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Supporting Information

# Late-Stage Photocatalytic Fluoroalkylation of Aromatic Crown Ethers in Aqueous Media

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## 1. General Information

All reactions were carried out without deoxygenation unless otherwise indicated. Water was purified with a Millipore system. Chromatography and extraction solvents such as ethyl acetate, acetonitrile (MeCN), dichloromethane (DCM) and *n*-hexane were of HPLC grade quality and used without further purification. 1,1,2,2-Tetrafluoro-1-iodoethane, 1-iodononafluorobutane (perfluorobutyl iodide), 1-iodotridecafluorohexane (perfluorohexyl iodide), 1-iodoheptadecafluorooctane (perfluorooctyl iodide) and 1-iodohenicosafluorodecane (perfluorodecyl iodide) were commercial reagents and used without further purification. A 0.6 M solution of trifluoromethyl iodide was prepared according to section 2.

*N,N,N′,N′*-Tetramethyl ethylenediamine (TMEDA), triethanolamine (TEOA) and triethylamine (TEA) were used as received from the supplier.

Eosin Y (2′,4′,5′,7′-Tetrabromofluorescein) was commercial and 99% pure. Rose Bengal (4,5,6,7-tetrachloro-3′,6′-dihydroxy- 2′,4′,5′,7′-tetraiodo-3H-spiroisobenzofuran-1,9′-xanthen]-3-one ) was 99.9% pure. Both dyes were used as received from the supplier.

Tetrabutylammonium chloride (TBACl), $Cs_2CO_3$, NaCl, KCl, LiCl, and $KPF_6$ were purchased and used without further purification.

Organic substrates benzo[12]crown-4 (B12C4), benzo[15]crown-5 (B15C5), benzo[18]crown-6 (B18C6), dibenzo[18]crown-6 (DB18C6) and dibenzo[24]crown-8 (DB24C8) and *N*-phenylaza[15]crown-5 were purchased from TCI® and used as received. Benzo[24]crown-8,[36] 3,5-di-tertbutylbenzoic anhydride[37] and 3,5-di-tert-butylbenzyl-4-hydroxymethylbenzylammonium hexafluorophosphate[38] were synthesized according to literature procedures.

2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO) and *p*-dinitrobenzene (*p*-DNB) were ultra-pure-grade reagents.

Analytical thin layer chromatography (TLC) was performed on silica gel 60 F254 pre-coated plates (0.25 mm, Merck). TLC plates were visualized with ultraviolet light or by treatment with ceric ammonium molybdate (CAM) solution followed by heating. Purification of the reaction products was carried out by column chromatography using standard silica-gel for column chromatography (60 mesh) or silica-gel for thin layer preparative chromatography with fluorescent indicator (rhodamine). Size exclusion chromatography was performed using Biorad Biobeads SX-1 as the stationary phase and dichloromethane as the eluent.

The light sources were commercially available high power LEDs (3 watts): green light, LED of $\lambda_{max}$ = 525nm ± 2nm, ET=10 mW.

$^1$H-NMR spectra were recorded on an Agilent DD2 500 (500 MHz), or a Bruker Avance 600 (600 MHz) spectrometers, and are reported in ppm using the solvent residual peak resonance as the internal standard ($CDCl_3$ at 7.26 ppm). $^1$H NMR data are reported as follows: chemical shift; number of hydrogen; multiplicity;

coupling constants (Hz). Multiplicity is abbreviated as follows: s = singlet, d = doublet, t = triplet, dd = double doublet, m = multiplet, br = broad. Proton-decoupled $^{13}$C-NMR spectra were recorded on an Agilent DD2 500 (at 125.758 MHz), or on a Bruker Avance 600 (at 150.903 MHz) spectrometers and are reported in ppm using the C resonance signal from the solvent as the internal standard ($CDCl_3$ at 77.00 ppm). $^{19}$F NMR spectra were recorded on a Agilent DD2 500 (at 470.592 MHz), or a Bruker Avance 600 (at 564.686 MHz) spectrometers and are reported in ppm using the internal standard signal from the spectrometer. High-resolution mass spectra (HRMS) were obtained using Xevo G2-XS QTof.

## 2. Preparation of $CF_3I$ Stock Solution in MeCN

MeCN was added to a 50 mL round-bottom flask under nitrogen atmosphere, the solvent was cooled to 0 °C using an ice bath and the flask vessel containing the solvent was sealed with a septum. Next, $CF_3I$ (99%) was introduced into MeCN using a canula until saturation. The concentration of the $CF_3I$ stock solution was then calculated based on $^{19}$F NMR spectroscopy analysis, using an internal standard of benzotrifluoride. The solution was stored in the dark at 0 °C for ulterior use without change in title.

## 3. Photocatalytic fluoroalkylation reactions of aromatic crown ethers. General procedure, isolation and characterization of reaction products

In a 4 mL glass reaction vial provided with screw-cap septum and micro stir bar, substrate (0.2 mmol), *N,N,N´,N´*-tetramethylethylenediamine (TMEDA, 3 equiv), Eosin Y (EY, 5 mol %), KCl, NaCl or LiCl (1.2 equiv) and 3 mL of solvent were introduced. When indicated, the mixture was purged with a stream of Ar for 10 minutes. Liquid fluorinated reagents (3 equiv) were introduced with a microliter syringe. For Ar-purged reactions, a slight stream of Ar was passed through for 1 additional minute and then the vial was sealed. The closed reaction vessel was placed on a stir plate above the heat dissipator, according to Figure S1, and stirred vigorously for 20 hrs. (at 22 °C) under constant irradiation with high power green LEDs (3 Watts, $\lambda_{max}$ = 525nm ± 2nm).
We determined that reducing the quantity of perfluoroalkyl iodides below 3 equiv considerably lowers product yield, most likely as a result of a slower radical reaction. On the other hand, increasing the amount of perfluoroalkyl iodides above 3 equiv. led to the formation of mixtures of mono- and di-substituted products.

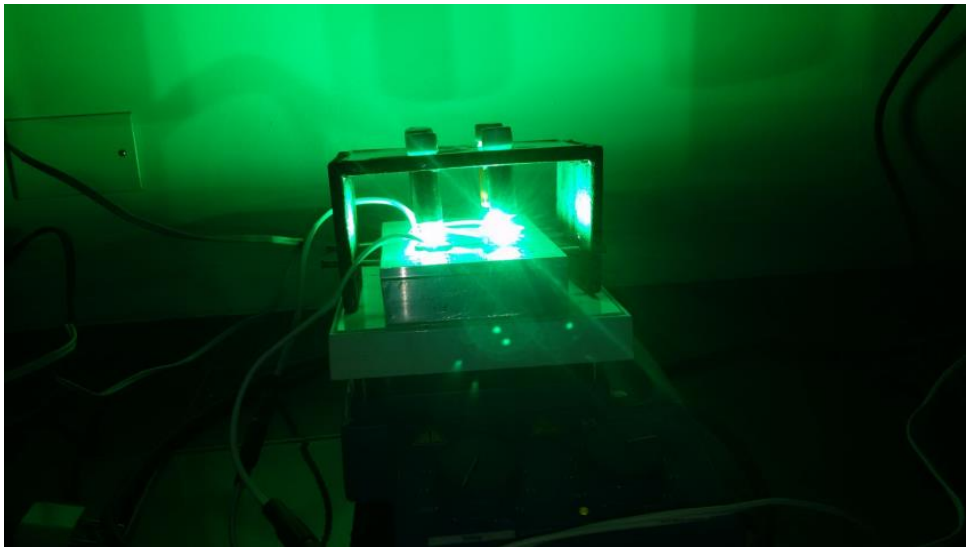


**Figure S1 -** Green (525 nm) LEDs set up for the photocatalytic fluoroalkylation reactions of aromatic crown ethers.

**Figure S2 –** Reaction vessels with: DB18C6 (0.2 mmol) in MeCN: $H_2O$ (1:1) (Right); DB18C6 (0.2 mmol) + KCl (1.2 equiv) in MeCN: $H_2O$ (1:1) (Left).

Figure S2 left shows the extolled effect of adding KCl to a sparingly soluble/precipitated mixture of DB18C6 in MeCN: $H_2O$, right.

After irradiation, the mixture was extracted thrice with $CH_2Cl_2$ / water. The organic layers were gathered and dried over anhydrous $Na_2SO_4$, filtered and evaporated under vacuo. The crude reaction mixture was purified by silica-gel (60 mesh) column chromatography, with the eluents indicated in the TLC conditions (*vide infra*, spectral data).
In all cases, the product obtained was the uncomplexed $R_F$-substitued crown ether, as shown in Figure **S3**.

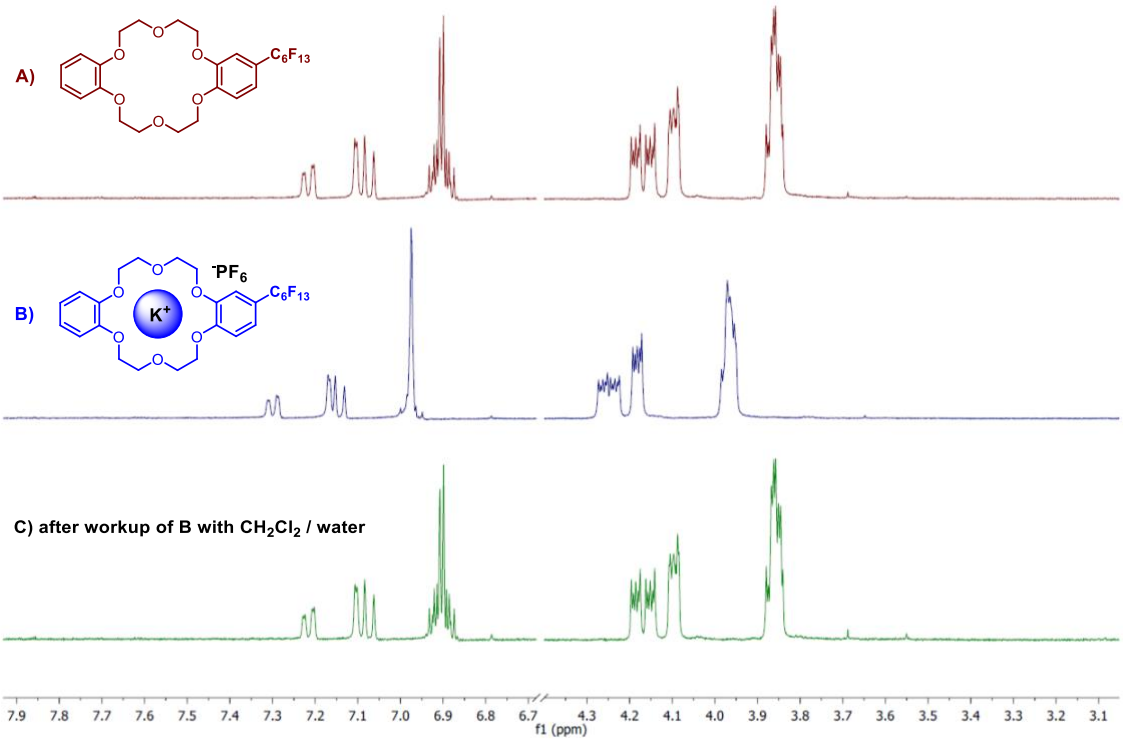
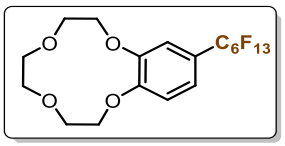



**Figure S3 –** $^{1}$HNMR (500 MHz) spectra of DB18C6-$C_6F_{13}$ in $CD_3CN$; DB18C6-$C_6F_{13}$ 0.025 mM (-); DB18C6-$C_6F_{13}$ + $KPF_6$ 0.025 mM (-); DB18C6-$C_6F_{13}$ + $KPF_6$ 0.025 mM after workup with $CH_2Cl_2$ / water (-).

Figure S3B shows the collapse of the aromatic signals and downfield shifts of all the resonance signals from DB18C6-$C_6F_{13}$ when complexed with $K^+$ cation, as opposed to the un-coordinated form (Figure S3A). Figure S3C depicts again the complex aromatic pattern of DB18C6-$C_6F_{13}$ when the $CD_3CN$ solution from Figure S3B is extracted into $CH_2Cl_2$ / water, and the upfield shifts of all the NMR signals, showing that the extracted product is not coordinated with the cation.

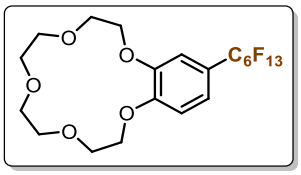
All products have not been previously reported, unless otherwise noted, and are reported as % yields obtained of isolated products. Characterizations employ $^{1}$H, $^{13}$C, $^{19}$F 1D-NMR techniques and HRMS measurements.



***12-(Perfluorohexyl)-2,3,5,6,8,9-hexahydrobenzo[b][1,4,7,10]tetraoxacyclododecine (i.e.: perfluorohexylbenzo-12-crown-4)***[17] **(3)** obtained as white solid (60 %, 65 mg). TLC: $CH_2Cl_2$ / Acetone (9:1)

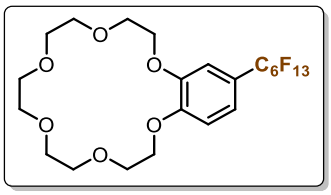
**$^{1}$H NMR (500 MHz, $CDCl_3$):** δ (ppm): 7.21 (1H, dd, *J* = 8.4 Hz, *J* = 1.8 Hz), 7.18 (1H, d, *J* = 1.9 Hz), 7.03 (1H, d, *J* = 8.4 Hz), 4.24-4.20 (4H, m), 3.89 (2H, t, *J* = 4.1 Hz), 3.85 (2H, t, *J* = 4.1 Hz), 3.79 (4H, s);

**$^{13}$C NMR (125 MHz, $CDCl_3$):** δ (ppm): 154.06, 150.44, 122.58 (t, *J* = 25.0 Hz), 122.19 (t, *J* = 6.8 Hz), 117.62 (t, *J* = 6.3 Hz), 116.81, 72.88, 71.56, 71.24, 71.21, 69.86, 69.85;
**$^{19}$F NMR (470.585 MHz, $CDCl_3$):** δ (ppm): -80.80, -109.77, -121.50, -121.87, -122.83, -126.13;
**HRMS (ESI $[M+Na]^+$):** *m/z* calc. for $C_{18}H_{15}F_{13}O_4Na$: 565.0660, found for: $C_{18}H_{15}F_{13}O_4Na$: 565.0660.



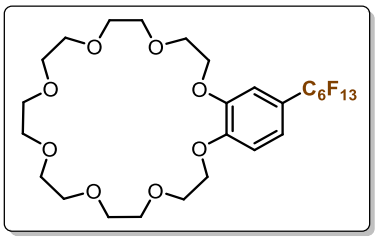

***15-(Perfluorohexyl)-2,3,5,6,8,9,11,12-octahydrobenzo[b][1,4,7,10,13]pentaoxacyclopentadecine (i.e.: perfluorohexylbenzo-12-crown-4)***[17] **(4)** obtained as white solid (70 %, 82 mg). TLC: $CH_2Cl_2$ / Acetone (9:1)

**$^{1}$H NMR (500 MHz, $CDCl_3$):** δ (ppm): 7.14 (1H, dd, *J* = 8.5 Hz, *J* = 2.1 Hz), 7.02 (1H, d, *J* = 1.3 Hz), 6.91 (1H, d, *J* = 8.5 Hz), 4.18-4.14 (4H, m), 3.93-3.89 (4H, m), 3.76-3.73 (8H, m);
**$^{13}$C NMR (125 MHz, $CDCl_3$):** δ (ppm): 152.20, 149.02, 121.27 (t, *J* = 24.9 Hz), 120.72 (t, *J* = 6.9 Hz), 112.78, 112.27 (t, *J* = 6.4 Hz), 71.26, 71.23, 70.57, 70.48, 69.46, 69.39, 69.33, 68.84;
**$^{19}$F NMR (470.585 MHz, $CDCl_3$):** δ (ppm): -80.87, -109.71, -121.54, -121.96, -122.87, -126.18;
**HRMS (ESI $[M+Na]^+$):** *m/z* calc. for $C_{20}H_{19}F_{13}O_5Na$: 609.0923, found for: $C_{20}H_{19}F_{13}O_5Na$: 609.0923.



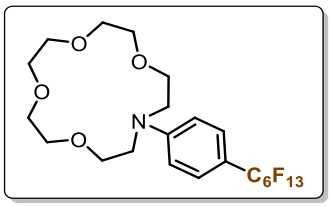

***18-(Perfluorohexyl)-2,3,5,6,8,9,11,12,14,15-decahydrobenzo[b][1,4,7,10,13,16]hexaoxacyclopentadecine (i.e.: perfluorohexylbenzo-16-crown-6)*** **(5)** obtained as white solid (75 %, 94 mg). TLC: $CH_2Cl_2$ / Acetone (9:1)

**$^{1}$H NMR (500 MHz, $CDCl_3$):** δ (ppm): 7.14 (1H, dd, *J* = 8.5 Hz, *J* = 1.6 Hz), 7.03 (1H, d, *J* = 1.7 Hz), 6.92 (1H, d, *J* = 8.5 Hz), 4.20-4.17 (4H, m), 3.94-3.91 (4H, m), 3.77-3.74 (4H, m), 3.72-3.69 (4H, m), 3.68 (4H, s);
**$^{13}$C NMR (125 MHz, $CDCl_3$):** δ (ppm): 151.98, 148.81, 121.23 (t, *J* = 24.9 Hz), 120.66 (t, *J* = 6.8 Hz), 112.75, 112.16 (t, *J* = 6.3 Hz), 71.05, 71.02, 70.91, 70.85, 70.81, 70.78, 69.52, 69.46, 69.36, 69.00;
**$^{19}$F NMR (470.585 MHz, $CDCl_3$):** δ (ppm): -80.81, -109.69, -121.48, -121.94, -122.84, -126.15;
**HRMS (ESI $[M+Na]^+$):** *m/z* calc. for $C_{22}H_{23}F_{13}O_6Na$: 653.1185, found for: $C_{22}H_{23}F_{13}O_6Na$: 653.1185.



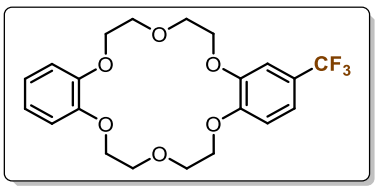

***24-(Perfluorohexyl)-2,3,5,6,8,9,11,12,14,15,17,18,20,21-tetradecahydrobenzo[b][1,4,7,10,13,16,19,22]octaoxacyclotetracosine (i.e.: perfluorohexylbenzo-20-crown-8)*** **(6)** obtained as white solid (70 %, 100 mg). TLC: $CH_2Cl_2$ / Acetone (3:2)

**$^1$H NMR (500 MHz, $CDCl_3$):** δ (ppm): 7.15 (1H, dd, *J* = 8.5 Hz, *J* = 1.8 Hz), 7.06 (1H, d, *J* = 1.8 Hz), 6.95 (1H, d, *J* = 8.5 Hz), 4.21-4.18 (4H, m), 3.94-3.90 (4H, m), 3.80-3.77 (4H, m), 3.72-3.69 (4H, m), 3.67-3.65 (12H, m);
**$^{13}$C NMR (125 MHz, $CDCl_3$):** δ (ppm): 152.12, 148.86, 121.39 (t, *J* = 24.8 Hz), 120.84 (t, *J* = 6.5 Hz), 113.19, 112.86 (t, *J* = 6.4 Hz), 71.42, 71.35, 71.09, 71.06, 71.02, 71.00, 70.90, 69.83, 69.73, 69.36;
**$^{19}$F NMR (470.585 MHz, $CDCl_3$):** δ (ppm): -80.80, -109.68, -121.51, -121.90, -122.82, -126.13;
**HRMS (ESI [M+Na]$^+$):** *m/z* calc. for $C_{26}H_{31}F_{13}O_8Na$: 741.1709, found for: $C_{26}H_{31}F_{13}O_8Na$: 741.1709.



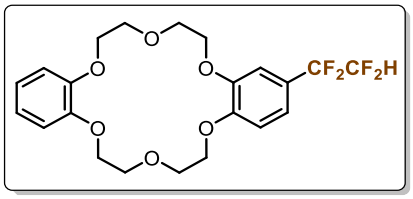

***13-[4-(Perfluorohexyl)phenyl]-1,4,7,10-tetraoxa-13-azacyclopentadecane (i.e.: perfluorohexyl-N-phenylaza-15-crown-5)*** **(7)** obtained as white solid (99 %, 120 mg). TLC / $CH_2Cl_2$: Acetone (9:1)

**$^1$H NMR (500 MHz, $CDCl_3$):** δ (ppm): 7.37 (2H, d, *J* = 8.6 Hz), 6.71 (2H, d, *J* = 8.6 Hz), 3.76 (4H, t, J = 6.1 Hz), 3.69-3.63 (16H, m);
**$^{13}$C NMR (125 MHz, $CDCl_3$):** δ (ppm): 150.04, 128.19 (t, *J* = 6.4 Hz), 111.09, 70.44, 70.42, 70.20, 68.31;
**$^{19}$F NMR (470.585 MHz, $CDCl_3$):** δ (ppm): -80.84, -109.21, -121.52, -121.93, -122.84, -126.15;
**HRMS (ESI [M+Na]$^+$):** *m/z* calc. for $C_{22}H_{24}F_{13}NO_4Na$: 636.1395, found for: $C_{22}H_{24}F_{13}O_4Na$: 636.1395.



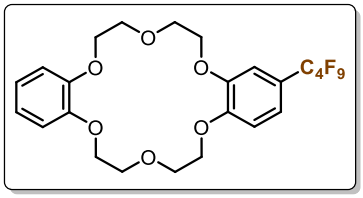

***2-(Trifluoromethyl)-6,7,9,10,17,18,20,21,-octahydrodibenzo[b,k][1,4,7,10,13,16,]hexaoxacyclooctadecine (i.e.: trifluoromethyldibenzo-18-crown-6)*** **(8)** obtained as white solid (85 %, 72 mg). TLC: $CH_2Cl_2$ / Acetone (2:8)

**$^{1}$H NMR (500 MHz, $CDCl_3$):** δ (ppm): 7.18, (1H, d, *J* = 8.31 Hz), 7.06 (1H, d, *J* = 1.54 Hz), 6.90-6.85 (5H, m), 4.20 (4H, t, *J* = 4.3 Hz), 4.17 (4H, t, *J* = 4.4 Hz), 4.05-4.00 (8H, m);
**$^{13}$C NMR (125 MHz, $CDCl_3$):** δ (ppm): 151.43, 148.84, 148.79, 148.72, 124.30 (q, *J* = 271.3 Hz), 123.26 (q, *J* = 32.7 Hz), 121.47, 121.41, 118.79 (q, *J* = 4.2 Hz), 113.63, 113.56, 112.39, 110.10 (q, *J* = 3.5 Hz), 70.15, 70.10, 69.72, 69.71, 69.11, 68.88, 68.75, 68.66;
**$^{19}$F NMR (470.585 MHz, $CDCl_3$):** δ (ppm): -61.55;
**HRMS (ESI [M+Na]$^{+}$):** *m/z* calc. for $C_{21}H_{23}F_3O_6Na$: 451.1344, found for: $C_{21}H_{23}F_3O_6Na$: 451.1344.




***2-(1,1,2,2-Tetrafluoroethyl)-6,7,9,10,17,18,20,21,-octahydrodibenzo[b,k][1,4,7,10,13,16,]hexaoxacyclooctadecine (i.e.: 1,1,2,2-tetrafluoroethyldibenzo-18-crown-6)*** **(9)** obtained as white solid (70 %, 64 mg). TLC: $CH_2Cl_2$ / Acetone (8:2)

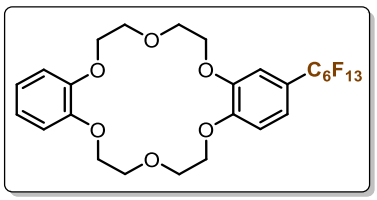
**$^{1}$H NMR (500 MHz, $CDCl_3$):** δ (ppm): 7.09, (1H, dd, *J* = 8.4 Hz, *J* = 1.3 Hz), 6.99 (1H, d, *J* = 1.7 Hz), 6.90-6.84 (5H, m), 5.86 (1H, tt, *J* = 54.3 Hz, *J* = 2.5 Hz), 4.20 (4H, t, *J* = 4.5 Hz), 4.16 (4H, t, *J* = 4.9 Hz), 4.04-4.01 (8H, m);
**$^{13}$C NMR (125 MHz, $CDCl_3$):** δ (ppm): 151.12, 148.78, 148.73, 148.64, 121.37, 121.32, 119.86 (t, *J* = 6.5 Hz), 113.33, 113.27, 112.33, 111.06, 70.07, 70.02, 69.71, 69.68, 68.98, 68.77, 68.62, 68.56;
**$^{19}$F NMR (470.585 MHz, $CDCl_3$):** δ (ppm): -112.69, -134.14;
**HRMS (ESI [M+Na]$^{+}$):** *m/z* calc. for $C_{22}H_{24}F_4O_6Na$: 483.1407, found for: $C_{22}H_{24}F_4O_6Na$: 483.1407.




***2-(Perfluorobutyl)-6,7,9,10,17,18,20,21,-octahydrodibenzo[b,k][1,4,7,10,13,16,]hexaoxacyclooctadecine (i.e.: perfluorobutyldibenzo-18-crown-6)*** **(10)** obtained as white solid (75 %, 86 mg). TLC: $CH_2Cl_2$ / Acetone (8:2)

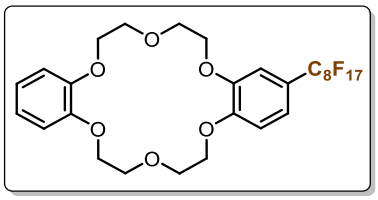
**$^{1}$H NMR (500 MHz, $CDCl_3$):** δ (ppm): 7.14, (1H, d, *J* = 8.4 Hz), 7.00 (1H, s), 6.91-6.84 (5H, m), 4.21-4.15 (8H, m), 4.04-4.01 (8H, m);
**$^{13}$C NMR (125 MHz, $CDCl_3$):** δ (ppm): 151.60, 148.69, 148.64, 148.57, 121.31, 121.25, 120.48 (t, *J* = 6.6 Hz), 113.07, 113.01, 112.00, 111.06, 70.02, 69.97, 69.59, 69.56, 68.91, 68.68, 68.45, 68.40;
**$^{19}$F NMR (470.585 MHz, $CDCl_3$):** δ (ppm): -81.03, -109.93, -122.85, -125.61;

**HRMS (ESI [M+Na]$^+$):** *m/z* calc. for $C_{24}H_{23}F_9O_6Na$: 601.1249, found for: $C_{24}H_{23}F_9O_6Na$: 601.1249.



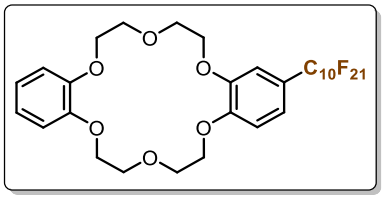

***2-(Perfluorohexyl)-6,7,9,10,17,18,20,21,-octahydrodibenzo[b,k][1,4,7,10,13,16,]hexaoxacyclooctadecine (i.e.: perfluorohexyldibenzo-18-crown-6)***[17] **(2)** obtained as white solid (90 %, 122 mg). TLC: $CH_2Cl_2$ / MeOH (9:1)

**$^1$H NMR (500 MHz, $CDCl_3$):** δ (ppm): 7.14 (1H, dd, *J* = 8.6 Hz, *J* = 1.4 Hz), 7.00 (1H, d, *J* = 1.6 Hz), 6.91-6.84 (5H, m), 4.21-4.15 (8H, m), 4.05-4.01 (8H, m);
**$^{13}$C NMR (125 MHz, $CDCl_3$):** δ (ppm): 151.70, 148.80, 148.75, 148.63, 121.40, 121.34, 120.57 (t, *J* = 6.7 Hz), 113.42, 113.35, 112.21, 111.39, 70.12, 70.06, 69.68, 69.64, 69.08, 68.78, 68.64, 68.58;
**$^{19}$F NMR (470.585 MHz, $CDCl_3$):** δ (ppm): -80.78, -109.70, -121.49, -121.97, -122.82, -126.13;
**HRMS (ESI [M+Na]$^+$):** *m/z* calc. for $C_{26}H_{23}F_{13}O_6Na$: 701.1185, found for: $C_{26}H_{23}F_{13}O_6Na$: 701.1185.



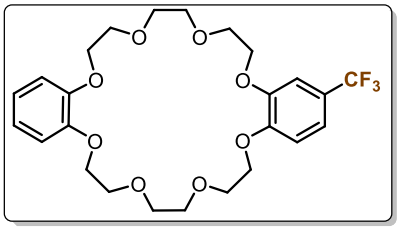

***2-(Perfluorooctyl)-6,7,9,10,17,18,20,21,-octahydrodibenzo[b,k][1,4,7,10,13,16,]hexaoxacyclooctadecine (i.e.: perfluorooctyldibenzo-18-crown-6)*** **(11)** obtained as white solid (70 %, 108 mg). TLC: $CH_2Cl_2$ / Acetone (8:2)

**$^1$H NMR (500 MHz, $CDCl_3$):** δ (ppm): 7.14 (1H, dd, *J* = 8.5 Hz, *J* = 1.4 Hz), 7.00 (1H, d, *J* = 1.7 Hz), 6.91-6.84 (5H, m), 4.20-4.14 (8H, m), 4.04-4.01 (8H, m);
**$^{13}$C NMR (125 MHz, $CDCl_3$):** δ (ppm): 151.59, 148.69, 148.64, 148.56, 121.28, 121.23, 120.48 (t, *J* = 6.8 Hz), 113.03, 112.97, 111.96, 111.05 (t, *J* = 5.9 Hz), 70.00, 69.96, 69.58, 69.54, 68.88, 68.66, 68.43, 68.38;
**$^{19}$F NMR (470.585 MHz, $CDCl_3$):** δ (ppm): -80.79, -109.70, -121.29, -121.91 (6F), -122.72, -126.12;
**HRMS (ESI [M+Na]$^+$):** *m/z* calc. for $C_{28}H_{23}F_{17}O_6Na$: 801.1121, found for: $C_{28}H_{23}F_{17}O_6Na$: 801.1121.



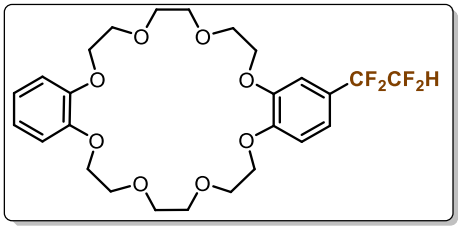
***2-(Perfluorodecyl)-6,7,9,10,17,18,20,21,-octahydrodibenzo[b,k][1,4,7,10,13,16,]hexaoxacyclooctadecine (i.e.: perfluorodecyldibenzo-18-crown-6)*** **(12)** obtained as white solid (65 %, 114 mg). TLC: AcOEt / Hexane (9:1)

**$^{1}$H NMR (500 MHz, $CDCl_3$):** δ (ppm): 7.15 (1H, d, *J* = 8.5 Hz), 7.02 (1H, s), 6.93-6.86 (5H, m), 4.22-4.16 (8H, m), 4.04 (8H, br s);
**$^{13}$C NMR (125 MHz, $CDCl_3$):** δ (ppm): 151.99, 149.07, 149.05, 148.81, 121.58, 121.56, 120.73 (t, *J* = 6.6 Hz), 114.21, 114.18, 112.75, 112.24 (t, *J* = 6.4 Hz), 71.57, 71.49, 71.41, 71.39, 70.08, 69.83, 69.55, 69.47;
**$^{19}$F NMR (470.585 MHz, $CDCl_3$):** δ (ppm): -80.74, -109.69, -121.25, -121.73 to -121.88 (10F, m), -122.68, -126.08;
**HRMS (ESI $[M+Na]^+$):** *m/z* calc. for $C_{30}H_{23}F_{21}O_6Na$: 901.1057, found for: $C_{30}H_{23}F_{21}O_6Na$: 901.1057.



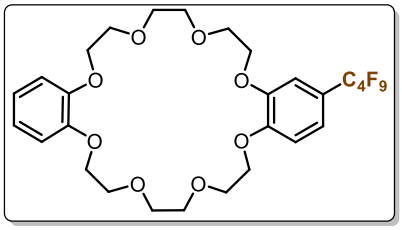

***2-(Trifluoromethyl)-6,7,9,10,12,13,20,21,23,24,26,27-dodecahydrodibenzo[b,n][1,4,7,10,13,16,19,22]octaoxacyclotetracosine (i.e.: trifluoromethyldibenzo-24-crown-8)*** **(13)** obtained as white solid (85 %, 87 mg). TLC: $CH_2Cl_2$ / Acetone (8:2)

**$^{1}$H NMR (500 MHz, $CDCl_3$):** δ (ppm): 7.17, (1H, d, *J* = 8.3 Hz), 7.06 (1H, d, *J* = 1.7 Hz), 6.89-6.85 (5H, m), 4.18-4.13 (8H, m), 3.94-3.89 (8H, m), 3.83-3.82 (8H, m);
**$^{13}$C NMR (125 MHz, $CDCl_3$):** δ (ppm): 151.64, 149.02, 149.00, 148.86, 124.29 (q, *J* = 282.2 Hz), 123.3 (q, *J* = 32.8 Hz), 121.56, 121.53, 118.87 (q, *J* = 4.1 Hz), 114.15, 114.13, 112.81, 110.70 (q, *J* = 3.4 Hz), 71.52, 71.46, 71.37, 71.36, 70.05, 69.81, 69.76, 69.74, 69.50, 69.44;
**$^{19}$F NMR (470.585 MHz, $CDCl_3$):** δ (ppm): -61.56;
**HRMS (ESI $[M+Na]^+$):** *m/z* calc. for $C_{25}H_{31}F_3O_8Na$: 539.1869, found for: $C_{25}H_{31}F_3O_8Na$: 539.1869.



