The Journal of Organic Chemistry

[2]Catenanes Displaying Switchable Gin Trap–Like Motion

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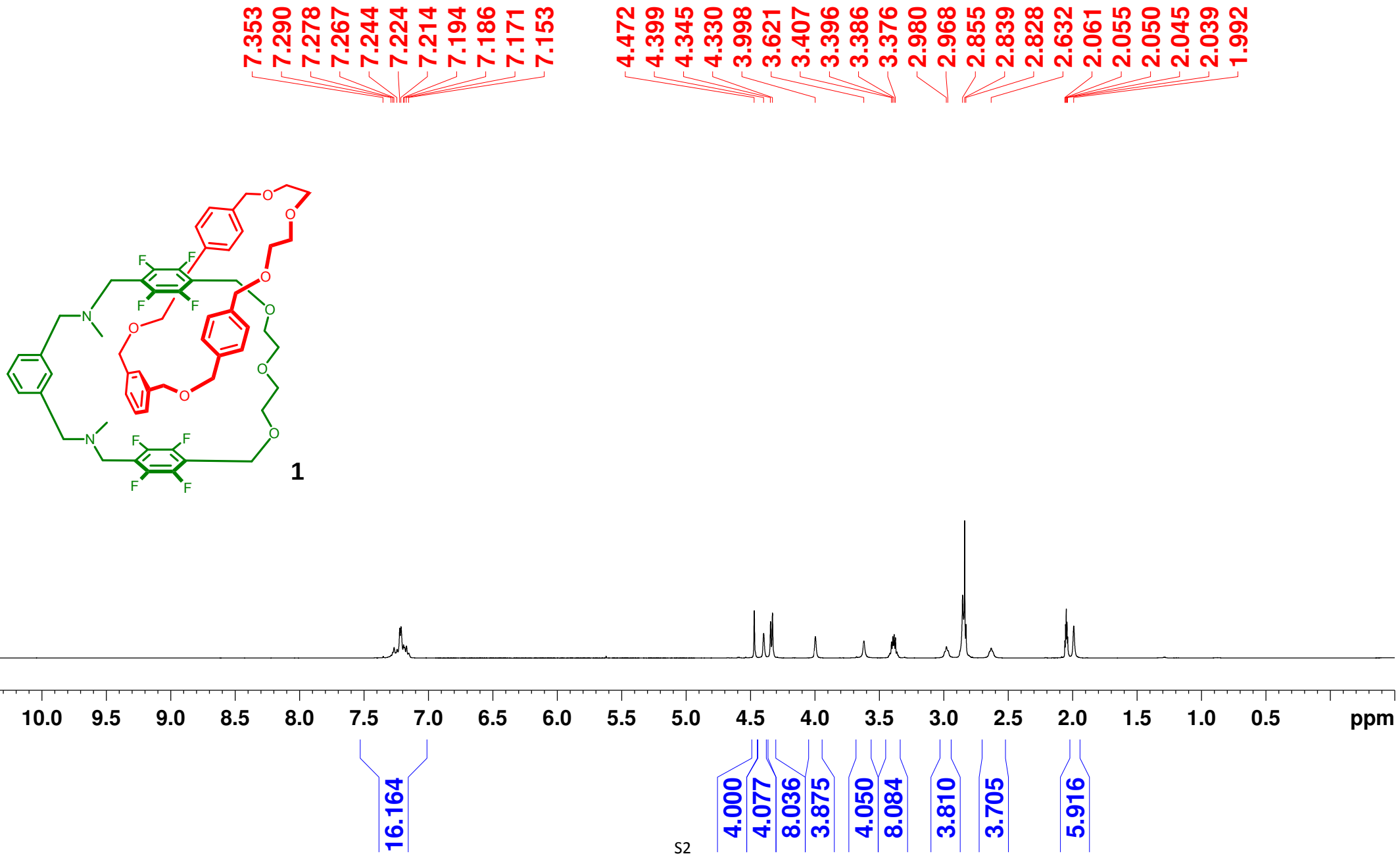
Supplementary Material

Page Numbers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4.345
4.330
3.998
3.621
3.407
3.396
3.386
3.376
2.980
2.968
2.855
2.839
2.828
2.632
2.061
2.055
2.050
2.045
2.039
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6.0
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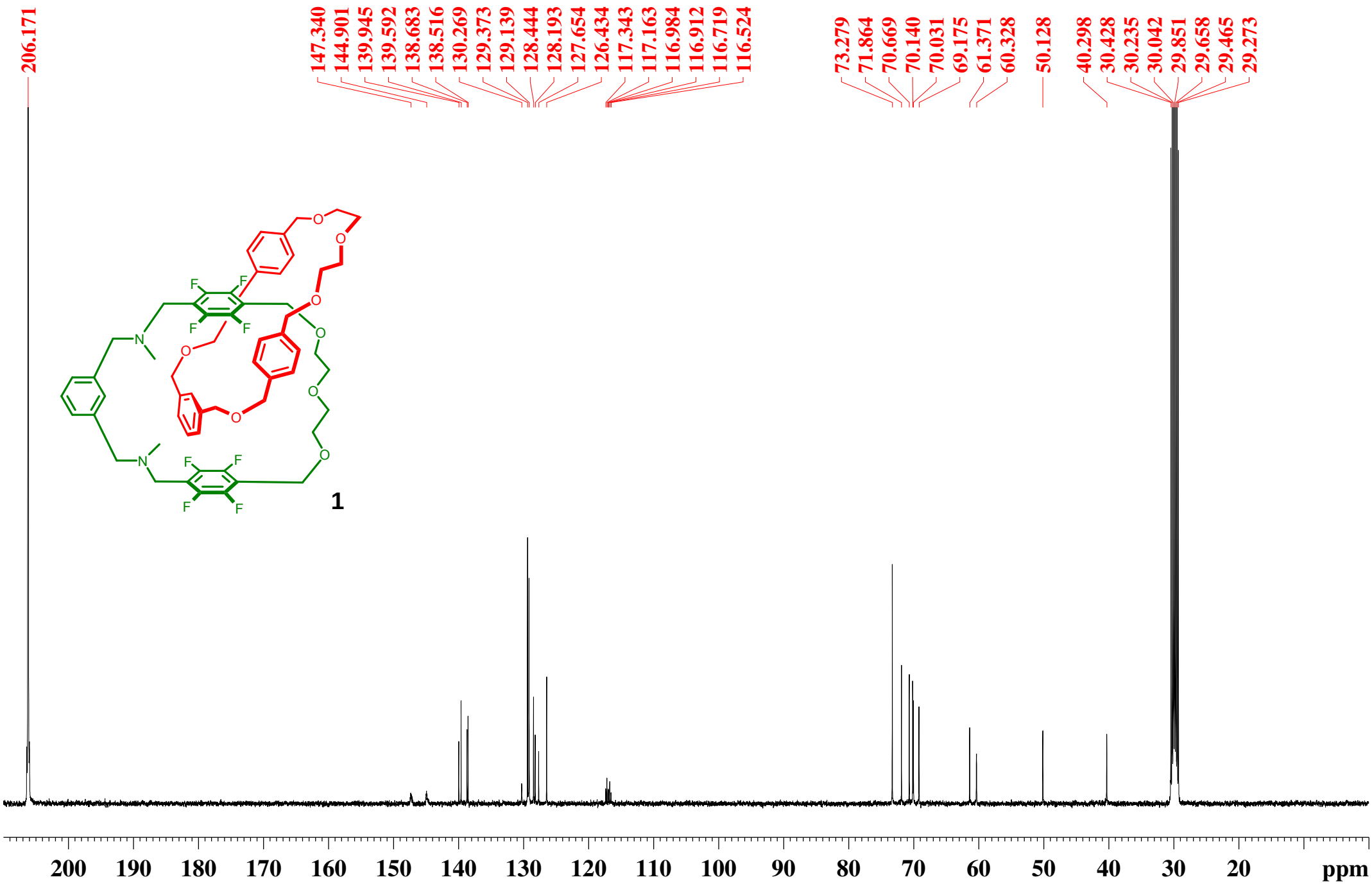
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126.434
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117.163
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116.912
116.719
116.524
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29.851
29.658
29.465
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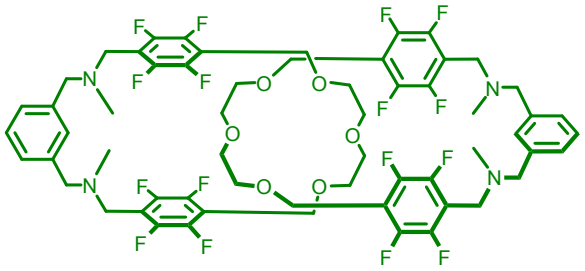

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3.124
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9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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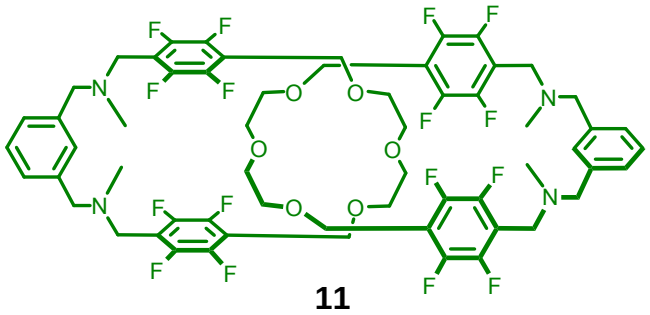

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146.305
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129.403
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127.530
115.710
115.548
115.367
115.178
77.323
77.006
76.689
69.579
68.960
60.742
59.902
49.523
39.699
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150
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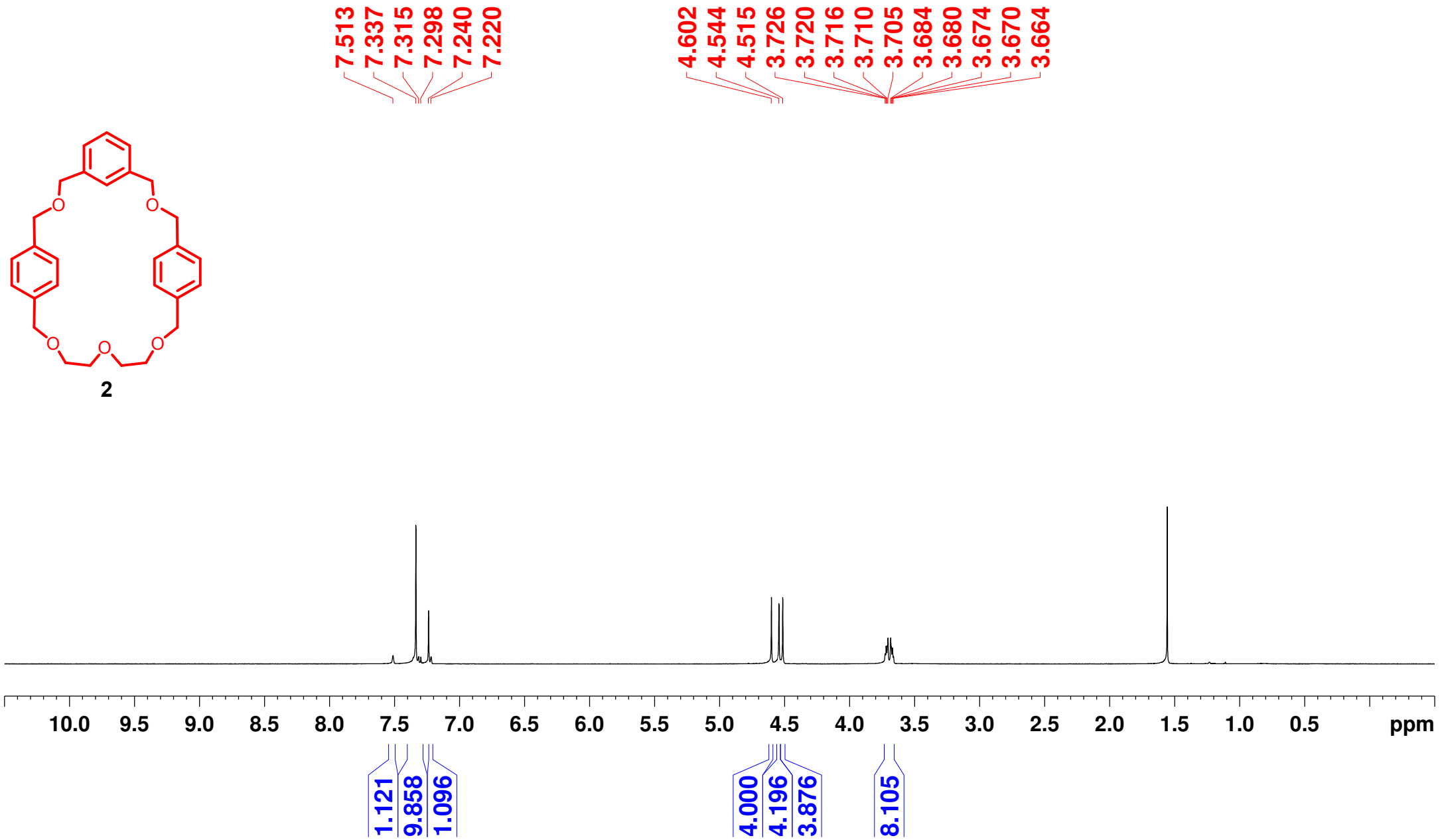
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3.720
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3.710
3.705
3.684
3.680
3.674
3.670
3.664
2
10.0
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9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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1.0
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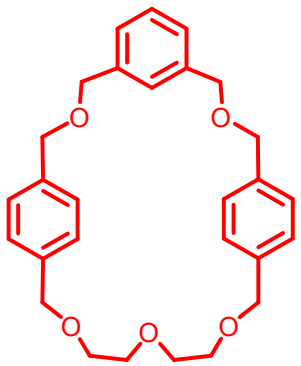

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137.808
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127.542
126.930
126.872
77.307
76.989
76.670
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71.314
71.279
70.847
69.423
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150
140
130
120
110
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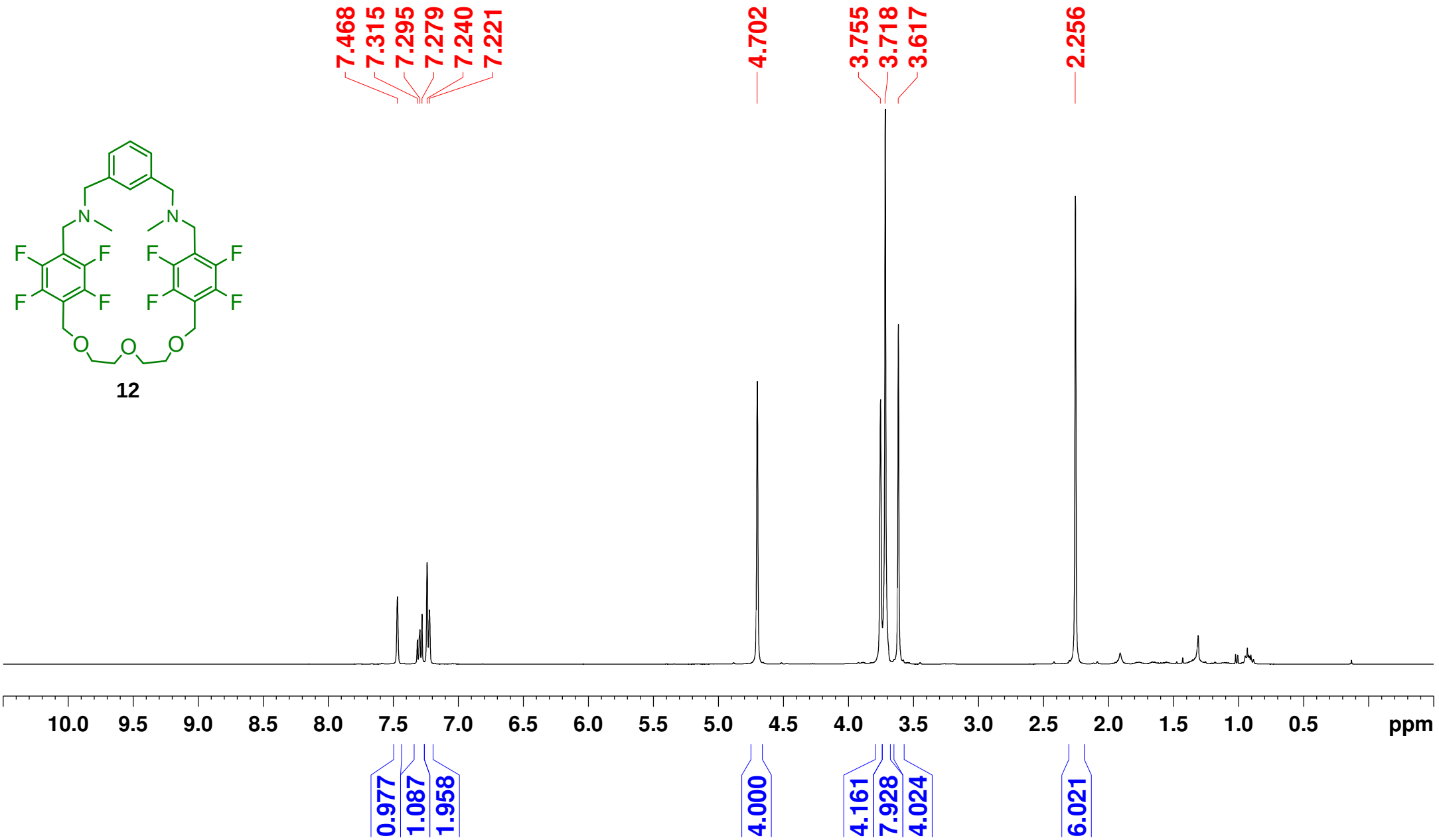
90
80
70
60
50
40
30
20
ppm

S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3.718
3.617
2.256
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F
F
F
F
F
F
F
O
O
O
12
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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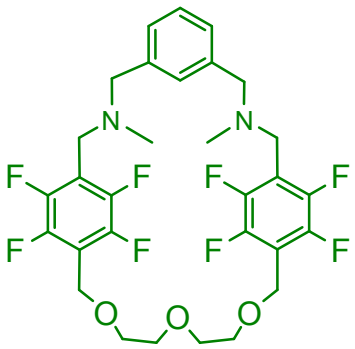
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F
F
O
O
O

12

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127.763
127.565
117.171
116.993
116.813
115.291
115.113
114.937
77.321
77.003
76.686
70.416
69.853
61.717
60.179
48.225
41.750
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150
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130
120
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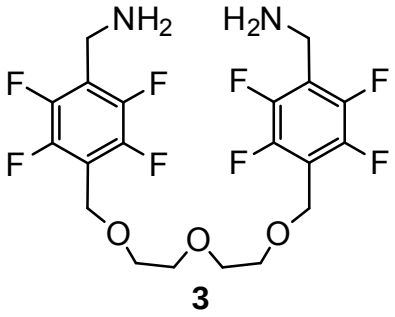
80
70
60
50
40
30
20
ppm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F
F
F
F
O
O
O

