Supporting Information

Catenation of Calixarene Annulus

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TABLE OF CONTENTS

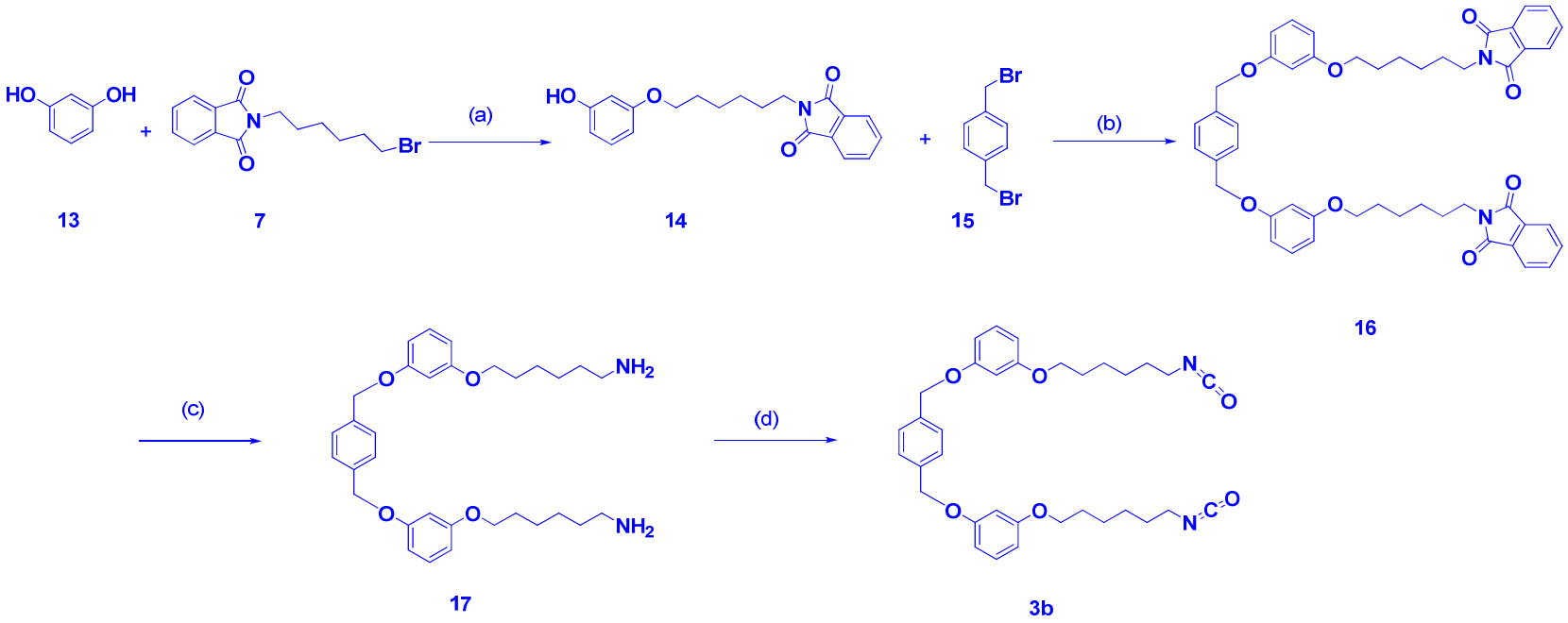
GENERAL COMMENTS

ESI-MS$^+$ measurements for calix[2]catenanes **4**$^+$·TFPB$^-$ and **12**$^+$·TFPB$^-$ were performed on a Waters Q-Tof Premiere mass spectrometer equipped with electrospray ion source, using a mixture of CH_2Cl_2/CH_3OH/HCOOH (80:18:2) as solvent. All the others ESI-MS$^+$ measurements were performed on a Micromass Bio-Q triple quadrupole mass spectrometer equipped with electrospray ion source, using a mixture of H_2O/CH_3CN (1:1) and 5% HCOOH as solvent. Flash chromatography was performed on Merck silica gel (60, 40-63 μm). All chemicals were reagent grade and were used without further purification. Anhydrous solvents were purchased from Aldrich. When necessary compounds were dried *in vacuo* over $CaCl_2$. Reaction temperatures were measured externally. Reactions were monitored by TLC on Merck silica gel plates (0.25 mm) and visualized by UV light, or by sprying with H_2SO_4-$Ce(SO_4)_2$ or phosphomolybdic acid. Derivatives **1a**,[1] **1b**,[2] **3a**,[3] **10**,[4] and sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate[5] were synthesized according to literature procedures.

1D and 2D NMR spectra were recorded on a Bruker Avance-400 spectrometer [400 (^{1}H) and 100 MHz (^{13}C)], Bruker Avance-300 spectrometer [300 (^{1}H) and 75 MHz (^{13}C)], or Bruker Avance-250 spectrometer [250 (^{1}H) and 63 MHz (^{13}C)]; chemical shifts are reported relative to the residual solvent peak (C*H*Cl$_3$: δ 7.26, *C*DCl$_3$: δ 77.23; $C_6H_5CH_3$: δ 2.09, $C_6D_5CD_3$: δ 20.4; CD_3OH: δ 4.87, *C*D$_3$OD: δ 49.0; THF-d_8: 3.58, 1.73). Standard pulse programs, provided by the manufacturer, were used for 2D COSY-45 and 2D ROESY experiments. Molecular modeling studies were performed with a combined use of the MacroModel-9/Maestro-4.1 program and the Gaussian-09 software package.

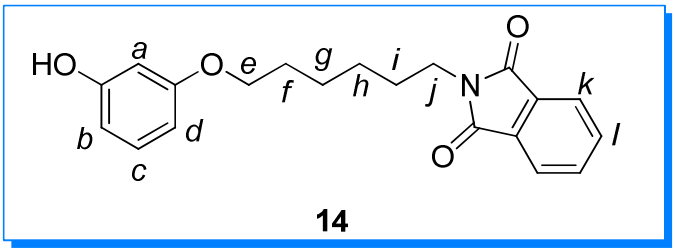
[1] Gutsche, C. D.; Lin, L. G. *Tetrahedron* **1986**, *42*, 1633.
[2] Gaeta, C.; Troisi, F.; Neri, P. *Org. Lett.* **2010**, *12*, 2092.
[3] Ovalos, M.; Babiano, R.; Cintas, P.; Gomez-Carretero, A.; Jimenez, J. L.; Lozano, M.; Ortiz, A. L.; Palacios, J. C.; Pinazo, A. *Chem. Eur. J.* **2008**, *14*, 5656.
[4] Pierro, T.; Gaeta, C.; Talotta, C.; Casapullo, A.; Neri, P. *Org. Lett.* **2011**, *13*, 2650.
[5] Nishida, H.; Takada, N.; Yoshimura, M.; Sonoda, T.; Kobayashi, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2600.

Synthesis of Diisocyanate Derivative 3b



Scheme S1. Synthesis of derivative **3b**. Reagents and conditions: (a) K_2CO_3, [18]crown-6, dry CH_3CN, RT, 4 h; (b) K_2CO_3, [18]crown-6, dry CH_3CN, reflux, 25 h; (c) NH_2NH_2, EtOH, reflux, 1 h; (d) triphosgene/dry toluene, dry NEt_3, reflux, 5h.

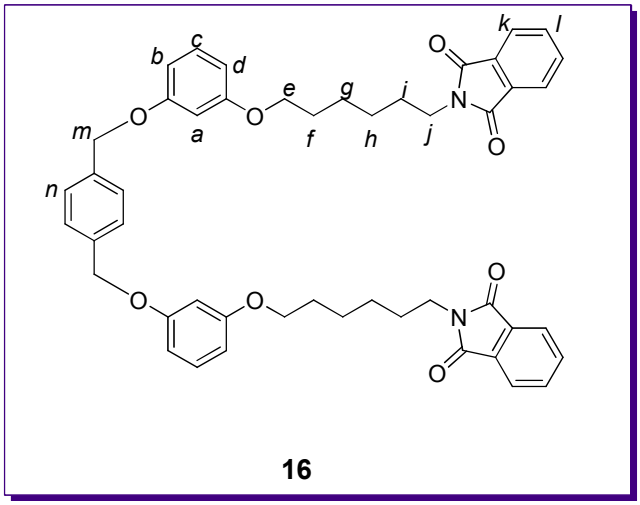
Derivative **14**



14

To a solution of resorcinol **13** (1.76 g, 16.0 mmol) in 60 mL of dry acetonitrile were added K_2CO_3 (1.1 g, 8.0 mmol) and [18]crown-6 (0.21 g, 0.81 mmol) under stirring. The mixture was refluxed for 1h, then a solution of derivative **7** (2.48 g, 8.02 mmol) in 20 mL of dry acetonitrile was slowly added and the mixture was refluxed for 3h. After concentration under vacuum, the mixture was partitioned between AcOEt (80 mL) and water (80 mL), then the organic layer was dried over $MgSO_4$ filtered and evaporated under reduced pressure. The crude product was subjected to flash chromatography on silica gel (CH_2Cl_2/Et_2O, 90/10, *v/v*), to give derivative **14** as a white solid (0.95 g, 35%). ESI-MS$^+$: *m/z* = 340 (MH^+); **^{1}H NMR** (250 MHz, $CDCl_3$, 298 K): δ 1.41-1.78 (overlapped, 8H, $H_{f+g+h+i}$), 3.70 (t, J = 7.3 Hz, 2H, H_j), 3.92 (t, J = 6.5 Hz, 2H, H_e), 5.09 (s, 1H, OH), 6.40-6.47 (overlapped, 3H, H_{a+b+d}), 7.01 (t, J = 8.8 Hz, 1H, H_c), 7.69-7.85 (overlapped, 4H, H_{k+l}); **^{13}C NMR** (63 MHz, $CDCl_3$, 298 K): δ 26.2, 27.2, 29.0, 29.5, 68.4, 102.5, 107.7, 108.2, 123.9, 130.7, 132.7, 134.6, 157.4, 161.0, 169.2. Anal. Calcd for $C_{20}H_{21}NO_4$: C, 70.78; H, 6.24. Found: C, 70.87; H, 6.15.

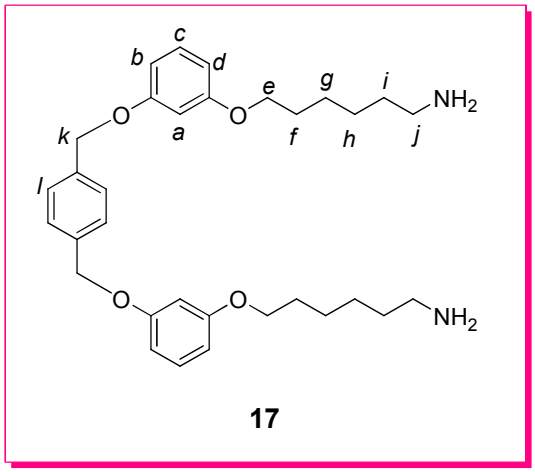
Derivative **16**



16

To a solution of derivative **14** (0.95 g, 2.8 mmol), in 30 mL of dry acetonitrile were added K_2CO_3 (1.9 g, 14.0 mmol) and [18]crown-6 (0.81 g, 3.1 mmol) under stirring. The mixture was refluxed for 1 h, then a solution of derivative **15** (0.34 g, 1.3 mmol) in 10 mL of dry acetonitrile was slowly added and the mixture was refluxed for 24 h. After concentration under vacuum, the mixture was partitioned between AcOEt (80 mL) and water (80 mL), then the organic layer was dried over $MgSO_4$ filtered and evaporated under reduced pressure to give **16** as a yellow solid (0.56 g, 55%). ESI-MS$^+$: m/z = 781 (MH^+); **^{1}H NMR** (250 MHz, $CDCl_3$, 298 K): δ 1.43-1.79 (overlapped, 16H, $H_{f+g+h+i}$), 3.69 (t, J = 7.3 Hz, 4H, H_j), 3.91 (t, J = 6.3 Hz, 4H, H_e), 5.04 (s, 4H, H_m), 6.47-6.57 (overlapped, 6H, H_{a+b+d}), 7.15 (t, J = 8.8 Hz, 2H, H_c), 7.44 (s, 4H, H_n), 7.68-7.85 (overlapped, 8H, H_{k+l}); **^{13}C NMR** (63 MHz, $CDCl_3$, 298 K): δ 26.2, 27.1, 29.0, 29.6, 38.4, 68.3, 70.2, 102.3, 107.4, 123.8, 128.2, 130.3, 132.7, 134.4, 137.4, 160.4, 160.8, 168.9, 169.7. Anal. Calcd for $C_{48}H_{48}N_2O_8$: C, 73.83; H, 6.20. Found: C, 73.92; H, 6.11.

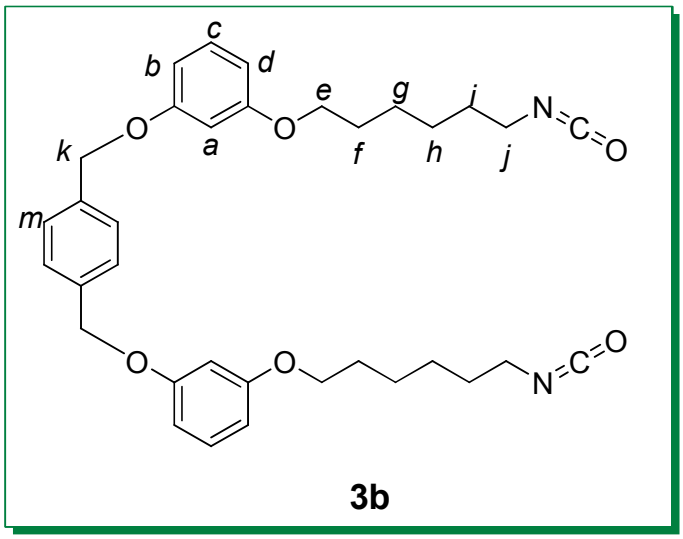
Derivative **17**



17

A solution of derivate **16** (0.6 g, 0.8 mmol) and hydrazine (144.0 mmol, 9.20 mL, 50-60% *v*/*v* solution in H_2O) in EtOH (8 mL) was refluxed for 1 h under N_2. The solution was cooled at room temperature and H_2O (100 mL) was added. The product was extracted with CH_2Cl_2 (3×50 mL) and the organic layers were collected and dried over $MgSO_4$, filtered and evaporated under reduced pressure to give **17** as a white solid (0.33 g, 88%).**^{1}H NMR** (250 MHz, $CDCl_3$, 298 K): δ 1.26-1.80 (overlapped, 16H, $H_{f+g+h+i}$), 2.69 (t, J =6.0 Hz, 4H, H_j), 3.93 (t, J = 6.5 Hz, 4H, H_e), 5.05 (s, 4H, H_k), 6.50-5.57 (overlapped, 6H, H_{a+b+d}), 7.17 (t, J = 9.0 Hz, 2H, H_c), 7.45 (s, 4H, H_l); **^{13}C NMR** (63 MHz, $CDCl_3$, 298 K): δ 26.5, 27.2, 29.8, 34.4, 42.8, 68.4, 70.3, 102.4, 107.4, 107.7, 128.3, 130.4, 137.3, 160.5, 160.9. Anal. Calcd for $C_{32}H_{44}N_2O_4$: C, 73.81; H, 8.52. Found: C, 73.90; H, 8.43.

Derivative **3b**



3b

A mixture of derivative **17** (0.33 g, 0.60 mmol), triphosgene (0.19 g, 0.60 mmol) and NEt_3 (0.14 g, 0.20 mL, 1.4 mmol) in 150 mL of dry toluene was refluxed for 5 h. The mixture was cooled to room temperature and filtered under a stream of N_2. The solvent was removed under reduced pressure to give derivative **3b** as a white solid (0.30 g, 82%). **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ 1.46−1.82 (overlapped, 16H, $H_{f+g+h+i}$), 3.32 (t, J =6.8 Hz, 4H, H_j), 3.95 (t, J = 6.4 Hz, 4H, H_e), 5.06 (s, 4H, H_k), 6.52-6.59 (overlapped, 6H, H_{a+b+d}), 7.18 (t, J = 8.4 Hz, 2H, H_c), 7.46 (s, 4H, H_m); **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K): δ 26.1, 26.9, 29.7, 31.8, 43.5, 68.3, 70.3, 102.4, 107.5, 107.7, 125.9, 128.3, 128.8, 129.6, 130.5, 137.3, 160.5, 160.9. Anal. Calcd for $C_{34}H_{40}N_2O_6$: C, 71.31; H, 7.04. Found: C, 71.40; H, 6.95.

^{1}H and ^{13}C NMR spectra of derivatives 14, 16, 17, and 3b

Derivative 14

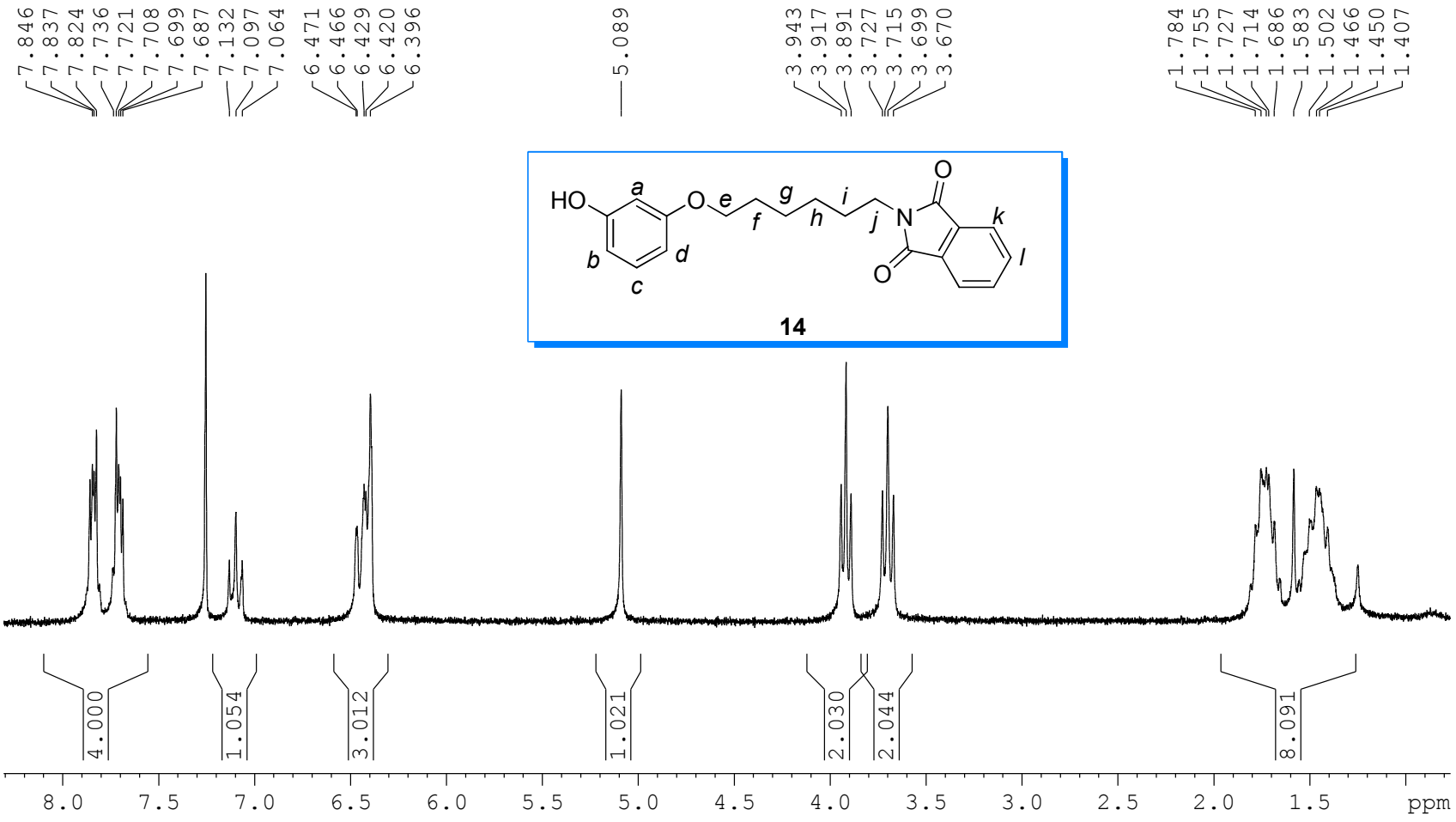


Figure S1. ^{1}H NMR spectrum of derivative **14** (250 MHz, $CDCl_3$, 298 K).

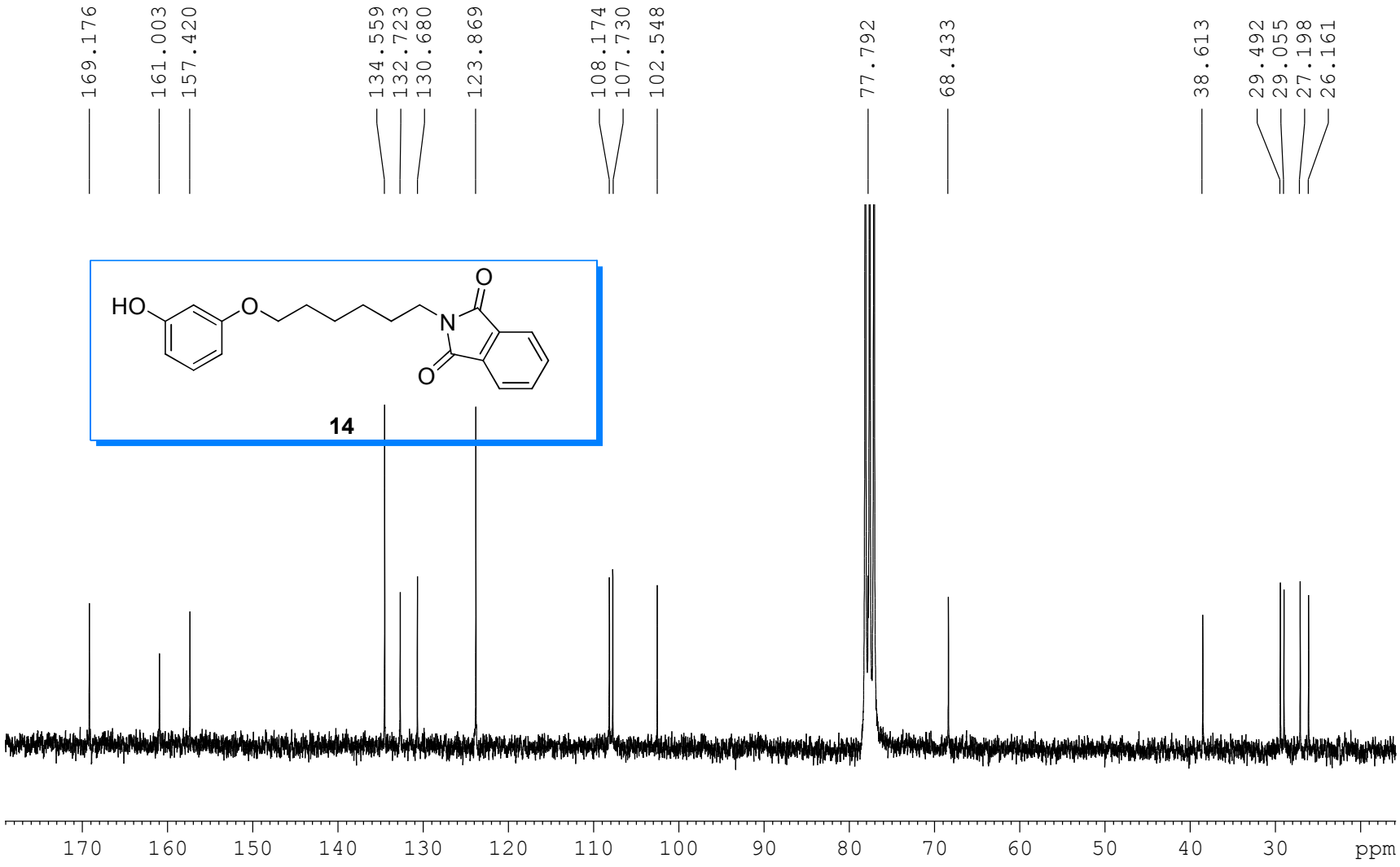


Figure S2. ^{13}C NMR spectrum of derivative **14** (63 MHz, $CDCl_3$, 298 K).

