

Supplementary Information

Synthesis of a cross-chain bridging cryptand

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Experimental

Materials and General Methods

The compounds **7** and **9a** were prepared according to literature procedures.^{S1} DMF and CH₂Cl₂ were dried over 4 Å molecular sieves. Other solvents and commercially available chemicals were used as received. ¹H and ¹³C NMR spectra were recorded using JEOL ECX-500II and ECA-600II spectrometers, with tetramethylsilane (0 ppm) and C₆H₅ (7.15 ppm) for ¹H NMR and with CDCl₃ (71.0 ppm) and C₆D₆ (128.0 ppm) for ¹³C NMR as the internal standard. Mass spectra were recorded using JEOL JMS-700T (FAB) and JMS-S3000 (MALDI) spectrometers. Infrared spectra were recorded using a Shimadzu FTIR-8600PC spectrometer. All reactions were performed under a positive atmosphere of dry N₂ except for hydrogenation (conversion of mixtures of compounds **10** and **11** to compounds **3** and **12**). All solvents were removed through rotary evaporation under reduced pressure. Silica gel column chromatography was performed using Kanto Chemical silica gel 60N. Thin layer chromatography was performed using Merck Kieselgel 60PF₂₅₄. For reactions that require heating used an oil bath as the heat source. HPLC was performed using a JASCO LC-NetII/ADC and a PU-2080 plus detector, with GL Sciences Inertsil ODS-3 5 μm column (10 × 250 mm) for separation of isomers **1** and **6** and a Shimadzu SDD-M20A detector, with DAICEL CHIRALPAK IG-3 for analysis of compound **1c**. GPC was performed using a Japan Analytical Industry LC-5060 apparatus and JAIGEL (2H and 2.5H).

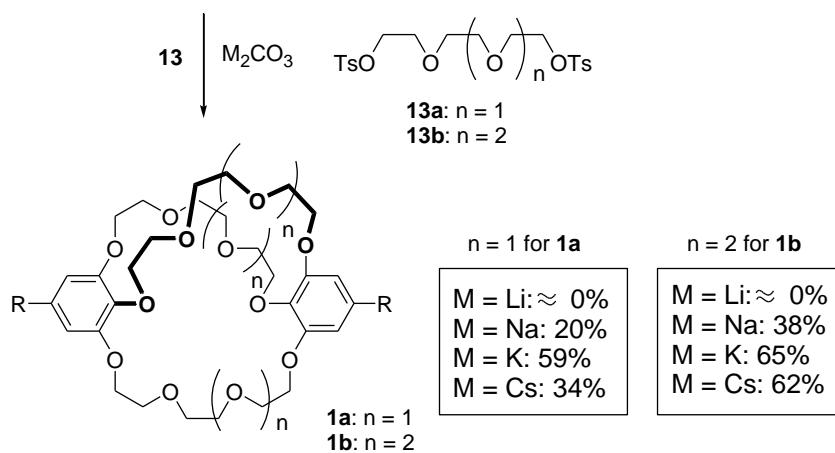
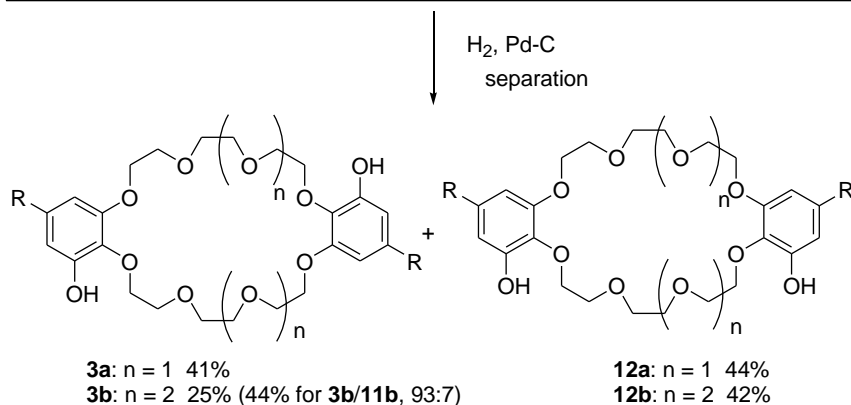
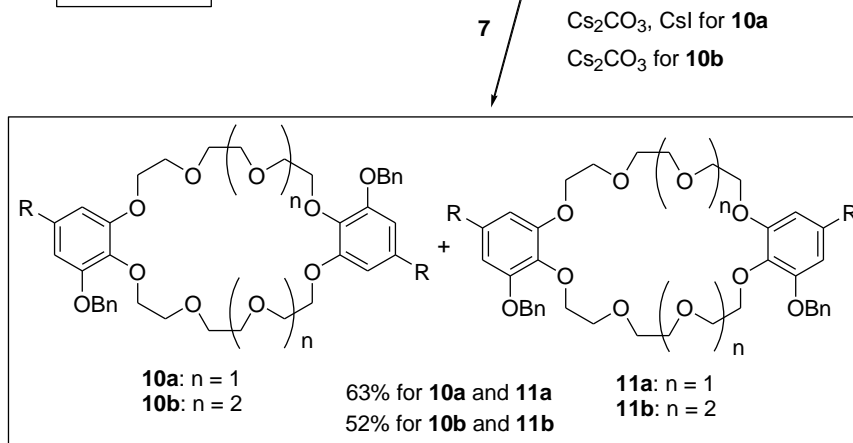
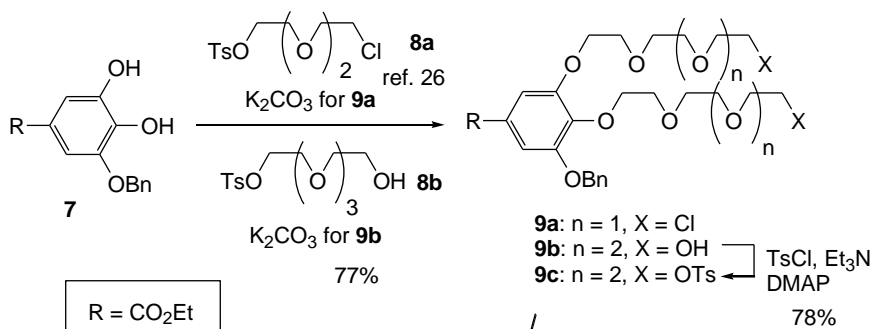
References

S1. H. Fujihara, M. Naito, T. Yashima, Y. Okada, N. Kobayashi, S. Miyagawa, H. Takaya, Y. Tokunaga, *Org. Lett.*, 2023, **25**, 8959–8964.

XRD structure determination

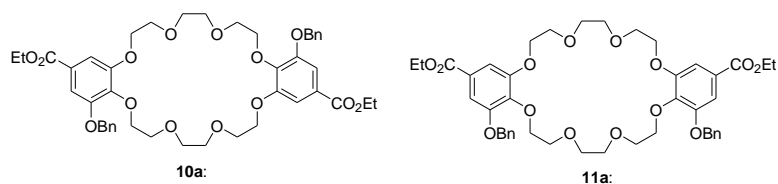
A crystal suitable for XRD was analyzed using a Rigaku R-Axis RAPID diffractometer and graphite-monochromated Mo_{Kα} radiation ($\lambda = 0.71075 \text{ \AA}$). The structure of **1a** was solved using direct methods and refined by applying the full-matrix least-squares method. In subsequent refinement, the function $\Sigma\omega(F_o^2 - F_c^2)^2$ was minimized, where F_o and F_c are the observed and calculated structure factor amplitudes, respectively. The positions of non-hydrogen atoms were determined from difference Fourier electron density maps and were refined anisotropically. All calculations were performed using the Rigaku CrystalStructure crystallographic software package; illustrations were generated in the ORTEP style. Details of the structural determinations are provided in Figures 6, S21 and Table S1. CCDC 2392777 contains the supplementary crystallographic data for this paper.

Method B



Synthesis of cryptand **1a**.

A mixture of crown ethers **10a** and **11a**



A suspension of dichloride **9a** (2.61 g, 4.43 mmol), gallate **7** (1.28 g, 4.43 mmol), Cs₂CO₃ (4.33 g, 13.3 mmol), and CsI (345 mg, 1.33 mmol) in DMF (90 mL) was stirred at 100 °C for 60 h. After evaporation of the solvent, 10% HCl (aq.) was added to the residue and the aqueous phase was extracted with AcOEt. The organic extract was washed with water, dried (MgSO₄), and concentrated. The residue was purified by column chromatography (SiO₂; toluene/AcOEt, 2:1) to afford a white solid (2.26 g, 63%), as a 1:1 mixture of crown ethers **10a** and **11a**.

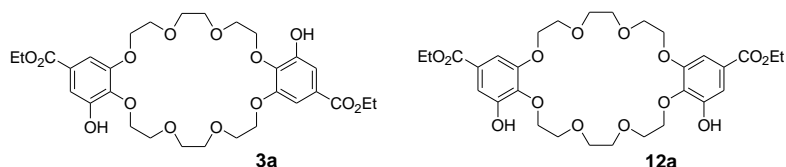
IR (KBr, ν_{max}) cm⁻¹: 2931, 2873, 1713, 1588, 1504, 1428, 1366, 1231, 1123, 1032, 763.

¹H NMR (500 MHz, CDCl₃) δ : 7.48–7.42 (m, 4H), 7.40–7.34 (m, 6H), 7.31 (br t, $J = 7.4$ Hz, 2H), 7.27 (br s, 2H), 5.13 (s, 4H), 4.34 (q, $J = 7.0$ Hz, 4H), 4.27–4.17 (m, 8H), 3.95–3.88 (m, 4H), 3.86–3.80 (m, 6H), 3.78–3.72 (m, 6H), 1.37 (t, $J = 7.0$ Hz, 6H).

¹³C NMR (125 MHz, CDCl₃) δ : 166.1, 152.5, 152.4, 152.2, 152.1, 142.5, 142.4, 136.8, 128.5, 127.9, 127.4, 127.3, 125.4, 125.3, 109.1, 108.3, 72.55, 72.45, 71.2, 71.1, 70.7, 70.6, 69.7, 69.6, 69.0, 61.1, 14.4. Six aliphatic/carbonyl and seven aromatic carbon signals were overlapping/missing.

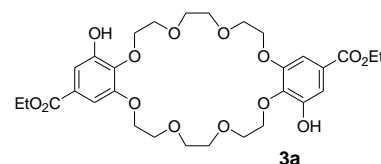
MS (FAB): m/z calcd for C₄₄H₅₃O₁₄⁺ [M+H]⁺: 805.3430; found: 805.3459.

Crown ethers **3a** and **12a**



A suspension of a 1:1 mixture of crown ethers **10a** and **11a** (430 mg, 0.534 mmol), 10% Pd-C (121 mg) in EtOH (10 mL) and CHCl₃ (5 mL) was stirred for 2 d under hydrogen. After the mixture was filtered through celite, the filtrate was concentrated. The residue was purified through column chromatography (SiO₂; toluene/CHCl₃/AcOEt, 1:1:1) to give the crown ether **3a** as a colorless solid and (SiO₂; toluene/CHCl₃/AcOEt, 1:1:2) to give the crown ether **12a** as a colorless solid. Both crown ethers were washed with iPr₂O to afford **3a** (136 mg, 41%) and **12a** (146 mg, 44%) as colorless solids, respectively.

Crown ether **3a**



IR (KBr, ν_{\max}) cm^{-1} : 3303, 2972, 2876, 1714, 1592, 1509, 1445, 1398, 1369, 1237, 1214, 1094, 1038, 957, 903, 867, 766.

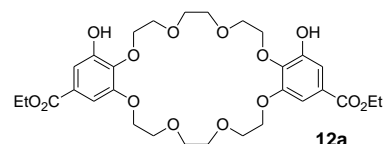
^1H NMR (500 MHz, CDCl_3) δ : 7.64 (s, 2H), 7.24 (br s, 2H), 7.11 (br s, 2H), 4.33 (q, $J = 7.1$ Hz, 4H), 4.24–4.19 (m, 4H), 4.16–4.11 (m, 4H), 3.86–3.78 (m, 12H), 3.78–3.72 (m, 4H), 1.37 (t, $J = 7.1$ Hz, 6H).

^{13}C NMR (125 MHz, CDCl_3) δ : 166.3, 152.0, 150.6, 139.2, 126.4, 110.7, 105.4, 73.5, 71.9, 70.0, 69.8, 69.3, 67.6, 60.9, 14.3.

MS (FAB): m/z calcd for $\text{C}_{30}\text{H}_{41}\text{O}_{14}^+$ $[\text{M}+\text{H}]^+$: 625.2491; found: 625.2520.

mp: 181–183 °C (acetone).

Crown ether **12a**



IR (KBr, ν_{\max}) cm^{-1} : 3407, 2980, 2873, 1714, 1593, 1508, 1445, 1364, 1342, 1237, 1215, 1098, 1034, 955, 888, 762.

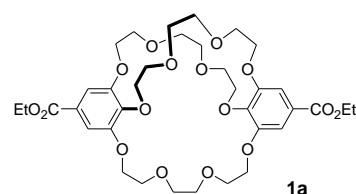
^1H NMR (500 MHz, CDCl_3) δ : 7.29 (d, $J = 1.7$ Hz, 2H), 7.16 (d, $J = 1.7$ Hz, 2H), 6.98 (s, 2H), 4.33 (q, $J = 7.1$ Hz, 4H), 4.26–4.18 (m, 8H), 3.85–3.78 (m, 8H), 3.77 (s, 4H), 3.69 (s, 4H), 1.37 (t, $J = 7.1$ Hz, 6H).

^{13}C NMR (125 MHz, CDCl_3) δ : 166.2, 151.5, 150.0, 139.4, 126.2, 110.6, 106.8, 72.8, 71.2, 70.8, 70.4, 69.6, 68.7, 61.0, 14.3.

MS (FAB): m/z calcd for $\text{C}_{30}\text{H}_{41}\text{O}_{14}^+$ $[\text{M}+\text{H}]^+$: 625.2491; found: 625.2498.

mp: 192–194 °C (CHCl_3).

Cryptand **1a**



Using Cs_2CO_3

A suspension of the crown ether **3a** (80.3 mg, 0.129 mmol), tri(ethylene glycol) ditosylate **13a** (58.9 mg, 0.129 mmol), and Cs_2CO_3 (126 mg, 0.386 mmol) in DMF (16 mL) was heated at 95 °C for 43 h. After evaporation of the solvent, 10% HCl (aq.) was added to the residue and the aqueous phase was

extracted with AcOEt. The organic extract was washed with water, dried (Na₂SO₄), and concentrated. The residue was purified by GPC (eluent CHCl₃) to afford a white solid (27.3 mg, 34%).

Using K₂CO₃

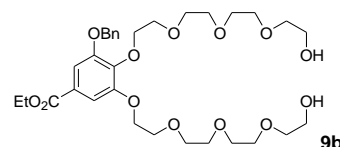
The cryptand **1a** (56.0 mg, 59%) was synthesized from the crown ether **3a** (80.1 mg, 0.128 mmol) and K₂CO₃ (53.2 mg, 0.384 mmol) instead of Cs₂CO₃, using the procedure described above, as a white solid.

Using Na₂CO₃

The cryptand **1a** (19.0 mg, 20%) was synthesized from the crown ether **3a** (79.4 mg, 0.127 mmol) and Na₂CO₃ (40.6 mg, 0.383 mmol) instead of Cs₂CO₃, using the procedure described above, as a white solid.

Synthesis of cryptand **1b**.

Compound **9b**



A suspension of ethyl gallate (**7**) (9.40 g, 32.7 mmol), tetra(ethylene glycol) monotosylate **8b** (28.4 g, 81.6 mmol), and K₂CO₃ (11.3 g, 81.6 mmol) in acetonitrile (111 mL) and DMF (38 mL) was heated at 95 °C for 17 h. After evaporation of the solvent, 10% HCl (aq.) and water were added to the residue and the aqueous phase was extracted with AcOEt. The organic extract was dried (Na₂SO₄), and concentrated. The residue was purified through column chromatography (SiO₂; CHCl₃/MeOH, 20:1) to a colorless oil (16.13 g, 77%).

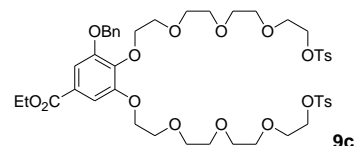
IR (KBr, ν_{max}) cm⁻¹: 3443, 2873, 1713, 1589, 1502, 1430, 1368, 1333, 1236, 1213, 1120, 1030, 947, 766.

¹H NMR (500 MHz, CDCl₃) δ : 7.48–7.44 (m, 2H), 7.41–7.36 (m, 2H), 7.37 (d, J = 2.1 Hz, 1H), 7.34–7.30 (m, 1H), 7.31 (d, J = 2.1 Hz, 1H), 5.14 (s, 2H), 4.35 (q, J = 7.0 Hz, 2H), 4.26–4.20 (m, 4H), 3.90–3.87 (m, 2H), 3.81–3.78 (m, 2H), 3.76–3.73 (m, 2H), 3.73–3.65 (m, 12H), 3.65–3.62 (m, 2H), 3.65–3.56 (m, 8H), 1.38 (t, J = 7.0 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃) δ : 166.0, 152.2, 152.1, 142.4, 136.7, 128.4, 127.9, 127.4, 125.3, 109.0, 108.8, 72.5, 71.1, 70.7, 70.53, 70.47, 70.4, 70.24, 70.18, 69.5, 68.7, 61.6, 61.0, 14.3. Six aliphatic carbon signals were overlapping/missing.

MS (FAB): m/z calcd for C₃₂H₄₉O₁₃⁺ [M+H]⁺: 641.3168; found: 641.3188.

Compound **9c**



Et₃N (0.55 mL, 3.95 mmol) was added to a solution of diol **9b** (1.00 g, 1.56 mmol), *p*-toluenesulfonyl chloride (0.685 g, 3.59 mmol), and 4-dimethylaminopyridine (DMAP, 19.5 mg, 0.160 mmol) in CH₂Cl₂ (20 mL) at 0 °C. After stirring at room temperature for 13 h, the mixture concentrated. Water was added to the residue, the aqueous phase was extracted with AcOEt. Combined organic phase was washed with sat. NaCl (aq.), dried (Na₂SO₄), and concentrated. The residue was purified through column chromatography (SiO₂; hexane/ethyl acetate, 1:3) to a colorless oil (1.16 g, 78%).

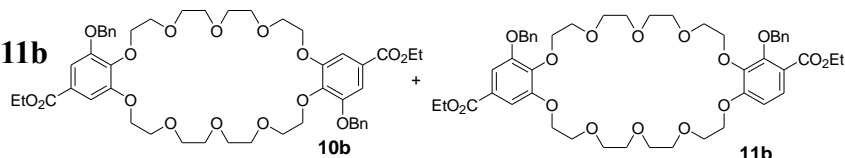
IR (KBr, ν_{\max}) cm⁻¹: 2872, 1714, 1430, 1358, 1333, 1212, 1177, 1112, 1019, 923, 816, 769.

¹H NMR (500 MHz, CDCl₃) δ : 7.80–7.76 (m, 4H), 7.47–7.44 (m, 2H), 7.40–7.35 (m, 3H), 7.35–7.29 (m, 6H), 5.13 (s, 2H), 4.34 (q, $J = 7.2$ Hz, 2H), 4.24–4.18 (m, 4H), 4.16–4.11 (m, 4H), 3.88–3.85 (m, 2H), 3.79–3.76 (m, 2H), 3.72–3.61 (m, 10H), 3.59–3.57 (m, 4H), 3.55–3.51 (m, 6H), 2.431 (s, 3H), 2.427 (s, 3H), 1.38 (t, $J = 7.2$ Hz, 3H).

¹³C NMR (125 MHz, CDCl₃) δ : 166.0, 152.2, 152.1, 144.7, 142.4, 136.7, 132.8, 129.7, 128.4, 127.9, 127.4, 125.3, 109.0, 108.8, 72.4, 71.1, 70.7, 70.63, 70.59, 70.51, 70.44, 70.37, 69.5, 69.2, 68.7, 68.6, 68.5, 61.0, 21.6, 14.3. Five aliphatic and five aromatic carbon signals were overlapping/missing.

MS (FAB): m/z calcd for C₄₆H₆₁O₁₇S₂⁺ [M+H]⁺: 949.3345; found: 949.3351.

A mixture of crown ethers **10b** and **11b**



A suspension of ditosylate **9c** (1.99 g, 2.09 mmol), ethyl gallate (**7**) (0.618 g, 2.14 mmol), and cesium carbonate (2.14 g, 6.56 mmol) in DMF (100 mL) was stirred at 100 °C for 72 h. After evaporation of the solvent, dil HCl (aq.) was added to the residue and the aqueous phase was extracted with AcOEt. The organic extract was dried (Na₂SO₄), and concentrated. The residue was purified through column chromatography (SiO₂; toluene/acetone, 4:1) to give a 1:1 mixture of crown ethers **10b** and **11b** (0.983 g, 52%) as a colorless solid.

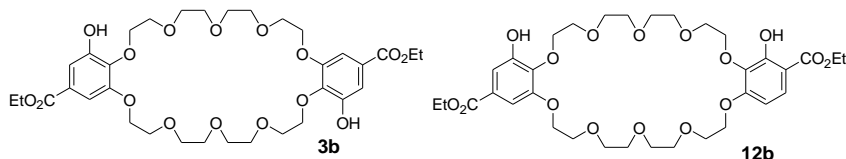
IR (KBr, ν_{\max}) cm⁻¹: 2873, 1712, 1589, 1503, 1429, 1367, 1336, 1233, 1213, 1120, 1031, 763.

