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ORIGINAL ARTICLE

# A facile and green microwave-assisted synthesis of new functionalized picolinium-based ionic liquids

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**Abstract** A facile preparation of a series of 17 new functionalized picolinium-based ionic liquids under "green chemistry" conditions is described. For the first time, target ionic liquids were prepared using standard methodology and under microwave irradiation in short duration of time with quantitative yields. Their structures were characterized by FT-IR, $^{1}$H NMR, $^{13}$C NMR, $^{11}$B, $^{19}$F, $^{31}$P and mass spectra.

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## 1. Introduction

Considerable stress to replace a lot of volatile organic compounds that were used as solvents in synthetic organic chemistry has been laid on many chemical industries. Chlorinated hydrocarbons and many other toxic substances having hazardous effect caused many serious environmental problems which led to make their use prohibitive. A suitable solution for these problems is found by using the ionic liquid as a clean medium of working and avoiding the solvent effect as well as the catalyst recycling problems (Sheldon, 2001; Carmichael, 2000; Seddon, 1998).

Ionic liquids (ILs) are salts consisting of ions, which exist in the liquid state at ambient temperatures. They have many unique physicochemical properties, such as negligible vapor pressure, high thermal and chemical stabilities, high ionic conductivity, excellent solubility with many substances (Davis, 2004). They 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 (Endres, 2002; Lin and Sun, 1999), electrolyte for electrochemical devices such as battery (Takahashi et al., 1999; Brennecke and Magin, 2001), supercapacitors (Ue et al., 2003; Balducci et al., 2004) and, in particular, fluids for thermal storage and exchange in solar concentrating power plants (Moens et al., 2003).

It is found that the cation and anion modifications with special functional groups led to a pronounced change in the properties of ionic liquids (ILs). Incorporating of the ILs with more than one functional group has attractive great interest in chemical synthesis, separation science, electrochemistry, instrumental analysis and energy sources (Chen, 2010).

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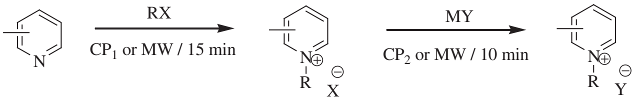
On the other hand, different procedures are recommended for green chemistry (Anastas and Warner, 1998) involving: solvent-free reactions, non-classical modes of activation such as ultrasounds or microwaves. The use of MW irradiation leads to large reductions in reaction times, enhancements in conversions, sometimes in selectivity, with several advantages of the eco-friendly approach (Loupy, 2004; Aupoix et al., 2010; Yi et al., 2005; Singh et al., 2005; Deetlefs and Seddon, 2003).

## 2. Materials and methods

### 2.1. Experimental

All new compounds were synthesized and characterized by $^1$H NMR, $^{13}$C NMR, IR and LCMS.

$^1$H NMR (400 MHz) and $^{13}$C NMR (100 MHz) spectra were measured in DMSO at room temperature at 400 MHz. Chemical shifts (d) were reported in ppm to a scale calibrated for tetramethylsilane (TMS), which is used as an internal standard. The LCMS spectra were measured with a Micromass, LCT mass spectrometer. IR spectra were recorded in NaCl disc on a Schimadzu 8201 PC, FTIR spectrophotometer ($v_{max}$ in cm$^{-1}$). The microwave-assisted reactions were performed using a controllable single-mode microwave reactor, CEM Discovery, designed for synthetic use. The reactor is equipped with a magnetic stirrer as well as pressure, temperature and power controls. The maximum operating pressure of the reactor is 20 bar. The power and temperature ranges are 15–300 W and 60–250 °C, respectively.



R = $NC(CH_2)_3$, $EtO_2C(CH_2)_3$, $EtO_2C(CH_2)_4$
X = Cl, Br
MY = $NaBF_4$, $KPF_6$

$CP_1$: toluene, 80 °C, 18h; $CP_2$: Acetonitrile, 70 °C, 3h

**Scheme 1** Synthesis of picolinium-based ionic liquids by conventional preparation (CP) and under microwave irradiation (MW).

