Supplementary Information for:

Towards Safer Electrolytes: Comparing the Air Stability and Electrochemical Properties of $NaPF_6$, NaTFSI and Na[B(hfip)$_4$]·DME for Sodium-Ion Batteries

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S1 Electrochemistry measurements.

S1.1 Conductivity measurement experimental.

Figure S1 Two-electrode platinum cell designed to perform ionic conductivity measurements.

The cell constant was determiend by measuring the impedance spectra of 0.01 M, 0.1 M and 1 M aqueous solutions of KCl, which have known ionic conductivity values, at 25°C, 35°C and 45°C. The high frequency region on the impedance spectra were fitted using the equivalent circuit $R_1 + (R_2 + Q_2) \times Q_1$ (Figure S2). An average of the cell constant values gave the value 10.2 ± 0.3 cm^{-1}.

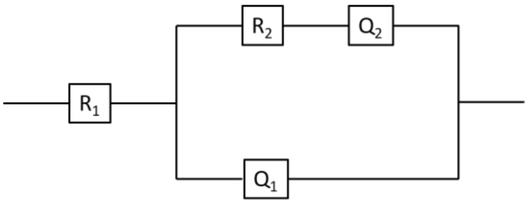


Figure S2 Equivalent circuit used to determine the cell constant.

Table S1 Bulk conductivity values for 1 M $NaPF_6$, 1 M NaTFSI and 1 M $Na[B(hfip)_4)]$·DME in EC:DEC (1:1 v/v). Recorded at 25°C, 35°C, 45°C and 55°C.

Electrolyte	Conductivity at 25°C	Conductivity at 35°C	Conductivity at 45°C	Conductivity at 55°C
1 M $NaPF_6$ in EC:DEC (1:1 v/v)	8.6	10.0	11.2	12.9
1 M NaTFSI in EC:DEC (1:1 v/v)	6.6	7.5	8.9	10.1
1 M $Na[B(hfip)_4)]$·DME in EC:DEC (1:1 v/v)	5.1	6.1	7.0	8.2

S1.2 Cyclic voltammetry.

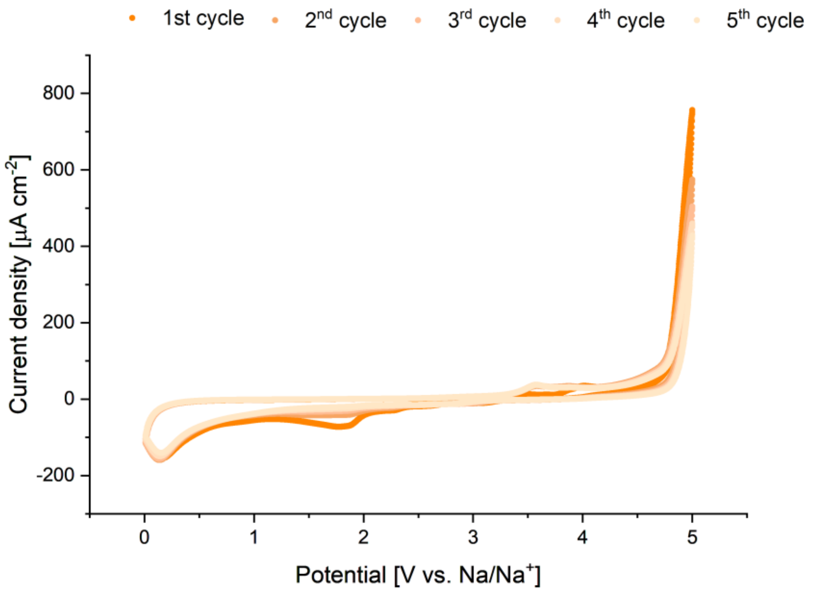


Figure S3 Cyclic voltammogram of 1 M $NaPF_6$ in EC:DEC (1:1 v/v). Working electrode is glassy carbon, counter electrode is platinum and the pseudo reference electrode is sodium. First five cycles, measured between 0.01 V and 5.0 V vs. Na/Na^+ at 10 mV s^{-1}.

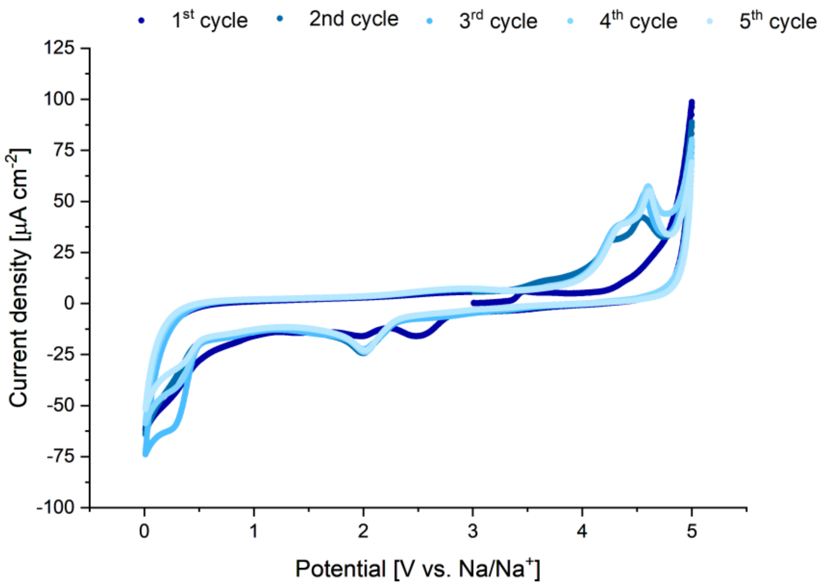


Figure S4 Cyclic voltammogram of 1 M NaTFSI in EC:DEC (1:1 v/v). Working electrode is glassy carbon, counter electrode is platinum and the pseudo reference electrode is sodium. First five cycles, measured between 0.01 V and 5.0 V vs. Na/Na^+ at 10 mV s^{-1}.

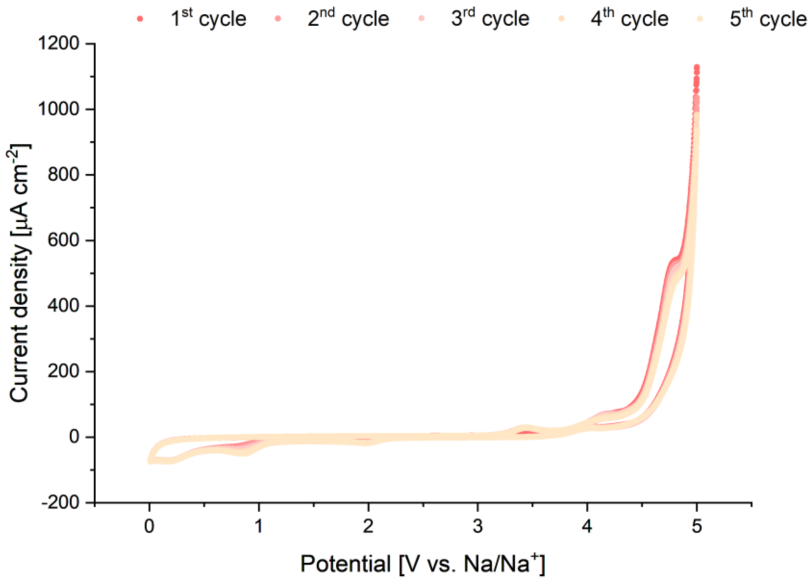


Figure S5 Cyclic voltammogram of 1 M Na[B(hfip)$_4$]·DME in EC:DEC (1:1 v/v). Working electrode is glassy carbon, counter electrode is platinum and the pseudo reference electrode is sodium. First five cycles, measured between 0.01 V and 5.0 V vs. Na/Na$^+$ at 10 mV s^{-1}.

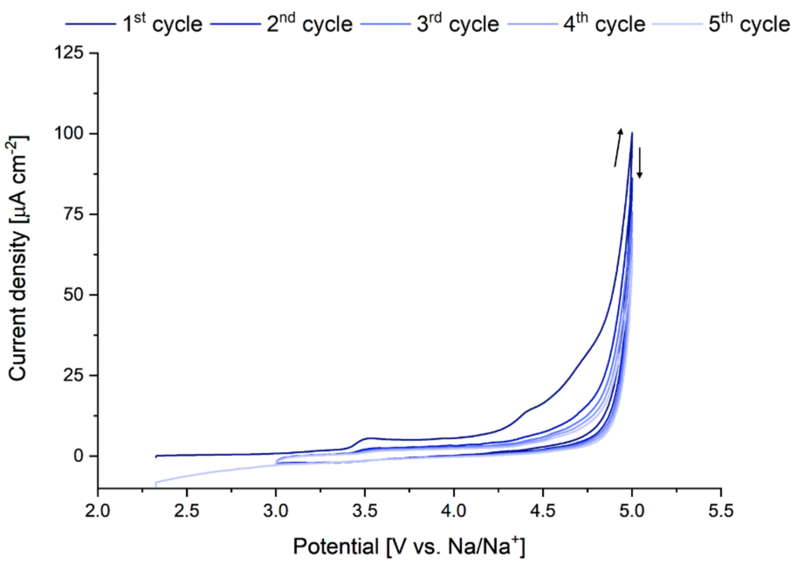


Figure S6 Cyclic voltammogram of 1 M NaTFSI in EC:DEC (1:1 v/v). Working electrode is glassy carbon, counter electrode is platinum and the pseudo reference electrode is sodium. First five cycles, measured between 3.0 V and 5.0 V vs. Na/Na$^+$ at 10 mV s^{-1}. Arrows indicate direction of experiment.

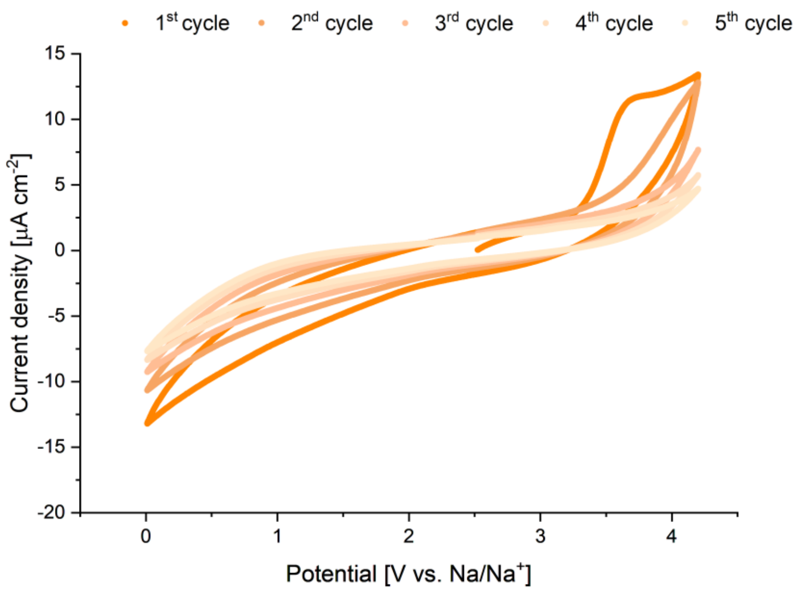


Figure S7 Cyclic voltammogram of 1 M $NaPF_6$ in EC:DEC (1:1 v/v). Working electrode is aluminium, counter electrode is platinum and the pseudo reference electrode is sodium. First five cycles, measured between 0.01 V and 4.2 V vs. Na/Na^+ at 5 mV s^{-1}.

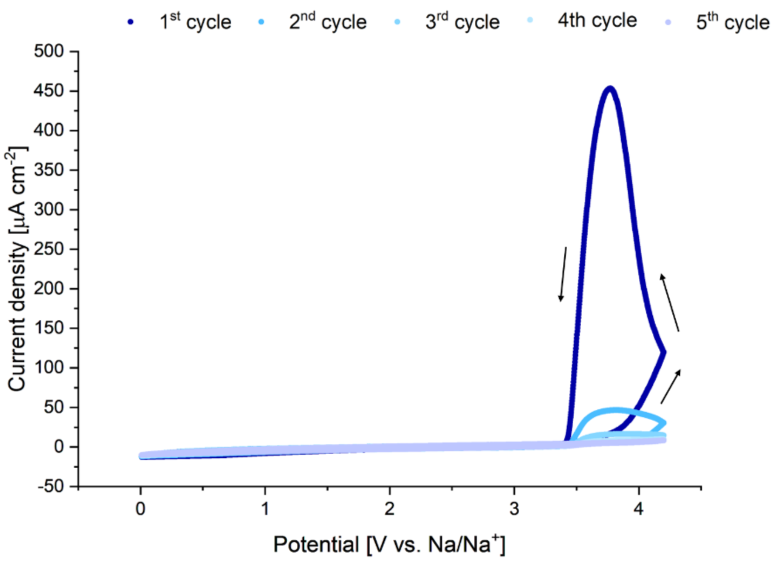


Figure S8 Cyclic voltammogram of 1 M NaTFSI in EC:DEC (1:1 v/v). Working electrode is aluminium, counter electrode is platinum and the pseudo reference electrode is sodium. First five cycles, measured between 0.01 V and 4.2 V vs. Na/Na^+ at 5 mV s^{-1}.

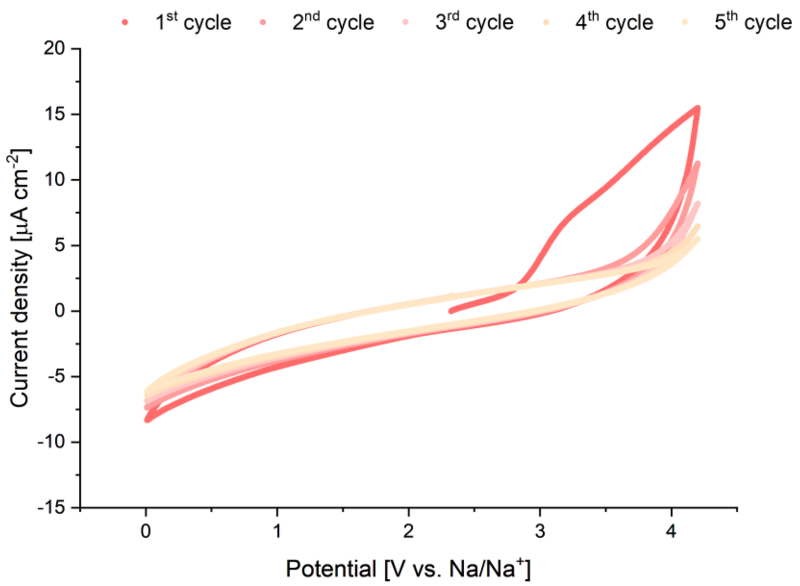


Figure S9 Cyclic voltammogram of 1 M Na[B(hfip)$_4$]·DME in EC:DEC (1:1 v/v). Working electrode is aluminium, counter electrode is platinum and the pseudo reference electrode is sodium. First five cycles, measured between 0.01 V and 4.2 V vs. Na/Na$^+$ at 5 mV s^{-1}.

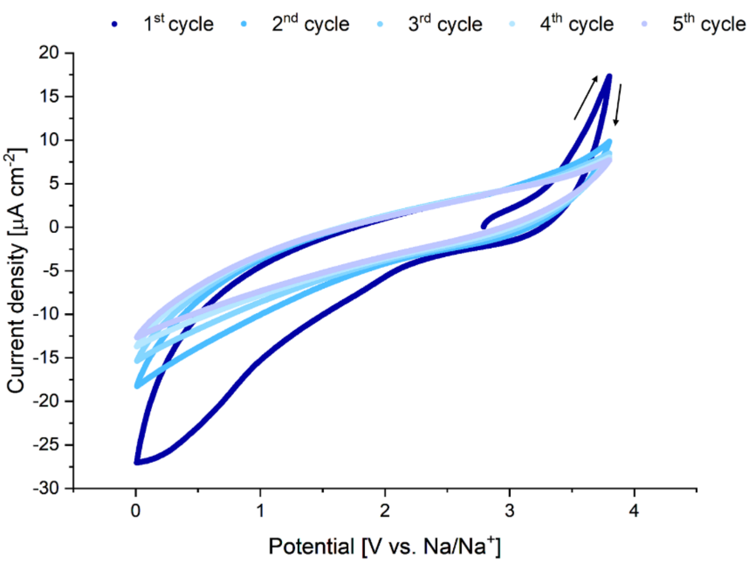


Figure S10 Cyclic voltammogram of 1 M NaTFSI in EC:DEC (1:1 v/v). Working electrode is aluminium, counter electrode is platinum and the pseudo reference electrode is sodium. First five cycles, measured between 0.01 V and 3.8 V vs. Na/Na$^+$ at 5 mV s^{-1}.

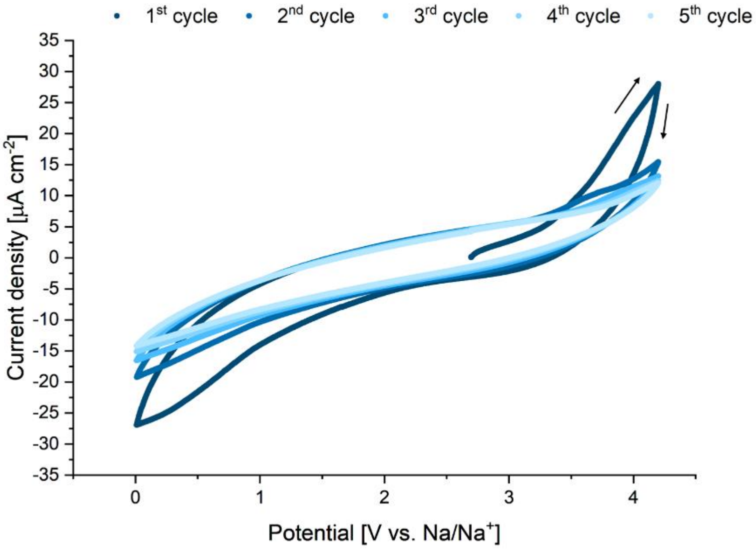


Figure S11 Cyclic voltammogram of 1 M NaTFSI in EC:DEC (1:1 v/v) + 2 wt% $NaPF_6$. Working electrode is aluminium, counter electrode is platinum and the pseudo reference electrode is sodium. First five cycles, measured between 0.01 V and 4.2 V vs. Na/Na^+ at 5 mV s^{-1}.

S1.3 Coin cell cycling.

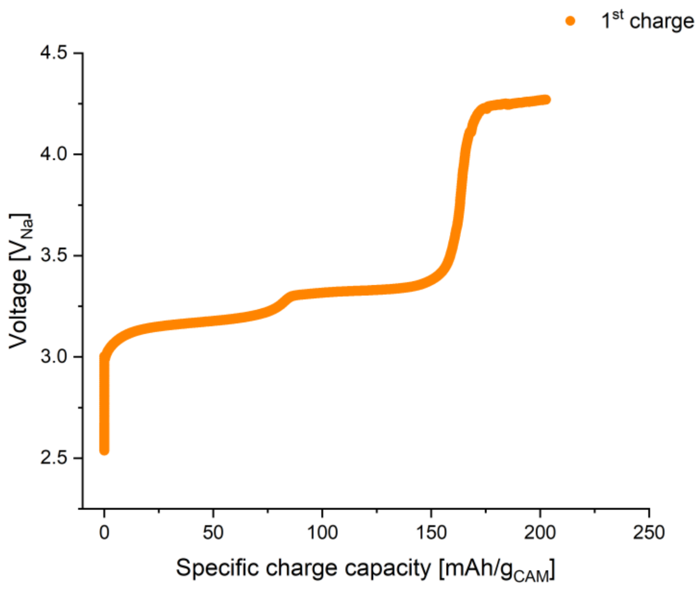


Figure S12 Voltage vs specific charge capacity, normalised by the mass of cathode active material (CAM). Prussian white, $Na_2Fe[Fe(CN)_6]$, cathode in a coin half-cell vs. sodium metal with 100 µl of 1 M $NaPF_6$ in EC:DEC (1:1 v/v) as electrolyte. The cell was charged at C/20 to 4.3 V_{Na} at 21°C.

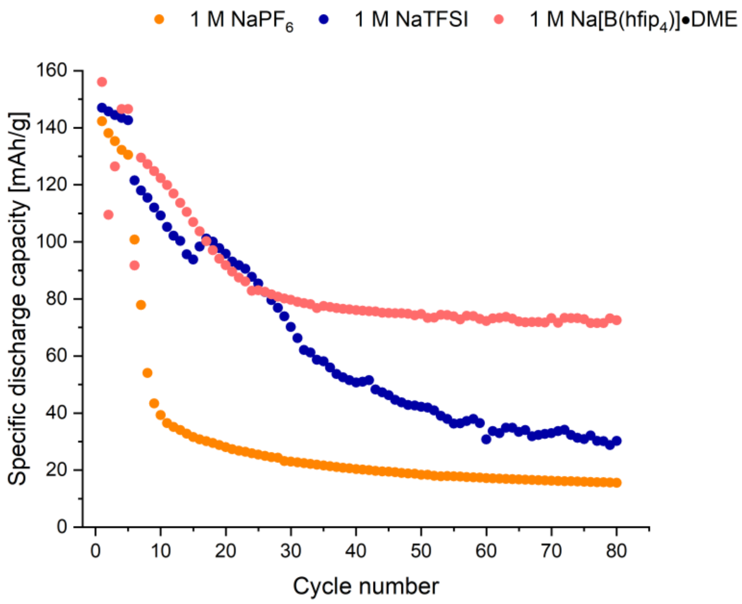


Figure S13 Specific discharge capacity vs. cycle number using Prussian white cathode and sodium metal anode. Electrolytes are 1 M $NaPF_6$ (orange), 1M NaTFSI (blue) and 1 M $Na[B(hfip)_4]\cdot DME$ in EC:DEC (1:1 v/v). Cycling protocol involved five C/10 rate formation cycles, followed by 80 C/2 rate cycles between voltage limits of 1.5–3.8 V. Cells cycled at 25°C.