¹H NMR (500 MHz, CDCl₃) δ : 7.47–7.42 (m, 4H), 7.40–7.34 (m, 6H), 7.34–7.29 (m, 2H), 7.29–7.26 (m, 2H), 5.13 (s, 4H), 4.34 (q, $J = 7.2$ Hz, 4H), 4.26–4.17 (m, 8H), 3.92–3.87 (m, 4H), 3.83–3.79 (m, 4H), 3.78–3.73 (m, 4H), 3.72–3.65 (m, 8H), 3.65–3.60 (m, 4H), 1.37 (t, $J = 7.2$ Hz, 6H).

¹³C NMR (125 MHz, CDCl₃) δ : 166.1, 152.4, 152.1, 142.5, 136.7, 128.5, 127.9, 127.4, 125.3, 109.1, 108.6, 108.5, 72.5, 71.2, 70.9, 70.71, 70.67, 70.6, 70.5, 69.6, 68.9, 61.0, 14.3. Ten aliphatic and eleven aromatic/carbonyl carbon signals were overlapping/missing.

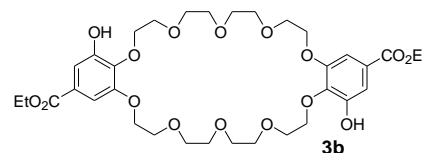
MS (FAB): m/z calcd for $C_{48}H_{61}O_{16}^+$ $[M+H]^+$: 893.3954; found: 893.3995.

Crown ethers **3b** and **12b**



A suspension of 1:1 mixture of the crown ethers **10b** and **11b** (0.960 g, 1.07 mmol) and 10% Pd-C (0.337 g) in EtOH/ $CHCl_3$ (39 mL, 2:1) was stirred at room temperature for 23 h under hydrogen atmosphere. After filtration through celite, the filtrate was concentrated. The residue was crystallized from MeOH to give a 93:7 mixture of the crown ethers **3b** (339 mg, 44%), which was washed with EtOH to afford the crown **3b** (190 mg, 25%) as a white solid. After concentration of the above first filtrate, the residue was treated with cold iPrOH to give the crown ether **12b** (323 mg, 42%) as a white solid.

Crown ether **3b**



IR (KBr, ν_{max}) cm^{-1} : 3423, 2929, 2872, 1698, 1592, 1507, 1445, 1370, 1349, 1229, 1102, 1044, 878, 768.

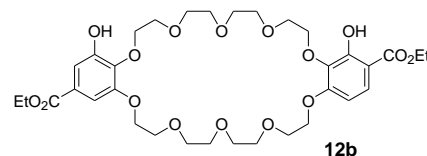
1H NMR (500 MHz, $CDCl_3$) δ : 7.42 (s, 2H), 7.24 (br s, 2H), 7.08 (br s, 2H), 4.32 (q, $J = 7.2$ Hz, 4H), 4.27–4.21 (m, 4H), 4.20–4.15 (m, 4H), 3.89–3.84 (m, 4H), 3.75–3.61 (m, 20H), 1.36 (t, $J = 7.2$ Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ : 166.2, 151.9, 150.6, 138.7, 126.2, 110.6, 105.9, 72.5, 70.8, 70.7, 70.5, 70.4, 69.5, 68.2, 60.9, 14.3. One aliphatic carbon signal was overlapping/missing.

MS (FAB): m/z calcd for $C_{34}H_{49}O_{16}^+$ $[M+H]^+$: 713.3015; found: 713.3047.

mp: 128–129 °C ($CHCl_3$ /hexane).

Crown ether **12b**



IR (KBr, ν_{max}) cm^{-1} : 3421, 3128, 2901, 2873, 1714, 1699, 1592, 1510, 1431, 1370, 1348, 1234, 1103, 1029, 768.

1H NMR (600 MHz, $CDCl_3$) δ : 7.53 (s, 2H), 7.29 (d, $J = 1.7$ Hz, 2H), 7.13 (d, $J = 1.7$ Hz, 2H), 4.33

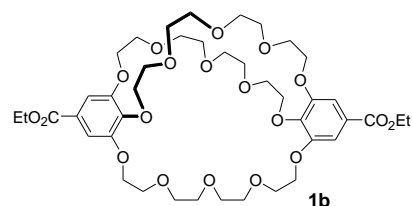
(q, $J = 7.0$ Hz, 4H), 4.21–4.17 (m, 8H), 3.87–3.84 (m, 4H), 3.74–3.68 (s, 16H), 3.67–3.64 (s, 4H), 1.36 (t, $J = 7.0$ Hz, 6H).

^{13}C NMR (150 MHz, CDCl_3) δ : 166.2, 152.0, 150.7, 139.0, 126.3, 110.8, 106.1, 72.7, 71.0, 70.80, 70.77, 70.3, 69.7, 69.6, 68.7, 61.0, 14.3.

MS (FAB): m/z calcd for $\text{C}_{34}\text{H}_{49}\text{O}_{16}^+$ $[\text{M}+\text{H}]^+$: 713.3015; found: 713.3001.

mp: 99–100 °C (EtOH).

Cryptand **1b**



Using Cs_2CO_3

The cryptand **1b** (60.5 mg, 62%) was synthesized from the crown ether **3b** (80.1 mg, 0.112 mmol) and tetra(ethyleneglycol) ditosylate (56.5 mg, 0.112 mmol), using the procedure for synthesis of the cryptand **1a**, as a white solid.

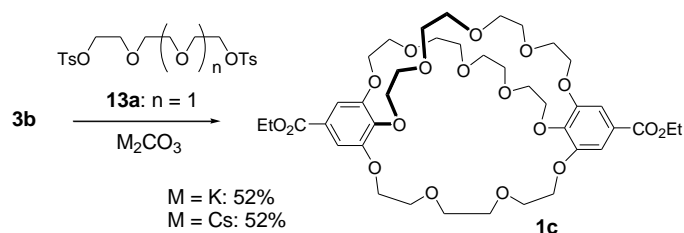
Using K_2CO_3

The cryptand **1b** (63.1 mg, 65%) was synthesized from the crown ether **3b** (80.1 mg, 0.128 mmol) and K_2CO_3 (46.9 mg, 0.338 mmol) instead of Cs_2CO_3 , using the procedure described above, as a white solid.

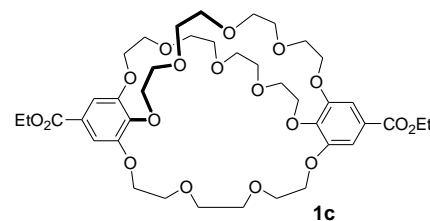
Using Na_2CO_3

The cryptand **1b** (37.5 mg, 38%) was synthesized from the crown ether **3b** (79.4 mg, 0.127 mmol) and Na_2CO_3 (40.6 mg, 0.383 mmol) instead of Cs_2CO_3 , using the procedure described above, as a white solid.

Synthesis of cryptand **1c**.



Cryptand **1c**



Using K_2CO_3

A suspension of crown **3b** (200 mg, 0.281 mmol), tri(ethylene glycol) ditosylate **13a** (128 mg, 0.280 mmol), and K_2CO_3 (156 mg, 1.13 mmol) in DMF (80 mL) was stirred 3 d at 100 °C. After evaporation of the solvent, the residue was neutralized with dil. HCl (aq.). The aqueous mixture was extracted with AcOEt. Combined extracts were dried (Na_2SO_4), and concentrated. The residue was purified through GPC to give the crude product, which was washed with $i\text{Pr}_2\text{O}$ and hexane to the cryptand **1c** (118 mg, 52 %) as a white solid.

Using Cs_2CO_3

The cryptand **1c** (119 mg, 52%) was synthesized from the crown ether **3b** (200 mg, 0.281 mmol) and Cs_2CO_3 (367 mg, 1.13 mmol) instead of K_2CO_3 , using the procedure described above, as a white solid.

IR (KBr, ν_{max}) cm^{-1} : 2872, 1717, 1589, 1501, 1431, 1368, 1331, 1245, 1206, 1121, 1030, 940, 768.

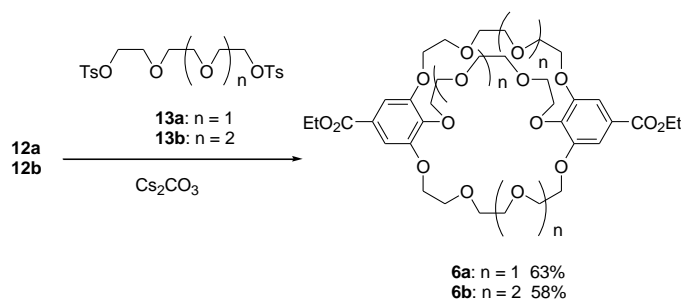
^1H NMR (600 MHz, C_6D_6) δ : 7.554 (d, $J = 1.7$ Hz, 2H), 7.548 (d, $J = 1.7$ Hz, 2H), 4.51 (dt, $J = 10.6$ and 5.2 Hz, 2H), 4.44 (dt, $J = 10.6$ and 5.2 Hz, 2H), 4.19 (q, $J = 7.2$ Hz, 4H), 3.94 (q, $J = 5.2$ Hz, 4H), 3.89–3.85 (m, 4H), 3.70–3.66 (m, 4H), 3.64 (td, $J = 4.8$ and 2.1 Hz, 4H), 3.62–3.58 (m, 2H), 3.55–3.45 (m, 14H), 3.44–3.38 (m, 6H), 3.34 (ddd, $J = 11.5$, 4.6, and 2.2 Hz, 2H), 1.07 (t, $J = 7.2$ Hz, 6H).

^{13}C -NMR (150 MHz, C_6D_6) δ : 166.2, 153.1, 153.0, 143.9, 125.6, 109.6, 109.5, 73.1, 71.4, 71.3, 71.1, 71.0, 70.9, 69.8, 69.7, 69.6, 69.1, 60.9, 14.4. One aliphatic carbon signal was overlapping/missing.

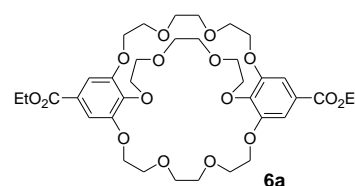
MS (MALDI): m/z calcd for $\text{C}_{40}\text{H}_{58}\text{O}_{18}\text{Na}^+$ [$\text{M}+\text{Na}$] $^+$: 849.3515; found: 849.3499.

mp: 121 °C (acetone).

Synthesis of cryptands **6**.



Cryptand **6a**



A suspension of the crown ether **12a** (200 mg, 0.32 mmol), tri(ethylene glycol) ditosylate **13a** (147 mg, 0.32 mmol), and Cs_2CO_3 (153 mg, 0.96 mmol) in DMF (15 mL) was heated at 100 °C for 16 h. After evaporation of the solvent, 10% HCl (aq.) was added to the residue and the aqueous phase was extracted with AcOEt. The organic extract was dried (MgSO_4), and concentrated. The residue was purified by GPC (eluent CHCl_3) to afford a white solid, which was washed with hexane (150 mg, 63%). IR (KBr, ν_{max}) cm^{-1} : 2936, 1707, 1593, 1504, 1432, 1334, 1252, 1209, 1118, 1031, 769.

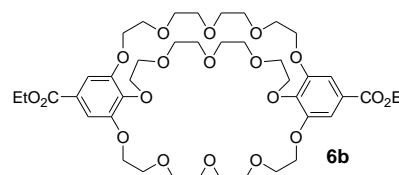
^1H NMR (600 MHz, CDCl_3) δ : 7.20 (s, 4H), 4.31 (q, $J = 7.1$ Hz, 4H), 4.18–4.13 (m, 12H), 3.98–3.95 (m, 4H), 3.90–3.87 (m, 8H), 3.80 (s, 8H), 3.79 (s, 4H), 1.35 (t, $J = 7.1$ Hz, 6H).

^{13}C NMR (150 MHz, CDCl_3) δ : 166.1, 152.2, 142.5, 125.1, 108.3, 72.5, 71.5, 70.9, 70.8, 69.6, 69.5, 61.0, 14.3.

MS (MALDI): m/z calcd for $\text{C}_{36}\text{H}_{50}\text{O}_{16}\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 761.2991; found: 761.2994.

mp: 95–96 °C (EtOH).

Cryptand **6b**



A suspension of the crown ether **12b** (200 mg, 0.28 mmol), tetra(ethylene glycol) ditosylate **13b** (140.7 mg, 0.28 mmol), and Cs_2CO_3 (274 mg, 0.84 mmol) in DMF (15 mL) was heated at 95 °C for 20 h. After evaporation of the solvent, 10% HCl (aq.) and water were added to the residue and the aqueous phase was extracted with AcOEt. The organic extract was dried (MgSO_4), and concentrated. The residue was purified by column chromatography (SiO_2 ; $\text{CHCl}_3/\text{MeOH}$, 10:1) to afford a crude product, which was recrystallized from EtOH (colorless solid, 141 mg, 58%).

IR (KBr, ν_{max}) cm^{-1} : 2931, 2871, 1715, 1587, 1505, 1430, 1336, 1240, 1213, 1128, 1034.

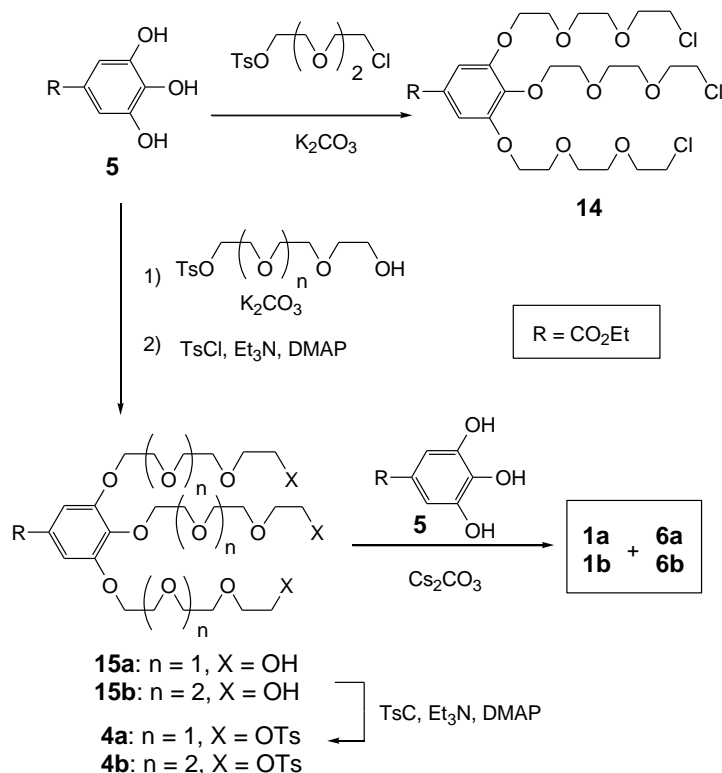
^1H NMR (600 MHz, CDCl_3) δ : 7.22 (s, 4H), 4.33 (q, $J = 7.1$ Hz, 4H), 4.23–4.19 (m, 4H), 4.17–4.13 (m, 8H), 3.88–3.84 (m, 12H), 3.76–3.65 (m, 24H), 1.36 (t, $J = 7.1$ Hz, 6H).

^{13}C NMR (150 MHz, CDCl_3) δ : 166.1, 152.2, 142.5, 125.1, 108.6, 72.5, 71.1, 70.9, 70.8, 70.63, 70.59, 69.6, 69.0, 61.0, 14.4.

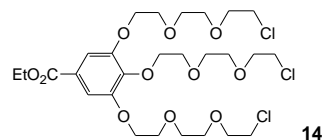
MS (MALDI): m/z calcd for $\text{C}_{42}\text{H}_{62}\text{O}_{19}\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 893.3778; found: 893.3775.

mp: 93–94 °C (EtOH).

Method C



Compound 14



A suspension of ethyl gallate (**5**) (0.512 g, 2.58 mmol), tri(ethylene glycol) monotosylate (3.27 g, 10.1 mmol), K_2CO_3 (1.75 g, 12.7 mmol) in DMF (15 mL) and 1,2-dichlorobenzene (3.0 mL) was heated at 90 °C for 20 h. After evaporation of the solvent, 10% HCl (aq.) was added to the residue and the aqueous phase was extracted with AcOEt and CH_2Cl_2 . The organic extract was dried (Na_2SO_4), and concentrated. The residue was purified by column chromatography (SiO_2 ; toluene/AcOEt, 2:1) to afford a pale yellow oil (1.21 g, 78%).

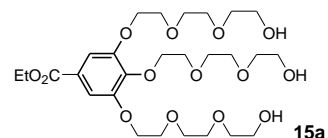
IR (KBr, ν_{max}) cm^{-1} : 2873, 1714, 1586, 1499, 1429, 1368, 1332, 1299, 1213, 1120, 1032.

^1H NMR (500 MHz, CDCl_3) δ : 7.30 (s, 2H), 4.35 (q, $J = 7.1$ Hz, 2H), 4.25–4.19 (m, 6H), 3.90–3.87 (m, 4H), 3.84–3.80 (m, 2H), 3.78–3.65 (m, 18H), 3.65–3.61 (m, 6H), 1.38 (t, $J = 7.1$ Hz, 3H).

^{13}C NMR (125 MHz, CDCl_3) δ : 165.9, 152.1, 142.2, 125.2, 108.7, 72.2, 71.21, 71.18, 70.6, 70.5, 70.4, 69.5, 68.7, 60.9, 42.6, 14.2. Three aliphatic carbon signals were overlapping/missing.

MS (MALDI): m/z calcd for $\text{C}_{27}\text{H}_{43}\text{Cl}_3\text{O}_{11}\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 671.1763; found: 671.1733.

Compound 15a



A suspension of ethyl gallate (0.513 g, 2.52 mmol), tri(ethylene glycol) monotosylate (3.07 g, 10.1 mmol), K_2CO_3 (1.74 g, 12.6 mmol) in DMF (15 mL) was heated at 90 °C for 19 h. After evaporation of the solvent, 10% HCl (aq.) was added to the residue and the aqueous phase was extracted with CH_2Cl_2 . The organic extract was dried (Na_2SO_4), and concentrated. The residue was purified by column chromatography (SiO_2 ; acetone/AcOEt, 2:1) to afford a pale yellow oil (0.832 g, 64%).

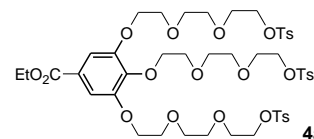
IR (KBr, ν_{max}) cm^{-1} : 3421, 2874, 1713, 1587, 1499, 1430, 1368, 1332, 1244, 1214, 1121, 938, 888, 767.

1H NMR (500 MHz, $CDCl_3$) δ : 7.30 (s, 2H), 4.35 (q, $J = 7.1$ Hz, 2H), 4.29–4.25 (m, 2H), 4.24–4.20 (m, 4H), 3.92–3.84 (m, 6H), 3.77–3.64 (m, 18H), 3.62–3.57 (m, 6H), 1.38 (t, $J = 7.1$ Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ : 166.1, 152.1, 142.2, 125.4, 108.8, 72.8, 72.7, 72.5, 70.8, 70.6, 70.5, 70.4, 69.6, 68.7, 61.7, 61.6, 61.1, 14.4. One aliphatic carbon signal was overlapping/missing.

MS (MALDI): m/z calcd for $C_{27}H_{46}O_{14}Na^+$ $[M+Na]^+$: 617.2780; found: 617.2768.

Compound 4a



Et_3N (3.15 mL, 22.6 mmol) was added to a solution of triol **15a** (2.56 g, 5.02 mmol), *p*-toluenesulfonyl chloride (3.36 g, 17.6 mmol), and DMAP (0.179 g, 1.46 mmol) in CH_2Cl_2 (30.0 mL) under ice bath, then the mixture was stirred for 90 min at room temperature. The mixture was neutralized with dil. HCl (aq), and extracted with CH_2Cl_2 . The combined extracts were dried (Na_2SO_4), and concentrated to give a residue, which was chromatographed (SiO_2 ; hexane/AcOEt, 1:2) to give a pale yellow oil (3.25 g, 67%).

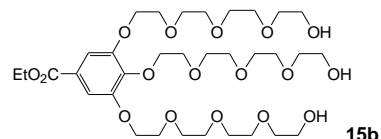
IR (KBr, ν_{max}) cm^{-1} : 2874, 1713, 1597, 1497, 1429, 1356, 1333, 1213, 1189, 1176, 1121, 1019, 923, 818, 769, 664.

1H NMR (500 MHz, $CDCl_3$) δ : 7.81–7.76 (m, 6H), 7.36–7.31 (m, 6H), 7.29 (s, 2H), 4.35 (q, $J = 7.1$ Hz, 2H), 4.21–4.12 (m, 12H), 3.85–3.81 (m, 4H), 3.78–3.75 (m, 2H), 3.71–3.63 (m, 12H), 3.62–3.56 (m, 6H), 2.43 (s, 9H), 1.38 (t, $J = 7.1$ Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ : 166.0, 152.1, 144.8, 142.3, 132.8, 129.8, 127.8, 125.3, 108.8, 72.3, 70.7, 70.6, 70.5, 70.3, 69.6, 69.24, 69.20, 68.7, 68.61, 68.58, 61.0, 21.5, 14.3. Four aromatic carbon signals were overlapping/missing. Two aliphatic carbon signals were overlapping/missing.

MS (MALDI): m/z calcd for $C_{48}H_{64}O_{20}S_3Na^+$ $[M+Na]^+$: 1079.3045; found: 1079.3037.

Compound **15b**



A suspension of ethyl gallate (**5**) (0.714 g, 3.60 mmol), tetra (ethylene glycol) monotosylate (5.00 g, 14.4 mmol), K_2CO_3 (2.50 g, 18.1 mmol) in DMF (25 mL) was heated at 90 °C for 20 h. After evaporation of the solvent, 10% HCl (aq.) was added to the residue and the aqueous phase was extracted with CH_2Cl_2 . The organic extract was dried (Na_2SO_4), and concentrated. The residue was purified by column chromatography (SiO_2 ; $CHCl_3/MeOH$, 20:1) to afford a pale yellow oil (1.57 g, 60%).