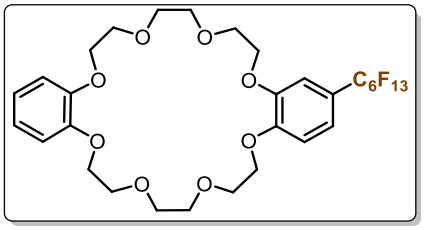

***2-(1,1,2,2-Tetrafluoroethyl)-6,7,9,10,12,13,20,21,23,24,26,27-dodecahydrodibenzo[b,n][1,4,7,10,13,16,19,22]octaoxacyclotetracosine (i.e.: 1,1,2,2-tetrafluoroethyldibenzo-24-crown-8)*** **(14)** obtained as off-white solid (70 %, 76 mg). TLC / $CH_2Cl_2$: Acetone (8:2)

**$^{1}$H NMR (500 MHz, $CDCl_3$):** δ (ppm): 7.10, (1H, d, *J* = 8.3 Hz), 7.01 (1H, s), 6.92-6.86 (5H, m), 5.86 (1H, tt, J = 54 Hz, J = 2.04 Hz), 4.19-4.14 (8H, m), 3.94-3.90 (8H, m), 3.83-3.82 (8H, m);
**$^{13}$C NMR (125 MHz, $CDCl_3$):** δ (ppm): 151.41, 149.06, 149.04, 148.83, 121.60, 121.59, 120.09, 114.21, 113.02, 112.01, 110.37 (t, *J* = 43.6 Hz), 71.52, 71.38, 71.37, 70.08, 70.07, 69.86, 69.79, 69.56, 69.49, 69.46;
**$^{19}$F NMR (470.585 MHz, $CDCl_3$):** δ (ppm): -112.61, -134.10;
**HRMS (ESI $[M+Na]^+$):** *m/z* calc. for $C_{26}H_{32}F_4O_8Na$: 571.1931, found for: $C_{26}H_{32}F_4O_8Na$: 571.1931.




***2-(Perfluorobutyl)-6,7,9,10,12,13,20,21,23,24,26,27-dodecahydrodibenzo[b,n][1,4,7,10,13,16,19,22]octaoxacyclotetracosine (i.e.: perfluorobutyl dibenzo-24-crown-8)*** **(15)** obtained as off-white solid (70 %, 93 mg). TLC: $CH_2Cl_2$ / Acetone (8:2)

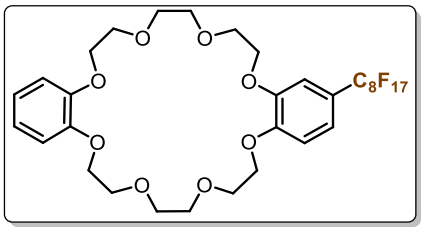
**$^{1}$H NMR (500 MHz, $CDCl_3$):** δ (ppm): 7.14, (1H, d, *J* = 8.8 Hz), 7.02 (1H, s), 6.92-6.85 (5H, m), 4.19-4.14 (8H, m), 3.94-3.90 (8H, m), 3.83-3.82 (8H, m);
**$^{13}$C NMR (125 MHz, $CDCl_3$):** δ (ppm): 151.96, 149.04, 149.03, 148.79, 121.58, 121.55, 121.29 (t, *J* = 24.7 Hz), 120.71 (t, *J* = 6.9 Hz), 114.16, 114.14, 112.73, 112.18 (t, *J* = 6.1 Hz), 71.58, 71.49, 71.41, 71.40, 70.09, 69.83, 69.82, 69.76, 69.53, 69.47, 69.46;
**$^{19}$F NMR (470.585 MHz, $CDCl_3$):** δ (ppm): -81.03, -109.90, -122.77, -125.61;
**HRMS (ESI $[M+Na]^+$):** *m/z* calc. for $C_{28}H_{31}F_9O_8Na$: 689.1773, found for: $C_{28}H_{31}F_9O_8Na$: 689.1773.




***2-(Perfluorohexyl)-6,7,9,10,12,13,20,21,23,24,26,27-dodecahydrodibenzo[b,n][1,4,7,10,13,16,19,22]octaoxacyclotetracosine (i.e.: perfluorohexyl dibenzo-24-crown-8)***[26] **(16)** obtained as an amorphous off-white solid (86 %, 131 mg). TLC: AcOEt / *n*-Hexane (9:1)

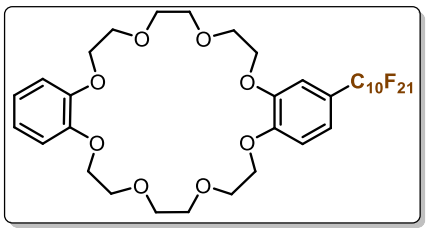
**$^{1}$H NMR (600 MHz, $CDCl_3$):** δ (ppm): 7.14, (1H, d, *J* = 6.5 Hz), 7.02 (1H, s), 6.92-6.85 (5H, m), 4.19-4.14 (8H, m), 3.95-3.91 (8H, m), 3.84-3.82 (8H, m);
**$^{13}$C NMR (150.903 MHz, $CDCl_3$):** δ (ppm): 151.97, 149.05, 149.03, 148.80, 121.59, 121.56, 121.92 (t, *J* = 25.0 Hz), 120.73 (t, *J* = 6.8 Hz), 114.17, 114.15, 112.73, 112.21 (t, *J* = 9.3 Hz), 71.59, 71.51, 71.42, 71.41, 70.10, 69.84, 69.83, 69.76, 69.54, 69.48, 69.47;
**$^{19}$F NMR (564.603 MHz, $CDCl_3$):** δ (ppm): -80.78, -109.66, -121.49, -121.89, -122.81, -126.10;

**HRMS (ESI [M+Na]$^+$):** *m/z* calc. for $C_{30}H_{31}F_{13}O_8Na$: 789.1709, found for: $C_{30}H_{31}F_{13}O_8Na$: 789.1709.




***2-(Perfluorooctyl)-6,7,9,10,12,13,20,21,23,24,26,27-dodecahydrodibenzo[b,n][1,4,7,10,13,16,19,22]octaoxacyclotetracosine (i.e.: perfluorooctyl dibenzo-24-crown-8)*** **(17)** obtained as an off-white solid (70 %, 121 mg). TLC: AcOEt / *n*-Hexane (9:1)

**$^1$H NMR (500 MHz, $CDCl_3$):** δ (ppm): 7.14, (1H, dd, *J* = 8.5 Hz, *J* = 1.9 Hz), 7.02 (1H, d, *J* = 2.0 Hz), 6.92-6.85 (5H, m), 4.19-4.14 (8H, m), 3.94-3.90 (8H, m), 3.83-3.82 (8H, m);
**$^{13}$C NMR (125 MHz, $CDCl_3$):** δ (ppm): 151.97, 149.05, 149.04, 148.79, 121.58, 121.55, 121.31 (t, *J* = 25.10), 120.72 (t, *J* = 6.8 Hz), 114.17, 114.15, 112.72, 112.20 (t, *J* = 6.5 Hz), 71.59, 71.50, 71.42, 71.41, 70.09, 69.84, 69.83, 69.76, 69.54, 69.48, 69.47;
**$^{19}$F NMR (470.585 MHz, $CDCl_3$):** δ (ppm): -80.77, -109.66, -121.28, -121.84 (6F), -122.70, -126.10;
**HRMS (ESI [M+Na]$^+$):** *m/z* calc. for $C_{32}H_{31}F_{17}O_8Na$: 889.1645, found for: $C_{32}H_{31}F_{17}O_8Na$: 889.1645.

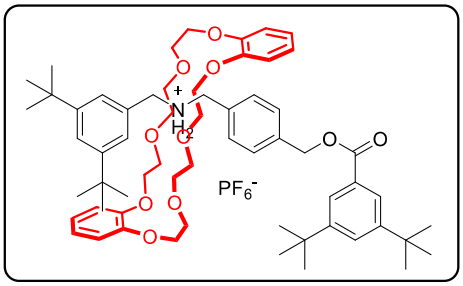



***2-(Perfluorodecyl)-6,7,9,10,12,13,20,21,23,24,26,27-dodecahydrodibenzo[b,n][1,4,7,10,13,16,19,22]octaoxacyclotetracosine (i.e.: perfluorodecyl dibenzo-24-crown-8)*** **(18)** obtained as an off-white solid (70 %, 135 mg). TLC: AcOEt / *n*-Hexane (9:1)

**$^1$H NMR (500 MHz, $CDCl_3$):** δ (ppm): 3.83 (8H, d), 3.92 (8H, m), 4.16 (8H, m), 6.86 (4H, m), 6.91 (1H, d, *J* = 8.5 Hz), 7.02 (1H, d, *J* = 2.0 Hz), 7.13, (1H, dd, *J* = 8.5 Hz, *J* = 2.0 Hz);
**$^{13}$C NMR (125 MHz, $CDCl_3$):** δ (ppm): 69.47, 69.55, 69.75, 69.83, 69.84, 70.08, 71.39, 71.41, 71.49, 71.57, 71.59, 112.24 (t, *J* = 7.8 Hz), 112.75, 114.18, 114.21, 120.73 (t, *J* = 7.9 Hz), 121.34 (t, *J* = 25.0 Hz), 121.56, 121.58, 148.81, 149.05, 149.07, 151.99;
**$^{19}$F NMR (470.585 MHz, $CDCl_3$):** δ (ppm): -126.10, -122.69, -121.82 to -121.73 (10F, m), -121.27, -109.67, -80.76;
**HRMS (ESI [M+Na]$^+$):** *m/z* calc. for $C_{34}H_{31}F_{21}O_8Na$: 989.1581, found for: $C_{34}H_{31}F_{21}O_8Na$: 989.1581.

## 4. Synthetic protocol and characterization for rotaxane 20

Compound **20** was obtained according to an adapted literature procedure.[39] 3,5-Di-tert-butylbenzyl-4-hydroxymethylbenzylammonium hexafluorophosphate (0.65 g, 0.34 mmol) and DB24C8 (0.24 g, 0.53 mmol) were suspended in $CH_2Cl_2$ (2 ml), and the mixture was stirred until the solid completely dissolved. Tributylphosphine (0.017 ml, 0.07 mmol) and 3,5-di-tertbutylbenzoic anhydride (0.24 g, 0.53 mmol) were added and the solution was stirred at room temperature for 4 hours. The reaction mixture was diluted with $CH_2Cl_2$ (10 ml) and washed with water (10 ml) twice. The organic phase was dried over $Na_2SO_4$ and the solvent removed under vacuum. The product was purified over silica column (eluent: $CH_2Cl_2$ then $CH_2Cl_2$ : MeOH 98:2). The isolated fraction containing the product was further purified by size exclusion chromatography. Product **20** was a white solid obtained in 66% yield (260 mg).



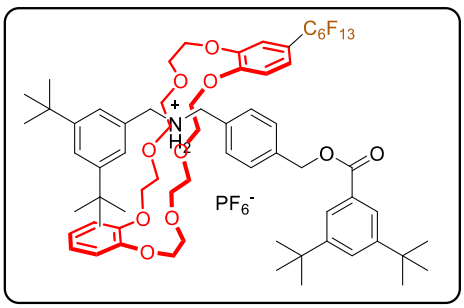

***Compound* 20** was obtained as a white solid (66 %, 260 mg). TLC: $CH_2Cl_2$ / MeOH (98:2)

**$^1$H NMR (500 MHz, $CDCl_3$):** δ (ppm): 7.91 (2H, d, *J* = 1.8 Hz, 7.65 (1H, t, *J* = 1.8 Hz), 7.37 (1H, br s), 7.63 (2H, br s), 7.30 (2H, d, *J* = 1.5 Hz), 7.15 (2H, d, *J* = 7.8 Hz), 7.07 (2H, d, *J* = 7.8 Hz), 6.84-6.74 (8H, m), 5.17 (2H, s), 4.72 (2H, t, *J* = 6.5 Hz), 4.58 (2H, t, *J* = 6.5 Hz), 4.12-4.05 (8H, m), 3.83-3.80 (4H, m), 3.75-3.72 (4H, m), 3.65-3.62 (4H, m), 3.49-3.46 (4H, m), 1.35 (18H, s),1.20 (18H, s);

**$^{13}$C NMR (125 MHz, $CDCl_3$):** δ (ppm): 167.1, 151.7, 151.3, 147.4, 137.7, 131.4, 130.9, 129.6, 129.5, 128.0, 127.5, 124.0, 123.8, 123.4, 121.8, 112.6, 70.7, 70.3, 68.0, 65.8, 53.2, 52.6, 35.1, 35.0, 31.6, 31.5;

**$^{19}$F NMR (470.585 MHz, $CDCl_3$):** δ (ppm): -73.5 (d, $J_{F-P}$ = 712.4 Hz).

## 5. Characterization of rotaxane 21




***Compound* 21** was obtained as a white solid (50 %, 130 mg). TLC: AcOEt / *n*-hexane (9:1)

**$^1$H NMR (500 MHz, $CDCl_3$):** δ (ppm): 7.91 (2H, d, *J* = 1.9 Hz), 7.65 (1H, t, *J* = 1.9 Hz), 7.64 (2H, br s), 7.35 (1H, t, *J* = 1.7 Hz), 7.27 (2H, d, *J* = 1.7 Hz), 7.17 (2H,

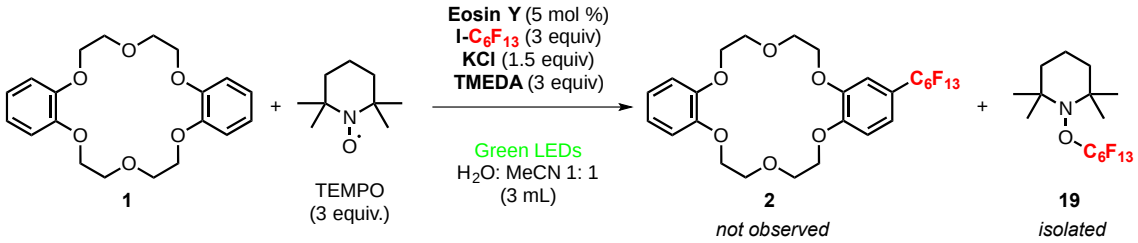
d, *J* = 8.1 Hz), 7.12 (1H, dd, *J* = 8.5 Hz, *J* = 1.8 Hz), 7.06 (2H, d, *J* = 8.1 Hz), 6.91 (1H, s),1.17 (18H, s), 6.90 (1H, d, *J* = 5.3 Hz), 6.78-6.76 (2H, m), 6.67-6.63 (2H, m), 5.15 (2H, s), 4.74 (2H, t, *J* = 6.8 Hz), 4.59 (2H, t, *J* = 6.7 Hz), 4.22-4.11 (4H, m), 4.10-4.03 (2H, m), 4.01-3.92 (4H, m), 3.90-3.86 (2H, m), 3.75-3.66 (5H, m), 3.63-3.57 (5H, m), 3.48-3.45 (1H, m), 3.42-3.38 (1H, m), 1.35 (18H, s), 1.17 (18H, s);
**$^{13}$C NMR (125 MHz, $CDCl_3$):** δ (ppm): 167.08, 151.77, 151.37, 150.84, 147.83, 146.90, 137.88, 131.35, 130.83, 129.52, 129.50, 127.96, 127.55, 123.97, 123.60, 123.48, 121.80, 121.73, 121.58 (t, *J* = 23.2 Hz), 121.14 (t, *J* = 7.5 Hz), 112.30, 112.24, 112.20, 110.79 (t, *J* = 7.4 Hz), 70.93, 70.89, 70.70, 70.51, 70.38, 70.28, 70.02, 69.94, 68.43, 68.29, 68.02, 67.93, 65.65, 53.22, 52.56, 34.96,35.10, 31.50, 31.42;
**$^{19}$F NMR (470.585 MHz, $CDCl_3$):** δ (ppm): -73.41 (6F, d, $J_{F-P}$ = 712.4 Hz), -80.77, -109.69, -121.53 (4F), -122.80, -126.10;
**HRMS (ESI $[M]^+$):** *m/z* calc. for $C_{68}H_{85}F_{19}NO_{10}$: 1322.5960, found for: $C_{68}H_{85}F_{19}NO_{10}$: 1322.5966.

## 6. Gram-scale photocatalytic fluoroalkylation reaction of dibenzo[24]crown-8 (DB24C8)

In a 50 mL glass reaction flask provided with a septum and a stir bar, dibenzo[18]crown-6 (DB24C8) (2.0 mmol, 0.9 g), *N,N,N´,N´*-tetramethylethylenediamine (6 mmol, 0.890 mL), EY (0.1 mol, 0.065 g), KCl (3 mmol, 0.224 g) and 35 mL of a solvent mixture MeCN : $H_2O$ (1:1) were introduced. Perfluorohexyliodide (6 mmol, 1.3 mL) was introduced and the flask was sealed. The reaction was stirred vigorously for 20 hours at 22 °C under constant irradiation with four high power LEDs (5 Watts, $\lambda_{max}$ = 525nm ± 2nm).
After the reaction time was completed, the mixture was extracted thrice with $CH_2Cl_2$ / water. The organic layers were gathered and dried over anhydrous $Na_2SO_4$, filtered and evaporated under vacuo. The crude reaction mixture was purified by silica-gel (60 mesh) column chromatography, employing the eluants indicated in the TLC conditions (*vide infra*, spectral data).

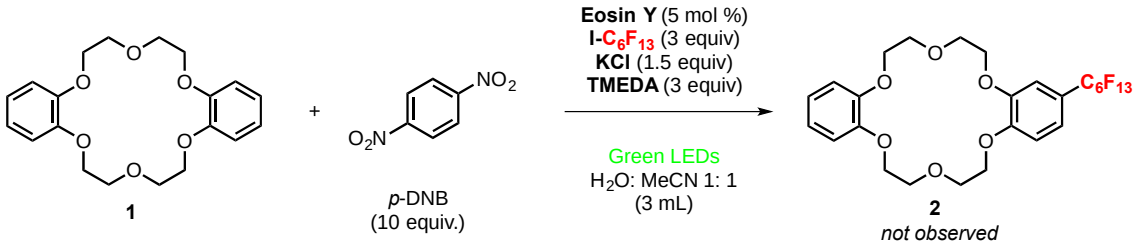
## 7. Mechanistic probe experiments for the perfluoroalkylation of dibenzo[18]crown-6 (DB18C6, 1)

Under standard conditions and employing **1** as substrate in the presence of TEMPO (3 equiv), product **2** formation was completely suppressed (Scheme S1) and a TEMPO-$C_6F_{13}$ adduct **19** was isolated (14% yield) and characterized by $^1$H, $^{13}$C, $^{19}$F 1D-NMR.



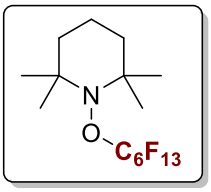

**Scheme S1 -** Mechanistic probe experiment for the perfluoroalkylation of DB18C6. Reaction performed in presence of 3 equiv of TEMPO.

When 1,4-dinitrobenzene (10 equiv) is added to the reaction medium and employing **1** as substrate, no product **2** formation is found (Scheme S2). This result could be explained taking into account that 1,4-dinitrobenzene is a better electron acceptor than $C_6F_{13}I$ and considering the presence of an ET process involving $EY^{3-\bullet}$ species. Indeed, the reductive quenching of $^3[EY^{2-}]^*$ with TMEDA to afford $EY^{3-\bullet}$ could be presumed.




**Scheme S2 -** Mechanistic probe experiment for the perfluoroalkylation of DB18C6. Reaction performed in presence of 10 equiv of *p*-dinitrobenzene.

## 8. Characterization of TEMPO-$C_6F_{13}$ adduct 19



***2,2,6,6-tetramethyl-1-(perfluorohexyl)piperidine***[40] **(19)** was obtained as a colorless oil (14 %). TLC: *n*-hexane (9:1)

