Electronic Supplementary Material (ESI) for Chemical Communications

Highly efficient non-covalent energy transfer in all-organic macrocycles

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Electronic Supporting Information

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Materials and Methods

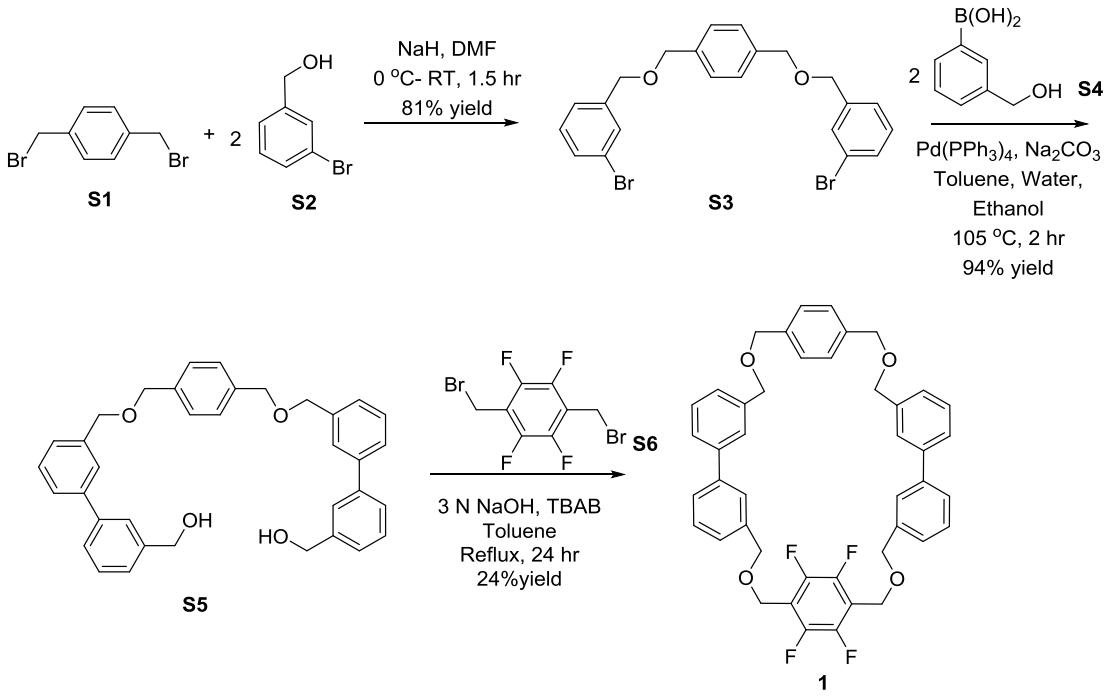
All reactions were carried out under an atmosphere of dry nitrogen unless otherwise noted. Solvents were dried using an MBraun dual solvent purification system prior to use. Starting materials, reagents and solvents were purchased from Aldrich Chemical Company, Acros Organics, or Fisher Scientific and were used as received. Reactions were all monitored via analytical thin layer chromatography (TLC) using polyester backed TLC plates. Visualization was accomplished with UV light at 254 nm. Column chromatography was performed with silica gel (230-400 mesh), obtained from Silicycle Incorporated.

^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker 300 MHz spectrometer. Multiplicity for ^{1}H NMR data is reported as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br =broad. ^{1}H NMR spectra were referenced to the residual solvent peaks: $CDCl_3$ (7.26 ppm), or d_6-DMSO (2.50 ppm). High resolution mass spectra were obtained and analyzed using a Bruker Daltonics APEXIV 4.7 Tesla Fourier Transform Ion Cyclotron Resonance Mass Spectrometer (FT-ICR-MS) at the Massachusetts Institute of Technology, in collaboration with Dr. Li Li. Absorbance measurements were recorded on an Agilent 8453 UV-visible spectrophotometer. Fluorescence measurements were recorded on Shimadzu RF 5301 spectrophotometer.

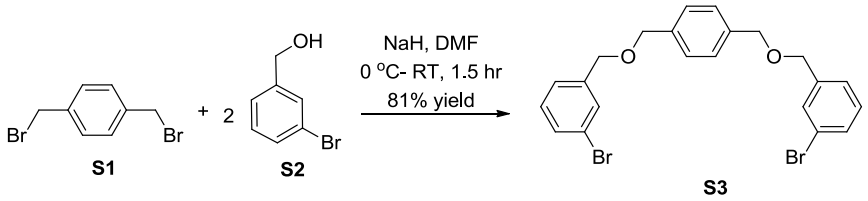
Synthetic Procedures:

Synthesis of Macrocycle 1:

Overall Scheme:

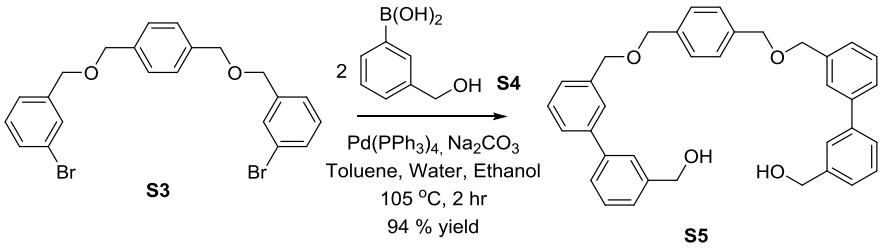


Reaction 1: Synthesis of compound S3:



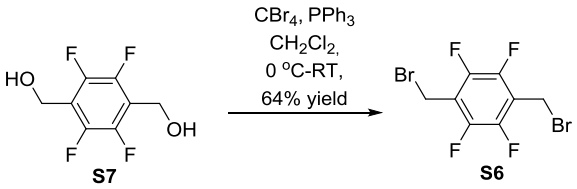
Compound **S1** (1.50 g, 5.68 mmol, 1.0 eq.) and 3-bromobenzyl alcohol **S2** (2.34 g, 12.50 mmol, 2.2 eq.) were dissolved in 20 mL of anhydrous dimethylformamide (DMF). The reaction mixture was stirred for 10 minutes at room temperature and was cooled to 0 °C in an ice bath. Sodium hydride (0.368 g, 15.34 mmol, 2.7 eq.) (60% in mineral oil) was then added to the reaction mixture and the reaction mixture was allowed to warm to room temperature. The reaction mixture was stirred at room temperature for 2 hours, at which point it was determined to be complete by TLC. Distilled water (10 mL) was added to quench the reaction, and the reaction mixture was then extracted with 3 portions of dichloromethane (20 mL each time). The combined organic extract was washed 9 times with distilled water (20 mL each time), followed by washing with brine. The organic extract was then dried over sodium sulfate, filtered, and concentrated via rotary evaporation to yield the crude product. The product was purified by flash chromatography (9:1 hexanes: ethyl acetate) to afford compound **S3** as a white solid in 81% isolated yield (2.18 grams). R_f: 0.85 (1:1 hexanes: ethyl acetate). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.52 (s, 2 H), 7.43 (d, 6 H, J = 7.8 Hz), 7.31-7.19 (m, 4 H), 4.56 (s, 4 H), 4.52 (s, 4 H); ^{13}C NMR ($CDCl_3$, 300 MHz): δ = 140.6, 137.5, 130.7, 130.6, 130.0, 128.0, 122.6, 72.1, 72.2; HRMS (ESI): Calcd for $[M+NH_4^+$, $C_{22}H_{20}Br_2O_2]^+$ 494.0157, found 494.0178.

Reaction 2: Synthesis of compound S5:



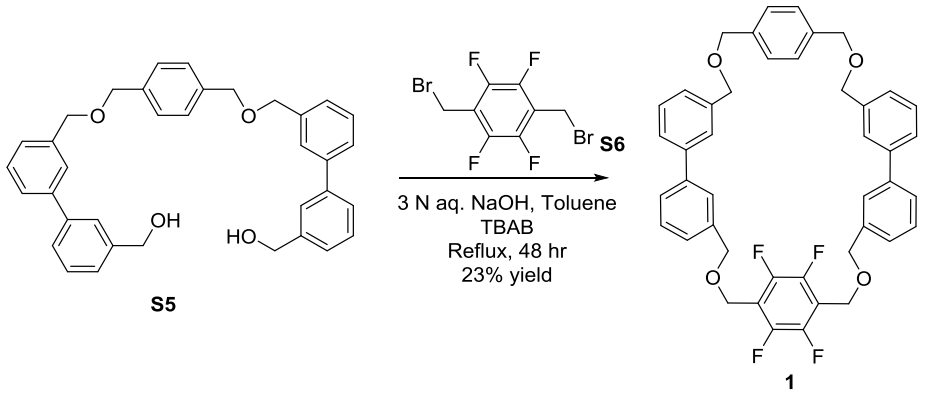
Compound **S3** (496 mg, 1.04 mmol, 1.0 eq.) was dissolved in anhydrous toluene (15 mL), 3-hydroxymethylphenyl boronic acid (compound **S4**) (481 mg, 3.17 mmol, 3.04 eq.) was dissolved in anhydrous ethanol (6.0 mL), and sodium carbonate (1.495 g, 14.11 mmol, 13.5 eq.) was dissolved in water (7.0 mL). The aqueous sodium carbonate solution was degassed under nitrogen for 30-60 minutes. All three solutions were combined in an oven-dried and nitrogen purged round-bottom flask and tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$) (156 mg, 0.14 mmol, 0.13 eq.) was added to the reaction mixture. The reaction mixture was refluxed at 105 °C for 3 hours under a nitrogen atmosphere, at which point the reaction was complete by TLC analysis. Water (6.0 mL) was added to quench the reaction and the reaction mixture was extracted with dichloromethane (3 portions of 20 mL each). The combined organic extract was dried over sodium sulfate, filtered, and concentrated via rotary evaporation. The product was further purified by flash chromatography using hexanes: ethyl acetate (4:6) to afford compound **S5** as an off-white solid (517 mg, 94 % yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.59 (s, 4 H), 7.52 (d, 4 H, J = 7.8 Hz), 7.43 (d, 4 H, J = 7.5 Hz) 7.41-7.34 (m, 8 H), 4.75 (d, 4 H, J = 5.7 Hz), 4.61 (d, 8 H, J = 5.1 Hz). ^{13}C NMR ($CDCl_3$, 300 MHz): δ = 141.4, 141.3, 141.1, 138.8, 129.0, 128.9, 128.0, 126.8, 126.6, 126.5, 126.4, 125.9, 125.8, 72.1, 72.0, 65.3. HRMS (ESI): Calcd for $[M+H^+, C_{36}H_{34}O_4]^+$ 530.2457, found 530.2454.

Reaction 3: Synthesis of compound S6:



Compound **S7** (1.20 g, 5.71 mmol, 1.0 eq.) was dissolved in dichloromethane (25 mL) and cooled to 0 °C. Carbon tetrabromide (4.73 g, 14.26 mmol, 2.5 eq.) and triphenylphosphine (3.74 g, 14.26 mmol, 2.5 eq.) were added to the reaction mixture. The reaction mixture was then warmed to room temperature and stirred at room temperature for 16 hours. The solvent was removed using a rotary evaporator, and the crude mixture was purified by flash chromatography (9:1 hexanes: ethyl acetate). The product was obtained as a white crystalline solid (1.21 g, 63 % yield). R_f: 0.80 (1:1 ethyl acetate: hexanes). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 4.50 (s, 4 H); ^{13}C NMR ($CDCl_3$, 300 MHz): δ = 146.1, 142.8, 117.5, 16.2; ^{19}F NMR ($CDCl_3$, 300 MHz): δ = -142.31; HRMS (ESI): Calcd for $[M+H^+, C_8H_4Br_2F_4]^+$ 333.8616, found 333.8612.