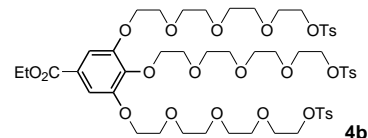
IR (KBr, ν_{max}) cm^{-1} : 3446, 2873, 1713, 1587, 1499, 1430, 1332, 1245, 1214, 1119, 945, 768.

1H NMR (500 MHz, $CDCl_3$) δ : 7.30 (s, 2H), 4.35 (q, $J = 7.2$ Hz, 2H), 4.26–4.19 (m, 6H), 3.90–3.86 (m, 4H), 3.84–3.80 (m, 2H), 3.76–3.69 (m, 12H), 3.69–3.64 (m, 18H), 3.61–3.57 (m, 6H), 3.35–2.70 (m, 3H), 1.38 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ : 166.0, 152.1, 142.2, 125.2, 108.7, 72.6, 72.5, 72.4, 70.7, 70.5, 70.3, 70.2, 69.5, 68.7, 61.5, 61.0, 14.3. Six aliphatic carbon signals were overlapping/missing.

MS (MALDI): m/z calcd for $C_{33}H_{58}O_{17}Na^+$ $[M+Na]^+$: 749.3566 ; found: 749.3571.

Compound **4b**



Tritosylate **4b** (0.467 g, 0.600 mmol) was synthesized from the triol **15b** (0.434 g, 0.600 mmol), using the procedure described above, as a pale yellow oil (65% yield) after chromatographic purification (SiO_2 ; hexane/AcOEt, 1:1).

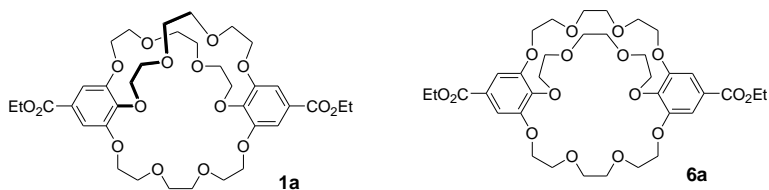
IR (KBr, ν_{max}) cm^{-1} : 2873, 1713, 1597, 1497, 1429, 1356, 1333, 1213, 1189, 1177, 1114, 1019, 923, 818, 769.

1H NMR (500 MHz, $CDCl_3$) δ : 7.81–7.76 (m, 6H), 7.36–7.32 (m, 6H), 7.29 (s, 2H), 4.35 (q, $J = 7.2$ Hz, 2H), 4.23–4.12 (m, 12H), 3.88–3.83 (m, 4H), 3.80–3.76 (m, 2H), 3.72–3.65 (m, 12H), 3.65–3.55 (m, 18H), 1.38 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ : 165.9, 152.1, 144.8, 142.3, 132.8, 129.8, 127.8, 125.3, 108.8, 72.3, 70.7, 70.6, 70.5, 70.3, 69.6, 69.23, 69.20, 68.7, 68.61, 68.58, 61.0, 21.5, 14.3. Four aromatic and six aliphatic carbon and signals were overlapping/missing.

MS (MALDI): m/z calcd for $C_{54}H_{76}O_{23}S_3Na^+$ $[M+Na]^+$: 1211.3832; found: 1211.3805.

Cryptands **1a** and **6a**



Using K_2CO_3

A suspension of the tritosylate **4a** (152 mg, 0.156 mmol), ethyl gallate (31.3 mg, 0.158 mmol), and K_2CO_3 (102 mg, 0.734 mmol) in DMF (7.7 mL) was heated at 100 °C for 23 h. After evaporation of the solvent, 10% HCl (aq.) was added to the residue and the aqueous phase was extracted with AcOEt and CH_2Cl_2 . Combined organic extract was dried (Na_2SO_4), and concentrated. The residue was purified by column chromatography (SiO_2 ; $CHCl_3/MeOH$, 10:1) and GPC ($CHCl_3$) to afford a mixture of two cryptands **1a** and **6a**, which was separated by HPLC (0.5 mM solution of Na_2HPO_4 and NaH_2PO_4 /acetonitrile/MeOH, 9:5:5, first peak: cryptand **1a**, second peak: cryptand **6a**). Each cryptand was purified by column chromatography (SiO_2 ; $CHCl_3/MeOH$, 10:1) to remove the salts to give the cross-chain bridging cryptand **1a** (19.7 mg, 17%) as a white solid and linear cryptand **6a** (16.6 mg 15%) as a white solid, respectively.

<HPLC conditions>

Column: GL Siences Inertsil ODS-3, 5 μm (10 \times 250 mm)

Eluent: buffer solution/acetonitrile/MeOH = 5/9/5 [$v/v/v$] (buffer solution, aqueous 1 mM sodium dihydrogen phosphate:1 mM disodium hydrogen phosphate = 1:1)

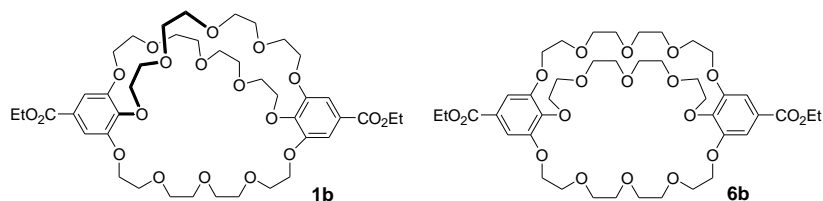
Flow rate: 2.0 mL/min

Wavelength: 254 nm

Using Cs_2CO_3

The cross-chain bridging cryptand **1a** (17.2 mg, 15%) and the linear cryptand **6a** (11.2 mg 10%) were synthesized from the tritosylate **4a** (152 mg, 0.156 mmol), ethyl gallate (30.9 mg, 0.156 mmol), and cesium carbonate (0.228 g, 0.698 mmol).

Cryptands **1b** and **6b**



Using K_2CO_3

A suspension of the tritosylate **4b** (152 mg, 0.128 mmol), ethyl gallate (25.5 mg, 0.129 mmol), and K_2CO_3 (80.5 mg, 0.582 mmol) in DMF (7.7 mL) was heated at 100 °C for 22 h. After evaporation of the solvent, 10% HCl (aq.) was added to the residue and the aqueous phase was extracted with AcOEt and CH_2Cl_2 . Combined organic extract was dried (Na_2SO_4), and concentrated. The residue was purified by column chromatography (SiO_2 ; $CHCl_3/MeOH$, 10:1) and GPC ($CHCl_3$) to afford a mixture of two

cryptands **1b** and **6b**, which was separated by HPLC (1.0 mM solution of Na₂HPO₄ and NaH₂PO₄/acetonitrile/MeOH, 6:11:5, first peak: cryptand **6b**, second peak: cryptand **1b**). Each cryptand was purified by column chromatography (SiO₂; CHCl₃/MeOH, 10:1) to remove the salts to give the cross-chain bridging cryptand **1b** (19.7 mg, 17%) as a white solid and linear cryptand **6b** (15.1 mg 13%) as a white solid, respectively.

<HPLC conditions>

Column: GL Siences Inertsil ODS-3, 5 μm (10 × 250 mm)

Eluent: buffer solution/acetonitrile/MeOH = 6/11/5 [v/v/v] (buffer solution, aqueous 1 mM sodium dihydrogen phosphate:1 mM disodium hydrogen phosphate = 1:1)

Flow rate: 3.0 mL/min

Wavelength: 254 nm

Using Cs₂CO₃

The cross-chain bridging cryptand **1b** (16.6 mg, 15%) and the linear cryptand **6b** (10.8 mg 9%) were obtained from the tritosylate **4a** (156 mg, 0.131 mmol), ethyl gallate (26.2 mg, 0.132 mmol), and cesium carbonate (0.196 g, 0.602 mmol), as described above.

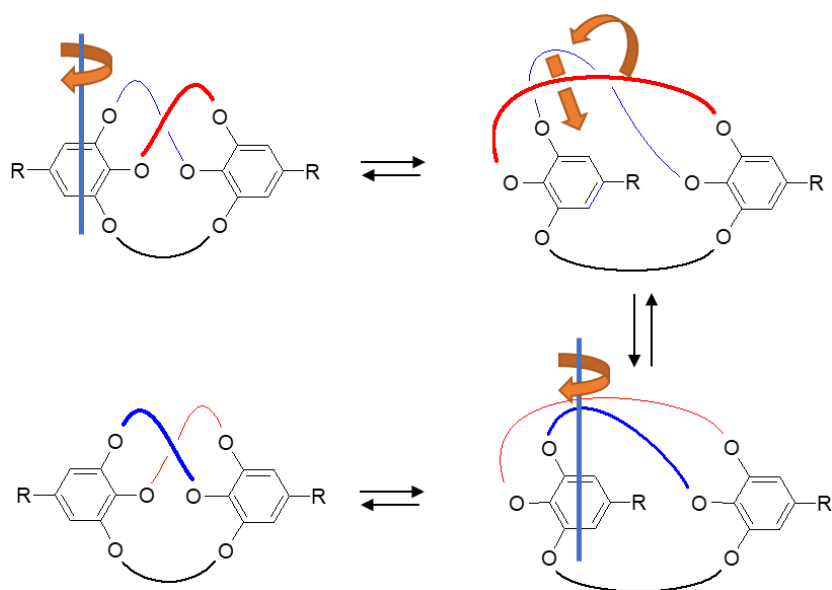
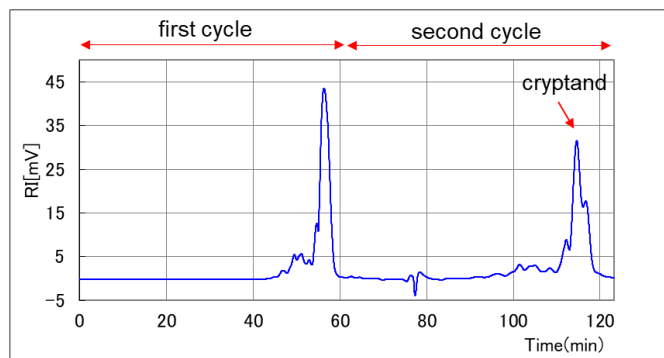
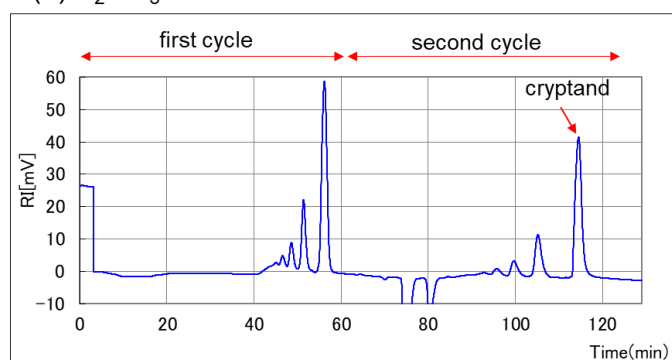


Figure S1. Interconversion of the cross-chain bridging cryptand **1b** between both enantiomers.

(a) Na_2CO_3



(b) K_2CO_3



(c) Cs_2CO_3

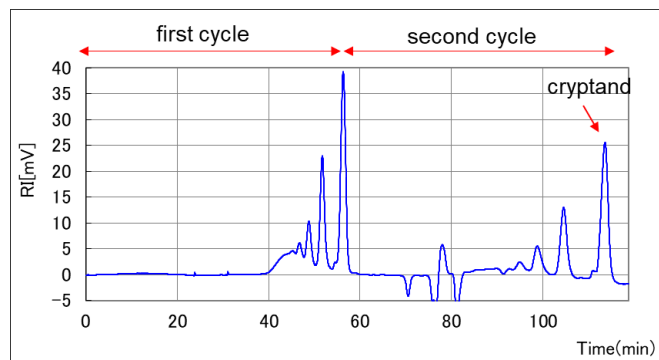
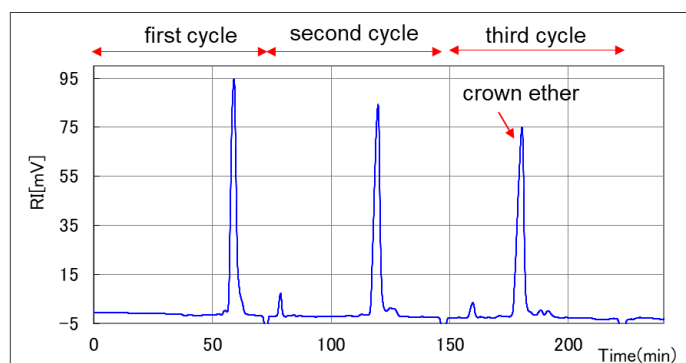
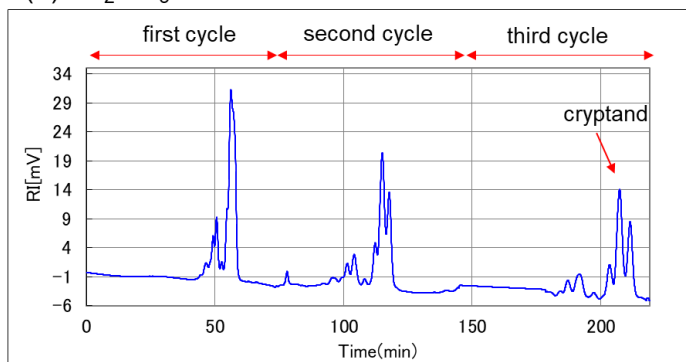


Figure S2. Recycle GPC analysis of the linking reaction of the crown ether **3a** using (a) Na_2CO_3 , (b) K_2CO_3 , and (c) Cs_2CO_3 as bases.

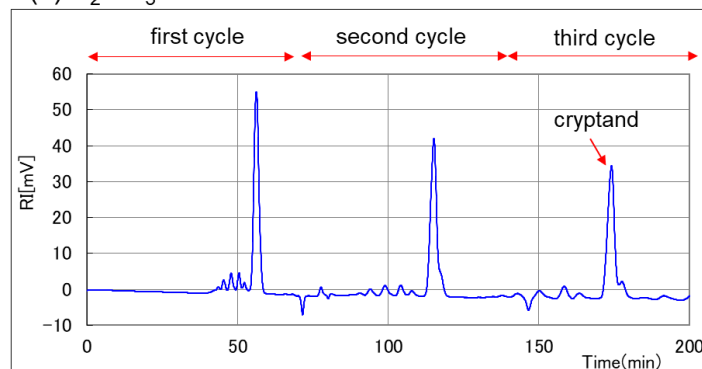
(a) Li_2CO_3



(b) Na_2CO_3



(c) K_2CO_3



(d) Cs_2CO_3

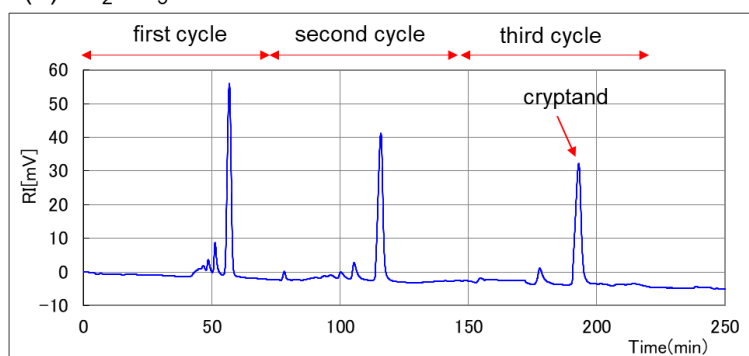


Figure S3. Recycle GPC analysis of the linking reaction of the crown ether **3b** using (a) Li_2CO_3 , (b) Na_2CO_3 , (c) K_2CO_3 , and (d) Cs_2CO_3 as bases.

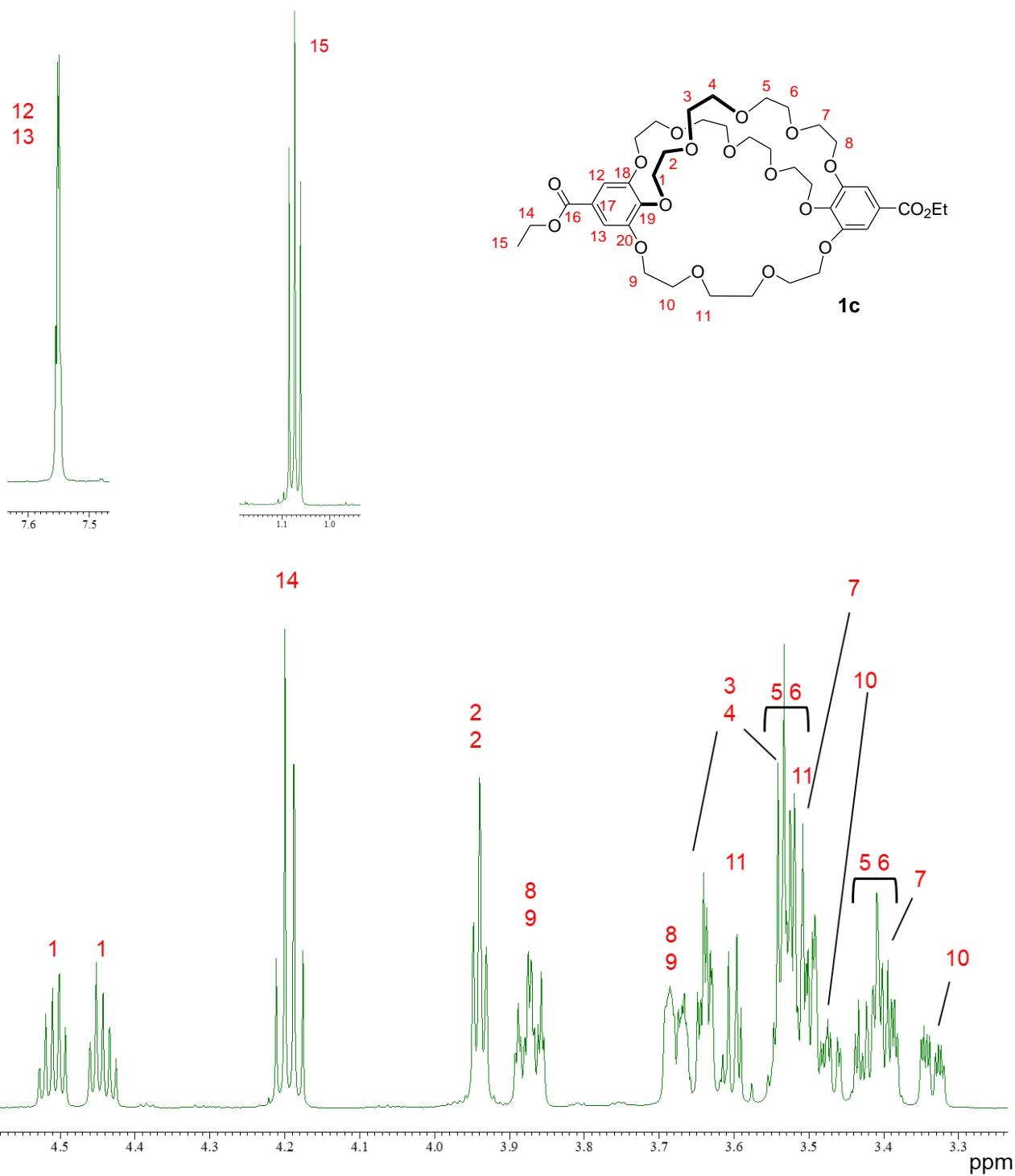


Figure S4. ^1H NMR spectrum (600 MHz, C_6D_6) of the cryptand **1c**.

