Electronic Supplementary Material (ESI) for Chemical Communications

Cavitand supported Tetraphosphine: Cyclodextrin offers a useful platform for Suzuki-Miyaura cross-coupling

Elena Zaborova, Julia Deschamp, Samuel Guieu, Yves Blériot, Giovanni Poli, Mickaël Ménand, David Madec*, Guillaume Prestat* and Matthieu Sollogoub*

UPMC Univ Paris 06, Institut Universitaire de France, Institut Parisien de Chimie Moléculaire (UMR CNRS 7201), FR 2769, C. 181, 4 place Jussieu, 75005 Paris, France

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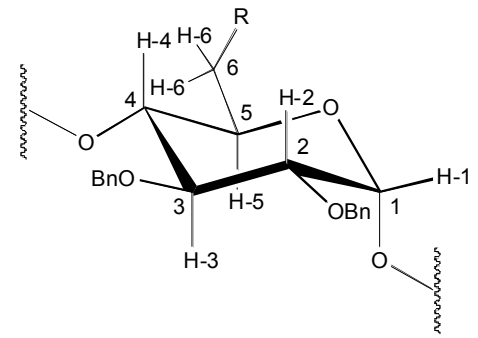
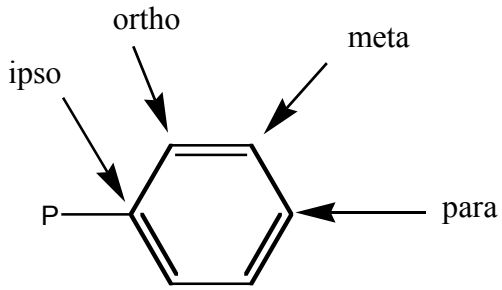
General :

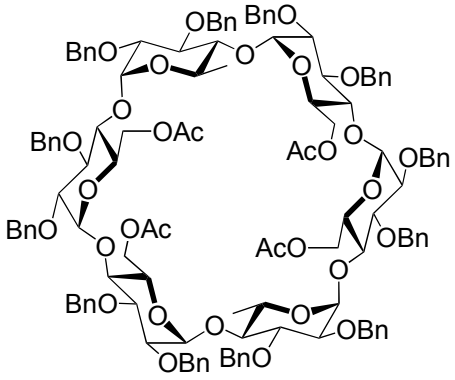
Solvents were freshly distilled from Na/benzophenone (THF, toluene), or P_2O_5 (CH_2Cl_2). Xylenes were freshly distilled over sodium, and degassed by freeze-pump-thaw method. Dichloromethane was freshly distilled on P_2O_5 and purged by bubbling argon for 2h. Reactions were carried under Ar. Optical rotations were measured on a Perkin Elmer 241 digital polarimeter with a path length of 1 dm. Fast Atom Bombardment Mass Spectra (FAB-MS) were obtained with a JMS-700 spectrometer. Elemental analyses were performed by the Centre Régional de Masures Physiques de l'Ouest in Rennes, France. ^{1}H NMR spectra were recorded with a Bruker DRX 400 for solutions in $CDCl_3$ at ambient temperature. Assignments were aided by COSY experiments. ^{13}C NMR spectra were recorded at 100.6 MHz with a Bruker DRX 400 spectrometer for solutions in $CDCl_3$ adopting 77.00 ppm for the central line of $CDCl_3$. Assignments were aided by J-mod technique and HMQC. The numbering of the atoms within a glucose unit is the usual one (see below). Reactions were monitored by thin-layer chromatography (TLC) on a precoated plate of silica gel 60 F_{254} (layer thickness 0.2 mm; E. Merck, Darmstadt, Germany) and detection by charring with sulfuric acid. Flash column chromatography was performed on silica gel 60 (230-400 mesh, E. Merck). Diisobutylaluminium was purchased from Aldrich as a 1.5 M solution in toluene.

Nomenclature for protons and carbons position is precised below:





6^{A}, 6^{D}-dideoxy-6^{B}, 6^{C}, 6^{E}, 6^{F} -Tetra-*O*-Acetate-$2^{A\text{-}F}$,$3^{A\text{-}F}$-Dodeca-*O*-Benzyl-α-cyclodextrin (3)



To a solution of cyclodextrin **2**[1] (4.1 g, 1.723 mmol, 1 eq.) in Ac_2O (50 mL) at –35°C under argon, was added dropwise a solution of TMSOTf (1.33 mL, 6.89 mmol, 4 eq.) in CH_2Cl_2 (5 mL). After 2 h stirring, saturated $NaHCO_3$ (10 mL) at –10°C was added, then water (10 mL). The aqueous layer was extracted with CH_2Cl_2 (3×30 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. Silica gel flash chromatography of the residue (cyclohexane/EtOAc: 2/1) afforded the cyclodextrin **3** (2.87 g, 76 %) as a white foam.

$[\alpha]_D^{20}$ +39.2 (*c* 1.0, $CHCl_3$) ;

R_f 0.25 (cyclohexane/AcOEt : 2/1) ;

^{1}H NMR ($CDCl_3$, 400 MHz) : δ 7.28-7.19 (m, 30H, H arom.), 5.46 (d, 1H, $^3J_{1,2}$ 3.7 Hz, H-1), 5.39 (d, 1H, ^2J 10.5 Hz, CHPh), 5.24 (d, 1H, ^2J 10.8 Hz, CHPh), 5.00 (d, 1H, ^2J 11.5 Hz, CHPh), 4.95 (d, 1H, ^2J 10.5 Hz, CHPh), 4.94 (d, 1H, ^2J 11.5 Hz, CHPh), 4.88 (d, 1H, ^2J 10.8 Hz, CHPh), 4.85 (d, 1H, $^3J_{1,2}$ 3.3 Hz, H-1), 4.72 (d, 1H, ^2J 12.3 Hz, CHPh), 4.70 (d, 1H, $^3J_{1,2}$ 3.5 Hz, H-1), 4.63 (d, 1H, ^2J 12.6 Hz, CHPh), 4.56-4.41 (m, 8H, 4×CHPh, 4×H-6), 4.36 (dd, 1H, $^3J_{2,3}$ 5.2, $^3J_{3,4}$ 11.9 Hz, H-3), 4.23 (dd, 1H, $^3J_{2,3}$ 8.3, $^3J_{3,4}$ 9.7 Hz, H-3), 4.17-4.05 (m, 4H, H-3, 3×H-5), 3.81 (dd, 1H, $^3J_{3,4}$ 9.9, $^3J_{4,5}$ 9.8 Hz, H-4), 3.68 (dd, 1H, $^3J_{3,4}$ 9.9, $^3J_{4,5}$ 9.8 Hz, H-4), 3.57 (dd, 1H, $^3J_{1,2}$ 3.7, $^3J_{2,3}$ 9.9 Hz, H-2), 3.52-3.48 (m, 3H, 2×H-2, H-4), 2.10 (s, 3H, $COCH_3$), 2.08 (s, 3H, $COCH_3$), 1.37 (d, 3H, $^3J_{5,6}$ 6.2 Hz, CH_3) ;

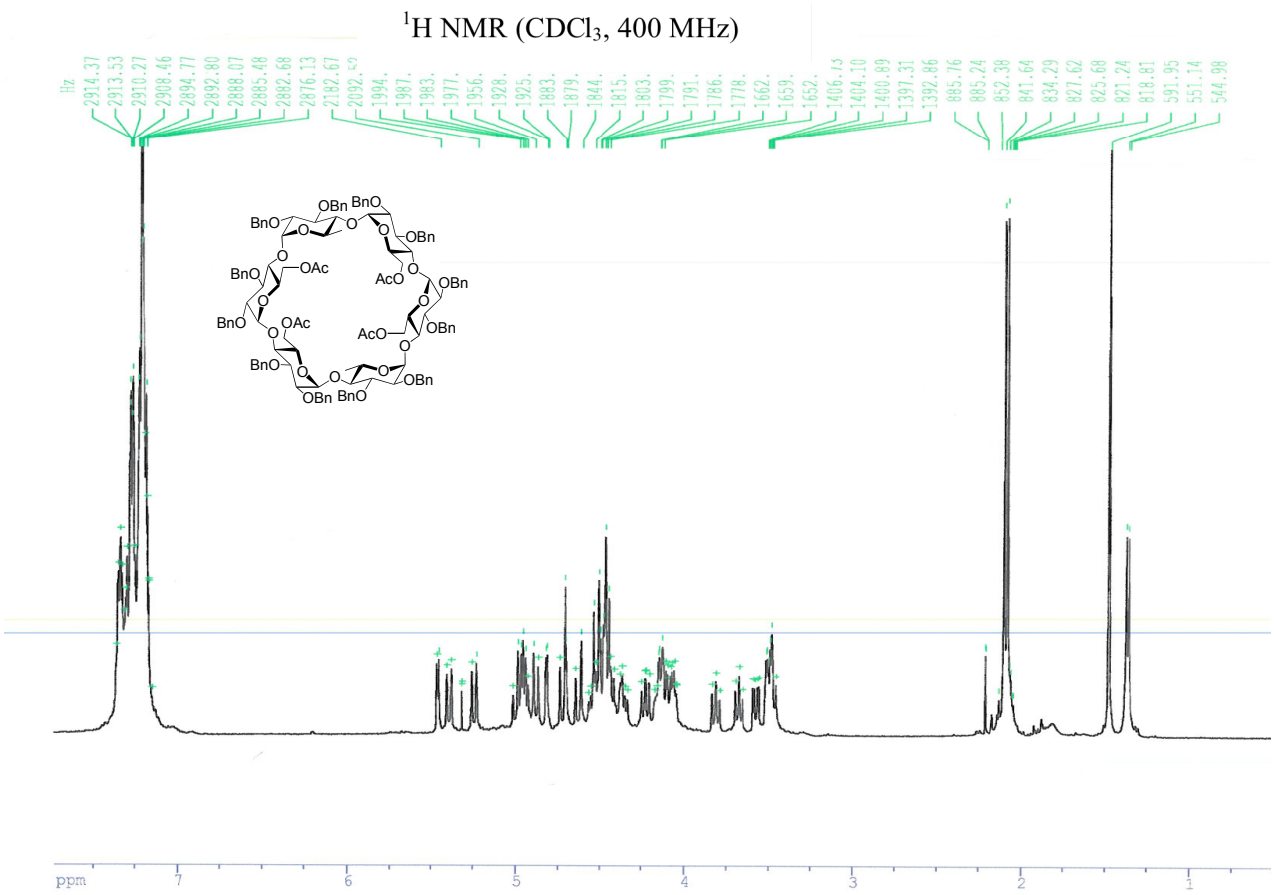
[1] O. Bistri, P. Sinaÿ, M. Sollogoub, *Tetrahedron Lett.* **2005**, *46*, 7757-7760 ; O. Bistri, P. Sinaÿ, J. Jimenez Barbero, M. Sollogoub, *Chem. Eur. J.* **2007,** *13*, 9757-9774.

