Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Vaporization of protic ionic liquids derived from organic superbases and short carboxylic acids

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1. Synthesis

General Procedure for the synthesis of distillable protic ionic liquids of 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) and 1,8-diazabicycloundec-7-ene (DBU) superbases with short-chain carboxylic acids:

The general synthetic procedure involves the exothermic neutralization of base with stoichiometric quantity of different acids as given in reaction Scheme 1. The synthesis of [DBUH][MeCOO] is described here and a similar procedure has been followed for other ILs. The quantity 15 mL (0.10 mol) of DBU was taken into 500 mL triple necked round bottomed flask fitted with a pressure equalizing dropping funnel in a water bath. An equimolar quantity (stoichiometric quantity) 5.9 mL (0.10 mol) of acetic acid was added drop wise through the dropping funnel in the presence of nitrogen gas. After completion of acid addition, the flask was brought to room temperature and stirred for 24 h. In order to remove the unreacted reactants (if any) and moisture from IL, high vacuum was applied for about 24 h. The dried pale yellow colour and viscus liquid was obtained, which is characterized by ^{1}H and ^{13}C NMR spectroscopic techniques given in the supporting information as Figs. S3– S12.

2. NMR spectroscopy

NMR description of the PILs synthetized:

[DBNH][MeCOO]: ^{1}H NMR (300 MHz, $CDCl_3$), δ / ppm, 10.77 (s, 1H), 3.66 (t, J = 7.2 Hz, 2H), 3.50-3.40 (m, 4H), 3.04 (t, J = 8.1 Hz, 2H), 2.17 (dt, $J_1 \approx J_2$ = 7.6 Hz, 2H), 2.05 (dt, $J_1 \approx J_2$ = 6.0 Hz, 2H), 1.94 (s, 3H); ^{13}C NMR (75 MHz, CDCl3), δ / ppm, 177.2, 163.8, 52.6, 42.2, 37.7, 29.4, 24.5, 18.6, 18.5.

[DBUH][MeCOO]: ^{1}H NMR (300 MHz, $CDCl_3$), δ / ppm, 3.55-3.40 (m, 6H), 2.94-2.81 (m, 2H), 2.03 (dt, $J_1 \approx J_2$ = 6.0 Hz, 2H), 1.97 (s, 3H), 1.83-1.62 (m, 6H); ^{13}C NMR (75 MHz, CDCl3), δ / ppm, 177.6, 165.8, 54.0, 48.4, 37.8, 31.7, 29.0, 26.9, 24.5, 24.0, 19.5.

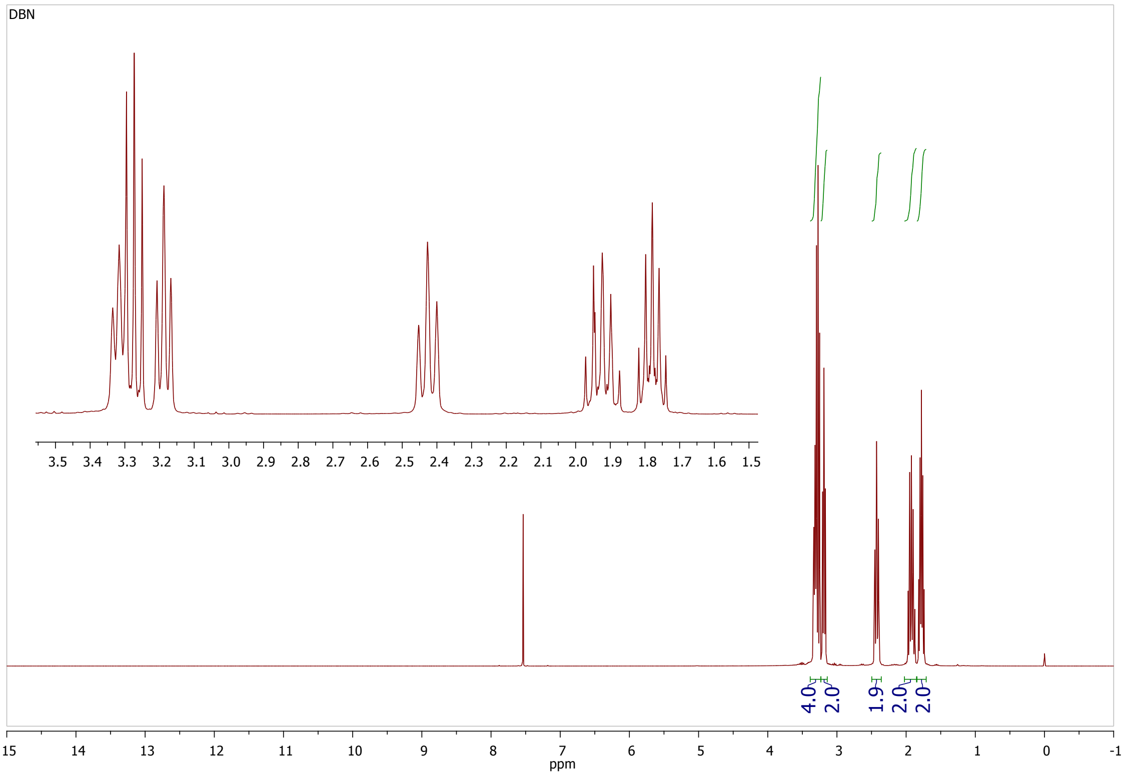
[DBNH][EtCOO]: ^{1}H NMR (300 MHz, $CDCl_3$), δ / ppm, 12.99 (s, 1H), 3.66 (t, J = 7.2 Hz, 2H), 3.52-3.41 (m, 4H), 3.07 (t, J = 8.1 Hz, 2H), 2.25-2.12 (m, 4H), 2.05 (dt, $J_1 \approx J_2$ = 6.0 Hz, 2H), 1.10 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, CDCl3), δ / ppm, 180.3, 163.7, 52.6, 42.1, 37.5, 30.6, 29.4, 18.6, 18.5, 10.7.

[DBUH][EtCOO]: ^{1}H NMR (300 MHz, $CDCl_3$), δ / ppm, 3.56-3.41 (m, 6H), 2.95-2.82 (m, 2H), 2.23 (q, J = 7.5 Hz, 2H), 2.02 (dt, $J_1 \approx J_2$ = 6.0 Hz, 2H), 1.85-1.62 (m, 6H), 1.11 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, CDCl3), δ / ppm, 180.7, 165.7, 53.9, 48.4, 37.8, 31.7, 30.8, 28.9, 26.8, 24.0, 19.5, 10.8.

[DBNH][nPrCOO]: ^{1}H NMR (300 MHz, $CDCl_3$), δ / ppm, 11.79 (s, 1H), 3.65 (t, J = 7.2 Hz, 2H), 3.51-3.40 (m, 4H), 3.07 (t, J = 8.1 Hz, 2H), 2.22-2.10 (m, 4H), 2.04 (dt, $J_1 \approx J_2$

= 6.0 Hz, 2H), 1.63 (sextet, J = 7.5 Hz, 2H), 0.94 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, CDCl3), δ / ppm, 179.7, 163.8, 52.6, 42.2, 40.0, 37.6, 29.4, 19.7, 18.6, 18.5, 14.1.

[DBUH][nPrCOO]: ^{1}H NMR (300 MHz, $CDCl_3$), δ / ppm, 3.57-3.41 (m, 6H), 2.96-2.84 (m, 2H), 2.18 (t, J = 7.5 Hz, 2H), 2.03 (dt, $J_1 \approx J_2$ = 6.0 Hz, 2H), 1.83-1.56 (m, 8H), 0.93 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, CDCl3), δ / ppm, 179.8, 165.5, 53.8, 48.3, 40.4, 37.7, 31.5, 28.8, 26.7, 23.9, 19.8, 19.4, 14.1.



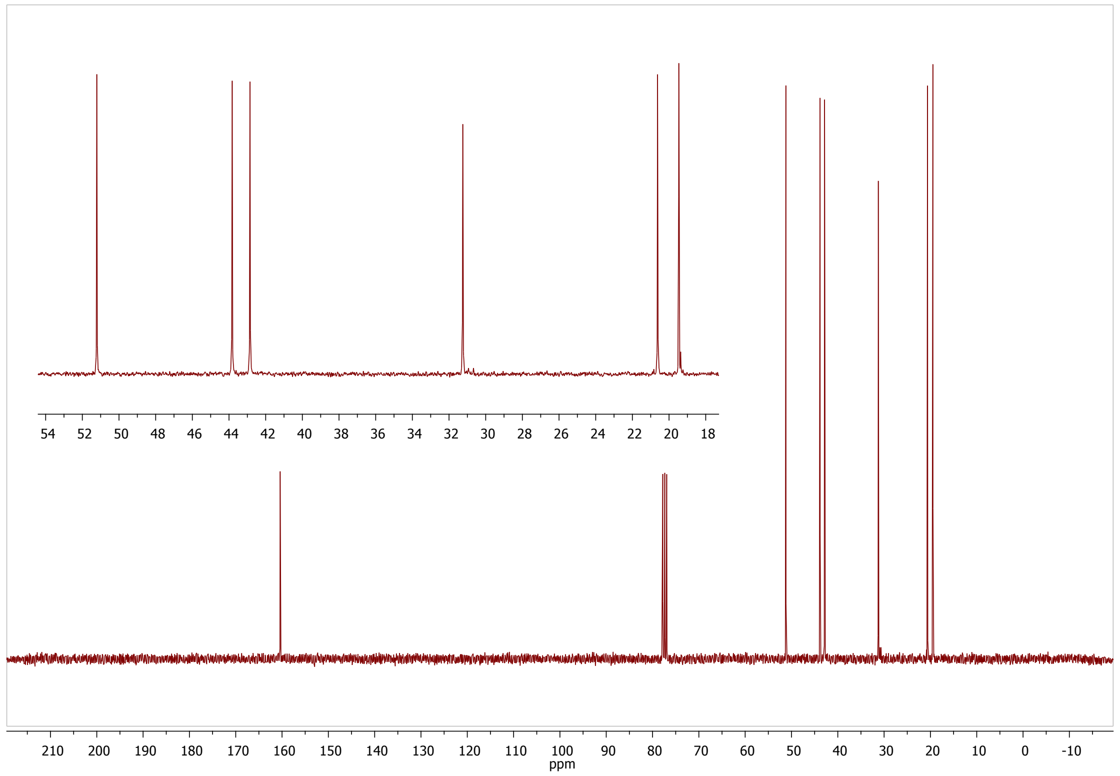
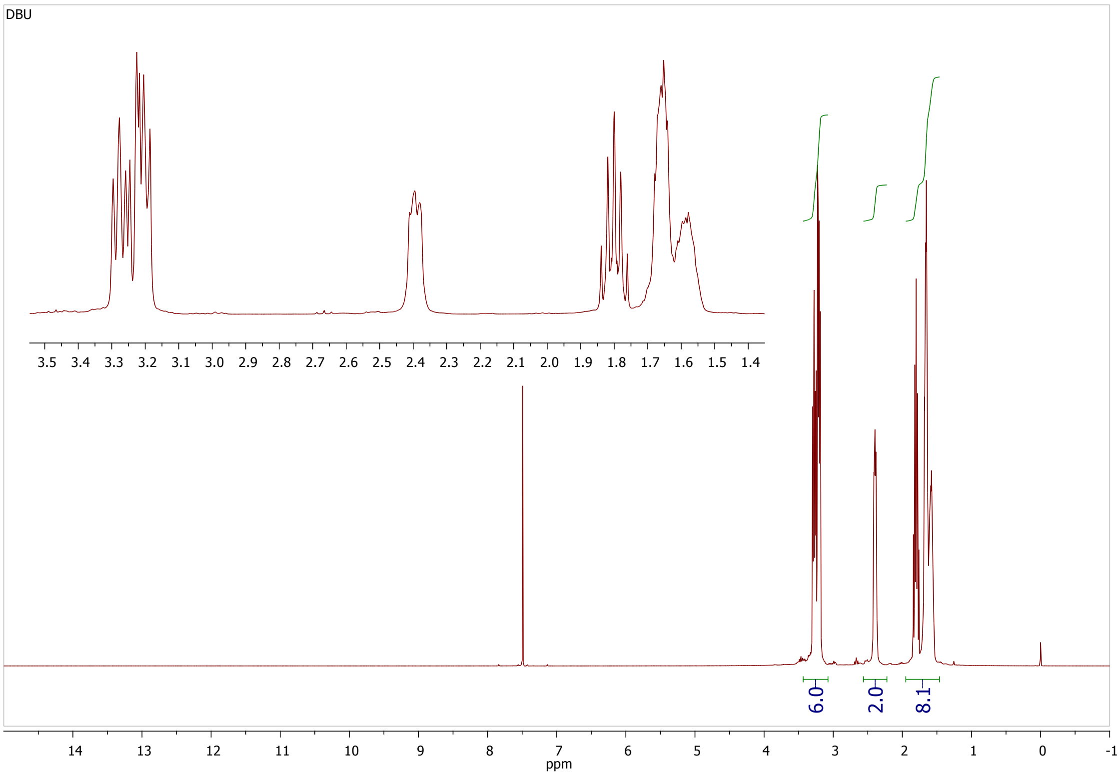


Figure S1. ^{1}H and ^{13}C NMR spectra of DBN in $CDCl_3$, at $T = 295$ K.



