

Hydrothermal Decarboxylation of Amino Acid derived Imidazolium Zwitterions: A Sustainable Approach towards Ionic Liquids

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Materials and Methods

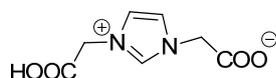
All chemicals were used as supplied. ^1H - and ^{13}C -NMR spectra were measured on a Bruker Spectrospin 400 MHz Ultrashield Spectrometer in deuterated solvents, with chemical shifts referenced to the residual solvent signals unless otherwise stated. ESI - Mass Spectra were recorded on a Thermo Scientific Velos Pro LC-MS (linear ion trap). Infrared spectra were recorded on a ThermoScientific Nicolet iS5 FT-IR spectrometer at a resolution of 4 cm^{-1} and 16 scans. Differential scanning calorimetry was performed on a Mettler-Toledo DSC1 Stare System. The samples were preheated at $130\text{ }^\circ\text{C}$ for 3h to evaporate off possible residual water, then cooled to $-50\text{ }^\circ\text{C}$ and heated to $130\text{ }^\circ\text{C}$ at a rate of 10 K/min . Glass transition temperatures were determined as inflection points using Mettler Toledo STARe software V9.30. For samples with Tgs below $-50\text{ }^\circ\text{C}$ DSC was performed on a Netzsch DSC 204 with the same temperature gradient but cooling down to $-150\text{ }^\circ\text{C}$. Elemental analysis was performed using a varioMICRO V 1.4.1 from Elementar Analysensysteme GmbH. TEM images were recorded using a Zeiss EM 912 Ω microscope operated at an acceleration voltage of 120 kV . GC-MS analysis was performed using an Agilent Technologies 5975 gas chromatograph equipped with a MS detector and a capillary column (HP-5MS, 30 m , 0.25 mm , 0.25 micron). The temperature program started with an isothermal step at $50\text{ }^\circ\text{C}$ for 2 min , the temperature was then increased to $300\text{ }^\circ\text{C}$ with a rate of $30\text{ }^\circ\text{C/min}$ and maintained for 1 min . Qualitative analysis was performed with MS library NIST 08 database with a retention index allowance of ± 100 . Viscosity was measured on an Anton Paar AVM automated Microviscometer with 70° angle, with measuring system MS 1.6 and 3.0. Density was measured on an Anton Paar DMA 5000 density meter. Electrical conductivity was measured on a Gamry Interface 1000 Potentiostat. TGA analysis was performed on a Netzsch TG209 F1 Libra coupled to a Pfeiffer vacuum Quadrupole Mass spectrometer with a heating rate of 5 K/min from 25 to $600\text{ }^\circ\text{C}$. Water content was determined using a Metrohm 756 KF Coulometer. Hydrothermal decarboxylation was performed on a ThalesNano X-Cube Flash flow reactor. Cellulose dissolution was assessed using a Linkam THMS 600 hot stage on a Hengtech NP-400 polarisation microscope without the polarization filter at $10\times$ magnification.

General procedure for the One-Pot synthesis of imidazolium zwitterions (a)

In a typical experiment dicarbonyl compound (pyruvaldehyde, glyoxal or butadione, 10 mmol), amino acid (20 mmol), formaldehyde (10 mmol) and acetic acid (60 mmol) were combined in 20 mL water and stirred at the desired temperature for a specified time. An aliquot was collected and analysed by NMR to quantify the yield. The mixture was freeze-dried unless otherwise stated.

Characterisation of imidazolium zwitterions

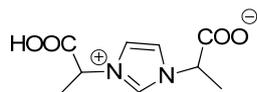
(1-ethanoyl-imidazol-1-ium)-acetate (SI1)



Following the general procedure **a** described above, **SI1** was obtained quantitatively (NMR) after stirring overnight at RT. The reaction mixture was then freeze-dried and the residue washed with MeOH to afford pure **SI1** in 98.2 % yield (1.807 g, 9.81 mmol).

$^1\text{H-NMR}$ (400 MHz, D_2O) δ_{H} 8.87 (s, 1H, ArH), 7.53 (s, 2H, ArH), 5.02 (s, 4H, CH_2); $^{13}\text{C-NMR}$ (101 MHz, D_2O) δ_{C} 170.88, 137.74, 123.33, 50.99; IR $\nu_{\text{max}}/\text{cm}^{-1}$ = 3158 (C-H), 3022 (C-O), 1661 (C=O), 1167 (OH), 680; ESI-MS (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_7\text{H}_9\text{N}_2\text{O}_4^+$: 185.06, found, 185.05; Elemental Analysis (calcd., found for $\text{C}_7\text{H}_8\text{N}_2\text{O}_4$): C, 45.66, 45.39; H, 4.38, 4.19; N, 15.21, 15.03.

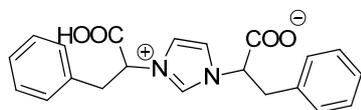
2-(1-((methyl)carboxymethyl)-imidazol-1-ium)-propanoate (**SI2**)



Following general procedure **a**, **SI2** was obtained in 67 % yield (1.42 g, 6.69 mmol) after stirring at room temperature overnight, freeze-drying and recrystallisation from hot H_2O .

$^1\text{H-NMR}$ (400 MHz, D_2O) δ_{H} 9.00 (s, 1H, ArH), 7.60 (s, 2H, ArH), 5.28 – 4.77 (m, 2H, CH), 1.83 (d, J = 7.4 Hz, 6H, Me); $^{13}\text{C-NMR}$ (101 MHz, D_2O) δ_{C} 173.80, 135.41, 121.67, 59.13, 17.18; ESI-MS (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_9\text{H}_{13}\text{N}_2\text{O}_4^+$: 213.09, found, 213.65; IR $\nu_{\text{max}}/\text{cm}^{-1}$ = 3144 (C-H), 2960 (C-O), 1682 (C=O), 1171 (OH), 662; Elemental analysis: (calcd., found for $\text{C}_9\text{H}_{12}\text{N}_2\text{O}_4$): C, 50.94, 51.55; H, 5.70, 5.52; N, 13.20, 13.37.

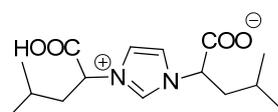
2-(1-((benzyl)carboxymethyl)-imidazol-1-ium)-3-phenylpropanoate (**SI3**)



Glyoxal (5 mmol), phenylalanine (10 mmol), formaldehyde (5 mmol) and acetic acid (30 mmol) were combined in 20 mL H_2O and stirred at 65 °C for 3h until **SI3** precipitated as a white solid. The precipitate was washed with water and dried. The supernatant was decanted and extracted with chloroform, and concentrated in vacuo. The combined residues accounted for the formation of **SI3** in 54 % yield (1.96 g, 5.38 mmol).

$^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ_{H} 9.36 (s, 1H, ArH), 7.46 (s, 2H, ArH), 7.20 – 7.13 (m, 6H, Ph), 6.97 – 6.92 (m, 4H, Phe), 5.22 (dd, J = 11.3, 4.0 Hz, 2H, CH), 3.48 (dd, J = 14.6, 4.0 Hz, 2H, CH_2), 3.19 (dd, J = 14.6, 11.3 Hz, 2H, CH_2); $^{13}\text{C-NMR}$ (101 MHz, DMSO) δ_{C} 168.70, 136.46, 136.35, 128.58, 128.39, 126.66, 121.45, 64.61, 38.18; ESI-MS (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{21}\text{H}_{21}\text{N}_2\text{O}_4^+$: 365.15, found, 365.57; IR $\nu_{\text{max}}/\text{cm}^{-1}$ = 3139 (C-H), 1675 (C=O), 1243 (C=N aromatic), 715, 697; Elemental analysis: (calcd., found for $\text{C}_{21}\text{H}_{21}\text{N}_2\text{O}_4$): C, 69.22, 68.62; H, 5.53, 5.52; N, 7.69, 7.64.

2-(1-((isobutyl)carboxymethyl)-imidazol-1-ium)-4-methyl-pentanoate (**SI4**)

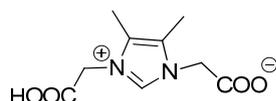


The reaction was performed following procedure **a**, with heating at 65 °C for 3 h. A white precipitate formed upon cooling down of the reaction mixture, which did not dissolve in common deuterated

solvents. The precipitate was washed with ACN and EtOH and filtered, affording **SI4** in 40 % yield (1.16 g, 3.9 mmol)

Elemental analysis: (calcd., found for $C_{15}H_{24}N_2O_4$): C, 60.79, 57.82; H, 8.16, 8.39; N, 9.54, 9.45; IR ν_{max}/cm^{-1} = 2957 (C-H), 1555 (C=O), 1174 (OH), 685, 669.

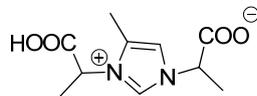
(1-ethanoyl-4, 5-dimethyl-imidazol-1-ium)-acetate (SI5)



Following procedure **a**, the reaction was performed at 50 °C for 2 h, with a yield of 70.5 % (NMR). The reaction mixture was freeze-dried and the residue redissolved in a small amount of water. THF was slowly added at room temperature until precipitation occurred affording **SI5** in 51.3 % yield (1.09 g, 5.1 mmol).

1H -NMR (400 MHz, D_2O) δ_H 8.68 (s, 1H, ArH), 4.91 (s, 4H, CH_2), 2.22 (s, 6H, Me); ^{13}C NMR (101 MHz, D_2O) δ_C 171.14, 135.41, 127.67, 48.62, 7.27; ESI-MS (m/z): $[M+H]^+$ calcd. for $C_9H_{13}N_2O_4^+$: 213.09, found 213.09; IR = 2998 (C-H), 1694 (C=O), 1335(C=N ar), 1200 (OH), 697; EA (calcd., found for $C_9H_{12}N_2O_4$): C, 50.94,50.07; H, 5.70, 5.332; N,13.20,12.78.

2-(1-((methyl)carboxymethyl)-4-methyl-imidazol-1-ium)- propanoate (SI6)



Following procedure **a**, the reaction mixture was stirred at room temperature overnight, which yielded 87 % as judged by NMR. The reaction mixture was freeze-dried and the product was recrystallised from hot H_2O yielding pure **SI6** in 53.3 % yield (1.21 g, 5.3 mmol).

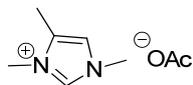
1H NMR (400 MHz, D_2O) δ_H 8.87 (s, 1H, ArH), 7.34 (s, 1H, ArH), 5.13 (q, J = 7.4 Hz, 1H, CH), 5.01 (q, J = 7.3 Hz, 1H, CH), 2.25 (s, 3H, Me), 1.81 (dd, J = 12.1, 7.3 Hz, 6H, Me); ^{13}C NMR (101 MHz, D_2O) δ_C 174.18, 173.82, 133.89, 131.84, 118.79, 58.83, 56.89, 17.04, 16.63, 8.31; ESI-MS (m/z): $[M+H]^+$ calcd. for $C_{10}H_{15}N_2O_4^+$: 227.10, found, 227.22; IR ν_{max}/cm^{-1} = 3409 (C-H), 3068 (O-H), 1619 (C=O), 1167 (CO), 682; Elemental analysis: (calcd., found for $C_{10}H_{14}N_2O_4$): C, 53.09, 51.27; H, 6.24, 6.33; N, 12.38, 11.93.

