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Regioselective Double Capping of Cyclodextrin Scaffolds

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Abstract: Four different regioselective double capping reactions were applied either to α- or β-cyclodextrin (CD) scaffolds. The first, which relied on the use of a rigid, bulky dialkylating reagent containing two trityl-like subunits, gave access to an A,B,D,E-tetrafunctionalised β-CD regioisomer in large scale reactions. Two further capping reactions, involving the dianions PhP^{2-} and S^{2-}, led to the synthesis of new C_1-symmetrical β-cyclodextrins in which pairs of neighbouring glucose units are linked by very short spacers. The last double capping reaction described allowed the high-yield preparation of unprecedented α- and β-cyclodextrins containing two sulfate handles. Proximal capping turned out to be favoured for each of the above difunctional reagents. The structural characterisation of the capped species was achieved by thorough NMR investigations as well as by single-crystal X-ray diffraction studies.

Keywords: cavitands · cyclodextrins · ligand design · macrocyclic ligands · regioselectivity

Introduction

The past decade has seen renewed interest in the chemical modification of cyclodextrins (CDs) as very selective methods have become available for differentiating the many identical hydroxyl groups present in these naturally occurring cyclic oligosaccharides.[1] Access to specific regioisomers in gram-scale quantities is of paramount importance[2] for taking full advantage of the ubiquitous CD cavity, in particular, for topics such as supramolecular chemistry[3] and catalysis.[4–7] So far, most of the methods developed for discriminating between identical hydroxyl groups focussed on disubstituted CDs.[1,8] The more challenging task of obtaining tetrafunctionalised species in a regioselective manner has been recently addressed by several groups. For example, one-step diisobutylaluminum hydride (DIBAL-H) induced deprotections of perbenzylated[9] CDs have been employed to produce tetrafunctionalised α-, β- and γ-CDs in low to moderate yields, but with high regioselectivity.[10] Tetrafunctionalised α- and β-CDs are also accessible through multistep syntheses involving two non-consecutive debenzylation steps.[11] In the case of perbenzylated species, deprotection usually takes place at the primary rim, although the O-3 positions of the secondary rim are also affected by C–O bond cleavage for the more sterically demanding perbenzylated α-CD.[12] On the other hand, permethylated β-CD undergoes tetrademethylation solely at the secondary rim.[13,14] Another strategy that has been applied to α-CD, consists of reacting the cyclic oligosaccharide with an excess of bulky monoalkylating agents such as trityl[15,16] or supertrityl chlorides,[17] thereby giving rise to tetrasubstituted species at the primary rim with good regioselectivity. Surprisingly, little attention has been paid to double capping reactions for targeting tetrasubstituted CDs since the early work of Tabushi, who relied on the use of rigid disulfonyl chlorides.[18–20] In the present paper, we describe a short and convenient synthesis of a $6^A,6^B$:$6^D,6^E$-doubly capped β-CD, which provides easy access to valuable $6^A,6^B,6^D,6^E$-functionalised β-CDs in gram-scale quantities. Capping methodology was also used for the preparation of new α- and β-CD-derived phosphanes, phosphane oxides, thioethers and sulfates.

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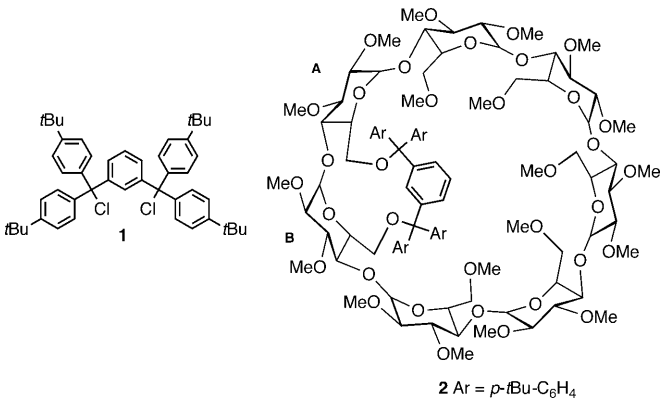
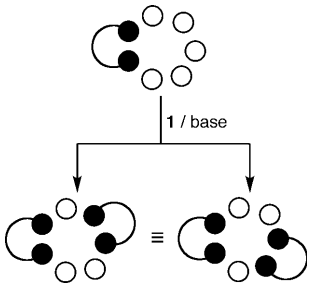
Results and Discussion

Tetrafunctionalisation of native β-CD: Our strategy for the preparation of A,B,D,E-tetrasubstituted β-CDs relied on the use of a particular alkylating reagent, namely "bis-trityl" dichloride **1**. As shown recently, alkylation of β-CD with one equivalent of **1** and subsequent methylation of the non-alkylated hydroxyl groups led to the A,B-capped CD **2**.[21] We anticipated that the use of two equivalents of **1** for the first alkylation step would regioselectively lead to an A,B:D,E doubly capped β-CD, as a result of both the capacity of the difunctional reagent to strap adjacent glucose units and the

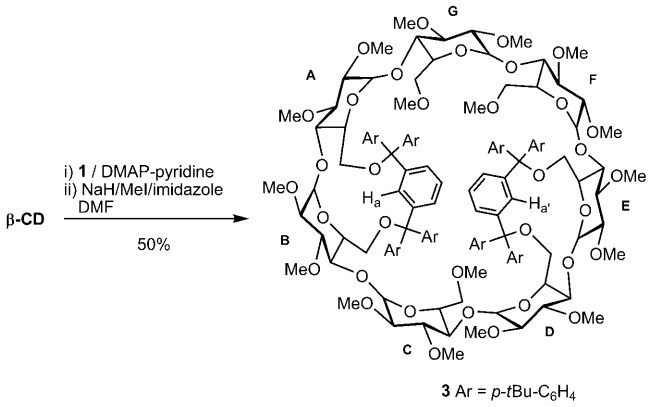


steric bulk of the "bis-trityl" cap, which possibly prevents attachment of two distinct "bis-trityl" units onto adjacent sugar units. Thus, once an A,B cap is formed, the second "bis-trityl" unit should form either a D,E or an E,F cap, with both routes leading to the same regioisomer (Scheme 1).



Scheme 1. Double capping strategy based on the use of the bulky reagent **1**.

In fact, doubly capped **3** could be prepared in 50% isolated yield by reacting **β-CD** with two equivalents of "bis-trityl" dichloride **1**[21] in pyridine in the presence of 4-(*N*,*N*-dimethylamino)pyridine (DMAP) at 70°C, followed by methylation with NaH/MeI in *N*,*N*-dimethylformamide (DMF) (Scheme 2). Only one doubly capped species was detected (see below). The product was conveniently separated from over- and under-tritylated species as well as non-bridged species by standard column chromatography. Note that applying the same reaction conditions to the smaller **α-CD** were rather ineffective because they led to only very small amounts of doubly capped compound.[22] Clearly, only a wide enough macrocyle, such as the β-CD torus is able to accommodate two such large handles.



Scheme 2. Synthesis of the doubly capped β-CD derivative **3**.

Characterisation of 3: The formation of a doubly capped product was inferred from the ESI-MS spectrum of **3**, which showed intense peaks at *m*/*z* 2673.4 and 2657.4, with isotopic profiles exactly as expected for the $[M + K]^+$ and $[M + Na]^+$ ions, respectively. Proof for A,B,D,E-substitution came from a single-crystal X-ray diffraction study on the phosphorus-containing CD **4** (see Scheme 3), which is derived from **3**. The ^{1}H NMR spectrum of **3** displays 17 singlets arising from methoxy groups, in agreement with the expected double cyclisation (Figure 1). The specific formation of A,B and D,E caps was deduced from a combination of COSY, TOCSY, HMQC and ROESY experiments (see the Supporting Information). Once the connectivity between the individual glucose units was established, ROESY experiments unambiguously showed that a number of the H-6 protons of the neighbouring capped sugar units correlate with the central aromatic proton (H_a or $H_{a'}$) of the capping unit; this observation constituted the ultimate proof for A,B:D,E double capping (Figure 2). It is worth mentioning here that the aromatic region of the ^{1}H NMR spectrum of **3** bears strong resemblance to the singly capped-CD **2**.[21] In particular, two low-field signals for the H_a and $H_{a'}$ protons of the central aromatic rings of the "bis-trityl" fragments at $\delta = 7.61$ and 7.72 ppm, respectively, are typical of non-dangling 6^A,6^B-capping units.[21]

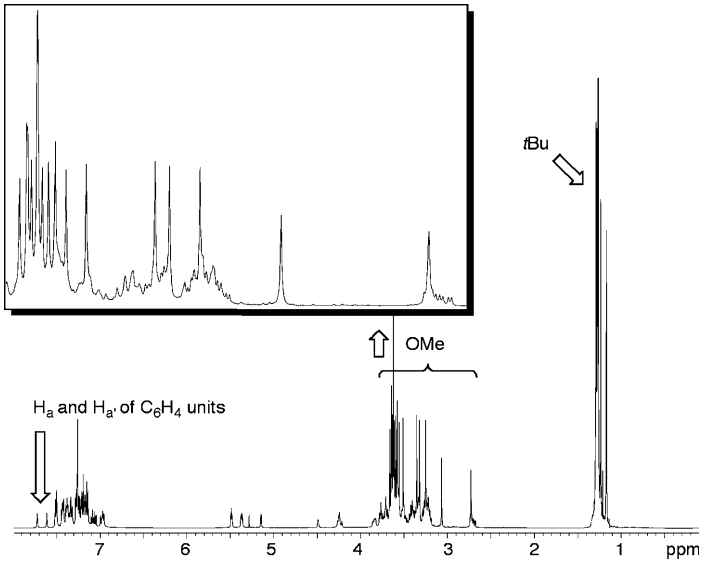


Figure 1. ^{1}H NMR spectrum of **3** recorded in $CDCl_3$ (500.1 MHz) and expansion showing the 17 singlets for the methoxy groups (top left).

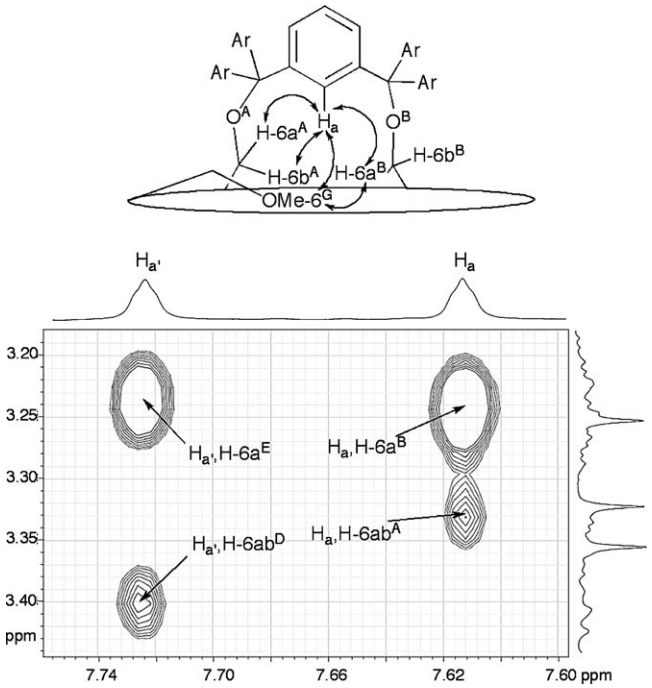


Figure 2. Part of the ROESY spectrum of compound **3** recorded in $CDCl_3$ at 500.1 MHz. The drawing above the spectrum represents one of the two capping units (A,B). The arrows represent important through-space correlations involving the A,B cap. H_a and $H_{a'}$ represent the central, *endo*-oriented aromatic protons of each capping unit.