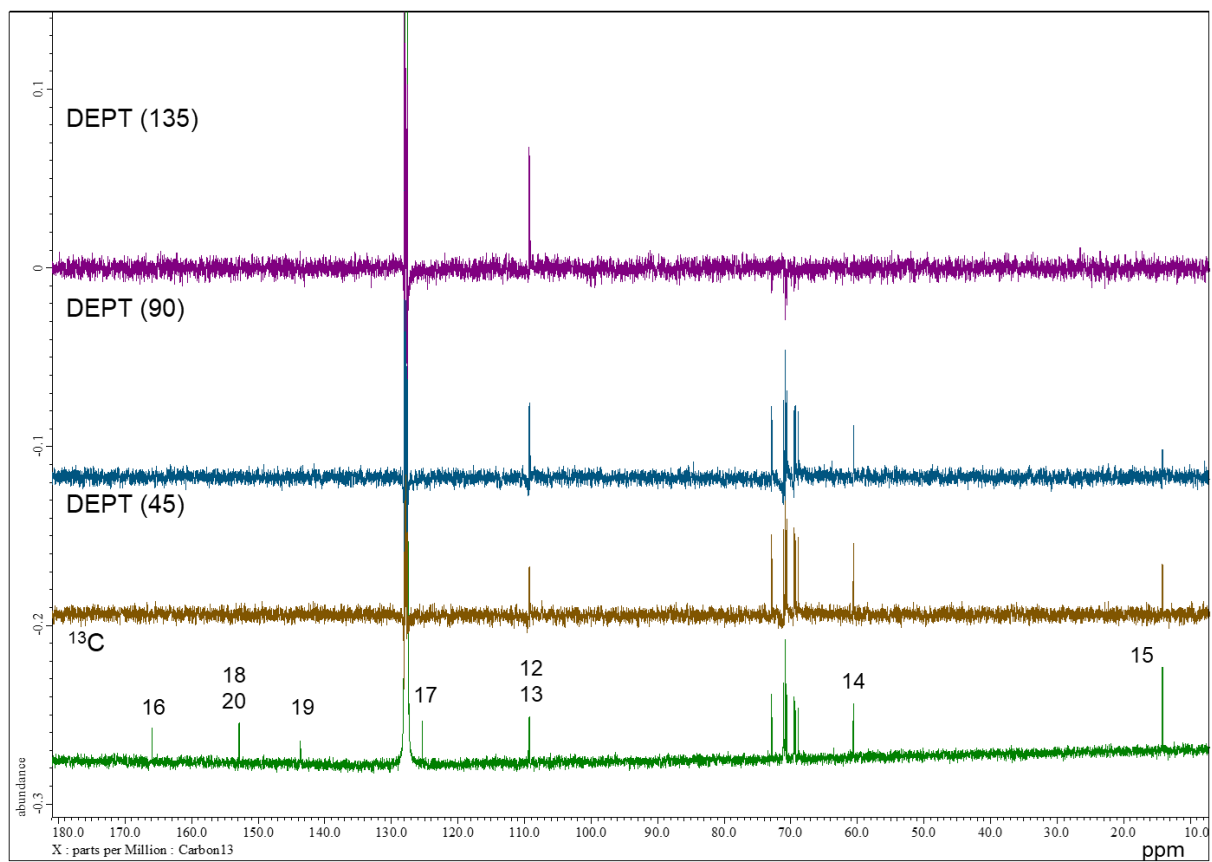
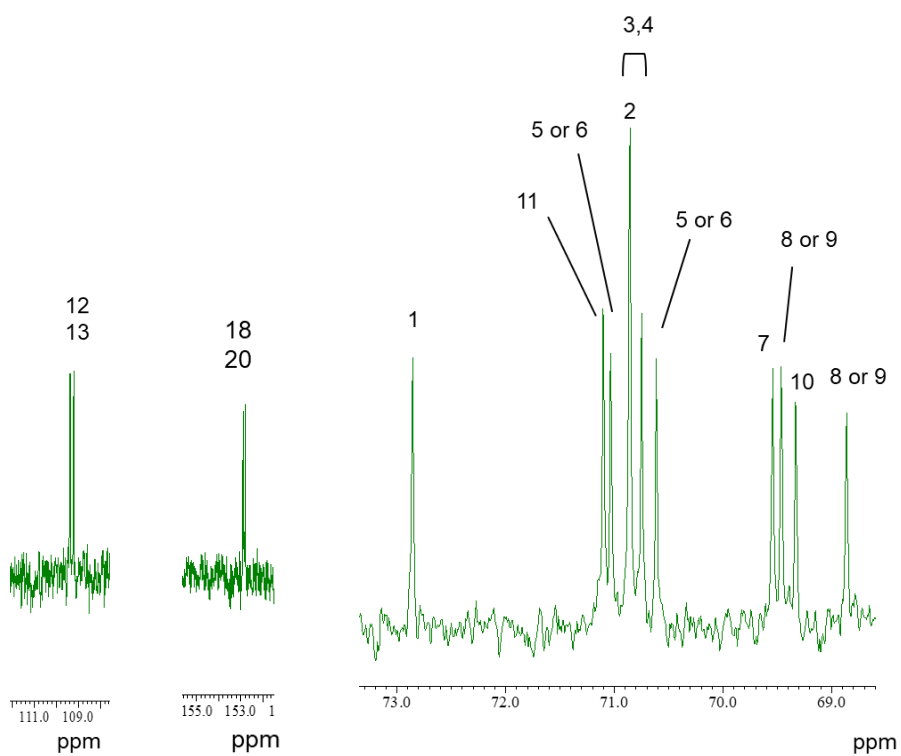


Figure S5. ^{13}C NMR spectra (150 MHz, C_6D_6) of the cryptand **1c**.

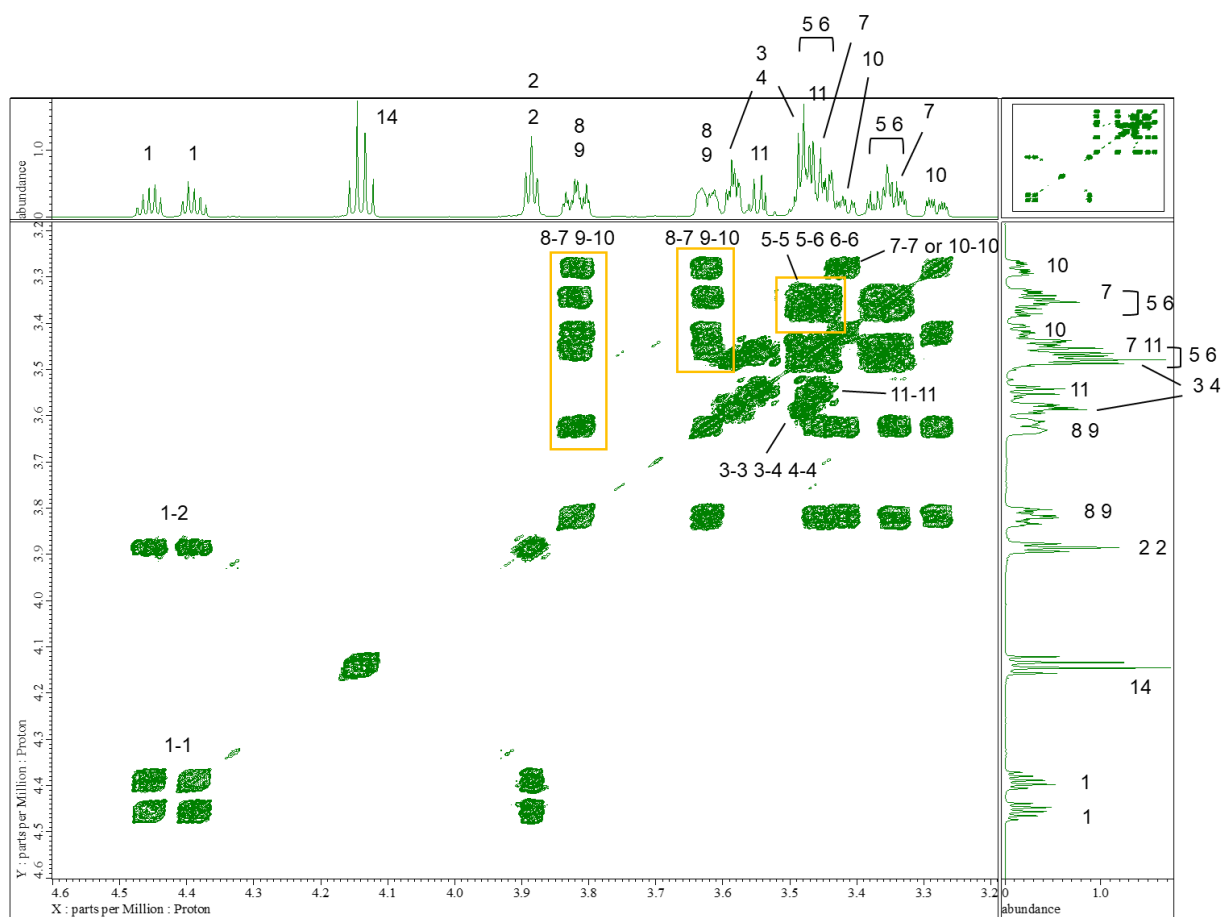
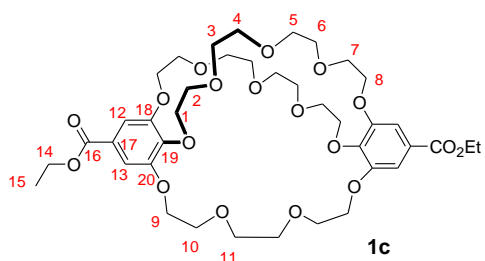


Figure S6. COSY spectrum (600 MHz, C_6D_6) of the cryptand **1c**.

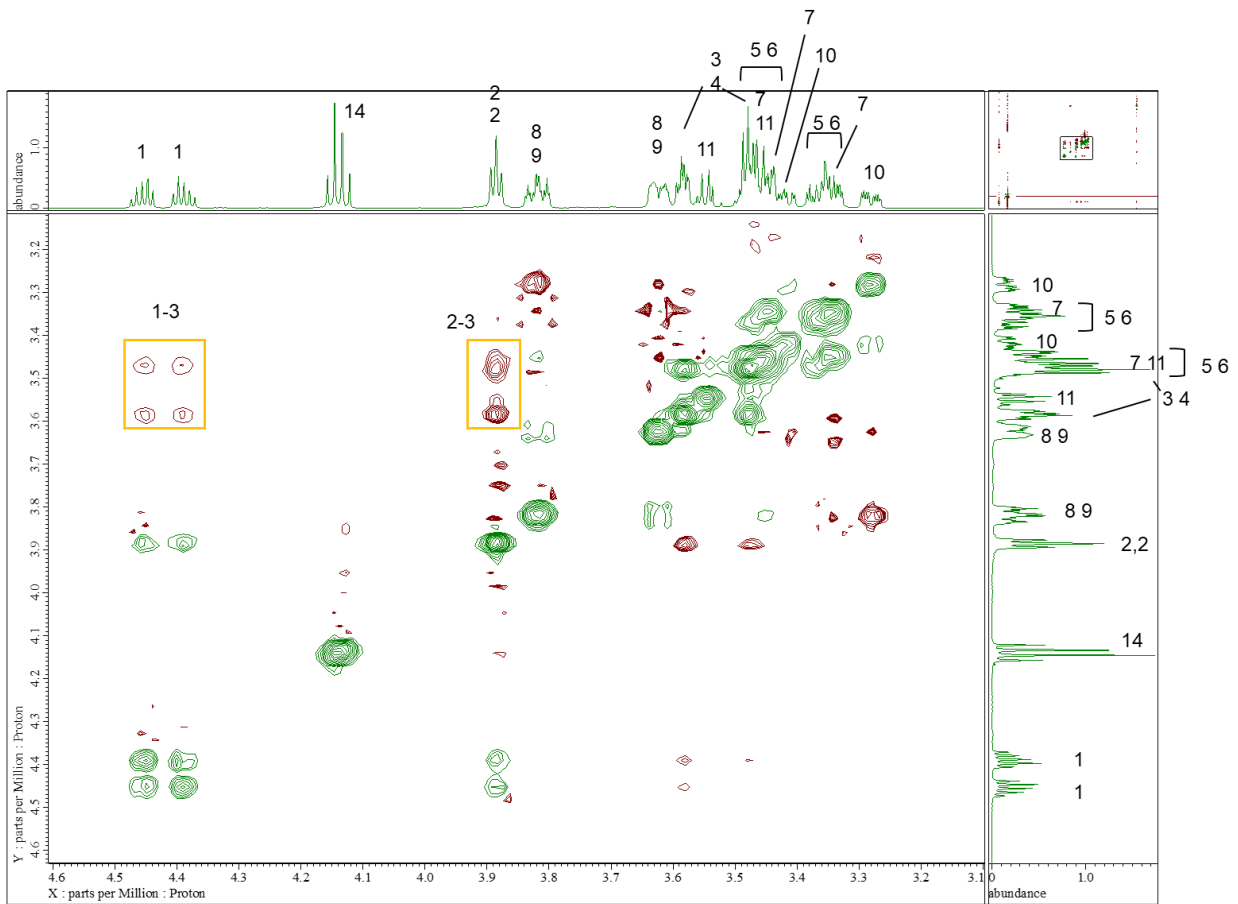
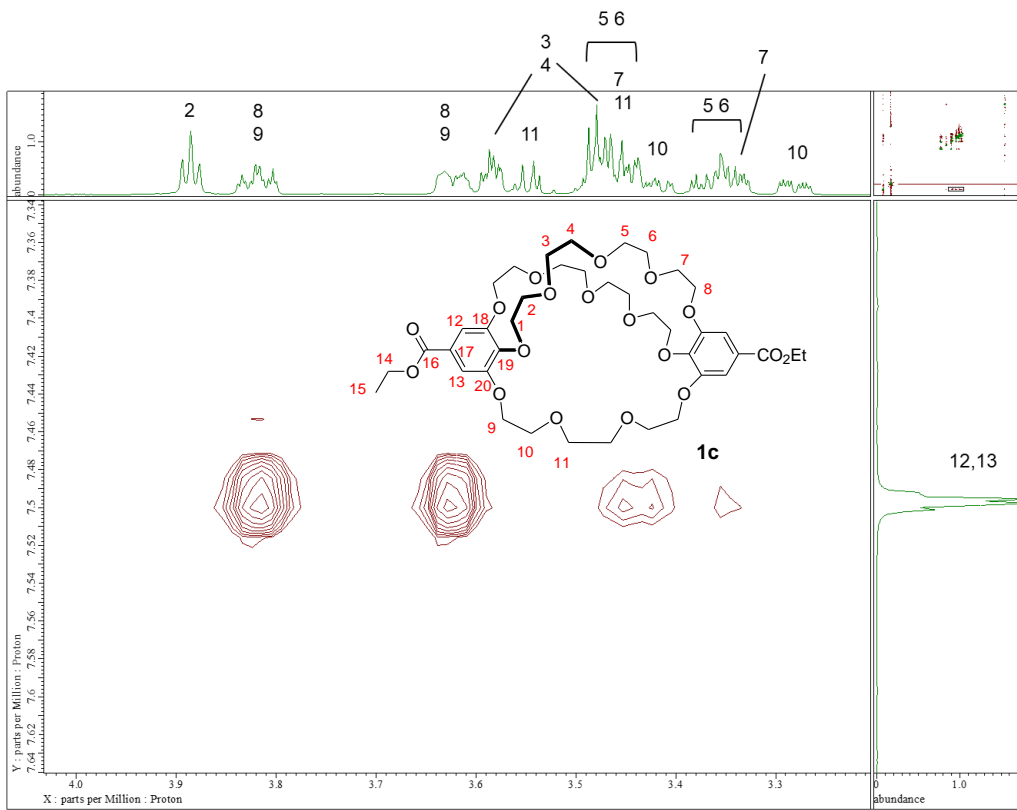


Figure S7. ROESY spectrum (600 MHz, C₆D₆) of the cryptand **1c**.

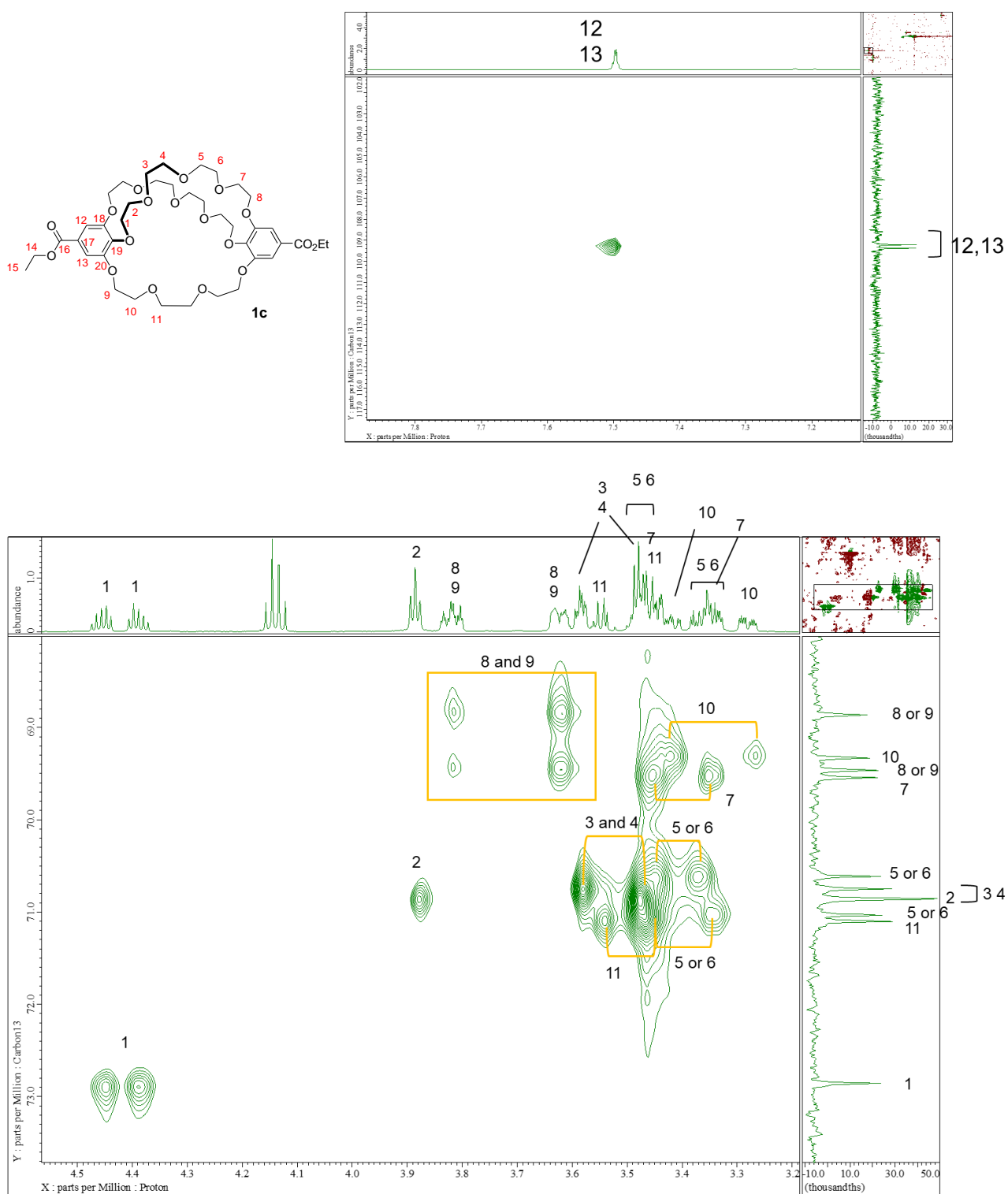
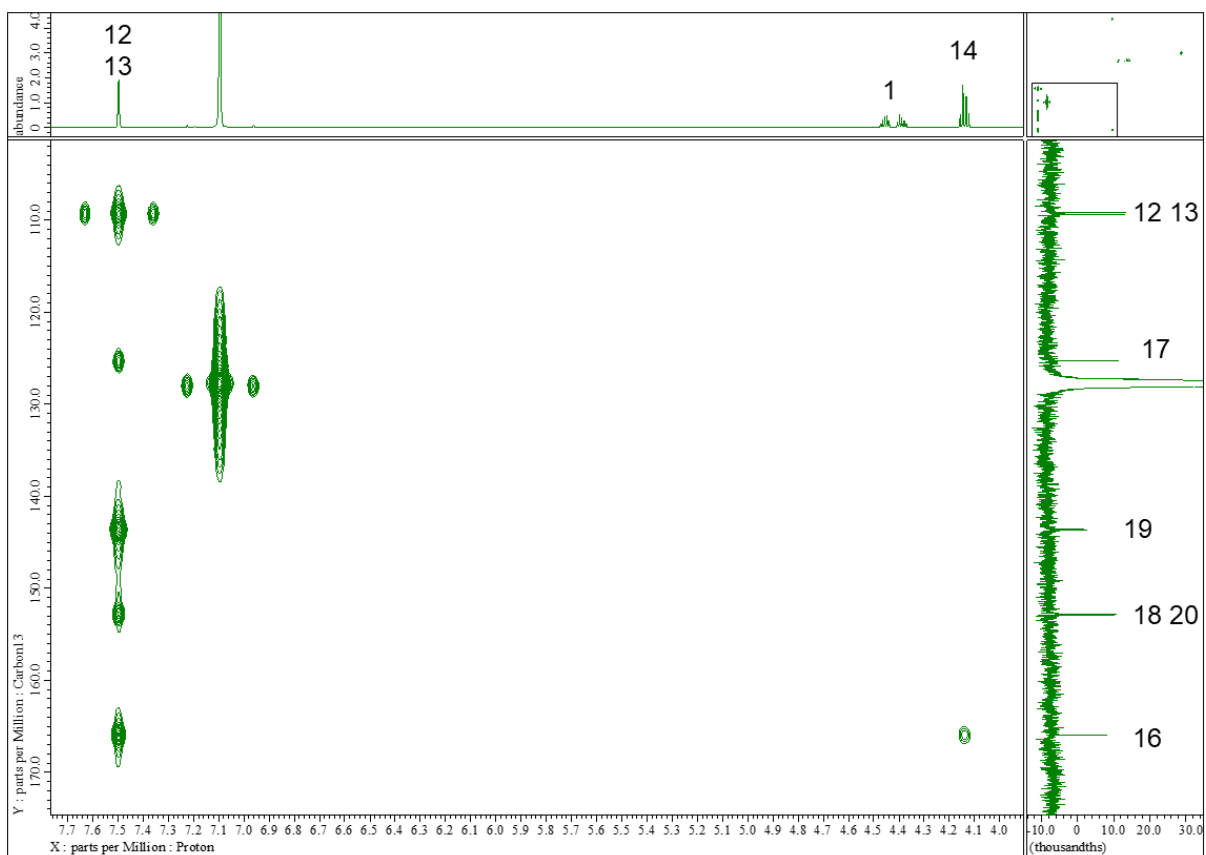
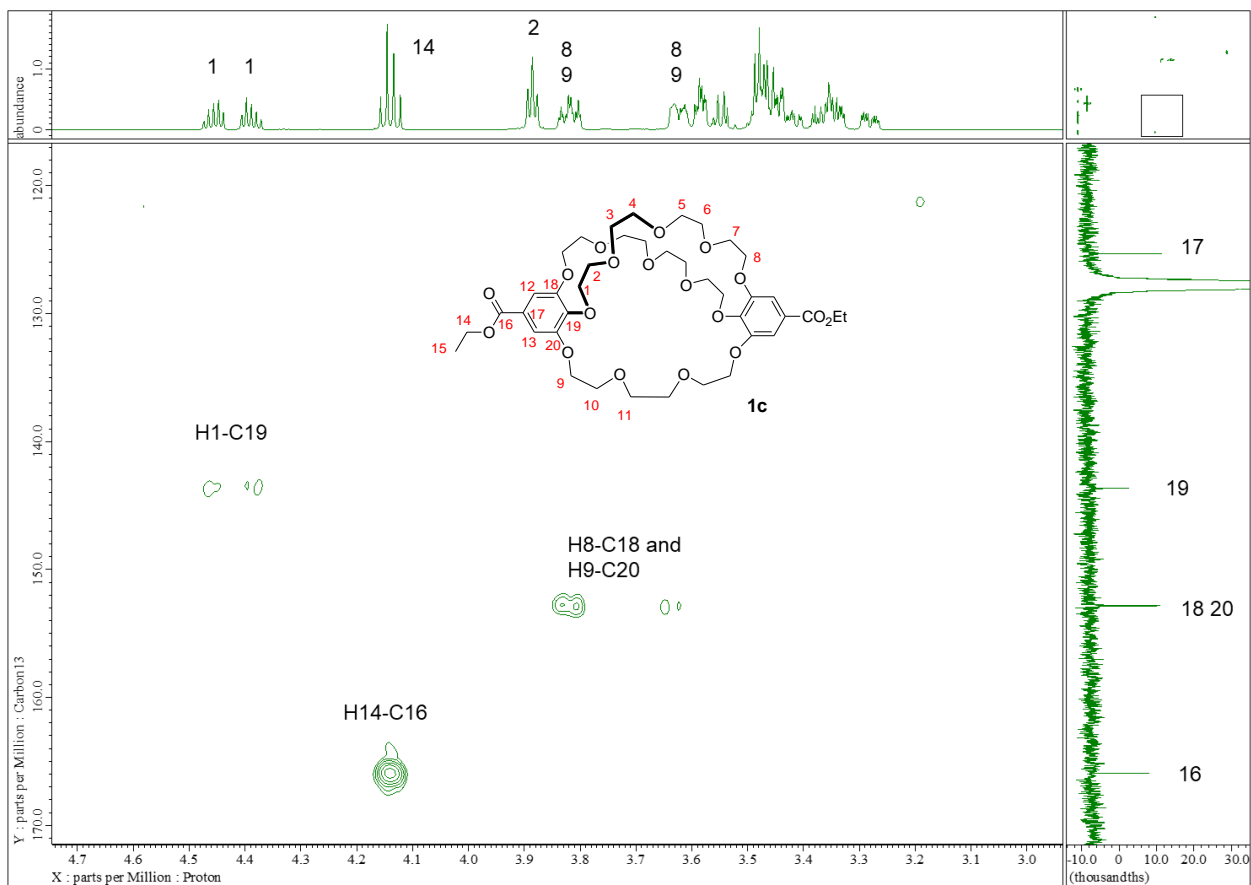


Figure S8. HSQC spectrum (600 MHz, C₆D₆) of the cryptand **1c**.