General procedure for the hydrothermal decarboxylation of zwitterionic imidazolium compounds (b)

Decarboxylations were performed using a flow reactor (X-Cube Flash, Thales Nano) equipped with a 4 mL Hastelloy reaction loop. After equilibrating the system at the desired temperature over a period of 2 min, 5 mL of a solution of the desired zwitterionic compound with 2 equivalents of acetic acid were injected and allowed to react at optimised concentration, temperature and pressure settings (table 1). The residence time was controlled by adjusting the flow rate. At the end of the reaction, the eluate was collected by an autosampler.

Characterisation of ionic liquids

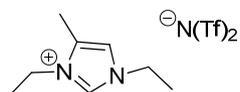
1,3-dimethyl-4-methyl-imidazolium acetate (1)



Compound **1** was obtained following general procedure **b**, using a 0.25 M Gly-pyruvaldehyde zwitterion¹ solution (1.25 mmol). The reaction mixture was washed 3 times with diethyl ether and freeze-dried, affording **1** in 90 % yield (0.19 g, 1.13 mmol).

¹H-NMR (D₂O) δ_{H} 8.490 (s, 1H, ArH), 7.114 (s, 1H, ArH), 3.780 (s, 3H, Me), 3.711 (s, 3H, Me), 2.246 (s, 3H, Me), 1.888 (s, 3H, MeCOO); ¹³C-NMR (D₂O) δ_{C} 135.641, 132.124, 119.998, 35.290, 32.741, 7.933 ppm; IR $\nu_{\text{max}}/\text{cm}^{-1}$ = 3340 (C-H), 1615 (C=O), 1387 (C=C ring), 1187 (C-N ring), 599.

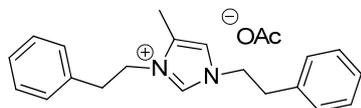
1,3-diethyl-4-methyl-imidazolium bis(trifluoromethane)sulfonamide (2)



Using a 0.125 M Ala-pyruvaldehyde zwitterion¹ solution (0.625 mmol), the acetate of **2** was obtained via procedure **b**. The reaction mixture was freeze-dried and redissolved in a small amount of water. A slight excess of lithium bistriflimide was added and stirred at room temperature for an hour, during which the product precipitated from solution as an oil. The supernatant was decanted and the product washed twice with water and then dried in vacuo, to obtain **2** in 65.4 % yield (0.17 g, 0.41 mmol).

¹H-NMR (400 MHz, DMSO-*d*₆) δ_{H} 9.07 (d, *J* = 1.8 Hz, 1H, ArH), 7.54 (s, 1H, ArH), 4.12 (dq, *J* = 12.2, 7.3 Hz, 4H, CH₂), 2.29 (d, *J* = 1.2 Hz, 3H, Me), 1.39 (tdd, *J* = 7.4, 3.2, 1.1 Hz, 6H, Me); ¹³C-NMR (101 MHz, DMSO-*d*₆) δ_{C} 134.73, 130.69, 121.06, 118.88, 117.86, 44.00, 41.46, 14.97, 14.46, 8.46; IR $\nu_{\text{max}}/\text{cm}^{-1}$ = 3369 (C-H), 3358 (C-H), 1452 (C=C ring), 1329 (C-H), 1052 (C-N ring); EA (calcd.; found for C₁₀H₁₅F₆N₃O₄S₂): C 28.64; 26.18, H: 3.61, 2.92, N: 10.02, 10.61.

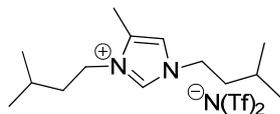
1,3-di(2-phenylethyl)-4-methylimidazolium acetate (3)



After decarboxylation of a 0.05 M Phe-pyruvaldehyde¹ zwitterion solution (0.25 mmol) following procedure **b** the reaction mixture was extracted with chloroform and dried by evaporation. The residue was redissolved in water to precipitate possible side products. The supernatant was freeze-dried and excess acetic acid was removed under vacuum, to obtain **3** in 89 % yield (0.078 g, 0.22 mmol).

¹H-NMR (400 MHz, DMSO-*d*₆) δ_{H} 9.143 (s, 1H, ArH), 7.442 (s, 1H, ArH), 7.38 – 7.07 (m, 10H, Ph), 4.34 (dt, *J* = 23.8, 7.2 Hz, 4H, CH₂), 3.04 (dt, *J* = 26.2, 7.2 Hz, 4H, CH₂), 2.046 (s, 3H, Me), 1.68 (s, 3H, MeCOO); ¹³C-NMR (101 MHz, DMSO-*d*₆) δ_{C} 173.15, 136.84, 136.19, 130.72, 128.81, 128.63, 128.54, 126.88, 126.80, 119.01, 49.49, 47.22, 35.36, 24.03, 8.26; ESI-MS (*m/z*): [M]⁺ calcd. for C₂₀H₂₃N₂⁺, 291.19; found, 291.87; IR $\nu_{\text{max}}/\text{cm}^{-1}$ = 3002 (C-H), 1651 (C=O), 1571 (C=C ring), 1213 (C-N ring), 749.

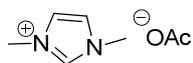
1,3-di(3-methylbutyl)-4-methyl-imidazolium bis(trifluoromethane)sulfonimide (4)



Following procedure **b** and using a Leu-pyruvaldehyde zwitterion¹ concentration of 0.03 M (0.15 mmol) the acetate of **4** was obtained in 41 % yield as assessed by NMR. The reaction mixture was washed 3 times with diethyl ether and freeze-dried. The residue was redissolved in water and an aqueous solution of lithium bistriflimide was added. The mixture was stirred overnight at room temperature. When the stirring was stopped, the product precipitated as an oil and was washed with H₂O to obtain **4** in 17.9 % (0.013 g, 0.027 mmol).

¹H-NMR (400 MHz, DMSO-*d*₆) δ_H 9.12 (s, 1H, ArH), 7.55 (s, 1H, ArH), 4.10 (dt, *J* = 15.4, 7.6 Hz, 4H, CH₂), 2.292 (s, 3H, Me), 1.89 – 1.54 (m, 4H, CH₂), 1.54-1.44 (m, 2H, CH), 0.92 (ddd, *J* = 11.4, 6.5, 1.1 Hz, 12H, Me); ¹³C-NMR (101 MHz, DMSO-*d*₆) δ_C 135.34, 130.78, 124.26, 121.06, 119.25, 117.86, 114.66, 47.09, 44.65, 39.94, 37.96, 37.48, 25.05, 24.76, 22.01, 21.93, 8.50; ESI-MS (*m/z*): [M]⁺ calcd. for C₁₄H₂₇N₂⁺, 223.22; found, 223.54; IR ν_{max}/cm⁻¹ = 3141 (C-H), 2939 (C-H ring), 1470 (C=C ring), 1347 9 (C-N ring), 1053; EA (calcd.; found for C₁₆H₂₇F₆N₃O₄S₂): C 38.17, 36.72; H 5.40, 4.830; N 8.35, 8.66.

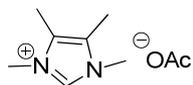
1,3-dimethyl-imidazolium acetate (5)



Following procedure **b** and using a Gly-glyoxal zwitterion concentration of 0.25 M (1.25 mmol), decarboxylation afforded **5** quantitatively as judged by NMR. The reaction mixture was freeze-dried, redissolved in a small amount of ethanol and poured into diethyl ether to obtain **5** as a precipitate in 95.9 % (0.19 g, 1.20 mmol).

¹H-NMR (400 MHz, D₂O) δ_H 8.64 (s, 1H, ArH), 7.41 (s, 2H, ArH), 3.88 (s, 6H, Me), 1.94 (s, 3H, MeCOO); ¹³C-NMR (101 MHz, D₂O) δ_C 180.56, 123.31, 35.52, 22.79; IR ν_{max}/cm⁻¹ = 3352 (C-H), 3099 (C-H ring), 1563 (C=C ring), 1392 (C-N ring), 712.

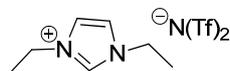
1,3-dimethyl-4,5-methyl-imidazolium acetate (6)



Following procedure **b** and using a Gly-butadione zwitterion concentration of 0.125 M (0.625 mmol), decarboxylation afforded **6** quantitatively as judged by NMR. The reaction mixture was freeze-dried, redissolved in a small amount of ethanol and poured into diethyl ether, which caused the compound to precipitate. Excess acetic acid was removed under vacuum, to obtain **6** in 98 % yield (0.113 g, 0.61 mmol).

$^1\text{H-NMR}$ (400 MHz, D_2O) δ_{H} 8.44 (s, 1H, ArH), 3.71 (s, 6H, Me), 2.21 (s, 6H, Me), 1.92 (s, 3H, MeCOO); $^{13}\text{C-NMR}$ (101 MHz, D_2O) δ_{C} 179.97, 133.91, 127.33, 32.82, 22.41, 7.22; IR $\nu_{\text{max}}/\text{cm}^{-1}$ = 3276 (C-H), 1557 (C=C ring), 1393 (C-N), 1261 (C-O), 603.

1,3-diethyl-imidazolium bis(trifluoromethane)sulfonamide (7)



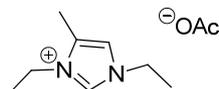
Following procedure **b** with a Ala-glyoxal zwitterion concentration of 0.125 M (0.625 mmol), hydrothermal decarboxylation proceeded in 21 % yield as assessed by NMR. The reaction mixture was freeze-dried and redissolved in a small amount of water. An aqueous solution of lithium bistriflimde was added and stirred at room temperature for 1 hour after which **7** precipitated from solution in 12.5 % yield (0.032 g, 0.078 mmol).

$^1\text{H-NMR}$ (400 MHz, DMSO-d_6) δ_{H} 9.17 (s, 1H, ArH), 7.78 (s, 2H, ArH), 4.19 (q, J = 7.3 Hz, 4H, CH_2), 1.43 (t, J = 7.3 Hz, 6H, Me); $^{13}\text{C-NMR}$ (101 MHz, DMSO-d_6) δ_{C} 135.35, 124.27, 122.07, 121.07, 117.87, 114.67, 44.18, 14.97; IR $\nu_{\text{max}}/\text{cm}^{-1}$ = 3118 (C-H), 1382 (C=C ring), 1178 (C-N ring), 1132, 739; Elemental analysis: (calcd., found for $\text{C}_9\text{H}_{13}\text{F}_6\text{N}_3\text{O}_4\text{S}_2$): C, 26.67, 26.18; H, 3.23, 2.92; N, 10.37, 10.61.