**$^1$H NMR (600 MHz, $CDCl_3$):** δ (ppm): 1.65-1.54 (m, 6H), 1.18 (s, 12H);

**$^{13}$C NMR (125 MHz, $CDCl_3$):** δ (ppm): 62.07, 40.61, 33.62 (t, J = 5.4 Hz), 20.83, 16.96;

**$^{19}$F NMR (470.585 MHz, $CDCl_3$):** δ (ppm): -78.52, -80.86, -121.91, -122.86, -123.64, -126.16.

## 9. $^{1}H$, $^{13}C$, $^{19}F$ -NMR and HRMS spectra

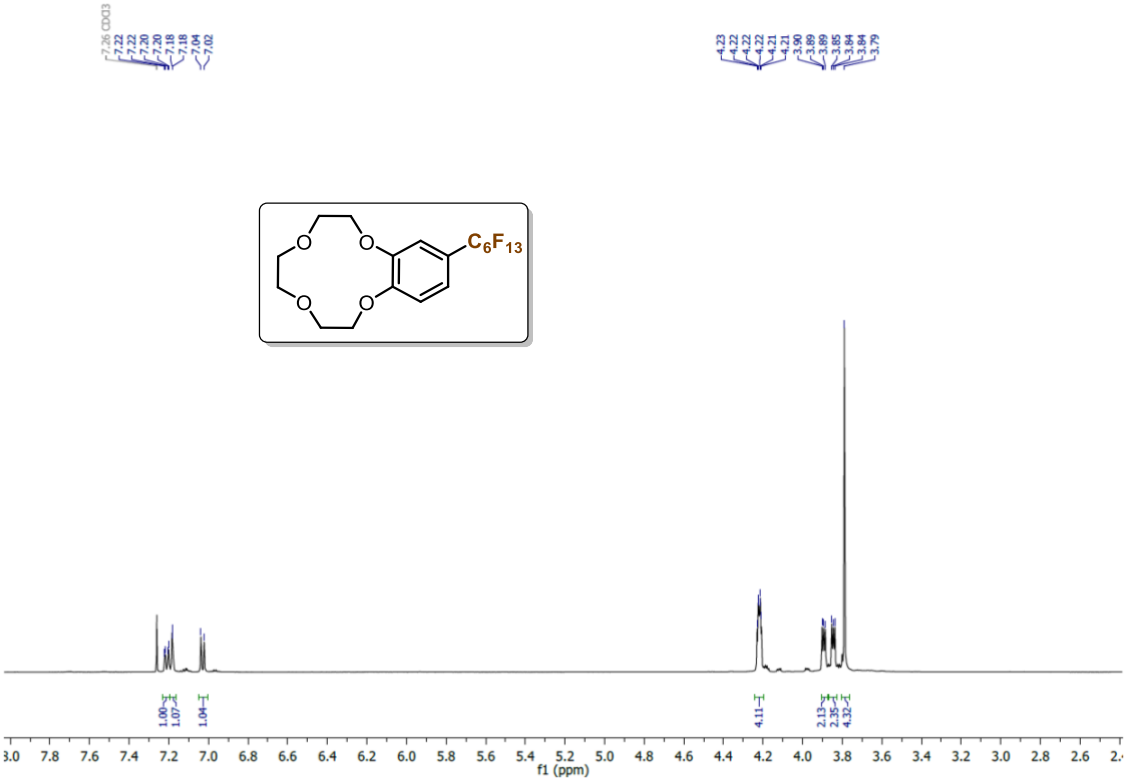



**Figure S4** – $^{1}H$ NMR spectrum of **3** (Chloroform-*d,* 298 K, 500 MHz).

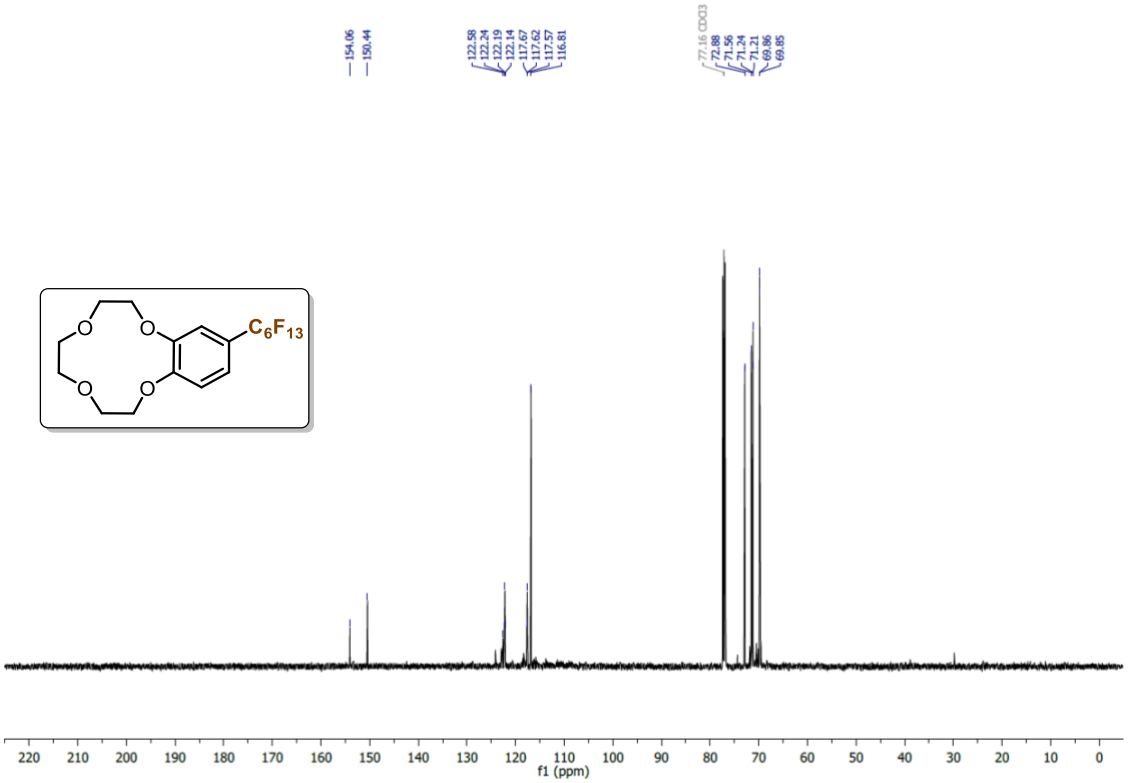



**Figure S5** – $^{13}C$ NMR spectrum of **3** (Chloroform-*d,* 298 K, 125 MHz).

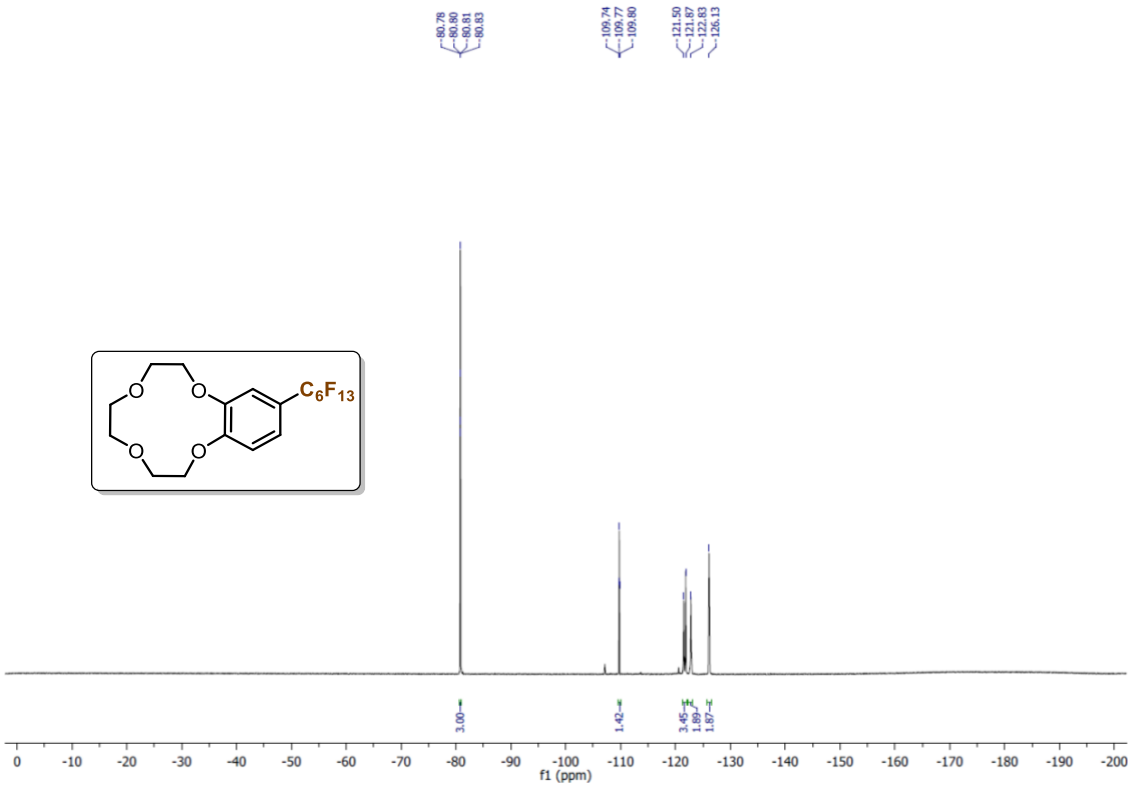



**Figure S6** – $^{19}$F NMR spectrum of **3** (Chloroform-*d,* 298 K, 470.585 MHz).

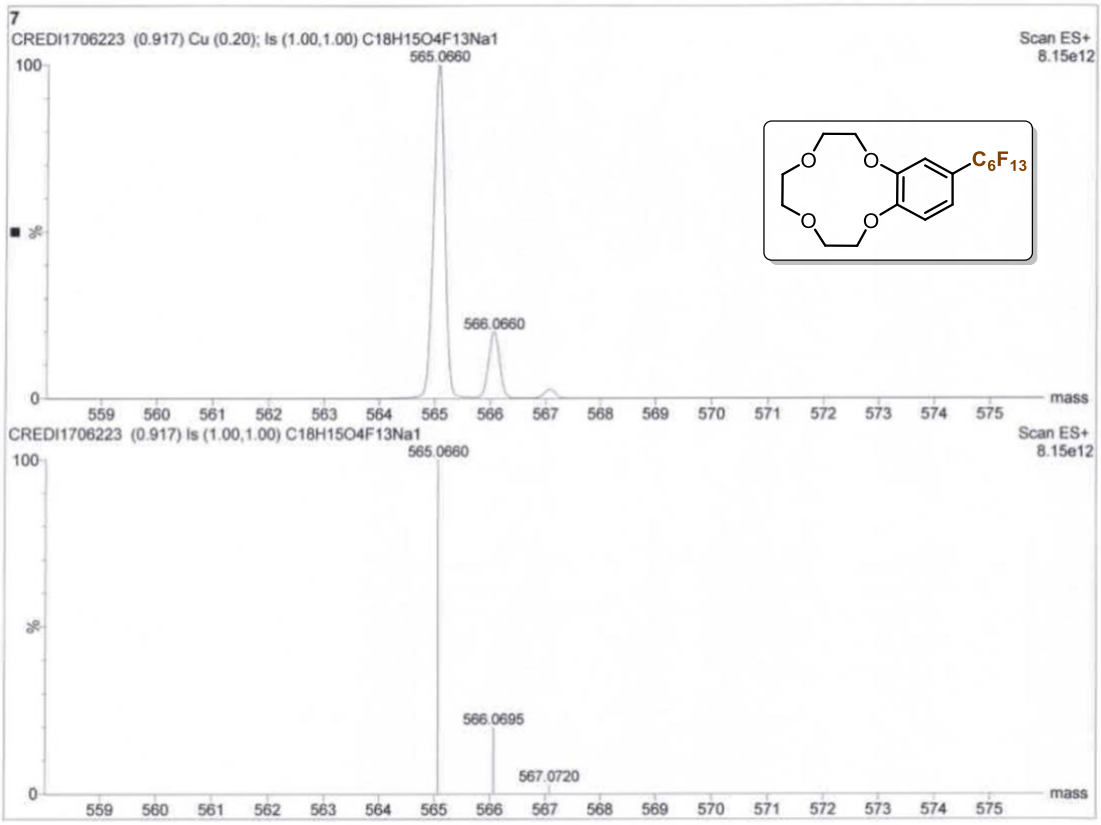



**Figure S7** – HRMS (ESI) spectrum of **3.**

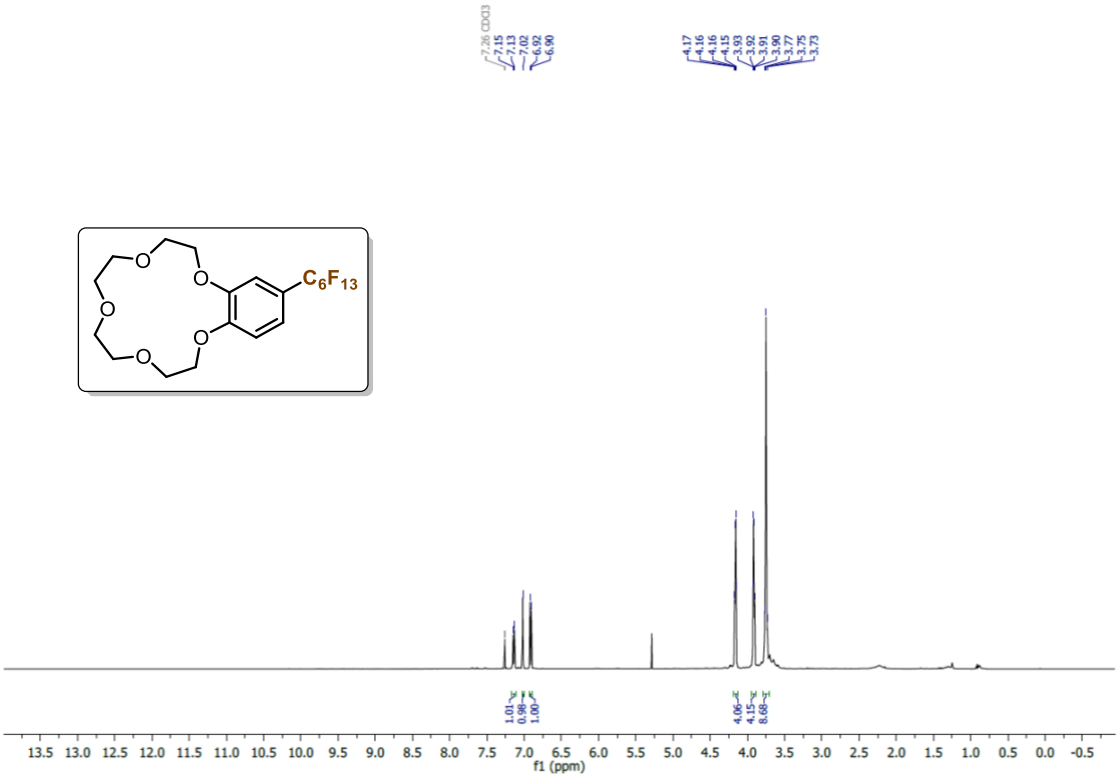



**Figure S8** – $^{1}$H NMR spectrum of **4** (Chloroform-*d,* 298 K, 500 MHz).

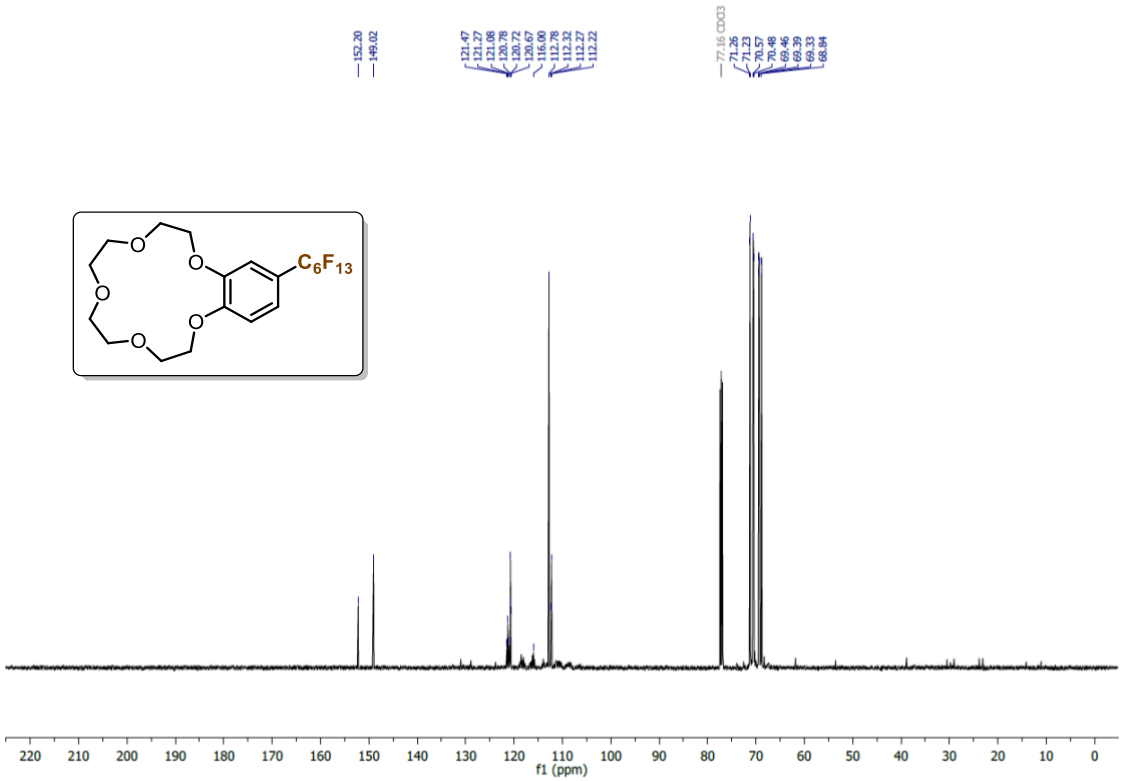



**Figure S9** – $^{13}$C NMR spectrum of **4** (Chloroform-*d,* 298 K, 125 MHz).

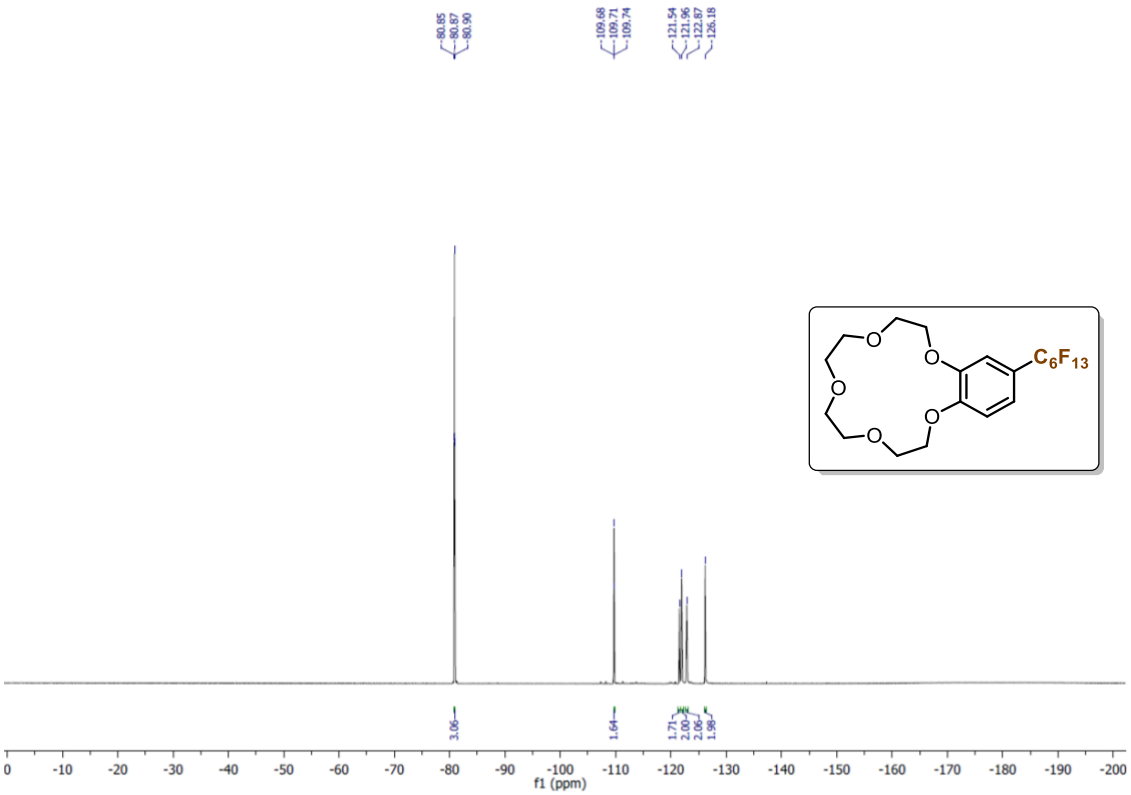



**Figure S10** – $^{19}$F NMR spectrum of **4** (Chloroform-*d,* 298 K, 470.585 MHz).

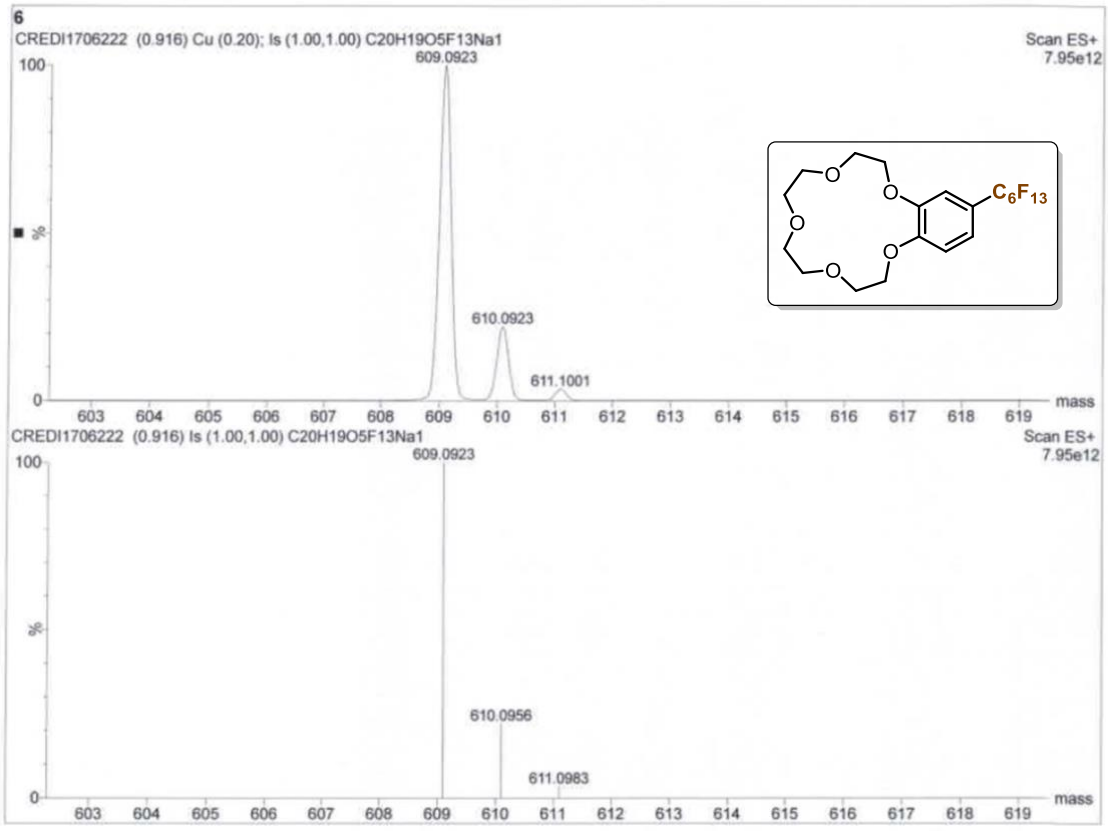



**Figure S11** – HRMS (ESI) spectrum of **4.**

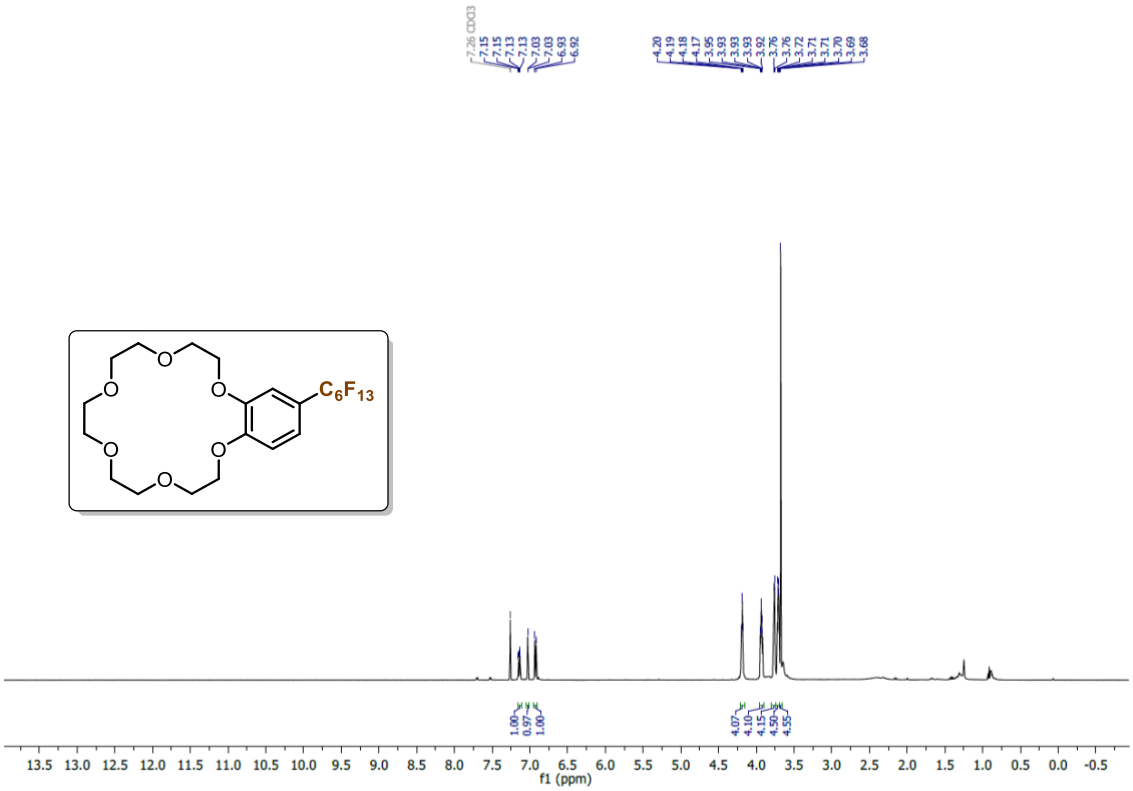



**Figure S12** – $^{1}$H NMR spectrum of **5** (Chloroform-*d,* 298 K, 500 MHz).

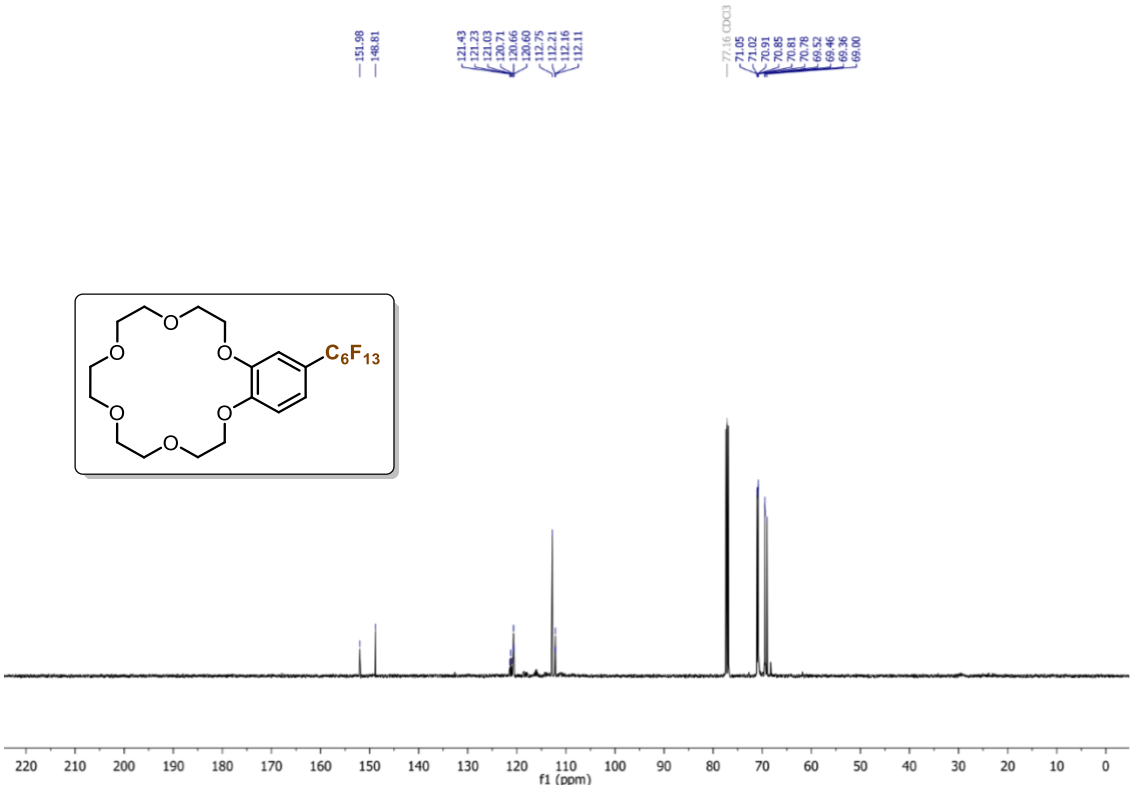



**Figure S13** – $^{13}$C NMR spectrum of **5** (Chloroform-*d,* 298 K, 125 MHz).

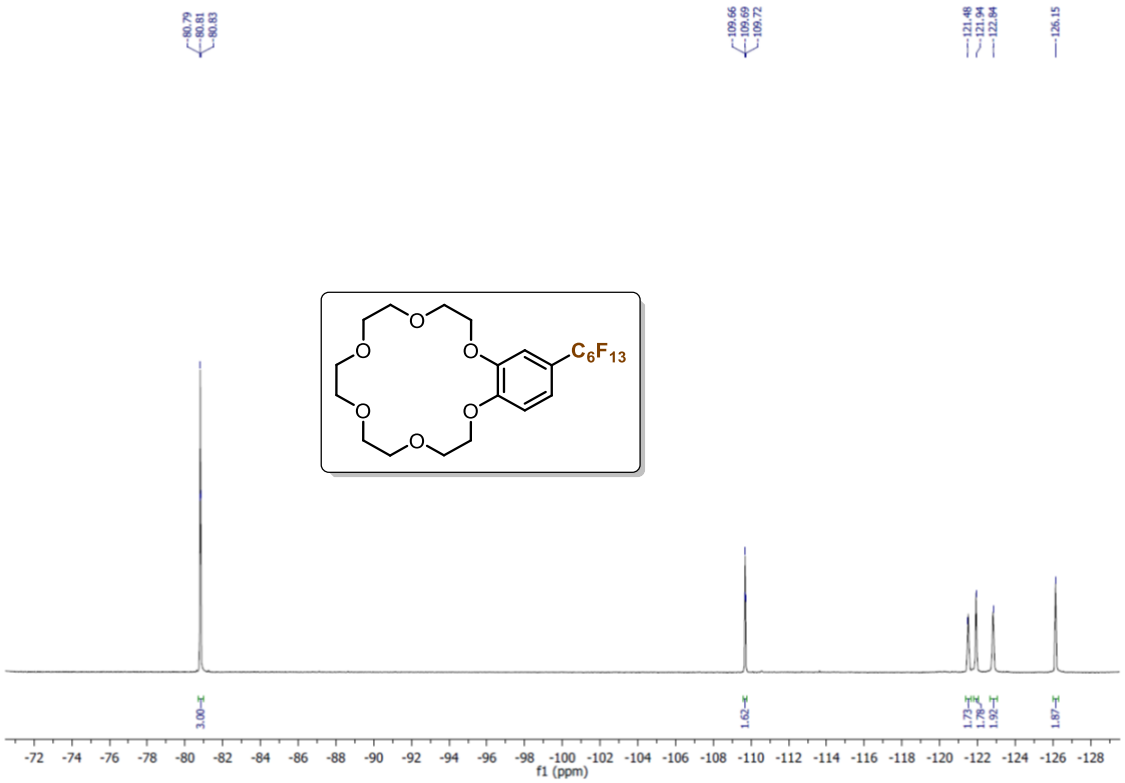