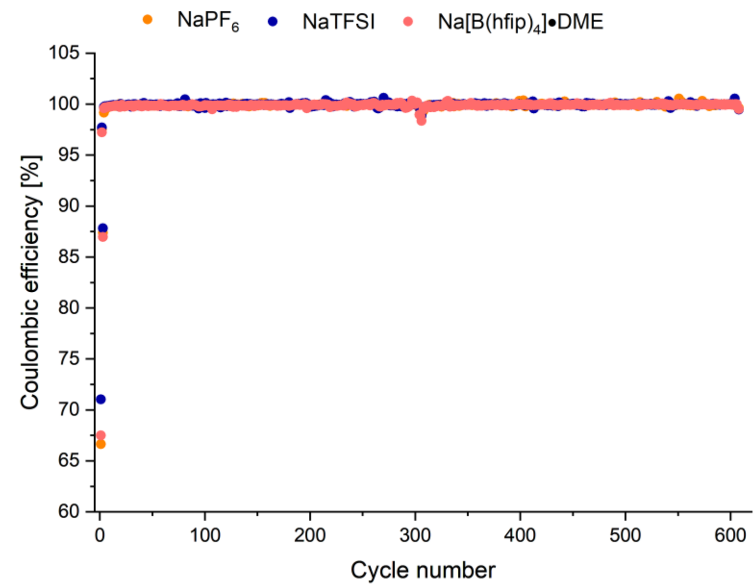


Figure S14 Coulombic efficiency vs. cycle number using Prussian white cathode and hard-carbon anode, using cell voltage limits of 1.5 and 3.8 V. Electrolytes are 1 M $NaPF_6$ (orange), 1M NaTFSI (blue) and 1 M $Na[B(hfip)_4]\cdot DME$ in EC:DEC (1:1 v/v). Cells cycled at 21°C.

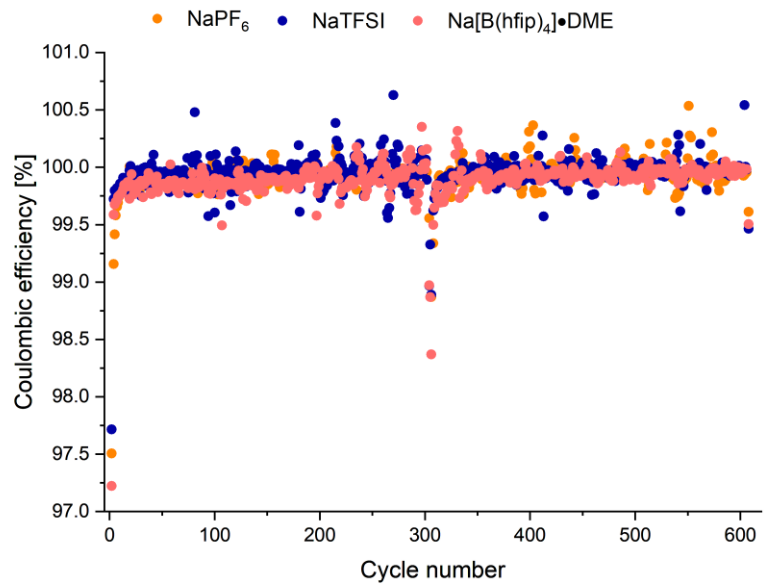


Figure S15 Coulombic efficiency vs. cycle number zoomed in using Prussian white cathode and hard-carbon anode, using cell voltage limits of 1.5 and 3.8 V. Electrolytes are 1 M $NaPF_6$ (orange), 1M NaTFSI (blue) and 1 M $Na[B(hfip)_4]\cdot DME$ in EC:DEC (1:1 v/v). Cells cycled at 21°C.

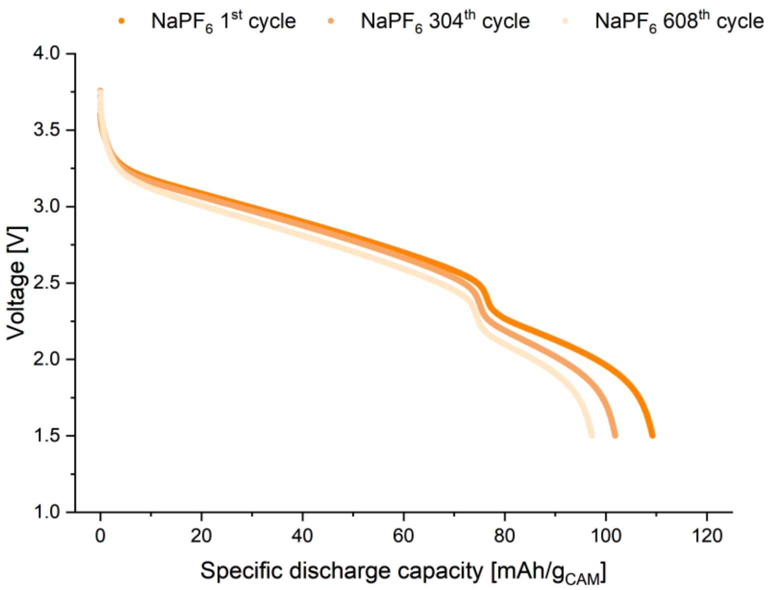


Figure S16 Voltage vs. specific discharge capacity of the initial, middle (304th) and last (608th) C/20 cycle. Cycling from coin cells using a Prussian white cathode and hard-carbon anode. The applied C-rate of C/20 was calculated based on the theoretical capacity of 150 mAh g^{-1} of the cathode, using cell voltage limits of 1.5 and 3.8 V. Electrolyte is 1 M $NaPF_6$ in EC:DEC (1:1 v/v). Cells cycled at 21°C.

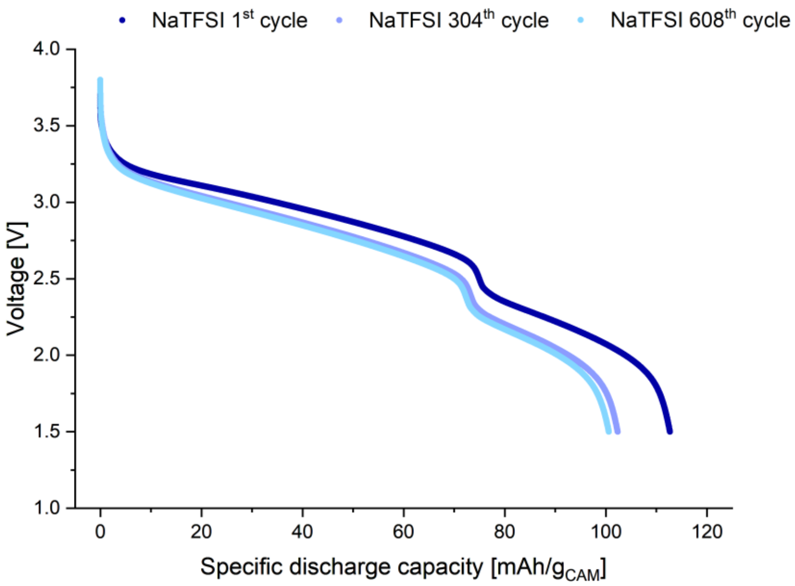


Figure S17 Voltage vs. specific discharge capacity of the initial, middle (304th) and last (608th) C/20 cycle. Cycling from coin cells using a Prussian white cathode and hard-carbon anode. The applied C-rate of C/20 was calculated based on the theoretical capacity of 150 mAh g^{-1} of the cathode, using cell voltage limits of 1.5 and 3.8 V. Electrolyte is 1 M NaTFSI in EC:DEC (1:1 v/v). Cells cycled at 21°C.

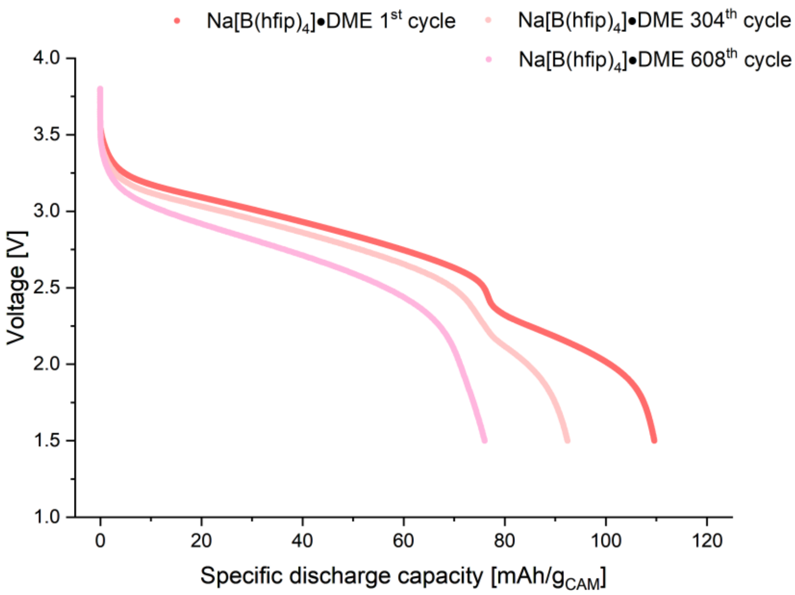


Figure S18 Voltage vs. specific discharge capacity of the initial, middle (304th) and last (608th) C/20 cycle. Cycling from coin cells using a Prussian white cathode and hard-carbon anode. The applied C-rate of C/20 was calculated based on the theoretical capacity of 150 mAh g^{-1} of the cathode, using cell voltage limits of 1.5 and 3.8 V. Electrolyte is 1 M Na[B(hfip)$_4$]·DME in EC:DEC (1:1 v/v). Cells cycled at 21°C.

S2 XPS data.

<u>Post-cycled Prussian white cathode</u>

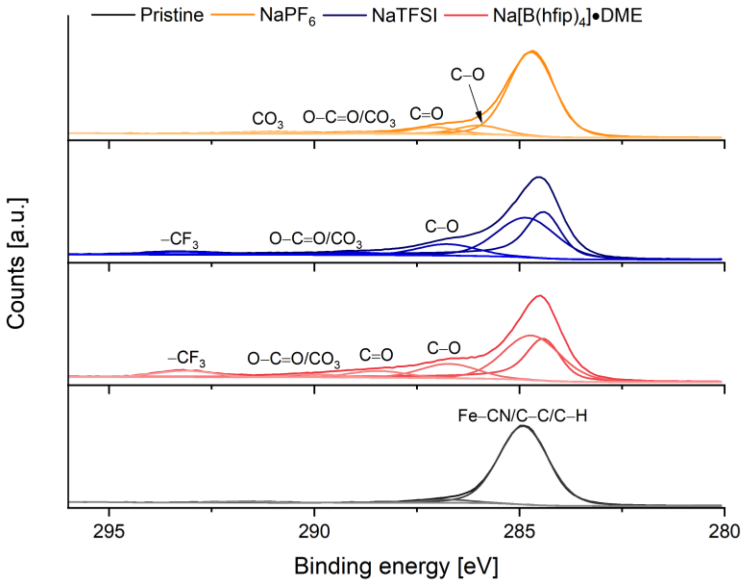


Figure S19 C1s XPS spectra of the pristine (black) and post-cycled Prussian white cathode using 1 M $NaPF_6$ (orange), 1 M NaTFSI (blue) and 1 M $Na[B(hfip)_4]{\cdot}DME$ in EC:DEC.

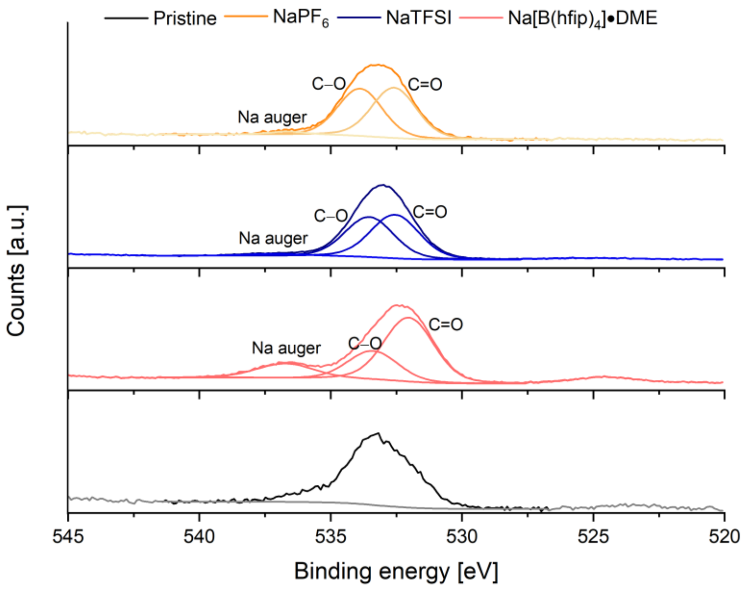


Figure S20 O1s XPS spectra of the pristine (black) and post-cycled Prussian white cathode using 1 M $NaPF_6$ (orange), 1 M NaTFSI (blue) and 1 M $Na[B(hfip)_4]{\cdot}DME$ in EC:DEC.

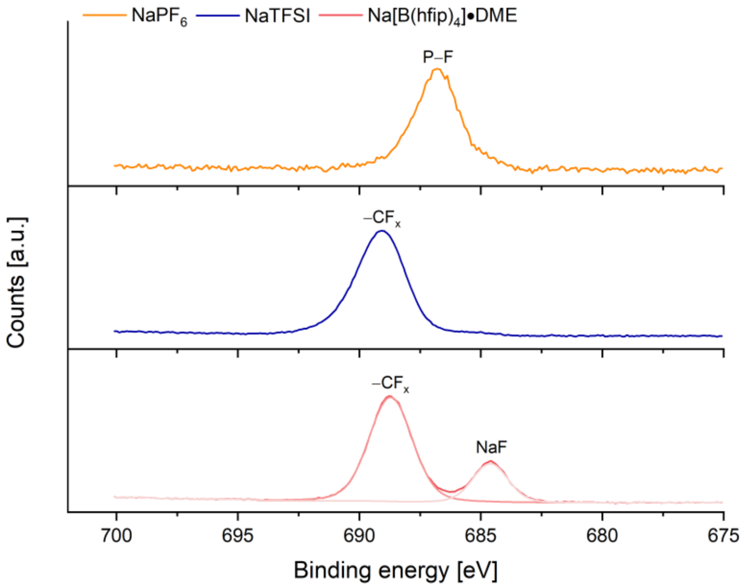


Figure S21 F1s XPS spectra of the post-cycled Prussian white cathode using 1 M $NaPF_6$ (orange), 1 M NaTFSI (blue) and 1 M $Na[B(hfip)_4]$·DME in EC:DEC. No fluorine was detected in the pristine Prussian white cathode.

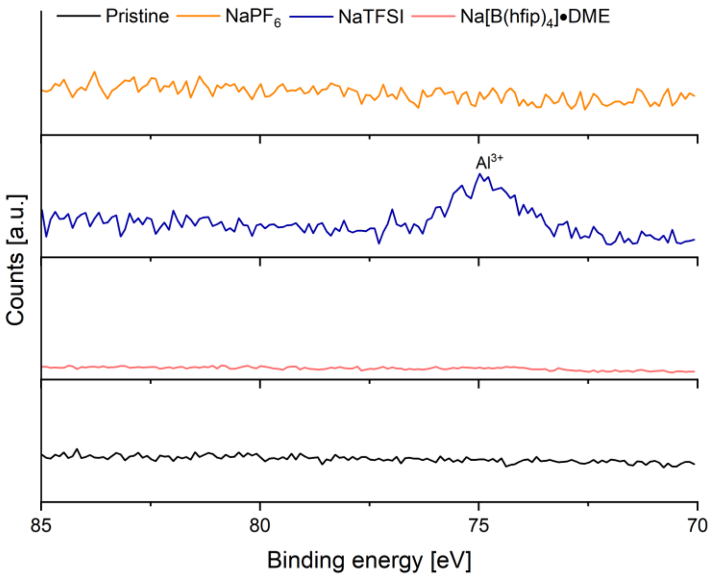


Figure S22 Al2p XPS spectra of the pristine (black) and post-cycled Prussian white cathode using 1 M $NaPF_6$ (orange), 1 M NaTFSI (blue) and 1 M $Na[B(hfip)_4]$·DME in EC:DEC.

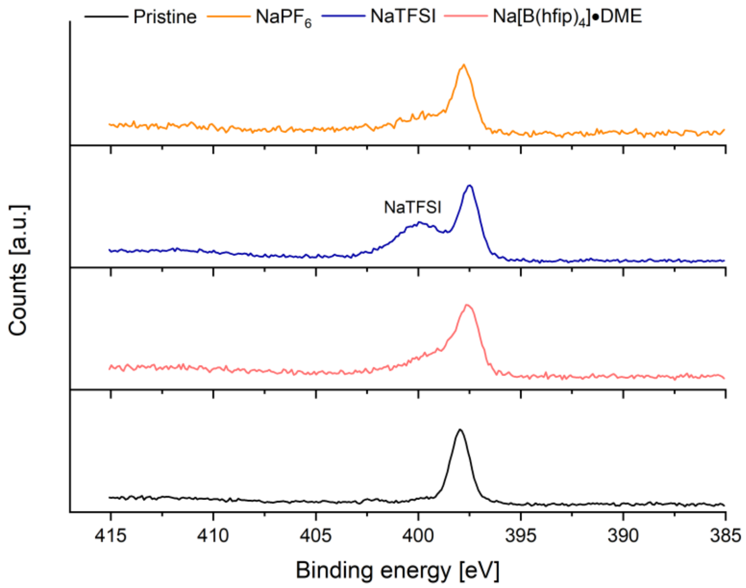


Figure S23 N1s XPS spectra of the pristine (black) and post-cycled Prussian white cathode using 1 M $NaPF_6$ (orange), 1 M NaTFSI (blue) and 1 M Na[B(hfip)$_4$]·DME in EC:DEC.

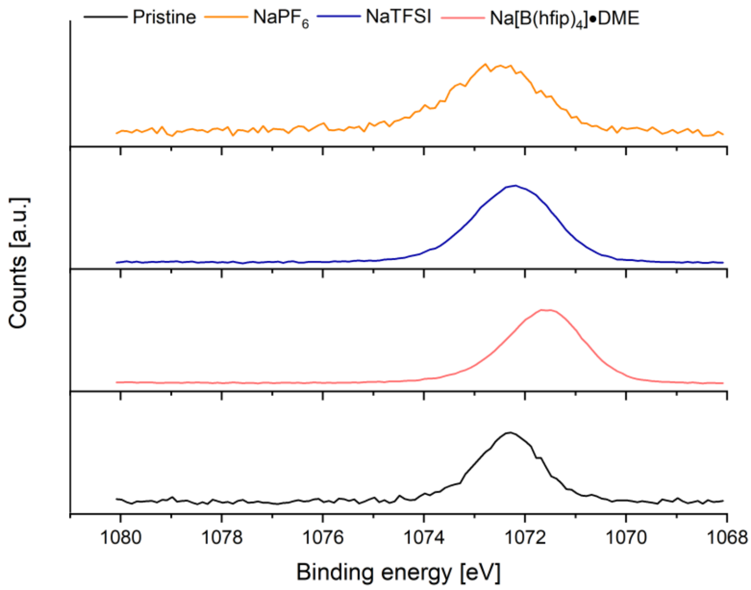


Figure S24 Na1s XPS spectra of the pristine (black) and post-cycled Prussian white cathode using 1 M $NaPF_6$ (orange), 1 M NaTFSI (blue) and 1 M Na[B(hfip)$_4$]·DME in EC:DEC.

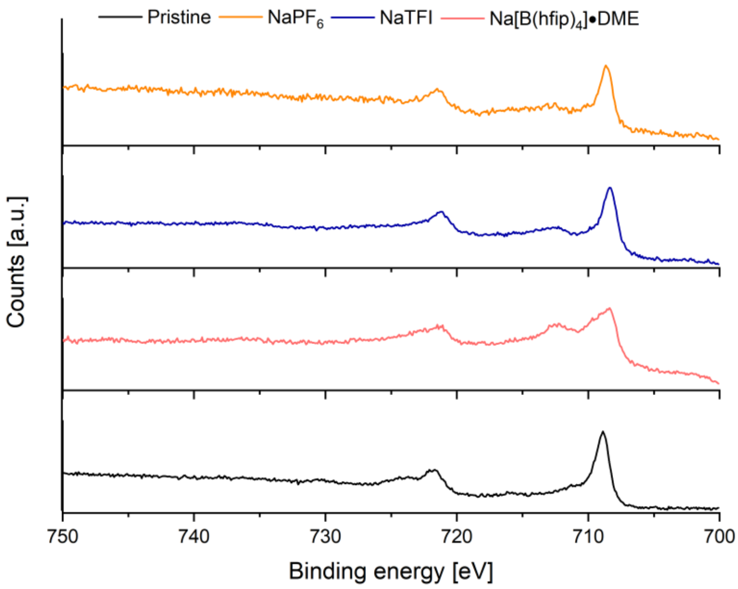


Figure S25 Fe2p XPS spectra of the pristine (black) and post-cycled Prussian white cathode using 1 M $NaPF_6$ (orange), 1 M NaTFSI (blue) and 1 M Na[B(hfip)$_4$]·DME in EC:DEC.

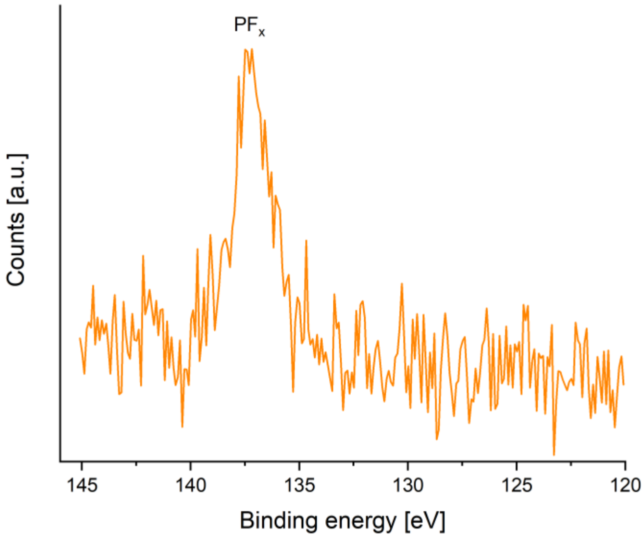


Figure S26 P2p XPS spectra of the post-cycled Prussian white cathode using 1 M $NaPF_6$ in EC:DEC. No phosphorus was detected in the pristine Prussian white cathode.