3

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10.0
9.5
9.0
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8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.0
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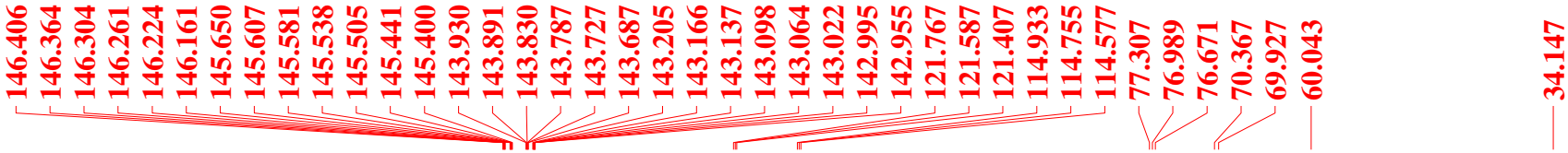
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145.505
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145.400
143.930
143.891
143.830
143.787
143.727
143.687
143.205
143.166
143.137
143.098
143.064
143.022
142.995
142.955
121.767
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114.577
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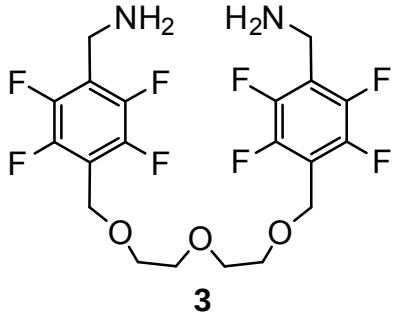
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F
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F
F
F
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F
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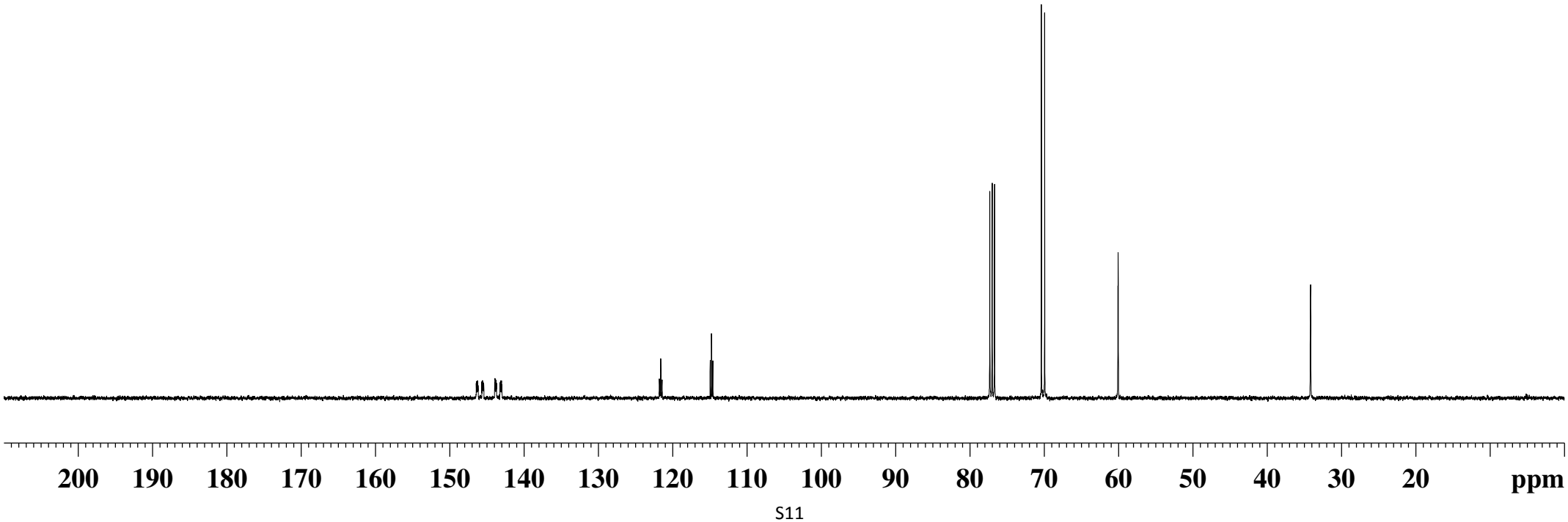
O
O

3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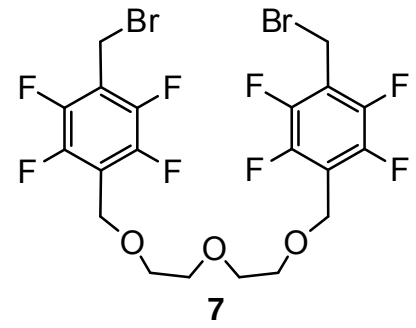
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


Br
Br
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F
F
F
F
F
F
F
O
O
O

7

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3.671
3.665
3.658
3.651
3.647
3.641
3.636
3.633
3.629
3.622
3.616
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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0.5
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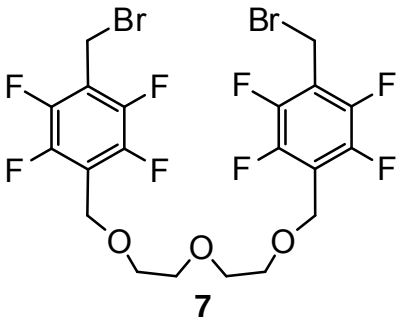
Br
Br
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F
F
F
F
F
F
F
O
O
O

7

146.586
146.528
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145.698
145.564
144.010
143.957
143.860
143.199
143.017
117.238
117.073
117.029
116.909
116.855
116.680
77.317
77.000
76.682
70.525
70.291
60.225
16.330
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150
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80
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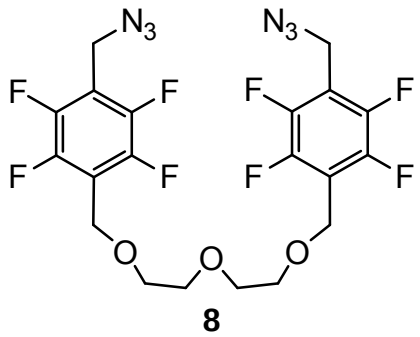
30
20
ppm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F
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8

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3.672
3.658
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3.647
3.643
3.640
3.636
3.629
3.623
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9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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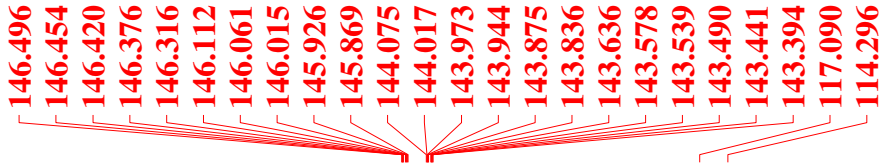
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144.017
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143.875
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143.636
143.578
143.539
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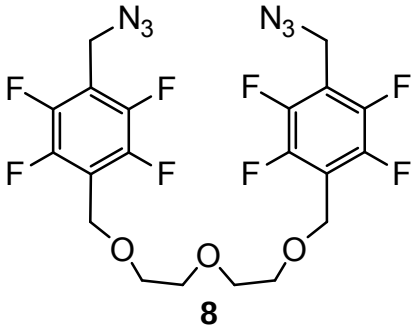
41.857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F
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F
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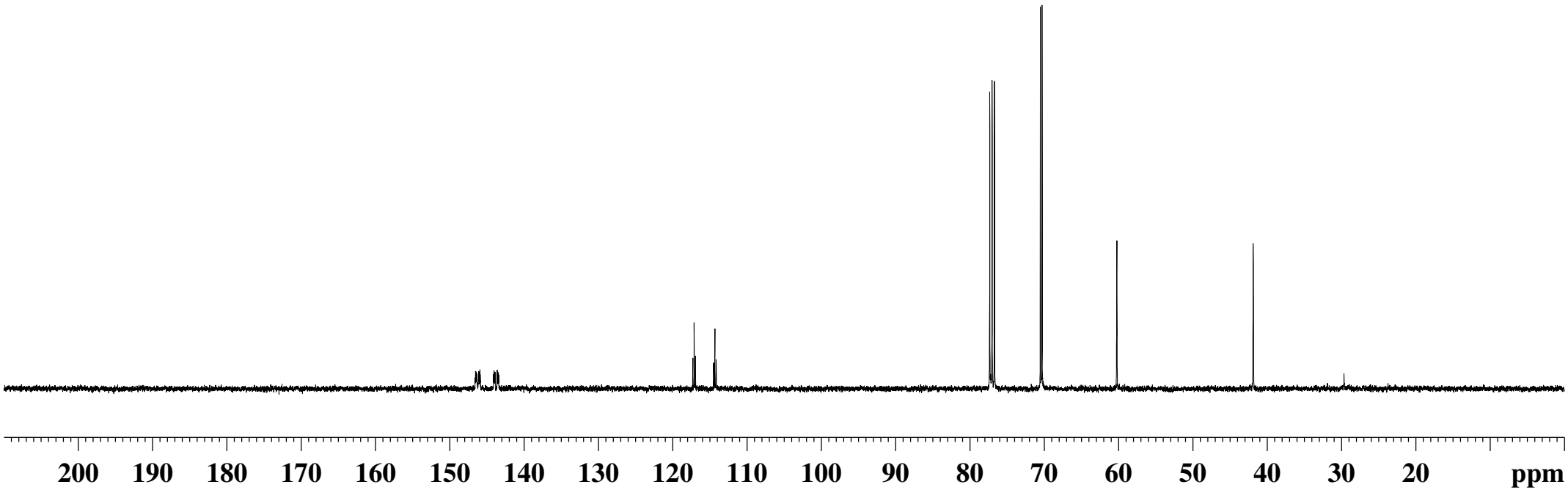
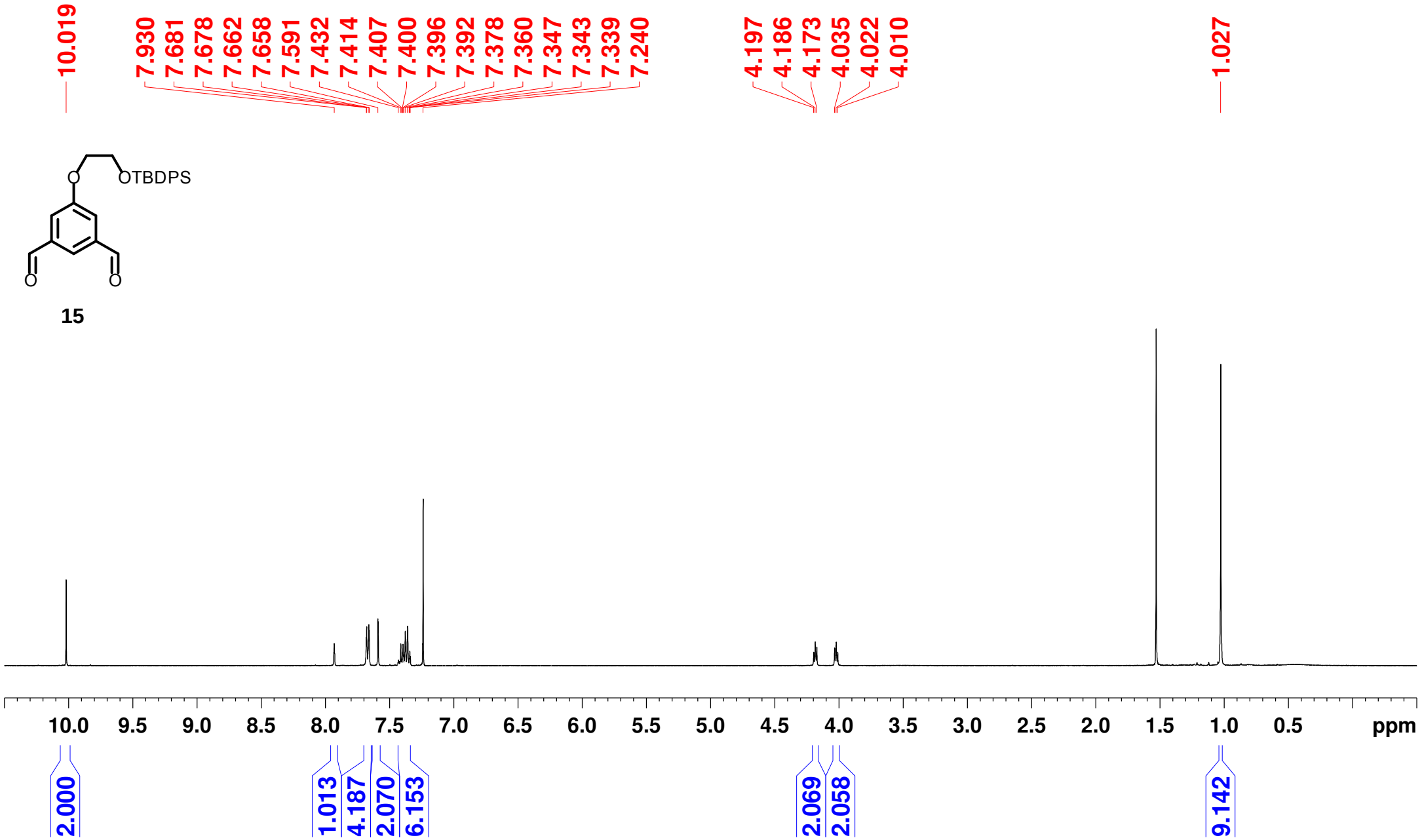
F
O
O
O

8


200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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7.400
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7.392
7.378
7.360
7.347
7.343
7.339
7.240
4.197
4.186
4.173
4.035
4.022
4.010
1.027
OTBDPS
O
O
O
15
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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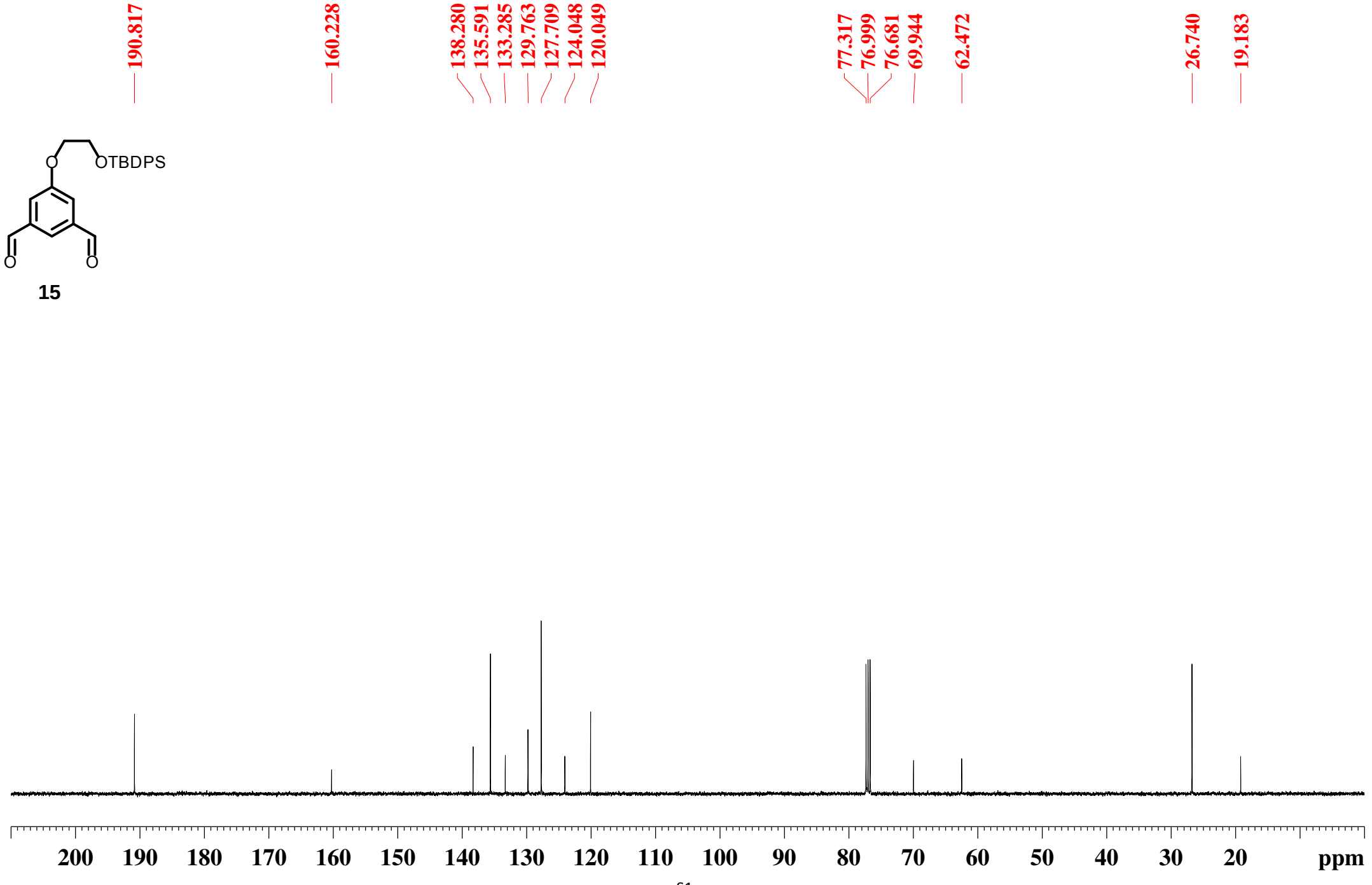
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127.709
124.048
120.049
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76.999
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69.944
62.472
26.740
19.183
OTBDPS
O
O
O
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150
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70
60
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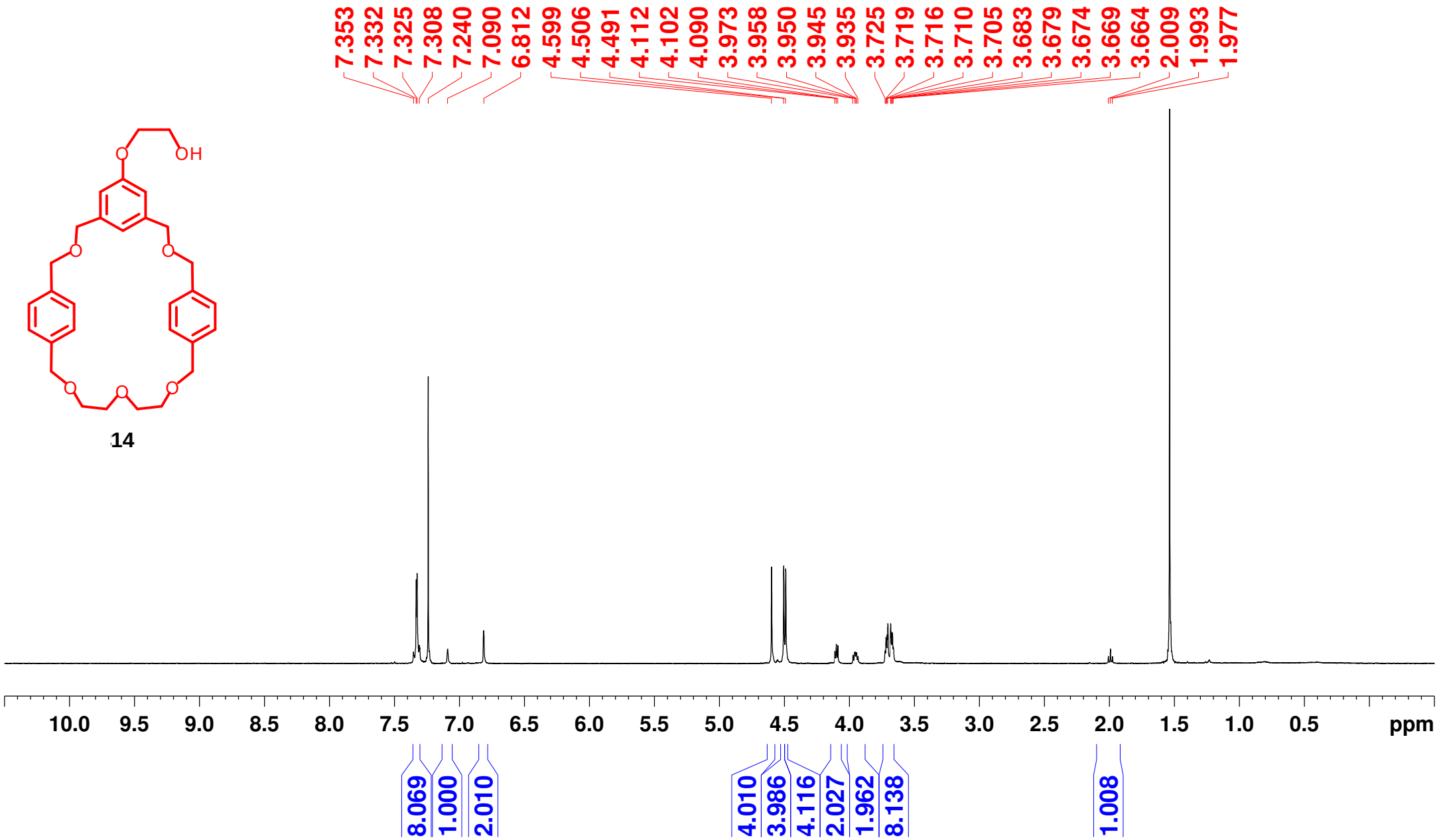
40
30
20
ppm

