

A Benzo-21-Crown-7/Secondary Ammonium Salt [c2]Daisy Chain

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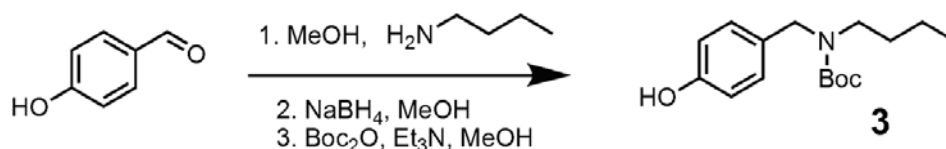
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1. Materials and methods

All reagents were commercially available and used as supplied without further purification. Compound **2** and model compounds were prepared according to the published procedures.^{S1,S2} ¹H NMR spectra were collected on a temperature-controlled 400 MHz or 500 MHz spectrometer. ¹³C NMR spectra were recorded on a Bruker AVANCE DMX-500 spectrometer. MALDI-TOF spectrometry was performed on a 4700 MALDI-TOF-TOF (Applied Biosystems, U.S.A). Low-resolution electrospray ionization (LRESI) mass spectra were obtained on a Bruker Esquire 3000 plus mass spectrometer (Bruker-Franzen Analytik GmbH Bremen, Germany) equipped with ESI interface and ion trap analyzer. High-resolution electrospray ionization (HRESI) mass spectra were obtained on a Bruker 7-Tesla FT-ICR mass spectrometer equipped with an electrospray source (Billerica, MA, USA).

2. Synthesis of compound 3



A solution of 4-hydroxybenzaldehyde (2.44 g, 20.0 mmol) and butan-1-amine (1.46 g, 20.0 mmol) in MeOH (50 mL) was stirred at room temperature overnight. Then NaBH₄ (0.91 g) was added. The reaction was quenched by addition of water. The resulting solution was extracted with dichloromethane (3 × 50 mL). The organic layer was dried over anhydrous Na₂SO₄ and evaporated to afford a crude product. The mixture of the crude product, di-*tert*-butyl dicarbonate (4.59 mL, 20.0 mmol) and Et₃N (2.79 mL, 20.0 mmol) in MeOH (100 mL) was stirred at room temperature overnight. The solvent was removed and the residue was purified by column chromatography on silica gel (ethyl acetate : petroleum ether = 1 : 30, v/v) to afford **3** as a white solid (3.63 g, 65%), mp 54–56 °C. The proton NMR spectrum of **3** is shown in Figure S1. ¹H NMR (500 MHz, acetone-*d*₆, room temperature) δ (ppm): 7.10 (d, *J* = 4.0 Hz, 2H), 6.77 (d, *J* = 4.0 Hz, 2H), 4.32 (s, 2H), 3.11 (br, 2H),

1.41–1.48 (m, 11H), 1.21–1.28 (m, 2H), 0.85 (t, $J = 4.0$ Hz, 3H). The ^{13}C NMR spectrum of **1** is shown in Figure S2. ^{13}C NMR (125 MHz, acetone- d_6 , room temperature) δ (ppm): 157.35, 130.63, 129.75, 79.37, 49.99, 46.51, 30.90, 28.48, 20.64, 14.15. LRESIMS is shown in Figure S3: m/z 581.3 $[2\text{M} + \text{Na}]^+$ (100%). HRESIMS (Figure S4): m/z calcd for $[\text{M}]^+$ $\text{C}_{16}\text{H}_{25}\text{NO}_3$, 279.1829; found 279.1837, error 2.9 ppm.

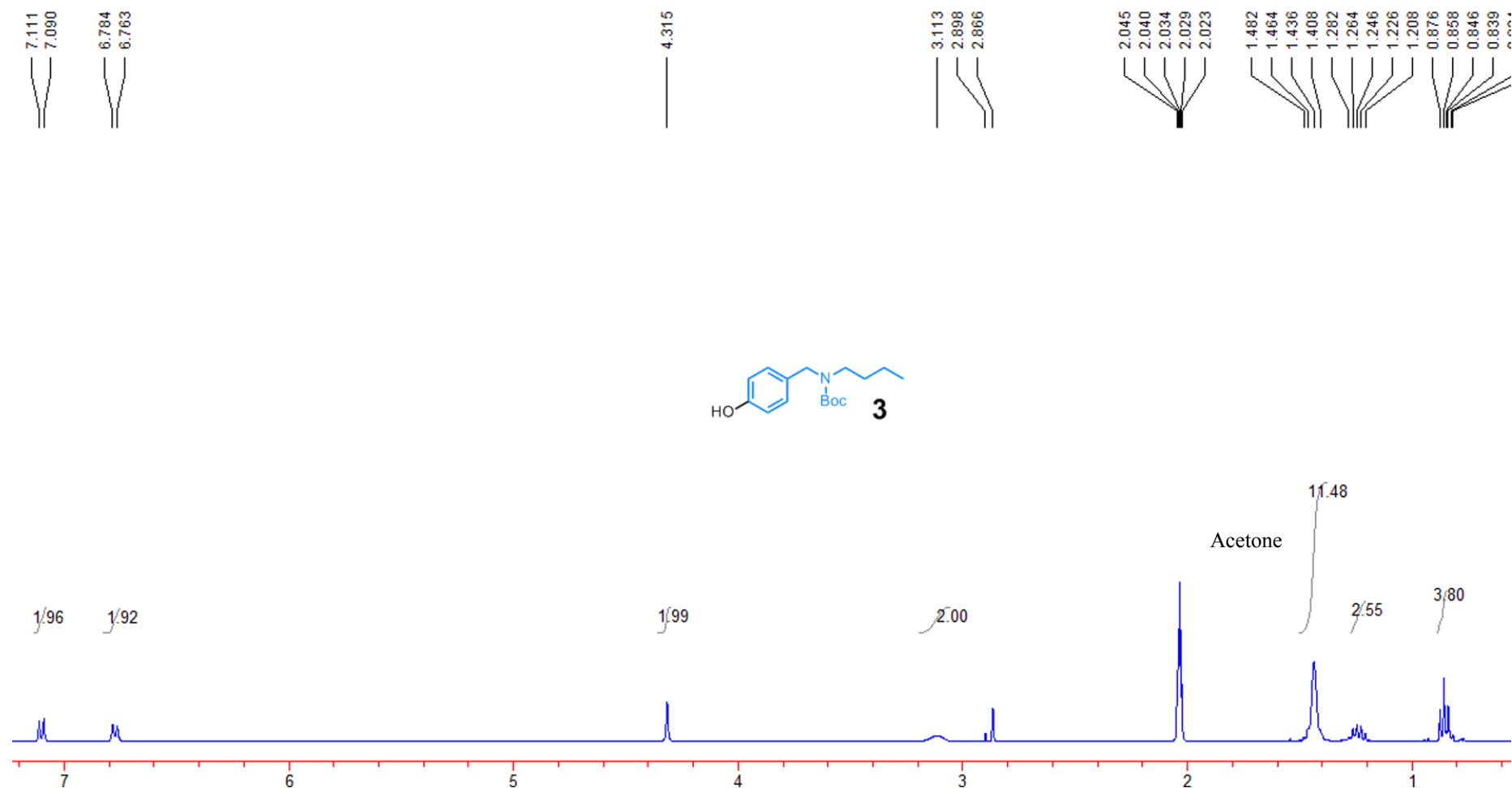


Figure S1. ¹H NMR spectrum (500 MHz, acetone-*d*₆, room temperature) of **3**.

