Electronic Supplementary Information

Electrochemical process to prepare and to recycle biobased ionic liquids

Antoine Fournier, Jihane Bousfiha, Guillaume de Robillard,

Charles H. Devillers* and Jacques Andrieu*

Institut de Chimie Moléculaire de l'Université de Bourgogne, UMR CNRS 6302, Université de Bourgogne Franche-Comté, 9 av. Alain Savary, 21078 DIJON, France.

E-mail: jacques.andrieu@u-bourgogne.fr and charles.devillers@u-bourgogne.fr

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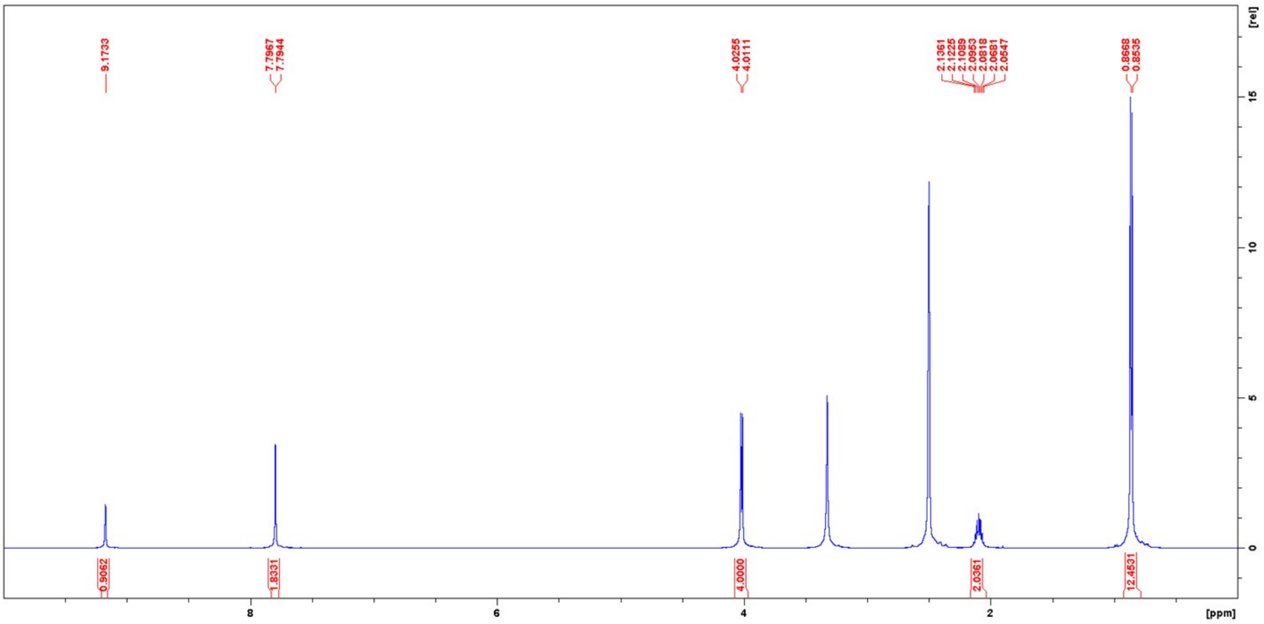
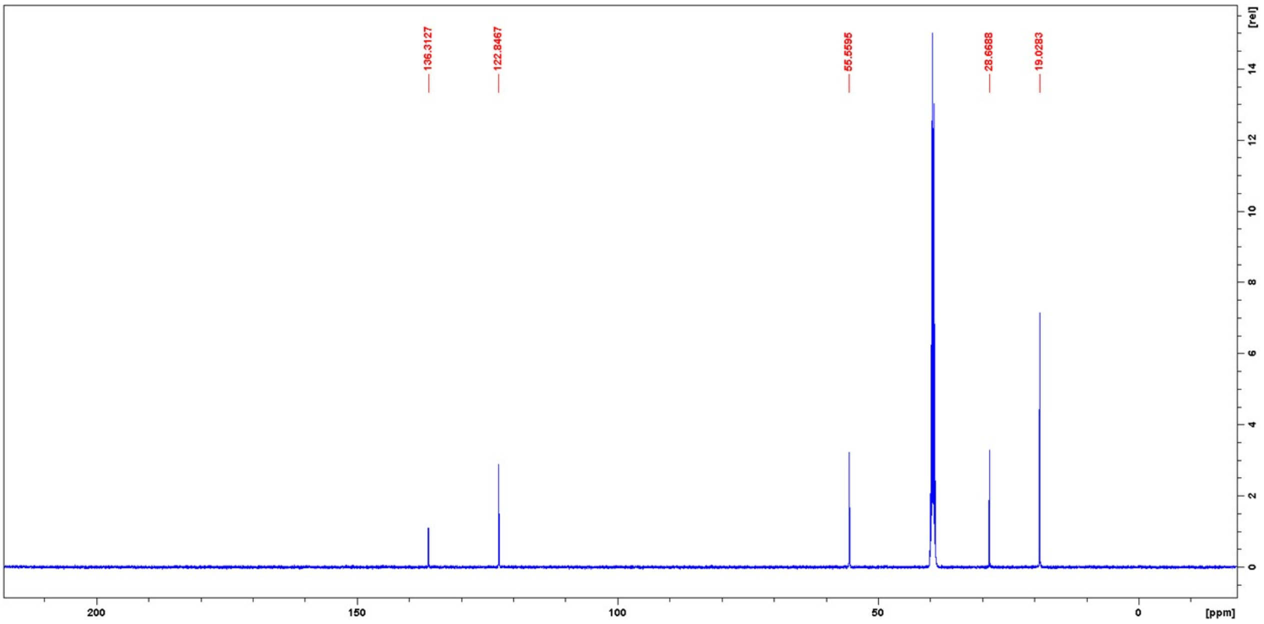
^{1}H- and ^{13}C-NMR spectra for $[iBu_2IM](BF_4)$ (recording conditions, see manuscript)