### 2.2. Synthesis

#### *2.2.1. General procedures for the synthesis of picolinium halides (1, 4, 7, 10, 13 and 16) using conventional method*

To the solution of picoline (1 eq) in toluene, was added alkyl halide (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 from the initially obtained clear and homogenous mixture of picoline and alkyl halide in toluene. The product was isolated by extraction to remove the unreacted starting materials and solvent. Subsequently, the picolinium salt was washed with ethyl acetate. In each case, the IL/

**Table 1** Different entries, reaction conditions and reaction yields for the synthesis of picolinium-based ionic liquids using conventional preparation (CP) and under microwave irradiation (MW).

| Entry | Amine | RX | Yield (%) N-alkylation (first step) | | MY | Yield (%) Anion metathesis (second step) | |
|---|---|---|---|---|---|---|---|
| | | | CP[a] | MW[b] | | CP[c] | MW[d] |
| 1 | 2-Picoline | $NC(CH_2)_3Cl^*$ | 67 | 78 | | | |
| 2 | | | | | $NaBF_4$ | 91 | 98 |
| 3 | | | | | $KPF_6$ | 92 | 98 |
| 4 | 3-Picoline | $NC(CH_2)_3Cl^*$ | 64 | 76 | | | |
| 5 | | | | | $NaBF_4$ | 92 | 98 |
| 6 | | | | | $KPF_6$ | 93 | 98 |
| 7 | | $EtO_2C(CH_2)_3$ Br | 78 | 89 | | | |
| 8 | | | | | $NaBF_4$ | 94 | 97 |
| 9 | | | | | $KPF_6$ | 93 | 97 |
| 10 | | $EtO_2C(CH_2)_4$ Br | 81 | 90 | | | |
| 11 | | | | | $NaBF_4$ | 92 | 97 |
| 12 | | | | | $KPF_6$ | 94 | 98 |
| 13 | 4-Picoline | $EtO_2C(CH_2)_3$ Br | 79 | 90 | | | |
| 14 | | | | | $NaBF_4$ | 94 | 98 |
| 15 | | | | | $KPF_6$ | 93 | 97 |
| 16 | | $EtO_2C(CH_2)_4$ Br | 81 | 91 | | | |
| 17 | | | | | $NaBF_4$ | 92 | 98 |
| 18 | | | | | $KPF_6$ | 94 | 97 |

[a] Time (18 h), temperature (80 °C) in toluene.
[b] Time (15 min), temperature (80 °C), power (240 W), pressure (40 Psi).
[c] Time (3 h), temperature (80 °C).
[d] Time (10 min), temperature (70 °C), power (300 W), pressure (40 Psi).
* Higher temperatures and longer reaction times are required in CP.