Double capping of β-CD with dianions: Recent studies on the double capping of $6^A,6^B,6^D,6^E$-tetramesylated α-CD **5** with small phenylphosphide,[23,24] or very small sulfide dianions,[25,26] showed that these cyclisation processes are highly regioselective, even regiospecific (because only adjacent glucose units were being bridged) in the case of the more sterically crowded phenylphosphide, towards $6^A,6^B$:$6^D,6^E$-double capped ligands **6** (TRANSDIP)[27] or **7**.[25]

The synthesis of $6^A,6^B$:$6^D,6^E$-doubly capped **3** made it possible to access further double capping reactions on a β-CD scaffold. To this end, we first prepared $6^A,6^B,6^D,6^E$-tetramesylated β-CD **9**, which was obtained in 96% yield from **3** after hydrolysis of the "bis-trityl" caps with aqueous HBF_4 in CH_3CN followed by reaction of the intermediate tetrol **8** with methylsulfonylchloride in pyridine/DMAP (Scheme 3). Evidence for the cleavage of the capping units came from the presence of four triplets at $\delta = 2.61$, 2.68, 2.78 and 2.96 ppm, respectively, in the ^1H NMR spectrum of **8**, corresponding to the four non-equivalent hydroxyl protons. As expected, the reaction of excess Li_2PPh in tetrahydrofuran (THF) with **9** afforded the "introverted" diphosphane **10** as the major product, together with unidentified side products.[28]

To purify **10**, the reaction mixture required treatment with BH_3·THF to afford the protected diphosphane **4**, which was isolated in 40% overall yield from **9** after standard column chromatography. Removal of the BH_3 protecting groups was carried out quantitatively in boiling $HNEt_2$.[29] The ^{31}P NMR spectrum of pure diphosphane **10**, recorded in C_6D_6, displayed two nearly identical singlets at $\delta = -15.2$ and -15.0 ppm; values that are typical of dialkylphenylphosphanes. The "introverted" character of diphosphane **10** was revealed by a ^{31}P–^{31}P COSY NMR experiment (Figure 3).

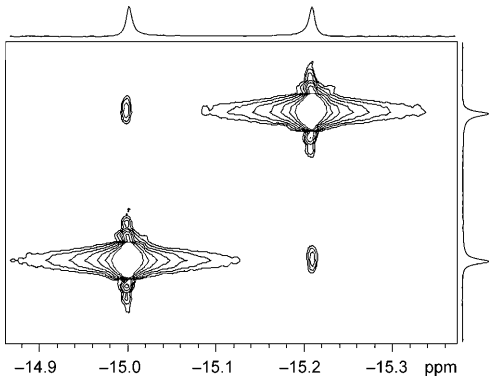
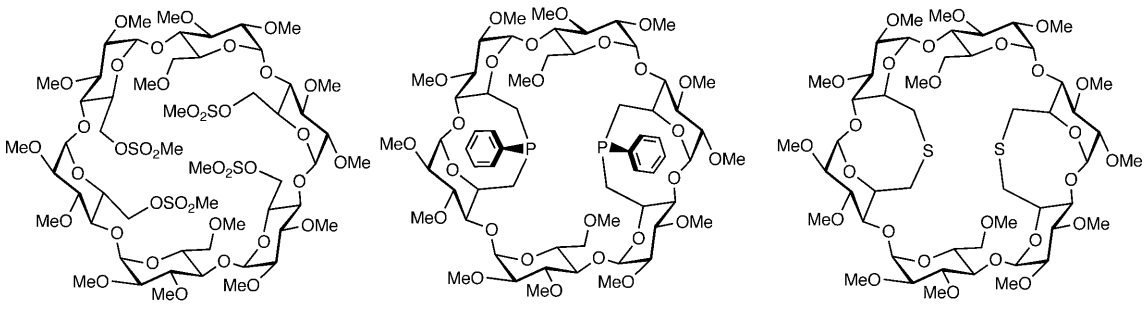
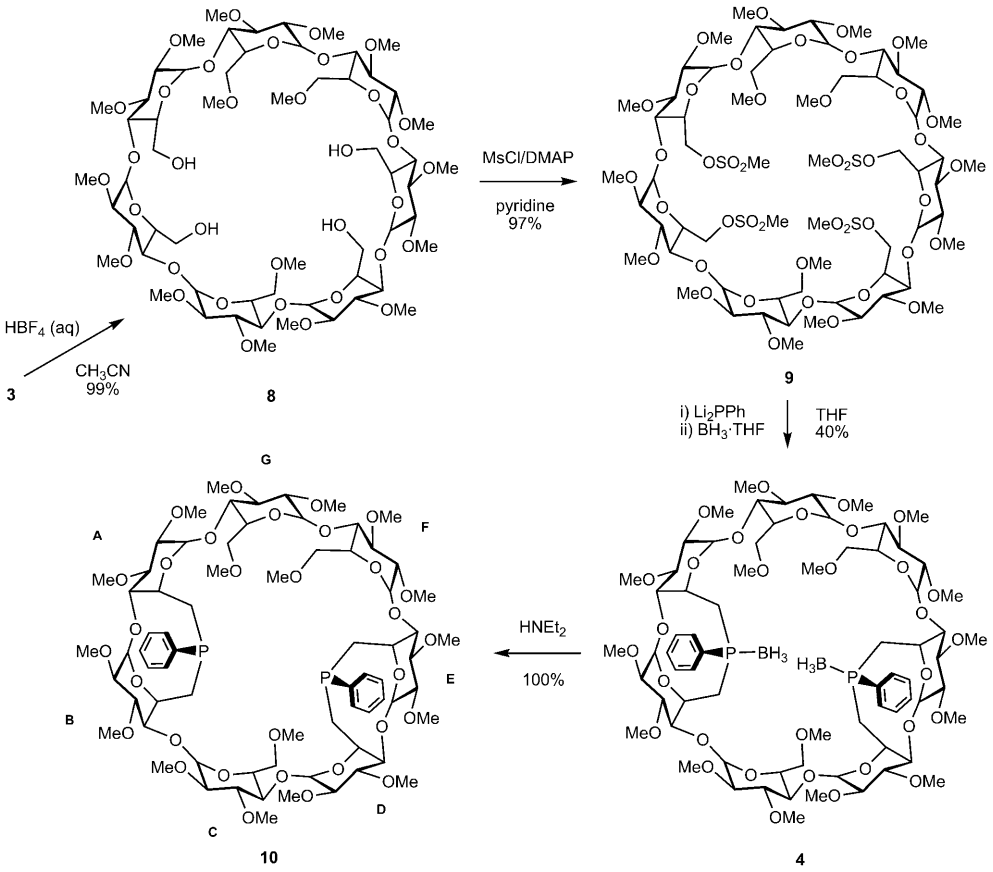


Figure 3. ^{31}P–^{31}P COSY NMR spectrum of diphoshine **10** recorded in C_6D_6 at 202.5 MHz.

Although the two non-equivalent phosphorus atoms are too far apart for significant ^{31}P–^{31}P through-space coupling constants[30] to be observed, the ^{31}P–^{31}P COSY NMR spectrum displayed correlations between the two P signals, thus proving that the two phosphorus lone pairs temporarily overlap. Clearly, the only diastereomer that would be expected to give rise to the previous observation is the one in which two phosphorus lone pairs face each other within the cavity.

Interestingly, a rare ^{31}P–^{13}C through-space spin coupling ($^{TS}J(P,C\text{-}6^C) = 2.6$ Hz) was observed between the C-6 atom





Scheme 3. Synthesis of the 6^A,6^B:6^D,6^E doubly capped diphosphane **10**.

of the non-bridged glucose unit C and one of the introverted P atoms (Figure 4).

Note that, despite its strong basicity, diphosphane **10** is difficult to oxidise with air, probably because access of oxygen to the buried phosphorus lone pairs is restricted. The solid state structure of the phosphane–borane adduct **4** was determined by a single-crystal X-ray diffraction study (Figure 5).

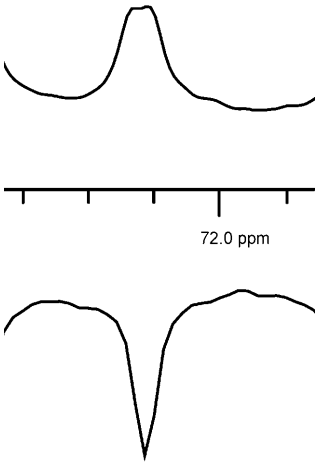


Figure 4. $^{13}C\{^1H\}$ NMR (top) and $^{13}C\{^1H,^{31}P\}$ NMR (bottom) spectra of **10** (C_6D_6, 125.8 MHz) showing the C-6^C signal.

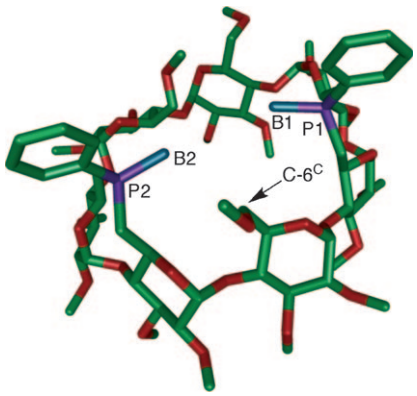
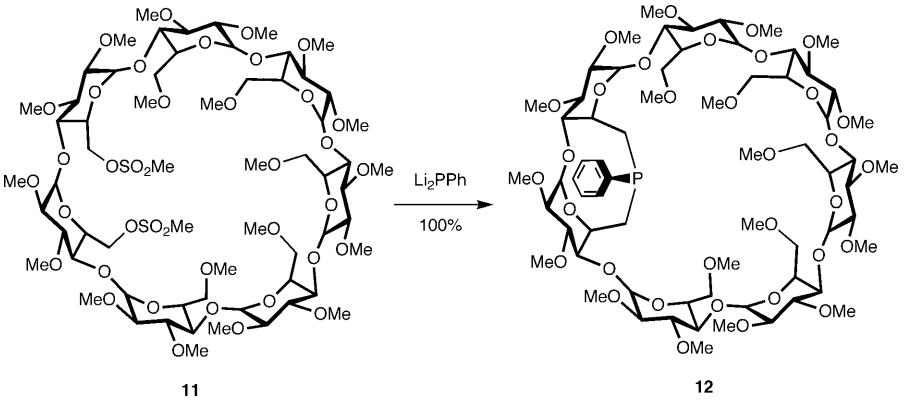


Figure 5. X-ray structure of the borane–diphosphane adduct **4** (top view). For clarity, the solvent molecules have been omitted. Important distances: P1···P2 8.23, B1···B2 4.67 Å.

This study confirmed the bridging of adjacent A,B as well as D,E glucose units. The cavity, which hosts a molecule of pentane, has a familiar circular shape, with all the glucose units adopting the standard $^4C_1$ conformation. The observed absence of deformation is not surprising because all the anomeric CD protons resonate within a narrow range ($\Delta\delta =$ 0.2 ppm) in the ^{1}H NMR spectrum of **4**.[31] Both P–B vectors are almost perpendicular to the axis that runs through the middle of the cavity and point towards its centre. They are

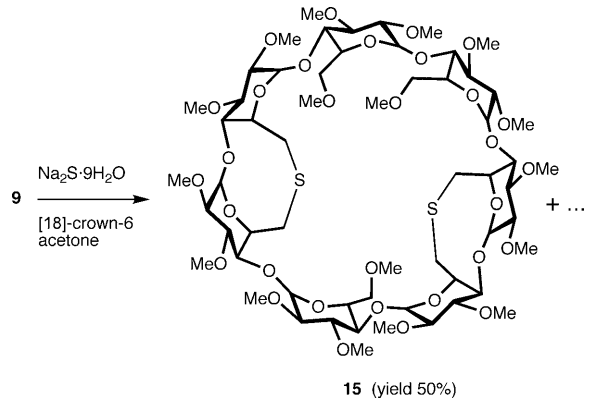
not aligned because of the non-symmetrical nature of the molecule (angle between the P–B vectors = 146.5°). The P···P distance (8.23 Å) is rather large compared with that observed in TRANSDIP. Moreover, the BH_3 protecting groups, which tend to repel each other, undoubtedly increase the P···P separation. We note also that one of the phosphorus atoms is relatively close to the C-6 atom of the neighbouring C glucose unit (C-6^C···P2 distance = 4.72 Å). This finding is consistent with the existence of a through-space spin coupling between these two nuclei in diphosphane **10**.