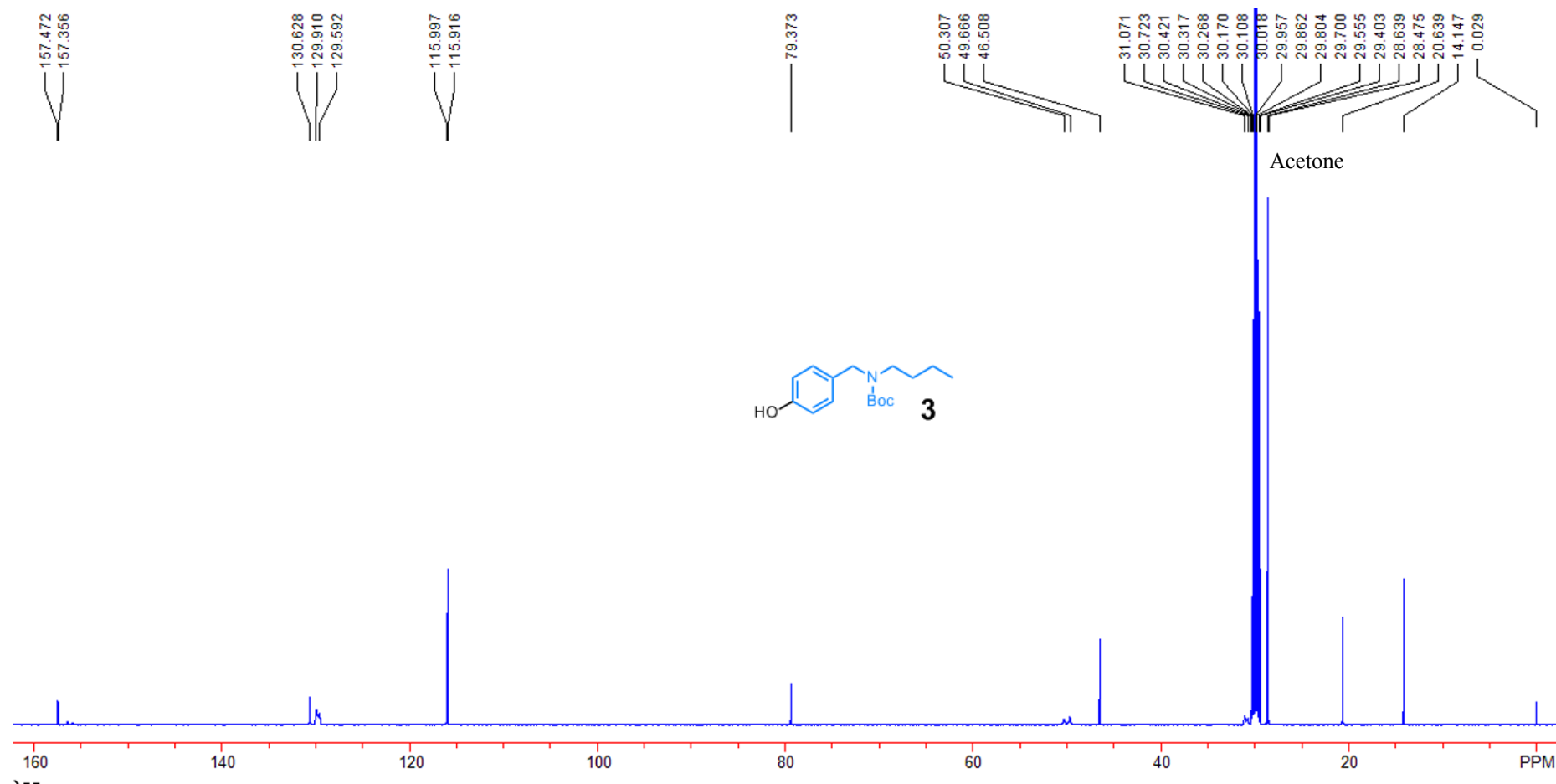


Figure S2. ¹³C NMR spectrum (125 MHz, acetone-*d*₆, room temperature) of **3**.

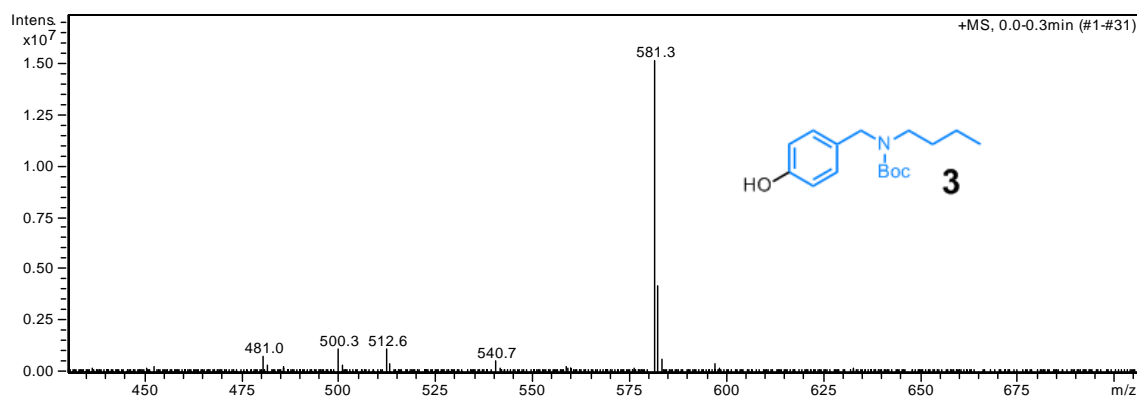
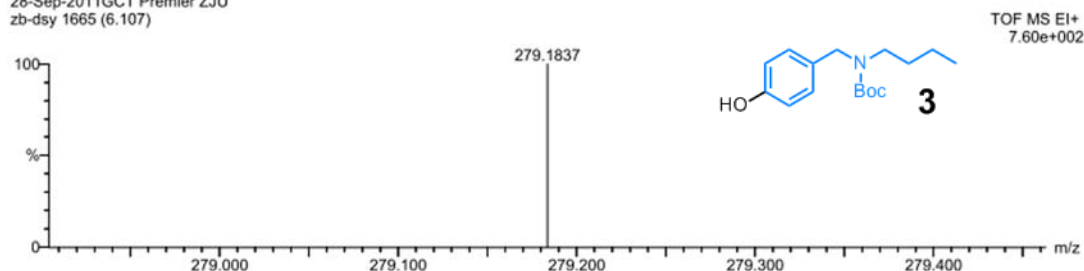


Figure S3. Electrospray ionization mass spectrum of **3**. Assignment of the main peak: m/z 581.31 $[2M + Na]^+$ (100%).

Tolerance = 1.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off

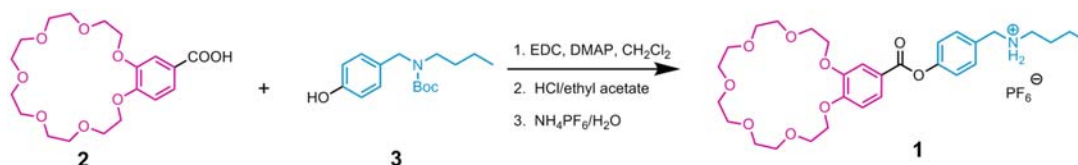
Monoisotopic Mass, Odd and Even Electron Ions
173 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-100 H: 0-300 N: 0-6 O: 0-6
28-Sep-2011 GCT Premier ZJU
zb-dsy 1665 (6.107)



Minimum:				-1.5			
Maximum:	1.0	10.0		50.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula	
279.1837	279.1834	0.3	1.1	5.0	5546386.0	C16	H25 N 03

Figure S4. High-resolution TOF mass spectrum of **3**.