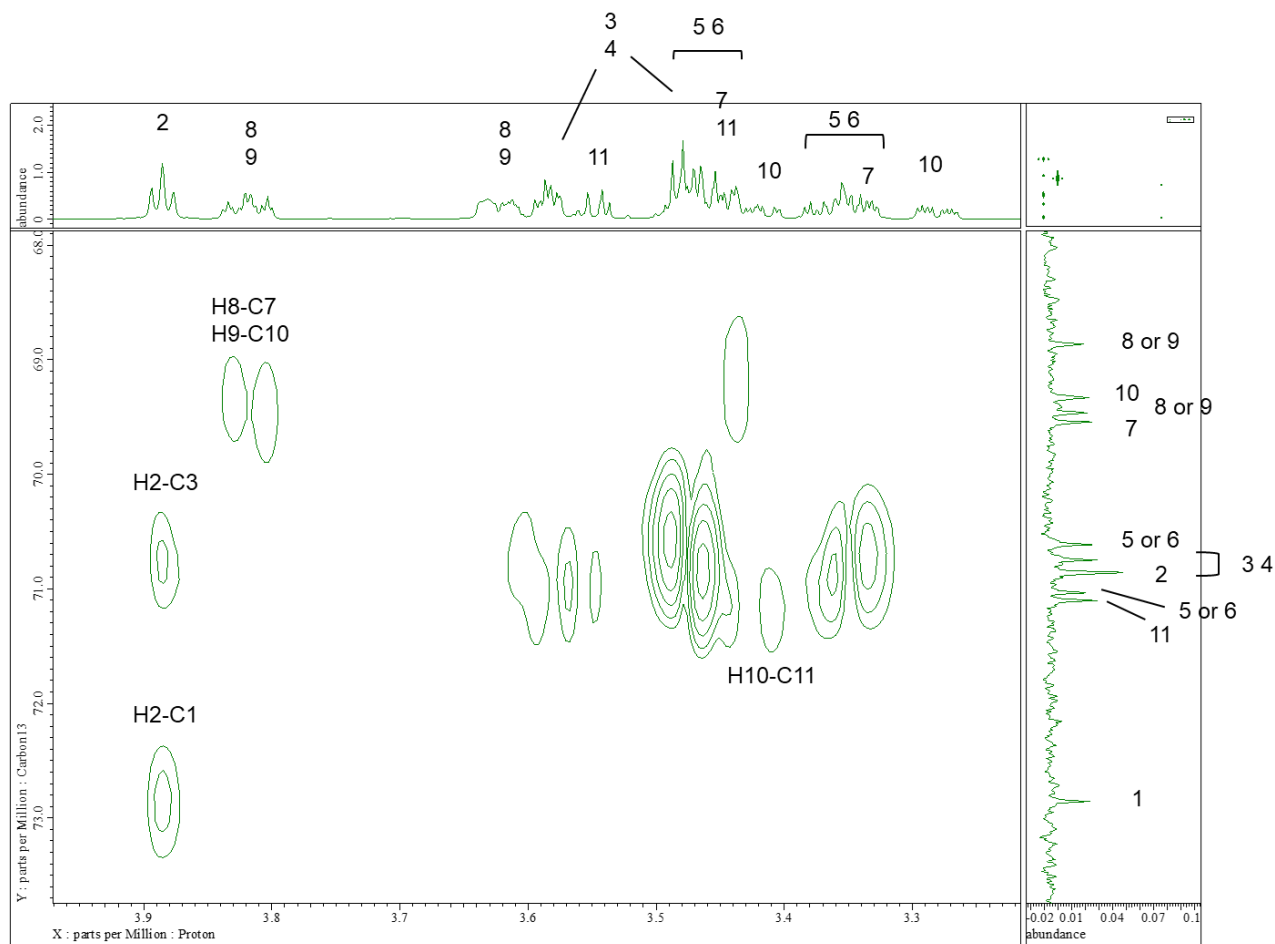
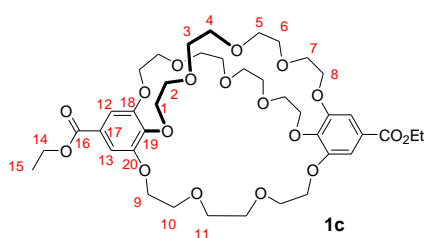


Figure S9. HMBC spectrum (600 MHz, C₆D₆) of the cryptand **1c**.

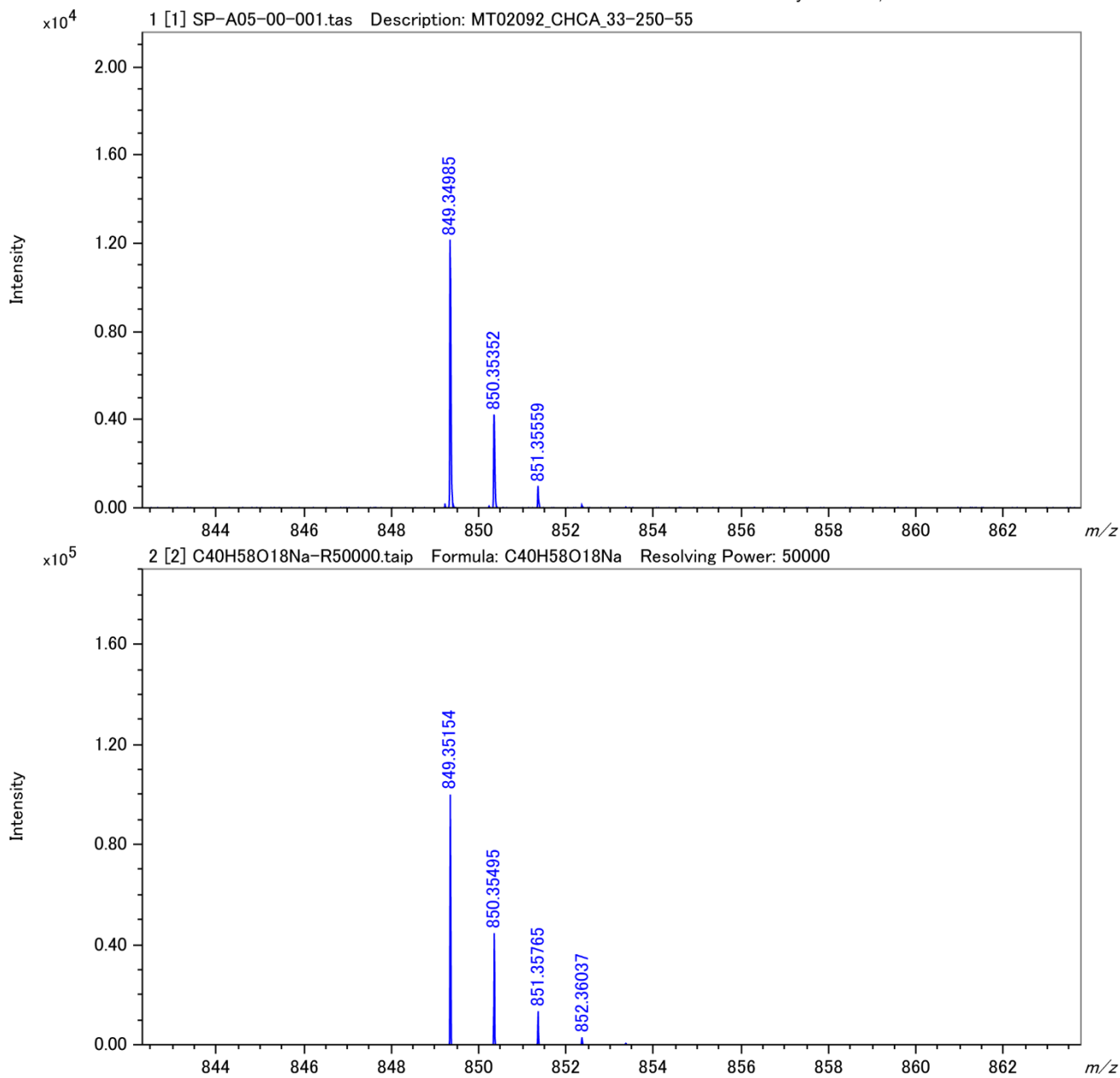


Figure S10. Mass spectrum (MALDI) of the cryptand **1c**: experimental (top) and calculated (bottom) isotopic patterns.

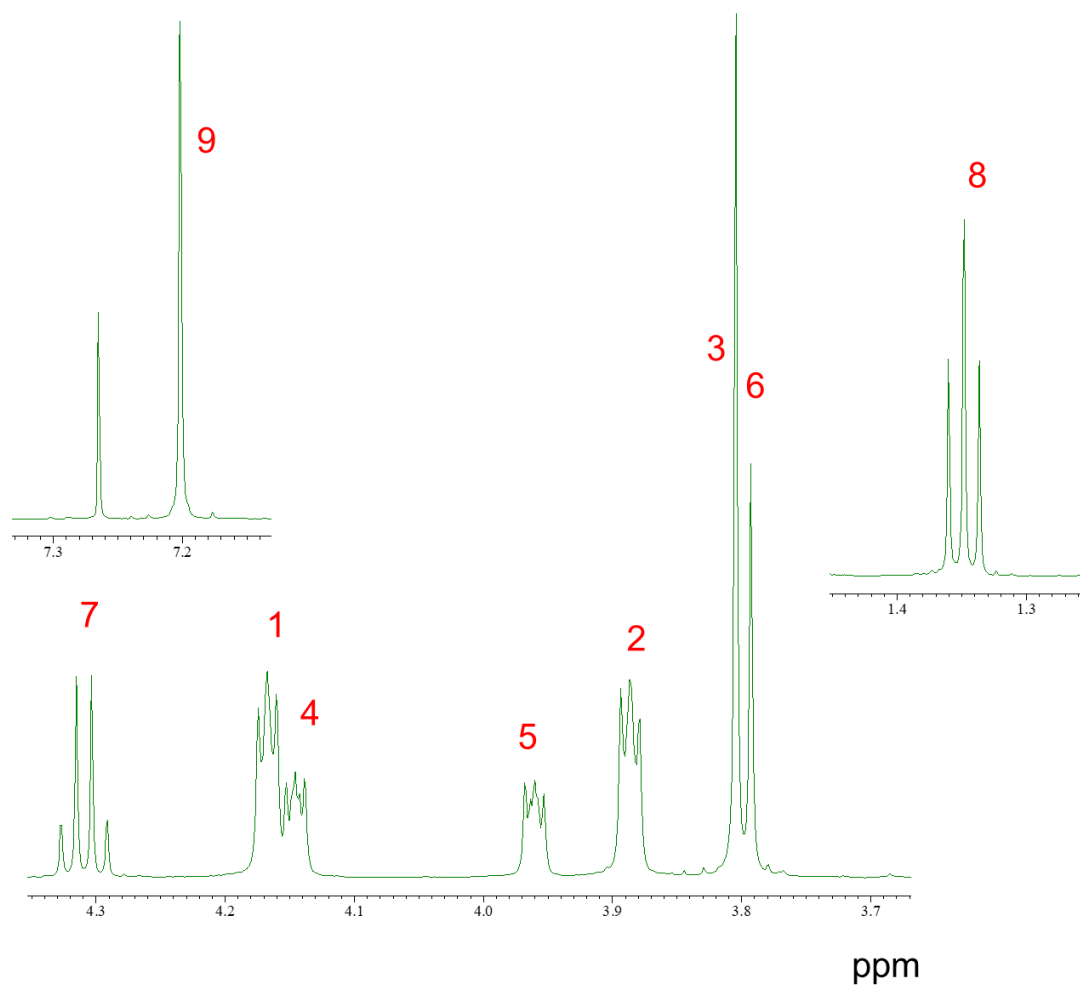
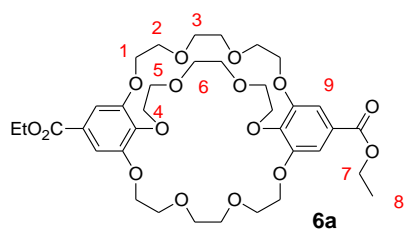


Figure S11. ^1H NMR spectrum (600 MHz, CDCl_3) of the linear cryptand **6a**.

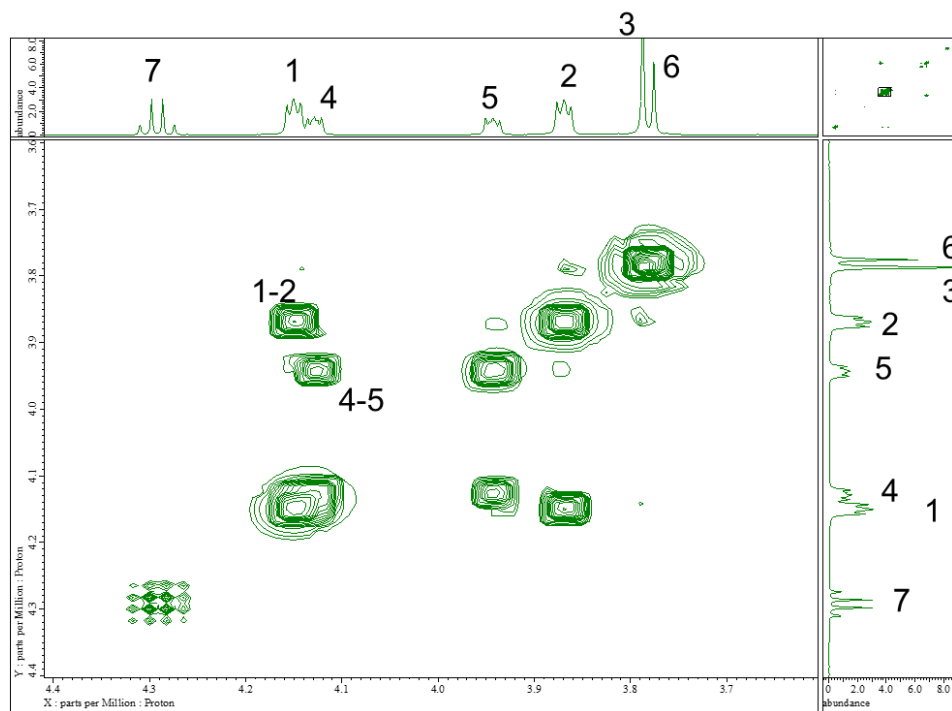
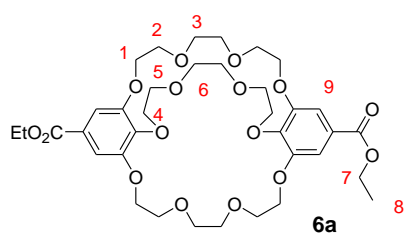


Figure S12. COSY spectrum (600 MHz, CDCl_3) of the linear cryptand **6a**.

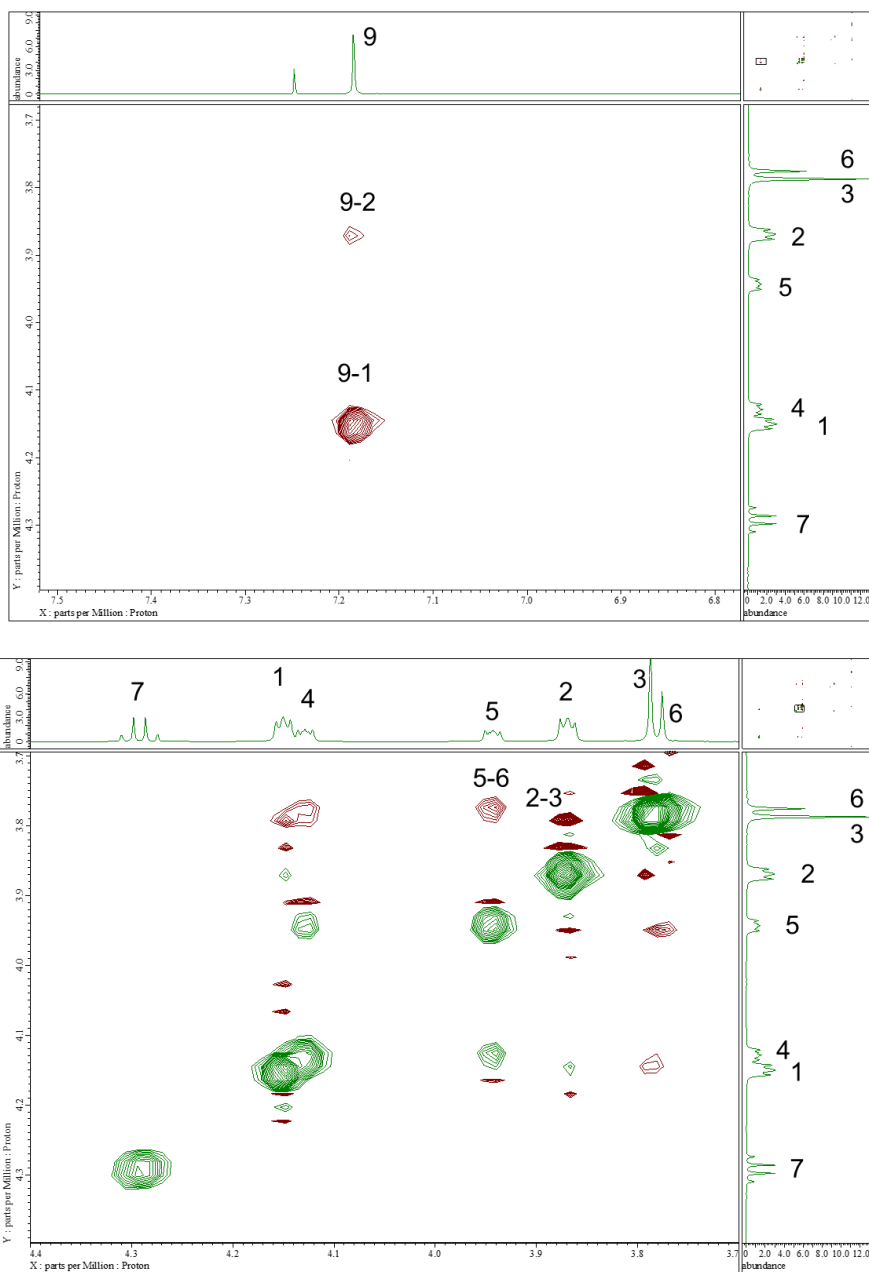
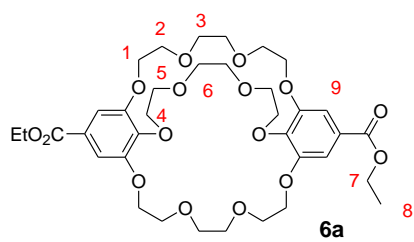


Figure S13. ROESY spectrum (600 MHz, CDCl₃) of the linear cryptand **6a**.

