

Supporting Information for  
Boronic ester functionalised 1,8-diboryl-naphthalene scaffolds:  
fluoride versus oxide chelation

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## 1. Additional synthetic/characterizing data

**Bis(methoxy)ester of 1:** A round-bottomed flask was charged with solid **1** (ca. 0.5 g) and a minimal volume of methanol added. The reaction was heated to reflux and more methanol added until the solid just dissolved. The solution was allowed to slowly cooled to room temperature, and colourless crystals of the product isolated in ca. 80 % yield.

Spectroscopic Data:  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta_{\text{H}}$  8.38 (dd,  $^3J_{\text{HH}} = 6.7$  Hz,  $^4J_{\text{HH}} = 1.2$  Hz, 2H, Naph CH), 7.72 (dd,  $^3J_{\text{HH}} = 8.3$  Hz,  $^4J_{\text{HH}} = 1.2$  Hz, 2H, Naph CH), 7.35 (dd,  $^3J_{\text{HH}} = 8.2$  Hz,  $^3J_{\text{HH}} = 6.7$  Hz, 2H, 3,6-Naph-CH), 3.64 (s, 6H,  $\text{OCH}_3$ ).  $^{11}\text{B}\{^1\text{H}\}$  NMR (128 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta_{\text{B}}$  29 (br s, BOMe).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta_{\text{C}}$  142.3 (Naph C), 134.5 (Naph CH), 132.3 (Naph C), 132.1 (Naph CH), 125.9 (3,6-Naph CH), 50.5 ( $\text{OCH}_3$ ). Elemental Microanalysis: calc. for  $\text{C}_{12}\text{H}_{12}\text{B}_2\text{O}_3$  (%): C 63.82, H 5.36; meas. C 63.73, H 5.22.

## 2. Additional crystal structure figures

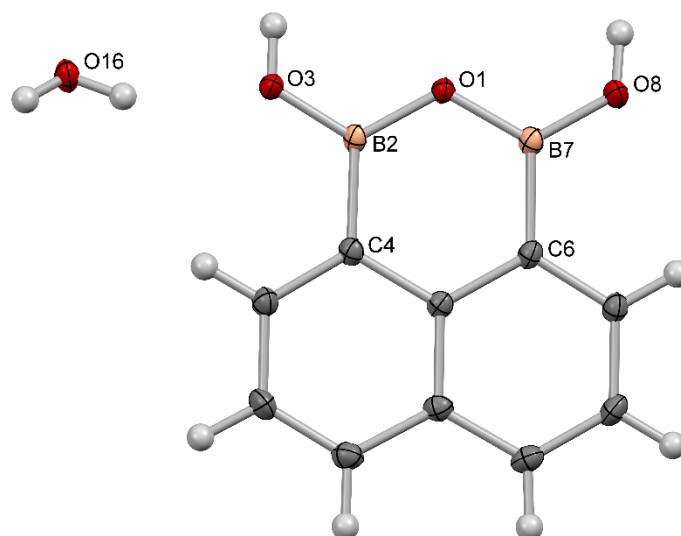


Figure S1 – Molecular structure of **1** in the solid state as determined by X-ray crystallography. Thermal ellipsoids set at 40% probability level. For previous disclosure of the X-ray crystal structure of this compound (as a CSD communication) see CCDC 1906117 and 2002648.

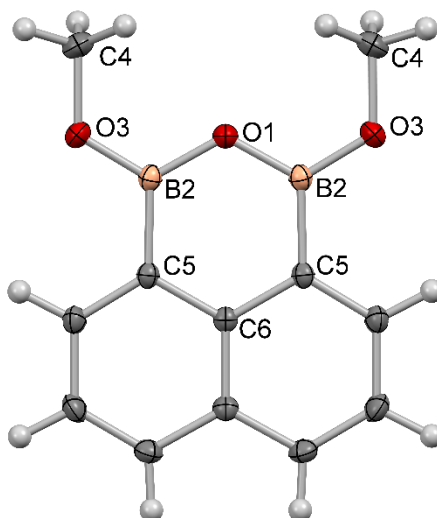


Figure S2 – Molecular structure of the bis(methoxy)ester of **1** in the solid state as determined by X-ray crystallography. Crystals obtained from slow cooling of a hot methanol solution. Thermal ellipsoids set at 40% probability level.

### 3. Kinetic studies

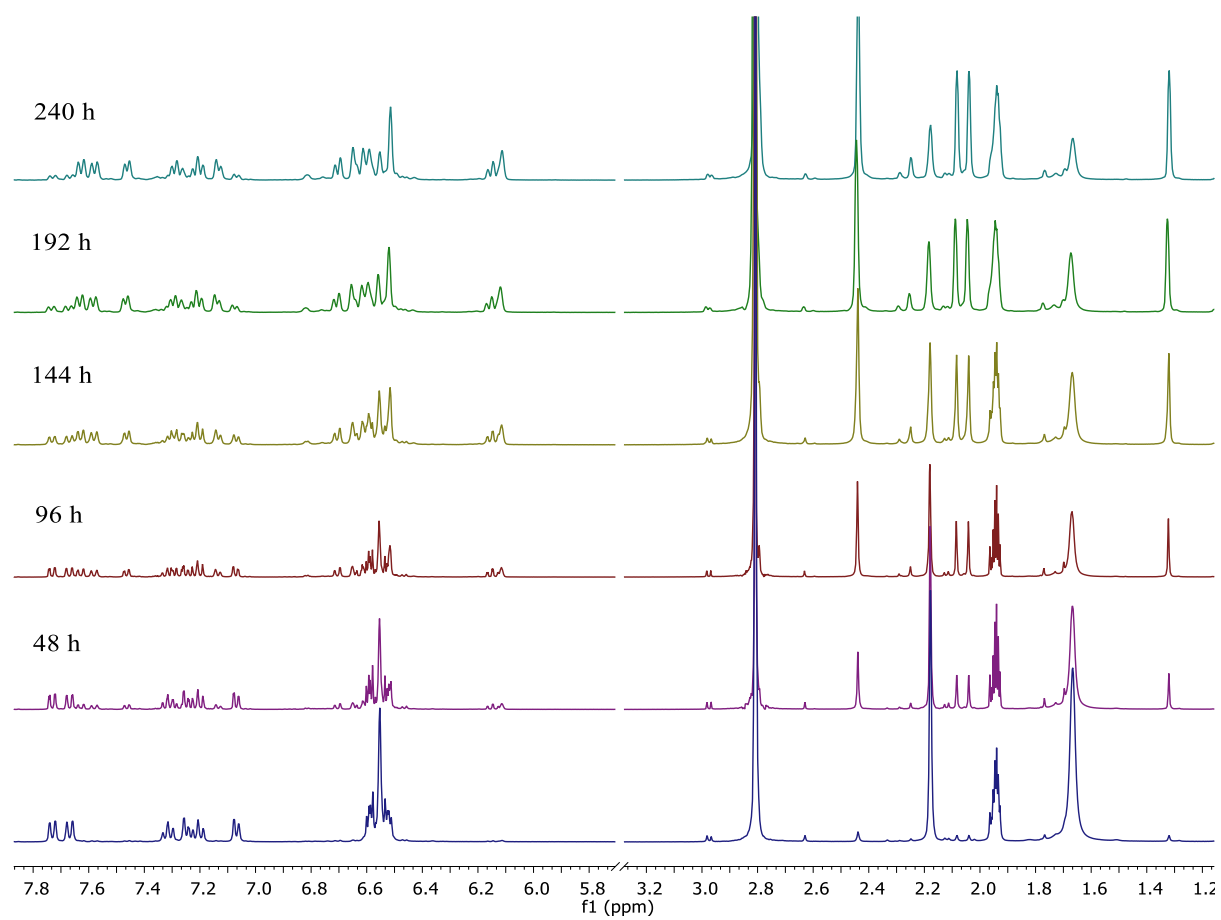


Figure S3 -  $^1\text{H}$  NMR spectra showing the conversion of  $[4]^-$  to  $[5]^-$  in  $\text{CD}_3\text{CN}$