3. Synthesis of compound **1**



A solution of **2** (175 mg, 0.43 mmol), **3** (121 mg, 0.43 mmol), EDC (83.3 mg, 0.43 mmol) and DMAP (53.0 mg, 0.43 mmol) in dichloromethane (30 mL) was stirred for 24 h at room temperature. The solvent was removed to give a crude product. The

crude product was dissolved in 10% HCl/ethyl acetate (25 mL) and stirred overnight. The white solid was filtered, washed with ethyl acetate thoroughly, and dissolved in warm deionized water (50 mL). The saturated aqueous solution of NH_4PF_6 was added to afford a white precipitate, which was filtered off and washed with deionized water to afford monomer **1** as a white solid (182 mg, 60%), mp 115–117 °C. The proton NMR spectrum of **1** is shown in Figure S5. ^1H NMR (500 MHz, $\text{DMSO}-d_6$, room temperature) δ (ppm): 8.50–8.80 (br, 2H), 7.75–7.79 (m, 1H), 7.55–7.60 (m, 3H), 7.37 (d, $J = 8.5$ Hz, 2H), 7.17 (d, $J = 9.0$ Hz, 1H), 4.20–4.24 (m, 2H), 4.15–4.20 (m, 4H), 3.76–3.82 (m, 4H), 3.65–3.47 (m, 16H), 2.94 (t, $J = 7.5$ Hz, 2H), 1.57–1.63 (m, 2H), 1.32–1.38 (m, 2H), 0.90 (t, $J = 7.5$ Hz, 3H). The ^{13}C NMR spectrum of **1** is shown in Figure S6. ^{13}C NMR (125 MHz, $\text{DMSO}-d_6$, room temperature) δ (ppm): 164.65, 153.59, 151.66, 148.32, 131.73, 130.08, 124.75, 122.82, 121.21, 114.05, 112.87, 70.83, 70.70, 70.66, 70.59, 70.33, 69.27, 69.15, 69.03, 50.00, 46.95, 27.90, 19.72, 13.93. LRESIMS is shown in Figure S7: m/z 562.1 $[\text{M} - \text{PF}_6]^+$ (100%). HRESIMS (Figure S8): m/z calcd for $[\text{M} - \text{PF}_6]^+$ $\text{C}_{30}\text{H}_{44}\text{NO}_9$, 562.3011; found 562.3021, error 1.8 ppm.

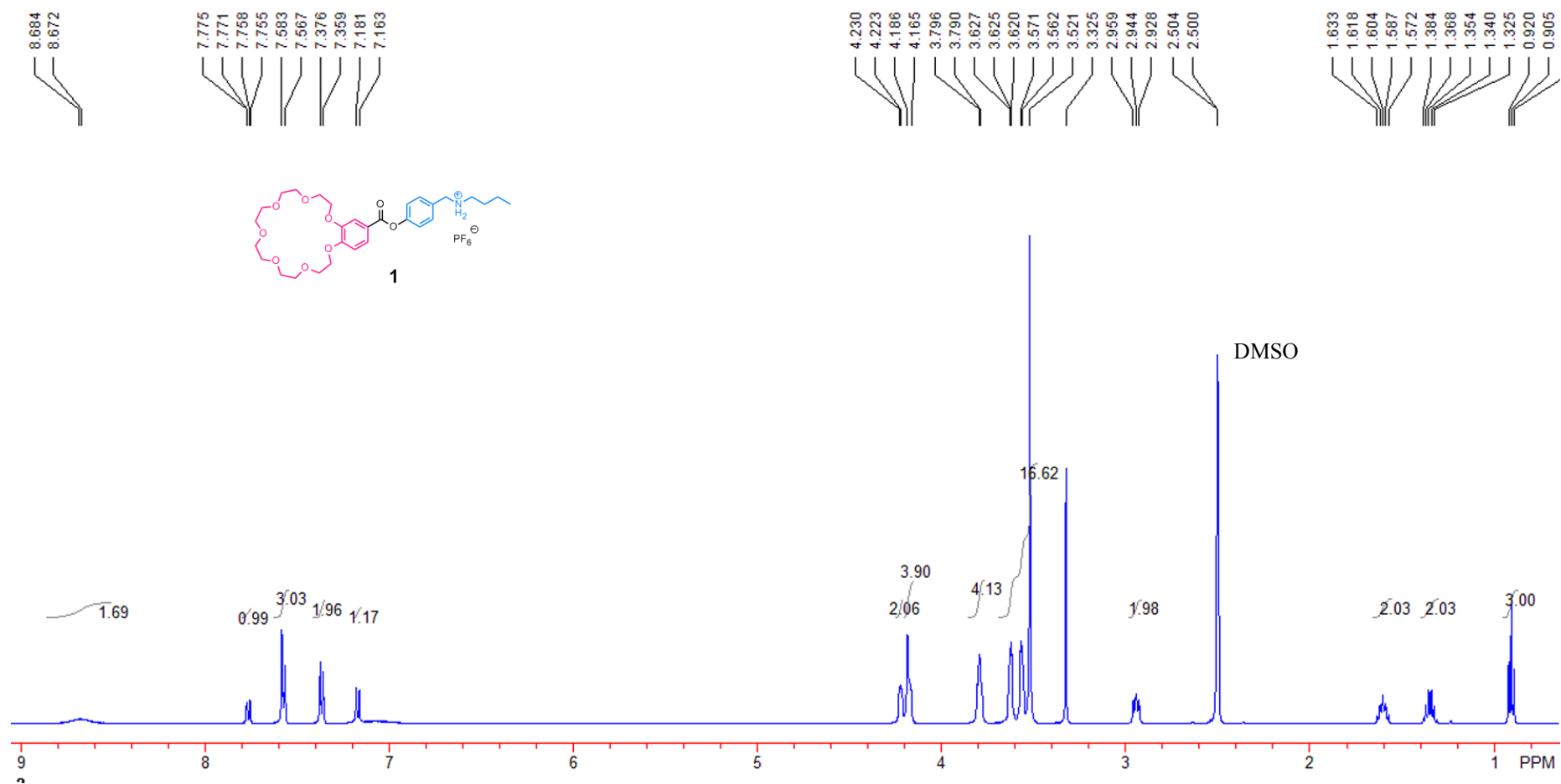


Figure S5. ¹H NMR spectrum (500 MHz, DMSO-*d*₆, room temperature) of **1**.