15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3.973
3.958
3.950
3.945
3.935
3.725
3.719
3.716
3.710
3.705
3.683
3.679
3.674
3.669
3.664
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1.993
1.977
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9.0
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5.5
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4.5
4.0
3.5
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1.5
1.0
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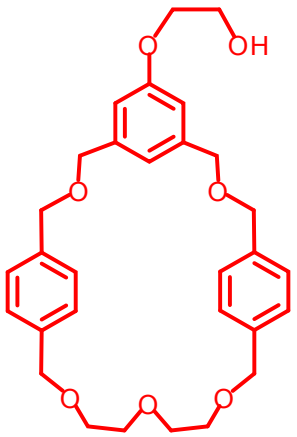
1.008


OH

14

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76.684
72.734
71.216
71.132
70.854
69.461
69.235
61.285
200
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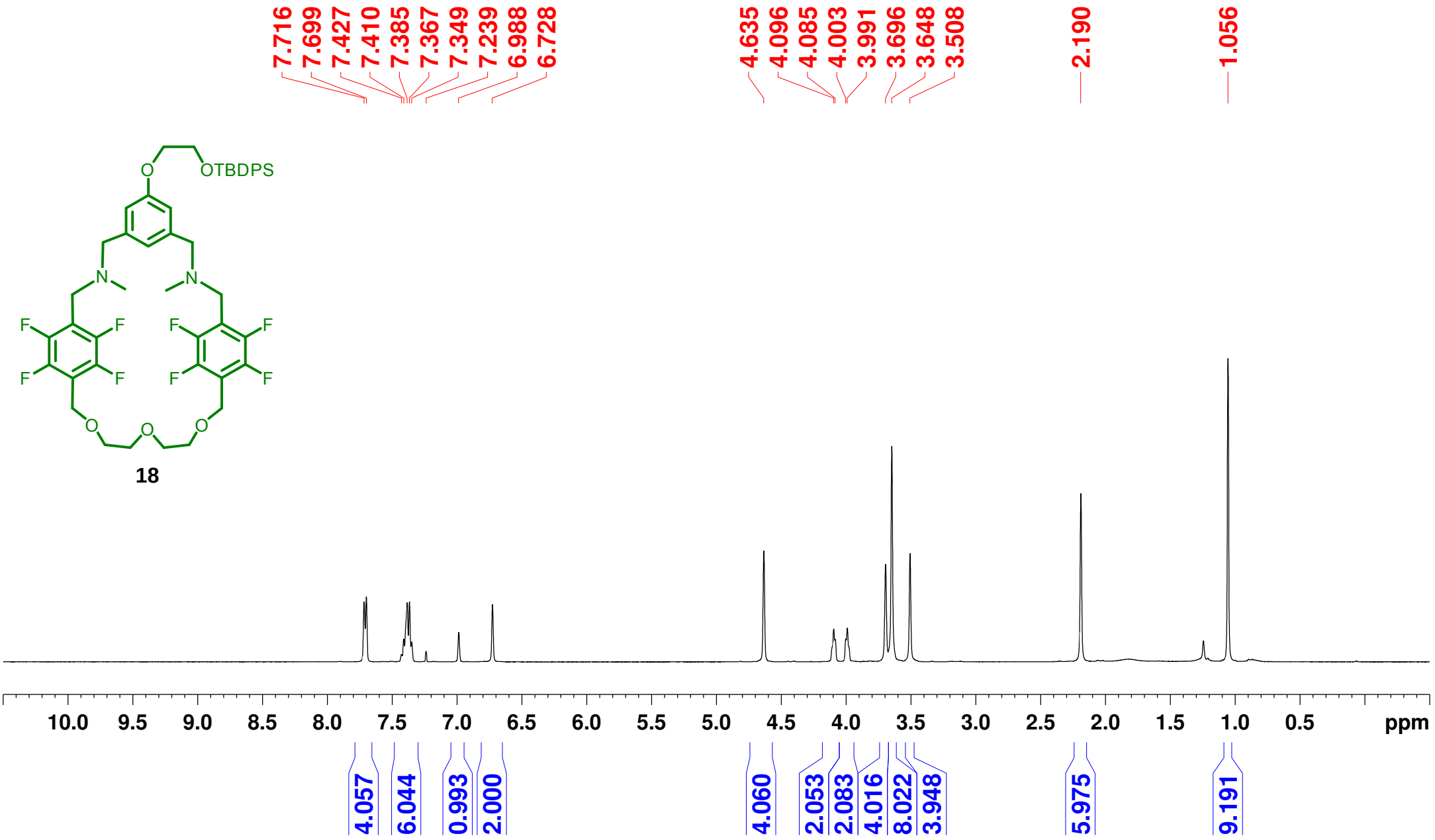
20
ppm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7.385
7.367
7.349
7.239
6.988
6.728
4.635
4.096
4.085
4.003
3.991
3.696
3.648
3.508
2.190
1.056
O
OTBDPS
N
N
F
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F
F
F
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F
F
O
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O
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9.0
8.5
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6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
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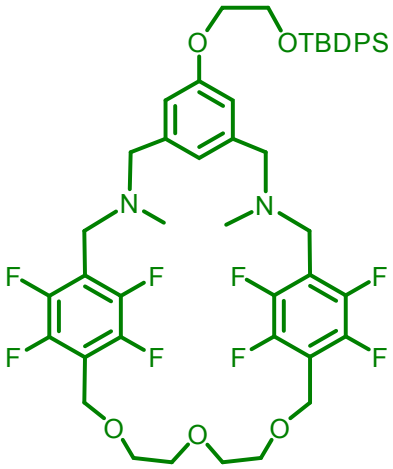
5.975
9.191

18



18

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146.348
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140.141
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133.579
129.616
127.630
122.016
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115.312
115.136
114.959
113.670
77.312
76.995
76.677
70.411
69.857
69.058
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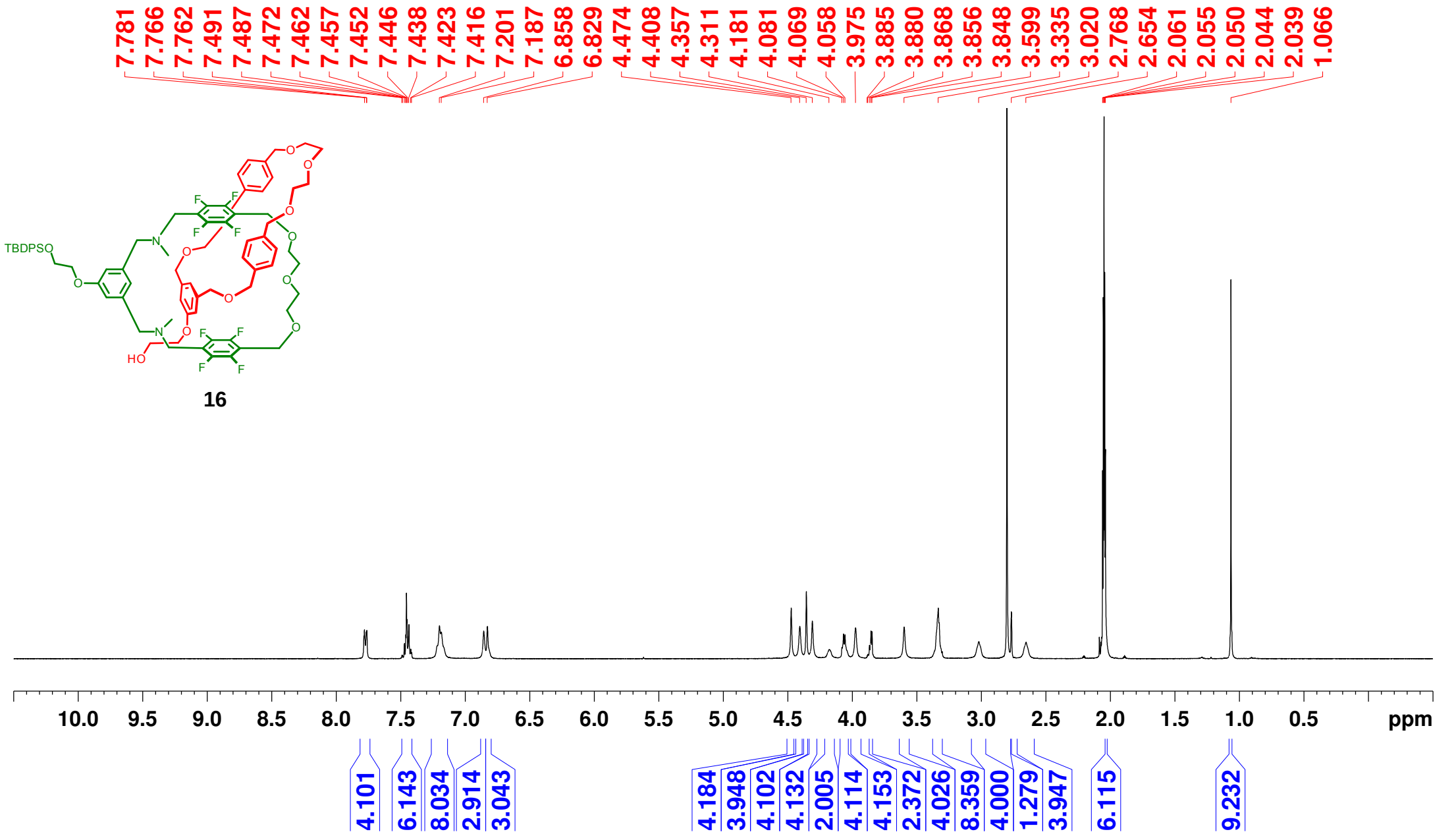
60.196
48.225
41.763
26.777
19.218

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm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7.446
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7.201
7.187
6.858
6.829
4.474
4.408
4.357
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4.069
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3.975
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3.848
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2.654
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2.055
2.050
2.044
2.039
1.066
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N
F
HO
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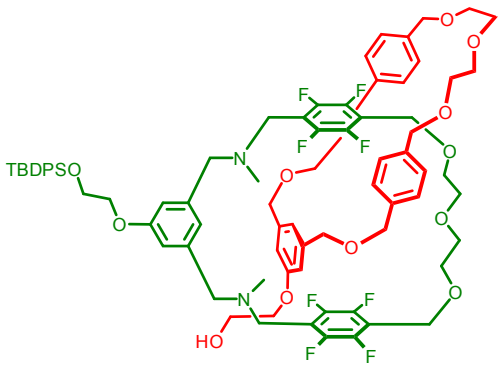
16



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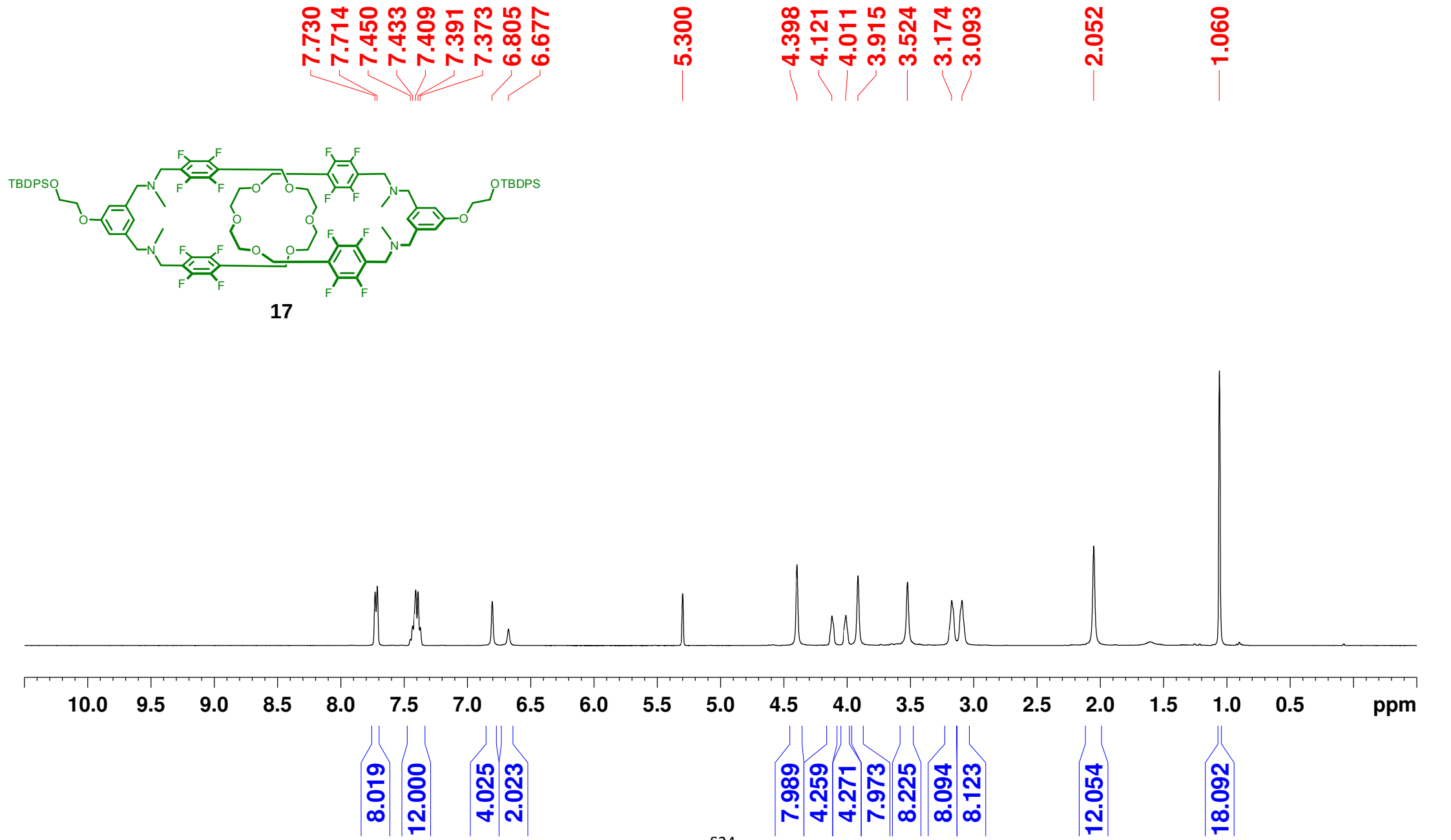
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OTBDPS
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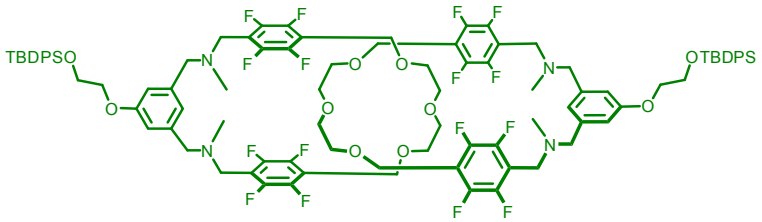

