

Electronic supporting information

A bifunctional chiral [2]catenane based on 1,1'-binaphthyl-phosphates

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General information:

Analytical methods

The melting point of (*S*)-**4** was measured with a Büchi Melting-Point B-540 apparatus with open end glass capillary tubes. All IR spectra were measured on a Jasco FT/IR-430 spectrometer. The NMR spectra were recorded with a Bruker DMX 600 spectrometer [¹H: 600 MHz, ¹³C: 151 MHz, ³¹P: 243 MHz]. All measurements were performed at room temperature, using d₁-chloroform (CDCl₃), d₆-benzene (C₆D₆) or d₆-DMSO as solvents. The chemical shifts are referenced relative to the residual proton signals of the solvents in the ¹H-NMR (CDCl₃: δ = 7.24 ppm, C₆D₆: δ = 7.15 ppm, d₆-DMSO: δ = 2.50 ppm) or relative to the solvent signal in the ¹³C-NMR (CDCl₃: δ = 77.16 ppm, C₆D₆: δ = 128.0 ppm, d₆-DMSO: δ = 39.51 ppm). The apparent coupling constants are given in Hertz. The description of the fine structure means: s = singlet, br s = broad singlet, d = doublet, ps d = pseudo doublet, br d = broad doublet, t = triplet, m = multiplet. Low resolution ESI mass spectra were recorded on a Bruker Amazon SL spectrometer. High resolution ESI mass spectra were recorded on a Bruker Maxis 4G spectrometer. The high resolution mass spectrum for the precatenane (*S,S*)-**8** was recorded using a Bruker Maxis 4G spectrometer with an APCI 2 source.

Reversed phase medium performance liquid chromatography (MPLC) was performed with the following setup: Armen Instrument Spot Liquid Chromatography Flash system (detection wavelength: 263 nm), YMC GEL ODS-AQ 12 nm, S-50 μm in Kronlab glass columns with 10 mm diameter and 500 mm length. Methanol for MPLC was distilled with ILUDEST MICROPURE distillation system. Water for MPLC was purified with a TKA MicroPure ultrapure water system. Normal phase analytical high performance liquid chromatography (HPLC) was performed with the following setup: Erma Degasser ERC-3512, Merck Hitachi Intelligent Pump L-6200A, Chiralcel OD-H column (0.46 x 25 cm), Knauer Smartline UV-Detector 2600 (detection wavelength 225 nm). Reversed phase analytical high performance liquid chromatography (HPLC) was performed with the following setup: Dionex HPLC system: P680 pump, ASI-100 automated sample injector, UVD-340U UV detector (detection wavelength: 263 nm), UltiMate 3000 Column Compartment; YMC-Pack ODS-A column (3.0 x 150 mm, 5 μm, 12 nm; type: AA12S05-1503QT).

Materials and Methods

For thin layer chromatography (TLC) analysis throughout this work, Polygram® SIL G/UV254 TLC plates (silica gel 0.2 mm, 40 × 80 mm) were used. Visualization of the spots was carried under a 254 nm UV light source. The products were purified by flash column chromatography on silica gel 60M (40-63 μm) which was purchased from MACHEREY-NAGEL GmbH & Co. KG. Dichloromethane, toluene and pyridine were distilled from CaH₂ and stored over molecular sieves under argon. Dimethoxyethane (DME) and aqueous sodium carbonate solution (2 M) were degassed by bubbling with argon for 15 minutes. Phosphoryl chloride (POCl₃) was distilled under vacuum and stored in a Schlenk flask under argon. Aqueous work-ups and column chromatographies were carried out using technical grade solvents. MOM-Cl, *p*-toluenesulfonyl chloride, Pd(PPh₃)₄, Amberlyst® 15 hydrogen form and Grubbs' 2nd generation catalyst were purchased Sigma-Aldrich and used without further purification. 4-hydroxyphenylboronic acid, D-arginine methyl ester bishydrochloride,

D/L-lysine methylester bishydrochloride, (*S,S*)-1,2-diaminocyclohexane and (*R,R*)-1,2-diaminocyclohexane were purchased from TCI and used without further purification. L-arginine methyl ester bishydrochloride was purchased from Bachem and used without further purification. (*S*)-**3**^[1] and O-allyl-hexaethyleneglycol-tosylate^[2] were synthesized according to literature procedures.

Synthetic procedures

Overview:

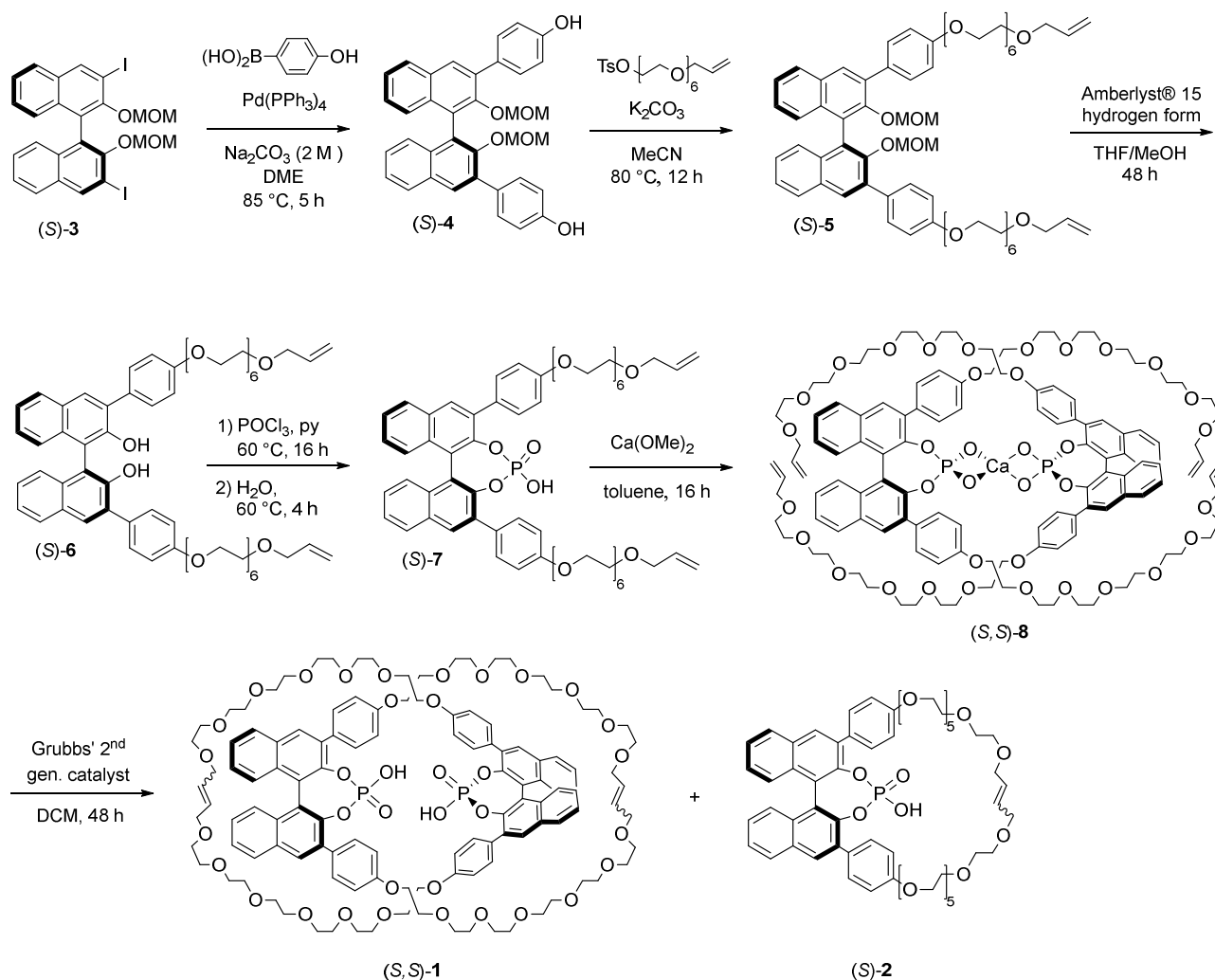
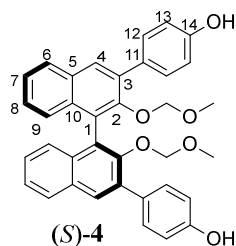


Figure S 1: Overview for the synthesis of (*S,S*)-1

Compound (S)-4:



(S)-3 (1.92 g, 3.07 mmol, 1 equiv), 4-hydroxyphenylboronic acid (1.69 g, 12.3 mmol, 4 equiv) and tetrakis(triphenylphosphine)palladium(0) (0.355 g, 0.307 mmol, 0.1 equiv) were dissolved in degassed dimethoxyethane (DME, 50 mL) under argon atmosphere. To that yellow solution, a degassed sodium carbonate solution (2 M, 8.00 mL, 16.0 mmol, 5.2 equiv) was added. The reaction mixture was refluxed under argon atmosphere and monitored by thin layer chromatography. After 5 h, the reaction mixture was allowed to come to room temperature and tetrahydrofuran (200 ml) was added. The organic layer was washed with a saturated ammonium chloride solution (50 mL). The aqueous layer was further extracted with tetrahydrofuran (3 × 100 mL). All organic layers were combined, dried over anhydrous sodium sulfate, filtered and concentrated in the rotary evaporator. The crude product was purified by a silica gel flash column chromatography using a cyclohexane/ethyl acetate mixture (2:1) to obtain (S)-4 as a yellowish white solid (1.43 g, 2.55 mmol; yield 82.7%).

M.p.: 124 °C. **Anal. Calcd** for C₃₆H₃₀O₆ (558.63): C, 77.40; H, 5.41. Found: C, 77.1; H, 5.51. **IR** (ATR) $\bar{\nu}$ 3489, 3052, 2925, 1610, 1512, 1418, 1382, 1359, 1261, 1233, 1171, 1145, 1125, 1066, 1015, 993, 933, 897, 833, 781, 694, 661, 639, 614, 576 cm⁻¹. **¹H NMR** (600 MHz, CDCl₃) δ 7.90 (s, 2H, H-4), 7.86 (d, J = 8.2 Hz, 2H, H-6), 7.62 (ps d, J = 8.7 Hz, 4H, H-12), 7.39 (ddd, J = 8.1, 5.5, 2.4 Hz, 2H, H-7), 7.27 – 7.23 (m, 4H, H-9 and H-8, merged with CHCl₃ peak), 6.88 (ps d, J = 8.7 Hz, 4H, H-13), 5.24 (br s, 2 H, OH), 4.42 (d, J = 5.7 Hz, 2H, OCH₂), 4.35 (d, J = 5.7 Hz, 2H, OCH₂), 2.35 (s, 6H, OCH₃). **¹³C{¹H} NMR** (151 MHz, CDCl₃) δ 155.3 (C-14), 151.3 (C-2), 135.1 (C-3), 133.5 (C-10), 131.5 (C-11), 131.1 (C-5), 131.0 (C-12), 130.4 (C-4), 127.9 (C-6), 126.7 (C-1), 126.5 (C-9), 126.3 (C-8), 125.4 (C-7), 115.5 (C-13), 98.4 (OCH₂), 56.1 (OCH₃). **COSY** (600 MHz/600 MHz, CDCl₃) δ 7.90/7.86 (H-4/H-6), 7.86/7.90, 7.39 (H-6/H-4, H-7), 7.62/6.88 (H-12/H-13), 7.39/7.86, 7.25 (H-7/ H-6, H-9 and H-8), 7.27 – 7.23/7.39 (H-9 and H-8/H-7), 6.88/7.62 (H-13/H-12). **HSQC** (600 MHz/151 MHz, CDCl₃) δ 7.90/130.4 (H-4/C-4), 7.86/127.9 (H-6/C-6), 7.62/131.0 (H-12/C-12), 7.39/125.4 (H-7/C-7), 7.27 – 7.23/126.5, 126.3 (H-9 and H-8/C-9, C-8), 6.88/115.5 (H-13/C-13), 4.42, 4.35 /98.4 (OCH₂/ OCH₂), 2.35/56.1 (OCH₃/OCH₃). **HMBC** (600 MHz/151 MHz, CDCl₃) δ 7.90/151.3, 133.5, 131.5, 127.9, 126.5 (H-4/C-2, C-10, C-11, C-6, C-9), 7.86/133.5, 130.4, 126.3 (H-6/C-10, C-4, C-8), 7.62/155.3, 135.1, 131.0, (H-12/C-14, C-3, C-12), 7.39/131.1, 126.5 (H-7/C-5, C-9), 7.27 – 7.23/133.5, 131.1, 127.9, 125.4 (H-9 and H-8/C-10, C-5, C-6, C-7), 6.88/155.3, 131.5, 115.5 (H-13/C-14, C-11, C-13), 4.42, 4.35/151.3, 56.1 (OCH₂/ C-2, OCH₃), 2.35/98.4 (OCH₃/ OCH₂). **ESI-pos** (MeOH): m/z = 576.3 ([M+NH₄]⁺), 581.2 ([M+Na]⁺). **HR-ESI-pos** (MeOH): m/z = 581.1928 (calcd 581.1934 for [M+Na]⁺). **HR-ESI-neg** (MeOH): m/z = 557.1960 (calcd 557.1969 for [M-H]⁻).

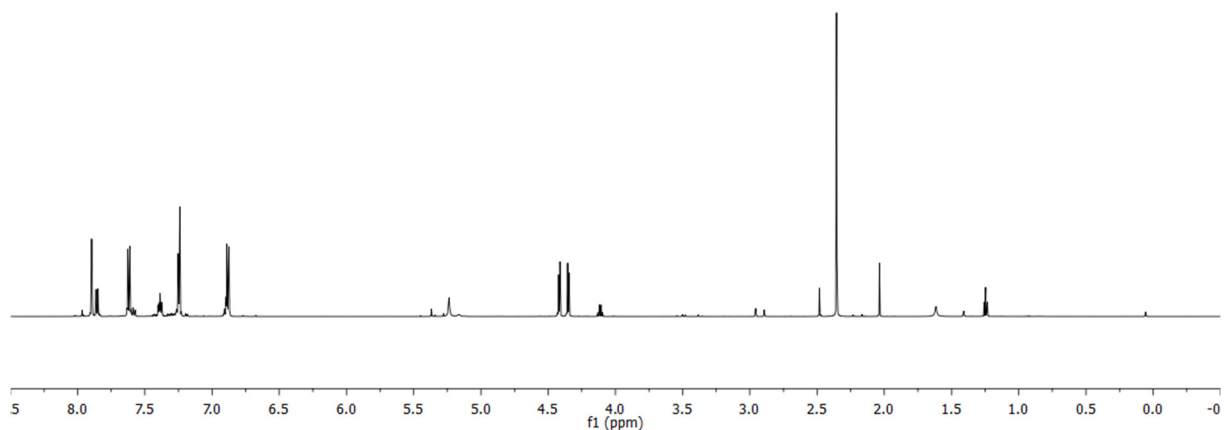


Figure S 2: ^1H NMR of (*S*)-**4** (600 MHz, CDCl_3).

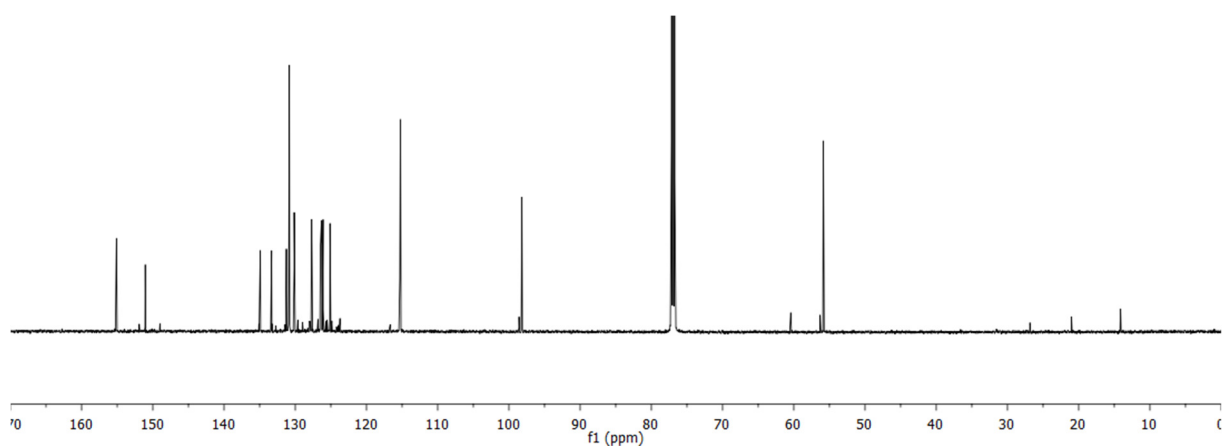
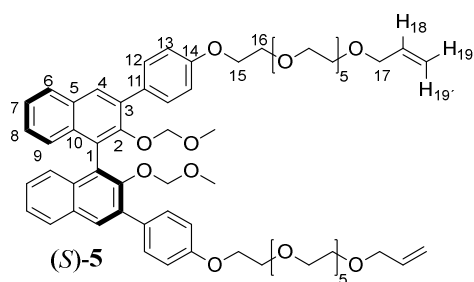


Figure S 3: $^{13}\text{C}\{^1\text{H}\}$ NMR of (*S*)-**4** (151 MHz, CDCl_3).

Compound (*S*)-**5**:



(*S*)-**4** (1.17 g, 2.09 mmol, 1 equiv) and potassium carbonate (0.723 g, 5.24 mmol, 2.5 equiv) were added to acetonitrile (60 mL). The mixture was stirred for 30 minutes, followed by addition of a solution of *O*-allyl-hexaethyleneglycol-tosylate (2.19 g, 4.60 mmol, 2.2 equiv) in acetonitrile (20 mL). The reaction mixture was refluxed overnight. After that, it was allowed to

come to room temperature and filtered. The solvent was removed to give a brown residue. The residue was re-dissolved in ethyl acetate (100 mL) and the organic layer was washed with a saturated brine solution (2 x 20 mL). The organic layer was dried over anhydrous sodium sulfate, filtered and concentrated in the rotary evaporator. The crude product was purified by a silica gel flash column chromatography using an ethyl acetate/methanol mixture (40:1) to obtain (*S*)-**5** as a yellowish viscous liquid (1.73 g, 1.48 mmol; yield 70.8%).

Anal. Calcd for $\text{C}_{66}\text{H}_{86}\text{O}_{18}$ (1167.40): C, 67.91; H, 7.43. Found: C, 67.9; H, 7.37. **IR** (ATR) $\bar{\nu}$ 2871, 1608, 1511, 1455, 1392, 1349, 1267, 1244, 1179, 1099, 995, 969, 924, 835, 730, 700,

618, 576 cm^{-1} . **^1H NMR** (600 MHz, CDCl_3) δ 7.89 (s, 2H, H-4), 7.84 (d, $J = 8.3$ Hz, 2H, H-6), 7.66 (ps d, $J = 8.8$ Hz, 4H, H-12), 7.38 (ddd, $J = 8.1, 5.8, 2.1$ Hz, 2H, H-7), 7.29 – 7.18 (m, 4H, H-9 and H-8, merged with CHCl_3 peak), 6.99 (ps d, $J = 8.8$ Hz, 4H, H-13), 5.89 (ddt, $J = 17.2, 10.4, 5.6$ Hz, 2H, H-18), 5.25 (ddt, $J = 17.2, 1.6, 1.6$ Hz, 2H, H-19'), 5.15 (ddt, $J = 10.4, 1.6, 1.3$ Hz, 2H, H-19), 4.38 (d, $J = 5.8$ Hz, 2H, MOM-OCH₂), 4.34 (d, $J = 5.8$ Hz, 2H, MOM-OCH₂'), 4.20 – 4.13 (m, 4H, H-15), 4.00 (dt, $J = 5.6, 1.4$ Hz, 4H, H-17), 3.91 – 3.82 (m, 4H, H-16), 3.76 – 3.51 (m, 40H, core glycol-OCH₂), 2.32 (s, 6H, MOM-OCH₃). **$^{13}\text{C}\{^1\text{H}\}$ NMR** (151 MHz, CDCl_3) δ 158.4 (C-14), 151.5 (C-2), 135.1 (C-3), 134.9 (C-18), 133.6 (C-10), 131.7 (C-11), 131.0 (C-5), 130.8 (C-12), 130.3 (C-4), 127.9 (C-6), 126.7 (C-1), 126.6 (C-9), 126.2 (C-8), 125.2 (C-7), 117.2 (C-19), 114.6 (C-13), 98.5 (MOM-OCH₂), 72.4 (C-17), 71.0 (core glycol-OCH₂), 70.78, 70.76 (core glycol-OCH₂), 70.7 (core glycol-OCH₂), 69.9 (C-16), 69.6 (core glycol-OCH₂), 67.6 (C-15), 56.0 (MOM-OCH₃). **COSY** (600 MHz/600 MHz, CDCl_3) δ 7.89/7.84 (H-4/H-6), 7.84/7.89, 7.38 (H-6/H-4, H-7), 7.66/6.99 (H-12/H-13), 7.38/7.84, 7.29-7.18 (H-7/ H-6, H-9 and H-8), 7.29 – 7.18/7.38 (H-9 and H-8/H-7), 6.99/7.66 (H-13/H-12), 5.89/5.25, 5.15, 4.00 (H-18/H-19', H-19, H17), 5.25/5.89, 5.15, 4.00 (H-19'/H-18, H-19, H-17), 5.15/5.89, 5.25, 4.00 (H-19/H-18, H-19', H17), 4.38/4.34 (MOM-OCH₂/MOM-OCH₂'), 4.34/4.38 (MOM-OCH₂'/MOM-OCH₂), 4.20 – 4.13/3.91 – 3.82 (H-15/H-16), 4.00/5.89, 5.25, 5.15 (H-17/H-18, H-19', H-19), 3.91 – 3.82/4.20 – 4.13 (H-16/H-15). **HSQC** (600 MHz/151 MHz, CDCl_3) δ 7.89/130.3 (H-4/C-4), 7.84/127.9 (H-6/C-6), 7.66/130.8 (H-12/C-12), 7.38/125.2 (H-7/ C-7z), 7.29 – 7.18/126.6, 126.2 (H-9 and H-8/C-9, C-8), 6.99/114.6 (H-13/C-13), 5.89/135.1 (H-18/C-18), 5.25, 5.15/117.4 (H-19', H-19/C-19), 4.38, 4.34 (MOM-OCH₂, MOM-OCH₂'/MOM-OCH₂), 4.20 – 4.13/98.5 (MOM-OCH₂/MOM-OCH₂'), 4.20 – 4.13/67.6 (H-15/C-15), 4.00/72.4 (H-17/C-17), 3.91 – 3.82/69.9 (H-16/C-16), 3.76 – 3.51/ 71.0, 70.78, 70.76, 70.7, 69.6 (core glycol-OCH₂/core glycol-OCH₂), 2.32/56.0 (MOM-OCH₃/ MOM-OCH₃). **HMBC** (600 MHz/151 MHz, CDCl_3) δ 7.89/151.5, 133.6, 131.7, 127.9, 126.6 (H-4/C-2, C-10, C-11, C-6, C-9), 7.84/133.6, 130.3, 126.2 (H-6/C-10, C-4, C-8), 7.66/158.4, 135.1, 130.8, 114.6 (H-12/C-14, C-3, C-12, C-13), 7.38/131.0, 126.6 (H-7/C-5, C-9), 7.29 – 7.18/133.6, 131.0, 127.9, 126.7, 125.2 (H-9 and H-8/C-10, C-5, C-6, C-1, C-7), 6.99/158.4, 131.7, 114.6 (H-13/C-14, C-11, C-13), 5.89/72.4 (H-18/C-17), 5.25/134.9, 72.4 (H-19'/C-18, C-17), 5.15/72.4 (H-19/C-17), 4.38, 4.34/151.4, 56.0 (MOM-OCH₂/C-2, MOM-OCH₃), 4.20 – 4.13/158.4, 69.9 (H-15/C-14, C-16), 4.00/134.9, 117.2, 69.6 (H-17/C-18, C-19, core glycol-OCH₂), 3.91 – 3.82/71.0, 67.6 (H-16/core glycol-OCH₂, C-15), 3.76 – 3.51/ 71.0, 70.78, 70.76, 70.7, 69.9, 69.6 (core glycol-OCH₂, C-16), 2.32/98.5 (MOM-OCH₃/ MOM-OCH₂). **ESI-pos** (MeOH): $m/z = 1184.7$ ($[\text{M}+\text{NH}_4]^+$), 1189.7 ($[\text{M}+\text{Na}]^+$), 606.3 ($[\text{M}+2\text{Na}]^{2+}$).

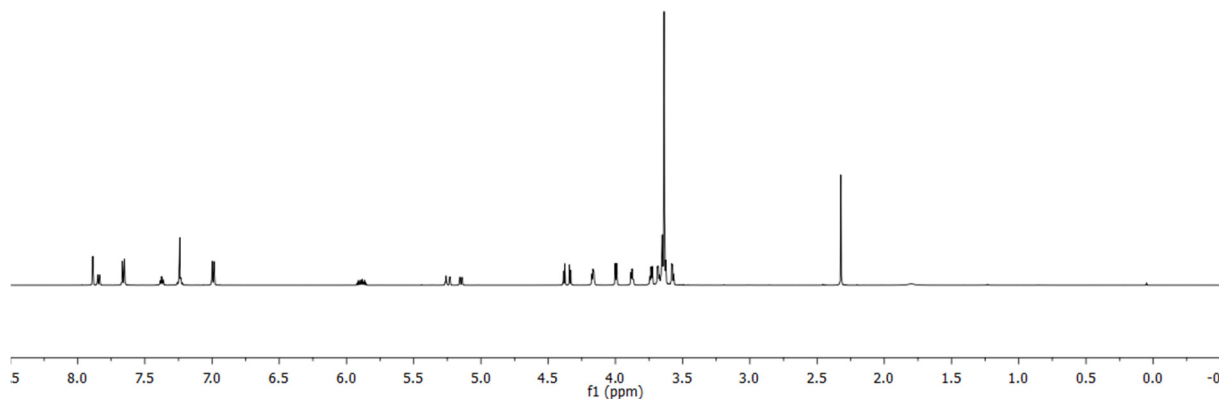


Figure S 4: ^1H NMR of (*S*)-**5** (600 MHz, CDCl_3).

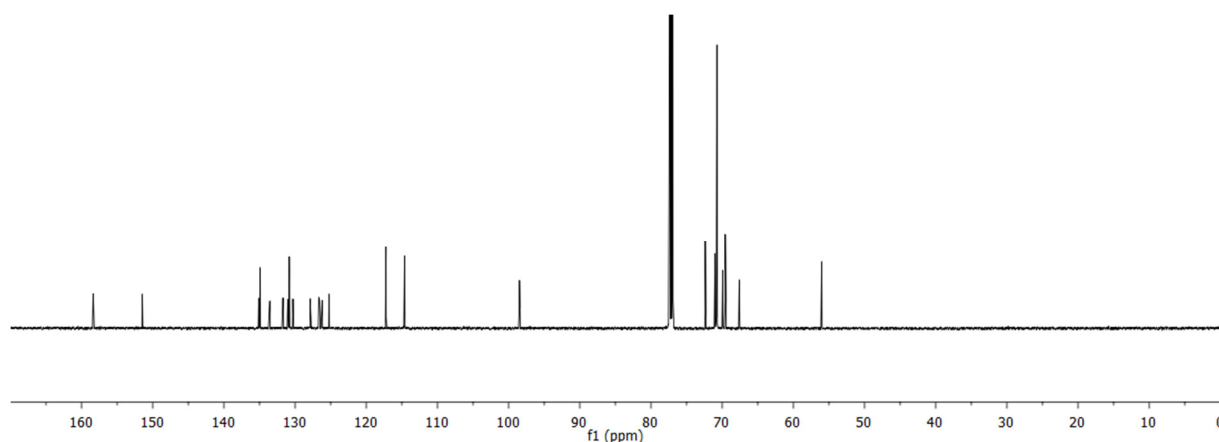
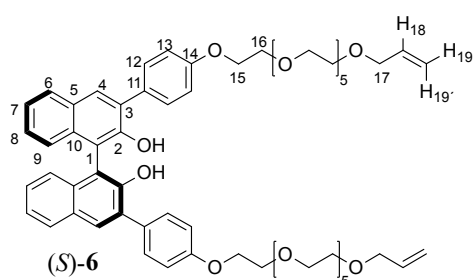


Figure S 5: $^{13}\text{C}\{^1\text{H}\}$ NMR of (*S*)-**5** (151 MHz, CDCl_3).

