

Solution and Solid-Phase Halogen and C–H Hydrogen Bonding to Perrhenate

Casey J. Massena,^[+] Asia Marie S. Riel,^[+] George F. Neuhaus, Daniel A. Decato and Orion Berryman*

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General:

All materials were obtained from Sigma-Aldrich, Acros, TCI-America, and Strem Chemicals and used without further purification. Nuclear Magnetic Resonance ^1H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on Varian Direct Drive 500 MHz and Bruker Avance 400 MHz spectrometers. Chemical shifts (δ) expressed as ppm. For the ^{19}F NMR spectra C_6F_6 (δ -164.9 ppm) was used as an internal standard. Signal splitting patterns are indicated as s, singlet; d, doublet; t, triplet; m, multiplet; b, broad. Coupling constants (J) are given in Hz. Melting points were determined with a Mel-temp. Compounds were analyzed via HPLC-ESI-MS to obtain accurate mass data. HPLC was performed with a reverse-phase HPLC column: an Agilent PLRP-S PSDVB column with 3.0 μm particles and dimensions of 50 mm length and 1.0 mm diameter (P/N PL1312-1300) was used with an Agilent 1290 HPLC system. The column was maintained at 40 °C with a flow rate of 0.6 mL/min. Chromatography was as follows: solvent consisted of methanol with 0.1% (v/v) formic acid for channel "A". Channel "B" was a (1:1 v/v) mixture of isopropanol and acetone. Following column equilibration at 20% B, the sample was injected via autosampler, and the column was flushed for 1.0 min to waste. From 1.0 min to the end of the run, the column eluent was directed to the MS source. From 1.0 min to 4.0 min, the gradient was linearly ramped from 20% to 95% B. From 4.8 to 5.0 min, the solvent mixture was held at 20% B. A Bruker micrOTOF mass spectrometer with ESI source was used: resolution was approximately 10,000 and accuracy 1 ppm. Source parameters were as follows: drying gas 7.0 L/min, drying gas heat at 180 °C, nebulizer 3 bar, capillary voltage 4500 V, capillary exit 100 V. Spectra were collected in negative or positive mode as appropriate from 50 to 1700 m/z at a rate of 2 Hz. Theoretical spectra were generated in Bruker Data Analysis to compare against experimental spectra.

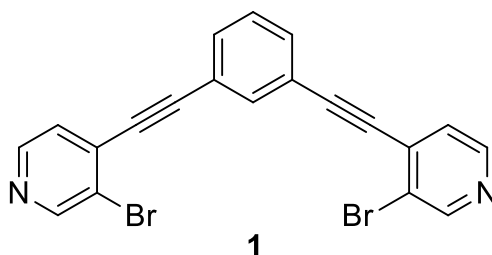
Synthesis:

General Procedure for Methylation. In an oven dried round bottom, **2** or **5** (1 equiv) was dissolved in dry DCM. In a separate round bottom, methyl triflate (4.1 equiv) was dissolved in dry DCM. Both round bottoms were sparged with dry N_2 gas for 15 min. The methyl triflate solution was then added dropwise to the solution of **2** or **5**. The solution was stirred for 16 h under inert atmosphere. Removal of the DCM by roto-evaporation left a solid that was triturated with hexanes followed by filtration.

General Procedure for Octylation. In an oven dried round bottom, **2** or **5** (1 equiv) was dissolved in dry DCM. Octyl triflate (4.5 equiv, prepared according to literature procedure¹) was dissolved in dry DCM. Both round bottoms were sparged with dry N_2 gas for 15 min. The octyl triflate solution was then added dropwise to the solution of **2** or **5**. The solution was stirred for 16 h under inert

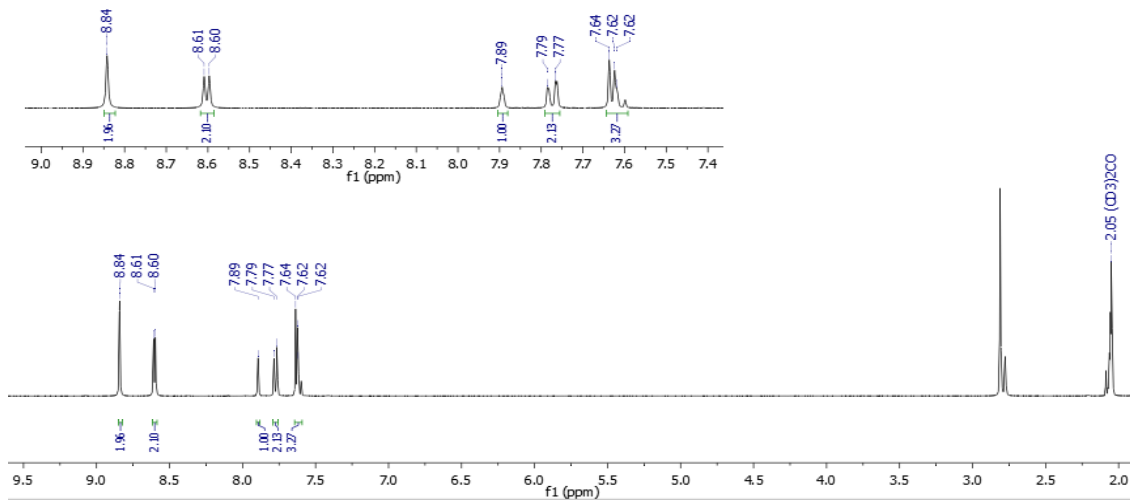
atmosphere. Removal of the DCM by roto-evaporation left a solid/oil that was triturated with hexanes followed by filtration.

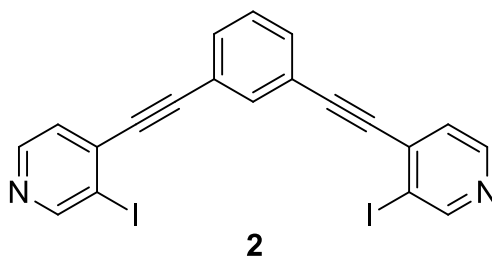
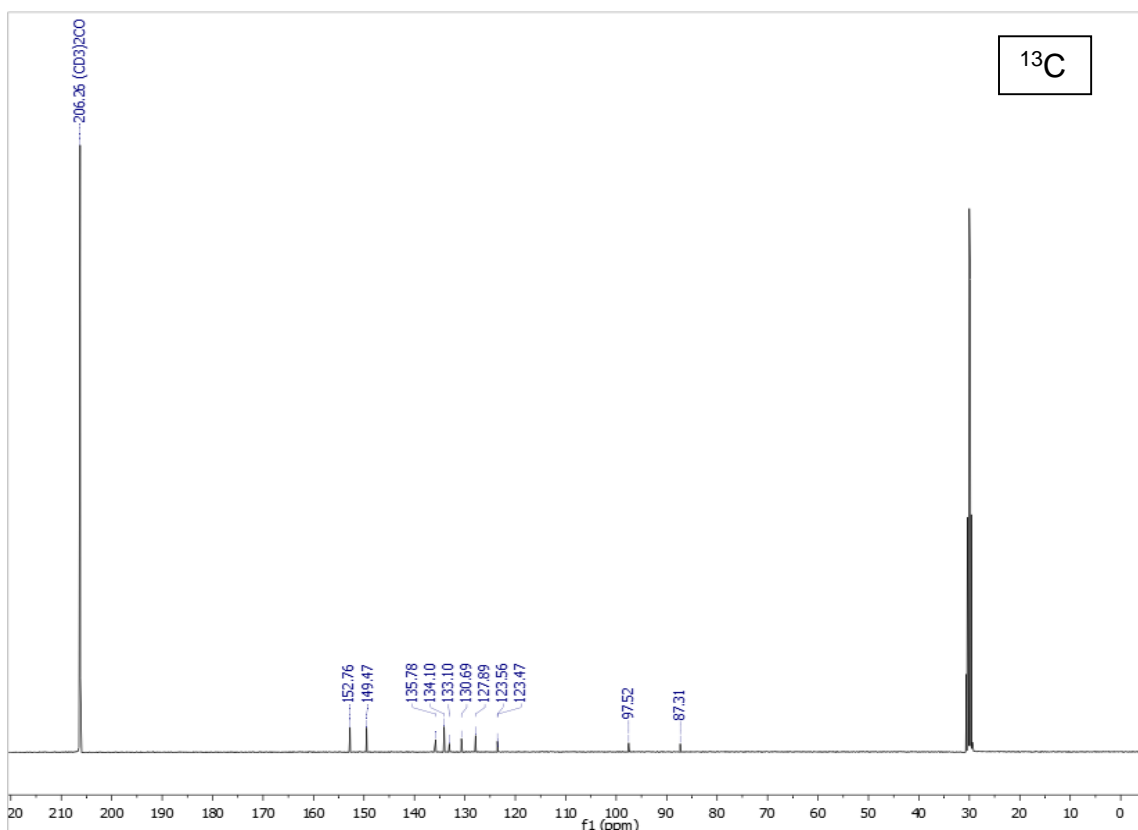
General Procedure for Anion Metathesis. In a one dram scintillation vial, **3** or **6** (1 equiv) and tetra-*n*-butylammonium chloride (2.2 equiv) were dissolved in DCM. Vapor diffusion of Et₂O afforded a precipitate that was isolated by filtration. To remove excess tetra-*n*-butylammonium chloride, the precipitate was washed with acetone which left a powder/oil.



1,3-bis(4-ethynyl-3-bromopyridinyl)benzene (1). To an oven dried 25 mL round bottom flask was added *N,N*-diisopropylamine (2.46 mL, 14.1 mmol), 1,3-diethynylbenzene (0.693 mL, 5.22 mmol), and 15 mL of DMF. To another dry 25 mL round bottom flask was added 10 mL DMF. Both 25 mL round bottoms were sparged for 20 min with dry N₂ gas. An oven dried Schlenk flask was charged with 3-bromo-4-iodopyridine (4.00 g, 14.1 mmol), then vacuumed and backfilled with dry N₂ gas (3x). Bis(triphenylphosphine)palladium (II) dichloride (0.219 g, 0.313 mmol) was added, vacuumed and backfilled with dry N₂ (3x). Copper (I) iodide (0.099 g, 0.522 mmol) was added, vacuumed and backfilled with dry N₂ (3x). The acetylene solution was transferred by cannula to the Schlenk flask. Excess DMF was used to wash the acetylene round bottom, which was then transferred to the Schlenk flask. The flask was carefully vacuumed and backfilled with dry N₂ (3x). The orange solution stirred for 20 h and subsequent removal of DMF by roto-evaporation left an orange solid that was purified by column chromatography (2:1 hexanes/EtOAc) to afford **1** (2.00 g, 4.56 mmol, 88%) as a cream colored solid. Mp: 111–112 °C. ¹H NMR (400 MHz, (CD₃)₂CO; 25 °C) δ 8.84 (s, 2H), 8.60 (d, *J* = 4.9 Hz, 2H), 7.89 (s, 1H), 7.78 (d, *J* = 7.7 Hz, 2H), 7.65 – 7.59 (m, 3H). ¹³C NMR (100.6 MHz, (CD₃)₂CO; 25 °C) δ 152.76, 149.47, 135.78, 134.10, 133.10, 130.69, 127.89, 123.56, 123.47, 97.52, 87.31. HRMS (CI pos) *m/z*: 438.903 (M²⁺+2, 100%), 436.905 (M²⁺+2, 51.4), 440.901 (M²⁺+2, 48.6); C₂₀H₁₀Br₂N₂²⁺+2 (438.93).

^1H

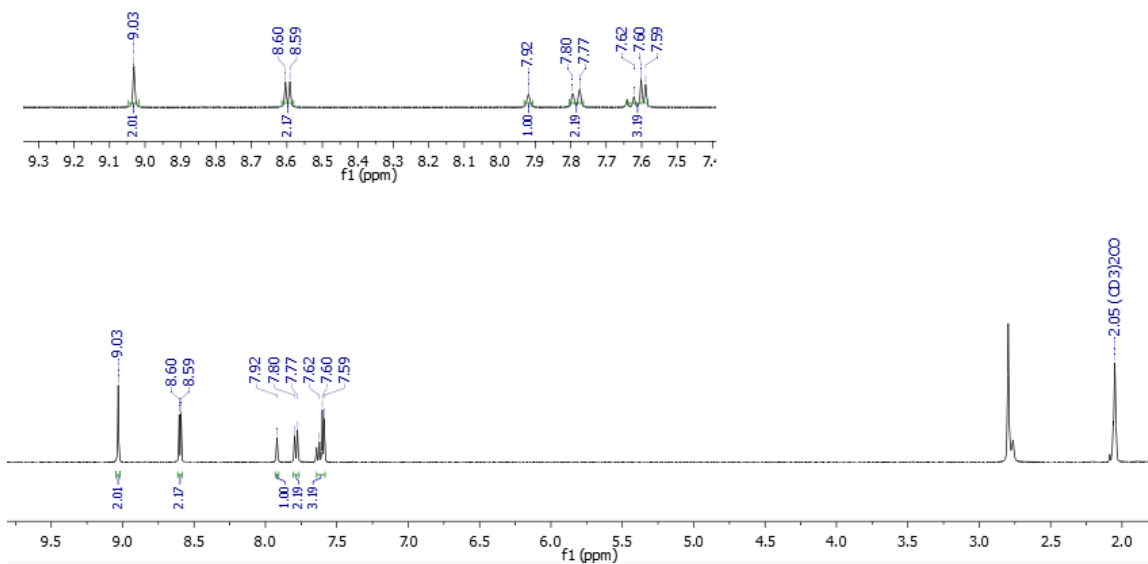


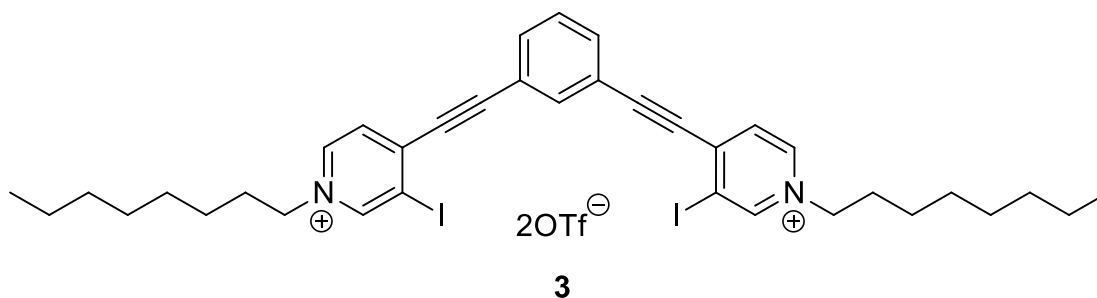
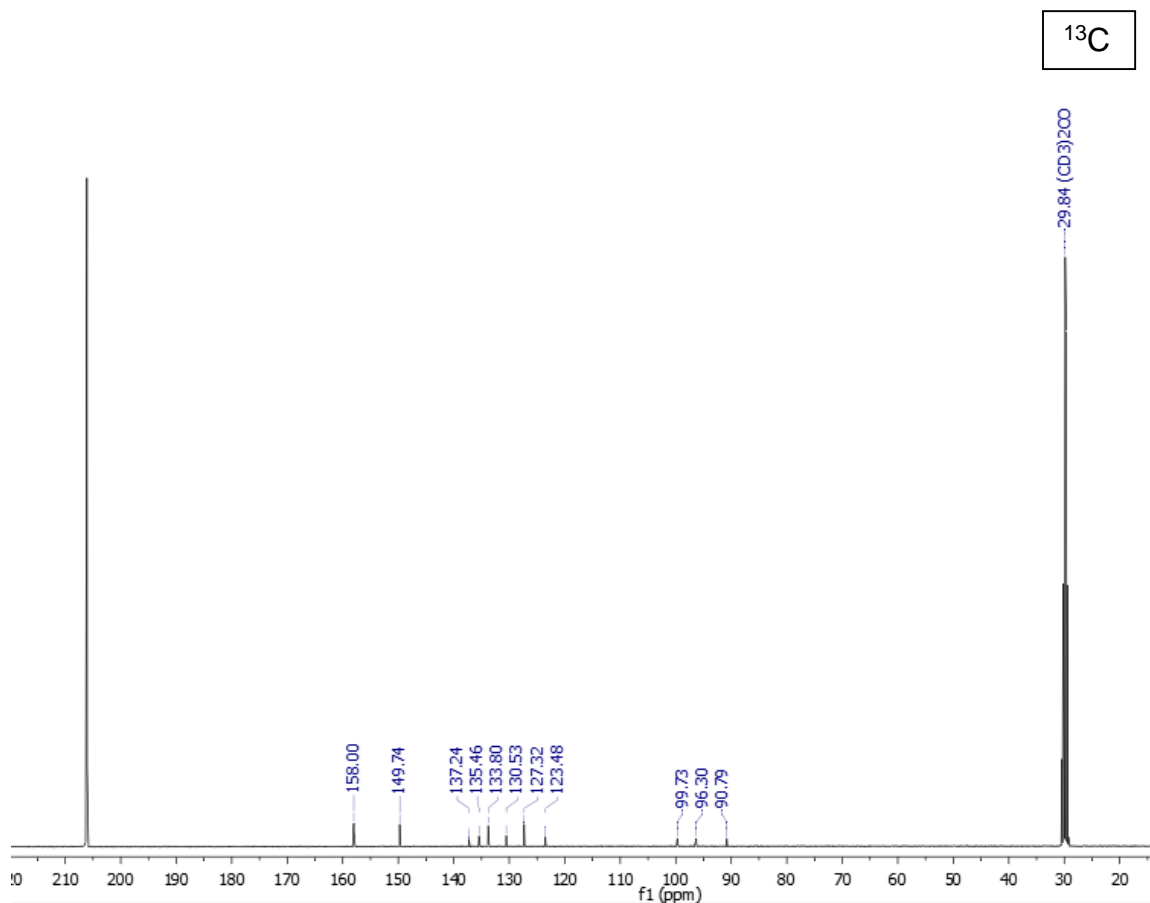


1,3-bis(4-ethynyl-3-iodopyridinyl)benzene (2). Adapted from literature procedure², an oven dried round bottom (50 mL) was charged with **1** (0.200 g, 0.457 mmol) which was subsequently dissolved in 20 mL of THF, cooled to -67 °C and sparged with dry N₂ gas for 20 min. N-butyllithium (2.3 M in hexanes, 0.50 mL, 1.15 mmol) was added dropwise to the light yellow solution of **1**. The deep green mixture was stirred for 30 min at -67 °C and was monitored by TLC. Iodine (0.571 g, 2.25 mmol) in 5 mL of THF was added dropwise keeping the temperature below -65 °C. The red solution was allowed to gradually warm to room temperature and stirred for 18 h. The red solution was washed with sat. Na₂S₂O₃ and extracted with Et₂O. The organic layers were combined and dried with MgSO₄. Removal of Et₂O by roto-evaporation left an orange solid that was purified via column chromatography (7:3 hexanes/EtOAc) to yield a beige solid (0.250 g, 0.469 mmol, 41%). Mp: 147–149 °C. ¹H NMR (400 MHz, (CD₃)₂CO; 25 °C) δ 9.03 (s, 2H), 8.60 (d, *J* = 4.9 Hz, 2H), 7.92 (s, 1H), 7.78 (d, *J* = 8.8 Hz,

2H), 7.67-7.56 (m, 3H). ^{13}C NMR (100.6 MHz, $(\text{CD}_3)_2\text{CO}$; 25°C) δ 158.00, 149.74, 137.24, 135.46, 133.80, 130.58, 127.32, 123.48, 99.73, 96.30, 90.79. HRMS (CI pos) m/z : 532.901 ($\text{M}^{2+}+2$, 100%), 533.904 ($\text{M}^{2+}+2$, 22.4), 534.907 ($\text{M}^{2+}+2$, 2.3); $\text{C}_{20}\text{H}_{10}\text{I}_2\text{N}_2^{2+}+2$ (532.90).