Synthesis of ILs **8** and **2** from ethylamine using the Debus-Radziszewski reaction

Pyruvaldehyde (50 mmol, 7.7 mL of 40 % aq solution), ethylamine (100 mmol, 7.9 mL of 70 % aq solution), formaldehyde (50 mmol, 3.7 mL 37 % aq solution) and acetic acid (300 mmol, 17.14 mL) were dissolved in 64 mL water and stirred at room temperature for 2 hours. The reaction mixture was freeze-dried and excess acetic acid was removed under high vacuum. The compound was redissolved in water and stirred with activated carbon at 65 °C for 3 days, filtered and the water removed by evaporation, to obtain **8** in 93 % yield (46.50 mmol, 9.22 g) after extensive drying. Compound **2** was obtained from **8** by redissolution in a small amount of H_2O , followed by the addition of an aqueous solution of lithium bis(trifluoromethane)sulfonimide (50 mmol, 14.35 g) under stirring at room temperature. **2** formed almost instantly and precipitated out of the water phase yielding pure IL in 88.1 % yield (44.04 mmol, 18.47 g). The product was washed twice with H_2O and dried in the vacuum oven over night before use.

1,3-diethyl-4 methylimidazolium acetate (8)

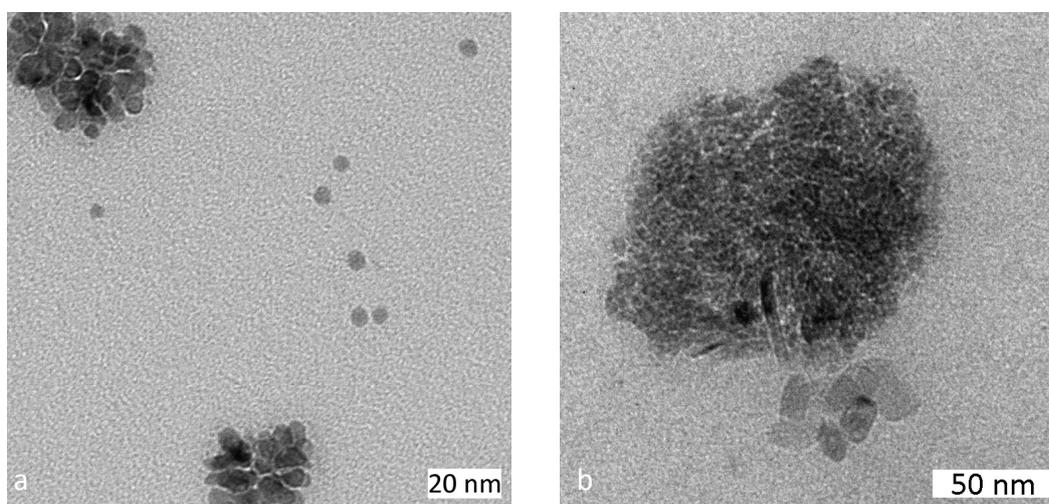


$^1\text{H-NMR}$ (400 MHz, D_2O) δ_{H} 8.62 (s, 1H, ArH), 7.21 (s, 1H, ArH), 4.11 (dq, J = 14.4, 7.3 Hz, 4H, CH_2), 2.28 (s, 3H, Me), 1.91 (s, 3H, MeCOO), 1.44 (td, J = 7.4, 1.9 Hz, 6H, Me); $^{13}\text{C-NMR}$ (101 MHz, D_2O) δ_{C} 180.19, 133.59, 131.52, 118.72, 44.50, 41.87, 22.68, 14.42, 14.01, 8.08. IR $\nu_{\text{max}}/\text{cm}^{-1}$ = 2977 (C-H), 1575 (C=C ring), 1378 (C-N ring), 1159 (C-O), 637.

General procedure for the Heck reaction (c)

$\text{Pd}(\text{OAc})_2$ (0.02 mmol, 4.5 mg) was dissolved in 4 mL of **2** and heated at 80 °C for 30 mins. The flask was conditioned with argon, and iodobenzene (10 mmol, 1.13 mL), triethylamine (14.3 mmol, 2.0 mL) and methyl acrylate (12.5 mmol, 1.13 mL) were added. The reaction was heated at 80 °C for 1 hour and at 100 °C for an additional 2.5 hours. The reaction mixture was extracted five times with toluene. The combined organic phases were evaporated to yield pure product. The IL phase was recycled without further purification. Alternatively, extraction with water followed by drying was used to remove excess ammonium salts prior to further utilisation.

TEM images of Pd-nanoparticles formed during the Heck reaction in the ionic liquid phase

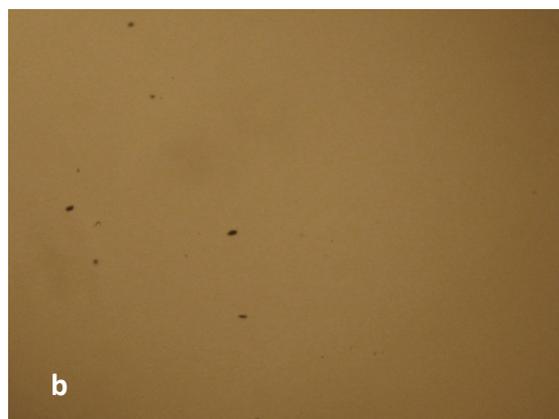
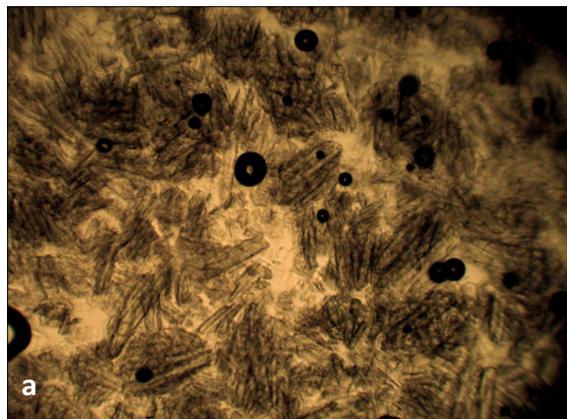


a) after 2nd run b) after 5th run

Dissolution of cellulose in ionic liquid

7.8 g of **8** were placed in a round bottom flask and microcrystalline cellulose (MCC) (0.3915 g, Aldrich) was added initially. The solution was stirred with a mechanical stirrer under air at 100 °C. As soon as the solution became visually clear, another aliquot of cellulose (0.2 g) was added. The process could be repeated until 16.9 wt% cellulose was dissolved. Dissolution was then confirmed at 10x magnification under a light microscope with a hot stage at 100 °C.

Light microscopy images of microcrystalline cellulose before and after dissolution in **8**.

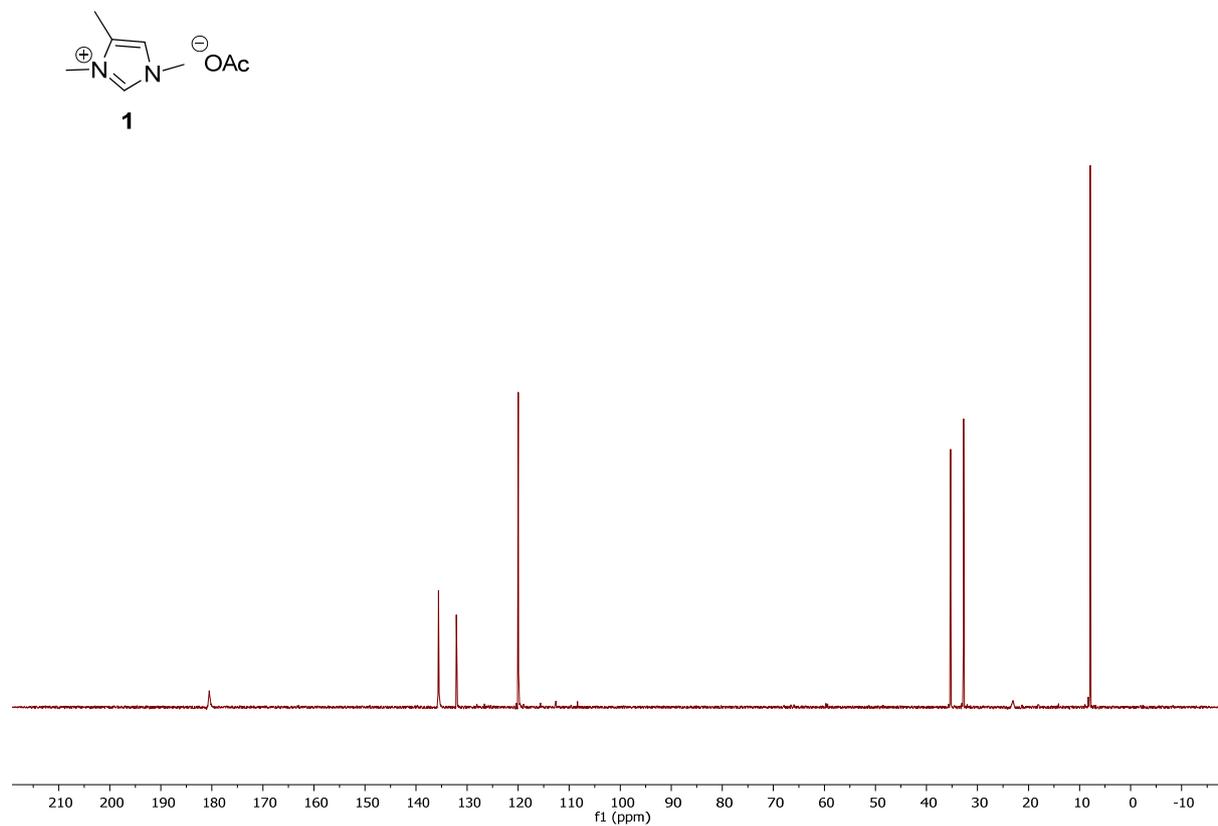
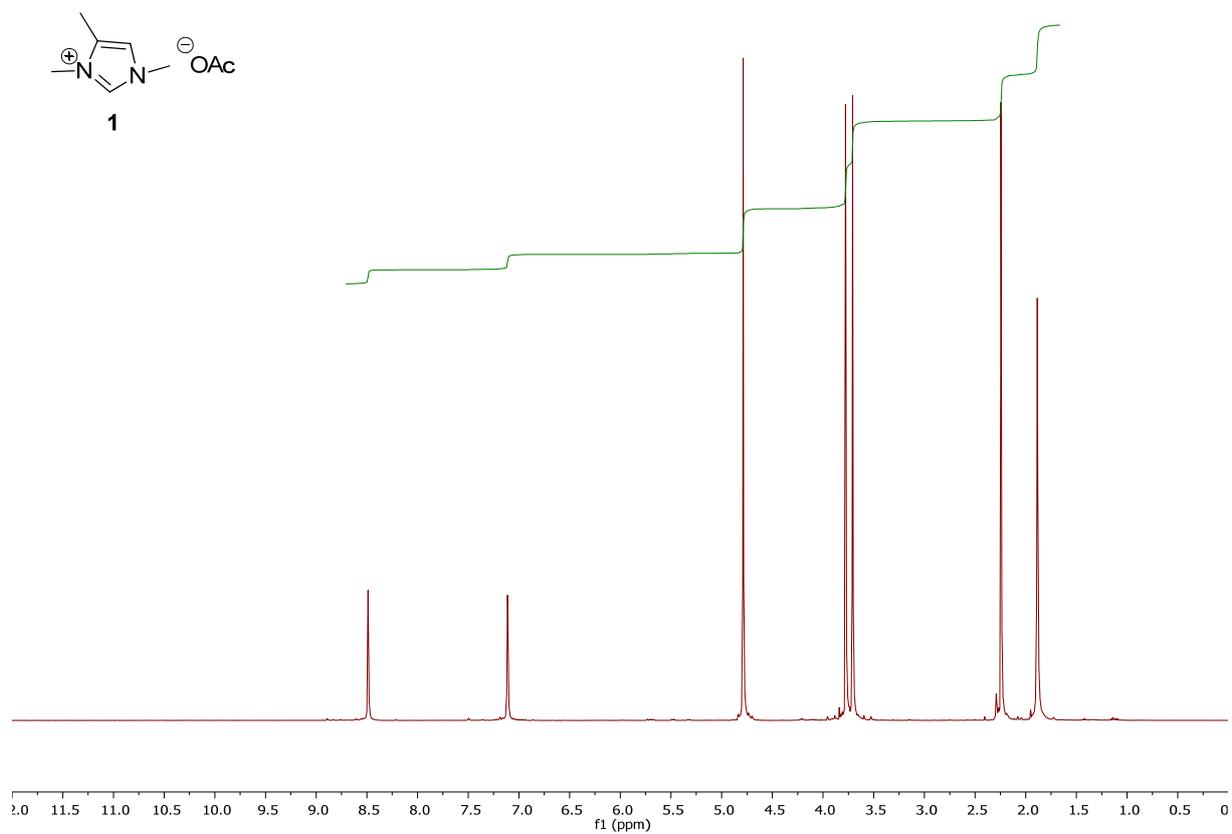