**Table 2** Spectroscopic data for the newly synthesized ionic liquids.

| Entry | $^1$H NMR | $^{13}$C NMR | IR (cm$^{-1}$) | LCMS |
|---|---|---|---|---|
| **1** | 2.33–2.41 (quint, *J* = 7.2, 2H), 2.72–2.75 (t, *J* = 7.2, 2H), 2.89 (s, 3H); 4.69–4.72 (t, *J* = 7.2, 2H), 7.89–7.97 (m, 2H), 8.39–8.44 (m, 1H) 8.78–8.79 (m, 1H) | 13.9, ($CH_2$); 19.5 ($CH_3$); 24.9 ($CH_2$); 56.2 ($CH_2$); 119.9 (C); 125.9 (CH); 130.4 (CH); 144.9 (CH); 145.6 (CH); 155.9 (C) | 2247 (CN) | (M-Cl) 161 found for $C_{10}H_{13}N_2^+$ |
| **2** | 2.17–2.24 (quint, *J* = 7.2, 2H); 2.66–2.69 (t, *J* = 7.2, 2H); 2.83 (s, 3H); 4.55–4.59 (t, *J* = 7.2, 2H); 7.92–8.02 (m, 2H); 8.42–8.46 (m, 1H) 8.89–8.91 (m, 1H) | 13.9, ($CH_2$); 19.7 ($CH_3$); 25.2 ($CH_2$); 56.1 ($CH_2$); 119.8 (C); 125.9 (CH); 130.3 (CH); 145.6 (CH); 155.7 (C) | 2246 (CN) | (M-$BF_4$) 161 found for $C_{10}H_{13}N_2^+$ |
| **3** | 2.19–2.23 (quint, *J* = 7.2, 2H); 2.68–2.72 (t, *J* = 7.2, 2H); 2.84 (s, 3H); 4.57–4.51 (t, *J* = 7.2, 2H); 7.97–8.05 (m, 2H); 8.45–8.47 (m, 1H) 8.94–8.96 (m, 1H) | 13.6, ($CH_2$); 19.6 ($CH_3$); 24.9 ($CH_2$); 55.8 ($CH_2$); 119.6 (C); 125.6 (CH); 130.0 (CH); 145.4 (CH); 145.5 (CH); 155.5 (C) | 2247 (CN) | (M-$PF_6$) 161 found for $C_{10}H_{13}N_2^+$ |
| **4** | 2.44–2.49 (quint, *J* = 7.2, 2H); 2.68–2.72 (t, *J* = 7.2, 2H); 4.73–4.76 (t, *J* = 7.2, 2H); 4.79 (s, 3H); 8.00–8.03 (m, 1H); 8.44–8.46 (d, *J* = 8, 1H) 8.75–8.77 (d, *J* = 5.6, 1H); 8.81 (s, 1H) | 16.3, ($CH_2$); 20.3 ($CH_3$); 28.7 ($CH_2$); 62.4 ($CH_2$); 122.4 (C); 130.3 (CH); 142.8 (CH); 144.1 (CH); 146.5 (CH); 149.2 (C) | 2245 (CN) | (M-Cl) 161 found for $C_{10}H_{13}N_2^+$ |
| **5** | 2.26–2.32 (quint, *J* = 7.2, 2H); 2.60–2.63 (t, *J* = 7.2, 2H); 3.54 (s, 3H); 4.58–4.61 (t, *J* = 7.2, 2H); 8.00–8.04 (m, 1H); 8.42–8.44 (d, *J* = 8, 1H) 8.73–8.75 (d, *J* = 5.6, 1H); 8.91 (s, 1H) | 13.6, ($CH_2$); 18.0 ($CH_3$); 26.3 ($CH_2$); 59.6 ($CH_2$); 119.7 (C); 127.7 (CH); 139.3 (CH); 142.3 (CH); 144.6 (CH); 146.3 (C) | 2247 (CN) | (M-$BF_4$) 161 found for $C_{10}H_{13}N_2^+$ |
| **6** | 2.26–2.30 (quint, *J* = 7.2, 2H); 2.61–2.65 (t, *J* = 7.2, 2H); 3.33 (s, 3H); 4.59–4.62 (t, *J* = 7.2, 2H); 8.05–8.07 (m, 1H); 8.44–8.46 (d, *J* = 8, 1H) 8.88–8.89 (d, *J* = 5.6, 1H); 8.97 (s, 1H) | 13.5, ($CH_2$); 17.8 ($CH_3$); 26.0 ($CH_2$); 59.4 ($CH_2$); 119.5 (C); 127.4 (CH); 138.9 (CH); 142.2 (CH); 144.5 (CH); 146.0 (C) | 2246 (CN) | (M-$PF_6$) 161 found for $C_{10}H_{13}N_2^+$ |