Compound (*S*)-**6**:



(*S*)-**5** (978 mg, 0.838 mmol, 1 equiv) was dissolved in a tetrahydrofuran/methanol-mixture (1:1, 50 mL). To that solution, Amberlyst[®] 15 (419 mg, 1 g/2 mmol) was added and the heterogeneous mixture was refluxed. The reaction was monitored by ^1H NMR. After two days, the reaction was judged to be complete. The mixture was allowed to come to room

temperature and filtered to remove the Amberlyst[®] 15. The catalyst was washed thoroughly with fresh tetrahydrofuran (2 x 5 mL) and the solvent was removed to give pure (*S*)-**6** (824 mg, 0.763 mmol; yield 91.1%) as a viscous colourless oil.

Anal. Calcd for $\text{C}_{62}\text{H}_{78}\text{O}_{16}$ (1079.29): C, 69.00; H, 7.28. Found: C, 69.8; H, 7.90. **IR** (ATR) $\bar{\nu}$ 2868, 1608, 1511, 1441, 1407, 1358, 1243, 1179, 1098, 994, 926, 831, 731, 697, 668, 617, 564 cm^{-1} . **^1H NMR** (600 MHz, CDCl_3) δ 7.96 (s, 2H, H-4), 7.88 (d, $J = 8.3$ Hz, 2H, H-6), 7.64 (ps d, $J = 8.8$ Hz, 4H, H-12), 7.35 (t, $J = 6.9$ Hz, 2H, H-7), 7.27 (t, $J = 6.9$ Hz, 2H, H-8), 7.18 (d, $J = 8.4$ Hz, 2H, H-9), 7.01 (ps d, $J = 8.8$ Hz, 4H, H-13), 5.88 (ddt, $J = 17.2, 10.4, 5.6$ Hz,

2H, H-18), 5.36 (br s, 2H, OH), 5.24 (ddt, $J = 17.2, 1.6, 1.6$ Hz, 2H, H-19'), 5.14 (ddt, $J = 10.4, 1.6, 1.3$ Hz, 2H, H-19), 4.21 – 4.12 (m, 4H, H-15), 3.98 (dt, $J = 5.6, 1.4$ Hz, 4H, H-17), 3.89 – 3.81 (m, 4H, H-16), 3.75 – 3.48 (m, 40H, core glycol-OCH₂). **¹³C{¹H} NMR** (151 MHz, CDCl₃) δ 158.7 (C-14), 150.4 (C-2), 134.9 (C-18), 132.9 (C-10), 131.1 (C-4), 130.9 (C-12), 130.4 (C-3), 130.1 (C-11), 129.6 (C-5), 128.5 (C-6), 127.2 (C-8), 124.42 (C-9), 124.37 (C-7), 117.2 (C-19), 114.8 (C-13), 112.6 (C-1), 72.4 (C-17), 71.0 (core glycol-OCH₂), 70.8 (core glycol-OCH₂), 70.7 (core glycol-OCH₂), 69.9 (C-16), 69.5 (core glycol-OCH₂), 67.7 (C-15). **COSY** (600 MHz/600 MHz, CDCl₃) δ 7.96/7.88 (H-4/H-6), 7.88/7.96, 7.35 (H-6/H-4, H-7), 7.64/7.01 (H-12/H-13), 7.35/7.88, 7.27 (H-7/ H-6, H-8), 7.27/7.35, 7.18 (H-8/H-7, H-9), 7.18/7.27 (H-9/H-8), 7.01/7.64 (H-13/H-12), 5.88/5.24, 5.14, 3.98 (H-18/H-19', H-19, H17), 5.24/5.88, 5.14, 3.98 (H-19'/H-18, H-19, H-17), 5.14/5.88, 5.24, 3.98 (H-19/H-18, H-19', H17), 4.21 – 4.12/3.89 – 3.81 (H-15/H-16), 3.98/5.88, 5.27, 5.14 (H-17/H-18, H-19', H-19), 3.89 – 3.81/4.21 – 4.12 (H-16/H-15). **HSQC** (600 MHz/151 MHz, CDCl₃) δ 7.96/131.1 (H-4/C-4), 7.88/128.5 (H-6/C-6), 7.64/130.9 (H-12/C-12), 7.35/124.37 (H-7/C-7), 7.27/127.2 (H-8/C-8), 7.18/124.42 (H-9/C-9), 7.01/114.8 (H-13/C-13), 5.88/134.9 (H-18/C-18), 5.24, 5.14/117.2 (H-19', H-19/C-19), 4.21 – 4.12/67.7 (H-15/C-15), 3.98/72.4 (H-17/C-17), 3.89 – 3.81/69.9 (H-16/C-16), 3.75 – 3.48/71.0, 70.8, 70.7, 69.5 (core glycol-OCH₂/core glycol-OCH₂). **HMBC** (600 MHz/151 MHz, CDCl₃) δ 7.96/150.4, 132.9, 130.1, 128.5, 112.6 (H-4/C-2, C-10, C-11, C-6, C-1), 7.88/132.9, 131.1, 127.2 (H-6/C-10, C-4, C-8), 7.64/158.7, 130.9, 114.8 (H-12/C-14, C-12, C-13), 7.35/129.6, 124.42 (H-7/C-5, C-9), 7.27/132.9, 128.5 (H-8/C-10, C-6), 7.18/132.9, 129.6, 124.4, 112.6 (H-9/C-10, C-5, C-7, C-1), 7.01/158.7, 130.1, 114.8 (H-13/C-14, C-11, C-13), 5.88/72.4 (H-18/C-17), 5.36/150.4, 130.4, 112.6 (OH/C-2, C-3, C-1), 5.24/72.4 (H-19'/C-17), 5.24/134.9, 72.4 (H-19'/C-18, C-17), 5.14/72.4 (H-19/C-17), 4.21 – 4.12/158.7, 69.9 (H-15/C-14, C-16), 3.98/134.9, 117.2, 69.5 (H-17/C-18, C-19, core glycol-OCH₂), 3.89 – 3.81/71.0, 67.7 (H-16/core glycol-OCH₂, C-15), 3.75 – 3.48/71.0, 70.8, 70.7, 69.9, 69.5 (core glycol-OCH₂/core glycol-OCH₂, C-16). **ESI-neg** (MeOH): m/z 1077.7 ([M-H]⁻). **HR-ESI-neg** (MeOH): $m/z = 1077.5195$ (calcd 1077.5217 for [M-H]⁻). **NP HPLC** (Chiralcel OD-H, EtOH : hexane = 80 : 20, 0.4 ml/min): t_R (area): 62.9 min (0.61%), 99.9 min (99.4%).

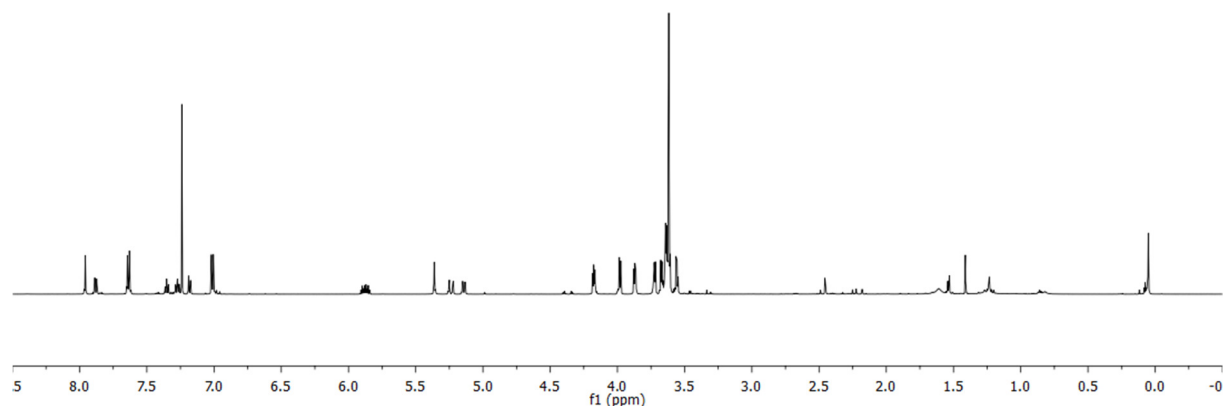


Figure S 6: ¹H NMR of (*S*)-**6** (600 MHz, CDCl₃).

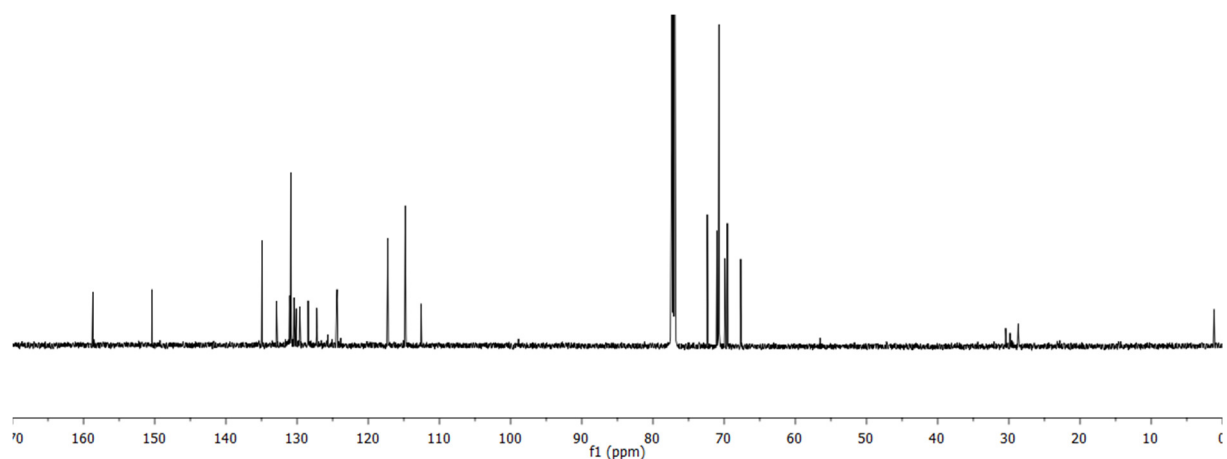
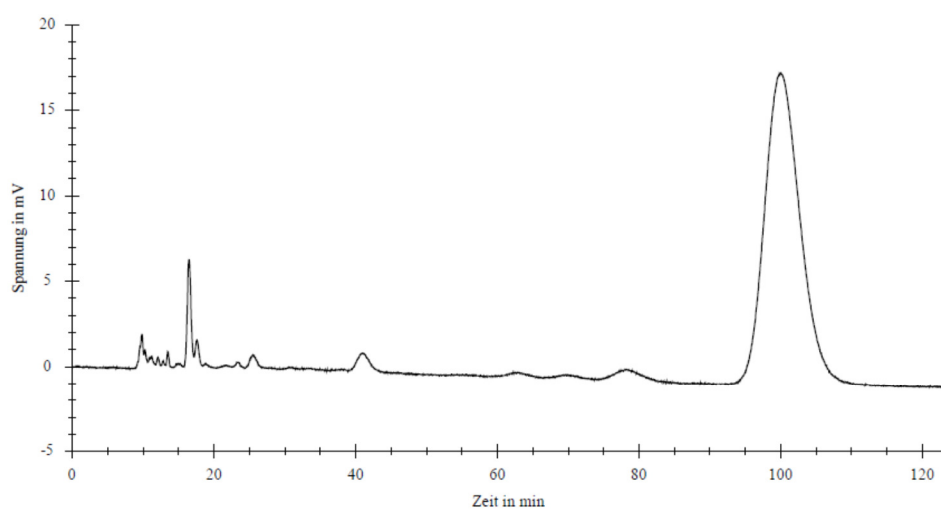


Figure S 7: $^{13}\text{C}\{^1\text{H}\}$ NMR of (*S*)-**6** (151 MHz, CDCl_3).



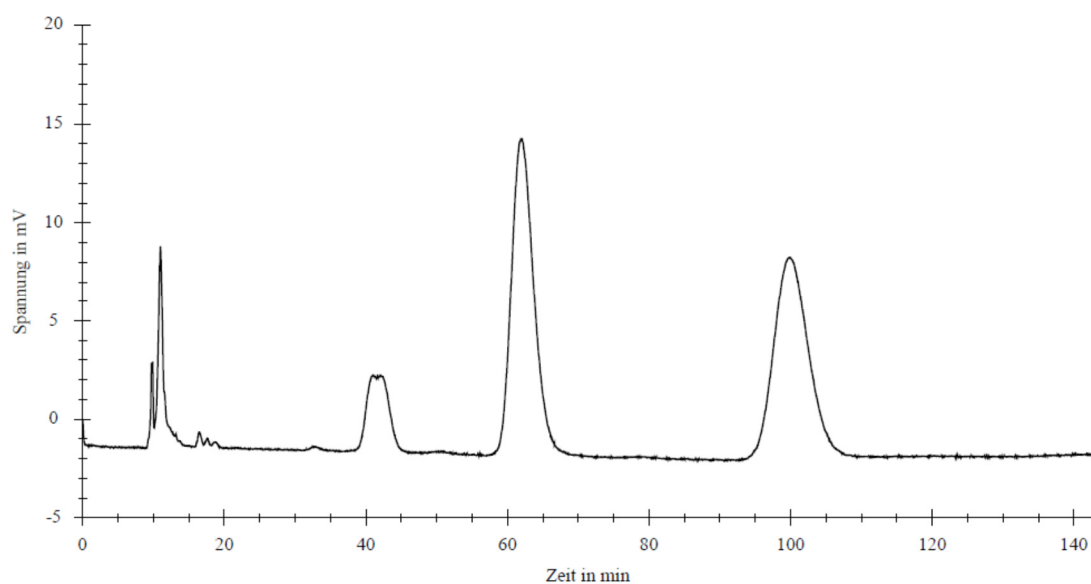
Berechnungsmethode:		Percent					
Peak-Nr.	Peak Start (min)	Peak Ende (min)	Ret. Zeit (min)	Fläche	Höhe (mV)	Percent	Name
1	59.558	65.592	62.850	38500.83	0.23	0.612	
2	91.958	111.817	99.900	6256743.00	18.07	99.388	

Figure S 8: Normal-phase HPLC-chromatogram of (*S*)-**6**

(rac)-6:

The diol (*rac*)-**6** was prepared accordingly starting from (*rac*)-**3**. All analytical data is identical with that for (*S*)-**6**.

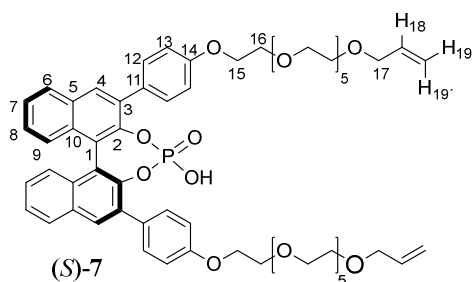
NP HPLC (Chiralcel OD-H, EtOH : hexanes = 80 : 20, 0.4 ml/min): t_R (area): 62.0 min (50.3%), 99.9 min (49.7%).



Berechnungsmethode:		Percent					
Peak-Nr.	Peak Start (min)	Peak Ende (min)	Ret. Zeit (min)	Fläche	Höhe (mV)	Percent	Name
1	56.500	70.125	61.967	3491343.00	15.95	50.287	
2	92.400	111.367	99.875	3451554.00	10.21	49.713	

Figure S 9: Normal-phase HPLC-chromatogram of (*rac*)-**6** (signals at $t_R = 40$ - 45 min belong to remainders of (*rac*)-**5** due to incomplete MOM-deprotection).

Compound (*S*)-**7**:



(*S*)-**6** (700 mg, 0.649 mmol, 1 equiv) was charged in a Schlenk flask and set under argon. Dry pyridine (2.62 mL, 32.5 mmol, 50 equiv) was added and the mixture was stirred for 15 minutes at room temperature. To that solution, freshly distilled POCl₃ (303 μ L, 498 mg, 3.25 mmol, 5 equiv) was added. The mixture was heated at 60 °C for 16 h under argon atmosphere. Then the reaction mixture was cooled to room temperature, followed by addition of water (2.50 mL). The resulting mixture was heated to 60 °C for 3 h. After cooling to room temperature, it was concentrated under reduced pressure. The residue was dissolved in dichloromethane (20 mL) and washed with 2 M HCl (4 x 10 mL). The organic layer was dried over anhydrous sodium sulfate, filtered and the solvent was removed to give (*S*)-**7** as viscous colourless oil (705 mg, 0.618 mmol; yield 95.2%).

Anal. Calcd for C₆₂H₇₇O₁₈P (1141.25): C, 65.25; H, 6.80. Found: C, 65.0; H, 7.01. **IR** (ATR) $\bar{\nu}$ 2867, 1608, 1513, 1455, 1406, 1348, 1245, 1180, 1097, 996, 954, 884, 833, 776, 753, 729, 700, 645, 615, 603, 569, 554 cm⁻¹. **¹H NMR** (600 MHz, C₆D₆) δ 7.85 (s, 2H, H-4), 7.71-7.64

(m, 6H, H-6, H-12), 7.38 (d, $J = 8.3$ Hz, 2H, H-9), 7.20 (t, $J = 7.6$ Hz, 2H, H-7) 6.98 (t, $J = 7.6$ Hz, 2H, H-8), 6.84 (d, $^3J = 8.3$ Hz, 4H, H-13), 5.76 (ddt, $J = 17.2, 10.4, 5.4$ Hz, 2H, H-18), 5.14 (ddt, $J = 17.2, 1.6, 1.6$ Hz, 2H, H-19'), 4.99 (ddt, $J = 10.4, 1.6, 1.3$ Hz, 2H, H-19), 3.81-3.73 (m, 8 H, H-17), 3.50-3.33 (m, 44 H, H-15, H-16, core glycol-OCH₂). **¹H NMR** (600 MHz, CDCl₃) δ 7.97 (s, 2H, H-4), 7.91 (d, $J = 8.2$ Hz, 2H, H-6), 7.61 (ps d, $J = 8.6$ Hz, 4H, H-12), 7.45 (t, $J = 7.4$ Hz, 2H, H-7), 7.31 (d, $J = 8.5$ Hz, 2H, H-9), 7.26 (t, $J = 7.2$ Hz, 2H, H-8), 6.92 (ps d, $J = 8.7$ Hz, 4H, H-13), 5.83 (ddt, $J = 17.2, 10.4, 5.6$ Hz, 2H, H-18), 5.57 (br s, 1H, P(O)OH), 5.20 (ddt, $J = 17.2, 1.6, 1.6$ Hz, 2H, H-19'), 5.11 (ddt, $J = 10.4, 1.6, 1.3$ Hz, 2H, H-19), 4.11 – 4.02 (m, 4H, H-15), 3.93 (dt, $J = 5.6, 1.4$ Hz, 4H, H-17), 3.80 – 3.69 (m, 4H, H-16), 3.67 – 3.46 (m, 40H, core glycol-OCH₂). **¹³C{¹H} NMR** (151 MHz, CDCl₃) δ 158.5 (C-14), 145.0 (d, $J_{C-P} = 9.6$ Hz, C-2), 134.7 (C-18), 133.8 (d, $J_{C-P} = 2.1$ Hz, C-3), 131.9 (C-10), 131.7 (C-5), 131.2 (C-12), 131.0 (C-4), 129.8 (C-11), 128.4 (C-6), 127.2 (C-9), 126.4 (C-8), 125.9 (C-7), 122.7 (d, $J_{C-P} = 1.9$ Hz, C-1), 117.3 (C-19), 114.6 (C-13), 72.3 (C-17), 70.8 (core glycol-OCH₂), 70.7 (core glycol-OCH₂), 70.6 (core glycol-OCH₂), 69.8 (C-16), 69.4 (core glycol-OCH₂), 67.5 (C-15). **³¹P{¹H} NMR** (243 MHz, CDCl₃) δ 1.72 (s, $\nu_{1/2} = 21$ Hz, P(O)OH). **COSY** (600 MHz/600 MHz, CDCl₃) δ 7.91/7.45 (H-6/H-7), 7.61/6.92 (H-12/H-13), 7.45/7.91, 7.26 (H-7/ H-6, H-8), 7.31/7.26 (H-9/H-8), 7.26/7.45, 7.31 (H-8/H-7, H-9), 6.92/7.61 (H-13/H-12), 5.83/5.20, 5.11, 3.93 (H-18/H-19', H-19, H17), 5.20/5.83, 5.11, 3.93 (H-19'/H-18, H-19, H-17), 5.11/5.83, 5.20, 3.93 (H-19/H-18, H-19', H17), 4.11 – 4.02/3.80 – 3.69 (H-15/H-16), 3.93/5.83, 5.20, 5.14 (H-17/H-18, H-19', H-19), 3.80 – 3.69/4.11 – 4.02 (H-16/H-15). **HSQC** (600 MHz/151 MHz, CDCl₃) δ 7.97/131.0 (H-4/C-4), 7.91/128.4 (H-6/C-6), 7.61/131.2 (H-12/C-12), 7.45/125.9 (H-7/C-7), 7.31/127.2 (H-9/C-9), 7.26/126.4 (H-8/C-8), 6.92/114.6 (H-13/C-13), 5.83/134.7 (H-18/C-18), 5.20, 5.11/117.2 (H-19', H-19/C-19), 4.11 – 4.02/67.5 (H-15/C-15), 3.93/72.3 (H-17/C-17), 3.80 – 3.69/69.8 (H-16/C-16), 3.75 – 3.48/70.8, 70.7, 70.6, 69.4 (core glycol-OCH₂/core glycol-OCH₂). **HMBC** (600 MHz/151 MHz, CDCl₃) δ 7.97/145.0, 131.9, 129.8, 128.4, 122.7 (H-4/C-2, C-10, C-11, C-6, C-1), 7.91/131.9, 126.4 (H-6/C-10, C-8), 7.61/158.5, 133.8, 131.2, 114.6 (H-12/C-14, C-3, C-12, C-13), 7.45/131.7, 127.2 (H-7/C-5, C-9), 7.31/131.7, 125.9, 122.7 (H-9/C-5, C-7, C-1), 7.26/131.9, 128.4 (H-8/C-10, C-6), 6.92/158.5, 129.8, 114.6 (H-13/C-14, C-11, C-13), 5.83/72.3 (H-18/C-17), 5.20/134.7, 72.3 (H-19'/C-18, C-17), 5.11/72.8 (H-19/C-17), 4.11 – 4.02/158.5, 69.8 (H-15/C-14, C-16), 3.93/134.7, 117.2, 69.4 (H-17/C-18, C-19, core glycol-OCH₂), 3.80 – 3.69/70.8, 67.5 (H-16/C-16, C-15), 3.67 – 3.46/70.8, 70.7, 70.6, 69.4 (core glycol-OCH₂/core glycol-OCH₂). **ESI-neg** (MeOH): $m/z = 1139.6$ ([M-H]⁻). **HR-ESI-neg** (MeOH): $m/z = 1139.4755$ (calcd 1139.4775 for [M-H]⁻). **RP HPLC** (RP C18, MeOH with 0.05% TFA : water with 0.05% TFA = 70 : 30 gradient flow up to 100:0 within 50 min, 0.43 ml/min): t_R (area): 22.9 min (90.74%), 47.3 (9.26%, elutes at 100% methanol, possibly remainder on column).

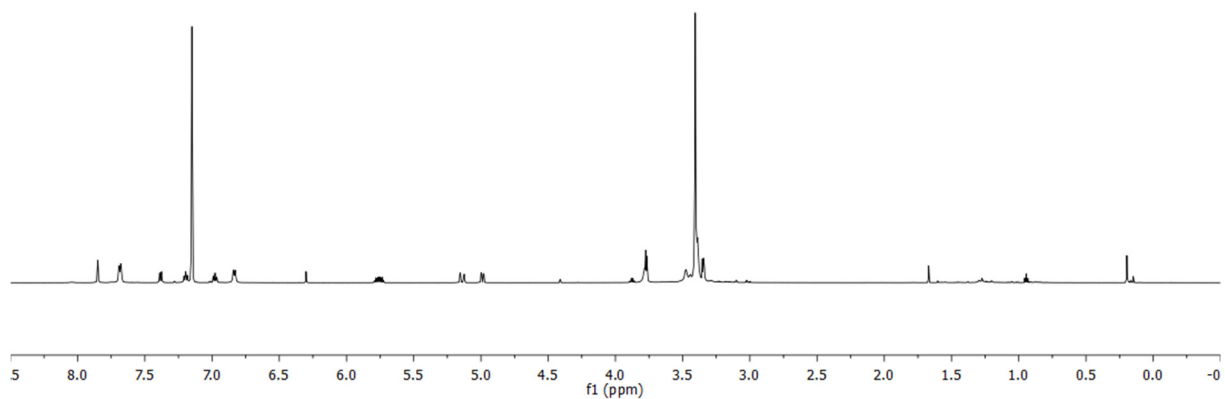


Figure S 10: ^1H NMR of (S)-7 (600 MHz, C_6D_6).

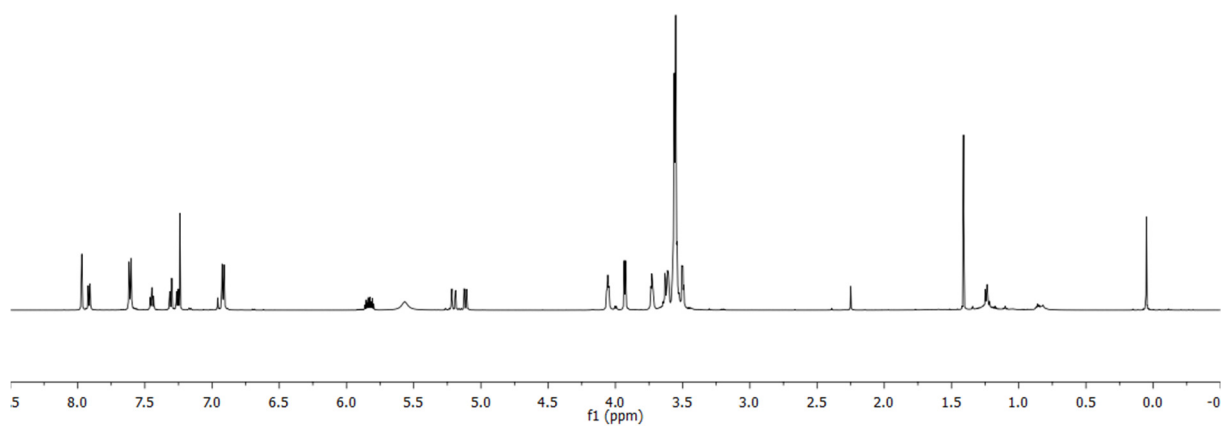


Figure S 11: ^1H NMR of (S)-7 (600 MHz, CDCl_3).

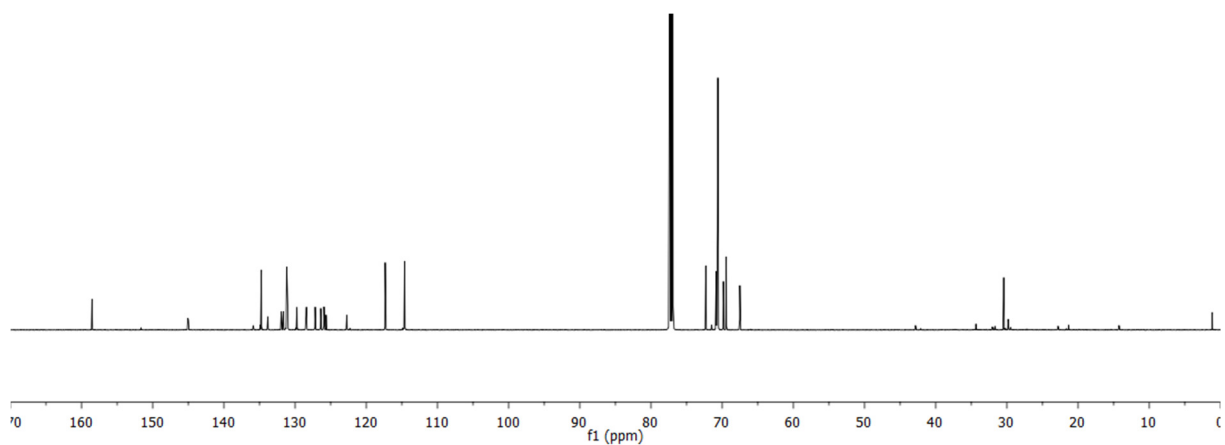


Figure S 12: $^{13}\text{C}\{^1\text{H}\}$ NMR of (S)-7 (151 MHz, CDCl_3).