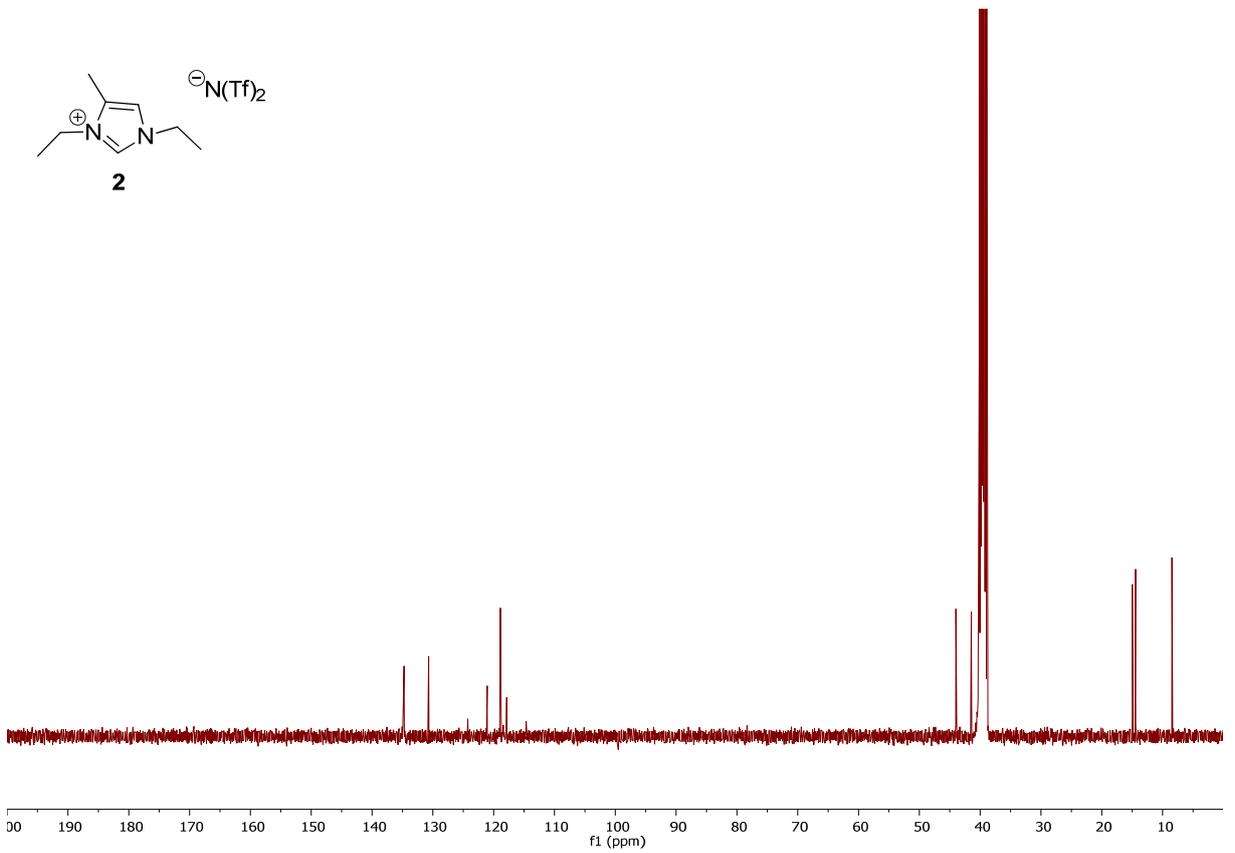
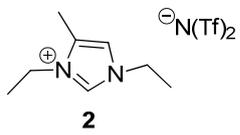
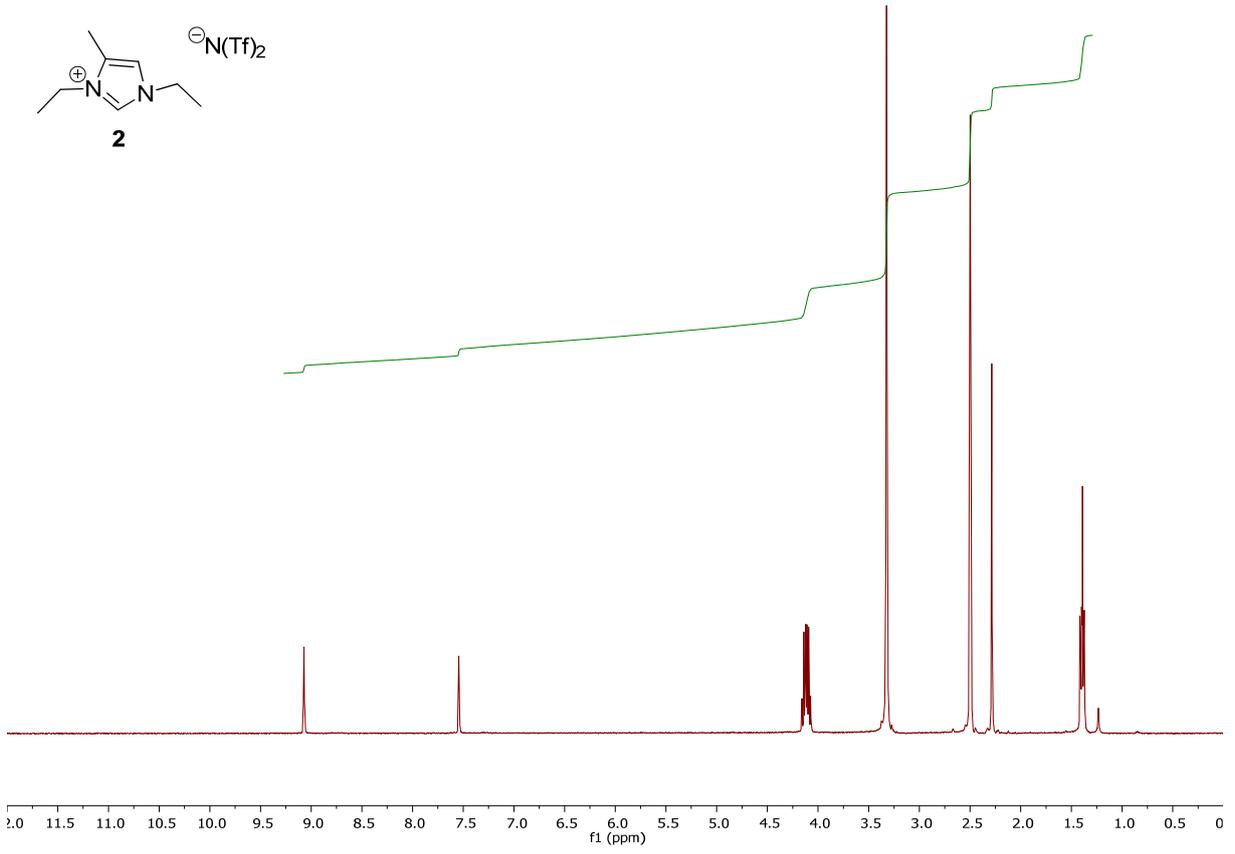
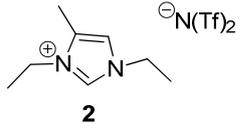
Microscope images of MCC in **8**, taken at 10x magnification. a) before, b) after dissolution at 100 °C. Some dust and air bubbles are visible.

