Supplementary Information

Evaluation of a Lab-scale Ionic Liquid Synthesis using Life Cycle Assessment

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Nuclear Magnetic (NMR) Resonance Spectra

1. 1-ethyl-3-methylimidazolium bromide, $[C_2C_1im]Br$

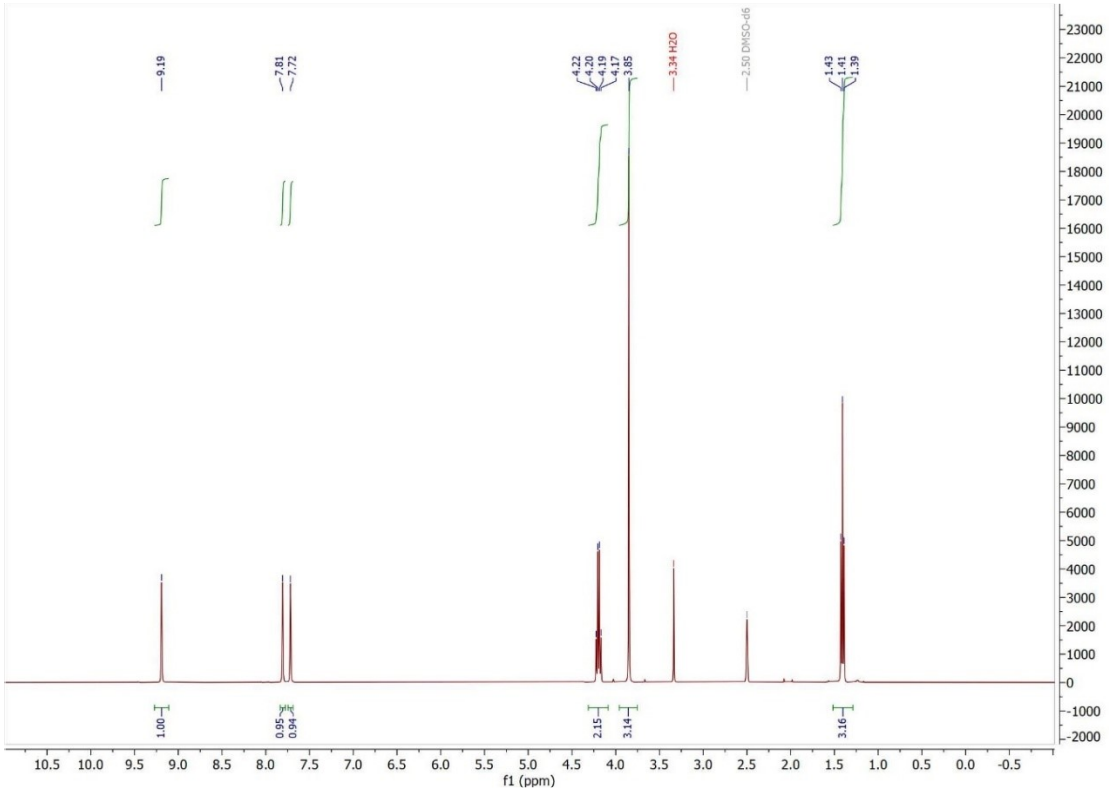


Figure S1: ^{1}H NMR spectrum of $[C_2C_1im]Br$

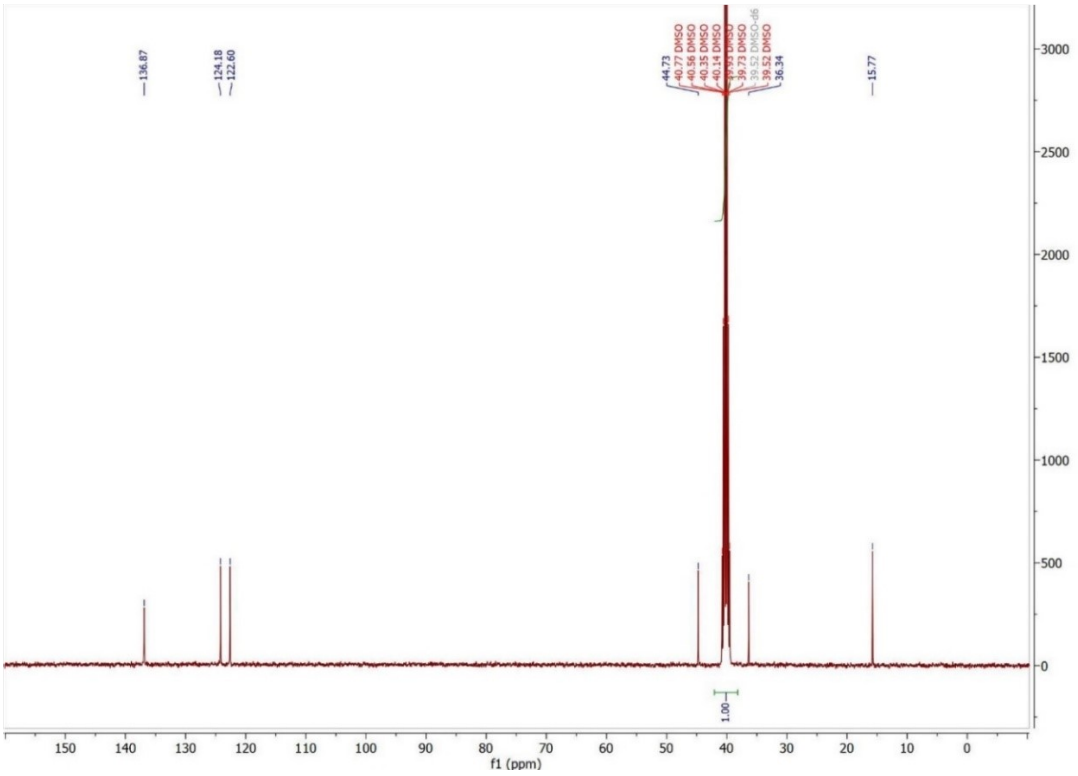


Figure S2: ^{13}C NMR spectrum of $[C_2C_1im]Br$

2. [C_2C_1im][OAc] synthesised by silver(I) acetate metathesis from a halide precursor

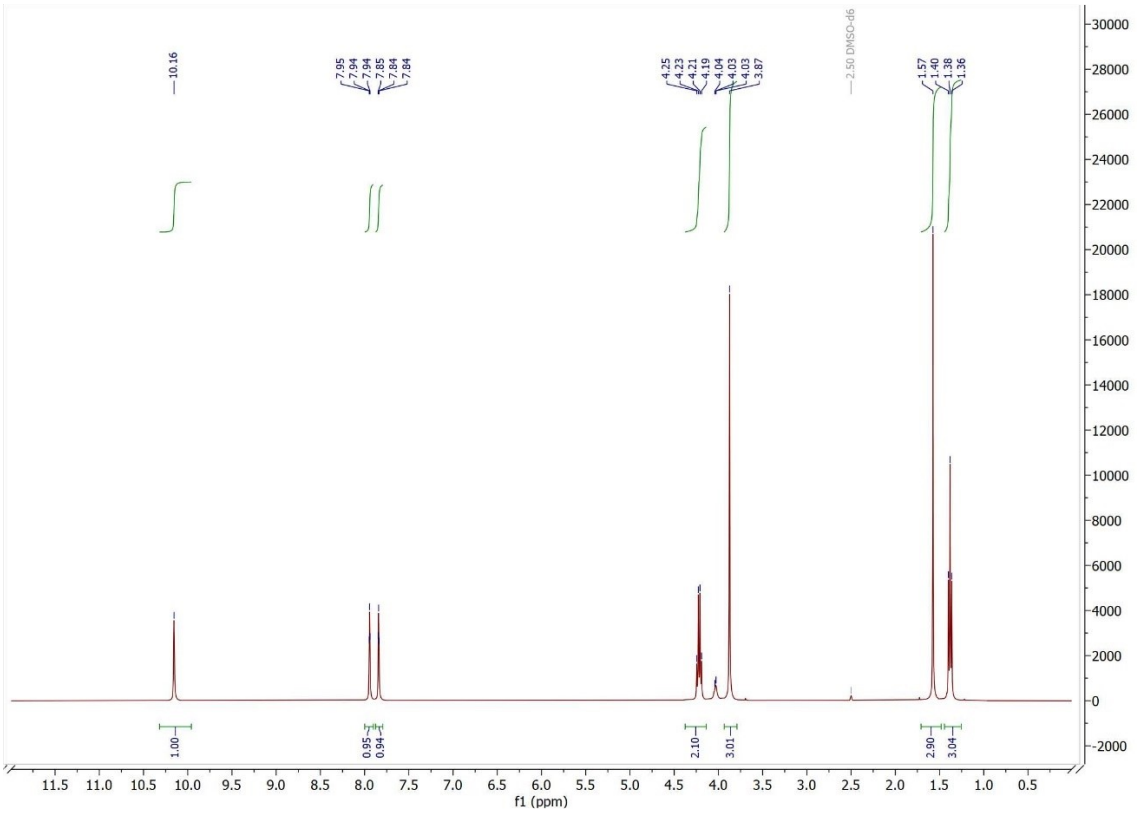


Figure S3: ^{1}H NMR spectrum of [C_2C_1im][OAc] synthesised by silver(I) acetate metathesis