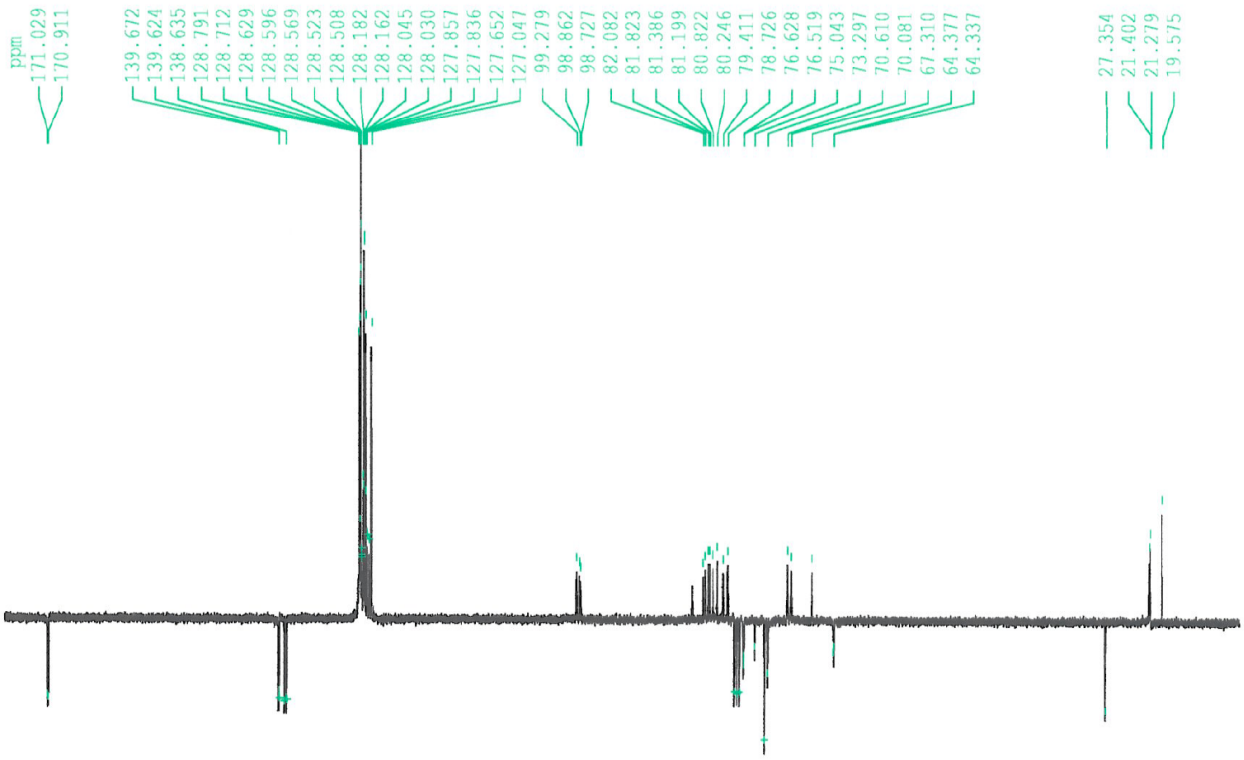
^{13}C RMN ($CDCl_3$, 100 MHz) : δ 171.03, 170.91 (2× $\underline{C}OCH_3$), 139.67, 139.62, 139.54, 138.86, 138.64, 138.51 (6×C arom. quat.), 128.79-127.05 (m, 30×C arom. tert.), 99.28, 98.86, 98.73 (3×C-1), 83.58, 82.08, 81.82 (3×C-4), 81.39, 81.20, 80.82 (3×C-3), 80.25, 79.41, 78.73 (3×C-2), 76.63, 76.52, 75.04, 73.75 (2C), 73.30 (6×CH_2Ph), 70.61, 70.08, 67.31 (3×C-5), 64.38, 64.34 (2×C-6), 21.40, 21.28 (2×CO$\underline{C}H_3$), 19.58 (CH_3) ;

FAB MS $(M+Na)^+$: m/z 2212.8 ;

Anal. Calcd for C_{128} H_{140} O_{32} · 2 CH_3OH: C, 69.26 ; H, 6.62. Found: C, 68.99 ; H, 6.38.

^{1}H NMR ($CDCl_3$, 400 MHz)

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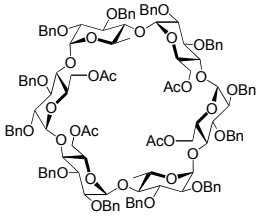
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BnO


ppm
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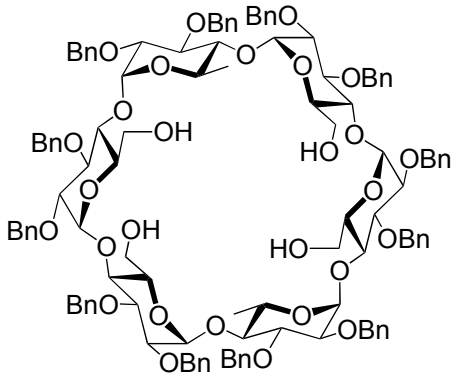
6^{A}, 6^{D}-dideoxy-2^{A-F},3^{A-F}-Dodeca-*O*-Benzyl-α-cyclodextrin (4)



To a solution of cyclodextrin **3** (1.3 g, 594 µmol, 1 eq.) in MeOH (50 mL) was added sodium (285 mg, 11.88 mmol, 20 eq.) in small fractions. After 3 h stirring, IR120 was added untill a pH of 6, the resin was filtrated, and the solvent was evaporated to afford the cyclodextrin **4** (1.197 g, quant.) as a white foam.

$[\alpha]_D^{20}$ +46.5 (*c* 1.0, $CHCl_3$) ;

R_f 0.40 (CH_2Cl_2/MeOH : 95/5) ;