Derivative 16

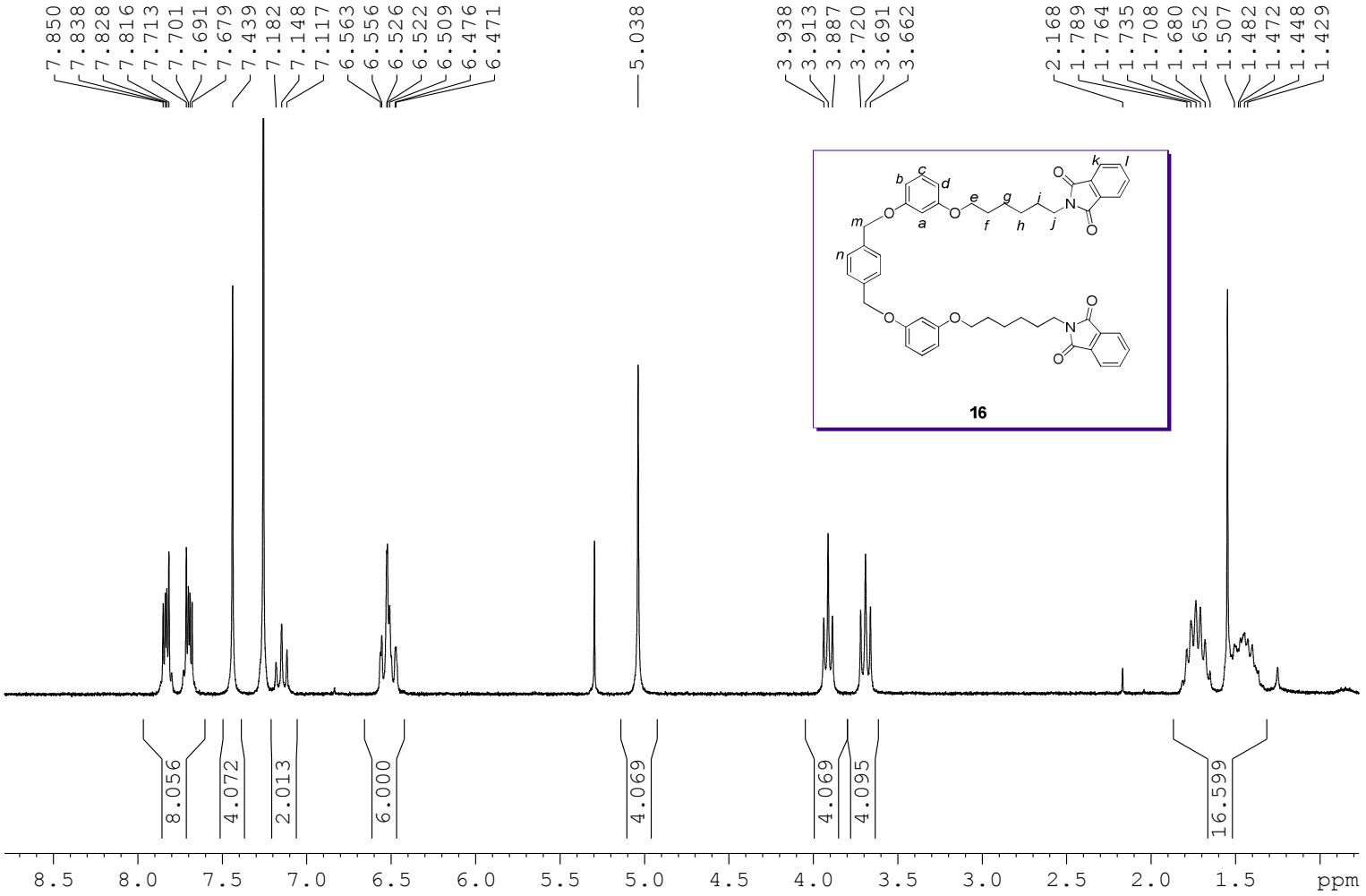


Figure S3. ^{1}H NMR spectrum of derivative **16** (250 MHz, $CDCl_3$, 298 K).

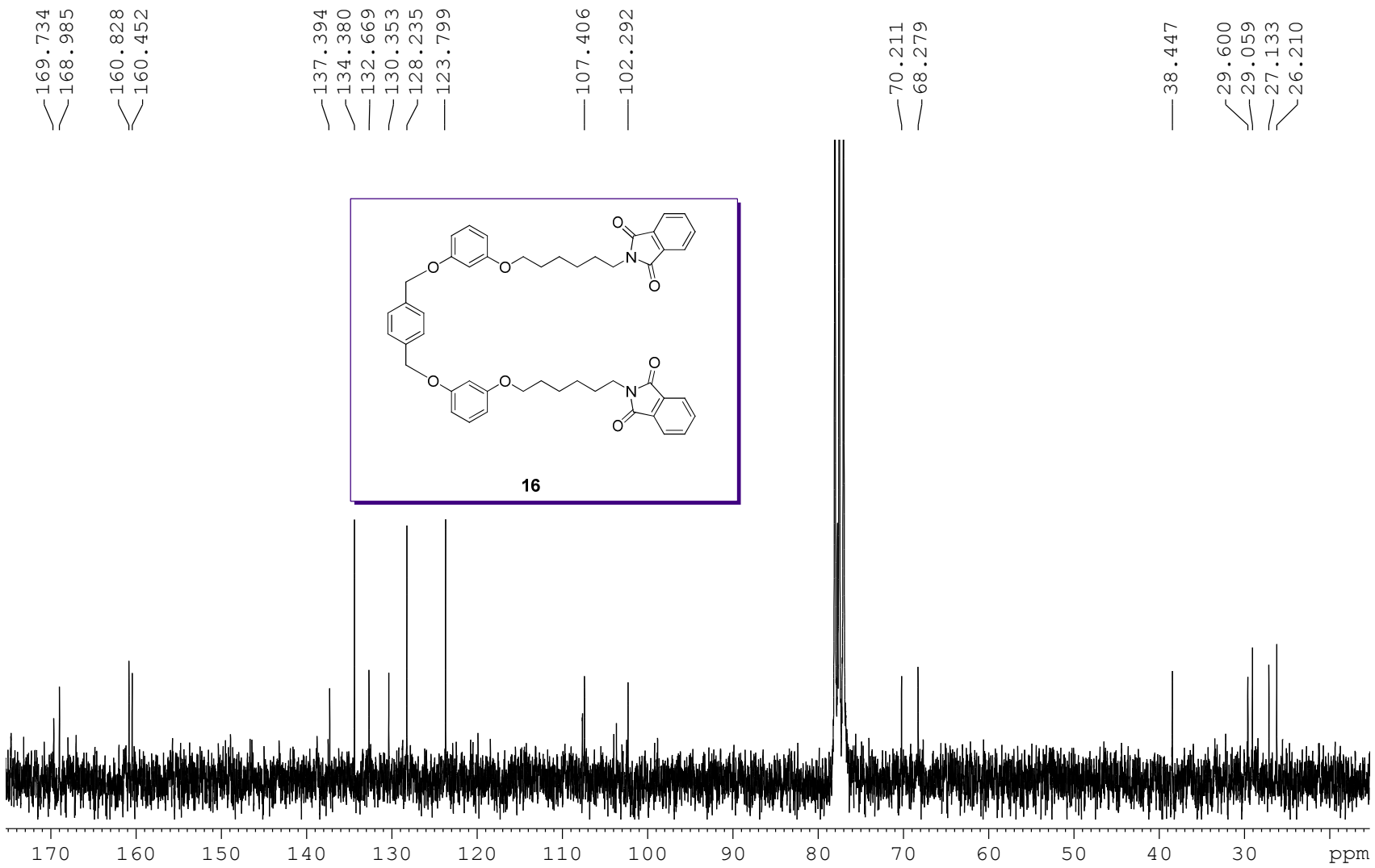


Figure S4. ^{13}C NMR spectrum of derivative **16** (63 MHz, $CDCl_3$, 298 K).

Derivative 17

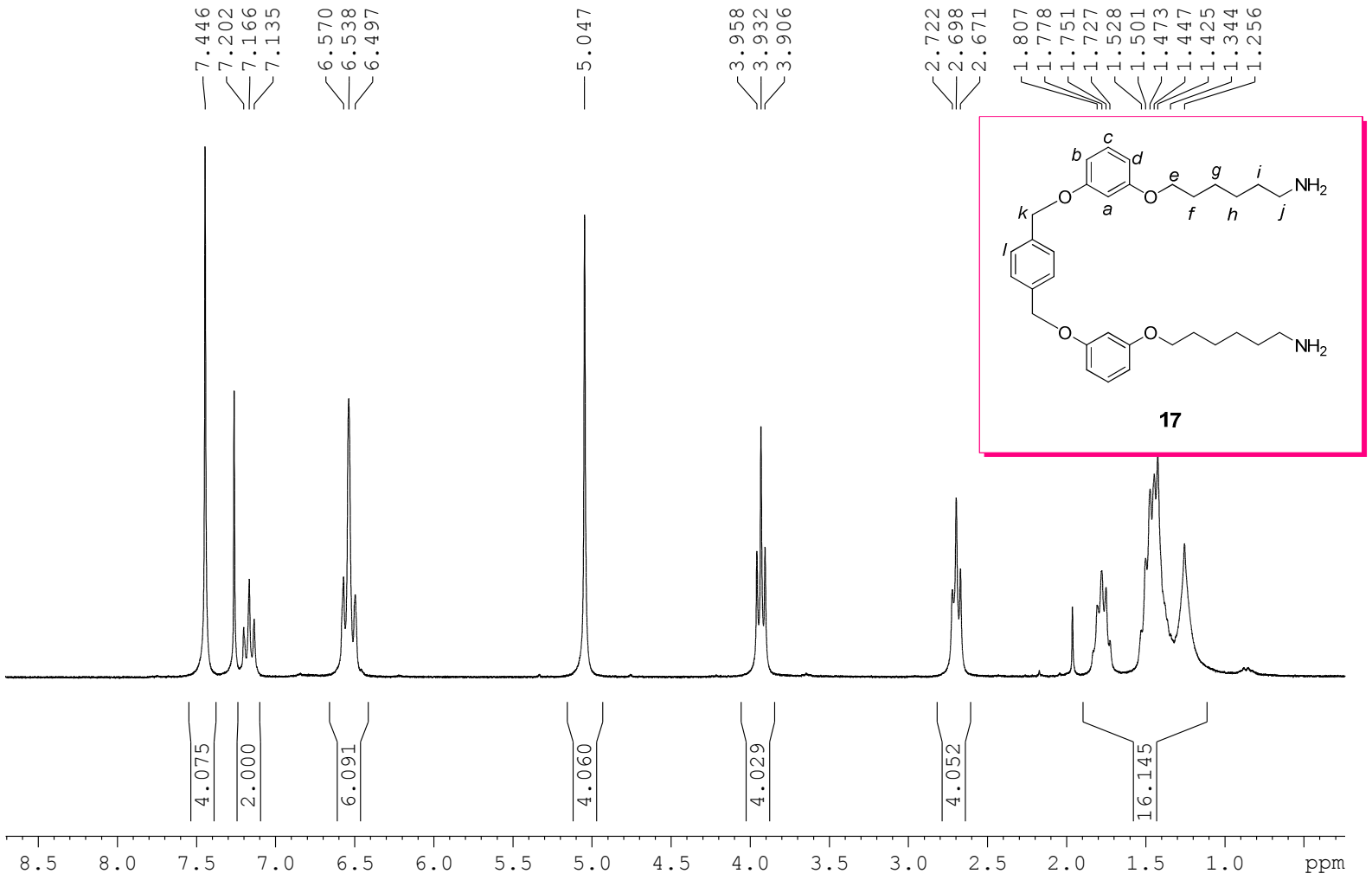


Figure S5. ^{1}H NMR spectrum of derivative **17** (250 MHz, $CDCl_3$, 298 K).

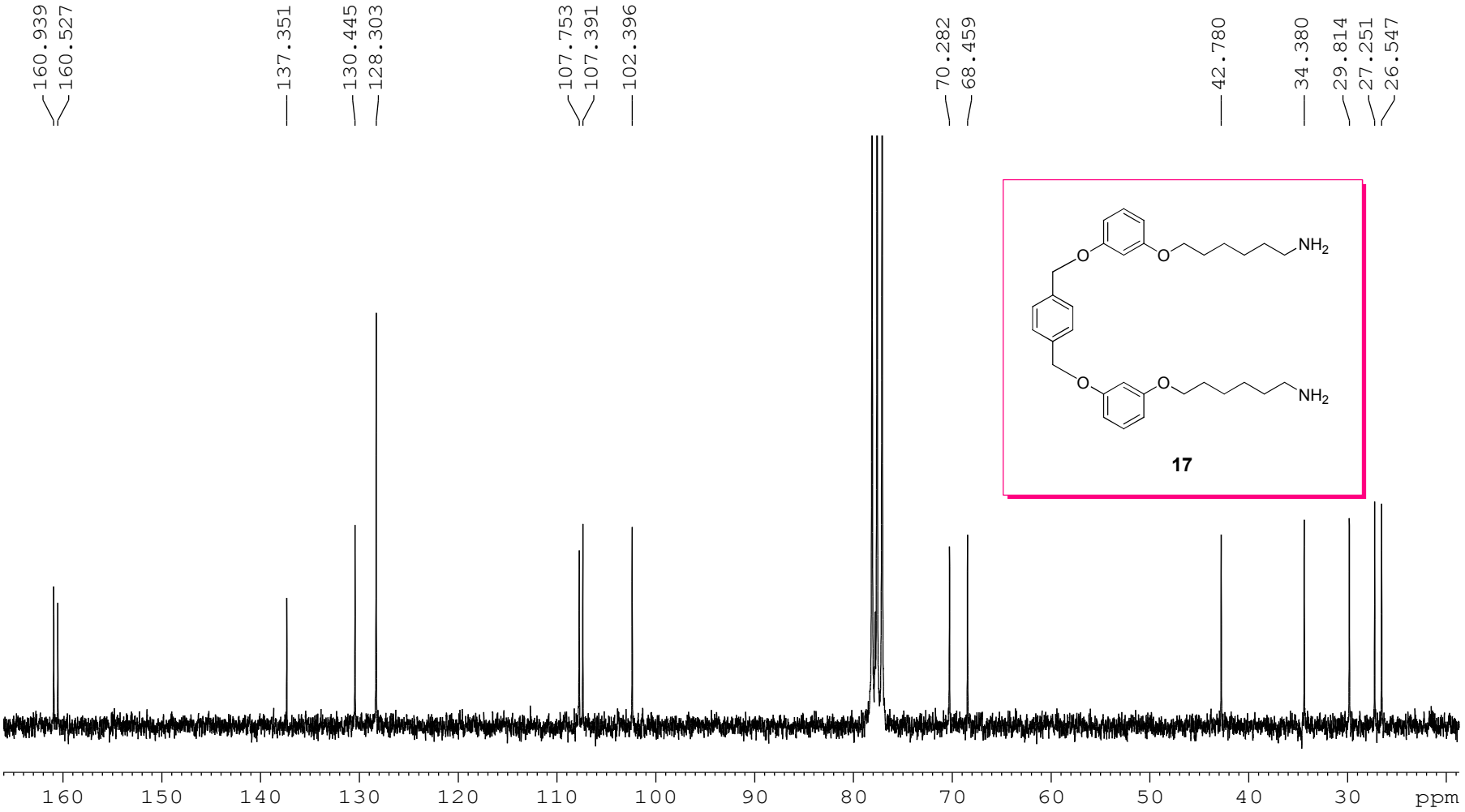


Figure S6. ^{13}C NMR spectrum of derivative **17** (63 MHz, $CDCl_3$ 298 K).

Diisocyanate Derivative 3b

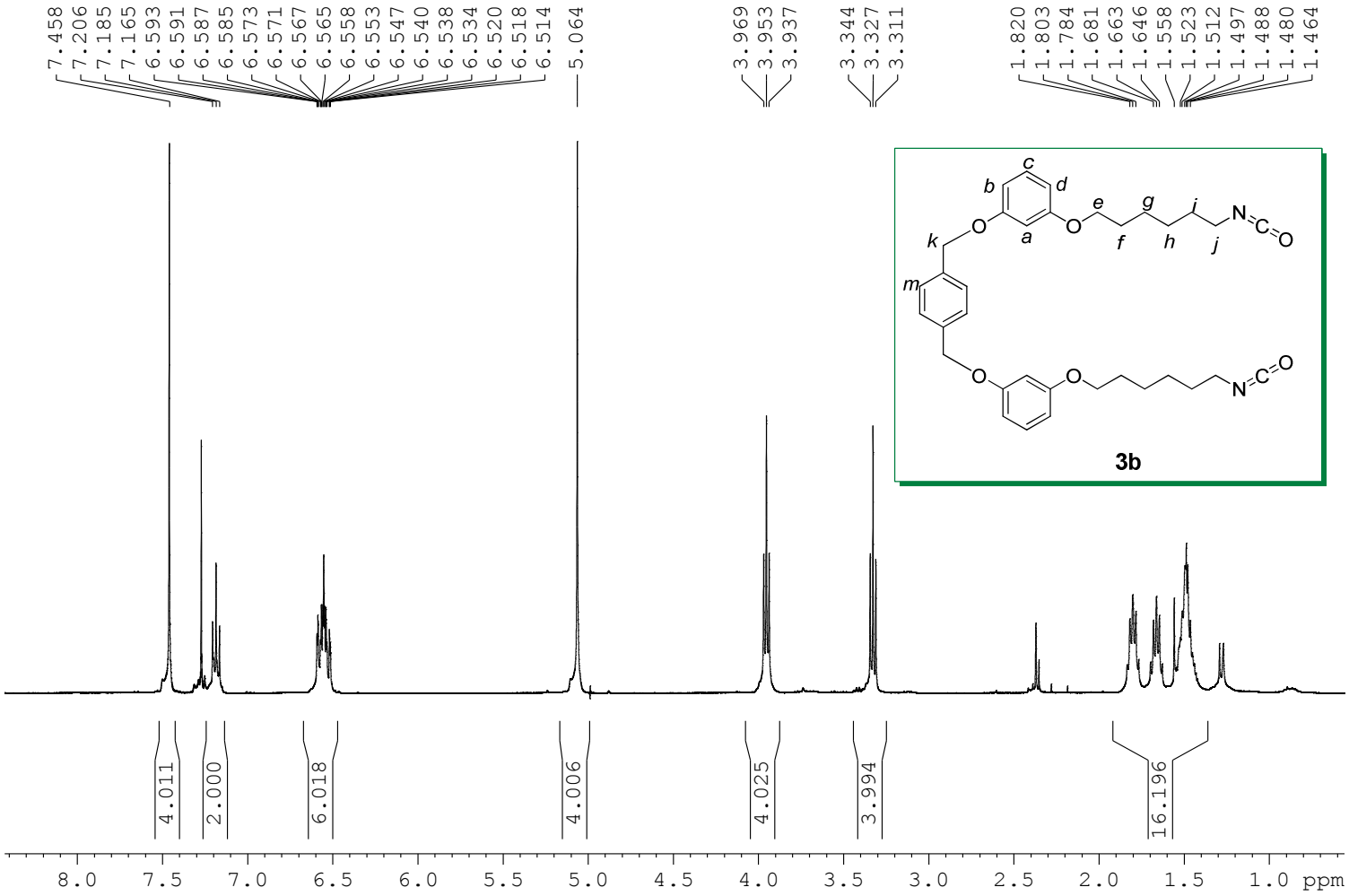


Figure S7. ^{1}H NMR spectrum of diisocyanate derivative **3b** (400 MHz, $CDCl_3$, 298 K).

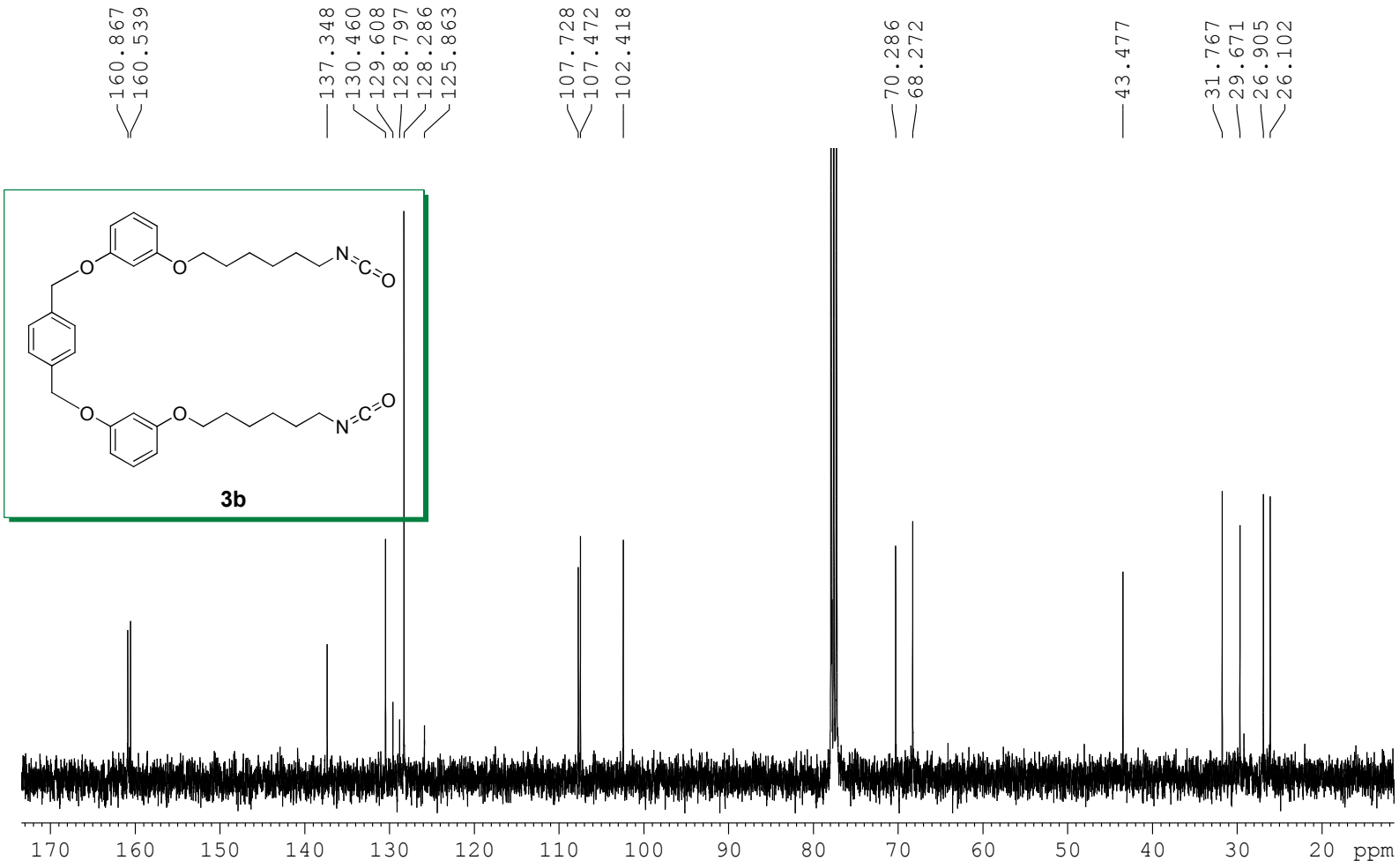
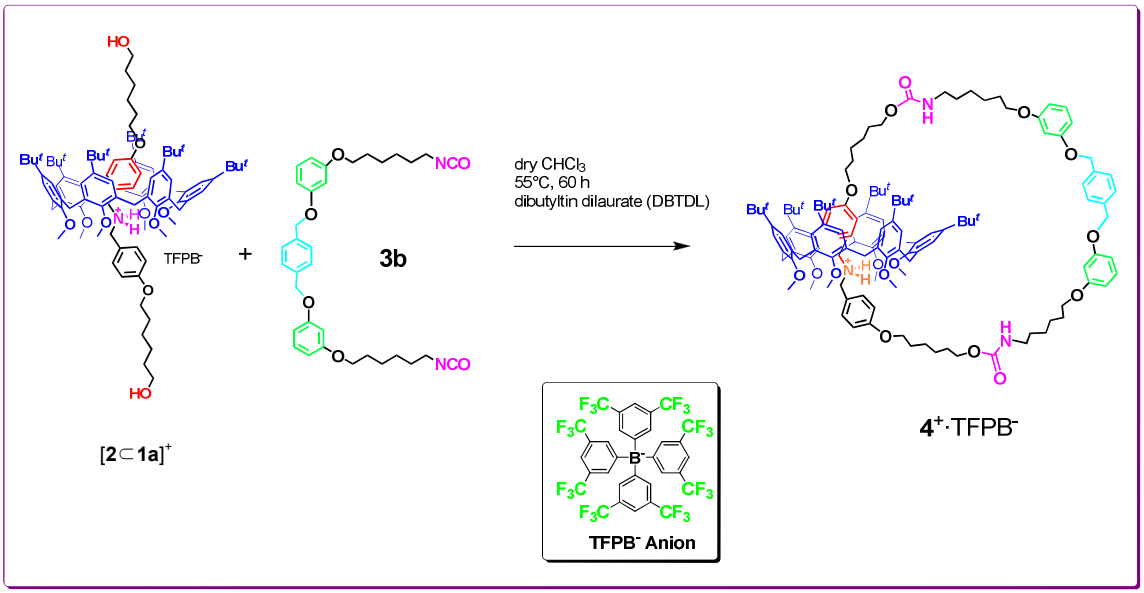


Figure S8. ^{13}C NMR spectrum of diisocyanate derivative **3b** (100 MHz, $CDCl_3$, 298 K).

Synthesis of Calix[2]catenane $4^{+}\cdot TFPB^{-}$



Scheme S2. Synthesis of calix[2]catenane $\mathbf{4}^{+}\cdot TFPB^{-}$.

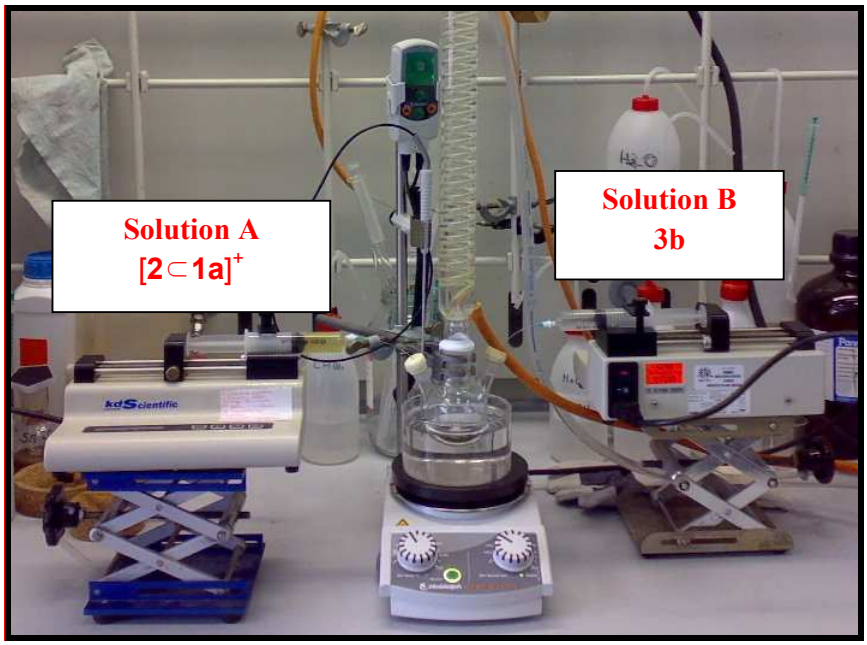


Figure S9. Apparatus assembled for the synthesis of calix[2]catenane $\mathbf{4}^{+}\cdot TFPB^{-}$.

