Electronic Supplementary Information (ESI)

Regioselective opening of proximally sulfato-capped cyclodextrins

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General methods

All commercial reagents were used as supplied. All manipulations were performed in Schlenk-type flasks under N₂ with degassed solvent. Solvents were dried by conventional methods and distilled immediately prior to use. Column chromatography was performed on silica gel 60 (particle size 40-63 µm, 230-240 mesh). CDCl₃ was passed down a 5-cm-thick alumina column and stored under N₂ over molecular sieves (3 Å). Routine ¹H, ³¹P{¹H} and ¹³C{¹H} NMR spectra were recorded with Bruker FT instruments (AVANCE 300, 400, 500, 600 spectrometers). ¹H NMR spectral data were referenced to residual protiated solvents (δ = 7.26 ppm for CDCl₃), ¹³C chemical shifts are reported relative to deuterated solvents (δ = 77.00 ppm for CDCl₃), and the ³¹P NMR data are given relative to external H₃PO₄. Mass spectra were recorded with a Bruker MicroTOF spectrometer (ESI) using CH₂Cl₂, MeCN or MeOH as solvent. Elemental analyses were performed by the Service de Microanalyse, Institut de Chimie UMR 7177, Strasbourg. Melting points were determined with a Büchi 535 capillary melting point apparatus. High pressure liquid chromatography were performed on a Varian Prostar instrument (Prostar 230 solvent delivery module, Prostar 355 differential refractor and Prostar 335 UV detector with reverse-phase column Pursuit C18). 2²,²B,²C,²D,²E,²F,³A,³B,³C,³D,³E,³F,⁶C,⁶D,⁶E,⁶F-Hexadeca-O-methyl-α-cyclodextrin,¹ 2²,²B,²C,²D,²E,²F,²G,³A,³B,³C,³D,³E,³F,³G,⁶C,⁶D,⁶E,⁶F,⁶G-Nonadeca-O-methyl-β-cyclodextrin,² and 3³ were synthesized according to literature procedures. In this publication, the cyclodextrins are depicted as seen from the secondary face, the glucose units being ranged counterclockwise in the following order: A, B, C, D, E, F, G. When not indicated, the letter A refers to a glucose unit bearing a corresponds The numbering of the atoms within a glucose unit is as follows:

![Diagram of cyclodextrin structure]
Synthesis and characterisation

6^A,6^B-Dideoxy-6^A,6^B-sulfato-2^A,2^B,2^C,2^D,2^E,
2^F,3^A,3^B,3^C,3^D,3^E,6^C,6^D,6^E,6^F-hexadeca-O-methyl-
\alpha-cyclodextrin (1):

A solution of freshly distilled thionyl chloride (0.112 g, 69 \( \mu\)L, 0.94 mmol) in CH\(_2\)Cl\(_2\) (10 mL) was added dropwise to a solution of 2^A,2^B,2^C,2^D,2^E,3^A,3^B,3^C,3^D,3^E,6^C,6^D,6^E,6^F-hexadeca-O-methyl- 
\alpha-cyclodextrin (0.500 g, 0.42 mmol) and NEt\(_3\) (0.106 g, 145 \( \mu\)L, 1.05 mmol) in CH\(_2\)Cl\(_2\) (100 mL) at \(-78^\circ\)C. The reaction mixture was stirred for 1 h at \(-78^\circ\)C whereupon it was allowed to reach room temperature for an additional 1 h, quenched with saturated aqueous NaHCO\(_3\) (80 mL), and extracted with CHCl\(_3\) (3 \times 50 mL). The combined organic extracts were dried (MgSO\(_4\)) before being evaporated to dryness to afford a colourless residue, which was dissolved in a mixture of CH\(_2\)Cl\(_2\) (6 mL), MeCN (6 mL) and water (12 mL). Ruthenium trichloride (0.005 g, 30 \times 10^{-3} mmol) and sodium periodate (0.225 g, 1.05 mmol) were then added and the reaction mixture was stirred for 12 h at room temperature before adding saturated aqueous NaHCO\(_3\) (200 mL). Subsequent extraction with CHCl\(_3\) (3 \times 50 mL) was followed by drying of the organic extracts (MgSO\(_4\)). Removal of the solvent in vacuo gave a colourless residue, which was subjected to column chromatography (SiO\(_2\); CH\(_2\)Cl\(_2\)/MeOH, 97:3 to 95:5, v/v) to afford 1 (0.498 g, 96%) as a colourless solid. \( R_f \) (SiO\(_2\), CH\(_2\)Cl\(_2\)/MeOH, 90:10, v/v) = 0.63; m.p. 147°C; \(^1\)H NMR (400.1 MHz, CDCl\(_3\), 25°C): \( \delta \) (assignment by COSY) = 3.08 (t, 1 H, \( ^3J_{H4-H3} = ^3J_{H4-H2} = 9.3 \) Hz, H-4\(^A\) or B), 3.12–3.21 (6 H, H-2), 3.26 (t, 1 H, \( ^3J_{H4-H3} = ^3J_{H4-H5} = 9.5 \) Hz, H-4\(^B\) or A), 3.37 (s, 6 H, OMe), 3.38 (s, 3 H, OMe), 3.39 (s, 3 H, OMe), 3.47 (s, 6 H, OMe), 3.49 (s, 6 H, OMe), 3.50 (s, 3 H, OMe), 3.53 (s, 3 H, OMe), 3.61 (s, 3 H, OMe), 3.62 (s, 3 H, OMe), 3.63 (s, 3 H, OMe), 3.64 (s, 3 H, OMe), 3.65 (s, 3 H, OMe), 3.66 (s, 3 H, OMe), 3.45–3.67 (12 H, H-3, H-6), 3.72–3.85 (8 H, H-4, H-5, H-6a or H-6b), 3.89–3.96 (2 H, H-5, H-6a or H-6b), 4.11 (t, 1 H, \( ^2J_{H6a-H6b} = ^2J_{H6a-H5} = 11.3 \) Hz, H-6a\(^A\) or B), 4.15 (dd, 1 H, \( ^3J_{H5-H6b} = 3.5 \) Hz, \( ^3J_{H5-H4} = 9.5 \) Hz, H-5\(^B\) or A), 4.30 (d, 1 H, \( ^2J_{H6a-H6b} = 10.0 \) Hz, H-6a\(^B\) or A), 4.43 (ddd, 1 H, \( ^3J_{H5-H6a} = 11.3 \) Hz, \( ^3J_{H5-H4} = 8.2 \) Hz, \( ^3J_{H5-H6b} = 1.8 \) Hz , H-5\(^A\) or B), 4.90 (d, 1 H, \( ^3J_{H11-H2} = 2.7 \) Hz, H-1), 4.91 (dd, 1 H, \( ^2J_{H6b-H6a} = 10.0 \) Hz, \( ^3J_{H6b-H5} = 3.5 \) Hz, H-6b\(^B\) or A), 5.03 (d, 1 H, \( ^3J_{H11-H2} = 3.3 \) Hz, H-1), 5.06 (d, 1 H, \( ^3J_{H11-H2} = 3.4 \) Hz, H-1), 5.07–5.10 (3 H, H-1), 5.11 (dd, 1 H, \( ^2J_{H6b-H6a} = 11.3 \) Hz, \( ^3J_{H6b-H5} = 9.5 \) Hz, H-5\(^A\) or B)
1.8, H-6b\(^{A}\) or \(^{B}\)) ppm; 13C \(^{1}\)H NMR (100.6 MHz, CDCl\(_3\), 25°C): δ (assignment by HMQC) = 57.85, 58.05, 58.17, 58.28, 58.41, 58.60, 59.06, 59.15, 59.24, 59.32, 61.85, 61.92 [\(\times 2\)], 62.07, 62.14, 62.32 (OMe), 67.57, 70.07 (C-5), 70.44, 70.82 (C-6), 70.90, 71.25, 71.29 (C-5), 71.41 [\(\times 2\)], 71.86 (C-5), 73.94 (C-6\(^{A}\) or \(^{B}\)), 75.76 (C-6\(^{B}\) or \(^{A}\)), 81.44, 81.54, 81.63, 81.72 [\(\times 3\)], 81.81 [\(\times 2\)], 81.91, 81.96, 82.07 [\(\times 2\)], 82.28, 82.31, 82.35, 82.47 (C-2, C-3, C-4), 83.98 (C-4\(^{A}\) or \(^{B}\)), 86.63 (C-4\(^{B}\) or \(^{A}\)), 98.81, 99.89, 100.04, 100.09, 100.26, 101.12 (C-1) ppm; elemental analysis (%) calc'd for C\(_{52}\)H\(_{90}\)O\(_{32}\)S-C\(_{7}\)H\(_{8}\) (1281.50 + 92): C 52.43, H 7.31, found: C 52.25, H 7.53; MS (ESI-TOF): \(m/z\) (%): 1281.50 (100) [M + Na]+.

