

ELECTRONIC SUPPORTING INFORMATION

Adjustment of the Structure of the Simplest Amino Acid Present in Nature— Glycine, toward More Environmentally Friendly Ionic Forms of Phenoxypropionate-Based Herbicides

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The structures of the obtained products were confirmed with the use of ^1H and ^{13}C NMR analyses:

Octyldimethylglycine hydrochloride [C₈-Bet]/[HCl] (3)

^1H NMR (CD_3OD) δ [ppm] = 0.90 (t, J = 6.8 Hz, 3H), 1.34 (s, 10H), 1.78 (m, 2H), 3.31 (s, 6H), 3.60 (m, 2H), 4.35 (s, 2H), 11.00 (s, 1H); ^{13}C NMR (CD_3OD) δ [ppm] = 167.3; 66.6; 61.9; 52.1; 32.9; 30.2; 27.3; 23.7; 23.6; 14.5.

Decyldimethylglycine hydrochloride [C₁₀-Bet]/[HCl] (4)

^1H NMR ($\text{DMSO}-d_6$) δ [ppm] = 0.86 (t, J = 6.7 Hz, 3H), 1.24 (s, 14H), 1.67 (m, 2H), 3.22 (s, 6H), 3.52 (m, 2H), 4.42 (s, 2H), 11.01 (s, 1H); ^{13}C NMR ($\text{DMSO}-d_6$) δ [ppm] = 166.2; 64.0; 60.5; 50.5; 31.2; 28.6; 25.7; 22.0; 21.7; 13.9.

Dodecyldimethylglycine hydrochloride [C₁₂-Bet]/[HCl] (5)

^1H NMR (CD_3OD) δ [ppm] = 0.89 (t, J = 6.6 Hz, 3H), 1.29 (s, 18H), 1.78 (m, 2H), 3.31 (s, 6H), 3.60 (m, 2H), 4.34 (s, 2H), 11.03 (s, 1H); ^{13}C NMR (CD_3OD) δ [ppm] = 167.3; 66.5; 61.9; 52.1; 33.1; 30.5; 27.3; 23.7; 23.6; 14.5.

Tetradecyldimethylglycine hydrochloride [C₁₄-Bet]/[HCl] (6)

^1H NMR (CD_3OD) δ [ppm] = 0.89 (t, J = 6.8 Hz, 3H), 1.28 (s, 22H), 1.78 (m, 2H), 3.30 (s, 6H), 3.59 (m, 2H), 4.33 (s, 2H), 11.00 (s, 1H); ^{13}C NMR (CD_3OD) δ [ppm] = 167.3; 66.5; 61.9; 52.1; 33.1; 30.6; 27.3; 25.6; 23.7; 14.5.

Hexadecyldimethylglycine hydrochloride [C₁₆-Bet]/[HCl] (7)

^1H NMR (CD_3OD) δ [ppm] = 0.90 (t, J = 6.9 Hz, 3H), 1.28 (s, 26H), 1.77 (m, 2H), 3.30 (s, 6H), 3.58 (m, 2H), 4.32 (s, 2H), 11.00 (s, 1H); ^{13}C NMR (CD_3OD) δ [ppm] = 167.3; 66.5; 61.9; 52.1; 33.1; 30.7; 27.3; 25.6; 23.7; 14.5.

Butyldimethylglycinium 2-(2,4-dichlorophenoxy)propionate [C₄-Bet]/[2,4-DP] (8)

^1H NMR (CDCl_3) δ [ppm] = 0.93 (t, J = 7.3 Hz, 3H), 1.30 (q, J = 7.33 Hz, 2H), 1.62 (d, J = 6.7 Hz, 3H), 1.69 (s, 2H), 3.16 (s, 6H), 3.47 (m, 2H), 3.89 (s, 2H), 4.65 (q, J = 6.7 Hz, 1H), 6.83 (d, J = 8.9 Hz, 1H), 7.11 (dd, $J_{1,3}$ = 8.8 Hz, $J_{1,2}$ = 2.5 Hz, 1H), 7.32 (d, J = 2.5 Hz, 1H), 10.95 (s, 1H); ^{13}C NMR (CDCl_3) δ [ppm] = 174.2; 166.1; 152.4; 129.6; 127.4; 125.7; 123.6; 115.4; 74.4; 64.4; 63.9; 51.0; 24.4; 19.4; 18.4; 13.3.