Preparation[6] of calix[6]arene-based pseudo[2]rotaxane [2⊂1a]$^{+}$·TFPB^{-} (**solution A**, Figure S9): calix[6]arene **1a** (0.15 g, 0.14 mmol) and dibenzylammonium derivative **2**$^{+}$·TFPB^{-} (0.15 g, 0.12 mmol) were dissolved in 20 mL dry $CHCl_3$ and the mixture was stirred for 72 h at 60 °C under a nitrogen atmosphere. The reaction was checked by ^{1}H NMR and the solution of pseudo[2]rotaxane [**2**⊂**1a**]$^{+}$·TFPB^{-} was used without further purification.

Preparation of solution B (Figure S9): diisocyanate derivative **3b** (0.07 g, 0.12 mmol) was dissolved in 20 mL of dry $CHCl_3$.

The solutions **A** and **B** were simultaneously and slowly added dropwise over 33 h by means of the two electronically controlled siringe pumps in Figure S9 (flow: 0.6 mL/min) and mixed in a reaction flask containing 2 mL of dry $CHCl_3$ at 55 °C in the presence of catalytic amount of dibutyltin dilaurate (DBTDL, 4 drops). After completion of the addition, the mixture was stirred at 55 °C for additional 27 h, and then cooled at room temperature. The solvent was removed under reduced pressure and the solid obtained was subjected to flash chromatography on silica gel (gradient of *n*-hexane/CH_2Cl_2, from 30/70 to 10/90 *v*/*v*, and to pure CH_2Cl_2). The product obtained was further purified by semipreparative HPLC on a Spherisorb Cyano (CN) column, with mobile phase *n*-hexane/*i*-PrOH 90/10, flow rate of 0.8 mL/min, to give calix[2]catenane **4**$^{+}$·TFPB^{-} as a white solid (0.105 g, 0.036 mmol, 30.0 %). **ESI-MS**$^{+}$: *m/z* = 2060.21 [M - TFPB]$^{+}$; **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): δ 1.12 (s, Bu^t_{calix}, 54H), 1.25-1.73 (overlapped, 32H, CH_2), 1.48 ($^{+}NH_2(CH_2)_\alpha Ar$, 2H) 3.17-3.21 [overlapped, 4H, $(CH_2)_i$+$(CH_2)_j$], 3.32 [t, *J* = 6.41 Hz, 2H, $(OCH_2)_k$], 3.44 and 4.38 (AX, *J* = 14.4 Hz, 12H, $ArCH_2Ar_{calix}$), 3.75 (s, 18H, OCH_{3calix}), 3.88-4.05 [overlapped, 12H, OCH_2 + $(CH_2)_{\alpha'}$], 4.50 (d, *J* = 8.3 Hz, 2H, ArH^a), 4.59 (overlapped, 2H, H_g+H_h) 5.00 [s, 4H, $(CH_2)_c$], 5.08 (d, *J* = 8.3 Hz, 2H, ArH^b), 6.07 (bs, 2H, NH_2^{+}), 7.48-6.56 (overlapped, 6H, ArH), 7.12 (t, *J* = 8.8 Hz, 2H, ArH), 7.16 (s, 12H, ArH_{calix}), 7.16 (d, *J* = 8.2 Hz, 2H, ArH), 7.41 (s, 4H, ArH), 7.51 (s, 4H, ArH_{TFPB}), 7.71 (s, 8H, ArH_{TFPB}), 7.81 (d, *J* = 8.2 Hz, 2H, ArH); **^{13}C NMR** (63 MHz, $CDCl_3$, 298 K): δ 23.2, 25.3, 25.9, 26.3, 27.0, 28.8, 29.4, 29.7, 30.3, 31.8, 32.1, 34.7, 41.4, 54.0, 62.4, 65.0,68.4, 68.6, 70.3, 102.5, 107.5, 114.5, 116.0, 118.0, 119.3, 123.0, 123.9, 126.8, 127.3, 128.2, 129.2, 129.6, 130.3, 130.5, 131.6, 132.4, 132.9, 135.4, 137.3, 147.7, 153.3, 157.4, 158.9, 160.5, 160.9. Anal. Calcd for $C_{164}H_{188}BF_{24}N_3O_{16}$: C, 67.36; H, 6.48. Found: C, 67.42; H, 6.40.

[6] Pierro, T.; Gaeta, C.; Talotta, C.; Casapullo, A.; Neri, P. *Org. Lett.* **2011**, *13*, 2650.

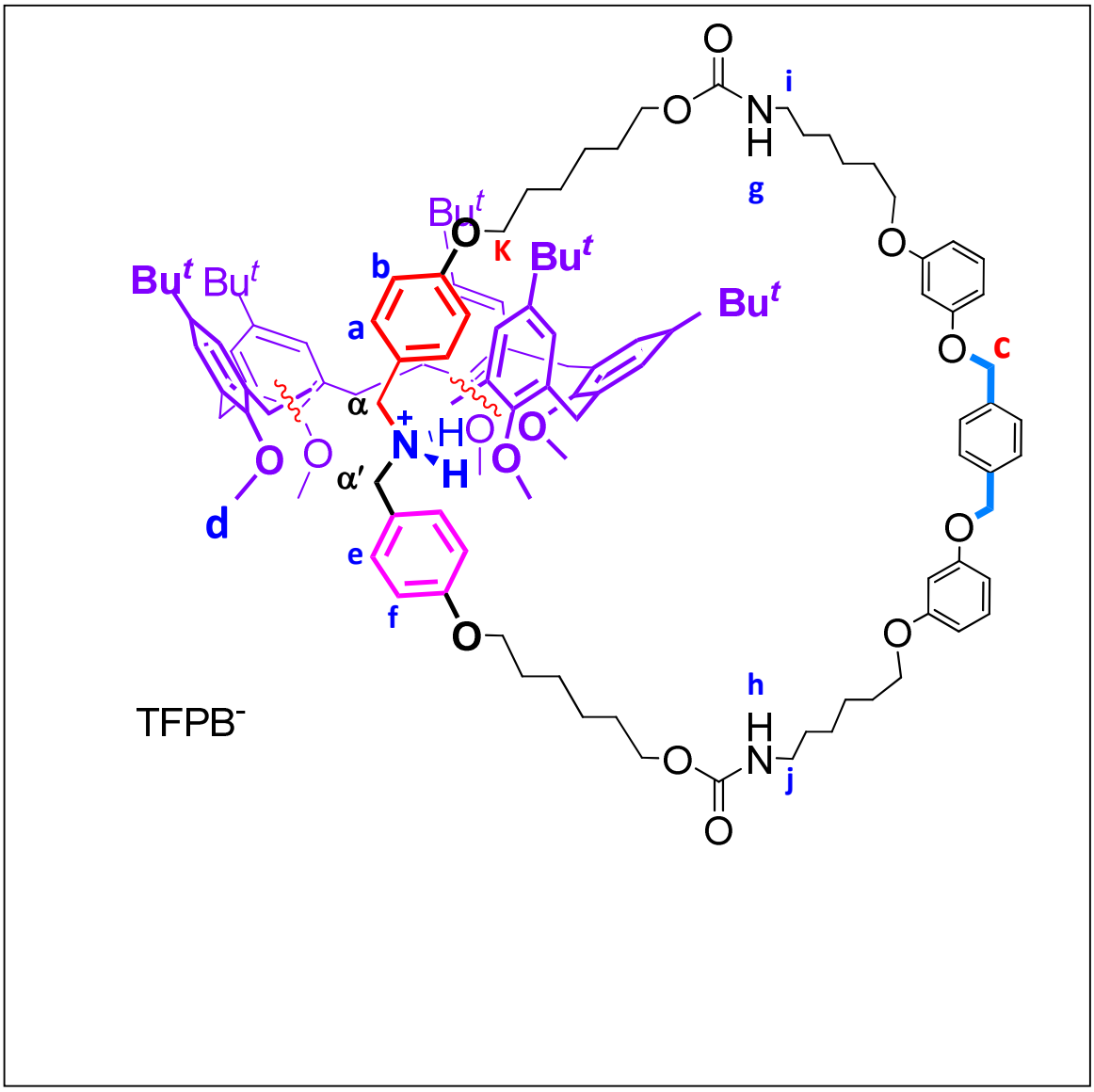


Figure S10.

ESI-MS$^+$ Spectrum of Calix[2]catenane 4$^+$·TFPB$^-$

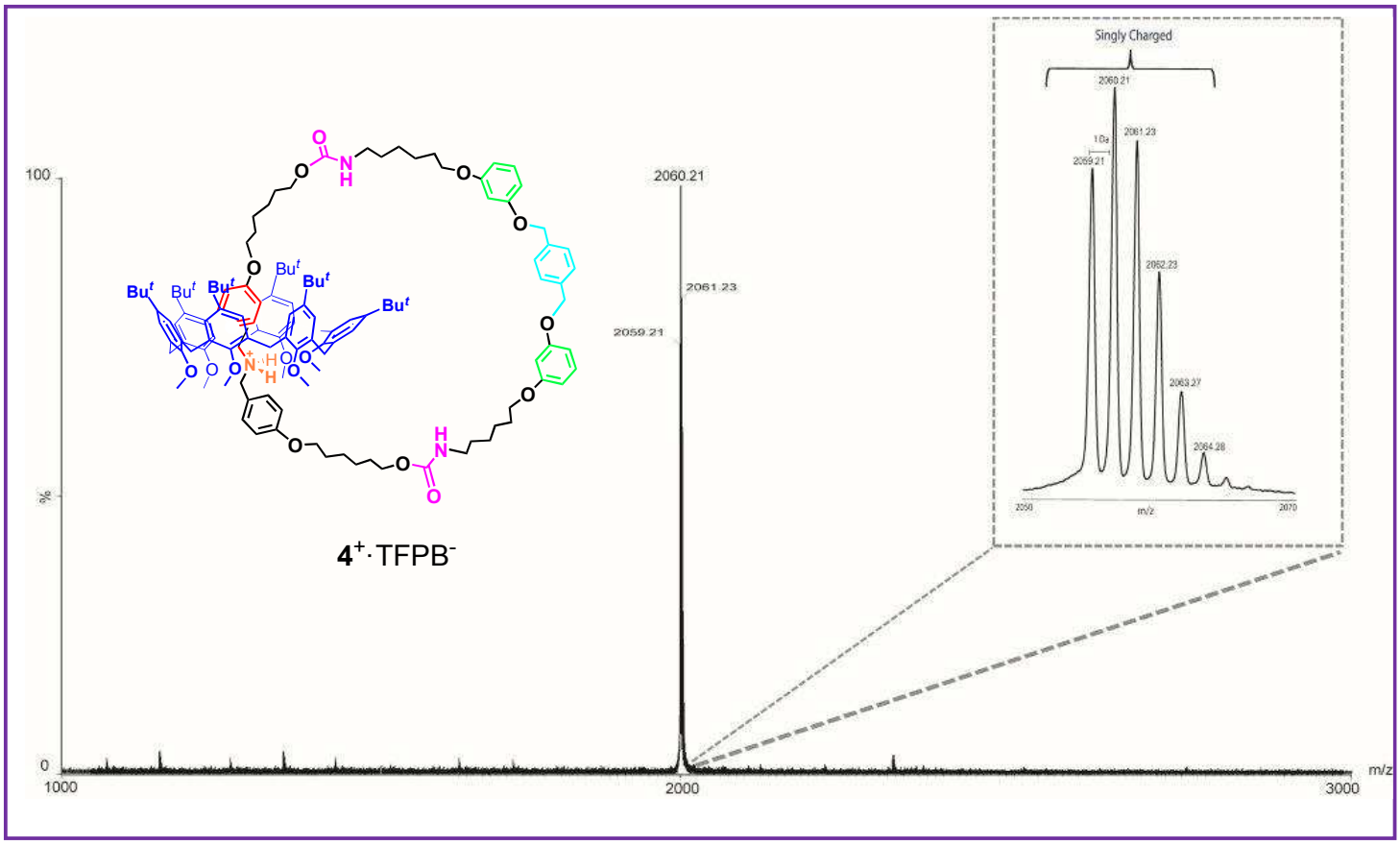


Figure S11. ESI-MS$^+$ spectrum of calix[2]catenane **4$^+$TFPB$^-$**.

^{1}H and ^{13}C NMR Spectra of Calix[2]catenane $4^{+}\cdot TFPB^{-}$

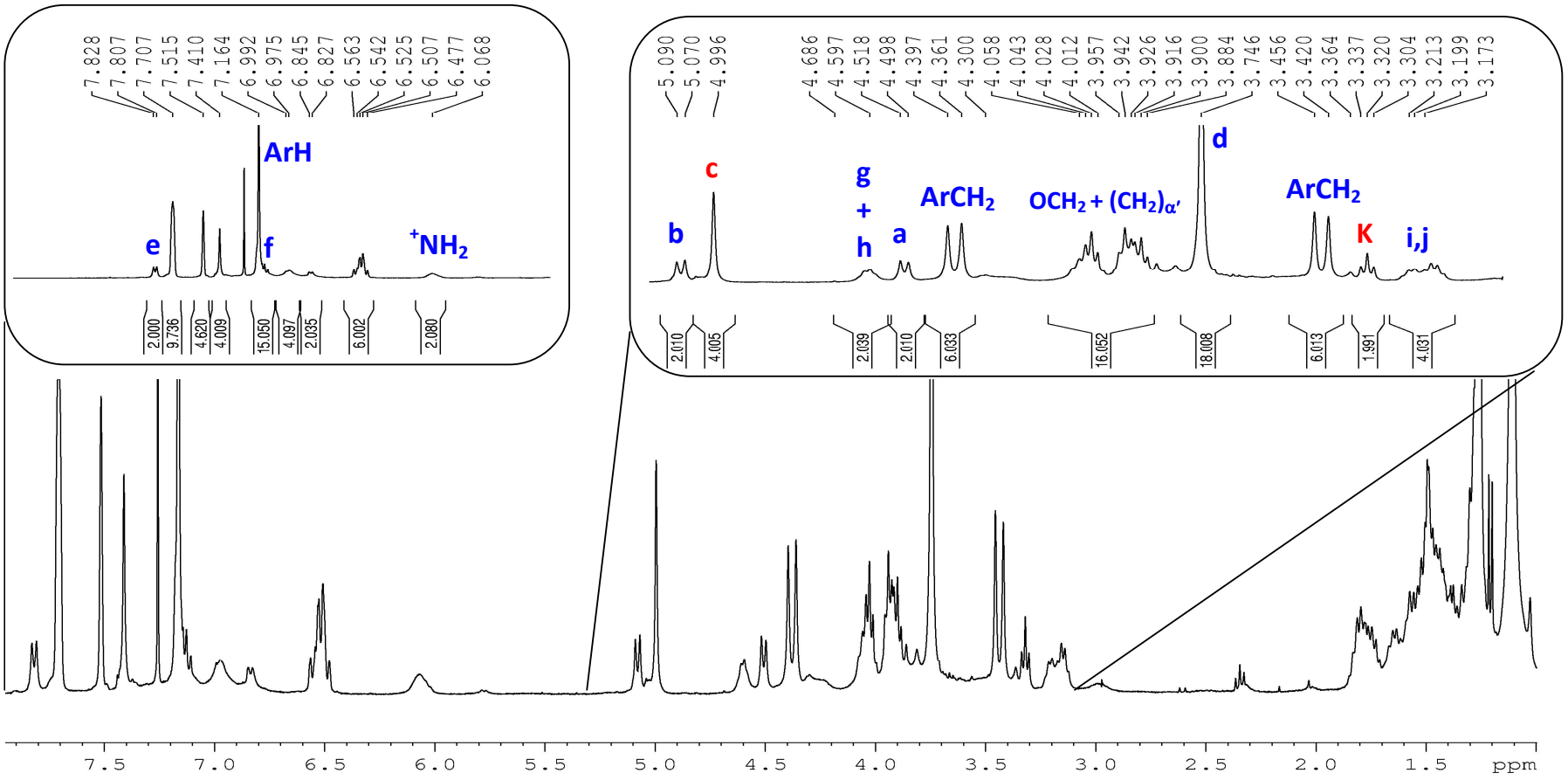


Figure S12. ^{1}H NMR spectrum of calix[2]catenane $\mathbf{4}^{+}\cdot$ $TFPB^{-}$ (400 MHz, $CDCl_3$, 298 K).

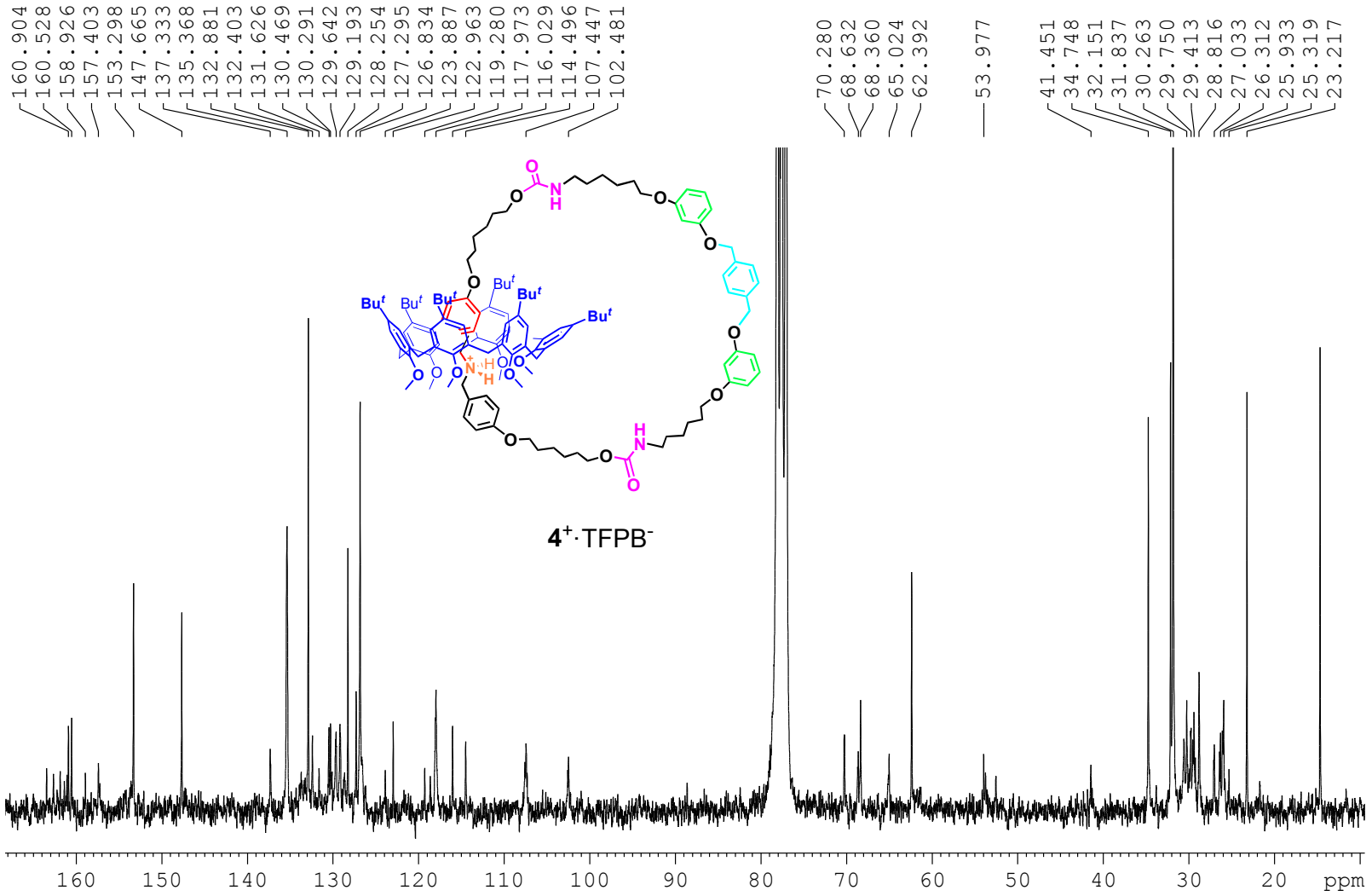
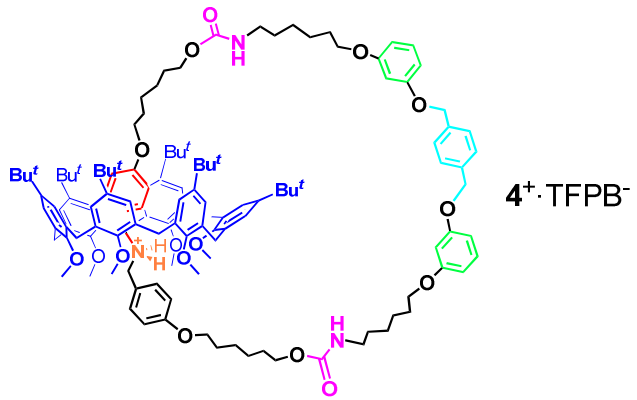
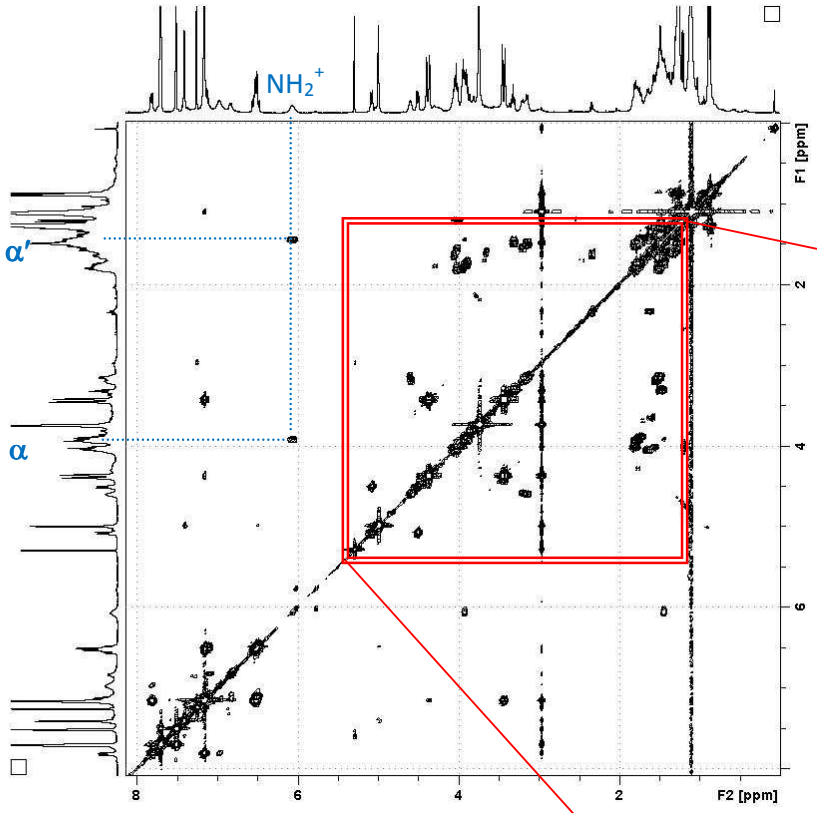


Figure S13. ^{13}C NMR spectrum of calix[2]catenane $\mathbf{4}^{+}\cdot$ TFPB^{-} (100 MHz, $CDCl_3$, 298 K).

2D COSY Spectrum of Calix[2]catenane $4^{+}\cdot TFPB^{-}$





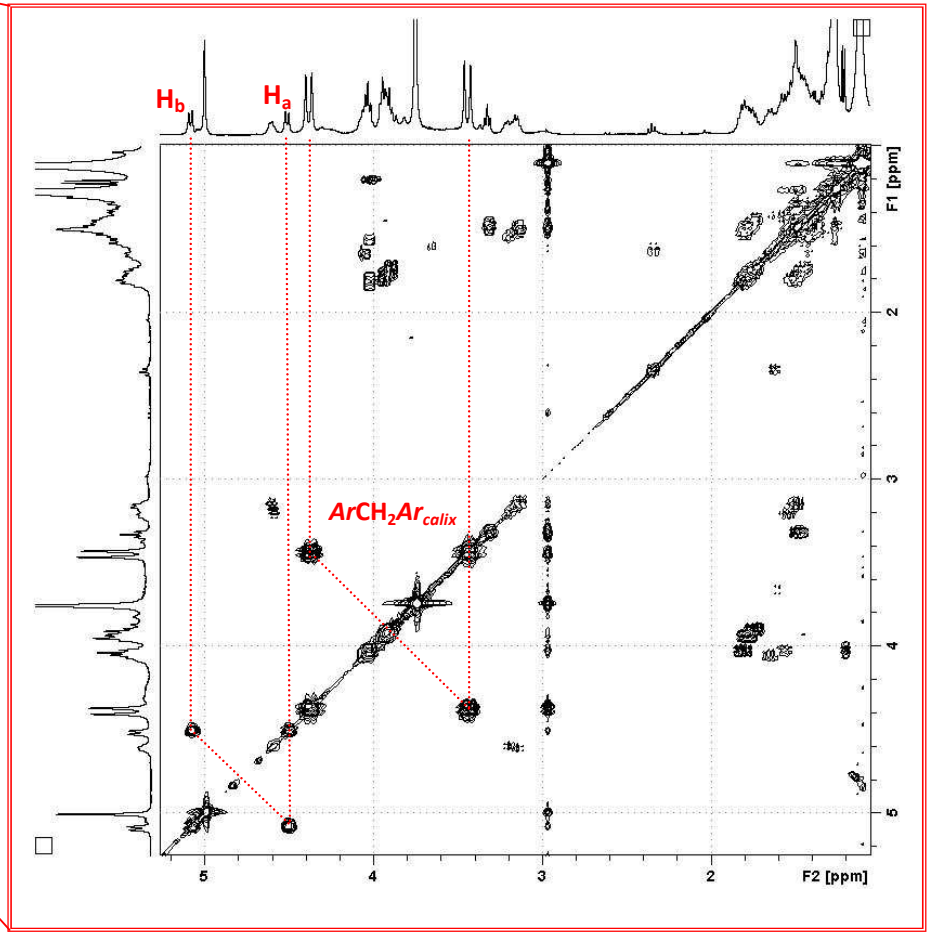


Figure S14. 2D COSY spectrum (400 MHz, $CDCl_3$, 298 K) of calix[2]catenane $\mathbf{4}^{+}\cdot$ $TFPB^{-}$.