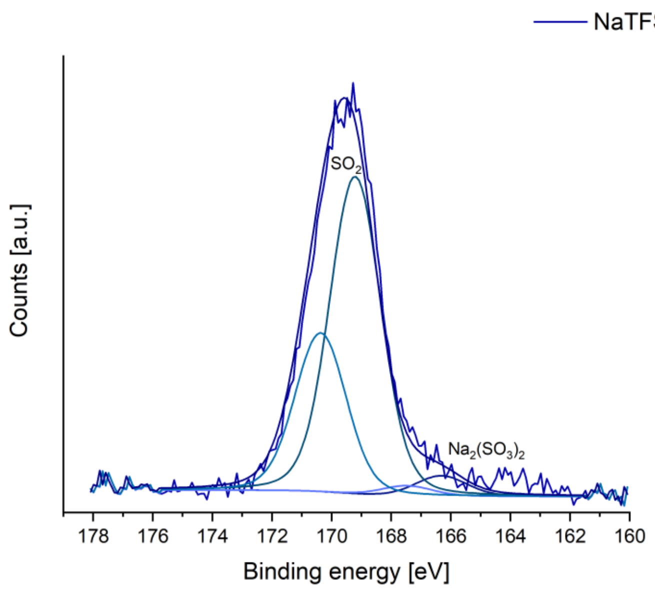


Figure S27 S2p XPS spectra of the post-cycled Prussian white cathode using 1 M NaTFSI in EC:DEC. No sulfur was detected in the pristine Prussian white cathode.

<u>Post-cycled hard carbon anode</u>

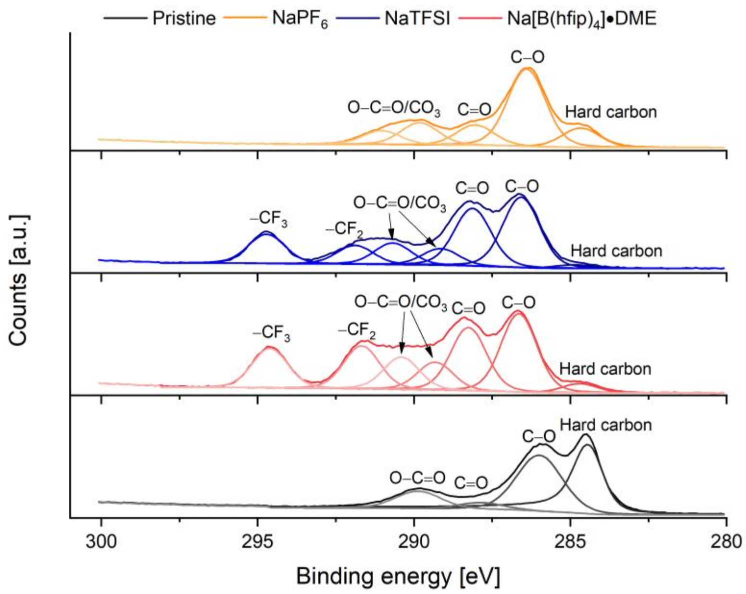


Figure S28 C1s XPS spectra of the pristine (black) and post-cycled hard carbon anode using 1 M $NaPF_6$ (orange), 1 M NaTFSI (blue) and 1 M Na[B(hfip)$_4$]·DME in EC:DEC.

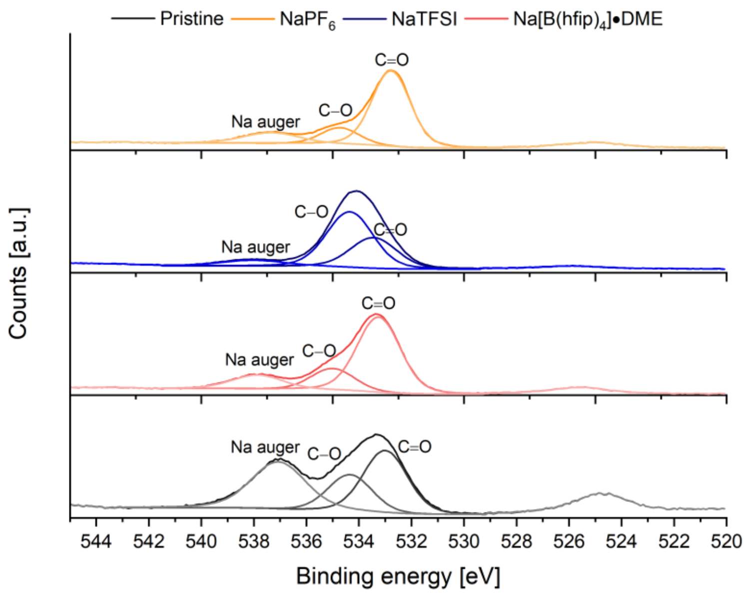


Figure S29 O1s XPS spectra of the pristine (black) and post-cycled hard carbon anode using 1 M $NaPF_6$ (orange), 1 M NaTFSI (blue) and 1 M Na[B(hfip)$_4$]·DME in EC:DEC.

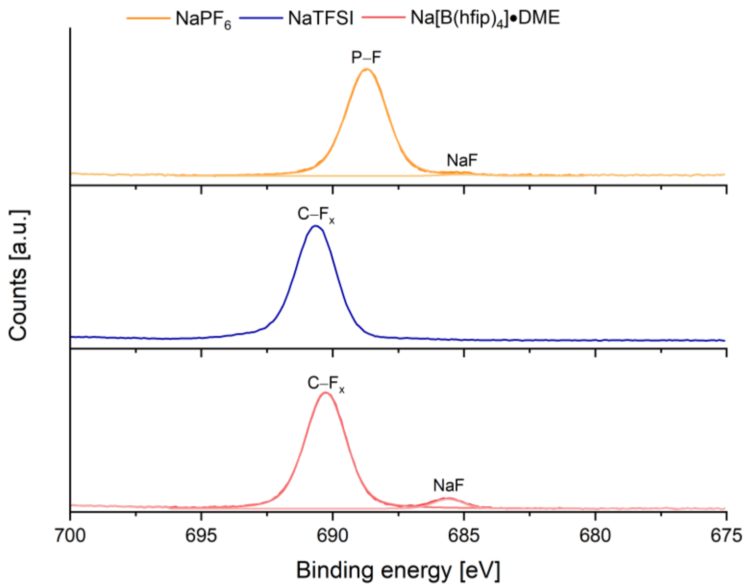


Figure S30 F1s XPS spectra of the post-cycled hard carbon anode using 1 M $NaPF_6$ (orange), 1 M NaTFSI (blue) and 1 M Na[B(hfip)$_4$]·DME in EC:DEC. No fluorine was detected in the pristine hard carbon anode.

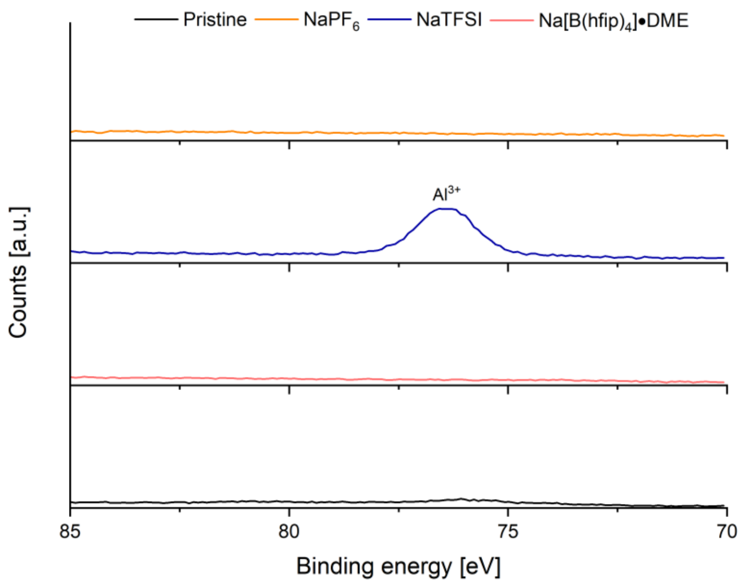


Figure S31 Al2p XPS spectra of the pristine (black) and post-cycled hard carbon anode using 1 M $NaPF_6$ (orange), 1 M NaTFSI (blue) and 1 M $Na[B(hfip)_4]\cdot DME$ in EC:DEC.

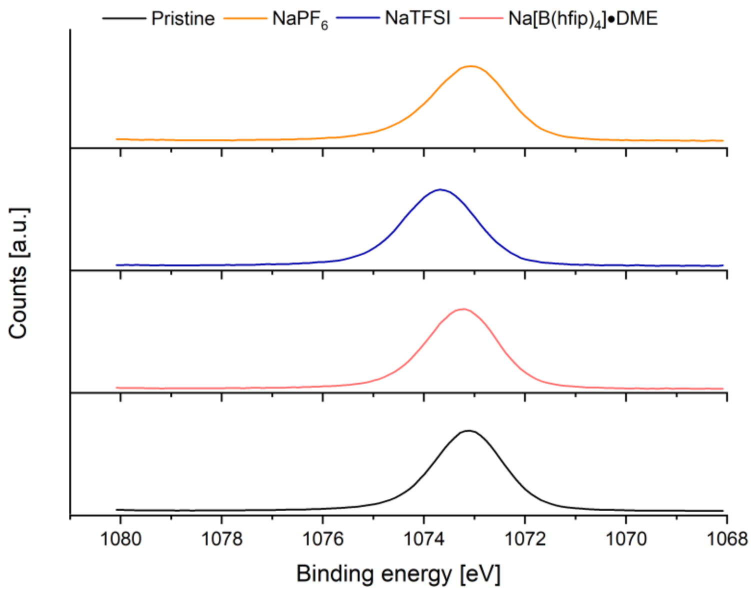


Figure S32 Na1s XPS spectra of the pristine (black) and post-cycled Prussian white cathode using 1 M $NaPF_6$ (orange), 1 M NaTFSI (blue) and 1 M $Na[B(hfip)_4]\cdot DME$ in EC:DEC.

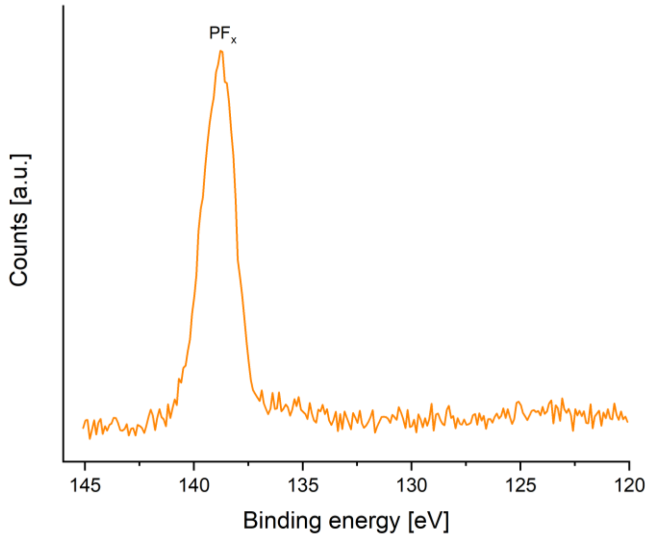


Figure S33 P2p XPS spectra of the post-cycled hard carbon anode using 1 M $NaPF_6$ in EC:DEC. No phosphorus was detected in the hard carbon anode.

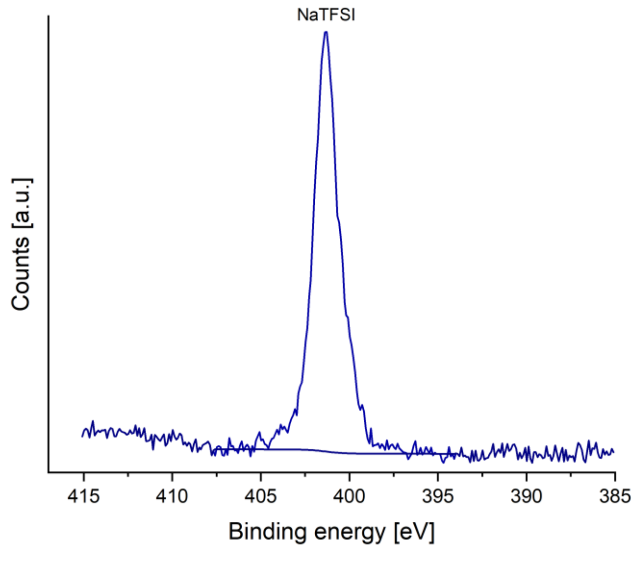


Figure S34 N1s XPS spectra of the post-cycled hard carbon anode using 1 M NaTFSI in EC:DEC. No nitrogen was detected in the hard carbon anode.

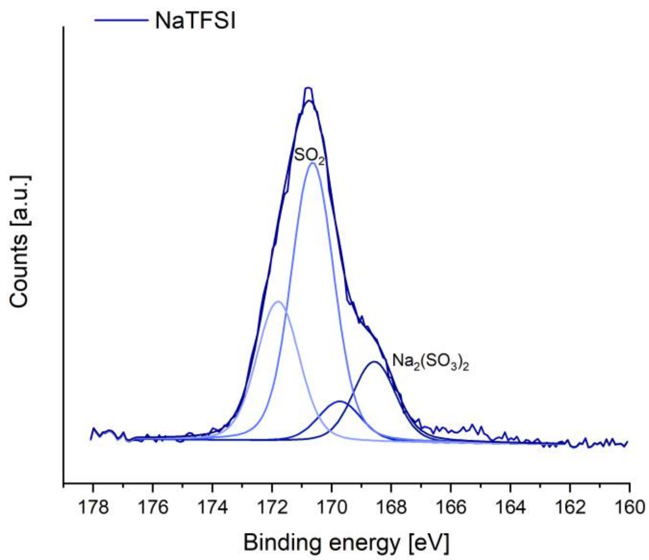


Figure S35 S2p XPS spectra of the post-cycled hard carbon anode using 1 M NaTFSI in EC:DEC. No sulfur was detected in the pristine Prussian white cathode.

S3 Scanning electron microscopy (SEM) and digital microscopy images.

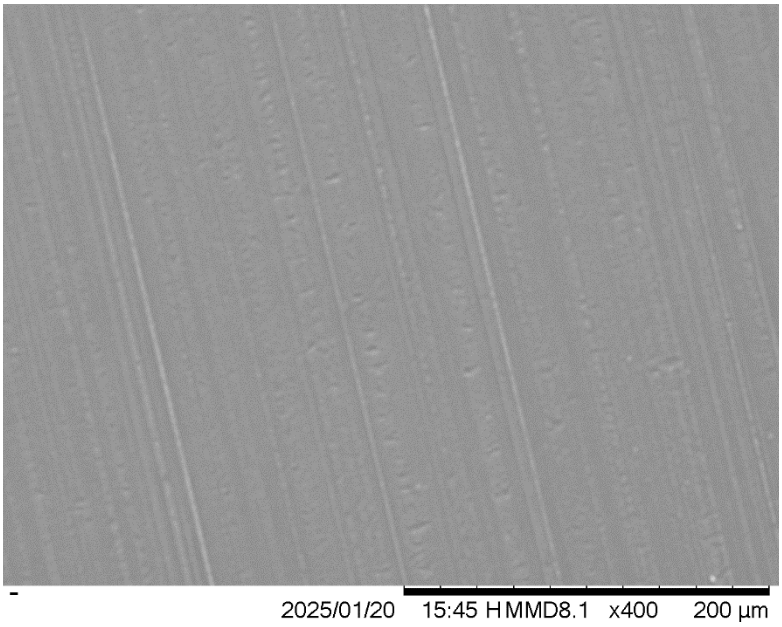


Figure S36 Representative SEM surface image of pristine aluminium foil.

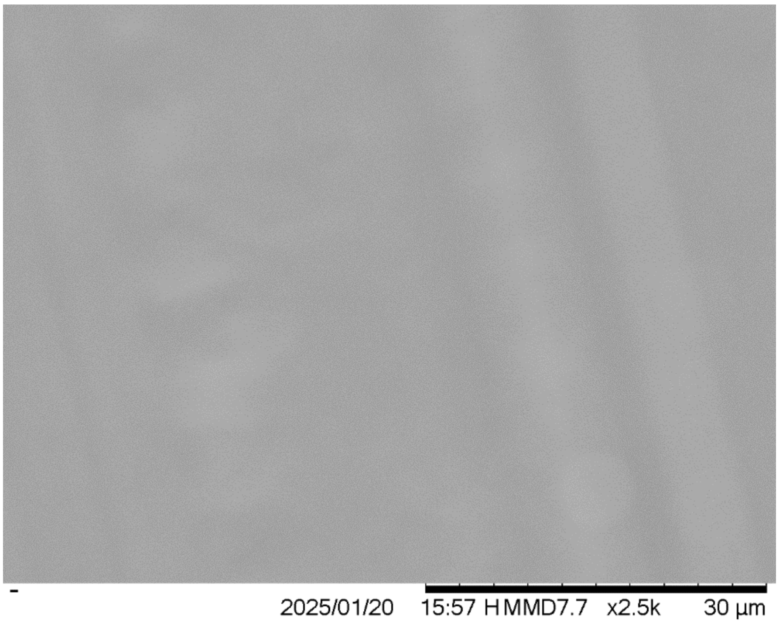


Figure S37 Representative SEM surface image of pristine aluminium foil.

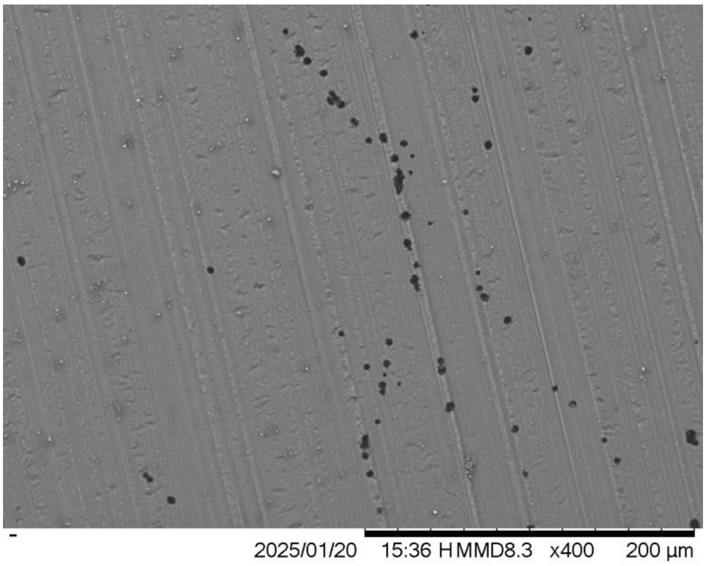


Figure S38 SEM surface image of the aluminium working electrode that was used in the cyclic voltammetry experiment using 1 M NaTFSI measured between 0.01–4.2 V vs. Na/Na$^+$.

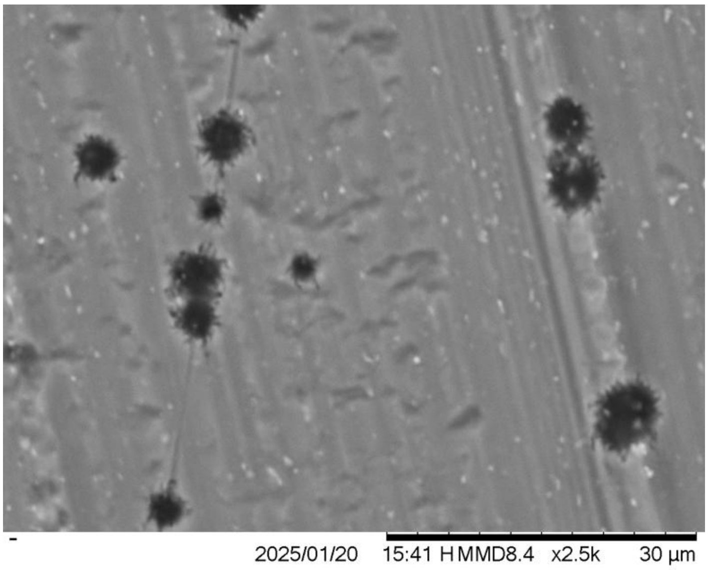


Figure S39 SEM surface image of the aluminium working electrode that was used in the cyclic voltammetry experiment using 1 M NaTFSI measured between 0.01–4.2 V vs. Na/Na$^+$.

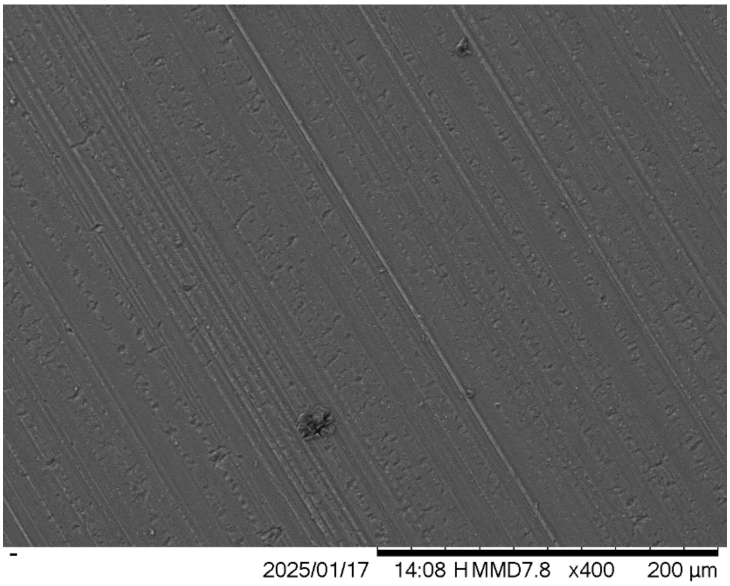


Figure S40 Representative SEM surface image of the aluminium working electrode that was used in the cyclic voltammetry experiment using 1 M NaTFSI measured between 0.01–3.8 V vs. Na/Na$^+$.

