Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Vinyl sulfonyl chemistry-driven unidirectional transport of a macrocycle through a [2]rotaxane

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- Electronic Supporting Information -

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1. Experimental Section

1.1. General Methods

Unless otherwise noted, commercially available reagents, solvents and anhydrous solvents were used as purchased without further purification. Freshly distilled THF was distilled over Na/benzophenone. Compounds **4**,[S1] **S3**[S1] and **S6**[S2] were prepared according to literature procedures.

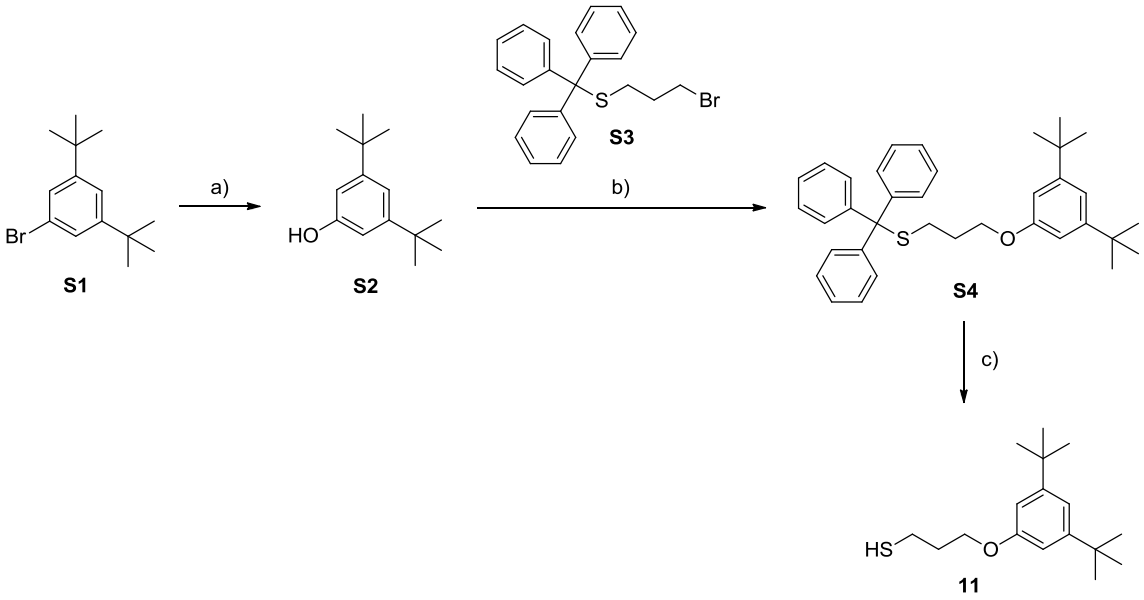
TLC was performed on Merck Silica gel 60 F_{254} aluminum sheets. The TLC plates were stained with potassium permanganate (1% w/v in water), cerium molybdate stain (Hanessian's stain) or ninhydrin (0.3% w/v in ethanol) or observed under UV light when applicable. Flash column chromatography was performed with Silica Gel 60 (VWR, 40-63 μm). Gel permeation chromatography was performed with Biobeads® SX−1 resin beads.

^{1}H and ^{13}C NMR spectra were recorded at room temperature on a Varian Direct Drive (400 MHz or 500 MHz), Bruker Avance III HD NanoBay (400 MHz) or Bruker Avance Neo (400 MHz, 500 MHz or 600 MHz) spectrometers at a constant temperature of 298 K. Chemical shifts are given in ppm and referenced to the signal of the residual protiated solvent (^{1}H: δ=7.26 for $CDCl_3$) or the ^{13}C signal of the solvents (^{13}C: δ=77.16 for $CDCl_3$) or to the signal of the residual TMS (^{1}H: δ=0.00). Coupling constant (J) values are given in Hz. Abbreviations indicating multiplicity were used as follow: m = multiplet, p = quintet, q = quartet, t = triplet, d = doublet, dd = doublet of doublets, s = singlet, br = broad. Signals were assigned by means of 2D NMR spectroscopy (COSY, HSQC, HMBC).

Electrospray (ESI) HRMS spectra were recorded on a Waters Xevo G2-XS QTOF or on a Bruker Maxis II spectrometer. Melting points were measured with a Stuart® melting point apparatus SMP3 and are uncorrected. IR spectra were recorded with a Perkin-Elmer Spectrum Two FTIR ATR spectrometer.

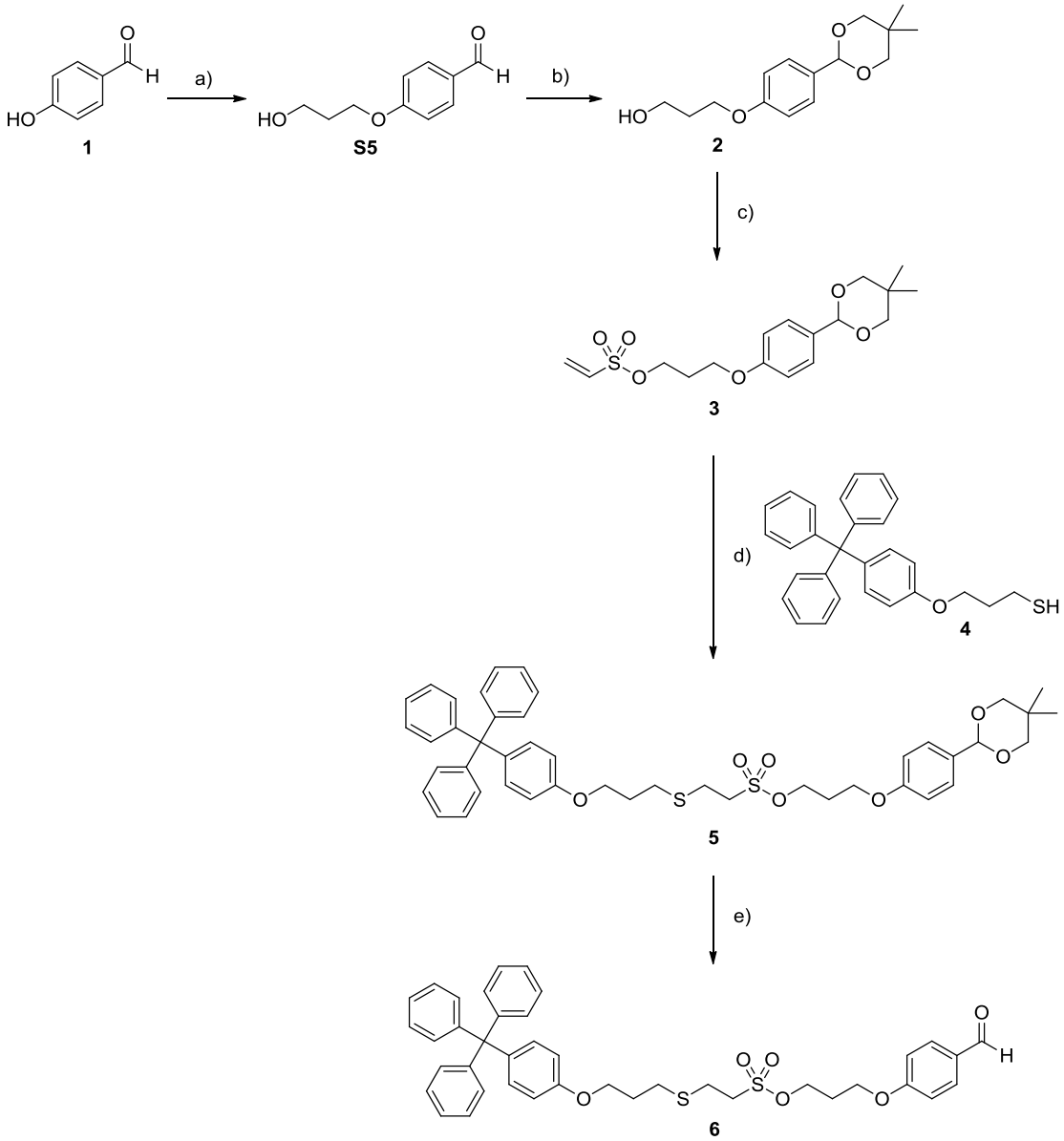
1.2 Synthesis Overview

1.2.1 Synthesis of stopper 11

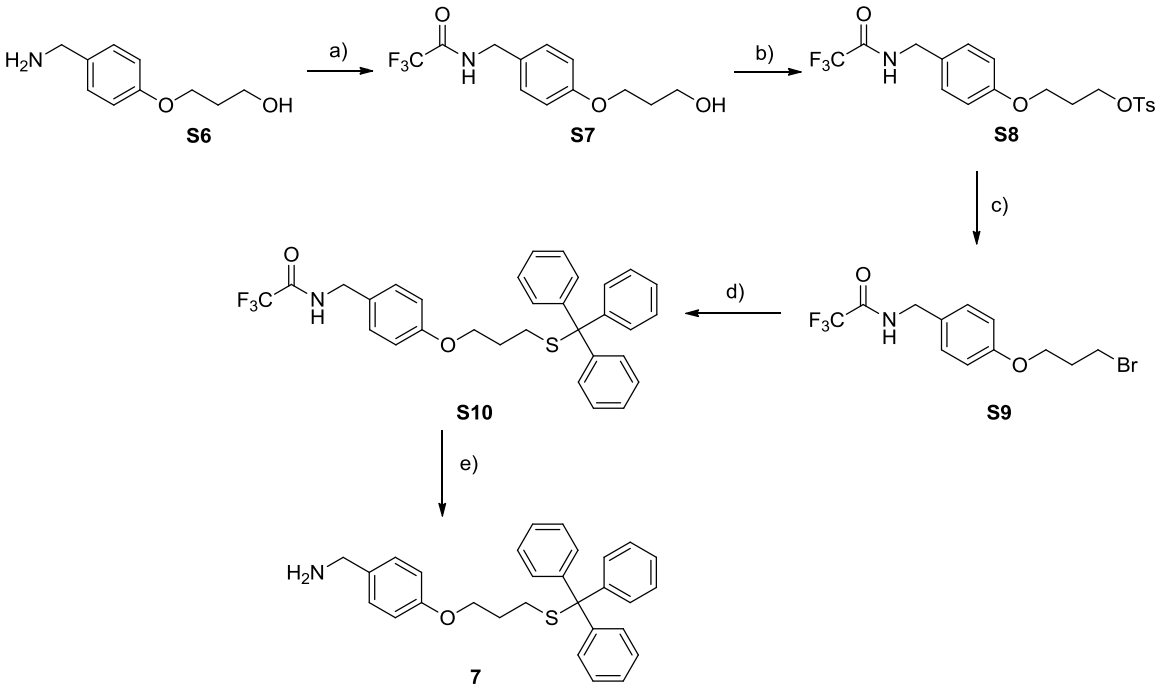


Scheme S1: Synthesis of stopper **11**: Reagents and conditions: a) 1. ^{n}BuLi (2.5 M in hexane), THF, –78 ºC, 20 min; 2. $B(OMe)_3$, THF, –78 ºC, 20 min, then 0-4 ºC, 2 h; 3. H_2O_2 (33% in H_2O), 0-4 ºC, 30 min, then r.t., 1 h, 61%. b) K_2CO_3, CH_3CN, 75 ºC, 22 h, 66 %. c) CF_3CO_2H, Et_3SiH, CH_2Cl_2, r.t., 4 h, 79%.

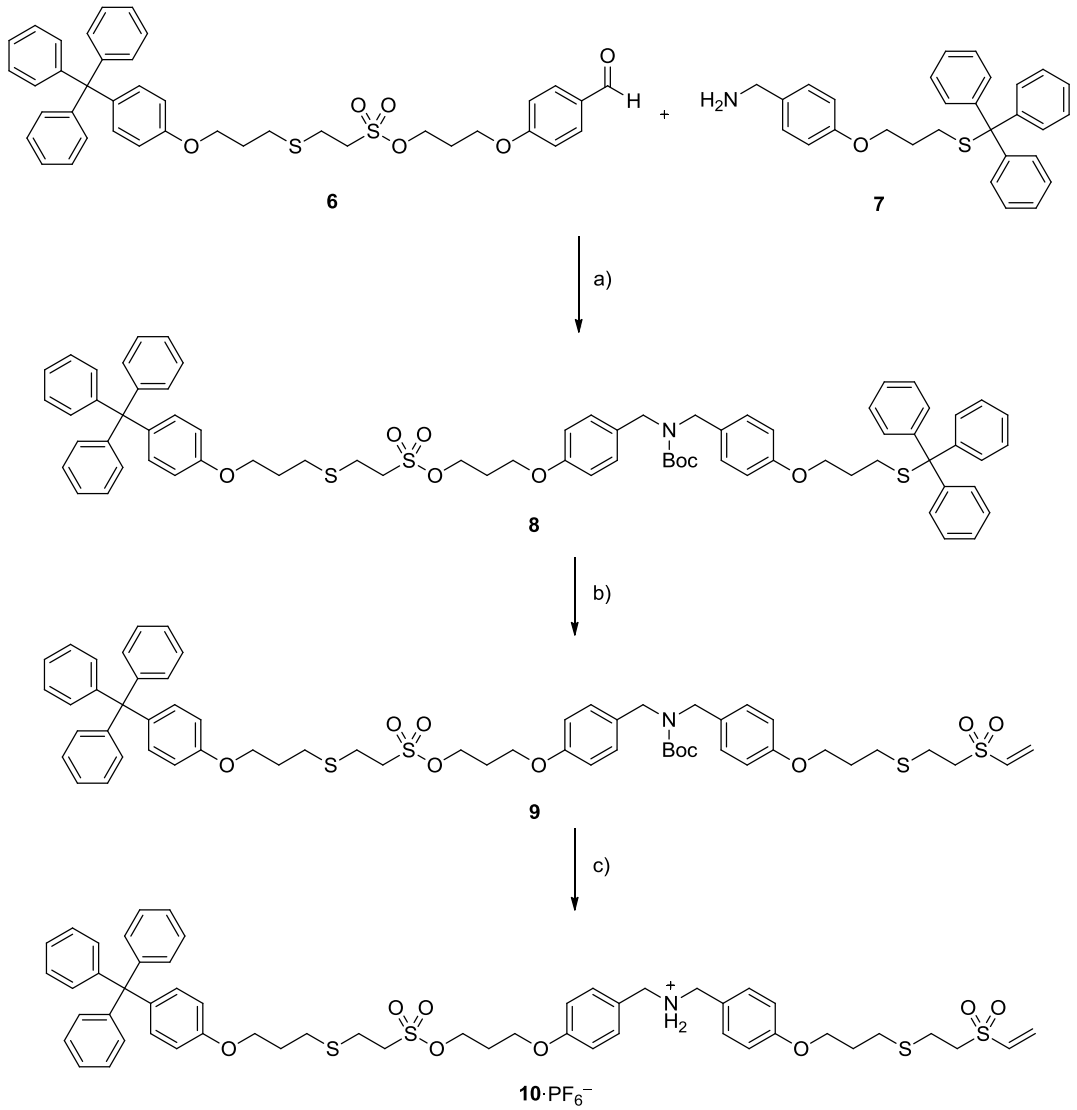
1.2.2 Synthesis of axle $10 \cdot PF_6^-$



Scheme S2: Synthesis of compound **6**: Reagents and conditions: a) 3-Bromo-1-propanol, K_2CO_3, CH_3CN, 75 ºC, 24 h, 85%. b) 2,2-Dimethyl-1,3-propanediol, DL-10-camphorsulfonic acid, molecular sieves (3Å), toluene, 100 ºC, 18 h, 73%. c) 2-Chloroethanesulfonyl chloride, Et_3N, CH_2Cl_2, 0-4 ºC, 1 h, 80%. d) Et_3N, PPh_3, $CH_2Cl_2/^iPrOH$ (8:1), r.t., 24 h, quant. e) CF_3CO_2H, H_2O, CH_2Cl_2, r.t., 5 h, 95%.

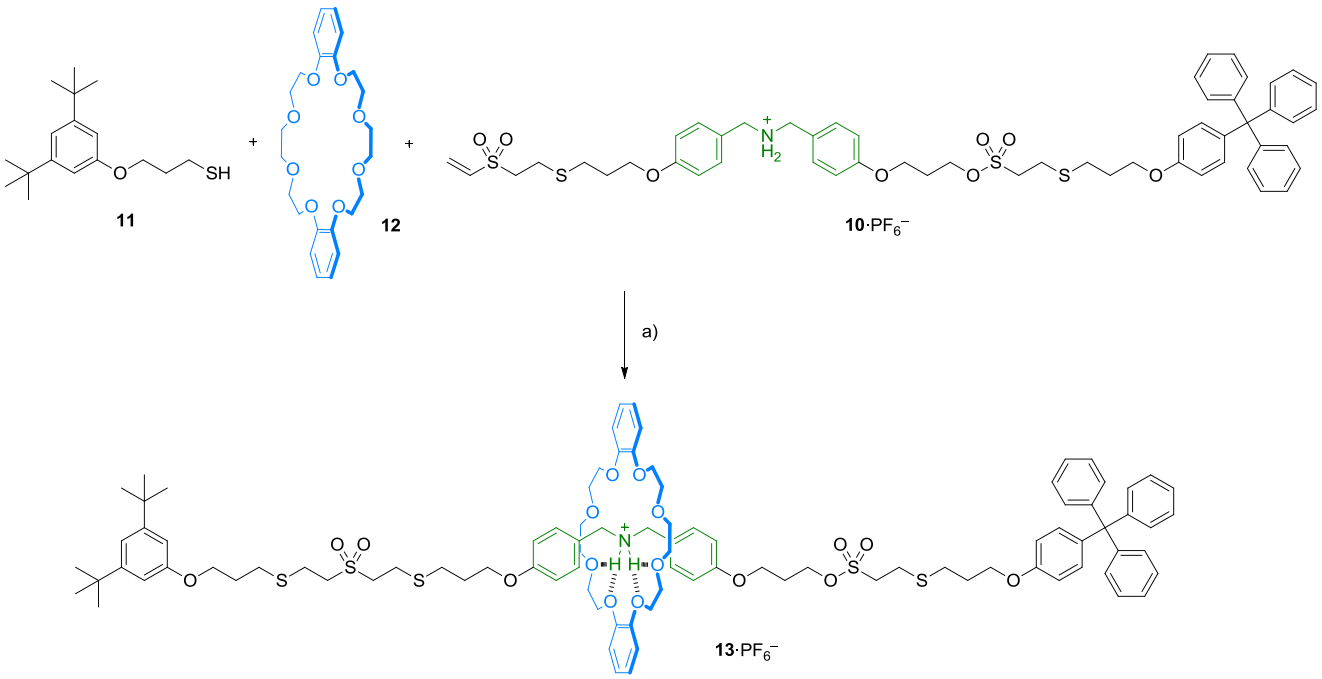


Scheme S3: Synthesis of compound **7**: Reagents and conditions: a) Ethyl trifluoroacetate, Et_3N, MeOH, r.t., 2 h, 89%. b) TsCl, Et_3N, $DMAP_{(cat)}$, CH_2Cl_2, r.t., 18 h, 99%. c) LiBr, acetone, reflux, 18 h, 86%. d) Triphenylmethanethiol, LiHMDS (1 M in THF), THF, 0-4 ºC to r.t., 70 min, 85%. e) NaOH, H_2O, MeOH, r.t., 20 h, 76%.

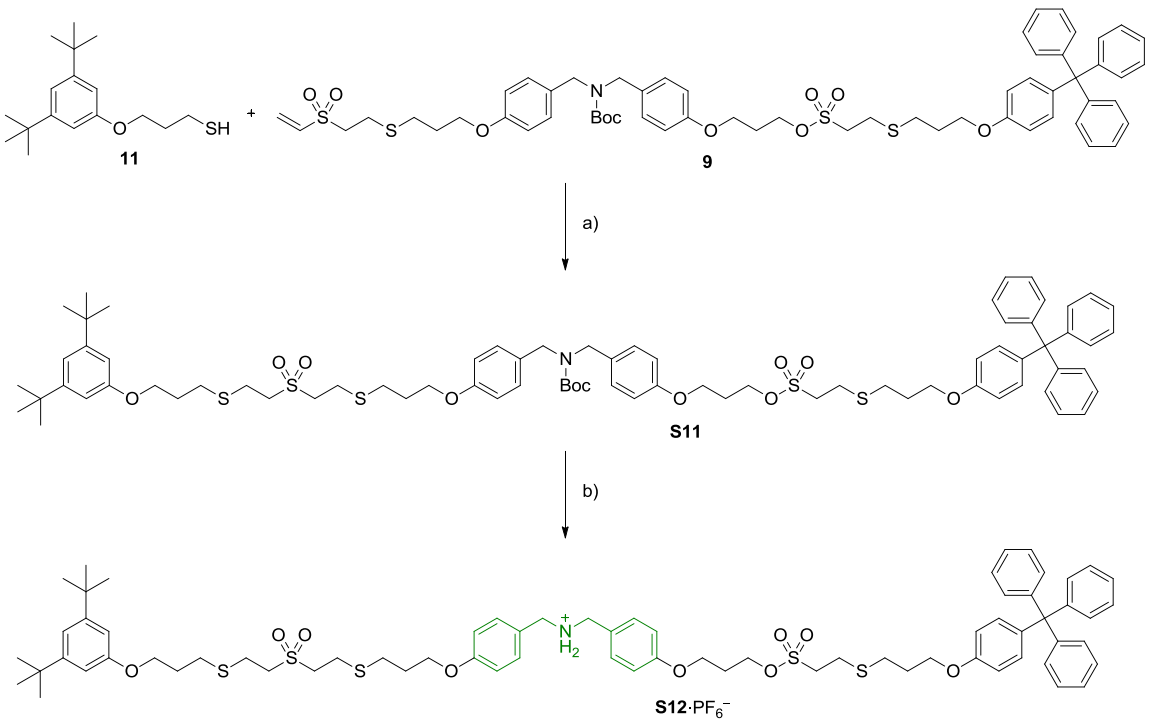


Scheme S4: Synthesis of axle **10**·PF_6^-: Reagents and conditions: a) 1. MeOH/THF (8:5), r.t., 24 h; 2. $NaBH_4$, MeOH/THF (8:5), r.t., 24 h; 3. Boc_2O, Et_3N, CH_2Cl_2, r.t., 24 h, 80%. b) 1. CF_3CO_2H, Et_3SiH, CH_2Cl_2, r.t., 6 h; 2. Boc_2O, Et_3N, CH_2Cl_2, r.t., 5 h; 3. Divinyl sulfone, Et_3N, CH_2Cl_2, r.t., 14 h, 52% (over 3 steps). c) 1. CF_3CO_2H, CH_2Cl_2, r.t., 5 h; 2. HCl (2 M in Et_2O), CH_2Cl_2, r.t., 3 h; 3. KPF_6, CH_2Cl_2/acetone/H_2O (4:5:5), r.t., 18 h, 84% (over 3 steps).

1.2.3 Synthesis of rotaxane 13·PF_6^-

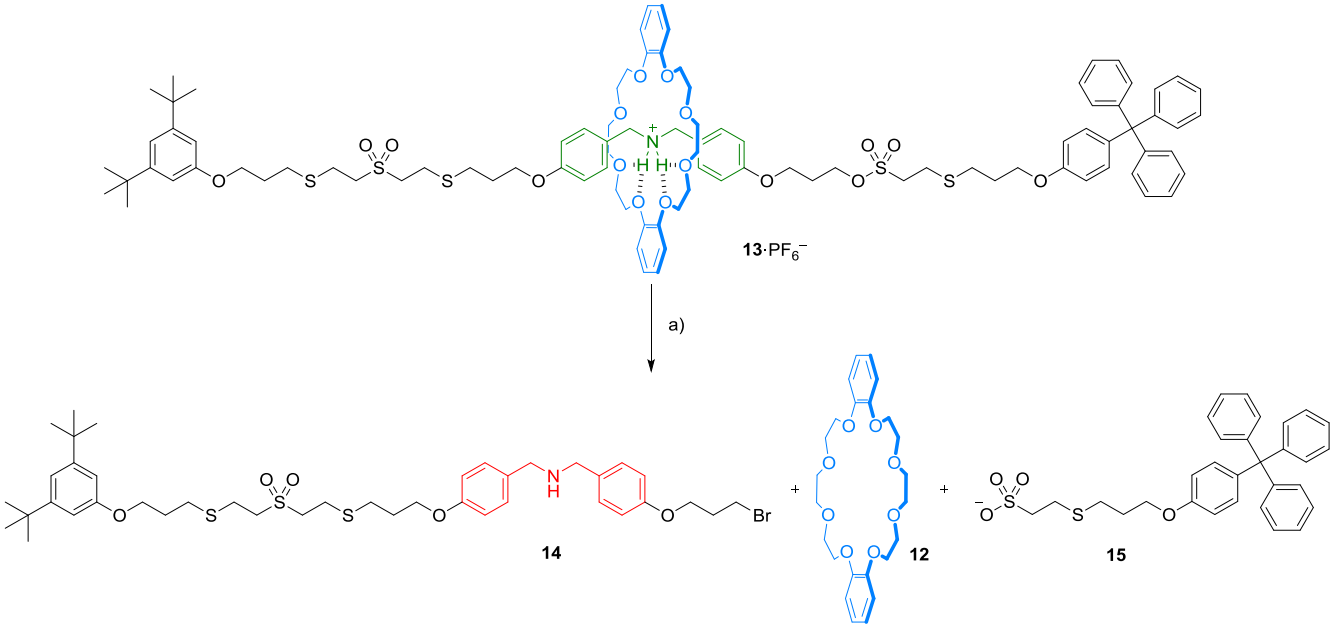


Scheme S5: Synthesis of rotaxane **13**·PF_6^-: Reagents and conditions: $DMAP_{(cat)}$, $CHCl_3$, 0 ºC, 72 h, 66%.

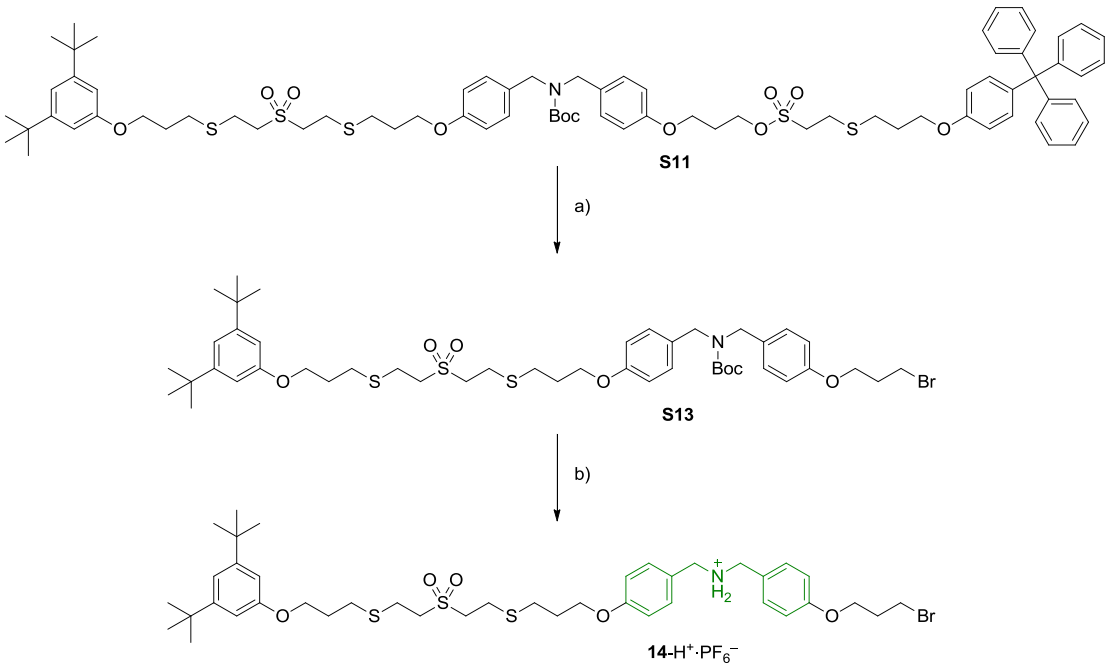


Scheme S6: Synthesis of thread **S12**·PF_6^-: Reagents and conditions: a) Et_3N, $CHCl_3$, r.t., 18 h, 90%. b) CF_3CO_2H, CH_2Cl_2, r.t., 2 h; 2. HCl (2 M in Et_2O), CH_2Cl_2, r.t., 3 h; 3. KPF_6, CH_2Cl_2/acetone/H_2O (4:5:5), r.t., 18 h, 83%.

1.2.4 Cleavage of rotaxane 13·PF_6^-

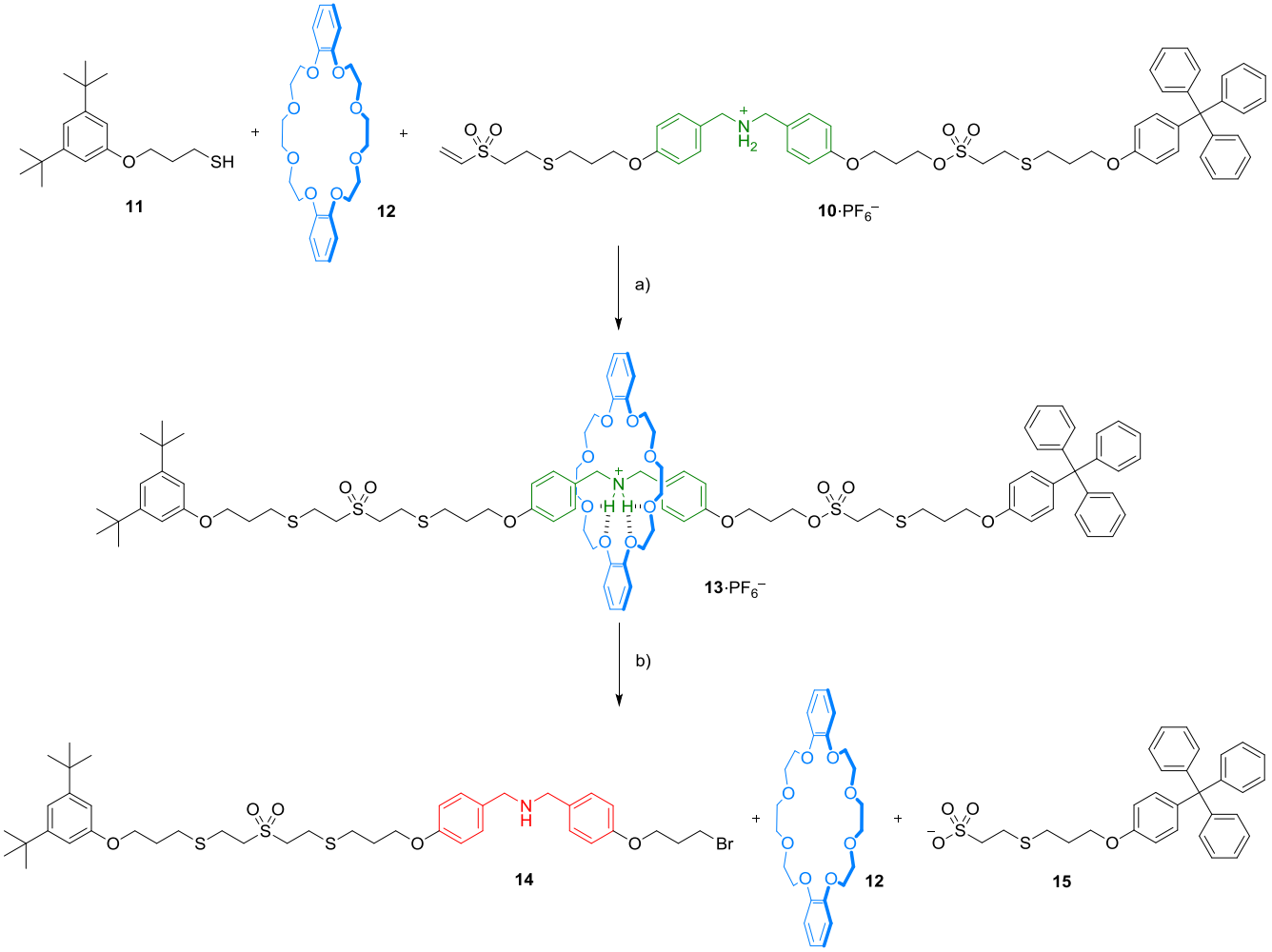


Scheme S7: Cleavage of rotaxane **13**·PF_6^-: Reagents and conditions: a) 1. $MgBr_2$, $CHCl_3$, r.t., 48 h; 2. Et_3N, $CDCl_3$, r.t., 10 min, 92% (for **12**) and 77% (for **14**/**15** (1:1)).



Scheme S8: Cleavage of thread **S11**: Reagents and conditions: a) $MgBr_2$, CH_2Cl_2, r.t., 48 h, 96%. b) CF_3CO_2H, CH_2Cl_2, r.t., 2 h; 2. HCl (2 M in Et_2O), CH_2Cl_2, r.t., 4 h; 3. KPF_6, CH_2Cl_2/acetone/H_2O (4:5:5), r.t., 18 h, 95%.

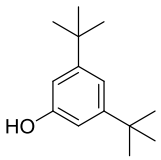
1.2.5 *In situ* unidirectional transport of macrocycle 12



Scheme S9: *In situ* unidirectional transport of macrocycle **12**: Reagents and conditions: a) $DMAP_{(cat)}$, $CDCl_3$, 0 °C, 96 h. b) 1. $MgBr_2$, $CDCl_3$, r.t., 48 h; 2. Et_3N, $CDCl_3$, r.t., 60 min.

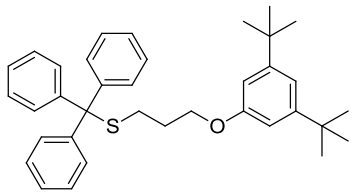
1.3 Synthetic procedures and characterization details

Compound S2:



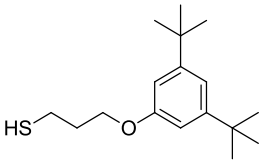
To a degassed solution of 1-bromo-3,5-di-*tert*-butylbenzene (1.29 g, 4.79 mmol) in freshly distilled THF (15 mL) at –78 ºC was added ^{n}BuLi (2.5 M in hexane, 2.30 mL, 5.75 mmol) dropwise. The solution was stirred for 20 min at –78 ºC and trimethyl borate (800 µL, 7.19 mmol) was added. The solution was stirred for 25 min at –78 ºC. The mixture was allowed to warm up to 0-4 ºC and was further stirred for 2 h at 0-4 ºC. Subsequently, H_2O_2 (33% in H_2O, 875 µL, 9.58 mmol) was added and the resulting mixture was stirred for 30 min at 0-4 ºC then, 1 h at room temperature. The reaction mixture was cooled in a water-ice bath and was slowly treated with an aqueous solution of Na_2SO_3 (0.63 M, 15 mL). The mixture was then stirred for 15 min at 0-4 ºC and 5 min at room temperature. The resulting mixture was extracted with EtOAc (3 × 50 mL) and the combined extracts were washed with H_2O (2 × 100 mL) and brine (2 × 100 mL). The organic layer was dried over anhydrous Na_2SO_4 and the solvent was evaporated under vacuum. The crude material was purified by column chromatography (SiO_2, EtOAc/hexane 10:90) to give **S2** (599 mg, 61%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.06 (s, 1H), 6.76 (s, 2H), 5.59 (br, 1H), 1.34 (s, 18H). HRMS (ESI$^-$): *m/z*: 205.1593 $[M–H]^-$ (calcd for $C_{14}H_{21}O$: 205.1592). Characterization data are in agreement with those from literature.[S3]

Compound S4:



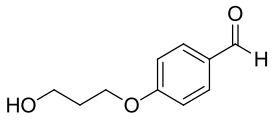
To a degassed solution of **S2** (520 mg, 2.52 mmol) in anhydrous CH_3CN (30 mL) were added **S3** (2.00 g, 5.03 mmol) and K_2CO_3 (1.74 g, 12.6 mmol). The suspension was stirred for 22 h at 75 ºC. The solvent was evaporated under reduced pressure and the solid was dissolved in CH_2Cl_2/H_2O (1:1, 200 mL). Layers were separated and the aqueous one was extracted with CH_2Cl_2 (50 mL). The combined extracts were dried over anhydrous Na_2SO_4 and the solvent was removed under vacuum. The crude material was purified by column chromatography (SiO_2, CH_2Cl_2/hexane 20:80) to yield **S4** (864 mg, 66%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.43 (m, 6H), 7.28 – 7.15 (m, 9H), 7.01 (s, 1H), 6.69 (s, 2H), 3.92 (m, 2H), 2.38 (m, 2H), 1.84 (m, 2H), 1.31 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$): δ=158.50, 152.21, 145.05, 129.75, 127.98, 126.71, 115.02, 108.95, 66.77, 66.14, 35.11, 31.62, 28.75. IR (neat): ν=2958, 2866, 1591, 1443, 1427, 1299, 1053, 744, 699 cm^{-1}. HRMS (ESI$^+$): *m/z*: 545.2856 $[M+Na]^+$ (calcd for $C_{36}H_{42}ONaS$: 545.2854).

Compound 11:



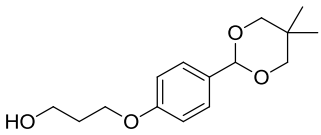
Under argon, to a solution of **S4** (800 mg, 1.53 mmol) in dry CH_2Cl_2 (10 mL) were added CF_3CO_2H (2 mL) and Et_3SiH (1 mL). The solution was stirred for 4 h at room temperature and the solvent was removed under reduced pressure. Subsequently, the solid was dissolved in toluene (20 mL) and the solvent was evaporated under vacuum. The crude material was purified by column chromatography (SiO_2, CH_2Cl_2/hexane 20:80) to afford **11** (340 mg, 79%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.07 (t, J = 1.7 Hz, 1H), 6.80 (d, J = 1.7 Hz, 2H), 4.12 (t, J = 5.9 Hz, 2H), 2.79 (q, J = 7.1 Hz, 2H), 2.12 (p, J = 6.5 Hz, 2H), 1.45 (t, J = 8.1 Hz, 1H), 1.35 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$): δ=158.52, 152.35, 115.21, 108.92, 65.51, 35.12, 33.76, 31.59, 21.50. IR (neat): ν=2956, 2866, 1591, 1427, 1298, 1217, 1203, 1061, 863, 764, 750, 707 cm^{-1}. HRMS (ESI$^+$): *m/z*: 303.1754 $[M+Na]^+$ (calcd for $C_{17}H_{28}ONaS$: 303.1753).

Compound S5:



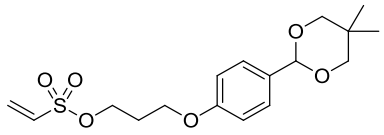
To a degassed solution of 4-hydroxybenzaldehyde (1.00 g, 8.19 mmol) in dry CH_3CN (30 mL) were added K_2CO_3 (5.66 g, 41.0 mmol) and 3-bromo-1-propanol (0.960 mL, 10.7 mmol). The suspension was stirred for 24 h at 75 ºC. The mixture was cooled to room temperature, filtered and the solvent was evaporated under reduced pressure. The syrup was dissolved in CH_2Cl_2 (50 mL) and washed with H_2O (50 mL). The aqueous layer was extracted with CH_2Cl_2 (50 mL) and the combined organic phases were dried over anhydrous Na_2SO_4. The solvent was removed under vacuum and the crude material was purified by column chromatography (SiO_2, CH_2Cl_2/EtOAc 85:15) to yield **S5** (1.25 g, 85%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ=9.88 (s, 1H), 7.83 (d, J = 8.8 Hz, 2H), 7.01 (d, J = 8.8 Hz, 2H), 4.21 (t, J = 6.1 Hz, 2H), 3.88 (t, J = 5.9 Hz, 2H), 2.08 (p, J = 6.0 Hz, 2H). Characterization data are in agreement with those from literature.[S4]

Compound 2:



To a degassed solution of **S5** (6.45 g, 35.8 mmol) in dry toluene (300 mL) were added 2,2-dimethyl-1,3-propanediol (5.59 g, 53.7 mmol), DL-10-camphorsulfonic acid (1.66 g, 7.16 mmol) and molecular sieves (3Å, 10 g). The suspension was stirred for 18 h at 100 ºC. The resulting mixture was cooled to room temperature and Et_3N (15 mL) was added. The solution was concentrated to dryness and the crude material was purified by column chromatography (SiO_2, CH_2Cl_2/EtOAc 85:15) to afford **2** (6.92 g, 73%) as a white solid. M.p. 55–57 ºC. ^{1}H NMR (500 MHz, $CDCl_3$): δ=7.42 (d, J = 8.7 Hz, 2H), 6.89 (d, J = 8.7 Hz, 2H), 5.34 (s, 1H), 4.11 (t, J = 6.0 Hz, 2H), 3.83 (t, J = 5.9 Hz, 2H), 3.75 (d, J = 11.3 Hz, 2H), 3.63 (d, J = 10.5 Hz, 2H), 2.02 (p, J = 6.0 Hz, 2H), 1.29 (s, 3H), 0.79 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ=159.29, 131.40, 127.58, 114.40, 101.76, 77.79, 65.90, 60.55, 32.08, 30.31, 23.18, 22.02. IR (neat): ν=3400 (br), 2953, 2858, 1614, 1516, 1387, 1245, 1097, 1059, 1036, 1012, 987, 827, 764, 749 cm^{-1}. HRMS (ESI$^+$): *m/z*: 289.1415 $[M+Na]^+$ (calcd for $C_{15}H_{22}O_4Na$: 289.1416).

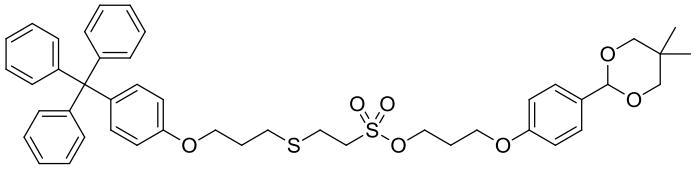
Compound 3:



Under an argon atmosphere, to a solution of **2** (2.29 g, 8.58 mmol) in anhydrous CH_2Cl_2 (250 mL), in a water-ice bath, were added Et_3N (5.96 mL, 42.9 mmol) and a solution of 2-chloroethanesulfonyl chloride (1.35 mL, 12.9

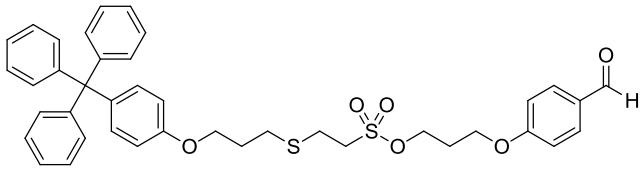
mmol) in anhydrous CH_2Cl_2 (25 mL). The solution was stirred for 1 h at 0-4 ºC. Subsequently, the mixture was diluted with CH_2Cl_2 (50 mL) and washed with H_2O (250 mL). The aqueous layer was then extracted with CH_2Cl_2 (250 mL). The combined organic phases were dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The crude material was purified by column chromatography (SiO_2, EtOAc/hexane 35:65) to yield **3** (2.46 g, 80%) as a white solid. M.p. 57–58 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.43 (d, J = 8.7 Hz, 2H), 6.87 (d, J = 8.7 Hz, 2H), 6.46 (dd, J = 16.6, 9.3 Hz, 1H), 6.38 (d, J = 16.7 Hz, 1H), 6.06 (d, J = 9.3 Hz, 1H), 5.34 (s, 1H), 4.32 (t, J = 6.1 Hz, 2H), 4.06 (t, J = 5.9 Hz, 2H), 3.75 (d, J = 11.2 Hz, 2H), 3.64 (d, J = 10.5 Hz, 2H), 2.19 (p, J = 6.0 Hz, 2H), 1.29 (s, 3H), 0.79 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ=158.96, 132.31, 131.69, 130.46, 127.66, 114.34, 101.67, 77.78, 67.49, 63.28, 30.30, 29.04, 23.17, 22.00. IR (neat): ν=2954, 2848, 1614, 1516, 1358, 1244, 1169, 1097, 974, 944, 828, 761 cm^{-1}. HRMS (ESI$^+$): *m/z*: 379.1188 [M+Na]$^+$ (calcd for $C_{17}H_{24}O_6SNa$: 379.1191).

Compound 5:



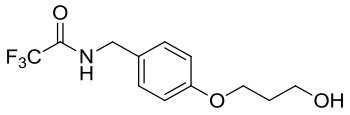
To a degassed solution of **3** (1.15 g, 3.23 mmol) in CH_2Cl_2/^{i}PrOH (8:1, 90 mL) were added **4** (2.15 g, 5.24 mmol), Et_3N (225 µL, 1.62 mmol) and PPh_3 (169 mg, 0.646 mmol). The solution was stirred for 24 h at room temperature. The solvent was then evaporated under reduced pressure and the crude material was purified by column chromatography (SiO_2, CH_2Cl_2/EtOAc 98:2) to give **5** (2.46 g, quant) as a white solid. M.p. 70–73 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.43 (d, J = 8.7 Hz, 2H), 7.30 – 7.14 (m, 15H), 7.11 (d, J = 8.9 Hz, 2H), 6.88 (d, J = 8.7 Hz, 2H), 6.76 (d, J = 8.9 Hz, 2H), 5.33 (s, 1H), 4.44 (t, J = 6.2 Hz, 2H), 4.08 (t, J = 5.9 Hz, 2H), 3.99 (t, J = 5.9 Hz, 2H), 3.74 (d, J = 11.2 Hz, 2H), 3.62 (d, J = 10.6 Hz, 2H), 3.34 (m, 2H), 2.92 (m, 2H), 2.69 (t, J = 7.2 Hz, 2H), 2.21 (p, J = 6.0 Hz, 2H), 2.01 (p, J = 6.4 Hz, 2H), 1.28 (s, 3H), 0.79 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ=158.95, 156.79, 147.15, 139.32, 132.36, 131.77, 131.24, 127.70, 127.56, 125.99, 114.38, 113.36, 101.66, 77.78, 67.05, 65.81, 64.45, 63.41, 50.66, 30.31, 29.30, 29.19, 29.01, 25.37, 23.19, 22.03. IR (neat): ν=3055, 2956, 2849, 1611, 1508, 1244, 1167, 1099, 828, 734, 702 cm^{-1}. HRMS (ESI$^+$): *m/z*: 789.2890 [M+Na]$^+$ (calcd for $C_{45}H_{50}NaO_7S_2$: 789.2896).