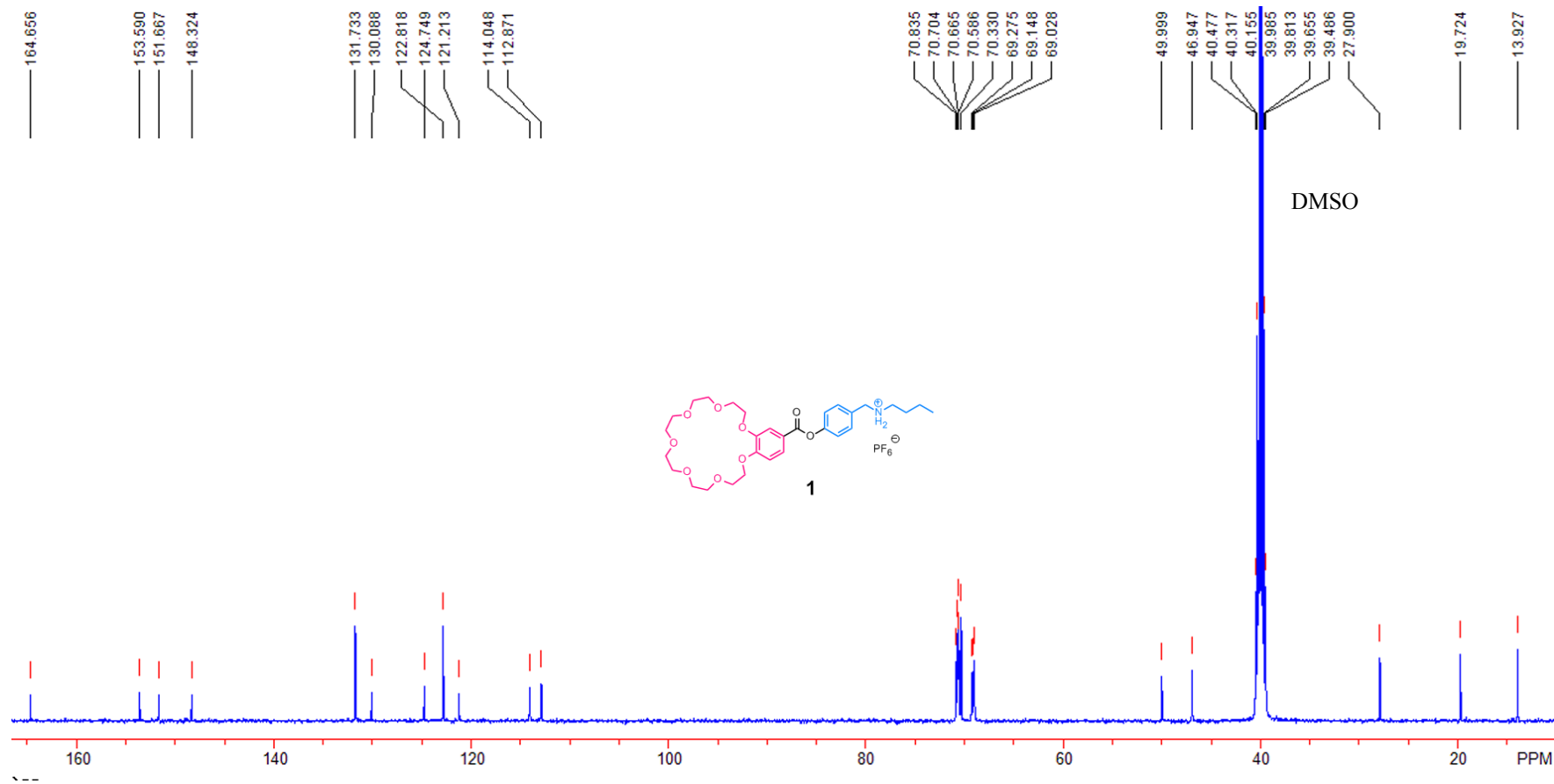


Figure S6. ^{13}C NMR spectrum (125 MHz, $\text{DMSO}-d_6$, room temperature) of **1**.

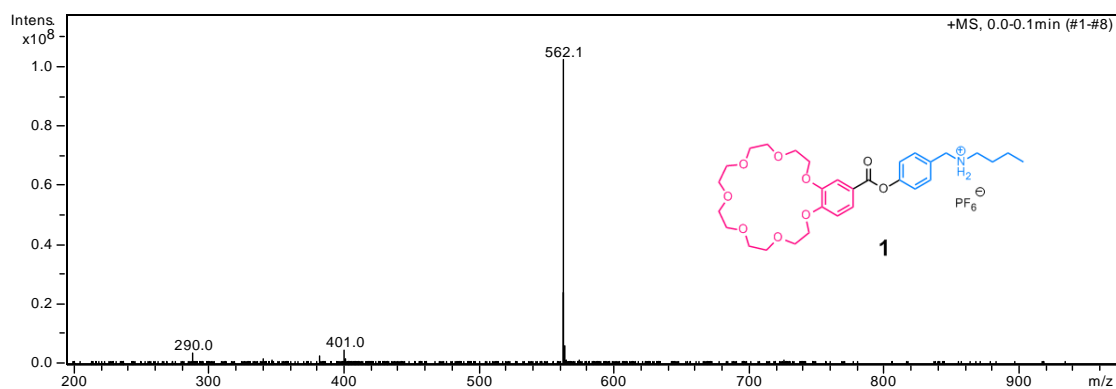


Figure S7. Electrospray ionization mass spectrum of **1**. Assignment of the main peak: m/z 562.1 $[\text{M} - \text{PF}_6]^+$ (100%).

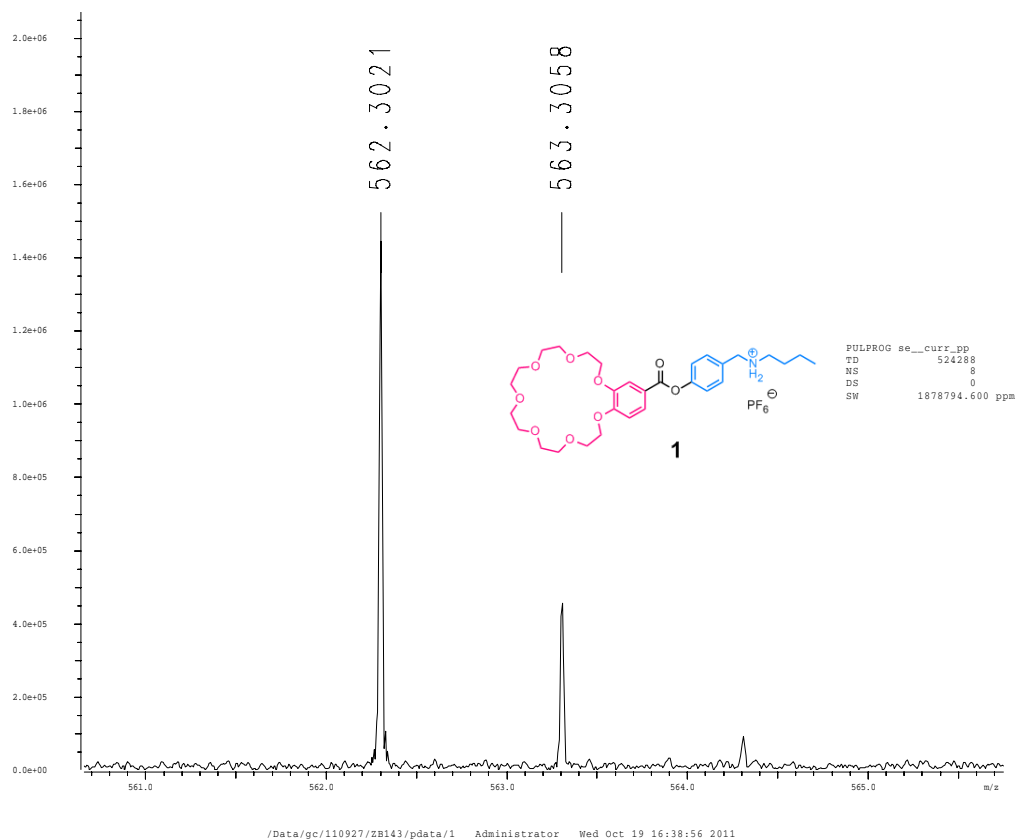


Figure S8. High-resolution ESI-MS spectra of **1**.