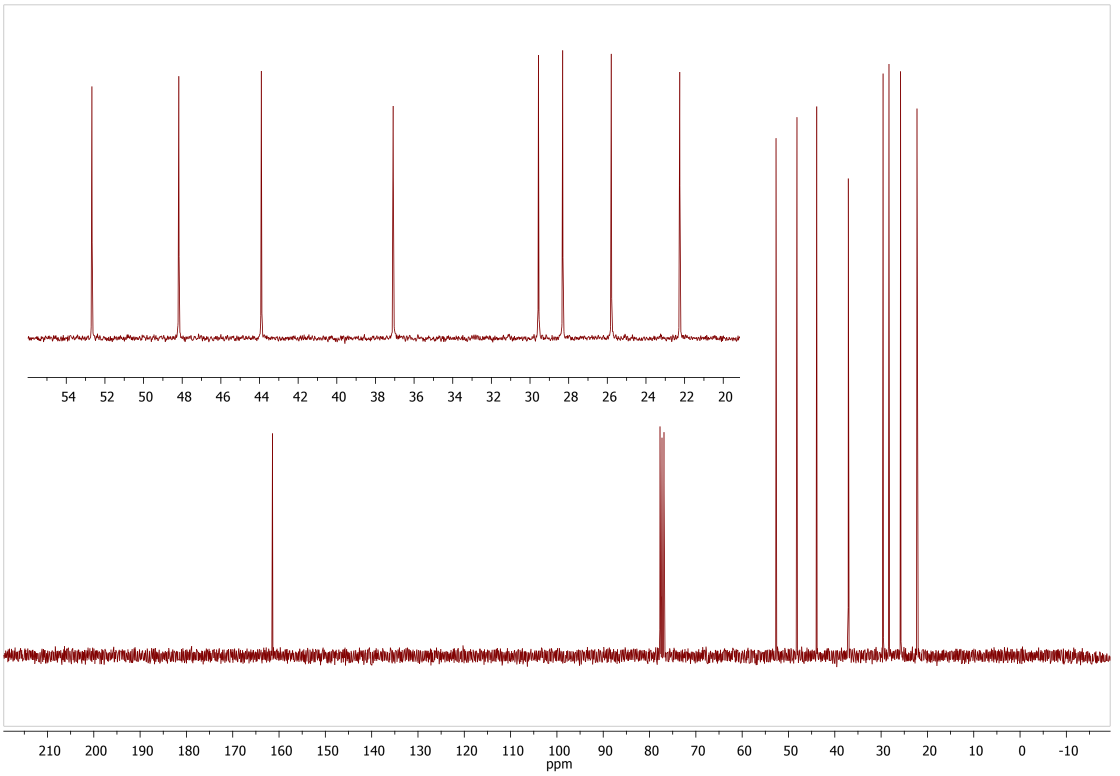
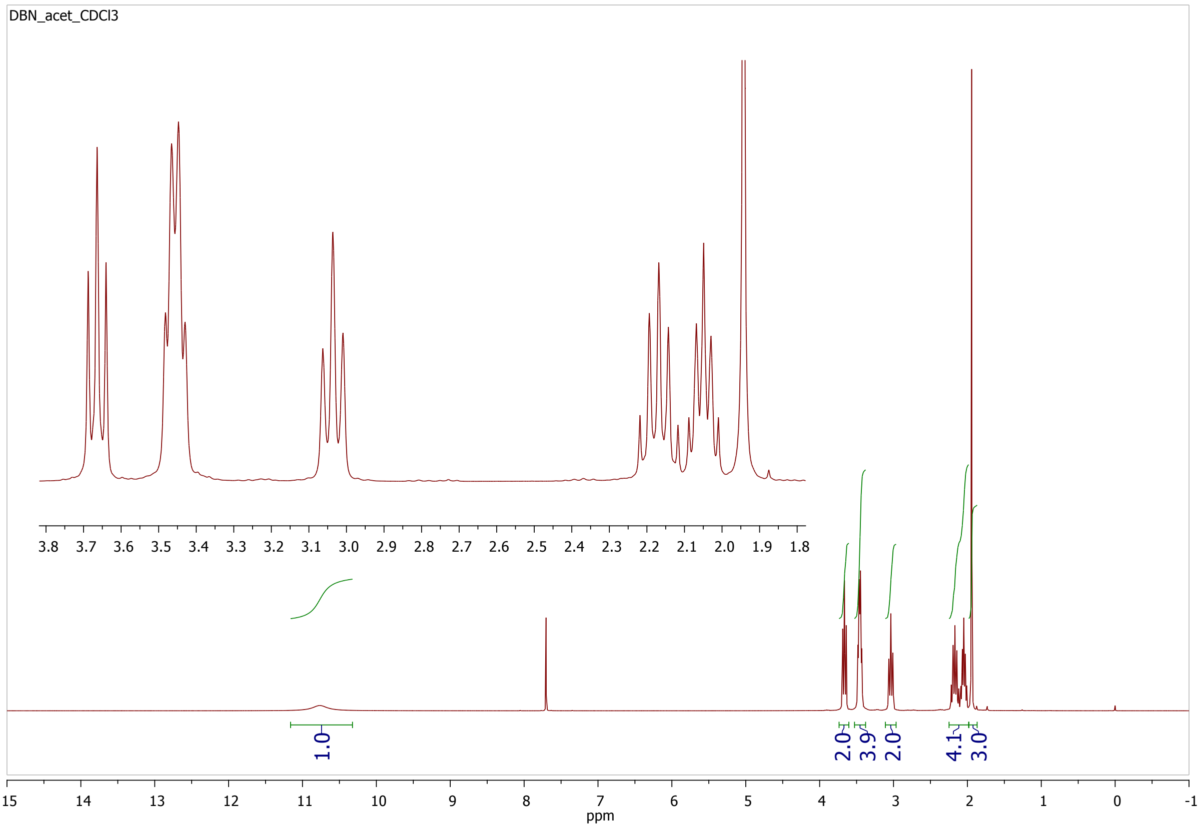


Figure S2. ^{1}H and ^{13}C NMR spectra of DBU in CDCl$_3$, at $T = 295$ K.



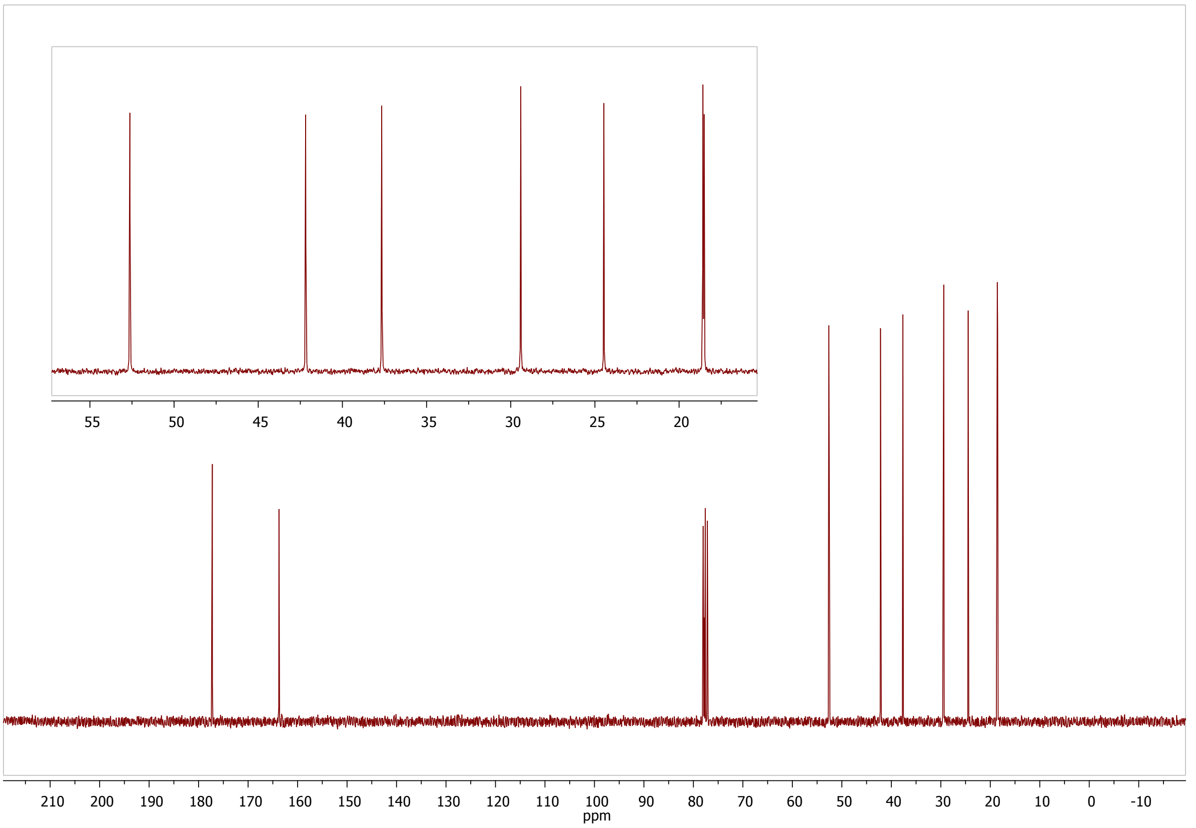
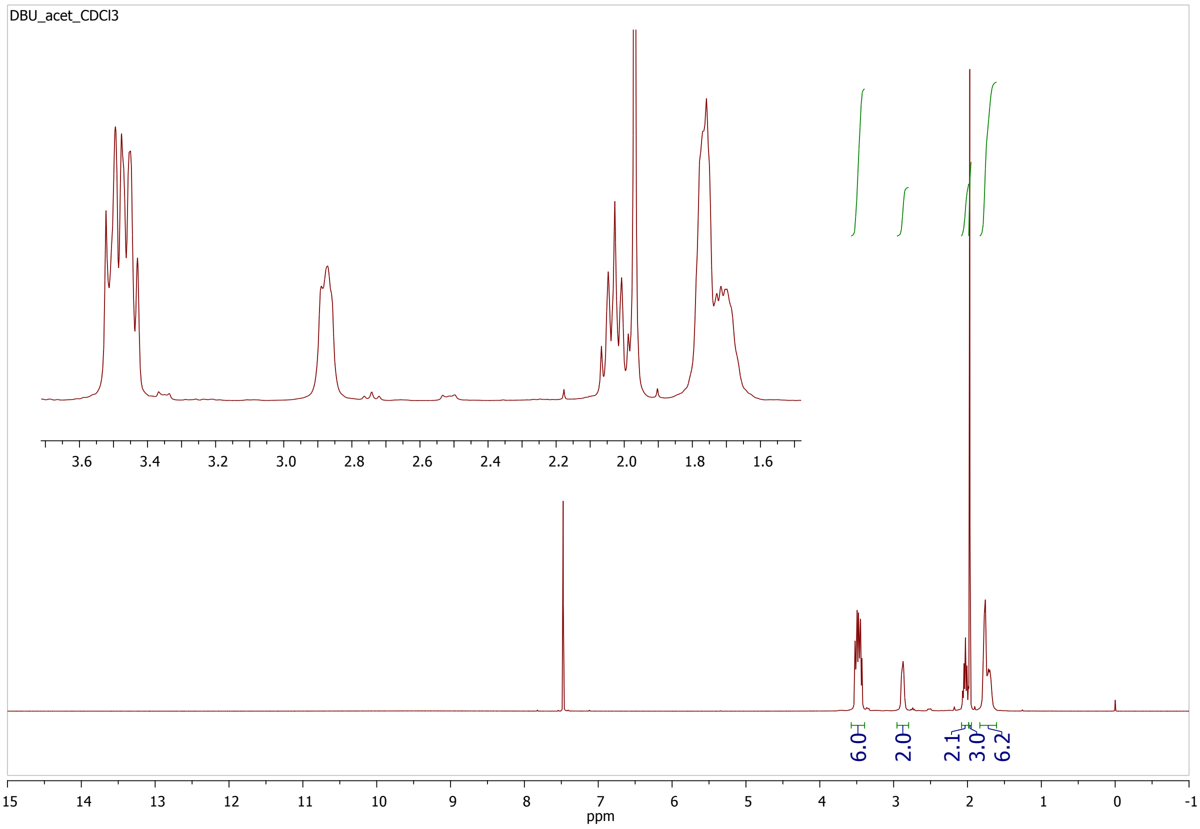


Figure S3. ^{1}H and ^{13}C NMR spectra of [DBNH][MeCOO] in $CDCl_3$, at $T = 295$ K.



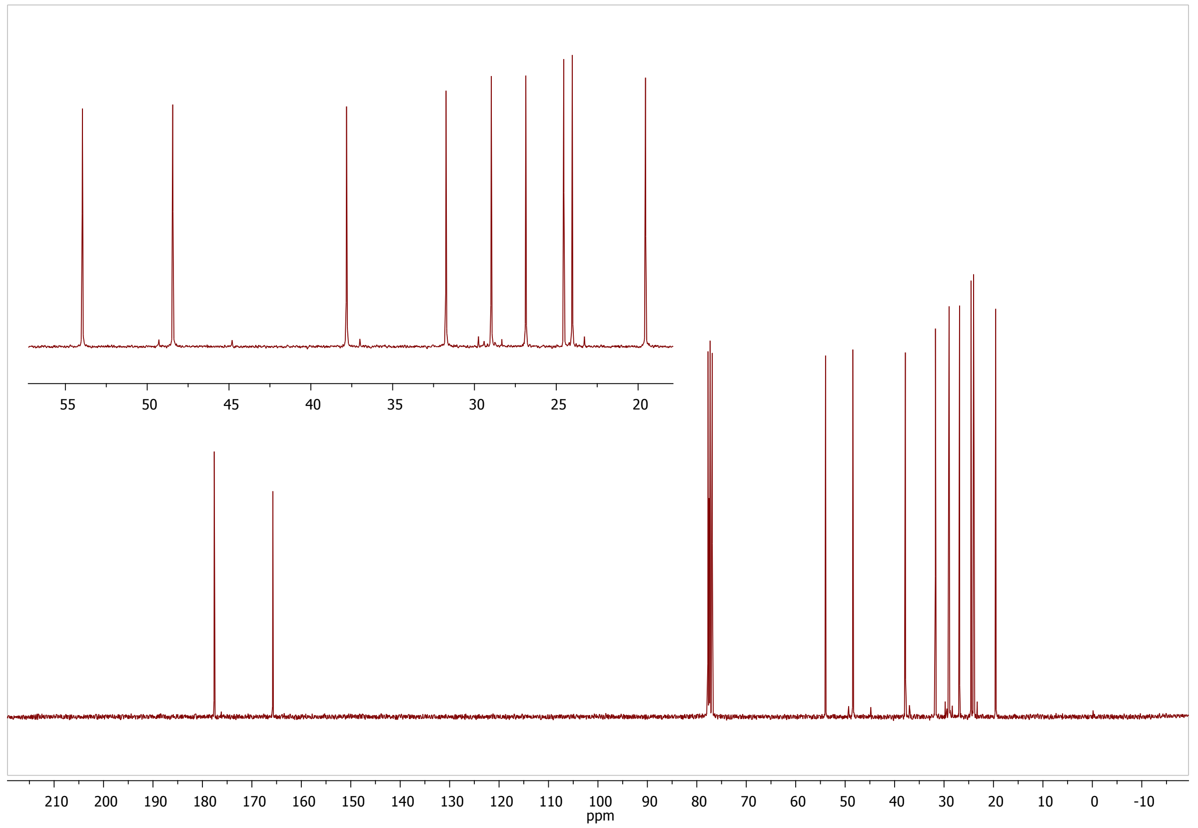


Figure S4. ^{1}H and ^{13}C NMR spectra of [DBUH][MeCOO] in $CDCl_3$, at $T = 295$ K.