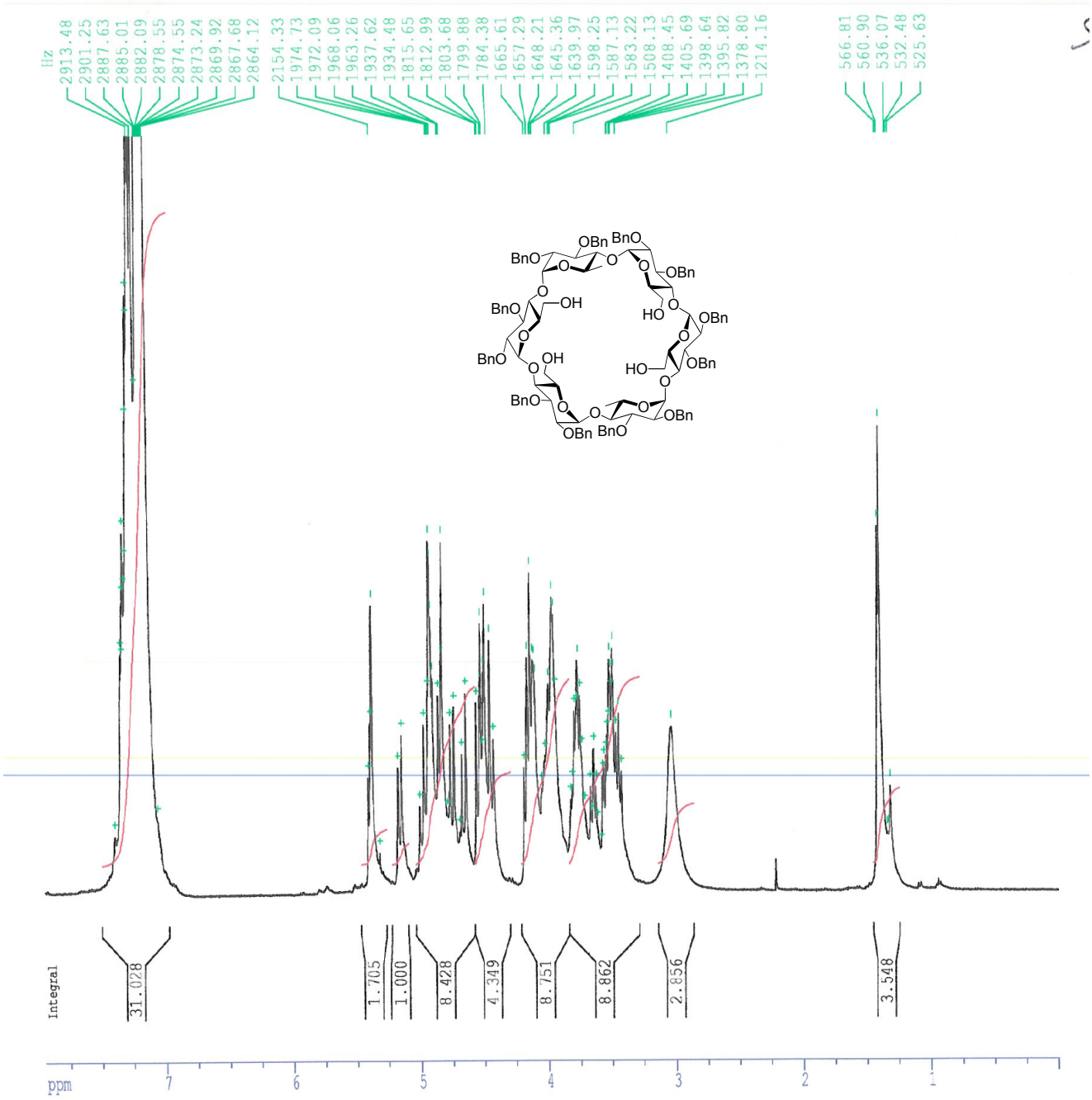
^{1}H NMR ($CDCl_3$, 400 MHz) : δ 7.28-7.16 (m, 30H, H arom.), 5.40 (d, 1H, ^2J 10.1 Hz, CHPh), 5.39 (d, 1H, $^3J_{1,2}$ 3.9 Hz, H-1), 5.16 (d, 1H, ^2J 10.8 Hz, CHPh), 4.99 (d, 1H, ^2J 11.5 Hz, CHPh), 4.94-4.91 (m, 3H, H-1, 2×CHPh), 4.85 (d, 1H, ^2J 10.9 Hz, CHPh), 4.84 (d, 1H, $^3J_{1,2}$ 3.1 Hz, H-1), 4.75 (d, 1H, ^2J 12.1 Hz, CHPh), 4.66 (d, 1H, ^2J 12.4 Hz, CHPh), 4.55 (d, 1H, ^2J 12.5 Hz, CHPh), 4.52 (d, 1H, ^2J 12.0 Hz, CHPh), 4.52 (d, 1H, ^2J 13.3 Hz, CHPh), 4.45 (d, 1H, ^2J 12.3 Hz, CHPh), 4.19-4.10 (m, 4H, 3×H-3, H-6), 4.05-3.94 (m, 5H, 3×H-5, 2×H-6), 3.81-3.74 (m, 2H, H-4, H-6), 3.64 (dd, 1H, $^3J_{3,4}$ 9.3, $^3J_{4,5}$ 8.4 Hz, H-4), 3.55 (dd, 1H, $^3J_{1,2}$ 3.7, $^3J_{2,3}$ 9.9 Hz, H-2), 3.51 (dd, 1H, $^3J_{1,2}$ 3.2, $^3J_{2,3}$ 9.7 Hz, H-2), 3.50 (dd, 1H, $^3J_{1,2}$ 2.8, $^3J_{2,3}$ 9.9 Hz, H-2), 3.45 (dd, 1H, $^3J_{3,4}$ 8.8, $^3J_{4,5}$ 8.1 Hz, H-4), 3.03 (bs, 2H, 2×OH), 1.40 (d, 3H, $^3J_{5,6}$ 5.9 Hz, CH_3) ;

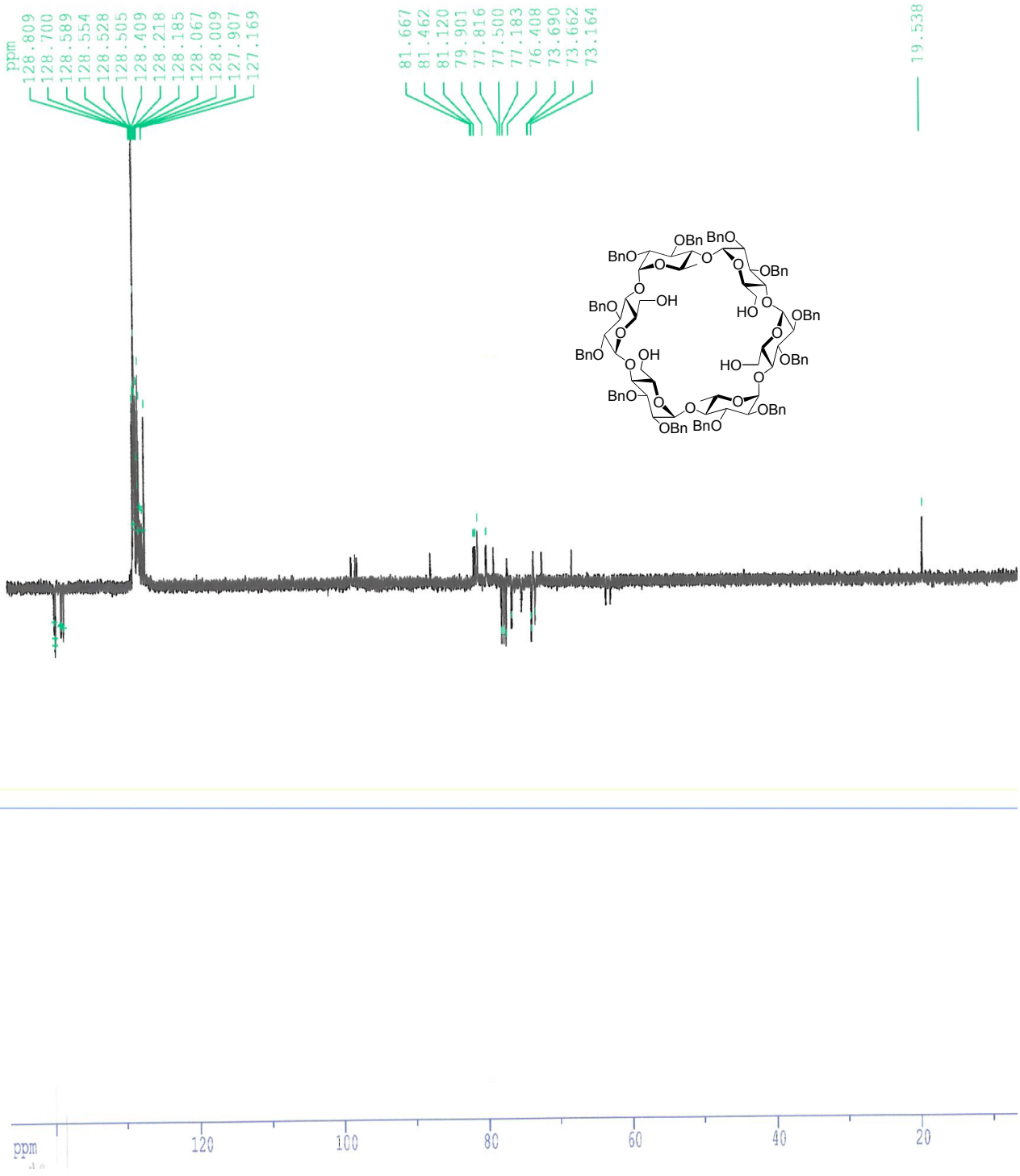
^{13}C RMN ($CDCl_3$, 100 MHz) : δ 139.77, 139.72, 139.64, 138.95, 138.76, 138.68 (6×C arom. quat.), 128.81-127.17 (m, 30×C arom. tert.), 98.64, 98.10, 97.86 (3×C-1), 87.64 (C-2), 81.67 (C-3), 81.46 (C-4), 81.12 (2×C-3), 79.95 (C-2), 79.80 (C-4), 78.88 (C-2), 76.34 (C-4), 76.24, 76.21, 74.98, 73.58,

73.55 (5×CH_2Ph), 73.41 (C-5), 73.20 (CH_2Ph), 72.18, 68.10 (2×C-5), 63.34, 62.73 (2×C-6), 19.54 (CH_3) ;

FAB MS $(M+Na)^+$: m/z 2044.7 ;

Anal. Calcd for C_{120} H_{132} O_{28}: C, 71.27 ; H, 6.58. Found: C, 70.91 ; H, 6.62.

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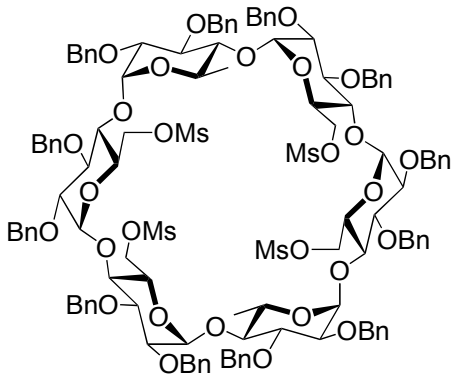
80
60
40
20

6^{A}, 6^{D}-dideoxy-6^{B}, 6^{C}, 6^{E}, 6^{F} -Tetra-*O*-Mesylate-2^{A-F},3^{A-F}-Dodeca-*O*-Benzyl-α-cyclodextrin (5)



To a solution of cyclodextrin **4** (1.197 g, 593 µmol, 1 eq.) in CH_2Cl_2 (10 mL) were added Et_3N (660 µL, 4.74 mmol, 8 eq.) and MsCl (370 µL, 4.74 mmol, 8 eq.) at 0°C. The reaction mixture was stirred at r.t. for 1 h under argon, then water (5 mL) was added, the phases were separated and the aqueous layer was extracted with CH_2Cl_2 (3×10 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated. Silica gel flash chromatography of the residue (CH_2Cl_2/MeOH : 95/5) afforded the mesylated cyclodextrin **5** (1.317 g, 95 %) as a white foam.