17

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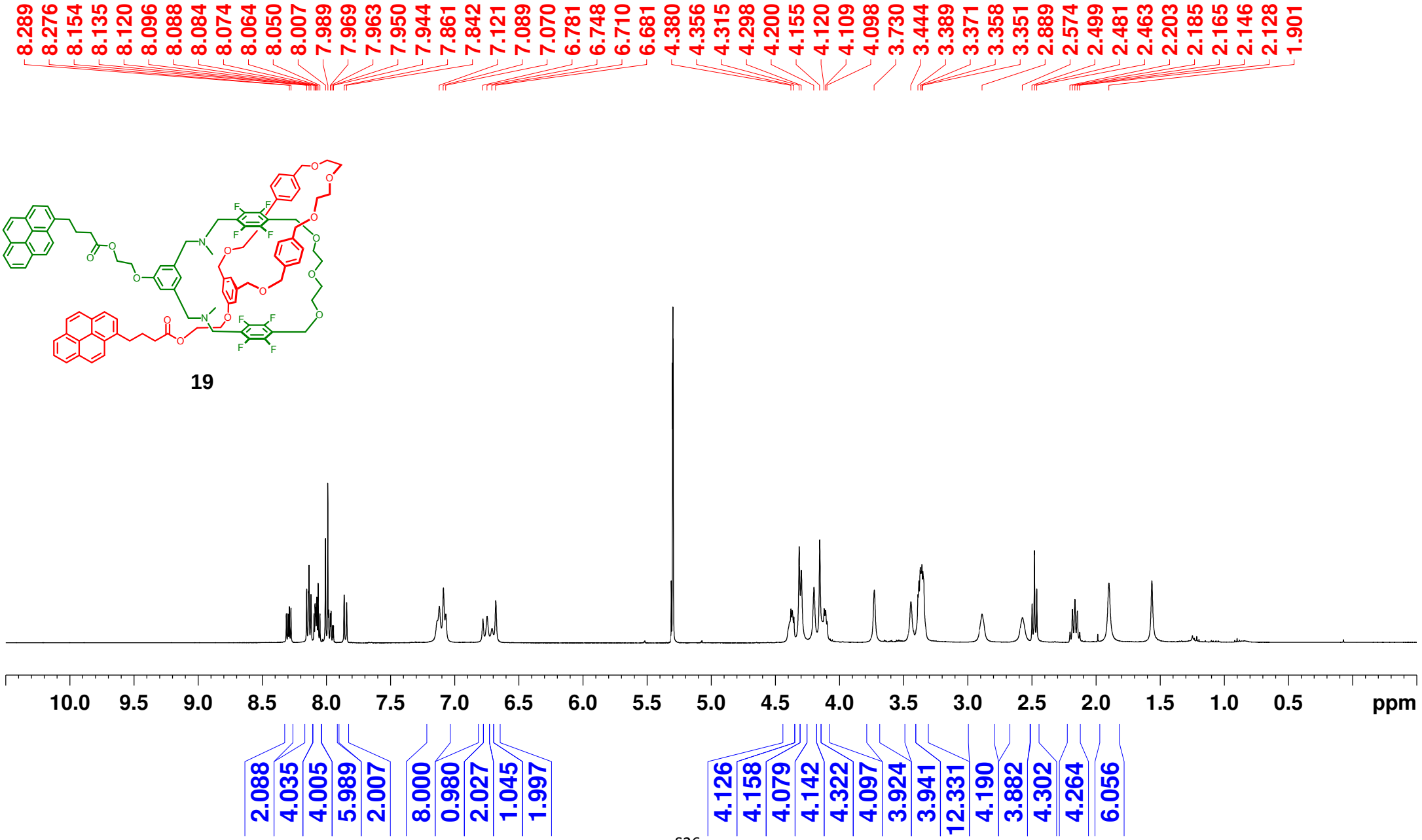
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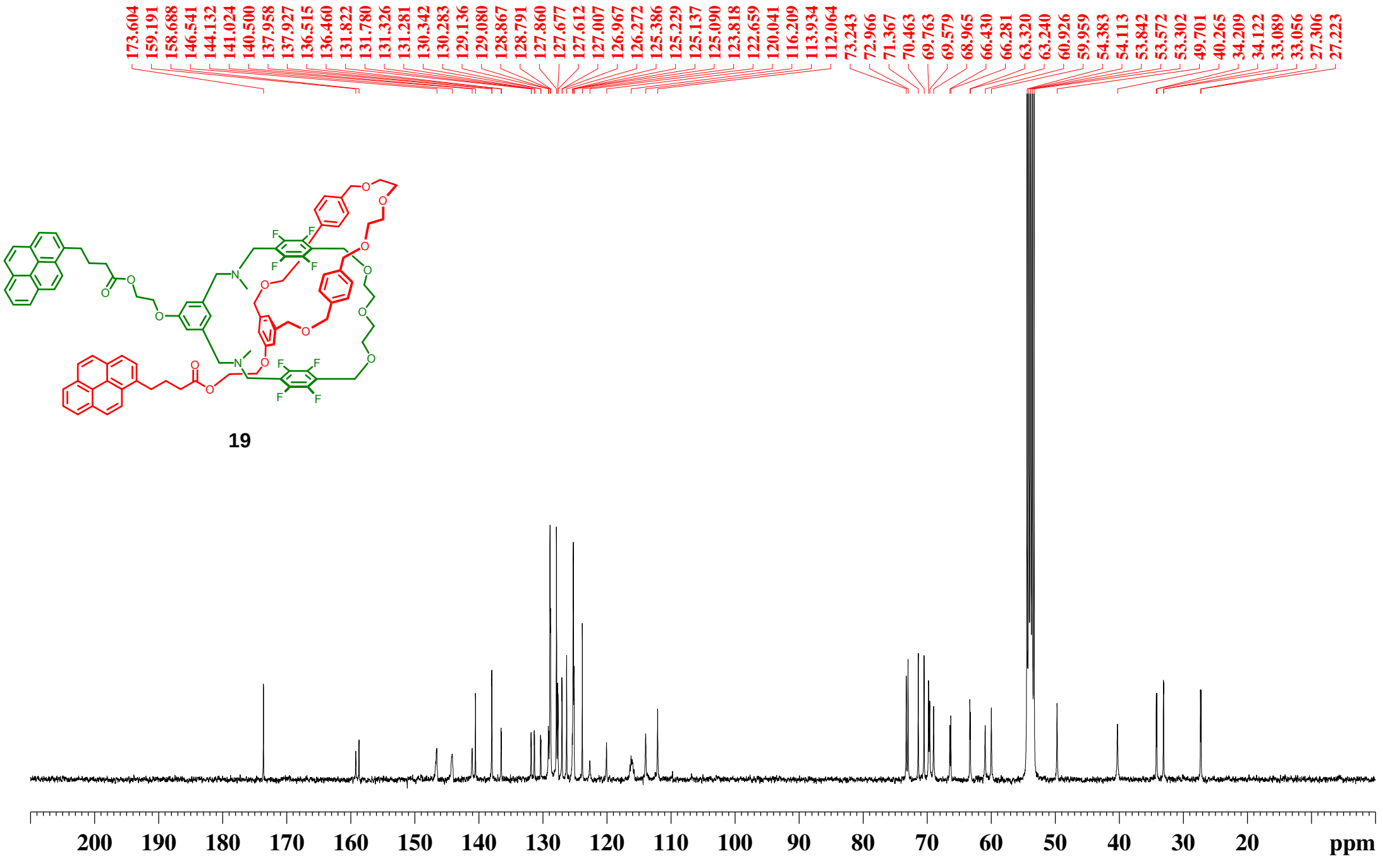
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200
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180
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160
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140
130
120
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30
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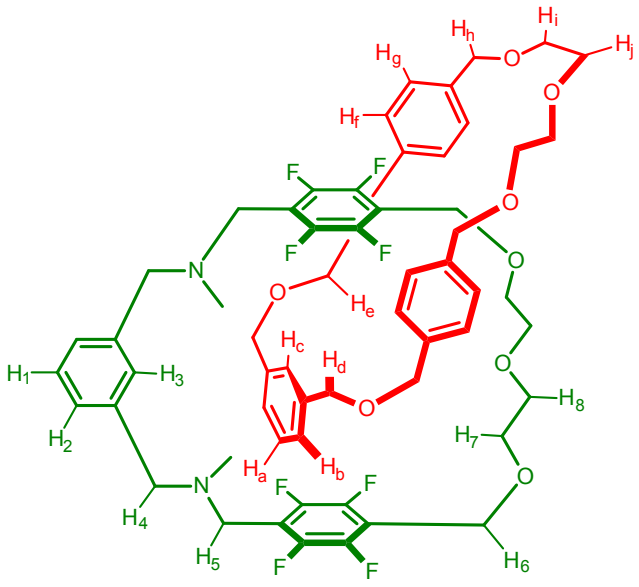
ppm

19

Figure S1 COSY Spectrum (400 MHz, CD_2Cl_2, 5 mM, 298 K)



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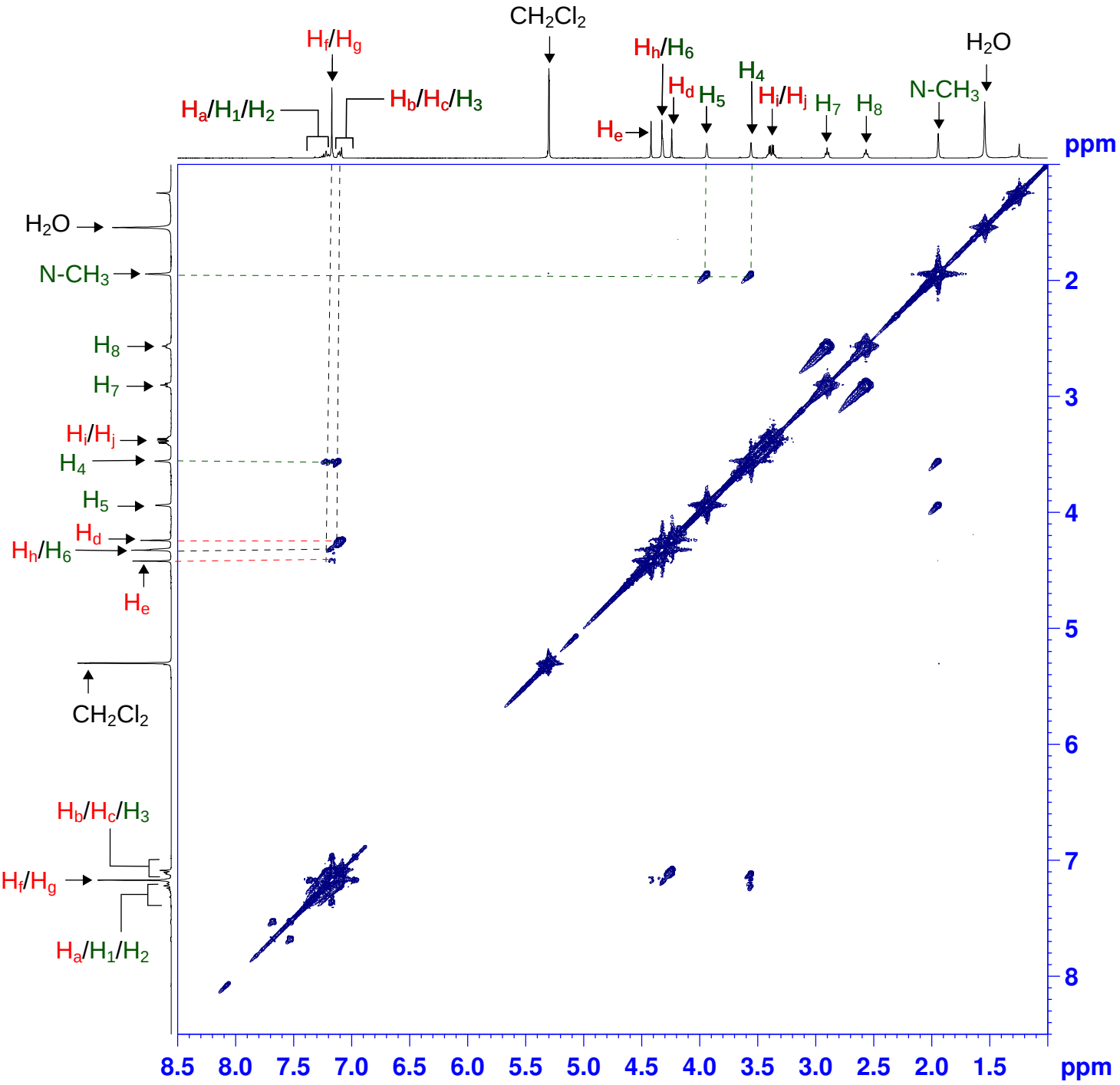


Figure S2 NOESY Spectrum (400 MHz, CD_2Cl_2, 5 mM, 298 K)

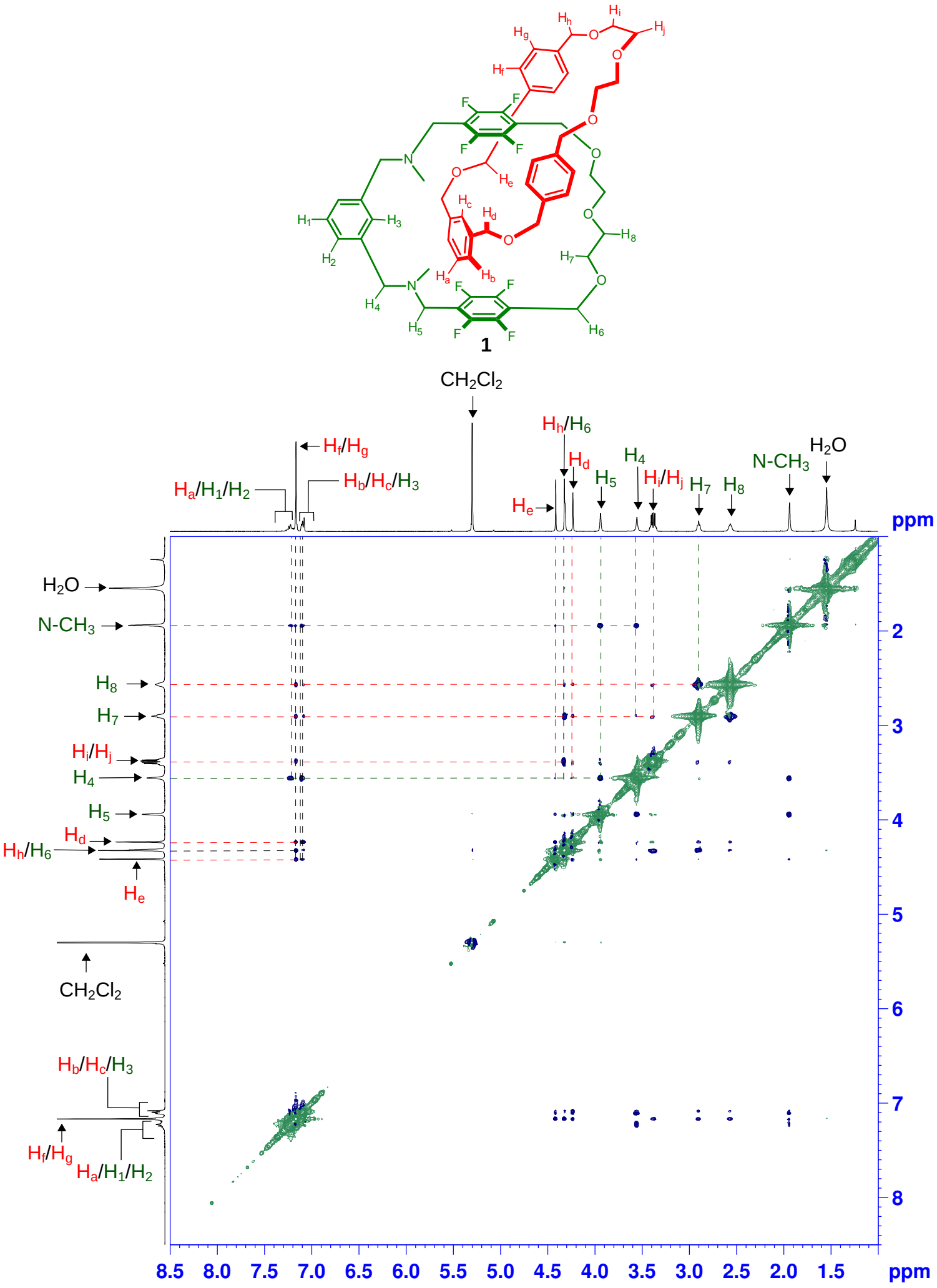
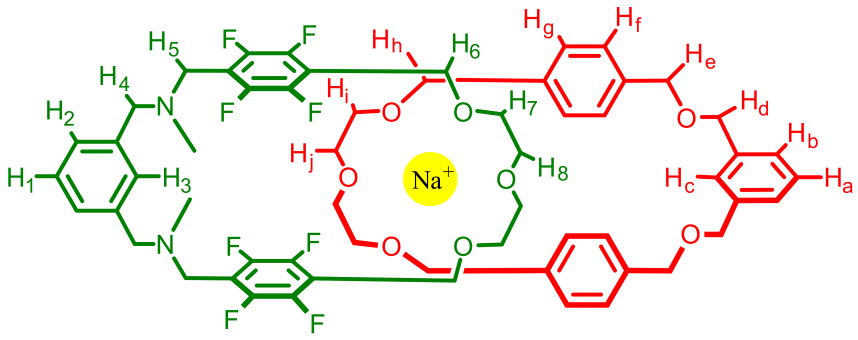


Figure S3 COSY Spectrum (400 MHz, CD_2Cl_2, 5 mM, 298 K)



[1·Na][TFPB]

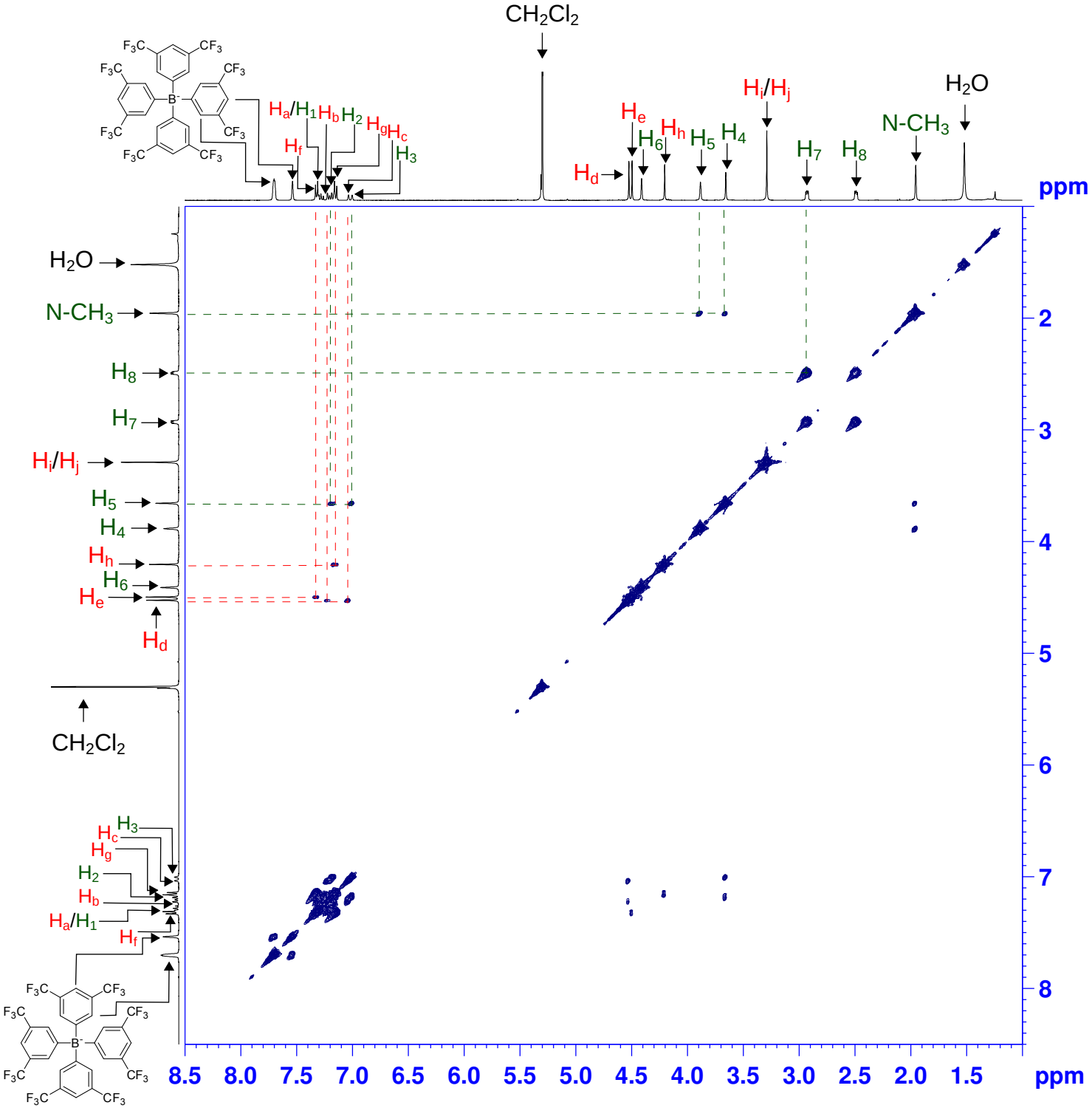
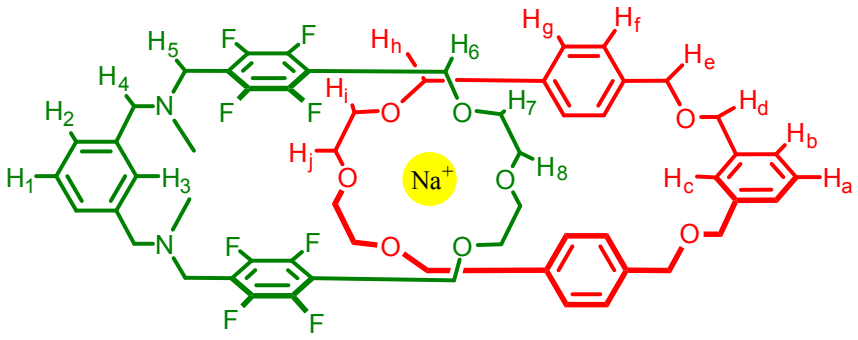


