Photodriven [2]Rotaxane - [2]Catenane Interconversion

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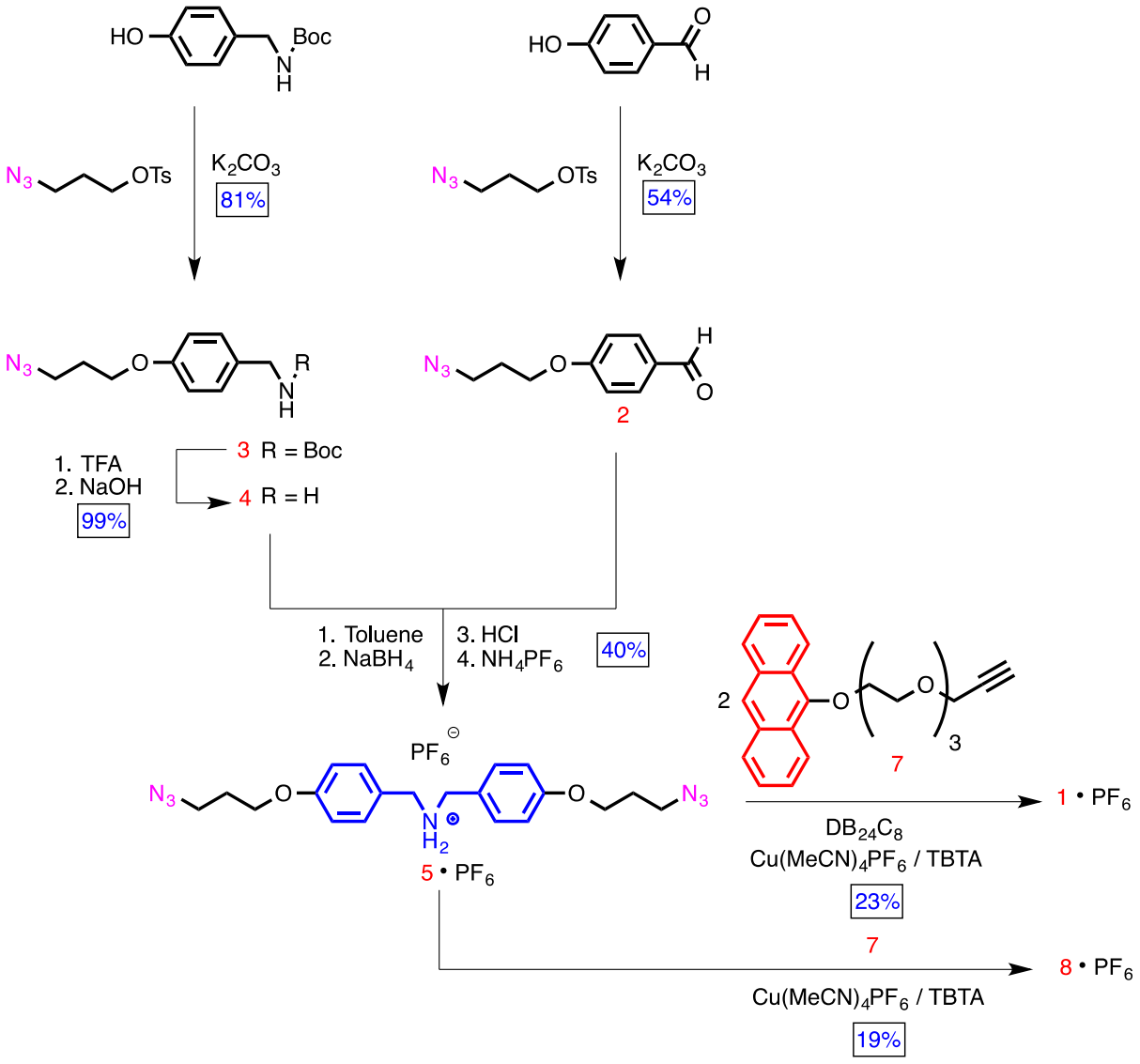
1. Materials and Methods

^{1}H NMR and ^{13}C NMR spectra were recorded at 600, 300 and 200 MHz, on Bruker Avance 300 and 200 spectrometers and a Avance III 600 spectrometers. Proton chemical shifts (δ) are reported in ppm downfield from tetramethylsilane (TMS). Reagent grade tetrahydrofuran (THF) was distilled under argon over sodium benzophenone ketyl. CH_2Cl_2 was distilled over CaH_2 under argon. All other reagents were purchased from commercial suppliers and used without further purification. Flash column chromatography was carried out using silica gel (230-400 mesh). Thin layer chromatography (TLC) was carried out on plates coated with silica gel 40 F254 purchased from Aldrich. All reactions were conducted under dry oxygen free atmosphere using oven-dried glassware unless otherwise stated. *N*-Boc-4-hydroxybenzylamine was prepared using literature procedures.[S1] Mass spectrometry was performed by the CESAMO analytical centre (University of Bordeaux, France) on a QStar Elite mass spectrometer (Applied Biosystems). The instrument is equipped with an ESI source and spectra were recorded in the positive mode. The electrospray needle was maintained at 5000 V and operated at room temperature. Samples were introduced by injection through a 20 μL sample loop into a 4500 μL/min flow of methanol from the LC pump. Electronic absorption spectra were measured on a Varian Cary 5000 UV-vis-NIR spectrophotometer. .Steady-state emission spectra were recorded on a Horbiba Jobin-Yvon Fluorolog-3 spectrofluorometer equipped with a R928P PMT and were corrected.

Fluorescence and Photodimerization Quantum Yield. The fluorescence and reaction quantum yield were determined in quartz cells using acetonitrile solution, which were degassed by multiple freeze-pump-thaw cycles and were blowtorch sealed. The luminescence quantum yield [S2] (Φ) was calculated by using the equation $\Phi = \Phi_r(I/I_r)(A_r/A)(\eta^2/\eta_r^2)$ in which

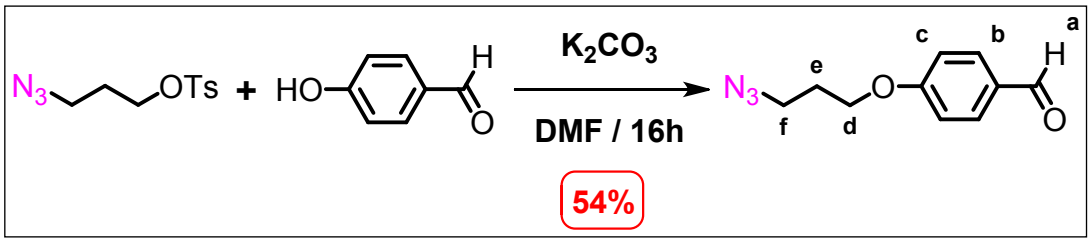
Φ_r refers to the quantum yield reference, I is the integrated emission intensity, A is the absorbance at the excitation wavelength and η is the refractive index of the solvent. An optically dilute solution of quinine sulphate in 1N sulphuric acid was used as the standard, Φ_f = 0.54. Photoreaction quantum yields were determined upon excitation at 365 nm using the couple potassium ferrioxalate-phenanthroline as a chemical actinometer[S3] on an optical bench equipped with a 150 W Hg-Xe lamp and a monochromator. Samples (100 μM) were stirred during the irradiation and the amount of converted material was determined at 5 min intervals by UV-vis following the disappearance of the ^1L_a absorption band of the anthracene moieties at 370 nm.

2. Synthesis and Characterization of the Compounds



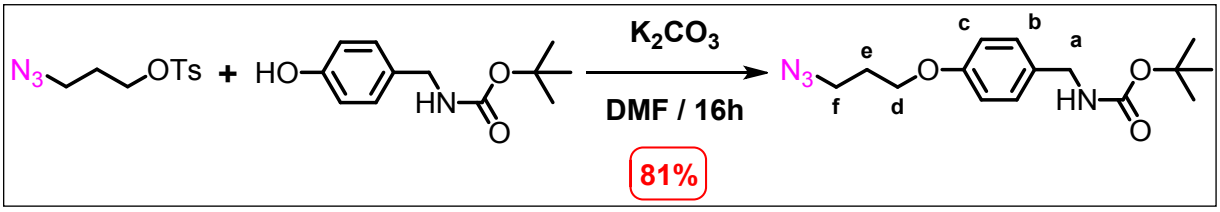
Scheme S1: Synthesis of [2]rotaxane **1•PF$_6$** from commercially available materials.

Synthesis of 4-(3-azido-propoxy)benzaldehyde (2)



To a solution of 4-hydroxybenzaldehyde (500 mg, 4.09 mmol, 1 equiv.) and 3-azidopropyl tosylate[S4] (1.14 g, 4.47 mmol, 1.1 equiv.) in DMF (10 mL) was added K_2CO_3 (1.13 g, 8.18 mmol, 2 equiv.). The reaction mixture was stirred at 80 °C overnight. The mixture was then diluted with H_2O (20 mL) and extracted with CH_2Cl_2 (3 × 30 mL). The organic layer was dried ($MgSO_4$), and the solvent was removed. The crude product was purified by column chromatography (SiO_2, Cyclohexane/AcOEt, 90:10, v/v), affording **2** as a white oily solid in 54% yield (455 mg). ^{1}H NMR (300 MHz, $CDCl_3$, 25ºC): δ (ppm) = 9.89 (s, 1H, H_a), 7.84 (d, J = 8.8 Hz, 2H, H_b), 7.00 (d, J = 8.7 Hz, 2H, H_c), 4.14 (t, J = 6.5 Hz, 2H, H_d), 3.54 (t, J = 6.5 Hz, 2H, H_f), 2.09 (p, J = 6.5 Hz, 2H, H_e). ^{13}C NMR (75 MHz, $CDCl_3$, 25ºC): δ (ppm) = 190.8, 163.7, 132.1, 130.2, 114.8, 65.0, 48.1, 28.7. HRMS (EI) calcd for $C_{10}H_{11}N_3O_2$ m/z = 205.0851 $[M]^+$, found m/z = 205.0844 $[M]^+$. IR (KBr): 2832 (CHO), 2743 (CHO), 2098 (N_3), 1689 cm^{-1} (C=O).

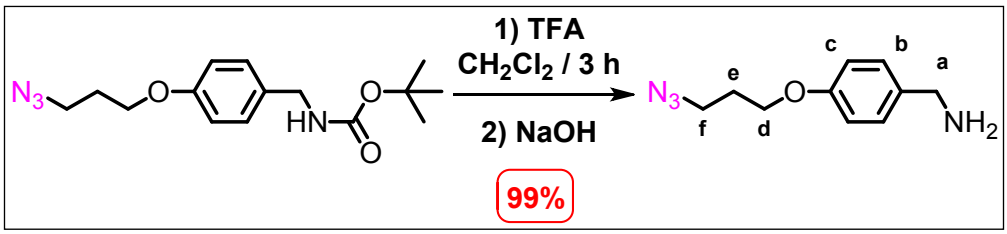
Synthesis of *tert*-Butyl-4-(3-azido-propoxy)benzyl carbamate (3)



To a solution of *tert*-Butyl(4-hydroxybenzyl)carbamate[S1] (500 mg, 2.24 mmol, 1 equiv.) and 3-azidopropyl tosylate[S1] (634 mg, 2.48 mmol, 1.1 equiv.) in DMF (10 mL) was added K_2CO_3 (660 mg, 4.78 mmol, 2.1 equiv.). The reaction mixture was stirred at 80 °C overnight. The mixture was then diluted with H_2O (20 mL) and extracted with CH_2Cl_2 (3 × 30 mL). The organic layer was dried ($MgSO_4$), and the solvent was removed. The crude product was purified by column chromatography (SiO_2, Cyclohexane/AcOEt, 80:20, v/v), affording **3** as a

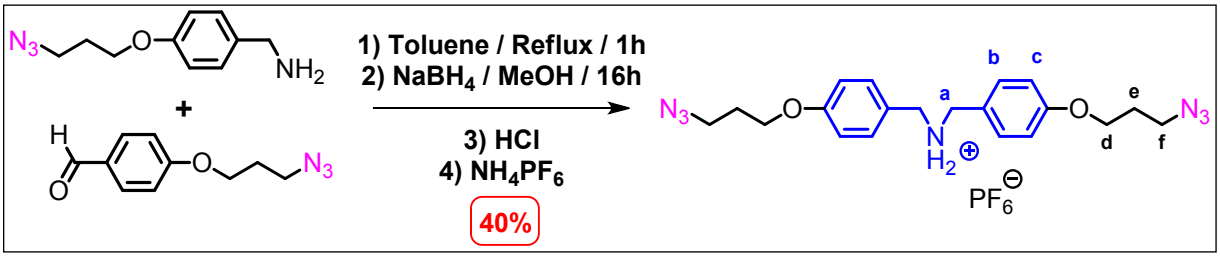
white oil in 81% yield (556 mg). ^{1}H NMR (300 MHz, $CDCl_3$, 25ºC): δ (ppm) = 7.20 (d, *J* = 8.5 Hz, 2H, H_b), 6.85 (d, *J* = 8.5 Hz, 2H, H_c), 4.24 (s, 2H, H_a), 4.03 (t, *J* = 6.0 Hz, 2H, H_d), 3.51 (t, *J* = 6.0 Hz, 2H, H_f), 2.04 (p, *J* = 6.0 Hz, 2H, H_e), 1.46 (s, 9H, ^{t}Bu). ^{13}C NMR (75 MHz, $CDCl_3$, 25ºC): δ (ppm) = 158.1, 155.9, 131.5, 129.0, 114.7, 80.1, 64.7, 48.4, 44.3, 28.9, 28.5. HRMS (ESI) calcd for $C_{15}H_{22}N_4O_3Na$ *m/z* = 329.1576 $[M+Na]^+$, found *m/z* = 329.1584 $[M+Na]^+$. IR (KBr): 2098 (N_3), 1699 cm^{-1} (C=O).

Synthesis of 4-(3-azido-propoxy)benzylamine (4)



To a solution of *tert*-Butyl-4-(3-azido-propoxy)benzyl carbamate (**3**) (270 mg, 0.88 mmol, 1 equiv.) in CH_2Cl_2 (25 mL) was added trifluoroacetic acid (1.8 mL). The reaction mixture was stirred at 23°C for 3 hours. The mixture was then neutralized with a 3 M solution of NaOH (30 mL) and extracted with CH_2Cl_2 (3 × 30 mL). The organic layer was dried ($MgSO_4$), and the solvent was removed. Compound **4** was isolated as a white solid in quantitative yield (180 mg) and was used without further purification. ^{1}H NMR (300 MHz, $CDCl_3$, 25ºC): δ (ppm) = 7.23 (d, *J* = 8.5 Hz, 2H, H_b), 6.86 (d, *J* = 8.5 Hz, 2H, H_c), 4.04 (t, *J* = 6.0 Hz, 2H, H_d), 3.80 (s, 2H, H_a), 3.51 (t, *J* = 6.0 Hz, 2H, H_f), 2.04 (p, *J* = 6.0 Hz, 2H, H_e). ^{13}C NMR (75 MHz, $CDCl_3$, 25ºC): δ (ppm) = 157.8, 135.6, 128.5, 114.7, 64.7, 48.4, 45.8, 28.9. HRMS (EI) calcd for $C_{10}H_{14}N_4O$ *m/z* = 206.1167 $[M]^+$, found *m/z* = 206.1158 $[M]^+$. IR (KBr): 2098 cm^{-1} (N_3).

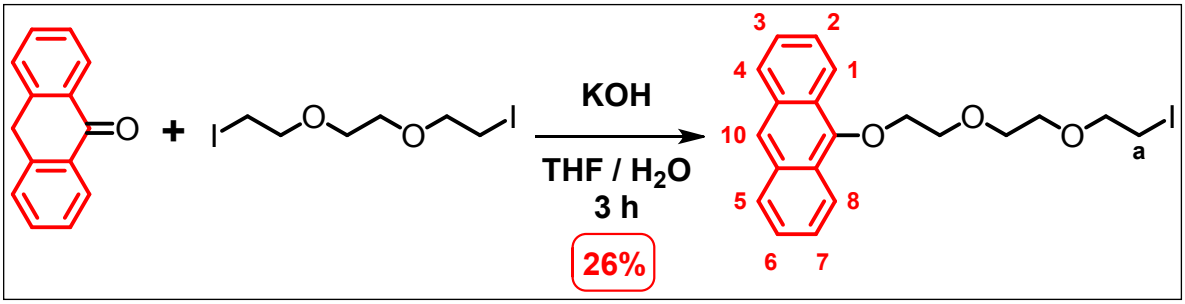
Synthesis of the dumbbell precursor (5•PF_6)



A solution of 4-(3-azido-propoxy)benzaldehyde (**2**) (169 mg, 0.82 mmol, 1 equiv.) and 4-(3-azido-propoxy)benzylamine (**4**) (170 mg, 0.82 mmol, 1 equiv.) was reflux in toluene (30 mL)

for 2 hours. The mixture was allowed to 23°C and the solvent was removed under vacuum. The crude Schiff base was then solubilized in MeOH (10 mL) and $NaBH_4$ (5 × 54 mg) was added to the mixture during 1.5 h. The reaction mixture was stirred at 23°C for 18 h. The mixture was then neutralized with a 3 M solution of HCl (30 mL), basified with a 3M solution of NaOH to pH 12 and extracted with CH_2Cl_2 (3 × 30 mL). The organic layer was dried ($MgSO_4$), and the solvent was removed. The residue was then dissolved in concentrated HCl (3 mL). After evaporation of the solvent under vacuum, the solid was dissolved in MeOH (10 mL) and saturated NH_4PF_6 solution in water (3 mL) was added to the mixture. After evaporation of MeOH, the precipitate was then filtrated to afford **5**•PF_6 as a white solid in 40% yield (180 mg). ^{1}H NMR (300 MHz, CD_3CN, 25ºC): δ (ppm) = 7.39 (d, J = 8.5 Hz, 2H, H_c), 6.98 (d, J = 8.5 Hz, 2H, H_b), 4.15 (s, 2H, H_a), 4.08 (t, J = 6.5 Hz, 2H, H_d), 3.50 (t, J = 6.5 Hz, 2H, H_f), 2.02 (p, J = 6.5 Hz, 2H, H_e). ^{13}C NMR (75 MHz, CD_3CN, 25ºC): δ (ppm) = 160.8, 132.8, 123.4, 115.8, 65.9, 51.7, 49.0, 29.3. HRMS (ESI) calcd for $C_{20}H_{26}N_7O_2$ m/z = 396.2142 $[M–PF_6]^+$, found m/z = 396.2148 $[M–PF_6]^+$. IR (KBr): 2099 cm^{-1} (N_3).