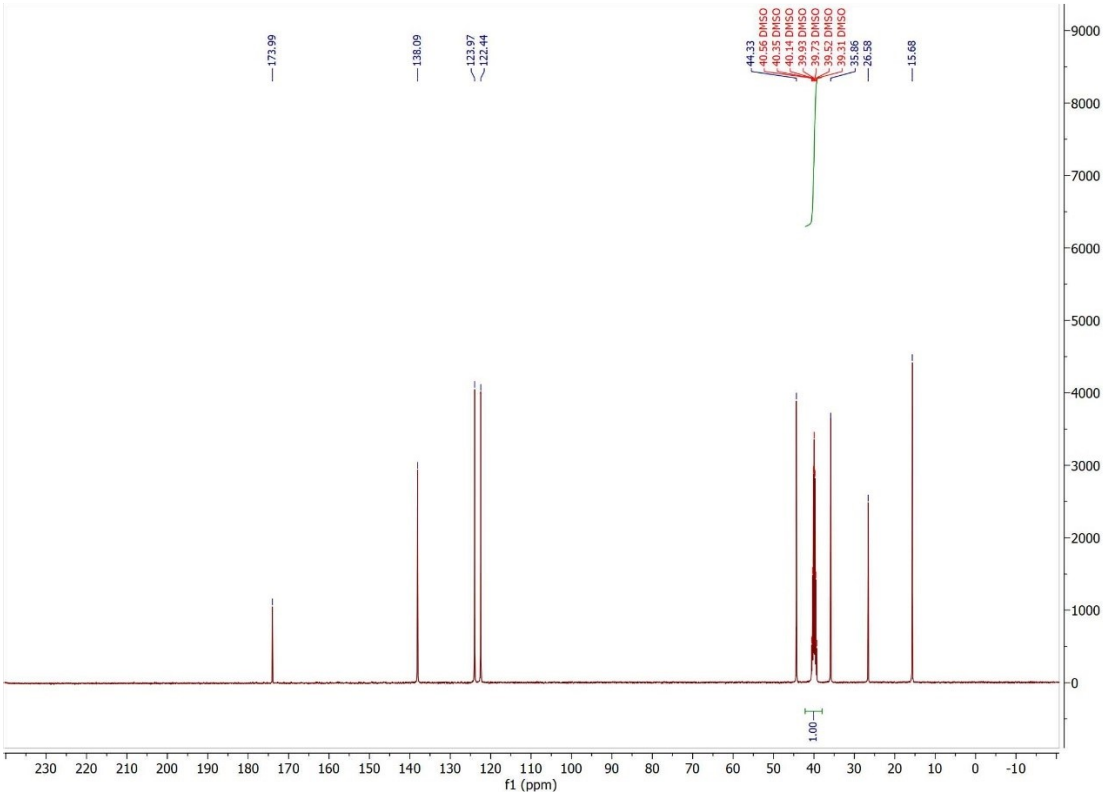


Figure S4: ^{13}C NMR spectrum of [C_2C_1im][OAc] synthesised by silver(I) acetate metathesis

3. [C_2C_1im][OAc] synthesised via anion-exchange method from a halide precursor

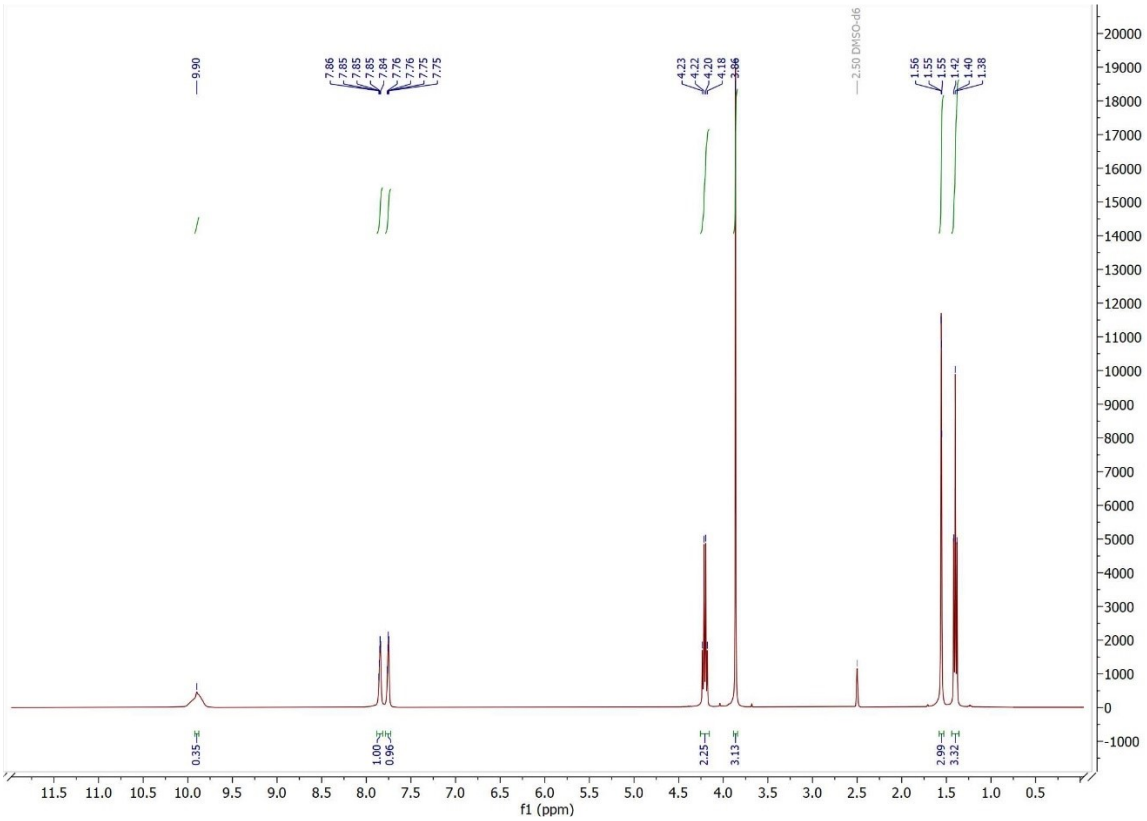


Figure S5: ^{1}H NMR spectrum of [C_2C_1im][OAc] synthesised by anion-exchange method

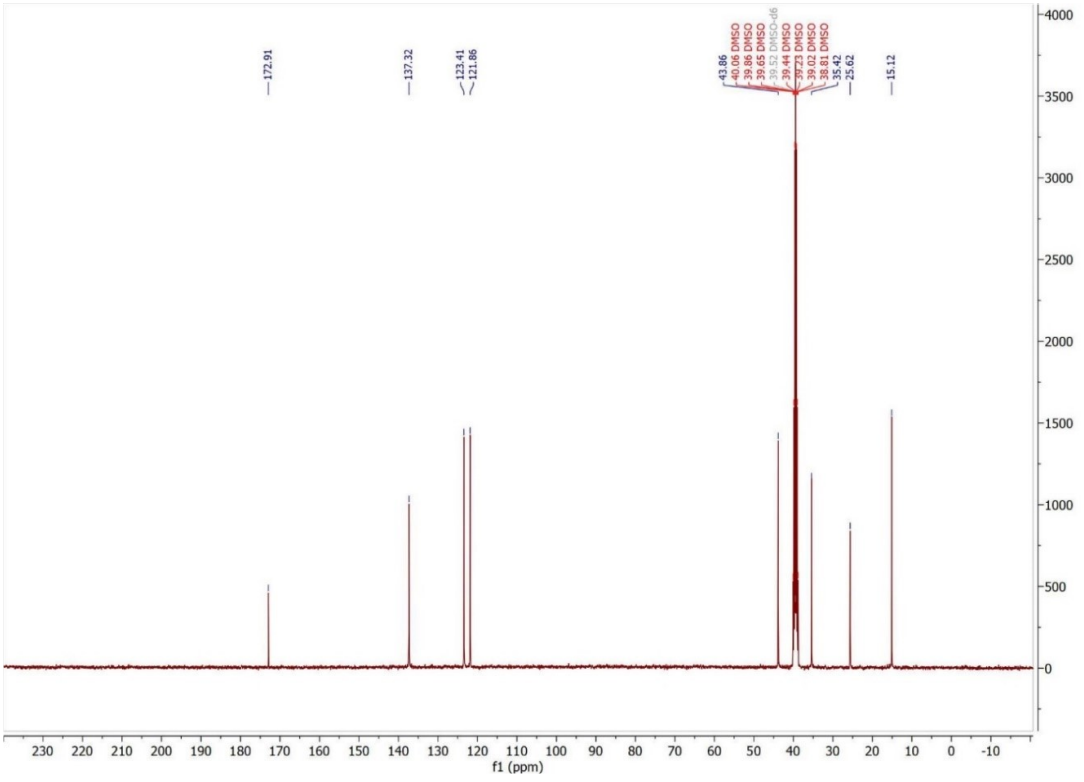


Figure S6: ^{13}C NMR spectrum of [C_2C_1im][OAc] synthesised by anion-exchange method

4. [C_2C_1im][OAc] synthesised via dimethyl carbonate route (pressure tube)