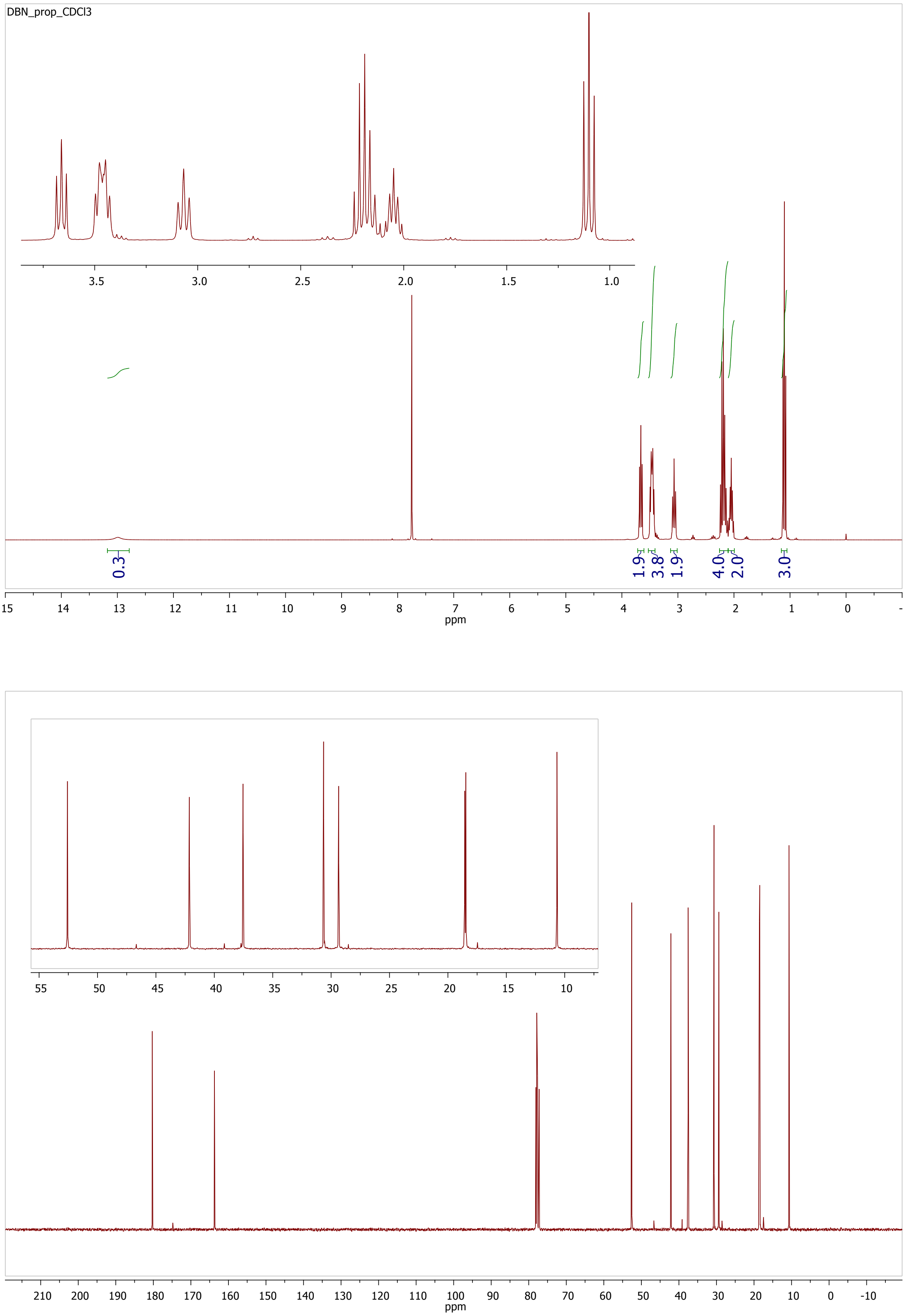


Figure S5. ^1H and ^{13}C NMR spectra of [DBNH][EtCOO] in $CDCl_3$, at $T = 295$ K.

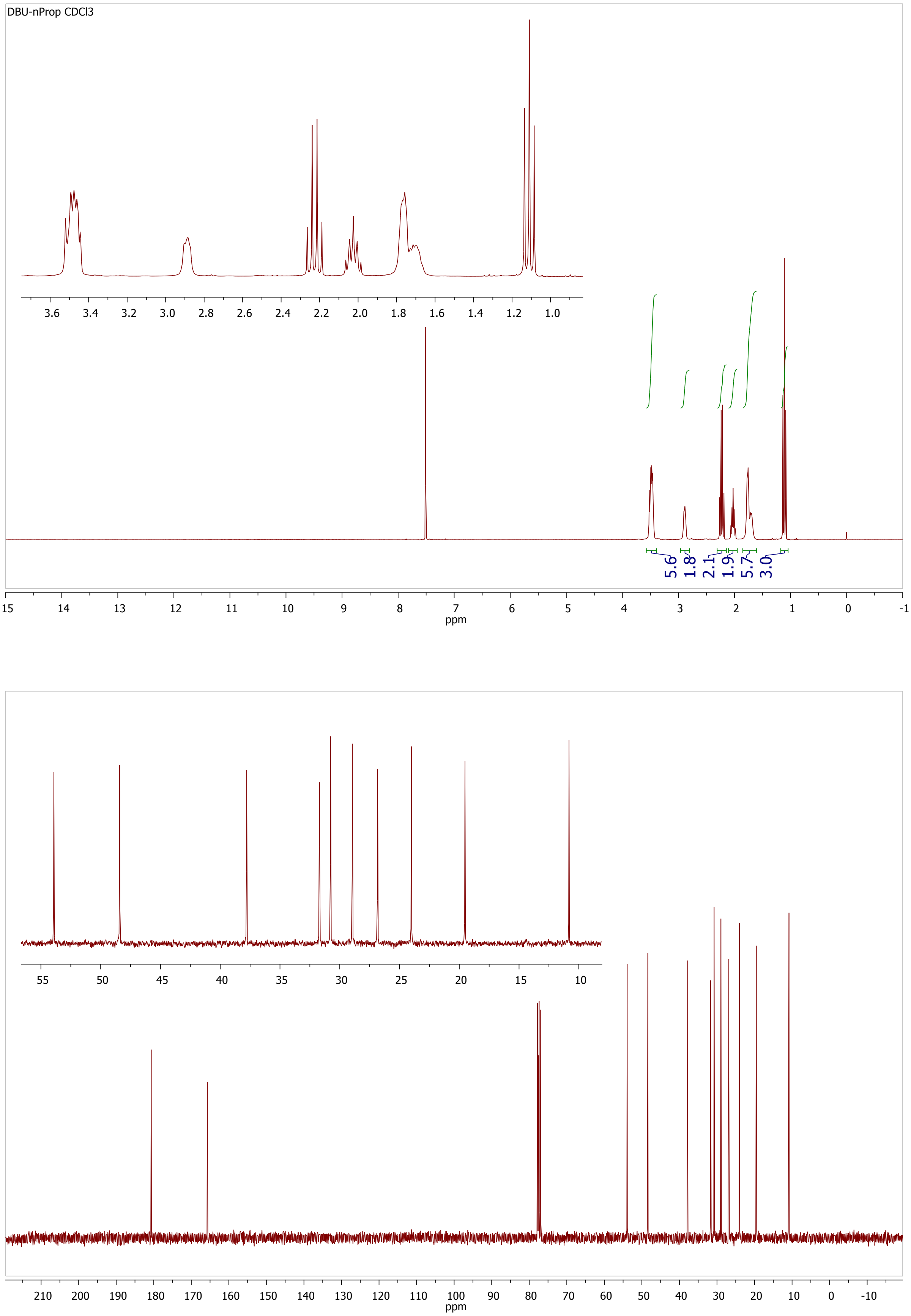


Figure S6. ^{1}H and ^{13}C NMR spectra of [DBUH][EtCOO] in $CDCl_3$, at $T = 295$ K.

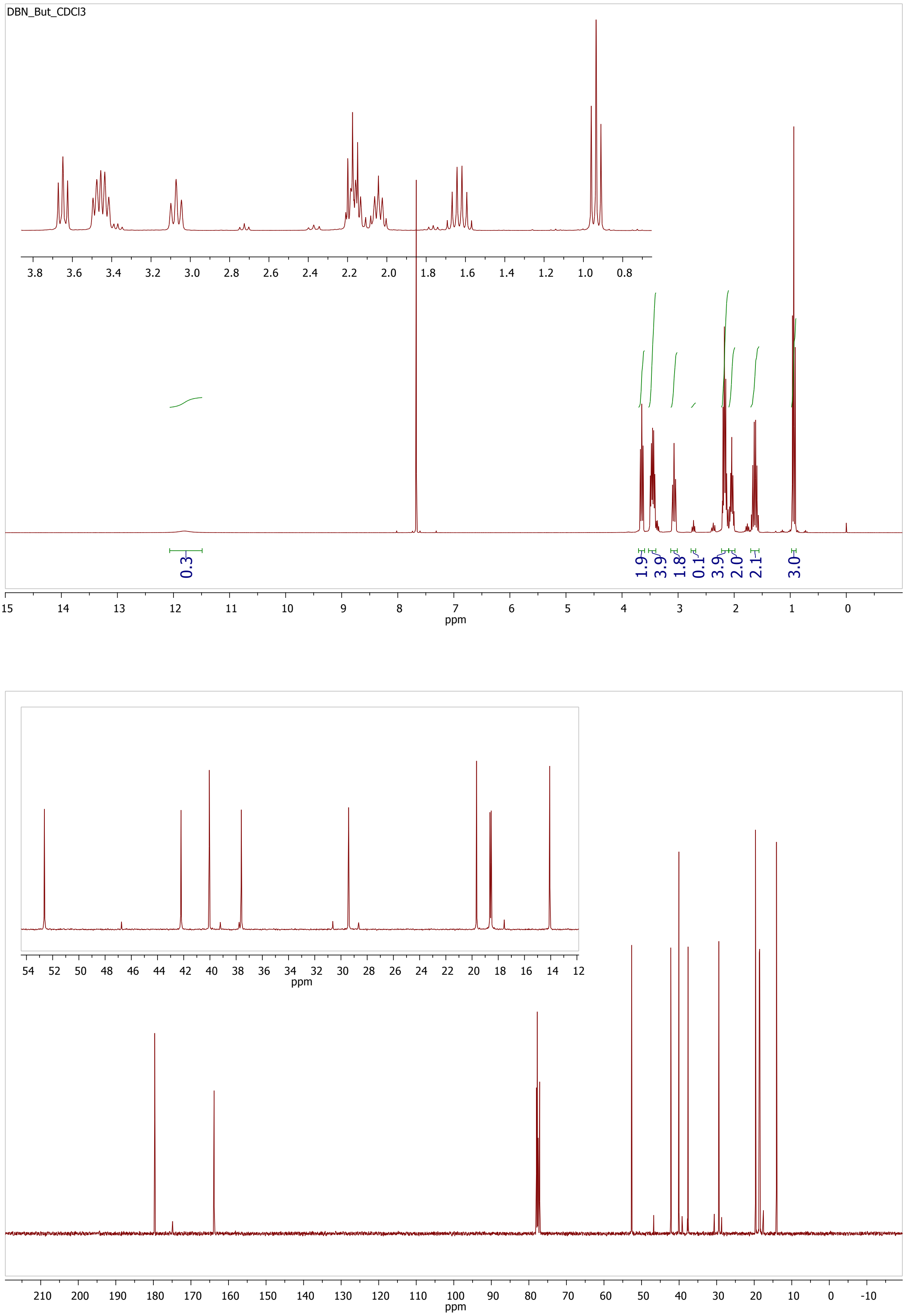


Figure S7. ^{1}H and ^{13}C NMR spectra of [DBNH][nPrCOO] in $CDCl_3$, at $T = 295$ K.

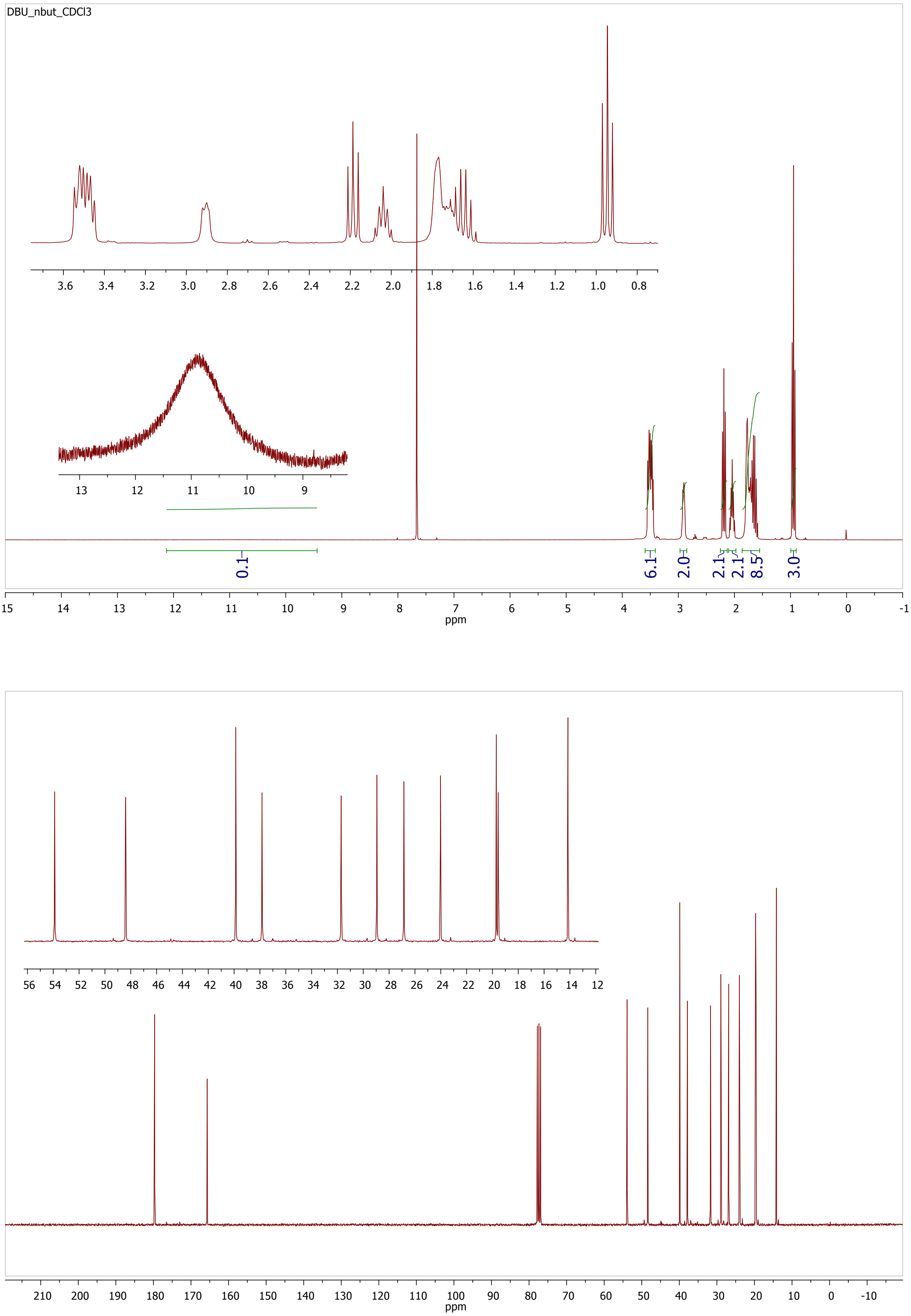


Figure S8. ^{1}H and ^{13}C NMR spectra of [DBUH][nPrCOO] in $CDCl_3$, at $T = 295$ K.