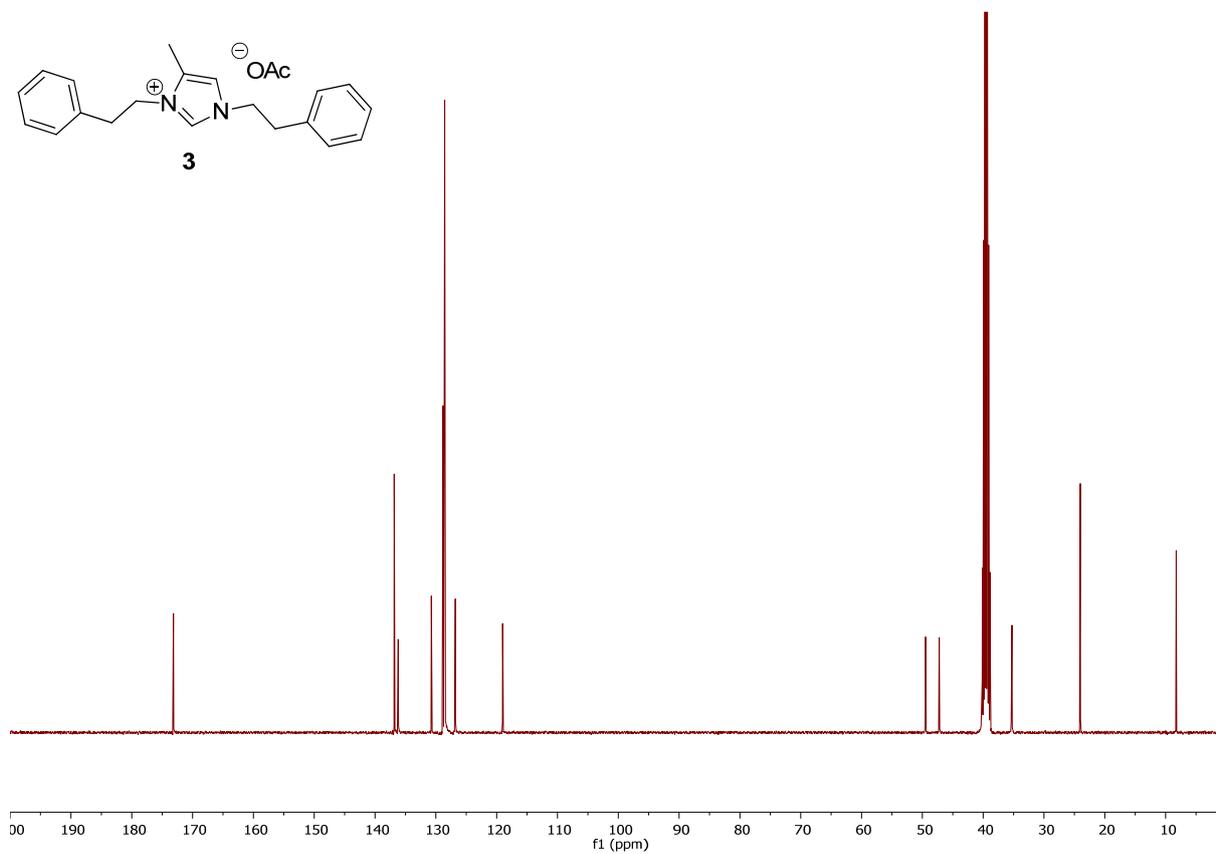
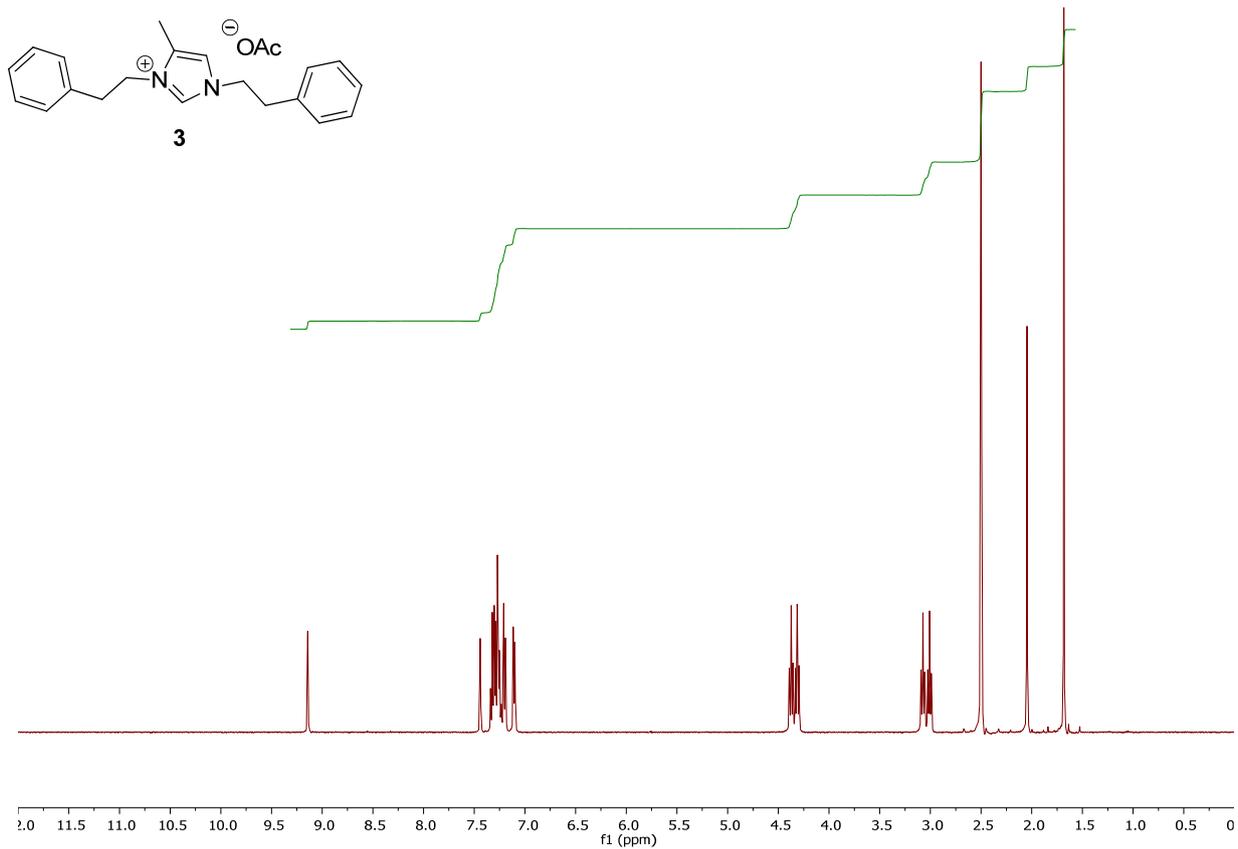
References

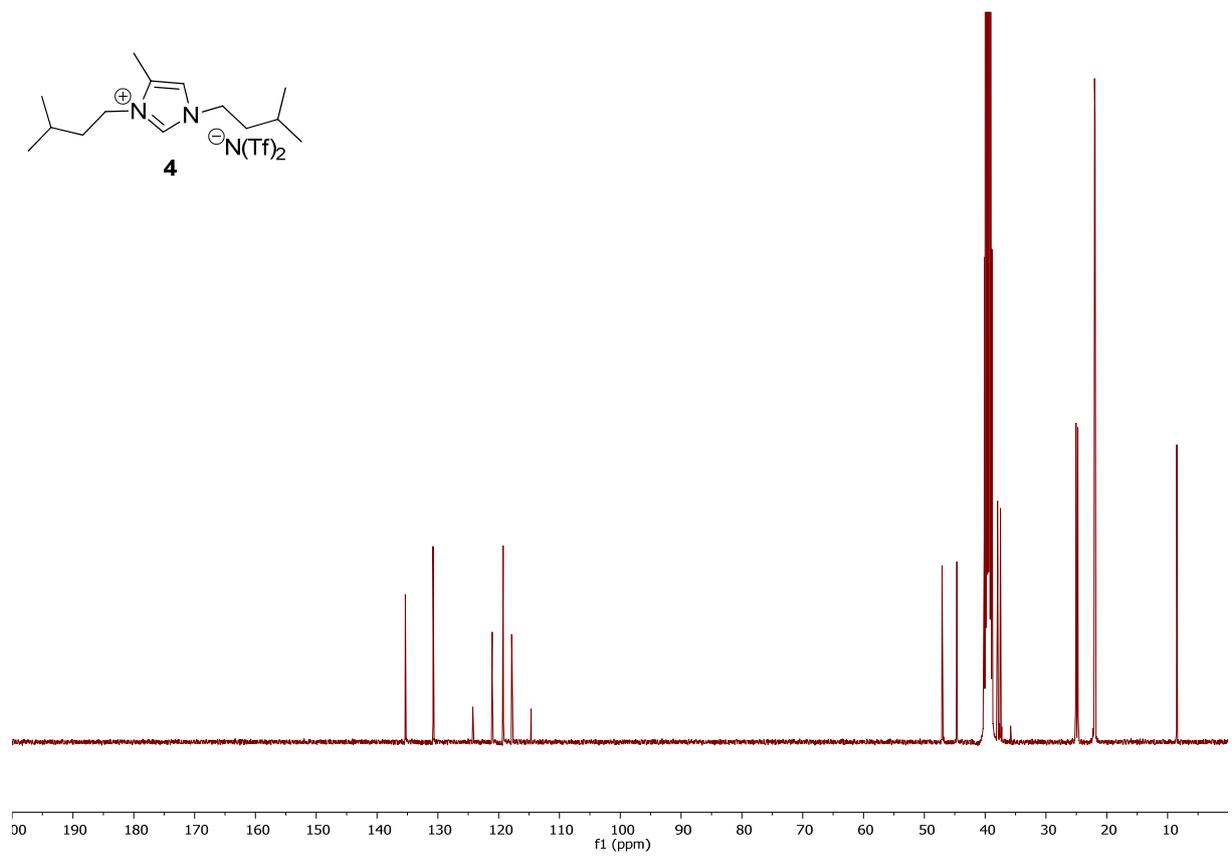
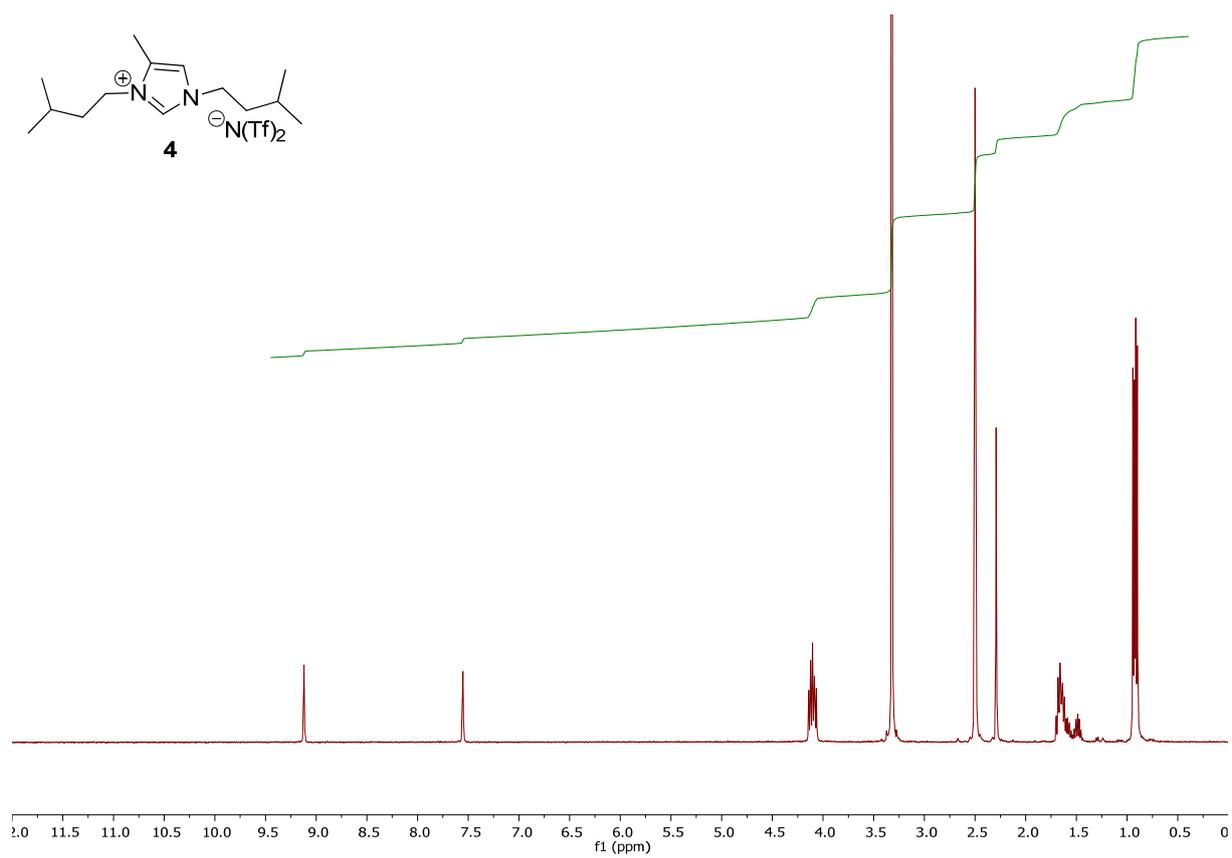
- 1) Esposito, D.; Kirchhecker, S.; Antonietti, M. *Chem. Eur. J.* **2013**, *19*, 15097–15100.