^1H

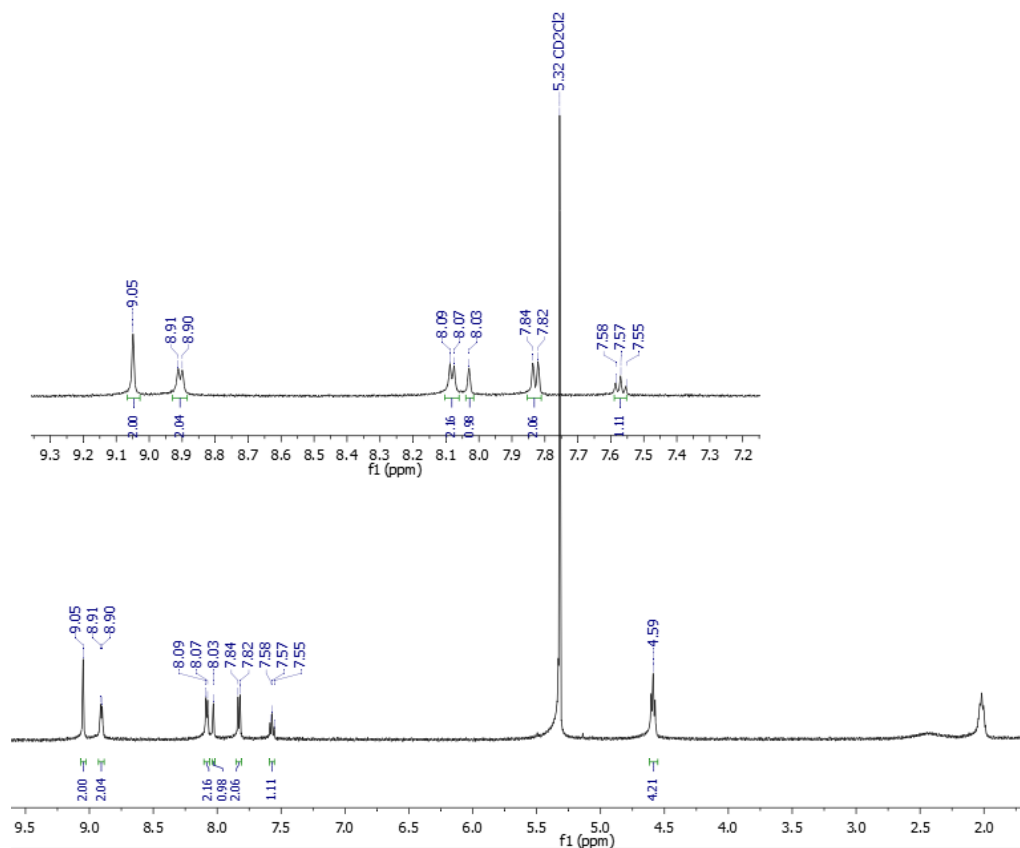




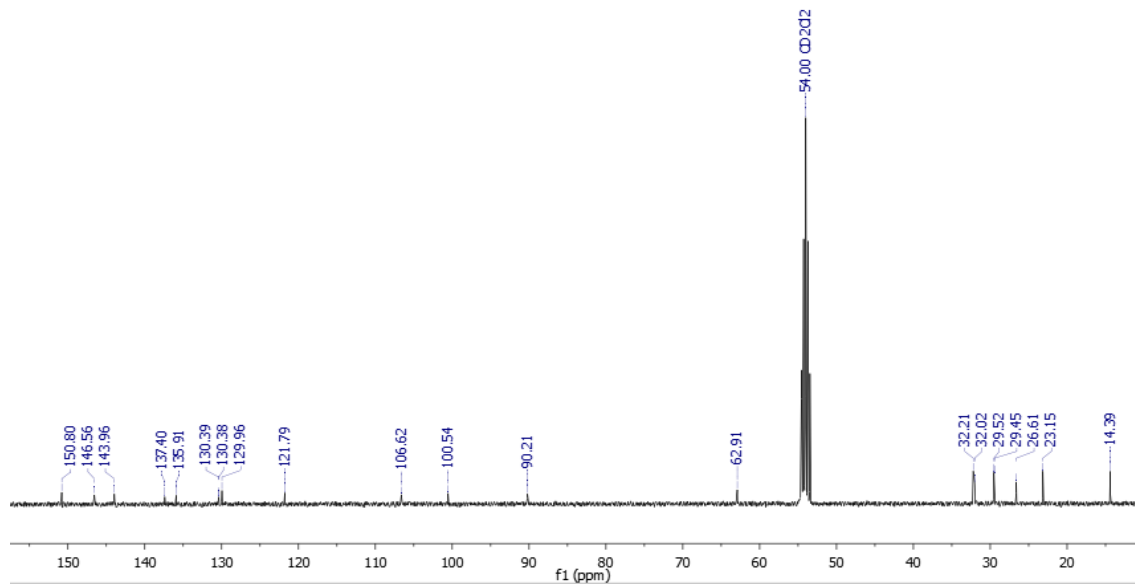
1,3-bis(4-ethynyl-N-octyl-3-iodopyridinium)benzene ditriflate (3). 2 (0.189 g, 3.55 mmol) was reacted with octyl triflate (0.616 mL, 3.94 mmol of 1-octanol) according to general procedure for octylation. The product was a beige solid (0.318 g, 0.301 mmol, 85%). Mp: 113–115 °C. ¹H NMR (500 MHz, CD₂Cl₂; 25 °C) δ 9.05 (s, 1H), 8.91 (d, *J* = 5.9 Hz, 2H), 8.08 (d, *J* = 6.4 Hz, 2H), 8.03 (s, 1H), 7.83 (d, *J* = 7.3 Hz, 2H), 7.57 (t, *J* = 7.9 Hz, 1H), 4.58 (t, *J* = 1.6 Hz, 4H), 1.38 (b, 8H), 1.28 (b, 16H), 0.88 (b, 6H). ¹³C NMR (100.6 MHz, CD₂Cl₂; 25 °C) δ 150.80, 146.56, 143.96, 137.40, 135.91, 130.39, 130.38, 129.96, 121.79, 106.62, 100.54,

90.21, 62.91, 32.21, 32.02, 29.52, 29.45, 26.61, 23.15, 14.39. ^{19}F NMR (376.3 MHz, CD_3CN ; 25°C) δ -76.89. HRMS (CI pos) m/z : 379.079 (M^{+2} , 100%), 379.581 (M^{+2} , 39.7), 380.082 (M^{+2} , 7.6); $\text{C}_{38}\text{H}_{44}\text{I}_2\text{N}_2^{2+}$ (379.08).

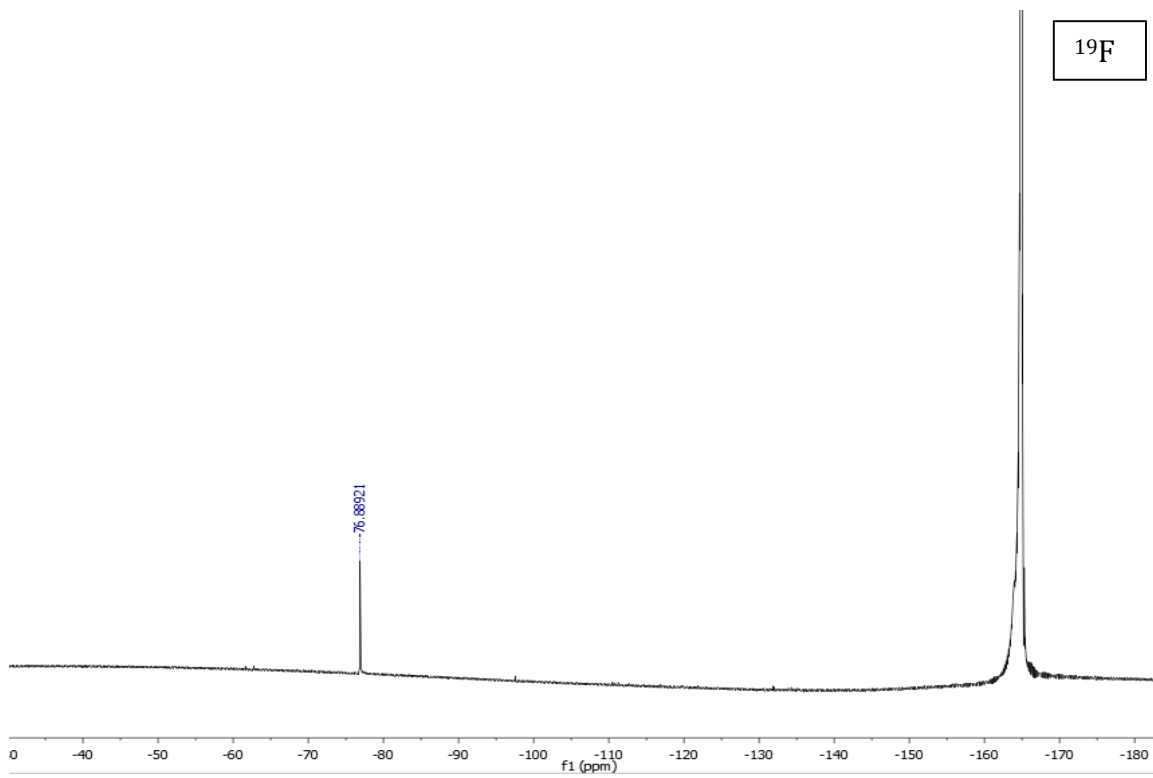
^1H

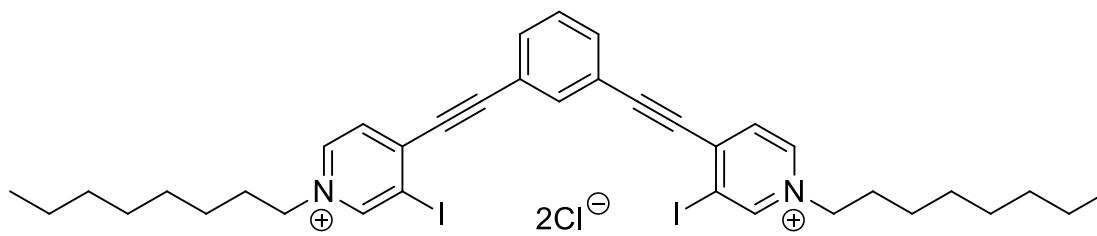


¹³C



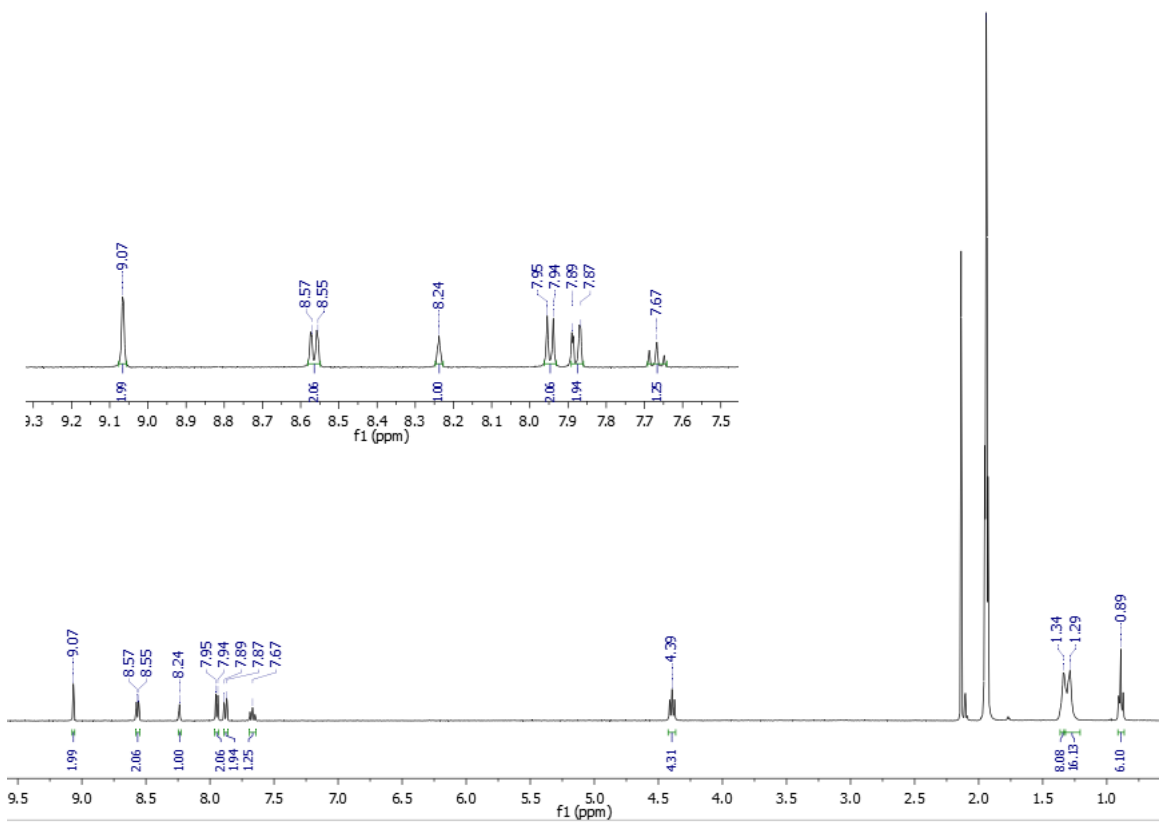
¹⁹F



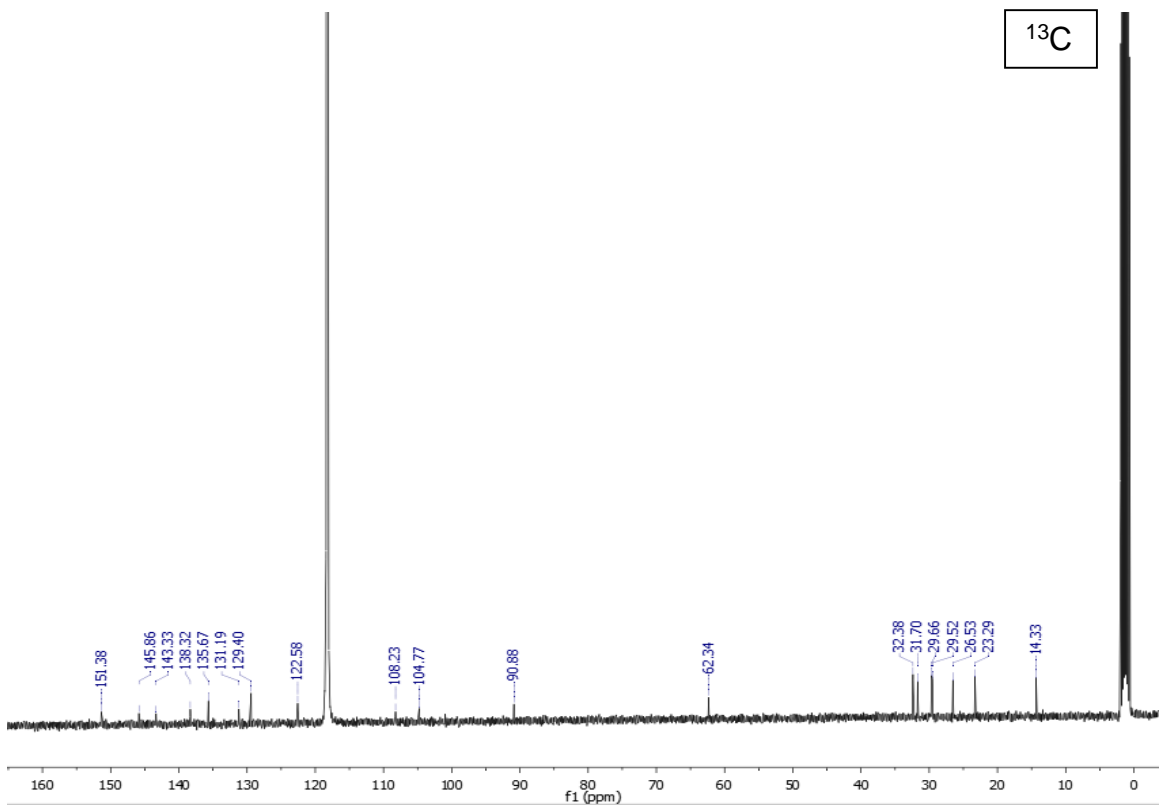


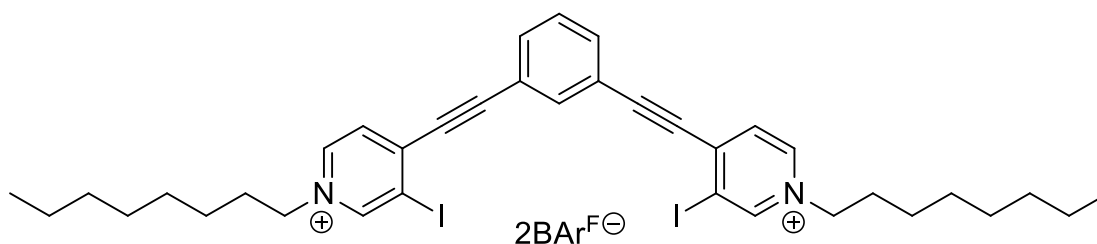
1,3-bis(4-ethynyl-N-octyl-3-iodopyridinium)benzene dichloride (4). **3** (0.156 g, 0.147 mmol) and tetra-*n*-butylammonium chloride (0.0975 g, 0.351 mmol) were reacted according to the general procedure for anion metathesis. The product was isolated as a yellow powder (0.060 g, 0.0791 mmol, 55%). Mp: 182–184 °C. ¹H NMR (400 MHz, CD₃CN; 25 °C) δ 9.07 (s, 2H), 8.56 (d, *J* = 6.4 Hz, 2H), 8.24 (s, 1H), 7.95 (d, *J* = 6.4 Hz, 2H), 7.88 (d, *J* = 9.4 Hz, 2H), 7.67 (t, *J* = 16.0 Hz, 1H), 4.39 (t, *J* = 15.2 Hz, 4H), 1.34 (b, 8H), 1.29 (b, 16H), 0.89 (b, 6H). ¹³C NMR (100.6 MHz, CD₃CN; 25 °C) δ 151.38, 145.86, 143.33, 138.32, 135.67, 131.19, 129.40, 122.58, 108.23, 104.77, 90.88, 62.34, 32.38, 31.70, 29.66, 29.52, 26.53, 23.29, 14.33.

¹H



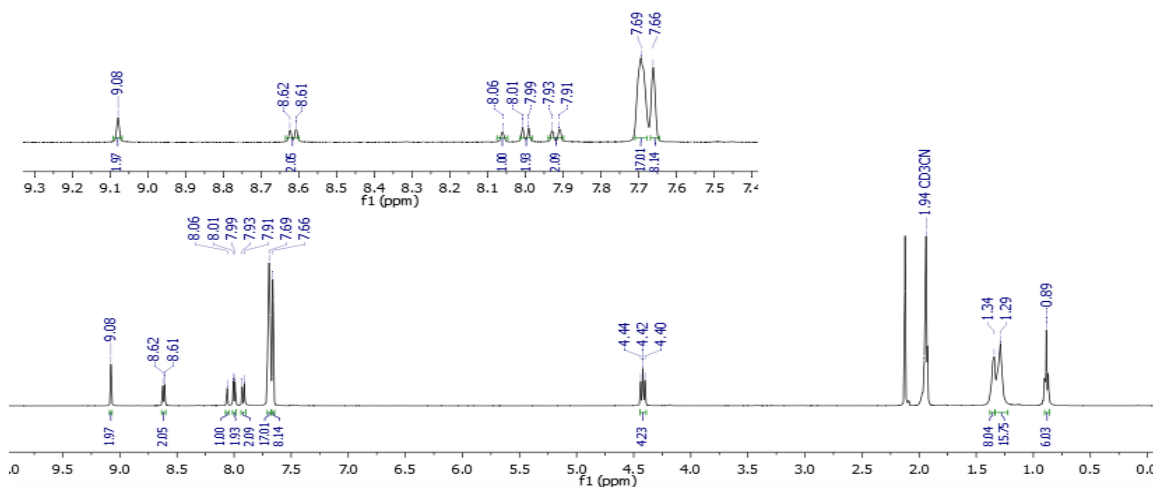
¹³C

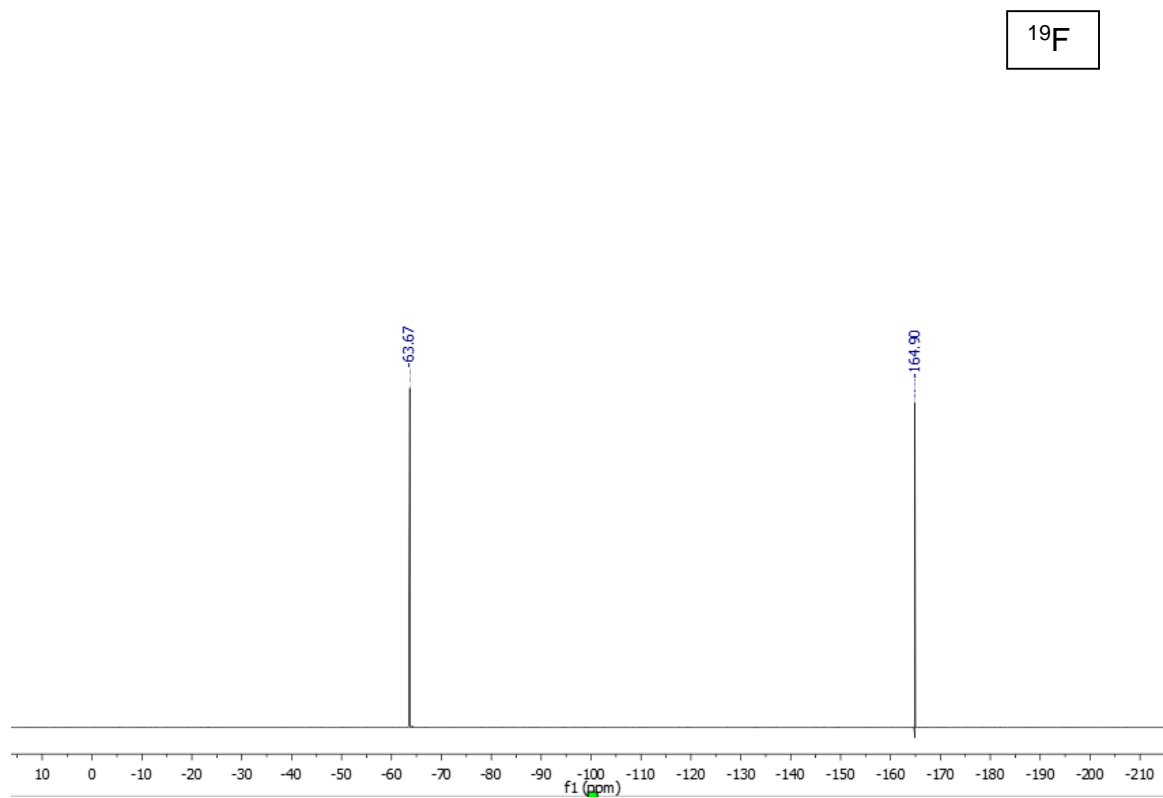
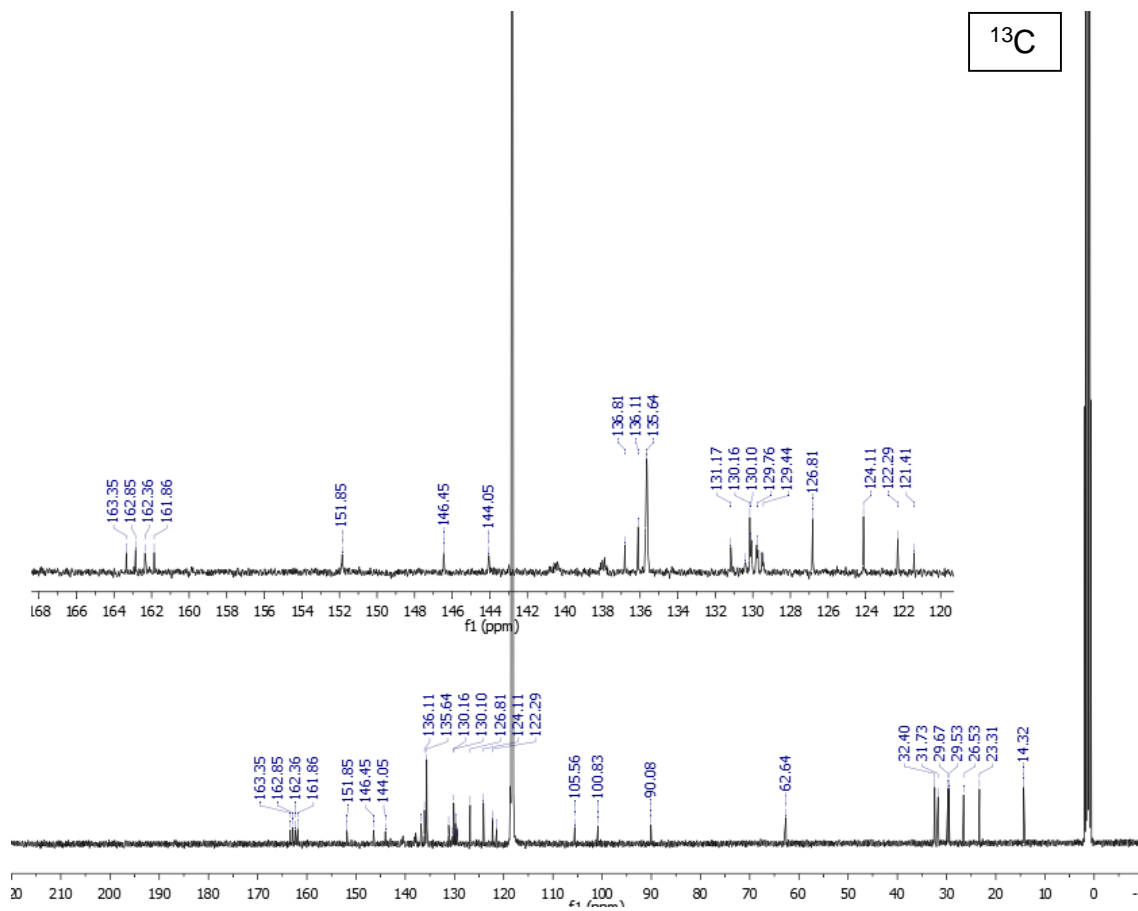