**Figure S14** – $^{19}$F NMR spectrum of **5** (Chloroform-*d,* 298 K, 470.585 MHz).

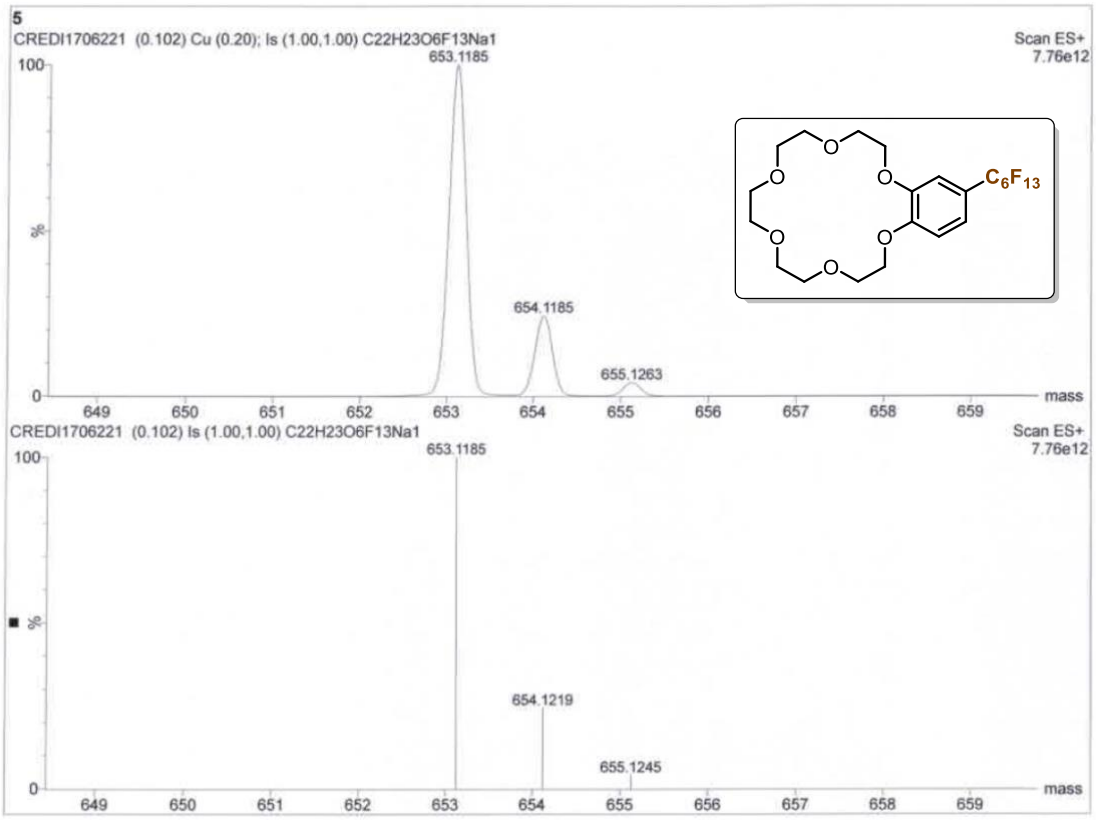



**Figure S15** – HRMS (ESI) spectrum of **5.**

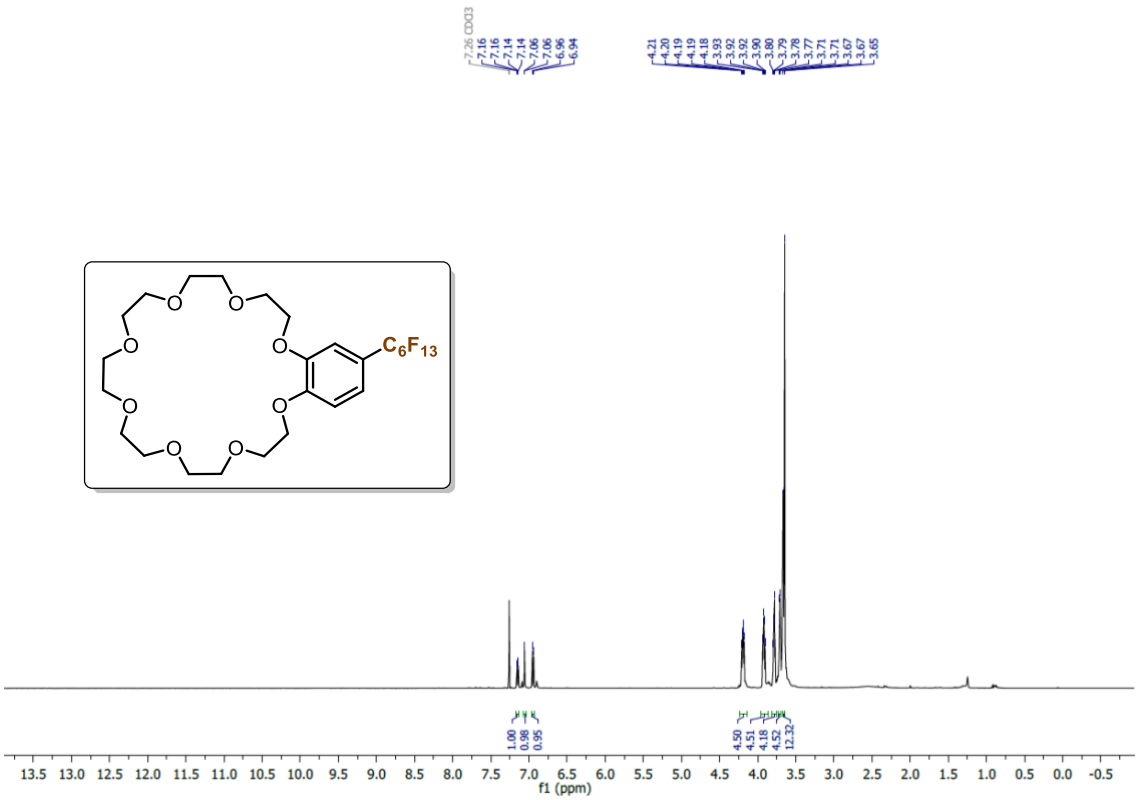



**Figure S16** – $^{1}$H NMR spectrum of **6** (Chloroform-*d,* 298 K, 500 MHz).

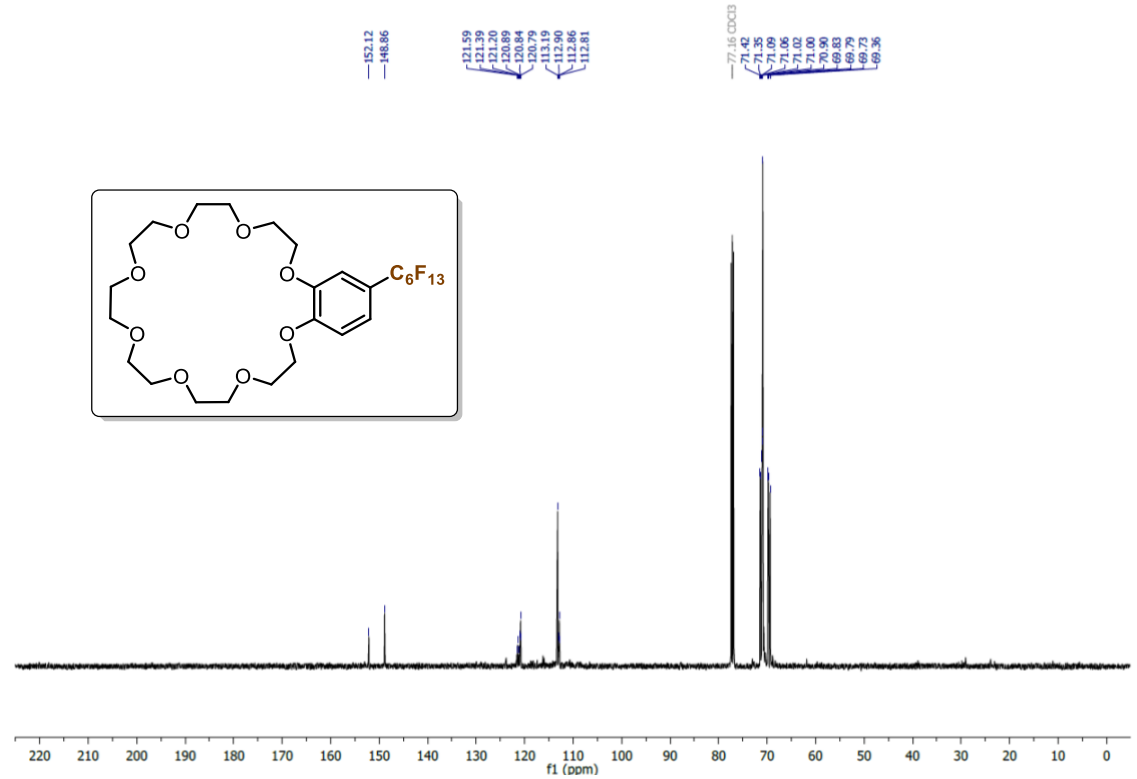



**Figure S17** – $^{13}$C NMR spectrum of **6** (Chloroform-*d,* 298 K, 125 MHz).

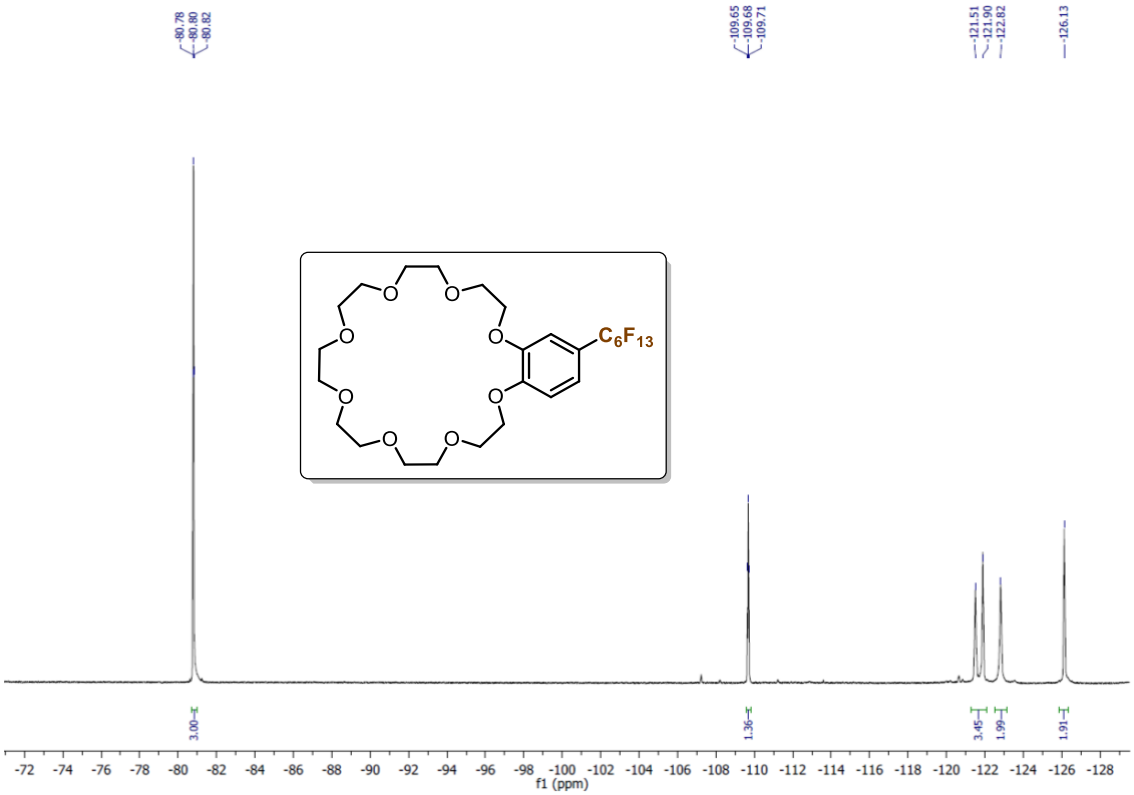



**Figure S18** – $^{19}$F NMR spectrum of **6** (Chloroform-*d,* 298 K, 470.585 MHz).

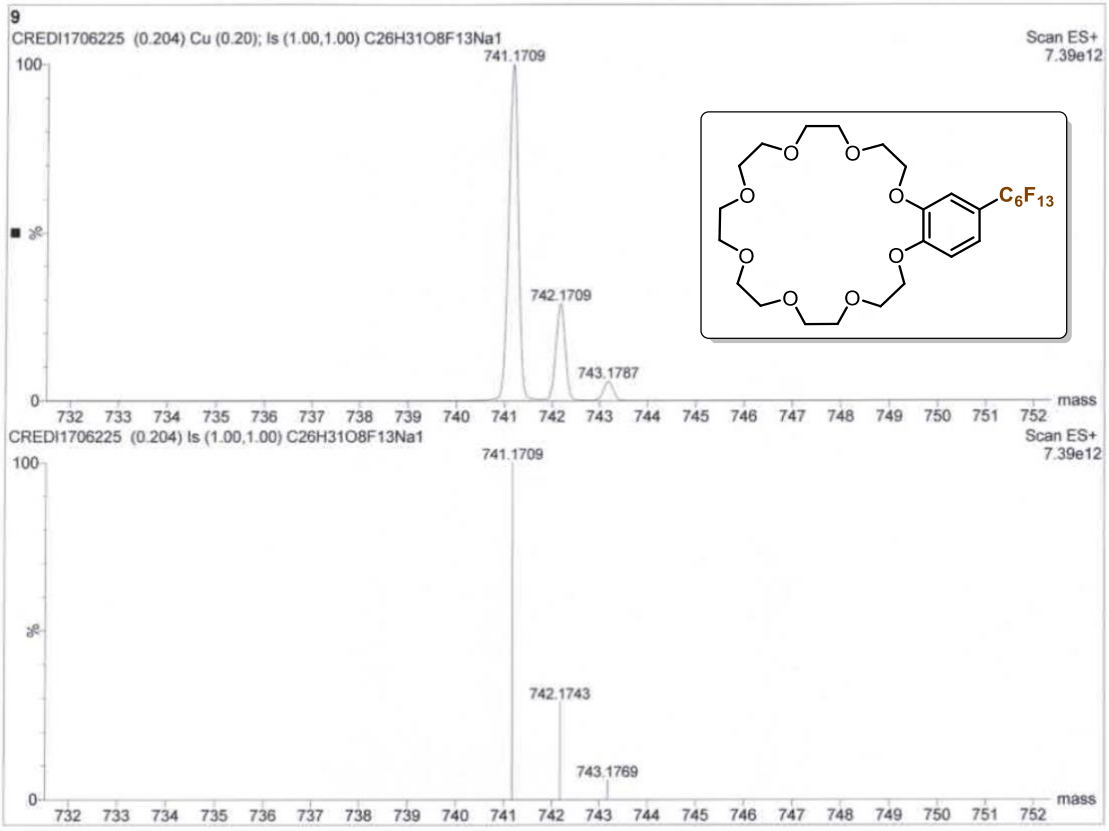



**Figure S19** – HRMS (ESI) spectrum of **6.**

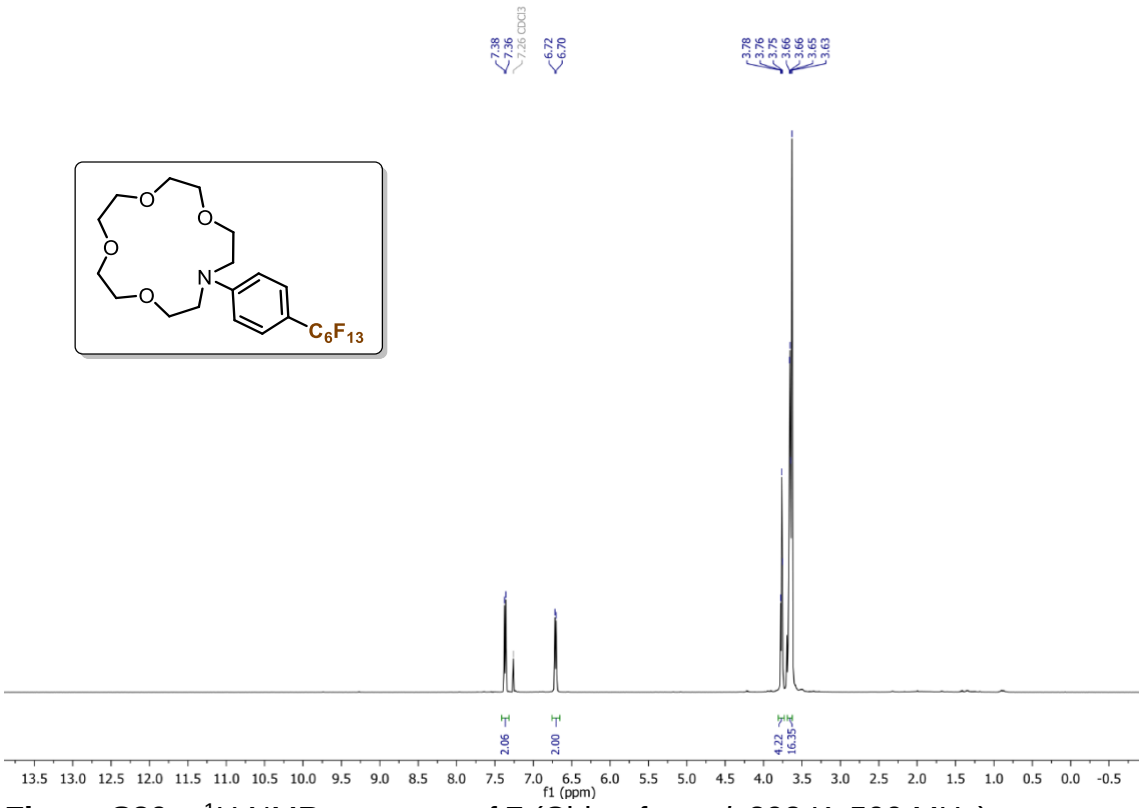



**Figure S20** – $^{1}$H NMR spectrum of **7** (Chloroform-*d*, 298 K, 500 MHz).

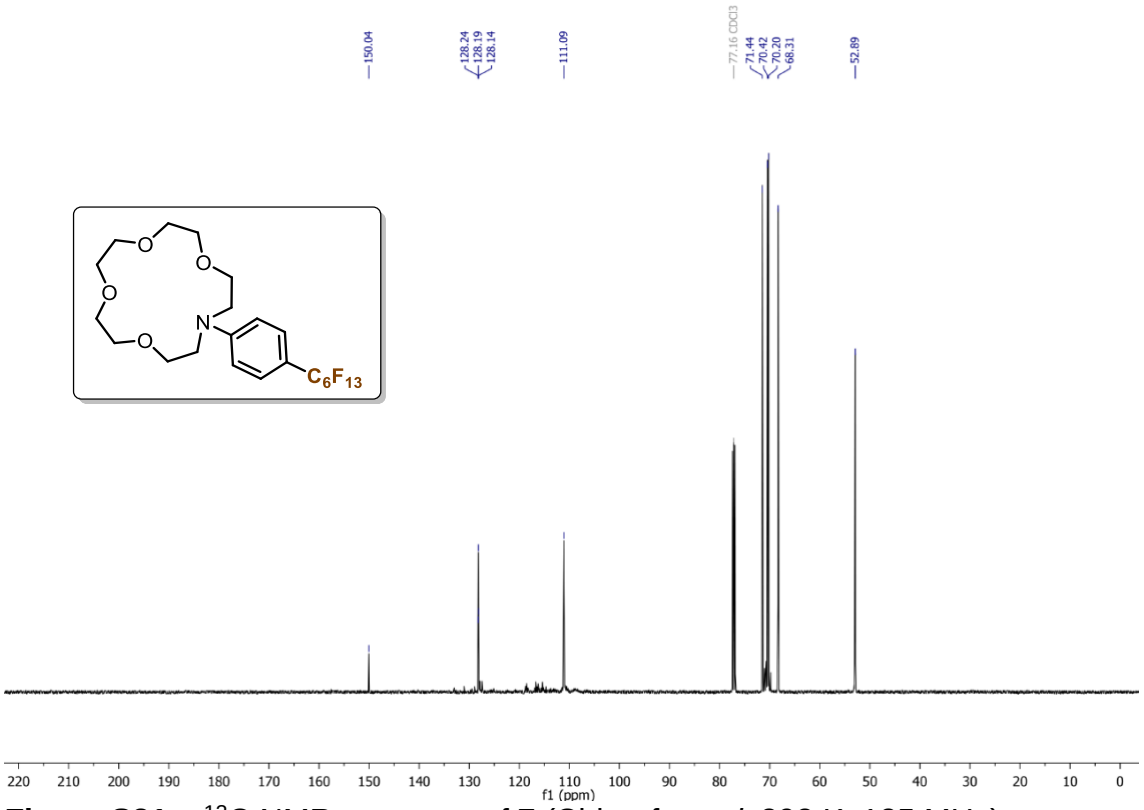



**Figure S21** – $^{13}$C NMR spectrum of **7** (Chloroform-*d,* 298 K, 125 MHz).

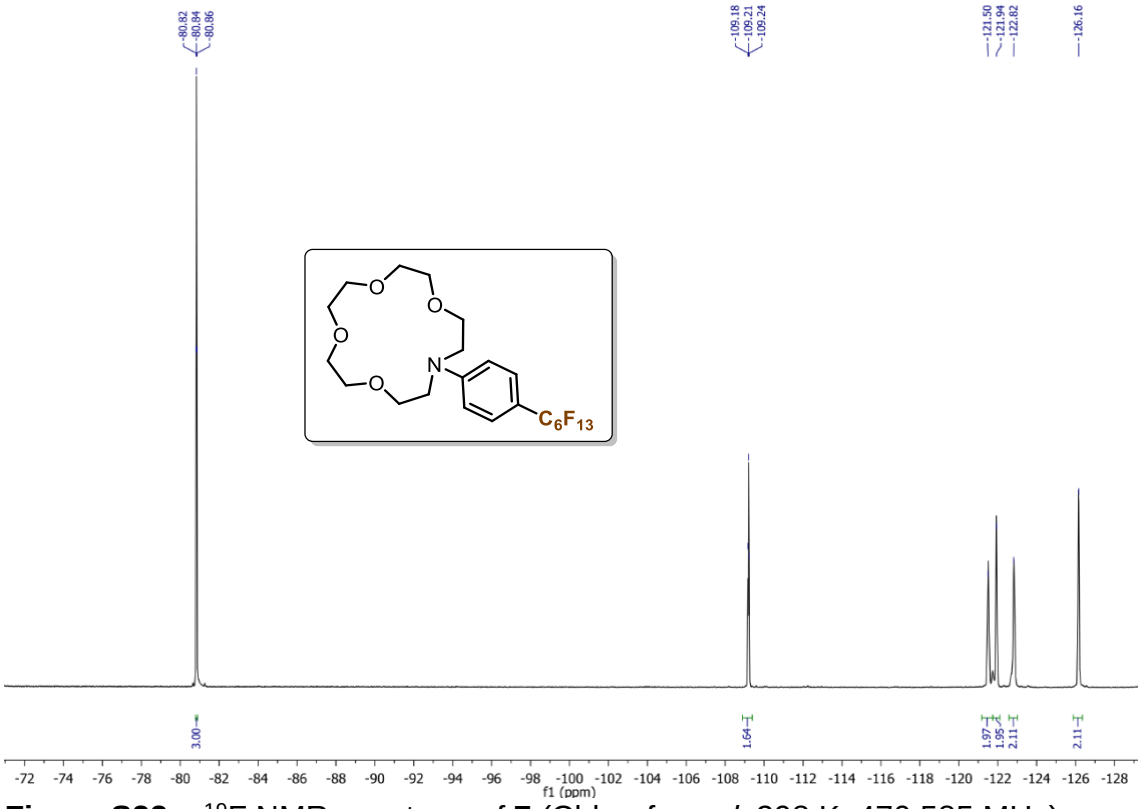



**Figure S22** – $^{19}$F NMR spectrum of **7** (Chloroform-*d,* 298 K, 470.585 MHz).

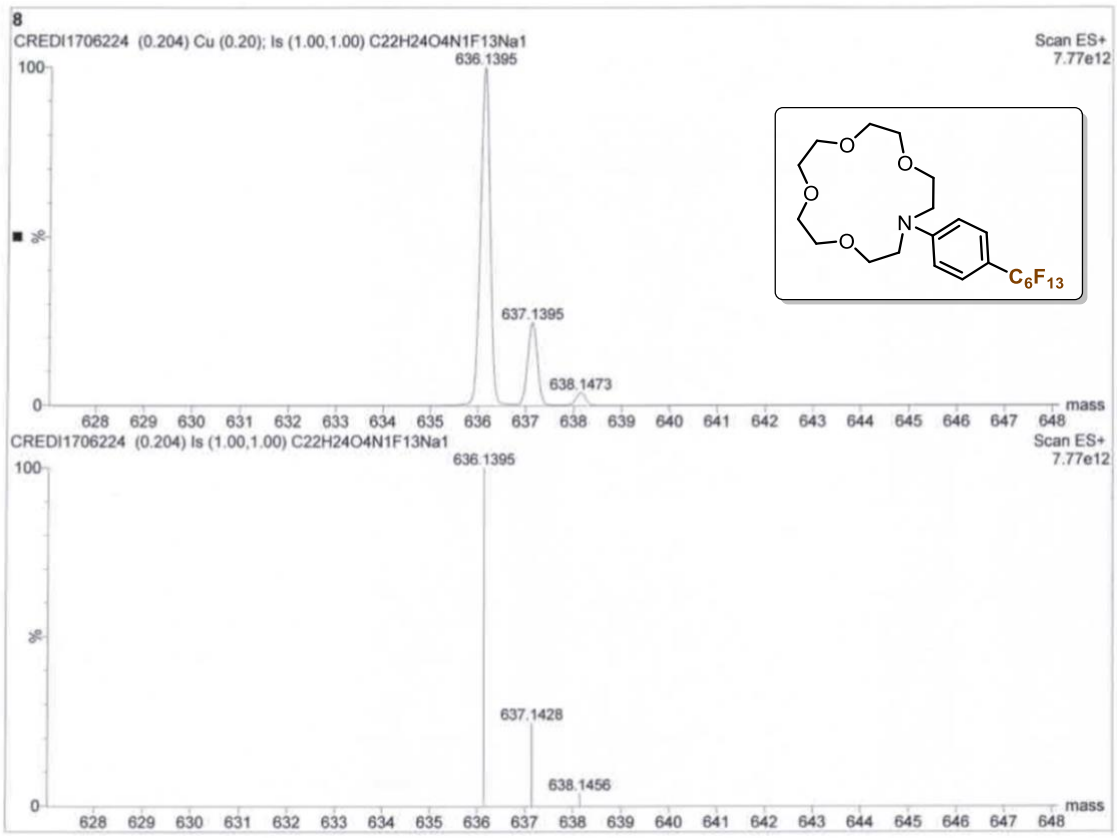



**Figure S23** – HRMS (ESI) spectrum of **7.**

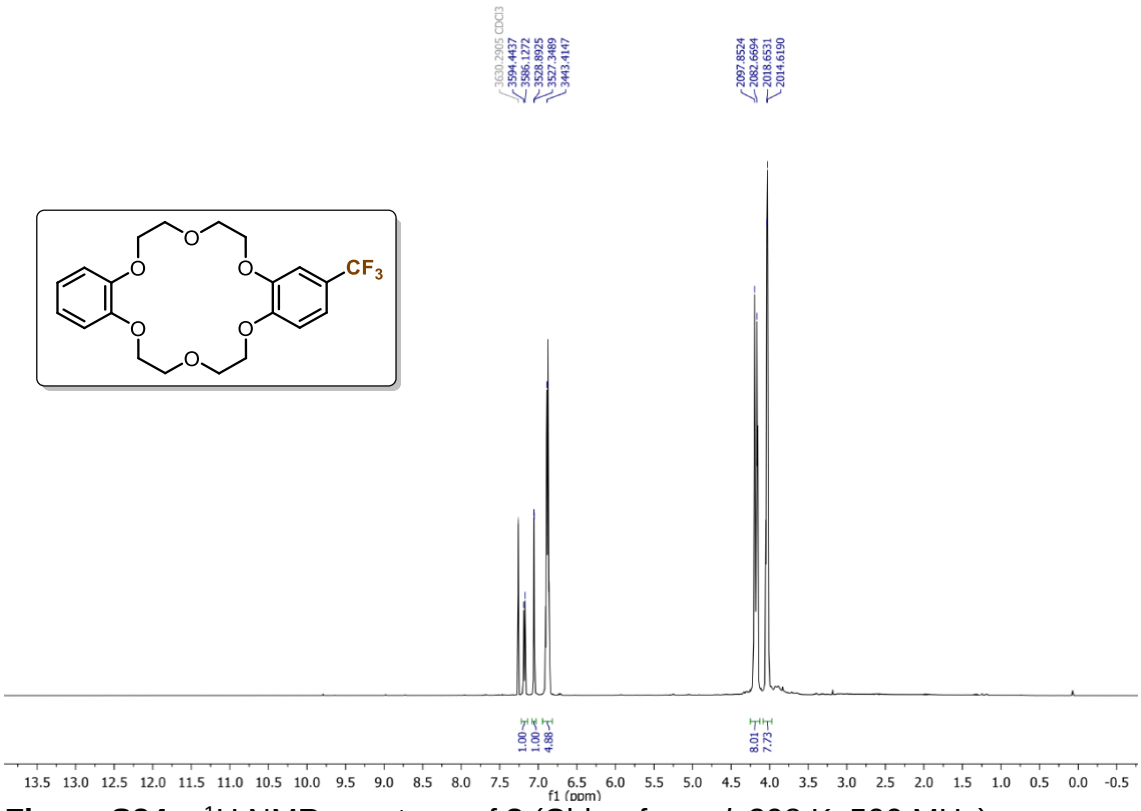



**Figure S24** – $^{1}$H NMR spectrum of **8** (Chloroform-*d*, 298 K, 500 MHz).

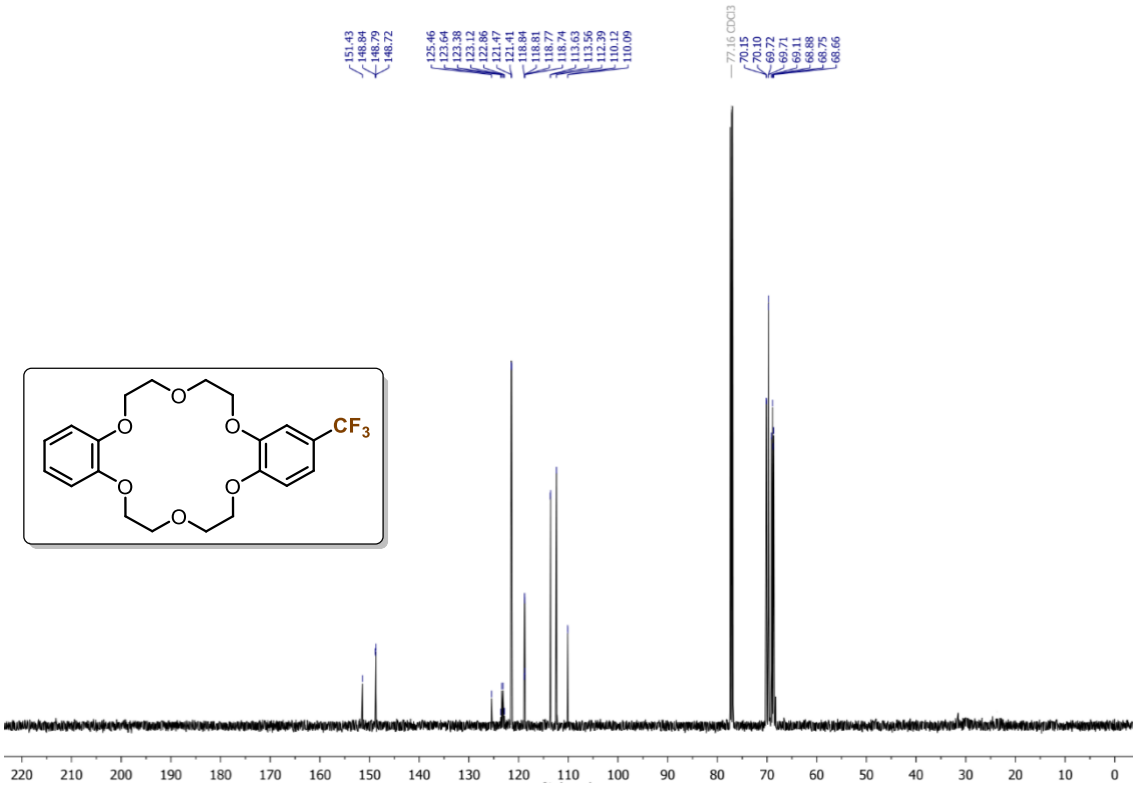



**Figure S25** – $^{13}$C NMR spectrum of **8** (Chloroform-*d,* 298 K, 125 MHz).

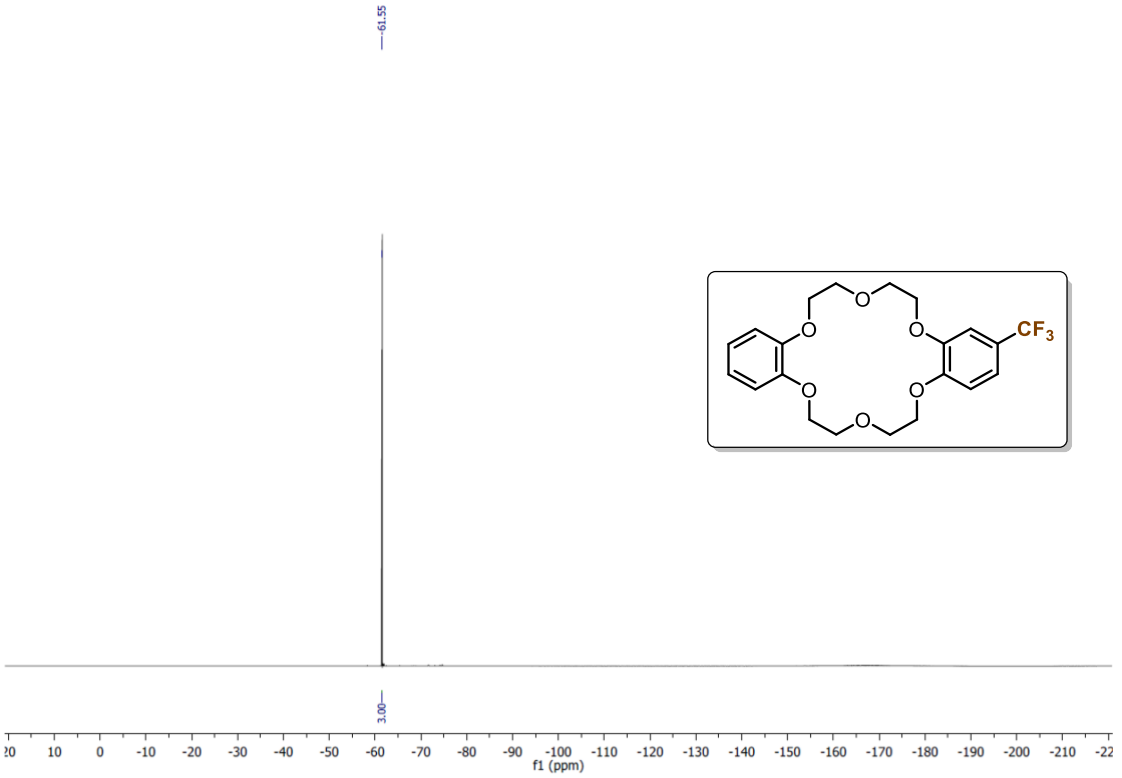



**Figure S26** – $^{19}$F NMR spectrum of **8** (Chloroform-*d,* 298 K, 470.585 MHz).

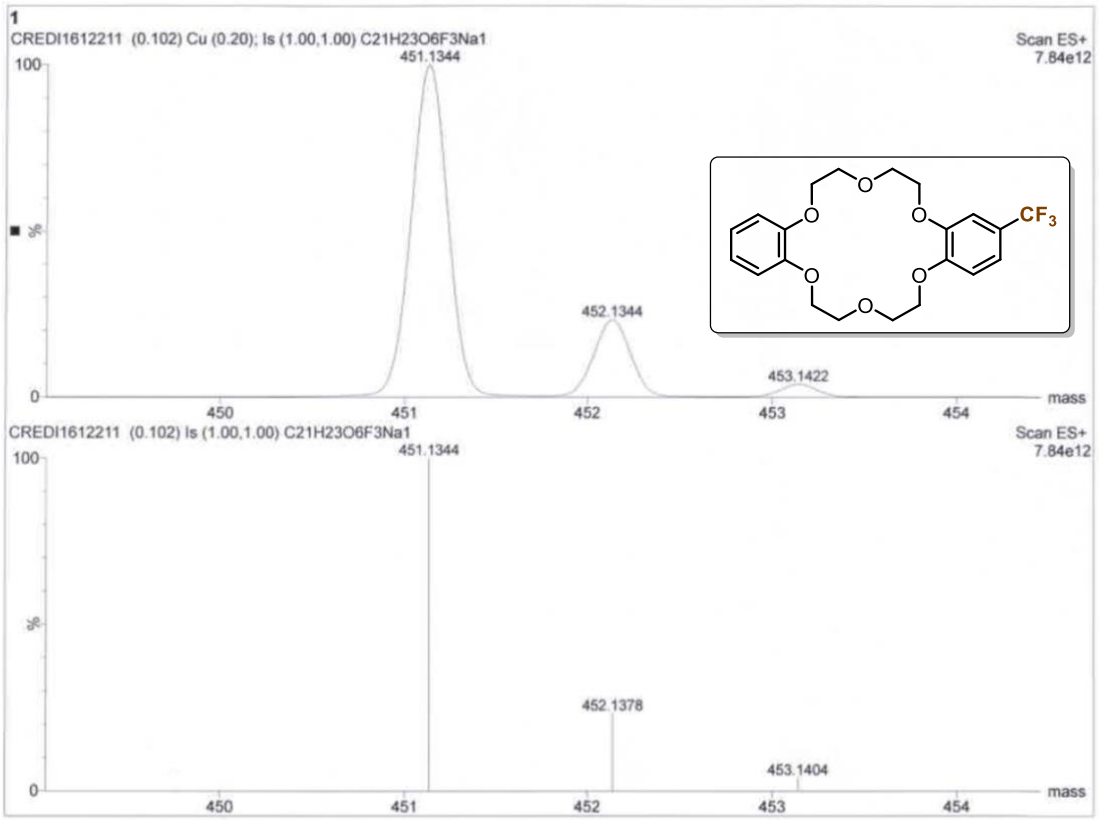



