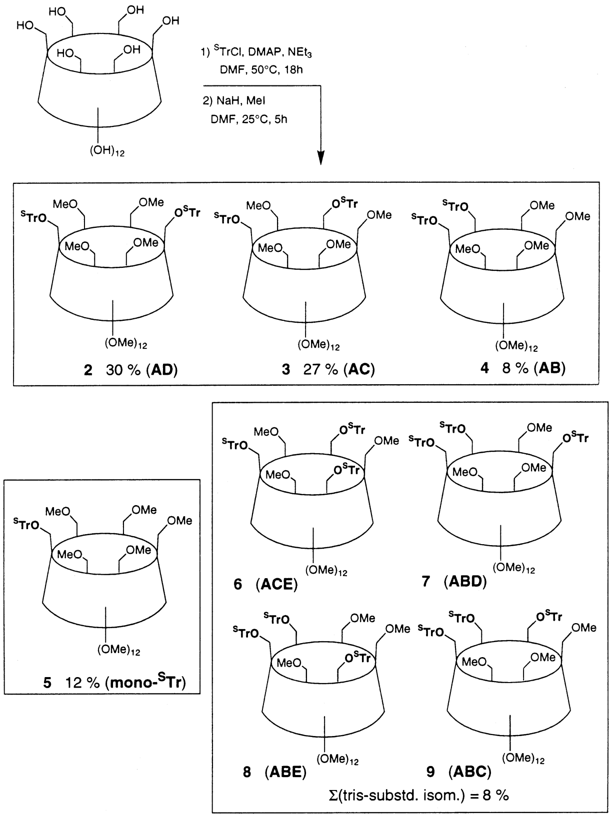
1 (^{S}TrCl)

Reaction of a solution of α-CD in *N*,*N*-dimethylformamide with the triarylmethyl chloride **1** (3 equiv) in the presence of 4-*N*,*N*-dimethylaminopyridine (DMAP) and Et_3N at 50 °C for 18 h [23] gave a mixture of polysubstituted species. The latter was treated in *N*,*N*-dimethylformamide with iodomethane after deprotonation of the remaining hydroxyl groups using sodium hydride (Scheme 1). This methylation facilitates product separation. Flash chromatography then afforded the **AD** isomer **2** (30%, R_f 0.43), the **AC** isomer **3** (27%, R_f 0.26), the **AB** isomer **4** (8%, R_f 0.12) as well as small amounts of trisubstituted (8%) and monosubstituted (12%) species.

Stoddart et al. [24] reported that 4-*tert*-butyltriphenylmethyl ethers undergo spontaneous cleavage, even in the absence of acids. Such instability was not observed in our case since all products are stable in the solid state as well as in solution. They can be submitted to chromatography over silica gel without noticeable hydrolysis occurring.

The ^{1}H NMR spectra (Fig. 1) reflect the symmetry of the difunctionalised CDs. For example, three signals are observed for the anomeric protons (H-1) in **2** in agreement with its expected C_2 symmetry. For asymmetrical **3** and **4**, the number of H-1 signals is doubled. Furthermore, whereas all H-1 protons in **2** and **3** as well as in monosubstituted **5** appear in the same relatively narrow chemical shift region ($\Delta\delta = 0.45$ ppm), this is not the case in **4** whose H-1 signals are much more widespread ($\Delta\delta = 1.3$ ppm). Considerable steric interaction between the tris(4-*tert*-butylphenyl)methyl groups in **4** is probably responsible for such a dramatic change.

In terms of availability, we believe that our method based on the use of "supertrityl" offers significant advantages over previous methodologies since gram-scale quantities of pure disubstituted α-CDs can be prepared without using HPLC purification procedures. The regioselectivity of such difunctionalisation could be further improved by using even larger groups such as dendrimers.



Scheme 1.