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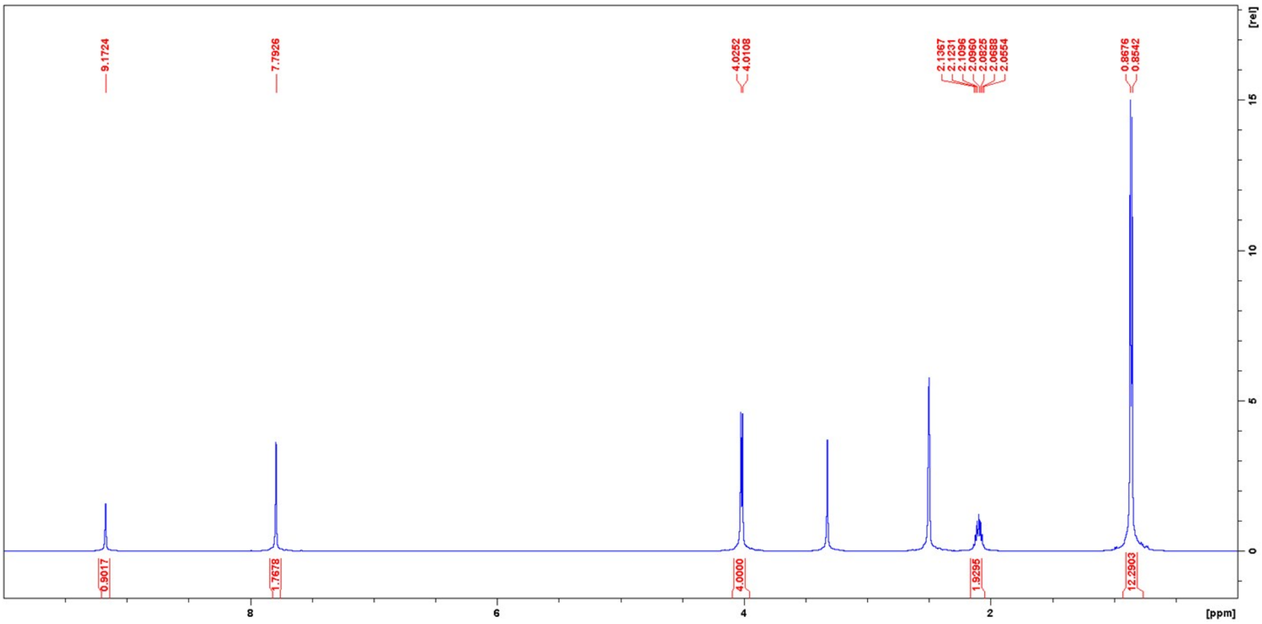

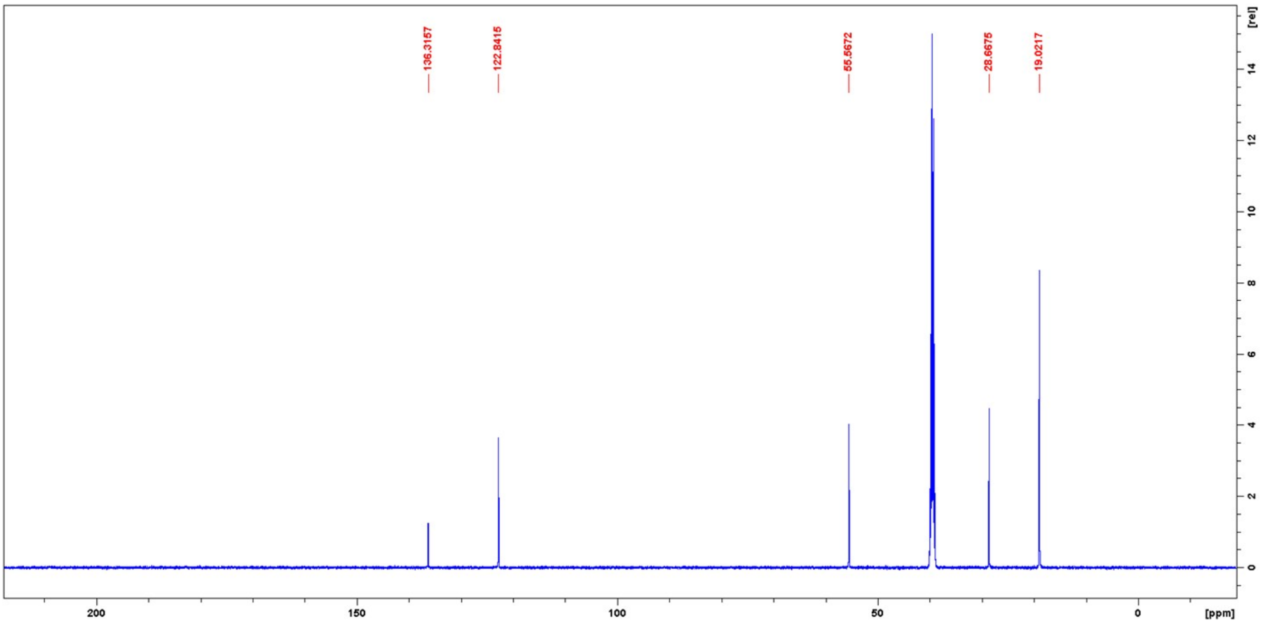

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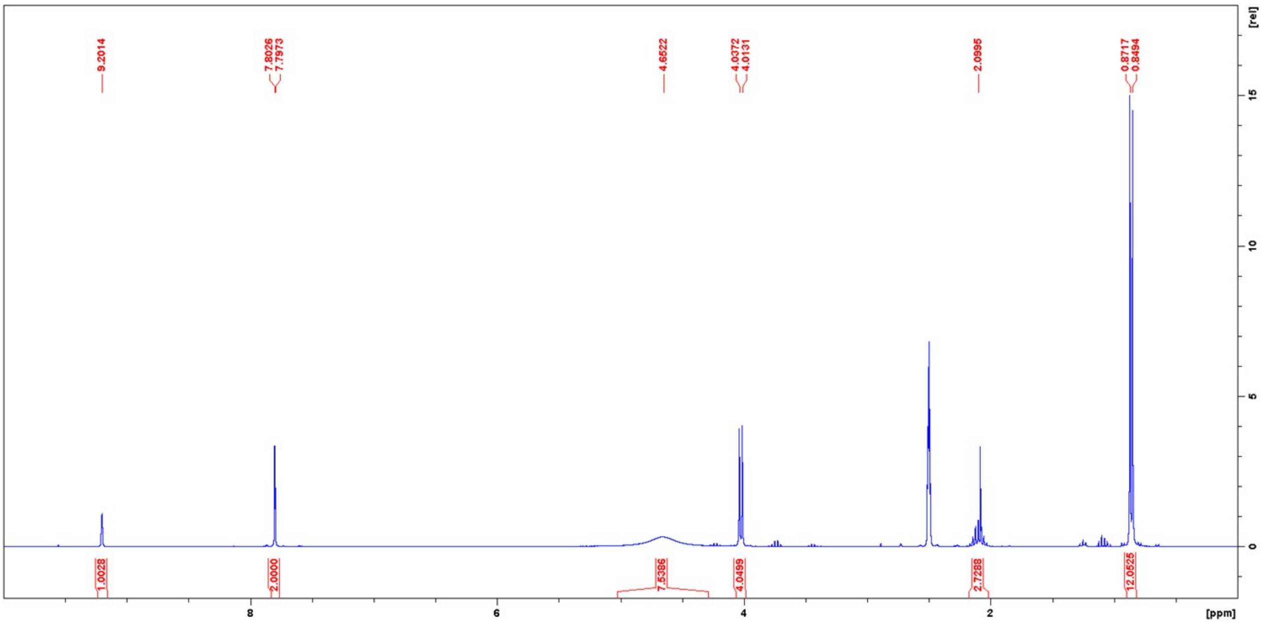

