Supplementary Data for: Towards macrocyclic frustrated Lewis pairs

Jason Yeung,[a] Matthias Becker [a] and Douglas W. Stephan*[a]

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Chemicals and Materials

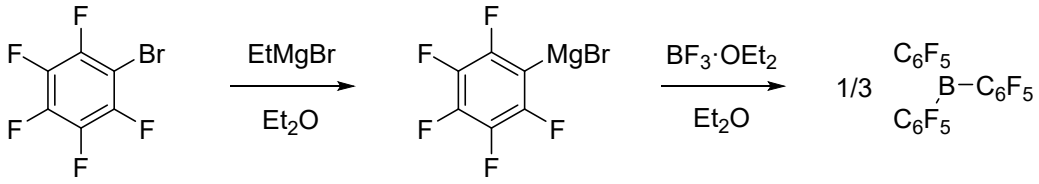
All manipulations were performed under an atmosphere of dry and deoxygenated N_2 under standard glovebox or Schlenk techniques unless otherwise stated. All glassware was dried in an oven at 200°C followed by dynamic vacuum over several hours prior to use. After suitable drying procedures, all solvents were stored over 4 Å molecular sieves for a minimum of 24 h prior to use. 4 Å molecular sieves were activated by heating in a sand bath (>200°C) under dynamic vacuum over 48 h. Plastic syringes and disposable needles were evacuated in the antechamber of the glovebox prior to use. Toluene, dichloromethane, diethyl ether and n-pentane were purchased from Sigma Aldrich and were dried using a Grubbs-type Innovative Technologies solvent purification system prior to use. Benzene-d_6 and chloroform-d were dried over CaH_2 and distilled prior to use. Ethylmagnesium bromide 3M diethyl ether solution, boron trifluoride diethyl etherate, borane dimethyl sulfide complex, magnesium turnings, lithium aluminum hydride, sodium borohydride, phosphorus pentabromide, sodium iodide, acetyl chloride, copper(I) iodide, [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II), and methyl 2,2-difluoro-2-(fluorosulfonyl)acetate were purchased from Sigma Aldrich and were used without further purification. 4-Hydroxypyridine-2,6-dicarboxylic acid and dimethyl 4-chloropyridine-2,6-dicarboxylate were purchased from Combi-Blocks and were used without further purification. 2-Bromomesitylene was purchased from TCI America and was used without further purification. Triethyl borate was purchased from Sigma Aldrich and was purified by drying over sodium followed by distillation prior to use. Bromopentafluorobenzene and trimethylsilyl chloride were purchased from Sigma Aldrich and were purified by distillation prior to use.

Physical Methods

All NMR spectra were collected at 298 K on Bruker Avance III 400 MHz, Agilent DD2 400 MHz, Agilent DD2 500 MHz, or Agilent DD2 600 MHz spectrometers in 3- or 5-mm diameter NMR tubes or in a J-Young tube. Chemical shifts (δ) are reported in ppm and absolute values of coupling constants are listed in Hz. Multiplicity is reported as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. ^{1}H NMR spectra are referenced related to residual deuterated-solvent or protio-solvent signals. Mass spectra were obtained on JEOL AccuTOF model JMS-T1000LC mass spectrometer equipped with a Direct Analysis in Real Time (DART) ion source. The samples were dissolved in a suitable solvent and introduced to the DART source using a glass melting point capillary. X-ray diffraction data were collected using a graphite monochromator with MoK(α) radiation (λ = 0.71073 Å) and the Bruker APEX2 software package. Single crystals were coated in paratone-N oil, mounted on a Bruker Kappa Apex II diffractometer, and placed in a cold stream of N_2 prior to collection. Data reduction was performed using the SAINT software package and an absorption correction was applied using SADABS. The structures were solved by direct methods using XS and refined by full-matrix least-squares on F2 using XL as implemented in the SHELXTL suite of programs. All non-hydrogen atoms were refined anisotropically. Carbon-bound hydrogen atoms were placed in calculated positions using an appropriate riding model and coupled isotropic temperature factors.

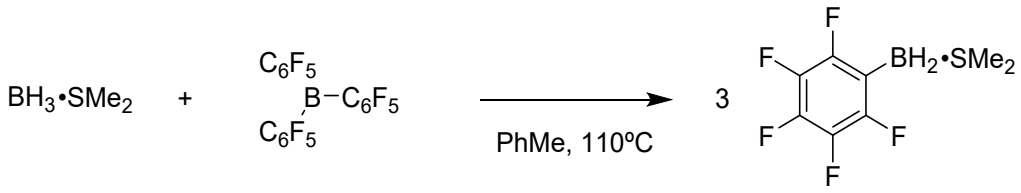
Preparation of starting materials

Preparation of tris(pentafluorophenyl)borane



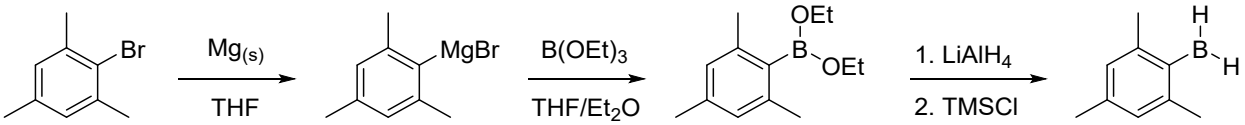
Tris(pentafluorophenyl)borane was synthesized according to modified literature procedures.[1] Using basic Schlenk line techniques, ethylmagnesium bromide 3 M diethyl ether solution (20 mL, 60.0 mmol) was added slowly (dropwise) to a solution of bromopentafluorobenzene (14.82 g, 60 mmol) in diethyl ether (125 mL) at -78°C. The reaction mixture was warmed to room temperature and stirred for 3 h. In an inert atmosphere glovebox, added the resulting pentafluorophenylmagnesium bromide solution to a solution of boron trifluoride diethyl etherate (2.84 g, 20.0 mmol) in diethyl ether (150 mL). Stirred reaction mixture at room temperature for 18 h. The volatiles were removed under reduced pressure to give a sticky white solid. Added pentane (5 x 20 mL) while stirring and evacuated to pull out any residual ether from solid, resulting in a powdery white solid. Purified crude product by sublimation (120°C on full vacuum) to yield a white solid. Recrystallized from warm hexanes to give a fluffy white solid (Yield: 8.10 g, 79.1%). The product was characterized by NMR spectroscopy. ^{11}B NMR (C_6D_6, 128 MHz, 298 K): δ (ppm) 60.4 (br s). ^{19}F NMR (C_6D_6, 376 MHz, 298 K): δ (ppm) -128.76 (br s, 2F, *o*-F), -141.59 (br s, 1F, *p*-F), -159.91 (m, 2F, *m*-F).

Preparation of $C_6F_5BH_2{\cdot}SMe_2$



$C_6F_5BH_2{\cdot}SMe_2$ was synthesized according to modified literature procedures.[2] Using basic Schlenk line techniques, an excess of $BH_3{\cdot}SMe_2$ (742 mg, 9.77 mmol) was added to a solution of $B(C_6F_5)_3$ (1.0 g, 2.0 mmol) in toluene (16 mL). The reaction mixture was stirred at 80°C for 5 h. After cooling to room temperature, removed all volatiles under reduced pressure to give a white solid. In an inert atmosphere glovebox, recrystallized from a dichloromethane-pentane solution at -17°C to give a white solid (Yield: 1.19 g, 84%). The product was characterized by NMR spectroscopy. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ (ppm) 2.98 (br s, 2H, BH_2), 2.25 (s, 6H, CH_3). ^{11}B NMR ($CDCl_3$, 128 MHz, 298 K): δ (ppm) -17.1 (t, $^1J_{B\text{-}H}$ = 105.0 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz, 298 K): δ (ppm) -130.46 (d, $^3J_{F\text{-}F}$ = 18.8 Hz, 2F, *o*-F), -157.20 (t, $^3J_{F\text{-}F}$ = 20.7 Hz, 1F, *p*-F), -163.68 (m, 2F, *m*-F).

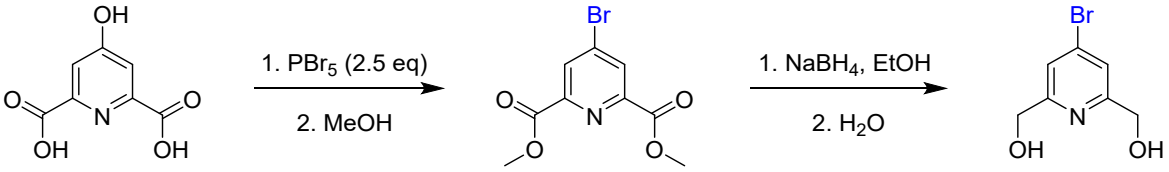
Preparation of mesitylborane ($MesBH_2$)



Mesitylborane was synthesized according to modified literature procedures.[3] Using Schlenk line techniques, magnesium turnings (2.93 g, 120 mmol) were added to dry THF (70 mL), then 2-bromomesitylene (20 g, 0.10 mol) was added slowly (dropwise) into the reaction flask at room temperature. The reaction mixture was stirred at 70°C for 4 h. After cooling to room temperature, the resulting Grignard solution was added to a 0°C solution of triethyl borate (29.3 g, 201 mmol) in dry THF (70 mL) under positive nitrogen flow. During the addition, a white salt precipitates out of solution. Let reaction mixture warm up to room temperature, then stirred at room temperature for 16 h. In an inert atmosphere glovebox, the reaction mixture was vacuum filtered, then washed with pentane (2 x 10 mL). The volatiles were removed under reduced pressure to give a clear colourless liquid (Yield: 13.8 g, 62%). ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ (ppm) 6.80 (s, 2H, ArH), 3.83 (q, $^{3}J_{H\text{-}H}$ = 7.2 Hz, 4H, CH_2), 2.26 (s, 3H, *p*-CH_3), 2.25 (s, 6H, *o*-CH_3), 1.21 (t, $^{3}J_{H\text{-}H}$ = 7.2 Hz, 6H, CH_3). ^{11}B NMR ($CDCl_3$, 128 MHz, 298 K): δ (ppm) 30.6 (s).

In an inert atmosphere glovebox, the resulting diethoxymesitylborane (13.8 g, 62.8 mmol) was added to diethyl ether/pentane (200 mL/50 mL), then a solution of $LiAlH_4$ (2.5 g, 66 mmol) in diethyl ether (100 mL) was added slowly (dropwise) at room temperature. The reaction mixture was stirred at room temperature for 16 h. The reaction mixture was vacuum filtered, then washed with diethyl ether (10 mL) and pentane (2 x 10 mL). To the filtrate, trimethylsilyl chloride (8.4 mL, 66 mmol) was added slowly (dropwise) at room temperature. The reaction mixture was stirred at room temperature for 5 h. The reaction mixture was vacuum filtered, then washed with diethyl ether (10 mL) and pentane (2 x 10 mL). The volatiles were removed under reduced pressure and the product was recrystallized from pentane at -17°C to give a white crystalline solid (Yield: 4.21 g, 51%). The product was characterized by NMR spectroscopy. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ (ppm) 6.91 (s, 2H, ArH), 2.37 (s, 6H, *o*-CH_3), 2.31 (s, 3H, *p*-CH_3). ^{11}B NMR ($CDCl_3$, 128 MHz, 298 K): δ (ppm) 22.0 (s).

Preparatbion of 4-bromo-2,6-pyridinedimethanol

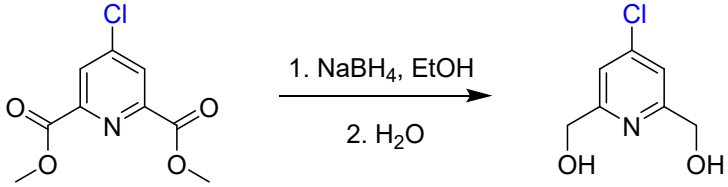


4-Bromo-2,6-pyridinedimethanol was synthesized according to modified literature procedures.[4] Using Schlenk line techniques, 4-hydroxypyridine-2,6-dicarboxylic acid (2.0 g, 11 mmol) and phosphorus pentabromide (11.75 g, 27.3 mmol) were mixed together. The solid mixture was stirred at 90°C for 16 h. After cooling to room temperature, methanol (25 mL) was

added to the reaction mixture and stirred at room temperature for 1 h. The volatiles were removed under reduced pressure, then partitioned crude product between chloroform and water. Extracted with chloroform (2x), washed with water (2x) and saturated $NH_4Cl_{(aq)}$ (2x). The organic phases were combined, dried over $MgSO_4$, vacuum filtered, and the solvent was removed under reduced pressure to give a light-orange solid (Yield: 2.5 g, 84%). ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ (ppm) 8.46 (s, 2H, ArH), 4.04 (s, 6H, CH_3).

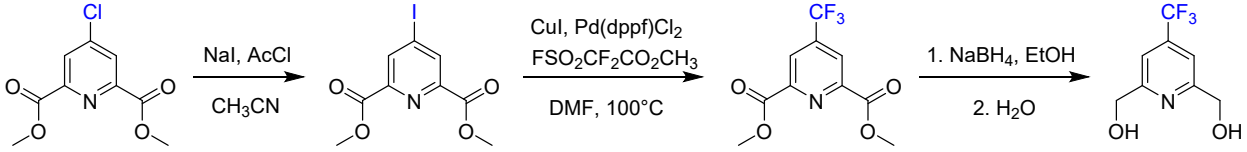
Added the resulting dimethyl 4-bromopyridine-2,6-dicarboxylate (1.5 g, 5.5 mmol) into ethanol (55 mL). Cooled reaction mixture to 0°C in an ice bath, then added excess $NaBH_4$ (828 mg, 22 mmol) slowly into the reaction flask while stirring. Stirred reaction mixture at 60°C for 3 h. Poured reaction mixture into cold H_2O and stirred for 30 min. Extracted with ethyl acetate (3x) and washed with brine. The organic phases were combined, dried over $MgSO_4$, and vacuum filtered. The solvent was removed under reduced pressure and the product was recrystallized from hot dichloromethane to give a white solid (686 mg, 57%). The product was characterized by NMR spectroscopy. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ (ppm) 7.42 (s, 2H, ArH), 4.76 (s, 4H, CH_2), 2.96 (br s, 2H, OH).

Preparation of 4-chloro-2,6-pyridinedimethanol



4-Chloro-2,6-pyridinedimethanol was synthesized according to modified literature procedures.[5] Using basic Schlenk line techniques, added dimethyl 4-chloropyridine-2,6-dicarboxylate (500 mg, 2.18 mmol) into ethanol (20 mL). Cooled reaction mixture to 0°C in an ice bath, then added excess $NaBH_4$ (330 mg, 8.71 mmol) slowly into the reaction flask while stirring. Stirred reaction mixture at 60°C for 3 h. Poured reaction mixture into cold H_2O and stirred for 30 min. Extracted with ethyl acetate (3x) and washed with brine. The organic phases were combined, dried over $MgSO_4$, vacuum filtered, and the solvent was removed under reduced pressure to give a light-yellow solid (246 mg, 65%). The product was characterized by NMR spectroscopy. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ (ppm) 7.36 (s, 2H, ArH), 5.57 (t, $^3J_{H\text{-}H}$ = 6.0 Hz, 2H, OH), 4.51 (d, $^3J_{H\text{-}H}$ = 6.0 Hz, 4H, CH_2).

Preparation of 4-trifluoromethyl-2,6-pyridinedimethanol



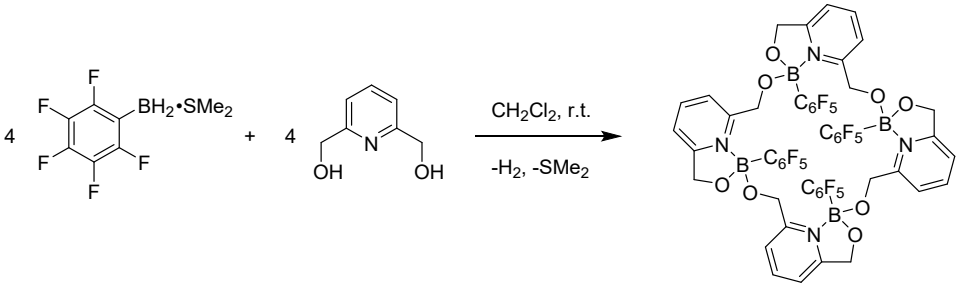
4-Trifluoromethyl-2,6-pyridinedimethanol was synthesized according to modified literature procedures.[6] Dimethyl 4-chloropyridine-2,6-dicarboxylate (3.0 g, 13.1 mmol) and sodium iodide (19.6 g, 131 mmol) were added to acetonitrile (150 mL). The suspension was sonicated for 30 min. at room temperature. Acetyl chloride (2.8 mL, 39 mmol) was added to the reaction mixture and sonicated for 60 min. at room temperature. The reaction mixture was partitioned between dichloromethane and saturated aqueous sodium carbonate. Extracted with dichloromethane (2x), washed with saturated sodium thiosulfate (2x), then washed with brine (2x). The organic phases were combined, dried over $MgSO_4$, and vacuum filtered. The volatiles were removed under reduced pressure and the product was recrystallized from methanol/water solution to give a light-red solid (Yield: 3.33 g, 79%). ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ (ppm) 8.66 (s, 2H, ArH), 4.03 (s, 6H, CH_3).