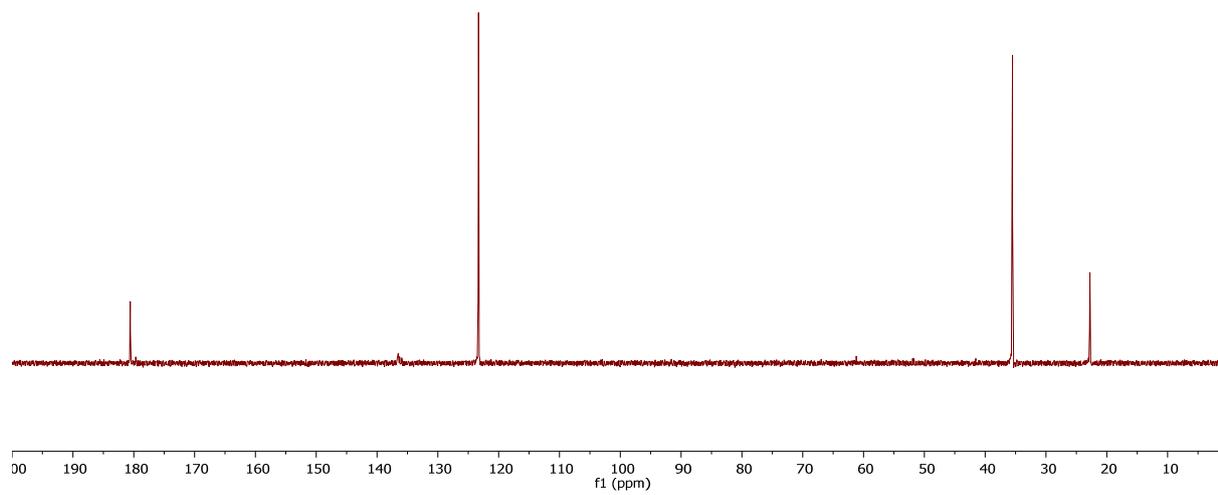
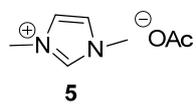
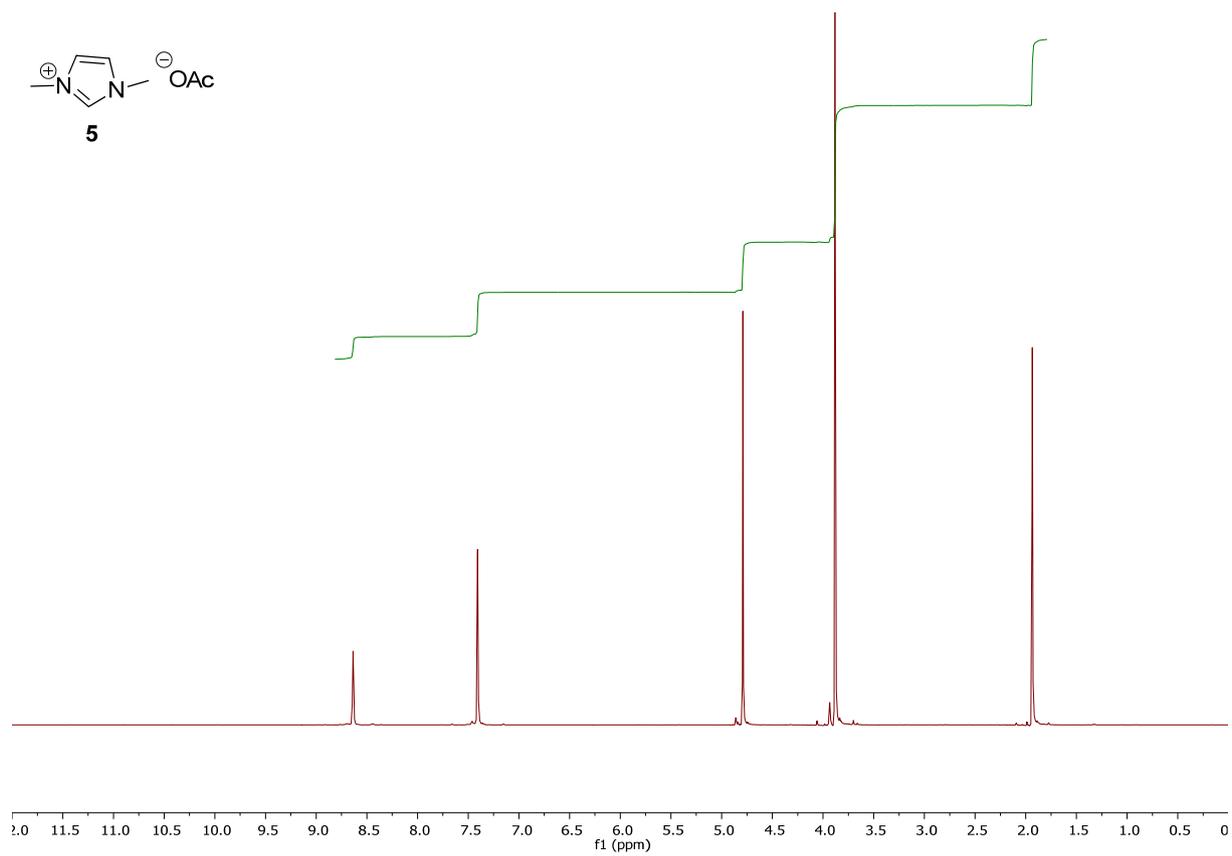
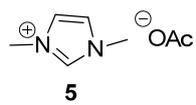
S18. NMR spectra of compounds 1 – 9

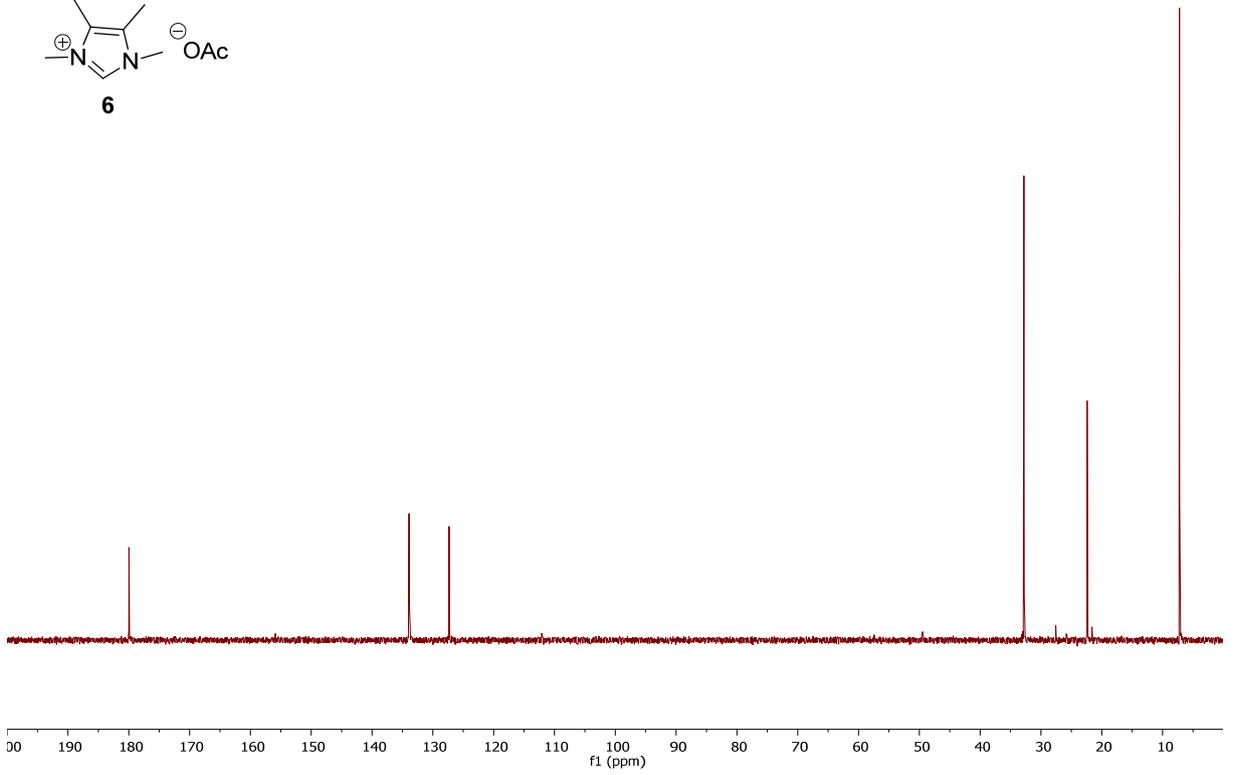
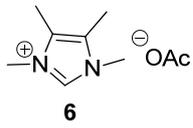
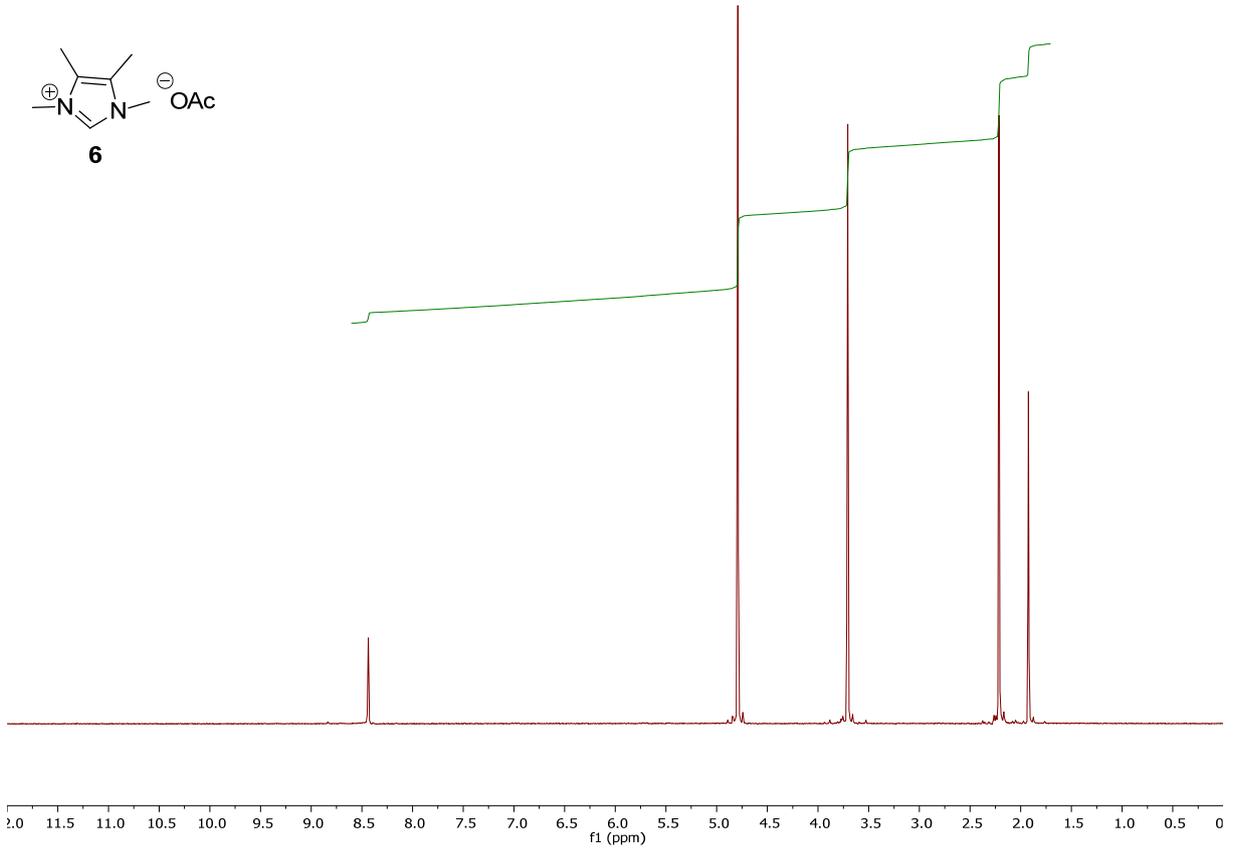
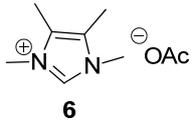


