Supporting Information for

An electrochemically controlled supramolecular zip tie based on host-guest chemistry of CB[8]

Iago Neira,[a] Olaya Domarco,[a] Jose L. Barriada,[a] Paola Franchi,[b] Marco Lucarini,[b] Marcos D. García*[a] and Carlos Peinador*[a]

[a]Departamento de Química and Centro de Investigaciones, Científicas Avanzadas (CICA), Universidade da Coruña, Facultad de Ciencias, E-15071 A Coruña, Spain.

[b]Department of Chemistry "G. Ciamician" – Alma Mater Studiorum-University of Bologna, Via San Giacomo 11, Bologna, Italy

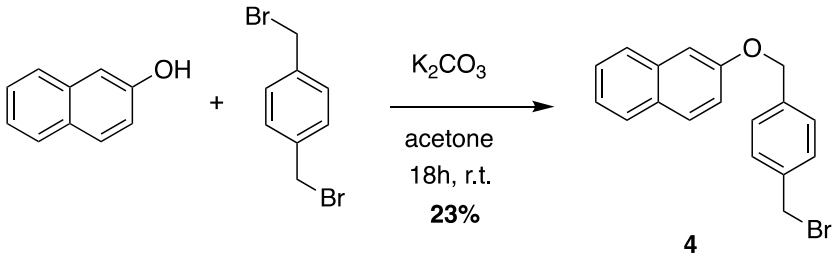
General

The chemicals used in this work were purchased from commercial suppliers and used without further purification. Compound **8**·PF_6 was prepared using a modified procedure.[1] The purity of the CB[8] was assessed as previously reported by Kaifer *et al.*[2] Milli-Q water was purified with a Millipore Gradient A10 apparatus. Merck 60 F254 foils were used for thin layer chromatography, and Merck 60 (230-400 mesh) silica gel was used for flash chromatography. NMR spectra were recorder on a Bruker Advance 400 or 500 MHz for ^{1}H, and 100 or 125 MHz for ^{13}C, equipped each other with a dual cryoprobe. The solvent for NMR experiments was deuterium oxide (D_2O), methanol (CD_3OD) and acetonitrile (CD_3CN). Mass spectrometry experiments were carried out in a LCQ-q-TOF Applied Biosystems QSTAR Elite spectrometer for low and high resolution ESI. UV/Vis spectra were recorded on a Jasco V-650 spectrometer. Microwave-assisted reactions were carried out in an Anton Paar Monowave 300 reactor operating at 2455 MHz in a sealed reaction vial using microwave power between 0-850 W. The samples were irradiated with the microwave power necessary for reaching the temperature of 150 °C heating with a "as fast as possible" protocol. The reaction mixture temperature was monitored via built-in IR sensor.

EPR measurements. Compounds **1**$^{4+}$- **3**$^{4+}$ were added to a water/CH_3CN (3/2, v/v) solution saturated with $Na_2S_2O_4$. The samples under nitrogen were immediately sealed in a capillary EPR tube. The EPR spectra were recorded on a Bruker ESP300 spectrometer equipped with an NMR gaussmeter for field calibration and Bruker ER033M field-frequency lock. The instrument settings were as follows: microwave power 0.79 mW, modulation amplitude 1.0 - 0.2 G, modulation frequency 100 kHz, scan time 180 s, 2 K data points.

Synthetic procedures:

Synthesis and characterization of 2-((4-(bromomethyl)benzyl)oxy)naphthalene **(4)**.



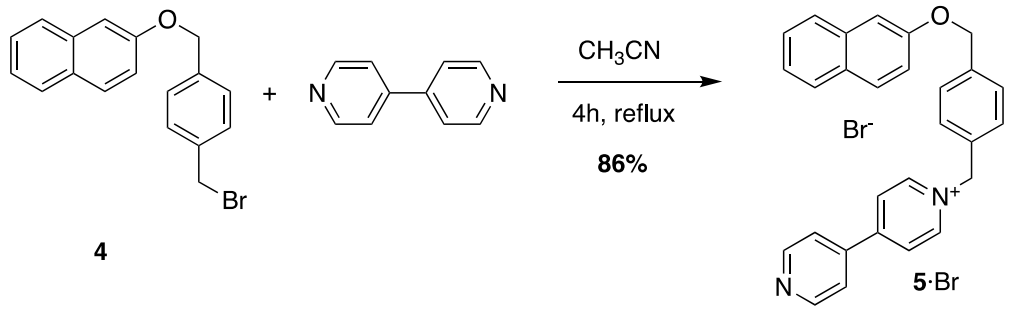
To a solution of 2-hydroxynaphthalene (1.4 g, 9.8 mmol) and K_2CO_3 (6.8 g, 50 mmol) in 60 mL of acetone α,α'-dibromo-*p*-xylene (2.0 g, 7.6 mmol) was added. The mixture was left under stirring at room temperature for 18 hours. After stirring for 20 hours at room temperature, the resulting mixture was filtered off and purified by column chromatography (SiO_2, EtOAc:Hex 1:7) to give **4** as a

[1] J. M. Weber, M. T. Rawls, V. J. MacKenzie, B. R. Limoges, C. M. Elliott, *J. Am. Chem. Soc.* 2007, **129**, 313.

[2] S. Yi and A. E. Kaifer, *J. Org. Chem*. 2011, **76**, 10275.

white solid (0.6 g, 23%). *^{1}H NMR (500 MHz, $CDCl_3$)* δ: 7.77 (m, 2H), 7.72 (d, *J* = 8.7 Hz, 1H) 7.43 (m, 5H), 7.32 (t, *J* = 7.48 Hz, 1H), 7.21 (m, 2H), 5.17 (s, 2H), 4.51 (s, 2H) ppm. *^{13}C NMR (125 MHz, $CDCl_3$)* δ: 156.73 (C), 137.69 (C), 137.40 (C), 134.60 (C), 129.67 (CH), 129.48 (C), 129.26 (CH), 128.05 (CH), 127.81 (CH), 126.94 (CH), 126.57 (CH), 123.93 (CH), 119.17 (CH), 107.30 (CH), 69.69 (CH_2), 33.30 (CH_2) ppm. *HRMS-ESI (m/z)*: calcd. $[M]^+$: 247.1117, found 247.1115.

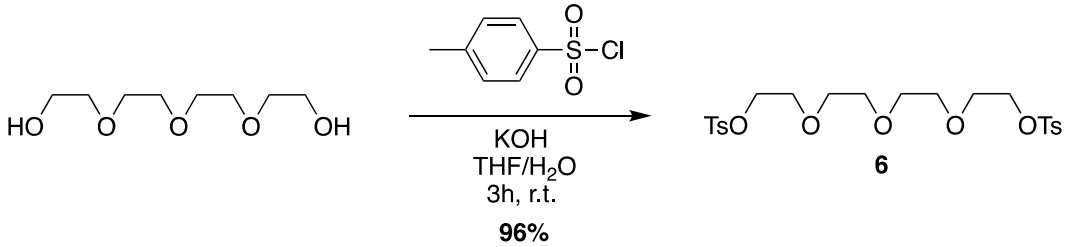
Synthesis and characterization of 1-(4-((naphthalen-2-yloxy)methyl)benzyl)-[4,4'-bipyridin]-1-ium bromide **(5·Br)**.



To a solution of **4** (470 mg, 1.40 mmol) in 50 mL of CH_3CN, 4,4'-bipyridine was added (560 mg, 3.60 mmol) and the mixture was left under reflux. After for 4 hours the mixture was cooled down to reach room temperature and 200 mL of Et_2O was added. The precipitate formed was filtered off and washed with 25 mL of toluene to give **5**·Br (480 mg, 70%) as a yellow solid. *^{1}H NMR (500 MHz, CD_3OD)* δ: 9.18 (d, *J* = 7.0 Hz, 2H), 8.83 (d, *J* = 6.3 Hz, 2H), 8.52 (d, *J* = 7.0 Hz, 2H), 7.97 (d, *J* = 6.3 Hz, 2H), 7.77 (d, *J* = 8.9 Hz, 2H), 7.72 (d, *J* = 7.3 Hz, 1H), 7.66 (d, *J* = 8.1 Hz, 2H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.41 (ddd, *J* = 8.1, 6.8, 1.3 Hz, 1H), 7.36 – 7.27 (m, 2H), 7.20 (dd, *J* = 9.0, 2.6 Hz, 1H), 5.92 (s, 2H), 5.27 (s, 2H) ppm. *^{13}C NMR (125 MHz, CD_3OD)* δ: 156.4 (C), 154.22 (C), 150.41 (CH), 145.10 (CH), 142.12 (C), 139.63 (C), 134.63 (C), 132.59 (C), 129.10 (CH), 128.99 (CH), 128.35 (CH), 127.19 (CH), 126.42 (CH), 126.01 (CH), 125.98 (CH), 123.42 (CH), 122.14 (CH), 118.36 (CH), 106.97 (CH), 68.74 (CH_2), 63.73 (CH_2) ppm. *HRMS-ESI (m/z)*: calcd: $[C_{28}H_{23}N_2O]^+$: 403.1804, found 403.1807.

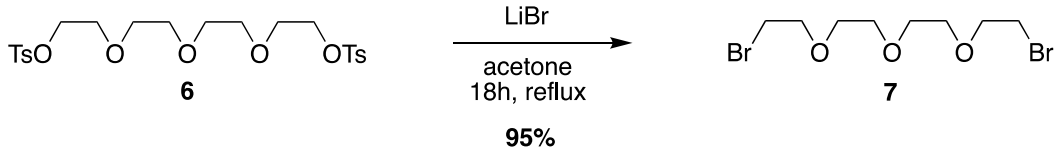
Finally, **5**·Br was dissolved in 100 mL of MeOH and KPF_6 was added until no more precipitation was observed. The MeOH was removed under reduced pressure to leave a yellow crude. The crude was suspended into 100 mL of H_2O and the yellow powder was filtered off to afford **5**·PF_6 (540 mg, 98%). *^{1}H NMR* (400 MHz, CD_3CN) δ: 8.82 (d, *J* = 6.3 Hz, 4H), 8.29 (d, *J* = 7.0 Hz, 2H), 7.80 (d, *J* = 9.3 Hz, 2H), 7.78 – 7.73 (m, 3H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 8.3 Hz, 2H), 7.46 – 7.42 (m, 1H), 7.38 – 7.30 (m, 2H), 7.20 (dd, *J* = 9.0, 2.6 Hz, 1H), 5.74 (s, 2H), 5.24 (s, 2H) ppm. *^{13}C NMR* (100 MHz, CD_3CN) δ: 157.07 (C), 155.24 (C), 151.76 (CH), 145.53 (CH), 141.72 (C), 139.93 (C), 135.17 (C), 133.13 (C), 130.10 (CH), 129.95 (CH), 129.27 (CH), 128.16 (CH), 127.26 (CH), 127.18 (CH), 126.89 (CH), 124.49 (CH), 122.44 (CH), 119.33 (CH), 107.94 (CH), 69.61 (CH_2), 64.44 (CH_2). *HRMS-ESI (m/z)*: calcd. $[C_{28}H_{23}N_2O]^+$: 403.1804, found 403.1807.

Synthesis and characterization of ((oxybis(ethane-2,1-diyl))bis(oxy))bis(ethane-2,1-diyl) bis(4-methylbenzenesulfonate) **(6)**.



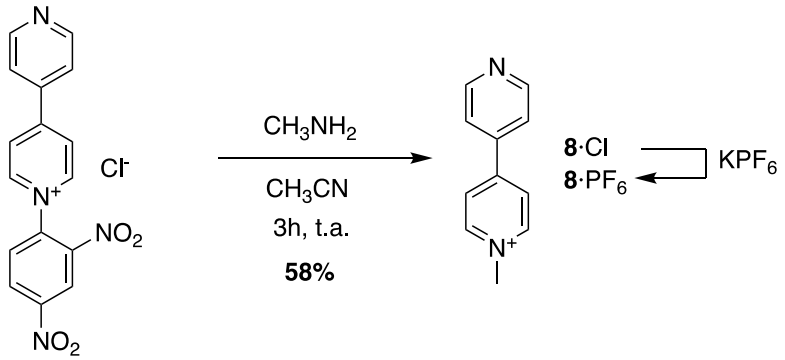
A solution of 2,2'-((oxybis(ethane-2,1-diyl))bis(oxy))bis(ethan-1-ol) (5.0 g, 25,7 mmol) and 4-methylbenzenesulfonyl chloride (14.7 g, 77.2 mmol) in 100 mL of THF was stirred for 15 minutes at 0°C in an ice bath. Then, a solution of KOH (10.1 g, 180.2 mmol) in 25 mL of H_2O was added dropwise for 1 hour. After the complete addition, the solution was left 2 h under stirring at room temperature. Consecutively, a mixture of 150 mL H_2O/Et_2O (1:3) was added and the organic phase was separated from the aqueous phase. The aqueous phase was extracted again with Et_2O (3 × 75 mL). The product-containing organic fractions were combined and washed with 200 mL of a saturate solution of NH_4Cl and 200 mL of H_2O. Finally, the organic phase was dried with $MgSO_4$ and the solvent was removed under reduced pressure to afford **6** as a yellow oil (12.4 g, 96%). *^{1}H NMR (500 MHz, $CDCl_3$)* δ: 7.79 (d, *J* = 8.4 Hz, 4H), 7.34 (d, *J* = 8.5 Hz, 4H), 4.15 (t, *J* = 5.4, 4.5 Hz, 4H), 3.67 (t, *J* = 5.4, 4.5 Hz, 4H), 3.56 (m, 8H), 2.44 (s, 3H) ppm. *^{13}C NMR (125 MHz, $CDCl_3$)* δ: 144.96 (C), 132.91 (C), 129.97 (CH), 128.12 (CH), 70.89 (CH_2), 70.70 (CH_2), 69.39 (CH_2), 68.84 (CH_2), 21.79 (CH_3) ppm. *HRMS-ESI (m/z)*: calcd. $[C_{22}H_{30}O_9S_2 + Na^+]^+$: 525.1223, found 525.1202.

Synthesis and characterization of 1-bromo-2-(2-(2-(2-bromoethoxy)ethoxy)ethoxy)ethane **(7)**.



A solution of **6** (10.0 g, 19.8 mmol) and LiBr (6.9 g, 79.5 mmol) in 100 mL of acetone was left under reflux for 18 hours. Then, the solvent was removed under reduced pressure and the crude was dissolved in 200 mL of a mixture of H_2O/Et_2O (1:1). The organic phase was separated from the aqueous phase and this one was extracted again with Et_2O (3 × 75 mL). The product-containing organic fractions were combined, dried with $MgSO_4$ and the solvent was removed under reduced pressure to afford **7** as a yellow oil (6.1 g, 95%). *^{1}H NMR (500 MHz, $CDCl_3$)* δ: 3.79 (t, *J* = 6.3 Hz, 4H), 3.65 (d, *J* = 1.1 Hz, 8H), 3.45 (t, *J* = 6.3 Hz, 4H) ppm. *^{13}C NMR (125 MHz, $CDCl_3$)* δ: 71.1 (CH_2), 70.64 (CH_2), 70.53 (CH_2), 30.36 (CH_2) ppm. *HRMS-ESI (m/z)*: calcd. $[C_8H_{17}Br_2O_3]^+$: 318.9538, found 318.9536.

Synthesis and characterization of 1-methyl-[4,4'-bipyridin]-1-ium hexafluorophosphate **(8)**.

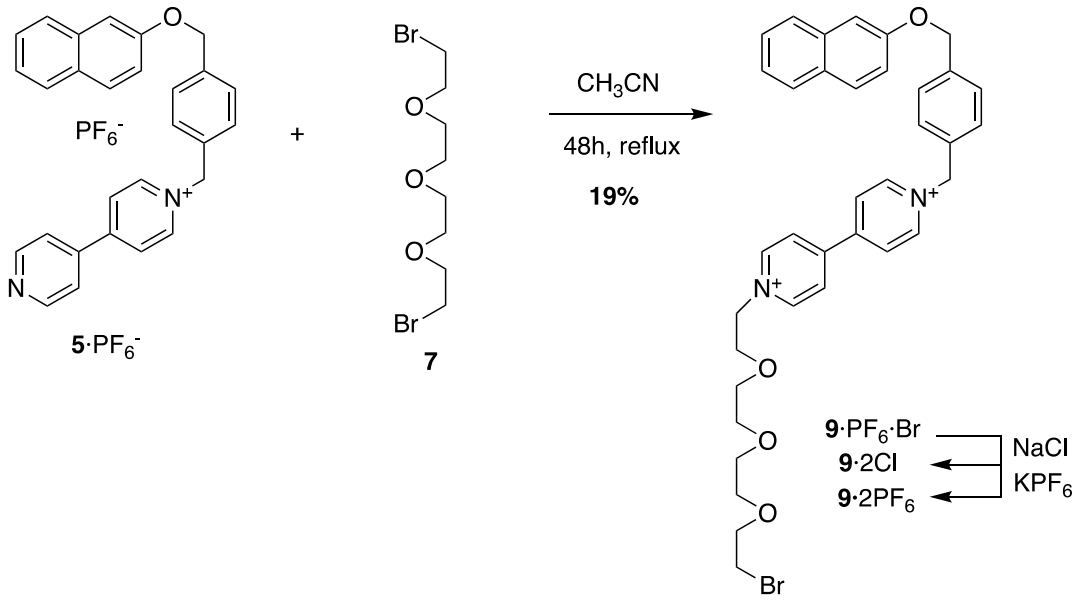


A solution of 1-(2,4-dinitrophenyl)-[4,4'-bipyridin]-1-ium[3] (3.2 g, 9 mmol) and methanamine (1.7 mL, 19.8 mmol) in a mixture 100 mL EtOH and 30 mL of H_2O was stirring at room temperature for 3 hours. Then, the solvent was removed under reduced pressure and the crude was dissolved in 200 mL of a mixture of H_2O/EtOAc (1:1). The organic phase was separated from the aqueous phase and this one was extracted again with EtOAc (3 × 75 mL). The product-containing organic fractions were

[3] D. Bongard, M. Möller, S. Nagaraja Rao, D. Corr, and L. Walder, *Helv. Chim. Acta,* **2005**, *88*, 3200-3209.

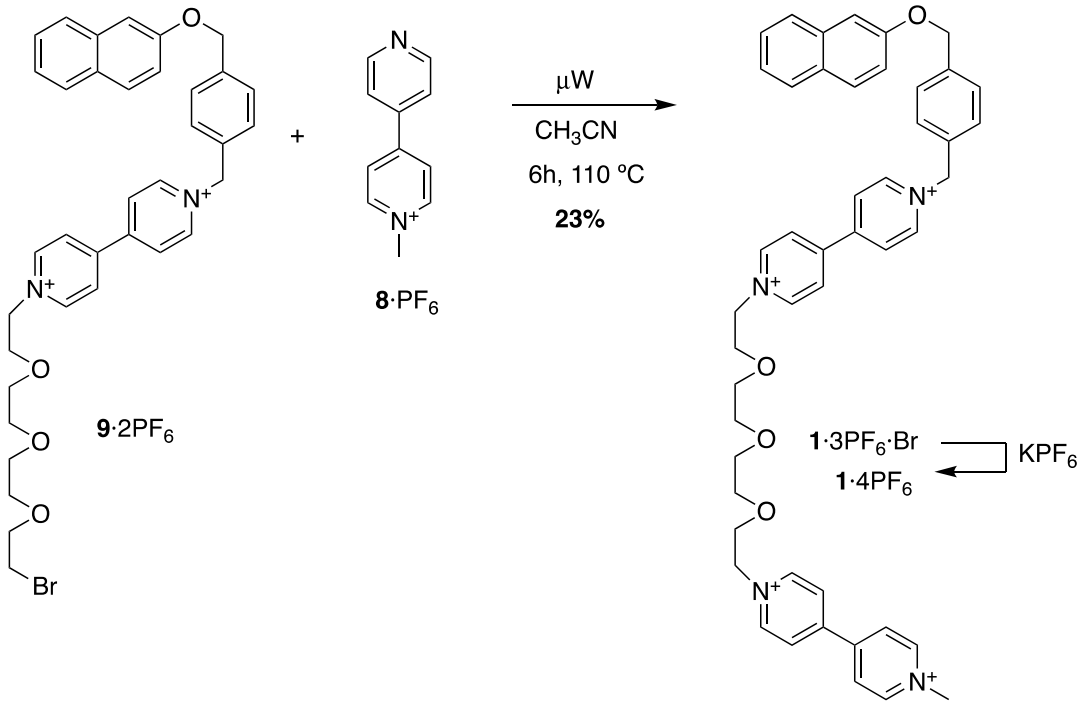
combined and KPF_6 was added until no more precipitation was observed. The solid was filtered off and washed with 50 mL of H_2O to leave **8**·PF_6 (1.64 g, 58%) as a brown solid. *^{1}H NMR (500 MHz, CD_3CN)* δ: 8.85 (d, *J* = 5.8 Hz, 2H), 8.71 (d, *J* = 7.7 Hz, 2H), 8.29 (d, *J* = 6.4 Hz, 2H), 7.79 (d, *J* = 6.2 Hz, 2H), 4.33 (s, 3H) ppm. *^{13}C NMR (125 MHz, CD_3CN)* δ: 155.14 (C), 152.48 (CH), 147.10 (CH), 142.50 (C), 126.68 (CH), 123.10 (CH), 49.23 (CH_3) ppm. *HRMS-ESI (m/z)*: calcd. $[C_{11}H_{11}N_2]^+$: 171.0916, found 171.0917.

Synthesis and characterization of 1-(2-(2-(2-(2-bromoethoxy)ethoxy)ethoxy)ethyl)-1'-(4-((naphthalen-2-yloxy)methyl)benzyl)-[4,4'-bipyridine]-1,1'-diium hexafluorophosphate (**9·2PF$_6$**).



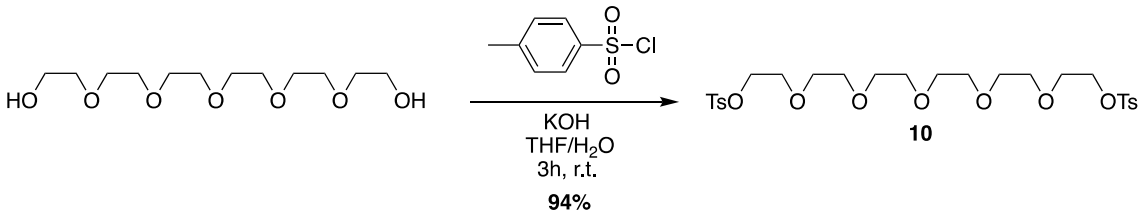
A solution of **5**·PF_6 (0.48 g, 0.88 mmol) and **7** (1.60 g, 4.44 mmol) in 50 mL of CH_3CN was left under reflux for 48 hours. Then, the solvent was removed under reduced pressure to leave a solid residue, which was subjected to flash chromatography (SiO_2, CH_3CN/NaCl (0.6 M)/MeOH 4/1/1). The product-containing fractions were combined and the solvents evaporated. The residue was suspended in EtOH and filtered off to remove NaCl. The EtOH was removed under reduced pressure to afford **9**·2Cl as a yellow oil. The yellow oil was dissolved in the minimal amount of H_2O and KPF_6 was added until no more precipitation was observed. The solid was filtered off and washed with 50 mL of H_2O to leave **9**·2PF_6 (155 mg, 19%) as an orange oil. *^{1}H NMR (400 MHz, CD_3CN)* δ: 8.94 (d, *J* = 6.9 Hz, 2H), 8.90 (d, *J* = 7.0 Hz, 2H), 8.32 (dd, *J* = 9.0, 7.0 Hz, 4H), 7.75 (d, *J* = 9.4 Hz, 2H), 7.71 (dd, *J* = 8.3, 1.1 Hz, 1H), 7.59 (d, *J* = 8.5 Hz, 2H), 7.50 (d, *J* = 8.3 Hz, 2H), 7.40 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 7.33 – 7.27 (m, 2H), 7.17 (dd, *J* = 9.0, 2.6 Hz, 1H), 5.79 (s, 2H), 5.21 (s, 2H), 4.76 – 4.69 (m, 2H), 3.97 – 3.91 (m, 2H), 3.69 (dd, *J* = 6.1, 5.3 Hz, 2H), 3.60 – 3.56 (m, 2H), 3.56 – 3.51 (m, 2H), 3.51 – 3.46 (m, 4H), 3.43 (dd, *J* = 6.1, 5.2 Hz, 2H) ppm. *^{13}C NMR (100 MHz, CD_3CN)* δ: 157.02 (C), 150.99 (C), 150.53 (C), 146.83 (CH), 146.13 (CH), 140.04 (C), 135.12 (C), 132.80 (C), 130.12 (CH), 130.07 (CH), 129.61 (C), 129.28 (CH), 128.13 (CH), 128.05 (CH), 127.32 (CH), 127.16 (CH), 127.16 (CH), 124.46 (CH), 119.32 (CH), 107.89 (CH), 71.25 (CH_2), 70.88 (CH_2), 70.54 (CH_2), 70.53 (CH_2), 70.49 (CH_2), 69.56 (CH_2), 69.11 (CH_2), 65.02 (CH_2), 62.23 (CH_2), 32.23 (CH_2) ppm. *HRMS-ESI (m/z)*: calcd. $[C_{36}H_{39}BrN_2O_4F_6P]^+$: 787.1729, found 787.1749; calcd. $[C_{36}H_{39}BrN_2O_4]^{+2}$: 321.1041 , found 321.1050.

Synthesis and characterization of 1-methyl-1'-(2-(2-(2-(2-(1'-(4-((naphthalen-2-yloxy)methyl)benzyl)-[4,4'-bipyridin]-1,1'-diium-1-yl)ethoxy)ethoxy)ethoxy)ethyl)-[4,4'-bipyridine]-1,1'-diium hexafluorophosphate **(1·4PF$_6$)**.



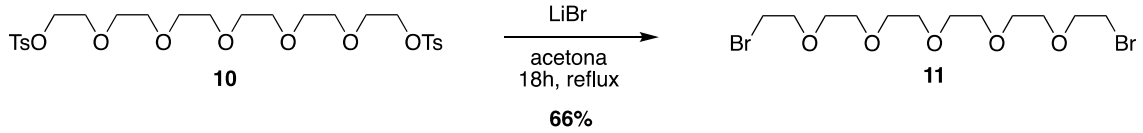
A mixture of **9**·2PF$_6$ (155 mg, 0.16 mmol) and **8**·PF$_6$ (525 mg, 1.6 mmol) in 7 mL of CH_3CN was heated up to 110 °C for 6 hours using microwave-assisted heating. Then, the solvent was removed under reduced pressure to leave a solid residue, which was subjected to flash chromatography (SiO_2) using two different eluent phases: CH_3CN/NaCl (0.6 M)/MeOH 4/1/1) to remove impurities and CH_3CN/KPF_6 (0.6 M)/MeOH 4/1/1) to elute the compound. The product-containing fractions were combined and the solvents evaporated. The obtained residue was then suspended in 100 mL H_2O and filtered off to remove excess KPF_6 and dissolved in CH_3CN. Finally, the CH_3CN was removed under reduced pressure to leave **1**·4PF$_6$ as a brown oil (51 mg, 23%). *^{1}H NMR (500 MHz, CD$_3$CN)* δ: 9.01 (d, *J* = 6.9 Hz, 2H), 8.91 (d, *J* = 5.7 Hz, 4H), 8.85 (d, *J* = 6.8 Hz, 2H), 8.41 – 8.34 (m, 8H), 7.81 (d, *J* = 8.8 Hz, 2H), 7.76 (d, *J* = 8.9 Hz, 1H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.57 – 7.52 (m, 2H), 7.46 (ddd, *J* = 8.2, 6.7, 1.2 Hz, 1H), 7.39 – 7.32 (m, 2H), 7.21 (dd, *J* = 9.0, 2.6 Hz, 1H), 5.84 (s, 2H), 5.26 (s, 2H), 4.76 (t, *J* = 4.9, 4.5 Hz, 4H), 4.40 (s, 3H), 3.95 (t, *J* = 4.6 Hz, 4H), 3.64 – 3.55 (m, 4H), 3.55 – 3.48 (m, 4H) ppm. *^{13}C NMR (125 MHz, CD$_3$CN)* δ: 157.45 (C), 151.42 (C), 151.15 (C), 151.11 (C), 150.58 (C), 147.49 (CH), 147.15 (CH), 147.15 (CH), 146.61 (CH), 140.47 (C), 135.56 (C), 133.26 (C), 130.54 (CH), 130.51 (CH), 130.06 (C), 129.73 (CH), 128.57 (CH), 128.49 (CH), 127.81 (CH), 127.79 (CH), 127.72 (CH), 127.68 (CH), 127.60 (CH), 124.91 (CH), 119.73 (CH), 108.32 (CH), 71.28 (CH_2), 70.85 (CH_2), 70.00 (CH_2), 69.55 (CH_2), 65.46 (CH_2), 62.67 (CH_2), 49.59 (CH_3) ppm. *HRMS-ESI (m/z)*: calcd. $[C_{47}H_{50}N_4O_4F_{18}P_3]^+$: 1169.2752, found 1169.2710; calcd. $[C_{47}H_{50}N_4O_4F_{12}P_2]^{+2}$: 512.1552, found 512.1531.

Synthesis and characterization of 3,6,9,12,15-pentaoxaheptadecane-1,17-diyl bis(4-methylbenzenesulfonate) **(10)**.



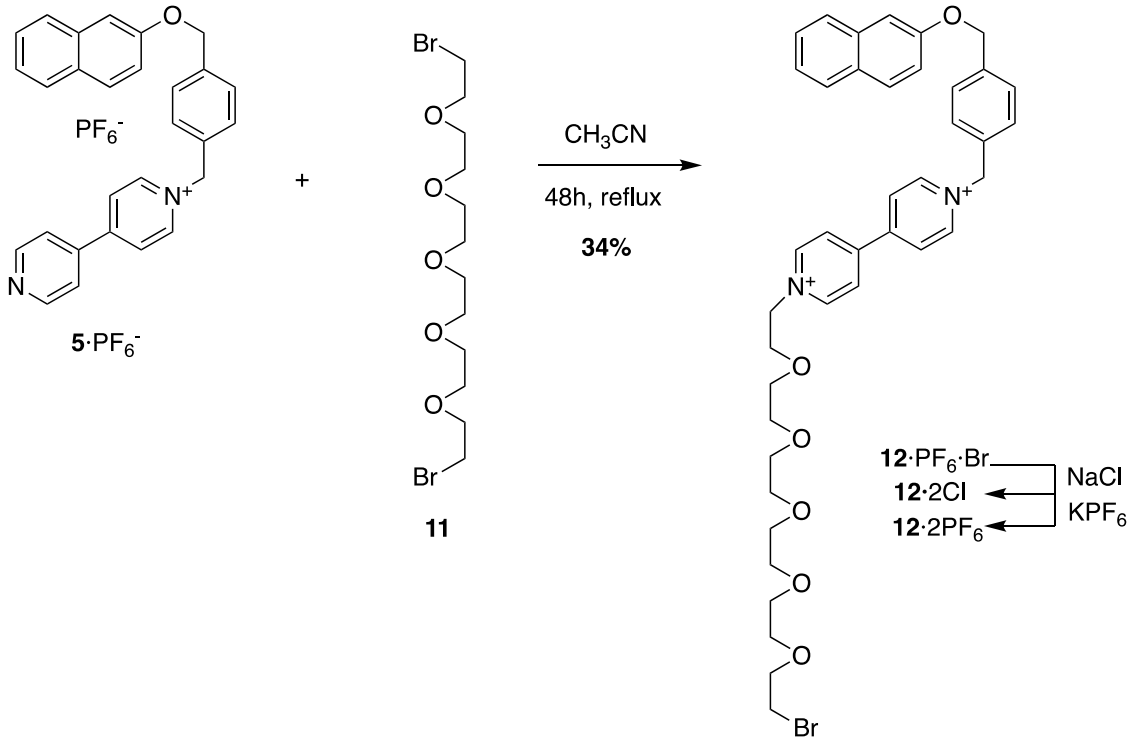
A solution of 3,6,9,12,15-pentaoxaheptadecane-1,17-diol (2.0 g, 7.1 mmol) and 4-methylbenzenesulfonyl chloride (4.0 g, 21.3 mmol) in 50 mL of THF was stirred for 15 minutes at 0 °C in an ice bath. Then, a solution of KOH (2.8 g, 49.7 mmol) in 25 mL of H_2O was added dropwise for 1 hour. After the complete addition, the solution was left 2 h under stirring at room temperature. Consecutively, a mixture of 150 mL H_2O/Et_2O (1:3) was added and the organic phase was separated from the aqueous phase. The aqueous phase was extracted again with Et_2O (3 × 75 mL). The product-containing organic fractions were combined and washed with 200 mL of a saturate solution of NH_4Cl and 200 mL of H_2O. Finally, the organic phase was dried with $MgSO_4$ and the solvent was removed under reduced pressure to afford **10** (3.9 g, 94%) as a yellow oil. *^{1}H NMR (500 MHz, $CDCl_3$)* δ: 7.78 (d, *J* = 8.4 Hz, 4H), 7.33 (d, *J* = 8.5 Hz, 4H), 4.18 – 4.09 (m, 4H), 3.70 – 3.64 (m, 4H), 3.61 (q, *J* = 1.3 Hz, 8H), 3.57 (s, 8H), 2.44 (s, 6H) ppm. *^{13}C NMR (125 MHz, $CDCl_3$)* δ: 144.86 (C), 132.83 (C), 129.85 (CH), 127.99 (CH), 70.71 (CH_2), 70.58 (CH_2), 70.52 (CH_2), 70.47 (CH_2), 69.29 (CH_2), 68.65 (CH_2), 21.69 (CH_3). *HRMS-ESI (m/z)*: calcd. $[C_{26}H_{39}O_{11}S_2]^+$: 591.1928, found 591.1966.

Synthesis and characterization of 1,17-dibromo-3,6,9,12,15-pentaoxaheptadecane **(11)**.



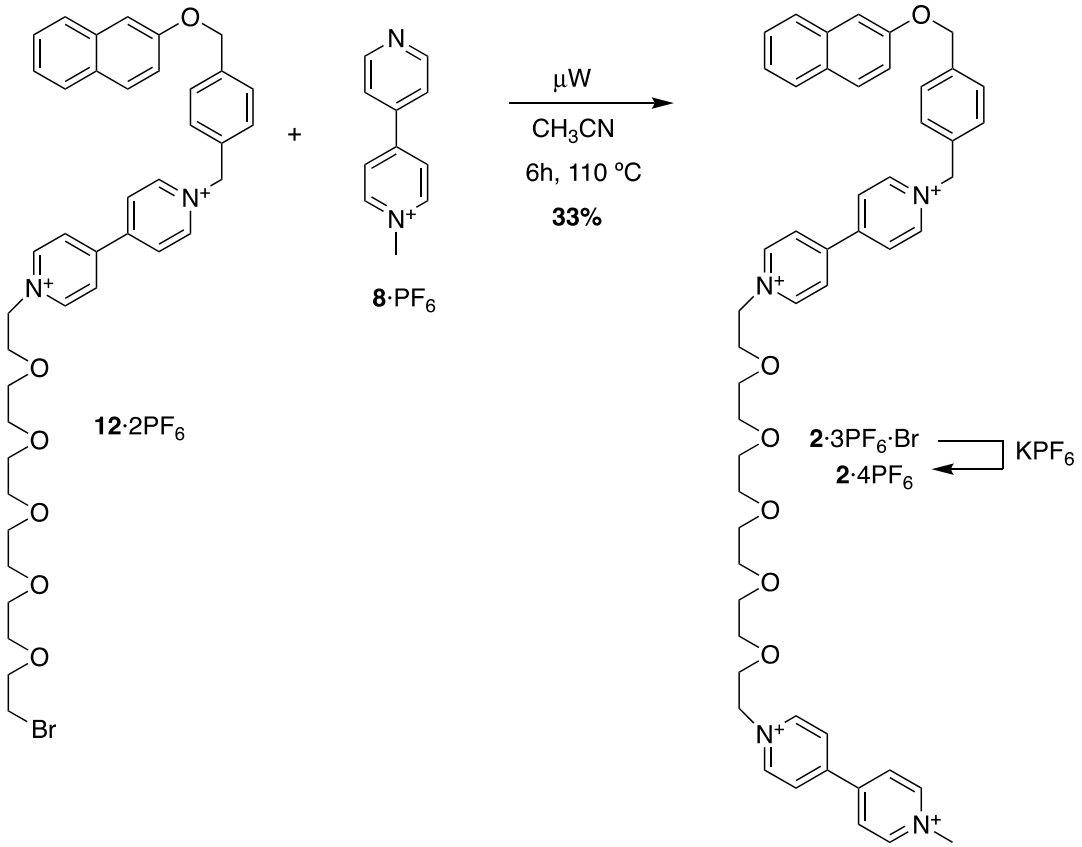
A solution of **10** (3.9 g, 6.7 mmol) and LiBr (2.3 g, 26.7 mmol) in 60 mL of acetone was left under reflux for 18 hours. Then, the solvent was removed under reduced pressure and the crude was dissolved in 200 mL of a mixture of H_2O/Et_2O (1:1). The organic phase was separated from the aqueous phase and this one was extracted again with Et_2O (3 × 75 mL). The product-containing organic fractions were combined, dried with $MgSO_4$ and the solvent was removed under reduced pressure to afford **11** (1.8 g, 66%) as a yellow oil. *^{1}H NMR (500 MHz, $CDCl_3$)* δ: 3.83 (t, J = 6.3 Hz, 4H), 3.72 – 3.65 (m, 16H), 3.49 (t, J = 6.3 Hz, 4H) ppm. *^{13}C NMR (125 MHz, $CDCl_3$)* δ: 71.19 (CH_2), 70.66 (CH_2), 70.58 (CH_2), 70.57 (CH_2), 70.52 (CH_2), 30.38 (CH_2) ppm. *HRMS-ESI (m/z)*: calcd. $[C_{12}H_{25}O_5Br_2]^+$: 407.0063, found 407.0083.

Synthesis and characterization of 1-(17-bromo-3,6,9,12,15-pentaoxaheptadecyl)-1'-(4-((naphthalen-2-yloxy)methyl)benzyl)-[4,4'-bipyridine]-1,1'-diium hexafluorophosphate **(12·2PF$_6$)**.



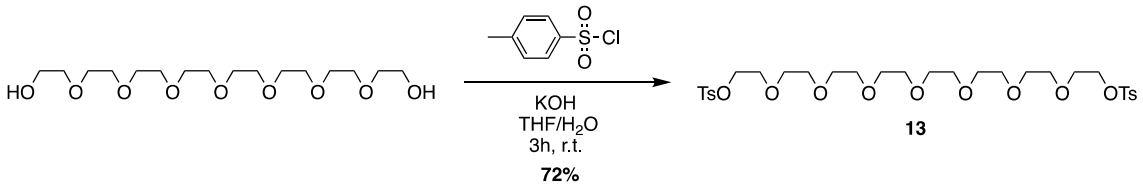
A solution of **5**·PF$_6$ (250 mg, 0.47 mmol) and **11** (950 mg, 2.34 mmol) in 25 mL of CH_3CN was left under reflux for 48 hours. Then, the solvent was removed under reduced pressure to leave a solid residue, which was subjected to flash chromatography (SiO_2, CH_3CN/NaCl (0.6 M)/MeOH 4/1/1). The product-containing fractions were combined and the solvents evaporated. The residue was suspended in EtOH and filtered off to remove NaCl. The EtOH was removed under reduced pressure to afford **12**·2Cl as a yellow oil. The yellow oil was dissolved in the minimal amount of H_2O and KPF_6 was added until no more precipitation was observed. The solid was filtered off and washed with 50 mL of H_2O to leave **12**·2PF$_6$ (163 mg, 34%) as an orange oil. *^{1}H NMR (500 MHz, CD$_3$CN)* δ: 8.99 (d, *J* = 7.0 Hz, 2H), 8.97 (d, *J* = 7.0 Hz, 2H), 8.42 (d, *J* = 7.0 Hz, 2H), 8.40 (d, *J* = 6.9 Hz, 2H), 7.80 (d, *J* = 8.7 Hz, 2H), 7.76 (dd, *J* = 8.3, 1.1 Hz, 1H), 7.64 (d, *J* = 8.3 Hz, 2H), 7.55 (d, *J* = 8.3 Hz, 2H), 7.45 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 7.40 – 7.31 (m, 2H), 7.21 (dd, *J* = 9.0, 2.6 Hz, 1H), 5.83 (s, 2H), 5.25 (s, 2H), 4.77 (t, *J* = 4.7 Hz, 2H), 3.98 (t, *J* = 4.9 Hz, 2H), 3.70 – 3.64 (m, 2H), 3.64 – 3.59 (m, 2H), 3.55 – 3.46 (m, 14H), 3.46 – 3.41 (m, 2H). *^{13}C NMR (125 MHz, CD$_3$CN)* δ: 156.04 (C), 150.05 (C), 149.43 (C), 145.95 (CH), 145.18 (CH), 139.05 (C), 134.16 (C), 131.94 (C), 129.17 (CH), 129.14 (CH), 128.64 (C), 128.35 (CH), 127.20 (CH), 127.15 (CH), 126.41 (CH), 126.31 (CH), 126.23 (CH), 123.53 (CH), 118.39 (CH), 106.85 (CH), 70.22 (CH_2), 69.80 (CH_2), 69.69 (CH_2), 69.68 (CH_2), 69.62 (CH_2), 69.61 (CH_2), 69.51 (CH_2), 69.50 (CH_2), 69.47 (CH_2), 68.55 (CH_2), 68.16 (CH_2), 64.03 (CH_2), 61.21 (CH_2), 31.20 (CH_2). *HRMS-ESI (m/z)*: calcd. $[C_{40}H_{47}N_2O_6F_6PBr]^+$: 875.2253, found 875.2252.

Synthesis and characterization of 1-methyl-1'-(17-(1'-(4-((naphthalen-2-yloxy)methyl)benzyl)-[4,4'-bipyridin]-1,1'-diium-1-yl)-3,6,9,12,15-pentaoxaheptadecyl)-[4,4'-bipyridine]-1,1'-diium (**2·4PF$_6$**).



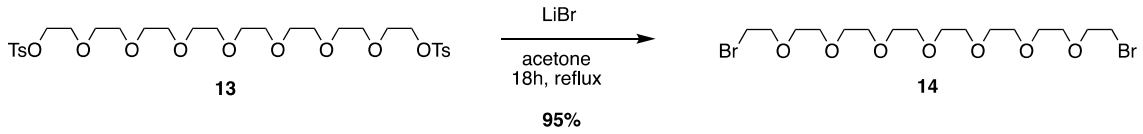
A mixture of **12**·2PF$_6$ (163 mg, 0.16 mmol) and **8**·PF$_6$ (505 mg, 1.6 mmol) in 7 mL of CH_3CN was heated up to 110 °C for 6 hours using microwave-assisted heating. Then, the solvent was removed under reduced pressure to leave a solid residue, which was subjected to flash chromatography (SiO_2) using two different eluent phases: CH_3CN/NaCl (0.6 M)/MeOH 4/1/1) to remove impurities and CH_3CN/KPF_6 (0.6 M)/MeOH 4/1/1) to elute the compound. The product-containing fractions were combined and the solvents evaporated. The obtained residue was then suspended in 100 mL H_2O and filtered off to remove excess KPF_6 and dissolved in CH_3CN. Finally, the CH_3CN was removed under reduced pressure to leave **2**·4PF$_6$ as a brown oil (74 mg, 33%). *^{1}H NMR (500 MHz, CD$_3$CN)* δ: 8.99 (d, *J* = 6.8 Hz, 2H), 8.95 – 8.89 (m, 4H), 8.84 (d, *J* = 6.9 Hz, 2H), 8.42 – 8.34 (m, 8H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.64 (d, *J* = 8.1 Hz, 2H), 7.55 (d, *J* = 8.3 Hz, 2H), 7.48 – 7.43 (m, 1H), 7.38 – 7.32 (m, 2H), 7.21 (dd, *J* = 8.9, 2.6 Hz, 1H), 5.84 (s, 2H), 5.25 (s, 2H), 4.74 (q, *J* = 5.0 Hz, 4H), 4.39 (s, 3H), 3.94 (q, *J* = 4.6 Hz, 4H), 3.61 – 3.45 (m, 16H). *^{13}C NMR (125 MHz, CD$_3$CN)* δ: 156.29 (C), 150.29 (C), 149.85 (C), 149.84 (C), 149.41 (C), 146.29 (CH), 146.03 (CH), 146.03 (CH), 145.42 (CH), 139.30 (C), 134.38 (C), 132.10 (C), 129.38 (CH), 129.35 (CH), 128.88 (C), 128.55 (CH), 127.40 (CH), 127.33 (CH), 126.63 (CH), 126.61 (CH), 126.54 (CH), 126.52 (CH), 126.44 (CH), 123.75 (CH), 118.57 (CH), 107.14 (CH), 70.10 (CH_2), 69.91 (CH_2), 69.87 (CH_2), 69.62 (CH_2), 68.83 (CH_2), 68.37 (CH_2), 64.29 (CH_2), 61.45 (CH_2), 48.43 (CH_3). *HRMS-ESI (m/z)*: calcd. $[C_{51}H_{58}N_4O_6F_{18}P_3]^+$: 1257.3276, found 1257.3273; calcd. $[C_{51}H_{58}N_4O_6F_{12}P_2]^{+2}$: 556.1814, found 556.1813; calcd. $[C_{51}H_{58}N_4O_6F_6P]^{+3}$: 322.4660, found 322.4662.

Synthesis and characterization of 3,6,9,12,15,18,21-heptaoxatricosane-1,23-diyl bis(4-methylbenzenesulfonate) **(13)**.



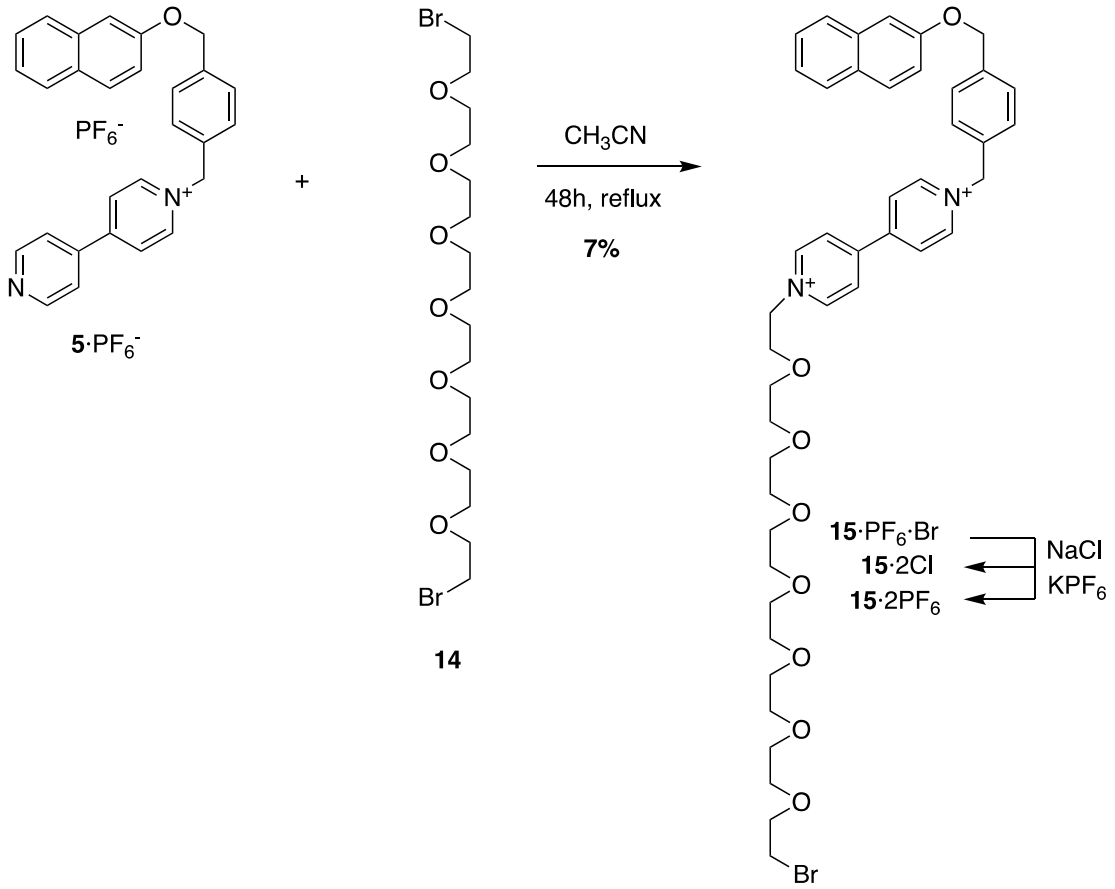
A solution of 3,6,9,12,15,18,21-heptaoxatricosane-1,23-diol (1.0 g, 2.7 mmol) and 4-methylbenzenesulfonyl chloride (1.5 g, 8.1 mmol) in 50 mL of THF was stirred for 15 minutes at 0°C in an ice bath. Then, a solution of KOH (1.1 g, 18.9 mmol) in 25 mL of H_2O was added dropwise for 1 hour. After the complete addition, the solution was left 2 h under stirring at room temperature. Consecutively, a mixture of 150 mL H_2O/CH_2Cl_2 (1:3) was added and the organic phase was separated from the aqueous phase. The aqueous phase was extracted again with CH_2Cl_2 (3 × 50 mL). The product-containing organic fractions were combined and washed with 200 mL of a saturate solution of NH_4Cl and 200 mL of H_2O. Finally, the organic phase was dried with $MgSO_4$ and the solvent was removed under reduced pressure to afford **13** as a yellow oil (1.3 g, 72%). *^{1}H NMR (500 MHz, $CDCl_3$)* δ: 7.79 (d, *J* = 8.3 Hz, 4H), 7.34 (d, *J* = 8.0 Hz, 4H), 4.21 – 4.12 (m, 4H), 3.71 – 3.65 (m, 4H), 3.66 – 3.60 (m, 16H), 3.58 (s, 8H), 2.44 (s, 6H) ppm. *^{13}C NMR (125 MHz, $CDCl_3$)* δ: 144.79 (C), 132.98 (C), 129.82 (CH), 127.98 (CH), 70.73 (CH_2), 70.58 (CH_2), 70.54 (CH_2), 70.49 (CH_2), 69.24 (CH_2), 68.67 (CH_2), 21.64 (CH_3) ppm. *HRMS-ESI (m/z)*: calcd. $[C_{30}H_{47}O_{13}S_2]^+$: 679.2452, found 679.2462.

Synthesis and characterization of 1,23-dibromo-3,6,9,12,15,18,21-heptaoxatricosane **(14)**.



