

Procedures for the Synthesis of Compounds 7 and 8

Cs₂7(ione): The dinitrile **6** (1.2 g, 1.53 mmol, dried in vacuum for 12 h at 40 °C) was stirred with a mixture of toluene (15 ml) and ethylene glycol dimethyl ether (DME) (5 ml) in a 100 ml flask until the main portion of the calixarene dissolved (ca. 30 min. – 1 h), solid NaH (95 %, 80 mg, 3.15 mmol) was added with stirring. After 2 h a solution of the Cosan-dioxane **5** (1.26 g, 3.07 mmol) in toluene/DME (3:1, 15 ml) was injected and the mixture was stirred 48 h at room temperature. The resulting solution was neutralized with a small amount of acetic acid/water (1:3) and evaporated. The crude product was dissolved in Et₂O (25 ml) and washed twice with water. The organic layer was filtered to remove a small amount of unreacted **6** and evaporated after addition of water (10 mL) almost to dryness. Water (10 ml) was added followed by ethanol until the dissolution of the orange mass. An excess of an aqueous solution of CsCl was added. The precipitate was filtered or centrifuged, shortly dried, dissolved in benzene (30 ml), (eventually with addition of CH₂Cl₂, ca. 15 mL), and left to crystallize overnight. The resulting solids were filtered or decanted and dried. Final purification by column chromatography on silica gel (column 25 x 2.5 cm I.D) using CH₂Cl₂/CH₃CN (1:3) as eluent. Isolated yield of Cs₂7(ione) 0.86 g, 30 %. M. S. (-80 eV, ESI) m/e: 804.6 [M]²⁻ 20 % (calc. 804. 6), [M]⁻; R_f = 0.27 (CH₂Cl₂/CH₃CN = 3:1, silica gel TLC plates Silufol®); m.p. 175-178 °C;

¹¹B NMR (128 MHz, [D₆]acetone, 25 °C, BF₃.Et₂O): δ = 23.0 (s, 1B; B8), 3.8 (d, ¹J(B,H) = 142 Hz, 1B; B8'), 0.3 (d, ¹J(B,H) = 139 Hz, 1B; B10'), -2.5 (d, ¹J(B,H) = 142 Hz, 1B; B10), -4.5 (d, ¹J(B,H) = 153 Hz, 2B; B4', 7'), -7.8, -8.2 (2d, overlap, 6B; B4, 7, 9, 12, 9', 12'), -17.6 (d, ¹J(B,H) = 146 Hz, 2B; B5', 11'), -20.7 (d, ¹J(B,H) = 153 Hz, 2B; B5, 11), -21.7 (d, ¹J(B,H) = 173, Hz, 1B; B6'), -29.0 ppm (d, ¹J(B,H) = 139 Hz, 1B; B6);

¹H NMR (400 MHz, [D₆]acetone, 25 °C, TMS): 7.22 (s, 4H; ArH), 6.63 (s, 2H; ArH), 4.39 (d, ²J(H,H) = 11 Hz, 4H; ArCH₂Ar, H_{ax}), 4.30, 4.27 (2s, 8H; cage CH), 4.163 (t, ²J(H,H) = 8 Hz, 4H; CH₂O), 3.98 (t, J(H,H) = 5 Hz, 4H; CH₂O), 3.89 (t, J(H,H) = 5 Hz, 4H; CH₂O), 2.83 (br. t, 4H; CH₂CN), 3.67 (m, 8H; CH₂O), 3.24 (d, ²J(H,H) = 13 Hz, 4H; ArCH₂Ar, H_{eq}), 2.83 (m, 4H; CH₂), 2.49 (m, 4H; CH₂), 1.34 (s, 18H; *t*Bu), 0.90 ppm (s, 18H; *t*Bu);

B-H signals from **¹H{¹¹Bselective} NMR** (400 MHz, [D₆]acetone, 25 °C, TMS): δ = 2.93 (H10'), 2.78 (H(4', 7')), 2.70 (H10), 2.41 (H8'), 2.94, 2.02, 1.80 (H 4,7, 9, 12, 9', 12'), 1.68 (H5', 11'), 1.58 (H5, 11), 1.44 (H6'), 1.33 ppm (H6);