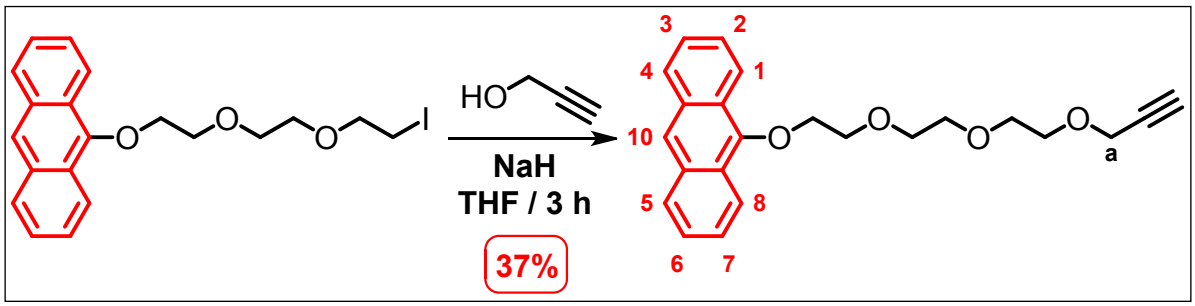
Synthesis of 9-(2-[2-(2-iodo-ethoxy)-ethoxy]ethoxy)anthracene (6)



A solution of 1-iodo-2-[2-(2-iodo-ethoxy)-ethoxy]ethane[S5] (20 g, 54 mmol) in THF/H_2O (2:1, v/v, 300 mL) was degassed by bubbling nitrogen for 10 min. Then KOH (6.2 g, 111 mmol) was added and nitrogen was bubbled for 10 more minutes. After addition of anthrone (3.1 g, 16 mmol), the mixture was refluxed for 3 days. After evaporation of THF, the crude material was extracted from CH_2Cl_2 (100 mL), washed with H_2O (50 mL). The organic layer was dried ($MgSO_4$), and the solvent was removed. The crude product was purified by column chromatography (SiO_2, Cyclohexane/AcOEt, 90:10, v/v), affording **7** as a white solid in 42% yield (2.96 g). ^{1}H NMR (300 MHz, $CDCl_3$, 25ºC): δ (ppm) = 8.42 – 8.36 (m, 2H, $H_{4/5}$), 8.23 (s, 1H, H_{10}), 8.04 – 7.97 (m, 2H, $H_{1/8}$), 7.53 – 7.42 (m, 4H, $H_{2/7\text{-}3/6}$), 4.45 – 4.37 (m, 2H), 4.06 – 3.98 (m, 2H), 3.90 – 3.74 (m, 6H), 3.30 (t, J = 7.0 Hz, 2H, H_a). ^{13}C NMR (75 MHz, $CDCl_3$)

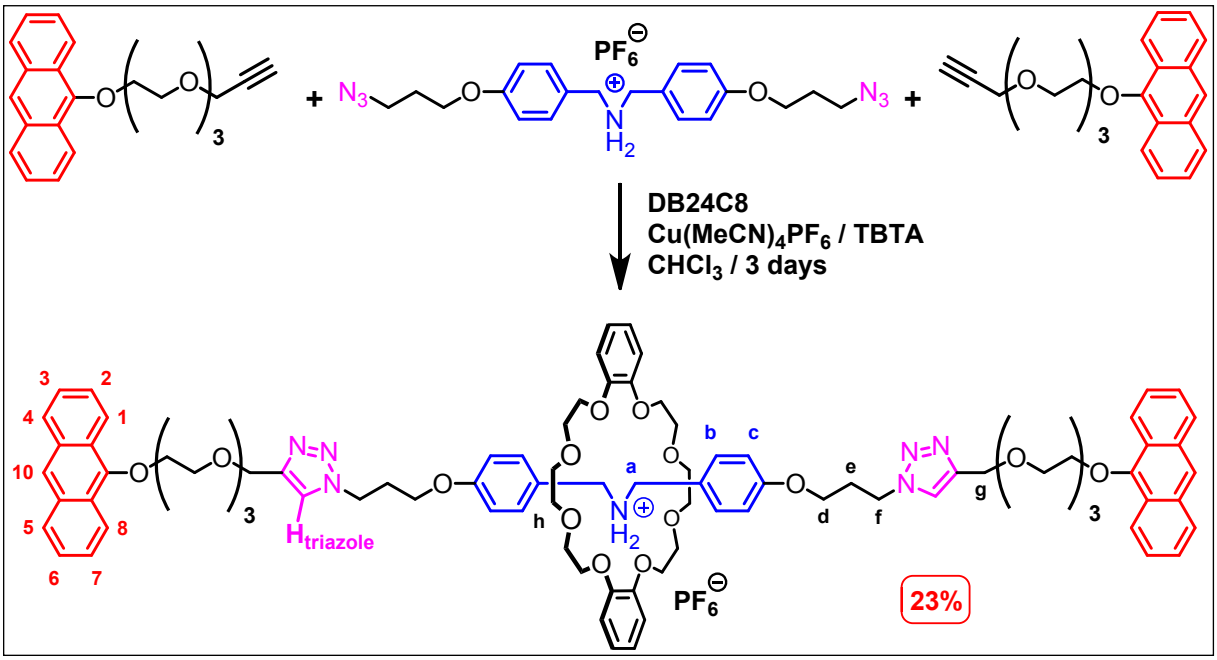
: δ (ppm) = 150.8, 132.4, 128.3, 125.4, 125.1, 124.7, 122.5, 122.3, 74.8, 72.1, 71.0, 70.7, 70.4, 2.9. HRMS (FD) calcd for $C_{20}H_{21}IO_3$ m/z = 436.0535 $[M]^+$, found m/z = 436.0515 $[M]^+$.

Synthesis of the stopper precursor (7)



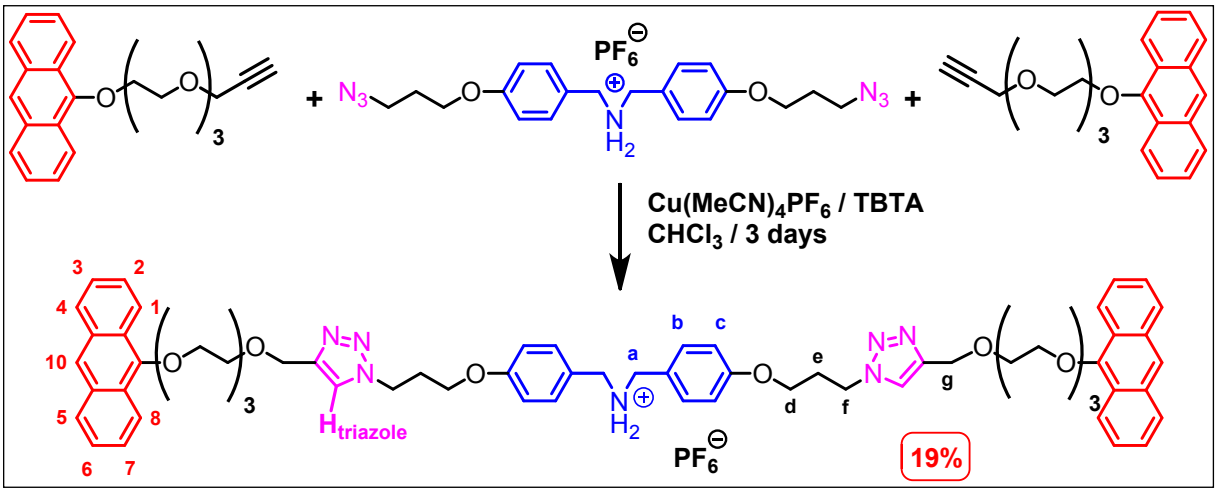
To a solution of propargyl alcohol (0.15 mL, 2.52 mmol, 1.1 equiv.) in THF (10 mL) was added NaH 95% (66 mg, 2.75 mmol, 1.2 equiv.). After 15 min at 23 °C, 9-(2-[2-(2-iodo-ethoxy)-ethoxy]ethoxy)anthracene (**7**) (1 g, 2.25 mmol, 1 equiv.) was added to the mixture and the reaction was stirred at 23°C for 3 h. The solvent was removed and the crude product was purified by column chromatography (SiO_2, Cyclohexane/AcOEt, 90:10, v/v), affording **6** as a white solid in 37% yield (340 mg). ^{1}H NMR (300 MHz, $CDCl_3$, 25ºC): δ (ppm) = 8.42 (m, 2H, $H_{4/5}$), 8.20 (s, 1H, H_{10}), 7.97 (m, 2H, $H_{1/8}$), 7.56 – 7.39 (m, 4H, $H_{2/7\text{-}3/6}$), 4.41 – 4.31 (m, 2H, H_{glycol}), 4.23 (d, J = 2.5 Hz, 2H, H_a), 4.08 – 3.93 (m, 2H, H_{glycol}), 3.88 – 3.69 (m, 8H, H_{glycol}), 2.45 (t, J = 2.5 Hz, 1H, H_{alkyne}). ^{13}C NMR (75 MHz, $CDCl_3$) : δ (ppm) = 150.8, 132.3, 128.3, 125.5, 125.2, 125.1, 124.7, 123.1, 122.5, 122.2, 79.7, 74.7, 70.9, 70.7, 70.5, 69.1, 58.3. HRMS (ESI) calcd for $C_{23}H_{24}O_4Na$ m/z = 387.1566 $[M+Na]^+$, found m/z = 387.1550 $[M+Na]^+$. IR (KBr): 3222 (C≡C), 2111 cm^{-1} (≡C–H).

Synthesis of the [2]rotaxane (1•PF_6)



The stopper precursor (**6**) (73 mg, 0.20 mmol, 2.2 equiv.) and **DB24C8** (60 mg, 0.13 mmol, 1.4 equiv.) were added to a degassed solution of the diazide dumbbell precursor (**5**•PF_6) (50 mg, 0.09 mmol, 1 equiv.) in $CHCl_3$ (0.5 mL). The reaction mixture was stirred for 1 h at 23ºC before a catalytic amount of $Cu(MeCN)_4PF_6$ and tris[(1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl]amine (TBTA) were added. The reaction mixture was stirred for an additional 3 days at 23ºC. After evaporation of the solvents, the crude product was subjected to column chromatography (SiO_2, CH_2Cl_2/MeOH, 95:5, v/v then 90:10, v/v). The [2]rotaxane **1•PF_6** was obtained as a yellowish solid (36 mg, 23%).^{1}H NMR (600 MHz, CD_3CN, 25ºC): δ (ppm) 8.42 – 8.36 (m, 4H, $H_{4/5}$), 8.29 (s, 2H, H_{10}), 8.03 (m, 4H, $H_{1/8}$), 7.69 (s, 2H, $H_{triazole}$), 7.50 – 7.47 (m, 8H, $H_{2/7\text{-}3/6}$), 7.15 (d, J = 8.5 Hz, 4H, H_b), 6.78 – 6.71 (m, 8H, H_{24C8}), 6.52 (d, J = 8.5 Hz, 4H, H_c), 4.57 (s, 4H, H_g), 4.51 – 4.47 (m, 4H), 4.43 (t, J = 6.8 Hz, 4H), 4.33 – 4.29 (m, 4H), 3.99 – 3.94 (m, 8H), 3.90 (m, 4H), 3.74 – 3.65 (m, 20H), 3.64 (s, 8H, H), 3.51 (s, 8H, H_h), 2.02 (p, J = 6.5 Hz, 4H, H_e). ^{13}C NMR (151 MHz, CD_3CN): δ (ppm) 159.9, 151.8, 148.3, 145.6, 133.4, 131.7, 129.2, 126.7, 126.3, 125.6, 125.2, 124.3, 123.4, 123.1, 122.1, 115.1, 113.3, 75.9, 71.5, 71.5, 71.3, 71.2, 71.1, 71.0, 70.4, 68.7, 65.3, 64.8, 52.6, 47.6, 30.4. HRMS (ESI) calcd for $C_{90}H_{106}N_7O_{18}$ m/z = 1572.7588 $[M–PF_6]^+$, found m/z = 1572.7865 $[M–PF_6]^+$. UV/Vis (CH_3CN, 298 K) λ_{max} (ε) = 277 (9800), 365 nm (6700 $M^{-1}\cdot cm^{-1}$)

Synthesis of the [2]rotaxane thread (8•PF_6)



The stopper precursor (**6**) (152 mg, 0.42 mmol, 4.2 equiv.) was added to a degassed solution of the diazide (**5**•PF_6) (90 mg, 0.10 mmol, 1 equiv.) in $CHCl_3$ (1 mL). The reaction mixture was stirred for 1 h at 23ºC before a catalytic amount of $Cu(MeCN)_4PF_6$ and tris[(1-benzyl-1*H*-1,2,3-triazol-4-yl)methyl]amine (TBTA) were added. The reaction mixture was stirred for an additional 2 days at 23ºC. After evaporation of the solvents, the crude product was subjected to column chromatography (SiO_2, CH_2Cl_2/MeOH, 95:5, v/v). The product was obtained as a yellowish solid (25 mg, 19%). ^{1}H NMR (300 MHz, CD_3CN, 25ºC): δ (ppm) 8.39 – 8.33 (m, 4H, $H_{4/5}$) ; 8.28 (s, 2H, H_{10}), 8.04 – 7.99 (m, 4H, $H_{1/8}$), 7.65 (s, 2H, $H_{triazole}$), 7.53 – 7.44 (m, 8H, $H_{2/7\text{-}3/6}$), 7.23 (d, J = 7.5 Hz, 2H, H_b), 6.78 (d, J = 7.5 Hz, 2H, H_c), 4.52 (s, 4H, H_g), 4.42 (t, J = 6.5 Hz, 4H, H_f), 4.33 – 4.28 (m, 4H), 3.92 – 3.88 (m, 4H), 3.82 (t, J = 6.5 Hz, 4H, H_d), 3.71 – 3.70 (m, 4H), 3.66 – 3.65 (m, 4H), 3.63 – 3.58 (m, 8H), 2.20 (p, J = 6.5 Hz, 4H, H_e). ^{13}C NMR (75 MHz, CD_3CN) δ 158.9, 158.8, 150.8, 144.5, 132.4, 130.8, 128.3, 125.7, 125.4, 124.6, 123.4, 122.4, 122.1, 114.5, 74.9, 70.4, 70.3, 70.2, 70.2, 69.4, 64.4, 63.8, 46.7, 29.4. HRMS (ESI) calcd for $C_{66}H_{73}N_7O_{10}$ m/z = 1124.5491 $[M–PF_6]^+$, found m/z = 1124.5491 $[M–PF_6]^+$. UV/Vis (CH_3CN, 298 K) λ_{max} (ε) = 277 (7400), 365 nm (6700 $M^{-1}\cdot cm^{-1}$)

3. Molecular Modeling

The molecular structure of [2]rotaxane $\mathbf{1}^+$ (without PF_6^-) and [2]catenane $\mathbf{1}^+$ (without PF_6^-) were calculated with AMPAC 10.1. A geometry optimization was performed by energy minimization using the PM6 method.

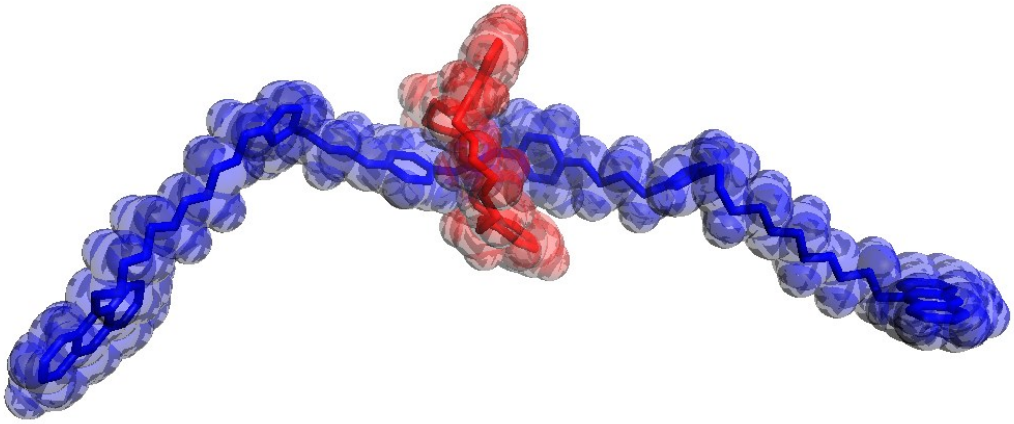


Figure S1: Calculated structure of [2]rotaxane **1**•PF_6 (PM6 minimization). Hydrogen atoms are omitted for clarity.

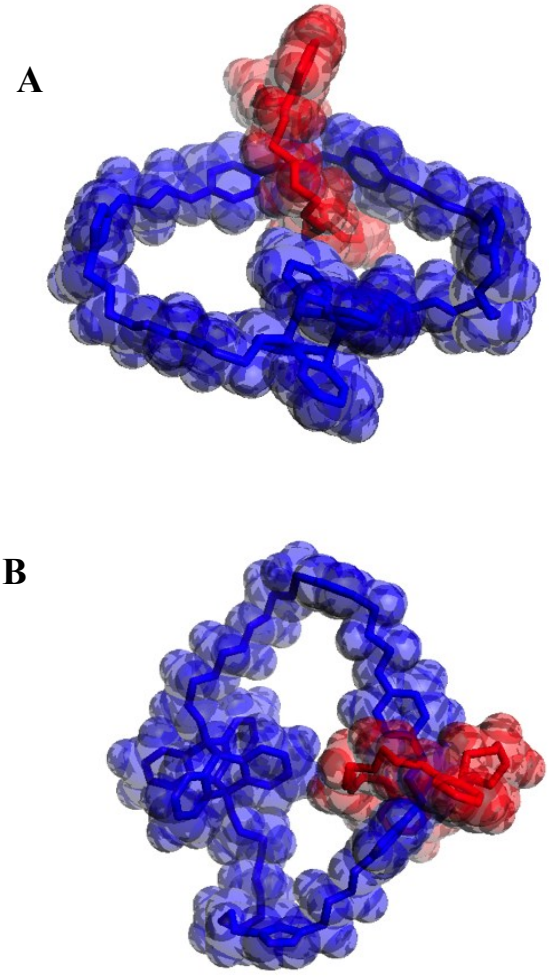


Figure S2: Calculated structure of HT isomer of [2]catenane **1**•PF_6 (PM6 minimization). Hydrogen atoms are omitted for clarity. A) Side-view, B) Top-view.