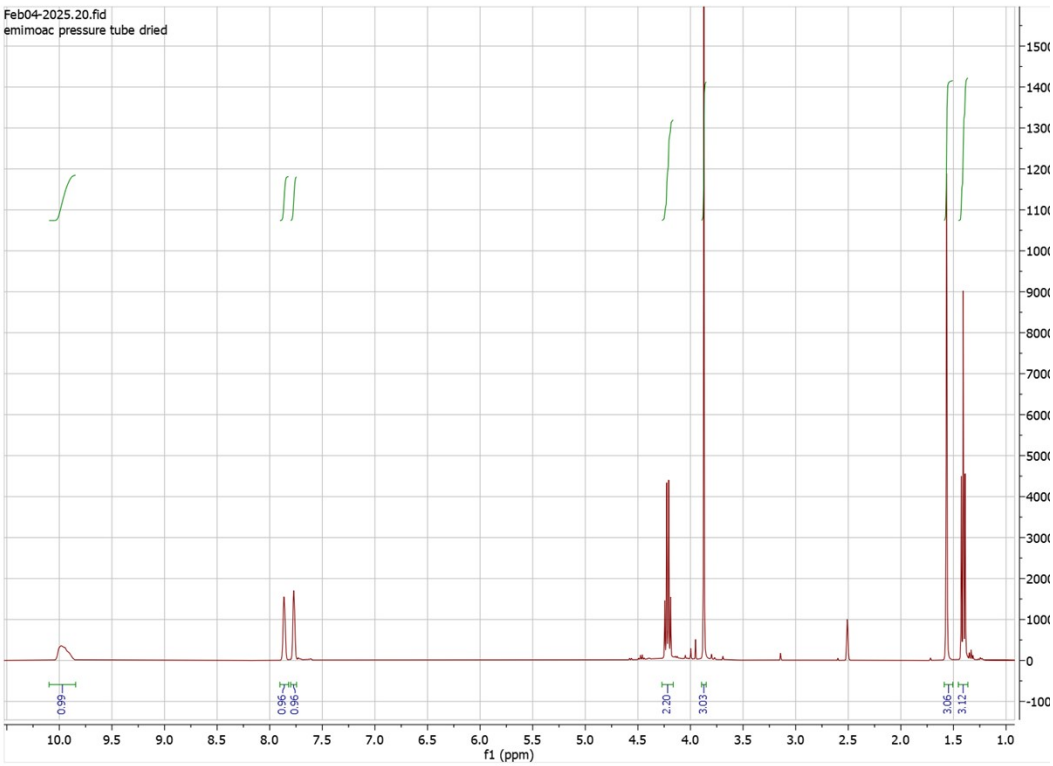


Figure S7: ^{1}H NMR spectrum of [C_2C_1im][OAc] synthesised by the dimethyl carbonate route (pressure tube)

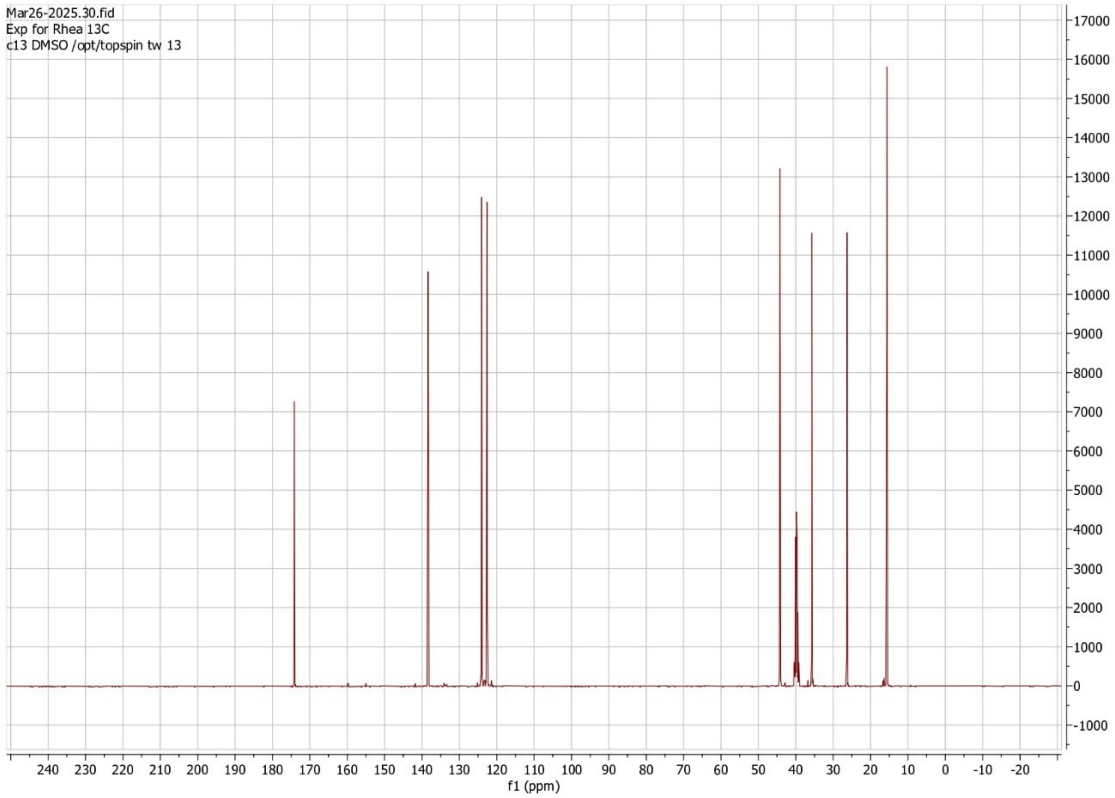


Figure S8: ^{13}C NMR spectrum of [C_2C_1im][OAc] synthesised by the dimethyl carbonate route (pressure tube)

5. [C_2C_1im][OAc] synthesised via dimethyl carbonate route in a high-pressure benchtop reactor

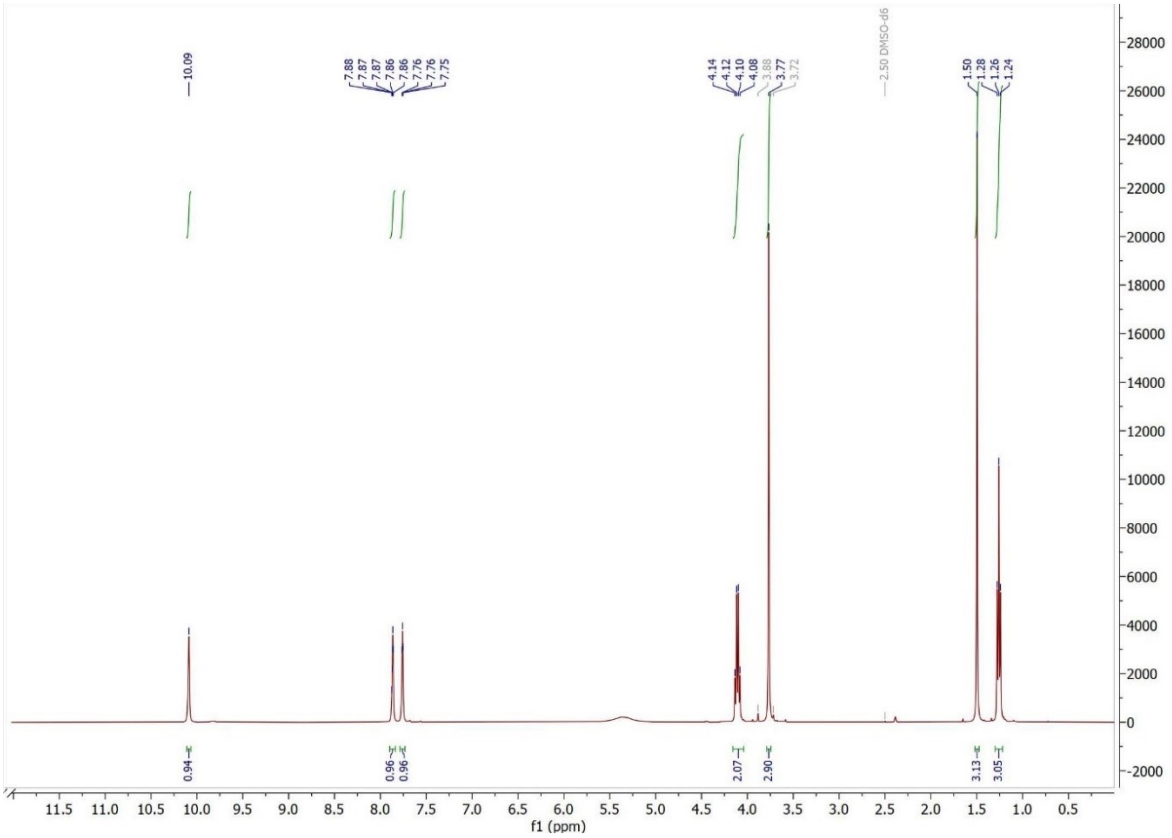


Figure S9: ^{1}H NMR spectrum of [C_2C_1im][OAc] synthesised by dimethyl carbonate route (high pressure benchtop reactor)

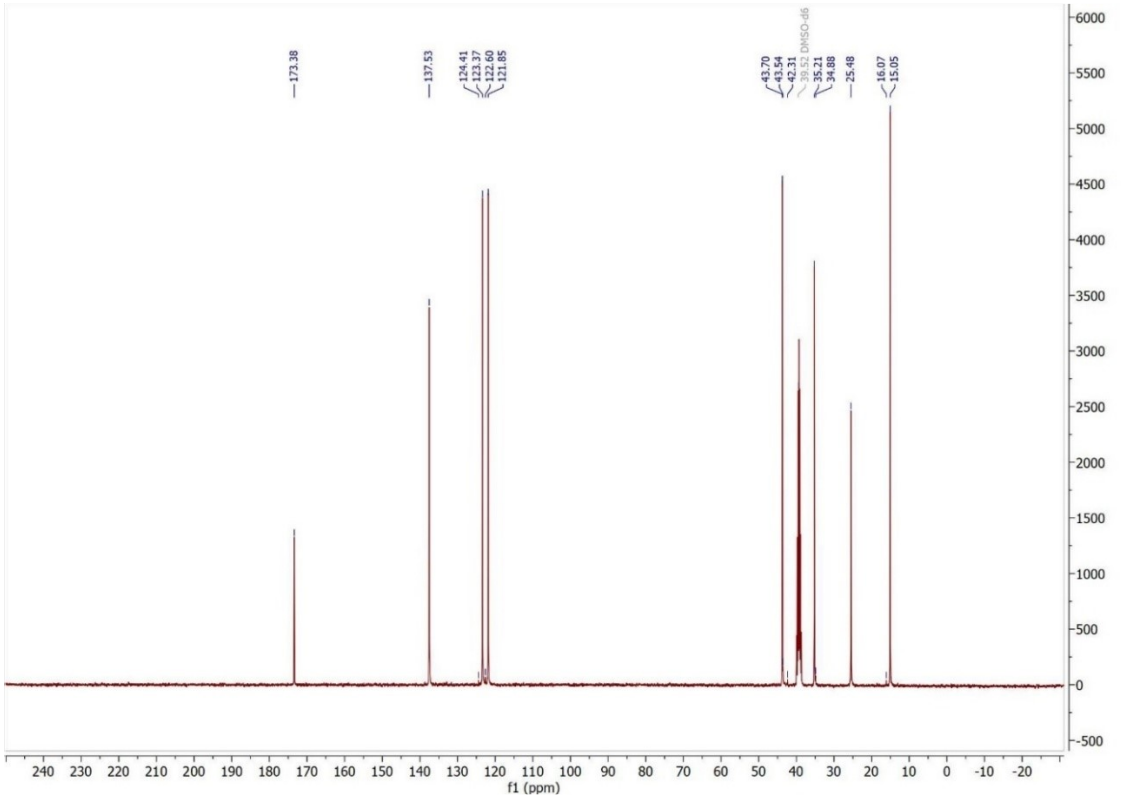


Figure S10: ^{13}C NMR spectrum of [C_2C_1im][OAc] synthesised by dimethyl carbonate route (high pressure benchtop reactor)

