

Supplementary Information for:

## Sodium Tetrphenylborate: A Fluorine-Free Electrolyte Salt for Sodium-Ion Batteries

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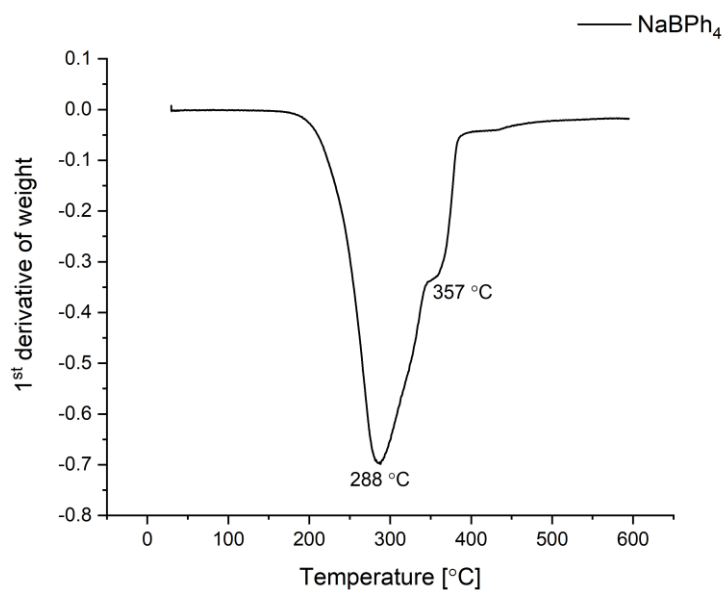
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## S1 Thermal measurements.



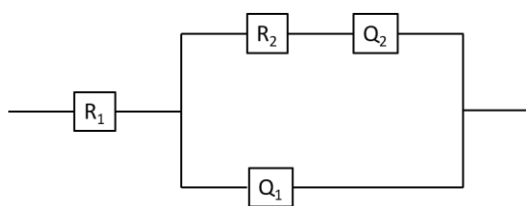
**Figure S1** 1<sup>st</sup> derivative of the Weight vs. Temperature plot for NaBPh<sub>4</sub>, showing the inflection point temperature.

## S2 Bulk conductivity.



**Figure S2** Two-electrode platinum cell designed to perform ionic conductivity measurements.

The cell constant was determined 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 equivalence circuit  $R_1 + (R_2 + Q_2) \times Q_1$  (Figure S3). An average of the cell constant values gave the value  $10.2 \pm 0.3 \text{ cm}^{-1}$ .



**Figure S3** Equivalence circuit used to determine the cell constant.

### S3 Viscosity.

**Table S1:** Newtonian viscosity measurements of EC:DEC (1:1 v/v) solvent and different electrolyte concentrations of NaBPh<sub>4</sub> in EC:DEC.

Concentration (M)	Newtonian Viscosity (mPa.s)				
	Run 1	Run 2	Run 3	Mean	Standard deviation
Neat EC:DEC solvent	1.51	1.50	1.42	1.48	0.05
0.1	1.80	1.79	1.69	1.76	0.06
0.25	2.15	2.37	2.15	2.22	0.12
0.5	3.65	3.56	3.80	3.67	0.12
1.0	10.46	9.47	10.37	10.10	0.55
1.5	36.45	36.75	36.65	36.62	0.15

#### S4 DOSY NMR spectroscopy.

Solution NMR experiments were conducted on a Bruker 9.4 T magnet ( $\nu_0(^1\text{H}) = 400 \text{ MHz}$ ) equipped with an Avance IIIHD console. A 5 mm BBO probe was used for all experiments. The Bruker dstebpgp3s convection corrected pulse sequence was used, with a diffusion delay of  $\Delta = 60 \text{ ms}$  and a gradient pulse length of  $\delta = 2 \text{ ms}$ . Spectra were obtained over an 8 step gradient range from 10–90%. Spectra were processed using Topspin and Dynamics Center.

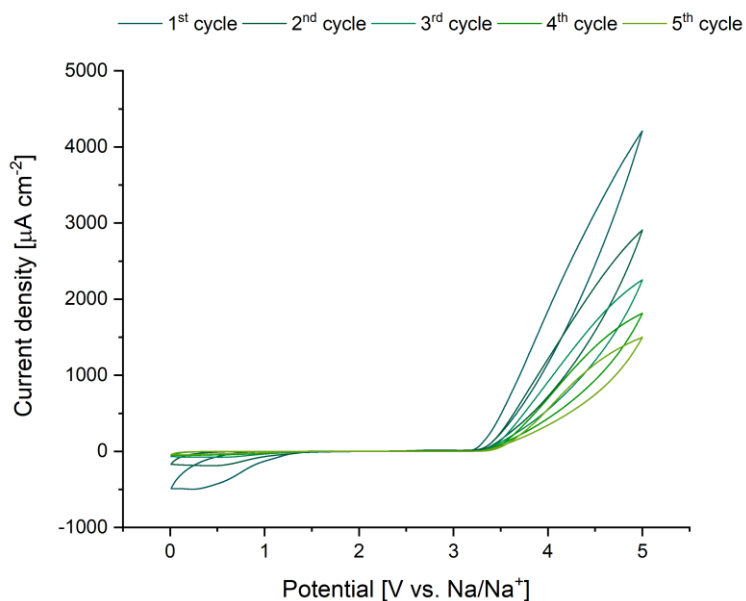
**Table S2:** Diffusion coefficients of ethylene carbonate (EC), diethyl carbonate (DEC) and  $\text{BPh}_4^-$  anion. Measured by  $^1\text{H}$  DOSY NMR spectroscopy. Diffusion coefficients in units of  $10^{-10} \text{ m}^2 \text{ s}^{-1}$ .

Concentration (M)	$D_{\text{EC}}$	$D_{\text{DEC (ethyl)}}$	$D_{\text{DEC (methyl)}}$	$D_{\text{BPh}_4^-}$	$D_{\text{EC}} - D_{\text{BPh}_4^-}$
0.1	7.89	6.92	7.13	2.95	4.94
0.25	6.27	6.17	6.01	2.28	3.99
0.5	4.03	3.80	3.94	1.47	2.56
1.0	1.78	1.72	1.88	0.68	1.10
1.5	0.70	0.81	0.72	0.26	0.44

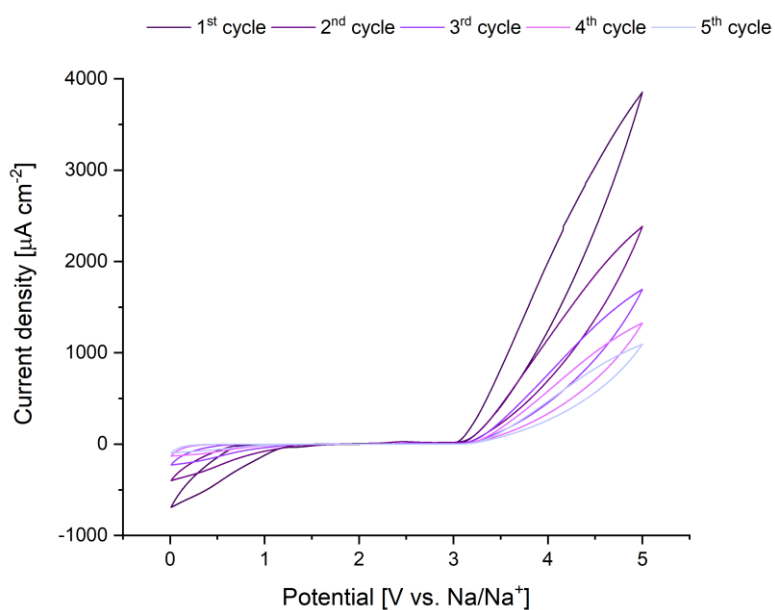
To determine the percentage of free EC solvent molecules (i.e. not coordinated to  $\text{Na}^+$ ) in the  $\text{NaBPh}_4$  electrolyte solutions, we assume 4 EC solvent molecules are coordinated to one  $\text{Na}^+$  cation at all electrolyte concentrations. This is because  $\text{Na}^+$  favours a five- or six-coordination geometry and cyclic carbonates preferentially coordinate to  $\text{Na}^+$  over linear carbonates, thus in the coordination shell of  $\text{Na}^+$  the ratio of EC to DEC is greater than 1:1.<sup>1</sup> From this assumption, the percentage of free EC solvent molecules decreases from 90% in the 0.1 M  $\text{NaBPh}_4$  electrolyte, 87% in the 0.25 M  $\text{NaBPh}_4$  electrolyte, 73% in the 0.5 M  $\text{NaBPh}_4$  electrolyte, 47% in the 1 M  $\text{NaBPh}_4$  electrolyte and 20% in the 1.5 M  $\text{NaBPh}_4$  electrolyte.

If the amount of coordinated EC solvent molecules is lower and we assume that 3 EC solvent molecules are coordinated to the  $\text{Na}^+$  cation at all electrolyte concentrations, then the percentage of free EC solvent molecules (not coordinated to  $\text{Na}^+$ ) decreases from 96% in the 0.1 M  $\text{NaBPh}_4$  electrolyte to 90% in the 0.25 M  $\text{NaBPh}_4$  electrolyte, 80% in the 0.5 M  $\text{NaBPh}_4$  electrolyte, 60% in the 1 M  $\text{NaBPh}_4$  sample and 40% in the 1.5 M  $\text{NaBPh}_4$  sample. A similar discussion to this investigating the percentage of free EC solvent molecules in  $\text{NaPF}_6$  in EC:DEC (1:1 v/v) electrolytes has previously been reported.<sup>2</sup>

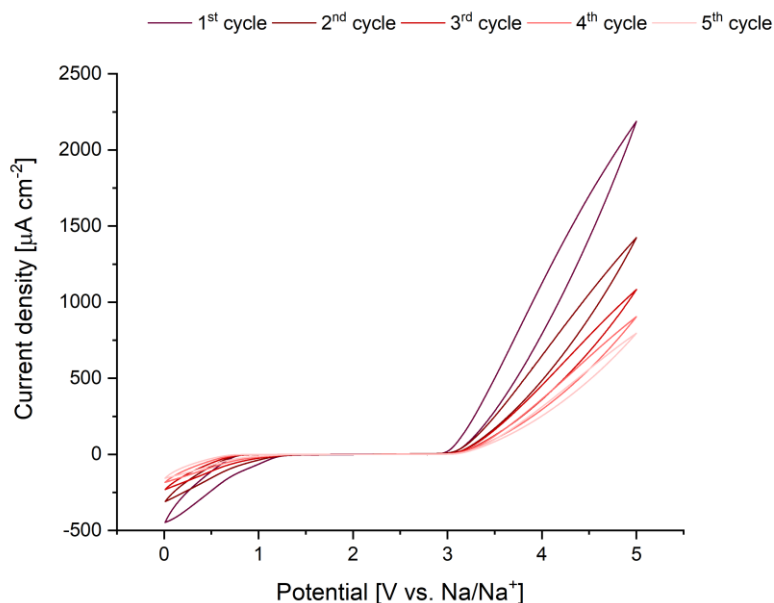
## S5 Cyclic voltammetry.



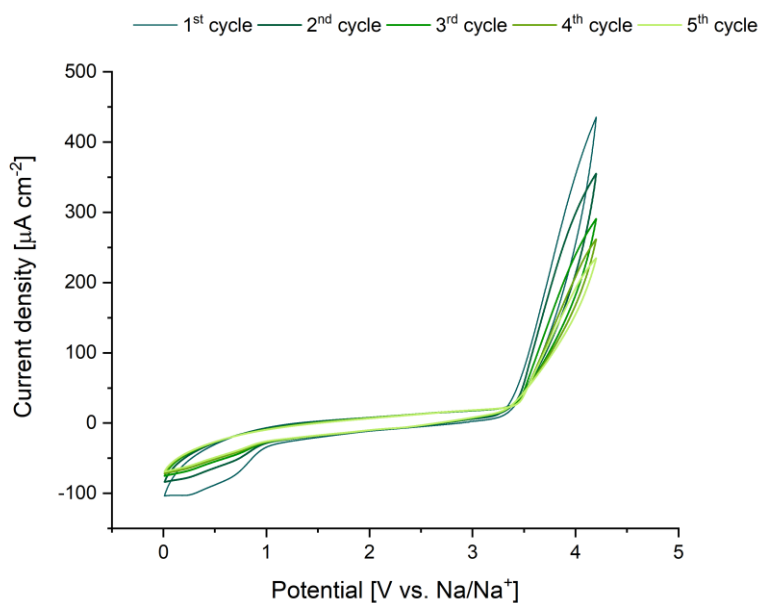
**Figure S4** Cyclic voltammogram of 0.5 M NaBPh<sub>4</sub> in EC:DEC (1:1 v/v). Working electrode is glassy carbon, counter electrode is platinum and the pseudo reference electrode is sodium. First five cycles, measured between 0.01 V and 5 V vs. Na/Na<sup>+</sup> at 10 mV s<sup>-1</sup>.



