Supplementary Data

For the article

An unexpected increase of toxicity of amino acid-containing ionic liquids

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1-Butyl-3-methylimidazolium glycinate ([BMIM][Gly])

Obtained 0.160 g (75%) light yellow oil.
^{1}H NMR (600 MHz, dmso-d_6) δ, ppm: 0.89 (t, J=7.3 Hz, 3H), 1.25 (sext, J=7.3 Hz, 2H), 1.76 (pent, J=7.3 Hz, 2H), 2.69 (s, 2H), 3.87 (s, 3H), 4.19 (t, J=7.2 Hz, 2H), 7.77 (s, 1H), 7.83 (s, 1H), 9.75 (s, 1H); NH_2 may appear as very broad signal around 1.5 ppm.
^{13}C{^{1}H} NMR (150.9 MHz, dmso-d_6) δ, ppm: 13.2; 18.7; 31.4; 35.5; 46.6; 48.3; 122.2; 123.5; 137.6; 175.3.
Confirmed according to the literature data.[1]
HRMS (ESI): found m/z 139.1232; calculated for cation $C_8H_{15}N_2$ m/z 139.1230 (Δ=1.4 ppm).

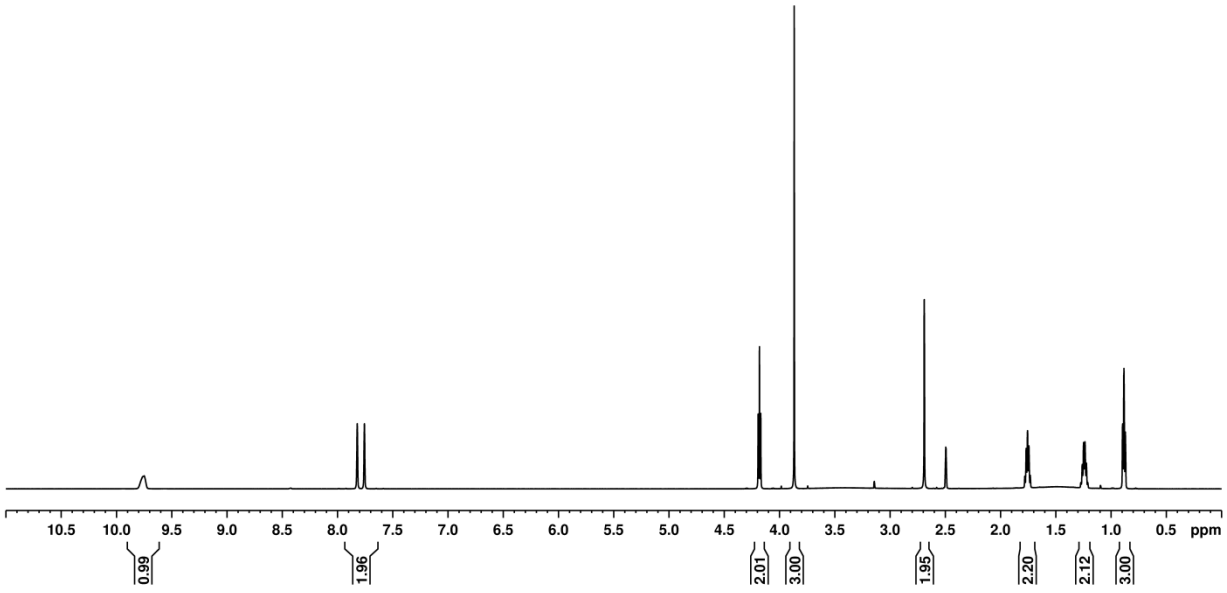

Figure S1. ^{1}H NMR spectrum of [BMIM][Gly].

[1] Li, M.; Wang, T.; Pham, P. J.; Pittman, C. U.; Li, T. *Sep. Sci. Technol*,. 2008, **43**, 828.

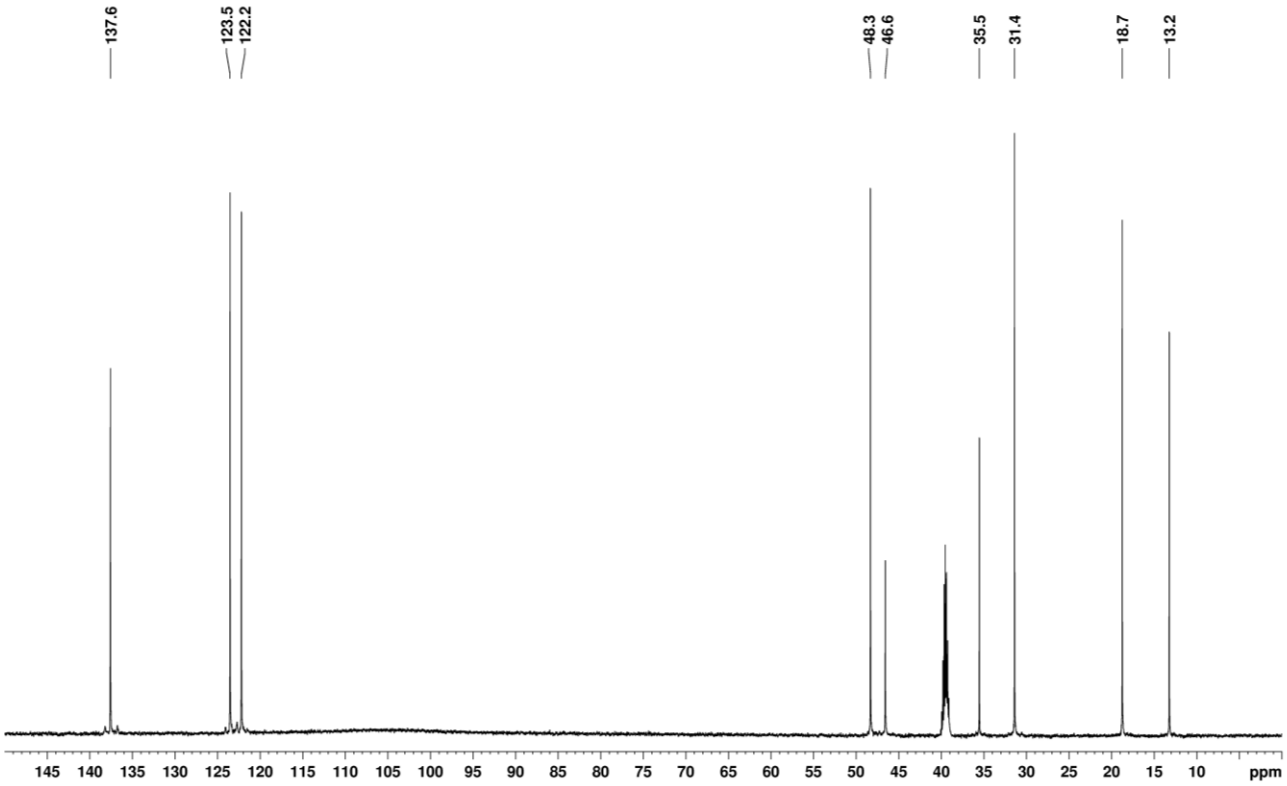

Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of [BMIM][Gly].