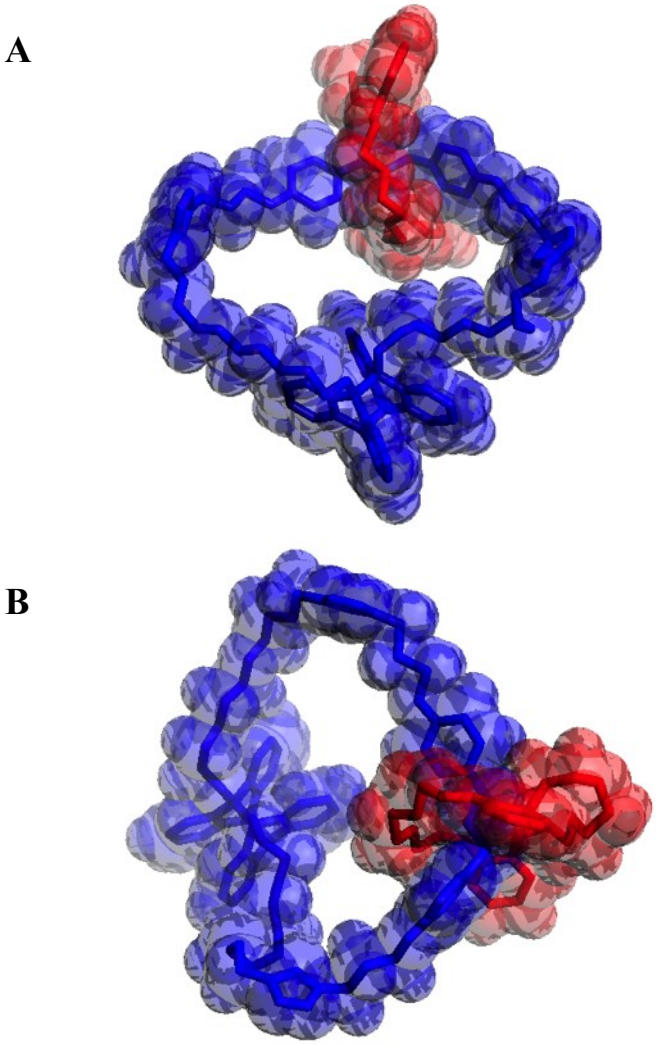


Figure S3: Calculated structure of HH isomer of [2]catenane **1**•PF_6 (PM6 minimization). Hydrogen atoms are omitted for clarity. A) Side-view, B) Top-view.

4. ^{1}H NMR comparison of macrocycle and thread components and rotaxane 1•PF_6

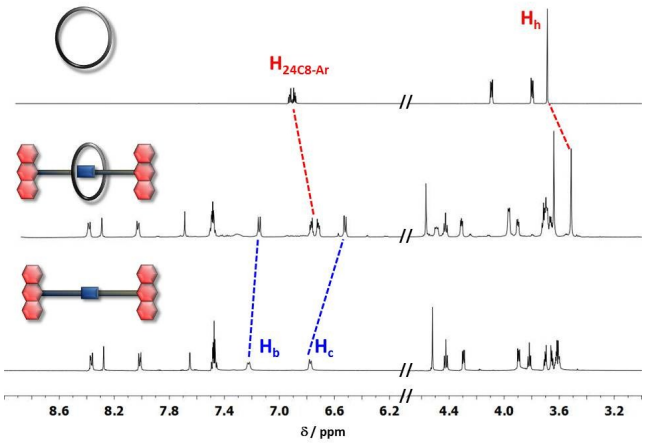


Figure S4. ^{1}H NMR (CD_3CN, 600 MHz, 25 °C) spectra of a 1 mM solution of the DB24C8 macrocycle (top), the [2]rotaxane **1**•PF_6 (middle) and corresponding dumbbell (bottom).

5. UV-Vis and Fluorescence Studies

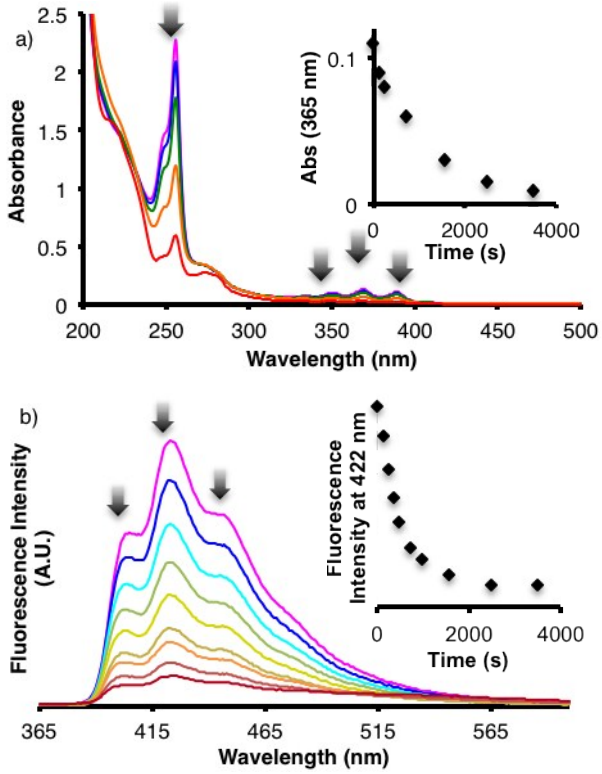


Figure S5. UV-visible spectra (a) and fluorescence spectra (b) of a 2×10^{-5} M solution of the [2]rotaxane **1**•PF_6 in CH_3CN. Upon irradiation at 365 nm, the $S_1 \leftarrow S_0$ absorption band of the anthracene monomer decreases as does anthracene monomer emission.

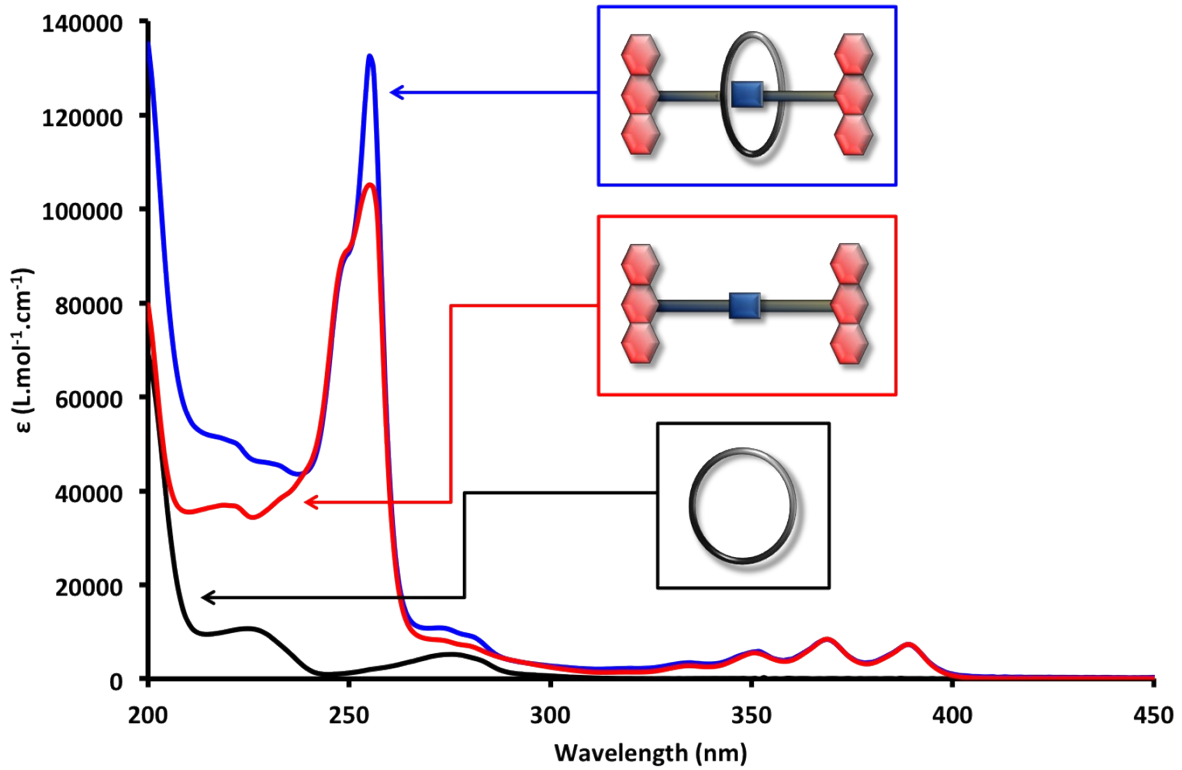


Figure S6a — Electronic absorption spectra of **1**•PF_6, **8**•PF_6 and the DB24C8 macrocycle in CD_3CN.

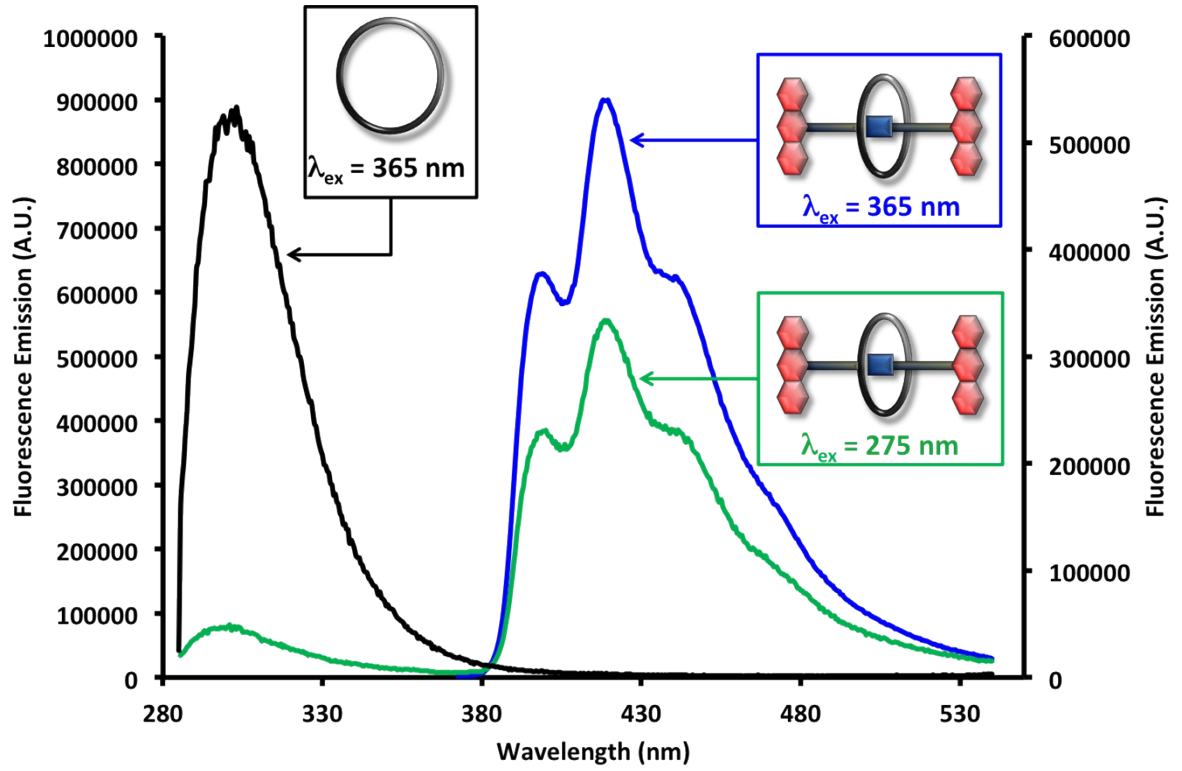


Figure S6b — Emission spectra of **1**•PF_6 (λ_{ex} = 275 nm and 365 nm) and the DB24C8 (λ_{ex} = 275 nm) in CD_3CN.

Table 1. Absorption properties of 1•PF_6, 8•PF_6 and the DB24C8 macrocycle in CH_3CN.

	λ (nm)	ε ($L.mol^{-1}.cm^{-1}$)
[2]Rotaxane (**1**•PF_6)	256	130000
	277	9800
	365	6700
Thread **8**•PF_6	256	104000
	277	7400
	365	6700
DB24C8	225	10700
	277	5100

6. Photoreaction: Procedure and NMR Characterization

Procedure

Solutions of **1**•PF_6 were degassed by three freeze-pump-thaw cycles on a high-vacuum (P = 10^{-5} bar) line and blowtorch sealed under vacuum. Irradiation at 365 nm and 254 nm were performed with a 12W TLC lamp (Bioblock Scientific VL-6 LC). Irradiations at 280 nm were performed with a 150 W Xe-Hg lamp (Schoeffel instrument GmbH) coupled to a monochromator Oriel Stratford (model 77250).

Analysis after photoirradiation (1h, λ_{exc} = 365 nm)

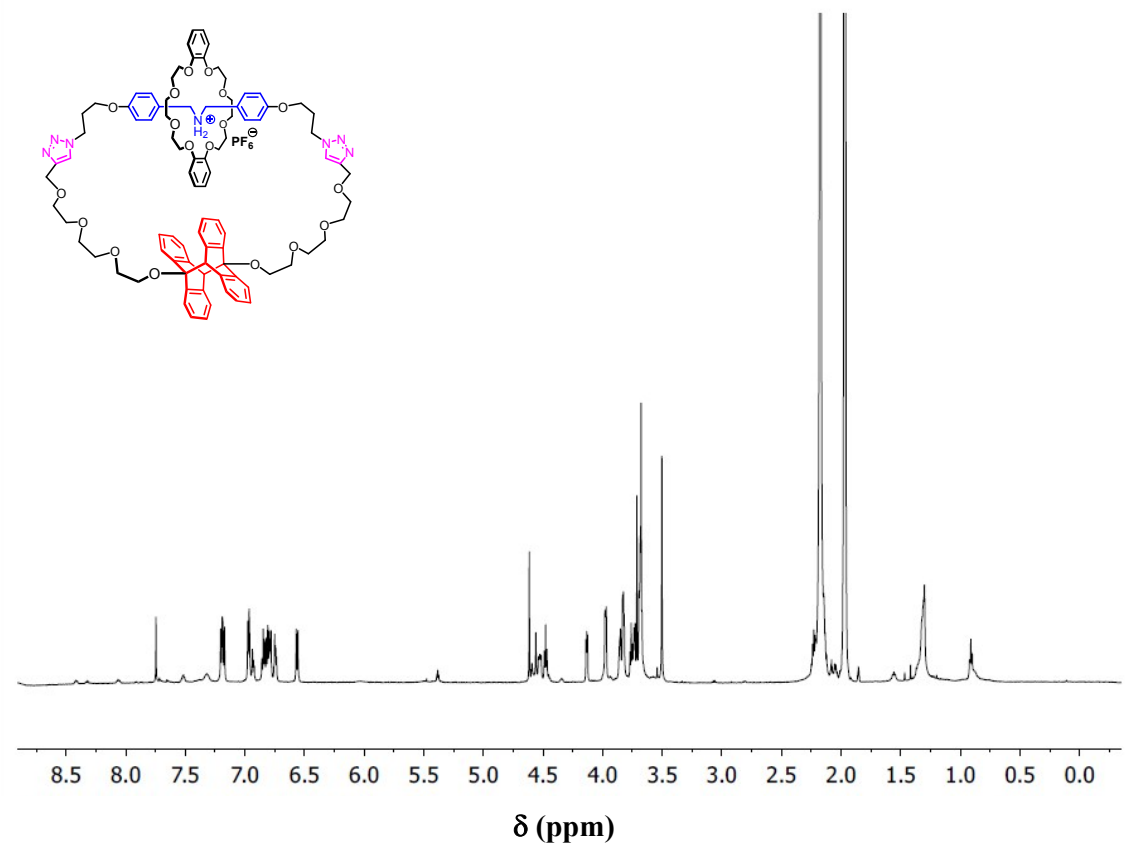


Figure S7a — ^{1}H NMR following irradiation (1h, λ_{ex} = 365 nm) of **1**•PF_6 in CD_3CN at 298 K on a 600 MHz spectrometer.

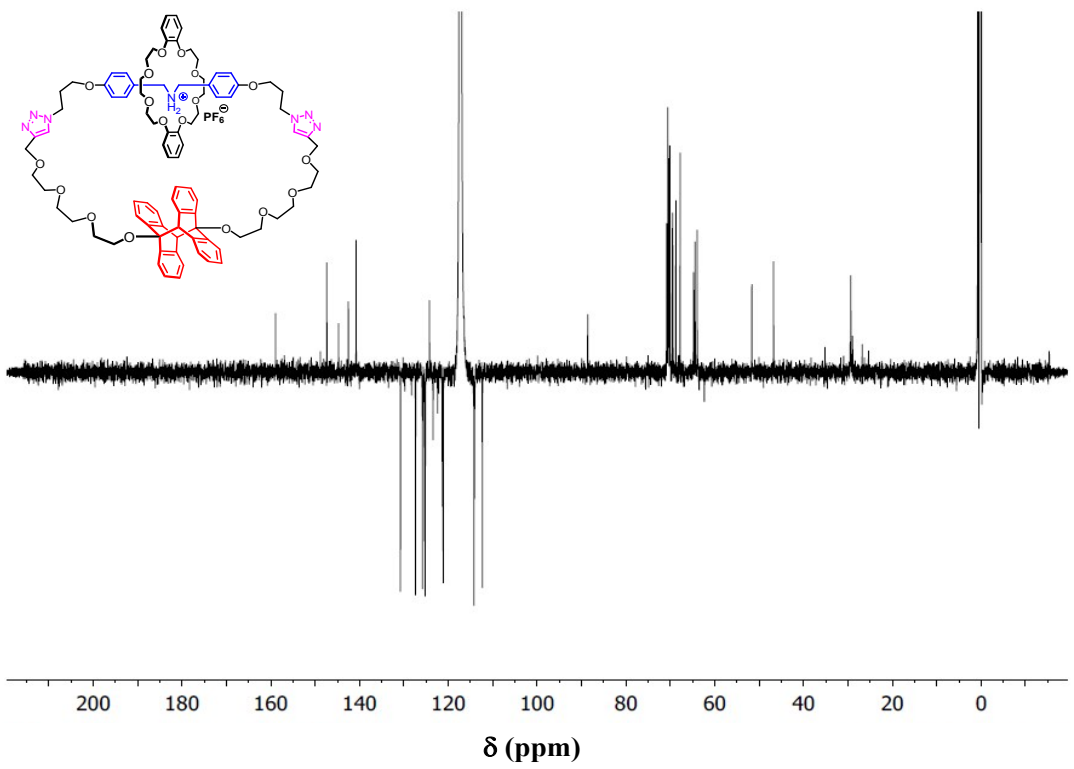


Figure S7b — ^{13}C NMR following irradiation (1h, λ_{ex} = 365 nm) of **1**•PF_6 in CD_3CN at 298 K on a 150 MHz spectrometer.