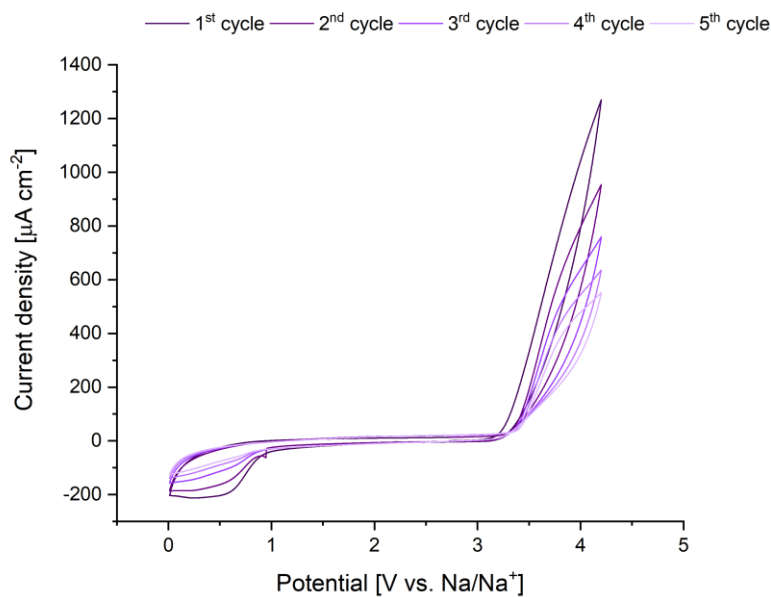
**Figure S5** Cyclic voltammogram of 1 M NaBPh<sub>4</sub> in EC:DEC (1:1 v/v). Working electrode is glassy carbon, counter electrode is platinum and the pseudo reference electrode is sodium. First five cycles, measured between 0.01 V and 5 V vs. Na/Na<sup>+</sup> at 10 mV s<sup>-1</sup>.



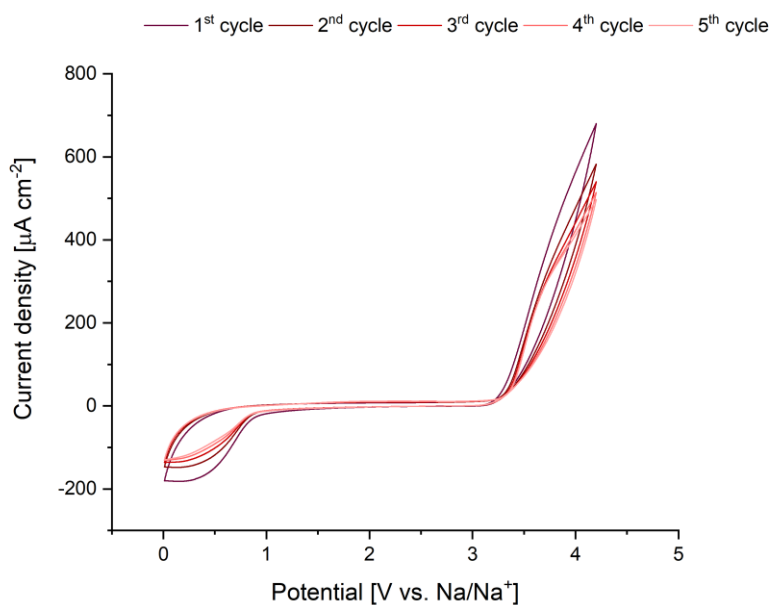
**Figure S6** Cyclic voltammogram of 1.5 M NaBPh<sub>4</sub> in EC:DEC (1:1 v/v). Working electrode is glassy carbon, counter electrode is platinum and the pseudo reference electrode is sodium. First five cycles, measured between 0.01 V and 5 V vs. Na/Na<sup>+</sup> at 10 mV s<sup>-1</sup>.



**Figure S7** Cyclic voltammogram of 0.5 M NaBPh<sub>4</sub> 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<sup>+</sup> at 5 mV s<sup>-1</sup>.



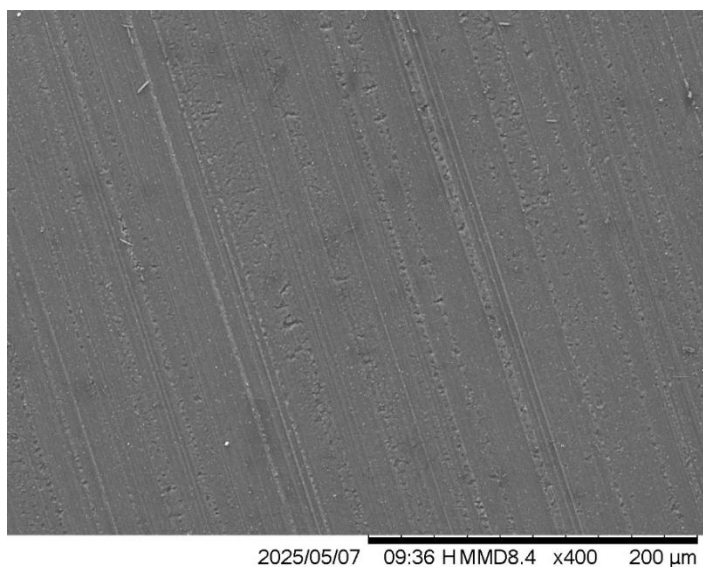
**Figure S8** Cyclic voltammogram of 1 M NaBPh<sub>4</sub> in EC:DEC (1:1 v/v). Working electrode is aluminium, counter electrode is platinum and the pseudo reference electrode is sodium. First five cycles, measured between 0.01 V and 4.2 V vs. Na/Na<sup>+</sup> at 5 mV s<sup>-1</sup>.



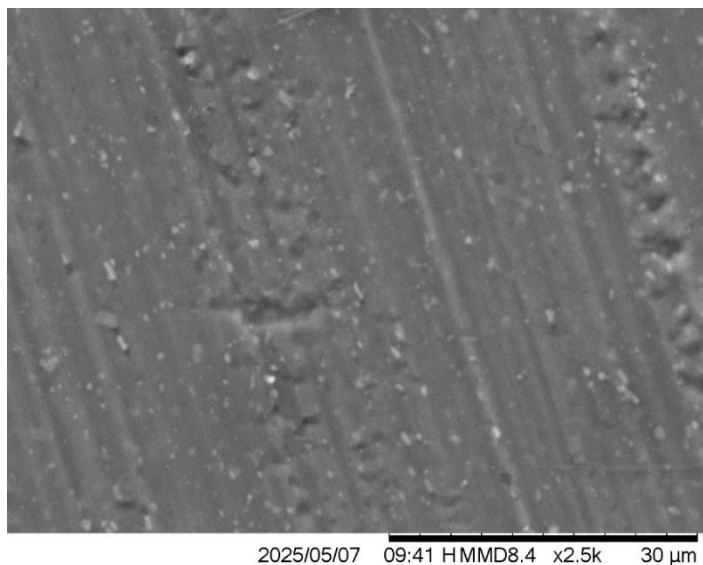
**Figure S9** Cyclic voltammogram of 1.5 M NaBPh<sub>4</sub> in EC:DEC (1:1 v/v). Working electrode is aluminium, counter electrode is platinum and the pseudo reference electrode is sodium. First five cycles, measured between 0.01 V and 4.2 V vs. Na/Na<sup>+</sup> at 5 mV s<sup>-1</sup>.

## S6 Scanning electron microscopy (SEM) images.

Electron microscopy was performed using a Hitachi TM3030Plus tabletop microscope with an Oxford Instruments EDS X-stream-2 and MicsF+. Images were captured using the TM3030 software version 01-05-02, with additional images captured and EDX spectra obtained and analysed with AztecOne Sp1 3.1 software.

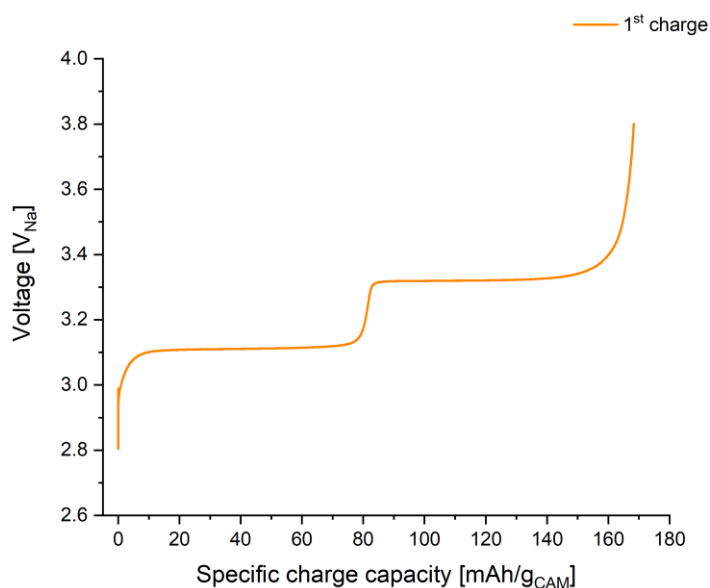


**Figure S10** Representative SEM surface image of the post-cycled aluminium working electrode that was used in the cyclic voltammetry experiment using 0.5 M NaBPh<sub>4</sub> measured between 0.01–4.2 V vs. Na/Na<sup>+</sup>.

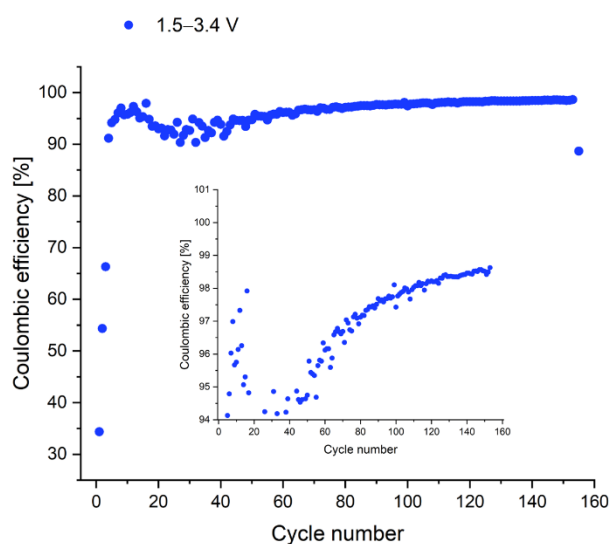


**Figure S11** Representative SEM surface image of the post-cycled aluminium working electrode that was used in the cyclic voltammetry experiment using 0.5 M NaBPh<sub>4</sub> measured between 0.01–4.2 V vs. Na/Na<sup>+</sup>.

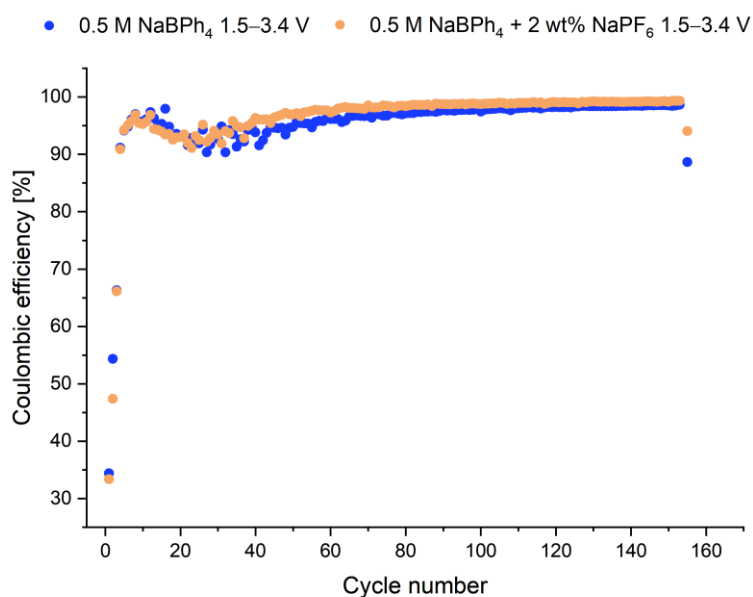
## S7 Sodium-ion cycling.