1-Butyl-3-methylimidazolium alaninate ([BMIM][Ala])

Obtained 0.177 g (78%) light yellow oil.
^{1}H NMR (600 MHz, dmso-d_6) δ, ppm: 0.89 (t, J=7.4 Hz, 3H), 1.01 (d, J=6.8 Hz, 3H), 1.24 (sext, J=7.5 Hz, 2H), 1.76 (pent, J=7.5 Hz, 2H), 2.84 (q, J=6.7 Hz, 1H), 3.87 (s, 3H), 4.19 (t, J=7.2 Hz, 2H), 7.76 (s, 1H), 7.82 (s, 1H), 9.81 (s, 1H); NH_2 may appear as very broad signal around 1.5 ppm.
$^{13}C\{^{1}H\}$ NMR (150.9 MHz, dmso-d_6) δ, ppm: 13.2; 18.7; 22.9; 31.4; 35.5; 48.3; 51.8; 122.2; 123.5; 137.4; 177.9.
Confirmed according to the literature data.[2]
HRMS (ESI): found m/z 139.1233; calculated for cation $C_8H_{15}N_2$ m/z 139.1230 (Δ=2.2 ppm).

[2] Fang, D. W.; Guan, W.; Tong, J.; Wang, Z. W.; Yang, J. Z. *J. Phys. Chem , B* 2008, **112**, 7499.

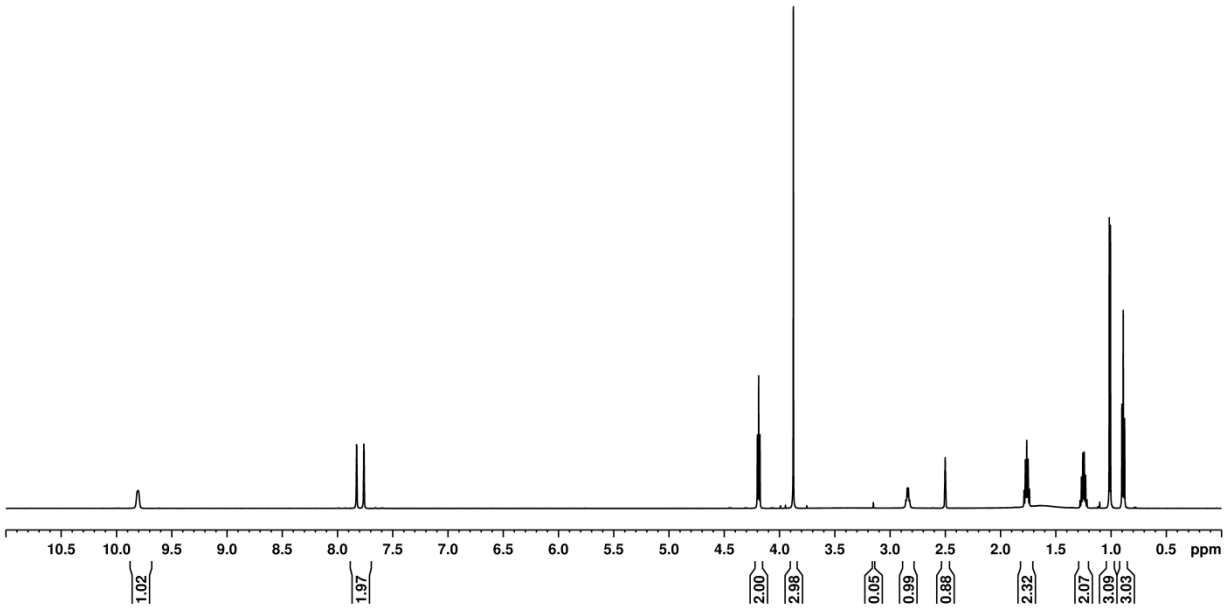

Figure S3. ^{1}H NMR spectrum of [BMIM][Ala].

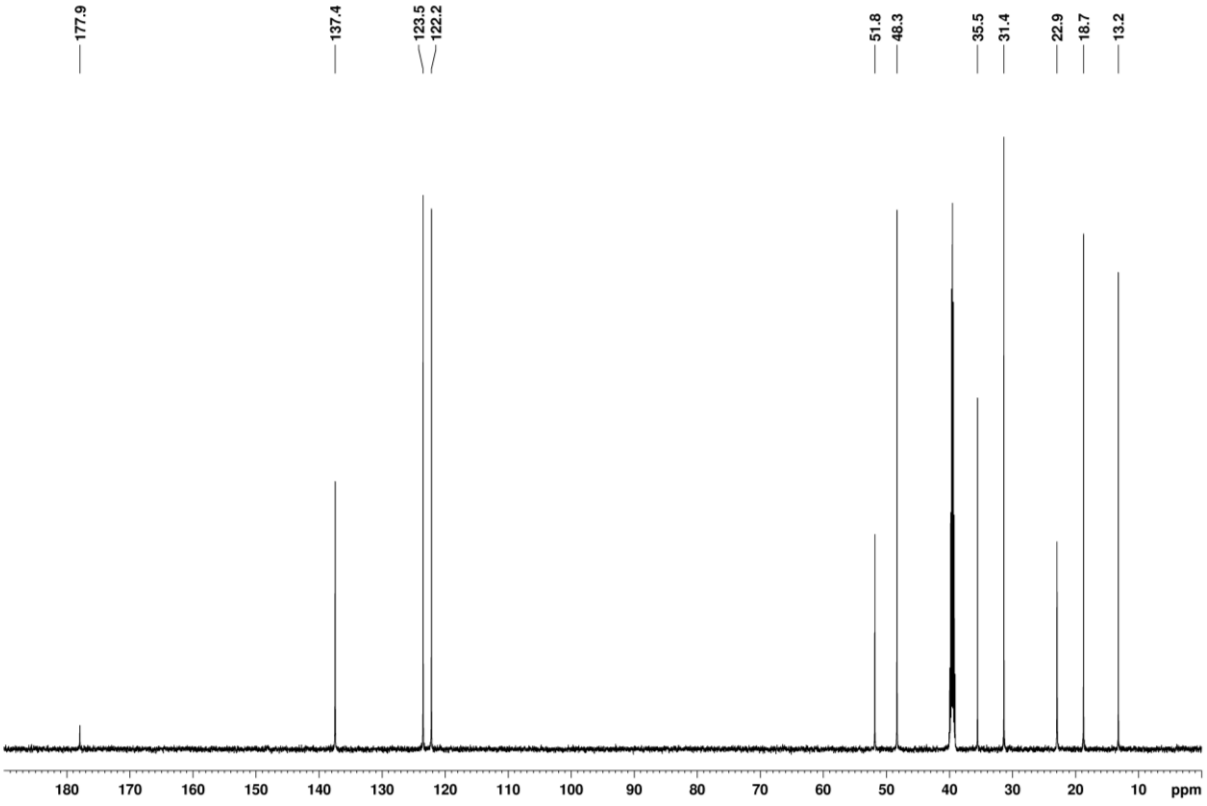

Figure S4. ^{13}C{^{1}H} NMR spectrum [BMIM][Ala].