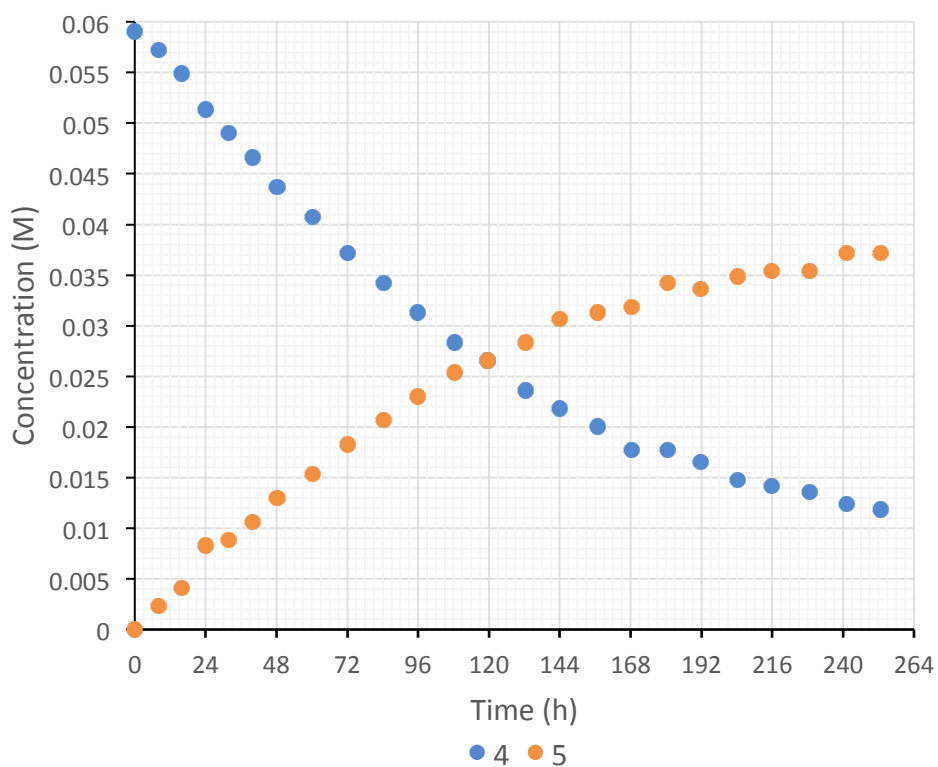


Figure S4 - Plot showing change in concentration of [4]<sup>-</sup> and [5]<sup>-</sup> against time

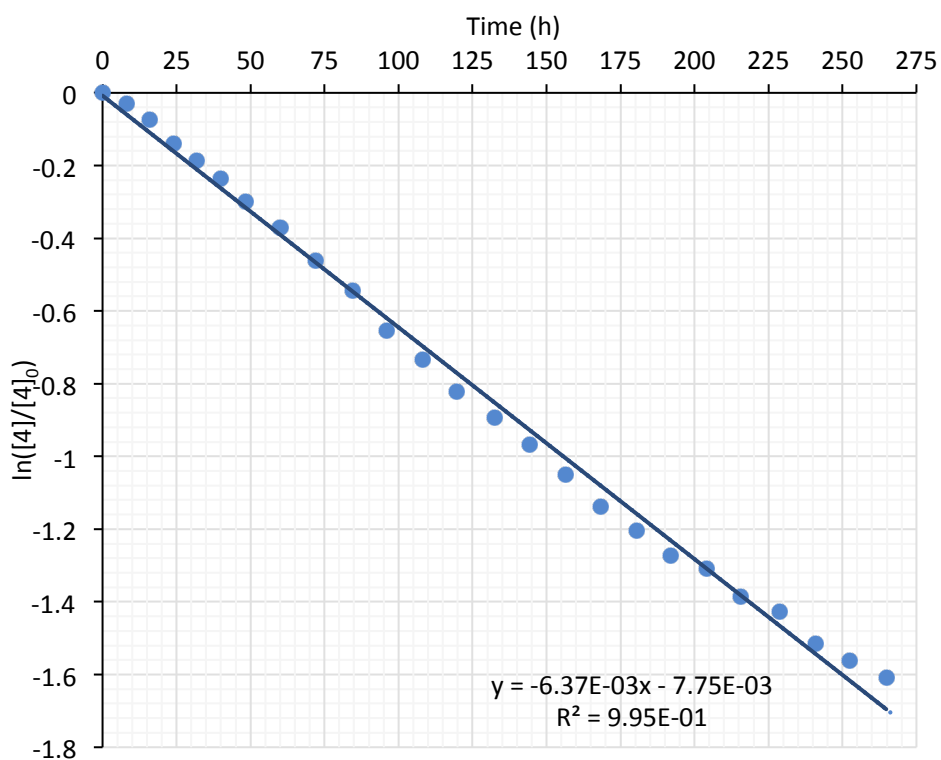


Figure S5 - First order log plot of the concentration of anion [4]<sup>-</sup> against time

#### 4. Representative NMR spectra

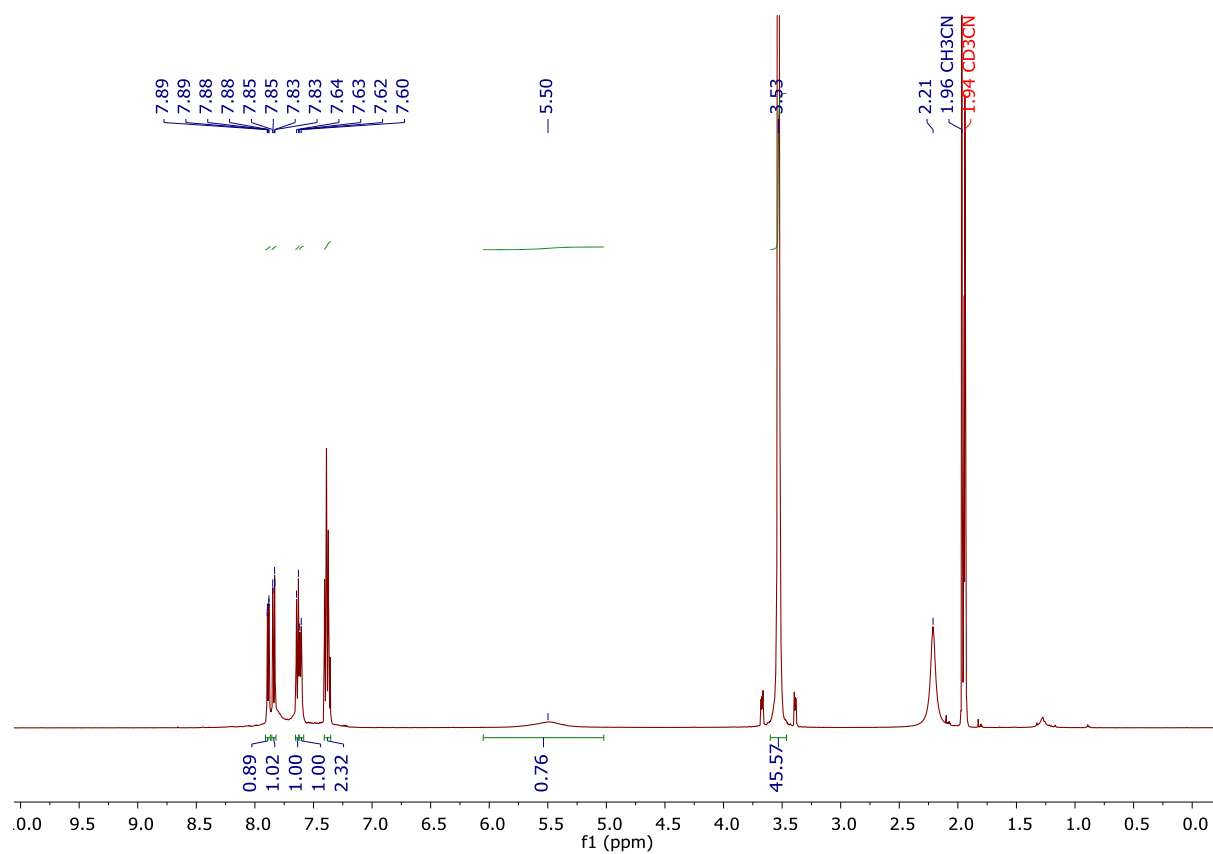


Figure S6 –  $^1\text{H}$  NMR spectrum of  $[\text{K}(18\text{-crown-6})][\mathbf{2}]$  in  $\text{CD}_3\text{CN}$