Compound 6:



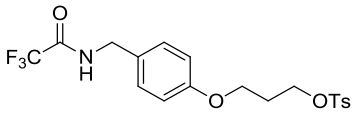
Under argon, to a solution of **5** (2.28 g, 2.97 mmol) in CH_2Cl_2 (50 mL) were added CF_3CO_2H (20 mL) and H_2O (2 mL). The solution was stirred for 5 h at room temperature and concentrated to dryness. The crude material was purified by column chromatography (SiO_2, CH_2Cl_2/EtOAc 99:1) to afford **6** (1.93 g, 95%) as a white solid. M.p. 91–93 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ=9.87 (s, 1H), 7.82 (d, J = 8.7 Hz, 2H), 7.26 – 7.15 (m, 15H), 7.10 (d, J = 8.9 Hz, 2H), 6.99 (d, J = 8.7 Hz, 2H), 6.75 (d, J = 8.9 Hz, 2H), 4.45 (t, J = 6.1 Hz, 2H), 4.16 (t, J = 5.9 Hz, 2H), 4.00 (t, J = 5.8 Hz, 2H), 3.35 (m, 2H), 2.92 (m, 2H), 2.71 (t, J = 7.2 Hz, 2H), 2.25 (p, J = 6.0 Hz, 2H), 2.02 (p, J = 6.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ=190.82, 163.54, 156.73, 147.11, 139.42, 132.38, 132.16, 131.22, 130.43, 127.56, 126.00, 114.87, 113.34, 66.67, 65.78, 64.44, 63.80, 50.76, 29.27, 29.22, 29.07, 25.41. IR (neat): ν=2929, 1688, 1600, 1508, 1357, 1253, 1162, 1035, 942, 831, 750, 703 cm^{-1}. HRMS (ESI$^+$): *m/z*: 703.2158 [M+Na]$^+$ (calcd for $C_{40}H_{40}NaO_6S_2$: 703.2164).

Compound S7:



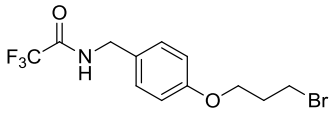
To a degassed solution of **S6** (2.61 g, 14.4 mmol) in dry MeOH (90 mL) were added Et_3N (2.00 mL, 14.4 mmol) and ethyl trifluoroacetate (2.22 mL, 18.7 mmol). The solution was stirred for 2 h at room temperature. The resulting solution was diluted with H_2O (100 mL) and brine (150 mL) and then extracted with EtOAc (3 × 250 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and the solvent was removed under vacuum. The crude material was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH 96:4) to afford **S7** (3.55 g, 89%) as a white solid. M.p. 81–84 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.20 (d, J = 8.6 Hz, 2H), 6.88 (d, J = 8.6 Hz, 2H), 6.72 (br, 1H), 4.44 (d, J = 5.7 Hz, 2H), 4.10 (t, J = 6.0 Hz, 2H), 3.84 (t, J = 5.9 Hz, 2H), 2.03 (p, J = 6.0 Hz, 2H), 1.85 (br, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ=158.93, 157.18 (q, J = 37.2 Hz), 129.59, 128.26, 116.01 (q, J = 287.8 Hz), 115.08, 65.87, 60.41, 43.56, 32.05. IR (neat): ν=3300, 2948, 2878, 1697, 1555, 1513, 1188, 1167, 1061 cm^{-1}. HRMS (ESI$^+$): *m/z*: 300.0824 [M+Na]$^+$ (calcd for $C_{12}H_{14}NO_3F_3Na$: 300.0823).

Compound S8:



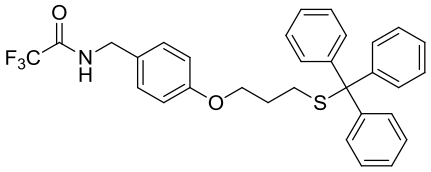
To a degassed solution of **S7** (3.38 g, 12.2 mmol) in anhydrous CH_2Cl_2 (150 mL) were added Et_3N (6.80 mL, 48.8 mmol), TsCl (4.65 g, 24.4 mmol) and a catalytic amount of DMAP. The solution was stirred for 18 h at room temperature and concentrated to dryness. The crude material was purified by column chromatography (SiO_2, CH_2Cl_2, to CH_2Cl_2/MeOH 98:2) to yield **S8** (5.24 g, 99%) as a white solid. M.p. 122–125 ºC. ^{1}H NMR (500 MHz, $CDCl_3$): δ=7.76 (d, J = 8.3 Hz, 2H), 7.27 (d, J = 8.5 Hz, 2H), 7.19 (d, J = 8.7 Hz, 2H), 6.77 (d, J = 8.6 Hz, 2H), 6.48 (br, 1H), 4.46 (d, J = 5.7 Hz, 2H), 4.24 (t, J = 6.0 Hz, 2H), 3.96 (t, J = 5.9 Hz, 2H), 2.39 (s, 3H), 2.12 (p, J = 6.0 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ= 158.69, 157.13 (q, J = 37.3 Hz), 144.95, 133.01, 129.98, 129.55, 128.32, 128.01, 116.01 (q, J = 287.9 Hz), 115.07, 67.09, 63.42, 43.59, 29.02, 21.76. IR (neat): ν=3323, 2934, 1688, 1517, 1358, 1251, 1166, 951, 749 cm^{-1}. HRMS (ESI$^+$): *m/z*: 454.0912 [M+Na]$^+$ (calcd for $C_{19}H_{20}NF_3O_5SNa$: 454.0912).

Compound S9:



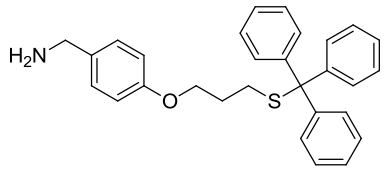
Under an argon atmosphere, to a solution of **S8** (2.92 g, 6.77 mmol) in dry acetone (180 mL) was added LiBr (5.88 g, 67.7 mmol). The suspension was stirred for 18 h at reflux and concentrated to dryness. The resulting solid was dissolved in CH_2Cl_2/H_2O (1:1, 500 mL). Layers were separated and the aqueous one was extracted with CH_2Cl_2 (2 × 250 mL). The combined organic phases were dried over anhydrous Na_2SO_4 and the solvent was evaporated under vacuum. The crude material was purified by column chromatography (SiO_2, CH_2Cl_2) to give **S9** (1.97 g, 86%) as a white solid. M.p. 106–109 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.22 (d, J = 8.6 Hz, 2H), 6.90 (d, J = 8.6 Hz, 2H), 6.50 (br, 1H), 4.46 (d, J = 5.7 Hz, 2H), 4.11 (t, J = 5.8 Hz, 2H), 3.60 (t, J = 6.4 Hz, 2H), 2.32 (p, J = 6.1 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ=158.89, 157.12 (q, J = 36.9 Hz), 129.64, 128.30, 116.00 (q, J = 287.9 Hz), 115.17, 65.56, 43.61, 32.40, 30.01. IR (neat): ν=3288, 1698, 1551, 1515, 1248, 1181, 1159, 823, 754 cm^{-1}. HRMS (ESI$^-$): *m/z*: 338.0003 [M–H]$^-$ (calcd for $C_{12}H_{12}NO_2F_3Br$: 338.0004).

Compound S10:



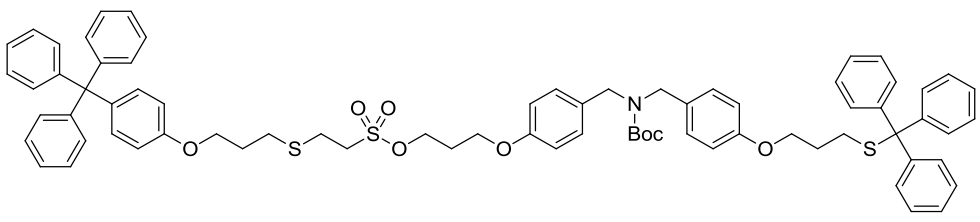
To a degassed solution of triphenylmethanethiol (955 mg, 3.46 mmol) in anhydrous THF (9 mL), in a water-ice bath, was added LiHMDS (1 M in THF, 3.50 mL, 3.46 mmol). The mixture was stirred at 0-4 ºC until the thiolate precipitates (approximately 10 min). Subsequently, the suspension was allowed to warm up to room temperature and a degassed solution of **S9** (980 mg, 2.88 mmol) in dry THF (4 mL) was added. The mixture was further stirred for 1 h at room temperature and was concentrated to dryness. The resulting syrup was dissolved in CH_2Cl_2 (100 mL) and washed with H_2O (2 × 100 mL). The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The crude material was purified by column chromatography (SiO_2, Hexane/CH_2Cl_2 20:80) to give **S10** (1.31 g, 85%) as a white solid. M.p. 111–113 ºC. ^{1}H NMR (500 MHz, $CDCl_3$): δ=7.44 (m, 6H), 7.34 – 7.19 (m, 11H), 6.84 (d, J = 8.6 Hz, 2H), 6.58 (br, 1H), 4.46 (d, J = 5.7 Hz, 2H), 3.92 (t, J = 6.2 Hz, 2H), 2.39 (t, J = 7.1 Hz, 2H), 1.84 (p, J = 6.7 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ=158.97, 157.09 (q, J = 36.9 Hz), 144.95, 129.70, 129.51, 127.99, 126.75, 115.99 (q, J = 287.9 Hz), 115.11, 66.76, 66.44, 43.60, 28.54, 28.38. IR (neat): v=3307, 3058, 2932, 1705, 1512, 1443, 1246, 1202, 1172, 1033, 743, 700 cm^{-1}. HRMS (ESI$^+$): m/z: 558.1691 $[M+Na]^+$ (calcd for $C_{31}H_{28}NO_2SF_3Na$: 558.1691).

Compound 7:



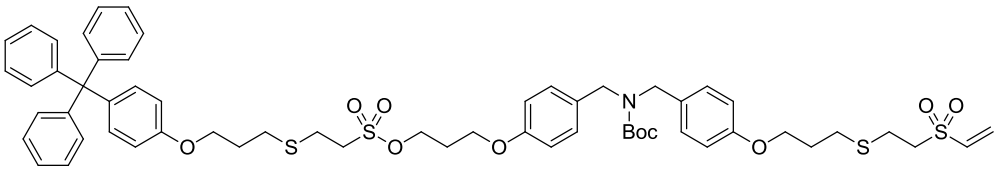
S10 (1.95 g, 3.64 mmol) was dissolved in MeOH (30 mL) upon sonication. Then, a solution of NaOH (728 mg, 18.2 mmol) in H_2O (8 mL) was added. The mixture was stirred for 20 h at room temperature. MeOH was evaporated under reduced pressure and the resulting mixture was diluted with H_2O/CH_2Cl_2 (2:3, 150 mL). Layers were separated and the aqueous one was extracted with CH_2Cl_2 (2 × 100 mL). The combined extracts were dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The crude material was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH 95:5, to CH_2Cl_2/MeOH/NH_3 (30% in H_2O) 90:10:2) to yield **7** (1.21 g, 76%) as a light-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.44 (m, 6H), 7.31 – 7.19 (m, 11H), 6.80 (d, J = 8.6 Hz, 2H), 3.90 (t, J = 6.2 Hz, 2H), 3.80 (s, 2H), 2.38 (t, J = 7.1 Hz, 2H), 2.29 (br, 2H), 1.82 (p, J = 6.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ=157.96, 144.96, 129.68, 128.49, 127.95, 126.70, 114.71, 66.70, 66.39, 45.71, 28.58, 28.45. IR (neat): v=3056, 2925, 1609, 1510, 1488, 1444, 1243, 1033, 764, 748, 700 cm^{-1}. HRMS (ESI$^+$): m/z: 462.1869 $[M+Na]^+$ (calcd for $C_{29}H_{29}NOSNa$: 462.1868); 440.2042 $[M+H]^+$ (calcd for $C_{29}H_{30}NOS$: 440.2048)

Compound 8:



6 (1.66 g, 2.44 mmol) and **7** (1.07 g, 2.44 mmol) were dissolved in degassed anhydrous MeOH/THF (8:5, 65 mL) upon sonication. Then, the solution was stirred for 24 h at room temperature. $NaBH_4$ (369 mg, 9.76 mmol) was added and the solution was further stirred for 24 h at room temperature. H_2O (50 mL) was added, the mixture was stirred for 15 min and diluted with brine (100 mL). The resulting mixture was extracted with CH_2Cl_2 (3 × 150 mL). The combined extracts were dried over anhydrous Na_2SO_4 and the solvent was removed under vacuum. Subsequently, the solid was dissolved in degassed CH_2Cl_2 (60 mL) and Et_3N (1.00 mL, 7.19 mmol) and a solution of Boc_2O (691 mg, 3.17 mmol) in CH_2Cl_2 (5 mL) were added dropwise. The solution was stirred for 24 h at room temperature and was concentrated to dryness. The crude material was purified by column chromatography (SiO_2, CH_2Cl_2, to CH_2Cl_2/EtOAc 96:4) to yield **8** (2.34 g, 80%) as a light-yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ=7.42 (m, 6H), 7.29 – 7.07 (m, 30H), 6.85 (d, J = 8.6 Hz, 2H), 6.77 (m, 4H), 4.45 (t, J = 6.2 Hz, 2H), 4.28 (br, 4H), 4.07 (t, J = 5.8 Hz, 2H), 4.01 (t, J = 5.9 Hz, 2H), 3.91 (t, J = 6.1 Hz, 2H), 3.35 (m, 2H), 2.94 (m, 2H), 2.73 (t, J = 7.2 Hz, 2H), 2.37 (t, J = 7.1 Hz, 2H), 2.22 (p, J = 6.0 Hz, 2H), 2.03 (p, J = 6.6 Hz, 2H), 1.82 (p, J = 6.7 Hz, 2H), 1.50 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ=158.19, 157.81, 156.74, 156.06, 147.12, 144.98, 139.36, 132.37, 131.22, 130.77, 130.14, 129.72, 129.56, 128.00, 127.56, 126.74, 125.99, 114.64, 114.60, 113.34, 80.06, 67.13, 66.73, 66.35, 65.76, 64.43, 63.38, 50.67, 48.45, 48.37, 48.16, 48.09, 29.39, 29.20, 29.02, 28.64, 28.47, 25.37. IR (neat): ν=2928, 1688, 1610, 1510, 1364, 1244, 1166, 764, 749, 702 cm^{-1}. HRMS (ESI$^+$): *m/z*: 1226.4707 $[M+Na]^+$ (calcd for $C_{74}H_{77}NO_8S_3Na$: 1226.4709).

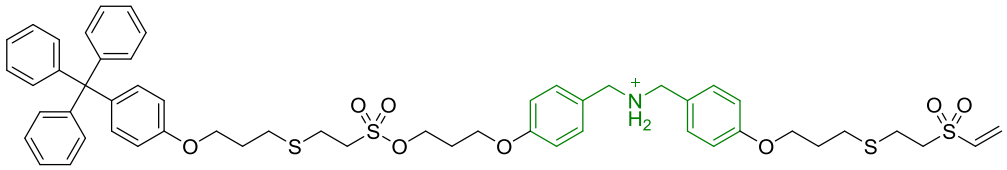
Compound 9:



Note: Divinyl sulfone is very toxic by inhalation or contact with skin. It should only be handle inside a well-ventilated fumehood while wearing adequate gloves, lab coat and face protection to avoid skin contact.

Under an argon atmosphere, to a solution of **8** (2.16 g, 1.79 mmol) in anhydrous CH_2Cl_2 (80 mL) were added CF_3CO_2H (15 mL) and Et_3SiH (7 mL). The solution was stirred for 6 h at room temperature and was concentrated to dryness. The crude was dissolved in toluene (70 mL) and the solvent was evaporated under reduced pressure. Then, the solid was dissolved in degassed CH_2Cl_2 (80 mL) and Et_3N (8 mL) and Boc_2O (391 mg, 1.79 mmol) were added. The mixture was stirred for 5 h at room temperature. Subsequently, divinyl sulfone (1.40 mL, 14.3 mmol) was added and the solution was stirred for another 14 h at room temperature. The solvent was evaporated under vacuum and the crude material was purified by column chromatography (SiO_2, CH_2Cl_2, to CH_2Cl_2/EtOAc 98:2) to afford **9** (1.01 g, 52%) as a light-yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ=7.27 – 7.08 (m, 21H), 6.85 (d, J = 8.6 Hz, 4H), 6.76 (d, J = 8.9 Hz, 2H), 6.64 (dd, J = 16.6, 9.8 Hz, 1H), 6.45 (d, J = 16.6 Hz, 1H), 6.17 (d, J = 9.8 Hz, 1H), 4.45 (t, J = 6.1 Hz, 2H), 4.28 (br, 4H), 4.09 – 3.99 (m, 6H), 3.35 (m, 2H), 3.24 (m, 2H), 2.92 (m, 4H), 2.74 (m, 4H), 2.22 (p, J = 5.9 Hz, 2H), 2.05 (m, 4H), 1.50 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ=158.06, 157.82, 156.73, 156.03, 147.10, 139.35, 136.13, 132.35, 131.31, 131.20, 130.72, 130.47, 129.51, 128.97, 127.53, 125.97, 114.60, 113.33, 80.08, 67.12, 65.92, 65.77, 64.42, 63.40, 54.54, 50.66, 48.50, 48.19, 29.81, 29.37, 29.19, 29.00, 28.96, 28.62, 25.35, 24.34. IR (neat): ν=2928, 1685, 1610, 1510, 1318, 1241, 1164, 764, 750, 703 cm^{-1}. HRMS (ESI$^+$): *m/z*: 1102.3708 $[M+Na]^+$ (calcd for $C_{59}H_{69}NO_{10}NaS_4$: 1102.3702).

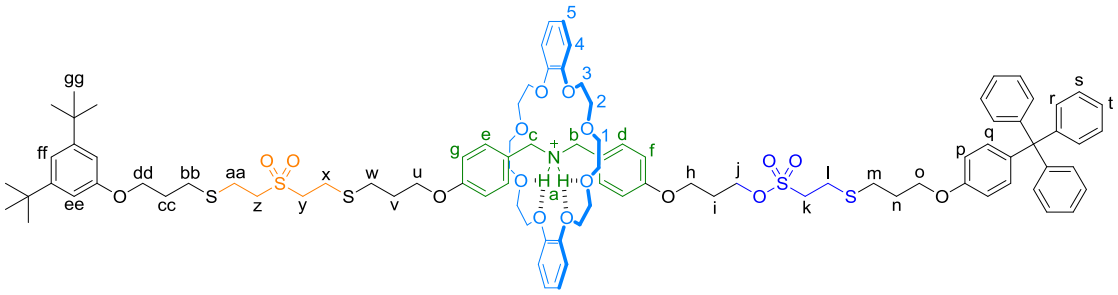
Compound 10·PF_6^-:



Note: HCl in Et_2O solution is corrosive and toxic by inhalation. It should be handled only inside a well-ventilated fumehood. When evaporating the reaction mixture, the exhaust gases of the vacuum pump must be directed to a fumehood with appropriate tubing.

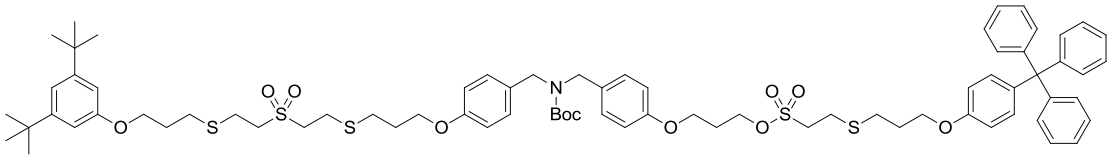
To a solution of **9** (519 mg, 0.480 mmol) in CH_2Cl_2 (30 mL) was added CF_3CO_2H (6 mL). The solution was stirred for 5 h at room temperature and was concentrated to dryness. The solid was then dissolved in CH_2Cl_2 (20 mL) and HCl (2 M in Et_2O, 3.6 mL, 7.2 mmol) was added. The mixture was stirred for 3 h at room temperature. The solvent was evaporated under reduced pressure. The resulting solid was dissolved in CH_2Cl_2/acetone/H_2O (4:5:5, 70 mL) and an excess of KPF_6 was added. The mixture was stirred for 18 h at room temperature and was diluted with H_2O (35 mL). The resulting mixture was extracted with CH_2Cl_2 (3 × 50 mL) and the combined organic phases were dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to give **10**·PF_6^- (456 mg, 84%) as a white solid. M.p. 154–156 ºC (decomp.). ^{1}H NMR (500 MHz, $CDCl_3$): δ=8.49 (br, 2H), 7.33 – 7.14 (m, 19H), 7.10 (d, J = 8.8 Hz, 2H), 6.89 (d, J = 8.2 Hz, 4H), 6.75 (d, J = 8.6 Hz, 2H), 6.63 (dd, J = 16.6, 9.9 Hz, 1H), 6.42 (d, J = 16.6 Hz, 1H), 6.18 (d, J = 9.9 Hz, 1H), 4.41 (t, J = 6.2 Hz, 2H), 4.05 – 3.87 (m, 10H), 3.34 (m, 2H), 3.18 (m, 2H), 2.92 (m, 2H), 2.83 (m, 2H), 2.72 (m, 4H), 2.28 (m, 2H), 2.02 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$): δ=159.82, 159.60, 156.76, 147.14, 139.41, 136.02, 132.39, 131.69, 131.51, 131.24, 127.58, 126.01, 122.35, 122.20, 115.33, 113.37, 66.98, 65.98, 65.84, 64.46, 63.52, 54.46, 53.12, 50.74, 49.48, 49.43, 29.33, 29.23, 29.05, 28.80, 25.38, 24.34. IR (neat): ν=2932, 1655, 1611, 1515, 1250, 829, 749, 702 cm^{-1}. HRMS (ESI$^+$): m/z: 980.3353 [M–PF_6^-]$^+$ (calcd for $C_{54}H_{62}NO_8S_4$: 980.3358).

Compound 13·PF_6^-:



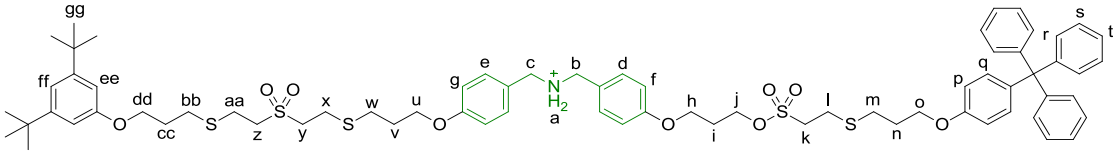
10·PF_6^- (22 mg, 20 µmol) and **12** (44 mg, 98 µmol) were dissolved in $CHCl_3$ (7 mL) upon sonication. The solvent was removed under vacuum and the syrup was dissolved in degassed $CHCl_3$ (700 µL). The mixture was cooled to 0 ºC and stirred for 1 h. To this solution were added a degassed solution of **11** (11 mg, 39 µmol) in $CHCl_3$ (100 µL) and a catalytic amount of DMAP. The solution was stirred for 72 h at 0 ºC. Then, the solvent was evaporated under reduced pressure and the crude material was purified by gel permeation chromatography (Bio-Beads® SX−1, CH_2Cl_2) to yield **13**·PF_6^- (24 mg, 66%) as a white solid. M.p. 165–168 ºC (decomp.). ^{1}H NMR (500 MHz, $CDCl_3$): δ= 7.46 (br, 2H, H_a), 7.25 – 7.15 (m, 19H, $H_{e+d+r+s+t}$), 7.09 (d, J = 8.8 Hz, 2H, H_q), 7.02 (t, J = 1.6 Hz, 1H, H_{ff}), 6.93 – 6.80 (m, 8H, H_{4+5}), 6.76 (m, 8H, $H_{f+g+p+ee}$), 4.44 (m, 6H, H_{j+b+c}), 4.17 – 3.99 (m, 16H, $H_{3+h+o+u+dd}$), 3.75 (m, 8H, H_2), 3.46 – 3.26 (m, 14H, $H_{1+k+y+z}$), 3.18 – 2.72 (m, 12H, $H_{l+m+w+x+aa+bb}$), 2.19 (m, 2H, H_i), 2.06 (m, 6H, H_{n+v+cc}), 1.31 (s, 18H, H_{gg}). ^{13}C NMR (126 MHz, $CDCl_3$): δ= 159.52, 159.29, 158.45, 156.78, 152.38, 148.97, 147.67, 147.13, 139.31, 132.35, 131.22, 130.96, 127.56, 125.98, 124.11, 123.87, 121.97, 121.62, 115.25, 114.72, 113.37, 113.05, 108.95, 71.31, 70.84, 70.31, 70.07, 69.43, 68.53, 67.34, 66.19, 65.88, 64.44, 63.57, 53.92, 53.83, 52.13, 50.72, 35.13, 31.60, 29.83, 29.43, 29.27, 29.09, 28.97, 28.80, 25.32, 23.96, 23.85. IR (neat): ν=2937, 1655, 1590, 1506, 1275, 1256, 1214, 1180, 1121, 1055, 951, 841, 764, 750 cm^{-1}. HRMS (ESI$^+$): m/z: 1708.7335 [M–PF_6^-]$^+$ (calcd for $C_{95}H_{122}NO_{17}S_5$: 1708.7316).

Compound S11:



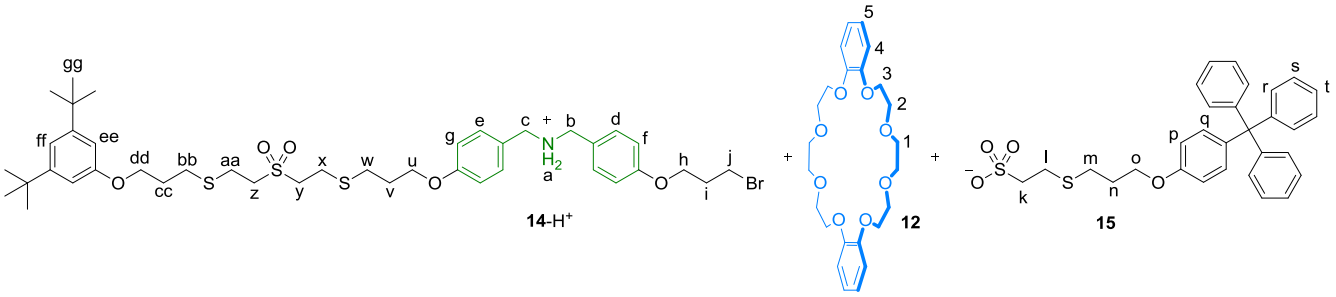
To a degassed solution **9** (54 mg, 0.049 mmol) and **11** (28 mg, 0.10 mmol) in $CHCl_3$ (3 mL) were added 2 drops of Et_3N. The solution was stirred for 18 h at room temperature and was concentrated to dryness. The crude material was purified by column chromatography (SiO_2, CH_2Cl_2, to CH_2Cl_2/EtOAc 97:3) to afford **S11** (61 mg, 90%) as a white syrup. ^{1}H NMR (500 MHz, $CDCl_3$): δ=7.27 – 7.07 (m, 21H), 7.04 (t, J = 1.7 Hz, 1H), 6.85 (d, J = 8.6 Hz, 4H), 6.77 (m, 4H), 4.45 (t, J = 6.1 Hz, 2H), 4.28 (br, 4H), 4.10 – 3.98 (m, 8H), 3.35 (m, 2H), 3.28 (m, 4H), 2.95 (m, 6H), 2.83 – 2.70 (m, 6H), 2.22 (p, J = 6.0 Hz, 2H), 2.05 (m, 6H), 1.50 (s, 9H), 1.32 (s, 18H). ^{13}C NMR (126 MHz, $CDCl_3$): δ=158.39, 158.07, 157.82, 156.74, 156.03, 152.41, 147.11, 139.35, 132.35, 131.21, 130.74, 130.47, 129.52, 128.97, 127.54, 125.98, 115.33, 114.61, 113.34, 108.90, 80.07, 67.12, 65.95, 65.77, 65.72, 64.43, 63.40, 53.83, 53.81, 50.68, 48.49, 48.15, 35.12, 31.58, 29.82, 29.40, 29.23, 29.20, 29.12, 29.01, 28.63, 25.37, 24.12, 24.07. IR (neat): ν=2948, 1687, 1608, 1591, 1510, 1242, 1164, 1119, 1038, 828, 703 cm^{-1}. HRMS (ESI$^+$): m/z: 1382.5573 [M+Na]$^+$ (calcd for $C_{76}H_{97}NO_{11}S_5Na$: 1382.5563).

Compound S12·PF_6^-:



To a solution of **S11** (7 mg, 5.1 μmol) in CH_2Cl_2 (2 mL) was added CF_3CO_2H (500 μL). The solution was stirred for 2 h at room temperature and was concentrated to dryness. The solid was then dissolved in CH_2Cl_2 (3 mL) and HCl (2 M in Et_2O, 40 μL, 80 μmol) was added. The solution was stirred for 3 h at room temperature. The solvent was removed under reduced pressure. The resulting solid was dissolved in CH_2Cl_2/acetone/H_2O (4:5:5, 14 mL) and an excess of KPF_6 was added. The mixture was stirred for 18 h at room temperature and was diluted with H_2O (10 mL). The resulting mixture was extracted with CH_2Cl_2 (3 × 10 mL) and the combined organic layers were dried over anhydrous Na_2SO_4. The solvent was evaporated under vacuum to give **S12**·PF_6^- (6 mg, 83%) as a white solid. M.p. 151–153 ºC (decomp.). ^{1}H NMR (500 MHz, $CDCl_3$): δ=8.49 (br, 2H, H_a), 7.35 – 7.14 (m, 19H, $H_{d+e+r+s+t}$), 7.10 (d, J = 8.5 Hz, 2H, H_q), 7.03 (s, 1H, H_{ff}), 6.87 (d, J = 6.7 Hz, 4H, H_{f+g}), 6.75 (m, 4H, H_{p+ee}), 4.39 (t, J = 6.1 Hz, 2H, H_j), 4.10 – 3.83 (m, 12H, $H_{b+c+h+o+u+dd}$), 3.34 (m, 2H, H_k), 3.28 – 3.19 (m, 4H, H_{y+z}), 3.00 –2.86 (m, 6H, H_{l+x+aa}), 2.82 – 2.66 (m, 6H, H_{m+w+bb}), 2.17 (m, 2H, H_i), 2.10 – 1.97 (m, 6H, H_{n+v+cc}), 1.31 (s, 18H, H_{gg}). ^{13}C NMR (126 MHz, $CDCl_3$): δ=158.45, 156.78, 152.45, 147.15, 147.10, 139.42, 136.40, 132.45, 132.39, 131.86, 131.81, 131.25, 127.58, 126.02, 115.36, 115.28, 113.40, 108.97, 67.01, 66.02, 65.88, 65.81, 64.48, 63.54, 53.79, 50.79, 49.40, 35.16, 32.08, 31.61, 29.86, 29.51, 29.46, 29.35, 29.26, 29.08, 28.97, 25.38, 24.09, 24.05, 22.84. IR (neat): ν=2920, 2850, 1608, 1514, 1275, 1256, 843, 764, 750 cm^{-1}. HRMS (ESI$^+$): m/z: 1260.5226 [M–PF_6^-]$^+$ (calcd for $C_{71}H_{90}NO_9S_5$: 1260.5219).

Compounds 12, 14-H$^+$ and 15 from the cleavage of rotaxane 13·PF$_6^-$:



Under an Ar atmosphere, to a solution of **13**·PF$_6^-$ (18 mg, 9.7 μmol) in non-anhydrous $CHCl_3$ (2 mL) was added $MgBr_2$ (18 mg, 97 μmol). The suspension was stirred for 48 h at room temperature. The solvent was removed under vacuum. The resulting solid was dissolved in $CDCl_3$ (1 mL) and Et_3N (14 μL, 97 μmol) was added. The solvent solution was stirred for 10 min and filtered through a 0.22 μm filter. The solvent was evaporated under reduced pressure and the crude was purified by gel permeation chromatography (Bio-Beads® SX−1, CH_2Cl_2) to yield an equimolar fraction of **14**-H$^+$/**15** (10 mg, 70%)* as a white solid and a mixed fraction of **12** with Et_3N. The latter was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH 95:5) to afford **12** (4 mg, 92%) as a white solid.

12: ^{1}H NMR (500 MHz, $CDCl_3$): δ=6.89 (s, 8H, H_{4+5}), 4.16 (br, 8H, H_3), 3.91 (t, J = 4.3 Hz, 8H, H_2), 3.82 (s, 8H, H_1). HRMS (ESI$^+$): *m/z*: 471.1992 [M+Na]$^+$ (calcd for $C_{24}H_{32}O_8Na$: 471.1995). Characterization data match those of the commercially available compound.

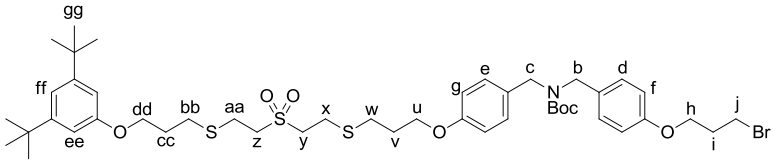
14-H$^+$/**15** (1:1): ^{1}H NMR (500 MHz, $CDCl_3$): δ= 9.19 (br, 2H, H_a), 7.40 (d, J = 8.1 Hz, 4H, H_{d+e}), 7.25 – 7.14 (m, 15H, H_{r+s+t}), 7.08 (d, J = 8.9 Hz, 2H, H_q), 7.03 (t, J = 1.7 Hz, 1H, H_{ff}), 6.88 (m, 4H, H_{f+g}), 6.75 (m, 4H, H_{p+ee}), 4.09 – 3.94 (m, 8H, $H_{h+o+u+dd}$), 3.85 (br, 4H, H_{b+c}), 3.53 (t, J = 6.4 Hz, 2H, H_j), 3.30 – 3.09 (m, 6H, H_{k+y+z}), 3.04 – 2.66 (m, 12H, $H_{l+m+w+x+aa+bb}$), 2.25 (p, J = 6.1 Hz, 2H, H_i), 2.04 (m, 6H, H_{n+v+cc}), 1.31 (s, 18H, H_{gg}). ^{13}C NMR (126 MHz, $CDCl_3$): δ= 159.52, 158.27, 156.77, 152.30, 147.03, 139.08, 132.20, 131.89, 131.87, 131.11, 127.46, 127.43, 125.85, 122.27, 115.21, 115.00, 113.26, 108.78, 66.07, 65.84, 65.62, 65.33, 64.31, 53.70, 53.65, 48.73, 46.13, 32.22, 31.94, 30.95, 29.87, 29.72, 29.38, 28.97, 28.87, 23.87.

14-H$^+$: HRMS (ESI$^+$): *m/z*: 822.2892 [M–PF$_6^-$]$^+$ (calcd for $C_{41}H_{61}NBrO_5S_3$: 822.2895).

15: HRMS (ESI$^-$): *m/z*: 517.1507 [M]$^-$ (calcd for $C_{30}H_{29}O_4S_2$: 517.1507).

* As seen in the ^{1}H NMR spectrum, the cleaved thread is isolated in its protonated form (**14**-H$^+$) after removal under reduced pressure of the solvents and, therefore, triethylamine and gel permeation chromatography (Figure S5c). This counterintuitive result can be explained by the acid-base equilibrium being displaced towards the protonated dibenzylammonium motif upon removal of the amine base under vacuum.[S5] In this way, we repeated the cleavage following the same procedure but with an additional treatment of the mixture with an OH$^-$ ion exchange resin, resulting in the isolation of a mixture of deprotonated **14** and **15** (Figure S5g).

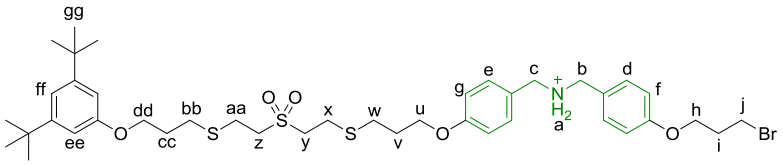
Compound S13:



Under Ar, to a solution of **S11** (20 mg, 15 μmol) in dry CH_2Cl_2 (2 mL) was added $MgBr_2$ (27 mg, 0.15 mmol). The suspension was stirred for 48 h at room temperature. The solvent was evaporated under reduced pressure and the crude material was purified by column chromatography (SiO_2, CH_2Cl_2/EtOAc 96:4) to afford **S13** (13 mg,

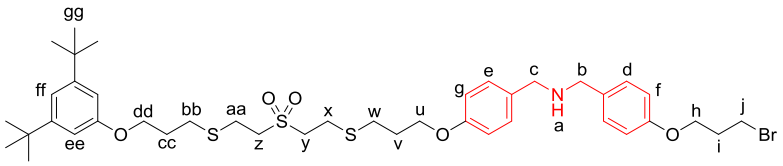
96%) as a white syrup. ^{1}H NMR (500 MHz, $CDCl_3$): δ=7.13 (br, 4H, H_d,H_e), 7.03 (t, J = 1.7 Hz, 1H, H_{ff}), 6.85 (m, 4H, H_f,H_g), 6.75 (d, J = 1.7 Hz, 2H, H_{ee}), 4.28 (br, 4H, H_b,H_c), 4.12 – 4.02 (m, 6H, H_h,H_u,H_{dd}), 3.61 (t, J = 6.4 Hz, 2H, H_j), 3.27 (m, 4H, H_y,H_z), 2.97 (br, 4H, H_x,H_{aa}), 2.79 (m, 4H, H_w,H_{bb}), 2.32 (p, J = 6.1 Hz, 2H, H_i), 2.07 (p, J = 6.3 Hz, 4H, H_v,H_{cc}), 1.50 (s, 9H,H_{tBuBoc}), 1.31 (s, 18H,H_{gg}). ^{13}C NMR (126 MHz, $CDCl_3$): δ=158.41, 158.08, 156.08, 152.44, 130.54, 129.54, 128.98, 115.35, 114.68, 114.62, 108.92, 80.09, 65.97, 65.75, 65.50, 53.87, 53.84, 48.49, 48.20, 35.15, 32.54, 31.60, 30.17, 29.43, 29.26, 29.22, 29.15, 28.65, 24.15, 24.11. IR (neat): ν=2959, 2923, 1688, 1610, 1591, 1511, 1299, 1241, 1164, 1119, 1037 cm^{-1}. HRMS (ESI$^+$): m/z: 944.3236 $[M+Na]^+$ (calcd for $C_{46}H_{68}NO_7S_3NaBr$: 944.3239).

Compound 14-H$^+$·PF$_6^-$:



To a solution of **S13** (11 mg, 12 µmol) in CH_2Cl_2 (2 mL) was added CF_3CO_2H (500 µL). The solution was stirred for 2 h at room temperature and was concentrated to dryness. The solid was then dissolved in CH_2Cl_2 (2 mL) and HCl (2 M in Et_2O, 90 µL, 0.18 mmol) was added. The solution was stirred for 4 h at room temperature. The solvent was removed under reduced pressure. The resulting solid was dissolved in CH_2Cl_2/acetone/H_2O (4:5:5, 14 mL) and an excess of KPF_6 was added. The mixture was stirred for 18 h at room temperature and was diluted with H_2O (10 mL). The resulting mixture was extracted with CH_2Cl_2 (3 × 20 mL) and the combined organic extracts were dried over anhydrous Na_2SO_4. The solvent was evaporated under vacuum to yield **14**-H$^+$·PF$_6^-$ (11 mg, 95%) as a white solid. M.p. 173–175 ºC (decomp.). ^{1}H NMR (500 MHz, $CDCl_3$): δ=8.43 (br, 2H, H_a), 7.33 (m, 4H, H_{d+e}), 7.03 (br, 1H, H_{ff}), 6.88 (d, J = 5.8 Hz, 4H, H_{f+g}), 6.75 (s, 2H, H_{ee}), 4.09 – 3.97 (m, 6H, H_{h+u+dd}), 3.91 (m, 4H, H_{b+c}), 3.55 (t, J = 6.4 Hz, 2H, H_j), 3.24 (m, 4H, H_{y+z}), 2.99 – 2.68 (m, 8H, $H_{w+x+aa+bb}$), 2.27 (p, J = 6.0 Hz, 2H, H_i), 2.10 – 1.99 (m, 4H, H_{v+cc}), 1.31 (s, 18H, H_{gg}). ^{13}C NMR (126 MHz, $CDCl_3$): δ=159.61, 158.29, 152.30, 147.00, 131.66, 131.10, 127.43, 122.16, 115.22, 115.13, 113.24, 108.81, 65.85, 65.66, 65.39, 53.68, 53.65, 35.00, 32.22, 31.93, 31.46, 29.36, 29.11, 28.94, 28.84, 28.51, 23.95, 23.92, 22.69. IR (neat): ν=2919, 1611, 1515, 1275, 1260, 1180, 1030, 843, 764, 750 cm^{-1}. HRMS (ESI$^+$): m/z: 822.2895 $[M–PF_6^-]^+$ (calcd for $C_{41}H_{61}NO_5S_3Br$: 822.2895).

Compound 14:



To a solution of **S13** (13 mg, 14 µmol) in CH_2Cl_2 (2 mL) was added CF_3CO_2H (500 µL). The solution was stirred for 2 h at room temperature and was concentrated to dryness. The solid was then dissolved in CH_2Cl_2 (20 mL) and washed with NaOH (1 M, 10 mL). The organic phase was dried over anhydrous Na_2SO_4. The solvent was evaporated under vacuum to yield **14** (11 mg, 95%) as a white syrup. ^{1}H NMR (500 MHz, $CDCl_3$): δ= 7.25 (d, J = 7.9 Hz, 4H, H_{d+e}), 7.03 (t, J = 1.7 Hz, 1H, H_{ff}), 6.86 (m, 4H, H_{f+g}), 6.75 (d, J = 1.6 Hz, 2H, H_{ee}), 4.10 – 4.03 (m, 6H, H_{h+u+dd}), 3.73 (s, 4H, H_{b+c}), 3.60 (t, J = 6.5 Hz, 2H, H_j), 3.26 (m, 4H, H_{y+z}), 2.96 (m, 4H, H_{x+aa}), 2.78 (m, 4H, H_{w+bb}), 2.31 (p, J = 6.1 Hz, 2H, H_i), 2.10 – 2.03 (m, 4H, H_{v+cc}), 1.31 (s, 18H, H_{gg}). ^{13}C NMR (126 MHz, $CDCl_3$): δ=158.40, 158.02, 158.01, 152.43, 129.77, 129.74, 115.35, 114.62, 114.57, 108.91, 65.90, 65.73, 65.48, 53.81, 52.24, 35.15, 32.54, 31.60, 30.19, 29.85, 29.41, 29.24, 29.20, 29.12, 24.11. IR (neat): ν=2924, 1591, 1510, 1428, 1298, 1244, 1116, 1039 824 cm^{-1}. HR-MS (ESI$^+$): m/z: 822.2908 $[M+H]^+$ (calcd for $C_{41}H_{61}NO_5S_3Br$: 822.2895).

Assembly of pseudorotaxane 12+10·PF_6^-:

Under Ar, **10**·PF_6^- (14.4 mg, 12.8 μmol) and **12** (71 mg, 63.9 μmol) were dissolvend in $CDCl_3$ (0.6 mL). The resulting suspension was sonicated for 3 min and stirred until a clear solution was formed (typically 48-72 h). The resulting solution was analyzed by ^{1}H NMR spectroscopy.

***In situ* unidirectional transport of the macrocycle 12:**

Under Ar, a mixture of **10**·PF_6^- (36 mg, 32 μmol) and **12** (71 mg, 0.16 mmol) in $CDCl_3$ (1.5 mL) was sonicated for 3 min and stirred at room temperature until complete dissolution of the reagents and full complexation was observed by ^{1}H NMR. The resulting solution was cooled to 0 ºC and stirred for 1 h. To this solution were added a degassed solution of **11** (18 mg, 64 μmol) in $CDCl_3$ (100 μL) and a catalytic amount of DMAP. The solution was stirred at 0 ºC (typically 72 h) and then at room temperature (usually 24 h) until no signal of the vinyl sulfone moiety was observed by NMR. The resulting solution was allowed to warm up to room temperature and $MgBr_2$ (59 mg, 0.32 mmol) was added. The suspension was stirred for 48 h at room temperature. An aliquot of 0.6 mL was taken and filtered through a 0.22 μm filter before analysis.

Subsequently, to the remaining suspension (0.9 mL) was added Et_3N (26 μL, 0.19 mmol) was added and the mixture was stirred for 30 min at room temperature. The addition of Et_3N (26 μL, 0.19 mmol) was repeated and the mixture stirred additionally for 30 min. The mixture was filtered through a 0.22 μm filter before analysis.

The unidirectional transport process was monitored and analyzed by ^{1}H NMR and HRMS throughout the experiment.