Figure S4 NOESY Spectrum (400 MHz, CD_2Cl_2, 5 mM, 298 K)



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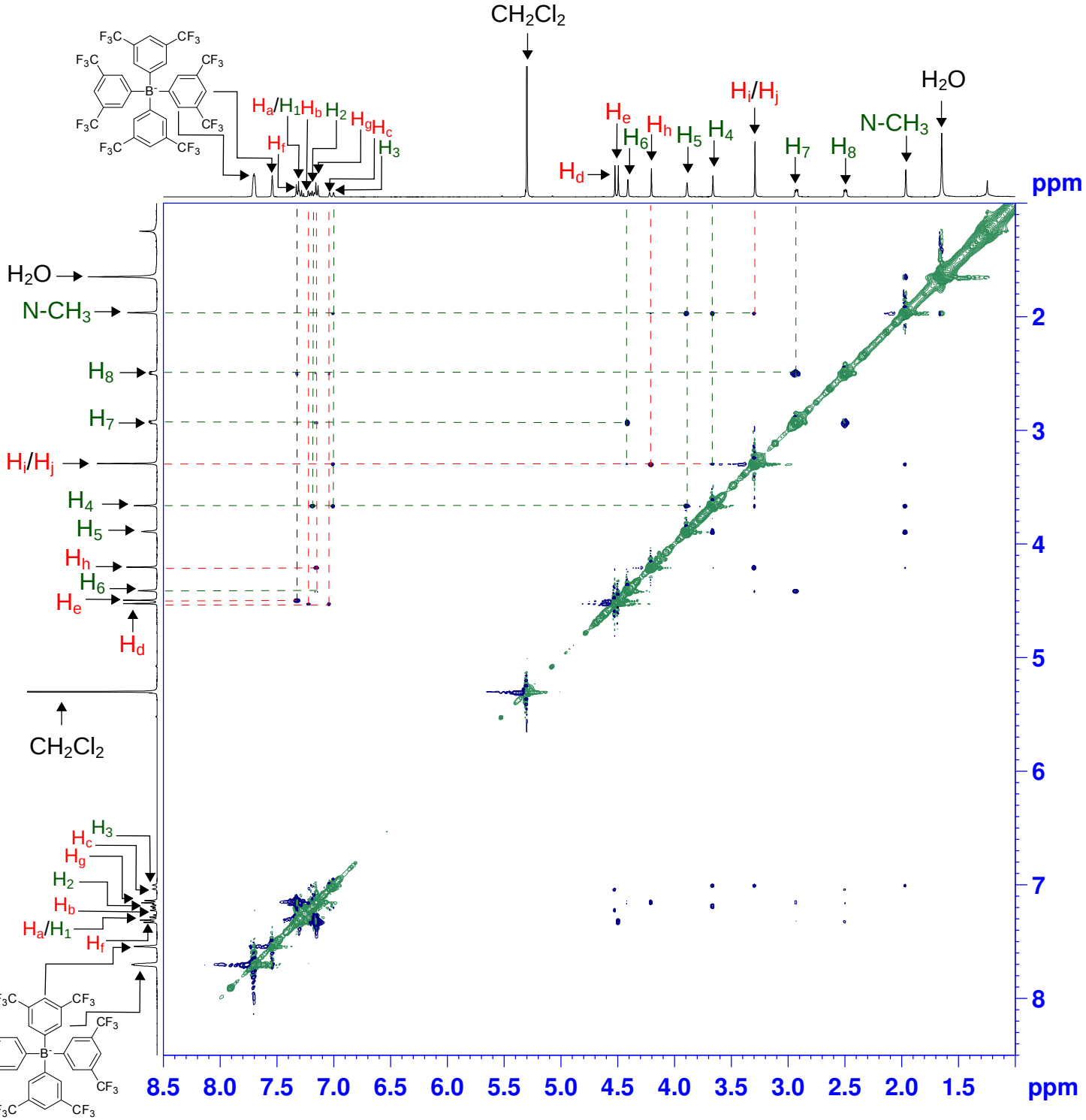
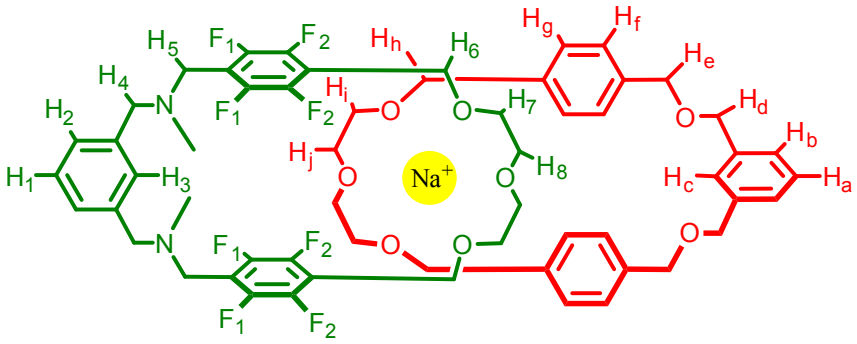


Figure S5 HOESY Spectrum (400 MHz, CD_2Cl_2, 5 mM, 298 K)



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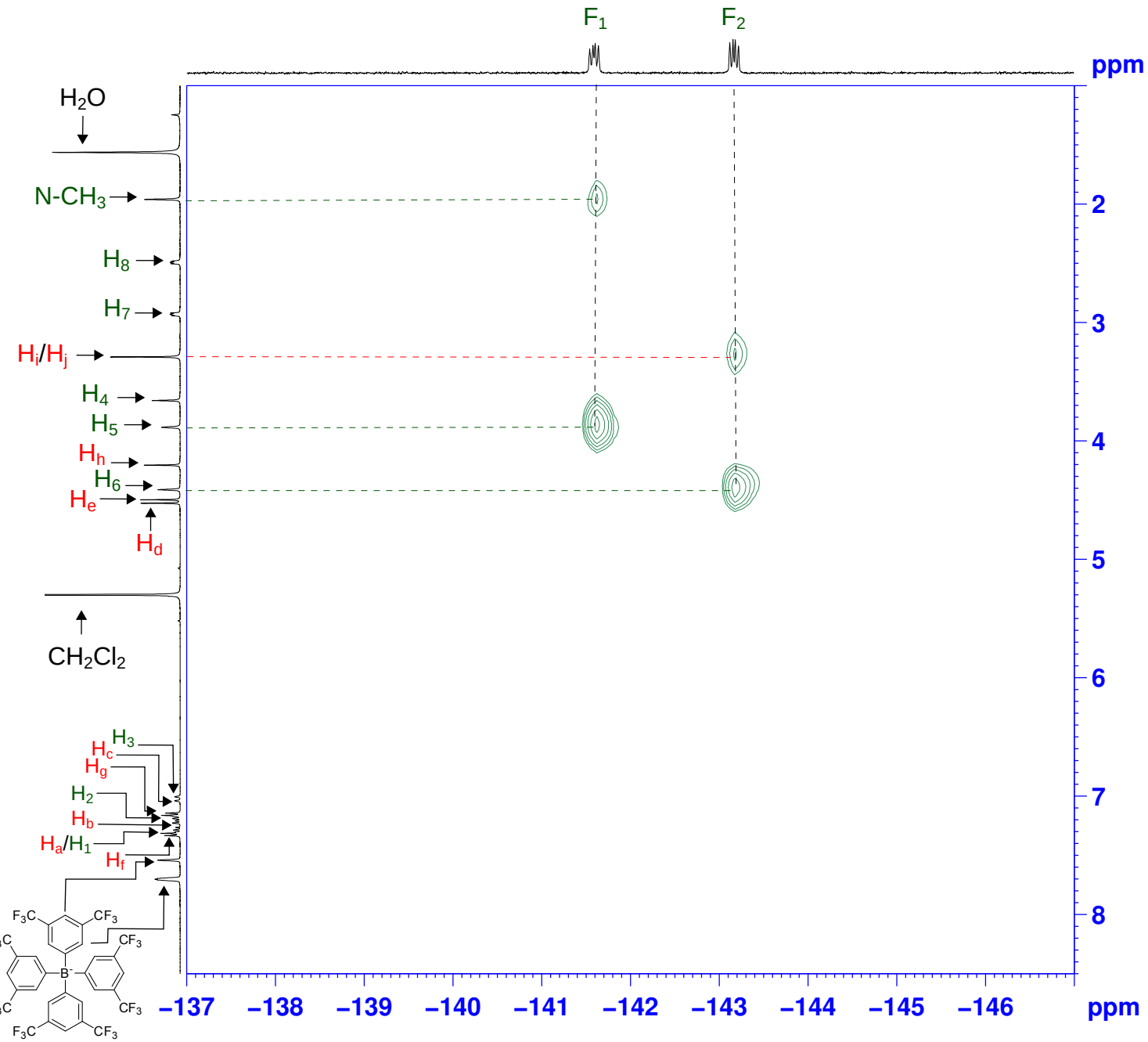
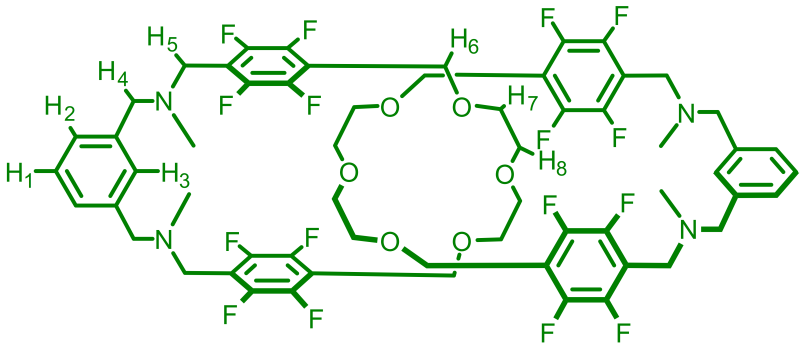


Figure S6 COSY Spectrum (400 MHz, CD_2Cl_2, 5 mM, 298 K)



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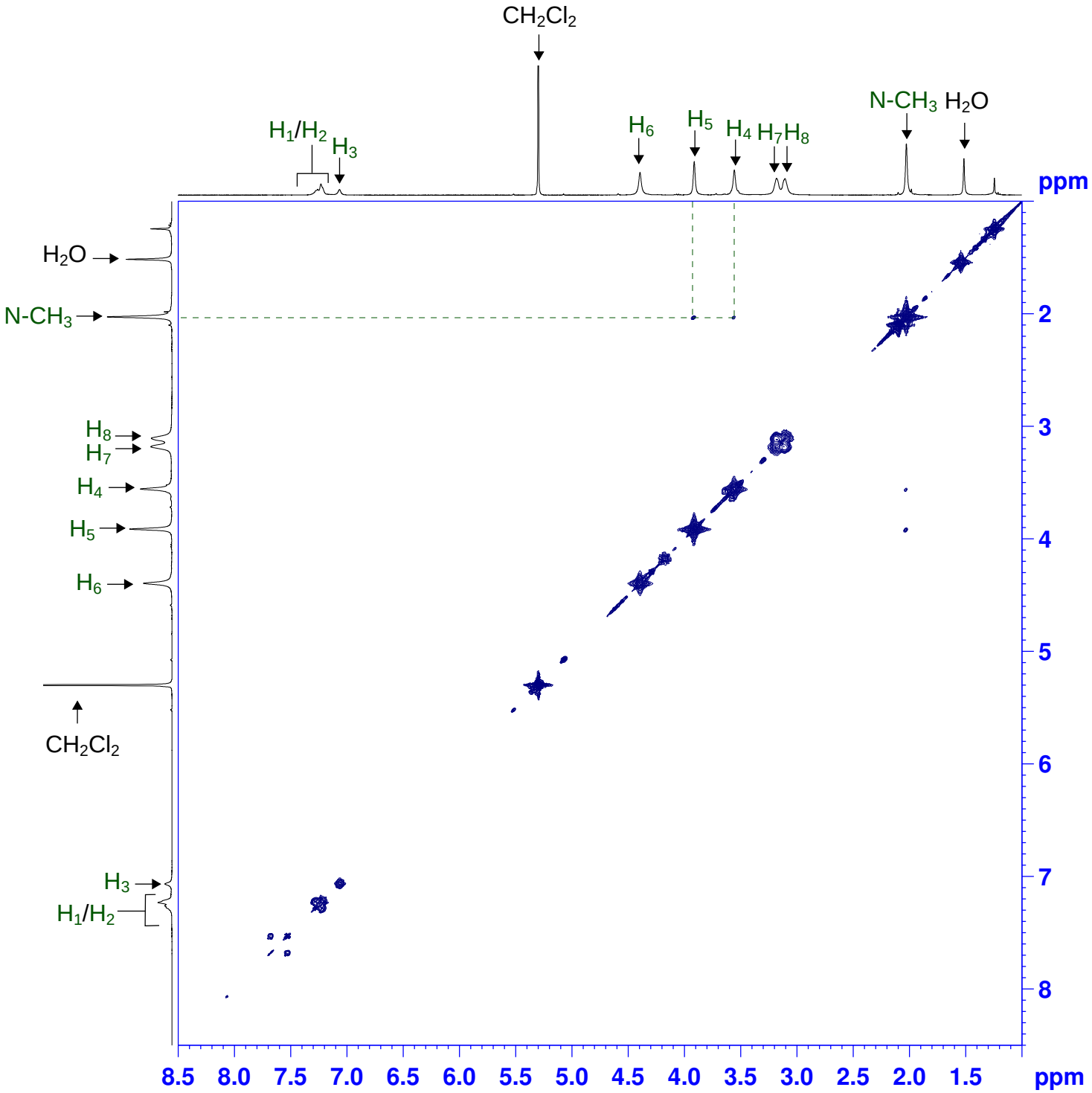
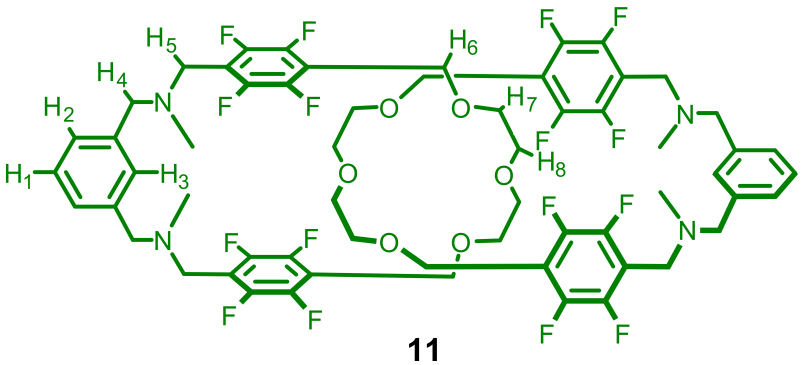


Figure S7 NOESY Spectrum (400 MHz, CD_2Cl_2, 5 mM, 298 K)



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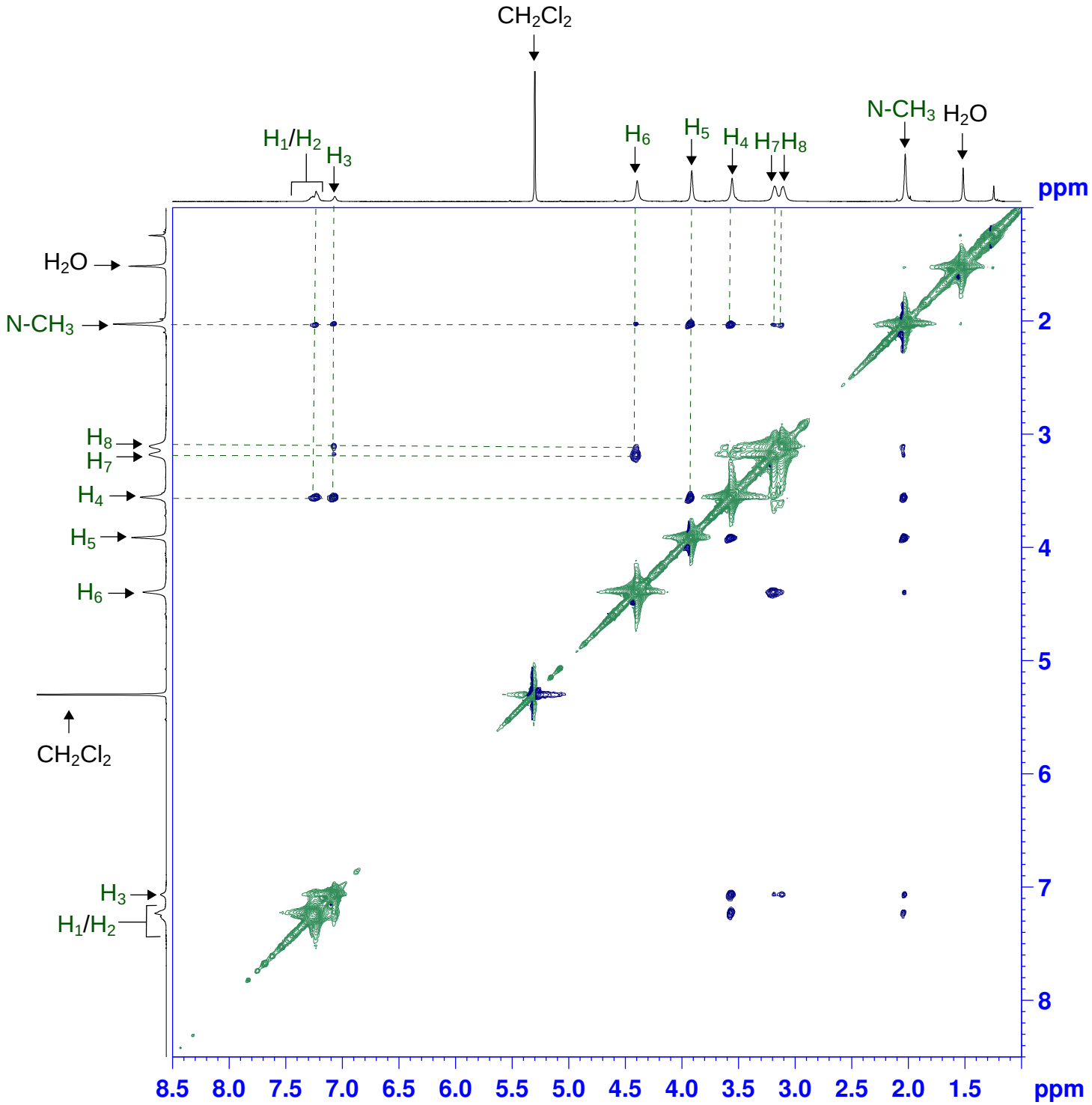


Figure S8 COSY Spectrum (400 MHz, CD_2Cl_2, 5 mM, 298 K)