$[\alpha]_D^{20}$ +38.5 (*c* 1.0, $CHCl_3$) ;

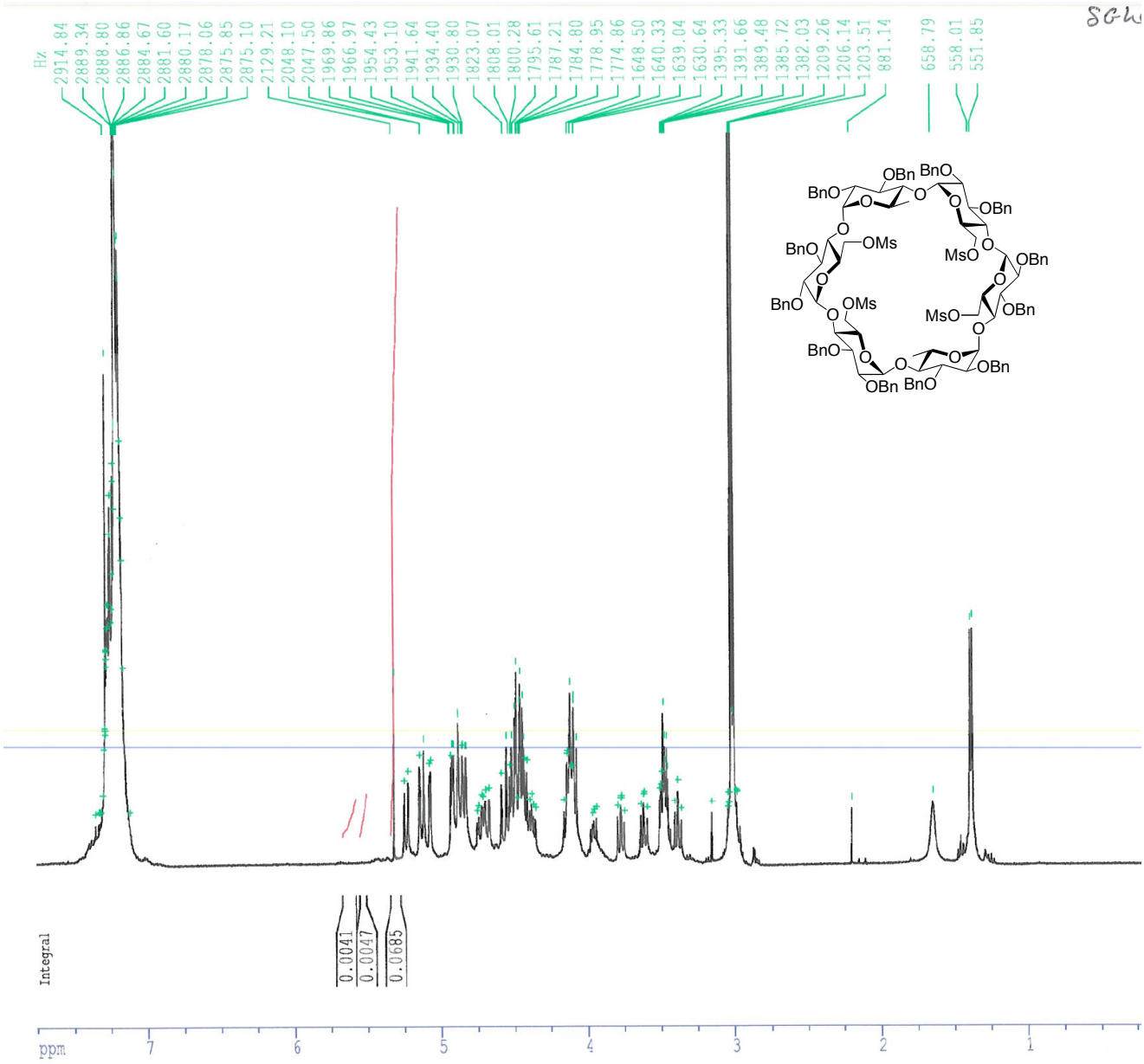
R_f 0.80 (CH_2Cl_2/MeOH : 95/5);

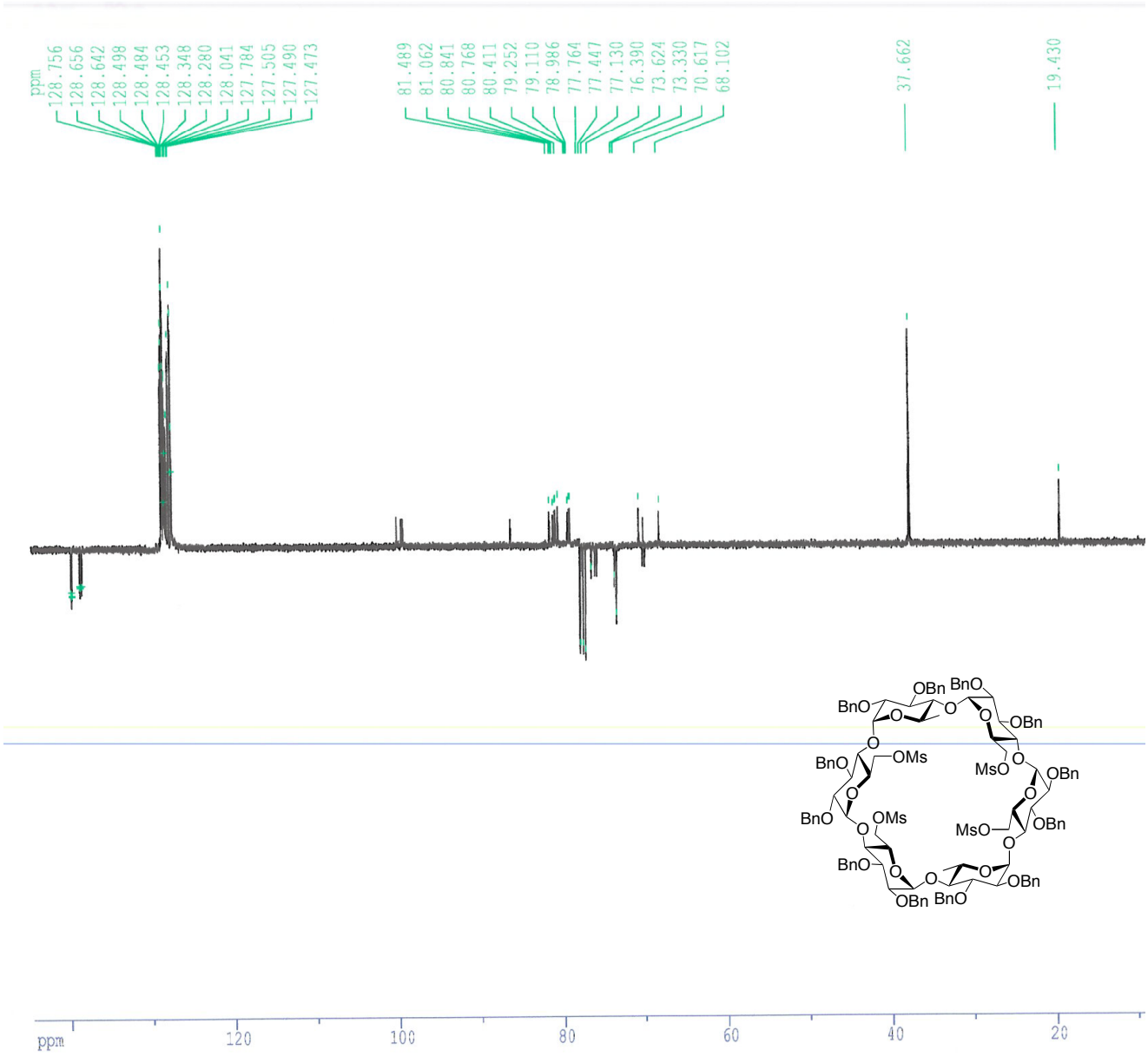
^{1}H NMR ($CDCl_3$, 400 MHz) : δ 7.28-7.19 (m, 30H, H arom.), 5.24 (d, 1H, ^2J 10.9 Hz, CHPh), 5.13 (d, 2H, ^2J 11.1 Hz, 2×CHPh), 5.08 (d, 1H, $^3J_{1,2}$ 3.5 Hz, H-1), 4.93 (d, 1H, $^3J_{1,2}$ 3.5 Hz, H-1), 4.90 (d, 1H, ^2J 12.5 Hz, CHPh), 4.87 (d, 1H, ^2J 11.0 Hz, CHPh), 4.87 (d, 1H, ^2J 11.5 Hz, CHPh), 4.83 (d, 1H, $^3J_{1,2}$ 3.6 Hz, H-1), 4.73 (dd, 1H, $^3J_{5,6}$ 3.8, ^2J 11.2 Hz, H-6), 4.69 (d, 2H, ^2J 9.5 Hz, 2×CHPh), 4.57 (d, 1H, ^2J 12.4 Hz, CHPh), 4.51 (dd, 1H, $^3J_{5,6}$ 4.8, ^2J 12.5 Hz, H-6), 4.50 (d, 1H, ^2J 12.5 Hz, CHPh) , 4.48 (d, 1H, ^2J 10.6 Hz, CHPh), 4.45 (d, 1H, ^2J 12.3 Hz, CHPh), 4.44 (dd, 1H, $^3J_{5,6}$ 5.9, ^2J 12.6 Hz, H-6), 4.38 (dd, 1H, $^3J_{5,6}$ 5.5, ^2J 10.9 Hz, H-6), 4.16-4.08 (m, 5H, 3×H-3, 2×H-5), 3.96 (dq, 1H, $^3J_{4,5}$ 9.1, $^3J_{5,6}$ 6.2 Hz, H-5), 3.77 (dd, 1H, $^3J_{3,4}$ 8.5, $^3J_{4,5}$ 9.5 Hz, H-4), 3.62 (dd, 1H, $^3J_{3,4}$ 8.4, $^3J_{4,5}$ 9.5 Hz, H-4), 3.51-3.45 (m, 3H, 3×H-2), 3.39 (dd, 1H, $^3J_{3,4}$ 8.8, $^3J_{4,5}$ 8.7 Hz, H-4), 3.02 (s, 3H, S-CH_3), 3.01 (s, 3H, S-CH_3), 1.39 (d, 3H, $^3J_{5,6}$ 6.2 Hz, CH_3) ;

^{13}C RMN ($CDCl_3$, 100 MHz) : δ 139.61, 139.56, 139.53, 138.56, 138.50, 138.32 (6×C arom. quat.), 128.76-127.47 (m, 30×C arom. tert.), 100.01, 99.43, 99.26 (3×C-1), 86.29, 81.49, 81.06 (3×C-4), 80.84, 80.76, 80.41 (3×C-3), 79.25, 79.11, 78.99 (3×C-2), 76.39, 75.98, 75.70, 73.62, 73.33 (2C) (6×CH_2Ph), 70.62 (C-5), 70.15 (C-6), 70.07 (C-5), 69.84 (C-6), 68.10 (C-5), 37.66 (2×S-CH_3), 19.43 (CH_3) ;

FAB MS $(M+Na)^+$: m/z 2356.3 ;

Anal. Calcd for C_{124} H_{140} O_{36} S_4: C, 63.79 ; H, 6.04. Found: C, 63.72 ; H, 6.13.