11 12

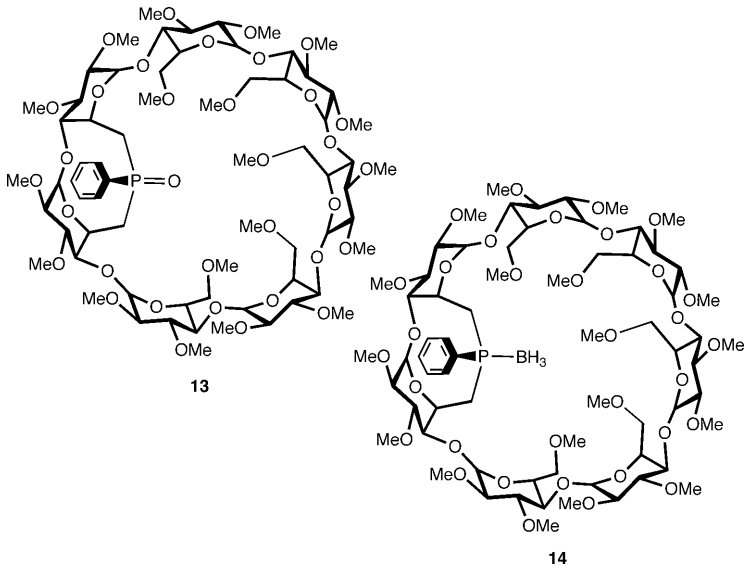
Scheme 4. Synthesis of the 6^A,6^B-capped monophosphane **12**.

Attempts were made to improve the synthesis of **10** by varying the solvents and temperature of the capping reaction, however, the composition of the reaction mixture varied little. It should be noted that the first cyclisation is probably quantitative, as observed for the synthesis of monophosphane **12**, which was obtained from dimesylate **11**[32] according to Scheme 4. Oxidation of **12** in air into the corresponding phosphane oxide **13** occurs readily, in contrast to that of diphosphane **10**. For storage purposes, **12** is best converted (see the Supporting Information) into the borane adduct **14**.



15 (yield 50%)

Scheme 5. Synthesis of the double sulfur-capped species **15**.



13 14

With the aim of achieving double capping reactions with a dianion smaller than the crowded phenylphosphide, we also decided to synthesise the β-CD version of **7**. Treatment of tetramesylate **9** with the small sulfide dianion in acetone, in the presence of [18]crown-6, gave the expected 6^A,6^B:6^D,6^E-sulfur-capped CD **15** in 50% isolated yield (Scheme 5). The ESI mass spectrum of **15** confirmed the formation of a doubly capped species, as revealed by the presence of a unique peak at m/z 1391.6 corresponding to the $[M + Na]^+$ ion.

As for the phosphinidene-capped derivative **10**, the ^{1}H NMR spectrum of **15** is in agreement with an overall circular CD torus, with all anomeric protons lying within a narrow resonance range ($\Delta\delta = 0.24$ ppm). Again, COSY, TOCSY, HMQC and ROESY experiments recorded at 500.1 MHz were used to establish the molecular structure of compound **15** (see the Supporting Information). In particular, these experiments allowed unambiguous identification of the C-6 atoms linked to a sulfur atom and the corresponding H-6 atoms. S-capping of the A and B units was inferred from ROESY experiments (Figure 6), which showed the close spatial proximity of the H-6a proton of glucose unit A and the H-5 proton of the neighbouring glucose unit B. The same H-$6a^A$ atom also correlates with the vicinal H-5^A proton. The observation of *both* correlations is only consistent with proximal S-capping (see also the Supporting Information). The same type of correlations were observed within the other pair of capped glucose units, namely D and E. Careful examination of the ^{1}H NMR spectrum of **15** further revealed a broadening of some H-6a, H-6b, H-5 and H-1 signals belonging to capped glucose units, suggesting rapid conformational mobility of the capped glucose residues.

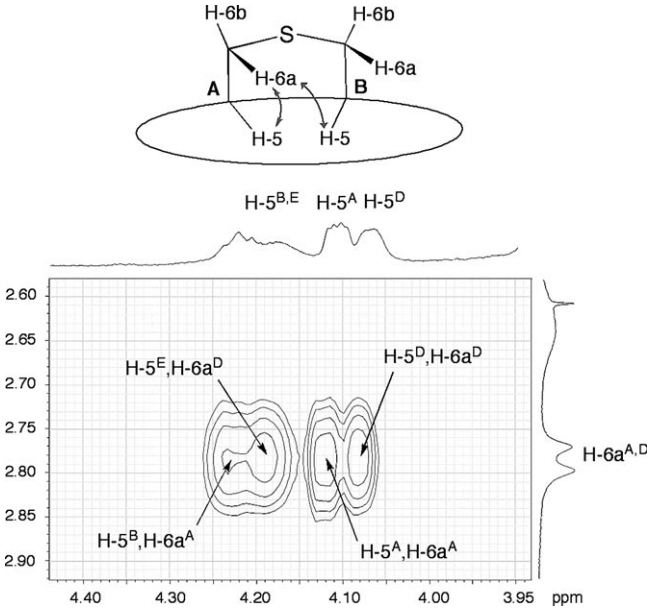


Figure 6. Part of the ROESY spectrum of compound **15** recorded in $CDCl_3$ at 500.1 MHz. The drawing above the spectrum shows one of the two capping units (A,B). The arrows represent through-space correlations involving the A,B cap.

Such a feature has previously been detected in another 6^A,6^B-sulfide-capped methylated β-CD, but not in its 6^A,6^C regioisomer,[3] nor in smaller α-CD analogues such as **7**.

It should be mentioned here that, beside **15**, a minor product was formed (**16**; see the Supporting Information), to which we tentatively assign a A,C:D,G doubly capped structure. This structural assignment was based on an MS analysis of **16** as well as on its ^{1}H NMR spectrum, in which the signals of the anomeric protons are much more widespread ($\Delta\delta = 0.93$ ppm) than those of **15**, thus reflecting a significant shape distortion of the macrocyclic core brought about by the A,C:D,G double capping.

Cyclodextrins capped with two sulfate moieties: Bols et al. were recently able to cap benzylated α- and β-CDs with a sulfate unit linking the 6^A and 6^D carbon atoms.[33] Double capping of methylated α- and β-CD scaffolds with sulfate units can also be achieved, provided Bols's reaction conditions are modified. Indeed, both tetrols **17** and **8** react with thionyl chloride in CH_2Cl_2 and NEt_3 at low temperature (−78 °C) to give a mixture of diastereomeric cyclic disulfites, the corresponding ESI-MS spectra of which displayed, in each case, a single signal for the corresponding $[M + Na]^+$ cation. Purification of these mixtures was not necessary because, in each case, a single product was formed after oxidation with $RuCl_3$/$NaIO_4$, namely disulfate **18** or **19** (Scheme 6). Remarkably, for both α- and β-CD disulfates, the overall yield was virtually quantitative (95 %). Only the use of a base, with the reaction mixture kept at low temperature, allowed these cyclisations to reach this level of regioselectivity.

The regioselectivity of the reaction leading to **18** was unambiguously established by a single-crystal X-ray diffraction study on this disulfate (Figure 7).

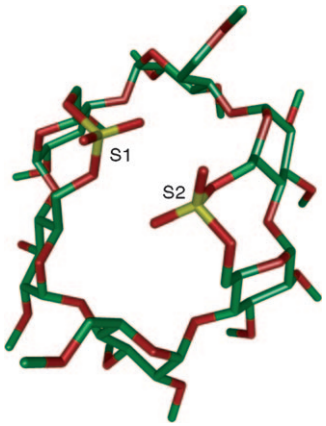
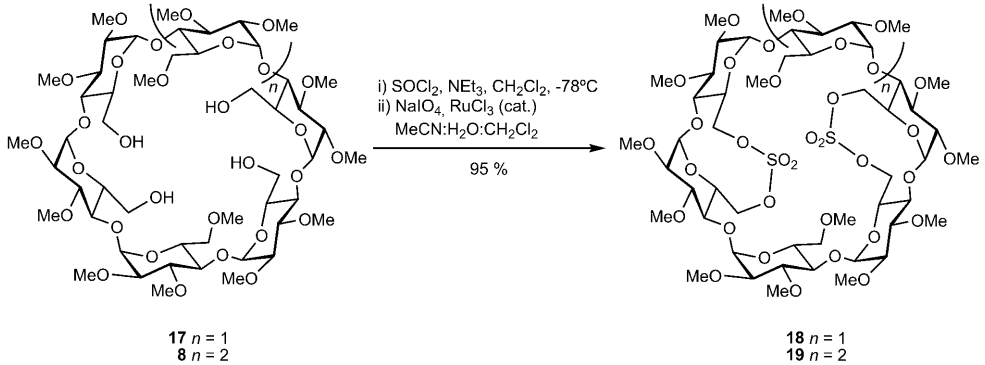


Figure 7. X-ray structure of disulfate doubly capped derivative **18** (view from the primary rim). For clarity, the solvent molecules that are hydrogen-bonded to a sulfate oxygen atom have been omitted. Important distance: S1···S2 4.01 Å.

Interestingly, the two sulfate caps of **18**, which link the A,B and D,E glucose units, respectively, are intertwined so as to block the cavity entrance. As for doubly capped CD **4**, the CD macrocycle hosts a molecule of pentane and comprises glucose units having all undistorted standard $^4C_1$ con-



Scheme 6. Synthesis of the disulfate doubly capped compounds **18** and **19**.

formations. However, those that are capped (A,B,D,E) are tilted towards the cavity interior. The cavity adopts a slightly elongated shape, the longest O(4)–O′(4) distance being 8.95 Å, and the shortest being 8.00 Å.

The capping mode in **19** was established by NMR analysis. Consistent with caps involving neighbouring glucose units, the H-1 protons of **19** resonate within a narrow range of chemical shifts ($\Delta\delta = 0.3$ vs. 0.15 ppm for **18**; see the Supporting Information), in agreement with the presence of undistorted glucose units.[31] Again, full structural characterisation was achieved through combined COSY, TOCSY, HMQC and ROESY studies (see the Supporting Information). As for **15**, ROESY cross peaks arising from through-space correlations between the H-6a proton of capped glucose unit A and two H-5 protons, namely H-5^{A} and H-5^{B}, unequivocally establish that proximal capping had occurred. Similar correlations could be seen between a H-6a atom of capped glucose D and H-5^{D} and H-5^{E}. Interestingly, the ROESY spectrum also showed a spatial proximity between the H-6b proton of glucose unit A and H-6a of glucose unit B, suggesting a high degree of flexibility of the AB cap.

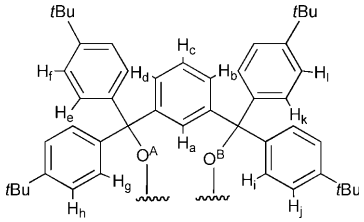
Conclusion

The present study has shown that double capping is a powerful means of tetrasubstituting native β-CD, as well as for introducing useful functionalities on methylated CDs. The introverted diphosphane **10** and the doubly sulfur-capped **15** constitute prototypes of a new class of bidentate ligands, the coordination chemistry and catalytic properties of which are currently under investigation. Furthermore, the cyclic sulfates reported in this study are promising starting materials for the tridifferentiation of methylated cyclodextrins, in particular as regards the synthesis of CD-based heterotetradentate ligands. Overall, these results usefully complement previous studies by us and others on the regiofunctionalisation of cyclodextrins, thereby opening the way to new, cavity-shaped ligand types.