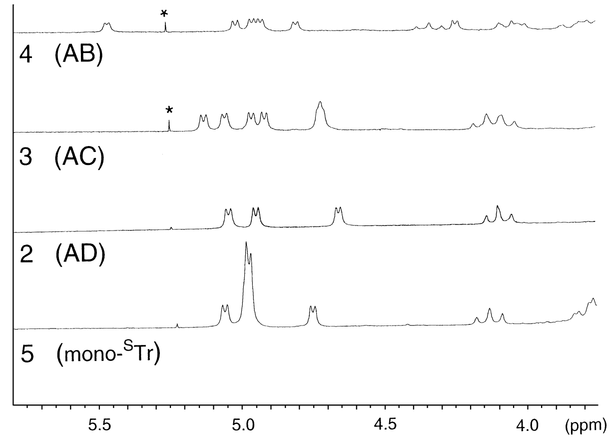


Fig. 1. Part of the ^{1}H NMR ($CDCl_3$) spectra (anomeric H region) of the disubstituted isomers **2**–**4** and the monosubstituted α-CD **5**. The asterisk indicates the presence of residual CH_2Cl_2.

1. Experimental

General methods.—Cyclomaltohexaose (α-CD, Wacker) was dried at 0.1 mmHg and 120 °C for 24 h. Solvents were dried by conventional methods and distilled just before use. $CDCl_3$ was passed down a 5 cm-thick alumina column and stored under nitrogen over molecular sieves (4 Å). ^{1}H and ^{13}C-{^{1}H} NMR spectra were recorded with an FT Bruker AC 200 instrument. ^{1}H NMR spectral data were referenced to residual protiated solvents (7.35 ppm for $CDCl_3$) and ^{13}C chemical shifts are reported relative to deuteriated solvents (77.0 ppm for $CDCl_3$). The mass spectra were recorded on a ZAB HF VG Analytical spectrometer using *m*-nitrobenzyl alcohol or tetraglyme (2,5,8,11,14-pentaoxapentadecane) as a matrix for FAB or a PerSeptive Biosystems Vestec spectrometer in positive linear mode at 5 kV acceleration voltage with 2,5-dihydroxybenzoic acid as matrix for MALDI-TOF. For column chromatography Geduran SI (E. Merck, 0.040–0.063 nm) was used. Routine thin-layer chromatography analysis were carried out on Silica Gel (Merck Kieselgel 60 GF_{254}) with detection by charring with H_2SO_4. Elemental analysis were performed by the Centre de Recherche Chimie, Strasbourg, analytical service.

Procedure for disubstitution.—To a solution of dry α-CD (7.000 g, 7.20 mmol) in anhydrous *N*,*N*-dimethylformamide (DMF) (175 mL) and triethylamine (7 mL) was added tris(*p*-*tert*-butylphenyl)methyl chloride (9.650 g, 21.60 mmol, 3 equiv) and 4-dimethylaminopyridine (DMAP) (0.400 g, 3.27 mmol). The solution was stirred overnight at 50 °C, then poured into water (600 mL), and the precipitate was collected by filtration over Celite. The Celite and precipitate mixture was dried under vacuum before being extracted several times with hot hexane to remove excess tris(*p*-*tert*-butylphenyl)methyl chloride. The residue was then extracted with dichloromethane and the filtrate evaporated to dryness. The resulting glassy solid was dried under high vacuum for 4 h at 110 °C to remove entrapped water. TLC (SiO_2, butanone/isopropanol/water 7:1:1) showed three spots, corresponding respectively to mixtures of tritritylated (R_f 0.62), ditritylated (R_f 0.55) and monotritylated species (R_f 0.40). To a solution of the crude product in dry *N*,*N*-dimethylformamide (200 mL) was added sodium hydride (10.5 g, 60% dispersion in oil). The mixture was stirred for 1 h, and then iodomethane (14 mL) was added dropwise so that the suspension temperature did not exceed 35 °C. Excess sodium hydride was destroyed by careful addition of methanol, water (600 mL) was subsequently added, and the mixture extracted several times with ether. The combined organic extract was washed with water and dried. Removal of the solvent in vacuo gave a glassy solid which was subjected to column chromatography (SiO_2, ethyl acetate/hexane, step gradient: 35:65→50:50→75:25→100/0), to give five fractions:

Fraction 1, mixture of $6^{A},6^{C},6^{E}$-tri-*O*-tris(*p*-*tert*-butylphenyl)methyl-$2^{A},2^{B},2^{C},2^{D},2^{E}, 2^{F},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F},6^{B},6^{D},6^{F}$-pentadeca-*O*-methyl-$\alpha$-cyclodextrin (**6**), $6^{A},6^{B},6^{D}$-tri-*O*-tris(*p*-*tert*-butylphenyl)methyl-$2^{A},2^{B},2^{C},2^{D},2^{E},2^{F},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F},6^{C},6^{E},6^{F}$-pentadeca-*O*-methyl-$\alpha$-cyclodextrin (**7**), $6^{A},6^{B},6^{E}$-tri-*O*-tris(*p*-*tert*-butylphenyl)methyl-$2^{A},2^{B},2^{C},2^{D},2^{E},2^{F},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F},6^{C},6^{D},6^{F}$-pentadeca-*O*-methyl-$\alpha$-cyclodextrin (**8**), $6^{A},6^{B},6^{C}$-tri-*O*-tris(*p*-*tert*-butylphenyl)methyl-$2^{A},2^{B},2^{C},2^{D},2^{E},2^{F},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F},6^{D},6^{E},6^{F}$-pentadeca-*O*-methyl-$\alpha$-cyclodextrin (**9**) (overall yield 1.5 g, 8%), R_f (hexane-EtOAc, 1: 1). MS (MALDI-TOF): *m*/*z*: 411 [tris(*p*-*tert*-butylphenyl)methyl$^+$], 2027 [M-tris(*p*-*tert*-butylphenyl)methyl + Na$^+$], 2044 [M-tris(*p*-*tert*-butylphenyl)methyl + K$^+$], 2438 [M + Na$^+$], 2454 [M + K$^+$].

Fraction 2, $6^{A},6^{D}$-di-*O*-tris(*p*-*tert*-butylphenyl)methyl-$2^{A},2^{B},2^{C},2^{D},2^{E},2^{F},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F},6^{B},6^{C},6^{E},6^{F}$-hexadeca-*O*-methyl-$\alpha$-cyclodextrin (**2**) (4.300 g, 30%). M.p. > 250 °C; ^{1}H NMR (200.1 MHz, $CDCl_3$, 25 °C): $\delta = 1.28$ (s, 18H, *tert*-butyl), 3.17 (s, 12H, 4×*O*-Me), 3.42 (s, 6H, 2×*O*-Me), 3.47 (s, 6H, 2×*O*-Me), 3.56 (s, 6H, 2×*O*-Me), 3.58 (s, 6H, 2×*O*-Me), 3.66 (s, 6H, 2×*O*-Me), 3.70 (s, 6H, 2×*O*-Me), 2.87–4.19 (m, 36H, H-2, H-3, H-4, H-5, H-6), 4.72 (d, 2H, ^3J(H-1,H-2) = 3.2 Hz, H-1), 4.99 (d, 2H, ^3J(H-1,H-2) = 3.2 Hz, H-1), 5.08 (d, 2H, ^3J(H-1,H-2) = 3.2 Hz, H-1), 7.23 (m, 12 H, AA′ part of AA′BB′ system of trityl), 7.33 (m, 12 H, BB′ part of AA′BB′ system of trityl); ^{13}C{^{1}H} NMR (50.3 MHz, $CDCl_3$, 25 °C): $\delta = 31.31$ (C(CH$_3$)$_3$), 34.24 (C(CH$_3$)$_3$), 57.36, 57.98, 58.09, 58.43, 58.87 (6-*O*-CH$_3$ and 2-*O*-CH$_3$), 61.40, 61.62, 61.88 (3-*O*-CH$_3$), 62.14 (C-$6^{A,D}$), 70.66, 70.71 (C-$5^{B,C,E,F}$), 71.07, 71.36 (C-$6^{B,C,E,F}$) 71.91 (C-$5^{A,D}$), 80.81, 80.99, 81.14, 81.32, 81.65, 82.06 [×2], 82.28 [×2] (C-2, C-3, C-4), 85.51 (O-C(Ph)$_3$), 97.31 (C-$1^{A,D}$), 100.07, 100.21 (C-$1^{B,C,E,F}$), 124.21, 128.20 (aromatic *C*H), 141.48, 148.98 (aromatic quaternary C); MS (MALDI-TOF): *m*/*z*: 411 [tris(*p*-*tert*-