Cs₂7(alt): The dinitrile **6** (700 mg, 0.89 mmol, dried in vacuum for 12 h at 40 °C) was dissolved in a mixture of toluene and DME (3:1, 15 ml) and stirred with solid Cs₂CO₃ (583 mg, 1.78 mmol) for 2 h. Then a solution of **5** (731 mg, 1.78 mmol) in the same solvent (15 ml) was injected and the mixture was stirred 6 d at room temperature. The resulting solution was neutralized with few drops of acetic acid (3 M) and evaporated. The crude products were dissolved in Et₂O (25 mL) and washed twice with water. The ether layer was filtered and evaporated after addition of water (10 ml) almost to dryness. The crude product was dissolved in hot ethanol (approx 70 %, ca. 30 mL) and left to crystallize overnight. The resulting microcrystalline orange solid was centrifuged off. This procedure was twice repeated. Final purification by column chromatography on silica gel (column 25 x 2.5 cm I.D.) with CH₂Cl₂/CH₃CN (1:3) as the mobile phase. Yield 810 mg, 48 %. *R*_f = 0.30 (CH₂Cl₂/CH₃CN 3:1); m.p. 196-200 °C, M.S. (-70 V, ESI) *m/e*: 804.6 [M]²⁻ 20 % (calc. 804. 6), [M]⁻.

¹¹B NMR (128 MHz, [D₆]acetone, 25 °C, BF₃.Et₂O): δ = 22.6 (s, 1B; B8), 3.3 (d, ¹*J*(B,H) = 125 Hz, 1B; B8'), 0.4 (d, ¹*J*(B,H) = 129 Hz, 1B; B10'), -2.4 (d, ¹*J*(B,H) = 142 Hz, 1B; B10), -4.1 (d, ¹*J*(B,H) = 153 Hz, 2B; B4', 7'), -7.9, -8.2 (2d, overlap, 6B; B4, 7, 9, 12, 9', 12'), -17.3 (d, ¹*J*(B,H) = 131 Hz, 2B; B5', 11'), -20.5 (d, ¹*J*(B,H) = 144 Hz, 2B; B5, 11), -21.7 (d, overlap, 1B; B6'), -28.5 ppm (d, ¹*J*(B,H) = 139 Hz, 1B; B6);

¹H NMR (400 MHz, [D₆]acetone, 25 °C, TMS): 7.2 (s, 4H; ArH), 7.17 (s, 2H; ArH), 4.32, 4.30 (2s, 8H; cage CH), 4.0 (d, ²*J*(H,H) = 16 Hz, 4H; ArCH₂Ar), 3.91 (d, ²*J*(H,H) = 17 Hz, 4H; ArCH₂Ar), 3.79 (br. s, 4H; CH₂O), 3.62 (t, ³*J*(H,H) = 7 Hz, 4H; CH₂O), 3.56 (m, 8H; CH₂O), 3.43 (t, ³*J*(H,H) = 5 Hz, 4H; CH₂O), 3.01 (br. t, 4H; CH₂CN), 2.11 (m, 4H; CH₂), 1.36 (s, 18H; *t*Bu), 1.35 ppm (s, 18H; *t*Bu);

B-H signals from **¹H{¹¹Bselective} NMR** (400 MHz, [D₆]acetone, 25 °C, TMS): δ = 2.94 (H10'), 2.79 (H(4', 7')), 2.71 (H10), 2.38 (H8'), 2.92, 1.99 (H 4,7, 9, 12, 9', 12') 1.69 (H5', 11'), 1.56 (H5, 11), 1.37 (H6'), 1.21 ppm (H6);

8(cone) and 8(alt): Vacuum dried (12 h at 40 °C) cesium salts of the isomers of **7** (0.5 mmol) were dissolved in THF and an excess of Me₂SBH₃ (0.6 ml) was added. The reaction mixture was stirred for 2 d at ambient temperature and then at 50 °C for 5 h (TLC monitoring, CH₂Cl₂/CH₃CN 19:1). The reaction mixture was poured carefully into methanol (15 ml), water (5 ml) was added after the gas evolution ceased, followed by diluted HCl (3 M, 3 ml). The organic solvents were evaporated and the residue extracted with Et₂O (3 x 20 ml). The ether extracts were washed with 3 M HCl (3 x 20 ml) followed by water (3 x 20 ml). After evaporation the crude products were crystallized from hot 70 % methanol and purified eventually by flash chromatography on silica gel (column 20 x 2 cm I. D.) using CH₂Cl₂/CH₃CN (1:5) as eluent.