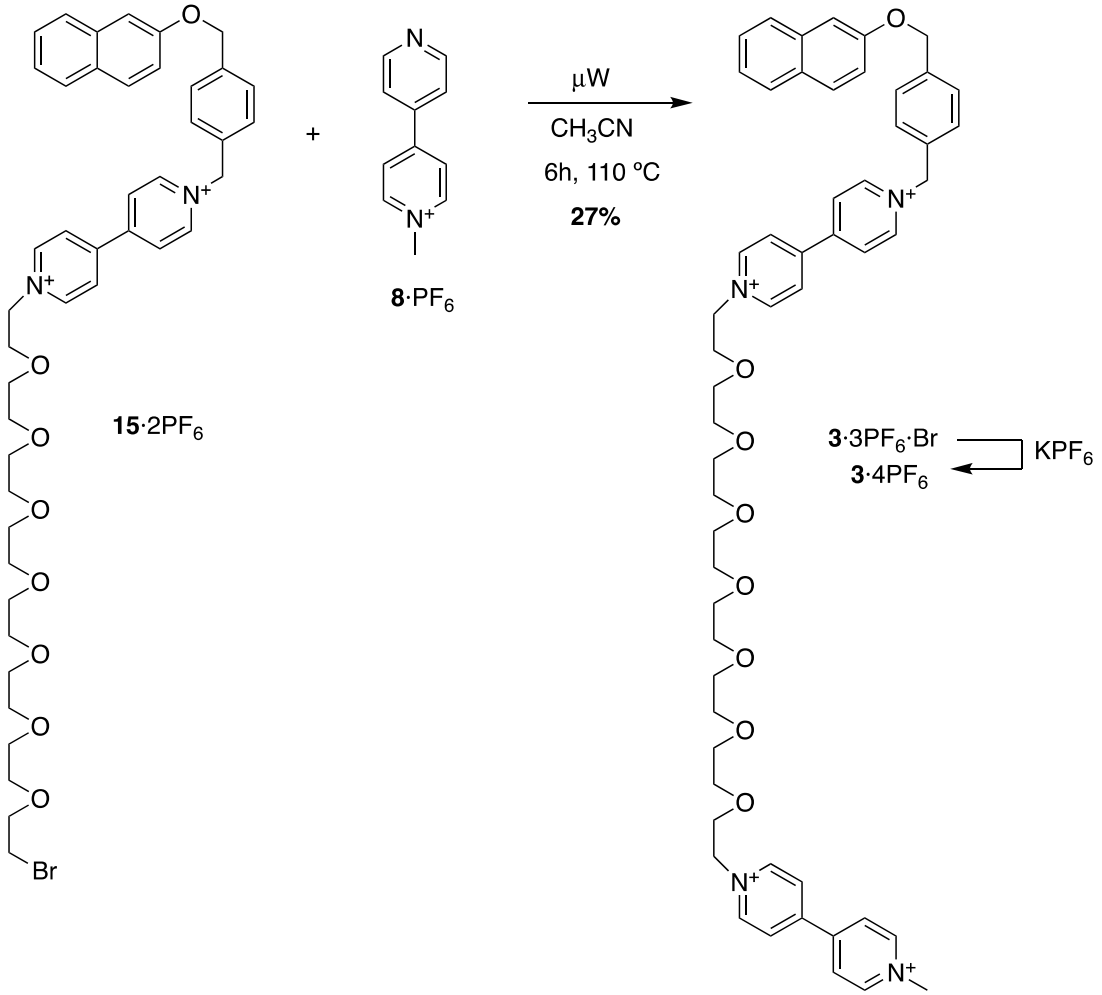
A solution of **13** (1.30 g, 1.9 mmol) and LiBr (0.67 g, 7.6 mmol) in 50 mL of acetone was left under reflux for 18 hours. Then, the solvent was removed under reduced pressure and the crude was dissolved in 100 mL of a mixture of H_2O/CH_2Cl_2 (1:1). The organic phase was separated from the aqueous phase and this one was extracted again with CH_2Cl_2 (3 × 50 mL). The product-containing organic fractions were combined, dried with $MgSO_4$ and the solvent was removed under reduced pressure to afford **14** (0.92 g, 95%) as a yellow oil. *^{1}H NMR (500 MHz, $CDCl_3$)* δ: 3.83 (t, *J* = 6.3 Hz, 4H), 3.69 – 3.65 (m, 24H), 3.49 (t, *J* = 6.3 Hz, 4H) ppm. *^{13}C NMR (125 MHz, $CDCl_3$)* δ: 71.21 (CH_2), 70.65 (CH_2), 70.58 (CH_2), 70.53 (CH_2), 30.32 (CH_2) ppm. *HRMS-ESI (m/z)*: calcd. $[C_{16}H_{33}O_7Br_2]^+$: 495.0587, found 495.0600.

Synthesis and characterization of 1-(23-bromo-3,6,9,12,15,18,21-heptaoxatricosyl)-1'-(4-((naphthalen-2-yloxy)methyl)benzyl)-[4,4'-bipyridine]-1,1'-diium hexafluorophosphate (**15·2PF$_6$**).



A solution of **5**·PF$_6$ (331 mg, 0.60 mmol) and **14** (1500 mg, 1.95 mmol) in 20 mL of CH_3CN was left under reflux for 48 hours. Then, the solvent was removed under reduced pressure to leave a solid residue, which was subjected to flash chromatography (SiO_2, CH_3CN/NaCl (0.6 M)/MeOH 4/1/1). The product-containing fractions were combined and the solvents evaporated. The residue was suspended in EtOH and filtered off to remove NaCl. The EtOH was removed under reduced pressure to afford **15**·2Cl as a yellow oil. The yellow oil was dissolved in the minimal amount of H_2O and KPF_6 was added until no more precipitation was observed. The solid was filtered off and washed with 50 mL of H_2O to leave **15**·2PF$_6$ (80 mg, 7%) as an orange oil. *^{1}H NMR (500 MHz, CD$_3$CN)* δ: 9.00 (d, *J* = 7.0 Hz, 2H), 8.95 (d, *J* = 7.0 Hz, 2H), 8.41 (t, *J* = 6.9 Hz, 2H), 7.81 (d, *J* = 9.0 Hz, 2H), 7.76 (dd, *J* = 8.3, 1.1 Hz, 1H), 7.64 (d, *J* = 8.3 Hz, 2H), 7.55 (d, *J* = 8.3 Hz, 2H), 7.46 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 7.39 – 7.33 (m, 2H), 7.22 (dd, *J* = 9.0, 2.6 Hz, 1H), 5.84 (s, 2H), 5.26 (s, 2H), 4.78 (t, *J* = 4.8 Hz, 2H), 3.97 (t, *J* = 4.5 Hz, 2H), 3.74 (t, *J* = 6.2, 5.2 Hz, 2H), 3.64 – 3.62 (m, 2H), 3.60 – 3.48 (m, 24H) ppm. *^{13}C NMR (125 MHz, CD$_3$CN)* δ: 159.21 (C), 153.17 (C), 152.75 (C), 149.03 (CH), 148.38 (CH), 142.25 (C), 137.33 (C), 135.06 (C), 132.30 (CH), 132.28 (CH), 131.83 (C), 131.49 (CH), 130.34 (CH), 130.30 (CH), 129.61 (CH), 129.45 (CH), 129.36 (CH), 126.67 (CH), 121.51 (CH), 110.09 (CH), 73.39 (CH_2), 72.97 (CH_2), 72.60 (CH_2), 72.53 (CH_2), 72.51 (CH_2), 72.50 (CH_2), 72.48 (CH_2), 72.41 (CH_2), 72.37 (CH_2), 72.35 (CH_2), 72.33 (CH_2), 71.75 (CH_2), 71.34 (CH_2), 67.23 (CH_2), 64.30 (CH_2), 34.22 (CH_2) ppm. *HRMS-ESI (m/z)*: calcd. $[C_{44}H_{55}N_2O_8F_6PBr]^+$: 963.2778, found 963.2787; calcd. $[C_{44}H_{55}N_2O_8Br]^{+2}$: 409.1565, found 409.1571.

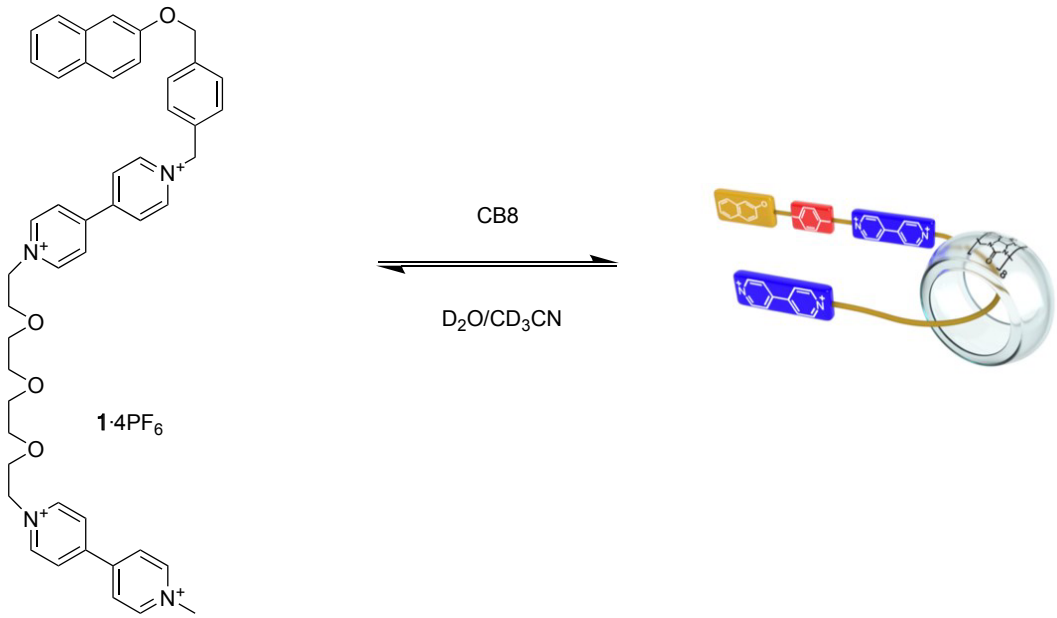
Synthesis and characterization of 1-methyl-1'-(23-(1'-(4-((naphthalen-2-yloxy)methyl)benzyl)-[4,4'-bipyridin]-1,1'-diium-1-yl)-3,6,9,12,15,18,21-heptaoxatricosyl)-[4,4'-bipyridine]-1,1'-diium hexafluorophosphate (**3·4PF$_6$**).



A mixture of **15**·2PF$_6$ (115 mg, 0.10 mmol) and **8**·PF$_6$ (329 mg, 1.0 mmol) in 5 mL of CH_3CN was heated up to 110 °C for 6 hours using microwave-assisted heating. Then, the solvent was removed under reduced pressure to leave a solid residue, which was subjected to flash chromatography (SiO_2) using two different eluent phases: CH_3CN/NaCl (0.6 M)/MeOH 4/1/1) to remove impurities and CH_3CN/KPF_6 (0.6 M)/MeOH 4/1/1) to elute the compound. The product-containing fractions were combined and the solvents evaporated. The obtained residue was then suspended in 100 mL H_2O and filtered off to remove excess KPF_6 and dissolved in CH_3CN. Finally, the CH_3CN was removed under reduced pressure to leave **3**·4PF$_6$ as a brown oil (42 mg, 27%). *^{1}H NMR (500 MHz, CD$_3$CN)* δ: 9.00 (d, *J* = 7.0 Hz, 2H), 8.93 (t, *J* = 6.8 Hz, 4H), 8.84 (d, *J* = 6.9 Hz, 2H), 8.42 – 8.36 (m, 8H), 7.80 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.75 (dd, *J* = 8.3, 1.0 Hz, 1H), 7.64 (d, *J* = 8.3 Hz, 2H), 7.55 (d, *J* = 8.3 Hz, 2H), 7.46 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 7.40 – 7.32 (m, 2H), 7.21 (dd, *J* = 9.0, 2.6 Hz, 1H), 5.84 (s, 2H), 5.25 (s, 2H), 4.79 – 4.72 (m, 4H), 4.39 (s, 3H), 3.95 (q, *J* = 4.9 Hz, 4H), 3.63 – 3.56 (m, 4H), 3.53 – 3.44 (m, 20H) ppm. *^{13}C NMR (125 MHz, CD$_3$CN)* δ: 156.19 (C), 150.20 (C), 149.72 (C), 149.70 (C), 149.31 (C), 146.23 (CH), 146.04 (CH), 146.01 (CH), 145.37 (CH), 139.19 (C), 134.30 (C), 132.12 (C), 129.32 (CH), 129.30 (CH), 128.79 (C), 128.51 (CH), 127.35 (CH), 127.30 (CH), 126.56 (CH), 126.50 (CH), 126.46 (CH), 126.44 (CH), 126.40 (CH), 123.70 (CH), 118.53 (CH), 106.97 (CH), 69.99 (CH_2), 69.75 (CH_2), 69.73 (CH_2), 69.56 (CH_2),

68.71 (CH_2), 68.34 (CH_2), 64.18 (CH_2), 61.35 (CH_2), 48.36 (CH_3) ppm. *HRMS-ESI (m/z)*: calcd. $[C_{55}H_{66}N_4O_8F_{12}P_2]^{+2}$: 600.2076, found 600.2094; calcd. $[C_{55}H_{66}N_4O_8F_6P]^{+3}$: 351.8168, found 351.8172.

Synthesis and characterization *of* **1**⊂CB[8]

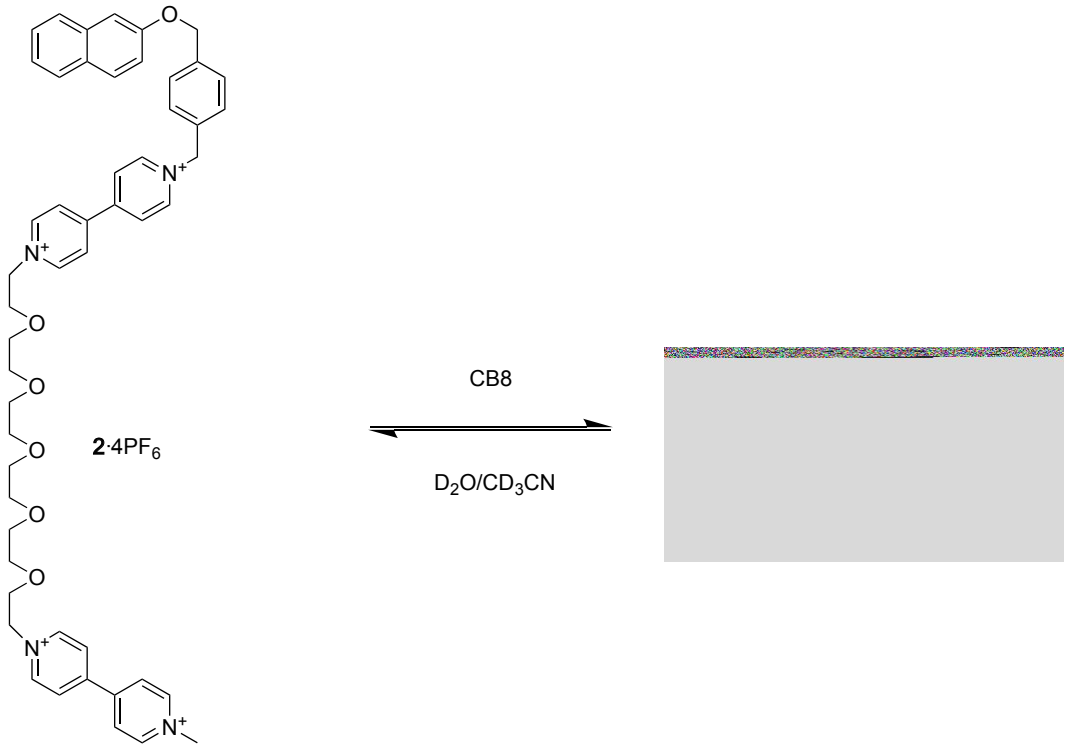


A solution of **1**·4PF_6 (6.5 mg, 0.005 mmol) in 2.5 mL of a mixture of H_2O/CH_3CN (3/2 v/v) was prepared and 1 equivalent of CB[8] was added. The mixture of the reaction was stirred for 10 minutes. A portion of 0.6 mL was taken from the resulting mixture and the solvent was evaporated under reduced pressure to leave the crude product. The solid was dissolved in D_2O/CD_3CN (3/2 v/v) (0.6 mL, 2 mM with respect to **1**·4PF_6). *^{1}H NMR (500 MHz, D_2O/CD_3CN (3/2)):* δ 9.46 (d, *J* = 6.3 Hz, 2H), 9.35 (d, *J* = 6.3 Hz, 2H), 9.06 (d, *J* = 6.4 Hz, 2H), 9.01 (t, *J* = 6.6 Hz, 4H), 8.94 (d, *J* = 6.3 Hz, 2H), 8.86 (d, *J* = 6.3 Hz, 2H), 8.83 – 8.77 (m, 8H), 8.18 (dd, *J* = 9.0, 4.2 Hz, 2H), 8.11 (d, *J* = 8.3 Hz, 1H), 7.90 (m, 4H), 7.82 (t, *J* = 7.6 Hz, 1H), 7.73 (t, *J* = 7.5 Hz, 1H), 7.68 (s, 1H), 7.58 (dd, *J* = 9.0, 2.5 Hz, 1H), 6.21 (s, 2H), 6.01 (dd, *J* = 25.3, 15.2 Hz, 16H), 5.70 (s, 16H), 5.58 (s, 1H), 4.45 (t, *J* = 14.9 Hz, 16H), 3.93 (s, 3H), 3.36 (bs, 4H), 2.54 (bs, 2H), 2.47 – 2.36 (bs, 2H), 2.19 – 2.14 (bs, 2H), 2.11 (bs, 2H) ppm. *^{13}C NMR (125 MHz, CD_3CN)*: δ 155.77 (C), 149.85 (C), 148.91 (C), 147.55 (C), 147.13 (CH), 146.92 (CH), 146.16 (CH), 145.97 (CH), 145.88 (CH), 145.46 (C), 137.76 (C), 134.99 (C), 132.29 (C), 130.41 (CH), 129.30 (CH), 129.27 (C), 128.50 (C), 127.80 (CH), 127.26 (CH), 127.16 (CH), 126.68 (CH), 126.46 (CH), 126.34 (CH), 125.98 (CH), 125.81 (CH), 123.82 (CH), 107.06 (CH), 102.04 (CH), 72.84 (CH_2), 71.25 (CH), 69.43 (CH_2), 69.30 (CH_2), 69.21 (CH_2), 68.64 (CH_2), 66.92 (CH_2), 66.64 (CH_2), 64.14 (CH_2), 61.11 (CH_2), 53.53 (CH_2), 47.80 (CH_3).

The solid was dissolved in CD_3CN (0.6 mL, 2 mM with respect to **1**·4PF_6). *^{1}H NMR (500 MHz, CD_3CN)* δ: 9.01 (d, *J* = 7.0 Hz, 2H), 8.92 (d, *J* = 7.0 Hz, 2H), 8.90 – 8.86 (m, 4H), 8.70 (d, *J* = 7.0 Hz, 2H), 8.67 (d, *J* = 7.1 Hz, 2H), 8.62 (d, *J* = 7.2 Hz, 2H), 8.58 (d, *J* = 7.2 Hz, 2H), 7.84 (d, *J* = 8.9 Hz, 2H), 7.79 (d, *J* = 8.3 Hz, 1H), 7.59 (s, 4H), 7.48 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 7.42 – 7.35 (m, 2H), 7.25 (dd, *J* = 9.0, 2.5 Hz, 1H), 5.84 (s, 2H), 5.77 (dd, *J* = 25.2, 14.9 Hz, 16H), 5.29 (s, 16H), 5.25 (s, 2H), 4.45– 4.55 (s, 2H), 4.40 (s, 3H), 4.08 (dd, *J* = 15.0, 10.7 Hz, 16H), 3.11 – 2.91 (m, 2H), 1.75 (s, 4H) ppm. *^{13}C NMR (125 MHz, CD_3CN)* δ: 156.36 (C), 155.64 (C), 155.57 (C), 148.46 (C), 148.26 (C), 147.05 (C), 146.76 (CH), 146.71 (CH), 145.91 (CH), 145.87 (CH), 138.95 (C), 134.41 (C), 132.39 (C), 129.74 (CH), 129.40 (CH), 128.89 (C), 128.57 (C), 128.20 (CH), 127.47 (CH), 127.23 (CH), 126.54 (CH), 126.54 (CH), 126.52 (CH), 126.09 (CH), 125.83 (CH), 123.84 (CH), 118.65 (CH), 107.16 (CH), 72.19 (CH_2), 71.31 (CH), 70.14 (CH_2), 70.11 (CH_2), 68.93 (CH_2), 67.26 (CH_2), 67.21 (CH_2), 63.82 (CH_2), 63.82 (CH_2), 60.98 (CH_2), 60.85 (CH_2), 53.08

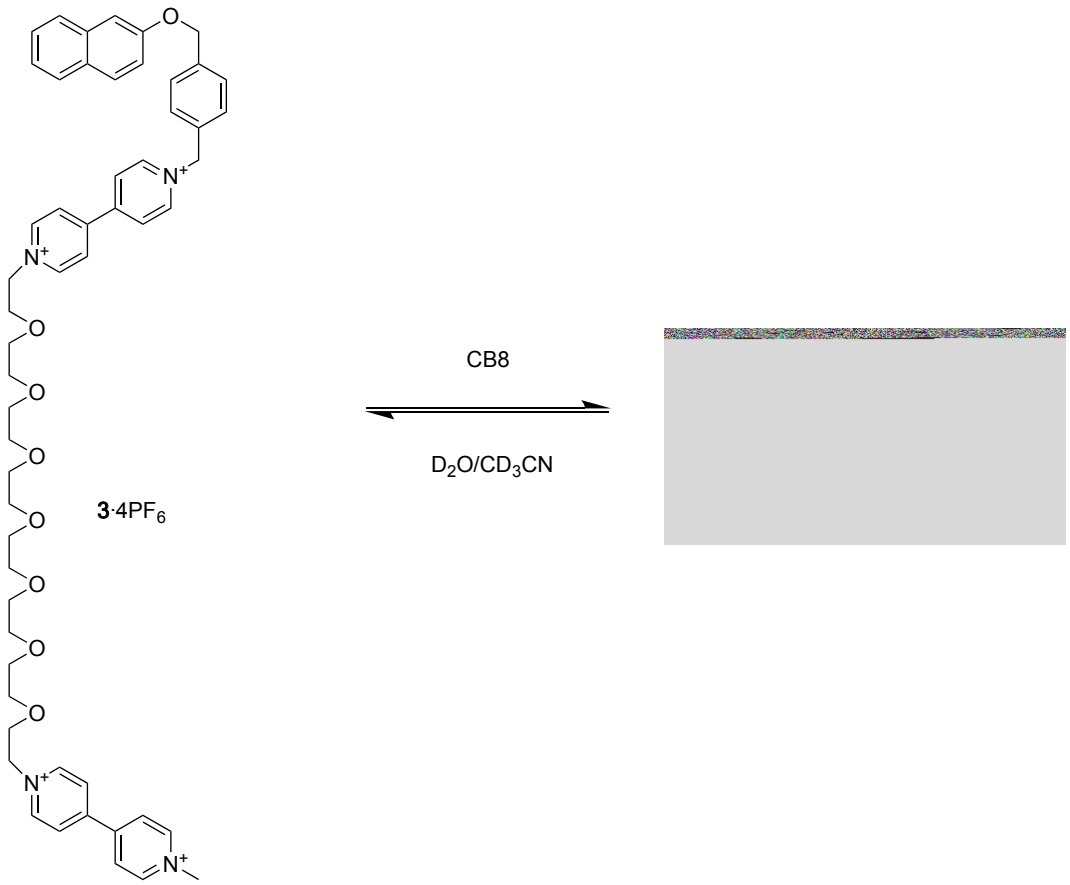
(CH_2), 53.03 (CH_2), 47.93 (CH_3) ppm. *HRMS-ESI (m/z)*: calcd. $[C_{95}H_{98}N_{36}O_{20}F_{12}P_2]^{+2}$: 1176.3515, found 1176.3417; calcd. $[C_{95}H_{98}N_{36}O_{20}F_6P]^{+3}$: 735.9127, found 735.9092.

Synthesis and characterization *of* **2**⊂CB[8]



A solution of **2**·$4PF_6$ (7.0 mg, 0.005 mmol) in 2.5 mL of a mixture of H_2O/CH_3CN (3/2 v/v) was prepared and 1 equivalent of CB[8] was added. The mixture of the reaction was stirred for 10 minutes. A portion of 0.6 mL was taken from the resulting mixture and the solvent was evaporated under reduced pressure to leave the crude product. The solid was dissolved in CD_3CN (0.6 mL, 2 mM with respect to **2**·$4PF_6$). *^{1}H NMR (500 MHz, CD_3CN)*: δ 8.99 (d, *J* = 6.5 Hz, 2H), 8.82 (m, 8H), 8.74 (d, *J* = 6.7 Hz, 2H), 8.57 (d, *J* = 6.5 Hz, 2H), 8.53 (d, *J* = 6.3 Hz, 2H), 7.83 (d, *J* = 8.3 Hz, 2H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.58 (s, 5H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.41 – 7.34 (m, 2H), 7.24 (d, *J* = 9.0 Hz, 1H), 5.81 (d, *J* = 6.4 Hz, 2H), 5.76 (d, *J* = 15.0 Hz, 16H), 5.28 (d, *J* = 3.0 Hz, 2H), 5.25 (s, 16H), 4.72 (s, 3H), 4.67 (m, 2H), 4.38 (m, 2H), 4.02 (d, *J* = 15.0 Hz, 16H), 3.68 (m, 2H), 3.41 (m, 2H), 3.27 (m, 2H), 3.15 (m, 2H), 2.93 (m, 2H), 2.90 (m, 2H), 2.66 (m, 2H), 2.63 (m, 2H), 2.36 (m, 2H), 2.29 (overlap) ppm. *^{13}C NMR (125 MHz, CD_3CN)*: δ 156.63 (C), 148.01 (CH), 147.27 (CH), 147.14 (CH), 146.39 (CH), 133.15 (CH), 131.58 (CH), 130.56 (CH), 129.87 (CH), 129.40 (CH), 128.87 (CH), 128.30 (CH), 127.70 (CH), 127.24 (CH), 125.00 (CH), 119.78 (CH), 108.34 (CH), 72.46 (CH), 72.20 (CH_2), 71.62 (CH_2), 71.29 (CH_2), 70.89 (CH_2), 70.49 (CH_2), 70.10 (CH_2), 69.32 (CH_2), 65.04 (CH_2), 64.24 (CH_2), 63.62 (CH_2), 55.22 (CH_2), 49.66 (CH_3). *HRMS-ESI (m/z)*: calcd. $[C_{99}H_{106}N_{36}O_{22}F_{12}P_2]^{+2}$: 1220.3777, found 1220.3758; calcd. $[C_{99}H_{106}N_{36}O_{22}F_6P]^{+3}$: 765.2635, found 765.2657.

Synthesis and characterization *of* **3**⊂CB[8]



A solution of **3**·4PF_6 (7.5 mg, 0.005 mmol) in 2.5 mL of a mixture of H_2O/CH_3CN (3/2 v/v) was prepared and 1 equivalent of CB[8] was added. The mixture of the reaction was stirred for 10 minutes. A portion of 0.6 mL was taken from the resulting mixture and the solvent was evaporated under reduced pressure to leave the crude product. The solid was dissolved in CD_3CN (0.6 mL, 2 mM with respect to **3**·4PF_6).*^{1}H NMR (500 MHz, CD_3CN):* δ 9.03 (d, *J* = 6.4 Hz, 2H), 8.98 (d, *J* = 6.4 Hz, 2H), 8.89 (d, *J* = 6.5 Hz, 2H), 8.86 (d, *J* = 6.5 Hz, 2H), 8.71 (d, *J* = 6.3 Hz, 2H), 8.59 (m, 2H), 8.48 (d, *J* = 6.3 Hz, 2H), 8.44 (m, 2H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.78 (d, *J* = 8.3 Hz, 1H), 7.58 (s, 4H), 7.48 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 7.40 – 7.36 (m, 1H), 7.35 (d, *J* = 2.5 Hz, 1H), 7.23 (dd, *J* = 8.9, 2.6 Hz, 1H), 5.83 (s, 2H), 5.76 (d, *J* = 14.9 Hz, 16H), 5.24 (s, 16H), 4.74 (m, 2H), 4.63 (m, 2H), 4.37 (s, 3H), 4.01 (d, *J* = 15.0 Hz, 16H), 3.78 (m, 2H), 3.52 (m, 2H), 3.45 (m, 2H), 3.29 (m, 2H), 3.23 (m, 2H), 3.13 (m, 2H), 3.09 (m, 2H), 2.92 (m, 4H), 2.82 (m, 6H), 2.74 (m, 2H), 2.55 (m, 2H).*^{13}C NMR (125 MHz, CD_3CN)*: δ 156.09 (C), 155.25 (C), 149.14 (C), 148.70 (C), 148.53 (C), 148.24 (CH), 146.76 (CH), 146.25 (CH), 145.99 (CH), 145.17 (CH), 138.67 (CH), 134.17 (CH), 132.39 (CH), 129.40 (CH), 129.16 (CH), 128.64 (CH), 128.06 (CH), 127.40 (CH), 127.25 (CH), 126.72 (CH), 126.33 (CH), 123.62 (CH), 71.96 (CH), 69.92 (CH_2), 69.53 (CH_2), 69.32 (CH_2), 69.25 (CH_2), 69.15 (CH_2), 69.10 (CH_2), 68.96 (CH_2), 68.71 (CH_2), 68.69 (CH_2), 68.41 (CH_2), 68.18 (CH_2), 68.00 (CH_2), 66.26 (CH_2), 63.59 (CH_2), 61.83 (CH_2), 61.16 (CH_2), 54.15 (CH_2), 52.24 (CH_2), 47.82 (CH_3) ppm. *HRMS-ESI (m/z)*: calcd. $[C_{103}H_{114}N_{36}O_{24}F_{12}P_2]^{+2}$: 1264.4039, found 1264.4003; calcd. $[C_{103}H_{114}N_{36}O_{24}F_6P]^{+3}$: 794.6144, found 794.6138.

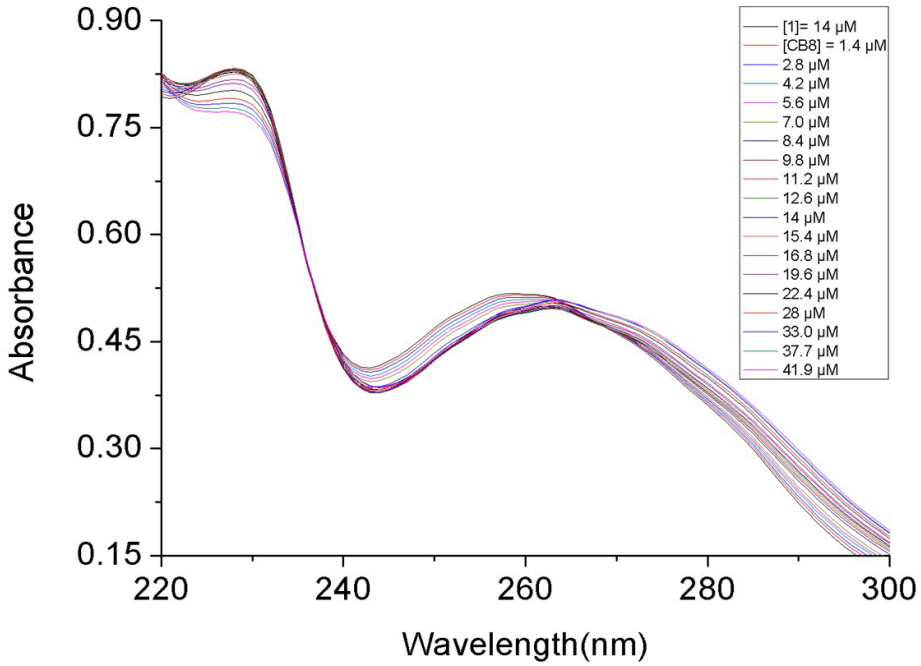


Figure S1 UV-VIS Titration data of **1**·4PF_6 with increasing amounts of CB[8] in H_2O/CH_3CN (3/2 v/v).

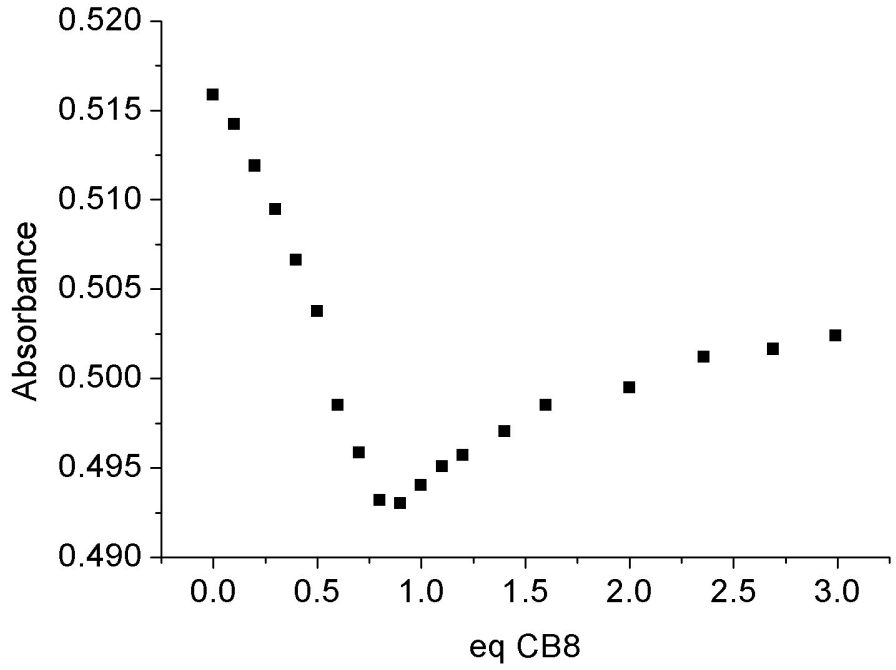


Figure S2 UV-VIS Representation of titration **1**·4PF_6 and CB[8] at λ_{obs}= 261 nm in H_2O/CH_3CN (3/2 v/v).

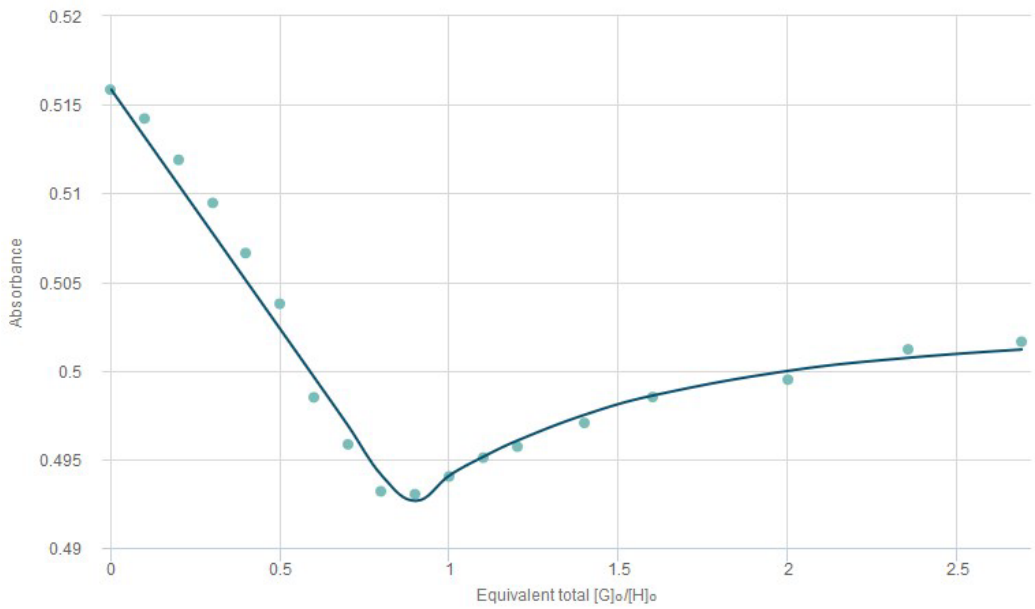


Figure S3 Fitting of titration of **1**·4PF_6 and CB[8] at λ_{obs}= 261 nm using supramolecular.org in H_2O/CH_3CN (3/2 v/v).

x1: Guest concentration / M	x2:Host concentration / M	x3: H/G equivalent total	y1: 261 nm
0.000014	0	0	0.51585
0.000014	0.0000014	0.1	0.51422
0.000014	0.0000028	0.2	0.51189
0.000014	0.0000042	0.3	0.50946
0.000014	0.0000056	0.4	0.50663
0.000014	0.000007	0.5	0.50377
0.000014	0.0000084	0.6	0.49849
0.000014	0.0000098	0.7	0.49584
0.000014	0.0000112	0.8	0.49319
0.000014	0.0000126	0.9	0.49303
0.000014	0.000014	1	0.49403
0.000014	0.0000154	1.1	0.49509
0.000014	0.0000168	1.2	0.49571
0.000014	0.0000196	1.4	0.49705
0.000014	0.0000224	1.6	0.49851
0.000014	0.000028	2	0.49949
0.000014	3.30103E-05	2.4	0.5012
0.000014	3.76667E-05	2.7	0.50163

K_{11}	K_{21}	K_{11} error (%)	K_{21} error (%)	SSR	Datapoints fitted	Params fitted
197160.507	-35726.9294	10.5280012	-0.14815273	1.5125E-05	18	4

H coeffs	HG coeffs	H2G coeffs	Raw coeffs 1	Raw coeffs 2	Raw coeffs 3
36846.4286	35955.7143	37620.1208	36846.4286	35955.7143	37620.1208

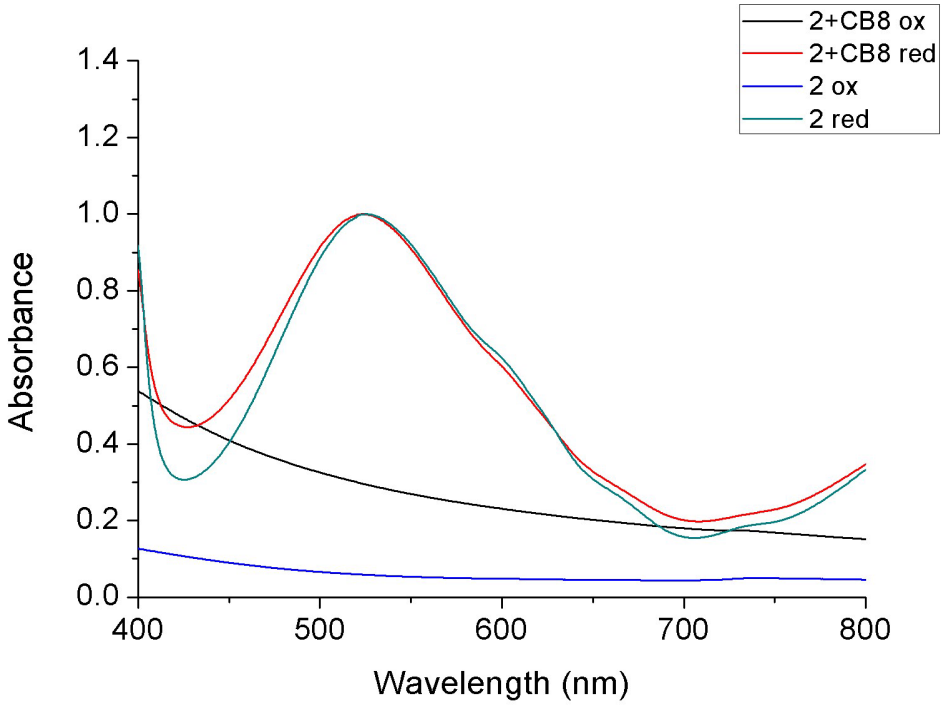


Figure S4 UV-visible spectrum of **2**·4PF_6 and **2**⊂CB[8] in H_2O/CH_3CN (3/2 v/v) before and after addition of an excess of $Na_2S_2O_4$ under N_2 atmosphere.

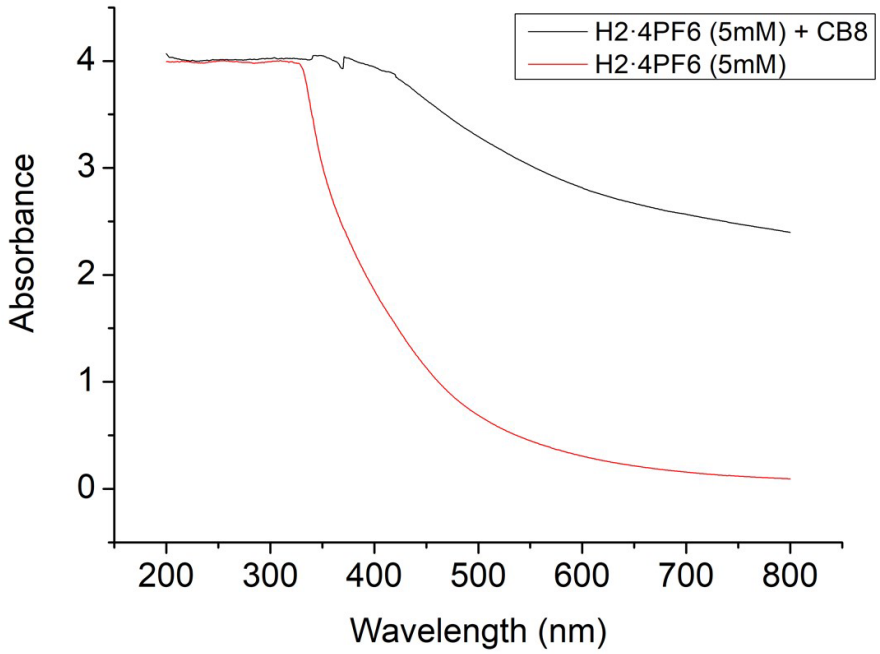


Figure S5 UV-visible spectrum of **2**·4PF_6 and **2**⊂CB[8] (5mM) in H_2O/CH_3CN (3/2 v/v) showing the increasing of the absorbance because of the charge-transfer band.

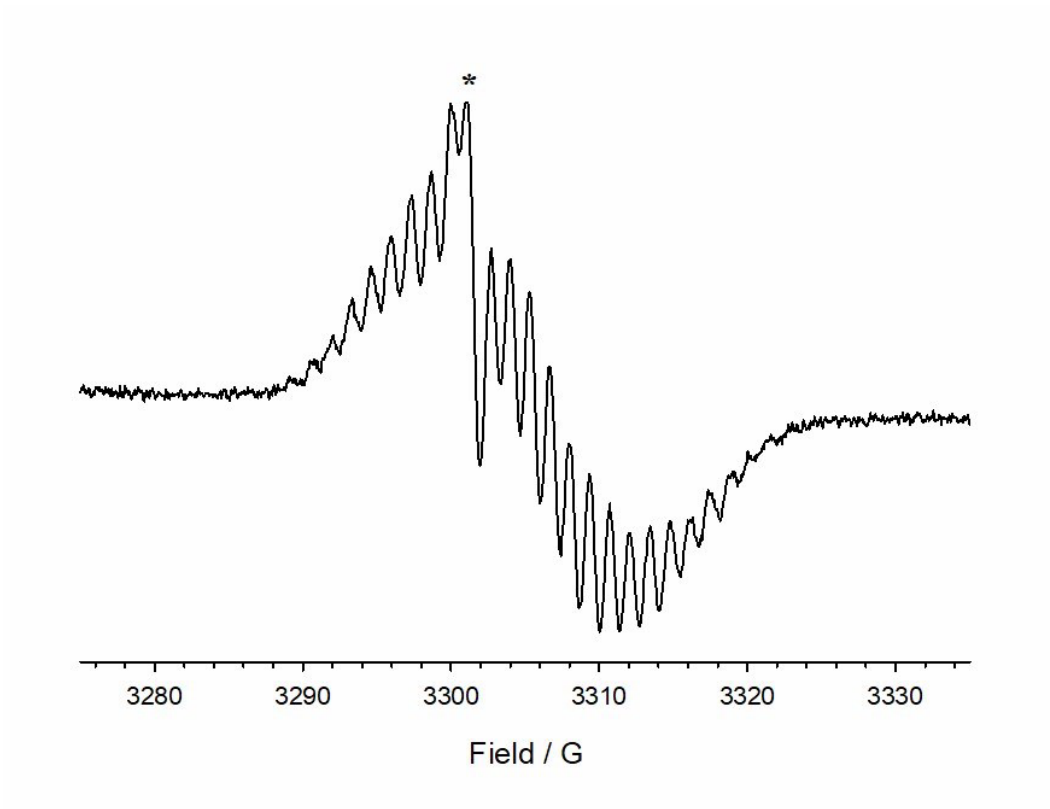


Figure S6 Room temperature EPR spectrum of a H_2O/CH_3CN (3/2, v/v) solution containing compound $\mathbf{3}^{4+}$ and $Na_2S_2O_4$. The asterisk indicates the signal due to $SO_2^{\bullet-}$ radical anion.

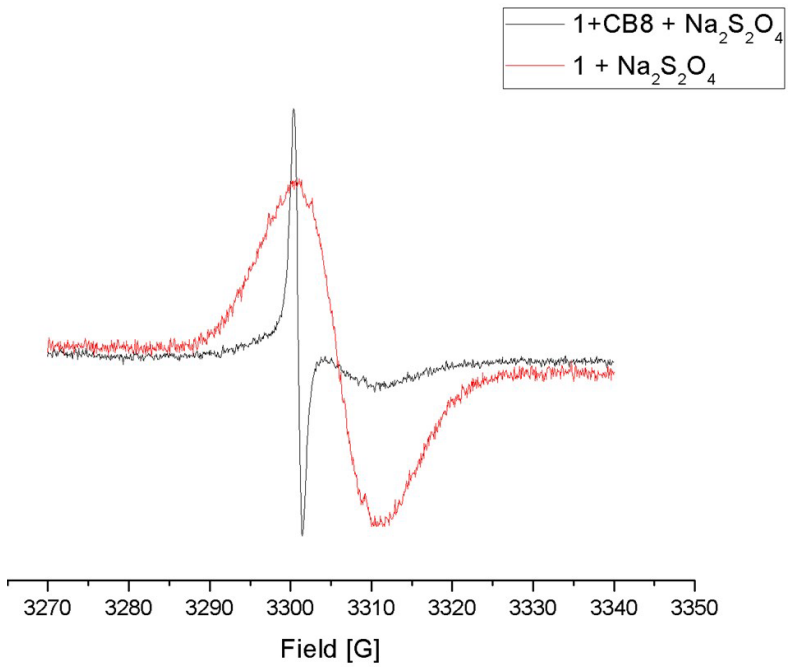


Figure S7 EPR spectroscopy of **1**·$4PF_6$ and **1⊂**CB[8] after addition of an excess of $Na_2S_2O_4$ under N_2 atmosphere.

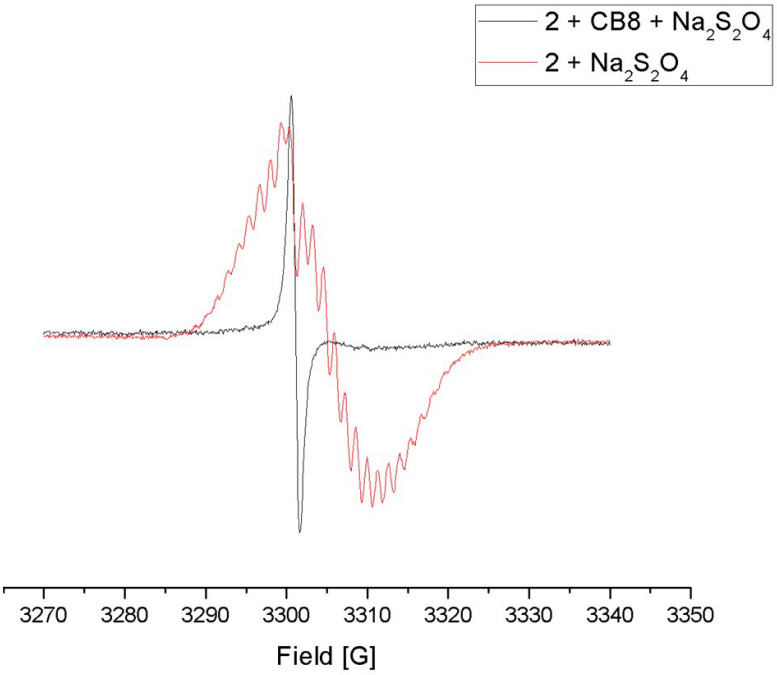


Figure S8 EPR spectroscopy of **2**·4PF_6 and **2**⊂CB[8] after addition of an excess of $Na_2S_2O_4$ under N_2 atmosphere.

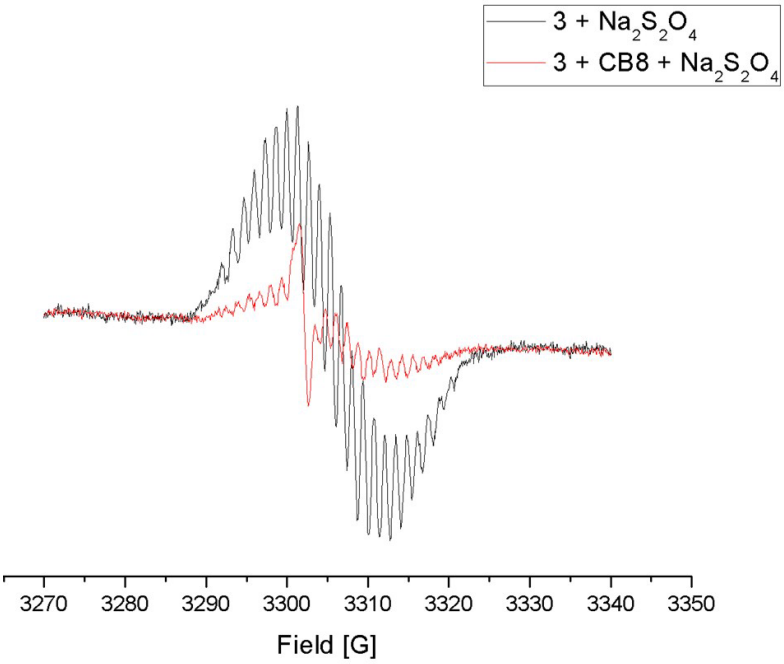


Figure S9 EPR spectroscopy of **2**·4PF_6 and **2**⊂CB[8] after addition of an excess of $Na_2S_2O_4$ under N_2 atmosphere.