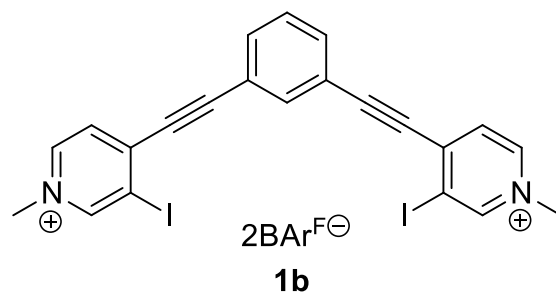


1a

1,3-bis(4-ethynyl-N-octyl-3-iodopyridinium)benzene bis(tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (1a). Adapted from literature procedure³, a 25 mL round bottom flask was charged with **4** (0.050 g, 0.0603 mmol) which was subsequently suspended in 8 mL DCM. Na⁺[BARF₄]⁻ (0.107 g, 0.121 mmol), prepared according to literature procedure⁴, was added to the solution of **4** and stirred for 15 min at rt during which Na⁺Cl⁻ precipitated from solution. The mixture was filtered through Celite and the filtrate concentrated under reduced pressure. Purification via HPLC afforded a dark yellow oil (0.0223 g, 0.0089 mmol, 79%). ¹H NMR (400 MHz, CD₃CN; 25 °C) δ 9.08 (s, 2H), 8.62 (d, *J* = 6.3 Hz, 2H), 8.06 (s, 1H), 8.00 (d, *J* = 6.4 Hz, 2H), 7.92 (d, *J* = 7.8 Hz, 2H), 7.69 (b, 17H), 7.66 (b, 8H), 4.42 (t, *J* = 15.2 Hz, 4H), 1.34 (b, 8H), 1.29 (b, 16H), 0.89 (m, 6H). ¹³C NMR (100.6 MHz, CD₃CN; 25 °C) δ 162.56 (q, *J* = 50.3 Hz), 151.85, 146.45, 144.05, 136.81, 136.11, 135.64, 131.17, 130.16, 129.80, 129.89 (qq, *J* = 34.2 Hz), 125.51 (q, *J* = 271.6 Hz), 122.29, 105.56, 100.83, 90.08, 62.64, 32.40, 31.73, 29.67, 26.53, 23.31, 14.32. ¹⁹F NMR (376.3 MHz, CD₃CN; 25 °C) δ -63.67. HRMS (CI pos) *m/z*: 379.075 (M⁺², 100%), 379.581 (M⁺², 39.7), 380.082 (M⁺², 7.6); C₃₆H₄₄I₂N₂²⁺ (379.08).

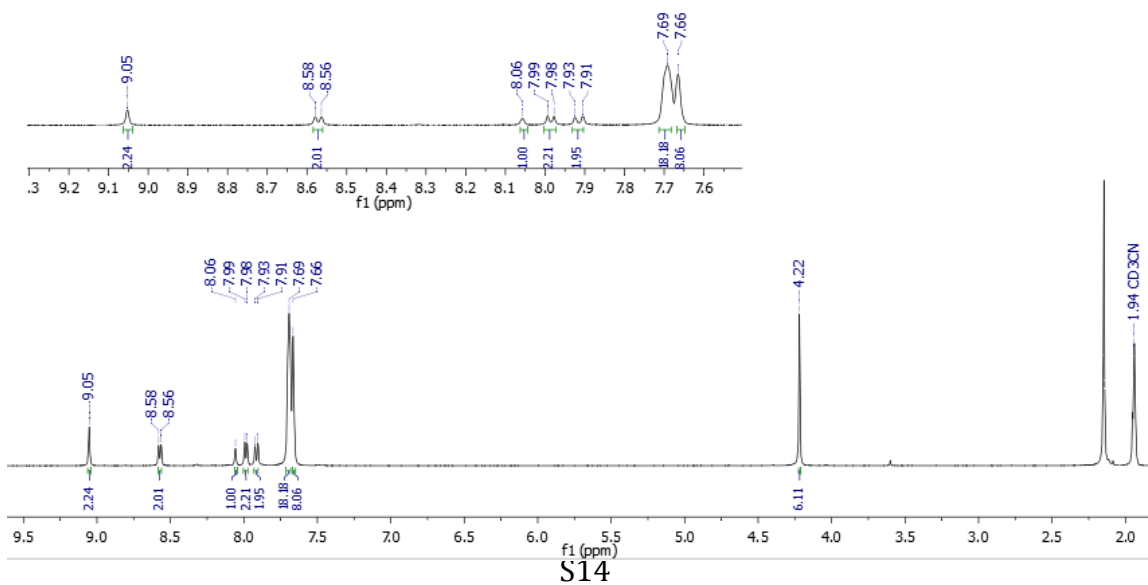




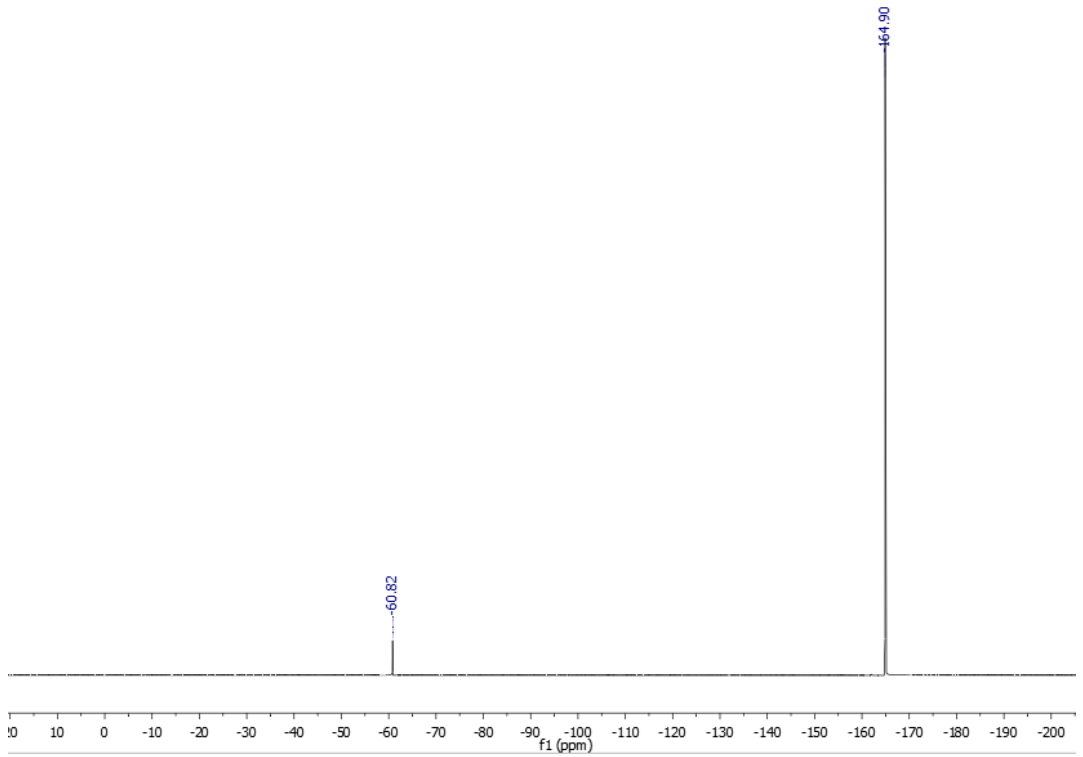
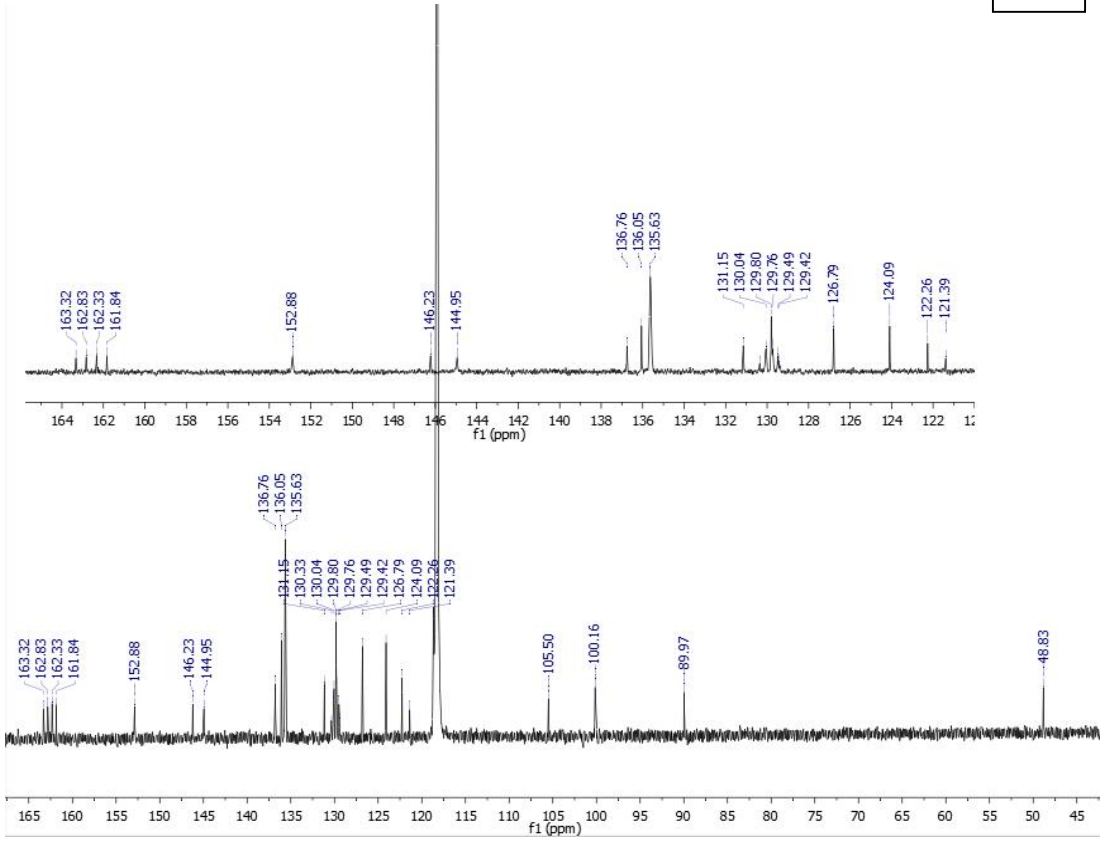


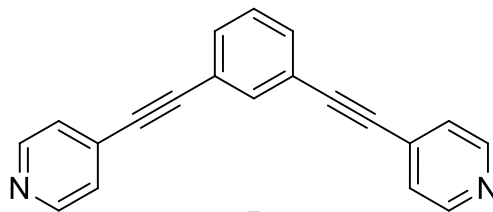
1,3-bis(4-ethynyl-N-methyl-3-iodopyridinium)benzene bis(tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (1b). 2 (0.06 g, 0.072 mmol) and $\text{Na}^+[\text{BAr}^{\text{F}}_4]^-$ (0.165 g, 0.181 mmol) were dissolved in 5 mL of DCM. The reaction was stirred for 30 min. A mixture of toluene and hexane (10 mL, 2:1 v/v) precipitated $\text{Na}^+[\text{OTf}]^-$ and was filtered off. Filtrate was concentrated under reduced pressure and purified via HPLC to afford an off white solid (0.105 g, 0.0459 mmol, 66%). ^1H NMR (400 MHz, CD_3CN ; 25°C) δ 9.05 (s, 2H), 8.57 (d, $J = 6.3$ Hz, 2H), 8.06 (s, 1H), 7.99 (d, $J = 6.4$ Hz, 2H), 7.92 (d, $J = 7.8$ Hz, 2H), 7.69 (b, 17H), 7.66 (b, 8H), 4.22 (s, 6H). ^{13}C NMR (100.6 MHz, CD_3CN ; 25°C) δ 162.58 (q, $J = 49.3$ Hz), 152.88, 146.23, 144.95, 136.76, 136.05, 135.63, 131.15, 129.88 (qq, $J = 26.2$ Hz), 122.26, 105.50, 100.16, 89.97, 48.83. ^{19}F NMR (376.3 MHz, CD_3CN ; 25°C) δ -60.82. HRMS (CI pos) m/z : 280.970 (M^{+2} , 100%), 281.471 (M^{+2} , 24.5), 281.973 (M^{+2} , 2.7); $\text{C}_{22}\text{H}_{16}\text{I}_2\text{N}_2^{2+}$ (280.97).

^1H



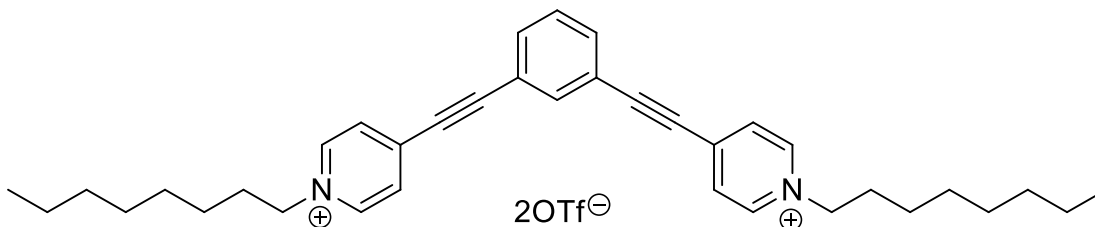
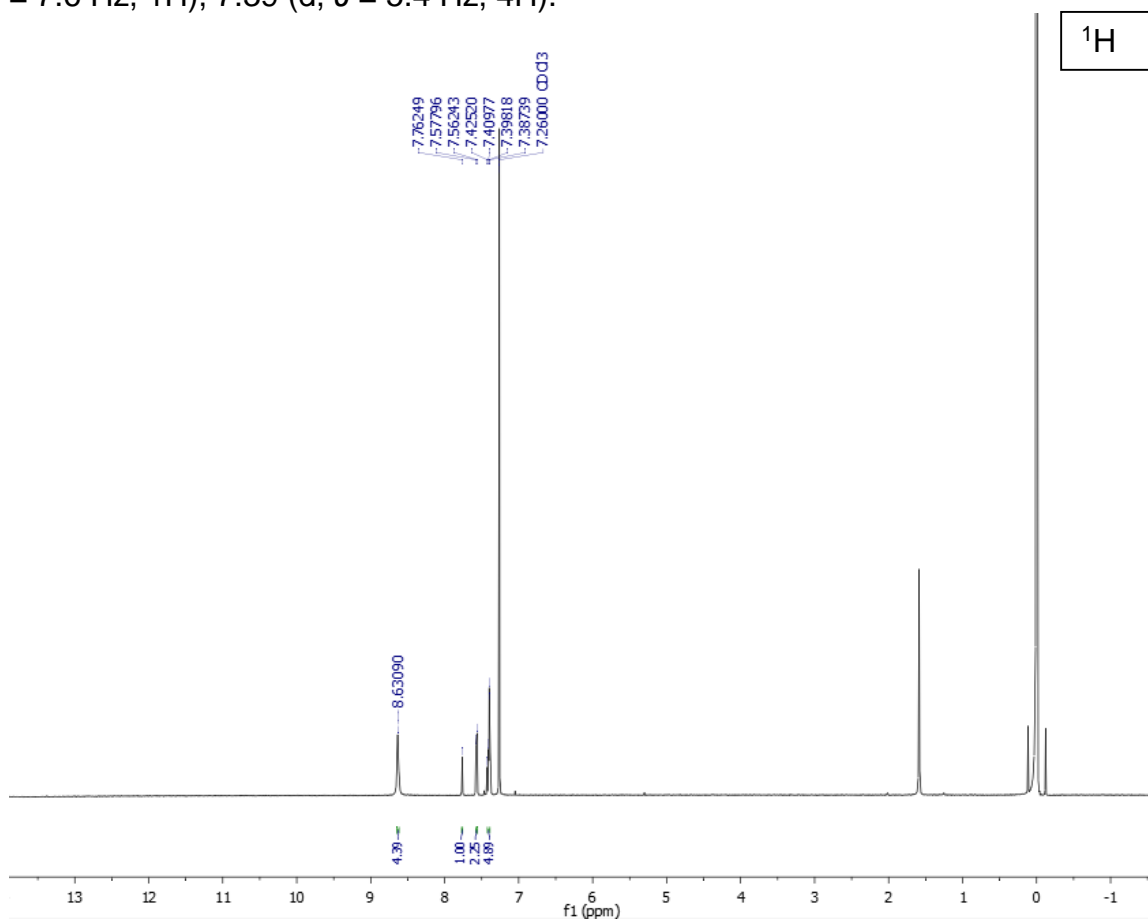
¹³C





5

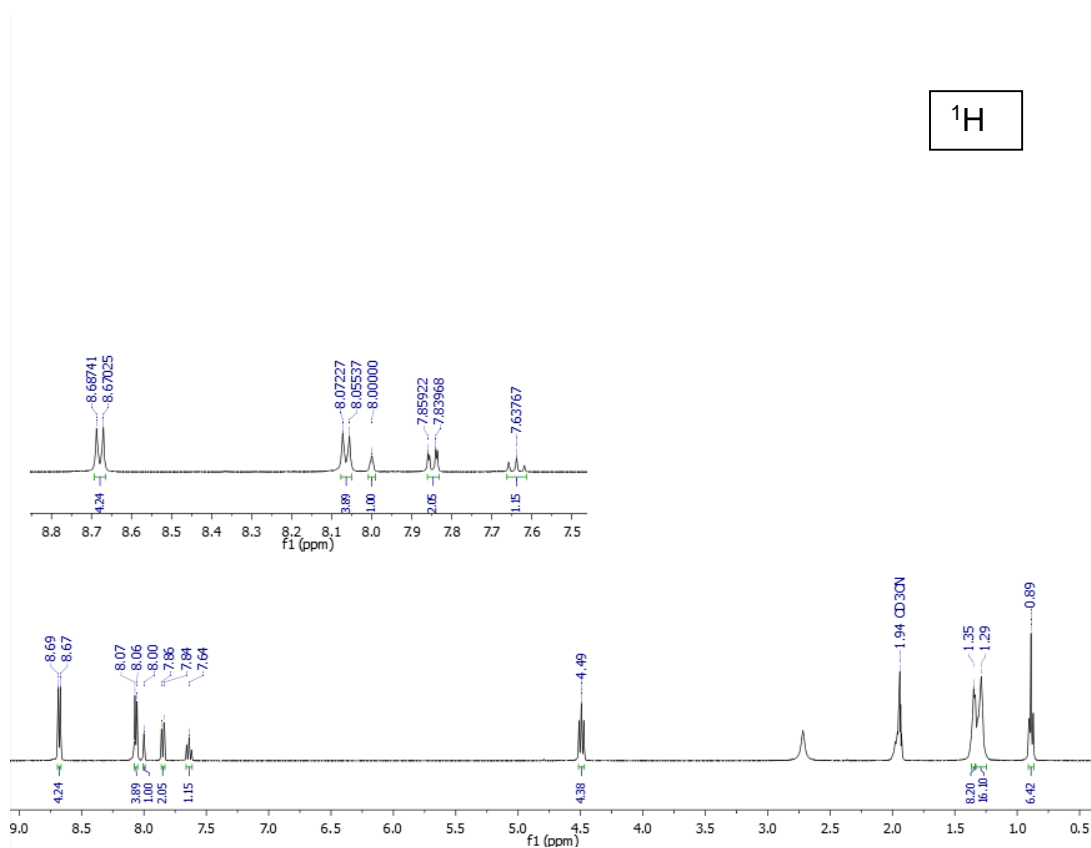
1,3-bis(4-ethynylpyridinyl)benzene (5) was prepared according to literature procedure⁵ affording a white solid (0.124 g, 0.597 mmol, 22%). ¹H NMR (500 MHz, CDCl₃; 25°C) δ 8.63 (b, 4H), 7.76 (s, 1H), 7.57 (d, *J* = 7.7 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.39 (d, *J* = 5.4 Hz, 4H).