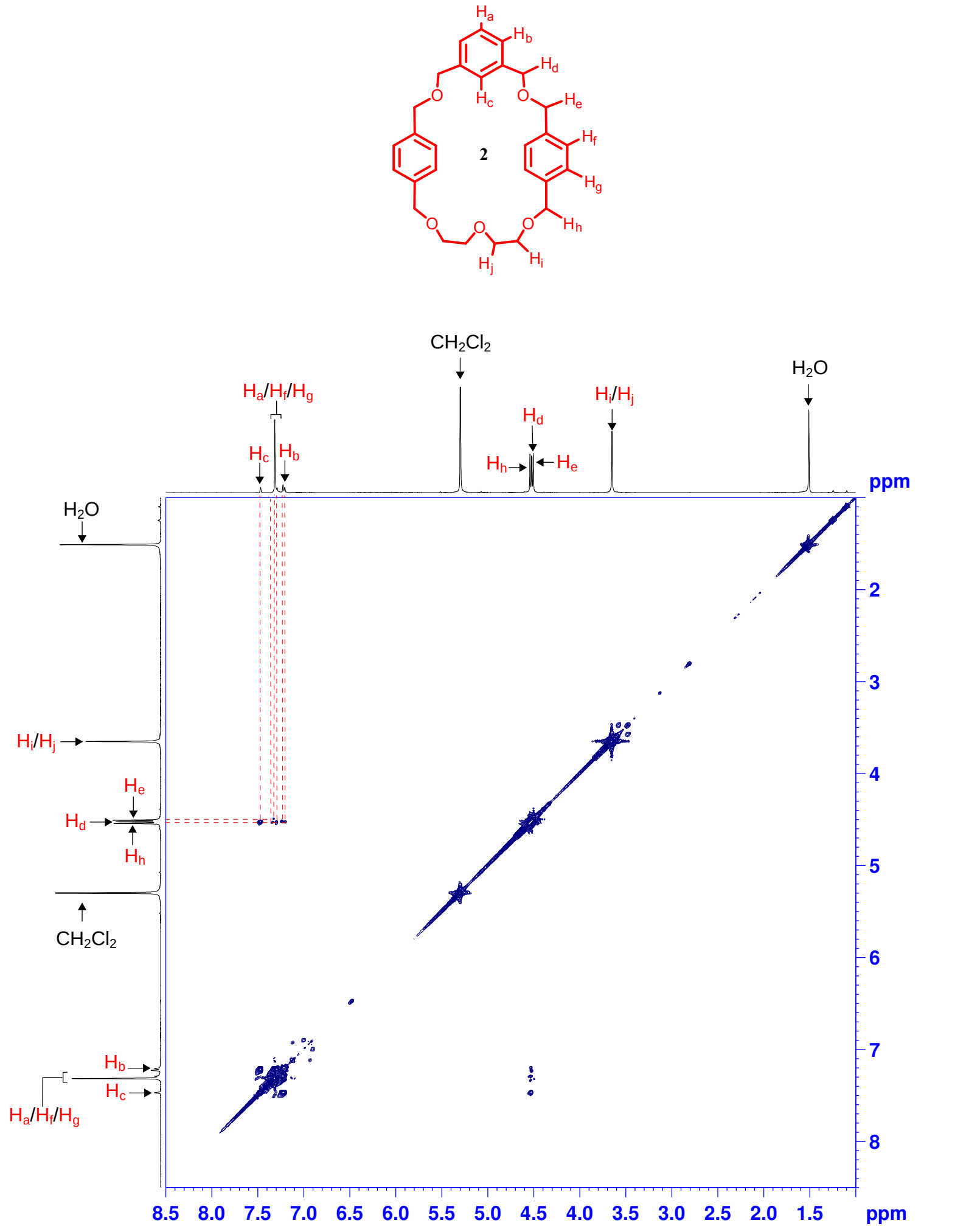


Figure S9 NOESY Spectrum (400 MHz, CD_2Cl_2, 5 mM, 298 K)

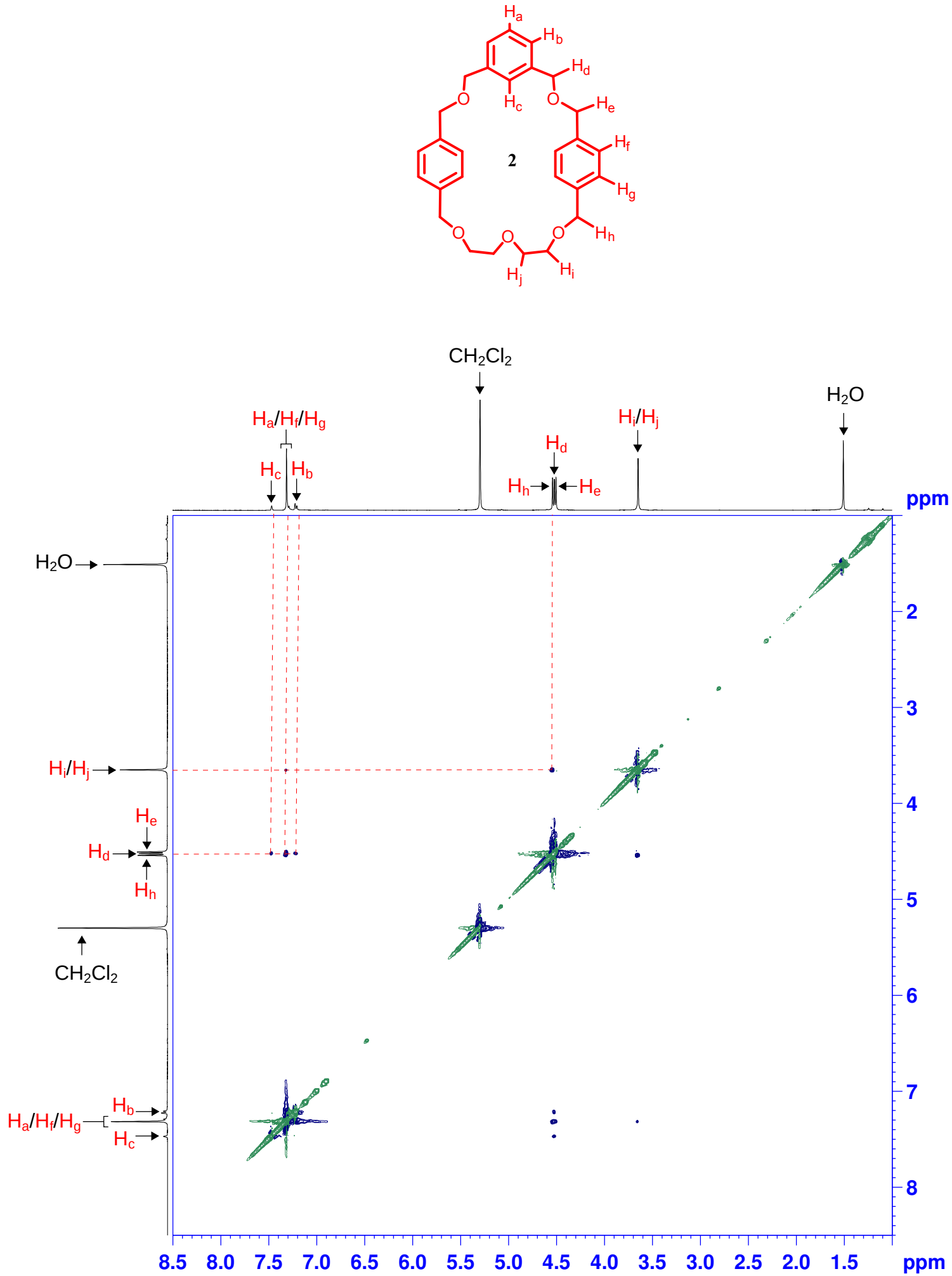


Figure S10 COSY Spectrum (400 MHz, CD_2Cl_2, 5 mM, 298 K)

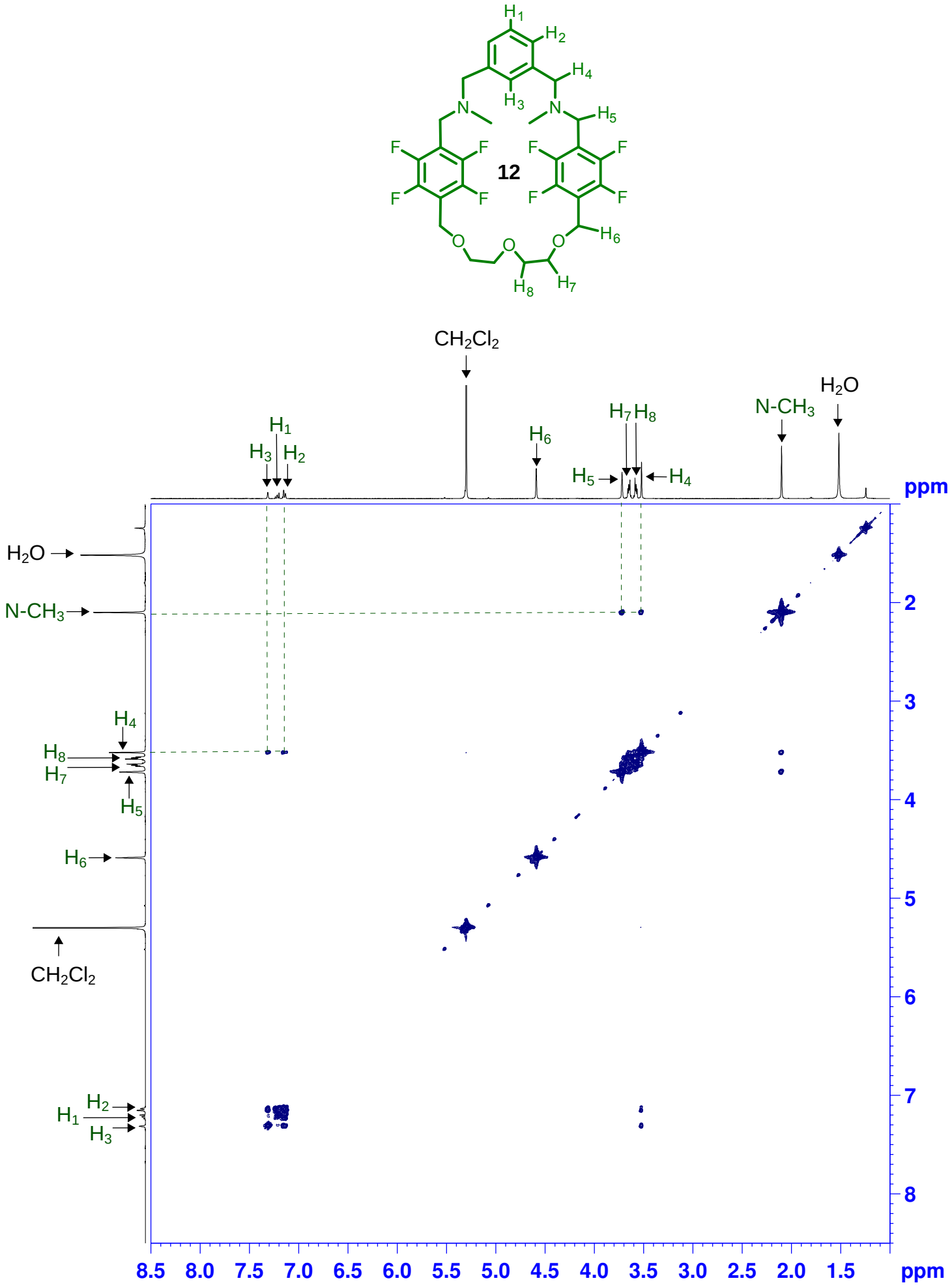
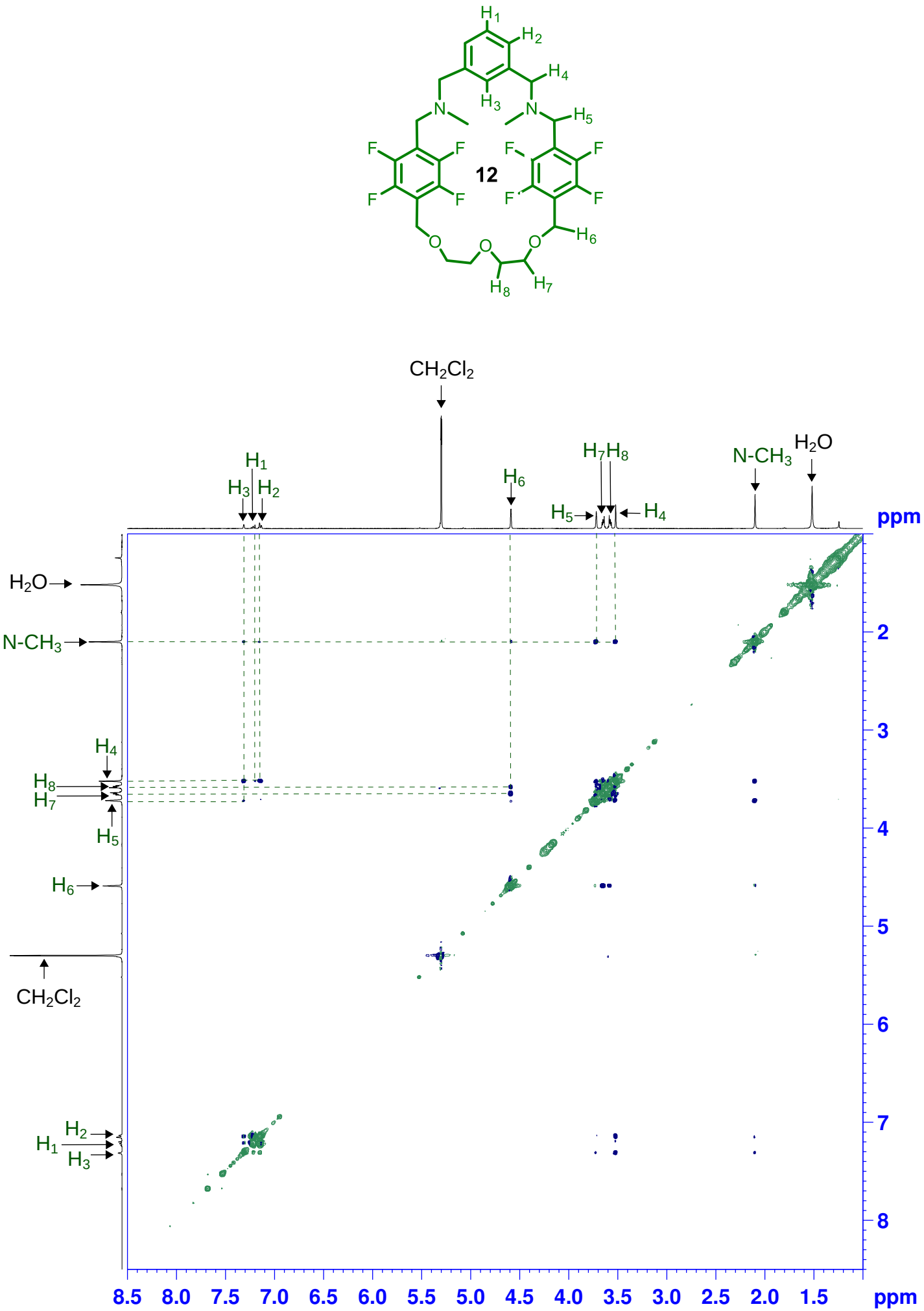


Figure S11 NOESY Spectrum (400 MHz, CD_2Cl_2, 5 mM, 298 K)



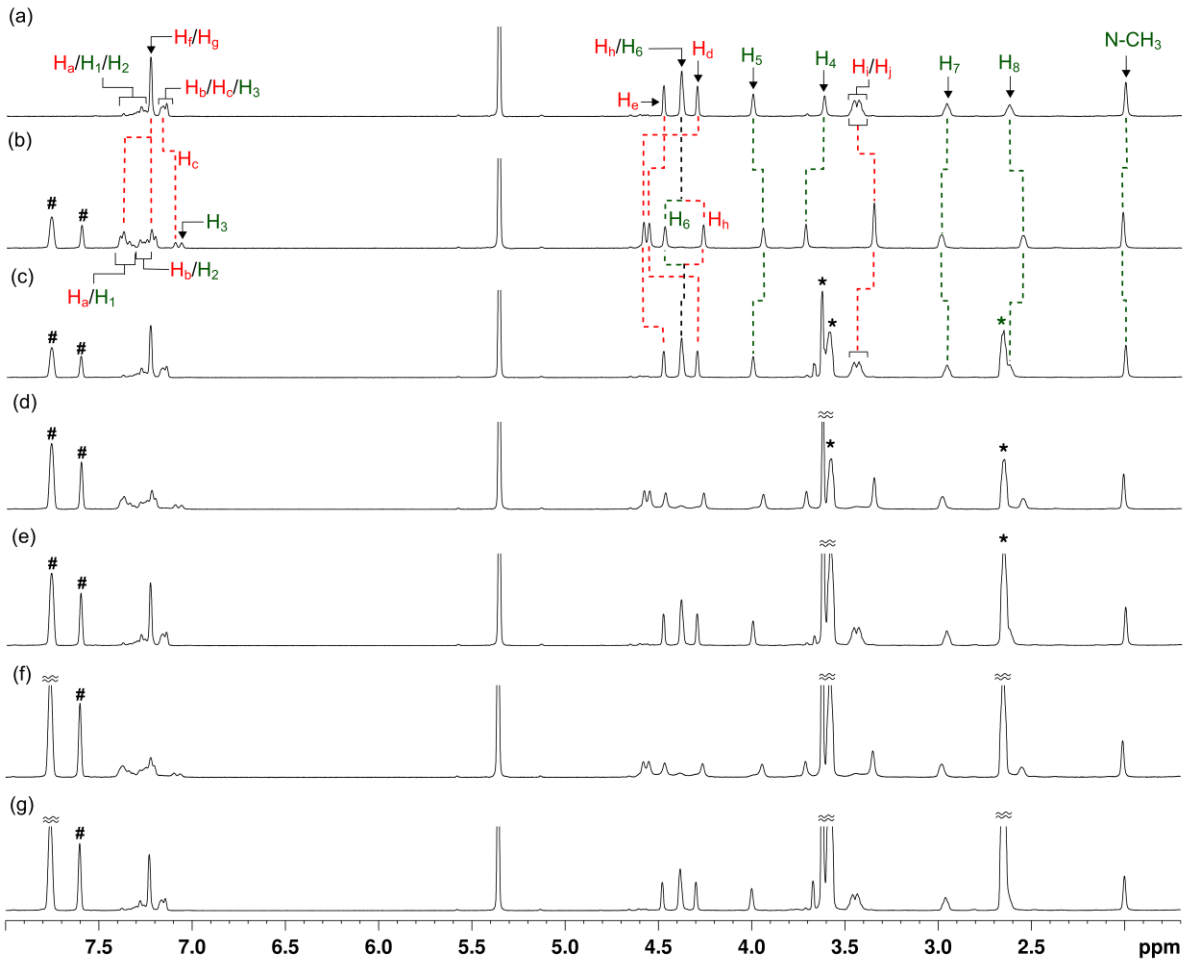


Figure S12. ^{1}H NMR spectra (400 MHz, CD_2Cl_2, 298K) of (a) the [2]catenane **1** (5 mM), (b) the sample obtained after addition of NaTFPB (1 equiv.) to the solution in (a), (c) the sample obtained after addition of [2.2.2]cryptand (1 equiv.) to the solution in (b), (d) the sample obtained after addition of NaTFPB (1 equiv.) to the solution in (c), (e) the sample obtained after addition of [2.2.2]cryptand (1 equiv.) to the solution in (d), (f) the sample obtained after addition of NaTFPB (1 equiv.) to the solution in (e), (g) the sample obtained after addition of [2.2.2]cryptand (1 equiv.) to the solution in (f).