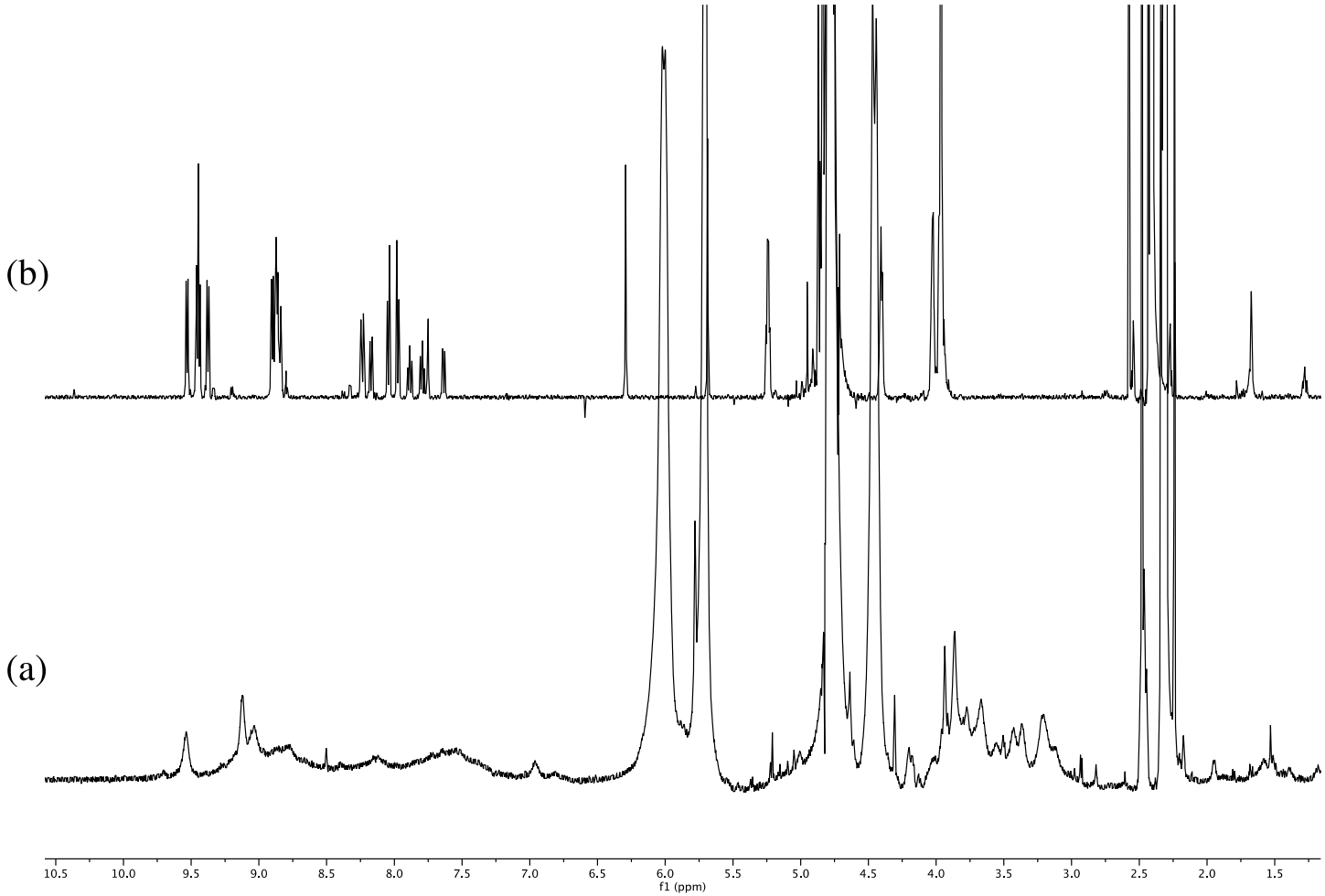


Figure S10 Partial ^{1}H NMR (500 MHz, D_2O/CD_3CN (3:2)) spectrum of: (a) 2 mM solution of **3**·4PF_6 (b) 2 mM solution of **3**⊂CB[8].

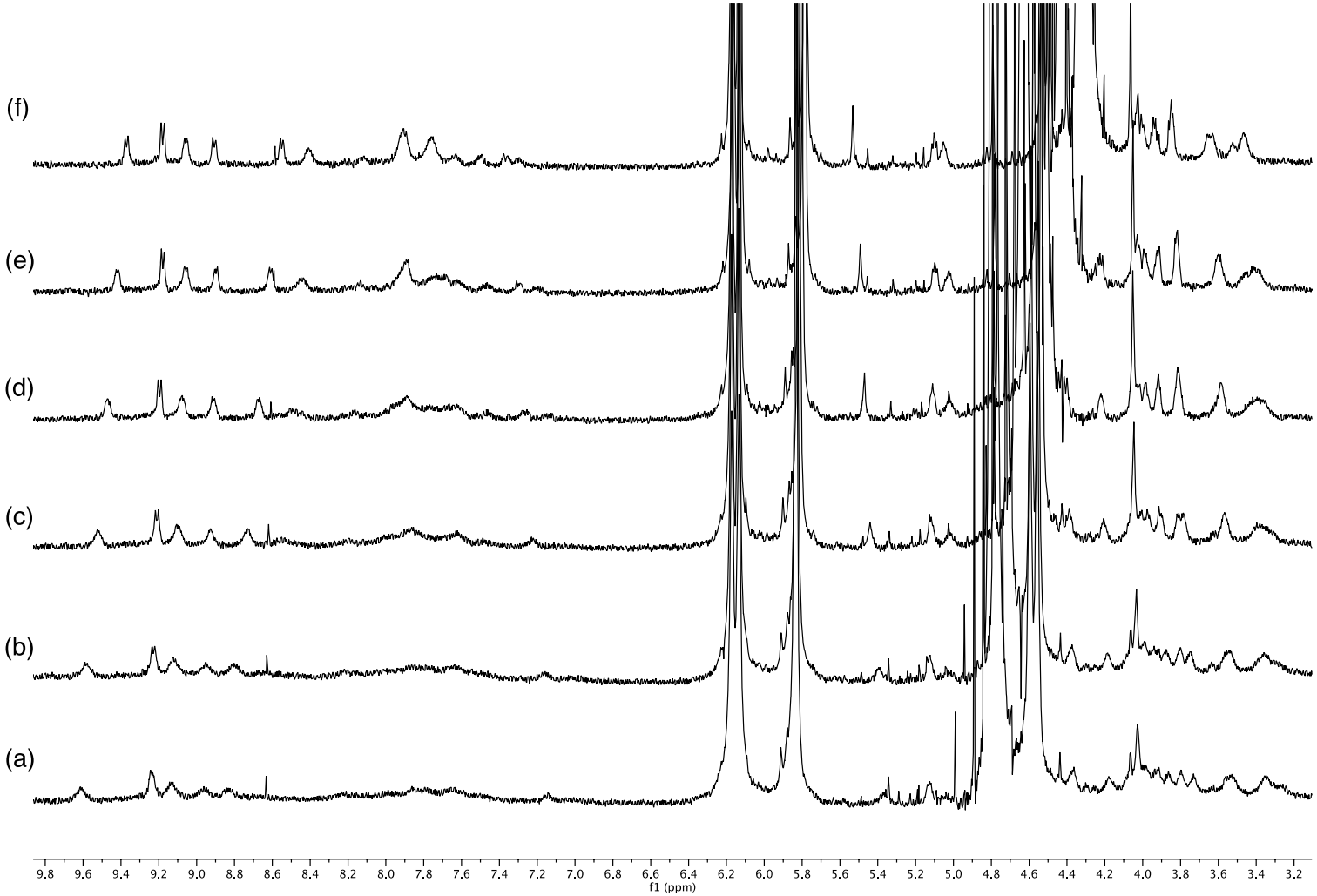


Figure S11. Partial ^{1}H VT-NMR (400 MHz, D_2O) spectra of a 2 mM solution of **3**⊂CB[8] (a) 298 K; (b) 303 K; (c) 313 K; (d) 323 K; (e) 333 K; (f) 343 K.

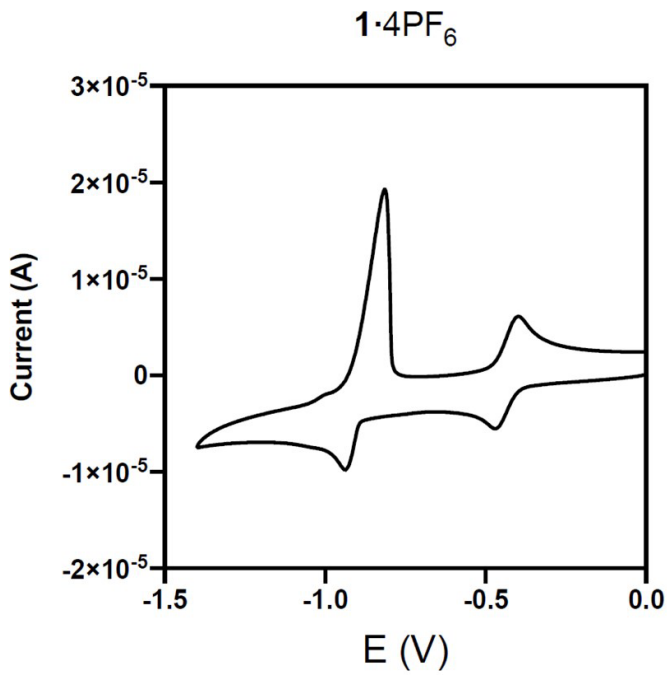


Figure S12 Cyclic voltammetric response on a glassy carbon electrode of 1.0 mM **1**·$4PF_6$ in H_2O/CH_3CN (3:2, v/v). Supporting electrolyte: 0.1 M KCl. Scan rate: 50 mV/s.

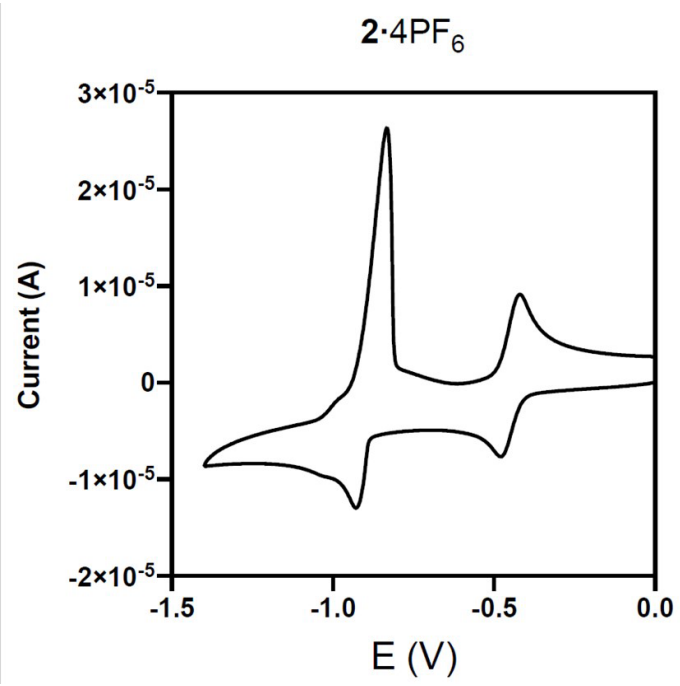


Figure S13 Cyclic voltammetric response on a glassy carbon electrode of 1.0 mM **2**·$4PF_6$ in H_2O/CH_3CN (3:2, v/v). Supporting electrolyte: 0.1 M KCl. Scan rate: 50 mV/s.

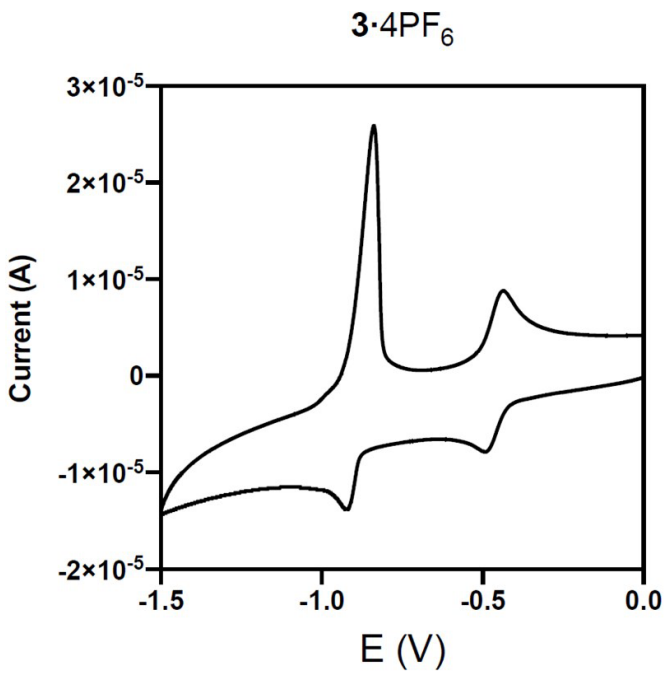


Figure S14 Cyclic voltammetric response on a glassy carbon electrode of 1.0 mM **3**·$4PF_6$ in H_2O/CH_3CN (3:2, v/v). Supporting electrolyte: 0.1 M KCl. Scan rate: 50 mV/s.

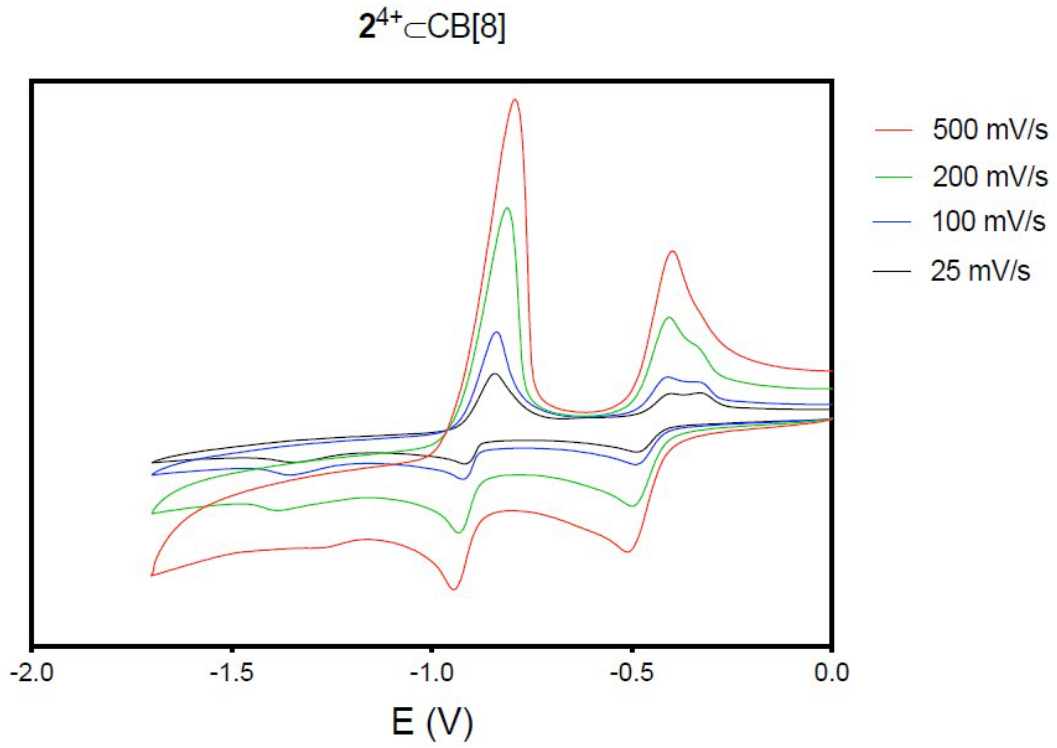


Figure S15 Cyclic voltammetric response on a glassy carbon electrode of 1.0 mM **2^{4+}⊂CB[8]** in H_2O/CH_3CN (3:2, v/v) at different scan rate. Supporting electrolyte: 0.1 M KCl.

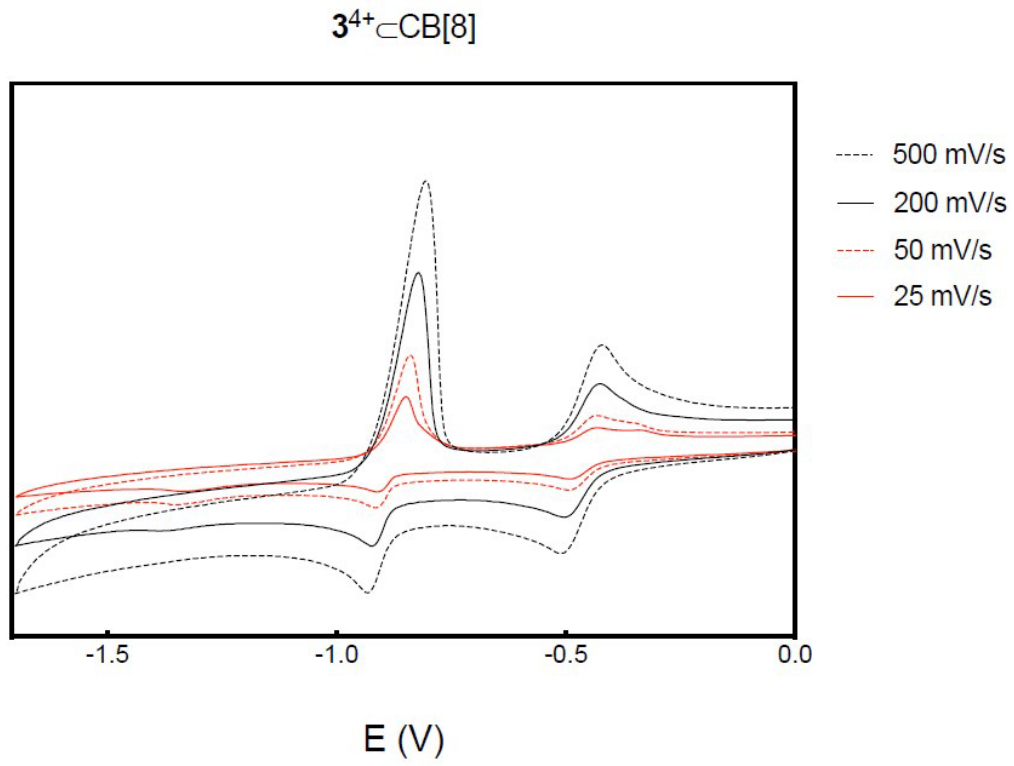


Figure S16 Cyclic voltammetric response on a glassy carbon electrode of 1.0 mM **3^{4+}⊂CB[8]** in H_2O/CH_3CN (3:2, v/v) at different scan rate. Supporting electrolyte: 0.1 M KCl.

NMR spectra

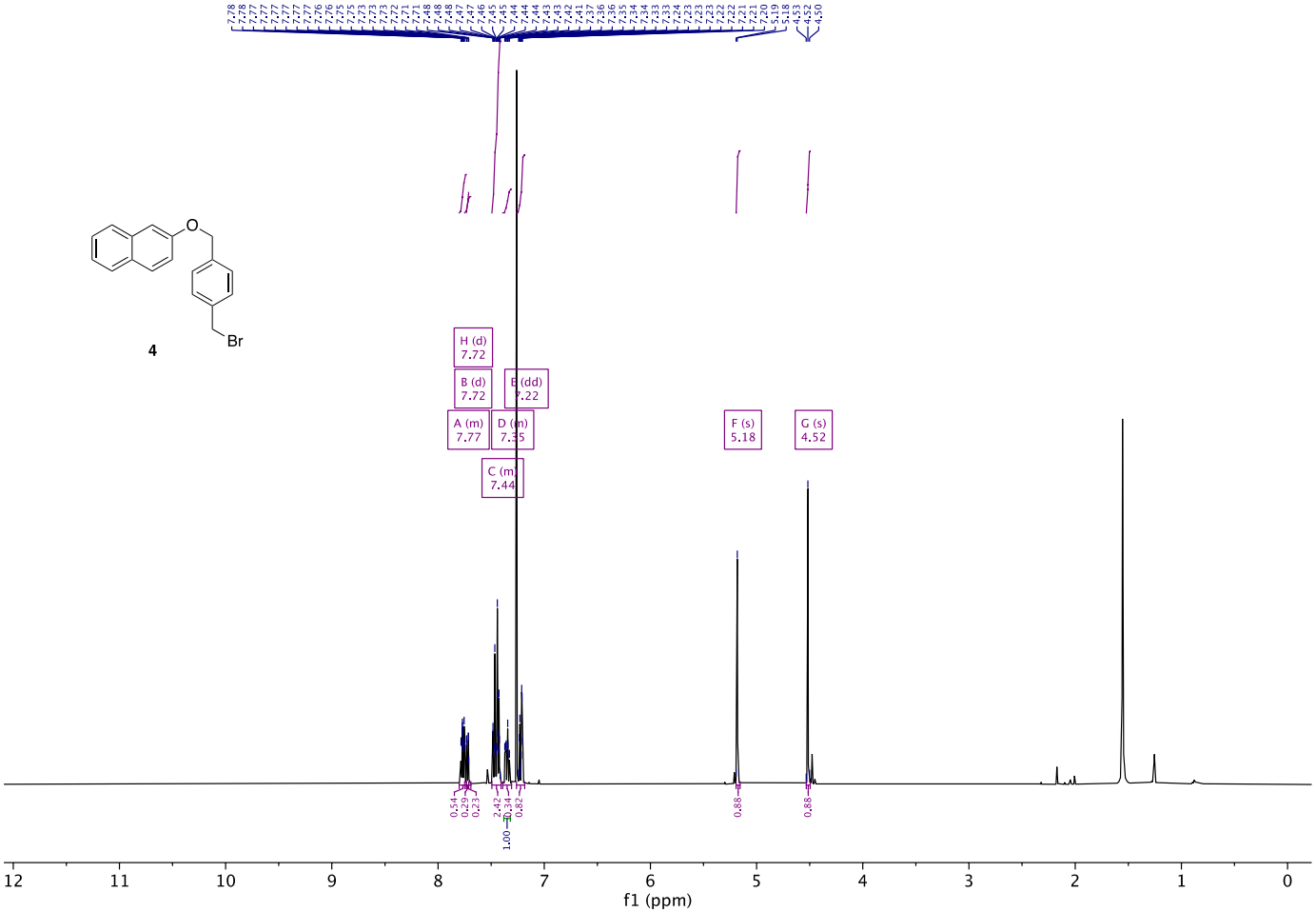


Figure S17 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **4**.

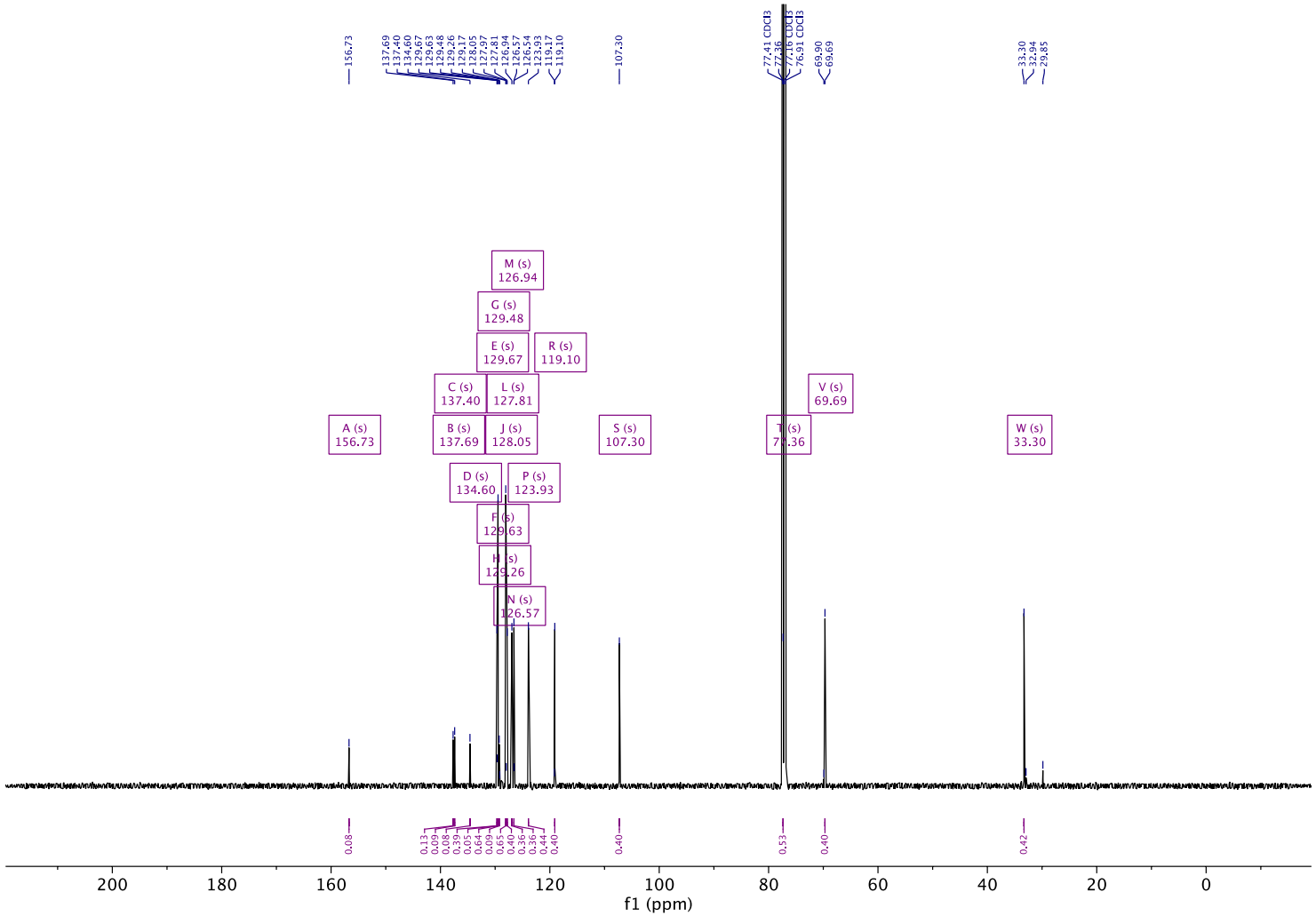


Figure S18 ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **4**.

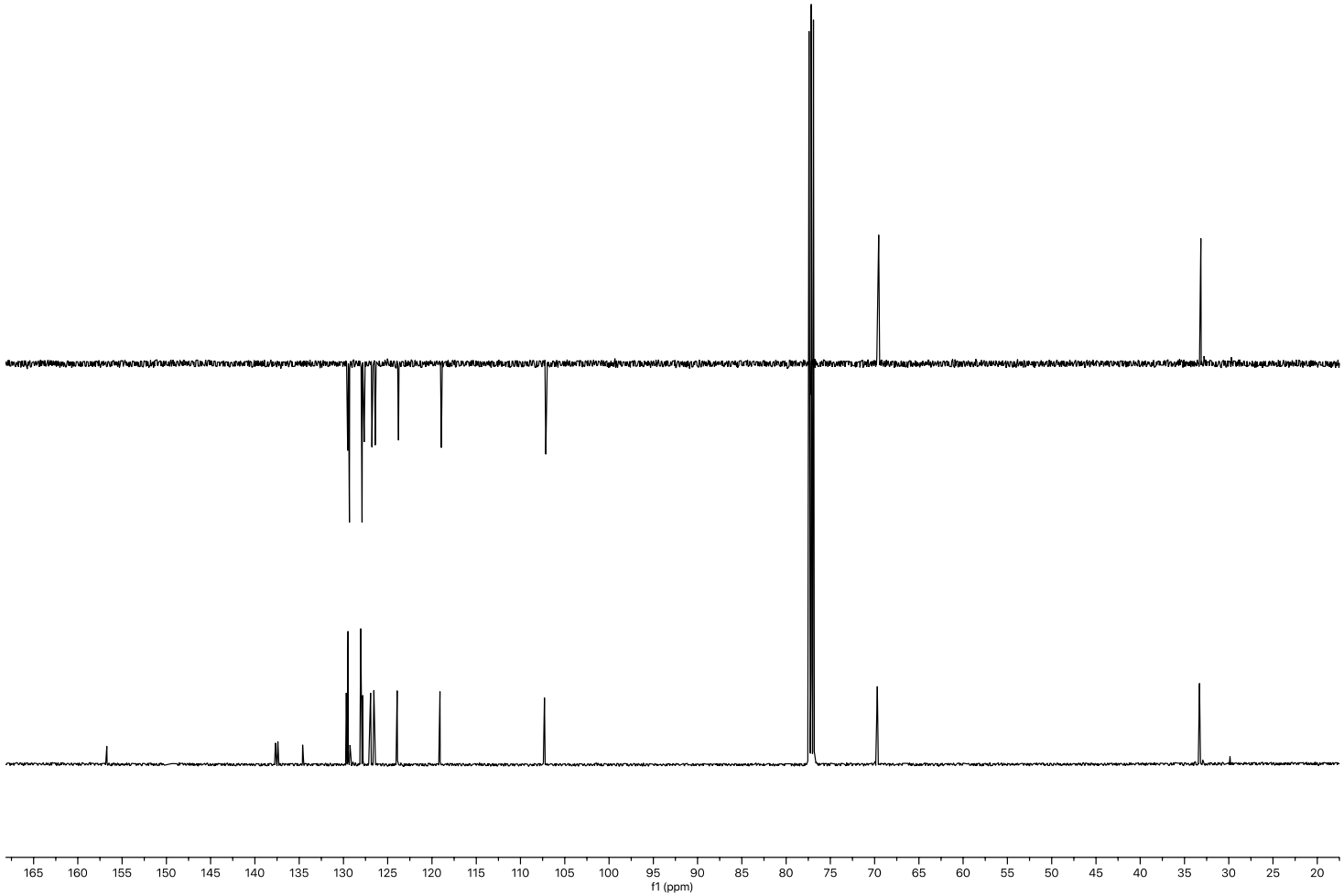


Figure S19 ^{13}C and DEPT NMR (125 MHz, $CDCl_3$) spectrum of **4**.

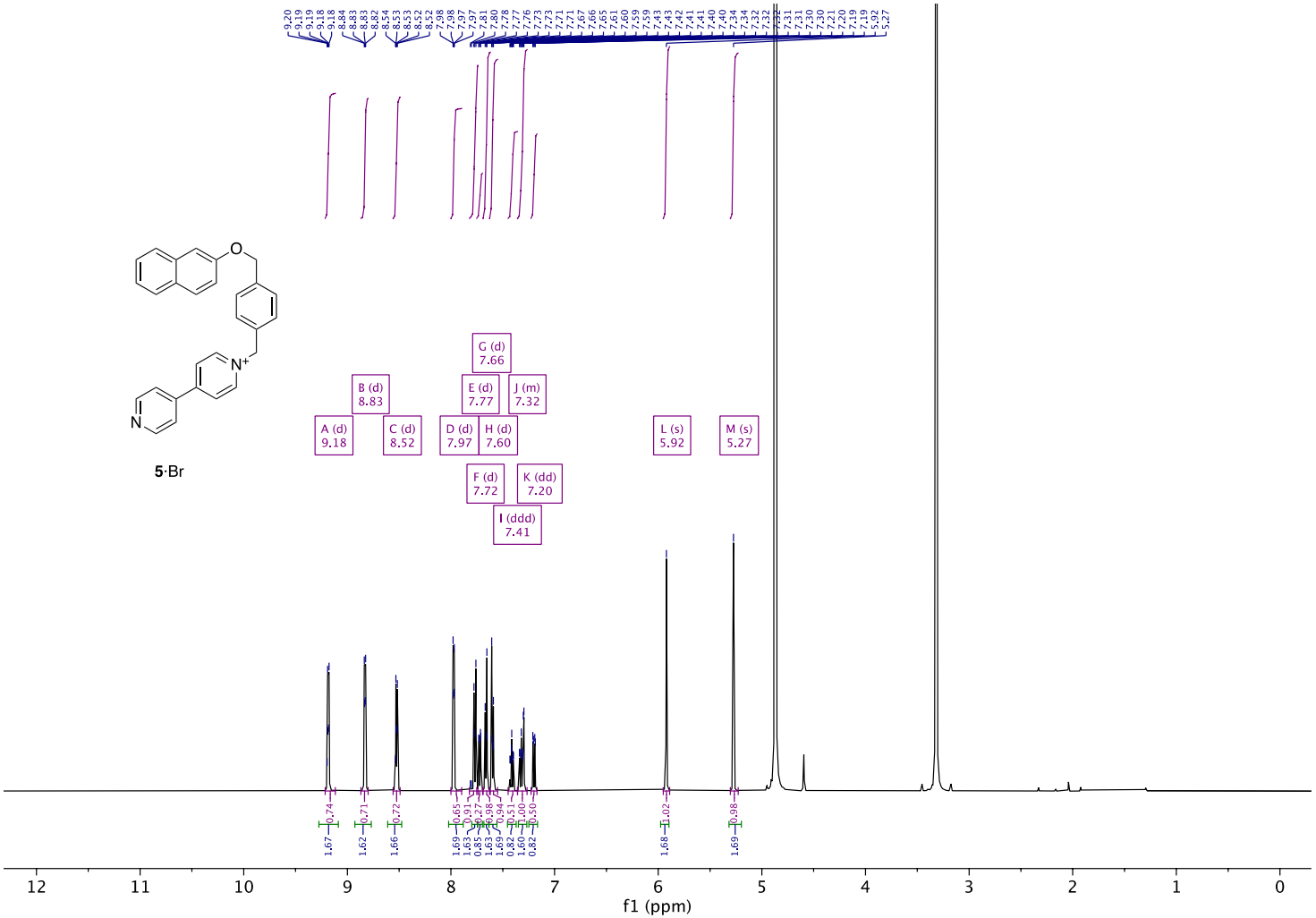


Figure S20 ^{1}H NMR (500 MHz, D_2O) spectrum of **5**·Br.

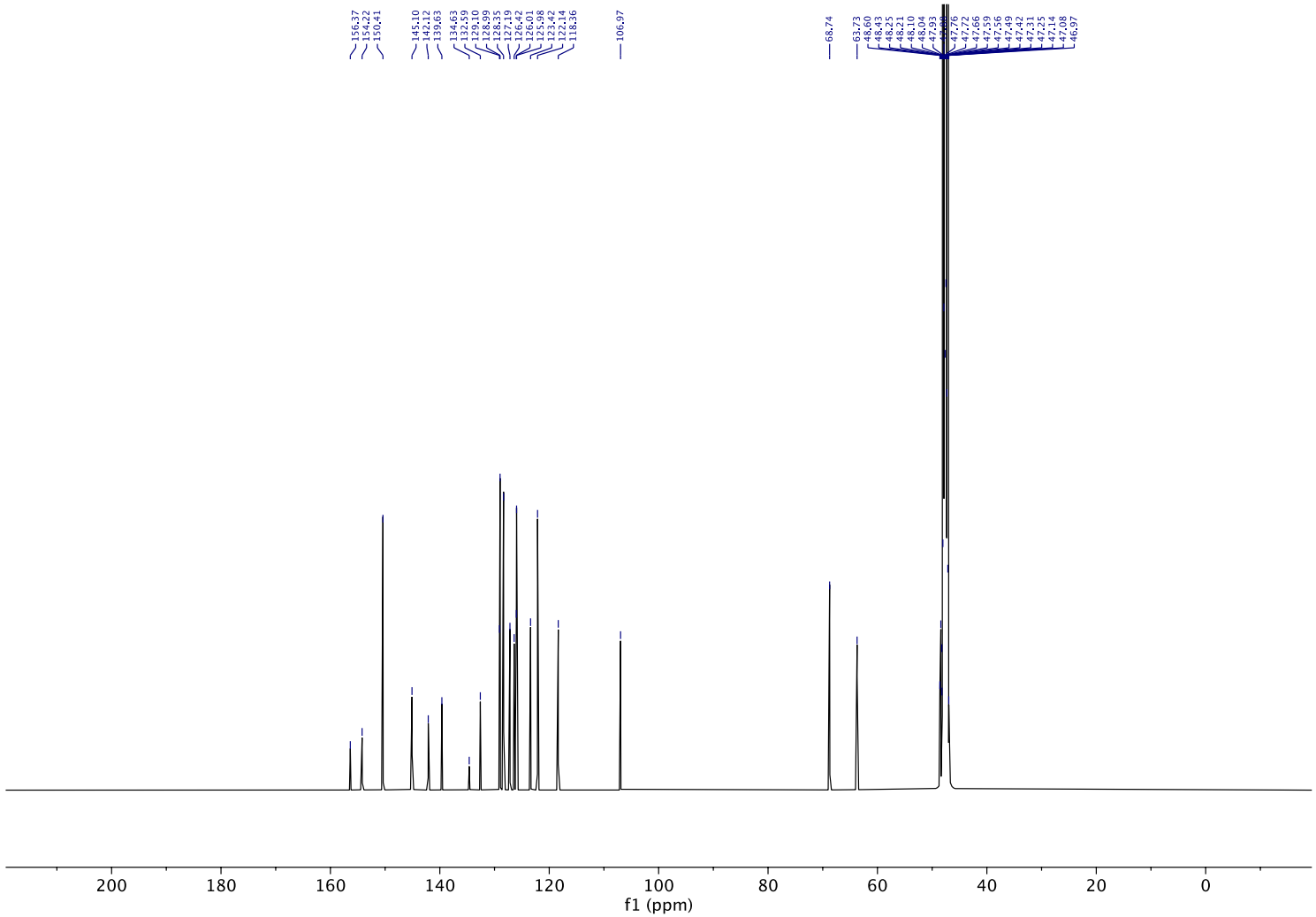


Figure S21 ^{13}C NMR (125 MHz, D_2O) spectrum of **5**·Br.

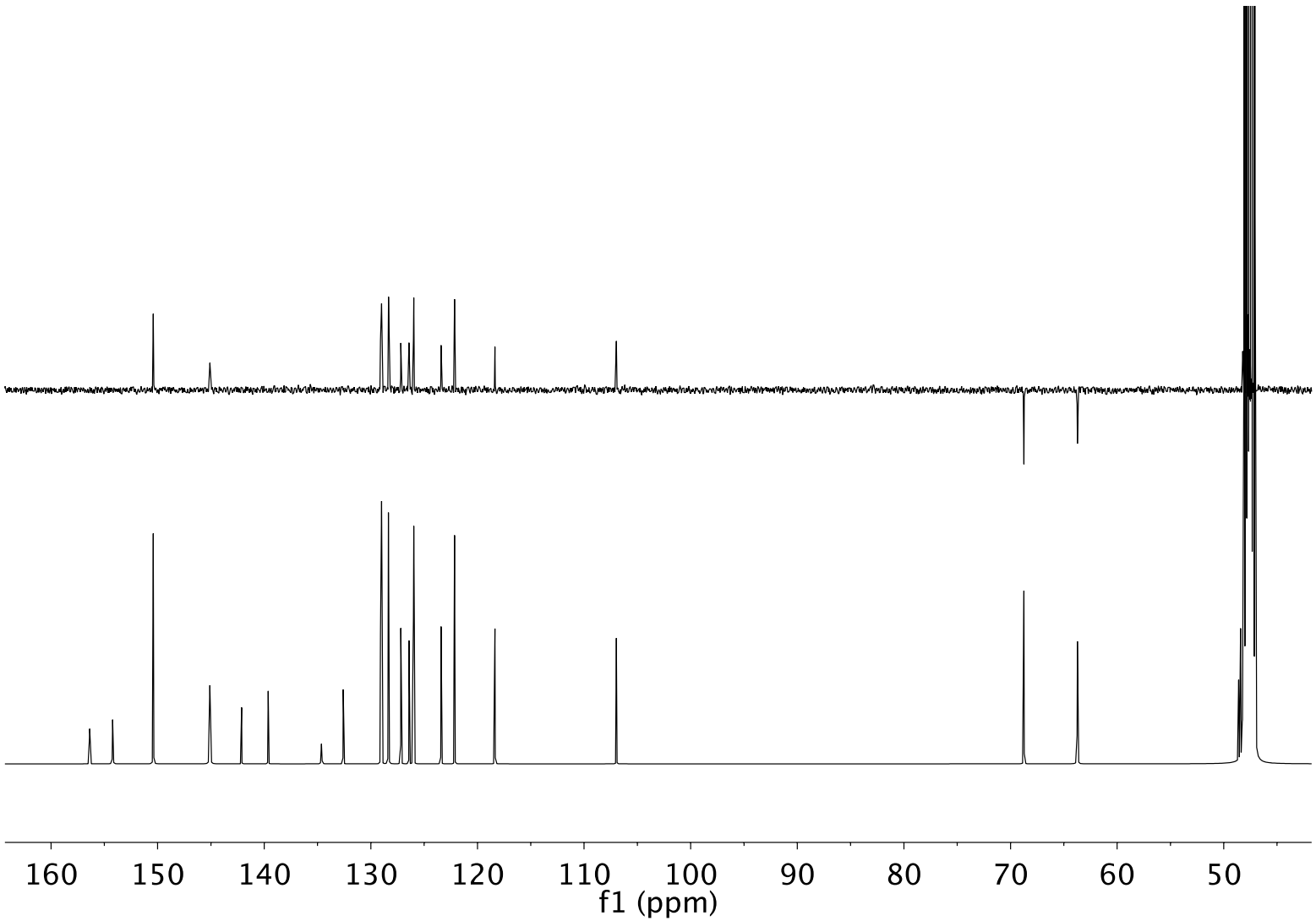


Figure S22 ^{13}C and DEPT NMR (125 MHz, D_2O) spectrum of **5**·Br.

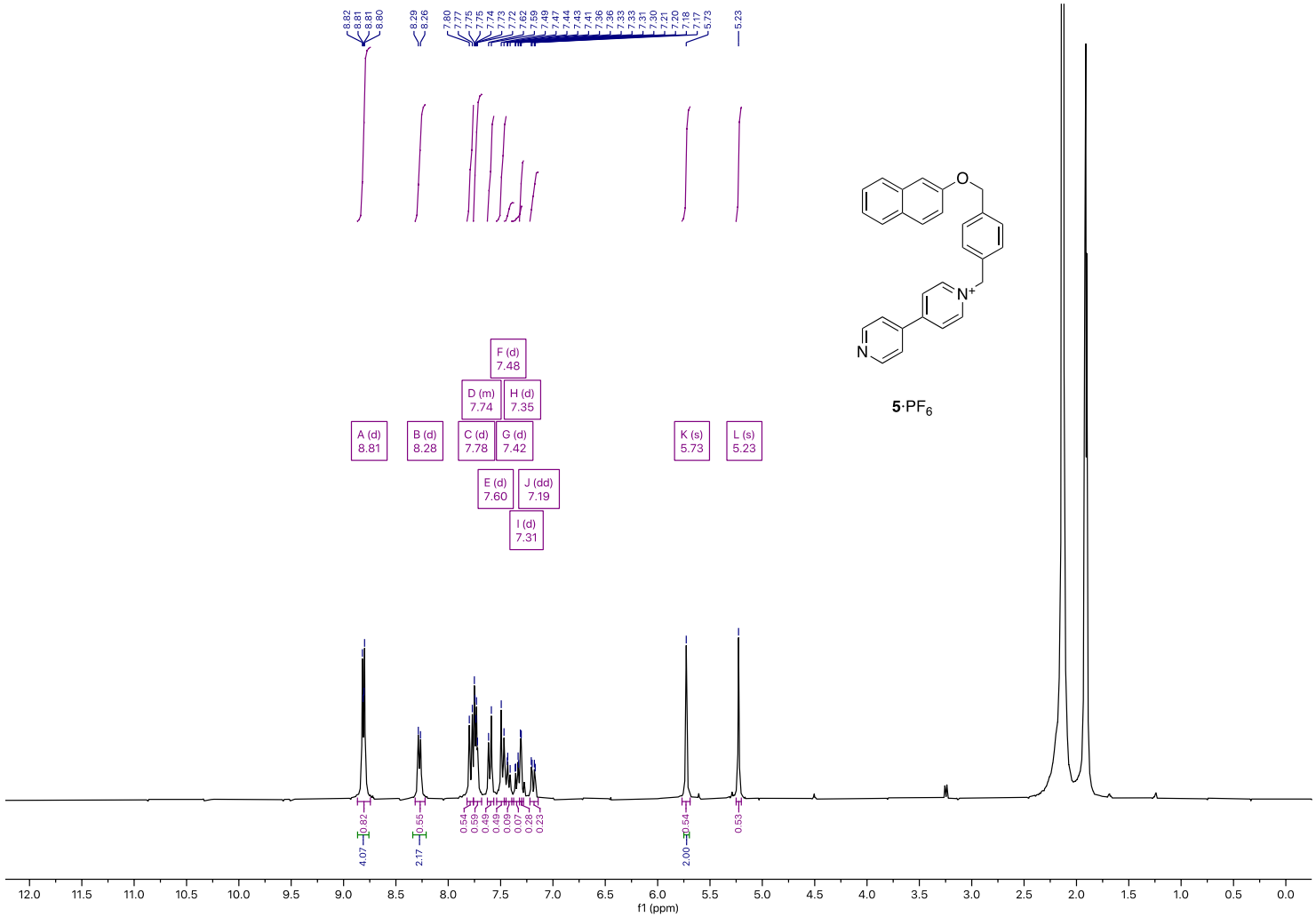


Figure S23 ^{1}H NMR (400 MHz, CD_3CN) spectrum of **5**·PF_6.

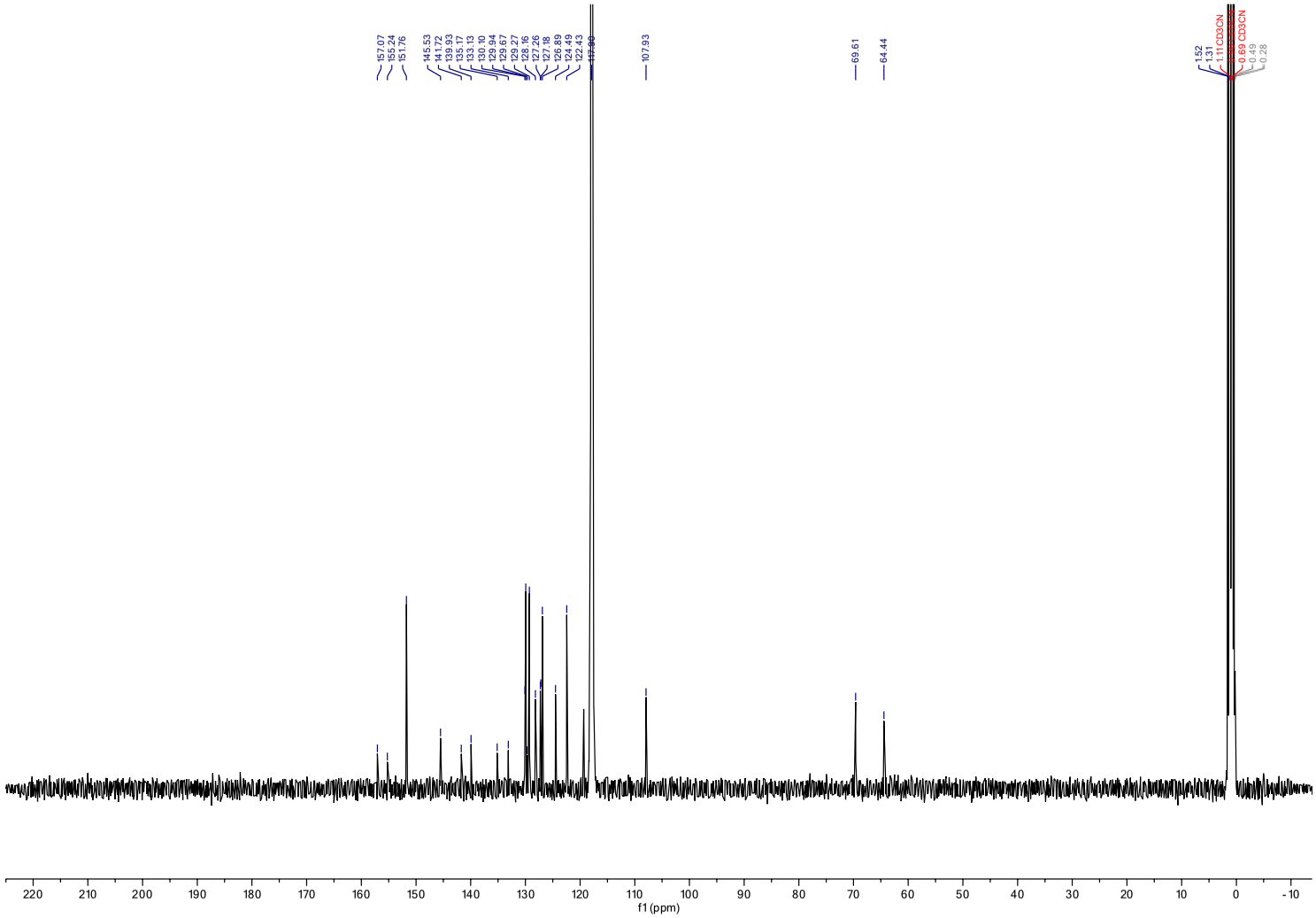


Figure S24 ^{13}C NMR (400 MHz, CD_3CN) spectrum of **5**·PF_6.

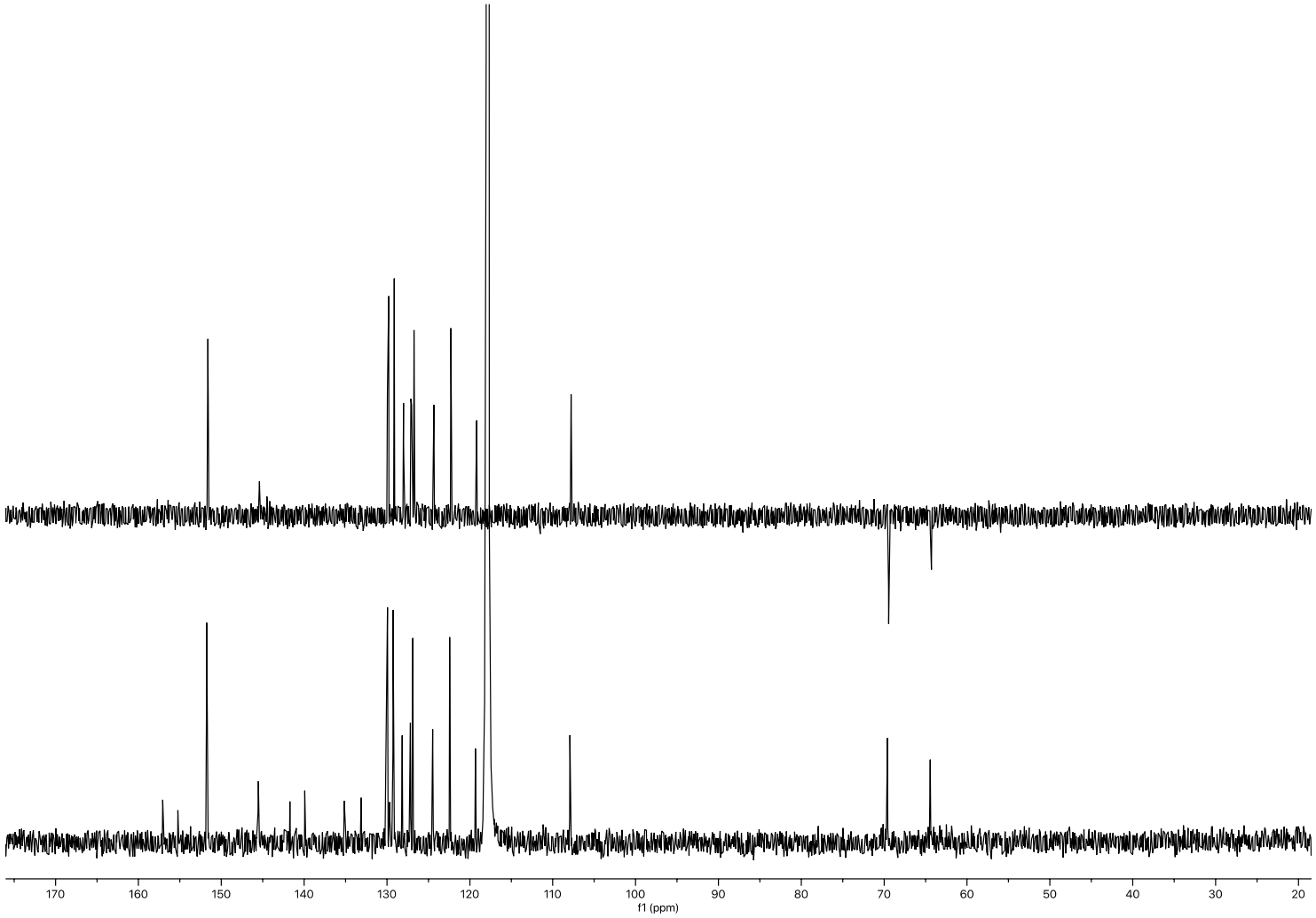


Figure S25 ^{13}C and DEPT NMR (400 MHz, CD_3CN) spectrum of **5**·PF_6.