Hexyldimethylglycinium 2-(2,4-dichlorophenoxy)propionate [C₆-Bet]/[2,4-DP] (9)

¹H NMR (CDCl₃) δ [ppm] = 0.88 (t, *J* = 6.7 Hz, 3H), 1.27 (s, 6H), 1.62 (d, *J* = 6.7 Hz, 3H), 2.17 (s, 2H), 3.14 (s, 6H), 3.44 (m, 2H), 3.88 (s, 2H), 4.64 (q, *J* = 6.8 Hz, 1H), 6.83 (d, *J* = 8.8 Hz, 1H), 7.10 (dd, *J*_{1,3} = 8.8 Hz, *J*_{1,2} = 2.6 Hz, 1H), 7.32 (d, *J* = 2.5 Hz, 1H), 10.95 (s, 1H); ¹³C NMR (CDCl₃) δ [ppm] = 174.3; 166.4; 152.4; 129.6; 127.1; 125.7; 123.5; 115.4; 74.5; 64.6; 64.0; 50.9; 31.0; 25.7; 22.5; 22.2; 18.4; 13.7.

Decyldimethylglycinium 2-(2,4-dichlorophenoxy)propionate [C₁₀-Bet]/[2,4-DP] (11)

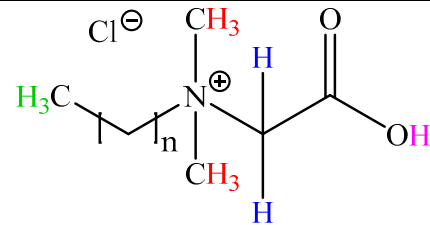
¹H NMR (CDCl₃) δ [ppm] = 0.88 (t, *J* = 6.9 Hz, 3H), 1.25 (s, 14H), 1.62 (d, *J* = 6.8 Hz, 3H), 2.09 (s, 2H), 3.13 (s, 6H), 3.43 (m, 2H), 3.88 (s, 2H), 4.65 (q, *J* = 6.8 Hz, 1H), 6.83 (d, *J* = 8.8 Hz, 1H), 7.11 (dd, *J*_{1,3} = 8.7 Hz, *J*_{1,2} = 2.5 Hz, 1H), 7.33 (d, *J* = 2.5 Hz, 1H), 11.00 (s, 1H); ¹³C NMR (CDCl₃) δ [ppm] = 174.1; 166.6; 152.4; 129.7; 127.4; 125.8; 123.7; 115.4; 74.3; 64.7; 64.0; 50.9; 31.7; 29.3; 29.0; 26.1; 22.5; 18.4; 14.0.

Dodecyldimethylglycinium 2-(2,4-dichlorophenoxy)propionate [C₁₂-Bet]/[2,4-DP] (12)

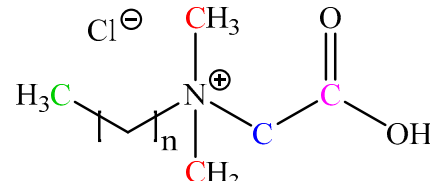
¹H NMR (CDCl₃) δ [ppm] = 0.88 (t, *J* = 6.8 Hz, 3H), 1.26 (s, 18H), 1.63 (d, *J* = 6.7 Hz, 3H), 2.17 (s, 2H), 3.17 (s, 6H), 3.45 (m, 2H), 3.89 (s, 2H), 4.65 (q, *J* = 6.8 Hz, 1H), 6.84 (d, *J* = 8.9 Hz, 1H), 7.10 (dd, *J*_{1,3} = 8.8 Hz, *J*_{1,2} = 2.6 Hz, 1H), 7.32 (d, *J* = 2.5 Hz, 1H), 11.00 (s, 1H); ¹³C NMR (CDCl₃) δ [ppm] = 174.4; 166.3; 152.5; 129.6; 127.3; 125.7; 123.6; 115.4; 74.5; 64.6; 64.0; 51.0; 31.7; 29.5; 26.1; 24.0; 22.5; 18.4; 13.9.