**Figure S27** – HRMS (ESI) spectrum of **8.**

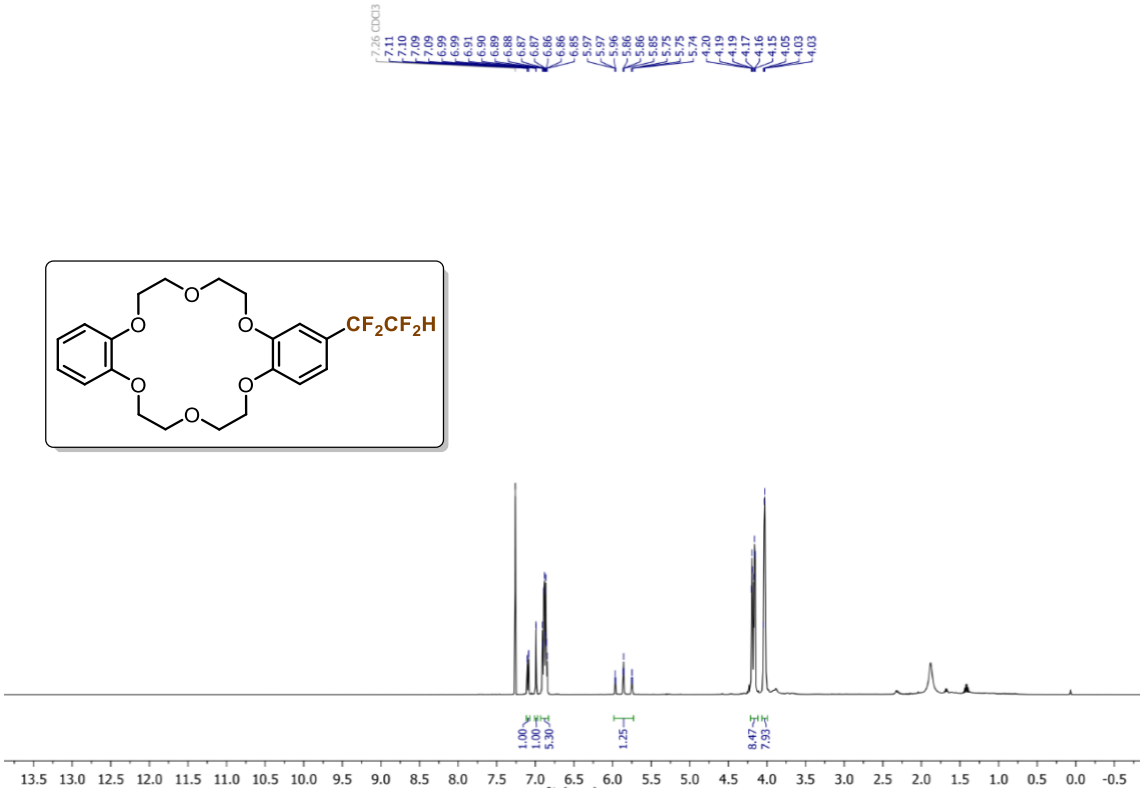



**Figure S28** – $^{1}$H NMR spectrum of **9** (Chloroform-*d*, 298 K, 500 MHz).

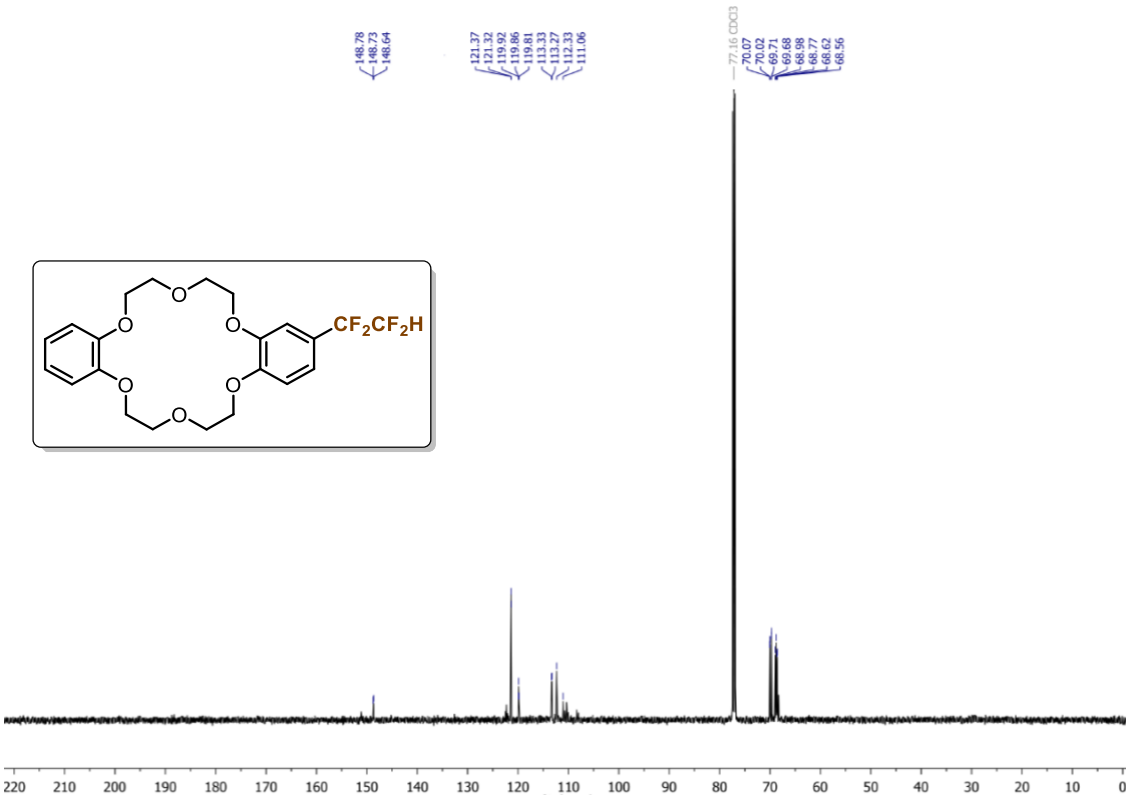



**Figure S29** – $^{13}$C NMR spectrum of **9** (Chloroform-*d,* 298 K, 125 MHz).

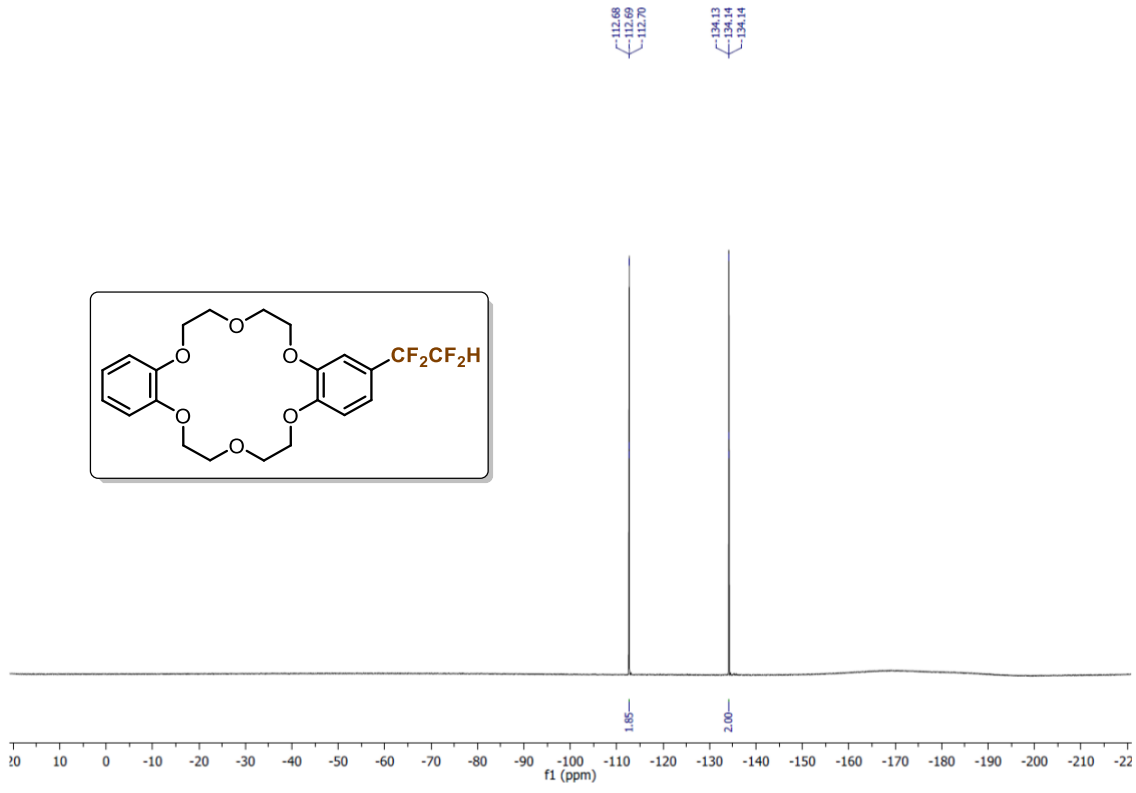



**Figure S30** – $^{19}$F NMR spectrum of **9** (Chloroform-*d,* 298 K, 470.585 MHz).

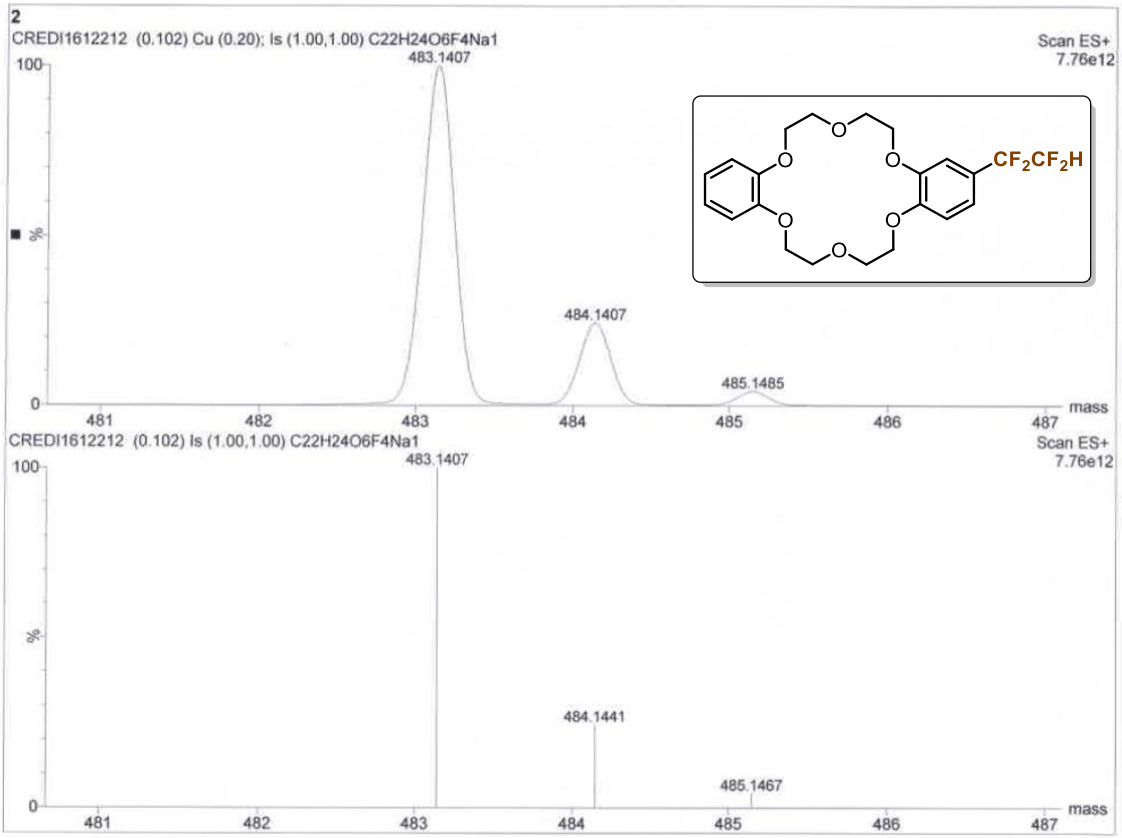



**Figure S31** – HRMS (ESI) spectrum of **9.**

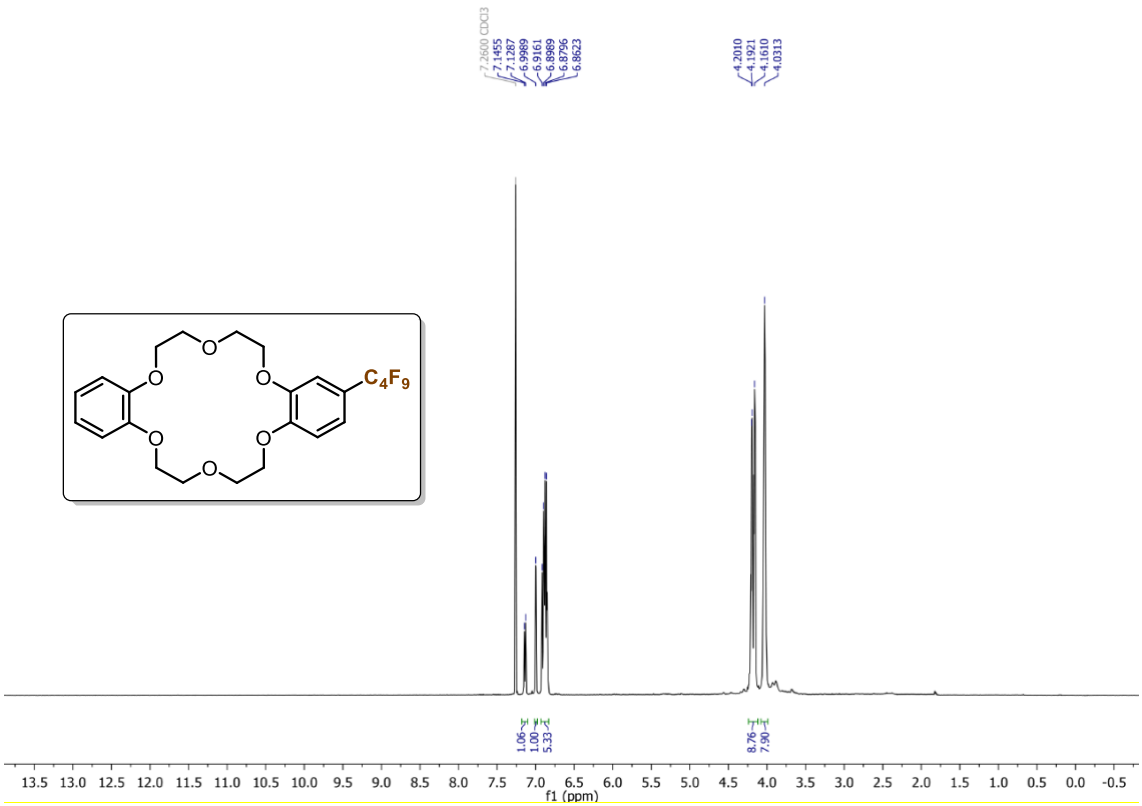



**Figure S32** – $^{1}$H NMR spectrum of **10** (Chloroform-*d,* 298 K, 500 MHz).

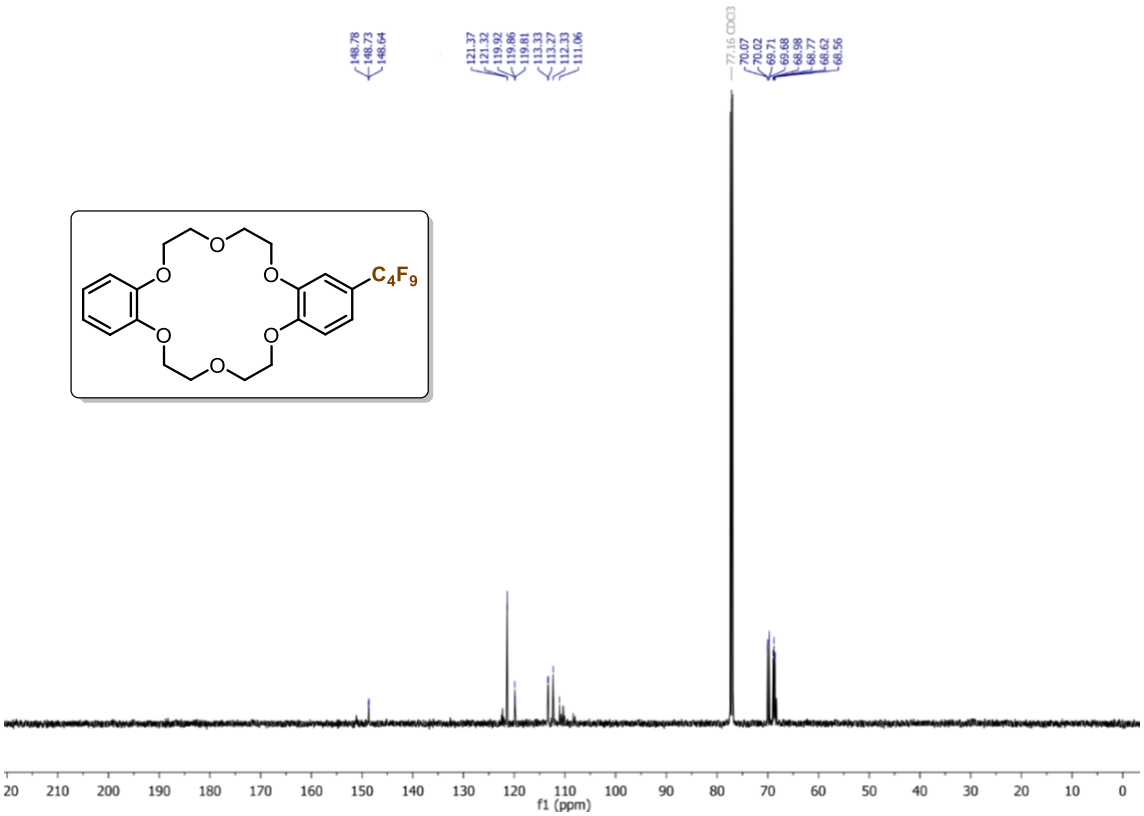



**Figure S33** – $^{13}$C NMR spectrum of **10** (Chloroform-*d*, 298 K, 125 MHz).

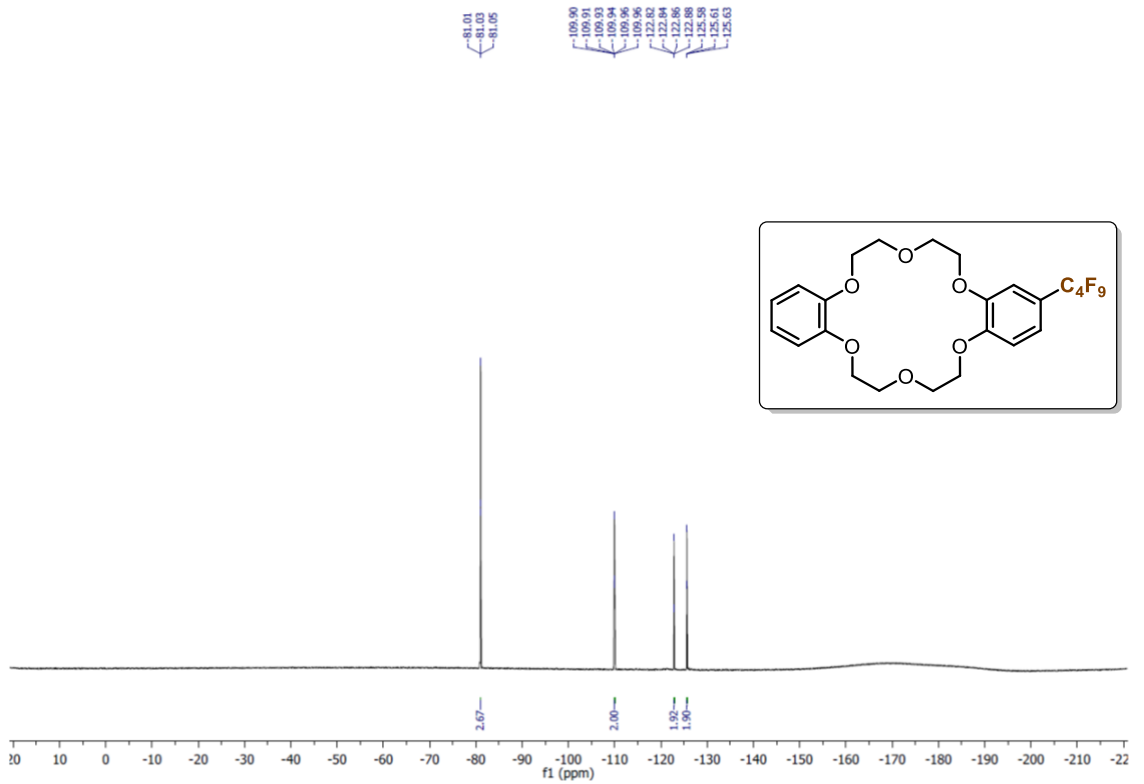



**Figure S34** – $^{19}$F NMR spectrum of **10** (Chloroform-*d*, 298 K, 470.585 MHz).

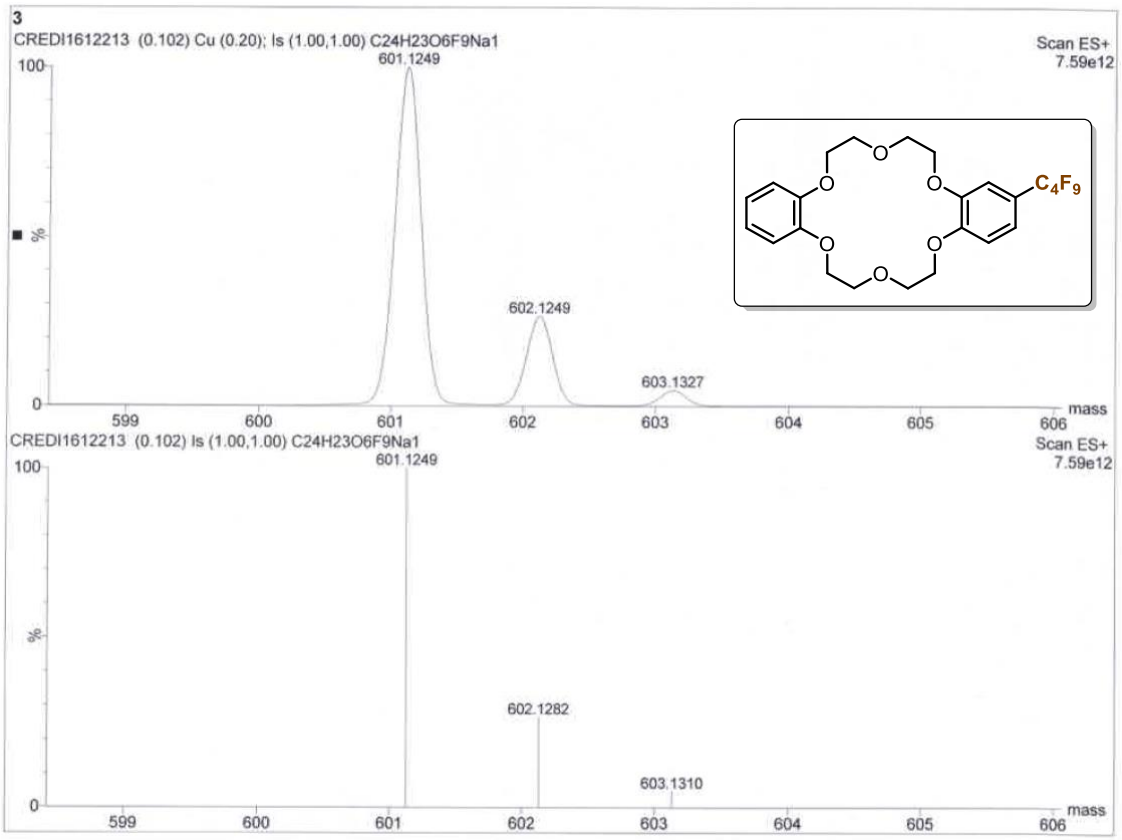



**Figure S35** – HRMS (ESI) spectrum of **10.**

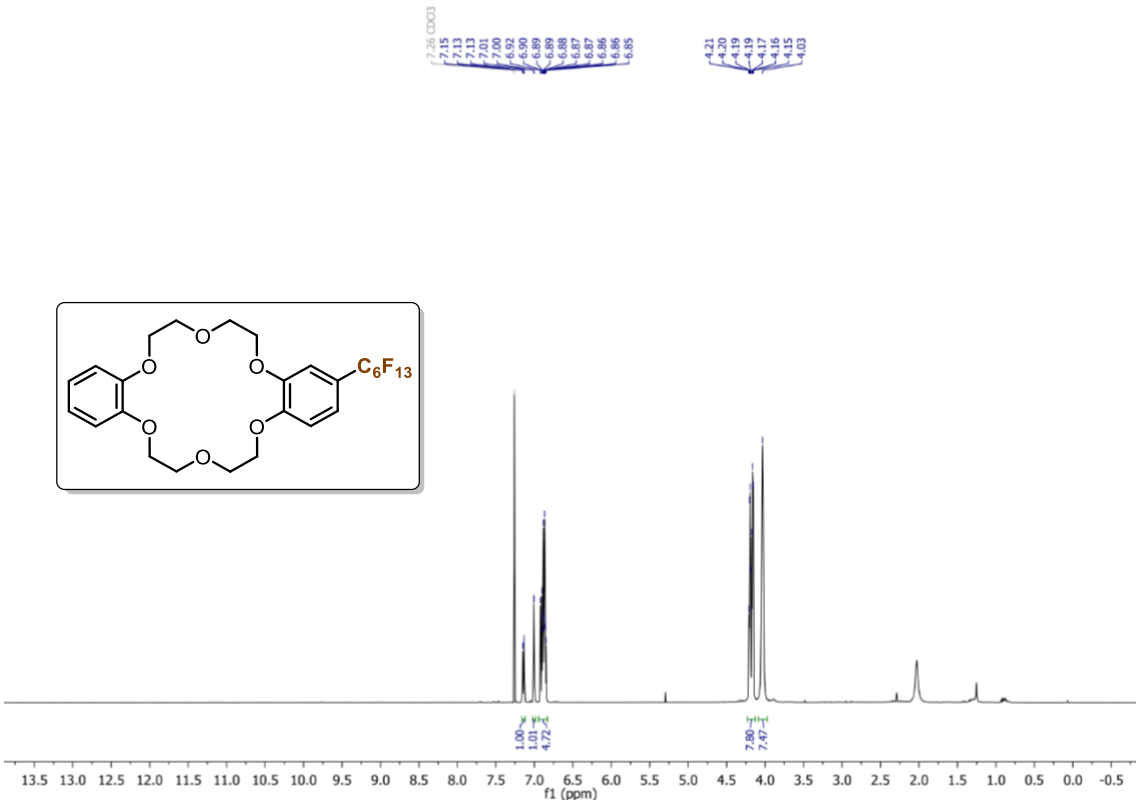



**Figure S36** – $^{1}$H NMR spectrum of **2** (Chloroform-*d,* 298 K, 500 MHz).

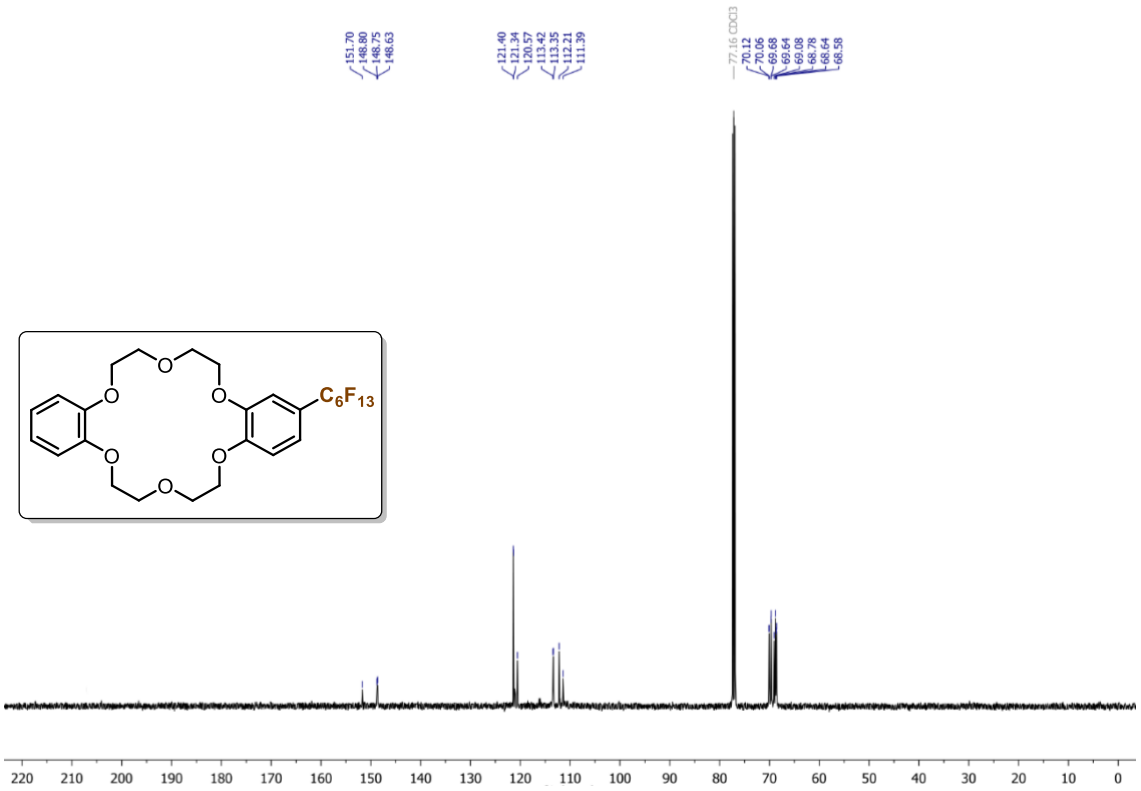



**Figure S37** – $^{13}$C NMR spectrum of **2** (Chloroform-*d,* 298 K, 125 MHz).

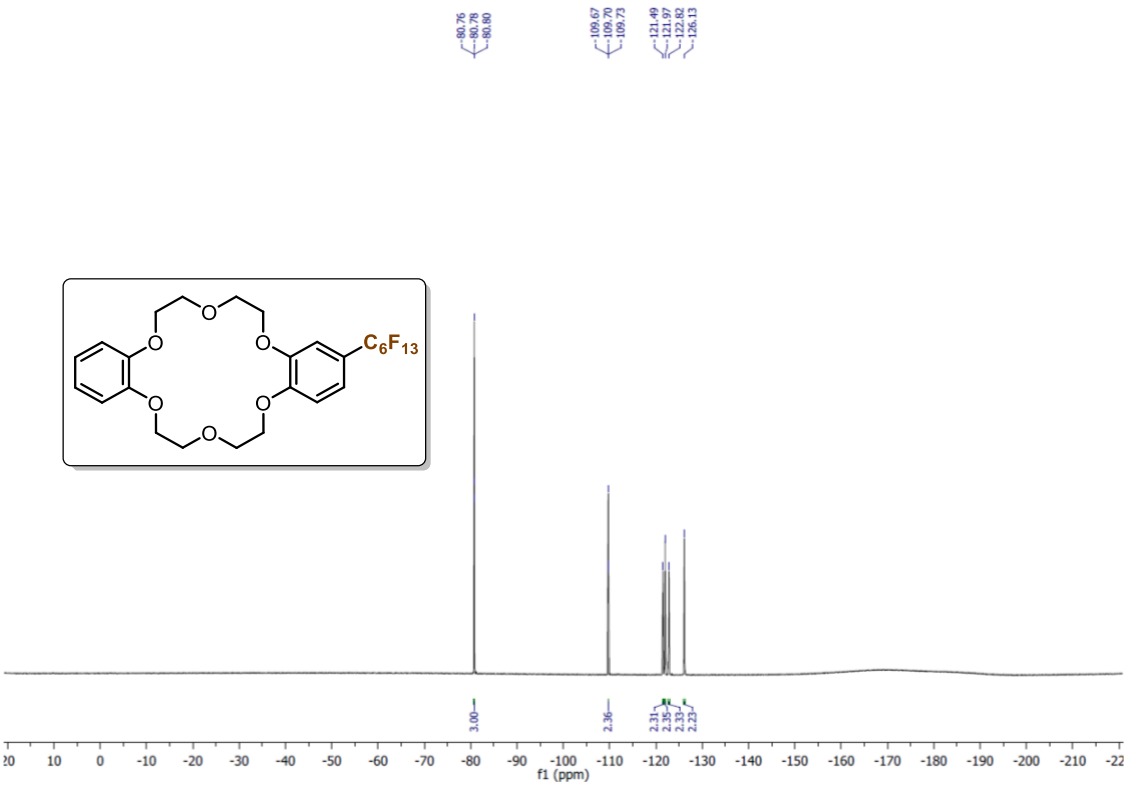



**Figure S38** – $^{19}$F NMR spectrum of **2** (Chloroform-*d,* 298 K, 470.585 MHz).

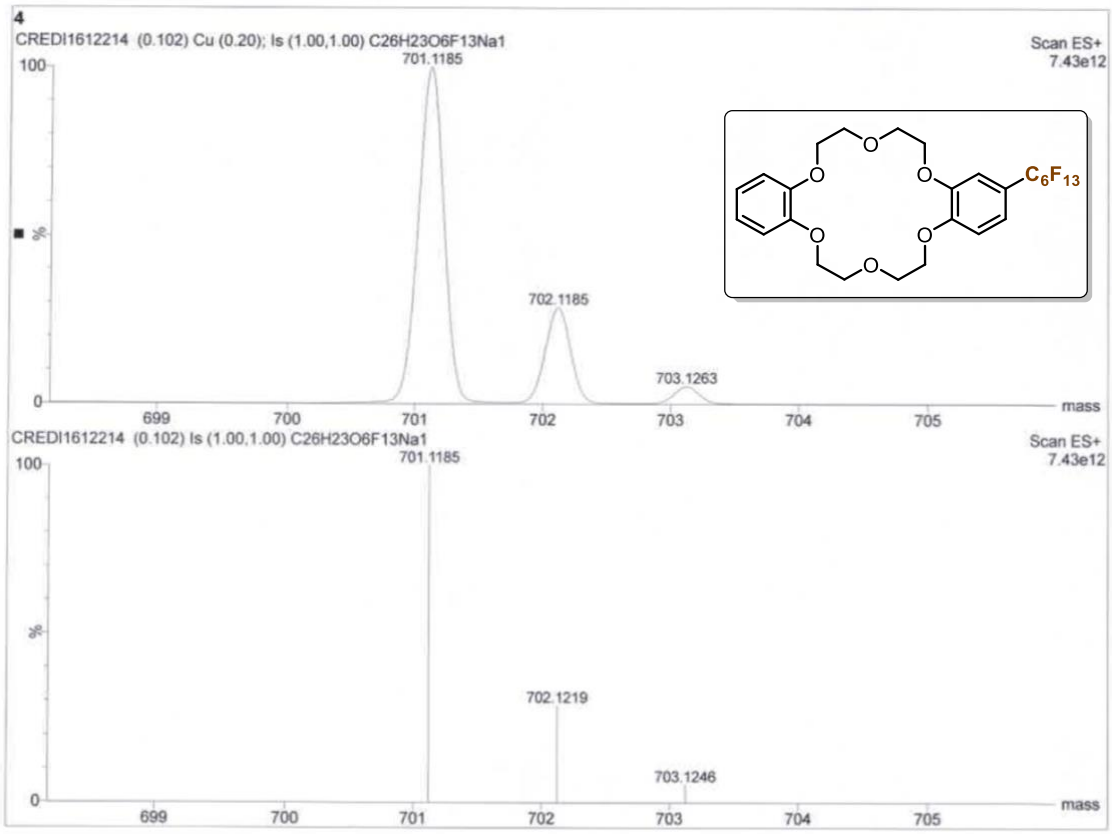



**Figure S39** – HRMS (ESI) spectrum of **2.**

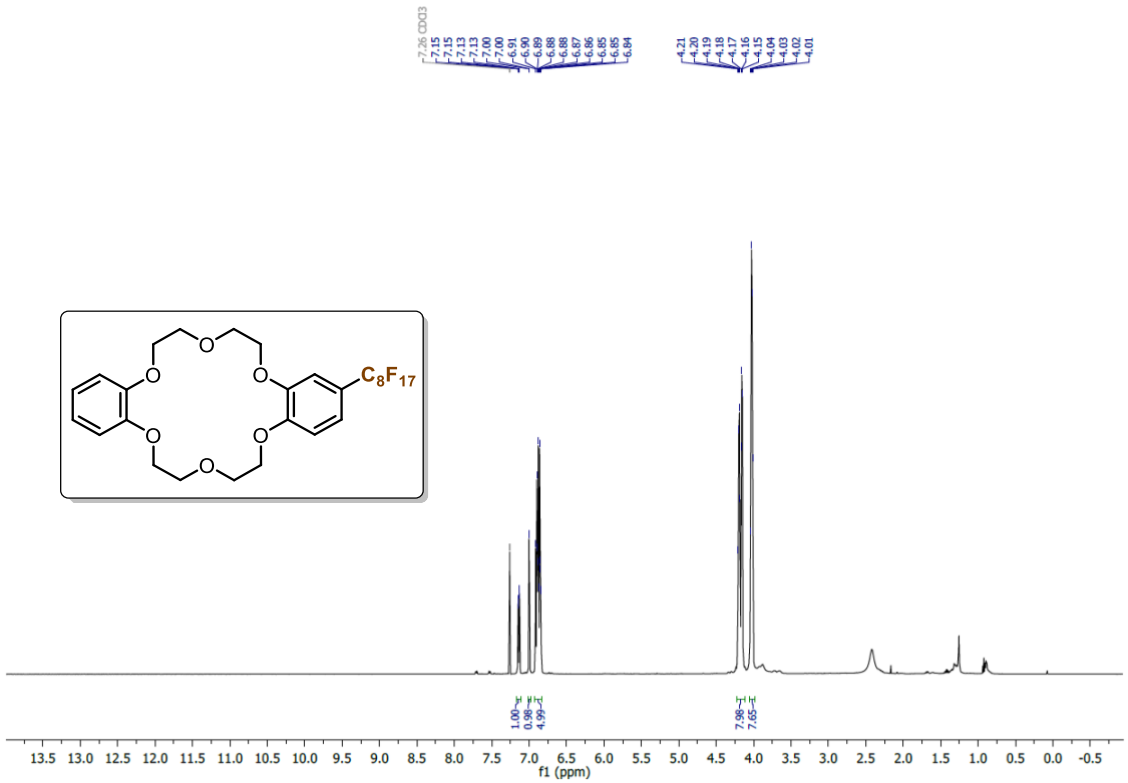