The resulting dimethyl 4-iodopyridine-2,6-dicarboxylate (3.33 g, 10.4 mmol), copper(I) iodide (11.85 g, 62.2 mmol), and Pd(dppf)Cl_2 catalyst (423 mg, 0.52 mmol) were added to DMF (80 mL), then a solution of methyl 2,2-difluoro-2-(fluorosulfonyl)acetate (8.0 mL, 62.2 mmol) in DMF (24 mL) was added to the reaction flask at room temperature. The reaction mixture was stirred at 100°C for 16 h. After cooling to room temperature, the dark brown solution was diluted with dichloromethane (250 mL) and filtered through a pad of celite. The filtrate was washed with water (3x), then washed with brine. The organic phases were combined, dried over $MgSO_4$, vacuum filtered, and the volatiles were removed under reduced pressure. The crude brown product was purified by silica column chromatography using 33% ethyl acetate in hexanes as the eluent. Collected desired fractions, removed solvent under reduced pressure, then recrystallized from ethyl acetate/diethyl ether solution to give a yellow solid (Yield: 1.92 g, 70%). ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ (ppm) 8.52 (s, 2H, ArH), 4.07 (s, 6H, CH_3). ^{19}F NMR ($CDCl_3$, 376 MHz, 298 K): δ (ppm) -64.70 (s, 3F, CF_3).

Using Schlenk line techniques, dimethyl 4-(trifluoromethyl)pyridine-2,6-dicarboxylate (500 mg, 1.90 mmol) was added into ethanol (20 mL). The reaction mixture was cooled to 0°C in an ice bath, then an excess of $NaBH_4$ (287 mg, 7.60 mmol) was slowly added into the reaction flask while stirring. The reaction mixture was stirred at 60°C for 3 h. The reaction mixture was poured into cold H_2O, stirred for 30 min., extracted with ethyl acetate (3x) and washed with brine. The organic phases were combined, dried over $MgSO_4$, and vacuum filtered. The solvent was removed under reduced pressure and the product was recrystallized from hot dichloromethane to give a white solid (Yield: 245 mg, 63%). The product was characterized by NMR spectroscopy. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ (ppm) 7.57 (s, 2H, ArH), 4.92 (s, 4H, CH_2), 2.79 (br s, 2H, OH). ^{19}F NMR ($CDCl_3$, 376 MHz, 298 K): δ (ppm) -64.84 (s, 3F, CF_3).

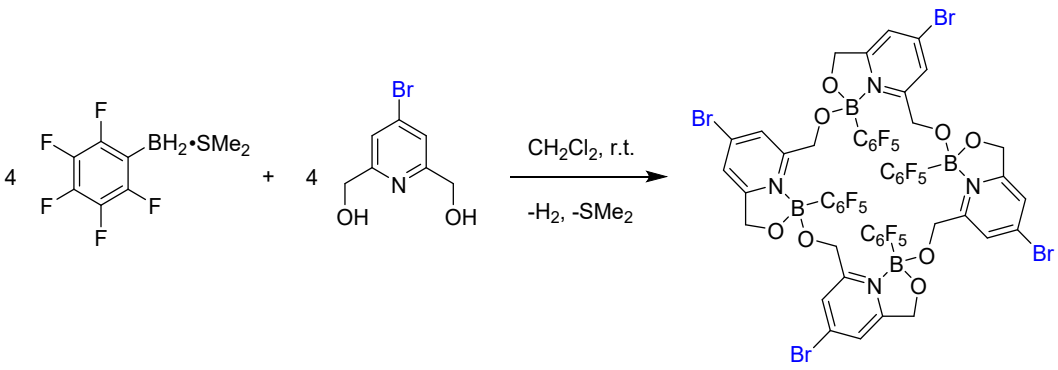
Preparation of macrocycles

Preparation of macrocycle 1



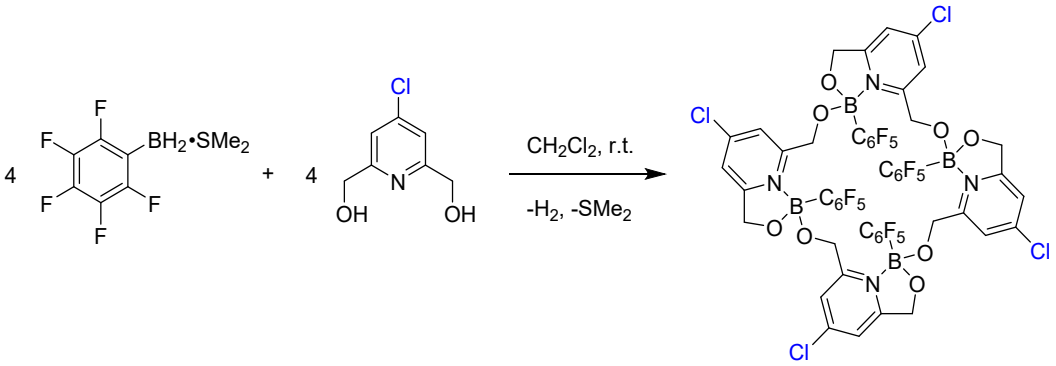
In an inert atmosphere glovebox, $C_6F_5BH_2{\cdot}SMe_2$ (246 mg, 1.02 mmol) was dissolved in 4.0 mL of CH_2Cl_2 and 2,6-pyridinedimethanol (135 mg, 0.971 mmol) was suspended in 6.0 mL of CH_2Cl_2. The borane solution was added dropwise to the 2,6-pyridinedimethanol suspension while stirring. Complete transfer of the borane solution was insured using an additional 2.0 mL of CH_2Cl_2 to rinse the vial. Immediately after the borane solution was added to the 2,6-pyridinedimethanol suspension, bubbling was observed. Within 30 min., the 2,6-pyridinedimethanol dissolves and a white solid began to precipitate out of solution. The reaction mixture was stirred at room temperature for 4 h. The volatiles were removed under reduced pressure and the resulting crude product was triturated with pentane (3 x 5 mL) and dried *in vacuo* to give a white solid (Yield: 299 mg, 98%). The product was characterized by NMR spectroscopy, mass spectrometry, and X-ray crystallography. Single crystals suitable for X-ray crystallography were grown by dissolving product into minimal amount of dichloromethane, layering with pentane, and storing in a freezer cooled to -17°C. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ (ppm) 8.09 (t, $^3J_{H\text{-}H}$ = 8.0 Hz, 4H, *p*-ArH), 7.59-7.65 (m, 8H, *m*-ArH), 5.32 (d, $^2J_{H\text{-}H}$ = 16.8 Hz, 4H, CH_2), 4.95 (d, $^2J_{H\text{-}H}$ = 17.2 Hz, 4H, CH_2), 4.16 (d, $^2J_{H\text{-}H}$ = 17.2 Hz, 4H, CH_2), 3.77 (d, $^2J_{H\text{-}H}$ = 17.2 Hz, 4H, CH_2). ^{11}B NMR ($CDCl_3$, 128 MHz, 298 K): δ (ppm) 8.7 (s). ^{19}F NMR ($CDCl_3$, 376 MHz, 298 K): δ (ppm) -135.30 (d, $^3J_{F\text{-}F}$ = 9.0 Hz, 4F, *o*-F), -135.36 (d, $^3J_{F\text{-}F}$ = 9.0 Hz, 4F, *o*-F), -155.43 (t, $^3J_{F\text{-}F}$ = 19.9 Hz, 4F, *p*-F), -163.59 (m, 8F, *m*-F). MS (DART) [M+H] $C_{52}H_{29}B_4F_{20}N_4O_8$ calc. 1261.2 m/z, found 1261.3 m/z.

Preparation of macrocycle 2



In an inert atmosphere glovebox, $C_6F_5BH_2{\cdot}SMe_2$ (52 mg, 0.22 mmol) was dissolved in 1.0 mL of CH_2Cl_2 and 4-bromo-2,6-pyridinedimethanol (45 mg, 0.21 mmol) was suspended in 2.0 mL of CH_2Cl_2. The borane solution was added dropwise to the 4-bromo-2,6-pyridinedimethanol suspension while stirring. Complete transfer of the borane solution was insured using an additional 1.0 mL of CH_2Cl_2 to rinse the vial. Immediately after the borane solution was added to the 4-bromo-2,6-pyridinedimethanol suspension, bubbling was observed. Within 30 min., all the 4-bromo-2,6-pyridinedimethanol dissolved. The reaction mixture was stirred at room temperature for 4 h. The volatiles were removed under reduced pressure and the resulting crude product was triturated with pentane (3 x 5 mL) and dried *in vacuo* to give a white solid (Yield: 81 mg, 100%). The product was characterized by NMR spectroscopy, mass spectrometry, and X-ray crystallography. Single crystals suitable for X-ray crystallography were grown by dissolving product into minimal amount of dichloromethane, layering with pentane, and storing in a freezer cooled to -17°C. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ (ppm) 8.00 (s, 4H, ArH), 7.75 (s, 4H, ArH), 5.25 (d, $^2J_{H\text{-}H}$ = 16.8 Hz, 4H, CH_2), 4.74 (d, $^2J_{H\text{-}H}$ = 17.2 Hz, 4H, CH_2), 4.05 (d, $^2J_{H\text{-}H}$ = 16.8 Hz, 4H, CH_2), 3.84 (d, $^2J_{H\text{-}H}$ = 17.2 Hz, 4H, CH_2). ^{11}B NMR ($CDCl_3$, 128 MHz, 298 K): δ (ppm) 8.9 (s). ^{19}F NMR ($CDCl_3$, 376 MHz, 298 K): δ (ppm) -135.10 (d, $^3J_{F\text{-}F}$ = 9.0 Hz, 4F, *o*-F), -135.16 (d, $^3J_{F\text{-}F}$ = 9.0 Hz, 4F, *o*-F), -154.82 (t, $^3J_{F\text{-}F}$ = 19.9 Hz, 4F, *p*-F), -163.02 (m, 8F, *m*-F). MS (DART) [M+H] $C_{52}H_{25}B_4{}^{79}Br_2{}^{81}Br_2F_{20}N_4O_8$ calc. 1576.8 m/z, found 1577.0 m/z.

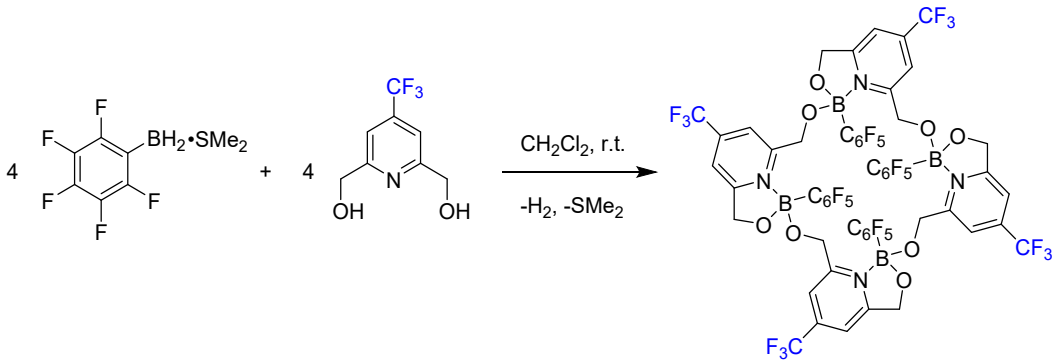
Preparation of macrocycle 3



In an inert atmosphere glovebox, $C_6F_5BH_2{\cdot}SMe_2$ (73 mg, 0.30 mmol) was dissolved in 1.0 mL of CH_2Cl_2 and 4-chloro-2,6-pyridinedimethanol (50 mg, 0.29 mmol) was suspended in 2.0 mL of CH_2Cl_2. The borane solution was added dropwise to the 4-chloro-2,6-pyridinedimethanol suspension while stirring. Complete transfer of the borane solution was insured using an additional 1.0 mL of CH_2Cl_2 to rinse the vial. Immediately after the borane solution was added to the 4-chloro-2,6-pyridinedimethanol suspension, bubbling was observed. Within 30 min., all the 4-chloro-2,6-pyridinedimethanol dissolved and a white solid began to precipitate from solution. The reaction mixture was stirred at room temperature for 4 h. The volatiles were removed under reduced pressure and the resulting crude product was triturated with pentane (3 x 5 mL) and dried *in vacuo* to give a white solid (Yield: 100 mg, 100%). The product was characterized by NMR

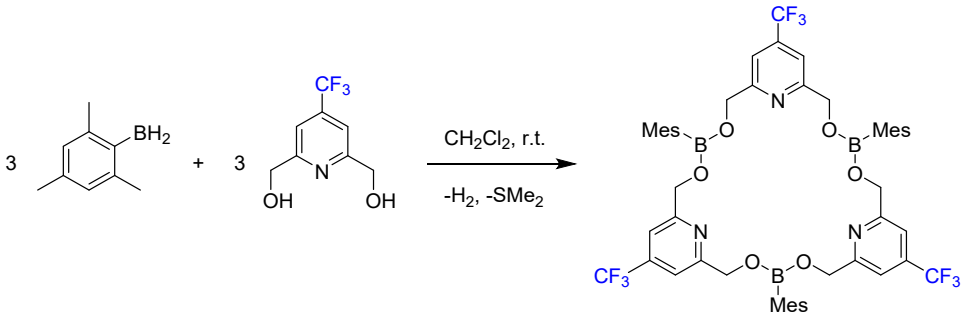
spectroscopy and mass spectrometry. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ (ppm) 7.78 (s, 4H, ArH), 7.58 (s, 4H, ArH), 5.28 (d, $^{2}J_{H\text{-}H}$ = 18.0 Hz, 4H, CH_2), 4.81 (d, $^{2}J_{H\text{-}H}$ = 17.2 Hz, 4H, CH_2), 4.11 (d, $^{2}J_{H\text{-}H}$ = 17.6 Hz, 4H, CH_2), 3.83 (d, $^{2}J_{H\text{-}H}$ = 17.6 Hz, 4H, CH_2). ^{11}B NMR ($CDCl_3$, 128 MHz, 298 K): δ (ppm) 9.3 (s). ^{19}F NMR ($CDCl_3$, 376 MHz, 298 K): δ (ppm) -135.24 (d, $^{3}J_{F\text{-}F}$ = 9.0 Hz, 4F, *o*-F), -135.30 (d, $^{3}J_{F\text{-}F}$ = 9.4 Hz, 4F, *o*-F), -154.70 (t, $^{3}J_{F\text{-}F}$ = 19.9 Hz, 4F, *p*-F), -163.01 (m, 8F, *m*-F). MS (DART) [M+H] $C_{52}H_{25}B_4Cl_4F_{20}N_4O_8$ calc. 1397.1 m/z, found 1398.2 m/z.

Preparation of macrocycle 4



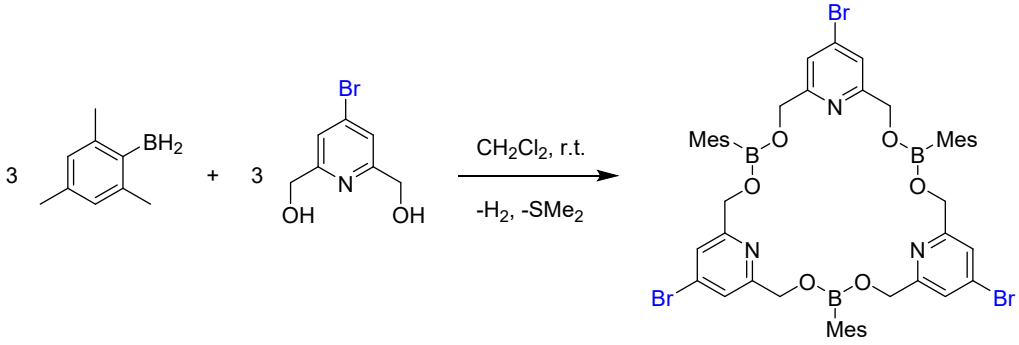
In an inert atmosphere glovebox, $C_6F_5BH_2{\cdot}SMe_2$ (59 mg, 0.24 mmol) was dissolved in 1.0 mL of CH_2Cl_2 and 4-trifluoromethyl-2,6-pyridinedimethanol (48 mg, 0.23 mmol) was dissolved in 2.0 mL of CH_2Cl_2. The borane solution was added dropwise to the 4-trifluoromethyl-2,6-pyridinedimethanol solution while stirring. Complete transfer of the borane solution was insured using an additional 1.0 mL of CH_2Cl_2 to rinse the vial. Immediately after the borane solution was added to the 4-trifluoromethyl-2,6-pyridinedimethanol solution, bubbling was observed. The reaction mixture was stirred at room temperature for 4 h. The volatiles were removed under reduced pressure and the resulting crude product was triturated with pentane (3 x 5 mL) and dried *in vacuo* to give a white solid (Yield: 78 mg, 88%). The product was characterized by NMR spectroscopy and mass spectrometry. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ (ppm) 8.11 (s, 4H, ArH), 7.82 (s, 4H, ArH), 5.36 (d, $^{2}J_{H\text{-}H}$ = 18.0 Hz, 4H, CH_2), 4.76 (d, $^{2}J_{H\text{-}H}$ = 18.4 Hz, 4H, CH_2), 4.00 (m, 8H, CH_2). ^{11}B NMR ($CDCl_3$, 128 MHz, 298 K): δ (ppm) 8.9 (s). ^{19}F NMR ($CDCl_3$, 376 MHz, 298 K): δ (ppm) -65.66 (s, 12F, CF_3), -135.31 (d, $^{3}J_{F\text{-}F}$ = 8.6 Hz, 4F, *o*-F), -135.37 (d, $^{3}J_{F\text{-}F}$ = 9.8 Hz, 4F, *o*-F), -154.16 (t, $^{3}J_{F\text{-}F}$ = 19.2 Hz, 4F, *p*-F), -162.55 (m, 8F, *m*-F). MS (DART) [M+H] $C_{56}H_{25}B_4F_{32}N_4O_8$ calc. 1533.2 m/z, found 1533.2 m/z.