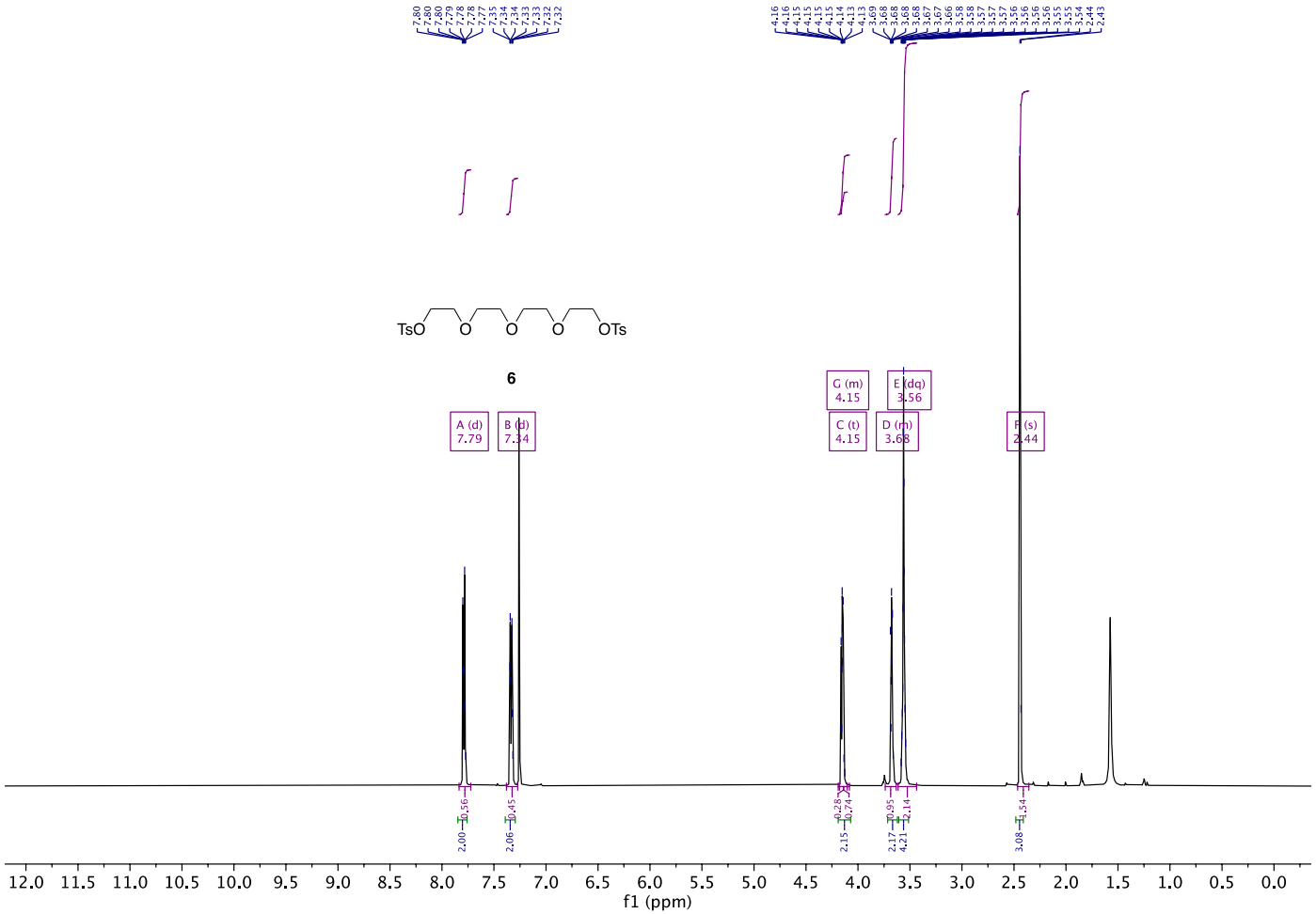


Figure S26 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **6**.

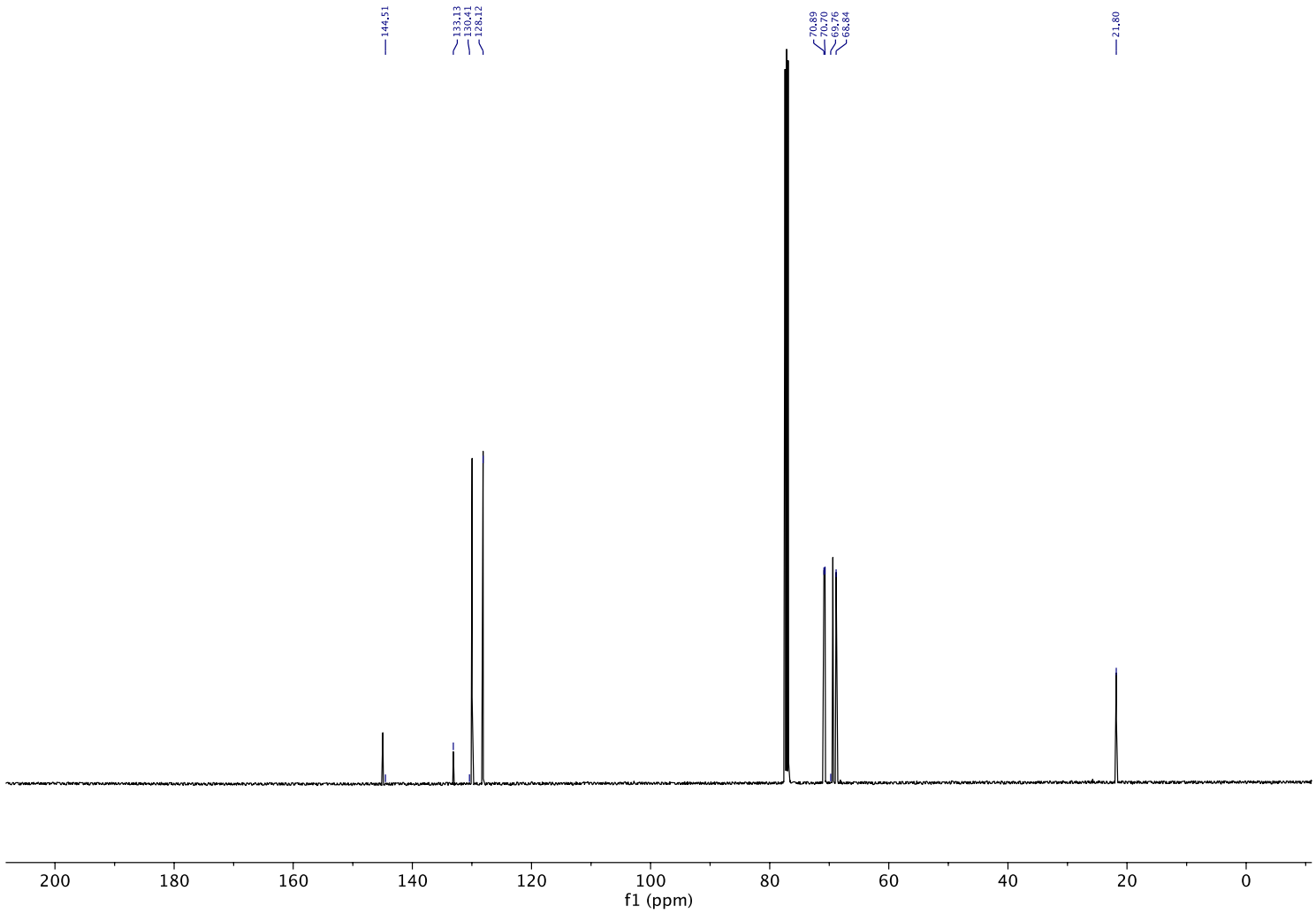


Figure S27 ^{13}C (125 MHz, $CDCl_3$) spectrum of **6**.

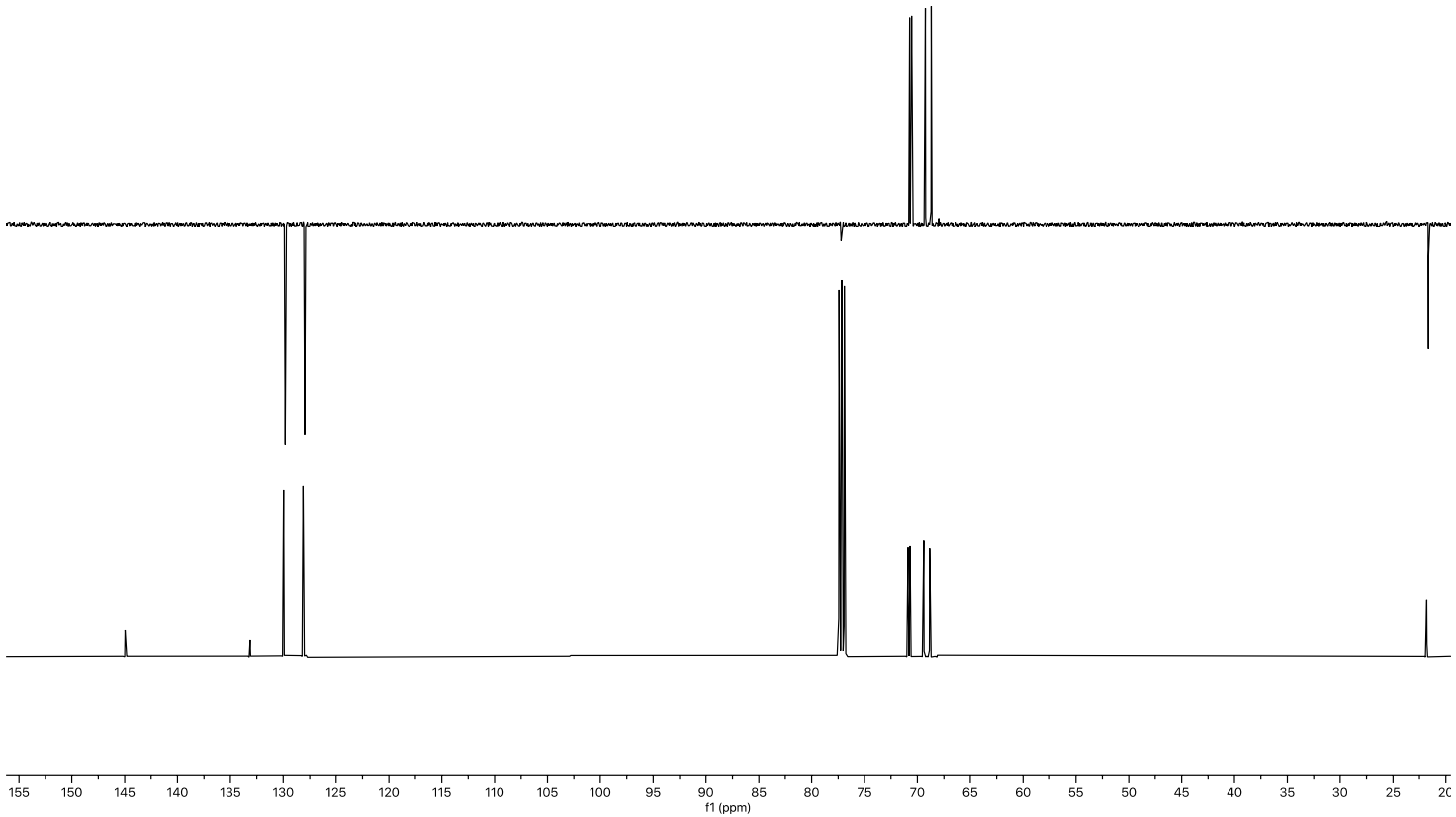


Figure S28 ^{13}C and DEPT NMR (125 MHz, $CDCl_3$) spectrum of **6**.

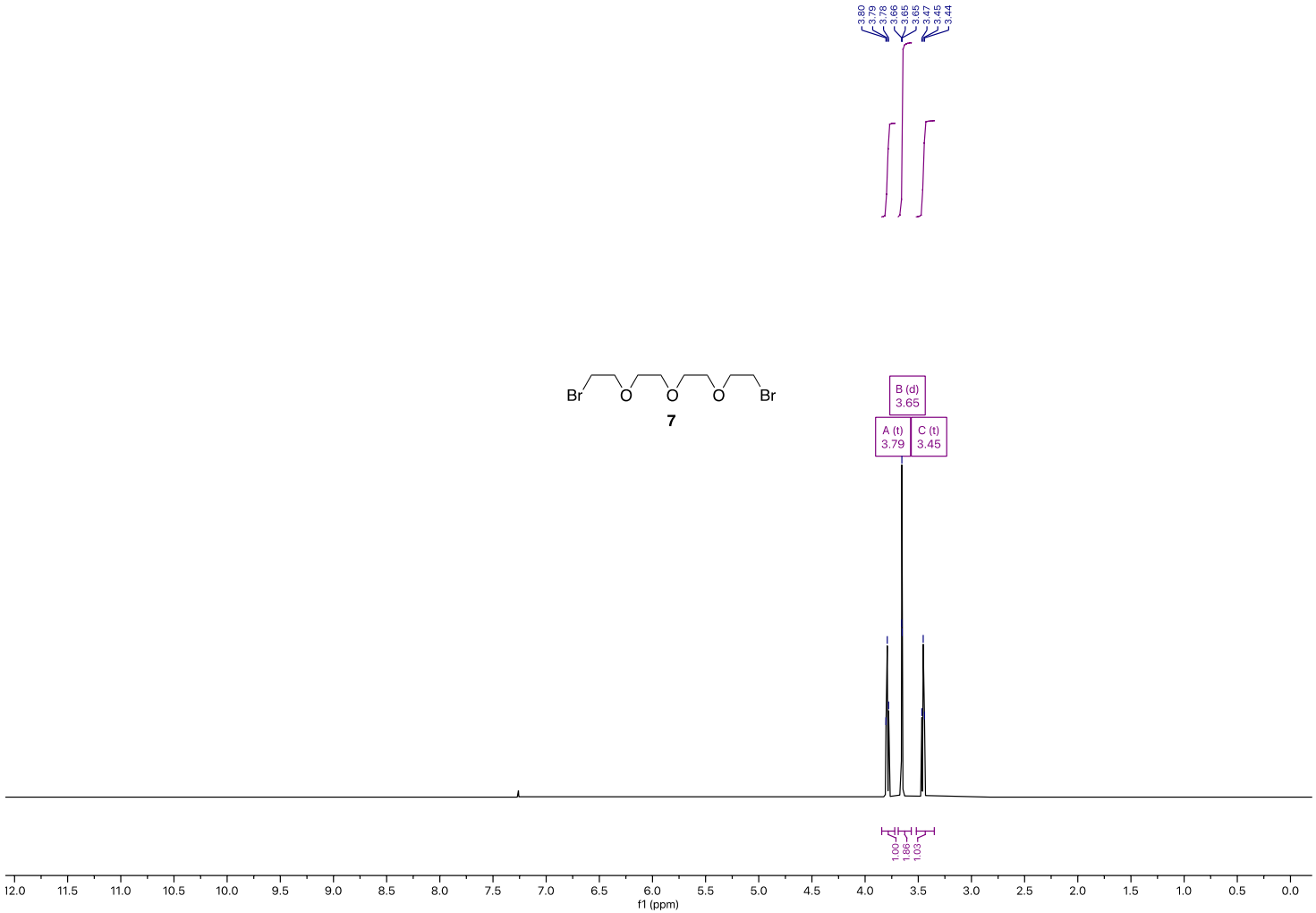


Figure S29 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **7**.

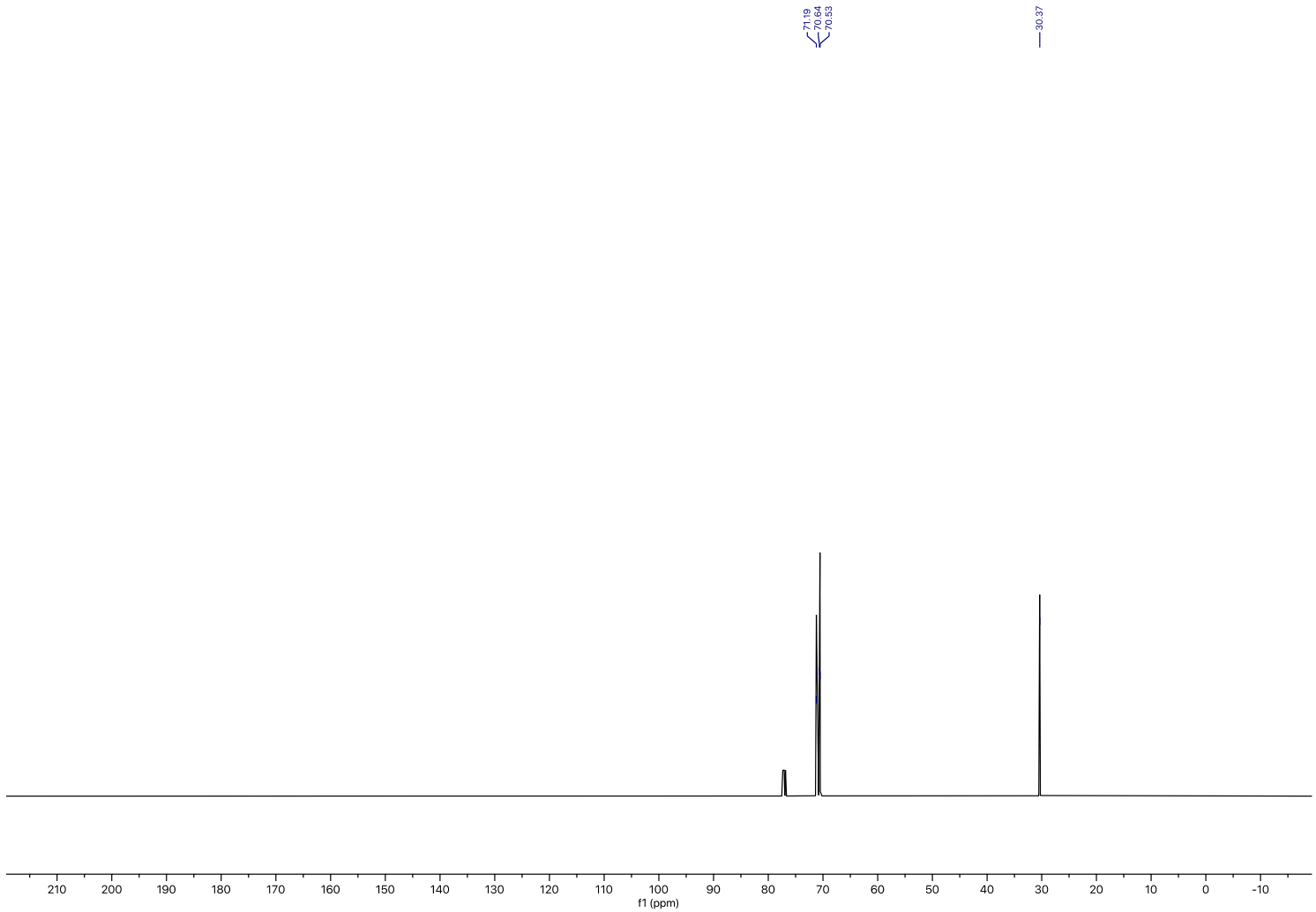


Figure S30 ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **7.**

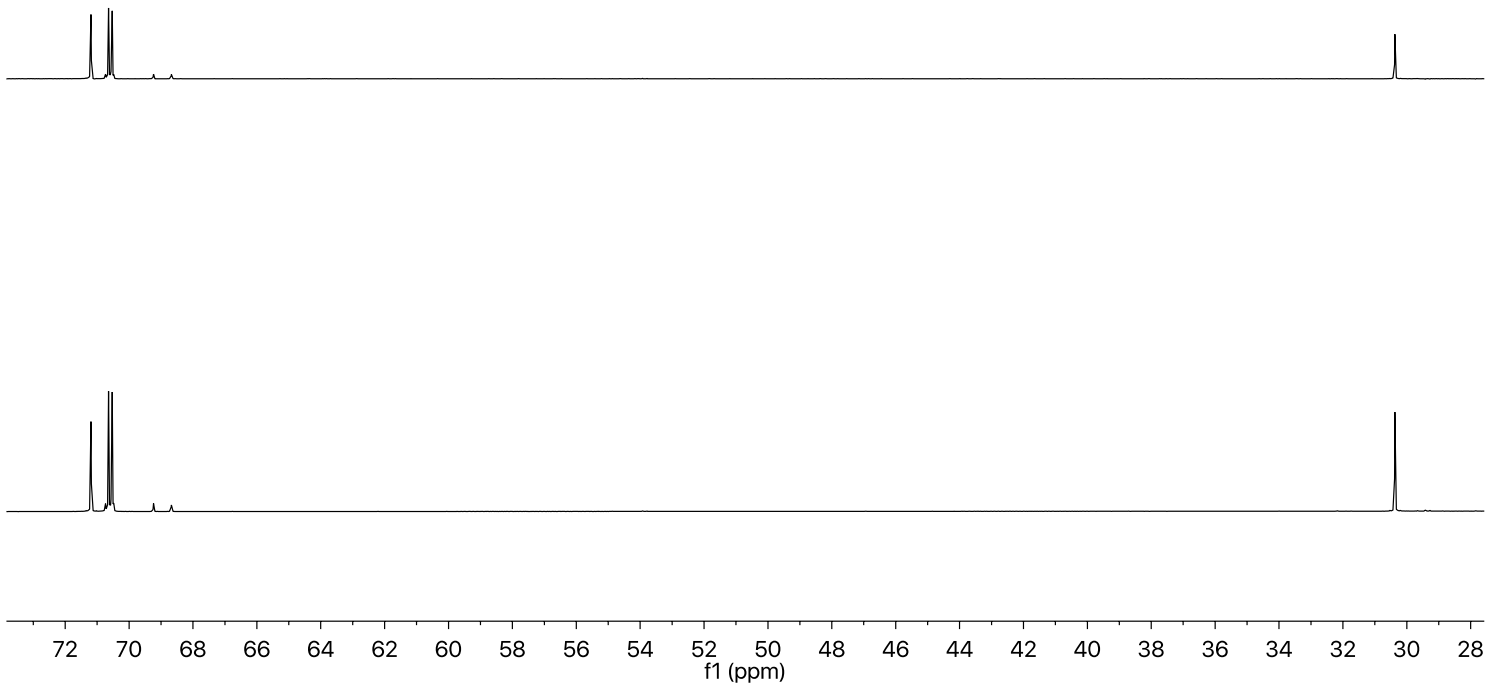


Figure S31 ^{13}C and DEPT NMR (125 MHz, $CDCl_3$) spectrum of **7.**

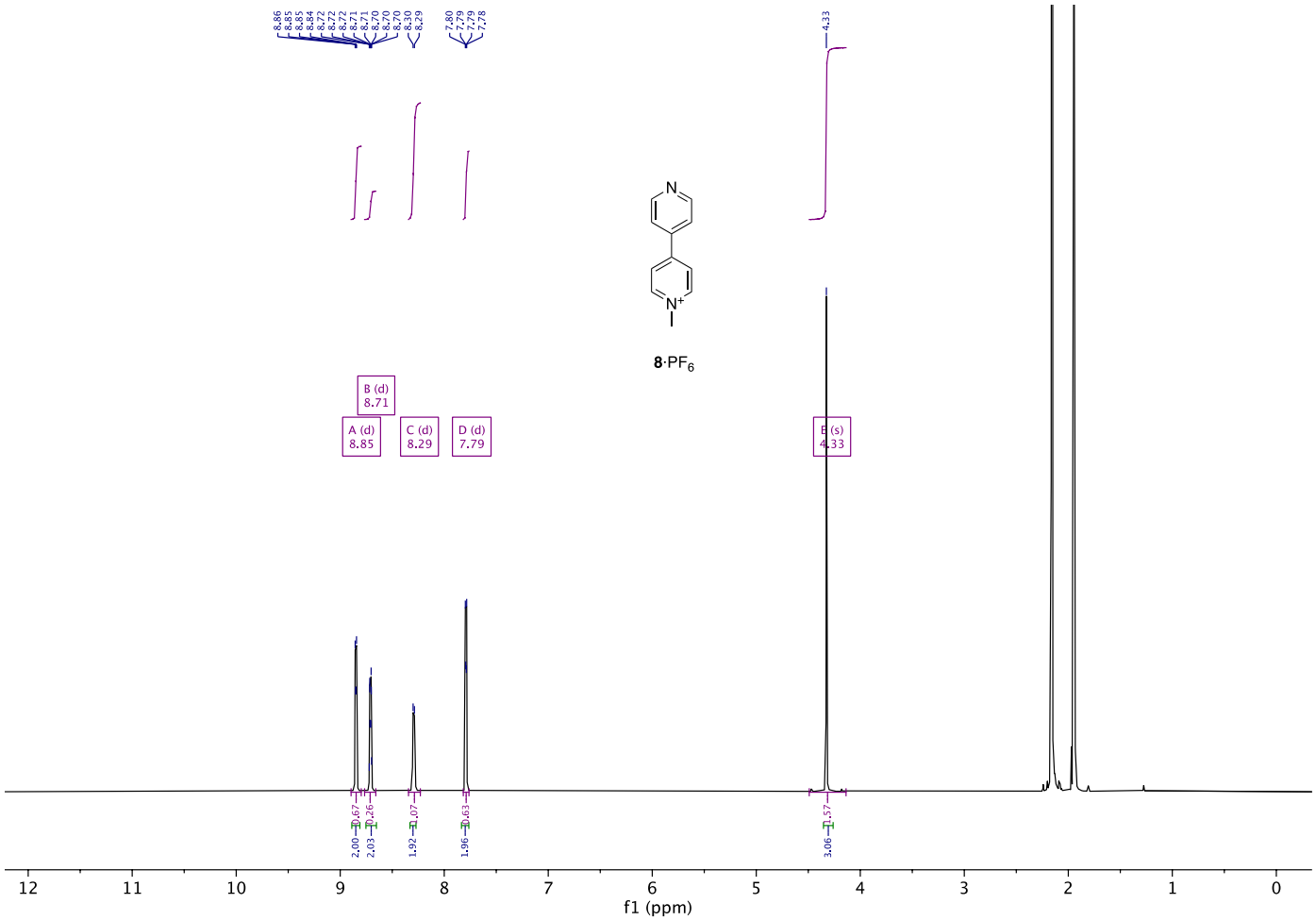


Figure S32 ^{1}H NMR (500 MHz, CD_3CN) spectrum of **8**·PF_6.

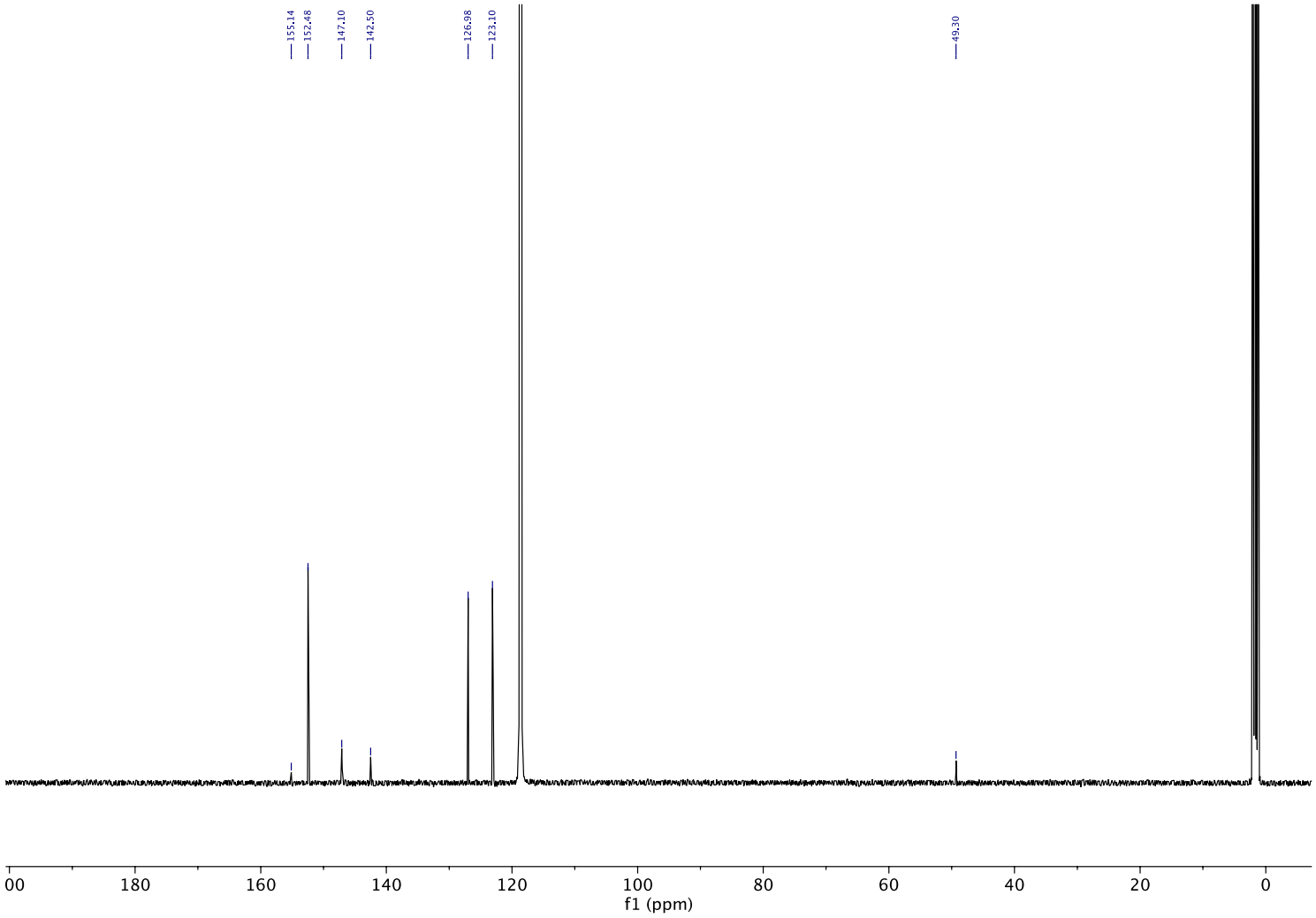


Figure S33 ^{13}C NMR (125 MHz, CD_3CN) spectrum of **8**·PF_6.

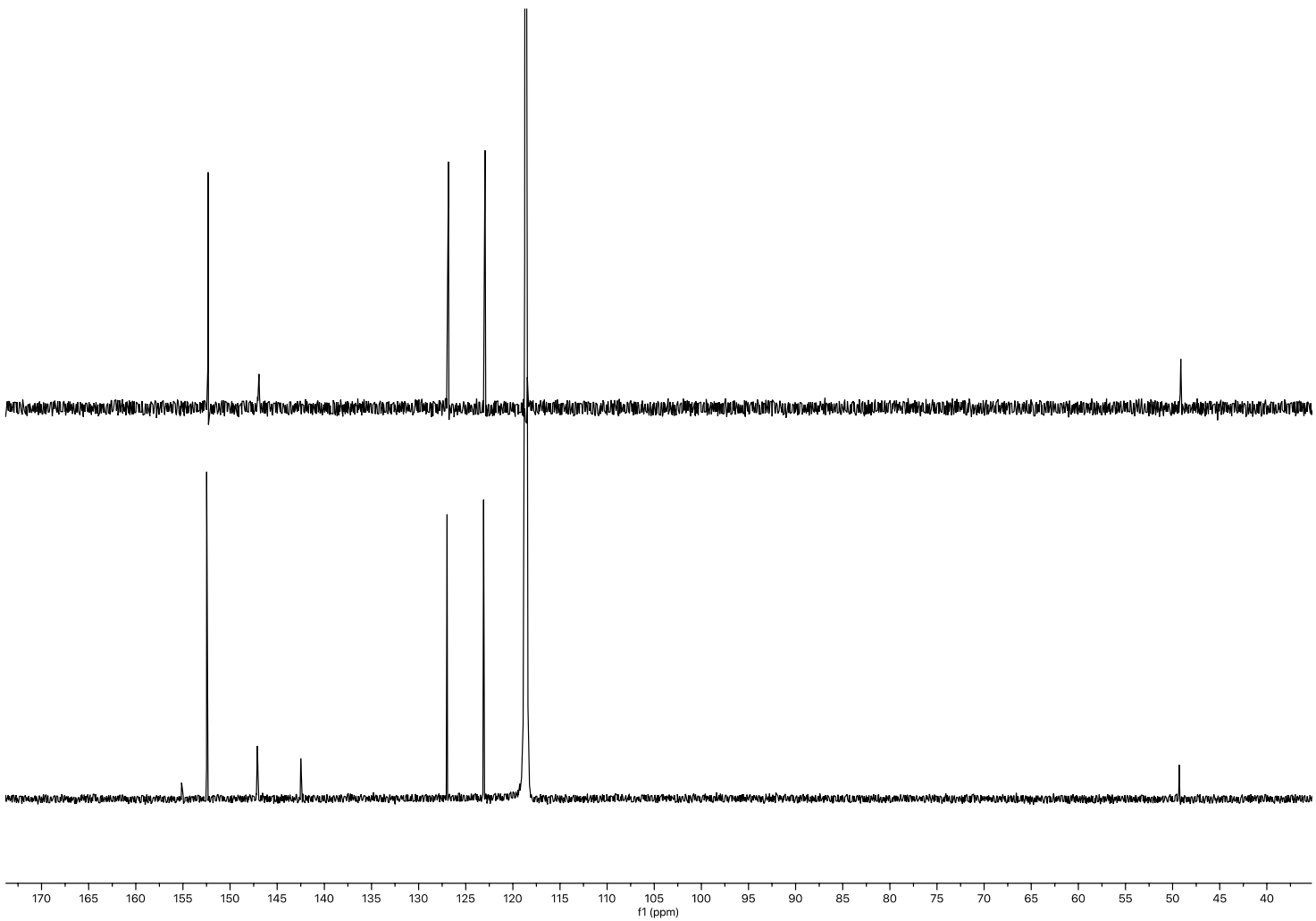


Figure S34 ^{13}C and DEPT NMR (125 MHz, CD_3CN) spectrum of **8**·PF_6.

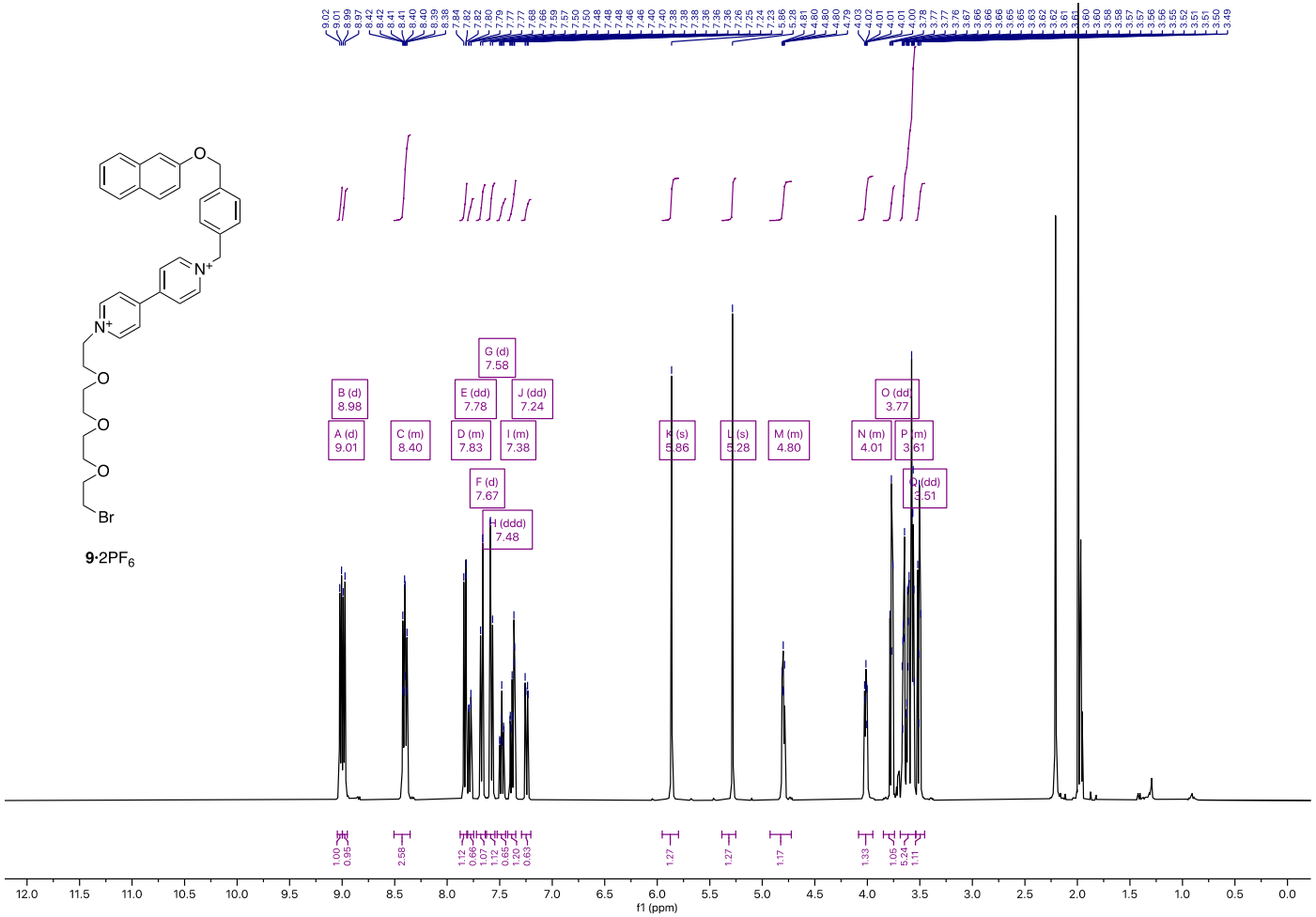


Figure S35 ^{1}H NMR (500 MHz, CD_3CN) spectrum of **9**·2PF_6.

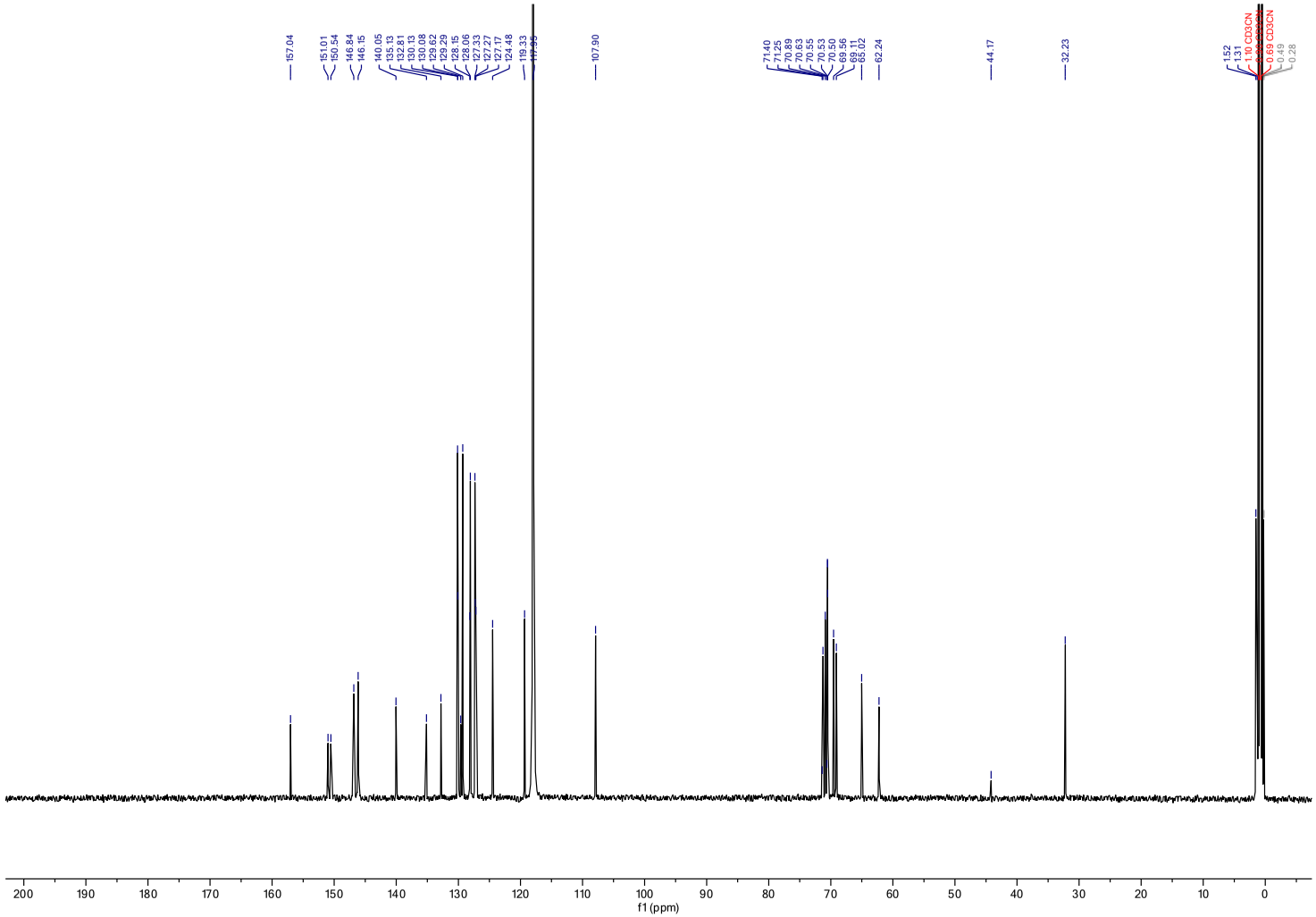


Figure S36 ^{13}C NMR (125 MHz, CD_3CN) spectrum of **9**·$2PF_6$

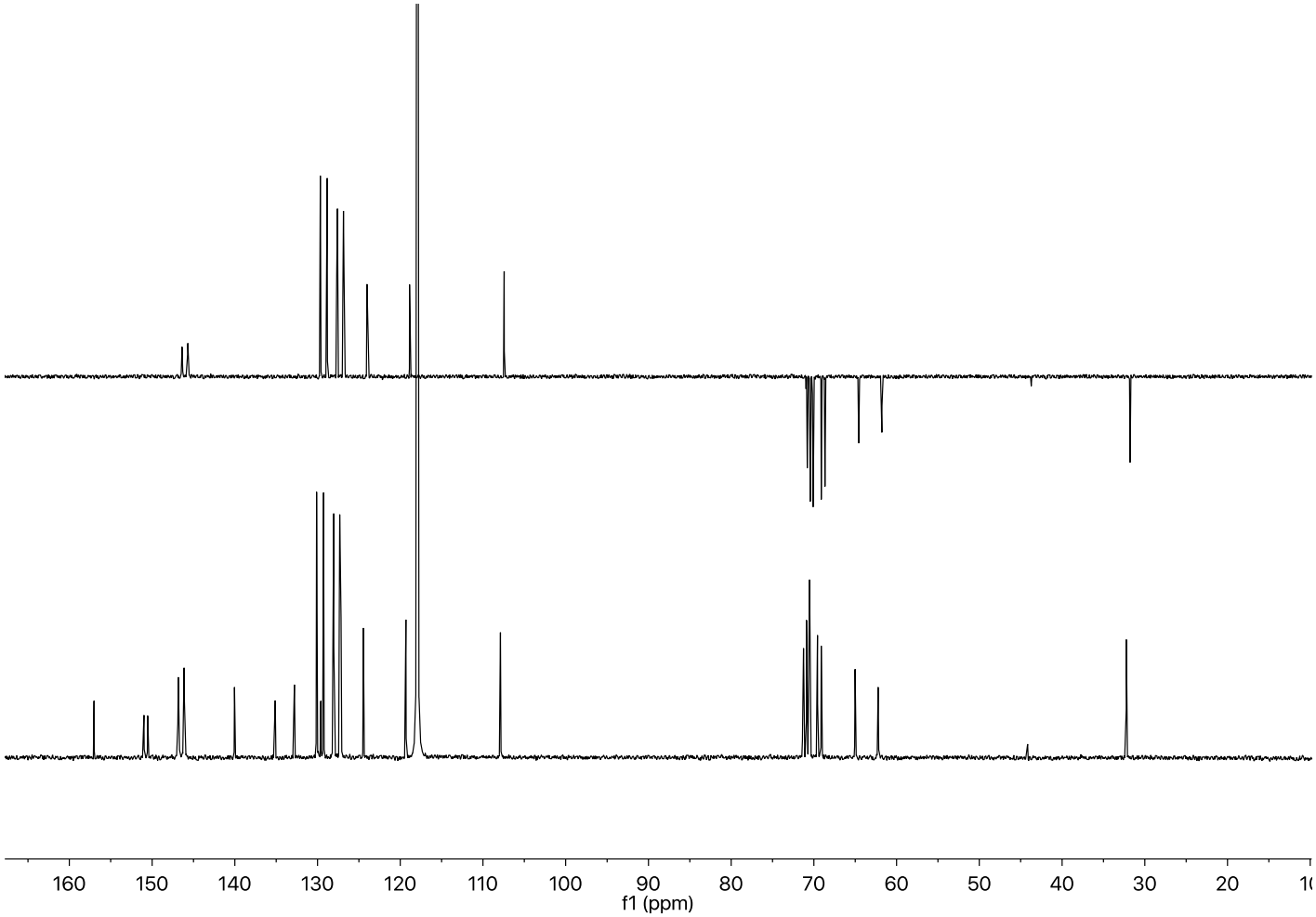


Figure S37 ^{13}C NMR and DEPT (125 MHz, CD_3CN) spectrum of **9**·$2PF_6$

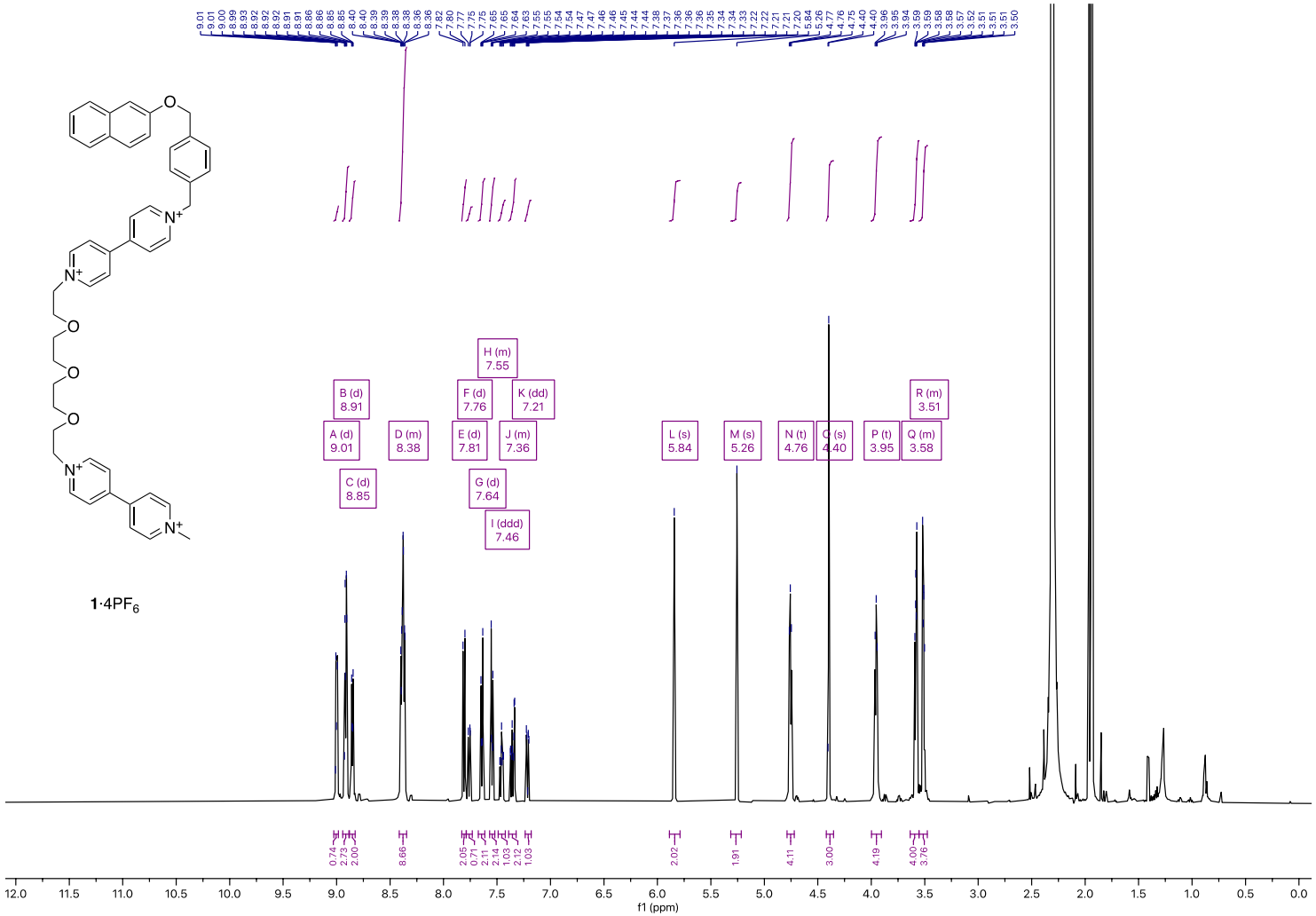


Figure S38 ^{1}H NMR (500 MHz, CD_3CN) spectrum of **1**·4PF_6.