| **7** | 1.20–1.23 (t, *J* = 7.2, 3H); 2.30–2.37 (quint, *J* = 7.2, 2H); 2.51–2.55 (t, *J* = 7.2, 2H); 2.55 (s, 3H); 4,07–4.12 (q, *J* = 7.2, 2H); 4.62–4.65 (t, *J* = 7.2, 2H); 7.95–7.98 (d, *J* = 7.2 1H); 8.38–8.40 (d, *J* = 8 1H); 8.68–8.70 (d, *J* = 5.2 1H); 8.75 (s, 1H) | 13.4 ($CH_3$); 17.8 ($CH_3$); 25.8 ($CH_2$), 30.5 ($CH_2$); 60.7 ($CH_2$), 62.0 ($CH_2$); 127.5 (CH); 140.1 (C); 141.5 (CH); 143.9 (CH); 146.4 (CH), 174.7 (C) | 1728 ($CO_2Et$) | (M-Br) 208 found for $C_{12}H_{18}NO_2^+$ |
| **8** | 1.15–1.18 (t, *J* = 7.2, 3H); 2.16–2.21 (quint, *J* = 7.2, 2H); 2.39–2.42 (t, *J* = 7.2, 2H); 2.50 (s, 3H); 4,00–4.05 (q, *J* = 7.2, 2H); 4.55–4.59 (t, *J* = 7.2, 2H); 8.02–8.06 (d, *J* = 7.2 1H); 8.43–8.45 (d, *J* = 8 1H); 8.87–8.88 (d, *J* = 6 1H); 8.96 (s, 1H) | 14.0 ($CH_3$); 17.8 ($CH_3$); 25.8 ($CH_2$), 30.0 ($CH_2$); 60.0 ($CH_2$), 60.1 ($CH_2$); 127.4 (CH); 138.8 (C); 142.0 (CH); 144.3 (CH); 145.8 (CH), 171.8 (C) | 1731 ($CO_2Et$) | (M-$BF_4$) 208 found for $C_{12}H_{18}NO_2^+$ |
| **9** | 1.15–1.18 (t, *J* = 7.2, 3H); 2.17–2.21 (quint, *J* = 7.2, 2H); 2.39–2.42 (t, *J* = 7.2, 2H); 2.50 (s, 3H); 4,00–4.05 (q, *J* = 7.2, 2H); 4.55–4.59 (t, *J* = 7.2, 2H); 8.02–8.05 (d, *J* = 7.2 1H); 8.42–8.44 (d, *J* = 8 1H); 8.86–8.88 (d, *J* = 6 1H); 8.95 (s, 1H) | 14.0 ($CH_3$); 17.8 ($CH_3$); 25.9 ($CH_2$), 30.1 ($CH_2$); 60.0 ($CH_2$), 60.1 ($CH_2$); 127.4 (CH); 138.9 (C); 142.0 (CH); 144.3 (CH); 145.8 (CH), 171.8 (C) | 1729 ($CO_2Et$) | (M-$PF_6$) 208 found for $C_{12}H_{18}NO_2^+$ |
| **10** | 1.24–1.25 (t, *J* = 7.2, 3H); 1.62–1.69 (quint, *J* = 7.2, 2H); 2.02–2.09 (quint, *J* = 7.2, 2H); 2.43–2.47 (t, *J* = 7.2, 2H); 2.56 (s, 2H); 4.11–4.16 (q, *J* = 7.2, 2H); 4.59–4.62 (t, *J* = 7.2, 2H); 7.94–7.98 (t, *J* = 7.2 1H); 8.38–8.40 (d, *J* = 8 1H); 8.68–8.70 (d, *J* = 6 1H); 8.75 (s, 1H) | 15.9 ($CH_3$); 20.3 ($CH_3$); 23.3 ($CH_2$); 32.4 ($CH_2$); 35.7 ($CH_2$); 63.7 ($CH_2$); 64.2 ($CH_2$); 130.0 (CH); 142.5 (C); 143.8 (CH); 146.3 (CH); 148.7 (CH); 178.5 (C) | 1730 ($CO_2Et$) | (M-Br) 222 found for $C_{12}H_{18}NO_2^+$ |