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79.110
78.986
77.764
77.447
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73.624
73.330
70.617
68.102
37.662
19.430
OBn
BnO
OMs
MsO
ppm
120
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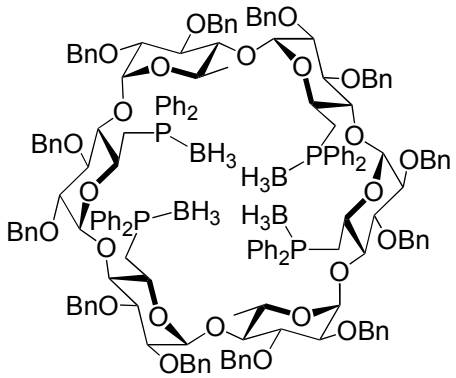
80
60
40
20

P, P', P'', P'''-{6^{A}, 6^{D}-dideoxy-6^{B}, 6^{C}, 6^{E}, 6^{F} -Tetra-(diphenylphosphinyl)-2^{A-F},3^{A-F}-Dodeca-*O*-Benzyl-α-cyclodextrin} Tetraborane (6)



^{n}BuLi (410 µL of a 2.5 M solution in hexane, 1.029 mmol, 8 eq.) was added dropwise at -78°C to a stirred solution of diphenylphosphane (180 µL, 1.029 mmol, 8 eq.) in THF (2 mL). After 30 min., the mesylated cyclodextrin **5** (300 mg, 129 µmol, 1 eq.) in THF (6 mL) was added dropwise. The solution was then allowed to reach room temperature. After 3 h, a BH_3·THF solution (1.0 M in THF, 2.58 mL, 2.58 mmol, 20 eq.) was added and the mixture was stirred for 12 h. MeOH (5 mL) was added dropwise, and the solvents were evaporated. Silica gel flash chromatography of the residue (cyclohexane/EtOAc: 8/1) afforded the cyclodextrin **6** (218 mg, 61 %) as a white foam.

$[\alpha]_D^{20}$ +87.0 (*c* 1.0, $CHCl_3$) ;

R_f 0.50 (cyclohexane/AcOEt : 2/1) ;

^{1}H NMR ($CDCl_3$, 400 MHz) : δ 7.92 (dd, 2H, $^3J_{H,P}$ 8.8, $^3J_{H,H}$ 9.0 Hz, 2×H_{ortho}), 7.61 (dd, 2H, $^3J_{H,P}$ 7.2, $^3J_{H,H}$ 10.7 Hz, 2×H_{ortho}), 7.45-6.93 (m, 36H, 4×$H_{méta}$, 2×H_{para}, 30×H arom. Bn), 5.39 (d, 1H, $^3J_{1,2}$ 3.3 Hz, H-1) , 5.38 (d, 1H, ^2J 12.1 Hz, CHPh), 5.22 (d, 1H, ^2J 10.7 Hz, CHPh), 4.96 (d, 1H, ^2J 11.0 Hz, CHPh), 4.86 (d, 1H, ^2J 10.7 Hz, CHPh), 4.81 (d, 1H, ^2J 11.6 Hz, CHPh), 4.64 (d, 1H, ^2J 11.6 Hz, CHPh), 4.58 (dd, 1H, $^3J_{3,4}$ 9.0, $^3J_{4,5}$ 9.0 Hz, H-4), 4.54 (d, 1H, $^3J_{1,2}$ 2.0 Hz, H-1), 4.53-4.47 (m, 3H, H-4, H-5, CHPh), 4.44 (d, 1H, ^2J 13.6 Hz, CHPh), 4.38 (d, 1H, ^2J 12.7 Hz, CHPh), 4.31 (s, 2H, CH_2Ph), 4.28 (d, 1H, ^2J 13.6 Hz, CHPh), 4.25-4.20 (m, 2H, H-1, H-5), 4.14 (dd, 1H, $^3J_{2,3}$ 8.5, $^3J_{3,4}$ 9.8 Hz, H-3), 4.06 (dd, 1H, $^3J_{2,3}$ 9.0, $^3J_{3,4}$ 9.6 Hz, H-3), 4.02-3.97 (m, 1H, H-5), 3.92 (dd, 1H, $^3J_{2,3}$ 8.6, $^3J_{3,4}$ 9.4 Hz, H-3), 3.73-3.67 (m, 1H, H-6), 3.50 (dd, 1H, $^3J_{1,2}$ 2.8, $^3J_{2,3}$ 8.7 Hz, H-2), 3.44 (dd, 1H, $^3J_{5,6}$ 6.8, ^2J 14.9 Hz, H-6), 3.35 (dd, 1H, $^3J_{1,2}$ 3.3, $^3J_{2,3}$ 9.8 Hz, H-2), 3.29 (dd, 1H, $^3J_{1,2}$ 3.3, $^3J_{2,3}$ 10.1 Hz, H-2),

3.10-3.00 (m, 1H, H-6), 2.95 (dd, 1H, $^{3}J_{3,4}$ 8.8, $^{3}J_{4,5}$ 9.0 Hz, H-4), 2.65-2.57 (m, 1H, H-6), 0.90-1.35 (m, 6H, 2×BH_3), 0.59 (d, 3H, $^{3}J_{5,6}$ 5.9 Hz, CH_3) ;

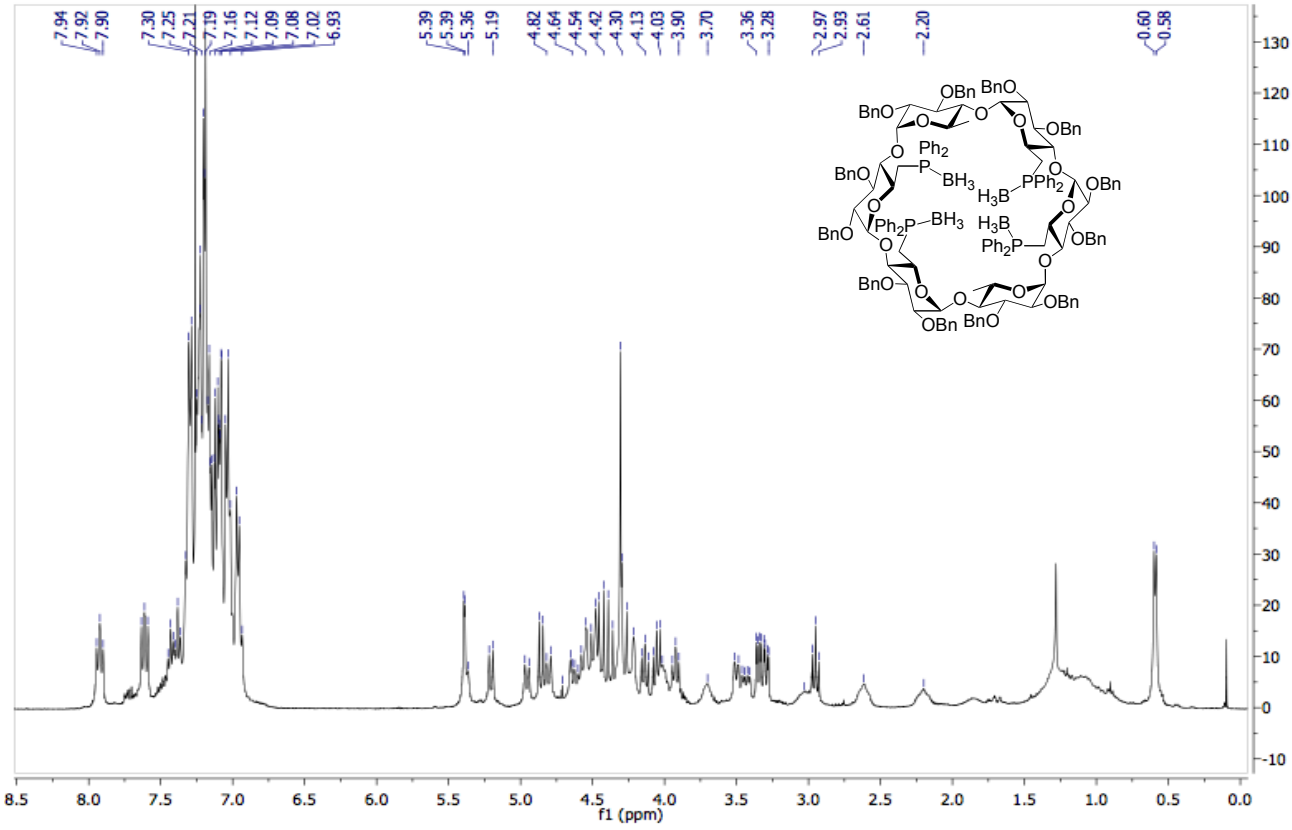
^{13}C RMN ($CDCl_3$, 100 MHz) : δ 140.01, 139.83, 139.77, 138.74, 138.50, 138.47 (6×C arom. quat. Bn), 132.98 (d, $^{2}J_{C,P}$ 9.5 Hz, 2×C_{ortho}), 132.58 (d, $^{2}J_{C,P}$ 9.5 Hz, 2×C_{ortho}), 132.40 (d, $^{2}J_{C,P}$ 8.6 Hz, 2×C_{ortho}), 132.38 (d, $^{1}J_{C,P}$ 59.1 Hz, 2×C_{ipso}), 131.83 (d, $^{2}J_{C,P}$ 8.6 Hz, 2×C_{ortho}), 131.10, 130.81, 130.66, 130.25 (4×C_{para}), 129.66 (d, $^{1}J_{C,P}$ 65.1 Hz, 2×C_{ipso}), 128.75-126.38 (m, 8×C_{meta}, 30×C arom. tert.), 100.63, 99.01, 98.92 (3×C-1), 88.52, 85.17, 83.51 (3×C-4), 80.19, 80.09, 80.03 (3×C-3), 79.93, 78.13, 77.62 (3×C-2), 76.19, 75.71, 74.32, 73.09, 72.97, 71.62 (6×CH_2Ph), 70.75, 69.23, 67.82 (3×C-5), 30.12 (d, $^{2}J_{C,P}$ 48.3 Hz, C-6), 27.14 (d, $^{2}J_{C,P}$ 31.0 Hz, C-6), 18.09 (CH_3) ;