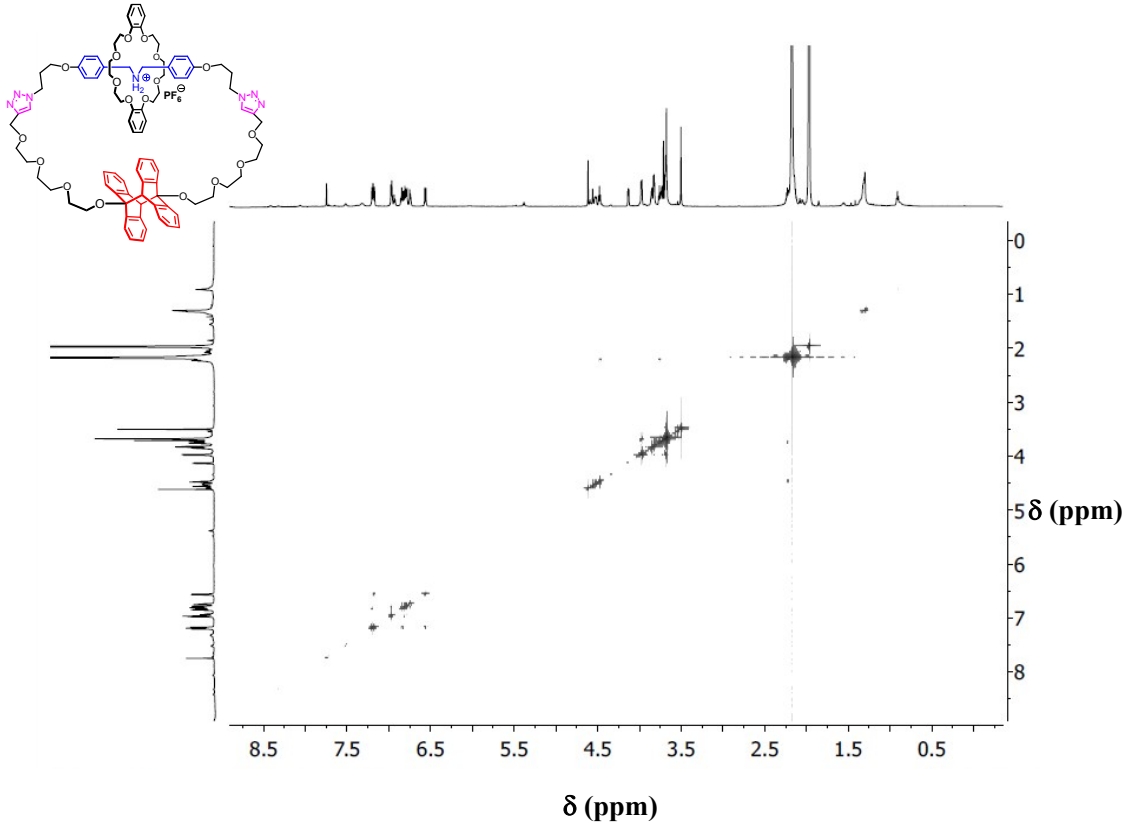


Figure S7c — ^{1}H-^{1}H Double quantum filtered COSY NMR 2D spectrum following irradiation (1h, λ_{ex} = 365 nm) of **1**•PF_6 in CD_3CN at 298 K on a 600 MHz spectrometer.

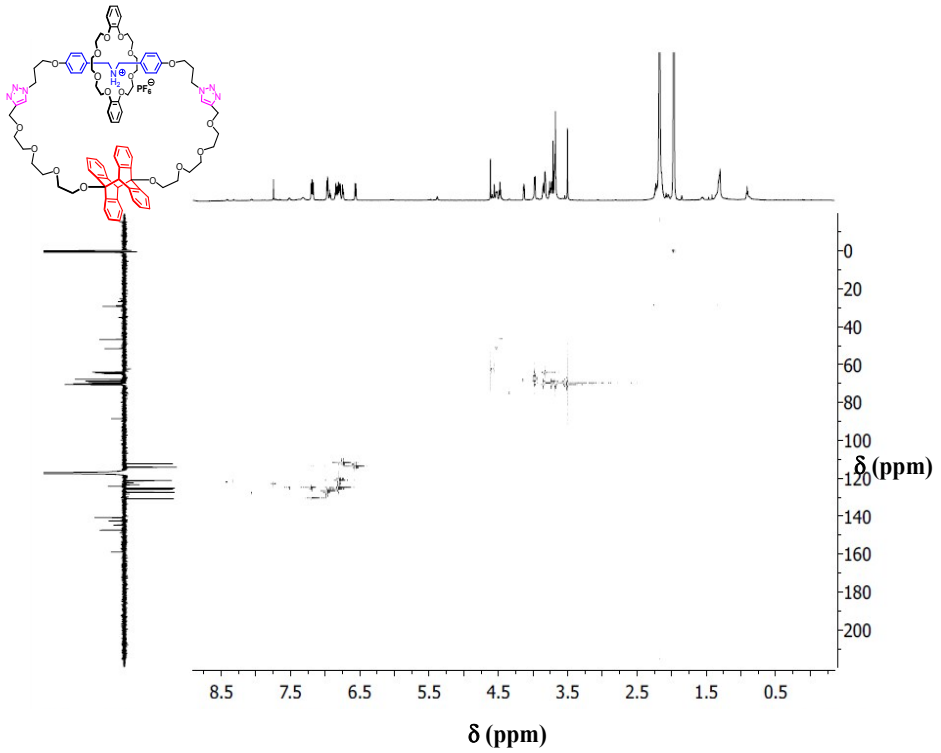


Figure S7d — ^{13}C Double quantum filtered HSQC NMR 2D spectrum following irradiation (1h, λ_{ex} = 365 nm) of **1**•PF_6 in CD_3CN at 298 K on a 600 MHz spectrometer.

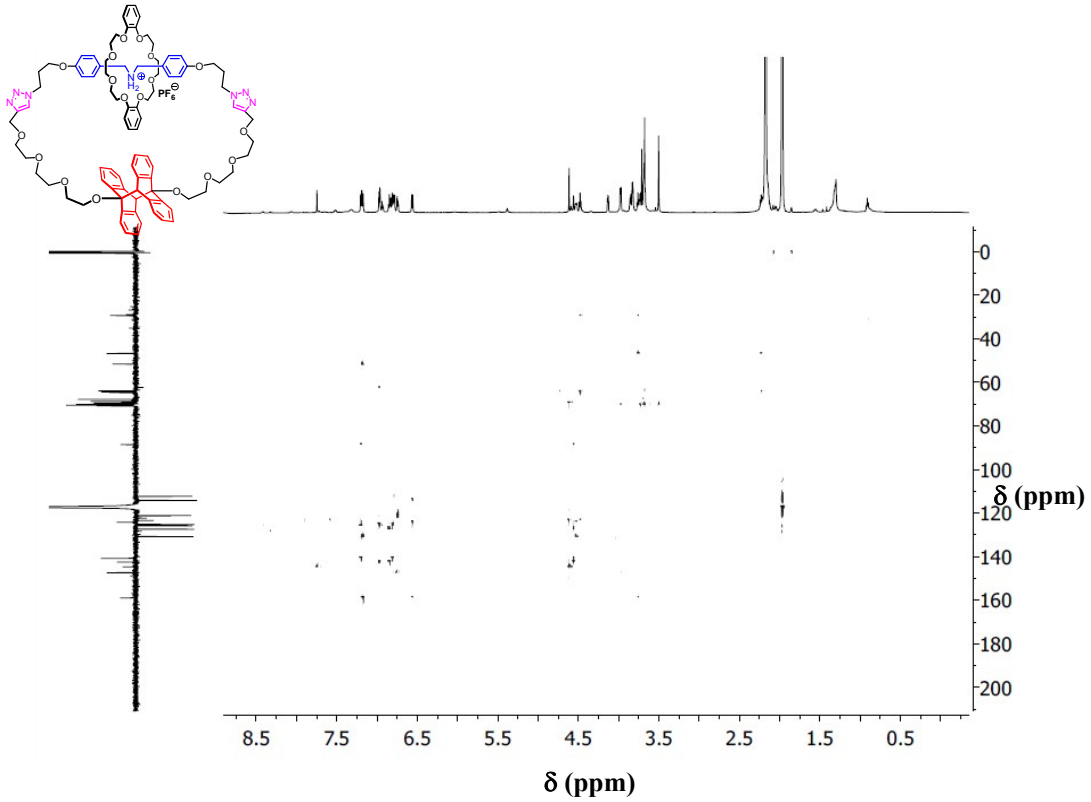


Figure S7f — ^{1}H-^{13}C Double quantum filtered HMBC NMR 2D spectrum following irradiation (1h, λ_{ex} = 365 nm) of **1**•PF_6 in CD_3CN at 298 K on a 600 MHz spectrometer.

7. Fatigue Study by Thermal-cycloreversion (120 °C)

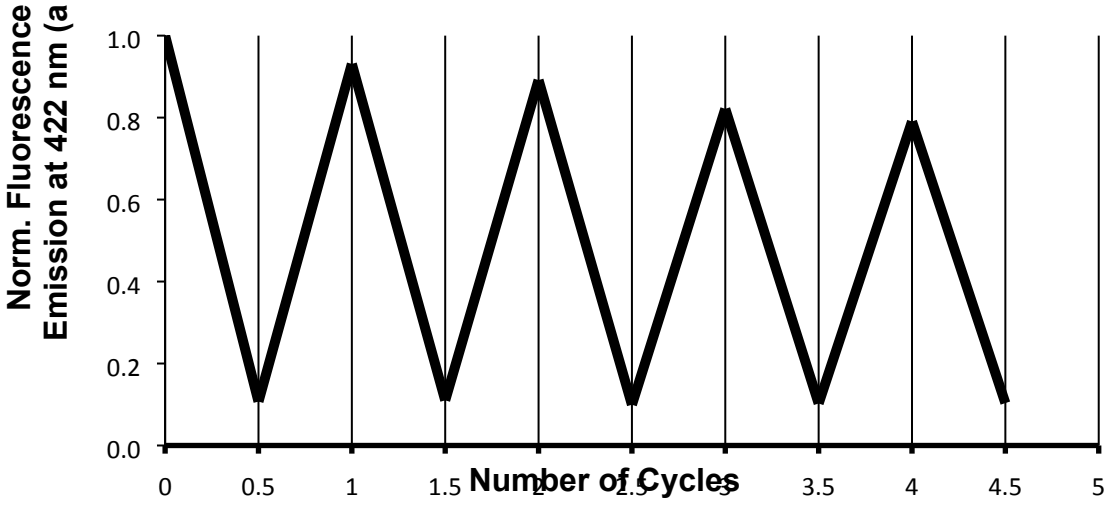


Figure S8 — Fatigue study of a 2×10^{-5} mol.L^{-1} solution of **1**•PF_6 in CH_3CN monitored by fluorescence emission at 422 nm. Each cycle corresponds to an irradiation at 365 nm (1 h) leading to the photocyclization followed by an heating at 120 °C (3 h) leading to the cycloreversion.

8. References

[S1] K. S. Chichak, A. J. Peters, S. J. Canrill and J. F. Stoddart, *J. Org. Chem.,* 2005, **70**, 7956-7962.

[S2] D. E. Eaton, *Handbook of Organic Photochemistry*, Vol 1; Scaiano, J. C., Ed.; CRC : Boca Raton, FL, 1989.

[S3] M. Montalti, A. Credi, L. Prodi and M. T. Gandolfi, *Handbook of Photochemistry*, edition taylor et Francis, 601-604.

[S4] V. Aucagne, K. D. Hänni, D. A. Leigh, P. J. Lusby and D. B. Walker, *J. Am. Chem. Soc.,* 2006, **128**, 2186–2187.

[S5] M. Shao, P. Dongare, L. N. Dawe, D. W. Thompson and Y. Zhao, *Org. Lett.,* 2010, **12**, 3050–3053.

9. ^{1}H NMR Characterization

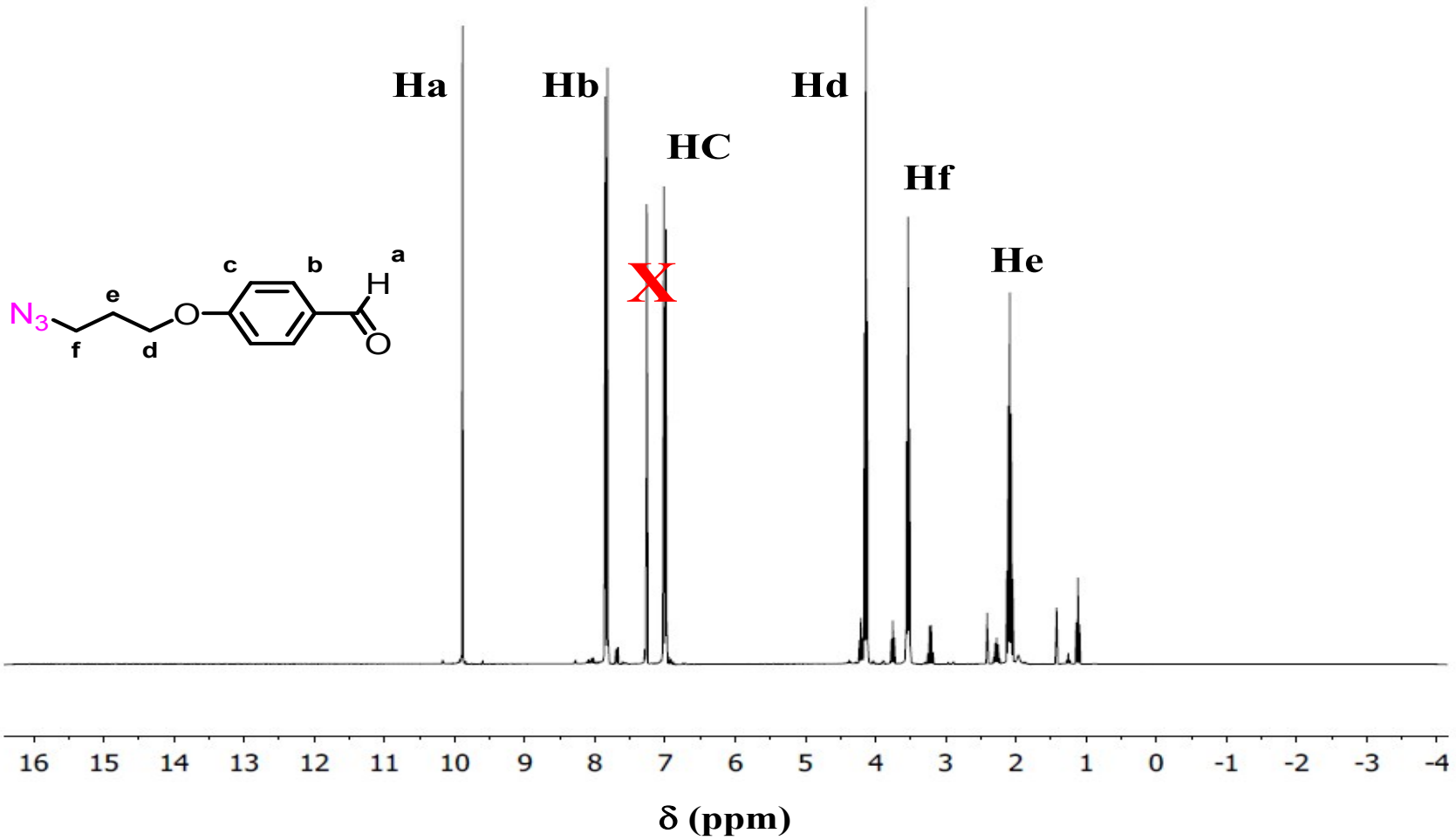


Figure S9a — ^{1}H NMR of **2** in CD_3Cl at 298 K on a 300 MHz spectrometer.

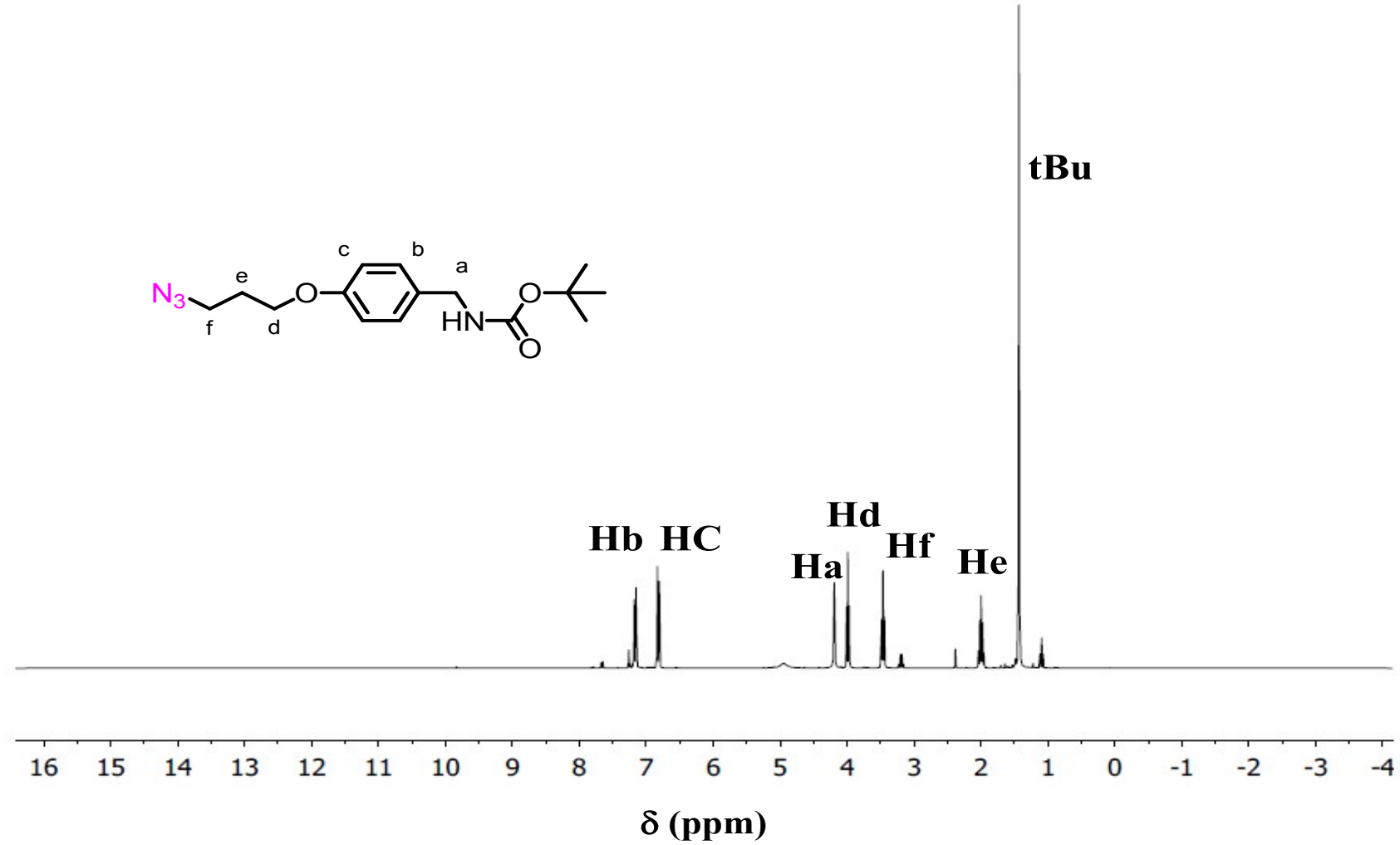


Figure S9b — ^{1}H NMR of **3** in $CDCl_3$ at 298 K on a 300 MHz spectrometer.