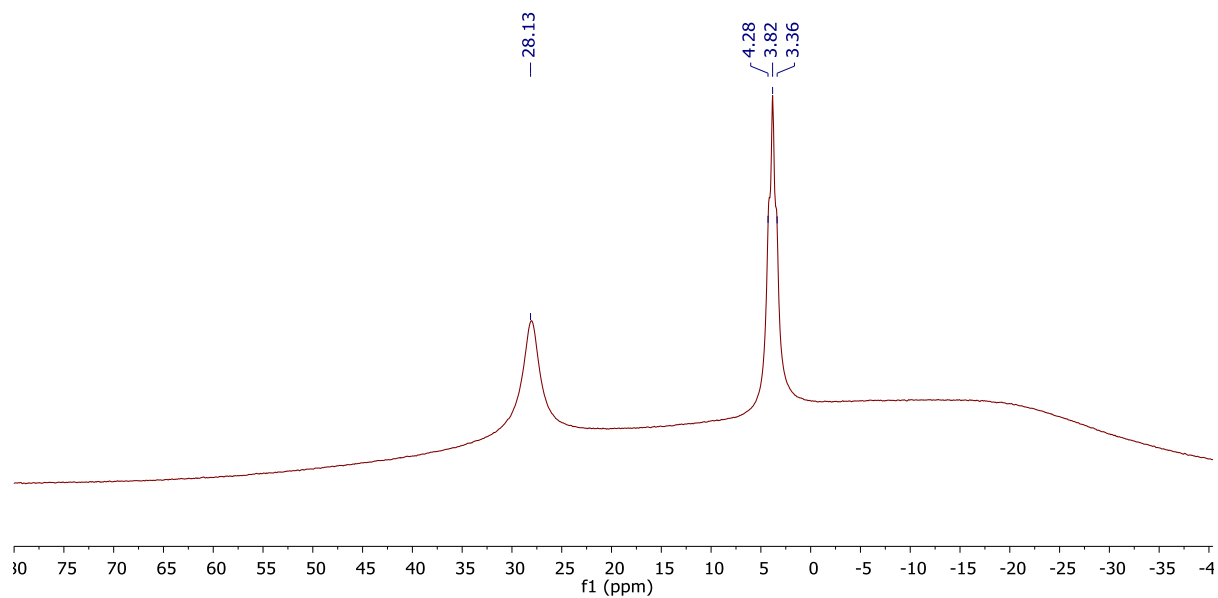


Figure S7 –  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of  $[\text{K}(18\text{-crown-6})][\mathbf{2}]$  in  $\text{CD}_3\text{CN}$

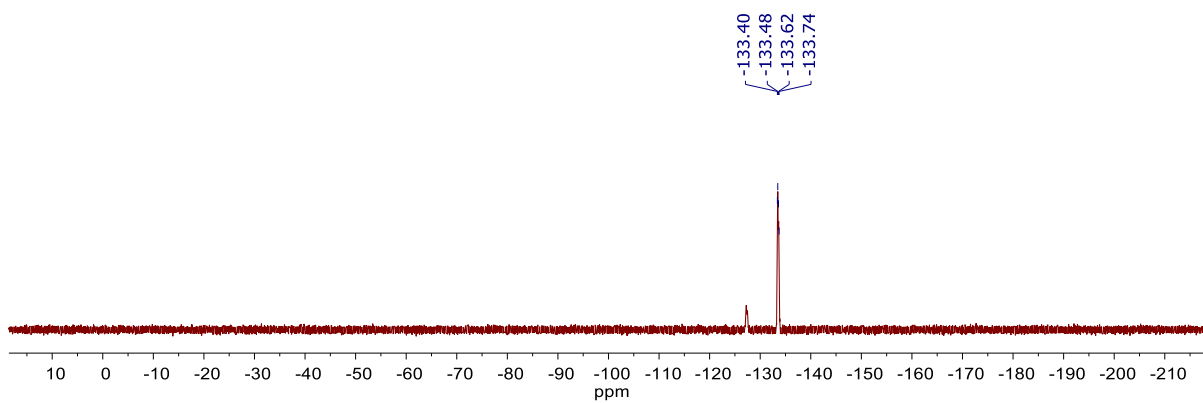


Figure S8 -  $^{19}\text{F}$  NMR spectrum of  $[\text{K}(\text{18-crown-6})][\mathbf{2}]$  in  $\text{CD}_3\text{CN}$

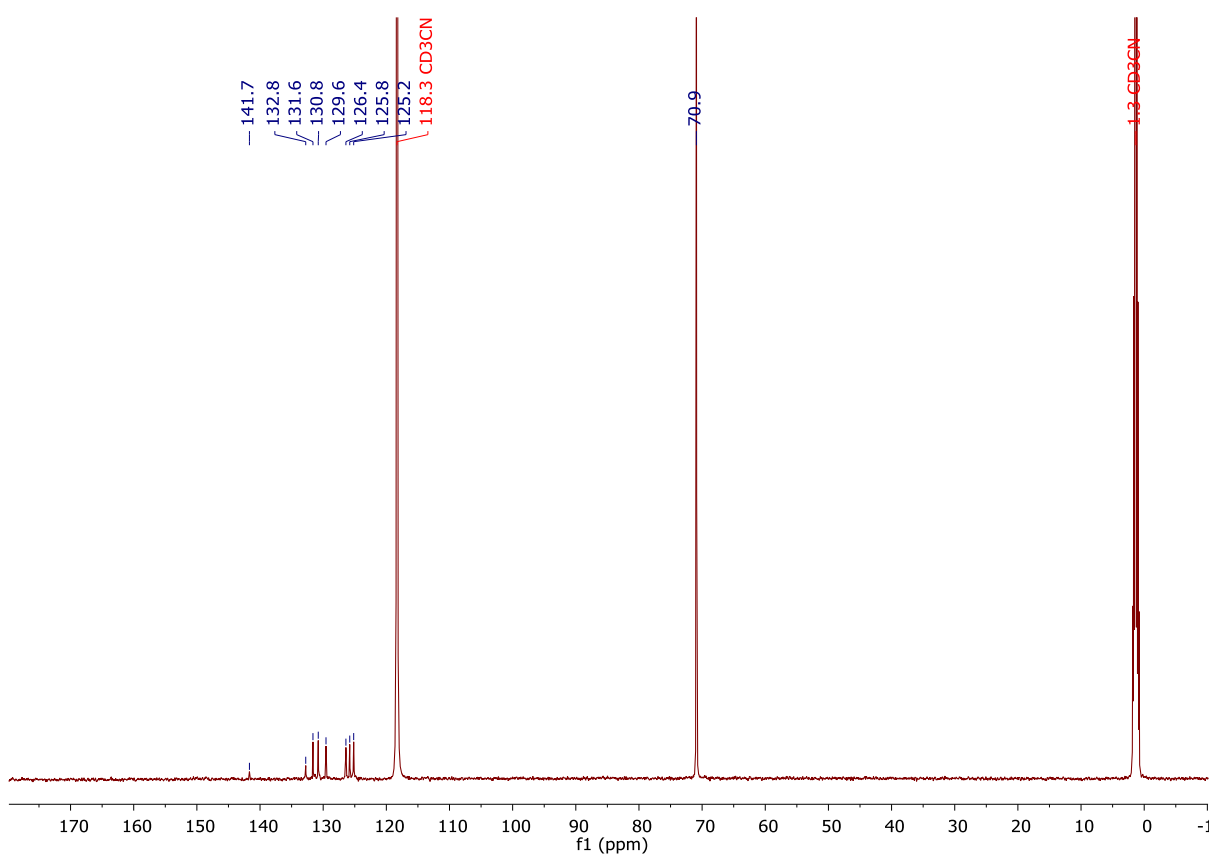


Figure S9 -  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $[\text{K}(\text{18-crown-6})][\mathbf{2}]$  in  $\text{CD}_3\text{CN}$