\(6^{A},6^{B}-\text{Dideoxy-}\(6^{A},6^{B}\)-sulfato-2\(^{A}\),2\(^{B}\),2\(^{C}\),2\(^{D}\),2\(^{E}\),2\(^{F}\),
2\(^{G}\),3\(^{A}\),3\(^{B}\),3\(^{C}\),3\(^{D}\),3\(^{E}\),3\(^{F}\),3\(^{G}\),6\(^{C}\),6\(^{D}\),6\(^{E}\),6\(^{F}\),6\(^{G}\)-nonadeca-O-
\text{methyl-}\(\beta\)-cyclodextrin (2):

This compound was prepared from

(0.530 g, 0.38 mmol) according to the above procedure (0.420 g, 76 %). \(R_{f}\) (SiO\(_2\), CH\(_{2}\)Cl\(_2\)/MeOH, 90:10, \(v/v\)) = 0.56; m.p.

150°C; \(^{1}\)H NMR (400.1 MHz, CDCl\(_3\), 25°C): δ (assignment by COSY) = 3.04–3.18 (8 H, H-2, H-4\(^{B}\) or \(^{A}\)), 3.30 (s, 3 H, OMe), 3.31 (s, 9 H, OMe), 3.31 (1 H, H-4\(^{A}\) or \(^{B}\)), 3.32 (s, 3 H, OMe), 3.41 (s, 3 H, OMe), 3.42 (s, 9 H, OMe), 3.43 (s, 3 H, OMe), 3.45 (s, 3 H, OMe), 3.49 (s, 3 H, OMe), 3.55 (s, 9 H, OMe), 3.56 (s, 3 H, OMe), 3.57 (s, 3 H, OMe), 3.58 (s, 3 H, OMe), 3.59 (s, 3 H, OMe), 3.59–3.68 (16 H, H-3, H-4, H-6), 3.69–3.80 (8 H, H-5, H-6), 3.81–3.87 (2 H, H-5, H-6), 3.90 (m, 1 H, H-5), 4.05 (ddd, 1 H, \(\text{J}_{\text{H5-H6a}} = 1.2 \text{ Hz}, \text{J}_{\text{H5-H6b}} = 3.5 \text{ Hz}, \text{J}_{\text{H5-H4}} = 9.8 \text{ Hz}, \text{H-5}^{A}\) or \(^{B}\)), 4.13 (ddd, 1 H, \(\text{J}_{\text{H6a-H6b}} = 10.5 \text{ Hz}, \text{J}_{\text{H6a-H5}} = 12.3 \text{ Hz}, \text{H-6}^{A}\) or \(^{B}\)), 4.28 (ddd, 1 H, \(\text{J}_{\text{H5-H6a}} = 12.3 \text{ Hz}, \text{J}_{\text{H5-H6b}} = 2.4 \text{ Hz}, \text{J}_{\text{H5-H4}} = 7.6 \text{ Hz}, \text{H-5}^{B}\) or \(^{A}\)), 4.33 (dd, 1 H, \(\text{J}_{\text{H6a-H6b}} = 10.0 \text{ Hz}, \text{J}_{\text{H6a-H5}} = 1.2 \text{ Hz}, \text{H-6}^{A}\) or \(^{B}\)), 4.60 (dd, 1 H, \(\text{J}_{\text{H6b-H6a}} = 10.0 \text{ Hz}, \text{J}_{\text{H6b-H5}} = 3.5 \text{ Hz}, \text{H-6}^{A}\) or \(^{B}\)), 4.82 (d, 1 H, \(\text{J}_{\text{H1-H2}} = 3.7 \text{ Hz}, \text{H-1}), 4.96 (dd, 1 H, \(\text{J}_{\text{H6b-H6a}} = 10.5 \text{ Hz}, \text{J}_{\text{H6b-H5}} = 2.4 \text{ Hz}, \text{H-6}^{B}\) or \(^{A}\)), 4.98 (d, 1 H, \(\text{J}_{\text{H1-H2}} = 3.6 \text{ Hz}, \text{H-1}), 5.02 (d, 1 H, \(\text{J}_{\text{H1-H2}} = 3.7 \text{ Hz}, \text{H-1}), 5.04 (d, 1 H, \(\text{J}_{\text{H1-H2}} = 3.6 \text{ Hz}, \text{H-1}), 5.05 (d, 1 H, \(\text{J}_{\text{H1-H2}} = 4.3 \text{ Hz}, \text{H-1}), 5.09 (d, 1 H, \(\text{J}_{\text{H1-H2}} = 3.9 \text{ Hz}, \text{H-1}), 5.19 (d, 1 H, \(\text{J}_{\text{H1-H2}} = 4.2 \text{ Hz}, \text{H-1}) \text{ ppm}; 13C \(^{1}\)H NMR (100.6 MHz, CDCl\(_3\), 25°C): δ (assignment by HMQC) = 57.97, 58.04, 58.17, 58.27, 58.56, 58.76, 58.81[\(\times 3\)], 58.87, 58.96, 59.02, 60.73, 61.13, 61.16, 61.34, 61.40, 61.52 [\(\times 2\)] (OMe), 68.06 (C-5\(^{B}\) or \(^{A}\)), 68.68 (C-5\(^{A}\) or \(^{B}\)), 70.23 (C-6), 70.31, 70.62, 70.70 (C-5), 70.85 (C-6), 70.88 (C-5), 71.00 [\(\times 2\)] (C-6),
71.26 (C-5), 71.30 (C-6), 73.93 (C-6\textsuperscript{B} or \textsuperscript{A}), 74.26 (C-6\textsuperscript{A} or \textsuperscript{B}), 77.96, 79.49, 80.01, 80.28, 80.80, 81.25, 81.30, 81.35 [\times2], 81.37 [\times2], 81.45, 81.55, 81.60, 81.69, 81.77, 81.80, 81.87, 82.06, 82.28, 82.48 (C-2, C-3, C-4), 98.22, 98.41, 98.46, 98.55, 98.63, 99.82, 100.39 (C-1) ppm; elemental analysis (%) calcd for C\textsubscript{61}H\textsubscript{166}O\textsubscript{37}S-CH\textsubscript{2}Cl\textsubscript{2} (1463.54 + 84.93): C 48.09, H 7.03, found: C 48.22, H 7.22; MS (ESI-TOF): m/z (%): 1485.60 (100) [M + Na]\textsuperscript{+}.

P-\{6\textsuperscript{A}-Deoxy-6\textsuperscript{A}-diphenylphosphinyl-2\textsuperscript{A},2\textsuperscript{B},2\textsuperscript{C},2\textsuperscript{D},2\textsuperscript{E},2\textsuperscript{F},3\textsuperscript{A},3\textsuperscript{B},3\textsuperscript{C},3\textsuperscript{D},3\textsuperscript{E},3\textsuperscript{F},6\textsuperscript{C},6\textsuperscript{D},6\textsuperscript{E},6\textsuperscript{F}-hexadeca-O-methyl-\alpha-cyclodextrin\} borane (5a):