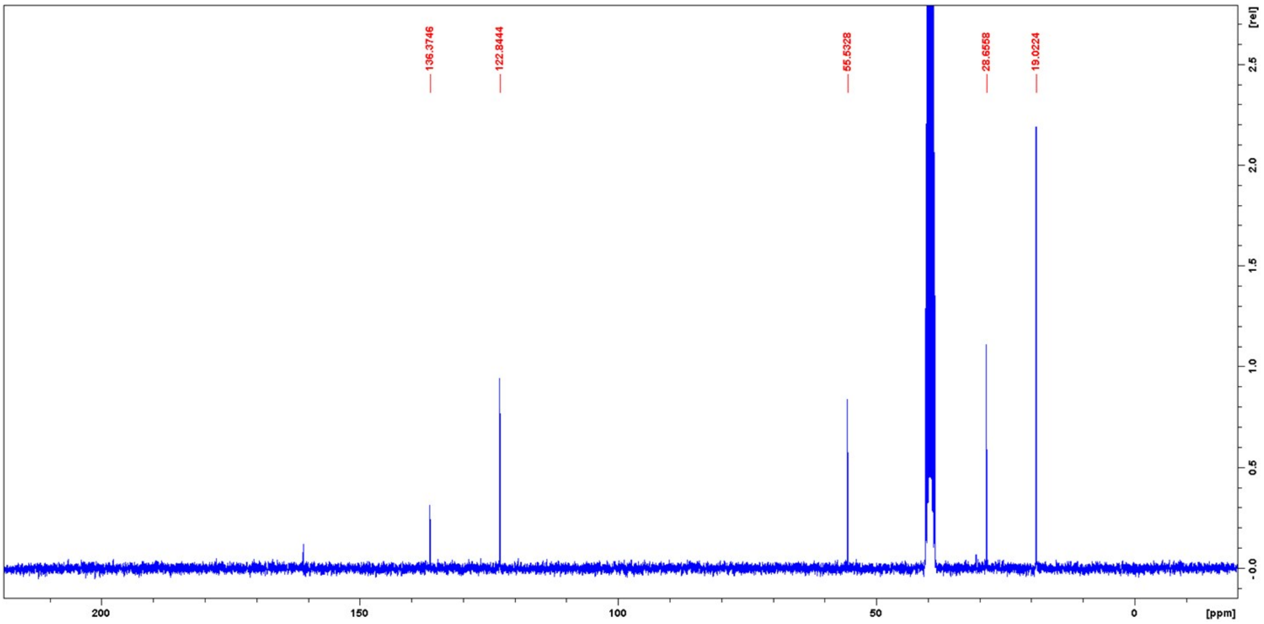

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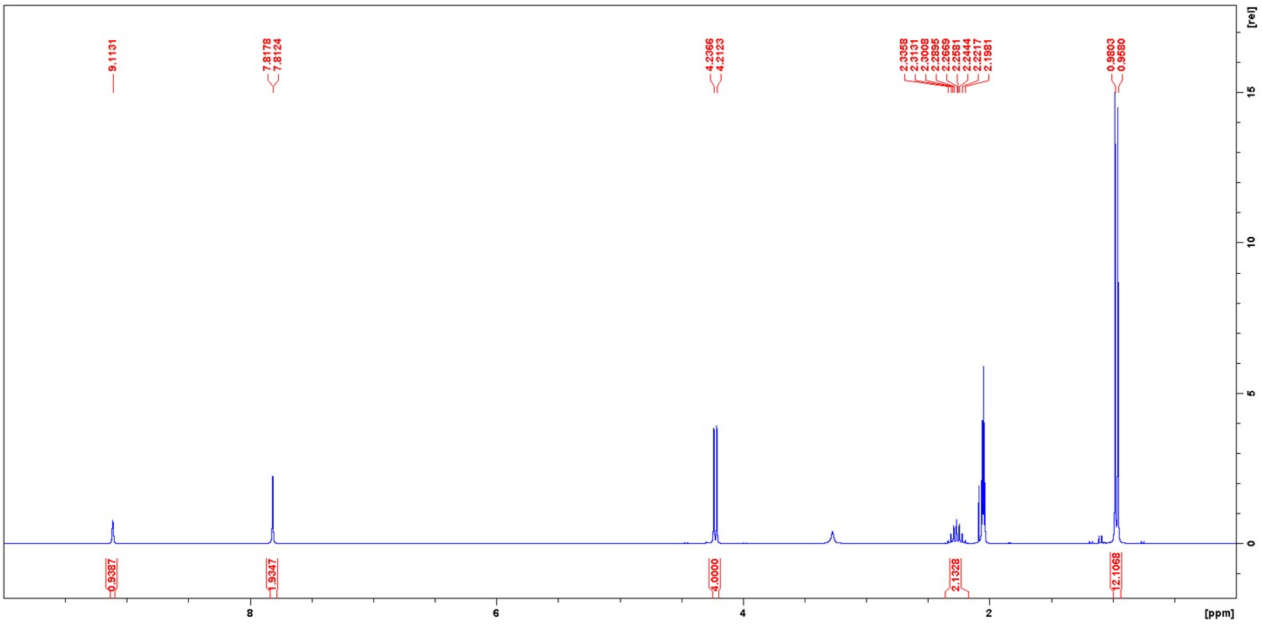