2D ROESY Spectrum of Calix[2]catenane $4^{+}\cdot TFPB^{-}$

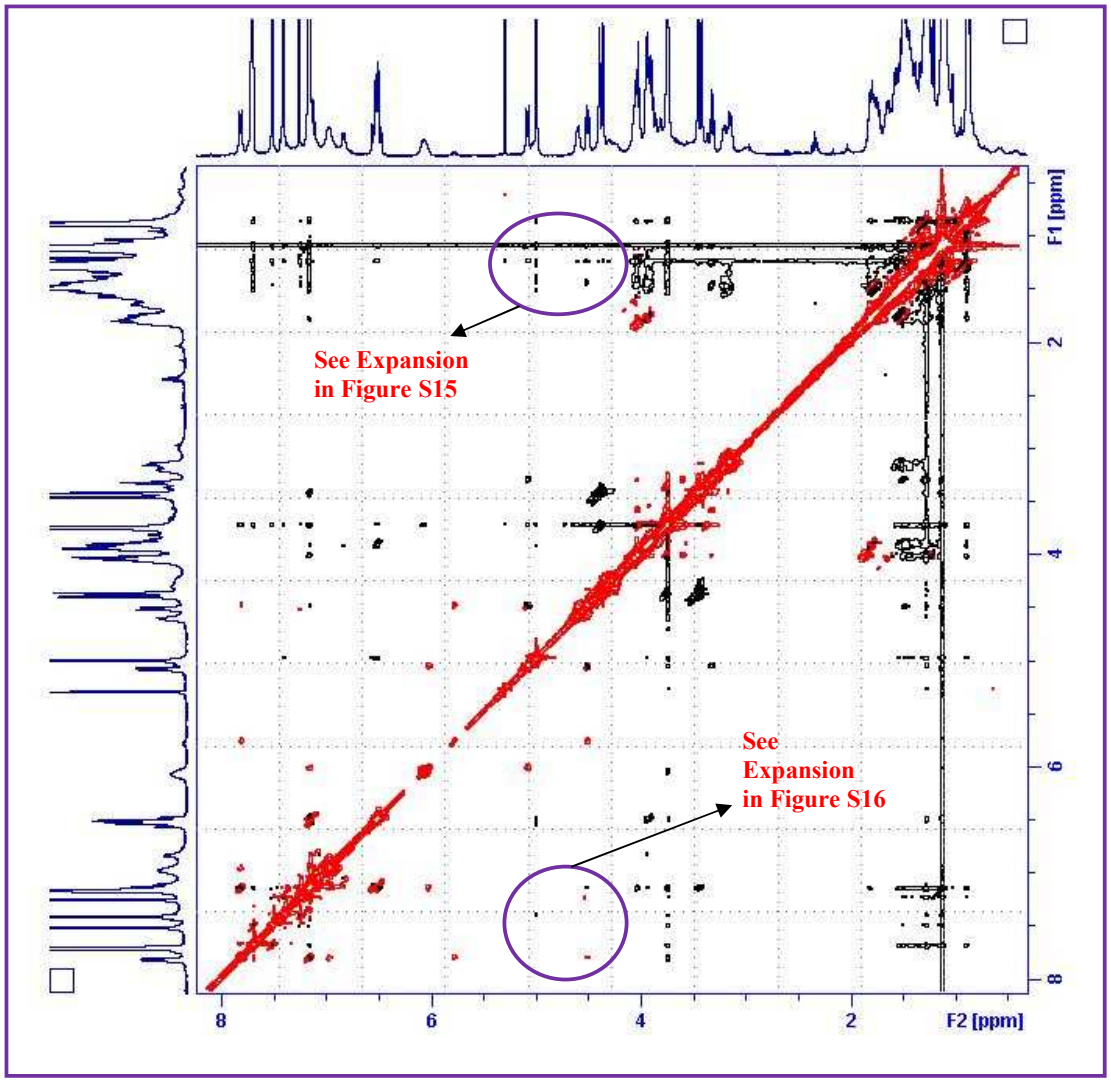
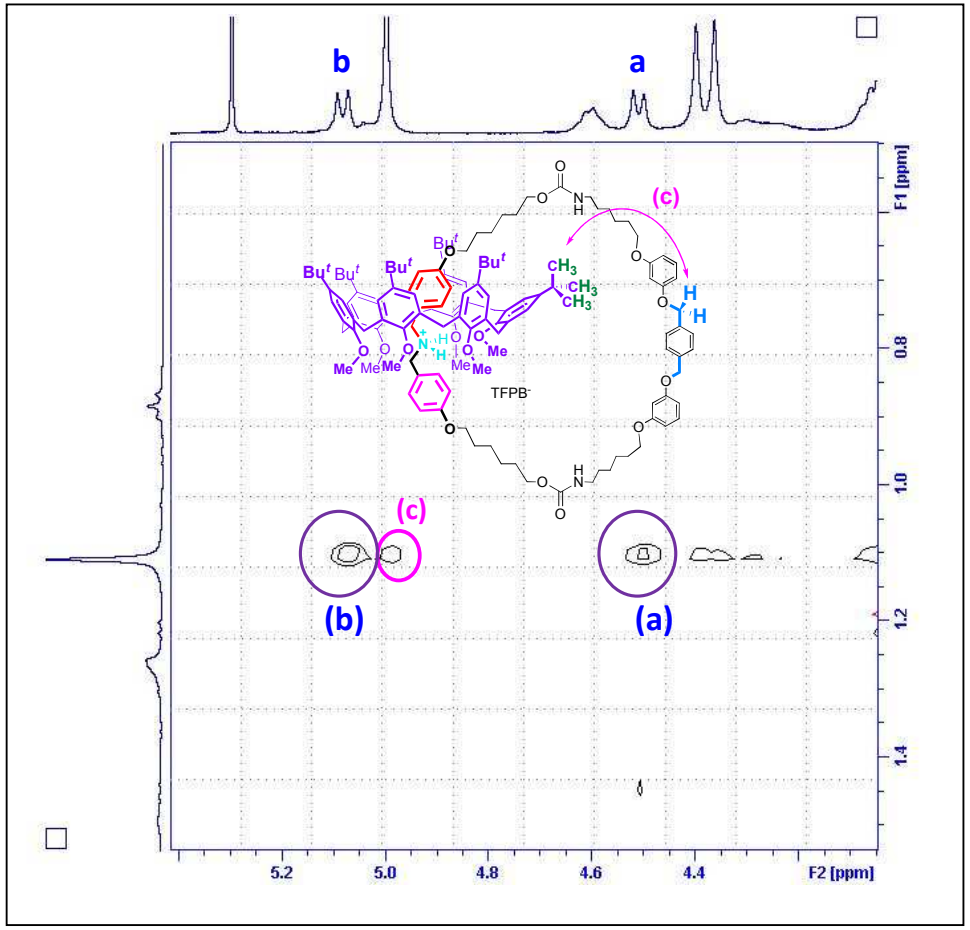


Figure S15. 2D ROESY spectrum (400 MHz, $CDCl_3$, 298 K) of calix[2]catenane $4^{+}\cdot TFPB^{-}$.



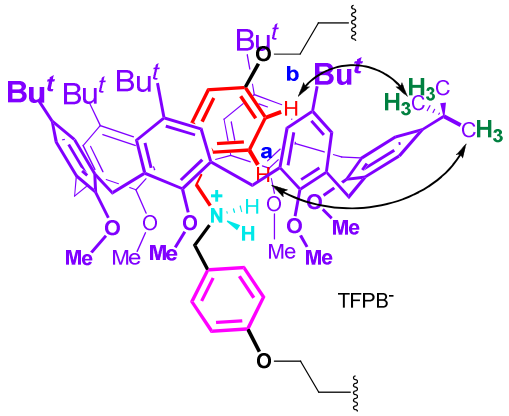


Figure S16. Expansion of the 2D ROESY spectrum (400 MHz, $CDCl_3$, 298 K) of calix[2]catenane $\mathbf{4}^{+\cdot}$ $TFPB^{-}$.

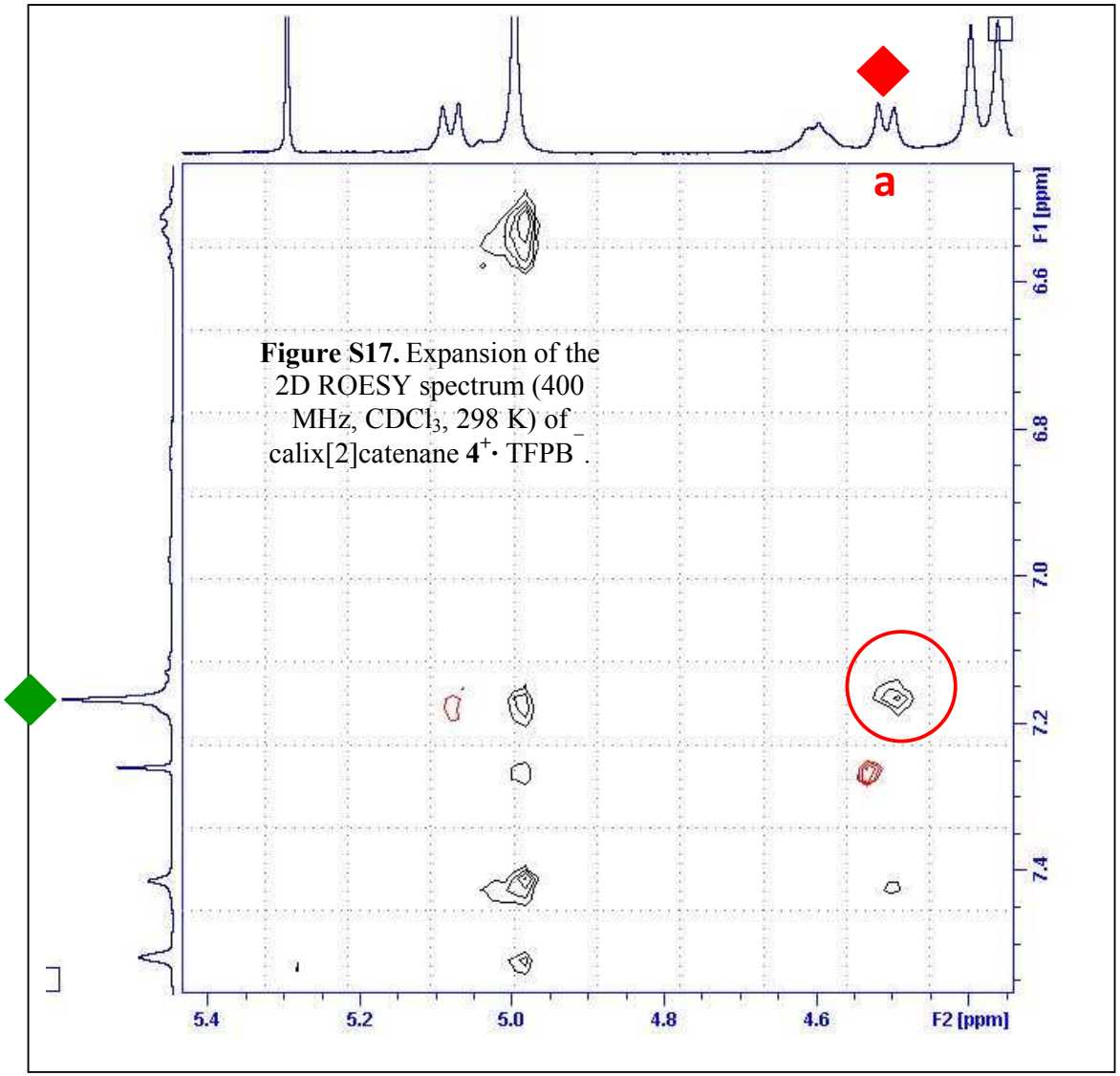
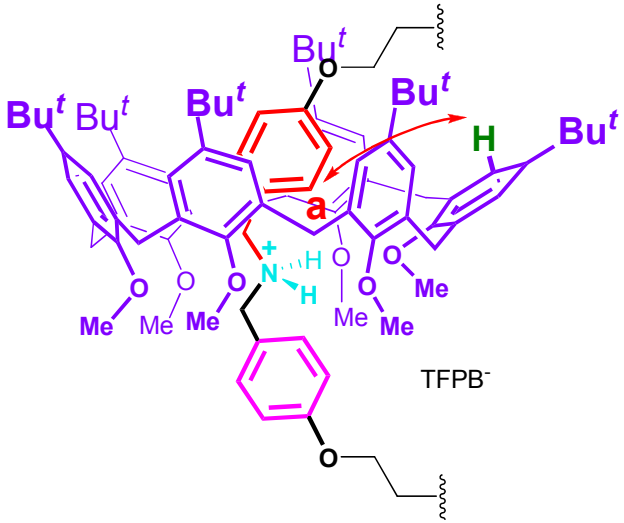


Figure S17. Expansion of the 2D ROESY spectrum (400 MHz, $CDCl_3$, 298 K) of calix[2]catenane $\mathbf{4}^{+}\cdot$ $TFPB^{-}$.



Molecular Modeling Studies of Calix[2]catenane 4^+

DFT calculations were performed with the Gaussian 09 Software Package.[7] Input structure files for DFT calculations were obtained by molecular modeling with MacroModel 9.0 program[8] (Schrödinger, LLC, New York, NY, 2005) using OPLS force field and $CHCl_3$ solvent (GB/SA model). The input structure files were optimized at the DFT B3LYP level of theory using the 6-31G* basis set for the entire system.

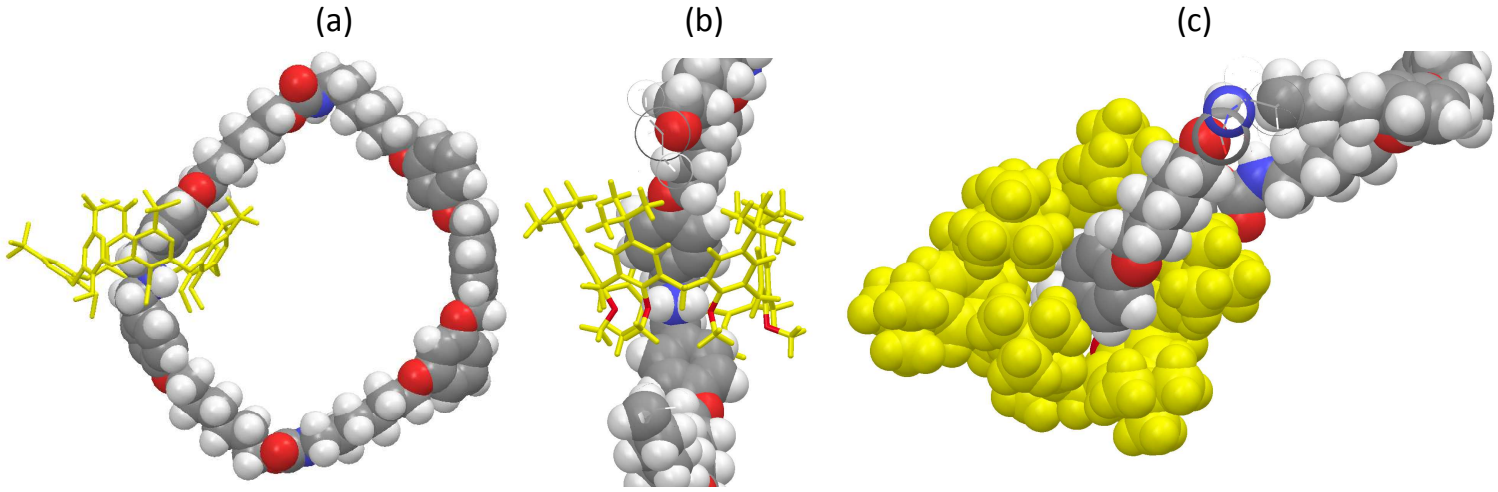


Figure S18. (a) Energy-minimized structure of calix-threaded [2]catenane $\mathbf{4}^+$ (B3LYP DFT calculation using the 6-31G* basis set). (b) Detailed view of the predicted $^+$N–H···OMe^{calix} H-bonds. (c) Detailed view of the filling of the aromatic cavity of the calixarene macrocycle through the threading with the benzylammonium unit.

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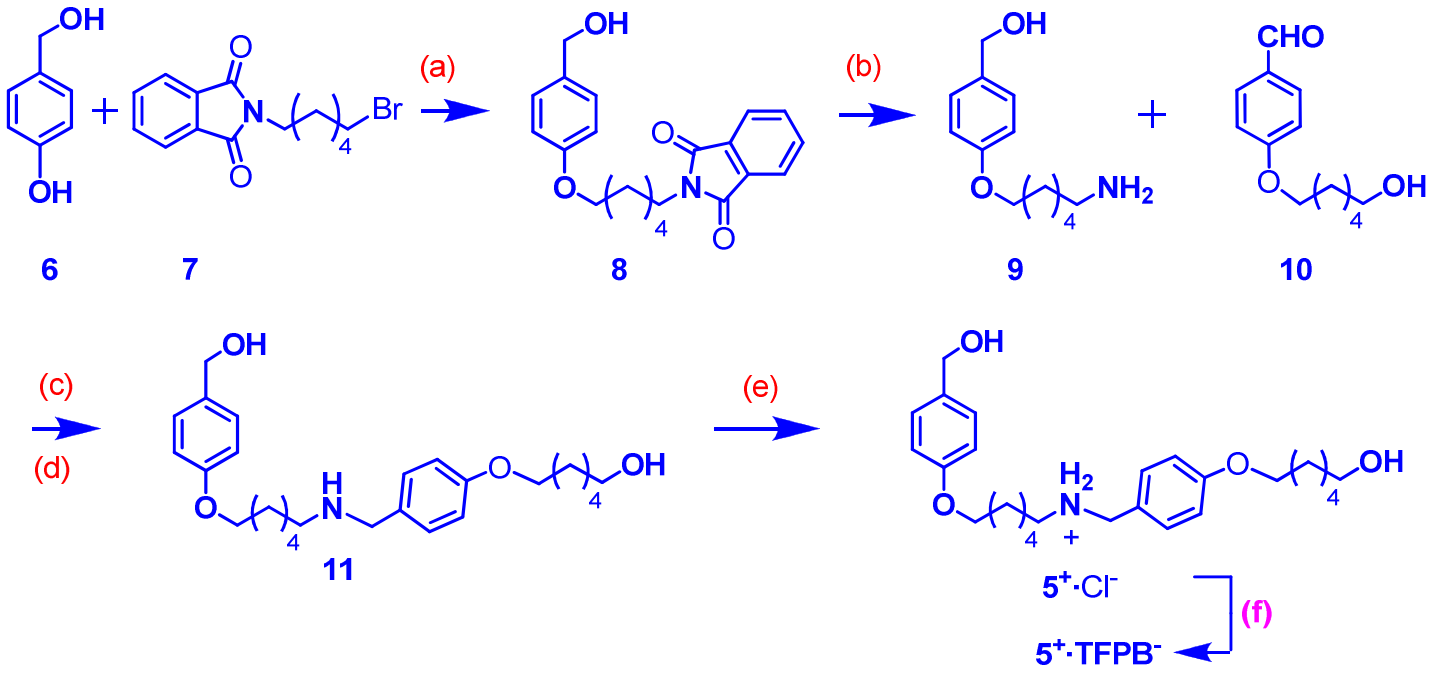
[7] Gaussian 09, Revision **A.1**, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

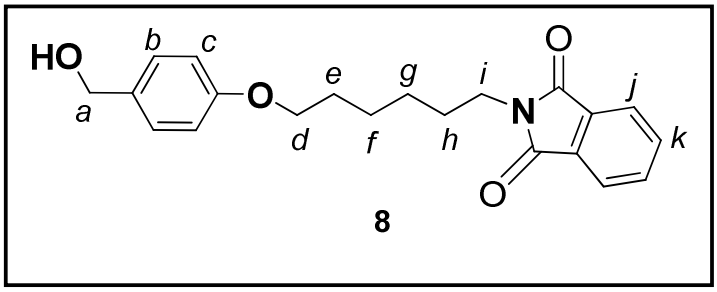
[8] MacroModel-9.0/Maestro-4.1 program: Mohamadi, F.; Richards, N. G.; Guida, W. C.; Liskamp, R.; Lipton, M.; Caufield, C.; Chang, G.; Hendrickson, T.; Still, W. C. *J. Comput. Chem.* **1990**, *11*, 440.

Synthesis of Directional Axle $5^{+}\cdot TFPB^{-}$



Scheme S3. Synthesis of directional axle $\mathbf{5^{+}\cdot TFPB^{-}}$. *Reagents and conditions:* (a) K_2CO_3, [18]crown-6, dry CH_3CN, RT, 25 h; (b) NH_2NH_2, EtOH, reflux, 1 h; (c) $CHCl_3$, RT, 30 min; (d) $NaBH_4$, MeOH, RT, 3 h; (e) HCl (4 M in MeOH), MeOH, 0 °C, quant.; (f) NaTFPB, dry MeOH, RT, 12 h.

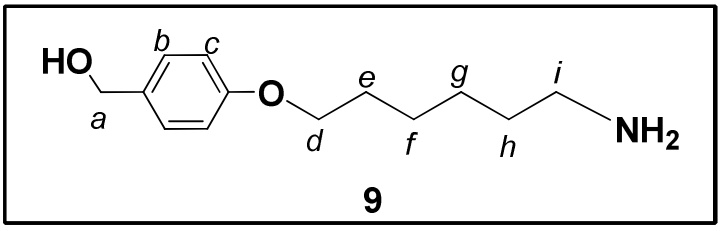
Derivative **8**



8

A mixture of derivative **6** (1.20 g, 9.7 mmol), [18]crown-6 (0.13 g, 0.5 mmol), and K_2CO_3 (0.67 g, 4.9 mmol) in 30 mL of dry acetonitrile was refluxed for 1 h. Then, the solution was cooled at room temperature and derivative **7** (1.50 g, 4.9 mmol) was added and then the mixture was refluxed again for 24 h. The solution was cooled at room temperature and the solvent was evaporated under reduced pressure. The residue was partitioned between AcOEt (100 mL) and water (100 mL), then the organic layer was dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The crude product was subjected to flash chromatography on silica gel (CH_2Cl_2/Et_2O, 98/2, *v/v*), to give derivative **8** as a white solid (0.79 g, 42%). ESI-MS^+: *m/z* = 354 (MH^+); **^{1}H NMR** (250 MHz, $CDCl_3$, 298 K): δ 1.40-1.80 (overlapped, 9H, $H_{e+f+g+h}$ + OH), 3.68 (t, J = 7.2 Hz, 2H, H_i), 3.93 (t, J = 6.5 Hz, 2H, H_d), 4.59 (s, 2H, H_a), 6.85 (d, J = 8.5 Hz, 2H, H_c), 7.25 (d, J = 8.5 Hz, 2H, H_b), 7.68-7.84 (overlapped, 4H, H_{j+k}); **^{13}C NMR** (63 MHz, $CDCl_3$, 298 K): δ 25.8, 26.8, 28.7, 29.2, 38.0, 65.2, 67.9, 114.6, 123.3, 128.8, 132.2, 133.1, 134.0, 158.8, 168.7. Anal. Calcd for $C_{21}H_{23}NO_4$: C, 71.37; H, 6.56. Found: C, 71.46; H, 6.47.