\(n\)-BuLi (1.60 M in hexane, 1.20 mL, 1.94 mmol) was added dropwise at \(-78^\circ\text{C}\) to a stirred solution of diphenylphosphine (0.347 g, 485 \(\mu\text{L}\) of 20.3 wt/wt in hexane, 0.37 mmol) in THF (10 mL). After 30 min, the dark red diphenylphosphine solution was transferred via a cannula to a stirred solution of 1 (0.200 g, 0.16 mmol) in THF (10 mL) kept at \(-78^\circ\text{C}\). The solution was further stirred at \(-78^\circ\text{C}\) for 1 h before being allowed to reach 0 \(^\circ\text{C}\) over 1 h. BH\textsubscript{3}-THF (1.00 M in THF, 10 mL, 10 mmol) was then added dropwise at 0 \(^\circ\text{C}\), and the reaction mixture allowed to reach room temperature before being stirred for an additional 12 h. Once the solvent was removed in vacuo, the solid was taken in THF (8 mL) and H\textsubscript{2}SO\textsubscript{4} (0.20 mL, 50% wt/wt solution in water) was added. The reaction mixture was stirred for 1 h at room temperature before adding saturated aqueous NaHCO\textsubscript{3} (50 mL). Subsequent extraction with CHCl\textsubscript{3} (3 \times 50 mL) was followed by drying of the organic extracts (MgSO\textsubscript{4}). Removal of the solvent under vacuum gave a colourless residue, which was subjected to column chromatography (SiO\textsubscript{2}; CH\textsubscript{2}Cl\textsubscript{2}/MeOH, 97:3, v/v) to afford 5a (0.215 g, 97%) as a colourless solid. \(R_f\) (SiO\textsubscript{2}, CH\textsubscript{2}Cl\textsubscript{2}/MeOH, 90:10, v/v) = 0.43; Retention time (reverse-phase column Pursuit C18, isocratic elution with MeCN:H\textsubscript{2}O, 1:1, with a flow rate of 1mL.min\textsuperscript{-1}) = 10.79 min; m.p. 210–212°C; \(^1\text{H} \text{NMR} (400.1 \text{MHz, CDCl}_3, 25^\circ\text{C})\): \(\delta\) (assignment by combined COSY, TOCSY, HMQC, and ROESY) = 0.86 (br s, 3 H, P-BH\textsubscript{3}), 2.39 (d, 1 H, \(\text{J}_{H-6a,H-6b} = 11.8 \text{ Hz, H-6a}^\text{B}\)), 2.52 (dd, 1 H, \(\text{J}_{H-6a,H-6b} = 11.5 \text{ Hz, H-6a}^\text{A}\)), 2.68 (dd, 1 H, \(\text{J}_{H-6a,H-6b} = 11.5 \text{ Hz, H-6a}^\text{F}\)), 2.76 (s, 3 H, OMe-6\textsuperscript{A}), 2.82 (d, \(\text{J}_{H-6b,H-6a} = 11.4 \text{ Hz, H-6b}^\text{B}\)), 2.89 (m, 1 H, H-6b\textsuperscript{A}), 2.99 (dd, 1 H, \(\text{J}_{H-2,H-3} = 9.5 \text{ Hz, } \text{J}_{H-2,H-1} = 3.4 \text{ Hz, H-2}^\text{B}\)), 3.03 (dd, 1 H, \(\text{J}_{H-2,H-3} = 9.9 \text{ Hz, } \text{J}_{H-2,H-1} = 3.4 \text{ Hz, H-2}^\text{A}\)), 3.11 (dd, 1 H, \(\text{J}_{H-2,H-3} = 9.8 \text{ Hz, } \text{J}_{H-2,H-1} = 2.9 \text{ Hz, H-2}^\text{A}\)), 3.13 (dd, 1 H, \(\text{J}_{H-2,H-3} = 9.3 \text{ Hz, } \text{J}_{H-2,H-1} = 2.9 \text{ Hz, H-2}^\text{C}\)), 3.17 (dd, 1 H, \(\text{J}_{H-2,H-3} = 9.5 \text{ Hz, } \text{J}_{H-2,H-1} = 3.1 \text{ Hz, H-2}^\text{E}\)), 3.18 (dd, 1 H, \(\text{J}_{H-2,H-3} = 9.5 \text{ Hz, } \text{J}_{H-2,H-1} = 2.7 \text{ Hz, H-2}^\text{D}\)), 3.20 (dd, 1 H, \(\text{J}_{H-4,H-3} = \text{J}_{H-4,H-2}\)).
12.1 (br s) ppm; C (C 61.90, 61.93, 62.01 (OMe 57.70, 58.25, 58.26, 58.88, 59.14, 59.25 [x2] (OMe), 60.43 (C-6), 61.34, 61.52, 61.86, 61.90, 61.93, 62.01 (OMe), 68.02 (C-6), 68.68 (C-5), 69.79 (C-6b), 70.74 [x2] (C-5), 70.98 (C-6), 71.15 [x2] (C-5), 71.28, 71.34 (C-6), 72.00 (C-5), 79.85, 80.74, 80.82, 81.11, 81.23, 81.28, 81.35, 81.40, 81.56, 81.72, 81.82, 81.92, 82.08, 82.27, 82.37, 82.79, 82.82 (C-2, C-3, C-4), 87.75 (d, 3J_C,P = 41.3 Hz, C-4A), 97.16, 99.40, 100.14, 100.37, 100.46, 100.84 (C-1), 128.92 (d, 3J_C,P = 10.0, C_meta), 128.99 (d, 3J_C,P = 10.0, C_meta), 130.51 (d, 1J_C,P = 53.4 , C_ipso), 131.27 (d, 2J_C,P = 8.3 Hz, C_ortho), 131.29 (s, C_para), 131.41 (s, C_para), 131.69 (d, 2J_C,P = 9.9 Hz, C_ortho), 132.24 (d, 1J_C,P = 56.7 , C_ipso) ppm; 31P{1H} NMR (121.5 MHz, CDCl3, 25°C): δ = 12.1 (br s) ppm; elemental analysis (%) calcd for C_6H_10_4BO_2P-2MeOH (1401.63 + 64): C 54.62, H 8.11, found: C 54.92, H 7.83; MS (ESI-TOF): m/z (%): 1401.63 (100) [M+Na]^+. 
5.03 (d, 1 H, \(J = 2.5\) Hz, H\(_{6b}\)), 3.64 (m, 1 H, H\(_{3}\)). 3.59 (s, 3 H, OMe), 3.60 (s, 3 H, OMe), 3.61 (s, 3 H, OMe), 3.61 (m, 1 H, H\(_{3}\)).

The organic extracts (MgSO\(_4\)) was subjected to column chromatography (SiO\(_2\); CH\(_2\)Cl\(_2\)/MeOH, 97:3, v/v) to afford 2 colourless solids, 5b (0.180 g, 87%) and 6b (0.006 g, 5%).

5b \(R_f\) (SiO\(_2\), CH\(_2\)Cl\(_2\)/MeOH, 90:10, v/v) = 0.58; m.p. 228–230°C; \(^1\)H NMR (400.1 MHz, CDCl\(_3\), 25°C): \(\delta\) (assignment by combined COSY, TOCSY, HMQC, and ROESY) = 2.24 (br s, 1 H, OH), 2.70 (dd, 1 H, \(J_{H_6aH_6b} = 10.3\) Hz, \(J_{H-6aH-5} = 1.5\) Hz, H-6a), 2.99 (s, 3 H, OMe), 3.06 (dd, 1 H, \(J_{H-2H-3} = 9.8\) Hz, \(J_{H-2,H-1} = 3.5\) Hz, H-2), 3.16 (m, 1 H, H-2\(^\alpha\)), 3.17 (m, 1 H, H-2\(^\beta\)), 3.18 (s, 3 H, OMe), 3.12–3.21 (3 H, H-2), 3.31 (t, 1 H, \(J_{H-H-4,H-3} = J_{H-4,H-5} = 9.3\) Hz, H-4\(^\alpha\)), 3.37 (s, 3 H, OMe), 3.34–3.38 (m, 1 H, H-5), 3.43 (s, 3 H, OMe), 3.44 (s, 3 H, OMe), 3.46 (s, 3 H, OMe), 3.47 (s, 3 H, OMe), 3.48 (s, 3 H, OMe), 3.49 (s, 3 H, OMe), 3.51 (s, 3 H, OMe), 3.52 (m, 1 H, H-3\(^\beta\)), 3.59 (s, 3 H, OMe), 3.60 (s, 3 H, OMe), 3.61 (s, 3 H, OMe), 3.61 (m, 1 H, H-4\(^\beta\)), 3.62 (s, 3 H, OMe), 3.64 (m, 1 H, H-3\(^\beta\)), 3.65 (s, 3 H, OMe), 3.67 (s, 3 H, OMe), 3.67–3.70 (12 H, H-4, H-6), 3.73–3.76 (m, 1 H, H-5), 3.79–3.86 (2 H, H-6a), 3.86–3.91 (2 H, H-6a or H-6b, H-6a\(^\beta\)), 3.92–4.03 (4 H, H-5, H-6a\(^\alpha\), H-6b\(^\beta\)), 4.12 (ddd, 1 H, \(J_{H-5,H-6a} = J_{H-5,H-4} = 9.0\) Hz, \(J_{H-5,H-6b} = 2.6\) Hz, H-5\(^\alpha\)), 4.15–4.19 (m, 1 H, H-6b\(^\beta\)), 4.34 (dd, 1 H, \(J_{H-6b,H-6a} = 14.2\) Hz, \(J_{H-6b,H-5} = 2.5\) Hz, H-6b\(^\alpha\)), 4.91 (d, 1 H, \(J_{H-H-2} = 2.8\) Hz, H-1\(^\alpha\)), 4.95 (d, 1 H, \(J_{H-H-2} = 3.1\) Hz, H-1), 5.03 (d, 1 H, \(J_{H-H-2} = 3.1\) Hz, H-1), 5.07 (d, 1 H, \(J_{H-H-2} = 3.1\) Hz, H-1), 5.09 (d, 1 H, \(J_{H-H-2} = 3.1\) Hz, H-1).