Life Cycle Inventory Data

Table S1. Material requirements for the Synthesis of 1 g of $[C_2C_1im]Br$

Material	Experimental (g)	Material input/output (g per g IL)	Waste Scenario
$[C_2C_1im]Br$	87.3	1.00	Product
1-Methylimidazole	41.2	0.472	Fully consumed
1-Bromoethane	147	1.68	Fully consumed
Ethyl acetate	1939	22.21	Hazardous waste for incineration (market, cut-off S)
Acetonitrile	156	1.79	Hazardous waste for incineration (market, cut-off S)
KOH	5.00	0.0573	Wastewater, average (market, Cut-off, S)
$NaHCO_3$	5.00	0.0573	Wastewater, average (market, Cut-off, S)
Sulphuric acid	45.0	0.516	Wastewater, average (market, Cut-off, S)
Dry ice	7000	80.24	Emissions to air: Carbon dioxide, indoor.
Liquid nitrogen	2017	23.10	Emissions to air: Nitrogen, indoor.
Ethanol	316	3.62	Hazardous waste for incineration (market, cut-off S)
Water	5330	61.1	Wastewater, average (market, Cut-off, S)

Table S2. Material requirements for the Synthesis of 1 g of $[C_2C_1im][OAc]$ via silver(I) acetate metathesis from halide precursor

Material	Experimental (g)	Material input/output (g per g IL)	Waste Scenario
$[C_2C_1im][OAc]$	3.61	1.00	Product
$[C_2C_1im]Br$	5.00	1.38	Fully consumed
Silver(I) acetate	4.82	1.34	Fully consumed
Silver(I) bromide	5.47	1.52	Wast
Dry ice	2500	692	Emissions to air: Carbon dioxide, indoor.
Ethanol	77.1	21.3	Hazardous waste for incineration (market, cut-off S)
Water	1900	526	Wastewater, average (market, Cut-off, S)

Table S3. Material requirements for the Synthesis of 1 g of [C_2C_1im][OAc] via anion exchange route from halide precursor

Material	Experimental (g)	Material input/output (g per g IL)	Waste Scenario
[C_2C_1im][OAc]	3.52	1.00	Product
[C_2C_1im]Br	5.00	1.42	Fully consumed
Acetic acid	1.53	0.434	Fully consumed
NaOH	10.0	2.84	Wastewater, average (market, Cut-off, S)
Dry Ice	5000	1420	Emissions to air: Carbon dioxide, indoor.
Ethanol	98.8	28.1	Hazardous waste for incineration (market, cut-off S)
Water	4800	1363	Wastewater, average (market, Cut-off, S)

Table S4. Material requirements for the Synthesis of 1 g of [C_2C_1im][OAc] via dimethyl carbonate route (pressure tube)

Material	Experimental (g)	Material input/output (g per g IL)	Waste Scenario
[C_2C_1im][OAc]	3.78	1.00	Product
1-Ethylimidazole	2.00	0.527	Fully consumed
Dimethyl carbonate	4.10	1.16	Fully consumed
Acetic acid	1.40	0.389	Fully consumed
Methanol	6.25	1.31	Hazardous waste for incineration (market, cut-off S)
Potassium hydroxide	1.00	0.265	Wastewater, average (market, Cut-off, S)
Charcoal	5.00	0.0350	Wastewater, average (market, Cut-off, S)
Dry Ice	2500	826	Emissions to air: Carbon dioxide, indoor.
Liquid Nitrogen	2500	533	Emissions to air: Atmospheric nitrogen, indoor.
Ethanol	30	6.27	Hazardous waste for incineration (market, cut-off S)
Water	350	92.6	Wastewater, average (market, Cut-off, S)

Table S5. Material requirements for the Synthesis of 1g of $[C_2C_1im][OAc]$ via dimethyl carbonate route (high-pressure benchtop reactor)

Material	Experimental (g)	Material input/output (g per g IL)	Waste Scenario
$[C_2C_1im][OAc]$	145	1.00	Product
1-ethylimidazole	85.0	0.586	Fully consumed
Dimethyl carbonate	198	1.37	Fully consumed
Acetic acid	53.6	0.369	Fully consumed
Methanol	261	1.81	Hazardous waste for incineration (market, cut-off S)
Potassium hydroxide	5.00	0.0345	Wastewater, average (market, Cut-off, S)
Charcoal	5.00	0.0345	Wastewater, average (market, Cut-off, S)
Dry Ice	1000	6.90	Emissions to air: Carbon dioxide, indoor.
Liquid Nitrogen	2017	13.93	Emissions to air: Atmospheric nitrogen, indoor.
Ethanol	873	6.02	Hazardous waste for incineration (market, cut-off S)
Water	2320	16.00	Wastewater, average (market, Cut-off, S)

Table S6. Experimental energy readings for the synthesis of $[C_2C_1im]Br$ and $[C_2C_1im][OAc]$ (kWh)

Process	87.25 g $[C_2C_1im]Br$	3.61 g $[C_2C_1im][OAc]$, silver(I) acetate metathesis	3.52 g $[C_2C_1im][OAc]$, anion-exchange method	3.78 g $[C_2C_1im][OAc]$, dimethyl carbonate route	145 g $[C_2C_1im][OAc]$, high-pressure benchtop reactor
Reagent purification	3.260	-	-	1.378	4.662
Synthesis (stirring and heating)	3.551	0.342	-	24.72	0.014
Pressure reactor	-	-	-	-	241.5
Drying, rotary evaporator	1.648	0.628	1.983	0.341	0.247
Drying, Schlenk line vacuum pump	14.46	0.522	0.507	0.191	-
Experimental total	22.92	1.492	2.492	26.63	246.4
Total (Wh/g IL)	**262.6**	**413.3**	**707.9**	**7046**	**1699**

Calculation of Green Metrics

Green metric calculations[1-3] were performed of the three routes (Schemes 2-3) to synthesise $[C_2C_1im][OAc]$. The calculations focused solely on the reaction itself, considering the yield of precursor materials to be 100 %. The molar weight of 1-ethyl-3-methylimidazolium cation was 170.21 g/mol.

Table S7: Green metrics used to evaluate process sustainability

Green Metric	Calculation	Definition
Percent Yield	$\frac{\text{Experimental yield}}{\text{Theoretical yield}} \times 100$	Percent ratio of actual yield to the theoretical yield.
Atom Economy (AE)	$\frac{\text{Molecular weight of desired product}}{\text{Molecular weight of reactants}} \times 100$	Atom percent of reactants in the final product.
Effective Mass Yield (EMY)	$\frac{\text{Mass of desired product}}{\text{Mass of non - benign reagents}} \times 100$	Percent mass of product to nonbenign inputs.
Sheldon E-factor (e-factor)	$\frac{\text{Total mass of waste}}{\text{Mass of desired product}}$	Mass of waste produced per unit mass of product.
Process Mass Intensity (PMI)	$\frac{\text{Total mass of input materials}}{\text{Mass of desired product}}$	Total mass of inputs per unit mass of product.

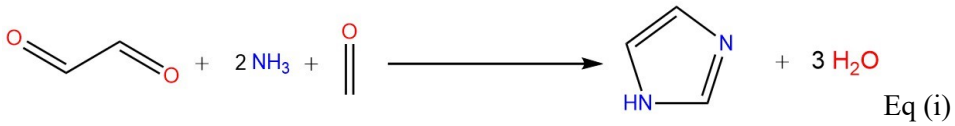
Table S8: Calculations of green metrics for the three routes to synthesis $[C_2C_1im][OAc]$

Route	Mass of Desired Product	Non-benign reagents	Mass of non-benign reagents	Effective Mass Yield (EMY)	Total mass of waste (g)	E-factor	Process Mass Intensity (PMI)
Silver(I) acetate route	3.61 g	$[C_2C_1im]Br$, CH_3COOAg	9.82 g	36.8 %	4866	1348	1349
Anion exchange Route	3.52 g	$[C_2C_1im]Br$, CH_3COOH	6.53 g	53.9 %	14320	4068	4069
DMC Route	3.78 g	Ethylimidazole, DMC, CH_3COOH	7.85 g	48.1 %	5528	1463	1464
DMC route using high-pressure benchtop reactor	145 g	Ethylimidazole, DMC, CH_3COOH	336 g	43.1 %	7002	48	49

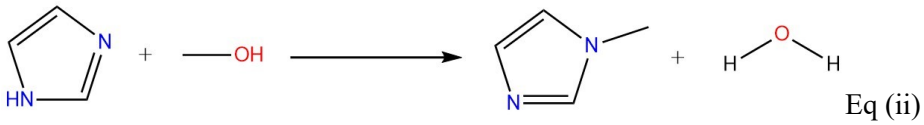
Estimation of Precursor Material Requirements