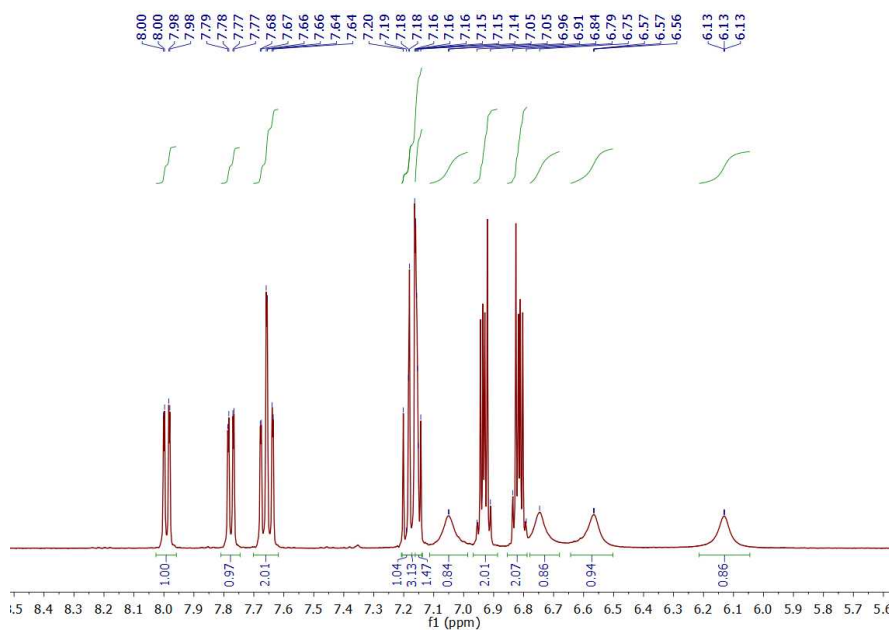
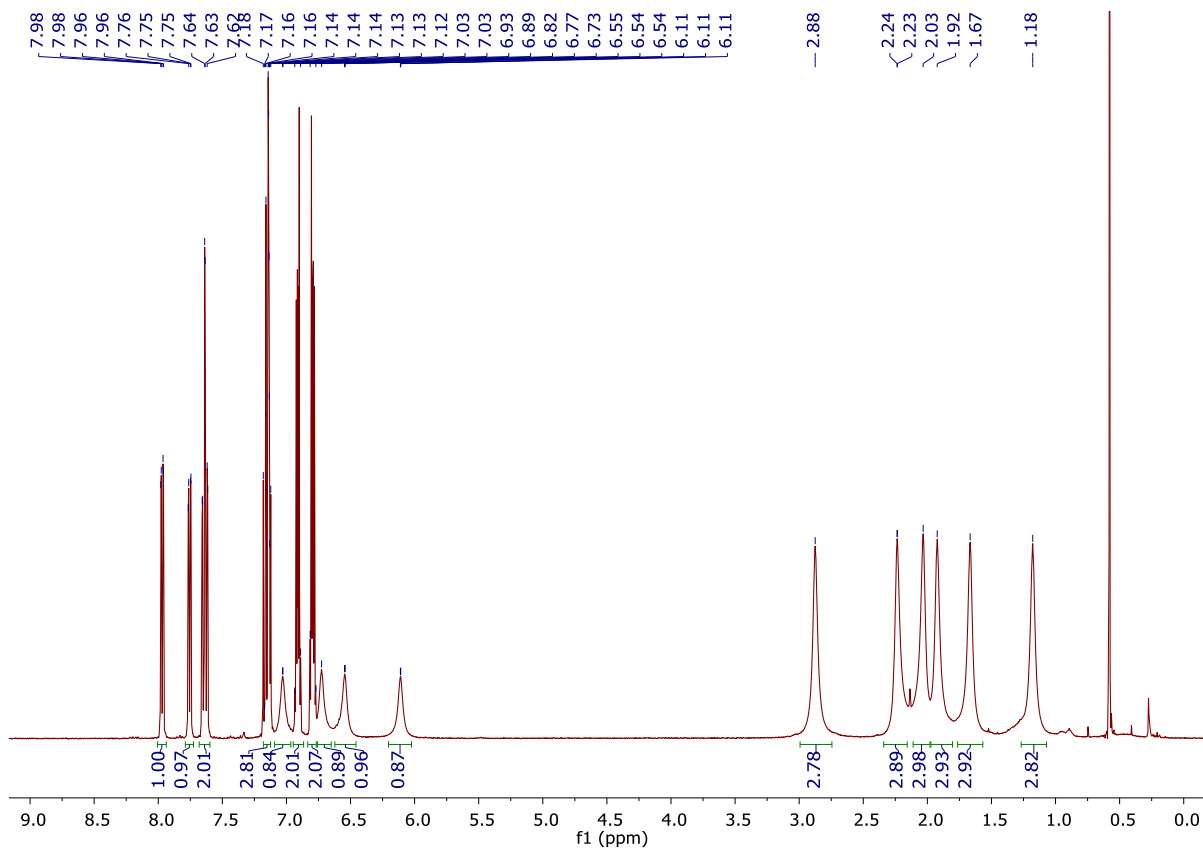


Figure S10 -  $^1\text{H}$  NMR spectrum of **3** in  $\text{C}_6\text{D}_6$  (plus expansion of aromatic region)



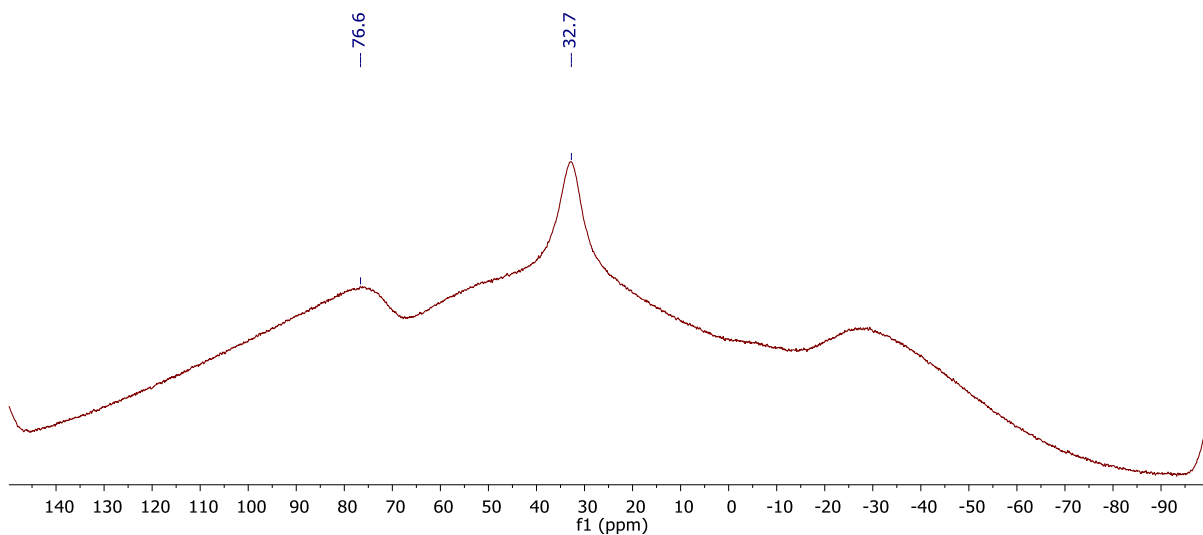


Figure S11 -  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of **3** in  $\text{C}_6\text{D}_6$