4. Comparison of the structures of a [2]rotaxane^{S1} and the [c2]daisy chain in the solid state

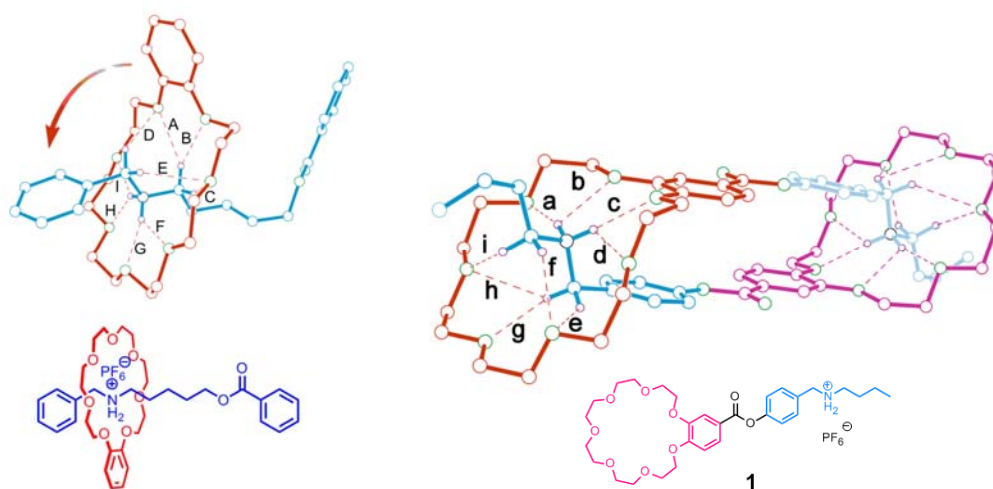


Figure S9. Crystal structure of the [2]rotaxane^{S1} (left) and the [c2]daisy chain **1**₂ (right). A PF₆ counterion, and hydrogens except the ones involved in hydrogen bonding have been omitted for clarity. **B21C7** parts are red or magenta, secondary ammonium salt parts are blue or light blue, hydrogens are purple, oxygens are green, and nitrogens are black. Hydrogen-bond parameters: H···O distances (Å), C(N)-H···O angles (deg) **A**, 2.48, 152; **B**, 2.48, 122; **C**, 2.43, 150; **D**, 2.56, 144; **E**, 2.72, 144; **F**, 2.50, 129; **G**, 2.04, 154; **H**, 2.11, 140; **I**, 2.33, 139.^{S1} From these two crystal structures, the benzene ring of B21C7 (left) flipped over to participate in face-to-face π -stacking interactions in order to stabilize the dimer structure (right). Both threaded structures are stabilized by [N⁺-H···O] and [C-H···O] hydrogen bonds. All oxygen atoms of the polyether rings of B21C7 and the ammonium and closest methylene hydrogens participate in the stabilization of the threaded structures.

5. MALDI-TOF spectrum of **1**

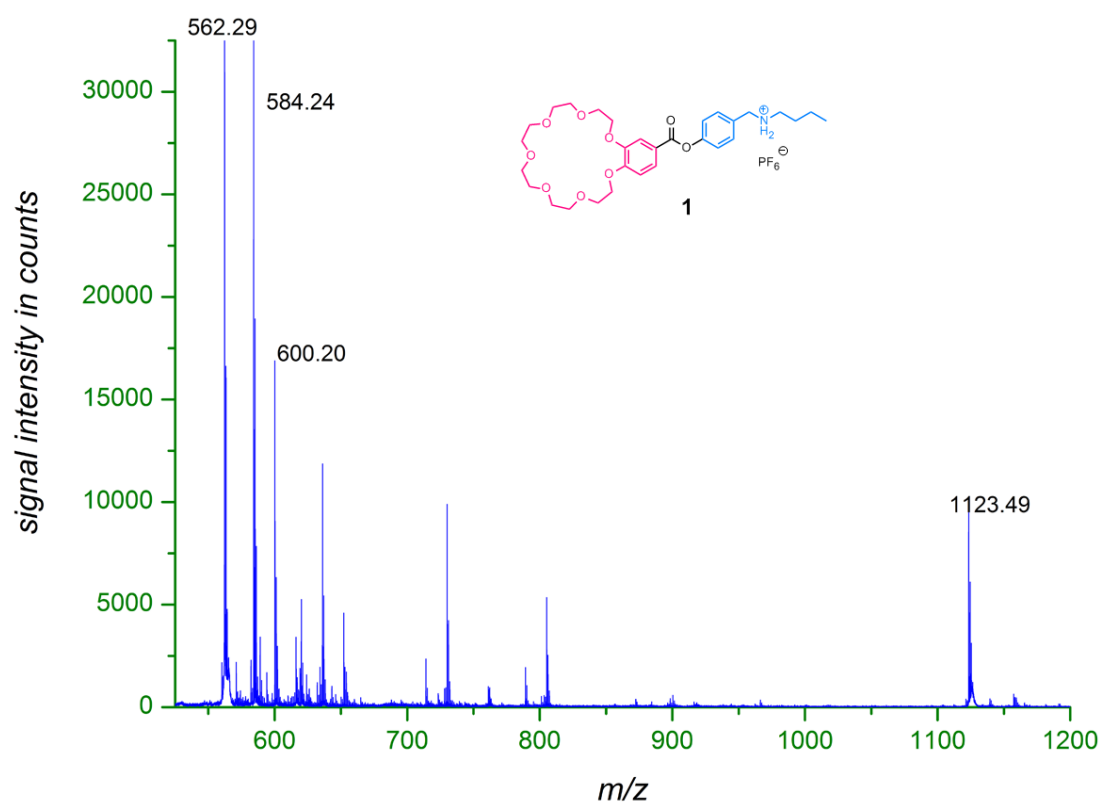


Figure S10. MALDI-TOF mass spectrum of **1**. The spectrum was measured in the positive-ion mode using α -cyano-4-hydroxycinnamic acid (CHCA) as the matrix and acetonitrile as the solvent. The spectrum revealed the existence of the dimer structure of **1**, m/z 1123.49 (25%), corresponding to $[\mathbf{1}_2 - \text{HPF}_6 - \text{PF}_6]^+$. The other main peaks at 562.29 (100%), 584.24 (98%) and 600.20 (57%), corresponding to $[\mathbf{1} - \text{PF}_6]^+$, $[\mathbf{1} - \text{HPF}_6 + \text{Na}]^+$ and $[\mathbf{1} - \text{HPF}_6 + \text{K}]^+$, respectively.