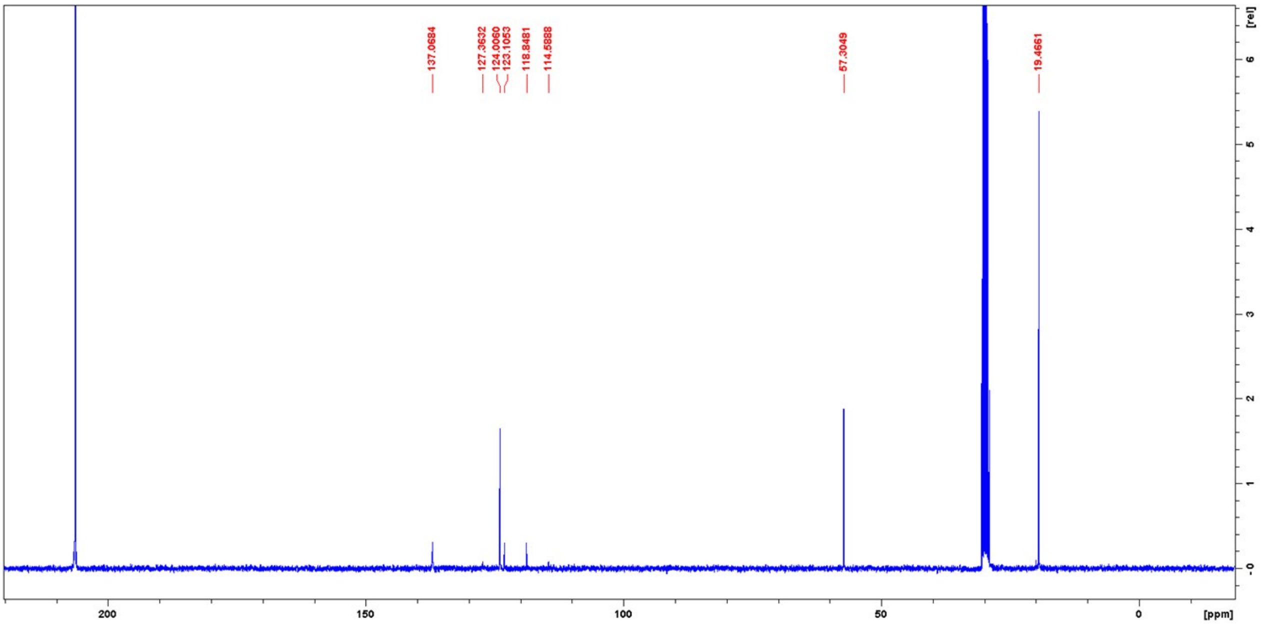
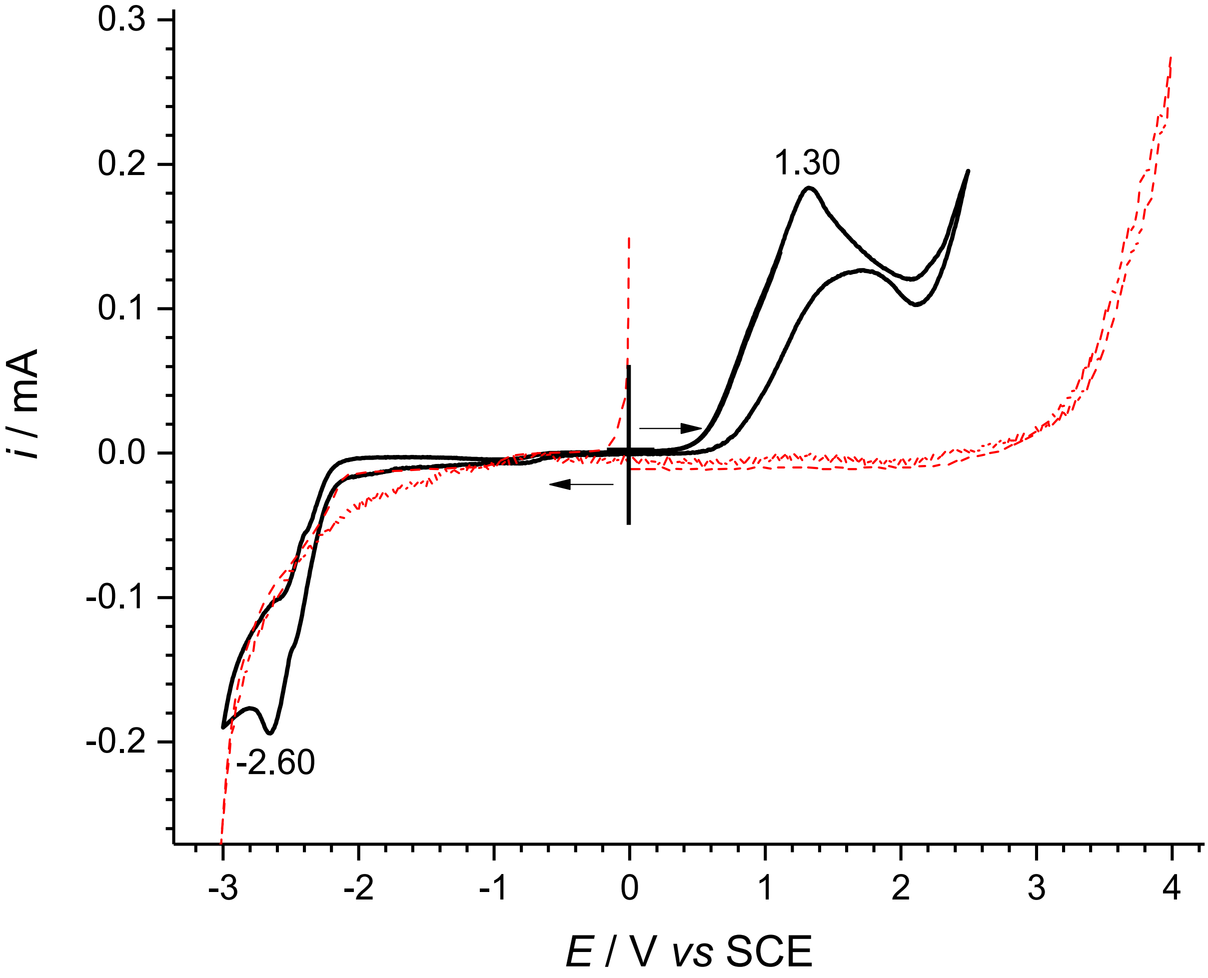