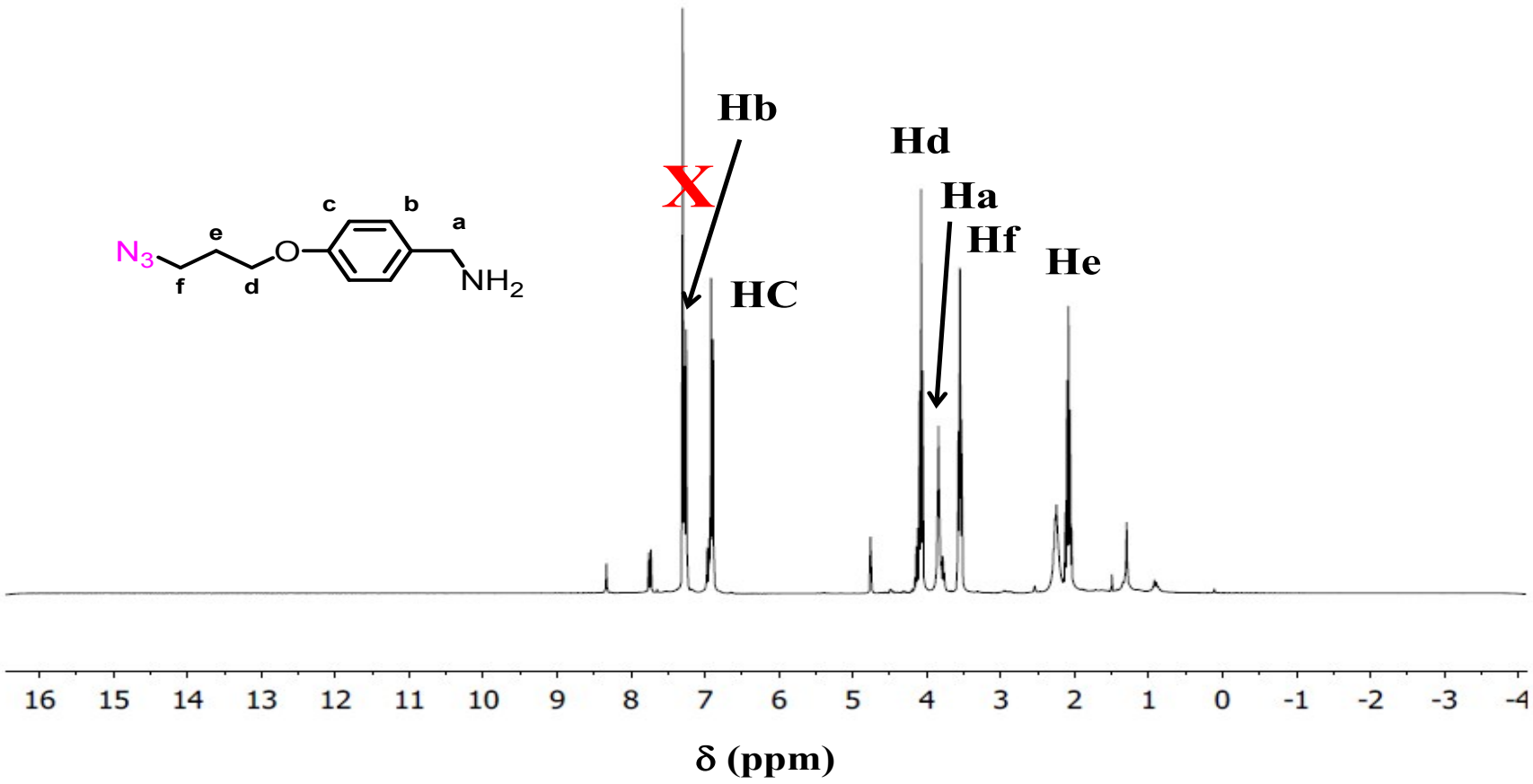


Figure S9c — ^{1}H NMR of **4** in $CDCl_3$ at 298 K on a 300 MHz spectrometer.

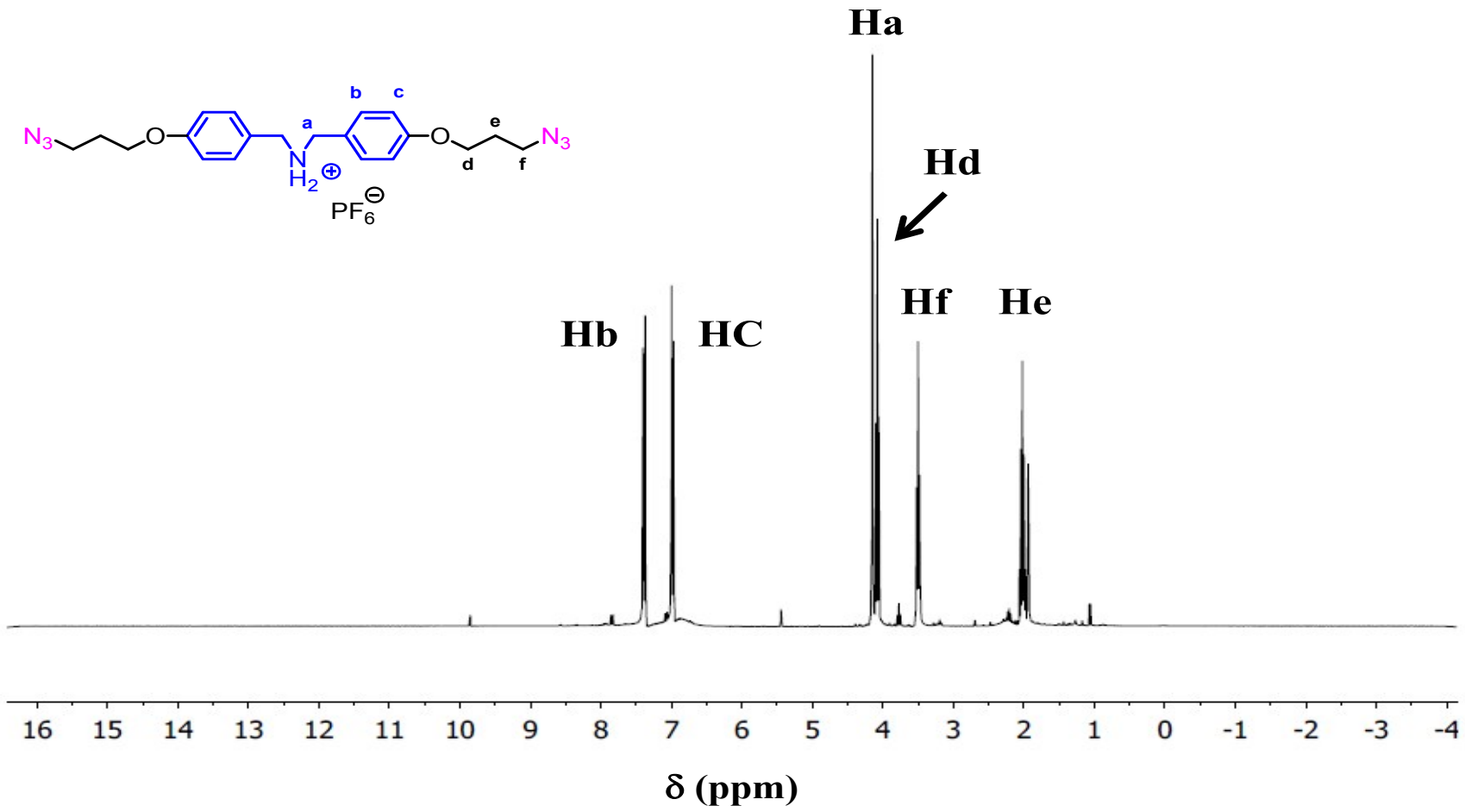


Figure S9d — ^{1}H NMR of **5**•PF_6 in CD_3CN at 298 K on a 300 MHz spectrometer.

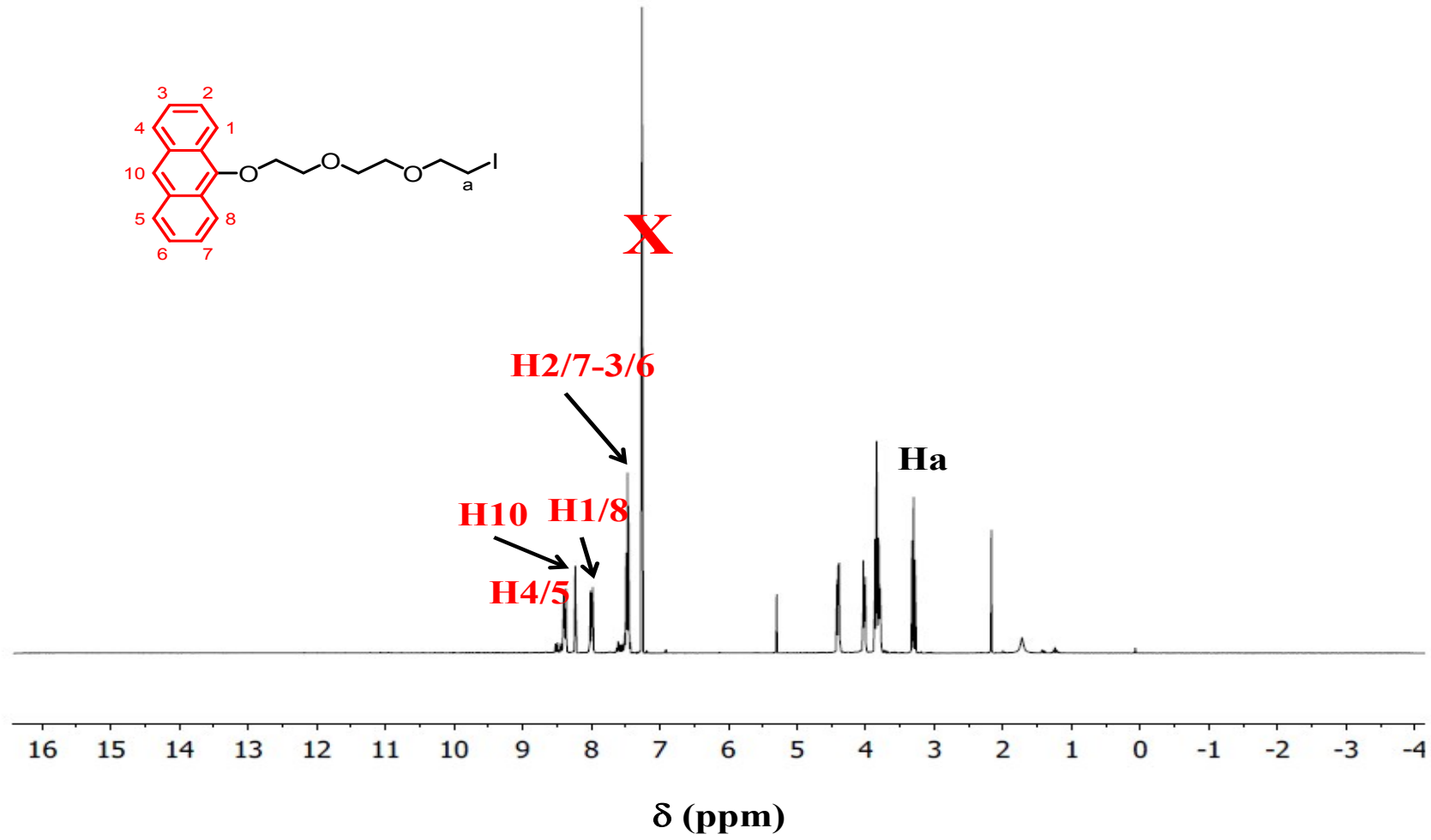


Figure S9e — ^{1}H NMR of **7** in $CDCl_3$ at 298 K on a 300 MHz spectrometer.

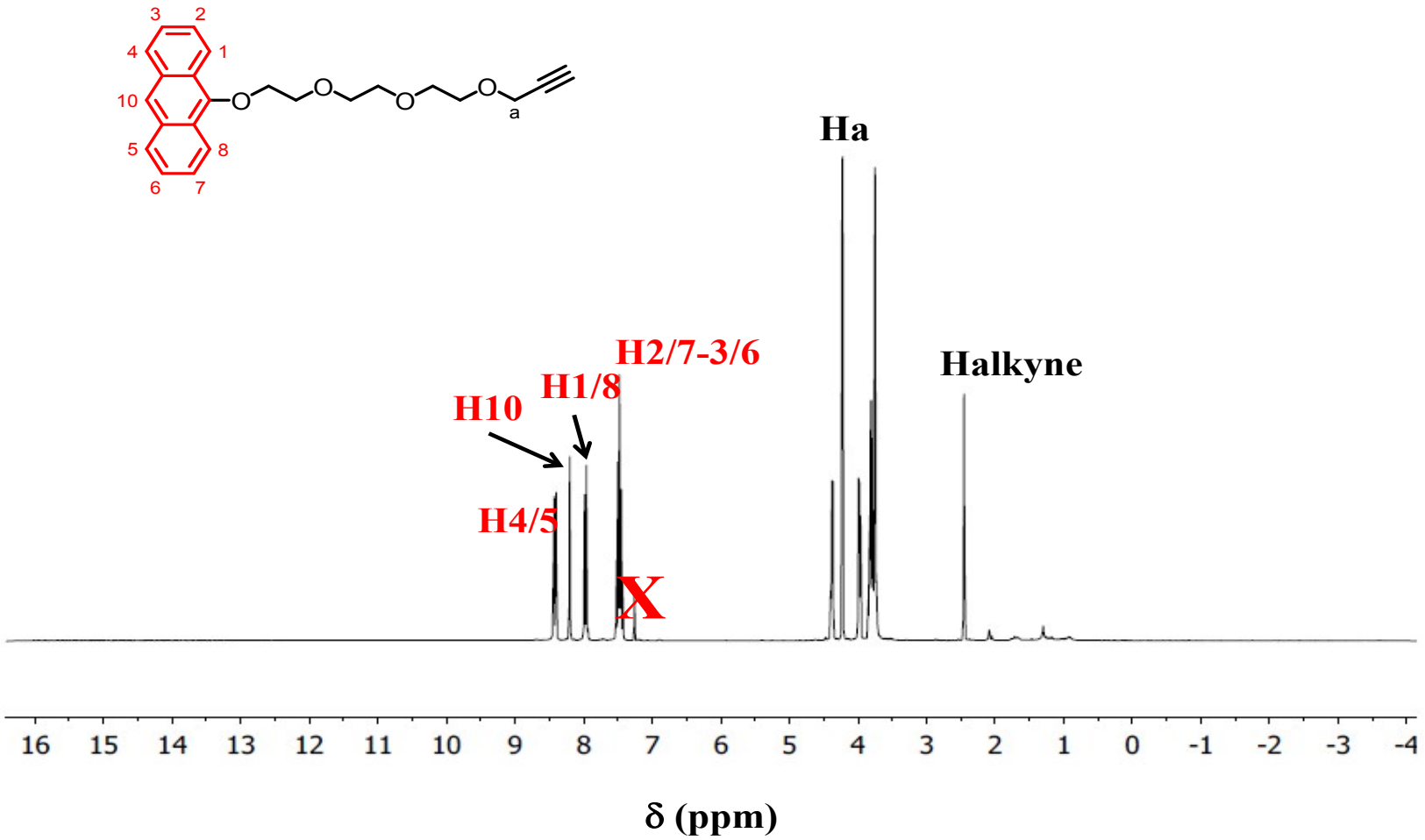


Figure S9f — ^{1}H NMR of **6** in $CDCl_3$ at 298 K on a 300 MHz spectrometer.