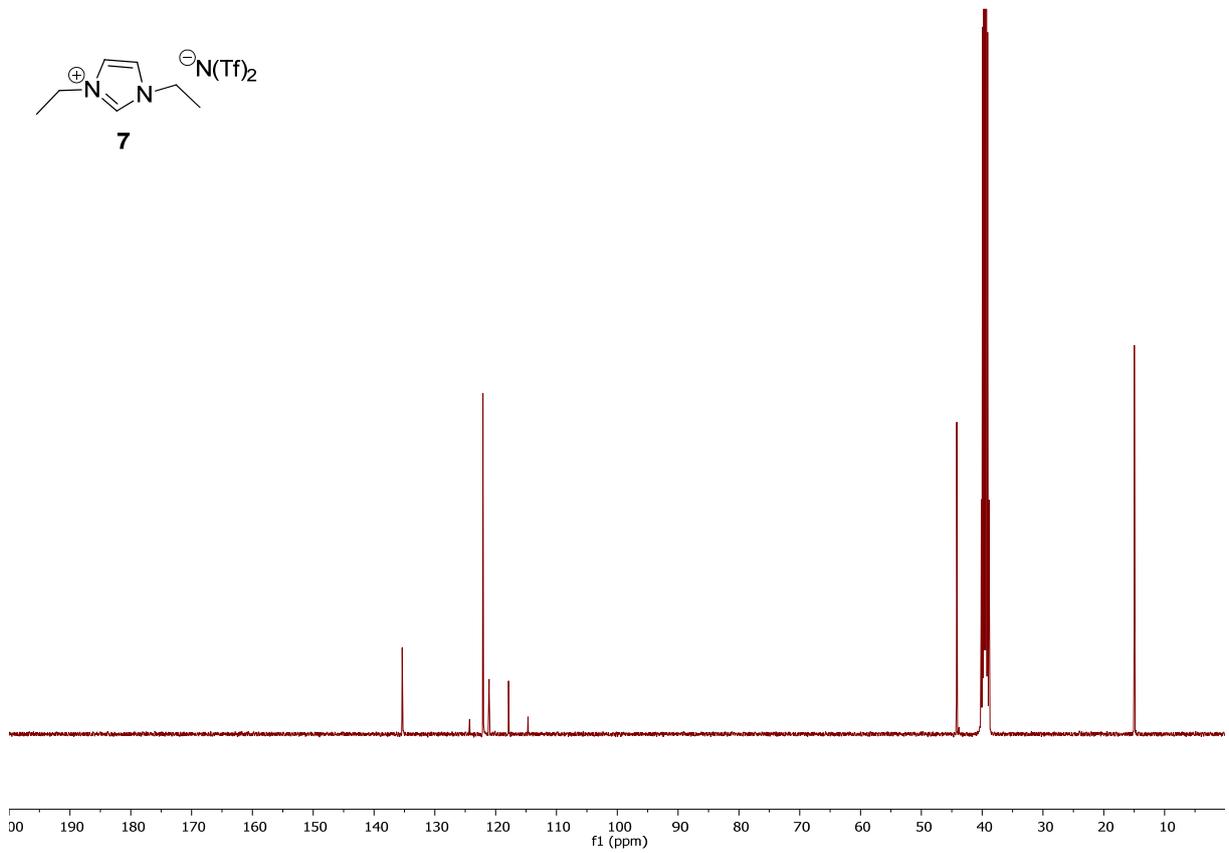
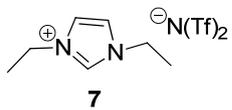
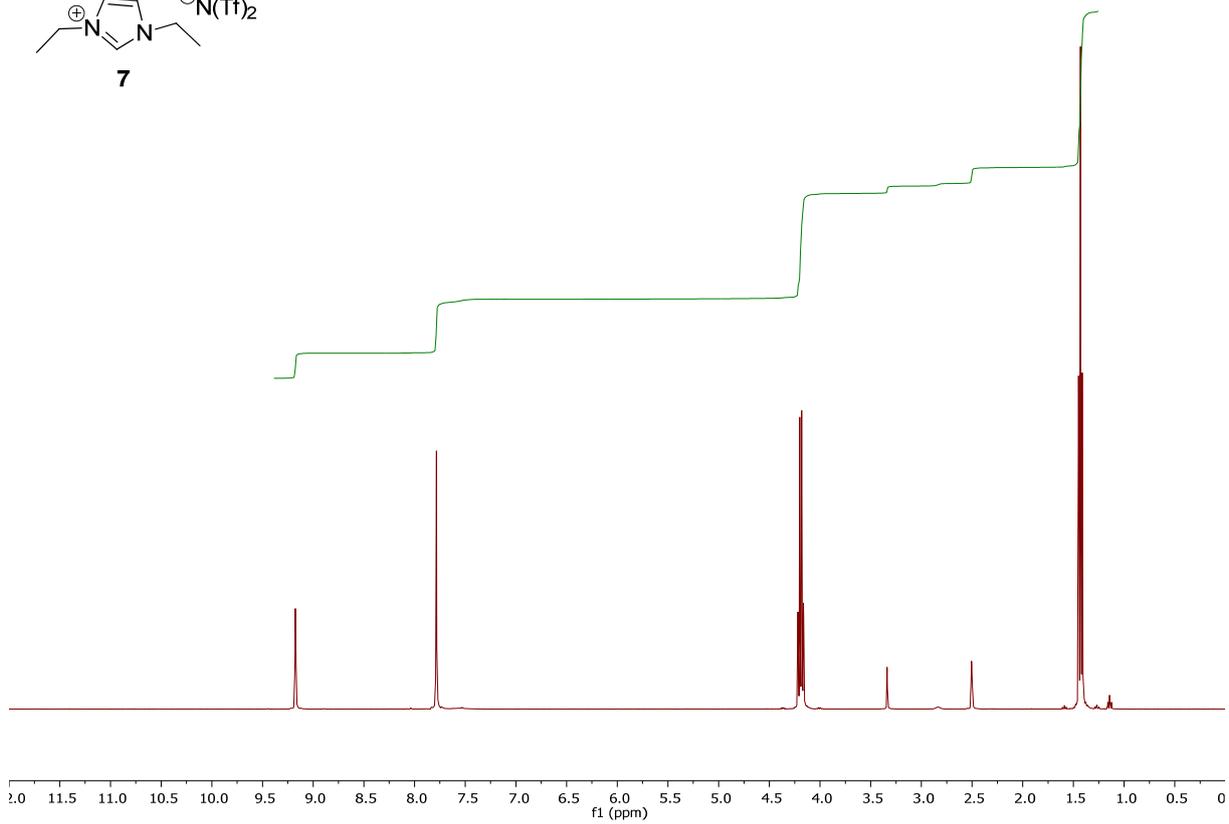
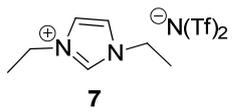