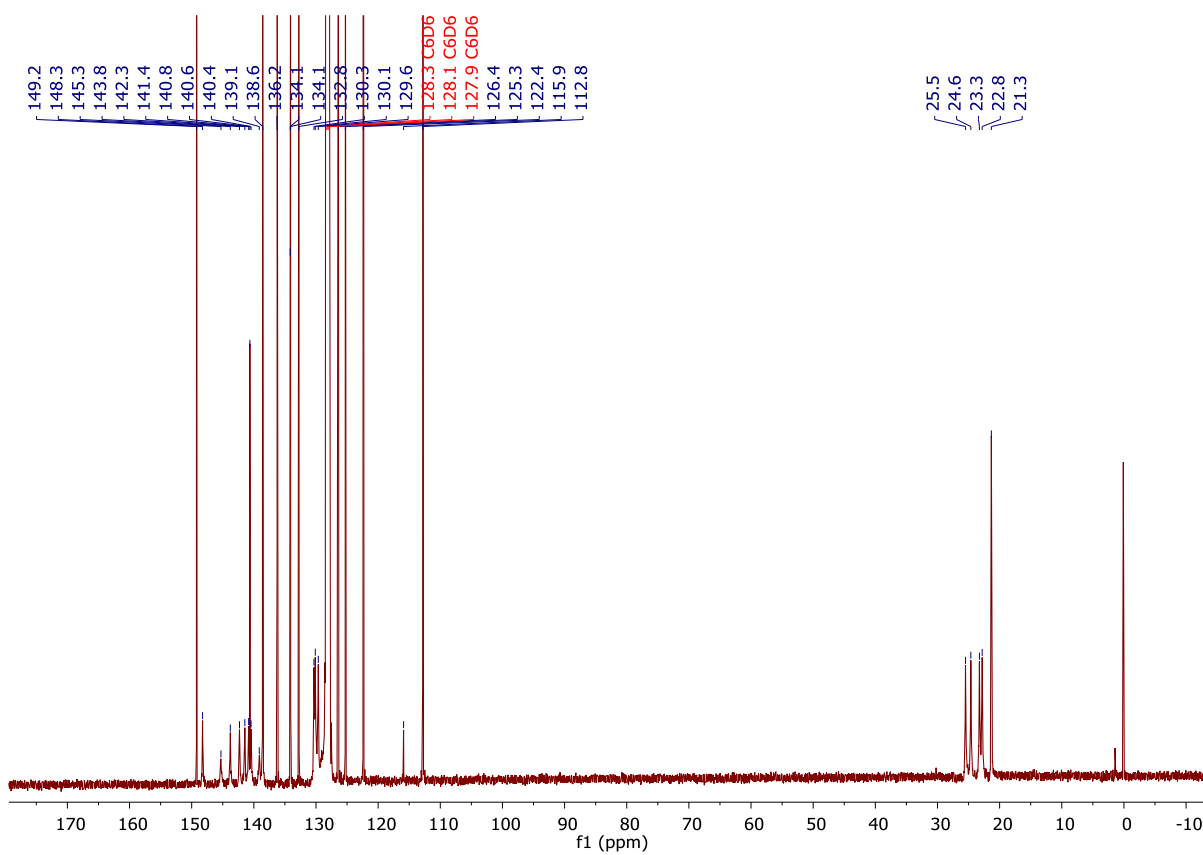


Figure S12 -  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **3** in  $\text{C}_6\text{D}_6$

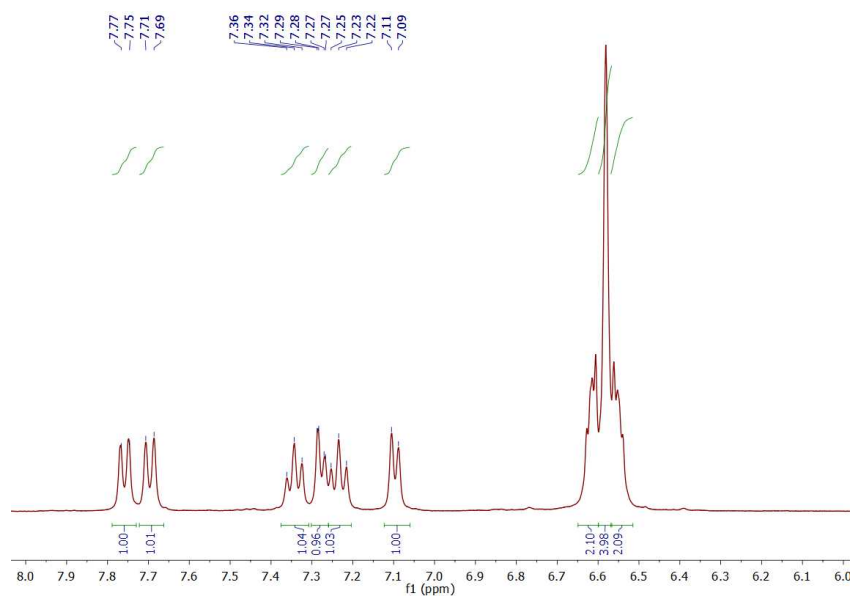
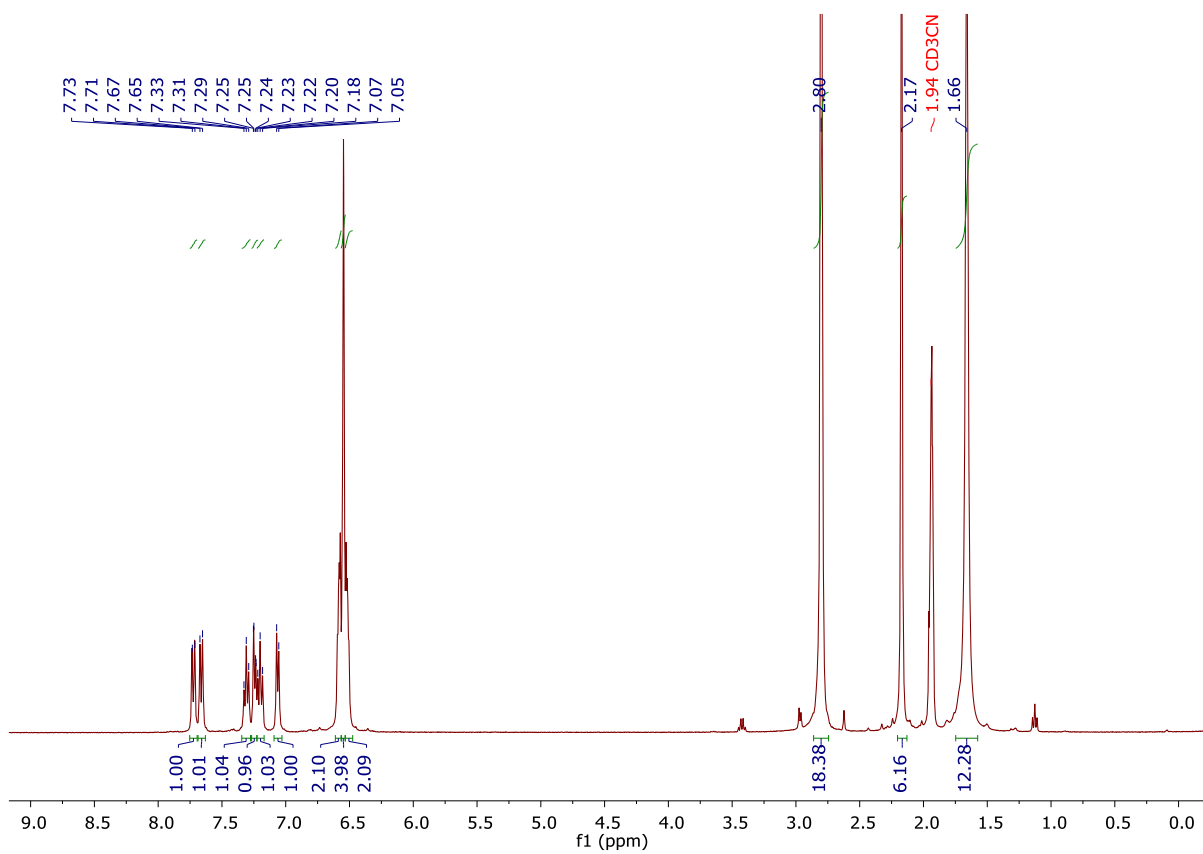