Hexadecyldimethylglycinium 2-(2,4-dichlorophenoxy)propionate [C₁₆-Bet]/[2,4-DP] (14)

¹H NMR (CDCl₃) δ [ppm] = 0.88 (t, *J* = 6.7 Hz, 3H), 1.26 (s, 26H), 1.64 (d, *J* = 6.9 Hz, 3H), 2.69 (s, 2H), 3.17 (s, 6H), 3.47 (m, 2H), 3.90 (s, 2H), 4.64 (d, *J* = 6.8 Hz, 1H), 6.83 (d, *J* = 8.9 Hz, 1H), 7.11 (dd, *J*_{1,3} = 8.8 Hz, *J*_{1,2} = 2.6 Hz, 1H), 7.32 (d, *J* = 2.6 Hz, 1H), 11.00 (s, 1H); ¹³C NMR (CDCl₃) δ [ppm] = 174.6; 166.5; 152.6; 129.7; 127.3; 125.7; 123.7; 115.4; 74.7; 64.7; 64.1; 51.0; 31.7; 29.5; 29.0; 26.1; 22.5; 18.5; 14.0.

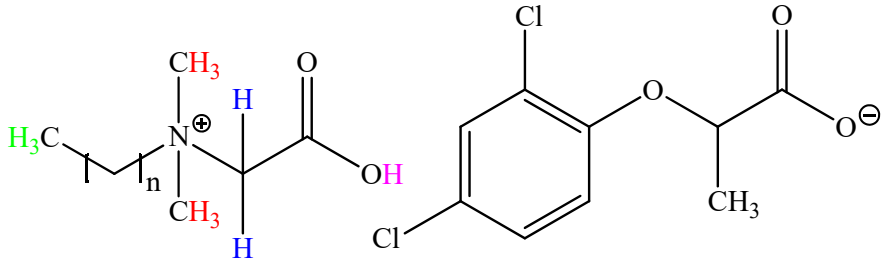
Table S1. Chemical shifts [ppm] of selected protons in ¹H NMR spectra of products (3–7).


No	n	CH ₃	N-(CH ₃) ₂	N-CH ₂ -CO	COOH
3 ^a	7	0.90(t)	3.31(s)	4.35(s)	11.00(s)
4 ^b	9	0.86(t)	3.22(s)	4.42(s)	11.01(s)
5 ^a	11	0.89(t)	3.31(s)	4.34(s)	11.03(s)
6 ^a	13	0.89(t)	3.30(s)	4.33(s)	11.00(s)
7 ^a	15	0.90(t)	3.30(s)	4.32(s)	11.01(s)

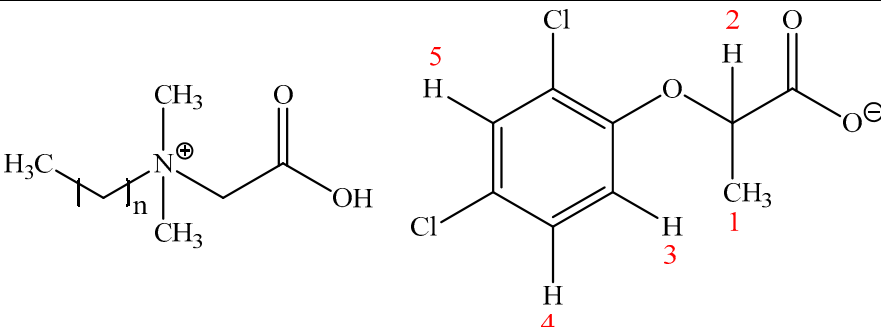
s – singlet, t – triplet, solvent - ^a CD₃OD, ^b DMSO-*d*₆**Table S2.** Chemical shifts [ppm] of selected carbons in ¹³C NMR spectra of products (3–7).