Powdered potassium phthalimide (0.135 g, 0.64 mmol) was added to a stirred solution of 1 at 0°C (0.200 g, 0.16 mmol) in DMF (0.80 mL). After 1 h, the reaction mixture was allowed to reach room temperature and then kept at this temperature for 12 h under stirring. It was then evaporated to dryness and the residue was retaken in THF (8 mL). H\(_2\)SO\(_4\) (0.20 mL, 50% wt/wt solution in water) was added and the reaction mixture was stirred for 1 h at room temperature before adding saturated aqueous NaHCO\(_3\) (50 mL). Subsequent extraction with CHCl\(_3\) (3 \times 50 mL) was followed by drying of the organic extracts (MgSO\(_4\)). Removal of the solvent in vacuo gave a colourless residue, which was subjected to column chromatography (SiO\(_2\); CH\(_2\)Cl\(_2\)/MeOH, 97:3, v/v) to afford 2 colourless solids, 5b (0.180 g, 87%) and 6b (0.006 g, 5%).
= 3.4 Hz, H-1), 5.18 (d, 1 H, \( ^3J_{H1-H2} = 3.3 \) Hz, H-1\(^B\)), 7.73–7.75 (2 H, m-H), 7.81–7.83 (2 H, o-H) ppm; \(^{13}\)C{\(^1\)H} NMR (100.6 MHz, CDCl\(_3\), 25°C): \( \delta \) (assignment by HMQC) = 39.78 (C-6\(^A\)), 57.83 [\( \times 3\)], 58.02 [\( \times 2\)], 58.13, 58.65, 58.96, 59.00, 59.14, 61.65, 61.80 [\( \times 3\)], 61.88, 61.98 (OMe), 62.14 (C-6\(^B\)), 69.44 (C-5), 69.68 (C-6), 70.92 (C-6), 70.94 (C-5), 70.98 (C-6), 71.23, 71.27, 71.34 (C-5), 71.66 (C-6), 72.25 (C-5), 80.92, 81.06, 81.17, 81.29, 81.30, 81.47, 81.60, 81.78, 81.87, 81.97, 82.19 [\( \times 2\)], 82.23 [\( \times 3\)], 82.37, 82.60, 85.43 (C-2, C-3, C-4), 99.15, 99.83, 99.88, 100.06, 100.11, 100.47 (C-1), 123.11 (C\(_{meta}\)), 132.17 (C\(_{ipso}\)), 134.06 (C\(_{ortho}\)), 168.08 (CO) ppm; elemental analysis (%) calcd for C\(_{60}\)H\(_{95}\)NO\(_{31}\)·CH\(_2\)Cl\(_2\) (1326.38 + 84.93): C 51.91, H 6.93, N 0.99, found: C 51.83, H 6.92, N 0.98; MS (ESI-TOF): \( m/z \) (%): 1348.58 (100) [\( M+Na\)]\(^+\).

**Electronic Supplementary Material (ESI) for Chemical Communications**

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Powdered sodium azide (0.042 g, 0.64 mmol) was added to a stirred solution of 1 (0.200 g, 0.16 mmol) in DMF (0.80 mL) at 0°C. The same procedure as that used for 5b/6b was then applied. The crude product consisted in an inseparable mixture of regioisomers 5c and 6c (0.180 g, 94 %). $R_f$ (SiO$_2$, CH$_2$Cl$_2$/MeOH, 90:10, v/v) = 0.70; Retention time (reverse-phase column Pursuit C18, isocratic elution with MeCN:H$_2$O, 1:1, with a flow rate of 1mL.min$^{-1}$) = 17.49 and 18.16 min; elemental analysis (%) calcd for C$_{52}$H$_{91}$N$_3$O$_{29}$·H$_2$O (1221.5 + 18.02): C 50.36, H 7.56, N 3.39, found: C 50.33, H 7.50, N 3.18; MS (ESI-TOF): $m/z$ (%): 1244.55 (100) [M + Na]$^+$. 

Powdered potassium thioacetate (0.073 g, 0.64 mmol) was added to a stirred solution of 1 (0.200 g, 0.16 mmol) in DMF (0.80 mL) at 0°C. The same procedure as that for 5b/6b was then applied. The crude product consisted in an inseparable mixture of regioisomers 5d and 6d (0.180 g, 91 %). $R_f$ (SiO$_2$, CH$_2$Cl$_2$/MeOH, 90:10, v/v) = 0.55; Retention time
(reverse-phase column Pursuit C18, elution with MeCN:H₂O 1:1 over 40 min with a flow rate of 1 mL min⁻¹) = 14.82 and 16.32 min; Selected ¹H NMR signals (400.1 MHz, CDCl₃, 25°C): δ = 2.30 (s, 0.87 H, CH₃(C(O)S) and 2.33 (s, 3 H, CH₃(C(O)S) ppm; elemental analysis (%) calcd for C₅₄Hₙ₄Oₙ₄S·0.5H₂O (1255.37 + 9.01): C 51.30, H 7.57, found: C 51.37, H 7.69; MS (ESI-TOF): m/z (%): 1277.54 (100) [M + Na]⁺.

P-{⁶ᴬ-Deoxy-⁶ᴮ-diphenylphosphinyl-²ᴬ,²ᴮ,²ᵀ,²ᴰ,²ᴱ,²ᴳ,³ᴬ,³ᴮ,³ᵀ,³ᴰ,³ᴱ,³ᴳ,⁶ᴰ,⁶ᴱ,⁶ᴳ- nonadeca-⁶⁻methyβ-cyclodextrin} borane (⁵ᵉ) and P-{⁶ᴮ-deoxy-⁶ᴮ-diphenylphosphinyl-²ᴬ,²ᴮ,²ᵀ,²ᴰ,²ᴱ,²ᴳ,³ᴬ,³ᴮ,³ᵀ,³ᴰ,³ᴱ,³ᴳ,⁶ᴰ,⁶ᴱ,⁶ᴳ- nonadeca-⁶⁻methyβ-cyclodextrin} borane (⁶ᵉ):

⁵ᵉ and ⁶ᵉ were prepared from 2 (0.200 g, 0.14 mmol) according to the procedure used for the synthesis of ⁵ᵃ. The crude product consisted in an inseparable mixture of regioisomers ⁵ᵉ and ⁶ᵉ (0.204 g, 96 %). Rᵣ (SiO₂, CH₂Cl₂/MeOH, 90:10, v/v) = 0.51; Selected ³¹P{¹H} NMR signals (121.5 MHz, CDCl₃, 25°C): δ = 13.43 and 14.25 ppm; elemental analysis (%) calcd for C₇₃H₁₂₀B₉O₃₄P·2CH₂Cl₂ (1583.50 + 169.87): C 51.38, H 7.13, found: C 51.45, H 7.10; MS (ESI-TOF): m/z (%): 1605.74 (100) [M + Na]⁺.
6^A-Deoxy-6^A-(1,3-dioxoisindolin-2-yl)-2^A,2^B,2^C,2^D,2^E,2^F,2^G,3^A,3^B,3^C,3^D,3^E,3^F,3^G,
6^C,6^B,6^E,6^F,6^C-nonadeca-O-methyl-β-cyclodextrin (5f) and 6^B-deoxy-6^B-(1,3-dioxoisindolin-2-yl)-
2^A,2^B,2^C,2^D,2^E,2^F,2^G,3^A,3^B,3^C,3^D,3^E,3^F,3^G,6^C,6^D,6^E, 
6^F,6^G-nonadeca-O-methyl-β-cyclodextrin (6f):
5f and 6f were prepared from 2 (0.200 g, 0.14 mmol) according to the procedure used for the synthesis of 5b. The crude product consisted in an inseparable mixture of regioisomers 5f and 6f (0.160 g, 76 %). R_f (SiO_2, CH_2Cl_2/MeOH, 90:10, v/v) = 0.46; elemental analysis (%) calcd for C_{69}H_{111}NO_{36}·CH_3C(O)OC_2H_5 (1530.60 + 88.11): C 54.17, H 7.41, N 0.87 found: C 54.23, H 7.39, N 0.89; MS (ESI-TOF): m/z (%): 1552.68 (100) [M + Na]^+.