2. Additional Supporting Figures

2.1. Additional stack plots and NMR spectra

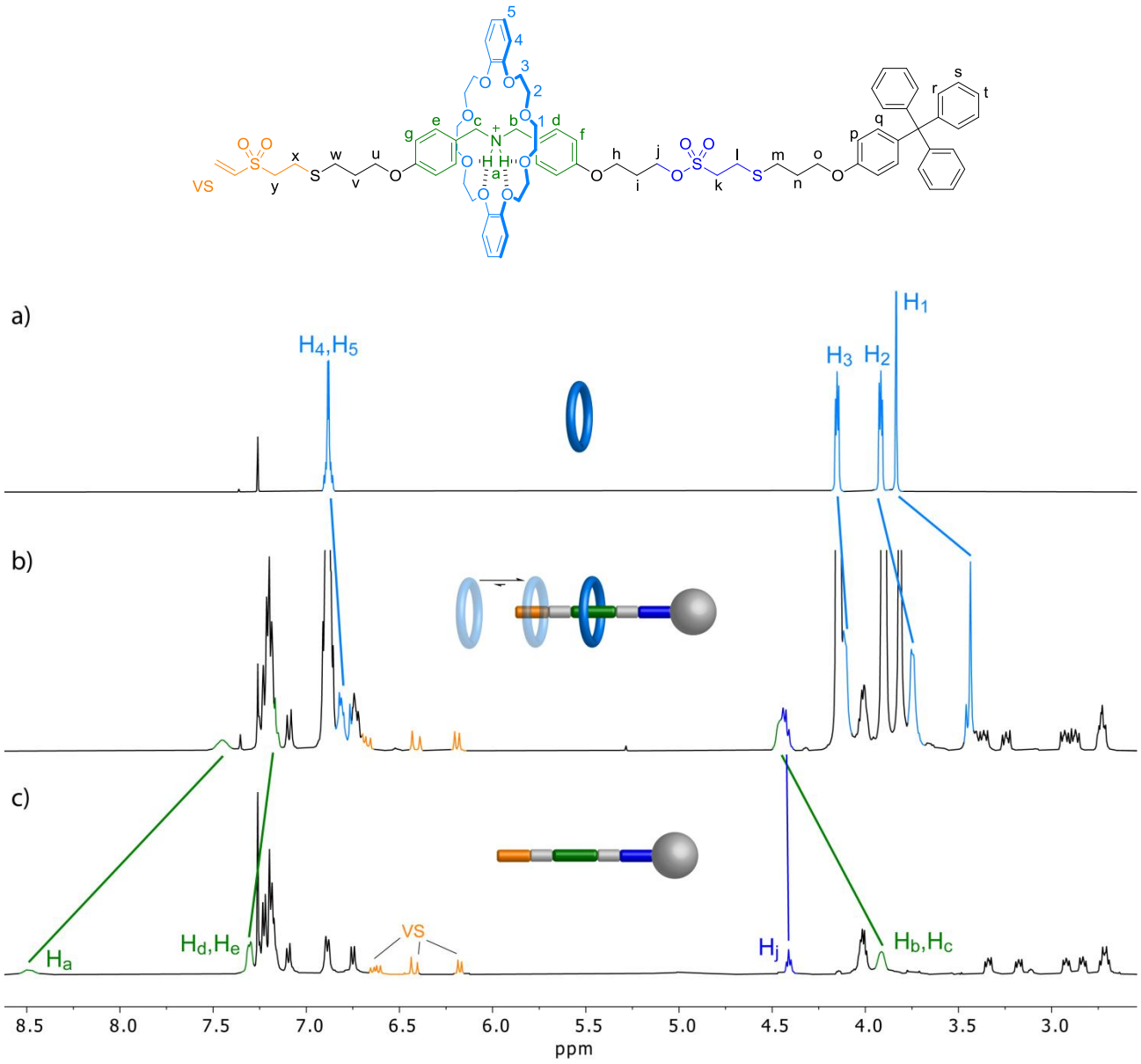


Figure S1: ^{1}H NMR ($CDCl_3$) spectrum of: a) DB24C8 (500 MHz). b) Pseudorotaxane assembled from **10**·PF_6^- (*ca.* 20 mM) and **12** (5 equiv) (400 MHz). c) Thread **10**·PF_6^- (500 MHz). A comparison between spectra b and c shows that the signals of Hd and He (green signals at 7.3 ppm) in the free thread are no longer present in the pseudorotaxane, supporting full complexation between the dibenzylammonium derivative and DB24C8.

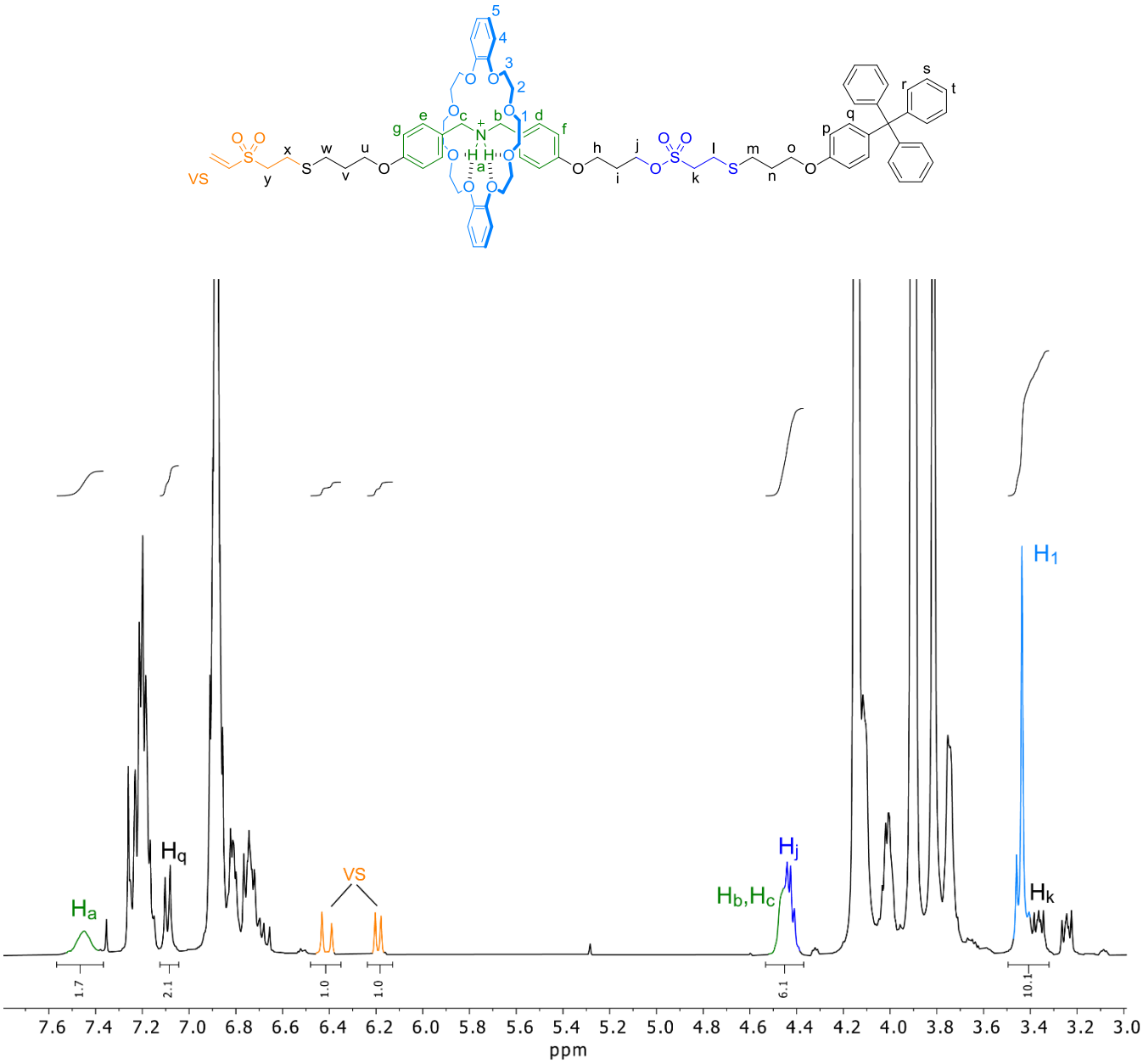


Figure S2: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of a mixture of thread **10**·PF_6^- (*ca.* 20 mM) and macrocycle **12** (5 equiv) showing the integration of the diagnostic signals that support the full complexation into the pseudorotaxane.

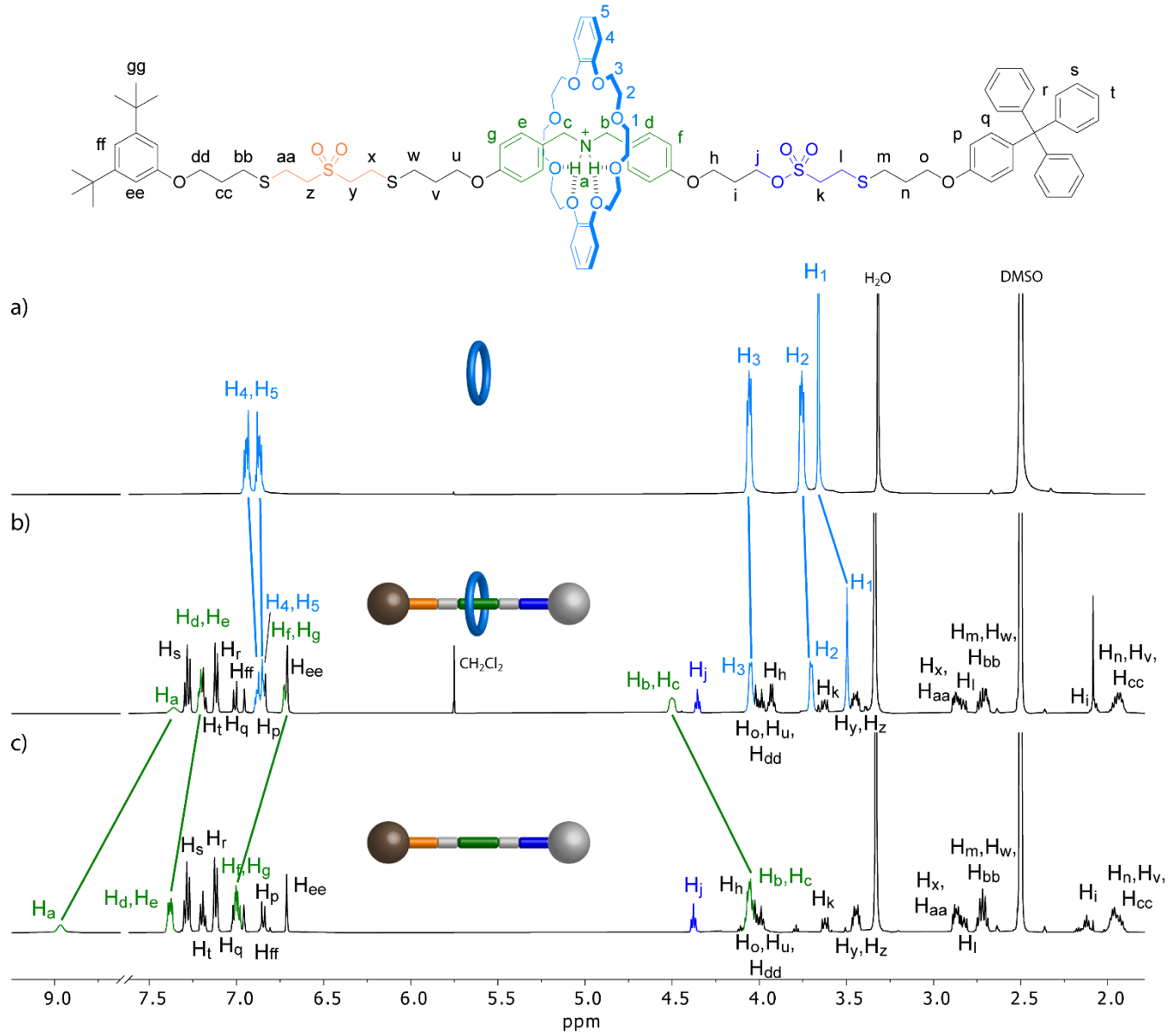


Figure S3: ^{1}H NMR (500 MHz, DMSO-d_6) spectra of: a) DB24C8. b) Rotaxane **13**·PF_6^-. c) Thread **10**·PF_6^-.

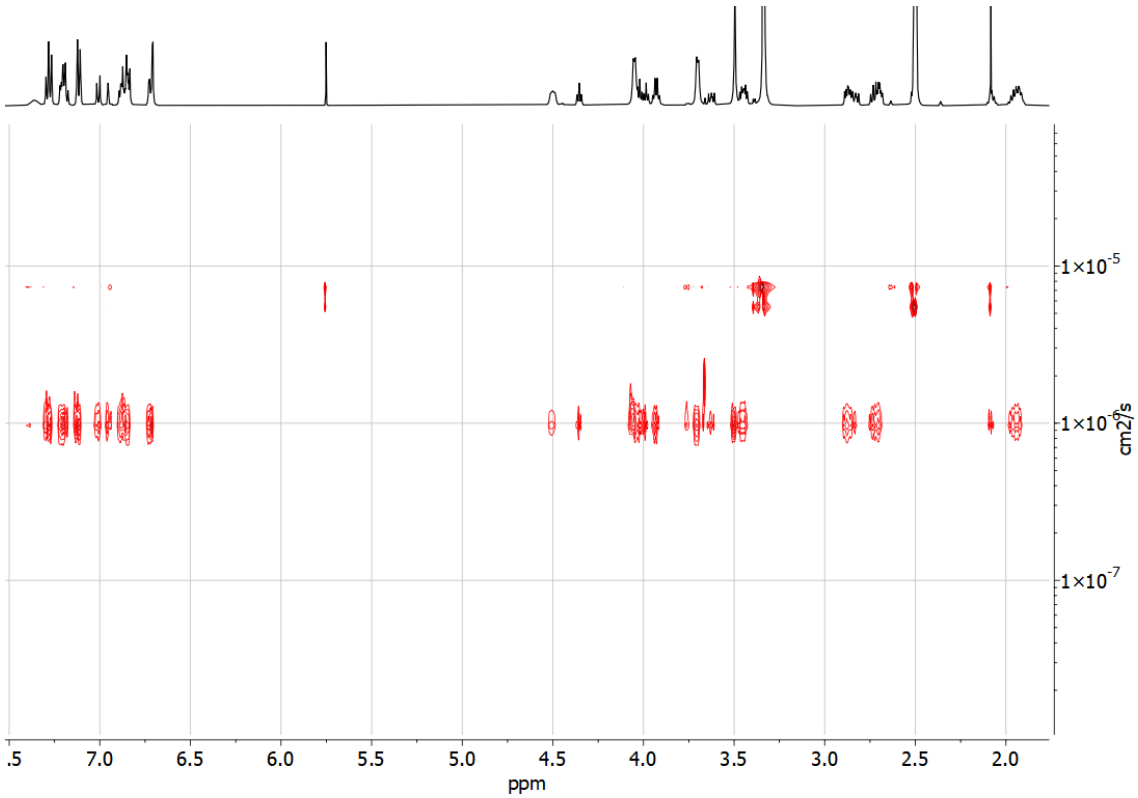


Figure S4: DOSY NMR (500 MHz, DMSO-d_6) experiment of rotaxane **13**·PF_6^-.

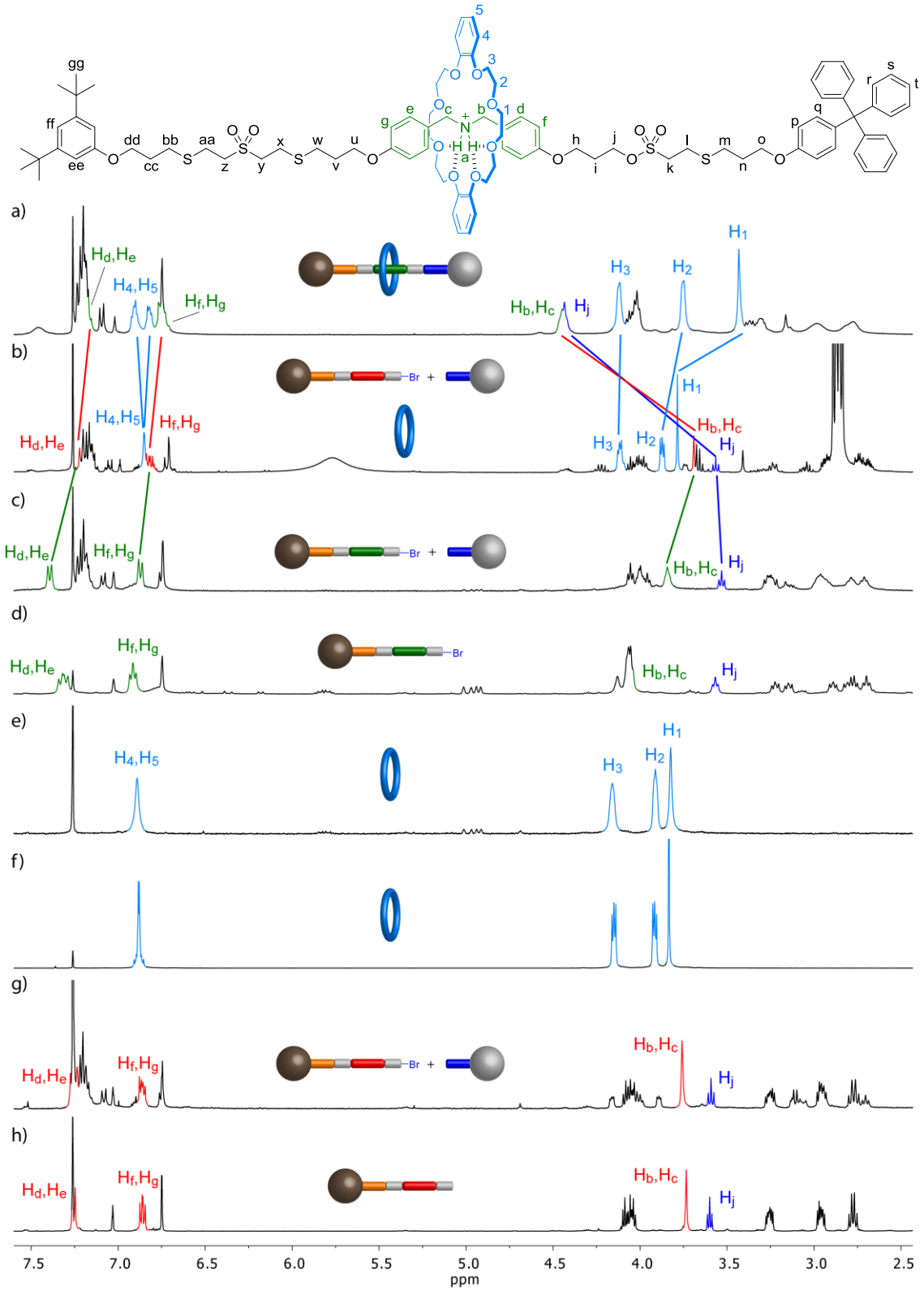


Figure S5: Cleavage and disassembly of rotaxane **13**·PF_6^-. a-g) ^{1}H NMR (400 MHz, $CDCl_3$) spectra of: a) Rotaxane **13**·PF_6^-. b) Crude mixture of the reaction of rotaxane **13**·PF_6^- with $MgBr_2$ after the addition of Et_3N. c) 1:1 mixture of **14**-H^+ and stopper **15** obtained after purification.* d) Compound **14**-H^+·PF_6^-. e) Macrocycle **12** obtained purification. f) Macrocycle **12**. g) Mixture of **14** and stopper **15** obtained after purification and treatment with DOWEX 550A (OH^-) resin. h) ^{1}H NMR (500 MHz, $CDCl_3$) spectra of compound **14**.

* As seen in the ^{1}H NMR spectrum, the cleaved thread is isolated in fact in its protonated form (**14**-H^+) after removal under reduced pressure of the solvents and, therefore, triethylamine and gel permeation chromatography (Figure S5c). This counterintuitive result can be explained by the acid-base equilibrium being displaced towards the protonated dibenzylammonium motif upon removal of the amine base under vacuum.[S5] In this way, we repeated the cleavage following the same procedure but with an additional treatment of the mixture with an OH^- ion exchange resin, resulting in the isolation of a mixture of deprotonated **14** and **15** (Figure S5g).

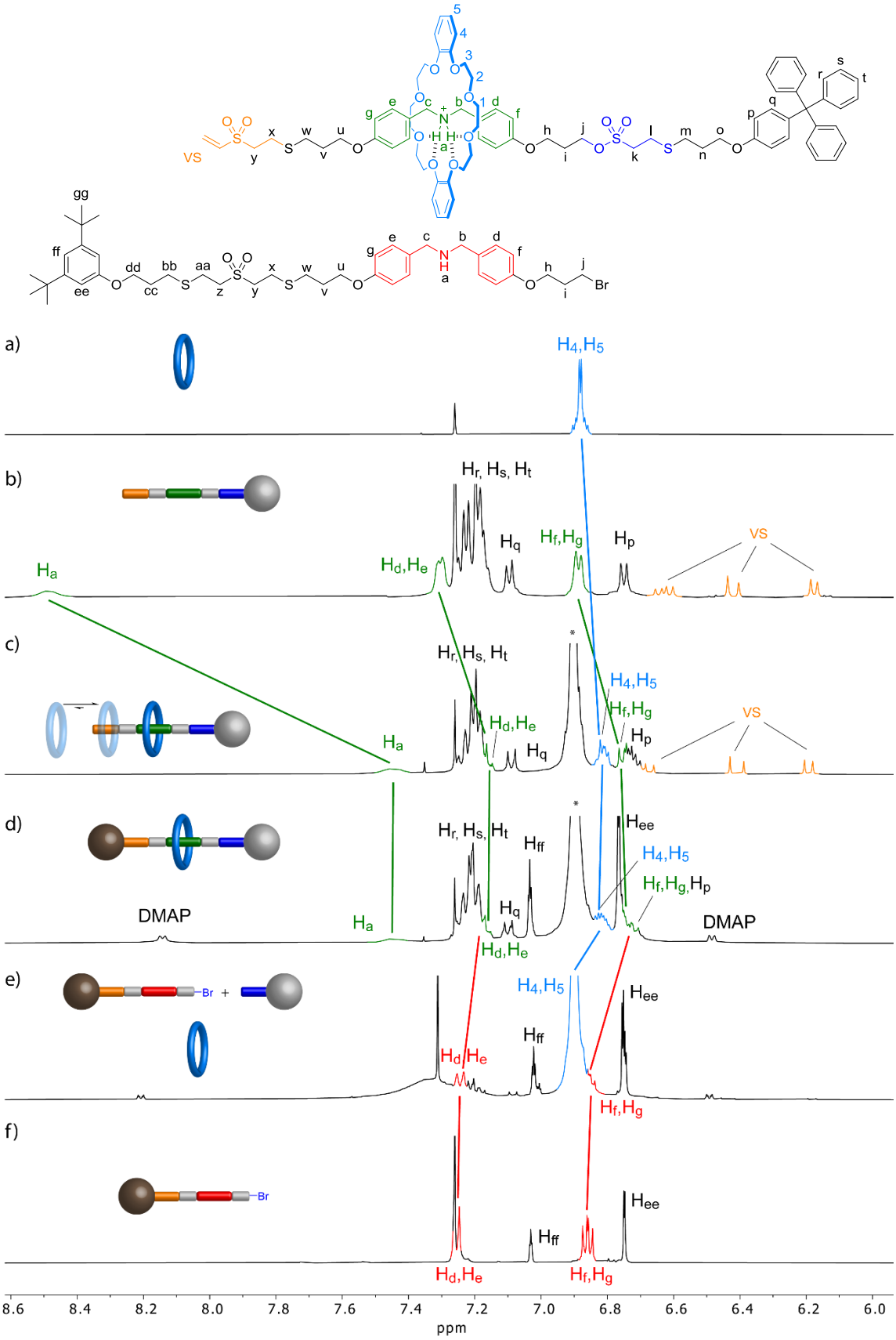


Figure S6: *In situ* unidirectional transport experiment of macrocycle **12**. Partial ^{1}H NMR ($CDCl_3$) spectra of: a) Macrocycle **12** (500 MHz). b) Thread precursor **10**·PF_6^- (500 MHz). c) Mixture of **10**·PF_6^- (21 mM) and **12** (5 equiv) (400 MHz). d) Mixture c 96 h after the addition of stopper **11** and $DMAP_{(cat)}$ (400 MHz). e) Mixture d stirred for 48 h in the presence of $MgBr_2$ and for additional 60 min after the addition of Et_3N (400 MHz). g) **14** (500 MHz). The signal marked with an asterisk correspond to the excess of DB24C8

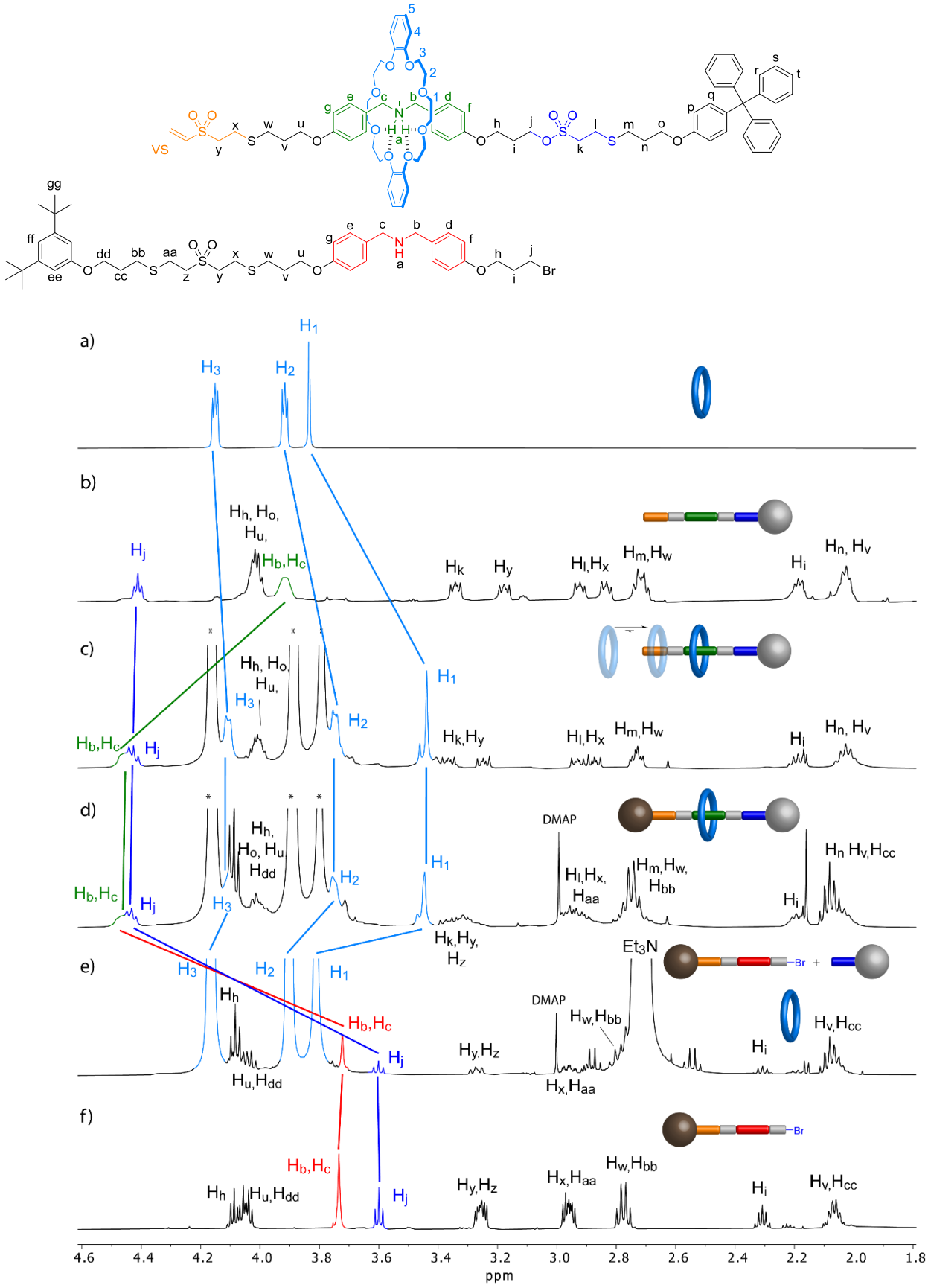


Figure S7: *In situ* unidirectional transport experiment of macrocycle **12**. Partial ^{1}H NMR ($CDCl_3$) spectra of: a) Macrocycle **12** (500 MHz). b) Thread precursor **10**·PF_6^- (500 MHz). c) Mixture of **10**·PF_6^- (21 mM) and **12** (5 equiv) (400 MHz). d) Mixture c 96 h after the addition of stopper **11** and $DMAP_{(cat)}$ (400 MHz). e) Mixture d stirred for 48 h in the presence of $MgBr_2$ and for additional 60 min after the addition of Et_3N (400 MHz). g) **14** (500 MHz). The signals marked with an asterisk correspond to the excess of DB24C8

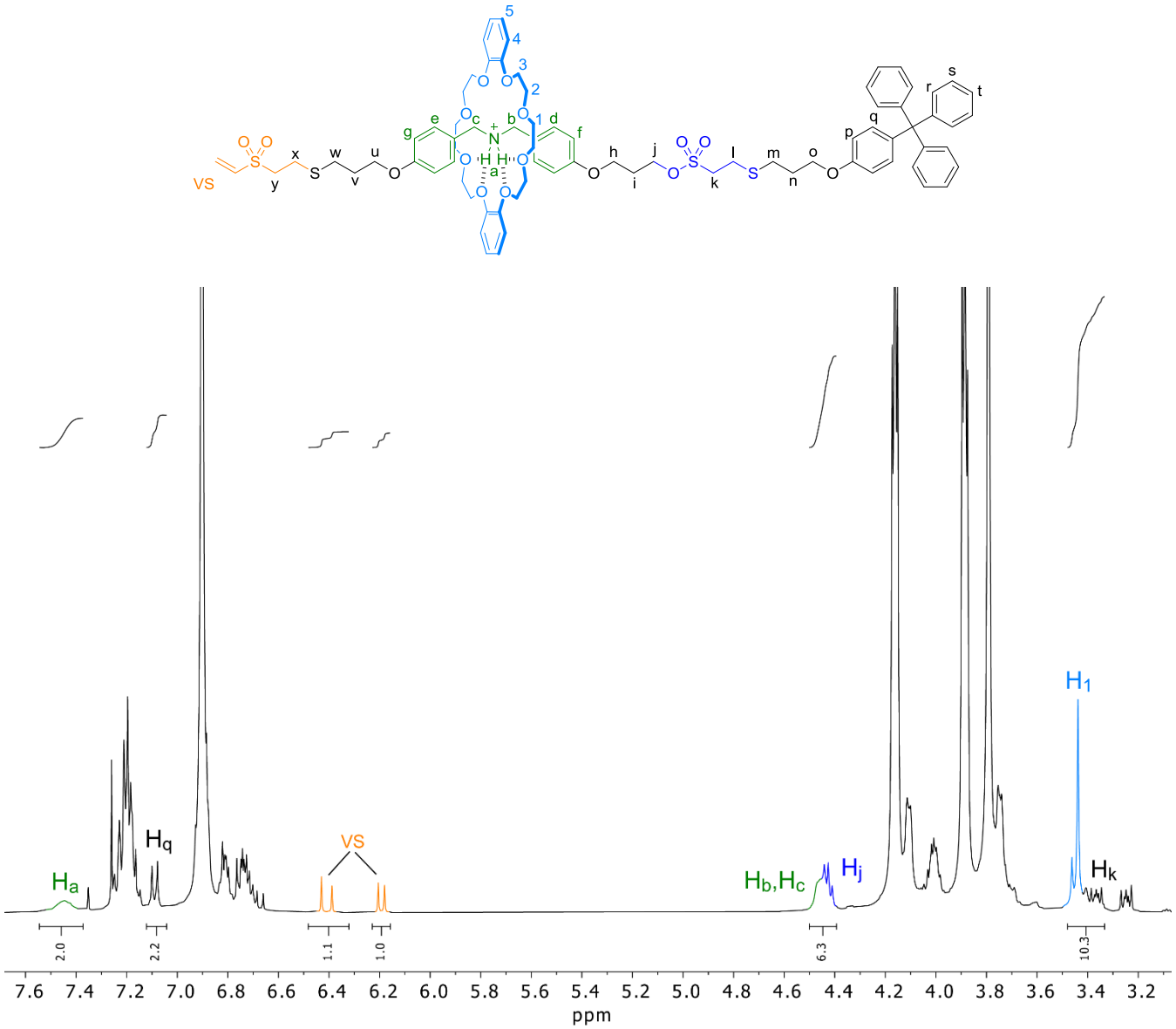


Figure S8: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of the *in situ* unidirectional transport experiment after stirring a mixture of **10**·PF_6^- (*ca.* 20 mM) and macrocycle **12** (5 equiv) for showing the integration of the diagnostic signals that support the full complexation into the pseudorotaxane.

2.2. HRMS spectra of the unidirectional transport process

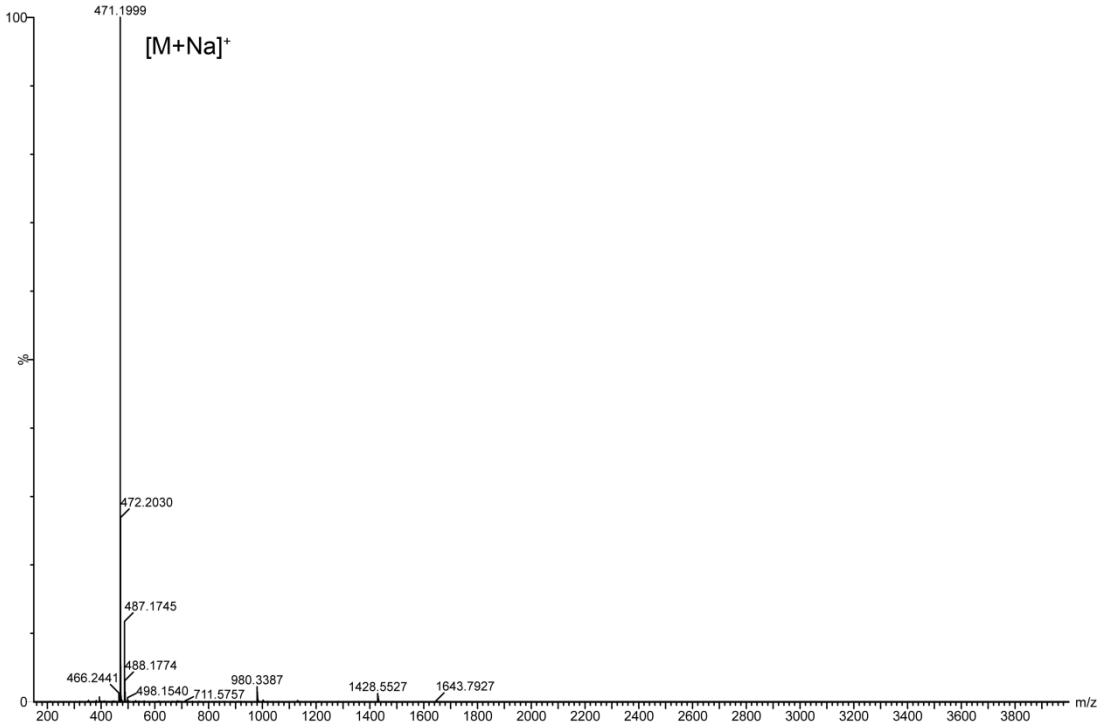


Figure S9: HRMS (ESI^+) spectrum of the *in situ* unidirectional transport experiment of macrocycle **12** after stirring **10**·PF_6^- and **12** for 72 h, showing the signal corresponding to macrocycle **12**: *m/z*: 471.1999 $[M+Na]^+$ (calcd for $C_{24}H_{32}NaO_8$: 471.1995).

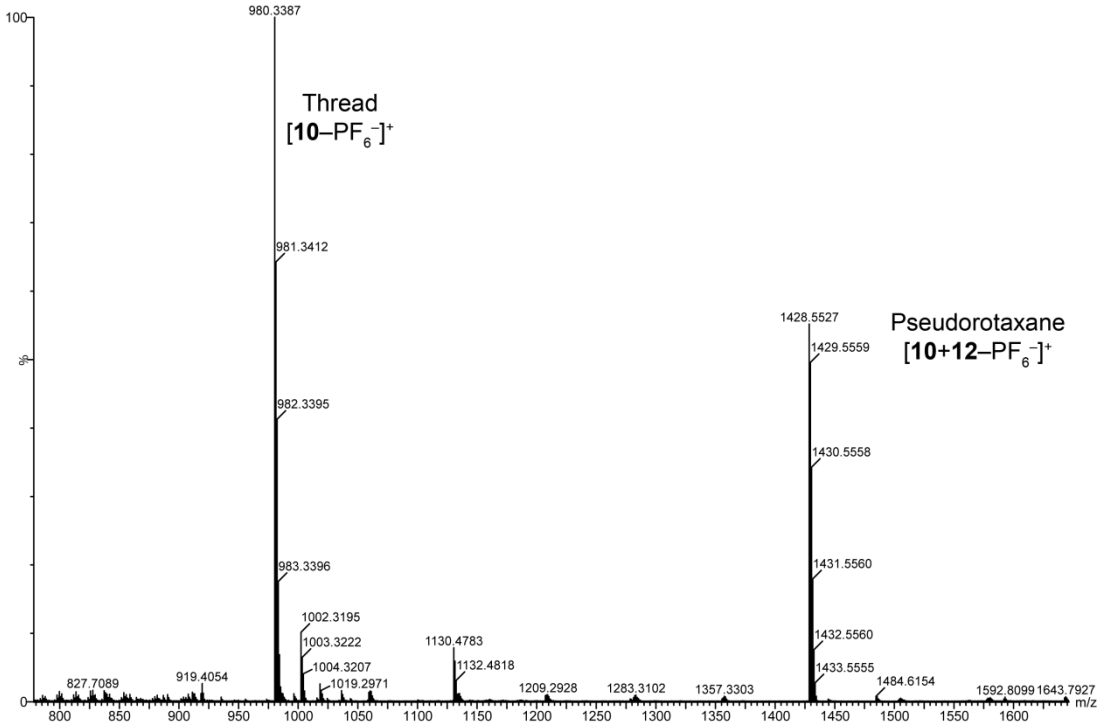


Figure S10: HRMS (ESI^+) spectrum of the *in situ* unidirectional transport experiment of macrocycle **12** after stirring **10**·PF_6^- and **12** for 72 h, showing a peak corresponding to thread **10**·PF_6^-: *m/z*: 980.3387 $[M–PF_6^-]^+$ (calcd for $C_{54}H_{62}NO_8S_4$: 980.3358) and pseudorotaxane **10**+**12**·PF_6^-: *m/z*: 1428.5527 $[M–PF_6^-]^+$ (calcd for $C_{78}H_{94}NO_{16}S_4$: 1428.5455).

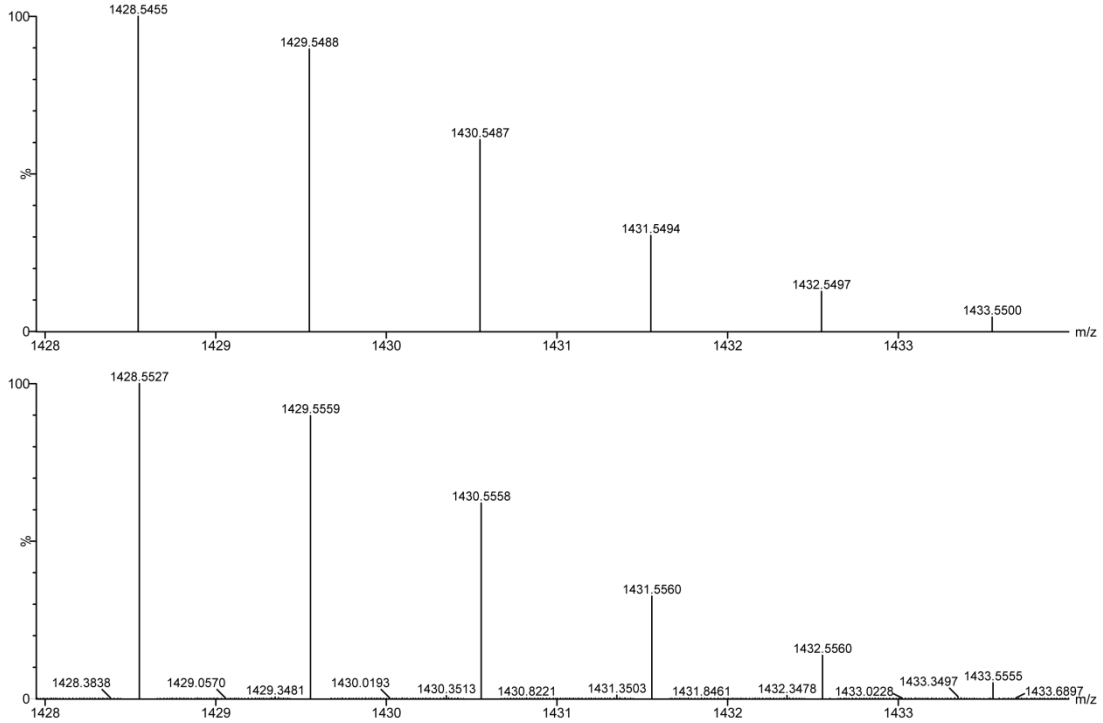


Figure S11: Experimental (bottom) and theoretical (top) isotopic distribution for the $[M–PF_6^–]^+$ ion of pseudorotaxane **10**+**12**·$PF_6^–$ obtained during the *in situ* unidirectional transport experiment.

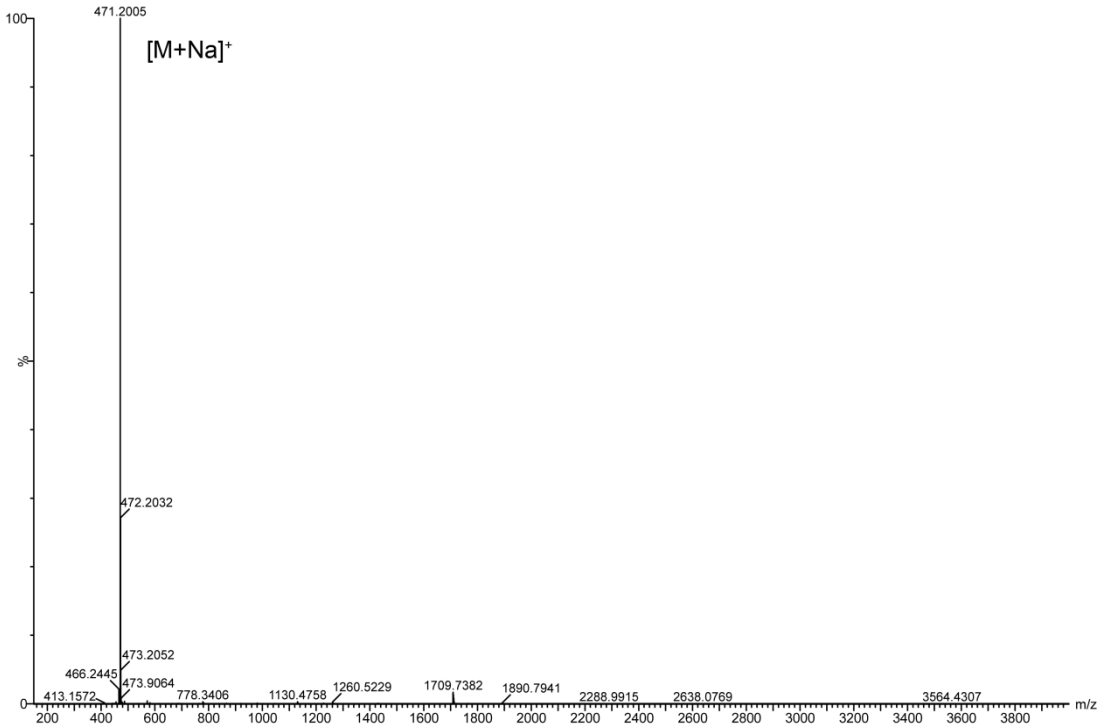


Figure S12: HRMS (ESI^+) spectrum of the *in situ* unidirectional transport experiment of macrocycle **12** 96 h after the addition of stopper **11** and DMAP, showing the peak corresponding to the excess macrocycle **12**: *m/z*: 471.2005 $[M+Na]^+$ (calcd for $C_{24}H_{32}NaO_8$: 471.1995).

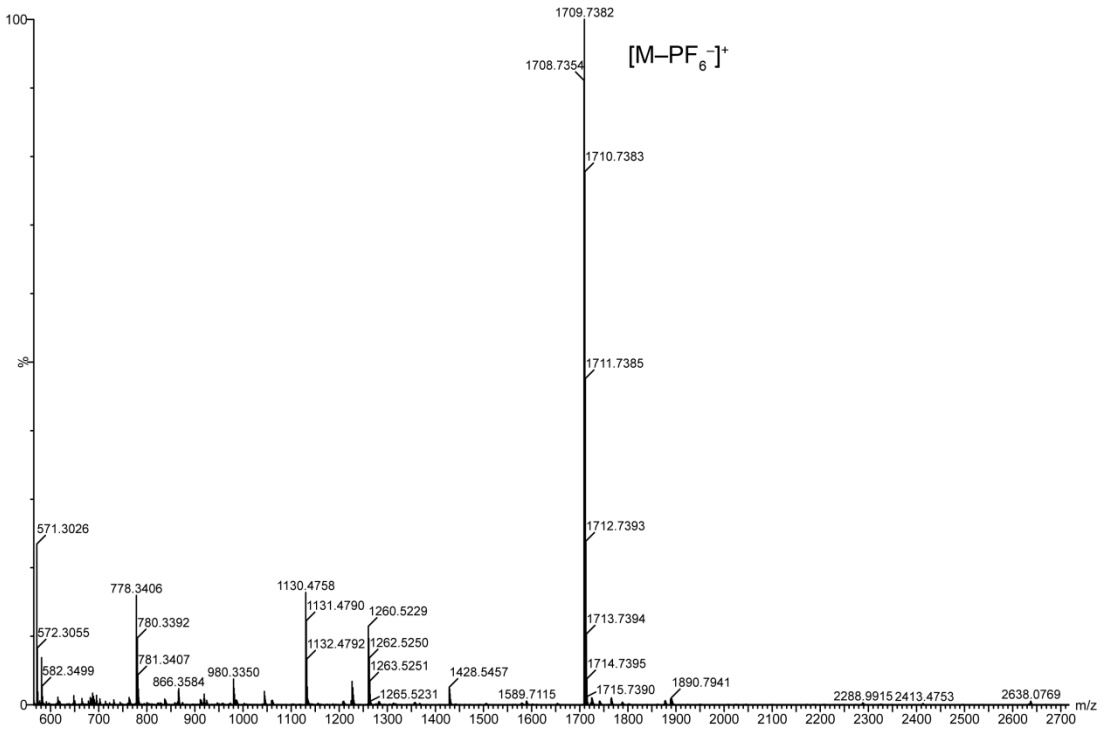


Figure S13: HRMS (ESI$^+$) spectrum of the *in situ* unidirectional transport experiment of macrocycle **12** 96 h after the addition of stopper **11** and DMAP, showing the signal corresponding to rotaxane **13**·PF_6^-: *m/z*: 1708.7354 $[M–PF_6^-]^+$ (calcd for $C_{95}H_{122}NO_{17}S_5$: 1708.7316).