6. Partial proton NMR spectra of **1**, B21C7 and a model secondary ammonium hexafluorophosphate salt

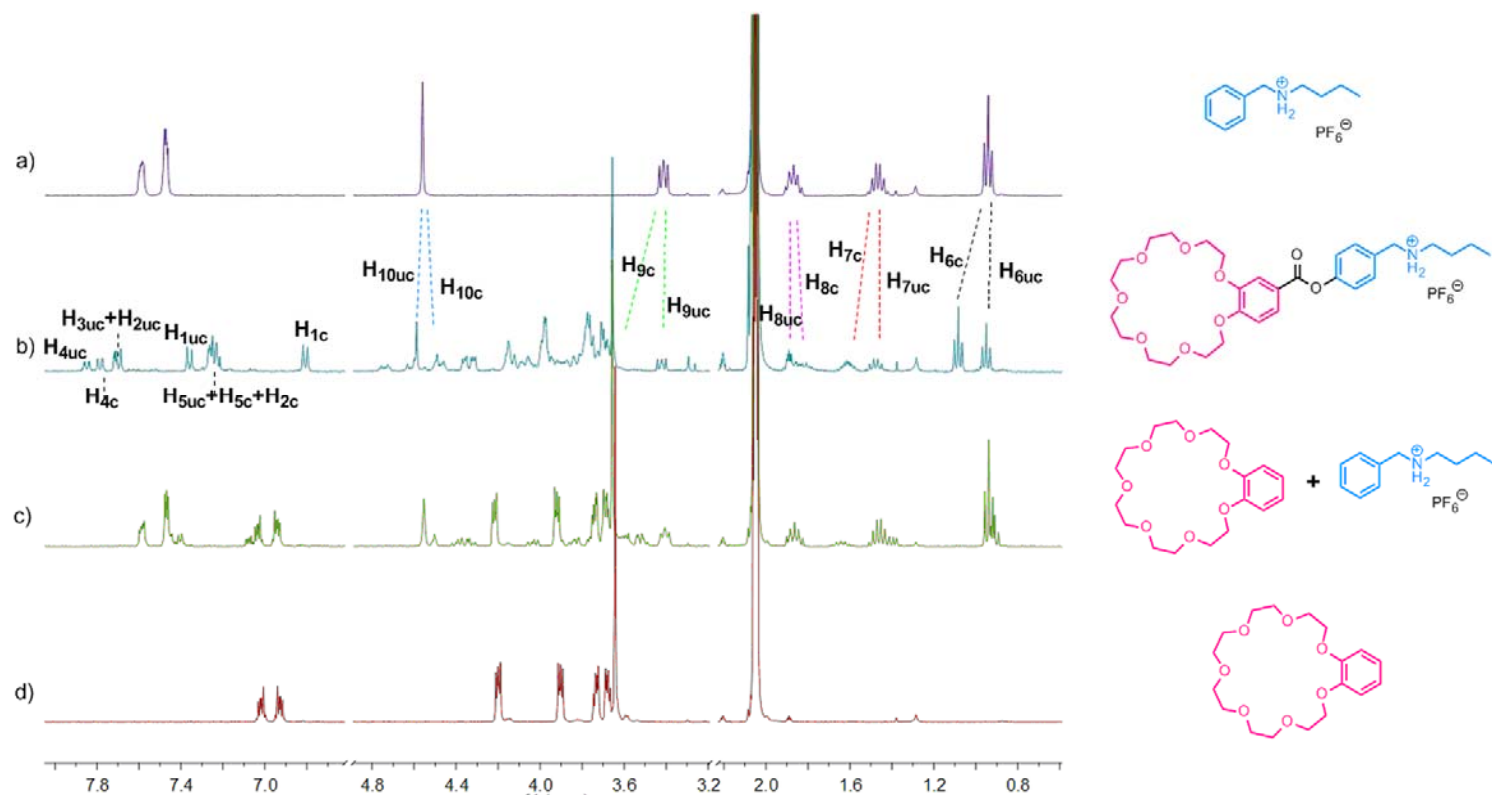


Figure S11. Partial proton NMR spectra (400 MHz, acetone- d_6 , room temperature) of (a) model secondary ammonium hexafluorophosphate salt (8.00 mM), (b) monomer **1** (8.00 mM), (c) an equimolar mixture of benzo-21-crown-7 and model secondary ammonium hexafluorophosphate salt (8.00 mM), and (d) benzo-21-crown-7 (8.00 mM). “c” and “uc” denote complexed and uncomplexed species, respectively.

7. Partial ^1H - ^1H COSY NMR spectrum of **1**

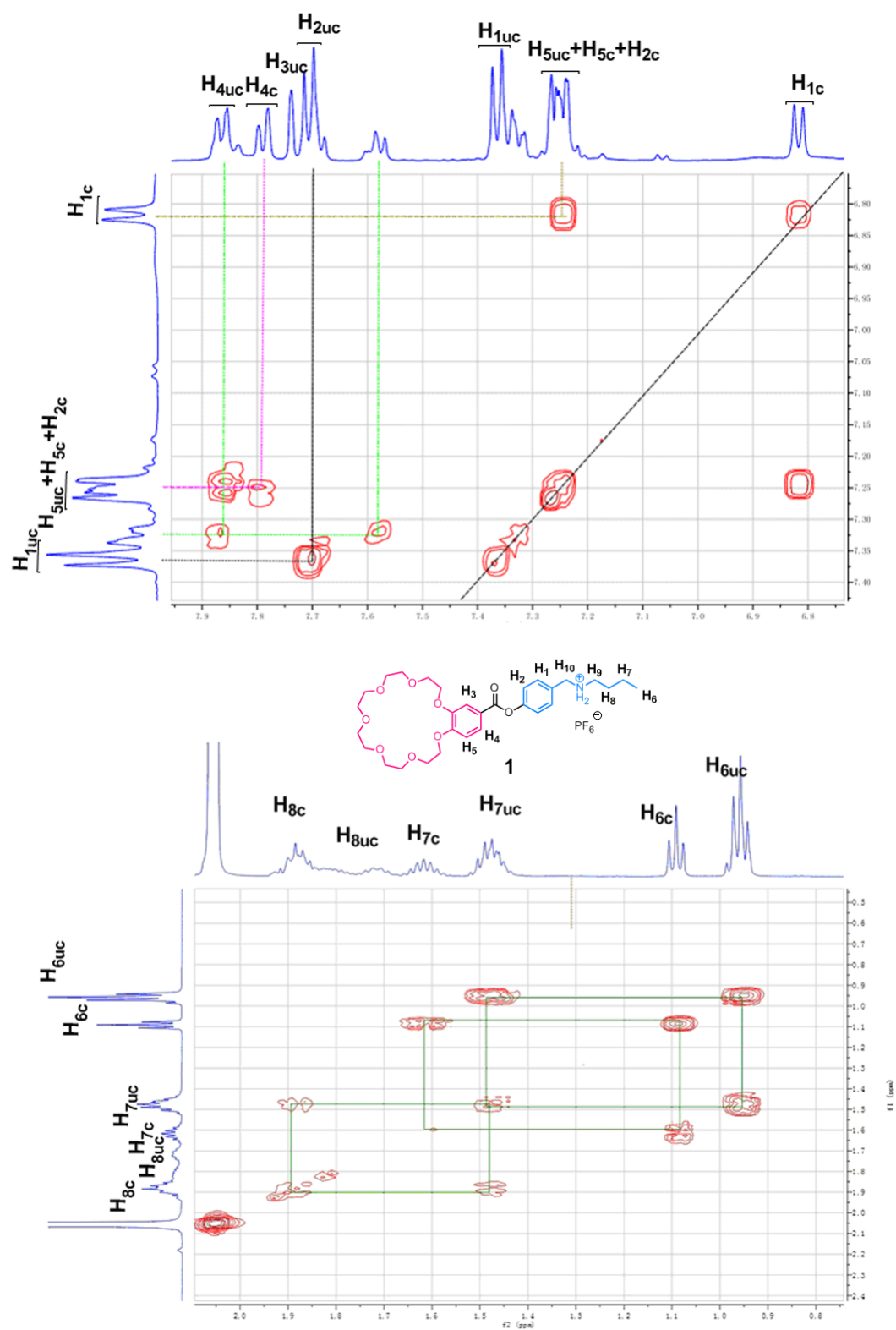


Figure S12. Partial ^1H - ^1H COSY NMR (500 MHz, acetone- d_6 , room temperature) spectrum of **1** (40.0 mM).

