Supporting Information

Deep eutectic solvents as recyclable solvent-electrolyte systems for electroreductive C-O cleavage of lignin models

Astrid Kjær Steffensen,[a] Helena Lundberg,[b]* Anders Riisager[a]*

[a]*Technical University of Denmark, Department of Chemistry, 2800 Kgs. Lyngby, Denmark*

[b]*Department of Chemistry, KTH Royal Institute of Technology, S-100 44 Stockholm, Sweden.*

Corresponding author e-mail: ar@kemi.dtu.dk, hellundb@kth.se

Table of Contents

1. Experimental

1.1 Materials

Unless otherwise stated, all solvents and chemicals were purchased from commercial suppliers and used without further purification. The electrolyte salt, tetrabutylammonium hexafluorophosphate (NBu_4PF_6), was first recrystallized from an ethanol:water (3:1) mixture and then recrystallized three times from ethanol. The resulting white crystals were dried over high vacuum. Prior to use, molecular sieves (4Å, powder) were activated by flame drying under vacuum for 15 min and then cooled in an argon atmosphere. Anhydrous *N,N*-dimethylformamide (DMF, 99.8%, Thermo Scientific) was dried over molecular sieves prior to use for CV measurements.

RVC electrodes (6 x 36 x 5 mm, IKA) were cleaned by submersion in 1 M HCl, followed by sonication in water and acetone, and oven drying. Glassy carbon (GC) and graphite (C_{gr}) electrodes (8 x 52.5 x 2 mm, IKA) were cleaned using the same procedure. Nickel (Ni), stainless steel (SS), zinc (Zn), magnesium (Mg), and aluminum (Al) electrodes (8 x 52.5 x 2 mm, IKA) were cleaned by thorough rinsing with water, acetone and ethanol. All electrodes, except RVC and GC electrodes, were polished using ultra-fine sandpaper (grade P800 & P1000).

1.2 Synthesis of deep eutectic solvents (DESs)

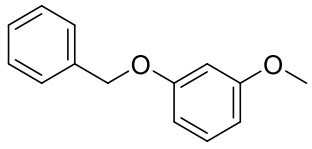
The hydrogen bond acceptor (0.375 mol, 1 eq.) was combined with the hydrogen bond donor (0.750 mol, 2 eq.) in a round bottomed flask. The mixture was heated to 80°C under vigorous stirring until a homogeneous clear liquid formed. The DES was then dried under high vacuum overnight at 80°C to remove residual water and stored under inert atmosphere.

^{1}H and ^{13}C NMR spectra of the synthesized DESs (DES-1 to DES-6) are shown in Figure S28-Figure **S33**.

1.3 Synthesis of ether substrates

Synthesis of the ether substrates **1b**-**1e** and **1h** was carried out using Williamson ether synthesis procedures reported in literature.[1] In a typical synthesis, benzyl bromide (4 mmol, 1 eq.) was dissolved in acetone (20 mL) and combined with K_2CO_3 (8 mmol, 2 eq.) and a phenol (6 mmol, 1.5 eq.) with stirring. The mixture was then heated to reflux for 18 h. After cooling, the mixture was filtered and concentrated by rotary evaporation. The product was purified by flash column chromatography using silica gel 60 (40-63µm) as the stationary phase.

Compound **1b**, 3-benzyloxyanisole, a colorless oil, was isolated by column chromatography (10% ethyl acetate, hexane). Yield 91% (isolated). The NMR data (Figure S36) is consistent with literature.[1]

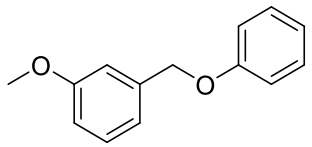


1b

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.5.-7.3 (m, 5H), 7.2 (t, *J* = 8.1, 0.5 Hz, 1H), 6.6-6.5 (m, 3H), 5.1 (s, 2H), 3.8 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0, 160.2, 137.1, 130.0, 128.7, 128.1, 127.7, 107.1, 106.7, 101.5, 70.2, 55.4.

Compound **1c**, 1-methoxy-3-(phenoxymethyl)benzene, a colorless oil, was isolated by column chromatography (10% ethyl acetate, hexane). Yield 79% (isolated). The NMR data (Figure S37) is consistent with literature.[2]

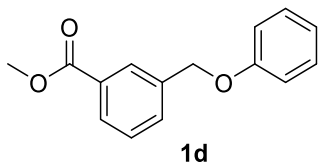


1c

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (ddd, *J* = 10.8, 5.9, 2.6 Hz, 3H), 7.05-6.92 (m, 5H), 6.87 (dd, *J* = 8.2, 2.6 Hz, 1H), 5.05 (s, 2H), 3.82 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 158.9, 138.8, 129.8, 129.6, 121.1, 119.8, 115.0, 113.6, 113.0, 69.9, 55.4.

Compound **1d**, methyl 3-phenoxymethylbenzoate, a colorless oil, was isolated by column chromatography (10% ethyl acetate, hexane). Yield 80% (isolated). The NMR data (Figure S38) is consistent with literature.[3]

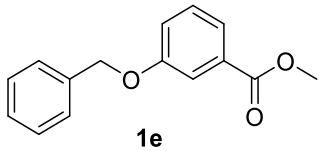


1d

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.2-8.1 (m, 1H), 8.0 (dt, *J* = 7.9, 1.5 Hz, 1H), 7.7-7.6 (m, 1H), 7.5 (t, *J* = 7.7 Hz, 1H), 7.4-7.3 (m, 2H), 7.0 (m, 3H), 5.1 (s, 2H), 4.0 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 158.7, 137.7, 132.0, 130.7, 129.7, 129.3, 128.9, 128.7, 121.3, 115.0, 69.5, 52.3.

Compound **1e**, methyl 3-(benzyloxy)benzoate, a white crystalline powder, was isolated by column chromatography (10% ethyl acetate, hexane). Yield 79% (isolated). The NMR data (Figure S39) is consistent with literature.[3]

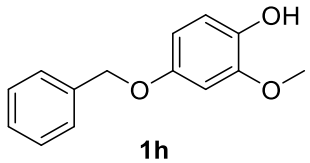


1e

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.7 (dd, *J* = 7.2, 1.6 Hz, 2H), 7.5-7.3 (m, 6H), 7.2-7.1 (m, 1H), 5.1 (s, 2H), 3.9 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 158.9, 136.7, 131.6, 129.6, 128.8, 128.3, 127.7, 122.4, 120.4, 115.2, 70.3, 52.3.

Compound **1h**, 4-(benzyloxy)-2-methoxyphenol, a colorless oil was isolated by column chromatography (10% ethyl acetate, hexane). Yield 21 %. The NMR data (Figure S40) is consistent with literature.[4]



1h

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.28 (m, 5H), 6.82 (d, *J* = 8.6 Hz, 1H), 6.57 (d, *J* = 2.7 Hz, 1H), 6.47 (dd, *J* = 8.6, 2.7 Hz, 1H), 5.22 (s, 1H), 5.00 (s, 2H), 3.85 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.9, 147.2, 140.1, 137.3, 128.7, 128.1, 127.7, 114.2, 105.6, 100.6, 71.0, 56.0.

1.4 General procedure for electrochemical C-O cleavage

Electrosynthesis was carried out with an Aim-TTi power source (MX100QP) using IKA ElectraSyn vials (5 mL) and caps to ensure consistent inter electrode gap between experiments. The Aim-TTi Test Bridge software was used to monitor voltage during the reaction.

In a typical experiment, benzyl ether (0.3 mmol, 1 eq.) was placed in an oven dried vial with molecular sieves (4Å, 60 mg) and a stir bar. The DES (3 mL) was added, and the vial was closed with an IKA cap, equipped with two electrodes. The vial was placed in an oil bath at 50°C and purged with argon for 10 min, where after the outlet needle was removed, ensuring a continuous argon atmosphere during the reaction.

Electrolysis was carried out by applying 10 mA until 2.5-10 F had passed. After electrolysis, the internal standard 4,4'-di-*t*-butylbiphenyl (0.1 M in acetonitrile) was added and samples prepared for high performance liquid chromatography (HPLC)

analysis by adding the reaction mixture to ethyl acetate and adding water if needed, to facilitate separation between the organic and DES phases (see Figure S1). Aliquot (400 μL) of the ethyl acetate phase was filtered through a syringe filter (0.22 nm), transferred to an HPLC vial and diluted with acetonitrile (1 mL).

1.5 Recycling of DESs

After sampling, the reaction mixture was filtered (frit size 4) to remove molecular sieves and any electrode deposits. Transfer of the DES was aided by using water, after which the DES-water phase was washed with ethyl acetate to remove any products or reactants (6 x 5 mL) and followed by drying under high vacuum at 80°C for 40 h.

1.6 Product analysis

HPLC analysis of electrolysis products was conducted using an Agilent 1200 instrument equipped with an inline degasser, a multiwavelength detector (254 nm, 265 nm) and a reversed phase column (Eclipse XDB-C18, 5 μm, 4.6 x 150 mm). A good separation of analytes was obtained using a gradient of acetonitrile, and 0.1% formic acid in Milli-Q® water with a flow rate of 1 mL/min at 30°C (see Figure S23). Commercially available reference compounds were used for calibrations (see Figure S24-Figure **S26**).

NMR spectra were recorded using a 400 MHz Bruker Ascend spectrometer at 298 K. Chemical shifts are reported in ppm relative to the residual solvent peak.

Gas chromatography-mass spectrometry (GC-MS) analysis of the reaction mixtures (extracted with ethyl acetate) was conducted using an Agilent GC-MS (7890A-5975C) equipped with a HP-5MS capillary column (30 m x 250 μm x 0.25 μm).

1.7 Statistical analysis

The average yield, conversion and selectivity were reported as the arithmetic mean, $\bar{X}$, calculated by equation (1) for 2-4 parallel reactions. The standard deviation, σ, was determined by equation (2).

$$\bar{X} = \frac{1}{n} \cdot \sum_{i=1}^{n} X_i \quad (1)$$

$$\sigma = \sqrt{\frac{\sum_{i=1}^{n}(X_i - \bar{X})^2}{n}} \quad (2)$$

n is the number of parallel reactions and X_i is the numerical value of individual measurements.

1.8 Electrochemical analysis

Cyclic voltammetry (CV) measurements were carried out using a WaveNow^{XV} Potentiostat (Pine Research). Measurements were performed in single compartment cell with a three-electrode set up, consisting of a glassy carbon (GC) disk electrode (diameter 1 mm, ALS catalogue no. 002411), Pt wire counter electrode and a saturated calomel reference electrode, separated from the sample by a glass frit (SCE, saturated KCl, ALS catalogue no. 013458). Prior to each measurement, the Pt wire was flame dried and the disk electrode was polished with 0.05 µm polishing alumina on a polishing pad.

All solutions were purged with argon for 15 min prior to measurements. Substrates were fully dissolved in neat DES (10-80 mM) prior to measurements. CV measurements of substrates in conventional electrolyte were conducted by measuring a DMF solution of substrate (10-80 mM) in 0.1 M NBu_4PF_6 purged with argon prior to measurements. All measurements were referenced to ferrocene/ferrocenium (Fc/Fc^+) redox couple ($E_{1/2}$ = 0.479 V vs SCE, see Figure S10). The CV measurements were performed at scan rates of 20-100 mV/s. The scan always started at the open circuit potential and continued in the direction indicated on the graph. The cyclic voltammograms are plotted using the IUPAC convention. The cathodic and anodic limit of the DESs were arbitrarily defined as the potential at which the current density reached 0.5 mA/cm^2. The onset potential was determined by the tangent method. The cyclic voltammetry data plotted represents the last cycle of at least four cycles to ensure that the behavior is stable and consistent over several cycles.

1.9 Characterization of DESs

The water content of dried DES was determined by coulometric Karl-Fischer titration. Samples of 0.1-0.2 g were analyzed using a Metrohm Eco Coulometer. The reported water content is an average of at least two independent measurements.

The viscosity of the DES was measured at 50°C using a discovery HR-2 rheometer (TA instruments), equipped with a parallel plate (steel, 40 mm). The reported viscosities are an average of three independent flow sweeps with shear rates varying from 1.25 to 125 s^{-1}.

The conductivity of the DES was measured at 50°C using a SevenCompact S230 (Mettler Toledo) conductivity meter equipped with an InLab® 731 ISM conductivity probe.

2. Physical properties of DESs

Table S1: Physical properties of synthesized DESs

DES	Water content (ppm)[a]	Viscosity (mPa·s)[b]
DES-1	1.213 ± 11	166
DES-2	14.900 ± 135	155
DES-3	10.700 ± 2.6	29
DES-4	4.801 ± 329	14
DES-5	17.870 ± 242	85

[a] Determined by Karl Fischer titration after drying for 18 h at 80 °C under vacuum. [b] Average viscosity over a range of shear rates at 50 °C, see section 1.9 for details.

Table S2: Water content of DES-1 after recycling in the C-O cleavage of **1a**.

Run	Water content (ppm)[a]
1	1.213 ±11
2	3.629 ± 383
3	10.180 ± 823
4	12.770 ± 13

[a] Determined by Karl Fischer titration after recovery of used DES and drying for 18 h at 80 °C under vacuum.

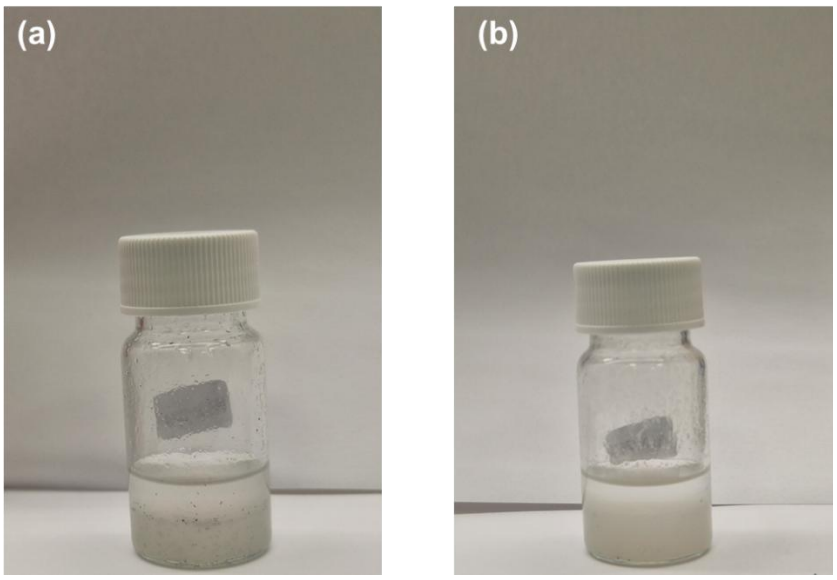


Figure S1: Phase separation after electrolysis reaction (a) DES-1/ethyl acetate and (b) DES-1+H_2O/ethyl acetate.

