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An efficient and green sonochemical synthesis of some new eco-friendly functionalized ionic liquids

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Abstract Considerable stress to replace a lot of volatile organic compounds which were used as solvents in synthetic organic chemistry has been done for many chemical industries. A suitable solution for these problems is found by using the ionic liquids as a clean medium of working and avoiding the solvent effect. The present work describes a facile and green ultrasound-assisted procedure as an environmentally friendly alternative to traditional methods for the preparation of a series of 26 new functionalized imidazolium-based ionic liquids. Their structures were characterized by FT-IR, ^{1}H, ^{13}C, ^{11}B, ^{19}F, ^{31}P NMR and mass spectra.

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1. Introduction

Over the past few decades the number of publications concerning room-temperature ionic liquids (RTILs) has increased substantially (Rogers and Seddon, 2002). (RTILs) provide a new class of solvents where molecules are composed of ions. At normal temperatures, ionic liquids have essentially zero-vapor pressure and are thermally stable over a wide range of temperature. Therefore, they are considered as environmentally friendly alternatives to the volatile organic compounds (VOCs).

RTILs have been also widely investigated for a variety of applications: the use as solvents or catalysts for chemical synthesis (Liu et al., 2003; Wang et al., 2007), media for electrodeposition of metals (Lin and Sun, 1999; Takahashi et al., 1999; Endres, 2002; Ibrahim and Messali, 2011), electrolyte for electrochemical devices such as battery (Brennecke and Magin, 2001), supercapacitors (Ue et al., 2003; Balducci et al., 2004), as inhibitors of corrosion (Messali, 2011; Zarrouk et al., 2012a; Zarrouk et al., 2012b; Ibrahim et al., 2011), as fluids for thermal storage and exchange in solar concentrating power plants (Moens et al., 2003) and a wide electrochemical potential window (Ngo et al., 2000; Forsyth et al., 2004; Endres et al., 2006; Al-Ghamdi et al., 2011).

Recently, many chemists promoted to explore new methods for the clean and efficient synthesis of ILs since from the point of green chemistry, the conventional syntheses of the ILs themselves are not benign. In recent reports, several modifications have been attempted including solvent-free reactions, microwave irradiation (Anastas and Warner, 1998; Messali, 2011) ultrasound assisted procedures (Leveque et al., 2006; Messali, 2013). The use of the green technologies leads to large reductions in reaction times, enhancements in conversions, sometimes in selectivity, with several advantages of the eco-friendly approach (Deetlefs and Seddon, 2003; Loupy, 2004; Yi et al., 2005; Singh et al., 2005; Aupoix et al., 2010; Messali and Ahmed, 2011).

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In continuation of our previous work dealing with the development of novel functionalized ionic liquids and our general interests in green technologies such a MW-assisted or ultrasound-assisted chemical processes (Messali, 2013; Messali et al., 2013; Messali, 2011; Messali and Asiri, 2013) we present in the following an overview of our new study of the ultrasound-assisted synthesis of new functionalized imidazolium-based ionic liquids, showing the scope of this method.

2. Materials and methods

2.1. Experimental

All new compounds were synthesized and characterized by ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, ^{11}B NMR, ^{31}P NMR, IR and LCMS. ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz), ^{19}F NMR (376.5 MHz), ^{31}P NMR (162 MHz) and ^{11}B NMR (128 MHz) spectra were measured in DMSO, $CDCl_3$ or D_2O at room temperature. Chemical shifts (δ) were reported in ppm to a scale calibrated for tetramethylsilane (TMS), which is used as an internal standard (Taibah University, Madinah, Saudi Arabia). The LCMS spectra were measured with a Micromass, LCT mass spectrometer (Mohamed First University, Oujda, Morocco). FT-IR spectra were recorded in NaCl or KBr disk on a Schimadzu 8201 PC, FTIR spectrophotometer (ν_{max} in cm^{-1}) (Taibah University, Madinah, Saudi Arabia). The ultrasound-assisted reactions were performed using a controllable laboratory ultrasonic bath.

3. Synthesis

3.1. General procedure for the synthesis of imidazolium halides (4–7) using conventional method

To the solution of *N*-alkylimidazole (**1–3**) (1 eq) in toluene, was added the appropriate alkyl bromide (1.1 eq) at room temperature, followed by stirring at 80 °C for 18 h. The completion of the reaction was marked by the separation of oil or solid from the initially obtained clear and homogenous mixture of *N*-alkylimidazole and alkyl halide in toluene. The product was isolated by extraction or filtration to remove the unreacted starting materials and solvent. Subsequently, the imidazolium salt was washed with ethyl acetate. In each case, the IL/salt (**4–7**) was finally dried at a reduced pressure to get rid of all the volatile organic compounds.

3.2. General procedure for the synthesis of imidazolium halides (4–7) using under Ultrasonic irradiation

N-alkylimidazole (**1–3**) (1 eq) and the appropriate alkyl bromide (1 eq) were placed in a closed vessel and exposed to ultrasound irradiation for 5 h at 80 °C using a sonication bath. The product was then collected as described in the conventional procedure outlined earlier.

3.3. General procedure for the methathesis reaction of (4–7) leading to compounds (8–31) using conventional method

The quaternary salt (**4–7**) (1 eq) was dissolved in acetonitrile to obtain a clear solution. To this solution of quaternary halide were added solution of sodium tetrafluoroborate, potassium hexafluorophosphate, trifluoroacetic acid sodium, sodium dicyanamide, sodium thiocyanate or sodium nitrate (1.2 eq), followed by stirring at 70 °C for 3 h. The cooled reaction mixture was filtered through Celite to remove solid metal halide. The evaporation of acetonitrile led quantitatively to the desired ionic liquids.

3.4. General procedure for the ultrasound-assisted methathesis reaction of (4–7) leading to compounds (8–31)

Imidazolium-halide salts (**4–7**) (1 eq) and $NaBF_4$, KPF_6, CF_3COONa, $NaN(CN)_2$, NaNCS or $NaNO_3$ (1 eq) were placed in a closed vessel and exposed to ultrasound irradiation for 45 min at 70 °C using a sonication bath. The product was then collected as described in the conventional procedure outlined earlier.

3.5. Characterization

3.5.1. 1-Benzyl-3-(2-ethoxy-2-oxoethyl)-1H-imidazol-3-ium chloride 4

White crystals, Mp 119–121 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.14 (t, J = 7.6, 3H), 4.07 (q, J = 6.8, 2H), 5.37 (s, 2H), 5.44 (s, 2H), 7.23–7.36 (m, 6H), 7.68 (d, 1H), 10.32 (s,1H), ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.9 (CH_3), 50.1 (CH_2), 53.1 (CH_2), 62.6 (CH_2), 121.5 (CH), 124.1 (CH), 128.7(CH), 129.2(CH), 133.1(C), 137.9(CH), 166.2(CO), IR (KBr): ν_{max} cm^{-1} 3132 (C–H, sp^2), 1726 (C═O), 1562–1448 (C═C), 1166 (C–N), 1030 (C–O), LCMS (M–Cl) 245 found for $C_{14}H_{17}N_2O_2^{+}$.

3.5.2. 1-Benzyl-3-(4-phenoxybutyl)-1H-imidazol-3-ium bromide 5

White crystals, Mp 153–155 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.77 (quint, J = 8, 2H), 2.07 (quint, J = 8, 2H), 3.91 (t, J = 8, 2H), 4.35 (t, J = 8, 2H), 5.52 (s, 2H), 6.77–6.88 (m, 3H), 7.17–7.55 (m, 9H), 10.45 (s, 1H), ^{13}C NMR (100 MHz, $CDCl_3$) δ: 25.7 (CH_2), 26.9 (CH_2), 49.7 (CH_2), 53.2 (CH_2), 66.7 (CH_2), 114.4 (CH), 120.8 (CH), 122.2 (CH), 122.6 (CH), 128.9 (CH), 129.4 (CH), 129.5 (CH), 133.0 (C), 135.5 (CH), 158.6 (C), IR (KBr): ν_{max} cm^{-1} 3132 (C–H, sp^2), 1599–1471 (C═C), 1165(C–N),1082(C–O), 815 (C–H , bending). LCMS (M–Br) 307 found for $C_{20}H_{23}N_2O^{+}$.

3.5.3. 3-(3-hydroxypropyl)-1-propyl-1H-imidazol-3-ium bromide 6

^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.82 (t, J = 7.2 , Hz 3H), 1.79 (t, J = 7.2 , Hz 2H), 2.01 (quint, J = 7.6 Hz , 2H), 2.18 (sixtet, J = 7.6 Hz , 2H), 4.12 (t, J = 7.6 Hz , 2H), 4.37 (t, J = 7.6 Hz , 2H), 5.11 (s , 1H), 7.48–7.50 (m, 2H), 9.90 (s, 1H), ^{13}C NMR (100 MHz, $CDCl_3$) δ: 8.8 (CH_3), 21.6 (CH_2), 29.0 (CH_2), 45.1 (CH_2), 49.6 (CH_2), 55.2 (CH_2), 119.9 (CH), 120.8 (CH), 135.1 (CH), IR (NaCl): ν_{max} cm^{-1} 3213 (O-H), 3161 (C–H, sp^2), 1566 (C═C), 1161 (C–N), 1157 (C–O), LCMS (M–Br) 169 found for $C_9H_{17}N_2O^{+}$.

3.5.4. 3-(3-Hydroxypropyl)-1-pentyl-1H-imidazol-3-ium bromide 7

^{1}H NMR (400 MHz, D_2O) δ: 0.67 (t, J = 7.6, 3H), 1.10–1.17 (m, 4H), 1.72 (quint, 2H), 1.94 (quint, J = 7.6, 2H), 3.41 (t,

J = 6.8, 2H), 4.12 (t, J = 7.6, 2H), 4.32 (t, J = 6.8, 2H), 7.37 (d, 1H), 7.64 (d, 1H), 9.73 (s,1H), ^{13}C NMR (100 MHz, D_2O) δ 11.7 (CH_3), 19.8 (CH_2), 26.0 (CH_2), 27.7 (CH_2), 30.6 (CH_2), 44.7 (CH_2), 47.8 (CH_2), 54.9 (CH_2), 120.0 (CH), 121.0 (CH), 134.3 (CH), IR (NaCl): ν_{max} cm^{-1} 3212 (O–H), 3160 (C–H, sp^2), 1565 (C═C), 1163 (C–N), 1158 (C–O), LCMS (M–Br 197 found for $C_{11}H_{21}N_2O^+$.

3.5.5. 1-Benzyl-3-(2-ethoxy-2-oxoethyl)-1H-imidazol-3-ium tetrafluoroborate ***8***

White crystals, Mp 110–111 °C, ^{1}H NMR (400 MHz, DMSO) δ: 1.24 (t, J = 7.6, 3H), 4.22 (q, J = 6.8, 2H), 5.24 (s, 2H), 5.51 (s, 2H),7.41–7.45 (m, 5H), 7.76 (d, 1H), 7.84 (d, 1H), 9.24 (s,1H), ^{13}C NMR (100 MHz, DMSO) δ: 13.8 (CH_3), 49.6 (CH_2), 52.0 (CH_2), 61.8 (CH_2), 122.2 (CH), 124.2 (CH), 128.2(CH), 128.8 (CH), 129.0 (CH), 134.6(C), 137.3 (CH), 166.7 (CO). ^{19}F NMR (376.5 MHz, DMSO) δ: −148.24, ^{11}B NMR (128 MHz, $CDCl_3$) δ: −1.26, IR (KBr): ν_{max} cm^{-1} 3131 (C–H, sp^2), 1728 (C═O), 1561–1447 (C═C), 1167 (C–N), 1030 (C–O), LCMS (M–BF_4) 245 found for $C_{14}H_{17}N_2O_2^+$.

3.5.6. 1-Benzyl-3-(2-ethoxy-2-oxoethyl)-1H-imidazol-3-ium hexafluorophosphate ***9***

White crystals, Mp 89–91 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.25 (t, J = 7.6, 3H), 4.22 (q, J = 6.8, 2H), 5.51 (s, 2H), 5.74 (s, 2H),7.41–7.46 (m, 5H), 7.76 (d, 1H), 7.78 (d, 1H), 9.225 (s,1H), ^{13}C NMR (100 MHz, $CDCl_3$) δ: 12.8 (CH_3), 48.6 (CH_2), 51.0 (CH_2), 61.8 (CH_2), 121.2 (CH), 123.2 (CH), 127.2(CH), 127.8 (CH), 128.0 (CH), 133.6(C), 136.3 (CH), 165.7 (CO). ^{19}F NMR (376.5 MHz, $CDCl_3$) δ: −71.10 (d, J = 711.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ: −144.16 (sep, J = 712.8 Hz), IR (KBr): ν_{max} cm^{-1} 3133 (C–H, sp^2), 1727 (C═O), 1562–1447 (C═C), 1165 (C–N), 1031 (C–O), LCMS (M–PF_6) 245 found for $C_{14}H_{17}N_2O_2^+$.

3.5.7. 1-Benzyl-3-(2-ethoxy-2-oxoethyl)-1H-imidazol-3-ium trifluoroacetate ***10***

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.17 (t, J = 7.6, 3H), 4.14 (q, J = 6.8, 2H), 5.18 (s, 2H), 5.30 (s, 2H), 7.12 (d, 1H), 7.27–7.29 (m, 5H), 7.40 (d, 1H), 10.15 (s,1H), ^{13}C NMR (100 MHz, $CDCl_3$) δ: 11.9 (CH_3), 48.0 (CH_2), 51.5 (CH_2), 51.6 (CH_2), 119.4 (CH), 122.0 (CH), 126.8(CH), 127.6 (CH), 127.7 (CH), 130.8(C), 137.0 (CH), 164.4 (CO), ^{19}F NMR (376.5 MHz, $CDCl_3$) δ: −75,41, IR (NaCl): ν_{max} cm^{-1} 3133 (C–H, sp^2), 1726 (C═O), 1563–1448 (C═C), 1165 (C–N), 1031 (C–O), LCMS (M–CF_3CO_2) 245 found for $C_{14}H_{17}N_2O_2^+$.

3.5.8. 1-Benzyl-3-(2-ethoxy-2-oxoethyl)-1H-imidazol-3-ium Dicyanoamine ***11***

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.20 (t, J = 7.6, 3H), 4.16 (q, J = 6.8, 2H), 5.05 (s, 2H), 5.30 (s, 2H), 7.30–7.33 (m, 6H), 7.47 (d, 1H), 9.13 (s,1H), ^{13}C NMR (100 MHz, $CDCl_3$) δ: 12.1 (CH_3), 48.2 (CH_2), 51.7 (CH_2), 61.2 (CH_2), 120.1 (CH), 122.4 (CH), 126.9 (CH), 127.7 (CH), 127.8 (CH), 130.5(C), 135.1 (CH), 164.0 (CO), IR (NaCl): ν_{max} cm^{-1} 3131 (C–H, sp^2), 1727 (C═O), 1559–1448 (C═C), 1164 (C–N), 1030 (C–O), LCMS (M–N(CN)$_2$) 245 found for $C_{14}H_{17}N_2O_2^+$.

3.5.9. 1-Benzyl-3-(2-ethoxy-2-oxoethyl)-1H-imidazol-3-ium thiocyanate 12

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.29 (t, J = 7.6, 3H), 4.16 (q, J = 6.8, 2H), 5.07 (s, 2H), 5.32 (s, 2H), 7.29–7.34 (m, 6H), 7.48 (d, 1H), 9.15 (s,1H), ^{13}C NMR (100 MHz, $CDCl_3$) δ: 12.2 (CH_3), 48.3 (CH_2), 51.8 (CH_2), 61.3 (CH_2), 120.2 (CH), 122.5 (CH), 127.0 (CH), 127.8 (CH), 127.9 (CH), 130.6 (C), 135.2 (CH), 164.1 (CO). IR (NaCl): ν_{max} cm^{-1} 3132 (C–H, sp^2), 1729 (C═O), 1562–1449 (C═C), 1165 (C–N), 1032 (C–O), LCMS (M–NCS) 245 found for $C_{14}H_{17}N_2O_2^+$.

3.5.10. 1-Benzyl-3-(2-ethoxy-2-oxoethyl)-1H-imidazol-3-ium Nitrate 13

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.20 (t, J = 7.6, 3H), 4.15 (q, J = 6.8, 2H), 5.19 (s, 2H), 5.36 (s, 2H), 7.28–7.35 (m, 6H), 7.59 (d, 1H), 9.88 (s,1H), ^{13}C NMR (100 MHz, $CDCl_3$) δ: 13.9 (CH_3), 49.9 (CH_2), 53.3 (CH_2), 62.7 (CH_2), 121.7 (CH), 124.2 (CH), 128.7 (CH), 129.4 (CH), 129.5 (CH), 133.0 (CH), 138.3 (C), 166.3 (CO). IR (NaCl): ν_{max} cm^{-1} 3132 (C–H, sp^2), 1729 (C═O), 1560–1446 (C═C), 1165 (C–N), 1031 (C–O), LCMS (M–NO_3) 245 found for $C_{14}H_{17}N_2O_2^+$.

3.5.11. 1-Benzyl-3-(4-phenoxybutyl)-1H-imidazol-3-ium tetrafluoroborate ***14***

Brown crystals, Mp 89–92 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.72 (quint, J = 8, 2H), 2.01 (quint, J = 8, 2H), 3.89 (t, J = 8, 2H), 4.20 (t, J = 8, 2H), 5.28 (s, 2H), 6.80–6.91 (m, 3H), 7.19–7.37 (m, 9H), 8.97 (s, 1H), ^{13}C NMR (100 MHz, $CDCl_3$) δ: 25.7 (CH_2), 26.9 (CH_2), 49.7 (CH_2), 53.2 (CH_2), 66.7 (CH_2), 114.4 (CH), 120.8 (CH), 122.2 (CH), 122.6 (CH), 128.9 (CH), 129.4 (CH), 129.5 (CH), 133.0 (C), 135.5 (CH), 158.6 (C), ^{19}F NMR (376.5 MHz, $CDCl_3$) δ: −150.08 ppm, ^{11}B NMR (128 MHz, $CDCl_3$) δ: −1.04 ppm, IR (KBr): ν_{max} cm^{-1} 3131 (C–H, sp^2), 1598–1470 (C═C), 1160(C–N),1081(C–O), 814 (C–H , bending). LCMS (M–BF_4) 307 found for $C_{20}H_{23}N_2O^+$.

3.5.12. 1-Benzyl-3-(4-phenoxybutyl)-1H-imidazol-3-ium hexafluorophospate ***15***

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.76 (quint, J = 8, 2H), 2.01 (quint, J = 8, 2H), 3.92 (t, J = 8, 2H), 4.18 (t, J = 8, 2H), 5.31 (s, 2H), 6.82–6.93 (m, 3H), 7.13–7.37 (m, 9H), 8.60 (s, 1H), ^{13}C NMR (100 MHz, $CDCl_3$) δ: 25.7 (CH_2), 26.9 (CH_2), 49.8 (CH_2), 53.4 (CH_2), 66.7 (CH_2), 114.4 (CH), 120.8 (CH), 122.1 (CH), 122.4 (CH), 128.9 (CH), 129.5 (CH), 129.6 (CH), 132.5 (C), 135.2 (CH), 158.6 (C), ^{19}F NMR (376.5 MHz, $CDCl_3$) δ: −72.54 (d, J = 711.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ: −139.77 (sep, J = 712.8 Hz), IR (NaCl): ν_{max} cm^{-1} 3132 (C–H, sp^2), 1599–1471 (C═C), 1165(C–N),1082 (C-O), 815 (C–H, bending), LCMS (M–PF_6) 307 found for $C_{20}H_{23}N_2O^+$.

3.5.13. 1-Benzyl-3-(4-phenoxybutyl)-1H-imidazol-3-ium trifluoroacetate ***16***

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.77 (quint, J = 8, 2H), 2.05 (quint, J = 8, 2H), 3.99 (t, J = 8, 2H), 4.32 (t, J = 8, 2H), 5.29 (s, 2H), 6.83–6.92 (m, 3H), 7.21–7.37 (m, 9H), 10.27 (s, 1H), ^{13}C NMR (100 MHz, $CDCl_3$) δ: 25.9 (CH_2), 27.3

(CH_2), 49.8 (CH_2), 53.4 (CH_2), 66.8 (CH_2), 114.5 (CH), 121.0 (CH), 122.0 (CH), 122.4 (CH), 129.0 (CH), 129.5 (CH), 129.6 (CH), 129.7, (CH), 133.5 (C), 136.2 (CH), 158.7 (C), ^{19}F NMR (376.5 MHz, $CDCl_3$) δ: −75.50, IR (NaCl): ν_{max} cm^{-1} 3130 (C–H, sp^2), 1560–1470 (C═C), 1164 (C–N), 1082(C–O), 816 (C–H, bending). LCMS (M–CF_3CO_2) 307 found for $C_{20}H_{23}N_2O^+$.

3.5.14. 1-Benzyl-3-(4-phenoxybutyl)-1H-imidazol-3-ium Dicyanoamine ***17***

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.76 (quint, J = 8, 2H), 2.04 (quint, J = 8, 2H), 3.91 (t, J = 8, 2H), 4.28 (t, J = 8, 2H), 5.37 (s, 2H), 6.78–6.87 (m, 3H), 7.16–7.44 (m, 9H), 9.72 (s, 1H), ^{13}C NMR (100 MHz, $CDCl_3$) δ: 25.8 (CH_2), 27.2 (CH_2), 48.8 (CH_2), 53.3 (CH_2), 66.7 (CH_2), 114.4 (CH), 120.8 (CH), 122.2 (CH), 128.9 (CH), 129.4 (CH), 129.5 (CH), 132.7 (C), 136.0 (CH), 158.5 (C), IR (NaCl): ν_{max} cm^{-1} 3132 (C–H, sp^2), 1598–1472 (C═C), 1167 (C–N), 1080 (C–O), 815 (C–H , bending). LCMS (M–$N(CN)_2$) 307 found for $C_{20}H_{23}N_2O^+$.

3.5.15. 1-Benzyl-3-(4-phenoxybutyl)-1H-imidazol-3-ium thiocyanate ***18***

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.80 (quint, J = 8, 2H), 2.11 (quint, J = 8, 2H), 3.95 (t, J = 8, 2H), 4.34 (t, J = 8, 2H), 5.45 (s, 2H), 6.82–6.91 (m, 3H), 7.22–7.46 (m, 9H), 9.34 (s, 1H), ^{13}C NMR (100 MHz, $CDCl_3$) δ: 24.0 (CH_2), 25.3 (CH_2), 48.2 (CH_2), 51.7 (CH_2), 64.9 (CH_2), 112.5 (CH), 118.9 (CH), 120.4 (CH), 120.7 (CH), 127.2 (CH), 127.6 (CH), 129.5 (CH), 131.0 (C), 134.0 (CH), 156.6 (C), IR (NaCl): ν_{max} cm^{-1} 3133 (C–H, sp^2), 1560–1471 (C═C), 1164 (C–N), 1081 (C–O), 814 (C–H , bending). LCMS (M-NCS) 307 found for $C_{20}H_{23}N_2O^+$.

3.5.16. 1-Benzyl-3-(4-phenoxybutyl)-1H-imidazol-3-ium Nitrate ***19***

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.68 (quint, J = 8, 2H), 1.99 (quint, J = 8, 2H), 3.83 (t, J = 8, 2H), 4.26 (t, J = 8, 2H), 5.43 (s, 2H), 6.71–6.81 (m, 3H), 7.10–7.54 (m, 9H), 10.29 (s, 1H), ^{13}C NMR (100 MHz, $CDCl_3$) δ: 25.8 (CH_2), 27.2 (CH_2), 49.6 (CH_2), 52.9 (CH_2), 66.6 (CH_2), 114.3 (CH), 120.7 (CH), 122.1 (CH), 122.7 (CH), 128.9 (CH), 129.2 (CH), 129.3 (CH), 129.4 (CH), 133.0 (C), 136.2 (CH), 158.4 (C), IR (NaCl): ν_{max} cm^{-1} 3132 (C–H, sp^2), 1597–1469 (C═C), 1166 (C–N),1082 (C-O), 816 (C–H , bending). LCMS (M–NO_3) 307 found for $C_{20}H_{23}N_2O^+$.

3.5.17. 3-(3-Hydroxypropyl)-1-propyl-1H-imidazol-3-ium tetrafluoroborate ***20***

^{1}H NMR (400 MHz, D_2O) δ: 0.98 (t, J = 7.2 , Hz 3H), 1.97 (t, J = 7.2 , Hz 2H), 2.20 (quint, J = 7.6 Hz , 2H), 3.72 (sixtet, J = 7.6 Hz , 2H), 4.24 (t, J = 7.6 Hz , 2H), 4.39 (t, J = 7.6 Hz , 2H), 7.58–7.60 (m, 2H), 8.83 (s, 1H), ^{13}C NMR (100 MHz, D_2O) δ: 9.9 (CH_3), 22.9 (CH_2), 31.8 (CH_2), 46.7 (CH_2), 51.3 (CH_2), 58.2 (CH_2), 122.5 (CH), 122.6 (CH), 135.5 (CH), ^{19}F NMR (376.5 MHz, D_2O) δ: −150.20, ^{11}B NMR (128 MHz, D_2O) δ: −1.26, IR (NaCl): ν_{max} cm^{-1} 3214 (O–H), 3162 (C–H, sp^2), 1567 (C═C), 1165 (C–N), 1160 (C–O), LCMS (M–BF_4) 169 found for $C_9H_{17}N_2O^+$.

3.5.18. 3-(3-Hydroxypropyl)-1-propyl-1H-imidazol-3-ium hexafluorophosphate ***21***

^{1}H NMR (400 MHz, D_2O) δ: 0.97 (t, J = 7.2 , Hz 3H), 1.95 (t, J = 7.2 , Hz 2H), 2.18 (quint, J = 7.6 Hz , 2H), 3.70 (sixtet, J = 7.6 Hz, 2H), 4.22 (t, J = 7.6 Hz , 2H), 4.37 (t, J = 7.6 Hz , 2H), 7.56–7.58 (m, 2H), 8.81 (s, 1H), ^{13}C NMR (100 MHz, D_2O) δ: 9.8 (CH_3), 22.8 (CH_2), 31.6 (CH_2), 46.5 (CH_2), 51.1 (CH_2), 58.0 (CH_2), 122.3 (CH), 122.4 (CH), 135.4 (CH), ^{19}F NMR (376.5 MHz, D_2O) δ: −71.15 (d, J = 711.6 Hz); ^{31}P NMR (162 MHz, D_2O) δ: −144.26 (sep, J = 712.8 Hz), IR (NaCl): ν_{max} cm^{-1} 3211 (O–H), 3159 (C–H, sp^2), 1566 (C═C), 1162 (C–N), 1159 (C–O), LCMS (M–PF_6) 169 found for $C_9H_{17}N_2O^+$.

3.5.19. 3-(3-Hydroxypropyl)-1-propyl-1H-imidazol-3-ium trifluoroacetate ***22***

^{1}H NMR (400 MHz, D_2O) δ: 1.05 (t, J = 7.2 , Hz 3H), 2.02 (t, J = 7.2 , Hz 2H), 2.21 (quint, J = 7.6 Hz , 2H), 3.77 (sixtet, J = 7.6 Hz , 2H), 4.31 (t, J = 7.6 Hz , 2H), 4.46 (t, J = 7.6 Hz , 2H), 7.65–7.67 (m, 2H), 8.89 (s, 1H), ^{13}C NMR (100 MHz, D_2O) δ: 9.0 (CH_3), 22.0 (CH_2), 30.9 (CH_2), 45.8 (CH_2), 50.3 (CH_2), 57.2 (CH_2), 121.7 (CH), 121.8 (CH), 134.5 (CH), ^{19}F NMR (376.5 MHz, D_2O) δ: −150.03 ppm, IR (NaCl): ν_{max} cm^{-1} 3211 (O–H), 3162 (C–H, sp^2), 1564 (C═C), 1165 (C–N), 1151 (C–O), LCMS (M–CF_3CO_2) 169 found for $C_9H_{17}N_2O^+$.

3.5.20. 3-(3-Hydroxypropyl)-1-propyl-1H-imidazol-3-ium Dicyanoamine ***23***

^{1}H NMR (400 MHz, D_2O) δ: 0.97 (t, J = 7.2 , Hz 3H), 1.96 (t, J = 7.2 , Hz 2H), 2.18 (quint, J = 7.6 Hz , 2H), 3.70 (sixtet, J = 7.6 Hz , 2H), 4.24 (t, J = 7.6 Hz , 2H), 4.38 (t, J = 7.6 Hz , 2H), 7.58–7.60 (m, 2H), 8.87 (s, 1H), ^{13}C NMR (100 MHz, D_2O) δ: 10.1 (CH_3), 23.1 (CH_2), 31.8 (CH_2), 46.7 (CH_2), 51.3 (CH_2), 58.2 (CH_2), 122.5 (CH), 122.6 (CH), 135.5 (CH), IR (NaCl): ν_{max} cm^{-1} 3214 (O–H), 3158 (C–H, sp^2), 1567 (C═C), 1162 (C–N), 1160 (C–O), LCMS (M–$N(CN)_2$) 169 found for $C_9H_{17}N_2O^+$.

3.5.21. 3-(3-Hydroxypropyl)-1-propyl-1H-imidazol-3-ium thiocyanate ***24***

^{1}H NMR (400 MHz, D_2O) δ: 1.12 (t, J = 7.2 , Hz 3H), 2.11 (t, J = 7.2 , Hz 2H), 2.34 (quint, J = 7.6 Hz , 2H), 3.85 (sixtet, J = 7.6 Hz , 2H), 4.43 (t, J = 7.6 Hz , 2H), 4.56 (t, J = 7.6 Hz , 2H), 7.75–7.77 (m, 2H), 8.03 (s, 1H), ^{13}C NMR (100 MHz, D_2O) δ 10.5 (CH_3), 23.3 (CH_2), 32.1 (CH_2), 47.0 (CH_2), 51.6 (CH_2), 58.4 (CH_2), 122.7 (CH), 122.8 (CH), 135.6 (CH), IR (NaCl): ν_{max} cm^{-1} 3216 (O–H), 3164 (C–H, sp^2), 1569 (C═C), 1168 (C–N), 1162 (C–O), LCMS (M–NCS) 169 found for $C_9H_{17}N_2O^+$.

3.5.22. 3-(3-Hydroxypropyl)-1-propyl-1H-imidazol-3-ium Nitrate ***25***

^{1}H NMR (400 MHz, D_2O) δ: 1.14 (t, J = 7.2 , Hz 3H), 2.13 (t, J = 7.2 , Hz 2H), 2.36 (quint, J = 7.6 Hz , 2H), 3.87 (sixtet, J = 7.6 Hz , 2H), 4.45 (t, J = 7.6 Hz , 2H), 4.58 (t, J = 7.6 Hz , 2H), 7.77–7.79 (m, 2H), 8.05 (s, 1H), ^{13}C NMR (100 MHz, D_2O) δ: 10.8 (CH_3), 23.6 (CH_2), 32.4 (CH_2), 47.3 (CH_2), 51.9 (CH_2), 58.7 (CH_2), 123.0 (CH), 123.1 (CH), 135.9 (CH), IR (NaCl): ν_{max} cm^{-1} 3210 (O–H), 3161 (C–H,

sp^2), 1567 (C═C), 1165 (C–N), 1160 (C–O), LCMS (M–NO_3) 169 found for $C_9H_{17}N_2O^+$.

3.5.23. 3-(3-Hydroxypropyl)-1-pentyl-1H-imidazol-3-ium tetrafluoroborate **26**

^{1}H NMR (400 MHz, D_2O) δ: 0.89 (t, J = 7.6, 3H), 1.29–1.36 (m, 4H), 1.91 (quint, 2H), 2.14 (quint, J = 7.6, 2H), 3.65 (t, J = 6.8, 2H), 4.22 (t, J = 7.6, 2H), 4.33 (t, J = 6.8, 2H), 7.54–7.55 (dd, 2H), 8.79 (s,1H), ^{13}C NMR (100 MHz, D_2O) δ: 13.1 (CH_3), 21.4 (CH_2), 27.6 (CH_2), 28.9 (CH_2), 31.7 (CH_2), 46.6 (CH_2), 49.7 (CH_2), 58.1 (CH_2), 122.5 (CH), 122.6 (CH), 135.3 (CH), ^{19}F NMR (376.5 MHz, D_2O) δ: −150.28, ^{11}B NMR (128 MHz, D_2O) δ: −1.31, IR (NaCl): ν_{max} cm^{-1} 3210 (O-H), 3159 (C–H, sp^2), 1563 (C═C), 1162 (C–N), 1158 (C–O), LCMS (M-BF_4) 197 found for $C_{11}H_{21}N_2O^+$.

3.5.24. 3-(3-Hydroxypropyl)-1-pentyl -1H-imidazol-3-ium hexafluorophosphate **27**

^{1}H NMR (400 MHz, D_2O) δ: 0.88 (t, J = 7.6, 3H), 1.27–1.33 (m, 4H), 1.88 (quint, J = 7.6, 2H), 2.12 (quint, J = 7.6, 2H), 3.64 (t, J = 6.8, 2H), 4.20 (t, J = 7.6, 2H), 4.32 (t, J = 6.8, 2H), 7.51–7.52 (dd, 2H), 8.78 (s,1H), ^{13}C NMR (100 MHz, D_2O) δ 13.1 (CH_3), 21.4 (CH_2), 27.5 (CH_2), 28.8 (CH_2), 31.6 (CH_2), 46.6 (CH_2), 49.7 (CH_2), 58.0 (CH_2), 122.4 (CH), 122.5 (CH), 135.3 (CH), ^{19}F NMR (376.5 MHz, D_2O) δ: −72.96 (d, J = 711.6 Hz); ^{31}P NMR (162 MHz, D_2O) δ: −144.96 (sep, J = 712.8 Hz) ppm, IR (NaCl): ν_{max} cm^{-1} 3212 (O–H), 3162 (C–H, sp^2), 1565 (C═C), 1164 (C–N), 1158 (C-O), LCMS (M-PF_6) 197 found for $C_{11}H_{21}N_2O^+$.

3.5.25. 3-(3-Hydroxypropyl)-1-pentyl -1H-imidazol-3-ium trifluoroacetate **28**

^{1}H NMR (400 MHz, D_2O) δ: 0.98 (t, J = 7.6, 3H), 1.36–1.44 (m, 4H), 2.03 (quint, J = 7.6, 2H), 2.28 (quint, J = 7.6, 2H), 3.78 (t, J = 6.8, 2H), 4.38 (t, J = 7.6, 2H), 4.49 (t, J = 6.8, 2H), 7.69–7.70 (dd, 2H), 8.99 (s,1H), ^{13}C NMR (100 MHz, D_2O) δ: 13.4 (CH_3), 21.7 (CH_2), 27.9 (CH_2), 29.5 (CH_2), 32.3 (CH_2), 46.7 (CH_2), 49.8 (CH_2), 57.2 (CH_2), 121.9 (CH), 122.8 (CH), 136.3 (CH), ^{19}F NMR (376.5 MHz, D_2O) δ: −75.72, IR (NaCl): ν_{max} cm^{-1} 3211 (O–H), 3161 (C–H, sp^2), 1564 (C═C), 1163 (C–N), 1158 (C–O), LCMS (M–CF_3CO_2) 197 found for $C_{11}H_{21}N_2O^+$.

3.5.26. 3-(3-Hydroxypropyl)-1-pentyl-1H-imidazol-3-ium Dicyanoamine **29**

^{1}H NMR (400 MHz, D_2O) δ: 0.96 (t, J = 7.6, 3H), 1.38–1.44 (m, 4H), 2.01 (quint, J = 7.6, 2H), 2.23 (quint, J = 7.6, 2H), 3.74 (t, J = 6.8, 2H), 4.33 (t, J = 7.6, 2H), 4.44 (t, J = 6.8, 2H), 7.66–7.67 (dd, 2H), 8.96 (s,1H), ^{13}C NMR (100 MHz, D_2O) δ: 13.5 (CH_3), 21.7 (CH_2), 27.8 (CH_2), 29.2 (CH_2), 31.9 (CH_2), 46.8 (CH_2), 49.9 (CH_2), 58.1 (CH_2), 122.7 (CH), 122.8 (CH), 135.5 (CH), IR (NaCl): ν_{max} cm^{-1} 3210 (O-H), 3160 (C–H, sp^2), 1562 (C═C), 1163 (C–N), 1160 (C-O), LCMS (M–$N(CN)_2$) 197 found for $C_{11}H_{21}N_2O^+$.

3.5.27. 3-(3-hydroxypropyl)-1-pentyl-1H-imidazol-3-ium thiocyanate **30**

^{1}H NMR (400 MHz, D_2O) δ: 0.98 (t, J = 7.6, 3H), 1.37–1.44 (m, 4H), 2.03 (quint, J = 7.6, 2H), 2.28 (quint, J = 7.6, 2H), 3.78 (t, J = 6.8, 2H), 4.39 (t, J = 7.6, 2H), 4.49 (t, J = 6.8, 2H), 7.69–7.70 (dd, 2H), 8.99 (s,1H), ^{13}C NMR (100 MHz, D_2O) δ 13.6 (CH_3), 21.8 (CH_2), 28.0 (CH_2), 29.4 (CH_2), 32.1 (CH_2), 47.0 (CH_2), 50.0 (CH_2), 58.3 (CH_2), 122.7 (CH), 122.8 (CH), 135.5 (CH), IR (NaCl): ν_{max} cm^{-1} 3213 (O–H), 3163 (C–H, sp^2), 1565 (C═C), 1166 (C–N), 1163 (C–O), LCMS (M–NCS) 197 found for $C_{11}H_{21}N_2O^+$.

3.5.28. 3-(3-Hydroxypropyl)-1-pentyl-1H-imidazol-3-ium Nitrate **31**

^{1}H NMR (400 MHz, D_2O) δ: 0.91 (t, J = 7.6, 3H), 1.32–1.38 (m, 4H), 1.93 (quint, J = 7.6, 2H), 2.18 (quint, J = 7.6, 2H), 3.68 (t, J = 6.8, 2H), 4.27 (t, J = 7.6, 2H), 4.38 (t, J = 6.8, 2H), 7.59–7.60 (dd, 2H), 8.89 (s,1H), ^{13}C NMR (100 MHz, D_2O) δ: 13.3 (CH_3), 21.5 (CH_2), 27.7 (CH_2), 29.0 (CH_2), 31.8 (CH_2), 46.7 (CH_2), 49.8 (CH_2), 58.1 (CH_2), 122.6 (CH), 122.7 (CH), 135.4 (CH), IR (NaCl): ν_{max} cm^{-1} 3211 (O–H), 3160 (C–H, sp^2), 1563 (C═C), 1163 (C–N), 1161 (C–O), LCMS (M–NO_3) 197 found for $C_{11}H_{21}N_2O^+$.

4. Results and discussion

The reason for popularity of imidazolium as an IL cation is due to the features which can be achieved. It is easy to modify, stable under acidic conditions, and its charge density is low due to the aromatic system. The low charge density means that it is relatively easy to construct low melting salts from imidazolium.

The universal method of preparing ionic liquids is the alkylation of a suitable heteroatom containing organic molecule to form the cation. After the alkylation the anion is changed to one desired. The chemistry has been quite simple, which makes it economic, but usually long reaction times are needed to complete the alkylation step, this is why the exploration of the sonochemistry will be beneficial.

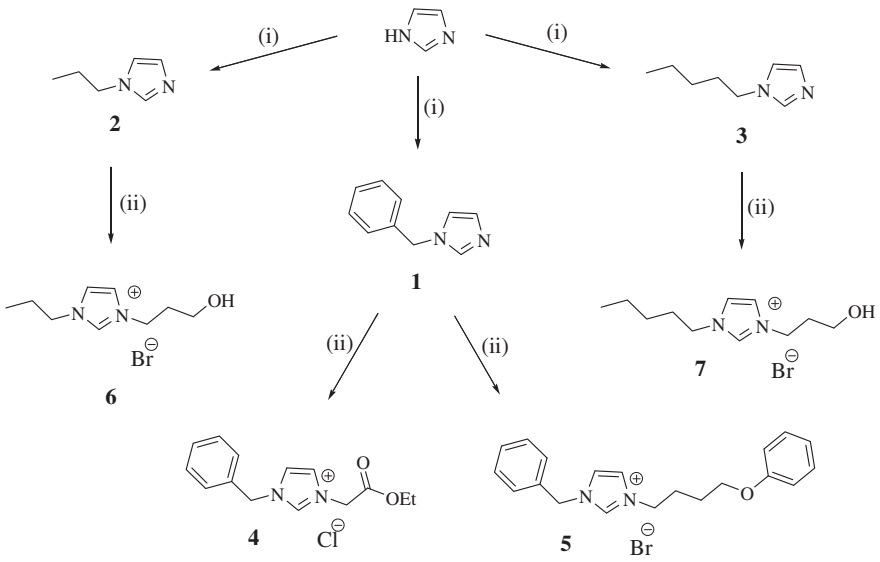
To the best of our knowledge, only compounds **5** and **14** have been previously reported by our team (Messali, 2013).

Initially, the known and commercially available N-alkylimidazoles (**1–3**) were easily prepared by treatment of imidazole with appropriate alkyl halides under basic conditions.

The quaternization reaction proceeds by an SN_2 mechanism. Therefore, both the nucleophile and the alkylating reagent have a strong influence on the reaction rate. The nucleophile in all the quaternization reactions was *N*-alkylimidazoles (**1–3**). In this way, the synthesis of imidazolium halides (**4–7**) is carried out by using different alkyl halides under conventional preparation (CP_1: toluene, 80 °C, 18 h) (Scheme 1).

On the other hand, the ultrasound-assisted preparation of imidazolium-based ionic liquids (**4–7**), already synthesized by conventional method, was explored further with the objective of shortening the reaction time. The reaction conditions were optimized by using a sonication bath with a strict control of temperature during the reaction process. The comparative results and the optimum reaction conditions determined for the synthesis of these unknown ionic liquids are summarized in Table 1.

Furthermore, ILs do not evaporate like volatile organic compounds do, but they will decompose at high temperatures. The decomposition temperature depends on the IL, and particularly on the anion. The low melting point and negligible



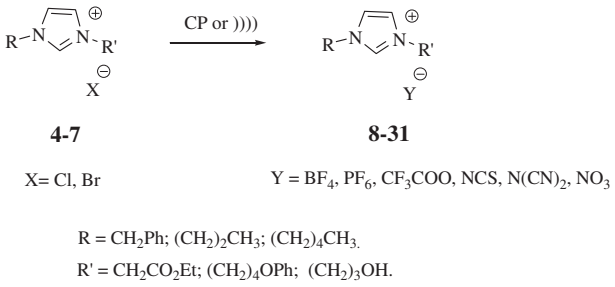
Scheme 1 (i) N-alkylation of imidazole: RBr, (KOH/K_2CO_3), acetonitrile, 80 °C, 24 h. R = CH_2Ph; $(CH_2)_2CH_3$; $(CH_2)_4CH_3$. (ii) N-alkylation of N-alkylimidazole: conventional preparation (CP_1) and ultrasonic irradiation conditions.(CP_1) : R'Br, toluene, 80 °C, 18 h; toluene, 80 °C, 5 h. R′ = CH_2CO_2Et; $(CH_2)_4OPh$; $(CH_2)_3OH$.

vapor pressure lead to a wide liquid range, often more than 300–400 °C (Holbrey and Seddon, 1999).

In This way, several alternative anions were subsequently introduced by a metathesis reaction (CP_2: Acetonitrile, 70 °C, 3 h) (Huddleston et al., 2001), with a slight excess of anions namely, sodium tetrafluoroborate, potassium hexafluorophosphate, trifluoroacetic acid sodium, sodium dicyanamide, sodium thiocyanate or sodium nitrate (Scheme 2). The pure metathesis products (**8–31**) were obtained after filtration of the salts (metal halides), then followed by filtrate evaporation and washing the residue with dichloromethane followed by further filtration to remove the excess of anion salts ($NaBF_4$, KPF_6, CF_3COONa, $NaN(CN)_2$, NaNCS, $NaNO_3$). Finally, evaporation of the filtrate afforded the desired ionic liquids in good yields.

The anion methathesis was easily carried out under ultrasound irradiation. The data in Table 2 indicated that very good yields were obtained within short reaction times. As observed, the anion nature of exchange agents did not affect the yields.

The preparations of the ionic liquids were monitored with ^1H NMR, ^{13}C NMR, ^{11}B NMR, ^{19}F NMR, ^{31}P NMR, FT-IR, and LCMS. NMR proved to be generally the most efficient method for monitoring the quaternization and methathesis reactions. The exchange of an anion from Cl^- or Br^- to BF_4^-, PF_6^- or other anions caused only slight changes in the NMR spectrum. The biggest difference in the ^1H NMR spectra is the chemical shift of the most acidic proton of the imidazolium ring. Furthermore the ^{11}B NMR, ^{19}F NMR, ^{31}P NMR spectra proved without ambiguity that the methathesis reactions were carried out successfully. Spectroscopic data of all newly synthesized room temperature ionic liquids are given in the experimental part.



Scheme 2 Anion metathesis using conventional preparation (CP_2) and ultrasonic irradiation conditions. (CP_2): MY, acetonitrile, 70 °C, 3 h;)))): acetonitrile, 70 °C, 45 min. M = Na, K.

Table 1 Reaction conditions and yields for the quaternization of N-alkylimidazole (1–3) using conventional preparation and ultrasound irradiation conditions.

Ionic liquid	R	R'	Yield (%) of the Quaternization step	
			CP_1[a]	))))[b]
4	CH_2Ph	CH_2CO_2Et	79	88
5	CH_2Ph	$(CH_2)_4OPh$	82	89
6	$(CH_2)_2CH_3$	$(CH_2)_3OH$	83	90
7	$(CH_2)_4CH_3$	$(CH_2)_3OH$	81	89

[a] Time (18 h), Temperature (80 °C) in Toluene;
[b] Time (5 h), Temperature (80 °C) in Toluene.

Table 2 Reaction conditions and yields for the anion metathesis reaction using conventional preparation and ultrasound irradiation conditions.

Ionic liquid	R	R′	X^-	MY	Yield (%) for the anion metathesis	
					CP_2[a]	))))[b]
8	CH_2Ph	CH_2CO_2Et	Cl^-	$NaBF_4$	95	98
9				KPF_6	93	96
10				$NaOOCCF_3$	95	97
11				$NaN(CN)_2$	94	97
12				NaNCS	94	95
13				$NaNO_3$	94	98
14	CH_2Ph	$(CH_2)_4OPh$	Br^-	$NaBF_4$	95	96
15				KPF_6	95	97
16				$NaOOCCF_3$	92	98
17				$NaN(CN)_2$	94	97
18				NaNCS	92	97
19				$NaNO_3$	94	95
20	$(CH_2)_2CH_3$	$(CH_2)_3OH$	Br^-	$NaBF_4$	94	97
21				KPF_6	93	96
22				$NaOOCCF_3$	95	97
23				$NaN(CN)_2$	92	96
24				NaNCS	93	95
25				$NaNO_3$	94	97
26	$(CH_2)_4CH_3$	$(CH_2)_3OH$	Br^-	$NaBF_4$	94	98
27				KPF_6	93	97
28				$NaOOCCF_3$	93	97
29				$NaN(CN)_2$	92	96
30				NaNCS	93	95
31				$NaNO_3$	92	96

[a] Time (3 h), Temperature (70 °C) in acetonitrile;
[b] Time (45 min), Temperature (70 °C) in acetonitrile.

5. Conclusion

In summary, new environmentally friendly functionalized imidazolium-based ionic liquids were prepared by using ultrasound irradiation. We indeed found that the simple, convenient and efficient sonochemistry methods could significantly enhance the yield of RTILs and decrease the reaction time. Further investigations on these new synthesized ionic-liquids as corrosion inhibitors will be discussed in detail in the forthcoming paper.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.arabjc.2013.08.023.

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