Experimental Section

General: All manipulations were performed in Schlenk-type flasks under dry nitrogen. Solvents were dried by conventional methods and distilled immediately prior to use. $CDCl_3$ was passed down a 5 cm-thick alumina column and stored under nitrogen over molecular sieves (4 Å). Routine ^{1}H and $^{13}C\{^{1}H\}$ spectra were recorded with Bruker FT instruments (AVANCE 300, 500, and 600 spectrometers). ^{1}H NMR spectral data were referenced to residual protiated solvent ($\delta = 7.26$ ppm for $CDCl_3$ and $\delta = 7.16$ ppm for C_6D_6); ^{13}C chemical shifts are reported relative to deuterated solvents ($\delta = 77.00$ ppm for $CDCl_3$ and $\delta = 128.06$ ppm for C_6D_6) and the ^{31}P NMR data are given relative to external H_3PO_4. Mass spectra were recorded either with a ZAB HF VG analytical spectrometer using *m*-nitrobenzyl alcohol as matrix or with a Bruker MicroTOF spectrometer (ESI) using CH_2Cl_2, MeCN or MeOH as solvent. Elemental analyses were performed by the Service de Microanalyse, Institut de Chimie, Strasbourg. Melting points were determined with a Büchi 535 capillary melting point apparatus. All commercial reagents were used as supplied. 1,3-Bis[bis(4-*tert*-butylphenyl)chloromethyl]benzene (**1**)[21] and dimesylate **11**[32] were synthesised according to literature procedures.

6^{A},6^{B}:6^{D},6^{E}-Tetra-*O*-bis{benzene-1,3-bis[bis(4-*tert*-butylphenyl)methyl]}-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^{F},6^{G}-heptadeca-*O*-methyl-β-cyclodextrin (3): Labelling of aromatic protons in the A,B cap (noted with a prime in the corresponding D,E cap):



Compound **1** (5.42 g, 7.7 mmol) was added to a solution of **β-CD** (3.97 g, 3.5 mmol) and DMAP (0.51 g, 4.2 mmol) in pyridine (90 mL). The reaction mixture was stirred at 70 °C for 12 h before being cooled to room temperature. Pyridine was then removed in vacuo and water (500 mL) was added to the residue to produce a suspension, which was filtered. The cake was dried in vacuo at 50 °C for 12 h. The colourless solid was dissolved in DMF (150 mL) and NaH (5.88 g, 147 mmol) was added carefully, followed by the addition of a catalytic amount of imidazole (0.010 g, 0.15 mmol). The reaction mixture was stirred at room temperature for 1 h before being cooled at 0 °C. MeI (17.88 g, 7.8 mL, 126 mmol) was added dropwise at 0 °C and the yellow suspension thus formed was stirred for 12 h at room temperature. MeOH (50 mL) was added slowly to quench excess NaH, and the reaction mixture was poured into water (500 mL) under stirring before being extracted with Et_2O (3×300 mL). The organic extract was dried ($MgSO_4$) and evaporated to dryness to afford a brown residue. The crude material was purified by column chromatography (SiO_2; petroleum ether/AcOEt, 80:20 to 65:35, v/v) to give the desired product **3** (4.63 g, 50 %) as a colourless solid. $R_f = 0.60$ (SiO_2; petroleum ether/AcOEt, 60:40, v/v); m.p. >250 °C (decomp); ^{1}H NMR (500.1 MHz, $CDCl_3$, 25 °C): δ (assignment by COSY, TOCSY and ROESY) = 1.17 (s, 6H; *t*Bu), 1.18 (s, 6H; *t*Bu), 1.20 (s, 6H; *t*Bu), 1.24 (s, 6H; *t*Bu), 1.27–1.29 (48H; *t*Bu), 2.69 (d, ^{3}J(H-2,H-1) = 4.0 Hz, 1H; H-2^{E}), 2.73 (s, 3H; OMe-6^{G}), 2.73 (d, ^{3}J(H-2,H-1) = 3.7 Hz, 1H; H-2^{B}), 3.07 (s, 3H; OMe-6^{C}), 3.25 (s, 3H; OMe-6^{F}), 3.32 (s, 3H; OMe-2^{B}), 3.36 (s, 3H; OMe-2^{E}), 3.51 (s, 3H; OMe-2^{G}), 3.56 (s, 3H; OMe-2^{A}), 3.58 (s, 3H; OMe-2^{F}), 3.60 (s, 3H; OMe-2^{C}), 3.62 (s, 3H; OMe-2^{D}), 3.63 (s, 9H; OMe-3), 3.64 (s, 3H; OMe-3), 3.65 (s, 3H; OMe-3), 3.66 (s, 3H; OMe-3), 3.67 (s, 3H; OMe-3), 3.20–4.05 (m, 38H; H-2, H-3, H-4, H-5, H-6a^{B,E}, H-6^{A,C,D,F,G}), 4.22–4.28 (m, 3H; H-1^{B}, H-6b^{B,E}), 4.49 (d, ^{3}J(H-1,H-2) = 3.5 Hz, 1H; H-1^{E}), 5.15 (d, ^{3}J(H-1,H-2) = 3.4 Hz, 1H; H-1^{G}), 5.36 (d, ^{3}J(H-1,H-2) = 3.8 Hz, 1H, H-1^{A}), 5.38 (d, ^{3}J(H-1,H-2) = 3.3 Hz, 1H; H-1^{F}), 5.48 (d, ^{3}J(H-1,H-2) = 3.9 Hz, 1H; H-1^{C}), 5.49 (d, ^{3}J(H-1,H-2) = 3.9 Hz, 1H; H-1^{D}), 6.96 (d, ^{3}J(H$_{d'}$,H$_{c'}$) = 7.5 Hz, 1H; H$_{d'}$), 6.97 (d, ^{3}J(H$_{b}$,H$_{c}$) = 7.9 Hz, 1H; H$_{b}$), 6.99 (d, ^{3}J(H$_{b'}$,H$_{c'}$) = 8.0 Hz, 1H; H$_{b'}$), 7.06 (t, ^{3}J(H$_{c'}$,H$_{b'}$) = ^{3}J(H$_{c'}$,H$_{d'}$) = 7.8 Hz, 1H; H$_{c'}$), 7.08 (t, ^{3}J(H$_{c}$,H$_{b}$) = ^{3}J(H$_{c}$,H$_{d}$) = 7.8 Hz, 1H; H$_{c}$), 7.14–7.29 (m, 17H; H$_{d}$, H$_{f}$, H$_{f'}$, H$_{h}$, H$_{h'}$, H$_{j}$, H$_{j'}$, H$_{l}$ and H$_{l'}$), 7.32–7.45 (m, 12H, H$_{e}$, H$_{e'}$, H$_{i}$, H$_{i'}$, H$_{k}$ and H$_{k'}$), 7.51 (d, ^{3}J(H$_{g}$,H$_{h}$) = ^{3}J(H$_{g'}$,H$_{h'}$) = 7.8 Hz, 4H; H$_{g}$ and H$_{g'}$), 7.61 (br s, 1H; H$_{a}$), 7.72 ppm (br s, 1H; H$_{a'}$); $^{13}C\{^{1}H\}$ NMR (75.5 MHz $CDCl_3$, 25 °C): δ (assignment by HMQC) = 31.4 (24C; Me of *t*Bu), 34.3 (8C; C of *t*Bu), 57.8, 57.9, 58.1, 58.1, 58.3, 58.4, 58.8, 59.0, 59.5, 59.7, 60.6, 61.0, 61.5, 61.7, 61.75, 61.84, 62.0 (OMe), 61.68, 61.70, 62.7, 63.2 (C-6^{A,B,D,E}), 71.1, 71.8, 72.5 (C-6^{C,F,G}), 70.46, 70.49, 70.6, 70.8, 71.2, 71.6, 71.7 (C-5), 77.2, 78.7, 80.2, 80.5, 80.98, 81.04, 81.2, 81.3, 81.6, 81.8 (4C), 82.1, 82.2, 82.3, 82.6 (2C), 82.7 (2C), 82.9 (C-2, C-3, C-4), 85.7, 86.1, 87.5, 87.9 [OC(Ar)$_3$], 97.7, 98.2, 98.5, 98.6, 98.8 (3C) (C-1), 124.1 (5C), 124.3, 124.4, 124.5 (2C), 124.6, 126.3, 126.4, 126.5, 126.8, 127.3, 127.5, 128.11, 128.14, 130.5, 131.0, 131.5, 131.9, 134.4, 135.0 (*o*-C and *m*-C), 140.1, 140.2, 140.4, 140.6, 140.9, 141.6, 141.9, 142.4, 142.8, 144.6, 145.0, 145.2, 148.5, 148.52, 148.54, 148.56, 148.60, 148.7 (2C), 148.9 ppm (*ipso*-C); elemental analysis calcd (%) for $C_{155}H_{212}O_{35}\cdot CH_2Cl_2$

(2635.32 + 83.95): C 68.88, H 7.93; found: C 68.77, H 8.09; MS (ESI-TOF): *m/z* (%): 2673.36 (15) $[M + K]^+$, 2657.38 (78) $[M + Na]^+$, 2641.41 (9) $[M + Li]^+$.

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^F,6^G-Heptadeca-*O*-methyl-β-cyclodextrin (8): HBF_4 (34 wt% aq, 7.5 g, 7.5 mL, 29 mmol) was added dropwise to a stirred solution of capped cyclodextrin **3** (2.55 g, 0.97 mmol) in MeCN (30 mL) at room temperature. After 30 min, NEt_3 (1.47 g, 2.0 mL) was added dropwise under stirring. Addition of water (100 mL) to the reaction mixture caused the carbinol to precipitate. The resulting suspension was filtered and the filtrate was extracted with $CHCl_3$ (3×50 mL). The combined organic extracts were washed with saturated aqueous $NaHCO_3$ (100 mL) then dried ($MgSO_4$). Removal of the solvent in vacuo gave tetrol **8** (1.32 g, 99%) as a colourless solid. R_f = 0.18 (SiO_2; CH_2Cl_2/MeOH, 92:8, v/v); m.p. 153 °C; ^{1}H NMR (300.1 MHz, $CDCl_3$, 25 °C): δ (assignment by COSY) = 2.61 (t, ^3J(OH,H-6) = 6.2 Hz, 1H; OH), 2.68 (t, ^3J(OH,H-6) = 5.9 Hz, 1H; OH), 2.78 (t, ^3J(OH,H-6) = 6.1 Hz, 1H, OH), 2.96 (t, ^3J(OH,H-6) = 5.8 Hz, 1H; OH), 3.17–3.22 (m, 7H; H-2), 3.30–4.00 (m, 35H; H-3, H-4, H-5, H-6), 3.37 (s, 9H; OMe), 3.49 (s, 9H; OMe), 3.51 (s, 6H; OMe), 3.52 (s, 3H; OMe), 3.53 (s, 3H; OMe), 3.62 (s, 9H; OMe), 3.63 (s, 3H; OMe), 3.64 (s, 6H; OMe), 3.65 (s, 3H; OMe), 5.01–5.03 (m, 2H; H-1), 5.09 (d, ^2J(H-1,H-2) = 3.8 Hz, 1H; H-1), 5.10 (d, ^2J(H-1,H-2) = 3.8 Hz, 1H; H-1), 5.17 (d, ^2J(H-1,H-2) = 3.5 Hz, 2H; H-1), 5.23 ppm (d, ^2J(H-1,H-2) = 3.8 Hz, 1H; H-1); ^{13}C{^{1}H} NMR (75.5 MHz $CDCl_3$, 25 °C): δ (assignment by HMQC) = 58.3 (3C), 58.7, 58.8, 58.95, 59.00, 59.1, 59.2 (2C), 61.05, 61.09, 61.25, 61.28, 61.5, 61.6, 61.78 (OMe), 61.78, 62.0 (2C), 62.1 (C-$6^{A,B,D,E}$), 71.2, 71.3, 71.5 (C-$5^{C,F,G}$), 71.4, 71.5, 71.7 (C-$6^{C,F,G}$), 71.8, 72.0, 72.3, 72.5 (C-$5^{A,B,D,E}$), 78.3, 79.1 (2C), 80.0, 80.4, 80.7, 81.1, 81.2, 81.4, 81.5, 81.6 (2C), 81.7, 81.8 (2C), 82.0 (4C), 82.07, 82.14 (C-2, C-3, C-4), 98.4, 98.6, 98.7 (2C), 98.85 (2C), 98.92 ppm (C-1); elemental analysis calcd for (%) $C_{59}H_{104}O_{35}$ (1373.44): C 51.60, H 7.63; found: C 51.68, H 7.57; MS (ESI-TOF): *m/z* (%): 1395.63 (100) $[M + Na]^+$.