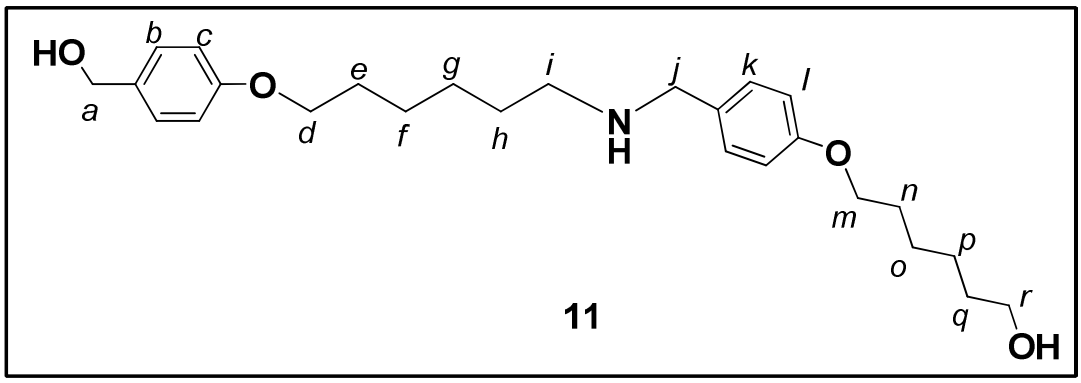
Derivative **9**



9

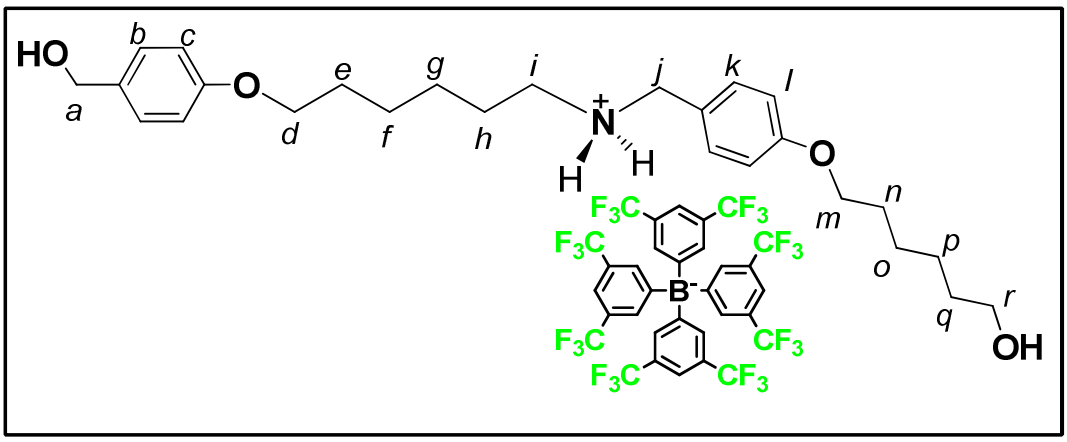
A solution of derivative **8** (0.79 g, 1.9 mmol) and hydrazine (190 mmol, 12 mL, 50-60% *v/v* solution in H_2O) in EtOH (10 mL) was refluxed for 1 h under N_2. The solution was cooled at room temperature and H_2O (100 mL) was added. The product was extracted with CH_2Cl_2 (3×80 mL) and the organic layers were collected and dried over $MgSO_4$, filtered, and evaporated under reduced pressure to give **9** as a white solid (0.42 g, 97%). ESI-MS^+: *m/z* = 224 (MH^+); **^{1}H NMR** (250 MHz, $CDCl_3$, 298 K): δ 1.41-1.81 (overlapped, 8H, $H_{e+f+g+h}$), 2.68 (t, J = 6.3 Hz, 2H, H_i), 3.95 (t, J = 6.5 Hz, 2H, H_d), 4.60 (s, 2H, H_a), 6.88 (d, J = 8.5 Hz, 2H, H_c), 7.28 (d, J = 8.5 Hz, 2H, H_b); **^{13}C NMR** (63 MHz, $CDCl_3$, 298 K): δ 26.1, 26.8, 29.4, 33.8, 42.2, 65.1, 68.0, 114.7, 128.7, 133.3, 158.8. Anal. Calcd for $C_{13}H_{21}NO_2$: C, 69.92; H, 9.48 Found: C, 70.00; H, 9.37.

Derivative **11**



A mixture of derivate **9** (0.41 g, 1.8 mmol) and derivate **10** (0.41 g, 1.8 mmol,) in $CHCl_3$ (5 mL) was stirred at room temperature for 30 min. The solvent was evaporated under reduced pressure to give the imine intermediate as a yellow oil in a quantitative yield. The imine intermediate was used for the next step without further purification. The imine was dissolved in dry MeOH (7 mL), and $NaBH_4$ (1.36 g, 36 mmol) was added at 0 °C and then the mixture was allowed to warm at room temperature. The solution was kept under stirring for 3 h. The solvent was removed under reduced pressure and the residue partitioned between AcOEt (50 mL) and an aqueous saturated solution of $NaHCO_3$ (100 mL). The organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure, to give amine derivate **11** as a white solid (0.67 g, 89%). ESI-MS^+: m/z = 430 (MH^+); **^{1}H NMR** (250 MHz, CD_3OD, 298 K): δ 1.48-1.82 (overlapped, 16H, $H_{e+f+g+h}$ +$H_{n+o+p+q}$), 3.01 (t, J = 7.7 Hz, 2H, H_i), 3.56 (t, J = 6.3 Hz, 2H, H_r), 3.94-4.01 (overlapped, 4H, H_{d+m}), 4.12 (s, 2H, H_j), 4.37 (s, 2H, H_a), 6.88 (d, J = 8.5 Hz, 2H, H_c), 6.98 (d, J = 8.7 Hz, 2H, H_l), 7.24 (d, J = 8.7 Hz, 2H, H_k), 7.41 (d, J = 8.5 Hz, 2H, H_b); **^{13}C NMR** (63 MHz, CD_3OD, 298 K): δ 27.0, 27.1, 27.3, 30.1, 30.3, 33.6, 51.8, 62.9, 68.7, 69.0, 75.3, 115.3, 116.0, 124.2, 130.7, 131.3, 132.6, 133.6, 160.2, 161.6. Anal. Calcd for $C_{26}H_{39}NO_4$: C, 72.69; H, 9.15; Found: C, 72.78; H, 9.06.

Directional Axle $5^{+}\cdot TFPB^{-}$



Derivative **11** (0.67 g, 1.6 mmol) was dissolved in MeOH (30 mL) at 0 °C and an aqueous solution of HCl (37% *w/w*, 0.2 mL) was added dropwise. The mixture was kept under stirring for 30 min, until the formation of a white precipitate. The solid was collected by filtration, washed with MeOH (10 mL) and CH_3CN (10 mL), and dried under vacuum, to give derivative $\mathbf{5^{+}\cdot Cl^{-}}$ as a white solid (0.79 g, 94%). Derivative $\mathbf{5^{+}\cdot Cl^{-}}$ (0.50 g, 1.08 mmol) was dissolved without further purification in warm dry MeOH (15 mL), then a solution of sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (0.96 g, 1.08 mmol) in dry MeOH (15 mL) was added. The mixture was kept under stirring overnight in the dark. The solvent was removed and deionized water was added, obtaining a brown precipitate that was filtered off and dried under vacuum for 48 h to give derivative $\mathbf{5^{+}\cdot TFPB^{-}}$ (1.24 g, 89%). **^{1}H NMR** (300 MHz, CD_3OD, 298 K): δ 1.46-1.77 (overlapped, 16H, $H_{e+f+g+h+n+o+p+q}$), 3.00 (t, J = 7.2 Hz, 2H, H_i), 3.53 (dt, J_1 = 18.6, J_1 = 18.6, 6.0 Hz, 2H, OCH_2), 3.97-4.10 (overlapped, 8H), 6.86 (d, J = 8.4 Hz, 2H, ArH), 6.98 (d, J = 8.7 Hz, 2H, ArH), 7.24 (d, J = 8.4 Hz, 2H, ArH), 7.38 (d, J = 8.7 Hz, 2H, ArH), 7.60 (overlapped, 12H, ArH_{TFPB}); **^{13}C NMR** (75 MHz, CD_3OD, 298 K): δ 26.6, 26.8, 27.1, 27.5, 29.8, 30.2, 30.7, 33.6, 51.7, 51.7, 62.7, 68.7, 69.2, 71.1, 73.6, 115.2, 116.3, 118.4, 120.4, 124.1, 127.6, 129.8, 130.3, 130.8, 131.5, 132.2, 136.2, 160.2, 161.7, 162.1, 163.1, 163.9. Anal. Calcd for $C_{58}H_{52}BF_{24}NO_4$: C, 52.84; H,4.05. Found: C, 52.93; H, 3.96.

^{1}H and ^{13}C NMR Spectra of Derivatives 8, 9, 11, and $5^{+}\cdot TFPB^{-}$

Derivative 8

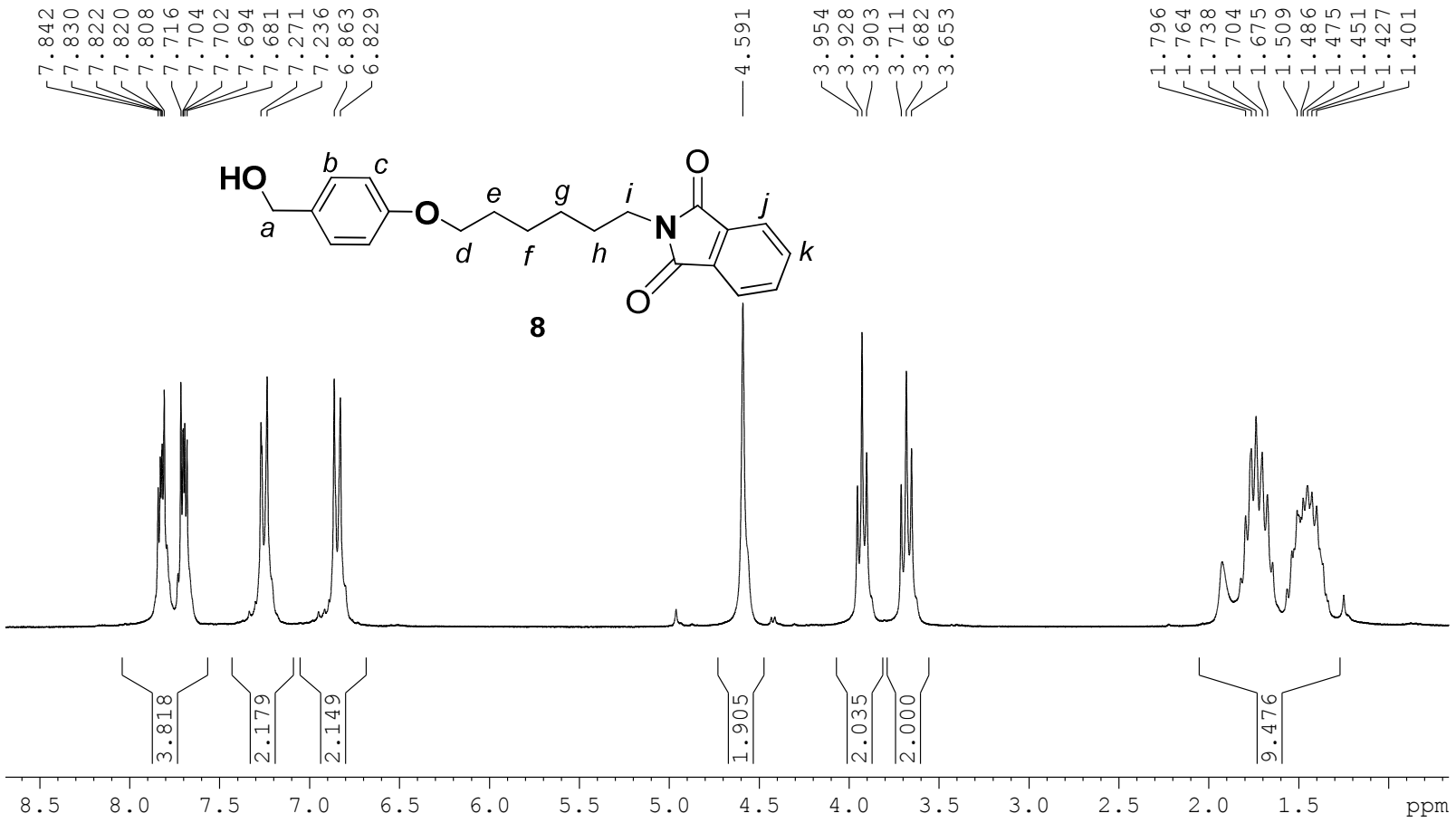


Figure S19. ^{1}H NMR spectrum of derivative **8** (250MHz, $CDCl_3$, 298 K).

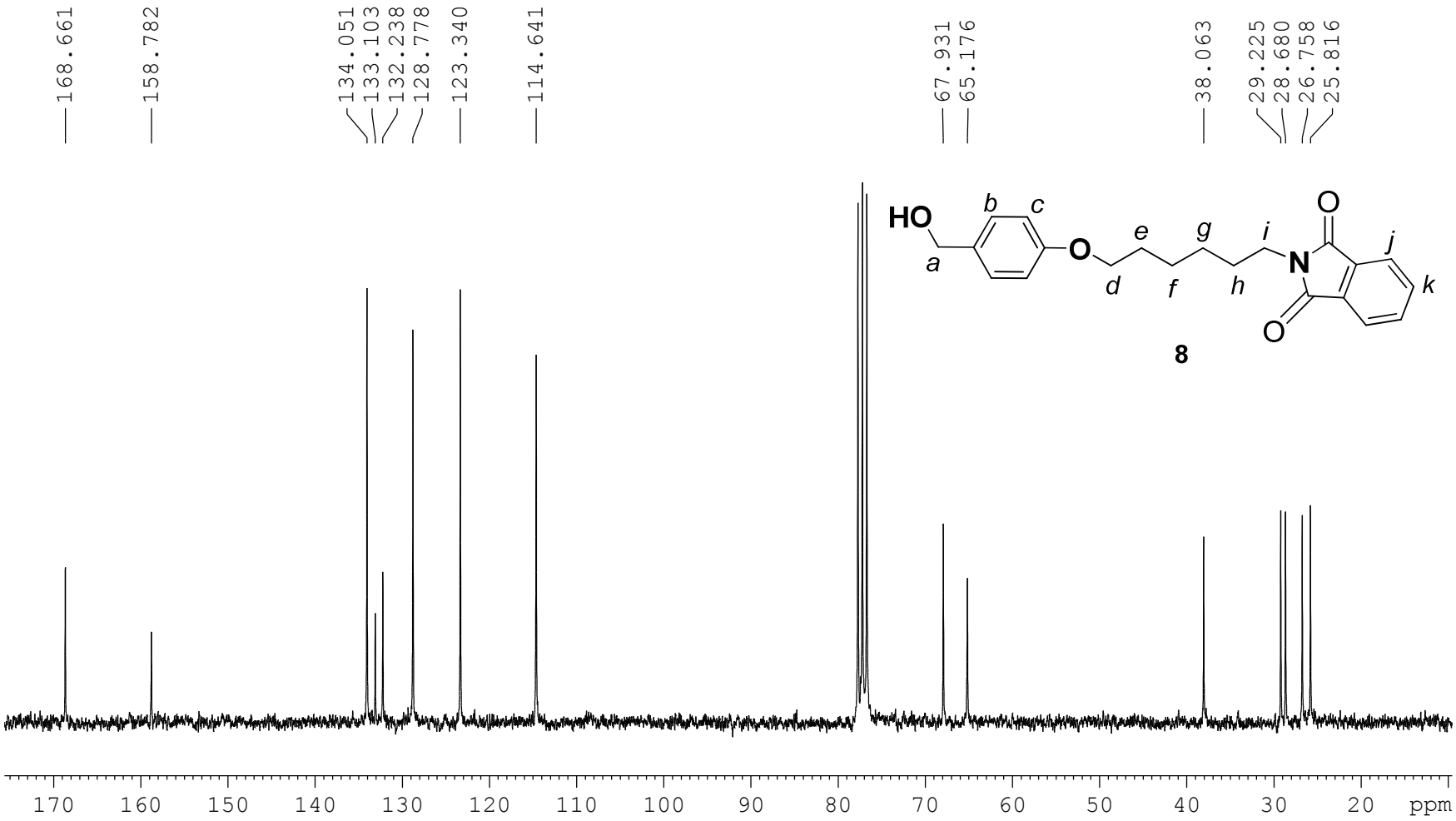


Figure S20. ^{13}C NMR spectrum of derivative **8** (63 MHz, $CDCl_3$, 298 K).

Derivative 9

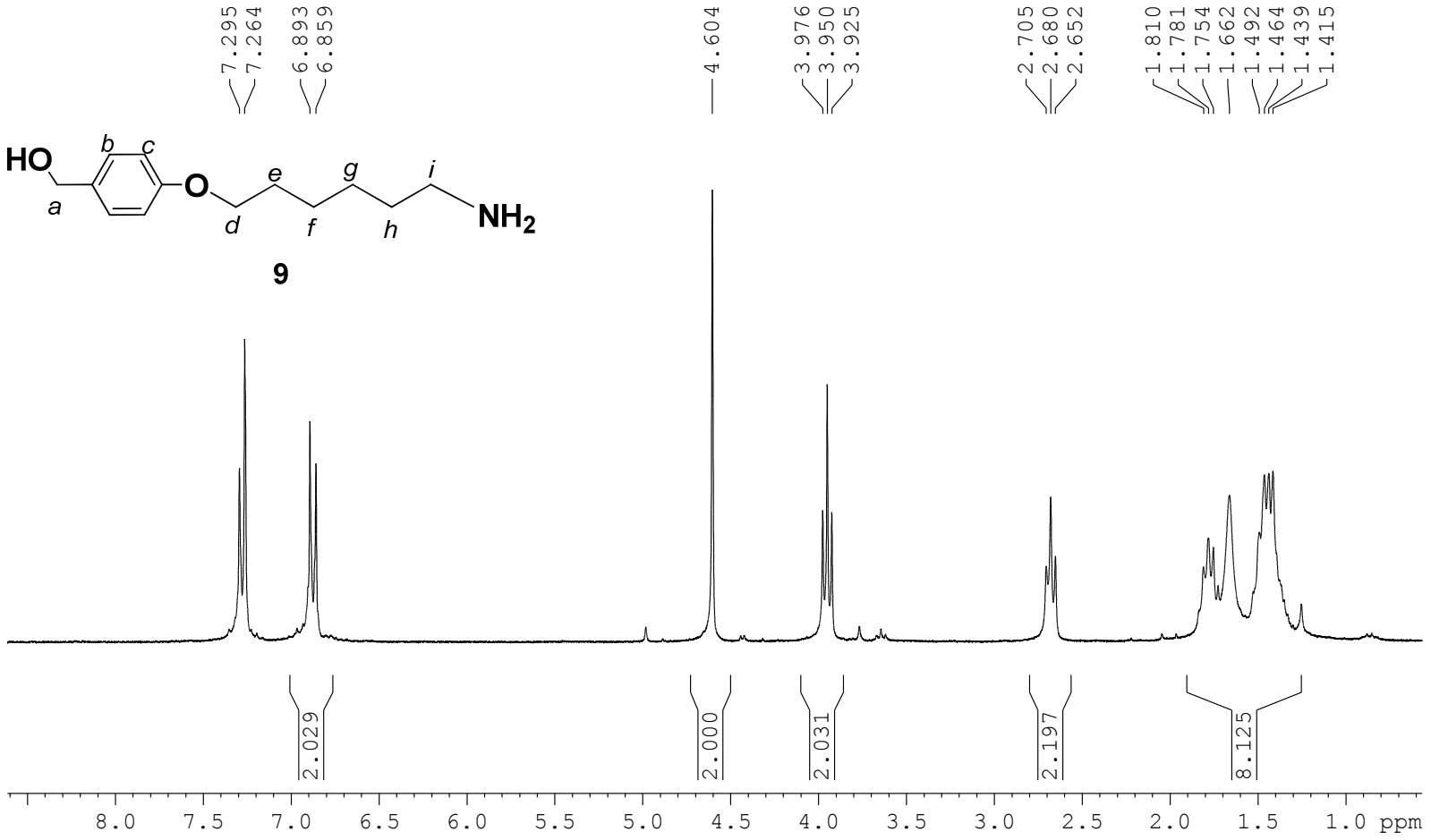


Figure S21. ^{1}H NMR spectrum of derivative **9** (250 MHz, $CDCl_3$, 298 K).

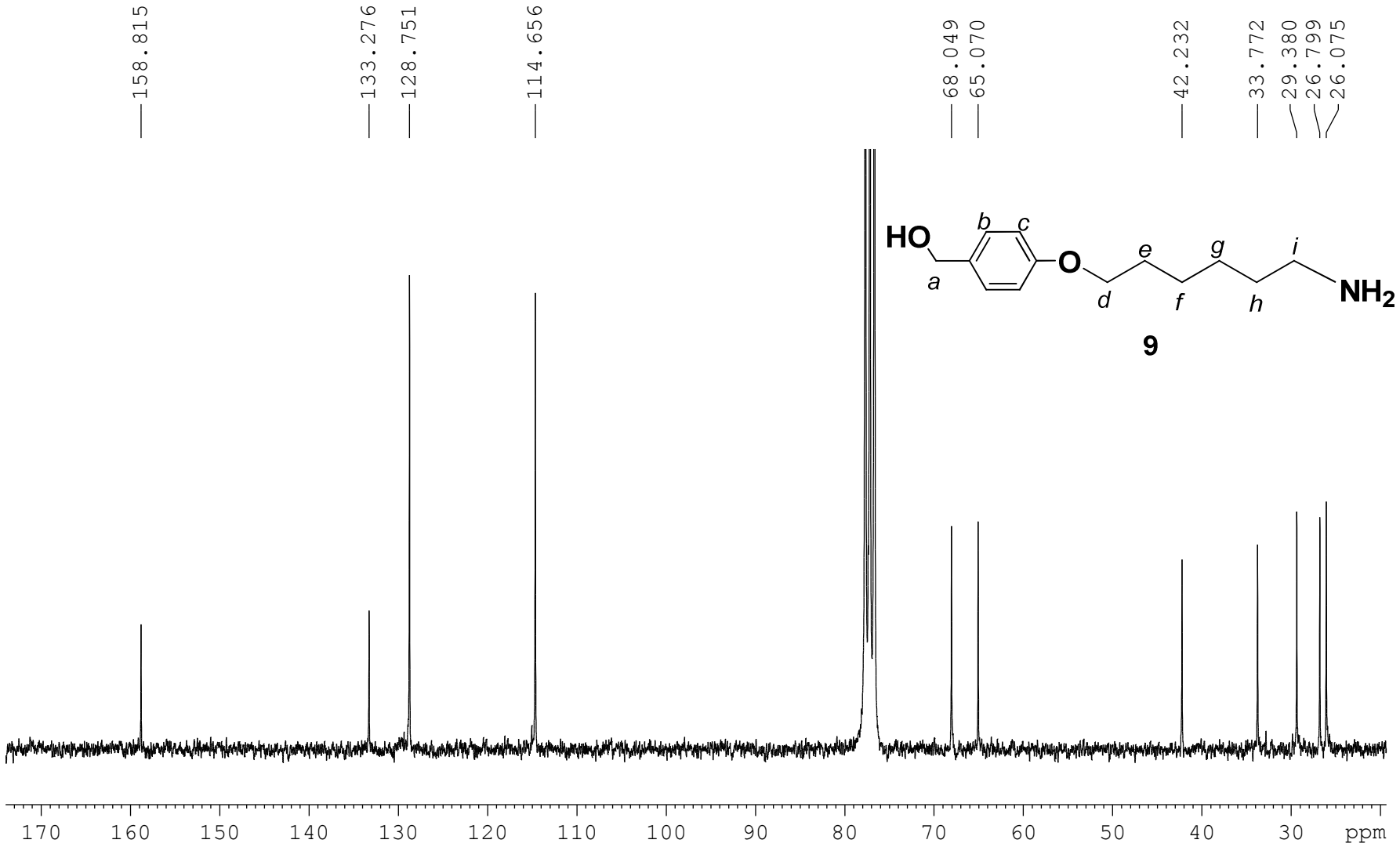


Figure S22. ^{13}C NMR spectrum of derivative **9** (63 MHz, $CDCl_3$, 298 K).

Derivative 11

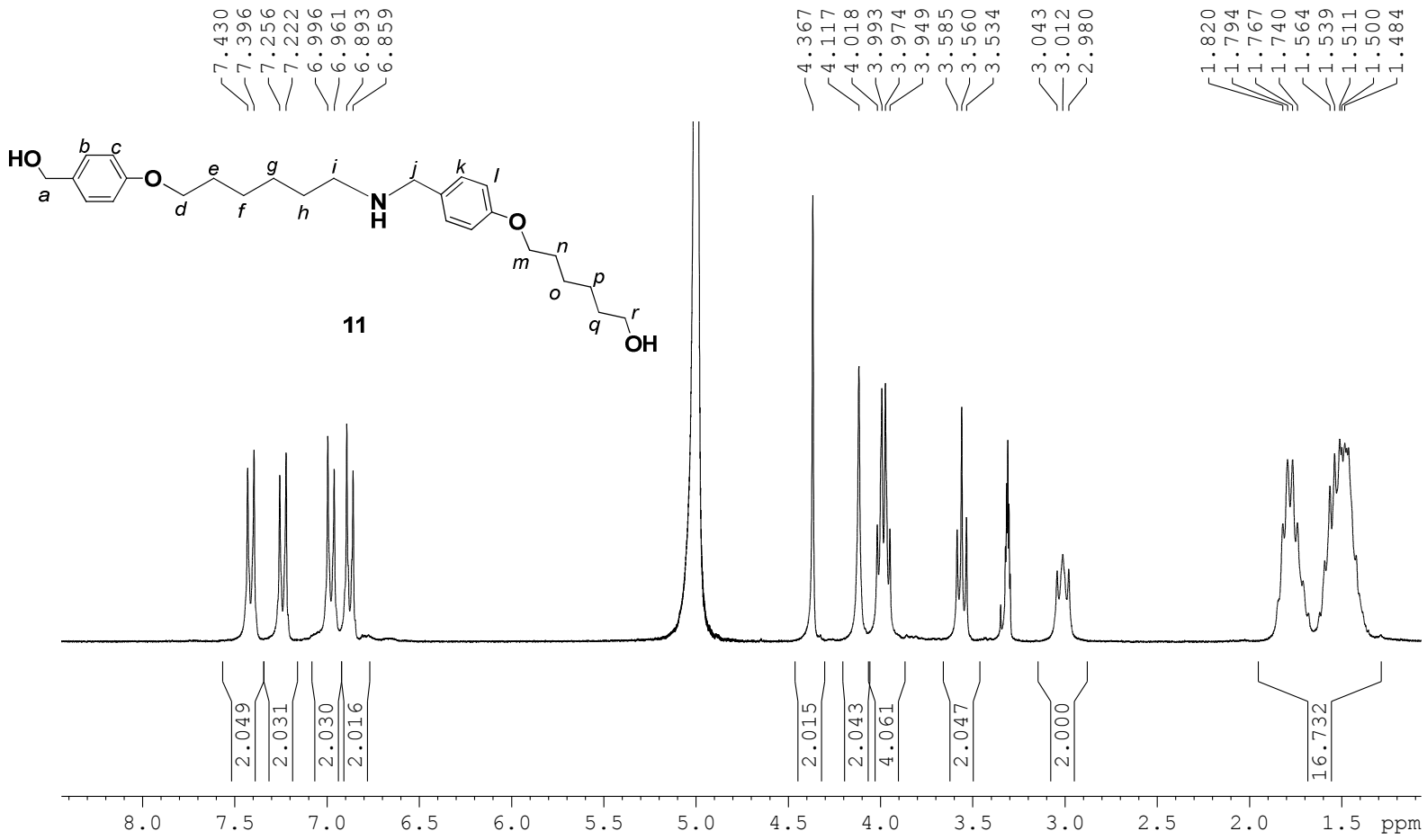


Figure S23. ^{1}H NMR spectrum of derivative **11** (250 MHz, CD_3OD, 298 K).