**Figure S40** – $^{1}$H NMR spectrum of **11** (Chloroform-*d,* 298 K, 500 MHz).

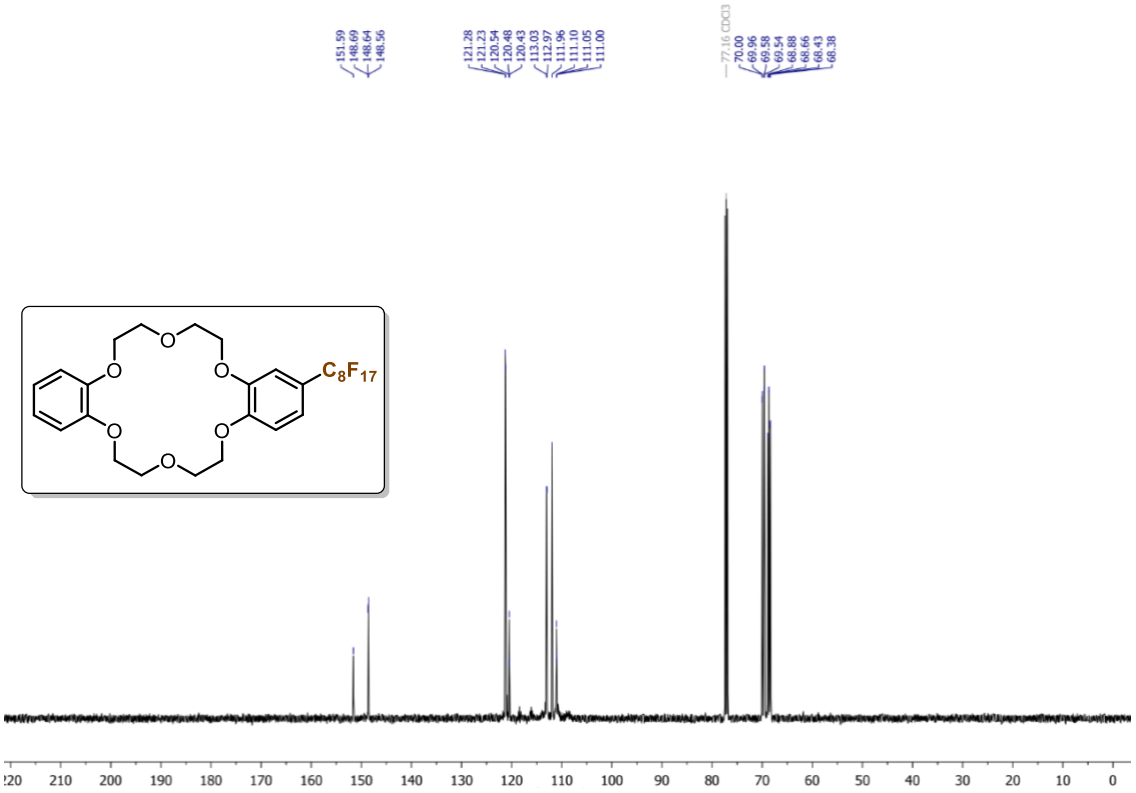



**Figure S41** – $^{13}$C NMR spectrum of **11** (Chloroform-*d,* 298 K, 125 MHz).

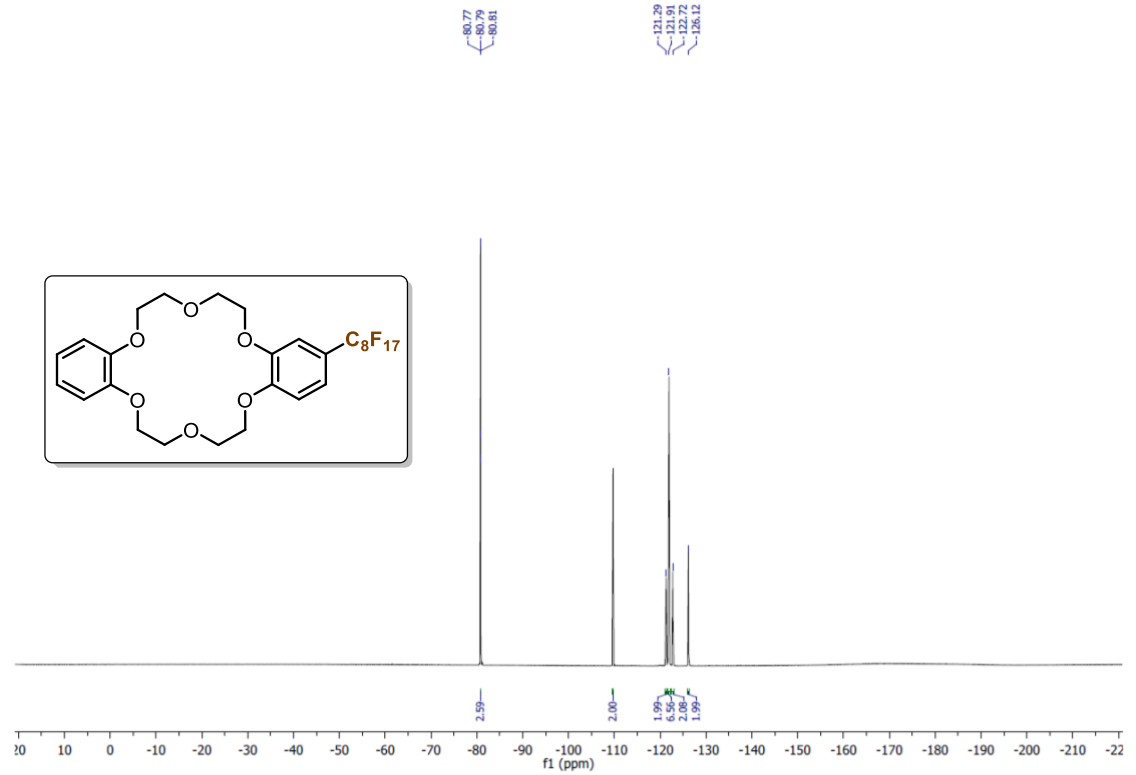



**Figure S42** – $^{19}$F NMR spectrum of **11** (Chloroform-*d,* 298 K, 470.585 MHz).

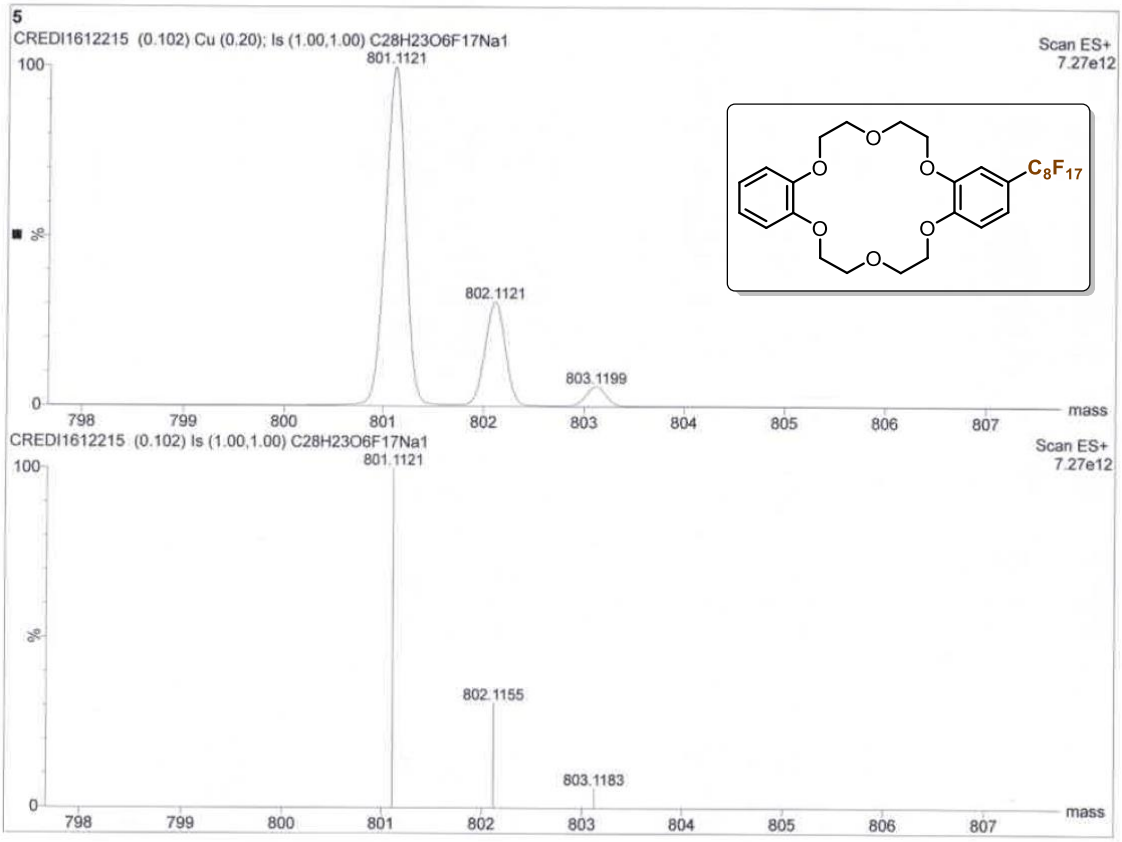



**Figure S43** – HRMS (ESI) spectrum of **11.**

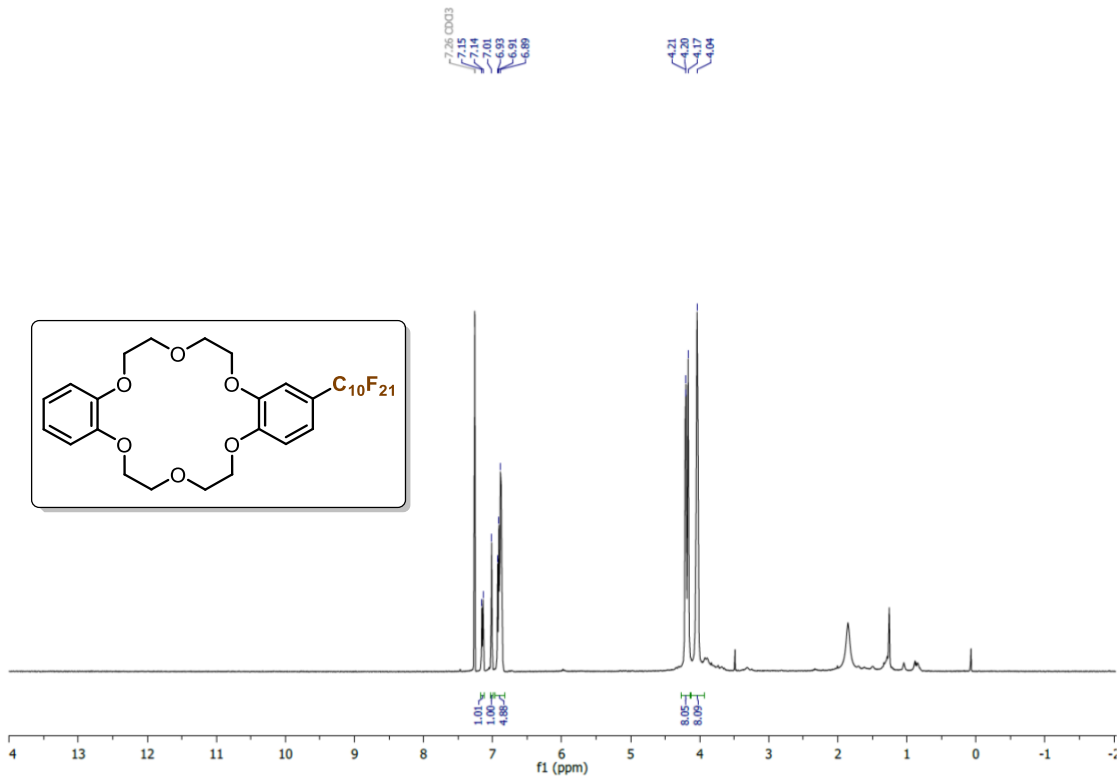



**Figure S44** – $^{1}$H NMR spectrum of **12** (Chloroform-*d,* 298 K, 500 MHz).

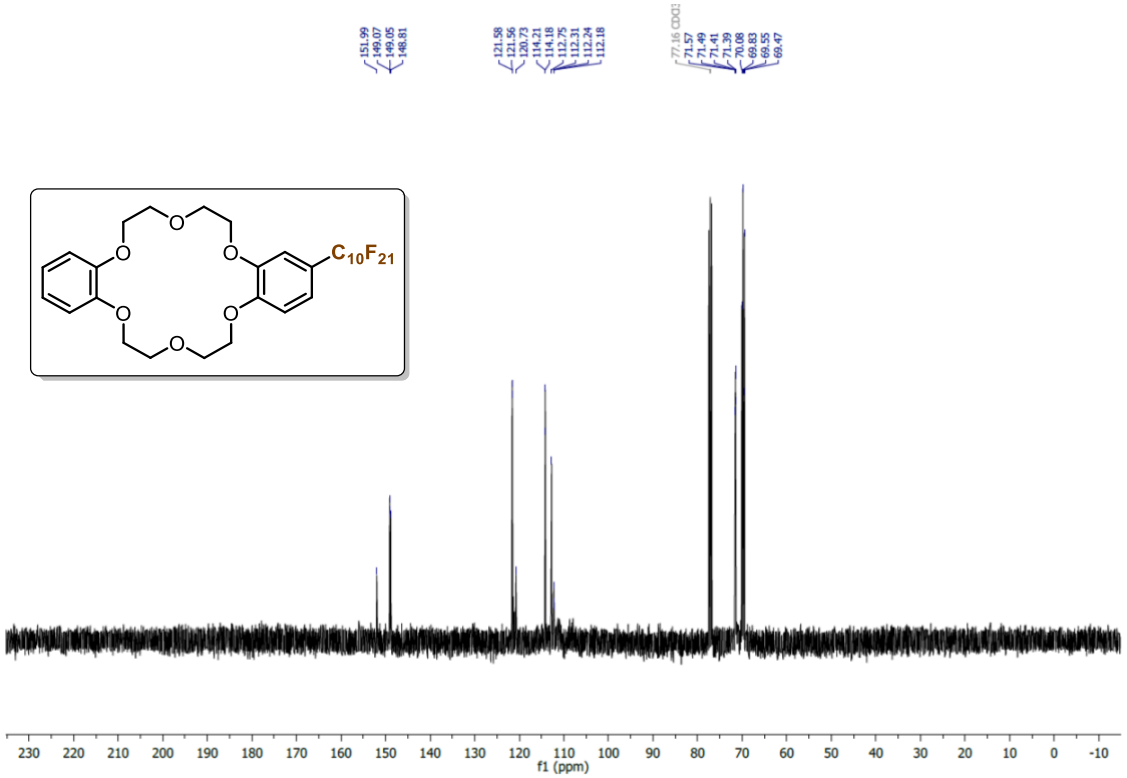



**Figure S45** – $^{13}$C NMR spectrum of **12** (Chloroform-*d,* 298 K, 125 MHz).

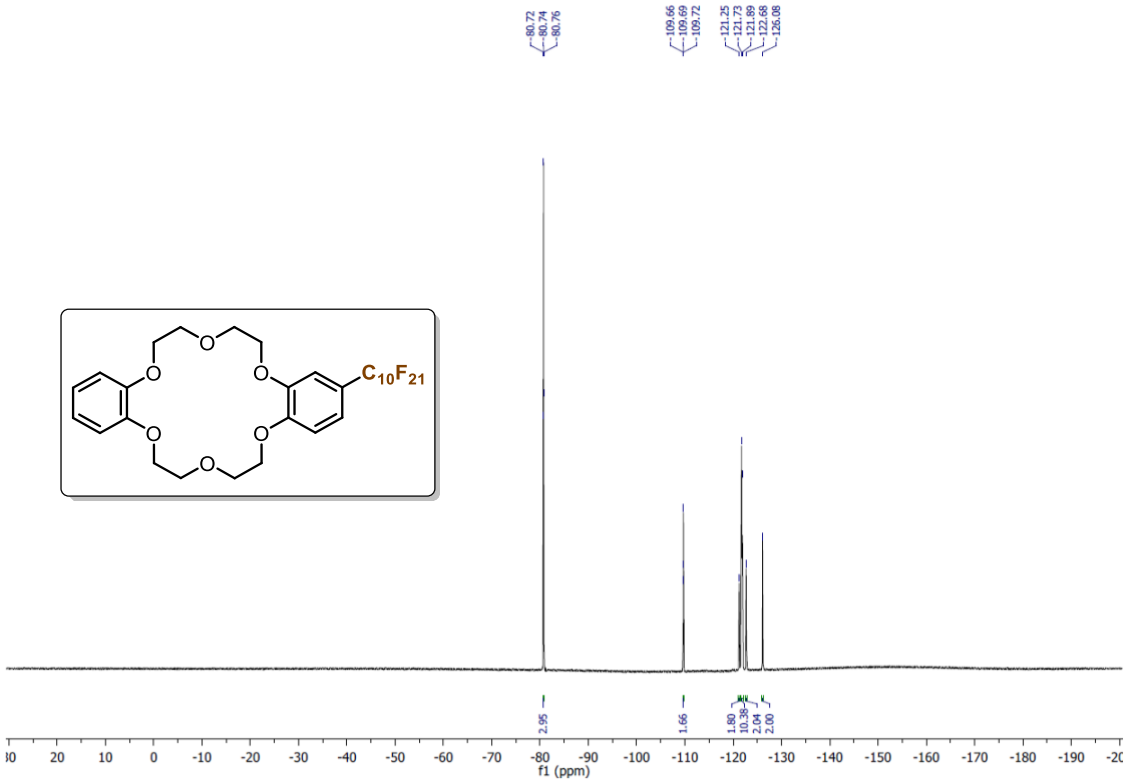



**Figure S46** – $^{19}$F NMR spectrum of **12** (Chloroform-*d,* 298 K, 470.585 MHz).

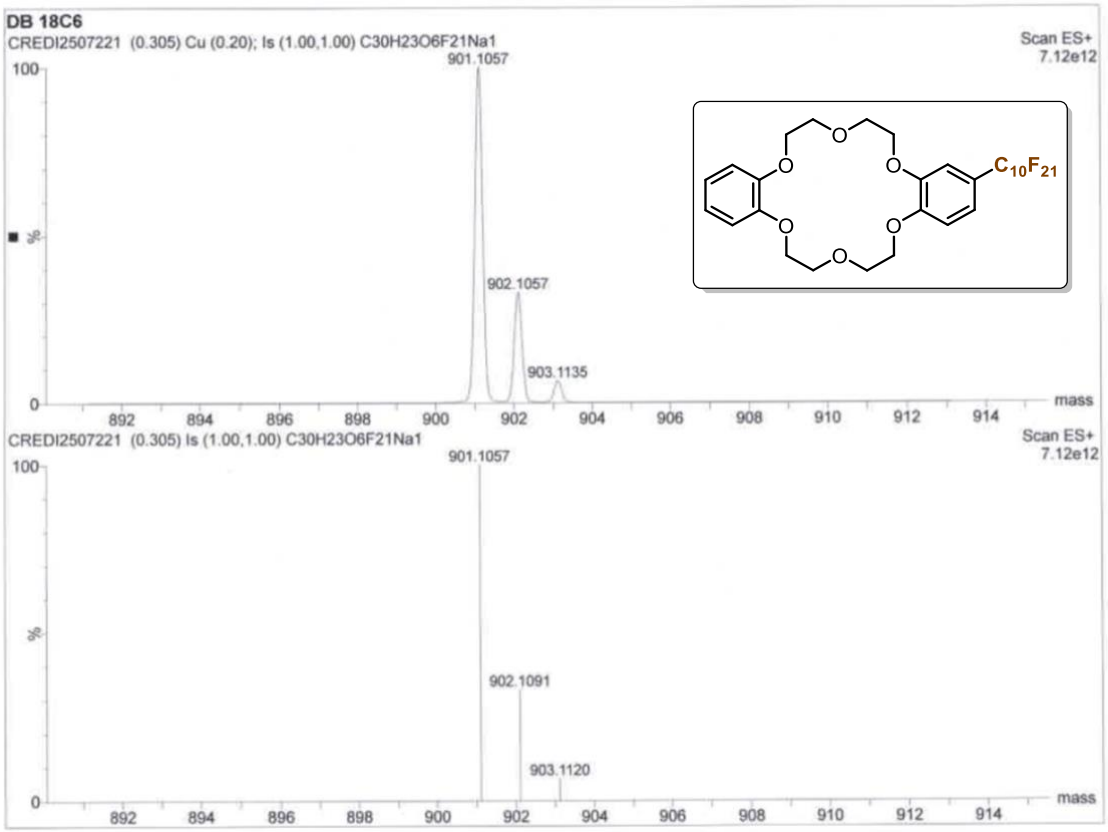



**Figure S47** – HRMS (ESI) spectrum of **12.**

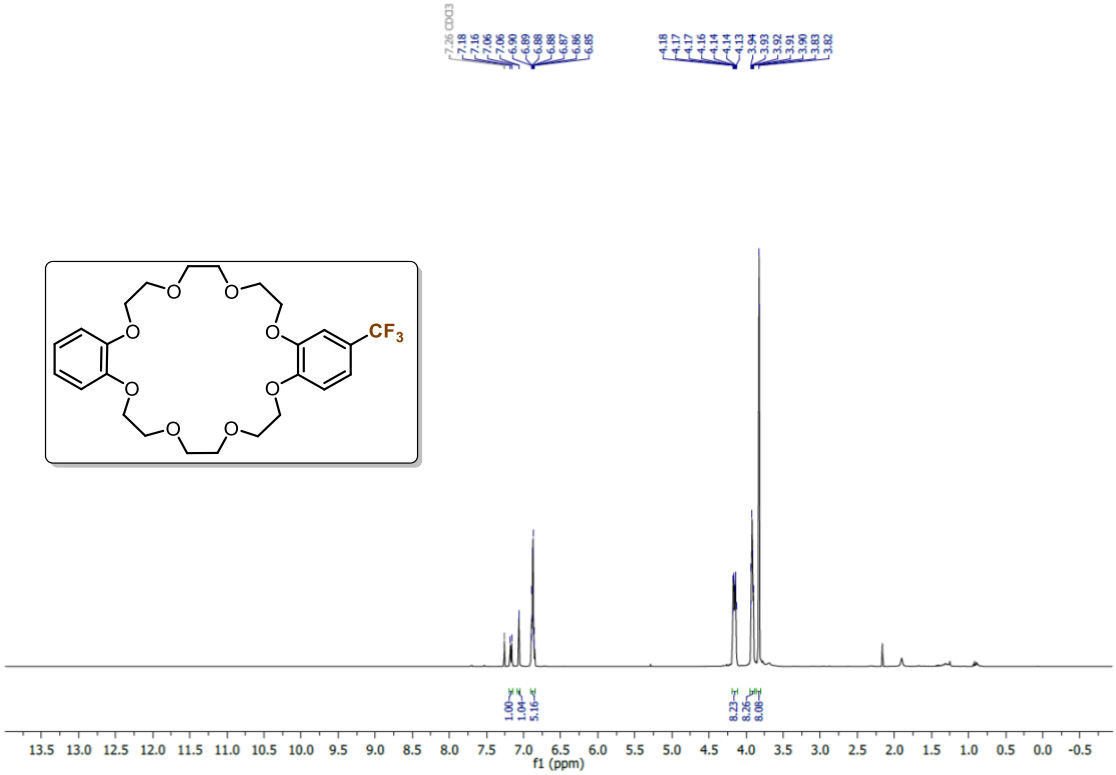



**Figure S48** – $^{1}$H NMR spectrum of **13** (Chloroform-*d,* 298 K, 500 MHz).

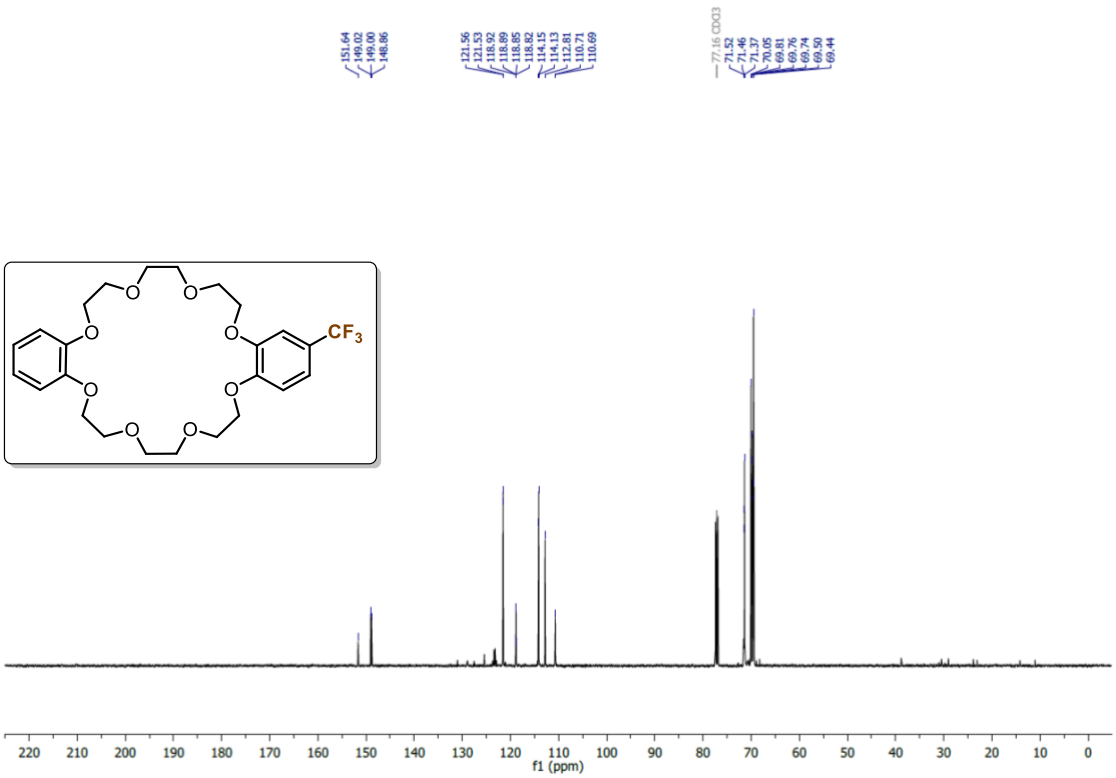



**Figure S49** – $^{13}$C NMR spectrum of **13** (Chloroform-*d,* 298 K, 125 MHz).

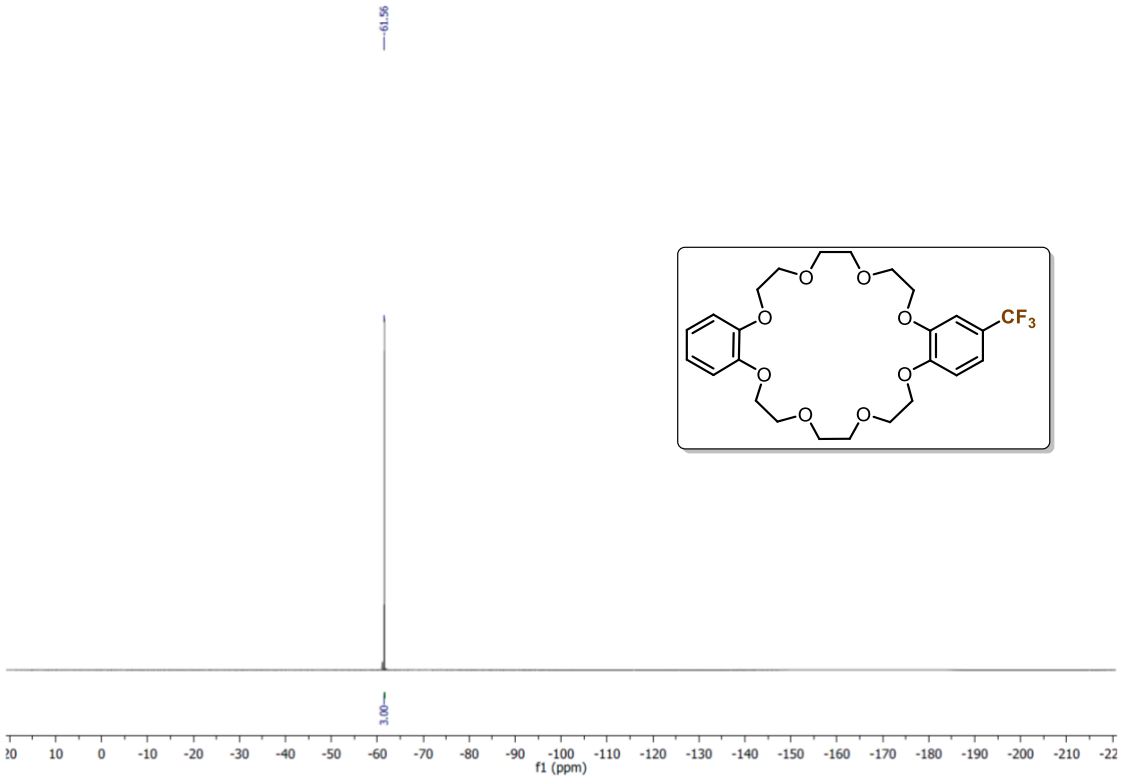



**Figure S50** – $^{19}$F NMR spectrum of **13** (Chloroform-*d,* 298 K, 470.585 MHz).

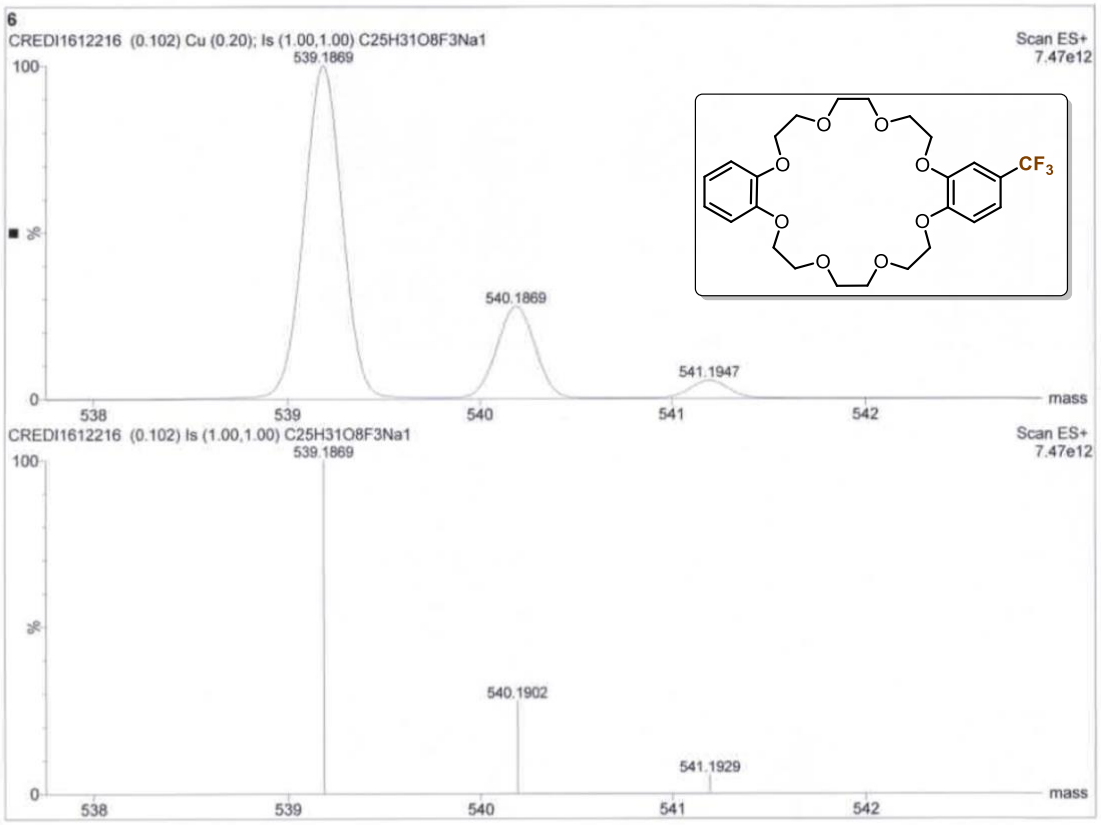



**Figure S51** – HRMS (ESI) spectrum of **13.**

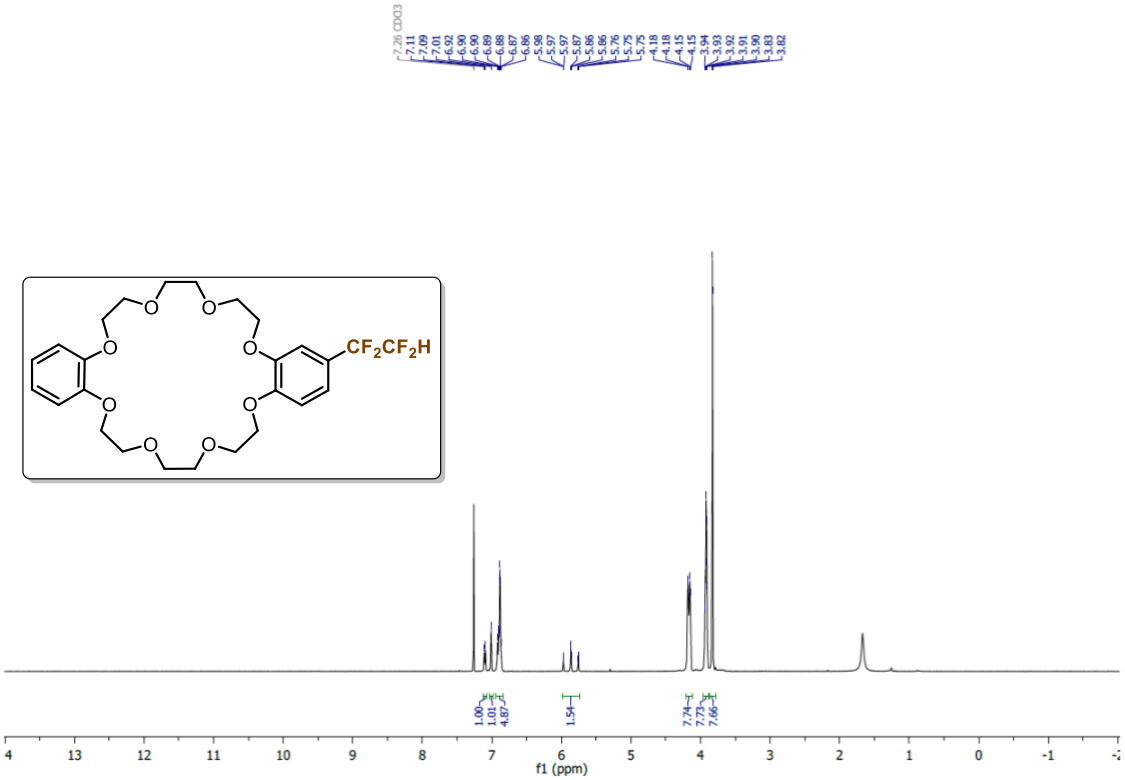



**Figure S52** – $^{1}$H NMR spectrum of **14** (Chloroform-*d*, 298 K, 500 MHz).

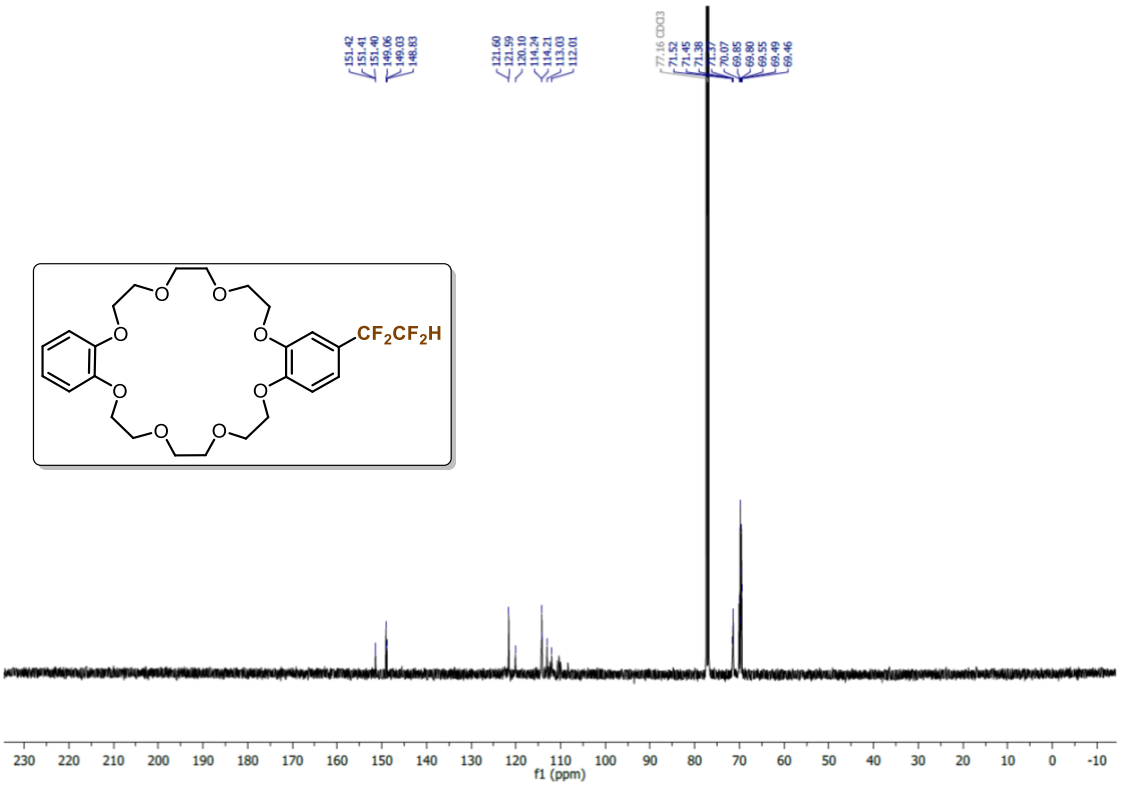