Molecular Mechanics Calculations

All molecular mechanics calculations were performed using the Merck Molecular Force Field (MMFF)[1-6] as implemented in Discovery Studio 2.1 (Accelrys, CA) with the dielectric constant set to 1 and no explicit solvent. Appropriate hydrogens were added to the solid state structure of [2]catenane **1**. The resulting structure was minimized by steepest descent followed by conjugated gradient. This structure was then subjected to simulated annealing protocols. In short, the system was equilibrated for 1 ps with 0.001 ps time steps and a target temperature of 300 K, and then heated to 1000 K over 3 ps with 0.001 ps time steps. Molecular dynamics was performed at 1000 K over 1 ns with 0.001 ps time steps, and the structure was saved every 1 ps. Each recorded structure was cooled to 300 K over 3 ps with 0.001 ps time steps, equilibrated at 300 K for 1 ps with 0.001 ps time steps, and then minimized by steepest descent followed by conjugated gradient. One of these structures with the *m*-xylyl ring sandwiched between the two tetrafluoro-*p*-xylyl rings in a face-to-face manner was particularly low in energy, whereas structures with the di(ethylene glycol) units on the two macrocycles in close proximity were higher in energy. Distance restraints were introduced to acheive the interstitial arrangement with sequential face-to-face π-stacking of the *p*-xylyl and tetrafluoro-*p*-xylyl rings; this conformation was then minimized by steepest descent followed by conjugated gradient without any restraints. A sodium ion was introduced into one of the structures with the di(ethylene glycol) units on the two macrocycles in close proximity to give [2]catenane [**1**·Na^+]. The system was then equilibrated for 1 ps with a target temperature of 300 K, and heated to 1000 K over 3 ps. Molecular dynamics was performed at 1000 K over 1 ns with 0.001 ps time steps, and the structure was saved every 1 ps. Each recorded structure was cooled to 300 K over 3 ps with 0.001 ps time steps, equilibrated at 300 K for 1 ps with 0.001 ps time steps, and then minimized by steepest descent followed by conjugated gradient. One of these structures with the sodium ion coordinated by six oxygen atoms on the ethylene glycol units was particularly low in energy.

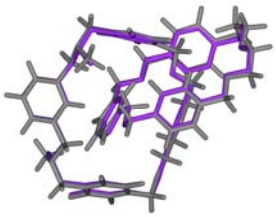
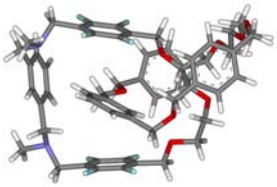


Figure S13. Superimposition of the solid state structure (magenta) and the corresponding energy minimized structure (gray) using the Merck Molecular Force Field. The root-mean square deviation (RMSD) for the non-hydrogen heavy atoms in the two structures was 0.18 Å.

(a)



(b)

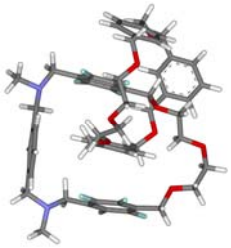


Figure S14. Energy-minimized structures of the [2]catenane **1** with (a) the two tetrafluoro-*p*-xylyl rings sandwiching to the *m*-xylyl ring in a face-to-face manner (generated by molecular dynamics calculations) and (b) sequential stacking to the two *p*-xylyl rings (forcing interstitial). Atom coloring: C: gray, H: white, N: blue, O: red, F: cyan.

Among these conformations, the structure featuring the *m*-xylyl ring sandwiched between the two tetrafluoro-*p*-xylyl rings in a face-to-face manner (Figure S14a) was energetically similar (ΔH = 0.4 kcal/mol) to the minimized solid state structure in Figure S13. The conformation featuring sequential face-to-face π-stacking of the *p*-xylyl and tetrafluoro-*p*-xylyl rings was not among the low-energy conformations; the structure obtained from forcing an interstitial arrangement (Figure S14b) was significantly higher in energy (ΔH = 6.7 kcal/mol) than the minimized solid state structure in Figure S13

References:

(1) Halgren, T. A. "Merck molecular force field. I. Basis, form, scope, parameterization, and performance of MMFF94" *J. Comput. Chem.* **1996**, *17*, 490.

(2) Halgren, T. A. "Merck molecular force field. III. Molecular geometries and vibrational frequencies for MMFF94" *J. Comput. Chem.* **1996**, *17*, 553.

(3) Halgren, T. A. “Merck molecular force field. IV. conformational energies and geometries for MMFF94” *J. Comput. Chem.* **1996**, *17*, 587.

(4) Halgren, T. A. “Merck molecular force field. V. Extension of MMFF94 using experimental data, additional computational data, and empirical rules” *J. Comput. Chem.* **1996**, *17*, 616.

(5) Halgren, T. A. “MMFF VI. MMFF94s option for energy minimization studies” *J. Comput. Chem.* **1999**, *20*, 720.

(6) Halgren, T. A. “MMFF VII. Characterization of MMFF94, MMFF94s, and other widely available force fields for conformational energies and for intermolecular-interaction energies and geometries” *J. Comput. Chem.* **1999**, *20*, 730.

Table S1. Minimized model of [2]catenane **1** based on crystal structure (*m*-xylene edge-to-face) Potential Energy(kcal/mol): 204.10662

F 18.8562 0.1515 6.1339	F 18.7082 2.8229 5.7694	F 19.6993 2.2529 1.1803
F 19.8462 -0.4170 1.5411	F 9.8595 -0.4889 2.8665	F 9.9974 2.1756 2.4829
F 10.0069 2.8472 7.1673	F 9.8284 0.1919 7.5478	O 17.8855 4.4621 2.5697
O 14.4318 5.2024 3.5558	O 11.6342 4.1480 3.9789	N 18.1559 -2.4793 3.8413
N 11.2101 -2.3625 5.6275	C 14.5879 -2.2890 4.5592	H 14.5549 -1.2096 4.4383
C 13.3872 -3.0156 4.5615	C 13.4436 -4.4052 4.7128	H 12.5251 -4.9878 4.7254
C 14.6742 -5.0478 4.8694	H 14.7083 -6.1271 4.9921	C 15.8610 -4.3098 4.8819
H 16.8127 -4.8203 5.0124	C 15.8309 -2.9205 4.7223	C 17.0917 -2.0814 4.7761
H 16.8193 -1.0335 4.6139	H 17.4664 -2.1504 5.8060	C 17.7241 -2.4824 2.4459
H 18.5496 -2.7743 1.7867	H 17.3519 -1.5087 2.1198	H 16.9345 -3.2213 2.2739
C 19.3973 -1.7077 4.0471	H 20.1840 -2.1181 3.3988	H 19.7696 -1.9088 5.0607
C 19.3306 -0.2128 3.8426	C 19.0518 0.6523 4.9048	C 18.9721 2.0348 4.7168
C 19.1747 2.6065 3.4611	C 19.4693 1.7485 2.4013	C 19.5497 0.3648 2.5898
C 19.0791 4.0897 3.2577	H 19.1742 4.6425 4.2006	H 19.9242 4.4111 2.6374
C 16.7621 4.6013 3.4421	H 16.9895 5.3257 4.2333	H 16.5424 3.6439 3.9217
C 15.5391 5.0737 2.6614	H 15.7484 6.0402 2.1878	H 15.3097 4.3579 1.8643
C 13.2364 5.5864 2.8663	H 13.0814 4.9220 2.0103	H 13.3650 6.6151 2.5132
C 12.0267 5.5156 3.8024	H 12.2677 5.9419 4.7810	H 11.1965 6.0707 3.3539
C 10.3559 4.0400 4.6006	H 9.5818 4.4577 3.9475	H 10.3540 4.5930 5.5465
C 10.0944 2.5802 4.8162	C 9.9951 1.7004 3.7371	C 9.9076 0.3211 3.9344
C 9.8936 -0.2276 5.2177	C 9.8971 0.6625 6.2936	C 9.9974 2.0412 6.0965
C 9.8956 -1.7207 5.4299	H 9.2528 -1.9543 6.2899	H 9.3870 -2.2063 4.5863
C 11.8809 -1.9115 6.8451	H 12.7148 -2.5710 7.1073	H 11.1993 -1.9523 7.7023
H 12.2707 -0.8917 6.7572	C 12.0645 -2.2864 4.4298	H 12.2653 -1.2420 4.1631
H 11.5364 -2.7272 3.5743	O 15.3739 1.3941 5.0642	O 11.6754 6.6628 7.5147
C 13.0062 6.5720 8.0301	H 12.9845 6.7191 9.1158	H 13.6306 7.3546 7.5820
C 11.2390 8.0217 7.4326	H 11.8625 8.5536 6.7054	H 11.3448 8.4851 8.4199
O 9.6402 7.7848 5.6116	O 8.7694 8.6117 2.8670	O 11.9517 3.3338 -0.0809
C 13.4066 1.8223 1.9165	H 12.4828 2.2518 2.2997	C 13.5571 1.6693 0.5290
C 14.7571 1.1485 0.0369	H 14.9050 1.0137 -1.0314	C 15.7860 0.8075 0.9142
H 16.7230 0.4197 0.5231	C 15.6198 0.9683 2.2912	H 16.4324 0.7032 2.9575
C 14.4295 1.4786 2.8132	C 14.2009 1.6889 4.2934	H 13.9195 2.7328 4.4516
H 13.3809 1.0357 4.6136	C 15.1204 1.3737 6.4746	H 16.0637 1.1268 6.9745
H 14.4214 0.5600 6.6998	C 14.6237 2.6961 7.0014	C 15.3936 3.8535 6.8434
H 16.3830 3.7894 6.3983	C 14.8775 5.1029 7.1913	H 15.4810 5.9888 7.0100
C 13.5840 5.2174 7.7154	C 12.8464 4.0502 7.9465	H 11.8453 4.1169 8.3670
C 13.3584 2.8006 7.5895	H 12.7423 1.9182 7.7400	C 9.7726 8.0819 7.0077
H 9.1804 7.3583 7.5790	H 9.3934 9.0931 7.1928	C 8.2952 7.9987 5.1678
H 8.0355 9.0537 5.3112	H 7.6245 7.3716 5.7660	C 8.1475 7.6219 3.6941
H 8.6205 6.6528 3.5114	H 7.0805 7.5648 3.4505	C 8.4262 8.4804 1.4857
H 8.8046 9.3705 0.9685	H 7.3355 8.5009 1.3673	C 9.0305 7.2547 0.8478
C 8.2392 6.1343 0.5606	H 7.1731 6.1449 0.7746	C 8.8098 4.9827 0.0136
H 8.1757 4.1222 -0.1860	C 10.1826 4.9287 -0.2596	C 10.9669 6.0602 0.0021
H 12.0347 6.0370 -0.2068	C 10.3998 7.2080 0.5612	H 11.0351 8.0619 0.7881
C 10.7987 3.6808 -0.8406	H 10.0738 2.8581 -0.8114	H 11.0829 3.8622 -1.8837
C 12.4268 2.0291 -0.4002	H 12.7616 2.0204 -1.4435	H 11.6261 1.2892 -0.2787

Table S2. Minimized model of [2]catenane **1** after molecular dynamics (*m*-xylene face-to-face) Potential Energy(kcal/mol): 203.71993

F 17.8427 1.1114 6.2161	F 16.3538 3.3471 6.2274	F 16.9073 3.7443 1.5420
F 18.4587 1.5513 1.5416	F 10.8945 -2.0204 1.5988	F 9.8405 0.4665 1.4473
F 8.8451 0.3228 6.0691	F 9.8721 -2.1626 6.2174	O 14.4235 4.5307 4.4690
O 10.9447 5.6983 4.0744	O 9.7854 2.8101 3.4217	N 18.4582 -1.1484 3.1672
N 12.2213 -3.6695 4.7637	C 15.8619 -2.8367 4.1065	H 15.9348 -3.1337 3.0607
C 14.6160 -2.8824 4.7526	C 14.5438 -2.4515 6.0850	H 13.5902 -2.4492 6.6090
C 15.6851 -2.0079 6.7551	H 15.6108 -1.6771 7.7877	C 16.9156 -1.9709 6.0995
H 17.7905 -1.6077 6.6330	C 17.0170 -2.3835 4.7673	C 18.3355 -2.3395 4.0284
H 19.1810 -2.4375 4.7226	H 18.3718 -3.2566 3.4221	C 19.2750 -1.4740 1.9946
H 20.2843 -1.7972 2.2754	H 19.3628 -0.6174 1.3196	H 18.8061 -2.2745 1.4104
C 19.0291 0.0063 3.8893	H 20.0041 0.3002 3.4746	H 19.2579 -0.2511 4.9312
C 18.1393 1.2207 3.8684	C 17.5839 1.7209 5.0484	C 16.7993 2.8779 5.0533
C 16.5223 3.5689 3.8733	C 17.0912 3.0826 2.6958	C 17.8910 1.9357 2.6944
C 15.6808 4.8093 3.8672	H 16.1787 5.5999 4.4394	H 15.5517 5.1728 2.8438
C 13.3457 5.2148 3.8298	H 13.2645 4.8715 2.7950	H 13.5446 6.2919 3.8124
C 12.0446 4.9388 4.5815	H 11.8137 3.8713 4.5898	H 12.1813 5.2369 5.6248
C 10.3437 5.1319 2.9073	H 11.0960 4.6905 2.2539	H 9.8854 5.9735 2.3774
C 9.2428 4.1261 3.2562	H 8.7287 4.4233 4.1772	H 8.5240 4.0950 2.4292
C 8.7624 1.8527 3.6793	H 8.0181 1.8682 2.8735	H 8.2507 2.1159 4.6122
C 9.3631 0.4823 3.7655	C 9.8893 -0.1505 2.6376	C 10.4239 -1.4410 2.7134
C 10.4455 -2.1467 3.9181	C 9.9160 -1.5129 5.0448	C 9.3837 -0.2232 4.9683
C 10.9689 -3.5579 3.9969	H 10.1761 -4.1459 4.4820	H 11.0808 -3.9964 2.9965
C 12.3802 -5.0414 5.2602	H 12.4025 -5.7744 4.4454	H 11.5558 -5.3009 5.9341
H 13.2986 -5.1538 5.8457	C 13.3902 -3.2857 3.9489	H 13.1494 -2.4164 3.3266
H 13.6528 -4.0973 3.2566	O 13.1332 1.5888 4.9986	O 11.8947 6.9393 9.1876
C 11.0843 5.7887 9.4413	H 10.0357 6.0121 9.2111	H 11.1461 5.5701 10.5130
C 11.5942 7.5590 7.9349	H 10.8697 8.3632 8.1062	H 11.1340 6.8618 7.2241
O 12.5776 8.7309 6.0772	O 14.5259 9.7607 3.1639	O 12.3520 4.0911 0.1950
C 13.0187 1.6741 2.0733	H 12.2241 2.1885 2.6119	C 13.1327 1.8397 0.6806
C 14.1613 1.1803 -0.0056	H 14.2741 1.2996 -1.0801	C 15.0511 0.3620 0.6813
H 15.8523 -0.1447 0.1499	C 14.9131 0.1884 2.0566	H 15.6159 -0.4613 2.5721
C 13.9017 0.8444 2.7754	C 13.7513 0.5460 4.2494	H 13.1363 -0.3521 4.3480
H 14.7446 0.3551 4.6702	C 13.0866 1.2368 6.3832	H 14.0888 0.9629 6.7359
H 12.4375 0.3630 6.5202	C 12.5622 2.3862 7.2026	C 13.4435 3.2210 7.8985
H 14.5156 3.0476 7.8507	C 12.9634 4.3027 8.6384	H 13.6708 4.9470 9.1569
C 11.5920 4.5867 8.6826	C 10.7066 3.7402 8.0054	H 9.6372 3.9332 8.0180
C 11.1892 2.6540 7.2689	H 10.4880 2.0300 6.7227	C 12.8776 8.1193 7.3300
H 13.3282 8.8570 8.0037	H 13.5983 7.3031 7.1973	C 13.7580 9.0527 5.3437
H 14.4092 8.1741 5.2612	H 14.3197 9.8385 5.8616	C 13.3561 9.5165 3.9481
H 12.7239 8.7482 3.4891	H 12.7616 10.4352 4.0128	C 14.2218 9.9593 1.7810
H 15.0740 10.4759 1.3251	H 13.3531 10.6185 1.6653	C 14.0288 8.6337 1.0870
C 12.7605 8.2336 0.6487	H 11.9021 8.8905 0.7693	C 12.5719 6.9656 0.0969
H 11.5728 6.6562 -0.2018	C 13.6442 6.0718 -0.0258	C 14.9207 6.4919 0.3674
H 15.7715 5.8198 0.2801	C 15.1098 7.7569 0.9284	H 16.1002 8.0478 1.2726
C 13.4216 4.6735 -0.5464	H 13.1596 4.7156 -1.6096	H 14.3346 4.0806 -0.4298
C 12.1576 2.7077 -0.0759	H 12.1936 2.5199 -1.1561	H 11.1420 2.4511 0.2458

Table S3. Minimized model of [2]catenane **1** with forced interstitial stacking (π-stacking) Potential Energy(kcal/mol): 210.76049