The section outlines the amounts of raw materials used to produce precursor materials. Life cycle data was not available for these materials. The materials were traced to products in the EcoInvent 3.9.1 database. The Debus-Radziszewski synthesis was used for imidazole production, followed by an alkylation reaction with methanol for 1-methylimidazolium production and ethanol for 1-ethylimidazolium production.[4]

1. 1-Methylimidazole



Eq (i)



Eq (ii)

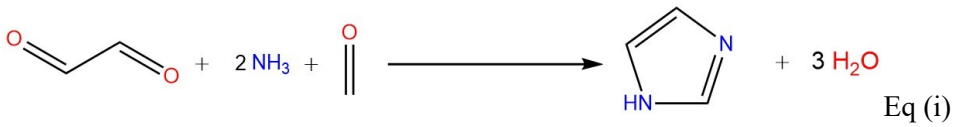
For the production of 1.0 kg of 1-methylimidazole (molecular weight = 82.10 g/mol)

Moles of 1-methylimidazole = $\frac{1000}{82.10} = 12.18\ moles$

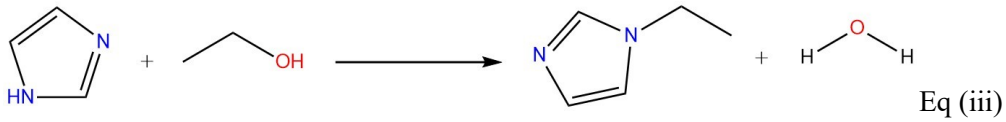
Table S9: Material requirements for 1-methylimidazole production.

Material Input	**Material Output**	**Molecular weight (g/mol)**	**Moles**	**Mass (g)**
Glyoxal		58.04	12.18	706.9
Ammonia		17.03	24.36	414.9
Formaldehyde		30.03	12.18	365.8
Methanol		32.04	12.18	390.3
	Water	18.01	48.72	877.5

2. 1-Ethylimidazole



Eq (i)



Eq (iii)

For the production of 1.0 kg of 1-ethylimidazole (molecular weight = 96.13 g/mol)

Moles of 1-ethylimidazole = $\frac{1000}{96.13} = 10.40\ moles$

Table S10: Material requirements for 1-ethylimidazole production.

Material Input	**Material Output**	**Molecular weight (g/mol)**	**Moles**	**Mass (g)**
Glyoxal		58.04	10.40	603.7
Ammonia		17.03	20.81	354.3
Formaldehyde		30.03	10.40	312.4
Ethanol		46.07	10.40	479.2
	Water	18.01	41.61	749.4

3. Silver(I) acetate

The silver(I) acetate process was created in SimaPro assuming that silver metal was converted to silver(I) nitrate[5], then silver(I) carbonate[6], and finally to silver(I) acetate[7].

$$Ag + 2HNO_3 + H_2O_2 \rightarrow 2AgNO3 + 2H2O \qquad \text{Eq (iv)}$$

$$AgNO_3 + Na_2CO_3 \rightarrow Ag_2CO_3 + 2NaNO_3 \qquad \text{Eq (v)}$$

$$Ag_2CO_3 + 2CH_3COOH \rightarrow H_2O + CO_2 + 2CH_3COOAg \qquad \text{Eq (vi)}$$

For the production of 1.0 kg of silver(I) acetate (molecular weight = 166.91 g/mol)

Moles of silver(I) acetate = $\frac{1000}{166.9} =$ 5.991 *moles*

Table S11: Material requirements for silver(I) acetate production

Material Input	**Material Output**	**Molecular weight (g/mol)**	**Moles**	**Mass (g)**
Silver metal		107.8	5.991	646.2
Nitric acid		63.01	5.991	377.5
Hydrogen peroxide		34.01	2.995	101.9
Sodium carbonate		106.0	2.995	317.5
Acetic Acid		60.05	5.991	359.8
	Water (i)	18.02	5.991	107.9
	Silver(I) nitrate	84.99	5.991	509.2
	Water (iii)	18.02	2.995	53.98
	Carbon Dioxide	44.01	2.995	131.8

Estimation of Precursor Energy Requirements

The energy requirements for the precursor materials were estimated using the following equations[8]

(Si) $Q - W = \Delta H + \Delta Ek + \Delta Ep$

(Sii) $\Delta H = \sum(n \times \hat{H})_{output} - \sum(n \times \hat{H})_{input}$

(Siii) $\hat{H} = \Delta\hat{H}f^{\circ} + \int_{T1}^{T2} Cp\, dT$

Where Q – heat consumption by reactor, W – work done, ΔEk – kinetic energy, ΔEp – potential energy, ΔH – enthalpy of reaction, n -moles of reactants, $\hat{H}$ - specific enthalpy of reactants, $\Delta\hat{H}f^{\circ}$ - heat of formation of reactants, Cp - calorific value of reactants, T1 – reference temperature, T2 – temperature of reactants.

If no work (W) is done, and the kinetic and potential energy are zero. Additionally, we assume that the temperature of the reactants is the same as the reference temperature. Thus, T1=T2=298.15 K, rendering the integral term zero.[9,10]

The resulting equations are as follows:

(Siv) $Q \approx \Delta H$

(Sv) $\Delta H = \sum(n \times \hat{H})_{output} - \sum(n \times \hat{H})_{input}$

(Svi) $\hat{H} \approx \Delta\hat{H}_f^{\circ}$

Thus, only the heat of formation of the chemical compounds are required to calculate the enthalpy of reaction. The theoretical heat requirements for endothermic reactions were multiplied by a factor of 4.2, assuming natural gas as the heat source. Similarly, the theoretical heat generated by exothermic reactions was converted to actual cooling electricity requirements using a factor of 3.2.[9-11]

Table S12: Heat of formation of chemical compounds used in the production of raw materials for IL synthesis

Chemical Compound	**Molecular Weight (g/mol)**	**Heat of Formation $\Delta_f H^{\circ}$ at 25°C (kJ/mol)**	**Source**
1-ethylimidazole	96.13	44.80	Da Silva et al.[12]
1-methylimidazole	82.10	70.70	Verevkin et al.[13]
Acetic acid	60.05	-484.0	NIST[14]
Ammonia	17.03	-45.90	NIST
Carbon dioxide	44.01	-393.5	NIST
Ethanol	46.07	-276.2	NIST
Formaldehyde	30.03	-112.3	NIST
Glyoxal	58.04	-212.0	NIST

Hydrogen peroxide	34.01	-187.3	Argonne National Laboratory[15]
Imidazole	68.08	54.30	NIST
Methanol	32.04	-238.9	NIST
Nitric acid	63.01	-174.1	Argonne National Laboratory
Silver	107.9	0.0	Argonne National Laboratory
Silver(I) acetate	166.9	-399.0	CRC Handbook[16]
Silver(I) carbonate	275.7	-505.8	CRC Handbook
Silver(I) nitrate	169.9	-124.4	Argonne National Laboratory
Sodium carbonate	105.9	-1130	CRC Handbook
Sodium nitrate	84.99	-467.0	NIST
Water	18.02	-285.8	NIST

1. **1-Methylimidazole**

The energy inventory for synthesising 1.0 kg of 1-methylimidazole has been estimated below based on the mole calculations done in Table S4 and the heat of formation values from Table S7.

$$12.18\ C_3H_4N_2 + 12.18\ CH_3OH \rightarrow 12.18\ C_4H_6N_2 + 12.18\ H_2O$$

The specific enthalpies were calculated as:

$$\hat{H}(CH_3OH) = \Delta\hat{H}f^\circ\ CH_3OH(25\ ^\circ C) + \int_{25\ ^\circ C}^{25\ ^\circ C} Cp\ dT = -238.9\ kJ/mol + 0\ kJ/mol = -238.9\ kJ/mol$$

$$\hat{H}(C_3H_4N_2) = \Delta\hat{H}f^\circ\ C_3H_4N_2(25\ ^\circ C) + \int_{25\ ^\circ C}^{25\ ^\circ C} Cp\ dT = 54.3\ kJ/mol + 0\ kJ/mol = 54.3\ kJ/mol$$

$$\hat{H}(C_4H_6N_2) = \Delta\hat{H}f^\circ\ C_4H_6N_2(25\ ^\circ C) + \int_{25\ ^\circ C}^{25\ ^\circ C} Cp\ dT = 70.7\ kJ/mol + 0\ kJ/mol = 70.7\ kJ/mol$$

$$\hat{H}(H_2O) = \Delta\hat{H}f^\circ\ H_2O\ (25\ ^\circ C) + \int_{25\ ^\circ C}^{25\ ^\circ C} Cp\ dT = -285.8\ kJ/mol + 0\ kJ/mol = -285.8\ kJ/mol$$

The total enthalpy is then calculated

$$\Delta H = \sum(n \times \hat{H})_{output} - \sum(n \times \hat{H})_{input}$$

$$= [(12.18 \times 70.7) + (12.18 \times -285.8)] - [(12.18 \times 54.3) + (12.18 \times -238.9)]\ kJ$$

$$= -371.49\ kJ$$

After applying correction factor 3.2. (electricity needed for cooling) = 1.118 MJ

Similarly, the energy required to synthesise 829.18 g of Imidazole (12.18 moles) via Debus Radziszewski reaction is estimated below.

$$12.18\ C_2H_2O_2 + 24.36\ NH_3 + 12.18\ CH_2O \rightarrow 12.18\ C_3H_4N_2 + 36.54\ H_2O$$