**Figure S53** – $^{13}$C NMR spectrum of **14** (Chloroform-*d,* 298 K, 125 MHz).

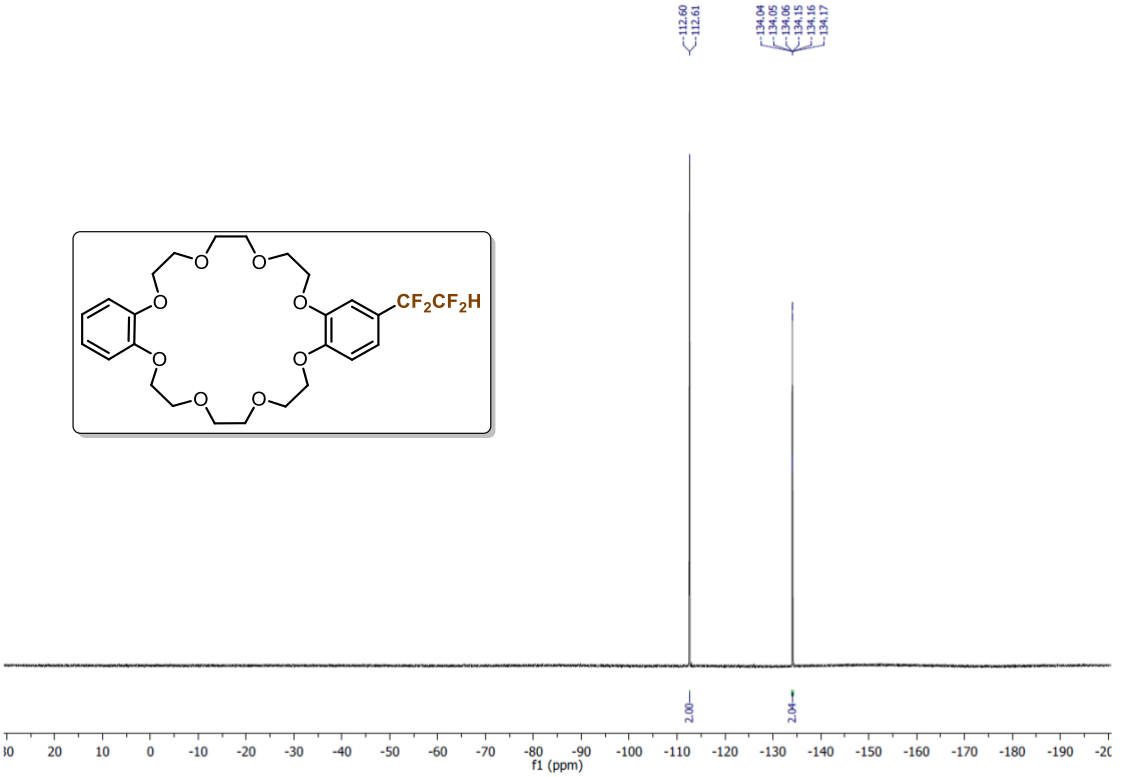



**Figure S54** – $^{19}$F NMR spectrum of **14** (Chloroform-*d,* 298 K, 470.585 MHz).

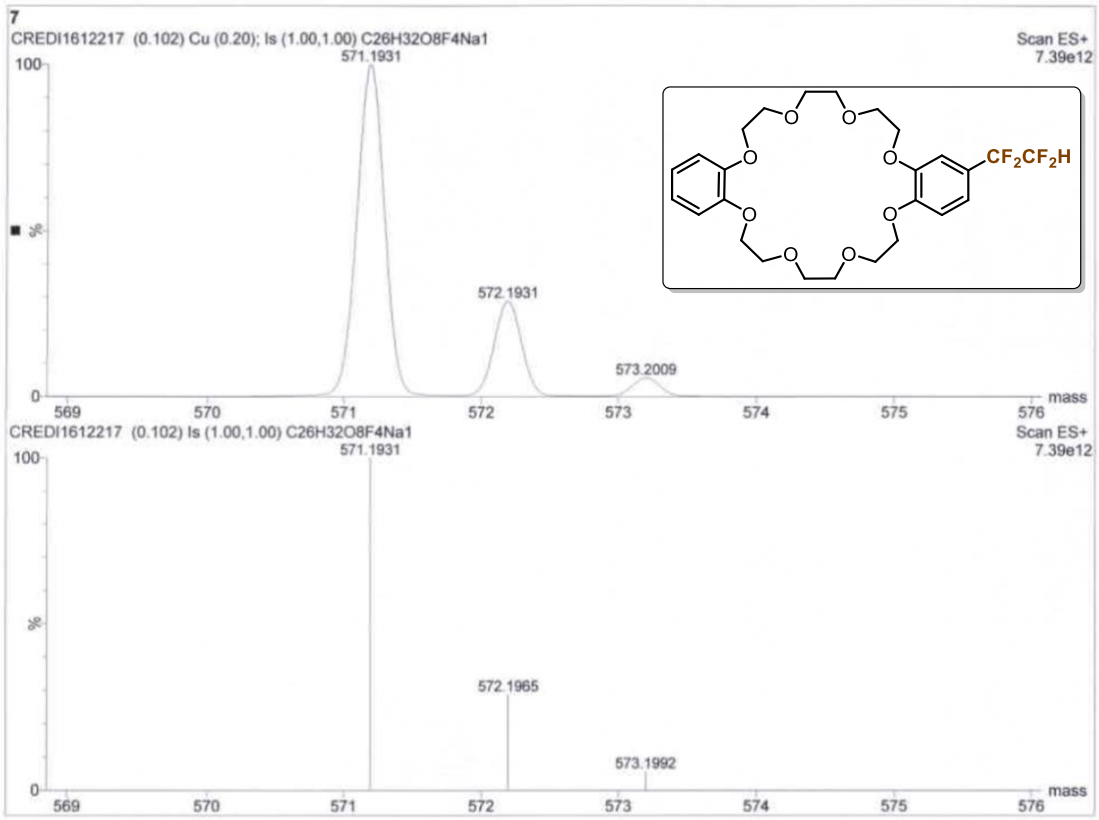



**Figure S55** – HRMS (ESI) spectrum of **14.**

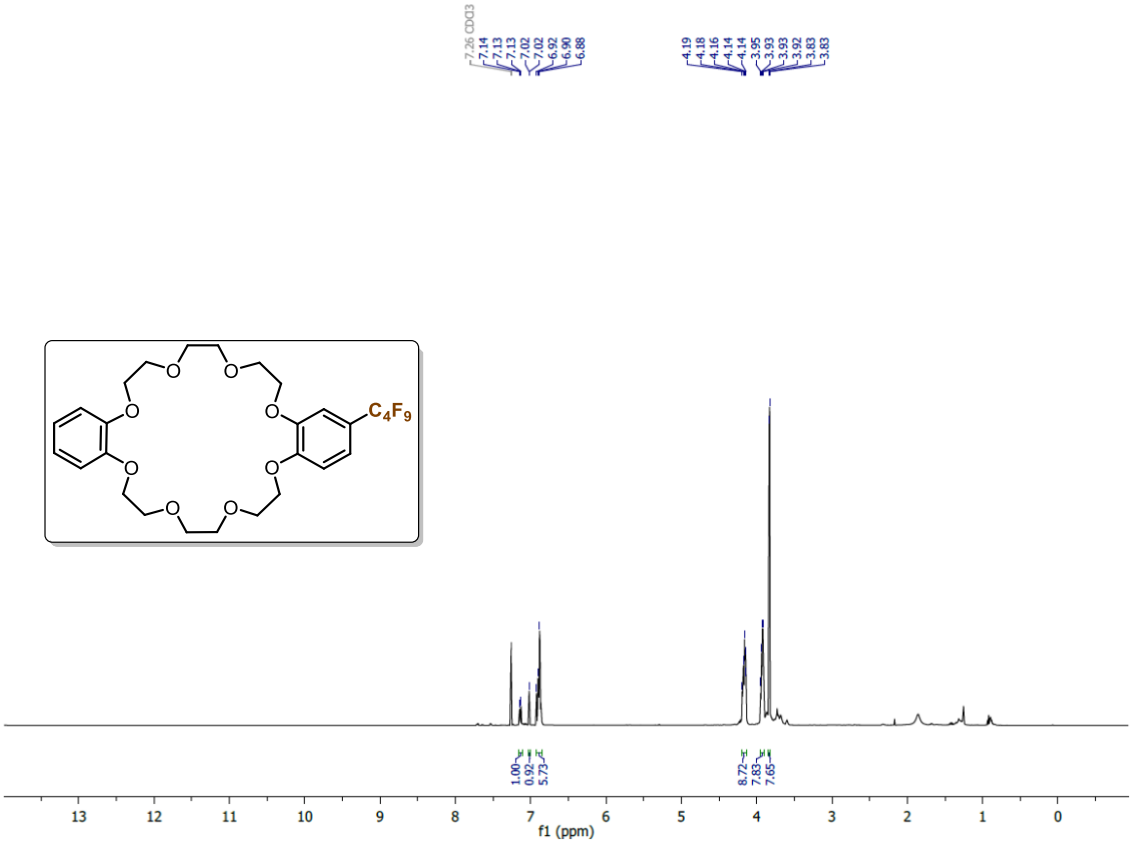



**Figure S56** – $^{1}$H NMR spectrum of **15** (Chloroform-*d,* 298 K, 500 MHz).

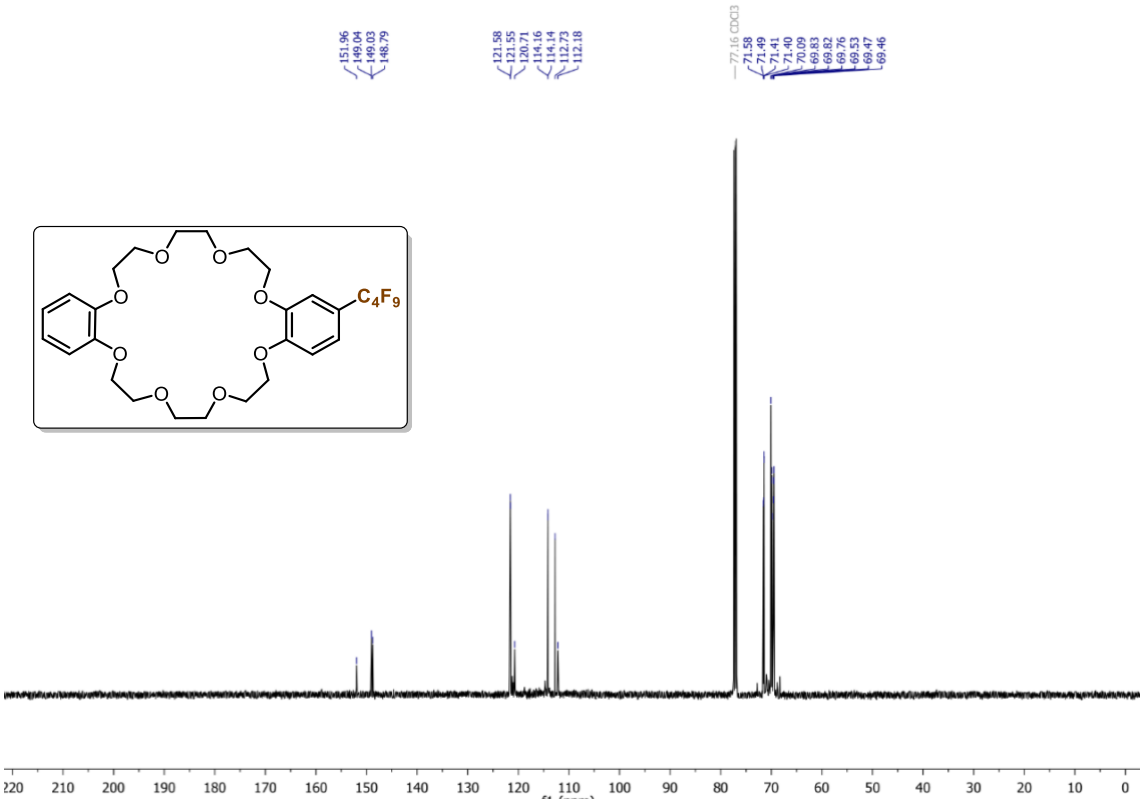



**Figure S57** – $^{13}$C NMR spectrum of **15** (Chloroform-*d,* 298 K, 125 MHz).

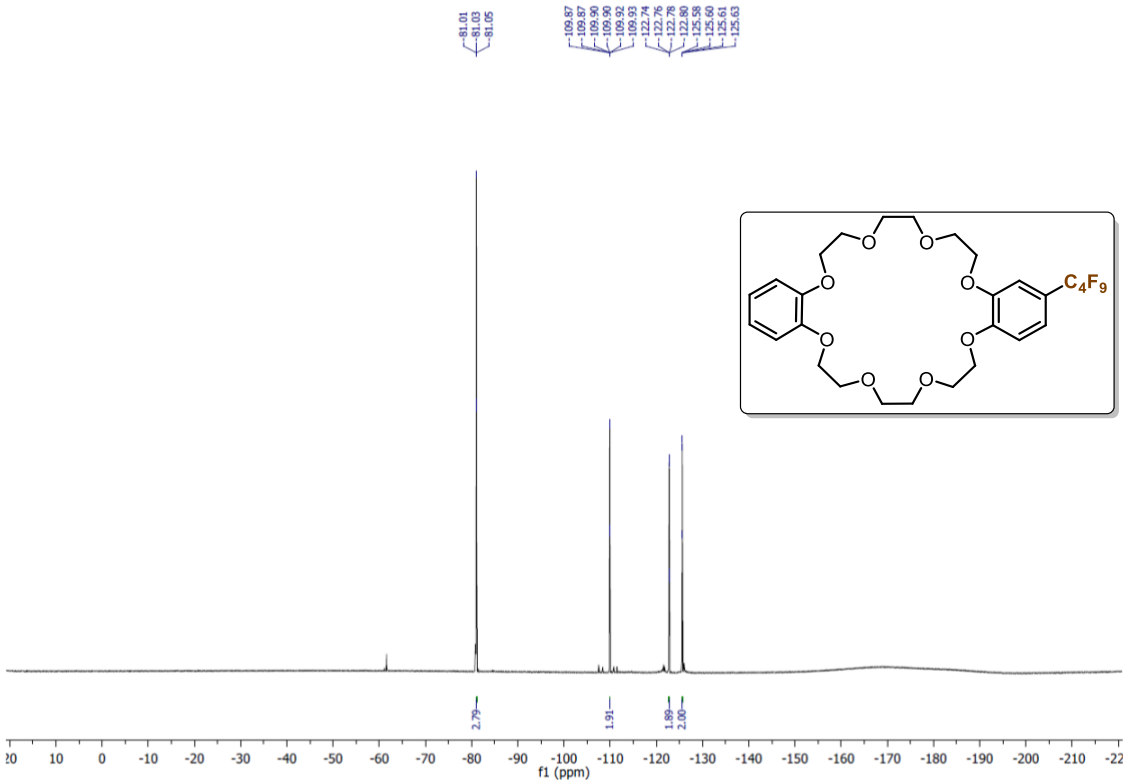



**Figure S58** – $^{19}$F NMR spectrum of **15** (Chloroform-*d,* 298 K, 470.585 MHz).

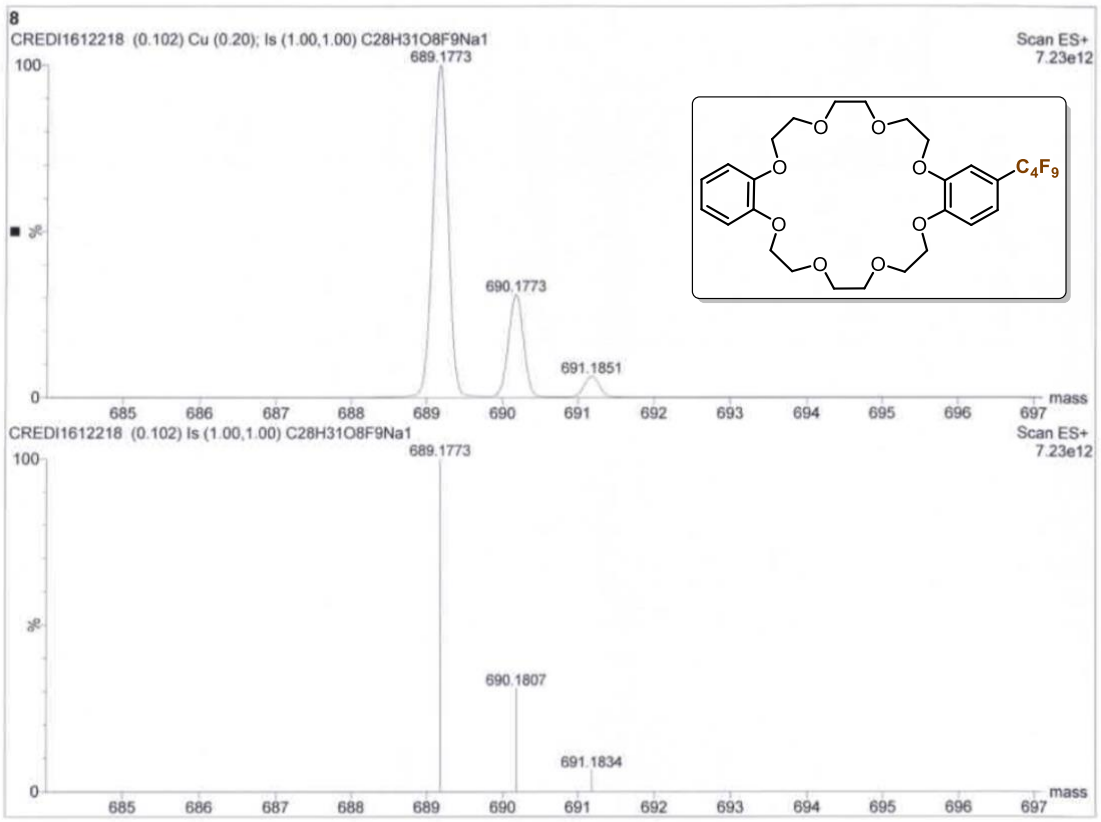



**Figure S59** – HRMS (ESI) spectrum of **15.**

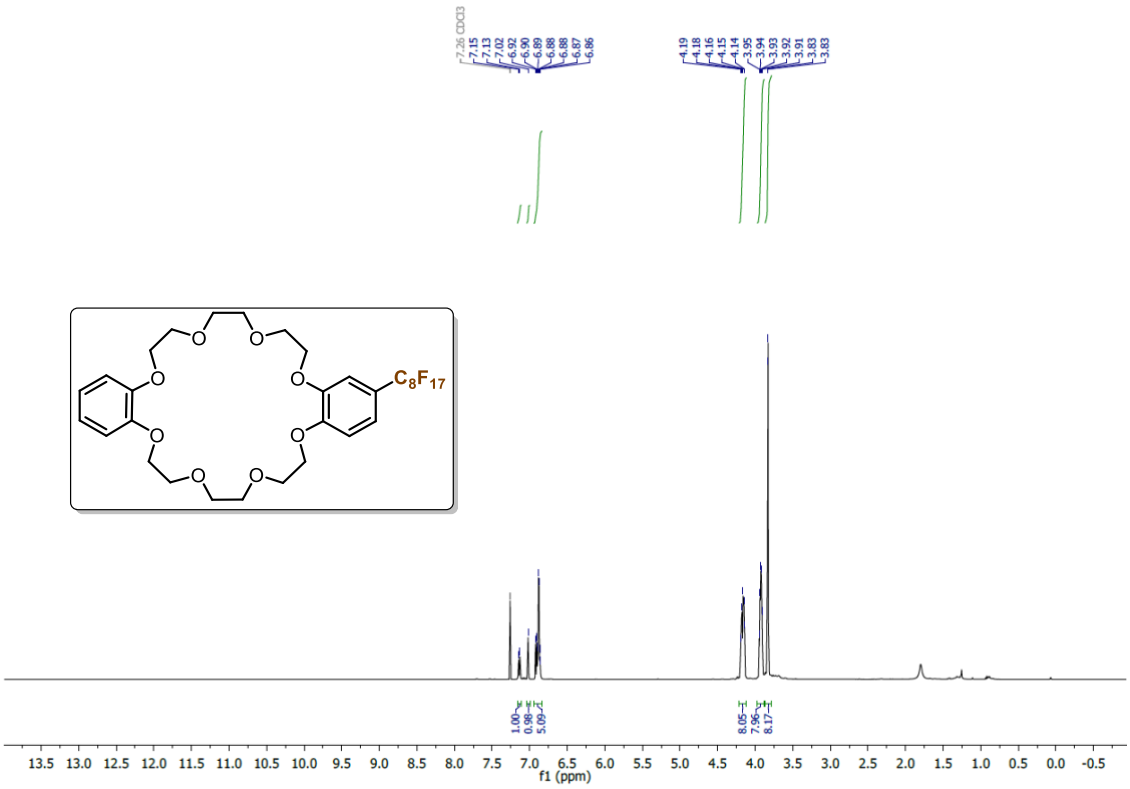



**Figure S60** – $^{1}$H NMR spectrum of **16** (Chloroform-*d,* 298 K, 500 MHz).

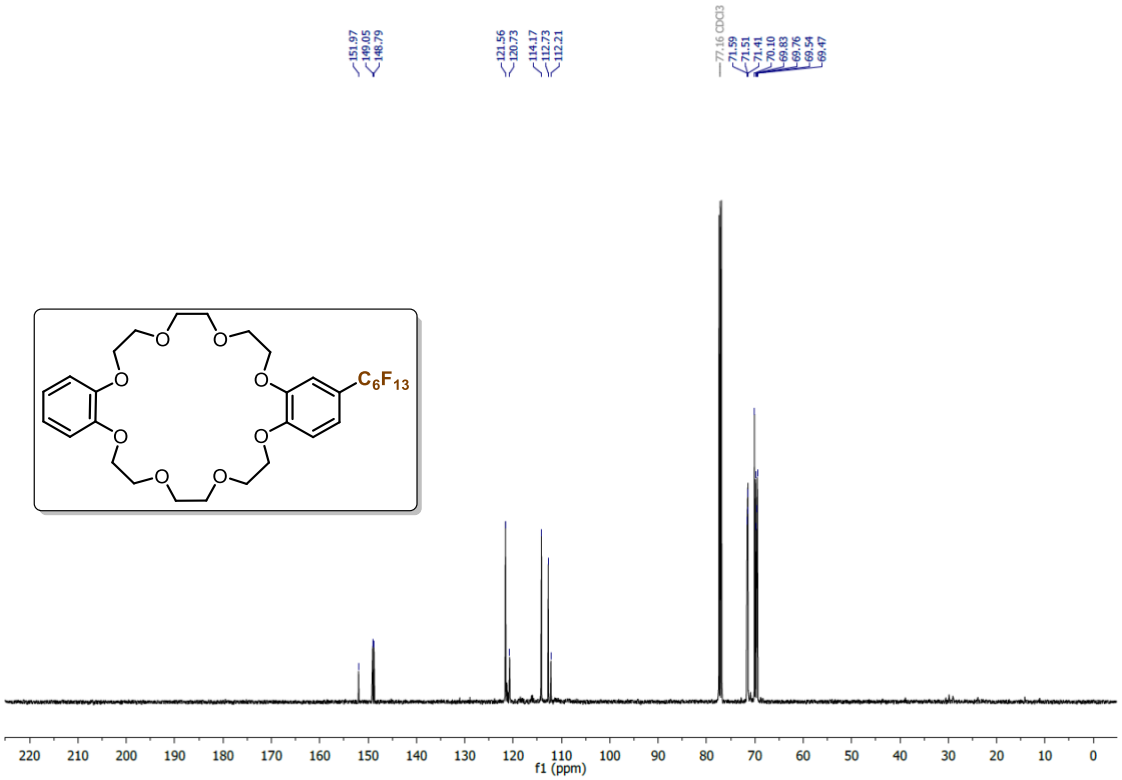



**Figure S61** – $^{13}$C NMR spectrum of **16** (Chloroform-*d,* 298 K, 125 MHz).

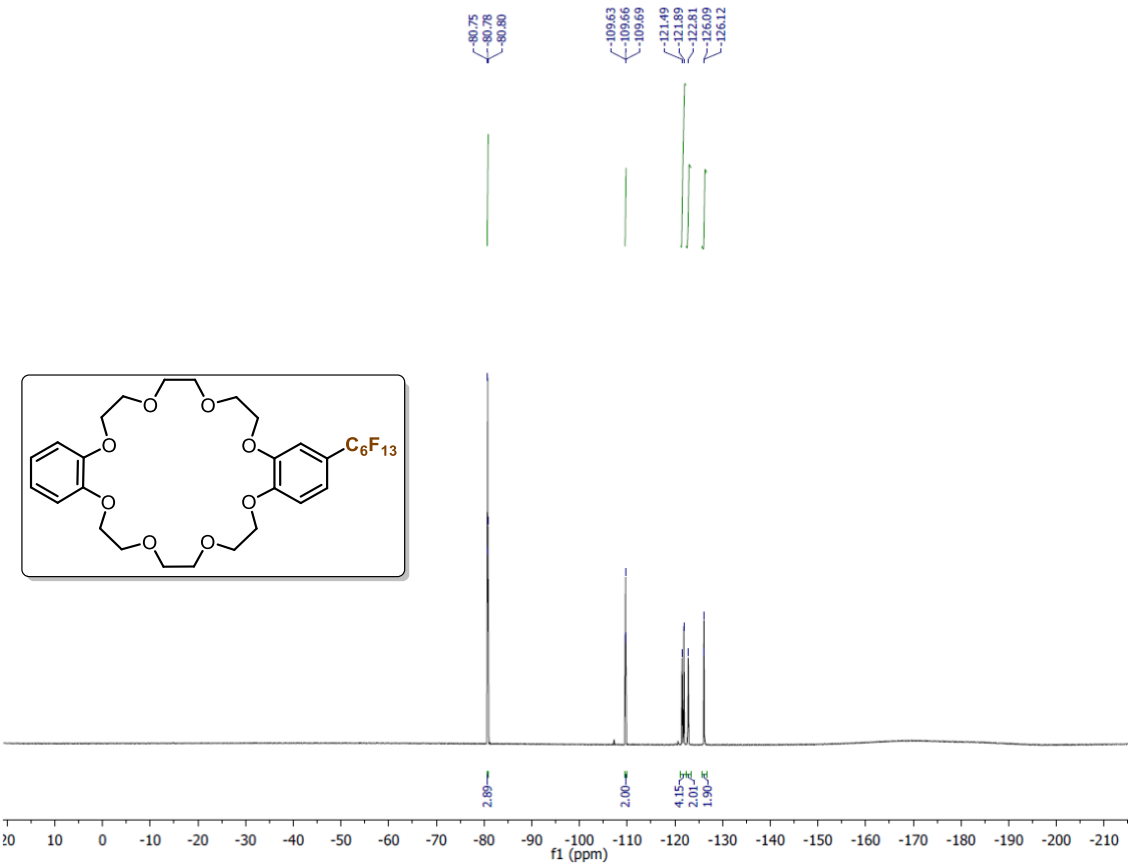



**Figure S62** – $^{19}$F NMR spectrum of **16** (Chloroform-*d,* 298 K, 470.585 MHz).

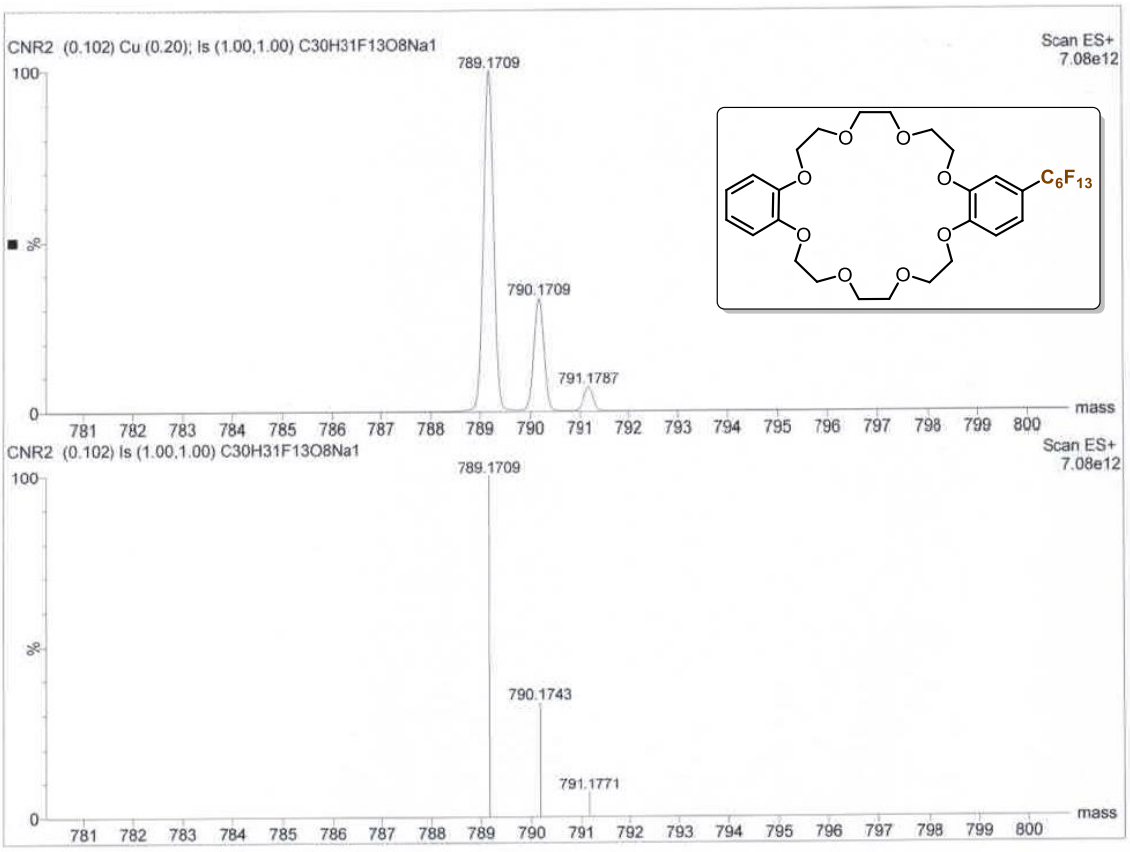



**Figure S63** – HRMS (ESI) spectrum of **16.**

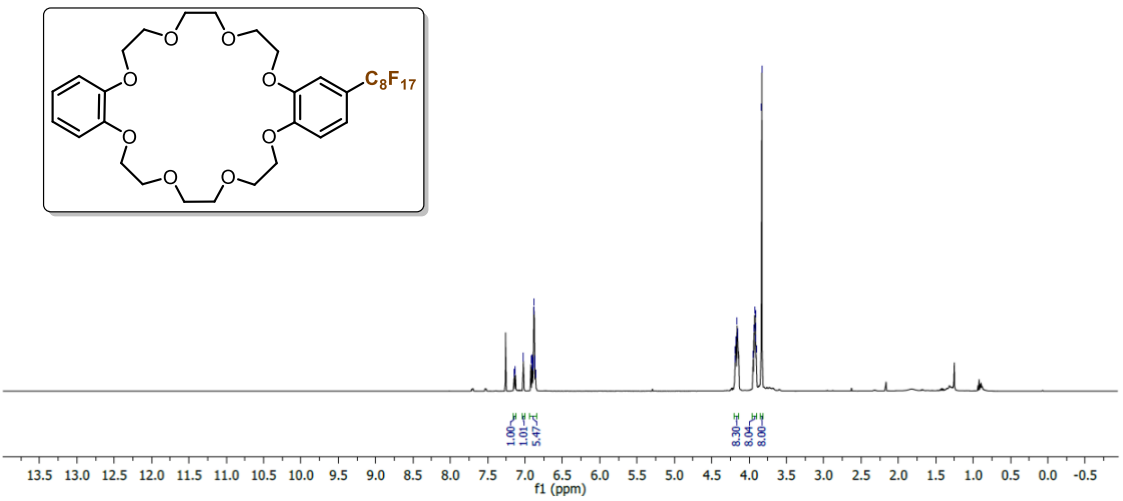



**Figure S64** – $^{1}$H NMR spectrum of **17** (Chloroform-*d,* 298 K, 500 MHz).

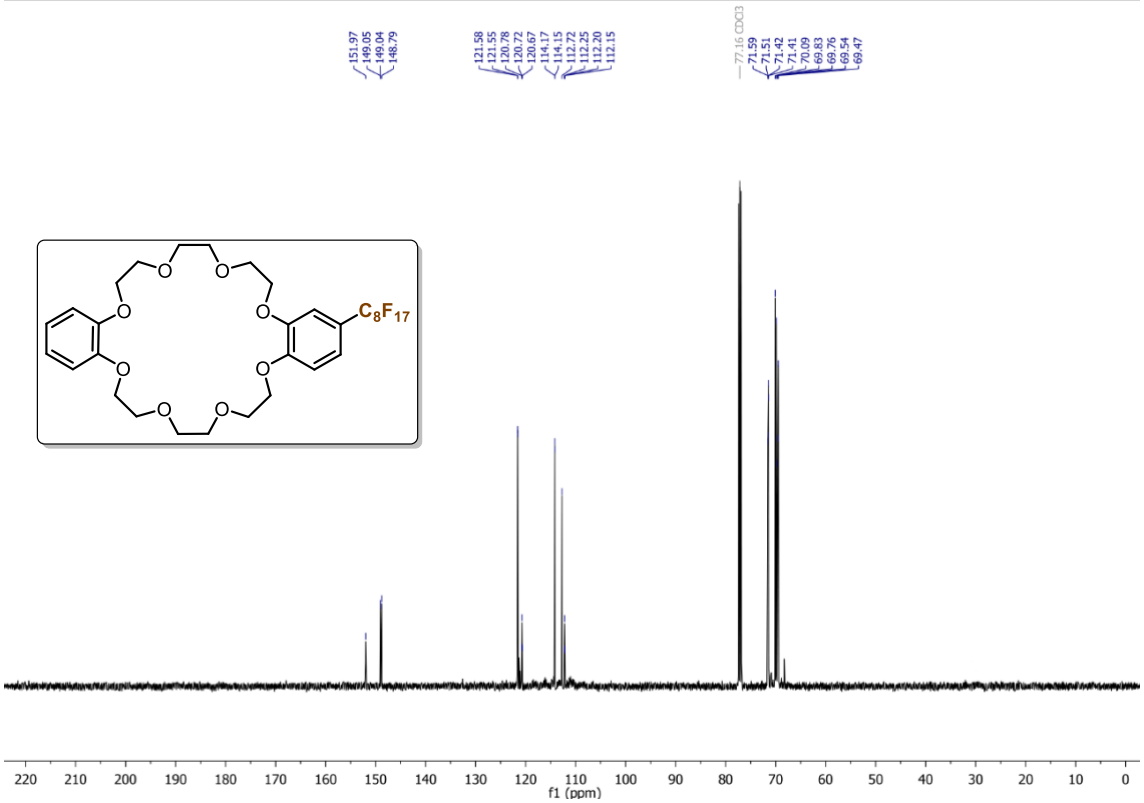



**Figure S65** – $^{13}$C NMR spectrum of **17** (Chloroform-*d,* 298 K, 125 MHz).

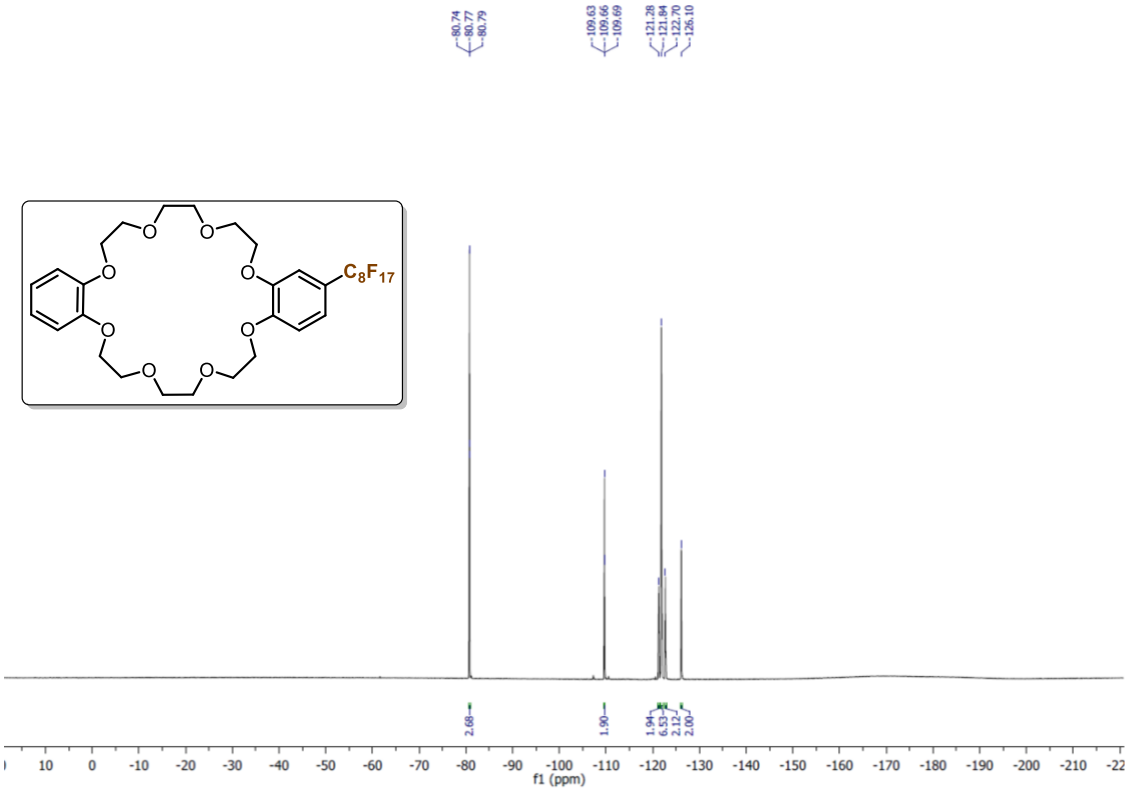