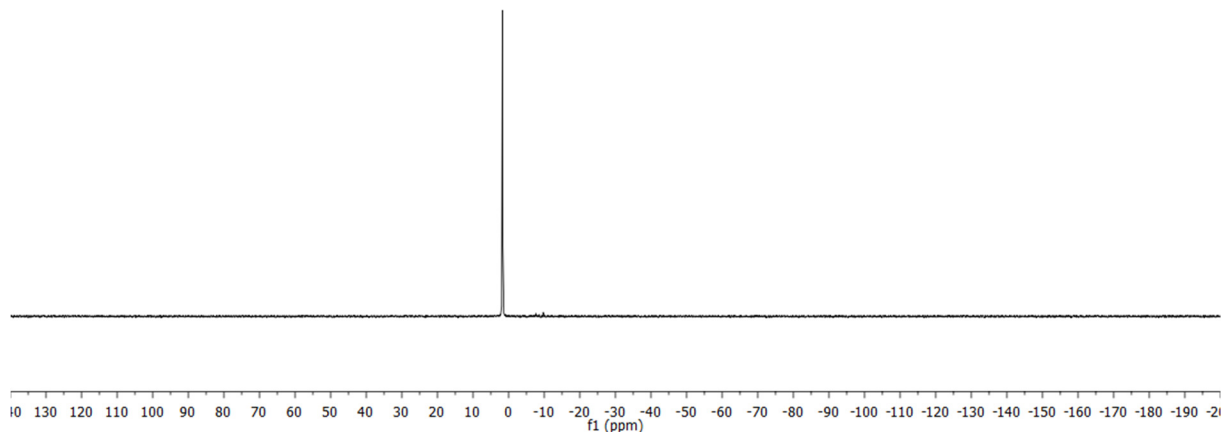


Figure S 13: $^{31}\text{P}\{^1\text{H}\}$ NMR of (*S*)-7 (243 MHz, CDCl_3).

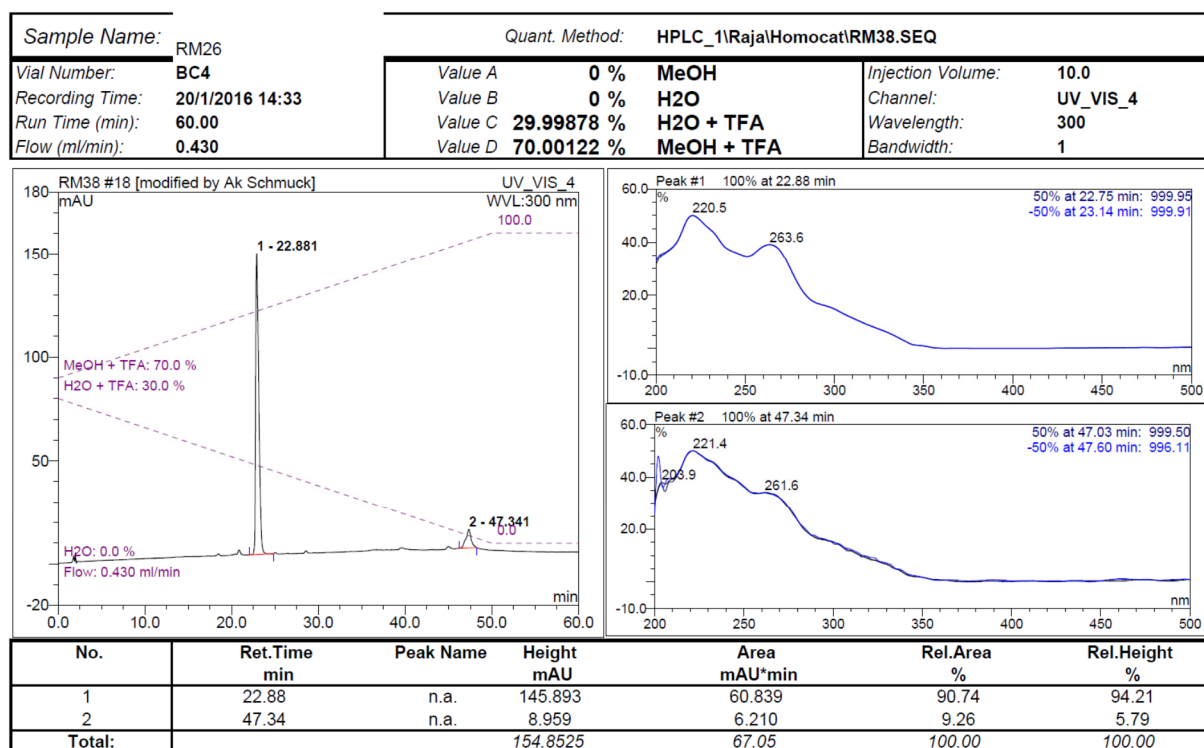


Figure S 14: Reversed-phase HPLC-chromatogram of (*S*)-7

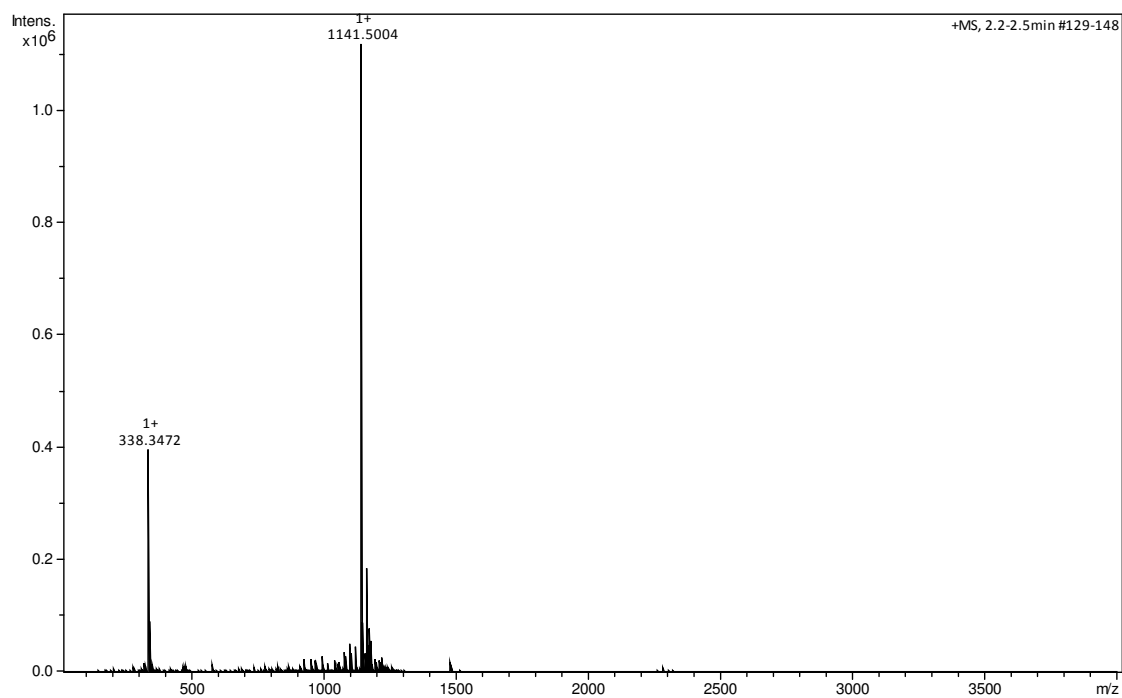


Figure S 15: HR-MS (APCI) spectrum of (S)-7 (full mass range).

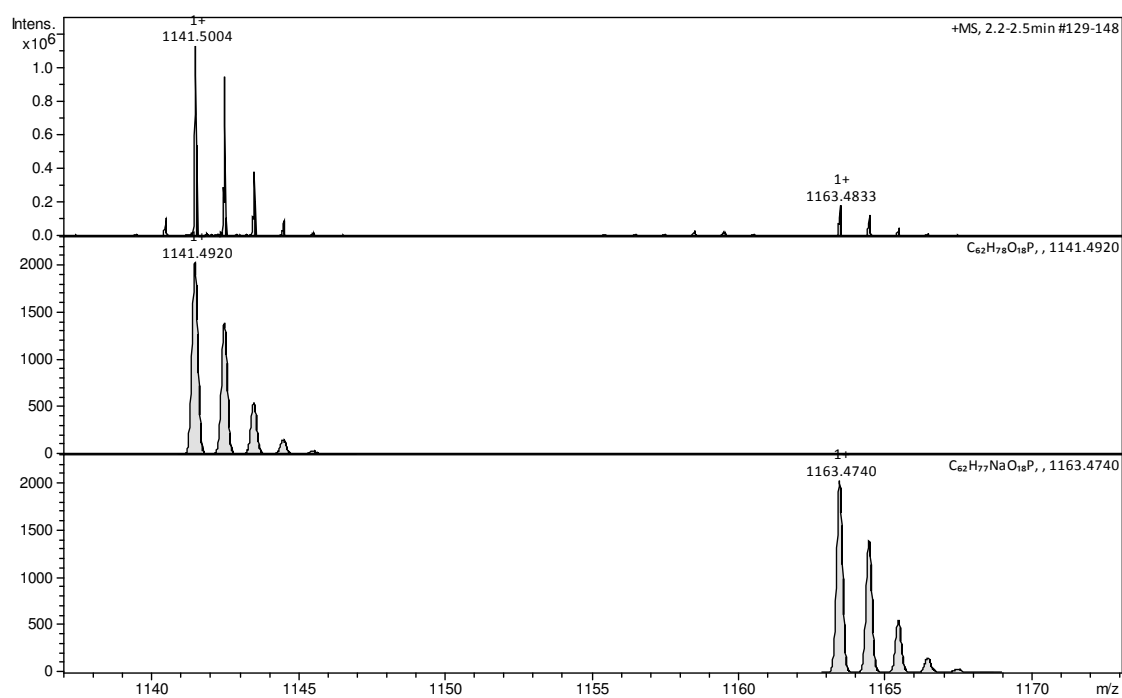
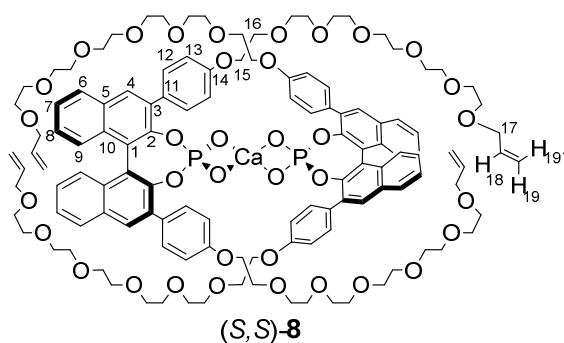


Figure S 16: HR-MS (APCI) spectrum of (S)-7 (Mass-range 1140-1170 (top: experimental data, middle: simulated for [M+H]⁺, bottom: simulated for [M+Na]⁺)).

Precatenane (*S,S*)-8:



(*S*)-7 (530 mg, 0.464 mmol, 1 equiv) was dissolved in dry toluene (30 mL) under argon atmosphere. Solid $\text{Ca}(\text{OMe})_2$ (23.7 mg, 0.232 mmol, 0.5 equiv) was added and the mixture was stirred at room temperature overnight. Then the reaction mixture was filtered to obtain a clear solution and the solvent was removed to give (*S,S*)-8 as viscous brown oil (510 mg, 0.220 mmol; yield 94.7%).

Anal. Calcd for $\text{C}_{124}\text{H}_{152}\text{CaO}_{36}\text{P}_2$ (2320.57): C, 65.05; H, 6.69. Found: C, 65.7; H, 6.87. **IR** (ATR) $\bar{\nu}$ 2870, 1680, 1513, 1454, 1426, 1405, 1348, 1246, 1183, 1097, 997, 970, 952, 885, 828, 729, 700, 646, 606, 581, 554 cm^{-1} . **$^1\text{H NMR}$** (600 MHz, C_6D_6) δ 7.90 (br s, 4H H-4), 7.84-7.69 (m, 12H, H-6, H-12), 7.41 (d, $J = 6.8$ Hz, H-9), 7.22 (t, $J = 7.1$ Hz, 4H, H-7), 6.98 (t, $J = 7.1$ Hz, 4H, H-8), 6.92 (br s, 8H, H-13), 5.78 (br s, 4H, H-18), 5.19 (br d, $J = 17.2$ Hz, 4H, H-19'), 5.10 (br d, $J = 10.3$ Hz, 4H, H-19), 3.85 (br s, 8H, H-15), 3.79 (br s, 8H, H-17), 3.53 (bs, 8H, H-16), 3.50 – 3.19 (m, 80H, core glycol-OCH₂). **$^1\text{H NMR}$** (600 MHz, CDCl_3) δ 7.89 (br s, 4H, H-6), 7.88 (br s, 4H, H-4), 7.56 (d, $J = 7.0$ Hz, 8H, H-12), 7.41 (t, $J = 7.1$ Hz, 4H, H-7), 7.25-7.16 (m, 8H, H-8, H-9), 6.79 (br s, 8H, H-13), 5.82 (br s, 4H, H-18), 5.18 (br s, 4H, H-19'), 5.10 (br s, 4H, H-19), 3.95 (br s, 16H, H-15, H-17), 3.67 (bs, 8H, H-16), 3.64 – 3.33 (m, 80H, core glycol-OCH₂). **$^{13}\text{C}\{^1\text{H}\}$ NMR** (151 MHz, CDCl_3) δ 158.3 (C-14), 145.7 (C-2), 134.7 (C-18), 134.0 (C-3), 132.0 (C-10), 131.3 (C-5), 131.2 (C-12), 130.9 (C-4), 130.0 (C-11), 128.3 (C-6), 127.1 (C-9), 126.2 (C-8), 125.7 (C-7), 122.9 (C-1), 117.4 (C-19), 114.5 (C-13), 72.3 (C-17), 70.7 (core glycol-OCH₂), 70.6 (core glycol-OCH₂), 69.8 (C-16), 69.4 (br, core glycol-OCH₂), 67.3 (C-15). **$^{31}\text{P}\{^1\text{H}\}$ NMR** (243 MHz, CDCl_3) δ 0.52 (s, $\nu_{1/2} = 219$ Hz, P(O)OCa). **COSY** (600 MHz/600 MHz, CDCl_3) δ 7.89, 7.88/7.41 (H-6, H-4/H-7), 7.56/6.79 (H-12/H-13), 7.41/7.89, 7.88, 7.25-7.16 (H-7/ H-6, H-4, H-8, H-9), 7.25-7.16/7.41 (H-8, H-9/H-7), 6.79/7.56 (H-13/H-12), 5.82/5.18, 5.10, 3.95 (H-18/ H-19', H-19, H-17), 5.18/5.82, 5.10 (H-19'/H-18, H-19), 5.10/5.82, 5.18 (H-19/H-18, H-19'), 3.95/5.82 (H-15, H-17/H-18). **HSQC** (600 MHz/151 MHz, CDCl_3) δ 7.89/130.9 (H-6/C-6), 7.88/128.3 (H-4/C-4), 7.56/131.2 (H-12/C-12), 7.41/125.7 (H-7/C-7), 7.25-7.16/127.1, 126.2 (H-8, H-9/C-9, C-8), 6.79/114.5 (H-13/C-13), 5.82/134.7 (H-18/C-18), 5.18, 5.10/117.4 (H-19', H-19/C-19), 3.95/72.3, 67.3 (H-15, H-17/C-17, C-15), 3.67/69.8 (H-16/C-16), 3.64 – 3.33/70.7, 70.6, 69.4 (core glycol-OCH₂/core glycol-OCH₂). **HMBC** (600 MHz/151 MHz, CDCl_3) δ 7.89, 7.88/145.7, 130.9, 130.0, 128.3, 126.2 (H-6, H-4/ C-2, C-4, C-11, C-6, C-8), 7.56/158.3, 131.2 (H12/C-14, C-12), 7.41/131.3, 127.1 (H-7/C-5, C-9), 7.25-7.16/132.0, 131.3, 128.3, 125.7 (H-8, H-9/C-10, C-5, C-6, C-7), 3.95/ 134.7, 117.4, 69.4 (H-15, H-17/ C-18, C-19, core glycol-OCH₂), 3.64 – 3.33/70.7, 70.6 (core glycol-OCH₂/core glycol-OCH₂). **APCI-pos** m/z 2319.9234 (calcd 2319.9237 for $[\text{C}_{124}\text{H}_{153}\text{CaO}_{36}\text{P}_2]^+$). **RP HPLC** (RP C18, MeOH with 0.05% TFA : water with 0.05% TFA = 70 : 30 gradient flow up to 100:0 within 50 min, 0.43 ml/min): t_R (area): 22.7 min (100%, liberation of the phosphoric acid (*S*)-7 from the Ca-salt in acidic medium).

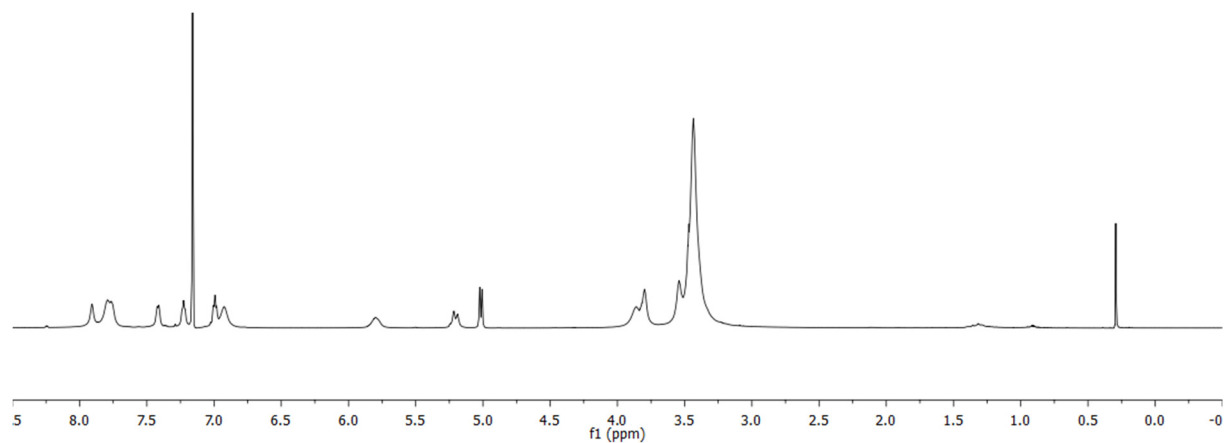


Figure S 17: ^1H NMR of *(S,S)*-**8** (600 MHz, C_6D_6).

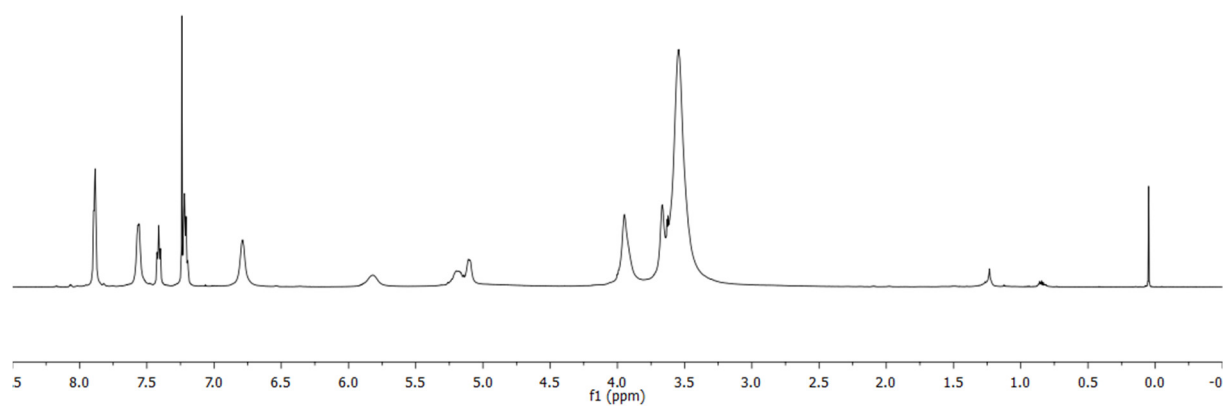


Figure S 18: ^1H NMR of *(S,S)*-**8** (600 MHz, CDCl_3).

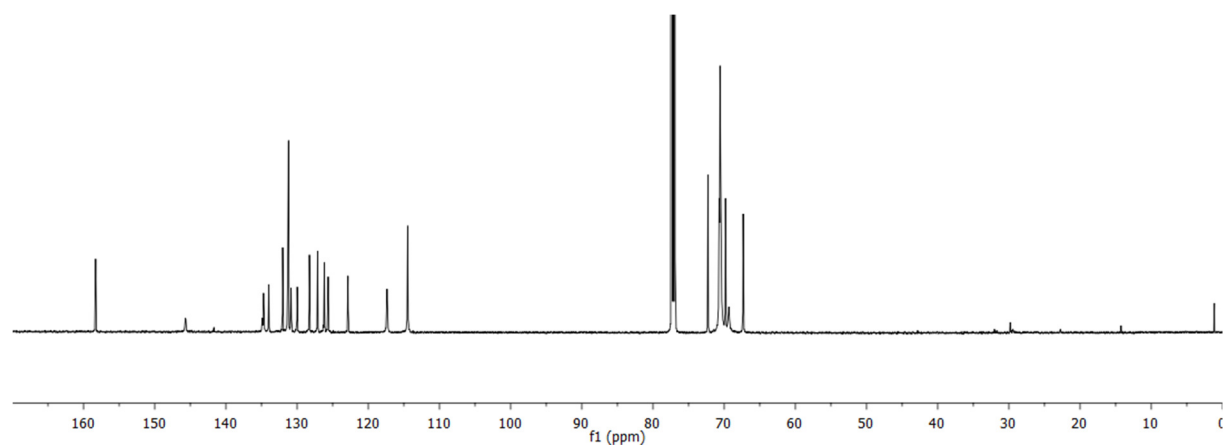


Figure S 19: $^{13}\text{C}\{^1\text{H}\}$ NMR of *(S,S)*-**8** (151 MHz, CDCl_3).

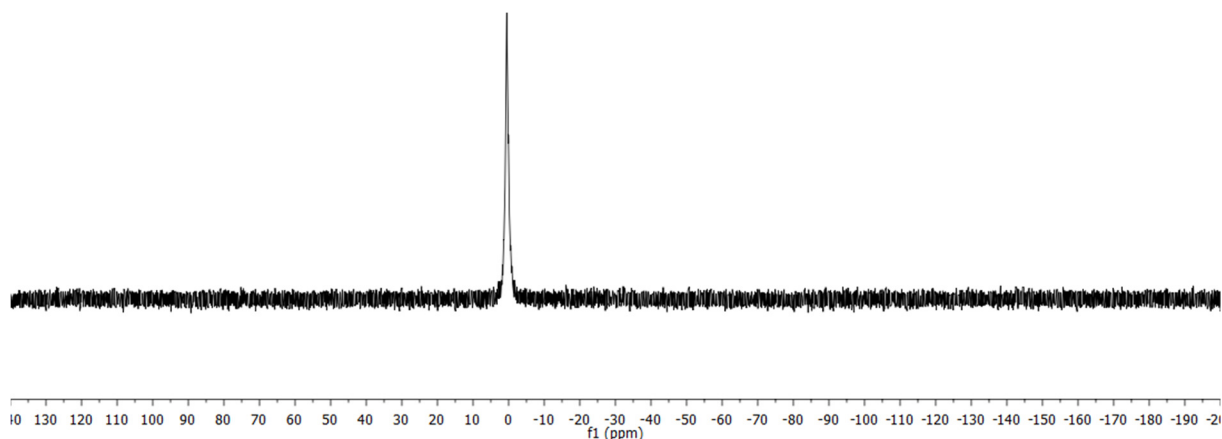


Figure S 20: $^{31}\text{P}\{^1\text{H}\}$ NMR of (*S,S*)-**8** (243 MHz, CDCl_3).

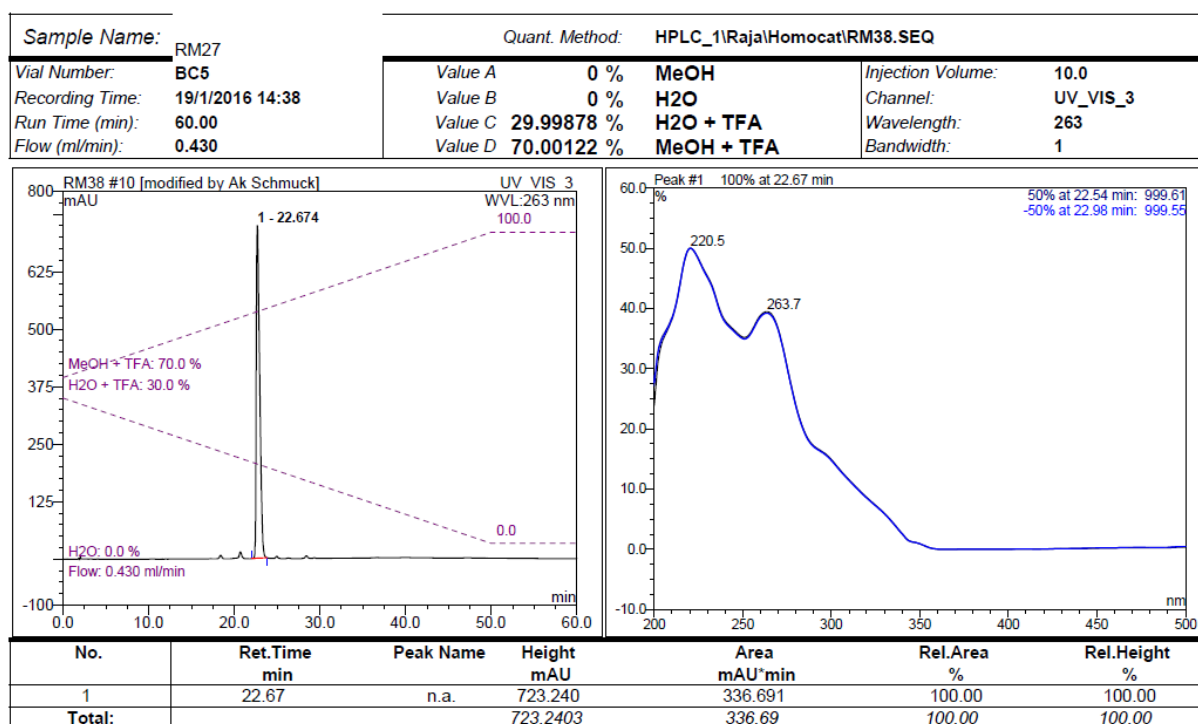


Figure S 21: Reversed-phase HPLC-chromatogram of (*S,S*)-**8** (detection of (*S*)-**7**).