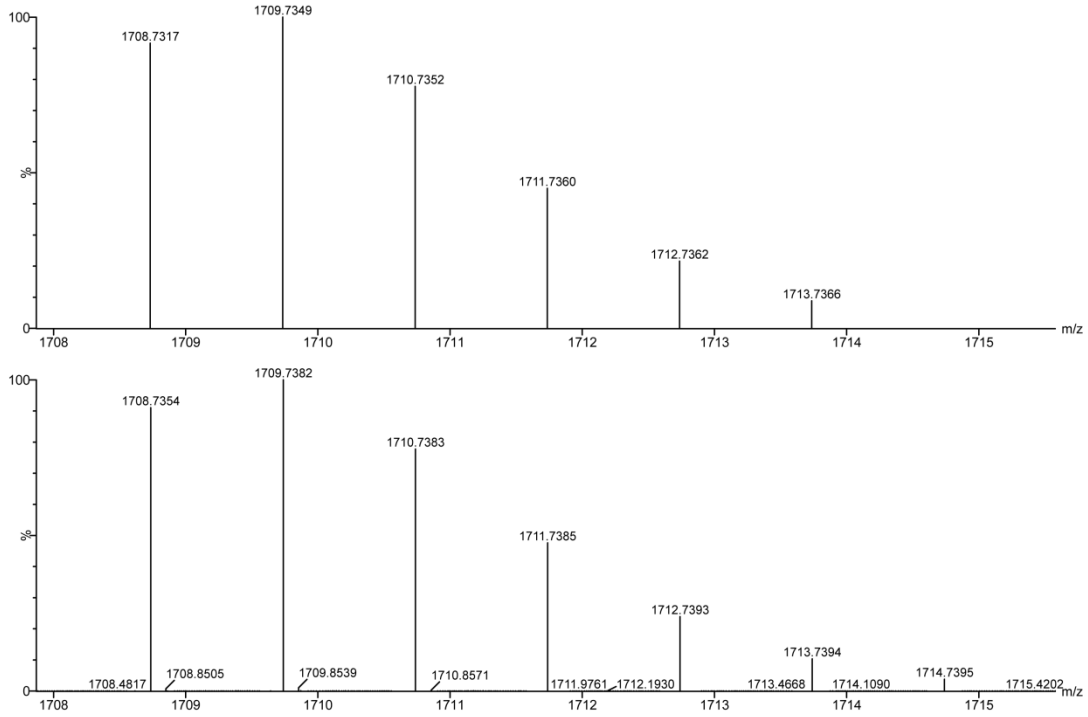


Figure S14: Experimental (bottom) and theoretical (top) isotopic distribution for the $[M–PF_6^-]^+$ ion of rotaxane **13**·PF_6^- obtained during the *in situ* unidirectional transport experiment.

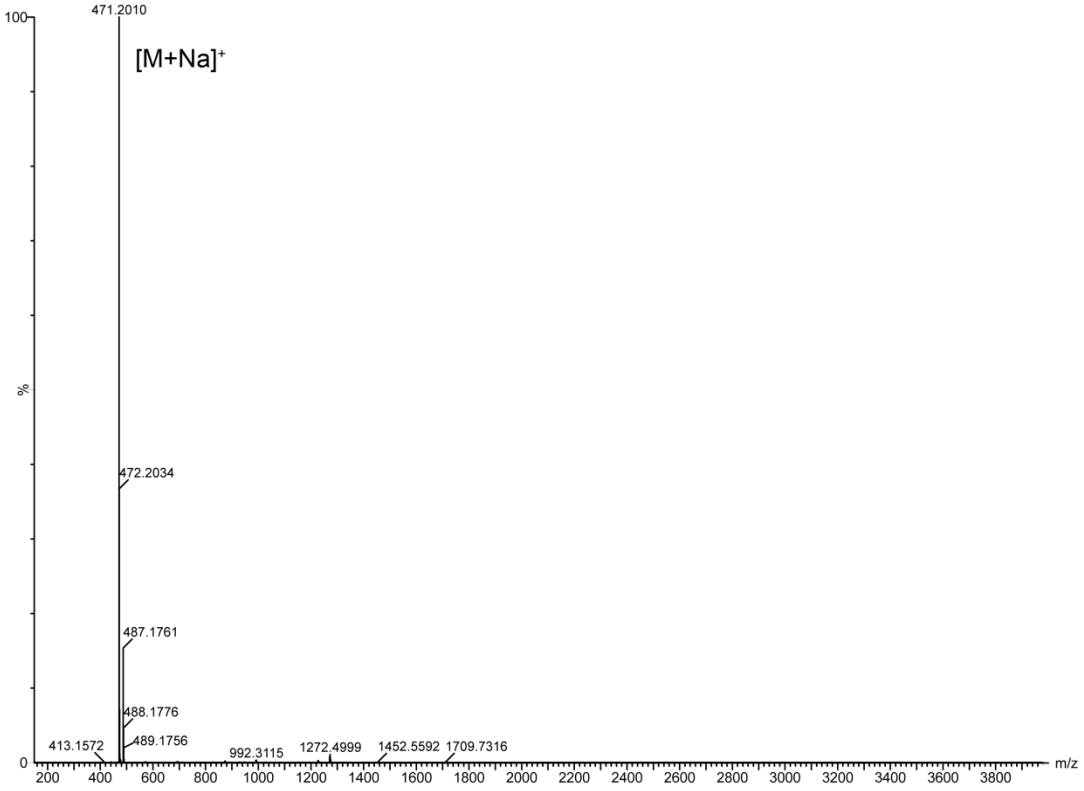


Figure S15: HRMS (ESI^+) spectrum of the *in situ* unidirectional transport experiment of macrocycle **12** 48 h after the addition of $MgBr_2$, showing the peak corresponding to the excess of macrocycle **12**: *m/z*: 471.2010 $[M+Na]^+$ (calcd for $C_{24}H_{32}NaO_8$: 471.1995).

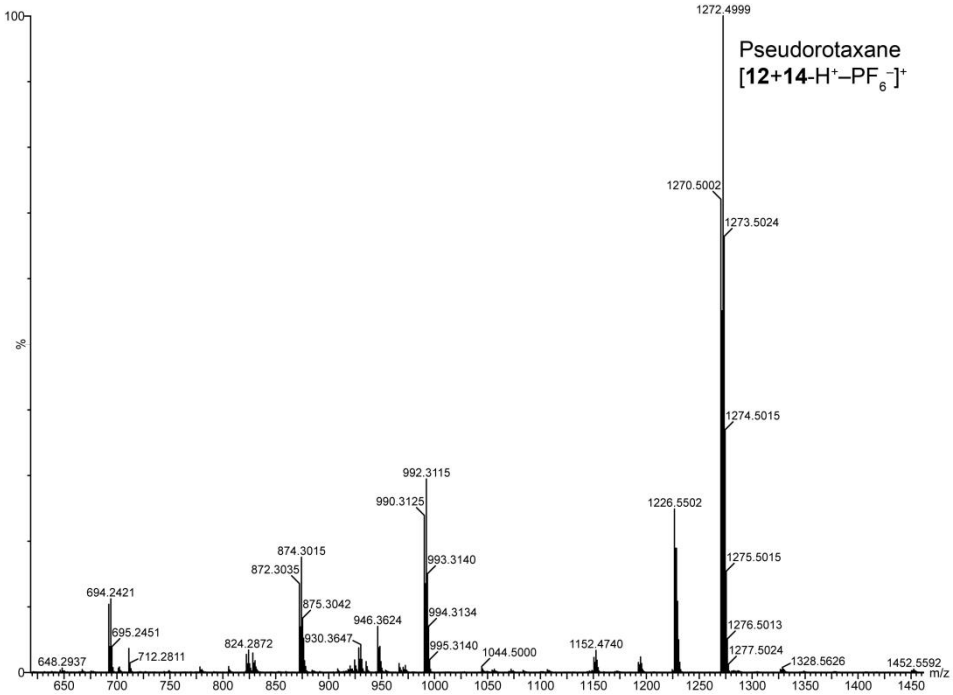


Figure S16: HRMS (ESI^+) spectrum of the *in situ* unidirectional transport experiment of macrocycle **12** 48 h after the addition of $MgBr_2$, showing a peak corresponding to pseudorotaxane **12**+**14**-$H^+ \cdot PF_6^-$: *m/z*: 1270.5002 $[M–PF_6^-]^+$ (calcd for $C_{65}H_{93}NBrO_{13}S_3$: 1270.4992).

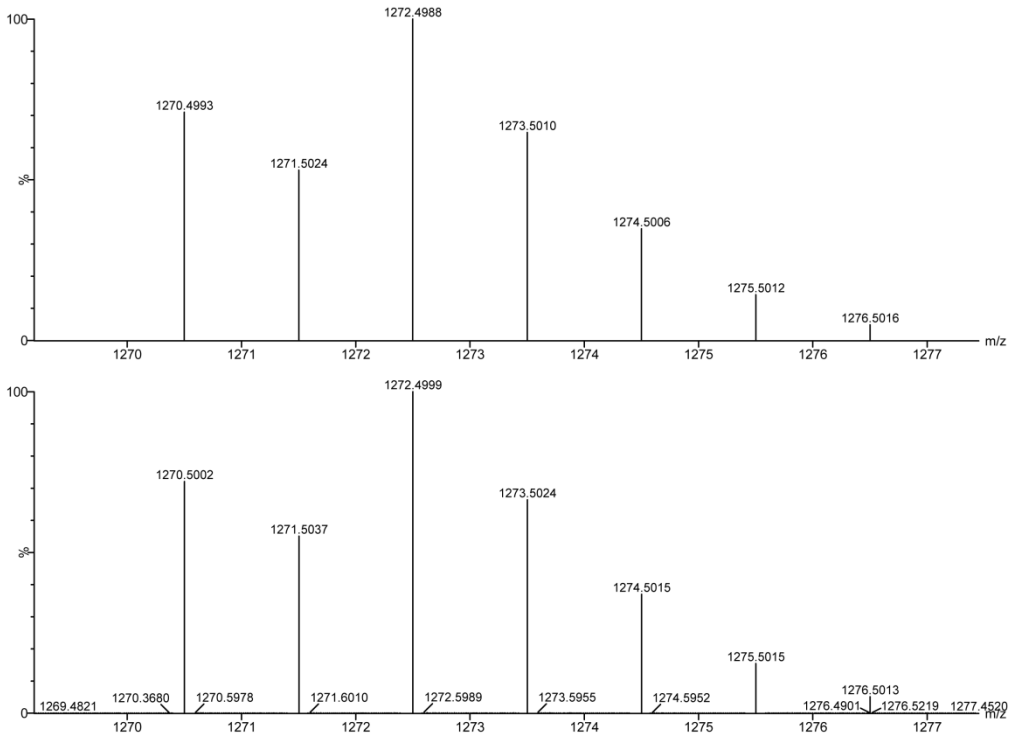


Figure S17: Experimental (bottom) and theoretical (top) isotopic distribution for the $[M–PF_6^-]^+$ ion of pseudorotaxane **12**+**14**-$H^+ \cdot PF_6^-$ obtained during the *in situ* unidirectional transport experiment.

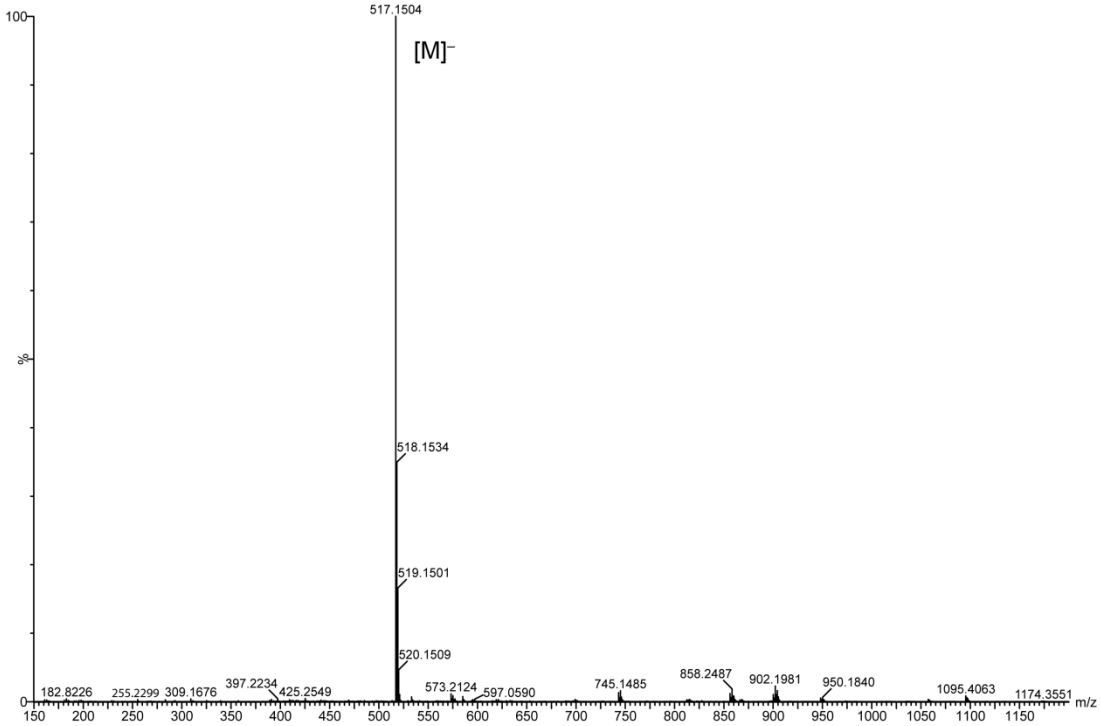


Figure S18: HRMS (ESI^-) spectrum of the *in situ* unidirectional transport experiment of macrocycle **12** 48 h after the addition of $MgBr_2$, showing the signal corresponding to stopper **15**: *m/z*: 517.1504 $[M]^-$ (calcd for $C_{30}H_{29}O_4S_2$: 517.1507).

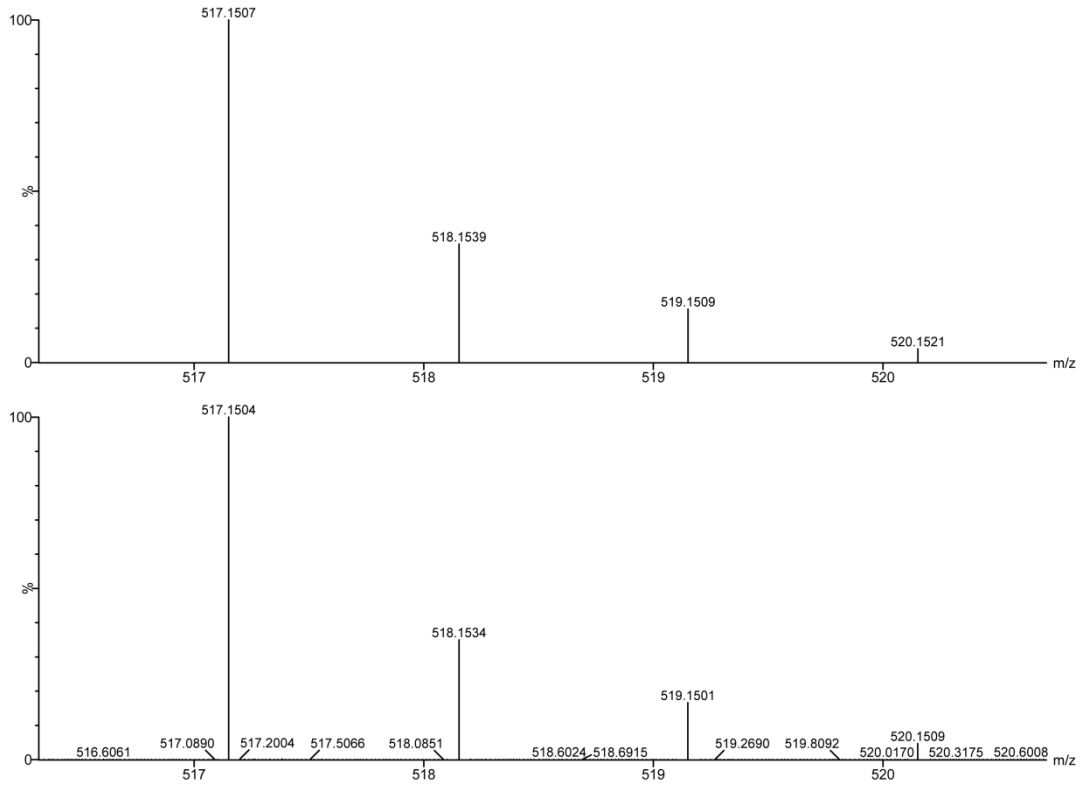


Figure S19: Experimental (bottom) and theoretical (top) isotopic distribution for the $[M]^-$ ion of stopper **15** obtained during the *in situ* unidirectional transport experiment.

3. NMR spectra of new compounds

Compound S4:

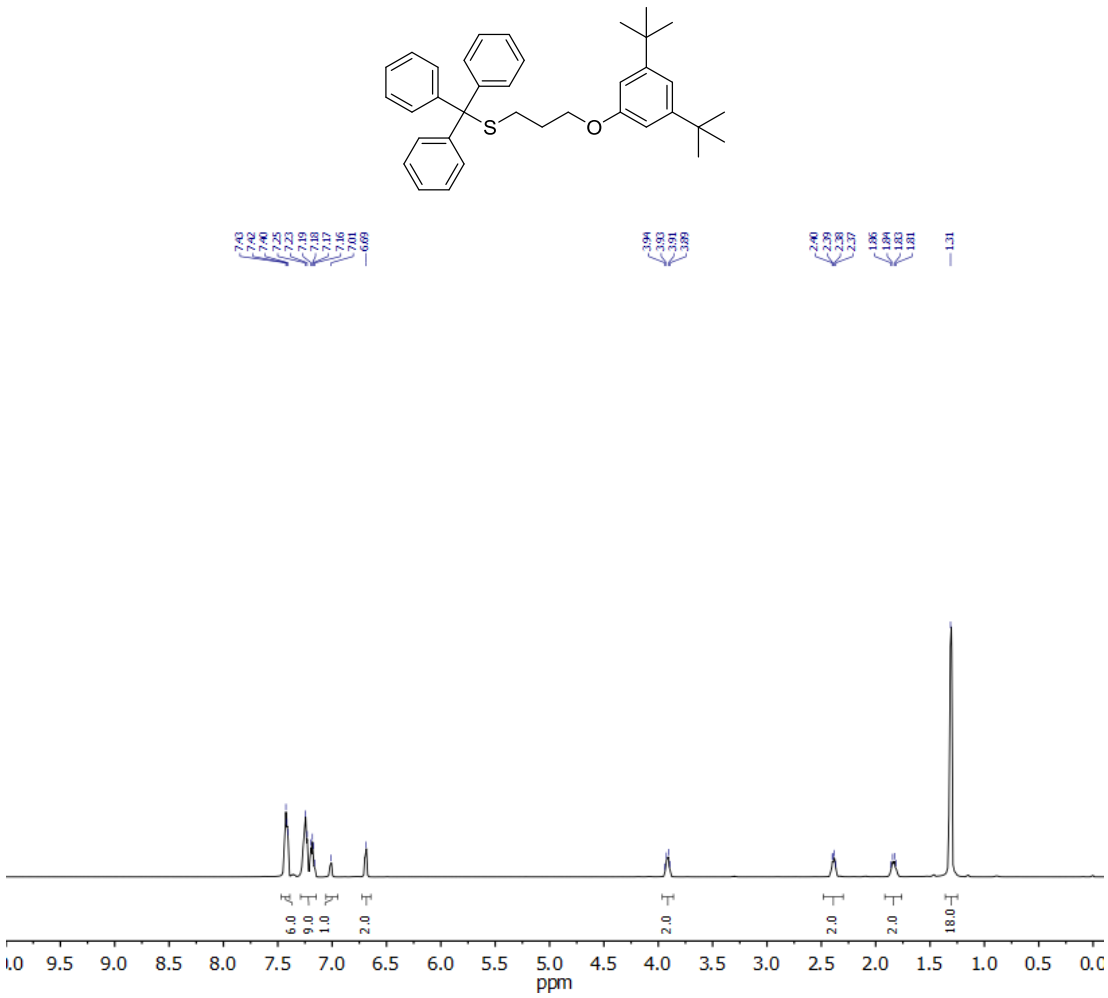


Figure S20: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **S4**.

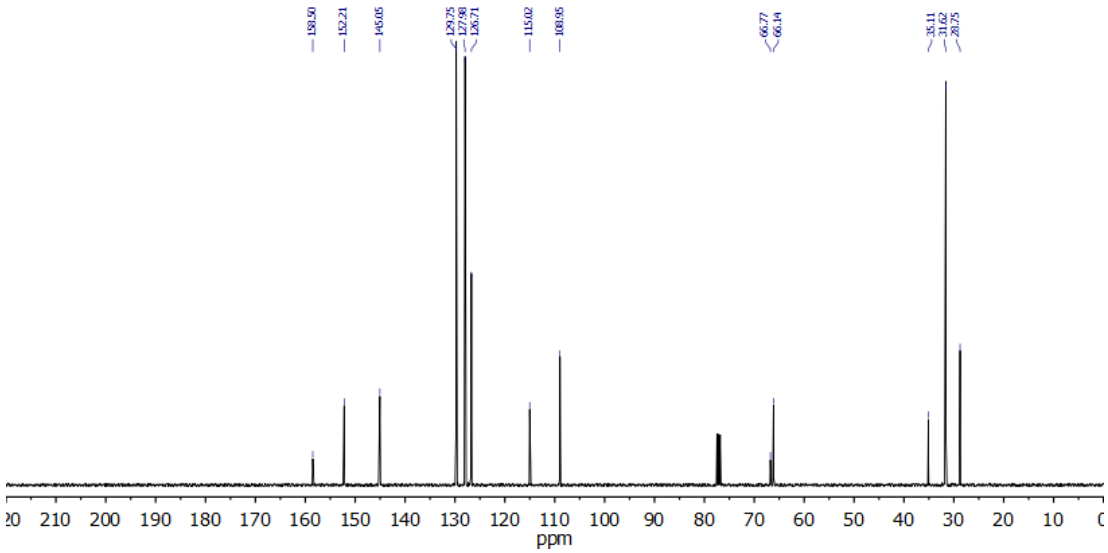


Figure S21: ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **S4**.

Compound 11:

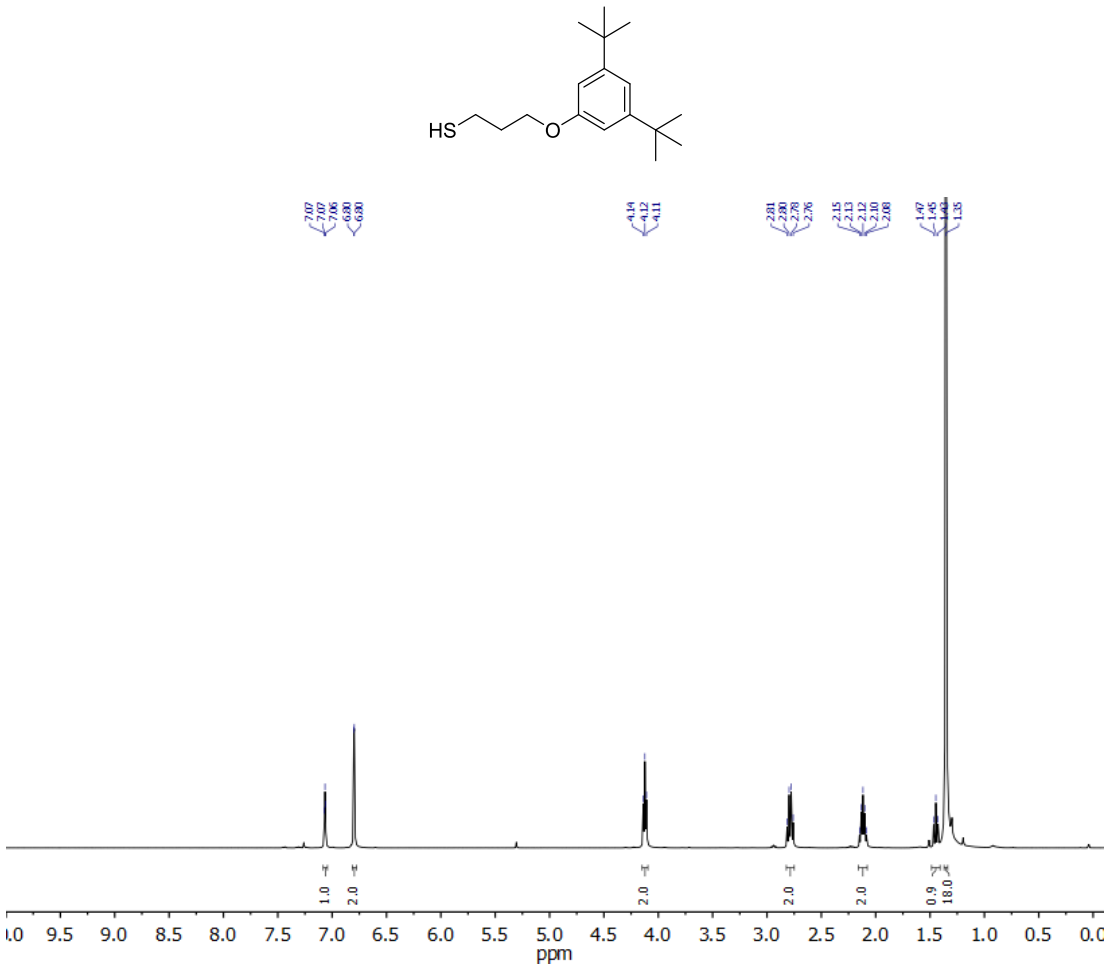


Figure S22: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **11**.

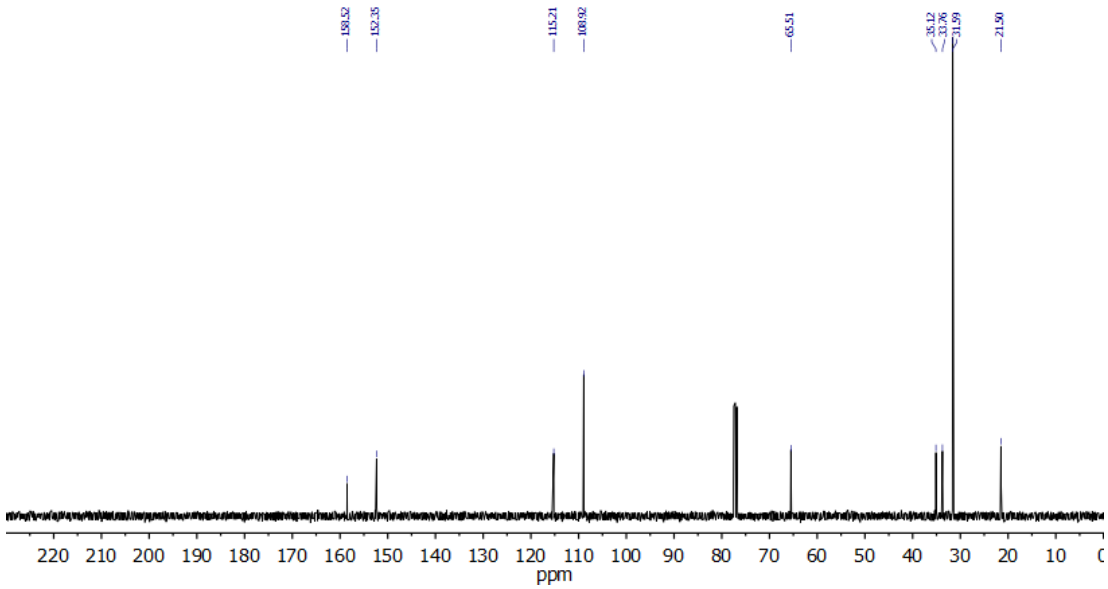


Figure S23: ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **11**.

Compound 2:

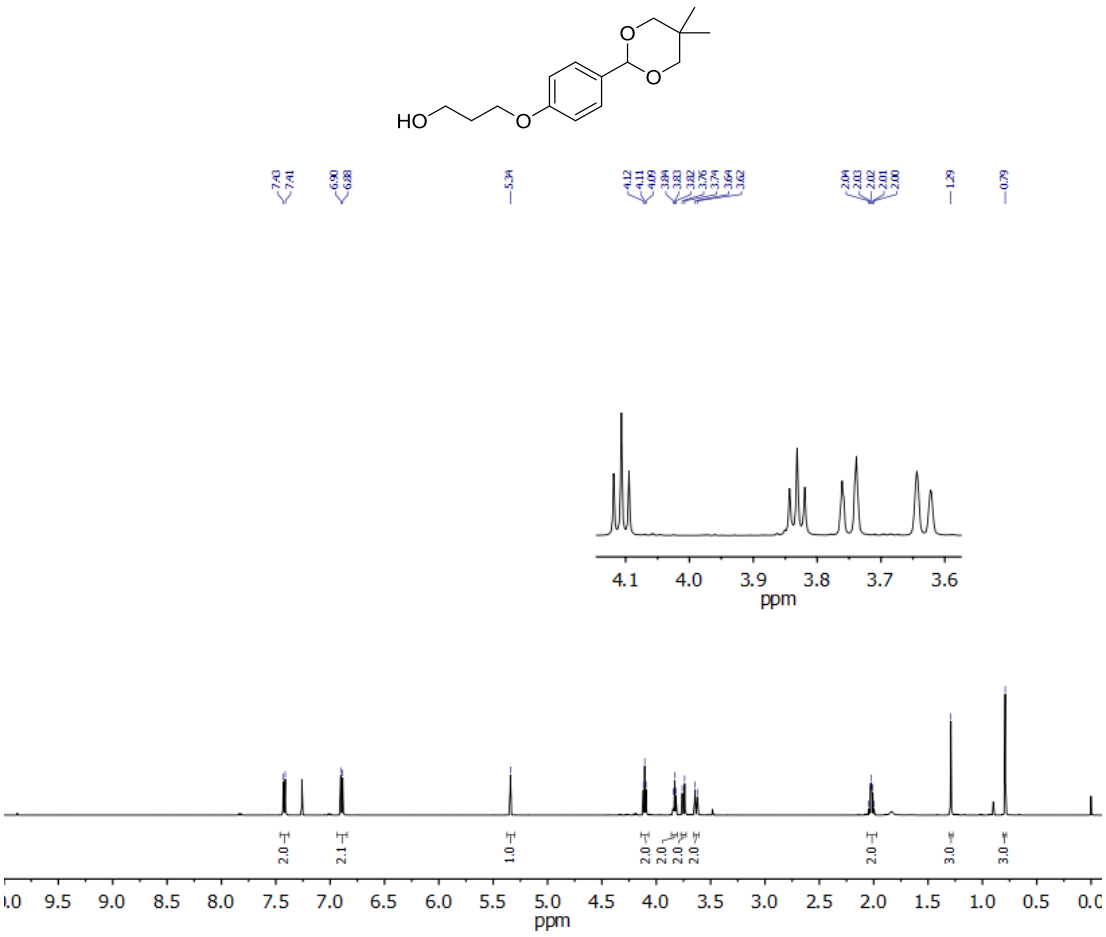


Figure S24: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2**.

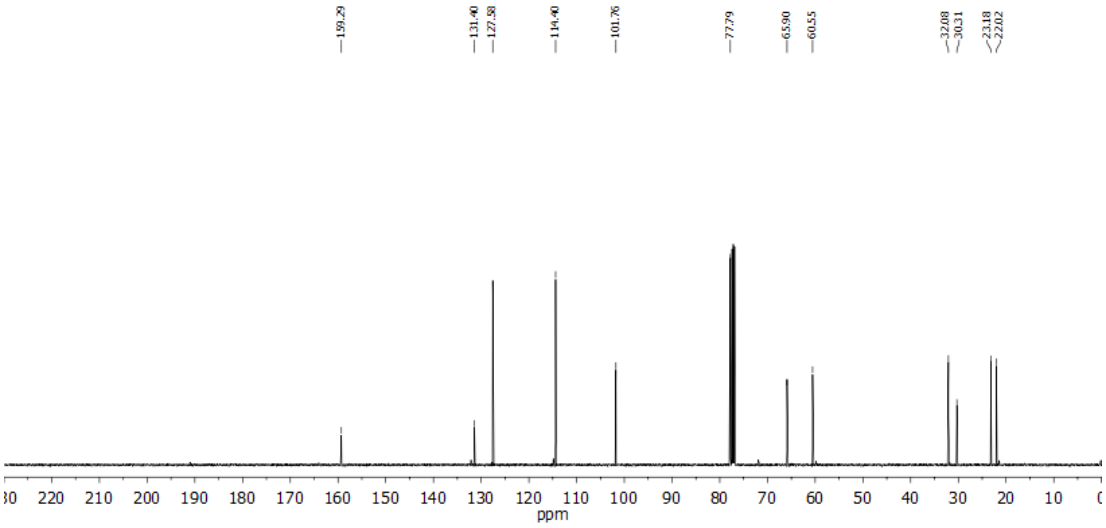


Figure S25: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **2**.

Compound 3:

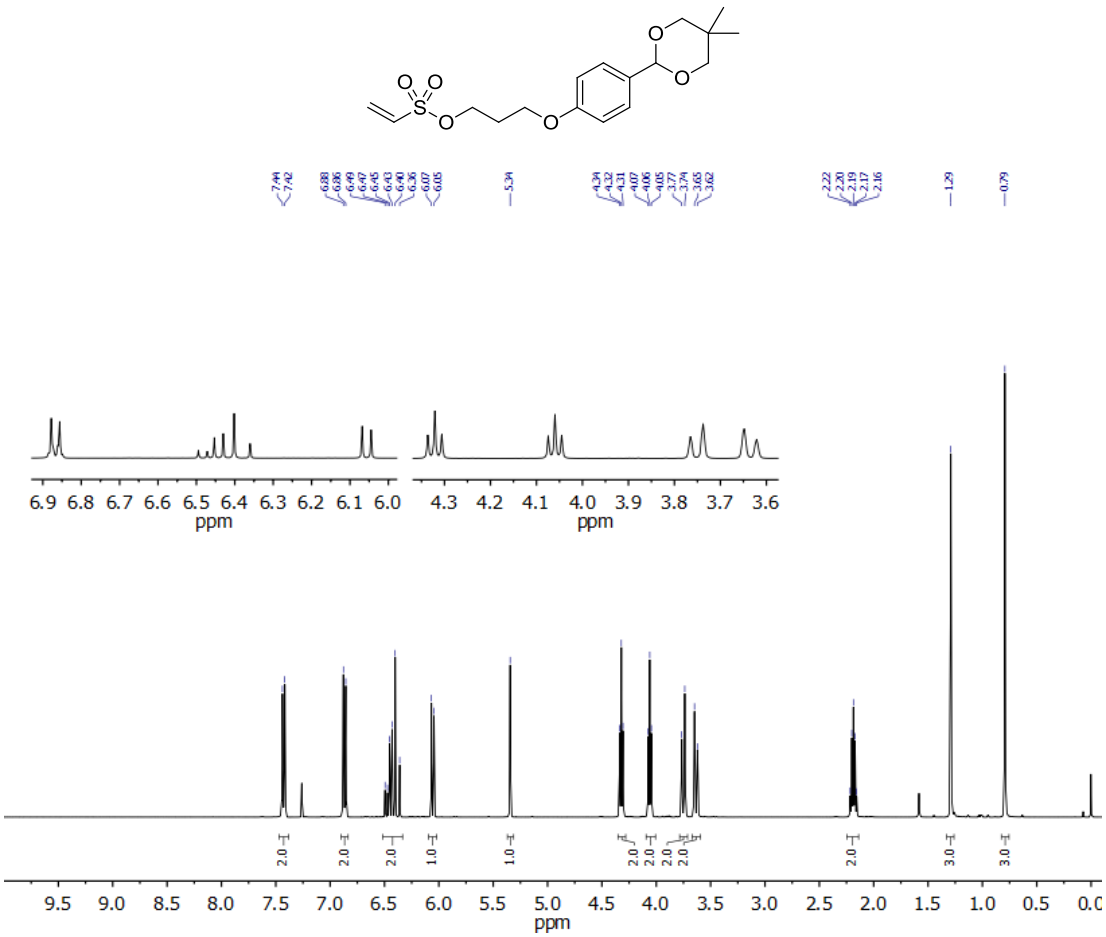


Figure S26: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3**.

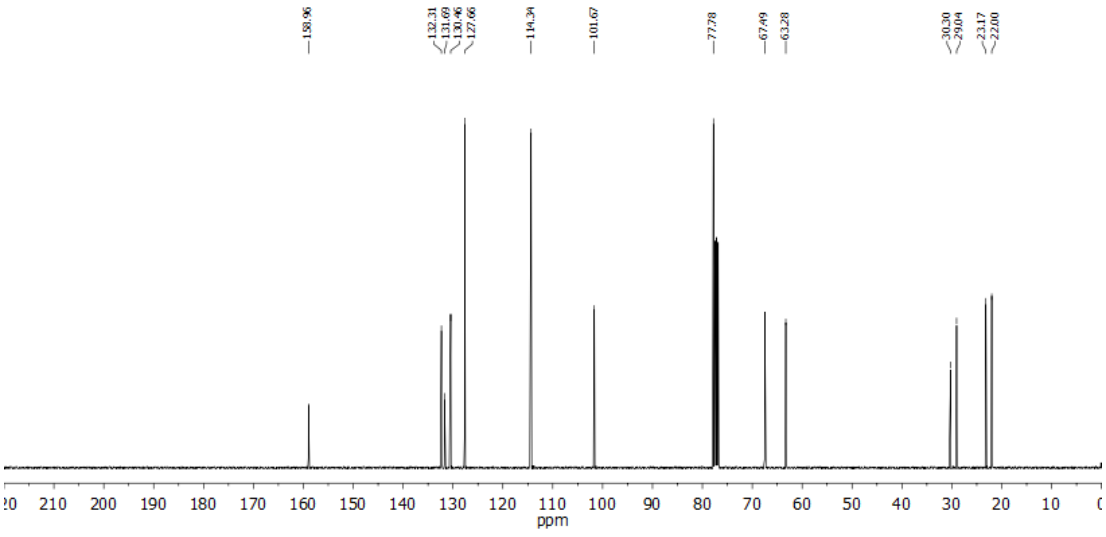


Figure S27: ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **3**.

Compound 5:

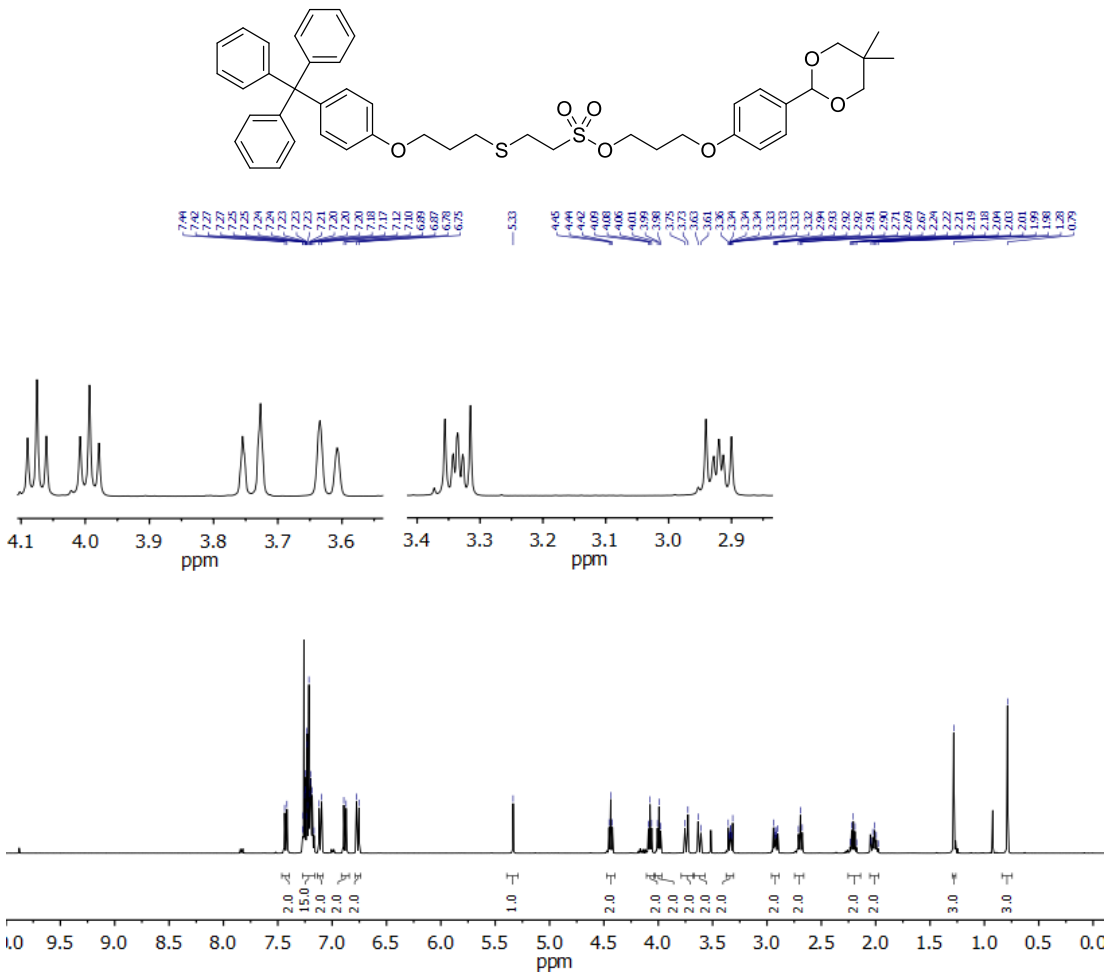


Figure S28: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5**.

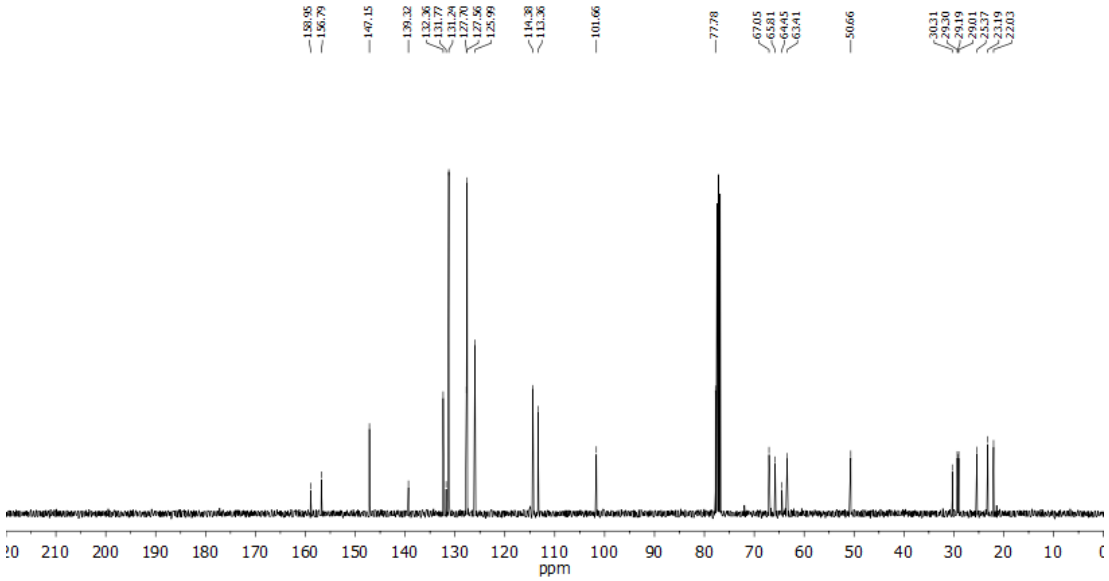


Figure S29: ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **5**.

Compound 6:

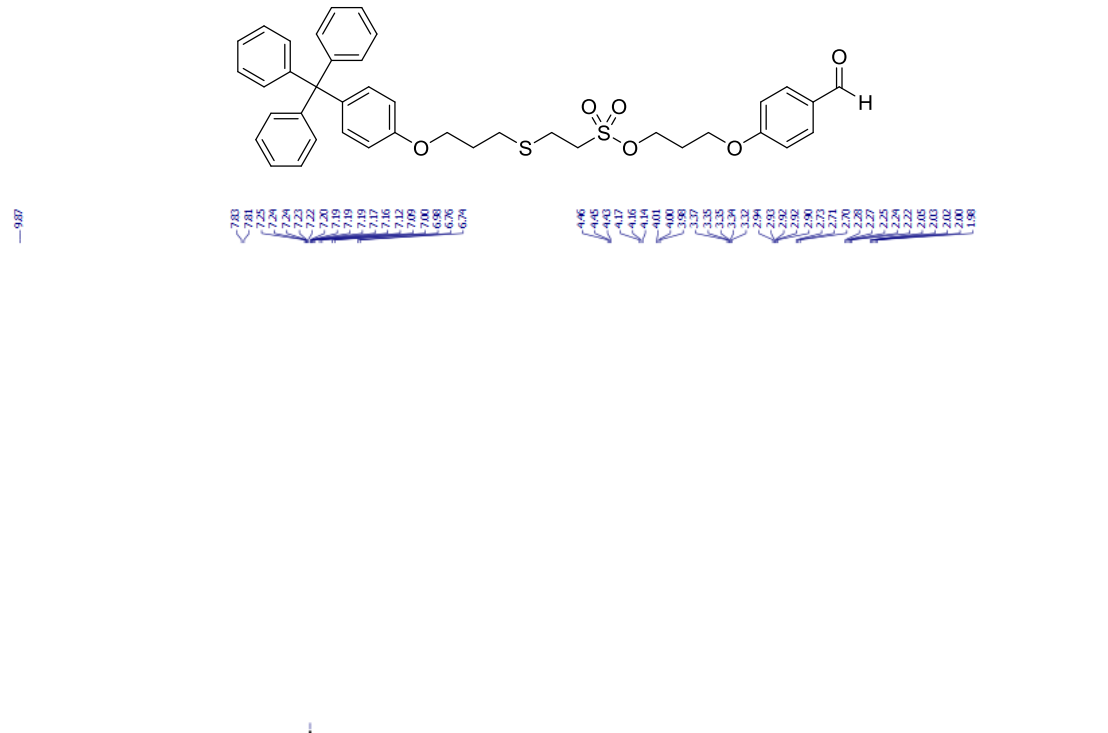


Figure S30: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **6**.