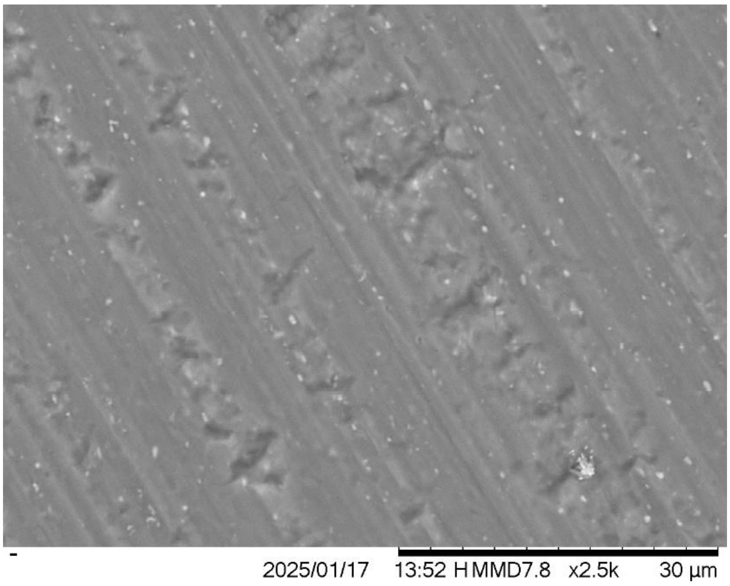


Figure S41 Representative SEM surface image of the aluminium working electrode that was used in the cyclic voltammetry experiment using 1 M NaTFSI measured between 0.01–3.8 V vs. Na/Na$^+$.

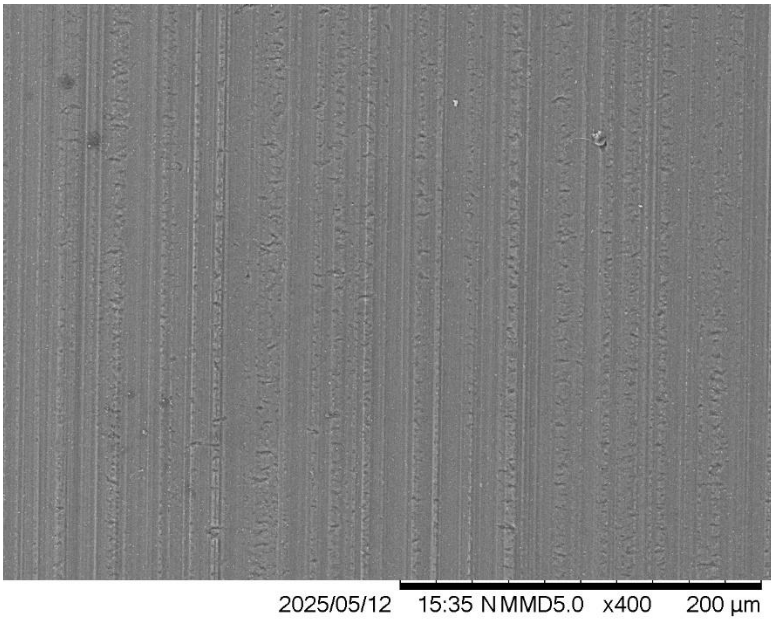


Figure S42 Representative SEM surface image of the aluminium working electrode that was used in the cyclic voltammetry experiment using 1 M NaTFSI + 2 wt% $NaPF_6$, measured between 0.01–4.2 V vs. Na/Na^+.

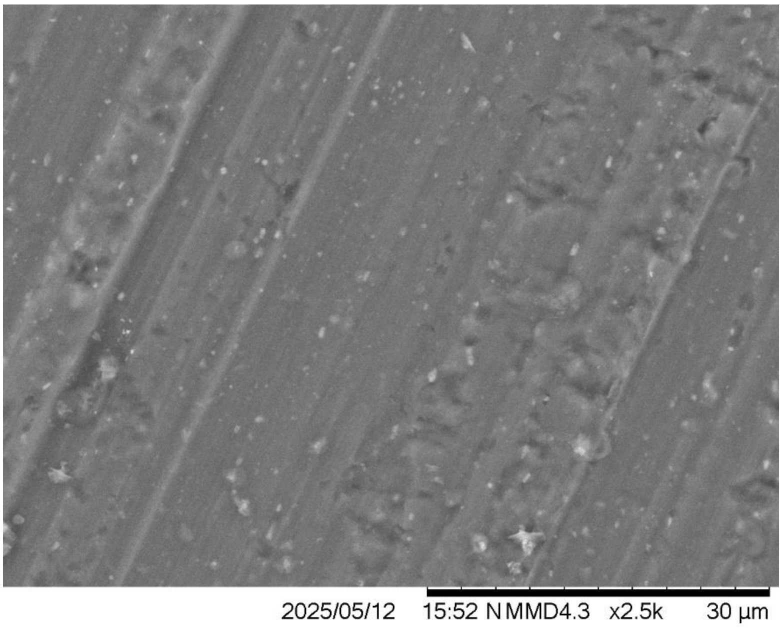


Figure S43 Representative SEM surface image of the aluminium working electrode that was used in the cyclic voltammetry experiment using 1 M NaTFSI + 2 wt% $NaPF_6$, measured between 0.01–4.2 V vs. Na/Na^+.

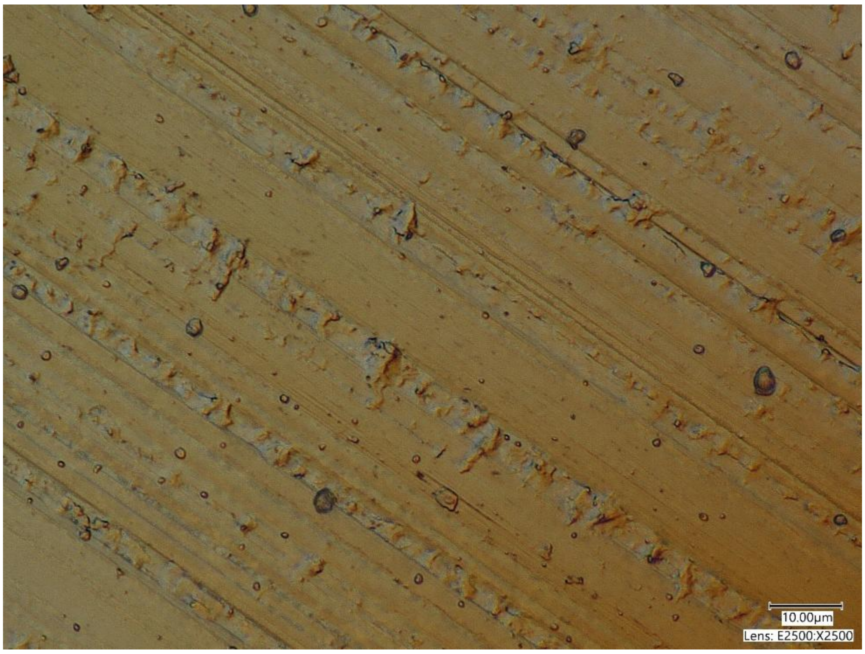


Figure S44 Digital microscope image of the pristine aluminium foil.

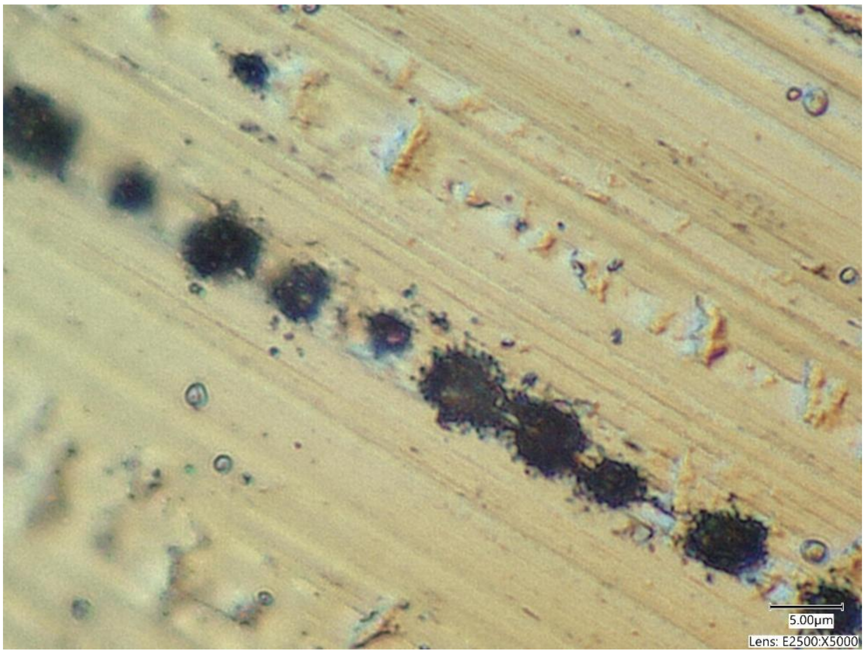


Figure S45 Digital microscope image of the aluminium working electrode that was used in the cyclic voltammetry experiment using 1 M NaTFSI measured between 0.01–4.2 V vs. Na/Na^+.

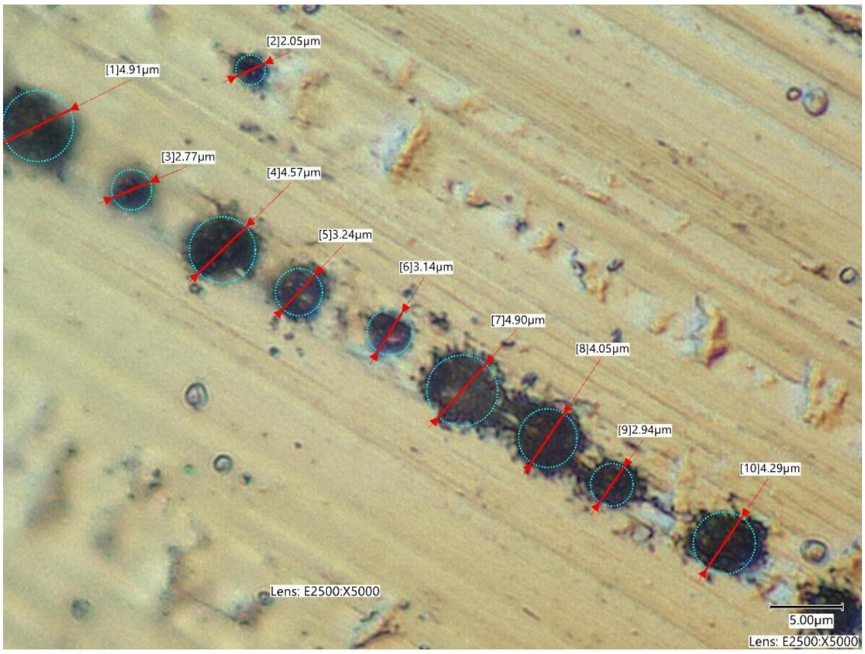
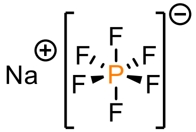


Figure S46 Digital microscope images of the aluminium working electrode that was used in the cyclic voltammetry experiment using 1 M NaTFSI measured between 0.01–4.2 V vs. Na/Na^+, showing the diameter of the pitting.

S4 NMR Spectroscopy.

S4.1 NMR spectra of synthesised electrolyte salts.

Figure S47 ^{1}H NMR (500 MHz, CD_3CN, 295 K) spectrum of $NaPF_6$.



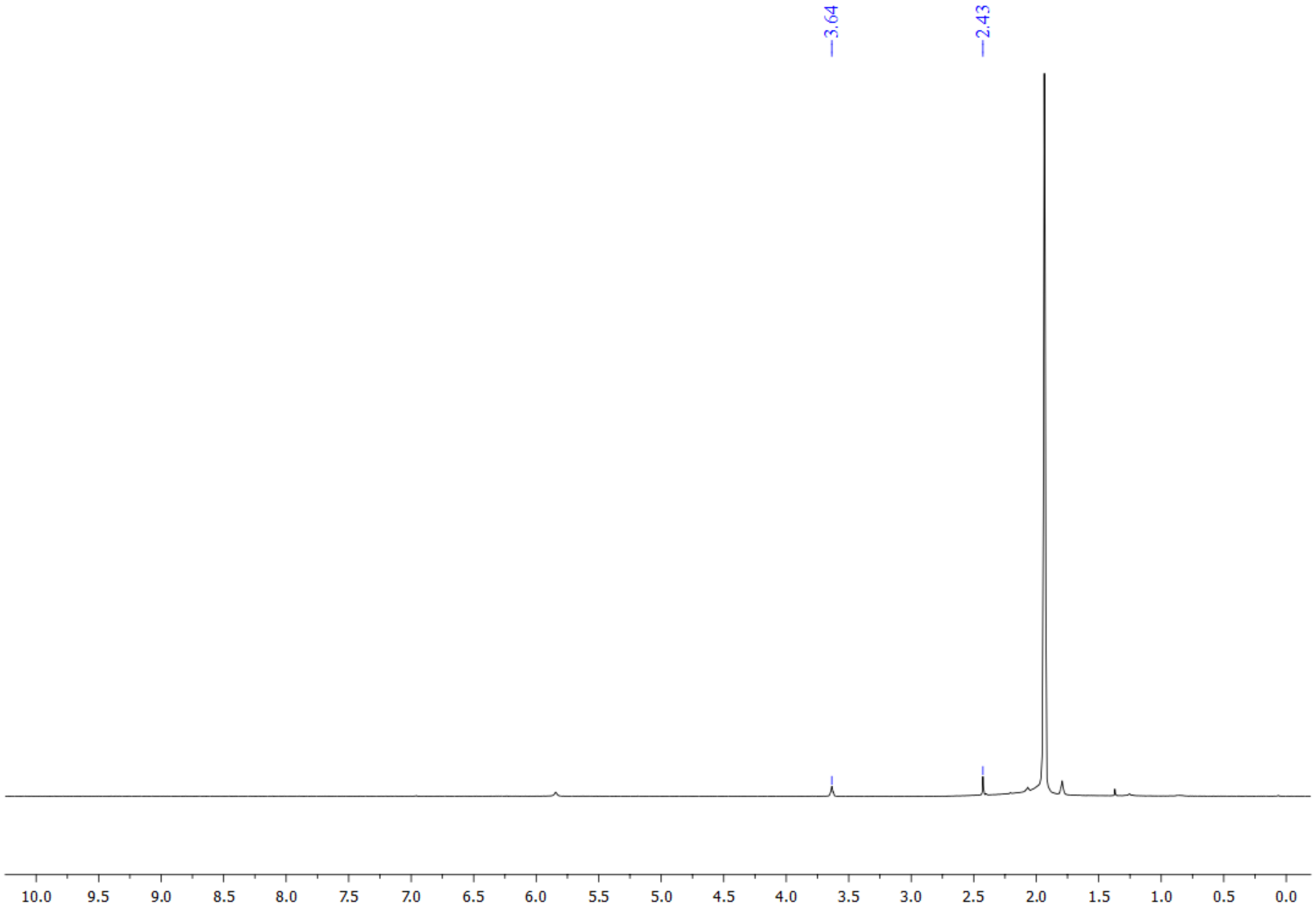
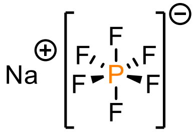


Figure S48 ^{19}F NMR (471 MHz, CD_3CN, 295 K) spectrum of $NaPF_6$.



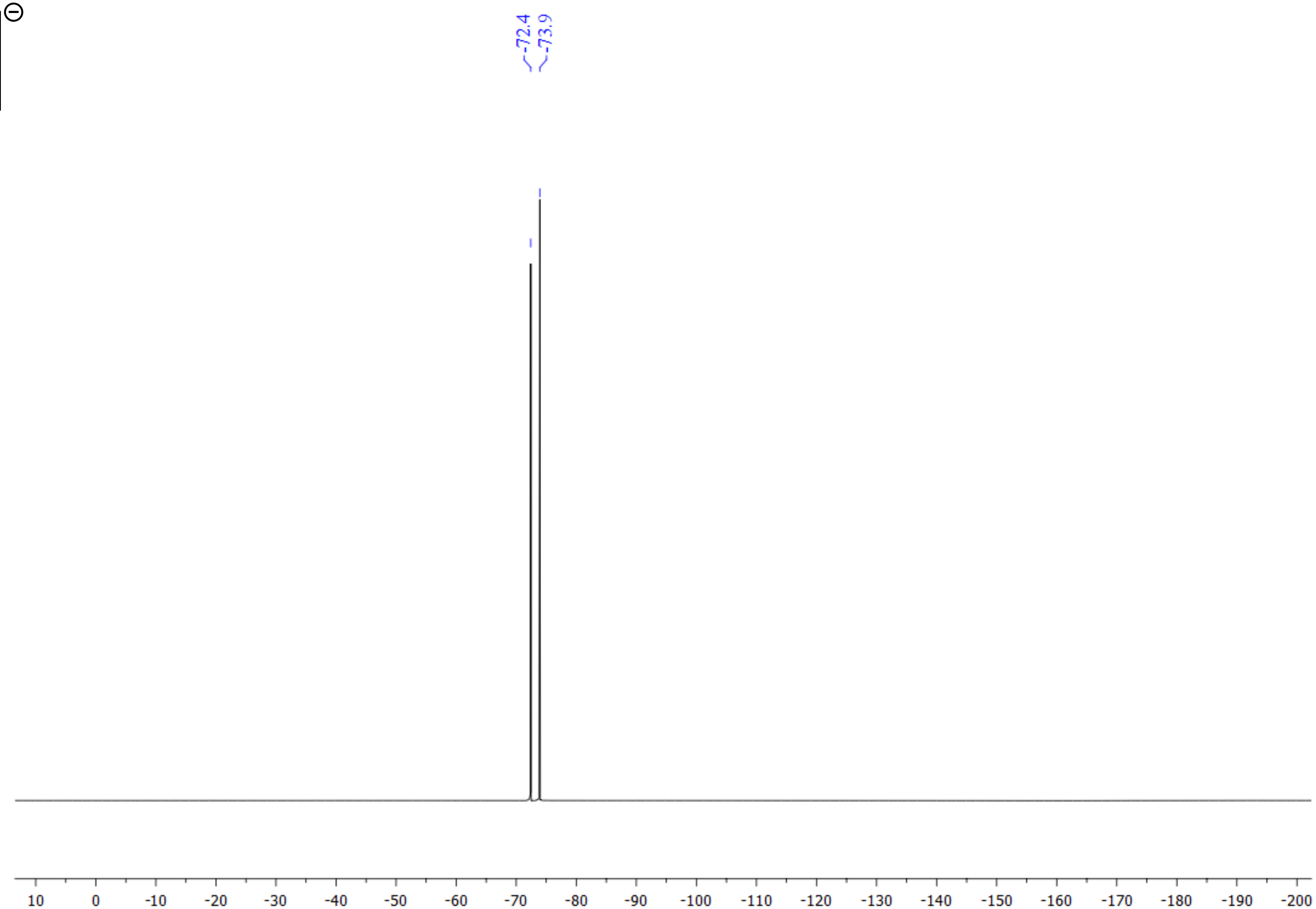
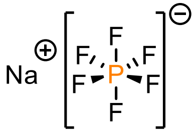


Figure S49 ^{31}P NMR (202 MHz, CD_3CN, 295 K) spectrum of $NaPF_6$.