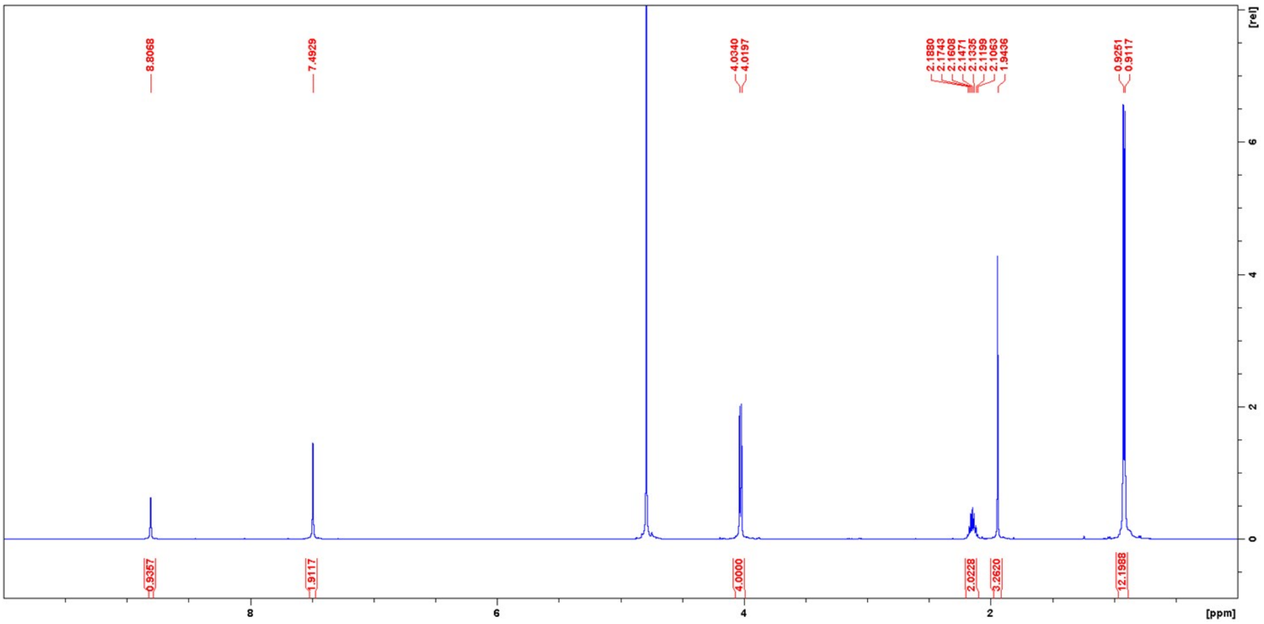
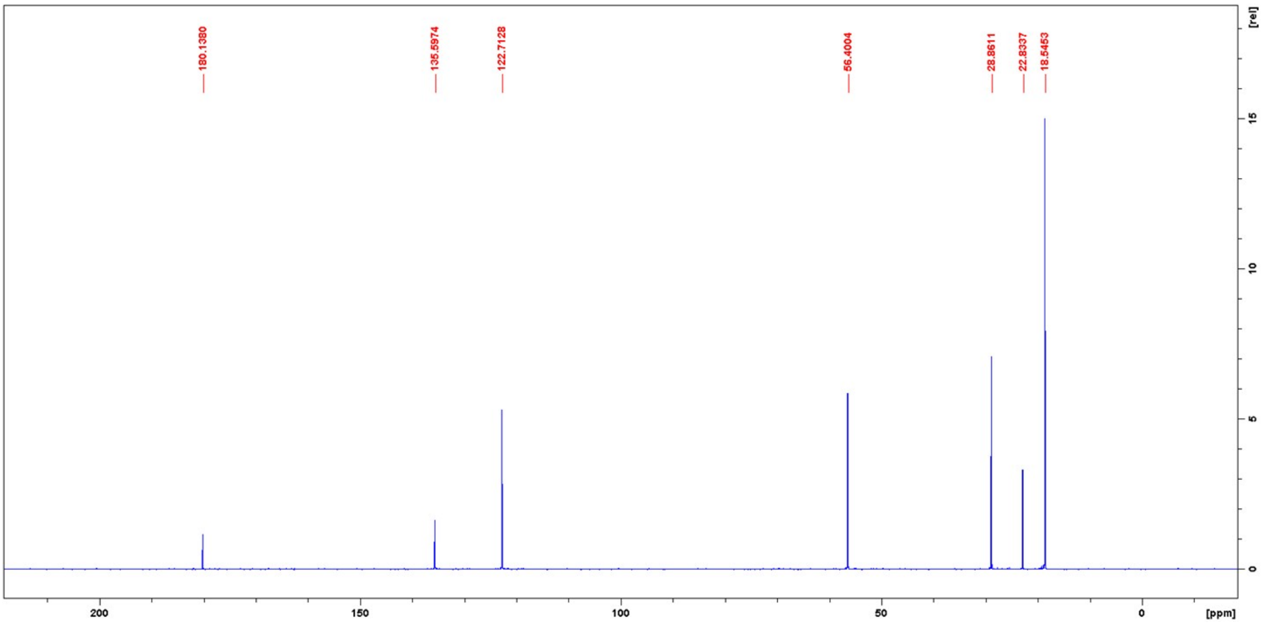