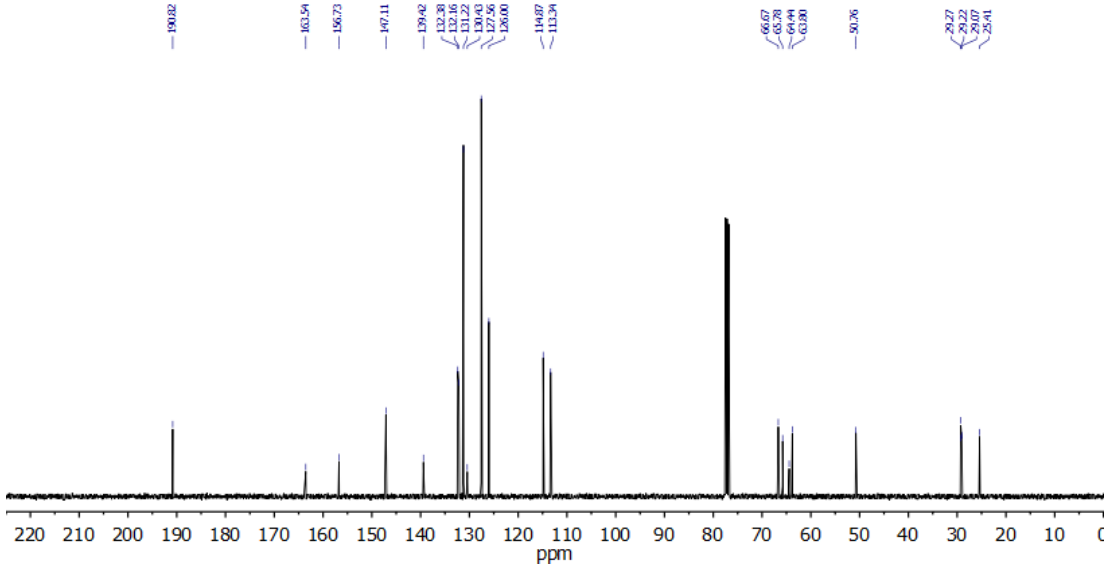


Figure S31: ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **6**.

Compound S7:

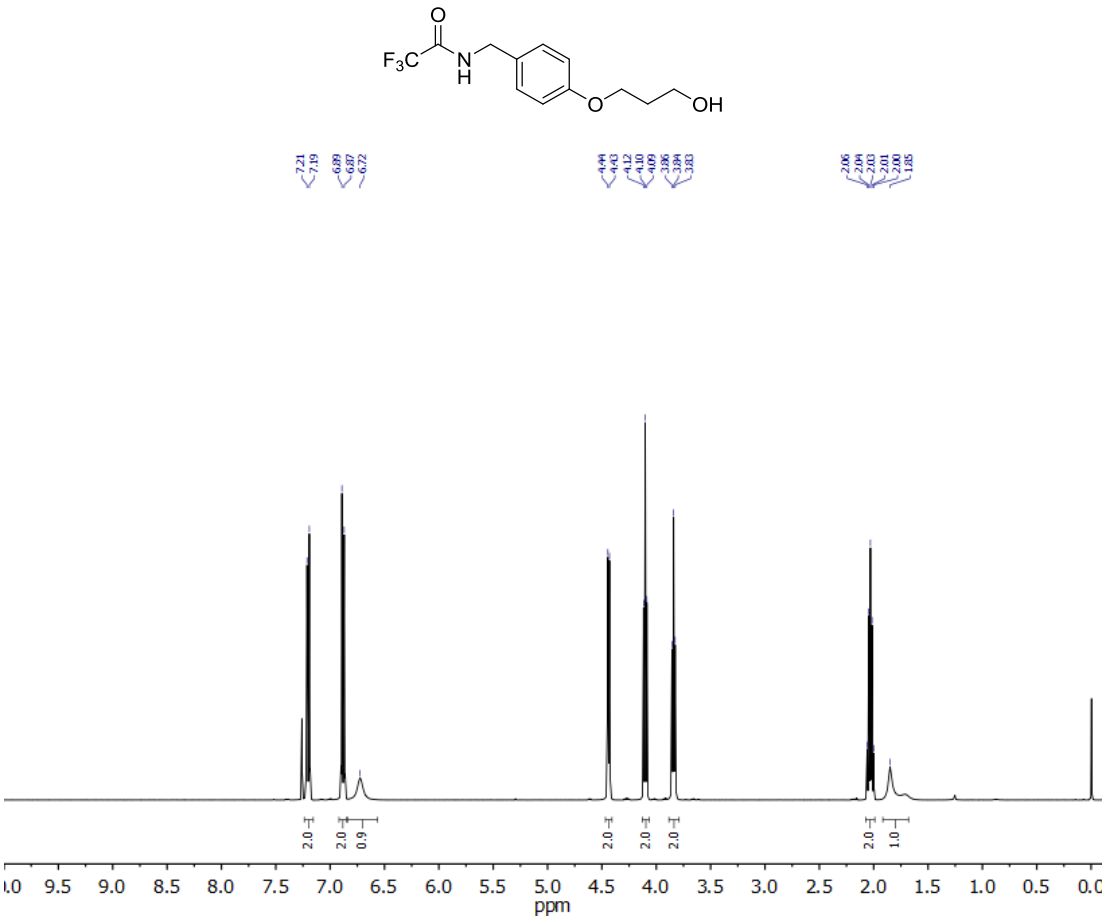


Figure S32: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **S7**.

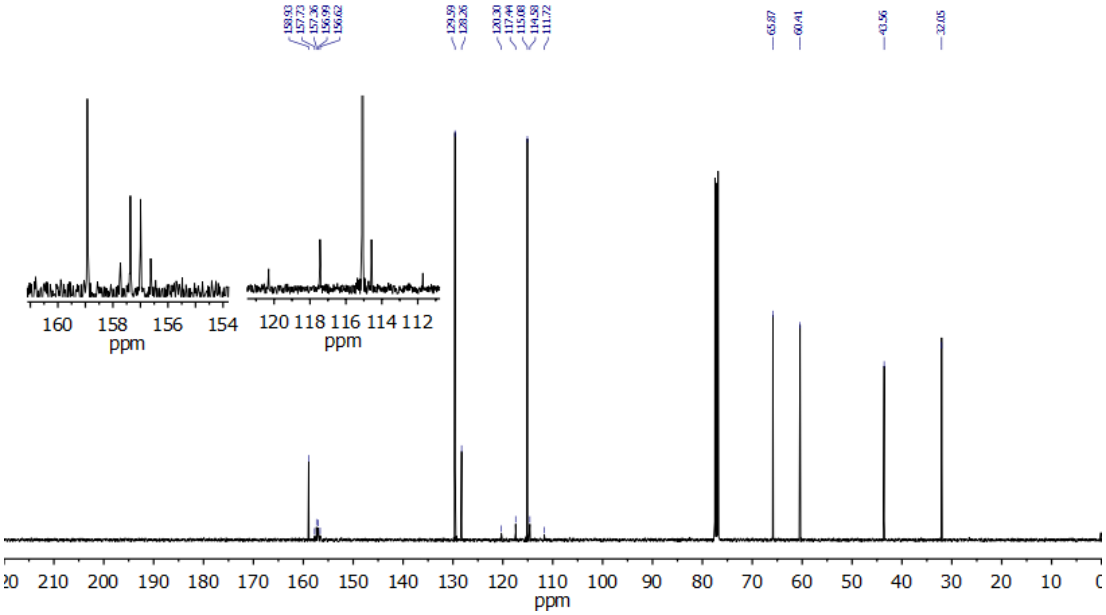


Figure S33: ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **S7**.

Compound S8:

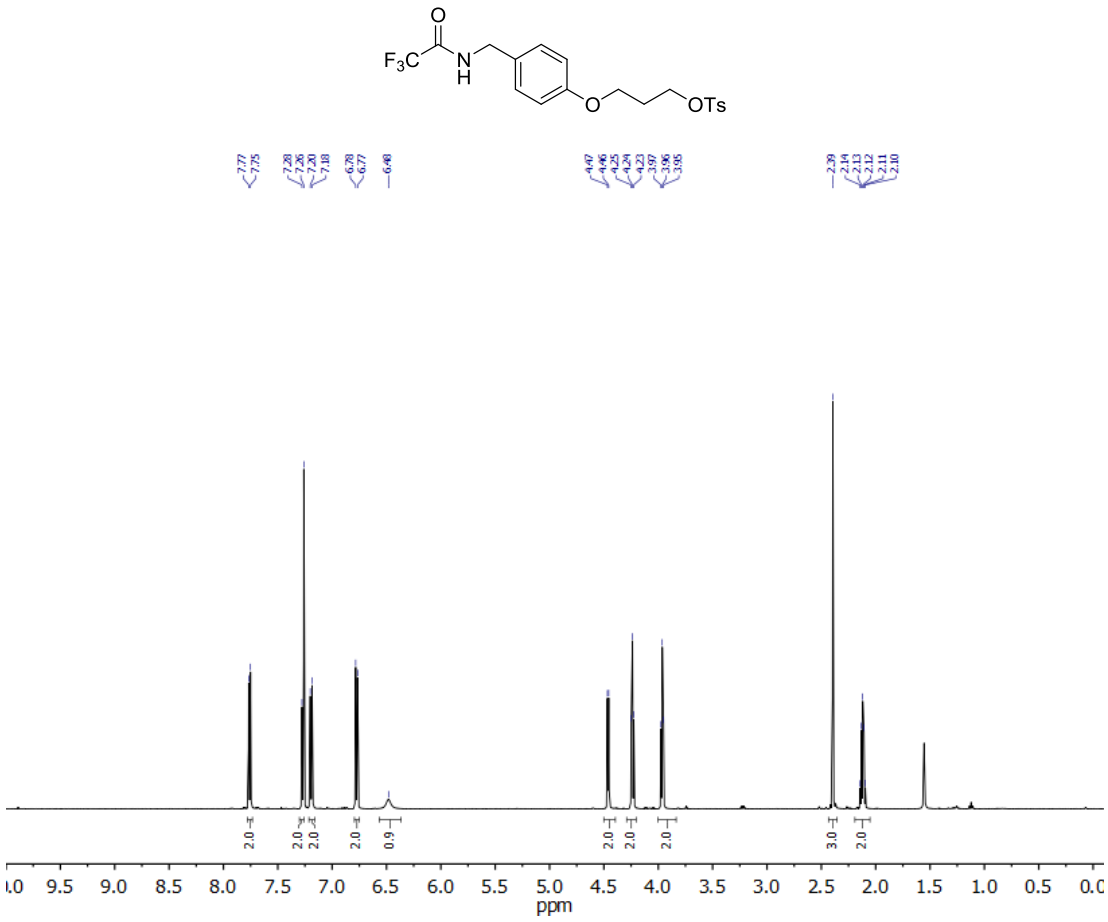


Figure S34: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **S8**.

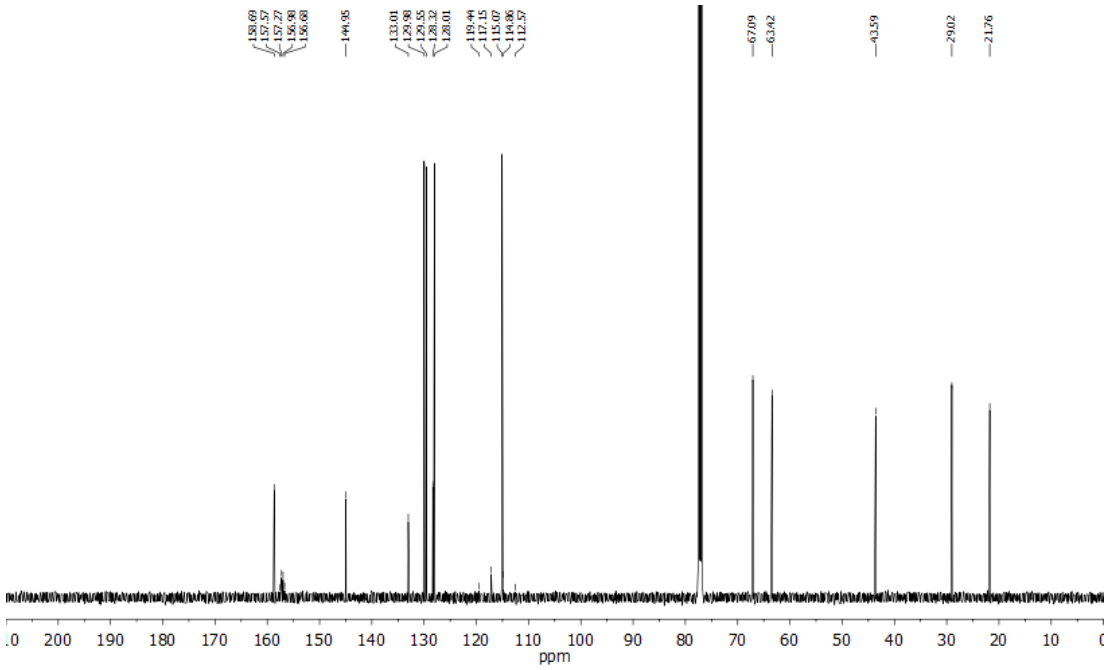


Figure S35: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **S8**.

Compound S9:

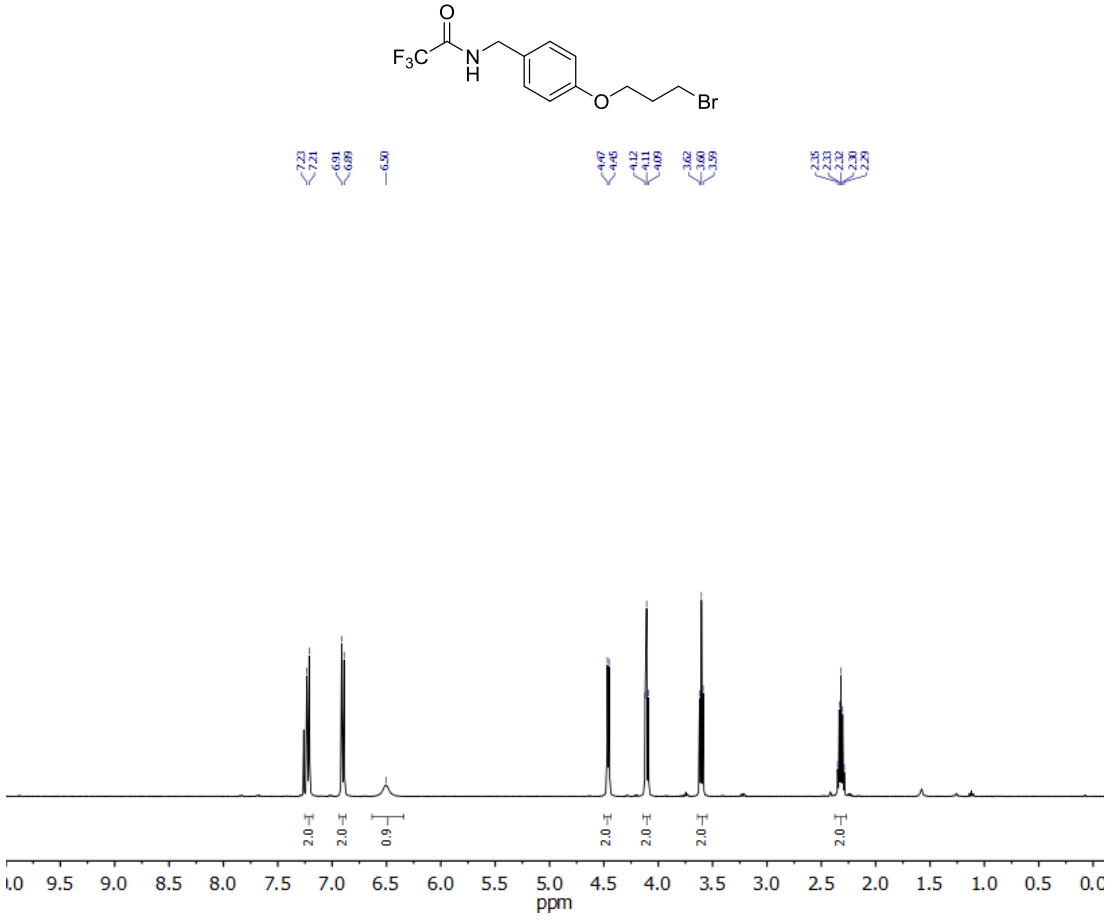


Figure S36: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **S9**.

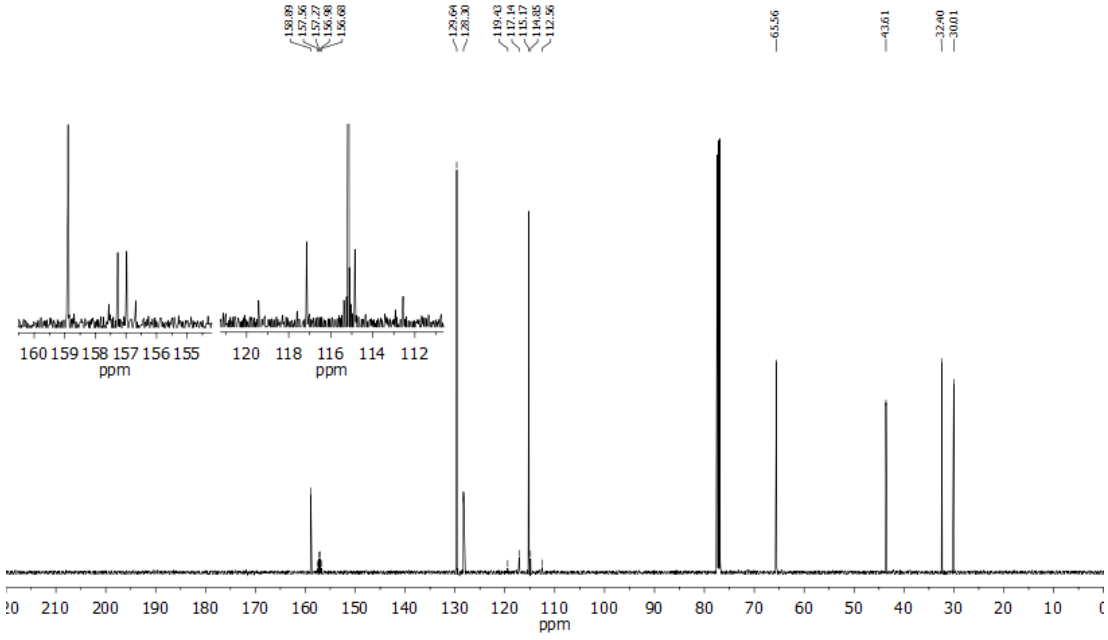
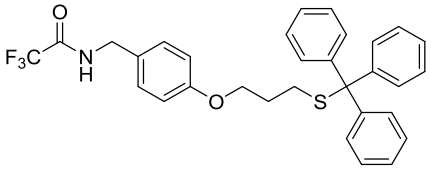


Figure S37: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **S9**.

Compound S10:



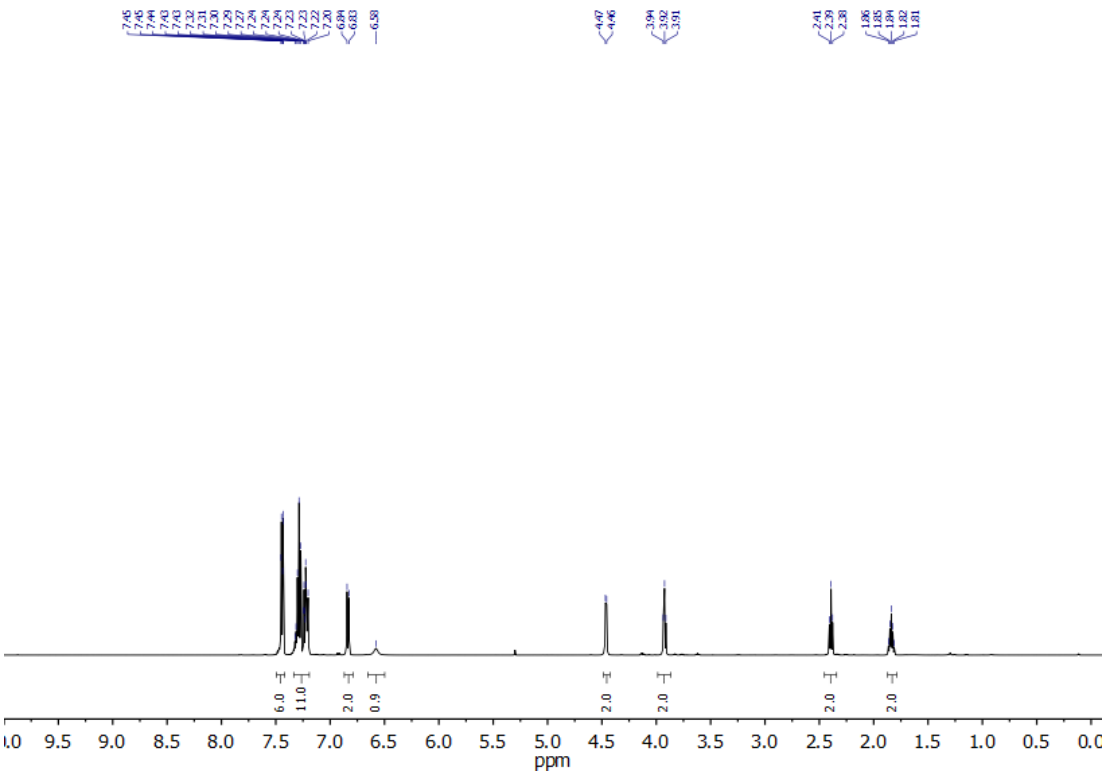


Figure S38: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **S10**.

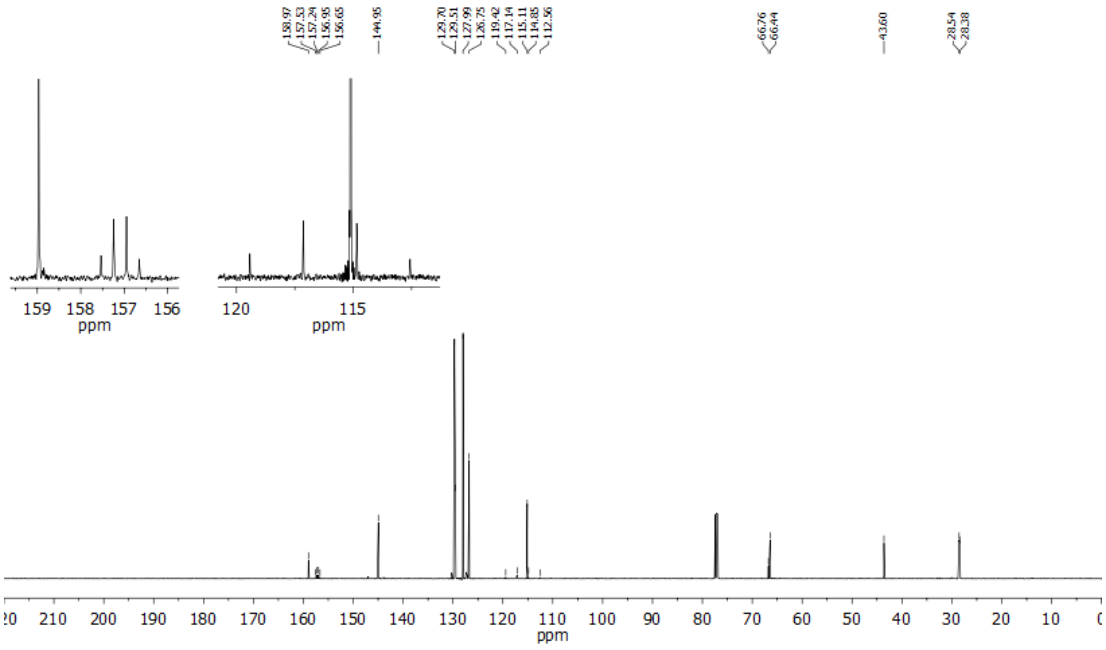


Figure S39: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **S10**.

Compound 7:

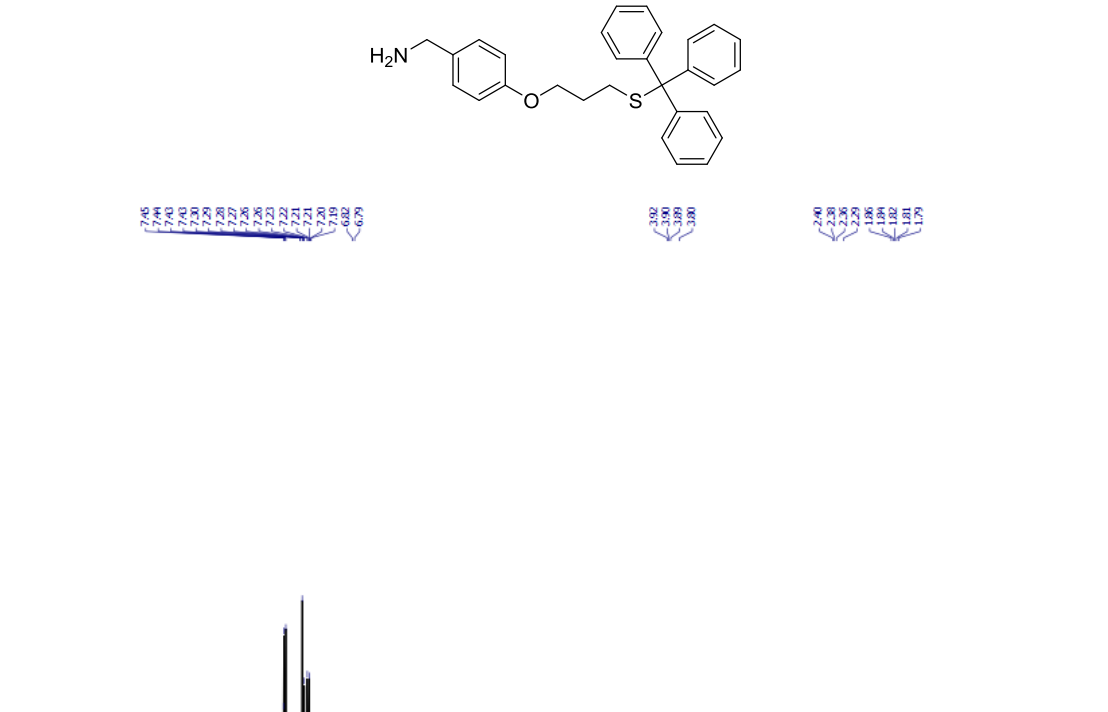


Figure S40: ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **7**.

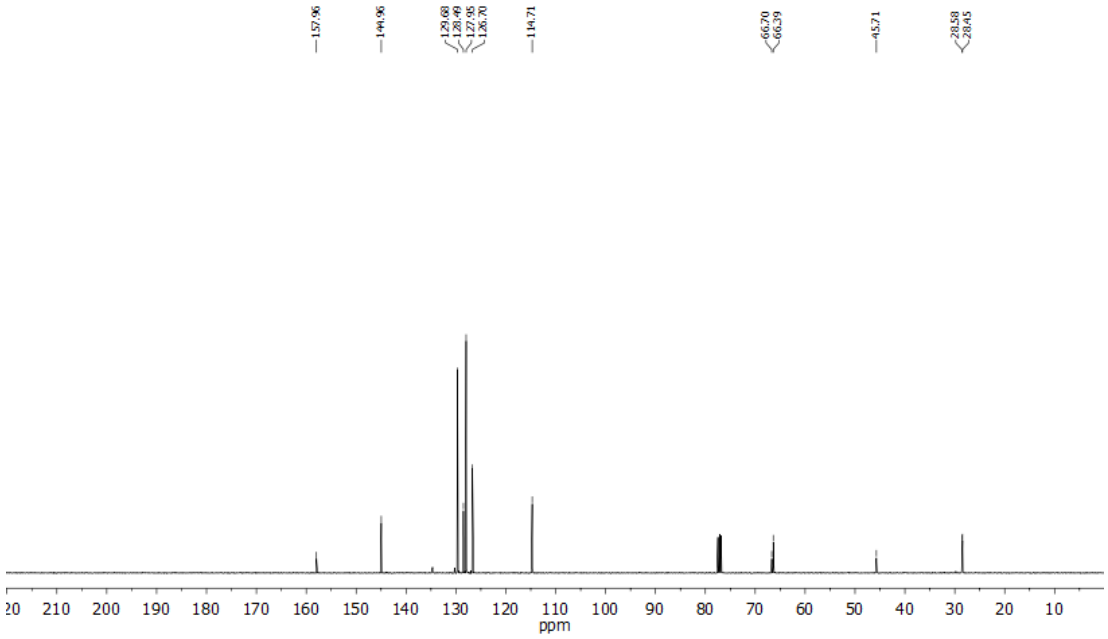


Figure S41: ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of **7**.

Compound 8:

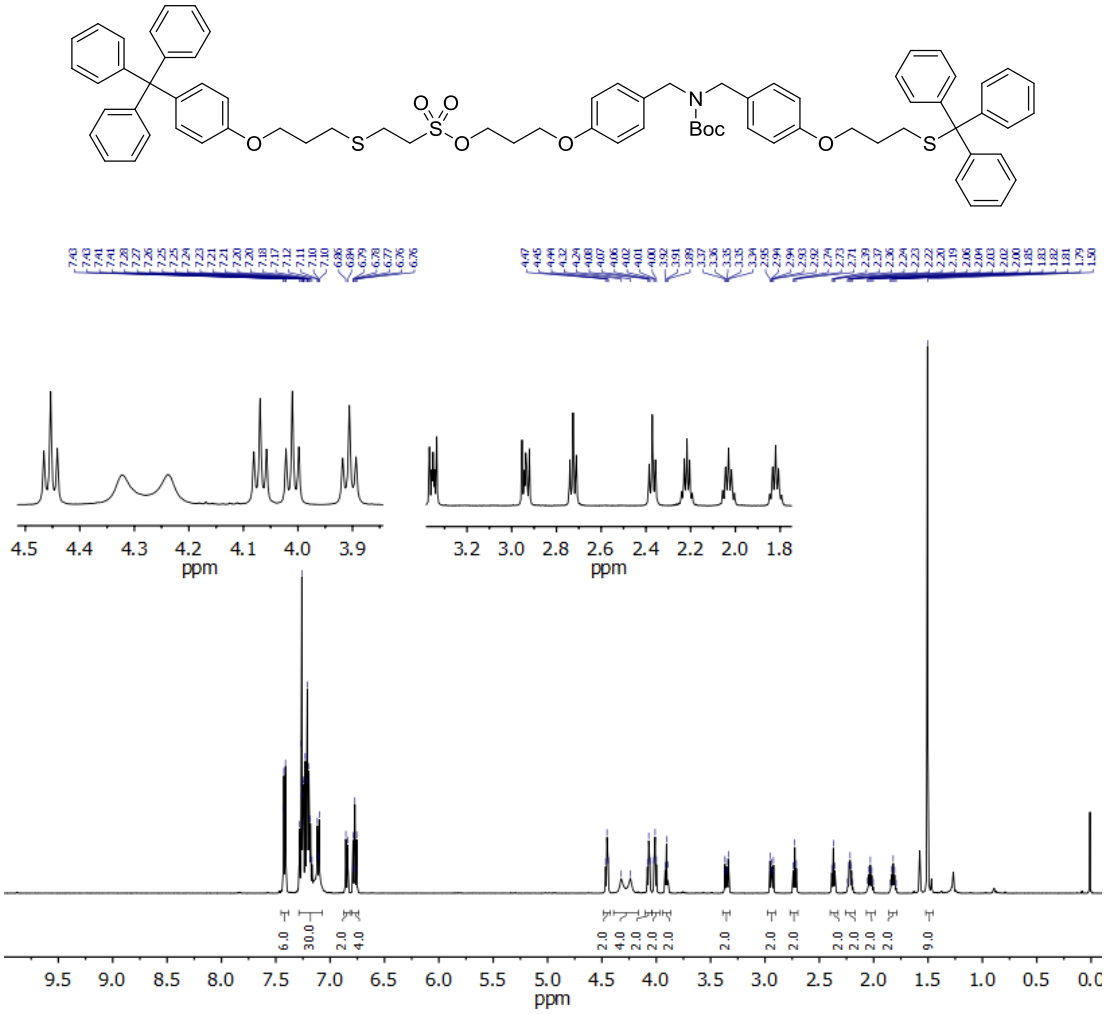


Figure S42: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **8**.

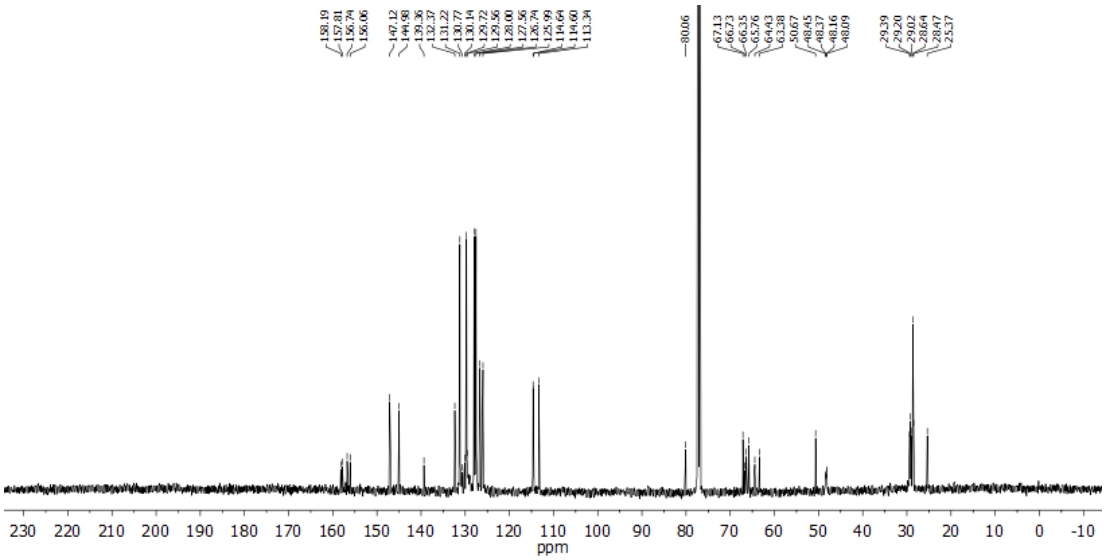


Figure S43: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **8**.

Compound 9:

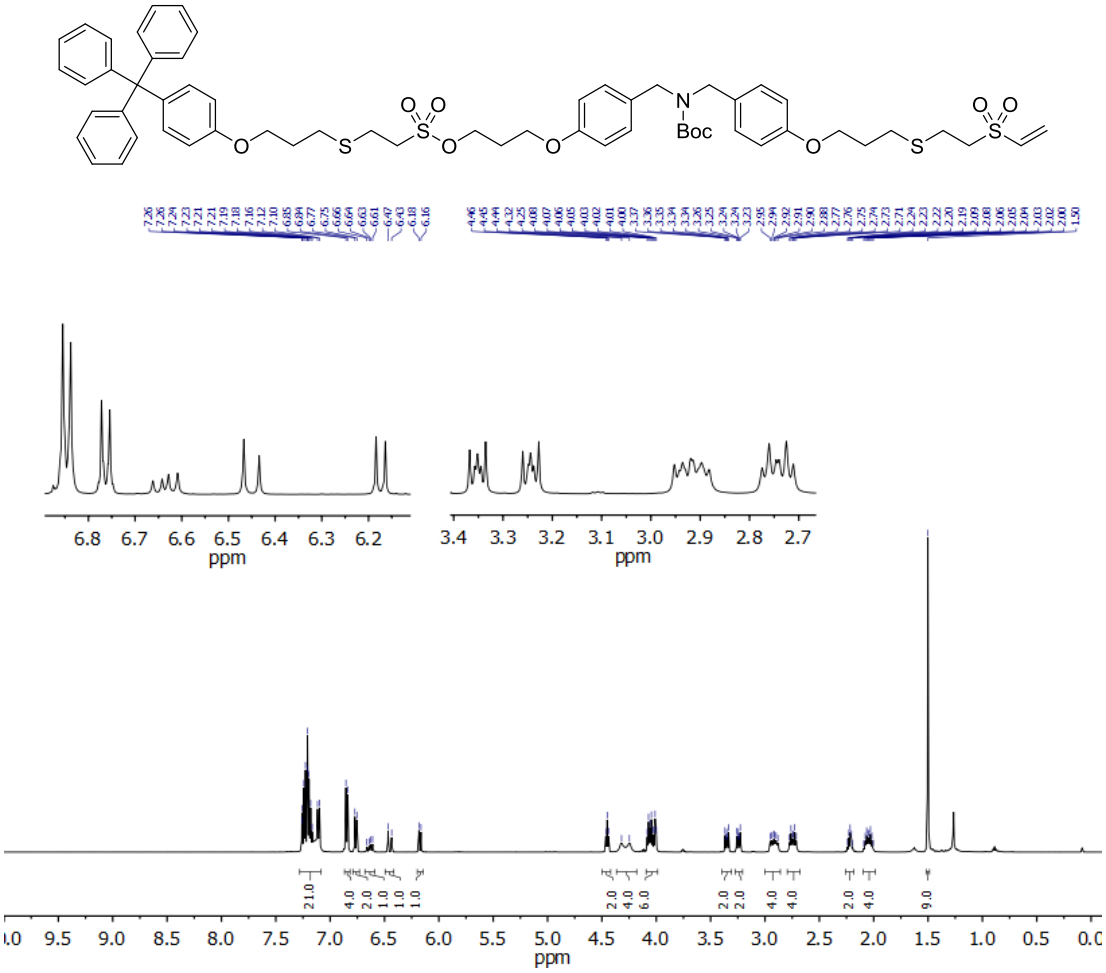


Figure S44: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **9**.

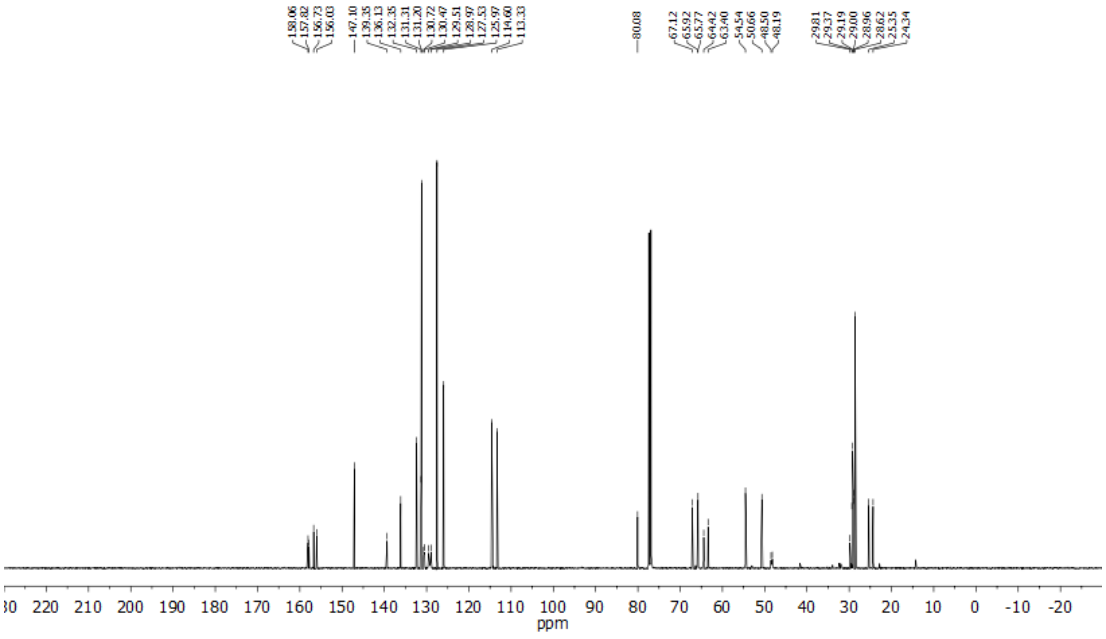
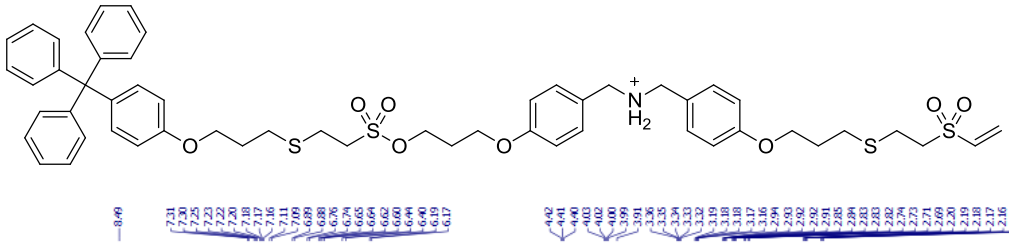


Figure S45: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **9**.

Compound 10·PF_6^-:



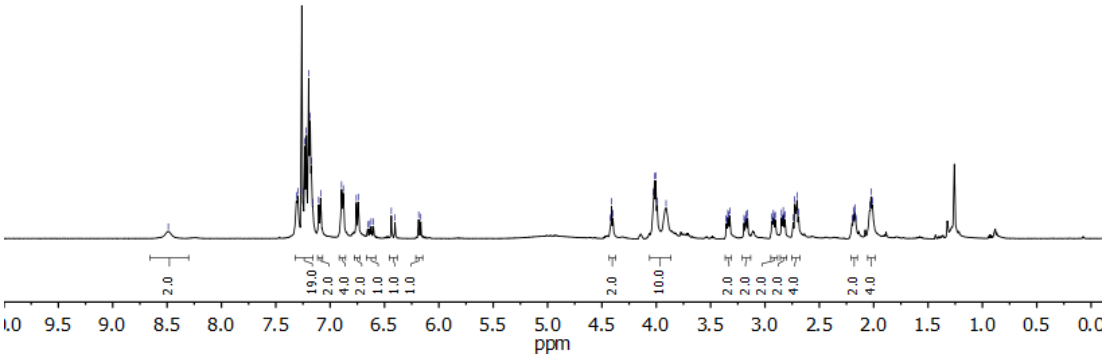


Figure S46: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **10**·PF_6^-.

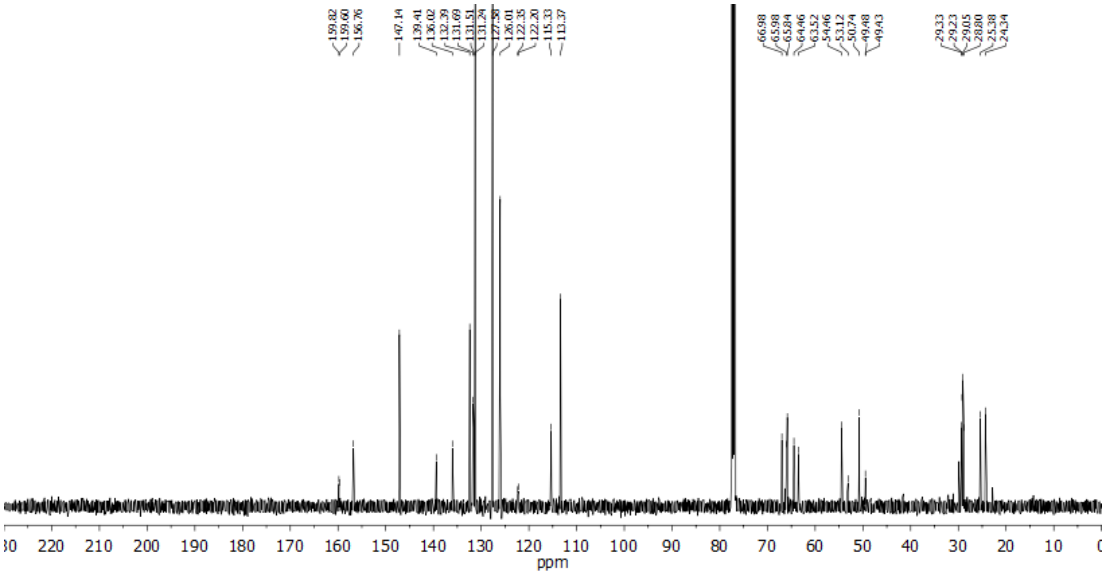


Figure S47: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **10**·PF_6^-.