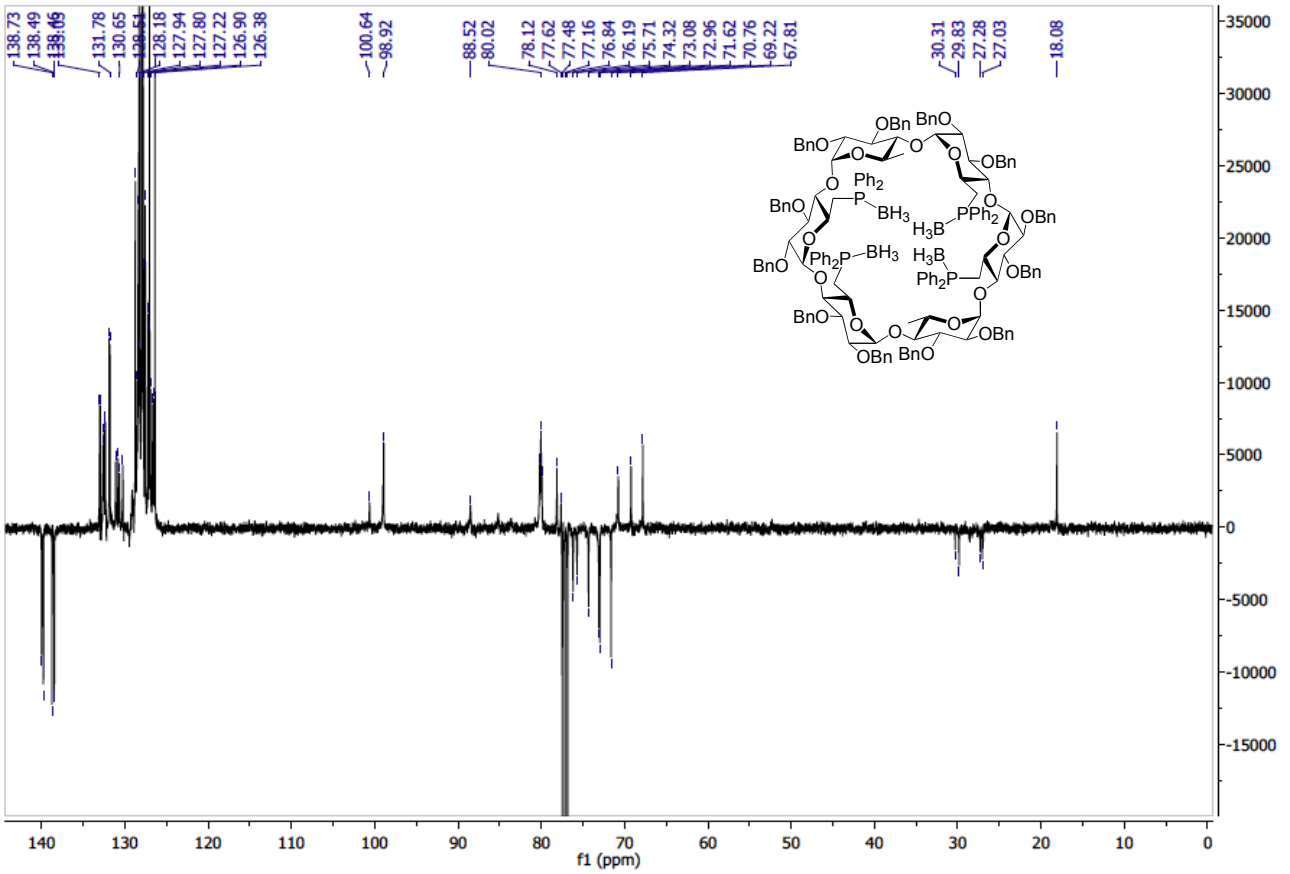
^{31}P RMN ($CDCl_3$, 100 MHz) : δ 15.17, 13.35;

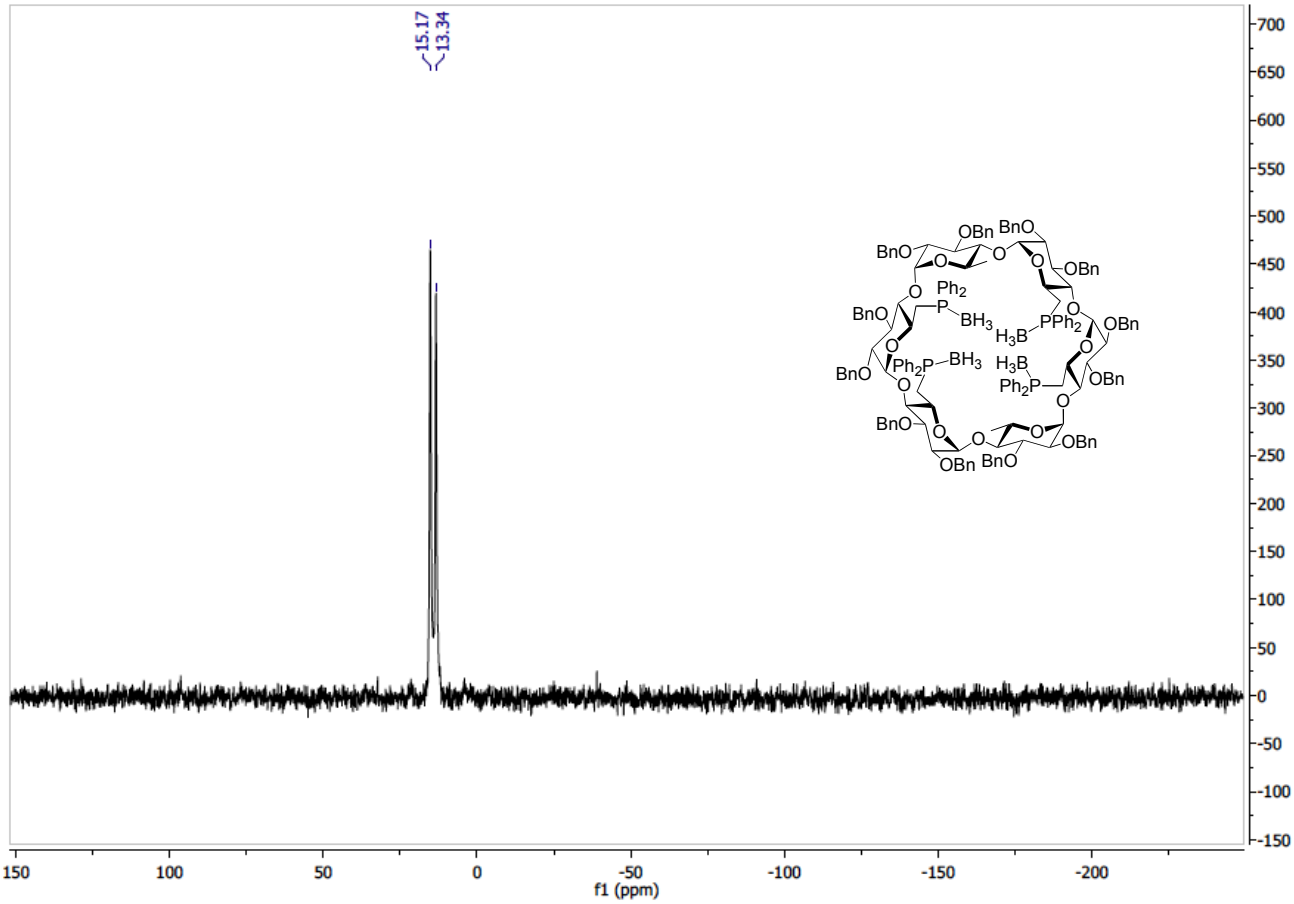
^{11}B NMR ($CDCl_3$, 125 MHz) : δ -37;

HRMS (ESI): calcd for C_{168} H_{180} B_4 K O_{24} P_4: 2788.1888, Found: 2788.1823 (+ 2.3 ppm) ;

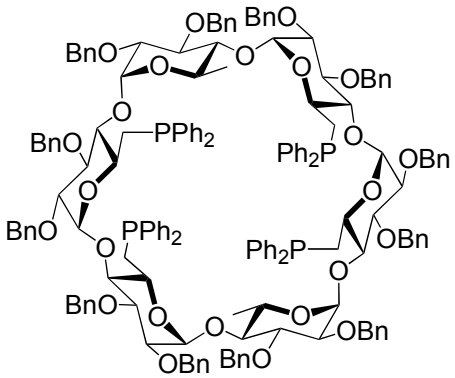
Anal. Calcd for C_{168} H_{180} O_{24} B_4 P_4 : C, 73.37 ; H, 6.60. Found: C, 73.01 ; H, 6.59.