butylphenyl)-methyl^{+}], 1219 [M-2×tris(*p-tert*-butylphenyl)-methyl + Na^{+}], 1235 [M-2×tris(*p-tert*-butylphenyl)-methyl + K^{+}], 1630 [M-tris(*p-tert*-butylphenyl)-methyl + Na^{+}], 1646 [M-tris(*p-tert*-butylphenyl)-methyl + K^{+}], 2041 [M + Na^{+}], 2057 [M + K^{+}]; $C_{114}H_{168}O_{30}$ (2018.6): calcd C 67.83, H 8.39; found: C, 67.84; H, 8.33.

Fraction 3, $6^{A},6^{C}$-di-*O*-tris(*p-tert*-butylphenyl)-methyl-$2^{A},2^{B},2^{C},2^{D},2^{E},2^{F},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F},6^{B},6^{D},6^{E},6^{F}$-hexadeca-*O*-methyl-*α*-cyclodextrin (**3**) (3.900 g, 27%). M.p. > 250 °C; ^{1}H NMR (200.1 MHz, $CDCl_3$, 25 °C): $\delta = 1.28$ (s, 9H, *tert*-butyl), 1.30 (s, 9H, *tert*-butyl), 3.07 (s, 3H, *O*-Me), 3.17 (s, 3H, *O*-Me), 3.25 (s, 3H, *O*-Me), 3.29 (s, 3H, *O*-Me), 3.43 (s, 3H, *O*-Me), 3.44 (s, 3H, *O*-Me), 3.45 (s, 3H, *O*-Me), 3.47 (s, 3H, *O*-Me), 3.56 (s, 3H, *O*-Me), 3.58 (s, 3H, *O*-Me), 3.60 (s, 3H, *O*-Me), 3.61 (s, 3H, *O*-Me), 3.62 (s, 3H, *O*-Me), 3.67 (s, 3H, *O*-Me), 3.70 (s, 3H, *O*-Me), 3.73 (s, 3H, *O*-Me), 2.86–4.24 (m, 36H, H-2, H-3, H-4, H-5, H-6), 4.79 (d, 1 H, ^{3}J(H-1,H-2) = 3.2 Hz, H-1), 4.80 (d, 1H, ^{3}J(H-1, H-2) = 3.2 Hz, H-1), 4.96 (d, 1H, ^{3}J(H-1, H-2) = 3.2 Hz, H-1), 5.00 (d, 2H, ^{3}J(H-1, H-2) = 3.2 Hz, H-1), 5.10 (d, 2H, ^{3}J(H-1, H-2) = 3.2 Hz, H-1), 5.17 (d, 2H, ^{3}J(H-1, H-2) = 3.2 Hz, H-1), 7.21–7.36 (m, 24 H, aromatic H): $^{13}C\{^{1}H\}$ NMR (50.3 MHz, $CDCl_3$, 25 °C): $\delta = 31.38$ [×2] ($C(CH_3)_3$), 34.32 [×2] ($C(CH_3)_3$), 57.36, 57.50, 57.82, 57.92, 57.99, 58.41, 58.55, 58.84 [×2], 59.04 (6-*O*-CH_3 and 2-*O*-CH_3), 61.17, 61.53, 61.72 [×2], 61.79, 61.89 (3-*O*-CH_3), 62.38, 62.80 (C-$6^{A,C}$), 70.05, 71.03 [×4], 71.20, 71.56 [×2], 71.72, 71.92 (C5, C-$6^{B,D,E,F}$), 80.41, 80.77, 81.90, 81.06 [×2], 81.29, 81.49, 81.58, 81.72 [×2], 81.94, 82.04, 82.21 [×2], 82.31 [×2], 82.47, 82.83 (C-2, C-3, C-4), 85.62 [×2] (O-*C*(Ph)$_3$), 97.22 [×2] (C-$1^{A,C}$), 99.99, 100.00, 100.14, 100.34 (C-$1^{B,C,E,F}$), 124.27, 128.50 [×2] (aromatic *C*H), 141.54, 141.74, 149.12 [×2] (aromatic quaternary C); MS (MALDI-TOF): *m*/*z*: 411 [tris(*p-tert*-butylphenyl)methyl^{+}], 1630 [M-tris(*p-tert*-butylphenyl)-methyl + Na^{+}], 1646 [M-tris(*p-tert*-butylphenyl)-methyl + K^{+}], 2041 [M + Na^{+}], 2057 [M + K^{+}]; $C_{114}H_{168}O_{30}\cdot CH_2Cl_2$ (2018.6 + 84.0): calcd C 65.67, H 8.15; found: C 65.15, H 8.22.