Figure 1. Cyclovoltammograms of [iBu$_2$IM](AcO) in CH$_3$CN at C = 2.1 x 10^{-2} M (black solid curve) and CH$_3$CN 0.1 M tetra-*n*-butylammonium hexafluorophosphate (dotted red curve). (WE: carbon 3 mm, reference electrode: SCE, CE: glassy carbon beaker, v = 100 mV s^{-1} at RT).

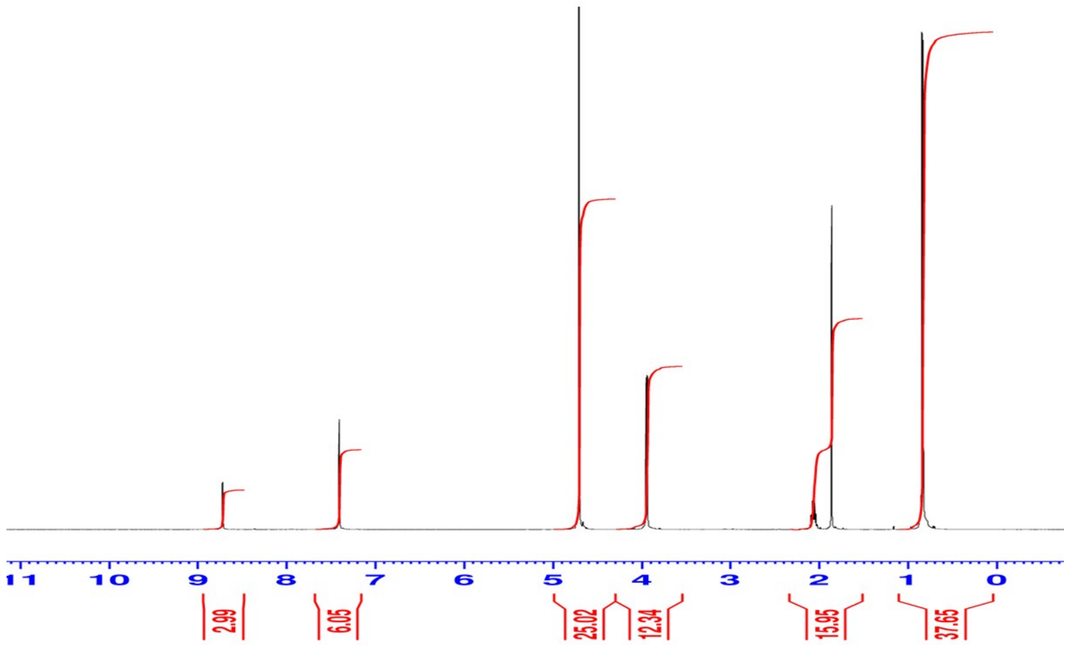


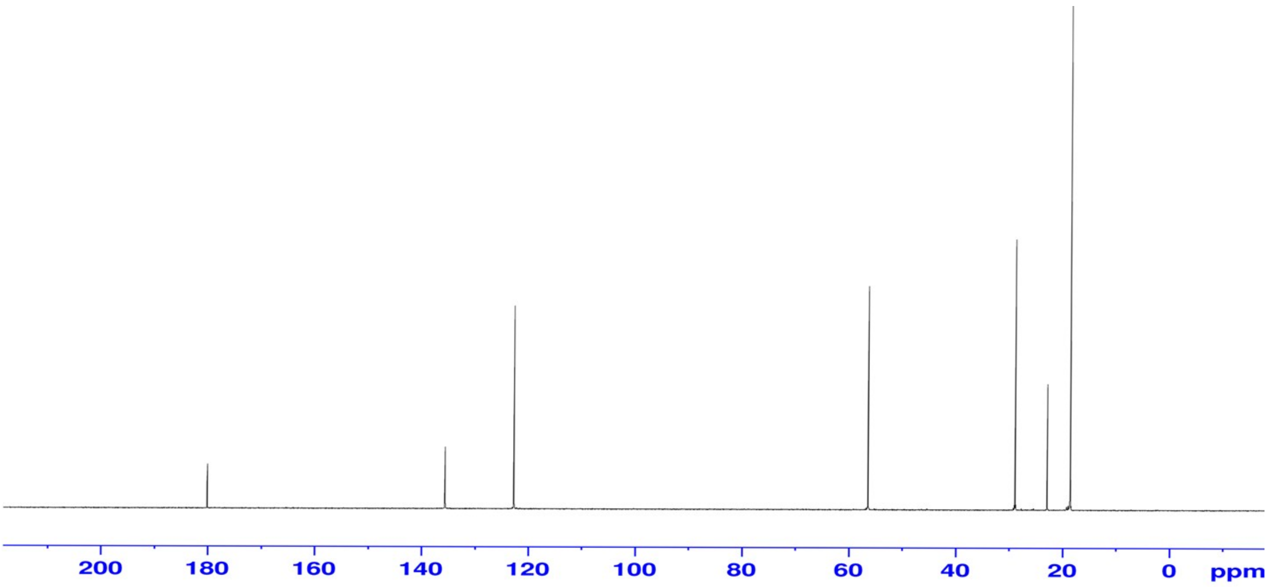
^{1}H- and ^{13}C-NMR spectra for [iBu$_2$IM](AcO) obtained by electrochemical synthesis (recording conditions, see manuscript)