1-Butyl-3-methylimidazolium valinate ([BMIM][Val])

Obtained 0.184 g (72%) light yellow oil.
^{1}H NMR (500 MHz, dmso-d_6) δ, ppm: 0.68 (d, J=6.7 Hz, 3H), 0.8 (d, J=6.7 Hz, 3H), 0.89 (t, J=7.4 Hz, 3H), 1.24 (sext, J=7.5 Hz, 2H), 1.76 (pent, J=7.3 Hz, 2H), 1.89 (m, J=6.7 Hz, 3.9 Hz, 1H), 2.64 (d, J=3.9 Hz, 1H), 3.88 (s, 3H), 4.19 (t, J=7.2 Hz, 2H), 7.78 (s, 1H), 7.85 (s, 1H), 9.93 (s, 1H)); NH_2 may appear as very broad signal around 1.5 ppm.
^{13}C{^{1}H} NMR (150.9 MHz, dmso-d_6) δ, ppm: 13.2; 17.0; 18.7; 20.6; 31.3; 31.6; 35.6; 48.3; 61.5; 122.2; 123.5; 137.2; 176.5.
HRMS (ESI): found m/z 139.1232; calculated for cation $C_8H_{15}N_2$ m/z 139.1230 (Δ=1.4 ppm).

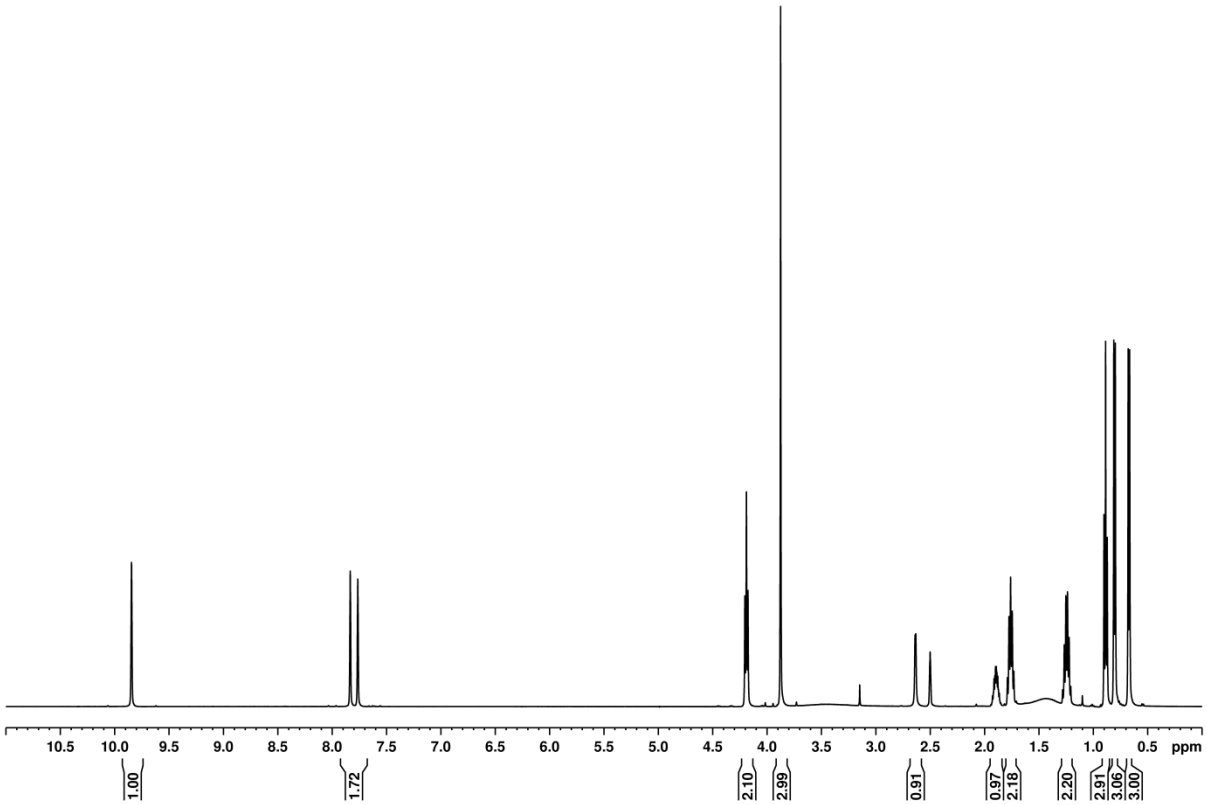

Figure S5. ^{1}H NMR spectrum of [BMIM][Val].