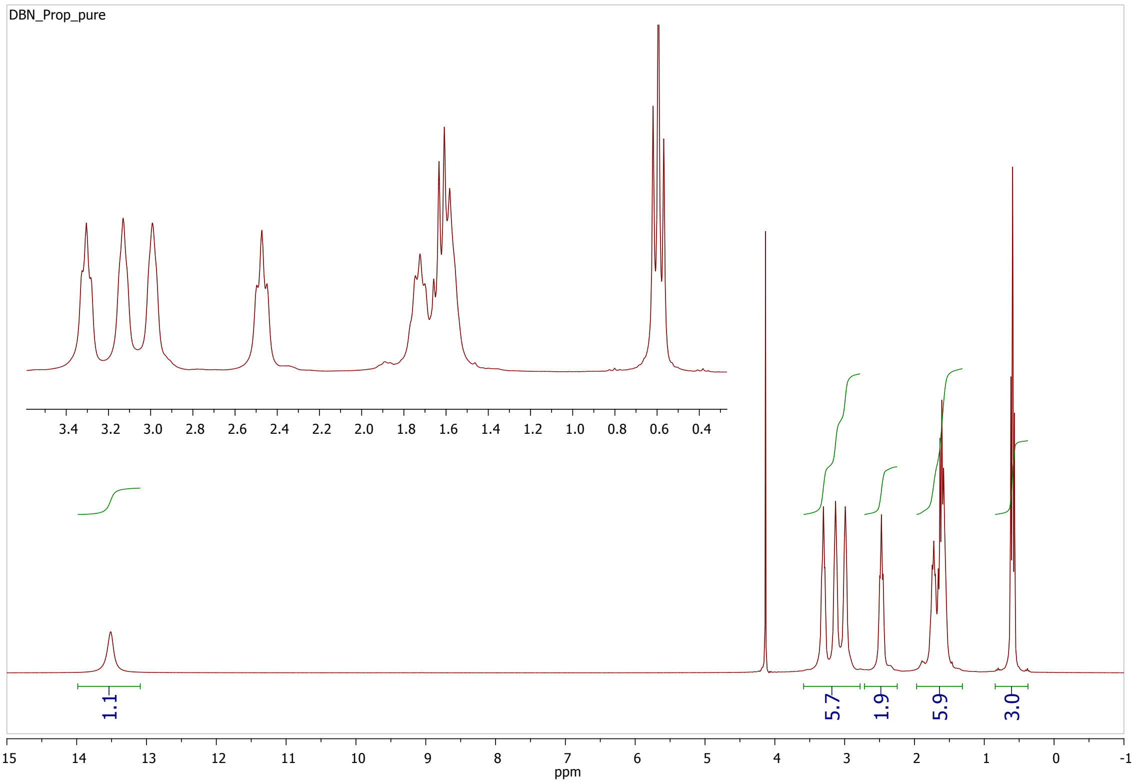


Figure S9. ^{1}H NMR spectrum of pure/neat [DBNH][EtCOO], at $T = 295$ K.

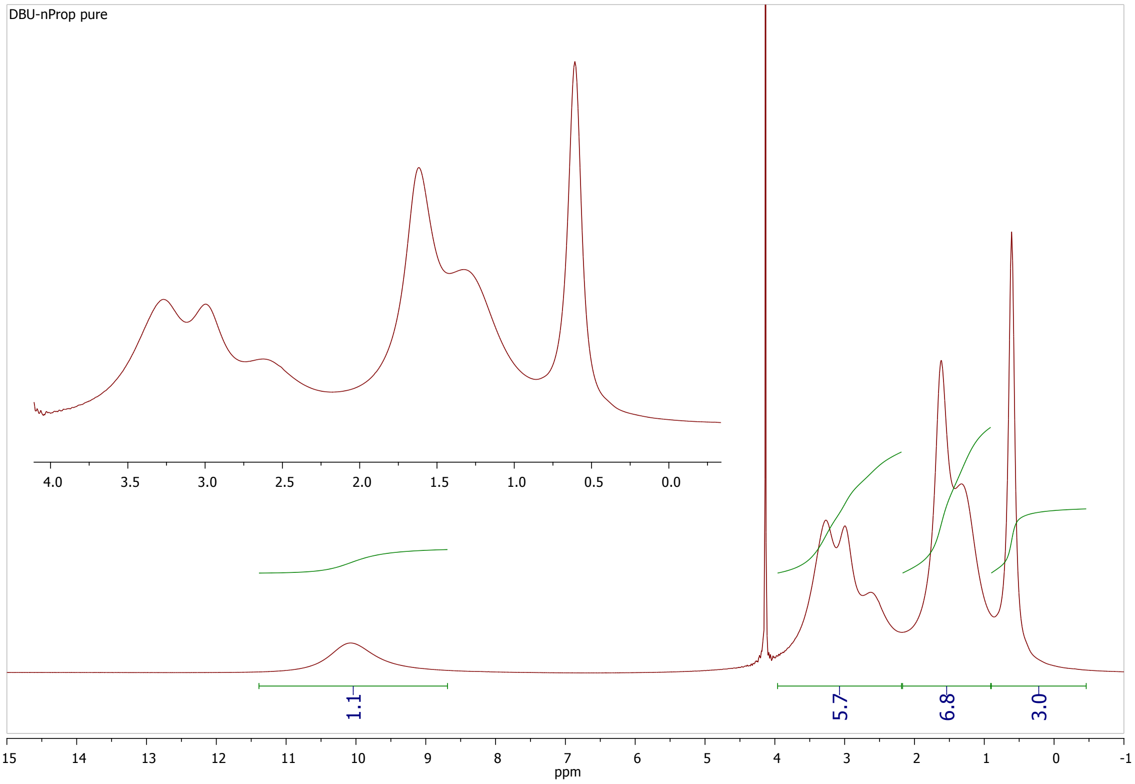


Figure S10. ^{1}H NMR spectrum of pure/neat [DBUH][EtCOO], at $T = 295$ K.

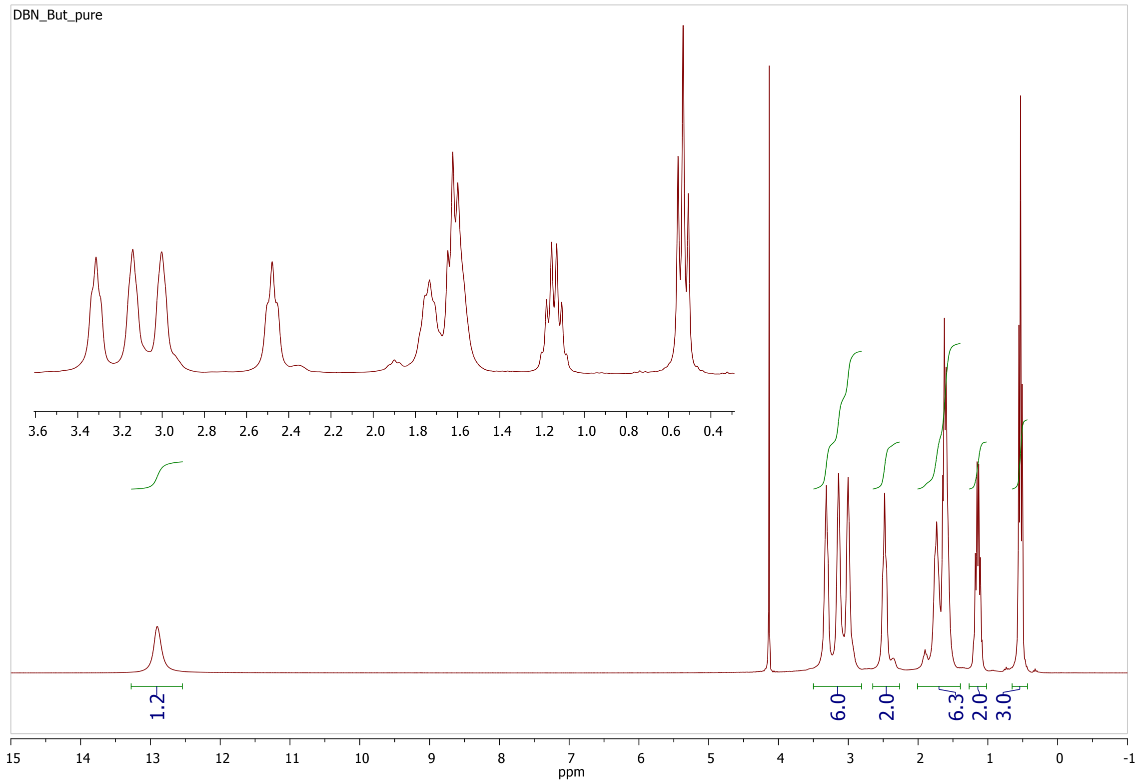


Figure S11. ^{1}H NMR spectrum of pure/neat [DBNH][nPrCOO], at $T = 295$ K.

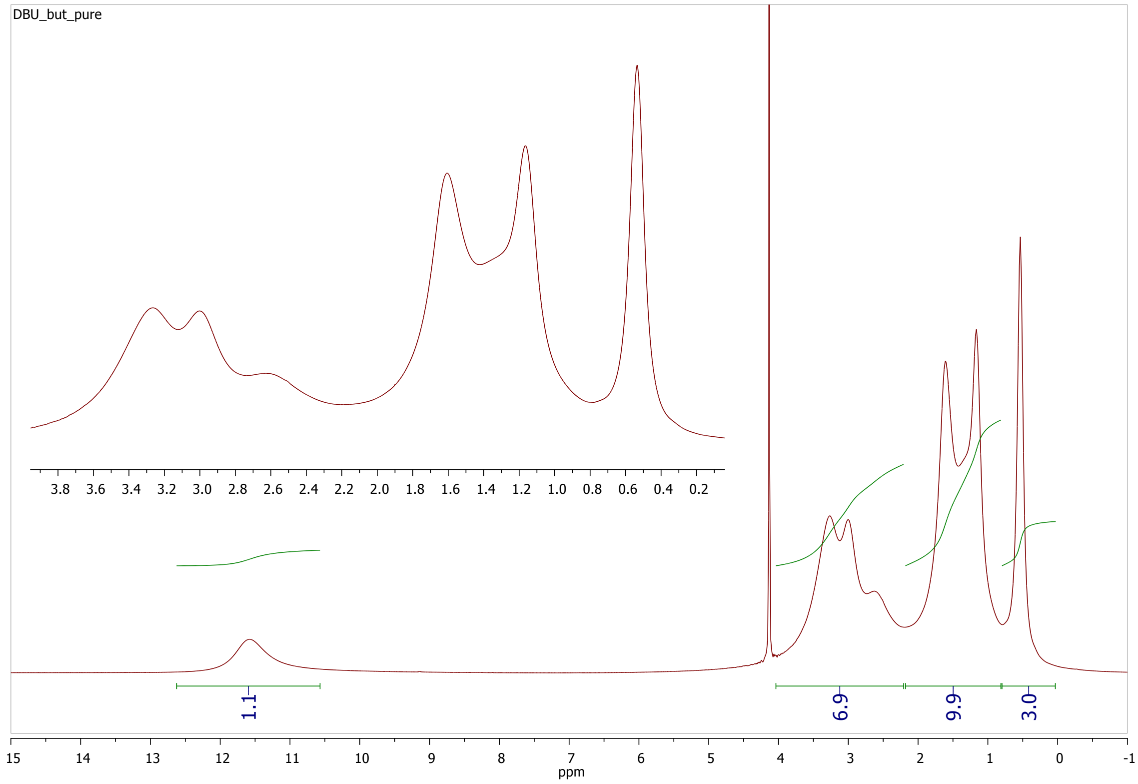


Figure S12. ^{1}H NMR spectrum of pure/neat [DBUH][nPrCOO], at $T = 295$ K.

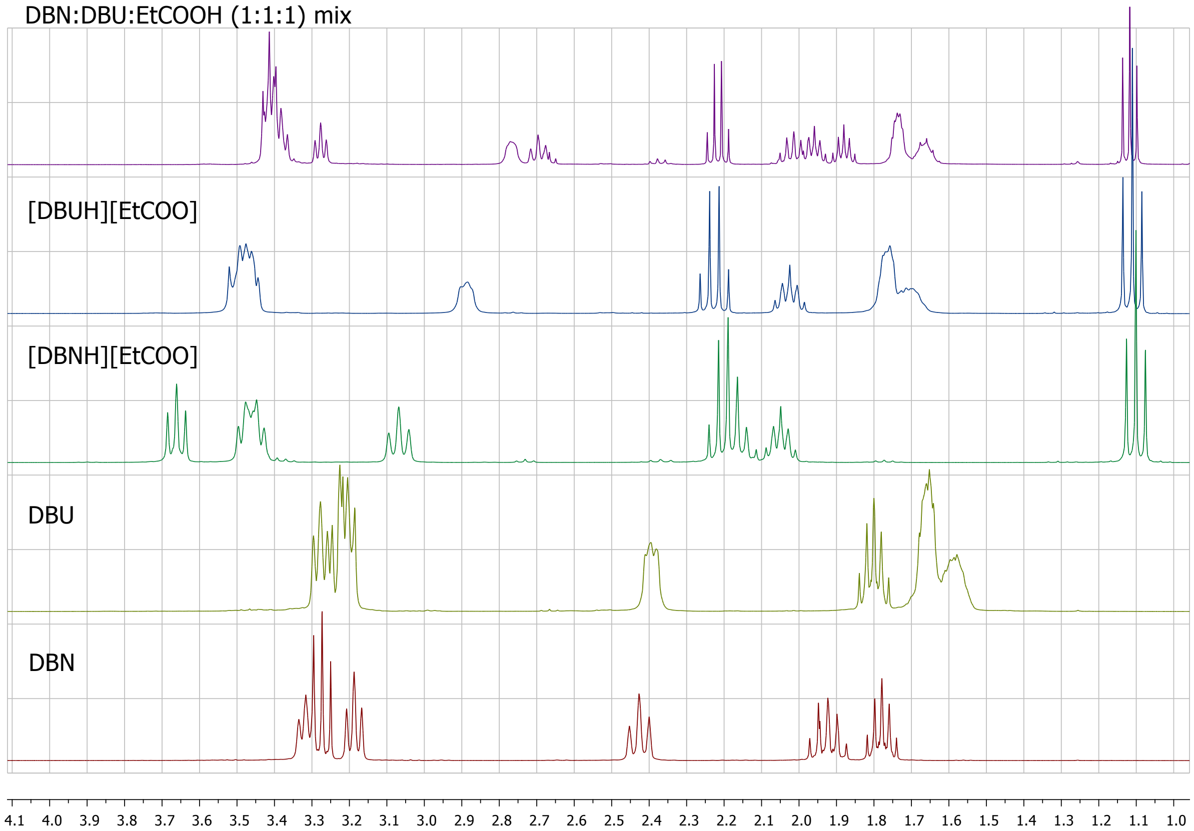


Figure S13. ^{1}H NMR spectra of the DBN:DBU:EtCOOH (1:1:1) mixture (top) in $CDCl_3$, at $T = 295$ K, and comparison with the relevant separated compounds.