Compound 13·PF_6^-:

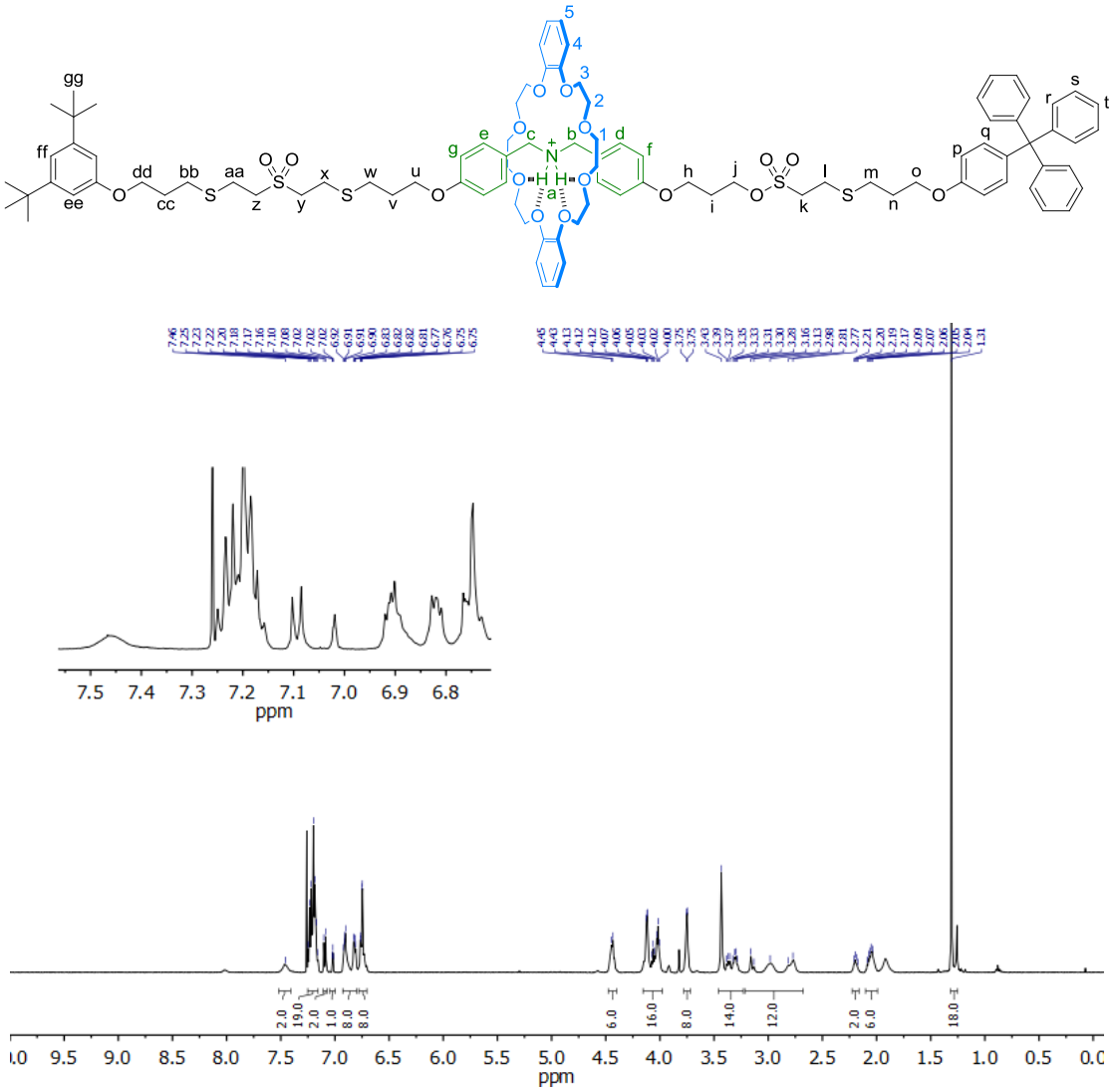


Figure S48: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **13**·PF_6^-.

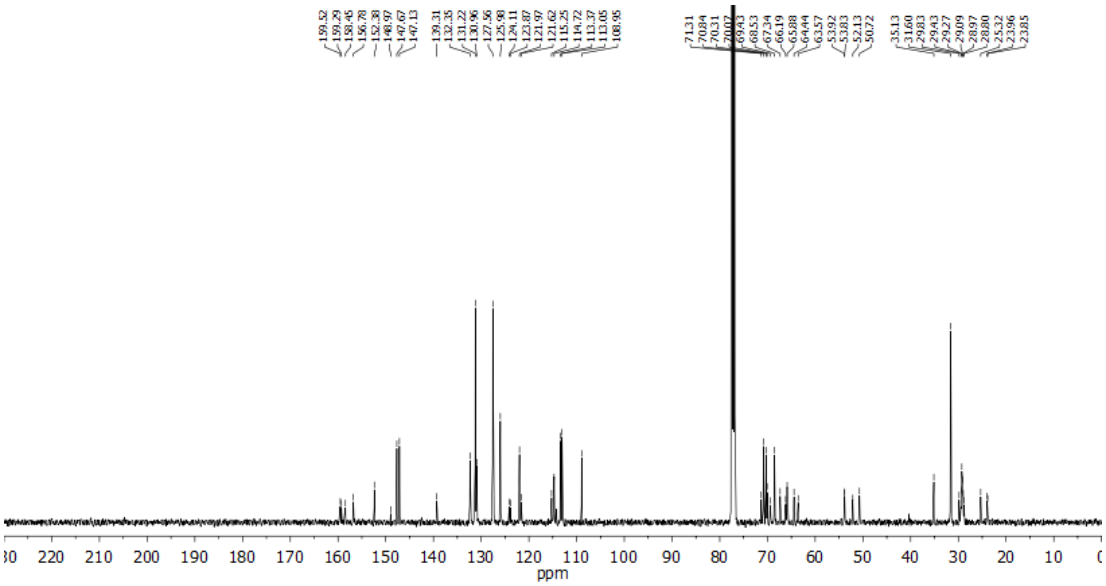


Figure S49: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **13**·PF_6^-.

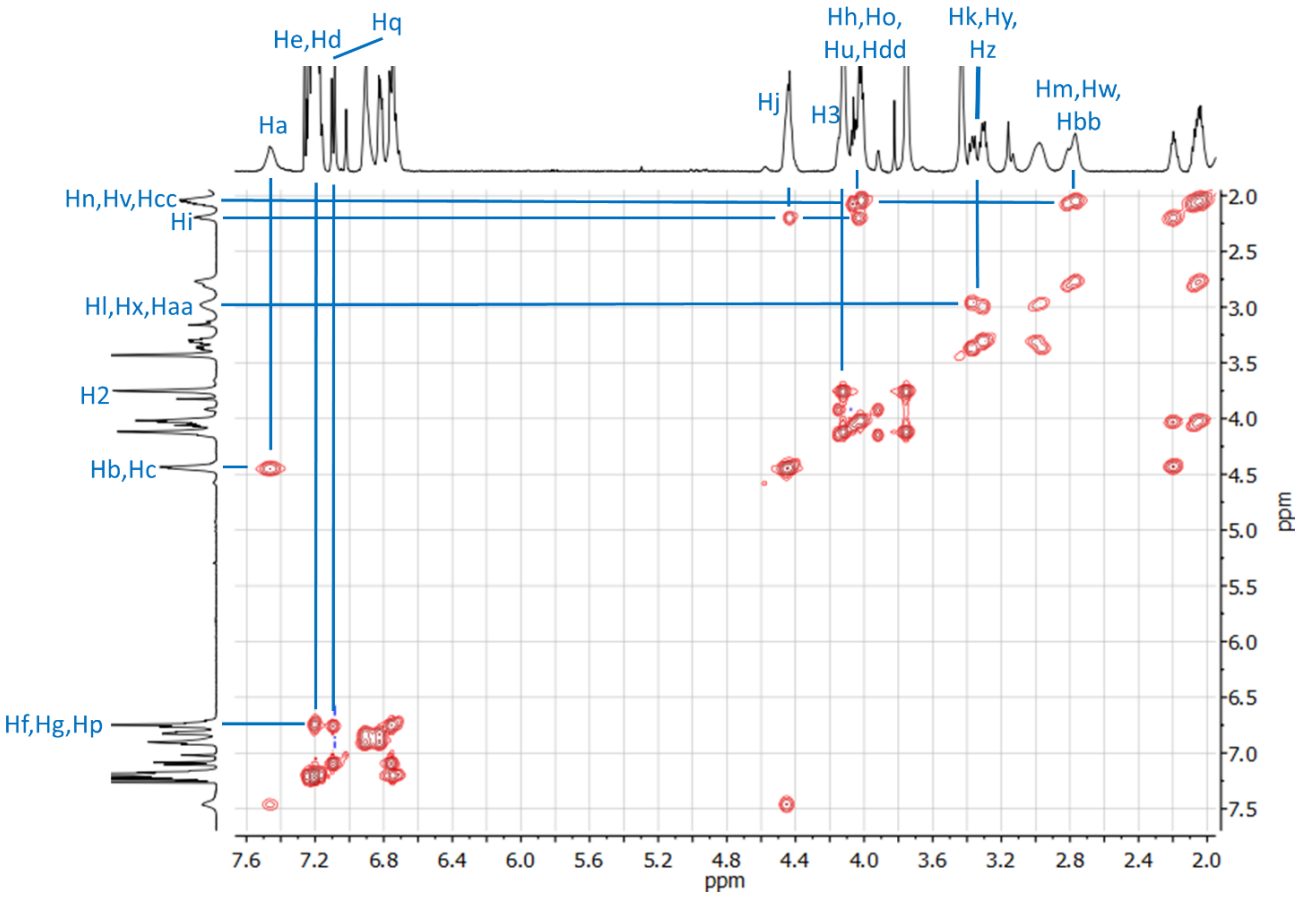


Figure S50: COSY NMR (500 MHz, $CDCl_3$) spectrum of **13**·PF_6^-.

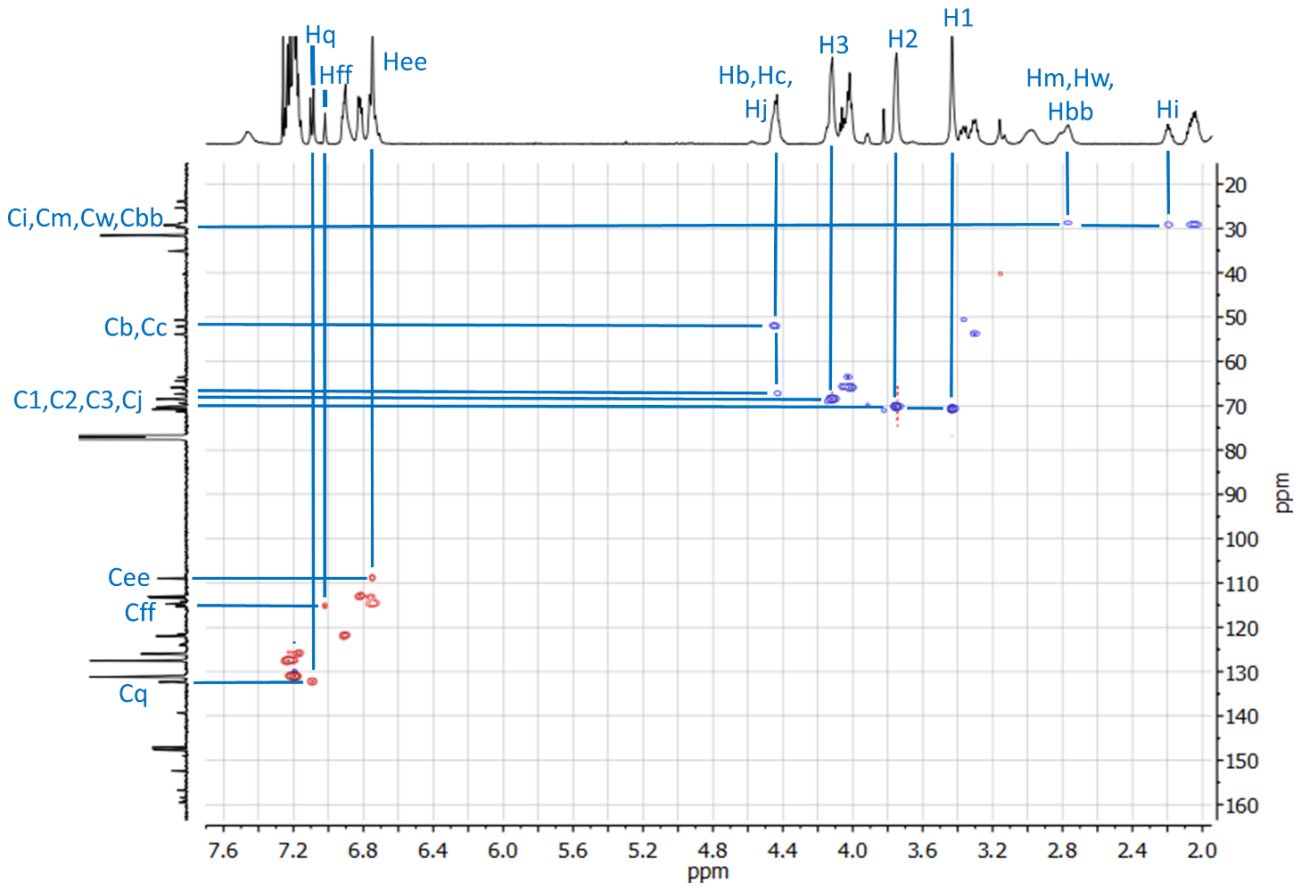


Figure S51: HSQC NMR (500 MHz and 126 MHz, $CDCl_3$) spectrum of **13**·PF_6^-.

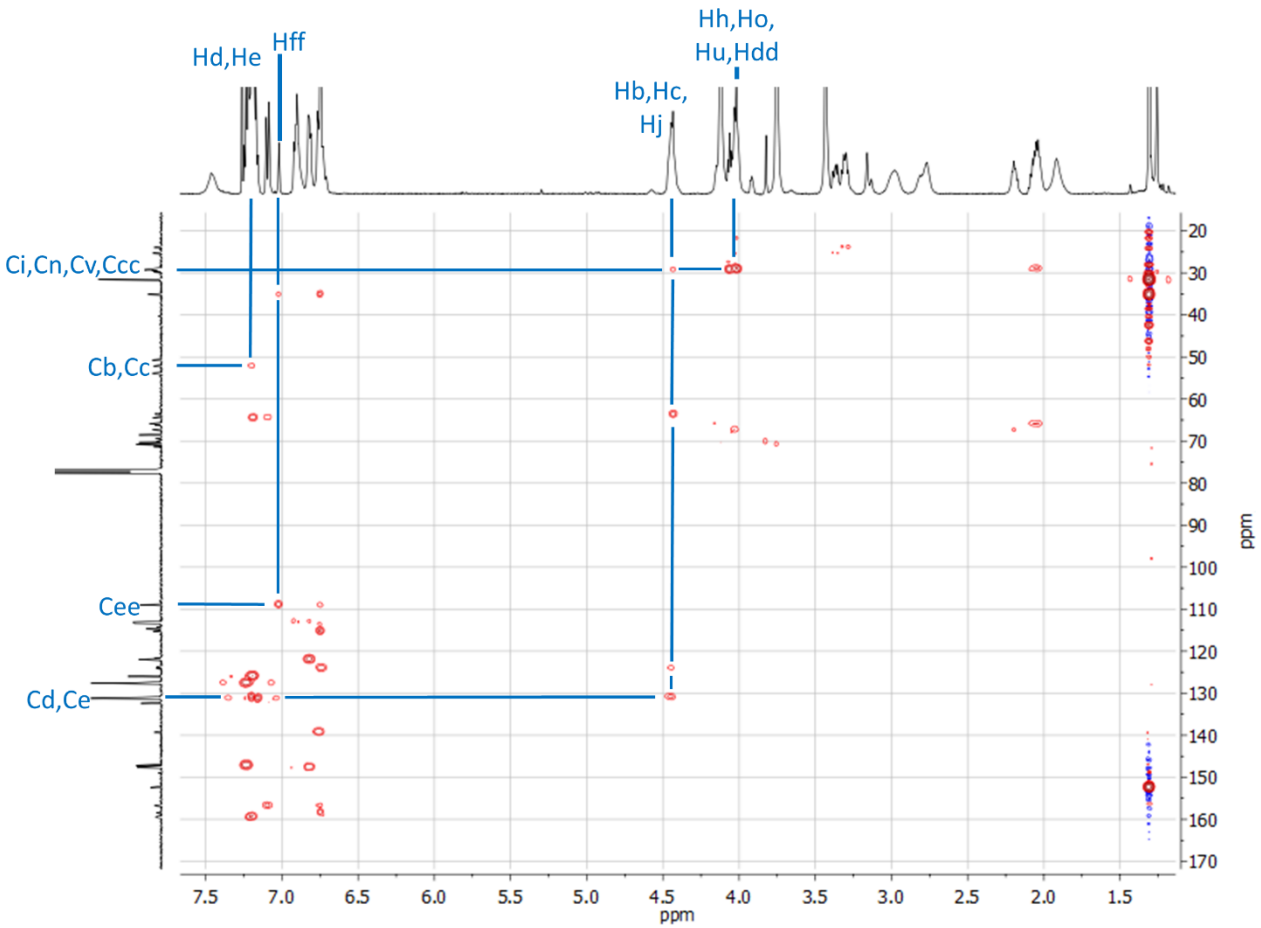


Figure S52: HMBC NMR (500 MHz and 126 MHz, $CDCl_3$) spectrum of **13**·PF_6^-.

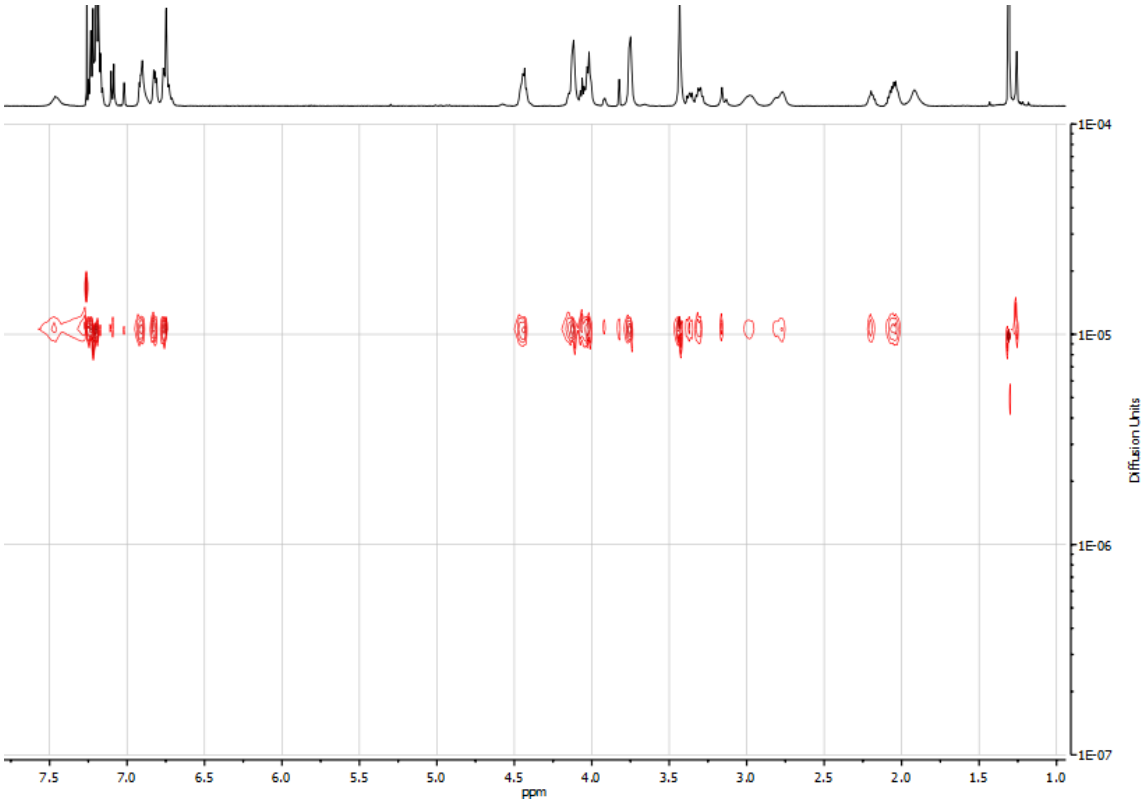


Figure S53: DOSY NMR (500 MHz, $CDCl_3$) spectrum of **13**·PF_6^-.

Compound S11:

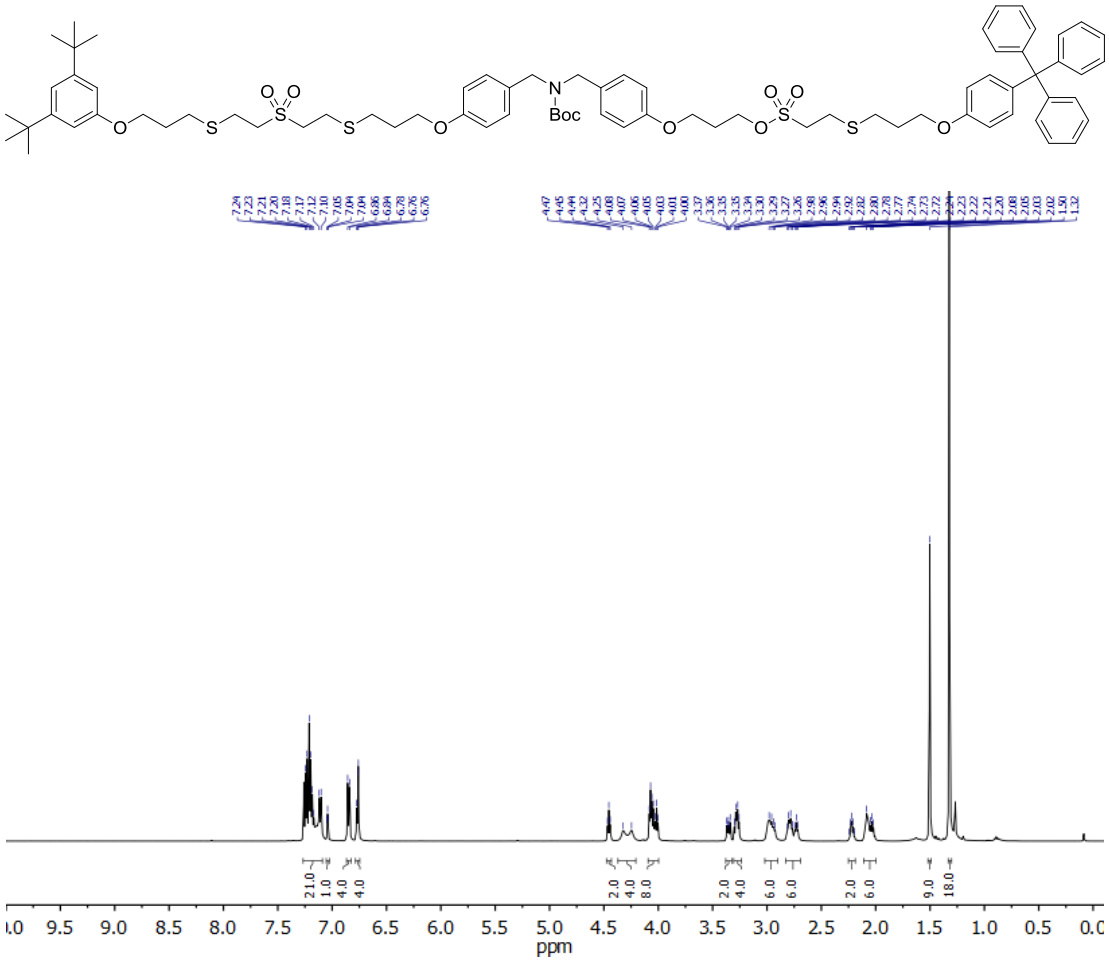


Figure S54: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **S11**.

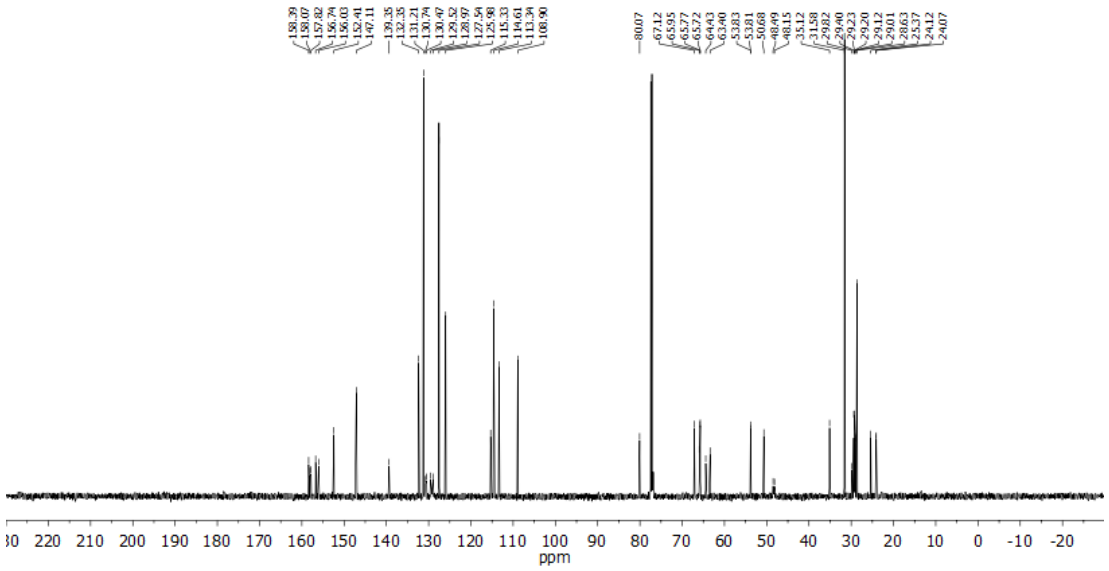


Figure S55: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **S11**.

Compound S12·PF_6^-:

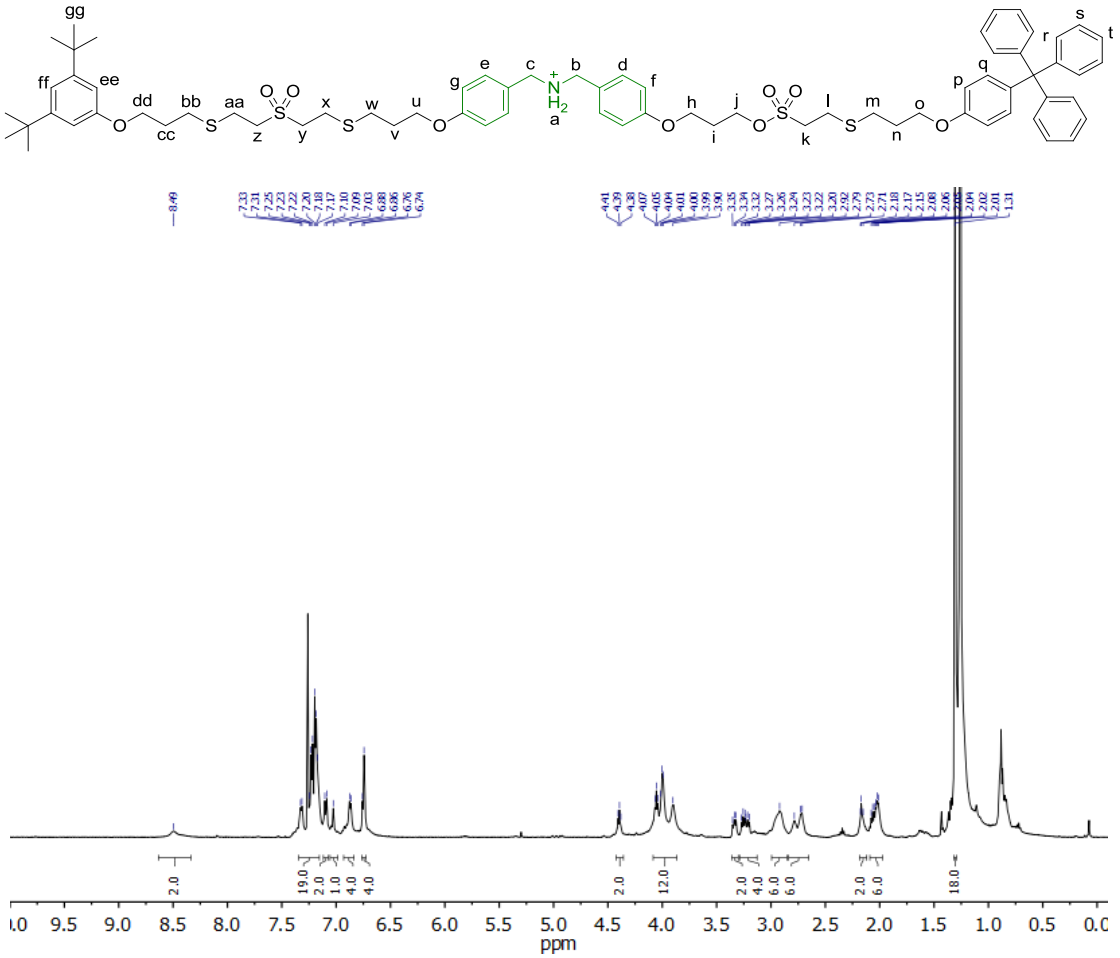


Figure S56: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **S12**·PF_6^-.

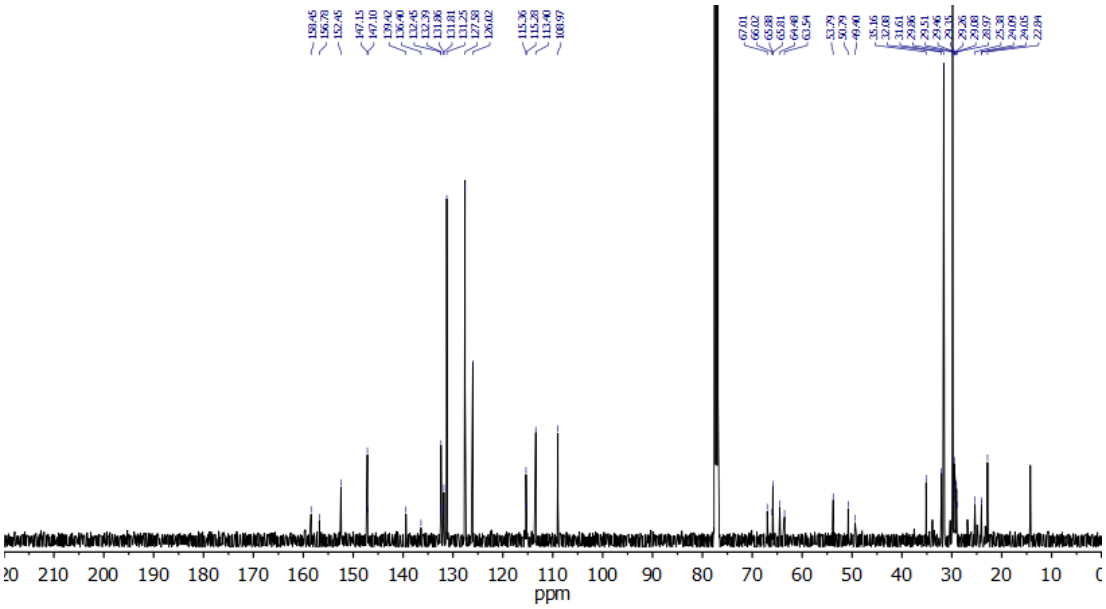


Figure S57: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **S12**·PF_6^-.

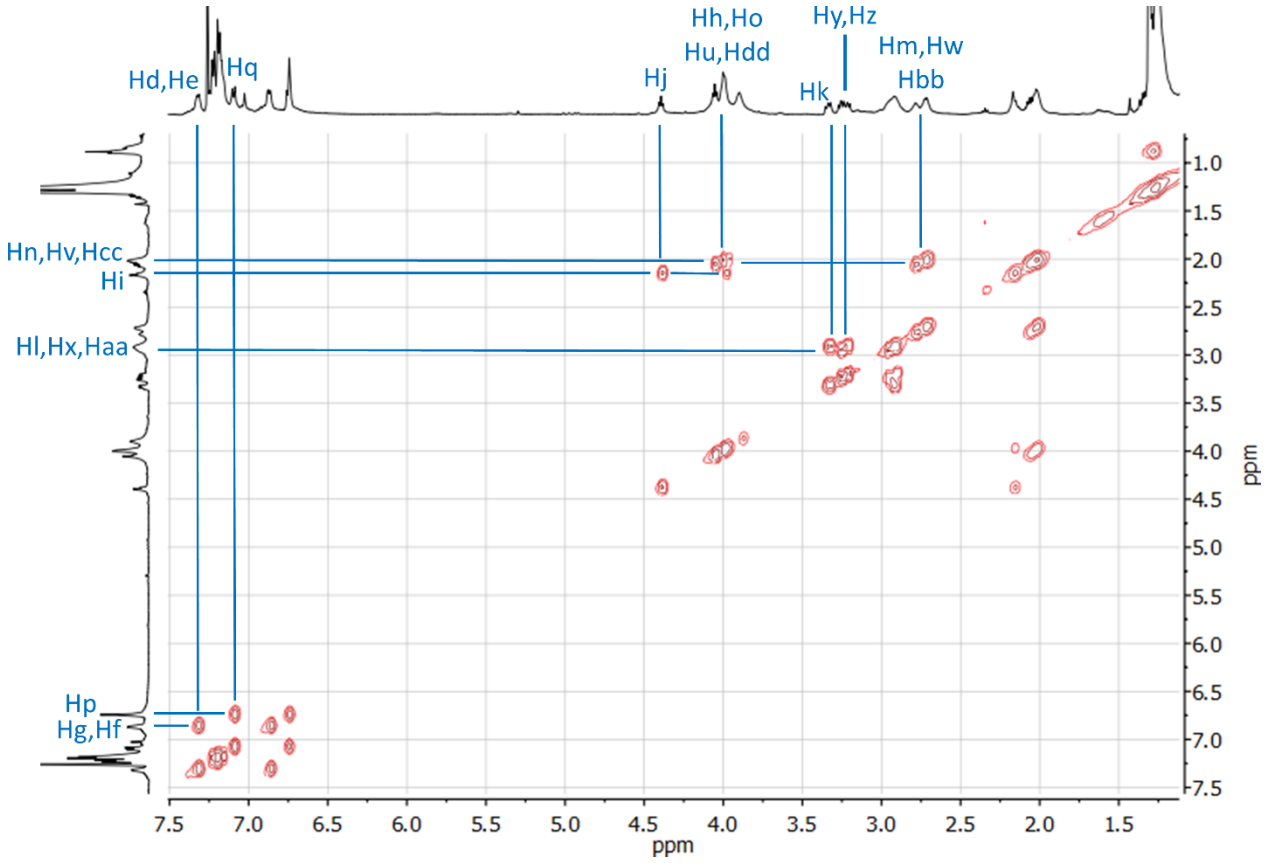


Figure S58: COSY NMR (500 MHz, $CDCl_3$) spectrum of **S12**·PF_6^-.

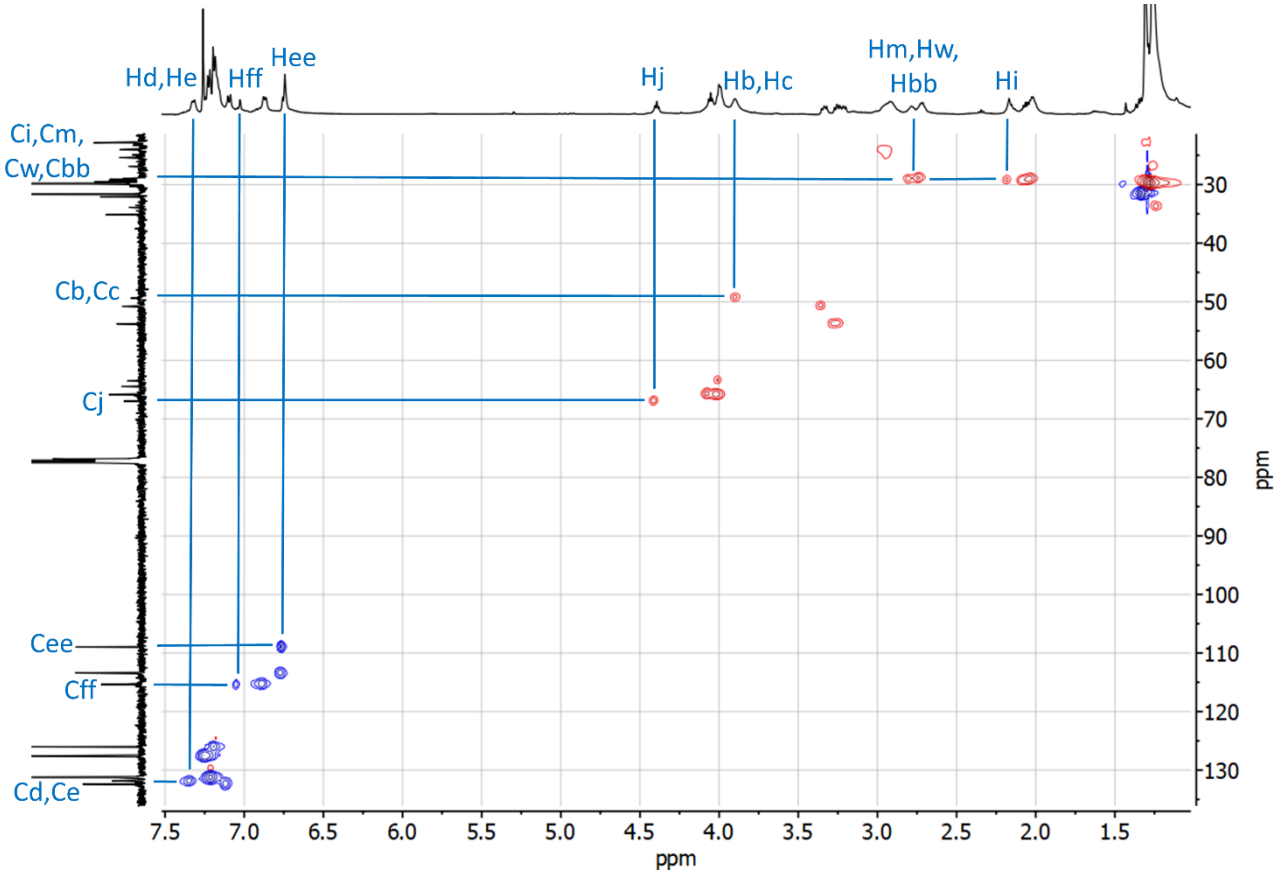


Figure S59: HSQC NMR (500 and 126 MHz, $CDCl_3$) spectrum of **S12**·PF_6^-.

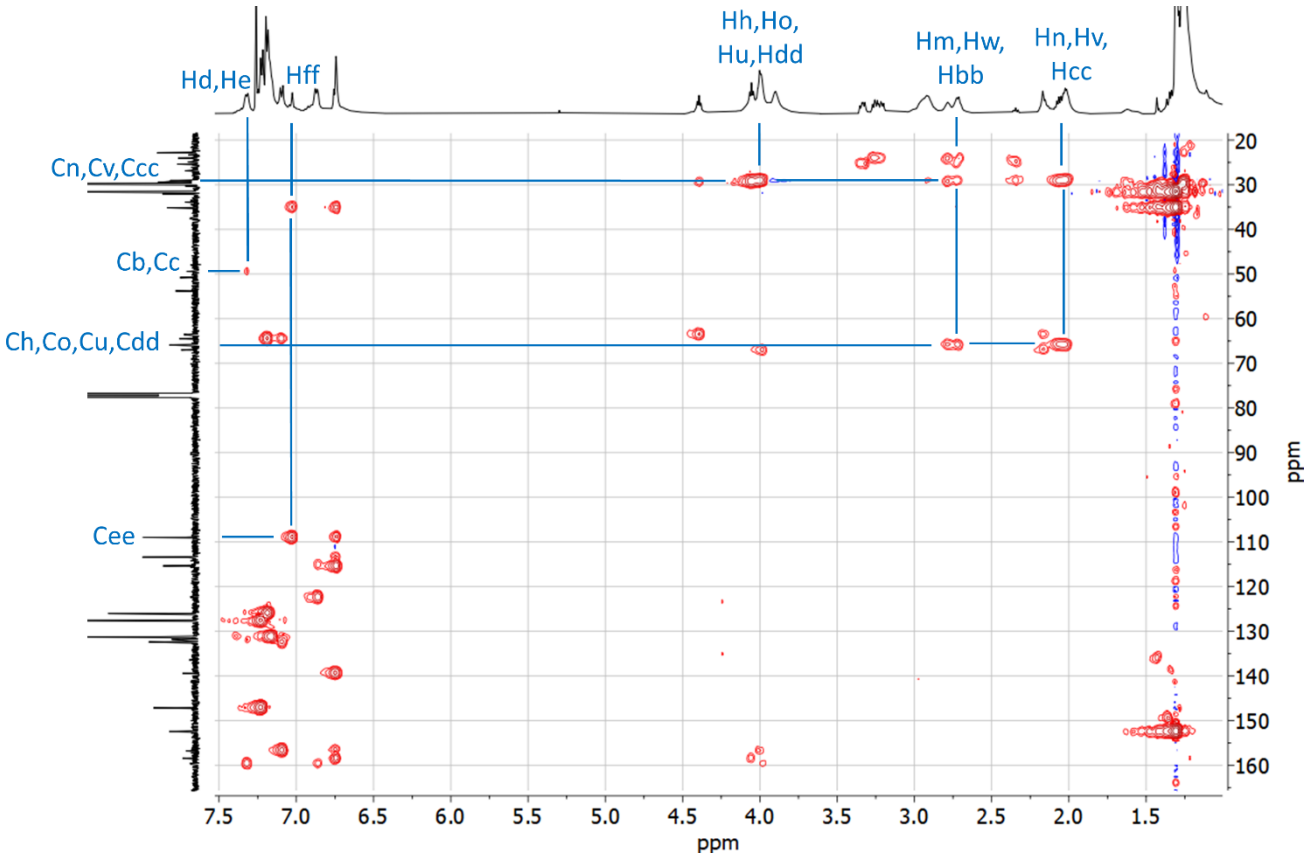


Figure S60: HMBC NMR (500 and 126 MHz, $CDCl_3$) spectrum of **S12**·PF_6^-.

Mixture of compounds 14-H$^+$/15 (1:1):

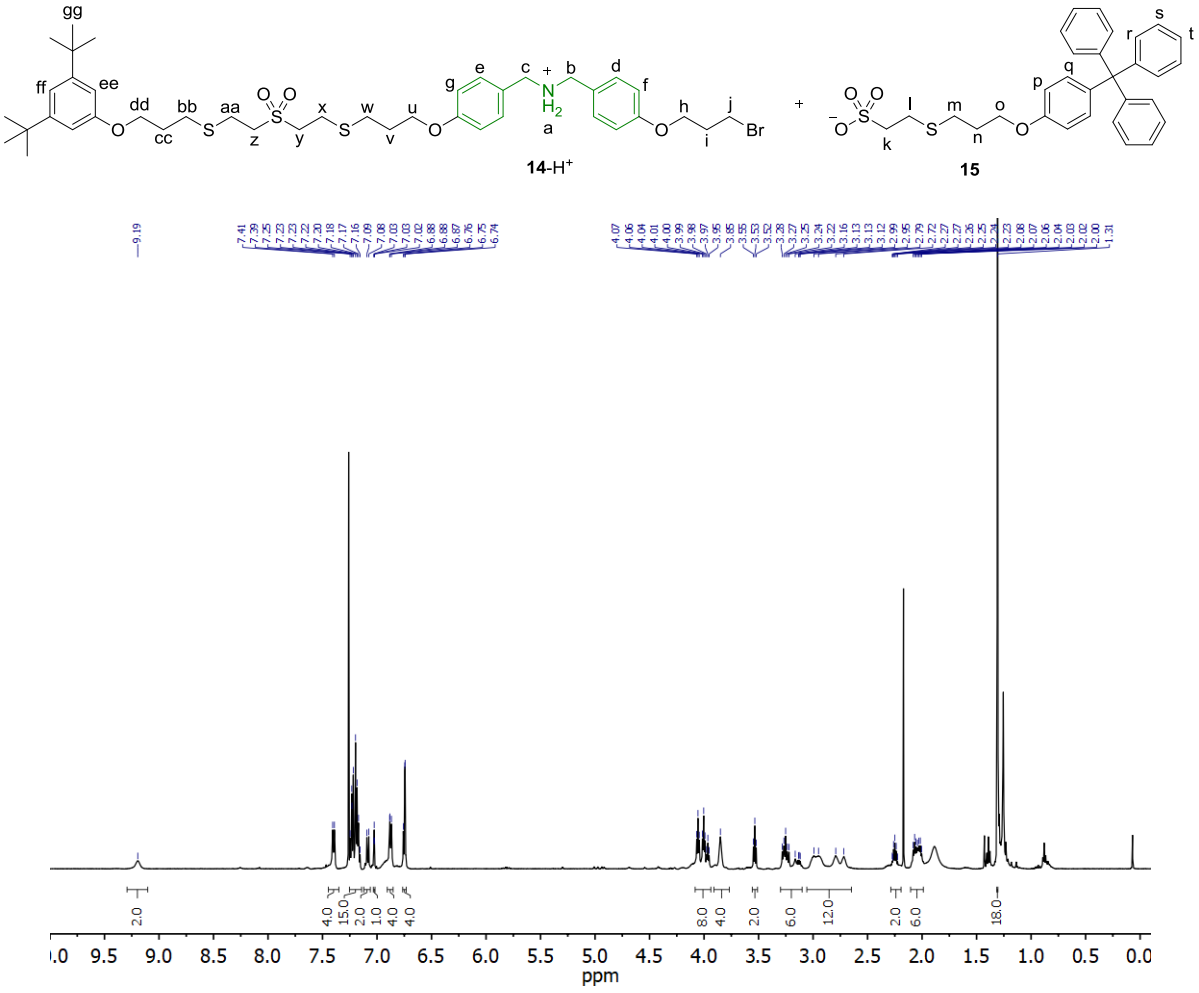


Figure S61: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of a mixture of compounds **14**-H$^+$/**15** (1:1) obtained from the cleavage of rotaxane **13**·PF_6^-.

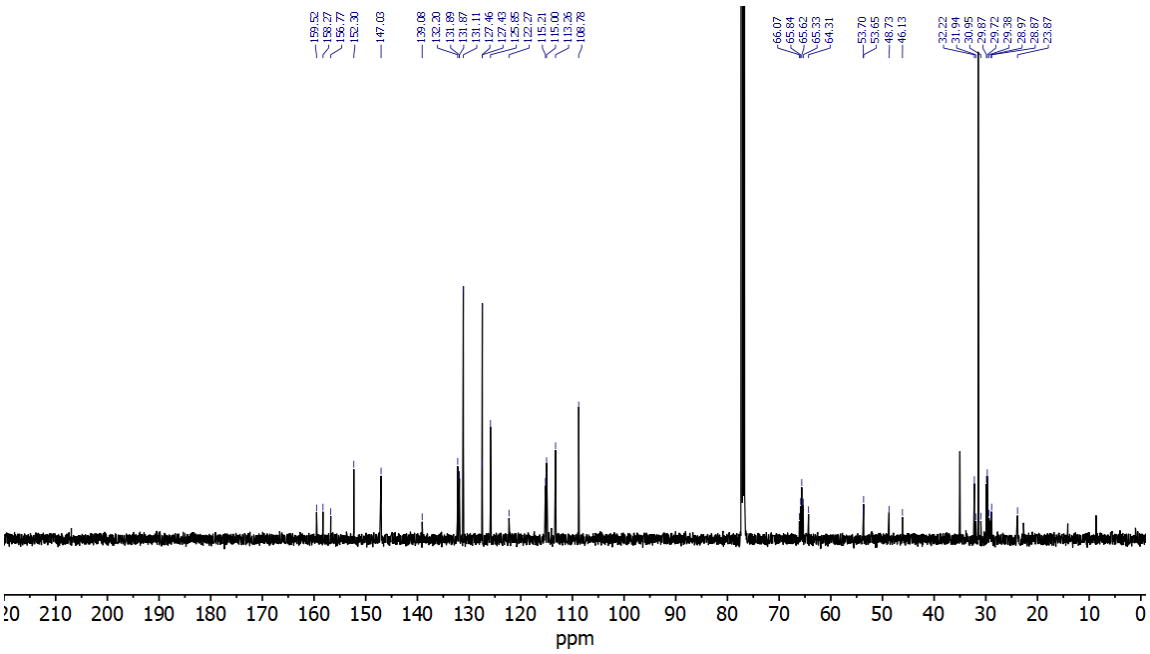


Figure S62: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of a mixture of compounds **14**-H$^+$/**15** (1:1) obtained from the cleavage of rotaxane **13**·PF_6^-.