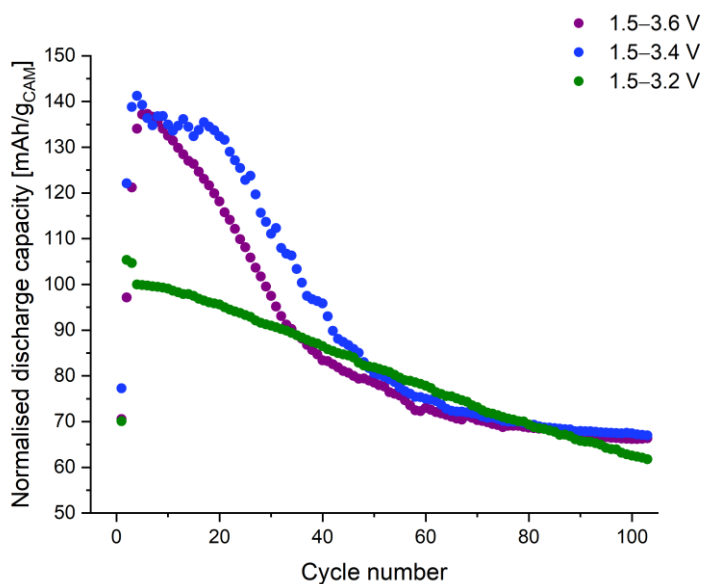
**Figure S12** Voltage vs specific charge capacity, normalised by the mass of cathode active material (CAM). Prussian white,  $\text{Na}_2\text{Fe}[\text{Fe}(\text{CN})_6]$ , cathode in a coin half-cell vs. sodium metal with 100  $\mu\text{l}$  of 1 M  $\text{NaPF}_6$  in EC:DEC (1:1 v/v) as electrolyte. The cell was charged at C/20 to 3.8 V<sub>Na</sub> at 21°C.



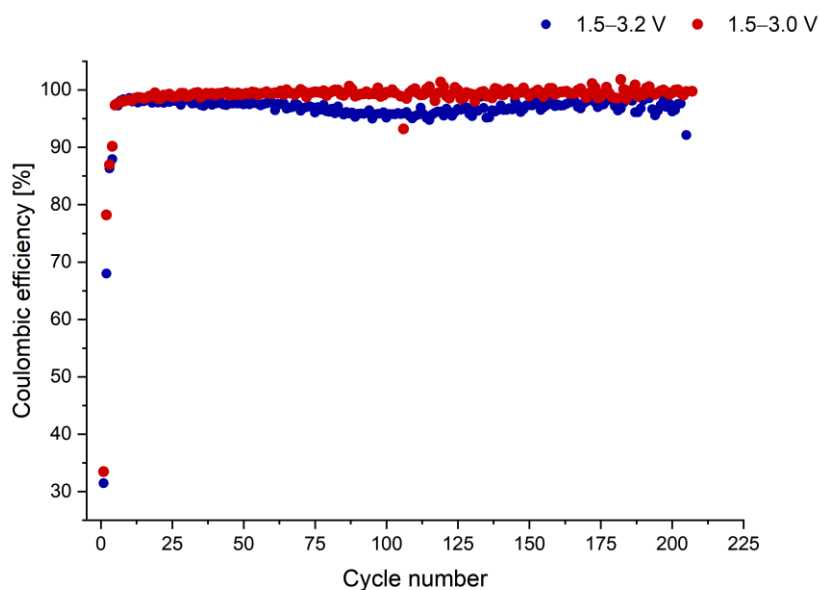
**Figure S13** Coulombic efficiency vs. cycle number using Prussian white cathode and hard-carbon anode, using cell voltage limits of 1.5 and 3.4 V. Electrolyte is 0.5 M  $\text{NaBPh}_4$  in EC:DEC (1:1 v/v). Cells cycled at 21°C.



**Figure S14** Coulombic efficiency vs. cycle number using Prussian white cathode and hard-carbon anode, using cell voltage limits of 1.5 and 3.4 V. Electrolyte is 0.5 M NaBPh<sub>4</sub> (blue) and 0.5 M NaBPh<sub>4</sub> + 2 wt% NaPF<sub>6</sub> (orange) in EC:DEC (1:1 v/v). Cells cycled at 21°C.

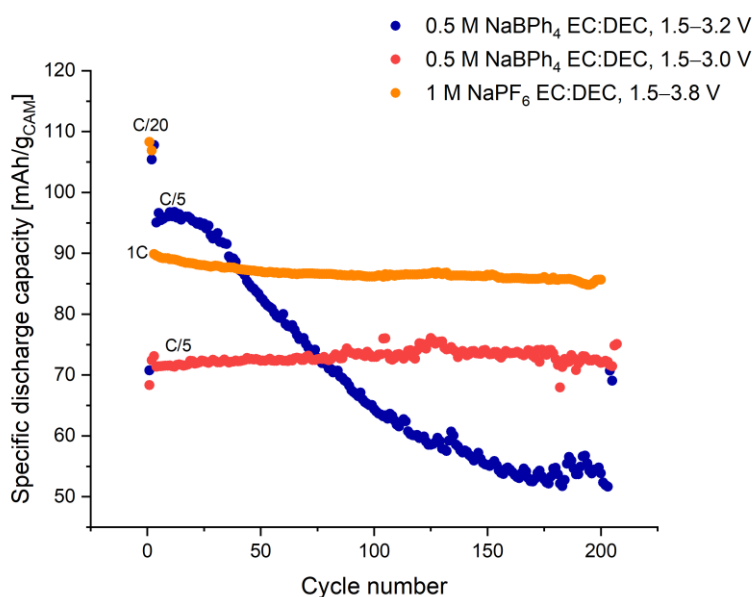


**Figure S15** Specific discharge capacity vs. cycle number using a Prussian white cathode and hard-carbon anode. Cell voltage limits of either 1.5–3.6 V (purple), 1.5–3.4 V (blue) or 1.5–3.2 V (green). The applied C-rates of C/20 and C/3 were calculated based on the theoretical capacity of 150 mAh g<sup>-1</sup> of the cathode. Electrolyte is 0.5 M NaBPh<sub>4</sub> in EC:DEC (1:1 v/v), cells cycled at 21°C.

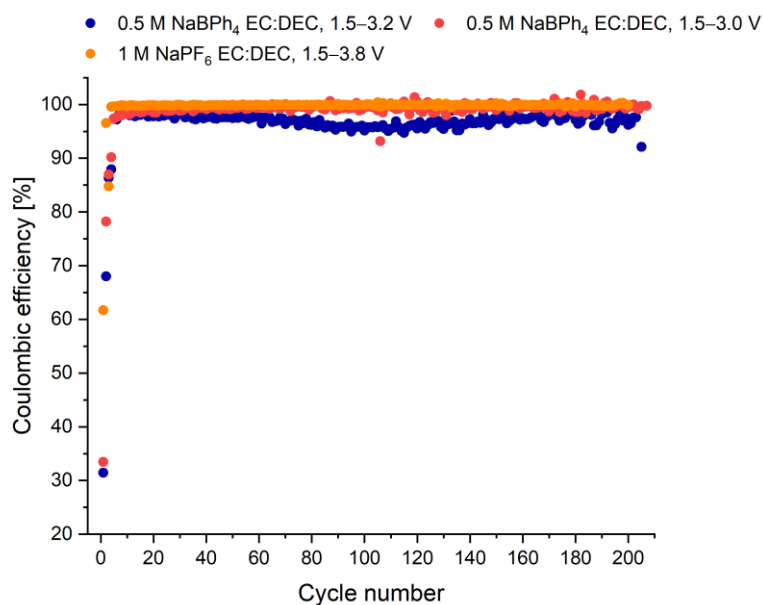


**Figure S16** Coulombic efficiency vs. cycle number using Prussian white cathode and hard-carbon anode, using cell voltage limits of either 1.5–3.2 V (blue) or 1.5–3.0 V (red) at rate C/5. Electrolyte is 0.5 M NaBPh<sub>4</sub> in EC:DEC (1:1 v/v). Cells cycled at 21°C.

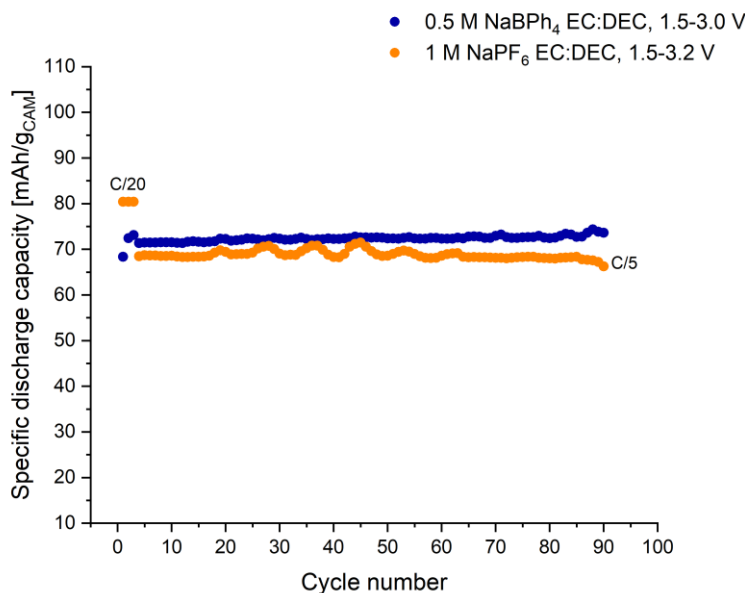
#### Comparison with NaPF<sub>6</sub>



**Figure S17** Specific discharge capacity vs. cycle number using Prussian white cathode and hard-carbon anode. Electrolyte is either 0.5 M NaBPh<sub>4</sub> (blue and red) or 1 M NaPF<sub>6</sub> (orange) in EC:DEC (1:1 v/v), cycled at 21°C. The applied C-rates of C/20, 1C (NaPF<sub>6</sub>) and C/5 (NaBPh<sub>4</sub>) were calculated based on the expected capacity of 150 mAh g<sup>-1</sup> of the cathode, using cell voltage limits of 1.5–3.2 V (blue), 1.5 V–3.0 (red) or 1.5 V–3.8 (orange, NaPF<sub>6</sub>).



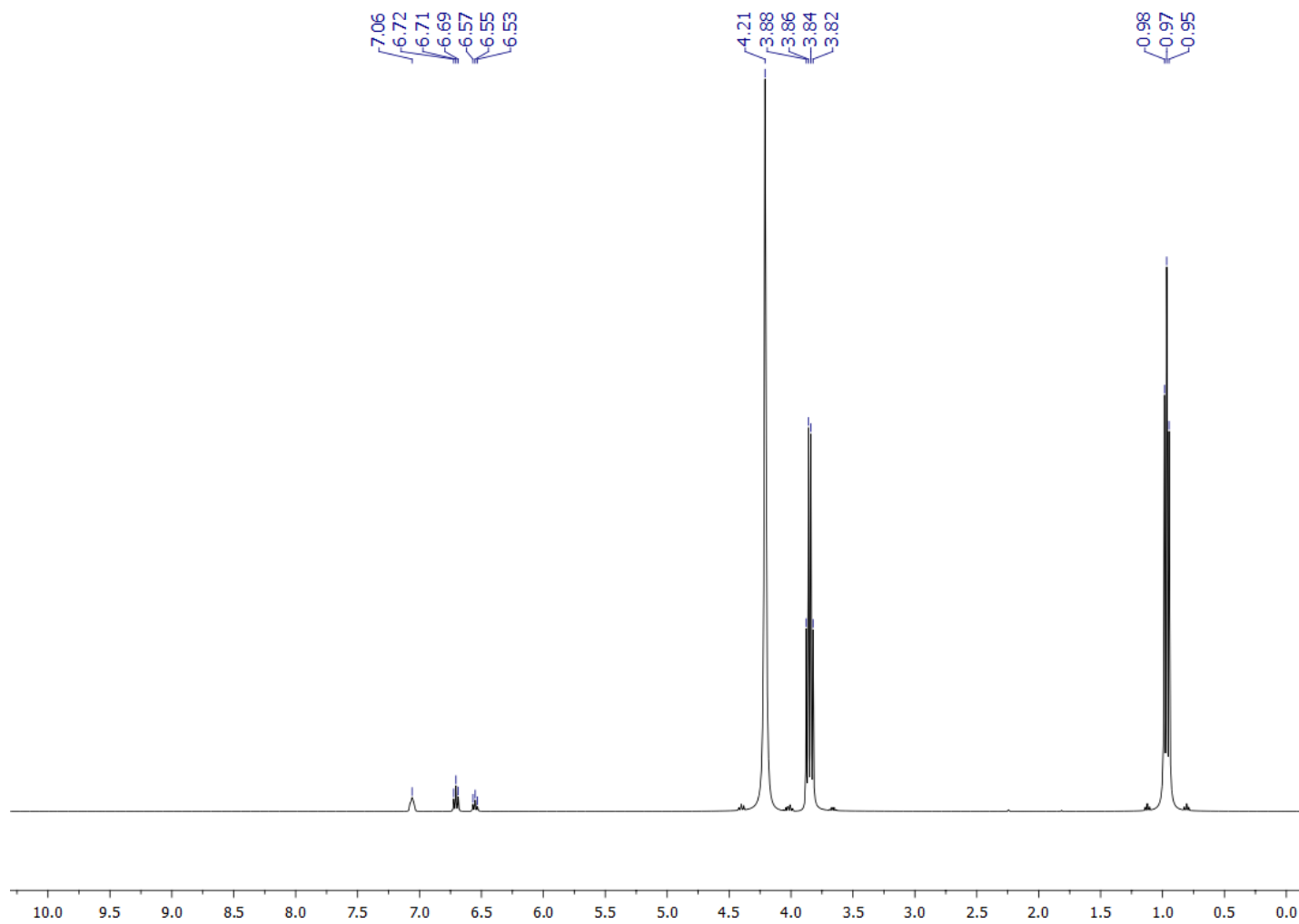
**Figure S18** Coulombic efficiency vs. cycle number using Prussian white cathode and hard-carbon anode. Electrolyte is either 0.5 M NaBPh<sub>4</sub> (blue and red) or 1 M NaPF<sub>6</sub> (orange) in EC:DEC (1:1 v/v), cycled at 21°C. Cell voltage limits of either 1.5–3.2 V (blue), 1.5–3.0 V (red) or 1.5–3.8 V (orange, NaPF<sub>6</sub>). The applied C-rates of C/20, 1C (NaPF<sub>6</sub>) and C/5 (NaBPh<sub>4</sub>) were calculated based on the expected capacity of 150 mAh g<sup>-1</sup> of the cathode.