No	n	CH ₃	N-(CH ₃) ₂	N-CH ₂ -CO	COOH
3 ^a	7	14.5	52.1	61.9	167.3
4 ^b	9	13.9	50.5	60.5	166.3
5 ^a	11	14.5	52.1	61.9	167.3
6 ^a	13	14.5	52.1	61.9	167.3
7 ^a	15	14.5	52.1	61.9	167.3

solvent - ^a CD₃OD, ^b DMSO-*d*₆

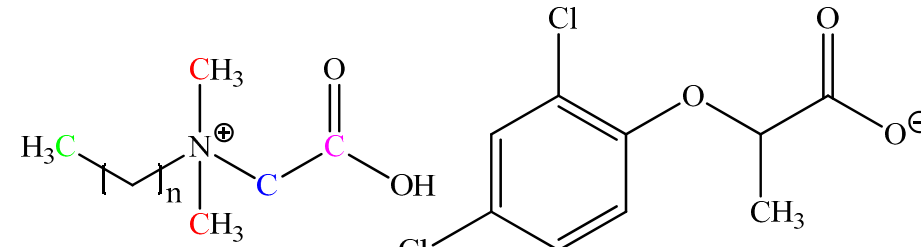
Table S3. Chemical shifts [ppm] of selected protons from cation in ^1H NMR spectra of ILs.


No	n	CH ₃ -R	N-(CH ₃) ₂	N-CH ₂ -CO	COOH
8	7	0.93(t)	3.16(s)	3.89(s)	10.95(s)
9	9	0.88(t)	3.14(s)	3.88(s)	10.95(s)
11	11	0.88(t)	3.13(s)	3.88(s)	11.00(s)
12	13	0.88(t)	3.17(s)	3.89(s)	11.00(s)
14	15	0.88(t)	3.17(s)	3.90(s)	11.01(s)

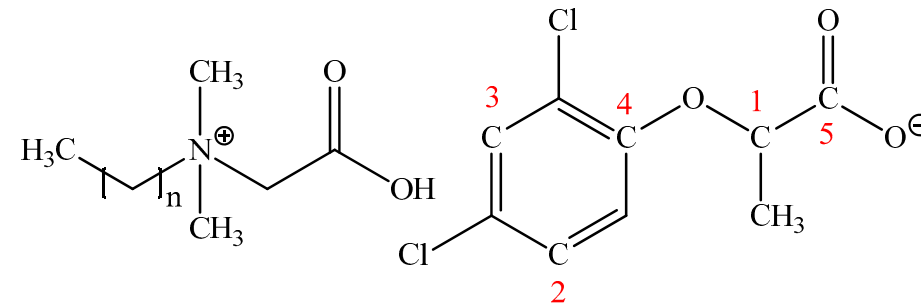
s – singlet, t – triplet, solvent – CDCl₃**Table S4.** Chemical shifts [ppm] of selected protons from anion in ^1H NMR spectra of ILs.


No	n	1	2	3	4	5
8	7	1.62(d)	4.64(q)	6.83(d)	7.11(dd)	7.32(d)
9	9	1.62(d)	4.64(q)	6.83(d)	7.10(dd)	7.32(d)
11	11	1.62(d)	4.65(q)	6.83(d)	7.11(dd)	7.33(d)
12	13	1.63(d)	4.65(q)	6.84(d)	7.10(dd)	7.32(d)
14	15	1.64(d)	4.64(d)	6.83(d)	7.11(dd)	7.32(d)

d – doublet; dd – doublet of doublets, q – quartet, solvent – CDCl₃

Table S5. Chemical shifts [ppm] of selected carbons from cation in ^{13}C NMR spectra of ILs.