P,P’-{6^A,6^D-Dideoxy-6^A,6^D-di(diphenylphosphinyl)-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-tetradeca-O-methyl-α-cyclodextrin} diborane (7a):

n-BuLi (1.60 M in hexane, 1.83 mL, 2.87 mmol) was added dropwise at −78°C to a stirred solution of diphenylphosphine (0.520 g, 725 µL of a 20.3% wt/wt solution in hexane, 0.57 mmol) in THF (10 mL). After 30 min, the dark red diphenylphosphide solution was transferred via a cannula to a stirred solution of 3 (0.200 g, 0.16 mmol) in THF (10 mL) kept at −78°C. The solution was further stirred at −78°C for 1 h before being allowed to reach 0°C over 1 h. BH_3·THF (1.00 M in THF, 10 mL, 10 mmol) was then added dropwise at 0°C, and the reaction mixture allowed to reach room temperature before being stirred for an additional 12 h. Once the solvent was removed in vacuo, the solid was taken in THF (8 mL) and H_2SO_4 (0.20 mL, 50% wt/wt solution in water) was added. The reaction mixture was stirred for 1 h at room temperature
before adding saturated aqueous NaHCO$_3$ (50 mL). Subsequent extraction with CHCl$_3$ (3 × 50 mL) was followed by drying of the organic extracts (MgSO$_4$). Removal of the solvent in vacuo gave a colourless residue, which was subjected to column chromatography (SiO$_2$; CH$_2$Cl$_2$/MeOH, 97:3, v/v) to afford 7a (0.140 g, 59%) as a colourless solid. $R_t$ (SiO$_2$, CH$_2$Cl$_2$/MeOH, 92:8, v/v) = 0.38; Retention time (reverse-phase column Pursuit C18, isocratic elution with MeCN:H$_2$O, 1:1, with a flow rate of 1mL.min$^{-1}$) = 18.27 min; m.p. 142-145 °C.; $^1$H NMR (300.1 MHz, CDCl$_3$, 25°C): $\delta$ (assignment by COSY) = 1.10 (br s, 6 H, P-BH$_3$), 2.77 (s, 6 H, OMe-6), 2.85 (d, 2 H, $^2$J$_{H-6a,H-6b}$ = 11.2 Hz, H-6a$_{C,F}$), 3.02 (d, 4 H, $^2$J$_{H-6a,H-6b}$ = 11.9 Hz, H-6b$_{C,F}$), 3.46 (s, 6 H, OMe), 3.47 (s, 6 H, OMe), 3.49 (s, 6 H, OMe), 3.59 (s, 6 H, OMe), 3.64 (s, 6 H, OMe), 3.69 (s, 6 H, OMe), 3.43–3.85 (18 H, H-3, H-4, H-5$_{B,C,E,F}$, OH), 4.39 (m, 2 H, H-5$_{A,D}$), 4.67 (d, 2 H, $^3$J$_{H-1,H-2}$ = 2.8 Hz, H-1$_{A,D}$), 5.01 (d, 2 H, $^3$J$_{H-1,H-2}$ = 3.1 Hz, H-1$_{C,F}$), 5.17 (d, 2 H, $^3$J$_{H-1,H-2}$ = 2.9 Hz, H-1$_{B,E}$), 7.36–7.50 (12 H, m-H, p-H), 7.73–7.86 (8 H, o-H) ppm; $^{13}$C\{$^1$H} NMR (75.5 MHz, CDCl$_3$, 25°C): $\delta$ (assignment by HMQC) = 26.91 (d, $^1$J$_{C,P}$ = 37 Hz, C-6$_{A,D}$), 58.09 [×2], 58.76, 61.29, 63.81, 61.47, 61.76 (OMe), 61.29 (C-6$_{B,E}$), 69.23, 71.12, 71.49 (C-5), 69.93 (C-6$_{C,F}$), 79.63, 80.76, 80.84, 81.15, 81.28, 81.41, 82.03, 82.55 (C-2, C-3, C-4), 86.26 (d, $^1$J$_{C,P}$ = 5.7 Hz, C-4$_{A,D}$), 97.60, 100.00, 100.23 (C-1), 128.66 (d, $^3$J$_{C,P}$ = 10.5, C$_{meta}$), 128.80 (d, $^3$J$_{C,P}$ = 10.5, C$_{meta}$), 130.04 (s, C$_{para}$), 131.03 (s, C$_{para}$), 130.83 (d, $^1$J$_{C,P}$ = 16.0 Hz, C$_{ipso}$), 131.32 (d, $^1$J$_{C,P}$ = 21.0 Hz, C$_{ipso}$), 131.78 (d, $^2$J$_{C,P}$ = 9.0 Hz, C$_{ortho}$), 131.87 (d, $^2$J$_{C,P}$ = 9.0 Hz, C$_{ortho}$) ppm; $^{31}$P\{$^1$H} NMR (121.5 MHz, CDCl$_3$, 25°C): $\delta$ = 12.5 (br s) ppm; elemental analysis (%) calcd for C$_{74}$H$_{112}$B$_2$O$_{28}$P$_2$·0.5MeOH (1532.70 + 16): C 57.76, H 7.42, found: C 57.97, H 7.36; MS (ESI-TOF): m/z (%): 1555.70 (100) [M + Na]$^+$. 

Electronic Supplementary Material (ESI) for Chemical Communications
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6^A,6^D-Dideoxy-6^A,6^D-di(1,3-dioxoisindolin-2-yl)-2^A,2^B,2^C,2^D,2^E,3^F,3^A,3^B,3^C,3^D,3^E,3^F,6^A,6^B,6^D-tetradeca-\textit{O}-methyl-\alpha\textit{-cyclodextrin} (7b) and

6^A,6^E-dideoxy-6^A,6^E-di(1,3-dioxoisindolin-2-yl)-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^A,6^B,6^E-tetradeca-\textit{O}-methyl-\alpha\textit{-cyclodextrin} (8b):