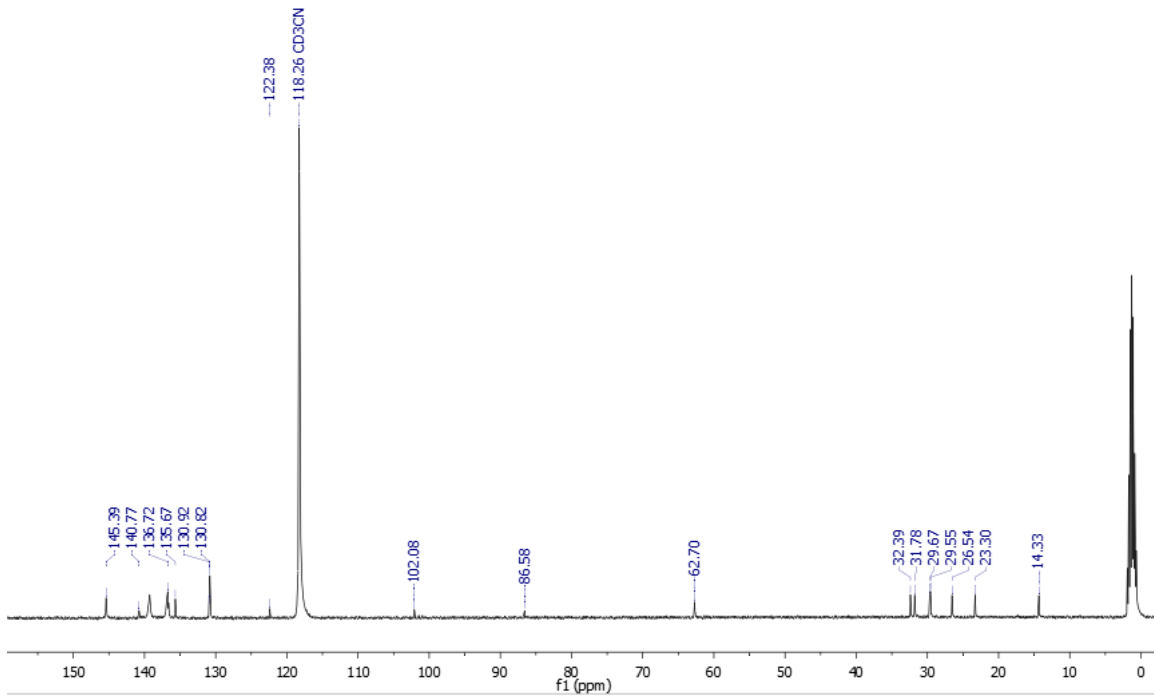
6

1,3-bis(4-ethynyl-N-octylpyridinium)benzene ditriflate (6). **5** (0.124 g, 0.597 mmol) was reacted with octyl triflate (0.631 mL, 3.99 mmol of 1-octanol)

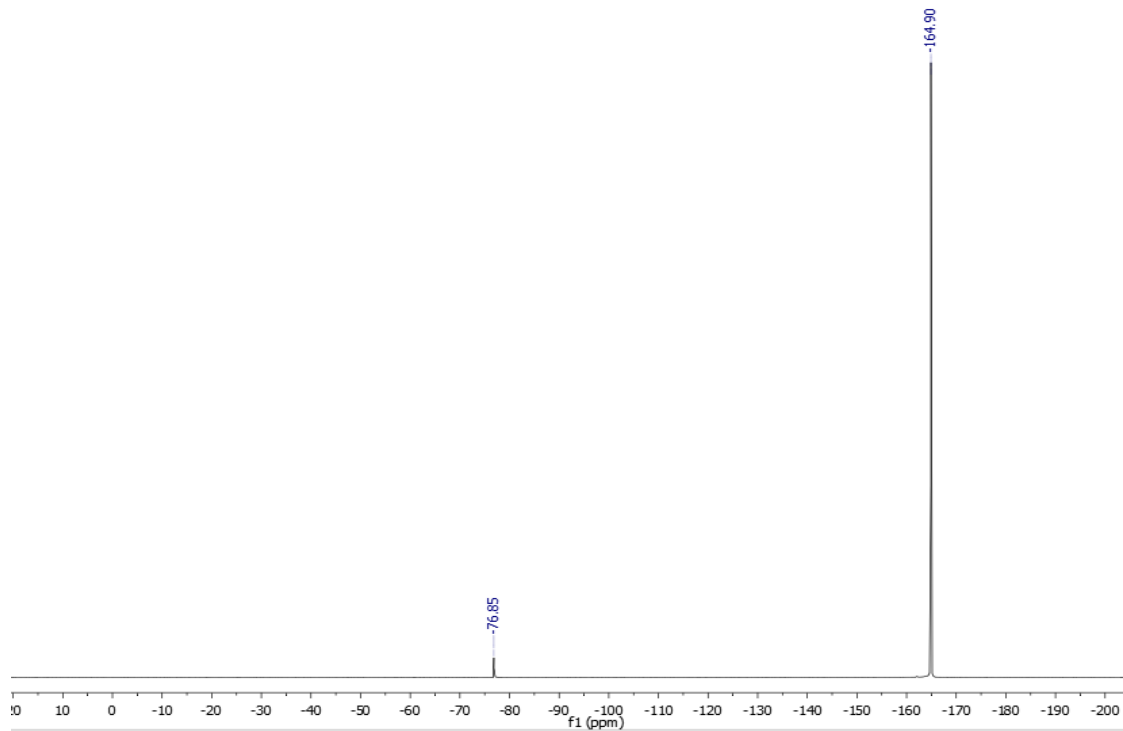
according to the general procedure for octylation. The product was isolated as a sticky light brown solid (0.349 g, 0.434 mmol, 97.7%). Mp: 96–98 °C. ^1H NMR (400 MHz, CD_3CN ; 25 °C) δ 8.68 (d, $J = 6.9$ Hz, 4H), 8.06 (d, $J = 6.8$ Hz, 4H), 8.00 (s, 1H), 7.85 (d, $J = 7.8$ Hz, 2H), 7.64 (t, $J = 16.0$ Hz, 1H), 4.49 (t, $J = 15.2$ Hz, 4H), 1.35 (b, 8H), 1.29 (b, 16H), 0.89 (s, 6H). ^{13}C NMR (100.6 MHz, CD_3CN ; 25 °C) δ 145.39, 140.77, 136.72, 135.67, 130.92, 130.82, 122.38, 102.08, 86.58, 62.70, 32.39, 31.78, 29.67, 29.55, 26.54, 23.30, 14.33. ^{19}F NMR (376.3 MHz, CD_3CN ; 25 °C) δ -76.85. HRMS (CI pos) m/z : 253.183 (M^{+2} , 100%), 253.683 (M^{+2} , 39.5), 254.186 (M^{+2} , 7.7); $\text{C}_{36}\text{H}_{46}\text{N}_2^{2+}$ (253.18).

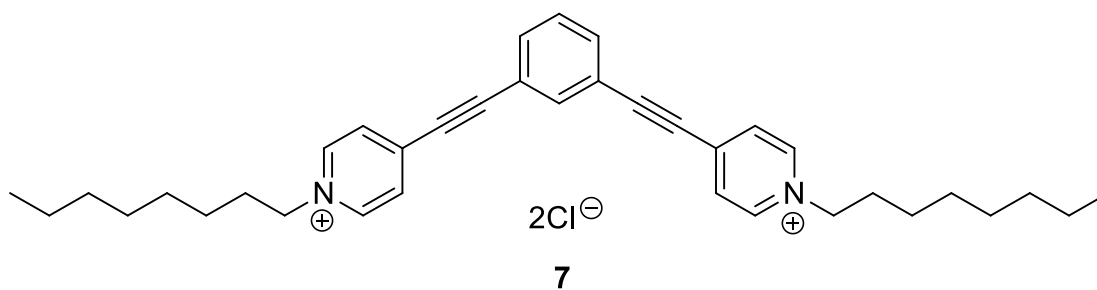


¹³C



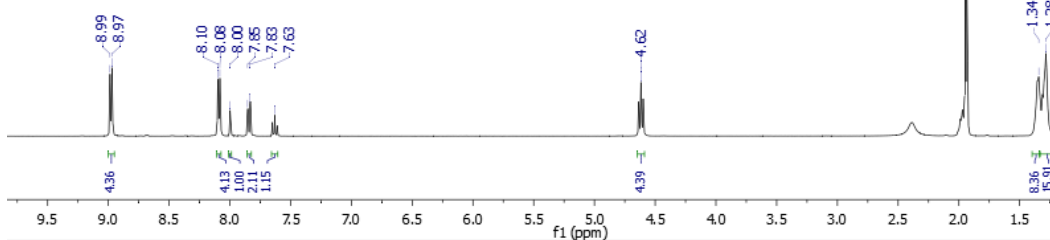
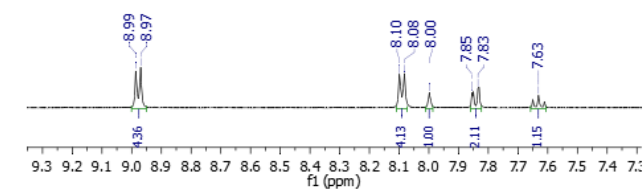
¹⁹F



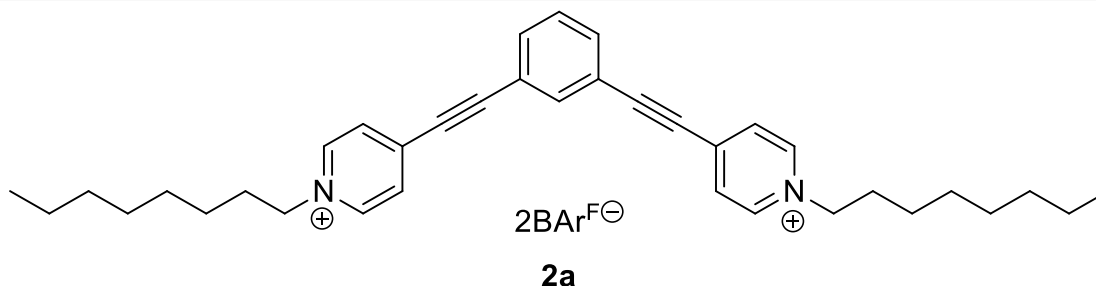
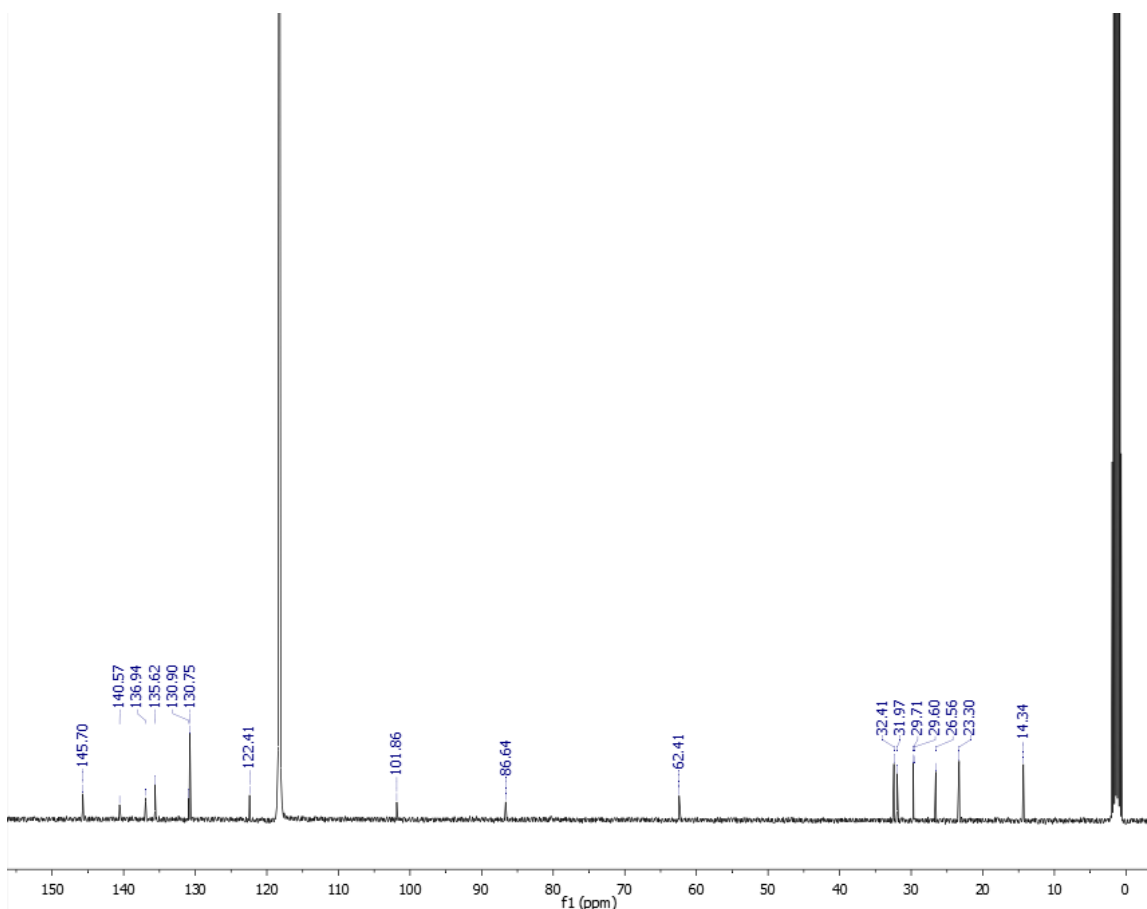


1,3-bis(4-ethynyl-N-octylpyridinium)benzene dichloride (7). 6 (0.010 g, 0.0124 mmol) and tetra-*n*-butylammonium chloride (0.0093 g, 0.0335 mmol) were reacted according to the general procedure for anion metathesis. The product was isolated as a golden yellow oil (0.0047 g, 0.00927 mmol, 74.7%). ^1H NMR (400 MHz, CD_3CN ; 25°C) δ 8.98 (d, $J = 6.8$ Hz, 4H), 8.09 (d, $J = 6.7$ Hz, 4H), 8.00 (s, 1H), 7.84 (d, $J = 7.8$ Hz, 2H), 7.63 (t, $J = 15.6$ Hz, 1H), 4.62 (t, $J = 14.8$ Hz, 4H), 1.34 (b, 8H), 1.28 (b, 16H), 0.89 (b, 6H). ^{13}C NMR (100.6 MHz, CD_3CN ; 25°C) δ 145.70, 140.57, 136.94, 135.62, 130.90, 130.75, 122.41, 101.86, 86.64, 62.41, 32.41, 31.97, 29.71, 29.60, 26.56, 23.30, 14.34.

^1H



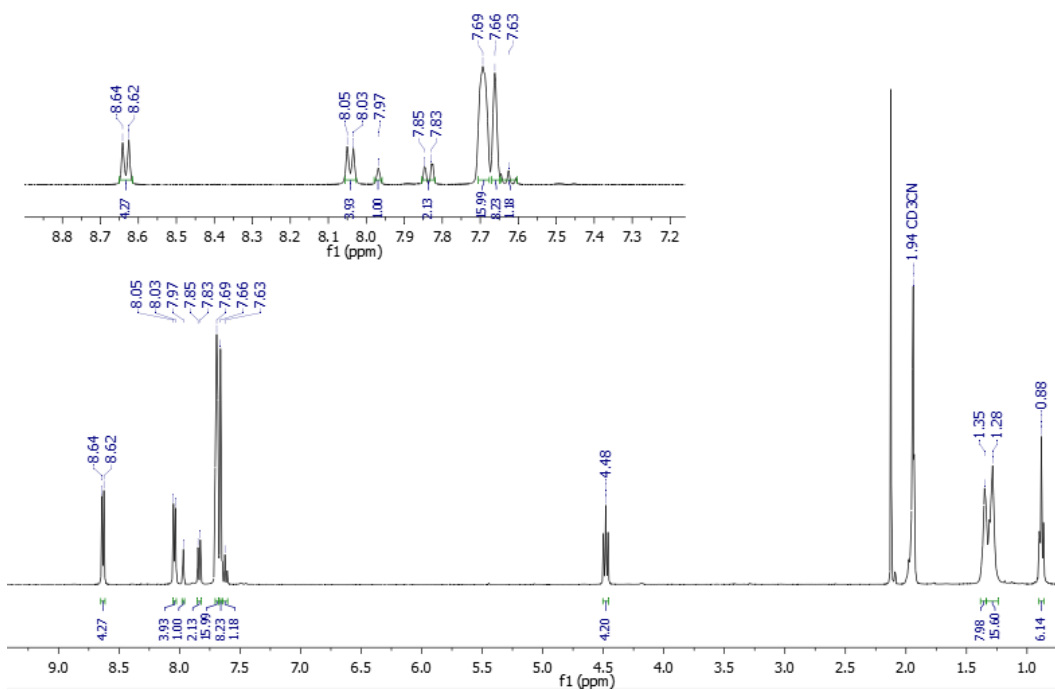
^{13}C



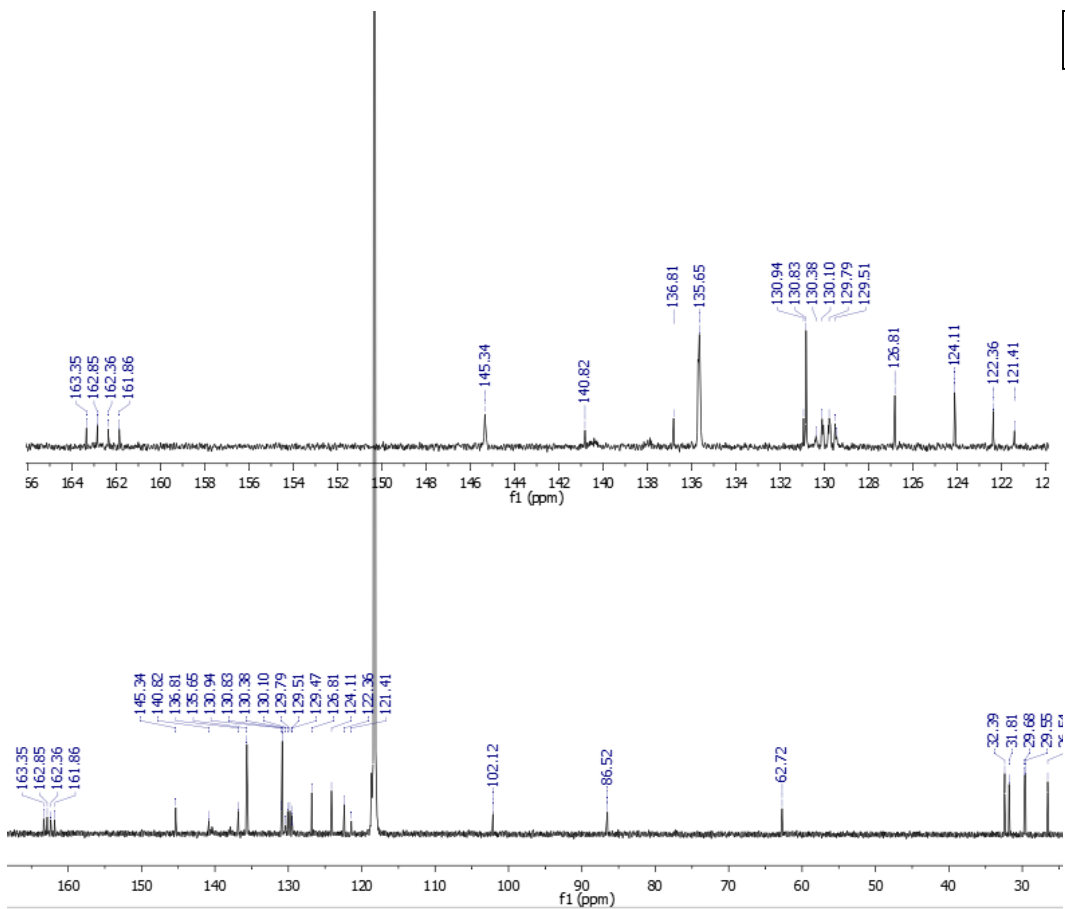
1,3-bis(4-ethynyl-N-octylpyridinium)benzene bis(tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (2a). Adapted from literature procedure³, a 25 mL round bottom flask was charged with **7** (0.004 g, 0.00813 mmol) which was subsequently suspended in 3 mL DCM. Na⁺[BARF₄]⁻ (0.0144 g, 0.0163 mmol), prepared according to literature procedure⁴, was added to the solution of **7** and stirred for 15 min at rt during which sodium chloride precipitated from solution. The mixture was filtered through Celite and the filtrate was concentrated under reduced pressure. Purification via HPLC afforded a yellow oil (0.0106 g, 0.00475 mmol, 58%). ¹H NMR (400 MHz, CD₃CN; 25 °C) δ 8.63 (d, *J* = 6.7 Hz, 4H), 8.04 (d, *J* = 6.6 Hz, 4H), 7.97 (s, 1H), 7.84 (d, *J* = 7.8 Hz, 2H), 7.69 (b, 16H), 7.66 (b, 8H), 7.63 (t, *J* = 5.6 Hz, 1H), 4.48 (t, *J* = 15.2 Hz, 1H), 1.35 (b, 8H), 1.28 (b, 16H), 0.88 (m, 6H). ¹³C NMR (100.6 MHz, CD₃CN; 25 °C) δ 162.61 (q, *J* = 50.3 Hz), 145.34, 140.82, 136.81, 135.65, 130.94, 130.83, 129.94 (qq, *J* = 28.2 Hz), 125.53 (q, *J* = 271.6 Hz), 102.12, 86.52, 62.72, 32.39, 31.81, 29.68, 29.55,

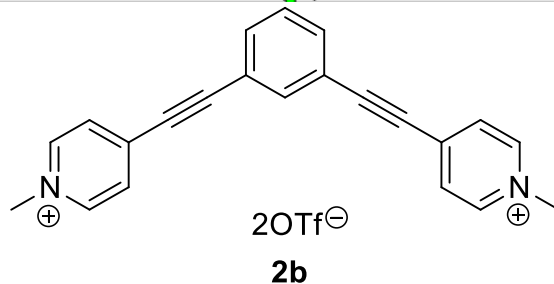
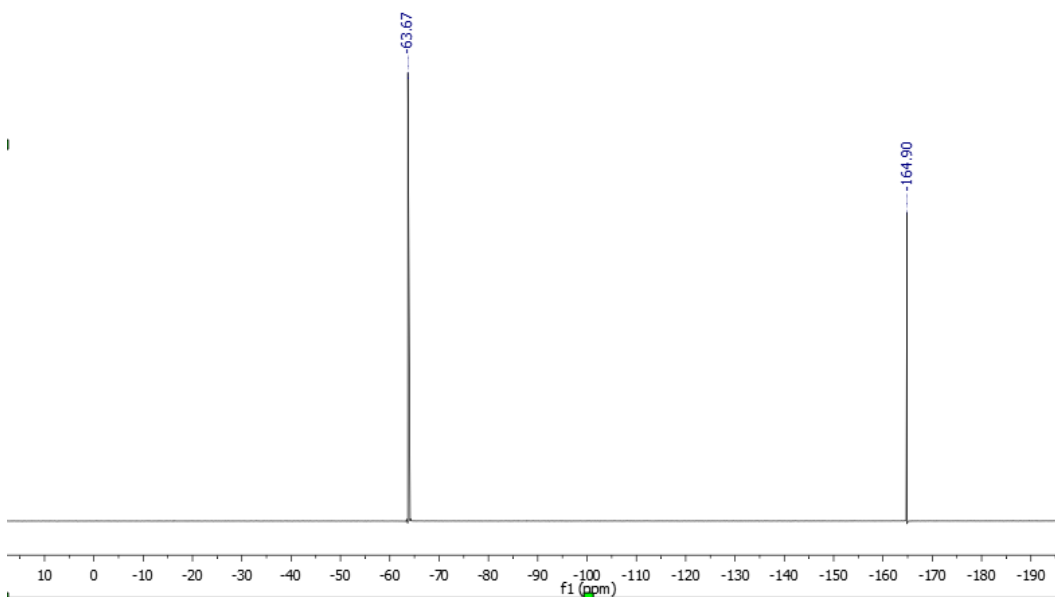
26.54, 23.30, 14.31. ^{19}F NMR (376.3 MHz, CD_3CN ; 25°C) δ -63.67. HRMS (CI pos) m/z : 253.183 (M^{+2} , 100%), 253.684 (M^{+2} , 39.5), 254.186 (M^{+2} , 7.7); $\text{C}_{36}\text{H}_{46}\text{N}_2^{2+}$ (253.18).