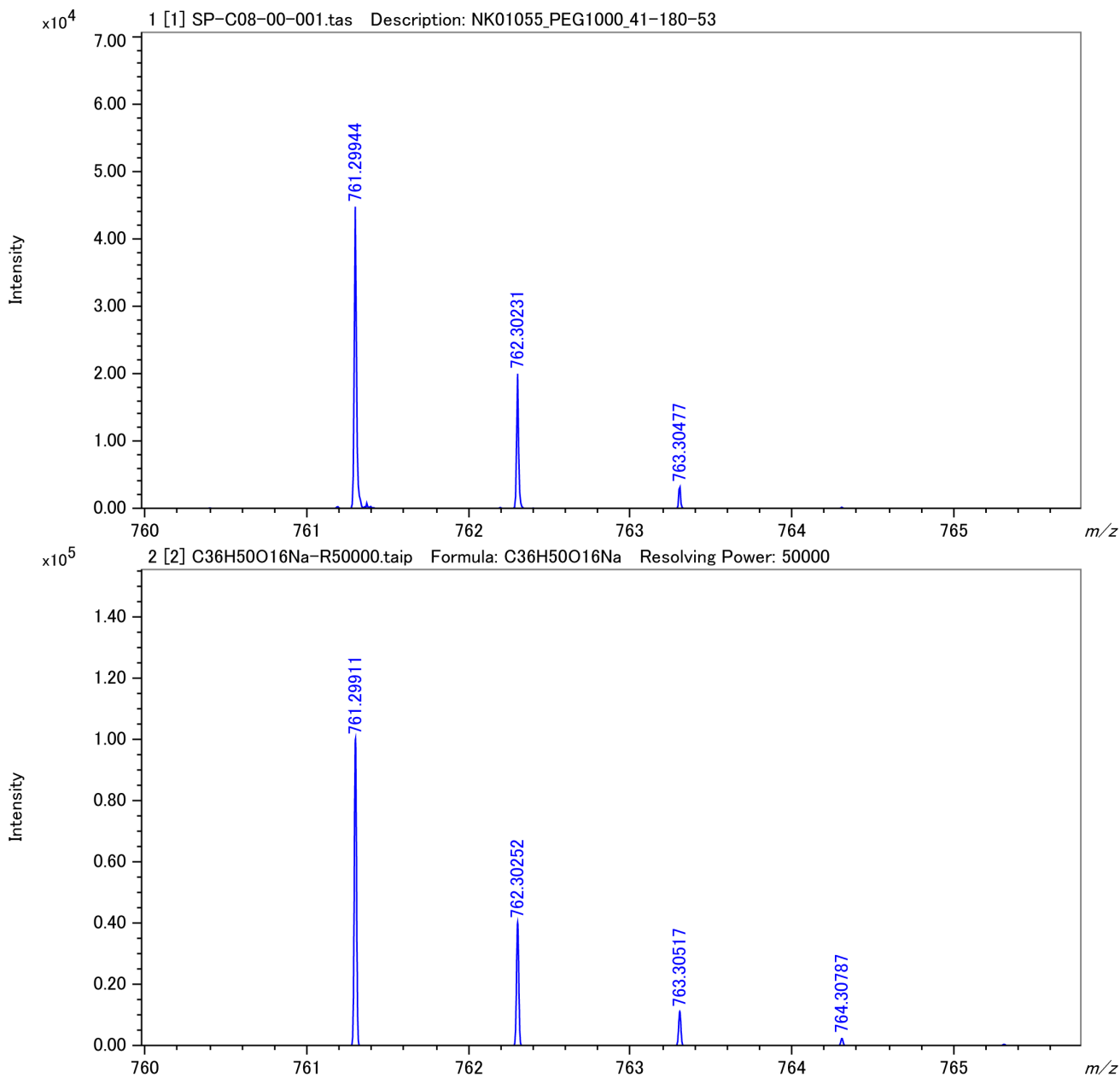


Figure S14. Mass spectrum of the cryptand **6a**: experimental (top) and calculated (bottom) isotopic patterns.

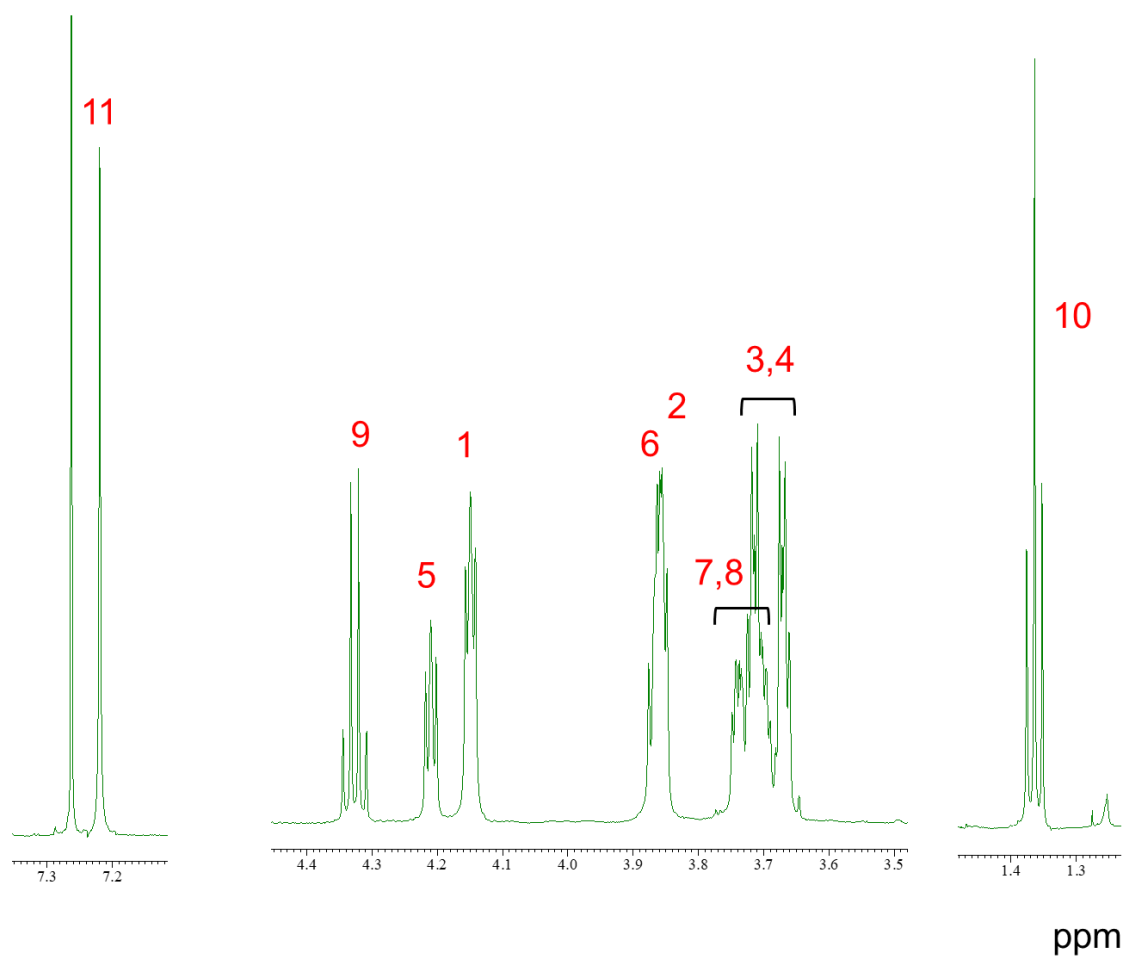
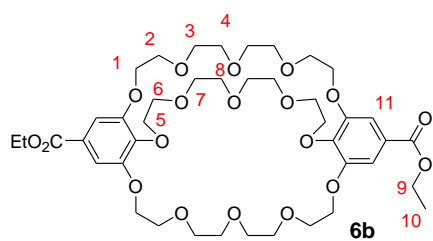


Figure S15. ¹H NMR spectrum (600 MHz, CDCl₃) of the cryptand **6b**.

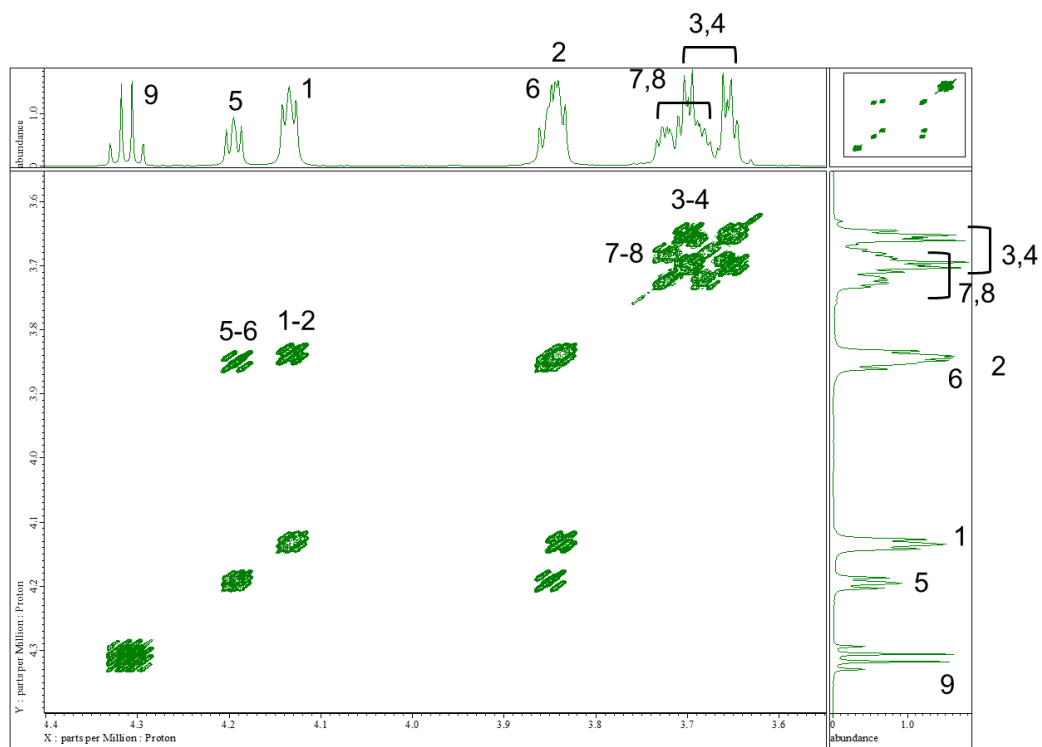
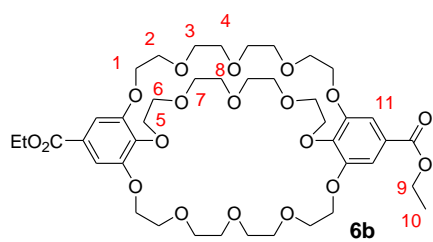


Figure S16. COSY spectrum (600 MHz, CDCl₃) of the linear cryptand **6b**.

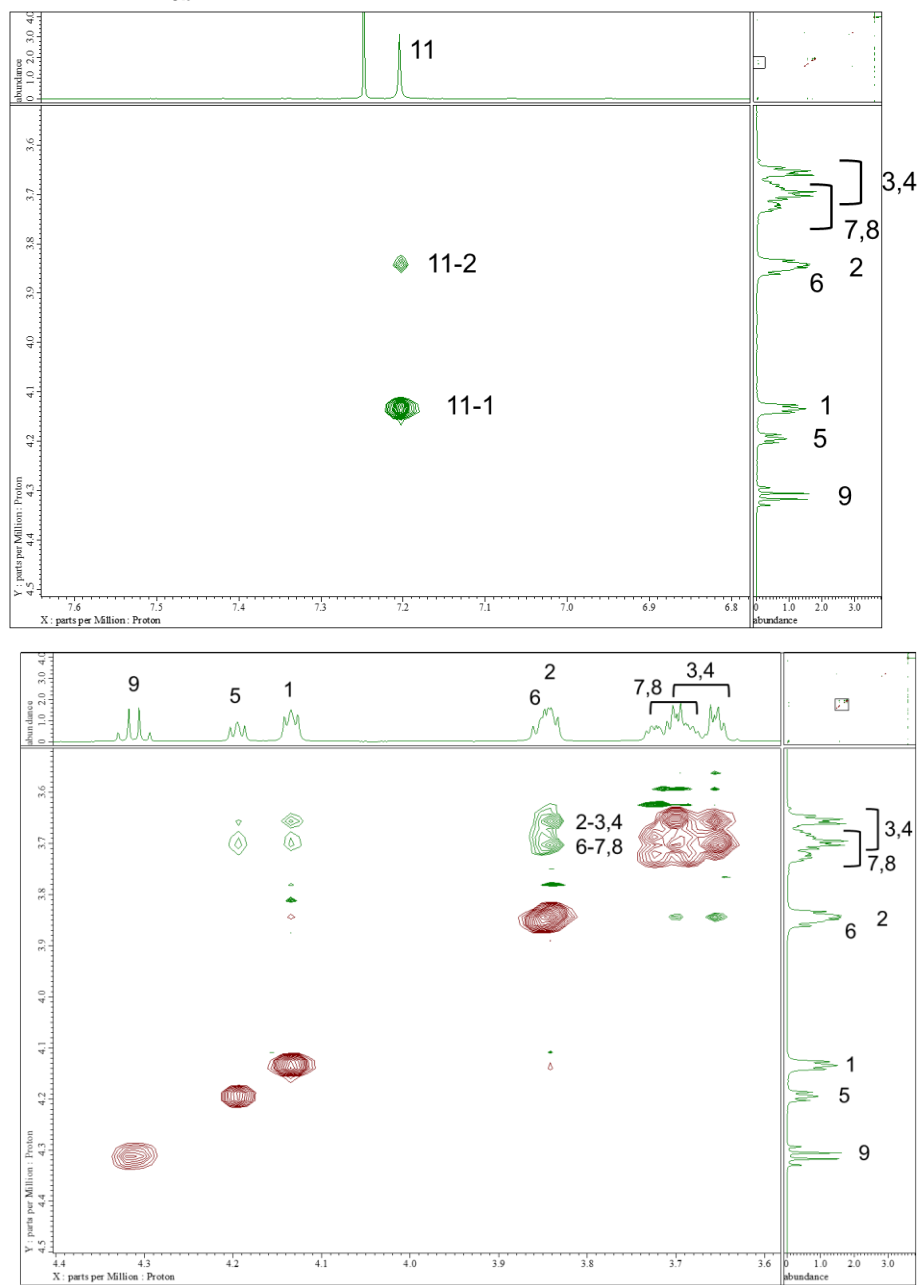
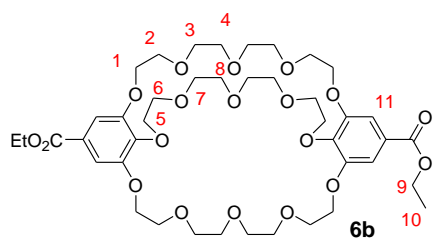


Figure S17. ROESY spectrum (600 MHz, CDCl_3) of the linear cryptand **6b**.

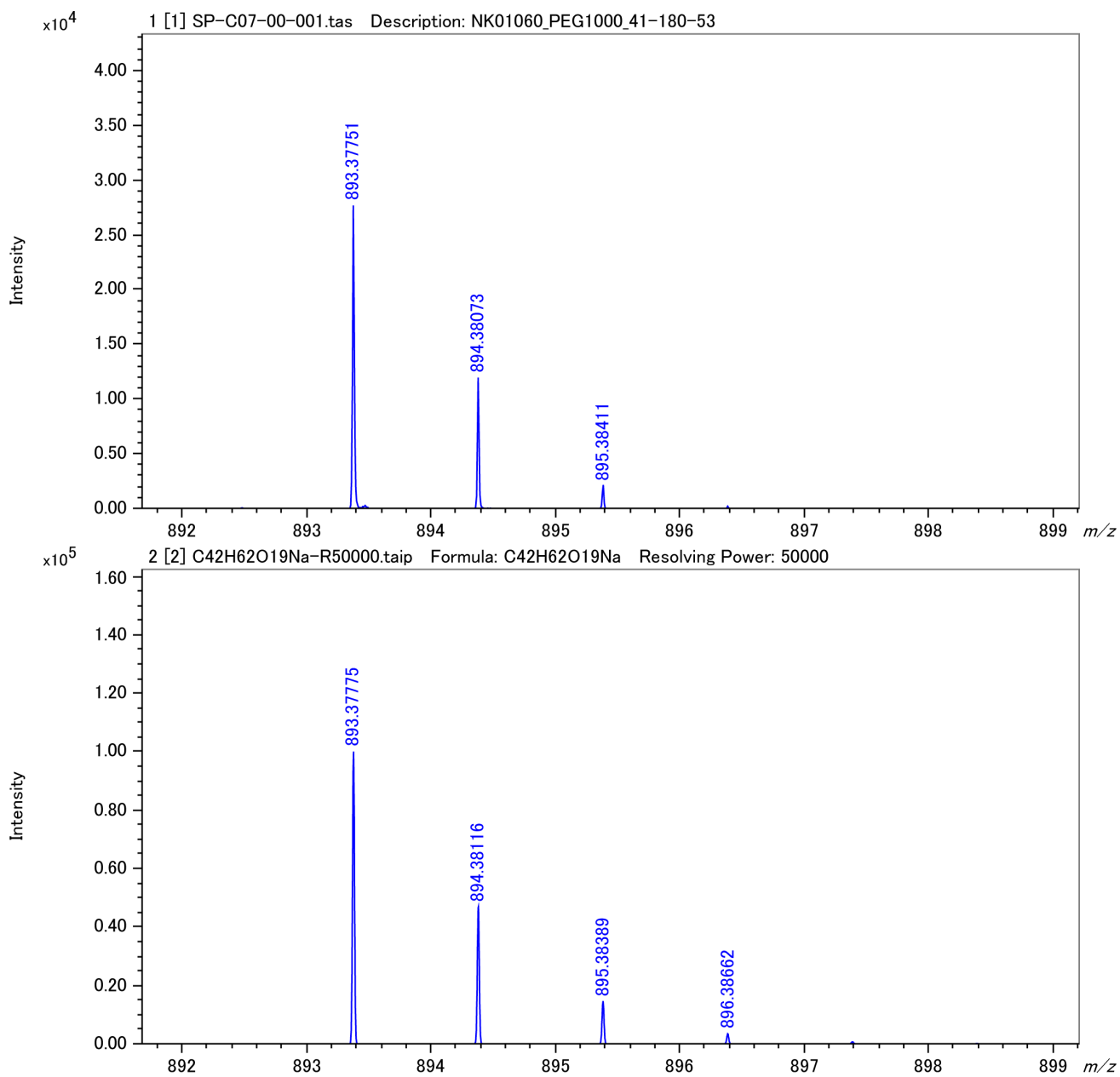


Figure S18. Mass spectrum of the cryptand **6b**: experimental (top) and calculated (bottom) isotopic patterns.

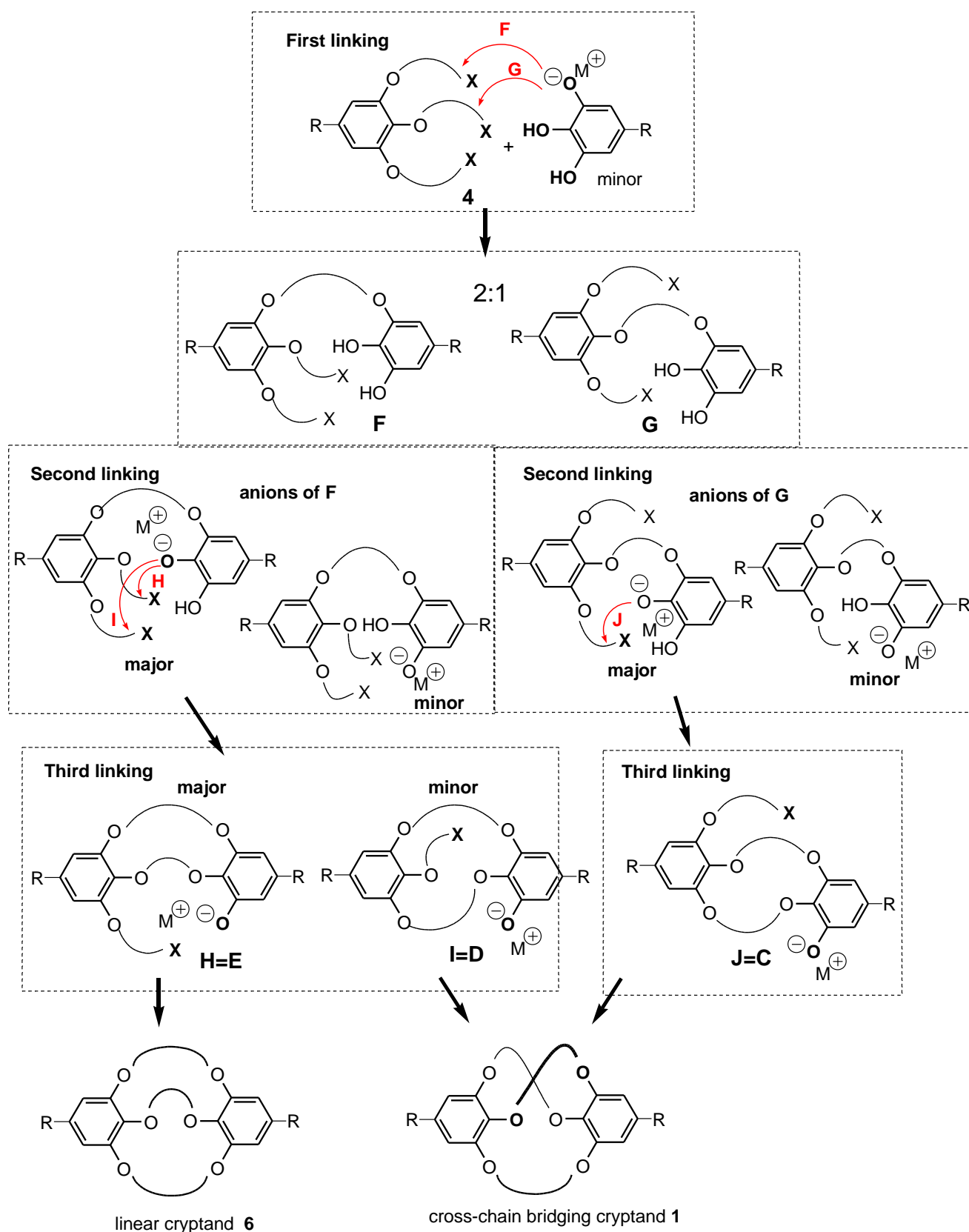
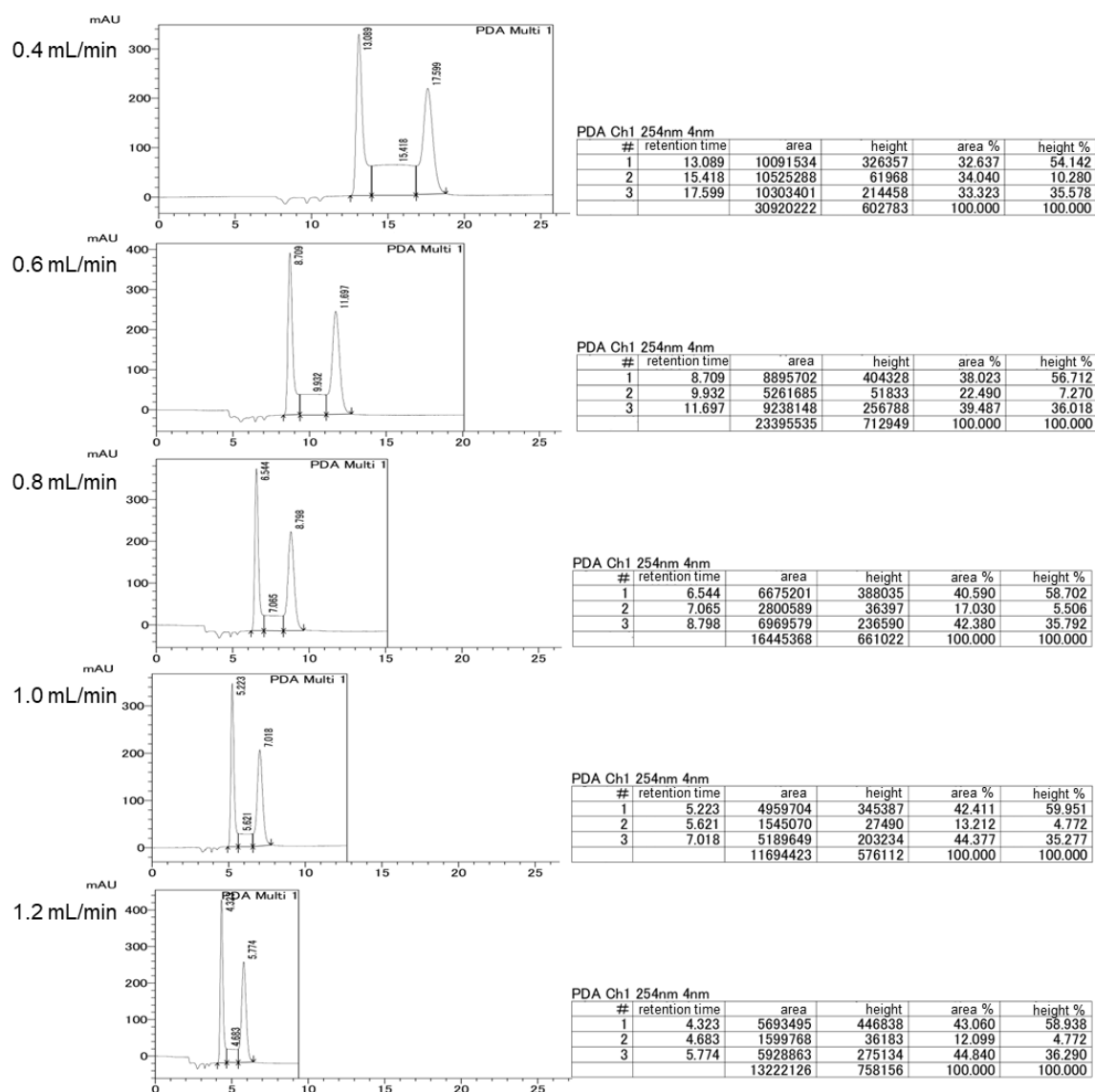