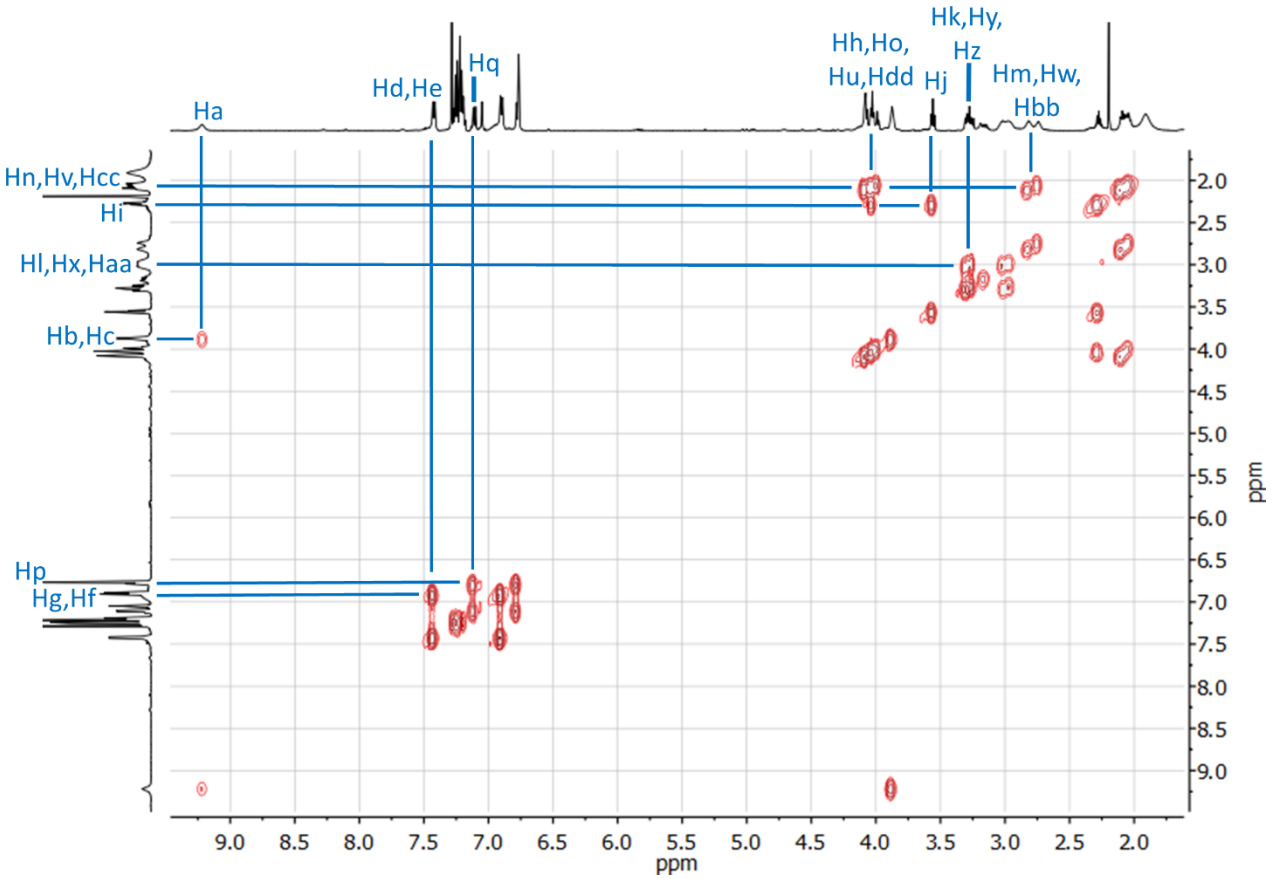


Figure S63: COSY NMR (500 MHz, $CDCl_3$) spectrum of a mixture of compounds **14**-H^+/**15** (1:1) obtained from the cleavage of rotaxane **13**·PF_6^-.

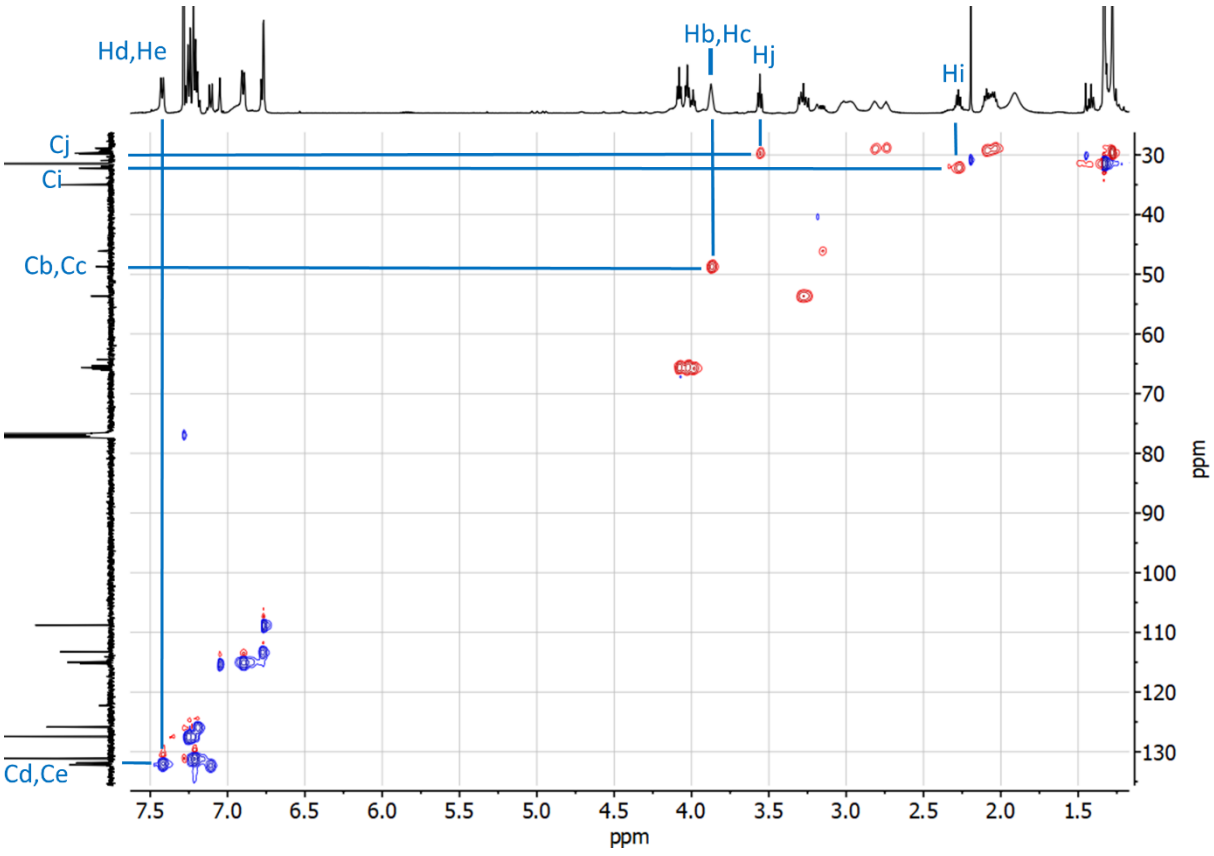


Figure S64: HSQC NMR (500 and 126 MHz, $CDCl_3$) spectrum of a mixture of compounds **14**-H^+/**15** (1:1) obtained from the cleavage of rotaxane **13**·PF_6^-.

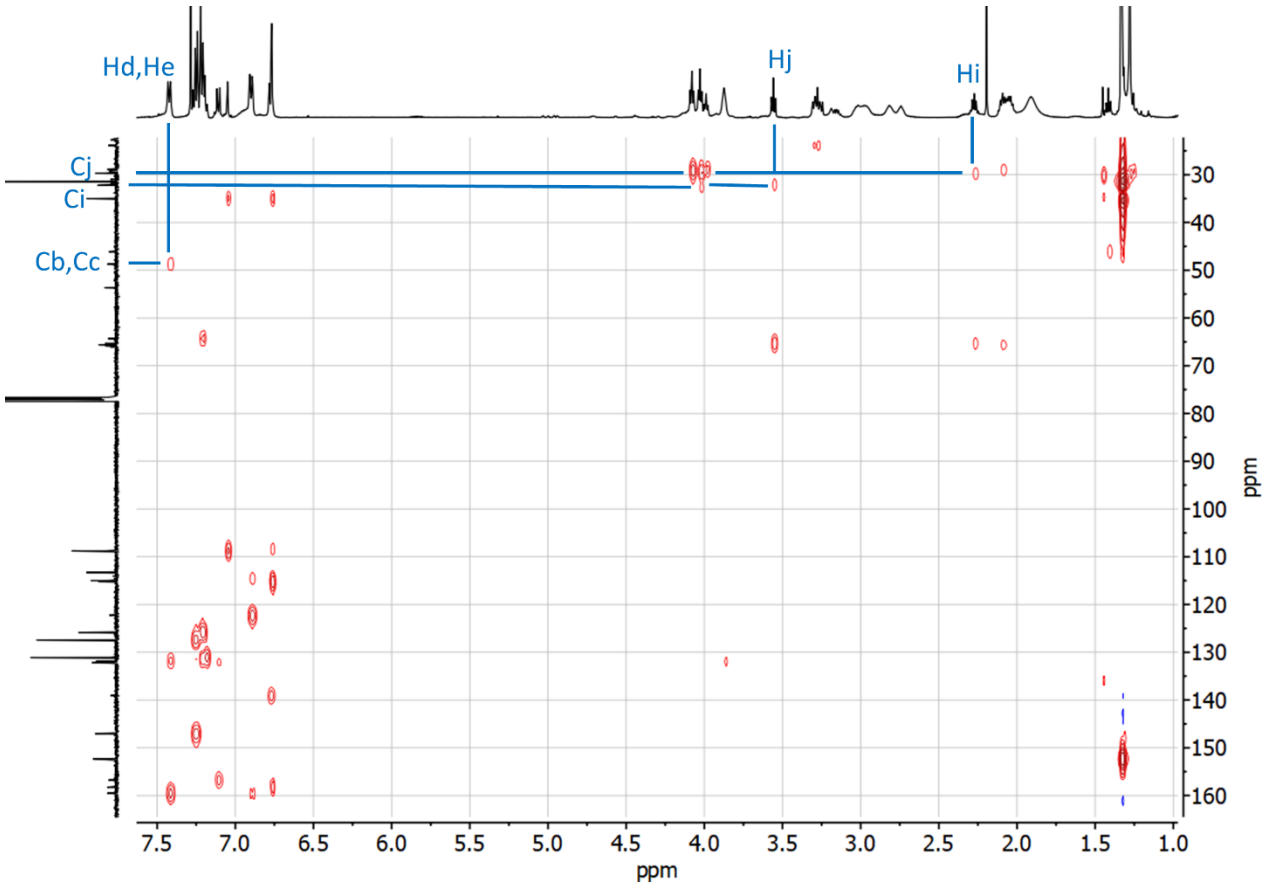


Figure S65: HMBC NMR (500 and 126 MHz, $CDCl_3$) spectrum of a mixture of compounds **14**-H^+/**15** (1:1) obtained from the cleavage of rotaxane **13**·PF_6^-.

Compound S13:

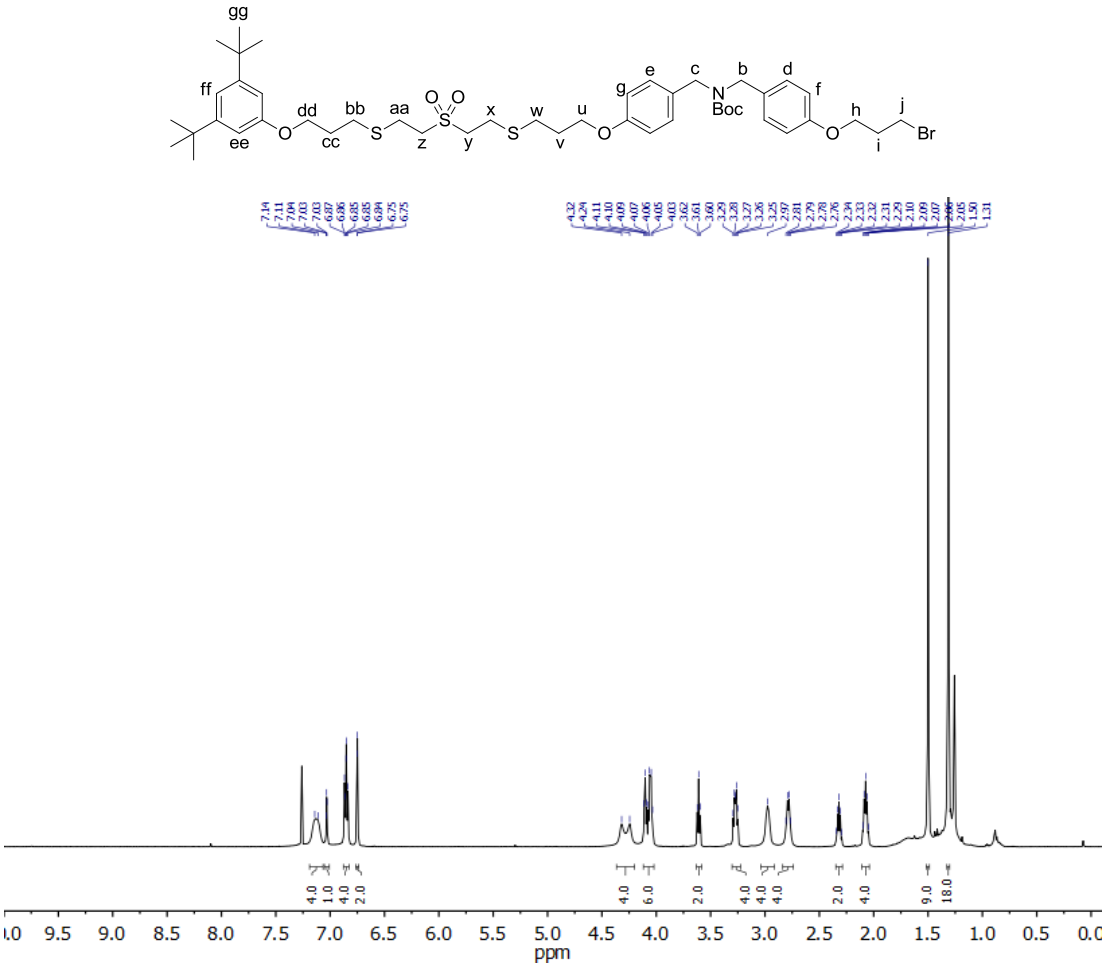


Figure S66: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **S13**.

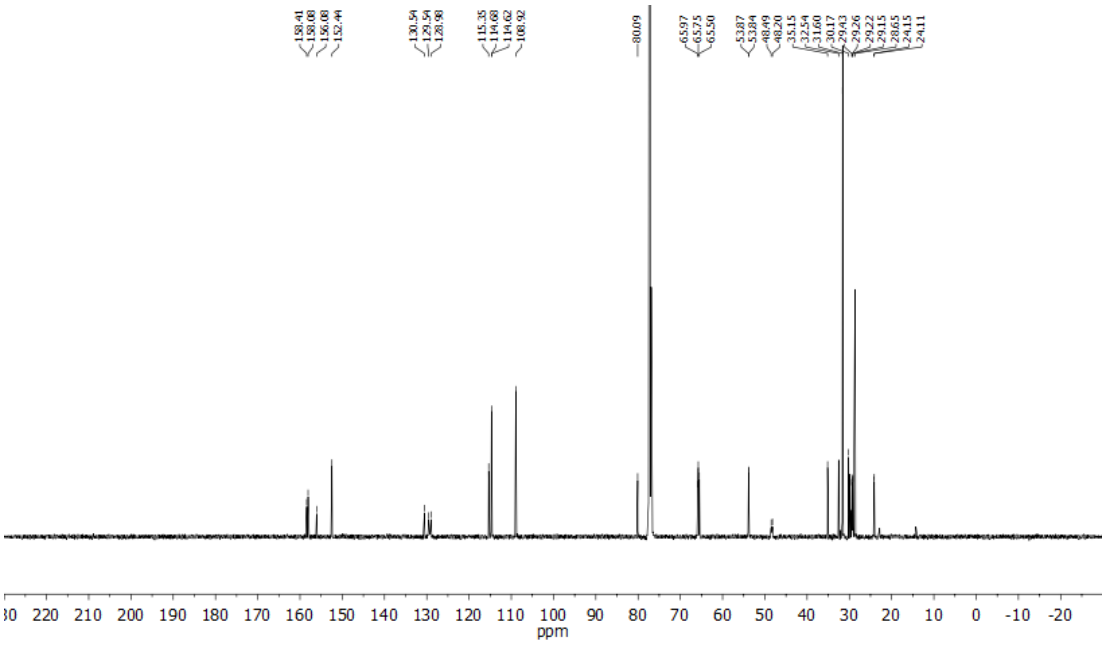


Figure S67: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **S13**.

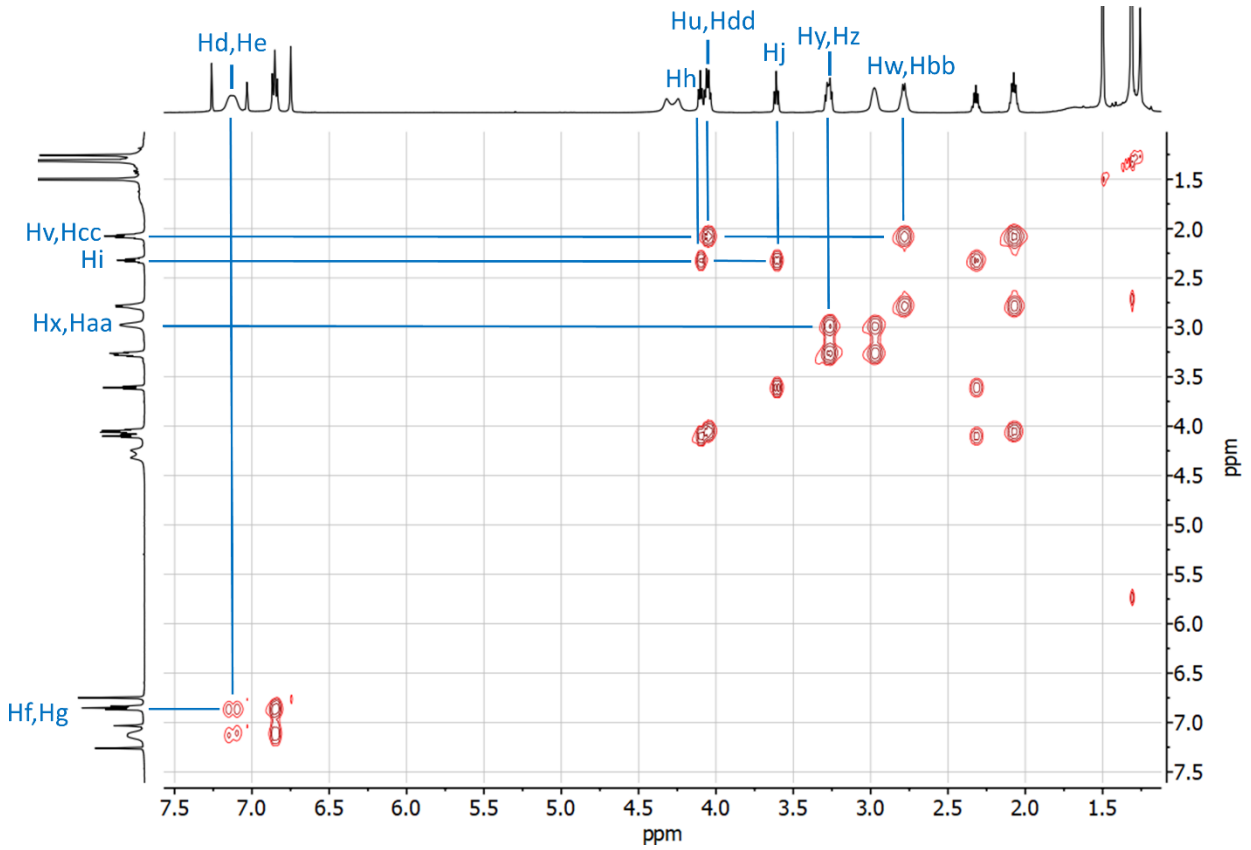


Figure S68: COSY NMR (500 MHz, $CDCl_3$) spectrum of **S13**.

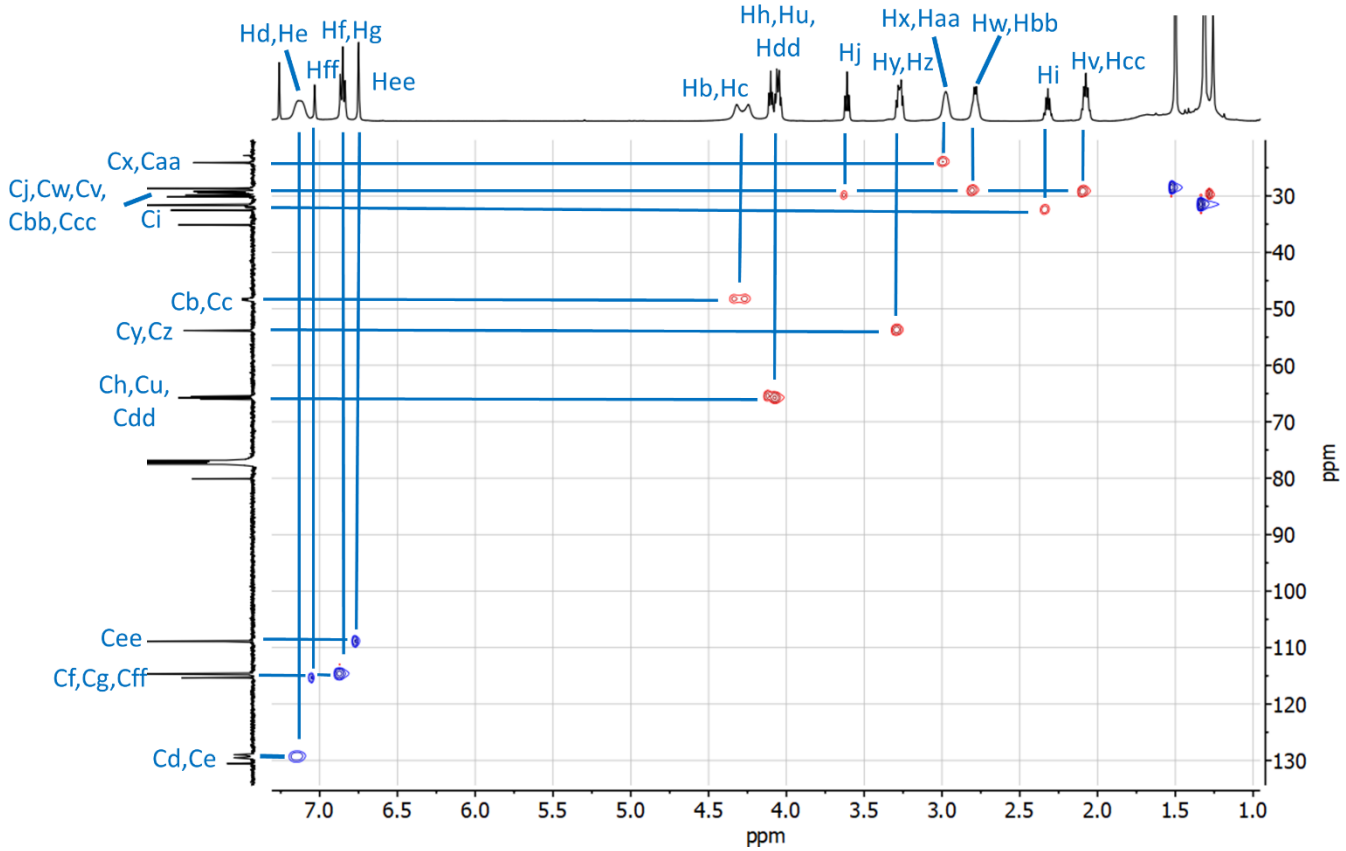


Figure S69: HSQC NMR (500 MHz and 126 MHz, $CDCl_3$) spectrum of **S13**.

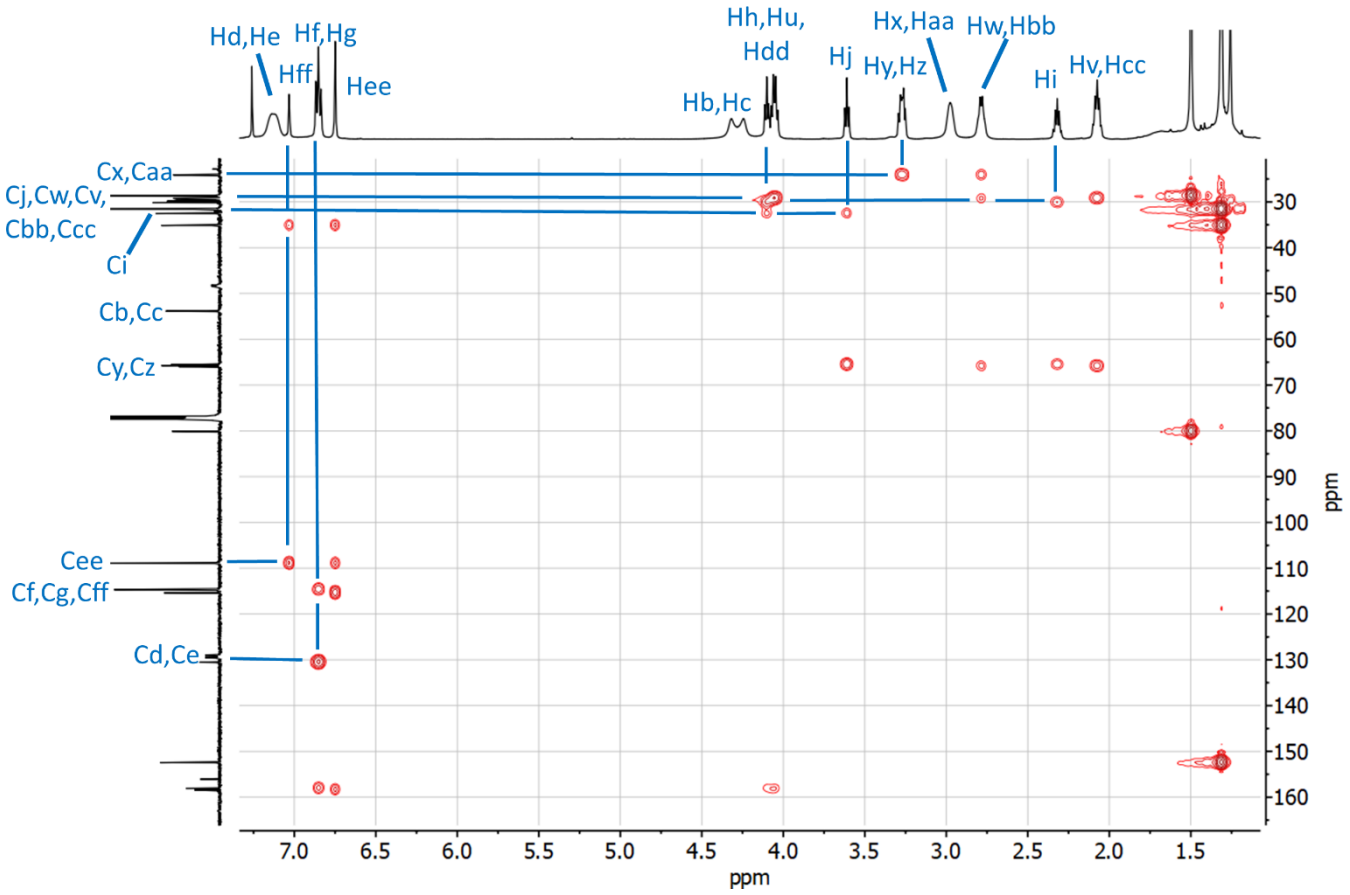


Figure S70: HMBC NMR (500 MHz and 126 MHz, $CDCl_3$) spectrum of **S13**.

Compound 14-$H^+ \cdot PF_6^-$:

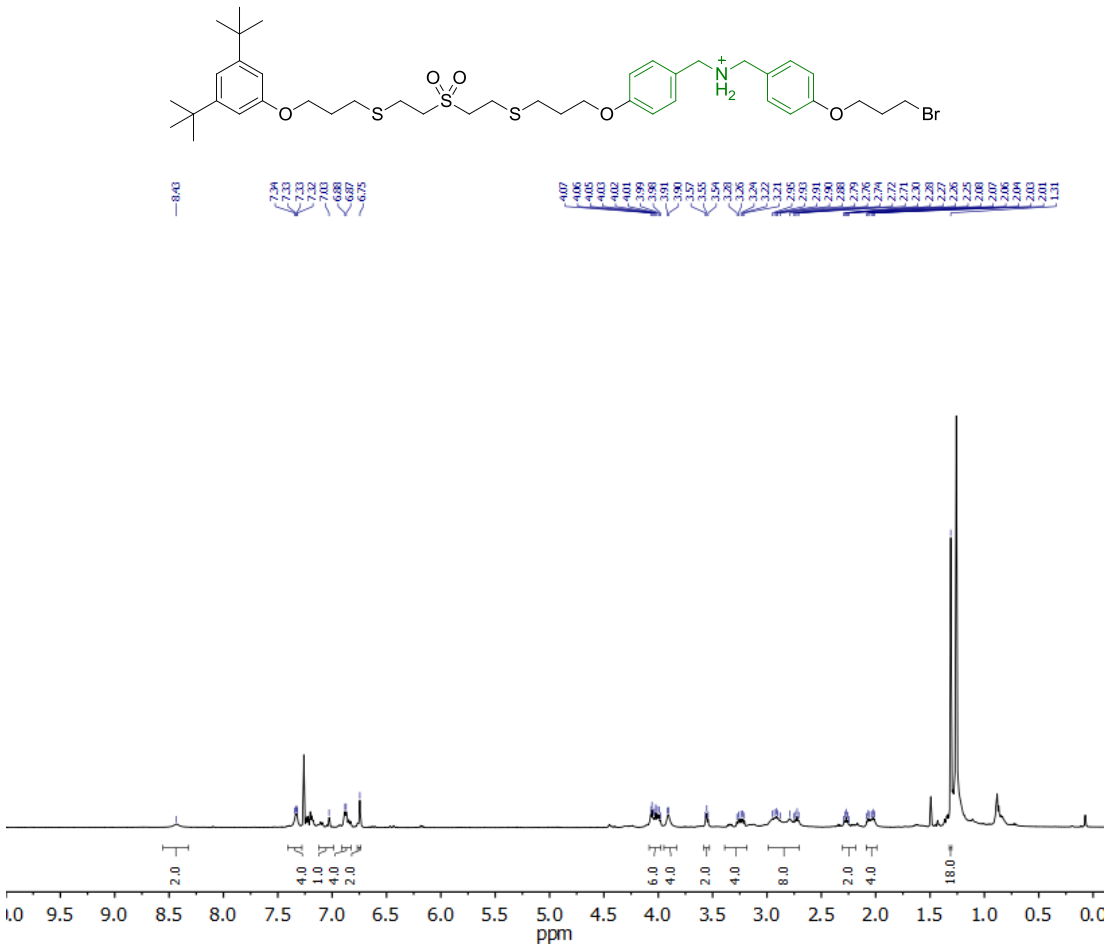


Figure S71: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **14**-$H^+ \cdot PF_6^-$.

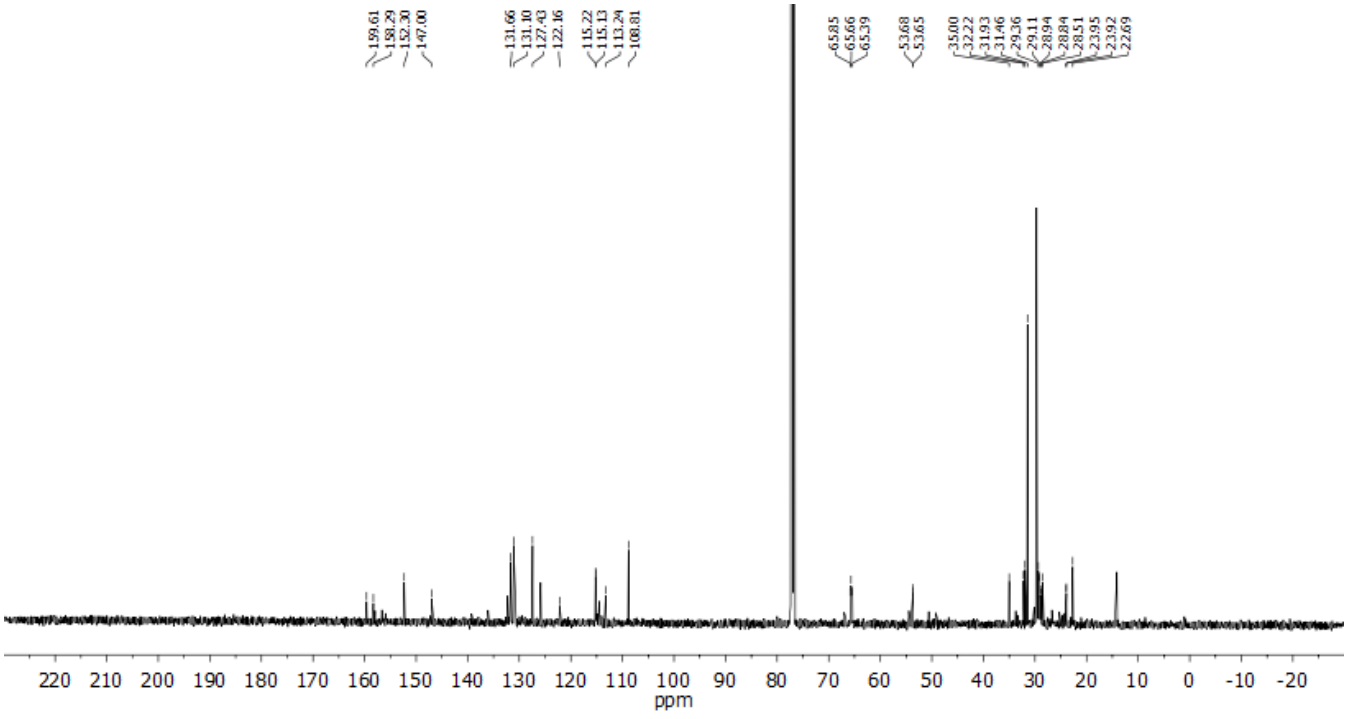


Figure S72: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **14**-$H^+ \cdot PF_6^-$.

Compound 14:

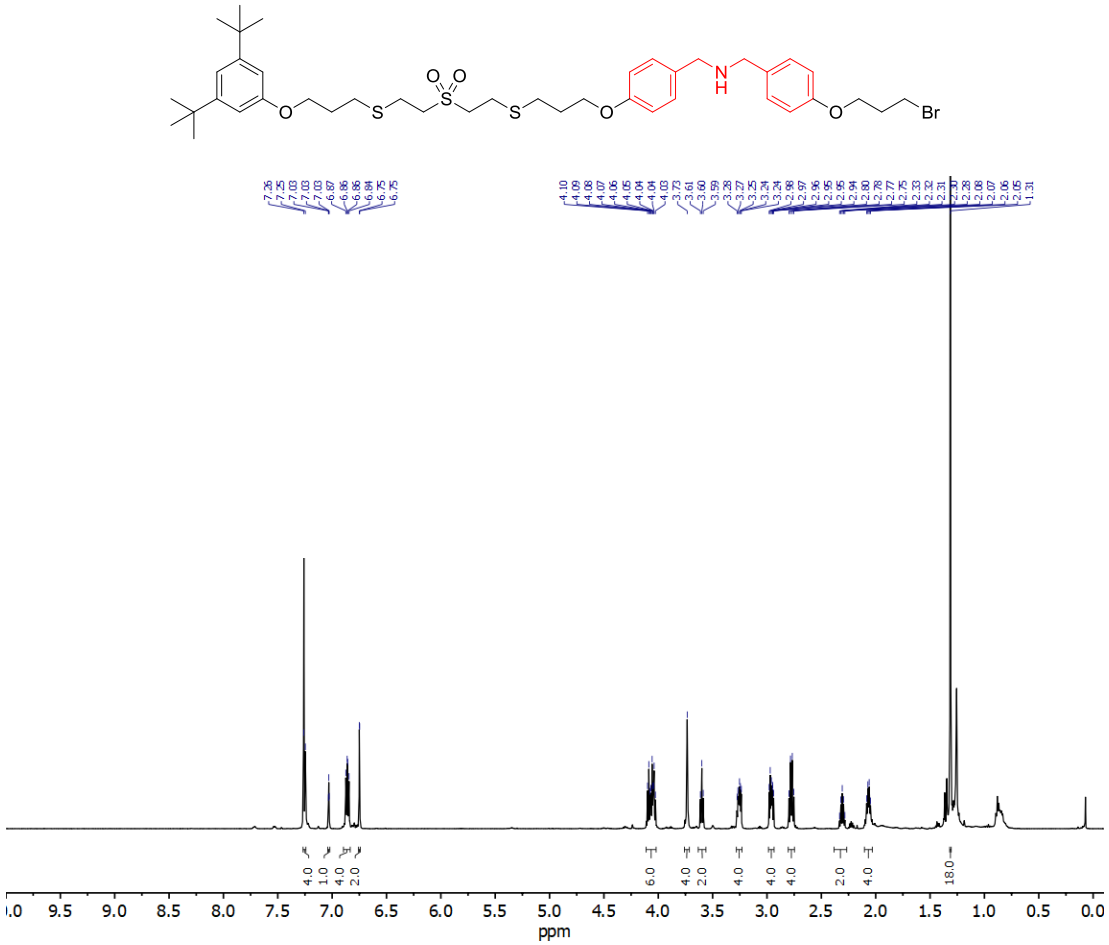


Figure S73: ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **14**.

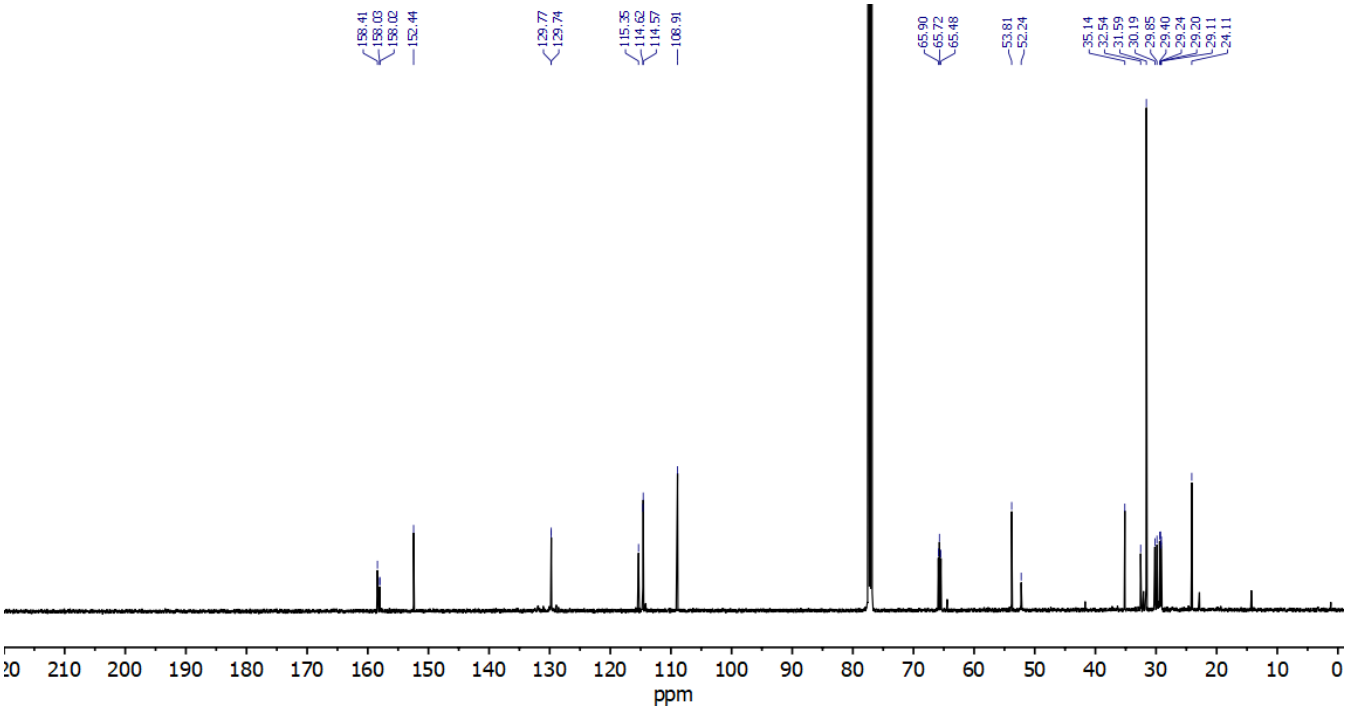


Figure S74: ^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **14**.

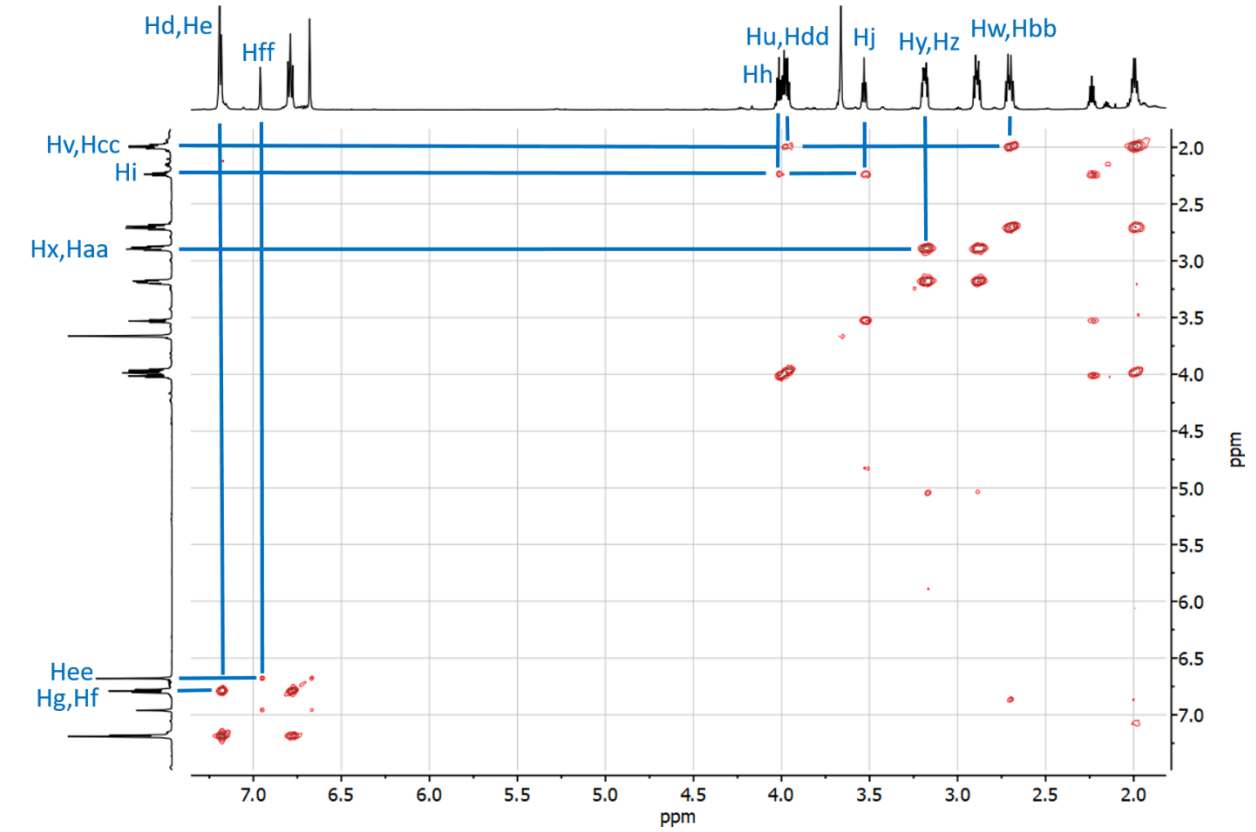


Figure S75: COSY NMR (600 MHz, $CDCl_3$) spectrum of **14**.