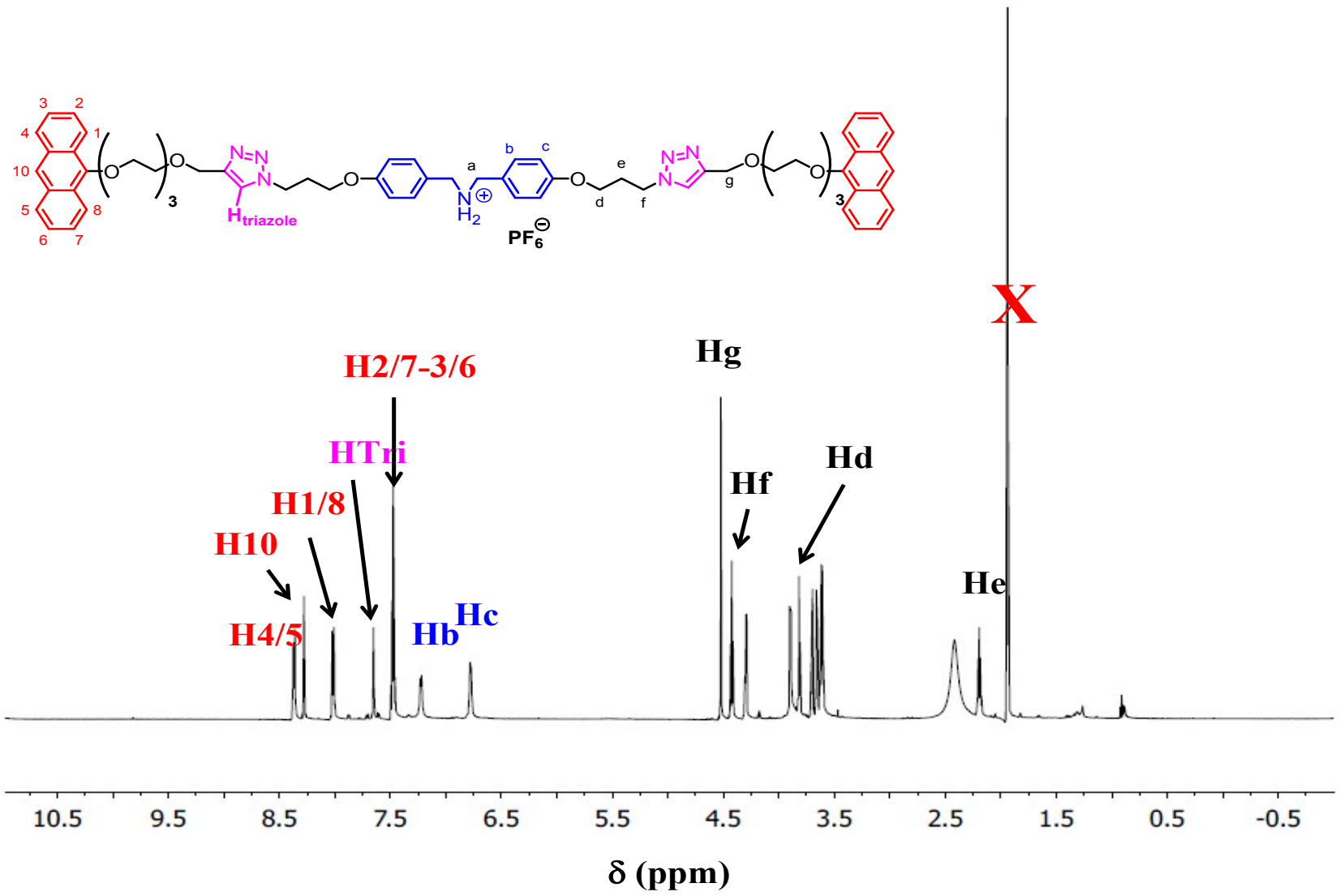


Figure S9g — ^{1}H NMR of the **8**•PF_6 in CD_3CN at 298K on a 300 MHz spectrometer.

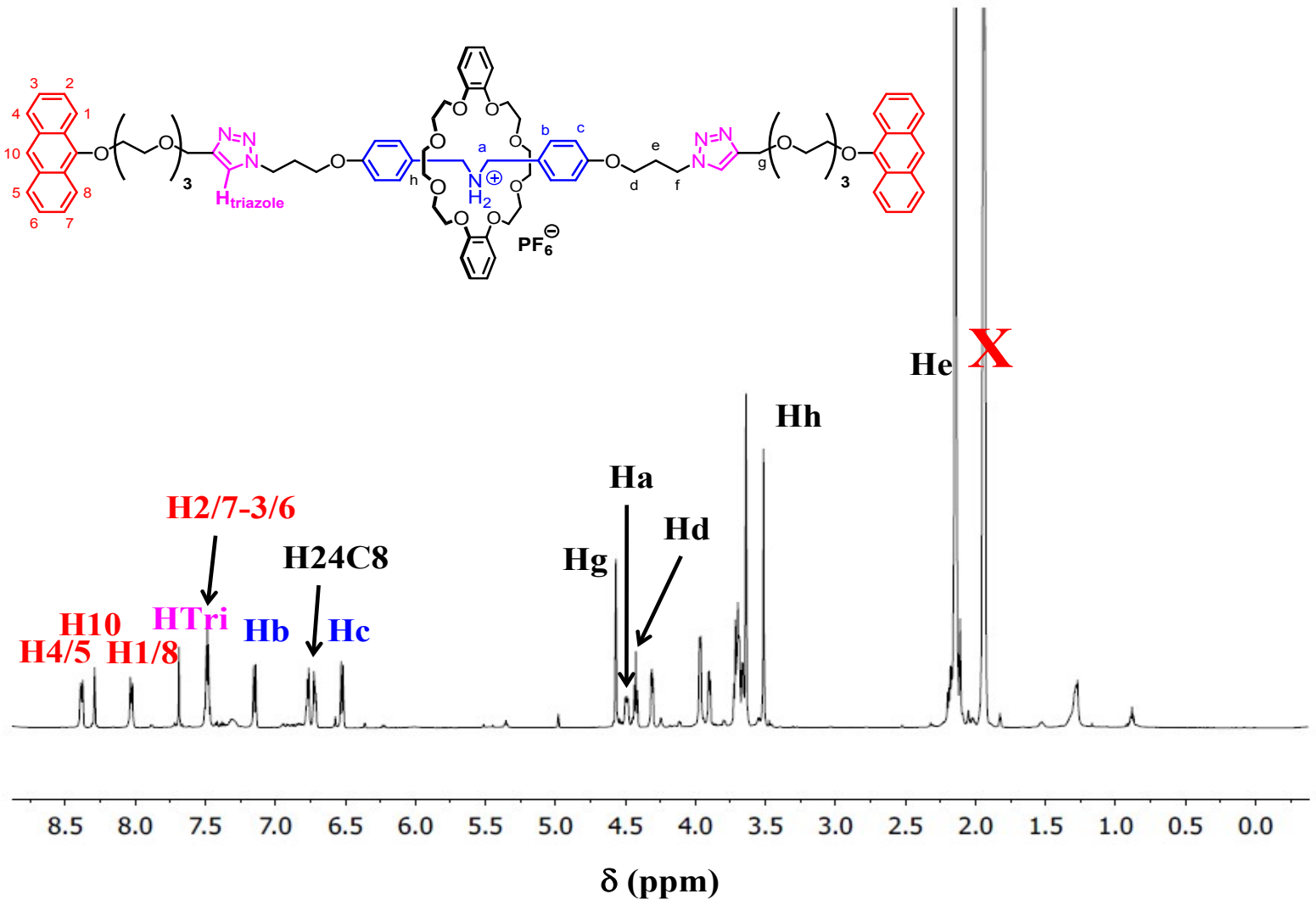


Figure S9h — ^{1}H NMR of the [2]Rotaxane **1**•PF_6 in CD_3CN at 298K on a 600 MHz spectrometer.

10. ^{13}C NMR Characterization

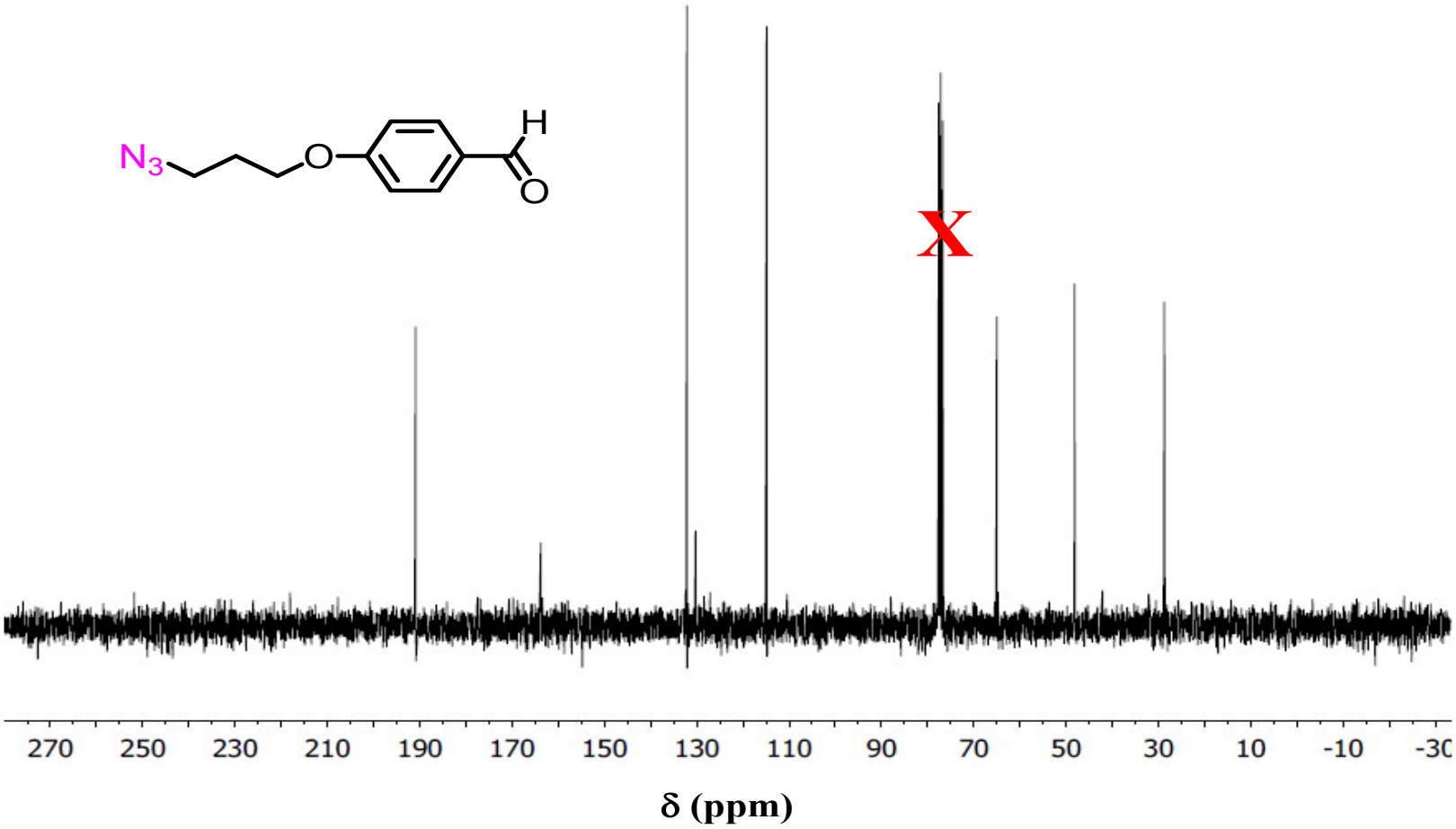


Figure S10a — ^{13}C NMR of **2** in $CDCl_3$ at 298 K (75 MHz).

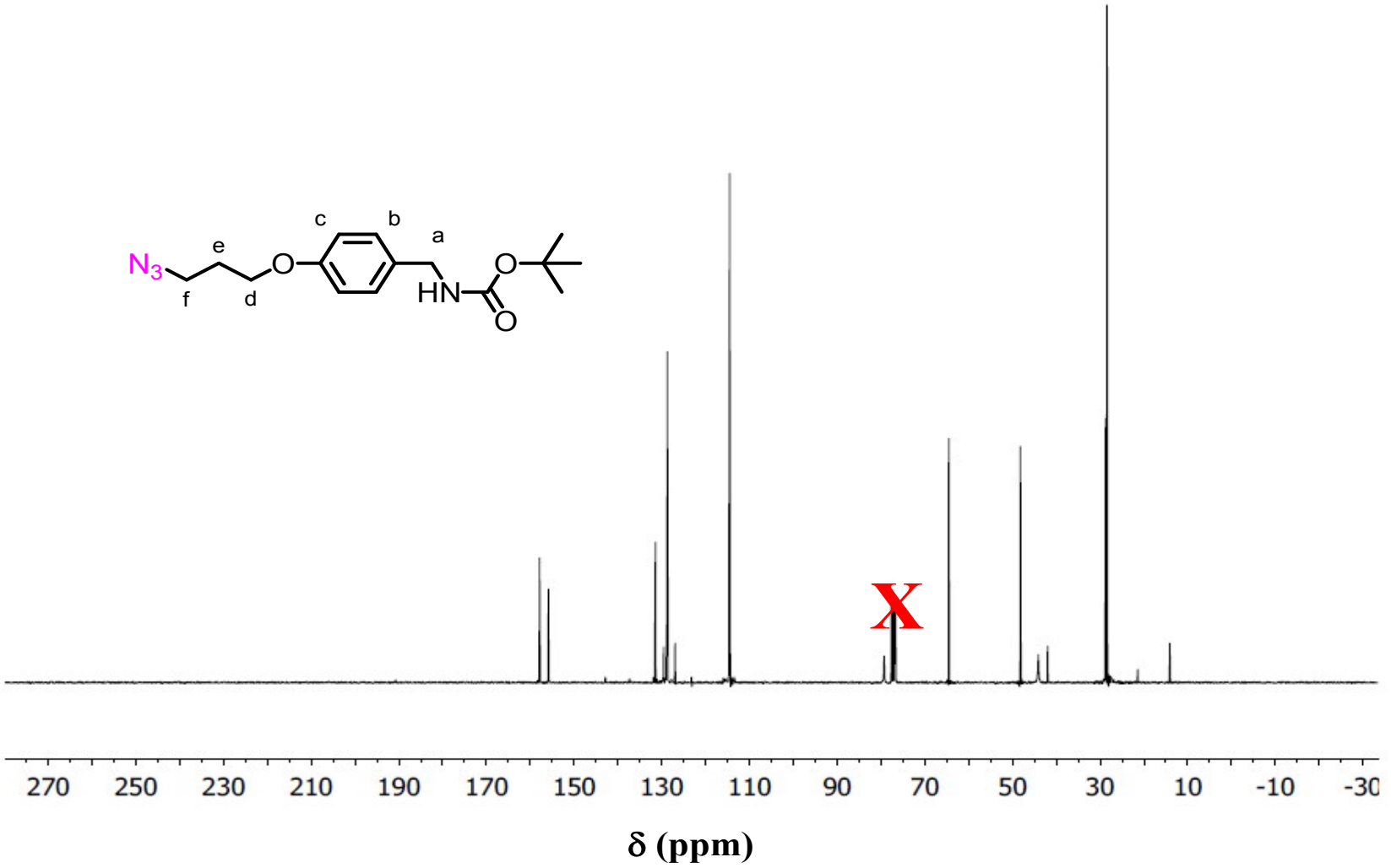


Figure S10b — ^{13}C NMR of **3** in $CDCl_3$ at 298 K (75 MHz).

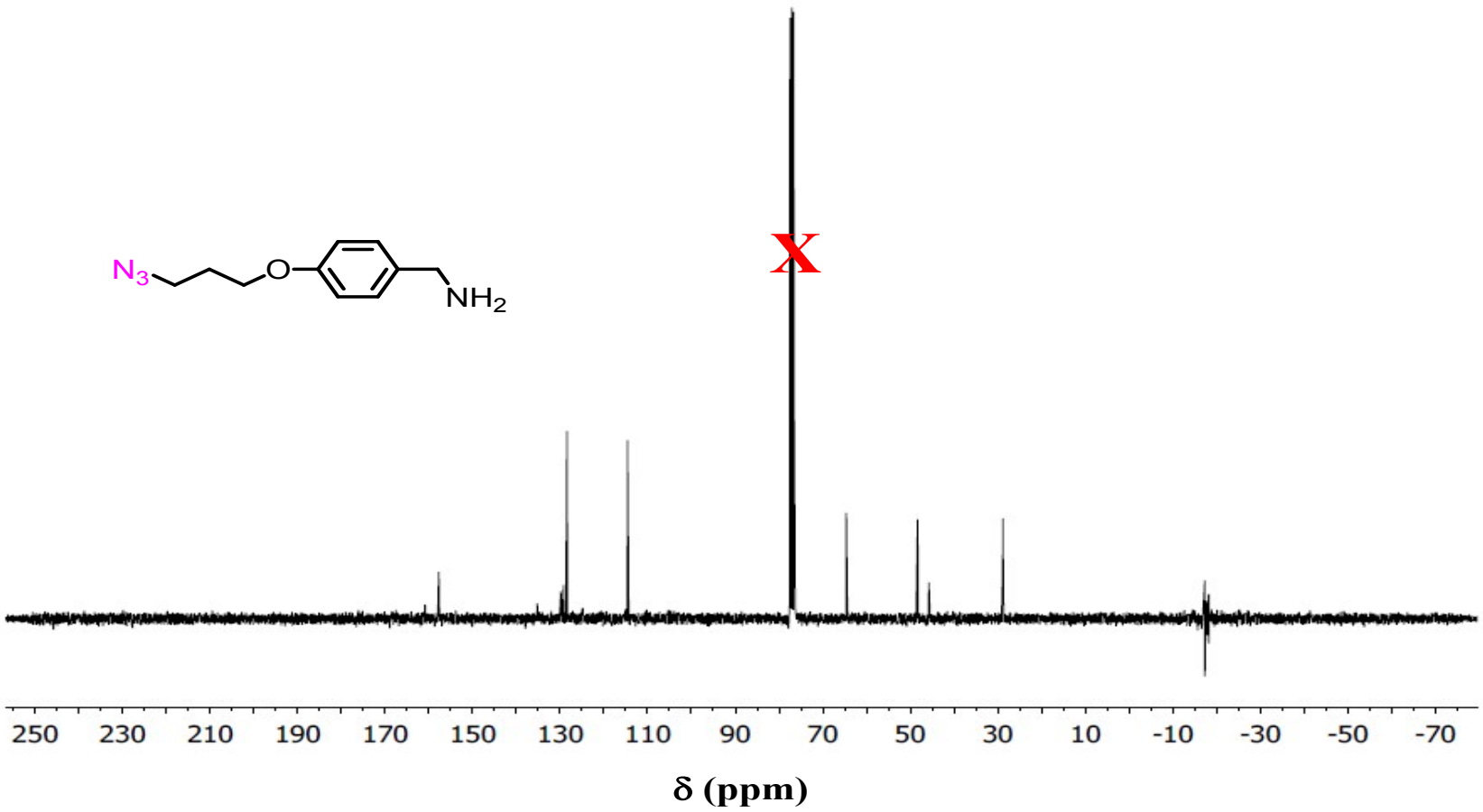


Figure S10c — ^{13}C NMR of **4** in $CDCl_3$ at 298 K (75 MHz).