Figure S13 - <sup>1</sup>H NMR spectrum of [TAS][4] in CD<sub>3</sub>CN (plus expansion of aromatic region)

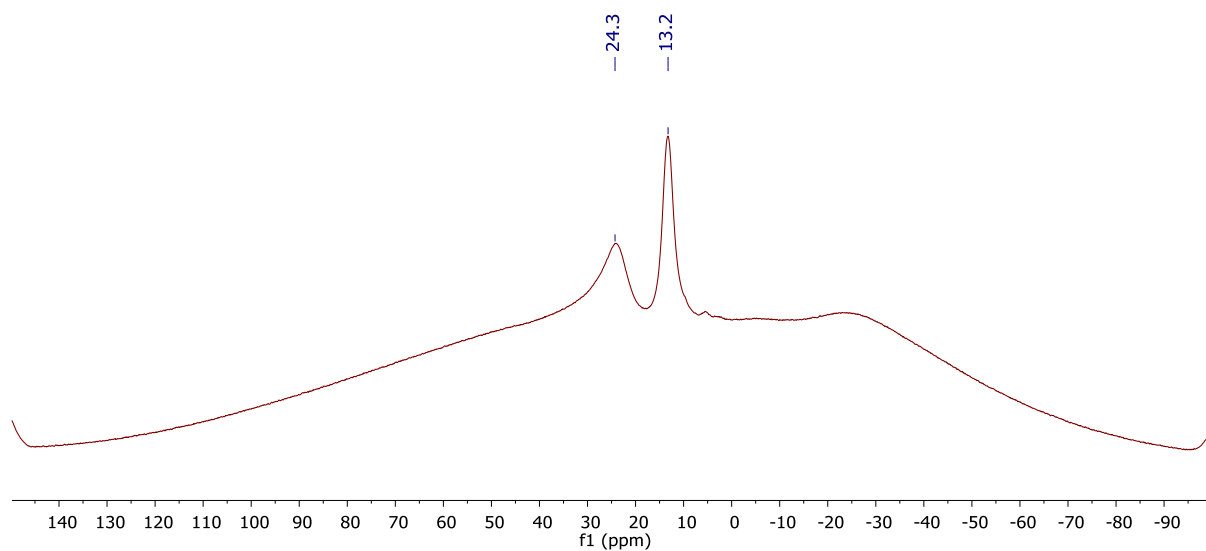


Figure S14 -  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of [TAS][4] in  $\text{CD}_3\text{CN}$

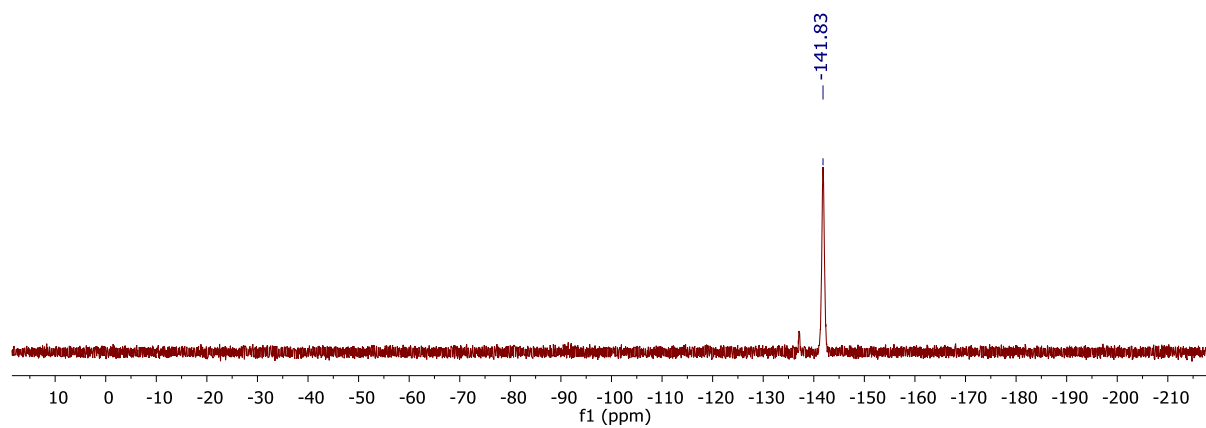


Figure S15 -  $^{19}\text{F}$  NMR of [TAS][4] in  $\text{CD}_3\text{CN}$

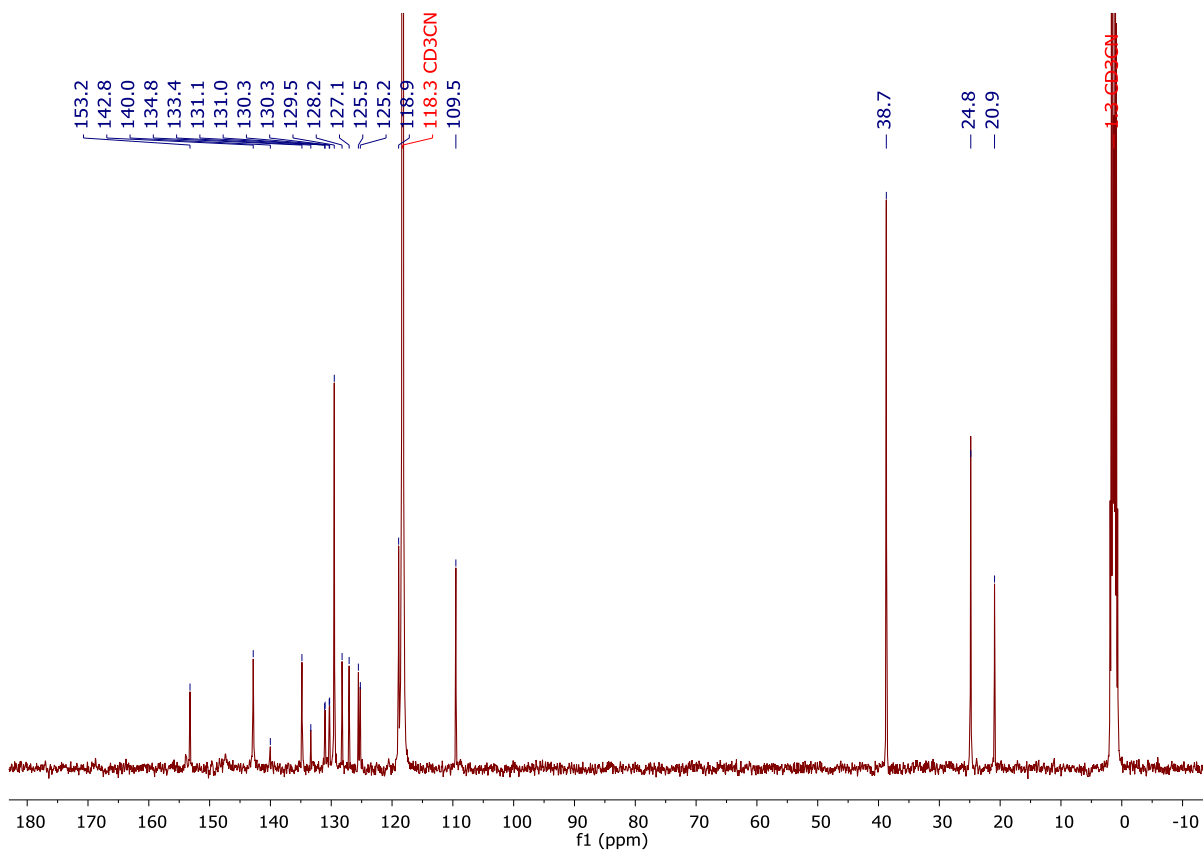


Figure S16 -  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of [TAS][4] in  $\text{CD}_3\text{CN}$