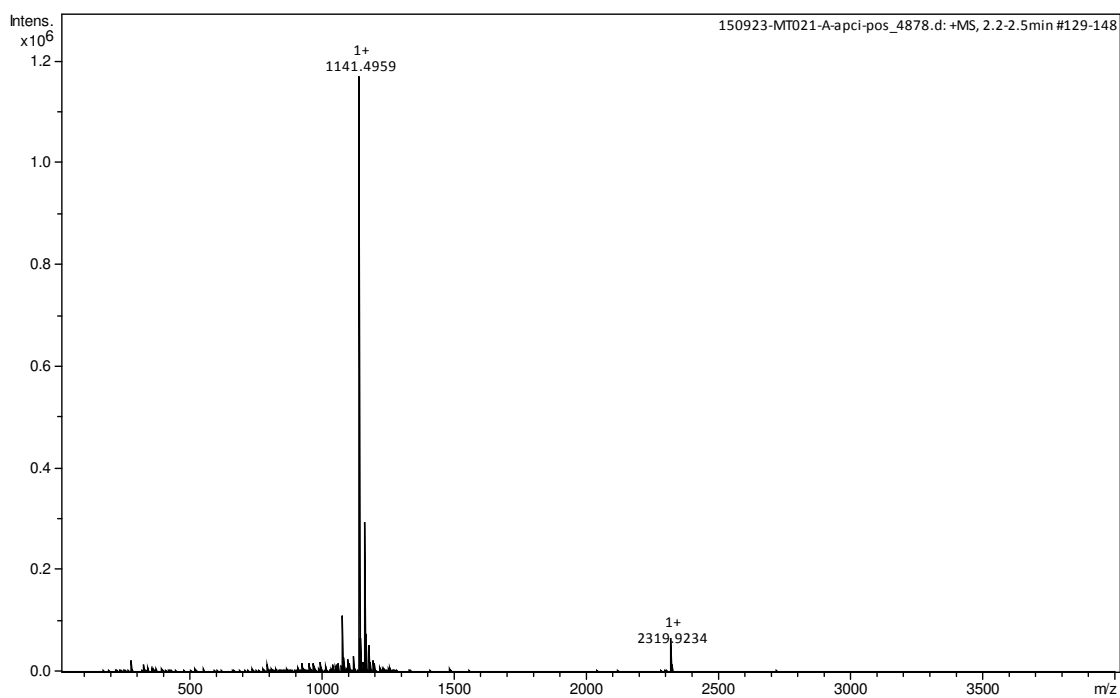


Figure S 22: HR-MS (APCI) spectrum of (*S,S*)-**8** (full mass range).

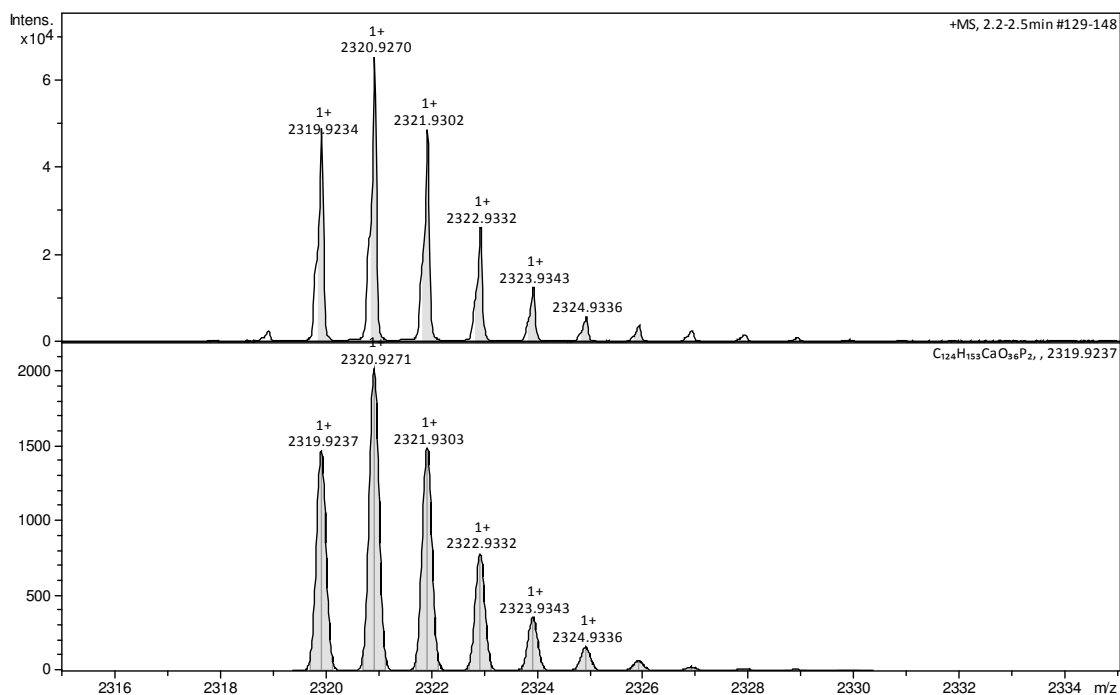


Figure S 23: HR-MS (APCI) spectrum of (*S,S*)-**8** (Mass-range 2316-2334 (top: experimental data, bottom: simulated for $[M+H]^+$)).

Macrocyclic (*S*)-**2** and Catenane (*S,S*)-**1**:

(*S,S*)-**8** (165 mg, 0.0711 mmol, 1 equiv) was dissolved in dry dichloromethane (50 mL) under argon atmosphere. To that solution, solid 2nd generation Grubbs' catalyst (6.04 mg, 7.11 μ mol, 0.1 equiv) was added and the mixture was stirred at room temperature in the dark. At different time points, 0.5 mL of reaction mixture was withdrawn and progress of the reaction was monitored by RP HPLC equipped with a C18 column. After 24 h, further 2nd generation Grubbs' catalyst (3.02 mg, 0.00356 mmol, 0.05 equiv) was added and the mixture was stirred for another 24 h. The reaction was judged to be complete and the solvent was removed to give a brown residue, which was dispersed in 50 mL of methanol and sonicated for 5 minutes. The methanol dispersion was filtered through a 0.22 μ PTFE syringe filter to obtain a clear brown solution and the solvent was evaporated in the rotary evaporator, followed by high vacuum to give the crude product as viscous oil (135 mg). The crude mixture was purified by MPLC equipped with a RP18 17g Kronlab column (MeOH with 0.05% TFA : water with 0.05% TFA = 65 : 35 gradient flow firstly up to 85:15 within 48 min, secondly up to 90:10 within 22 minutes, thirdly up to 100:0 within 10 minutes, 15 ml/min) as two major components, (*S*)-**2** (1st fraction) and (*S,S*)-**1** (2nd fraction). Purified compounds were then dissolved in dichloromethane (25 mL) and washed with 2 M HCl (2 x 10 mL) to remove the TFA, which was used for the MPLC. The organic layers were dried over anhydrous sodium sulfate, filtered, washed thoroughly with dichloromethane (2 x 5 mL) and the solvent was removed to give the desired products.

HPLC of the crude reaction mixture (135 mg):

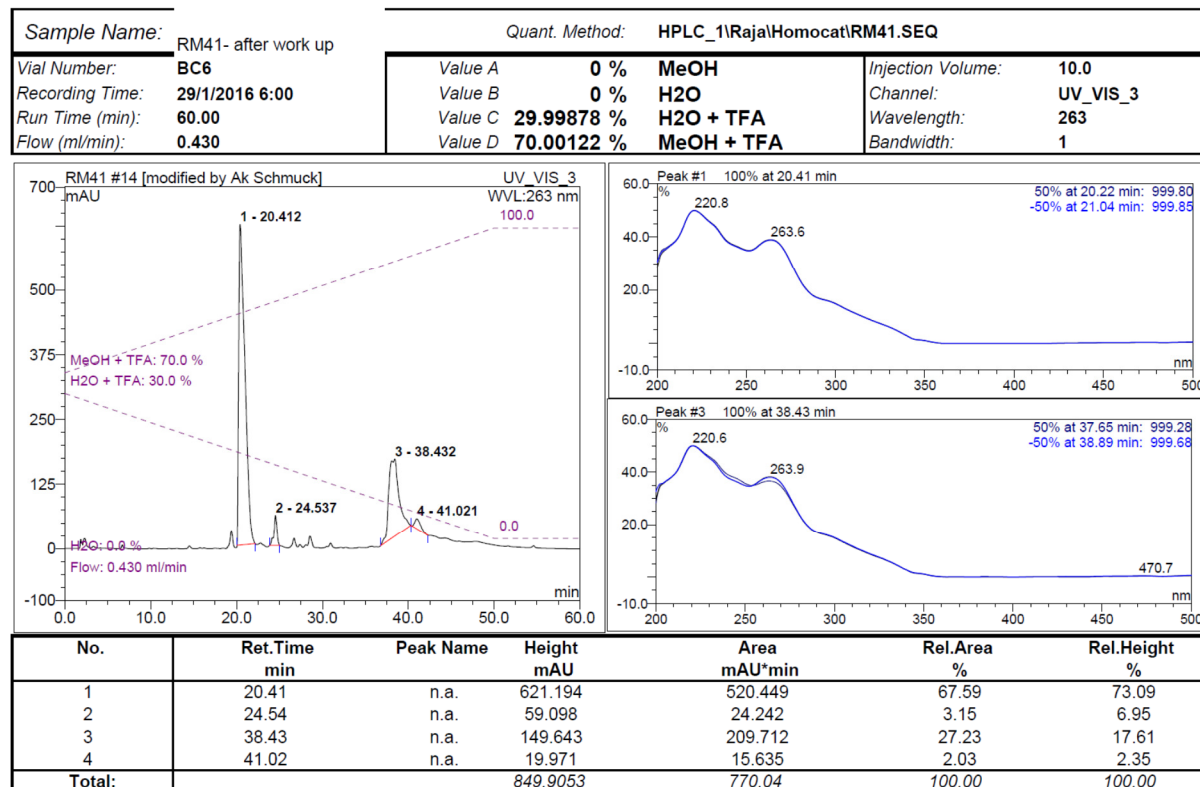
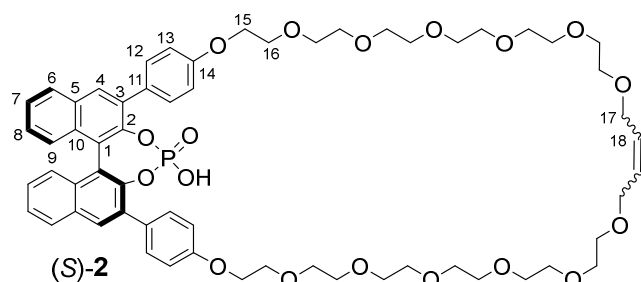


Figure S 24: Reversed-phase HPLC-chromatogram of the crude reaction mixture.

Macromolecule (*S*)-**2** was isolated as a brown oil with 22.2% yield (35.1 mg) after washing with HCl.



IR (ATR) $\bar{\nu}$ 2864, 1608, 1514, 1453, 1406, 1350, 1285, 1245, 1180, 1098, 995, 956, 885, 833, 753, 708, 666 cm^{-1} . **^1H NMR** (600 MHz, CDCl_3) δ 7.98 (s, 2H, H-4), 7.91 (d, $J = 8.2$ Hz, 2H, H-6), 7.68 (ps d, $J = 8.7$ Hz, 4H, H-12), 7.44 (t, $J = 7.5$ Hz, 2H, H-7), 7.31 (d, $J = 8.5$ Hz, 2H,

H-9), 7.25 (t, $J = 7.5$ Hz, 2H, H-8), 6.99 (ps d, $J = 8.7$ Hz, 4H, H-13), 5.65 (s, 2H, H-18 of (*Z*)-isomer, (*Z*)/(*E*)-ratio = 95:5), 5.57 (s, H-18 of (*E*)-isomer, other peaks for (*E*)-isomer not assignable), 5.07 (br s, 1H, P(O)OH), 4.23 – 4.13 (m, 4H, H-15), 3.88 – 3.85 (m, 8H, H-16, H-17), 3.75 – 3.37 (m, 40H, core glycol-OCH₂). **$^{13}\text{C}\{^1\text{H}\}$ NMR** (151 MHz, CDCl_3) δ 158.6 (C-14), 145.2 (d, $J_{\text{C-P}} = 9.6$ Hz, C-2), 133.8 (d, $J_{\text{C-P}} = 2.6$ Hz, C-3), 132.0 (C-10), 131.6 (C-5), 131.3 (C-12), 131.0 (C-4), 130.1 (C-11), 129.6 (C-18), 128.4 (C-6), 127.2 (C-9), 126.3 (C-8), 125.9 (C-7), 122.9 (d, $J_{\text{C-P}} = 2.2$ Hz, C-1), 114.6 (C-13), 71.13 (C-17), 71.08 (core glycol-OCH₂), 70.8 (core glycol-OCH₂), 70.70 (core glycol-OCH₂), 70.69 (core glycol-OCH₂), 70.68 (core glycol-OCH₂), 70.64 (core glycol-OCH₂), 70.62 (core glycol-OCH₂), 70.5 (core glycol-OCH₂), 69.9 (C-16), 69.4 (core glycol-OCH₂), 67.7 (C-15). **$^{31}\text{P}\{^1\text{H}\}$ NMR** (243 MHz, CDCl_3) δ 1.19 (s, $\nu_{1/2} = 7.5$ Hz, P(O)OH). **COSY** (600 MHz/600 MHz, CDCl_3) δ 7.91/7.44 (H-6/H-7), 7.68/6.99 (H-12/H-13), 7.44/7.91, 7.25 (H-7/H-6, H-8), 7.31/7.25 (H-9/H-8), 7.25/7.44, 7.31 (H-8/H-7, H-9), 6.99/7.68 (H-13/H-12), 5.65/3.88 – 3.85 (H-18/H-16, H-17), 4.23 – 4.13/3.88 – 3.85 (H-15/H-16, H-17), 3.88 – 3.85/4.23 – 4.13 (H-16, H-17/H-15). **HSQC** (600 MHz/151 MHz, CDCl_3) δ 7.98/131.0 (H-4/C-4), 7.91/128.4 (H-6/C-6), 7.68/131.3 (H-12/C-12), 7.44/125.9 (H-7/C-7), 7.31/127.2 (H-9/C-9), 7.25/126.3 (H-8/C-8), 6.99/114.6 (H-13/C-13), 5.65/129.6 (H-18/C-18), 4.23 – 4.13/67.7 (H-15/C-15), 3.88 – 3.85/71.13, 69.9 (H-16, H-17/C-16, C-17), 3.75 – 3.37/71.08, 70.8, 70.70, 70.69, 70.68, 70.64, 70.62, 70.5, 69.4 (core glycol-OCH₂). **HMBC** (600 MHz/151 MHz, CDCl_3) δ 7.98/145.2, 132.0, 130.1, 128.4, 122.9 (H-4/C-2, C-10, C-11, C-6, C-1), 7.91/132.0, 126.3 (H-6/C-10, C-8), 7.68/158.6, 133.8, 131.3 (H-12/C-14, C-3, C-12), 7.44/131.6, 127.2 (H-7/C-5, C-9), 7.31/131.6, 125.9, 122.9 (H-9/C-5, C-7, C-1), 7.25/132.0, 128.4 (H-8/C-10, C-6), 6.99/158.5, 130.1, 114.6 (H-13/C-14, C-11, C-13), 5.65/129.6, 71.13 (H-18/C-18, C-17), 4.23 – 4.13/158.5, 69.9 (H-15/C-14, C-16), 3.88 – 3.85/129.6, 71.13, 69.4, 67.7 (H-16, H-17/C-18, C-17, core glycol-OCH₂, C-15), 3.75 – 3.37/71.08, 70.8, 70.70, 70.69, 70.68, 70.64, 70.62, 70.5, 69.4 (core glycol-OCH₂/core glycol-OCH₂). **HR-ESI-pos** ($\text{CHCl}_3/\text{MeOH}$): $m/z = 1135.44271$ (calcd 1135.44267 for $[\text{C}_{60}\text{H}_{73}\text{O}_{18}\text{PNa}]^+$). **HR-ESI-neg** ($\text{CHCl}_3/\text{MeOH}$): $m/z = 1111.43870$ (calcd 1111.44617 for $[\text{C}_{60}\text{H}_{72}\text{O}_{18}\text{P}]^-$). **RP HPLC** (RP C18, MeOH with 0.05% TFA : water with 0.05% TFA = 70 : 30 gradient flow up to 100:0 within 50 min, 0.43 ml/min): t_R (area): 19.8 min (2.18%, (*Z*)-isomer), 20.8 min (97.82%, (*E*)-isomer).¹

¹ No satisfactory results of elemental analysis could be obtained for (*S*)-**2**. However, the purity of the material is clearly proven by NMR and HPLC-analysis.

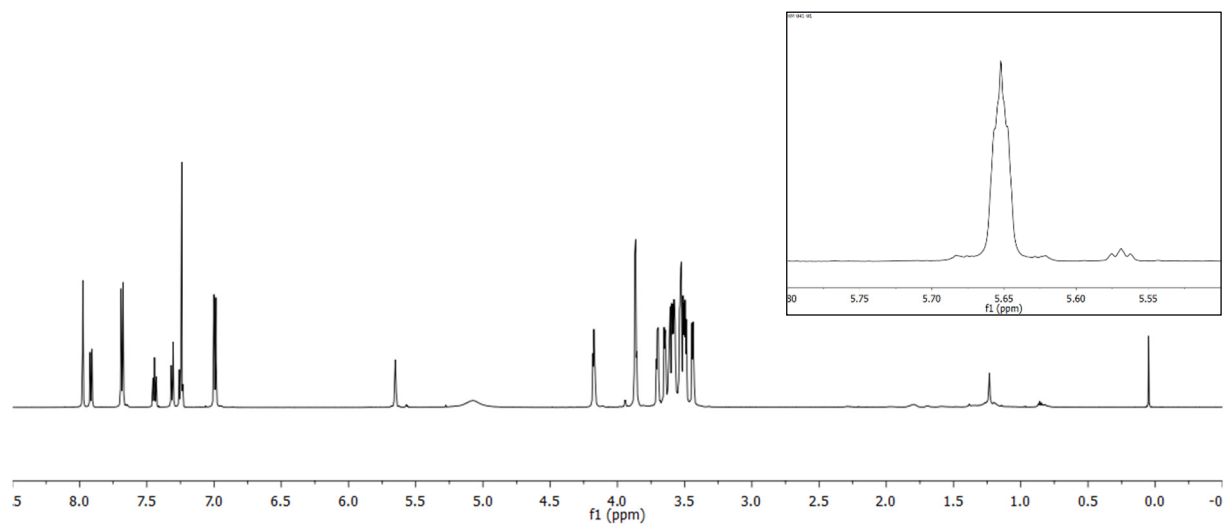


Figure S 25: ^1H NMR of (*S*)-**2** (600 MHz, CDCl_3). Insert: enlarged olefinic region.

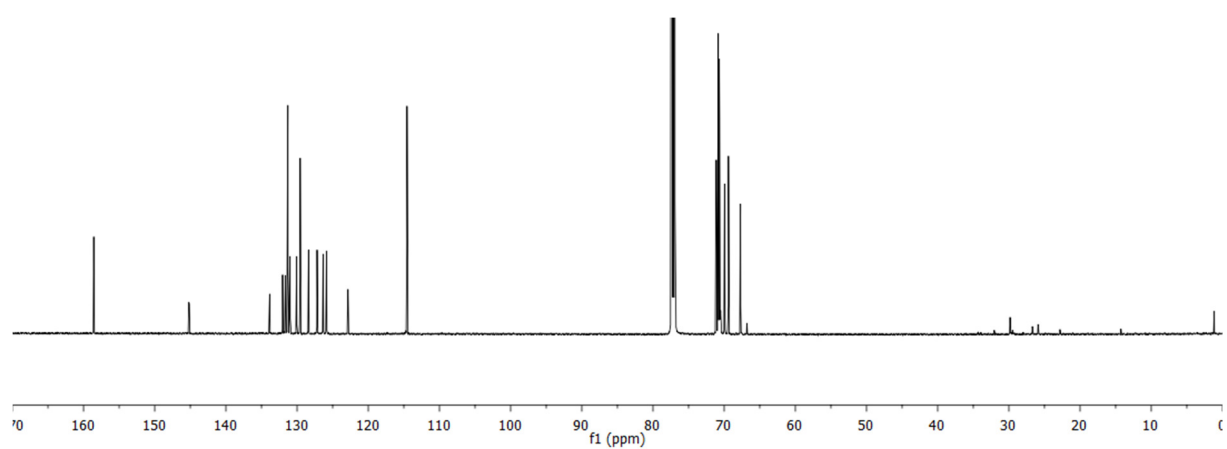


Figure S 26: $^{13}\text{C}\{^1\text{H}\}$ NMR of (*S*)-**2** (151 MHz, CDCl_3).

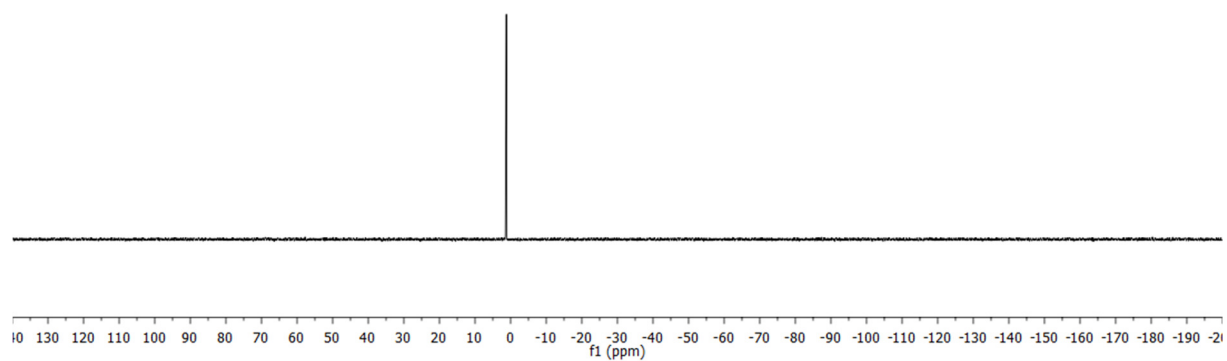


Figure S 27: $^{31}\text{P}\{^1\text{H}\}$ NMR of (*S*)-**2** (243 MHz, CDCl_3).

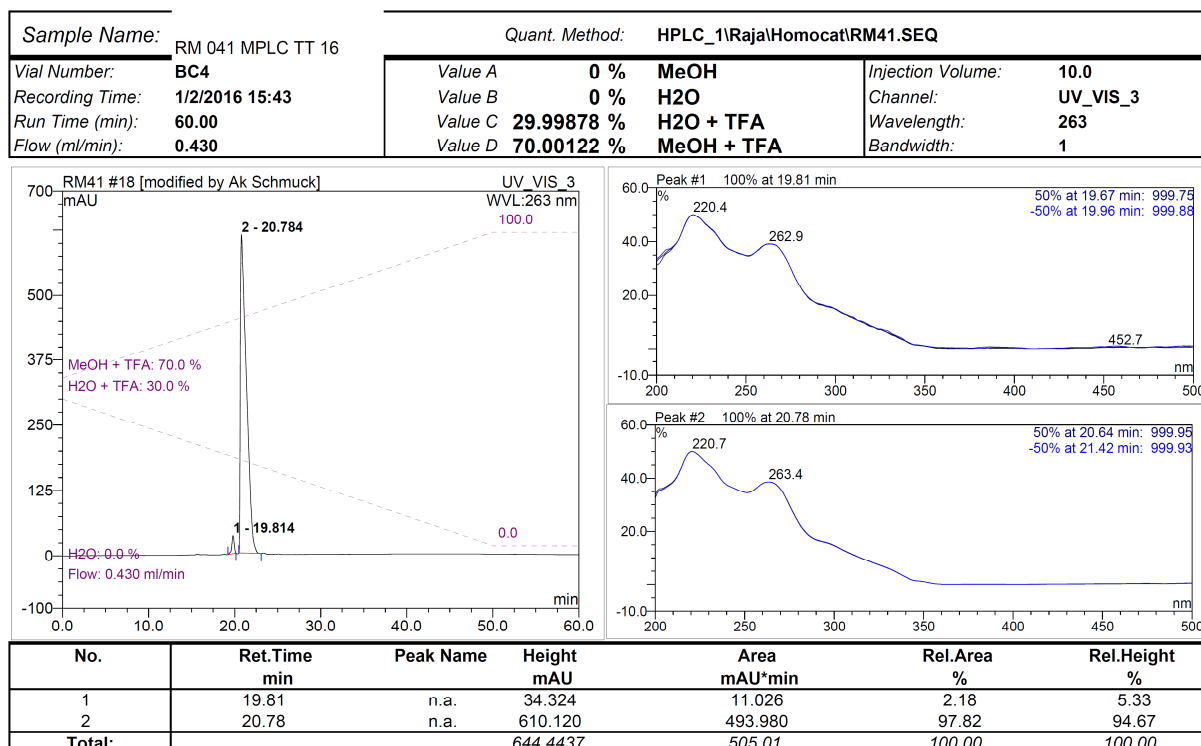
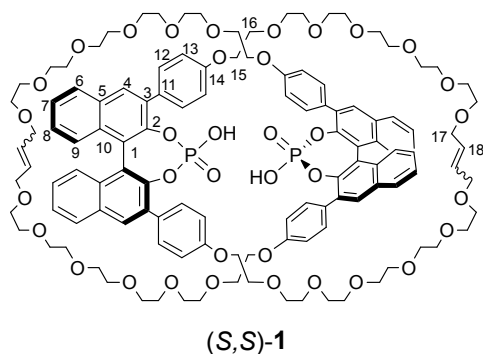


Figure S 28: Reversed-phase HPLC-chromatogram of (*S,S*)-**2**.

Catenane ((*S,S*)-**1**) was isolated as a brown oil with 13.9% yield (22.0 mg) after washing with HCl.