3. Additional bulk electrolysis experiments

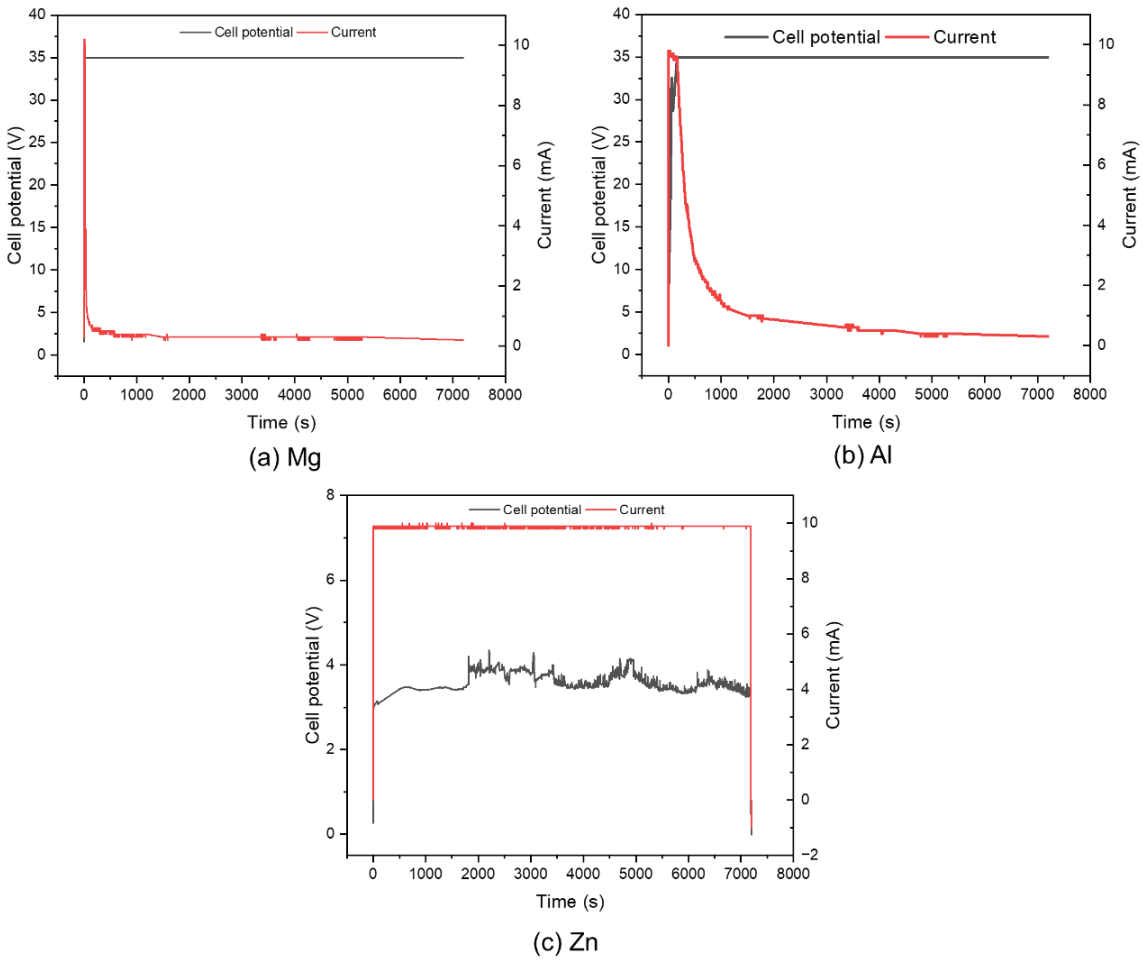
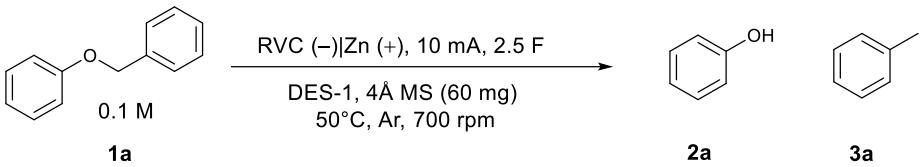


Figure S2: Representative voltage and current recording during the optimization of C-O cleavage of **1a** in DES-1 with different sacrifical anodes (a) Mg, (b) Al, and (c) Zn.

Table S3: Additional experiments



1a **2a** **3a**

Entry	Deviations	Conversion (%)	Selectivity / Yield (%)		Carbon balance (%)
			2a	**3a**	
1	None	36	82 / 29	56 / 20	89
2	None	45	76 / 34	42 / 19	81
3	None	36	62 / 22	51 / 18	84
4	GC(−)	29	62 / 18	21 / 6	73
5	GC(−)	30	47 / 14	15 / 4	79
6	GC(−)	24	50 / 9	16 / 4	83
7	C_{gr}(−)	41	22 / 9	20 / 8	68
8	C_{gr}(−)	29	12 / 4	12 / 3	74
9	Ni	3	-	-	97
10	Ni	-	-	-	100
11	SS	-	-	-	100
12	SS	7	-	-	93
13	Mg(+)[a]	19	13 / 2	14 / 3	83
14	Mg(+)[b]	19	14 / 3	-	82
15	Al(+)[c]	24	43 / 10	41 / 10	86
16	Al(+)[d]	25	33 / 8	32 / 8	83
17	NBu_4BH_4 (0.3 eq.)	47	64 / 30	32 / 15	75
18	NBu_4BH_4 (0.3 eq.)	41	61 / 25	29 / 12	77
19	NBu_4BH_4 (0.3 eq.) C_{gr}(+)	47	33 / 16	30 / 14	68
20	NBu_4BH_4 (0.3 eq.), C_{gr}(+)	55	41 / 23	45 / 25	69
21	No MS	43	70 / 30	51 / 22	83
22	No MS	25	78 / 19	40 / 10	90
23	No current	5	-	-	95
24	No current	3	-	-	97
25	1500 rpm	42	98 / 41	57 / 24	90
26	1500 rpm	46	97 / 45	78 / 36	94
27	1500 rpm	38	96 / 36	82 / 31	96
28	$NaHCO_3$ (10 eq), 1500 rpm	53	66 / 32	38 / 20	70
29	NBu_4PF_6 (2 eq), 1500 rpm	34	60 / 21	27 / 9	80
30	NBu_4PF_6 (10 eq), 1500 rpm	38	49 / 19	32 / 12	77
31	C_{gr}(−) (reuse), 700 rpm	20	41 / 8	-	84
31	C_{gr}(−) (reuse), 700 rpm	22	39 / 9	-	82

32	DMF/0.25 M NBu_4PF_6, 1500 rpm	77	85 / 65	76 / 59	85
33	DMF/0.25 M NBu_4PF_6, 1500 rpm	66	54 / 35	37 / 24	64
34	0.05 M substrate, 1500 rpm	29	86 / 25	34 / 10	88
35	0.05 M substrate, 1500 rpm	36	63 / 23	55 / 20	85
36	0.05 M substrate, 1500 rpm, 5 F	30	70 / 21	32 / 10	85
37	0.05 M substrate, 1500 rpm, 5 F	37	90 / 34	43 / 16	87

[a] Charge passed 2.5 C. [b] Charge passed 1.2 C. [c] Charge passed 8.0 C. [d] Charge passed 10 C.

4. Design of experiments

Table S4: Analysis of variance parameters for each response value on the 33 set of experiments for the DoE.

p-values[a]			
Factor	Conversion	Phenol yield	Toluene yield
A: Temperature	**0.0067 (-)**	**0.0435 (-)**	**0.0491 (-)**
B: Current	0.1250 (+)	0.4477 (+)	0.7868 (-)
C: Charge	**0.0117 (+)**	0.3876 (+)	0.2158 (+)
AB	0.5506 (+)	0.1068 (+)	**0.0369 (+)**
AC	0.5713 (-)	0.1874 (-)	0.1358 (-)
BC	0.0516 (+)	0.6924 (-)	0.5419 (-)
ABC	0.5480 (-)	0.1160 (-)	0.3084 (-)
R^2 (%)	74.9	60.1	62.7

[a] p-values marked in bold designate a statistically significant factor with a confidence level of 95%. By each p-value the sign denotes whether the corresponding parameter has a positive or negative effect on the variable.

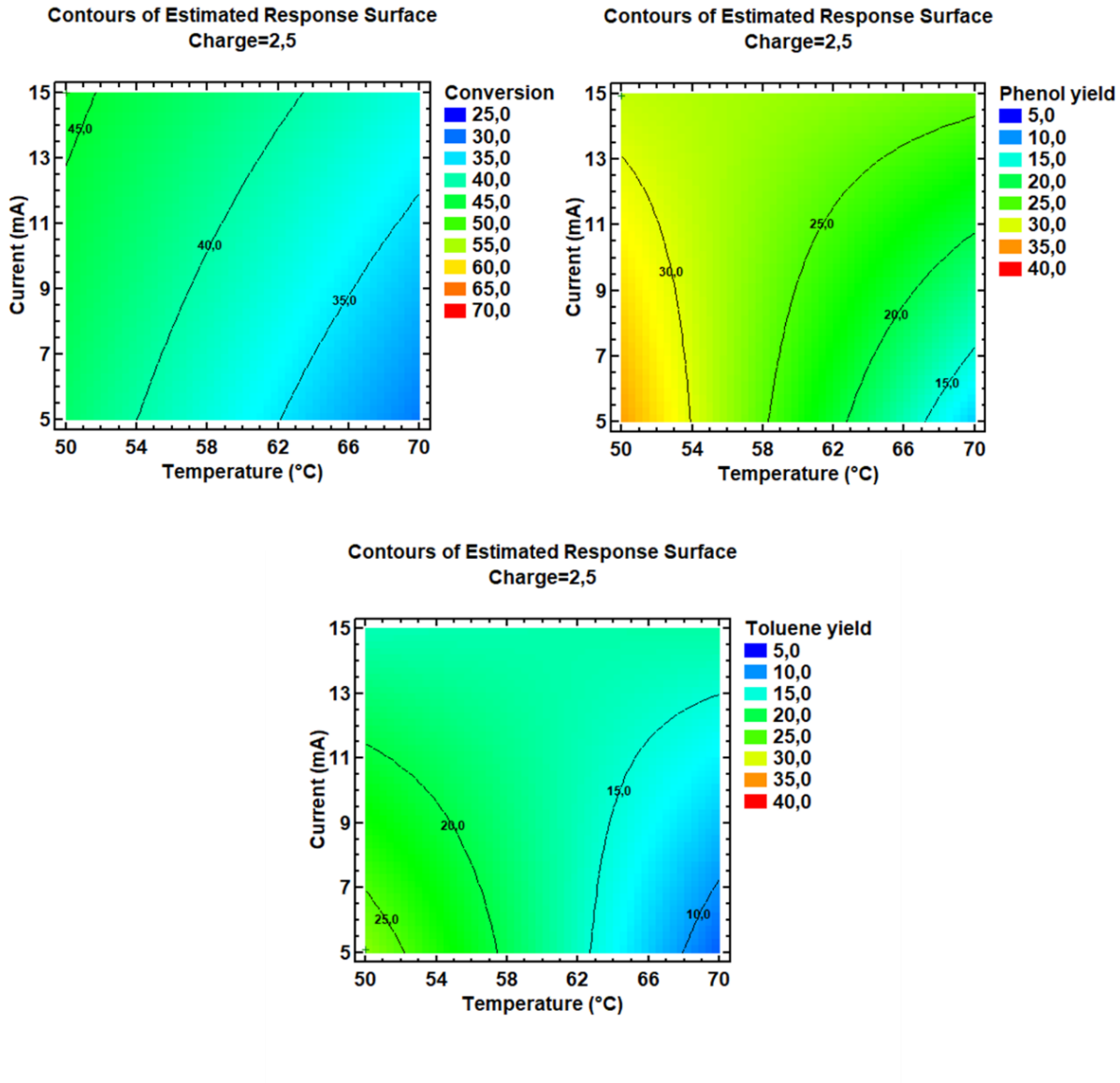


Figure S3: Contours plots from DoE showing temperature and applied current as a function of conversion, phenol yield and toluene yield.

5. Cyclic voltammetry

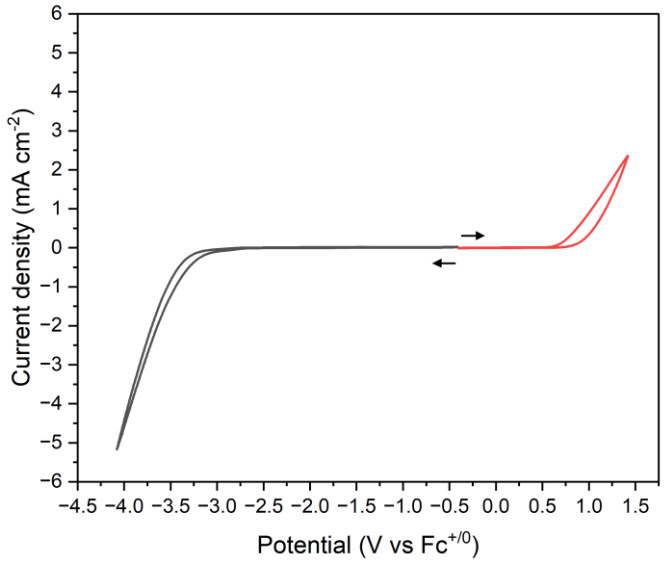


Figure S4: CV of DES-1 with anodic cycle (red) and separate cathodic cycle (black). Scan rate 100 mV/s. Arrows denote the direction of the scan.

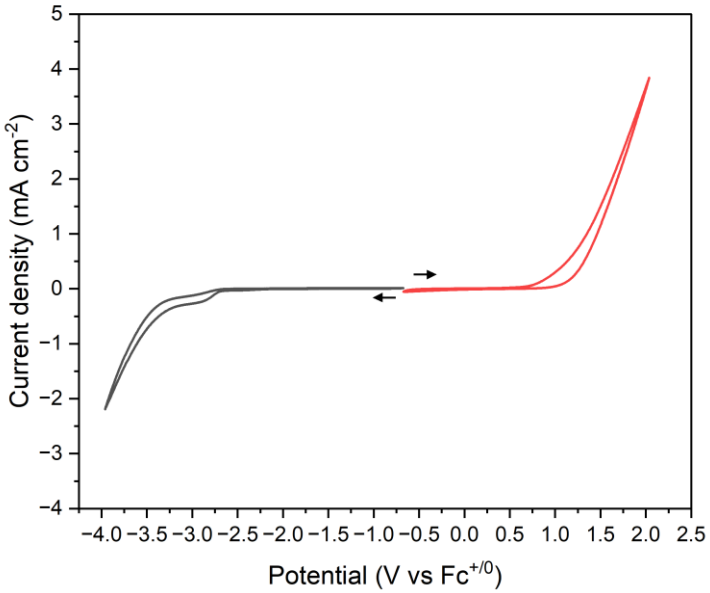


Figure S5: CV of DES-2 with anodic cycle (red) and separate cathodic cycle (black). Scan rate 100 mV/s. Arrows denote the direction of the scan.

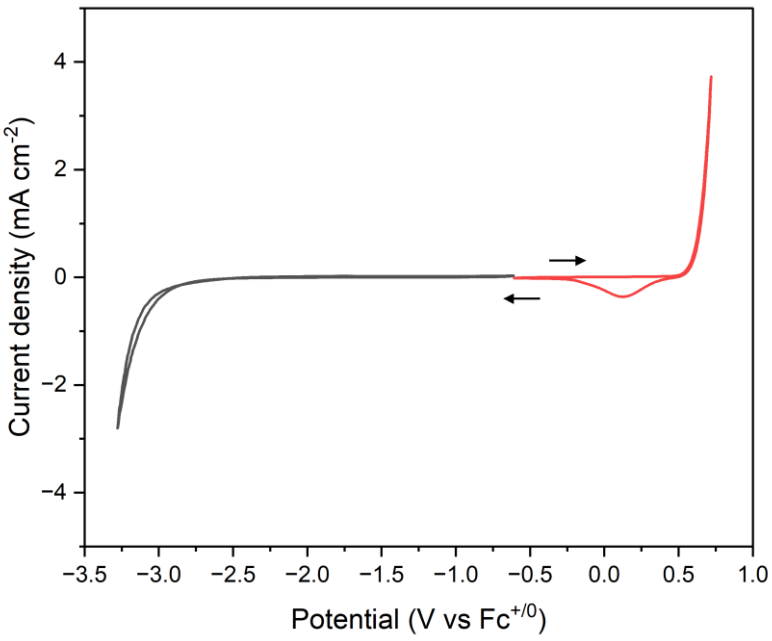


Figure S6: CV of DES-3 with anodic cycle (red) and separate cathodic cycle (black). Scan rate 100 mV/s. Arrows denote the direction of the scan.