No	n	CH ₃ -R	N-(CH ₃) ₂	N-CH ₂ -CO	COOH
8	7	13.3	51.0	63.9	166.6
9	9	13.7	50.9	64.0	166.4
11	11	14.0	50.9	64.0	166.6
12	13	13.9	51.0	64.0	166.3
14	15	14.0	51.0	64.1	165.5

solvent – CDCl₃**Table S6.** Chemical shifts [ppm] of selected carbons from anion in ^{13}C NMR spectra of ILs.


No	n	1	2	3	4	5
8	7	74.4	127.4	129.6	152.4	174.2
9	9	74.5	127.4	129.6	152.4	174.3
11	11	74.3	127.4	129.7	152.4	174.1
12	13	74.5	127.3	129.6	152.5	174.4
14	15	74.7	127.3	129.7	152.6	174.6

solvent – CDCl₃

Table S7. Densities [$\text{g}\cdot\text{cm}^{-3}$] of ILs **8–14** in a temperature range from 20 to 80 °C.

No	Temperature [°C]						
	20	30	40	50	60	70	80
8	1.23	1.22	1.21	1.21	1.20	1.19	1.18
9	1.21	1.20	1.19	1.18	1.18	1.17	1.16
10	1.16	1.15	1.14	1.13	1.13	1.12	1.11
11	1.15	1.14	1.13	1.12	1.11	1.10	1.10
12	1.13	1.12	1.11	1.10	1.09	1.09	1.08
13	1.08	1.07	1.07	1.06	1.05	1.04	1.04
14	1.08	1.07	1.06	1.05	1.05	1.04	1.03

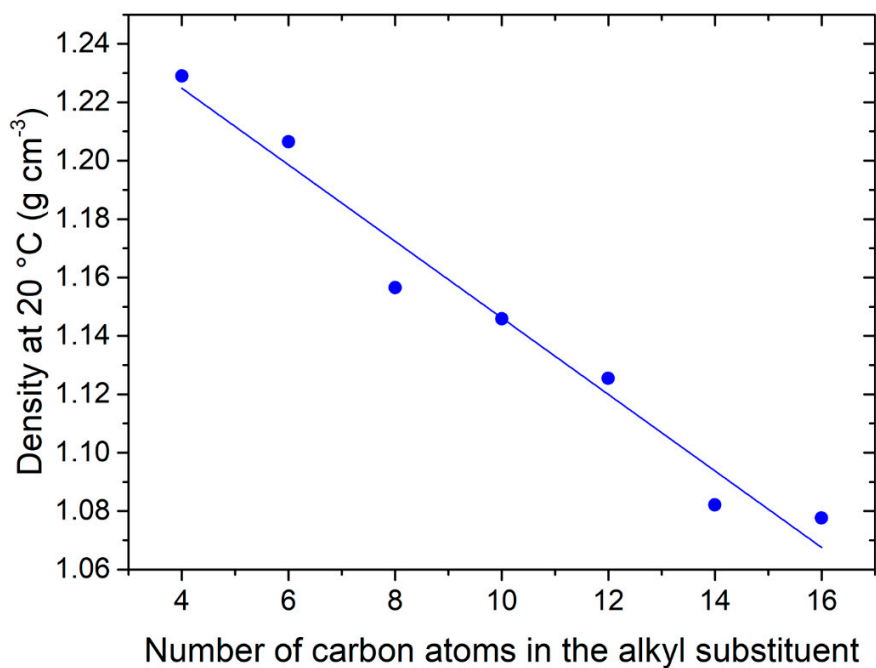


Figure S1. Relationship between alkyl substituent length in the cation and the densities of ILs **8–14** at 20 °C.

Table S8. Refractive indices of ILs **8–14** in a temperature range from 20 to 80 °C.