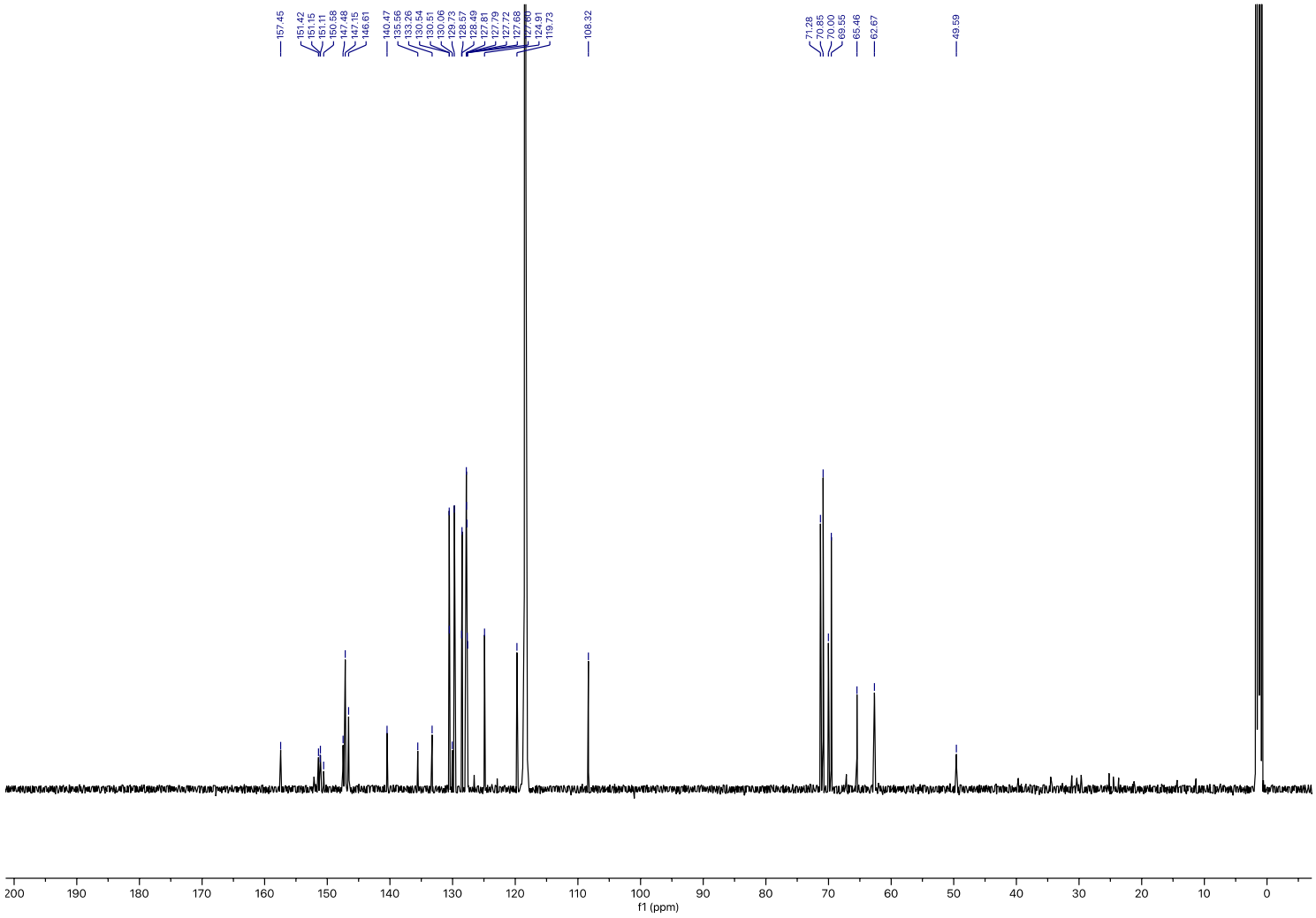


Figure S39 ^{13}C NMR (125 MHz, CD_3CN) spectrum of **1**·$4PF_6$.

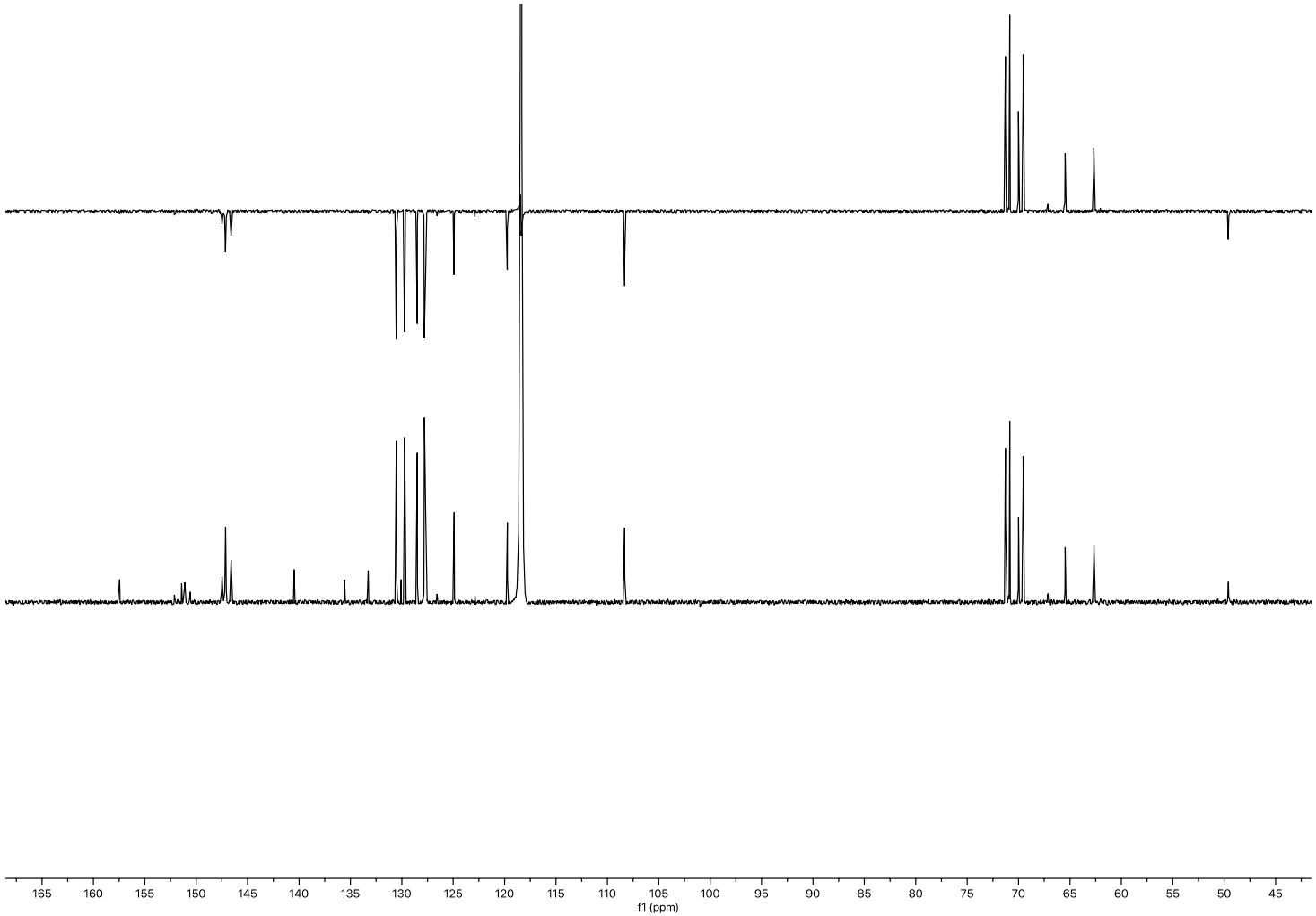


Figure S40 ^{13}C NMR and DEPT (125 MHz, CD_3CN) spectrum of **1**·4PF_6.

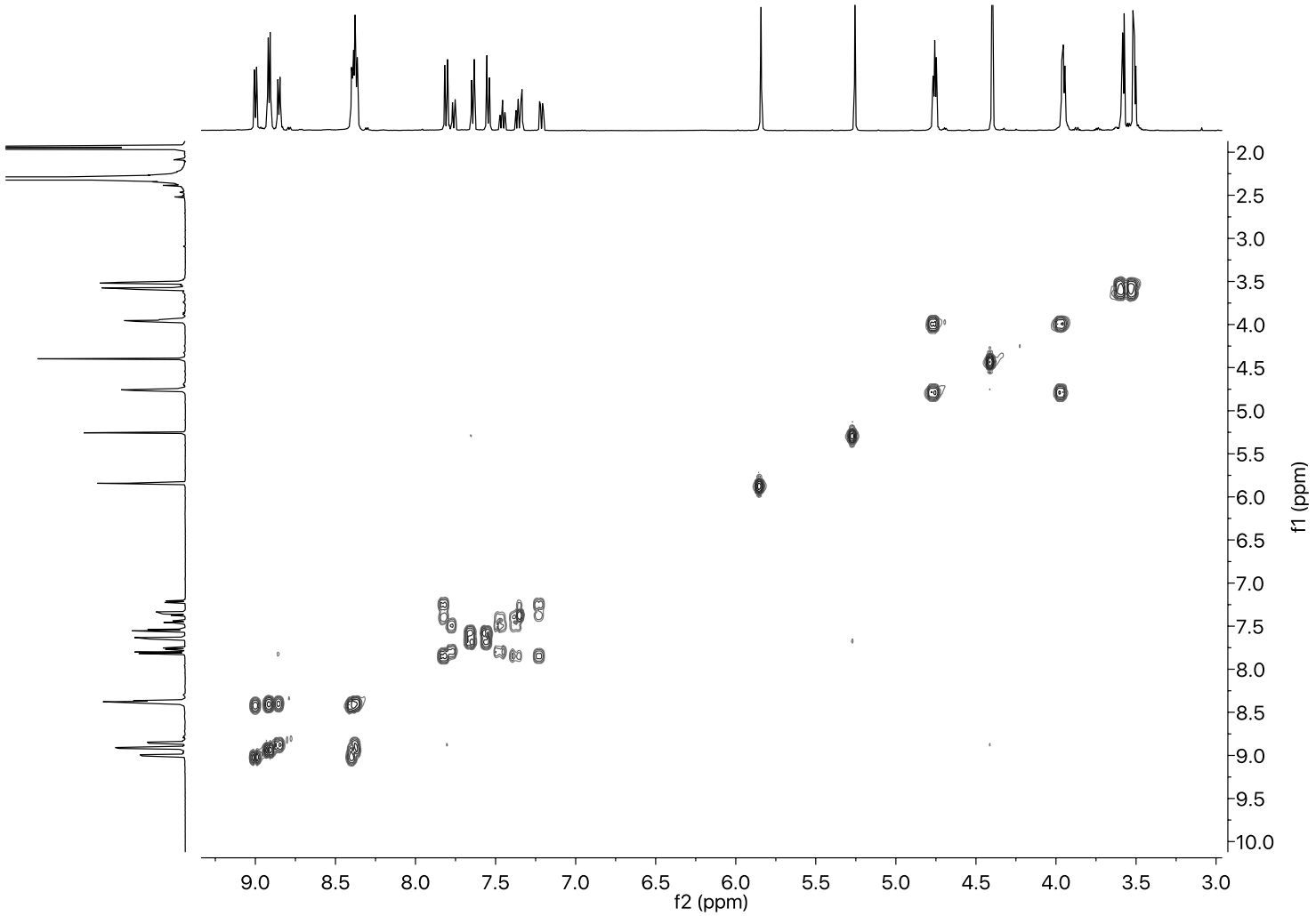


Figure S41 COSY (500 MHz, CD_3CN) spectrum of **1**·$4PF_6$.

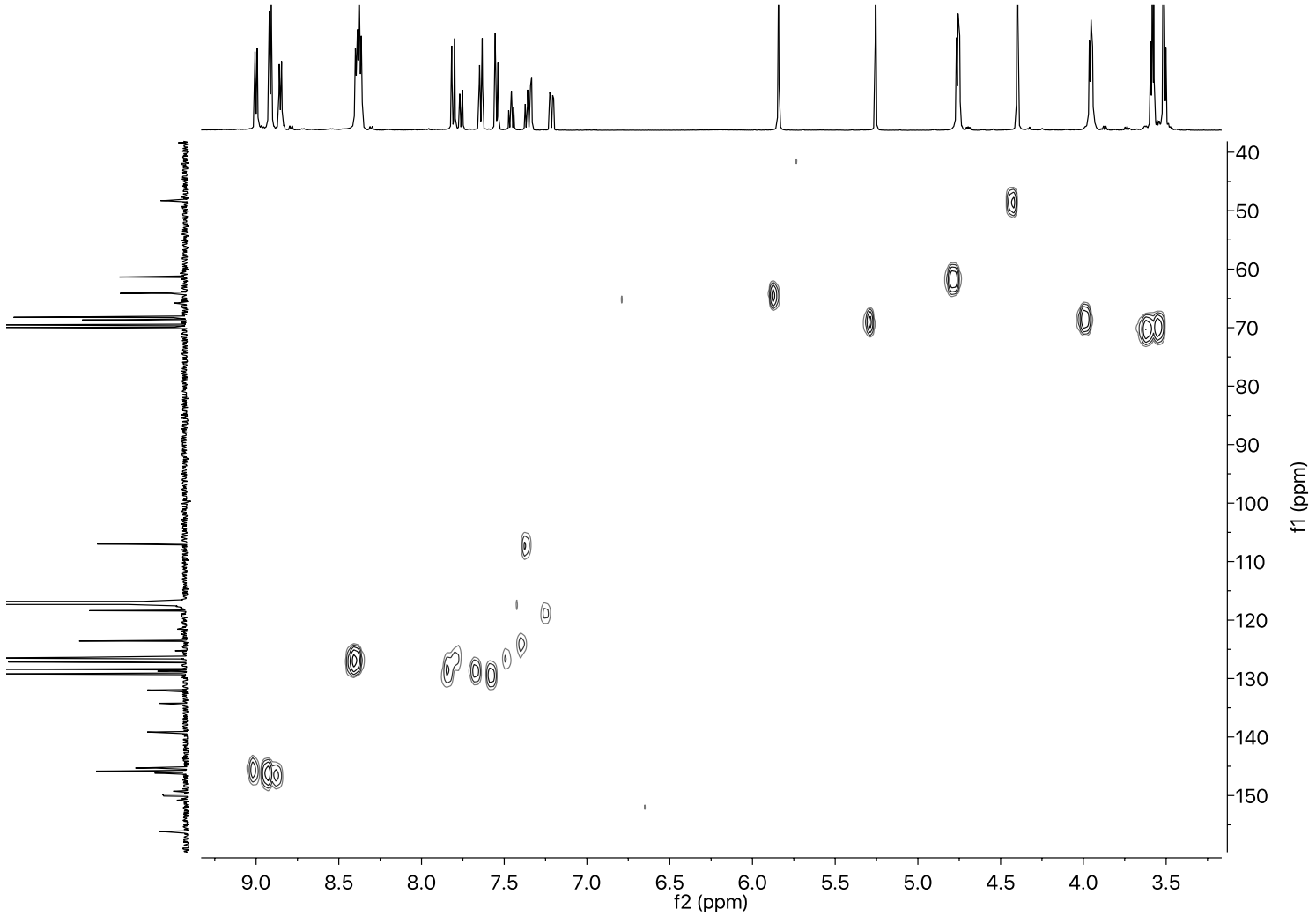


Figure S42 HSQC (500 MHz, CD_3CN) spectrum of **1**·$4PF_6$.

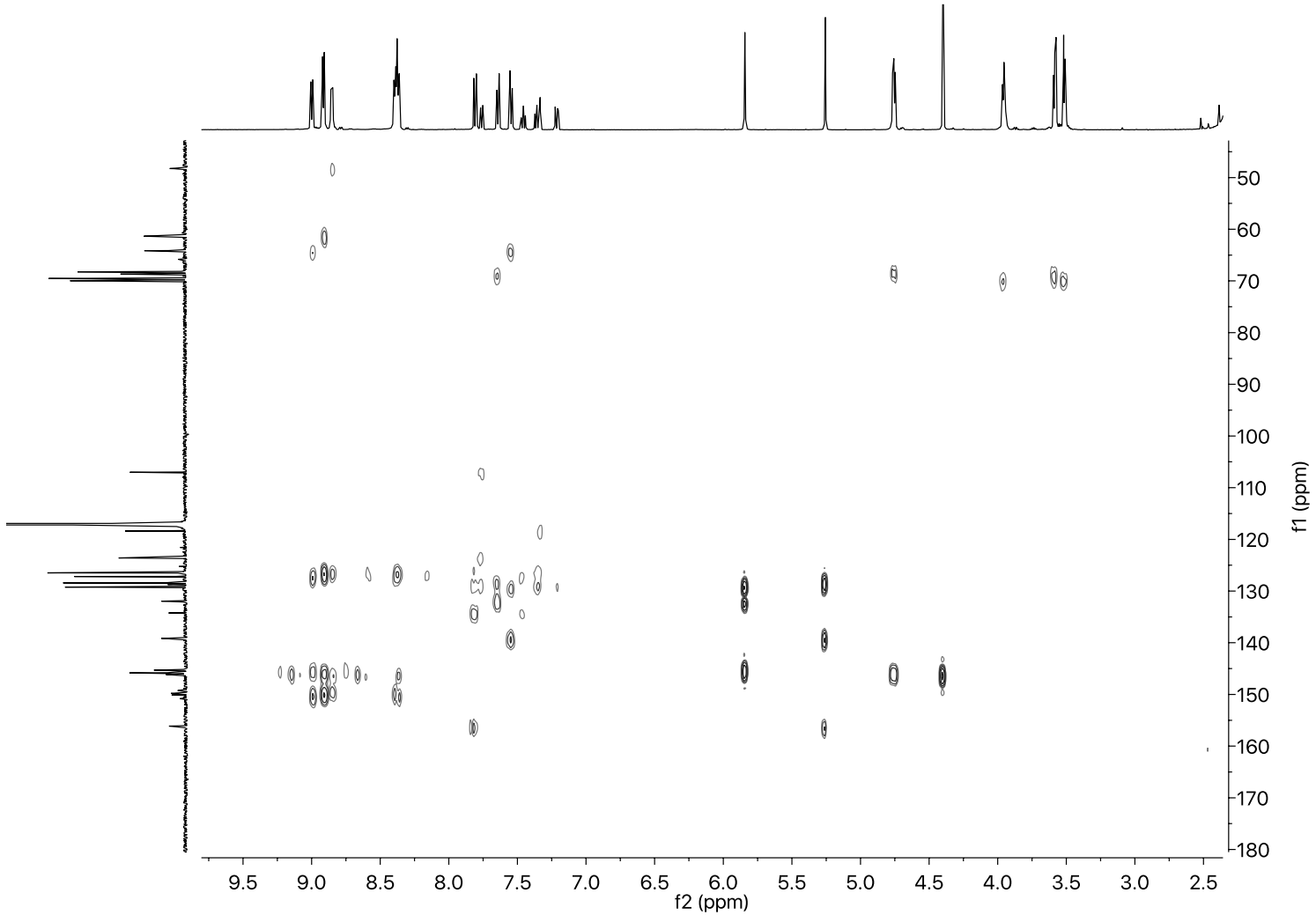


Figure S43 HMBC (500 MHz, CD_3CN) spectrum of **1**·$4PF_6$.

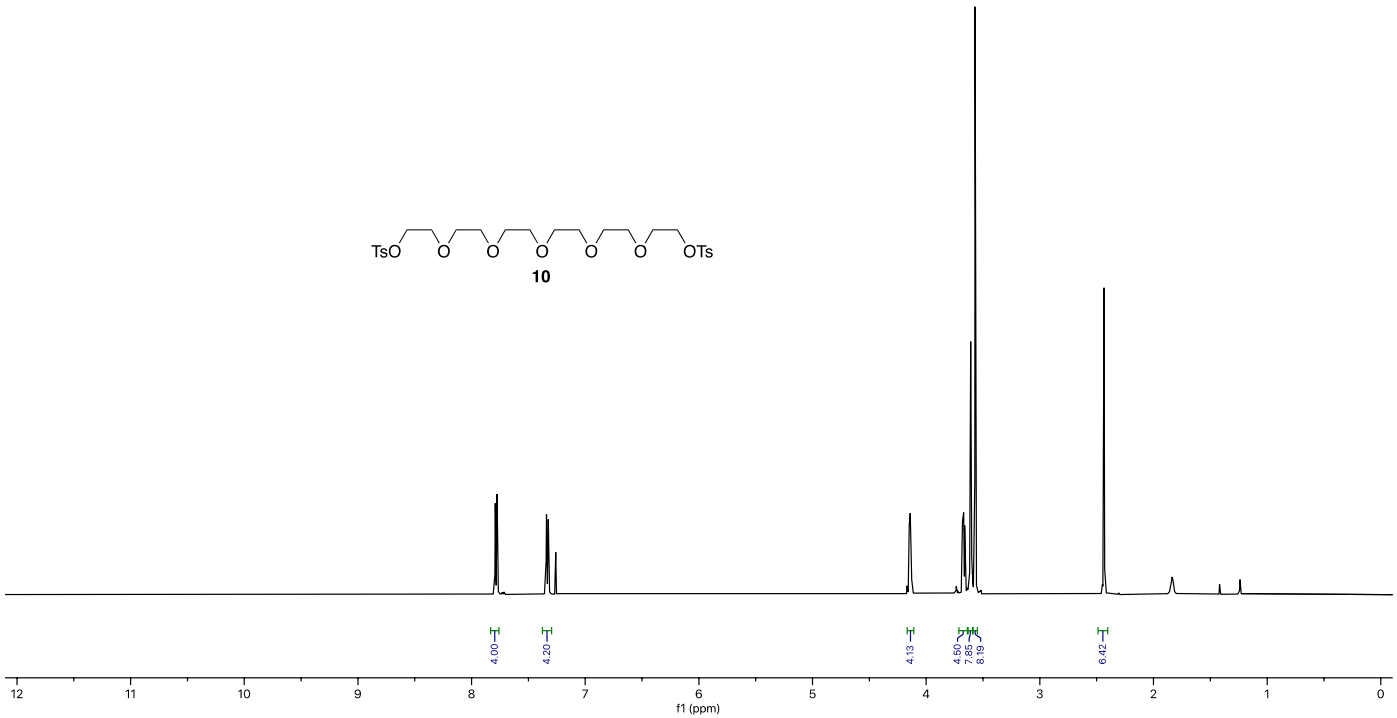


Figure S44 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **10**.

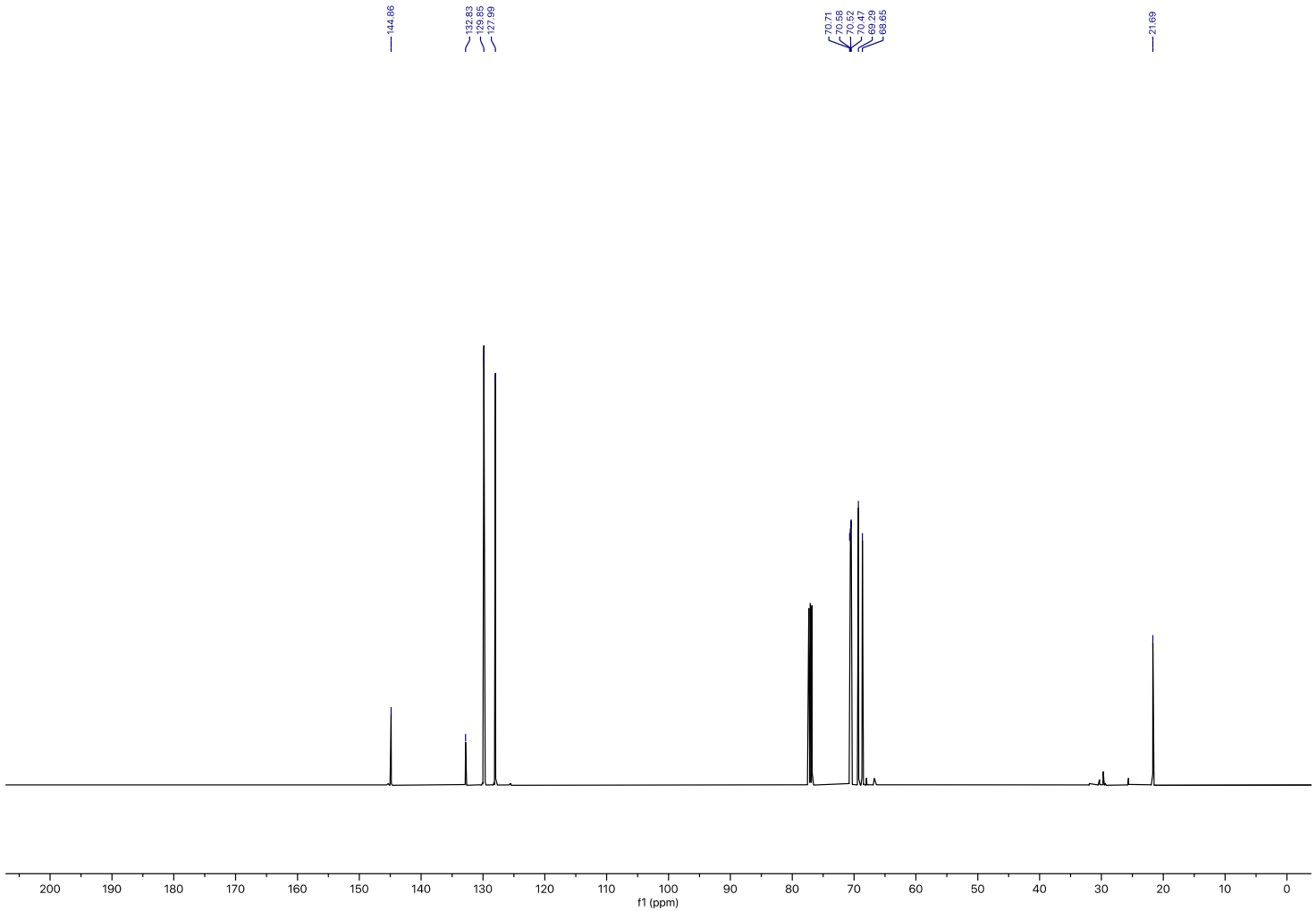


Figure S45 ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **10.**

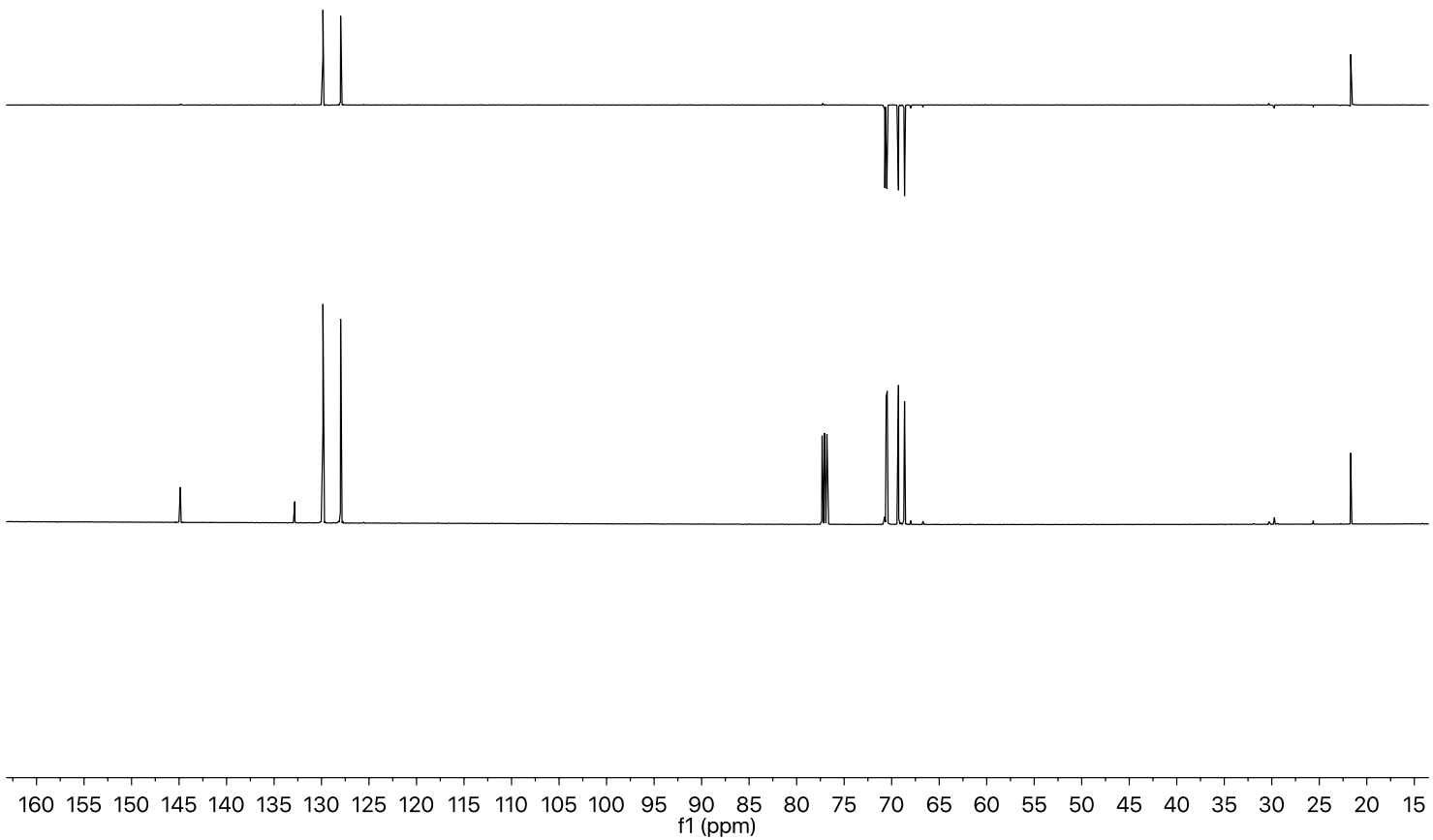


Figure S46 ^{13}C NMR and DEPT (125 MHz, $CDCl_3$) spectrum of **10**.

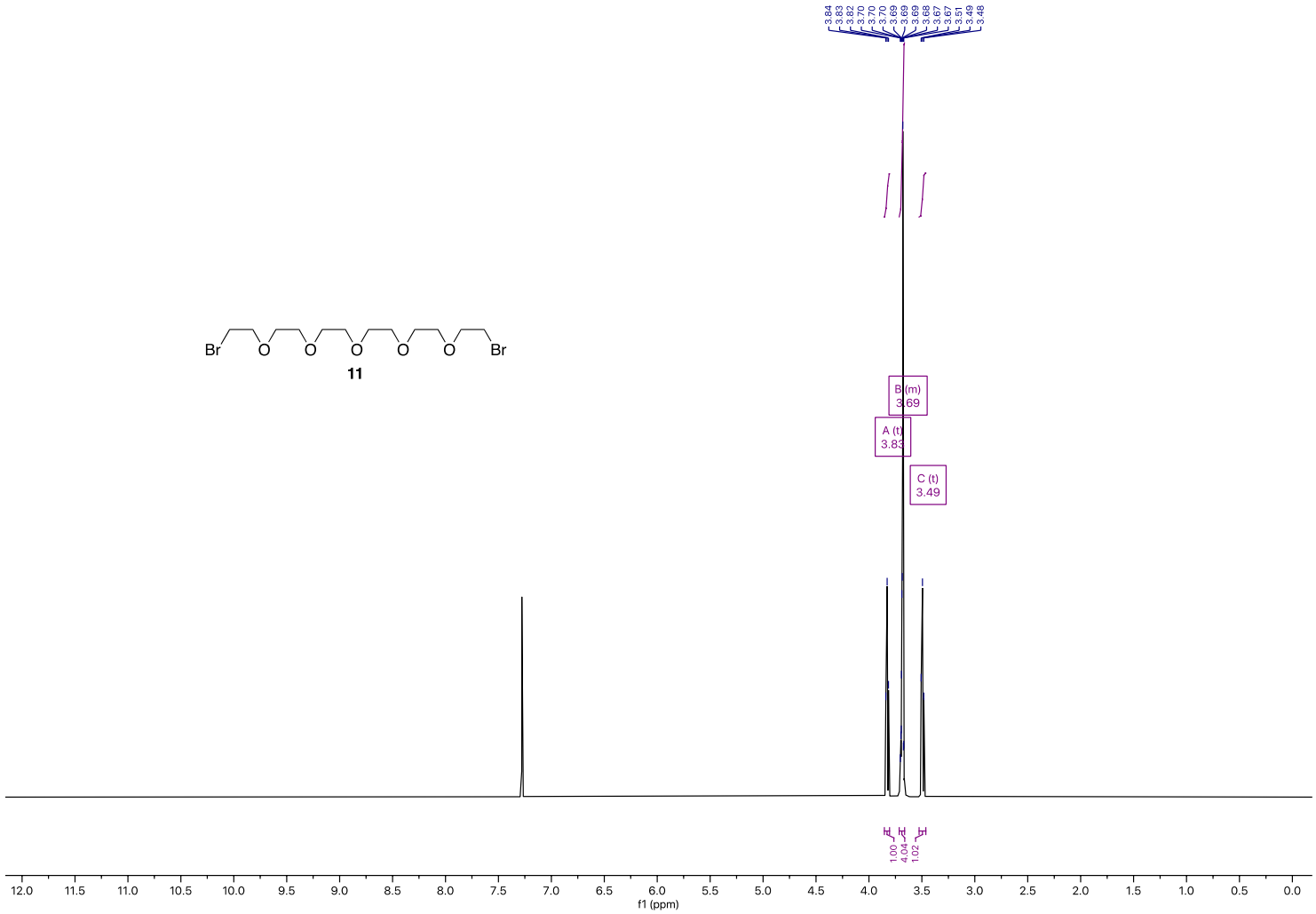


Figure S47 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **11**.

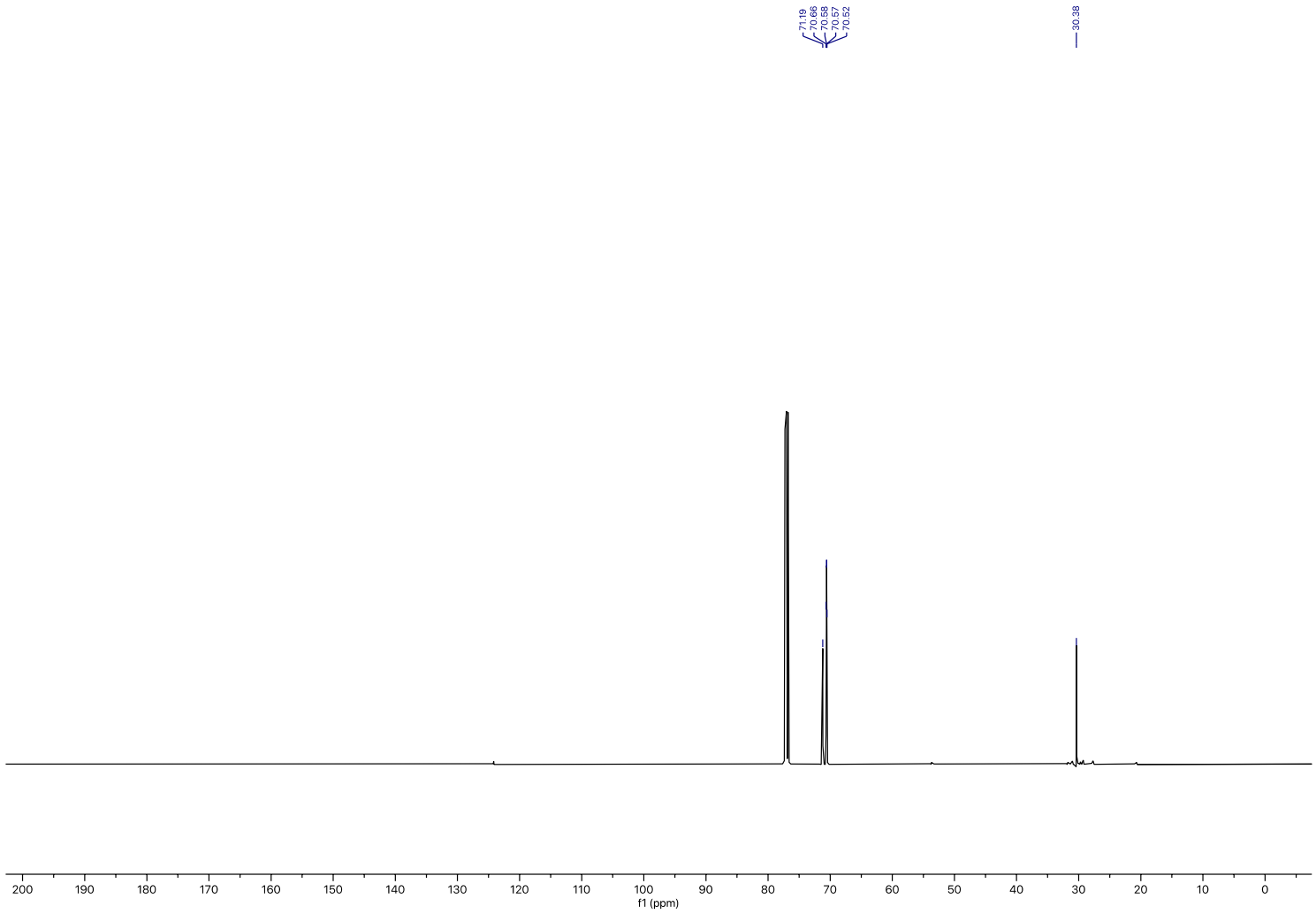


Figure S48 ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **11**.

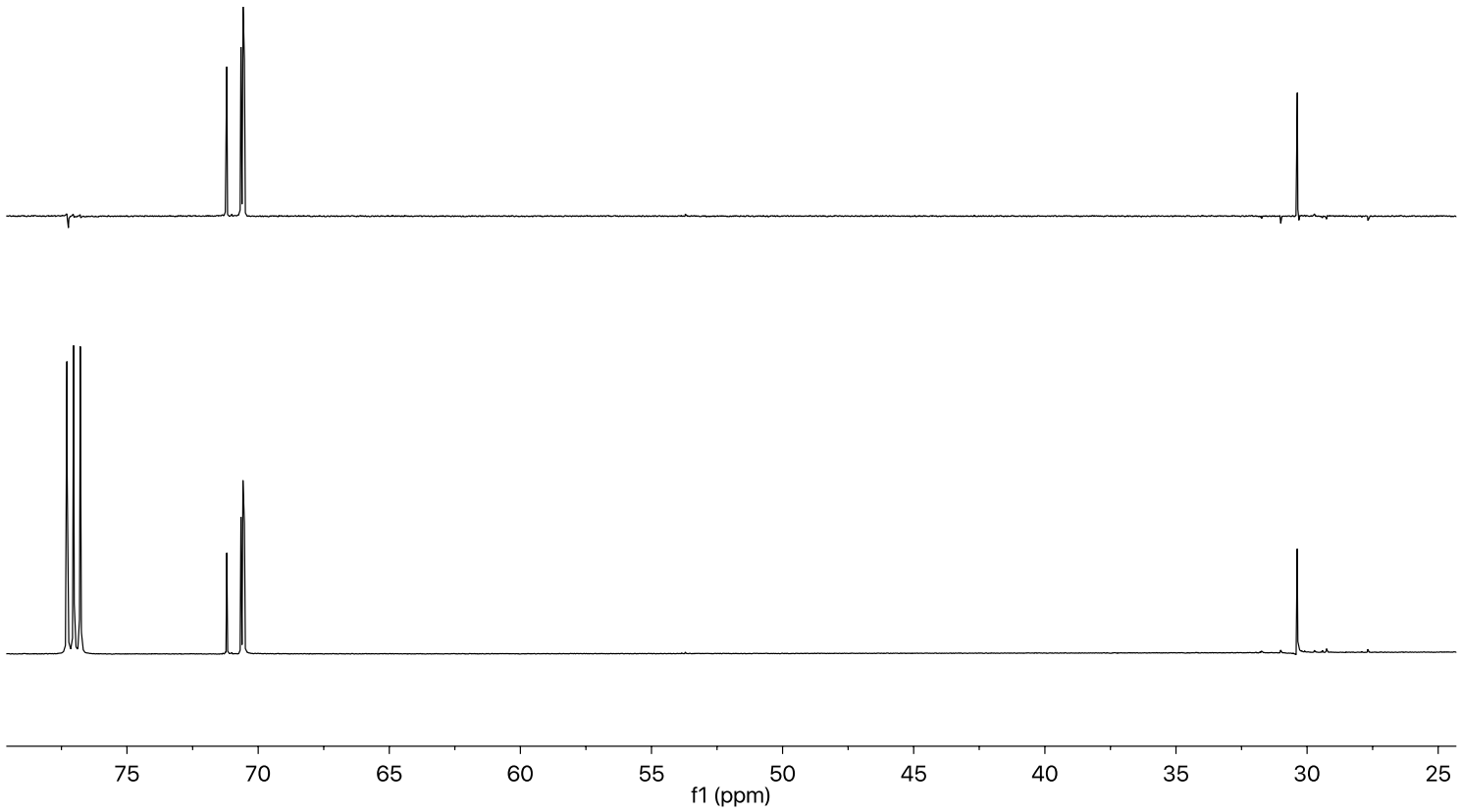


Figure S49 ^{13}C NMR and DEPT (125 MHz, $CDCl_3$) spectrum of **11**.

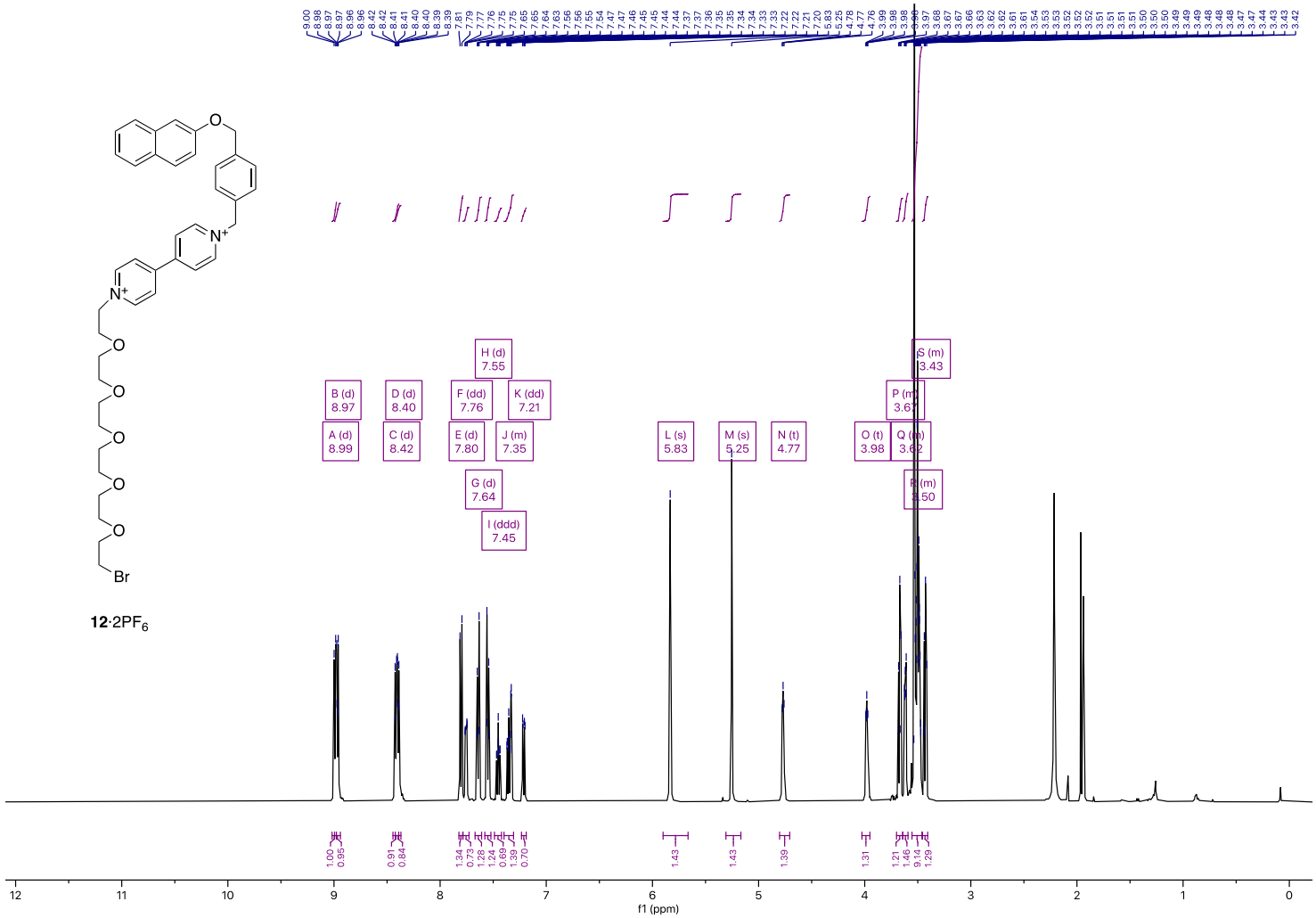


Figure S50 ^{1}H NMR (500 MHz, CD_3CN) spectrum of **12**·2PF_6.

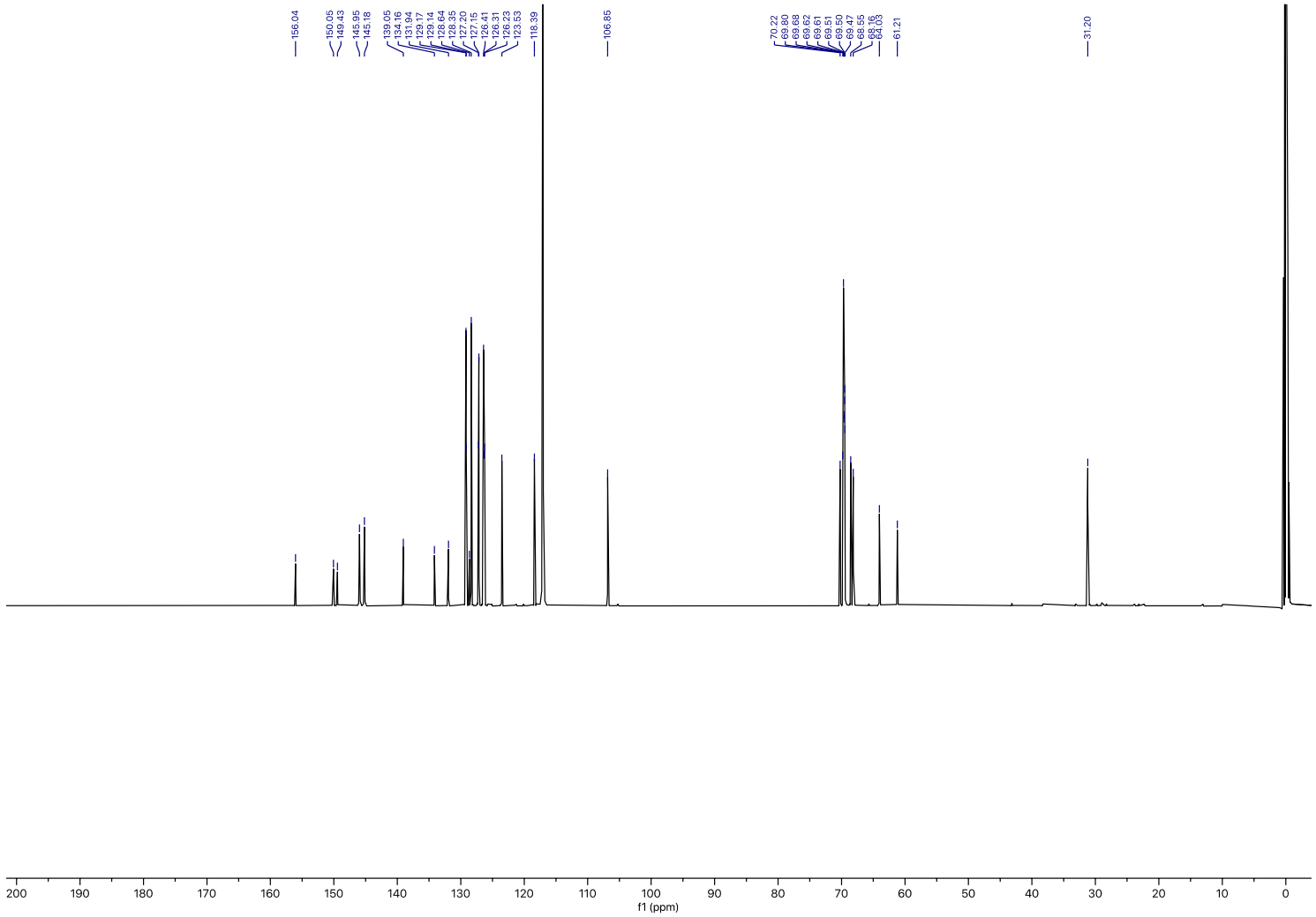


Figure S51 ^{13}C NMR (125 MHz, CD_3CN) spectrum of **12**·$2PF_6$.