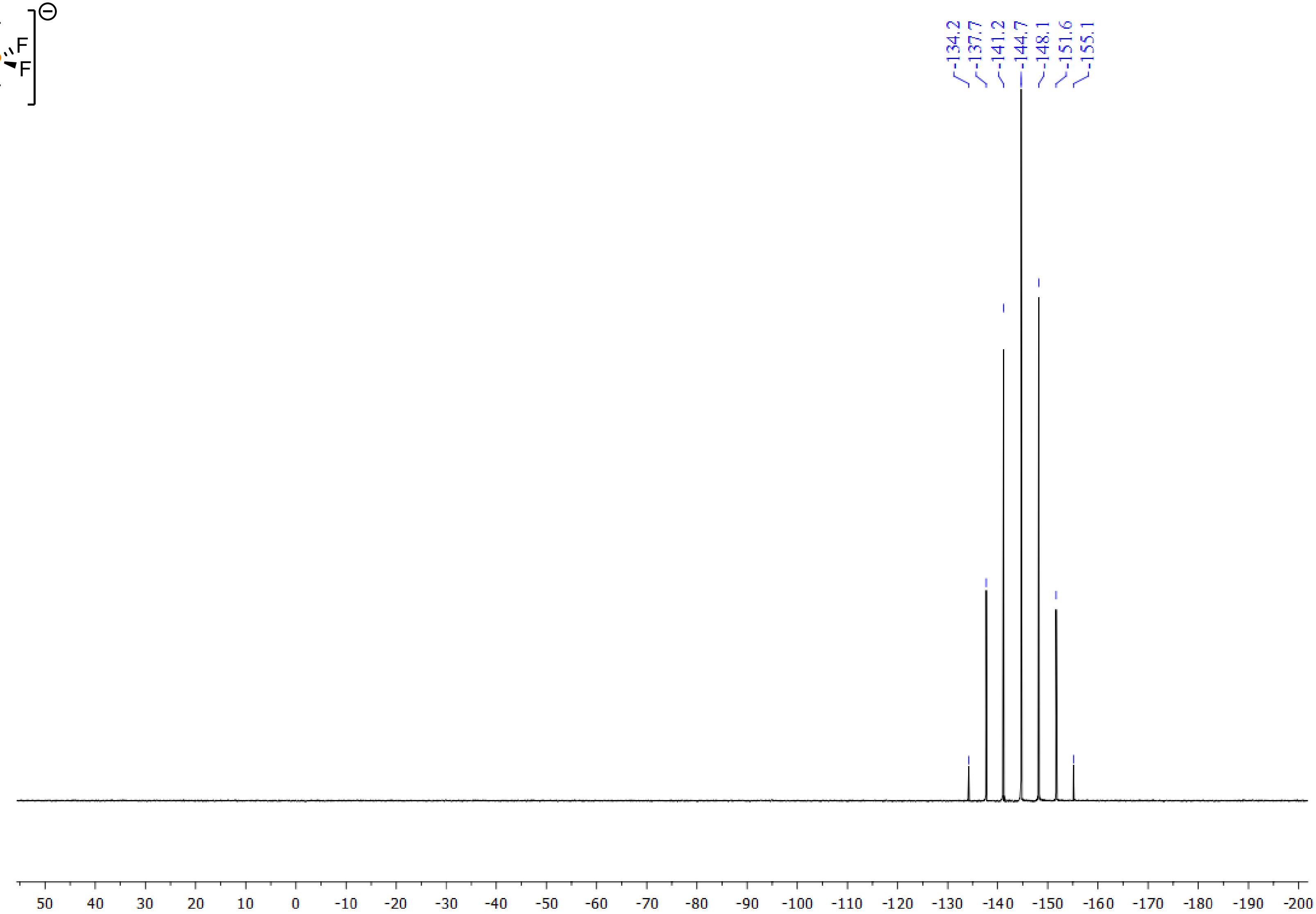
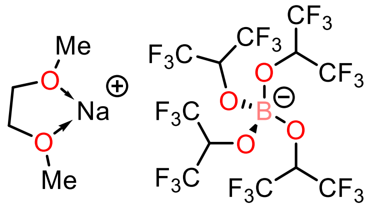


Figure S50 ^{1}H NMR (500 MHz, CD_3CN, 295 K) spectrum of Na[B(hfip)$_4$]·DME.



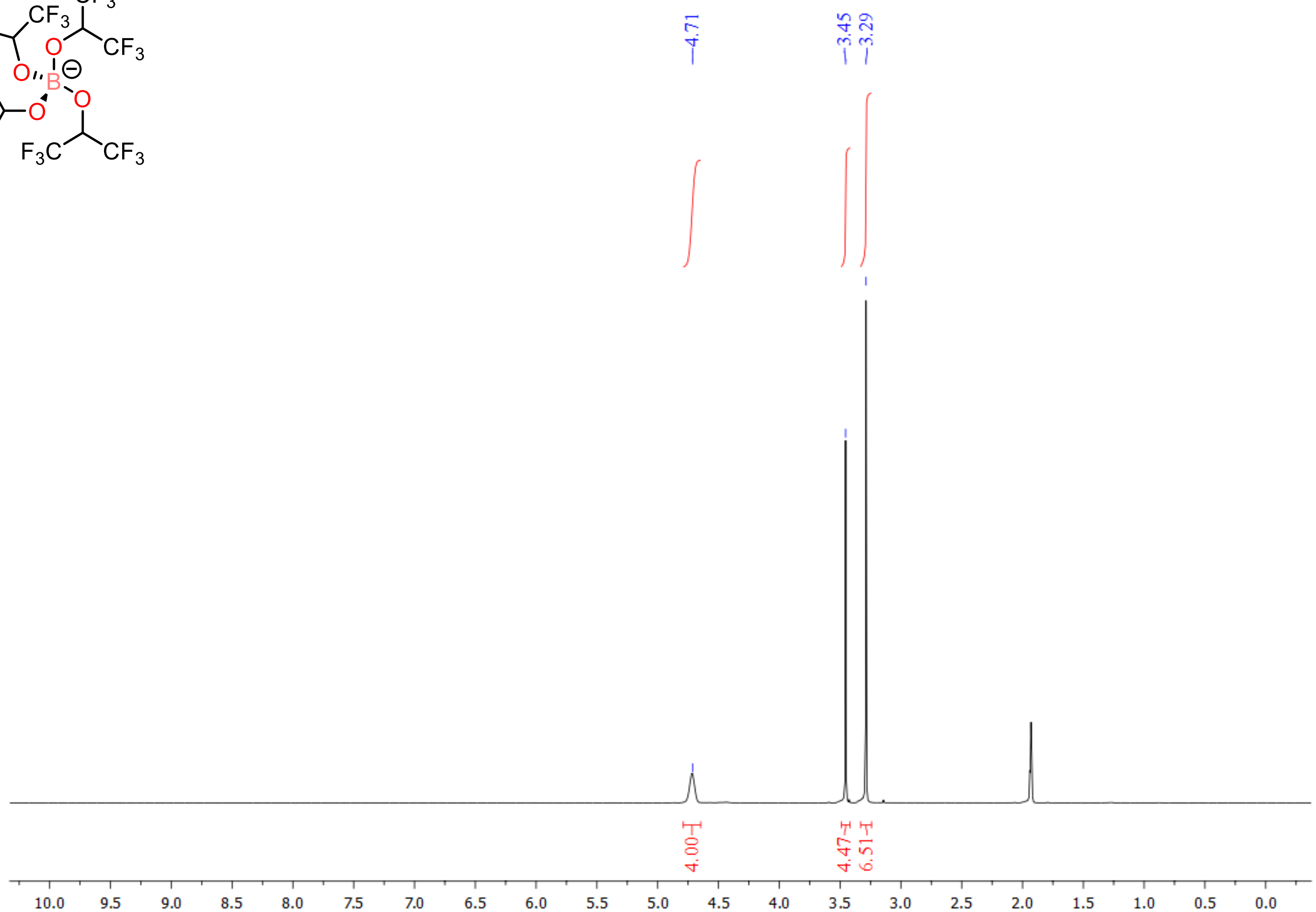


Figure S51 ^{19}F NMR (471 MHz, CD_3CN, 295 K) spectrum of $Na[B(hfip)_4]·DME$.

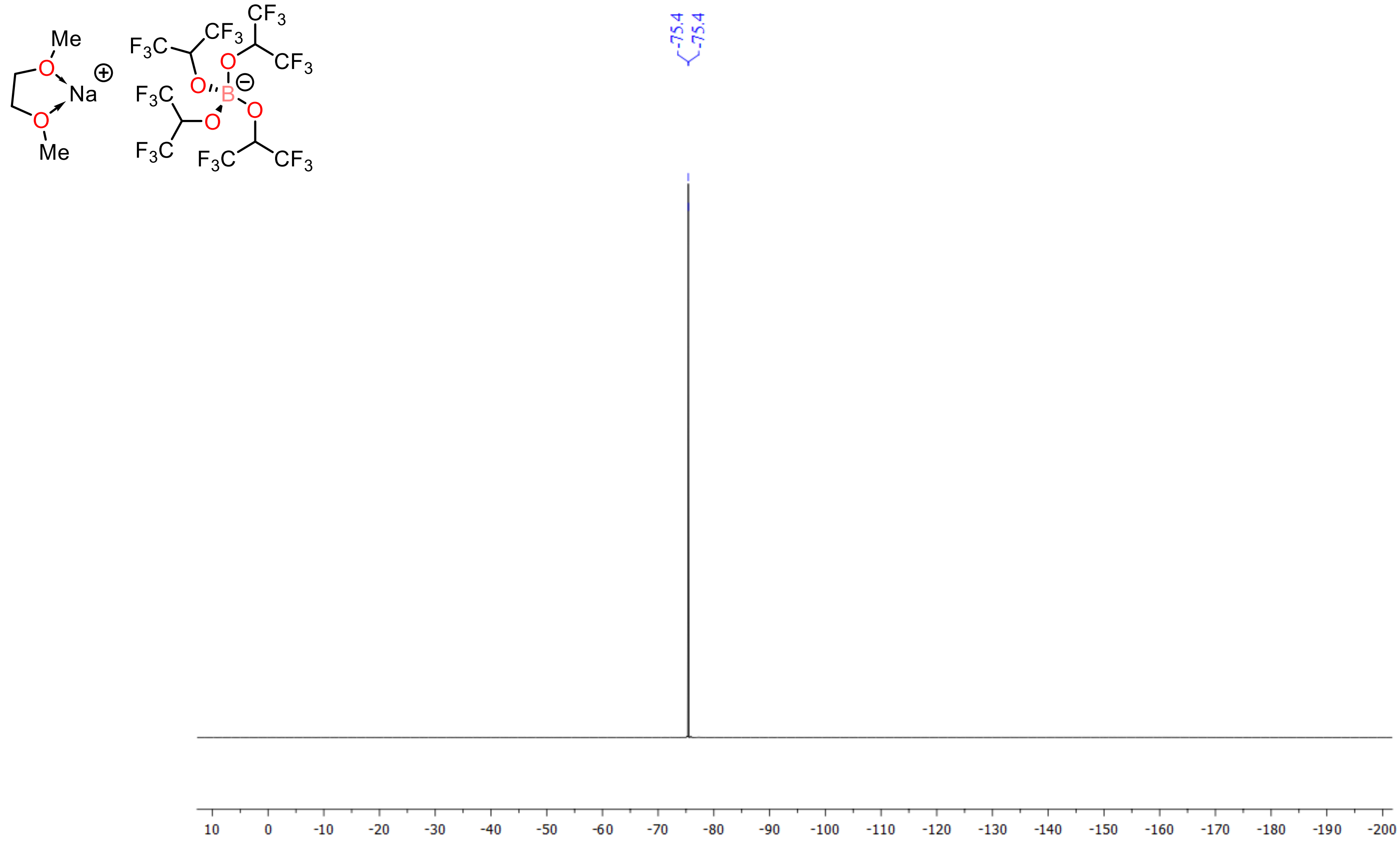
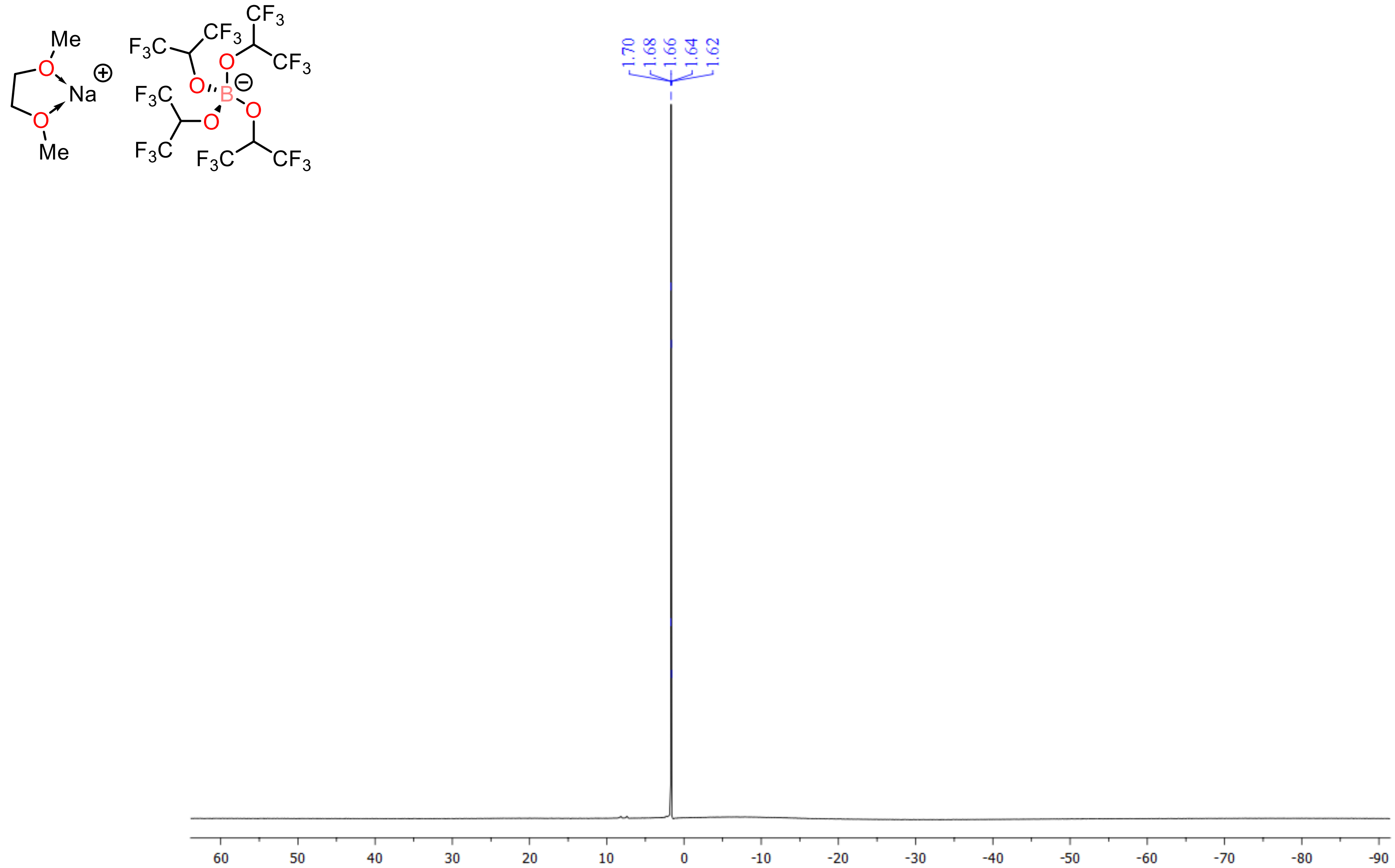


Figure S52 ^{11}B NMR (160 MHz, $(CD_3)_2SO$, 295 K) spectrum of Na[B(hfip)$_4$]·DME.



S4.2 NMR spectra of pristine electrolytes.

Figure S53 ^1H NMR (500 MHz, $(CD_3)_2SO$, 295 K) spectrum of pristine 1 M $NaPF_6$ in EC:DEC (1:1 v/v).

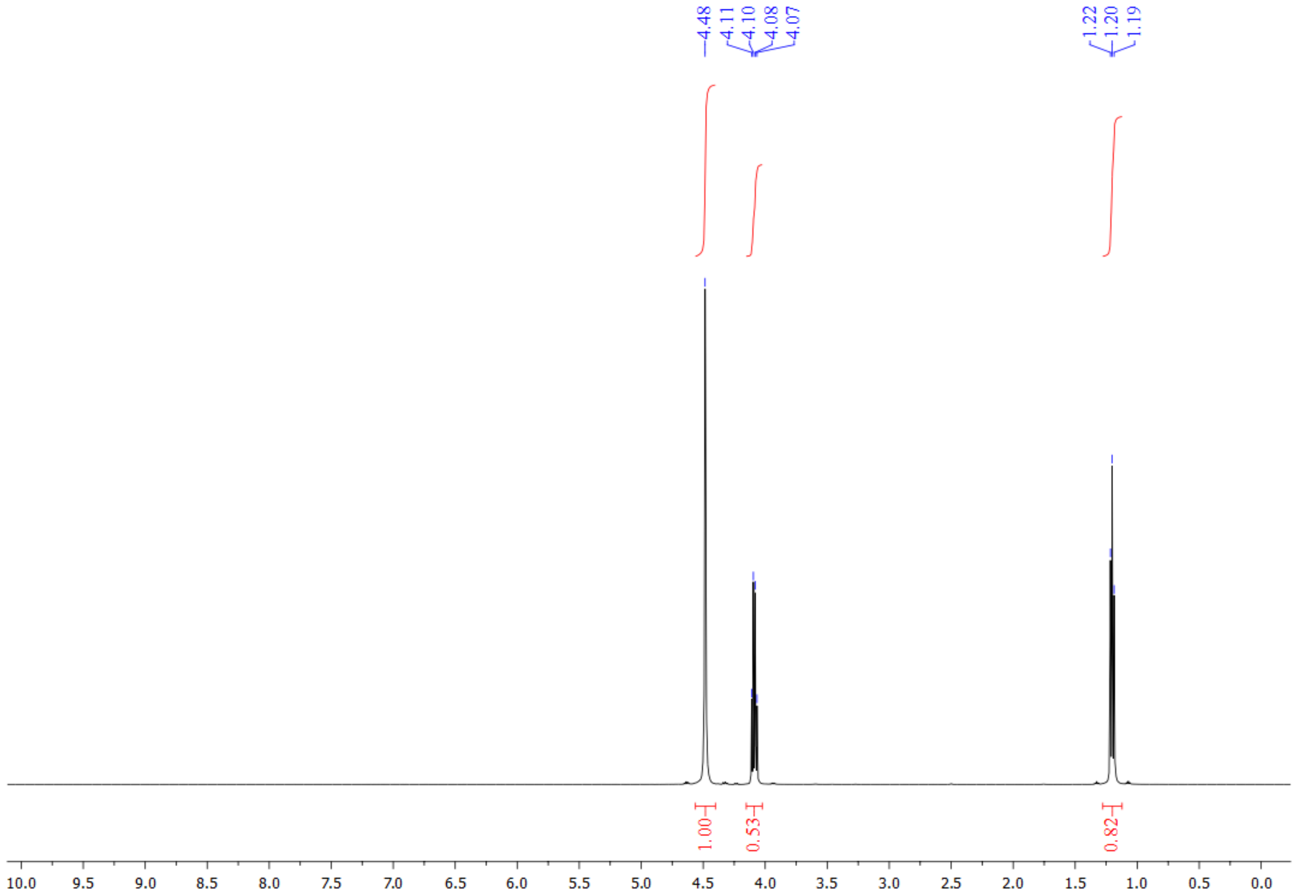


Figure S54 ^{19}F NMR (471 MHz, $(CD_3)_2SO$, 295 K) spectrum of pristine 1 M $NaPF_6$ in EC:DEC (1:1 v/v).

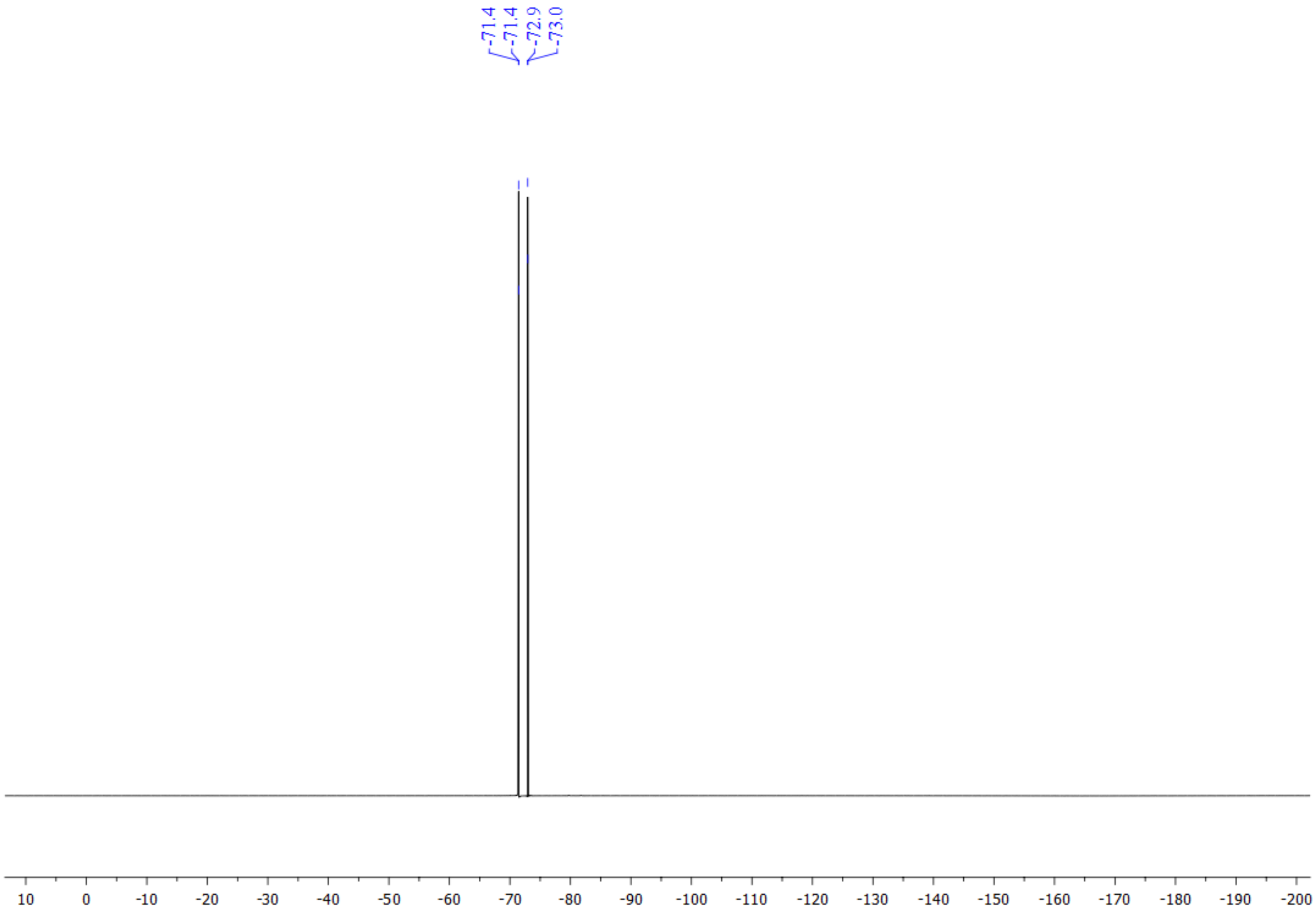


Figure S55 ^{31}P NMR (202 MHz, $(CD_3)_2SO$, 295 K) spectrum of pristine 1 M $NaPF_6$ in EC:DEC (1:1 v/v).