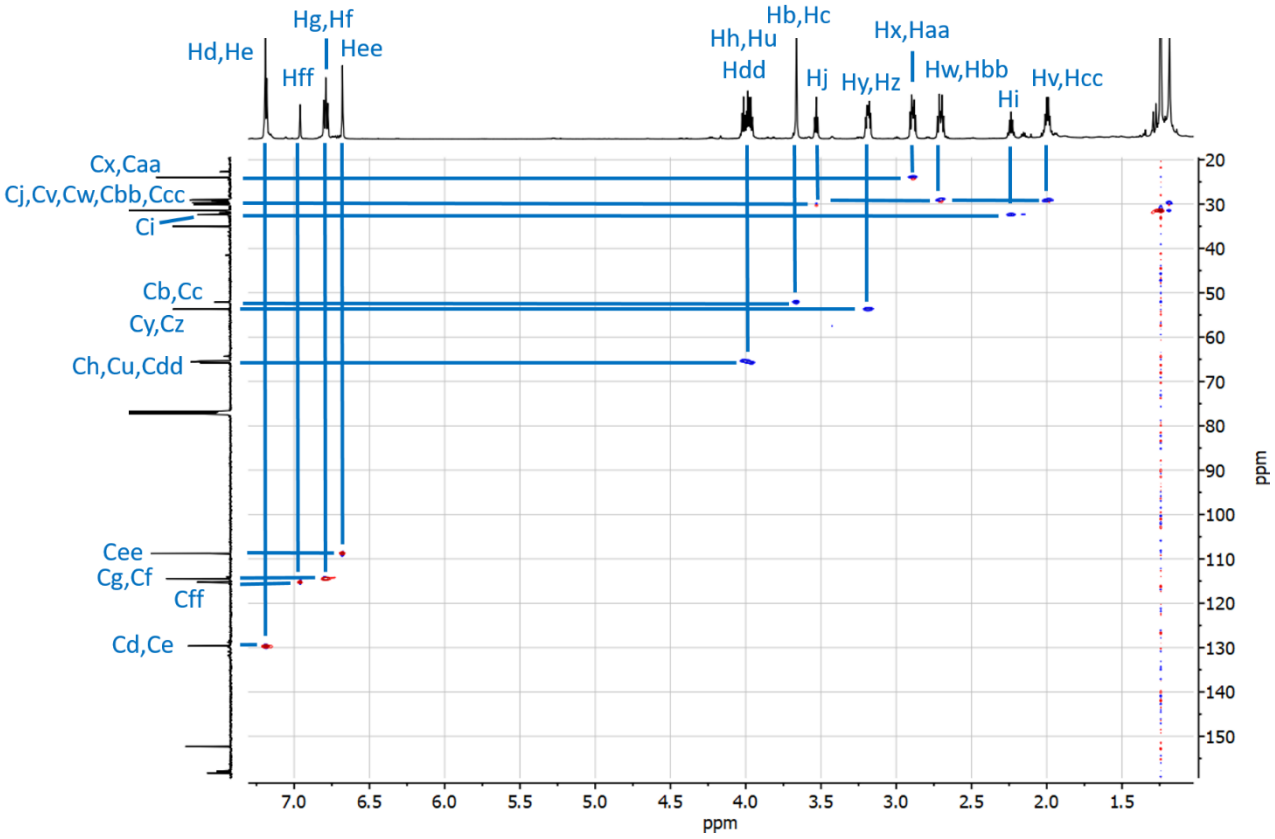


Figure S76: HSQC NMR (600 MHz and 151 MHz, $CDCl_3$) spectrum of **14**.

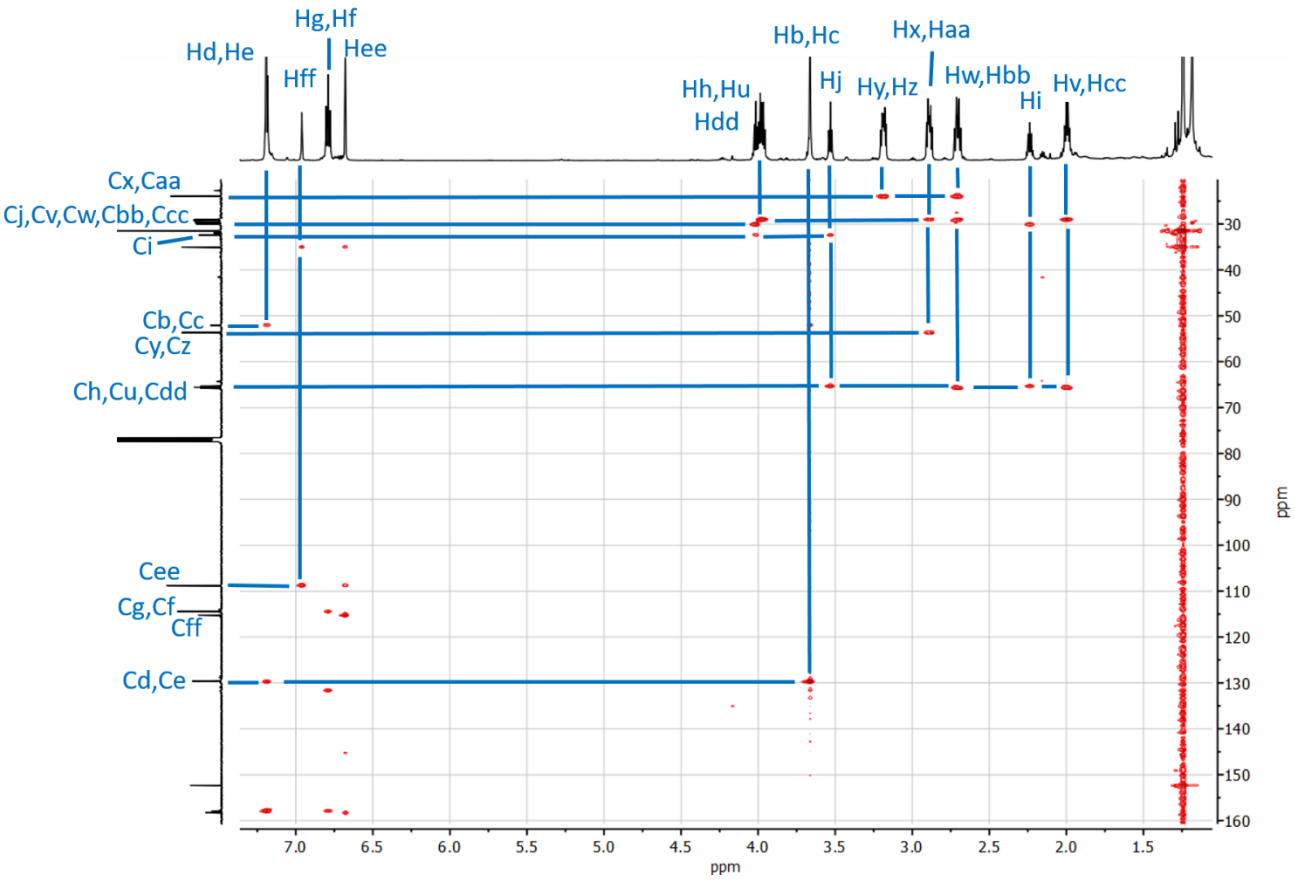


Figure S77: HMBC NMR (600 MHz and 151 MHz, $CDCl_3$) spectrum of **14**.

4. HRMS spectra of key compounds

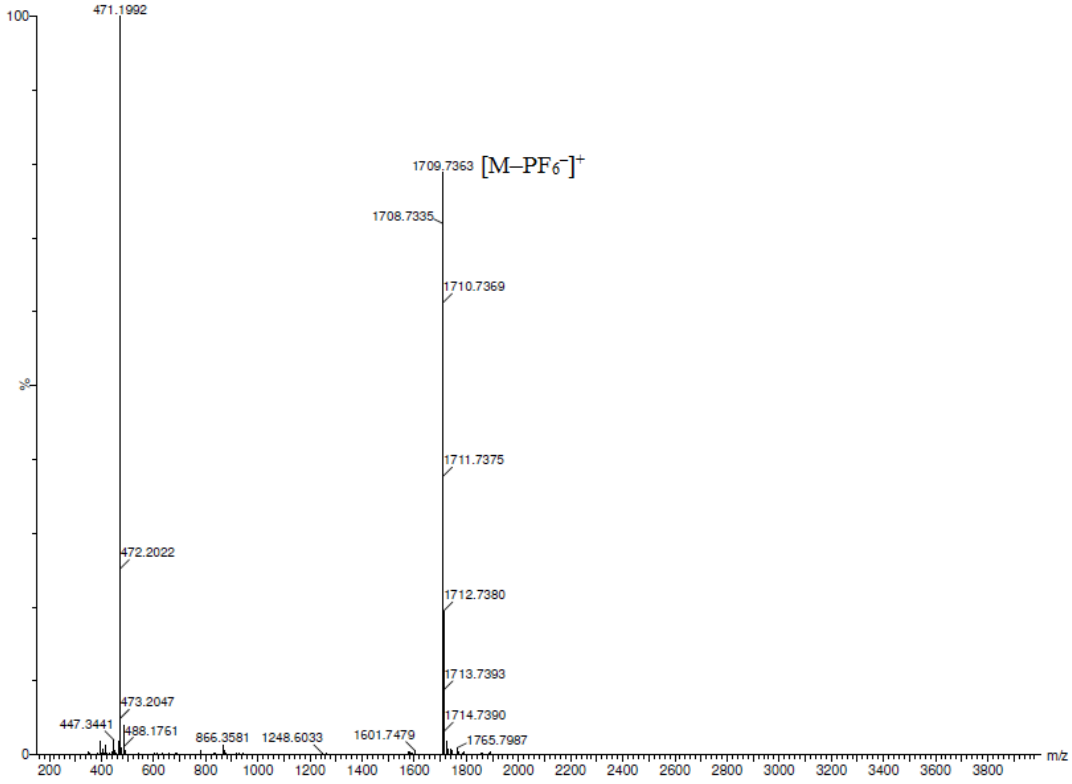


Figure S78: HRMS (ESI$^+$) spectrum of rotaxane **13**·PF_6^-.

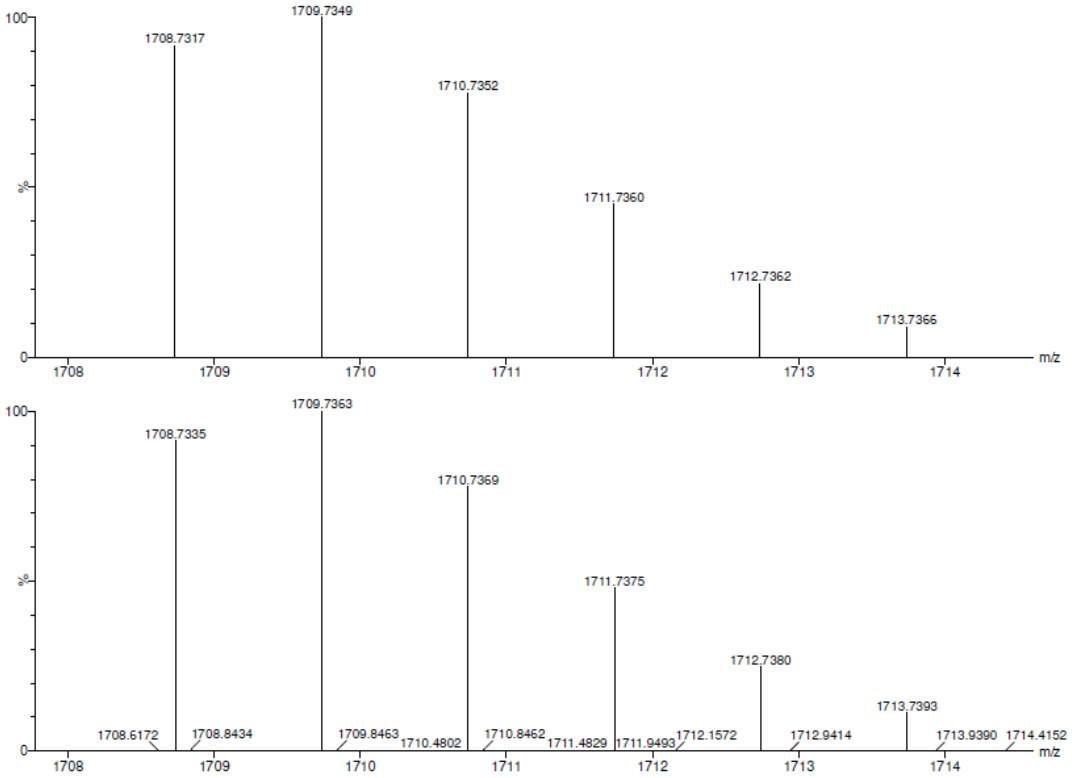


Figure S79: Experimental (bottom) and theoretical (top) isotopic distribution for the [M–PF_6^-]$^+$ ion of rotaxane **13**·PF_6^-.

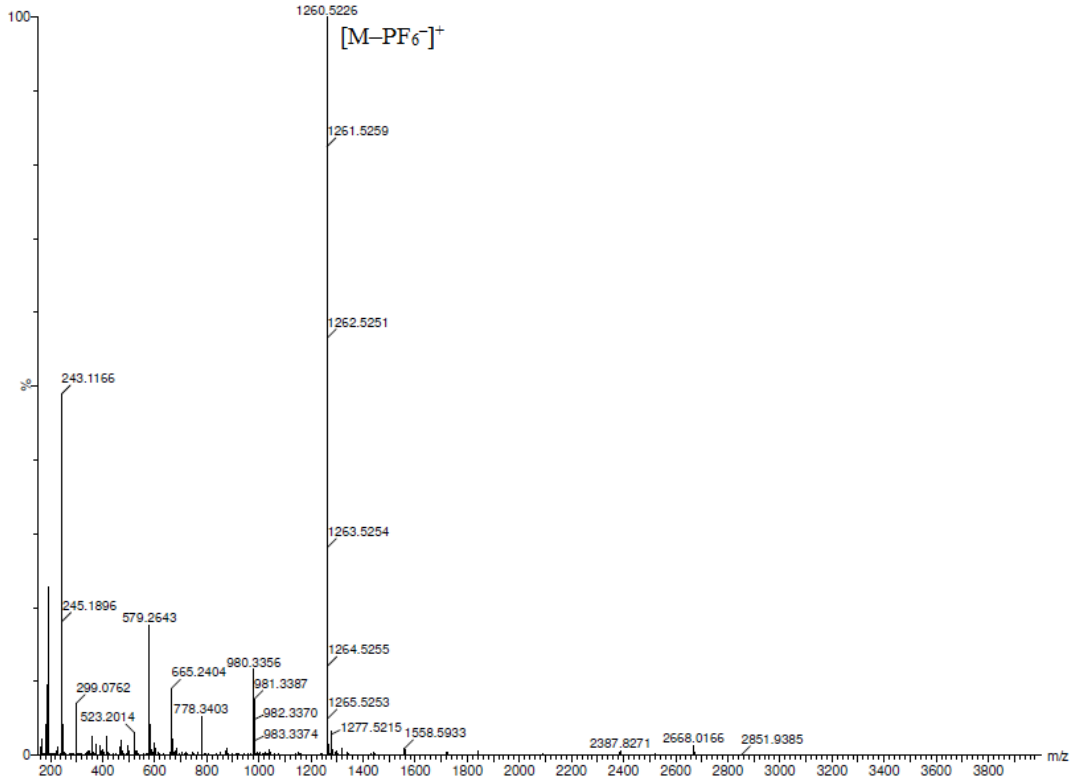


Figure S80: HRMS (ESI$^+$) spectrum of thread **S12**·PF_6^-.

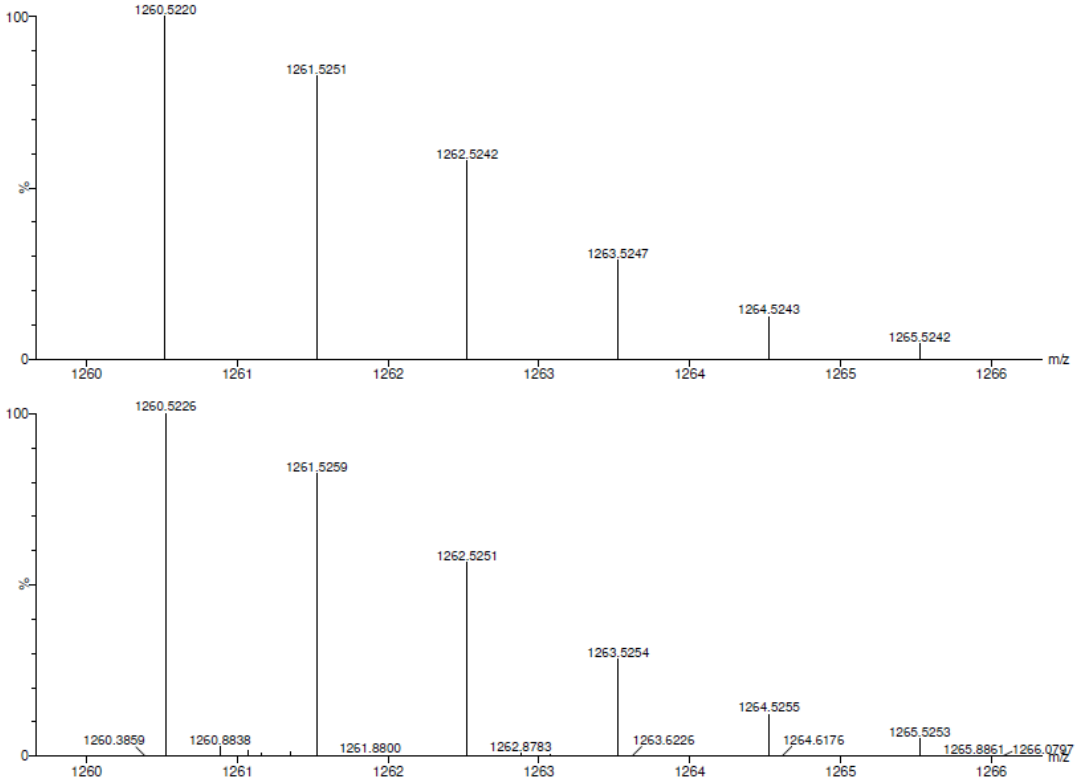


Figure S81: Experimental (bottom) and theoretical (top) isotopic distribution for the [M–PF_6^-]$^+$ ion of thread **S12**·PF_6^-.

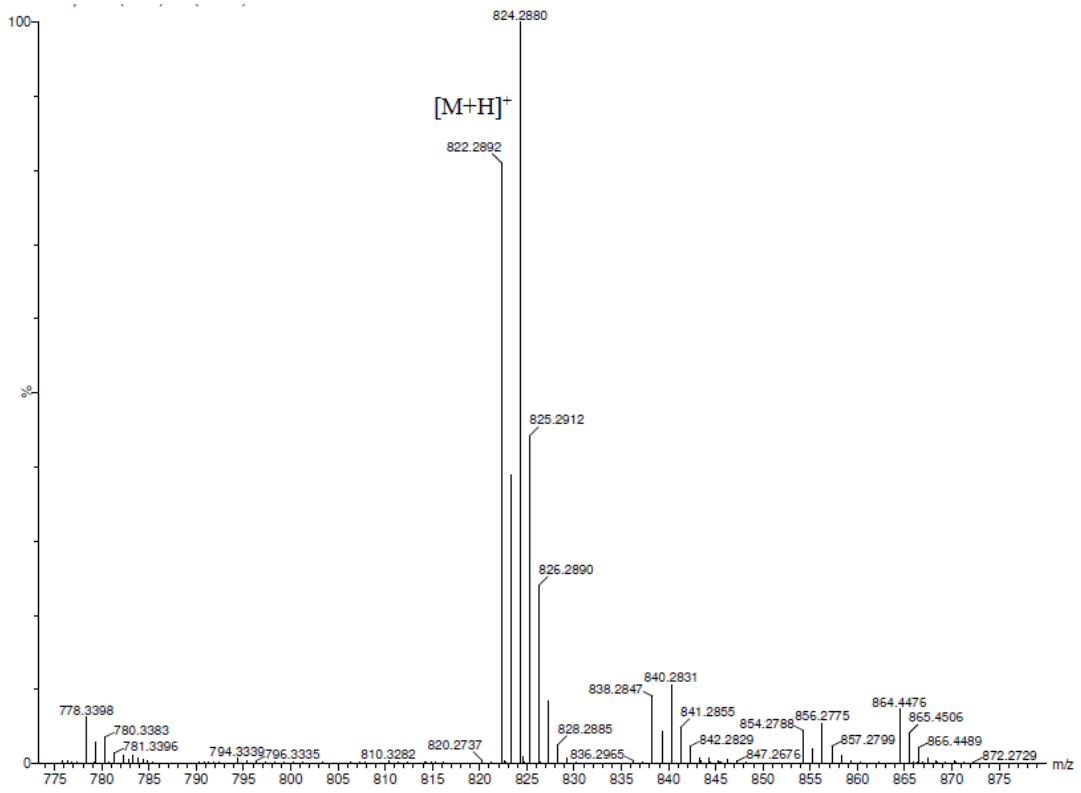


Figure S82: HRMS (ESI^+) spectrum of **14** obtained from the cleavage of rotaxane **13**·PF_6^-.

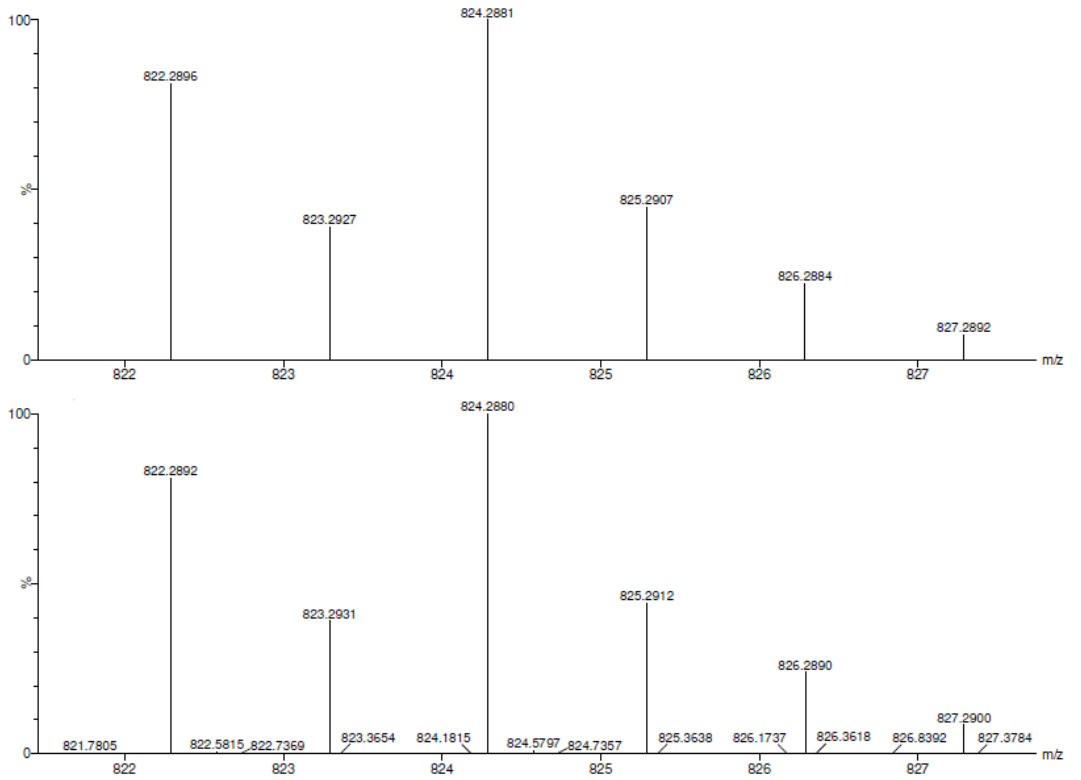


Figure S83: Experimental (bottom) and theoretical (top) isotopic distribution for **14** obtained from the cleavage of rotaxane **13**·PF_6^-.

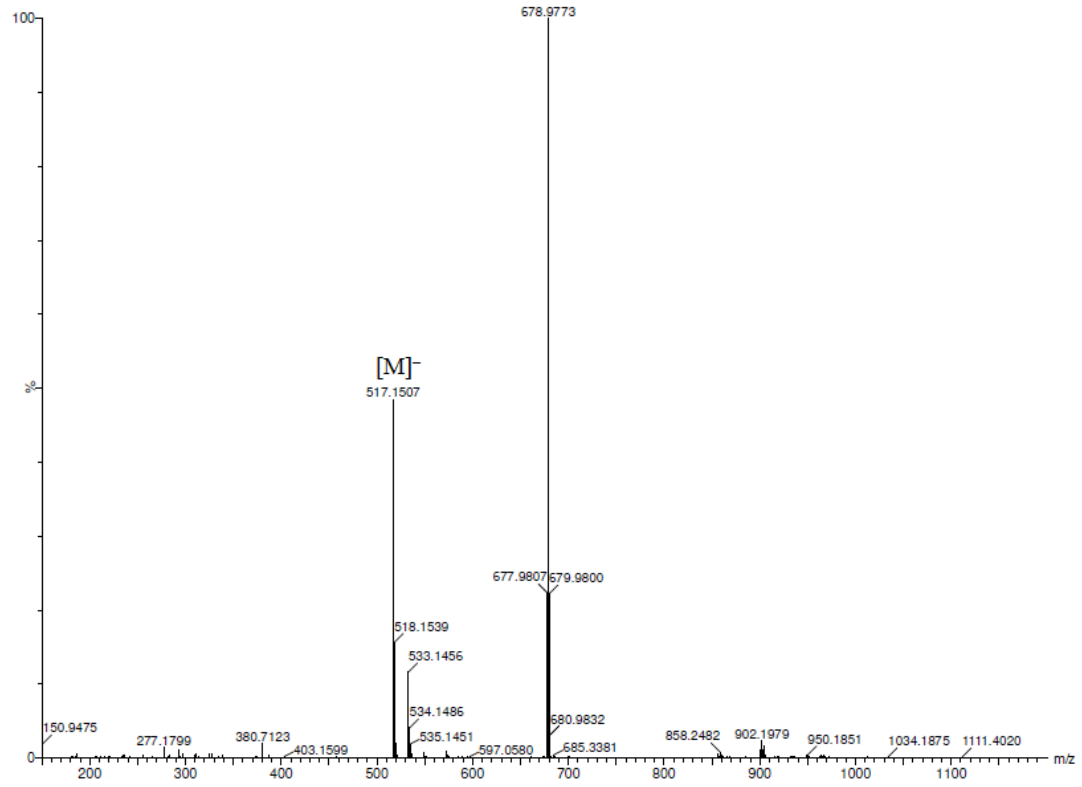


Figure S84: HRMS (ESI⁻) spectrum of **15** obtained from the cleavage of rotaxane **13**·PF_6^-.

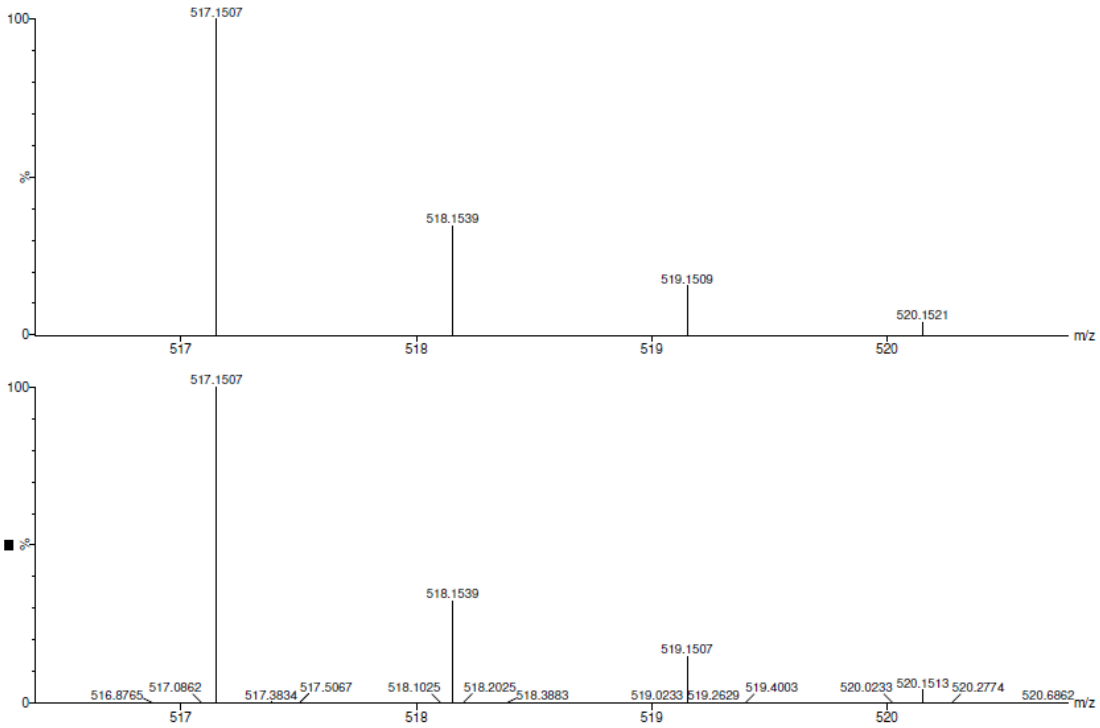


Figure S85: Experimental (bottom) and theoretical (top) isotopic distribution for the [M]⁻ ion of **15** obtained from the cleavage of rotaxane **13**·PF_6^-.

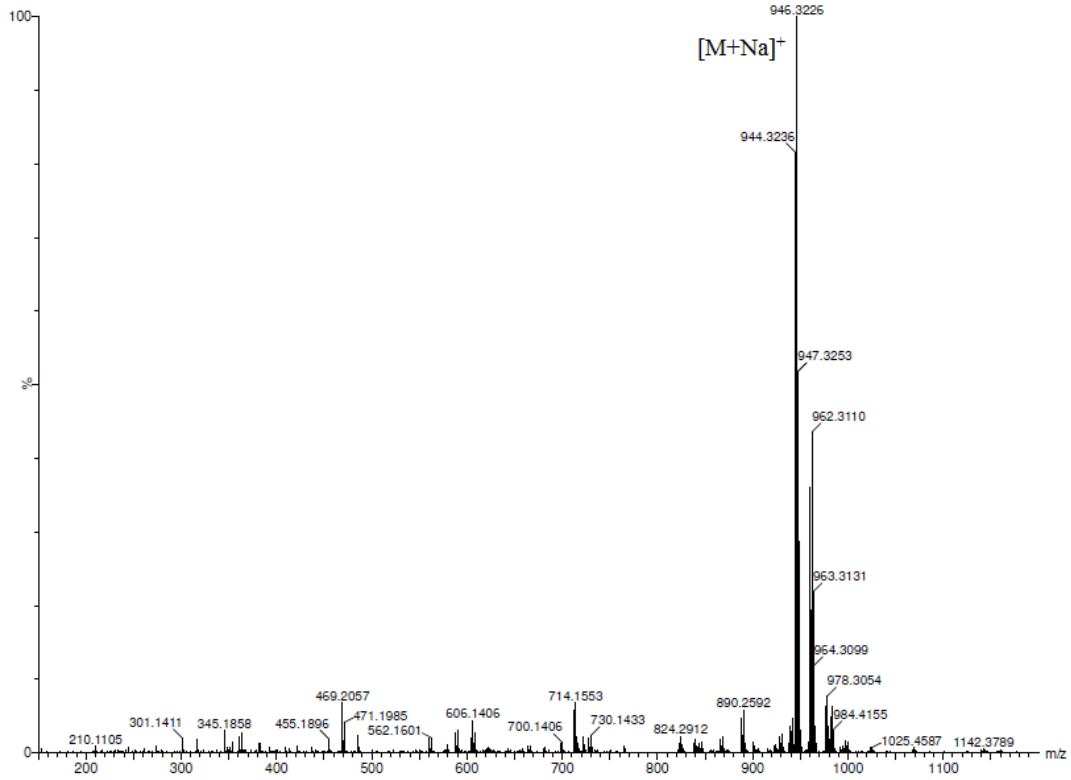


Figure S86: HRMS (ESI^+) spectrum of compound **S13**.

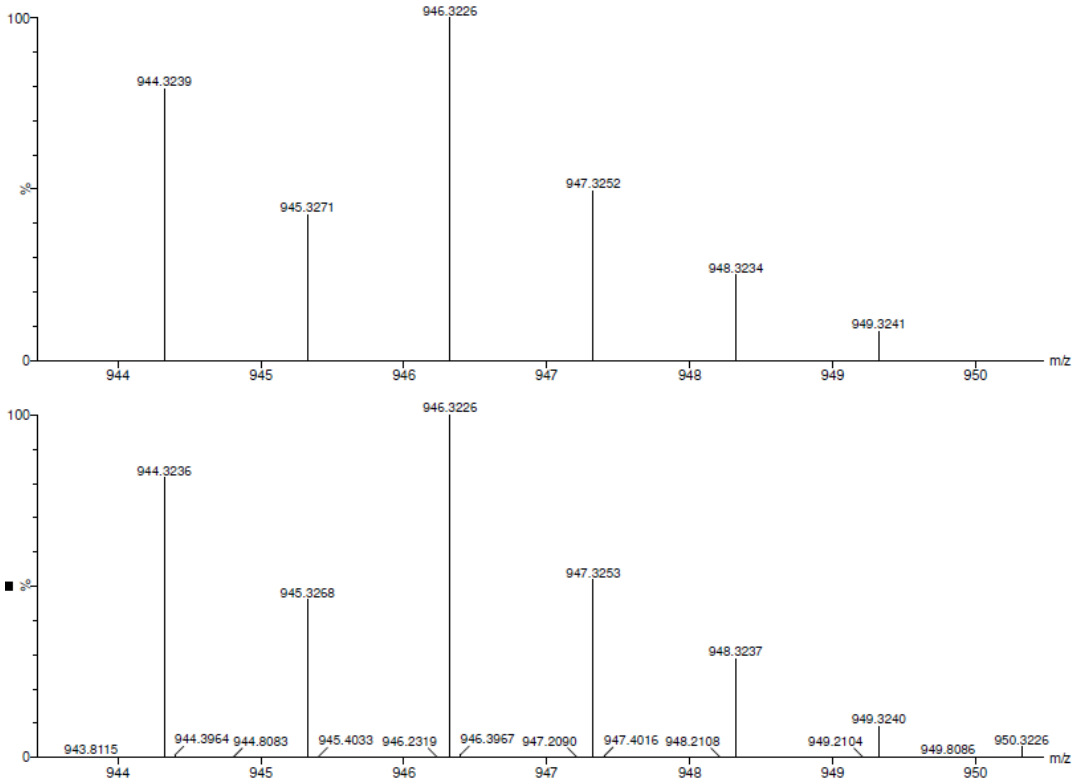


Figure S87: Experimental (bottom) and theoretical (top) isotopic distribution for the $[M+Na]^+$ ion of compound **S13**.

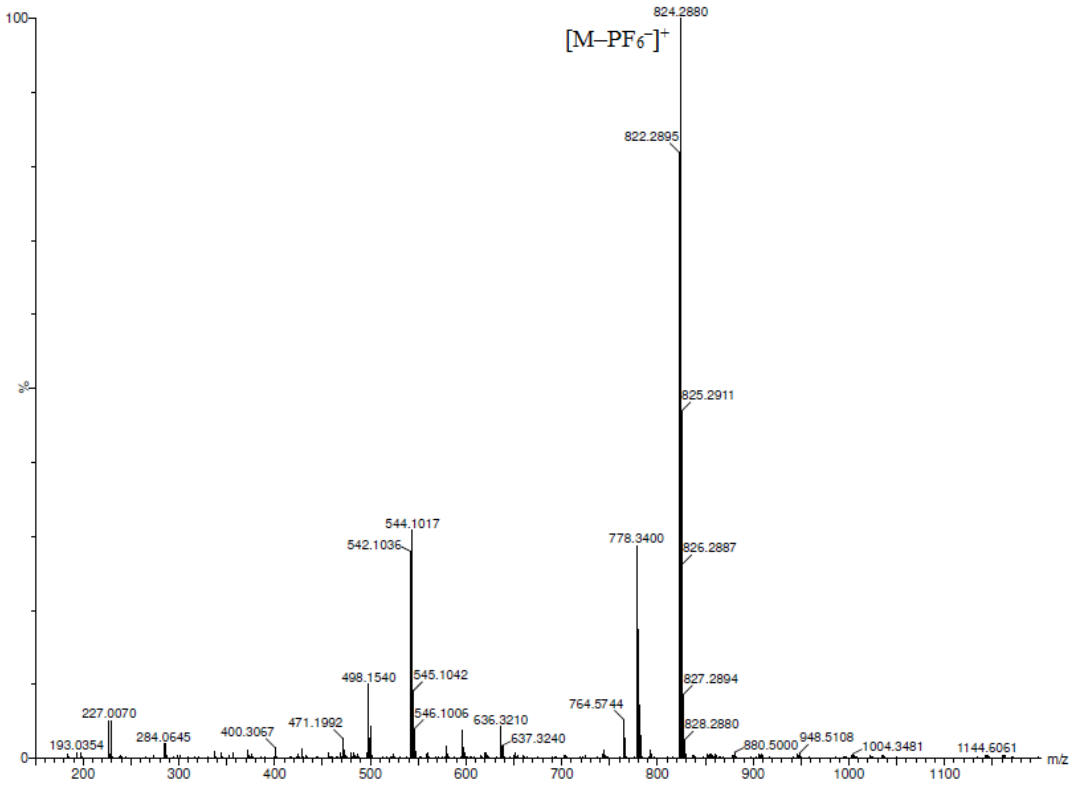


Figure S88: HRMS (ESI$^+$) spectrum of **14**-H$^+$·PF$_6^-$.

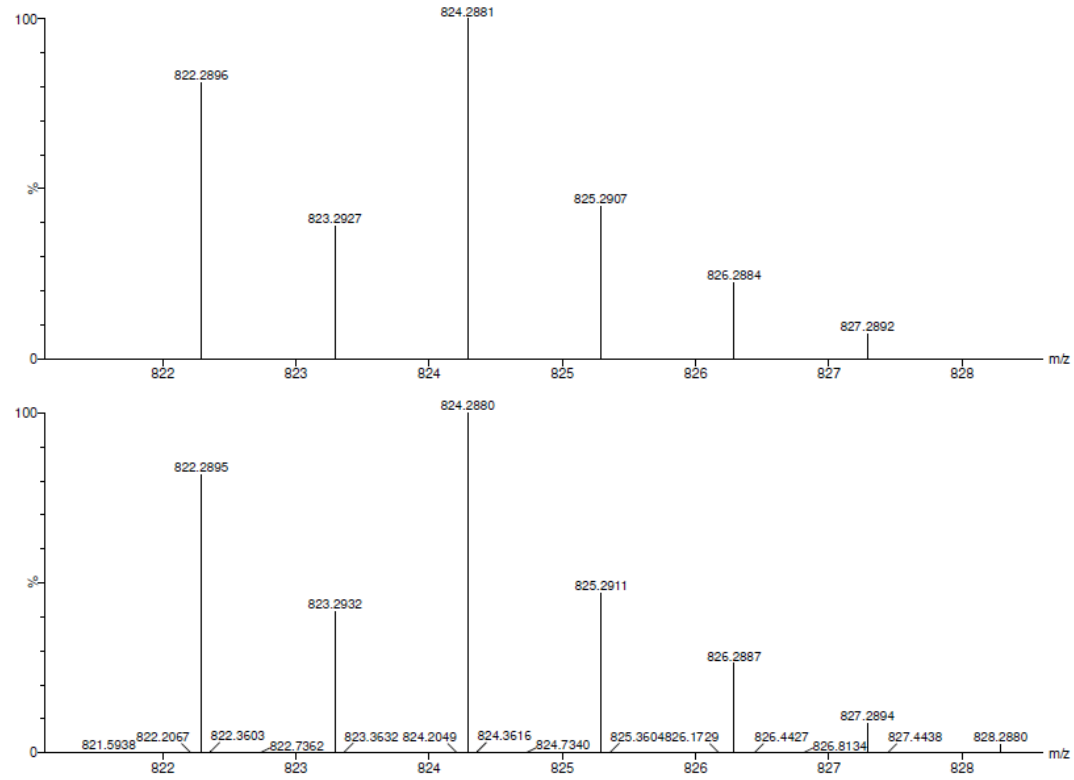


Figure S89: Experimental (bottom) and theoretical (top) isotopic distribution for the [M–PF$_6^-$]$^+$ ion of **14**-H$^+$·PF$_6^-$.

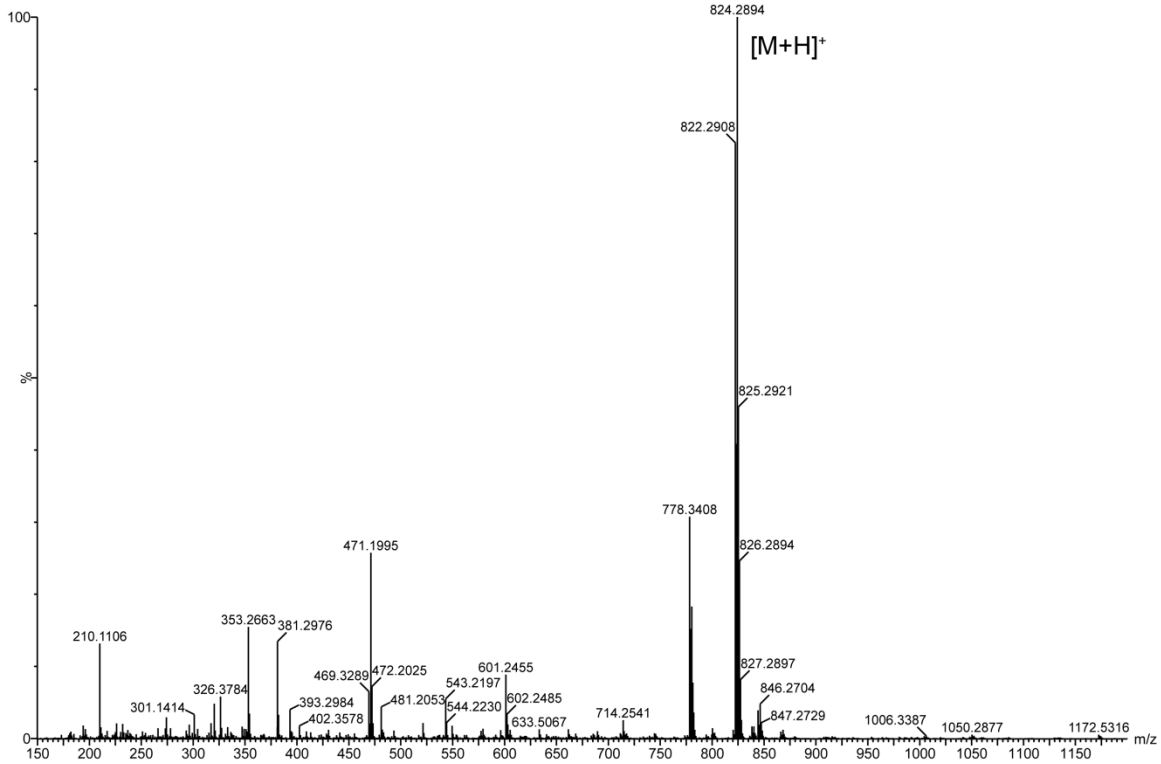


Figure S90: HRMS (ESI$^+$) spectrum of **14**.

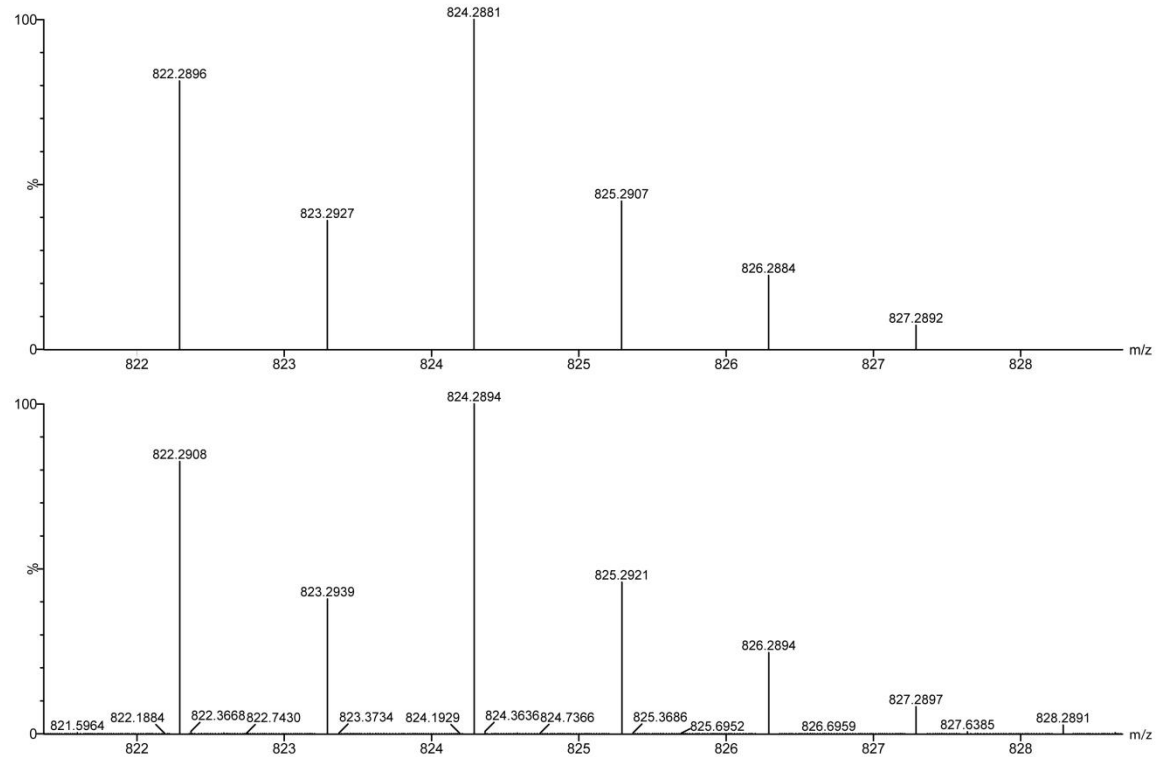


Figure S91: Experimental (bottom) and theoretical (top) isotopic distribution for the [M+H]$^+$ ion of **14**.

5. References

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S4 C. Sirichaiwat, C. Intaraudom, S. Kamchonwongpaisan, J. Vanichtanankul, Y. Thebtaranonth and Y. Yuthavong, Target Guided Synthesis of 5-Benzyl-2,4-diamonopyrimidines: Their Antimalarial Activities and Binding Affinities to Wild Type and Mutant Dihydrofolate Reductases from *Plasmodium falciparum*, *J. Med. Chem.*, 2004, **47**, 345–354.

S5 This effect has been pointed as a plausible explanation for the switching of DB24C8 in a dibenzylamine/ammonium rotaxane. See section 4.2.1 in: F. Coutrot, A Focus on Triazolium as a Multipurpose Molecular Station for pH-Sensitive Interlocked Crown-Ether-Based Molecular Machines, *ChemistryOpen*, 2015, **4**, 556–576.