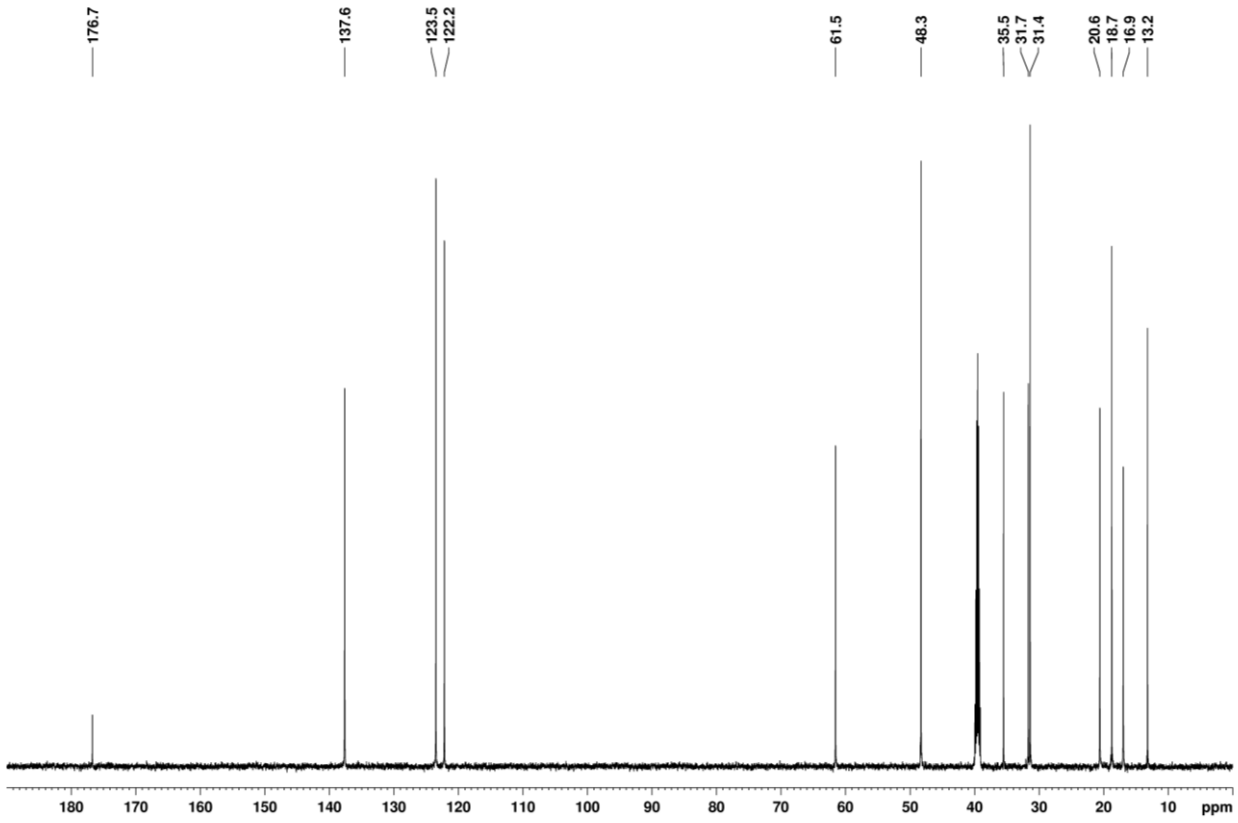

Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of [BMIM][Val].

O-Methylglycinate tetrafluoroborate ([Gly-OMe][BF_4])

Obtained 0.167 g (94%) light yellow oil, which crystallizes instantly.
^{1}H NMR (500 MHz, dmso-d_6) δ, ppm: 3.74 (s, 3H), 3.82 (s, 2H), 8.08 (br. s, NH_3)
$^{13}C\{^{1}H\}$ NMR (150.9 MHz, dmso-d_6) δ, ppm: 39.7, 52.6, 168.3
HRMS (ESI): found m/z 90.0556; calculated for cation $C_3H_8NO_2$ m/z 90.0550 (Δ=6.7 ppm).

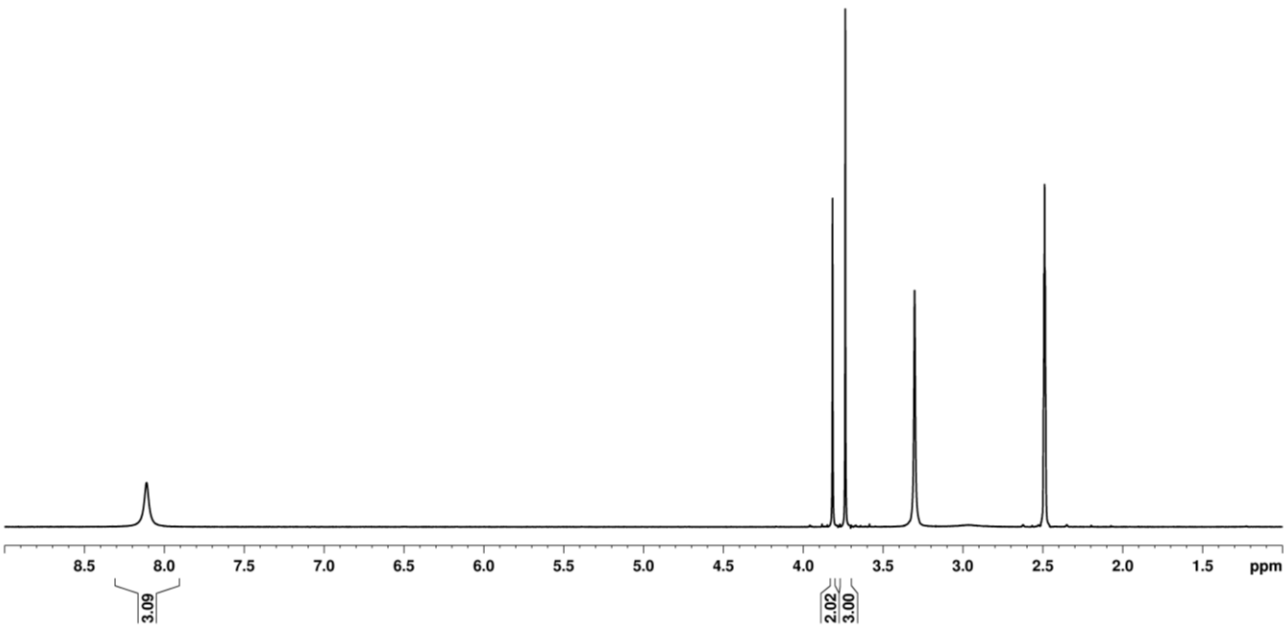

Figure S7. ^{1}H NMR spectrum of [Gly-OMe][BF_4].