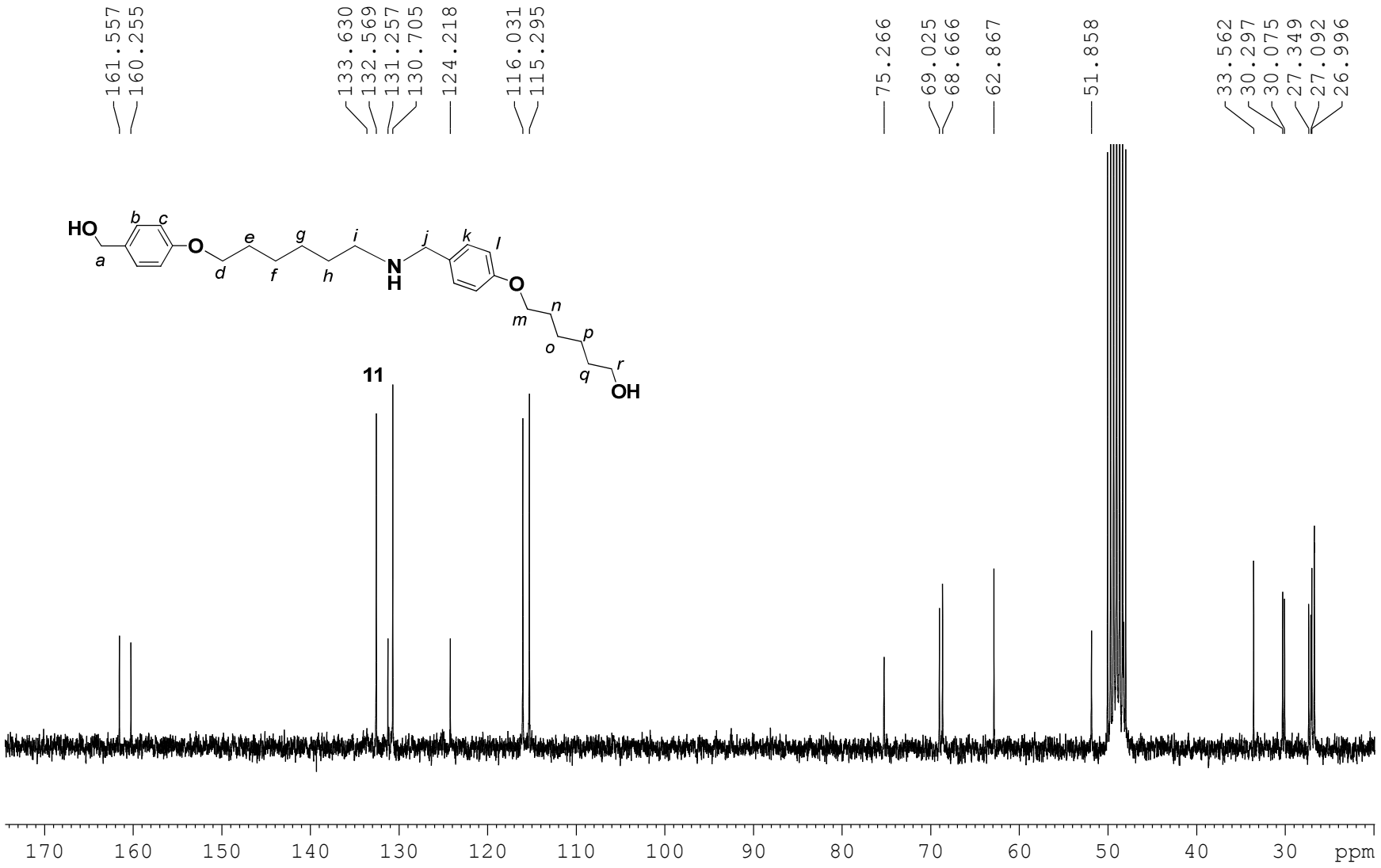


Figure S24. ^{13}C NMR spectrum of derivative **11** (63 MHz, CD_3OD, 298 K).

Directional Axle $5^{+}\cdot TFPB^{-}$

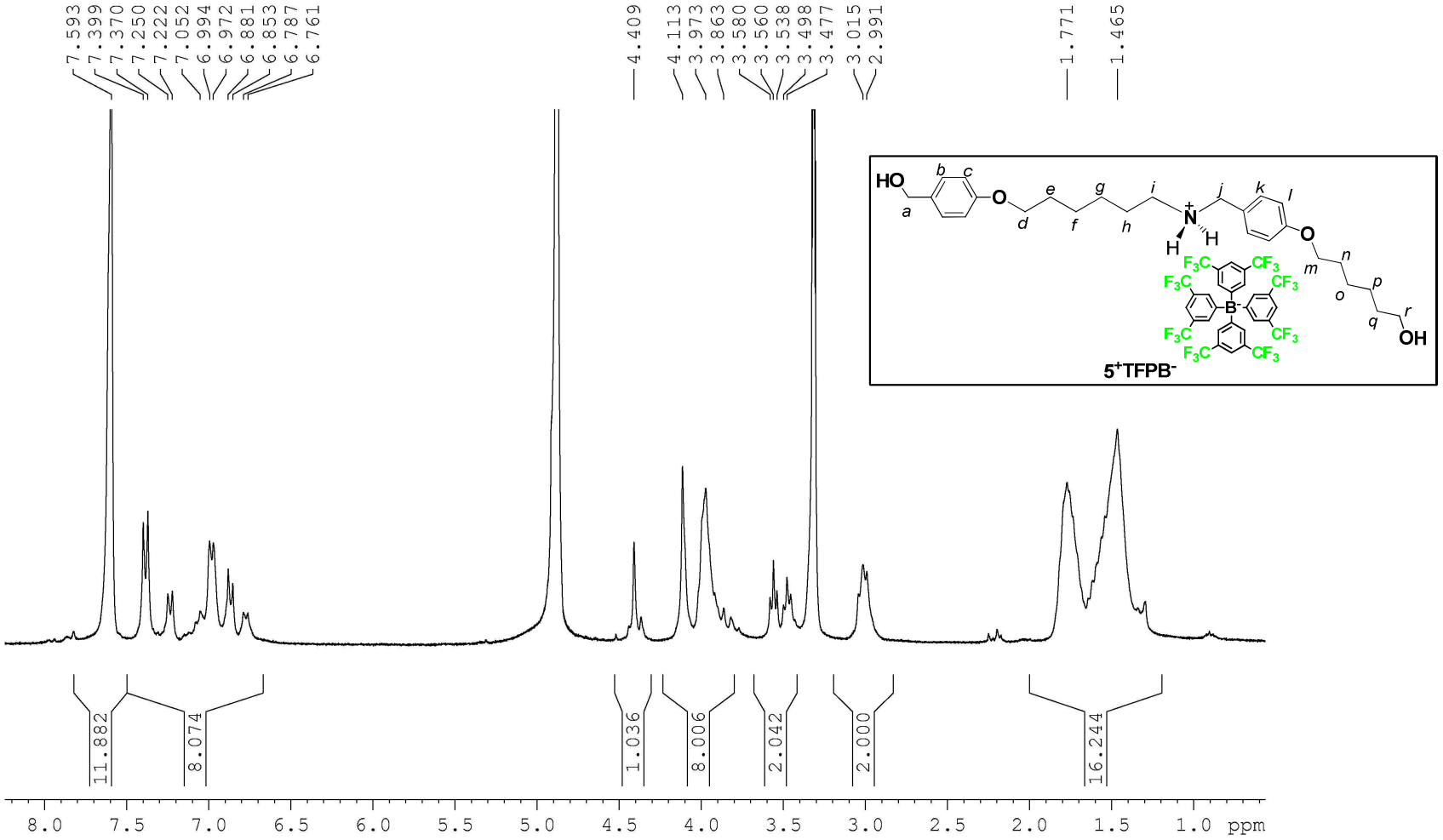


Figure S25. ^{1}H NMR spectrum of directional axle $\mathbf{5^{+}\cdot TFPB^{-}}$ (300 MHz, CD_3OD, 298 K).

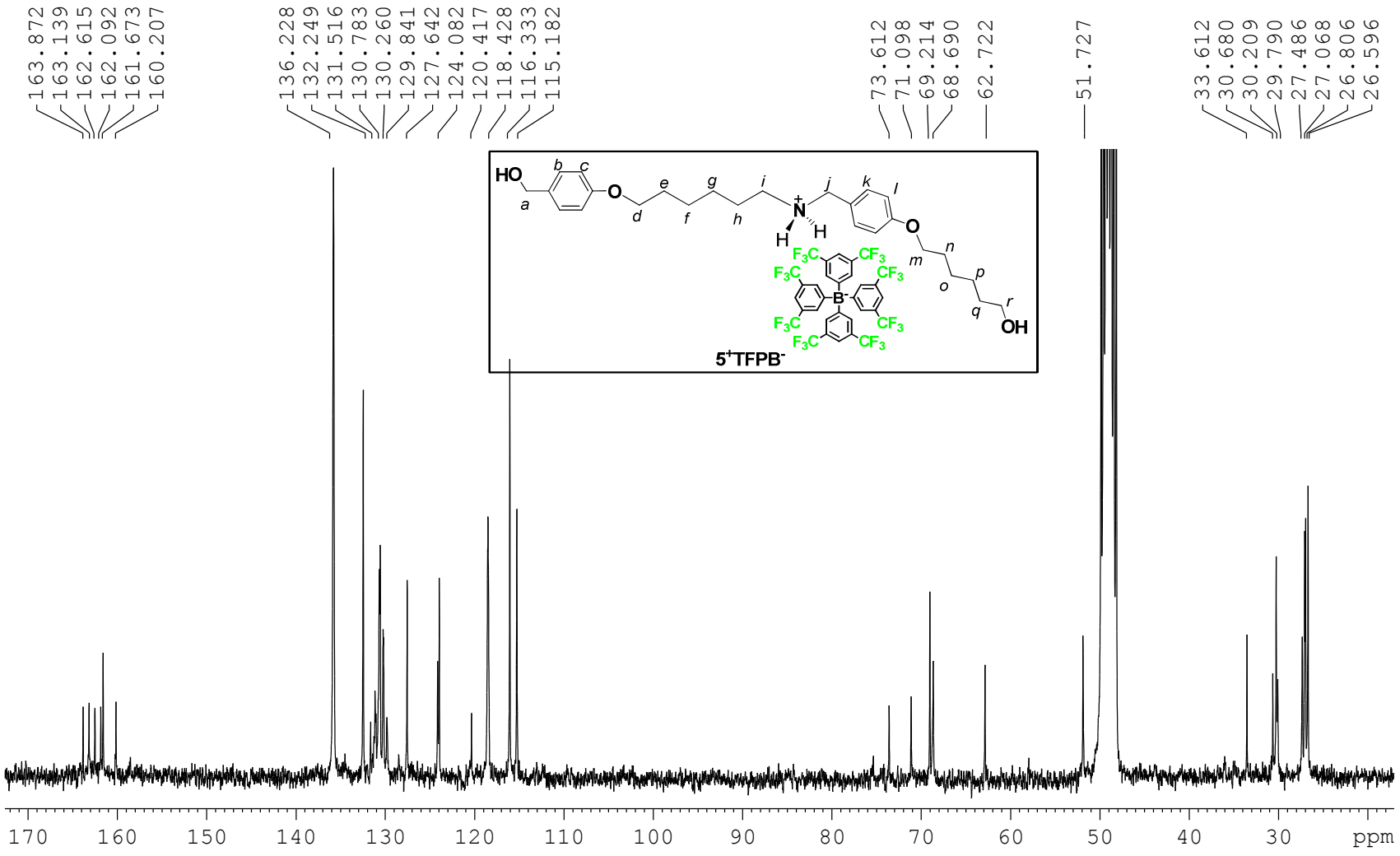
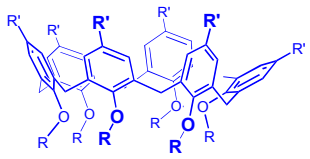


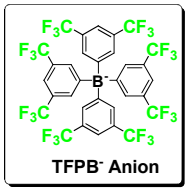
Figure S26. ^{13}C NMR spectrum of directional axle $\mathbf{5^{+}{\cdot}TFPB^{-}}$ (75 MHz, CD_3OD, 298 K).

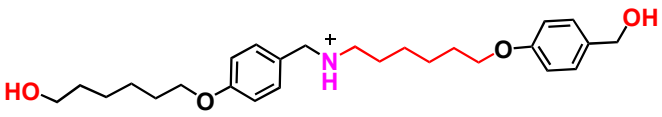
1D and 2D NMR Threading Studies of Calix[6]arenes 1a,b with Directional Axle $5^{+}\cdot TFPB^{-}$

Calix[6]arene derivative **1a** or **1b** (0.14 mmol) was dissolved in 15 mL of dry $CHCl_3$.Then, a solution of $\mathbf{5^{+}\cdot TFPB^{-}}$ (0.18 g, 0.14 mmol) in dry $CHCl_3$ (15 mL) was added and the mixture was stirred for 15 min at room temperature. The reaction was checked by ^1H NMR spectroscopy (see Figures S26 and S27).



1a) R' = *t*-Bu; R = Me
1b) R' = H; R =Me





$\mathbf{5^{+}\cdot TFPB^{-}}$

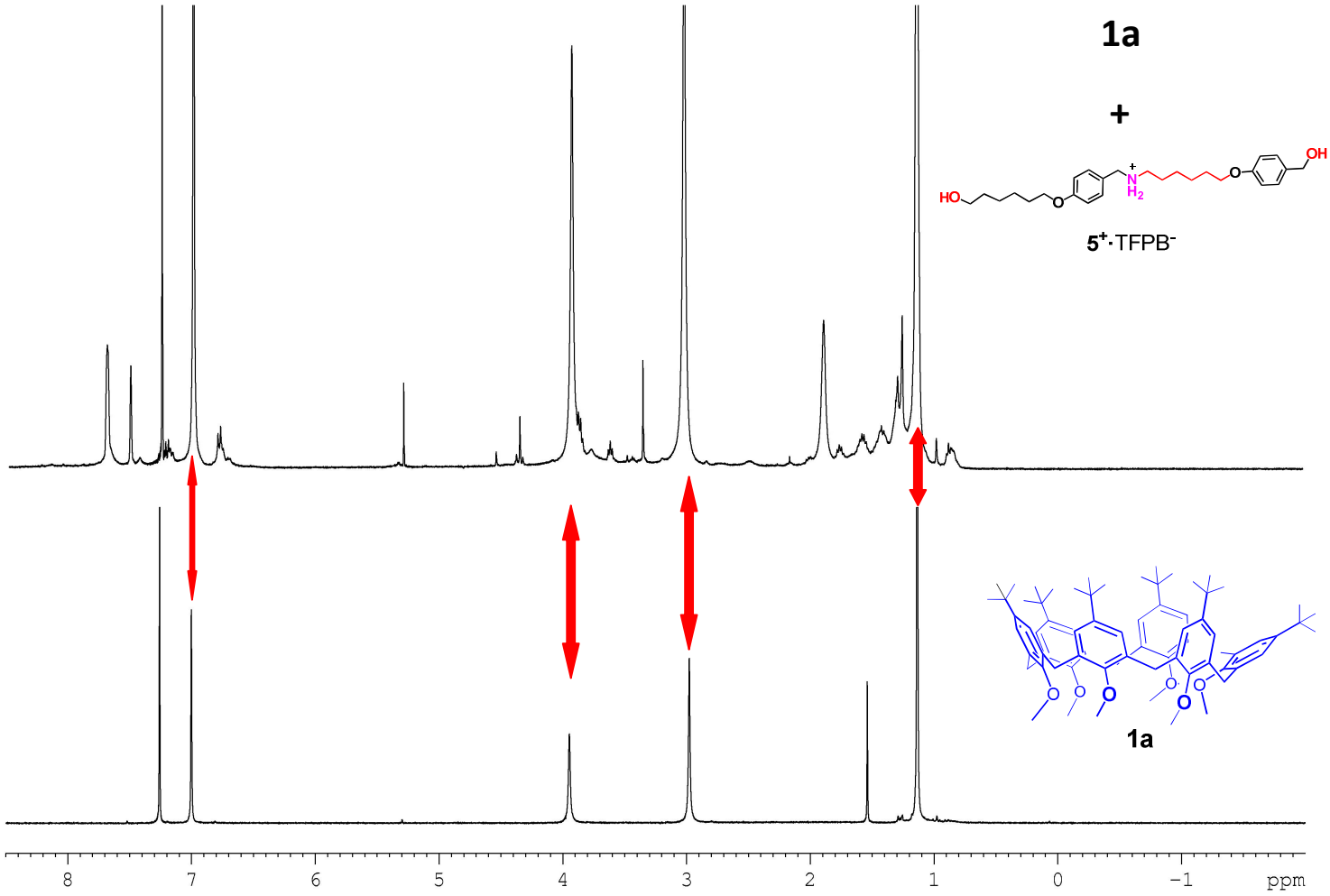


Figure S27. ^{1}H NMR spectra ($CDCl_3$, 400 MHz, 298 K) of **1a** (bottom) and an equimolar solution (9 mM) of **1a** and $\mathbf{5}^{+}$·TFPB^{-} (top).

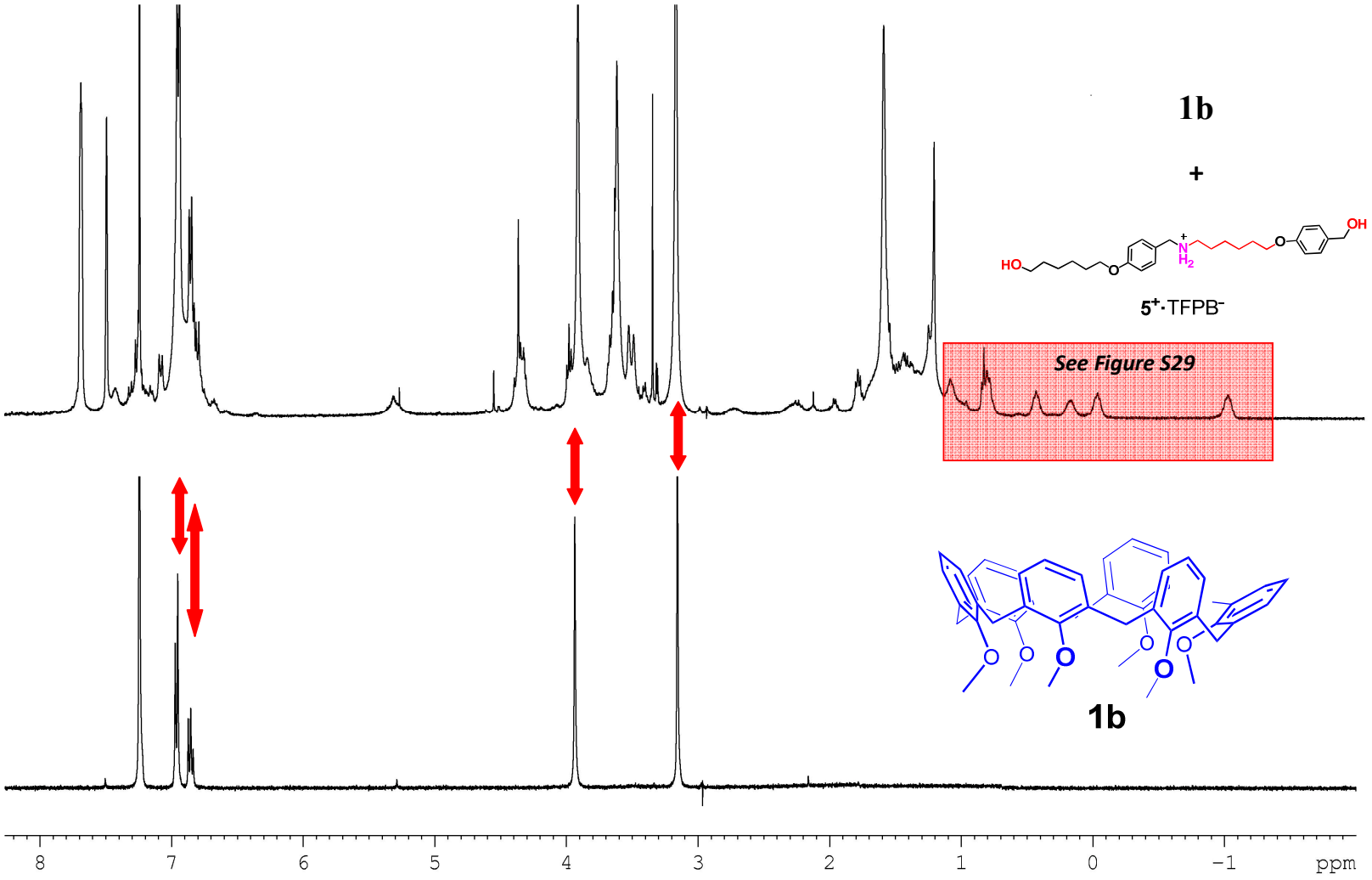


Figure S28. ^{1}H NMR spectra ($CDCl_3$, 400 MHz, 298 K) of **1b** (bottom) and an equimolar solution (9 mM) of **1b** and $\mathbf{5}^{+}$·$TFPB^{-}$ (top) .

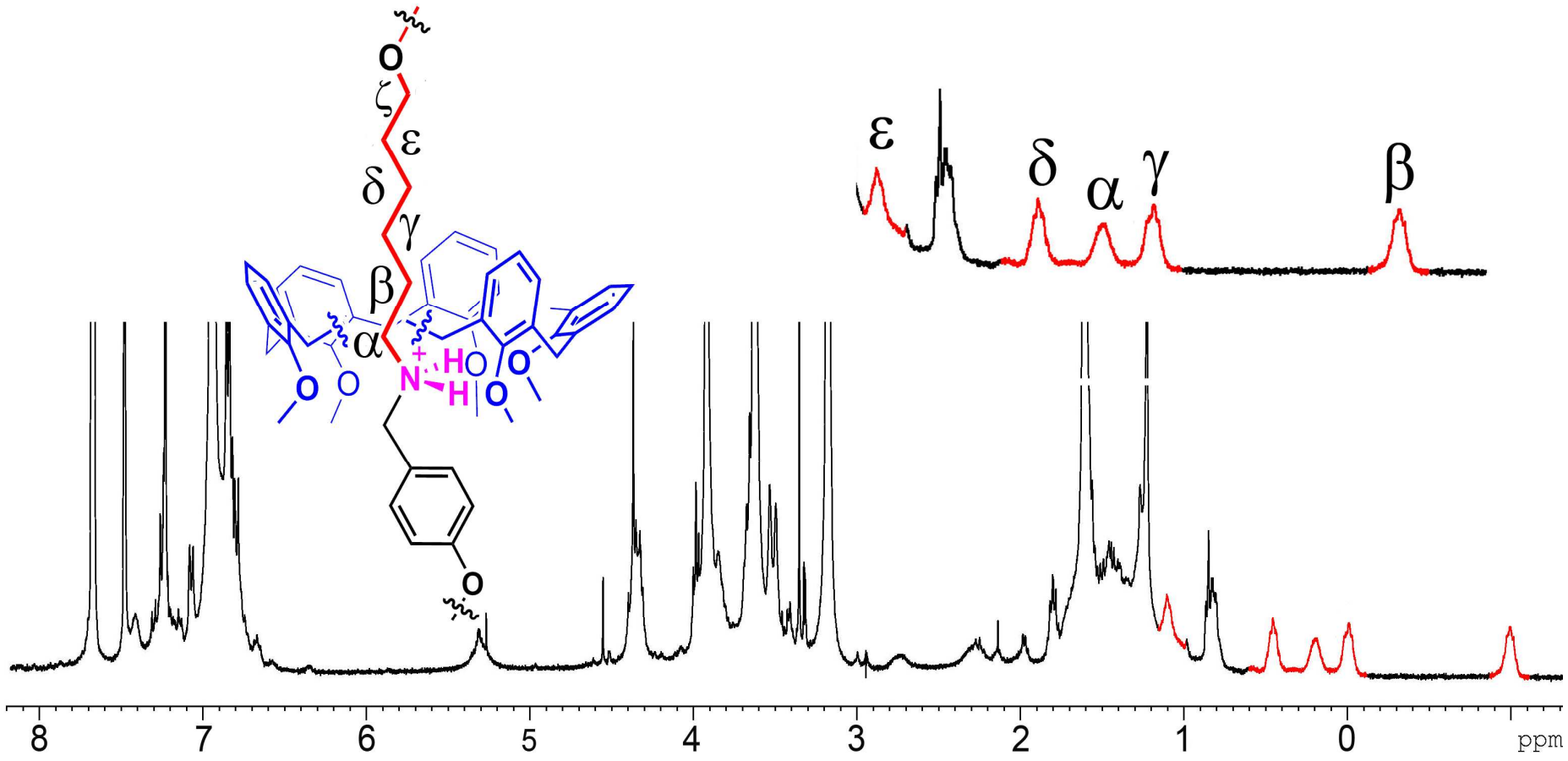


Figure S29. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of an equimolar solution (9 mM) of **1b** and **5**$^{+}$**· TFPB**$^{-}$.