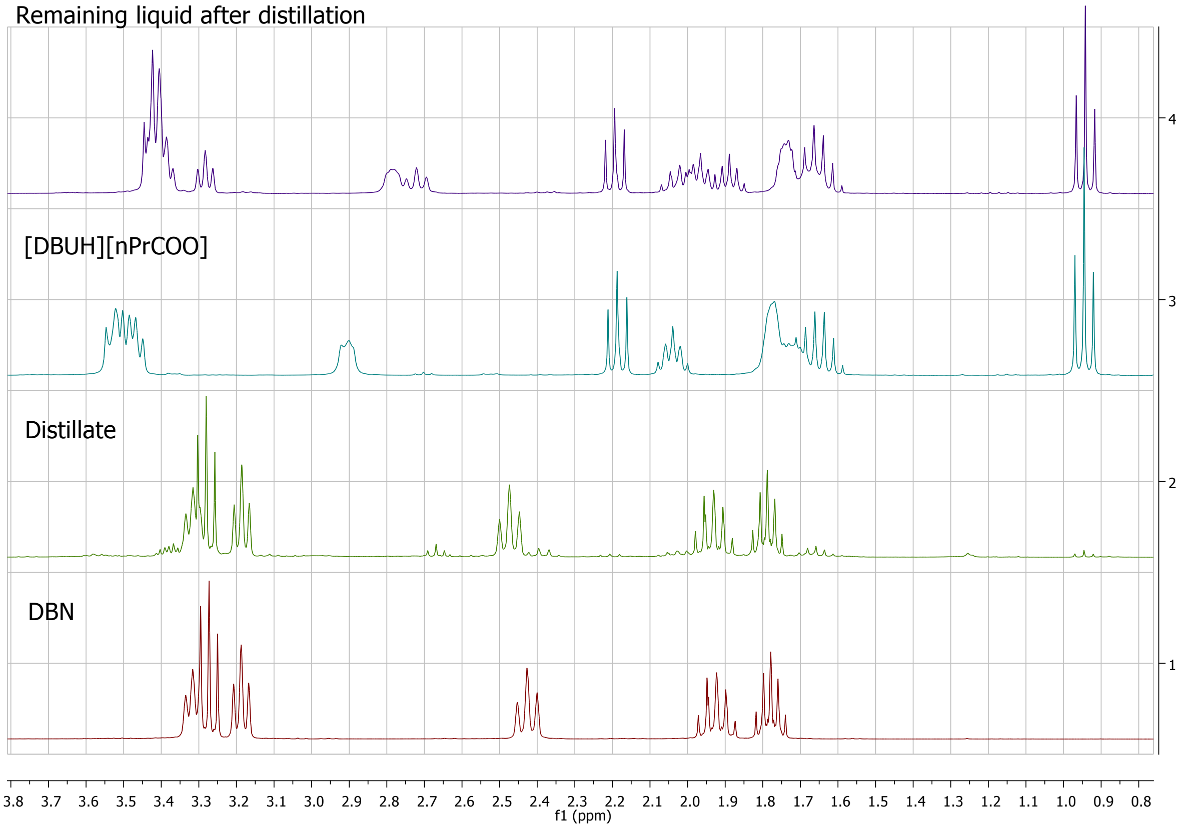


Figure S14. ^{1}H NMR results for the distillation of DBN:DBU:nPrCOOH (1:1:1) mixture; the spectra, in $CDCl_3$, at T = 295 K, of the remaining liquid and distillate are presented and compared with those of [DBUH][nPrCOO] and DBN.

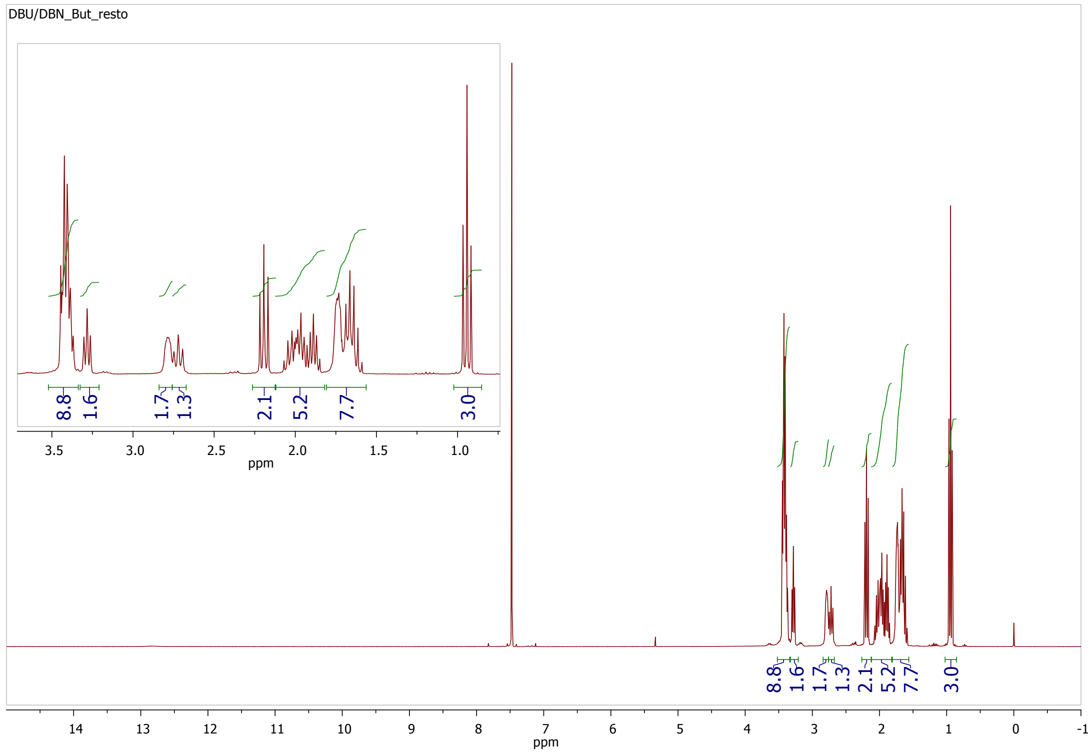


Figure S15. ^{1}H NMR spectrum of the remaining liquid after distillation of the DBN:DBU:nPrCOOH (1:1:1) mixture, in $CDCl_3$, at *T* = 295 K.

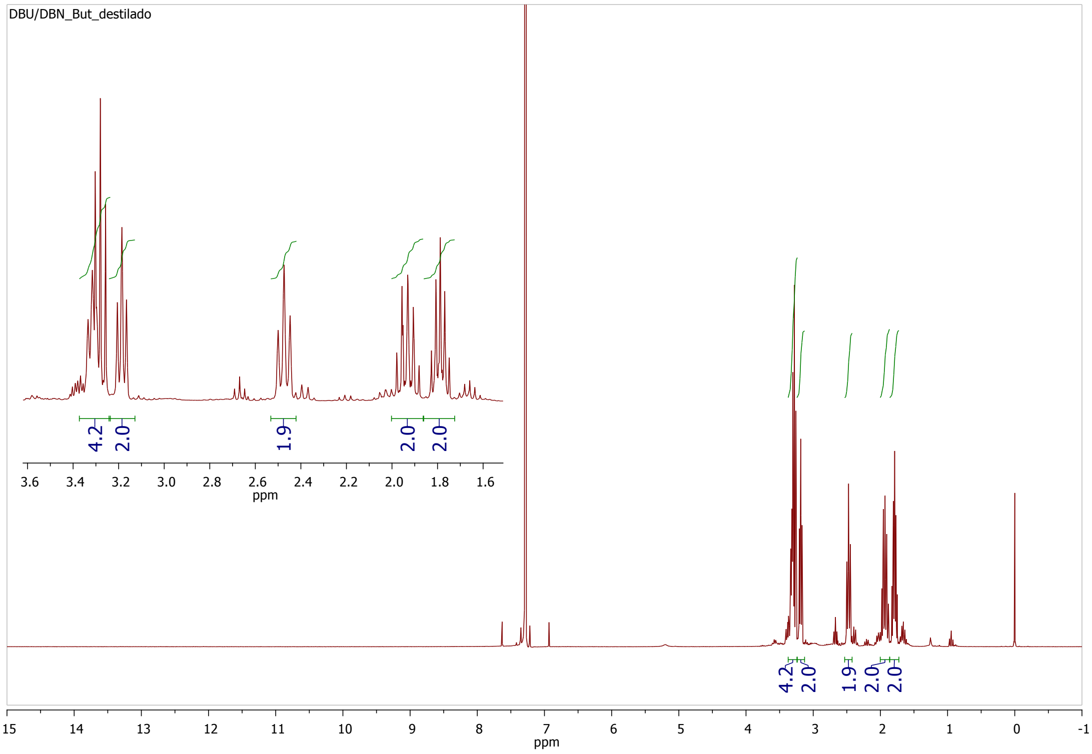


Figure S16. ^{1}H NMR spectrum of the distillate of the DBN:DBU:nPrCOOH (1:1:1) mixture, in $CDCl_3$, at *T* = 295 K.

3. FTIR spectroscopy

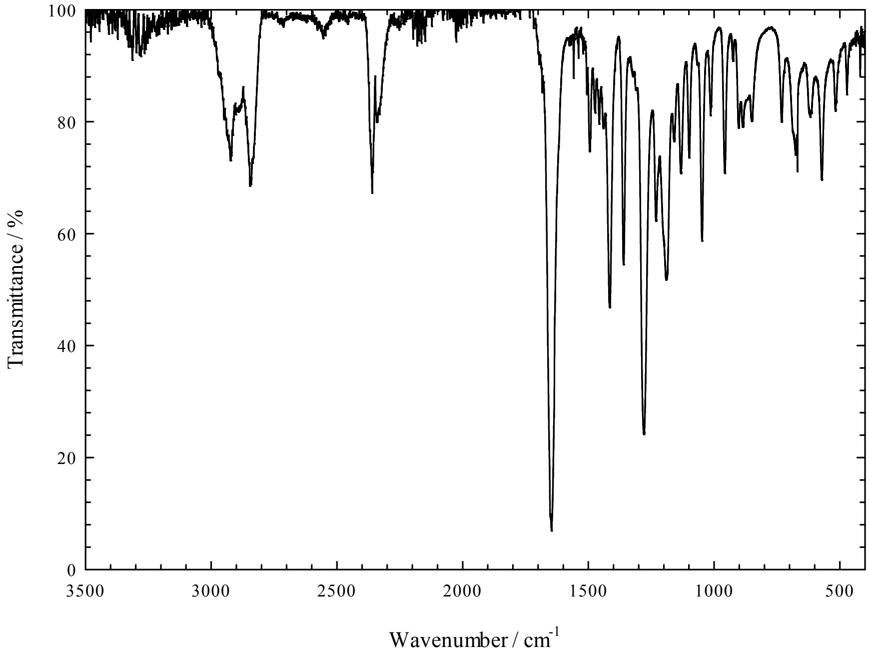


Figure S17. FTIR spectra of DBN, at *T* = 298 K.

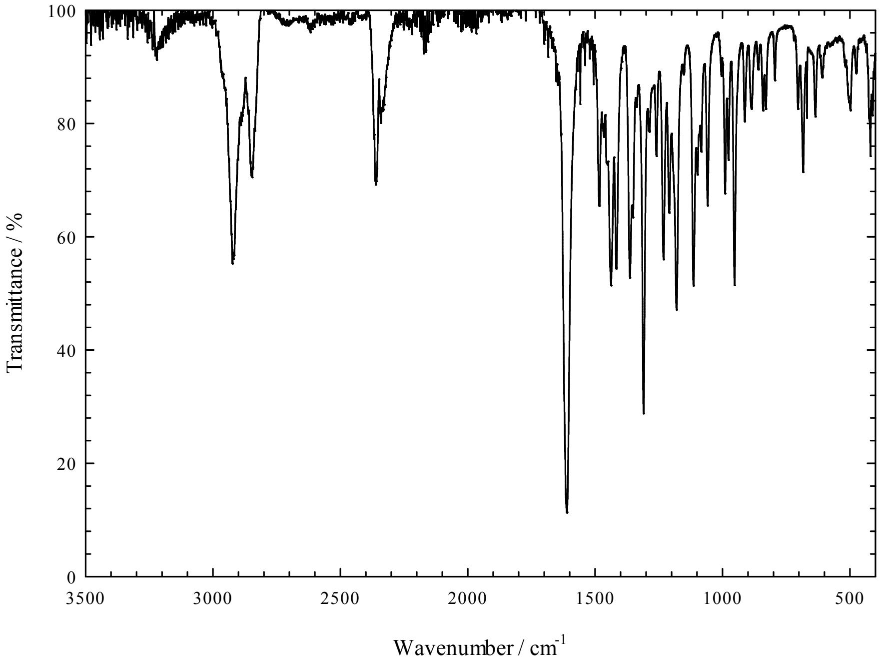


Figure S18. FTIR spectra of DBU, at *T* = 298 K.