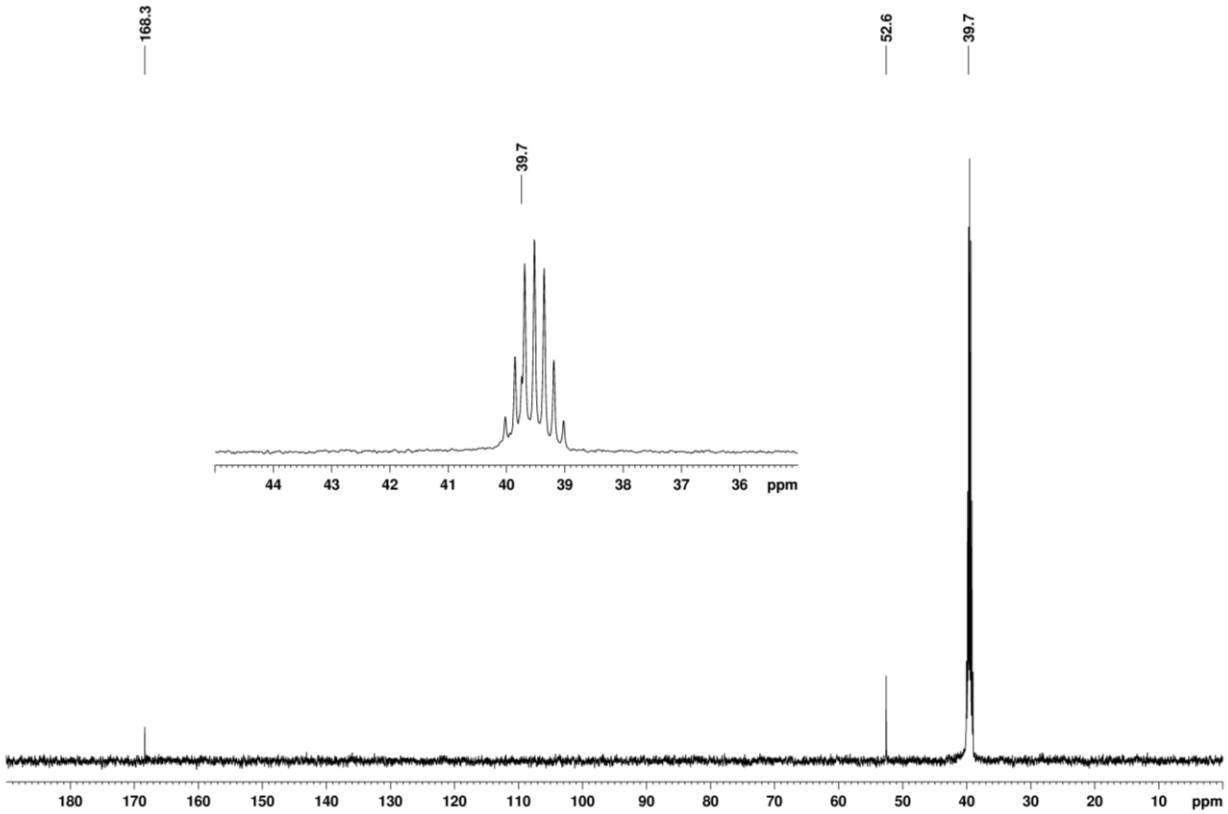

Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of [Gly-OMe][BF_4].

O-Methylalaninate tetrafluoroborate ([Ala-OMe][BF_4])

Obtained 0.176 g. (92%) light yellow oil, which crystallizes instantly.
^{1}H NMR (500 MHz, dmso-d_6) δ, ppm: 1.38 (d, J=7.2 Hz, 3H), 3.75 (s, 3H), 4.10 (q, J=7.2 Hz, 1H), 8.20 (br. s, 3H).
$^{13}C\{^{1}H\}$ NMR (128.5 MHz, dmso-d_6) δ, ppm 15.8, 48.0, 53.0, 170.5.
HRMS (ESI): found m/z 104.0709; calculated for cation $C_4H_{10}NO_2$ m/z 104.0706 (Δ=2.9 ppm).

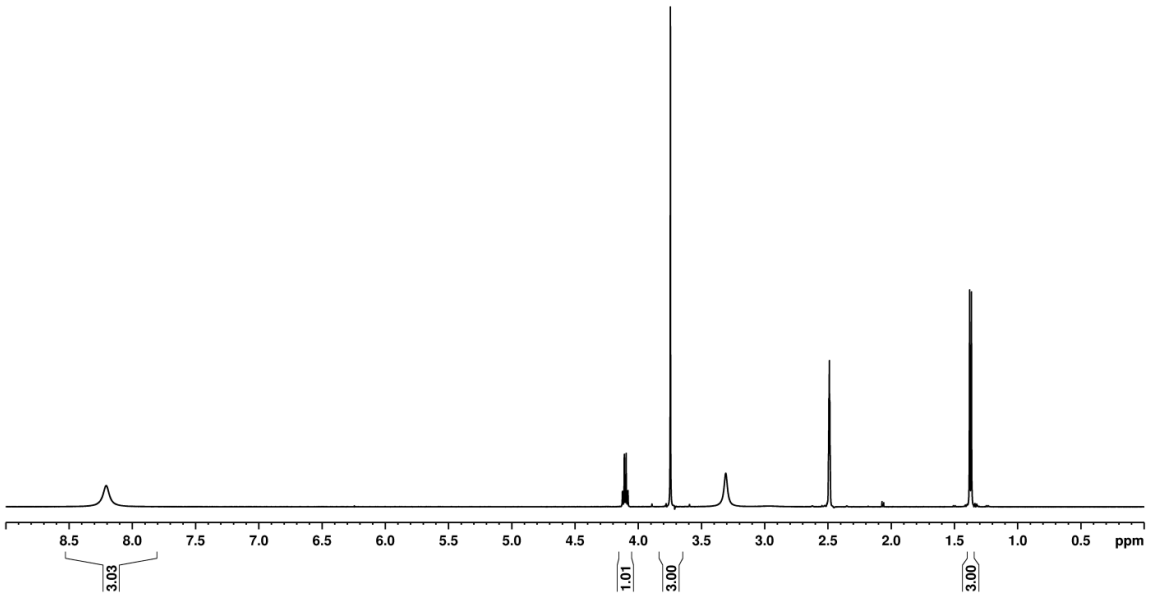

Figure S9. ^{1}H NMR spectrum of [Ala-OMe][BF_4].