Preparation of macrocycle 5



In an inert atmosphere glovebox, $MesBH_2$ (29 mg, 0.22 mmol) was dissolved in 1.0 mL of CH_2Cl_2 and 4-trifluoromethyl-2,6-pyridinedimethanol (44 mg, 0.212 mmol) was dissolved in 2.0 mL of CH_2Cl_2. The borane solution was added dropwise to the 4-trifluoromethyl-2,6-pyridinedimethanol solution while stirring. Complete transfer of the borane solution was insured using an additional 1.0 mL of CH_2Cl_2 to rinse the vial. Immediately after the borane solution was added to the 4-trifluoromethyl-2,6-pyridinedimethanol solution, bubbling was observed. The reaction mixture was stirred at room temperature for 4 h. The volatiles were removed under reduced pressure and the resulting crude product was triturated with pentane (3 x 5 mL) and dried *in vacuo* to give a yellow solid (Yield: 47 mg, 66%). The product was characterized by NMR spectroscopy and mass spectrometry. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ (ppm) 7.55 (s, 8H, ArH), 6.80 (s, 8H, ArH), 5.06 (s, 16H, CH_2), 2.25 (s, 12H, *p*-CH_3), 2.21 (s, 24H, *o*-CH_3). ^{11}B NMR ($CDCl_3$, 128 MHz, 298 K): δ (ppm) 33.9 (br s). ^{19}F NMR ($CDCl_3$, 376 MHz, 298 K): δ (ppm) -64.84 (s, 12F, CF_3). MS (DART) [M+H] $C_{51}H_{52}B_3F_9N_3O_6$ calc. 1006.4 m/z, found 1006.6 m/z.

Preparation of macrocycle 6



In an inert atmosphere glovebox, $MesBH_2$ (85 mg, 0.64 mmol) was dissolved in 1.5 mL of CH_2Cl_2 and 4-bromo-2,6-pyridinedimethanol (133 mg, 0.610 mmol) was suspended in 6.0 mL of CH_2Cl_2. The borane solution was added dropwise to the 4-trifluoromethyl-2,6-pyridinedimethanol suspension while stirring. Complete transfer of the borane solution was insured using an additional 1.5 mL of CH_2Cl_2 to rinse the vial. Immediately after the borane solution was added to the 4-trifluoromethyl-2,6-pyridinedimethanol suspension, bubbling was observed. Within 30 min. the 4-bromo-2,6-pyridinedimethanol dissolved. The reaction mixture

was stirred at room temperature for 4 h. The volatiles were removed under reduced pressure and the resulting crude product was triturated with pentane (3 x 5 mL) and dried *in vacuo* to give a white solid (Yield: 202 mg, 96%). The product was characterized by NMR spectroscopy and mass spectrometry. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ (ppm) 7.52 (s, 6H, ArH), 6.79 (s, 6H, ArH), 4.98 (s, 12H, CH_2), 2.25 (s, 9H, *p*-CH_3), 2.21 (s, 18H, *o*-CH_3). ^{11}B NMR ($CDCl_3$, 128 MHz, 298 K): δ (ppm) 33.4 (br s). MS (DART) [M+H] $C_{48}H_{52}B_3{}^{79}Br_2{}^{81}BrN_3O_6$ calc. 1038.2 m/z, found 1038.3 m/z.

Characterization of macrocycles

Characterization of macrocycle 1

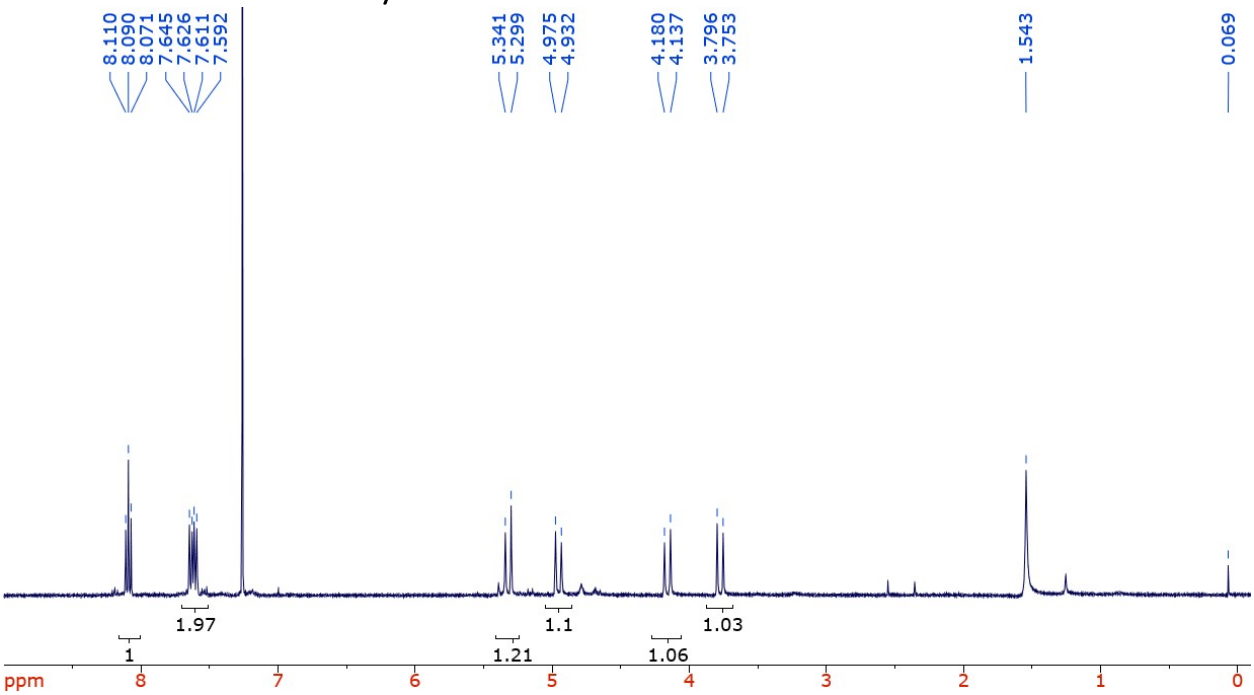


Figure S1. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) spectrum of macrocycle **1**.

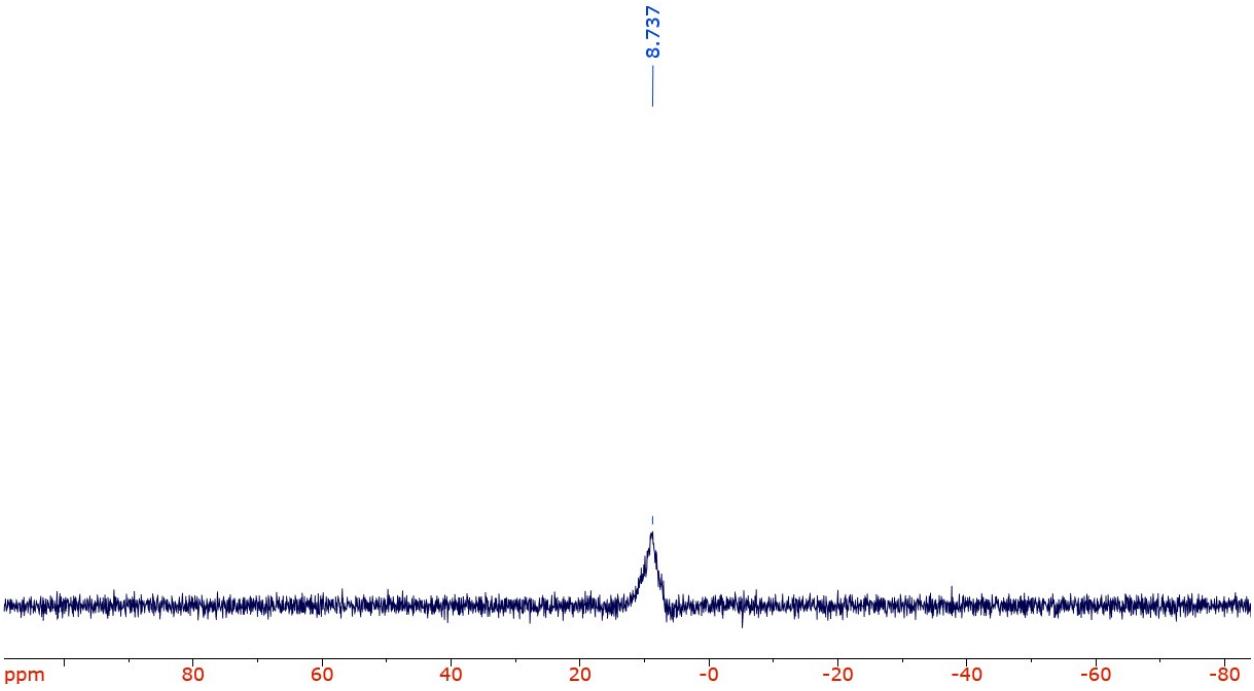


Figure S2. ^{11}B NMR ($CDCl_3$, 128 MHz, 298 K) spectrum of macrocycle **1**.

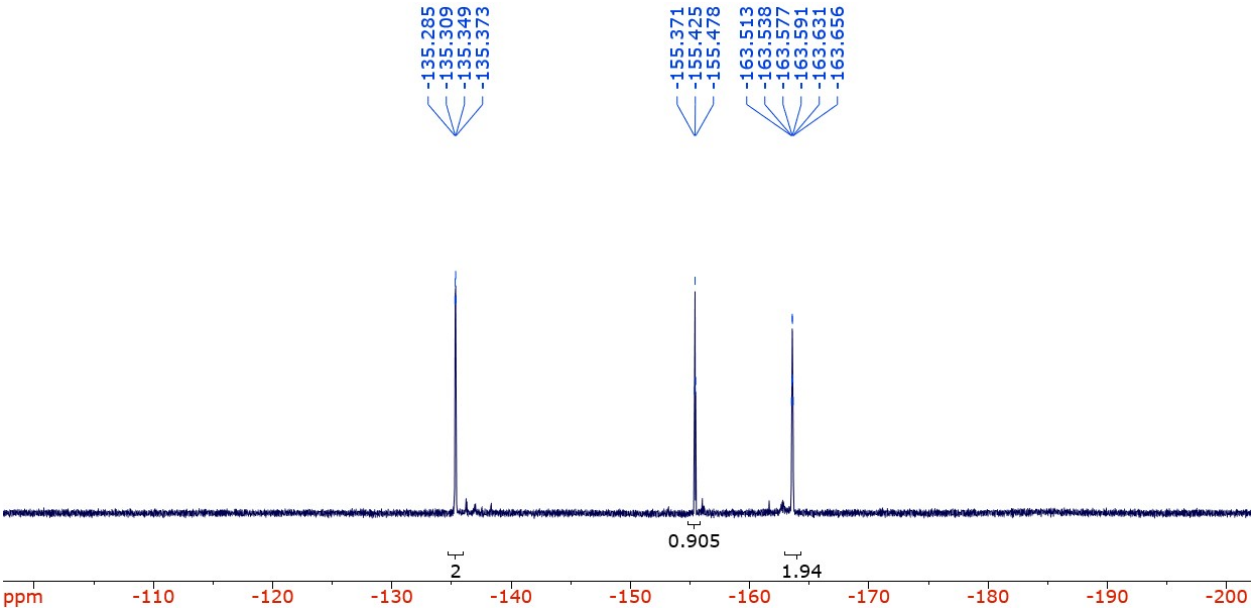


Figure S3. ^{19}F NMR ($CDCl_3$, 376 MHz, 298 K) spectrum of macrocycle **1**.

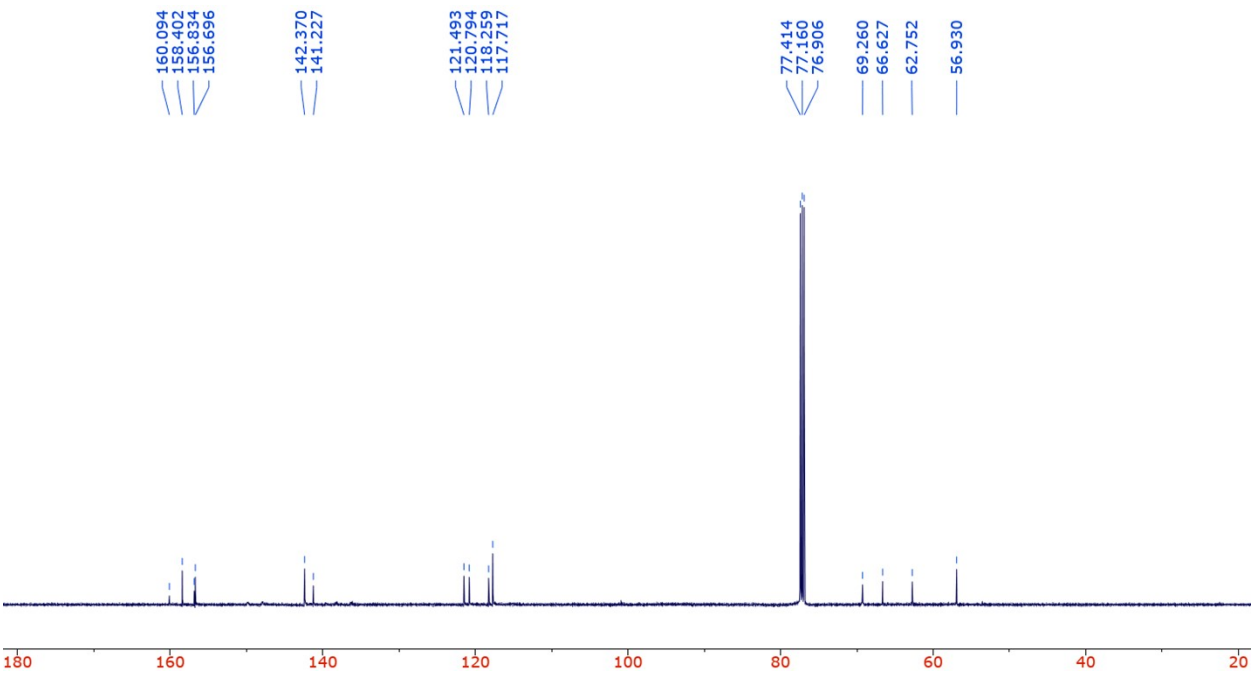


Figure S4. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz, 298 K) spectrum of macrocycle **1**.

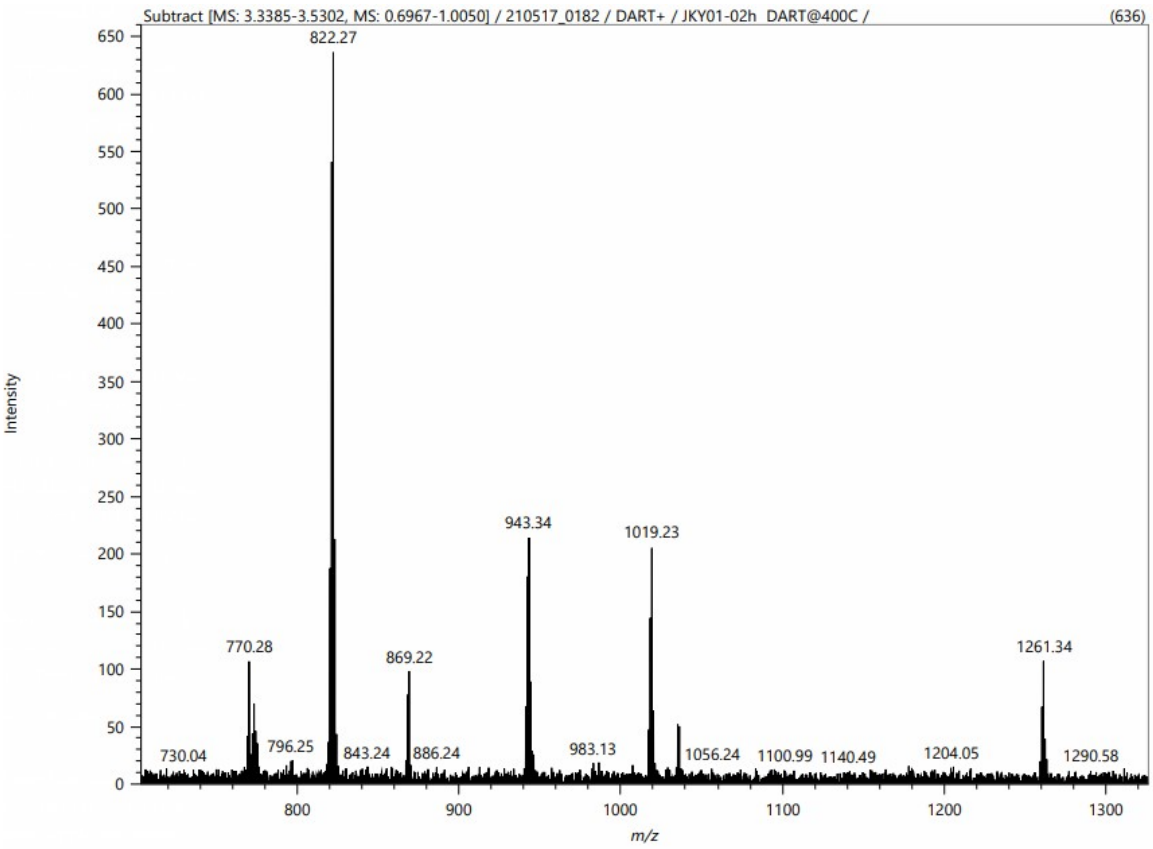


Figure S5. Mass spectrum (DART+) of macrocycle **1**.