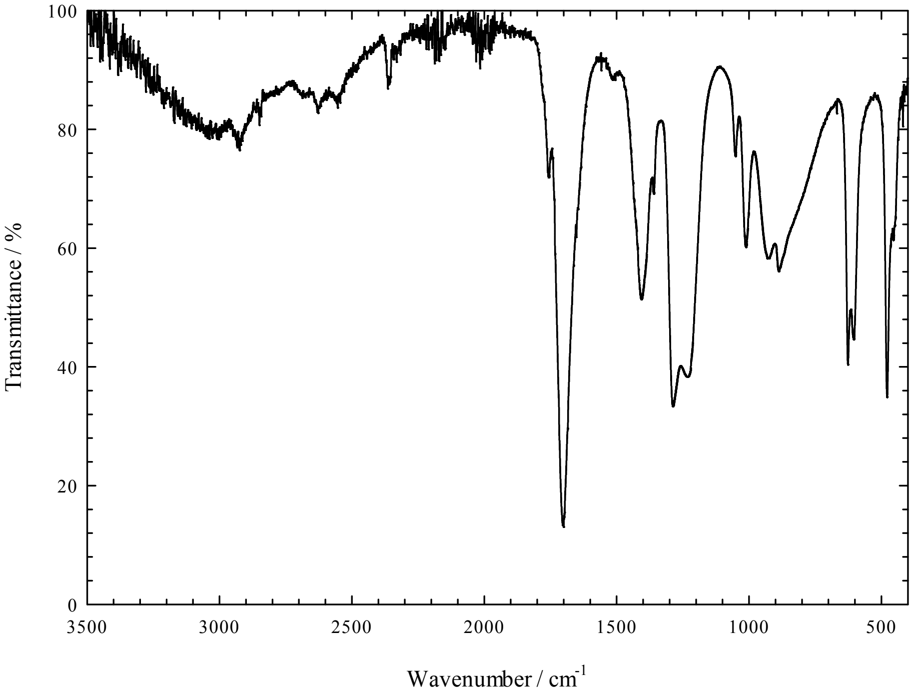


Figure S19. FTIR spectra of MeCOOH, at $T = 298$ K.

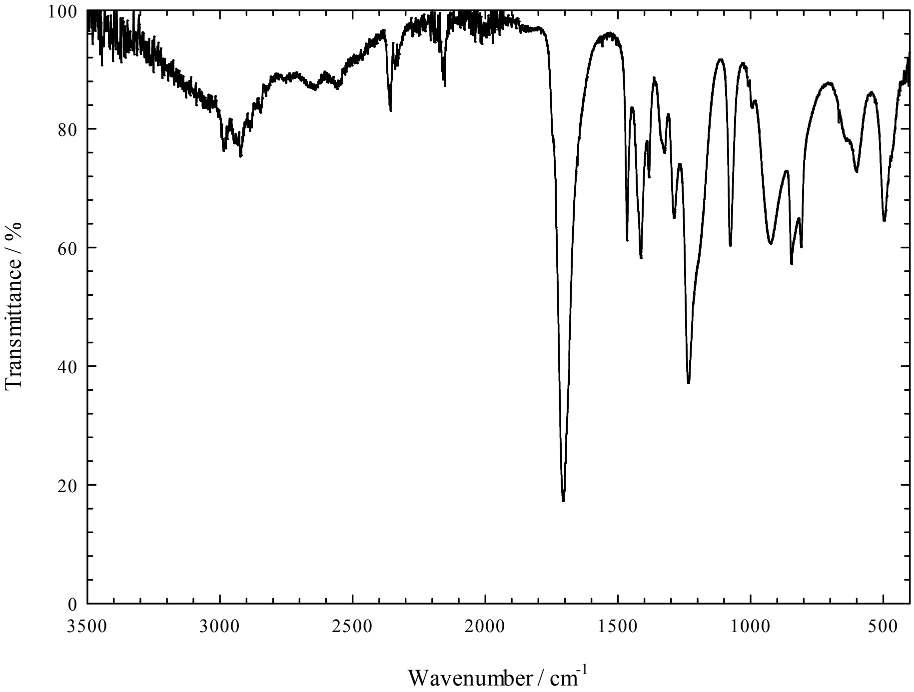


Figure S20. FTIR spectra of EtCOOH, at $T = 298$ K.

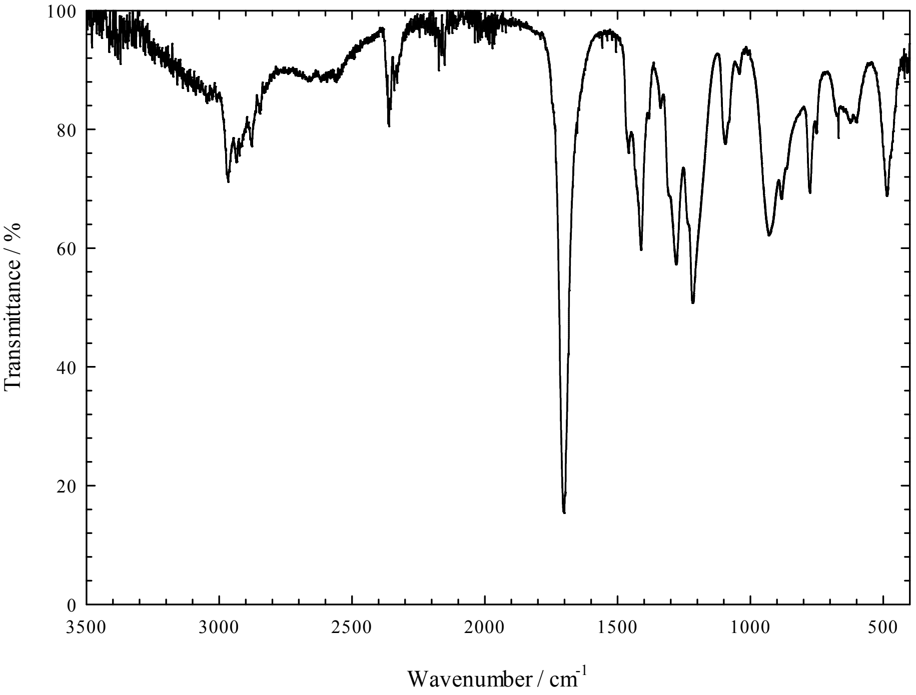


Figure S21. FTIR spectra of nPrCOOH, at T = 298 K.

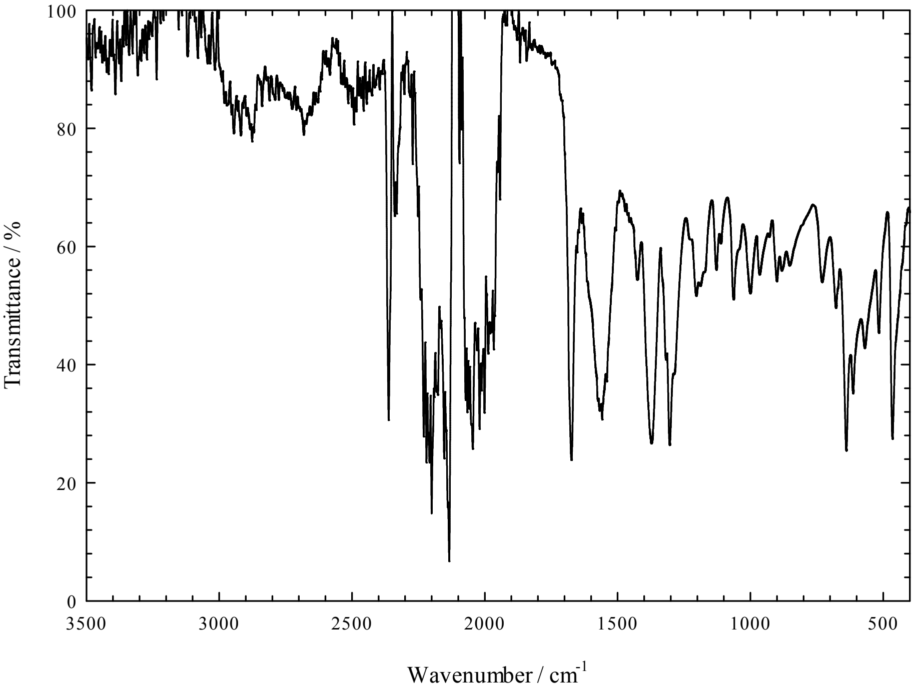


Figure S22. FTIR spectra of [DBNH][MeCOO], at T = 298 K.

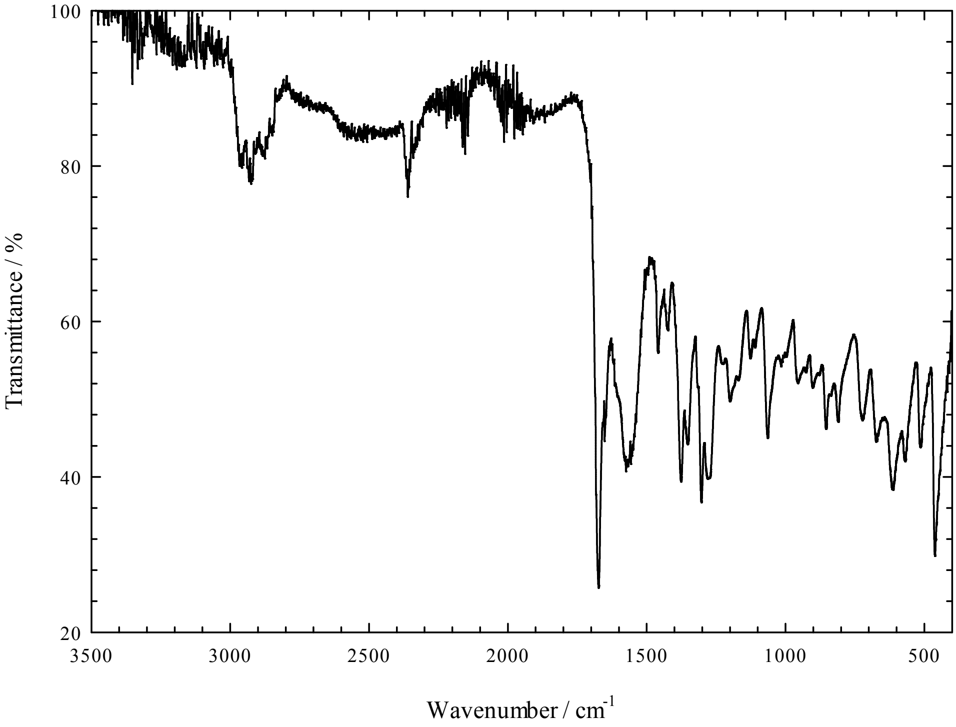


Figure S23. FTIR spectra of [DBNH][EtCOO], at T = 298 K.

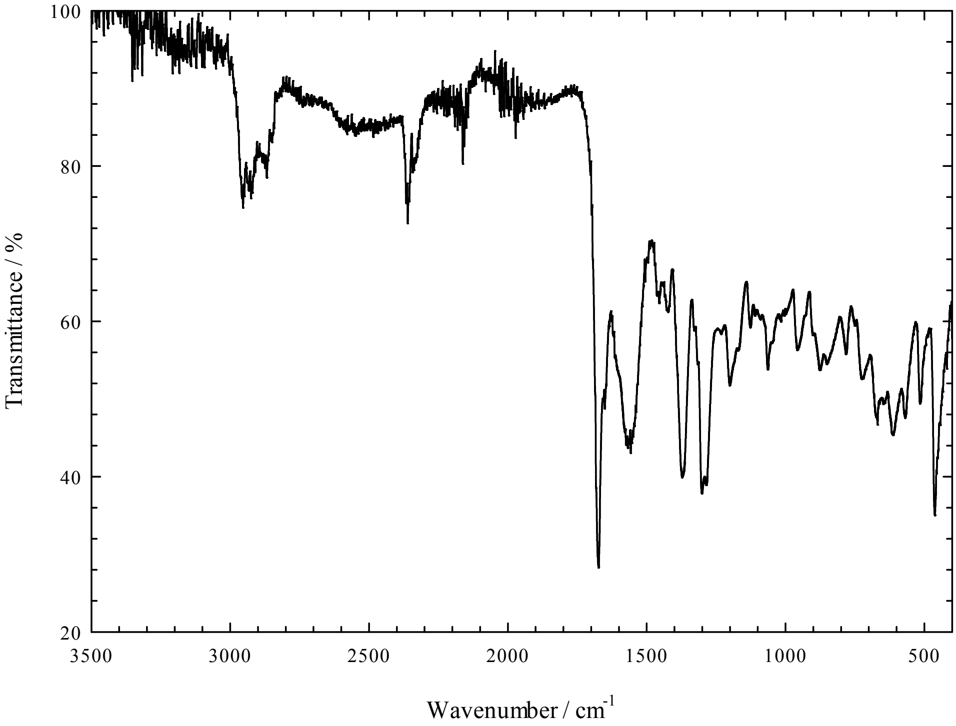


Figure S24. FTIR spectra of [DBNH][nPrCOO], at T = 298 K.

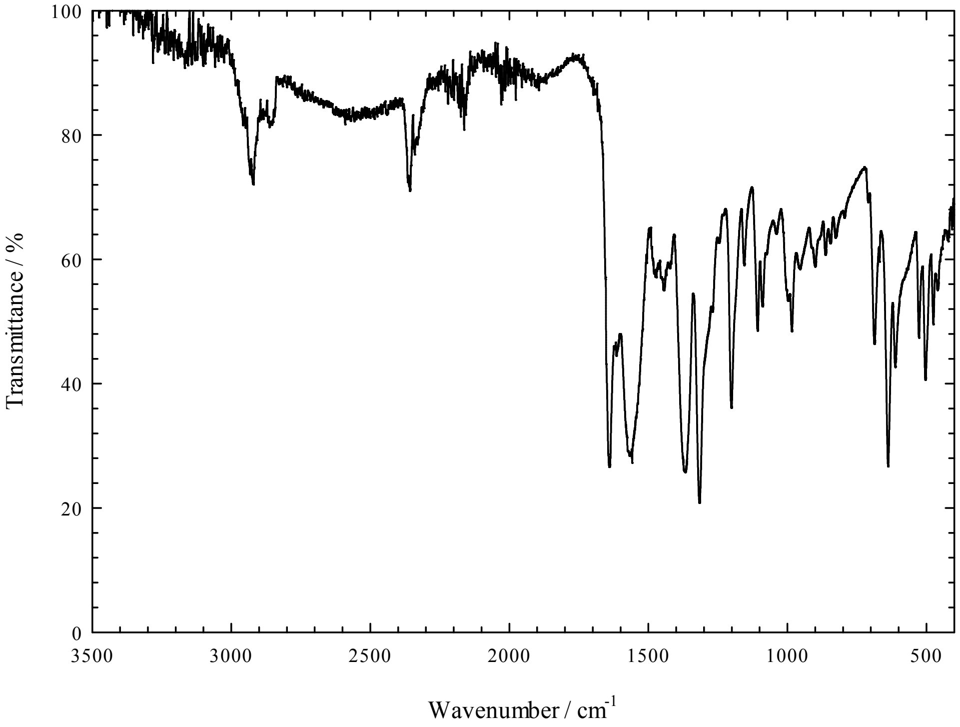


Figure S25. FTIR spectra of [DBUH][MeCOO], at $T = 298$ K.