IR (ATR) $\bar{\nu}$ 2865, 1608, 1514, 1454, 1406, 1350, 1284, 1246, 1180, 1095, 996, 956, 885, 833, 754 cm^{-1} . **¹H NMR** (600 MHz, CDCl_3) δ 7.96 (s, 4H, H-4), 7.92 (d, $J = 8.2$ Hz, 4H, H-6), 7.57 (ps d, $J = 8.5$ Hz, 8H, H-12), 7.45 (t, $J = 7.4$ Hz, 4H, H-7), 7.30 (d, $J = 8.4$ Hz, 4H, H-9), 7.25 (t, $J = 7.4$ Hz, 2H, H-8), 6.87 (ps d, $J = 8.6$ Hz, 8H, H-13), 5.71 (s, 4H, H-18 of (*Z,Z*)-isomer, (*Z,Z*)/(*Z,E*)-ratio = 95:5), 5.63 (s, H-18 of (*Z,E*)-isomer, other peaks for (*Z,E*)-isomer not assignable, (*E,E*)-isomer not detected), 5.02 (br s, 2H, P(O)OH), 4.03 – 3.94 (m, 8H, H-15), 3.92 (br s, 8H, H-17), 3.73 – 3.61 (m, 8H, H-16), 3.59 – 3.40 (m, 80H, core glycol-OCH₂). **¹³C NMR**{¹H} (151 MHz, CDCl_3) δ 158.6 (C-14), 145.0 (br, C-2), 133.8 (C-3), 131.9 (C-10), 131.7 (C-5), 131.1 (C-12, C-4), 129.6 (C-18, C-11), 128.4 (C-6), 127.2 (C-9), 126.4 (C-8), 126.0 (C-7), 122.7 (C-1), 114.6 (C-13), 71.2 (C-17), 70.8 (core glycol-OCH₂), 70.7 (core glycol-OCH₂), 70.6 (core glycol-OCH₂), 69.8 (C-16), 69.5 (core glycol-OCH₂), 67.5 (C-15). **³¹P NMR**{¹H} (243 MHz, CDCl_3) δ 2.25 (br s, $\nu_{1/2} = 49$ Hz, P(O)OH). **COSY** (600 MHz/600 MHz, CDCl_3) δ 7.92/7.45 (H-6/H-7), 7.57/6.87 (H-12/H-13), 7.45/7.92, 7.25 (H-7/ H-6, H-8), 7.30/7.25 (H-9/H-8), 7.25/7.45, 7.30 (H-8/H-7, H-9), 6.87/7.57 (H-13/H-12), 5.71/3.92 (H-18/H-17), 4.03 – 3.94/3.73 – 3.61 (H-15/H-16), 3.92/5.71 (H-17/H-18), 3.73 – 3.61/4.03 – 3.94 (H-16/H-15). **HSQC** (600 MHz/151 MHz, CDCl_3) δ 7.96/131.1 (H-4/C-4), 7.91/128.4

(H-6/C-6), 7.57/131.1 (H-12/C-12), 7.45/126.0 (H-7/C-7), 7.30/127.2 (H-9/C-9), 7.25/126.4 (H-8/C-8), 6.87/114.6 (H-13/C-13), 5.71/129.6 (H-18/C-18), 4.03 – 3.94/67.5 (H-15/C-15), 3.92/71.2 (H-17/C-17), 3.73 – 3.61/69.8 (H-16/C-16), 3.59 – 3.40/70.8, 70.7, 70.6, 69.5 (core glycol-OCH₂/core glycol-OCH₂). **HMBC** (600 MHz/151 MHz, CDCl₃) δ 7.96/145.0, 131.9, 129.6, 128.4, 122.7 (H-4/C-2, C-10, C-11, C-6, C-1), 7.92/131.9, 126.4 (H-6/C-10, C-8), 7.57/158.6, 133.8, 131.1, (H-12/C-14, C-3, C-12), 7.45/131.7, 127.2 (H-7/C-5, C-9), 7.30/131.7, 126.0, 122.7 (H-9/C-5, C-7, C-1), 7.25/131.9, 128.4 (H-8/C-10, C-6), 6.87/158.5, 129.5, 114.6 (H-13/C-14, C-11, C-13), 5.71/129.6, 71.2 (H-18/C-18, C-17), 4.03 – 3.94/158.5, 69.8 (H-15/C-14, C-16), 3.92/129.6, 69.5 (H-17/C-18, core glycol-OCH₂), 3.73 – 3.61/70.8, 67.5 (H-16/core glycol-OCH₂, C-15), 3.59 – 3.40/70.8, 70.7, 70.6, 69.5 (core glycol-OCH₂/core glycol-OCH₂). **HR-ESI-pos** (CHCl₃/MeOH): *m/z* = 1135.44307 (calcd 1135.44267 for [C₁₂₀H₁₄₆O₃₆P₂Na₂]²⁺), 2247.89412 (calcd 2247.89612 for [C₁₂₀H₁₄₅O₃₆P₂Na]⁺). **HR-ESI-neg** (CHCl₃/MeOH): *m/z* = 1111.43660 (calcd 1111.44617 for [C₁₂₀H₁₄₄O₃₆P₂]²⁻), 2223.88260 (calcd 2223.89963 for [C₁₂₀H₁₄₅O₃₆P₂]⁻). **RP HPLC** (RP C18, MeOH with 0.05% TFA : water with 0.05% TFA = 70 : 30 gradient flow up to 100:0 within 50 min, 0.43 ml/min): *t_R* (area): 39.2 min (93.47%), 43.7 min (6.53%).²

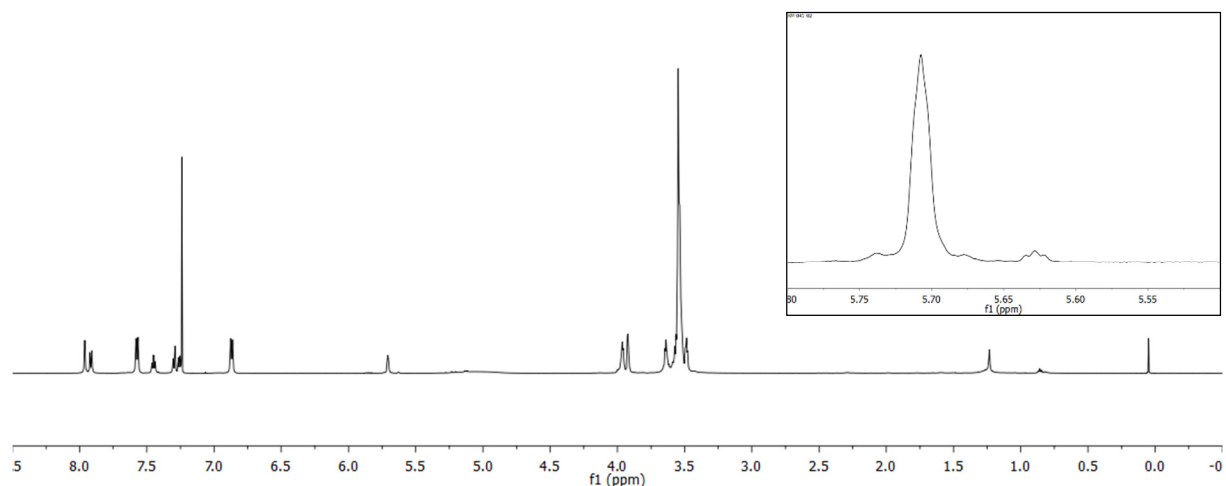


Figure S 29: ¹H NMR of (*S,S*)-**1** (600 MHz, CDCl₃). Insert: enlarged olefinic region.

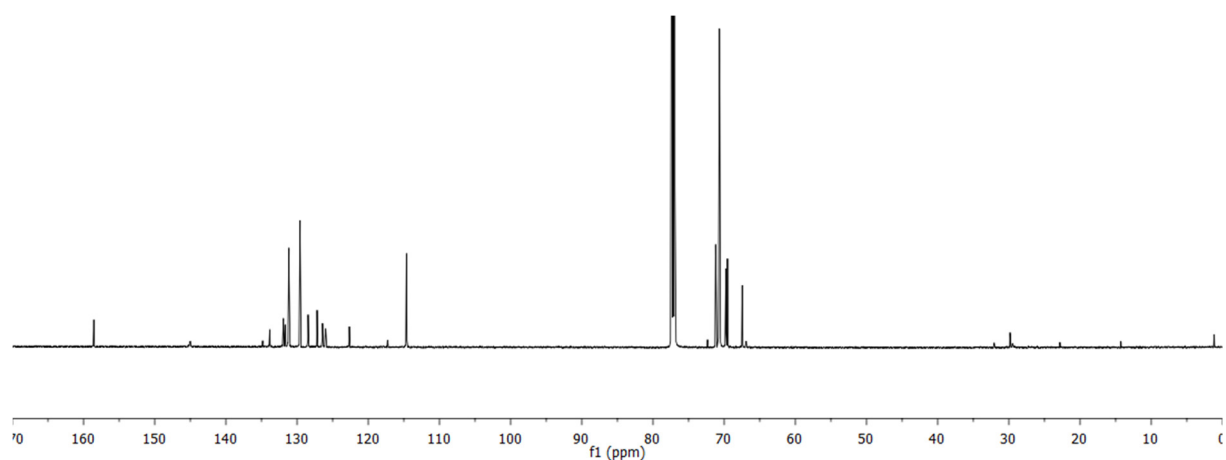


Figure S 30: ¹³C{¹H} NMR of (*S,S*)-**1** (151 MHz, CDCl₃).

² No satisfactory results of elemental analysis could be obtained for (*S,S*)-**1**. However, the purity of the material is clearly proven by NMR and HPLC-analysis.

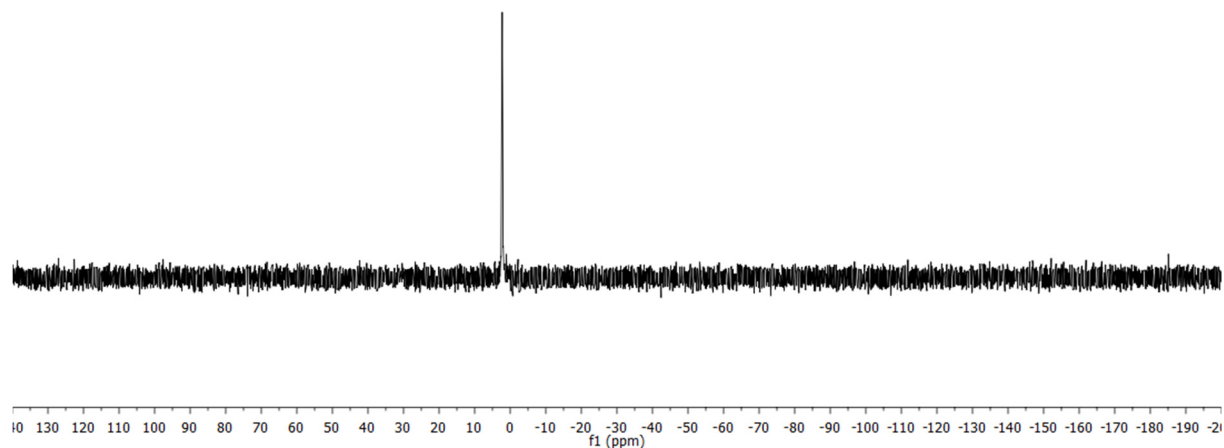


Figure S 31: $^{31}\text{P}\{^1\text{H}\}$ NMR of (*S,S*)-1 (243 MHz, CDCl_3).

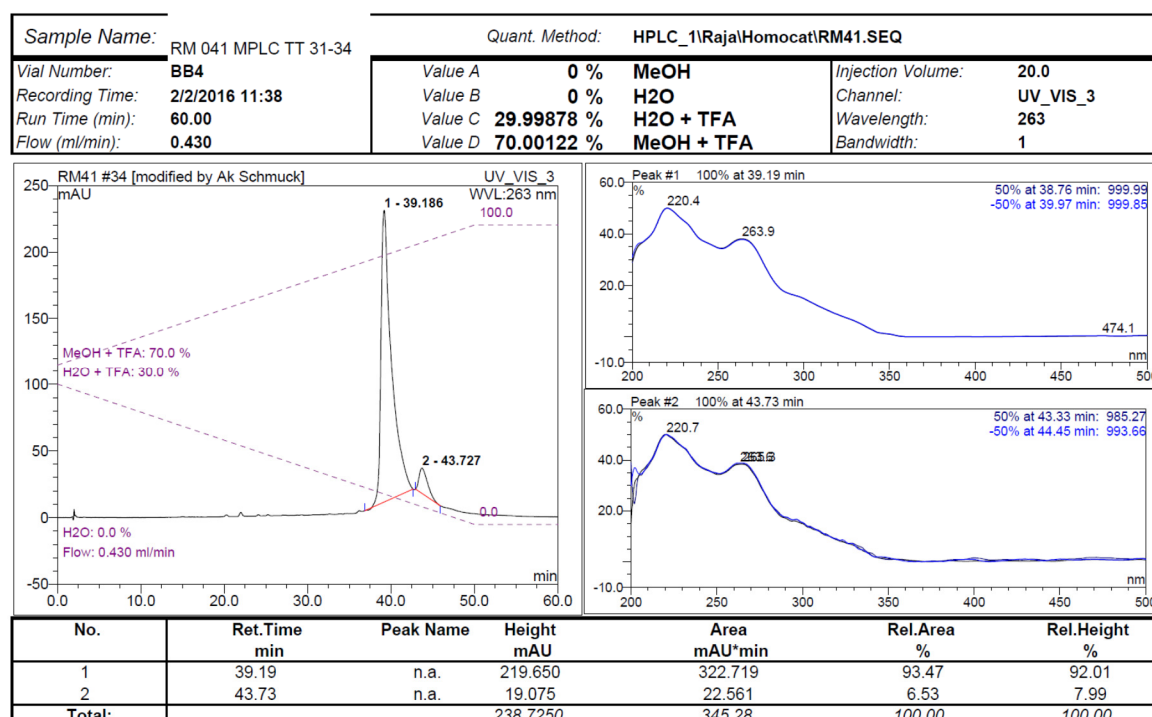


Figure S 32: Reversed-phase HPLC-chromatogram of (*S,S*)-1.

Independent synthesis of macrocycle (*S*)-2:

For the independent synthesis of the macrocycle (*S*)-2, the phosphoric acid (*S*)-7 was subjected to ring-closing metathesis in the absence of calcium:

(*S*)-7 (as the triethylammonium salt, $\text{C}_{68}\text{H}_{92}\text{NO}_{18}\text{P}$, $M = 1242.45$ g/mol, 16.0 mg, 12.9 μmol) was dissolved in dry toluene (5 ml) under argon atmosphere. To that solution, solid 1st generation Grubbs' catalyst (2.1 mg, 2.6 μmol , 0.2 equiv) was added and the mixture was stirred at room temperature in the dark. At different time points, 0.25 mL of reaction mixture was withdrawn and progress of the reaction was monitored by ^1H -NMR. After 24 h, further 1st generation Grubbs' catalyst (2.1 mg, 2.6 μmol , 0.2 equiv) was added and the mixture was stirred for another 24 h. The reaction was judged to be complete and the solvent was removed to give a brown residue. The mixture contained only the macrocycle (*S*)-2 and no catenane (*S,S*)-1 as judged by ^1H -NMR and ESI-MS.

DOSY-NMR

DOSY-spectra for (*S*)-7, (*S,S*)-8, (*S*)-2 and (*S,S*)-1:

DOSY-spectra were recorded on a Bruker DRX 500 spectrometer equipped with a gradient unit (maximum z-gradient of 1200 G/cm) and a DIFF30 probe equipped with a $^1\text{H}/^2\text{H}$ coil. Analysis of the data was performed using the Stejskal-Tanner-equation for relevant integral areas. Hydrodynamic radii were calculated using the Stokes-Einstein equation assuming spherical particles.

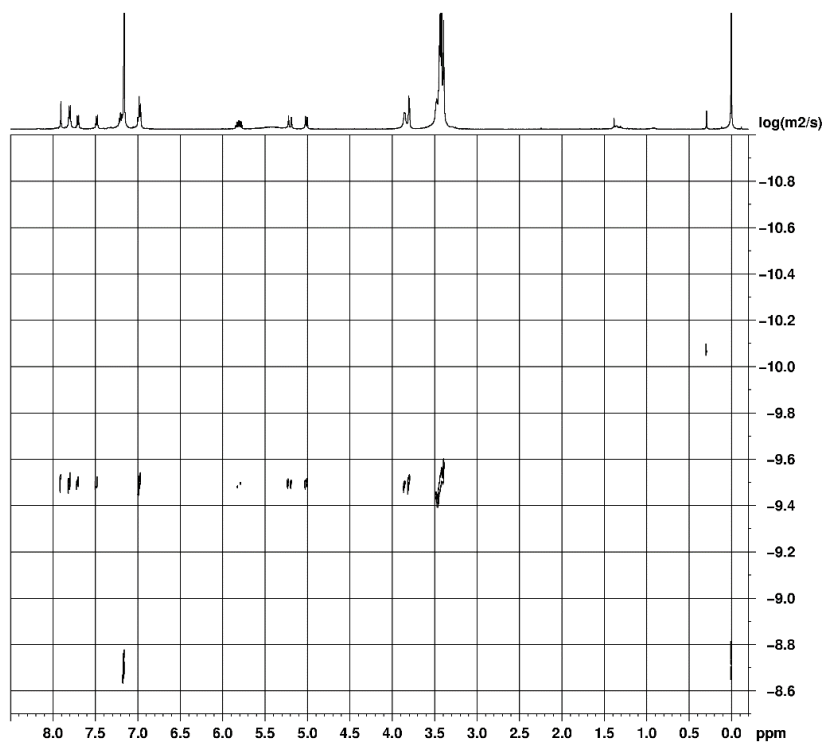


Figure S 33: DOSY NMR of (*S*)-7 (500 MHz, C_6D_6 , 298 K).

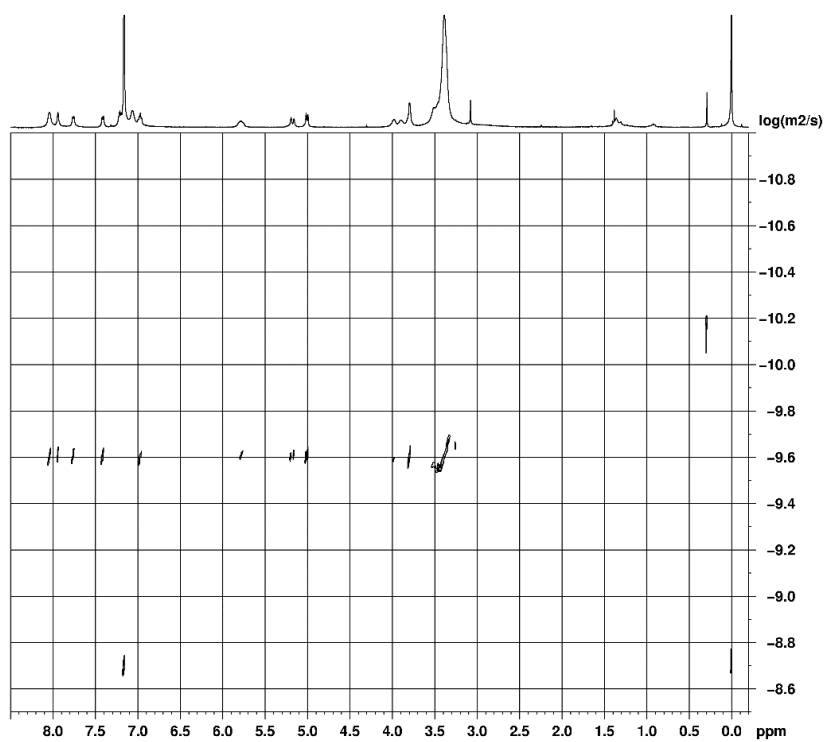


Figure S 34: DOSY NMR of (*S,S*)-**8** (500 MHz, C₆D₆, 298 K).

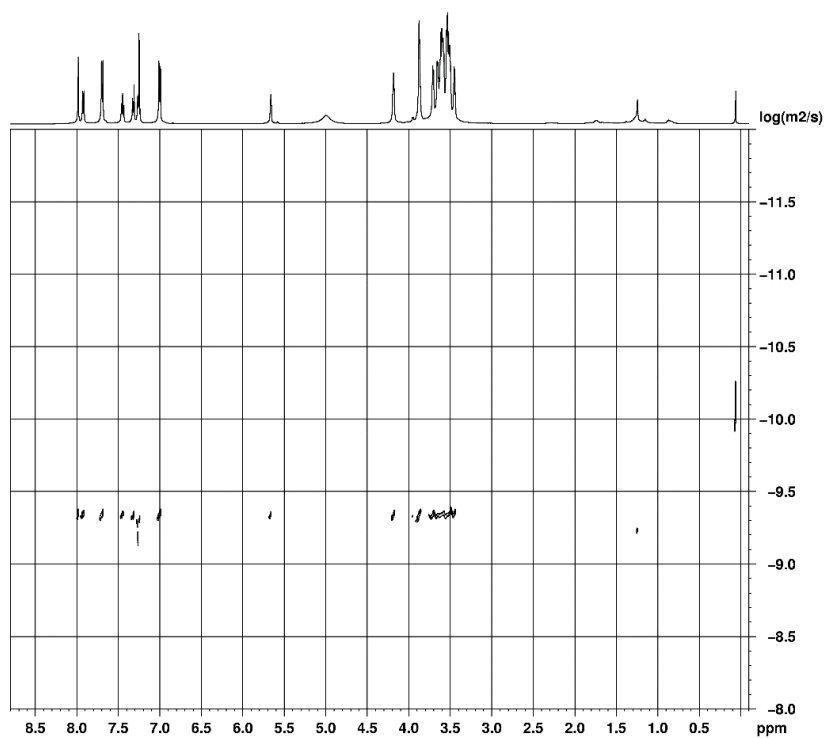


Figure S 35: DOSY NMR of (*S*)-**2** (500 MHz, CDCl₃, 298 K).

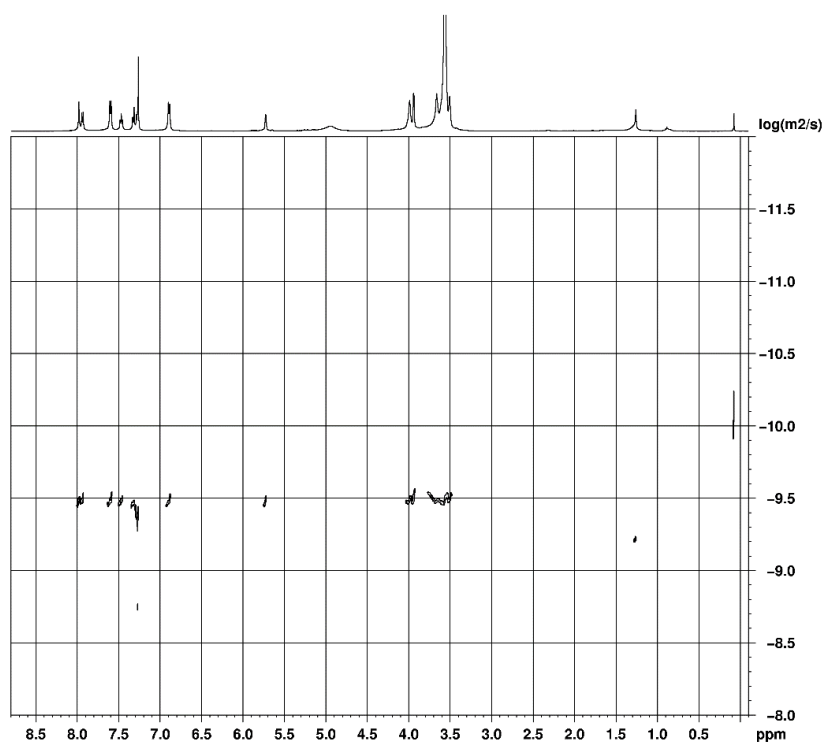


Figure S 36: DOSY NMR of (*S,S*)-**1** (500 MHz, CDCl₃, 298 K).

Table S 1: Analysis of the DOSY-data and calculation of the hydrodynamic radii

<i>(S)</i> - 7		<i>(S,S)</i> - 8		<i>(S)</i> - 2		<i>(S,S)</i> - 1	
Integral region [ppm]	Diffusion coefficient [10 ⁻¹⁰ m ² s ⁻¹]	Integral region [ppm]	Diffusion coefficient [10 ⁻¹⁰ m ² s ⁻¹]	Integral region [ppm]	Diffusion coefficient [10 ⁻¹⁰ m ² s ⁻¹]	Integral region [ppm]	Diffusion coefficient [10 ⁻¹⁰ m ² s ⁻¹]
8.065-7.599	3.165	8.327-7.560	2.452	8.232-7.565	4.552	8.186-7.796	3.192
7.592-7.382	3.103	-	-	7.124-6.702	4.540	7.770-7.401	3.261
6.028-5.543	3.213	6.104-5.466	2.433e	5.963-5.349	4.599	5.963-5.567	3.241
5.383-4.795	3.197	5.415-4.572	2.465	-	-	-	-
4.042-2.733	3.096	4.233-2.631	2.516	4.413-2.982	4.524	4.426-3.852	3.144
-	-	-	-	-	-	3.839-2.902	3.279
Mean diffusion coefficient [10 ⁻¹⁰ m ² s ⁻¹]	3.12		2.47		4.55		3.22
Hydrodynamic radius [Å]	11.5		14.6		8.85		12.5

Macromodel-calculations for (*S*)-**7**, (*S,S*)-**8**, (*S*)-**2** and (*S,S*)-**1**:

Schrödinger MacroModel 10.1 was used for the molecular modeling studies. The calculation was performed on the force field OPLS (optimized potentials for liquid simulations) 2005 choosing chloroform as the solvent. For the collapsed structures, a conformational search (mixed torsional/low-mode sampling) was performed and the lowest energy structure was used. For the extended structures, energy minimization (PCRG, convergence threshold 0.05) was performed using distance constraints, followed by a minimization with removed

constraints. The dimensions of the resulting structures were estimated by determining the widths and heights of the structures (see figure S37 to S41), which were then averaged. The resulting averaged diameters of the collapsed and extended structures were used to calculate a time-averaged mean diameter.

This is a rather crude methodology and does not take into account other possible conformations, does not account for the different occupancies of the calculated conformations and neglects the exact shape of the molecules for the estimation of their size. However, the resulting mean diameter was used as an indication for the molecular sizes and for comparison with the results obtained by diffusion ordered spectroscopy (see table S2).

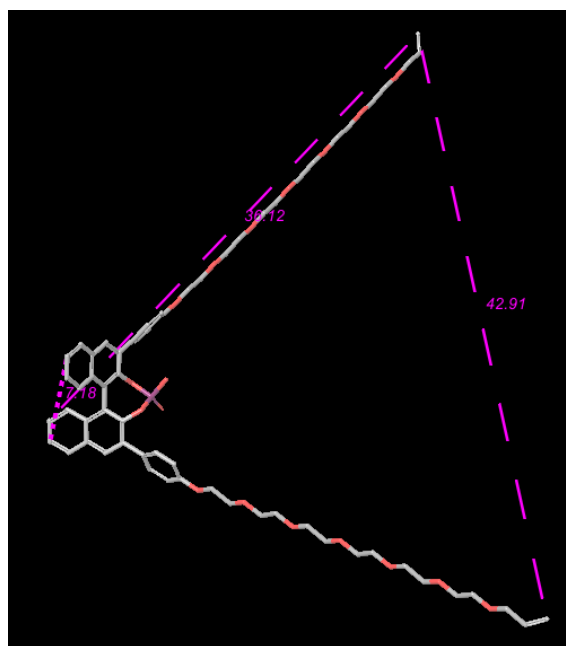
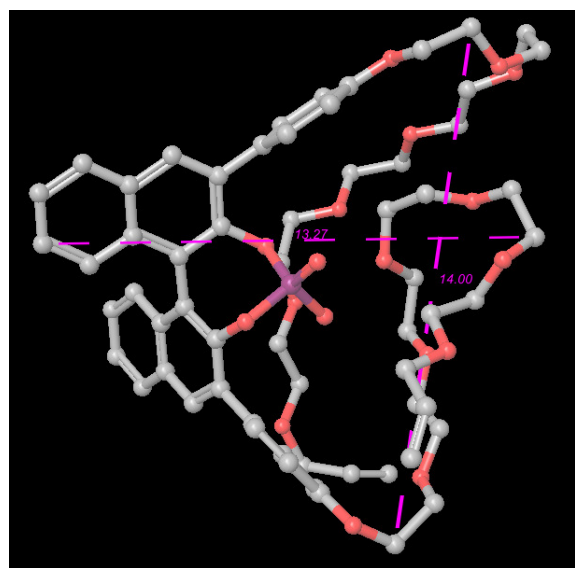


Figure S 37: Collapsed and extended structure for (*S*)-7 (calculated average diameter for both structures: $r_{\text{mean}} = 11.1 \text{ \AA}$).

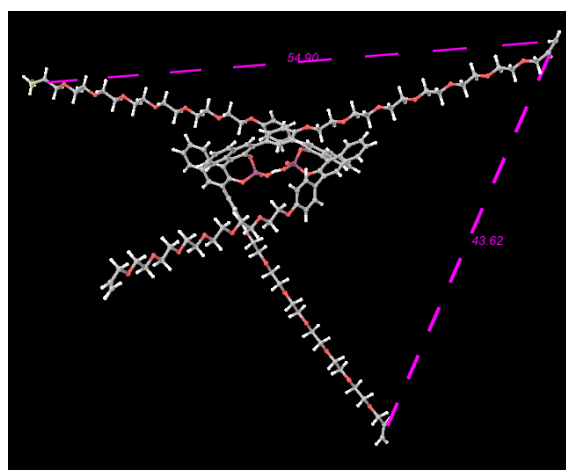
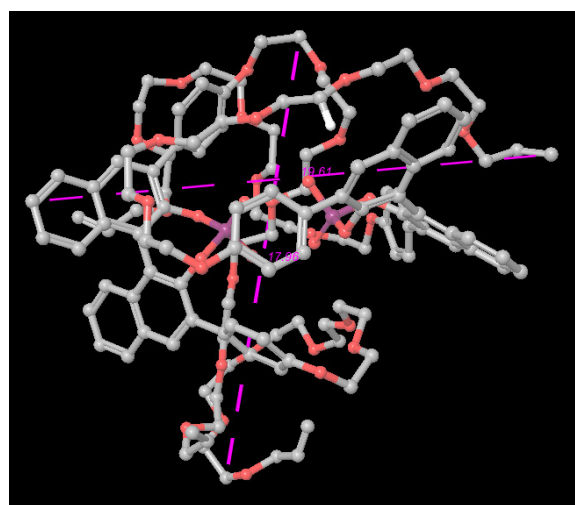


Figure S 38: Collapsed and extended structure for the precatenane (calculated as the hydrogen-bonded dimer instead of the Ca-bisphosphate; calculated average diameter for both structures: $r_{\text{mean}} = 17.1 \text{ \AA}$).