The specific enthalpies were calculated as:

$$\hat{H}(C_2H_2O_2) = \Delta\hat{H}f°C_2H_2O_2(25\ °C) + \int_{25\ °C}^{25\ °C} Cp\ dT = -212.0\ kJ/mol + 0\ kJ/mol = -212.0\ kJ/mol$$

$$\hat{H}(NH_3) = \Delta\hat{H}f\ °\ NH_3(25\ °C) + \int_{25\ °C}^{25\ °C} Cp\ dT = -45.9\ kJ/mol + 0\ kJ/mol = -45.9\ kJ/mol$$

$$\hat{H}(CH_2O) = \Delta\hat{H}f\ °\ CH_2O(25\ °C) + \int_{25\ °C}^{25\ °C} Cp\ dT = -112.3\ kJ/mol + 0\ kJ/mol = -112.3\ kJ/mol$$

$$\hat{H}(C_3H_4N_2) = \Delta\hat{H}f\ °\ C_3H_4N_2(25\ °C) + \int_{25\ °C}^{25\ °C} Cp\ dT = 54.3\ kJ/mol + 0\ kJ/mol = 54.3\ kJ/mol$$

$$\hat{H}(H_2O) = \Delta\hat{H}f\ °\ H_2O\ (25\ °C) + \int_{25\ °C}^{25\ °C} Cp\ dT = -285.8\ kJ/mol + 0\ kJ/mol = -285.8\ kJ/mol$$

The total enthalpy is then calculated

$$\Delta H = \sum(n \times \hat{H})_{output} - \sum(n \times \hat{H})_{input}$$

$$= [(12.18 \times 53.3) + (36.54 \times -285.8)] - [(12.18 \times -212.0) + + (24.36 \times 45.9) + (12.18 \times -112.3)]\ kJ$$

$$= -\ 4714.78\ kJ$$

After applying correction factor 3.2. (electricity needed for cooling) = 15.087 MJ

Total energy needed to synthesise 1 kg of 1-methylimidazole = 16.28 MJ

The energy required to produce 1-ethylimidazole and silver(I) acetate was calculated using similar assumptions, from mole calculations from tables S5-S6, using the heat of formation values from Table S7.

2. 1-Ethylimidazole

Table S13: Specific enthalpies of input and output materials to synthesise 1.0 kg 1-ethylimidazole

Input	**Output**	**Moles**	**n x $\hat{H}$ (kJ)**
Imidazole		10.40	564.7
Ethanol		10.40	-2872
	1-ethylimidazole	10.40	465.9
	Water	10.40	-2972

Enthalpy of reaction = -198.95 kJ

After applying correction factor 3.2. (electricity needed for cooling) = 0.64 MJ

Table S14: Specific enthalpies of input and output materials to synthesise 708 g of Imidazole**.**

Input	**Output**	**Moles**	**n x $\hat{H}$ (kJ)**

Glyoxal		10.40	-2205
Ammonia		20.80	-955.1
Formaldehyde		10.40	-1167
	Imidazole	10.40	564.7
	Water	31.20	-8918

Enthalpy of reaction = -4025.29 kJ

After applying correction factor 3.2. (electricity needed for cooling) = 12.88 MJ

Total energy needed to synthesise 1 kg of 1-ethylimidazole = 13.52 MJ

3. Silver(I) acetate

Table S15: Specific enthalpies of input and output materials to synthesise 1.0 kg silver(I) acetate.

Input	**Output**	**Moles**	**n x $\hat{H}$ (kJ)**
Silver(I) carbonate		2.995	-1517
Acetic acid		5.991	-2904
	Silver(I) acetate	2.995	-2394
	Carbon dioxide	2.995	-1180
	Water	2.995	-857.5

Enthalpy of reaction = -10.95 kJ

After applying correction factor 3.2. (electricity needed for cooling) = 0.03 MJ

Table S16: Specific enthalpies of input and output materials to synthesise 827.25 g of silver(I) carbonate.

Input	**Output**	**Moles**	**n x $\hat{H}$ (kJ)**
Silver(I) nitrate		5.991	-746.34
Sodium carbonate		2.995	-3392.1
	Sodium(I) nitrate	5.991	-2802
	Silver(I) carbonate	2.995	-1517.4

Enthalpy of reaction = -180.9 kJ

After applying correction factor 3.2. (electricity needed for cooling) = 0.58 MJ

Table S17: Specific enthalpies of input and output materials to synthesise 1019.2 g of silver(I) nitrate.

Input	Output	Moles	n x $\hat{H}$ (kJ)
Silver		6	0
Nitric acid		6	-1044.6
Hydrogen peroxide		3	-562.023
	Silver(I) nitrate	6	-746.34
	Water	6	-1714.98

Enthalpy of reaction = - 854.7 kJ

After applying correction factor 3.2. (electricity needed for cooling) = 2.74 MJ

Total energy needed to synthesise 1 kg of silver(I) acetate = 3.35 MJ

Water and Ethanol Consumption per Reaction

Table S18: Washing reagent usage of synthesis of 1-ethyl-3-methylimidazolium bromide, $[C_2C_1im]Br$.

Glassware	Number	Water used for washing each (mL)	Water (mL)	Ethanol used for washing each (mL)	EtOH total (mL)
Round Bottom Flask – 100 mL	2	150	300	7.5	15
Round Bottom Flask – 250 mL	4	250	1000	10	40
Water condenser	2	300	600	30	60
Measuring cylinder	6	30	180	10	60
Beaker – 500 mL	2	200	400	20	40
Connector for rotary evaporator	1	500	500	5	5
Separating flask	2	400	800	20	40
Glass funnel	7	200	1400	20	140
Sum for 87.25 g (mL)			5180		400
Mass (g per g of IL)			54.21		3.62

Table S19: Washing reagent usage of synthesis of 1-ethyl-3-methylimidazolium acetate, $[C_2C_1im][OAc]$, via silver(I) acetate metathesis from halide precursor.

Glassware	Number	Water used for washing each (mL)	Water (mL)	Ethanol used for washing each (mL)	EtOH total (mL)
Round Bottom Flask – 100 mL	3	150	450	7.5	22.5
Flask	1	250	250	10	10
Connector for rotavap	1	500	500	5	5
Glass funnel	2	200	400	20	40
Sum for 3.61 g			1600		77.5
Mass (g per g of IL)			4404		16.96

Table S20: Washing reagent usage of synthesis of 1-ethyl-3-methylimidazolium acetate, $[C_2C_1im][OAc]$, via anion exchange route from halide precursor.

Glassware	Number	Water used for washing each (mL)	Water (mL)	Ethanol used for washing each (mL)	EtOH total (mL)
Dropping funnel	3	400	1200	20	60
Beaker - 500 mL	1	200	200	20	20
Glass funnel	2	200	400	20	40
Connector for rotavap	1	500	500	5	5
Round Bottom Flask - 500 mL	1	500	500	15	15
Sum for 3.52 g			2800		125
Mass (g per g of IL)			795.5		28.05

Table S21: Washing reagent usage of synthesis of 1-ethyl-3-methylimidazolium acetate, [C_2C_1im][OAc], via dimethyl carbonate route in pressure tube.

Glassware	**Number**	**Water used for washing each (mL)**	**Water (mL)**	**Ethanol used for washing each (mL)**	**EtOH total (mL)**
Pressure Tube	1	100	100	20	20
Round Bottomed Flask - 50 mL	1	150	150	10	10
Sum for 3.78 g			350		30
Mass (g per g of IL)			92.6		6.27

Table S22: Washing reagent usage of synthesis 1-ethyl-3-methylimidazolium acetate, [C_2C_1im][OAc], via dimethyl carbonate route in high-pressure reactor.

Glassware	**Number**	**Water used for washing each (mL)**	**Water (mL)**	**Ethanol used for washing each (mL)**	**EtOH total (mL)**
Metal reactor flask	1	500	500	1000	1000
Measuring cylinder	4	30	120	10	40
Round Bottomed Flask - 250 mL	2	250	500	10	20
Round Bottomed Flask - 500 mL	1	500	500	15	15
Water condenser	1	300	300	30	30
Glass funnel	2	200	400	20	40
Sum for 145 g			2320		1105
Mass (g per g of IL)			16.00		6.02

LCI of Energy Requirements and Instrumentation Details

The energy readings for each instrument were measured manually using Energenie-ENER007 Energy Power Saving Meters. The details of the instruments measured is as follows

1. Magnetic stirrer - Heidolph magnetic stirrer, 825 W
2. Vacuum pump attached to Schlenk line - Oerlikon Leybold Vacuum Pump, 370 W
3. Water condenser with recirculating pump - Oerlikon Leybold Vacuum Pump, 370 W
4. High-pressure benchtop reactor - Parr 4520 Benchtop Reactor, 3750 W
5. High pressure reactor controller - Parr 4848 Reactor Controller, 1800 W
6. Rotary evaporator dry ice type - Heidolph Hei-VAP Rotary Evaporator, 1400W. Connected to Ilmvac Membrane Pump, 60W
7. Rotary evaporator water/ethylene glycol recirculatory type - Buchi Rotavapor® R-100, 30W connected to Heating Bath B-100, 1700 W

Table S23: Energy reading for synthesis of 1-ethyl-3-methylimidazolium bromide, $[C_2C_1im]Br$, per device.

Laboratory process	**Time (h)**	**Energy (kWh)**
Purification of 1-methylimidazole		
Stirring overnight (Room Temp, 400 rpm)	18	0.0855
Distillation – 70 degrees C		
Vacuum pump	1	0.435
Stirring on hot plate	1	0.137
Water condenser	1.5	0.581
Purification of bromoethane		
Stirring Overnight	18	0.0855
Distillation – 55 degrees C		
Stirring on hot plate	2	1.14
Water condenser	2.5	0.797
Synthesis and solvent removal		
Stirring for 5 days on hot plate	120	0.570
Heating and stirring for two days on hot plate	48	2.98
Drying on rotary evaporator	6	1.65
Vacuum drying on Schlenk Line	21	14.5
Sum for 87.25		22.9
Wh per g of IL		**263**

Table S24: Energy reading for synthesis of 1-ethyl-3-methylimidazolium acetate, $[C_2C_1im][OAc]$, via silver(I) acetate metathesis from halide precursor per device.