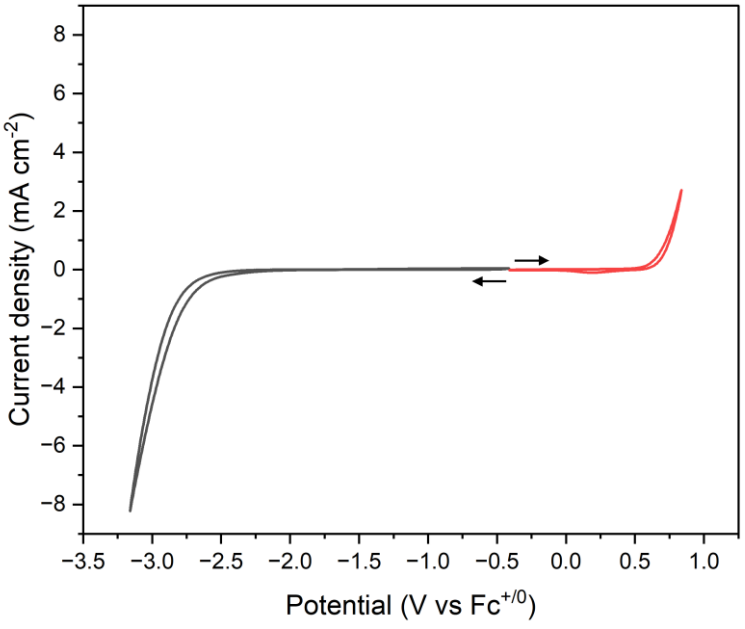


Figure S7: CV of DES-4 with anodic cycle (red) and separate cathodic cycle (black). Scan rate 100 mV/s. Arrows denote the direction of the scan.

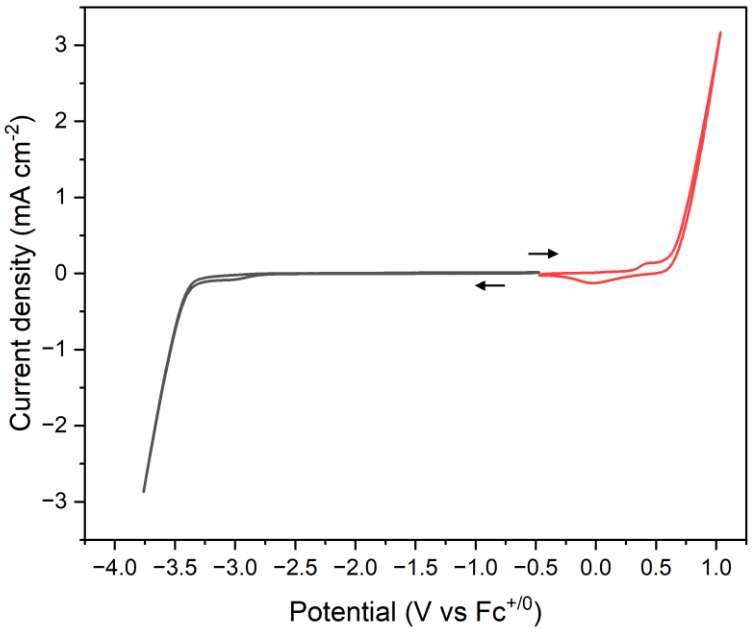


Figure S8: CV of DES-5 with anodic cycle (red) and separate cathodic cycle (black). Scan rate 100 mV/s. Arrows denote the direction of the scan.

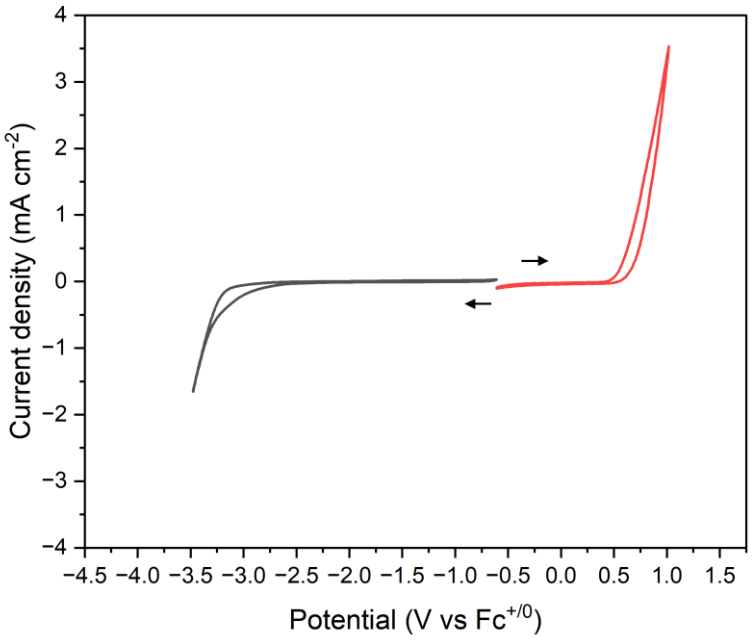


Figure S9: CV of DES-6 with anodic cycle (red) and separate cathodic cycle (black). Scan rate 100 mV/s. Arrows denote the direction of the scan.

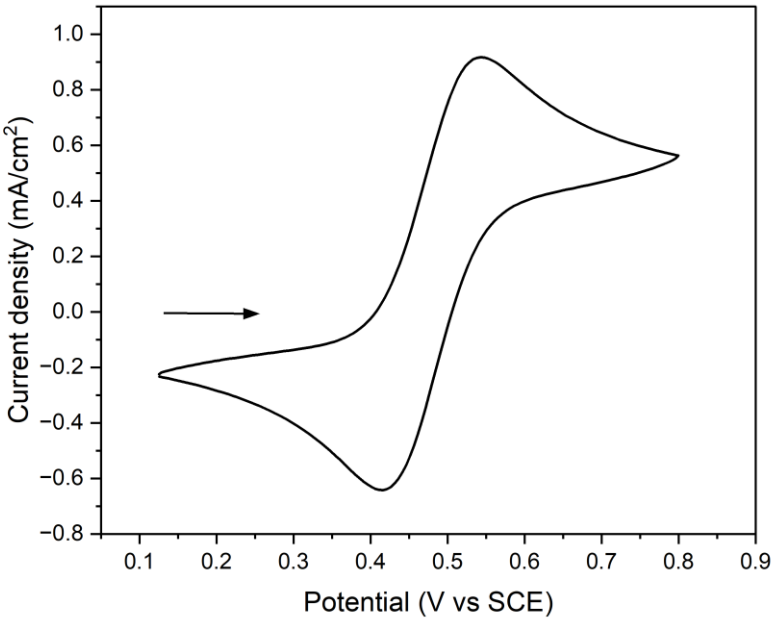


Figure S10: CV of ferrocene in DMF/NBu_4PF_6. Scan rate 100 mV/s. The arrow denotes the direction of the scan

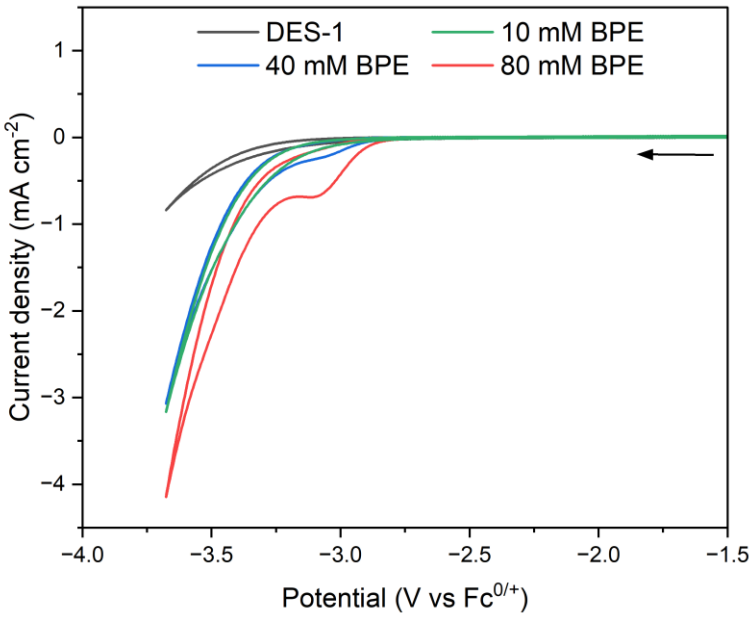


Figure S11: CV of **1a** at varying concentrations in DES-1. Scan rate 100 mV/s. The arrow denotes the direction of the scan.

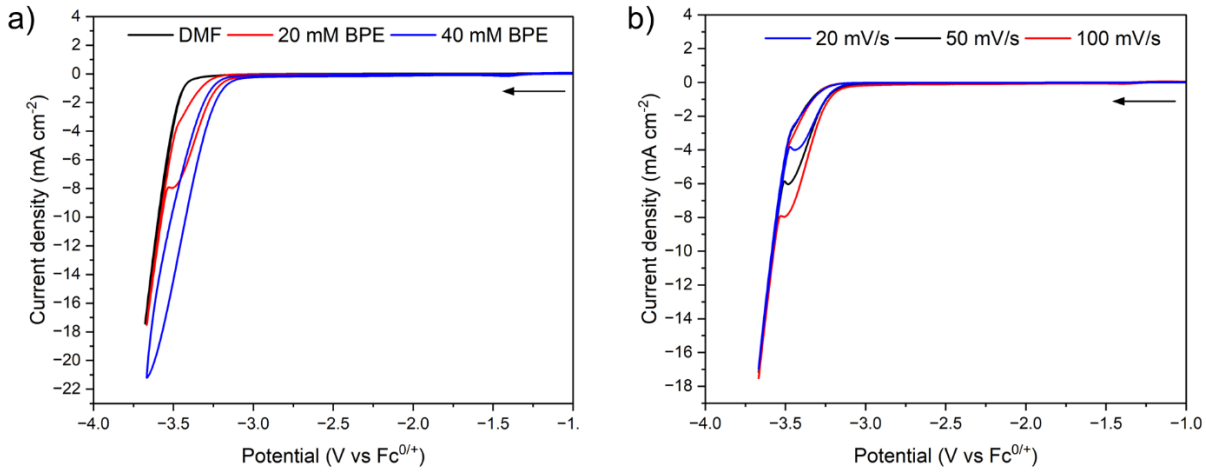


Figure S12: CV of **1a** in DMF/NBu_4PF_6 at a) varying concentrations with a scan rate 100 mV/s, and at b) concentration of 20 mM with varying scan rates. The arrow denotes the direction of the scan.

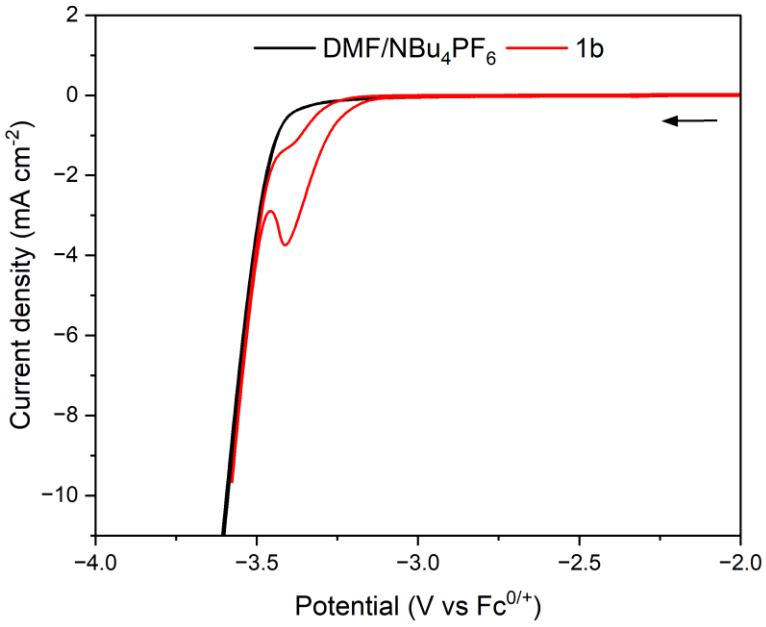


Figure S13: CV of **1b** (10 mM) in DMF/NBu_4PF_6. Scan rate 100 mV/s. The arrow denotes the direction of the scan.

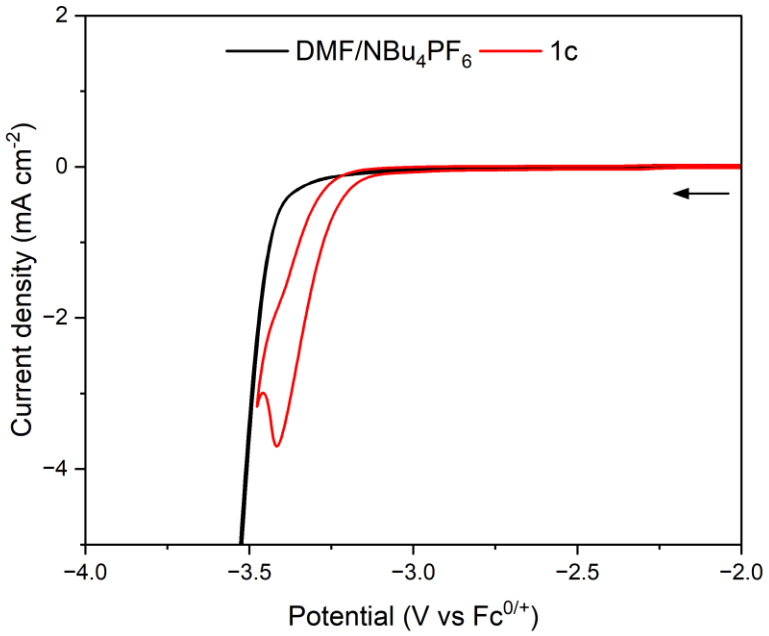


Figure S14: CV of **1c** (10 mM) in DMF/NBu_4PF_6. Scan rate 100 mV/s. The arrow denotes the direction of the scan.