Figure S19. Detailed minor processes of the triple linking reaction between the minor phenoxide ion of ethyl gallate in the first step and the tosylate 4.

Minor process

In the first linking step, the minor phenoxide anion might statistically attack to tosyloxy alkyl groups at 3- and 4-positions in **4** to afford a 2:1 mixture of intermediates **F** and **G**. 4-Hydroxy group of the intermediates **F** and **G** dominantly deprotonated because of electron-withdrawing effect of ethoxy carbonyl group. The second intramolecular linking of the intermediate **F** might give the crown ethers **H** (**E** in the Figure 4) and **I** (**D** in the Figure 4). In this step, the major phenoxide anion of **F** might predominantly attack to tosyloxy alkyl group at 4-position. Because alkyl chain of 4-position should inhibit the cross-linkage giving intermediate **I** (**D** in the Figure 4). Finally, crown ethers **H** (**E** in the Figure 4) and **I** (**D** in the Figure 4) are converted to the linear and cross-chain bridging cryptands **6** and **1**, respectively. In contrast, cross-chain bridging **1** should be mainly obtained by the second and third intramolecular linking of the intermediate **G** via intermediate **J** (**C** in the Figure 4). Therefore, this minor process gave linear cryptand **6** as a major product, totally, triple linking reaction may furnish a less than 2:1 mixture of the cross-chain bridging and linear cryptands **1** and **6**.

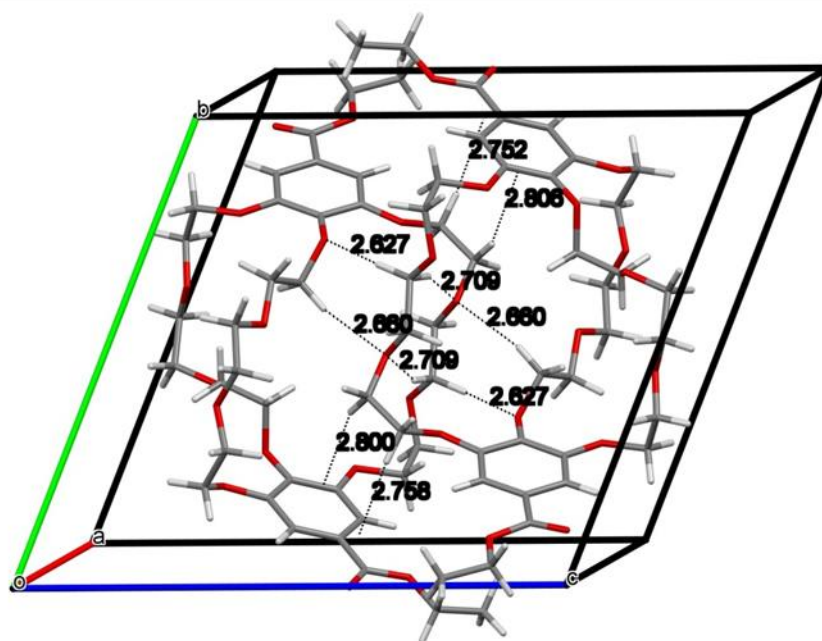


The relationship between flow rate and each area of each enantiomer and the middle of the enantiomers of **1c**.

Flow rate (mL/min)	Average of retention time (s)	Area of left peak (%)	Area of center (%)	Area of right peak (%)	Non-racemate (%)
0.4	922	32.6	34.0	33.3	66.0
0.6	607	38.0	22.5	39.5	77.5
0.8	448	40.6	17.0	42.4	83.0
1.0	357	42.4	13.2	44.4	86.8
1.2	296	43.1	12.1	44.8	87.9

Figure S20. Flow rate-dependent chiral HPLC analysis of the cryptand **1c** using CHIRALPAK IG-3 (4.6 mmI.D. × 25 cmL) as a stationary phase. Flow rate: 0.4–1.2 mL/min, eluent: AcOEt/Et₃N (100:0.5), detection: 254 nm, temp.: rt.

(a)



(b)

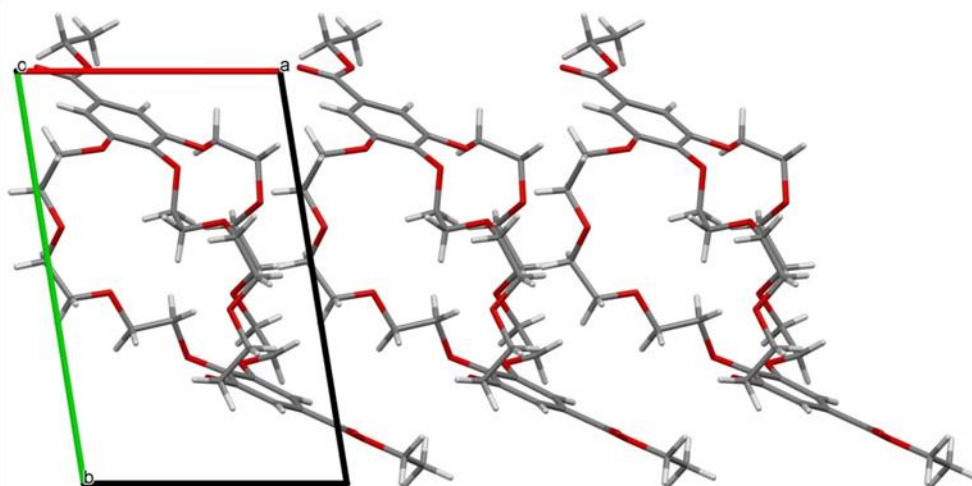


Figure S21. X-ray crystal structure of the racemic cryptand **1a**: (a) a crystal lattice, and (b) *c*-axis projection. Gray: carbon; red: oxygen.

Table S1. Crystal data of the racemic cryptand **1a**.

Parameter	(±)- 1a
Formula	C ₃₆ H ₅₀ O ₁₆
Formula weight	738.78
Temperature	−100 °C
Crystal color, habit	Colorless, platelet
Crystal size / mm	0.600 × 0.200 × 0.080
Crystal system	Triclinic
Space group	<i>P</i> -1 (#2)
<i>a</i> / Å	8.5825(5)
<i>b</i> / Å	14.5897(9)
<i>c</i> / Å	16.1070(10)
α / deg	68.243(5)
β / deg	83.475(6)
γ / deg	79.053(6)
<i>V</i> / Å ³	1837.0(2)
<i>Z</i>	2
<i>D</i> _{calcd} / g cm ^{−3}	1.336
<i>F</i> (000)	788.00
2 θ _{max} / deg	54.9
No. of reflns meads	36508
No. of obsd reflns	8379
No. of variables	488
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)] ^a	0.0550
<i>wR</i> ₂ (all reflns) ^b	0.1153
Goodness of fit	1.022

^a*R*₁ = $\Sigma (|F_o| - |F_c|) / \Sigma (|F_o|)$. ^b*wR*₂ = $\{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma w(F_o^2)^2 \}^{1/2}$.

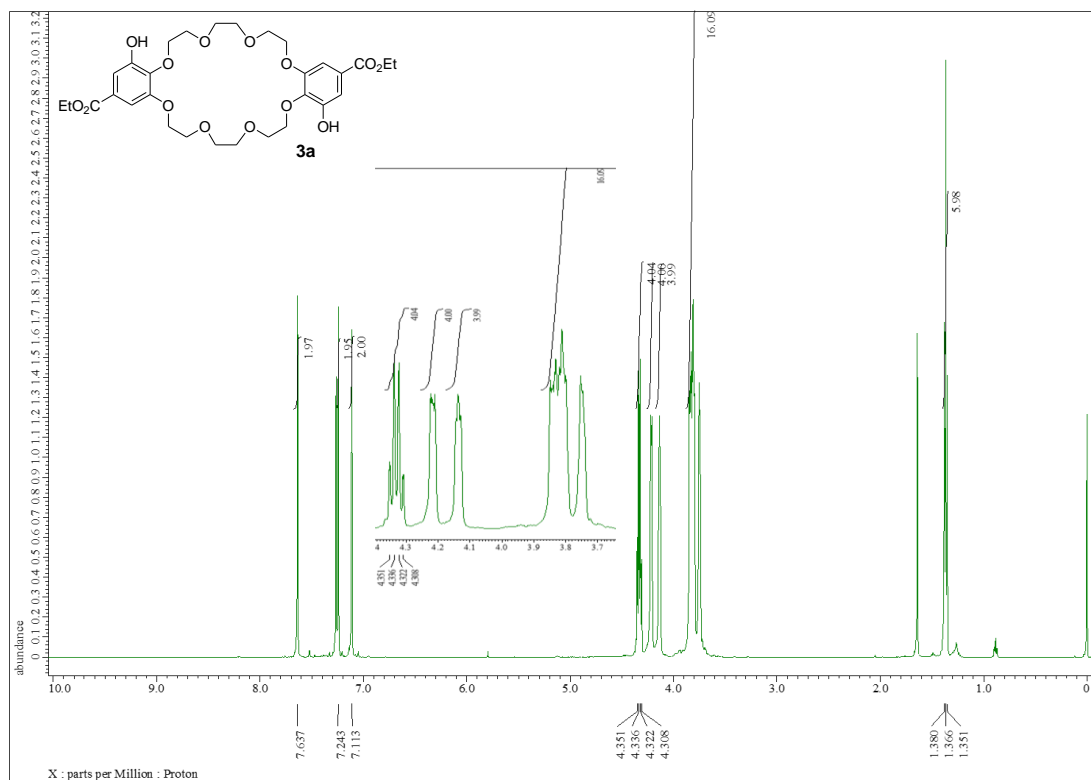


Figure. ¹H NMR (500 MHz, CDCl₃) spectrum of the crown ether **3a**.

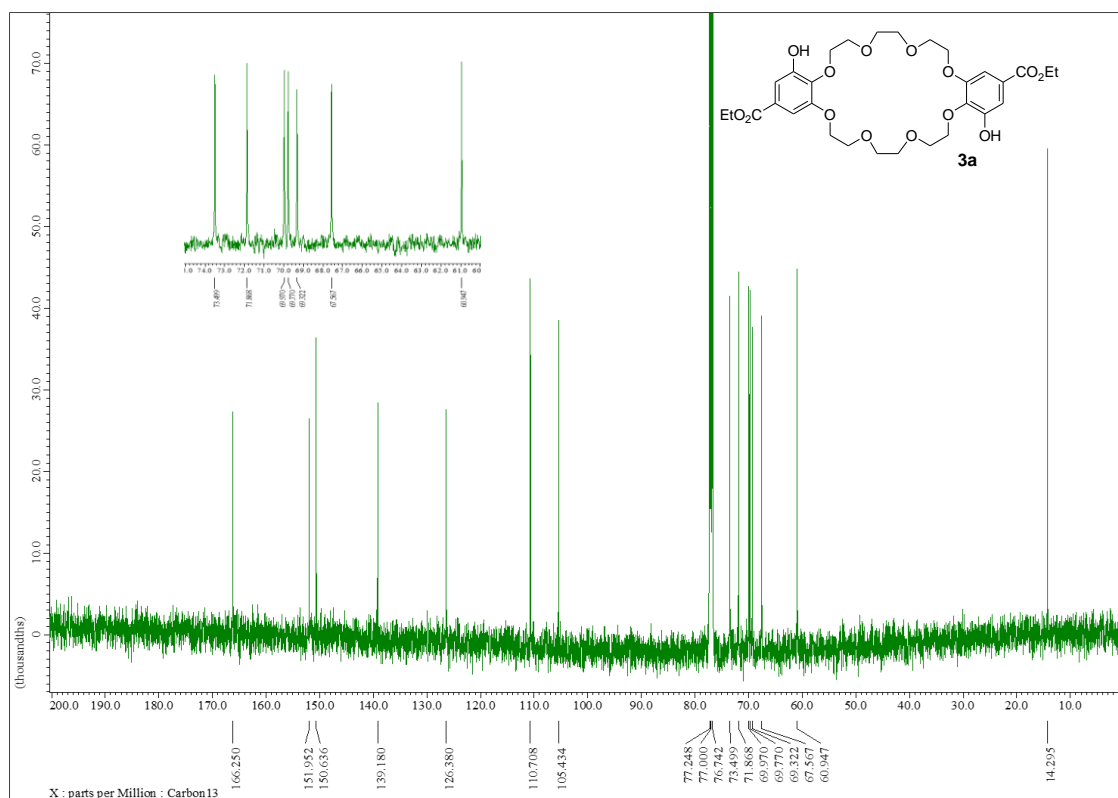


Figure. ¹³C NMR (125 MHz, CDCl₃) spectrum of the crown ether **3a**.

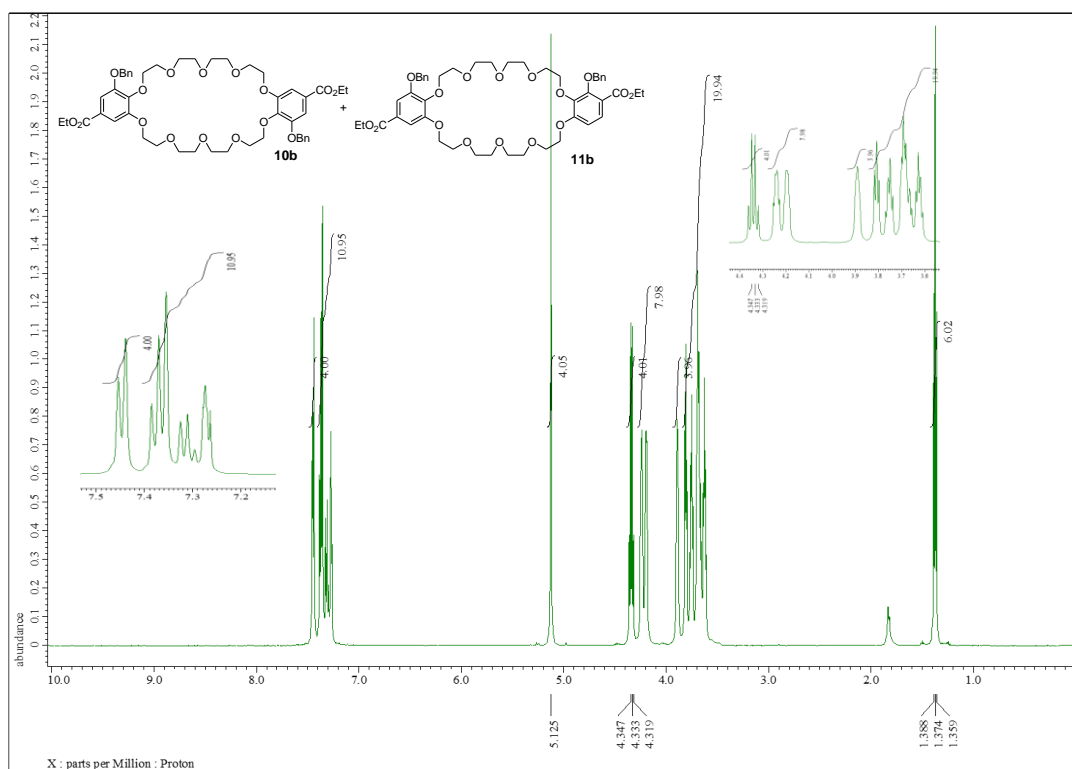


Figure. ¹H NMR (500 MHz, CDCl₃) spectrum of a mixture of the crown ethers **10b** and **11b**.

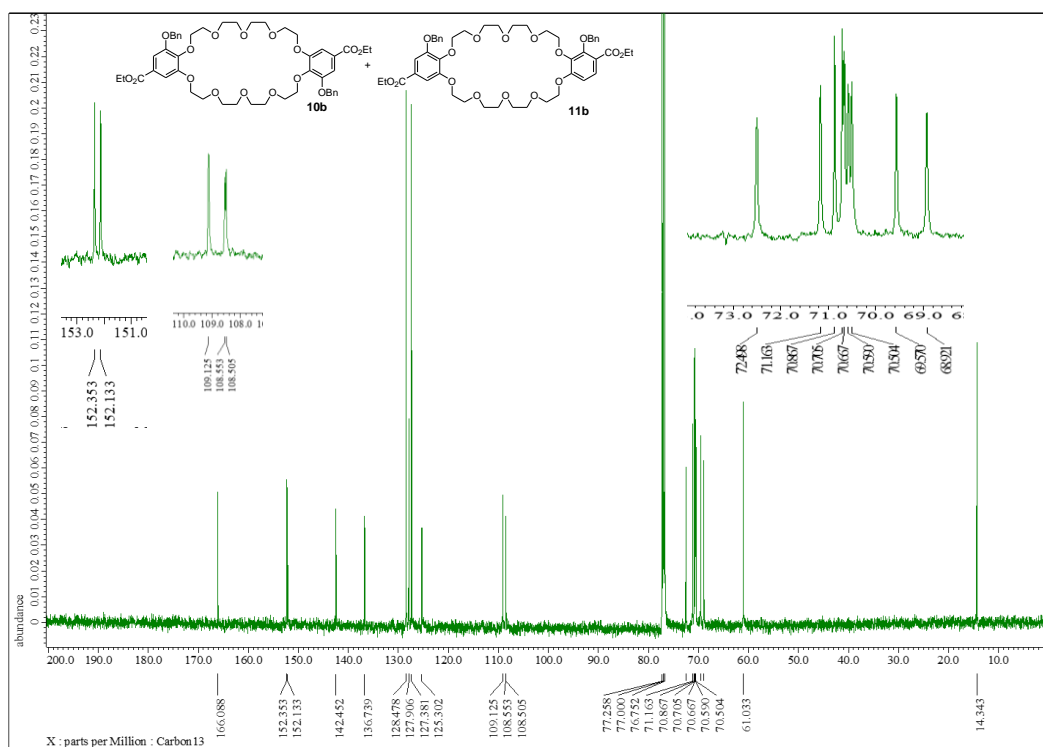


Figure. ¹³C NMR (125 MHz, CDCl₃) spectrum of a mixture of the crown ethers **10b** and **11b**.