138.73
138.49
131.78
130.65
128.18
127.94
127.80
127.22
126.90
126.38
100.64
98.92
88.52
80.02
78.12
77.62
77.48
77.16
76.84
76.19
75.71
74.32
73.08
72.96
71.62
70.76
69.22
67.81
30.31
29.83
27.28
27.03
18.08
f1 (ppm)


15.17
13.34
f1 (ppm)

6^{A},6^{D}-dideoxy-6^{B},6^{C},6^{E},6^{F} -Tetra-(diphenylphosphinyl)-2^{A-F},3^{A-F}-Dodeca-*O*-Benzyl-α-cyclodextrin (α-Cytep)



Tetraphosphine borane **6** (30 mg, 11 µmol) was refluxed in Et_2NH (3 mL) during 12 h, then cooled down to r.t., filtrated over a celite pad and Et_2NH was evaporated to afford tetraphosphine-CD **α-Cytep**(29 mg, quant.) as a white foam.

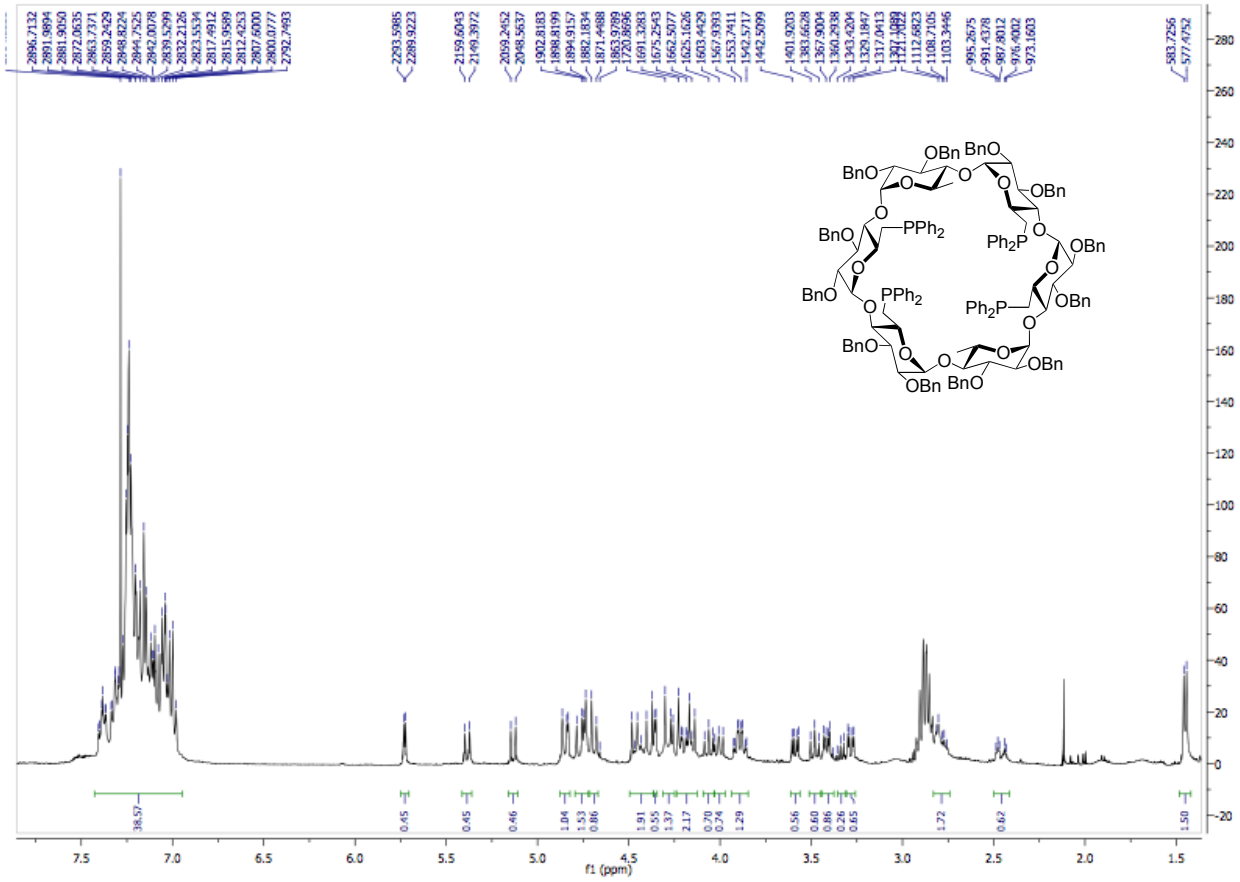
^{1}H NMR ($CDCl_3$, 400 MHz) : δ 7.41-6.97 (m, 50H, H arom.), 5.72 (d, 1H, $^{3}J_{1,2}$ 3.7 Hz, H-1), 5.38 (d, 1H, ^{2}J 10.2 Hz, CHPh), 5.13 (d, 1H, ^{2}J 10.7 Hz, CHPh), 4.86 (d, 1H, ^{2}J 10.0 Hz, CHPh), 4.85 (d, 1H, ^{2}J 12.8 Hz, CHPh), 4.78 (d, 2H, ^{2}J 11.9 Hz, CHPh), 4.76 (d, 1H, $^{3}J_{1,2}$ 4.0 Hz, H-1), 4.72 (d, 1H, ^{2}J 12.7 Hz, CHPh), 4.69 (d, 1H, ^{2}J 10.8 Hz, CHPh), 4.48 (d, 1H, ^{2}J 11.8 Hz, CHPh), 4.47-4.41 (m, 2H, 2×H-5), 4.38 (d, 1H, ^{2}J 12.5 Hz, CHPh), 4.36 (d, 1H, $^{3}J_{1,2}$ 3.0 Hz, H-1), 4.28 (d, 1H, ^{2}J 12.5 Hz, CHPh), 4.24 (d, 1H, ^{2}J 12.2 Hz, CHPh), 4.22-4.16 (m, 2H, H-3, H-5), 4.15 (d, 1H, ^{2}J 12.1 Hz, CHPh), 4.06 (dd, 1H, $^{3}J_{2,3}$ 9.3, $^{3}J_{3,4}$ 9.1 Hz, H-3), 4.01 (dd, 1H, $^{3}J_{2,3}$ 9.8, $^{3}J_{3,4}$ 8.3 Hz, H-3), 3.90 (ddd, 1H, $^{3}J_{3,4}$ 8.5, $^{3}J_{4,5}$ 8.0, $^{3}J_{H,P}$ 2.6 Hz, H-4), 3.88 (ddd, 1H, $^{3}J_{3,4}$ 8.9, $^{3}J_{4,5}$ 8.5, $^{3}J_{H,P}$ 2.4 Hz, H-4), 3.69 (dd, 1H, $^{3}J_{1,2}$ 3.7, $^{3}J_{2,3}$ 10.1 Hz, H-2), 3.48 (dd, 1H, $^{3}J_{3,4}$ 9.0, $^{3}J_{4,5}$ 9.2 Hz, H-4), 3.41 (dd, 1H, $^{3}J_{1,2}$ 3.0, $^{3}J_{2,3}$ 9.7 Hz, H-2), 3.28 (dd, 1H, $^{3}J_{1,2}$ 3.0, $^{3}J_{2,3}$ 9.9 Hz, H-2), 2.95-2.90 (m, 1H, H-6), 2.82-2.75 (m, 2H, 2×H-6), 2.46 (ddd, 1H, $^{3}J_{5,6}$ 3.2, $^{2}J_{H,H}$ 3.7, $^{2}J_{H,P}$ 15.0 Hz, H-6), 1.45 (d, 3H, $^{3}J_{5,6}$ 6.2 Hz, CH_3) ;