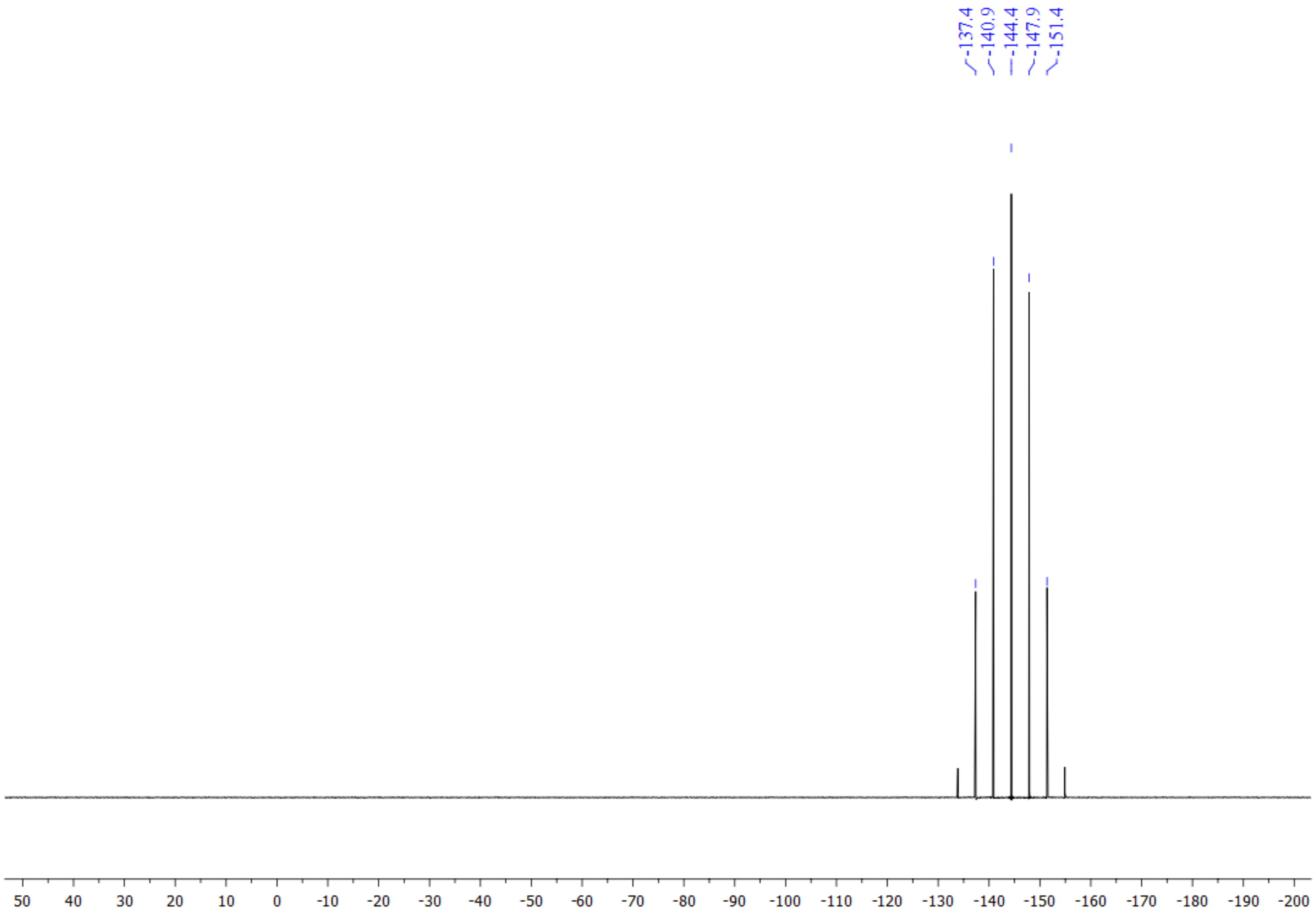


Figure S56 ^{1}H NMR (500 MHz, $(CD_3)_2SO$, 295 K) spectrum of pristine 1 M NaTFSI in EC:DEC (1:1 v/v).

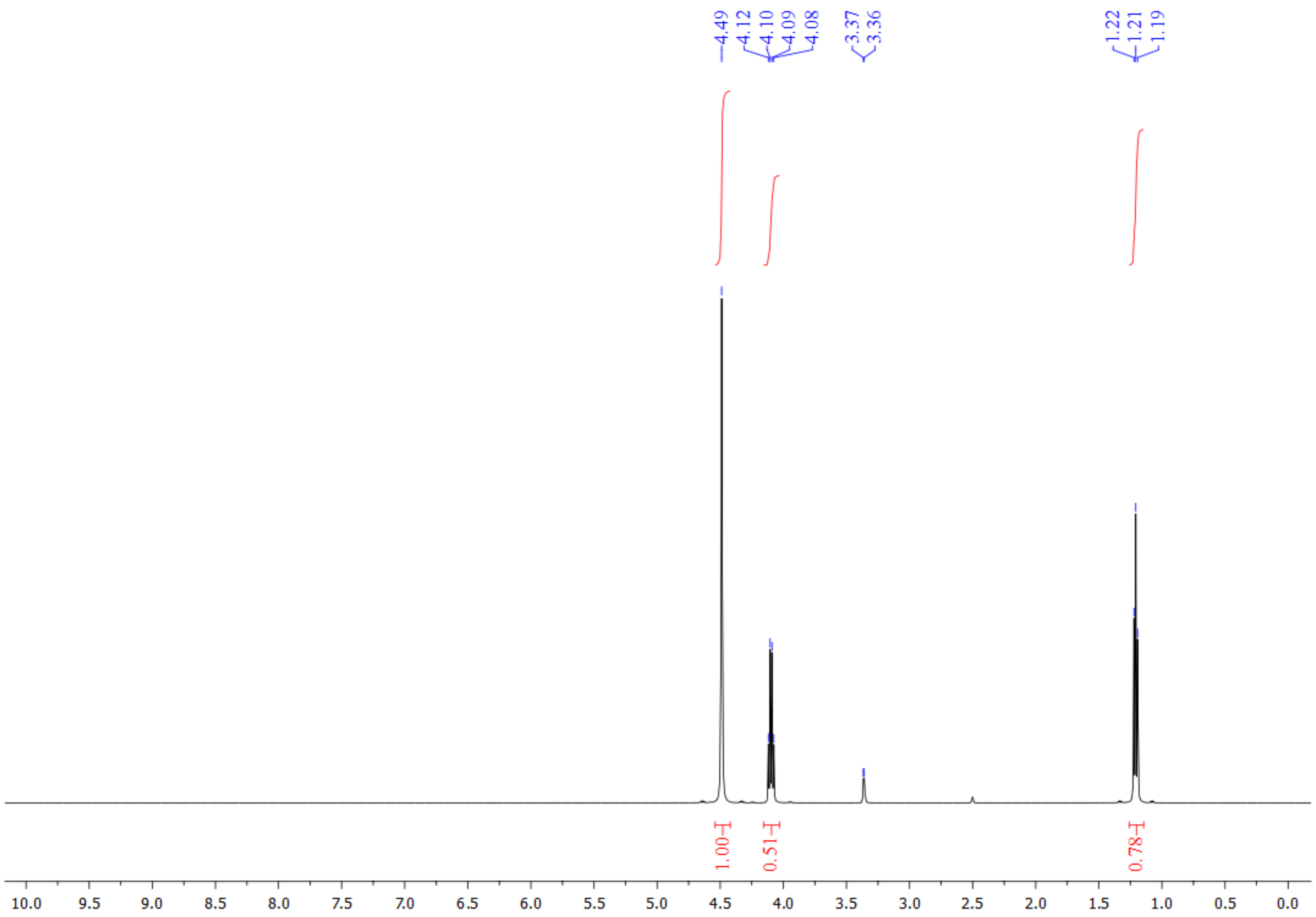


Figure S57 ^{19}F NMR (471 MHz, $(CD_3)_2SO$, 295 K) spectrum of pristine 1 M NaTFSI in EC:DEC (1:1 v/v).

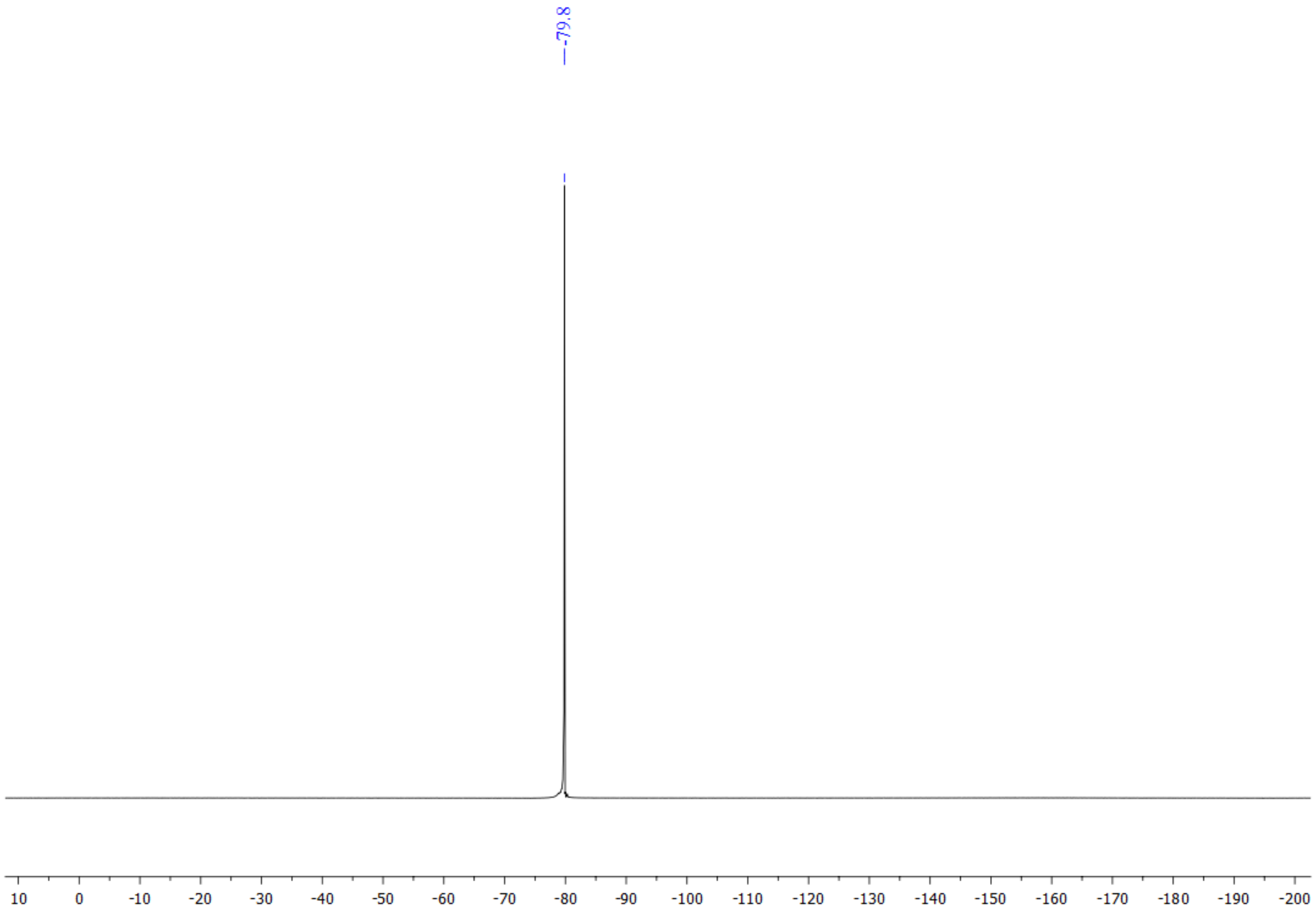


Figure S58 ^{1}H NMR (500 MHz, $(CD_3)_2SO$, 295 K) spectrum of pristine 1 M Na[B(hfip)$_4$]·DME in EC:DEC (1:1 v/v).

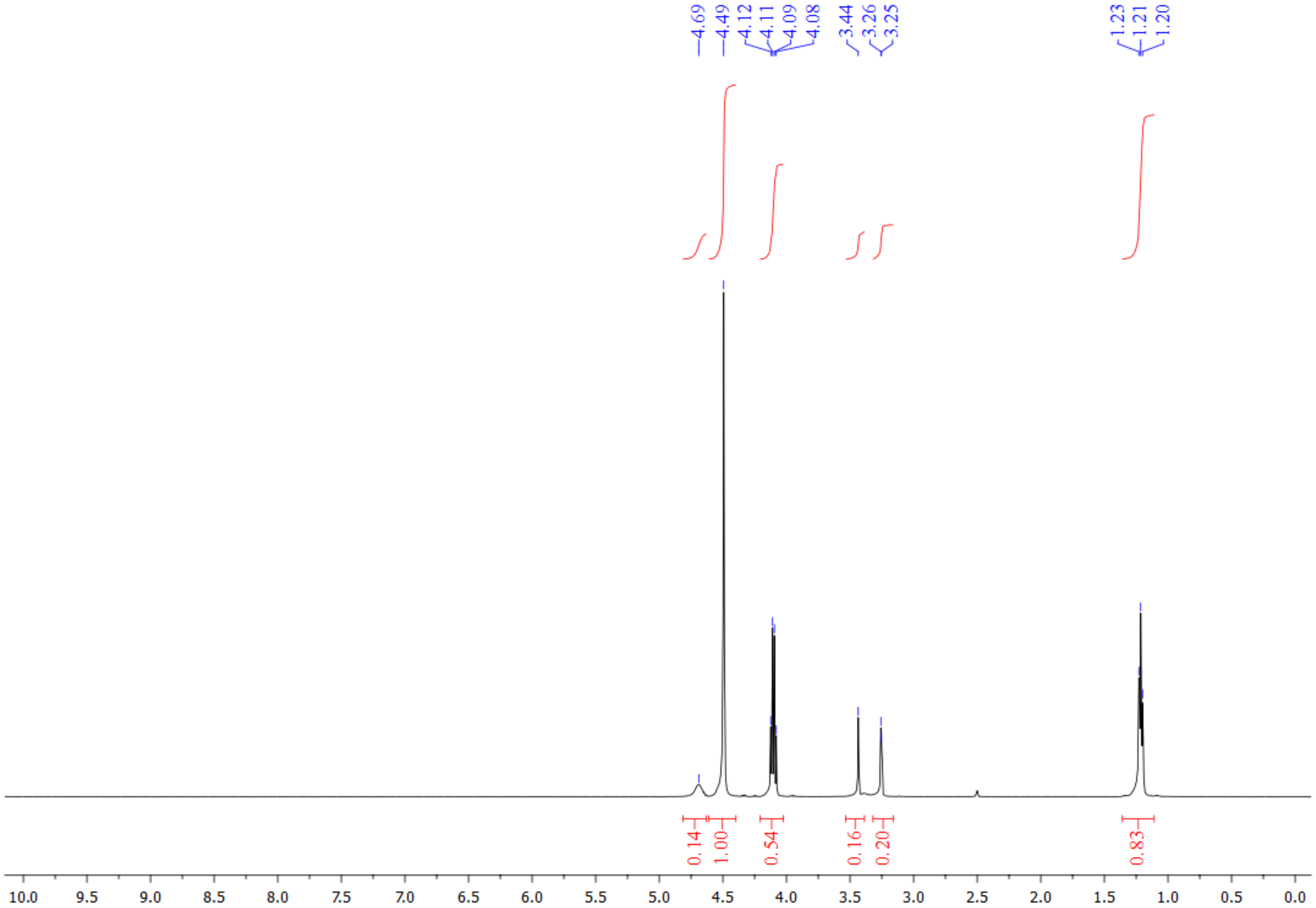


Figure S59 ^{19}F NMR (471 MHz, $(CD_3)_2SO$, 295 K) spectrum of pristine 1 M $Na[B(hfip)_4]\cdot DME$ in EC:DEC (1:1 v/v).

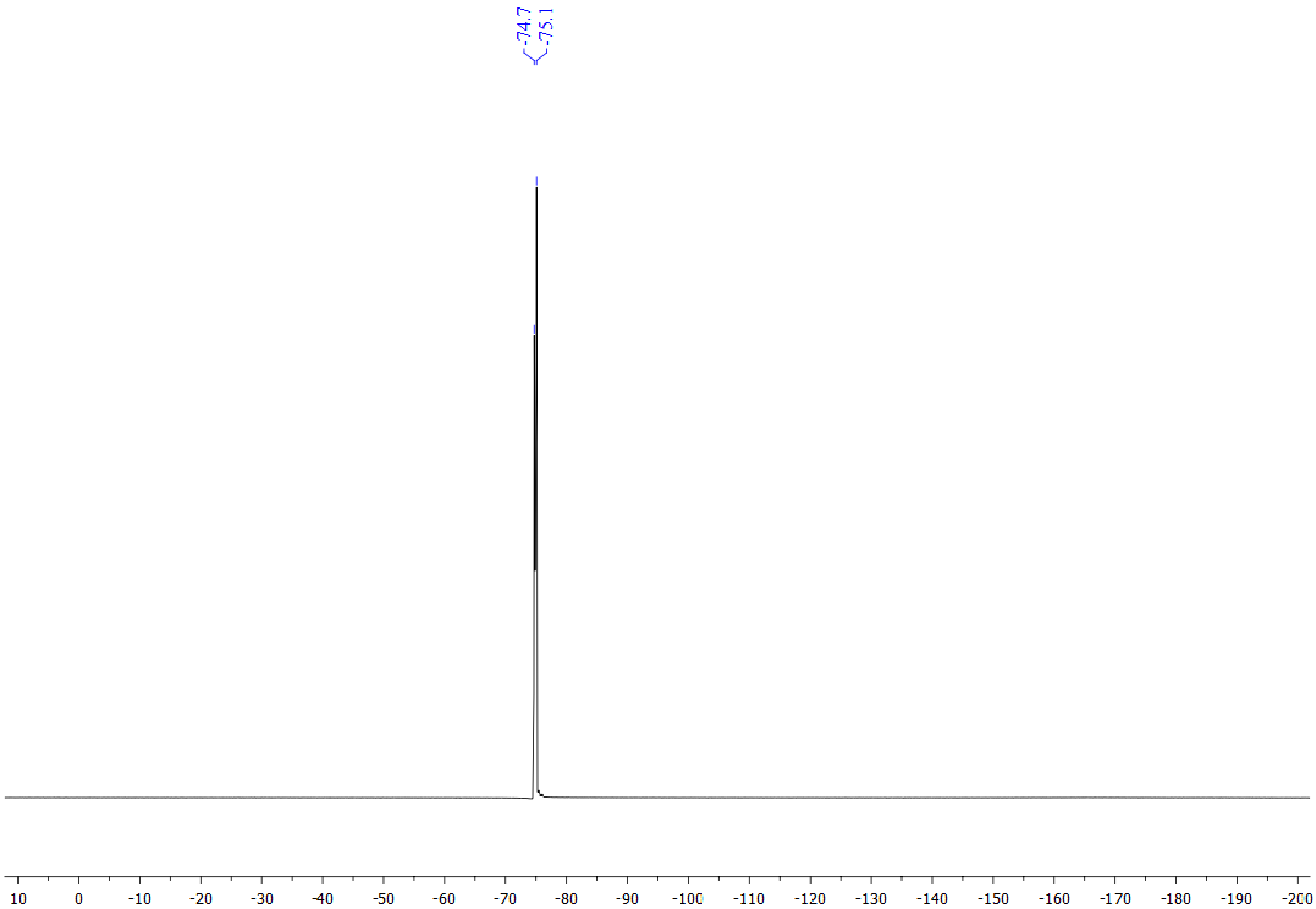
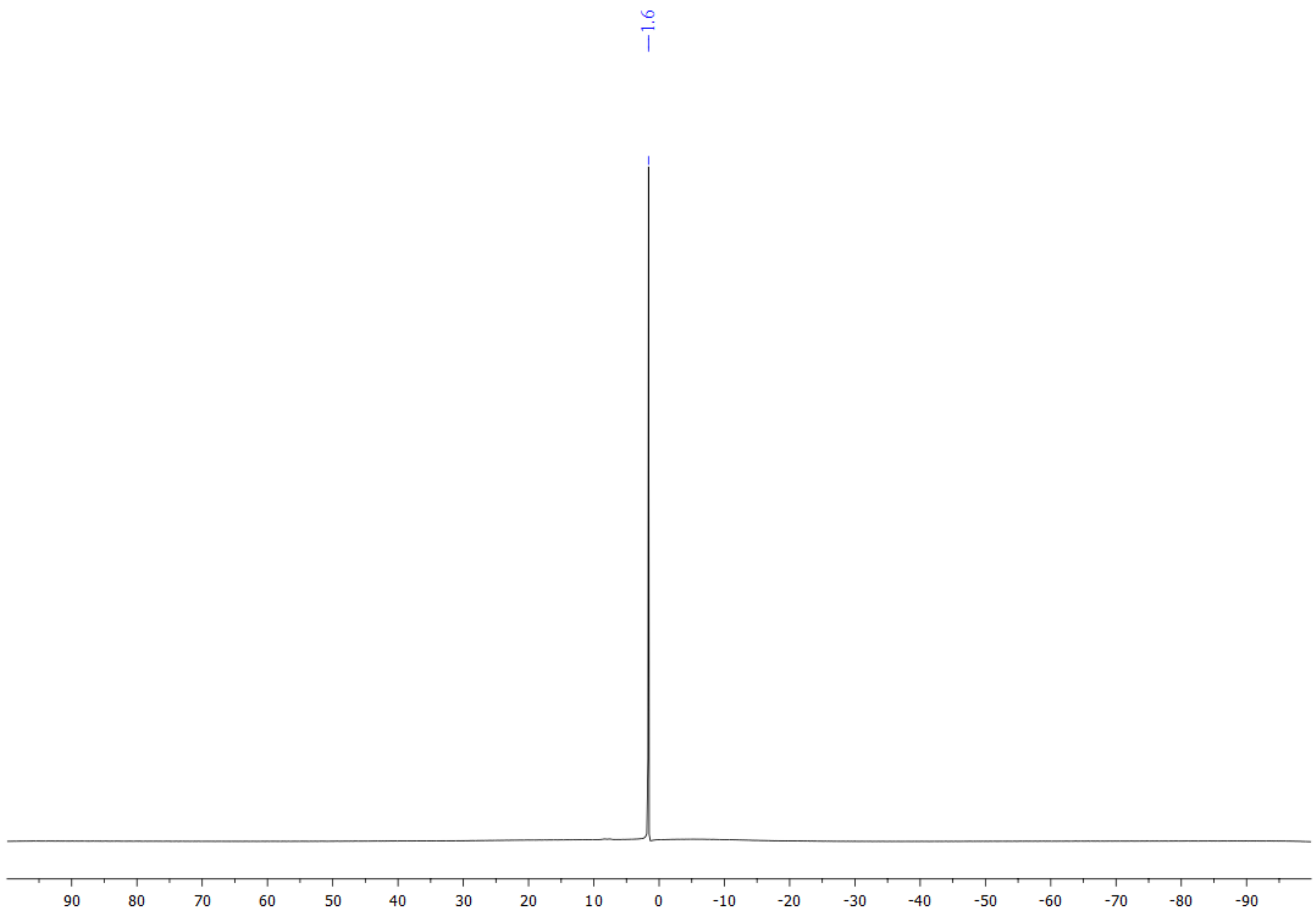


Figure S60 ^{11}B NMR (160 MHz, $(CD_3)_2SO$, 295 K) spectrum of pristine 1 M $Na[B(hfip)_4]\cdot DME$ in EC:DEC (1:1 v/v).