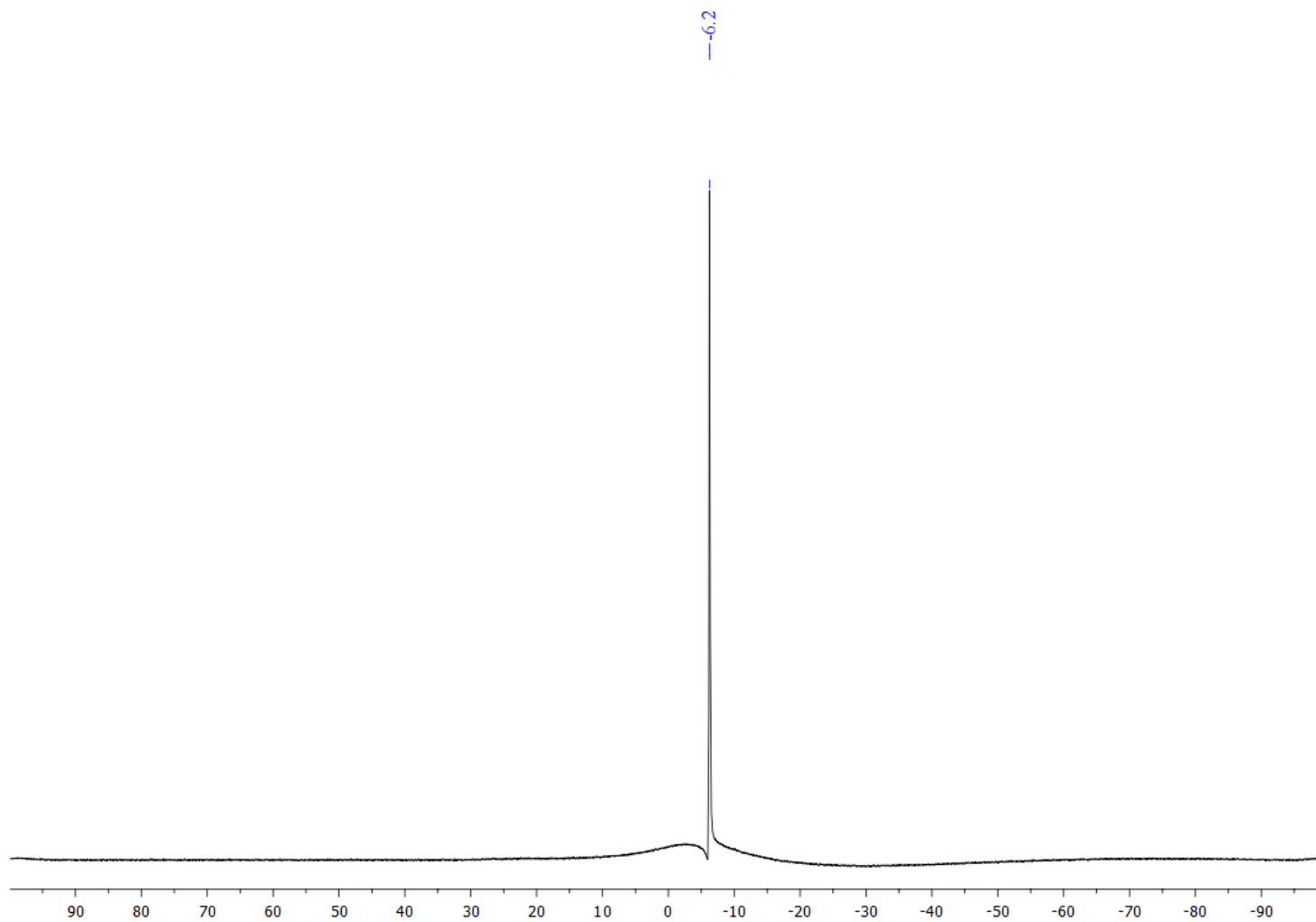
**Figure S19** Specific discharge capacity vs. cycle number using Prussian white cathode and hard-carbon anode. Electrolyte is either 0.5 M NaBPh<sub>4</sub> (blue) or 1 M NaPF<sub>6</sub> (orange) in EC:DEC (1:1 v/v), cycled at 21°C. The applied C-rates of C/20, and C/5 were calculated based on the expected capacity of 150 mAh g<sup>-1</sup> of the cathode, using cell voltage limits of 1.5–3.2 V (orange, NaPF<sub>6</sub>) or 1.5 V–3.0 (blue, NaBPh<sub>4</sub>).

# S8 NMR Spectroscopy

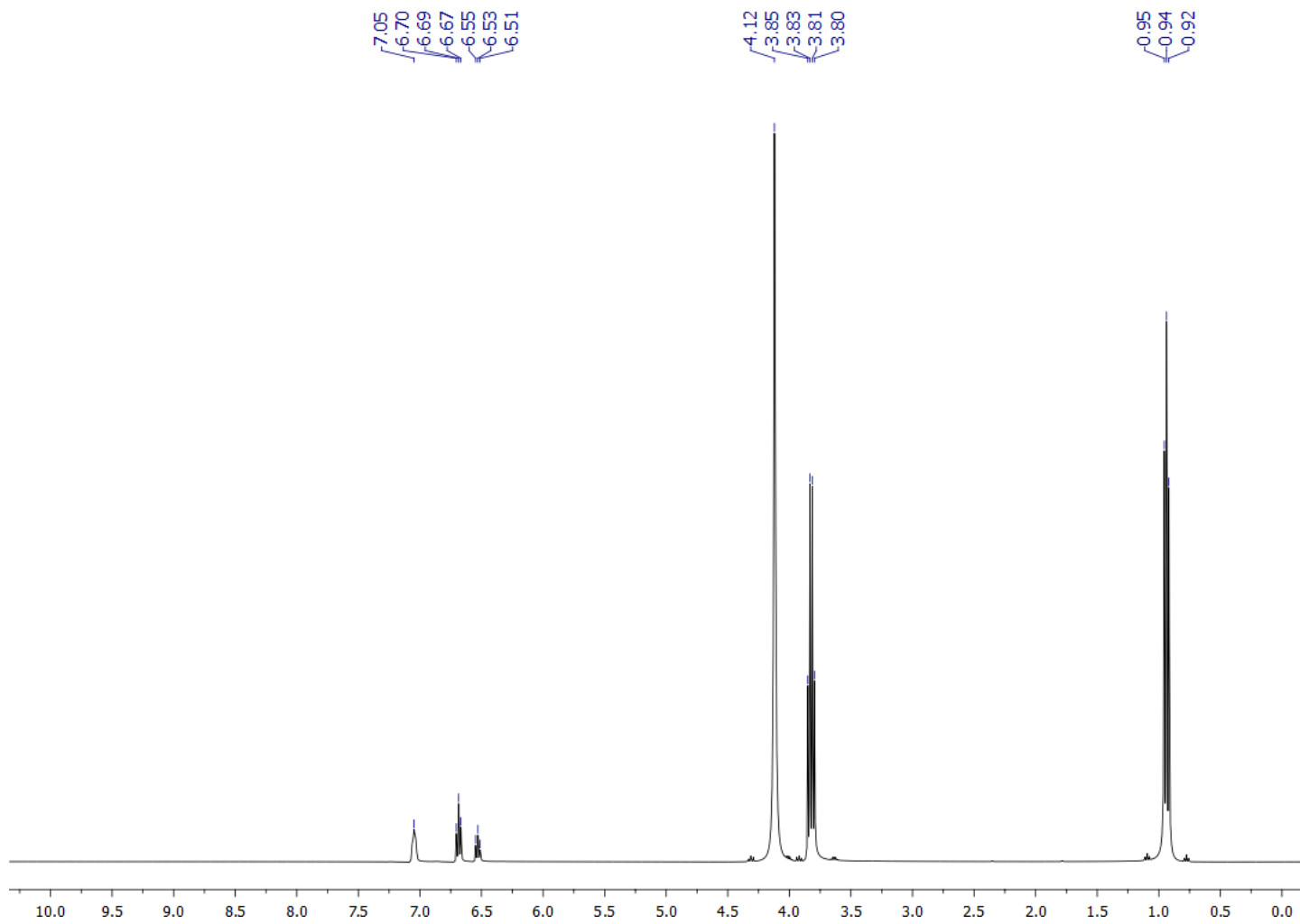
Figure S20  $^1\text{H}$  NMR (400 MHz, neat, 295 K) spectrum of pristine 0.1 M NaBPh<sub>4</sub> in EC:DEC (1:1 v/v).



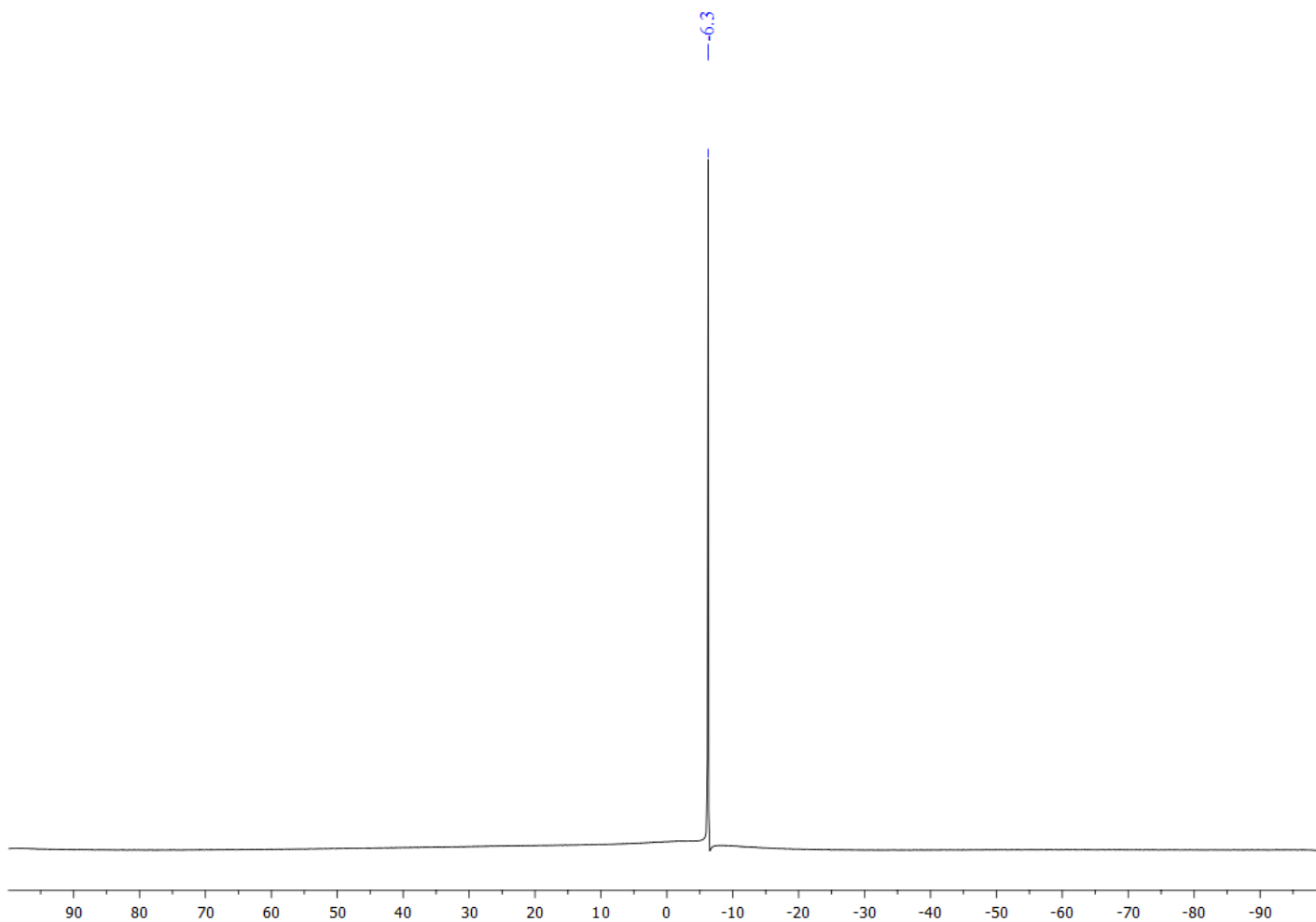
**Figure S21**  $^{11}\text{B}$  NMR (160 MHz,  $\text{CDCl}_3$ , 295 K) spectrum of pristine 0.1 M  $\text{NaBPh}_4$  in EC:DEC (1:1 v/v).