**Figure S66** – $^{19}$F NMR spectrum of **17** (Chloroform-*d,* 298 K, 470.585 MHz).

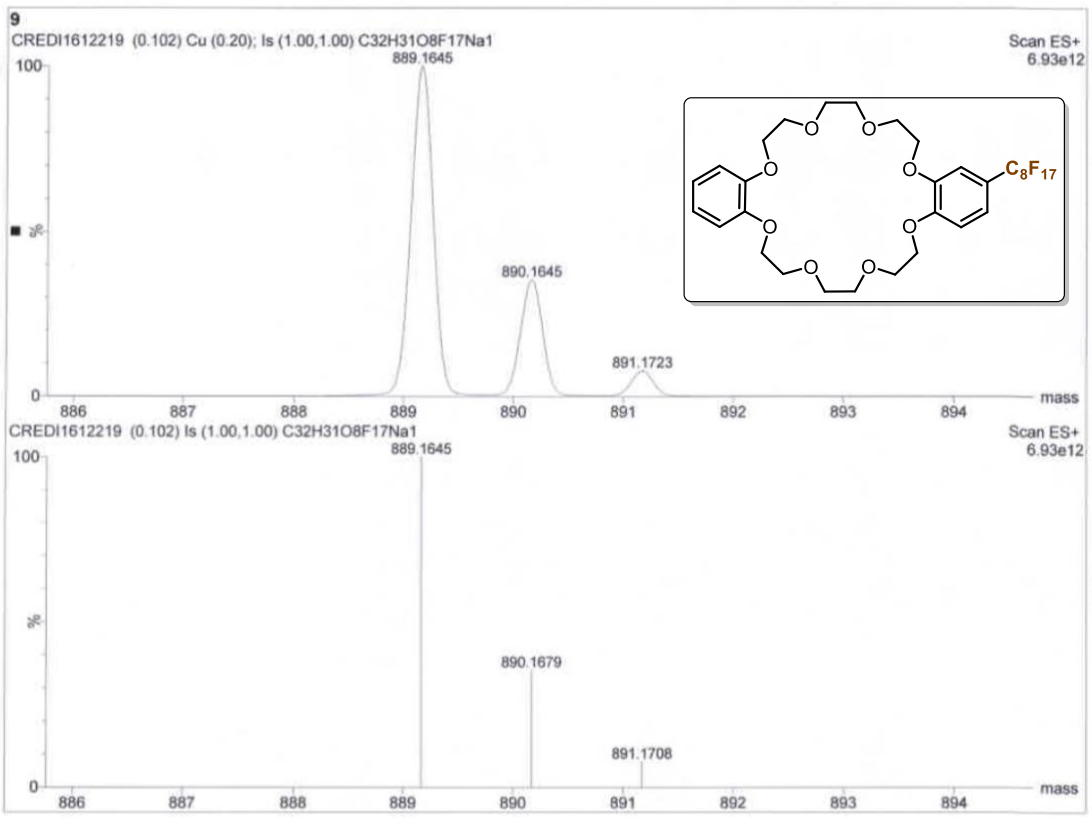



**Figure S67** – HRMS (ESI) spectrum of **17.**

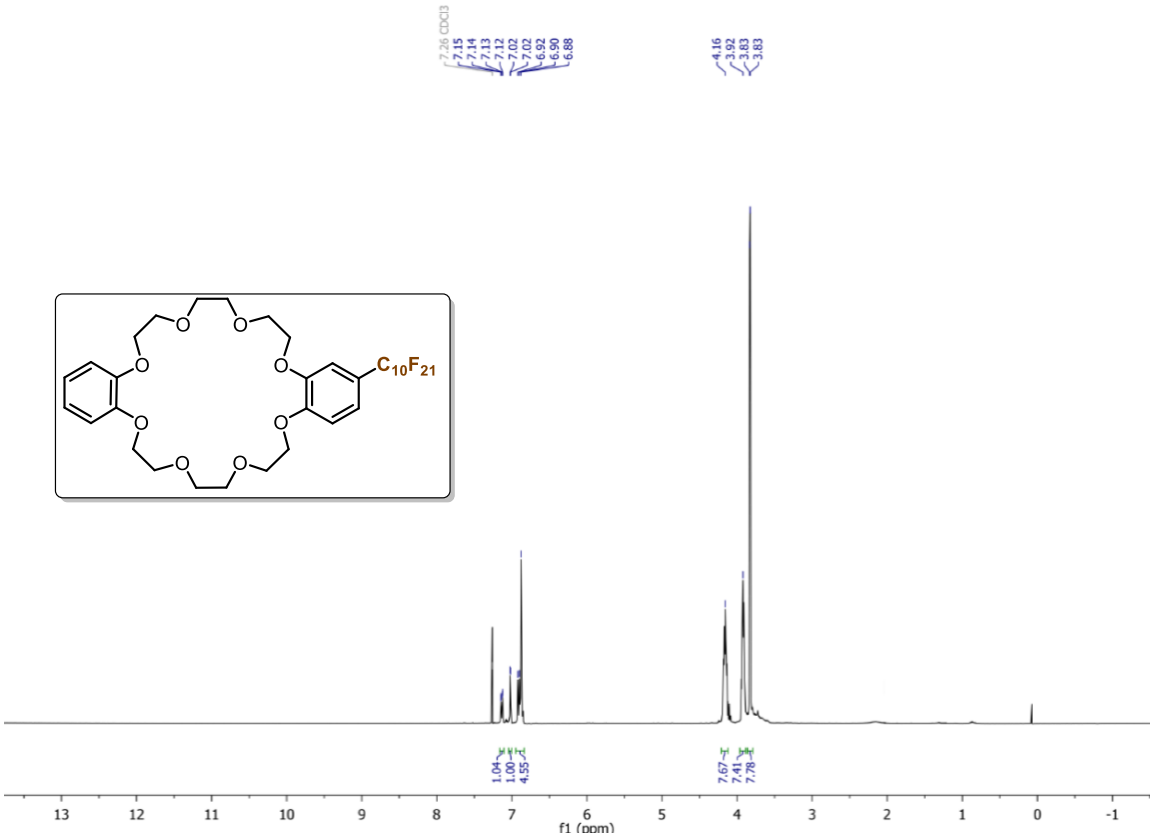



**Figure S68** – $^{1}$H NMR spectrum of **18** (Chloroform-*d,* 298 K, 500 MHz).

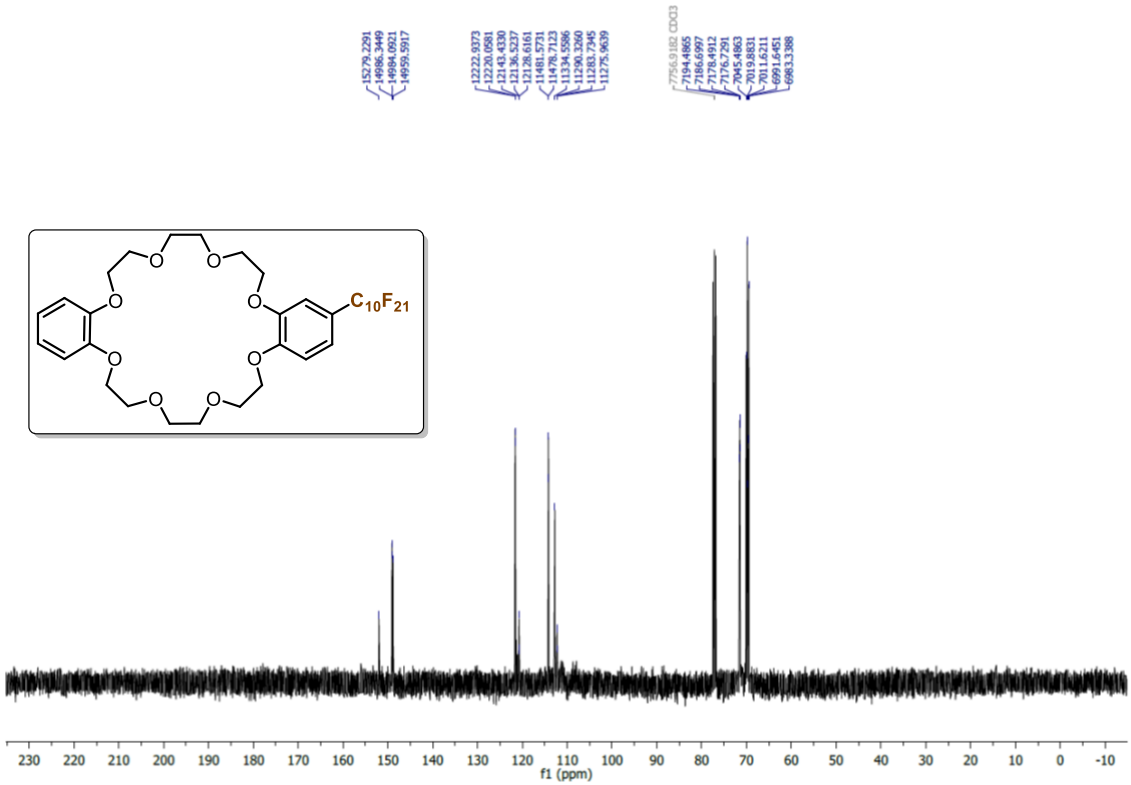



**Figure S69** – $^{13}$C NMR spectrum of **18** (Chloroform-*d,* 298 K, 125 MHz).

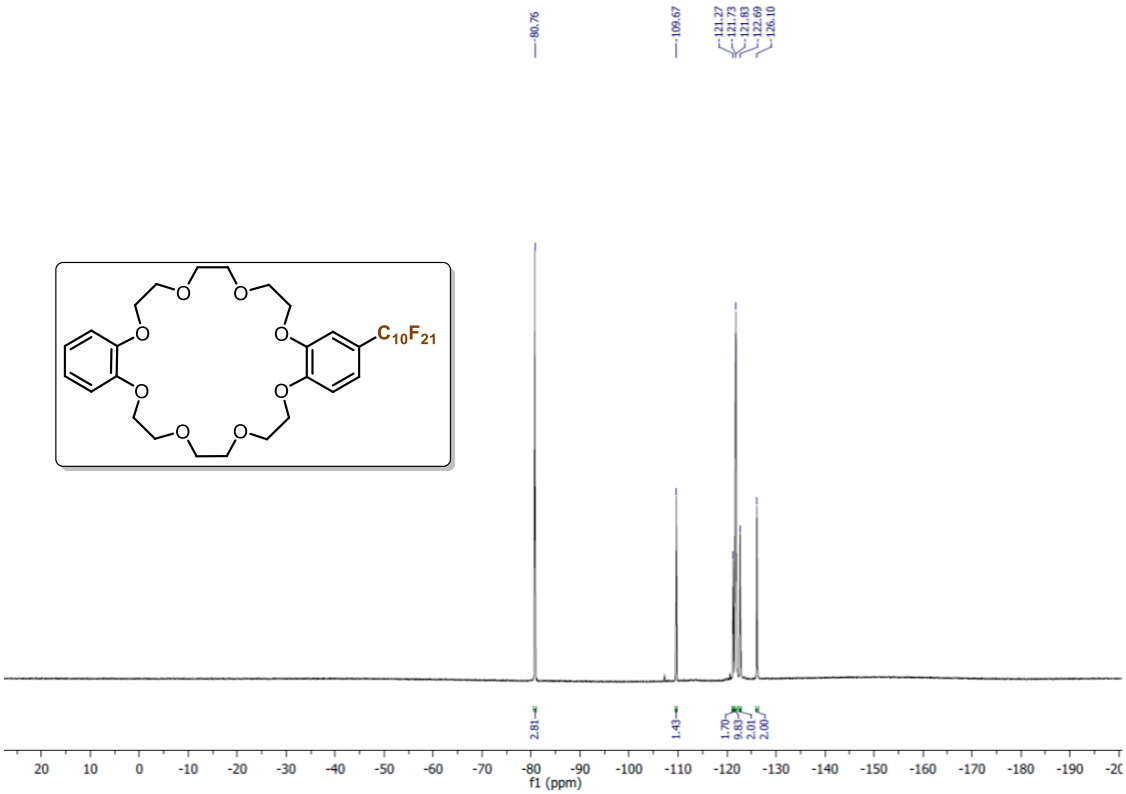



**Figure S70** – $^{19}$F NMR spectrum of **18** (Chloroform-*d,* 298 K, 470.585 MHz).

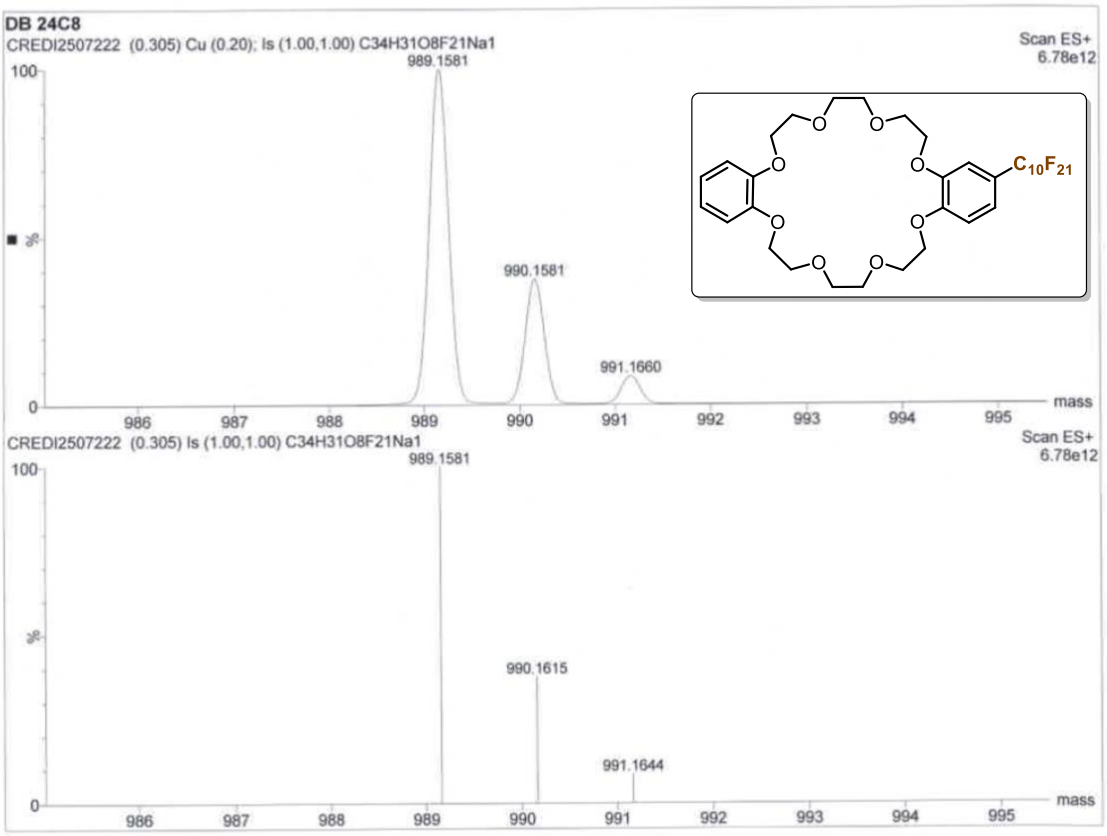



**Figure S71** – HRMS (ESI) spectrum of **18.**

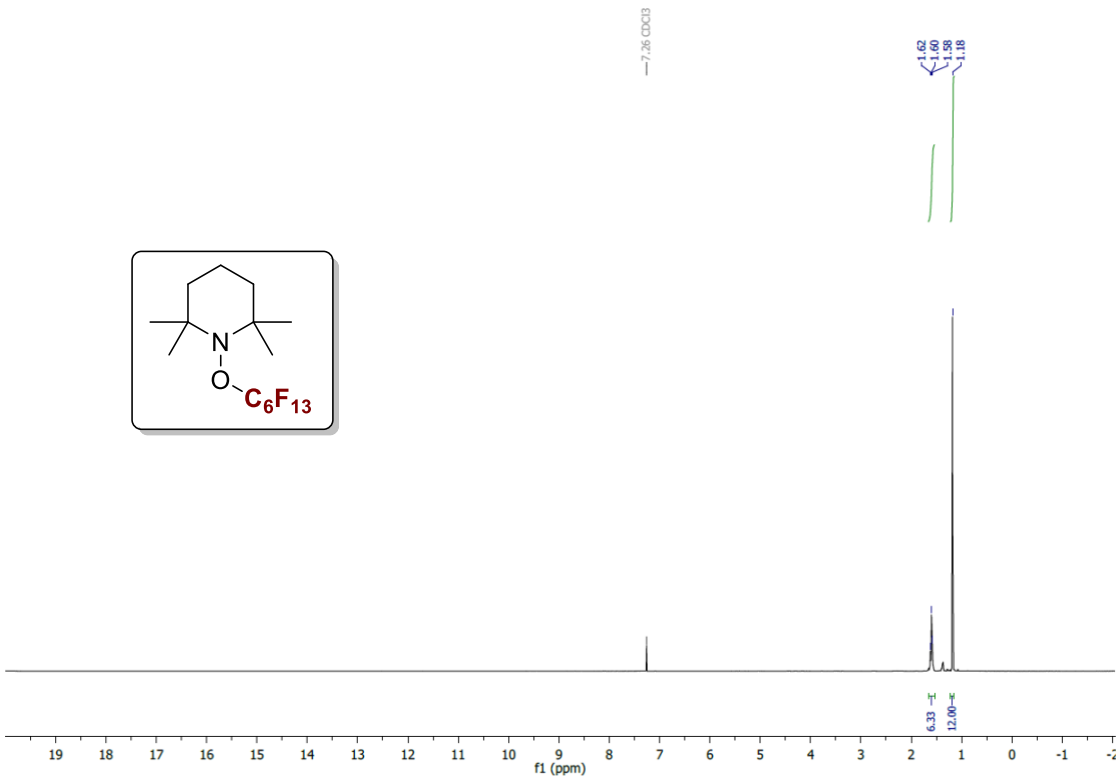



**Figure S76** – $^{1}$HNMR spectrum of **19** (Chloroform-*d,* 298 K, 600 MHz).

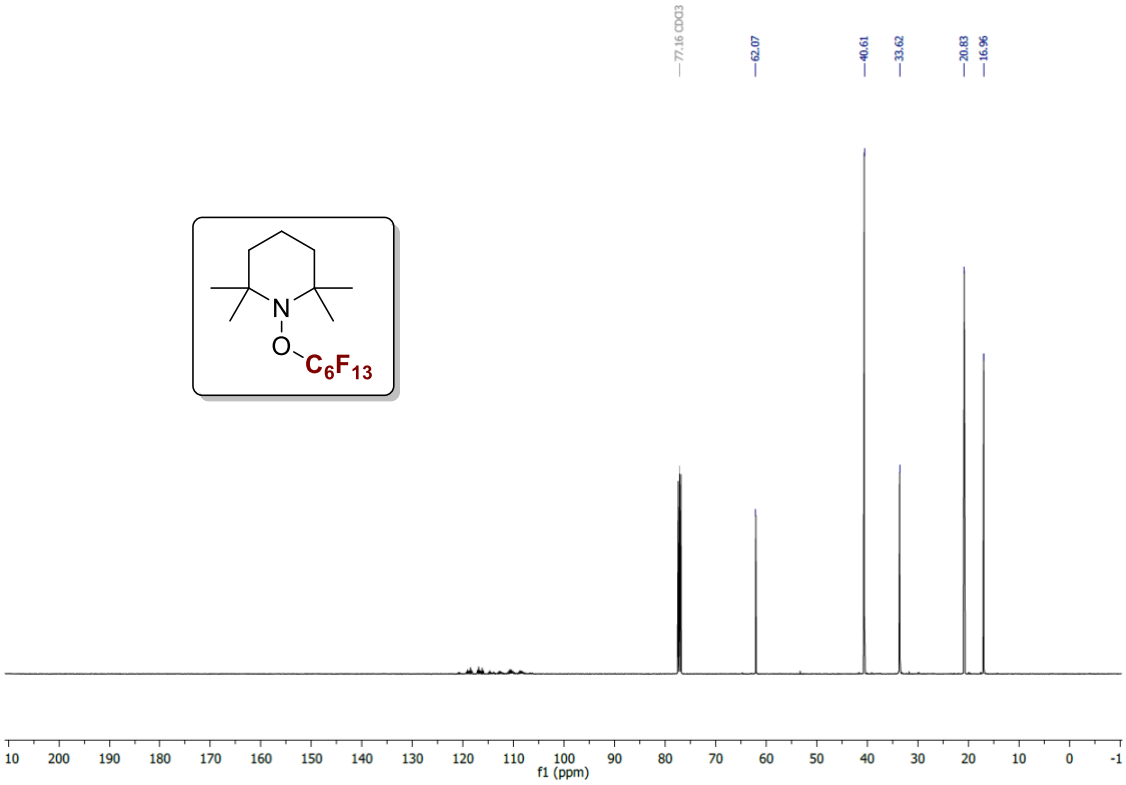



**Figure S77** – $^{13}$CNMR spectrum of **19** (Chloroform-*d,* 298 K, 125 MHz).

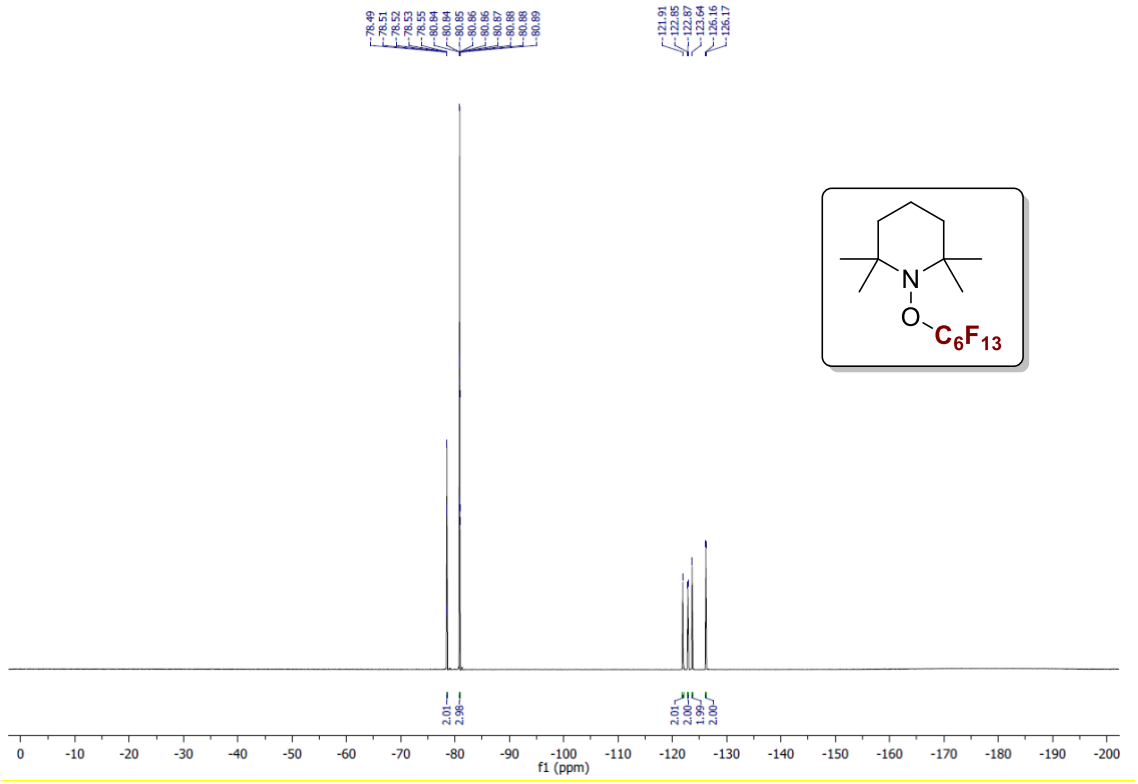



**Figure S78** – $^{19}$FNMR spectrum of **19** (Chloroform-*d,* 298 K, 470.585 MHz

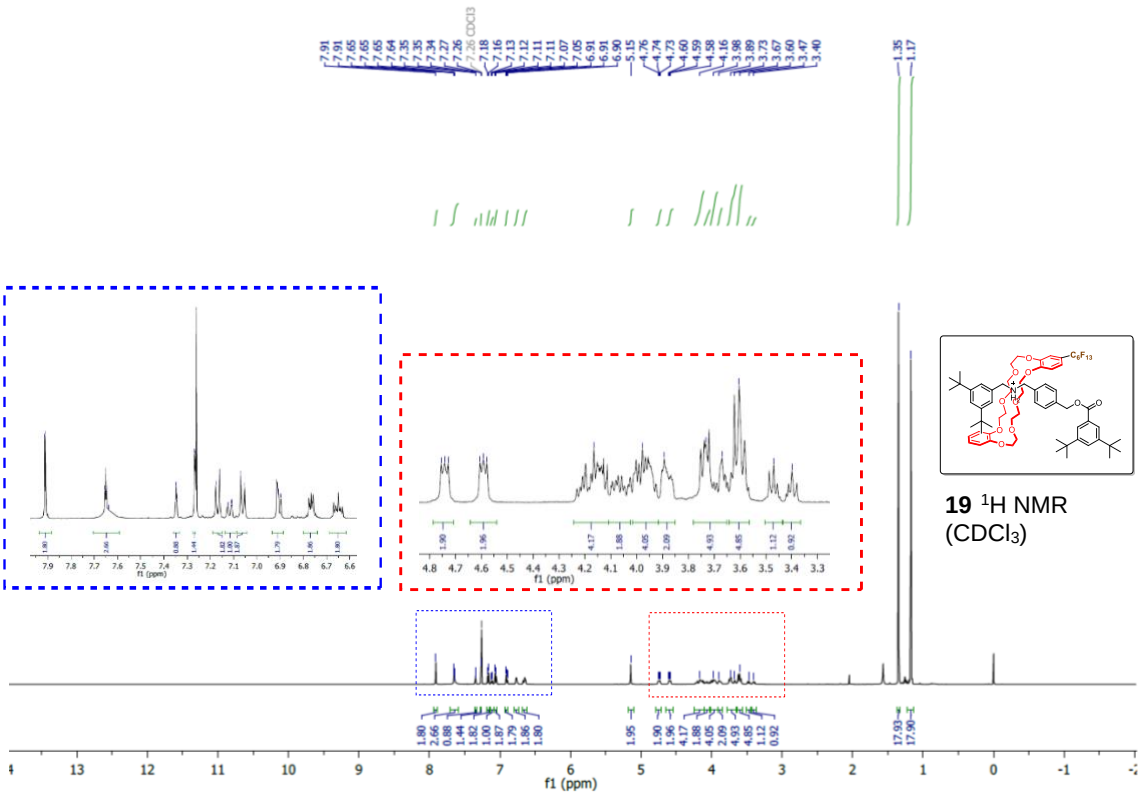



**Figure S72** – $^{1}$H NMR spectrum of **21** (Chloroform-*d*, 298 K, 500 MHz).

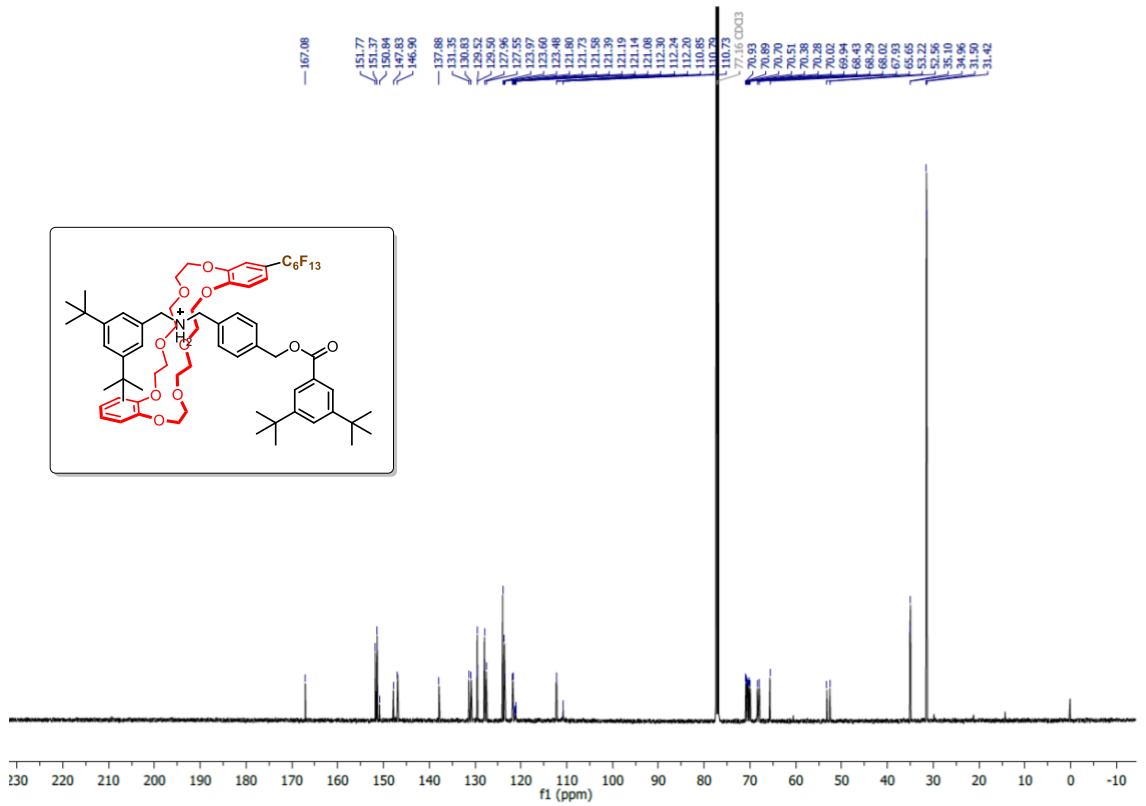



**Figure S73** – $^{13}$C NMR spectrum of **21** (Chloroform-*d*, 298 K, 125 MHz).

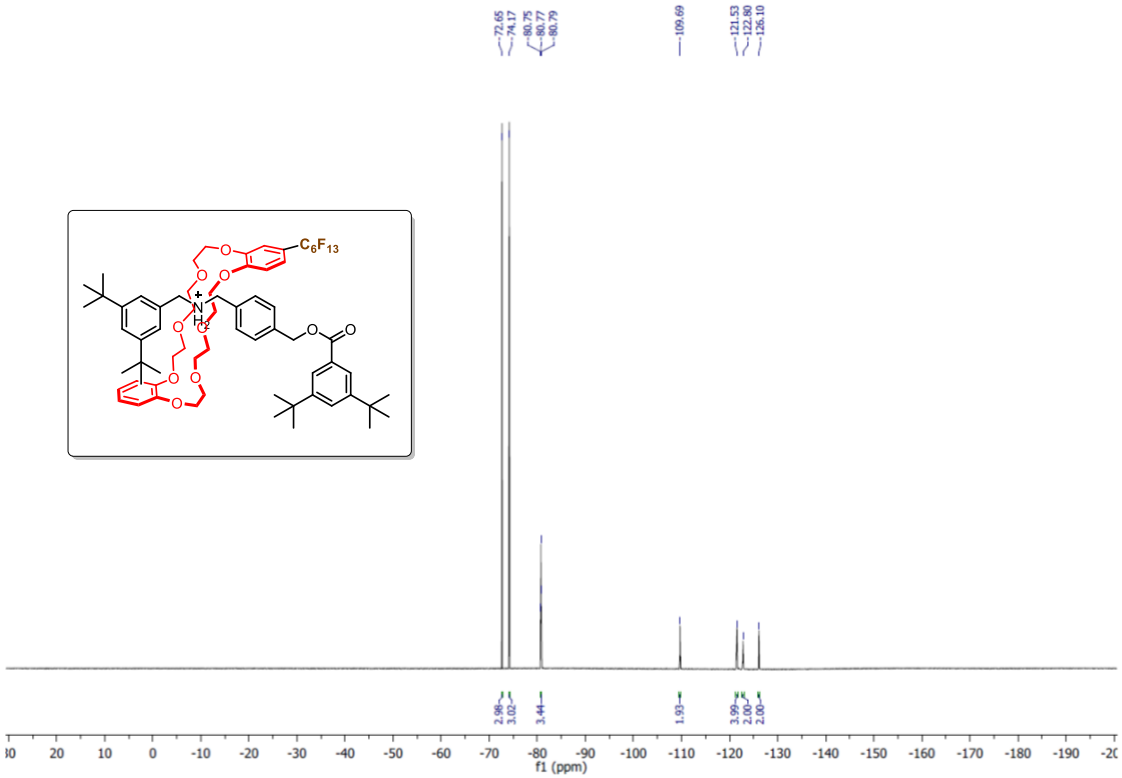



**Figure S74** – $^{19}$F NMR spectrum of **21** (Chloroform-*d,* 298 K, 470.585 MHz).

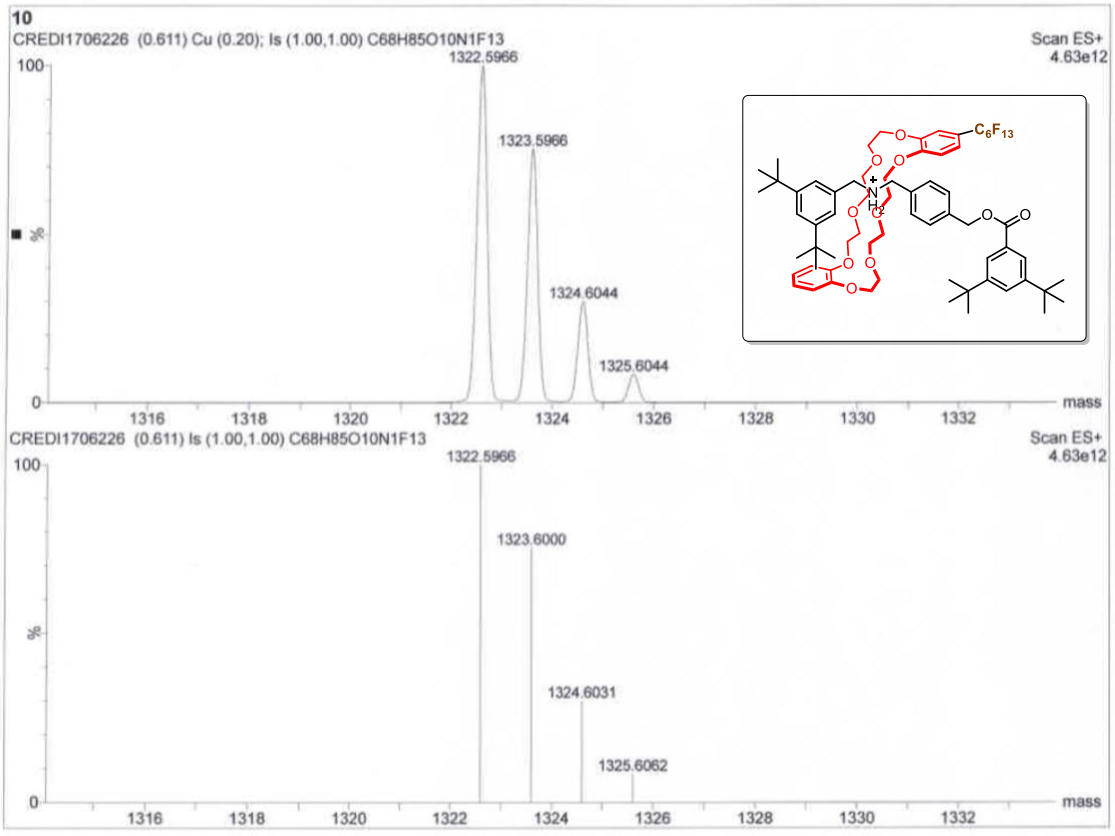



**Figure S75** – HRMS (ESI) spectrum of **21.**

## 10. References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