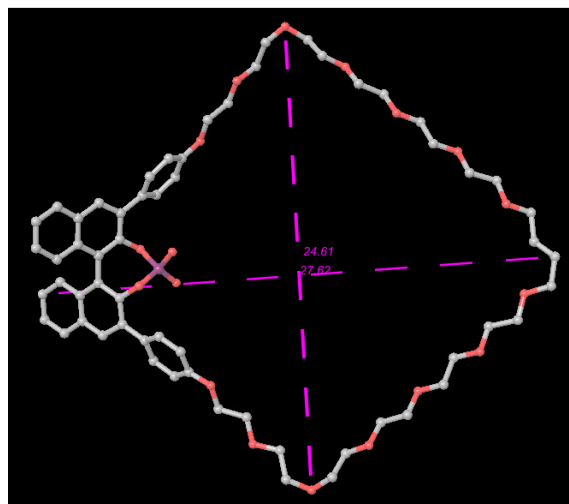
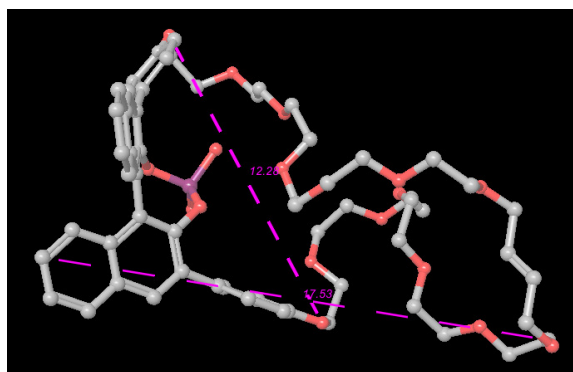


Figure S 39: Collapsed and extended structure for (*S*)-2 (calculated average diameter for both structures: $r_{\text{mean}} = 10.3 \text{ \AA}$).

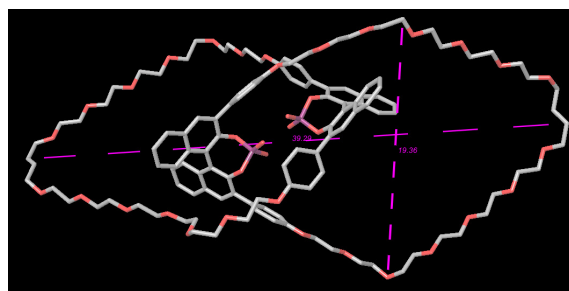
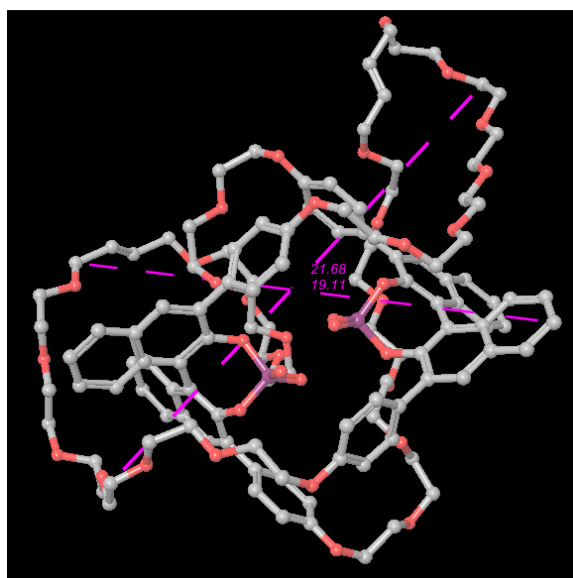


Figure S 40: Collapsed and extended structure for (*S,S*)-1 (calculated average diameter for both structures: $r_{\text{mean}} = 12.4 \text{ \AA}$).

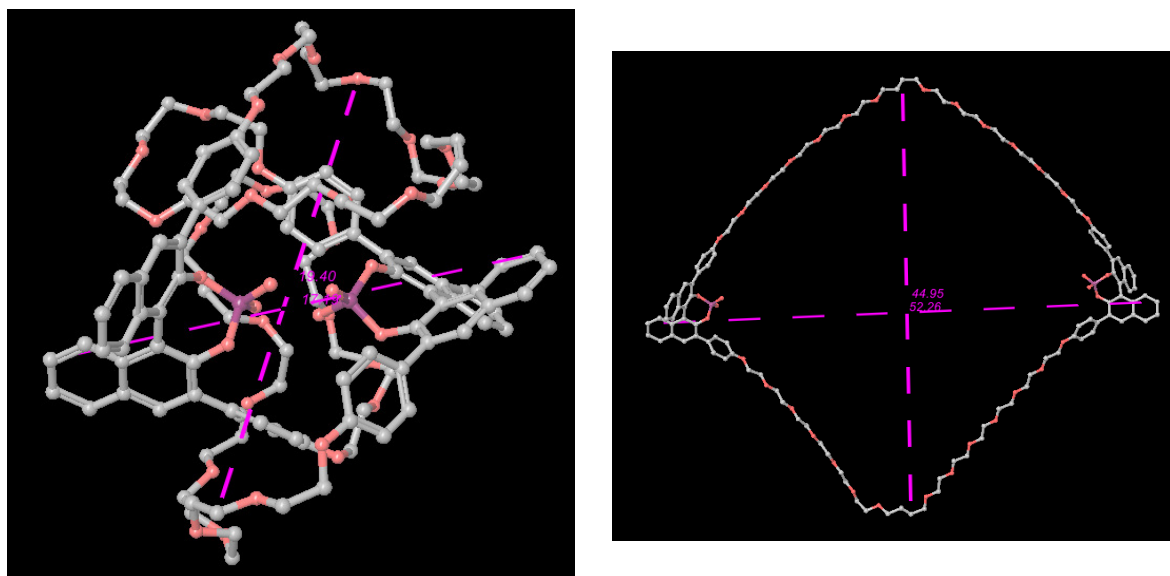


Figure S 41: Collapsed and extended structure for a potential [1+1]-macrocycle (calculated average diameter for both structures: $r_{\text{mean}} = 16.7 \text{ \AA}$).

Table S 2: Diffusion coefficients and hydrodynamic radii as determined per DOSY-NMR and calculated molecular radii. a) all: 500 MHz, 298 K, b) Calculated using the Stokes-Einstein-equation assuming spherical particles, c) Macro Model, average of chosen conformations, d) in C_6D_6 , e) in CDCl_3 , f) deviation from (S,S)-1.

	DOSY-results ^(a)		Calculated $r_{\text{Mean}} [\text{\AA}]^{(c)}$	Deviation
	D [$10^{-10} \text{ m}^2 \text{ s}^{-1}$]	$r_{\text{Hydrodyn.}} [\text{\AA}]^{(b)}$		
(S)-7	3.12 ^(d)	11.5	11.1	4%
(S,S)-8	2.47 ^(d)	14.6	17.1	17%
(S)-2	4.55 ^(e)	8.8	10.3	16%
(S,S)-1	3.22 ^(e)	12.5	12.4	1%
[1+1]macrocycle	-	-	16.7	34% ^(f)

ESI-MS/MS measurements

The MS and MS/MS spectra were recorded on a Thermo Scientific Orbitrap LTQ-XL mass spectrometer. MS/MS spectra were produced by CID in the LTQ.

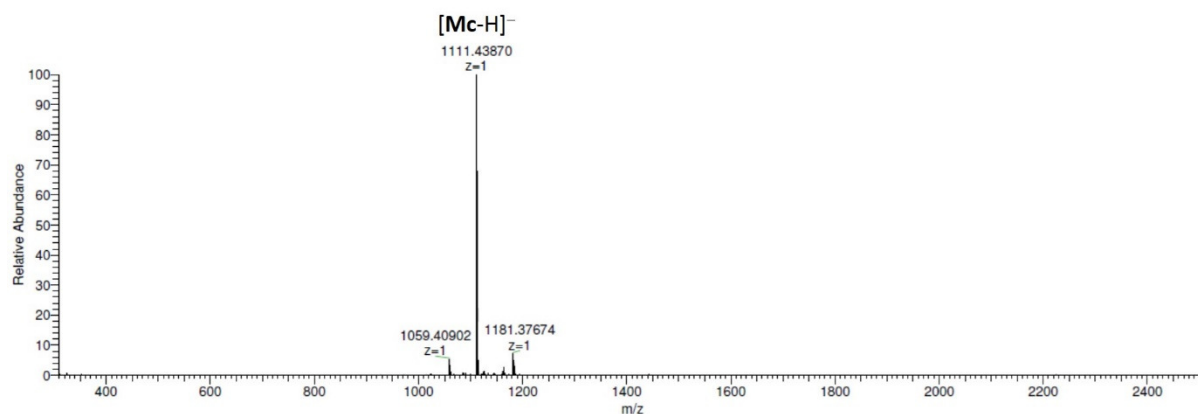


Figure S 42: ESI-negative MS spectrum of the macrocycle (S)-2 [Mc] (full mass range).

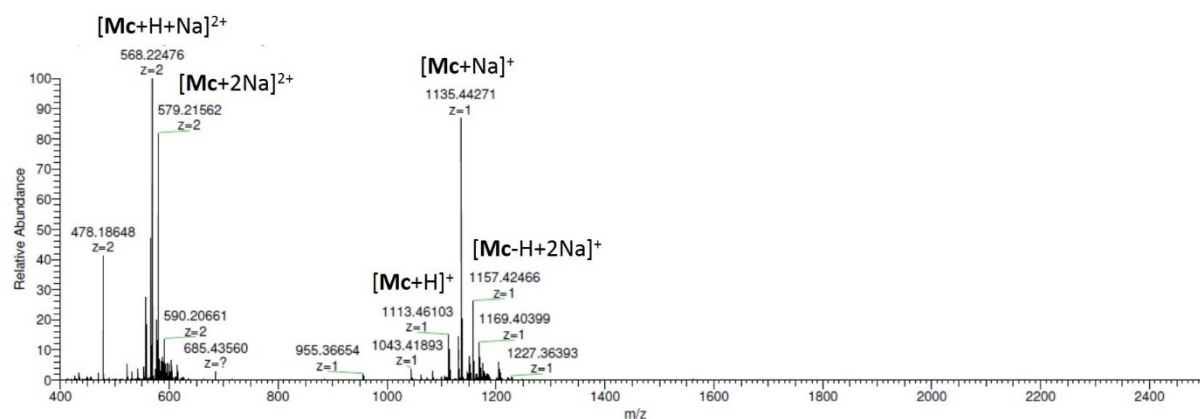


Figure S 43: ESI-positive MS spectrum of the macrocycle (S)-2 [Mc] (full mass range).

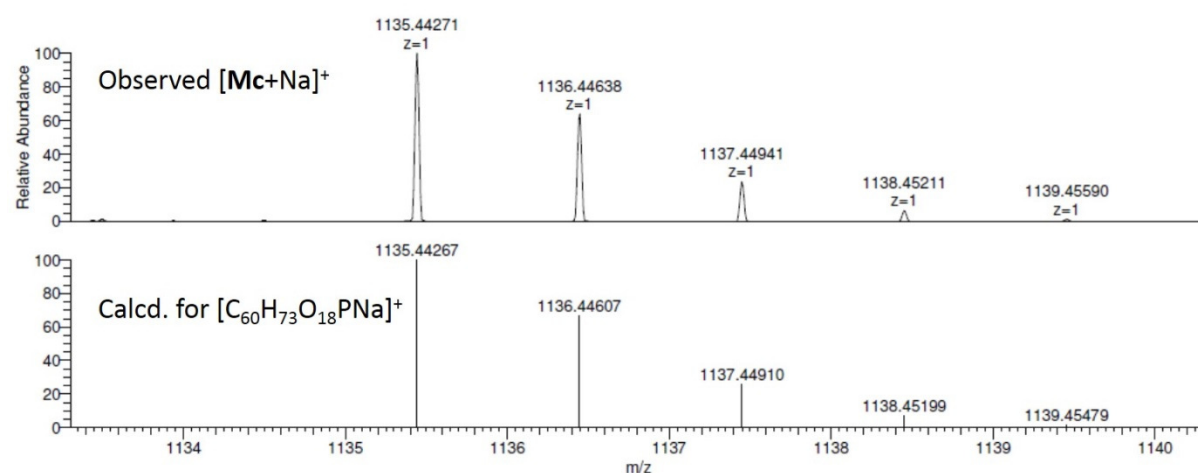


Figure S 44: ESI-positive MS spectrum of the macrocycle (S)-2 [Mc] (mass range m/z=1134-1140, top: experimental data, bottom: simulated for [M+Na]⁺).

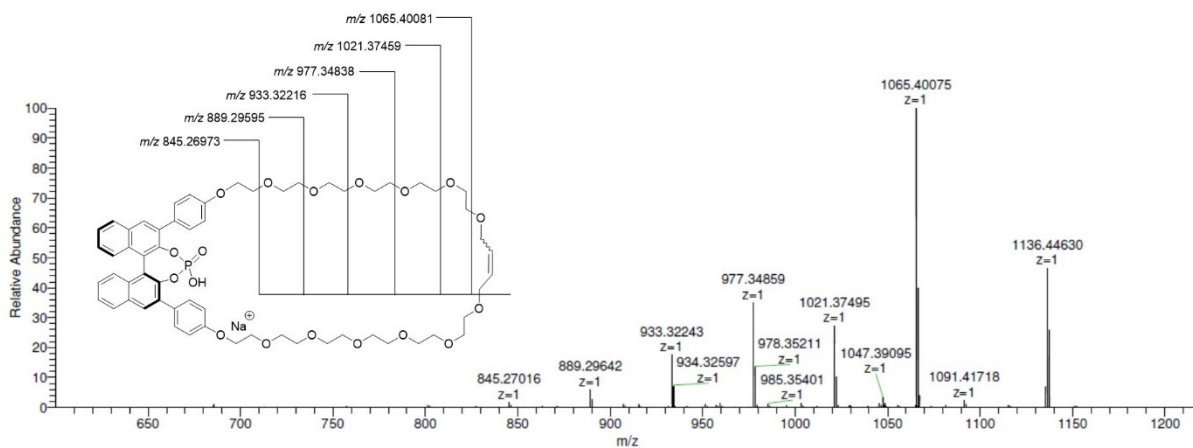


Figure S 45: ESI-positive CID-MS/MS spectrum of the macrocycle (*S*)-2 [Mc] ($m/z=1135.44@20\text{eV}$).

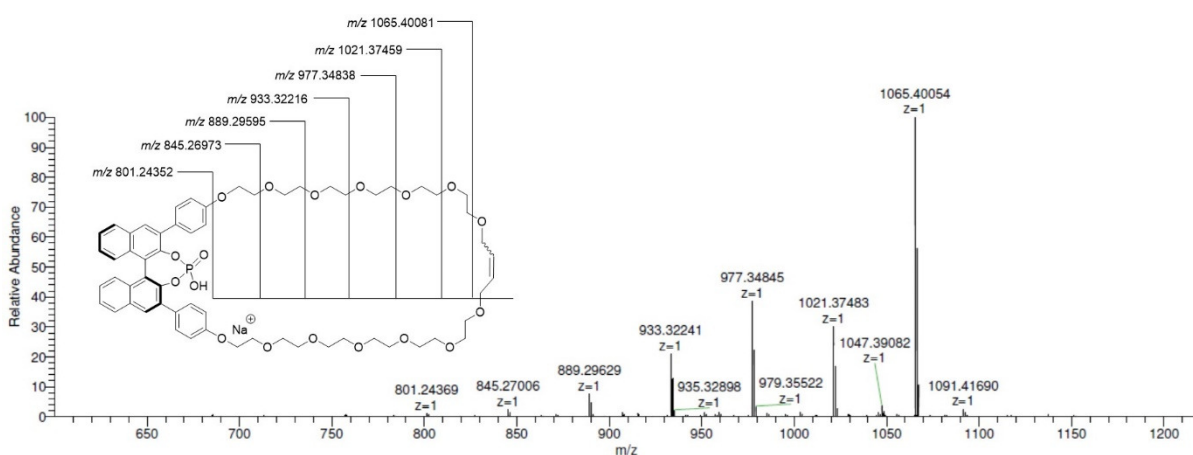


Figure S 46: ESI-positive CID-MS/MS spectrum macrocycle (*S*)-2 [Mc] ($m/z=1135.44@30\text{eV}$).

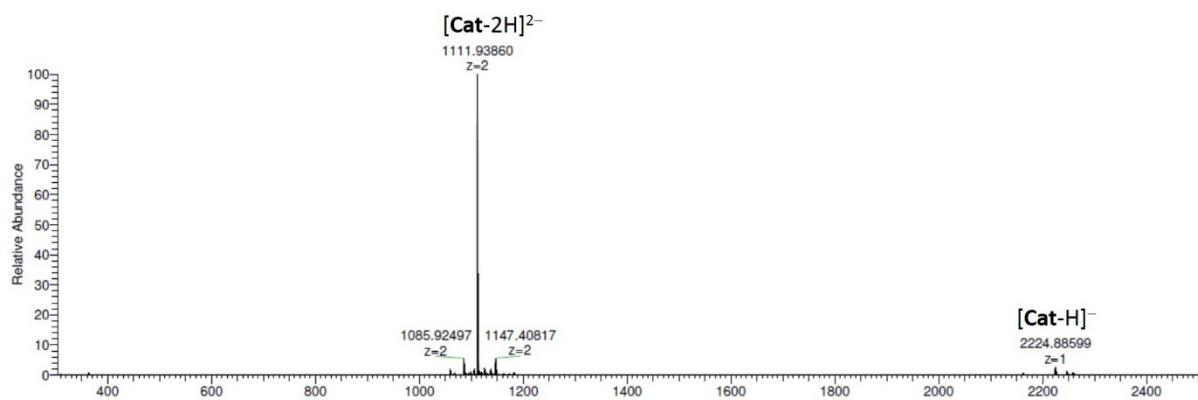


Figure S 47: ESI-negative MS spectrum of the catenane (*S,S*)-1 [Cat] (full mass range).

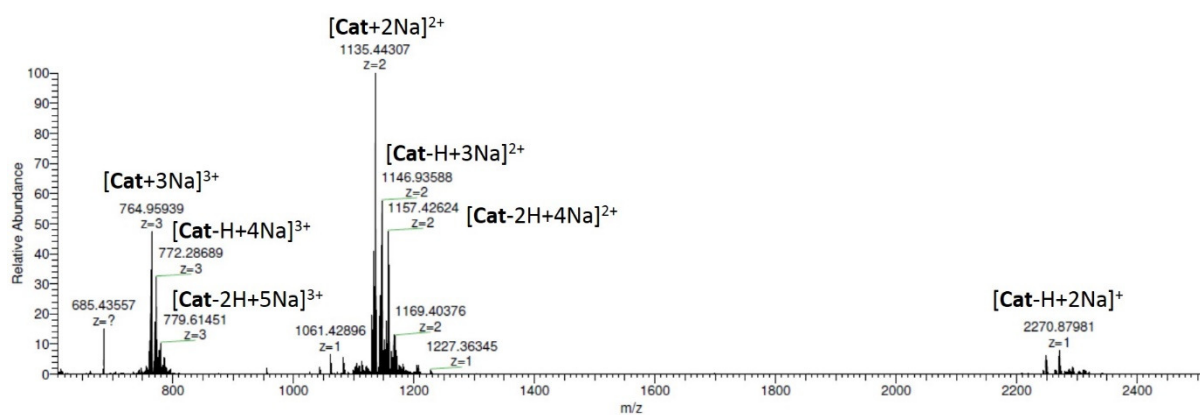


Figure S 48: ESI-positive MS spectrum of the catenane (*S,S*)-1 [Cat] (full mass range).

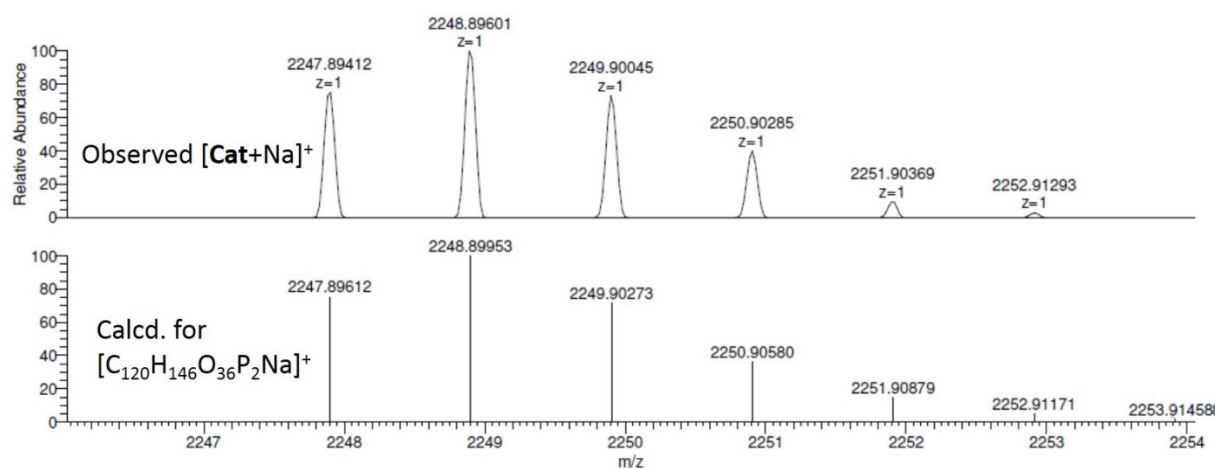


Figure S 49: ESI-positive MS spectrum of the catenane (*S,S*)-1 [Cat] (mass range $m/z=2247-2254$, top: experimental data, bottom: simulated for $[M+Na]^+$).

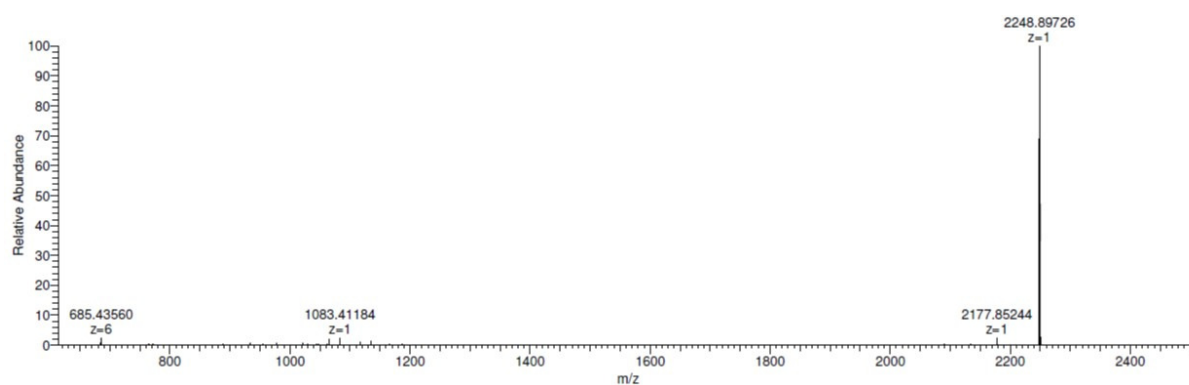


Figure S 50: ESI-positive CID-MS/MS spectrum of the catenane (*S,S*)-1 [Cat] ($m/z=2248.89@45eV$).

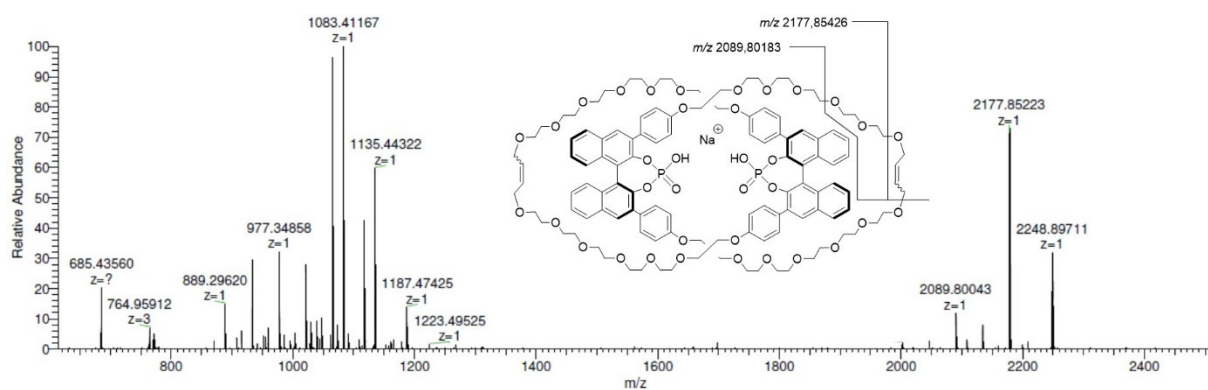


Figure S 51: Positive CID-MS/MS spectrum of the catenane (*S,S*)-1 [Cat] ($m/z=2248.89@50\text{eV}$, full mass range)

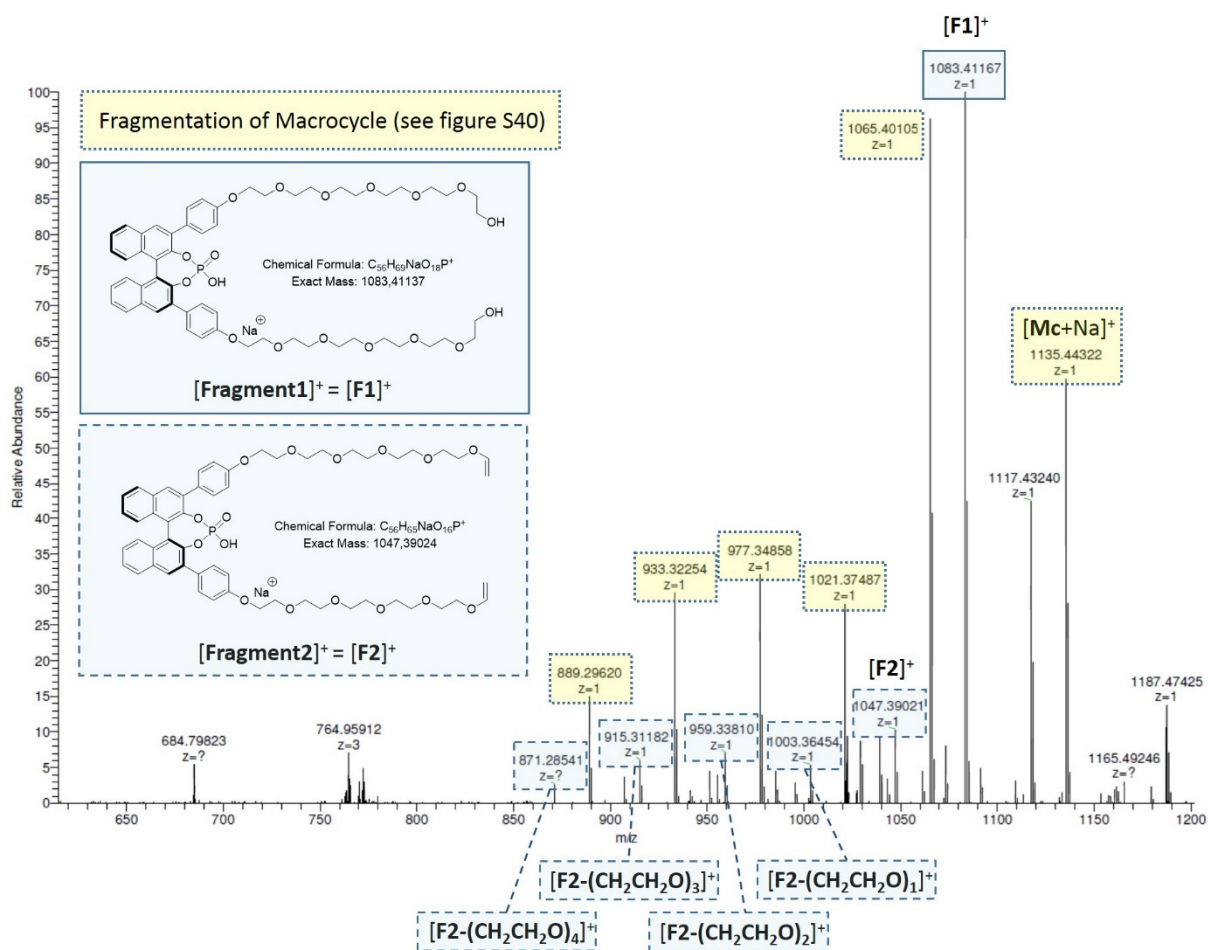


Figure S 52: Positive CID-MS/MS spectrum of (*S,S*)-1 ($m/z=2248.89@50\text{eV}$, mass range $m/z=600-1200$)

Determination of the binding constants

General:

The host-molecules were used as the corresponding tetrabutylammonium-salts. These were obtained by addition of a stoichiometric amount of tetrabutylammonium-hydroxide solution (0.1 M in ethanol) to a solution of the corresponding phosphoric acid [(*S*)-**2** or (*S,S*)-**1**] in methanol, followed by stirring for thirty minutes and removal of all volatiles *in vacuo*. The resulting tetrabutylammonium-salts [(*S*)-**2**⁻(Bu₄N⁺) or [(*S,S*)-**1**²⁻(Bu₄N⁺)₂] were dissolved in d₆-DMSO to give a clear solution (0.5 mM).