The zwitterionic amine derivatives (0.3 mmol, vacuum dried at 40 °C for 24 h) were dissolved in THF (20 ml), solid NaH (95 %, 0.6 mmol) was added, and the resulting slurry was stirred at room temperature for 2 h. A solution of the nitrophenyl ester **9** (0.36 mmol) in THF (15 ml) was added dropwise from a syringe during 30 min., the content of the reaction flask was stirred 12 h and then heated up to 60 °C and kept at this temperature for 6 h. After cooling down and standing overnight, sodium *p*-nitrophenolate which crystallized from this solution was filtered under nitrogen, solids were washed with dry THF (2 x 5 ml). Ethanol (5 ml) was carefully added to the combined THF filtrates, followed by water (15 ml) and several drops of 1 M HCl to adjust pH to approx. neutral. Solvents were evaporated almost to dryness and the residue was dissolved in CH₂Cl₂ (20 ml), and washed several times with 5 % aqueous solution of Na₂CO₃ (20 ml) to remove remaining nitrophenol, followed by brine (3 x 20 ml). Organic layer was then separated and after addition of water (10 ml), the solvents were evaporated to dryness. The residue was dissolved in benzene (30 ml) and an amount of dichloromethane required to complete the dissolution was added and the solution was over layered with hexane (75 ml) and left to crystallize for 3 d. The solvents were decanted from the orange solid material. The products were dissolved in CH₂Cl₂-CH₃CN solvent mixture (3:1) and purified by flash chromatography on a silica gel column using the same mobile phase for the elution.

Na₂8(cone), orange powder; yield 64 %, M. S. (-80 eV, ESI) m/z: 2122 (5 %) 2115 (100 %) [M+Na]⁺ (calc. 2122, 2115), R_f = 0.67 (CH₂Cl₂/CH₃CN = 3:1); m.p. 268-272 °C (decomp.);

¹¹B NMR (128 MHz, [D₆]acetone, 25 °C, BF₃.Et₂O): δ = 23.5 (s, 1B; B8), 4.5 (d, ¹J(B,H) = 142 Hz, 1B; B8'), 0.5 (d, ¹J(B,H) = 139 Hz, 1B; B10'), -2.5 (d, ¹J(B,H) = 145 Hz, 1B; B10), -4.4 (d, ¹J(B,H) = 154 Hz, 2B; B4', 7'), -7.5 (2d, overlap, 6B; B4, 7, 9, 12, 9', 12'), -17.3 (d,

$^1J(\text{B,H}) = 146 \text{ Hz}$, 2B; B5', 11'), -20.4 (d, $^1J(\text{B,H}) = 163 \text{ Hz}$, 2B; B5, 11), -21.6 (d, $^1J(\text{B,H}) = 173 \text{ Hz}$, 1B; B6'), -28.4 ppm (d, $^1J(\text{B,H}) = 139 \text{ Hz}$, 1B; B6);

$^1\text{H NMR}$ (400 MHz, $[\text{D}_6]$ acetone, 25 °C, TMS): 7.92 (t, $J(\text{H,H}) = 8 \text{ Hz}$, 8H; ArH), 7.63 (t, $J(\text{H,H}) = 8 \text{ Hz}$, 4H; ArH), 7.54 (m, 4H; ArH), 7.16 (s, 4H; ArH), 6.62 (s, 4H; ArH), 4.44 (d, $^2J(\text{H,H}) = 12 \text{ Hz}$, 4H; ArCH₂Ar, H_{ax}), 4.23, 4.21 (s, 8H; cage CH), 3.95 (t, $^3J(\text{H,H}) = 8 \text{ Hz}$, 4H; CH₂O), 3.87 (br t, 4H; CH₂O), 3.78 (t, $^3J(\text{H,H}) = 5 \text{ Hz}$, 4H; CH₂O), 3.78 (d, $^2J(\text{P,H}) = 6 \text{ Hz}$, 4H; CH₂P), 3.59 (t, $^3J(\text{H,H}) = 5 \text{ Hz}$, 8H; CH₂O), 3.24 (br. q, 4H; CH₂NCO), 3.17 (d, $^2J(\text{H,H}) = 12 \text{ Hz}$, 4H; ArCH₂Ar, H_{eq}), 1.95 (m, 4H; CH₂), 1.64 (m, 4H; CH₂), 1.31 (s, 18H; *t*Bu), 0.91 ppm (s, 18H; *t*Bu);

$^{31}\text{P}\{^1\text{H}\} \text{NMR}$ (400 MHz, $[\text{D}_6]$ acetone, 25 °C, H₃PO₄): 34.7 ppm (s).