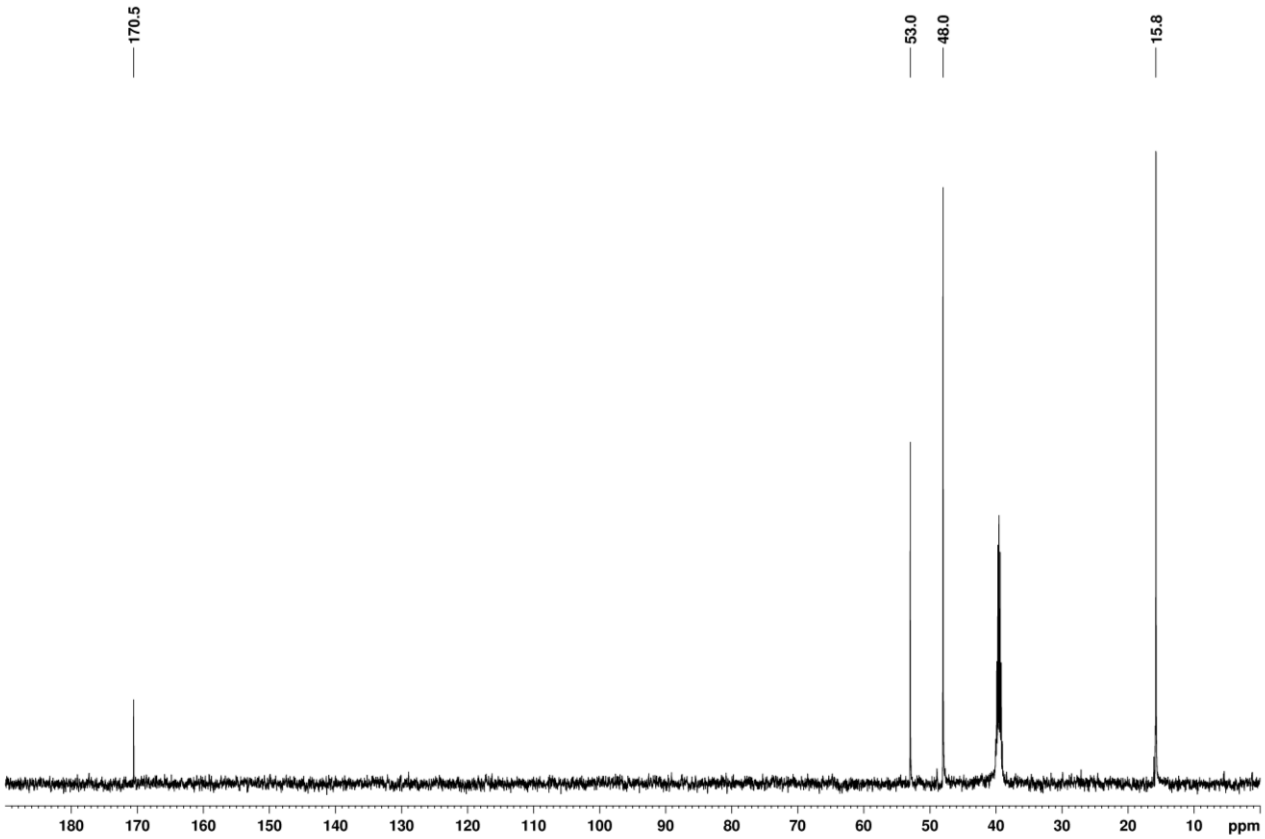

Figure S10. ^{13}C{^{1}H} NMR spectrum of [Ala-OMe][BF_4].

O-Methylvalinate tetrafluoroborate ([Val-OMe][BF_4])

Obtained 0.199 g (91 %) light oil, which crystallizes instantly.
^{1} H NMR (500 MHz, dmso-d_6) δ, ppm: 0.94 (d, J=6.7 Hz, 3H), 0.97 (d, J=6.7 Hz, 3H), 2.14 (dq, J=6.7 Hz, 4.8 Hz, 1H), 3.77 (s, 3H), 3.93 (d, J=4.8, 1H), 8.22 (br. s, 3H).
$^{13}C\{^1H\}$ NMR (128.5 MHz, dmso-d_6) δ, ppm: 17.6, 18.1, 29.4, 52.7, 57.4, 169.5.
HRMS (ESI): found m/z 132.1021; calculated for cation $C_6H_{14}NO_2$ m/z 132.1019 (Δ=1.5 ppm).

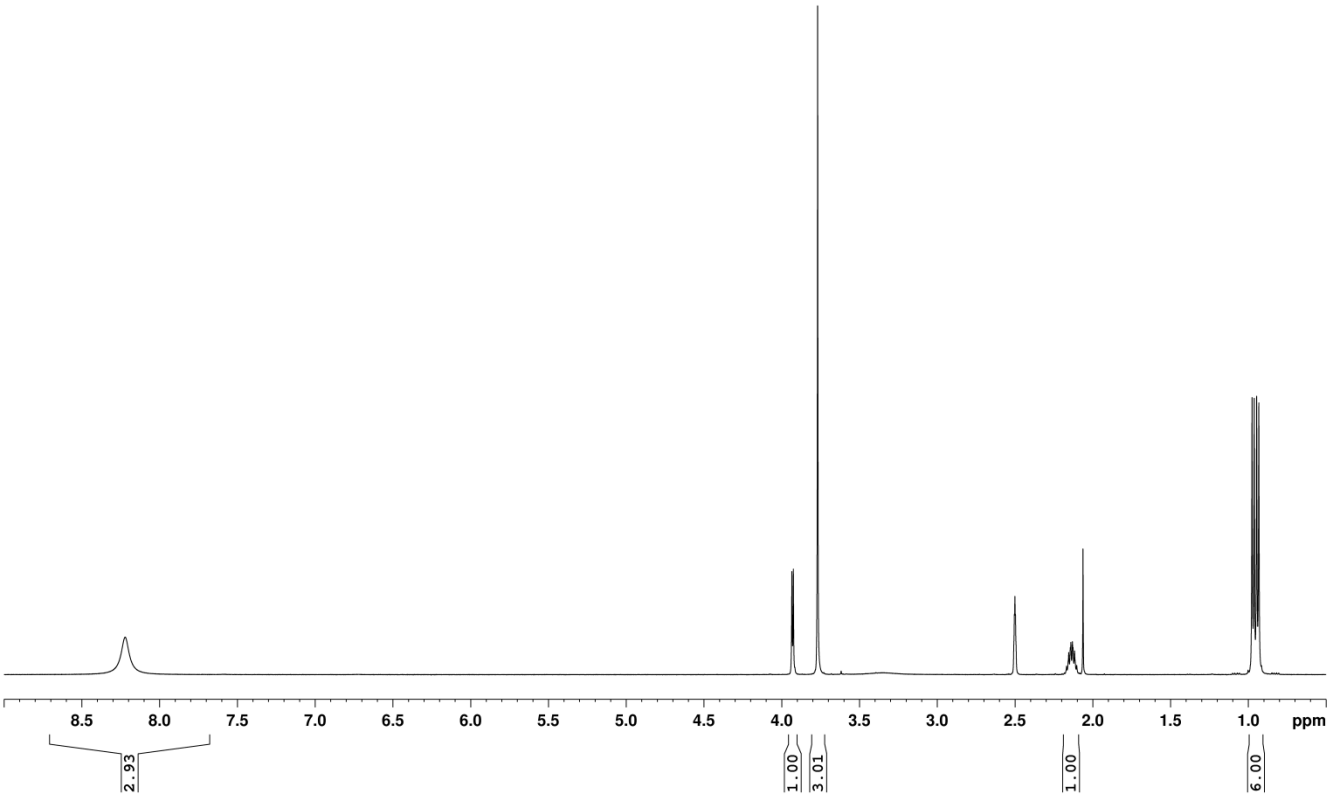

Figure S11. ^{1}H NMR spectrum of [Val-OMe][BF_4]. (residual organic solvent appears as a singlet at 2 ppm)