8. Partial NOSEY NMR spectrum of **1**

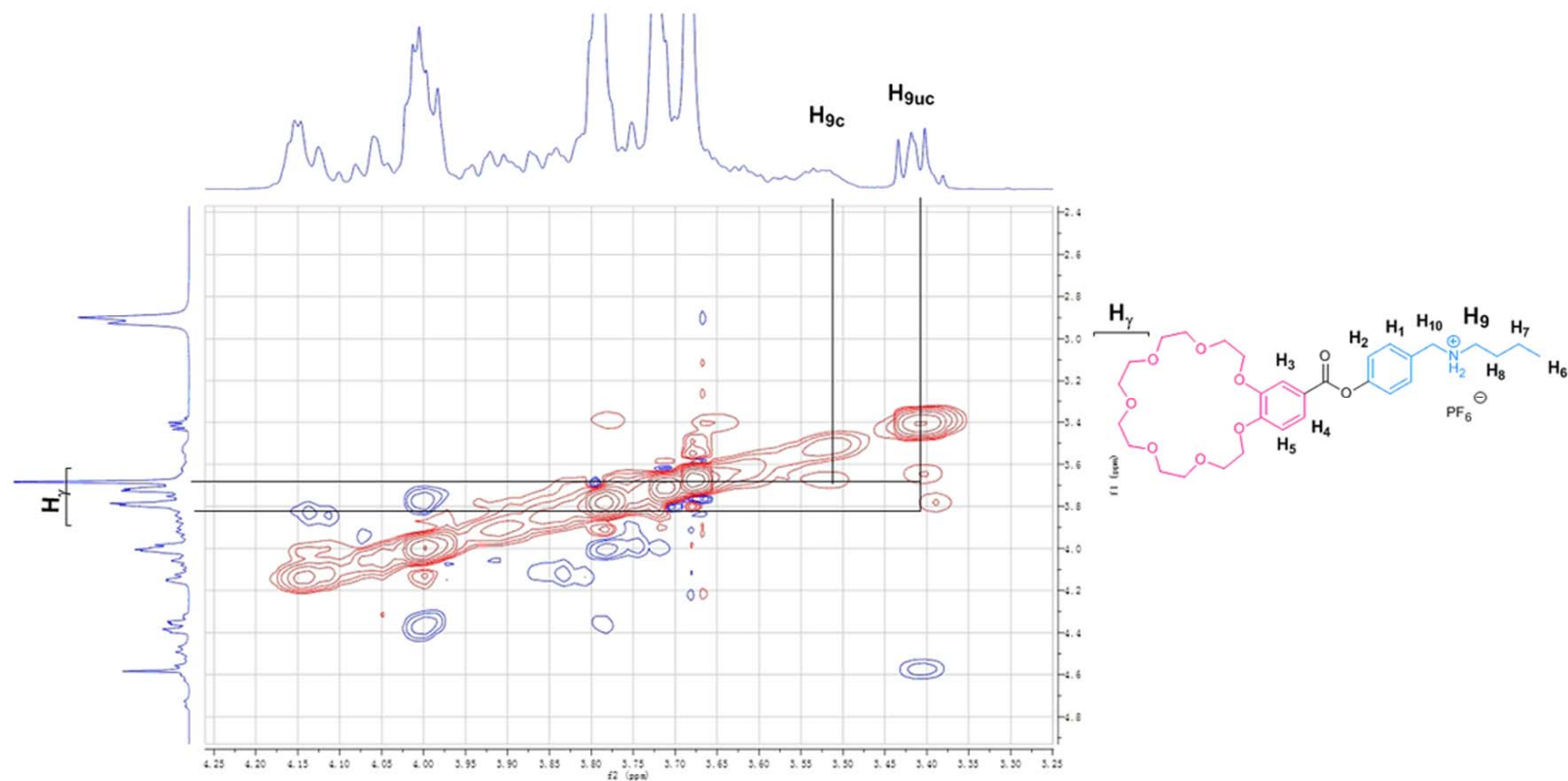


Figure S13. Partial NOESY NMR (500 MHz, acetone- d_6 , room temperature) spectrum of **1** (40.0 mM). Strong correlations were observed between the protons adjacent to secondary ammonium H_9 and the protons of the polyether macrocyclic ring, suggesting that secondary ammonium salt moieties NH_2^+ is located in the center of the macrocyclic ring.

9. Partial proton NMR spectra of the complexation of **1** controlled by pH value

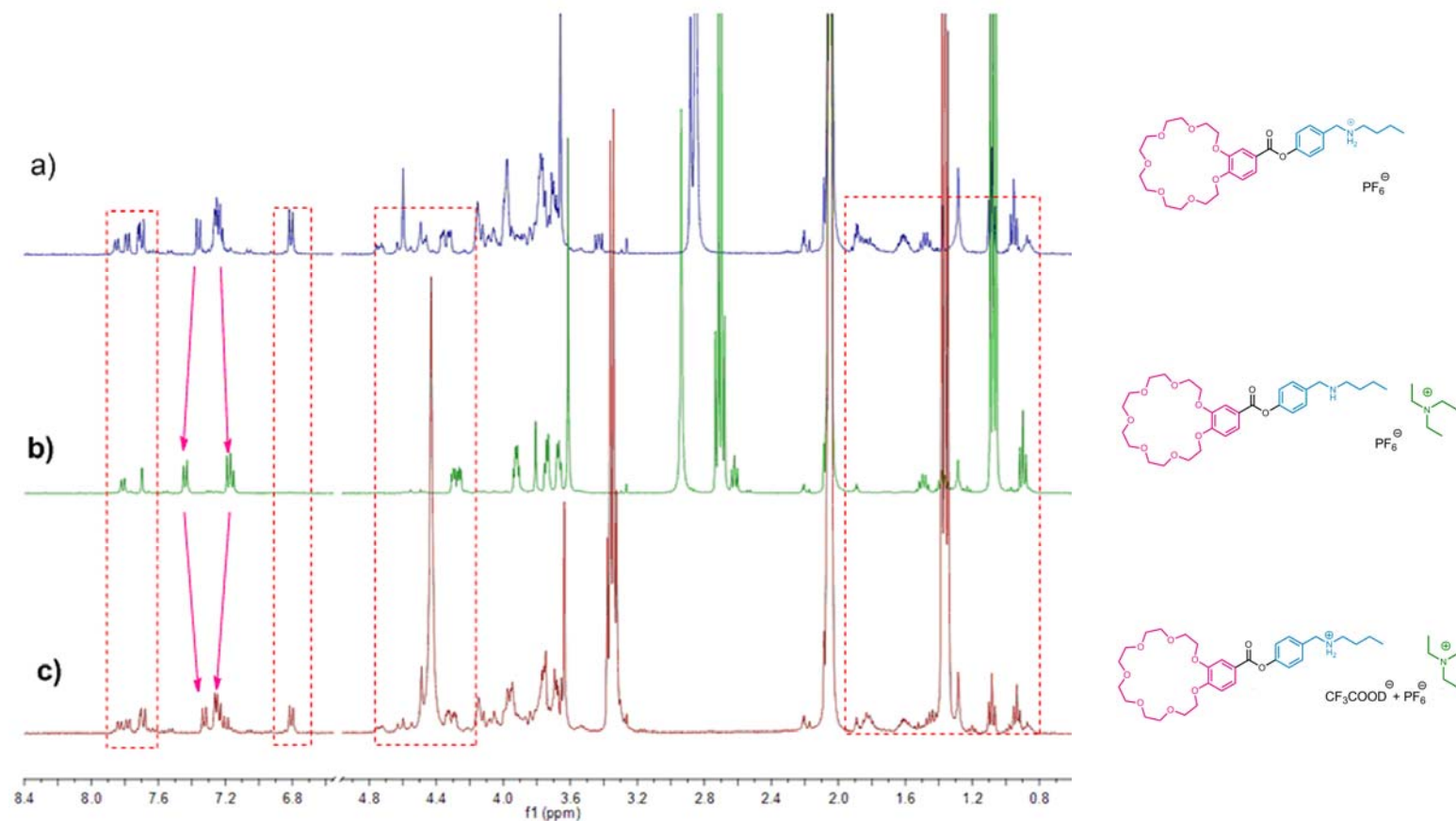


Figure S14. Partial ^1H NMR spectra (400 MHz, acetone- d_6 , room temperature) of (a) 8.00 mM compound **1**, (b) 8.00 mM compound **1** and 24.0 mM Et_3N , and (c) 8.00 mM compound **1**, 24.0 mM Et_3N and 32.0 mM CF_3COOD .