6^A,6^B,6^D,6^E-Tetra-*O*-methylsulfonyl-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^F,6^G-heptadeca-*O*-methyl-β-cyclodextrin (9): Methanesulfonyl chloride (0.34 g, 0.23 mL, 2.94 mmol) was added to a solution of tetrol **8** (0.96 g, 0.70 mmol) and DMAP (0.35 g, 2.87 mmol) in anhydrous pyridine (30 mL) at 0 °C. The reaction mixture was stirred at room temperature for 12 h before adding water (100 mL). The solution was extracted with AcOEt (3×50 mL) and the combined organic extracts were washed sequentially with HCl (2M; 2×50 mL), NaOH (2M; 2×50 mL) and water (50 mL) then dried ($MgSO_4$). Removal of the solvent in vacuo gave pure tetramesylate **9** (1.14 g, 97%) as a colourless solid. R_f = 0.40 (SiO_2; CH_2Cl_2/MeOH, 92:8, v/v); m.p. 201 °C; ^{1}H NMR (300.1 MHz, $CDCl_3$, 25 °C): δ (assignment by COSY) = 3.06 (s, 6H; OSO_2Me), 3.07 (s, 3H; OSO_2Me), 3.08 (s, 3H; OSO_2Me), 3.14–3.21 (m, 7H; H-2), 3.37 (s, 3H; OMe), 3.38 (s, 3H; OMe), 3.39 (s, 3H; OMe), 3.49 (s, 9H; OMe), 3.50 (s, 6H; OMe), 3.53 (s, 6H; OMe), 3.60 (s, 3H; OMe), 3.61 (s, 3H; OMe), 3.62 (s, 6H; OMe), 3.64 (s, 3H; OMe), 3.66 (s, 3H; OMe), 3.68 (s, 3H; OMe), 3.40–4.05 (m, 27H; H-3, H-4, H-5, H-$6^{C,F,G}$), 4.32–4.34 (m, 2H; H-$6a^{A,D\text{ or }B,E}$), 4.53–4.70 (m, 6H; H-$6a^{B,E\text{ or }A,D}$, H-$6b^{A,B,D,E}$), 5.08–5.11 (m, 4H; H-1), 5.14 (d, ^3J(H-1,H-2) = 3.6 Hz, 1H; H-1), 5.20 (d, ^3J(H-1,H-2) = 3.9 Hz, 1H, H-1), 5.22 ppm (d, ^3J(H-1,H-2) = 3.9 Hz, 1H; H-1); ^{13}C{^{1}H} NMR (75.5 MHz $CDCl_3$, 25 °C): δ (assignment by HMQC) = 37.2, 37.3 (2C), 37.5 (OSO_2Me), 58.3, 58.4 (2C), 58.5, 58.7, 59.1, 59.2 (2C), 59.36, 59.44, 61.1, 61.2, 61.6 (3C), 61.76, 61.80 (OMe), 69.3 (2C), 69.9 (2C) (C-$6^{A,B,D,E}$), 69.6 (2C), 69.7 (2C) (C-$5^{A,B,D,E}$), 70.9, 71.0 (2C) (C-$6^{C,F,G}$), 71.2 (2C), 71.3 (C-$5^{C,F,G}$), 78.1, 78.4, 80.1, 80.2, 80.6, 80.7 (2C), 81.0, 81.5, 81.6 (5C), 81.7, 81.8, 81.9 (3C), 81.95, 82.04 (C-2, C-3, C-4), 97.7, 98.4, 98.9 (2C), 99.1 (2C), 99.2 ppm (C-1); elemental analysis calcd (%) for $C_{63}H_{112}O_{43}S_4$ (1685.80): C 44.89, H 6.70; found: C 44.88, H 6.65; MS (ESI-TOF): *m/z* (%): 1707.54 (100) $[M + Na]^+$.

P,P′-{6^A,6^B,6^D,6^E-Tetradeoxy-6^A,6^B:6^D,6^E-bis[(*R*)-phenylphosphinidene]-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^F,6^G-heptadeca-*O*-methyl-β-cyclodextrin} diborane (4): A solution of *n*BuLi (1.60 M in hexane, 1.22 mL, 1.96 mmol) was added dropwise to a stirred solution of H_2PPh (0.098 g, 0.098 mL, 0.89 mmol) in THF (16.5 mL) at −78 °C. The temperature of the yellow solution was allowed to rise to room temperature over 1 h whereupon the phosphide dianion precipitated. The resulting yellow suspension was slowly cannulated, within 1 h, into a stirred solution of tetramesylate **9** (0.300 g, 0.18 mmol) in THF (25 mL). The reaction mixture was stirred for 12 h at room temperature, then the solvent was removed in vacuo and excess Li_2PPh was protonated with MeOH (15 mL). After removal of the solvent in vacuo, toluene (100 mL) was added and the resulting suspension was filtered over Celite. Evaporation of the solvent gave a colourless residue, which was dissolved in THF (10 mL) before a solution of BH_3·THF (1.00 M in THF, 0.9 mL, 0.9 mmol) was added dropwise at 0 °C. After stirring for 12 h at room temperature, the solvent was removed in vacuo and the resulting colourless residue was subjected to column chromatography (dried SiO_2; CH_2Cl_2/MeOH, 97:3, v/v) to afford pure **4** (0.120 g, 40%) as a colourless solid. R_f = 0.35 (SiO_2; CH_2Cl_2/MeOH, 92:8, v/v); m.p. 185 °C; ^{1}H NMR (300.1 MHz, $CDCl_3$, 25 °C): δ (assignment by COSY) = 0.89 (br s, 6H; P-BH_3), 1.62–1.64 (m, 4H; H-$6a^{A,B,D,E}$), 2.89–2.91 (m, 2H; H-$6b^{A,D\text{ or }B,E}$), 3.17 (s, 3H; OMe), 3.22 (s, 3H; OMe), 3.27 (s, 3H; OMe), 3.44 (s, 3H; OMe), 3.45 (s, 6H; OMe), 3.45 (s, 3H; OMe), 3.46 (s, 3H; OMe), 3.53 (s, 6H; OMe), 3.57 (s, 3H; OMe), 3.59 (s, 3H; OMe), 3.62 (s, 3H; OMe), 3.64 (s, 6H; OMe), 3.67 (s, 3H; OMe), 3.67 (s, 3H; OMe), 3.10–4.27 (m, 34H; H-2, H-3, H-4, H-$5^{B,E\text{ or }A,D}$, H-$5^{C,F,G}$, H-$6b^{B,E\text{ or }A,D}$, H-$6^{C,F,G}$), 4.60–4.62 (m, 2H; H-$5^{A,D\text{ or }B,E}$), 4.91 (d, ^3J(H-1,H-2) = 3.8 Hz, 1H; H-1), 4.94 (d, ^3J(H-1,H-2) = 3.3 Hz, 2H; H-1), 4.97–5.00 (m, 3H; H-1), 5.11 (d, ^3J(H-1,H-2) = 3.6 Hz, 1H; H-1), 7.46–7.47 (m, 6H; *m*-H, *p*-H), 7.77–7.83 ppm (m, 4H; *o*-H); ^{13}C{^{1}H} NMR (75.5 MHz $CDCl_3$, 25 °C): δ (assignment by HMQC) = 27.2 (d, ^1J(C,P) = 35.3 Hz), 27.9 (d, ^1J(C,P) = 34.4 Hz; C-$6^{A,D\text{ or }B,E}$), 34.3 (d, ^1J(C,P) = 30.0 Hz), 35.2 (d, ^1J(C,P) = 30.0 Hz; C-$6^{B,E\text{ or }A,D}$), 57.9 (3C), 58.0, 58.2, 58.45, 58.49, 58.7, 58.8, 58.9, 61.5, 61.6 (2C), 61.8, 61.9, 62.20, 62.22 (OMe), 64.5, 64.7 (C-$5^{A,D\text{ or }B,E}$), 68.7 (d, ^2J(C,P) = 6.4 Hz), 69.0 (d, ^2J(C,P) = 5.5 Hz) (C-$5^{B,E\text{ or }A,D}$), 70.57, 71.2, 71.42 (C-$6^{C,F,G}$), 70.9, 71.1, 71.44 (C-$5^{C,F,G}$), 80.1, 80.4, 80.5, 81.2, 81.3, 81.5, 81.8, 82.0, 82.3 (5C), 82.4, 82.5, 83.1, 83.3 (C-2, C-3, C-$4^{C,F,G}$), 86.7 (d, ^3J(C,P) = 10.1 Hz), 87.0 (d, ^3J(C,P) = 10.1 Hz) (C-$4^{A,D\text{ or }B,E}$), 89.1, 89.5 (C-$4^{B,E\text{ or }A,D}$), 98.46, 98.54, 99.6, 100.3, 100.5, 100.8, 101.2 (C-1), 128.7, 128.9 (*m*-C), 131.1, 131.2 (*p*-C), 131.6 (d, ^2J(C,P) = 3.7 Hz; *o*-C), 131.3 (d, ^1J(C,P) = 11.4 Hz; *ipso*-C), 131.7 (d, ^2J(C,P) = 3.7 Hz; *o*-C), 132.2 ppm (d, ^1J(C,P) = 11.4 Hz; *ipso*-C); ^{31}P{^{1}H} NMR (121.5 MHz $CDCl_3$, 25 °C): δ = 17.8 (s), 18.4 ppm (s); elemental analysis calcd (%) for $C_{71}H_{116}B_2O_{31}P_2$·MeOH (1549.23 + 32.04): C 54.69, H 7.65; found: C 54.56, H 7.69; MS (ESI-TOF): *m/z* (%): 1571.71 (100) $[M + Na]^+$.