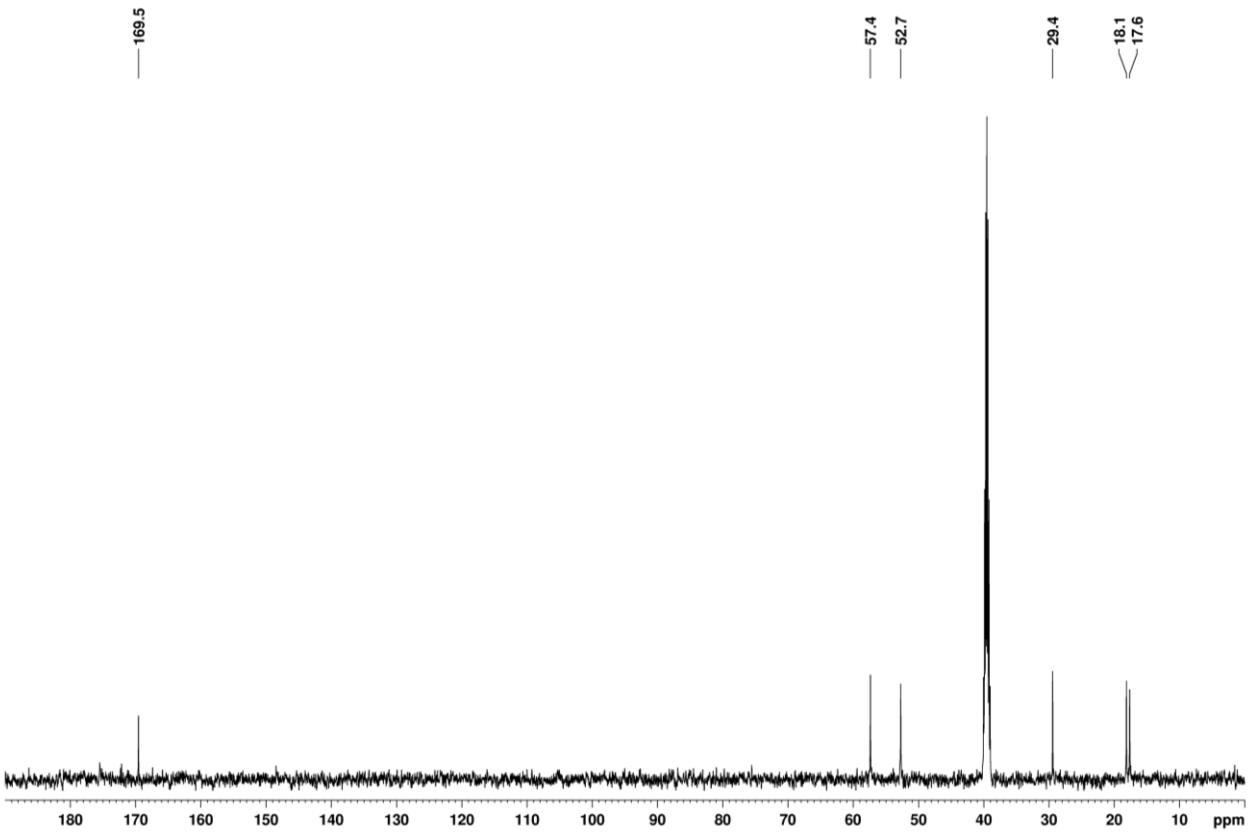

Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum of [Val-OMe][BF_4].

1-(2-(Glycyloxy)ethyl)-3-methylimidazolium tetrafluoroborate ([GlyO-EMIM][BF_4])

Obtained 0.493 g. (91%) beige powder

^{1} H NMR (500 MHz, dmso-d_6) δ, ppm: 3.83 (s, 2H), 3.88 (s, 3H), 4.50 (s, 4H), 7.73 (s, 1H), 7.83 (s, 1H), 8.48 (br. s, 2H), 9.28 (s, 1H).

$^{13}C\{^{1}H\}$ NMR (125.8 MHz, dmso-d_6) δ, ppm: 35.9; 39.7; 47.8; 63.5; 122.7; 123.6; 137.3; 167.3.

Confirmed according to the literature data.[3]

HRMS (ESI): found m/z 184.1082; calculated for cation $C_8H_{14}N_3O_2$ m/z 184.1081 (Δ=0.5 ppm).

[3] Debdab, M.; Mongin, F.; Bazureau, J.P. *Synthesis*, 2006, **23**, 4046.

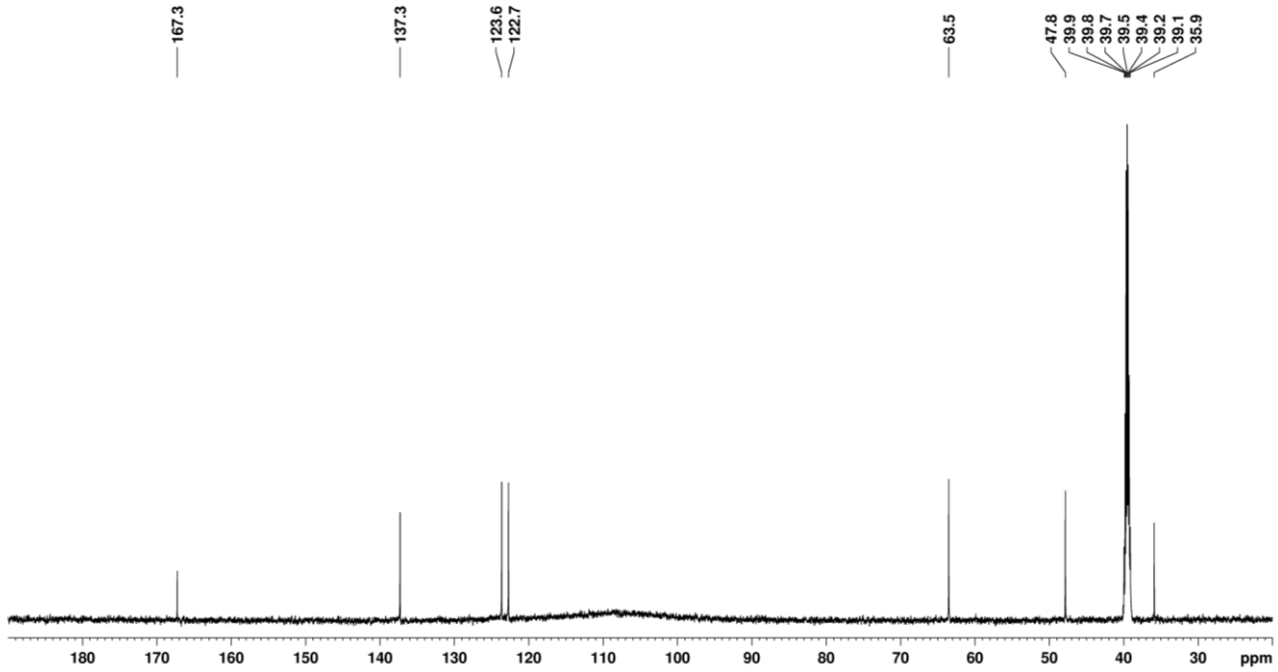

Figure S13. $^{13}C\{^{1}H\}$ NMR spectrum of [GlyO-EMIM][BF_4].