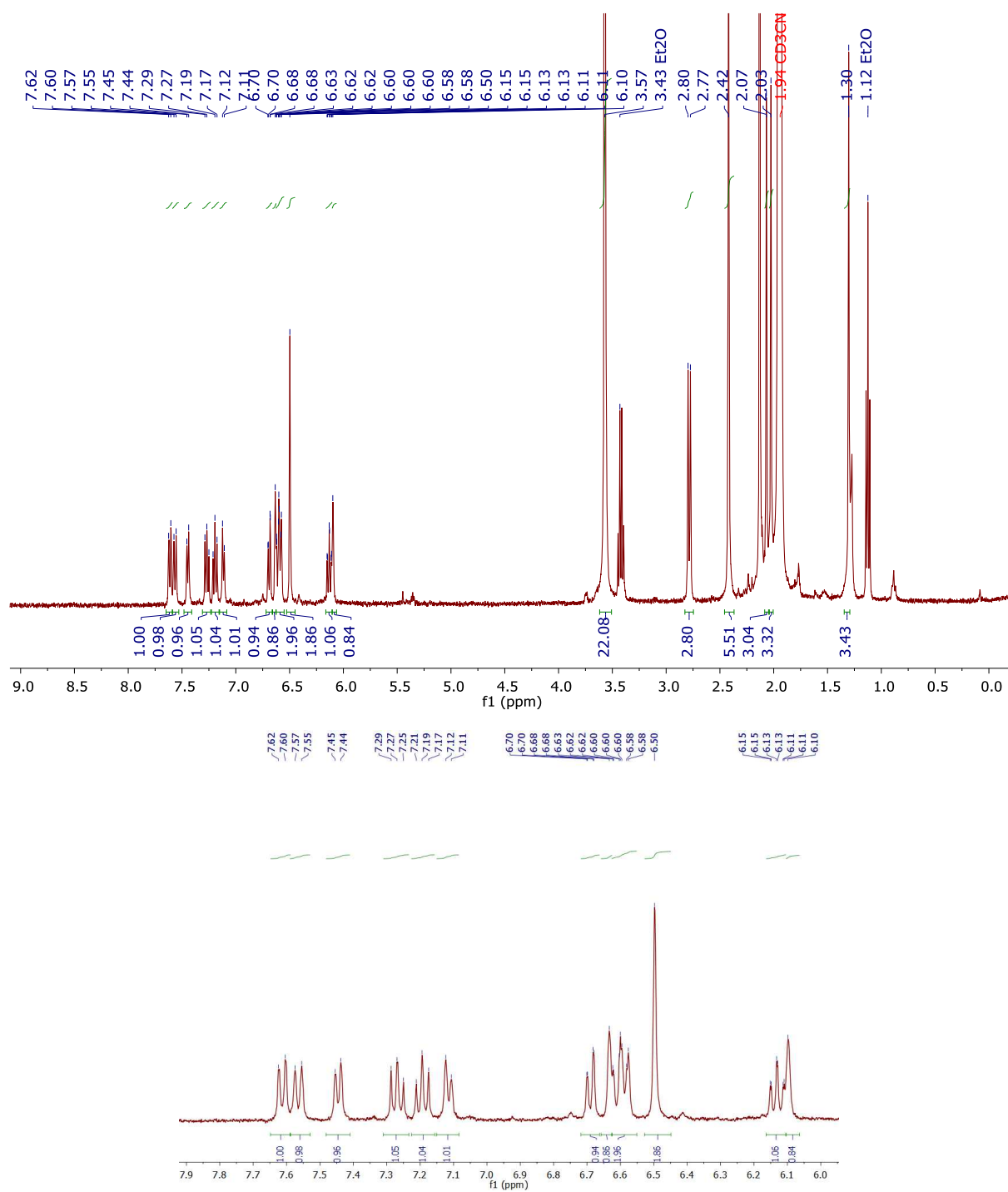


Figure S17 - <sup>1</sup>H NMR spectrum of [K(18-Crown-6)][5] in CD<sub>3</sub>CN (plus expansion of aromatic region)

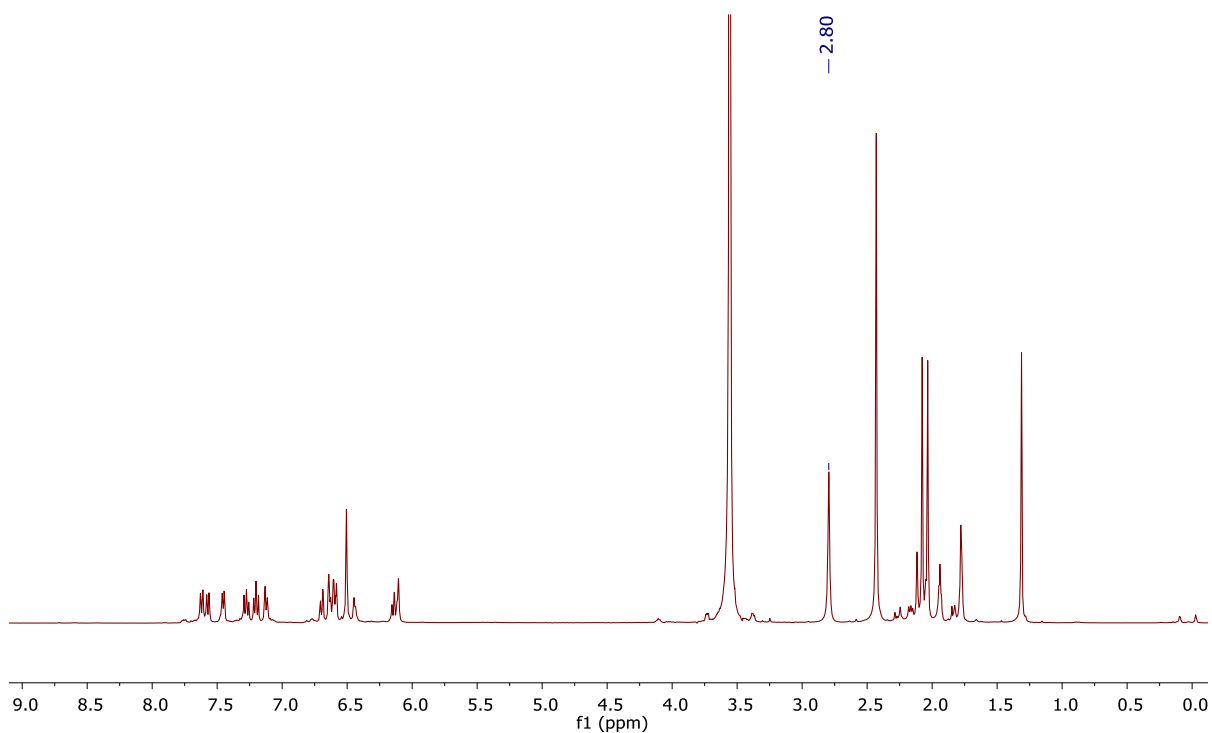


Figure S16 -  $^1\text{H}\{^{19}\text{F}\}$  NMR spectrum of  $[\text{K}(\text{18-Crown-6})][\mathbf{5}]$  in  $\text{CD}_3\text{CN}$