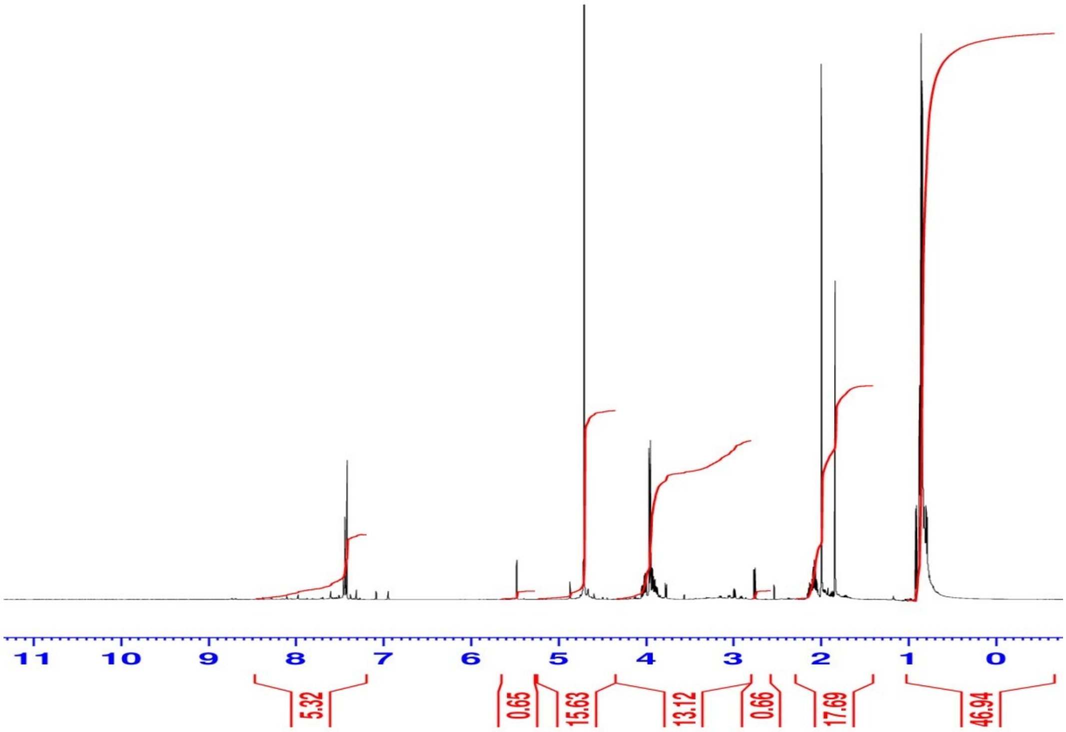


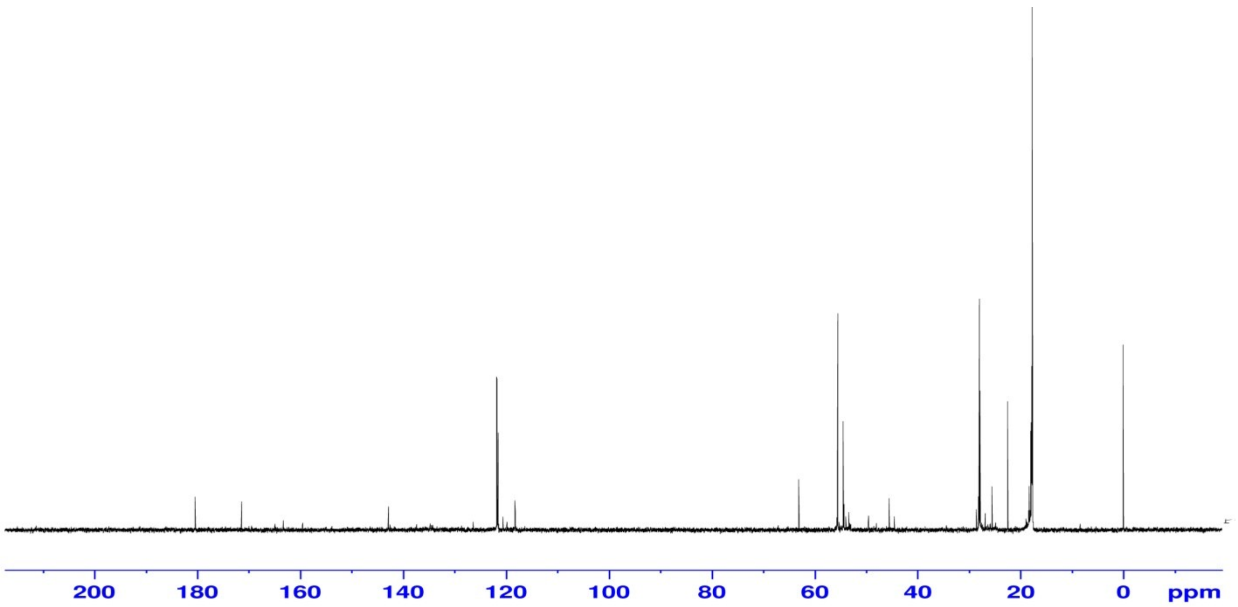
^{1}H- and ^{13}C-NMR spectra for [iBu$_2$IM](AcO) obtained by chemical synthesis (recording conditions, see manuscript)