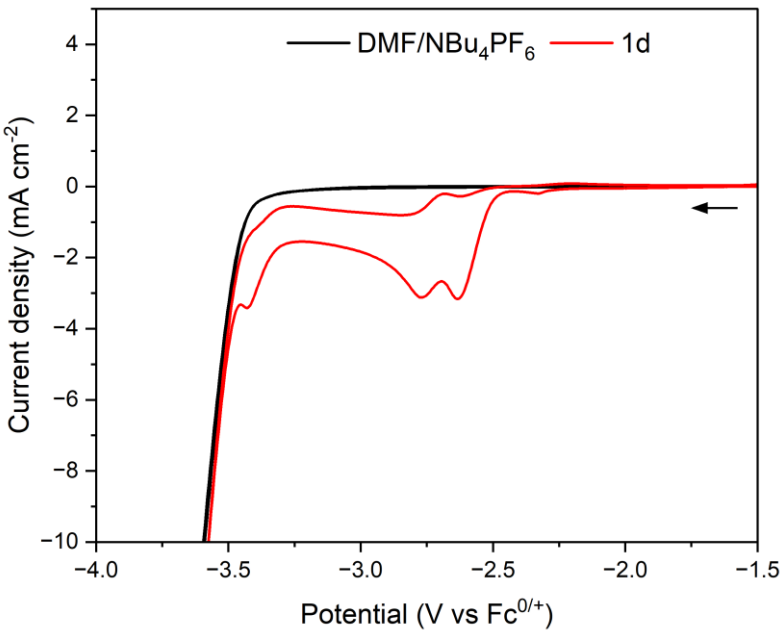


Figure S15: CV of **1d** (10 mM) in DMF/NBu_4PF_6. Scan rate 100 mV/s. The arrow denotes the direction of the scan.

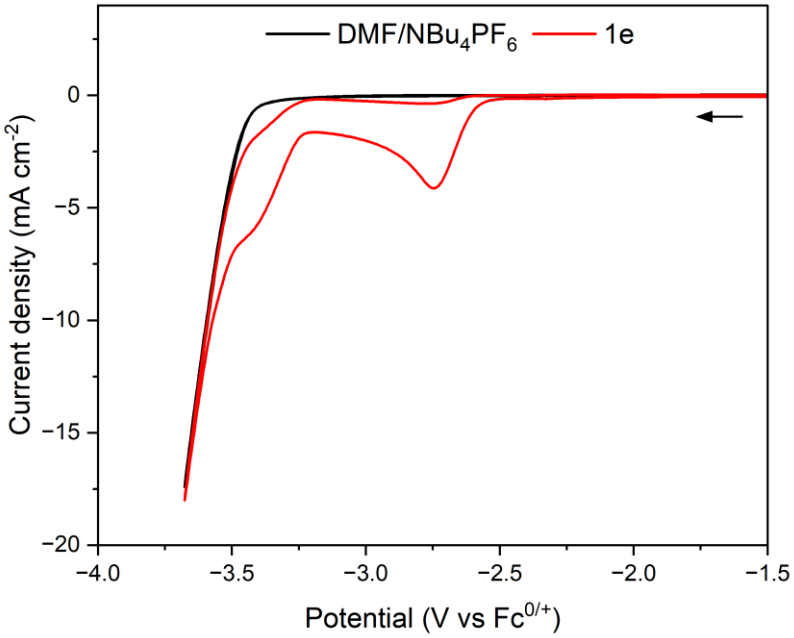


Figure S16: CV of **1e** (10 mM) in DMF/NBu_4PF_6. Scan rate 100 mV/s. The arrow denotes the direction of the scan.

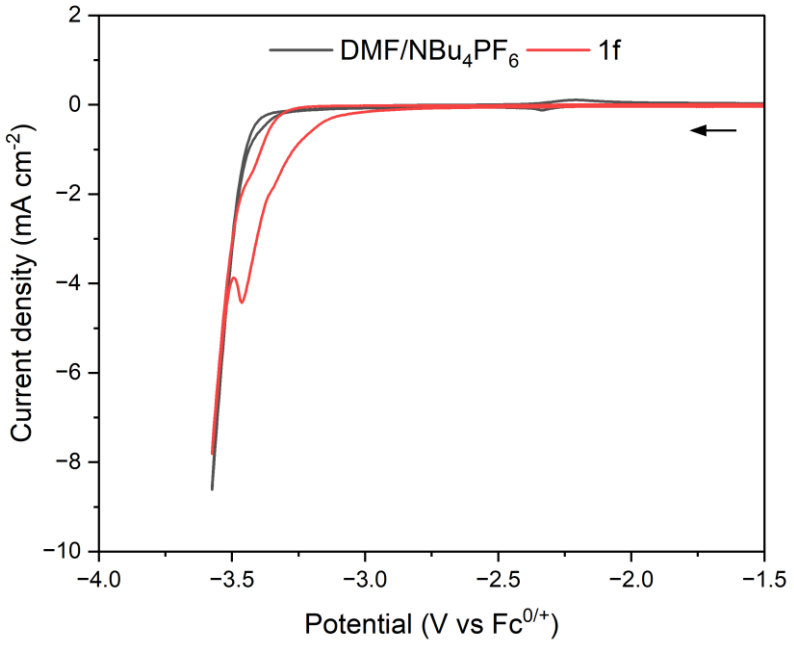


Figure S17: CV of **1f** (10 mM) in DMF/NBu_4PF_6. Scan rate 100 mV/s. The arrow denotes the direction of the scan.

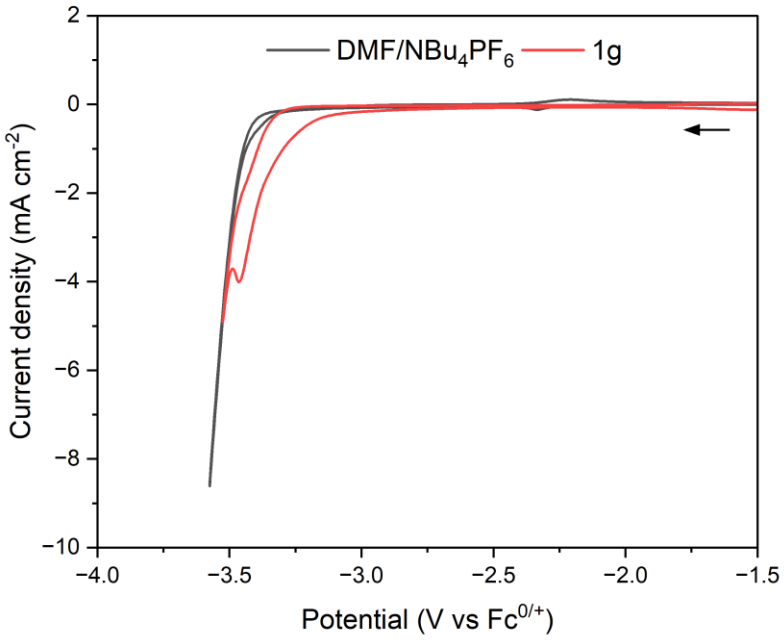


Figure S18: CV of **1g** (10 mM) in DMF/NBu_4PF_6. Scan rate 100 mV/s. The arrow denotes the direction of the scan.

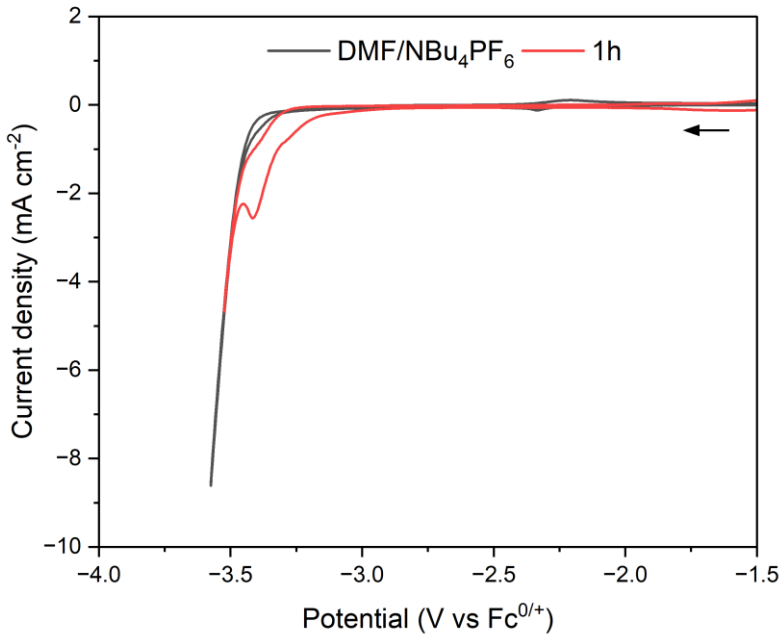


Figure S19: CV of **1h** (10 mM) in DMF/NBu_4PF_6. Scan rate 100 mV/s. The arrow denotes the direction of the scan.

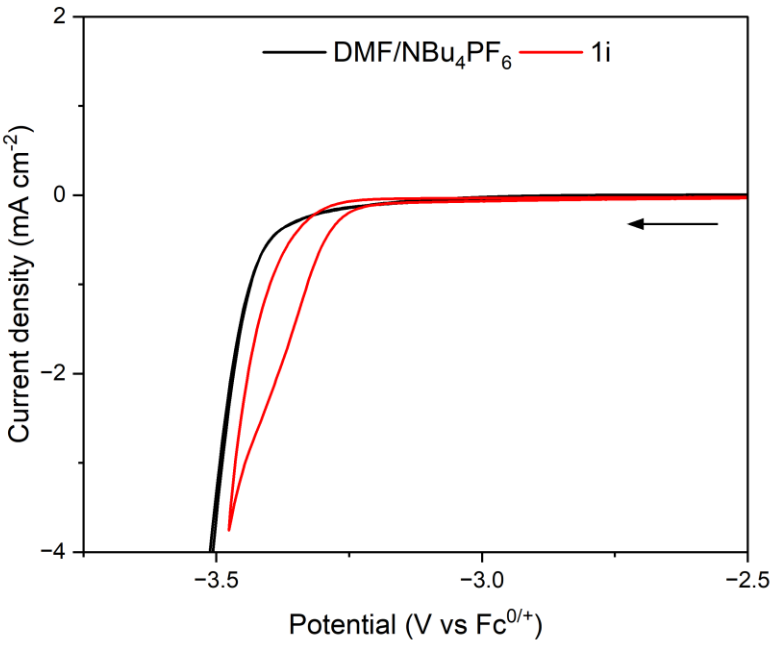


Figure S20: CV of **1i** (10 mM) in DMF/NBu_4PF_6. Scan rate 100 mV/s. The arrow denotes the direction of the scan.

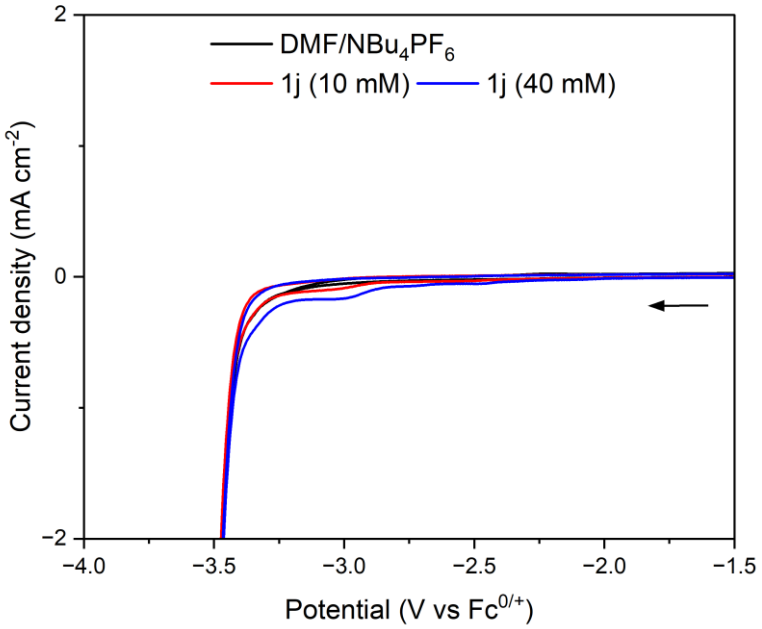


Figure S21: CV of **1j** in DMF/NBu_4PF_6. Scan rate 100 mV/s. The arrow denotes the direction of the scan.

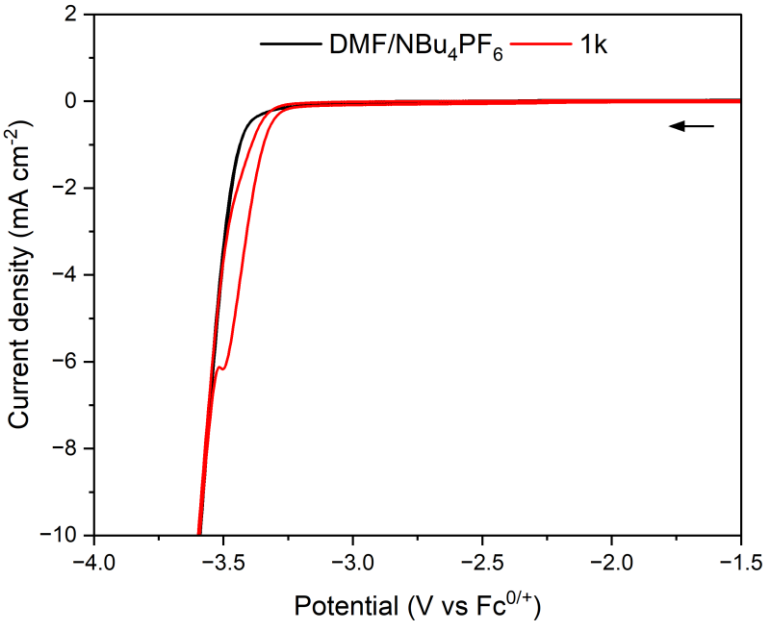


Figure S22: CV of **1k** (10 mM) in DMF/NBu_4PF_6. Scan rate 100 mV/s. The arrow denotes the direction of the scan.

6. HPLC chromatograms and calibrations

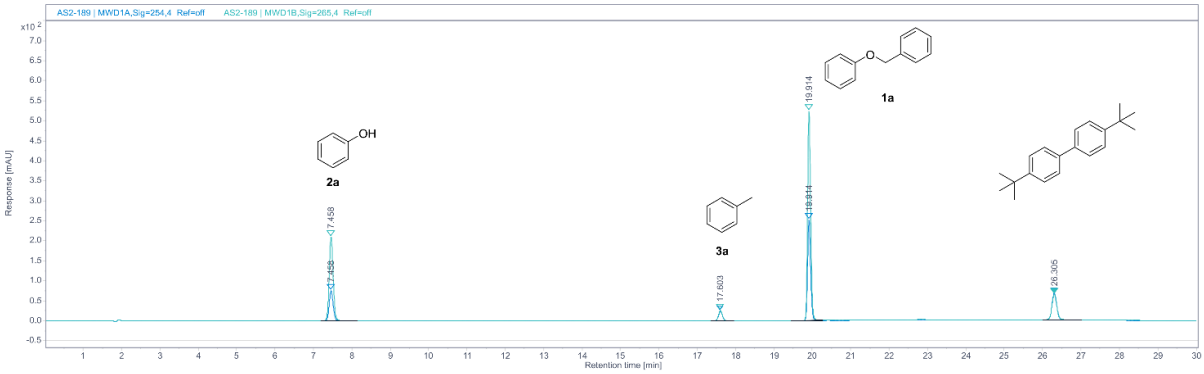


Figure S23: Representative HPLC chromatogram of a typical reaction mixture. MWD detector responses at 254.4 nm (blue) and 265.4 nm (green).