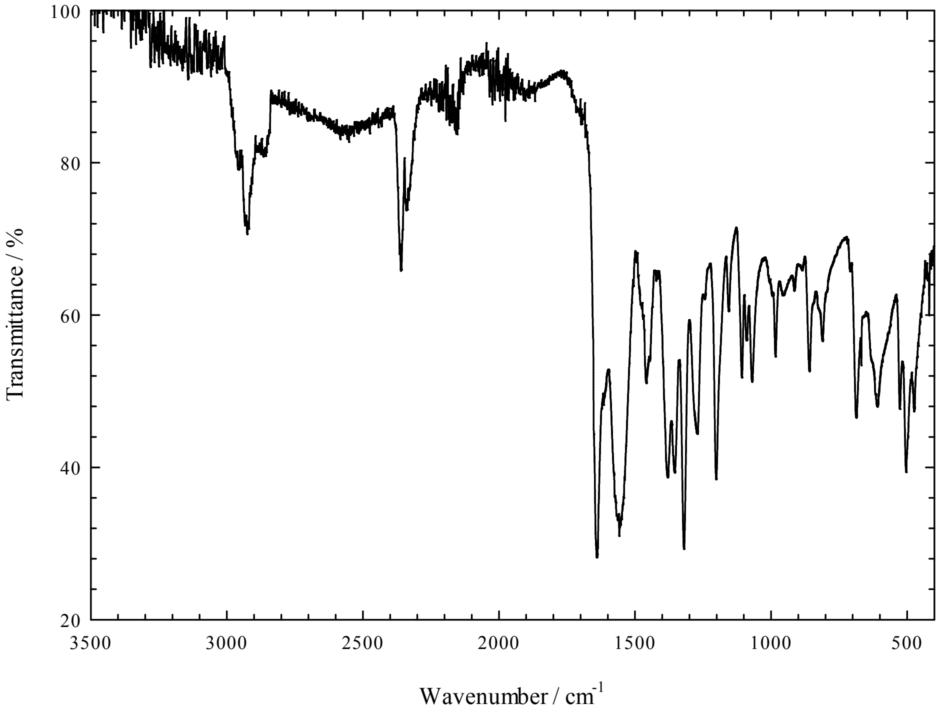


Figure S26. FTIR spectra of [DBUH][EtCOO], at $T = 298$ K.

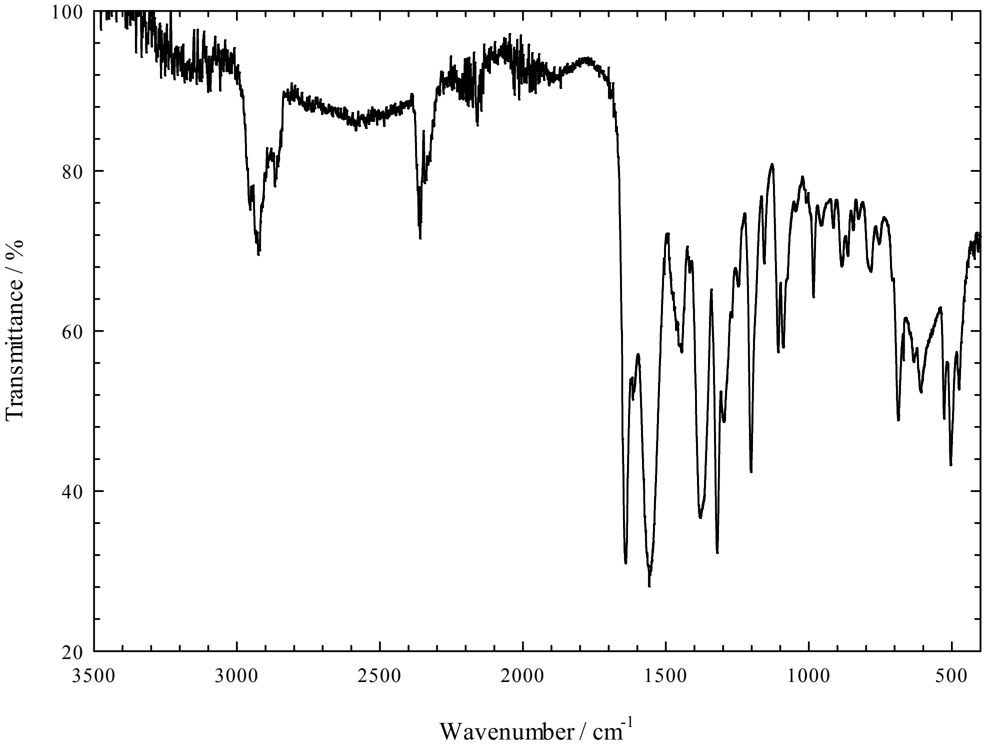


Figure S27. FTIR spectra of [DBUH][nPrCOO], at *T* = 298 K.

4. Calvet Microcalorimetry

Table S1 Experimental results obtained by Calvet microcalorimetry for the calibration experiments of each compound.

Compound	T / K	Calibrant	$\Delta_{\mathrm{cr}}^{\mathrm{g}} H_{\mathrm{m}}^{\mathrm{o}}$ (298.15 K)/ kJ·mol^{-1}	$H_{\mathrm{m}}^{\mathrm{o}}$ (g, T) - $H_{\mathrm{m}}^{\mathrm{o}}$ (g, 298.15 K) / kJ·mol^{-1}	n	k
DBN	340.0	Undecane	68.4 ± 1.2	11.8 ± 1.0	7	0.9974 ± 0.0180
DBU	340.0	Undecane	68.4 ± 1.2	11.8 ± 1.0	7	0.9974 ± 0.0180
[DBNH][MeCOO]	375.8	Ferrocene	87.6 ± 1.5	14.6 ± 1.0	7	0.9997 ± 0.0197
[DBNH][EtCOO]	375.9	Ferrocene	87.6 ± 1.5	14.6 ± 1.0	7	0.9997 ± 0.0197
[DBNH][nPrCOO]	375.7	Ferrocene	87.6 ± 1.5	14.6 ± 1.0	7	0.9997 ± 0.0197
[DBUH][MeCOO]	375.8	Ferrocene	87.6 ± 1.5	14.6 ± 1.0	7	0.9997 ± 0.0197
[DBUH][EtCOO]	375.9	Ferrocene	87.6 ± 1.5	14.6 ± 1.0	7	0.9997 ± 0.0197
[DBUH][nPrCOO]	375.9	Ferrocene	87.6 ± 1.5	14.6 ± 1.0	7	0.9997 ± 0.0197

Table S2 Experimental results obtained by Calvet microcalorimetry for the sublimation of DBN (*T*=340.0K).

m_{compound} / mg	$\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\text{o}}$ / kJ·mol⁻¹	$k\cdot<\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\text{o}}>$ / kJ·mol⁻¹	H_{m}^{o} (g, T) - H_{m}^{o} (g, 298.15 K) / kJ·mol⁻¹
4.00	68.67	70.3 ± 0.5	6.3 ± 1.0
3.10	71.42		
3.88	72.52		
4.27	70.35		
4.05	69.77		
2.39	68.95		
2.74	70.18		
$\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\text{o}}$ (298.15 K) / kJ·mol⁻¹ = (63.9 ± 1.5)			

Table S3 Experimental results obtained by Calvet microcalorimetry for the sublimation of DBU (*T*=340.0K).

m_{compound} / mg	$\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\text{o}}$ / kJ·mol⁻¹	$k\cdot<\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\text{o}}>$ / kJ·mol⁻¹	H_{m}^{o} (g, T) - H_{m}^{o} (g, 298.15 K) / kJ·mol⁻¹
3.84	76.71	77.9 ± 0.5	8.1 ± 1.0
4.00	78.51		
2.18	76.84		
3.58	77.21		
5.23	79.41		
4.45	79.57		
3.46	76.71		
$\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\text{o}}$ (298.15 K) / kJ·mol⁻¹ = (69.7 ± 1.5)			

Table S4 Experimental results obtained by Calvet microcalorimetry for the sublimation of [DBNH][MeCOO] (*T*=375.8K).

m_{compound} / mg	$\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\text{o}}$ / kJ·mol^{-1}	$k\cdot<\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\text{o}}>$ / kJ·mol^{-1}	H_{m}^{o} (g, T) - H_{m}^{o} (g, 298.15 K) / kJ·mol^{-1}
2.59	173.82	171.2 ± 0.7	18.3 ± 1.0
4.32	170.58		
4.63	169.60		
3.22	172.82		
6.01	168.26		
3.69	172.68		
4.62	171.91		
3.68	170.14		
$\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\text{o}}$ (298.15 K) / kJ·mol^{-1} = (152.9 ± 1.6)			

Table S5 Experimental results obtained by Calvet microcalorimetry for the sublimation of [DBNH][EtCOO] (*T*=375.9K).

m_{compound} / mg	$\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\text{o}}$ / kJ·mol^{-1}	$k\cdot<\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\text{o}}>$ / kJ·mol^{-1}	H_{m}^{o} (g, T) - H_{m}^{o} (g, 298.15 K) / kJ·mol^{-1}
6.25	180.87	179.5 ± 0.5	20.2 ± 1.0
6.29	181.55		
7.08	179.47		
6.42	181.20		
4.57	176.18		
5.15	178.08		
6.37	178.02		
5.70	180.41		
5.22	178.14		
5.88	179.44		
5.68	180.80		
$\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\text{o}}$ (298.15 K) / kJ·mol^{-1} = (159.3 ± 1.5)			

Table S6 Experimental results obtained by Calvet microcalorimetry for the sublimation of [DBNH][nPrCOO] (T=375.7K).

m_{compound} / mg	$\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\text{o}}$ / kJ·mol^{-1}	$k\cdot<\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\text{o}}>$ / kJ·mol^{-1}	H_{m}^{o} (g, T) - H_{m}^{o} (g, 298.15 K) / kJ·mol^{-1}
3.92	186.04	187.3 ± 0.4	22.0 ± 1.0
4.08	186.26		
3.82	187.76		
3.54	188.07		
3.36	186.70		
4.18	187.86		
3.30	188.62		
$\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\text{o}}$ (298.15 K) / kJ·mol^{-1} = (165.4 ± 1.5)			

Table S7 Experimental results obtained by Calvet microcalorimetry for the sublimation of [DBUH][MeCOO] (T=375.8K).

m_{compound} / mg	$\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\text{o}}$ / kJ·mol^{-1}	$k\cdot<\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\text{o}}>$ / kJ·mol^{-1}	H_{m}^{o} (g, T) - H_{m}^{o} (g, 298.15 K) / kJ·mol^{-1}
3.42	197.50	200.4 ± 1.0	21.8 ± 1.0
4.24	200.11		
3.68	202.38		
2.28	203.50		
3.41	198.47		
2.77	203.23		
4.90	197.44		
$\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\text{o}}$ (298.15 K) / kJ·mol^{-1} = (178.5 ± 1.7)			

Table S8 Experimental results obtained by Calvet microcalorimetry for the sublimation of [DBUH][EtCOO] (T=375.9K).

m_{compound} / mg	$\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$ / kJ·mol^{-1}	$k\cdot<\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}>$ / kJ·mol^{-1}	$H_{\mathrm{m}}^{\mathrm{o}}$ (g, T) - $H_{\mathrm{m}}^{\mathrm{o}}$ (g, 298.15 K) / kJ·mol^{-1}
3.48	210.84	208.6 ± 0.7	23.7 ± 1.0
3.65	210.00		
3.69	210.91		
4.78	205.26		
5.50	204.53		
4.26	209.60		
3.64	205.28		
3.76	208.37		
4.08	213.06		
7.76	209.17		
4.26	208.41		
5.04	211.07		
3.02	207.09		
3.87	206.89		
$\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$ (298.15 K) / kJ·mol^{-1} = (184.9 ± 1.6)			

Table S9 Experimental results obtained by Calvet microcalorimetry for the sublimation of [DBUH][nPrCOO] (T=375.9K).

m_{compound} / mg	$\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$ / kJ·mol^{-1}	$k\cdot<\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}>$ / kJ·mol^{-1}	$H_{\mathrm{m}}^{\mathrm{o}}$ (g, T) - $H_{\mathrm{m}}^{\mathrm{o}}$ (g, 298.15 K) / kJ·mol^{-1}
3.22	214.50	216.1 ± 1.6	25.6 ± 1.0
5.45	207.89		
3.41	219.99		
3.95	216.34		
3.77	213.95		
3.75	219.77		
3.39	208.58		
2.51	217.18		
2.63	221.37		
3.37	221.22		
$\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}$ (298.15 K) / kJ·mol^{-1} = (190.5 ± 2.1)			

5. Differential Scanning Calorimetry

The thermal analysis and phase behavior of all samples were explored in the temperature range of 173 K to 323 K, on a DSC, PerkinElmer, model Pyris Diamond using a heating rate of 5 $K \cdot min^{-1}$, a $N_2(g)$ flow of 50 ml/min and sealed aluminium crucibles. The crucibles were weighted using a Denver Instrument analytical balance with a readability of 0.01 mg and the typical sample load was of about 10 mg. Figures S28 to S35 present close-ups for all the experiments.

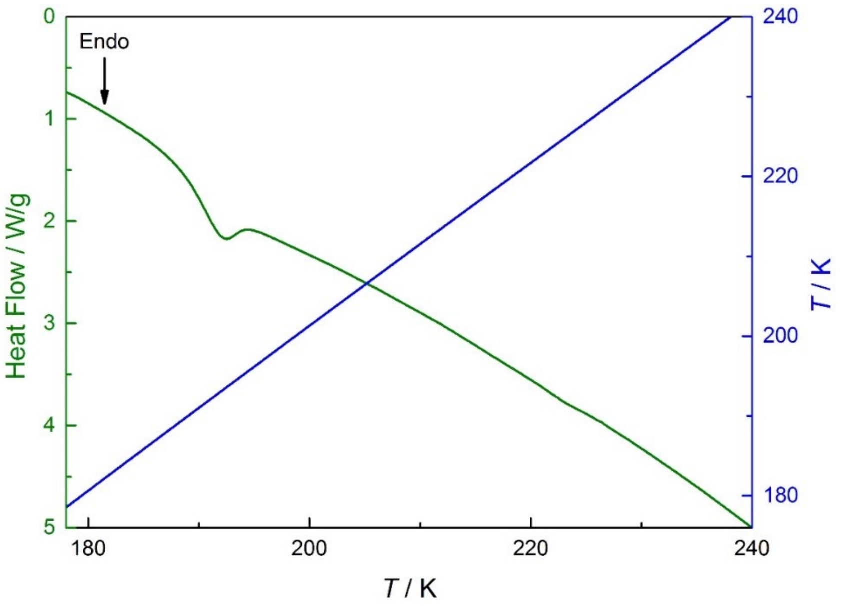


Figure S28. Thermogram for DBN.