2D COSY Spectrum of [(*endo*-alkyl)-**5**⊂**1b**]$^{+}$·TFPB^{-}

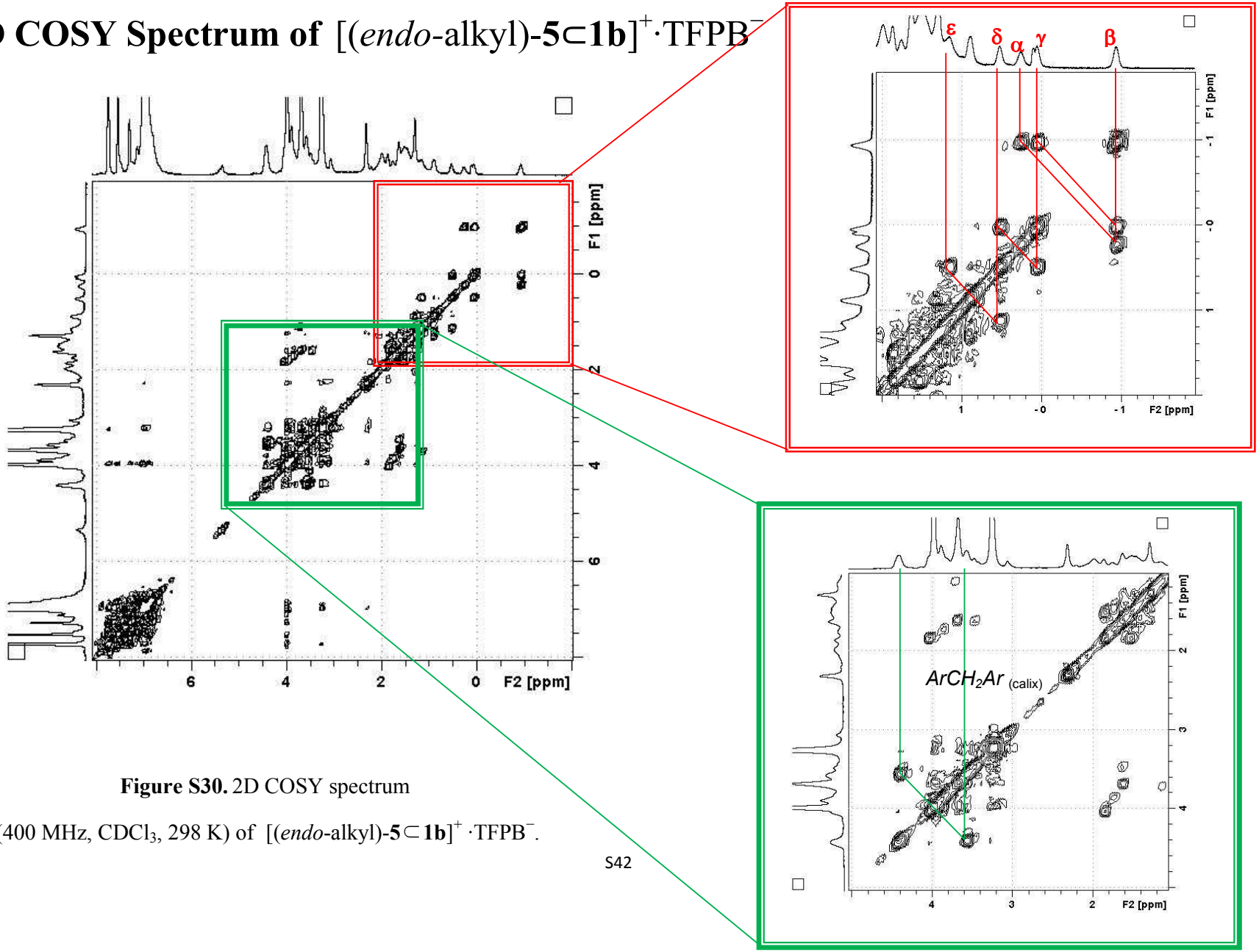
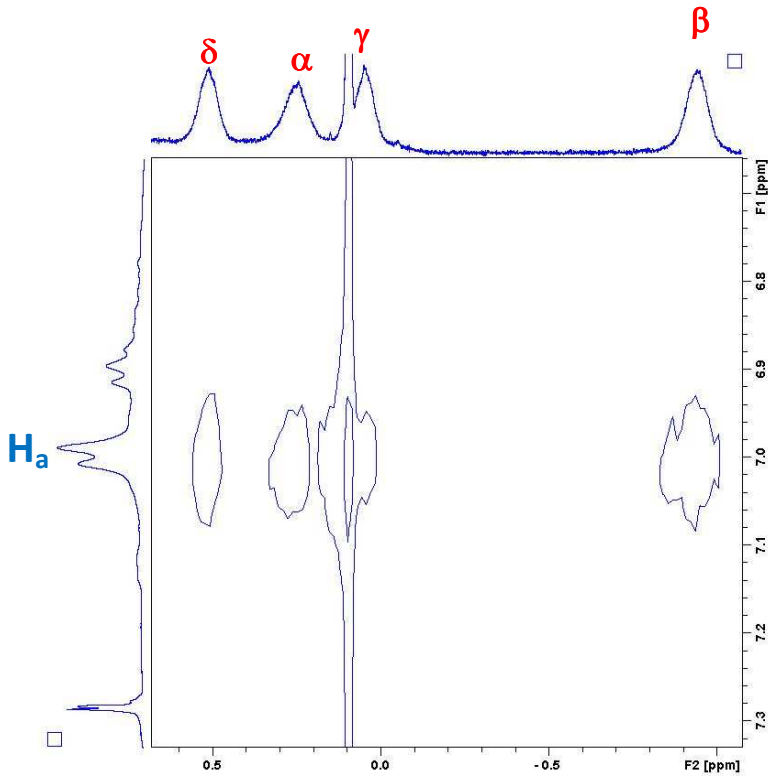


Figure S30. 2D COSY spectrum

(400 MHz, $CDCl_3$, 298 K) of [(*endo*-alkyl)-**5**⊂**1b**]$^{+}$·TFPB^{-}.

2D ROESY Spectrum of [(*endo*-alkyl)-**5⊂1b**]$^{+}$·TFPB^{-}



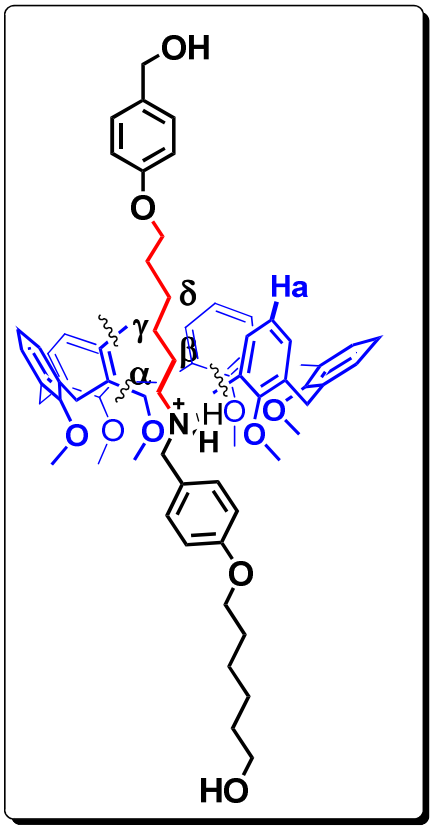


Figure S31. Expansion of the 2D ROESY spectrum (400 MHz, $CDCl_3$, 298 K) of [(*endo*-alkyl)-**5⊂1b**]$^{+}$ TFPB^{-}.

Molecular Modeling Studies of Pseudorotaxane $(5\subset 1b)^+$

DFT calculations were performed with the Gaussian 09 Software Package.[7] Input structure files for DFT calculations were obtained by molecular modeling with MacroModel 9.0 program[8] (Schrödinger, LLC, New York, NY, 2005) using OPLS force field and $CHCl_3$ solvent (GB/SA model). The input structure files were optimized at the DFT B3LYP level of theory using the 6-31G* basis set for the entire system.

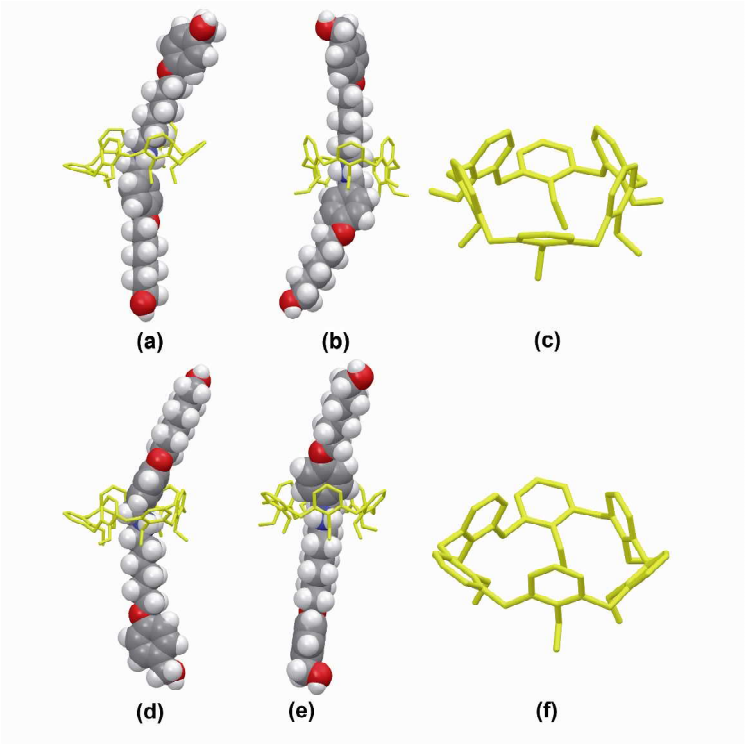
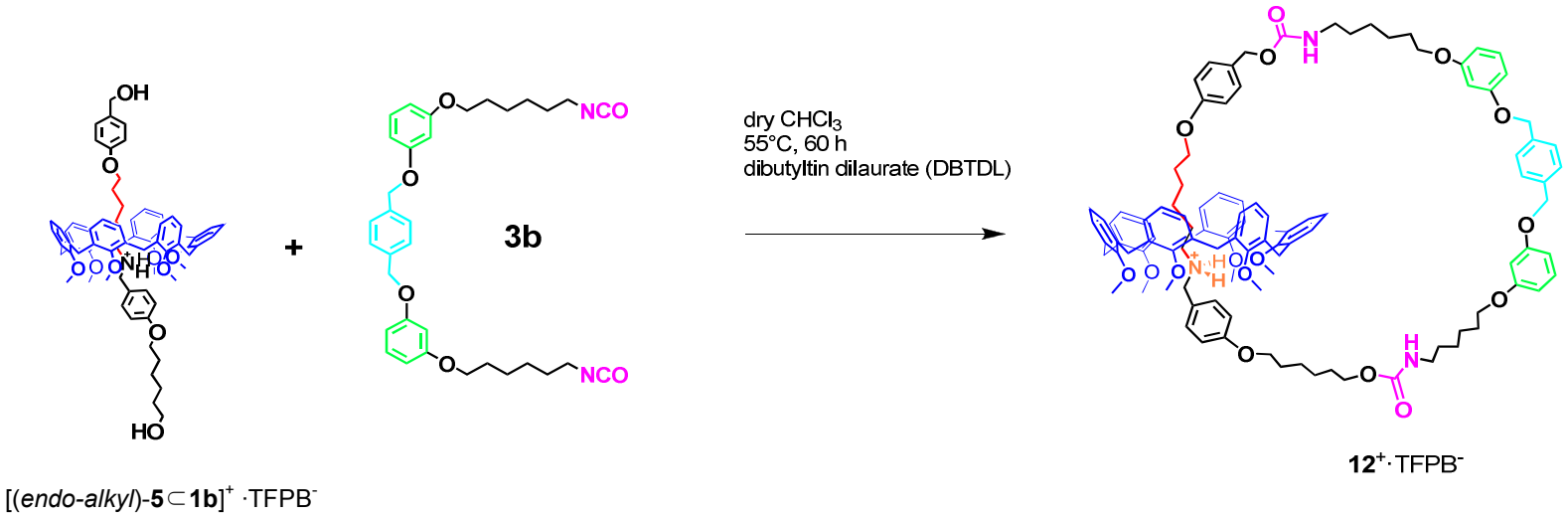


Figure S32. Different views of the energy-minimized structures of *endo*-alkyl (a-c) and *endo-benzyl* (d-f) stereoisomers of pseudo[2]-rotaxane $(\mathbf{5}\subset\mathbf{1b})^+$ (B3LYP DFT calculations using the 6-31G* basis set).

Synthesis of Oriented Calix[2]catenane $12^{+}\cdot TFPB^{-}$



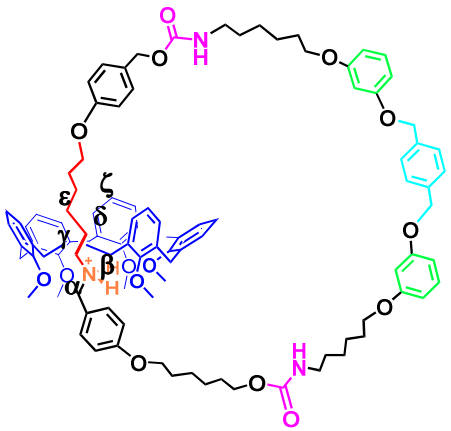
Scheme S4. Synthesis of oriented calix[2]catenane $\mathbf{12^{+}\cdot TFPB^{-}}$.

First Step: **Preparation of pseudo[2]rotaxane [(*endo*-alkyl)-5⊂1b]$^{+}$·TFPB^{-}**

Hexamethoxy-*p*-H-calix[6]arene **1b** (0.30 g, 0.23 mmol) and derivative **5**$^{+}$·TFPB^{-} (0.33 g, 0.46 mmol) were dissolved in dry $CHCl_3$ (38.0 mL) and the mixture was stirred for 1 h at room temperature under a nitrogen atmosphere. The reaction was checked by ^{1}H NMR and the solution of pseudo[2]rotaxane [(*endo*-alkyl)-**5**⊂**1b**]$^{+}$·TFPB^{-} was used without further purification for the successive macrocyclization step.

Second Step: **[1+1] Macrocyclization**

To the solution above described, a solution of diisocyanate derivative **3b** (0.13 g, 0.23 mmol, dissolved in 38 mL of dry $CHCl_3$) was slowly added dropwise over 21 h (flow rate: 0.6 mL/min) in the presence of a catalytic amount of dibutyltin dilaurate (DBTDL, 4 drops), at 55 °C. After the completion of the addition, the mixture was kept at 55 °C under stirring for additional 39 h. After cooling to room temperature, the solvent was removed under reduced pressure and the solid obtained was subjected to flash chromatography on silica gel (gradient of *n*-hexane/CH_2Cl_2, from 30/70 to 10/90 *v*/*v*, and to pure CH_2Cl_2) to give derivative **12**$^{+}$**·TFPB**$^{-}$ as a white solid (0.136 g, 0.053 mmol, 23%). **ESI-MS**$^{+}$: *m/z* = 1722.92 [M - TFBP]$^{+}$; **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): −0.98 (m, 2H, H_β), 0.05 (m, 2H, H_γ), 0.25 (broad t, 2H, H_α), 0.59 (m, 2H, H_δ), 1.09 (m, 2H, H_ε), 1.49−1.84 (overlapped, 24H, CH_2), 3.19 (broad, −OC(O)NHCH_2−, 2H), 3.52 and 4.38 [AX, (ArCH_2Ar)$_{calix}$, *J* = 14.1 Hz, 12H], 3.61 [s, 18H, (OCH_3)$_{calix}$], 3.69 (m, 2H, H_ζ), 3.90−4.08 (overlapped 10H, OCH_2 + $^{+}NH_2CH_2Ar$), 4,67 (s, 2H, $ArCH_2O$), 5.04 (s, 4H, $ArCH_2O$), 5.37 (broad, 2H, NH_2^{+}), 6.51-6.61 [overlapped, 4H, ArH), 6.88-7.44 [overlapped, 34H, ArH], 7.52 [s, 4H, (Ar*H*)$_{TFPB}^{-}$], 7.71 [s, 8H, (Ar*H*)$_{TFPB}^{-}$]; **^{13}C NMR** (63 MHz, $CDCl_3$ 298 K): *δ* 14.3, 23.1, 23.8, 24.0, 25.1, 25.8, 26.0, 26.7, 28.7, 29.1, 29.3, 29.6, 30.0, 30.2, 41.0, 52.0, 61.5, 64.7, 67.9, 68.3, 69.9, 77.5, 102.0, 107.0, 107.3, 114.3, 115.2, 117.6, 118.3, 122.5, 127.0, 128.0, 128.8, 129.3, 129.3, 129.8, 130.1, 130.9, 131.2, 132.3, 133.5, 135.0, 136.9, 155.4, 157.0, 160.0, 160.6, 160.8, 161.5, 162.2, 163.0 Anal. Calcd for $C_{140}H_{140}BF_{24}N_3O_{16}$: C, 64.99; H, 5.45. Found: C, 65.08; H, 5.36.



12^{+}·TFPB^{-}

ESI-MS^{+} Spectrum of Oriented Calix[2]catenane 12^{+}·TFPB^{-}

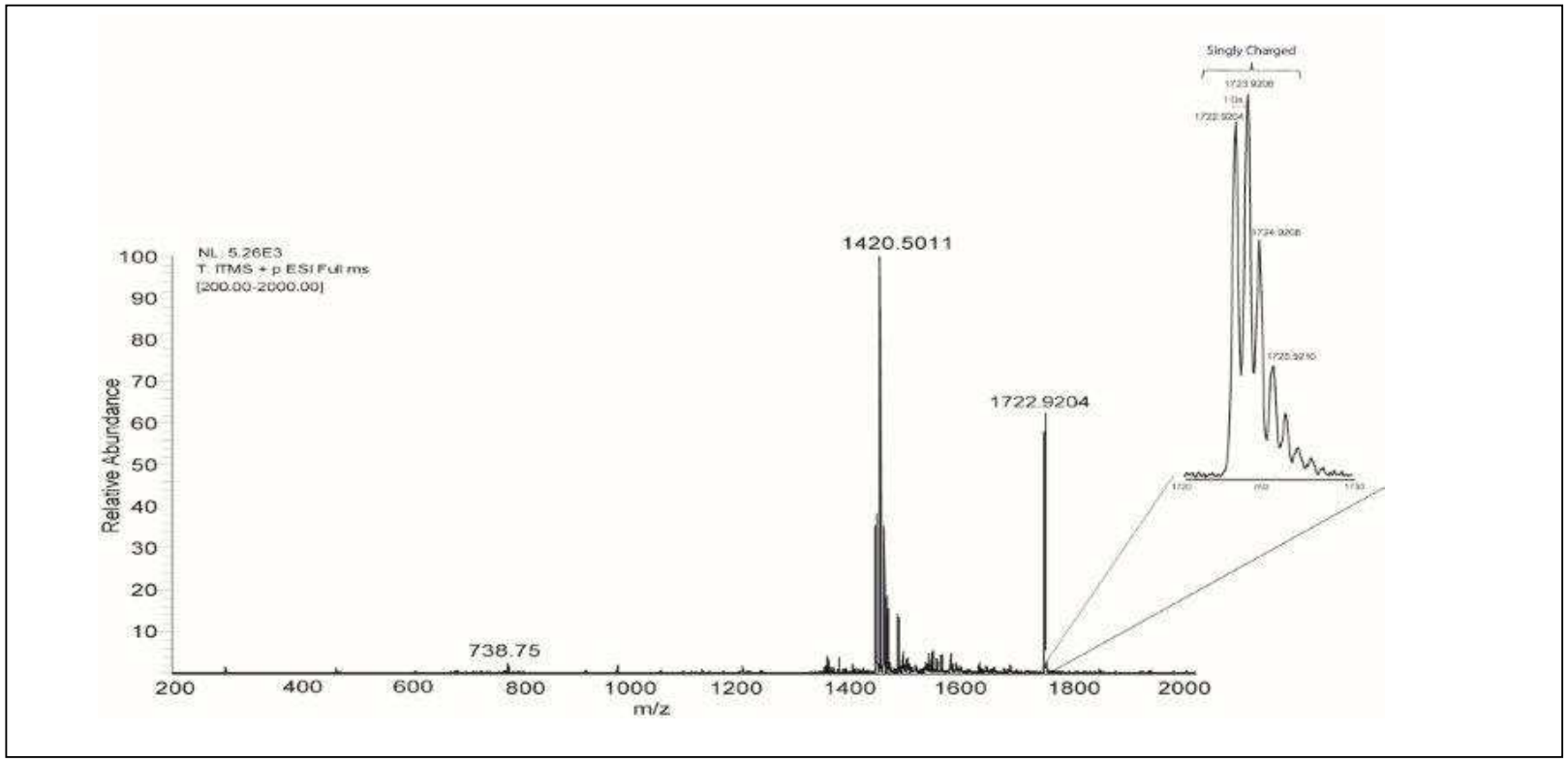


Figure S33. ESI-MS^{+} spectrum of oriented calix[2]catenane **12^{+}·TFPB^{-}**.

^{1}H and ^{13}C NMR Spectra of Oriented Calix[2]catenane $12^{+}\cdot TFPB^{-}$

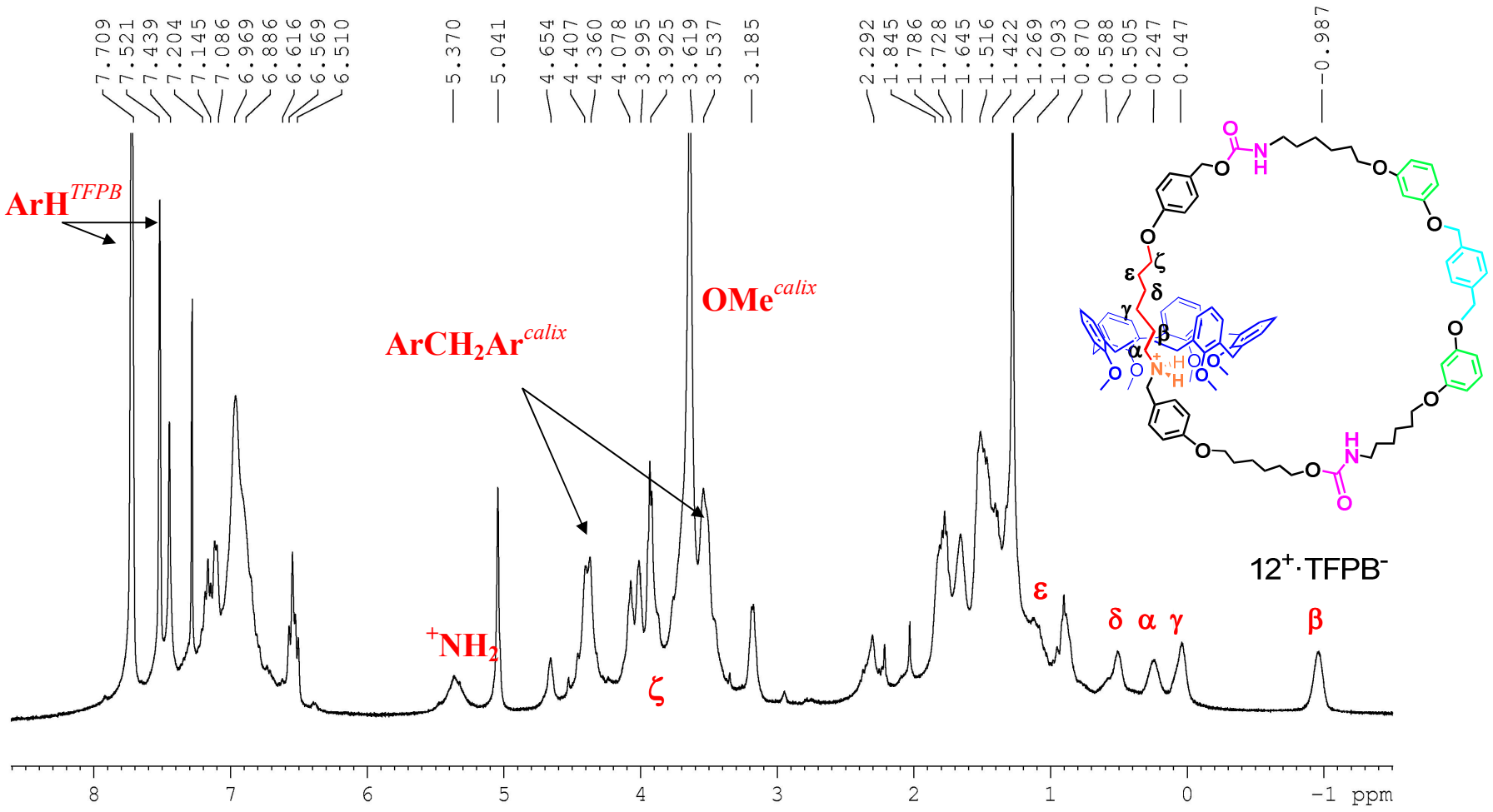


Figure S34. ^{1}H NMR spectrum of oriented calix[2]catenane **$12^{+}\cdot TFPB^{-}$** (400 MHz, $CDCl_3$, 298 K).