F 16.3473 1.5405 8.2708	F 17.1242 4.0037 7.5446	F 19.7309 2.1776 4.0484
F 18.9398 -0.3052 4.7509	F 11.3855 -0.7597 2.4012	F 12.8344 1.1787 1.2476
F 10.9832 4.3411 4.2267	F 9.5363 2.3977 5.3941	O 18.1003 4.8041 4.0690
O 16.3043 6.6973 2.2848	O 13.1997 4.8875 3.0284	N 16.9179 -1.2299 8.1949
N 10.1327 -0.6658 5.9762	C 13.5407 -1.8258 7.2756	H 13.8242 -2.5281 6.4945
C 12.2943 -1.1680 7.1929	C 11.9654 -0.2460 8.1986	H 11.0293 0.3079 8.1617
C 12.8435 0.0114 9.2517	H 12.5775 0.7371 10.0158	C 14.0772 -0.6317 9.3068
H 14.7696 -0.3909 10.1117	C 14.4468 -1.5530 8.3181	C 15.8209 -2.2021 8.3793
H 15.8940 -2.6672 9.3724	H 15.8962 -3.0251 7.6568	C 18.1738 -1.7628 8.7225
H 18.0833 -1.9703 9.7946	H 18.9838 -1.0334 8.6161	H 18.4742 -2.6892 8.2195
C 17.0641 -0.8489 6.7805	H 16.0896 -0.8498 6.2825	H 17.6549 -1.6090 6.2517
C 17.6320 0.5297 6.5410	C 17.1966 1.6624 7.2404	C 17.5869 2.9499 6.8550
C 18.4279 3.1579 5.7628	C 18.8962 2.0297 5.0884	C 18.4980 0.7429 5.4647
C 18.7796 4.5383 5.2981	H 18.4936 5.2870 6.0461	H 19.8638 4.6088 5.1475
C 18.3401 6.1385 3.6064	H 19.4226 6.2794 3.5131	H 17.9370 6.8512 4.3345
C 17.6970 6.3573 2.2297	H 18.1866 7.2137 1.7541	H 17.8363 5.4873 1.5781
C 15.4840 5.6005 2.6844	H 15.6564 5.3822 3.7424	H 15.7368 4.7163 2.0947
C 14.0084 5.9270 2.4825	H 13.7689 6.8510 3.0220	H 13.7821 6.1157 1.4249
C 12.7941 3.9117 2.0662	H 13.6823 3.4922 1.5828	H 12.1771 4.4036 1.3112
C 11.9891 2.8244 2.7253	C 12.0376 1.5078 2.2704	C 11.2814 0.4949 2.8699
C 10.4408 0.7572 3.9502	C 10.3595 2.0802 4.3835	C 11.1141 3.0893 3.7777
C 9.6576 -0.3430 4.6187	H 8.6169 0.0080 4.6634	H 9.6354 -1.2438 3.9918
C 9.1004 -1.4150 6.6998	H 8.1954 -0.8073 6.8137	H 9.4299 -1.6728 7.7119
H 8.8301 -2.3428 6.1820	C 11.4046 -1.4156 5.9788	H 12.0094 -1.1242 5.1131
H 11.2222 -2.4933 5.8735	O 16.2858 1.3787 -0.4266	O 14.0306 2.8626 5.8531
C 14.0984 1.4577 5.6305	H 13.0837 1.0646 5.5321	H 14.5900 0.9822 6.4793
C 13.1367 3.2052 6.9108	H 13.5936 2.9617 7.8762	H 12.1985 2.6451 6.8309
O 11.7599 5.0513 7.6875	O 9.1639 6.8765 5.8543	O 10.3015 3.7510 -0.1789
C 12.8624 2.2225 -1.4161	H 12.3651 1.2936 -1.1451	C 12.0861 3.3637 -1.6707
C 12.7371 4.5607 -1.9938	H 12.1582 5.4644 -2.1701	C 14.1290 4.6125 -2.0694
H 14.6242 5.5459 -2.3271	C 14.8883 3.4737 -1.7911	H 15.9737 3.5333 -1.8307
C 14.2676 2.2693 -1.4372	C 15.0700 1.0309 -1.0942	H 14.4643 0.3617 -0.4717
H 15.3232 0.4984 -2.0175	C 16.7184 0.3857 0.5080	H 17.8062 0.4808 0.6076
H 16.5159 -0.6233 0.1259	C 16.1053 0.6201 1.8667	C 16.2387 1.8648 2.4854
H 16.8137 2.6512 2.0014	C 15.6139 2.1277 3.7049	H 15.7136 3.1161 4.1457
C 14.8451 1.1540 4.3495	C 14.7731 -0.1189 3.7654	H 14.2094 -0.9112 4.2515
C 15.3894 -0.3826 2.5333	H 15.2786 -1.3686 2.0885	C 12.8384 4.6964 6.8170
H 13.7227 5.2803 7.0961	H 12.6062 4.9490 5.7783	C 11.0566 6.2034 7.2090
H 11.6502 6.7797 6.4886	H 10.8870 6.8656 8.0653	C 9.7063 5.7961 6.6196
H 9.8111 4.9009 6.0056	H 9.0176 5.5413 7.4345	C 7.9577 6.5124 5.1779
H 7.4242 7.4394 4.9373	H 7.3092 5.9404 5.8521	C 8.2038 5.7741 3.8819
C 7.5873 4.5401 3.6324	H 6.9383 4.0914 4.3822	C 7.8156 3.8519 2.4327
H 7.3276 2.8911 2.2786	C 8.6720 4.3797 1.4566	C 9.2610 5.6307 1.6951
H 9.9320 6.0662 0.9575	C 9.0334 6.3177 2.8937	H 9.5278 7.2708 3.0655
C 8.9254 3.6343 0.1664	H 8.6886 2.5703 0.2859	H 8.2887 4.0570 -0.6188
C 10.5890 3.3252 -1.5050	H 10.1115 3.9975 -2.2276	H 10.2092 2.3111 -1.6737

Table S4. Minimized model of [2]catenane **1** with sodium ion complexed Potential Energy(kcal/mol): 116.40577

F 16.9600 -0.8535 1.6854	F 16.4912 1.7333 1.0569	F 11.8764 0.8052 0.6320
F 12.3397 -1.7824 1.2356	F 9.9927 0.1553 7.2230	F 10.1237 2.7961 6.6406
F 13.4809 3.3635 9.9059	F 13.3242 0.7371 10.5344	O 13.8462 3.5169 1.8062
O 13.0744 5.4082 3.8612	O 12.5531 4.7069 6.6005	N 14.7193 -3.0166 3.3714
N 12.5176 -1.8778 8.2441	C 13.0511 -3.8699 5.8649	H 12.6124 -2.9739 5.4307
C 12.8158 -4.1708 7.2179	C 13.3638 -5.3456 7.7541	H 13.1884 -5.6140 8.7942
C 14.1467 -6.1874 6.9645	H 14.5643 -7.0964 7.3909	C 14.4025 -5.8603 5.6336
H 15.0232 -6.5269 5.0416	C 13.8666 -4.6935 5.0688	C 14.1481 -4.3632 3.6135
H 14.8086 -5.1282 3.1832	H 13.1860 -4.4472 3.0919	C 16.0184 -2.8828 4.0503
H 15.9128 -2.9752 5.1364	H 16.4488 -1.8907 3.8828	H 16.7424 -3.6341 3.7128
C 14.8892 -2.8147 1.9132	H 14.1666 -3.4222 1.3518	H 15.8703 -3.1634 1.5618
C 14.6602 -1.3850 1.5050	C 15.7020 -0.4591 1.4383	C 15.4594 0.8791 1.1189
C 14.1682 1.3408 0.8591	C 13.1329 0.4092 0.8886	C 13.3751 -0.9296 1.2012
C 13.9006 2.7836 0.5716	H 14.6988 3.1846 -0.0652	H 12.9518 2.9014 0.0327
C 13.5570 4.9004 1.5147	H 12.5019 4.9593 1.2508	H 14.1604 5.2424 0.6665
C 13.8568 5.7910 2.7140	H 14.9092 5.7045 2.9792	H 13.6336 6.8294 2.4535
C 13.3515 6.3083 4.9456	H 13.2291 7.3448 4.6101	H 14.3834 6.1554 5.2660
C 12.4098 6.0525 6.1177	H 12.6414 6.7633 6.9190	H 11.3716 6.1914 5.8036
C 11.8982 4.5788 7.8703	H 10.8837 4.9950 7.8176	H 12.4578 5.1499 8.6195
C 11.8190 3.1338 8.2418	C 10.9282 2.2889 7.5863	C 10.8611 0.9292 7.8916
C 11.6771 0.3682 8.8748	C 12.5409 1.2238 9.5610	C 12.6170 2.5820 9.2428
C 11.6340 -1.1108 9.1510	H 11.8603 -1.3183 10.2056	H 10.5885 -1.4257 9.0248
C 13.8892 -1.9030 8.7753	H 13.9473 -2.4001 9.7500	H 14.2858 -0.8896 8.8804
H 14.5766 -2.4060 8.0868	C 11.9870 -3.2563 8.1023	H 10.9852 -3.2139 7.6535
H 11.8656 -3.7159 9.0942	O 11.8640 8.1761 0.7929	O 10.5135 2.1330 3.3565
C 9.3058 2.7274 2.8569	H 8.5346 2.7435 3.6373	H 8.9338 2.1266 2.0182
C 10.1936 0.9080 4.0402	H 9.4975 0.3055 3.4434	H 9.7090 1.1634 4.9857
O 12.4659 0.9086 4.9262	O 15.0373 2.1037 5.2684	O 16.9438 7.5792 1.9278
C 14.7894 9.0954 0.6738	H 14.6270 8.9743 1.7431	C 16.0891 8.9610 0.1574
C 16.2880 9.1347 -1.2183	H 17.2852 9.0554 -1.6455	C 15.2113 9.4037 -2.0627
H 15.3791 9.5269 -3.1307	C 13.9220 9.5095 -1.5416	H 13.0947 9.7066 -2.2203
C 13.6961 9.3626 -0.1669	C 12.3031 9.4738 0.3964	H 12.3052 10.1471 1.2626
H 11.6196 9.8857 -0.3575	C 10.4983 8.1888 1.2027	H 9.8541 8.5077 0.3751
H 10.3662 8.8906 2.0342	C 10.1339 6.7912 1.6289	C 10.0572 6.4558 2.9857
H 10.2252 7.2145 3.7460	C 9.7861 5.1424 3.3772	H 9.7327 4.9015 4.4364
C 9.5882 4.1385 2.4216	C 9.6498 4.4748 1.0637	H 9.4977 3.7146 0.2991
C 9.9179 5.7902 0.6710	H 9.9837 6.0276 -0.3891	C 11.4587 0.0986 4.2966
H 11.2246 -0.7631 4.9316	H 11.8464 -0.2659 3.3448	C 13.6553 0.1282 5.1350
H 14.0981 -0.0943 4.1614	H 13.4057 -0.8012 5.6497	C 14.6475 0.9156 5.9764
H 14.1930 1.2161 6.9246	H 15.5252 0.2884 6.1734	C 16.1635 2.7055 5.9254
H 16.9718 1.9734 6.0425	H 15.8450 3.0433 6.9185	C 16.6791 3.8572 5.1056
C 16.8741 5.1172 5.6857	H 16.6403 5.2815 6.7367	C 17.3435 6.1886 4.9191
H 17.4505 7.1656 5.3845	C 17.6507 6.0142 3.5640	C 17.5004 4.7405 2.9964
H 17.7246 4.5798 1.9433	C 17.0215 3.6744 3.7607	H 16.9077 2.6978 3.2975
C 18.0723 7.1789 2.7063	H 18.4172 8.0168 3.3251	H 18.8971 6.8718 2.0510
C 17.2616 8.6701 1.0625	H 18.1426 8.4081 0.4639	H 17.4914 9.5613 1.6573
Na 12.8582 3.1335 4.1303		

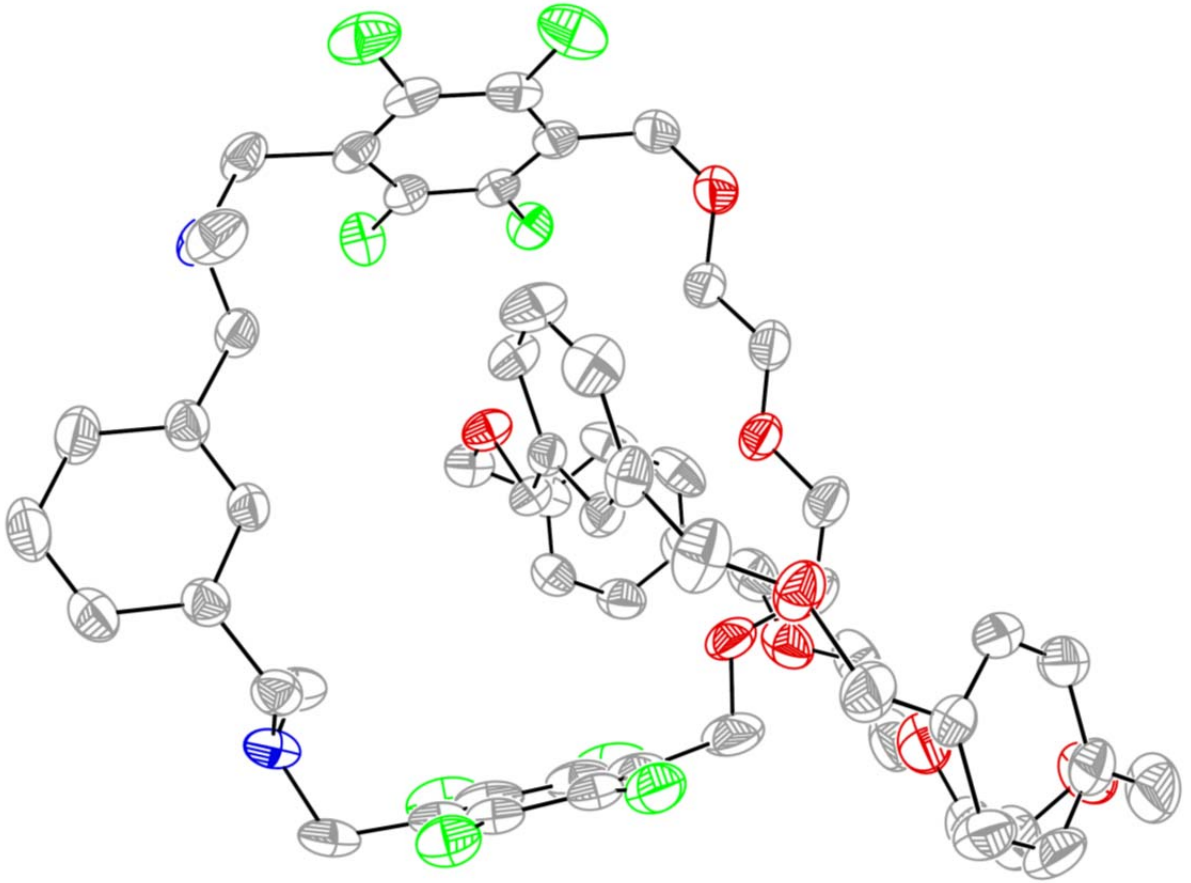


Figure S15. ORTEP diagram (50% ellipsoid probability) of the molecular structure of [2]catenane **1**.

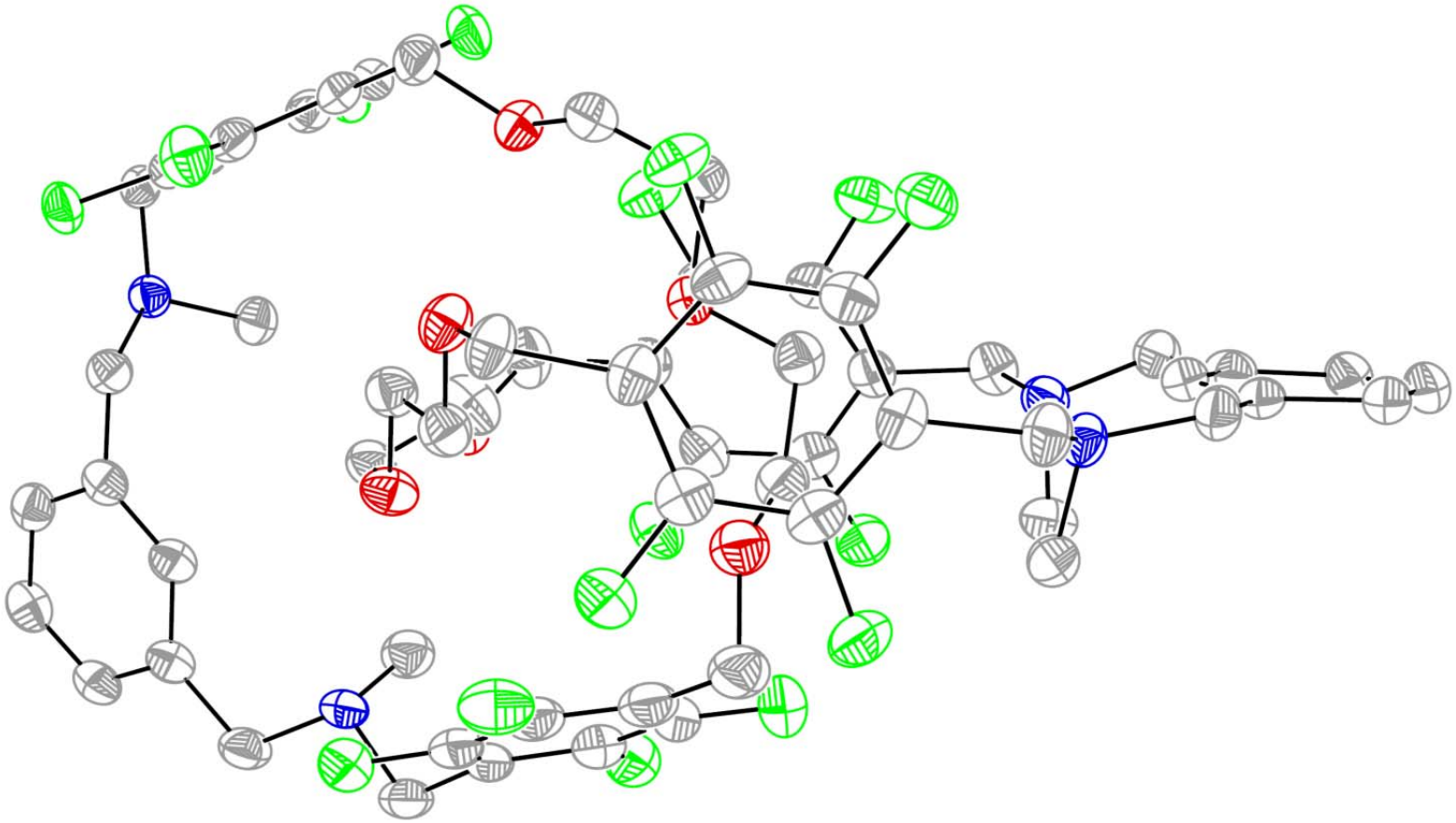


Figure S16. ORTEP diagram (50% ellipsoid probability) of the molecular structure of [2]catenane **11**.

Crystal Data of 1 and Methods for Growing and Analyzing the Single Crystals

Single crystals suitable for X-ray analysis were obtained after liquid diffusion of hexane into a CH_2Cl_2 solution of **1**.

Data were collected using an Agilent Xcalibur [Atlas, Gemini Enhance (Mo) X-ray Source] diffractometer with ω scans at 150(2) K. Integration and reduction of the data were performed using CrysAlisPRO. Absorption corrections were applied to the data using Multi-scan (CrysAlisPRO; Agilent, 2014). SHELXS-97 was applied to solve the structures by direct methods; subsequent refinement and extension were performed using SHELXL-97. Non-hydrogen atoms were refined anisotropically at large. Carbon-bound hydrogen atoms were included in idealized positions and refined using a riding model. The molecules were modeled using standard crystallographic methods, including constraints, restraints, and rigid bodies where necessary.

Crystal data for **1**: $[C_{58}H_{62}F_8N_2O_8]$; M_r = 1067.10; triclinic; space group *P-1*; a = 12.5540(6); b = 13.1199(7); c = 16.8258(8) Å; V = 2635.7(2) Å^3; ρ_{calcd} = 1.345 g cm^{-3}; $\mu(Cu_{K\alpha})$ = 0.912 mm^{-1}; T = 150(2) K; colorless plate; 9587 independent measured reflections; F^2 refinement; R_1 = 0.0550; wR_2 = 0.1616. CCDC-1814902 contains the supplementary crystallographic data for this structure. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal Data of 11 and Methods for Growing and Analyzing the Single Crystals

Single crystals suitable for X-ray analysis were obtained after liquid diffusion of hexane into a CH_2Cl_2 solution of **11**.

Data were collected using an Agilent Xcalibur [Atlas, Gemini Enhance (Mo) X-ray Source] diffractometer with ω scans at 150(2) K. Integration and reduction of the data were performed using CrysAlisPRO. Absorption corrections were applied to the data using Multi-scan (CrysAlisPRO; Agilent, 2014). SHELXS-97 was applied to solve the structures by direct methods; subsequent refinement and extension were performed using SHELXL-97. Non-hydrogen atoms were refined anisotropically at large. Carbon-bound hydrogen atoms were included in idealized positions and refined using a riding model. The molecules were modeled using standard crystallographic methods, including constraints, restraints, and rigid bodies where necessary.

Crystal data for **11**: $[C_{60}H_{60}F_{16}N_4O_6]$; M_r = 1237.12; orthorhombic; space group *Iba2*; a = 31.1008(7); b = 15.9050(6); c = 22.8099(7) Å; V = 11283.1(6) Å^3; ρ_{calcd} = 1.457 g cm^{-3}; $\mu(Cu_{K\alpha})$ = 1.129 mm^{-1}; T = 150(2) K; colorless column; 8124 independent measured reflections; F^2 refinement; R_1 = 0.0423; wR_2 = 0.1181. CCDC-1814903 contains the supplementary crystallographic data for this structure. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.