Laboratory process	**Time (h)**	**Energy (kWh)**
Stirring on hot plate	72	0.342
Drying on rotary evaporator	2	0.628
Vacuum drying on Schlenk Line	21	7.23
Sum for 3.61 g		1.49
Wh per g of IL		**413**

Table S25: Energy reading for synthesis of 1-ethyl-3-methylimidazolium acetate, $[C_2C_1im][OAc]$, via anion exchange route from halide precursor per device.

Laboratory process	**Time (h)**	**Energy (kWh)**
Drying on rotary evaporator	2	1.98
Vacuum drying on Schlenk Line	21	0.507
Sum for 3.61 g		2.49
Wh per g of IL		**707**

Table S26: Energy reading for synthesis of 1-ethyl-3-methylimidazolium acetate, $[C_2C_1im][OAc]$, via dimethyl carbonate route in pressure tube.

Laboratory process	**Time (h)**	**Energy (kWh)**
Purification of 1-ethylimidazole		
Stirring Overnight (Room Temp, 400 rpm)	18	0.0875
Distillation - 100 degrees C		
Vacuum pump	1	0.337
Stirring on hot plate	0.5	0.378
Water condenser	1	0.575
Synthesis and solvent removal		
Stirring on hot plate (Synthesis at 120 degrees C)	115	24.7
Drying on rotary evaporator	0.5	0.341
Vacuum drying on Schlenk Line	0.5	0.191
Sum for 3.78 g		26.6
Wh per g of IL		**7046**

Table S27: Energy reading for synthesis of 1-ethyl-3-methylimidazolium acetate, $[C_2C_1im][OAc]$, via dimethyl carbonate route in high-pressure reactor.

Laboratory process	**Time (h)**	**Energy (kWh)**
Purification of 1-ethylimidazole		
Stirring Overnight (Room Temp, 400 rpm)	18	0.0875
Distillation - 100 degrees C		
Vacuum pump	2.5	0.96
Stirring on hot plate	2.5	1.89
Water condenser	3	1.72
Synthesis		
Parr Reactor Benchtop (3450W)	46	158
Parr Reactor Benchtop (1800W)	46	82.8
Stirring on hot plate	3	0.014
Drying on rotary evaporator	<1	0.147
Sum for 145 g		246
Wh per g of IL		**1698**

LCA Results for Midpoint Categories

Key for the figures in this section:

A - Global warming, Human health. B - Global warming, Terrestrial ecosystems, C - Global warming, Freshwater ecosystems. D - Stratospheric ozone depletion, E - Ionizing radiation, F - Ozone formation, Human health, G - Fine particulate matter formation, H - Ozone formation, Terrestrial ecosystems, I - Terrestrial acidification, J - Freshwater eutrophication, K - Marine eutrophication, L - Terrestrial ecotoxicity, M - Freshwater ecotoxicity, N - Marine ecotoxicity, O - Human carcinogenic toxicity, P - Human non-carcinogenic toxicity, Q - Land use, R - Mineral resource scarcity, S - Fossil resource scarcity, T - Water consumption, Human health, U - Water consumption, Terrestrial ecosystem, V - Water consumption, Aquatic ecosystems.

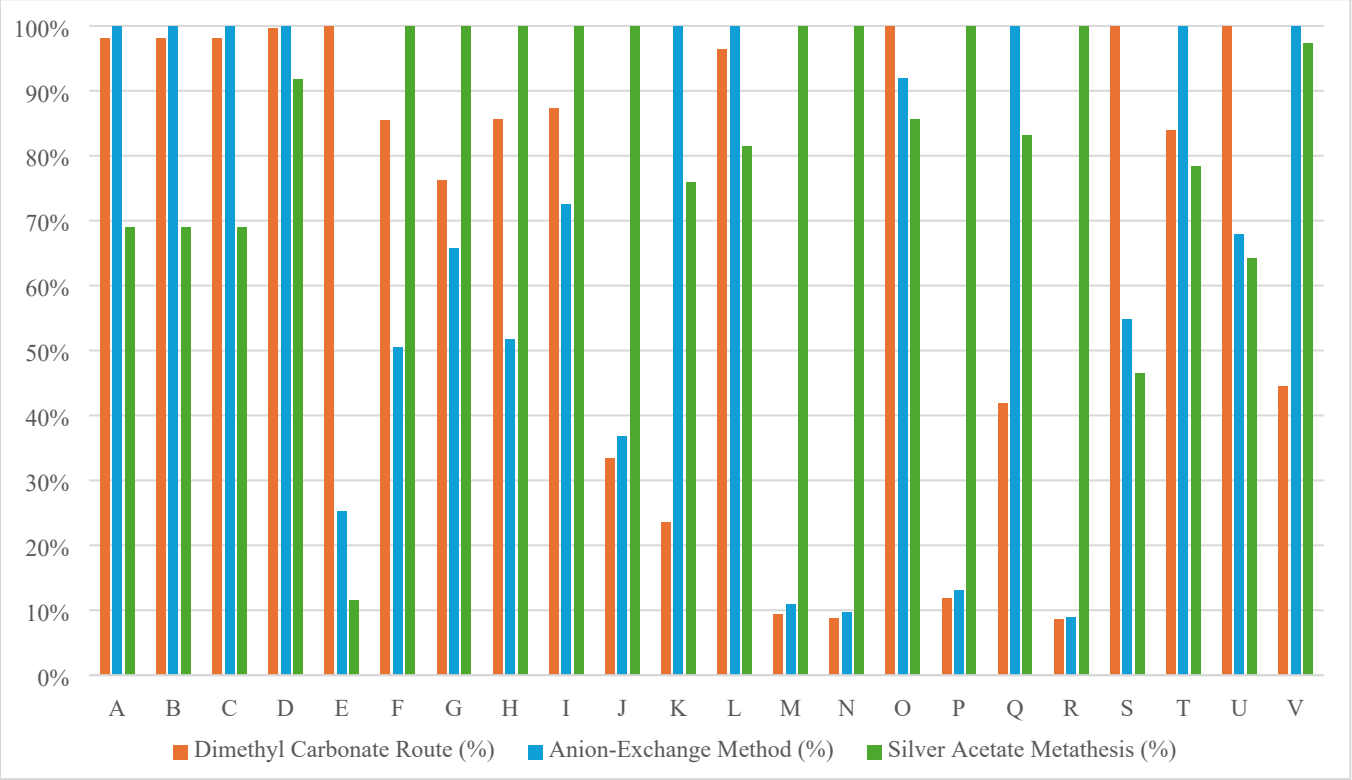


Figure S11: Impact in midpoint categories for the three [C_2C_1im][OAc] synthesis routes evaluated in this study, expressed as a percentage of the highest impact in each category.

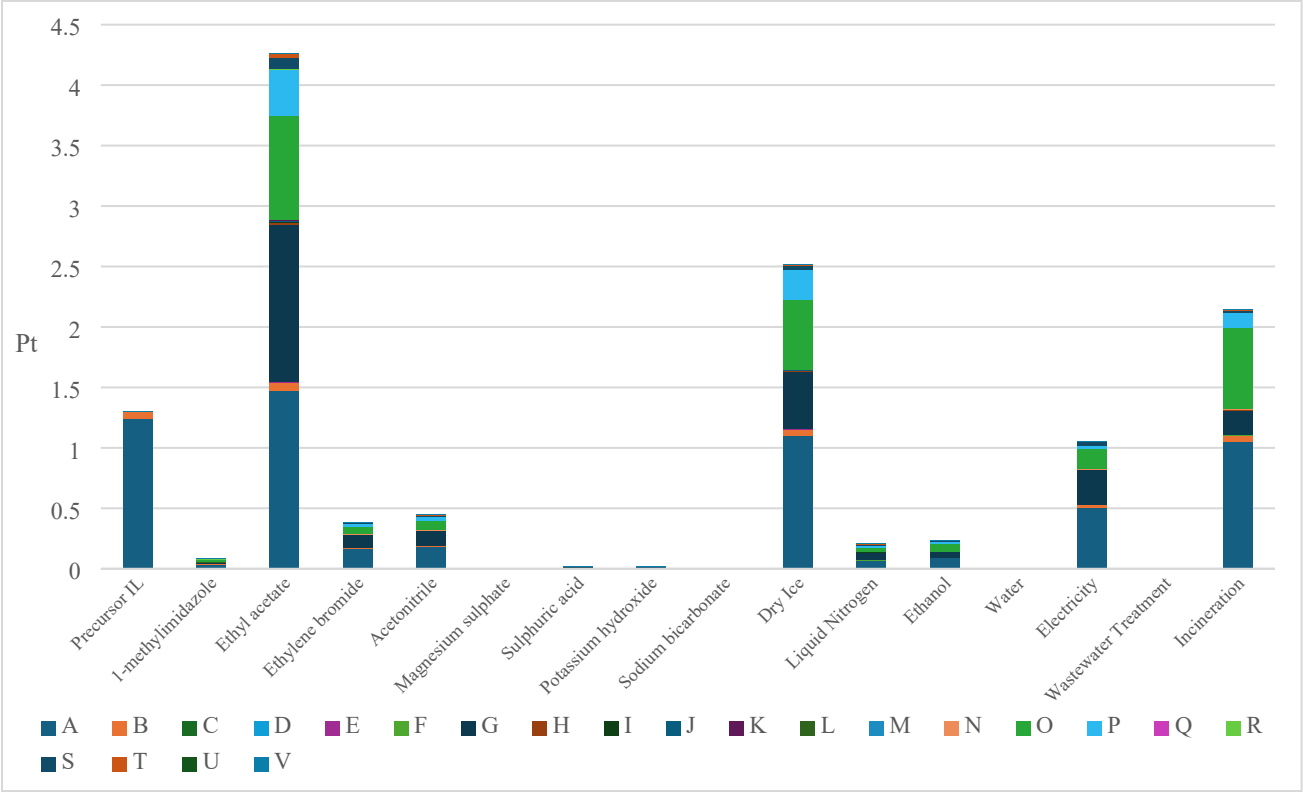


Figure S12: Single score contribution of each material flow for precursor ionic liquid synthesis showing midpoint categories, expressed as Pt.