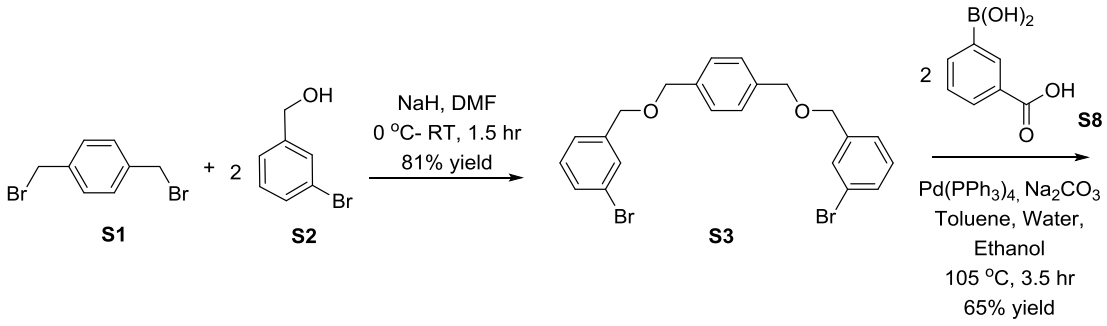
Reaction 4: Synthesis of compound 1:

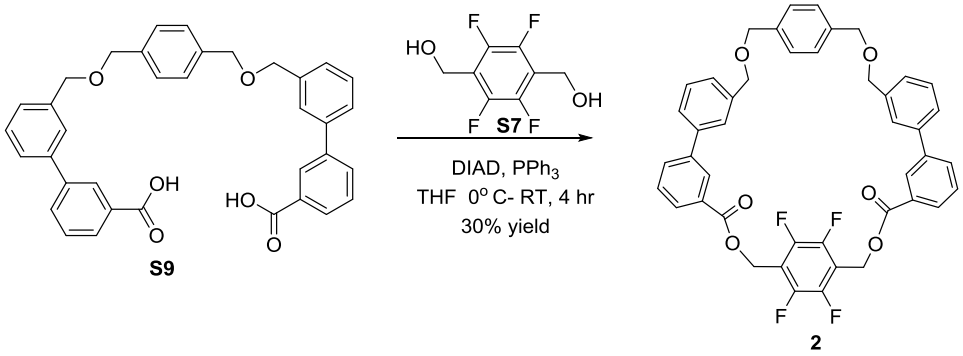


To a mixture of compound **S5** (50. mg, 0.094 mmol, 1.0 eq.), compound **S6** (34 mg, 0.101 mmol, 1.07 eq.) and tetrabutylammonium bromide (TBAB) (60 mg, 0.186 mmol, 1.98 eq.) in anhydrous toluene (50 mL) was added a solution of 3 N aqueous NaOH (8.0 mL). The reaction mixture was refluxed for 48 hours at 120 ^{o}C. After 48 hours, the reaction mixture was cooled to room temperature and toluene was removed via rotary evaporator. The reaction mixture was extracted with ethyl acetate (3 portions of 5.0 mL), and the combined organic extract was washed with brine solution, dried over anhydrous sodium sulfate, filtered and evaporated to yield the crude product as a yellow liquid. The product was purified via flash chromatography (3:7 ethyl acetate: hexanes) to afford the pale yellow liquid in 23% isolated yield (15 mg). R_f: 0.62 (1: 1 ethyl acetate: hexanes); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.55 (s, 4 H), 7.49 (d, 4 H, J = 7.8 Hz), 7.42 (d, 2 H, J = 7.5 Hz) 7.40-7.28 (m, 10 H), 4.68 (s, 4 H), 4.61 (s, 4 H), 4.59 (s, 4 H), 4.58 (s, 4 H). ^{13}C NMR ($CDCl_3$, 300 MHz): δ = 140.36, 140.13, 137.77, 136.88, 136.63, 127.78, 126.98, 125.89, 125.75, 125.72, 125.63, 125.46, 70.98, 70.91, 58.36; ^{19}F NMR ($CDCl_3$, 300 MHz): δ = -143.42; HRMS (ESI): Calcd for $[M+Na]^+$, $C_{44}H_{36}F_4O_4]^+$ 727.2447, found 727.2442.

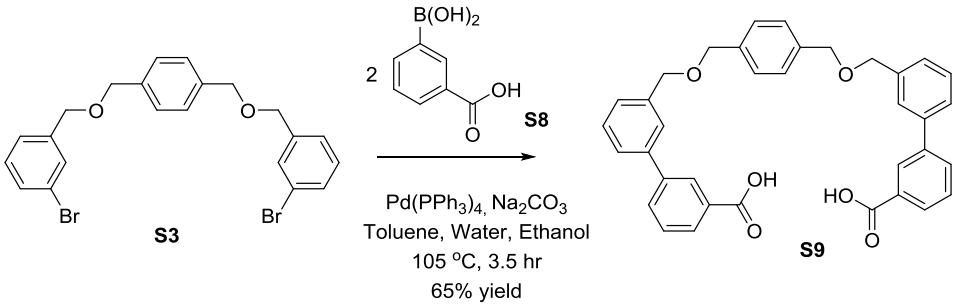
Synthesis of Macrocycle 2:

Overall Scheme:



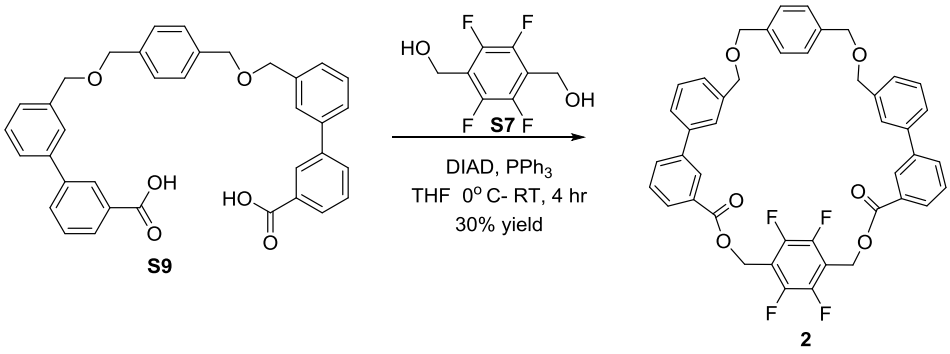


Reaction 5: Synthesis of compound S9:



Compound **S3** (500 mg, 1.05 mmol, 1.0 eq.) was dissolved in anhydrous toluene (15.0 mL), 3-carboxyphenyl boronic acid (compound **S8**) (400 mg, 2.41 mmol, 2.3 eq.) was dissolved in anhydrous ethanol (8.0 mL), and sodium carbonate (1.11 g, 10.47 mmol, 9.97 eq.) was dissolved in water (8.0 mL). The aqueous sodium carbonate solution was degassed under nitrogen for 30 minutes. All three solutions were combined in an oven-dried, nitrogen-purged round-bottom flask and tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$) (226 mg, 0.196 mmol, 0.19 eq.) was added to the reaction mixture. The reaction mixture was refluxed at 105 ^oC for 3.5 hours under a nitrogen atmosphere, until the reaction was complete by TLC analysis. The reaction mixture was acidified to pH 2 by adding 6N HCl dropwise (approximately 1.5-2 mL) then extracted with 3 portions of ethyl acetate (20 mL each). The combined organic extract was washed with brine and dried over sodium sulfate, filtered, and concentrated via rotary evaporation. The product was further purified by flash chromatography using hexanes: ethyl acetate (6:4) to afford a white solid (361 mg, 65 % yield). ^1H NMR (d_6-DMSO, 300 MHz): δ = 8.17 (s, 2 H), 7.92 (t, 4 H, J = 9 Hz), 7.66-7.56 (m, 6 H) 7.47 (t, 2 H, J = 7.5 Hz), 7.38 (d, 6 H, J = 9.3 Hz), 4.61 (s, 4 H), 4.57 (s, 4 H). ^{13}C NMR (d_6-DMSO, 300 MHz): δ = 167.2, 140.3, 139.3, 139.2, 137.9, 131.5, 131.0, 129.3, 129.1, 128.3, 127.6, 127.2, 127.0, 125.8, 125.8. HRMS (ESI): Calcd for $[M\text{-}H^-$, $C_{36}H_{30}O_6]^-$ 557.1970, found 557.1978.

Reaction 6: Synthesis of macrocycle 2:

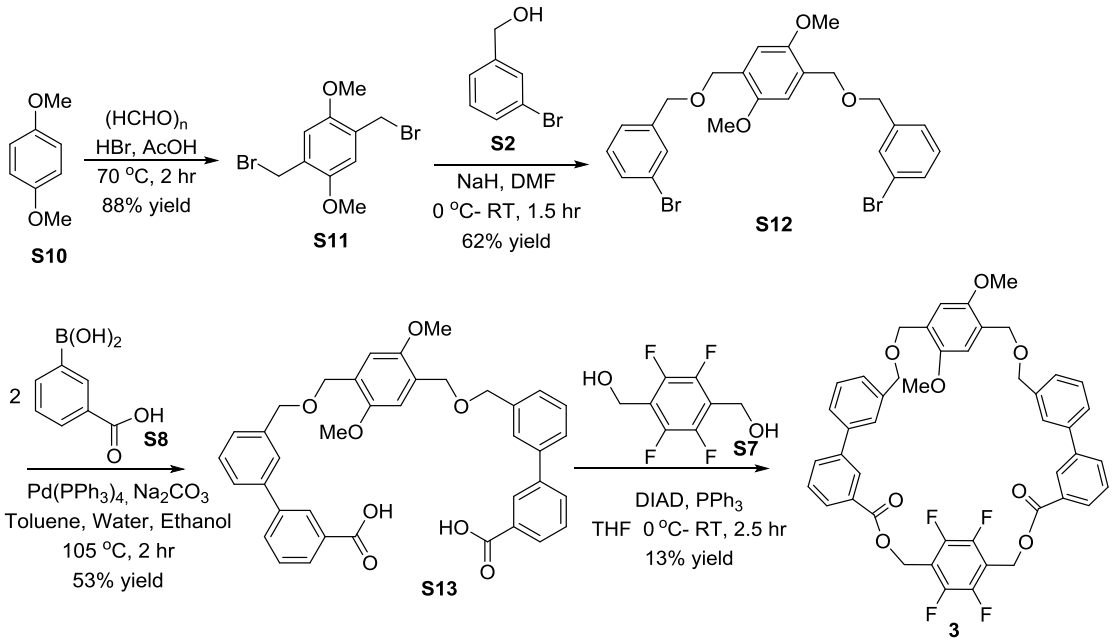


To compound **S9** (130.0 mg, 0.23 mmol, 1.0 eq.), compound **S7**, (54.0 mg, 0.25 mmol, 1.1 eq.) and triphenylphosphine (124.0 mg, 0.47 mmol, 2.04 eq.) in anhydrous THF (50 mL) was added a solution of diisopropylazodicarboxylate (0.096 mL, 0.49 mmol, 2.1 eq.) in anhydrous THF (5.0 mL) slowly at 0 ^0C. The reaction mixture was stirred for 15 min at 0 ^0C. The reaction mixture was allowed to warm to room temperature, and was stirred for 4 hours at room temperature. The reaction mixture was diluted with diethyl ether (15 mL), and washed with saturated $NaHCO_3$ (2 x 10 mL portions) and brine (10 mL). The organic layer was dried with sodium sulfate, filtered and evaporated. The residue was purified by column chromatography to afford macrocycle **2** as a white solid (51 mg, 30% yield). ^1H NMR ($CDCl_3$, 300 MHz): δ = 8.15 (s, 2 H), 8.03 (d, 2 H, J = 8.1 Hz), 7.77 (d, 2 H, J = 7.8 Hz), 7.50 (d, 4 H, J = 5.1 Hz), 7.45 (t, 4 H, J = 4.8 Hz), 7.39 (d, 2 H, J = 7.2 Hz), 7.33 (d, 2 H, J = 7.5 Hz), 7.31 (s, 4 H), 5.54 (s, 4 H), 4.57

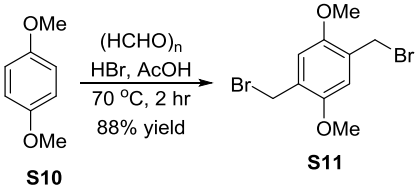
(s, 8 H). ^{13}C NMR ($CDCl_3$, 300 MHz): δ = 165.7, 141.7, 140.4, 139.0, 132.2, 129.8, 128.9, 127.9, 127.1, 126.6, 71.9, 71.7. ^{19}F NMR ($CDCl_3$, 300 MHz): δ = -141.8. HRMS (ESI): Calcd for [M+Na], [$C_{44}H_{32}F_4O_6$] 755.2028, found 755.2047.

Synthesis of Macrocycle 3:

Overall Scheme:

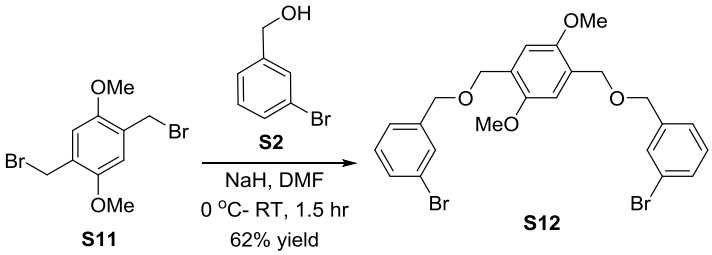


Reaction 7: Synthesis of compound S11:



Prepared according to the published procedure: Roviello, A.; Borbone, F.; Carella, A.; Diana, R.; Roviello, G.; Panunzi, B.; Ambrosio, A.; Maddalena, P. *J. Polym. Sci. A Polym. Chem.* **2009**, *47*, 2677-2689.