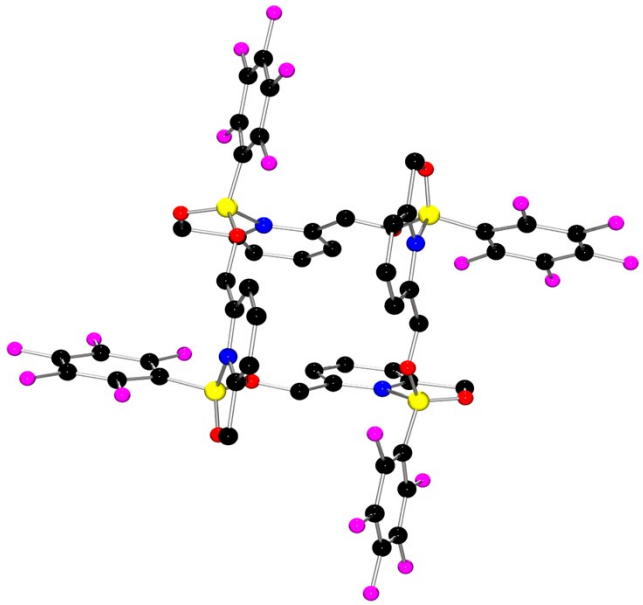


Figure S6. X-ray crystal structure of macrocycle **1**. C: black, O: red, B: yellow-green, N: blue, F: pink.

Characterization of macrocycle 2

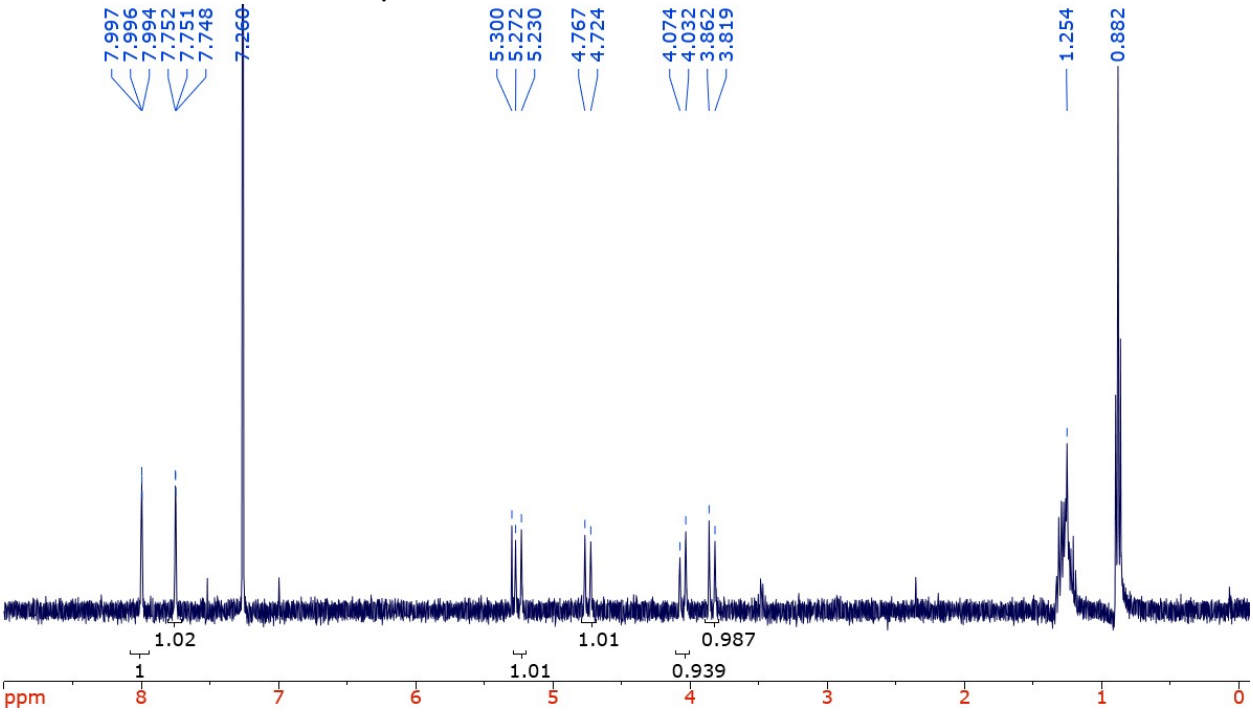


Figure S7. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) spectrum of macrocycle **2**.

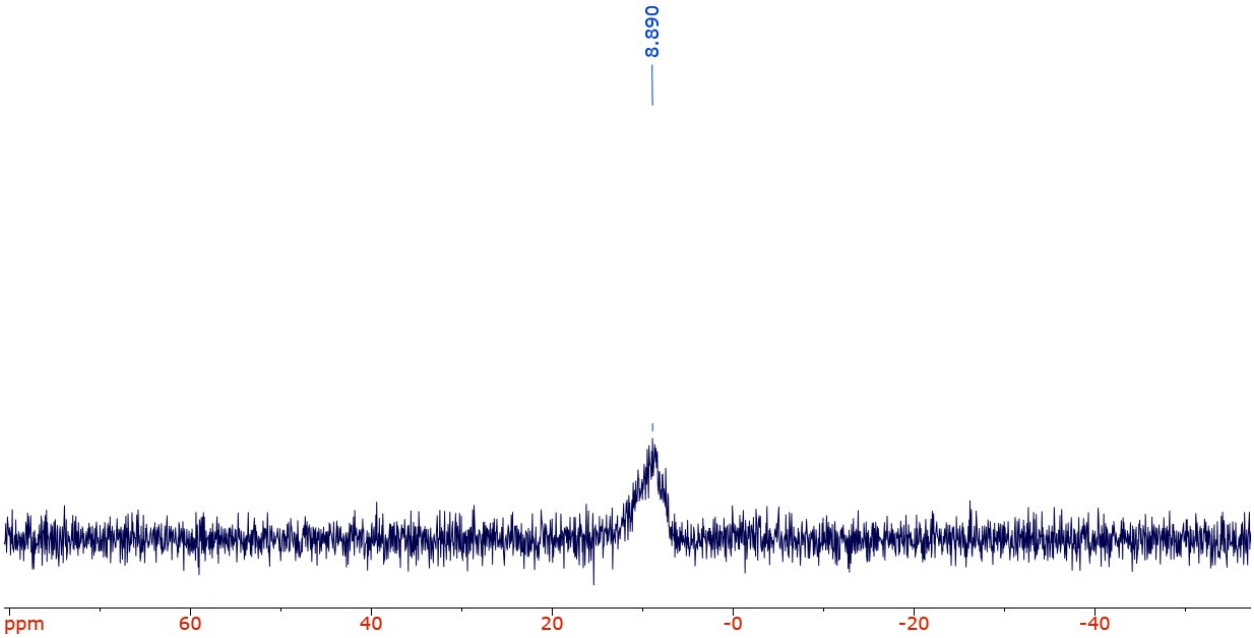


Figure S8. ^{11}B NMR ($CDCl_3$, 128 MHz, 298 K) spectrum of macrocycle **2**.

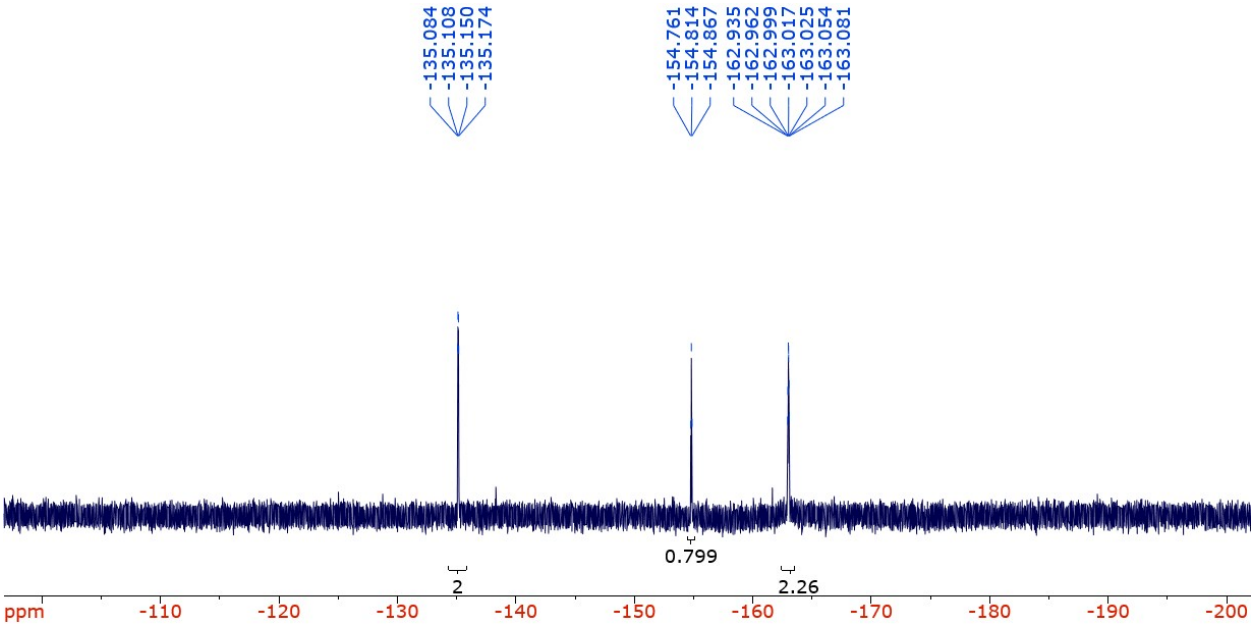


Figure S9. ^{19}F NMR ($CDCl_3$, 376 MHz, 298 K) spectrum of macrocycle **2**.

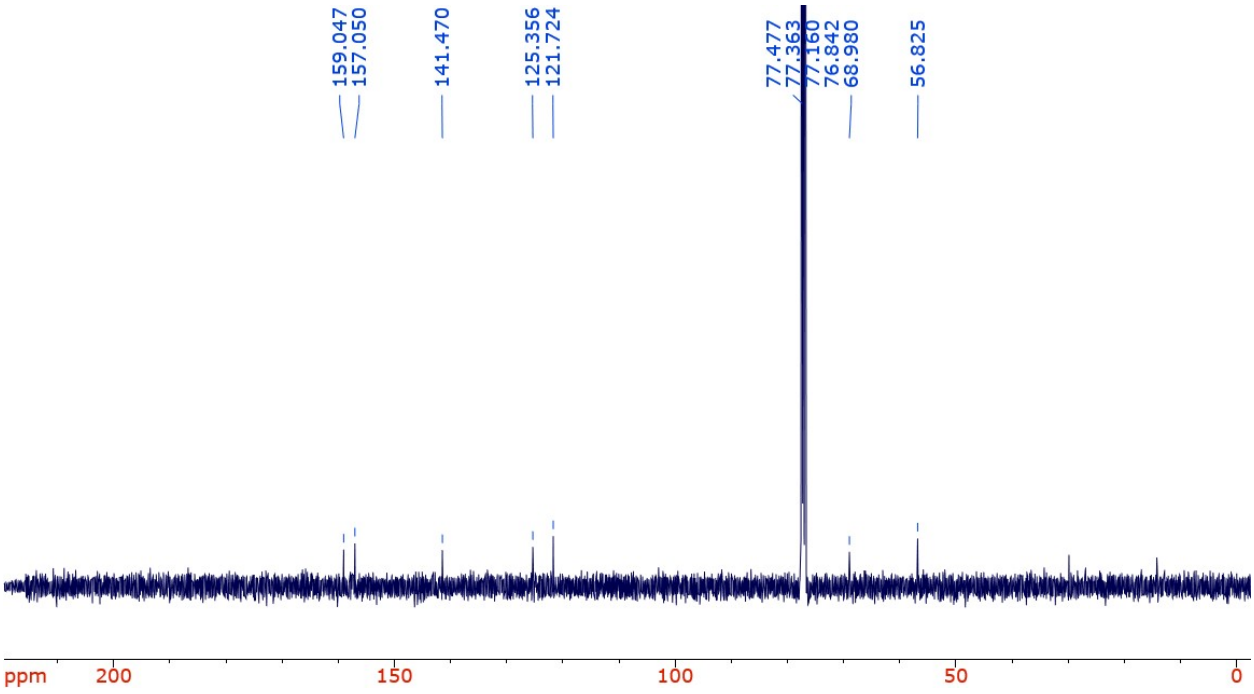


Figure S10. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz, 298 K) spectrum of macrocycle **2**.

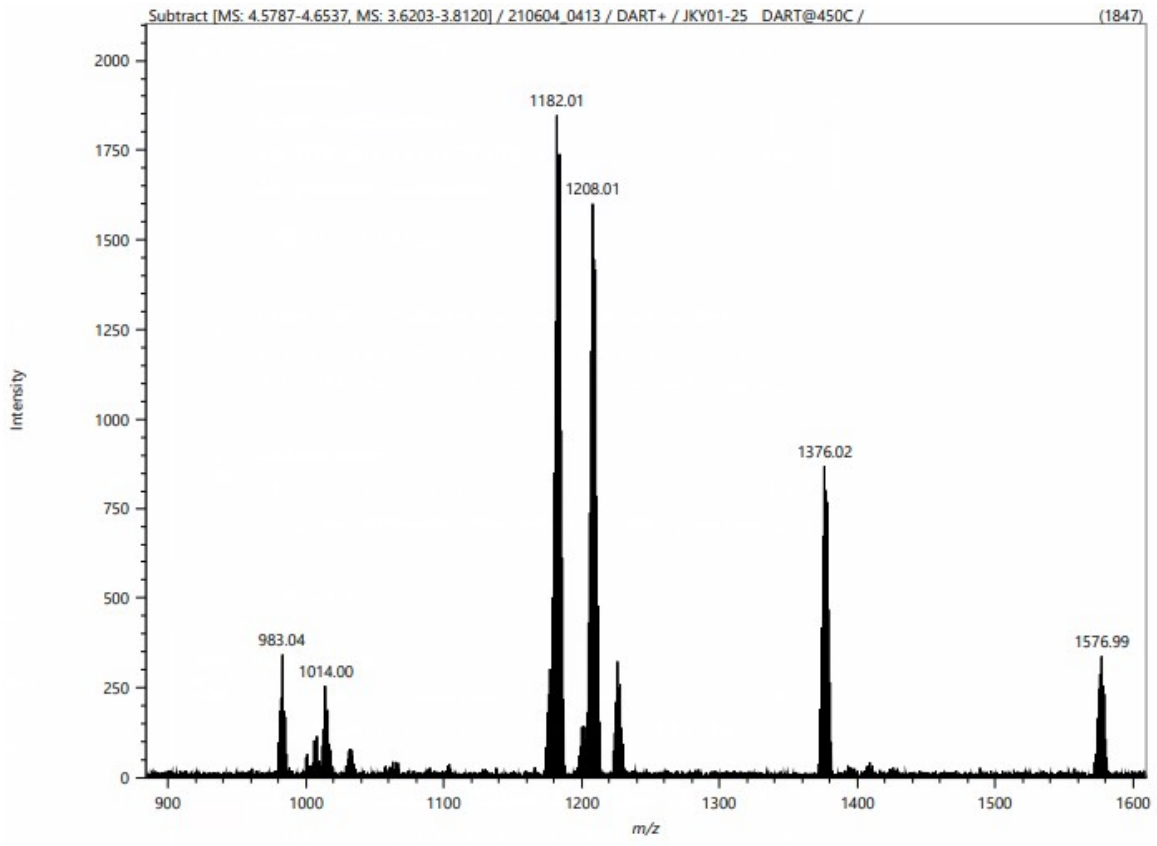


Figure S11. Mass spectrum (DART+) of macrocycle **2**.

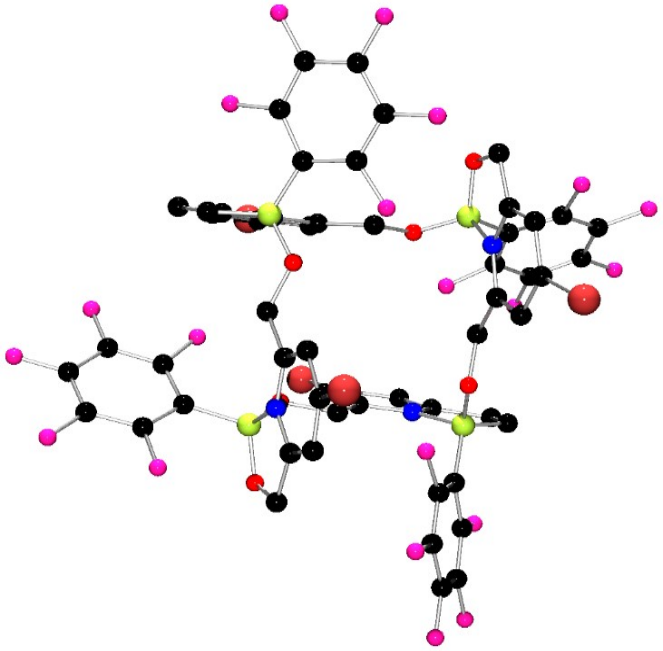


Figure S12. X-ray crystal structure of macrocycle **2**. C: black, O: red, B: yellow-green, N: blue, F: pink, Br: salmon-red.