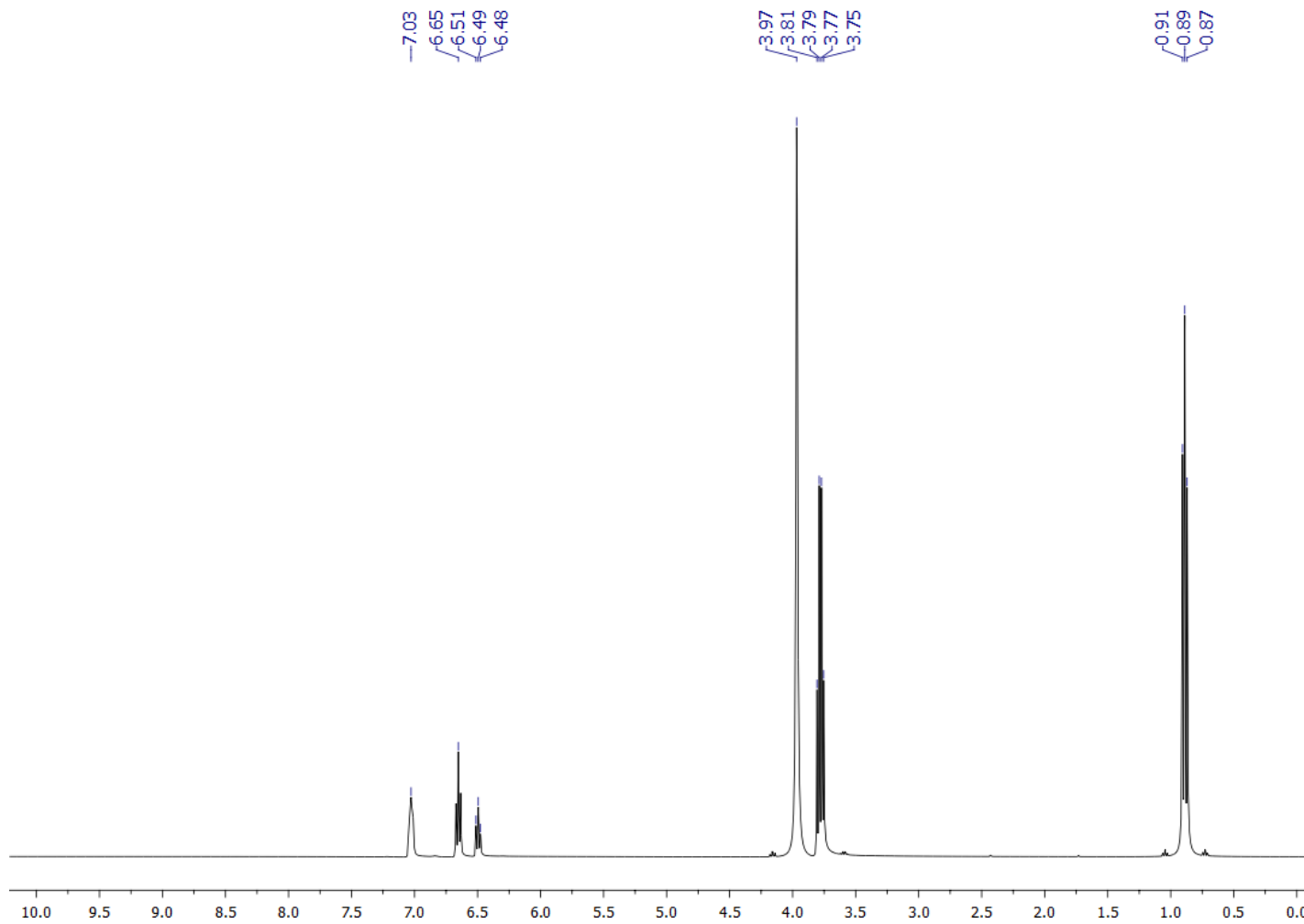
**Figure S22**  $^1\text{H}$  NMR (400 MHz, neat, 295 K) spectrum of pristine 0.25 M  $\text{NaBPh}_4$  in EC:DEC (1:1 v/v).



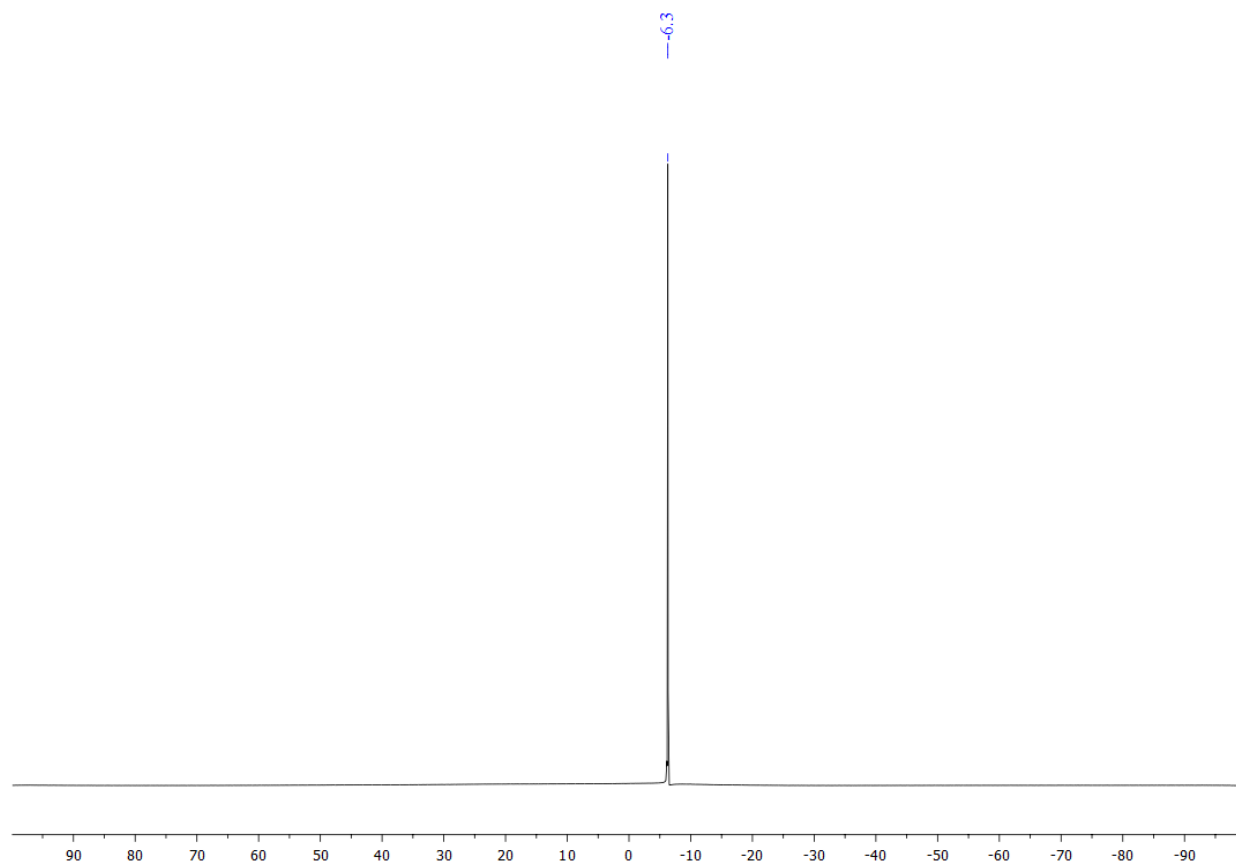
**Figure S23**  $^{11}\text{B}$  NMR (160 MHz,  $\text{CDCl}_3$ , 295 K) spectrum of pristine 0.25 M  $\text{NaBPh}_4$  in EC:DEC (1:1 v/v).



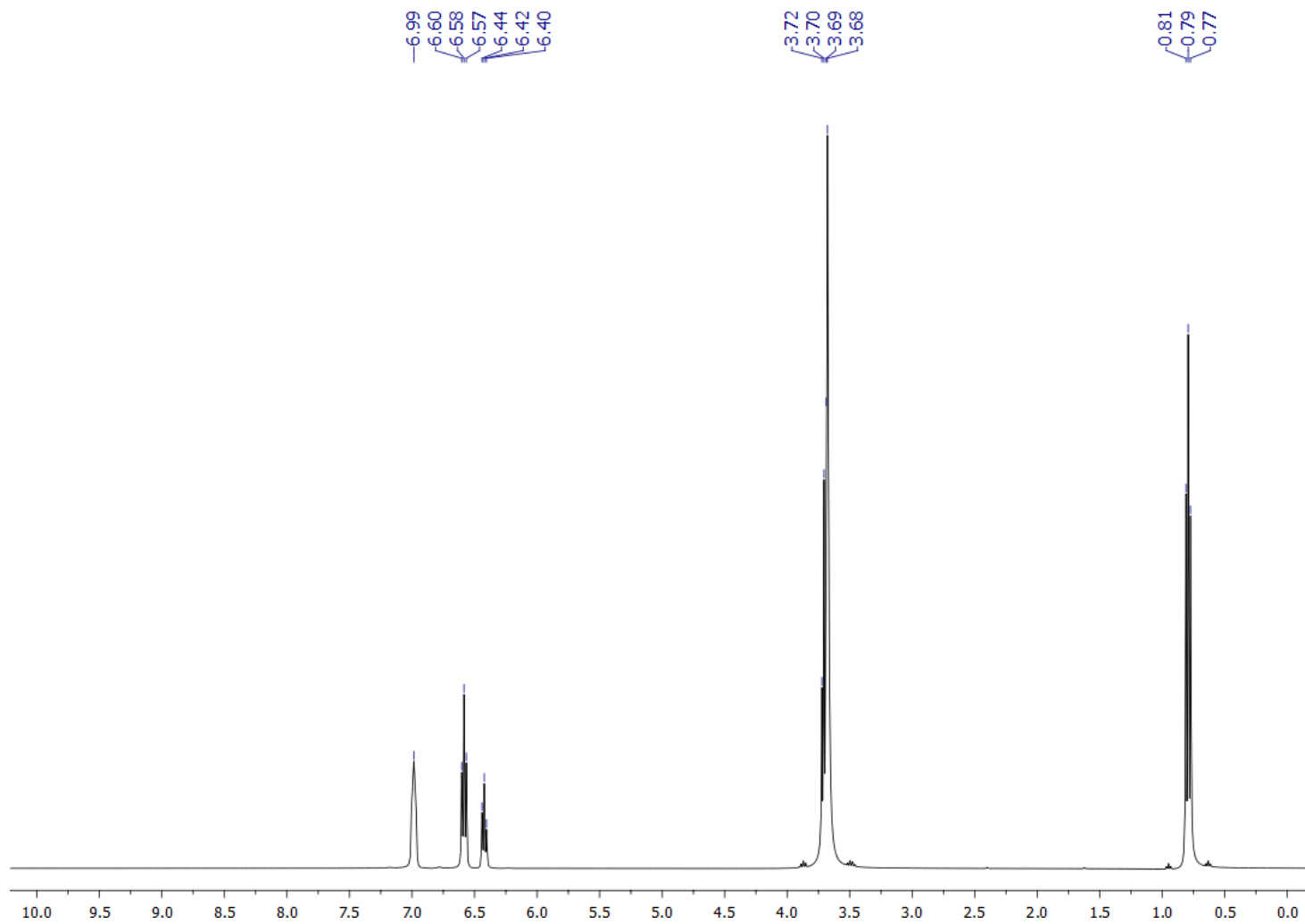
**Figure S24**  $^1\text{H}$  NMR (400 MHz, neat, 295 K) spectrum of pristine 0.5 M  $\text{NaBPh}_4$  in EC:DEC (1:1 v/v).