^1H



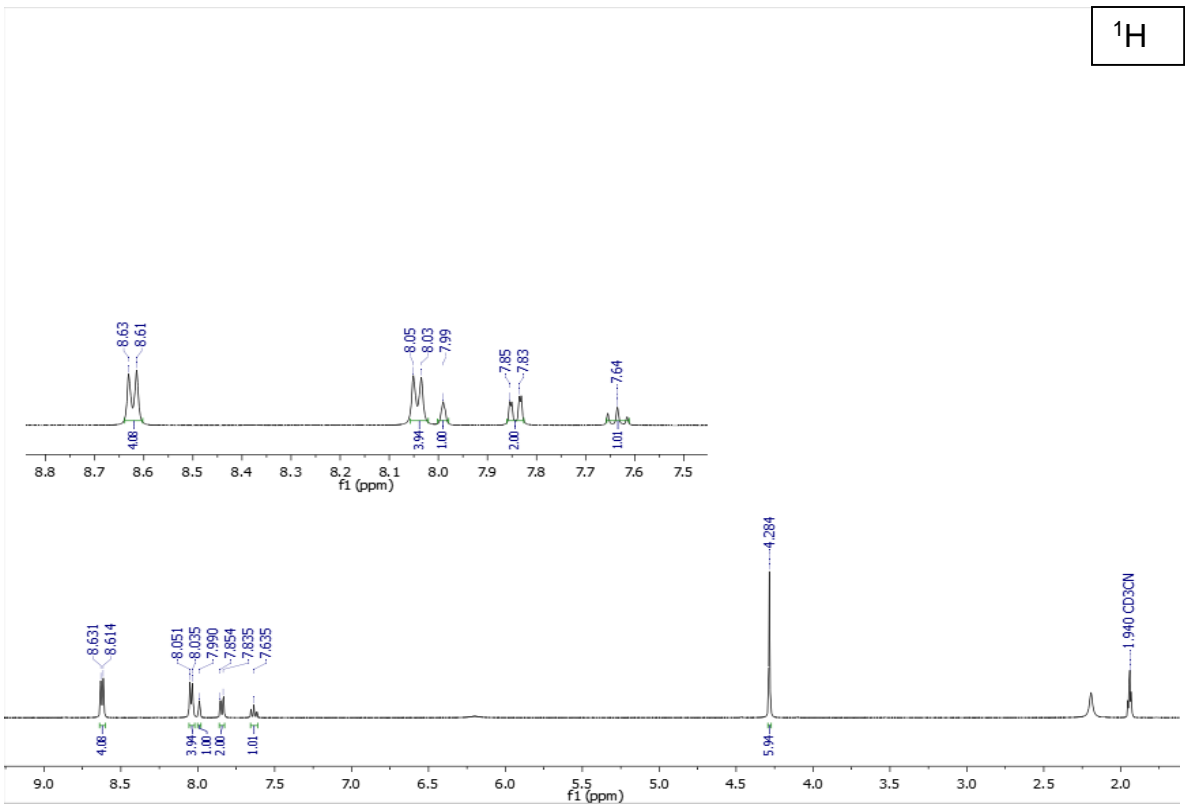
^{13}C



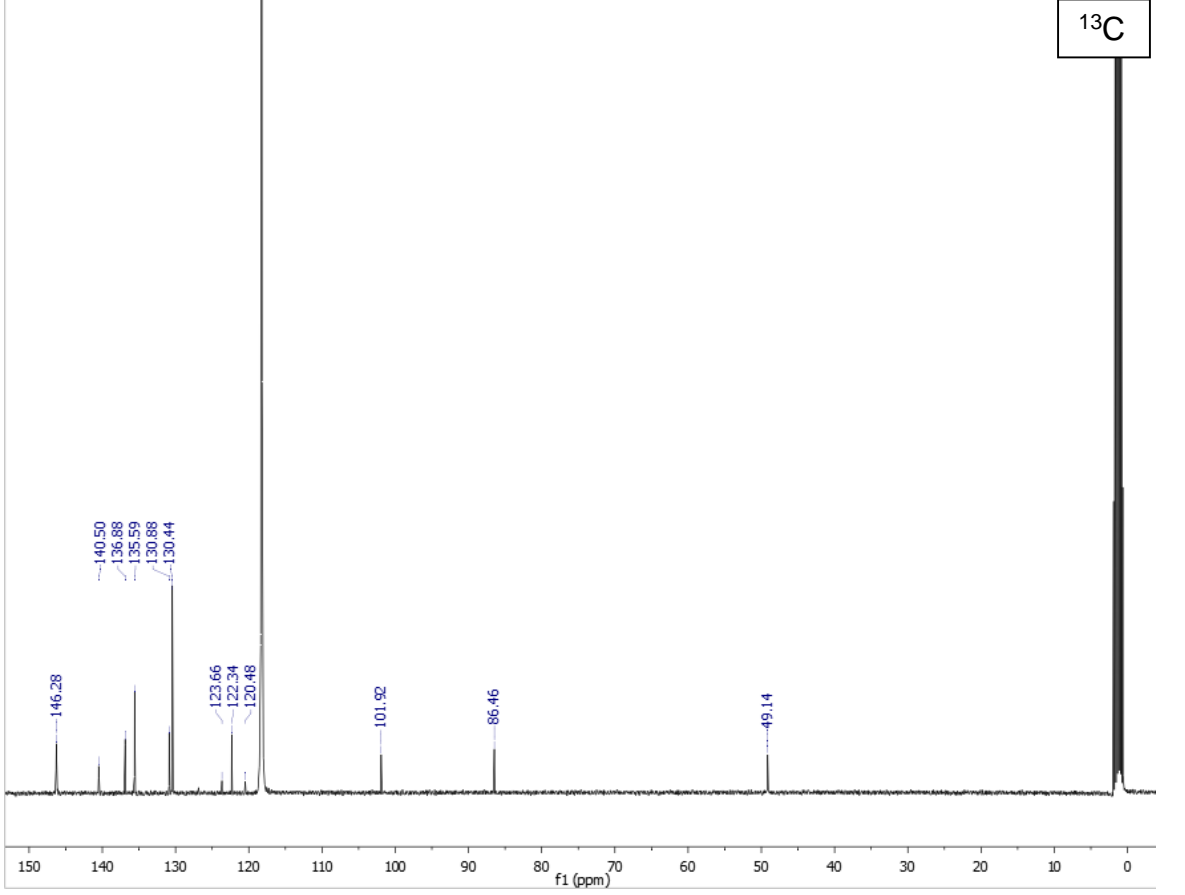
^{19}F 

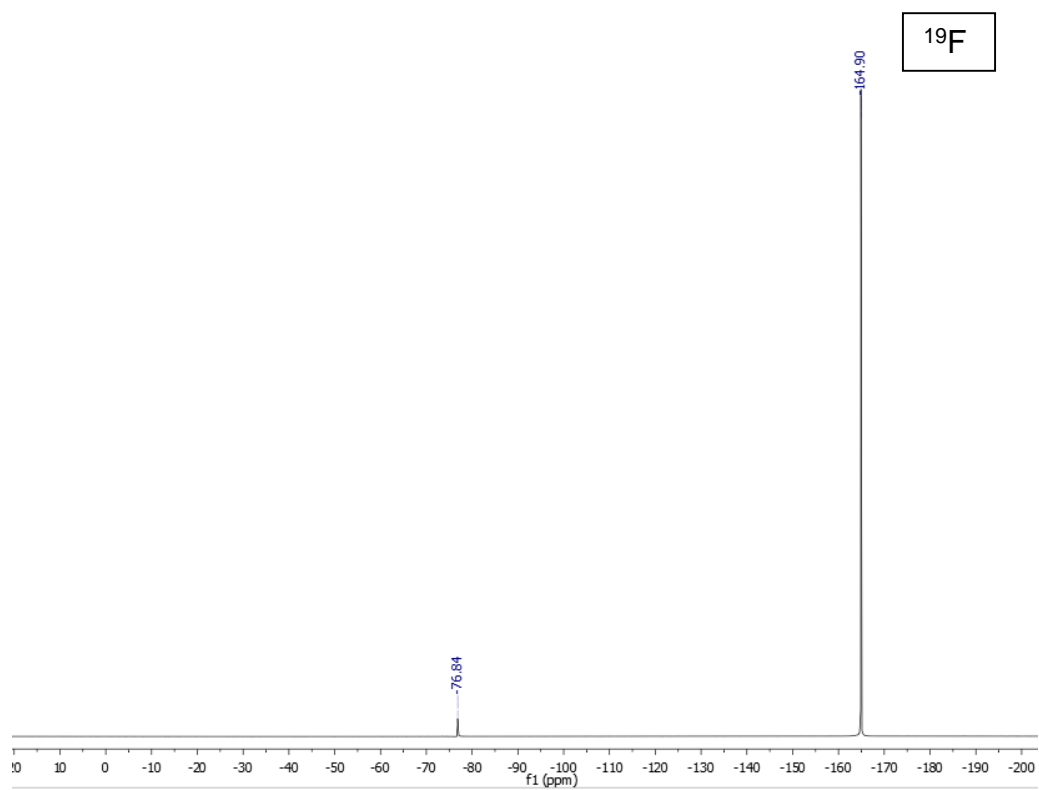
1,3-bis(4-ethynyl-N-methylpyridinium)benzene ditriflate (2b). 5 (0.020 g, 0.096 mmol) and methyl triflate (0.043 mL, 0.394 mmol) were reacted according to the general procedure for methylation. The product was isolated as a white solid (0.033 g, 0.054 mmol, 56%). ^1H NMR (400 MHz, CD_3CN ; 25°C) δ 8.62 (d, $J = 6.6$ Hz, 2H), 8.04 (d, $J = 6.6$ Hz, 2H), 7.99 (s, 1H), 7.84 (d, $J = 7.8$ Hz, 2H), 7.64 (t, $J = 15.6$ Hz, 1H), 4.28 (s, 6H). ^{13}C NMR (100.6 MHz, CD_3CN ; 25°C) δ 146.28, 140.50, 136.88, 135.59, 130.88, 130.44, 123.66, 122.34, 120.48, 101.92, 86.46, 49.14. ^{19}F NMR (376.3 MHz, CD_3CN ; 25°C) δ -76.84. HRMS (CI pos) m/z : 155.071 (M^{+2} , 100%), 155.573 (M^{+2} , 24), 156.079 (M^{+2} , 2.9); $\text{C}_{22}\text{H}_{18}\text{N}_2^{2+}$ (155.07).

¹H



¹³C





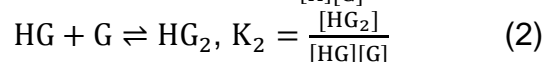
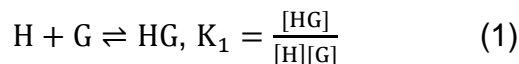
NMR Titrations

All experiments were performed on a Varian Drive Direct 500 MHz NMR Spectrometer. (CD₃)₂CO was stirred in Drierite (CaSO₄) under N₂ for 2 h, then used immediately after distillation. CDCl₃ was eluted through a column of activated alumina, and dried over 3 Å molecular sieves. TBA⁺ReO₄⁻ was dried under vacuum and stored in a desiccator.

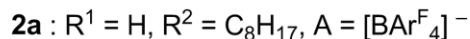
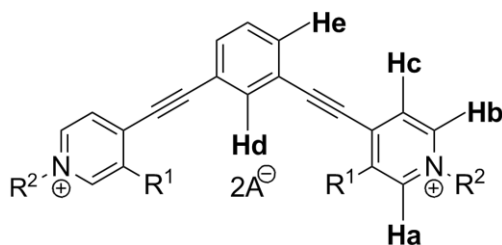
¹H Titrations

General:

Stock solutions of **1a** (1.561±0.012 mM) and **2a** (1.551±0.013 mM) were prepared in 3.840 mL of CDCl₃/(CD₃)₂CO (3:2 v/v). 0.500 mL aliquots from each stock solution were syringed into three separate NMR tubes with screw caps and septa. The stock solution of **1a** was then used to make three guest solutions corresponding to experiment number (13.90±0.30, 13.62±0.30, 13.62±0.30 mM, respectively). Likewise, the stock solution of **2a** was used to make three guest solutions (all 13.35±0.30 mM). After obtaining free-host spectra of **1a** and **2a**, aliquots of corresponding guest solution (containing **1a** or **2a**, and TBA⁺ReO₄⁻ at specified concentrations) were added to their respective NMR tubes. Spectra were obtained after each addition (20x). A constant host concentration was maintained, while TBA⁺ReO₄⁻ concentrations gradually increased throughout the titration (see data below). Intuitions of stoichiometric displacement led to the stepwise anion exchange model:



A simple 1:1 model, dimerization, and higher order binding were ruled out due to the emergence of an obvious pattern in residuals, unrealistic assigned shifts, poor convergence, and/or larger standard deviations. HypNMR 2008⁶ was used to refine the isothermal fits of multiple signals (**1a**: Ha, Hb, Hc, and Hd; **2a**: Ha/b, Hc, and Hd) simultaneously. For both **1a** and **2a**, hydrogen He and the sole phenyl core triplet were not followed due to limited shifting and/or residual solvent peak (CHCl₃) obstruction.



1a and TBA⁺ReO₄⁻ (Experiment 1)

1a (Exp.1)

Species	Log beta	ReO ₄ ⁻	1a	
1	3.9732	1	1	refine
2	6.2728	2	1	refine

Species concentrations/mol dm⁻³

Point	T(ReO ₄ ⁻)	T(1a)	F(ReO ₄ ⁻)	F(1a)	species	species
					1	2
1	0.00E+00	1.56E-03	4.77E-91	1.56E-03	7.00E-90	6.65E-18
2	5.35E-04	1.56E-03	4.72E-05	1.08E-03	4.79E-04	4.50E-06
3	1.03E-03	1.56E-03	1.32E-04	6.86E-04	8.53E-04	2.25E-05
4	1.49E-03	1.56E-03	2.80E-04	4.13E-04	1.09E-03	6.08E-05
5	1.92E-03	1.56E-03	4.95E-04	2.56E-04	1.19E-03	1.17E-04
6	2.32E-03	1.56E-03	7.48E-04	1.72E-04	1.21E-03	1.80E-04
7	2.69E-03	1.56E-03	1.01E-03	1.25E-04	1.19E-03	2.41E-04
8	3.04E-03	1.56E-03	1.28E-03	9.70E-05	1.17E-03	2.98E-04
9	3.37E-03	1.56E-03	1.54E-03	7.84E-05	1.13E-03	3.48E-04
10	3.68E-03	1.56E-03	1.79E-03	6.55E-05	1.10E-03	3.93E-04
11	4.25E-03	1.56E-03	2.27E-03	4.89E-05	1.04E-03	4.70E-04
12	4.76E-03	1.56E-03	2.70E-03	3.90E-05	9.90E-04	5.33E-04
13	5.21E-03	1.56E-03	3.10E-03	3.24E-05	9.45E-04	5.84E-04
14	5.63E-03	1.56E-03	3.47E-03	2.78E-05	9.07E-04	6.27E-04
15	6.00E-03	1.56E-03	3.80E-03	2.44E-05	8.74E-04	6.63E-04
16	6.35E-03	1.56E-03	4.11E-03	2.19E-05	8.46E-04	6.94E-04
17	6.66E-03	1.56E-03	4.40E-03	1.99E-05	8.21E-04	7.20E-04
18	6.95E-03	1.56E-03	4.66E-03	1.82E-05	8.00E-04	7.44E-04
19	7.22E-03	1.56E-03	4.91E-03	1.69E-05	7.81E-04	7.64E-04
20	7.47E-03	1.56E-03	5.14E-03	1.58E-05	7.64E-04	7.82E-04

Measured chemical shifts

Point	Ha	Hb	Hc	Hd
1	9.66E+00	9.23E+00	8.23E+00	8.04E+00
2	9.64E+00	9.20E+00	8.24E+00	8.09E+00
3	9.62E+00	9.19E+00	8.25E+00	8.13E+00
4	9.60E+00	9.18E+00	8.26E+00	8.16E+00
5	9.60E+00	9.17E+00	8.26E+00	8.17E+00
6	9.59E+00	9.16E+00	8.26E+00	8.18E+00
7	9.58E+00	9.16E+00	8.26E+00	8.18E+00
8	9.58E+00	9.16E+00	8.26E+00	8.19E+00
9	9.58E+00	9.16E+00	8.26E+00	8.19E+00
10	9.58E+00	9.15E+00	8.26E+00	8.19E+00

11	9.57E+00	9.15E+00	8.26E+00	8.19E+00
12	9.57E+00	9.15E+00	8.26E+00	8.19E+00
13	9.57E+00	9.15E+00	8.26E+00	8.19E+00
14	9.57E+00	9.15E+00	8.26E+00	8.19E+00
15	9.57E+00	9.15E+00	8.26E+00	8.19E+00
16	9.57E+00	9.15E+00	8.26E+00	8.19E+00
17	9.57E+00	9.14E+00	8.26E+00	8.19E+00
18	9.57E+00	9.14E+00	8.26E+00	8.19E+00
19	9.56E+00	9.14E+00	8.26E+00	8.19E+00
20	9.56E+00	9.14E+00	8.26E+00	8.19E+00

Calculated chemical shifts

Point	Ha	Hb	Hc	Hd
1	9.66E+00	9.23E+00	8.23E+00	8.04E+00
2	9.64E+00	9.21E+00	8.24E+00	8.09E+00
3	9.62E+00	9.19E+00	8.25E+00	8.13E+00
4	9.60E+00	9.18E+00	8.26E+00	8.16E+00
5	9.59E+00	9.17E+00	8.26E+00	8.17E+00
6	9.59E+00	9.16E+00	8.26E+00	8.18E+00
7	9.58E+00	9.16E+00	8.26E+00	8.18E+00
8	9.58E+00	9.16E+00	8.26E+00	8.19E+00
9	9.58E+00	9.16E+00	8.26E+00	8.19E+00
10	9.58E+00	9.15E+00	8.26E+00	8.19E+00
11	9.57E+00	9.15E+00	8.26E+00	8.19E+00
12	9.57E+00	9.15E+00	8.26E+00	8.19E+00
13	9.57E+00	9.15E+00	8.26E+00	8.19E+00
14	9.57E+00	9.15E+00	8.26E+00	8.19E+00
15	9.57E+00	9.15E+00	8.26E+00	8.19E+00
16	9.57E+00	9.15E+00	8.26E+00	8.19E+00
17	9.57E+00	9.15E+00	8.26E+00	8.19E+00
18	9.57E+00	9.14E+00	8.26E+00	8.19E+00
19	9.56E+00	9.14E+00	8.26E+00	8.19E+00
20	9.56E+00	9.14E+00	8.26E+00	8.19E+00

Chemical shifts for each nucleus

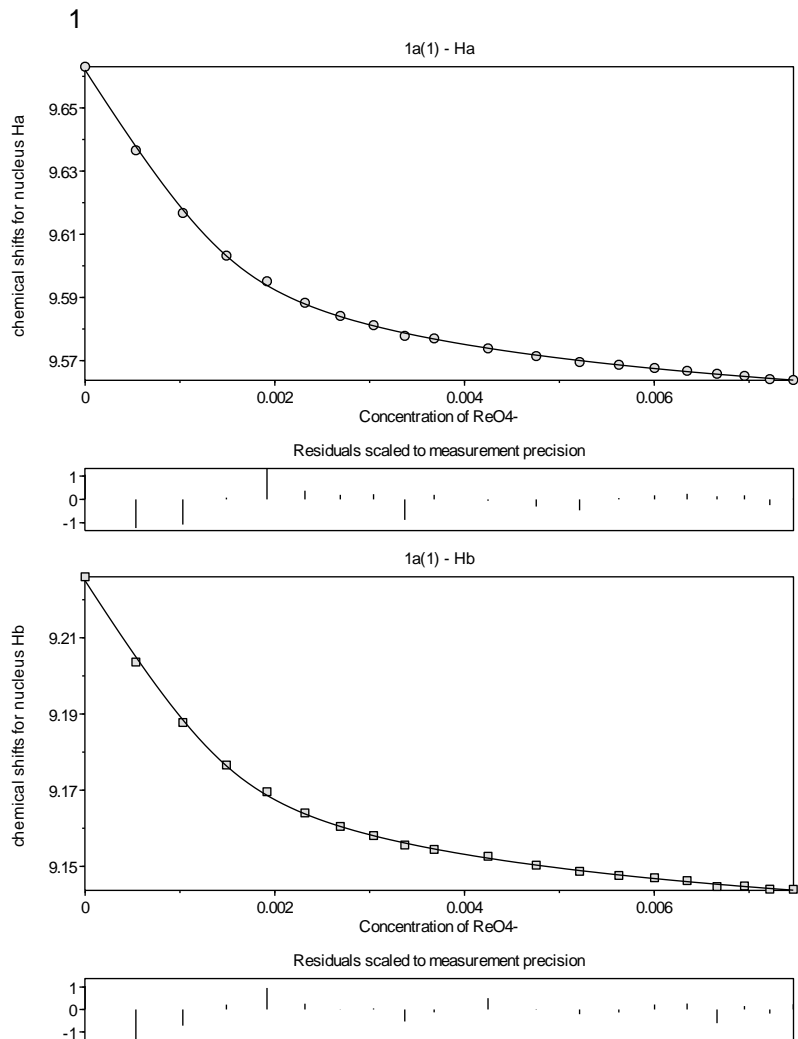
species	Ha	Hb	Hc	Hd
1a	9.66E+00	9.23E+00	8.23E+00	8.04E+00
(ReO ₄ ⁻)(1a)	9.58E+00	9.16E+00	8.27E+00	8.20E+00
(ReO ₄ ⁻) ₂ (1a)	9.54E+00	9.13E+00	8.25E+00	8.18E+00