The diamines which were employed as guest molecules were used as the corresponding bis-hydrochlorides. These were either purchased directly (for *D/L*-arginine methyl ester bis-hydrochloride, *D/L*-lysine methyl ester bis-hydrochloride) or the bis-hydrochlorides were generated from the free amines (for (*S,S*)- and (*R,R*)-1,2-diaminocyclohexane). This was done by addition of concentrated HCl (4 eq) to a solution of the free diamine in tetrahydrofurane, stirring for 30 minutes, filtration, washing of the solid with tetrahydrofurane and drying *in vacuo*. The resulting bis-hydrochlorides were dissolved in d₆-DMSO to give a clear solution (125 mM).

NMR-titrations:

The NMR-Titrations were performed on a Bruker DRX 500 spectrometer [¹H: 500 MHz]. The respective host (0.5 mM in 500 ml of d₆-DMSO) was titrated with a solution of the respective guest (125 mM in d₆-DMSO, 0.5 to 70 equivalents in 14 steps).

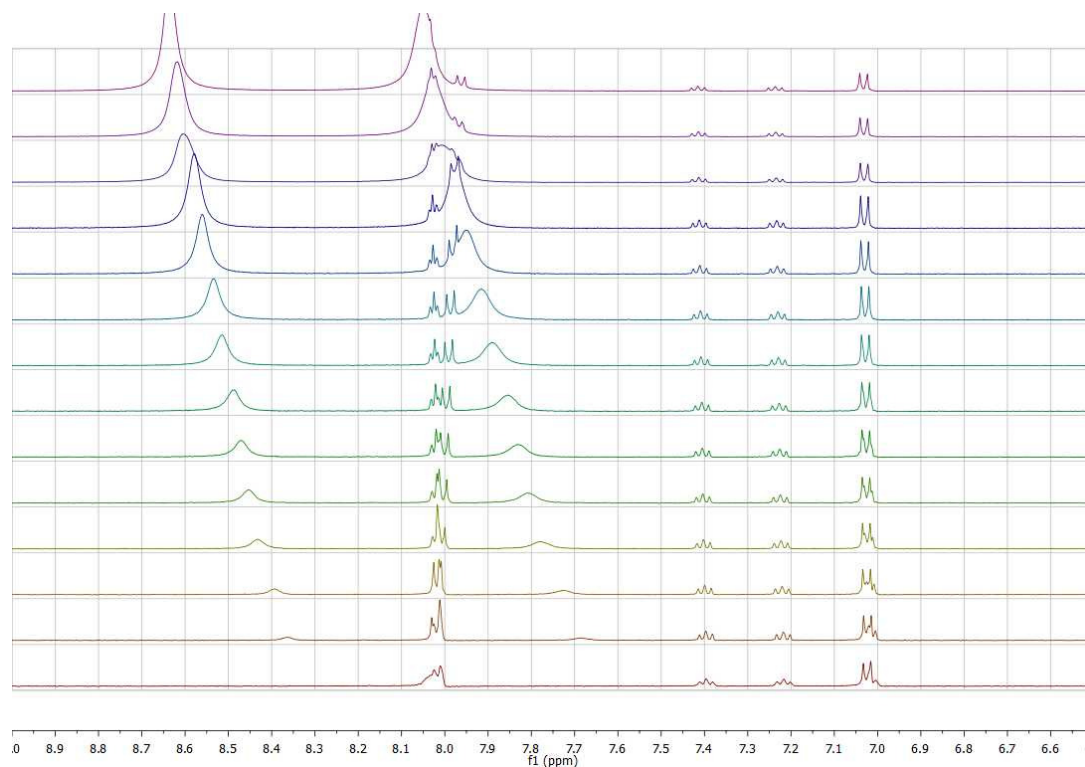


Figure S 53: Stacked NMR-spectra (aromatic region) for the binding of L-lysine methyl ester (0.5 to 70 equivalents, as the bis-HCl salt) to (*S*)-**2** (as the Bu₄N⁺-salt) [all: 500 MHz, d₆-DMSO, 298K, initial concentration of (*S*)-**2**: 0.5 mM].

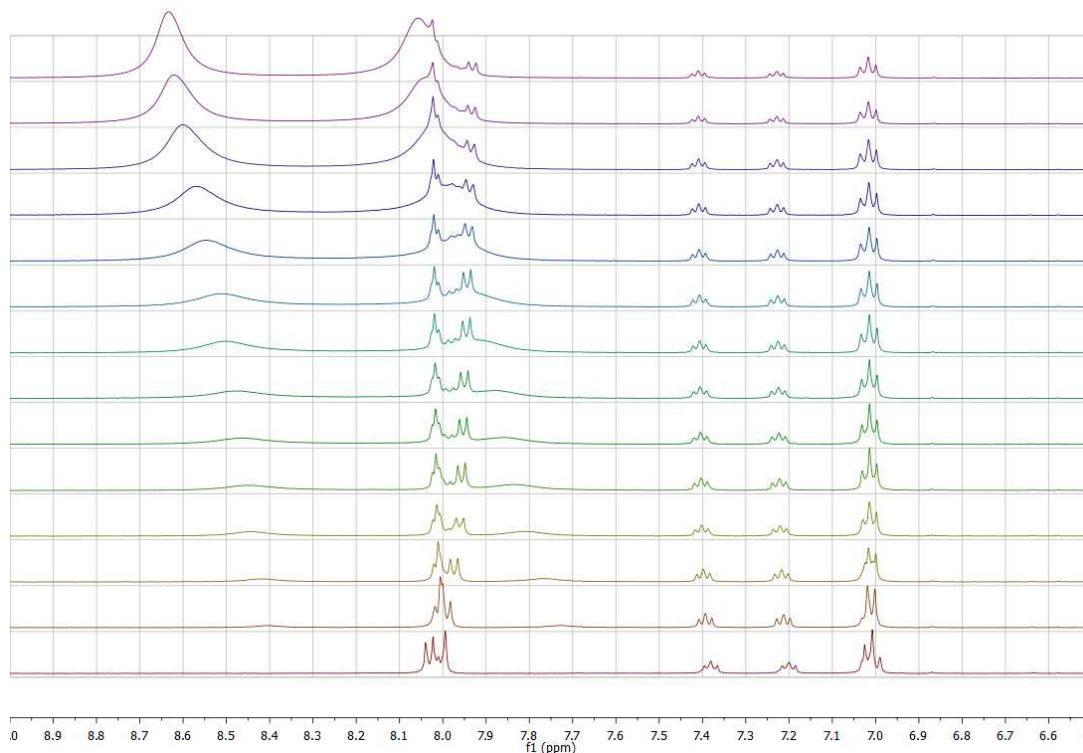


Figure S 54: Stacked NMR-spectra (aromatic region) for the binding of L- lysine methyl ester (0.5 to 70 equivalents, as the bis-HCl salt) to (*S,S*)-**1** (as the bis-Bu₄N⁺-salt) [all: 500 MHz, d₆-DMSO, 298K, initial concentration of (*S,S*)-**1**: 0.5 mM].

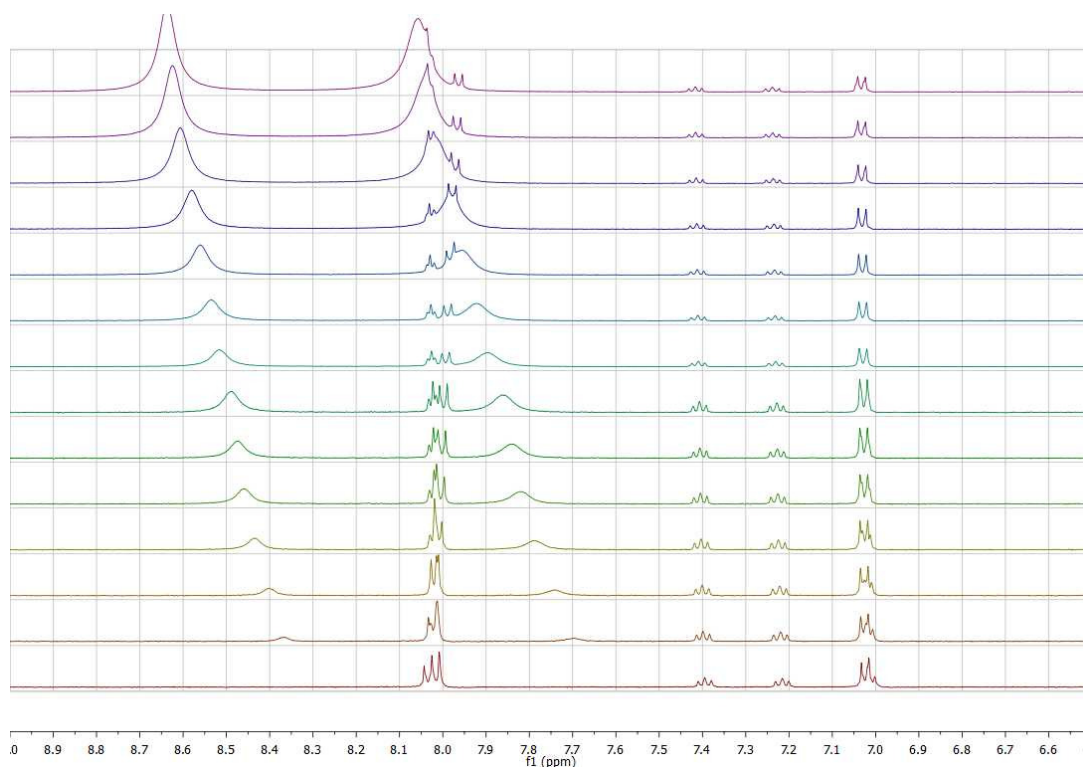


Figure S 55: Stacked NMR-spectra (aromatic region) for the binding of D-lysine methyl ester (0.5 to 70 equivalents, as the bis-HCl salt) to (*S*)-**2** (as the Bu₄N⁺-salt) [all: 500 MHz, d₆-DMSO, 298K, initial concentration of (*S*)-**2**: 0.5 mM].

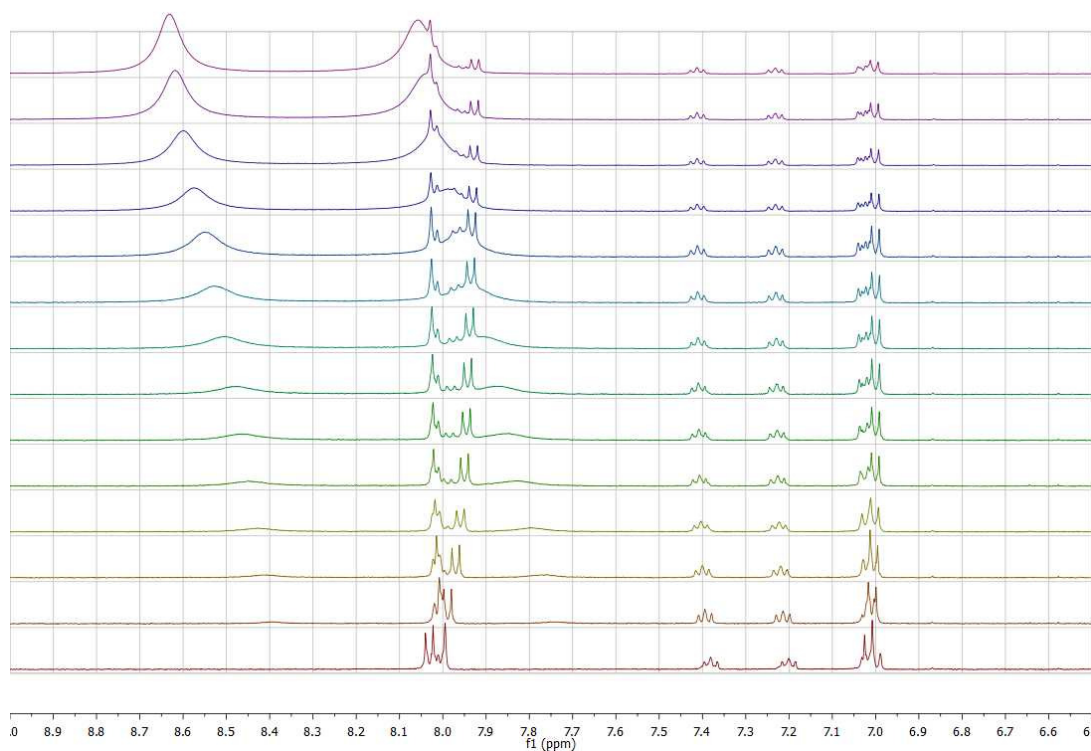


Figure S 56: Stacked NMR-spectra (aromatic region) for the binding of D-lysine methyl ester (0.5 to 70 equivalents, as the bis-HCl salt) to (*S,S*)-**1** (as the bis-Bu₄N⁺-salt) [all: 500 MHz, d₆-DMSO, 298K, initial concentration of (*S,S*)-**1**: 0.5 mM].

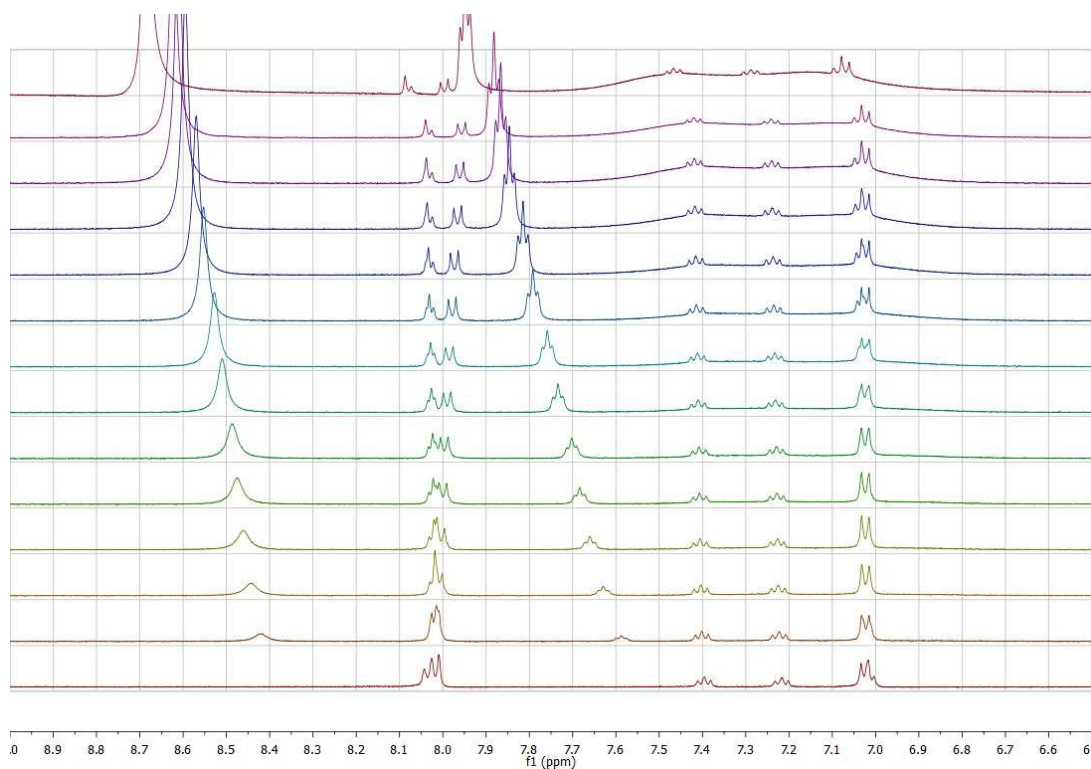


Figure S 57: Stacked NMR-spectra (aromatic region) for the binding of L-arginine methyl ester (0.5 to 70 equivalents, as the bis-HCl salt) to (*S*)-**2** (as the Bu₄N⁺-salt) [all: 500 MHz, d₆-DMSO, initial concentration of (*S*)-**2**: 0.5 mM].

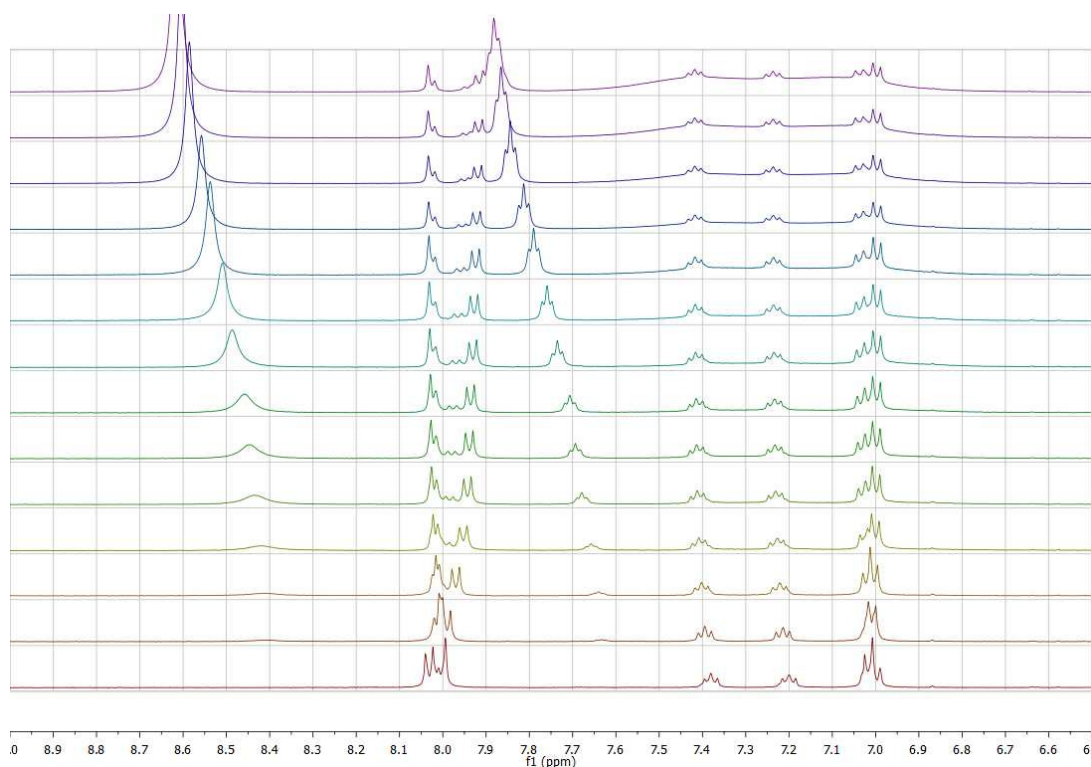


Figure S 58: Stacked NMR-spectra (aromatic region) for the binding of L-arginine methyl ester (0.5 to 70 equivalents, as the bis-HCl salt) to (*S,S*)-**1** (as the bis-Bu₄N⁺-salt) [all: 500 MHz, d₆-DMSO, 298K, initial concentration of (*S,S*)-**1**: 0.5 mM].

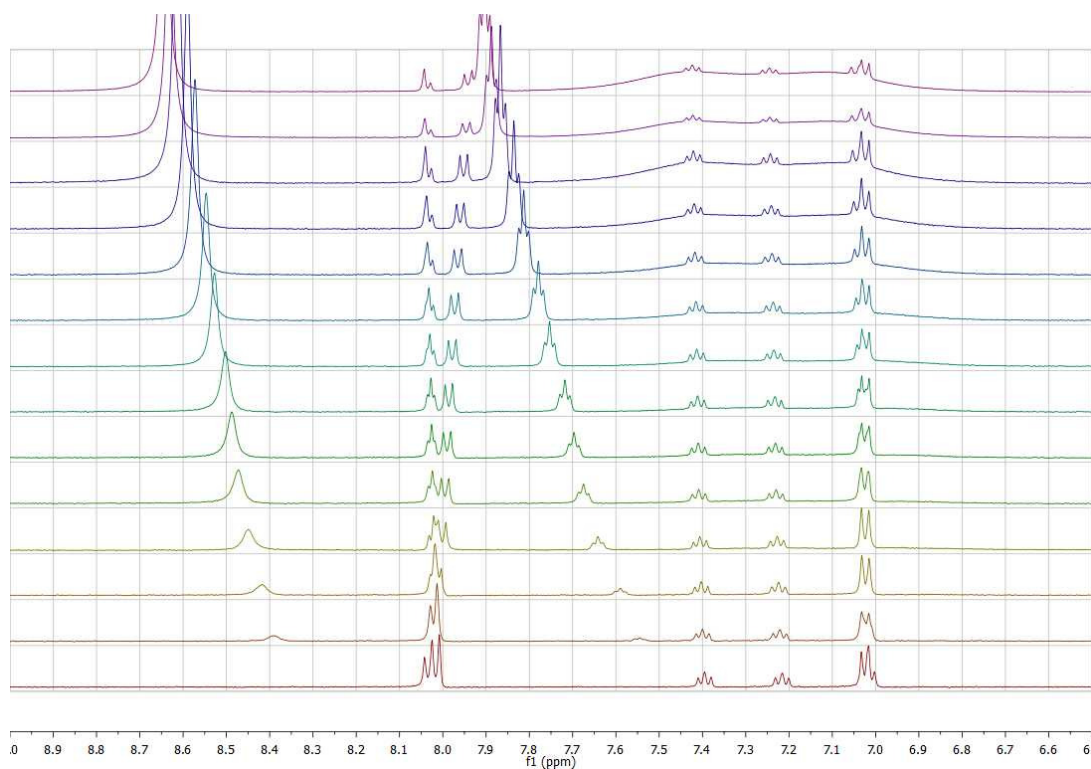


Figure S 59: Stacked NMR-spectra (aromatic region) for the binding of D-arginine methyl ester (0.5 to 70 equivalents, as the bis-HCl salt) to (*S*)-**2** (as the Bu₄N⁺-salt) [all: 500 MHz, d₆-DMSO, 298K, initial concentration of (*S*)-**2**: 0.5 mM].

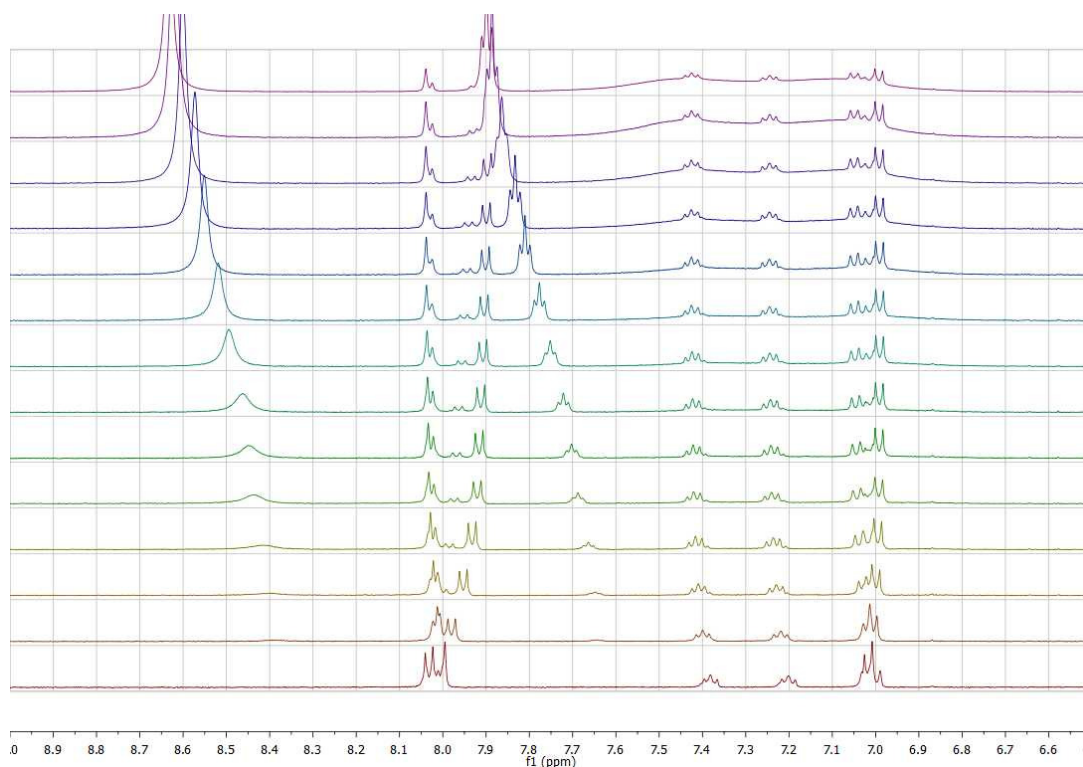


Figure S 60: Stacked NMR-spectra (aromatic region) for the binding of D-arginine methyl ester (0.5 to 70 equivalents, as the bis-HCl salt) to (*S,S*)-**1** (as the bis-Bu₄N⁺-salt) [all: 500 MHz, d₆-DMSO, 298K, initial concentration of (*S,S*)-**1**: 0.5 mM].

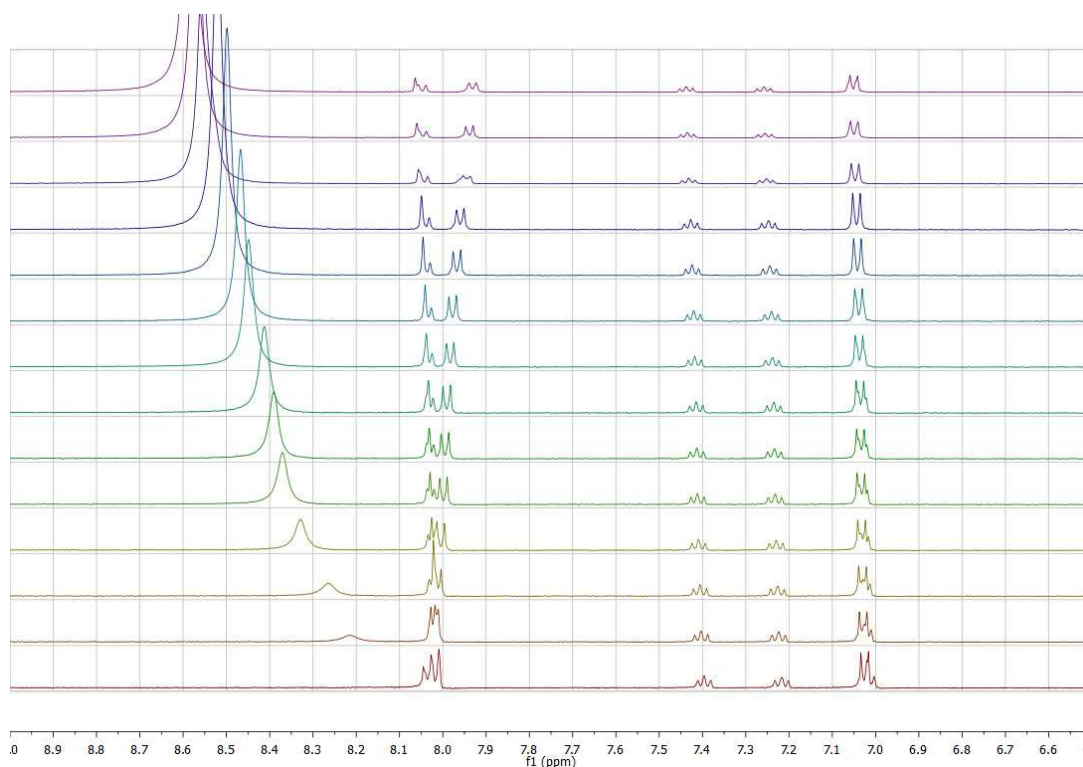


Figure S 61: Stacked NMR-spectra (aromatic region) for the binding of (*S,S*)-1,2-diaminocyclohexane (0.5 to 70 equivalents, as the bis-HCl salt) to (*S*)-**2** (as the Bu₄N⁺-salt) [all: 500 MHz, d₆-DMSO, 298K, initial concentration of (*S*)-**2**: 0.5 mM].