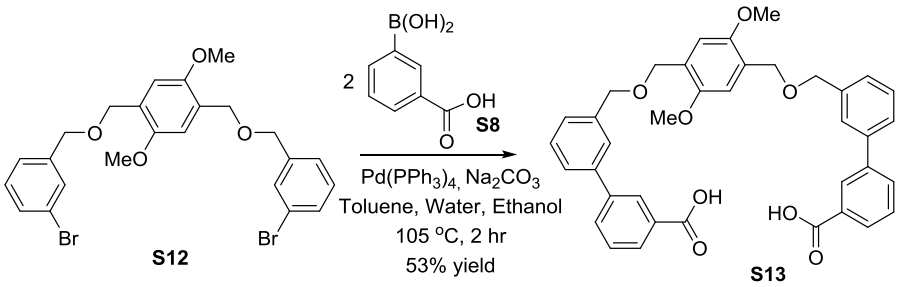
Reaction 8: Synthesis of compound S12:



Compound **S11** (1.0 g, 3.09 mmol, 1.0 eq.) and compound **S2** (1.26 g, 6.74 mmol, 2.2 eq.) were dissolved in 10 mL of anhydrous dimethylformamide. The reaction mixture was stirred for 10 minutes at room temperature and was cooled to 0 °C in an ice bath. Sodium hydride (0.200 g, 8.33 mmol, 2.7 eq.) (60% in

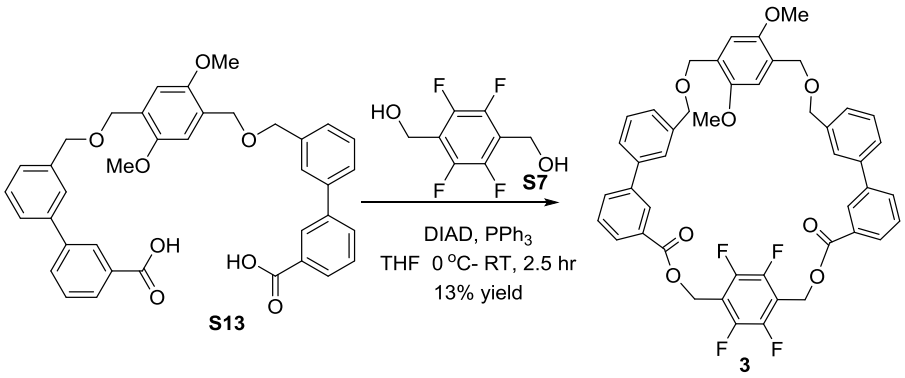
mineral oil) was then added to the reaction mixture and the mixture was allowed to warm to room temperature. The reaction mixture was stirred at room temperature for 2 hours, until it was determined to be complete by TLC. Excess distilled water (~ 15 mL) was added to quench the reaction, and the reaction mixture was then extracted multiple times with dichloromethane (3 X 20 mL). The combined organic extract was washed 10 times with distilled water (10 mL each time), followed by brine. The organic extract was then dried over sodium sulfate, filtered, and concentrated via rotary evaporation to yield the crude product. The crude product was purified by isopropanol (0.5 mL) and hexanes (10 mL) to afford the ether product as a white solid in 62% isolated yield (1.02 grams). R_f: 0.56 (9:1 hexanes: ethyl acetate). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.49 (s, 2 H), 7.34 (d, 2 H, J = 7.8 Hz), 7.23-7.11 (m, 4 H), 6.90 (s, 2 H), 4.51 (s, 4 H), 4.49 (s, 4 H), 3.74 (s, 6 H); ^{13}C NMR ($CDCl_3$, 300 MHz): δ = 151.1, 140.9, 130.67,129.9, 126.2, 126.1, 122.5, 71.5, 67.0, 56.1; HRMS (ESI): Calcd for $[M+NH_4^+$, $C_{24}H_{18}Br_2O_4]^+$ 552.0371, found 552.0367.

Reaction 9: Synthesis of compound S13:



Compound **S12** (0.505 g, 0.94 mmol, 1.0 eq.) was dissolved in anhydrous toluene (15 mL), 3-carboxyphenyl boronic acid (compound **S8**) (0.406 g, 2.45 mmol, 2.6 eq.) was dissolved in anhydrous ethanol (8.0 mL), and sodium carbonate (1.03 g, 9.72 mmol, 10.3 eq.) was dissolved in water (8.0 mL). The aqueous sodium carbonate solution was degassed under nitrogen for 30 minutes. All three solutions were combined in an oven-dried, nitrogen-purged round-bottom flask and tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$) (0.205 g, 0.18 mmol, 0.19 eq.) was added to the reaction mixture. The reaction mixture was refluxed at 105 ^{o}C for 3 hours under a nitrogen atmosphere, until the reaction was complete by TLC analysis. The reaction mixture was cooled to room temperature and acidified to pH 2 by adding 6N HCl dropwise (~2 mL), then extracted with ethyl acetate (3 portions of 20 mL each). The combined organic extract was washed with brine solution and dried over sodium sulfate, filtered, and concentrated via rotary evaporation. The product was further purified by flash chromatography using hexanes: ethyl acetate (1:1) to afford a white solid (307 mg, 53% yield). ^{1}H NMR (d_6-DMSO, 300 MHz): δ = 13.14 (s, 2 H), 8.19 (s, 2 H), 8.01-7.89 (m, 4 H), 7.70 (s, 2 H), 7.67-7.55 (m, 4 H), 7.49 (t, 2 H, J = 7.5 Hz), 7.41 (d, 2 H, J = 7.5 Hz), 7.04 (s, 2 H), 4.66 (s, 4 H), 4.55 (s, 4 H), 3.72 (s, 6 H). ^{13}C NMR (d_6-DMSO, 300 MHz): δ = 167.1, 150.4, 140.3, 139.4, 131.4, 131.0, 129.3, 129.0, 128.2, 127.2, 126.9, 126.0, 125.7, 111.4, 71.4, 66.3, 55.7. HRMS (ESI): Calcd for $[M-H^-$, $C_{36}H_{30}O_6]^-$ 618.6850, found 618.6858.

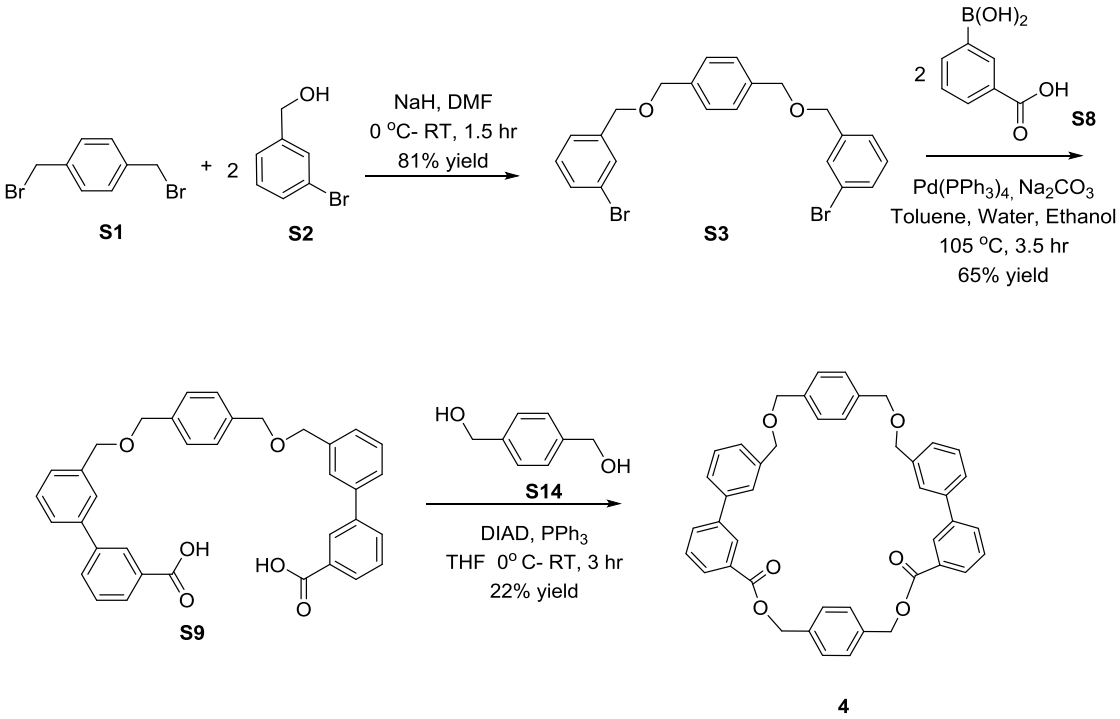
Reaction 10: Synthesis of macrocycle 3:



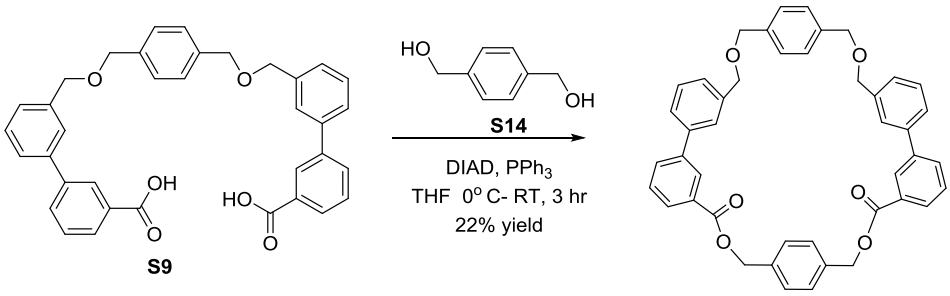
To compound **S13** (100.0 mg, 0.16 mmol, 1.0 eq.), compound **S7** (37.0 mg, 0.18 mmol, 1.1 eq.), and triphenylphosphine (86.0 mg, 0.33 mmol, 2.1 eq.) in anhydrous THF (50 mL) was added a solution of diisopropylazodicarboxylate (DIAD) (0.067 mL, 0.34 mmol, 2.1 eq.) in anhydrous THF (5.0 mL) slowly at 0 ^{0}C. The reaction mixture was stirred for 15 min at 0 ^{0}C. The reaction mixture was stirred for 2.5 hours at room temperature and then the reaction mixture was diluted with diethyl ether (10 mL). The organic phase was washed with saturated $NaHCO_3$ (2x10 mL) and brine (10 mL). The organic layer was dried with sodium sulfate, filtered and the solvent was removed on the rotary evaporator. The residue was purified by column chromatography (45% ethyl acetate: 55% hexanes) to afford macrocycle **3** as a white solid (17 mg, 13% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.14 (s, 2 H), 8.02 (d, 2 H, J = 7.8 Hz), 7.72 (d, 2 H, J = 8.1 Hz), 7.55-7.30 (m, 10 H), 6.88 (s, 2 H), 5.54 (s, 4 H), 4.61 (s, 4 H), 4.56 (s, 4 H), 3.62 (s, 6 H). ^{13}C NMR ($CDCl_3$, 300 MHz): δ = 165.7, 151.1, 141.8, 140.3, 139.3, 132.2, 129.8, 128.9, 128.8, 128.7, 128.4, 127.2, 126.8, 126.3, 111.9, 72.0, 66.8, 55.9, 54.1. ^{19}F NMR ($CDCl_3$, 300 MHz): δ = -141.85. HRMS (ESI): Calcd for $[M+NH_4]^+$, $C_{46}H_{36}F_4O_8$ 810.2685, found 810.2678.

Synthesis of Macrocycle 4:

Overall Scheme:



Reaction 11: Synthesis of macrocycle 4:



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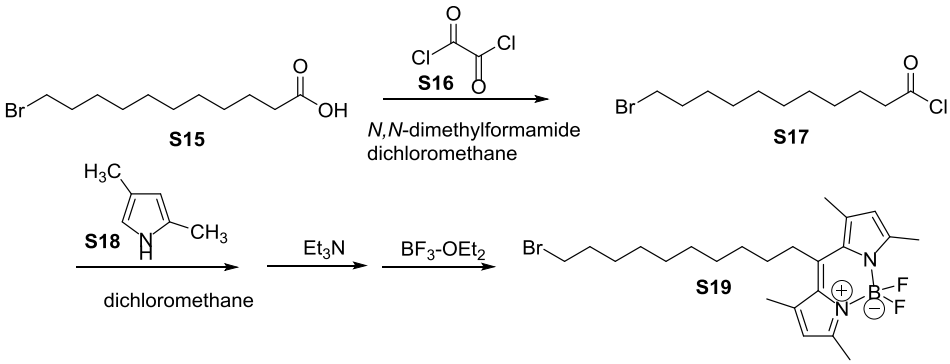
To compound **S9** (140.0 mg, 0.251 mmol, 1.0 eq.), compound **S14**, (58.0 mg, 0.276 mmol, 1.1 eq.) and triphenylphosphine (134.0 mg, 0.512 mmol, 2.04 eq.) in anhydrous THF (25 mL) was added a solution of diisopropylazodicarboxylate (0.096 mL, 0.49 mmol, 2.1 eq.) in anhydrous THF (5.0 mL) slowly at 0 ^{0}C. The reaction mixture was stirred for 15 min at 0 ^{0}C. The reaction mixture was allowed to warm to room temperature, and was stirred for 3 hours at room temperature. The reaction mixture was diluted with diethyl ether (10 mL), and washed with saturated $NaHCO_3$ (2 x 10 mL portions) and brine (10 mL). The organic layer was dried with sodium sulfate, filtered and evaporated. The residue was purified by column chromatography to afford macrocycle **4** as off-white solid (35 mg, 22% yield). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 8.29 (t, 1 H), 8.18 (t, 1 H), 8.05 (m, 2 H), 7.78 (d, 2 H, J = 7.8 Hz), 7.70 (m, 4 H), 7.62 (m, 2 H), 7.51 (m, 8 H), 7.39 (s, 2 H), 7.31 (s, 2 H), 5.41 (s, 2 H), 4.62 (d, 4 H, J = 7.5 Hz), 4.57 (s, 4H), 3.95 (s, 2H).

Synthesis of BODIPY 7:

The synthesis of BODIPY 7 was performed according to literature procedures:

Shepherd, J. L.; Kell, A.; Chung, E.; Sinclar, C. W.; Workentin, M. S.; Bizzotto, D. *J. Am. Chem. Soc.* **2004**, *126*, 8329-8335.