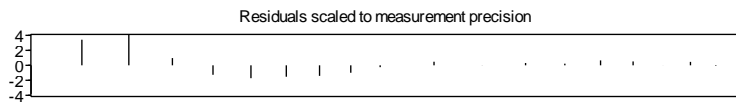
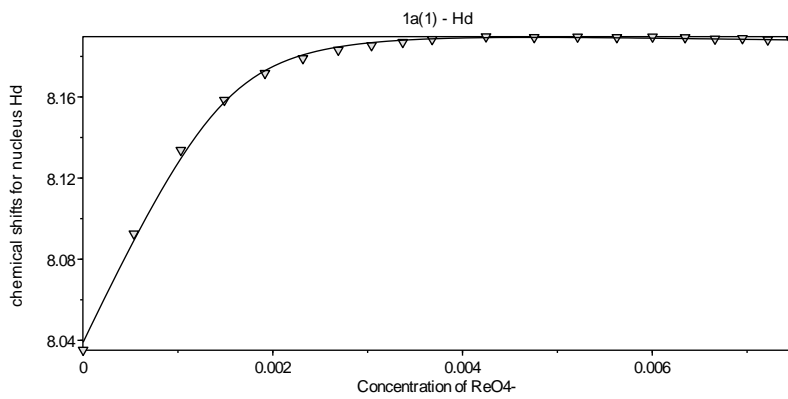
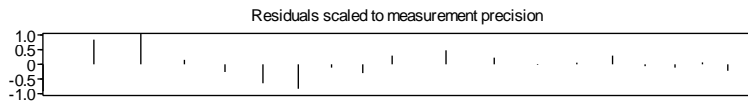
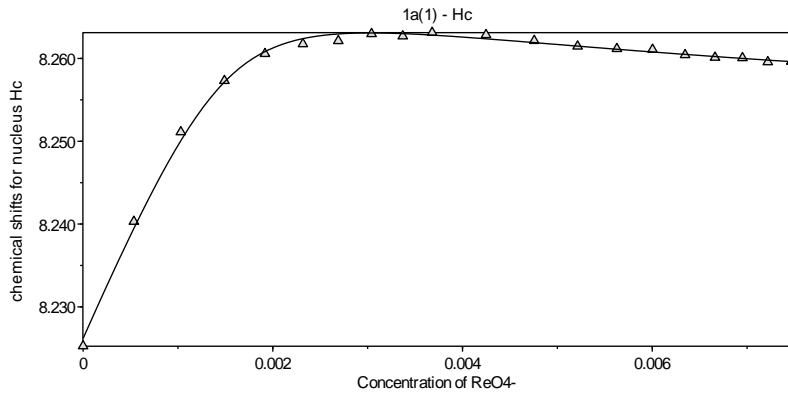
Converged in 6 iterations with sigma = 1.050141

	value	standard deviation	Comments
1 $\log \beta(\text{ReO}_4^-)(\mathbf{1a})$	3.9732	0.066	3.97(7)
2 $\log \beta(\text{ReO}_4^-)_2(\mathbf{1a})$	6.2727	0.1884	6.3(2)

Correlation coefficients between stability constants. Numbering as above

2 0.804





1a and TBA⁺ReO₄⁻ (Experiment 2)

1a (Exp.2)

Species	Log beta	ReO ₄ ⁻	1a	
1	3.9054	1	1	refine
2	6.1335	2	1	refine

Species concentrations/mol dm⁻³

Point	T(ReO ₄ ⁻)	T(1a)	F(ReO ₄ ⁻)	F(1a)	species 1	species 2
1	0.00E+00	1.56E-03	5.12E-91	1.56E-03	6.43E-90	5.57E-178
2	5.24E-04	1.56E-03	5.26E-05	1.09E-03	4.63E-04	4.12E-06
3	1.01E-03	1.56E-03	1.43E-04	7.16E-04	8.26E-04	2.00E-05
4	1.46E-03	1.56E-03	2.94E-04	4.48E-04	1.06E-03	5.27E-05
5	1.88E-03	1.56E-03	5.06E-04	2.88E-04	1.17E-03	1.00E-04
6	2.27E-03	1.56E-03	7.54E-04	1.99E-04	1.21E-03	1.54E-04
7	2.64E-03	1.56E-03	1.02E-03	1.48E-04	1.21E-03	2.07E-04
8	2.98E-03	1.56E-03	1.28E-03	1.16E-04	1.19E-03	2.57E-04
9	3.30E-03	1.56E-03	1.53E-03	9.44E-05	1.17E-03	3.02E-04
10	3.61E-03	1.56E-03	1.78E-03	7.95E-05	1.14E-03	3.43E-04
11	4.16E-03	1.56E-03	2.25E-03	6.02E-05	1.09E-03	4.13E-04
12	4.66E-03	1.56E-03	2.68E-03	4.84E-05	1.04E-03	4.71E-04
13	5.11E-03	1.56E-03	3.07E-03	4.06E-05	1.00E-03	5.20E-04
14	5.51E-03	1.56E-03	3.43E-03	3.50E-05	9.66E-04	5.60E-04
15	5.88E-03	1.56E-03	3.76E-03	3.10E-05	9.36E-04	5.95E-04
16	6.22E-03	1.56E-03	4.06E-03	2.78E-05	9.09E-04	6.24E-04
17	6.53E-03	1.56E-03	4.34E-03	2.54E-05	8.86E-04	6.50E-04
18	6.81E-03	1.56E-03	4.60E-03	2.34E-05	8.65E-04	6.73E-04
19	7.07E-03	1.56E-03	4.84E-03	2.17E-05	8.47E-04	6.93E-04
20	7.32E-03	1.56E-03	5.06E-03	2.04E-05	8.30E-04	7.11E-04

Measured chemical shifts

Point	Ha	Hb	Hc	Hd
1	9.66E+00	9.23E+00	8.23E+00	8.04E+00
2	9.64E+00	9.21E+00	8.24E+00	8.09E+00
3	9.62E+00	9.19E+00	8.25E+00	8.13E+00
4	9.61E+00	9.18E+00	8.26E+00	8.16E+00
5	9.60E+00	9.17E+00	8.26E+00	8.17E+00
6	9.59E+00	9.17E+00	8.26E+00	8.18E+00
7	9.59E+00	9.16E+00	8.26E+00	8.18E+00
8	9.58E+00	9.16E+00	8.26E+00	8.18E+00
9	9.58E+00	9.16E+00	8.26E+00	8.19E+00
10	9.58E+00	9.16E+00	8.26E+00	8.19E+00
11	9.58E+00	9.15E+00	8.26E+00	8.19E+00

12	9.57E+00	9.15E+00	8.26E+00	8.19E+00
13	9.57E+00	9.15E+00	8.26E+00	8.19E+00
14	9.57E+00	9.15E+00	8.26E+00	8.19E+00
15	9.57E+00	9.15E+00	8.26E+00	8.19E+00
16	9.57E+00	9.15E+00	8.26E+00	8.19E+00
17	9.57E+00	9.15E+00	8.26E+00	8.19E+00
18	9.57E+00	9.15E+00	8.26E+00	8.19E+00
19	9.57E+00	9.15E+00	8.26E+00	8.19E+00
20	9.57E+00	9.14E+00	8.26E+00	8.19E+00

Calculated chemical shifts

Point	Ha	Hb	Hc	Hd
1	9.66E+00	9.23E+00	8.23E+00	8.04E+00
2	9.64E+00	9.21E+00	8.24E+00	8.09E+00
3	9.62E+00	9.19E+00	8.25E+00	8.13E+00
4	9.61E+00	9.18E+00	8.26E+00	8.15E+00
5	9.60E+00	9.17E+00	8.26E+00	8.17E+00
6	9.59E+00	9.17E+00	8.26E+00	8.18E+00
7	9.59E+00	9.16E+00	8.26E+00	8.18E+00
8	9.58E+00	9.16E+00	8.26E+00	8.19E+00
9	9.58E+00	9.16E+00	8.26E+00	8.19E+00
10	9.58E+00	9.16E+00	8.26E+00	8.19E+00
11	9.58E+00	9.15E+00	8.26E+00	8.19E+00
12	9.57E+00	9.15E+00	8.26E+00	8.19E+00
13	9.57E+00	9.15E+00	8.26E+00	8.19E+00
14	9.57E+00	9.15E+00	8.26E+00	8.19E+00
15	9.57E+00	9.15E+00	8.26E+00	8.19E+00
16	9.57E+00	9.15E+00	8.26E+00	8.19E+00
17	9.57E+00	9.15E+00	8.26E+00	8.19E+00
18	9.57E+00	9.15E+00	8.26E+00	8.19E+00
19	9.57E+00	9.15E+00	8.26E+00	8.19E+00
20	9.56E+00	9.14E+00	8.26E+00	8.19E+00

Chemical shifts for each nucleus

species	Ha	Hb	Hc	Hd
1a	9.66E+00	9.23E+00	8.23E+00	8.04E+00
(ReO ₄ ⁻)(1a)	9.58E+00	9.16E+00	8.27E+00	8.20E+00
(ReO ₄ ⁻) ₂ (1a)	9.54E+00	9.12E+00	8.25E+00	8.18E+00

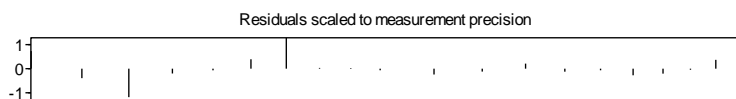
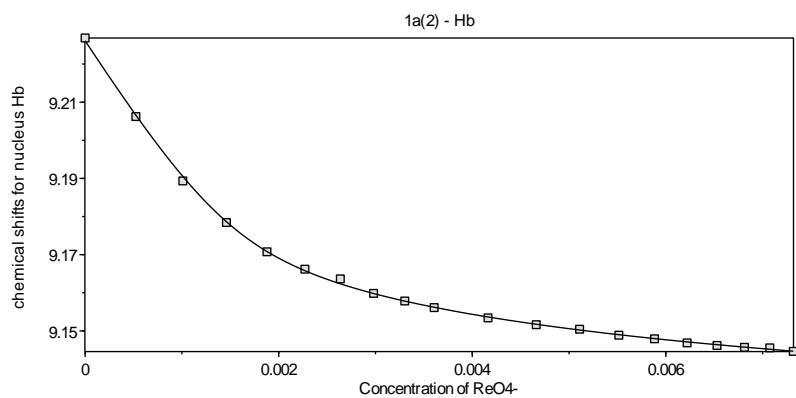
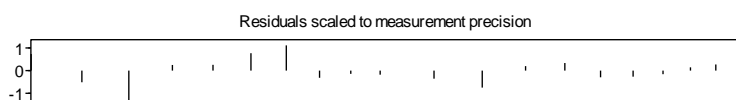
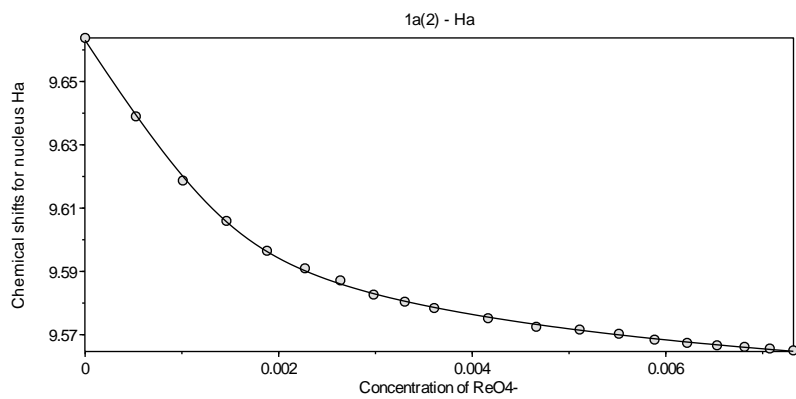
Converged in 8 iterations with sigma = 0.900117

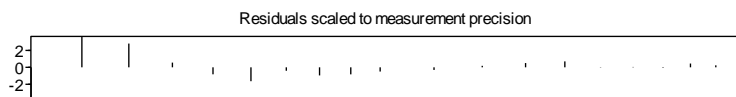
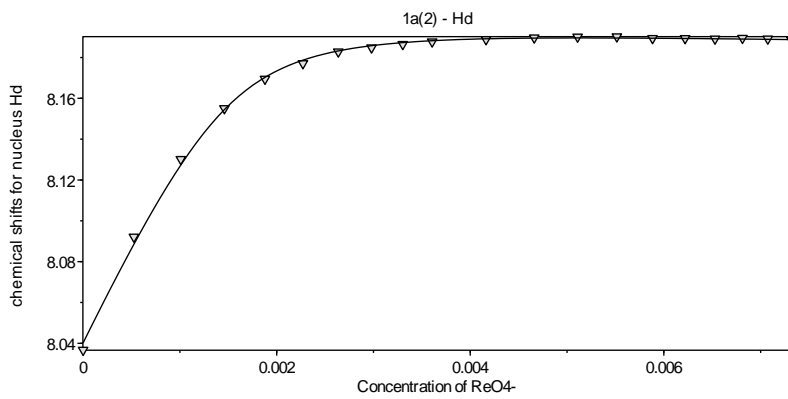
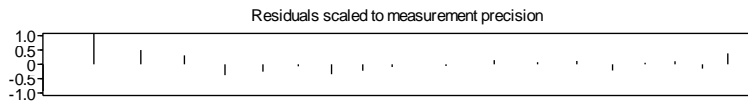
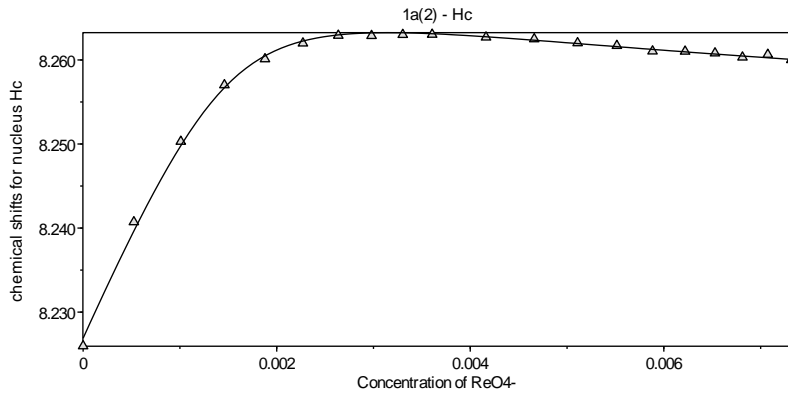
	value	standard deviation	Comments
1 log beta((ReO ₄ ⁻)(1a))	3.9054	0.0569	3.91(6)
2 log beta((ReO ₄ ⁻) ₂ (1a))	6.1335	0.1764	6.1(2)

Correlation coefficients between stability constants. Numbering as above

2 0.7997

1





1a and TBA⁺ReO₄⁻ (Experiment 3)

1a (Exp.3)

Species	Log beta	ReO ₄ ⁻	1a	
1	3.9794	1	1	refine
2	6.1451	2	1	refine

Species concentrations/mol dm⁻³

Point	T(ReO ₄ ⁻)	T(1a)	F(ReO ₄ ⁻)	F(1a)	species 1	species 2
1	0.00E+00	1.56E-03	4.74E-91	1.56E-03	7.05E-90	4.89E-178
2	5.24E-04	1.56E-03	4.56E-05	1.09E-03	4.72E-04	3.15E-06
3	1.01E-03	1.56E-03	1.28E-04	6.96E-04	8.49E-04	1.59E-05
4	1.46E-03	1.56E-03	2.74E-04	4.20E-04	1.10E-03	4.41E-05
5	1.88E-03	1.56E-03	4.90E-04	2.60E-04	1.21E-03	8.72E-05
6	2.27E-03	1.56E-03	7.48E-04	1.75E-04	1.25E-03	1.37E-04
7	2.64E-03	1.56E-03	1.02E-03	1.28E-04	1.25E-03	1.86E-04
8	2.98E-03	1.56E-03	1.29E-03	1.00E-04	1.23E-03	2.32E-04
9	3.30E-03	1.56E-03	1.55E-03	8.16E-05	1.21E-03	2.74E-04
10	3.61E-03	1.56E-03	1.80E-03	6.87E-05	1.18E-03	3.12E-04
11	4.16E-03	1.56E-03	2.28E-03	5.21E-05	1.13E-03	3.77E-04
12	4.66E-03	1.56E-03	2.71E-03	4.21E-05	1.09E-03	4.32E-04
13	5.11E-03	1.56E-03	3.11E-03	3.54E-05	1.05E-03	4.77E-04
14	5.51E-03	1.56E-03	3.47E-03	3.07E-05	1.02E-03	5.16E-04
15	5.88E-03	1.56E-03	3.80E-03	2.72E-05	9.86E-04	5.49E-04
16	6.22E-03	1.56E-03	4.11E-03	2.45E-05	9.60E-04	5.77E-04
17	6.53E-03	1.56E-03	4.39E-03	2.24E-05	9.37E-04	6.02E-04
18	6.81E-03	1.56E-03	4.65E-03	2.07E-05	9.17E-04	6.24E-04
19	7.07E-03	1.56E-03	4.89E-03	1.93E-05	8.99E-04	6.43E-04
20	7.32E-03	1.56E-03	5.11E-03	1.81E-05	8.83E-04	6.61E-04

Measured chemical shifts

Point	Ha	Hb	Hc	Hd
1	9.66E+00	9.23E+00	8.23E+00	8.04E+00
2	9.64E+00	9.20E+00	8.24E+00	8.09E+00
3	9.62E+00	9.19E+00	8.25E+00	8.13E+00
4	9.61E+00	9.18E+00	8.26E+00	8.16E+00
5	9.60E+00	9.17E+00	8.26E+00	8.17E+00
6	9.59E+00	9.17E+00	8.26E+00	8.18E+00
7	9.59E+00	9.16E+00	8.26E+00	8.18E+00
8	9.58E+00	9.16E+00	8.26E+00	8.19E+00
9	9.58E+00	9.16E+00	8.26E+00	8.19E+00
10	9.58E+00	9.16E+00	8.26E+00	8.19E+00
11	9.58E+00	9.15E+00	8.26E+00	8.19E+00

12	9.57E+00	9.15E+00	8.26E+00	8.19E+00
13	9.57E+00	9.15E+00	8.26E+00	8.19E+00
14	9.57E+00	9.15E+00	8.26E+00	8.19E+00
15	9.57E+00	9.15E+00	8.26E+00	8.19E+00
16	9.57E+00	9.15E+00	8.26E+00	8.19E+00
17	9.57E+00	9.15E+00	8.26E+00	8.19E+00
18	9.57E+00	9.15E+00	8.26E+00	8.19E+00
19	9.57E+00	9.14E+00	8.26E+00	8.19E+00
20	9.56E+00	9.14E+00	8.26E+00	8.19E+00

Calculated chemical shifts

Point	Ha	Hb	Hc	Hd
1	9.66E+00	9.23E+00	8.23E+00	8.04E+00
2	9.64E+00	9.21E+00	8.24E+00	8.09E+00
3	9.62E+00	9.19E+00	8.25E+00	8.13E+00
4	9.61E+00	9.18E+00	8.26E+00	8.16E+00
5	9.60E+00	9.17E+00	8.26E+00	8.17E+00
6	9.59E+00	9.17E+00	8.26E+00	8.18E+00
7	9.59E+00	9.16E+00	8.26E+00	8.18E+00
8	9.58E+00	9.16E+00	8.26E+00	8.19E+00
9	9.58E+00	9.16E+00	8.26E+00	8.19E+00
10	9.58E+00	9.16E+00	8.26E+00	8.19E+00
11	9.58E+00	9.15E+00	8.26E+00	8.19E+00
12	9.57E+00	9.15E+00	8.26E+00	8.19E+00
13	9.57E+00	9.15E+00	8.26E+00	8.19E+00
14	9.57E+00	9.15E+00	8.26E+00	8.19E+00
15	9.57E+00	9.15E+00	8.26E+00	8.19E+00
16	9.57E+00	9.15E+00	8.26E+00	8.19E+00
17	9.57E+00	9.15E+00	8.26E+00	8.19E+00
18	9.57E+00	9.15E+00	8.26E+00	8.19E+00
19	9.57E+00	9.15E+00	8.26E+00	8.19E+00
20	9.56E+00	9.14E+00	8.26E+00	8.19E+00

Chemical shifts for each nucleus

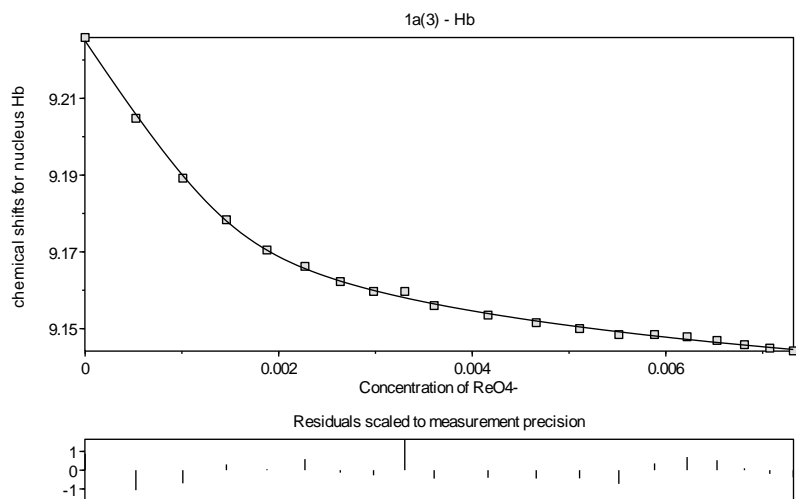
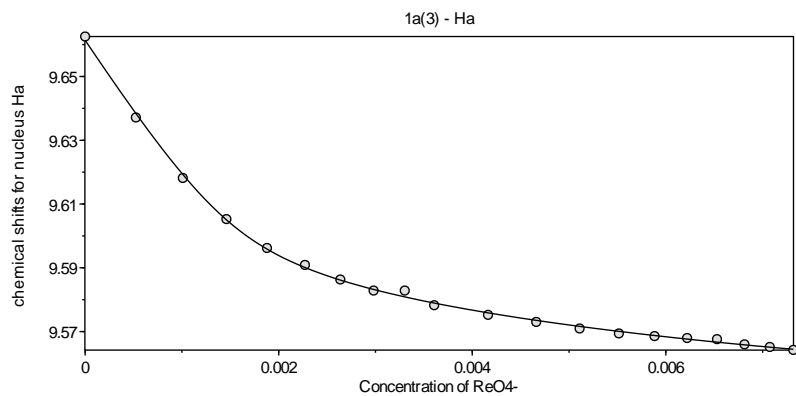
species	Ha	Hb	Hc	Hd
1a	9.66E+00	9.23E+00	8.23E+00	8.04E+00
(ReO ₄ ⁻)(1a)	9.59E+00	9.16E+00	8.27E+00	8.20E+00
(ReO ₄ ⁻) ₂ (1a)	9.53E+00	9.12E+00	8.25E+00	8.18E+00