No	Temperature [°C]						
	20	30	40	50	60	70	80
8	1.522	1.517	1.513	1.509	1.506	1.503	1.499
9	1.521	1.517	1.514	1.511	1.508	1.505	1.502
10	1.508	1.504	1.501	1.497	1.494	1.492	1.490
11	1.507	1.504	1.500	1.497	1.494	1.491	1.489
12	1.503	1.500	1.496	1.493	1.492	1.489	1.488
13	1.497	1.494	1.491	1.488	1.486	1.485	1.482
14	1.498	1.493	1.490	1.486	1.484	1.482	1.479

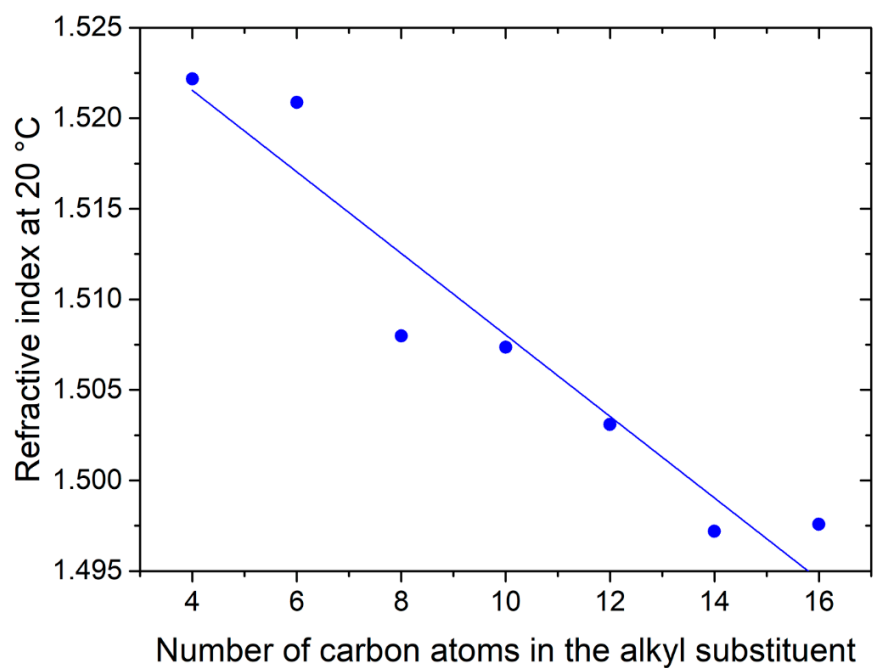


Figure S2. Relationship between alkyl substituent length in the cation and the refractive indices of ILs **8–14** at 20 °C.

Table S9. Viscosities [Pa·s] of ILs **8–14** in a temperature range from 20 to 80 °C.

No	Temperature [°C]						
	20	30	40	50	60	70	80
8	480.73	81.78	18.14	5.27	1.78	0.71	0.31
9	1725.30	257.93	53.04	14.25	4.70	1.85	0.80
10	1800.70	282.17	61.22	17.15	5.79	2.30	1.01
11	54.35	15.25	5.14	2.06	0.92	0.46	0.26
12	48.50	14.41	5.14	2.12	0.98	0.50	0.29
13	14.15	4.88	1.94	0.88	0.44	0.25	0.15
14	38.70	11.34	4.04	1.65	0.76	0.39	0.22