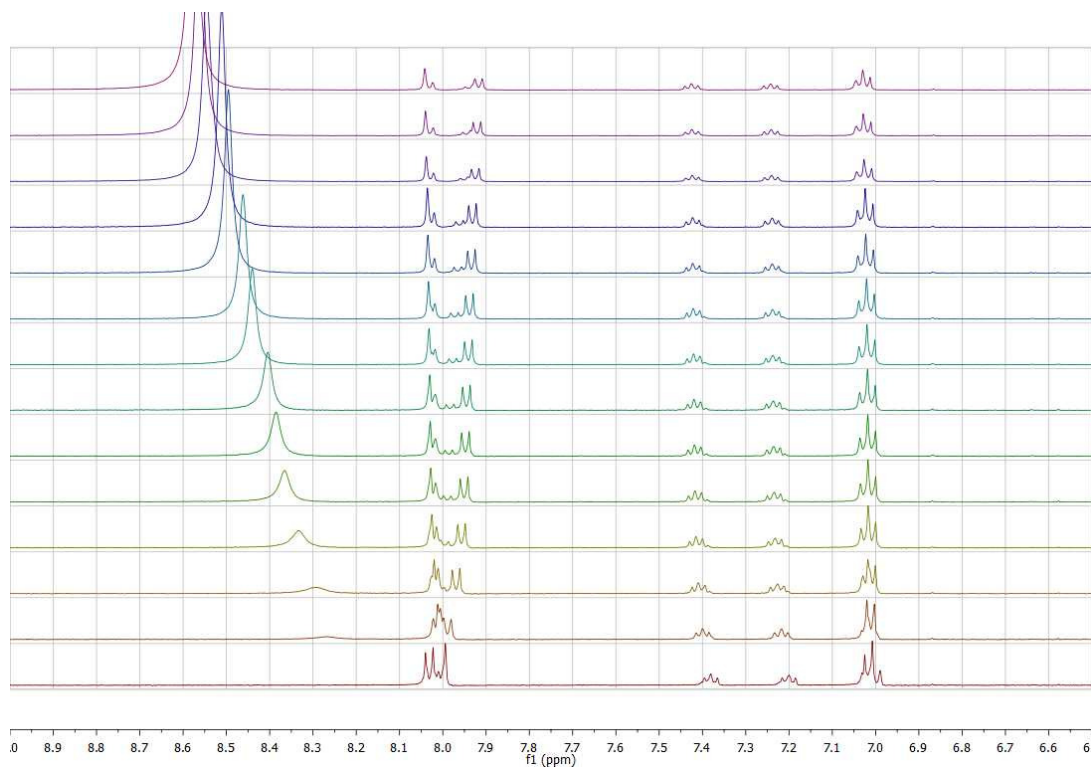


Figure S 62: Stacked NMR-spectra (aromatic region) for the binding of (*S,S*)-1,2-diaminocyclohexane (0.5 to 70 equivalents, as the bis-HCl salt) to (*S,S*)-**1** (as the bis-Bu₄N⁺-salt) [all: 500 MHz, d₆-DMSO, 298K, initial concentration of (*S,S*)-**1**: 0.5 mM].

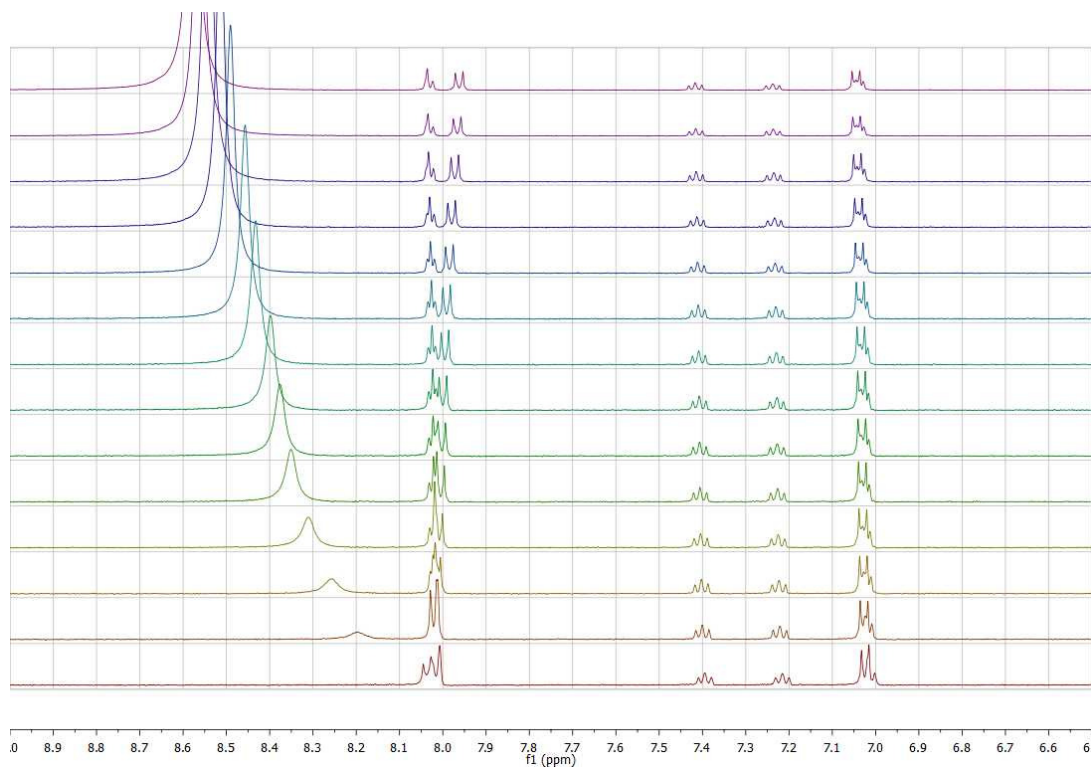


Figure S 63: Stacked NMR-spectra (aromatic region) for the binding of (*R,R*)-1,2-diaminocyclohexane (0.5 to 70 equivalents, as the bis-HCl salt) to (*S*)-**2** (as the Bu₄N⁺-salt) [all: 500 MHz, d₆-DMSO, 298K, initial concentration of (*S*)-**2**: 0.5 mM].

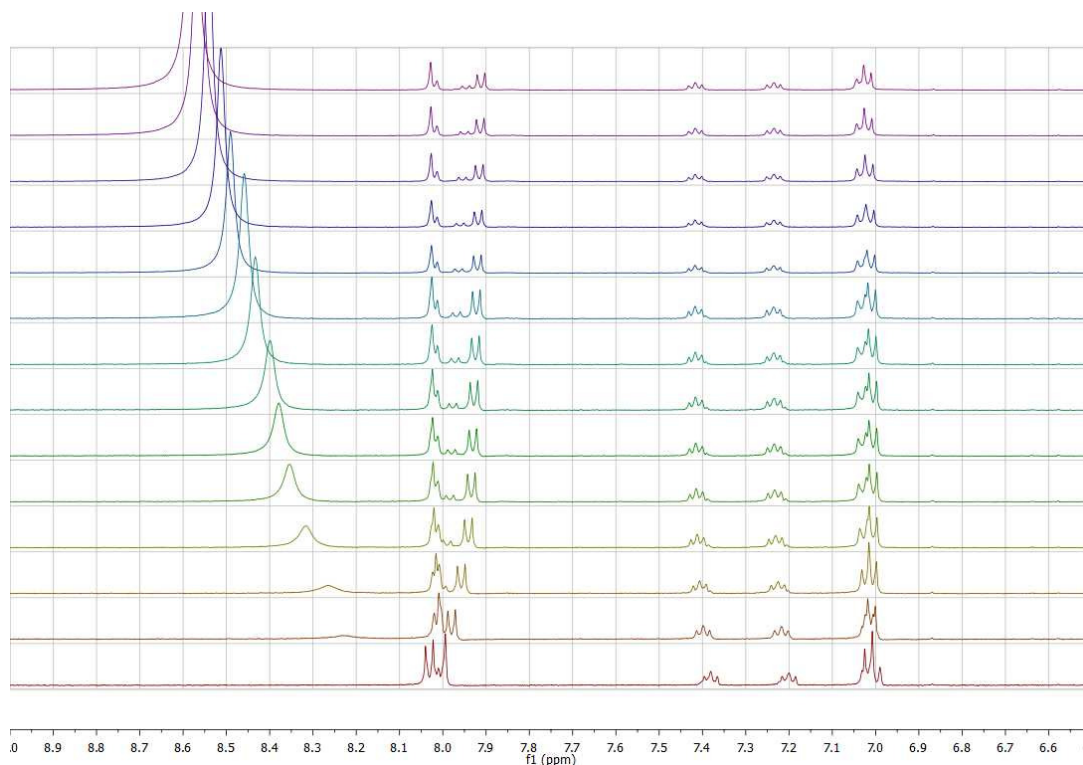


Figure S 64: Stacked NMR-spectra (aromatic region) for the binding of (*R,R*)-1,2-diaminocyclohexane (0.5 to 70 equivalents, as the bis-HCl salt) to (*S,S*)-**1** (as the bis-Bu₄N⁺-salt) [all: 500 MHz, d₆-DMSO, 298K, initial concentration of (*S,S*)-**1**: 0.5 mM].

Binding stoichiometries:

The stoichiometries of binding were identified for [(*S*)-**2**](Bu₄N⁺) and [(*S,S*)-**1**²⁻](Bu₄N⁺)₂] by using Job-Plots.

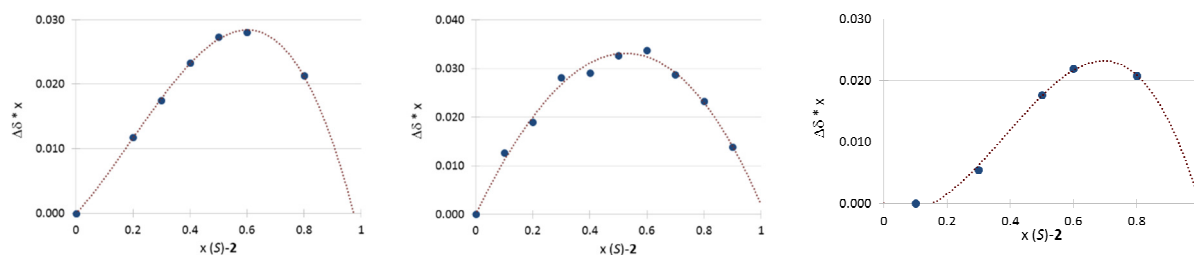


Figure S 65: Job-plots for the binding of L-lysine methyl ester (left), L-arginine methyl ester (middle) and (*S,S*)-1,2-diaminocyclohexane (right) (all as the bis-HCl salts) to (*S*)-**2** (as the mono-Bu₄N⁺-salt), plotted for arginine-NH, concentration of host+guest is 2.0 mM.

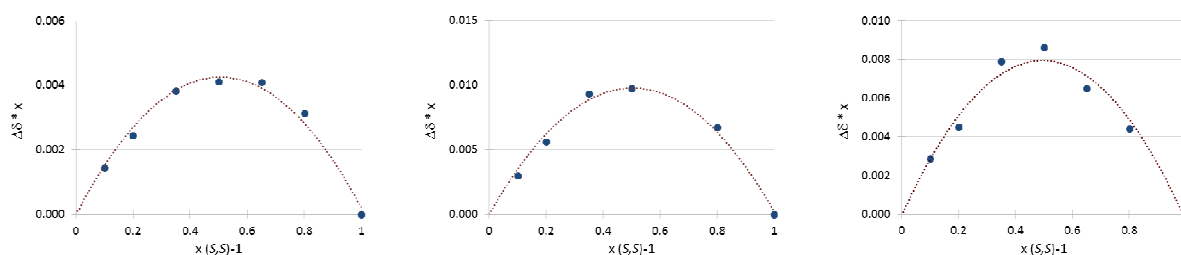


Figure S 66: Job-plots for the binding of L-lysine methyl ester (left), L-arginine methyl ester (middle) and (*S,S*)-1,2-diaminocyclohexane (right) (all as the bis-HCl salts) to (*S,S*)-1 (as the bis-Bu₄N⁺-salt), plotted for H-8 (for (*S,S*)-1), concentration of host+guest is 0.5 mM.

Data fitting:

The resulting binding isotherms were fitted using Origin® 9.0G and/or Microsoft Excel, respectively.^[3]

For Origin, the fitting was performed using the nonlinear-fit function, using two independent variables x1 and x2 (for [H]₀ and [G]₀) to take into account the dilution of [H]₀ in the course of the titration. Statistical values for fitting were reported by Origin.

For Microsoft Excel, fitting was performed using the SOLVER plugin. The sum of square residues for the calculated $\Delta\delta$ was minimized by changing K and $\Delta\delta_{max}$. The cubic equation for the 2:1 binding was solved using the CUBIC macro.^[4] Statistical values were obtained from the SOLVSTAT Macro written by E. J. Billo.^[5]

The following equations were used for the fitting:

1:1 binding stoichiometry:

Host:	H
Guest:	G
1:1-complex:	HG
Reaction:	$H + G \Rightarrow HG$
Equilibrium constant K:	$K = [HG]/([H]*[G])$
Total conc. of H:	$[H_0] = [H] + [HG]$
Total conc. of G:	$[G_0] = [G] + [HG]$
Equilibrium conc. of HG:	$[HG]=0.5*([G_0]+[H_0]+1/K)-((([G_0]+[H_0]+1/K)^2 - 4*[H_0]*[G_0])^{0.5})$
Observed chemical shift change:	$\Delta\delta_{Obs} = \delta_{Obs} - \delta_{Host}$
Maximum chemical shift change:	$\Delta\delta_{Max} = \delta_{HG} - \delta_{Host}$
$\Delta\delta$ calculated:	$\Delta\delta = ([HG]/[H_0])* \Delta\delta_{Max}$ $= (\Delta\delta_{Max}/(2*[H_0]))*([G_0]+[H_0]+1/K)-((([G_0]+[H_0]+1/K)^2 - 4*[H_0]*[G_0])^{0.5})$

2:1 binding stoichiometry:

Host: H
Guest: G

Complex: HHG

Reaction step 1: H + G \Rightarrow HG

Reaction step 1: HG + H \Rightarrow HHG

Total reaction: 2 H + G \Rightarrow HHG

Equilibrium constant K1: $K1 = [HG]/([G]*[H])$

Equilibrium constant K1: $K2 = [HHG]/([HG]*[H])$

Total equilibrium constant: $K1*K2 = K^2 = [HHG]/([G]*[H]^2)$

Total conc. of H: $[H0] = [H] + 2[HHG]$

Total conc. of G: $[G0] = [G] + [HHG]$

Equilibrium conc. of H: $K^2*[H]^3 + (2*K^2*[G0] - K^2*[H0])*[H]^2 + [H] - [H0] = 0$

$A*[H]^3 + B*[H]^2 + C*[H] + D = 0$

$A = K^2$

$B = 2*K^2*[G0] - K^2*[H0]$

$C = 1$

$D = -[H0]$

Equilibrium conc. of HHG: $[HHG] = K*[G]*[H]^2$

Observed chemical shift change: $\Delta\delta_{Obs} = \delta_{Obs} - \delta_{Host}$

Maximum chemical shift change: $\Delta\delta_{Max} = \delta_{HHG} - \delta_{Host}$

$\Delta\delta$ calculated: $\Delta\delta = ([HHG]/[H0])* \Delta\delta_{Max}$

For $[(S,S)\text{-1}^{2-}(\text{Bu}_4\text{N}^+)_2]$, the Job-plots clearly indicated a 1:1 stoichiometry, which was subsequently used for all data fitting procedures.

For $[(S)\text{-2}^-(\text{Bu}_4\text{N}^+)]$, the Job-plots hint at a 2:1 host:guest stoichiometry, although the data is not absolutely clear. For this reason, we have fitted the data for the binding to the macrocycle (S)-2 both for a 2:1 and a 1:1 stoichiometry.

Table S 3: Fitting results for binding to the catenane (S,S)-1 using a 1:1 complex stoichiometry

	L-Lys	D-Lys	L-Arg	D-Arg	SS-DACH	RR-DACH
K [M^{-1}]	4115	5691	5546	8202	15916	10060
Standard deviation [M^{-1}]	605	733	322	607	2870	1324
Standard deviation [%]	15	13	6	7	18	13
RMSD	0.96397	0.98026	0.99770	0.99549	0.98947	0.99067
Sum of square residues	3.12E-05	2.20E-05	3.51E-06	9.95E-06	1.32E-05	1.36E-05

Table S 4: Fitting results for binding to the macrocycle (S)-2 using a 2:1 complex stoichiometry

	L-Lys	D-Lys	L-Arg	D-Arg	SS-DACH	RR-DACH
K [M^{-1}]	633	695	573	768	874	842
Standard deviation [M^{-1}]	22	30	27	36	171	98
Standard deviation [%]	4	4	5	5	20	12
RMSD	0.99627616	0.99439987	0.99354889	0.9931271	0.93913199	0.976727815
Sum of square residues	2.24E-06	4.64E-06	6.54E-06	9.50E-06	2.28E-05	2.12E-05

Table S 5: Fitting results for binding to the macrocycle (S)-2 using a 1:1 complex stoichiometry

	L-Lys	D-Lys	L-Arg	D-Arg	SS-DACH	RR-DACH
K [M^{-1}]	450	566	366	596	1856	803
Standard deviation [M^{-1}]	31	65	41	66	543	204
Standard deviation [%]	7	11	11	11	29	25
RMSD	0.99395406	0.98386302	0.98494962	0.98458996	0.95431177	0.959723277
Sum of square residues	3.76E-06	1.36E-05	1.61E-05	2.17E-05	1.59E-05	3.98E-05

As can be seen from table S4 and S5, for binding to the macrocycle (S)-2 the 2:1 binding stoichiometry gives significantly better statistical results than the 1:1 binding stoichiometry. In conjunction with the Job-plot results and the underlying chemical process (binding of two monophosphates with one diammonium-species), the 2:1 binding stoichiometry seems to be prevalent. Thus, the calculated binding isotherms (see below) and the association constants for binding to the macrocycle (S)-2 were ultimately based on the 2:1 model.

Binding isotherms and calculated binding isotherms:

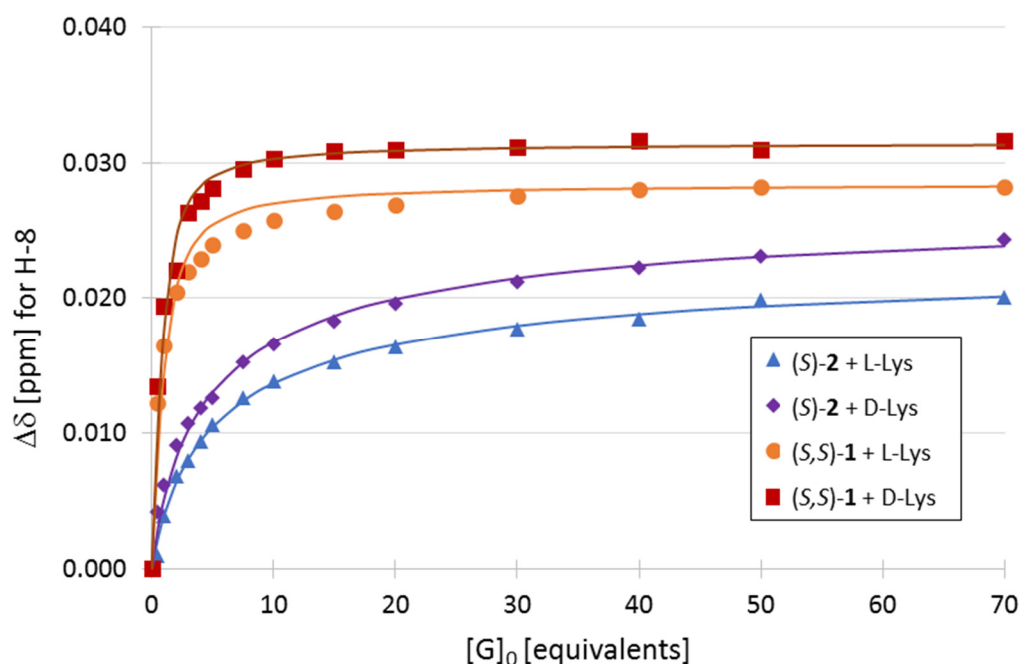


Figure S 67: Binding isotherms for the binding of D/L-lysine methyl esters (as the bis-HCl salts) to (S)-2 and (S,S)-1 (as the mono- or bis-Bu₄N⁺-salts) in d₆-DMSO, plotted for H-8 of the hosts. Data points: experimental data, lines: fitting data.

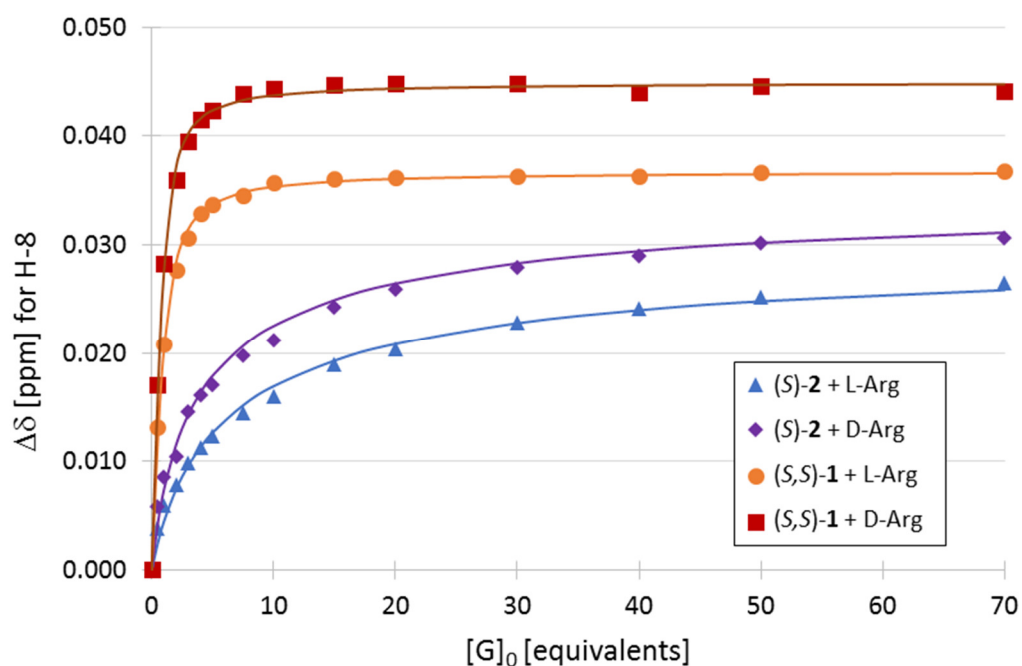


Figure S 68: Binding isotherms for the binding of D/L-arginine methyl esters (as the bis-HCl salts) to (S)-2 and (S,S)-1 (as the mono- or bis-Bu₄N⁺-salts) in d₆-DMSO, plotted for H-8 of the hosts. Data points: experimental data, lines: fitting data.

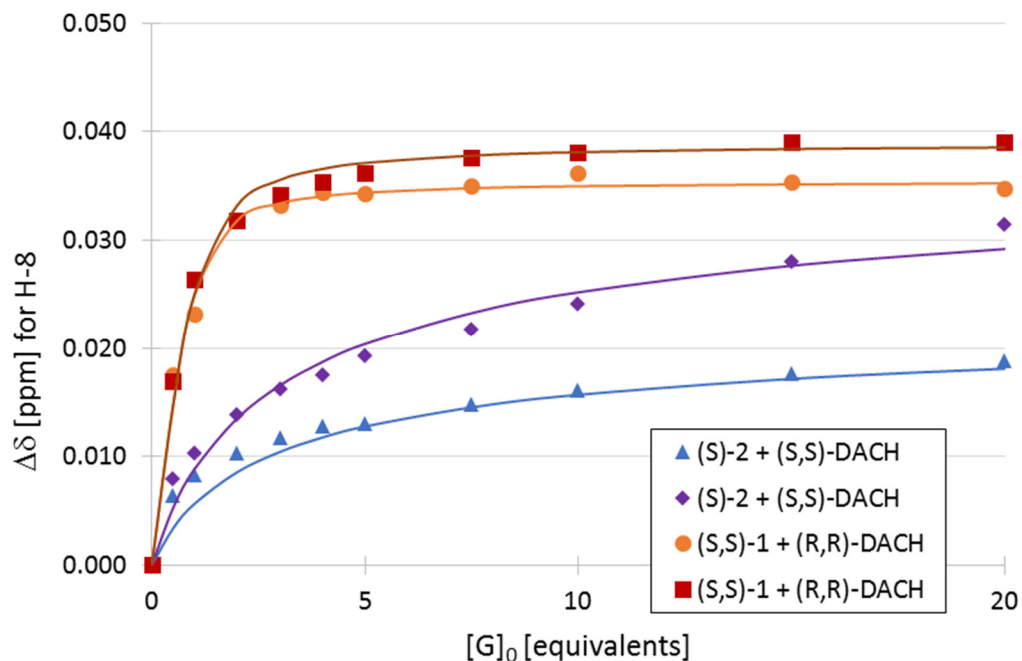


Figure S 69: Binding isotherms for the binding of (*S,S*)-/(*R,R*)-1,2-diaminocyclohexane (as the bis-HCl salt) to (*S,S*)-2 and (*S,S*)-1 (as the mono- or bis-Bu₄N⁺-salts) in d₆-DMSO, plotted for H-8 of the hosts. Data points: experimental data, lines: fitting data (only data points 1-11 could be used).

References:

- [1] a) N. Lv, M. Xie, W. Gu, H. Ruan, S. Qiu, C. Zhou and Z. Cui, *Org. Lett.*, 2013, **15**, 2382-2385; b) D. Cai, D. L. Hughes, T. R. Verhoeven and P. J. Reider, *Org. Synth.*, 1999, **76**, 1; c) T. R. Wu, L. Shen and J. M. Chong, *Org. Lett.*, 2004, **6**, 2701-2704.
- [2] a) M. G. Paulick, A. R. Wise, M. B. Forstner, J. T. Groves and C. R. Bertozzi, *J. Am. Chem. Soc.*, 2007, **129**, 11543-11550; b) J. F. Dellaria, Jr., J. F. Denissen, F. A. J. Kerdesky, R. G. Maki, D. J. Hoffman and H. N. Nellans, *J. Labelled Compd. Radiopharm.*, 1989, **27**, 1437-1450.
- [3] a) P. Thordarson, *Chem. Soc. Rev.*, 2011, **40**, 1305-1323; b) K. Hirose, in *Analytical Methods in Supramolecular Chemistry, Volume 1*, ed. C. Schalley, Wiley-VCH, Weinheim, 2012, p. 27-66; c) K. A. Connors, *Binding Constants*, John Wiley & Sons, New York, 1987.
- [4] CUBIC macro is included in the free *polynomial.zip*, copyright 2014 Interactive Design Services Pty Ltd.
- [5] E. J. Billo, *Excel for Chemists*, John Wiley & Sons, Hoboken, New Jersey, 2011.