6^A,6^B,6^D,6^E-Tetradeoxy-6^A,6^B:6^D,6^E-bis[(*R*)-phenylphosphinidene]-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^F,6^G-heptadeca-*O*-methyl-β-cyclodextrin (10): A solution of **4** (0.080 g, 0.52 mmol) in $HNEt_2$ (8 mL) was heated to reflux for 12 h. After cooling to room temperature, the suspension was filtered over Celite and the filtrate was evaporated to dryness in vacuo to afford analytically pure **10** (0.080 g, 99%). R_f = 0.40 (SiO_2; CH_2Cl_2/MeOH, 92:8, v/v); m.p. 195 °C; ^{1}H NMR (300.1 MHz, $CDCl_3$, 25 °C): δ (assignment by COSY) = 1.72–1.74 (m, 2H; H-$6a^{A,D\text{ or }B,E}$), 1.86–1.88 (m, 2H; H-$6a^{B,E\text{ or }A,D}$), 2.81 (td, ^2J(H-6b,P) = ^2J(H-6b,H-6a) = 13.5 Hz, ^3J(H-6b,H-5) = 3.9 Hz, 2H; H-$6b^{A,D\text{ or }B,E}$), 3.05–3.29 (m, 12H; H-2, H-$6a^{C,F,G}$, H-$6b^{B,E\text{ or }A,D}$), 3.11 (s, 3H; OMe), 3.20 (s, 3H; OMe), 3.27 (s, 3H; OMe), 3.30–3.72 (m, 14H; H-3, H-4), 3.47 (s, 3H; OMe), 3.48 (s, 3H; OMe), 3.49 (s, 3H; OMe), 3.50 (s, 6H; OMe), 3.55 (s, 6H; OMe), 3.60 (s, 3H; OMe), 3.62 (s, 3H; OMe), 3.65 (s, 9H; OMe), 3.66 (s, 6H; OMe), 3.81–3.42 (m, 8H; H-$5^{A,D\text{ or }B,E}$, H-$5^{C,F,G}$, H-$6b^{C,F,G}$), 4.29–4.31 (m, 2H; H-$5^{B,E\text{ or }A,D}$), 4.95–5.05 (m, 6H, H-1), 5.22 (d, ^3J(H-1,H-2) = 3.7 Hz, 1H; H-1), 7.20–7.28 (m, 6H; *m*-H, *p*-H), 7.41–7.51 ppm (m, 4H; *o*-H); ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6, 25 °C): δ (assignment by HMQC) = 28.66 (d, ^1J(C,P) = 15.4 Hz; C-$6^{A\text{ or }D}$), 28.69 (d, ^1J(C,P) = 16.2 Hz; C-$6^{D\text{ or }A}$), 35.0 (d, ^1J(C,P) = 19.1 Hz; C-$6^{B\text{ or }E}$), 35.1 (d, ^1J(C,P) = 19.7 Hz; C-$6^{E\text{ or }B}$), 58.1 (2C), 58.2, 58.3, 58.7, 59.10, 59.14, 59.4, 59.68, 59.74, 61.77, 61.79, 61.9, 62.0, 62.1, 62.3 (2C) (OMe), 67.5 (d, ^2J(C,P) = 11.7 Hz; C-$5^{A\text{ or }D}$), 67.6 (d, ^2J(C,P) = 11.7 Hz; C-$5^{D\text{ or }A}$), 71.5 (2C), 71.8 (C-$5^{C,F,G}$), 72.1 (d, ^{TS}J(C,P) = 2.6 Hz; C-6^C), 72.4 (2C; C-$6^{F,G}$), 74.0 (d, ^2J(C,P) = 14.3 Hz; C-$5^{B\text{ or }E}$), 74.3 (d, ^2J(C,P) = 13.6 Hz; C-$5^{E\text{ or }B}$), 79.8, 82.2, 82.3, 82.37, 82.42, 82.97, 83.15, 83.23, 83.36 (3C), 83.4, 83.5, 83.6, 84.1, 84.6, 84.7 (C-2, C-3, C-$4^{C,F,G}$), 87.2 (d, ^3J(C,P) = 8.0 Hz; C-$4^{B\text{ or }E}$), 87.3 (d, ^3J(C,P) = 8.0 Hz; C-$4^{E\text{ or }B}$), 90.2 (d, ^3J(C,P) = 2.7 Hz; C-$4^{A\text{ or }D}$), 90.4 (d, ^3J(C,P) = 2.6 Hz; C-$4^{D\text{ or }A}$), 99.27, 99.32, 99.7, 99.9, 100.0 (2C), 101.2 (C-1), 128.96, 129.03 (*p*-C), 129.15 (overlapping d, ^3J(C,P) = 4.8 Hz, 2C; *m*-C), 132.47

(d, ^2J(C,P) = 18.7 Hz), 132.51 (d, ^2J(C,P) = 18.7 Hz) (*o*-C), 142.3 ppm (d, ^1J(C,P) = 11.7 Hz, 2C; *ipso*-C); ^{31}P{^{1}H} NMR (202.5 MHz, C_6D_6, 25 °C): δ = −15.0 (s), −15.2 ppm (s); elemental analysis calcd (%) for $C_{71}H_{110}O_{31}P_2{\cdot}0.5CH_2Cl_2$ (1521.56 + 42.47): C 54.91, H 7.15; found: C 54.82, H 7.35; MS (ESI-TOF): *m*/*z* (%): 1521.57 (100) $[M + H]^+$.

6^A,6^B-Dideoxy-6^A,6^B-(*R*)-phenylphosphinidene-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 (12): A solution of *n*BuLi (1.60 M in hexane, 4.06 mL, 6.50 mmol) was added dropwise to a stirred solution of H_2PPh (0.35 g, 0.35 mL, 3.24 mmol) in THF (40 mL) at −78 °C. The temperature of the yellow solution was allowed to rise to room temperature over 1 h, whereupon the phosphide dianion precipitated. The resulting yellow suspension was slowly cannulated, within 1 h, into a stirred solution of dimesylate **11** (1.26 g, 0.81 mmol) in THF (110 mL). The reaction mixture was stirred for 12 h at room temperature, then the solvent was removed in vacuo and excess Li_2PPh was protonated with MeOH (75 mL). After removal of the solvent in vacuo, toluene (200 mL) was added and the resulting suspension was filtered over Celite. Evaporation of the solvent to dryness in vacuo afforded analytically pure **12** (1.16 g, 97%) as a white solid. R_f = 0.35 (SiO_2; CH_2Cl_2/MeOH, 92:8, v/v); ^{1}H NMR (300.1 MHz, $CDCl_3$, 25 °C): δ (assignment by COSY) = 1.77 (m, 1H; H-6a$^{A\text{ or }B}$), 1.85 (m, 1H; H-6a$^{B\text{ or }A}$), 2.86 (t, ^2J(H-6b,H-6a) = ^2J(H-6b,P) = 13.5 Hz, 1H; H-6b$^{A\text{ or }B}$), 3.16–3.46 (m, 17H; H-2, H-3, H-6b$^{B\text{ or }A}$, H-4^{A,B}), 3.23 (s, 3H; OMe), 3.28 (s, 3H; OMe), 3.35 (s, 3H; OMe), 3.37 (s, 6H; OMe), 3.47 (s, 3H; OMe), 3.50 (s, 9H; OMe), 3.51 (2×s, 6H; OMe), 3.54 (s, 3H; OMe), 3.61 (s, 3H; OMe), 3.65 (s, 9H; OMe), 3.66 (s, 6H; OMe), 3.67 (s, 3H; OMe), 3.95–3.32 (m, 20H; H-4^{C,D,E,F,G}, H-5^{C,D,E,F,G}, H-6^{C,D,E,F,G}), 4.00 (m, 1H; H-5$^{A\text{ or }B}$), 4.27 (m, 1H; H-5$^{B\text{ or }A}$), 5.00 (d, ^3J(H-1,H-2) = 4.8 Hz, 1H; H-1), 5.01 (d, ^3J(H-1,H-2) = 4.2 Hz, 1H; H-1), 5.02 (d, ^3J(H-1,H-2) = 4.2 Hz, 1H; H-1), 5.11 (d, ^3J(H-1,H-2) = 3.6 Hz, 1H; H-1), 5.15 (d, ^3J(H-1,H-2) = 3.9 Hz, 1H; H-1), 5.19 (d, ^3J(H-1,H-2) = 3.3 Hz, 1H; H-1), 5.24 (d, ^3J(H-1,H-2) = 3.9 Hz, 1H; H-1), 7.30–7.32 (m, 3H, *m*-H, *p*-H), 7.44–7.49 ppm (m, 2H, *o*-H); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 25 °C): δ (assignment by HMQC) = 27.5 (d, ^1J(C,P) = 14.3 Hz; C-6 $^{A\text{ or }B}$), 34.6 (d, ^1J(C,P) = 18.6 Hz; C-6$^{B\text{ or }A}$), 58.0, 58.25, 58.33, 58.4, 58.7 (3C), 58.9, 59.0 (3C), 59.1, 61.1, 61.3, 61.4 (2C), 61.5 (2C), 61.6 (OMe), 66.8 (d, ^2J(C,P) = 11.4 Hz; C-5$^{A\text{ or }B}$), 70.7 (2C), 70.99, 71.03 (2C), 71.27, 71.32 (2C), 71.6, 71.7 (C-5^{C,D,E,F,G}, C-6^{C,D,E,F,G}), 73.3 (d, ^2J(C,P) = 38.9 Hz; C-5$^{B\text{ or }A}$), 78.1, 79.3, 79.9, 80.5, 81.08 (C-4^{C,D,E,F,G}), 81.10 (2C), 81.8 (2C), 82.0 (3C), 82.1 (3C), 82.3 (2C), 83.7 (2C) (C-2, C-3), 86.1 (C-4$^{A\text{ or }B}$), 88.9 (C-4$^{B\text{ or }A}$), 98.4, 98.5 (2C), 98.7, 98.9, 99.1, 99.7 (C-1), 128.4 (d, ^3J(C,P) = 6.6 Hz; *m*-C), 128.6 (*p*-C), 131.6 (d, ^2J(C,P) = 18.7 Hz; *o*-C), 140.6 ppm (d, ^1J(C,P) = 9.6 Hz; *ipso*-C); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$): δ = −15.1 ppm (s); elemental analysis calcd (%) for $C_{67}H_{111}O_{33}P{\cdot}2CH_2Cl_2$: (1475.55 + 169.86): C 50.37, H 7.07; found: C 50.28, H 7.21; MS (ESI-TOF): *m*/*z* (%): 1497.7 $[M + Na]^+$.

6^A,6^B-Dideoxy-6^A,6^B-(*S*)-phenyloxophosphinidene-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 (13): The phosphane oxide **13** was obtained by bubbling air through a solution of **12** in MeOH for 1 h at room temperature. Removal of the solvent in vacuo gave analytically pure **13** as a white solid. R_f = 0.30 (SiO_2; CH_2Cl_2/MeOH, 98:2, v/v); m.p. 201 °C; ^{1}H NMR (300.1 MHz, $CDCl_3$, 25 °C): δ (assignment by COSY) = 1.93 (t, ^2J(H-6a,H-6b) = ^2J(H-6a,P) = 13.2 Hz, 1H; H-6a$^{A\text{ or }B}$), 2.15 (t, ^2J(H-6a,H-6b) = ^2J(H-6a,P) = 16.4 Hz, 1H; H-6a$^{B\text{ or }A}$), 2.90–3.03 (m, 2H; H-6b^{A,B}), 3.11 (s, 3H; OMe), 3.13 (s, 3H; OMe), 3.19–3.94 (m, 36H; H-2, H-3, H-4, H-5^{C,D,E,F,G}, H-6^{C,D,E,F,G}), 3.35 (s, 6H; OMe), 3.37 (s, 3H; OMe), 3.41 (s, 3H; OMe), 3.44 (s, 9H; OMe), 3.46 (s, 3H; OMe), 3.47 (s, 3H; OMe), 3.50 (s, 3H; OMe), 3.55 (s, 3H; OMe), 3.58 (s, 3H; OMe), 3.61 (s, 9H; OMe), 3.62 (s, 3H; OMe), 3.63 (s, 3H; OMe), 4.38 (m, 1H; H-5$^{A\text{ or }B}$), 4.62 (m, 1H; H-5$^{B\text{ or }A}$), 4.90 (d, ^3J(H-1,H-2) = 3.6 Hz, 1H; H-1), 4.94 (d, ^3J(H-1,H-2) = 3.3 Hz, 1H; H-1), 4.98 (d, ^3J(H-1,H-2) = 4.5 Hz, 1H; H-1), 5.05 (d, ^3J(H-1,H-2) = 3.3 Hz, 1H; H-1), 5.06 (d, ^3J(H-1,H-2) = 3.0 Hz, 1H; H-1), 5.10 (d, ^3J(H-1,H-2) = 3.6 Hz, 1H; H-1), 5.12 (d, ^3J(H-1,H-2) = 3.6 Hz, 1H; H-1), 7.41–7.49 (m, 3H; *m*-H, *p*-H), 7.64 ppm (m, 2H; *o*-H); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 25 °C): δ (assignment by HMQC) = 33.4 (d, ^1J(C,P) = 68.0 Hz; C-6$^{A\text{ or }B}$), 38.2 (d, ^1J(C,P) = 66.4 Hz; C-6$^{B\text{ or }A}$), 58.1, 58.3 (2C), 58.4, 58.5, 58.6, 58.7, 58.8 (2C), 59.0 (3C), 61.2, 61.4, 61.5, 61.6 (2C), 61.7, 61.9 (OMe), 63.2 (d, ^2J(C,P) = 5.7 Hz; C-5$^{A\text{ or }B}$), 66.3 (C-5$^{B\text{ or }A}$), 70.6 (4C), 70.9 (3C), 71.3 (3C) (C-5^{C,D,E,F,G}, C-6^{C,D,E,F,G}), 77.3, 78.7, 79.8, 80.5, 80.6, 81.0, 81.4, 81.5, 81.7 (2C), 81.8, 82.0, 82.1 (3C), 82.2, 82.4, 83.6, 86.1 (C-2, C-3, C-4^{C,D,E,F,G}), 86.2 (d, ^3J(C,P) = 11.3 Hz; C-4$^{A\text{ or }B}$), 88.9 (C-4$^{B\text{ or }A}$), 98.8, 98.9, 99.0, 99.2 (2C), 99.6, 100.3 (C-1), 128.8 (d, ^3J(C,P) = 11.3 Hz; *m*-C), 129.2 (d, ^2J(C,P) = 9.1 Hz; *o*-C), 132.0 (*p*-C), 135.0 ppm (d, ^1J(C,P) = 97.4 Hz; *ipso*-C); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 25 °C): δ = 35.9 ppm (s); elemental analysis calcd (%) for $C_{67}H_{111}O_{34}P{\cdot}2CH_2Cl_2$ (1491.55 + 169.86): C 49.88, H 6.98; found: C 50.20, H 7.15; MS (ESI-TOF): *m*/*z* (%): 1513.7 $[M + Na]^+$.