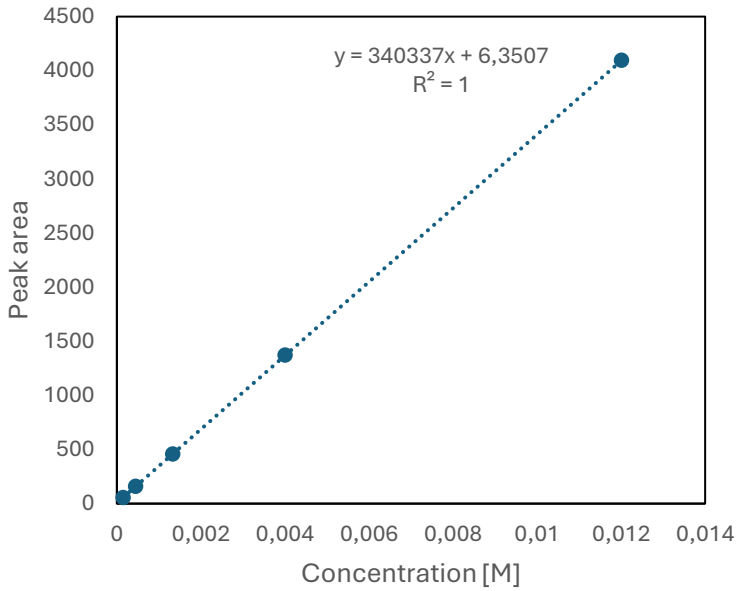


Figure S24: Calibration curve of **1a** (265 nm).

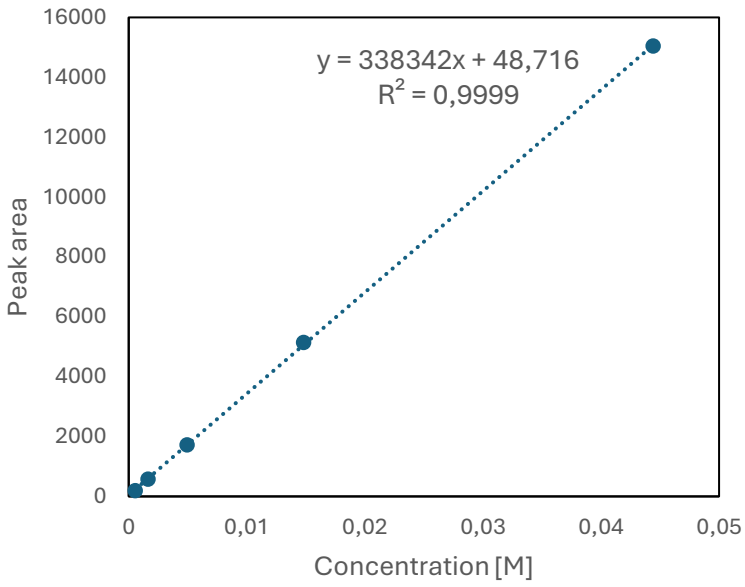


Figure S25: Calibration curve of **2a** (265 nm).

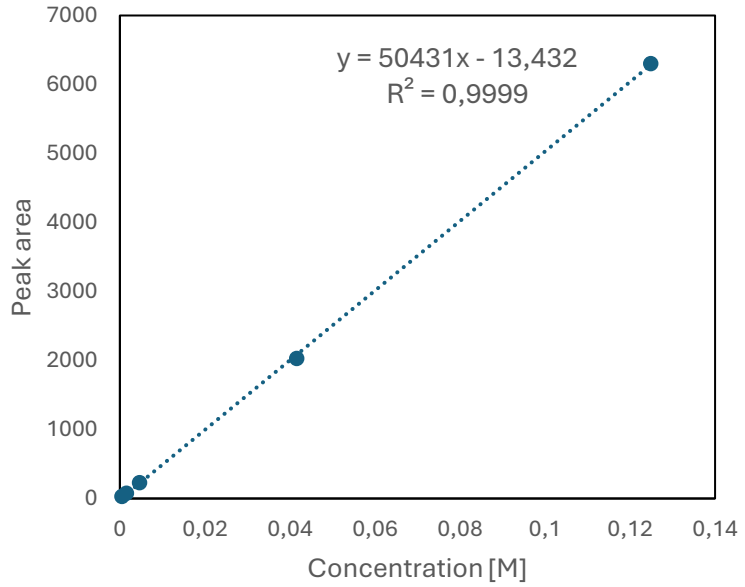


Figure S26: Calibration curve of **2a** (254 nm).

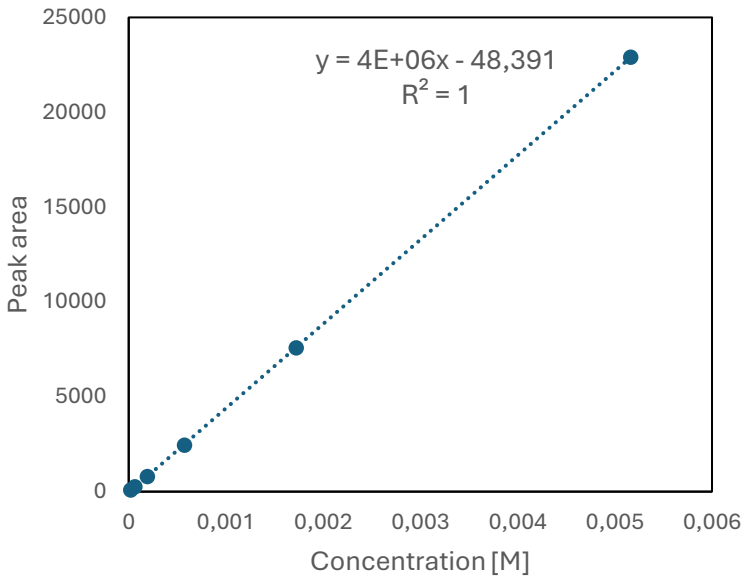


Figure S27: Calibration curve of internal standard (4,4'-di-*t*-butylbiphenyl, 254 nm).

7. NMR spectra of DESs

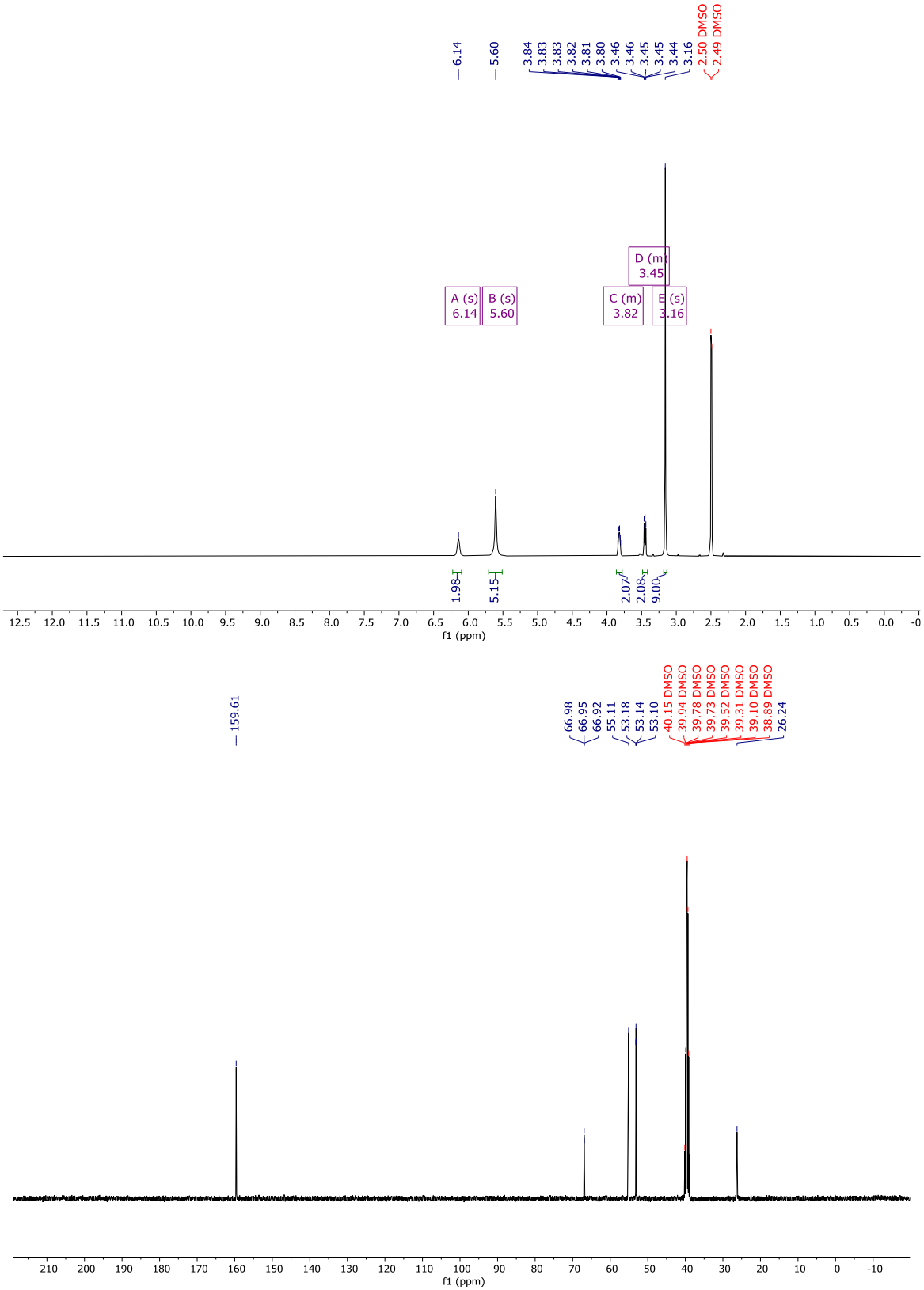


Figure S28: ^{1}H and ^{13}C NMR spectra of choline chloride:N-methyl urea (1:2) (DES-1)

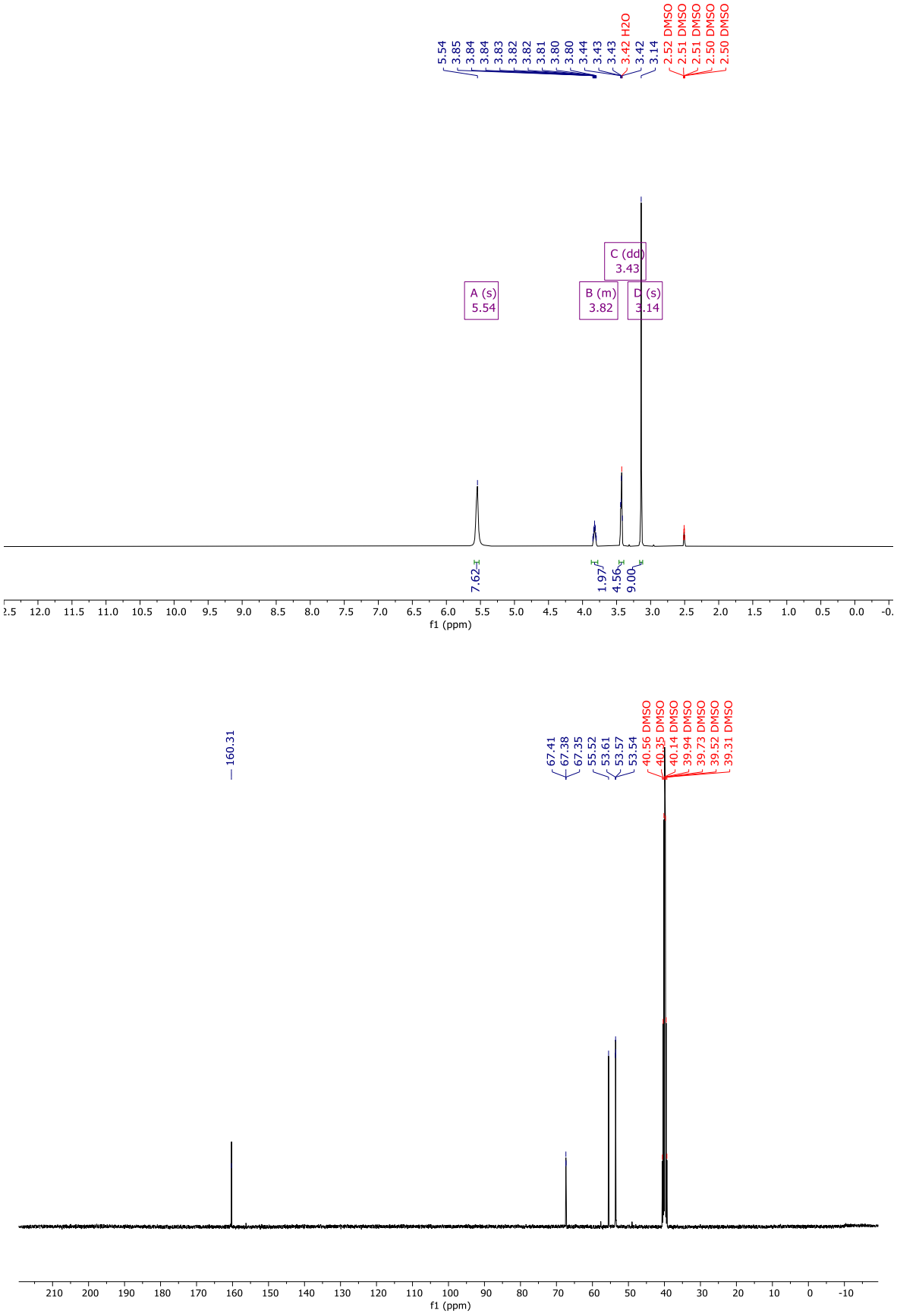


Figure S29: ^{1}H and ^{13}C NMR spectra of choline chloride:urea (1:2) (DES-2)

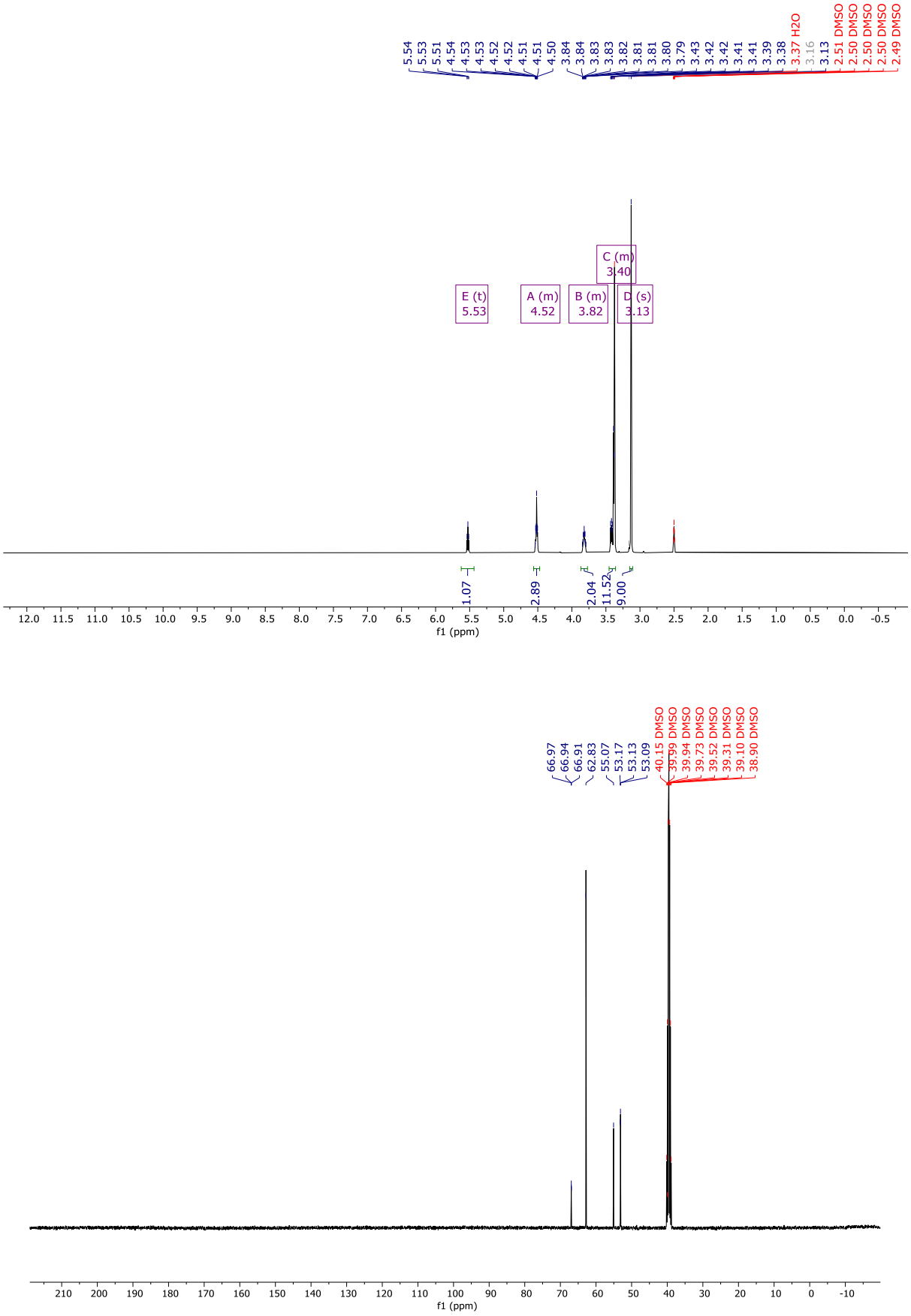


Figure S30: ^{1}H and ^{13}C NMR spectra of choline chloride:ethylene glycol (1:2) (DES-3)