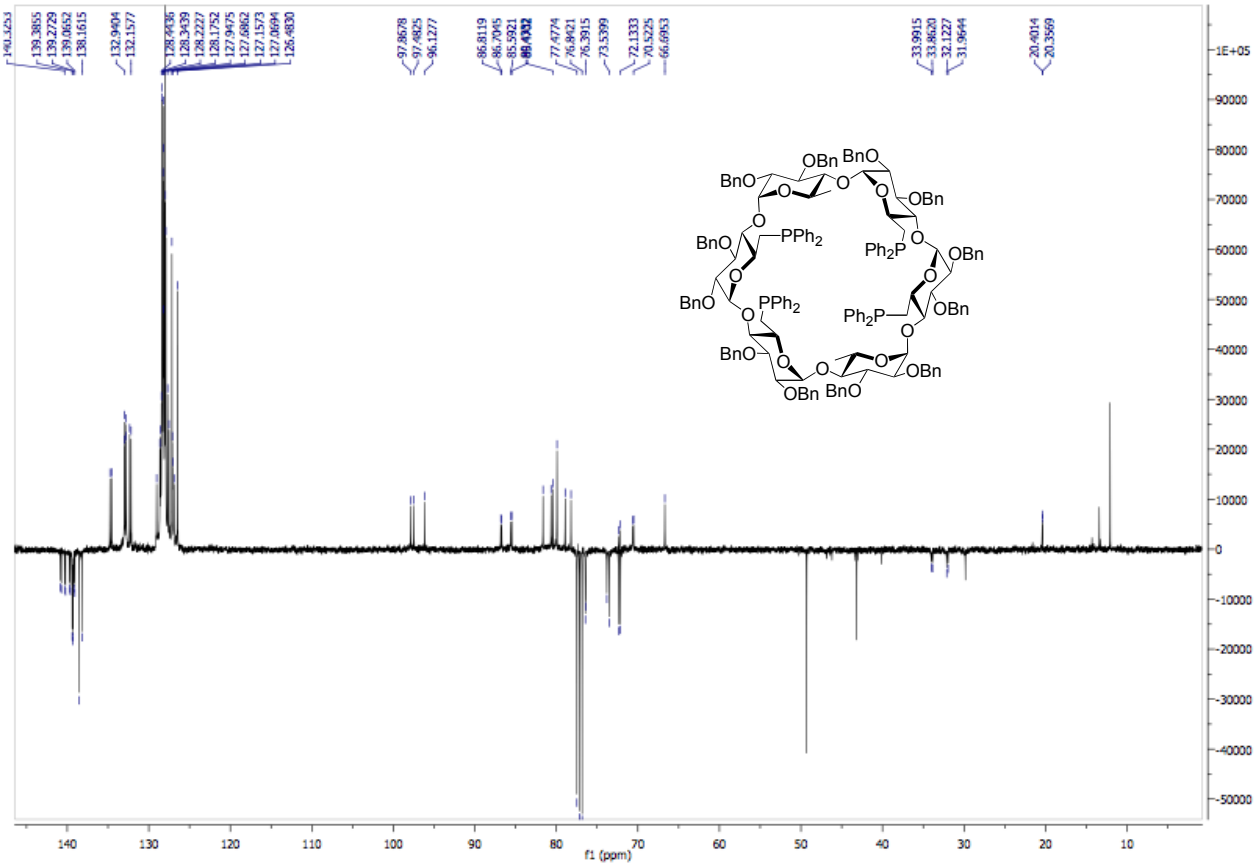
^{13}C RMN ($CDCl_3$, 100 MHz) : δ 140.58 (d, $^{1}J_{C,P}$ 52.3 Hz, C_{ipso}), 140.46 (d, $^{1}J_{C,P}$ 52.3 Hz, C_{ipso}), 139.45 (d, $^{1}J_{C,P}$ 55.2 Hz, C_{ipso}), 139.39 (C arom. quat. Bn), 139.33 (d, $^{1}J_{C,P}$ 54.9 Hz, C_{ipso}), 139.32, 139.27, 138.52 (2C), 138.16 (5×C arom. quat. Bn), 134.77 (C_{para}), 134.56 (C_{para}), 132.88 (d, $^{2}J_{C,P}$ 19.6 Hz, 2×C_{ortho}), 132.85 (d, $^{2}J_{C,P}$ 18.6 Hz, 2×C_{ortho}), 132.25 (d, $^{2}J_{C,P}$ 17.9 Hz, 4×C_{ortho}), 129.04-126.48 (m, 8×C_{meta}, 30×C arom. tert. Bn), 97.87, 97.48, 96.13 (3×C-1), 86.76 (d, $^{3}J_{C,P}$ 10.8 Hz, C-4), 85.53 (d, $^{3}J_{C,P}$ 12.3 Hz, C-4), 81.64, 80.66, 80.43 (3×C-3), 79.92 (2C), 78.93 (3×C-2), 78.20 (C-4), 76.45,

76.39, 73.81, 73.54, 72.38 (5×CH_2Ph), 72.26 (d, $^2J_{C,P}$ 12.8 Hz, C-5), 72.13 (CH_2Ph), 70.58 (d, $^2J_{C,P}$ 10.9 Hz, C-5), 66.70 (C-5), 33.92 (d, $^1J_{C,P}$ 13.0 Hz, C-6), 32.05 (d, $^1J_{C,P}$ 15.9 Hz, C-6), 20.40 (CH_3);

^{31}P RMN ($CDCl_3$, 100 MHz) : δ -20.87, -21.17 ;

HRMS (ESI): calcd for C_{168} H_{169} O_{24} Na P_4: 1359.04373, Found: 1359.04360 (- 0.2 ppm); calcd for C_{168} H_{170} O_{24} P_4: 1348.05275, Found: 1348.05334 (+ 0.5 ppm).

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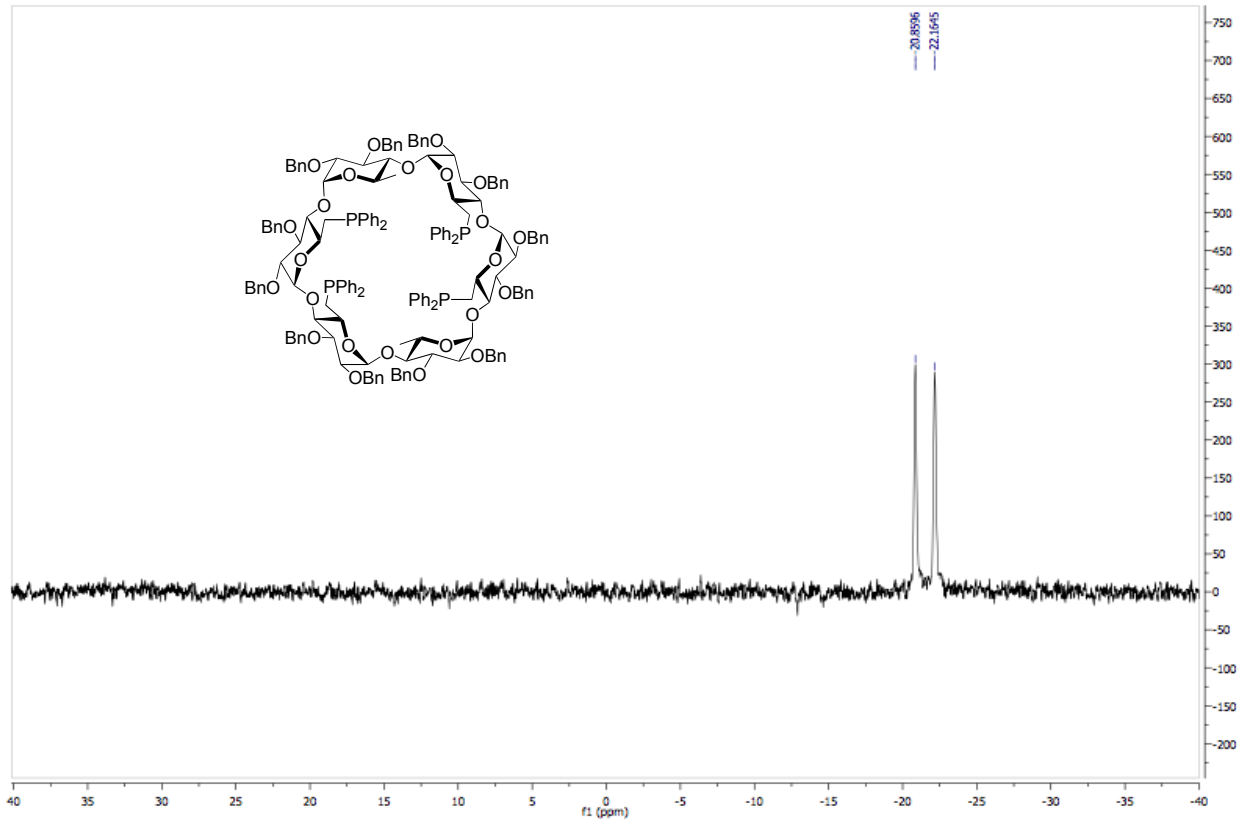
BnO
PPh2
Ph2P
f1 (ppm)


OBn
BnO
PPh2
Ph2P
f1 (ppm)

General procedure for Suzuki couplings

Preparation of the diluted $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ solution for C/S: 10^{-12}

In a flame-dried Schlenk tube reactor equipped with a magnetic stirrer, was introduced $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (3.0 mg, 8.20 µmol), which was purged under argon. The catalyst was dissolved in degassed dichloromethane (20.0 mL). The required amount of the catalyst solution (19.5 mL) was taken off *via* a syringe. To the remaining catalyst solution (0.5 mL) in the schlenk was again added degassed dichloromethane (19.5 mL) and the intended quantity of the diluted catalyst solution (19.5 mL) was once again taken off via a syringe. This operation was reiterated 4 times. To the last remaining catalyst solution (0.5 mL) in the schlenk was added degassed dichloromethane (1.5 mL) and the intended quantity of the diluted catalyst solution (1.5 mL) was once again taken off via a syringe to reach the expected dilution (0.5×10^{-12} mmol).

Preparation of the diluted Cytep solution for C/S: 10^{-12}

In a flame-dried Schlenk tube reactor equipped with a magnetic stirrer containing the deprotected **α-Cytep** (1.0 mg, 0.372 µmol) was introduced degassed dichloromethane (20 mL)(solution A). To a 100 µL of diluted solution A in a schlenk was added dichloromethane (19.9 mL) (solution B). This operation was reiterated 2 times (solution C and D) to obtain the desired concentration (0.430 mL of solution D for 1×10^{-12} mmol).

Coupling reaction

The appropriate solutions of $[Pd(C_3H_5)Cl]_2$ and of tetraphosphine **α-Cytep** were respectively prepared as previously described in degassed dichloromethane.

To the diluted solution of $[Pd(C_3H_5)Cl]_2$ in degassed dichloromethane was added via a purged syringe the diluted solution of tetraphosphine **α-Cytep** under argon atmosphere. This solution was stirred at room temperature for 15 min under argon atmosphere. To this catalyst solution were both introduced the aryl halide (1 mmol, 1 eq.), the arylboronic acid (2 mmol, 2 eq.) and potassium carbonate (2 mmol, 2 eq.). After stirring for 5 minutes at room temperature, degassed anhydrous xylene (4 mL) was added under argon and the reaction mixture was then warmed at 120°C. After complete evaporation of dichloromethane under a stream of argon, the reaction mixture was stirred at 120°C under argon. After the indicated time, the reaction was cooled to room temperature and was quenched by water (5 mL). The aqueous layer was extracted three times with dichloromethane. The combined organic layer was dried over magnesium sulfate and filtered on a pad of silica gel. Then, the solvent

was removed *in vacuo* to give a solid residue. The conversions were determined by integration of the different signals relative to the substrate and the products protons. The NMR yields were determined by using an external standard (butadienesulfone, 0.5 mmol, 0.5 eq.).