Fraction 4, $6^{A},6^{B}$-di-*O*-tris(*p-tert*-butylphenyl)-methyl-$2^{A},2^{B},2^{C},2^{D},2^{E},2^{F},3^{A},3^{B},3^{C},3^{D},3^{E},3^{F},6^{C},6^{D},6^{E},6^{F}$-hexadeca-*O*-methyl-*α*-cyclodextrin (**4**) (1.2 g, 8.2%). M.p. > 250 °C); ^{1}H NMR (200.1 MHz, $CDCl_3$, 25 °C: $\delta = 1.10$ (s, 9H, *tert*-butyl), 1.25 (s, 9H, *tert*-butyl), 3.08 (s, 3H, *O*-Me), 3.28 (s, 3H, *O*-Me), 3.30 (s, 3H, *O*-Me), 3.33 (s, 3H, *O*-Me), 3.43 (s, 6H, *O*-Me), 3.44 (s, 3H, *O*-Me), 3.45 (s, 3H, *O*-Me), 3.47 (s, 3H, *O*-Me), 3.55 (s, 3H, *O*-Me), 3.57 (s, 3H, *O*-Me), 3.59 (s, 3H, *O*-Me), 3.65 (s, 3H, *O*-Me), 3.69 (s, 6H, *O*-Me), 3.71 (s, 3H, *O*-Me), 2.78–4.42 (m, 36H, H-2, H-3, H-4, H-5, H-6), 4.28 (d, 1H, ^{3}J(H-1, H-2) = 3.2 Hz, H-1), 4.85 (d, 1H, ^{3}J(H-1, H-2) = 3.2 Hz, H-1), 4.97 (d, 1H, ^{3}J(H-1, H-2) = 3.2 Hz, H-1), 5.00 (d, 2H, ^{3}J(H-1, H-2) = 3.2 Hz, H-1), 5.05 (d, 2H, ^{3}J(H-1, H-2) = 3.2 Hz, H-1), 5.51 (d, 2H, ^{3}J(H-1, H-2) = 3.2 Hz, H-1), 7.09–7.25 (m, 12 H, aromatic H), 7.33–7.45 (m, 12 H, aromatic H); $^{13}C\{^{1}H\}$ NMR (50.3 MHz, $CDCl_3$, 25 °C): $\delta = 31.20$, 31.40 ($C(CH_3)_3$), 34.16 [×2] ($C(CH_3)_3$), 57.33, 57.40, 57.60, 58.05 [×2], 58.31, 58.64, 58.77, 58.90 [×2] (6-*O*-CH_3 and 2-*O*-CH_3), 61.23, 61.43, 61.69, 61.79 [×2], 61.89 (3-*O*-CH_3), 62.77, 63.20 (C-$6^{A,B}$), 70.77, 71.87, 70.93, 71.04, 71.07, 71.20, 72.90, 71.82, 72.54, 72.90 (C-5, C-$6^{C,D,E,F}$), 80.90 [×3], 81.11, 81.22 [×2], 81.36 [×2], 81.52, 81.85 [×3], 81.95 [×2], 82.03, 82.10, 82.18, 82.31 (C-2, C-3, C4), 85.49, 87.23 (O-*C*(Ph)$_3$), 97.65, 99.22, 99.42, 99.81 [×3] (C-1), 124.14, 124.47, 128.43, 128.66 (aromatic *C*H), 141.81, 142.23, 148.89, 149.02 (aromatic quaternary C); MS (MALDI-TOF): *m*/*z*: 411 [tris(*p-tert*-butylphenyl)methyl^{+}], 1630 [M-tris(*p-tert*-butylphenyl)methyl + Na^{+}], 1646 [M-tris(*p-tert*-butylphenyl)methyl + K^{+}], 2041 [M + Na^{+}], 2057 [M + K^{+}]; $C_{114}H_{168}O_{30}\cdot CH_2Cl_2$ (2018.6 + 84.0): calcd C 65.67, H 8.15; found: C 65.38, H 8.02.