10. Partial proton NMR spectra of the complexation of **1** controlled by K^+

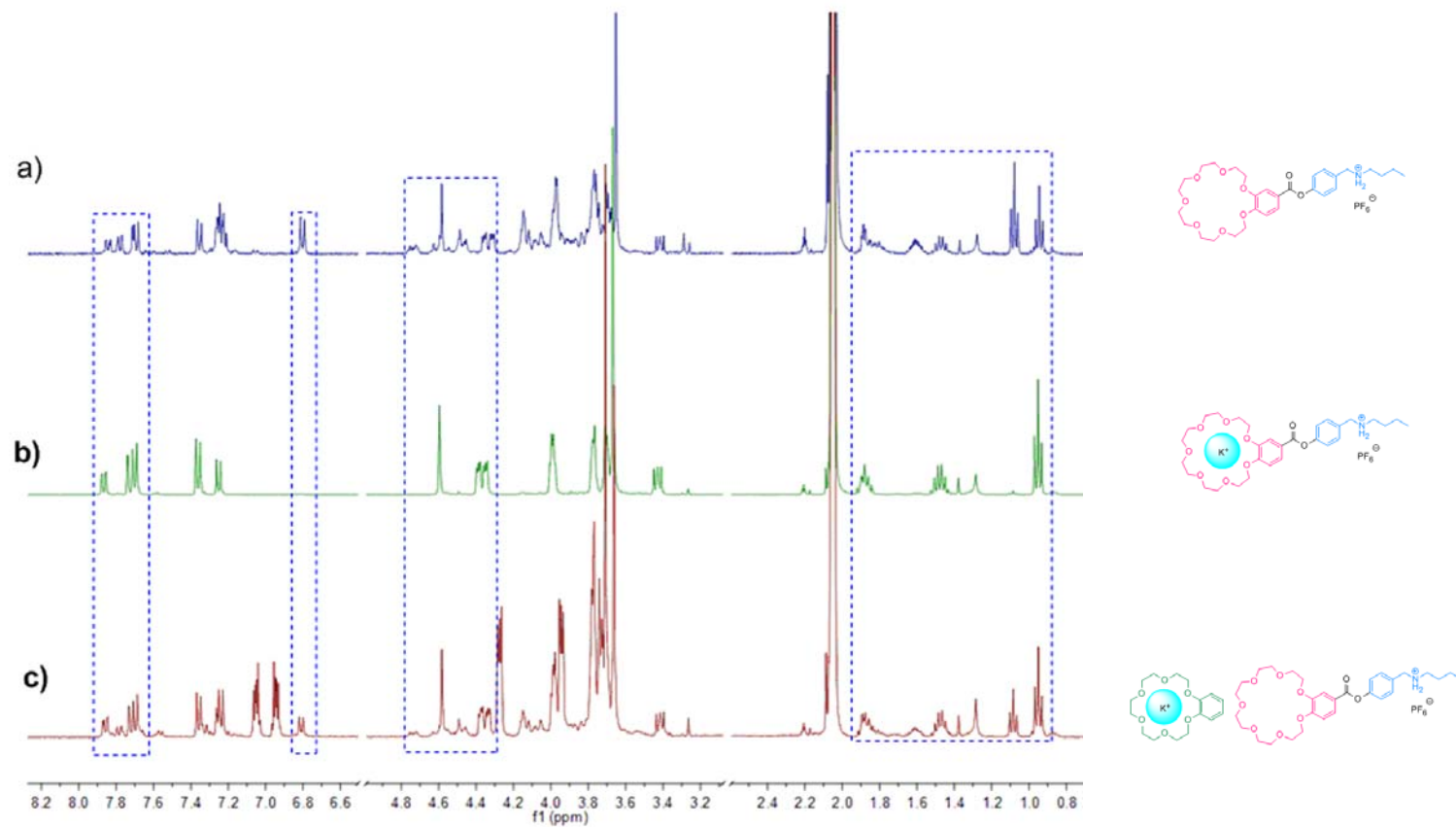
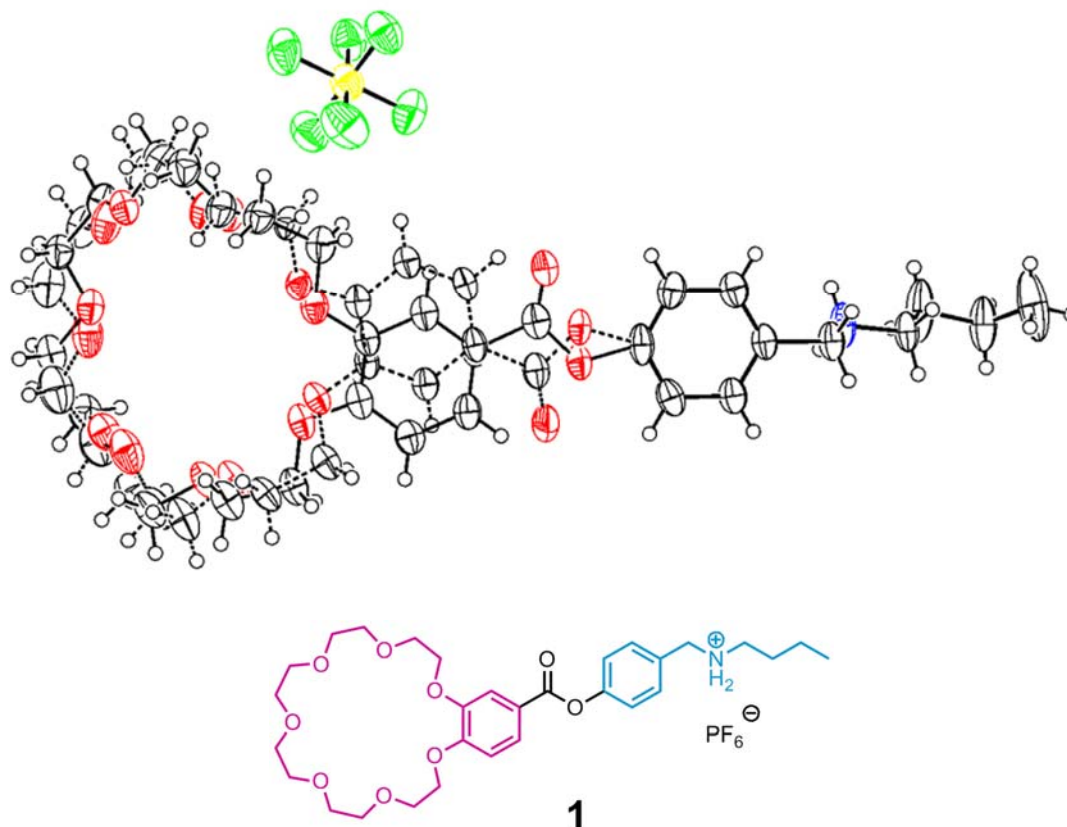


Figure S15. Partial ^1H NMR spectra (400 MHz, acetone- d_6 , room temperature) of (a) 8.00 mM compound **1**, (b) 8.00 mM compound **1** and 8.00 mM KPF_6 , and (c) 8.00 mM compound **1**, 8.00 mM KPF_6 and 8.00 mM benzo-18-crown-6.

11. X-ray analysis data of **1**



Crystallographic data: block, colorless, $C_{30}H_{44}NO_9F_6P$, FW 707.63, triclinic, space group $P\bar{1}$, $a = 7.9713(4)$, $b = 11.8560(8)$, $c = 19.9106(13)$ Å, $\alpha = 89.124(5)^\circ$, $\beta = 87.531(4)^\circ$, $\gamma = 86.362(5)^\circ$, $V = 1876.0(2)$ Å³, $Z = 2$, $D_c = 1.253$ g cm⁻³, $T = 120(2)$ K, $\mu = 1.333$ mm⁻¹, 6585 measured reflections, 4558 independent reflections, 654 parameters, 2905 restraints, $F(000) = 744$, $R_1 = 0.0738$, $wR_2 = 0.1110$ (all data), $R_1 = 0.0528$, $wR_2 = 0.1035$ [$I > 2\sigma(I)$], max. residual density 0.499 e•Å⁻³, and goodness-of-fit (F^2) = 1.018.

References:

- S1. Zhang, C.; Li, S.; Zhang, J.; Zhu, K.; Li, N.; Huang, F. *Org. Lett.* **2007**, *9*, 5553–5556.
S2. Dong, S.; Luo, Y.; Yan, X.; Zheng, B.; Ding, X.; Yu, Y.; Ma, Z.; Zhao, Q.; Huang, F. *Angew. Chem., Int. Ed.* **2011**, *50*, 1905–1909.