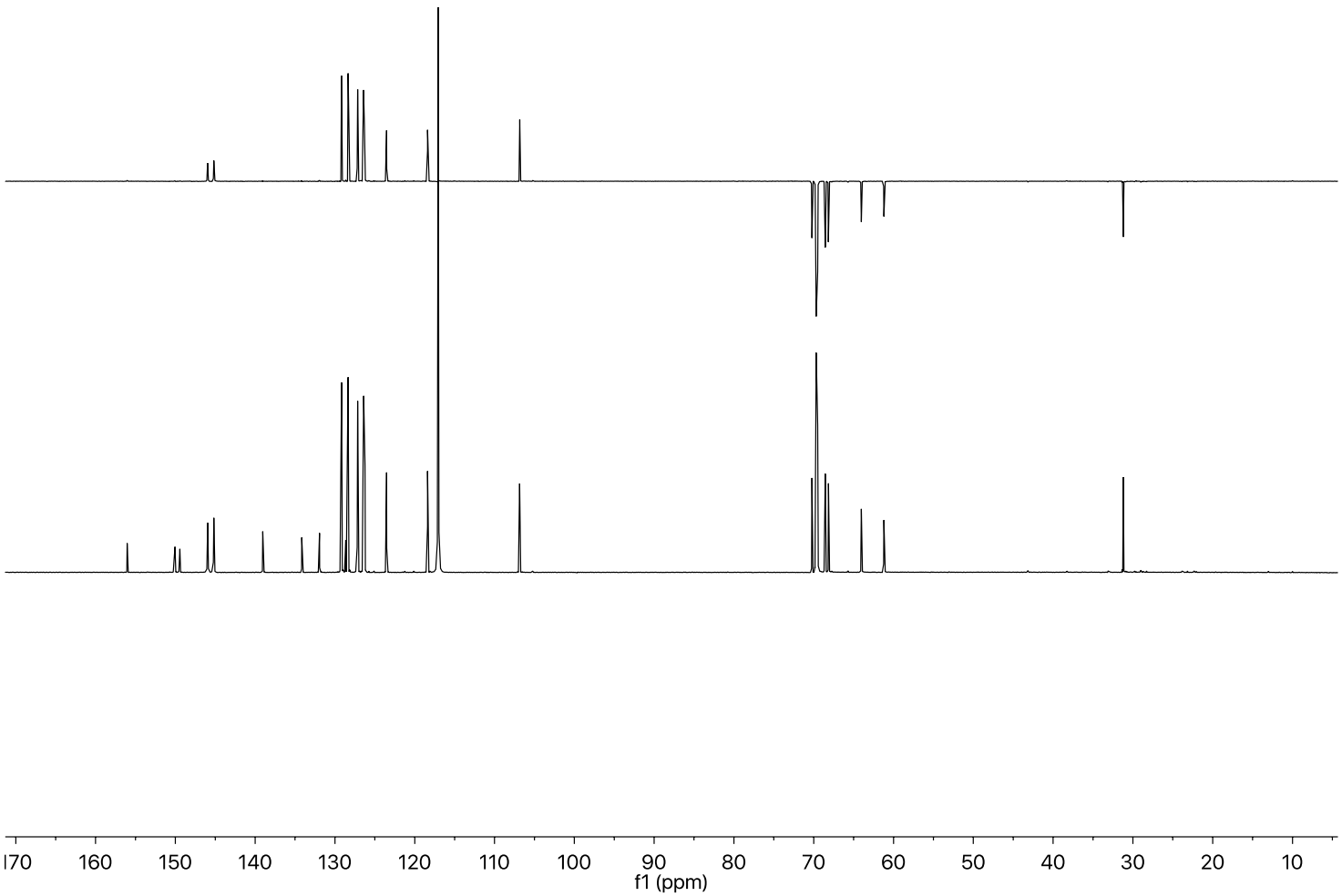


Figure S52 ^{13}C NMR and DEPT (125 MHz, CD_3CN) spectrum of **12**·$2PF_6$.

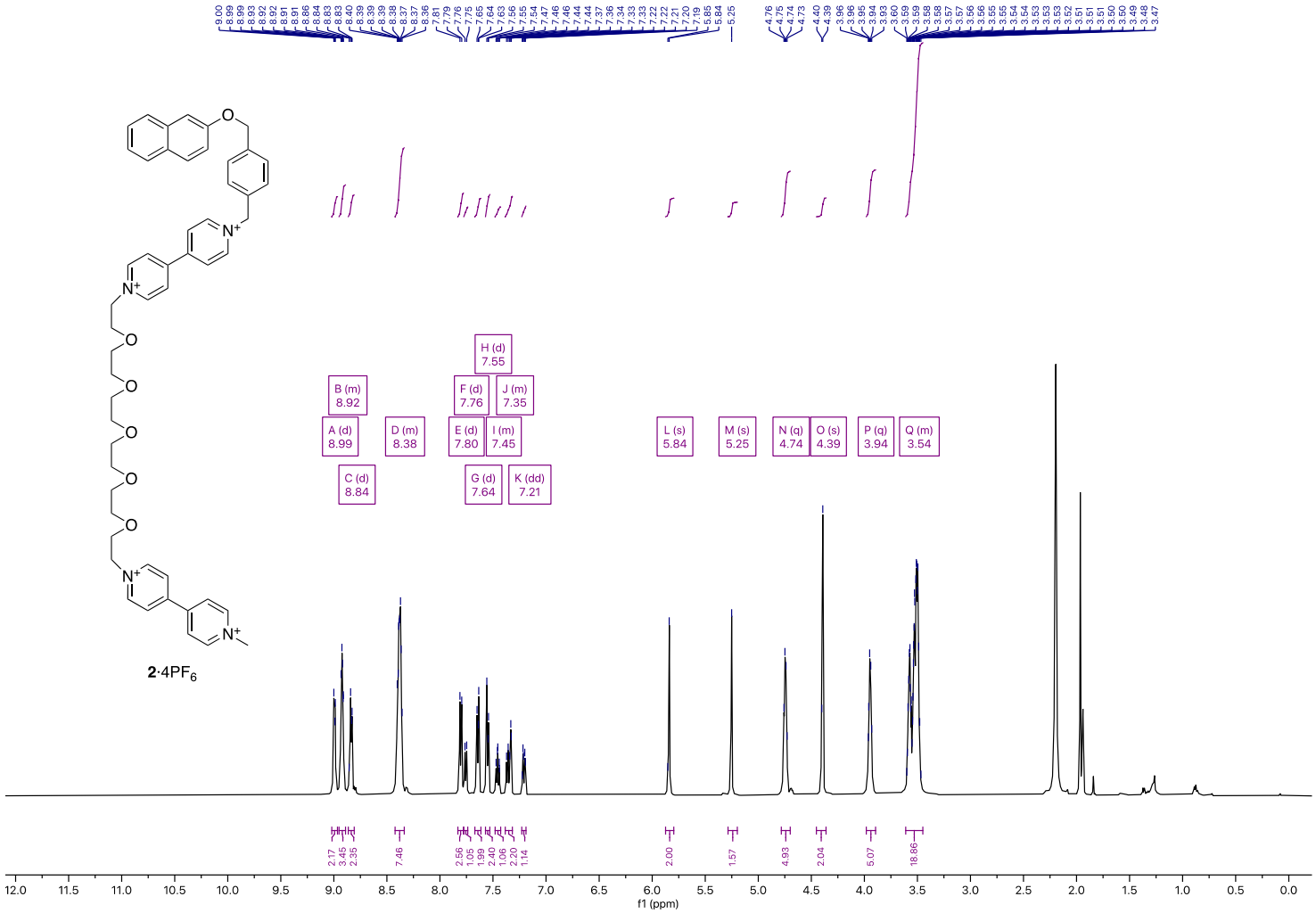


Figure S53 ^{1}H NMR (500 MHz, CD_3CN) spectrum of **2**·4PF_6.

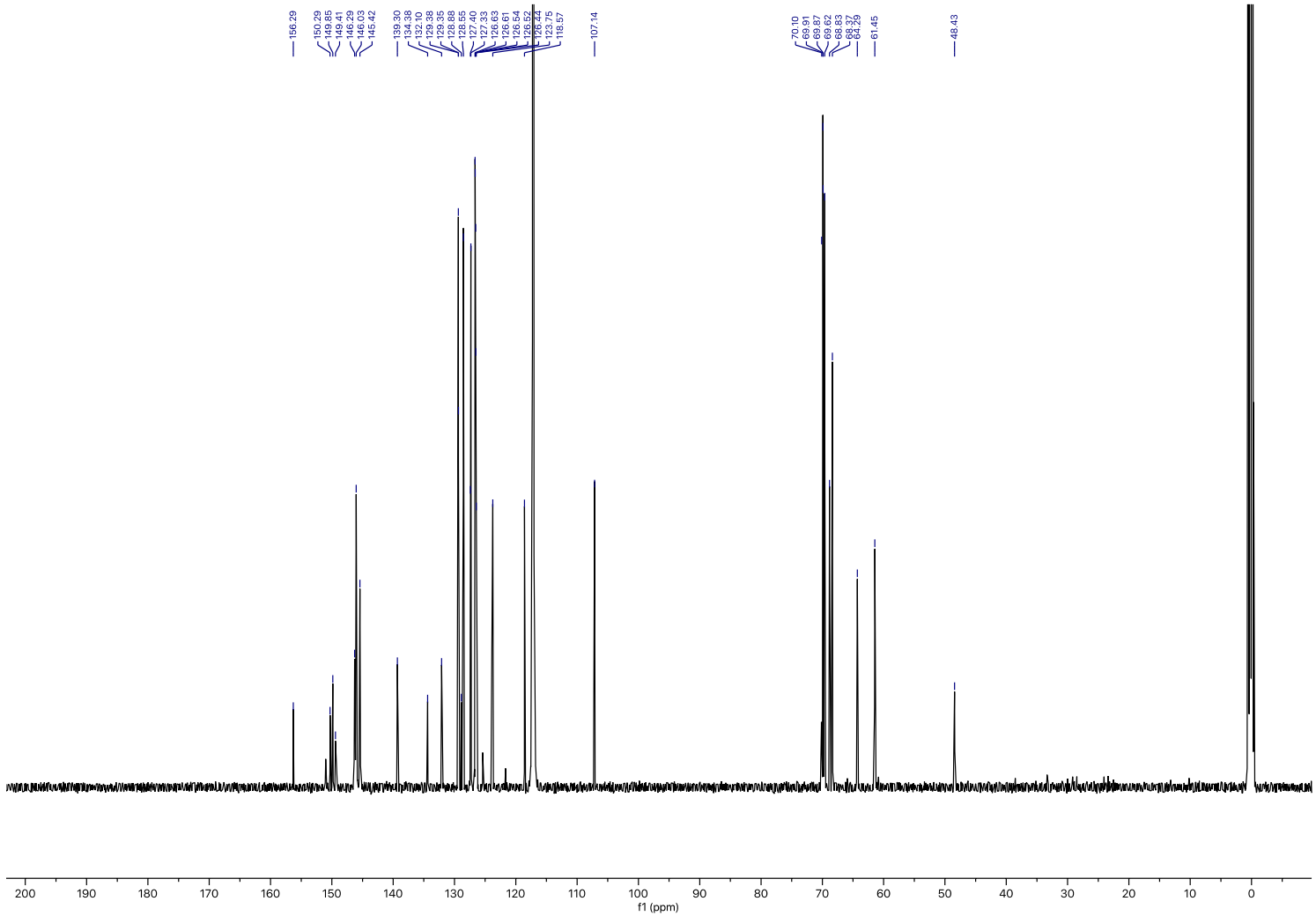


Figure S54 ^{13}C NMR (125 MHz, CD_3CN) spectrum of **2**·$4PF_6$.

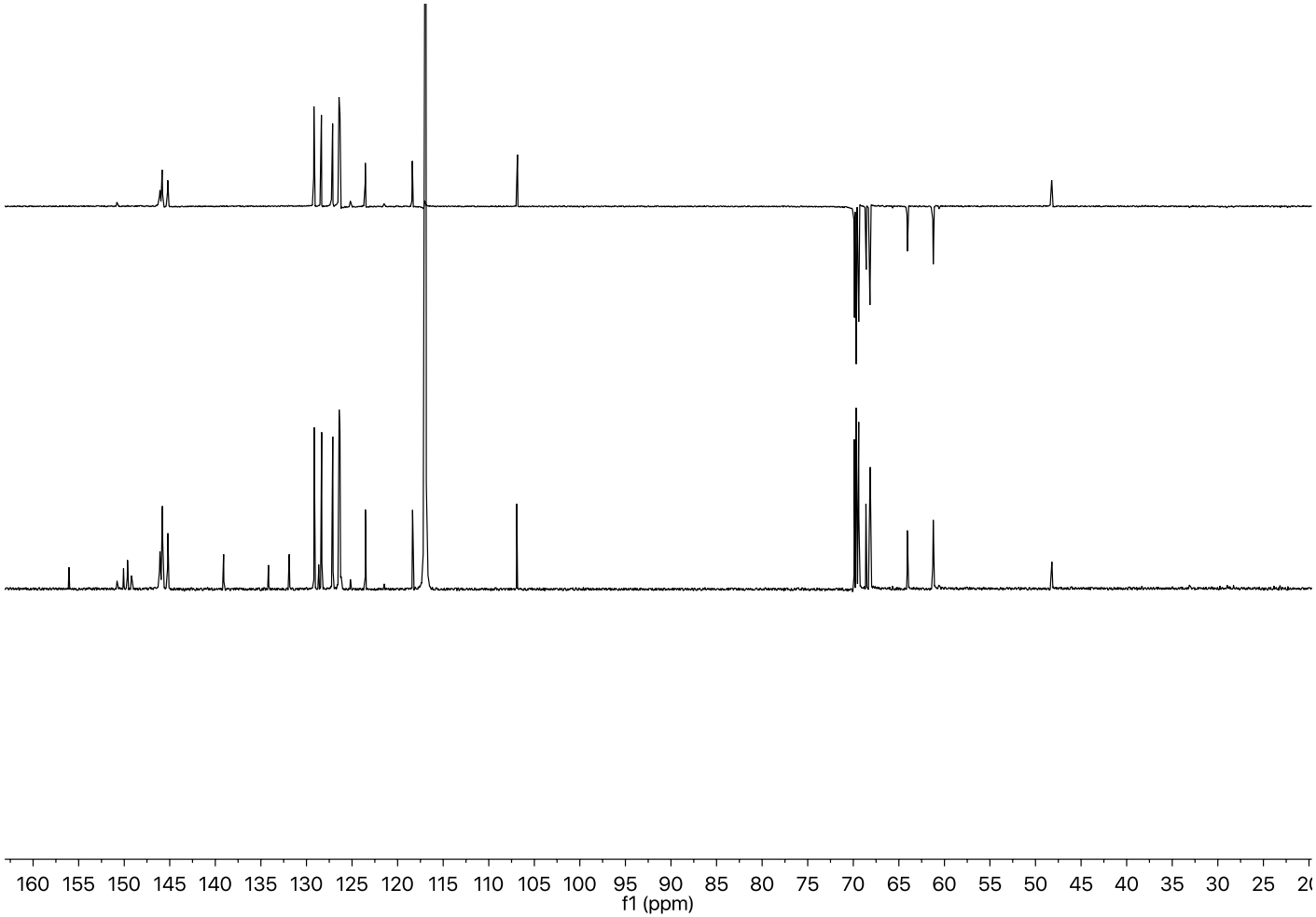


Figure S55 ^{13}C NMR and DEPT (125 MHz, CD_3CN) spectrum of **2**·$4PF_6$.

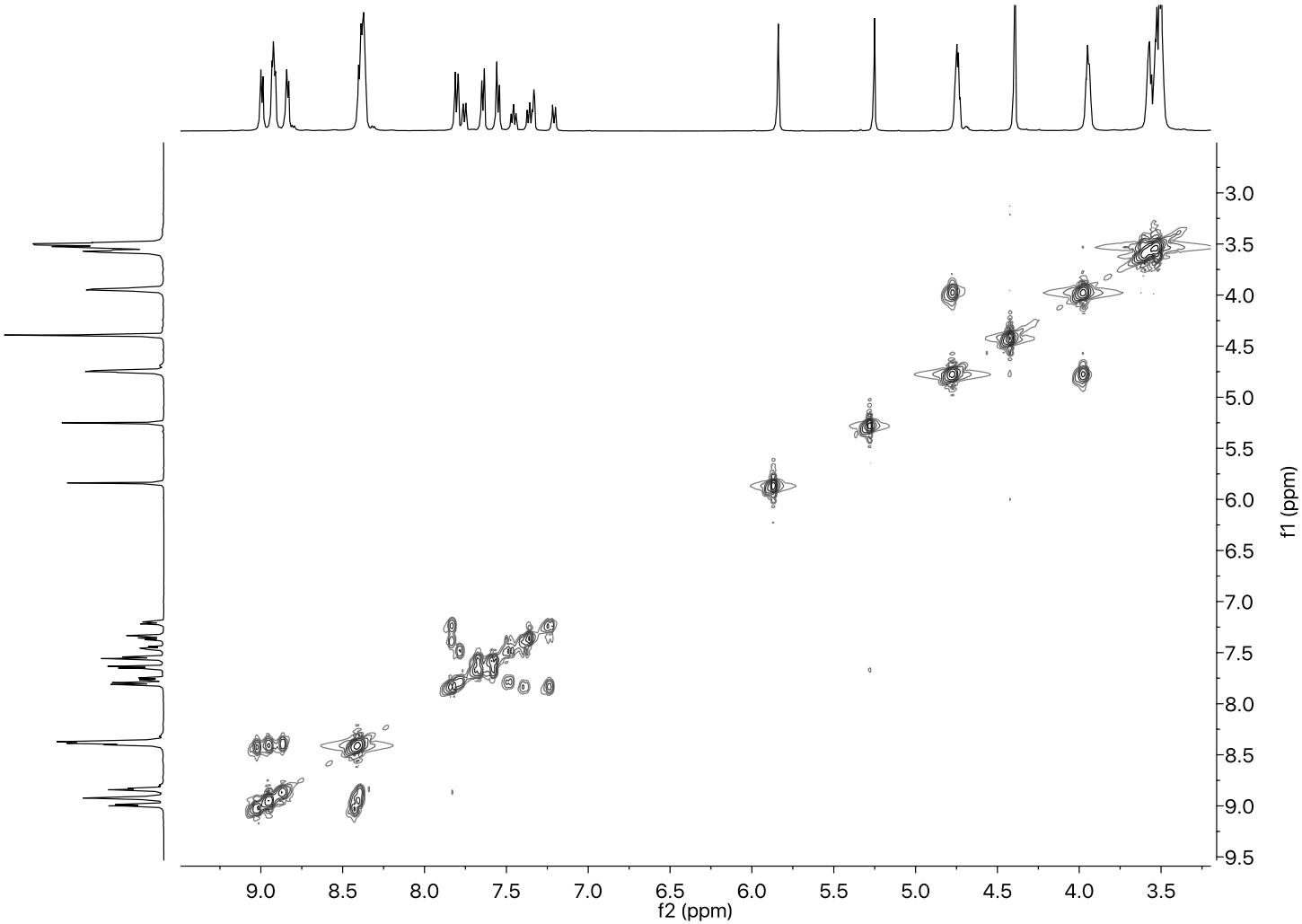


Figure S56 COSY (500 MHz, CD_3CN) spectrum of **2**·4PF_6.

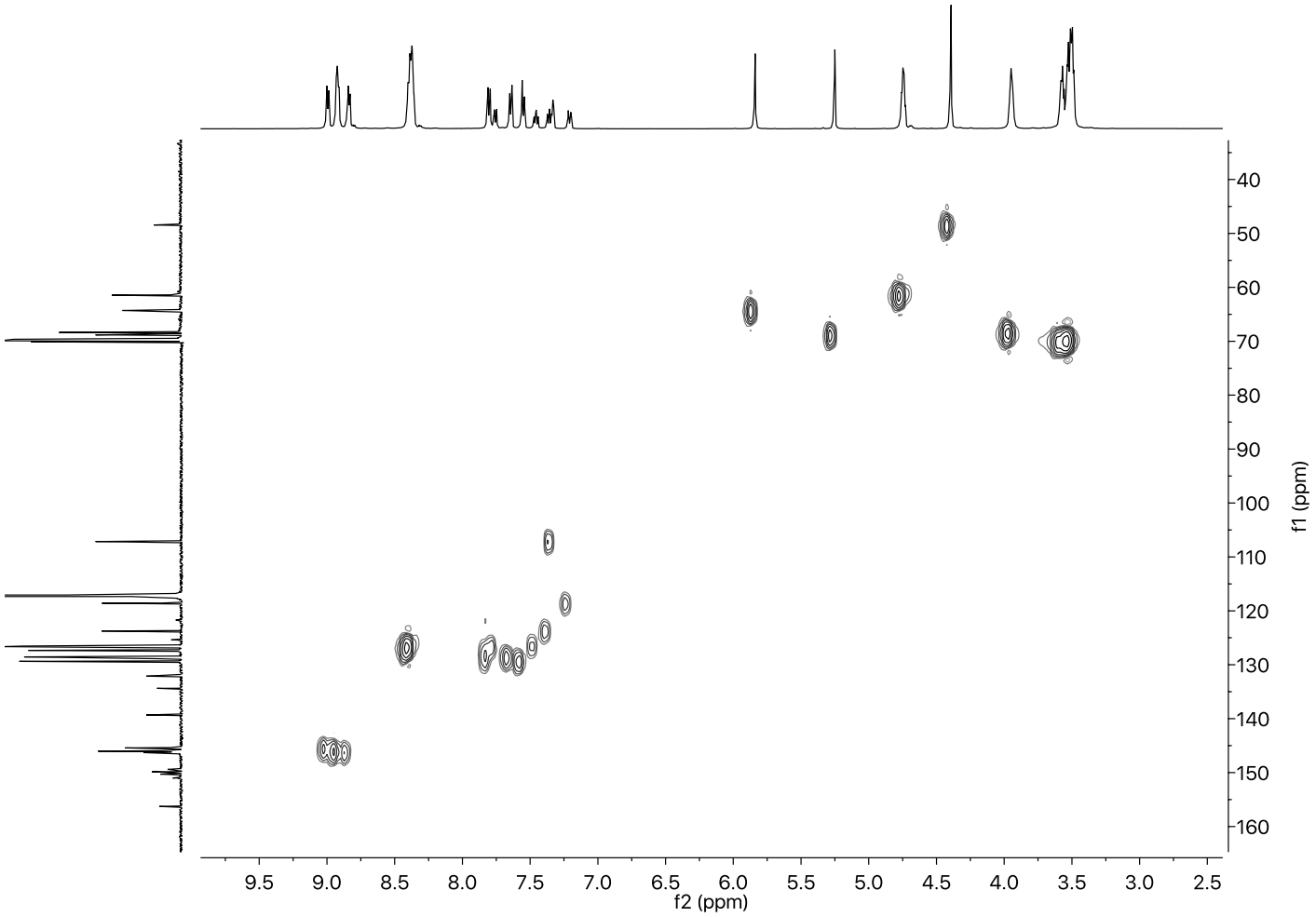


Figure S57 HSQC (500 MHz, CD_3CN) spectrum of **2**·$4PF_6$.

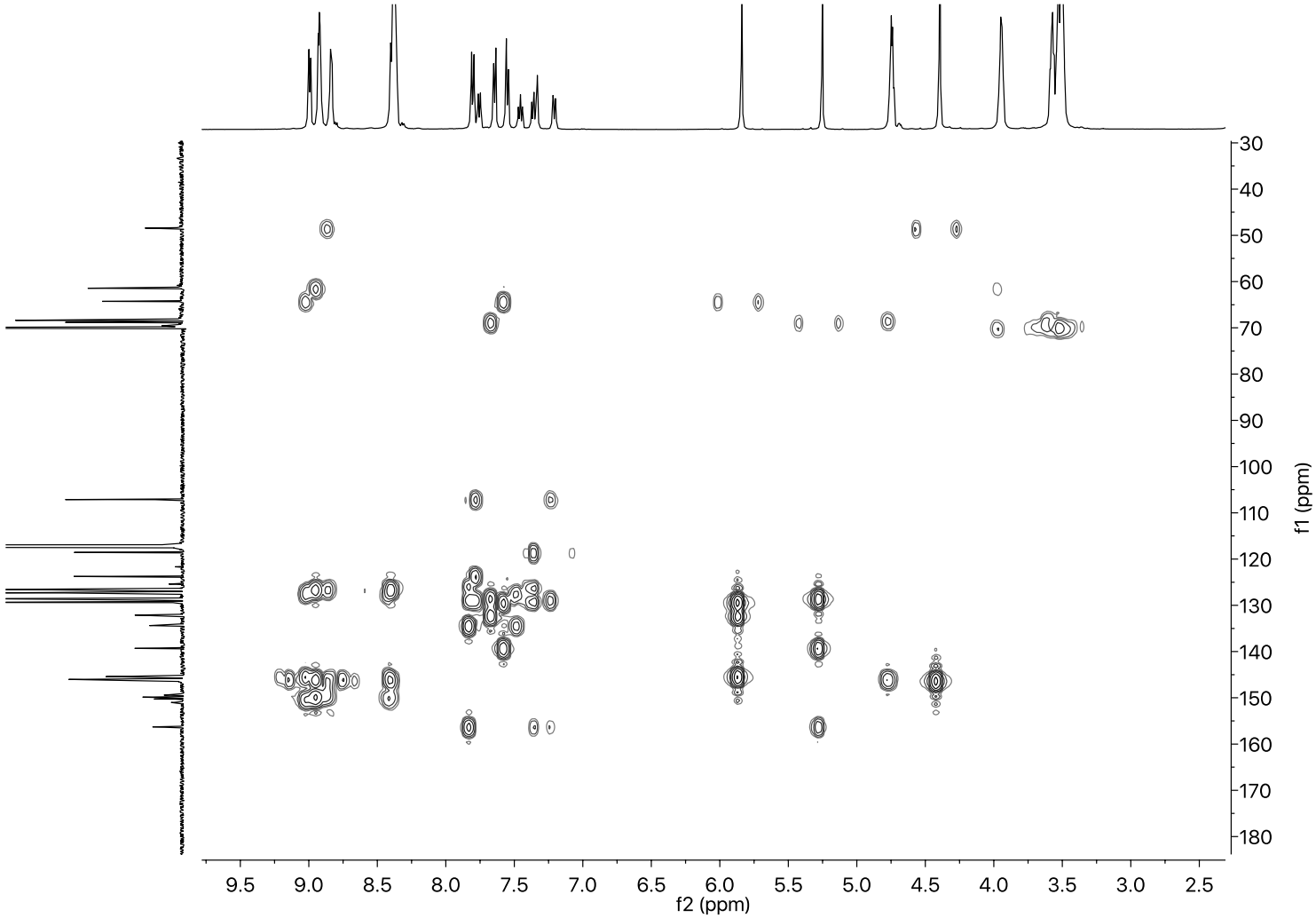


Figure S58 HMBC (500 MHz, CD_3CN) spectrum of **2**·$4PF_6$.

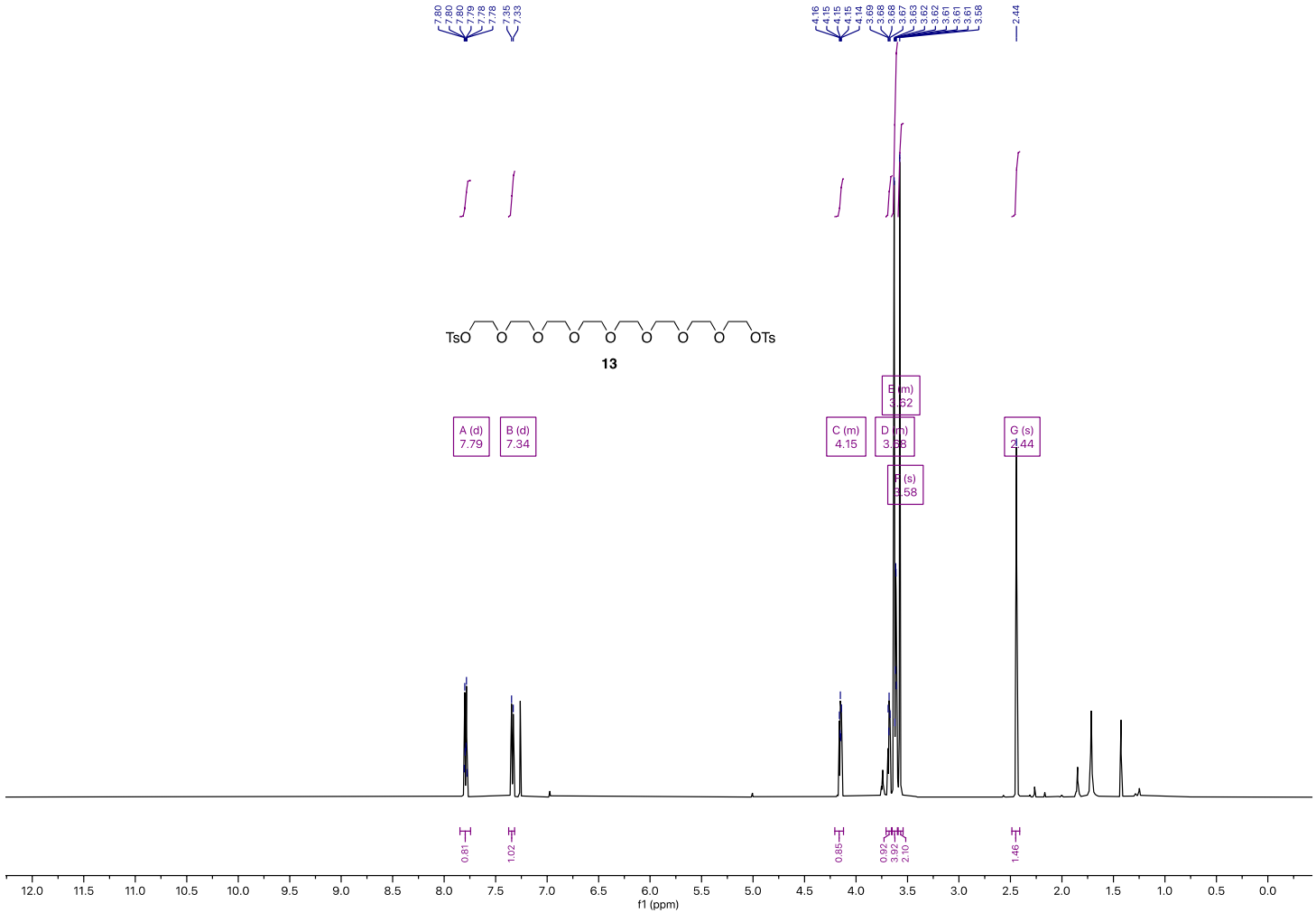


Figure S59 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **13**.

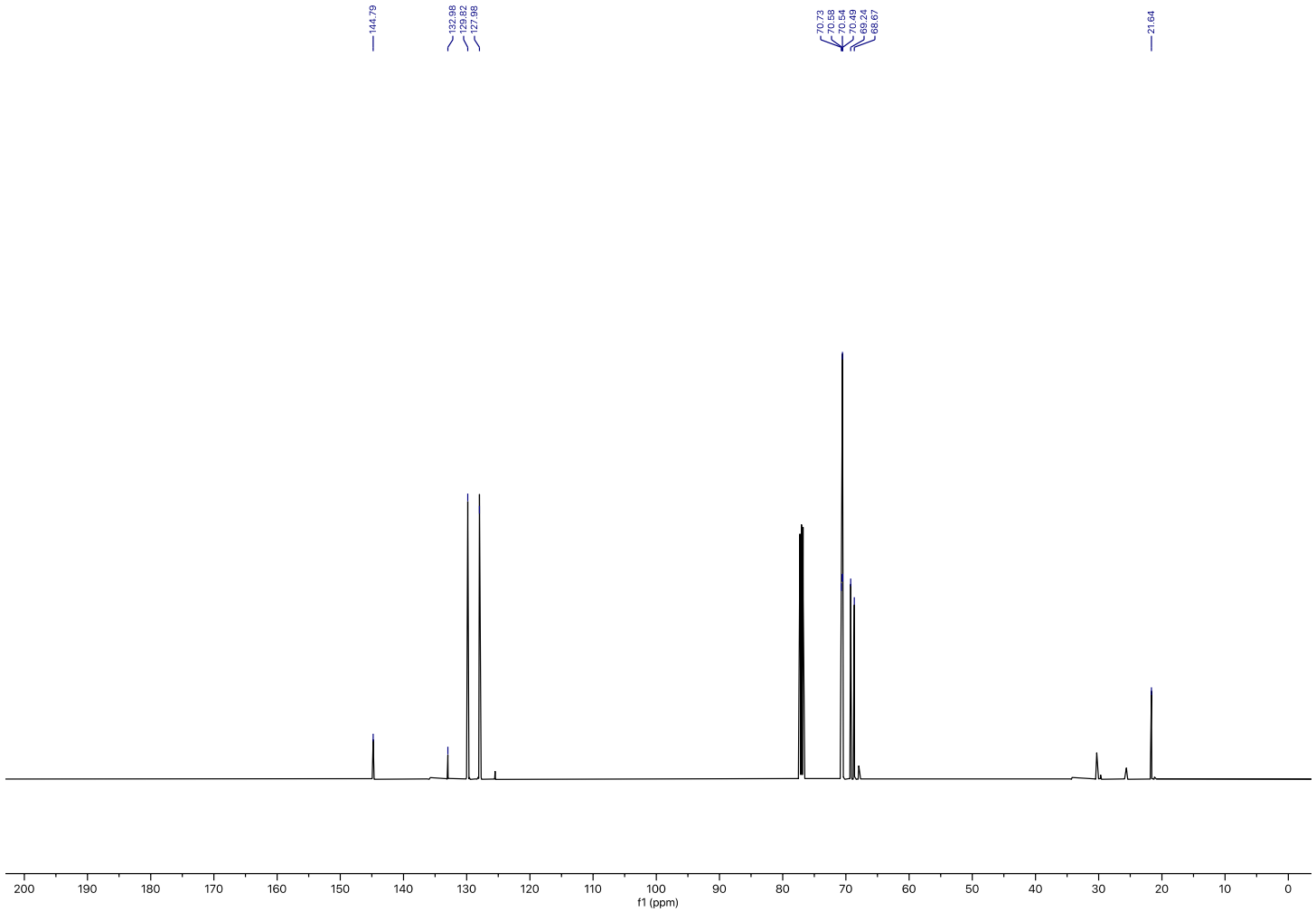


Figure S60 ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **13**.

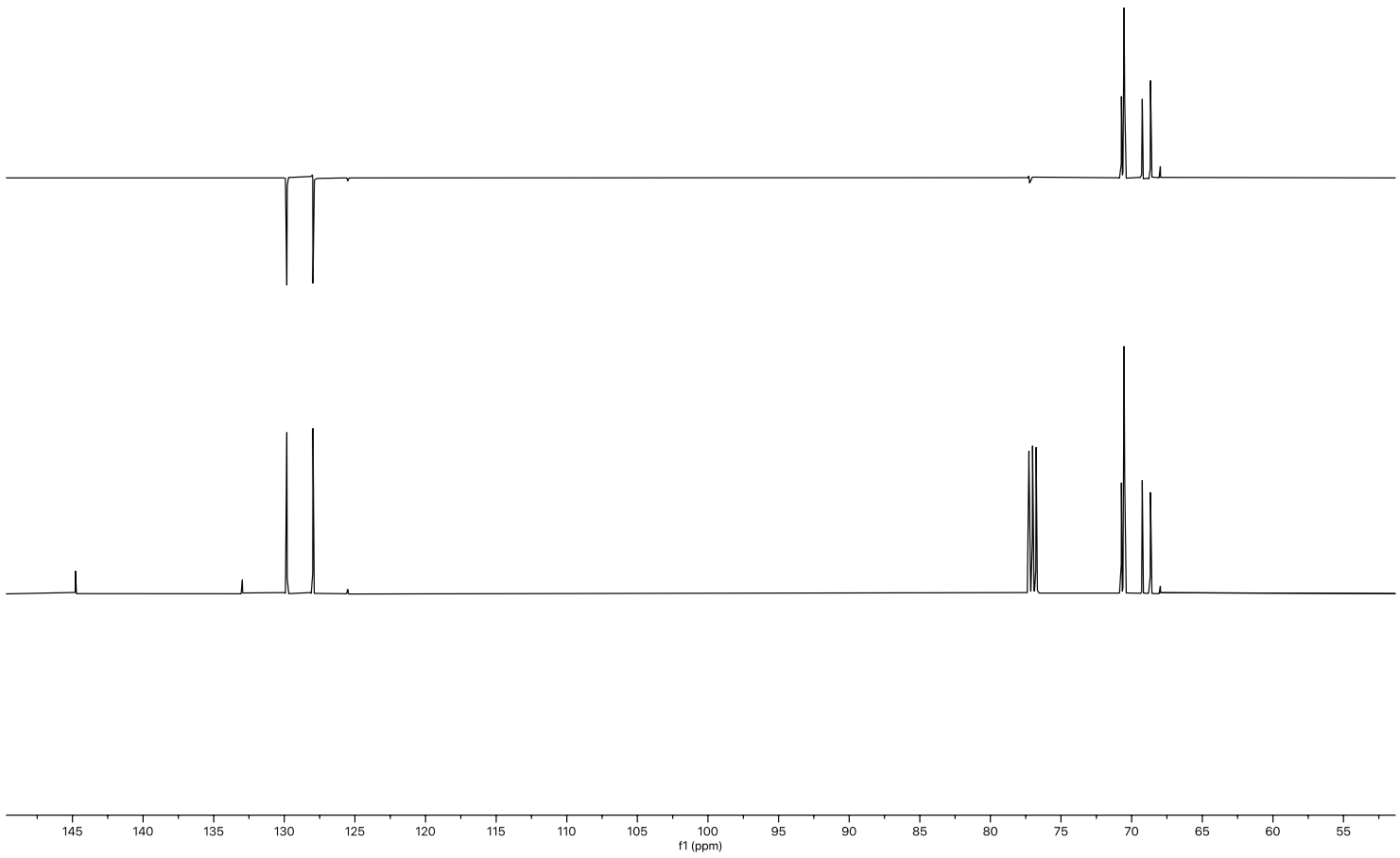


Figure S61 ^{13}C and DEPT NMR (125 MHz, $CDCl_3$) spectrum of **13**.

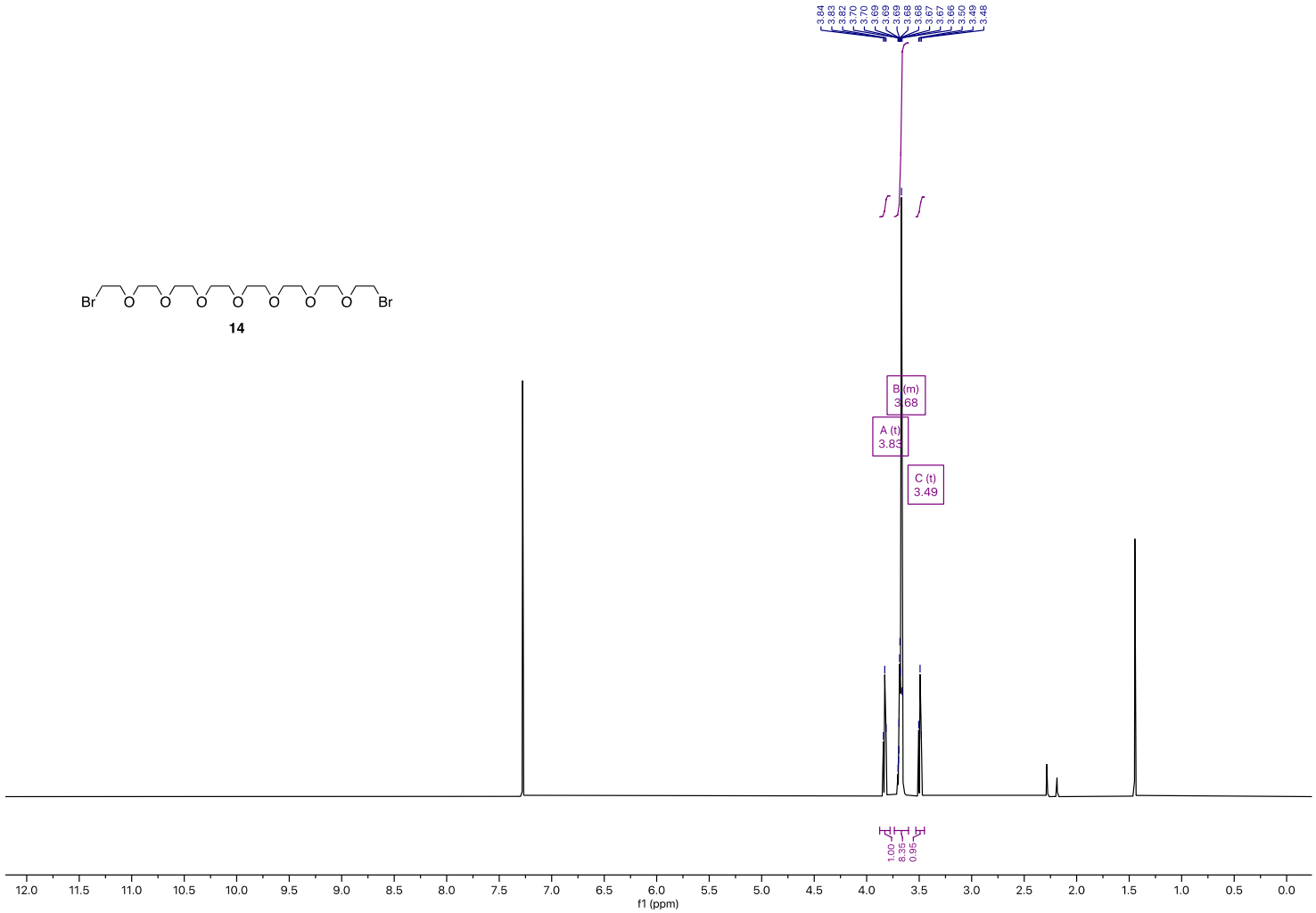


Figure S62 ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **14**.

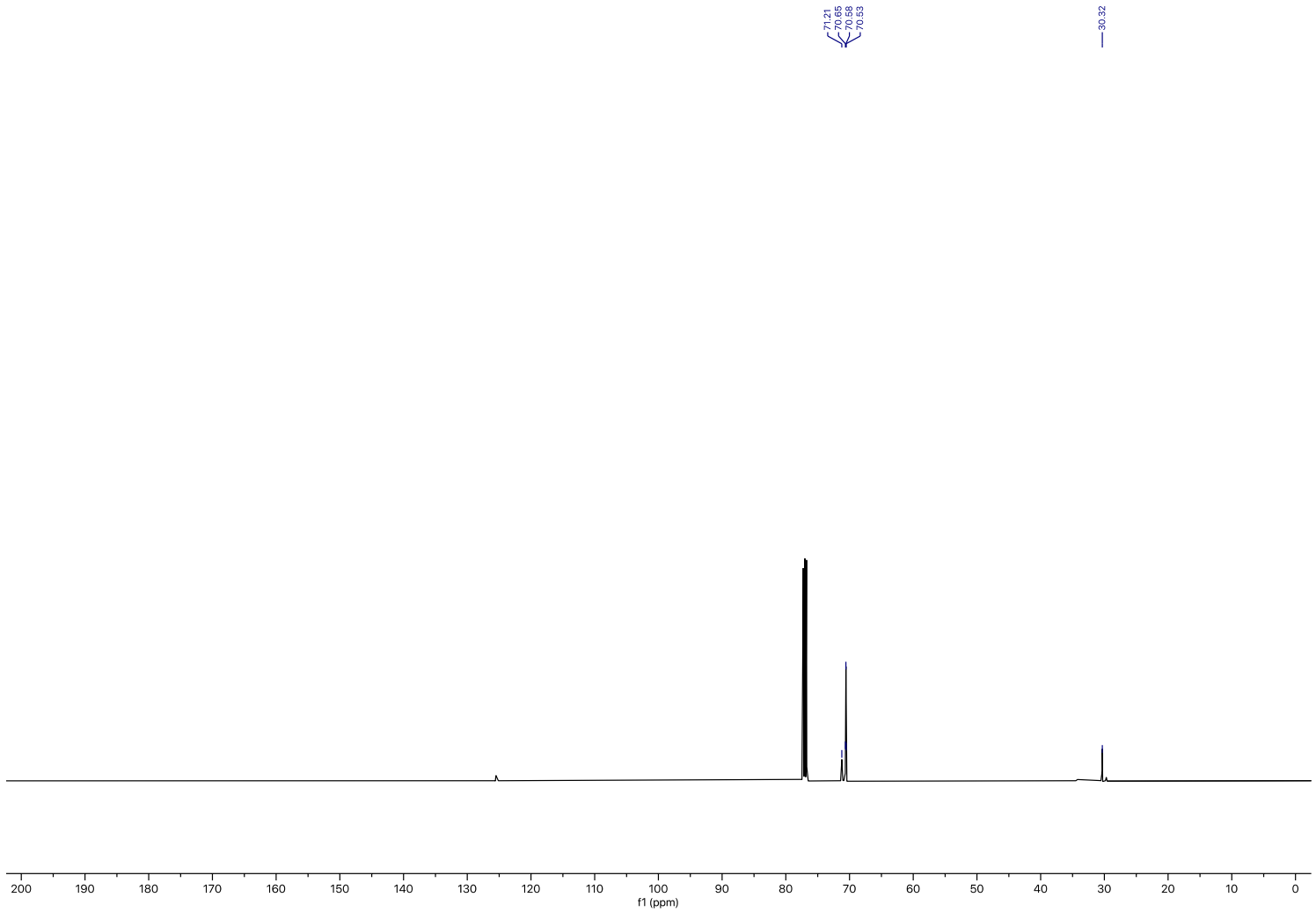


Figure S63 ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of **14**.

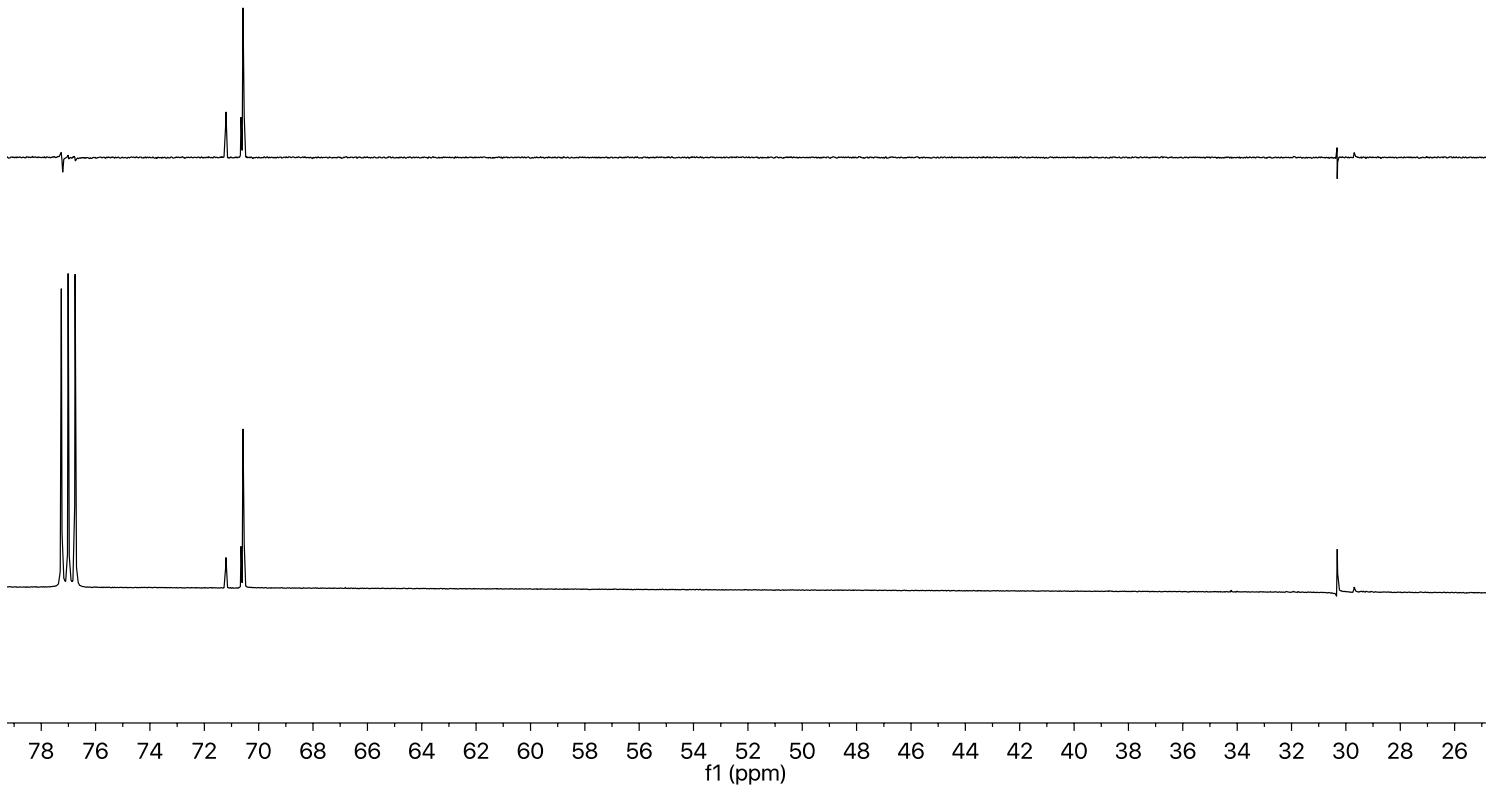


Figure S64 ^{13}C and DEPT NMR (125 MHz, $CDCl_3$) spectrum of **14**.

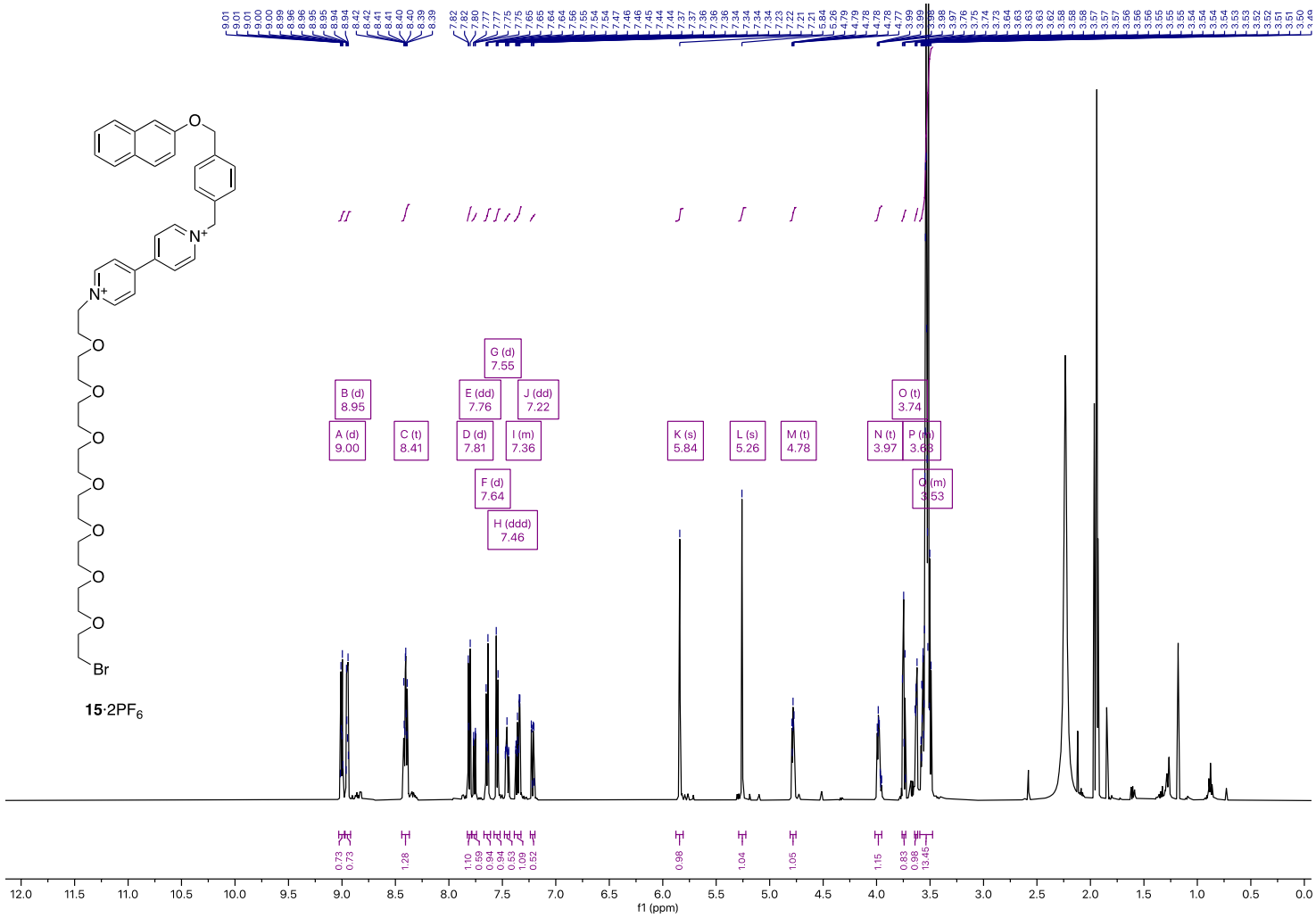


Figure S65 ^{1}H NMR (500 MHz, CD_3CN) spectrum of **15**·$2PF_6$.