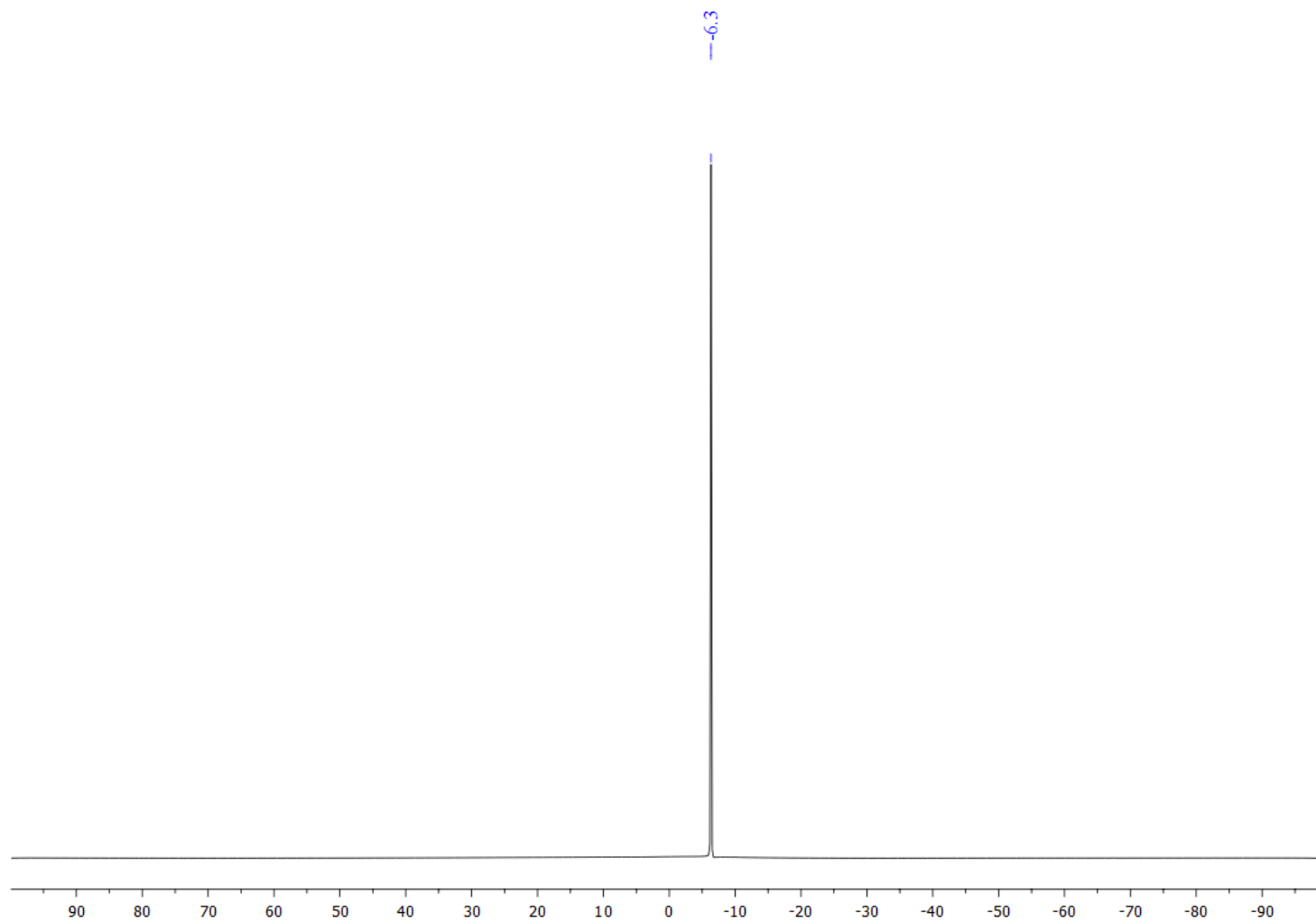
**Figure S25**  $^{11}\text{B}$  NMR (160 MHz,  $\text{CDCl}_3$ , 295 K) spectrum of pristine 0.5 M  $\text{NaBPh}_4$  in EC:DEC (1:1 v/v).



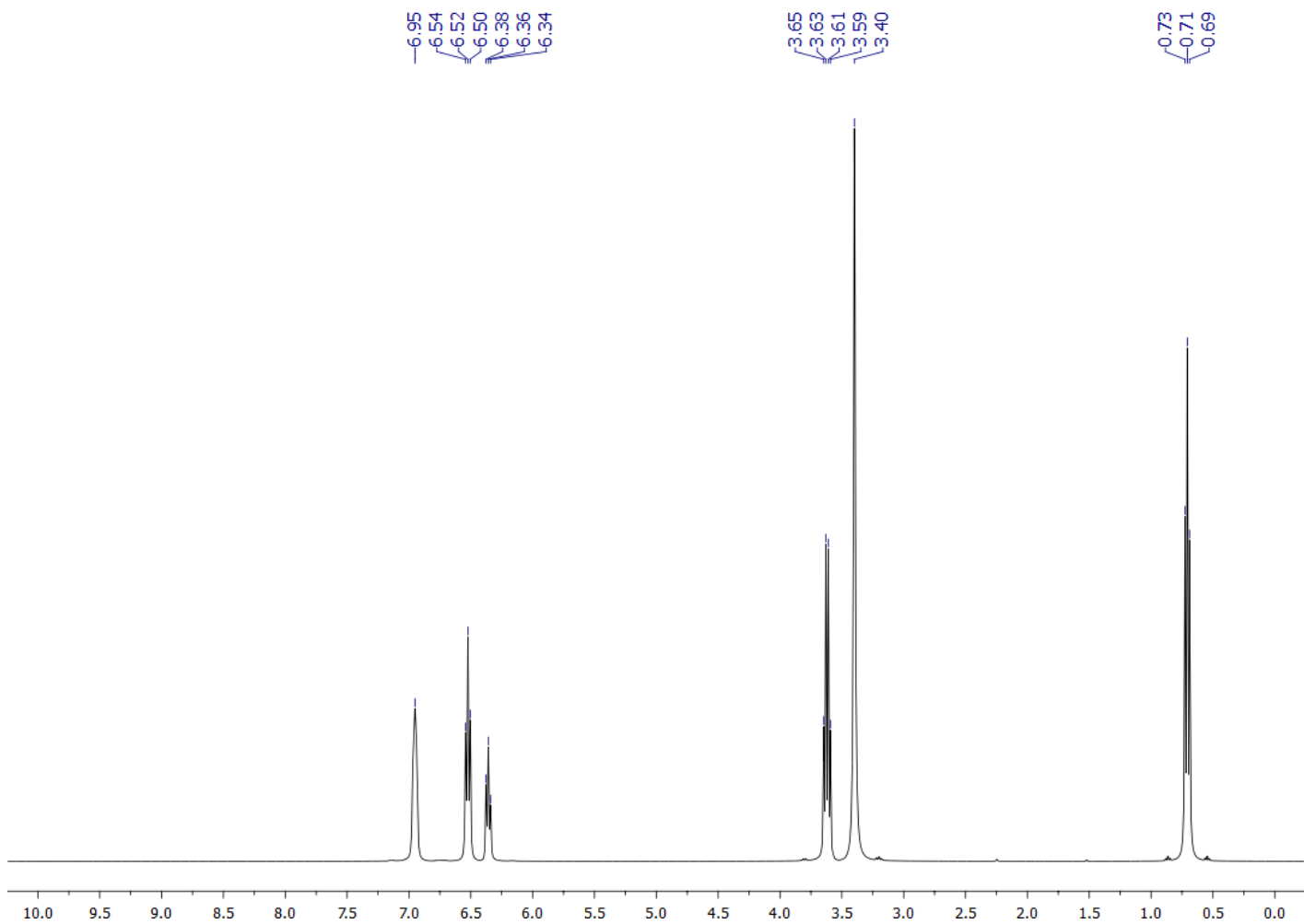
**Figure S26**  $^1\text{H}$  NMR (400 MHz, neat, 295 K) spectrum of pristine 1 M  $\text{NaBPh}_4$  in EC:DEC (1:1 v/v).



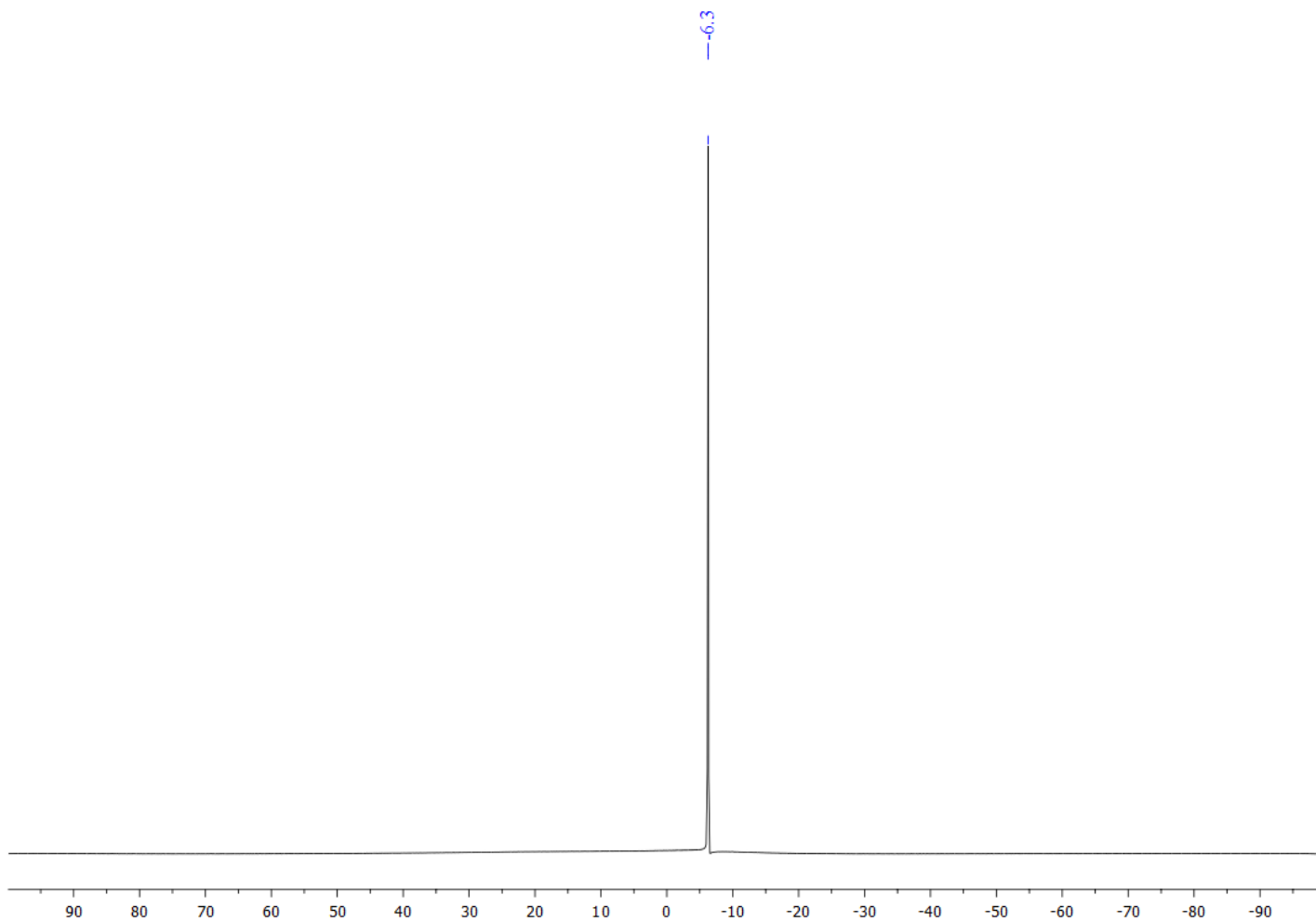
**Figure S27**  $^{11}\text{B}$  NMR (160 MHz,  $\text{CDCl}_3$ , 295 K) spectrum of pristine 1 M  $\text{NaBPh}_4$  in EC:DEC (1:1 v/v).