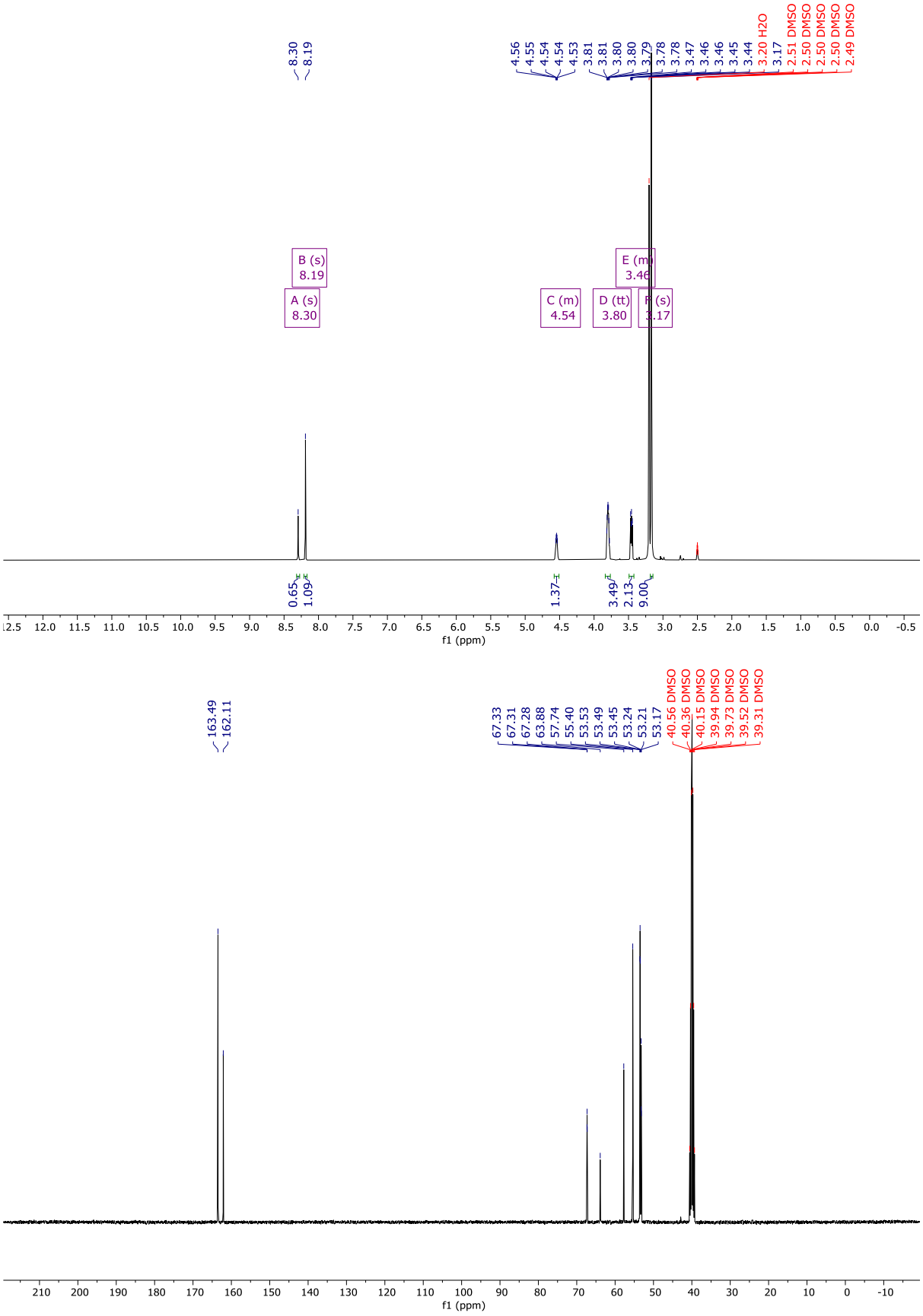


Figure S31: ^{1}H and ^{13}C NMR spectra of choline chloride:formic acid (1:2) (DES-4)

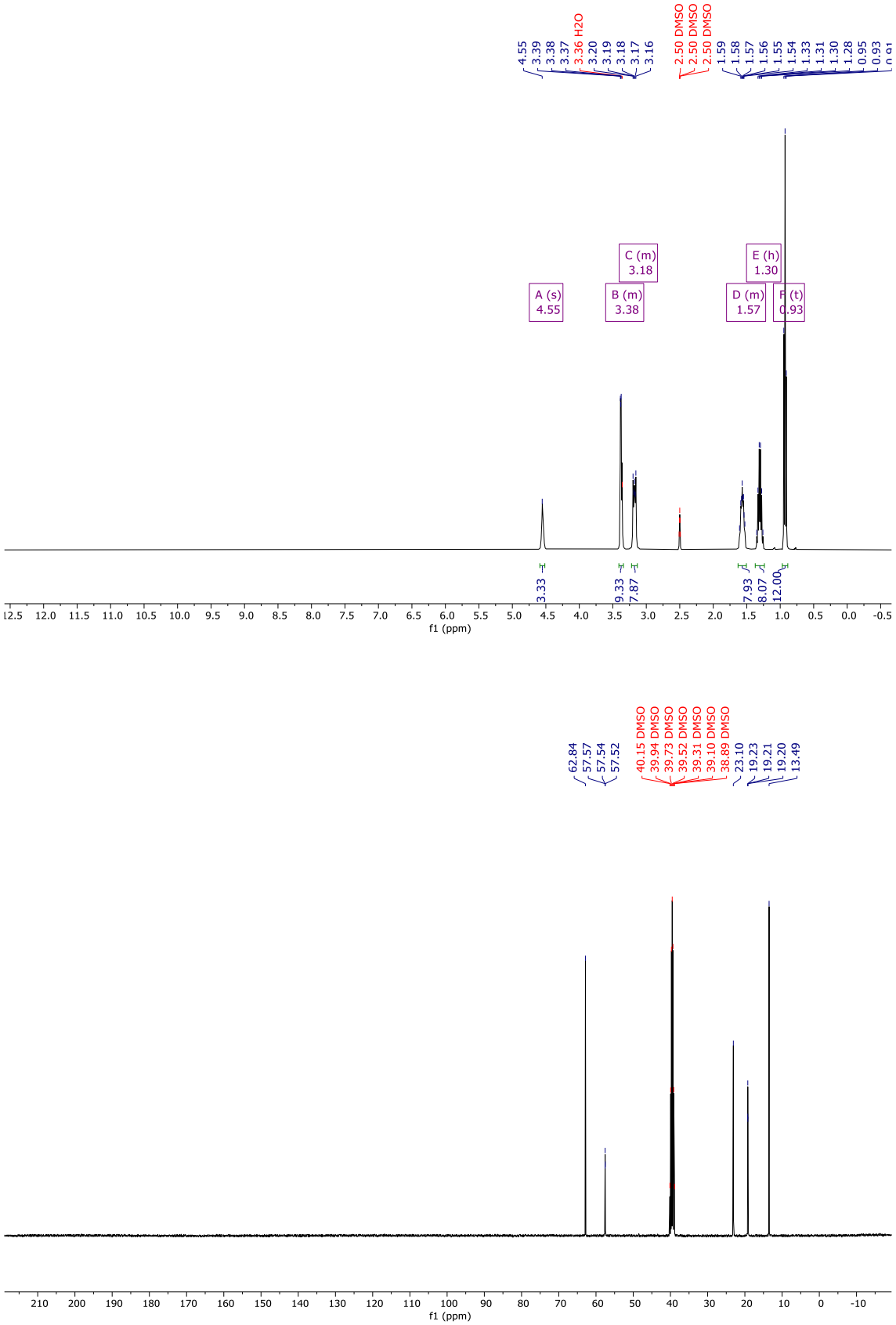


Figure S32: ^{1}H and ^{13}C NMR spectra of tetrabutylammonium chloride:ethylene glycol (1:2) (DES-5)

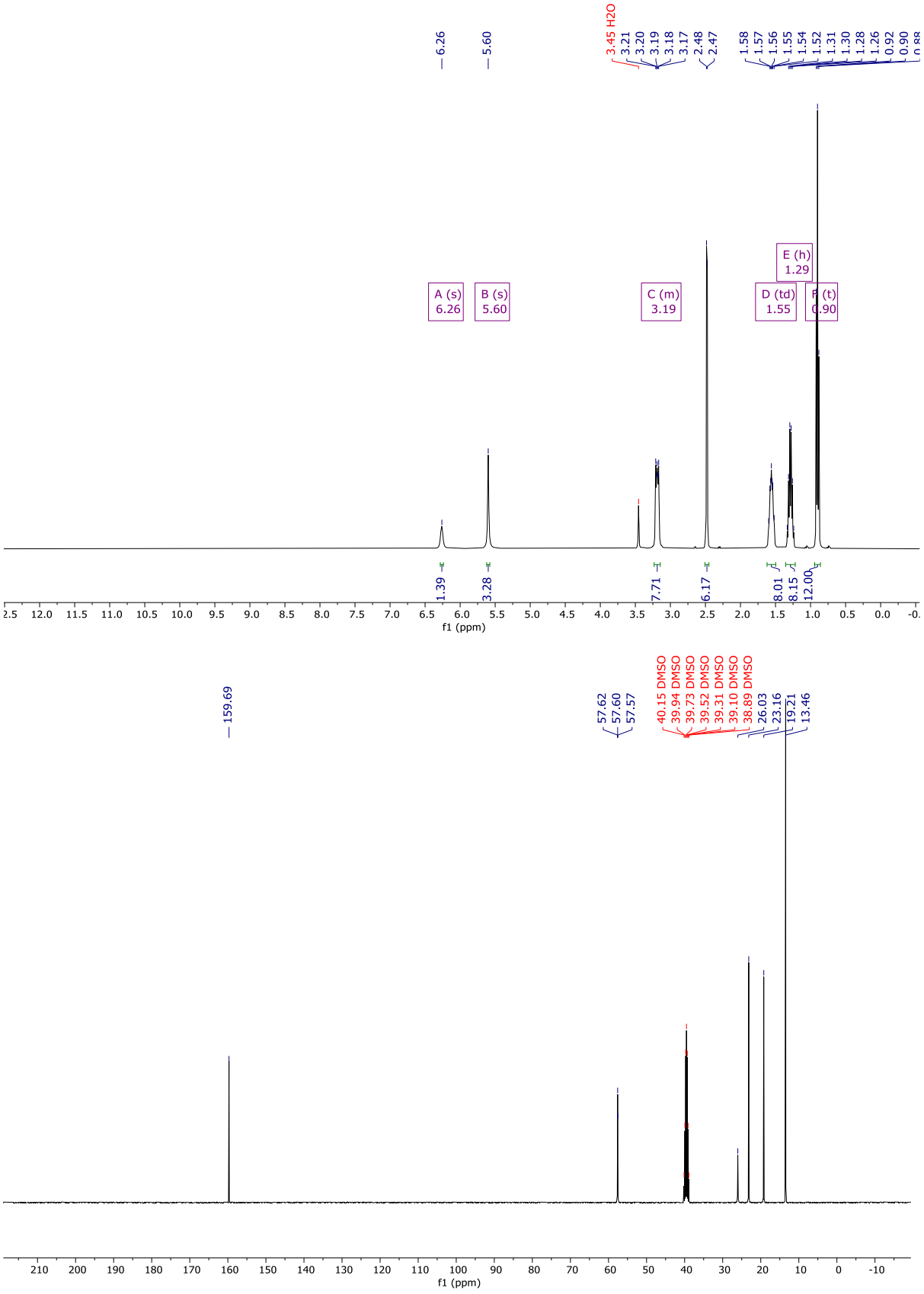
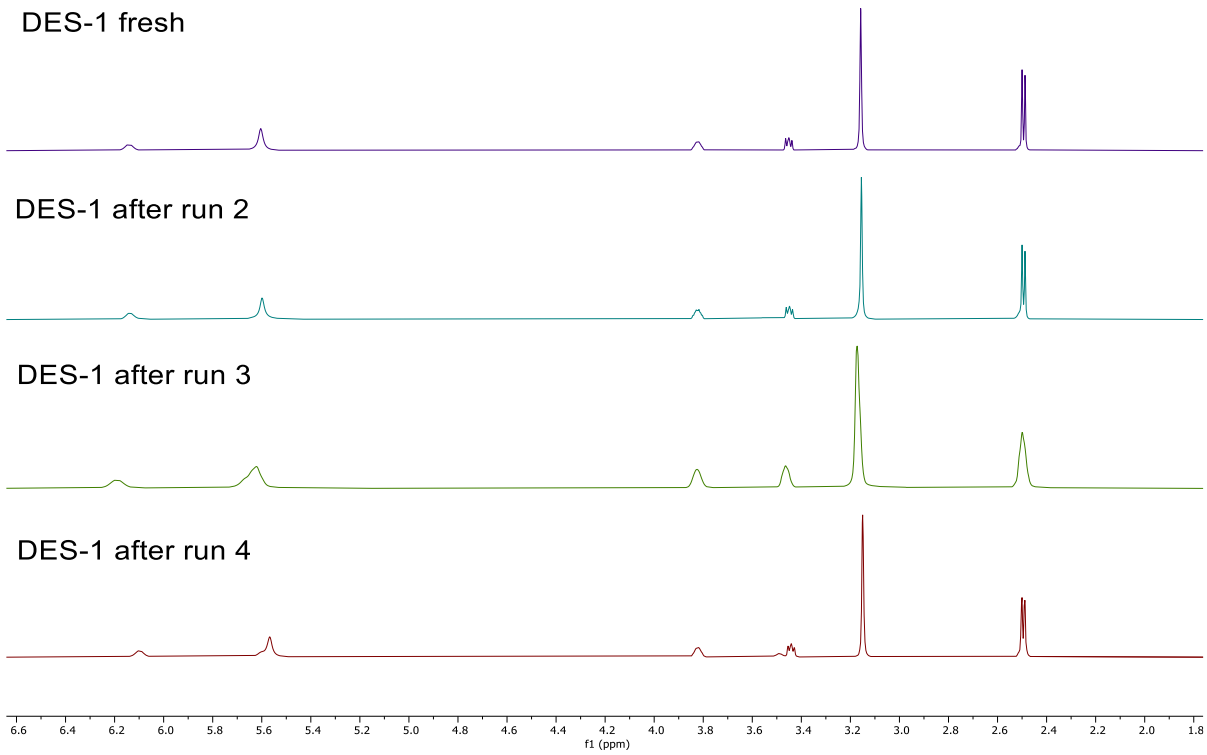