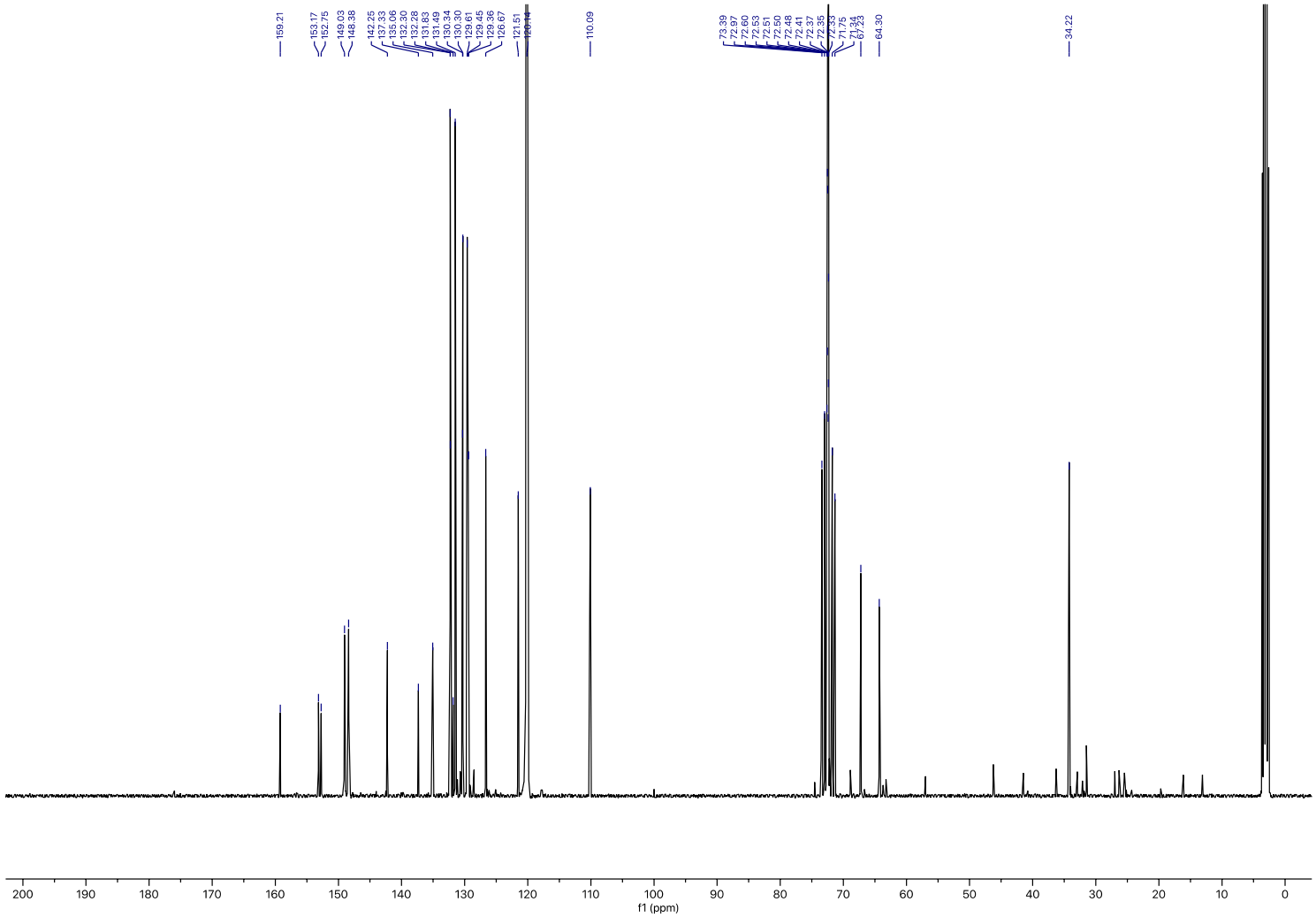


Figure S66 ^{13}C NMR (125 MHz, CD_3CN) spectrum of **15**·$2PF_6$.

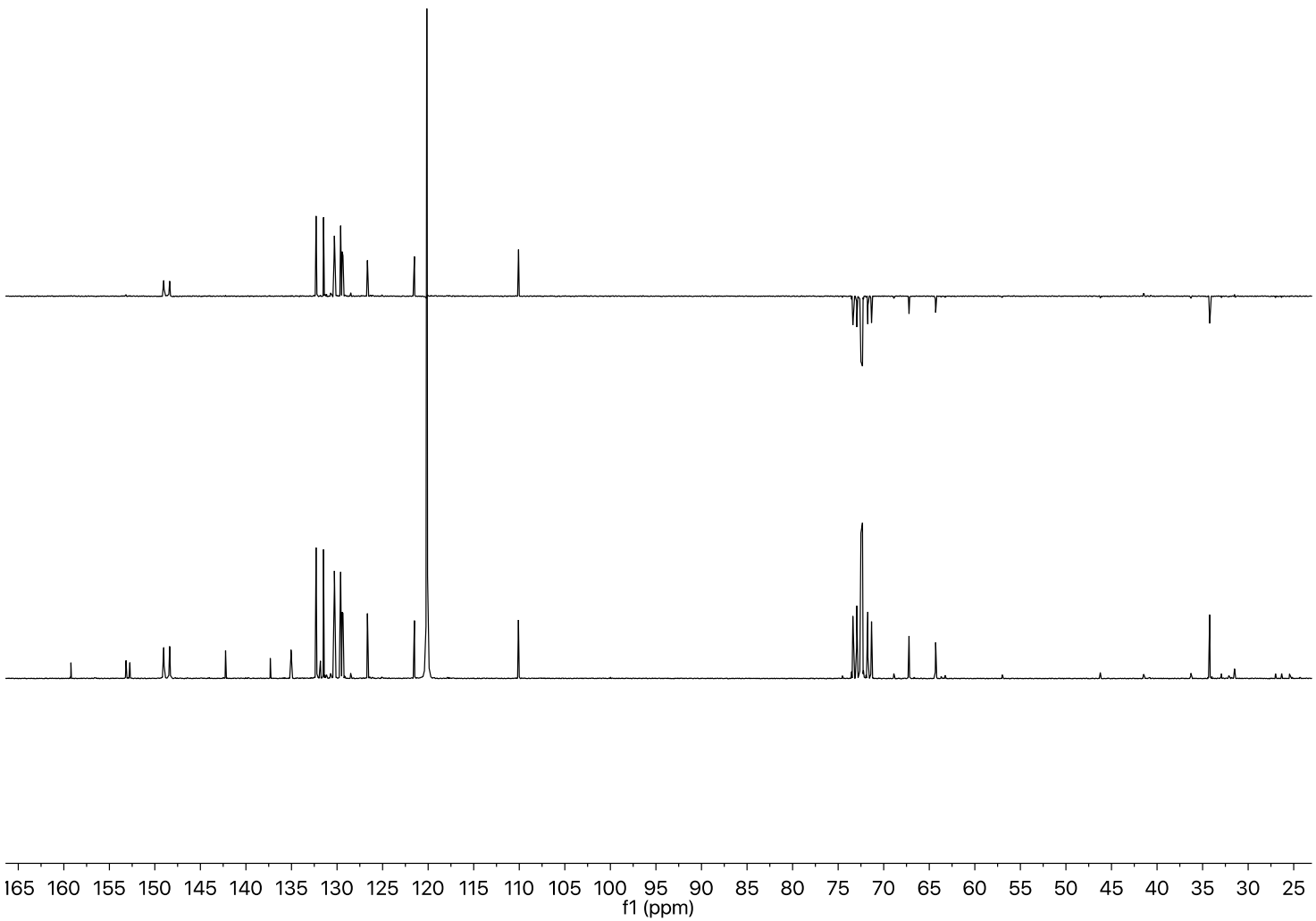


Figure S67 ^{13}C and DEPT NMR (125 MHz, CD_3CN) spectrum of **15**·$2PF_6$.

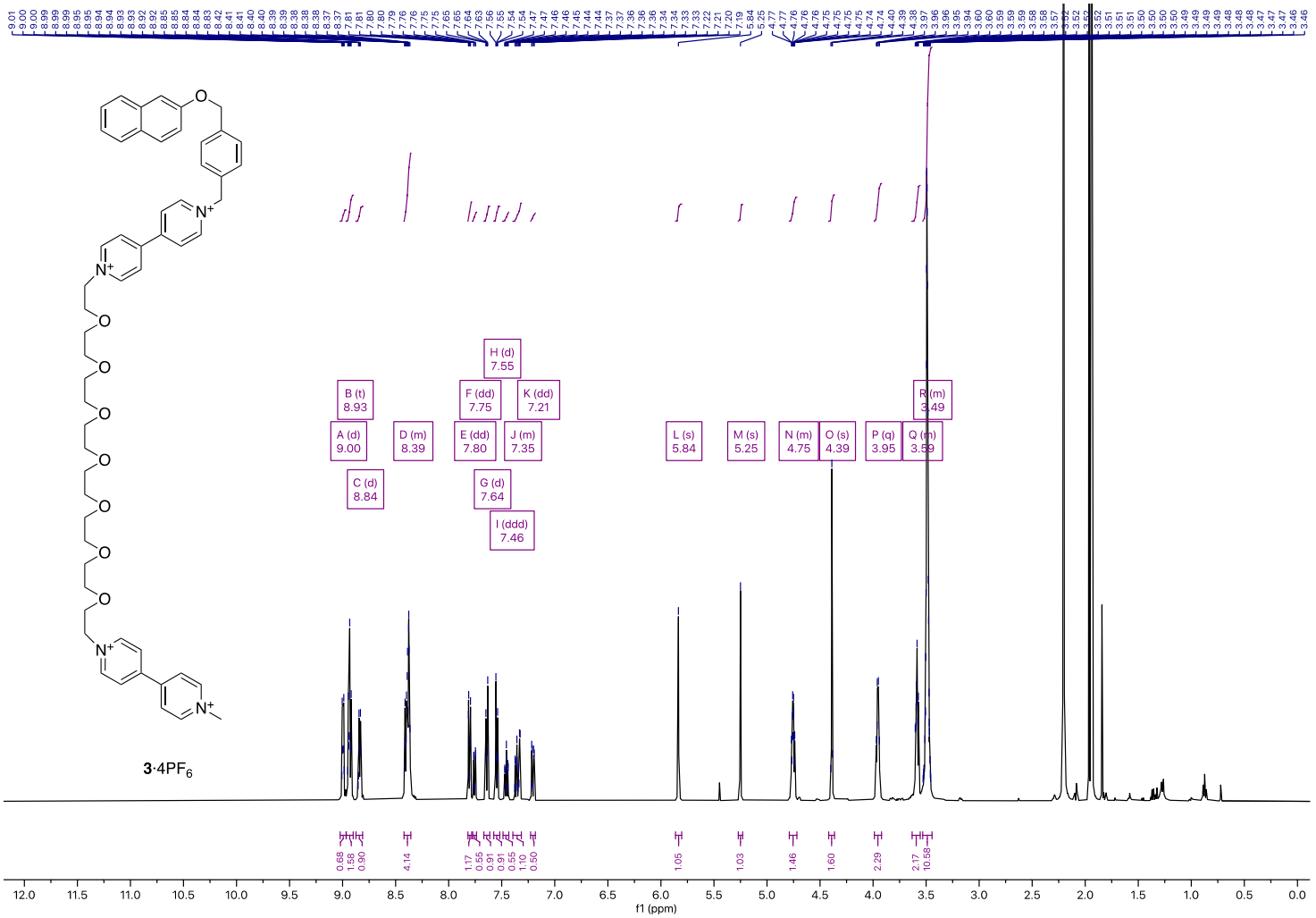


Figure S68 ^{1}H NMR (500 MHz, CD_3CN) spectrum of **3**·4PF_6.

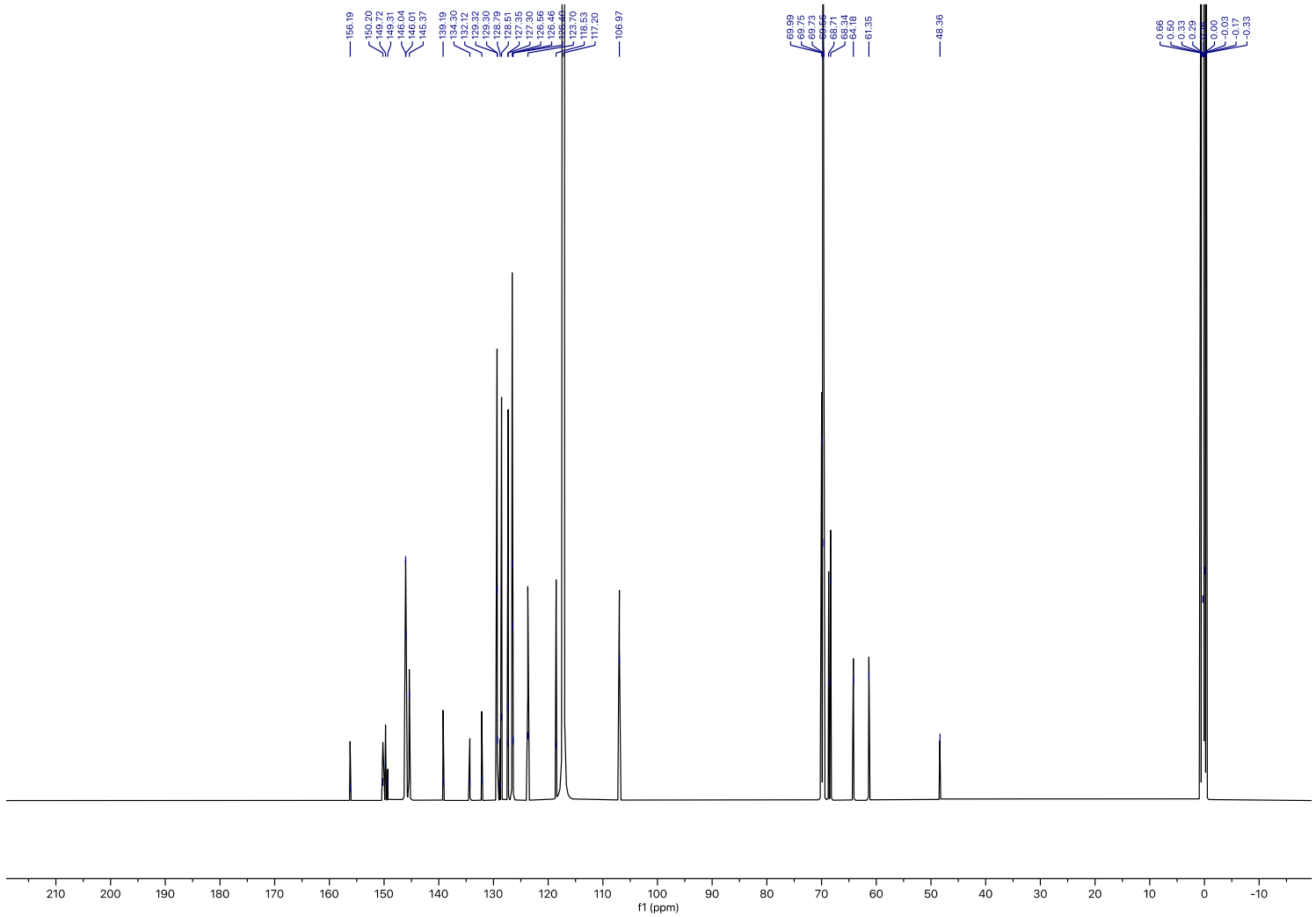


Figure S69 ^{13}C NMR (125 MHz, CD_3CN) spectrum of **3**·4PF_6.

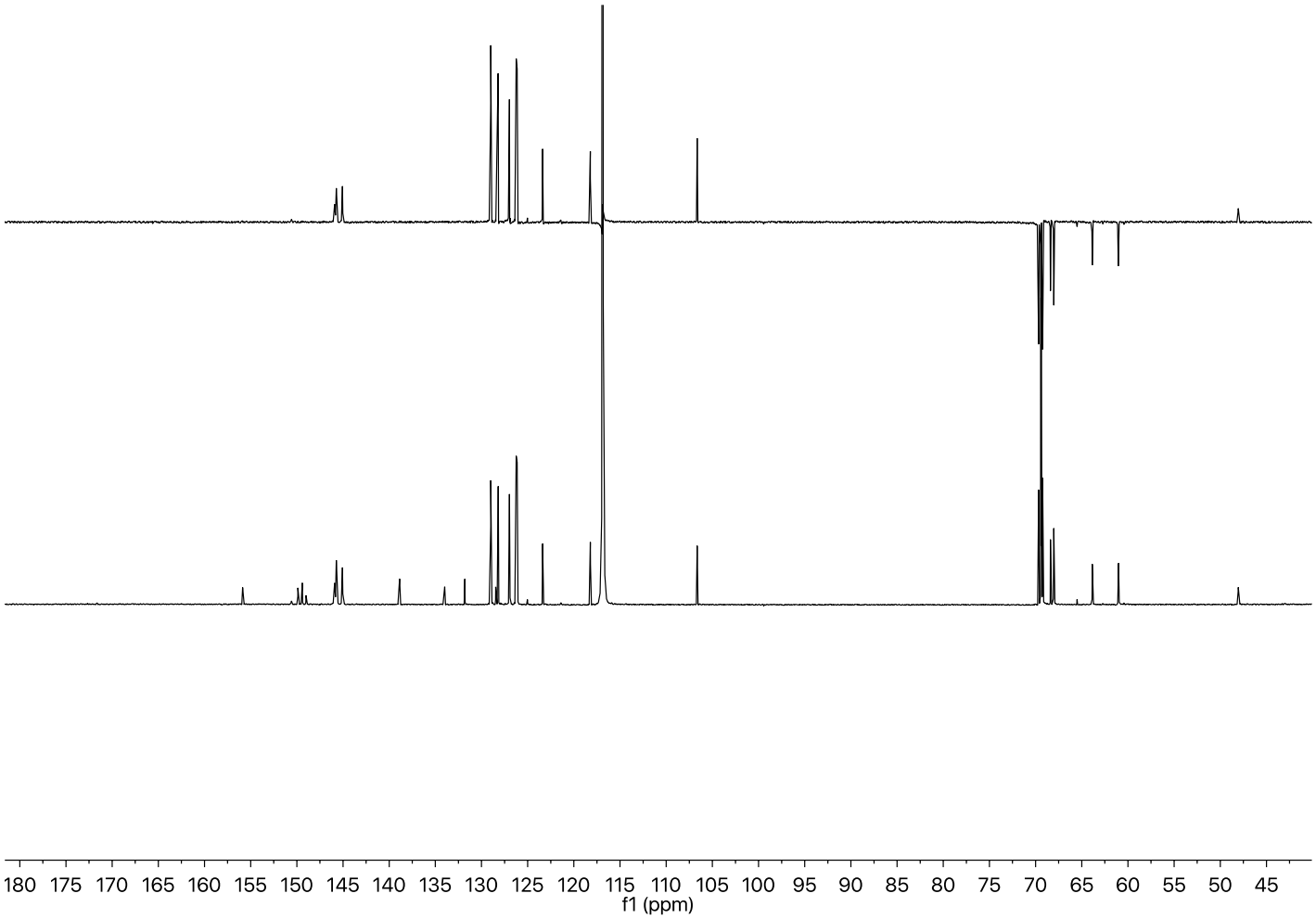


Figure S70 ^{13}C and DEPT NMR (125 MHz, CD_3CN) spectrum of **3**·$4PF_6$.

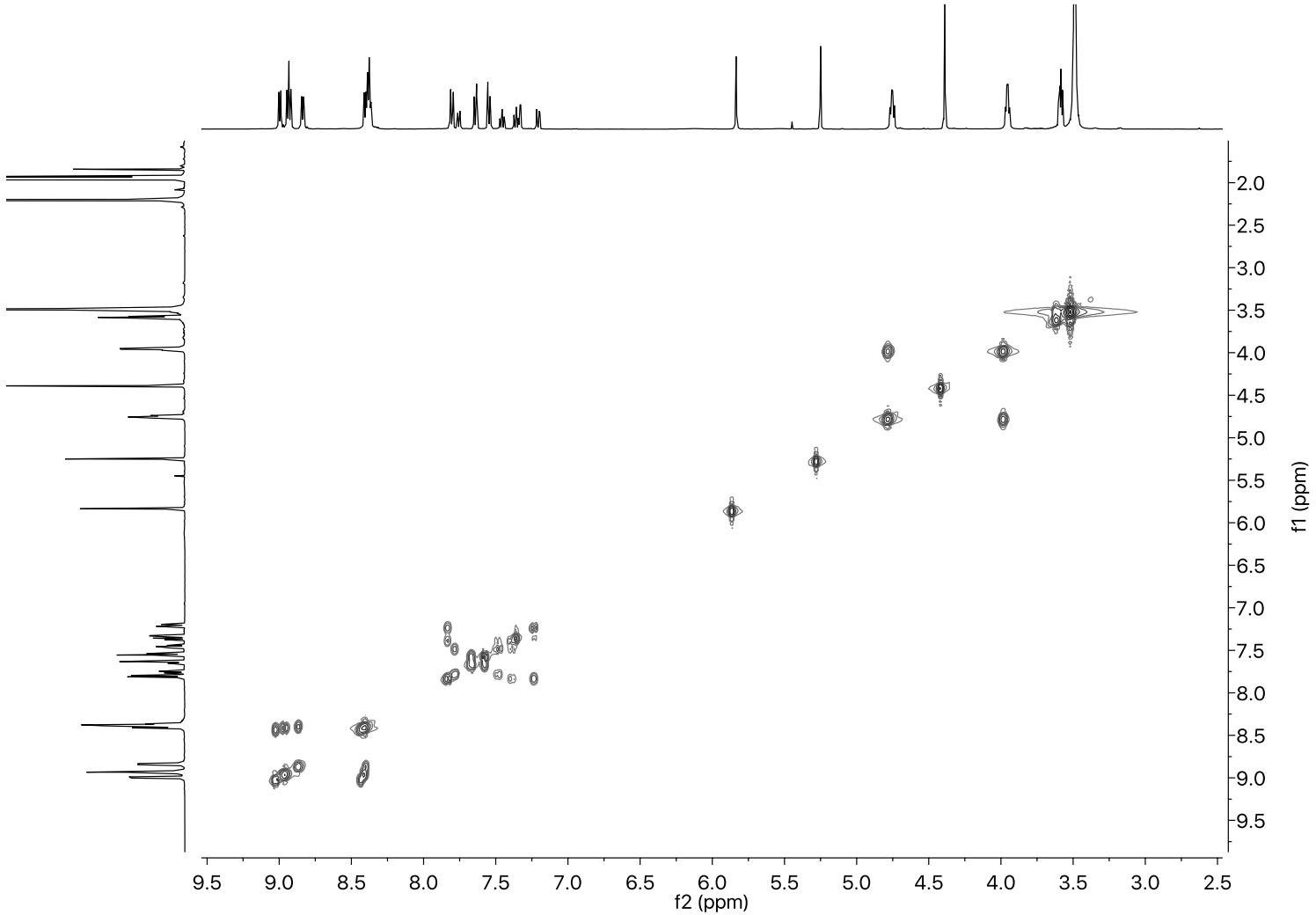


Figure S71 COSY (500 MHz, CD_3CN) spectrum of **3**·$4PF_6$.

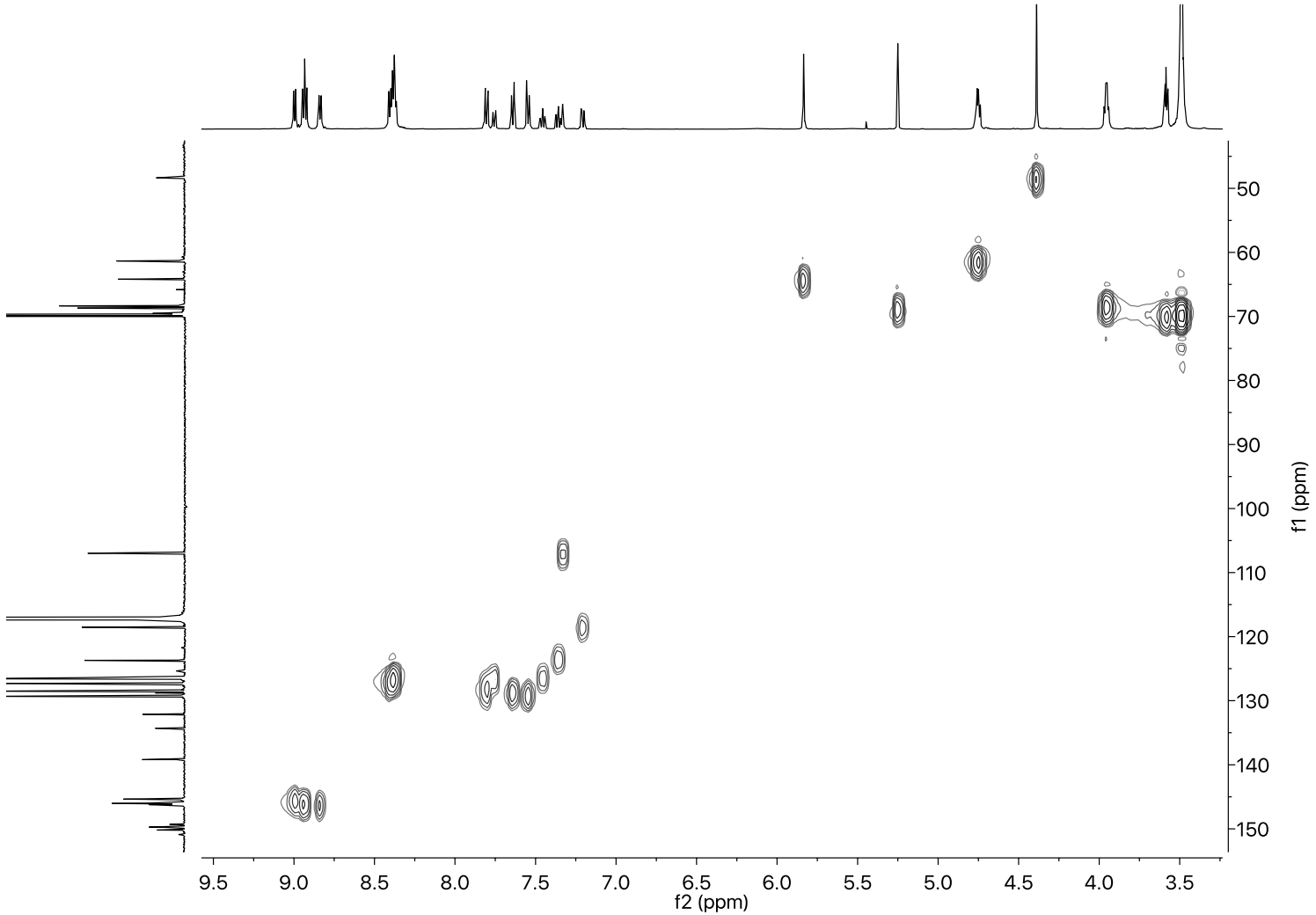


Figure S72 HSQC (500 MHz, CD_3CN) spectrum of **3**·$4PF_6$.

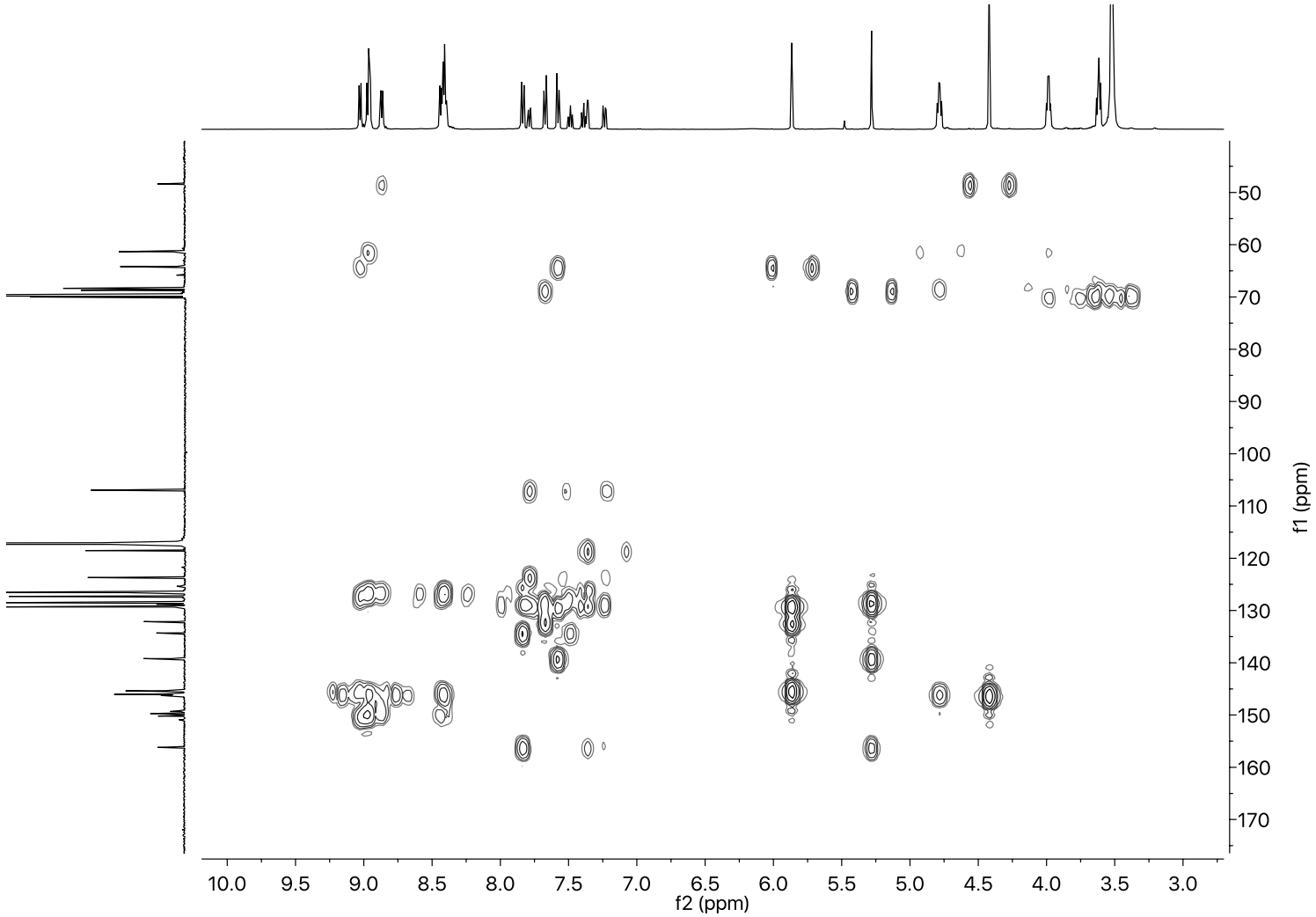


Figure S73 HMBC (500 MHz, CD_3CN) spectrum of **3**·$4PF_6$.

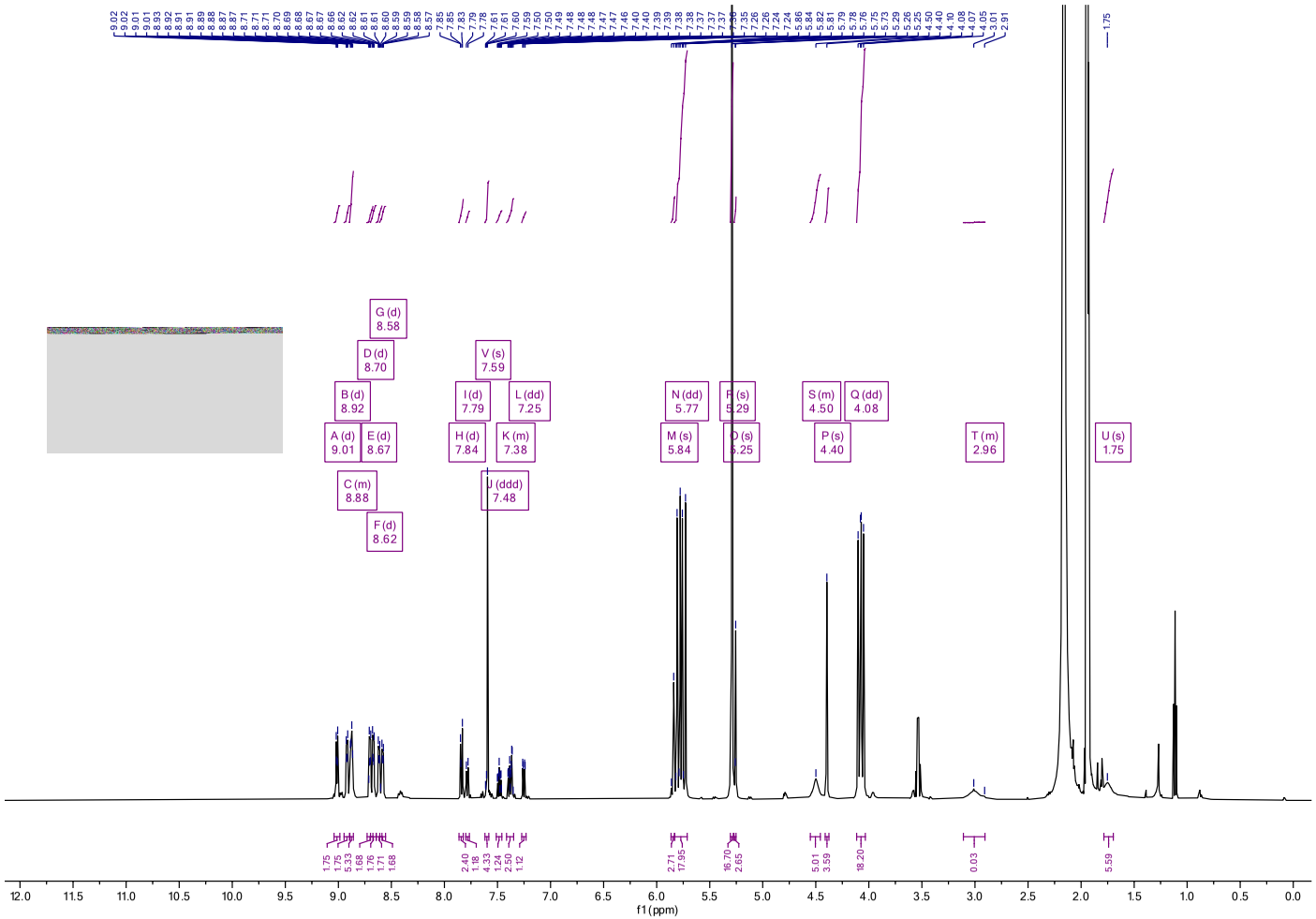


Figure S74 ^{1}H NMR (500 MHz, CD_3CN) spectrum of **1⊂CB[8]**.

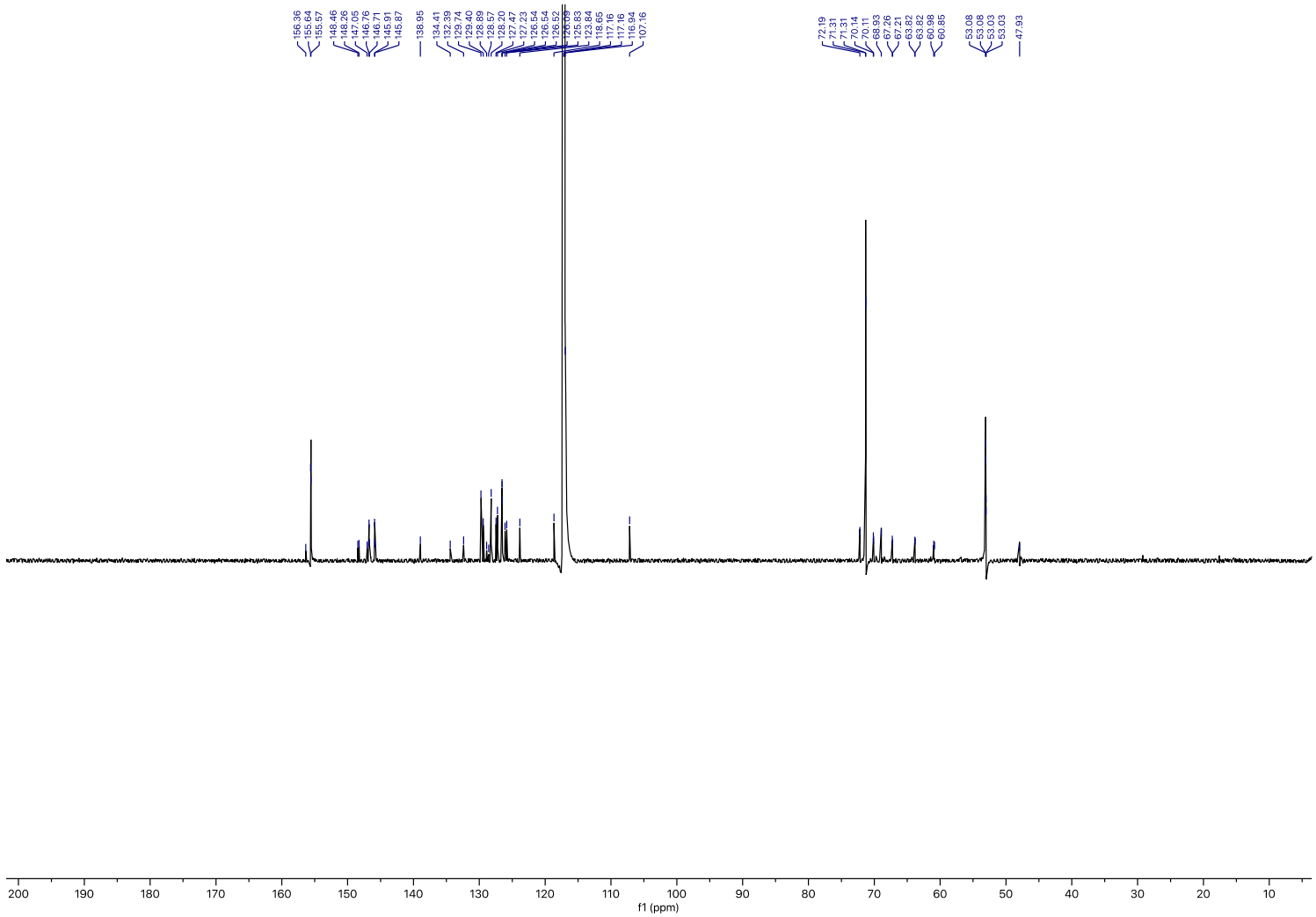


Figure S75 ^{13}C NMR (125 MHz, CD_3CN) spectrum of **1⊂CB[8]**.

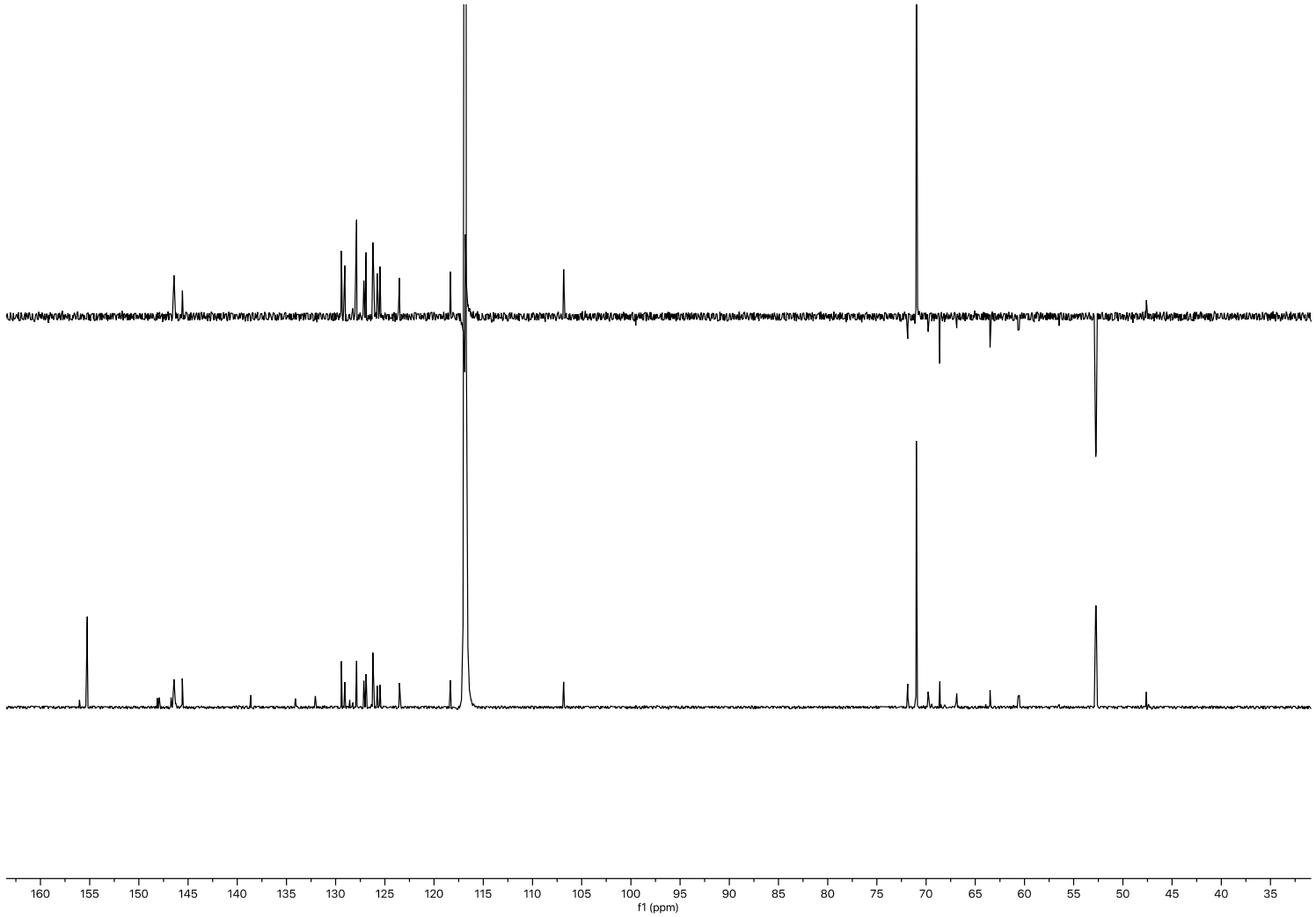


Figure S76 ^{13}C and DEPT NMR (125 MHz, CD_3CN) spectrum of **1⊂CB[8]**.

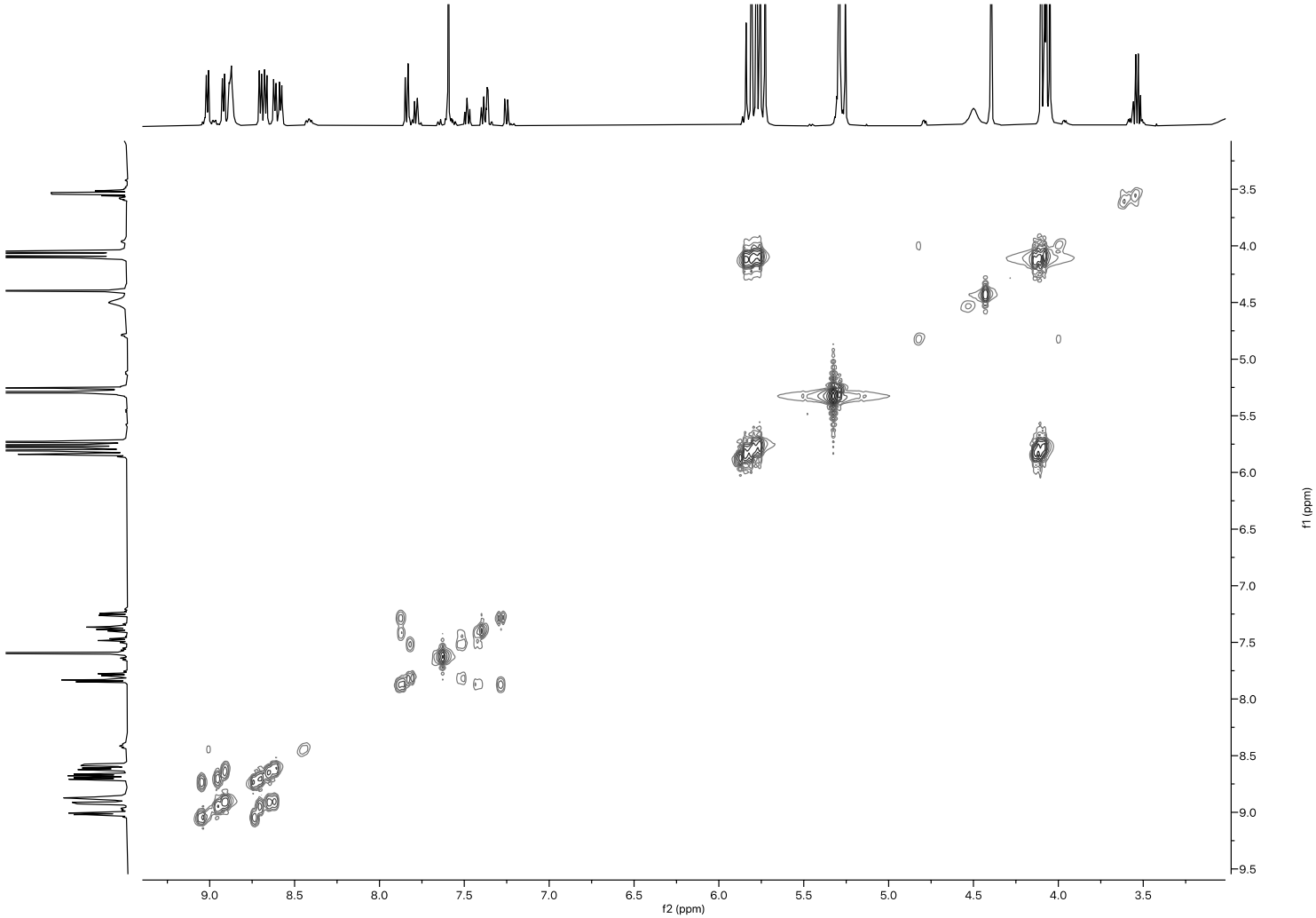


Figure S77 COSY (500 MHz, CD_3CN) spectrum of **1⊂CB[8]**.

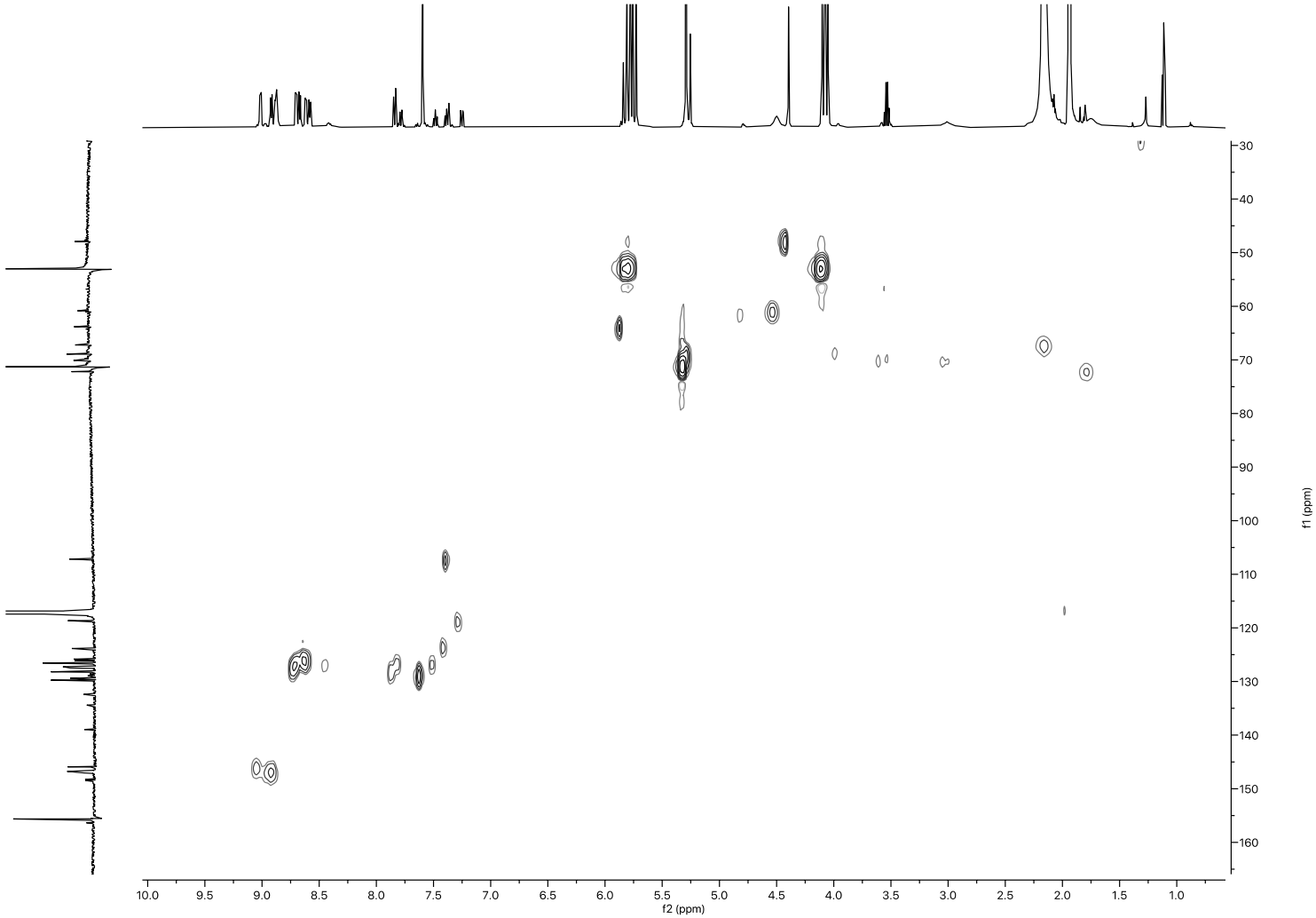


Figure S78 HSQC (500 MHz, CD_3CN) spectrum of **1⊂CB[8]**.