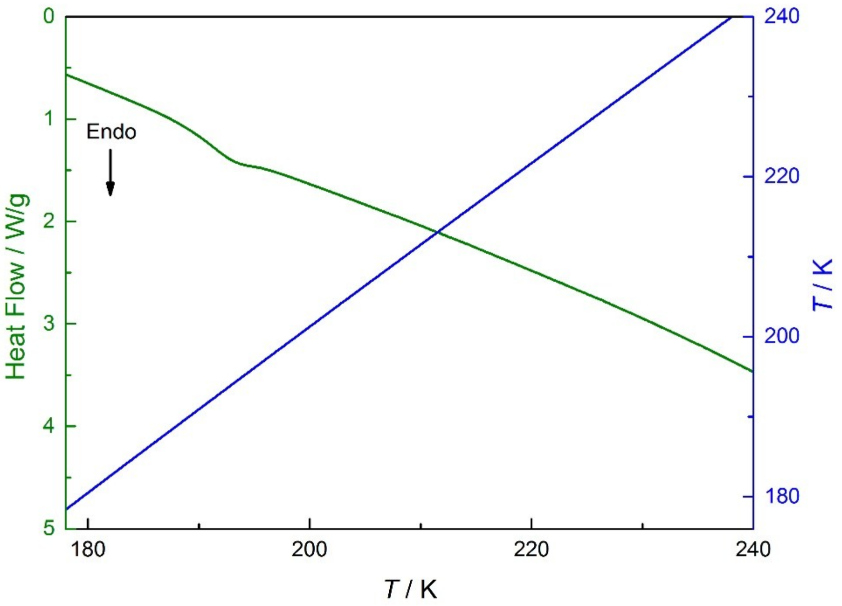


Figure S29. Thermogram for DBU.

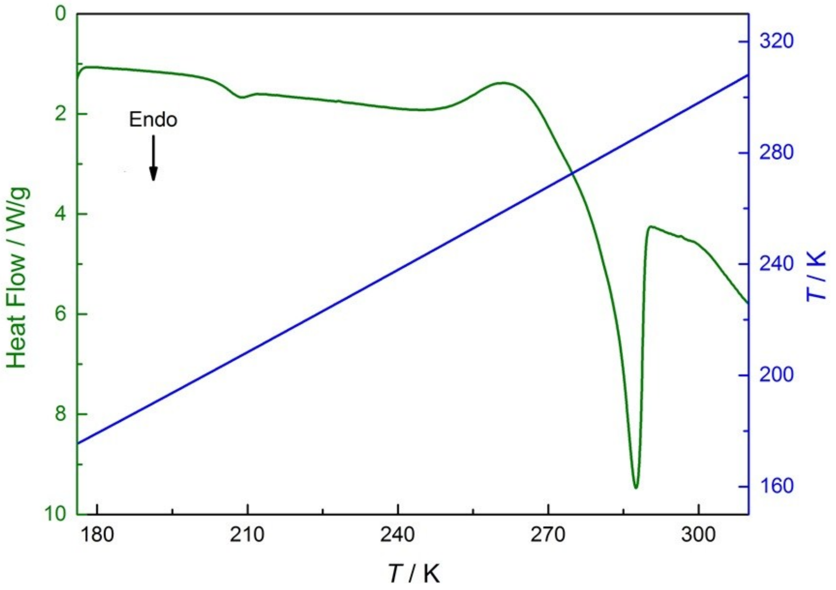


Figure S30. Thermogram for [DBNH][MeCOO]. For this protic ionic liquid, a cold-crystallization temperature T_{cc} of 257.8 K was measured.

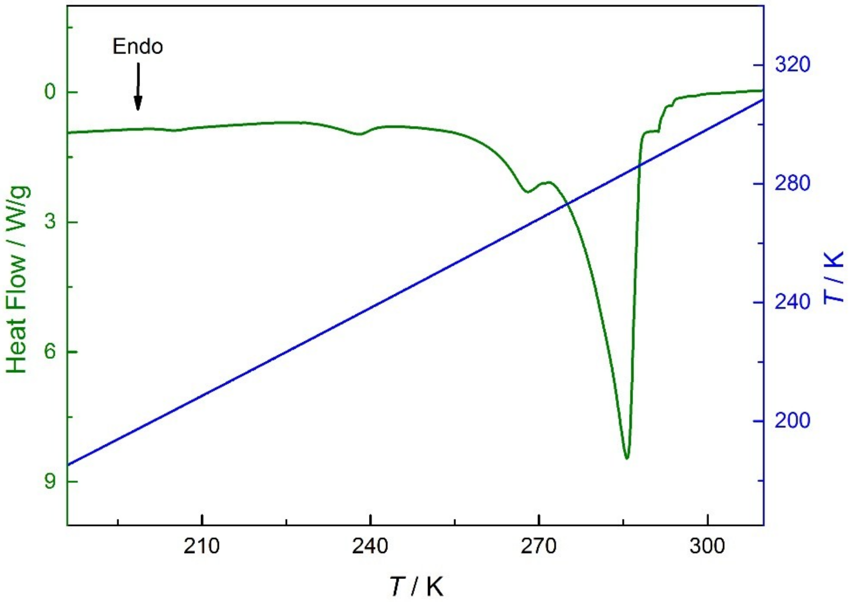


Figure S31. Thermogram for [DBNH][EtCOO]. For this protic ionic liquid, a crystallization temperature T_c of 245.3 K was measured.

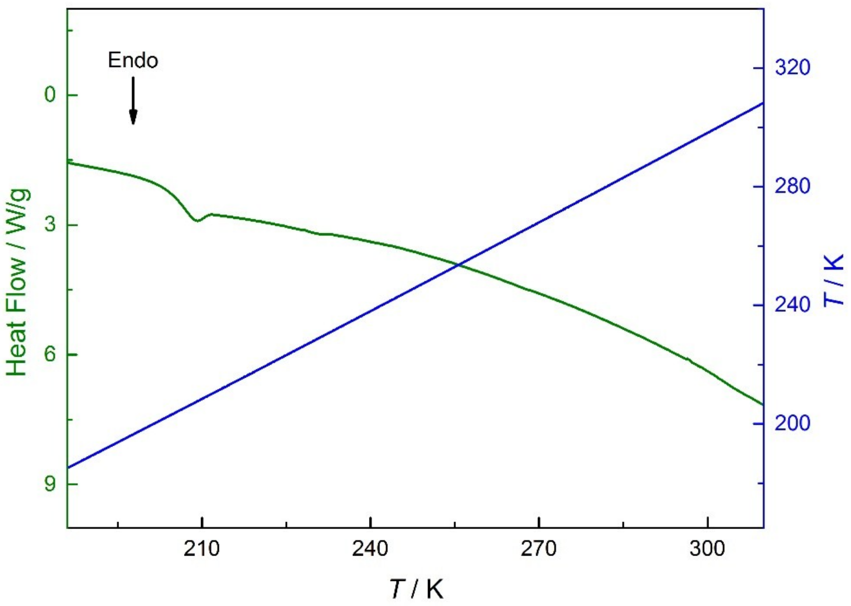


Figure S32. Thermogram for [DBNH][nPrCOO].

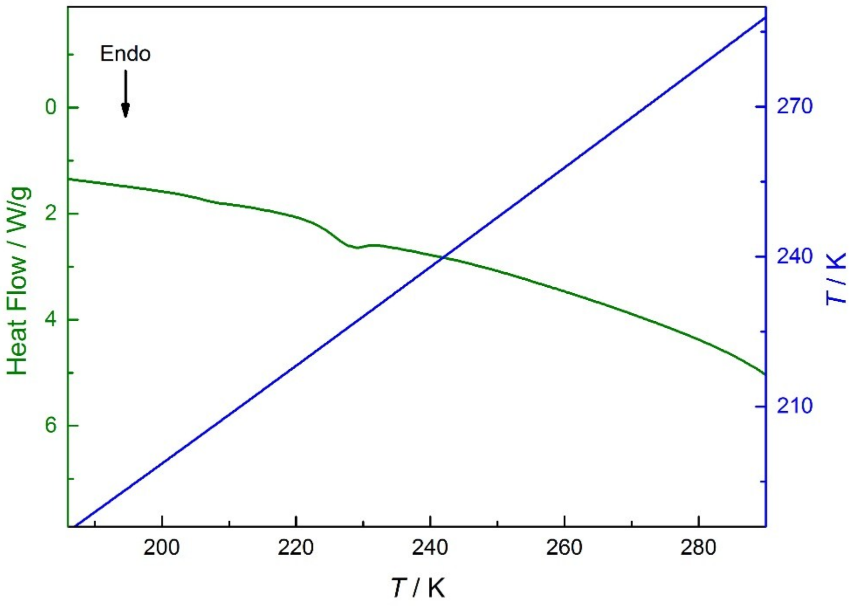


Figure S33. Thermogram for [DBUH][MeCOO].

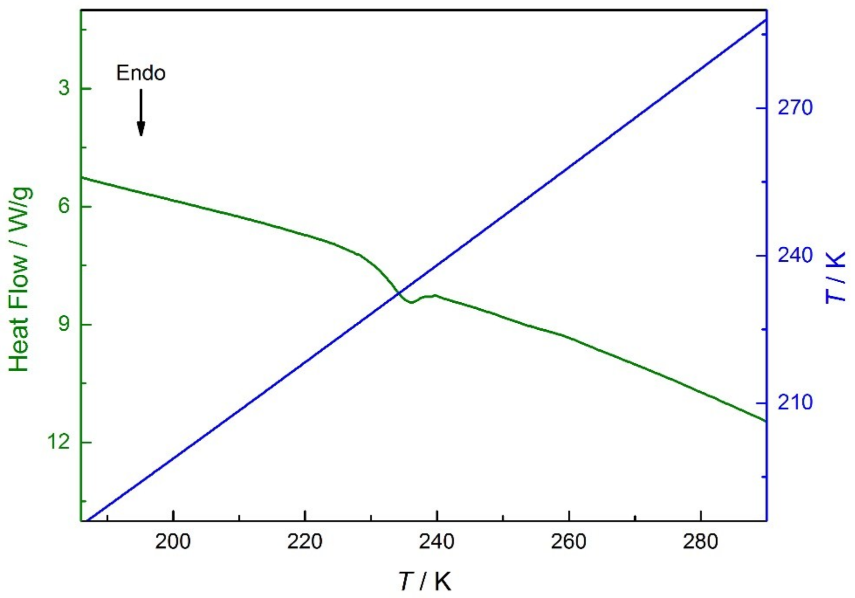


Figure S34. Thermogram for [DBUH][EtCOO].

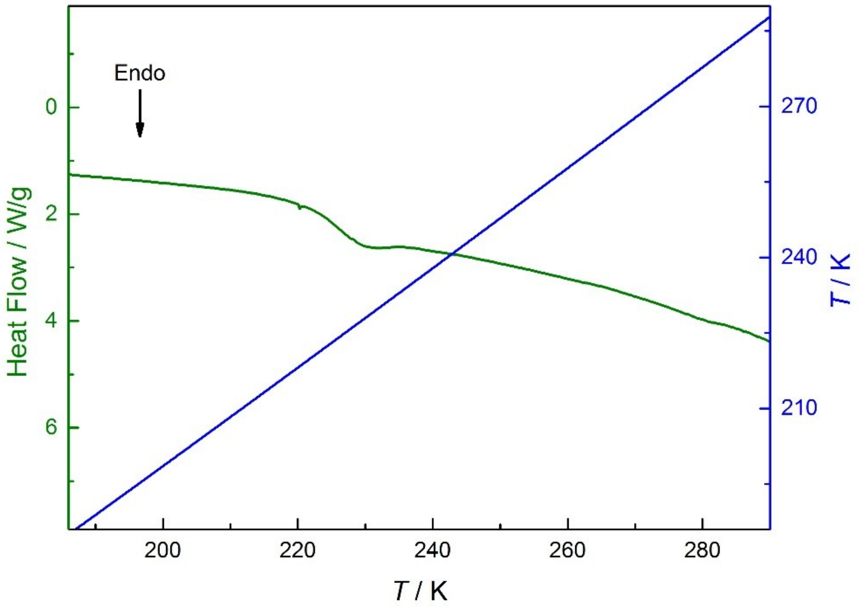


Figure S35. Thermogram for [DBUH][nPrCOO].

6. Computational Chemistry

Table S10 Electronic energies, E_{el}, at T = 0K, and enthalpies, at T = 298.15K ($H_{298.15}$), for the optimized geometries of the compounds considered in this work, at the B3LYP/6-311++G(d,p), M06-2X/6-311++G(d,p) and the MP2/cc-pVDZ, levels of theory.

Compound	E_{el} / Hartree·particle^{-1}			$H_{298.15}$ / Hartree·particle^{-1}		
	B3LYP	M06-2X	MP2	B3LYP	M06-2X	MP2
DBN	-383.57380	-383.39972	-382.27592	-383.37827	-383.20231	-382.07809
DBNH	-383.98440	-383.80645	-382.68517	-383.77385	-383.59418	-382.47232
DBU	-462.21207	-462.00293	-460.63336	-461.95627	-461.74479	-460.37463
DBUH	-462.62591	-462.41189	-461.04374	-462.35522	-462.13874	-460.77012
Acetic acid	-229.16483	-229.06486	-228.47198	-229.09778	-228.99683	-228.40406
Acetate	-228.60249	-228.50079	-227.88222	-228.55029	-228.44792	-227.82835
Propionic acid	-268.48961	-268.36908	-267.65379	-268.39281	-268.27105	-267.55562
Propanoate	-267.92770	-267.80575	-267.06732	-267.84589	-267.72178	-266.98420
Butyric acid	-307.81385	-307.67232	-306.83446	-307.68734	-307.54568	-306.70626
Butanoate	-307.25257	-307.10974	-306.24919	-307.14117	-306.99746	-306.13617
[DBNH][MeCOO]	-612.76062	-612.48972	-610.77499	-612.49615	-612.22269	-610.50695
[DBNH][EtCOO]	-652.08512	-651.79375	-649.95697	-651.79087	-651.49648	-649.65873
[DBNH][nPrCOO]	-691.40923	-691.09691	-689.13768	-691.08534	-690.76968	-688.80943
[DBUH][MeCOO]	-691.39471	-691.08971	-689.12892	-691.07034	-690.76190	-688.80021
[DBUH][EtCOO]	-730.71898	-730.39309	-728.31090	-730.36448	-730.03545	-727.95191
[DBUH][nPrCOO]	-770.04351	-769.69663	-767.49195	-769.66023	-769.30836	-767.10289

Table S11 Proton affinities for the optimized geometries of the bases considered in this work, at the B3LYP/6-311++G(d,p), M06-2X/6-311++G(d,p) and the MP2/cc-pVDZ, levels of theory.

Compound	Proton affinity / kJ·mol^{-1}		
	B3LYP	M06-2X	MP2
DBN ↔ DBNH	1039	1029	1035
DBU ↔ DBUH	1047	1034	1038