1-(2-Hydroxyethyl)-3-methylimidazolium tetrafluoroborate ([EMIMOH][BF_4])

Obtained 0.393 g (92%) yellow oil.
^{1}H NMR (500 MHz, dmso-d_6) δ, ppm: 3.72 (q, J=5 Hz, 2H), 3.86 (s, 3H), 4.21 (t, J=5 Hz, 2H), 5.13 (t, J=5 Hz, 1H), 7.67 (s, 1H), 7.70 (s, 1H), 9.06 (s, 1H).
$^{13}C\{^{1}H\}$ NMR (150.9 MHz, dmso-d_6) δ, ppm: 35. 7, 51.7, 59.3, 122.7, 123.3, 136.8.
Confirmed according to the literature data.[4]
HRMS (ESI): found m/z 127.0870; calculated for cation $C_6H_{11}N_2O$ m/z 127.0866 (Δ=3.2 ppm).

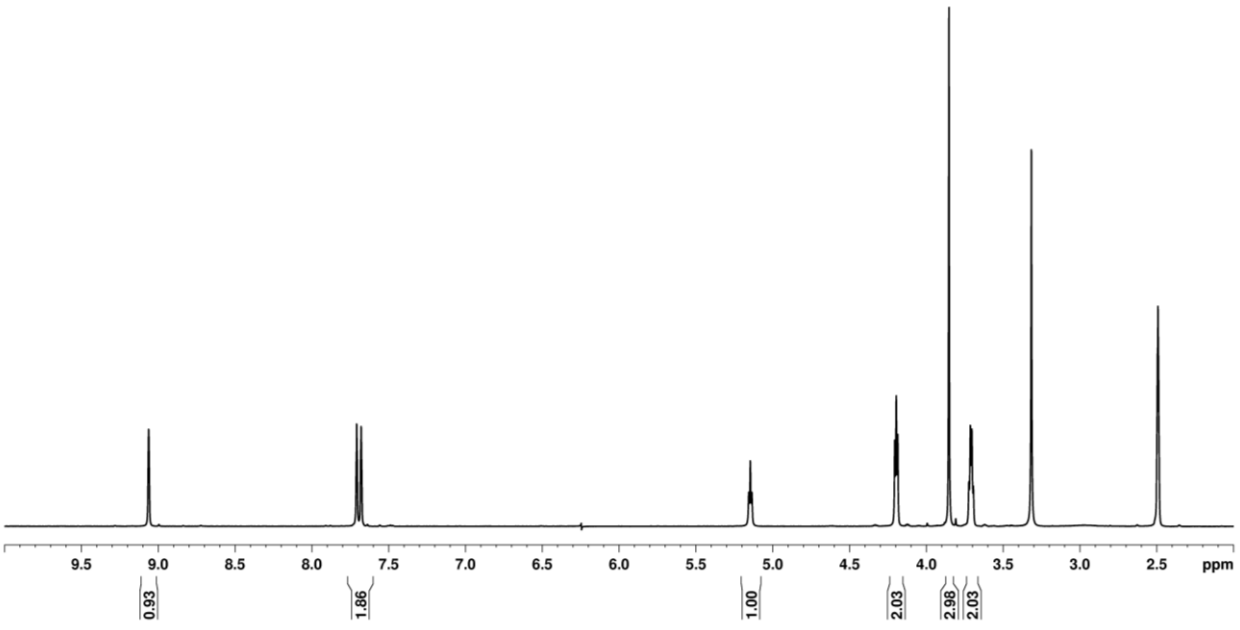

Figure S14. ^{1}H NMR spectrum of [EMIMOH][BF_4].

[4] L. C. Branco, J. N. Rosa, J. J. Moura Ramos and C. A. Afonso, *Chem.-Eur. J.*, 2002, **8**, 3671.

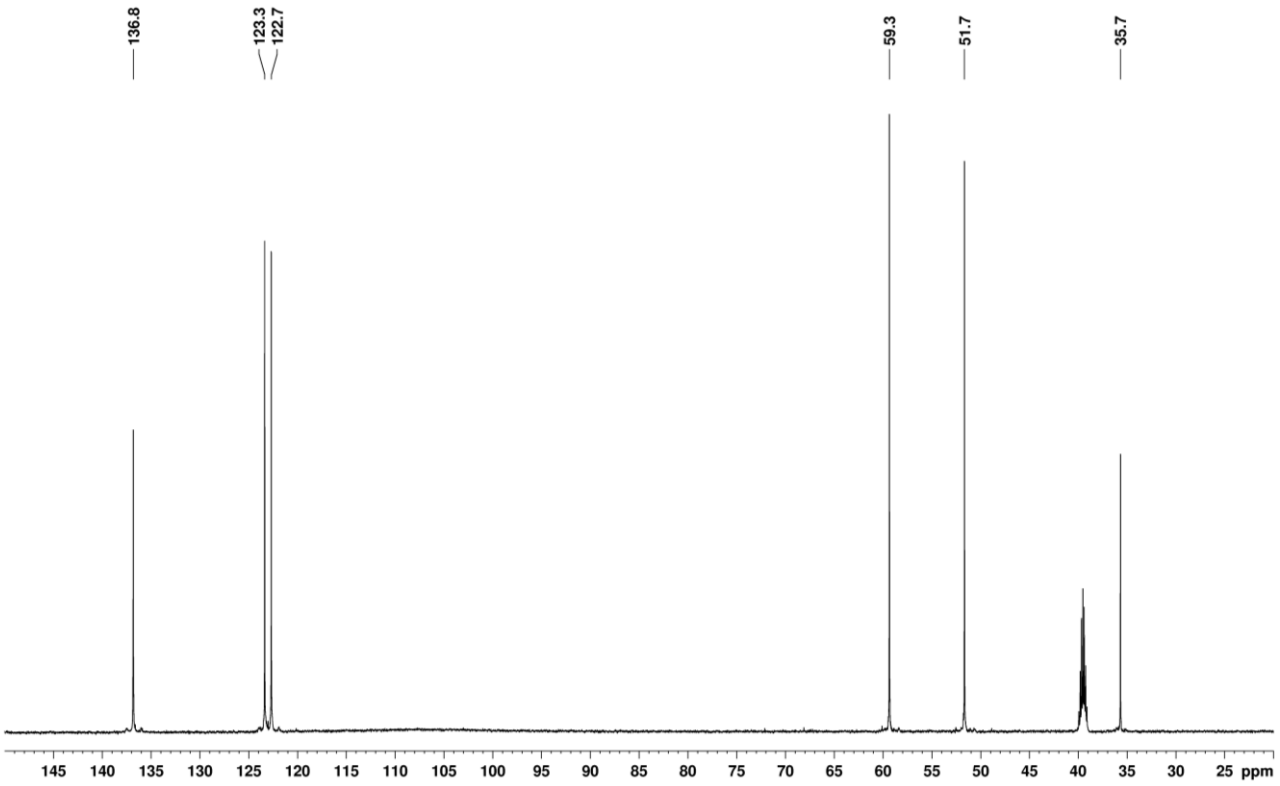

Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum of [EMIMOH][BF_4].