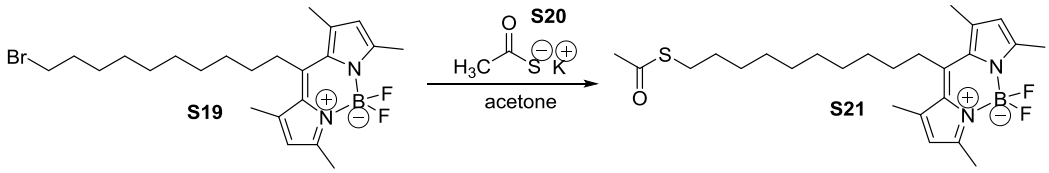
Reaction 1:



Procedure: 2.0 grams of 11-bromoundecanoic acid **S15** (7.54 mmol, 1.0 eq.) was combined with 2 drops of *N*,*N*-dimethylformamide in 40 mL of dichloromethane. 1.0 gram of oxalyl chloride **S16** (7.88 mmol, 1.05 eq.) was dissolved in 5.0 mL of dichloromethane and added dropwise. The reaction mixture was stirred for one hour, then the crude mixture was concentrated on the rotary evaporator and dried on a vacuum overnight to remove any unreacted oxalyl chloride. The resulting acid chloride **S17** was dissolved in 50 mL of dichloromethane. 0.772 mL of 2,4-dimethylpyrrole **S18** (7.50 mmol, 0.99 eq.) was dissolved in 5.0 mL of dichloromethane and added to the reaction mixture. The resulting reaction mixture was heated to reflux for 3 hours under a nitrogen atmosphere, during which time the mixture became a dark red color. After three hours, the reaction mixture was cooled to room temperature and solvent was removed on the rotary evaporator until approximately 5.0 mL of the dichloromethane solution remained.

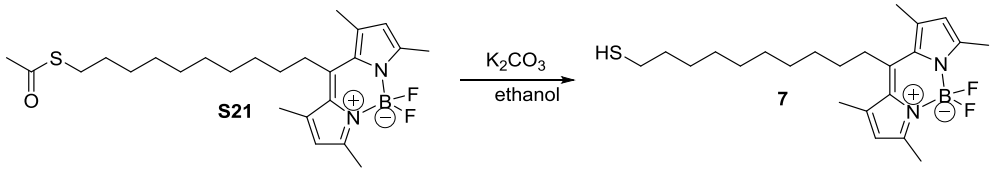
200 mL of *n*-hexanes were added to the flask, and the mixture was cooled overnight in the freezer at -20 °C. The hexanes were decanted from the insoluble oil and precipitate. The resulting crude product was dissolved in 75 mL of toluene and heated to 80 °C. 1.0 mL of triethylamine (7.17 mmol, 0.95 eq.) was added and the solution immediately turned light yellow. 1.0 mL of boron trifluoride etherate (8.10 mmol, 1.07 eq.) was then added and the reaction mixture was stirred at 80 °C for 30 minutes, during which time the color of the mixture darkened and became fluorescent. The reaction mixture was cooled to room temperature, and the product was extracted 3 times with brine (50 mL each time). The organic layer was dried over sodium sulfate, filtered, and concentrated. The crude product was purified by flash chromatography (1:1 dichloromethane: hexanes) to yield the desired product in 28% yield (comparable to the literature-reported 24% yield).

Reaction 2:



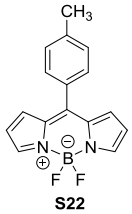
Procedure: Compound **S19** (0.968 g, 2.07 mmol, 1.0 eq.) and compound **S20** (0.27 grams, 2.36 mmol, 1.14 eq.) were dissolved in 50 mL of acetone. The reaction mixture was heated to reflux for two hours. After two hours, the reaction mixture was cooled to room temperature, acetone was removed, and the crude solid was re-dissolved in dichloromethane and washed with water. The organic extract was dried over sodium sulfate, filtered and concentrated, to yield compound **S21** in 97% yield (0.932 grams).

Reaction 3:



Procedure: Compound **S21** (0.932 grams, 2.01 mmol, 1.0 eq.) was dissolved in 150 mL of anhydrous ethanol that was purged with nitrogen. Potassium carbonate was added, and the reaction mixture was warmed to 30 °C. The reaction mixture was stirred under nitrogen for 4 hours at 30 °C. The contents of the flask were poured over 40 mL of aqueous saturated ammonium chloride, at which point the solution turned bright orange. The product was extracted with dichloromethane and washed several times with water. The organic layer was dried over sodium sulfate, filtered, and concentrated. The product was purified via flash chromatography (1:1 dichloromethane: hexanes) to yield compound **7** in 76% yield (674 mg).

Synthesis of control BODIPY (compound S22):



The synthesis of BODIPY **S22** was performed according to literature procedures: Cui, A.; Peng, X.; Fan, J.; Chen, X.; Wu, Y.; Guo, B. *J. Photochem. Photobiol. A Chem.* **2007**, *186*, 85-92.

Fluorescence Experimental Details:

All fluorescence spectra were recorded on a Shimadzu RF 5301 spectrophotometer. Binding experiments were conducted as follows:

The following stock solutions were made:

3 mg/mL of each macrocycle in THF

1 mg/mL of each PAH analyte in THF

Dilutions of the macrocycle stock solution were made to obtain solutions of 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 2.0 and 3.0 mg/mL solutions of the macrocycle.

20 μL of the PAH stock solution was added to 2.5 mL of phosphate buffered saline (PBS) at pH 7.4. 200 μL of each macrocycle solution was added, and the fluorescence of the solution was recorded with 360 nm excitation (scanned emission 370-710 nm). The fluorescence of the analyte was integrated with respect to wavenumber. The resulting data was plotted using a Benesi-Hildebrand plot, with 1/[macrocycle] (in M) on the X-axis and 1/integrated analyte emission on the Y-axis. Linear fits were obtained using macrocycle **2** as a host and anthracene and benzo[*a*]pyrene as guests (1:1 complex for anthracene and 1:2 complex for benzo[*a*]pyrene). The binding constant was calculated by dividing the y-intercept of the linear fit by the slope of the line.

Energy transfer experiments were conducted as follows:

A 1 mg/mL stock solution of BODIPY **7** in THF was made. 200 μL of the macrocycle host, 20 μL of the PAH analyte, and 20 μL of the BODIPY fluorophore were added to 2.5 mL of PBS. The solution was excited at 360 nm and 460 nm. The fluorescence emission of anthracene and of BODIPY were integrated with respect to wavenumber, and the efficiency of energy transfer was determined by measuring both the fractional quenching of anthracene emission in the presence of BODIPY, and the percentage of BODIPY emission from analyte excitation compared to direct excitation.

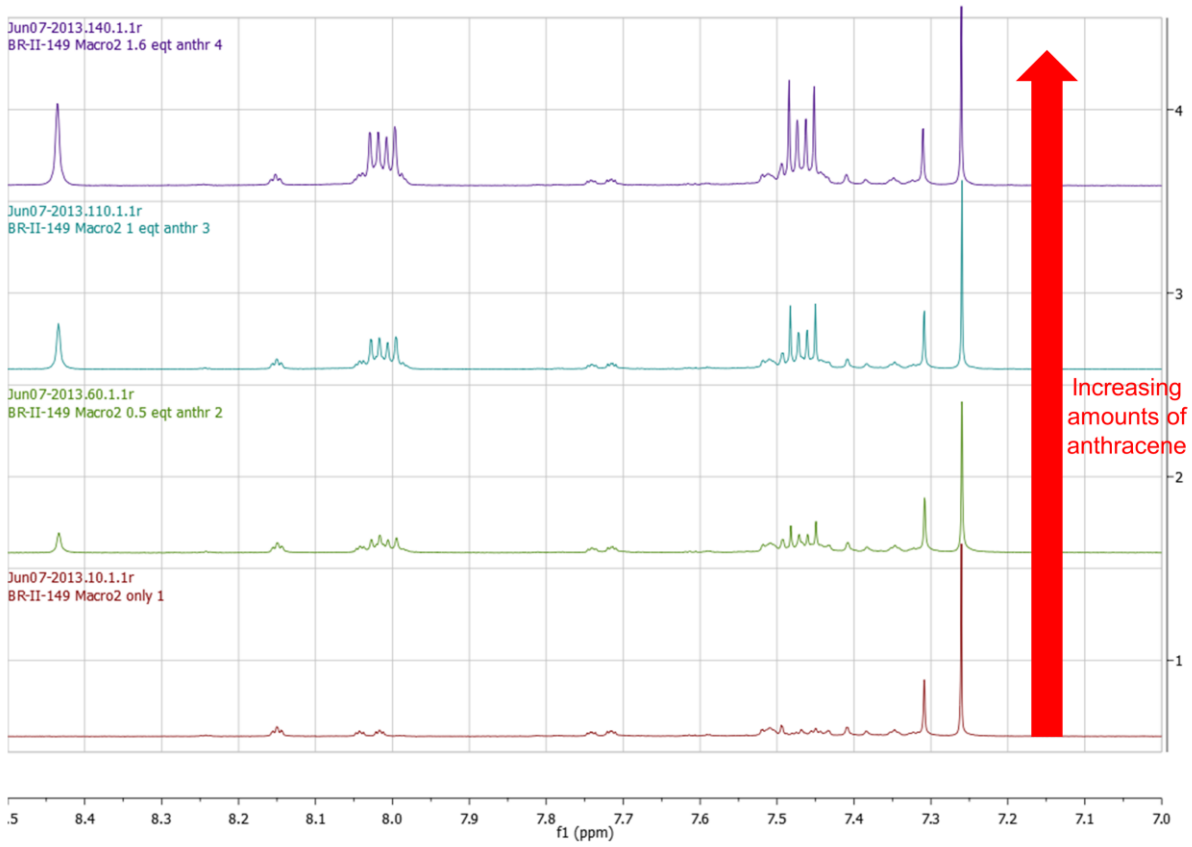
^{1}H NMR Titration Experiments:

All NMR titrations were carried out by adding aliquots of guest molecules in $CDCl_3$ to an NMR tube containing the host macrocycle. After each addition, spectra were recorded by using Bruker 300 MHz Instrument.

For the titration of macrocycle **2** with anthracene **5**: A $CDCl_3$ solution of macrocyle **2** (3.59 mg, 4.9 x 10^{-3} mmol, 0.5 mL) was titrated by adding an incremental amount (5 µL, 4.9 x 10^{-4} mmol, 0.1 equivalent) of anthracene from a stock solution (0.098 M in $CDCl_3$).

For the titration of macrocycle **2** with benzo[*a*]pyrene **6**: A $CDCl_3$ solution of macrocyle **2** (3.59 mg, 4.9 x 10^{-3} mmol, 0.5 mL) was titrated by adding an incremental amount (5 µL, 4.9 x 10^{-4} mmol, 0.1 equivalent) of benzo[*a*]pyrene from a stock solution (0.098 M in $CDCl_3$).

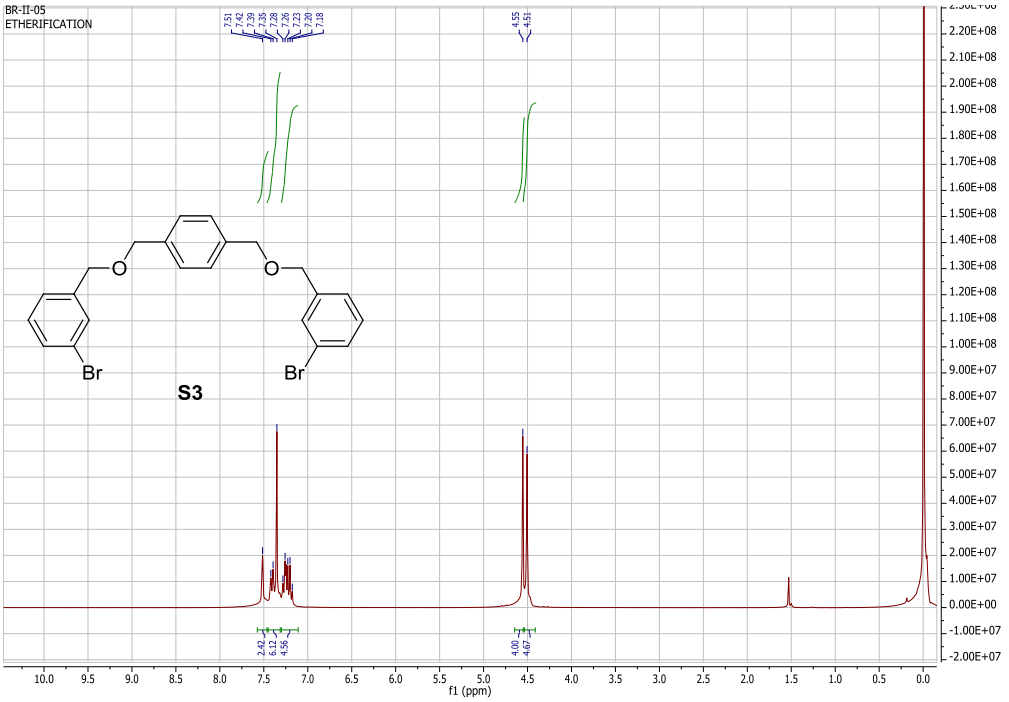
Benzo[*a*]pyrene showed clear evidence of binding in macrocycle **2** (see paper for details). Anthracene showed no shift in the ^{1}H NMR peaks, as shown below:



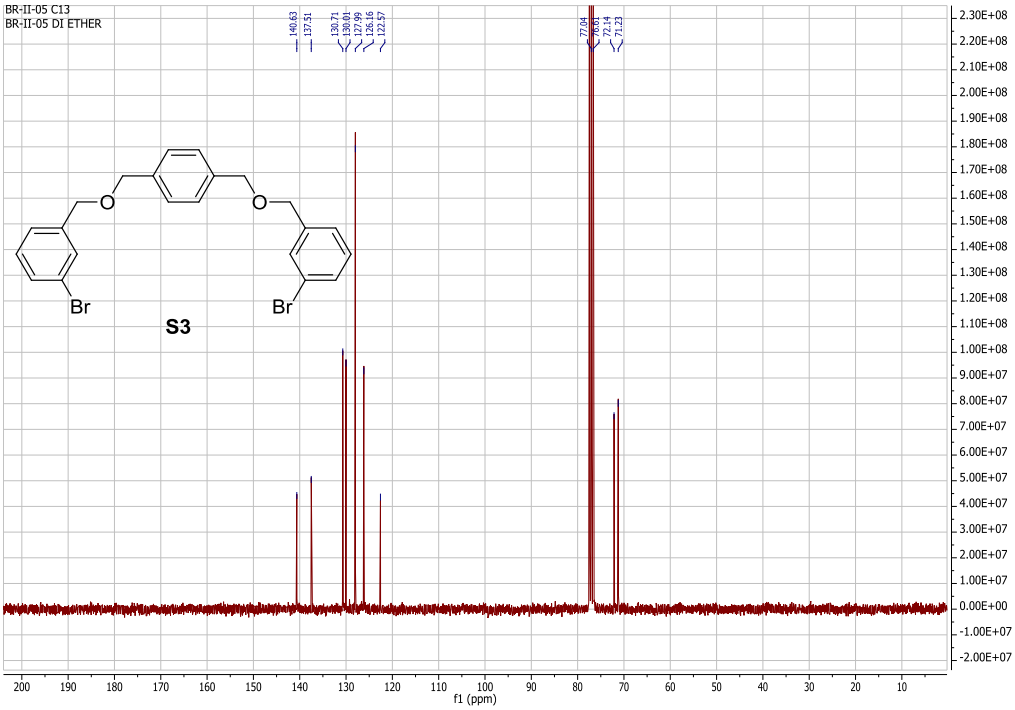
Spectral Copies:

Compound S3:

^{1}H NMR:

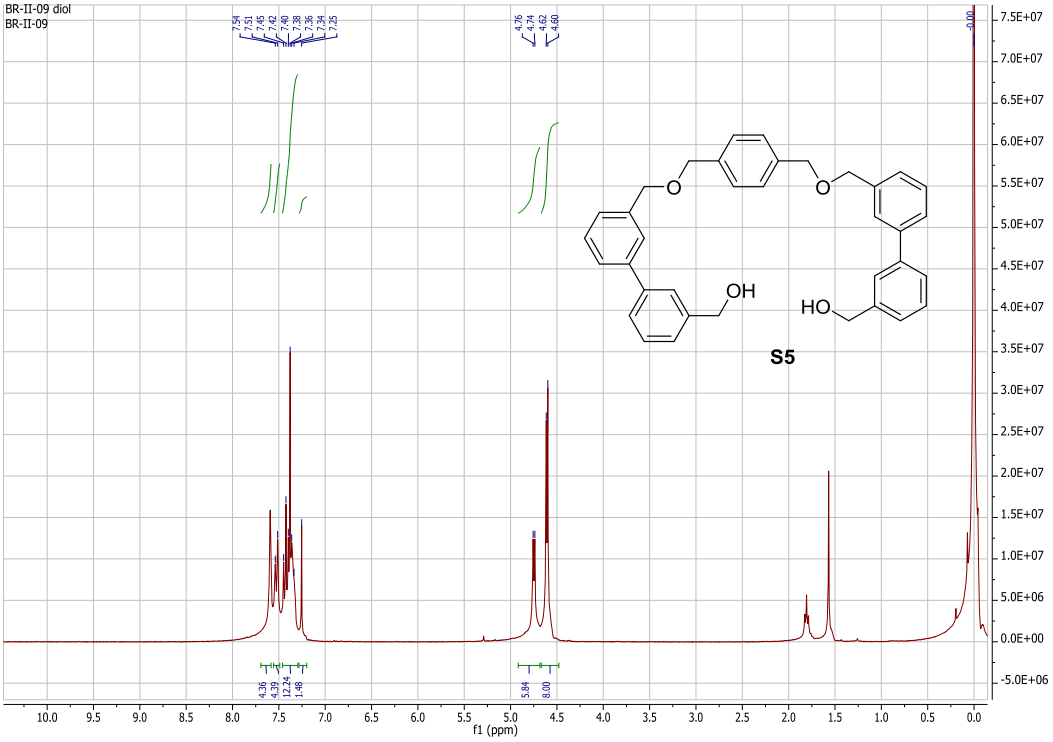


^{13}C NMR:

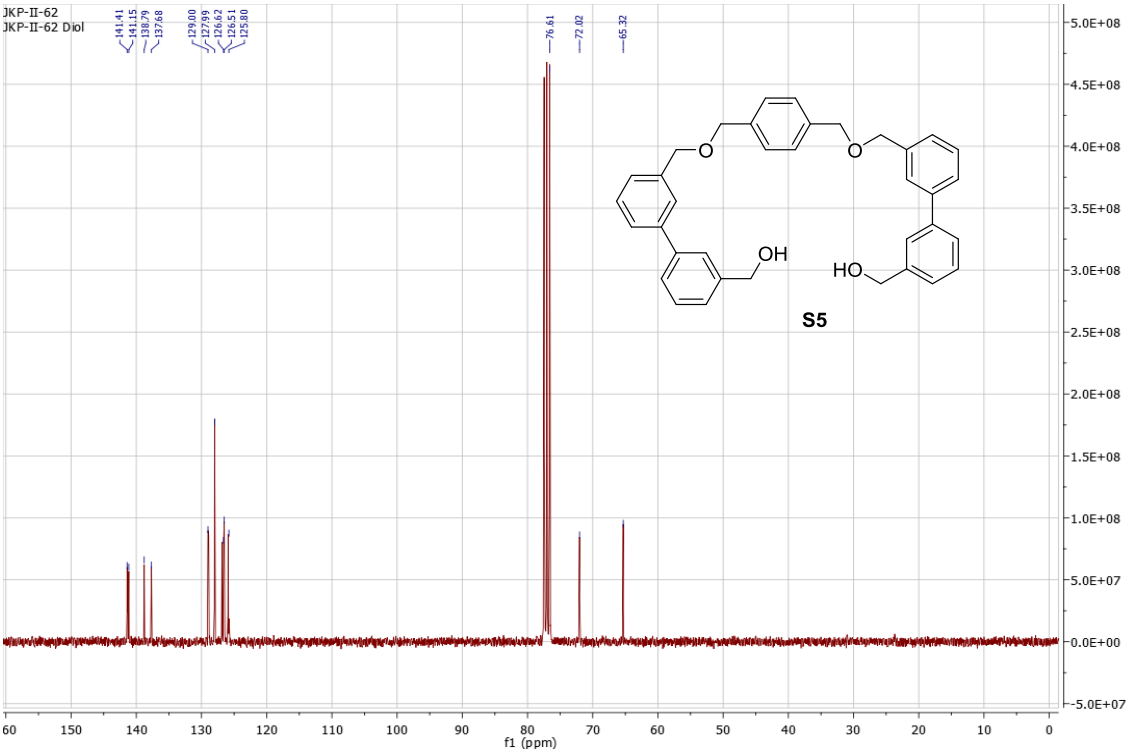


Compound S5:

^{1}H NMR:

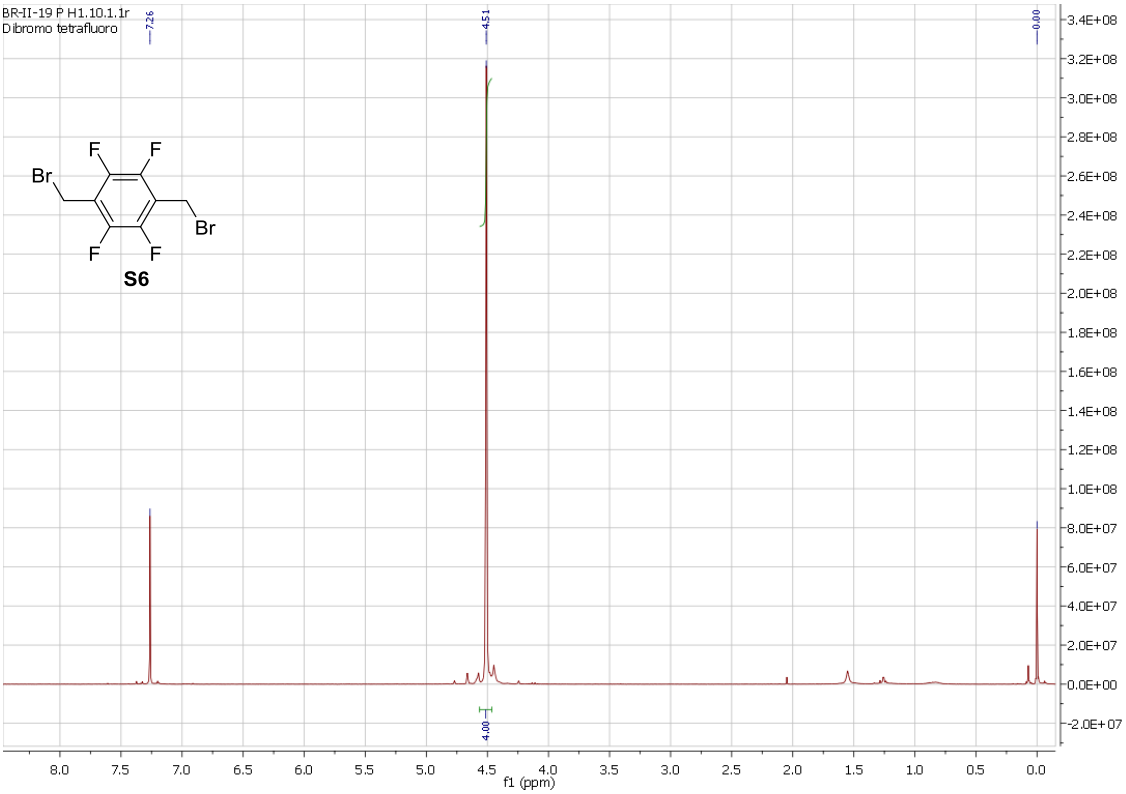


^{13}C NMR:

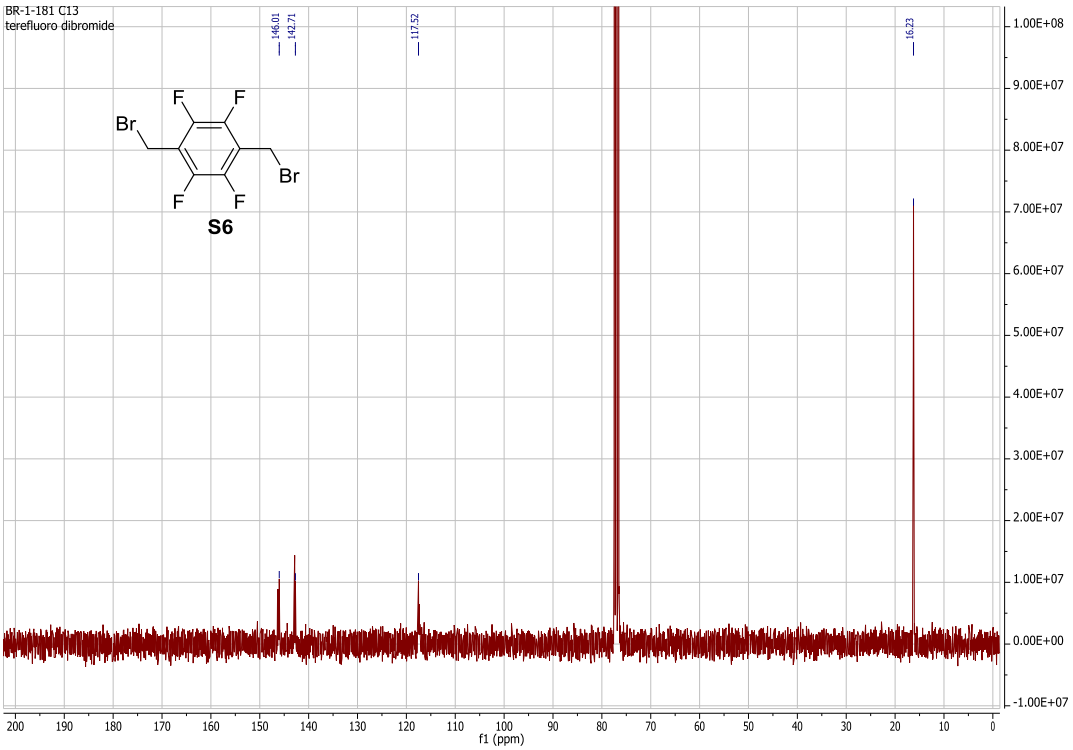


Compound S6:

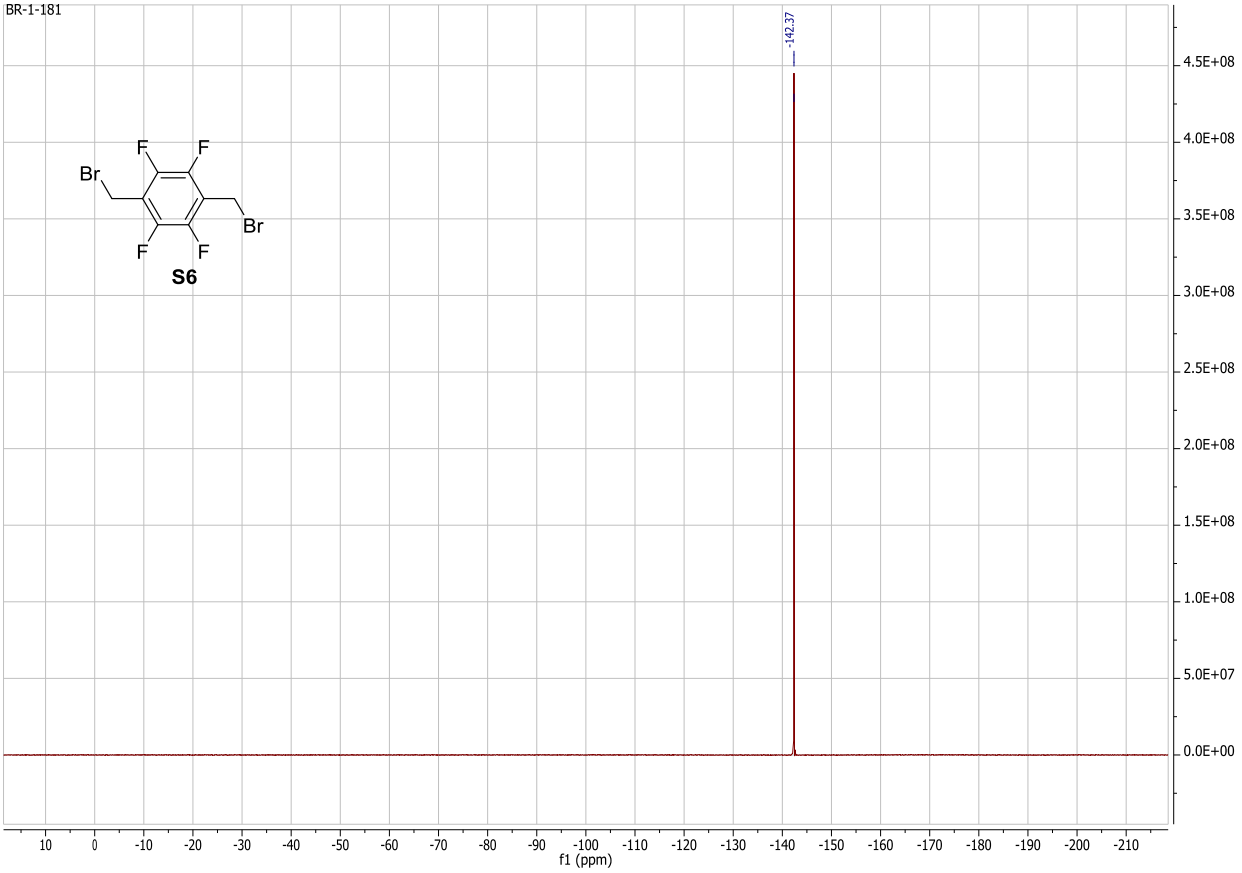
^{1}H NMR:



^{13}C NMR:

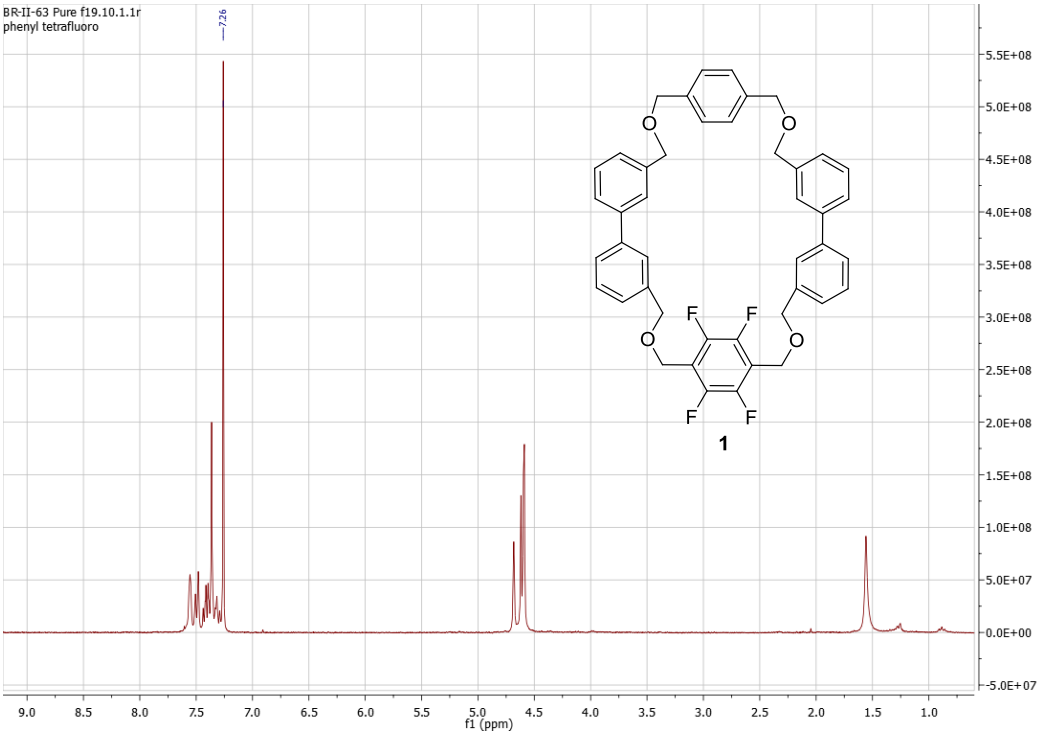


^{19}F NMR:

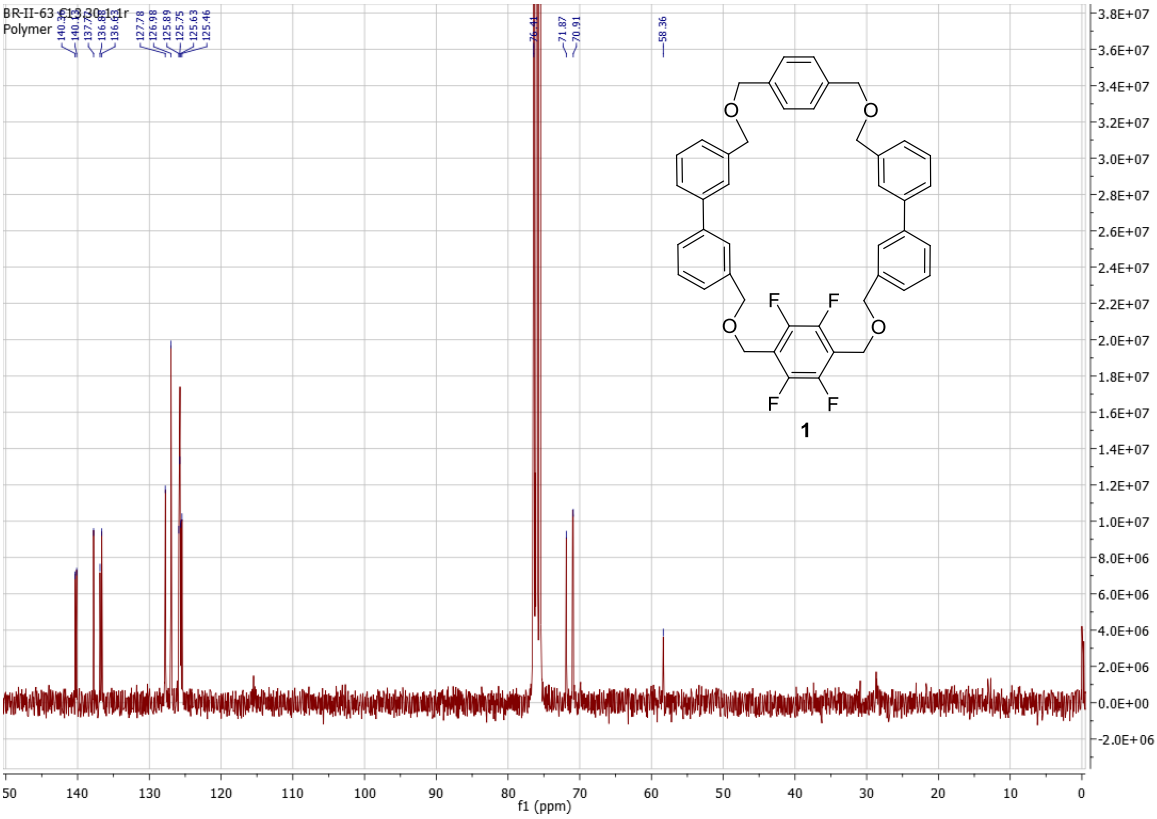

BR-1-181
-142.37
F
F
Br
Br
F
F
S6
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

Compound 1:

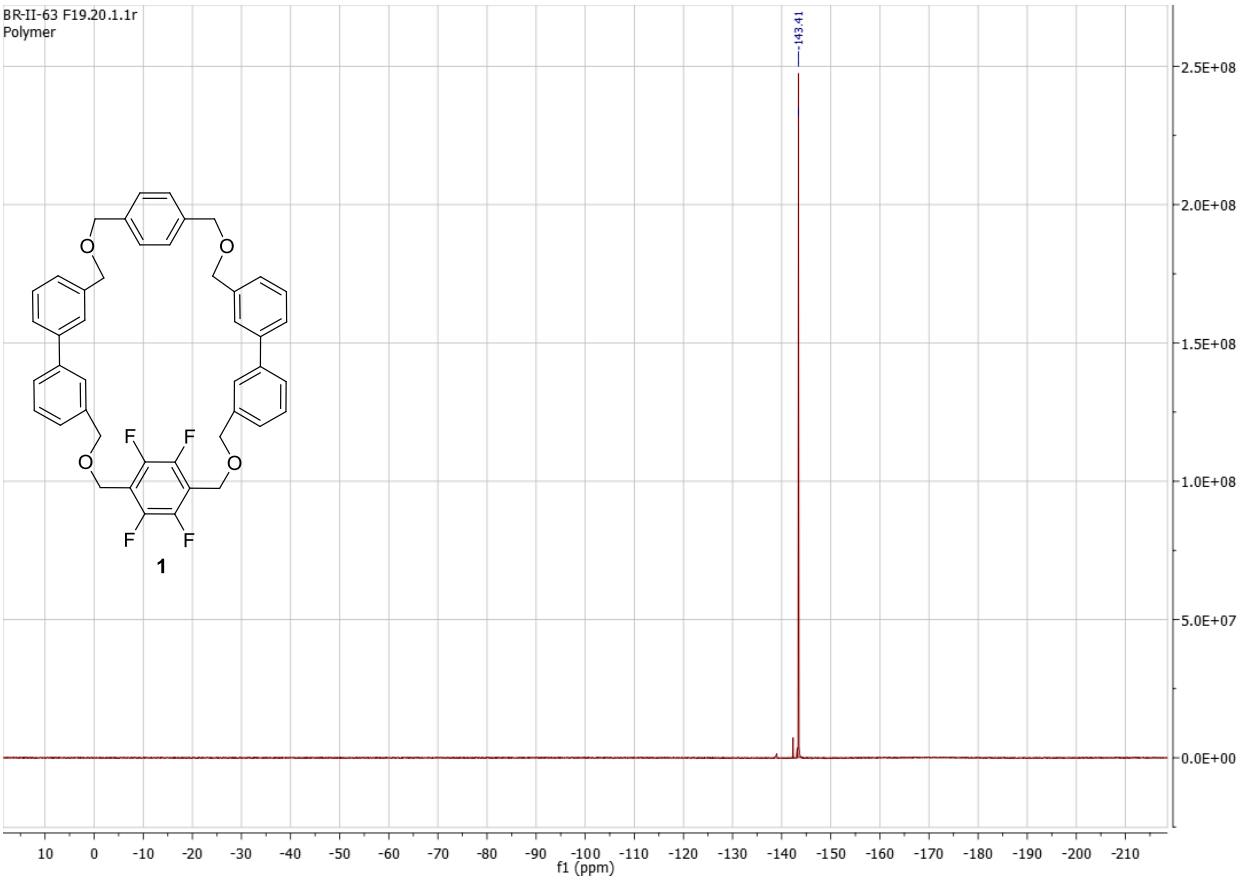
^{1}H NMR:



^{13}C NMR:

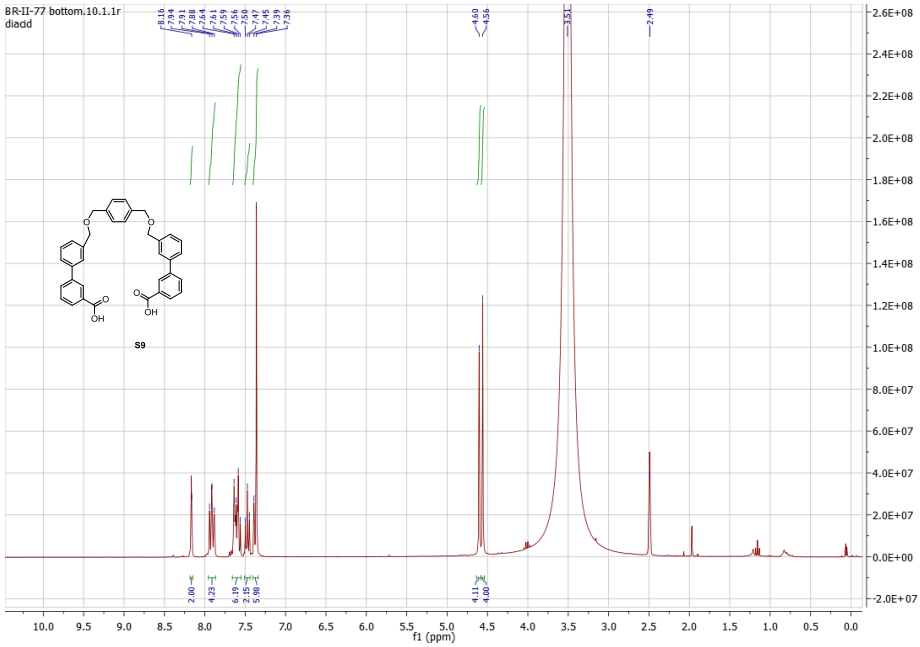


^{19}F NMR:

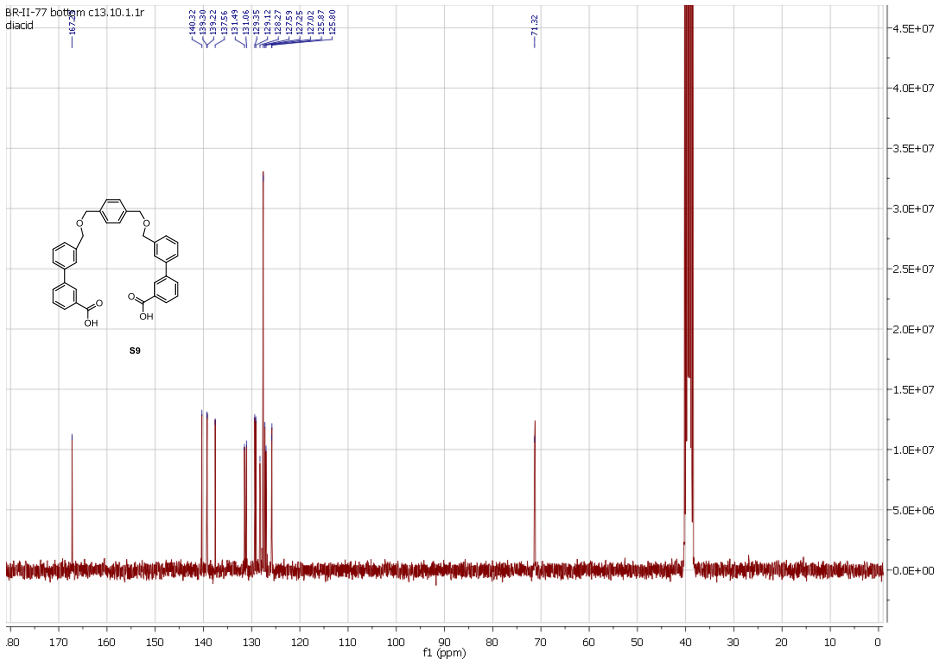

BR-II-63 F19.20.1.1r
Polymer
-143.41
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
O
O
O
O
F
F
F
F
1
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

Compound S9:

^{1}H NMR:

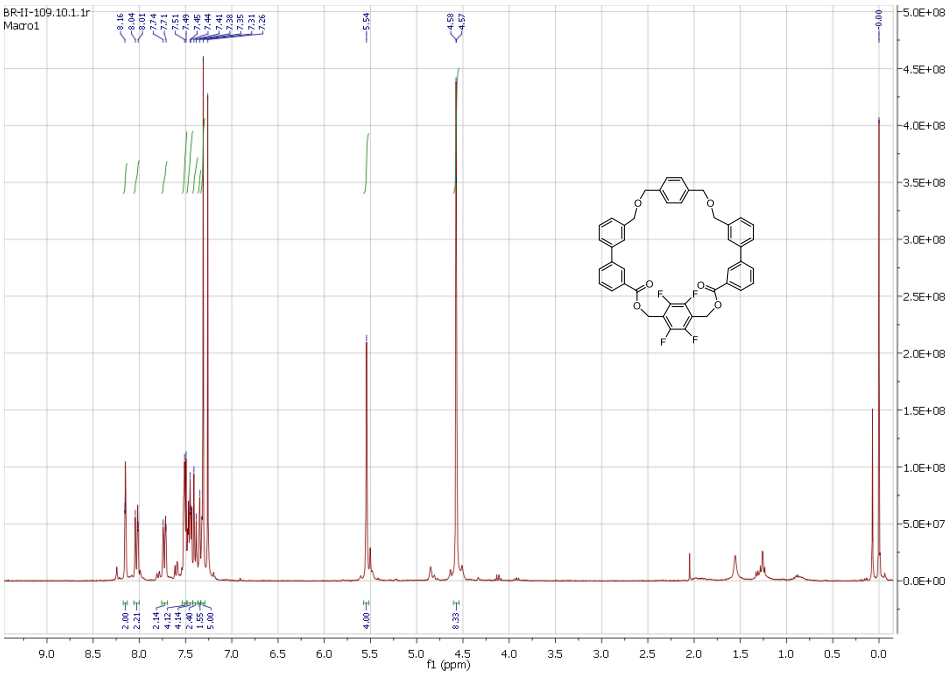


^{13}C NMR

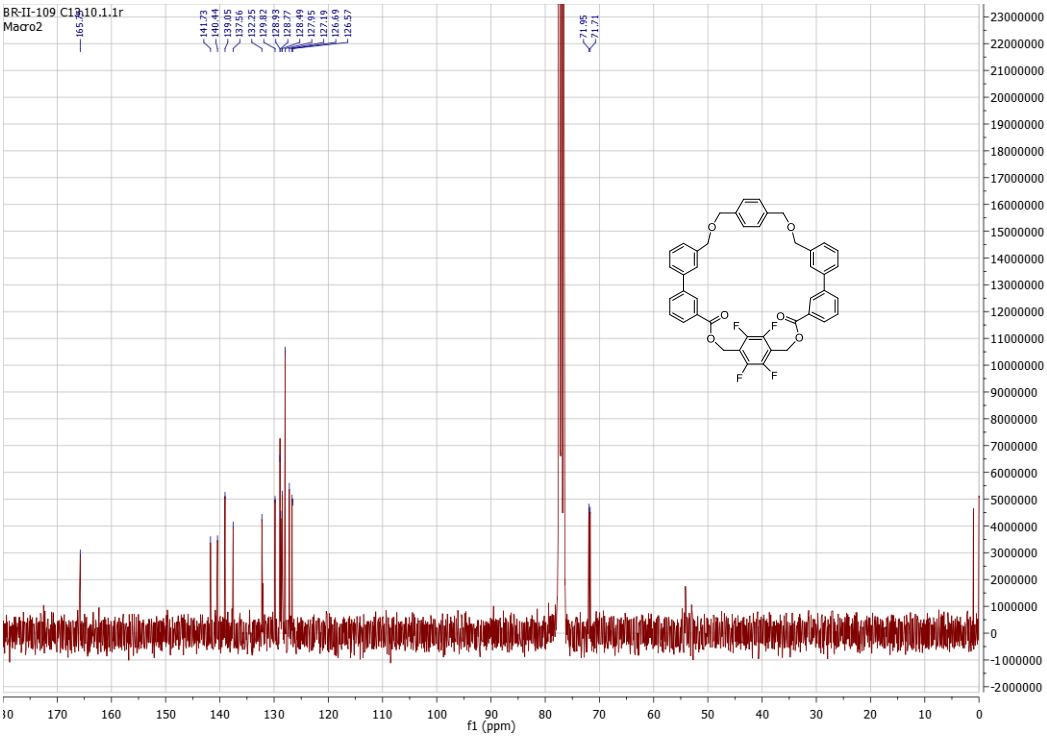


Macrocycle 2:

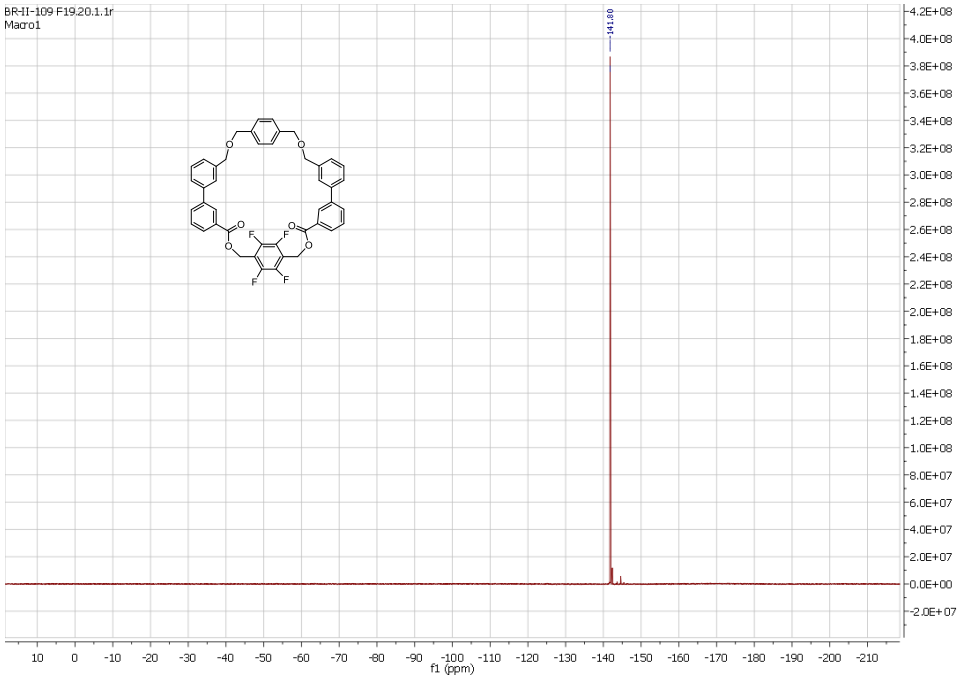
^{1}H NMR:



^{13}C NMR:

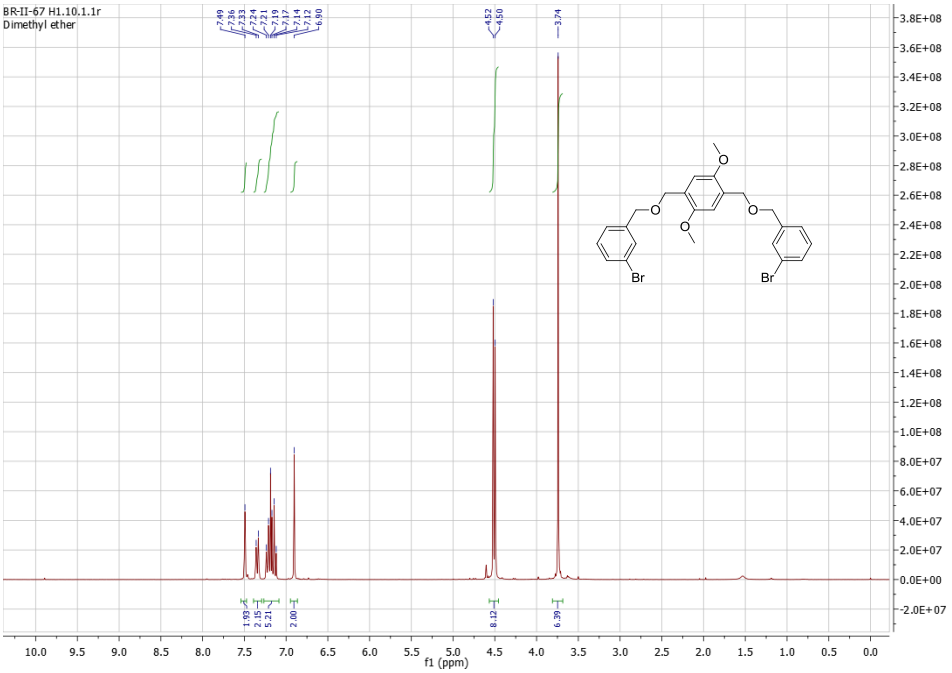


^{19}F NMR:

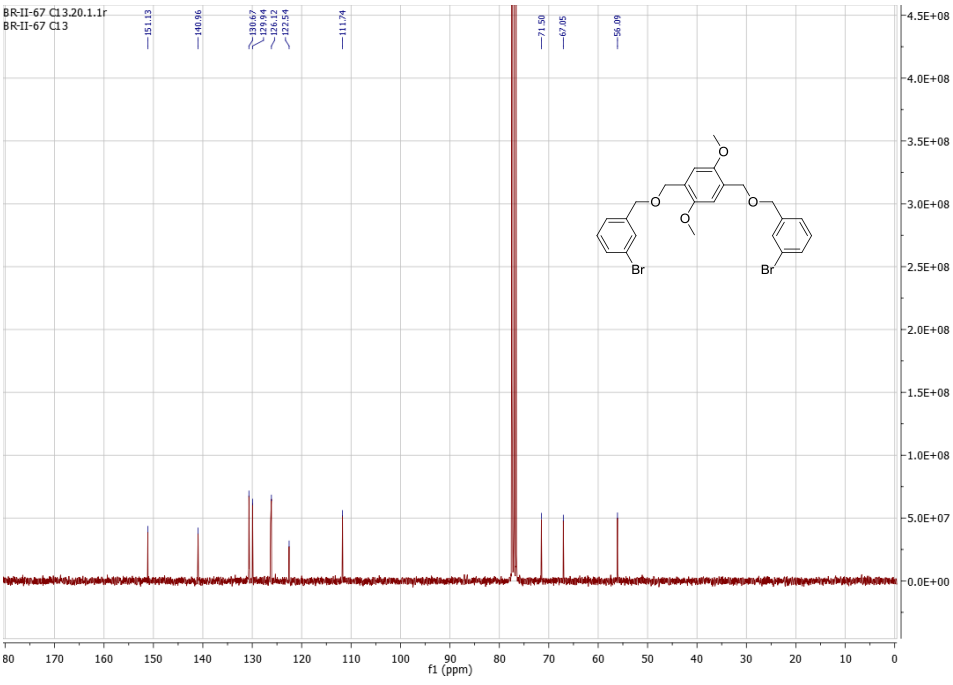

BR-II-109 F19.20.1.1r
Macro1
-141.60
4.2E+08
4.0E+08
3.8E+08
3.6E+08
3.4E+08
3.2E+08
3.0E+08
2.8E+08
2.6E+08
2.4E+08
2.2E+08
2.0E+08
1.8E+08
1.6E+08
1.4E+08
1.2E+08
1.0E+08
8.0E+07
6.0E+07
4.0E+07
2.0E+07
0.0E+00
-2.0E+07
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