Powdered potassium phthalimide (0.230 g, 1.24 mmol) was added to a stirred solution of 3 at 0°C (0.200 g, 0.16 mmol) in DMF (1.60 mL). The reaction mixture was allowed to reach room temperature in an ice bath for 12 h under stirring. It was then evaporated to dryness and the residue was retaken in THF (8 mL). H$_2$SO$_4$ (0.20 mL, 50% wt/wt solution in water) was added and the reaction mixture was stirred for 1 h at room temperature before adding saturated aqueous NaHCO$_3$ (50 mL). Subsequent extraction with CHCl$_3$ (3 × 50 mL) was followed by drying of the organic extracts (MgSO$_4$). Removal of the solvent in vacuo gave a colourless residue, which was subjected to column chromatography (SiO$_2$; CH$_2$Cl$_2$/MeOH, 97:3, v/v) to afford 2 colourless solids, 7b (0.110 g, 50%) and 8b (0.071 g, 28%). 7b $R_f$ (SiO$_2$, CH$_2$Cl$_2$/MeOH, 90:10, v/v) = 0.50; m.p. 164°C; $^1$H NMR (400.1 MHz, CDCl$_3$, 25°C): $\delta$ (assignment by combined COSY, TOCSY, HMOC, and ROESY) = 2.71 (d, 2 H, $^2$H$_{6a,H-6b}$ = 11.1 Hz, H-6a$^{CF}$), 2.72 (s, 3 H, OMe-6$^{CF}$), 3.08 (dd, 2 H, $^3$J$_{H-2,H-3}$ = 9.7 Hz, $^3$J$_{H-2,H-1}$ = 3.8 Hz, H-2$^{CF}$), 3.20 (dd, 2 H, $^3$J$_{H-2,H-3}$ = 9.9 Hz, $^3$J$_{H-2,H-1}$ = 2.7 Hz, H-2$^{AD}$), 3.23 (dd, 2 H, $^3$J$_{H-2,H-3}$ = 5.1, $^3$J$_{H-2,H-1}$ = 3.3 Hz, H-2$^{BE}$), 3.25 (t, 2 H, $^3$J$_{H-4,H-3}$ = 10.1 Hz, H-4$^{BE}$), 3.35 (t, 2 H, $^3$J$_{H-4,H-3}$ = 9.0 Hz, H-4$^{AD}$), 3.46 (s, 6 H, OMe-2), 3.50 (s, 6 H, OMe-2), 3.51 (s, 6 H, OMe-2), 3.52 (m, 2 H, H-6b$^{CF}$), 3.58 (m, 2 H, H-3$^{CF}$), 3.59 (m, 2 H, H-3$^{AD}$), 3.60 (m, 2 H, H-6a$^{BE}$), 3.61 (m, 2 H, H-3$^{BE}$), 3.62 (s, 6 H, OMe-3), 3.63 (s, 6 H, OMe-3), 3.66 (m, 4 H, H-4$^{CF}$, H-5$^{CF}$), 3.67 (m, 2 H, H-3$^{CF}$), 3.70 (s, 6 H, OMe-3), 3.99 (t, 2 H, $^2$J$_{H-6b,H-6a}$ = 12.8 Hz, H-6b$^{BE}$), 4.03 (d, 2 H, $^2$J$_{H-6a,H-6b}$ = 13.9 Hz, H-6a$^{AD}$), 4.30 (dd, 2 H, $^3$J$_{H-5,H-6b}$ = 12.8 Hz, $^3$J$_{H-5,H-4}$ = 10.1 Hz, H-5$^{BE}$), 4.45 (ddd, 2 H, $^3$J$_{H-5,H-6a}$ = 3.2 Hz, $^3$J$_{H-5,H-6b}$ = 17.4 Hz, $^3$J$_{H-5,H-4}$ = 9.0 Hz, H-5$^{AD}$), 4.87 (dd, 2 H, $^2$J$_{H-6b,H-6a}$ = 13.9 Hz, $^3$J$_{H-6b,H-5}$ = 3.2 Hz, H-6b$^{AD}$), 4.88 (d, 2 H, $^3$J$_{H-1,H-2}$ = 2.7 Hz, H-1$^{AD}$), 5.03 (d, 2 H, $^3$J$_{H-1,H-2}$ = 3.8 Hz, H-1$^{CF}$), 5.15 (d, 2 H, $^3$J$_{H-1,H-2}$ = 3.3 Hz, H-1$^{BE}$), 7.62–
A solution of diphenylphosphine (0.16 mmol) in THF (0.5 mL) of a 2,6-di(tert-butyl)pyridine (10 g, 0.1 mmol) solution in hexane, 0.57 mmol) was added dropwise at –78°C to a stirred solution of diphenylphosphine (0.520 g, 725 μL of a 20.3% wt/wt solution in hexane, 0.57 mmol) in THF (10 mL). After 30 min, the dark red diphenylphosphide solution was transferred via a cannula to a stirred solution of 3 (0.200 g, 0.16 mmol) in THF.
(10 mL) kept at −78°C. The solution was stirred at −78°C for a further 1 h. The reaction mixture was quenched at −78°C with distilled water (0.50 mL) and the colourless precipitate was filtered over Celite and the filtrate was evaporated to dryness. The dried filtrate was taken in THF (8 mL) and H₂SO₄ (0.20 mL, 50% wt/wt solution in water) was added. The reaction mixture was stirred for 1 h at room temperature before adding saturated aqueous NaHCO₃ (50 mL). Subsequent extraction with CHCl₃ (3 × 50 mL) was followed by drying of the organic extracts (MgSO₄). Removal of the solvent in vacuo gave a colourless residue which was dissolved in CH₂Cl₂ (20 mL) and then aqueous H₂O₂ (58 µL, 35% wt/wt solution in water, 0.56 mmol) was added. The mixture was stirred for 2 h at room temperature whereupon it was quenched with saturated aqueous NaHCO₃ (50 mL) then extracted with CHCl₃ (3 × 30 mL) and dried (MgSO₄). Evaporation of the solvents gave a colourless powder, which was subjected to column chromatography (SiO₂; CH₂Cl₂/Methanol, 97:3, v/v) to afford 10 (0.120 g, 50%) as a colourless solid. Rᵣ (SiO₂, CH₂Cl₂/Methanol, 92:8, v/v) = 0.42; m.p. 135-137 °C; ¹H NMR (400.1 MHz, CDCl₃, 25°C): δ (assignment by combined COSY, TOCSY, HMQC, and ROESY) = 2.53 (dd, 2 H, ²J_H6a_p = 15.3 Hz, ²J_H6a_p = 11.1 Hz, ²J_H6a_p = 3.2 Hz, H-6a²⁴), 2.63 (s, 6 H, OMe-6²⁴), 3.13 (dd, 2 H, ³J_H2_p,H-3 = 9.8 Hz, ³J_H2_p = 2.7 Hz, H-2²⁴), 3.16 (dd, 2 H, ³J_H2_p,H-3 = 10.1 Hz, ³J_H2_p,H-1 = 3.8 Hz, H-2²⁴), 3.17 (m, 2 H, H-6a²⁴), 3.29 (dd, 2 H, ³J_H2_p,H-3 = 9.5 Hz, ³J_H2_p,H-1 = 3.9 Hz, H-2²⁴), 3.39 (s, 6 H, OMe-3), 3.43–3.48 (4 H, H-6b²⁴, H-4²⁴), 3.51 (s, 6 H, OMe-2), 3.54 (s, 6 H, OMe-2), 3.57 (s, 6 H, OMe-2), 3.64 (m, 2 H, H-6b²⁴), 3.66 (m, 2 H, H-3²⁴), 3.68 (s, 6 H, OMe-3), 3.72 (dd, 2 H, ³J_H3_p,H-2 = 10.1 Hz, ³J_H3_p,H-4 = 18.1 Hz, H-3²⁴), 3.73 (dd, 2 H, ³J_H3_p,H-2 = 9.5 Hz, ³J_H3_p,H-4 = 18.1 Hz, H-3²⁴), 3.82 (dd, 2 H, ³J_H4_p,H-3 = 18.0 Hz, ³J_H4_p,H-5 = 8.8 Hz, H-4²⁴), 3.85 (s, 6 H, OMe-3), 3.89 (d, 2 H, ³J_H5_p,H-4 = 8.8 Hz, H-5²⁴), 3.95–4.03 (4 H, H-5²⁴, H-6a²⁴), 4.02 (dd, 2 H, ³J_H4_p,H-3 = 18.1 Hz, ³J_H4_p,H-5 = 10.3 Hz, H-4²⁴), 4.42 (d, 2 H, ²J_H6b_p,H-6a = 11.1 Hz, H-6b²⁴), 4.48 (dd, 2 H, ³J_H5_p,H-6a = 3.2 Hz, ²J_H5_p,H-6b = 17.4 Hz, ²J_H5_p,H-4 = 8.8 Hz, H-5²⁴), 4.69 (d, 2 H, ³J_H1_p,H-2 = 2.7 Hz, H-1²⁴), 4.94 (d, 2 H, ³J_H1_p,H-2 = 3.9 Hz, H-1²⁴), 5.58 (d, 2 H, ³J_H1_p,H-2 = 3.8 Hz, H-1²⁴), 6.03 (br s, 2 H, OH²⁴), 7.12 (td, 4 H, ³J_H-o,H-1 = 7.6, ³J_H-o,H-3 = 3.0 Hz, o-H), 7.23 (td, 2 H, ³J_H-o,H-1 = 7.6, ³J_H-o,H-3 = 1.3 Hz, m-H), 7.47–7.57 (10H, o-H, m-H, p-H), 7.78–7.84 (4H, m-H) ppm; ¹³C{¹H} NMR (100.6 MHz, CDCl₃, 25°C): δ (assignment by HMQC) = 32.26 (d, ¹J_C_P = 73.4 Hz, C-6²⁴), 56.98, 58.18, 58.32, 59.60, 59.65 (OMe), 60.08 (C-6²⁴), 61.82, 62.14 (OMe), 68.23 (d, ²J_C_P = 7.3 Hz, C-5²⁴), 70.43 (C-5), 70.88 [x2] (C-4, C-5), 71.54 (C-6²⁴), 80.40, 80.98, 81.16, 81.78 [x2], 81.88, 84.15, 88.08 (C-2, C-3, C-4), 96.81, 96.95, 97.01 (C-1), 128.46 (d, ³J_C_P = 11.7, C-meta), 128.53 (d, ³J_C_P = 11.7, C-meta), 130.34 (s, C-meta), 130.44 (s, C-para), 131.28 (d, ²J_C_P = 18.6 Hz, C-ortho), 131.41 (d, ²J_C_P = 26.1 Hz, C-ortho),
133.57 (d, $^1J_{C,P} = 100.8$, C$_{ipso}$), 135.40 (d, $^1J_{C,P} = 102.8$, C$_{ipso}$) ppm; $^{31}P$ ($^1$H) NMR (121.5 MHz, CDCl$_3$, 25°C): $\delta = 32.66$ (s) ppm; elemental analysis (%) calcd for C$_{74}$H$_{106}$O$_{30}$P$_2$·0.5CH$_2$Cl$_2$ (1537.56 + 42.5): C 56.63, H 6.83, found: C 56.81, H 7.10; MS (ESI-TOF): m/z (%): 1559.62 (100) [M + Na]$^+$. 