Characterization of macrocycle 3

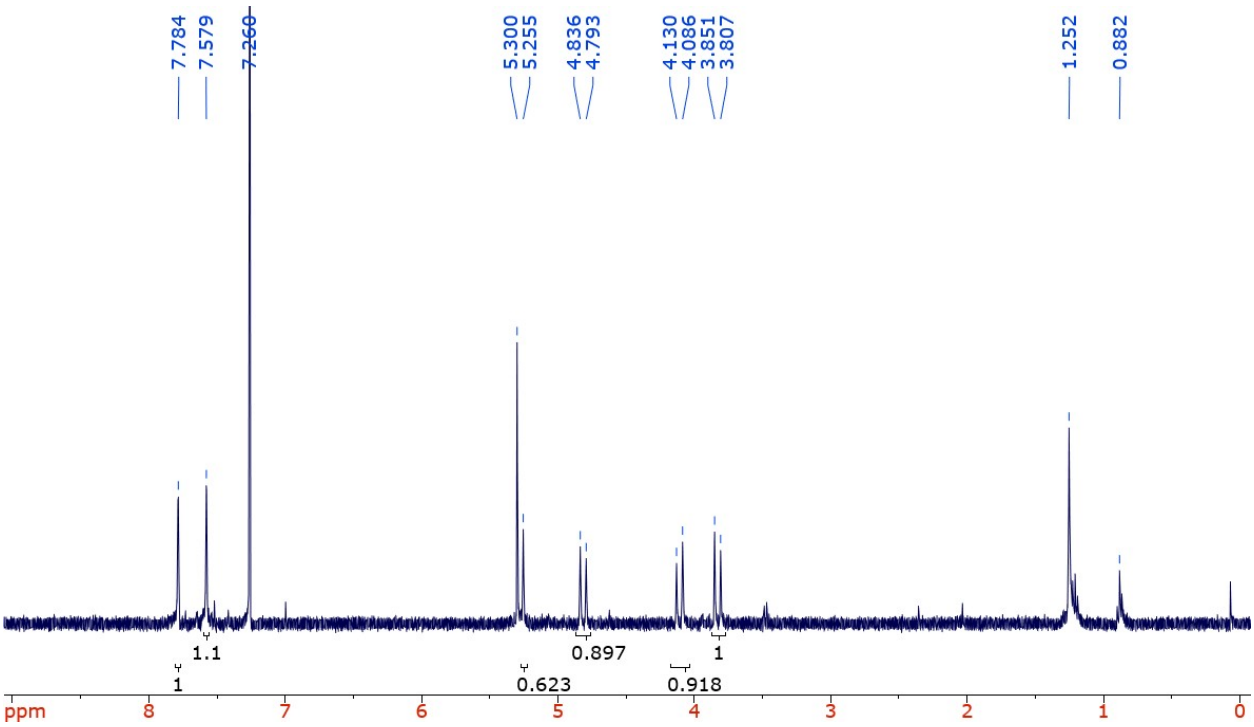


Figure S13. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) spectrum of macrocycle **3**.

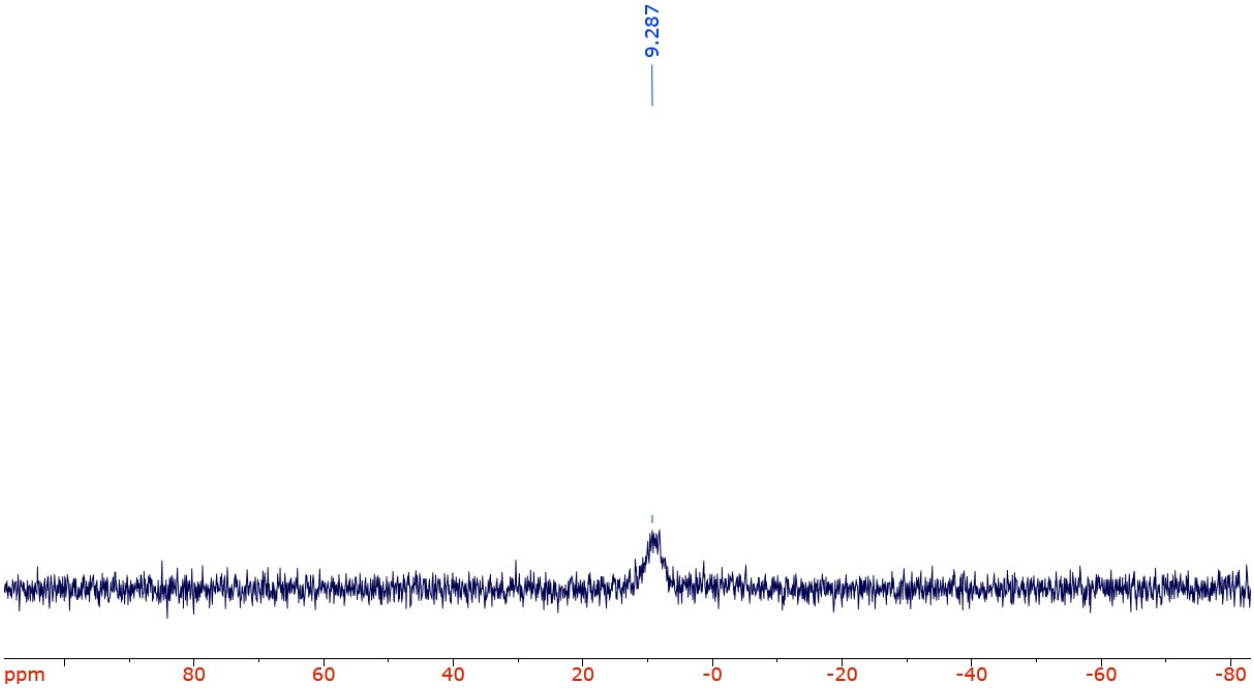


Figure S14. ^{11}B NMR ($CDCl_3$, 128 MHz, 298 K) spectrum of macrocycle **3**.

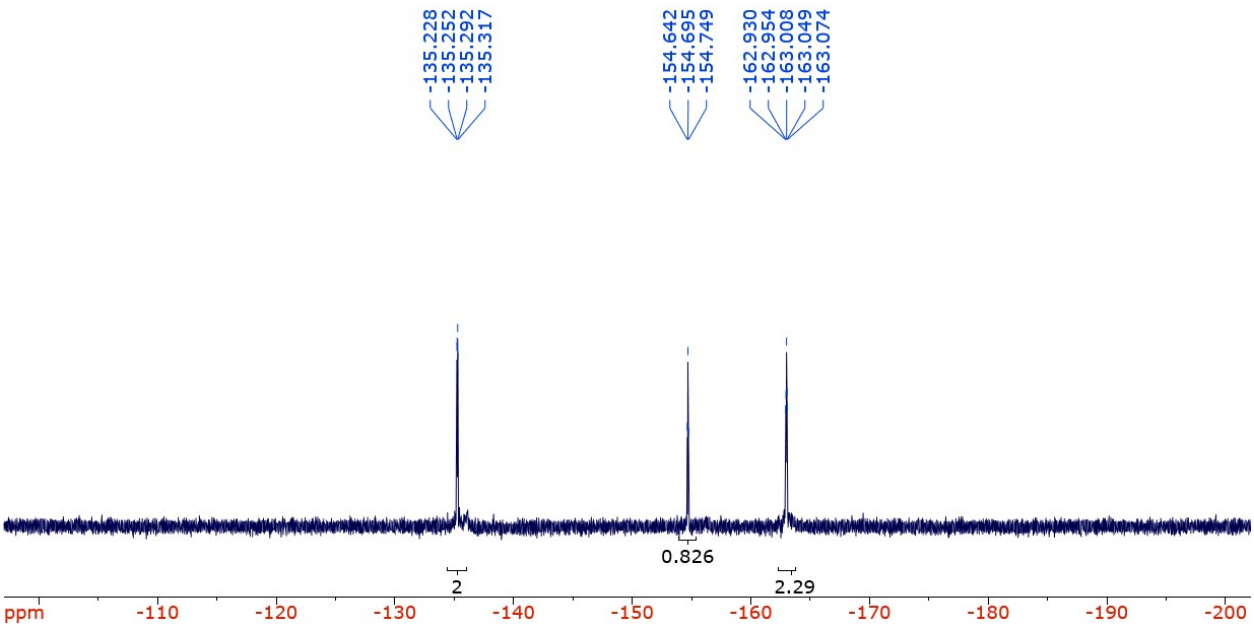


Figure S15. ^{19}F NMR ($CDCl_3$, 376 MHz, 298 K) spectrum of macrocycle **3**.

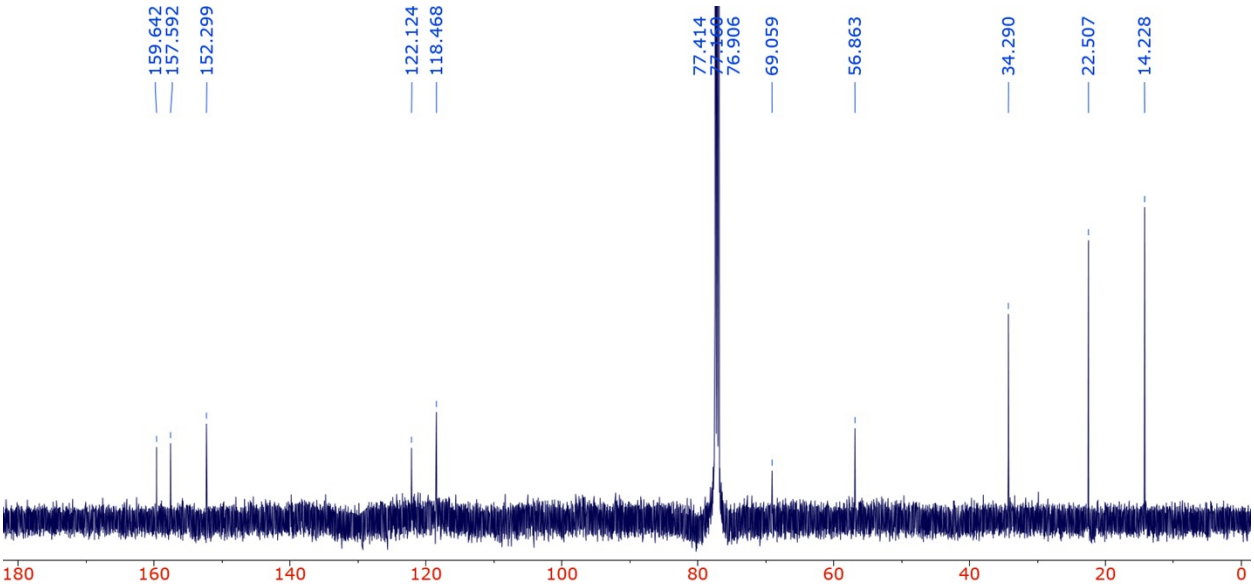


Figure S16. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 126 MHz, 298 K) spectrum of macrocycle **3**.

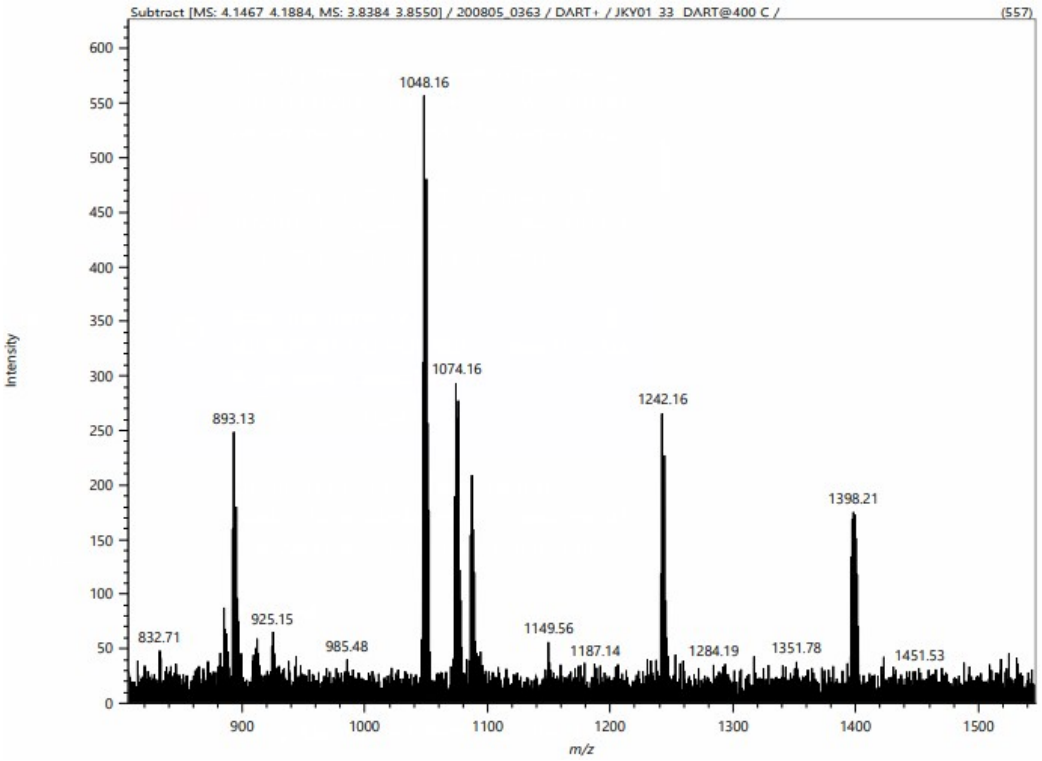


Figure S17. Mass spectrum (DART+) of macrocycle **3**.

Characterization of macrocycle 4

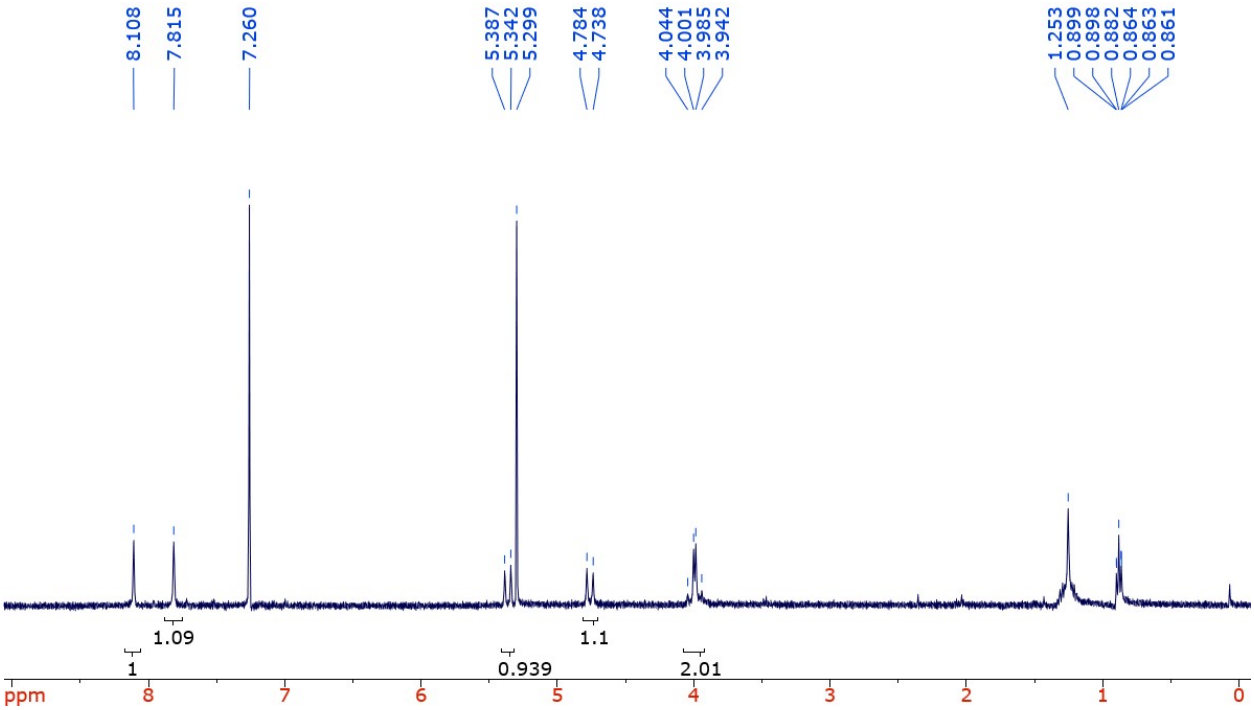


Figure S18. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) spectrum of macrocycle **4**.

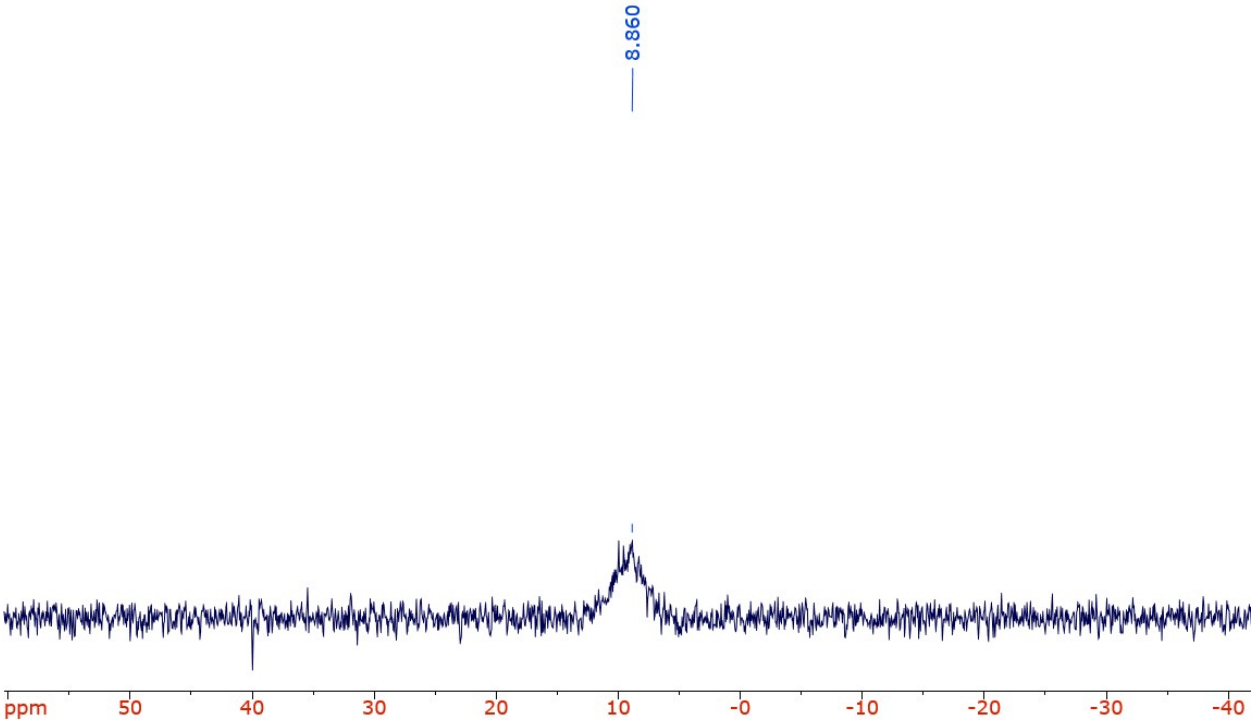


Figure S19. ^{11}B NMR ($CDCl_3$, 128 MHz, 298 K) spectrum of macrocycle **4**.