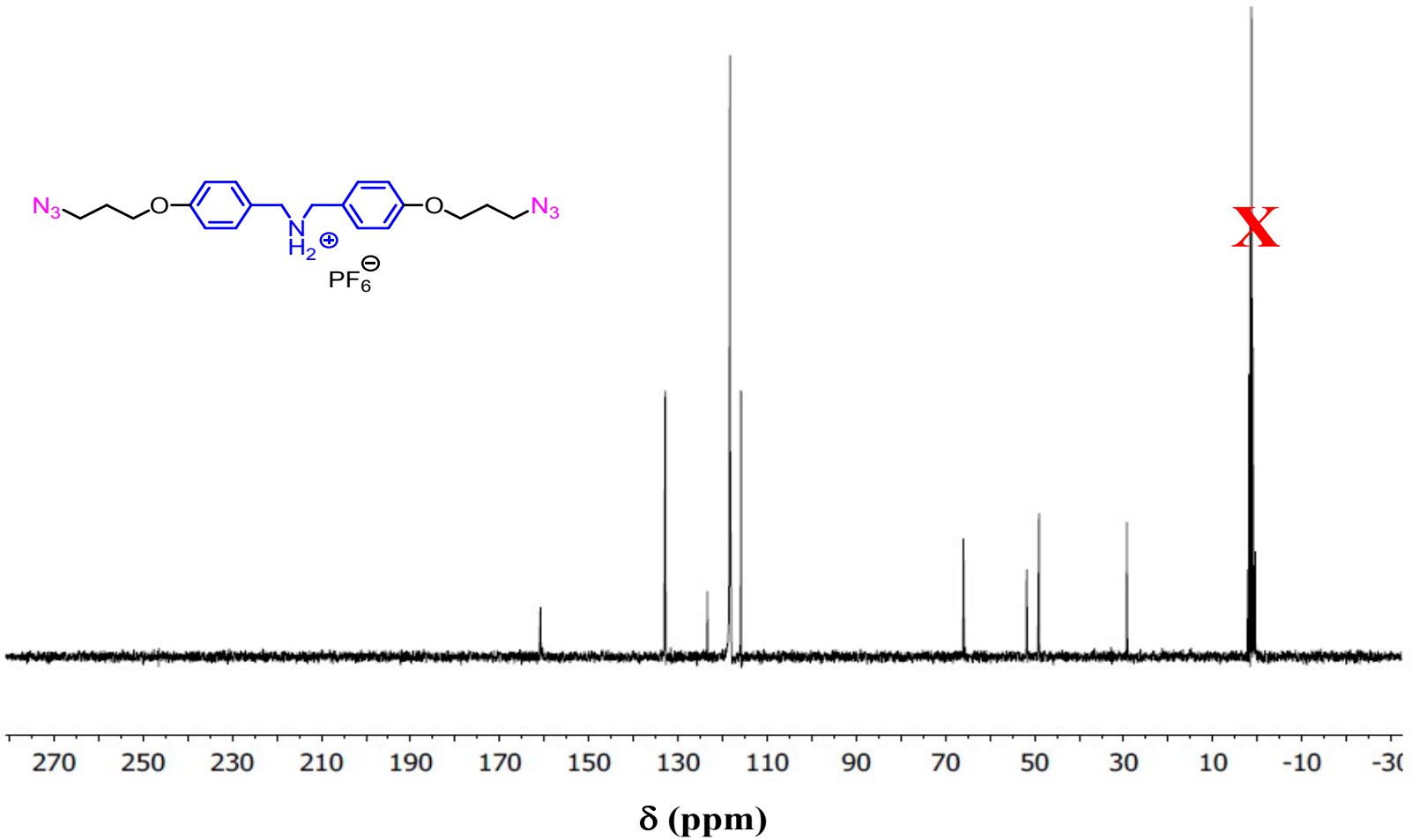


Figure S10d — ^{13}C NMR of **5**•PF_6 in CD_3CN at 298 K (75 MHz).

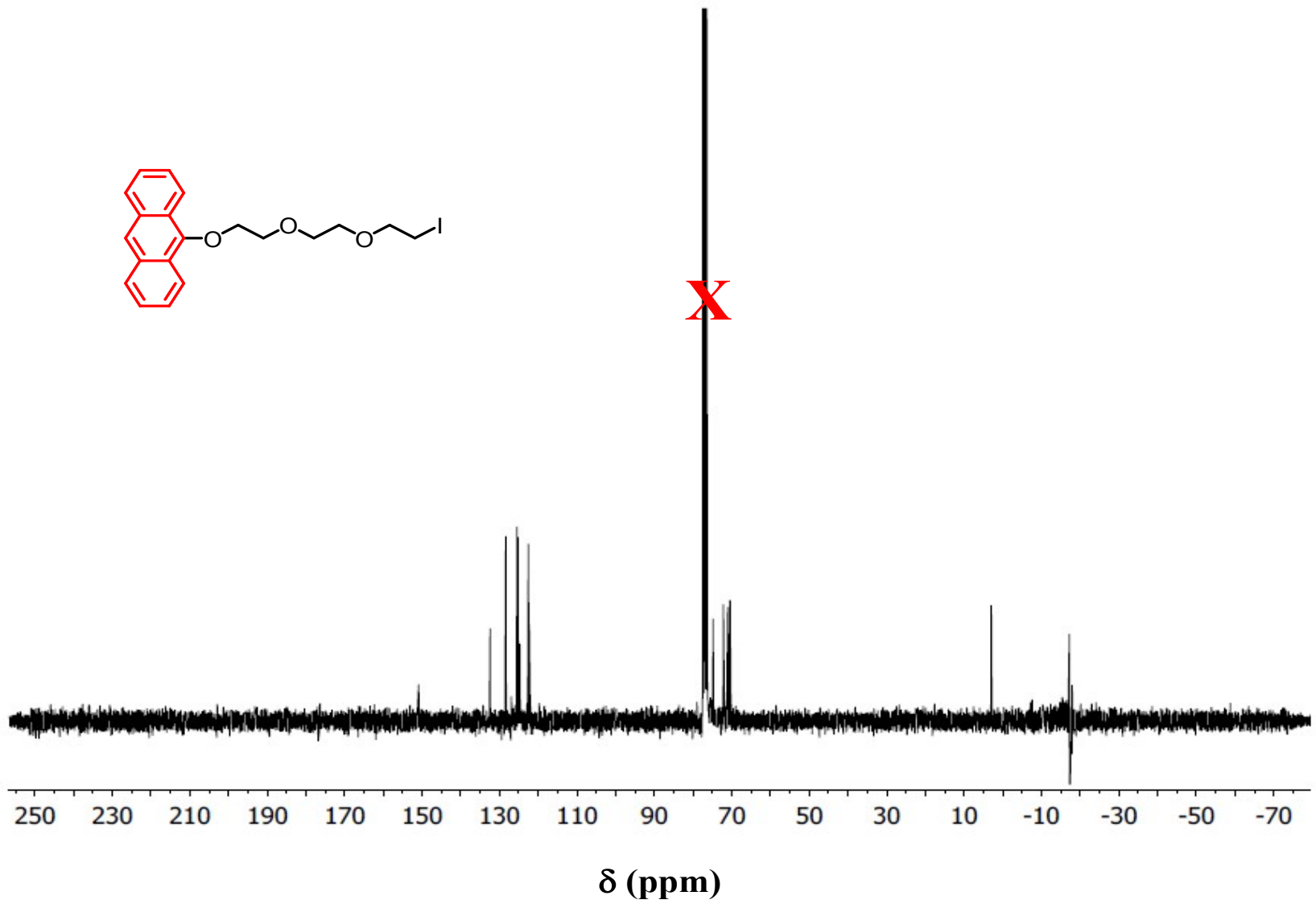


Figure S10e — ^{13}C NMR of **7** in $CDCl_3$ at 298 K (75 MHz).

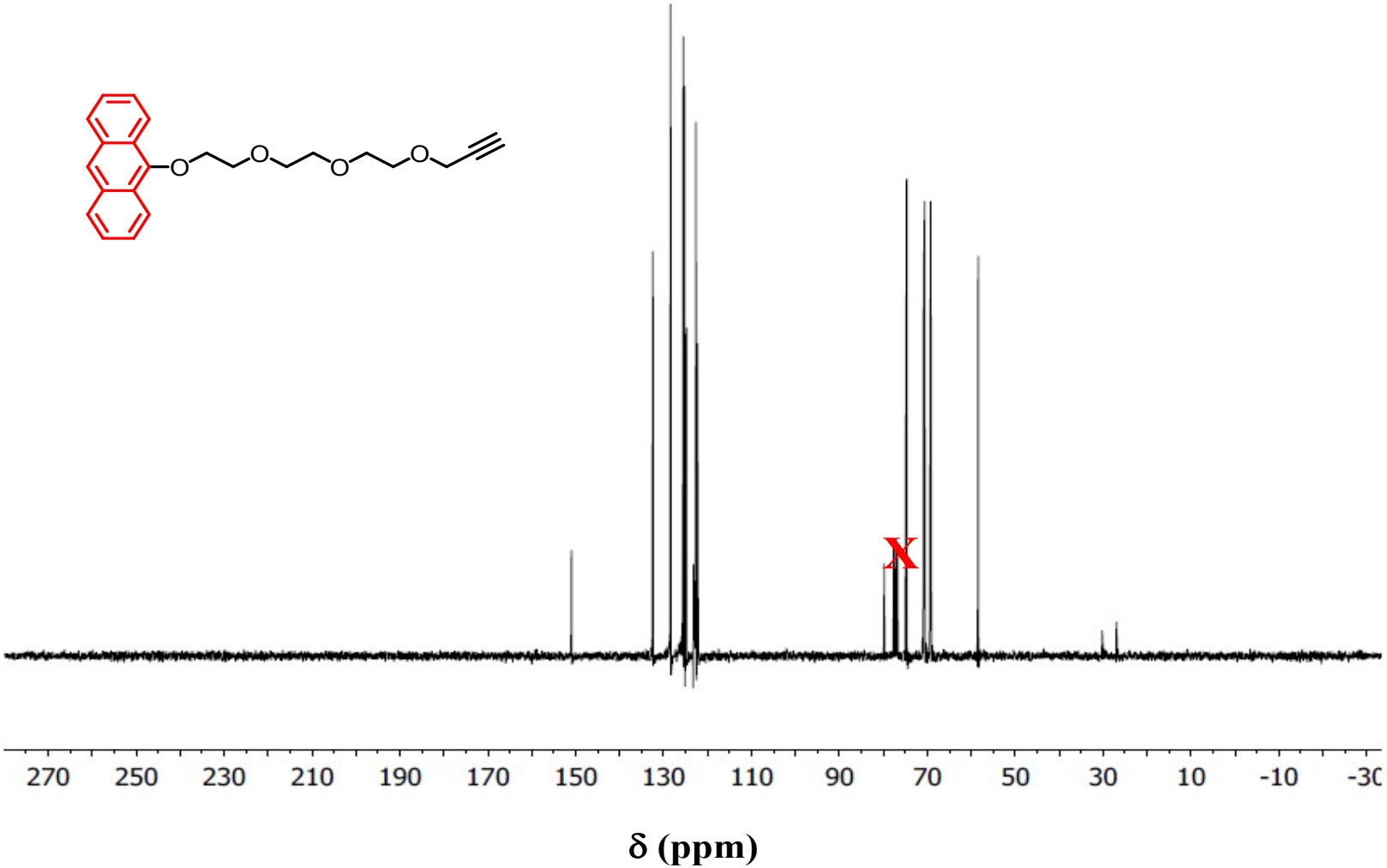


Figure S10f — ^{13}C NMR of **6** in $CDCl_3$ at 298 K (75 MHz).

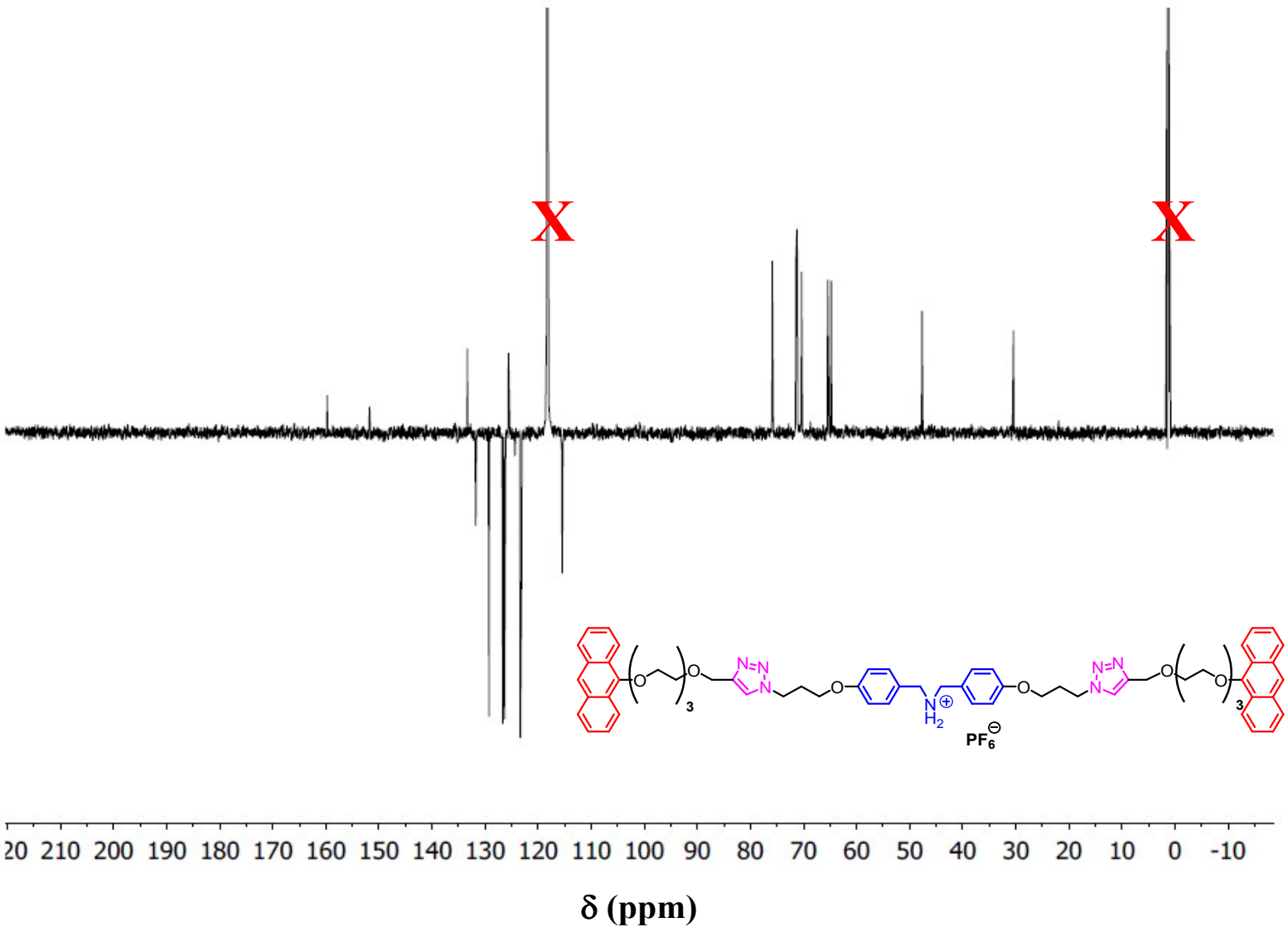


Figure S10g — ^{13}C NMR of the **8**•PF_6 in CD_3CN at 298 K (75 MHz).

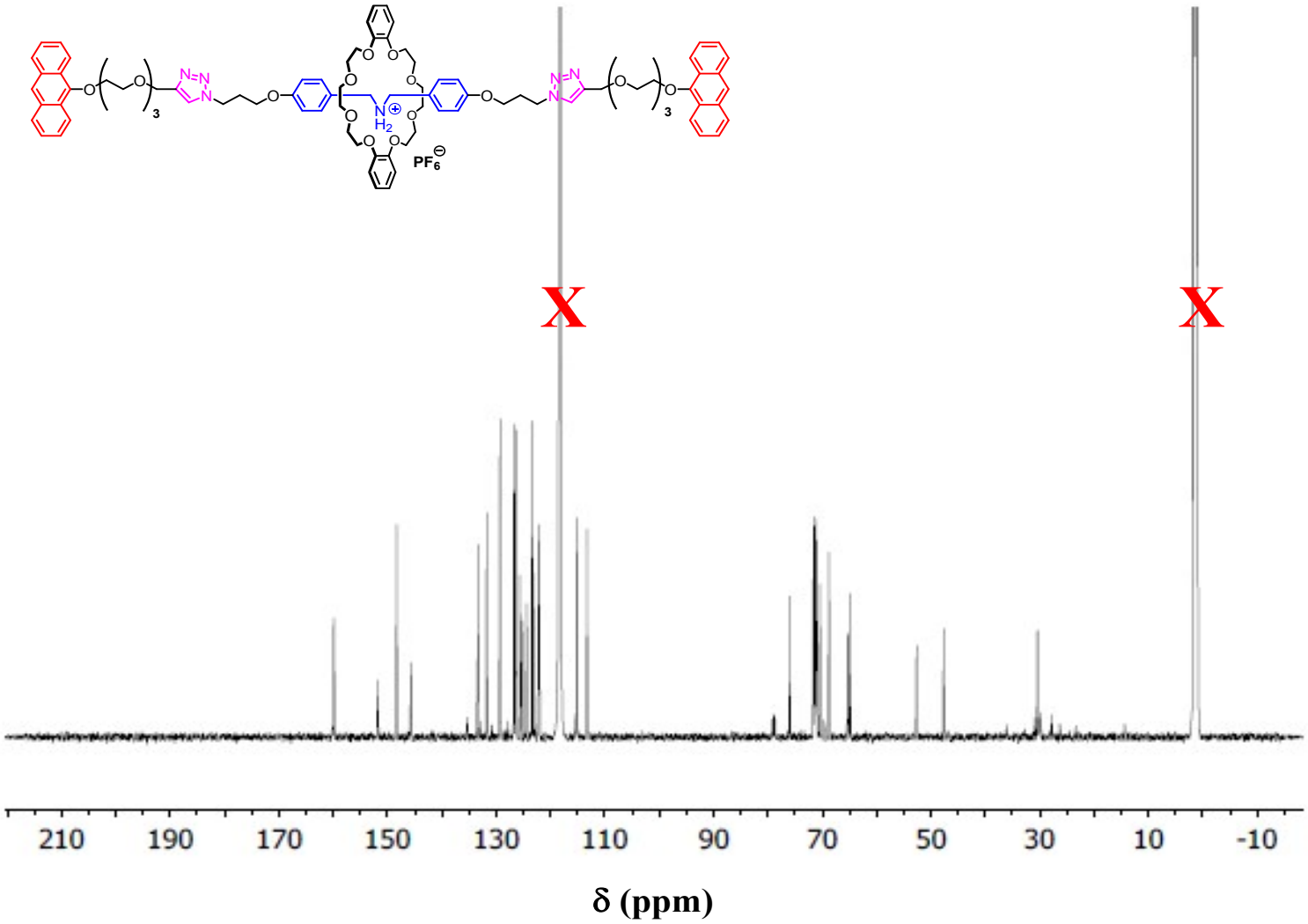


Figure S10h — ^{13}C NMR of the [2]rotaxane **1**•PF_6 in CD_3CN at 298 K (150 MHz).