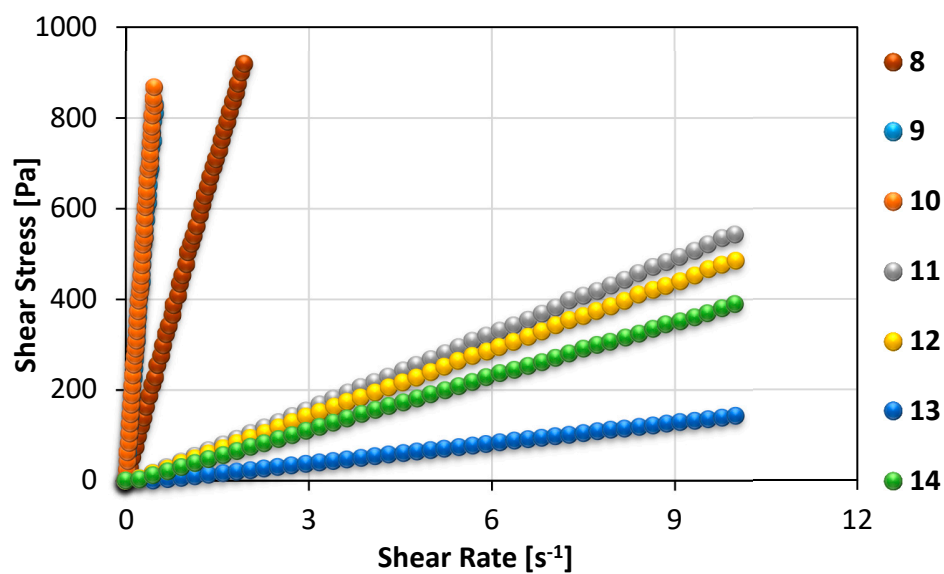


Figure S3. Shear stress versus shear rate for ILs **8–14**.

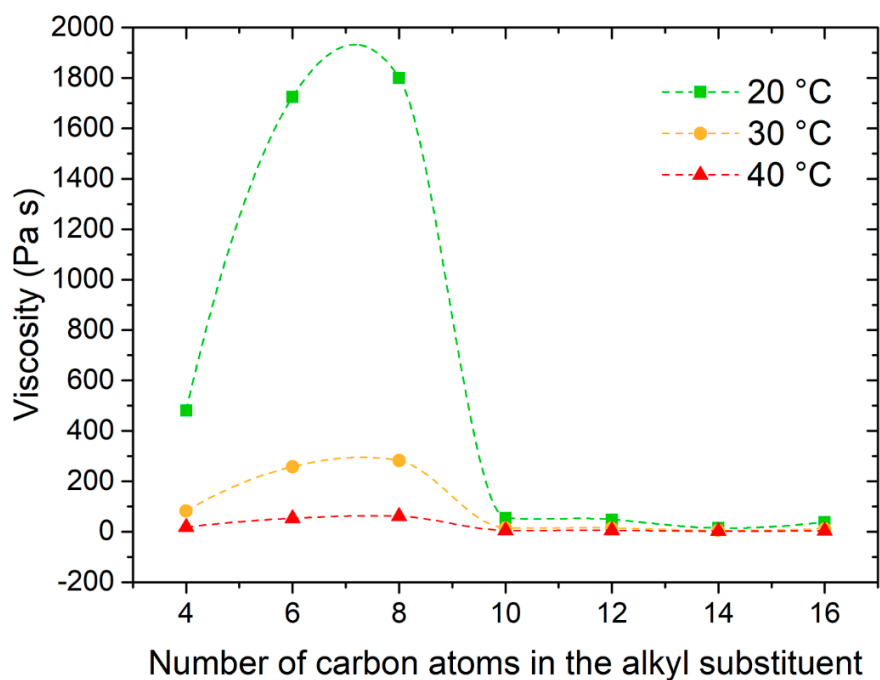


Figure S4. Relationship between alkyl substituent length in the cation and the viscosities of ILs **8–14** at 20, 30 and 40 °C.