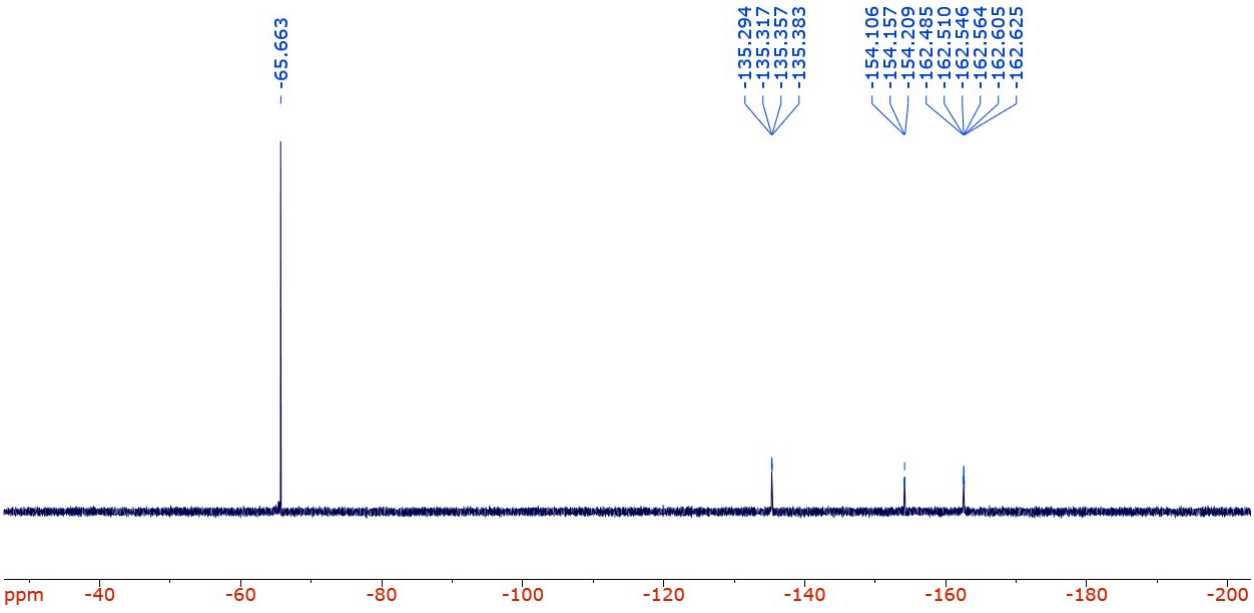


Figure S20. ^{19}F NMR ($CDCl_3$, 376 MHz, 298 K) spectrum of macrocycle **4**.

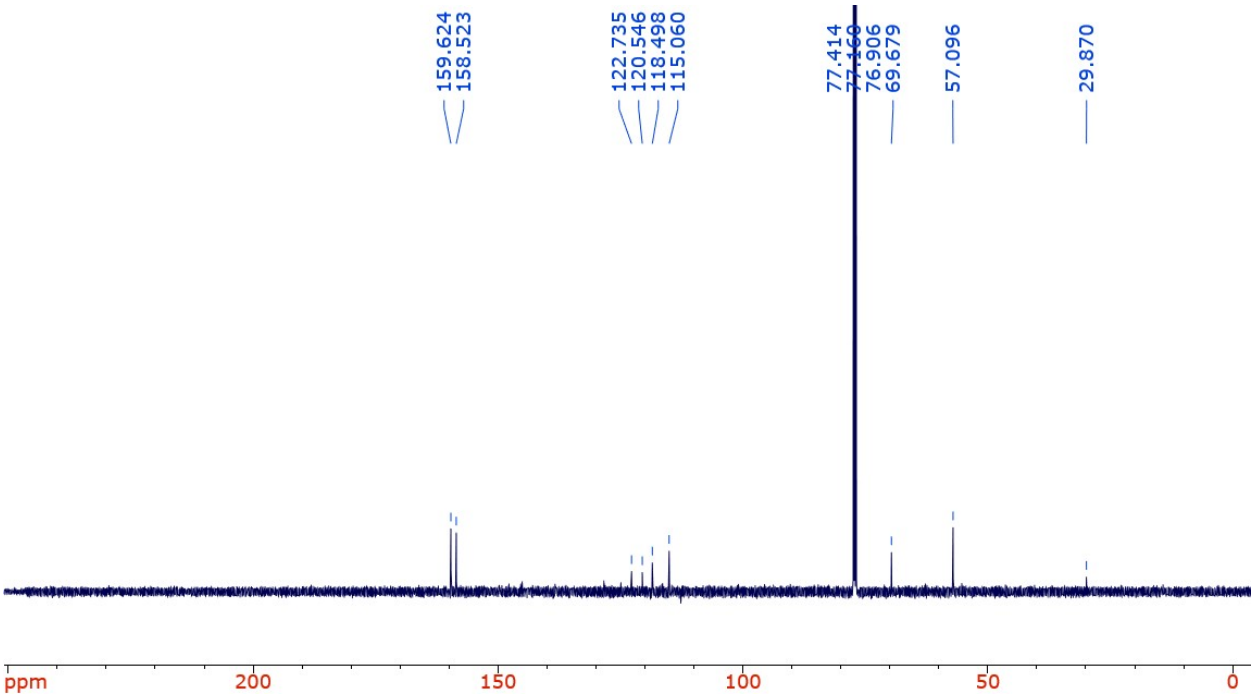


Figure S21. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz, 298 K) spectrum of macrocycle **4**.

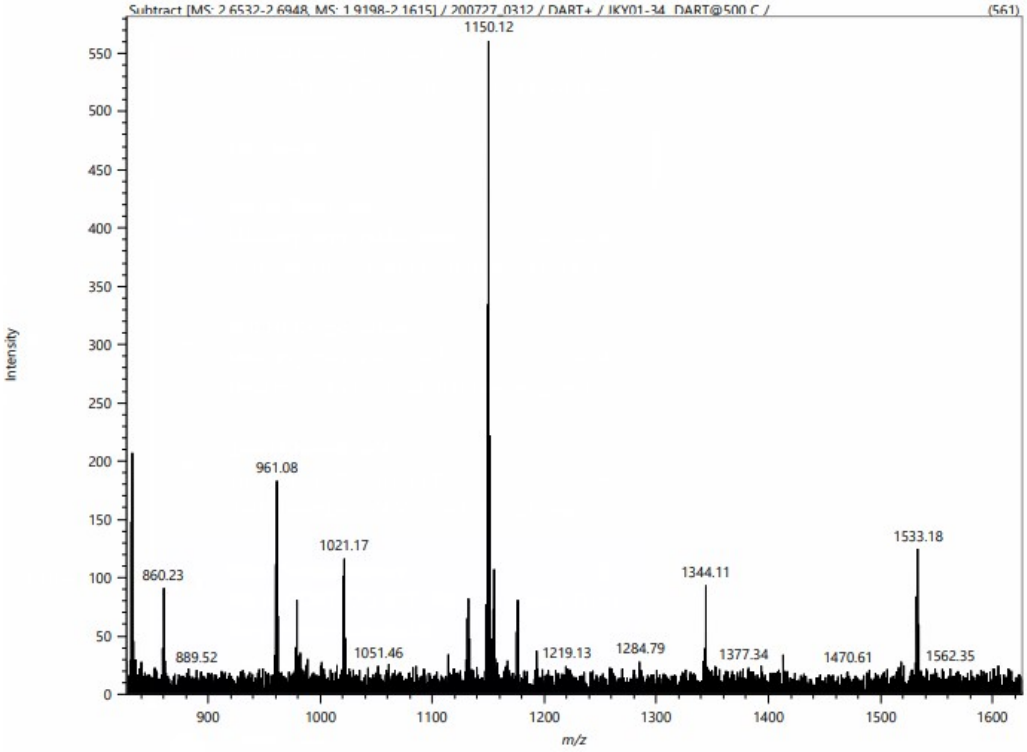


Figure S22. Mass spectrum (DART+) of macrocycle **4**.

Characterization of macrocycle 5

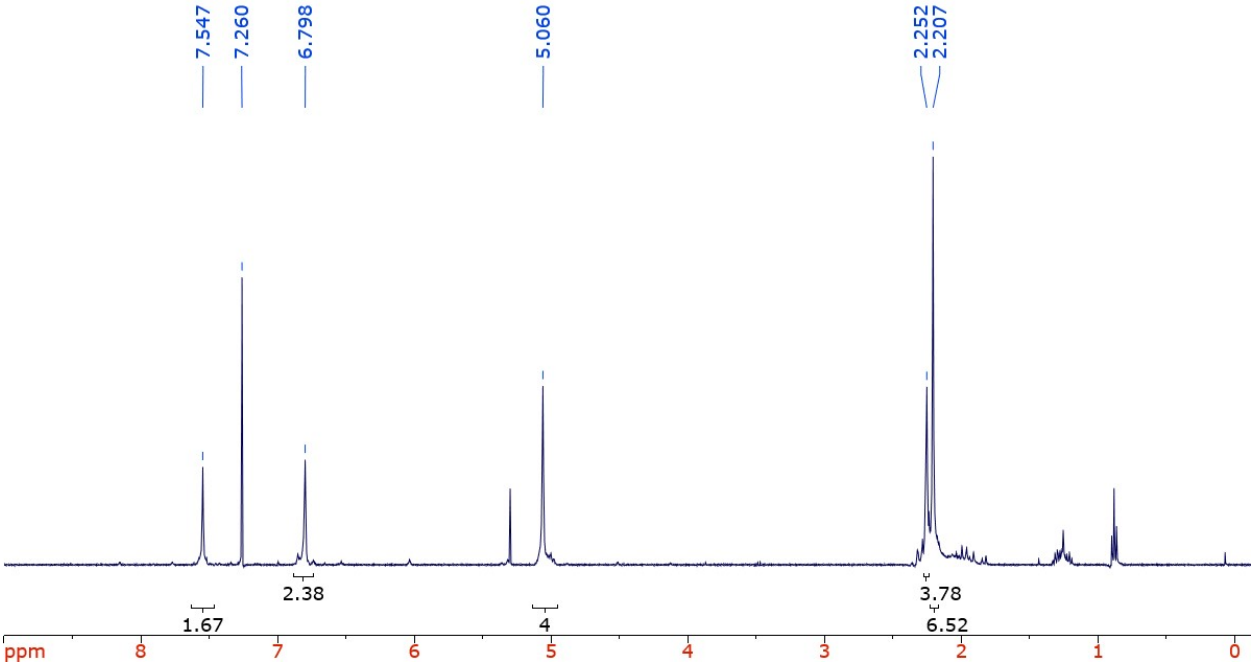


Figure S23. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) spectrum of macrocycle **5**.

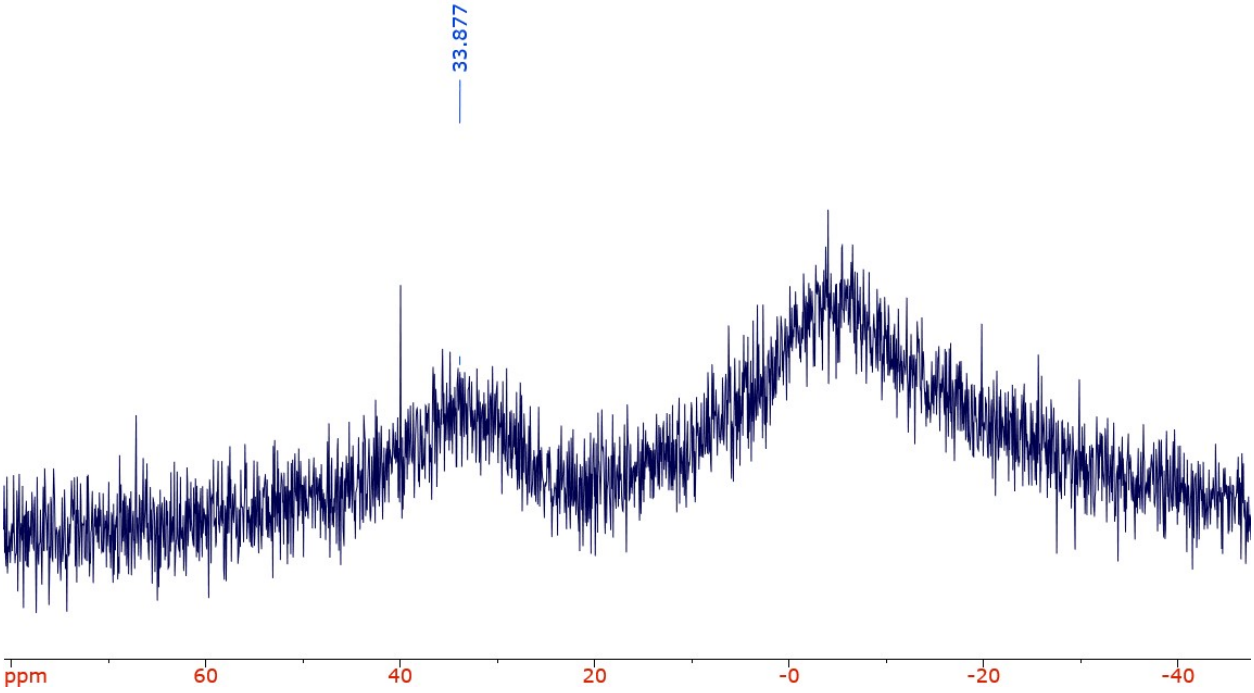


Figure S24. ^{11}B NMR ($CDCl_3$, 128 MHz, 298 K) spectrum of macrocycle **5**.

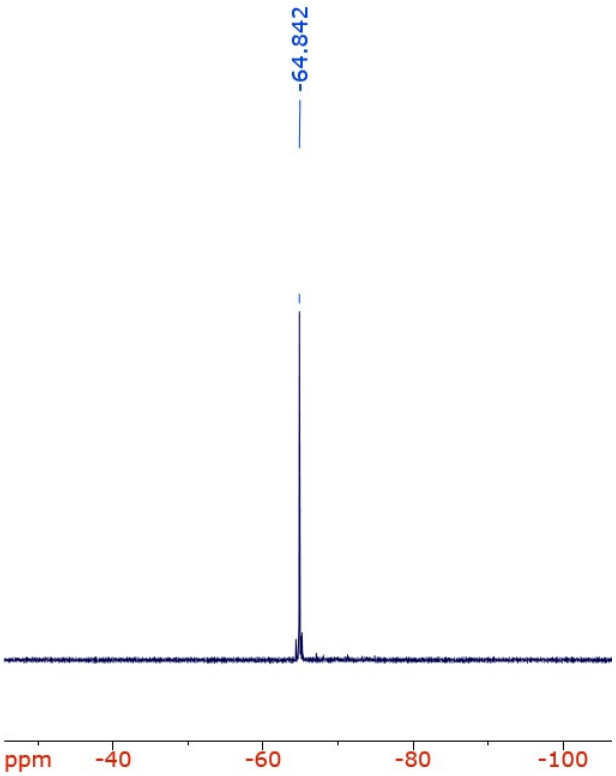


Figure S25. ^{19}F NMR ($CDCl_3$, 376 MHz, 298 K) spectrum of macrocycle **5**.

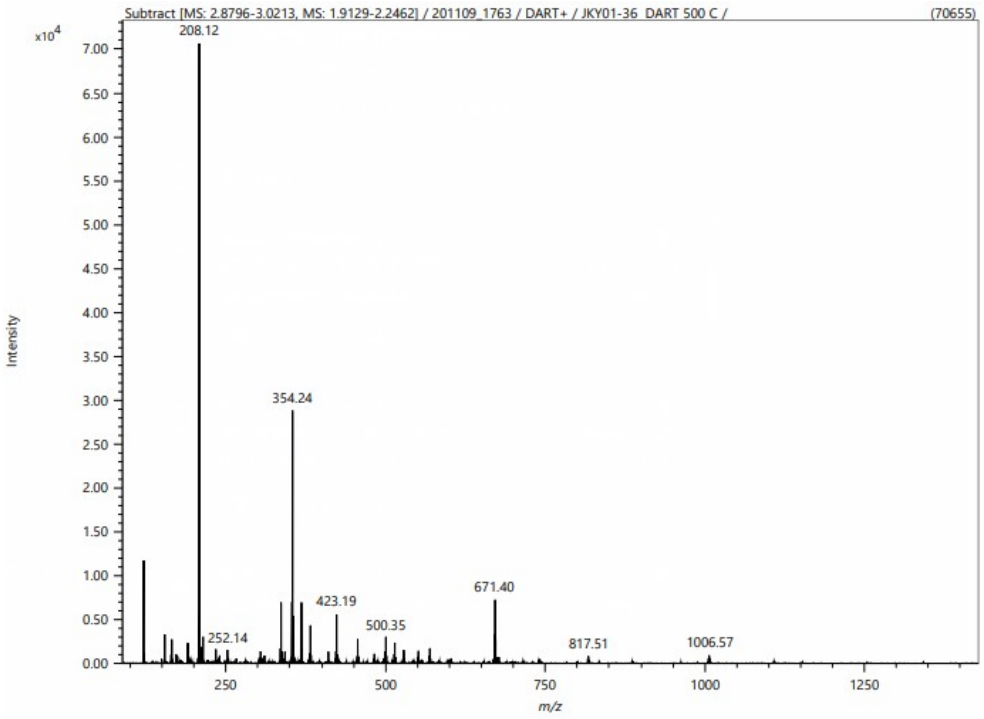


Figure S26. Mass spectrum (DART+) of macrocycle **5**.