Figure S33: ^{1}H and ^{13}C NMR spectra of tetrabutylammonium chloride:N-methyl urea (1:2) (DES-6)



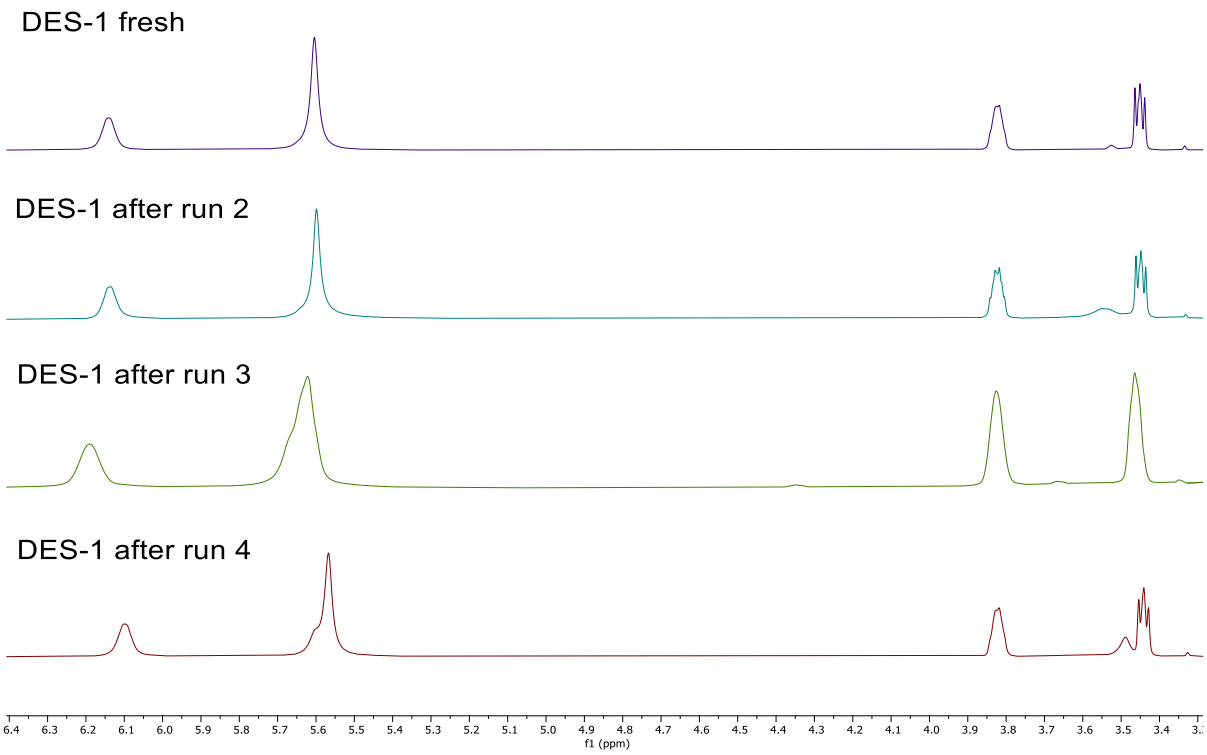


Figure S34: ^{1}H NMR spectra of fresh and recycled DES-1 after electroreductive C-O cleavage of **1a**.

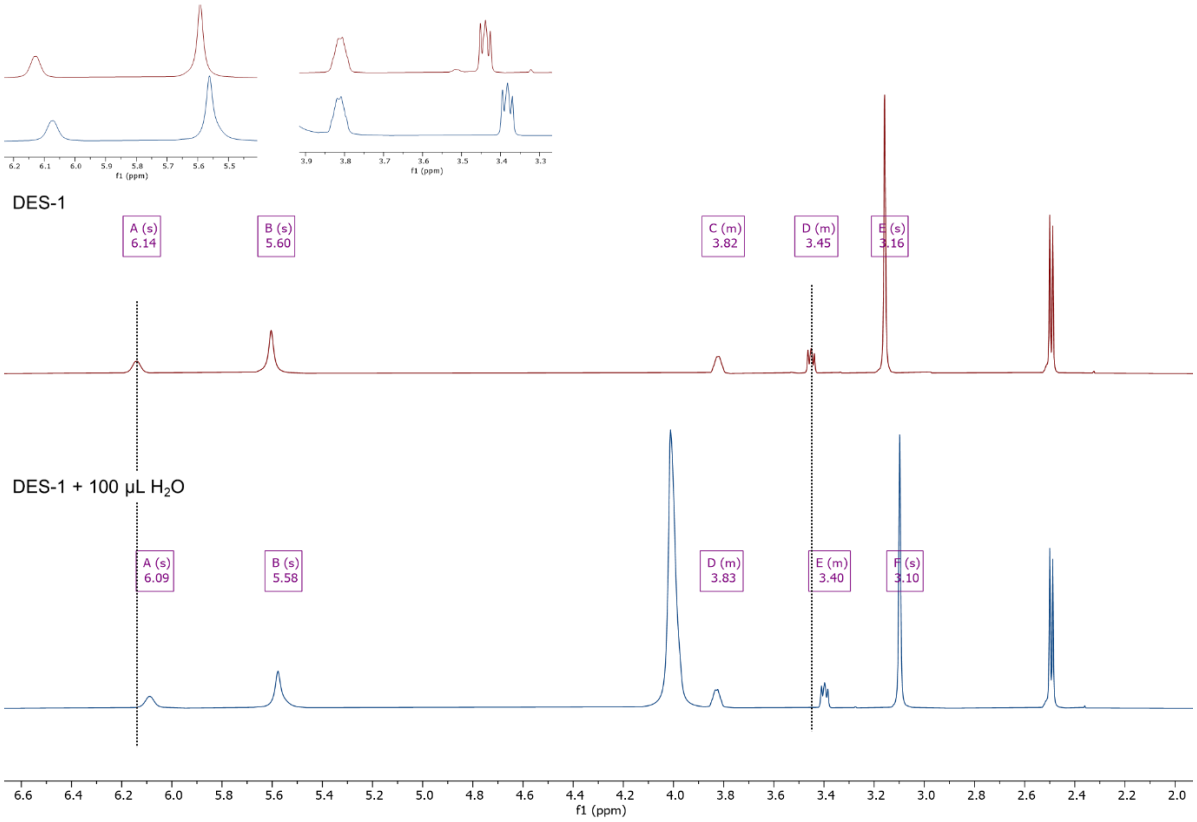
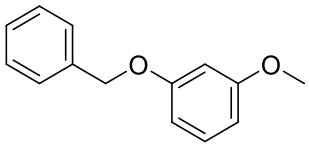


Figure S35: ^{1}H NMR spectra of fresh DES and DES with added water.

8. NMR spectra of 1b-1e & 1h



1b

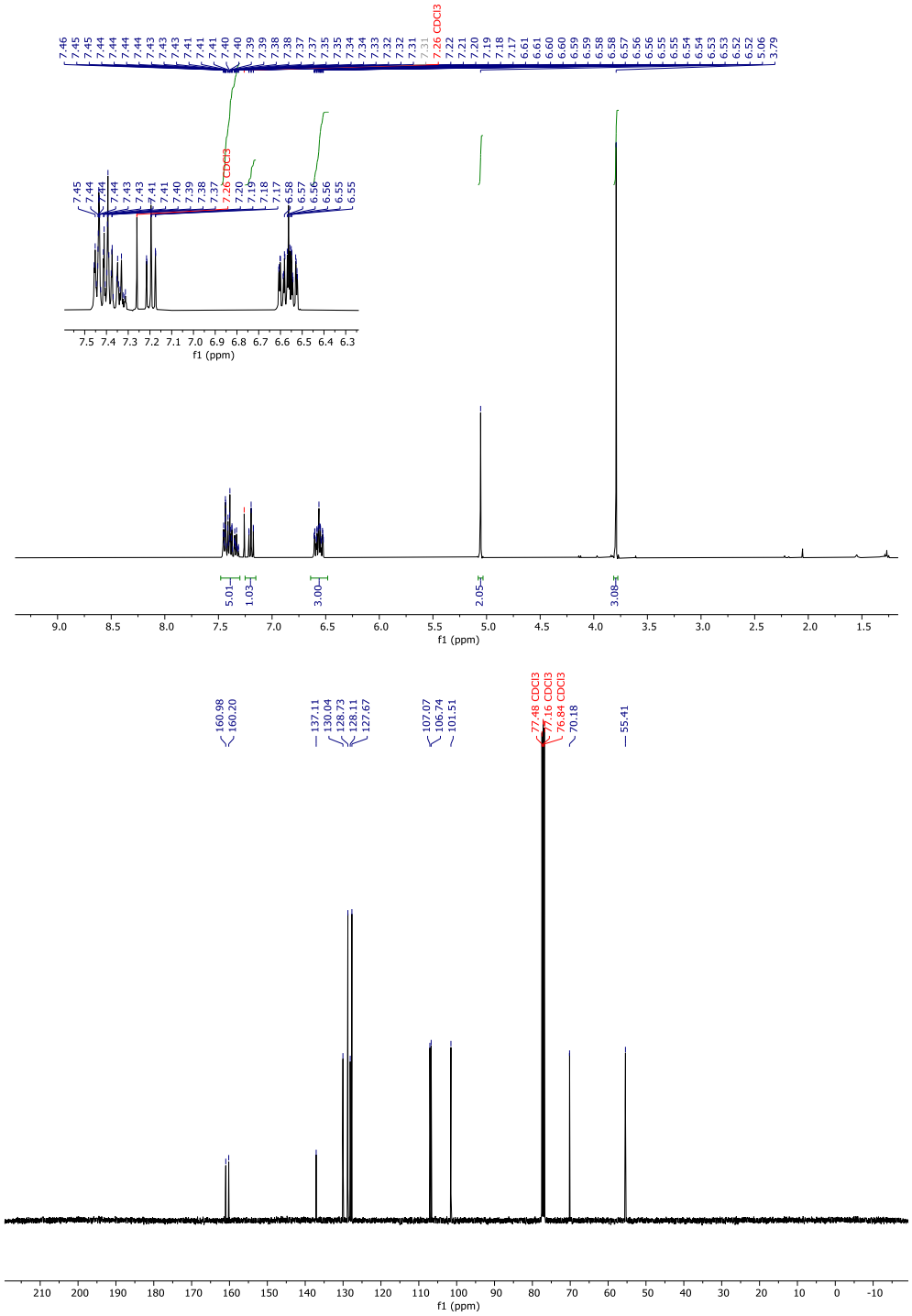


Figure S36: ^{1}H and ^{13}C NMR spectra of **1b**.

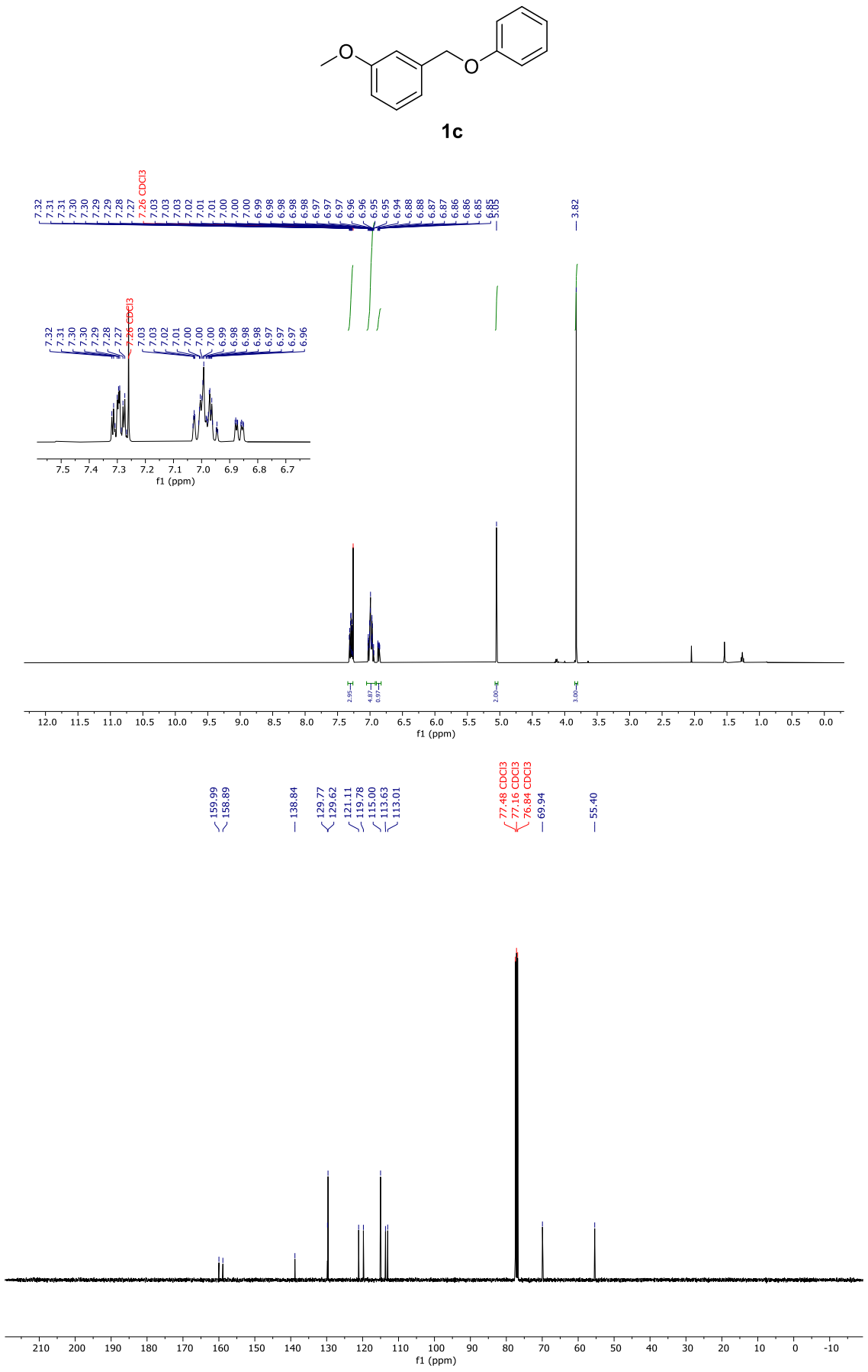


Figure S37: ^{1}H and ^{13}C NMR spectra of **1c**.