11. 2D NMR Characterization of 1•PF_6 and its thread

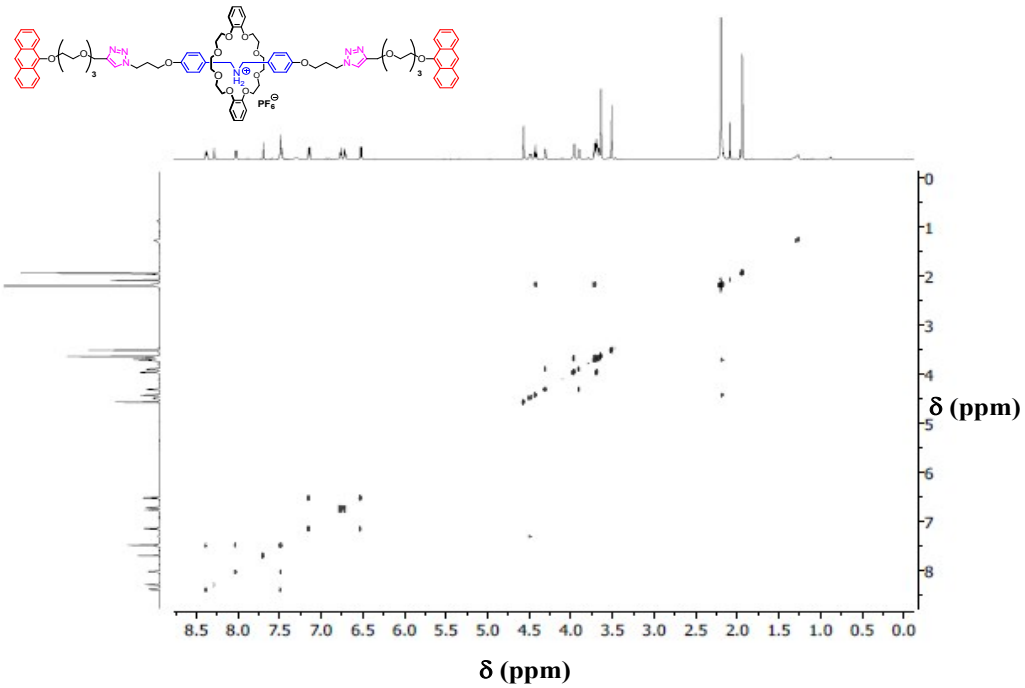


Figure S11a — ^{1}H-^{1}H Double quantum filtered COSY NMR 2D spectrum of the [2]rotaxane **1**•PF_6 in CD_3CN at 298 K on a 600 MHz spectrometer.

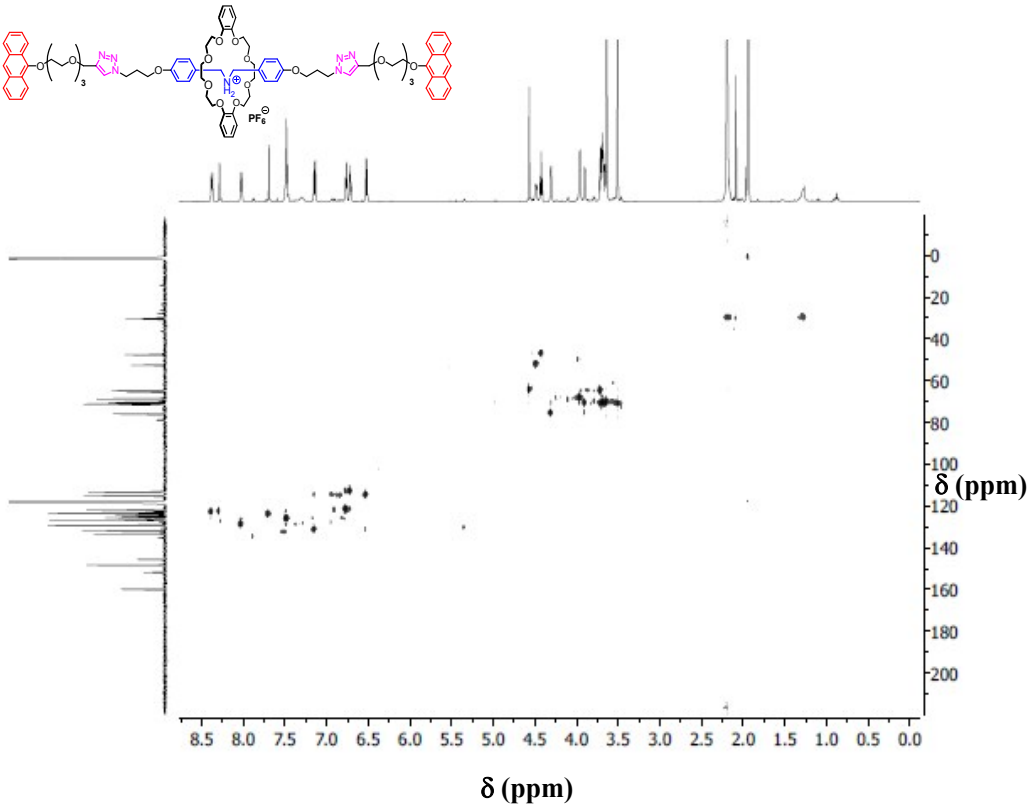


Figure S11b — ^{13}C Double quantum filtered HSQC NMR 2D spectrum of the [2]rotaxane **1**•PF_6 in CD_3CN at 298 K on a 600 MHz spectrometer.

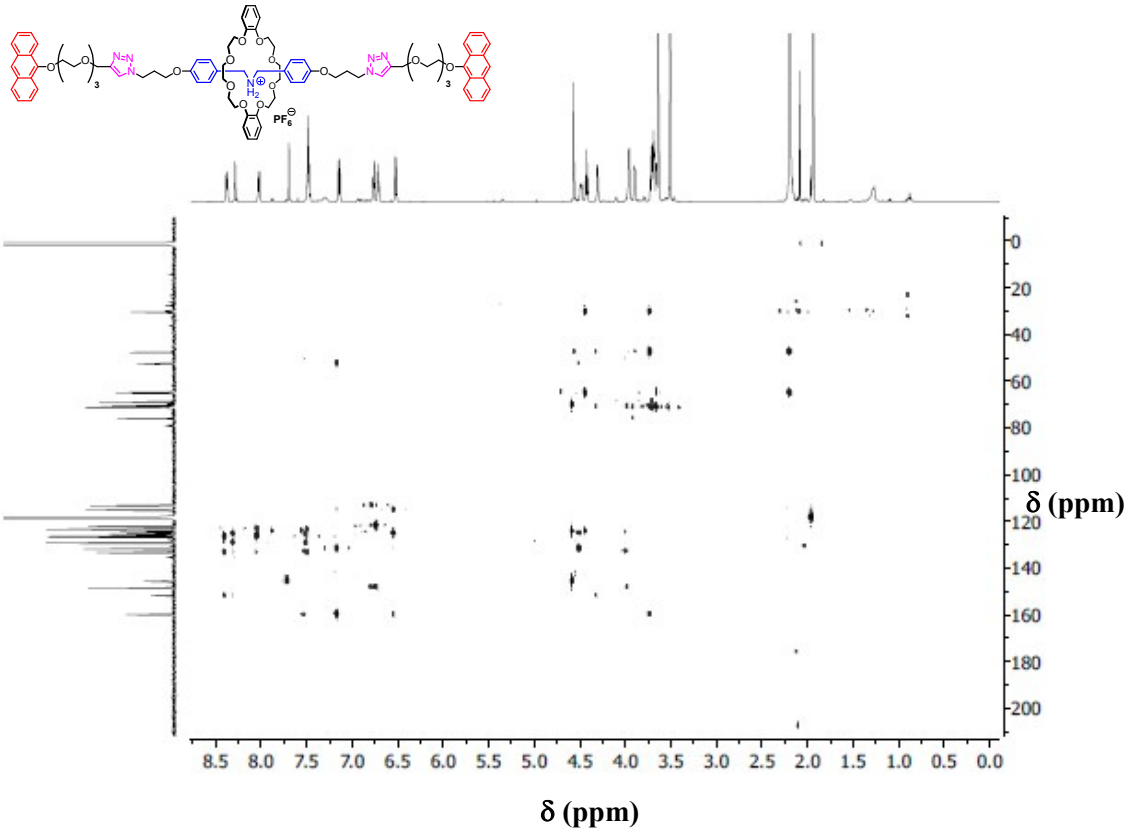


Figure S11c — ^{1}H-^{13}C Double quantum filtered HMBC NMR 2D spectrum of the [2]rotaxane **1**•PF_6 in CD_3CN at 298 K on a 600 MHz spectrometer.

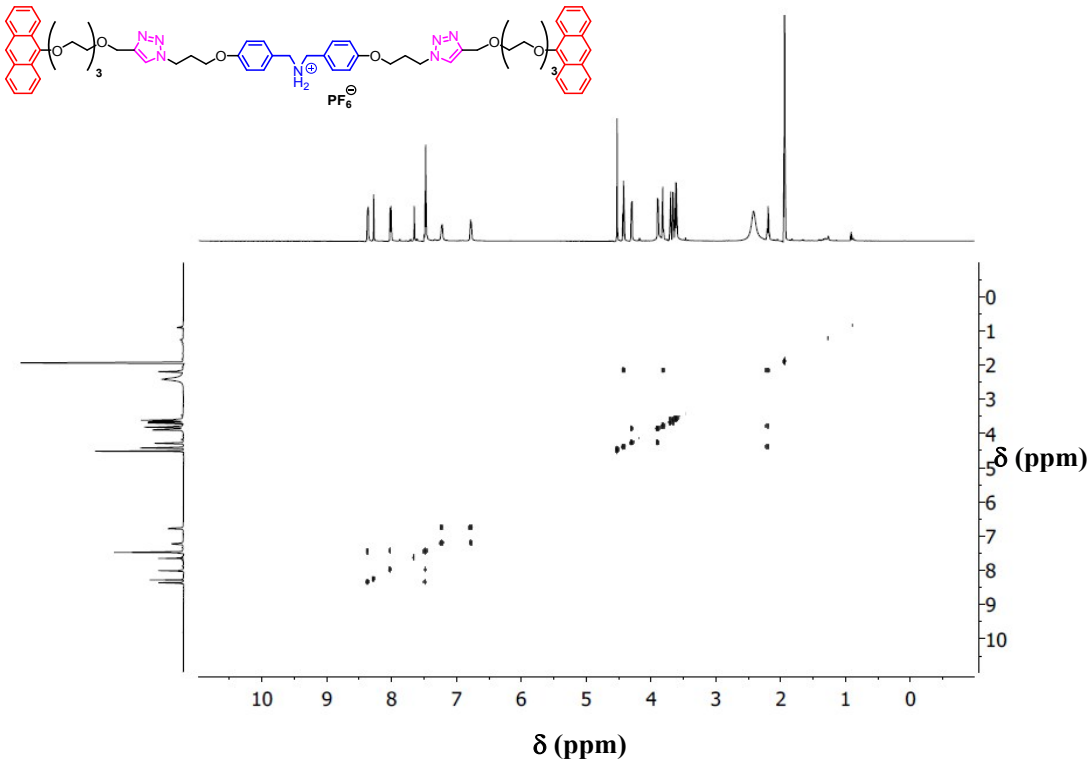


Figure S11d — ^{1}H-^{1}H Double quantum filtered COSY NMR 2D spectrum of the **8**•PF_6 in CD_3CN at 298 K on a 600 MHz spectrometer.

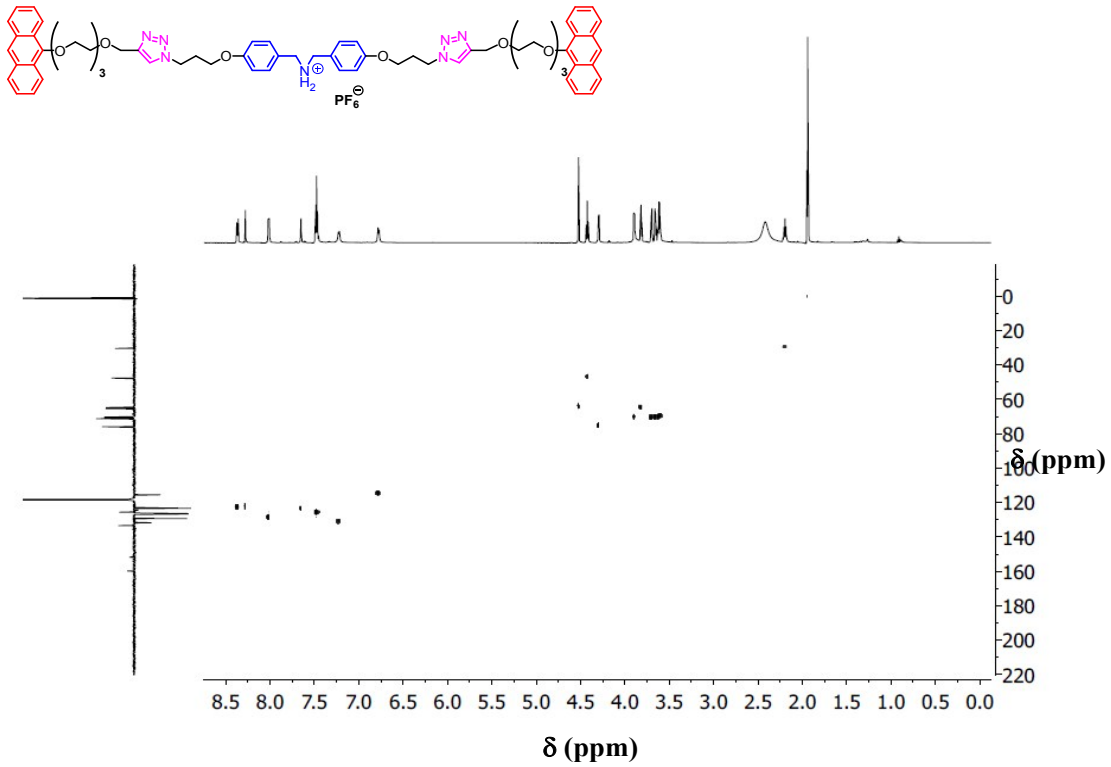


Figure S11e — ^{13}C Double quantum filtered HSQC NMR 2D spectrum of **8**•PF_6 in CD_3CN at 298 K on a 600 MHz spectrometer.

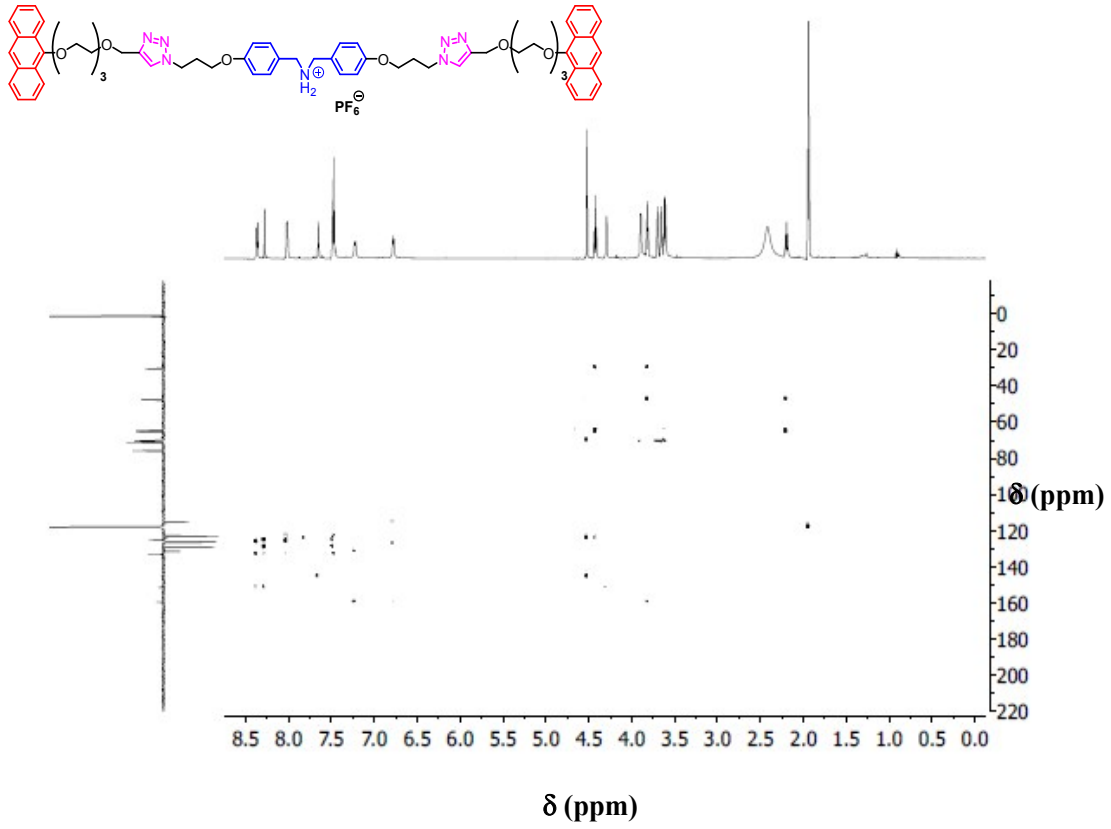


Figure S11f — ^{1}H-^{13}C Double quantum filtered HMBC NMR 2D spectrum of **8**•PF_6 in CD_3CN at 298 K on a 600 MHz spectrometer.