B-H signals from $^1\text{H}\{^{11}\text{Bselective}\} \text{NMR}$ (400 MHz, $[\text{D}_6]$ acetone, 25 °C, TMS): $\delta = 2.92$ (H10'), 2.76 (H(4', 7')), 2.72 (H10), 2.44 (H8'), 2.94, 2.02, 1.80 (H 4, 7, 9, 12, 9', 12'), 1.68 (H5',11'), 1.56 (H5, 11), 1.48 (H6'), 1.26 ppm (H6);

Na₂8(alt), orange powder; yield 56 %. $R_f = 0.84$ (CH₂Cl₂/CH₃CN = 3:1); m.p. 271-274 °C (decomp.), M.S. (-80 eV, ESI) m/z: 2122 (100 %) $[\text{M}+\text{Na}]^+$ (calc. 2122).

$^{11}\text{B NMR}$ (128 MHz, $[\text{D}_6]$ acetone, 25 °C, BF₃.Et₂O): $\delta = 22.6$ (s, 1B; B8), 3.5 (d, $^1J(\text{B,H}) = 144 \text{ Hz}$, 1B; B8'), 0.6 (d, $^1J(\text{B,H}) = 141 \text{ Hz}$, 1B; B10'), -2.4 (d, $^1J(\text{B,H}) = 140 \text{ Hz}$, 1B; B10), -4.0 (d, $^1J(\text{B,H}) = 154 \text{ Hz}$, 2B; B4', 7'), -7.6 (2d, overlap, 6B; B4, 7, 9, 12, 9', 12'), -17.3 (d, $^1J(\text{B,H}) = 147 \text{ Hz}$, 2B; B5', 11'), -20.3 (d, $^1J(\text{B,H}) = 152 \text{ Hz}$, 2B; B5, 11), -21.6 (d, overlap 1B; B6'), -28.5 ppm (d, $^1J(\text{B,H}) = 141 \text{ Hz}$, 1B; B6);

$^1\text{H NMR}$ (400 MHz, $[\text{D}_6]$ acetone, 25 °C, TMS): 7.88 (m, 8H; ArH), 7.64 (t, $J(\text{H,H}) = 7 \text{ Hz}$, 4H; ArH), 7.53 (m, 8H; ArH), 7.15 (s, 4H; ArH), 6.98 (s, 4H; ArH), 4.32, 4.29 (2s, 8H; cage CH), 3.93 (d, $^2J(\text{H,H}) = 16 \text{ Hz}$, 4H; ArCH₂Ar), 3.73 (d, $^2J(\text{H,H}) = 16 \text{ Hz}$, 4H; ArCH₂Ar), 3.63 (t, $^3J(\text{H,H}) = 6 \text{ Hz}$, 4H; CH₂O), 3.58 (d, $^2J(\text{H,P}) = 13 \text{ Hz}$, 4H; CH₂P), 3.57 (t, 4H; CH₂O), 3.45 (t, $^3J(\text{H,H}) = 5 \text{ Hz}$, 4H; CH₂O), 3.33 (t, $^3J(\text{H,H}) = 6 \text{ Hz}$, 4H; CH₂O), 3.16 (t, $^3J(\text{H,H}) = 6 \text{ Hz}$, 4H; CH₂O), 3.06 (br. q, 4H; CH₂NCO, H_{eq}), 1.79 (m, 4H; CH₂), 1.59 (m, 4H; CH₂), 1.36 (s, 18H; *t*Bu), 1.23 ppm (s, 18H; *t*Bu);

$^{31}\text{P}\{^1\text{H}\} \text{NMR}$ (400 MHz, $[\text{D}_6]$ acetone, 25 °C, H₃PO₄): 30.27 (s).