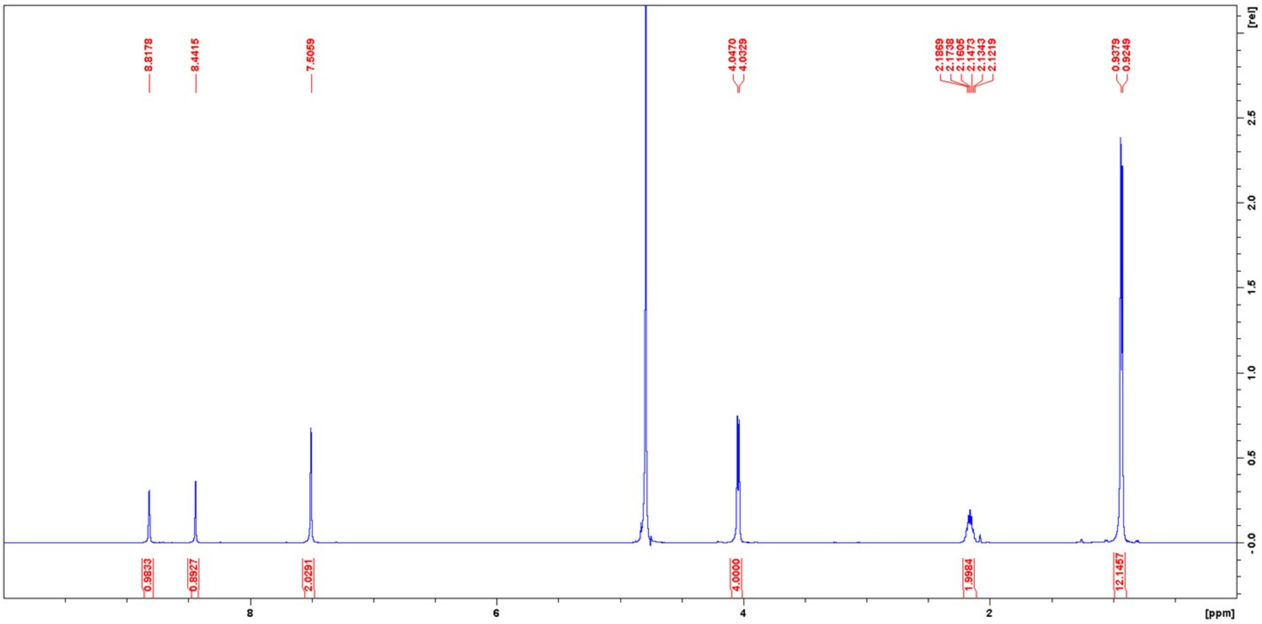


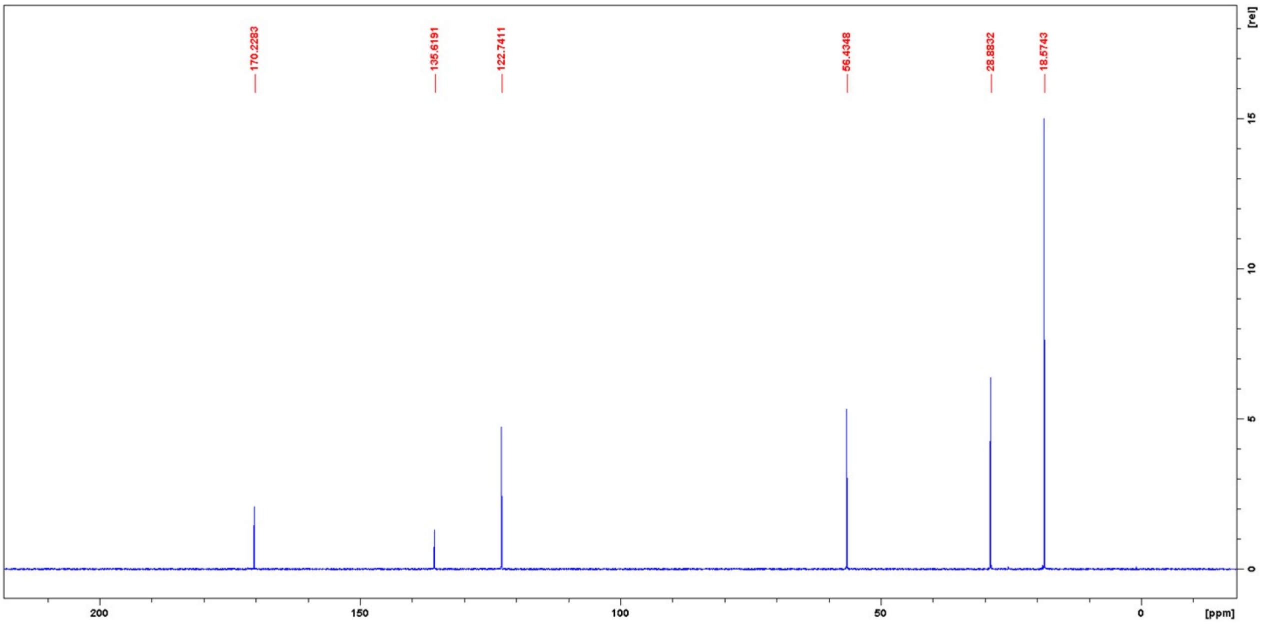
^1H- and ^{13}C-NMR spectra of crude evaporated solution after electrolysis of [iBu$_2$IM](AcO)




200
180
160
140
120
100
80
60
40
20
0
ppm

^{1}H- and ^{13}C-NMR spectra for [iBu$_2$IM](HCO$_2$) (recording conditions, see manuscript)





Calculation of environmental impacts

The toxicity of each ionic liquid recycling process were calculated as follow: the human toxicity data of the compound used in the process were found on the ReCiPe list.[33] The unit of these values is the equivalent in kilogram of 1,4-dichlorobenzene (1,4-DB), which serves as reference unit for the toxicity. These values were then multiplied by the mass of the compound used in the process and added to the others compounds of the process (Table 2).

Recycling Technologies RT:	**1**		**2**	**3**	**4**	**5**	
Compounds used	Diethyl ether	Ethyl acetate	CO_2	*tert*-butanol	-	Acetonitrile	Acetone
eq. kg 1,4-DB (x 10^{-3})	12	12	0	560	-	48	8.7
Mass used in the process (x 10^{-3} kg)	33.3	8.6	4.6	0.82	-	150	24
eq. kg 1,4-DB for the obtaining of 10 mmol of IL (x 10^{-4})	4.0	1.0	0	4.6	-	72	2.1
Total for the process (x10^{-4} eq. kg1,4-DB)	5.0		0	4.6	0	74	

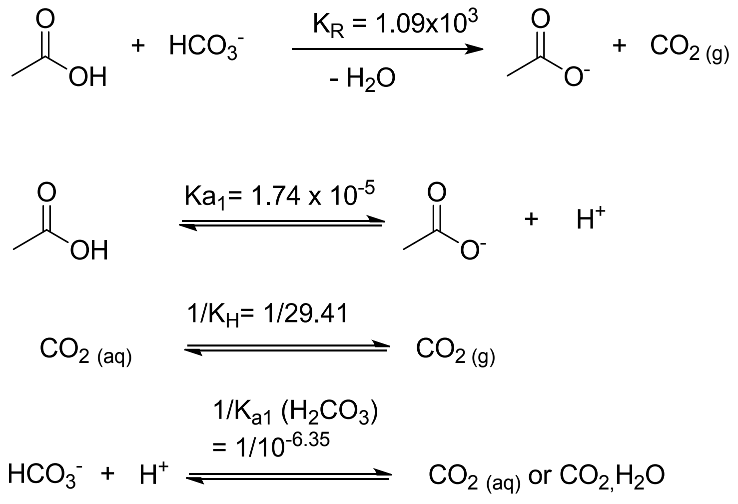
Table 2. Quantification of toxicity impacts of solvents used in recycling technologies

Calculation of energy consumption for ionic liquids recycling by direct distillation

To evaluate the energy consumption of the processes described in the literature, we measured the energy consumption of similar equipment with the Voltacraft Energy Monitor 3000. To model a Kugelrohr apparatus, we used a Buchi B-585 heating to 300°C and a vacuum pump Edwards RV3. After several minutes of equilibrium, the electric power was measured at 488 W, which was then used for the energy consumption of processes (by multiplying this value by the time).

Determination of equilibrium constants for protonation reactions with acetic/formic acids

With acetic acid:

	$K_R = \frac{[CH3COO-].pCO2}{[CH3COOH].[HCO3-]}$ $= \frac{[CH3COO-].[H+].pCO2.[CO2(aq)]}{[CH3COOH].[H+].[HCO3-].[CO2(aq}$ $= \frac{[CH3COO-].[H+].pCO2.[CO2(aq)]}{[CH3COOH].[CO2(aq)].[HCO3-].[H+}$ $= \frac{Ka(CH3COOH)xKH}{Ka1(CO2)}$ $= \frac{10-4.76\ x\ 29.41}{10-6.35}$ => $K_R =$ $1.15x10^3$

With formic acid:

$HCOOH + HCO_3^- \xrightarrow[- H_2O]{K_R = 1.17x10^4} HCOO^- + CO_{2\,(g)}$ $HCOOH \xrightleftharpoons{Ka_1 = 1.78x\ 10^{-4}} HCOO^- + H^+$ $CO_{2\,(aq)} \xrightleftharpoons{1/K_H = 1/29.41} CO_{2\,(g)}$ $HCO_3^- + H^+ \xrightleftharpoons{1/K_{a1}\ (H_2CO_3) = 1/10^{-6.35}} CO_{2\,(aq)}$ or $CO_2.H_2O$	$K_R = \frac{[HCOO-].pCO2}{[HCOOH].[HCO3-]}$ $= \frac{[HCOO-].[H+].pCO2.[CO2(aq)]}{[HCOOH].[H+].[HCO3-].[CO2(aq)]}$ $= \frac{[HCOO-].[H+].pCO2.[CO2(aq)]}{[HCOOH].[CO2(aq)].[HCO3-].[H+]}$

	$= \frac{Ka(HCOOH)xKH}{Ka1(CO2)}$ $= \frac{10 - 3.75\ x\ 29.41}{10 - 6.35}$ => K_R = 1.17x10^4