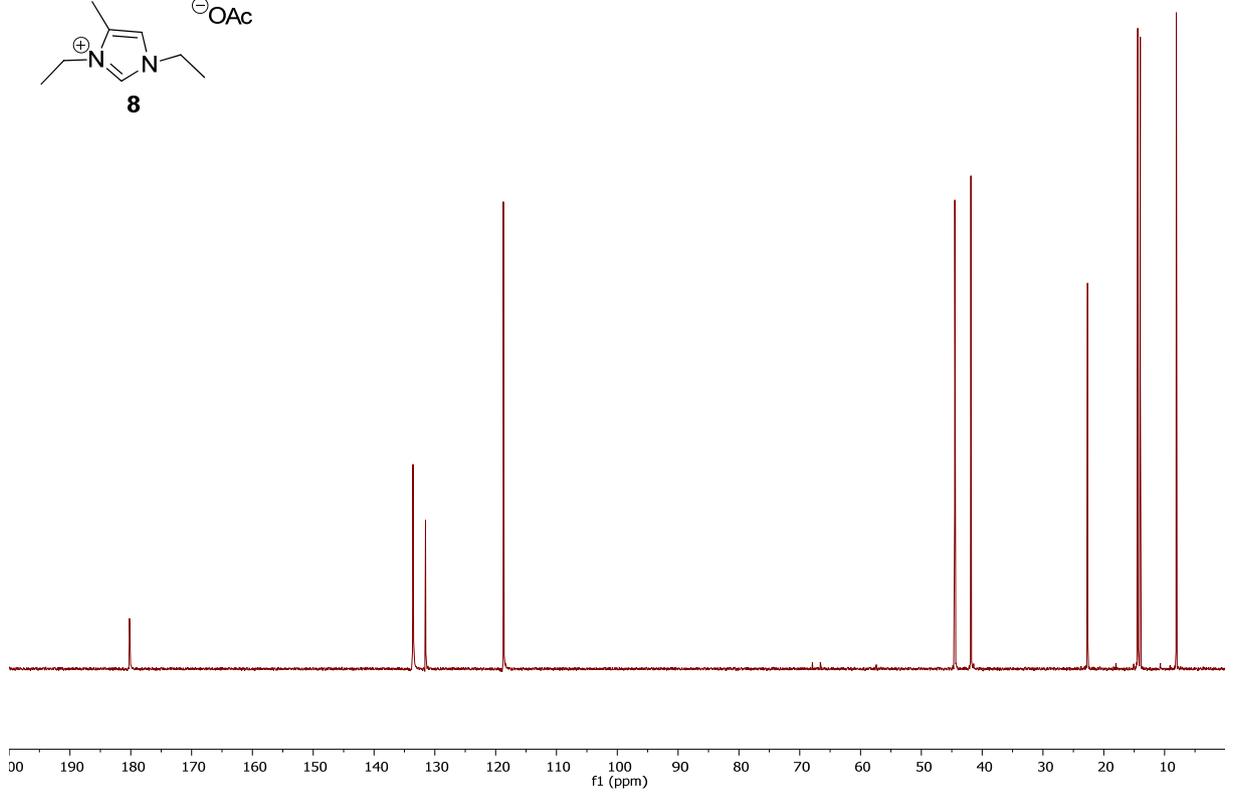
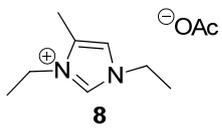
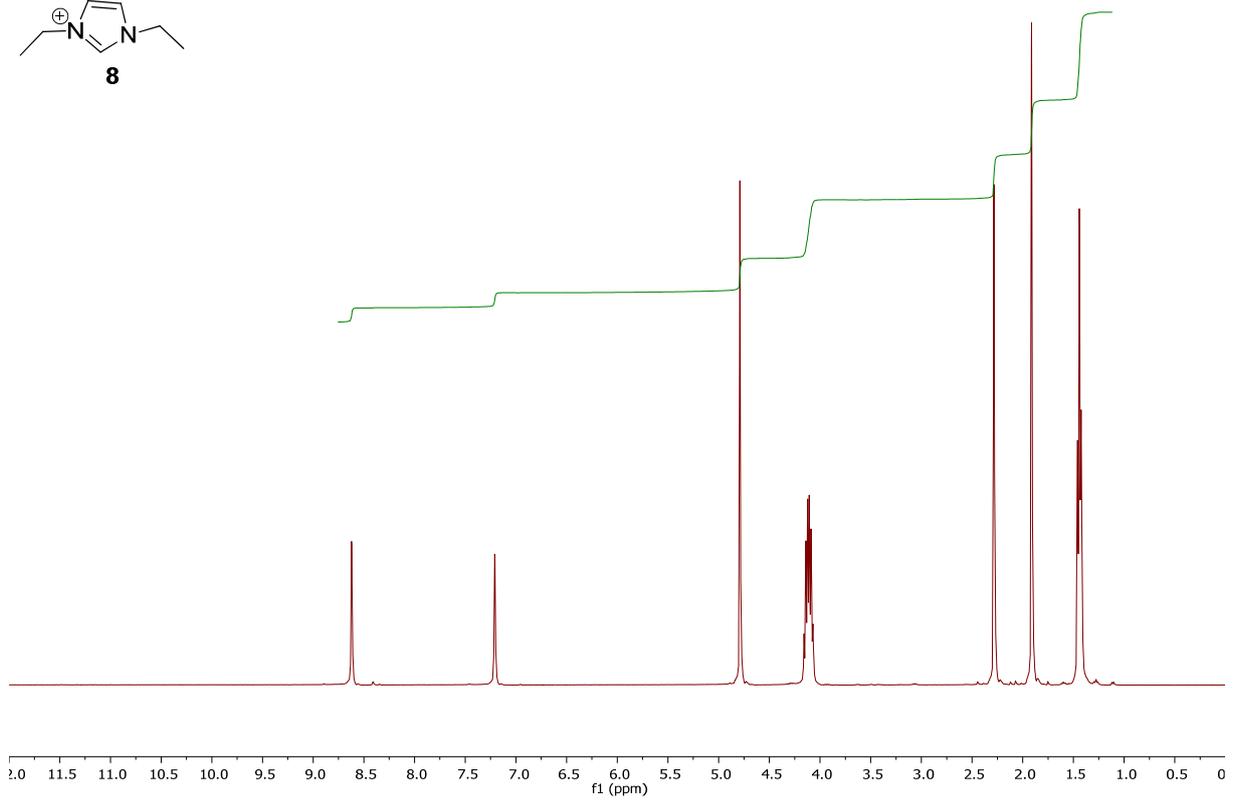
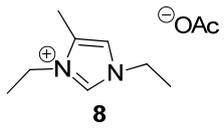


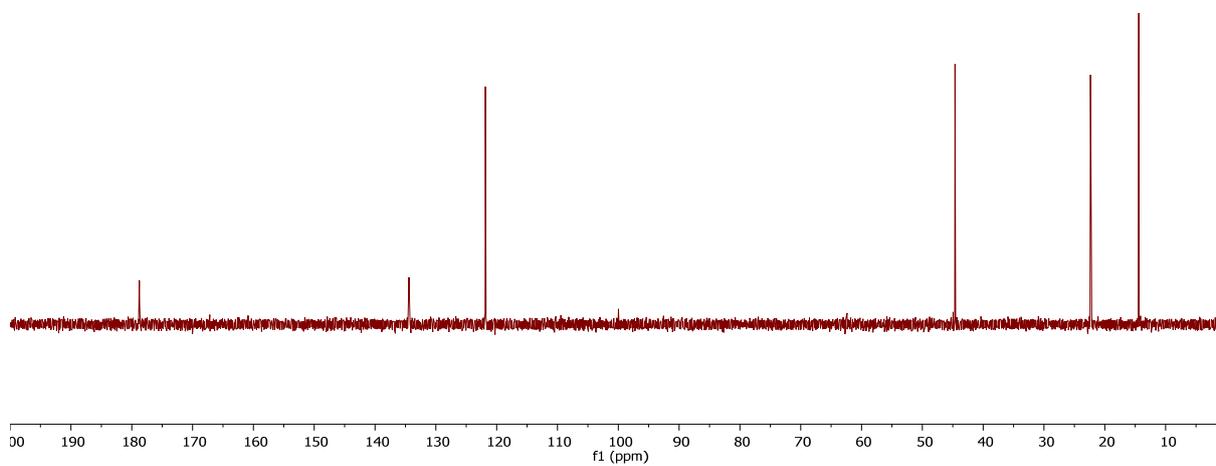
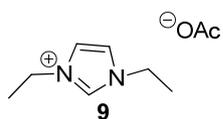
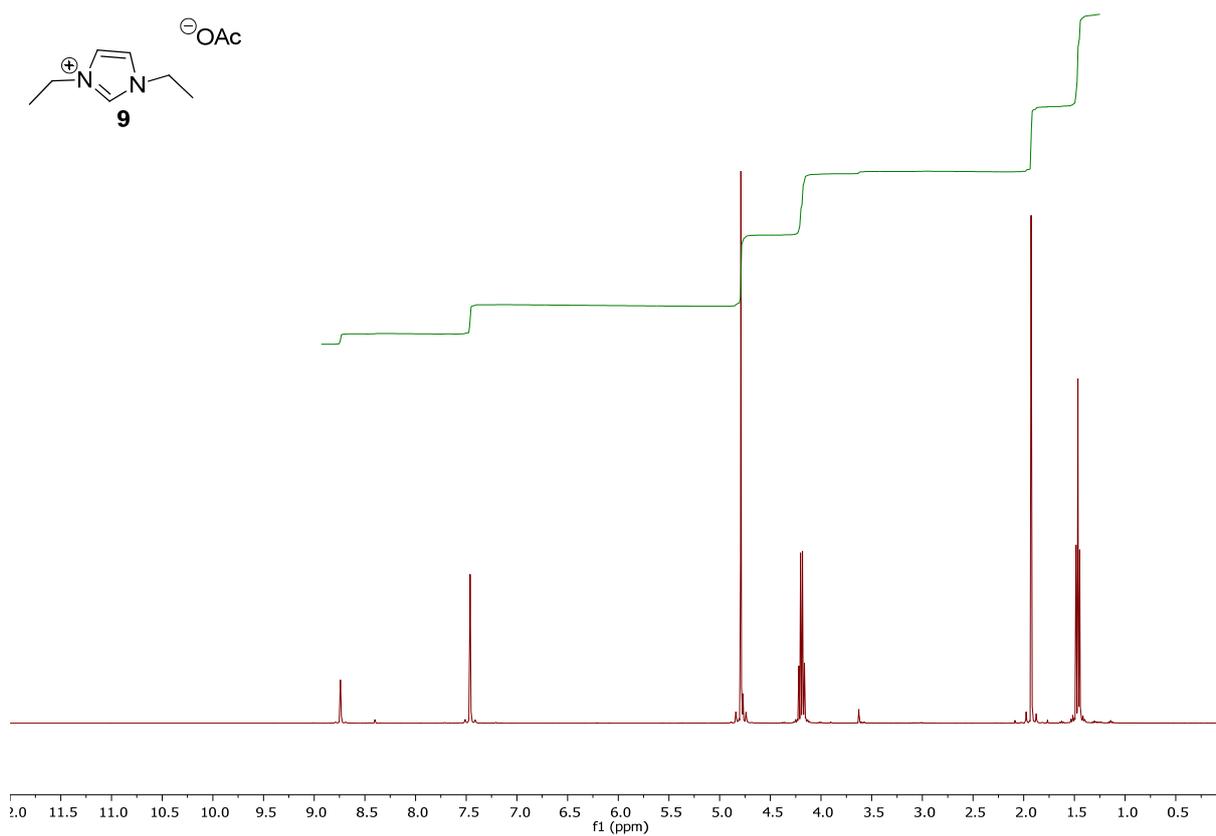
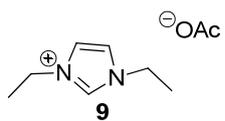












SI9. 1H- and 13C-NMR spectra for imidazolium zwitterions SI 1 – SI 6