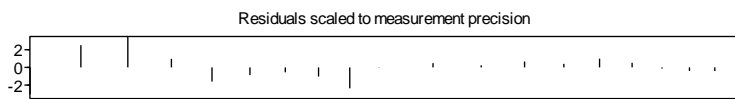
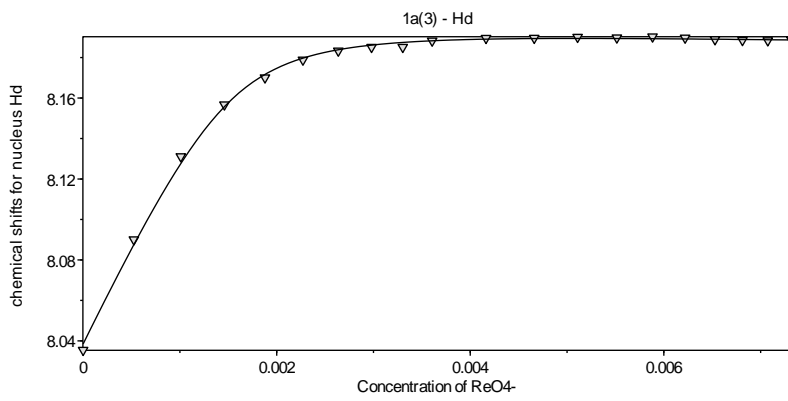
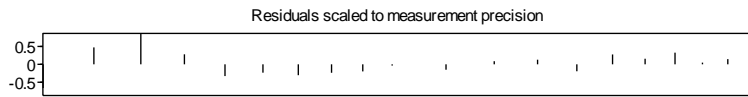
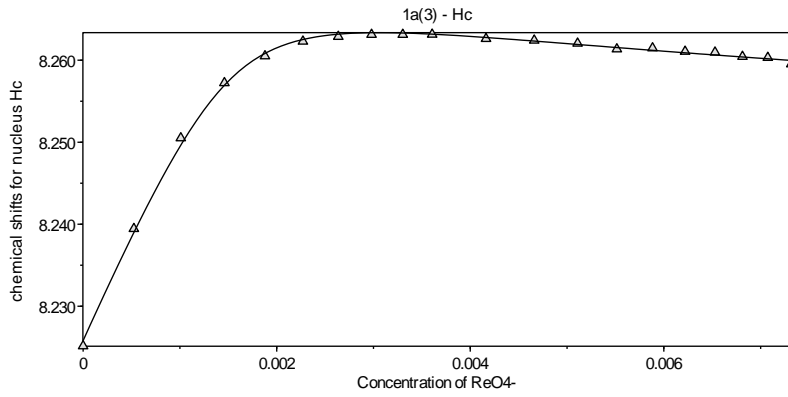
Converged in 7 iterations with sigma = 0.986089

	value	standard deviation	Comments
1 log beta((ReO ⁴⁻))(1a)	3.9794	0.0607	3.98(6)
2 log beta((ReO ⁴⁻) ₂ (1a))	6.1451	0.1901	6.1(2)

Correlation coefficients between stability constants. Numbering as above

2 0.7796
1





2a and TBA⁺ReO₄⁻ (Experiment 1)

2a (Exp.1)

Species	Log beta	ReO ₄ ⁻	2a	
1	3.8876	1	1	refine
2	6.0026	2	1	refine

Species concentrations/mol dm⁻³

Point	T(ReO ₄ ⁻)	T(2a)	F(ReO ₄ ⁻)	F(2a)	species 1	species 2
1	0.00E+00	1.55E-03	5.21E-91	1.55E-03	6.24E-90	4.24E-178
2	5.13E-04	1.55E-03	5.36E-05	1.09E-03	4.53E-04	3.17E-06
3	9.89E-04	1.55E-03	1.45E-04	7.24E-04	8.12E-04	1.54E-05
4	1.43E-03	1.55E-03	2.97E-04	4.59E-04	1.05E-03	4.07E-05
5	1.84E-03	1.55E-03	5.10E-04	2.98E-04	1.17E-03	7.81E-05
6	2.22E-03	1.55E-03	7.60E-04	2.08E-04	1.22E-03	1.21E-04
7	2.58E-03	1.55E-03	1.02E-03	1.56E-04	1.23E-03	1.64E-04
8	2.92E-03	1.55E-03	1.29E-03	1.23E-04	1.22E-03	2.05E-04
9	3.24E-03	1.55E-03	1.54E-03	1.01E-04	1.21E-03	2.43E-04
10	3.53E-03	1.55E-03	1.79E-03	8.60E-05	1.19E-03	2.77E-04
11	4.08E-03	1.55E-03	2.26E-03	6.59E-05	1.15E-03	3.37E-04
12	4.57E-03	1.55E-03	2.68E-03	5.36E-05	1.11E-03	3.88E-04
13	5.00E-03	1.55E-03	3.07E-03	4.54E-05	1.08E-03	4.30E-04
14	5.40E-03	1.55E-03	3.42E-03	3.96E-05	1.05E-03	4.66E-04
15	5.76E-03	1.55E-03	3.75E-03	3.52E-05	1.02E-03	4.98E-04
16	6.09E-03	1.55E-03	4.05E-03	3.18E-05	9.95E-04	5.25E-04
17	6.40E-03	1.55E-03	4.32E-03	2.92E-05	9.74E-04	5.49E-04
18	6.67E-03	1.55E-03	4.58E-03	2.70E-05	9.55E-04	5.70E-04
19	6.93E-03	1.55E-03	4.82E-03	2.52E-05	9.38E-04	5.88E-04
20	7.17E-03	1.55E-03	5.03E-03	2.37E-05	9.23E-04	6.05E-04

Measured chemical shifts

Point	Ha/b	Hc	Hd
1	9.22E+00	8.25E+00	7.93E+00
2	9.20E+00	8.25E+00	7.98E+00
3	9.19E+00	8.26E+00	8.01E+00
4	9.18E+00	8.26E+00	8.03E+00
5	9.17E+00	8.26E+00	8.05E+00
6	9.17E+00	8.26E+00	8.05E+00
7	9.16E+00	8.27E+00	8.06E+00
8	9.16E+00	8.26E+00	8.06E+00
9	9.16E+00	8.26E+00	8.06E+00
10	9.16E+00	8.26E+00	8.07E+00
11	9.15E+00	8.26E+00	8.07E+00

12	9.15E+00	8.26E+00	8.07E+00
13	9.15E+00	8.26E+00	8.07E+00
14	9.15E+00	8.26E+00	8.07E+00
15	9.15E+00	8.26E+00	8.07E+00
16	9.15E+00	8.26E+00	8.07E+00
17	9.15E+00	8.26E+00	8.07E+00
18	9.15E+00	8.26E+00	8.07E+00
19	9.15E+00	8.26E+00	8.07E+00
20	9.15E+00	8.26E+00	8.07E+00

Calculated chemical shifts

Point	Ha/b	Hc	Hd
1	9.22E+00	8.25E+00	7.93E+00
2	9.20E+00	8.25E+00	7.97E+00
3	9.19E+00	8.26E+00	8.01E+00
4	9.18E+00	8.26E+00	8.03E+00
5	9.17E+00	8.26E+00	8.05E+00
6	9.17E+00	8.26E+00	8.06E+00
7	9.16E+00	8.27E+00	8.06E+00
8	9.16E+00	8.26E+00	8.06E+00
9	9.16E+00	8.26E+00	8.06E+00
10	9.16E+00	8.26E+00	8.07E+00
11	9.15E+00	8.26E+00	8.07E+00
12	9.15E+00	8.26E+00	8.07E+00
13	9.15E+00	8.26E+00	8.07E+00
14	9.15E+00	8.26E+00	8.07E+00
15	9.15E+00	8.26E+00	8.07E+00
16	9.15E+00	8.26E+00	8.07E+00
17	9.15E+00	8.26E+00	8.07E+00
18	9.15E+00	8.26E+00	8.07E+00
19	9.15E+00	8.26E+00	8.07E+00
20	9.15E+00	8.26E+00	8.07E+00

Chemical shifts for each nucleus

species	Ha/b	Hc	Hd
2a	9.22E+00	8.25E+00	7.93E+00
(ReO ₄ ⁻)(2a)	9.16E+00	8.27E+00	8.08E+00
(ReO ₄ ⁻) ₂ (2a)	9.12E+00	8.25E+00	8.06E+00

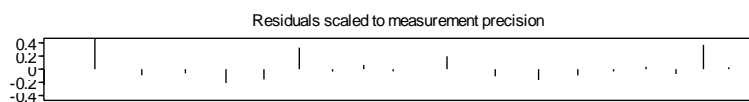
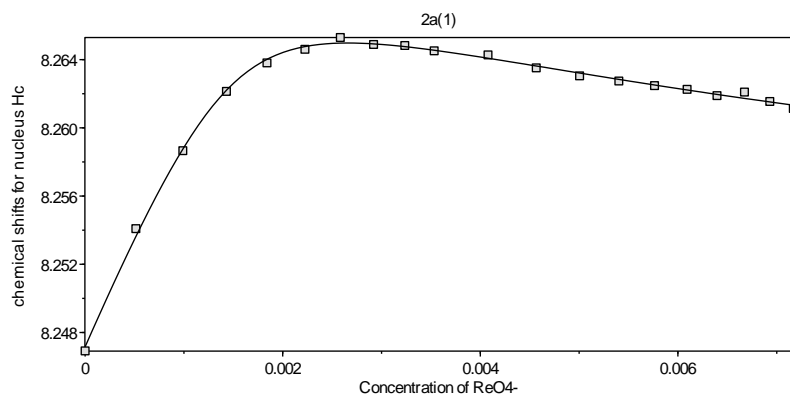
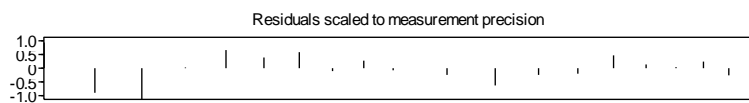
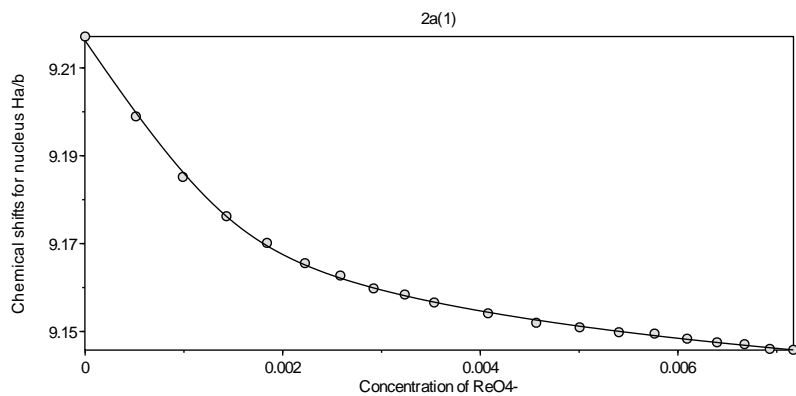
Converged in 1 iterations with sigma = 0.749908

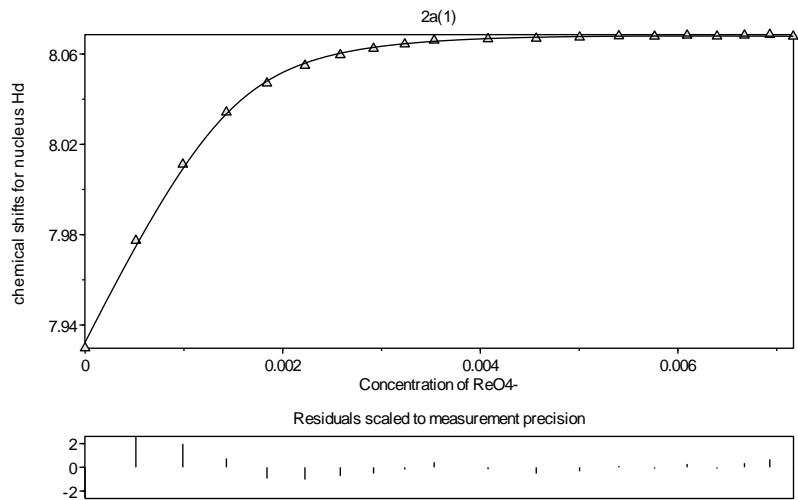
	value	standard deviation	Comments
1 log beta((ReO ₄ ⁻)(2a))	3.8876	0.0582	3.89(6)
2 log beta((ReO ₄ ⁻) ₂ (2a))	6.0026	0.2519	6.0(3)

Correlation coefficients between stability constants. Numbering as above

2 0.7668

1





2a and TBA⁺ReO₄⁻ (Experiment 2)

2a (Exp.2)

Species	Log beta	ReO ₄ ⁻	2a	
1	3.854	1	1	refine
2	6.0594	2	1	refine

Species concentrations/mol dm⁻³

Point	T(ReO ₄ ⁻)	T(2a)	F(ReO ₄ ⁻)	F(2a)	species 1	species 2
1	0.00E+00	1.55E-03	5.45E-91	1.55E-03	6.04E-90	5.28E-178
2	5.13E-04	1.55E-03	5.70E-05	1.10E-03	4.48E-04	4.10E-06
3	9.89E-04	1.55E-03	1.52E-04	7.34E-04	7.98E-04	1.95E-05
4	1.43E-03	1.55E-03	3.03E-04	4.74E-04	1.03E-03	4.99E-05
5	1.84E-03	1.55E-03	5.10E-04	3.14E-04	1.14E-03	9.36E-05
6	2.22E-03	1.55E-03	7.51E-04	2.21E-04	1.19E-03	1.43E-04
7	2.58E-03	1.55E-03	1.01E-03	1.66E-04	1.19E-03	1.92E-04
8	2.92E-03	1.55E-03	1.26E-03	1.31E-04	1.18E-03	2.39E-04
9	3.24E-03	1.55E-03	1.51E-03	1.08E-04	1.16E-03	2.82E-04
10	3.53E-03	1.55E-03	1.75E-03	9.11E-05	1.14E-03	3.20E-04
11	4.08E-03	1.55E-03	2.21E-03	6.94E-05	1.09E-03	3.88E-04
12	4.57E-03	1.55E-03	2.63E-03	5.60E-05	1.05E-03	4.43E-04
13	5.00E-03	1.55E-03	3.01E-03	4.72E-05	1.01E-03	4.90E-04
14	5.40E-03	1.55E-03	3.36E-03	4.08E-05	9.81E-04	5.29E-04
15	5.76E-03	1.55E-03	3.68E-03	3.62E-05	9.52E-04	5.63E-04
16	6.09E-03	1.55E-03	3.98E-03	3.26E-05	9.27E-04	5.92E-04
17	6.40E-03	1.55E-03	4.26E-03	2.97E-05	9.04E-04	6.18E-04
18	6.67E-03	1.55E-03	4.51E-03	2.74E-05	8.84E-04	6.40E-04
19	6.93E-03	1.55E-03	4.74E-03	2.56E-05	8.66E-04	6.60E-04
20	7.17E-03	1.55E-03	4.96E-03	2.40E-05	8.50E-04	6.77E-04

Measured chemical shifts

Point	Ha/b	Hc	Hd
1	9.22E+00	8.25E+00	7.93E+00
2	9.20E+00	8.25E+00	7.98E+00
3	9.19E+00	8.26E+00	8.01E+00
4	9.18E+00	8.26E+00	8.03E+00
5	9.17E+00	8.26E+00	8.05E+00
6	9.17E+00	8.27E+00	8.05E+00
7	9.16E+00	8.27E+00	8.06E+00
8	9.16E+00	8.27E+00	8.06E+00
9	9.16E+00	8.27E+00	8.06E+00
10	9.16E+00	8.26E+00	8.07E+00
11	9.16E+00	8.26E+00	8.07E+00

12	9.15E+00	8.26E+00	8.07E+00
13	9.15E+00	8.26E+00	8.07E+00
14	9.15E+00	8.26E+00	8.07E+00
15	9.15E+00	8.26E+00	8.07E+00
16	9.15E+00	8.26E+00	8.07E+00
17	9.15E+00	8.26E+00	8.07E+00
18	9.15E+00	8.26E+00	8.07E+00
19	9.15E+00	8.26E+00	8.07E+00
20	9.15E+00	8.26E+00	8.07E+00

Calculated chemical shifts

Point	Ha/b	Hc	Hd
1	9.22E+00	8.25E+00	7.93E+00
2	9.20E+00	8.25E+00	7.97E+00
3	9.19E+00	8.26E+00	8.01E+00
4	9.18E+00	8.26E+00	8.03E+00
5	9.17E+00	8.26E+00	8.05E+00
6	9.17E+00	8.27E+00	8.06E+00
7	9.16E+00	8.27E+00	8.06E+00
8	9.16E+00	8.27E+00	8.06E+00
9	9.16E+00	8.27E+00	8.06E+00
10	9.16E+00	8.27E+00	8.07E+00
11	9.16E+00	8.26E+00	8.07E+00
12	9.15E+00	8.26E+00	8.07E+00
13	9.15E+00	8.26E+00	8.07E+00
14	9.15E+00	8.26E+00	8.07E+00
15	9.15E+00	8.26E+00	8.07E+00
16	9.15E+00	8.26E+00	8.07E+00
17	9.15E+00	8.26E+00	8.07E+00
18	9.15E+00	8.26E+00	8.07E+00
19	9.15E+00	8.26E+00	8.07E+00
20	9.15E+00	8.26E+00	8.07E+00

Chemical shifts for each nucleus

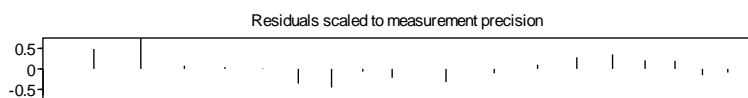
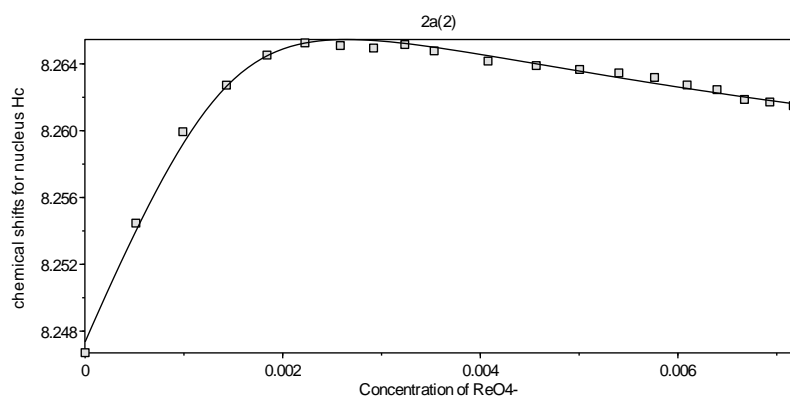
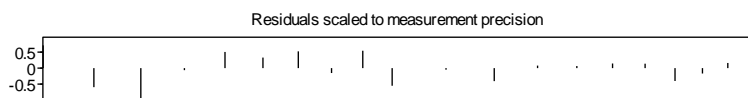
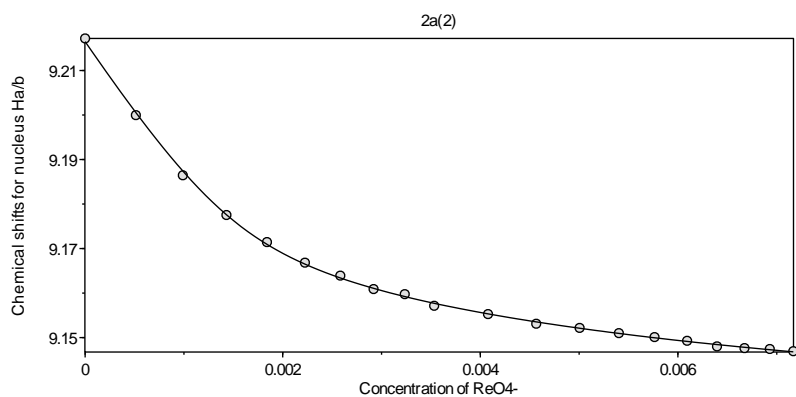
species	Ha/b	Hc	Hd
2a	9.22E+00	8.25E+00	7.93E+00
(ReO ₄ ⁻)(2a)	9.16E+00	8.27E+00	8.08E+00
(ReO ₄ ⁻) ₂ (2a)	9.13E+00	8.25E+00	8.06E+00

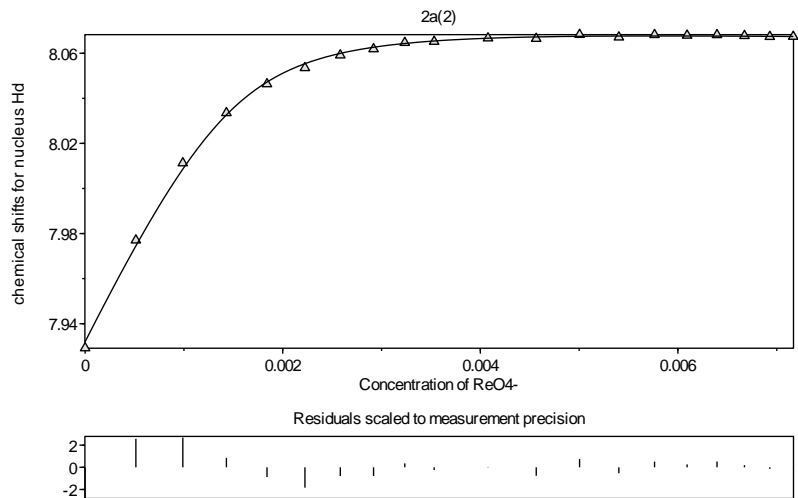
Converged in 11 iterations with sigma = 0.852949

	value	standard deviation	Comments
1 log beta((ReO ₄ ⁻)(2a))	3.854	0.0667	3.85(7)
2 log beta((ReO ₄ ⁻) ₂ (2a))	6.0594	0.2604	6.1(3)

Correlation coefficients between stability constants. Numbering as above

2 0.7736
1





2a and TBA⁺ReO₄⁻ (Experiment 3)

2a (Exp. 3)

Species	Log beta	ReO ₄ ⁻	2a	
1	3.8638	1	1	refine
2	6.0193	2	1	refine

Species concentrations/mol dm⁻³

Point	T(ReO ₄ ⁻)	T(2a)	F(ReO ₄ ⁻)	F(2a)	species 1	species 2
1	0.00E+00	1.55E-03	5.37E-91	1.55E-03	6.09E-90	4.68E-178
2	5.13E-04	1.55E-03	5.61E-05	1.10E-03	4.50E-04	3.61E-06
3	9.89E-04	1.55E-03	1.50E-04	7.31E-04	8.04E-04	1.73E-05
4	1.43E-03	1.55E-03	3.03E-04	4.69E-04	1.04E-03	4.49E-05
5	1.84E-03	1.55E-03	5.13E-04	3.09E-04	1.16E-03	8.50E-05
6	2.22E-03	1.55E-03	7.59E-04	2.17E-04	1.20E-03	1.31E-04
7	2.58E-03	1.55E-03	1.02E-03	1.63E-04	1.21E-03	1.77E-04
8	2.92E-03	1.55E-03	1.28E-03	1.29E-04	1.20E-03	2.20E-04
9	3.24E-03	1.55E-03	1.53E-03	1.06E-04	1.19E-03	2.60E-04
10	3.53E-03	1.55E-03	1.78E-03	8.98E-05	1.17E-03	2.96E-04
11	4.08E-03	1.55E-03	2.24E-03	6.87E-05	1.12E-03	3.59E-04
12	4.57E-03	1.55E-03	2.66E-03	5.58E-05	1.08E-03	4.12E-04
13	5.00E-03	1.55E-03	3.04E-03	4.71E-05	1.05E-03	4.56E-04
14	5.40E-03	1.55E-03	3.40E-03	4.09E-05	1.02E-03	4.94E-04
15	5.76E-03	1.55E-03	3.72E-03	3.63E-05	9.89E-04	5.26E-04
16	6.09E-03	1.55E-03	4.02E-03	3.28E-05	9.64E-04	5.54E-04
17	6.40E-03	1.55E-03	4.29E-03	3.00E-05	9.42E-04	5.79E-04
18	6.67E-03	1.55E-03	4.55E-03	2.78E-05	9.23E-04	6.01E-04
19	6.93E-03	1.55E-03	4.78E-03	2.59E-05	9.06E-04	6.20E-04
20	7.17E-03	1.55E-03	5.00E-03	2.43E-05	8.90E-04	6.37E-04

Measured chemical shifts

Point	Ha/b	Hc	Hd
1	9.22E+00	8.25E+00	7.93E+00
2	9.20E+00	8.25E+00	7.98E+00
3	9.19E+00	8.26E+00	8.01E+00
4	9.18E+00	8.26E+00	8.03E+00
5	9.17E+00	8.26E+00	8.05E+00
6	9.17E+00	8.27E+00	8.05E+00
7	9.16E+00	8.27E+00	8.06E+00
8	9.16E+00	8.27E+00	8.06E+00
9	9.16E+00	8.27E+00	8.06E+00
10	9.16E+00	8.26E+00	8.06E+00
11	9.16E+00	8.26E+00	8.07E+00

12	9.15E+00	8.26E+00	8.07E+00
13	9.15E+00	8.26E+00	8.07E+00
14	9.15E+00	8.26E+00	8.07E+00
15	9.15E+00	8.26E+00	8.07E+00
16	9.15E+00	8.26E+00	8.07E+00
17	9.15E+00	8.26E+00	8.07E+00
18	9.15E+00	8.26E+00	8.07E+00
19	9.15E+00	8.26E+00	8.07E+00
20	9.15E+00	8.26E+00	8.07E+00

Calculated chemical shifts

Point	Ha/b	Hc	Hd
1	9.22E+00	8.25E+00	7.93E+00
2	9.20E+00	8.25E+00	7.97E+00
3	9.19E+00	8.26E+00	8.01E+00
4	9.18E+00	8.26E+00	8.03E+00
5	9.17E+00	8.26E+00	8.05E+00
6	9.17E+00	8.26E+00	8.06E+00
7	9.16E+00	8.27E+00	8.06E+00
8	9.16E+00	8.27E+00	8.06E+00
9	9.16E+00	8.27E+00	8.06E+00
10	9.16E+00	8.26E+00	8.07E+00
11	9.16E+00	8.26E+00	8.07E+00
12	9.15E+00	8.26E+00	8.07E+00
13	9.15E+00	8.26E+00	8.07E+00
14	9.15E+00	8.26E+00	8.07E+00
15	9.15E+00	8.26E+00	8.07E+00
16	9.15E+00	8.26E+00	8.07E+00
17	9.15E+00	8.26E+00	8.07E+00
18	9.15E+00	8.26E+00	8.07E+00
19	9.15E+00	8.26E+00	8.07E+00
20	9.15E+00	8.26E+00	8.07E+00

Chemical shifts for each nucleus

species	Ha/b	Hc	Hd
2a	9.22E+00	8.25E+00	7.93E+00
(ReO ₄ ⁻)(2a)	9.16E+00	8.27E+00	8.08E+00
(ReO ₄ ⁻) ₂ (2a)	9.12E+00	8.25E+00	8.06E+00

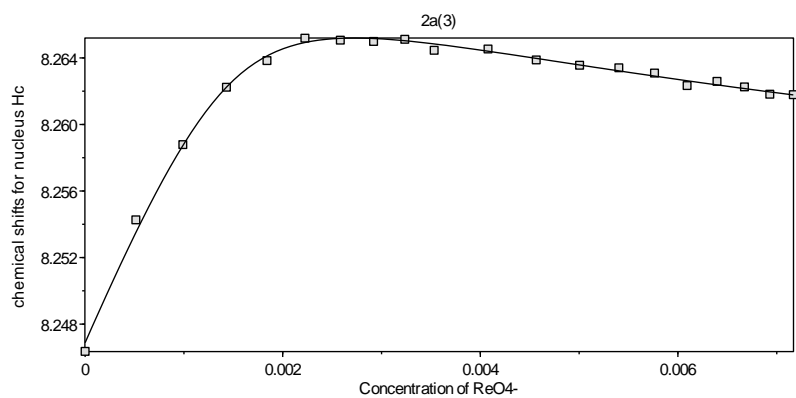
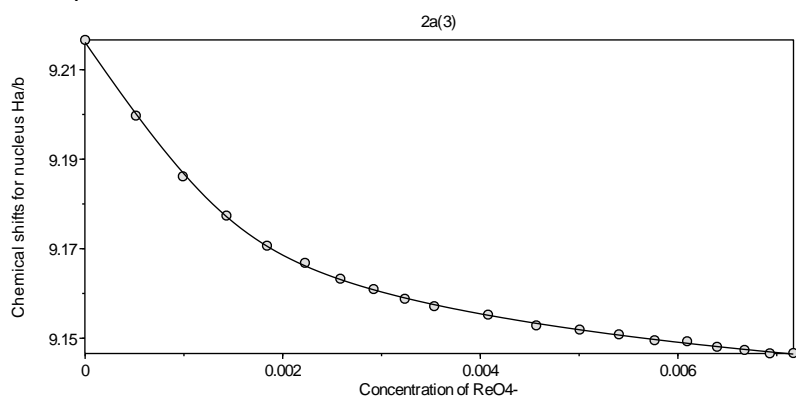
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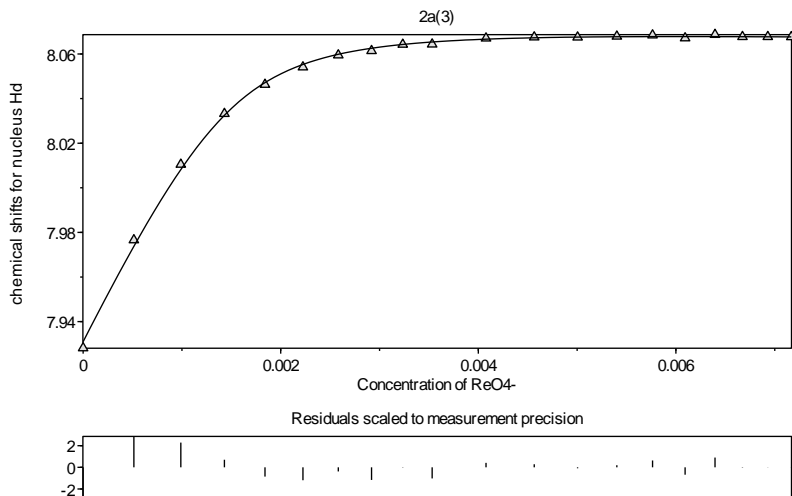
	value	standard deviation	Comments
1 log beta((ReO ₄ ⁻)(2a))	3.8638	0.0632	3.86(6)
2 log beta((ReO ₄ ⁻) ₂ (2a))	6.0193	0.2612	6.0(3)

Correlation coefficients between stability constants. Numbering as above

2 0.7716

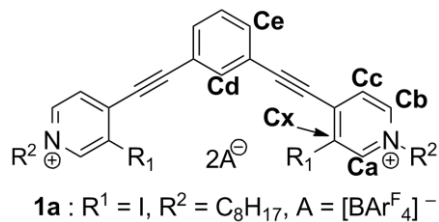
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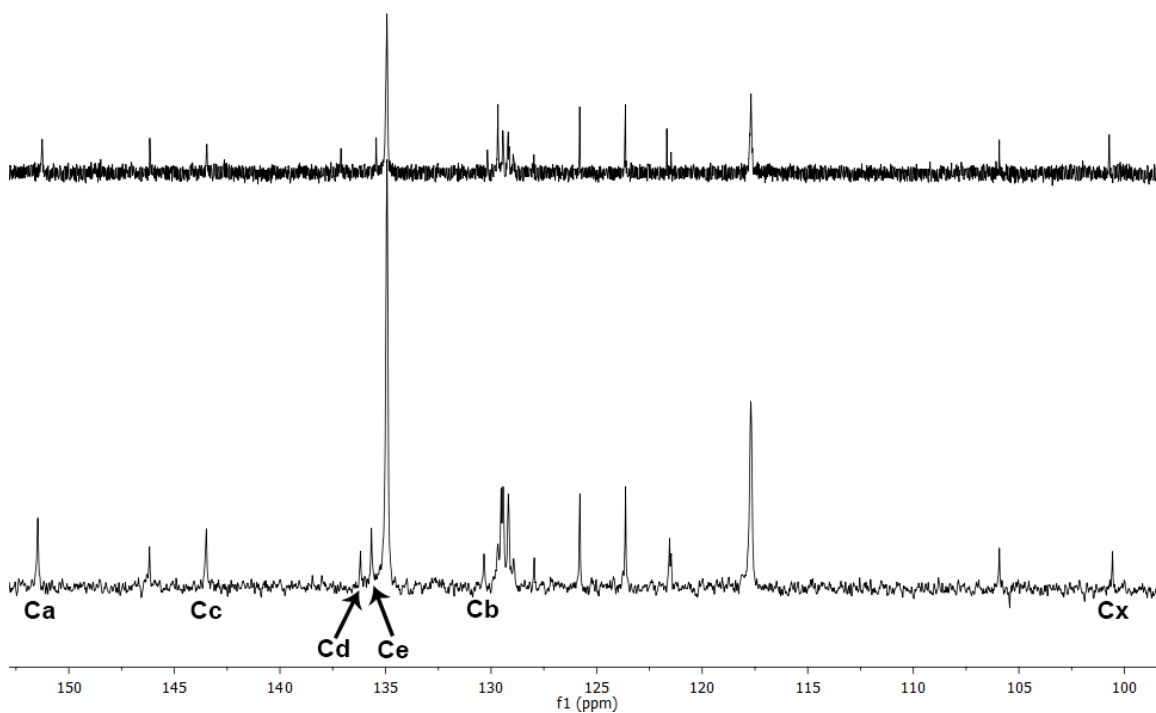




¹³C Titrations

A solution of **1a** (4.892 ± 0.092 mM) was dissolved in $\text{CDCl}_3/(\text{CD}_3)_2\text{CO}$ (3:2 v/v). ¹³C spectra were obtained prior to and directly after addition of $\text{TBA}^+\text{ReO}_4^-$, which resulted in a guest concentration of 8.76 ± 0.12 mM.





^{13}C NMR spectra of **1a** (bottom) and $\mathbf{1a}^{2+}\cdot 2\text{ReO}_4^-$ (top) upon titrating $\text{TBA}^+\text{ReO}_4^-$ (1.79 equiv, top).

Crystal Growth Conditions

Receptors (**1b** and **2b**, 0.001g) were dissolved in 1mL of MeOH in a 10x75mm test tube. $\text{TBA}^+\text{ReO}_4^-$ (0.0005g) was added to the test tube. For **1b**, DMF (0.5 mL) was added for solubility. The test tube was placed in a scintillation vial filled with Et_2O . After 2 days undisturbed, yellow ($\mathbf{1b}^{2+}\cdot 2\text{ReO}_4^-$) or colorless ($\mathbf{2b}^{2+}\cdot 2\text{ReO}_4^-$) single crystals were harvested for diffraction studies. Refer to .cif files for exact structural details.

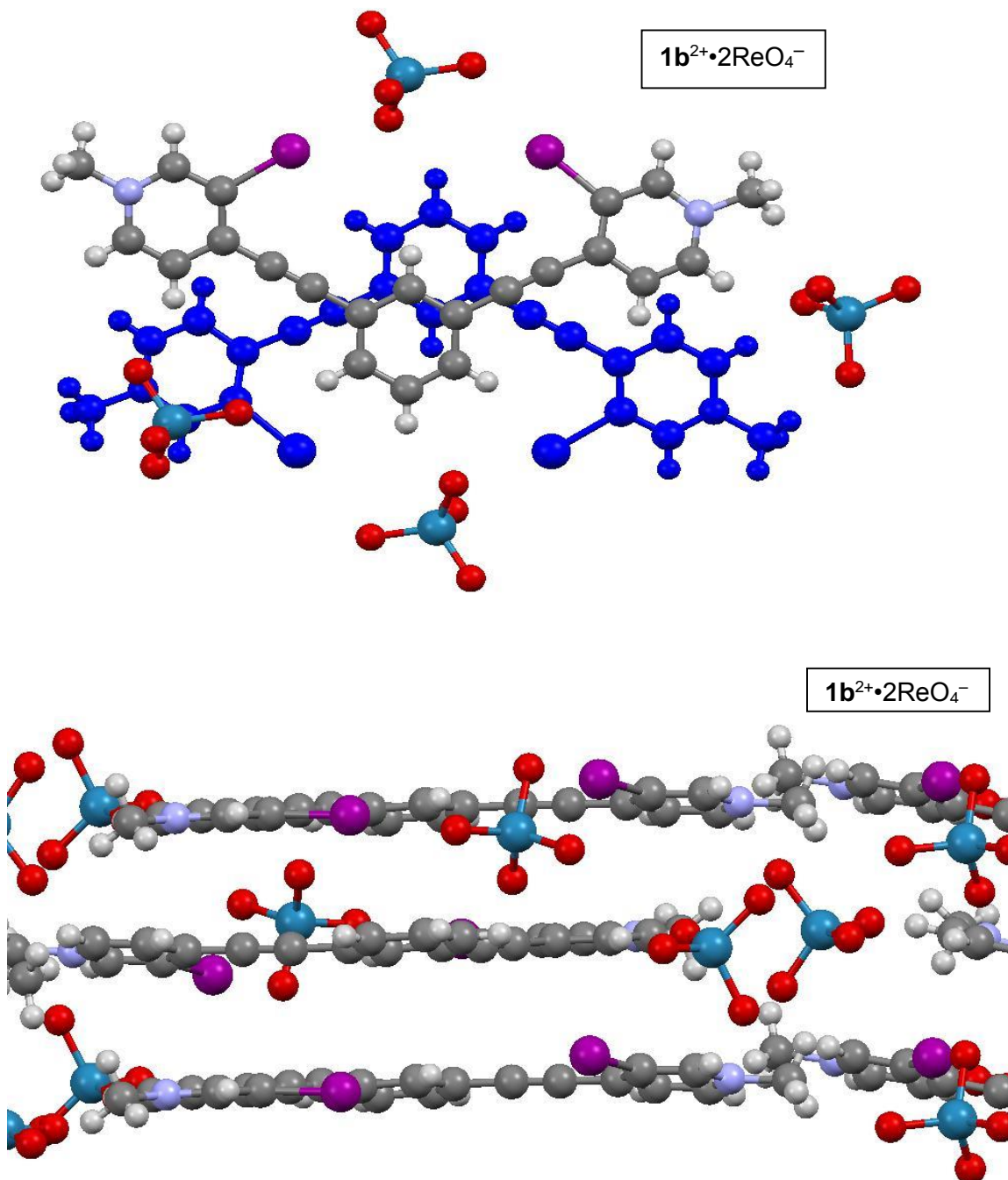
General X-ray Diffraction Experimental Procedure

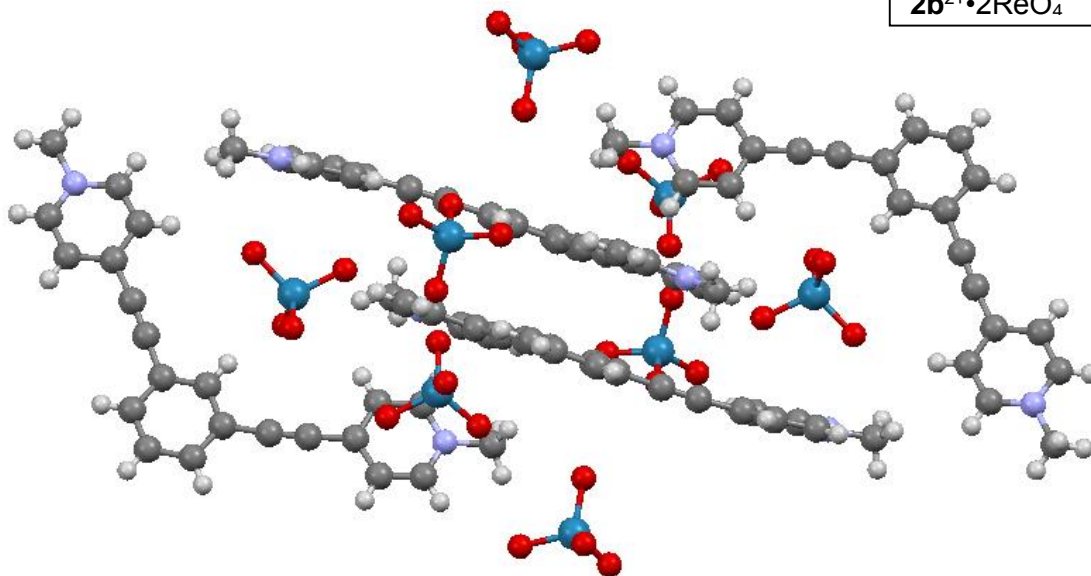
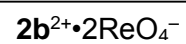
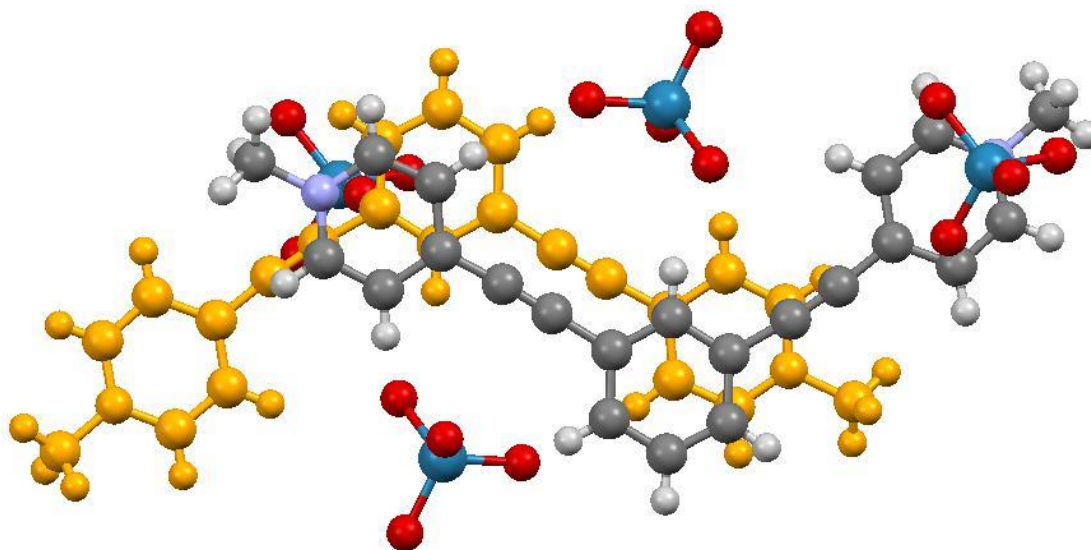
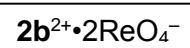
X-ray diffraction data for **1b** was collected at 150K and **2b** at 100K. Data were collected on a Bruker D8 Venture using $\text{MoK}\alpha$ -radiation ($\lambda=0.71073 \text{ \AA}$). Data have been corrected for absorption using the SADABS⁷ area detector absorption correction program. Using Olex2⁸, the structure was solved with the ShelXT structure solution program using Direct Methods and refined with the ShelXL refinement package using least squares minimization. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were refined in calculated positions in a ridged group model with isotropic thermal parameters $U(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for all C(H) groups and $U(\text{H})=1.5U_{\text{eq}}$

(C) for all C(H,H,H) groups. Calculations and refinement of structures were carried out using APEX2⁹, SHELXTL¹⁰, and Olex2 software.

After refinement both **1b** and **2b** continued to display a number of residual Q peaks greater than $1.0 \text{ e } \text{\AA}^{-3}$. All of which were observed less than 1 \AA from the large atoms (I or Re) regardless of the absorption correction applied. These Q peaks should be regarded as artifacts from these heavy atoms.

Crystal Structures





References:

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