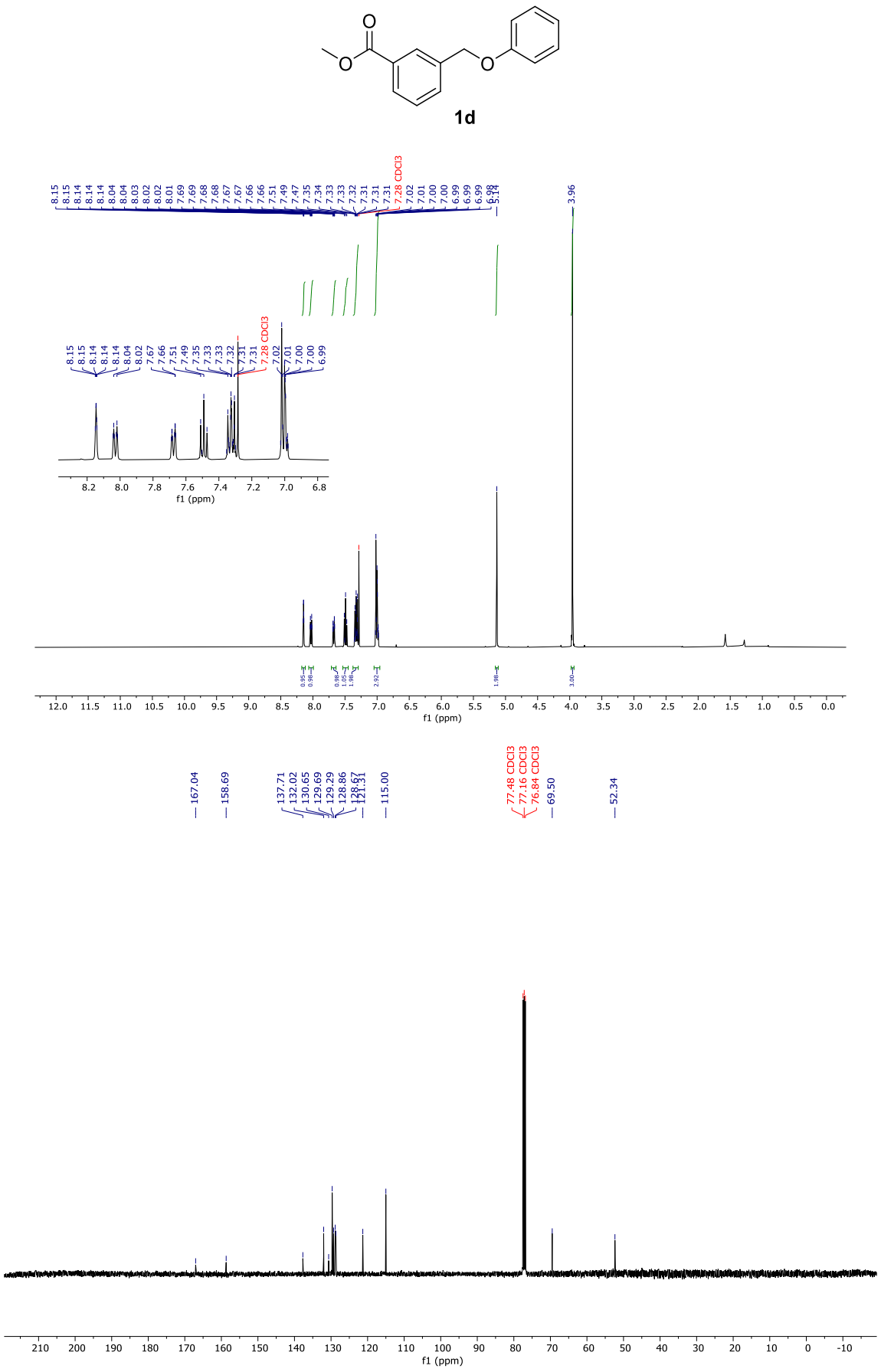


Figure S38: ^{1}H and ^{13}C NMR spectra of **1d**.

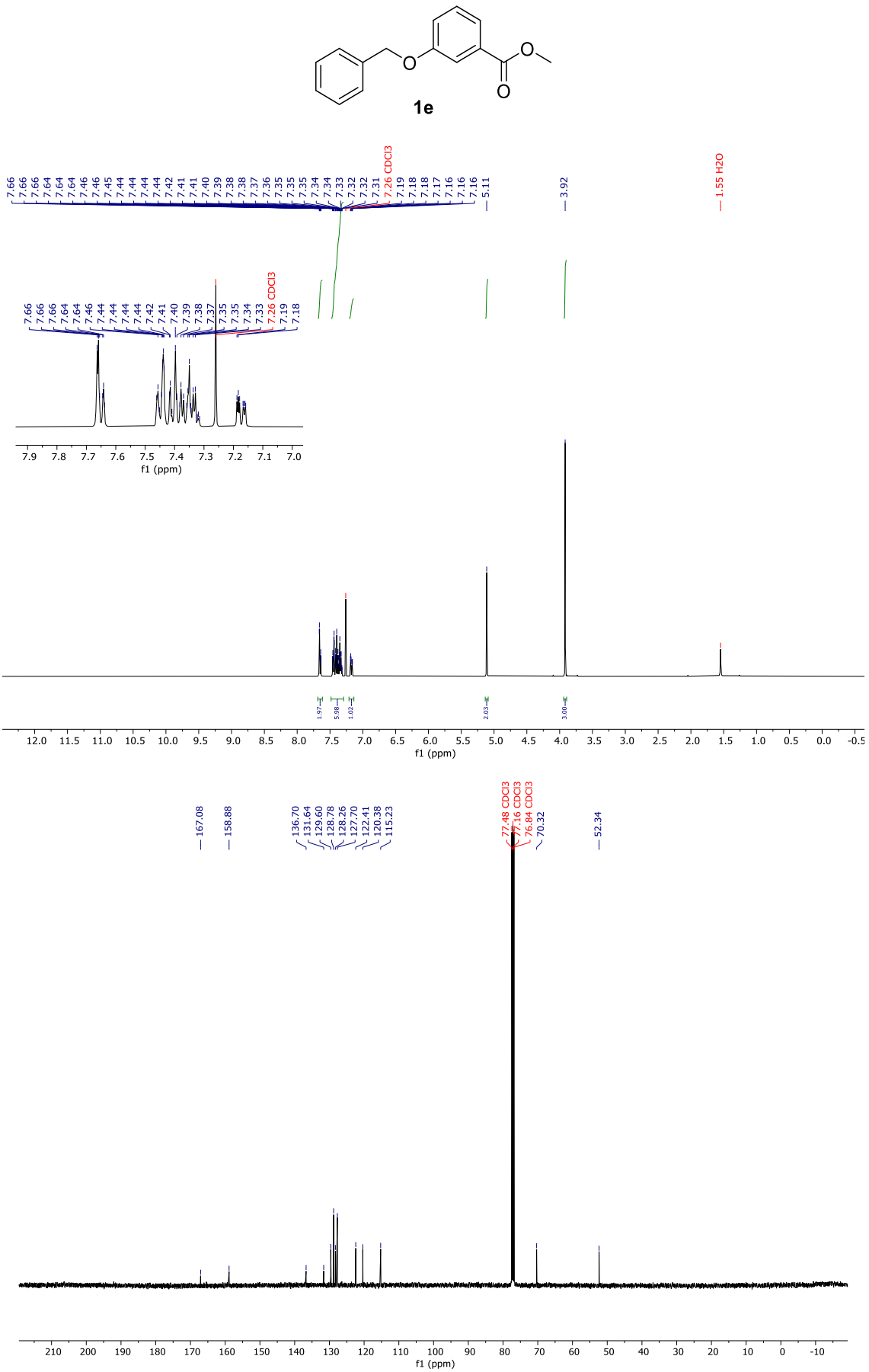


Figure S39: ^{1}H and ^{13}C NMR spectra of **1e**.

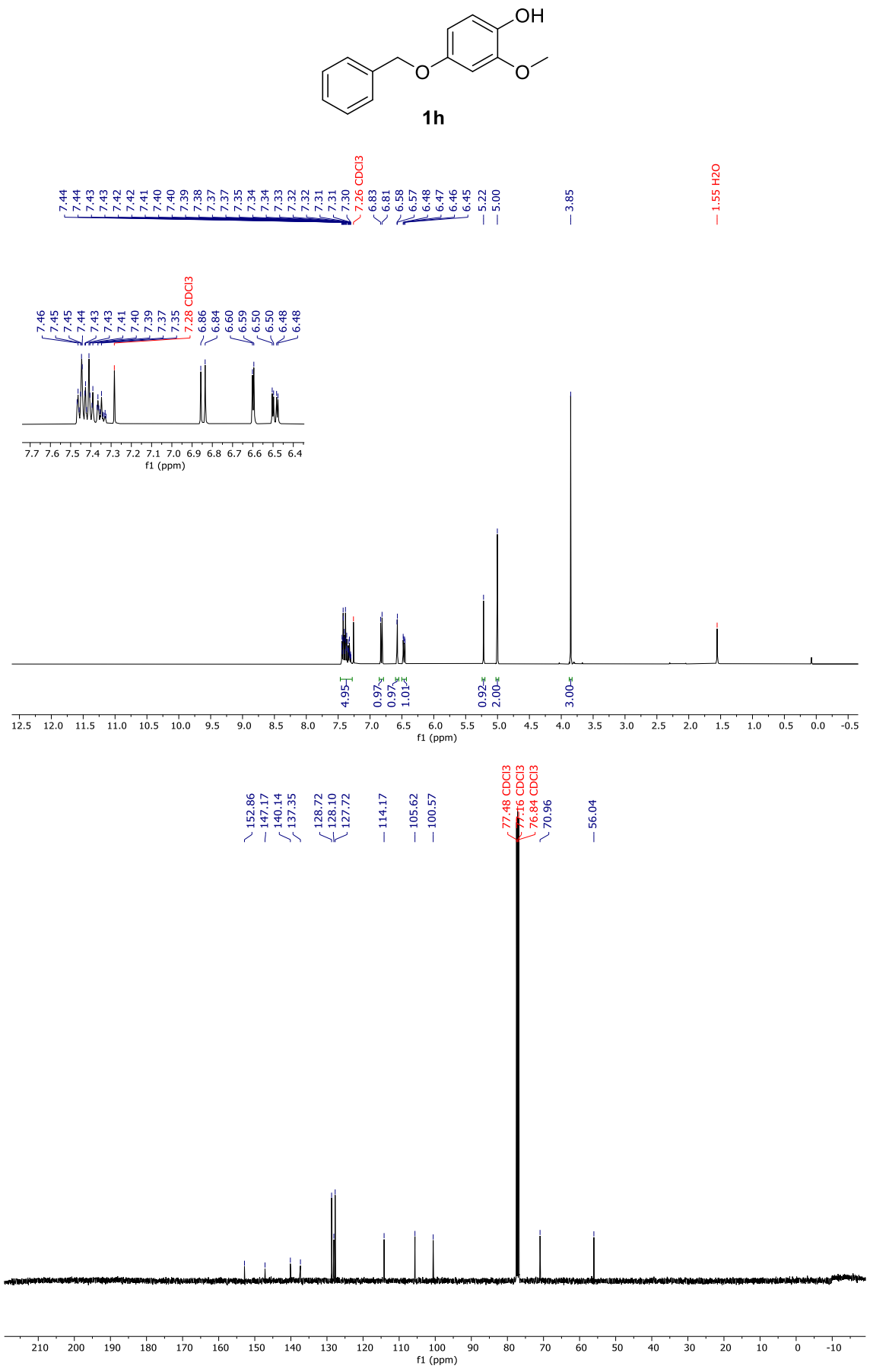


Figure S40: ^{1}H and ^{13}C NMR spectra of **1h**.

9. GC-MS analysis

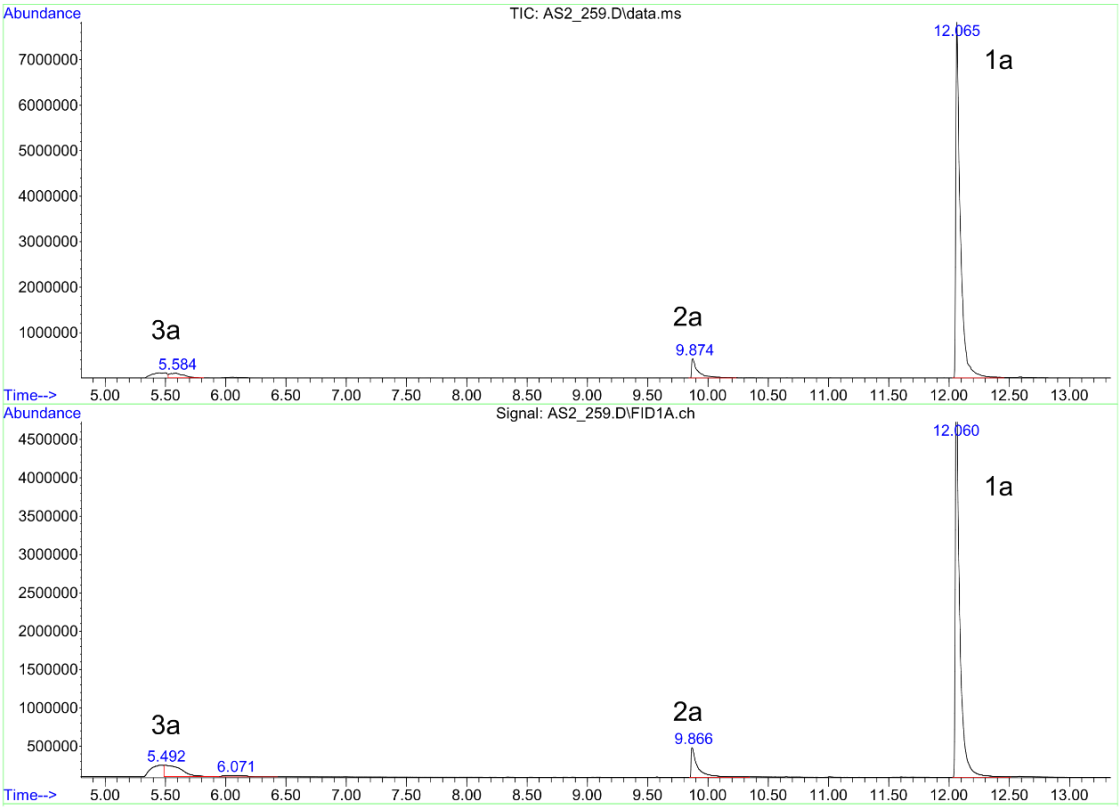


Figure S41: GC-MS spectra of reaction mixture from C-O cleavage of **1a** in DES-1 (50°C, 1500 rpm, 2.5 F).

10. References

1. L. Bering, K. Jeyakumar and A. P. Antonchick, *Org. Lett.*, 2018, **20**, 3911–3914.
2. K. A. C. Bastick and A. J. B. Watson, *Synlett*, 2023, **34**, 2097–2102.
3. T. Kronenberger, G. M. Ferreira, A. D. F. de Souza, S. da Silva Santos, A. Poso, J. A. Ribeiro, M. T. Tavares, F. R. Pavan, G. H. G. Trossini, M. V. B. Dias and R. Parise-Filho, *Bioorg. Med. Chem.*, 2020, **28**, 115600.
4. R. G. F. Giles, C. A. Joll, M. V Sargent, D. Matthew and G. Tilbrook, *J. Chem. Soc., Perkin Trans. 1*, 1999, 3029–3038.