S4.3 NMR spectra of air exposed salts.

Figure S61 ^{1}H NMR (500 MHz, $(CD_3)_2SO$, 295 K) spectrum of $NaPF_6$ exposed to atmospheric air in an uncapped vial at room temperature (17–20°C) for one day.

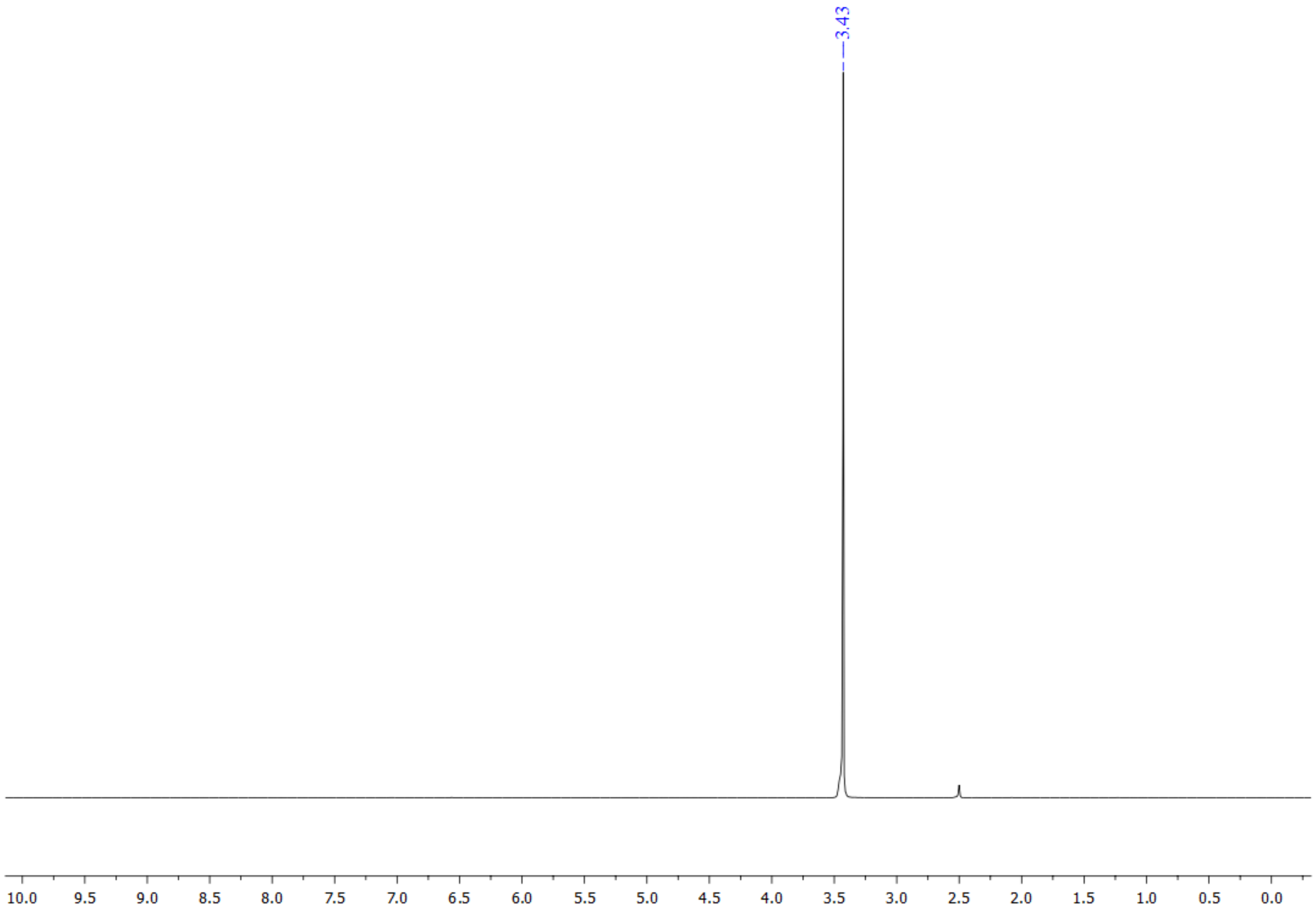


Figure S62 ^1H NMR (500 MHz, $(CD_3)_2SO$, 295 K) spectrum of $NaPF_6$ exposed to atmospheric air in an uncapped vial at room temperature (17–20°C) for one week.

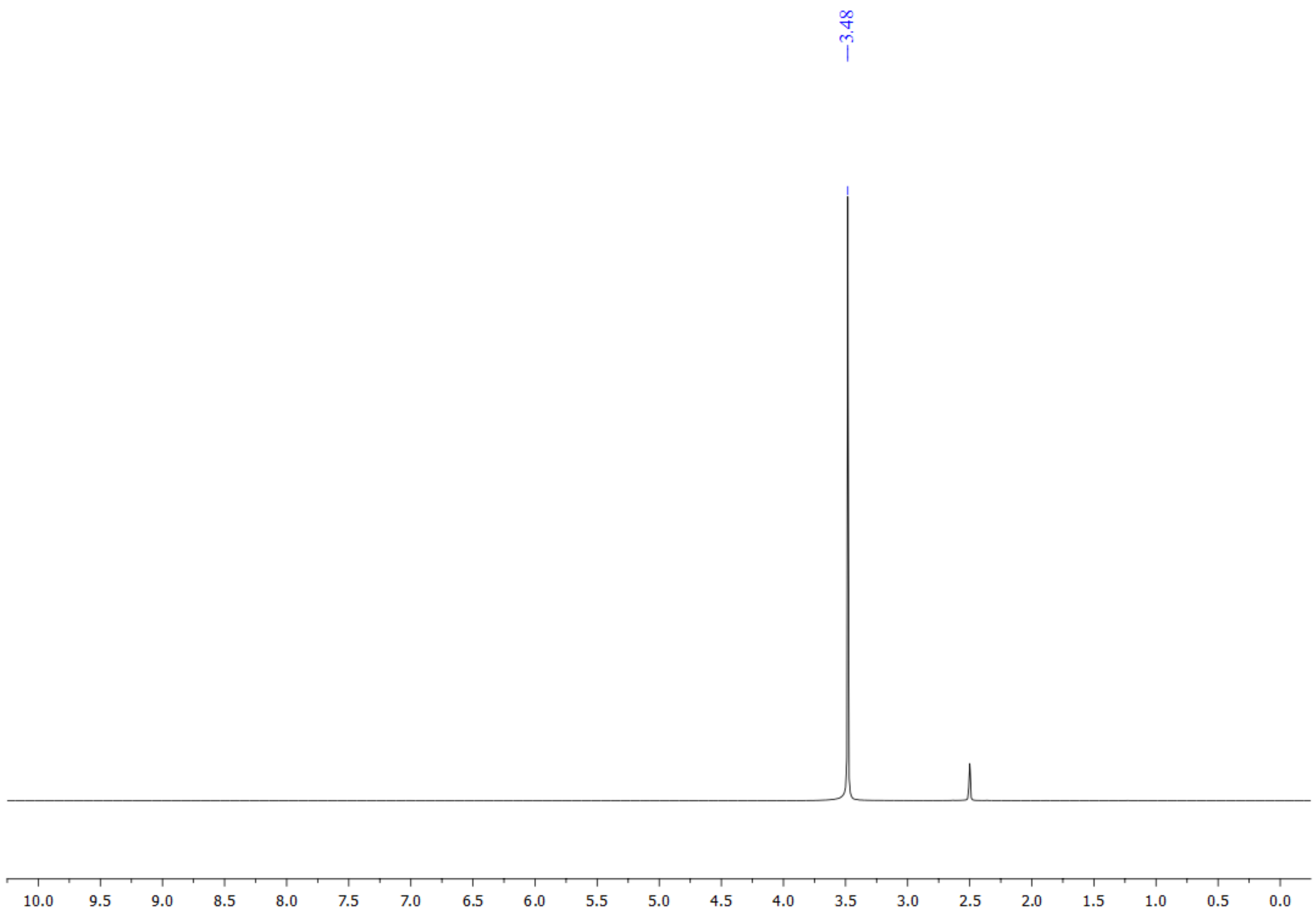


Figure S63 ^{1}H NMR (500 MHz, $(CD_3)_2SO$, 295 K) spectrum of $NaPF_6$ exposed to atmospheric air in an uncapped vial at room temperature (17–20°C) for one month.

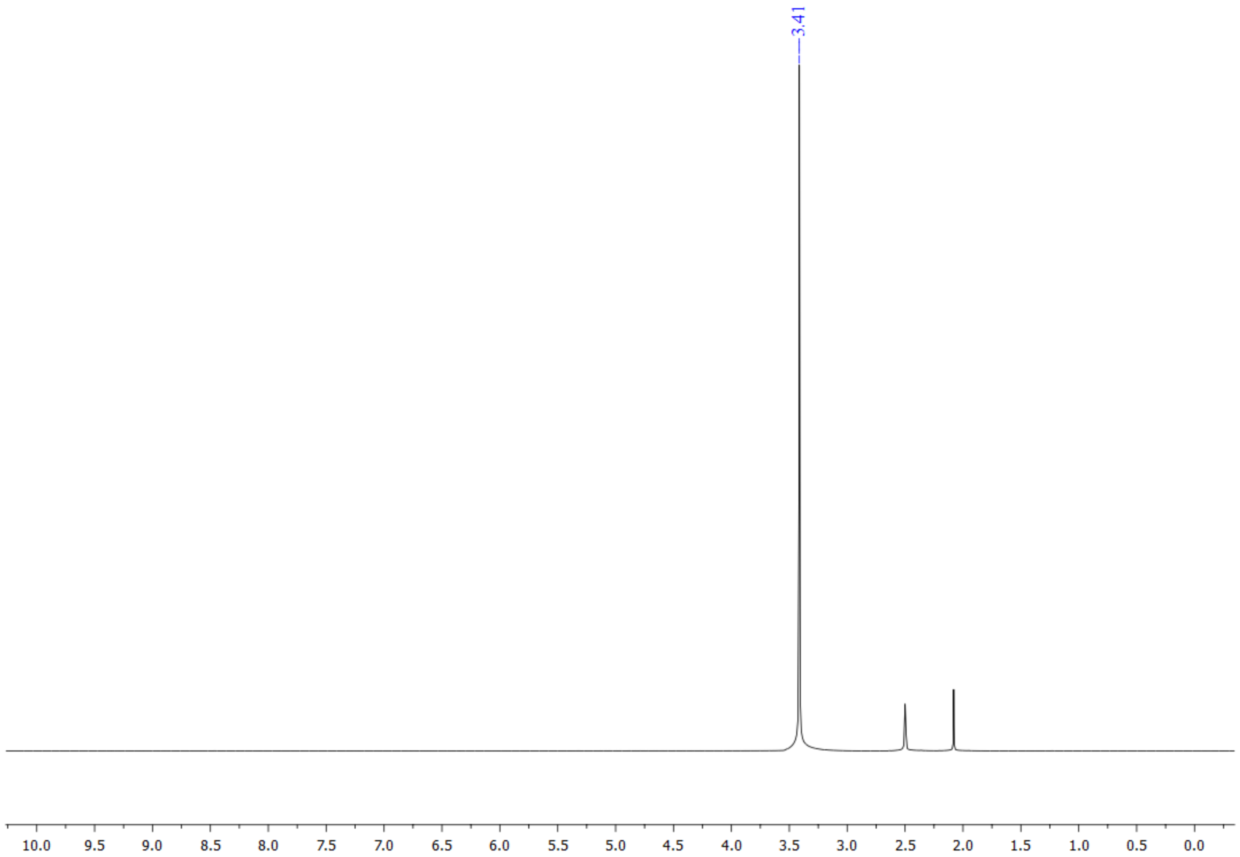


Figure S64 ^{31}P NMR (202 MHz, $(CD_3)_2SO$, 295 K) spectrum of $NaPF_6$ exposed to atmospheric air in an uncapped vial at room temperature (17–20°C) for 1 day, 1 week (7 days) and 1 month (30 days).

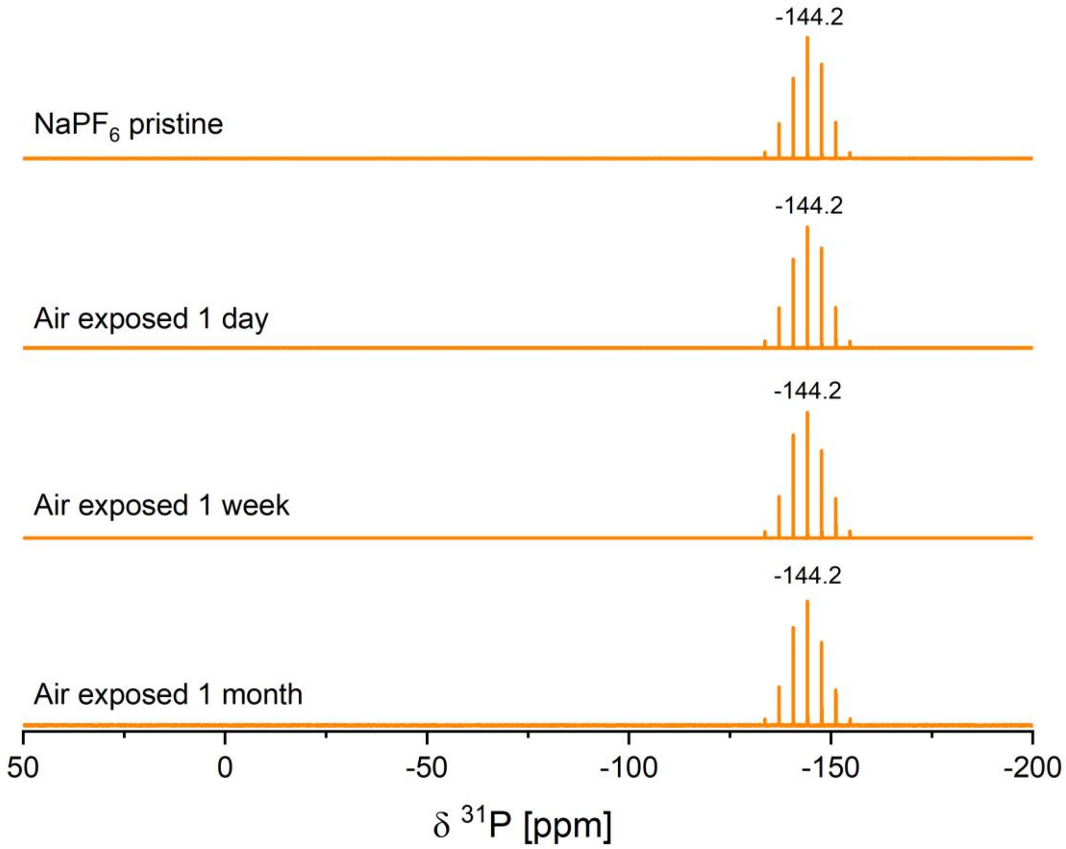


Figure S65 ^{1}H NMR (500 MHz, $(CD_3)_2SO$, 295 K) spectrum of NaTFSI exposed to atmospheric air in an uncapped vial at room temperature (17–20°C) for one day.

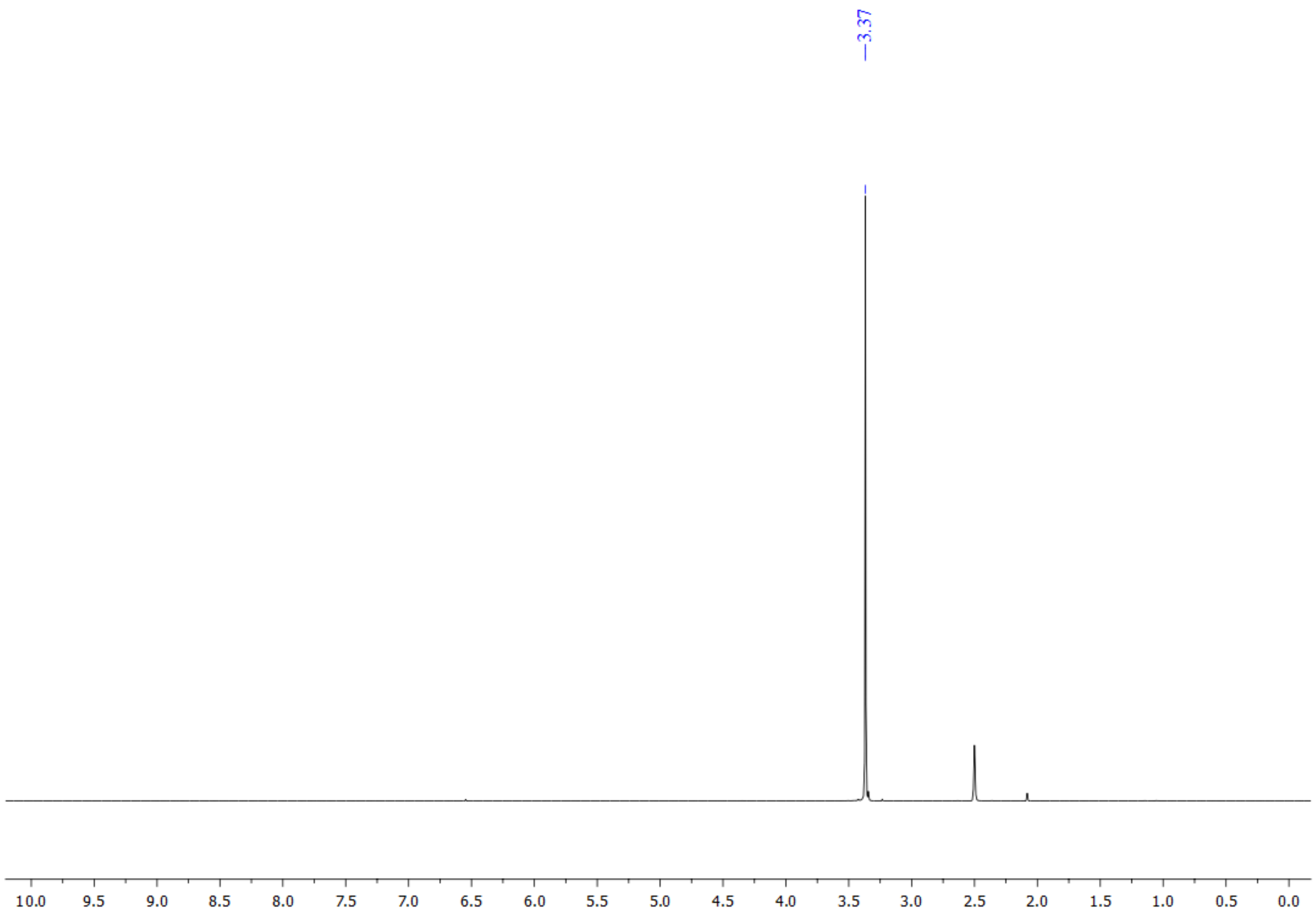


Figure S66 ^{1}H NMR (500 MHz, $(CD_3)_2SO$, 295 K) spectrum of NaTFSI exposed to atmospheric air in an uncapped vial at room temperature (17–20°C) for one week.