Compound S12:

^{1}H NMR:

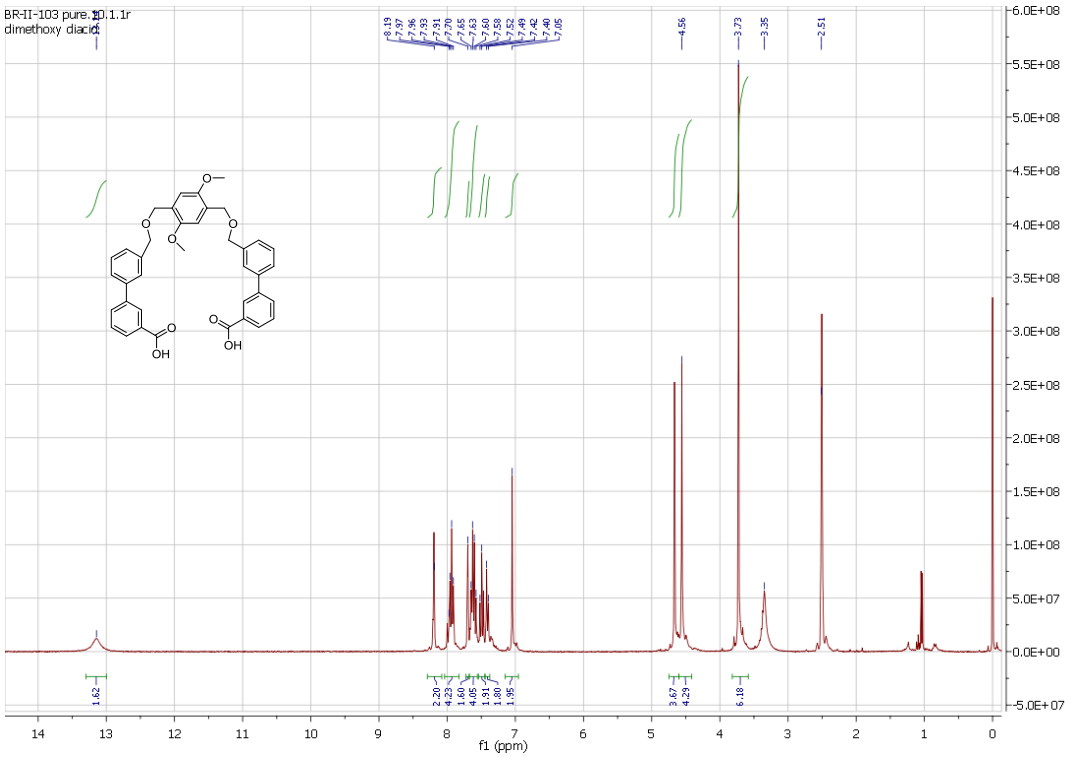


^{13}C NMR:

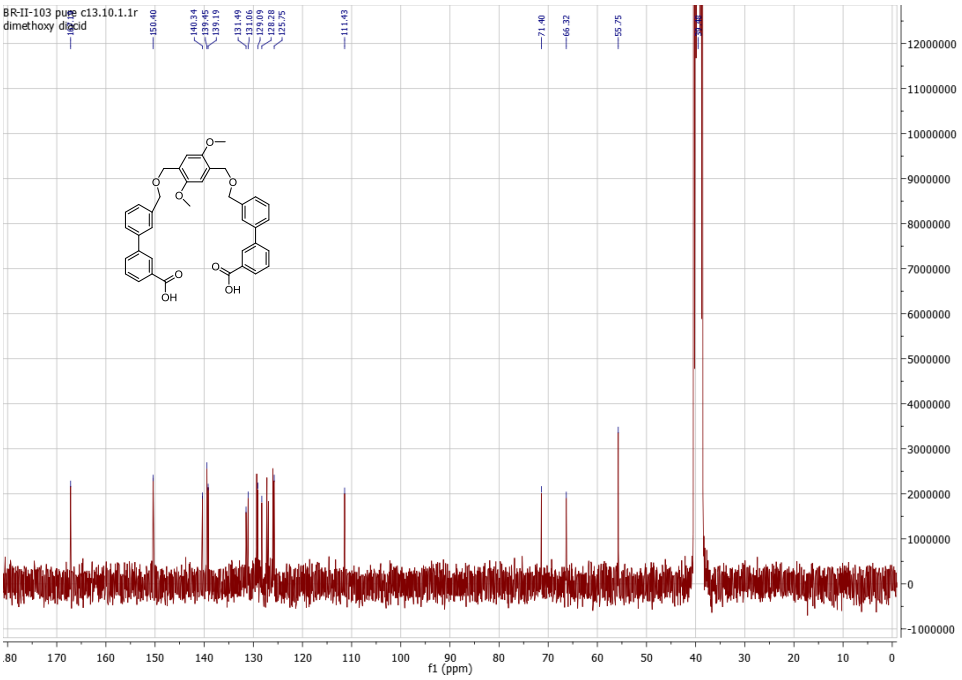


Compound S13:

^{1}H NMR:

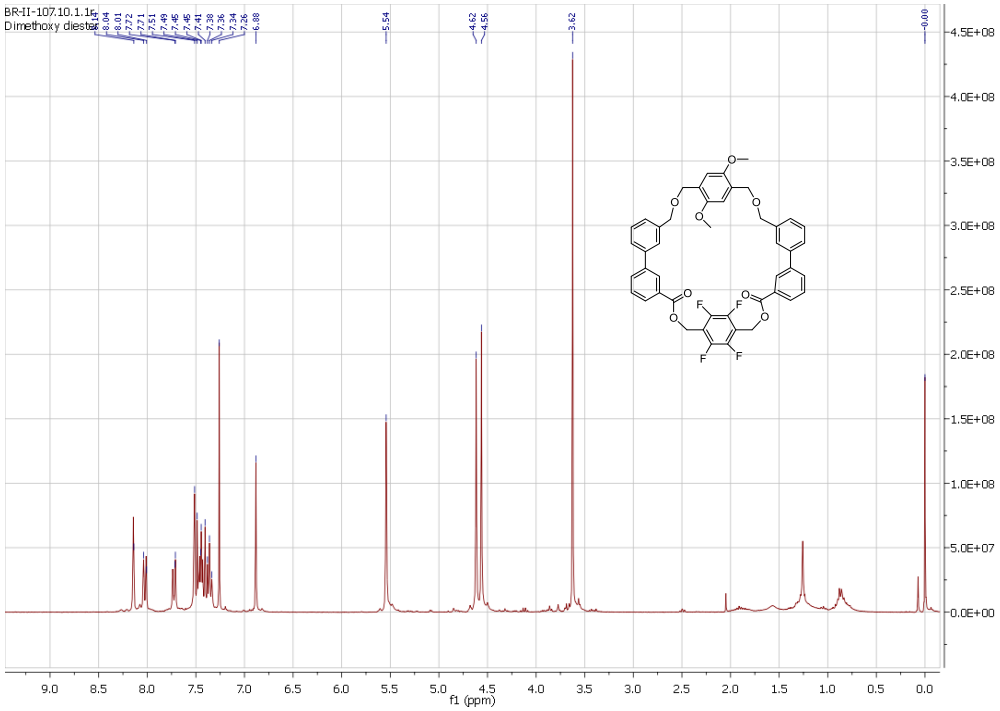


^{13}C NMR

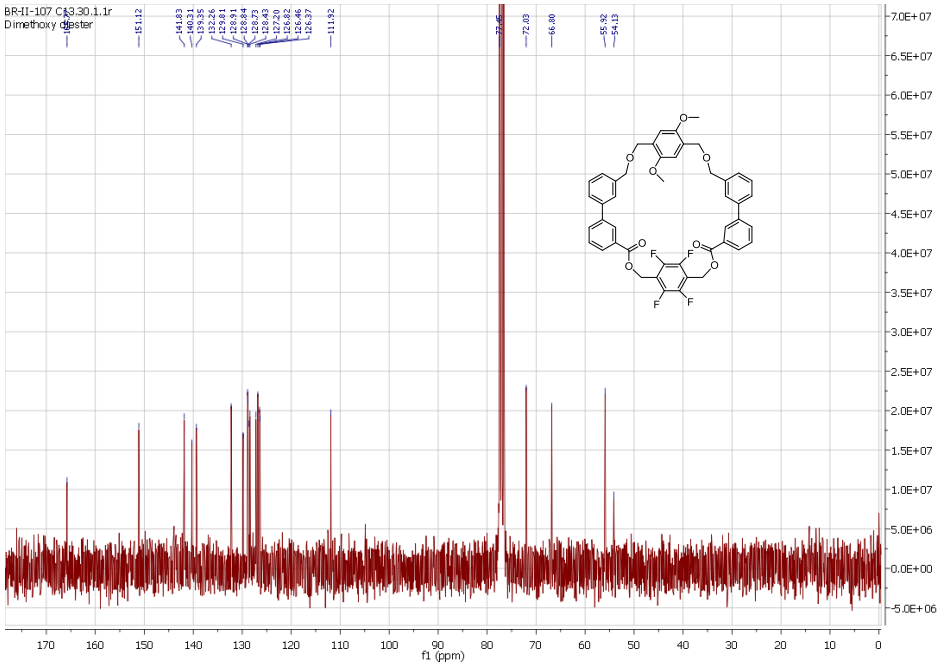


Macrocycle 3:

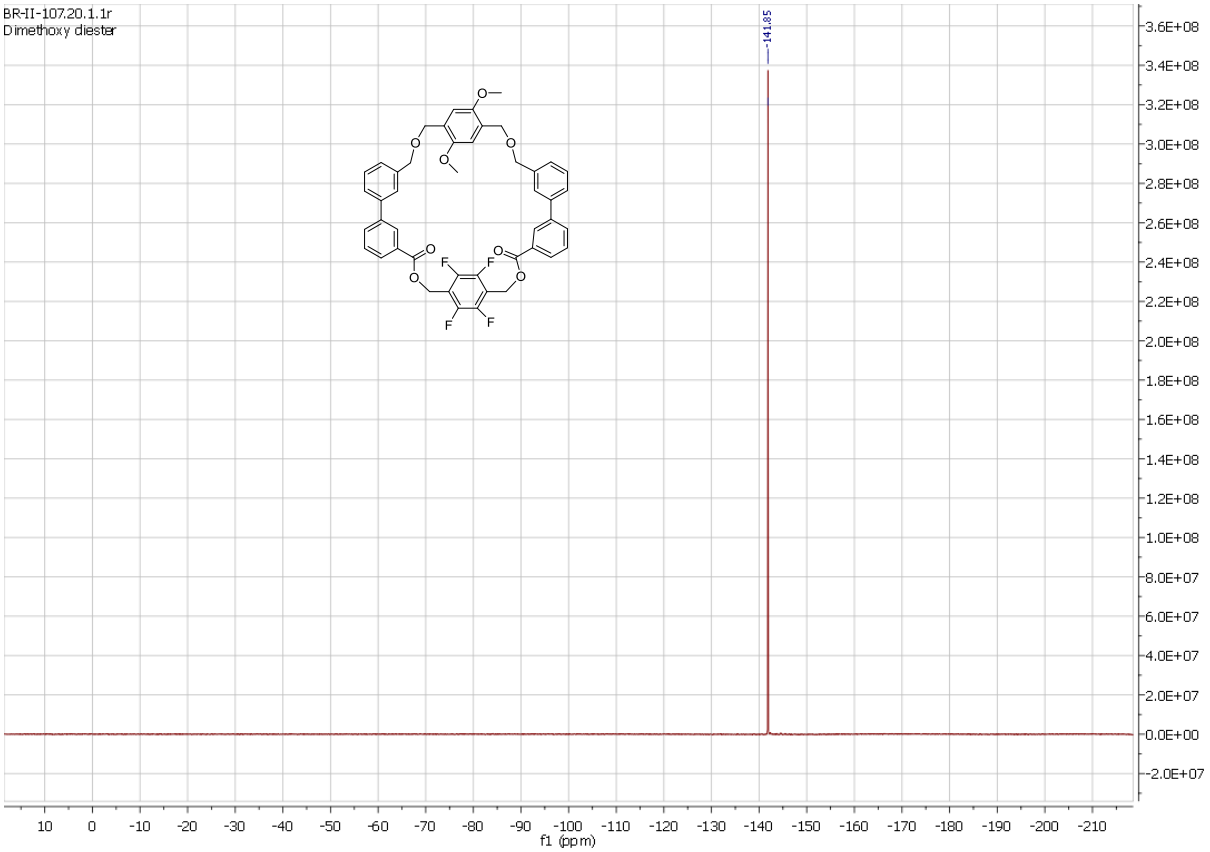
^{1}H NMR:



^{13}C NMR:



^{19}F NMR:


BR-II-107.20.1.1r
Dimethoxy diester
-141.85
3.6E+08
3.4E+08
3.2E+08
3.0E+08
2.8E+08
2.6E+08
2.4E+08
2.2E+08
2.0E+08
1.8E+08
1.6E+08
1.4E+08
1.2E+08
1.0E+08
8.0E+07
6.0E+07
4.0E+07
2.0E+07
0.0E+00
-2.0E+07
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

Macrocycle 4:

^{1}H NMR: