Supplementary Data

Synthesis of imidazolium-based ionic liquids with linear and branched alkyl side chains

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Materials

1-Methylimidazole (Aldrich) was distilled under reduced pressure prior to use and stored at room temperature. 1-Chloro-1-phenyl-ethane, 2-chloropropane and benzyl chloride (Across Organics), iodomethane (Riedel-de Haën), all other alkyl halides (Aldrich), sodium hydride, sodium tetrafluoroborate and silver tetrafluoroborate (Aldrich) were used as received. THF (Biosolve) was dried and deoxygenated using a solvent purification system (PURE SOLV 400-4-MD, Innovative Technology).

The synthesis of the ionic liquids was performed in a single-mode microwave reactor (Emrys Liberator, Biotage, Sweden).[1] The reactions were performed in glass vessels (2 to 5 mL) sealed with a septum. The pressure of the system was controlled by a load cell connected to the vessel and the temperature of the reaction mixture was monitored using a calibrated infrared sensor, which is located at the side of the reaction vessel. All experiments were performed using a Teflon®-coated magnetic stirring bar. In all microwave-assisted reactions a maximum microwave power of 150 W was used. A maximum pressure of 20 bar was set as a safety threshold.

An Infra-Red Vortex-Evaporator connected to a PoleStar Coldtrap System, both from HETTLAB, was used for drying the ionic liquids under vacuum. In this system the samples and a steel rack holder are heated by infrared light. The drying temperature was measured with a sensor connected to the steel rack. The maximum temperature for this system is 120 °C. To remove water after the anion exchange process a freeze dryer Alpha 1-2 LD from Christ was used. The dried ionic liquids were stored under dry conditions in an exsiccator.

^{1}H NMR spectra were recorded on Varian spectrometers (300 or 400 MHz) at 25 °C. Chemical shifts are given in ppm downfield from TMS. For FT-IR spectroscopy a

TENSOR 37™ from Bruker was used. The device is equipped with a HTS-XT (High Throughput Screening eXTension) compartment to perform an automatic measurement of the samples in transmission and/or diffuse reflection mode. For all measurements with this compartment the transmission mode was used. In addition, the FT-IR spectrometer is equipped with a microscope (HYPERION™ 3000), which was also used in transmission mode to characterize the samples. The samples were dissolved in methanol and spotted on a silica microtiter plate (96 well format). The background was measured on an empty spot on the microtiter plate. All MALDI experiments were performed on a Voyager-DE PRO Biospectrometry Workstation (Applied Biosystems, Foster City, CA) time-of-flight mass spectrometer in reflector mode. All spectra were obtained in the positive ion mode. Ionization was performed with a 337-nm pulsed nitrogen laser. Samples were dissolved in methanol and spotted on the target without using any matrix. All spectra are averaged over 500 laser shots over the complete sample area. All data were processed using the Data Explorer software package (Applied Biosystems).

Synthesis of the ionic liquids

General alkylation procedure of 1-methylimidazole

All experiments were performed in the microwave system Biotage Emrys Liberator.[33] A similar synthetic procedure as described in literature was used.[2,3,4] A mixture of 1-methylimidazole (5 to 13 mmol) and alkyl halide (6 to 16.9 mmol) was placed in a sealed reaction vessel (2 to 5 mL) with a magnetic stirrer. A 1.0 to 1.3 ratio of 1-methylimidazole to alkyl halide was used for all experiments. The reaction mixture was heated up to 170 °C at 150 W and then hold at this temperature for the required reaction times (1-11 minutes). The reaction mixture was cooled down to 40 °C in the microwave system and after that to room temperature. Not reacted alkyl halide was decanted from the reaction mixture and the conversion was determined by ^{1}H NMR spectroscopy. The raw product was dried under vacuum in the IR-Dancer at 120 °C until complete removal of 1-H-3-methylimidazolium chloride. The high viscous product was dissolved in methylene chloride or in a mixture of methylene chloride and methanol (95:5) and subsequently filtered over silica gel. The pure product was characterized by ^{1}H NMR spectroscopy.

Synthesis of 1-(1-ethylpropyl)-3-methylimidazolium iodide

1-(1-Ethylpropyl)-3-methylimidazolium iodide was synthesized according to a similar procedure described in literature.[5]

1-(1-Ethylpropyl)imidazole

A solution of imidazole (6 g, 88.2 mmol) in THF (80 mL) was slowly added into a solution of sodium hydride (2.46 g, 102.6 mmol) in THF (60 mL) at 0 °C. The mixture was stirred for 1 h at room temperature and subsequently 3-bromopentane (13.3 g, 11 mL, 88.2 mmol) was added slowly into this solution. The mixture was stirred for 5 d at 60 °C to obtain nearly quantitative conversion. This can be also achieved by heating the same mixture for 30 min at 120 °C using microwave irradiation. Water was added to the mixture (100 mL) and the water phase was extracted three times with ethyl acetate (40 mL). The collected ethyl acetate phases were washed with a saturated solution of

sodium chloride. The remaining ethyl acetate solution was dried over $MgSO_4$ and subsequently filtered. Ethyl acetate was removed under reduced pressure and the reaction mixture was separated by column chromatography on silica gel (methylene chloride: methanol = 95:5). The pure product was obtained as a slightly yellow liquid (5.9 g, 42.3 mmol, 48%).
^{1}H-NMR (400 MHz, DMSO, 25 °C): δ (ppm) = 0.66 (6 H, t, J = 7.4 Hz, CH_3), 1.57-1.79 (4 H, m, CH_2), 3.82 (1 H, m, *N*-CH), 6.88 (1 H, s), 7.14 (1 H, s), 7.60 (1 H, s).

1-(1-Ethylpropyl)-3-methylimidazolium iodide

Iodomethane (6.4 g, 44.7 mmol, 2.8 mL) was slowly added to 1-(1-ethylpropyl)imidazole (5.9 g, 42.3 mmol) in a pressure reaction tube at 0 °C. The reaction mixture was stirred until room temperature was reached. Subsequently water was added, and the aqueous phase was extracted three times with methylene chloride. The product was recovered by evaporation of the aqueous phase followed by freeze drying (6.59 g, 23.3 mmol, 55%).

The optimized reaction times obtained for the investigated ionic liquids are presented in Table 1.

Table 1: *Optimized reaction conditions for the synthesis of different branched ionic liquids according to Scheme 1 under microwave irradiation at 170 °C.*

Entry.	Cation	Anion	Time (min)	Conversion [b] (%)	Yield (%)
1	$[C_3MIM]^+$	Cl^-	9	100	95
2	$[C_4MIM]^+$	Cl^-	6	100	99
3	$[C_5MIM]^+$	Cl^-	8	100	98
4	$[BnMIM]^+$	Cl^-	1[a]	100	99
5	$[MC_2MIM]^+$	Cl^-	7	59	28
6	$[MC_3MIM]^+$	Cl^-	11	35	31
7	$[MC_4MIM]^+$	Cl^-	11	30	14
8	$[MBnMIM]^+$	Cl^-	7	51	39
9	$[EC_3MIM]^+$	Br^-	2	43	-[c]

[a] 100 °C.
[b] Determined by ^{1}H NMR spectroscopy.
[c] No separation/purification achieved.

Characterization of the synthesized ionic liquids

1-Methyl-3-propylimidazolium chloride
^{1}H-NMR (300 MHz, DMSO, 25 °C): δ (ppm) = 0.85 (3 H, t, J = 7.4 Hz, CH_3), 1.80 (2 H, m, CH_2), 3.86 (3 H, s, *N*-CH_3), 4.14 (2 H, t, J = 7.1 Hz, *N*-CH_2), 7.75 (1 H, s), 7.81 (1 H, s), 9.32 (1 H, s); IR (neat): 3414 (OH), 3150 (CH ring), 3096 (CH alkyl), 2970 (CH alkyl), 2880 (CH alkyl), 1638 (C=C, C=N), 1574 (C-C, C-N), 1462 (CH alkyl deform.), 1173 (CH ring deform.) cm^{-1}; MALDI-TOF-MS for $C_7H_{13}N_2^+$(125.1073): m/z 125 (100), 126 (5) Da.

1-(1-Methylethyl)-3-methylimidazolium chloride
^{1}H-NMR (300 MHz, DMSO, 25 °C): δ (ppm) = 1.46 (6 H, d, J = 6.7 Hz, CH_3), 3.85 (3 H, s, N-CH_3), 4.64 (1 H, m, N-CH), 7.75 (1 H, s), 7.92 (1 H, s), 9.39 (1 H, s); IR (neat): 3416 (OH), 3148 (CH ring), 3090 (CH alkyl), 2986 (CH alkyl), 2884 (CH alkyl), 2112 (N=C), 1638 (C=C, C=N), 1574 (C-C, C-N), 1468 (CH alkyl deform.), 1186 (CH ring deform.) cm^{-1}; MALDI-TOF-MS for $C_7H_{13}N_2^+$(125.1073): m/z 125 (100), 126 (25) Da.

1-Butyl-3-methylimidazolium chloride
^{1}H-NMR (300 MHz, DMSO, 25 °C): δ (ppm) = 0.89 (3 H, t, J = 7.4 Hz, CH_3), 1.25 (2 H, m, CH_2), 1.76 (2 H, m, CH_2), 3.86 (3 H, s, N-CH_3), 4.18 (2 H, t, J = 7.1 Hz, N-CH_2), 7.74 (1 H, s), 7.82 (1 H, s), 9.33 (0.9(1) H, s); IR (neat): 3410 (OH), 3148 (CH ring), 3088 (CH alkyl), 2963 (CH alkyl), 2876 (CH alkyl), 2112 (N=C), 1640 (C=C, C=N), 1572 (C-C, C-N), 1466(CH alkyl deform.), 1171 (CH ring deform.) cm^{-1}; MALDI-TOF-MS for $C_8H_{15}N_2^+$(139.1230): m/z 139 (100), 140 (10) Da.

1-(1-Methylpropyl)-3-methylimidazolium chloride
^{1}H-NMR (300 MHz, DMSO, 25 °C): δ (ppm) = 0.76 (3 H, t, J = 7.3 Hz, CH_3), 1.45 (3 H, d, J = 6.8 Hz, CH_3), 1.79 (2 H, m, CH_2), 3.86 (3 H, s, N-CH_3), 4.43 (1 H, m, N-CH), 7.78 (1 H, s), 7.92 (1 H, s), 9.43 (1 H, s); IR (neat): 3404 (OH), 3148 (CH ring), 3084 (CH alkyl), 2974 (CH alkyl), 2882 (CH alkyl), 2122 (N=C), 1640 (C=C, C=N), 1574 (C-C, C-N), 1464 (CH alkyl deform.), 1179 (CH ring deform.) cm^{-1}; MALDI-TOF-MS for $C_8H_{15}N_2^+$(139.1230): m/z 139 (100), 140 (15) Da.

1- Methyl-3-pentylimidazolium chloride
^{1}H-NMR (300 MHz, DMSO, 25 °C): δ (ppm) = 0.86 (3 H, t, J = 7.1 Hz, CH_3), 1.14-1.38 (4 H, m, CH_2), 1.78 (2 H, m, CH_2), 3.86 (3 H, s, N-CH_3), 4.17 (2 H, t, J = 7.2 Hz, N-CH_2), 7.74 (1 H, s), 7.81 (1 H, s), 9.31 (1 H, s); IR (neat): 3408 (OH), 3148 (CH ring), 3086 (CH alkyl), 2959 (CH alkyl), 2864 (CH alkyl), 2108 (N=C), 1638 (C=C, C=N), 1572 (C-C, C-N), 1466 (CH alkyl deform.), 1171 (CH ring deform.) cm^{-1}; MALDI-TOF-MS for $C_9H_{17}N_2^+$(153.1386): m/z 153 (100), 154 (15) Da.

1-(1-Methylbutyl)-3-methylimidazolium chloride
^{1}H-NMR (300 MHz, DMSO, 25 °C): δ (ppm) = 0.85 (3 H, t, J = 7.3 Hz, CH_3), 0.92-1.32 (2 H, m, CH_2), 1.43 (3 H, d, J = 6.7 Hz, CH_3), 1.65-1.81 (2 H, m, CH_2), 3.83 (3 H, s, N-CH_3), 4.48 (1 H, m, N-CH), 7.72 (1 H, s), 7.87 (1 H, s), 9.26 (1 H, s); IR (neat): 3424 (OH), 3144 (CH ring), 3078 (CH alkyl), 2963 (CH alkyl), 2876 (CH alkyl), 2116 (N=C), 1636 (C=C, C=N), 1572 (C-C, C-N), 1466 (CH alkyl deform.), 1175 (CH ring deform.) cm^{-1}; MALDI-TOF-MS for $C_9H_{17}N_2^+$(153.1386): m/z 153 (100), 154 (10) Da.

1-(1-Ethylpropyl)-3-methylimidazolium iodide
^{1}H-NMR (400 MHz, DMSO, 25 °C): δ (ppm) = 0.73 (6 H, t, J = 7.4 Hz, CH_3), 1.67-1.90 (4 H, m, CH_2), 3.85 (3 H, s, N-CH_3), 4.15 (1 H, m, N-CH), 7.75 (1 H, s), 7.84 (1 H, s), 9.16 (1 H, s); IR (neat): 3474 (OH), 3134 (CH ring), 3077 (CH alkyl), 2967 (CH alkyl), 2878 (CH alkyl), 1624 (C=C, C=N), 1572 (C-C, C-N), 1462 (CH alkyl deform.), 1171 (CH ring deform.) cm^{-1}; MALDI-TOF-MS for $C_9H_{17}N_2^+$(153.1386): m/z 153 (100), 154 (15) Da.

1-Benzyl-3-methylimidazolium chloride
^{1}H-NMR (300 MHz, DMSO, 25 °C): δ (ppm) = 3.85 (3 H, s, *N*-CH_3), 5.42 (2 H, s, *N*-CH_2), 7.38-7.45 (5 H, m, H_{aryl}), 7.72 (1 H, s), 7.79 (1 H, s), 9.24 (1 H, s); IR (neat): 3406 (OH), 3146 (CH ring), 3082 (CH alkyl), 2855 (CH alkyl), 2114 (N=C), 1634 (C=C, C=N), 1574 (C-C, C-N), 1456 (CH alkyl deform.), 1163 (CH ring deform.) cm^{-1}; MALDI-TOF-MS for $C_{12}H_{15}N_2^+$(187.1230): m/z 173 (100), 174 (20) Da.

1-(1-Methylbenzyl)-3-methylimidazolium chloride
Reaction time: 7 minutes, yield: 39%
^{1}H-NMR (300 MHz, DMSO, 25 °C): δ (ppm) = 1.87 (3 H, d, *J* = 7.1 Hz, CH_3), 3.86 (3 H, s, *N*-CH_3), 5.83 (1 H, m, *N*-CH), 7.33-7.48 (5 H, m, H_{aryl}), 7.76 (1 H, s), 7.91 (1 H, s), 9.56 (1 H, s); IR (neat): 3406 (OH), 3146 (CH ring), 3078 (CH alkyl), 2990 (CH alkyl), 2118 (N=C), 1638 (C=C, C=N), 1574 (C-C, C-N), 1456 (CH alkyl deform.), 1165 (CH ring deform.) cm^{-1}; MALDI-TOF-MS for $C_{12}H_{15}N_2^+$(187.1230): m/z 187 (100), 188 (10) Da.

Anion Exchange

The anion of the chloride containing ionic liquids was exchanged according to literature.[6] The ionic liquids were dissolved in water and the anion exchange salt was added in a ratio of 1.0 to 1.06 of ionic liquid to sodium tetrafluoroborate. The reaction mixture was stirred for 15 min and then methylene chloride was added. The aqueous phase was extracted with additional methylene chloride and the combined phases were washed with water containing sodium tetrafluoroborate. The methylene chloride was removed by evaporation under reduced pressure and the ionic liquid was freeze dried to remove remaining water. The completeness of the anion exchange was checked with silver nitrate. In addition, the OH stretching vibrations, which are very sensitive to hydrogen bonding, are shifted to higher wave numbers and instead of broad absorption bands for the chloride and iodide containing ionic liquids, two narrow bands typical for symmetric 1:2 H-bonded complexes (anion-HOH-anion) were observed.[7]

The anion of 1-(1ethylpropyl)-3-methylimidazolium iodide was exchanged by using silver tetrafluoroborate as exchange salt. The ionic liquid was dissolved in water and the anion exchange salt was added in a ratio of 1.0 to 1.06 of ionic liquid to silver tetrafluoroborate. The precipitated silver iodide was filtered off the solution and the aqueous phase was extracted three times with methylene chloride. The solvent was removed by evaporation under reduced pressure and the ionic liquid was freeze dried to remove remaining water. The completeness of the anion exchange was checked with silver nitrate.

The results of this anion exchange process are summarized in Table 2.

Table 2: *Results for the anion exchange process of the investigated ionic liquids.*

Entry	Cation	Anion	Anion exchange salt	Yield (%)
1	$[C_3MIM]^+$	Cl^-	$NaBF_4$	27
2	$[C_4MIM]^+$	Cl^-	$NaBF_4$	62
3	$[C_5MIM]^+$	Cl^-	$NaBF_4$	83
4	$[BnMIM]^+$	Cl^-	$NaBF_4$	72
5	$[MC_2MIM]^+$	Cl^-	$NaBF_4$	19
6	$[MC_3MIM]^+$	Cl^-	$NaBF_4$	30
7	$[MC_4MIM]^+$	Cl^-	$NaBF_4$	71
8	$[MBnMIM]^+$	Cl^-	$NaBF_4$	73
9	$[EC_3MIM]^+$	I^-	$AgBF_4$	50

Characterization of the ionic liquids after anion exchange

1-Methyl-3-propylimidazolium tetrafluoroborate
^{1}H-NMR (400 MHz, DMSO, 25 °C): δ (ppm) = 0.84 (3 H, t, J = 7.4 Hz, CH_3), 1.78 (2 H, m, CH_2), 3.83 (3 H, s, N-CH_3), 4.10 (2 H, t, J = 7.1 Hz, N-CH_2), 7.68 (1 H, s), 7.74 (1 H, s), 9.06 (1 H, s); IR (neat): 3642 (OH), 3563 (OH), 3161 (CH ring), 3125 (CH ring), 2972 (CH alkyl), 2943 (CH alkyl), 2884 (CH alkyl), 2116 (N=C), 1636 (C=C, C=N), 1576 (C-C, C-N), 1468 (CH deform. alkyl), 1175 (CH deform. ring), 1076 (B-F) cm^{-1}; MALDI-TOF-MS for $C_7H_{13}N_2^+$(125.1073): m/z 125 (100), 126 (10) Da.

1-(1-Methylethyl)-3-methylimidazolium tetrafluoroborate
^{1}H-NMR (400 MHz, DMSO, 25 °C): δ (ppm) = 1.45 (6 H, d, J = 6.7 Hz, CH_3), 3.82 (3 H, s, N-CH_3), 4.60 (1 H, m, N-CH), 7.69 (1 H, s), 7.85 (1 H, s), 9.14 (1 H, s); IR (neat): 3632 (OH), 3167 (OH), 3115 (CH ring), 2990 (CH alkyl), 2945 (CH alkyl), 1626 (C=C, C=N), 1572 (C-C, C-N), 1470 (CH deform. alkyl), 1188 (CH deform. ring), 1059 (B-F) cm^{-1}; MALDI-TOF-MS for $C_7H_{13}N_2^+$(125.1073): m/z 125 (100), 126 (20) Da.

1-Butyl-3-methylimidazolium tetrafluoroborate
^{1}H-NMR (400 MHz, DMSO, 25 °C): δ (ppm) = 0.88 (3 H, t, J = 7.4 Hz, CH_3), 1.24 (2 H, m, CH_2), 1.74 (2 H, m, CH_2), 3.83 (3 H, s, N-CH_3), 4.14 (2 H, t, J = 7.2 Hz, N-CH_2), 7.67 (1 H, s), 7.74 (1 H, s), 9.06 (1 H, s); IR (neat): 3644 (OH), 3559 (OH), 3165 (CH ring), 3125 (CH ring), 2967 (CH alkyl), 2940 (CH alkyl), 2880 (CH alkyl), 1630 (C=C, C=N), 1576 (C-C, C-N), 1470(CH deform. alkyl), 1173 (CH deform. ring), 1069 (B-F) cm^{-1}; MALDI-TOF-MS for $C_8H_{15}N_2^+$(139.1230): m/z 139 (100), 140 (15) Da.

1-(1-Methylpropyl)-3-methylimidazolium tetrafluoroborate
^{1}H-NMR (400 MHz, DMSO, 25 °C): δ (ppm) = 0.75 (3 H, t, J = 7.4 Hz, CH_3), 1.44 (3 H, d, J = 6.8 Hz, CH_3), 1.72-1.82 (2 H, m, CH_2), 3.83 (3 H, s, N-CH_3), 4.38 (1 H, m, N-CH), 7.70 (1 H, s), 7.83 (1 H, s), 9.13 (1 H, s); IR (neat): 3636 (OH), 3561(OH), 3159 (CH ring), 3117 (CH ring), 2976 (CH alkyl), 2945 (CH alkyl), 2886 (CH alkyl), 2118 (N=C), 1630 (C=C, C=N), 1576(C-C, C-N), 1466 (CH deform. alkyl), 1179 (CH deform. ring), 1069 (B-F) cm^{-1}; MALDI-TOF-MS for $C_8H_{15}N_2^+$(139.1230): m/z 139 (100), 140 (10) Da.

1-Methyl-3-pentylimidazolium tetrafluoroborate
^{1}H-NMR (400 MHz, DMSO, 25 °C): δ (ppm) = 0.86 (3 H, t, J = 7.2 Hz, CH_3), 1.16-1.35 (4 H, m, CH_2), 1.77 (2 H, m, CH_2), 3.83 (3 H, s, N-CH_3), 4.13 (2 H, t, J = 7.2 Hz, N-CH_2), 7.67 (1 H, s), 7.74 (1 H, s), 9.06 (1 H, s); IR (neat): 3642 (OH), 3563 (OH), 3163 (CH ring), 3123 (CH ring), 2963 (CH alkyl), 2936 (CH alkyl), 2874 (CH alkyl), 1631 (C=C, C=N), 1576 (C-C, C-N), 1468 (CH deform. alkyl), 1175 (CH deform. ring), 1072 (B-F) cm^{-1}; MALDI-TOF-MS for $C_9H_{17}N_2^+$(153.1386): m/z 153 (100), 154 (15) Da.

1-(1-Methylbutyl)-3-methylimidazolium tetrafluoroborate
^{1}H-NMR (400 MHz, DMSO, 25 °C): δ (ppm) = 0.85 (3 H, t, J = 7.4 Hz, CH_3), 0.99-1.29 (2 H, m, CH_2), 1.44 (3 H, d, J = 6.7 Hz, CH_3), 1.65-1.81 (2 H, m, CH_2), 3.82 (3 H, s, N-CH_3), 4.47 (1 H, m, N-CH), 7.69 (1 H, s), 7.84 (1 H, s), 9.13 (1 H, s); IR (neat): 3638 (OH), 3565 (OH), 3161 (CH ring), 3117 (CH ring), 2967 (CH alkyl), 2940 (CH alkyl), 2878 (CH alkyl), 2120 (N=C), 1628 (C=C, C=N), 1576 (C-C, C-N), 1468 (CH deform. alkyl), 1175 (CH deform. ring), 1065 (B-F) cm^{-1}; MALDI-TOF-MS for $C_9H_{17}N_2^+$(153.1386): m/z 153 (100), 154 (10) Da.

1-(1-Ethylpropyl)-3-methylimidazolium tetrafluoroborate
^{1}H-NMR (400 MHz, DMSO, 25 °C): δ (ppm) = 0.73 (6 H, t, J = 7.4 Hz, CH_3), 1.78 (4 H, m, CH_2), 3.84 (3 H, s, N-CH_3), 4.14 (1 H, m, N-CH), 7.74 (1 H, s), 7.83 (1 H, s), 9.14 (1 H, s); IR (neat): 3634 (OH), 3570 (OH), 3161 (CH ring), 3115 (CH ring), 2974 (CH alkyl), 2943 (CH alkyl), 2884 (CH alkyl), 1632 (C=C, C=N), 1576 (C-C, C-N), 1466 (CH deform. alkyl), 1173 (CH deform. ring), 1065 (B-F) cm^{-1}; MALDI-TOF-MS for $C_9H_{17}N_2^+$(153.1386): m/z 153 (100), 154 (5) Da.

1-Benzyl-3-methylimidazolium tetrafluoroborate
^{1}H-NMR (400 MHz, DMSO, 25 °C): δ (ppm) = 3.84 (3 H, s, N-CH_3), 5.39 (2 H, s, N-CH_2), 7.37-7.43 (5 H, m, H_{aryl}), 7.69 (1 H, s), 7.76 (1 H, s), 9.17 (1 H, s); IR (neat): 3642 (OH), 3559 (OH), 3159 (CH ring), 3111 (CH ring), 3040 (CH alkyl), 2963 (CH alkyl), 1626 (C=C, C=N), 1576 (C-C, C-N), 1458 (CH deform. alkyl), 1167 (CH deform. ring), 1072 (B-F) cm^{-1}; MALDI-TOF-MS for $C_{12}H_{15}N_2^+$(187.1230): m/z 173 (100), 174 (15) Da.

1-(1-Methylbenzyl)-3-methylimidazolium tetrafluoroborate
^{1}H-NMR (400 MHz, DMSO, 25 °C): δ (ppm) = 1.85 (3 H, d, J = 7.1 Hz, CH_3), 3.83 (3 H, s, N-CH_3), 5.75 (1 H, m, N-CH), 7.33-7.44 (5 H, m, H_{aryl}), 7.70 (1 H, s), 7.82 (1 H, s), 9.26 (1 H, s); IR (neat): 3644 (OH), 3561 (OH)*, 3161 (CH ring), 3125 (CH ring), 3038 (CH alkyl), 2965 (CH alkyl), 2110 (N=C), 1628 (C=C, C=N), 1578 (C-C, C-N), 1454 (CH deform. alkyl), 1167 (CH deform. ring), 1051 (B-F) cm^{-1}; MALDI-TOF-MS for $C_{12}H_{15}N_2^+$(187.1230): m/z 187 (100), 188 (20) Da.

References

1 www.biotage.com.
2 R. S. Varma, and V. V. Namboodiri, *Chem. Commun.*, 2001, 643-644.
3 B. M. Khadilkar, and G. L. Rebeiro, *Org. Process Res. Dev.*, 2002, **6**, 826-828.
4 M. Deetlefs, and K. R. Seddon, *Green Chem.*, 2003, **5**, 181-186.
5 J. Vitz, D. H. Mac, and S. Legoupy, *Green Chem.*, 2007, **9**, 431-433.
6 X. Creary, and E. D. Willis, *Organic Syntheses*, 2005, **82**, 166-169.
7 M. López-Pastor, M. J. Ayora-Cañada, M. Valcárcel, and B. Lendl, *J. Phys. Chem. B*, 2006, **110**, 10896-10902.