Electronic Supplementary Material (ESI) for Chemical Communications
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Crystal structure analyses

X-ray crystallographic data of 5b: Single crystals of 5b were obtained by slow diffusion of pentane into a dichloromethane solution of the compound. Crystal data for C_{60}H_{95}NO_{31}·0.5CH_{2}Cl_{2}·H_{2}O·1.5C_{5}H_{12} (5b·0.5CH_{2}Cl_{2}·H_{2}O·1.5C_{5}H_{12}), \( M_r = 1495.07 \), monoclinic, space group \( P2_1 \), \( a = 15.2970(10) \), \( b = 15.7262(8) \), \( c = 16.6710(10) \) Å, \( \beta = 90.778(6)° \), \( V = 4010.1(4) \) Å\(^3\), \( Z = 2 \), \( \rho_{\text{calc}} = 1.238 \) g cm\(^{-3}\), \( \lambda(\text{Mo}K\alpha) = 0.71073 \) Å, \( \mu = 0.129 \) mm\(^{-1}\), \( F(000) = 1608, T = 120 \) K. The sample (0.26 × 0.16 × 0.08 mm) was studied with an Oxford Diffraction Xcalibur Saphir 3 CCD with graphite monochromatised Mo K\( \alpha \) radiation. The structure was solved with SIR-97\(^4\) which revealed the non-hydrogen atoms of the molecule. After anisotropic refinement, many hydrogen atoms were found with a Fourier difference analysis. The whole structure was refined with SHELX-97\(^5\) and full-matrix least-square techniques. Use of \( F^2 \) magnitude; \( x, y, z, \beta_{ij} \) for C, O, S atoms, \( x, y, z, \) in riding mode for H atoms, 917 variables and 7789 observations with \([I > 2.0\sigma(I)]\), \( \text{calc} \ \rho = 1/[\varepsilon^2(F_o^2) + (0.1186 P)^2] \) where \( P = (F_o^2 + 2 F_c^2)/3 \) with the resulting \( R = 0.0680, R_w = 0.1911, \) and \( S_w = 0.830, \) \( \Delta \rho < 0.929 \) e Å\(^{-3}\). The compound was rather poorly diffracting. It crystallized with half a molecule of pentane inside the cavity and one molecule of pentane, half a molecule of CH\(_2\)Cl\(_2\) and one water molecule lying outside the CD. It must be emphasised that the O46-C49 O-methyl and C62...C67 aromatic groups are disordered. The disordered aromatic group was refined in the isotropical mode because of correlations in the anisotropic mode. The A-level alerts are mainly due to the external pentane molecule, which was difficult to refine. CCDC 826891.

X-ray crystallographic data of 7a: Single crystals of 7a were obtained by slow diffusion of pentane into a dichloromethane solution of the compound. Crystal data for C\(_{74}H_{112}B_2O_{28}P_2·3\)CH\(_2\)Cl\(_2·1.5\)C\(_5\)H\(_{12}\) (7a·3CH\(_2\)Cl\(_2·1.5\)C\(_5\)H\(_{12}\)), \( M_r = 1896.19 \), orthorhombic, space group \( P2_12_12_1 \), \( a = 16.0969(4) \), \( b = 22.4367(5) \), \( c = 27.7517(7) \) Å, \( V = 10022.8(4) \) Å\(^3\), \( Z = 4 \), \( \rho_{\text{calc}} = 1.257 \) g cm\(^{-3}\), \( \lambda(\text{Mo}K\alpha) = 0.71073 \) Å, \( \mu = 0.274 \) mm\(^{-1}\), \( F(000) = 4036, T = 120 \) K. The sample (0.22 × 0.12 × 0.10 mm) was studied with an Oxford Diffraction Xcalibur Saphir 3 CCD with graphite monochromatised Mo K\( \alpha \) radiation. The structure was solved with SIR-97\(^4\) which revealed the non-hydrogen atoms of the molecule. After anisotropic refinement, many hydrogen atoms were found with a Fourier difference analysis. The whole structure was refined with SHELX-97\(^5\) and full-matrix least-square techniques. Use of \( F^2 \)
magnitude; $x$, $y$, $z$, $\beta_{ij}$ for C, O, S atoms, $x$, $y$, $z$, in riding mode for H atoms, 1029 variables and 8413 observations with $[I > 2.0\sigma(I)]$, calcld $w = 1/[\sigma^2(F_o^2) + (0.1186 P)^2]$ where $P = (F_o^2 + 2 F_e^2)/3$ with the resulting $R = 0.0935$, $R_w = 0.2645$, and $S_w = 0.932$, $\Delta \rho < 0.658$ e Å$^{-3}$. CCDC 822184.

CCDC-822184 (7a) and CCDC-826891 (5b) contain the supplementary crystallographic data for this report. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
NMR and mass spectra

NMR spectra of all compounds were recorded in CDCl₃ at 25 °C.

6⁵,⁶⁷-Dideoxy-6⁵,⁶⁷-sulfato-2⁴,₂²,₂⁶,₂⁷,₂⁸,₂⁹,₃₀,₃₁,₃²,₃₃,₃₄,₃₅,₃₆,₃₇,₃₈,₃₉,₄₀,₄₁,₄₂,₄₃,₄₄-hexadeca-O-methyl-α-cyclodextrin (1):

¹H NMR spectrum .......................................................... 23
¹H/¹H COSY spectrum ......................................................... 24
¹³C{¹H} NMR spectrum ....................................................... 25
DEPT 135 spectrum .......................................................... 26
¹H/¹³C HMOC spectrum ...................................................... 27
Mass spectrum ............................................................... 28

6⁵,⁶⁷-Dideoxy-6⁵,⁶⁷-sulfato-2⁴,₂²,₂⁶,₂⁷,₂⁸,₂⁹,₃₀,₃₁,₃²,₃₃,₃₄,₃₅,₃₆,₃₇,₃₈,₃₉,₄₀,₄₁,₄₂,₄₃,₄₄-nonadeca-O-methyl-β-cyclodextrin (2):

¹H NMR spectrum .......................................................... 29
¹H/¹H COSY spectrum ......................................................... 30
¹³C{¹H} NMR spectrum ....................................................... 31
DEPT 135 spectrum .......................................................... 32
¹H/¹³C HMOC spectrum ...................................................... 33
Mass spectrum ............................................................... 34


¹H NMR spectrum .......................................................... 35
¹H/¹H COSY spectrum ......................................................... 36
¹H/¹H TOCSY spectrum ...................................................... 37
¹H/¹H ROESY spectrum ...................................................... 38
¹³C{¹H} NMR spectrum ....................................................... 39
DEPT 135 spectrum .......................................................... 40
¹H/¹³C HMOC spectrum ...................................................... 41
³¹P{¹H} NMR spectrum ....................................................... 42
Mass spectrum ............................................................... 43

6⁵-Deoxy-6⁵-(1,3-dioxisoindolin-2-y1)-2⁴,₂²,₂⁶,₂⁷,₂⁸,₂⁹,₃₀,₃₁,₃²,₃₃,₃₄,₃₅,₃₆,₃₇,₃₈,₃₉,₄₀,₄₁,₄₂,₄₃,₄₄-hexadeca-O-methyl-α-cyclodextrin (5b):

¹H NMR spectrum .......................................................... 44
¹H/¹H COSY spectrum ......................................................... 45
¹H/¹H TOCSY spectrum ...................................................... 46
¹H/¹H ROESY spectrum ...................................................... 47
¹³C{¹H} NMR spectrum ....................................................... 48
DEPT 135 spectrum .......................................................... 49
¹H/¹³C HMOC spectrum ...................................................... 50
Mass spectrum ............................................................... 51
6^A,6^D-Dideoxy-6^A,6^D-di(1,3-dioxoisooindolin-2-yl)-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^F-tetradeca-O-methyl-α-cyclodextrin (7b):

^1H NMR spectrum ........................................................................................................ 72
^1H/^1H COSY spectrum .................................................................................................. 73
^1H/^1H TOCSY spectrum .............................................................................................. 74
^1H/^1H ROESY spectrum .............................................................................................. 75
^13C{^1H} NMR spectrum ............................................................................................. 76
DEPT 135 spectrum ......................................................................................................... 77
^1H/^13C HMQC spectrum .............................................................................................. 78
Mass spectrum ................................................................................................................. 79

6^A,6^E-Dideoxy-6^A,6^E-di(1,3-dioxoisooindolin-2-yl)-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^F-tetradeca-O-methyl-α-cyclodextrin (8b):

^1H NMR spectrum ........................................................................................................ 80
^1H/^1H COSY spectrum .................................................................................................. 81
^13C{^1H} NMR spectrum ............................................................................................. 82
DEPT 135 spectrum ......................................................................................................... 83
^1H/^13C HMQC spectrum .............................................................................................. 84
Mass spectrum ................................................................................................................. 85

6^A,6^D-Dideoxy-6^A,6^D-di(diphenyloxophosphinyl)-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^F-tetradeca-O-methyl-α-cyclodextrin (10):