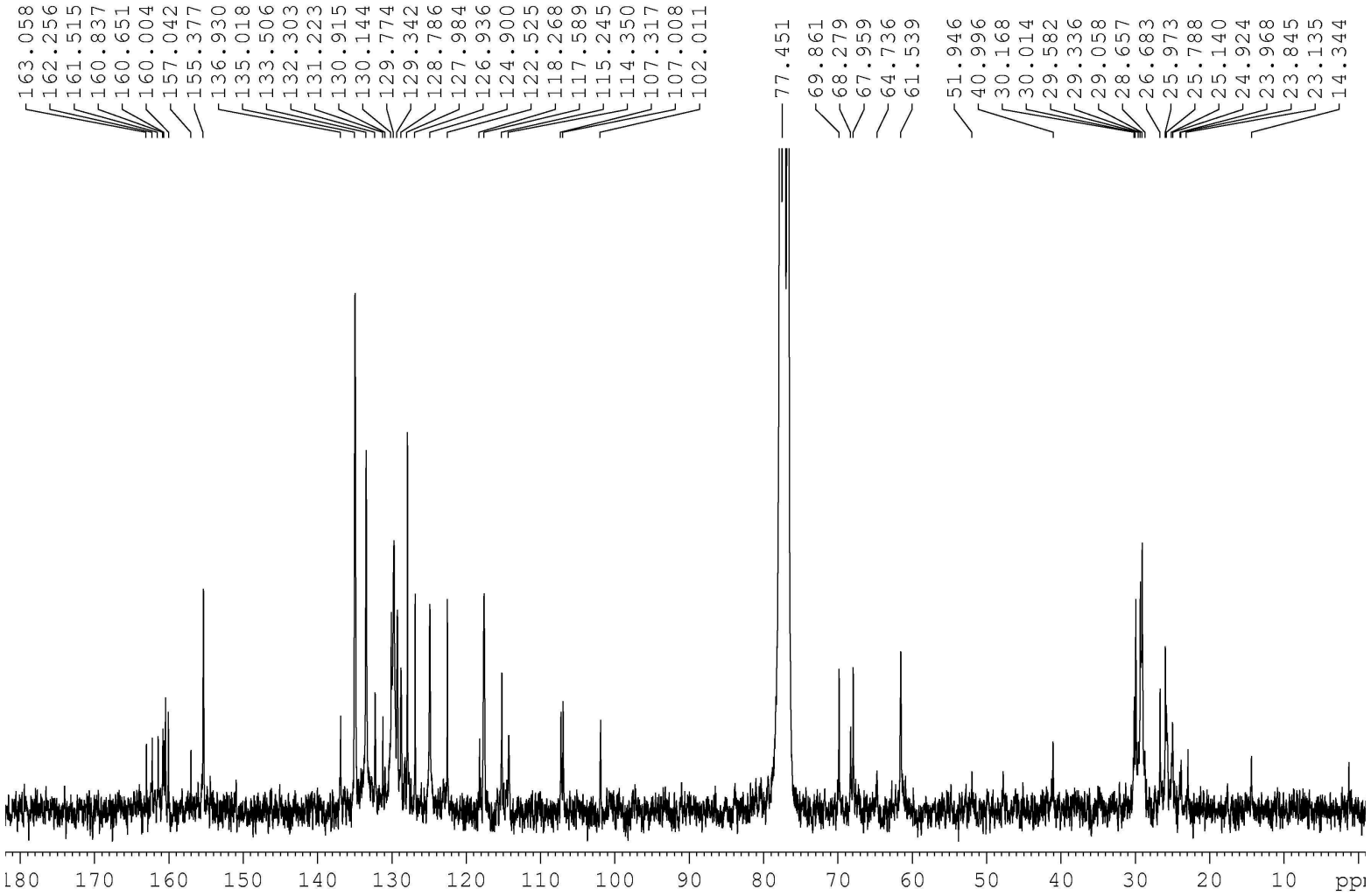


Figure S35. ^{13}C NMR spectrum of oriented calix[2]catenane **12^{+}·TFPB^{-}** (63 MHz, $CDCl_3$, 298 K).

2D COSY Spectrum of Oriented Calix[2]catenane $12^{+}\cdot TFPB^{-}$

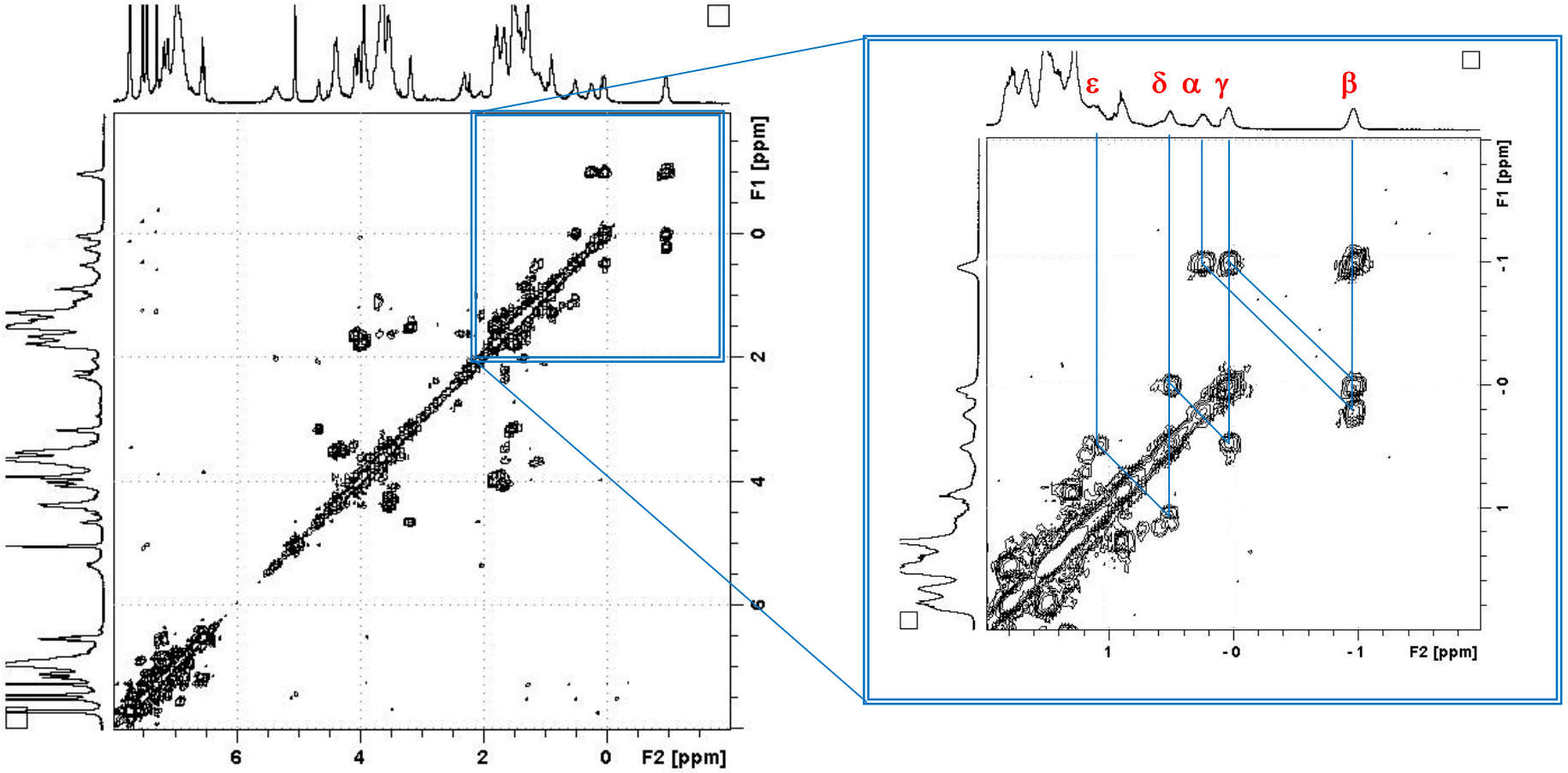


Figure S36. 2D COSY spectrum (400 MHz, $CDCl_3$, 298 K) of oriented calix[2]catenane **$12^{+}\cdot TFPB^{-}$**.

2D ROESY Spectrum of Oriented Calix[2]catenane $12^{+}\cdot TFPB^{-}$

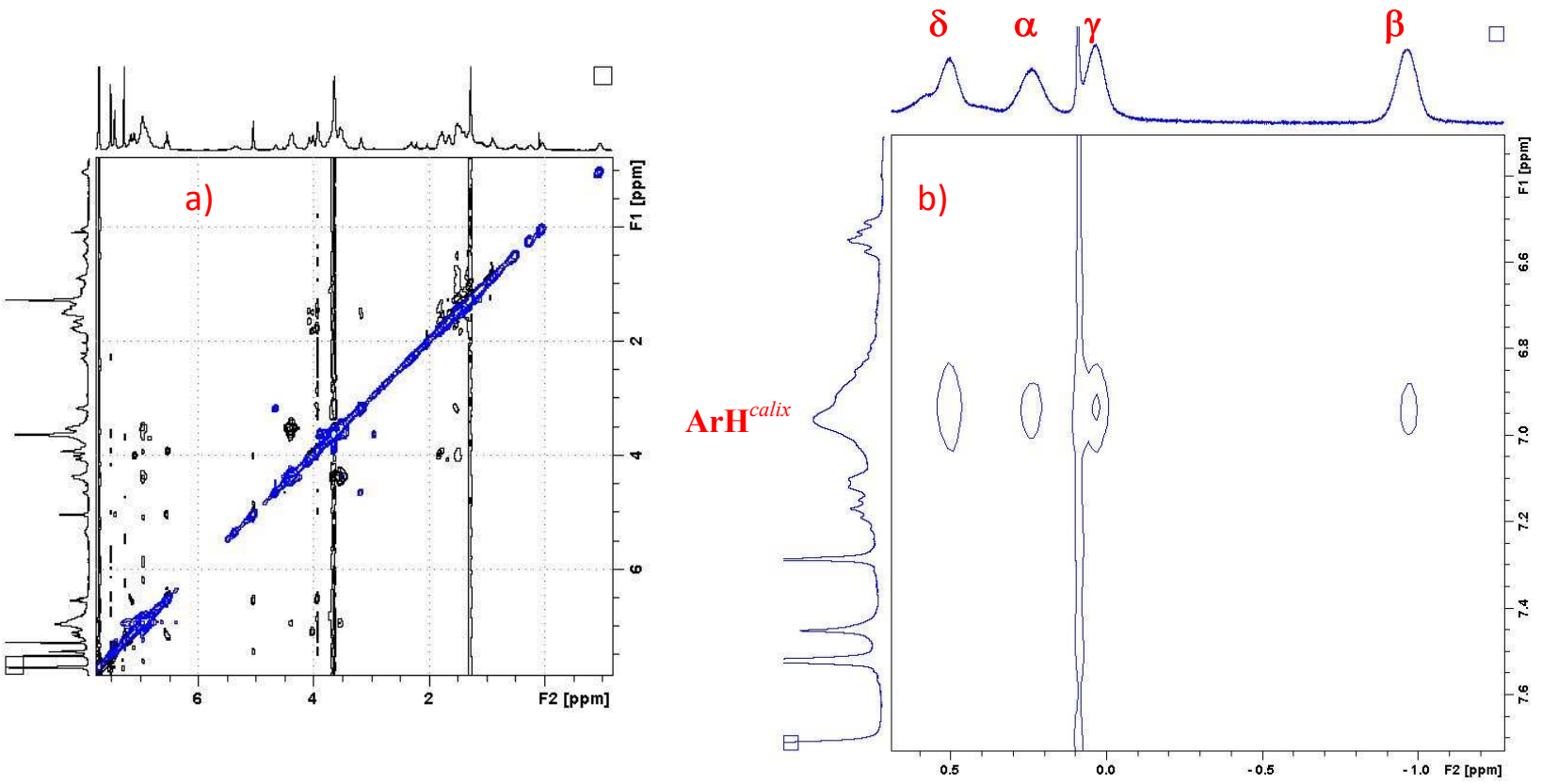


Figure S37. a) 2D ROESY spectrum (400 MHz, $CDCl_3$, 298 K) of oriented calix[2]catenane **$12^{+}\cdot TFPB^{-}$**. b) Expansion of the same spectrum showing the alkyl/ArH ROE correlations.

Molecular Modeling Studies of Oriented Calix[2]catenane 12^+

DFT calculations were performed with the Gaussian 09 Software Package.[7] Input structure files for DFT calculations were obtained by molecular modeling with MacroModel 9.0 program[8] (Schrödinger, LLC, New York, NY, 2005) using OPLS force field and $CHCl_3$ solvent (GB/SA model). The input structure files were optimized at the DFT B3LYP level of theory using the 6-31G* basis set for the entire system.

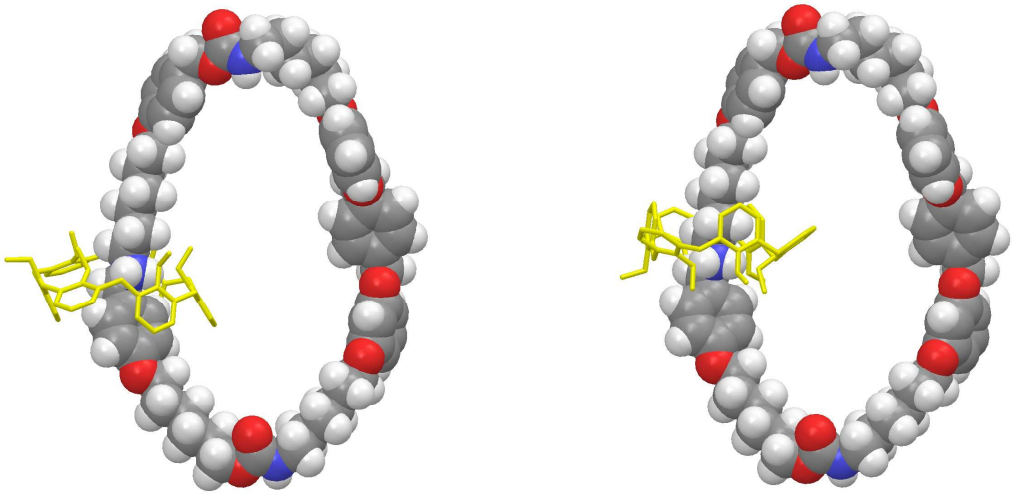


Figure S38. Energy-minimized structures of (*endo*-alkyl) (left) and (*endo*-benzyl) (right) orientational isomers of calix-threaded [2]catenane **12**$^+$ (B3LYP DFT calculation using the 6-31G* basis set).

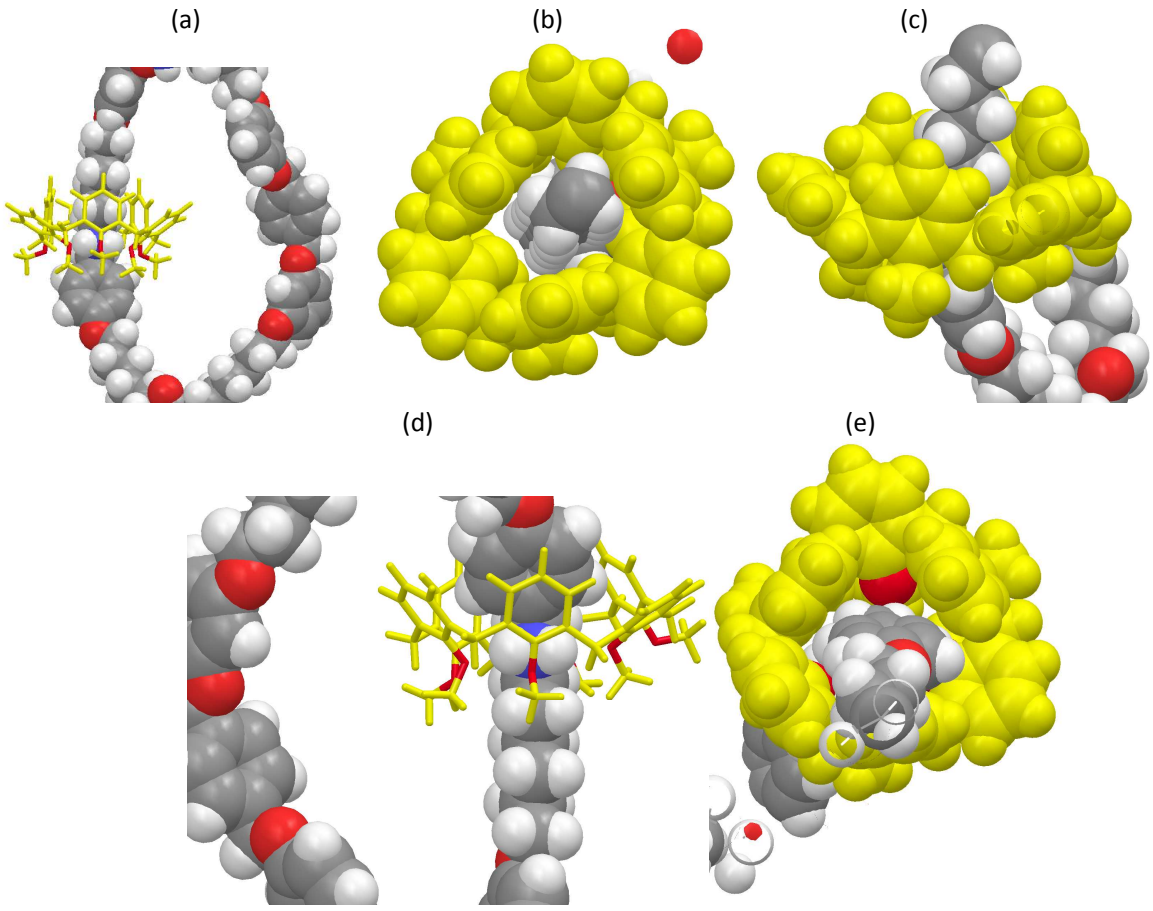
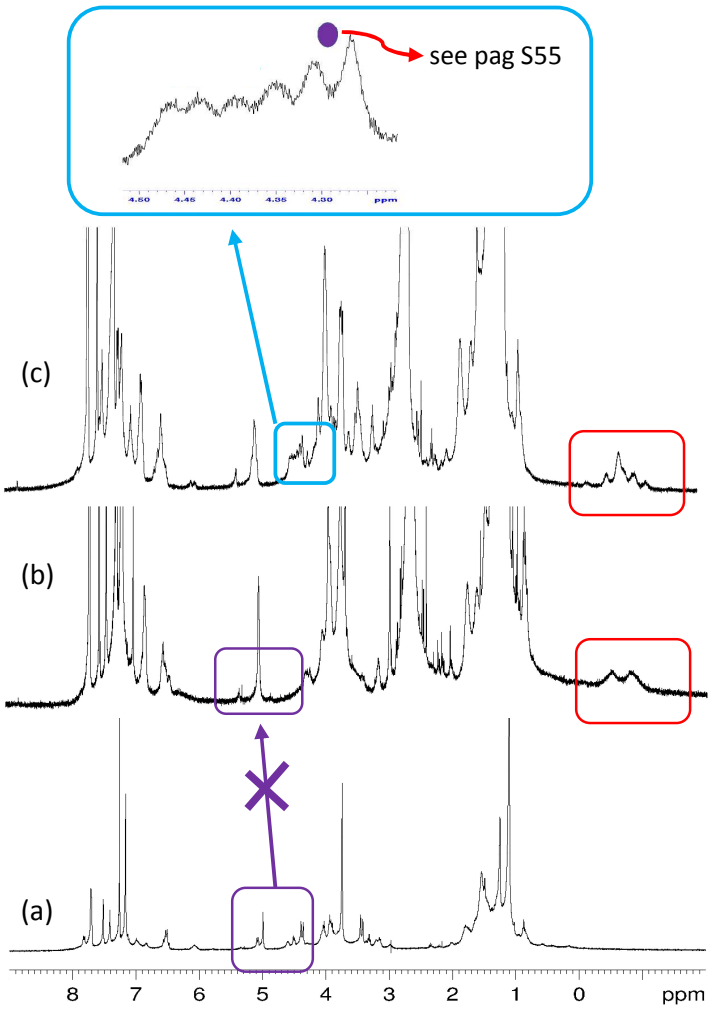


Figure S39. (a) Detailed view of the predicted $^{+}$N−H···OMe^{calix} H-bonds in the energy-minimized structure of (*endo*-alkyl) orientational isomer of calix-threaded [2]catenane **12**$^{+}$ (B3LYP DFT calculation using the 6-31G* basis set). (b and c) Detailed view of the filling of the aromatic cavity of the calixarene macrocycle **1b** through the threading with the alkyl chain unit. (d) Detailed view of the predicted $^{+}$N−H···OMe^{calix} H-bonds in the energy-minimized structure of (*endo*-benzyl) orientational isomer of calix-threaded [2]catenane **12**$^{+}$ (B3LYP DFT calculation using the 6-31G* basis set). (e) Detailed view of the filling of the aromatic cavity of the calixarene macrocycle **1b** through the threading with the benzyl unit.

Synthesis of Neutral [2]Catenane 4

To a solution of cationic [2]catenane $\mathbf{4}^+$ (0.010 g, 3.4×10^{-3} mmol) in $CDCl_3$ (2 mL) was added phosphazene base P1-*t*-Bu (0.22 M solution in $CDCl_3$, 1.9 µL, 8.5×10^{-3} mmol) and the mixture was stirred for 15 min to give neutral [2]catenane **4.** Subsequently ^{1}H VT NMR spectra (400 MHz, $CDCl_3$) were registered (Figure S40).



Neutral [2]catenane **4**, obtained upon deprotonation of $\mathbf{4}^+$, showed a broad ^{1}H NMR spectrum, in $CDCl_3$ at 298 K (Figure S40b), indicating a wheel dynamics comparable to the NMR time-scale. At a lower temperature the ^{1}H NMR spectrum of neutral **4** (400 MHz, $CDCl_3$, 233 K, Figures S40c) evidenced the presence of signals at negative values characteristic of an *endo*-alkyl inclusion. This implies that the calix[6]arene wheel move from the original dibenzyl-ammonium site to new positions in which an aliphatic chain is inside the calix-cavity (see Figure S41).

Figure S40. ^{1}H NMR Spectra (400 MHz, $CDCl_3$) of: (a) $\mathbf{4}^+\cdot TFPB^-$ (298 K), (b) neutral **4** at 298 K and (c) neutral **4** at 233 K.

On the basis of previous results,[9] among the four possibles isomers represented in Figure S41, the most favoured one is **4a**, which is stabilized by H-bonds between calixarene OMe atoms and urethane NH group. This is compatible with the main single $ArCH_2Ar$ AX system ● evidenced in Figure S40.

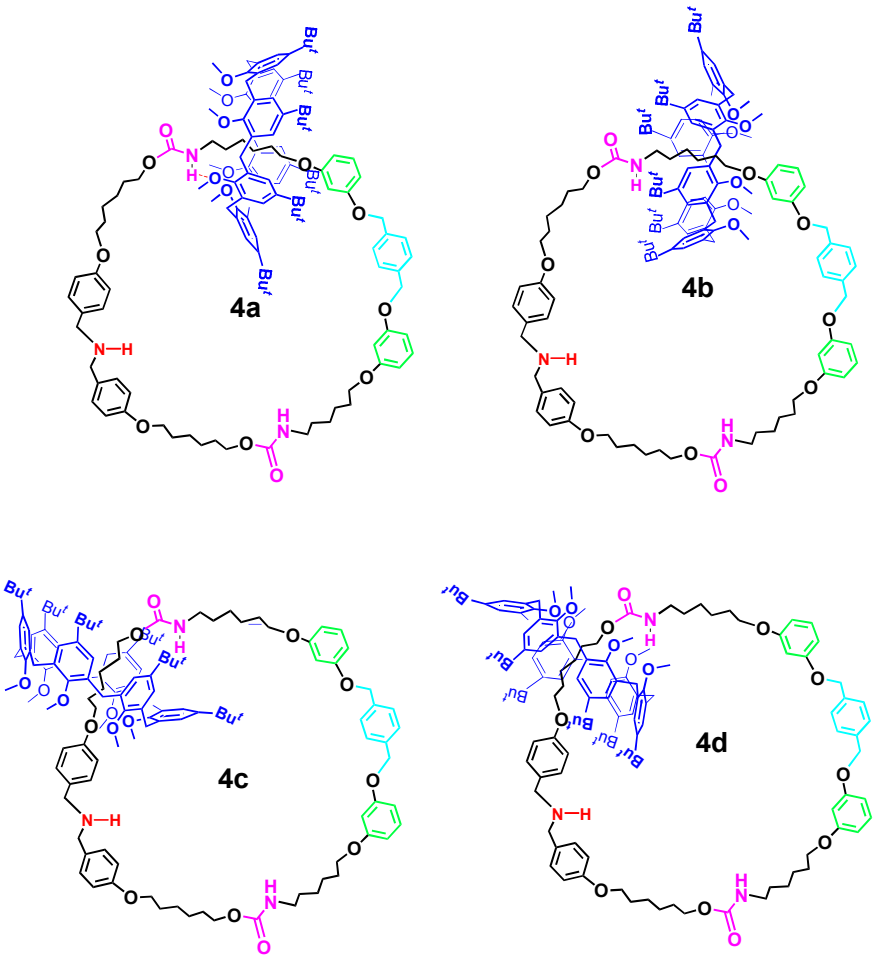


Figure S41.

[9] Pierro, T.; Gaeta, C.; Talotta, C.; Casapullo, A.; Neri, P. *Org. Lett.* **2011**, *13*, 2650. Talotta, C.; Gaeta, C.; Pierro, T.; Neri, P. *Org. Lett.* **2011**, *13*, 2098.