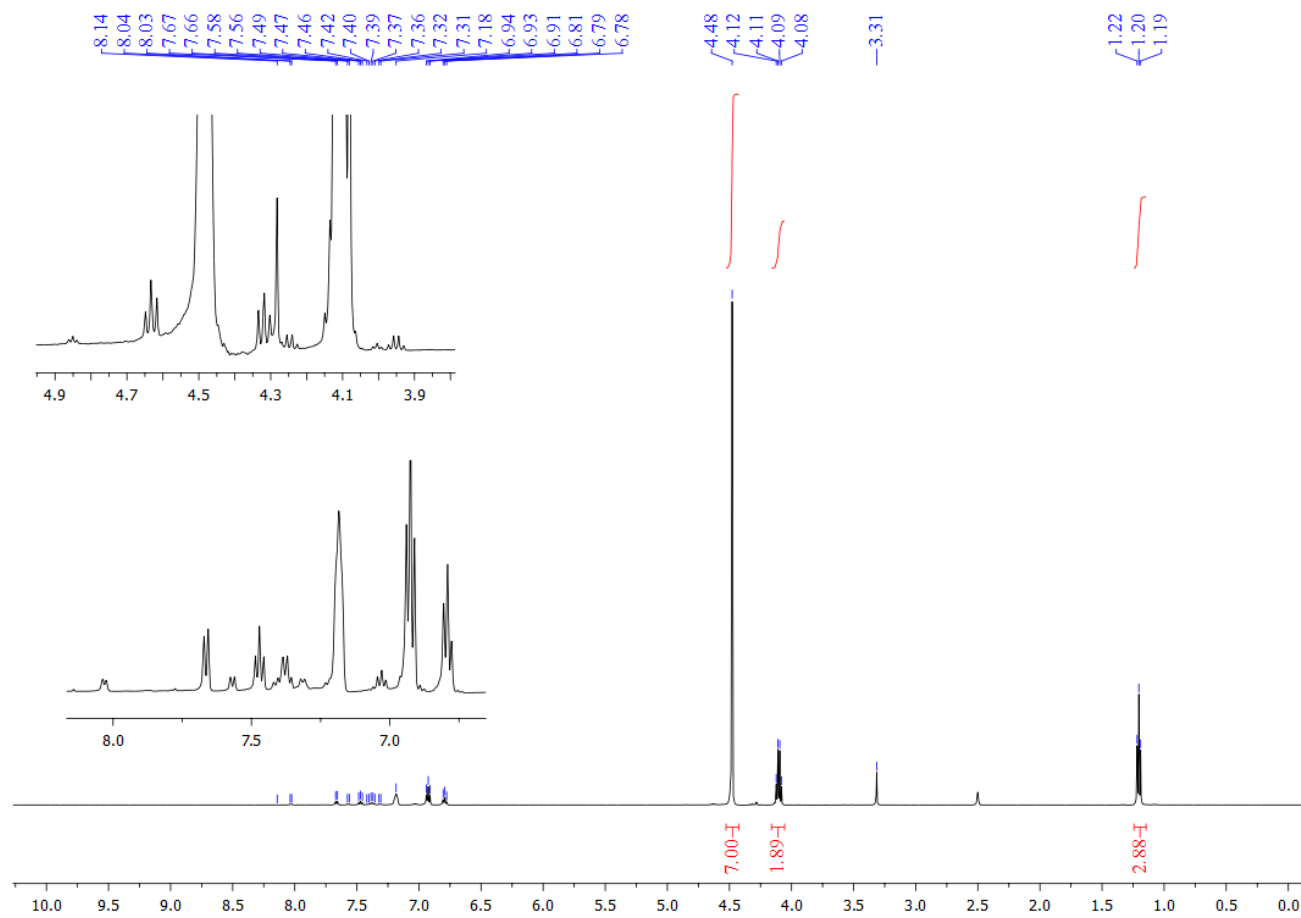
**Figure S28**  $^1\text{H}$  NMR (400 MHz, neat, 295 K) spectrum of pristine 1.5 M  $\text{NaBPh}_4$  in EC:DEC (1:1 v/v).



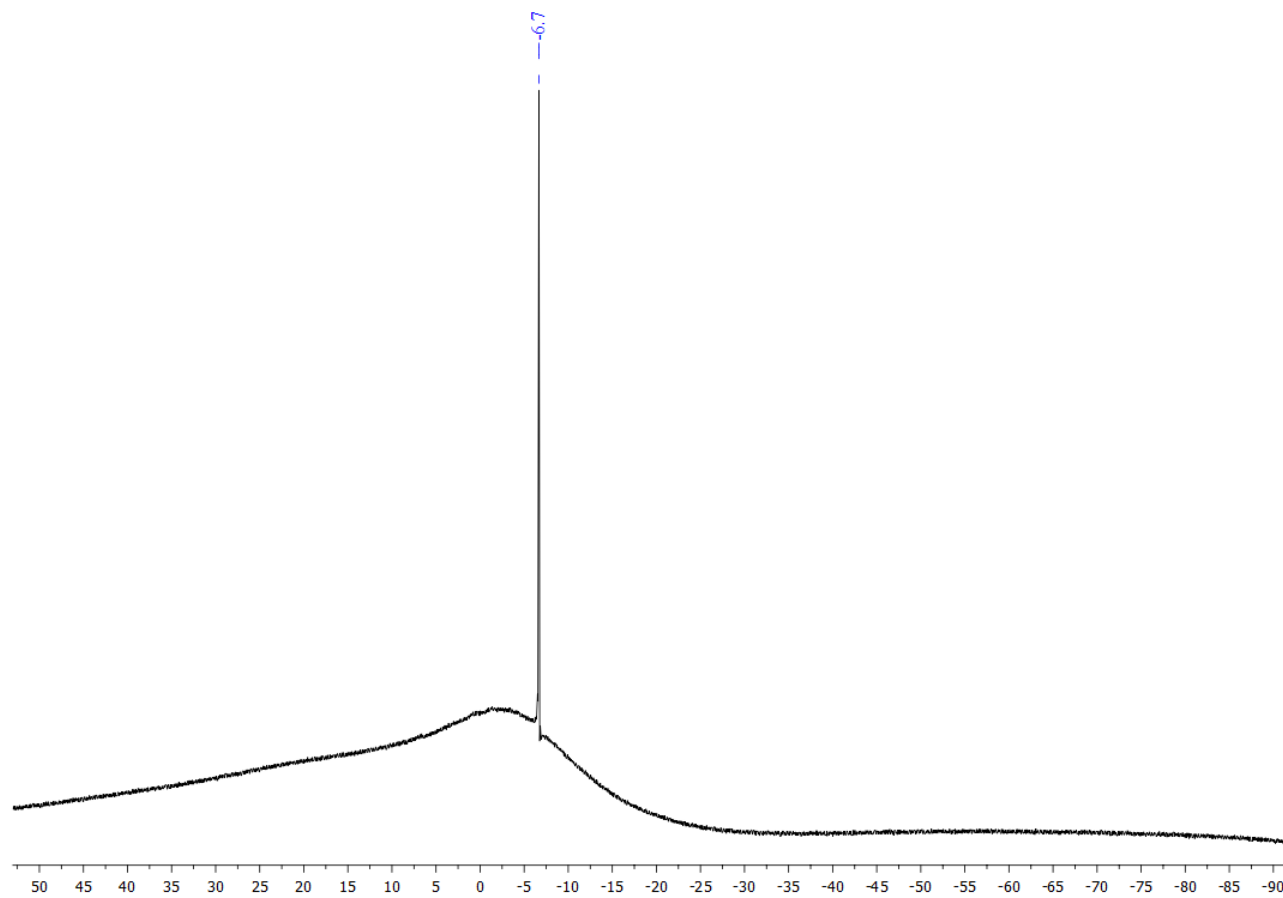
**Figure S29**  $^{11}\text{B}$  NMR (160 MHz,  $\text{CDCl}_3$ , 295 K) spectrum of pristine 1.5 M  $\text{NaBPh}_4$  in EC:DEC (1:1 v/v).



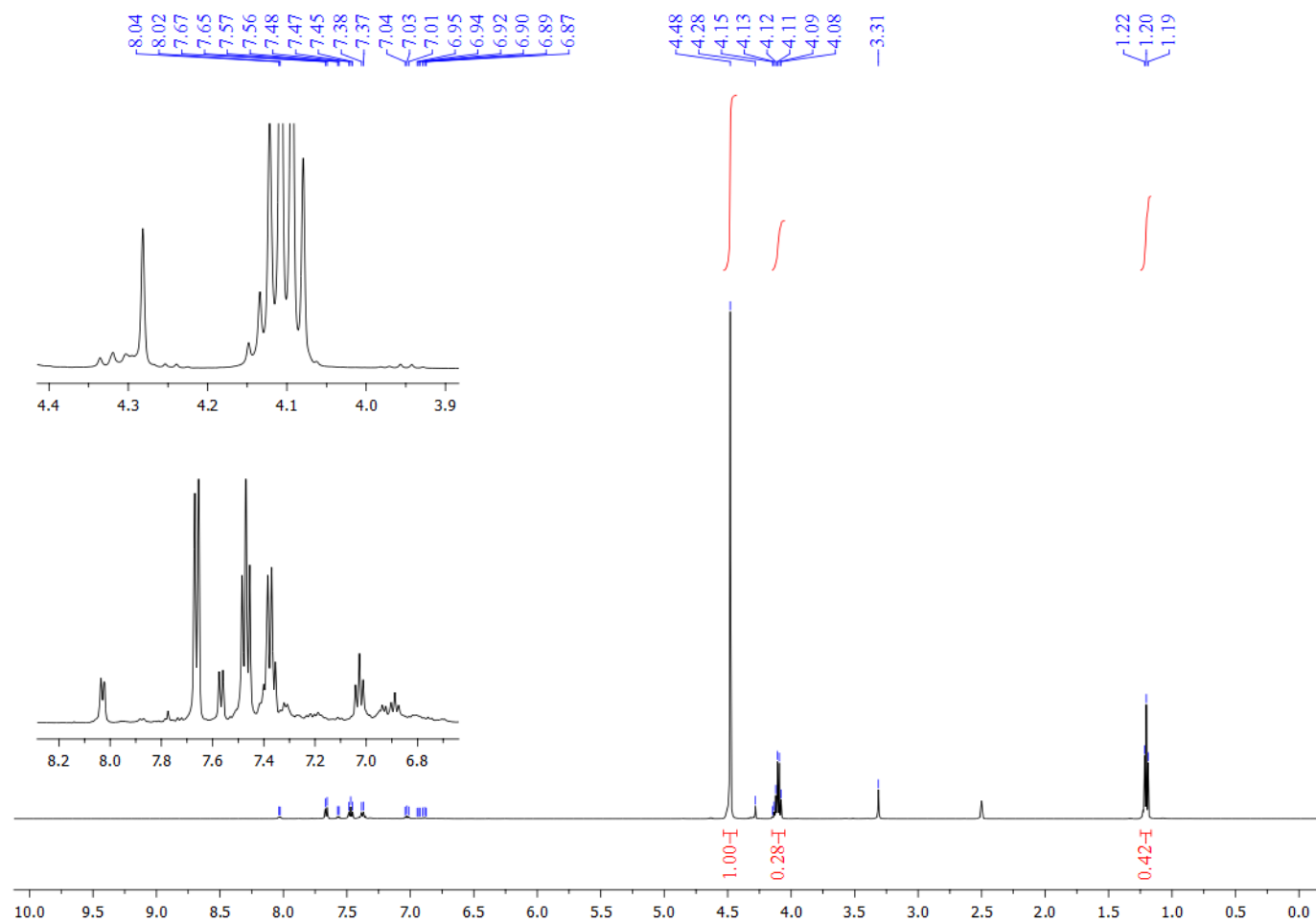
**Figure S30**  $^1\text{H}$  NMR (500 MHz,  $(\text{CD}_3)_2\text{SO}$ , 295 K) spectrum of post-cycled 0.5 M  $\text{NaBPh}_4$  in EC:DEC (1:1 v/v) cycled between 1.5–3.0 V.