^1H NMR spectrum ........................................................................................................ 86
^1H/^1H COSY spectrum .................................................................................................. 87
^1H/^1H TOCSY spectrum .............................................................................................. 88
^1H/^1H ROESY spectrum .............................................................................................. 89
^13C{^1H} NMR spectrum ............................................................................................. 90
DEPT 135 spectrum ......................................................................................................... 91
^1H/^13C HMQC spectrum .............................................................................................. 92
^31P{^1H} NMR spectrum .............................................................................................. 93
Mass spectrum ................................................................................................................. 94
$^1$H NMR spectrum of 1
$^1$H-$^1$H COSY NMR spectrum of 1
$^{13}$C NMR spectrum of 1
DEPT 135 NMR spectrum of 1
$^1$H-$^{13}$C HMQC NMR spectrum of 1
Service de spectrometrie de masse - Institut de Chimie - Strasbourg - UMR 7177 CNRS / ULP

Analysis Info
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Method: esi wide pos.m
Sample Name: MJ62
Comment:

Acquisition Parameter
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Ion Priority: Positive
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Nebulizer: 5.4 Bar
Dry Gas: 4.0 l/min
Corona: 21.8 mA
Set Heater RF: 200.0 V
Dry Heater: 180 °C
APCI Heater: 517 °C

Mass spectrum of 1

Stuker Daltronics Data/Analysis 3.1
Page 1 of 1
$^1$H NMR spectrum of 2
$^{1}$$H$$-^{1}$$H$ COSY NMR spectrum of 2
$^{13}$C NMR spectrum of 2
DEPT 135 NMR spectrum of 2
$^1$H-$^{13}$C HMQC NMR spectrum of 2
### Mass spectrum of 2

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- **Method**: esi wide pos.m
- **Sample Name**: M89
- **Comment**:

**Acquisition Parameter**
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- **Ion Priority**: Positive
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- **Nebulizer**: 5.4 Bar
- **Corona**: 210 nA
- **Dry Gas**: 4.0 L/min
- **sat Skimmer 1**: 50.0 V
- **Dry Heater**: 180 °C
- **APCI Heater**: 517 °C

![Mass spectrum of 2](chart)

**Studer Dalloros Data/Analysis 3.1**
- **Printed**: 11/10/2011 4:04:35 PM
$^1$H NMR spectrum of 5a
$^{1}H-^{1}H$ COSY NMR spectrum of 5a
$^1$H-$^1$H TOCSY NMR spectrum of 5a
$^1$H-$^1$H ROESY NMR spectrum of 5a
$^{13}$C NMR spectrum of 5a
DEPT 135 NMR spectrum of 5a
$^1$H-$^{13}$C NMR spectrum of 5a
$^{31}\text{P} \{^{1}\text{H}\}$ NMR spectrum of 5a
Mass spectrum of 5a
$^1$H NMR spectrum of 5b
\(^{1}\text{H}-^{1}\text{H} \text{ COSY NMR spectrum of 5b}\)
$^1$H-$^1$H TOCSY NMR spectrum of 5b
$^1$H-^1$H ROESY NMR spectrum of 5b
$^{13}$C NMR spectrum of 5b
DEPT 135 NMR spectrum of 5b
$^{1}{H}^{13}{C}$ HMQC NMR spectrum of 5b
Service de spectrometrie de masse - Institut de Chimie - Strasbourg - UMR 7177 CNRS / ULP

Analysis Info
Analysis Name: O1427Trm.d
Method: esi wide pos.m
Sample Name: MJ67
Comment:

Acquisition Parameter
Source Type: ESI
Ion Priority: Positive
Scan Range: n/a
Capillary: 4500 V
Nebulizer: 1.4 Bar
Dry Gas: 5.0 L/min
Set Skimmer 1: 50.0 V
Dry Heater: 180 °C
Corona: 218 mA
Set Heater RF: 200.0 V
APCI Heater: 517 °C

Mass spectrum of 5b
$^1$H NMR spectrum of 6b
Service de spectrometrie de masse - Institut de Chimie - Strasbourg - UMR 7177 CNRS / ULP

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Mass spectrum of 6b

![Mass spectrum graph](image_url)
$^1$H NMR spectrum of 5c and 6c (mixture)
Service de spectrometrie de masse - Institut de Chimie - Strasbourg - UMR 7177 CNRS / ULP

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| Operator | Administrator |
| Instrument | microOTOF |

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### Mass spectrum of 5c and 6c (mixture)
$^1$H NMR spectrum of 5d and 6d (mixture)
Mass spectrum of 5d and 6d (mixture)
$^1$H NMR spectrum of 5e and 6e (mixture)
Part of the $^1$H NMR spectrum showing the anomeric signals of both major (black dot) and minor (circle) isomers of the 5e/6e mixture.
$^{31}$P/$^1$H NMR spectrum of 5e and 6e (mixture)
Service de spectrometrie de masse - Institut de Chimie - Strasbourg - UMR 7177 CNRS / ULP

### Analysis Info

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### Mass spectrum of 5e and 6e (mixture)
$^1$H NMR spectrum of 5f and 6f (mixture)
Part of the $^1$H NMR spectrum showing the anomeric signals of both major (black dot) and minor (circle) isomers of the 5f/6f mixture. The peak marked with an asterisk corresponds to CH$_2$Cl$_2$. 
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Mass spectrum of 5f and 6f (mixture)

Electronic Supplementary Material (ESI) for Chemical Communications
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$^1$H NMR spectrum of 7a
$^1$H-$^1$H COSY NMR spectrum of 7a
DEPT 135 NMR spectrum of 7a
$^1$H-$^{13}$C HMQC NMR spectrum of 7a
$^{31}$P{$^1$H} NMR spectrum of 7a
Service de spectrometrie de masse - Institut de Chimie - Strasbourg - UMR 7177 CNRS / ULP

Analysis Info
- Analysis Name: O14089RC.d
- Method: esi brows
- Sample Name: MJ-48
- Comment

Acquisition Parameter
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- Nebulizer: 5.4 Bar
- Dry Gas: 3.0 l/min
- Dry Heater: 300 ºC
- ATP C Heater: 517 ºC

Mass spectrum of 7a

Studer Dalbanics Data/Analysis 3.1
printed: 4/7/2011 3:18:29 PM
Page 1 of 1
\(^1\)H NMR spectrum of 7b
$^1$H-$^1$H COSY NMR spectrum of 7b
$^1$H-$^1$H TOCSY NMR spectrum of 7b
\(^1\text{H}-^1\text{H}\) ROESY NMR spectrum of 7b
$^{13}$C NMR spectrum of 7b
DEPT 135 NMR spectrum of 7b
$^{1}H-^{13}C$ HMQC NMR spectrum of 7b
Service de spectrométrie de masse - Institut de Chimie - Strasbourg - UMR 7177 CNRS / ULP

Analysis info
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Acquisition Date: 10/5/2011 2:50:16 PM
Operator: Administrator
Instrument: microOTOF

Acquisition Parameter
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Corona: 218 V
Set Heatspray RF: 3000 V
Dry Heater: 180 °C
APCI Heater: 517 °C

Mass spectrum of 7b

Stuker Daltronics Data/Analysis 3.1
Page 1 of 1
$^1$H NMR spectrum of 8b
$^{1}\text{H}-^{1}\text{H}$ COSY NMR spectrum of 8b
$^{13}$C NMR spectrum of 8b
DEPT 135 NMR spectrum of 8b
$^1$H-$^{13}$C HMQC NMR spectrum of 8b
Mass spectrum of 8b
$\text{H NMR spectrum of 10}$
$^{1}H-^{1}H$ COSY NMR spectrum of 10
$^1$H-$^1$H TOCSY NMR spectrum of 10
$^1$H-$^1$H ROESY NMR spectrum of 10
$^{13}\text{C}$ NMR spectrum of 10
DEPT 135 NMR spectrum of 10
$^1$H-$^{13}$C HMQC NMR spectrum of 10
$^{31}$P NMR spectrum of 10
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Mass spectrum of 10
General procedure for determining the glucose units linked by a given capping unit.⁶

Our strategy for full structural assignment began with the differentiation between capped and non-capped C-6 carbon atoms by DEPT 135. These appear as two distinct sets of signals. The H-6 protons could then be identified using ¹H-¹³C HMQC (Heteronuclear Multiple Quantum Coherence spectroscopy). By using TOCSY (TOtal Correlation SpectroscopY) and COSY (COrrelated SpectroscopY), each H-6 proton was correlated to the set of protons belonging to the same glucose residue. The connectivity between individual glucose units was then established via a ROESY (Rotating frame Overhause Effect SpectroscopY) experiment showing the proximity between H-4N and H-1N⁺¹ protons (N and N+1 standing for neighbouring glucose moieties labeled in the alphabetical order).

References