P-{6^A,6^B-Dideoxy-6^A,6^B-(*R*)-phenylphosphinidene-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} borane (14): A solution of $BH_3{\cdot}THF$ (1.00 M in THF, 0.31 mL, 0.31 mmol) was added dropwise to a solution of monophosphane **12** (0.150 g, 0.10 mmol) in THF (10 mL) at 0 °C. After stirring for 12 h at room temperature, the solvent was removed in vacuo and the resulting colourless residue was subjected to column chromatography (dried SiO_2; CH_2Cl_2/MeOH, 97:3, v/v) to afford pure **14** (0.140 g, 95%) as a colourless solid. R_f = 0.35 (SiO_2; CH_2Cl_2/MeOH, 92:8, v/v); m.p. 183 °C; ^{1}H NMR (300.1 MHz, $CDCl_3$, 25 °C): δ = 0.70 (br s, 3H; P-BH_3), 1.78 (m, 1H; H-6a$^{A\text{ or }B}$), 1.98 (m, 1H; H-6a$^{B\text{ or }A}$), 2.85 (dd, ^2J(H-6b,H-6a) = 13.9 Hz, ^3J(H-6b,H-5) = 4.1 Hz, 1H; H-6b$^{B\text{ or }A}$), 3.21 (s, 3H; OMe), 3.26 (s, 3H; OMe), 3.34 (s, 3H; OMe), 3.37 (s, 3H; OMe), 3.42 (s, 3H; OMe), 3.45 (s, 3H; OMe), 3.48 (s, 9H; OMe), 3.50 (s, 3H; OMe), 3.52 (s, 3H; OMe), 3.54 (s, 3H; OMe), 3.61 (s, 3H; OMe), 3.64 (s, 6H; OMe), 3.65 (s, 3H; OMe), 3.68 (s, 9H; OMe), 3.09–4.18 (m, 38H; H-2, H-3, H-4, H-5$^{B\text{ or }A\text{ and }C,D,E,F,G}$, H-6b$^{A\text{ or }B}$, H-6^{C,D,E,F,G}), 4.50 (m, 1H; H-5$^{A\text{ or }B}$), 4.94 (d, ^3J(H-1,H-2) = 3.4 Hz, 1H; H-1), 5.00 (m, 2H; H-1), 5.13 (d, ^3J(H-1,H-2) = 2.6 Hz, 1H; H-1), 5.18 (d, ^3J(H-1,H-2) = 2.9 Hz, 1H; H-1), 5.26 (d, ^3J(H-1,H-2) = 3.7 Hz, 1H; H-1), 5.32 (d, ^3J(H-1,H-2) = 3.3 Hz, 1H; H-1), 7.44–7.48 (m, 3H; *m*-H, *p*-H), 7.71 ppm (t, ^3J(*o*-H,*m*-H) = 8.3 Hz, 2H; *o*-H); ^{13}C{^{1}H} NMR (75.5 MHz $CDCl_3$, 25 °C): δ = 27.9 (d, ^1J(C,P) = 34.9 Hz; C-6$^{B\text{ or }A}$), 34.2 (d, ^1J(C,P) = 31.4 Hz; C-6$^{A\text{ or }B}$), 57.8, 58.1, 58.15, 58.18, 58.5, 58.6, 58.8, 58.9 (2C), 59.0, 59.2, 59.3, 60.9, 61.1, 61.3, 61.5, 61.6, 61.8, 61.9 (OMe), 64.3 (C-5$^{B\text{ or }A}$), 68.1 (d, ^2J(C,P) = 6.8 Hz; C-5 $^{A\text{ or }B}$), 70.2, 70.7 (4C) (C-5^{C,D,E,F,G}), 70.4, 70.9, 71.1 (2C), 71.2 (C-6^{C,D,E,F,G}), 75.9, 78.3, 78.8, 79.9, 80.7, 80.9, 81.6, 81.65, 81.71, 81.9 (2C), 82.0 (4C), 82.1, 82.2, 82.6, 83.2 (C-2, C-3, C-4^{C,D,E,F,G}), 85.3 (d, ^3J(C,P) = 9.9 Hz; C-4$^{A\text{ or }B}$), 89.1 (C-4$^{B\text{ or }A}$), 97.6, 98.1, 98.20, 98.24, 98.3, 98.7, 99.7 (C-1), 128.8 (d, ^3J(C,P) = 9.7 Hz; *m*-C), 131.2 (d, ^2J(C,P) = 8.5 Hz; *o*-C), 131.3 (*p*-C), 131.7 ppm (d, ^1J(C,P) = 52.9 Hz; *ipso*-C); elemental analysis calcd (%) for $C_{67}H_{114}BO_{33}P{\cdot}EtOH$ (1489.39 + 46.06): C 53.97, H 7.88; found: C 53.83, H 8.00; MS (ESI-TOF): *m*/*z* (%): 1527.67 (25) $[M + K]^+$, 1511.70 (70) $[M + Na]^+$.

6^A,6^B,6^D,6^E-Tetradeoxy-6^A,6^B:6^D,6^E-bis(epithio)-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^F,6^G-heptadeca-*O*-methyl-β-cyclodextrin (15): A solution of tetramesylate **9** (0.150 g, 0.089 mmol) in degassed acetone (5 mL) was treated with [18]crown-6 (0.141 g, 0.534 mmol) followed by powdered hydrated sodium sulfide ($Na_2S{\cdot}9H_2O$; 0.064 g, 0.267 mmol). After 12 h stirring at room temperature, the reaction mixture was evaporated to dryness and the residue was dissolved in saturated aqueous KCl (30 mL) and extracted with CH_2Cl_2 (3×30 mL). The combined organic layers were dried ($MgSO_4$) before removing the solvent. The crude product was purified by column chromatography (SiO_2; CH_2Cl_2/MeOH, 97:3, v/v) to give the desired product **15** (0.061 g, 50%) as a white solid. R_f = 0.42 (SiO_2; CH_2Cl_2/MeOH, 92:8, v/v); m.p. 203 °C; ^{1}H NMR (500.1 MHz, $CDCl_3$, 25 °C): δ (assignment by COSY, TOCSY and ROESY) = 2.66 (m, 2H; H-6a^{B,E}), 2.79 (d, ^2J(H-6a,H-6b) = 16.6 Hz, 2H; H-6a^{A,D}), 3.13 (m, 2H; H-2^{A,D}), 3.17 (dd, ^3J(H-2,H-3) = 9.8 Hz, ^3J(H-1,H-2) = 3.6 Hz, 1H; H-2^G), 3.19 (dd, ^3J(H-2,H-3) = 9.8 Hz, ^3J(H-1,H-2) = 3.6 Hz, 1H; H-2^C), 3.22 (dd, ^3J(H-2,H-3) = 9.5 Hz, ^3J(H-1,H-2) = 3.6 Hz, 1H; H-2^F), 3.28 (d, ^2J(H-6b,H-6a) = 16.6 Hz, 2H; H-6b^{B,E}), 3.36–3.64 (m, 21H; H-2^{A,D}, H-3, H-4, H-6a^{C,F,G}, H-6b^{A,D}), 3.38 (s, 3H; OMe-6^G), 3.39 (s, 6H; OMe-6^{C,F}), 3.47 (s, 3H; OMe-2^G), 3.48 (s, 3H; OMe-2^C), 3.49 (s, 3H; OMe-2^F), 3.50 (s, 3H; OMe-2^A), 3.51 (s, 3H; OMe-2^D), 3.54 (s, 6H; OMe-2^{B,E}), 3.58 (s, 3H; OMe-3), 3.59 (s, 3H; OMe-3), 3.61 (s, 6H; OMe-3), 3.62 (s, 3H; OMe-3), 3.64 (s, 6H; OMe-3), 3.69 (dd, ^2J(H-6b,H-6a) = 10.3 Hz, ^3J(H-6b,H-5) = 3.8 Hz, 1H; H-6b^C), 3.77–3.82 (m, 3H; H-6b^{F,G}, H-5^G), 3.87–3.89 (m, 2H; H-5^{C,F}), 4.06–4.12 (m, 2H; H-5^{A,D}), 4.16–4.24 (m, 2H; H-5^{B,E}), 4.93 (d, ^3J(H-1,H-2) = 3.4 Hz, 1H; H-1^C), 4.97 (d, ^3J(H-1,H-2) = 3.6 Hz, 1H; H-1^F), 5.01 (d, ^3J(H-1,H-2) = 3.2 Hz, 2H; H-1^{A,D}), 5.05 (br s, 2H; H-1^{B,E}),

5.17 ppm (d, ^3J(H-1,H-2) = 2.7 Hz, 1H; H-1^G); ^{13}C{^{1}H} NMR (150.9 MHz $CDCl_3$, 25 °C): δ (assignment by HMQC) = 30.9 (br s, 2C; C-6^{B,E}), 35.4 (br s, 2C; C-6^{A,D}), 58.1, 58.3, 58.4 (2C), 58.5, 58.6, 59.0 (2C), 59.1, 59.2 , 61.3 (2C), 61.5 (3C), 61.6 (2C) (OMe), 70.7 (3C; C-5^{C,F,G}), 71.1 (3C; C-6^{C,F,G}), 73.5 (2C; C-5^{B,E}), 79.0 (2C; C-5^{A,D}), 80.7, 81.0 (2C), 81.2, 81.3, 81.76 (2C), 81.81 (3C), 81.83 (3C), 82.0 (2C), 82.1, 82.2, 83.5, 84.0, 84.6, 84.7 (C-2, C-3, C-4), 97.8, 98.0, 98.8 (2C), 99.0, 99.3, 99.5 ppm (C-1); elemental analysis calcd (%) for $C_{59}H_{100}O_{31}S_2$ (1369.54): C 51.74, H 7.36; found: C 51.56, H 7.59; MS (ESI-TOF): *m/z* (%): 1391.56 (100) [M + Na]$^+$.