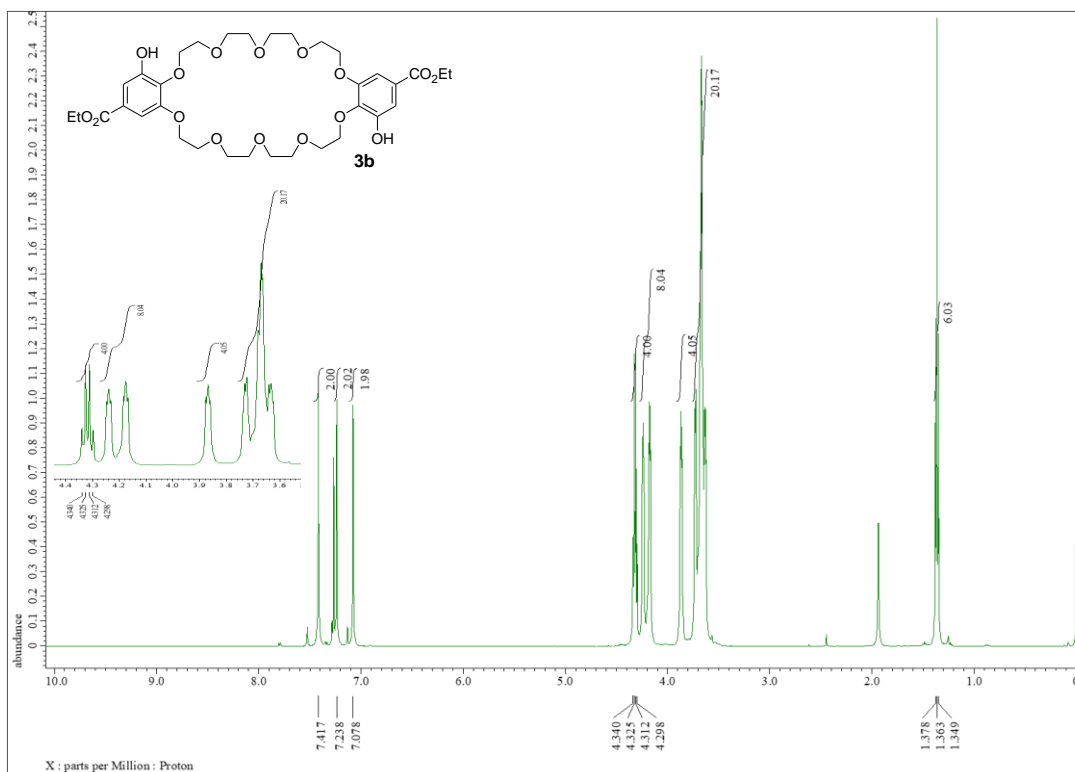


Figure. ¹H NMR (500 MHz, CDCl₃) spectrum of the crown ether **3b**.

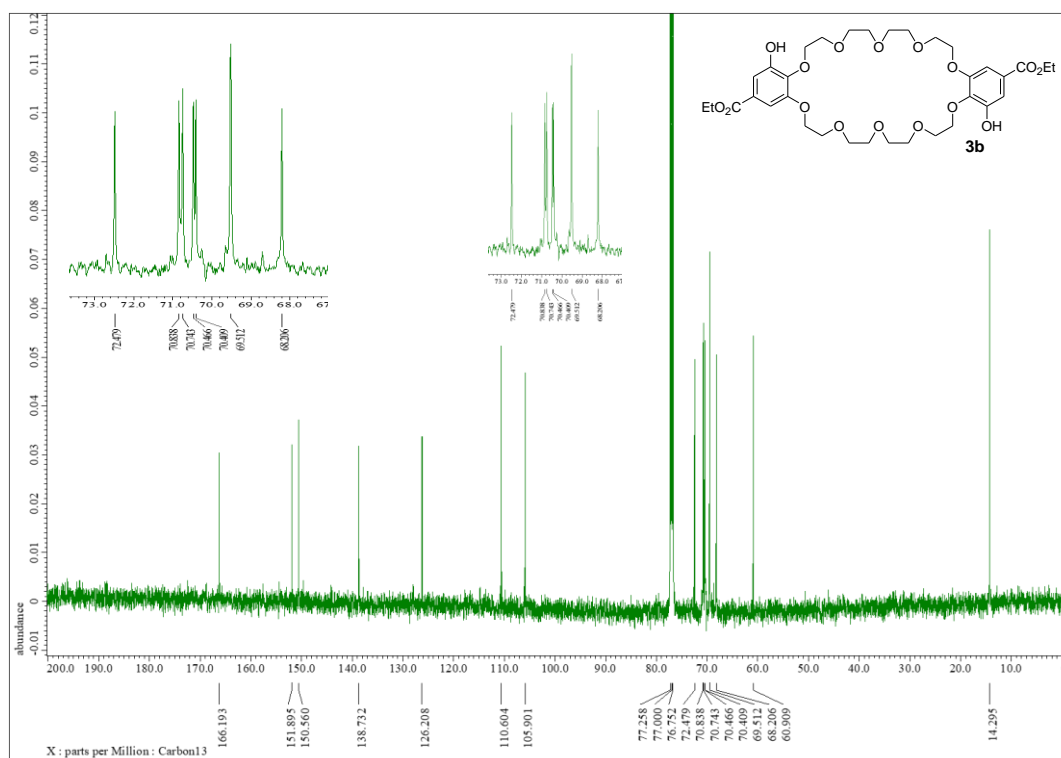


Figure. ¹³C NMR (125 MHz, CDCl₃) spectrum of the crown ether **3b**.

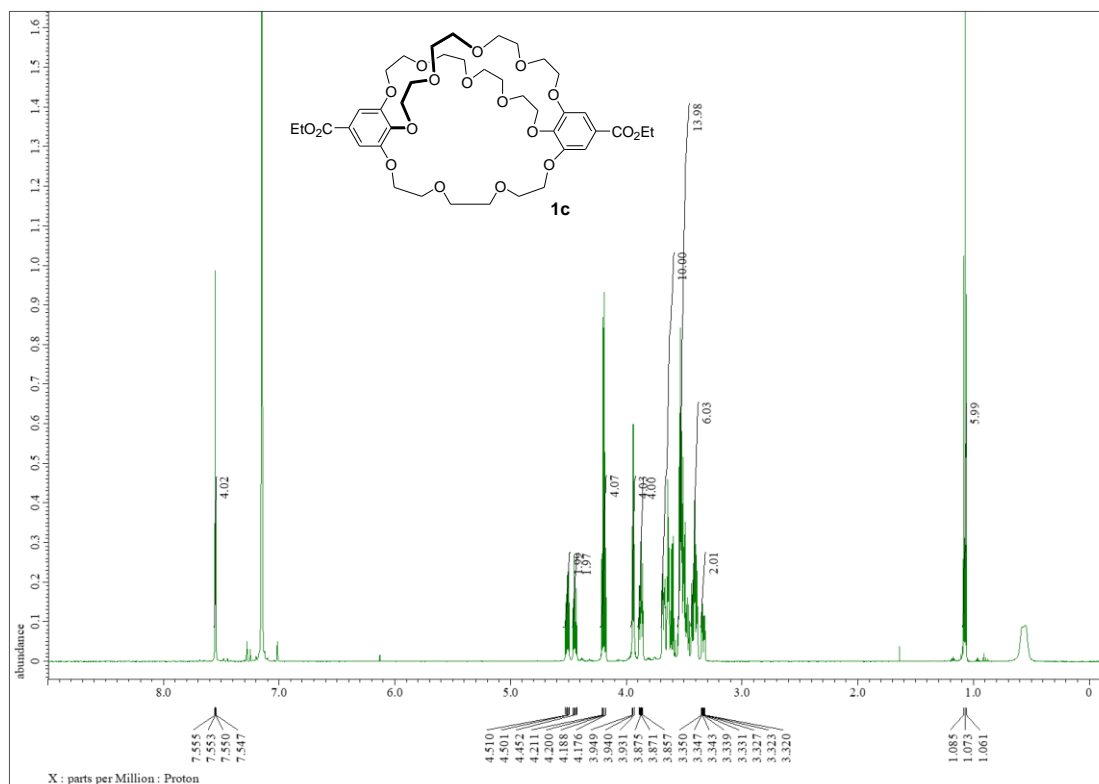


Figure. ¹H NMR (600 MHz, C₆D₆) spectrum of the cryptand **1c**.

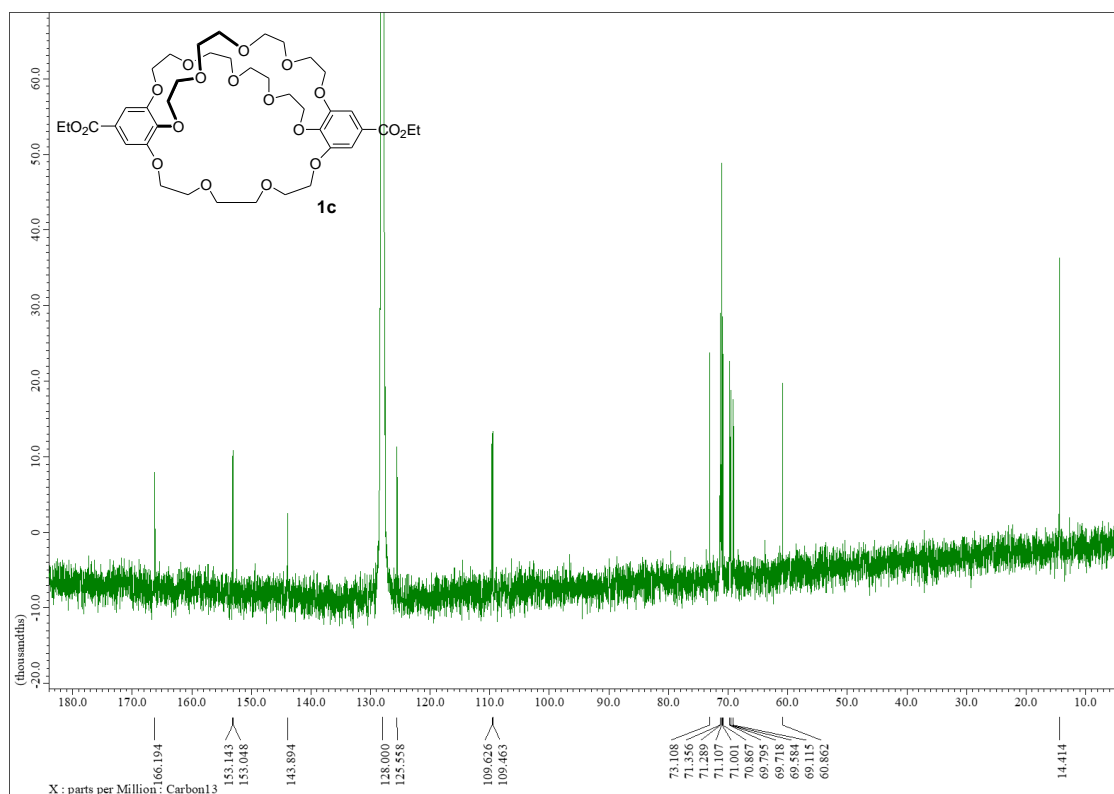


Figure. ¹³C NMR (150 MHz, C₆D₆) spectrum of the cryptand **1c**.

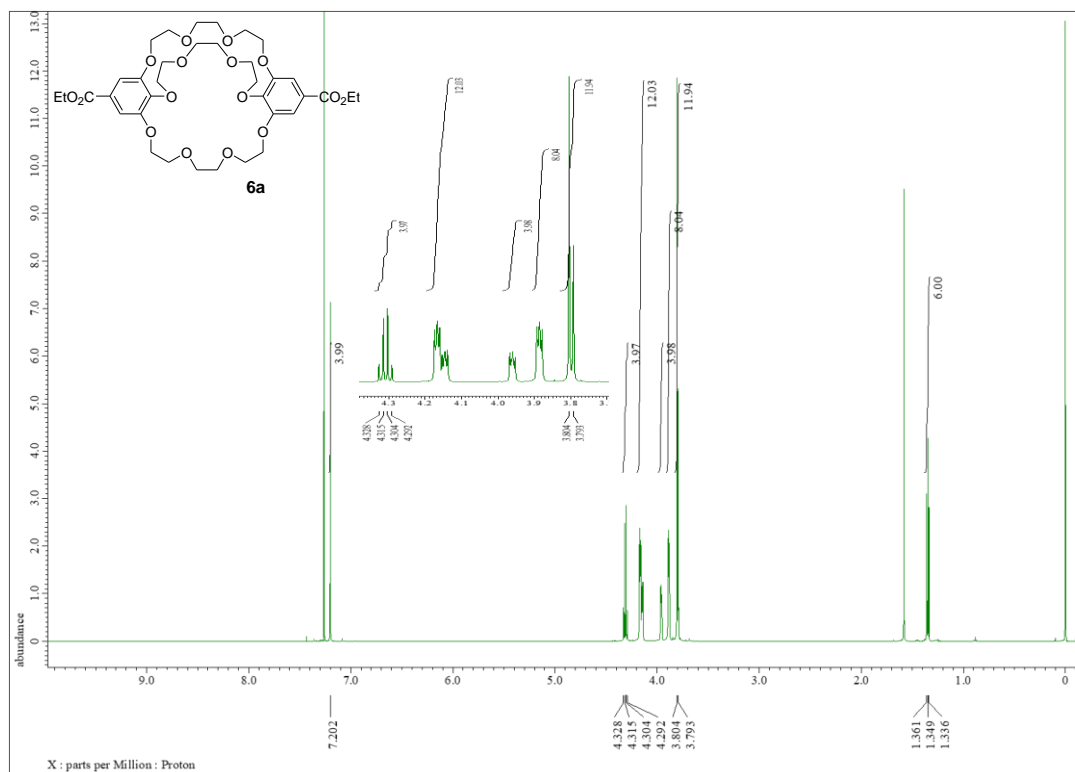


Figure. ^1H NMR (600 MHz, CDCl_3) spectrum of the cryptand **6a**.

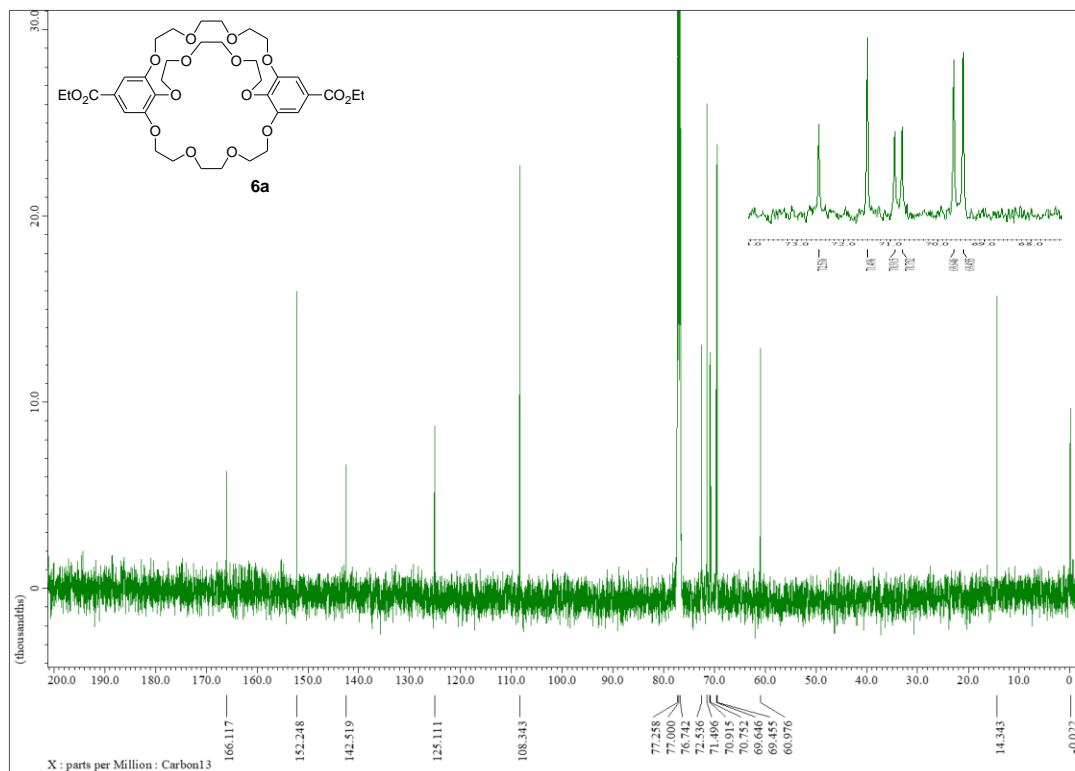


Figure. ^{13}C NMR (150 MHz, CDCl_3) spectrum of the cryptand **6a**.

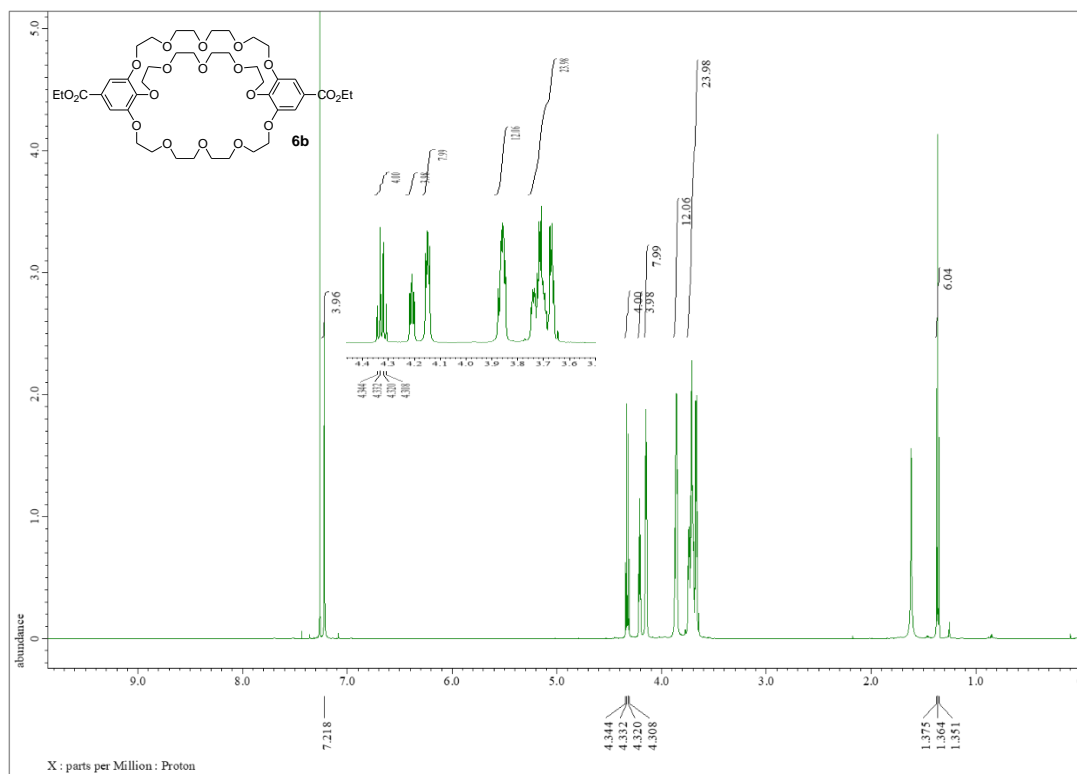


Figure. ^1H NMR (600 MHz, CDCl_3) spectrum of the cryptand **6b**.

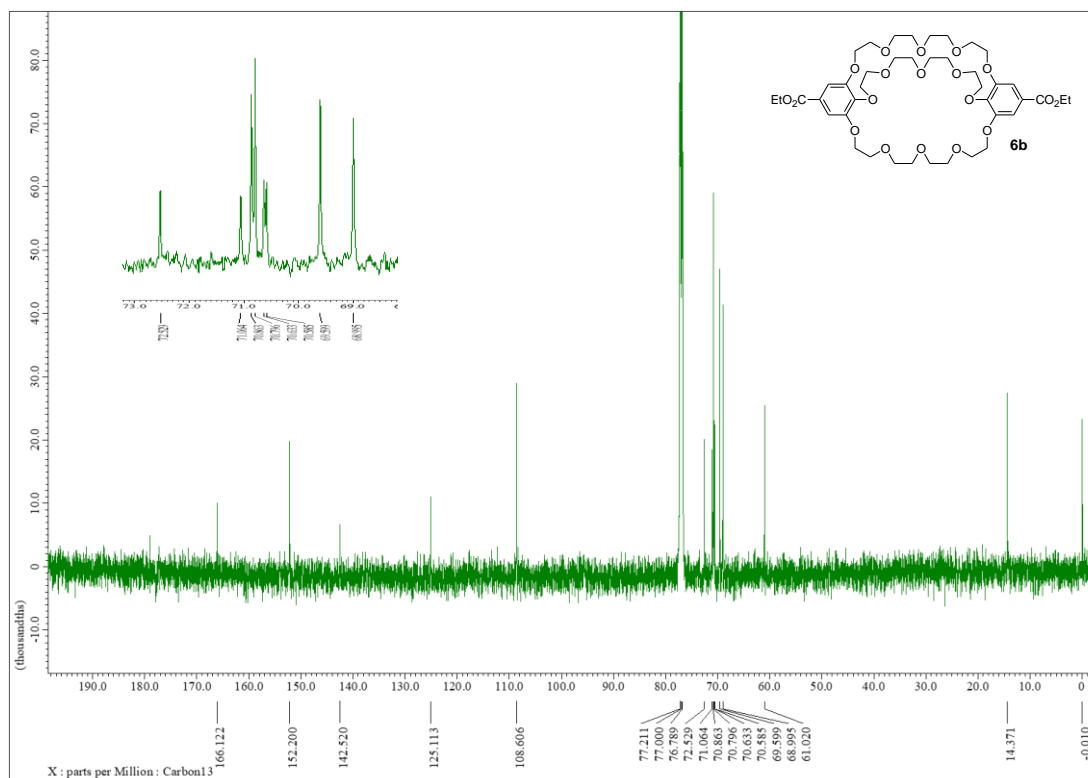


Figure. ^{13}C NMR (150 MHz, CDCl_3) spectrum of the cryptand **6b**.