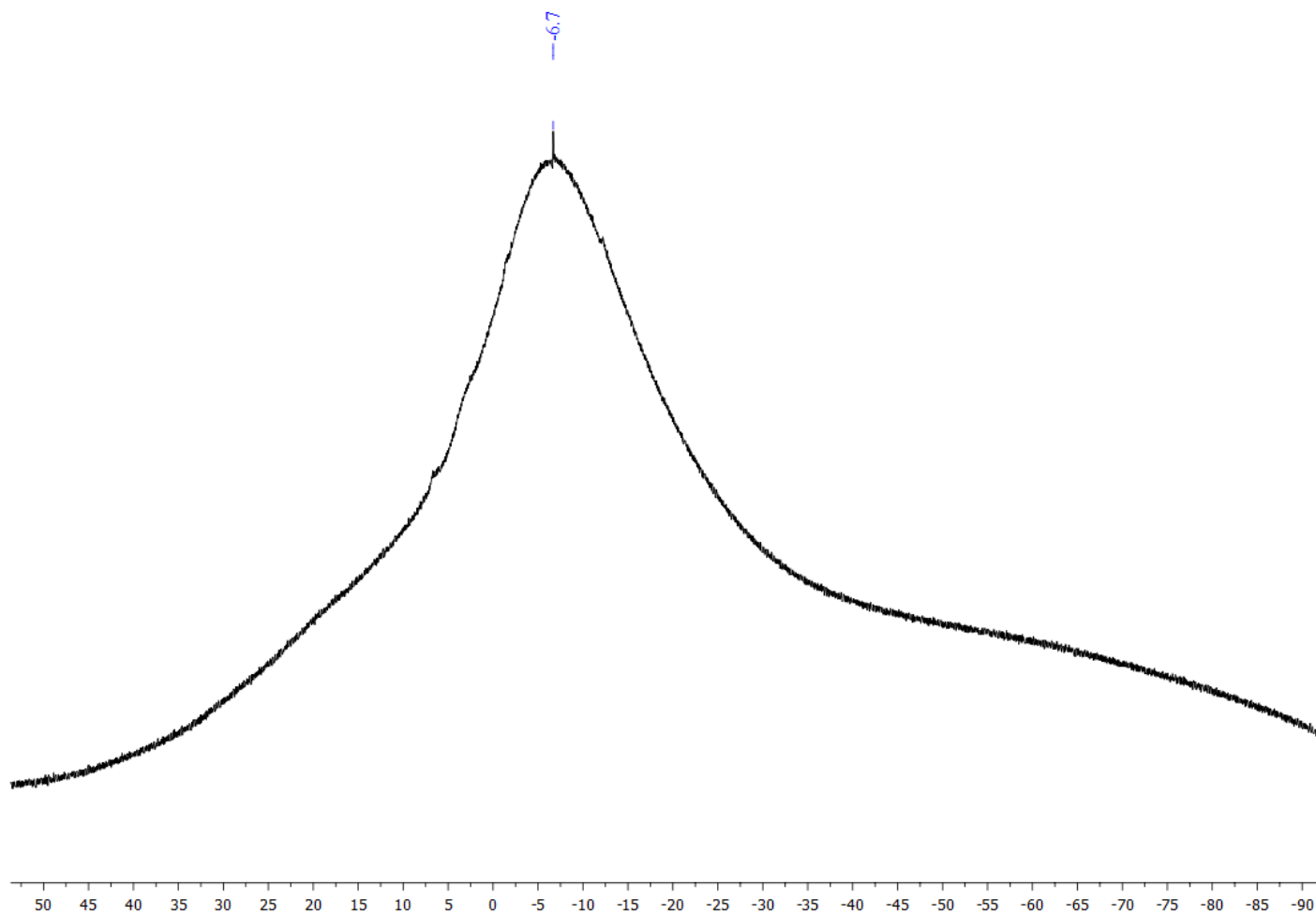
**Figure S31**  $^{11}\text{B}$  NMR (160 MHz,  $(\text{CD}_3)_2\text{SO}$ , 295 K) spectrum of post-cycled 0.5 M  $\text{NaBPh}_4$  in EC:DEC (1:1 v/v) cycled between 1.5–3.0 V.



**Figure S32**  $^1\text{H}$  NMR (500 MHz,  $(\text{CD}_3)_2\text{SO}$ , 295 K) spectrum of post-cycled 0.5 M  $\text{NaBPh}_4$  in EC:DEC (1:1 v/v) cycled between 1.5–3.2 V.



**Figure S33**  $^{11}\text{B}$  NMR (160 MHz,  $(\text{CD}_3)_2\text{SO}$ , 295 K) spectrum of post-cycled 0.5 M  $\text{NaBPh}_4$  in EC:DEC (1:1 v/v) cycled between 1.5–3.2 V.



**Figure S34**  $^1\text{H}$  NMR (400 MHz,  $(\text{CD}_3)_2\text{SO}$ , 295 K) spectrum of pristine biphenyl.

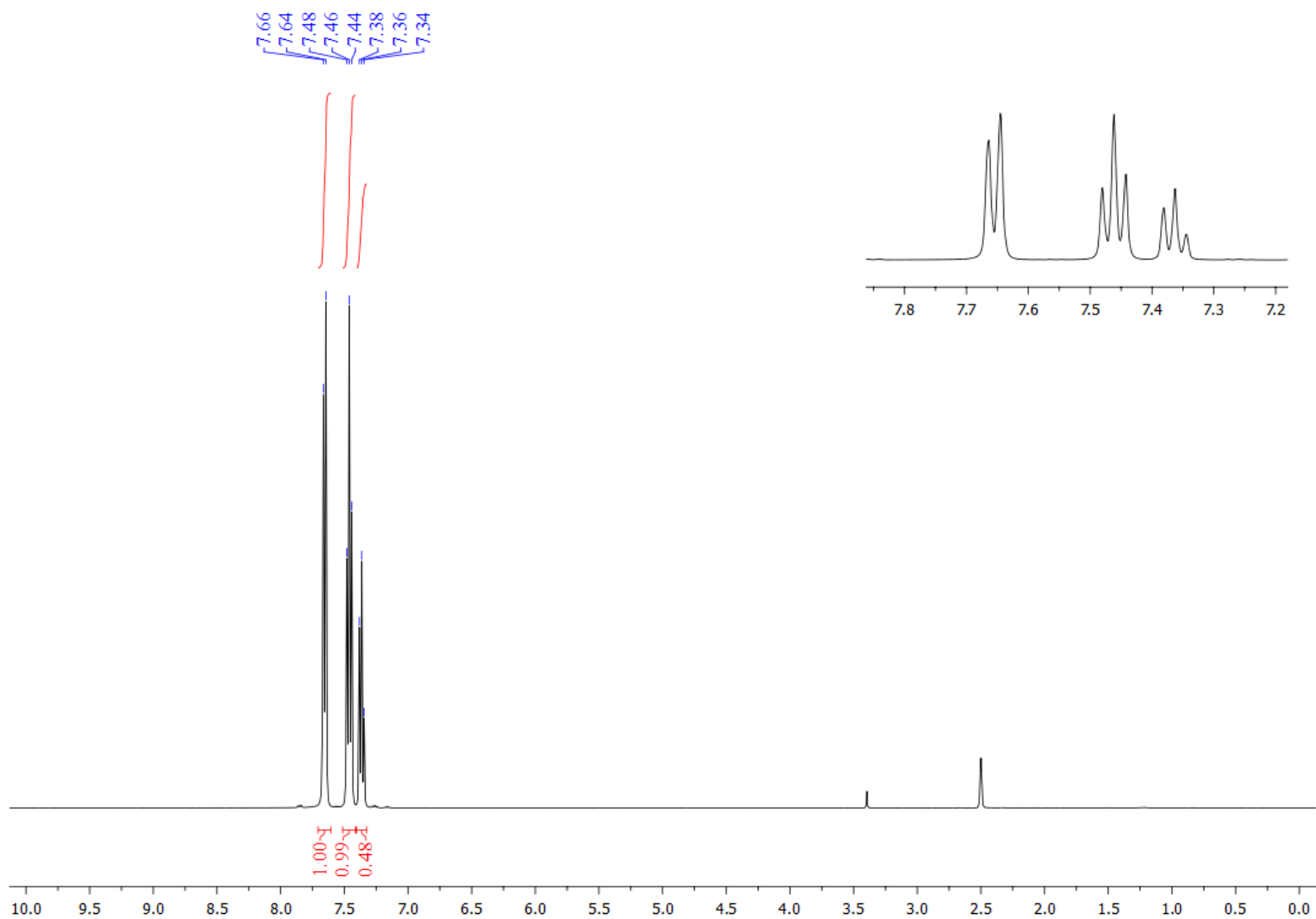
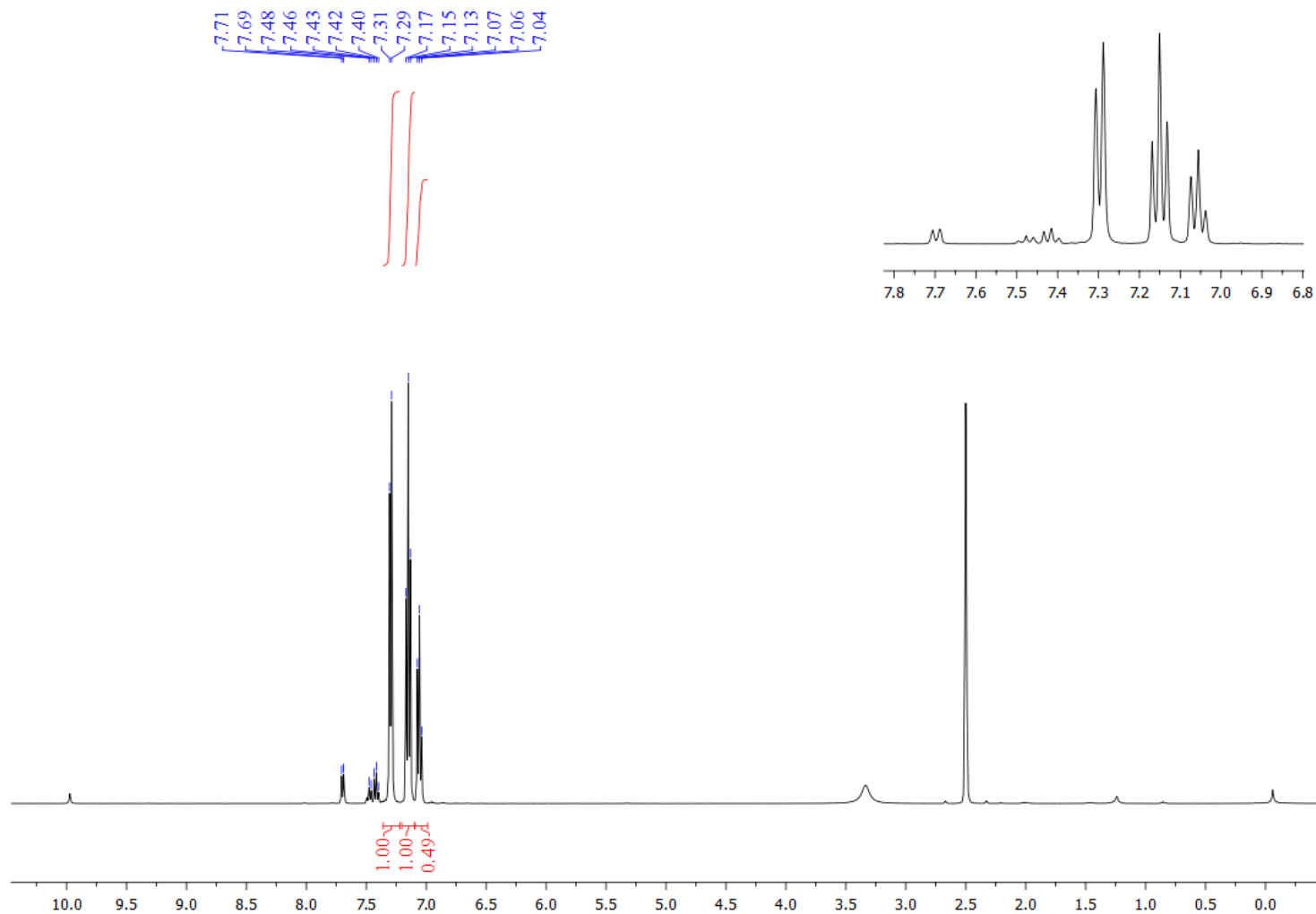


Figure S35  $^1\text{H}$  NMR (400 MHz,  $(\text{CD}_3)_2\text{SO}$ , 295 K) spectrum of pristine triphenylborane.



**Figure S36** Photo of NMR tubes containing post-cycled 0.5 M NaBPh<sub>4</sub> in EC:DEC electrolyte from cells cycled between 1.5–3.0 V and 1.5–3.2 V.



## S9 References.

- 1 D. Monti, E. Jónsson, A. Boschini, M. R. Palacín, A. Ponrouch and P. Johansson, *Phys. Chem. Chem. Phys.*, 2020, **22**, 22768–22777.
- 2 D. M. C. Ould, S. Oswald, H. E. Smith, C. A. O. Keefe, T. Song, E. Kendrick, D. S. Wright and C. P. Grey, *Chem. Commun.*, 2025, **61**, 8516–8519.