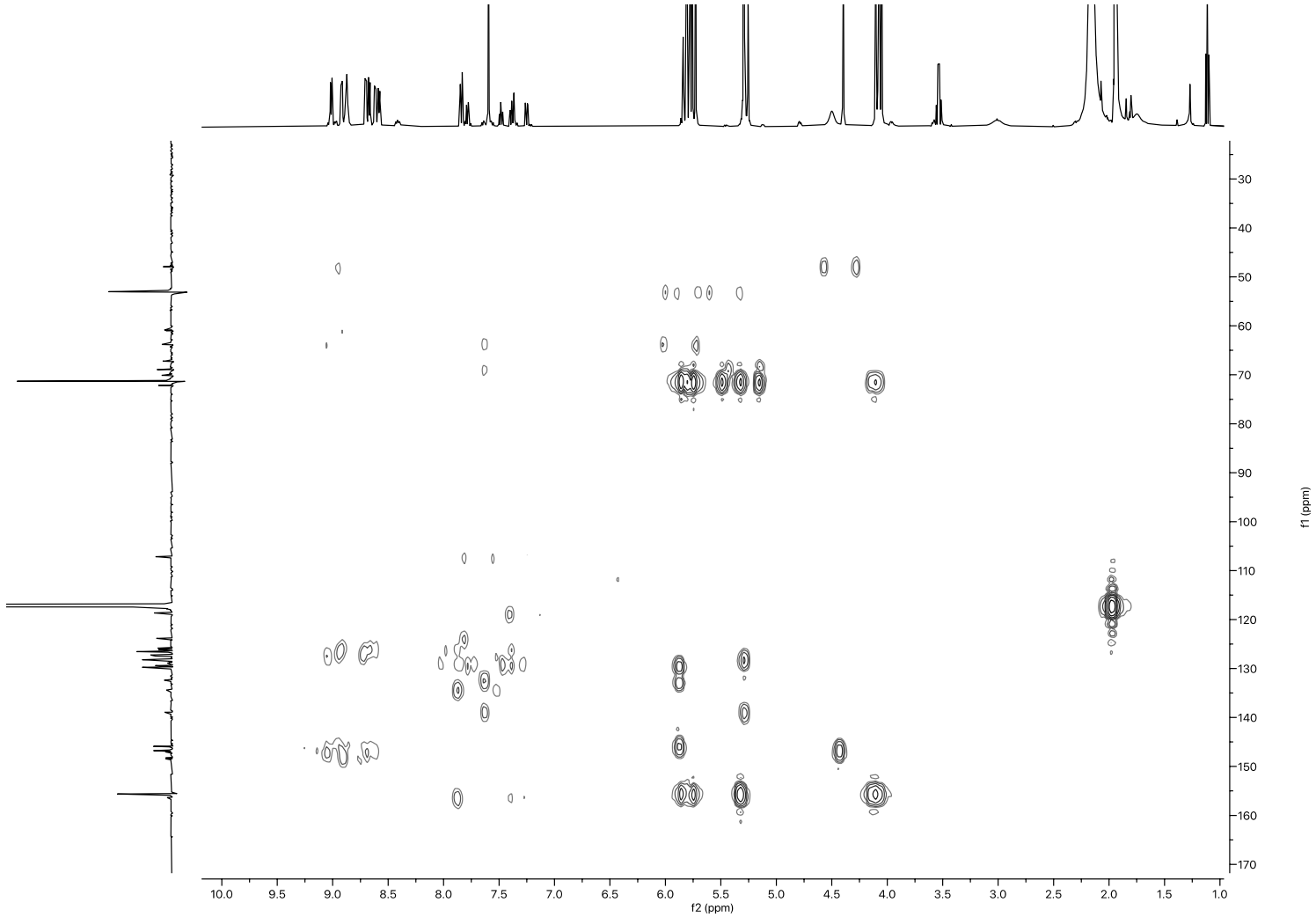


Figure S79 HMBC (500 MHz, CD_3CN) spectrum of **1⊂CB[8]**.

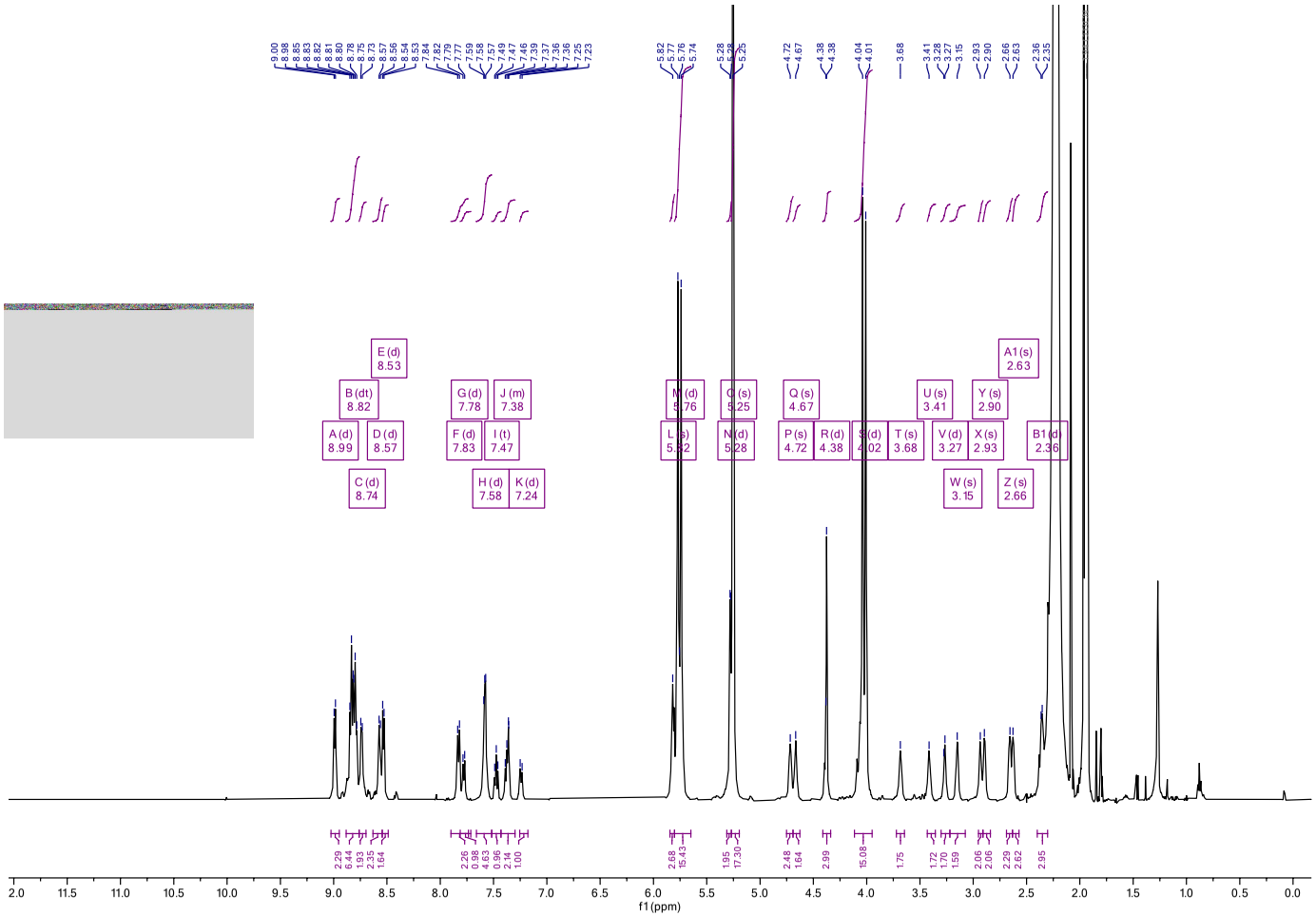


Figure S80 ^{1}H NMR (500 MHz, CD_3CN) spectrum of **2⊂CB[8]**.

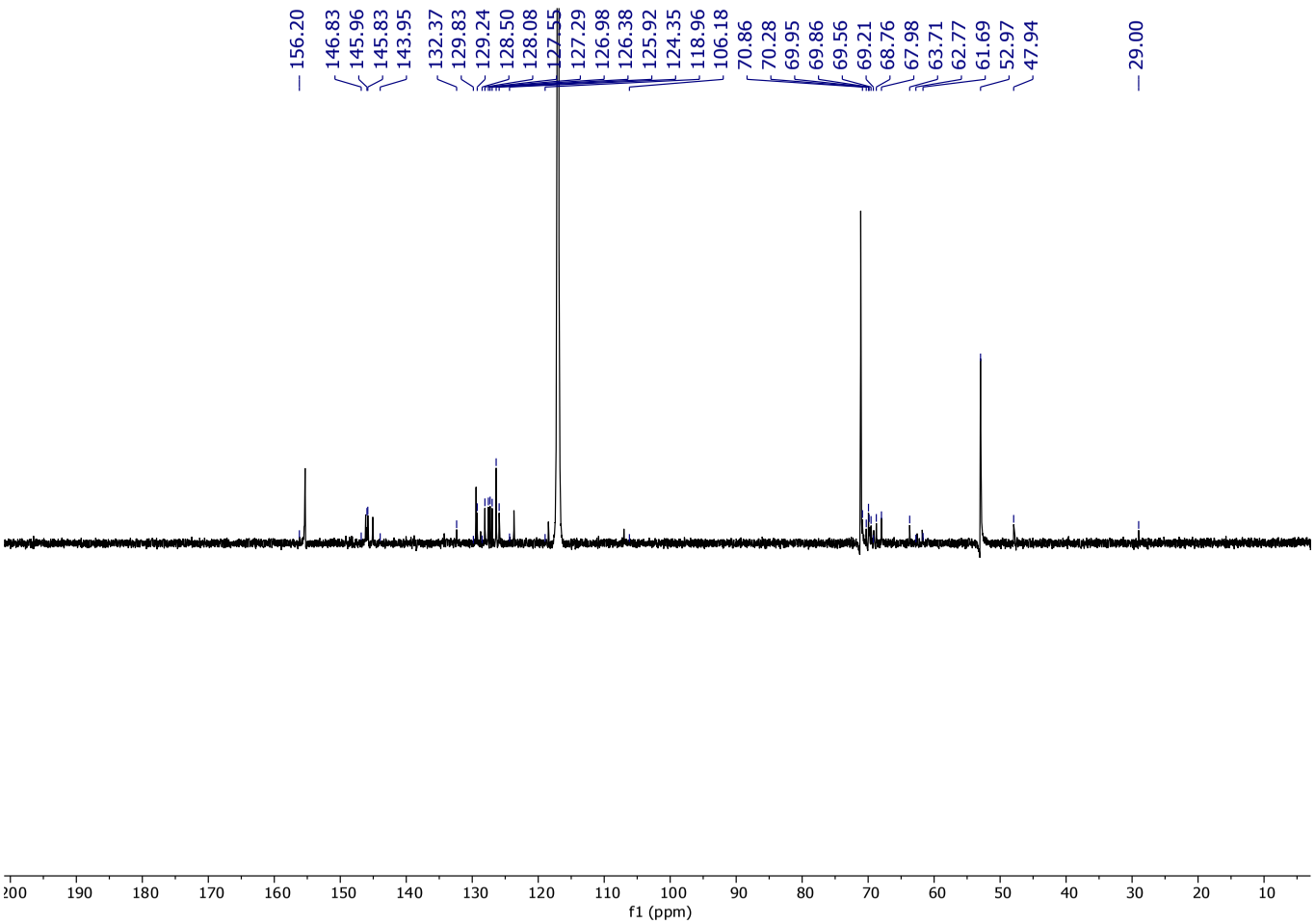


Figure S81 ^{13}C NMR (500 MHz, CD_3CN) spectrum of **2⊂CB[8]**.

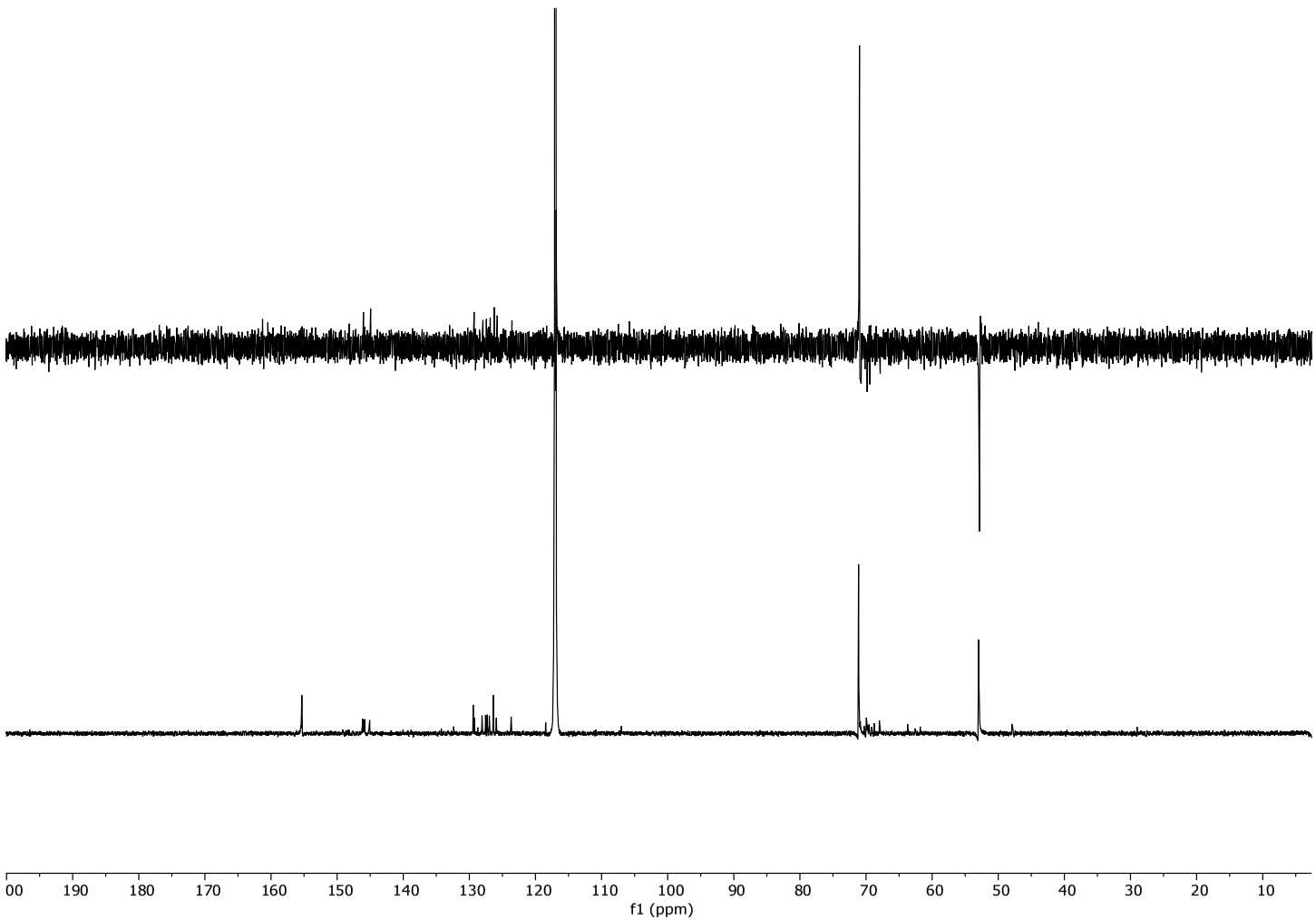


Figure S82 ^{13}C and DEPT NMR (500 MHz, CD_3CN) spectrum of **2⊂CB[8]**.

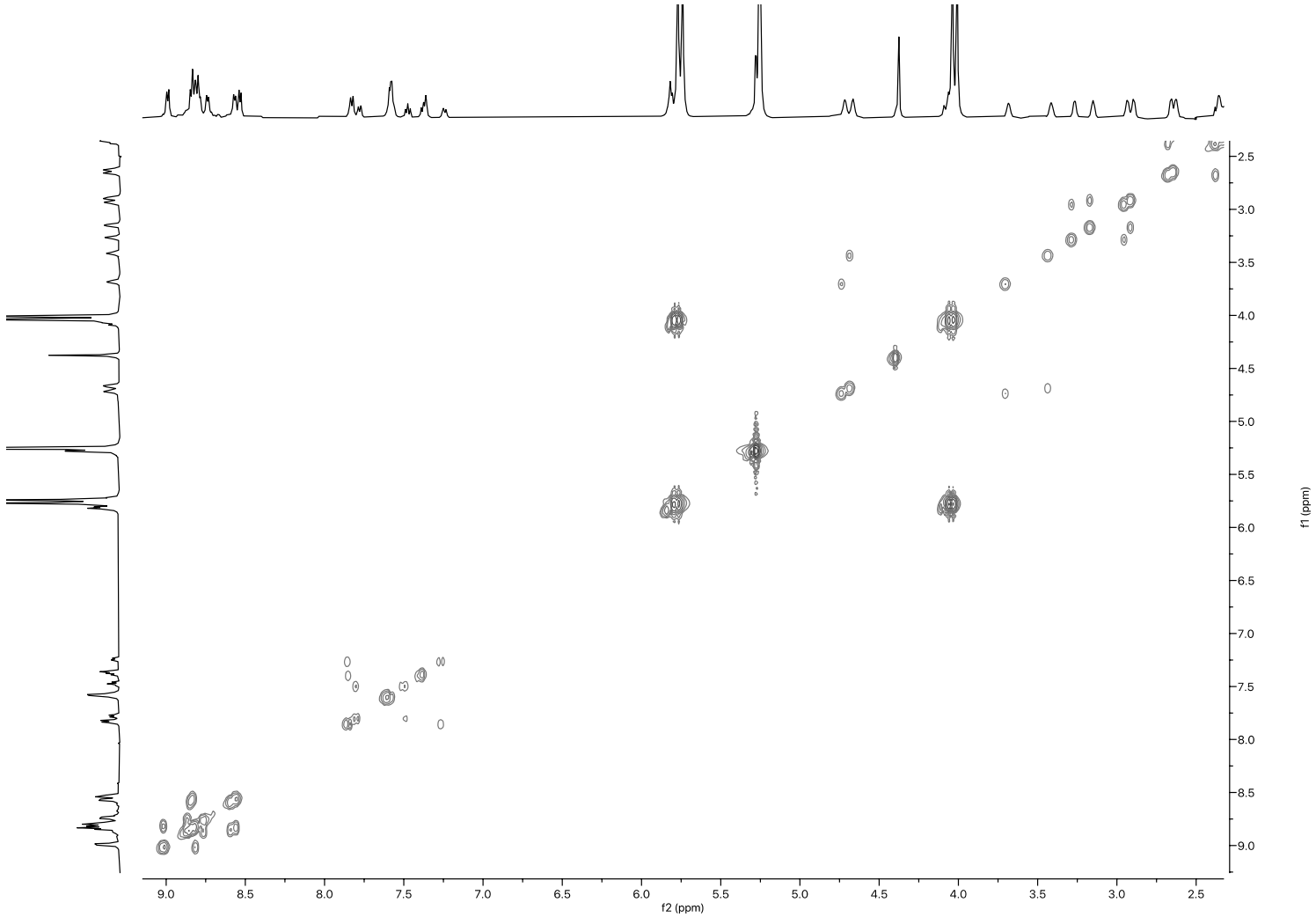


Figure S83 COSY (500 MHz, CD_3CN) spectrum of **2⊂CB[8]**.

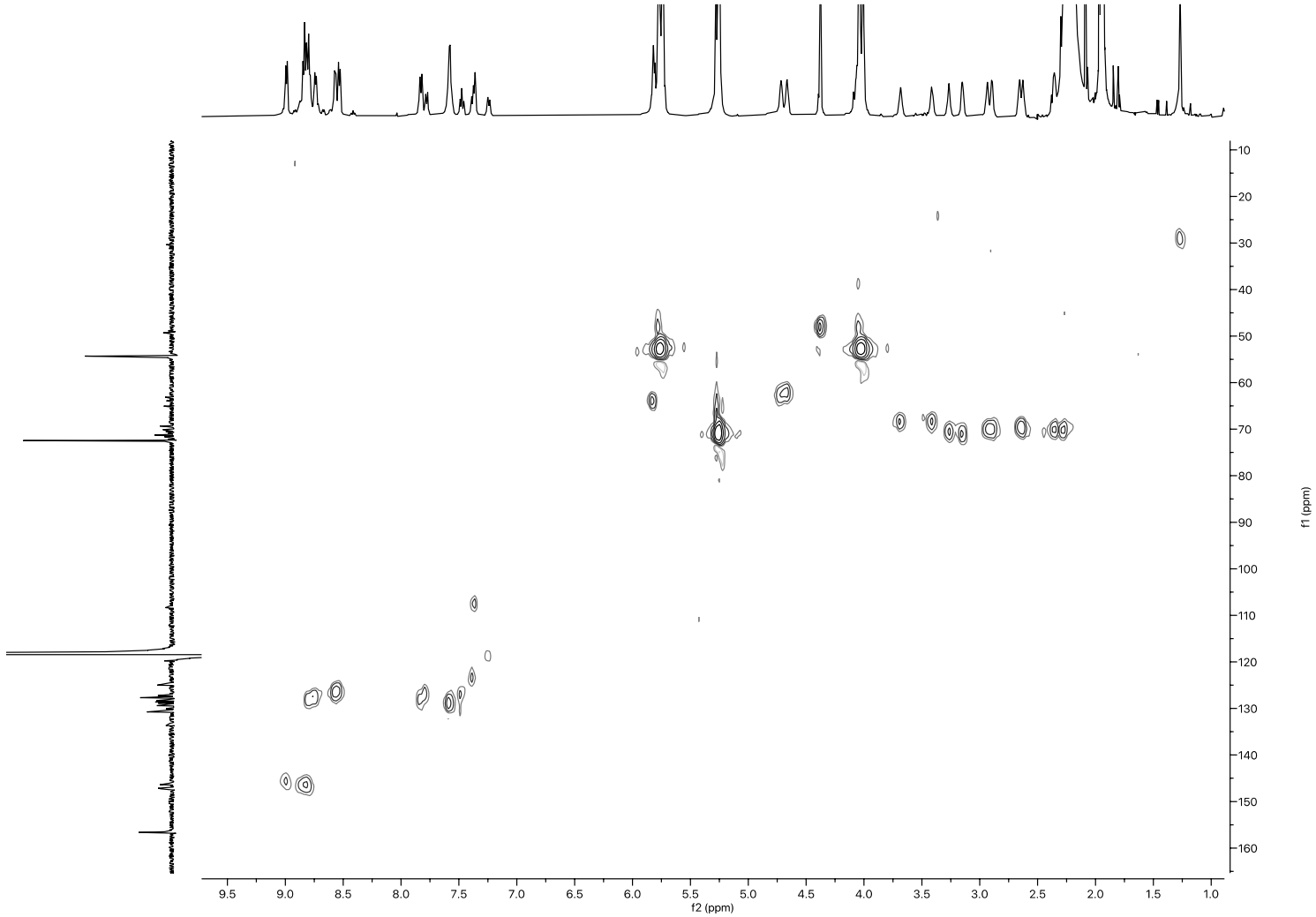


Figure S84 HSQC (500 MHz, CD_3CN) spectrum of **2⊂CB[8]**.

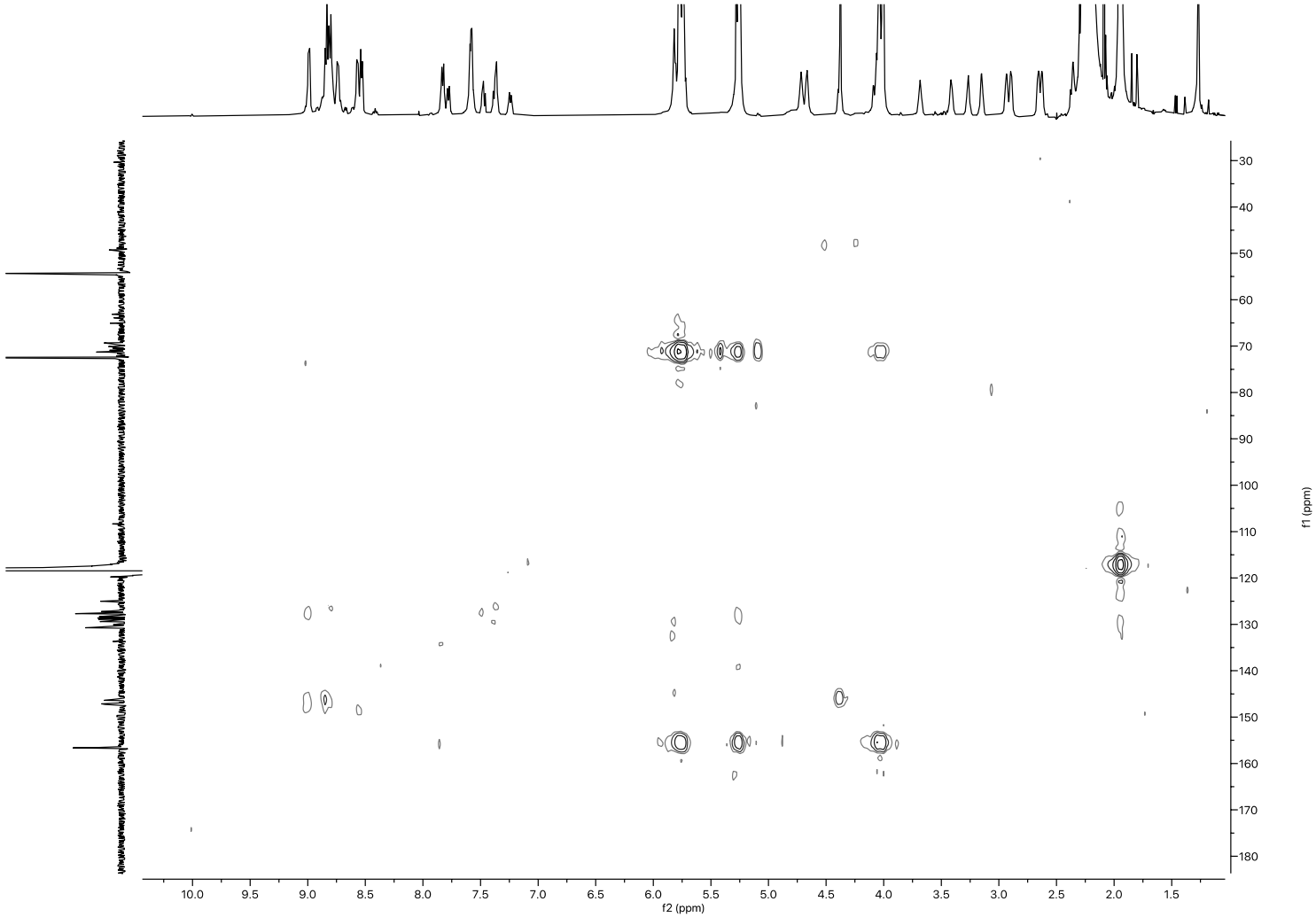


Figure S85 HMBC (500 MHz, CD_3CN) spectrum of **2⊂CB[8]**.

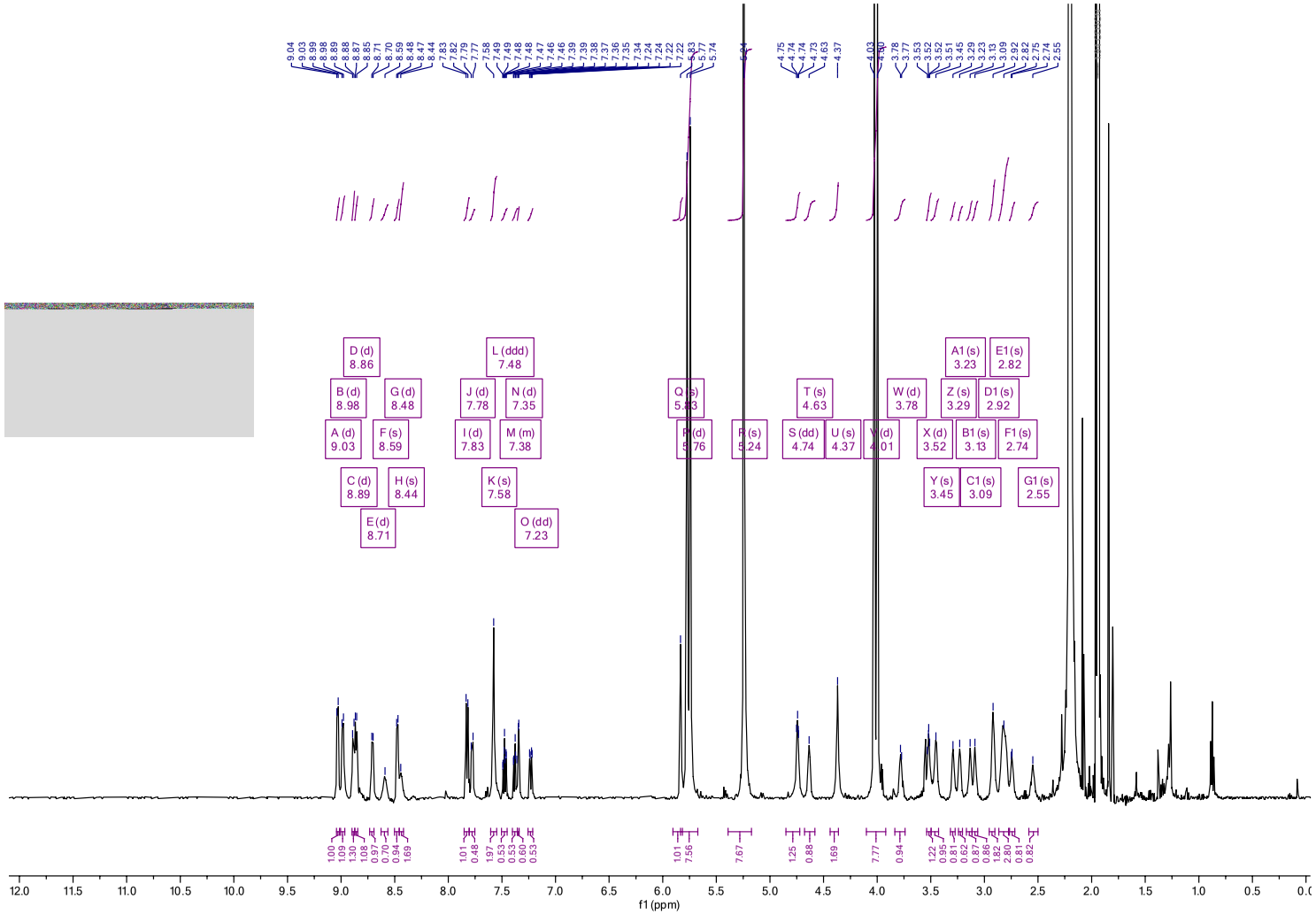


Figure S86 ^{1}H NMR (500 MHz, CD_3CN) spectrum of **3⊂CB[8]**.

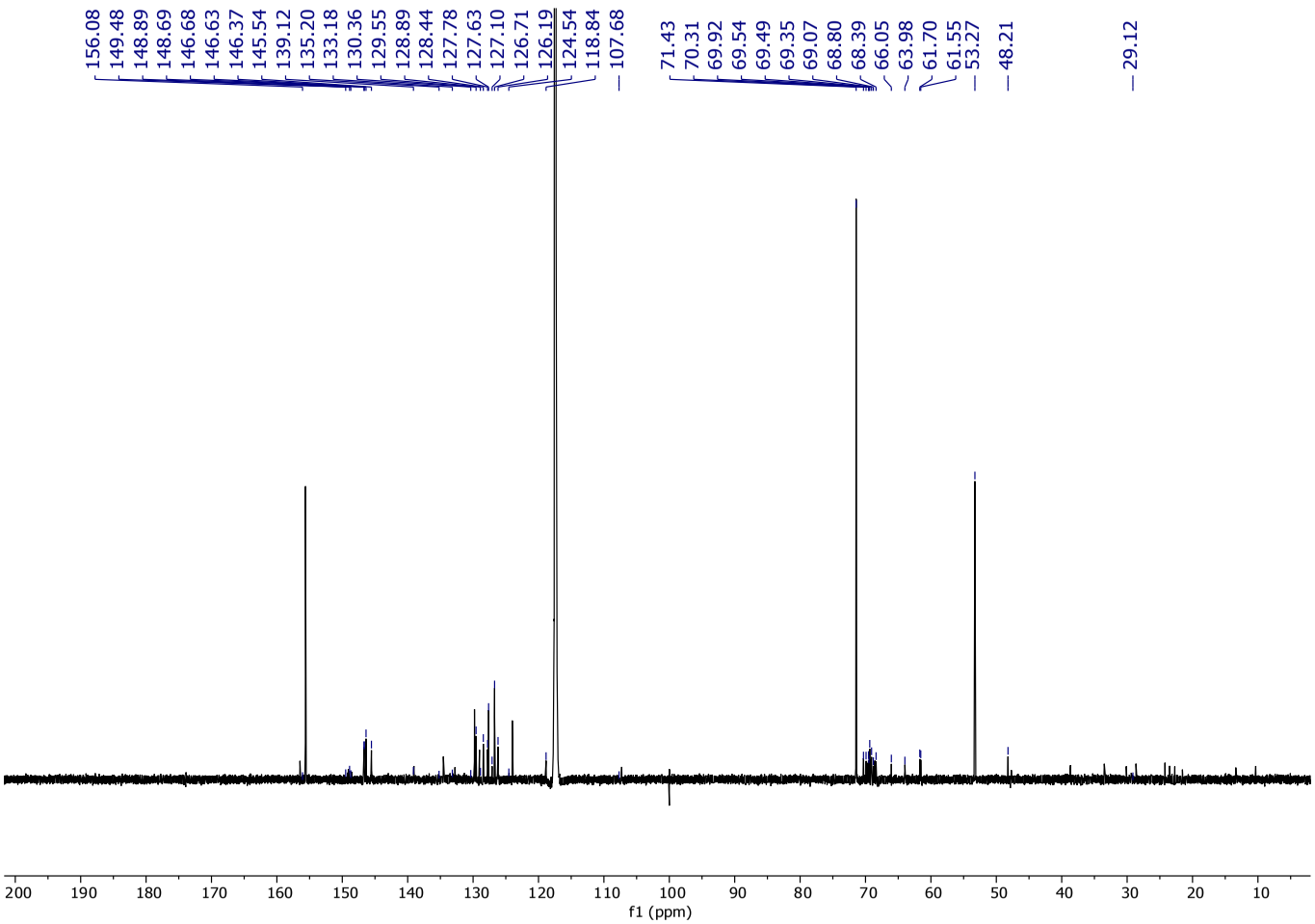


Figure S87 ^{13}C NMR (125 MHz, CD_3CN) spectrum of **3⊂CB[8]**.

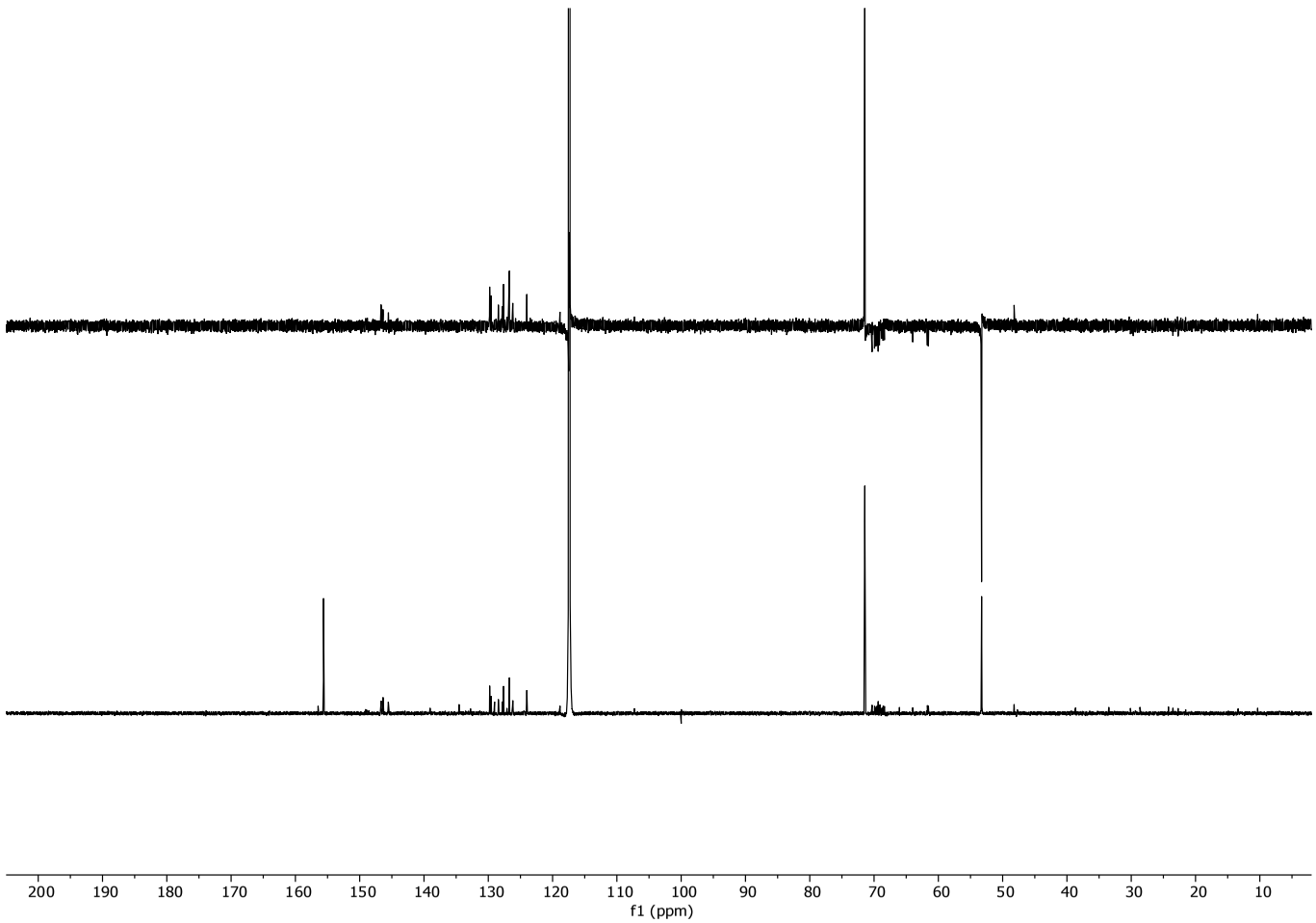


Figure S88 ^{13}C and DEPT NMR (125 MHz, CD_3CN) spectrum of **3⊂CB[8]**.

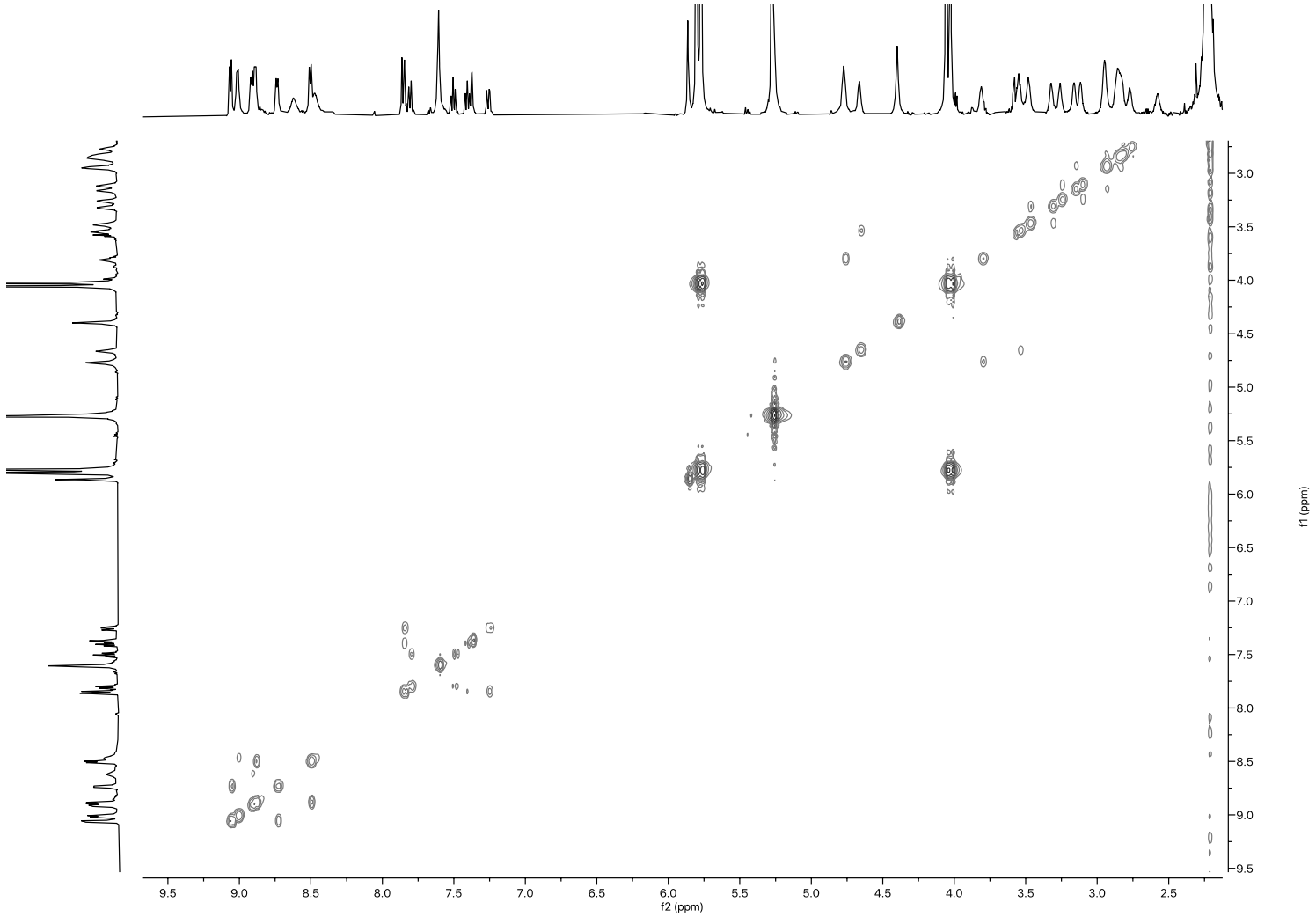


Figure S89 COSY (500 MHz, CD_3CN) spectrum of **3⊂CB[8]**.

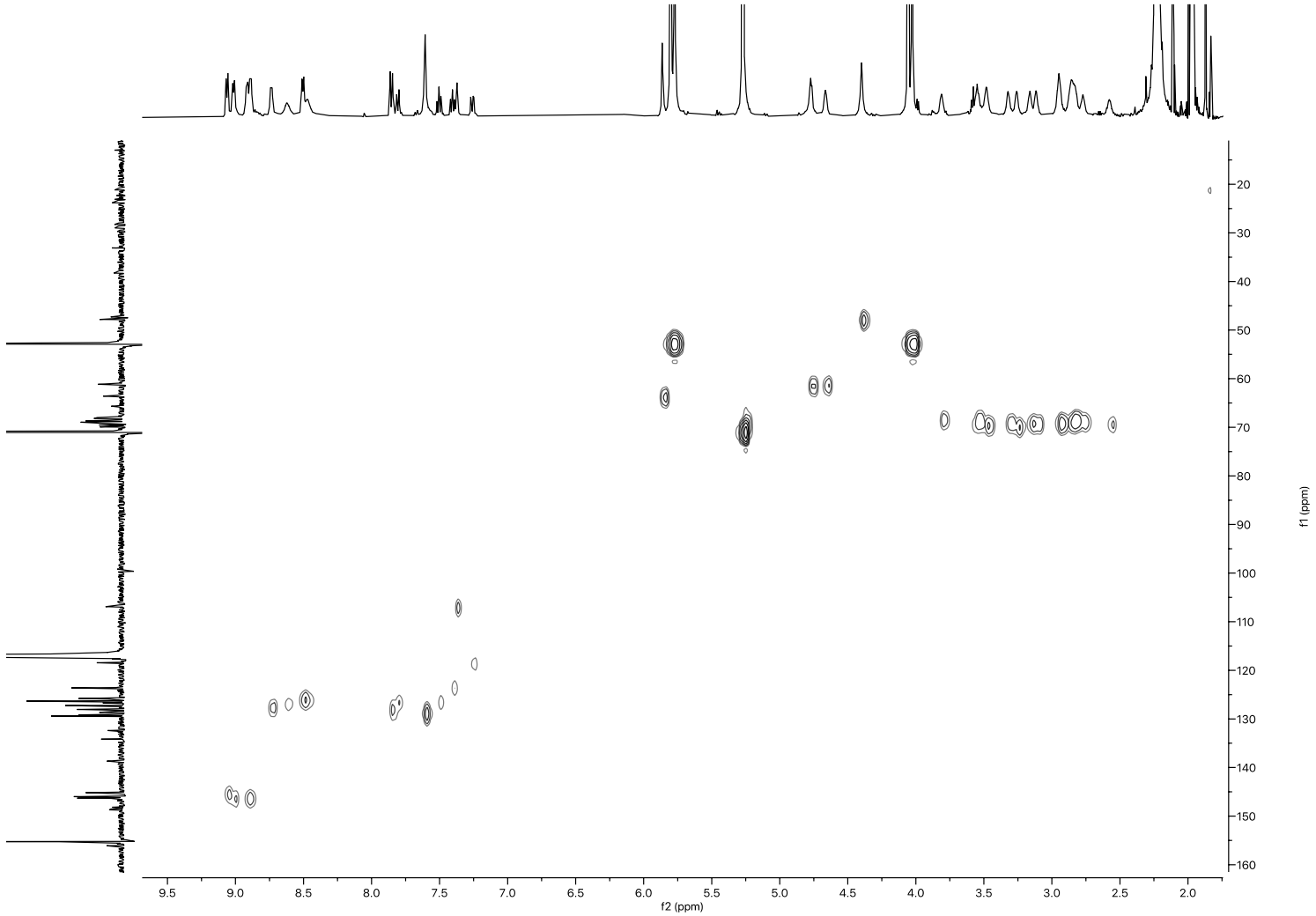


Figure S90 HSQC (500 MHz, CD_3CN) spectrum of **3⊂CB[8]**.

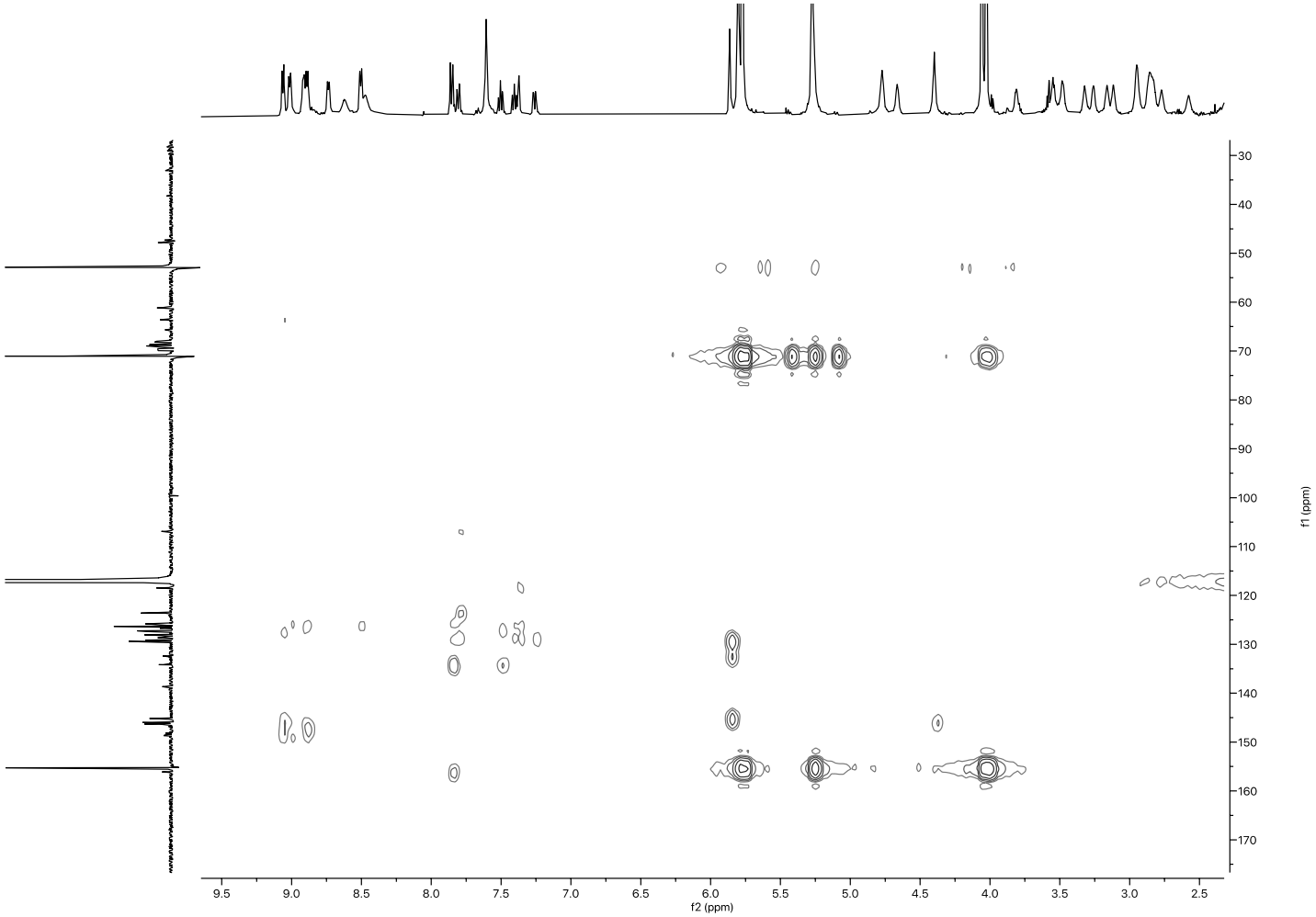


Figure S91 HMBC (500 MHz, CD_3CN) spectrum of **3⊂CB[8]**.