Characterization of macrocycle 6

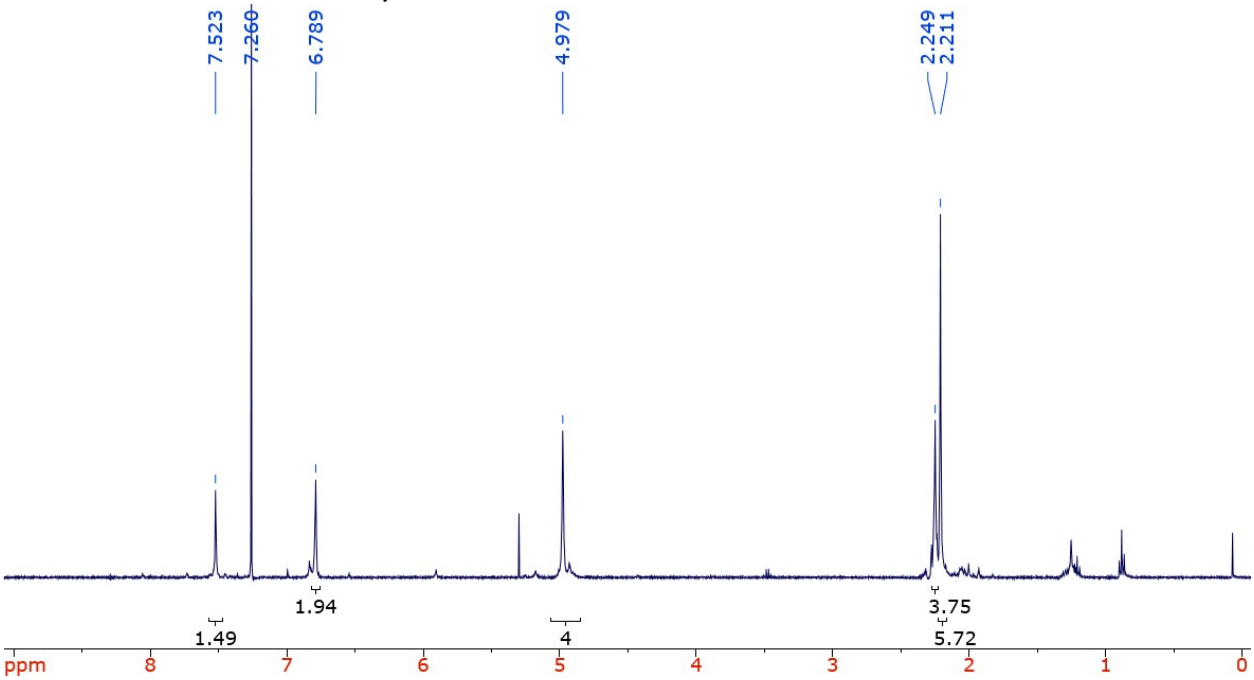


Figure S27. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) spectrum of macrocycle **6**.

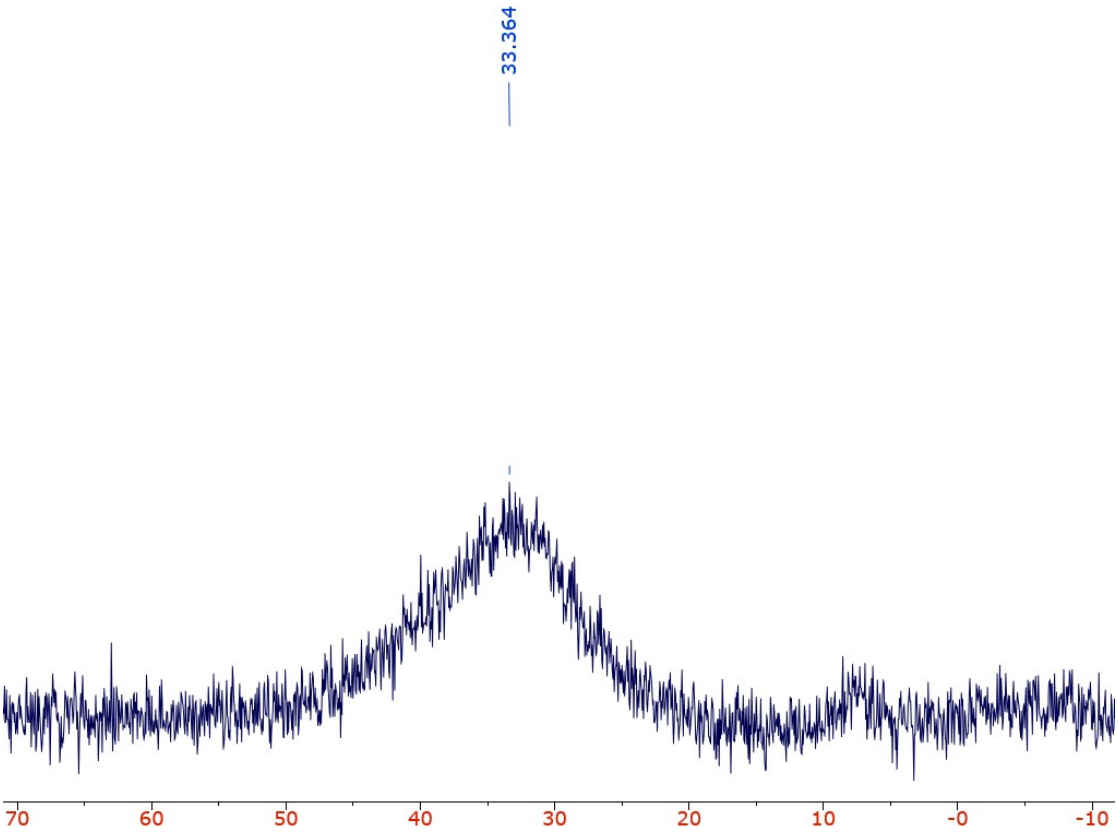


Figure S28. ^{11}B NMR ($CDCl_3$, 128 MHz, 298 K) spectrum of macrocycle **6**.

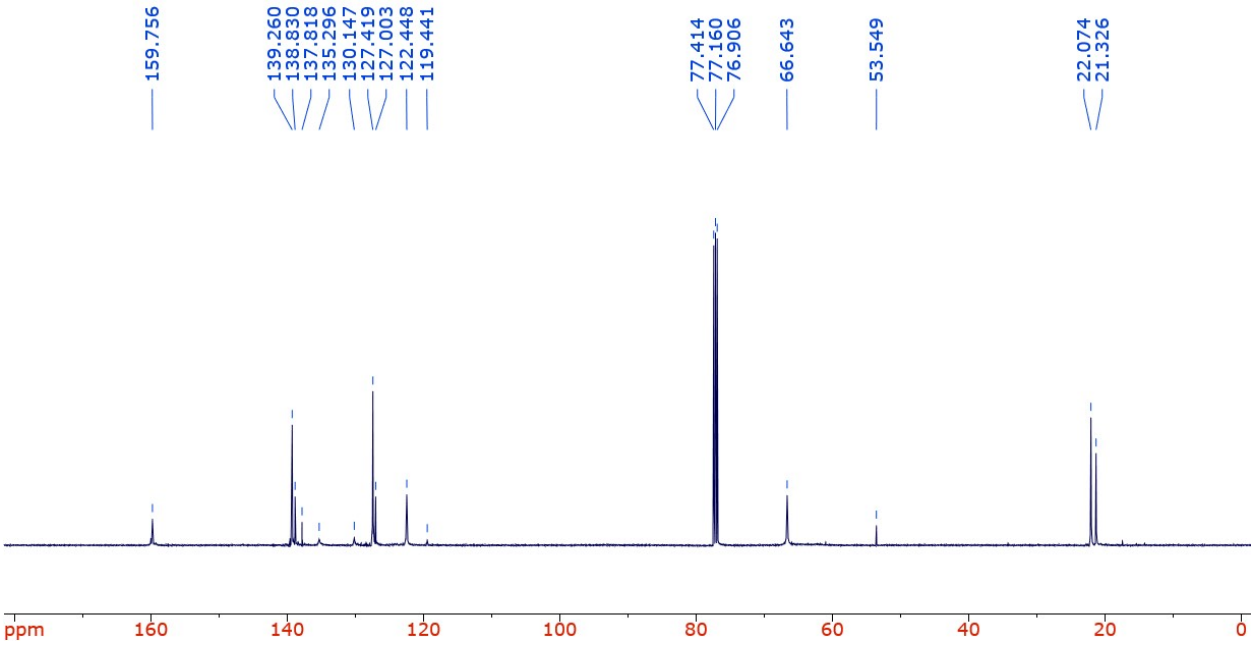


Figure S29. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 126 MHz, 298 K) spectrum of macrocycle **6**.

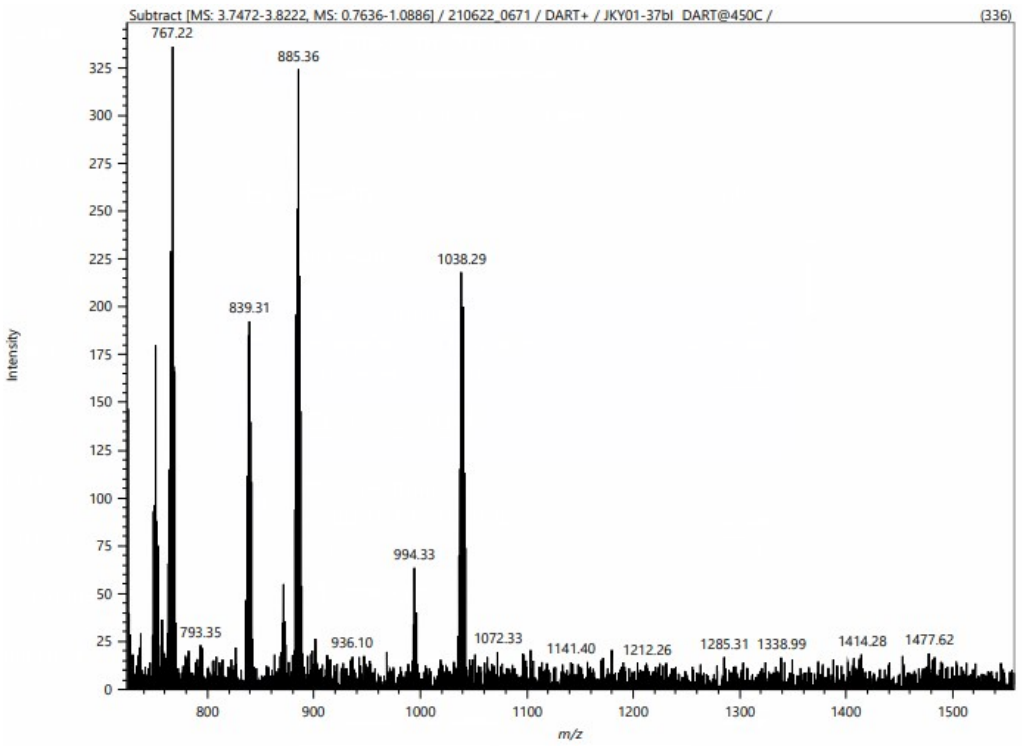


Figure S30. Mass spectrum (DART+) of macrocycle **6**.

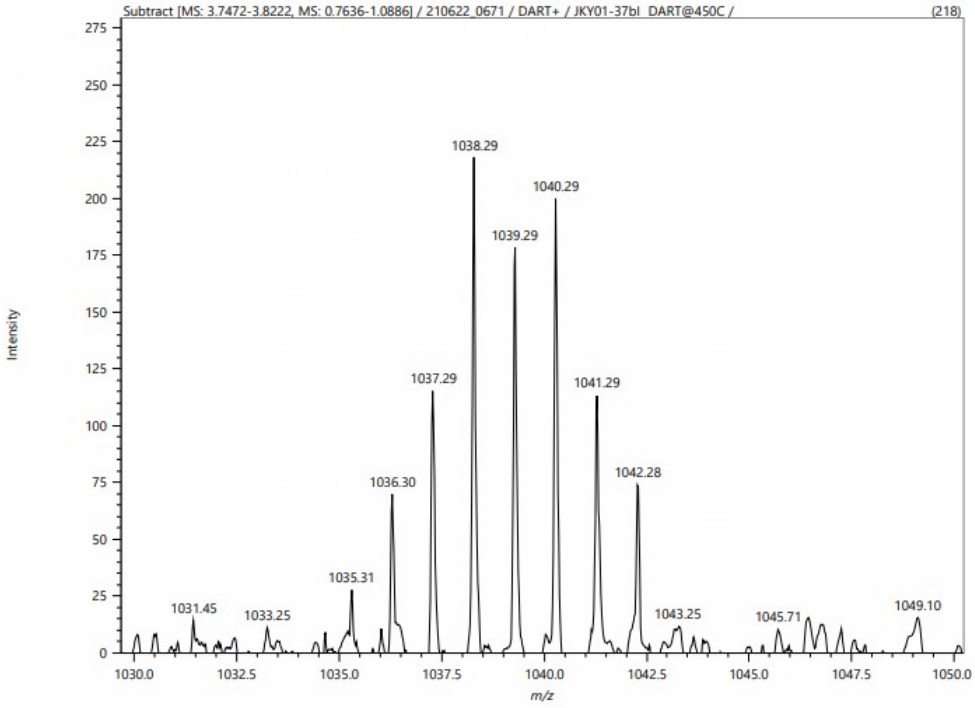


Figure S31. Intensity ratio of the molecular ion of macrocycle **6**.

Reaction of macrocycles

Reaction of macrocycle 2 with $B(C_6F_5)_3$

In an inert atmosphere glovebox, $B(C_6F_5)_3$ (12.8 mg, 25.0 μmol) was dissolved into $CDCl_3$ (0.5 mL), then added to macrocycle **2** (9.8 mg, 6.3 μmol). The solution was transferred to a J-Young tube and monitored by NMR spectroscopy.

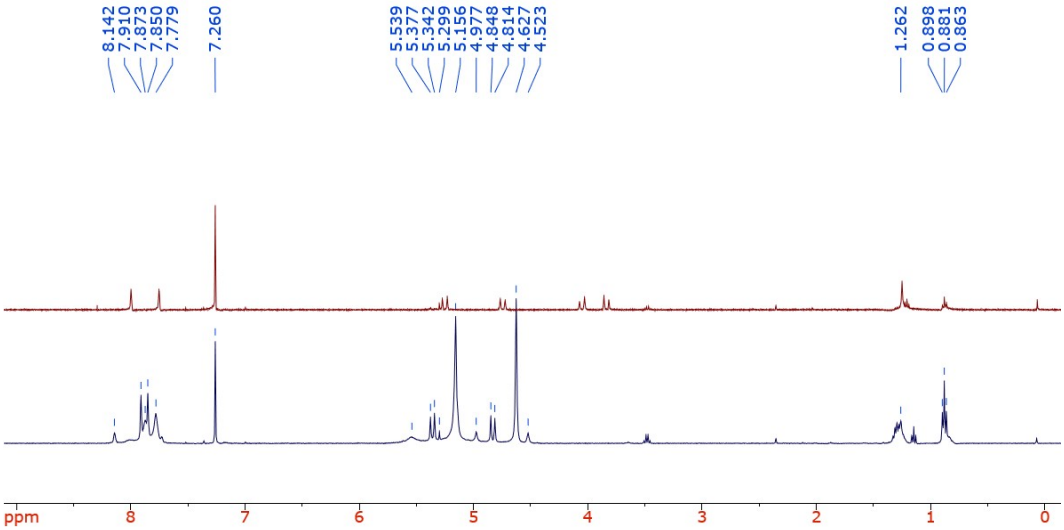


Figure S32. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) overlay of the reaction of macrocycle **2** with tris(pentafluorophenyl)borane (red trace is macrocycle **2**; blue trace is macrocycle **2** with tris(pentafluorophenyl)borane).

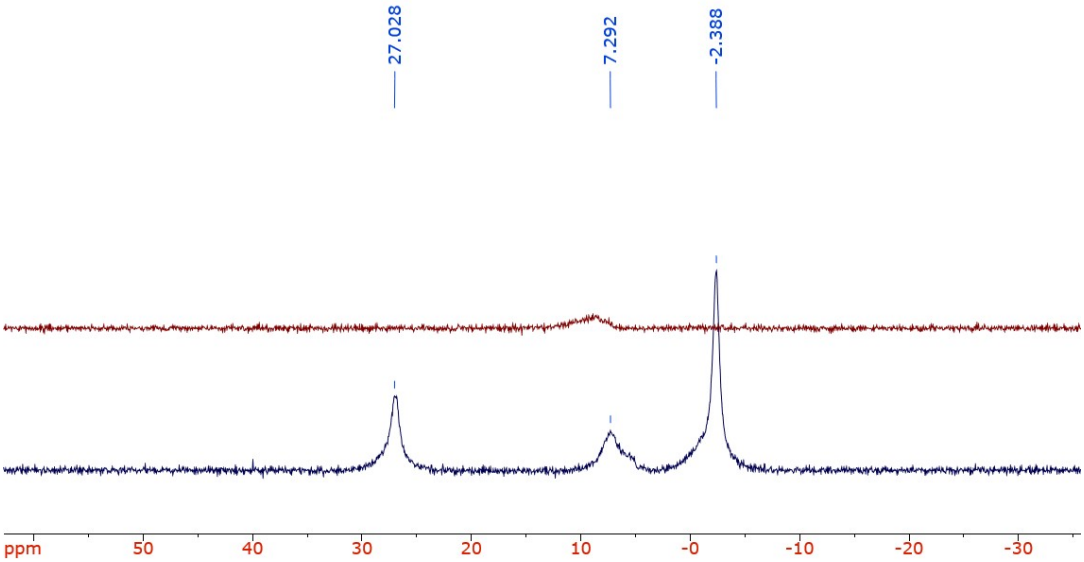


Figure S33. ^{11}B NMR ($CDCl_3$, 128 MHz, 298 K) overlay of the reaction of macrocycle **2** with tris(pentafluorophenyl)borane (red trace is macrocycle **2**; blue trace is macrocycle **2** with tris(pentafluorophenyl)borane).