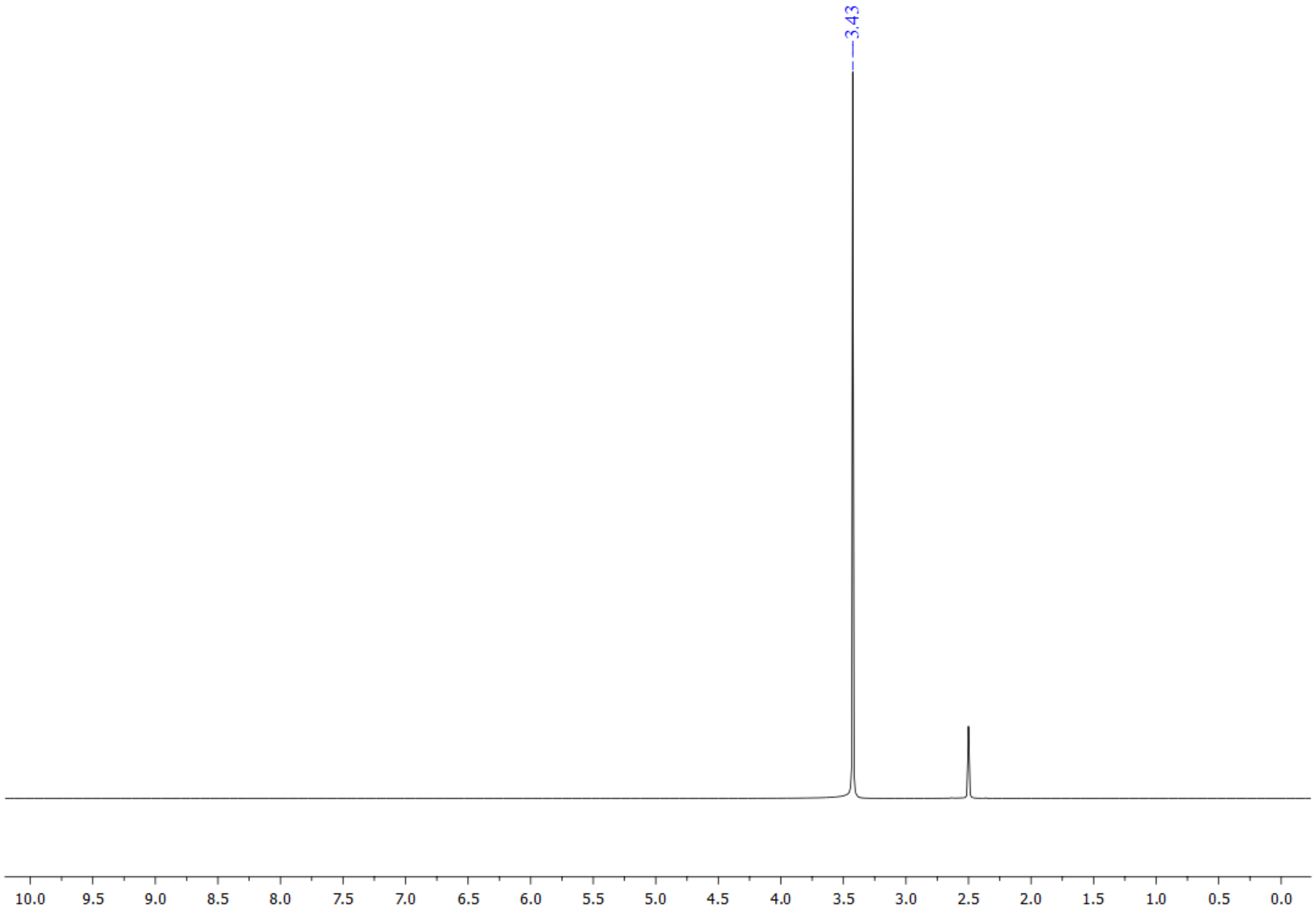


Figure S67 ^{1}H NMR (500 MHz, $(CD_3)_2SO$, 295 K) spectrum of NaTFSI exposed to atmospheric air in an uncapped vial at room temperature (17–20°C) for one month.

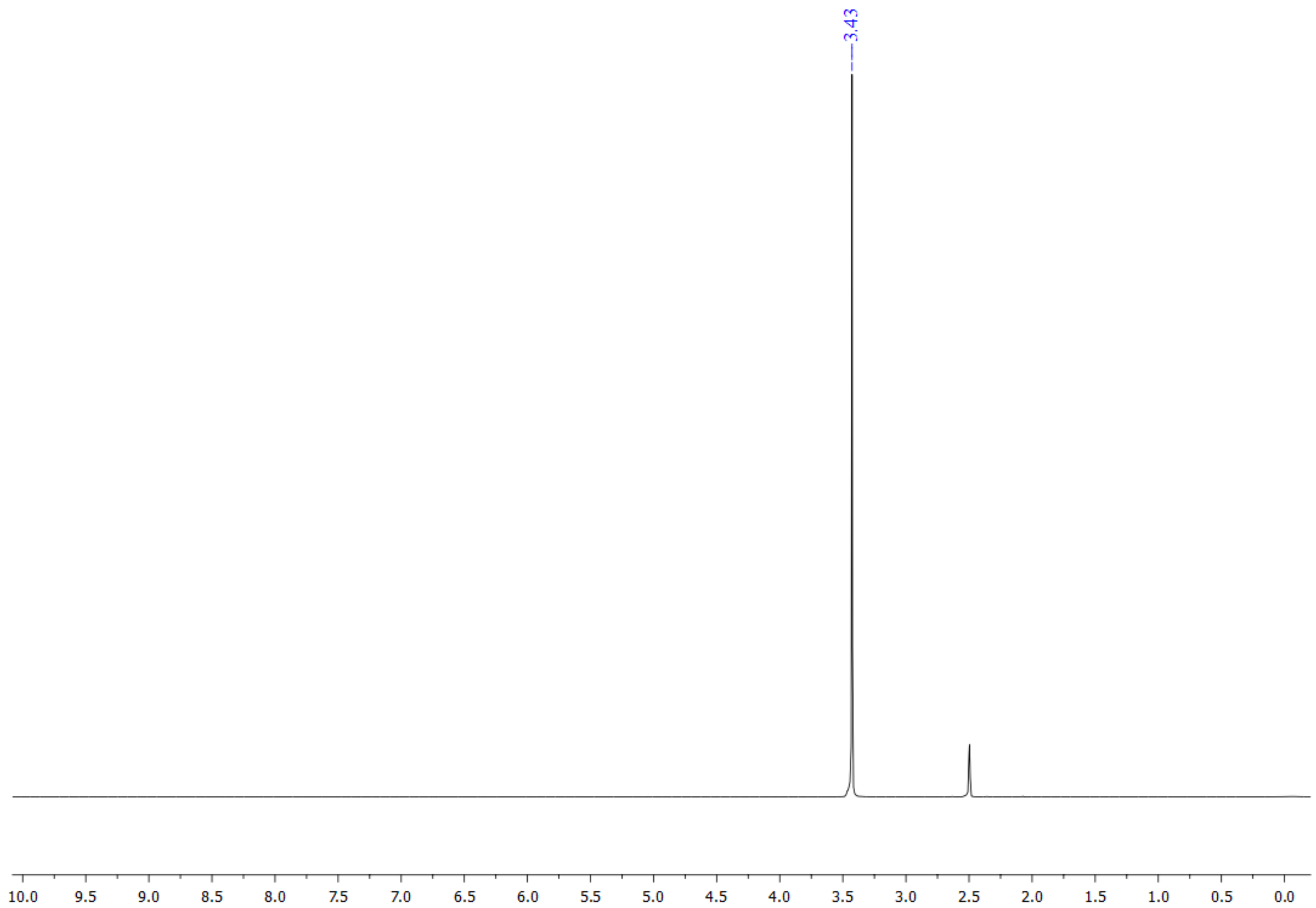


Figure S68 ^{1}H NMR (500 MHz, $(CD_3)_2SO$, 295 K) spectrum of Na[B(hfip)$_4$)]·DME exposed to atmospheric air in an uncapped vial at room temperature (17–20°C) for one day.

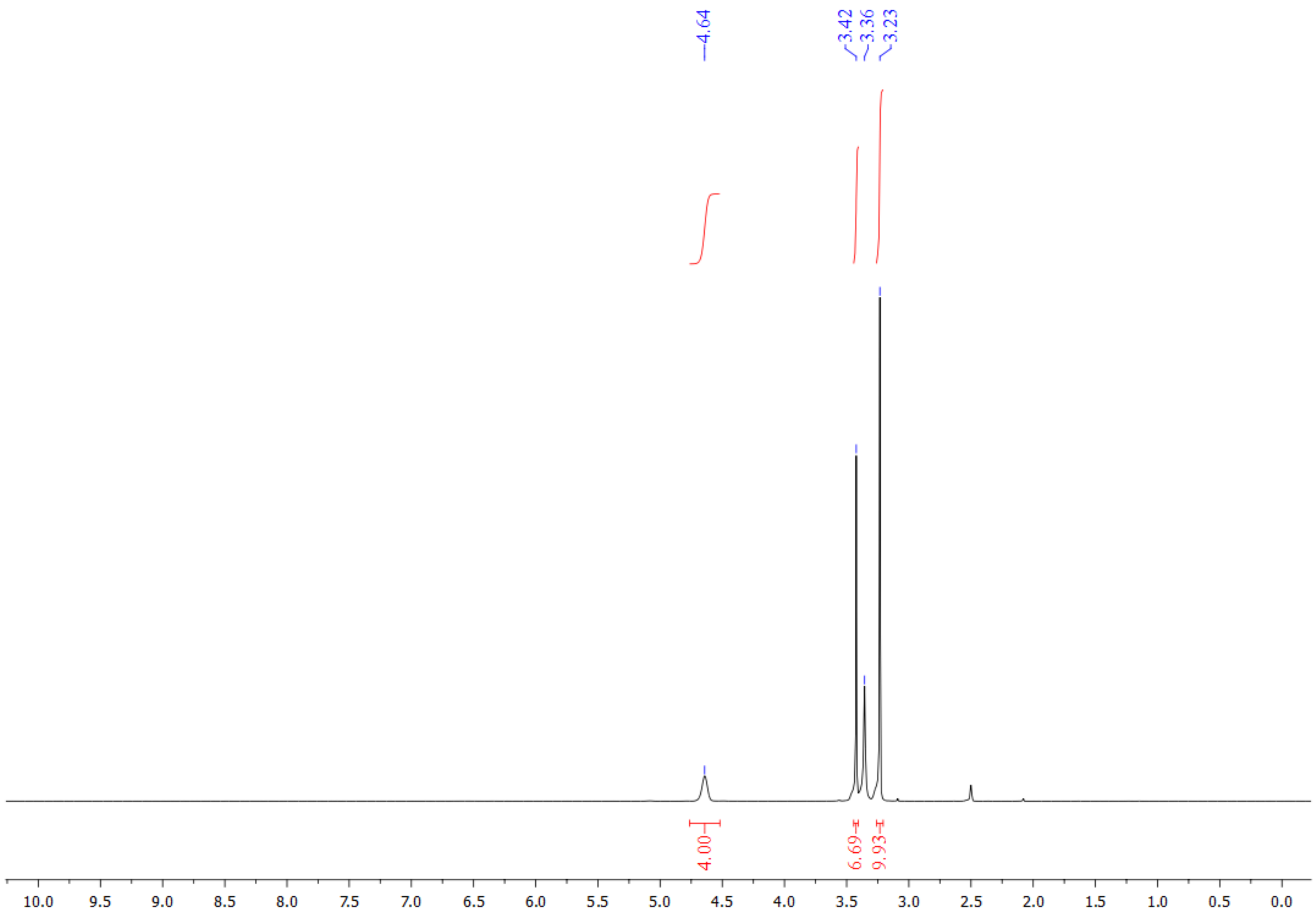


Figure S69 ^{1}H NMR (500 MHz, $(CD_3)_2SO$, 295 K) spectrum of Na[B(hfip)$_4$)]·DME exposed to atmospheric air in an uncapped vial at room temperature (17–20°C) for one week.

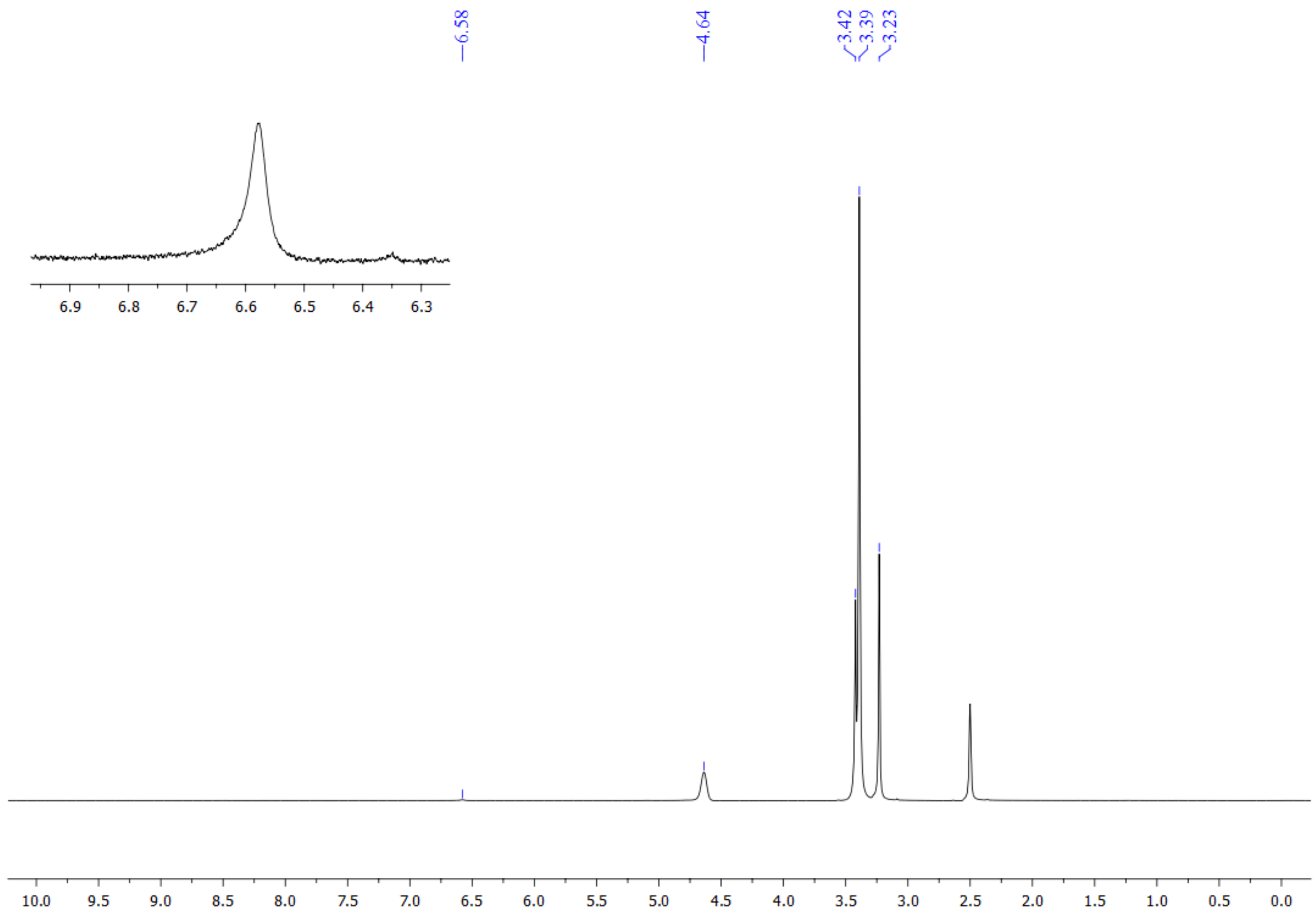


Figure S70 ^{1}H NMR (500 MHz, $(CD_3)_2SO$, 295 K) spectrum of Na[B(hfip)$_4$)]·DME exposed to atmospheric air in an uncapped vial at room temperature (17–20°C) for one month.

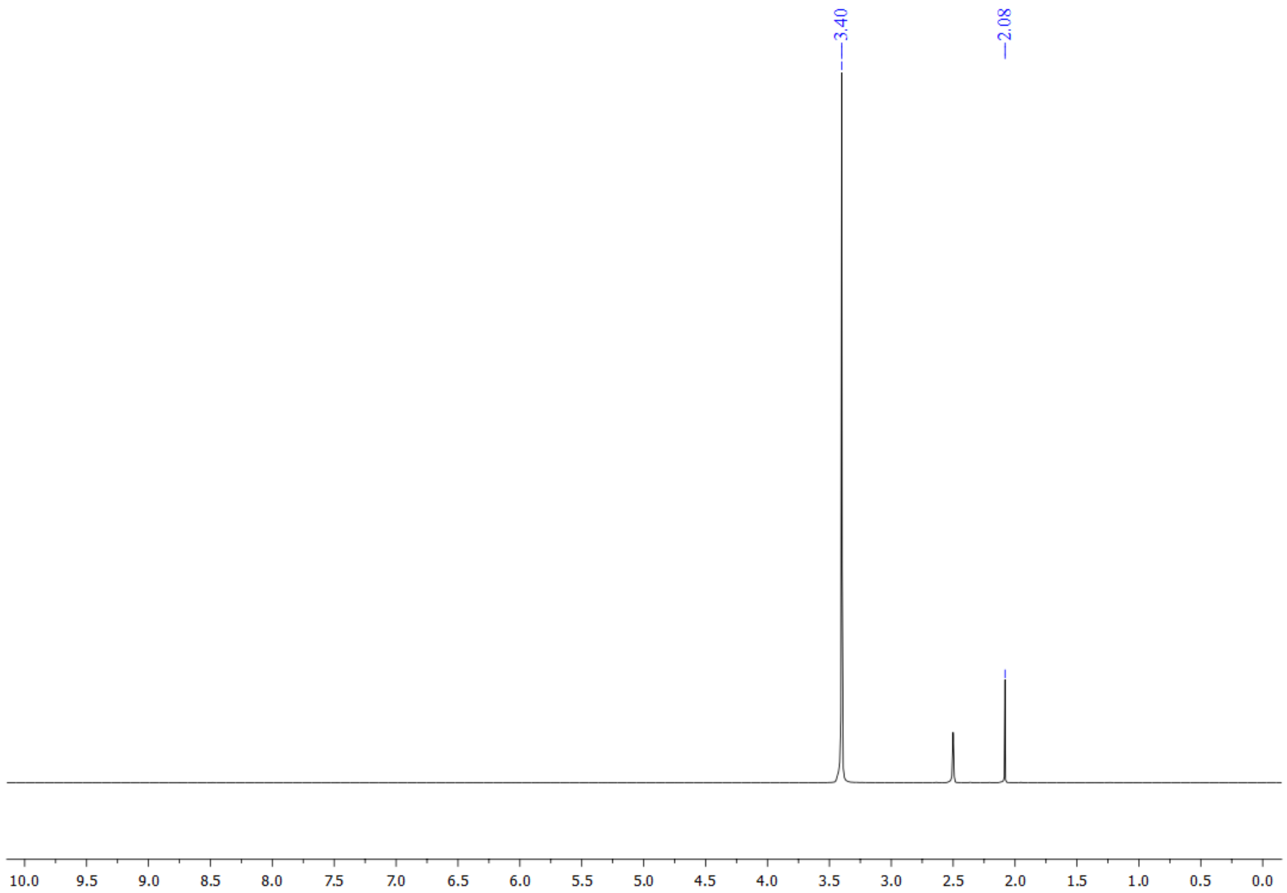
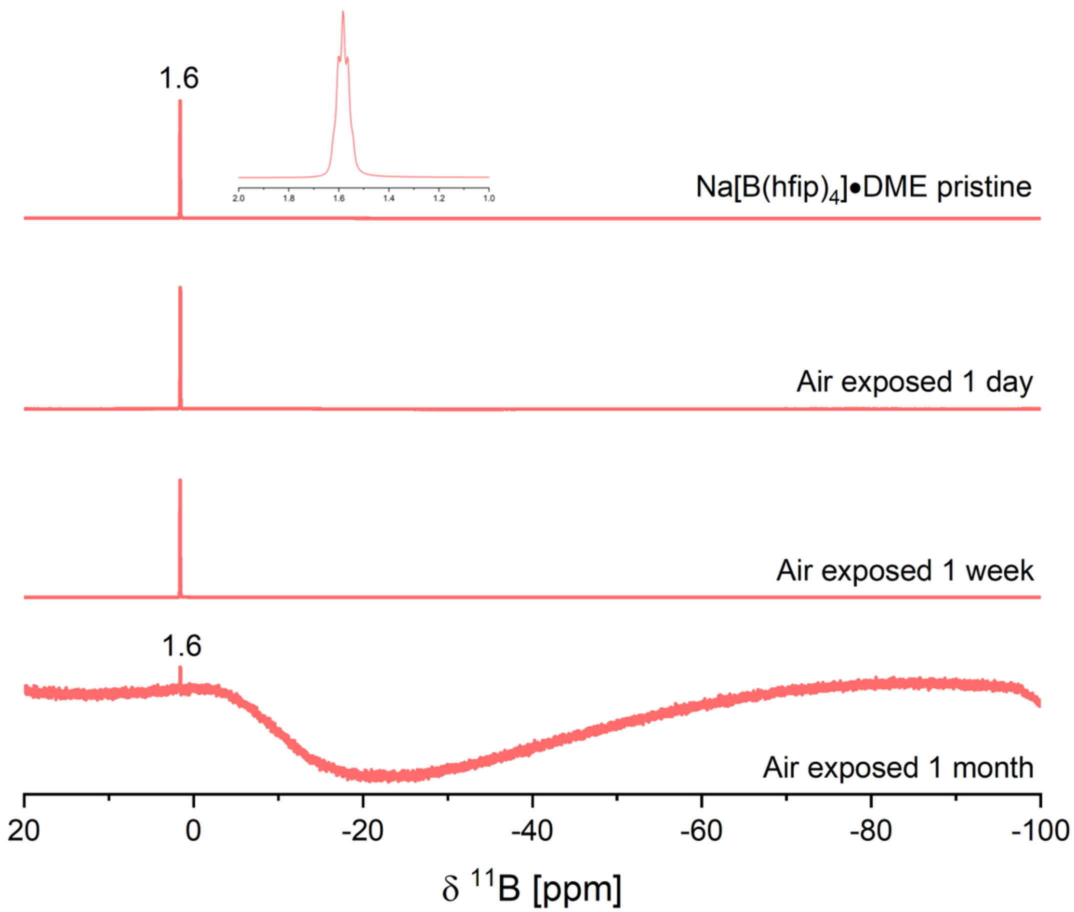


Figure S71 ^{11}B NMR (160 MHz, $(CD_3)_2SO$, 295 K) spectrum of Na[B(hfip)$_4$)]·DME exposed to atmospheric air in an uncapped vial at room temperature (17–20°C) for 1 day, 1 week (7 days) and 1 month (30 days).



S4.4 Other NMR spectra.

Figure S72 ^{31}P NMR (202 MHz, $(CD_3)_2SO$, 295 K) spectrum of crystalline phosphoric acid in DMSO-d_6 solvent.