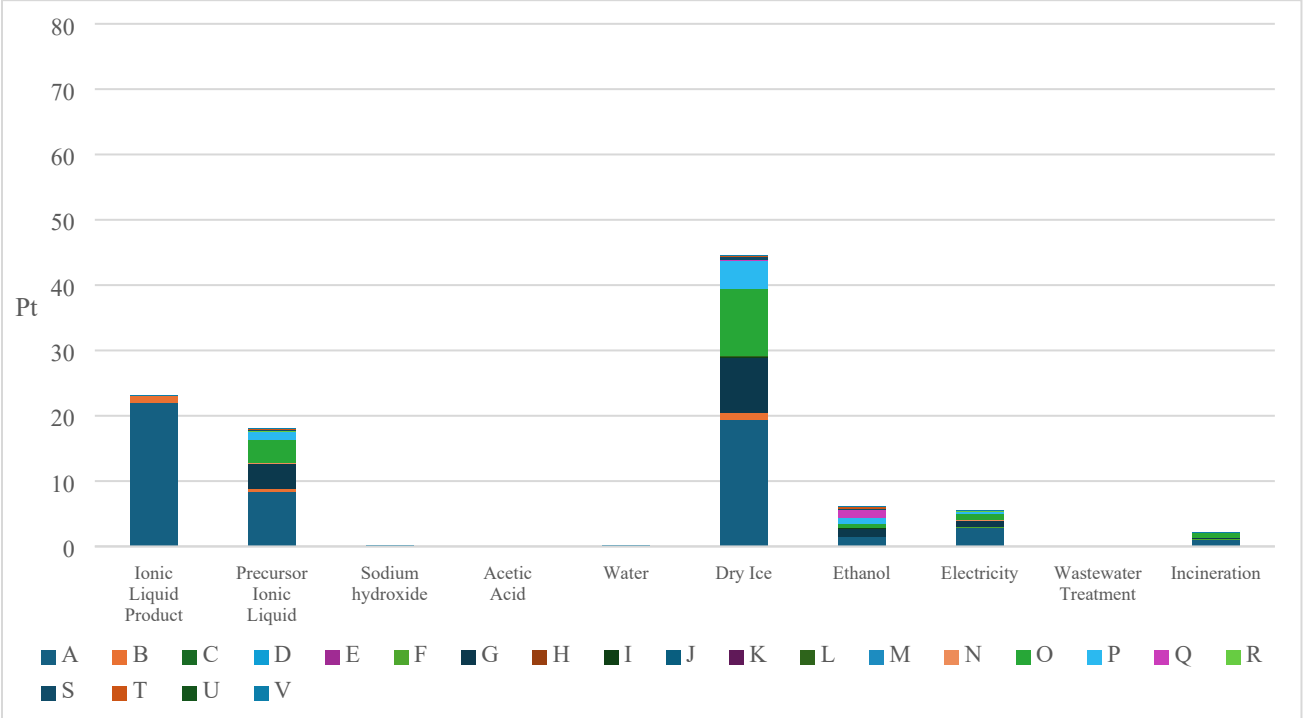


Figure S13: Single score contribution of each material flow for $[C_2C_1im][OAc]$ synthesis via the anion-exchange route showing midpoint categories, expressed as Pt.

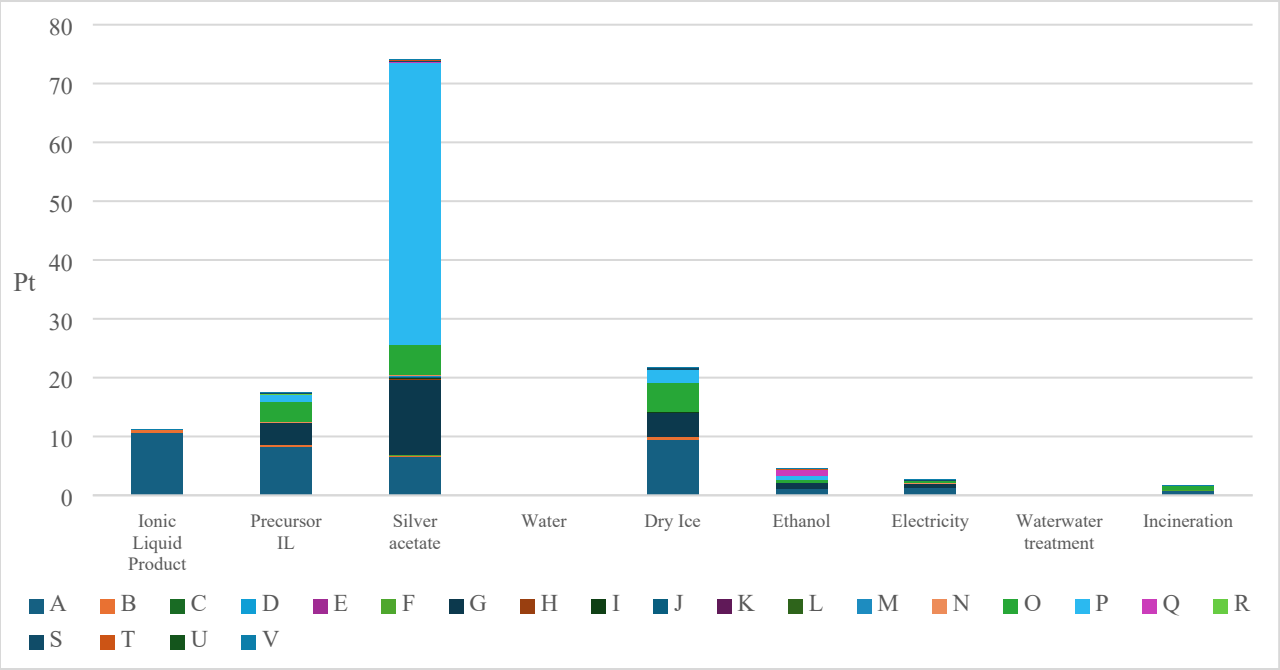


Figure S14: Single score contribution of each material flow for for $[C_2C_1im][OAc]$ synthesis via the silver acetate route showing midpoint categories, expressed as Pt.

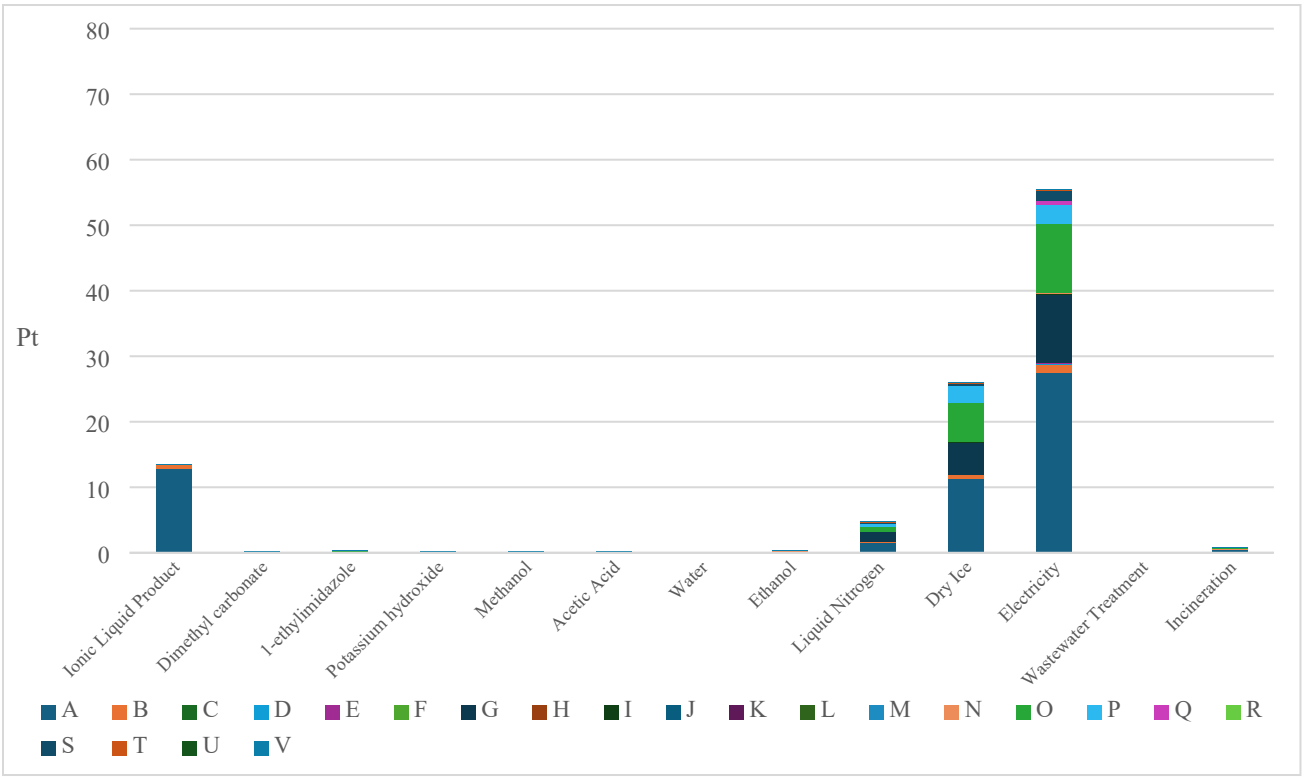


Figure S15: Single score contribution of each material flow for for $[C_2C_1im][OAc]$ synthesis via the dimethyl route showing midpoint categories, expressed as Pt.

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