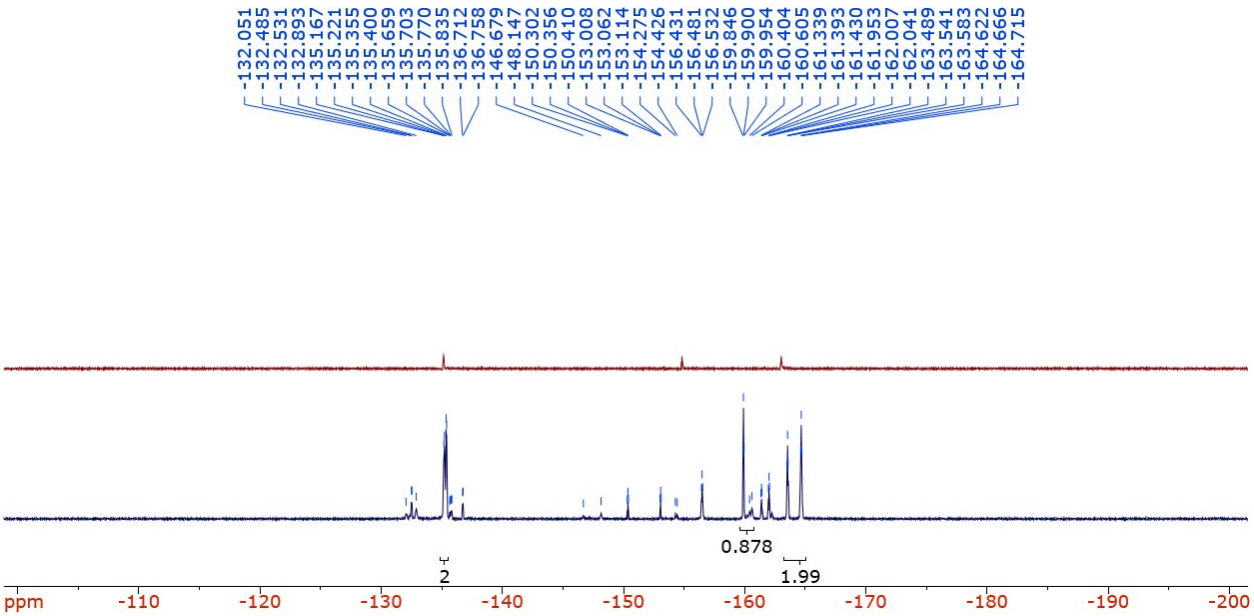


Figure S34. ^{19}F NMR ($CDCl_3$, 376 MHz, 298 K) overlay of the reaction of macrocycle **2** with tris(pentafluorophenyl)borane (red trace is macrocycle **2**; blue trace is macrocycle **2** with tris(pentafluorophenyl)borane).

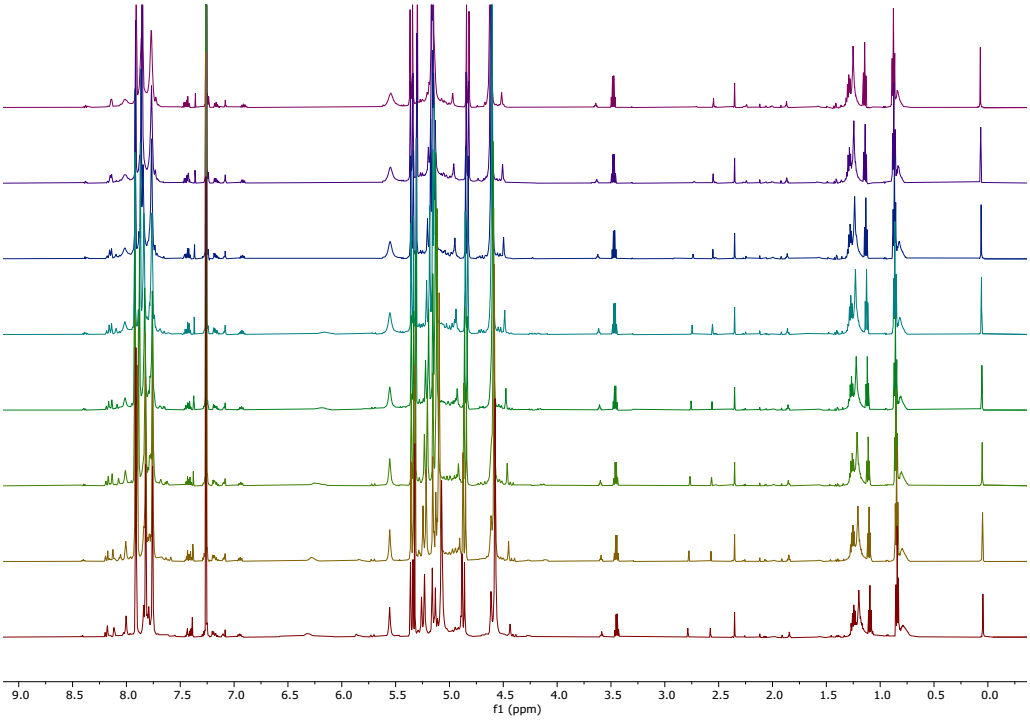


Figure S35. ^{1}H VT NMR ($CDCl_3$, 600 MHz) of the reaction of macrocycle **2** with tris(pentafluorophenyl)borane. Increments of 10°C starting from red trace at -50°C to purple trace at +20°C.

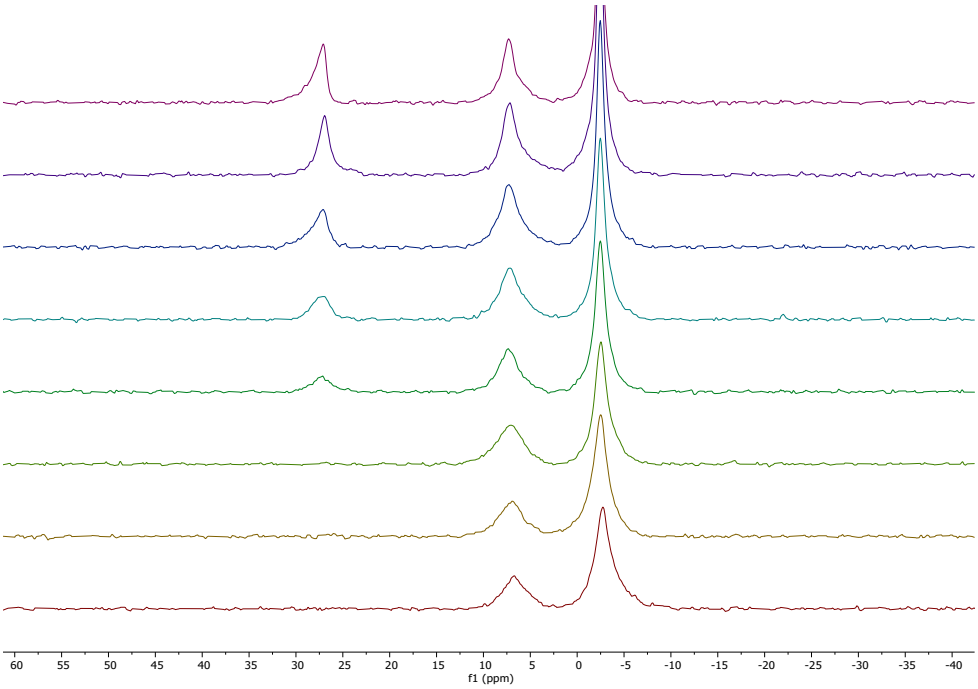


Figure S36. ^{11}B VT NMR ($CDCl_3$, 193 MHz) of the reaction of macrocycle **2** with tris(pentafluorophenyl)borane. Increments of 10°C starting from red trace at -50°C to purple trace at +20°C.

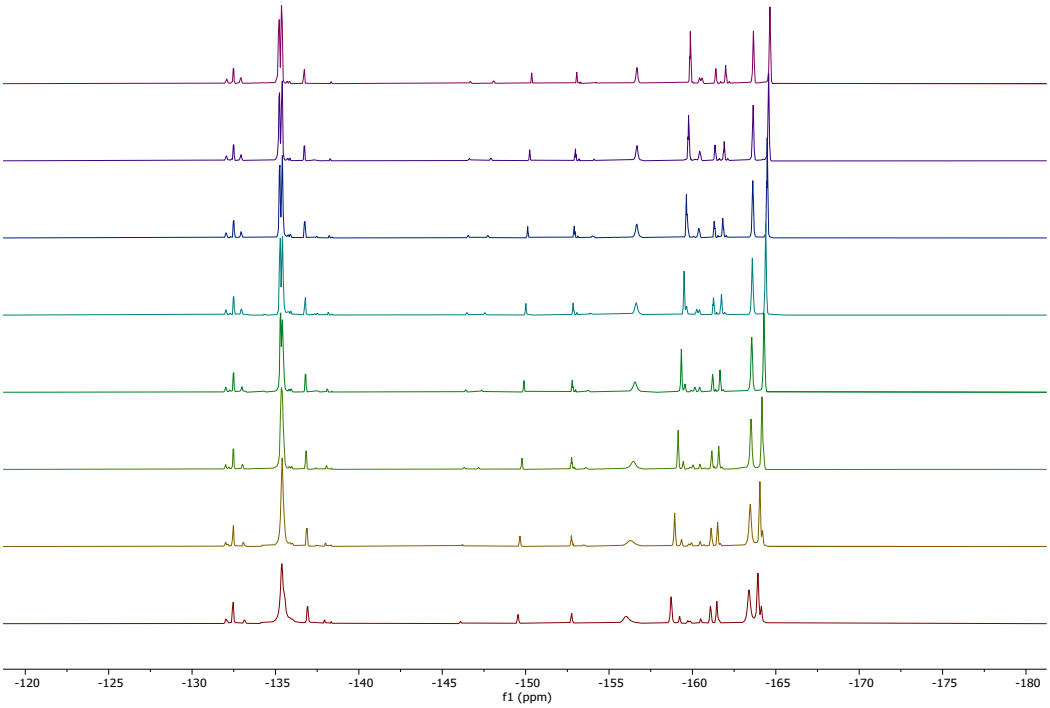


Figure S37. ^{19}F VT NMR ($CDCl_3$, 565 MHz) of the reaction of macrocycle **2** with tris(pentafluorophenyl)borane. Increments of 10°C starting from red trace at -50°C to purple trace at +20°C.

Reaction of macrocycle 6 with $B(C_6F_5)_3$

In an inert atmosphere glovebox, $B(C_6F_5)_3$ (12.9 mg, 25.0 μmol) was dissolved into $CDCl_3$ (0.5 mL), then added to macrocycle **6** (8.7 mg, 8.3 μmol). The reaction was monitored by NMR spectroscopy.

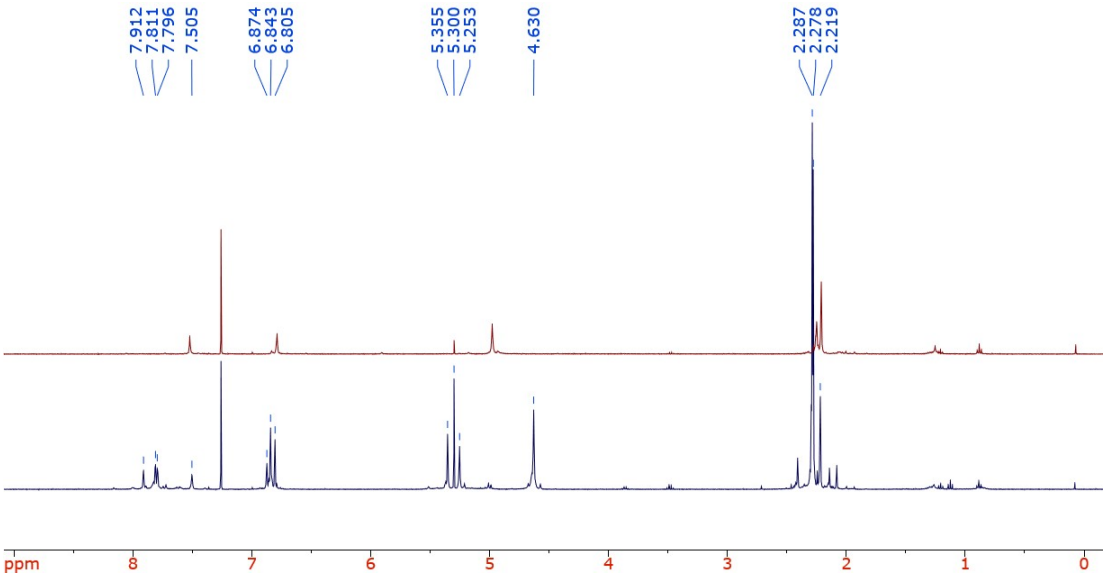


Figure S38. ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) overlay of the reaction of macrocycle **6** with tris(pentafluorophenyl)borane (red trace is macrocycle **6**; blue trace is macrocycle **6** with tris(pentafluorophenyl)borane).

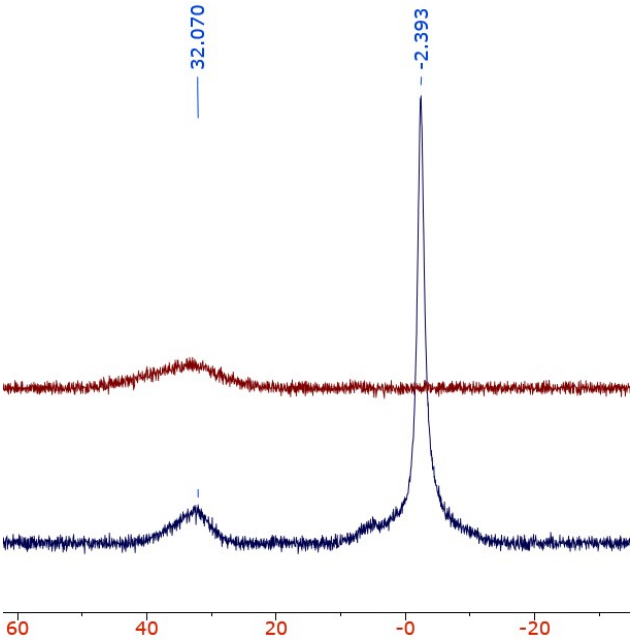


Figure S39. ^{11}B NMR ($CDCl_3$, 128 MHz, 298 K) overlay of the reaction of macrocycle **6** with tris(pentafluorophenyl)borane (red trace is macrocycle **6**; blue trace is macrocycle **6** with tris(pentafluorophenyl)borane).

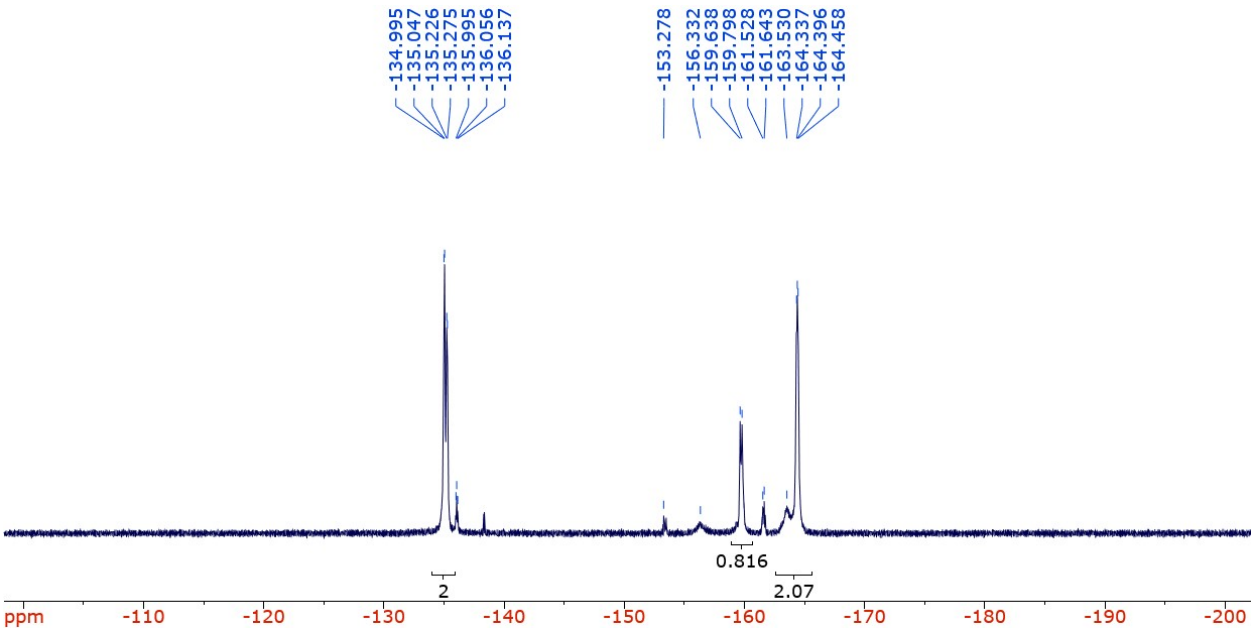


Figure S40. ^{19}F NMR ($CDCl_3$, 376 MHz, 298 K) of the reaction of macrocycle **6** with tris(pentafluorophenyl)borane.

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