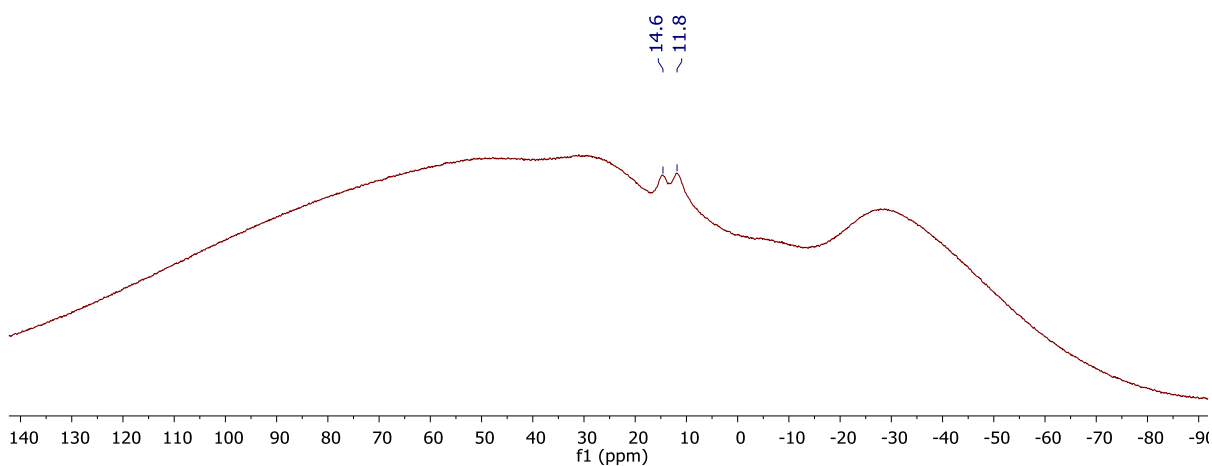


Figure S17 -  $^1\text{B}\{^1\text{H}\}$  NMR spectrum of  $[\text{K}(\text{18-Crown-6})][\mathbf{5}]$  in  $\text{CD}_3\text{CN}$

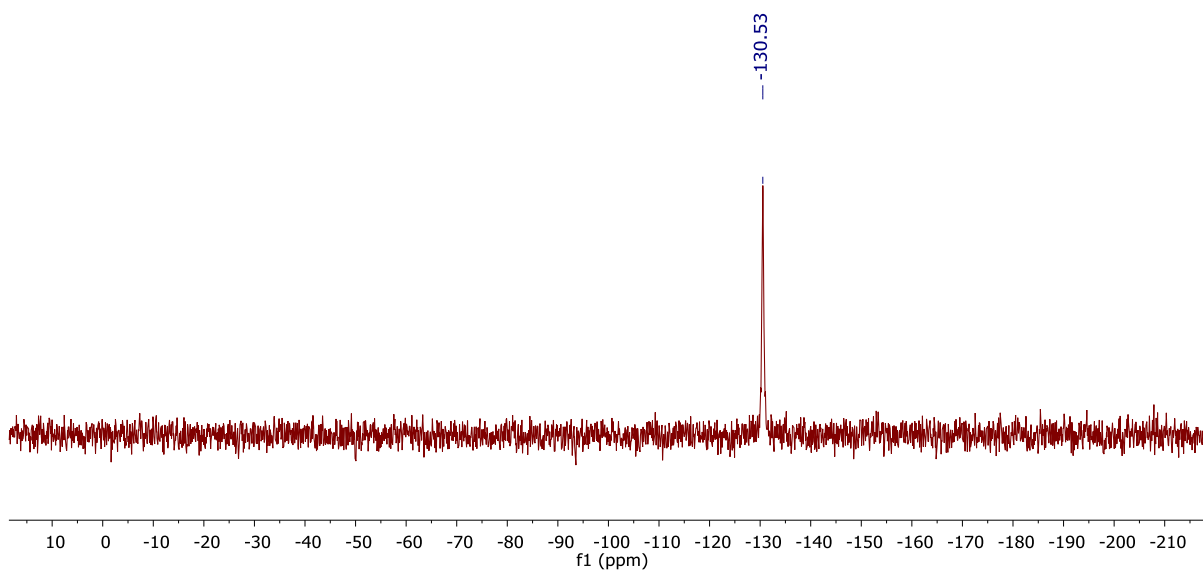


Figure S18 -  $^{19}\text{F}$  NMR spectrum of  $[\text{K}(18\text{-Crown-6})][5]$  in  $\text{CD}_3\text{CN}$

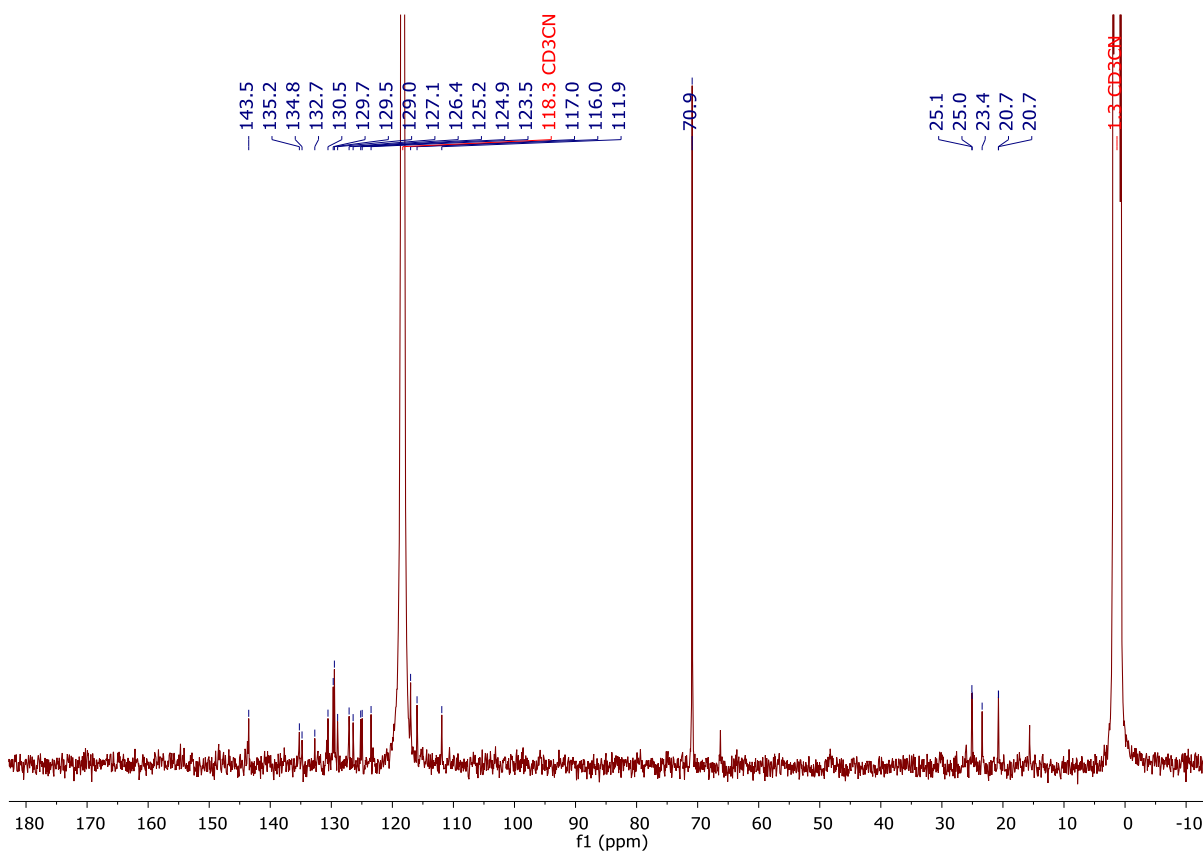


Figure S19 -  $^{13}\text{C}\{^1\text{H}\}$  NMR of  $[\text{K}(18\text{-Crown-6})][5]$  in  $\text{CD}_3\text{CN}$