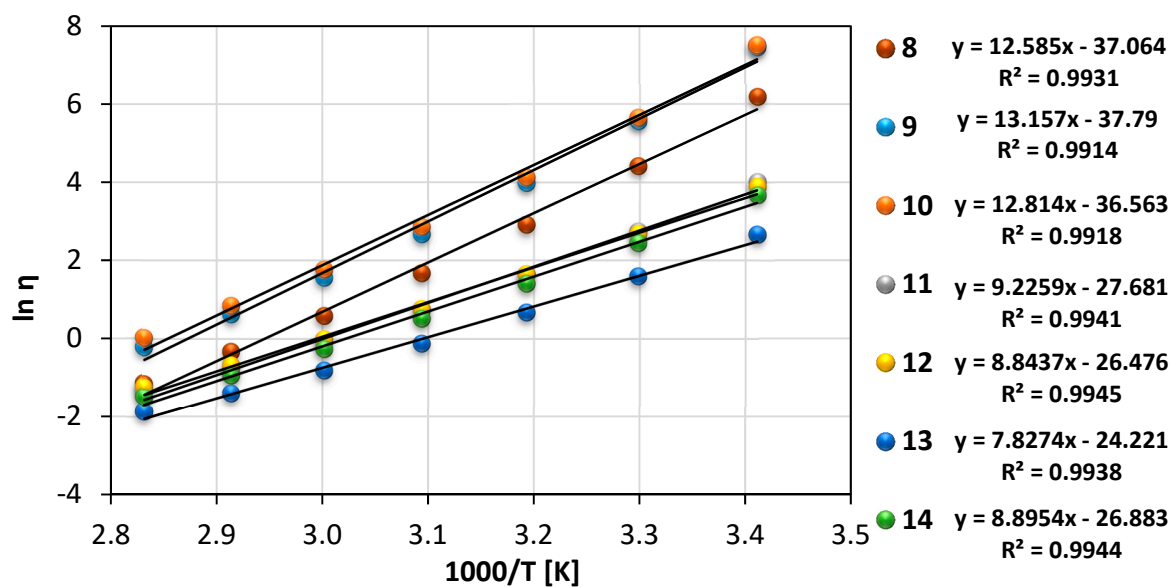


Figure S5. Arrhenius plots for ILs **8–14**, where η is viscosity and T is temperature.

Table S10. Biological activity of ILs **8–14** toward oilseed rape; **REF1** – potassium 2-(2,4-dichlorophenoxy)propionate, **REF2** – Aminopielik Standard 600 SL.

Substance*	R	SE** [%]	Mass reduction [%]
Untreated control	-	2.5	0 a***
8	C ₄ H ₉	4.9	16.8 b
9	C ₆ H ₁₃	4.3	19.0 b
10	C ₈ H ₁₇	2.1	44.7 cd
11	C ₁₀ H ₂₁	7.2	46.1 cd
12	C ₁₂ H ₂₅	3.5	55.5 d
13	C ₁₄ H ₂₉	3.7	50.9 cd
14	C ₁₆ H ₃₃	6.9	45.6 cd
REF1	-	2.8	42.4 c
REF2	-	3.7	11.3 b
HSD (0.05)			10.9
*All tested products were used in a dose of 400 g of active ingredient per hectare			
** SE – standard error			
*** a–d different letters indicate statistically different mean HSD (p < 0.05)			

Table S11. Green Chemistry Metrics. [1]

No	<i>Atom economy</i> (%)	<i>Percentage yield</i> (%)	<i>Reaction mass efficiency</i>	<i>Environmental factor*</i> (E-factor)
8	72	74	0.54	0.43
9	73	63	0.47	0.44
10	75	72	0.54	0.38
11	76	84	0.64	0.33
12	77	81	0.63	0.32
13	78	81	0.64	0.30
14	79	83	0.66	0.28

* Higher E-factors are relatively less desirable. For bulk chemicals, manufactured in amounts of hundreds of thousands to millions of tons per year, tolerable E-factors typically range from 1 to 5. For commercially produced pharmaceuticals E-factor is extremely high and generally exceeds 50. The elaborated methodology exhibits E-factor lower than 1, hence, can be considered as sustainable and appropriately developed in accordance to green chemistry principles.

[1] Sheldon, R.A. Metrics of Green Chemistry and Sustainability: Past, Present, and Future. *ACS Sustainable Chem. Eng.* **2018**, 6, 32–48, doi:10.1021/acssuschemeng.7b03505.