6^A,6^B,6^D,6^E-Tetradeoxy-6^A,6^B:6^D,6^E-bis(sulfate)-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 (18): A solution of freshly distilled thionyl chloride (0.72 g, 0.44 mL, 6.08 mmol) in CH_2Cl_2 (25 mL) was added dropwise to a solution of tetrol **17** (1.57 g, 1.35 mmol) and NEt_3 (0.68 g, 0.93 mL, 6.75 mmol) in CH_2Cl_2 (300 mL) at −78 °C. The reaction mixture was stirred for 1 h at −78 °C whereupon it was allowed to reach 0 °C, quenched with saturated aqueous $NaHCO_3$ (200 mL), and extracted with $CHCl_3$ (3 × 150 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_2Cl_2 (18 mL), MeCN (18 mL) and water (36 mL). Ruthenium trichloride (6 mg, 28×10^{-3} mmol) and sodium periodate (0.64 g, 2.97 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 × 100 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_2Cl_2/MeOH, 97:3, v/v) to afford **18** (1.66 g, 95%) as a colourless solid. R_f = 0.51 (SiO_2; CH_2Cl_2/MeOH, 90:10, v/v); m.p. 189 °C; ^{1}H NMR (300.1 MHz, $CDCl_3$, 25 °C): δ (assignment by COSY) = 3.07 (t, ^3J(H-4,H-3) = ^3J(H-4,H-5) = 9.4 Hz, 2H; H-4$^{A,D\text{ or }B,E}$), 3.13–3.21 (m, 6H; H-2), 3.28 (t, ^3J(H-4,H-3) = ^3J(H-4, H-5) = 9.4 Hz, 2H; H-4$^{B,E\text{ or }A,D}$), 3.38 (s, 6H; OMe), 3.48 (s, 12H; OMe), 3.54 (s, 6H; OMe), 3.61 (s, 6H; OMe), 3.65 (s, 6H; OMe), 3.66 (s, 6H; OMe), 3.42–3.60 (m, 8H; H-3$^{B,E\text{ or }A,D\text{ and }C,F}$, H-4^{C,F}, H-6b^{C,F}), 3.89–3.91 (m, 4H; H-3$^{A,D\text{ or }B,E}$, H-5^{C,F}), 4.01–4.09 (4H; H-6b$^{A,D\text{ or }B,E}$, H-6a^{C,F}), 4.17 (dd, ^3J(H-5,H-4) = 9.9, ^3J(H-5,H-6) = 4.6 Hz, 2H, H-5$^{B,E\text{ or }A,D}$), 4.37 (d, ^2J(H-6b,H-6a) = 9.8 Hz, 2H, H-6b$^{B,E\text{ or }A,D}$), 4.52 (t, ^3J(H-5,H-6a) = ^3J(H-5,H-6b) = 10.2 Hz, 2H; H-5$^{A,D\text{ or }B,E}$), 4.69 (dd, ^2J(H-6a,H-6b) = 9.8, ^3J(H-6a,H-5) = 5.1 Hz, 2H; H-6a$^{B,E\text{ or }A,D}$), 4.93 (d, ^3J(H-1,H-2) = 3.2 Hz, 2H; H-1), 4.98 (overlapping d, 2H; H-6a$^{A,D\text{ or }B,E}$), 5.01 (d, ^3J(H-1,H-2) = 3.2 Hz, 2H; H-1), 5.08 (d, ^3J(H-1,H-2) = 3.6 Hz, 2H; H-1) ppm; ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 25 °C): δ (assignment by HMQC) = 57.7, 58.0, 58.7, 59.2, 61.6, 61.95, 62.00 (OMe), 67.4 (C-5$^{A,D\text{ or }B,E}$), 69.1 (C-5$^{B,E\text{ or }A,D}$), 70.9 (C-6^{C,F}), 71.4 (C-5^{C,F}), 73.0 (C-6$^{A,D\text{ or }B,E}$), 75.0 (C-6$^{B,E\text{ or }A,D}$), 80.9, 81.2 (2C), 81.4, 81.5, 82.3 (2C), 83.6, 86.8 (C-2, C-3, C-4), 98.3, 100.3, 100.6 ppm (C-1); elemental analysis calcd (%) for $C_{50}H_{84}O_{34}S_2 \cdot 0.5CHCl_3$: (1293.31 + 59.69): C 44.83, H 6.29; found: C 44.91, H 6.37; MS (ESI-TOF): *m/z* (%): 1315.42 (100) [M + Na]$^+$.

6^A,6^B,6^D,6^E-Tetradeoxy-6^A,6^B:6^D,6^E-bis(sulfate)-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^F,6^G-heptadeca-*O*-methyl-β-cyclodextrin (19): Prepared from **8** (1.28 g, 0.93 mmol) according to the above procedure (1.34 g, 95%). R_f = 0.51 (SiO_2; CH_2Cl_2/MeOH, 90:10, v/v); m.p. 191 °C; ^{1}H NMR (600.1 MHz, $CDCl_3$, 25 °C): δ (assignment by COSY, TOCSY and ROESY) = 3.11–3.21 (m, 7H; H-2^{A,C,D,F,G}, H-4^{B,E}), 3.26 (dd, ^3J(H-2,H-3) = 9.1 Hz, ^3J(H-1,H-2) = 4.2 Hz, 1H; H-2^B), 3.28 (dd, ^3J(H-2,H-3) = 8.6 Hz, ^3J(H-1,H-2) = 4.2 Hz, 1H; H-2^E), 3.37–3.72 (m, 14H; H-3, H-4^{A,D,F,G}, H-6a^{C,F,G}), 3.39 (s, 3H; OMe-6^C), 3.39 (s, 3H; OMe-6^G), 3.40 (s, 3H; OMe-6^F), 3.49 (s, 12H; OMe-2^{B,C,E,G}), 3.50 (s, 3H; OMe-2^F), 3.56 (s, 3H; OMe-2^A), 3.57 (s, 3H; OMe-2^D), 3.60 (s, 6H; OMe-3), 3.62 (s, 6H; OMe-3), 3.64 (s, 3H; OMe-3),3.65 (s, 6H; OMe-3), 3.78–3.82 (m, 4H; H-4^C, H-5^{C,F,G}), 3.86 (dd, ^2J(H-6b,H-6a) = 10.9 Hz, ^3J(H-6b,H-5) = 3.2 Hz, 1H; H-6b^F), 3.94 (dd, ^2J(H-6b,H-6a) = 11.1 Hz, ^3J(H-6b,H-5) = 2.8 Hz, 1H; H-6b^G), 3.98 (d, ^2J(H-6b,H-6a) = 11.1 Hz, 1H, H-6b^C), 4.13–4.18 (m, 3H; H-5^{A,D}, H-6a^B), 4.24 (m, 1H; H-6a^E), 4.33 (td, ^3J(H-5,H-4) = ^3J(H-5,H-6a) = 10.0 Hz, ^3J(H-5,H-6b) = 1.1 Hz, 1H; H-5^B), 4.41 (td, ^3J(H-5,H-4) = ^3J(H-5,H-6a) = 9.9 Hz, ^3J(H-5,H-6b) = 1.4 Hz, 1H; H-5^E), 4.45 (dd, ^2J(H-6a,H-6b) = 10.1 Hz, ^3J(H-6a,H-5) = 1.0 Hz, 1H; H-6a^A), 4.50 (dd, ^2J(H-6a,H-6b) = 10.1 Hz, ^3J(H-6a,H-5) = 1.0 Hz, 1H; H-6a^D), 4.58 (dd, ^2J(H-6b,H-6a) = 10.1 Hz, ^3J(H-6b,H-5) = 4.2 Hz, 1H; H-6b^D), 4.61 (dd, ^2J(H-6b,H-6a) = 10.1 Hz, ^3J(H-6b,H-5) = 4.4 Hz, 1H; H-6b^A), 4.86 (d, ^3J(H-1,H-2) = 3.7 Hz, 1H, H-1^C), 4.87 (dd, ^2J(H-6b,H-6a) = 12.3 Hz, ^3J(H-6b,H-5) = 1.7 Hz, 1H; H-6b^E), 4.95 (d, ^3J(H-1,H-2) = 3.7 Hz, 1H; H-1^F), 4.97 (dd, ^2J(H-6b,H-6a) = 12.3 Hz, ^3J(H-6b,H-5) = 1.2 Hz, 1H; H-6b^B), 5.05 (d, ^3J(H-1,H-2) = 3.1 Hz, 1H; H-1^D), 5.06 (d, ^3J(H-1,H-2) = 3.1 Hz, 1H; H-1^A), 5.08 (d, ^3J(H-1,H-2) = 3.3 Hz, 1H; H-1^G), 5.14 (d, ^3J(H-1,H-2) = 4.1 Hz, 1H; H-1^E), 5.16 ppm (d, ^3J(H-1,H-2) = 4.1 Hz, 1H; H-1^B); ^{13}C{^{1}H} NMR (75.5 MHz $CDCl_3$, 25 °C): δ (assignment by HMQC) = 58.2 (3C), 58.5, 58.98, 59.03, 59.1 (3C), 59.4, 61.1, 61.2, 61.3, 61.5, 61.8 (3C) (OMe), 68.4 (3C), 68.6 (C-5^{A,D,B,E}), 70.6 (2C), 70.89 (C-6^{C,F,G}), 70.89, 71.2, 71.3 (C-5^{C,F,G}), 73.8 (3C), 73.9 (C-6^{A,D,B,E}), 80.0, 80.7, 81.2, 81.3 (3C), 81.5 (6C), 81.6, 81.65, 81.70, 81.8 (3C), 82.6, 82.8, 82.9 (C-2, C-3, C-4), 97.9, 98.9, 99.1, 99.7 (2C), 100.4, 100.5 ppm (C-1); elemental analysis calcd (%) for $C_{59}H_{100}O_{39}S_2$: (1497.53): C 47.32, H 6.73, found: C 47.55, H 6.67; MS (ESI-TOF): *m/z* (%): 1519.52 (100) [M + Na]$^+$.

X-ray crystallographic data of 4: Single crystals were obtained by slow diffusion of pentane into a commercial ethyl acetate solution of **4**. $C_{71}H_{116}B_2O_{31}P_2 \cdot 0.5(C_4H_8O_2) \cdot 0.5(C_5H_{12}) \cdot 0.5(H_2O)$; M_r = 1638.33; monoclinic; $P2_1$; a = 13.1531(2), b = 21.8818(3), c = 16.5539(2) Å, β = 104.303(1)°; V = 4616.75(11) Å^3; Z = 2; ρ_{calcd} = 1.179 Mg m^{-3}; $\lambda(Mo_{K\alpha})$ = 0.71073 Å; μ = 0.123 mm^{-1}; $F(000)$ = 1760; T = 150 K. The sample (0.35 × 0.35 × 0.32 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,[34] 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[35] and full-matrix least-square techniques. Use of F^2 magnitude; x, y, z, β_{ij} for C, B, O, P atoms, x, y, z, in riding mode for H atoms; 1033 variables and 15406 observations with $I > 2.0\sigma(I)$; calcd $w = 1/[\sigma^2(F_o^2) + (0.0840\ P)^2]$ where $P = (F_o^2 + 2\ F_o^2)/3$ with the resulting R = 0.0475, R_w = 0.1241, and S_w = 0.954; $\Delta\rho < 0.592$ e Å^{-3}. Flack parameter: 0.02(6).

X-ray crystallographic data of 18: Single crystals of **18** were obtained by slow diffusion of pentane into a dichloromethane solution of the compound. $C_{50}H_{84}O_{34}S_2 \cdot 2(CH_2Cl_2) \cdot 0.5(C_5H_{12})$; M_r = 1499.22; monoclinic; $P2_1$; a = 14.6490(2), b = 16.4157(2), c = 16.0156(2) Å, β = 109.185(1)°; V = 3637.43(8) Å^3; Z = 2; ρ_{calcd} = 1.369 Mg m^{-3}; $\lambda(Mo_{K\alpha})$ = 0.71073 Å; μ = 0.306 mm^{-1}; $F(000)$ = 1586; T = 150 K. The sample (0.26 × 0.22 × 0.22 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,[34] 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[35] and full-matrix least-square techniques. Use of F^2 magnitude; x, y, z, β_{ij} for C, O, S atoms, x, y, z, in riding mode for H atoms; 874 variables and 11936 observations with $I > 2.0\sigma(I)$; calcd $w = 1/[\sigma^2(F_o^2) + (0.1186\ P)^2]$ where $P = (F_o^2 + 2\ F_o^2)/3$ with the resulting R = 0.0506, R_w = 0.1476, and S_w = 0.842; $\Delta\rho < 1.306$ e Å^{-3}. Flack parameter: 0.00(5).

CCDC-744760 (**4**) and 738543 (**18**) contain the supplementary crystallographic data for this report. These data can be obtained free of charge from The Cambridge Christallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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