Fraction 5, 6^{A}-*O*-tris(*p-tert*-butylphenyl)methyl-$2^{A},2^{B},2^{C},2^{D},2^{E},2^{F},3^{A},3^{B}3^{C},3^{D},3^{E},3^{F},6^{B},6^{C},6^{D},6^{E},6^{F}$-heptadeca-*O*-methyl-*α*-eyclodextrin (**5**) (1.1 g, 12.8%) M.p. > 250 °C; ^{1}H NMR (200.1 MHz, $CDCl_3$, 25 °C): $\delta = 1.26$ (s, 9H, *tert*-butyl), 3.17 (s, 3H, *O*-Me), 3.25 (s, 3H, *O*-Me), 3.34 (s, 3H, *O*-Me), 3.35 (s, 3H, *O*-Me), 3.36 (s, 6H, *O*-Me), 3.43 (s, 3H, *O*-Me), 3.47 (s, 9H, *O*-Me), 3.48 (s, 3H, *O*-Me), 3.57 (s, 3H, *O*-Me), 3.59 (s, 3H, *O*-Me), 3.62 (s, 6H, *O*-Me), 3.64 (s, 3H, *O*-Me), 3.66 (s, 3H, *O*-Me), 3.71 (s, 6H, *O*-Me), 2.89–4.21 (m, 36H, H-2, H-3, H-4, H-5, H-6), 4.79 (d, 1H, ^{3}J(H-1, H-2) = 3.2 Hz, H-1), 5.01 (d, 4H, ^{3}J(H-1, H-2) = 3.2 Hz, H-1), 5.10 (d, 1H, ^{3}J(H-1, H-2) = 3.2 Hz, H-1), 7.24 (m, 12 H, AA′ part of AA′BB′ system of trityl), 7.34 (m, 12 H, BB′part of AA′BB′ system of trityl); $^{13}C\{^{1}H\}$ NMR (50.3 MHz, $CDCl_3$, 25 °C): $\delta = 31.37$ ($C(CH_3)_3$), 34.29 [×2] ($C(CH_3)_3$), 57.49, 57.69, 57.76, 57.82, 58.22, 58.35 [×2], 58.94 [×3], 59.03 (6-*O*-CH_3 and 2-*O*-CH_3), 61.39, 61.63, 61.76 [×2], 61.82, 61.89 (3-*O*-CH_3), 62.35 (C-6^{A}), 71.03, 71.30, 71.39 [×2], 71.65 (C-$6^{B,C,D,E,F}$), 70.67, 70.94, 71.00, 71.13 [×2], 71.95 (C-5), 80.90, 81.16, 81.19

[×2], 81.26 [×2], 81.62, 81.78, 81.92. 82.01, 82.08, 82.15 [×2], 82.24 [×2], 82.47 [×2], 82.54 (C-2, C-3, C-4), 85.68 (O-*C*(Ph)$_3$), 97.38, 99.68, 99.81, 100.08 [×2], 100.50 (C-1), 124.26, 128.53 (aromatic *C*H), 141.58, 149.12 (aromatic quaternary C); MS (FAB): *m*/*z*: 411 [tris(*p*-*tert*-butylphenyl)methyl$^+$], 1234 [M-tris(*p*-*tert*-butylphenyl)methyl + Na$^+$], 1644 [M + Na$^+$]; $C_{84}H_{132}O_{30}$ (1622.0): calcd C 62.20, H 8.20; found: C 62.05, H 8.04.

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