**Table 2** (*continued*)

| Entry | $^1$H NMR | $^{13}$C NMR | IR (cm$^{-1}$) | LCMS |
|---|---|---|---|---|
| **11** | 1.16–1.18 (t, *J* = 7.2, 3H); 1.50–1.54 (quint, *J* = 7.2, 2H); 1.92–1.96 (quint, *J* = 7.2, 2H); 2.33–2.37 (t, *J* = 7.2, 2H); 2.52 (s, 2H); 4.01–4.06 (q, *J* = 7.2, 2H); 4.53–4.57 (t, *J* = 7.2, 2H); 8.01–8.04 (t, *J* = 7.2 1H); 8.42–8.44 (d, *J* = 8 1H); 8.85–8.87 (d, *J* = 6 1H); 8.93 (s, 1H) | 14.2 ($CH_3$); 18.0 ($CH_3$); 21.2 ($CH_2$); 30.2 ($CH_2$); 32.8 ($CH_2$); 60.1 ($CH_2$); 60.5 ($CH_2$); 127.6 (CH); 139.2 (C); 142.0 (CH); 144.3 (CH); 146.0 (CH); 172.8 (C) | 1730 ($CO_2Et$) | (M-$BF_4$) 222 found for $C_{13}H_{20}NO_2^+$ |
| **12** | 1.18–1.21 (t, *J* = 7.2, 3H); 1.54–1.58 (quint, *J* = 7.2, 2H); 1.94–1.98 (quint, *J* = 7.2, 2H); 2.36–2.40 (t, *J* = 7.2, 2H); 2.53 (s, 2H); 4.05–4.10 (q, *J* = 7.2, 2H); 4.55–4.59 (t, *J* = 7.2, 2H); 8.01–8.04 (t, *J* = 7.2 1H); 8.42–8.44 (d, *J* = 8 1H); 8.86–8.88 (d, *J* = 6 1H); 8.93 (s, 1H) | 14.2 ($CH_3$); 18.0 ($CH_3$); 21.1 ($CH_2$); 30.1 ($CH_2$); 32.9 ($CH_2$); 60.2 ($CH_2$); 60.7 ($CH_2$); 127.6 (CH); 139.3 (C); 142.0 (CH); 144.3 (CH); 146.0 (CH); 172.9 (C) | 1730 ($CO_2Et$) | (M-$PF_6$) 222 found for $C_{13}H_{20}NO_2^+$ |
| **13** | 1.24–1.26 (t, *J* = 7.2, 3H); 2.32–2.37 (quint, *J* = 7.2, 2H); 2.54–2.56 (t, *J* = 7.2, 2H); 2.69 (s, 3H); 4,09–4.13 (q, *J* = 7.2, 2H); 4.14–4.68 (t, *J* = 7.2, 2H); 7.94–7.95 (d, *J* = 6 2H); 8.73–8.74 (d, *J* = 6.8 2H) | 13.6 ($CH_3$); 21.6 ($CH_3$); 25.8 ($CH_2$), 30.6 ($CH_2$); 60.8 ($CH_2$), 62.0 ($CH_2$); 128.6 (CH); 143.8 (CH); 160.4 (C), 174.7 (C) | 1729 ($CO_2Et$) | (M-Br) 208 found for $C_{12}H_{18}NO_2^+$ |
| **14** | 1.13–1.16 (t, *J* = 7.2, 3H); 2.13–2.17 (quint, *J* = 7.2, 2H); 2.36–2.40 (t, *J* = 7.2, 2H); 2.59 (s, 3H); 3.98–4.03 (q, *J* = 7.2, 2H); 4.51–4.54 (t, *J* = 7.2, 2H); 7.93–7.94 (d, *J* = 6 2H); 8.81–8.83 (d, *J* = 6.8 2H) | 14.2 ($CH_3$); 21.6 ($CH_3$); 26.2 ($CH_2$); 29.9 ($CH_2$); 30.3 ($CH_2$); 59.6 ($CH_2$); 60.6 ($CH_2$); 128.7 (CH); 143.9 (CH); 159.4(C); 172.2 (C) | 1729 ($CO_2Et$) | (M-$BF_4$) 208 found for $C_{12}H_{18}NO_2^+$ |
| **15** | 1.04–1.07 (t, *J* = 7.2, 3H); 2.04–2.08 (quint, *J* = 7.2, 2H); 2.27–2.30 (t, *J* = 7.2, 2H); 2.50 (s, 3H); 3.89–3.94 (q, *J* = 7.2, 2H); 4.42–4.46 (t, *J* = 7.2, 2H); 7.85–7.87 (d, *J* = 6 2H); 8.76–8.78 (d, *J* = 6.8 2H) | 14.0 ($CH_3$); 21.3 ($CH_3$); 25.8 ($CH_2$), 30.0 ($CH_2$); 59.3 ($CH_2$), 60.2 ($CH_2$); 128.4 (CH); 143.8 (CH); 159.0 (C), 171.8 (C) | 1731 ($CO_2Et$) | (M-$PF_6$) 208 found for $C_{12}H_{18}NO_2^+$ |
| **16** | 1.21–1.25 (t, *J* = 7.2, 3H); 1.64–1.68 (quint, *J* = 7.2, 2H); 2.02–2.07 (quint, *J* = 7.2, 2H);2.42–2.46 (t, *J* = 7.2, 2H); 2.66 (s, 3H); 4.09–4.15 (q, *J* = 7.2, 2H); 4.56–4.60 (t, *J* = 7.2, 2H); 7.90–7.92 (d, *J* = 6 2H); 8.68–8.70 (d, *J* = 6.8 2H) | 13.6 ($CH_3$); 20.9 ($CH_3$); 21.5 ($CH_2$); 29.9 ($CH_2$); 33.3 ($CH_2$); 60.6 ($CH_2$); 61.7 ($CH_2$); 128.8 (CH); 143.2 (CH); 160.2(C); 175.9 (C) | 1729 ($CO_2Et$) | (M-Br) 222 found for $C_{13}H_{20}NO_2^+$ |
| **17** | 1.13–1.17 (t, *J* = 7.2, 3H); 1.45–1.49 (quint, *J* = 7.2, 2H); 1.86–1.92 (quint, *J* = 7.2, 2H); 2.31–2.35 (t, *J* = 7.2, 2H); 2.59 (s, 3H); 4.00–4.05 (q, *J* = 7.2, 2H); 4.95–4.53 (t, *J* = 7.2, 2H); 7.93–7.95 (d, *J* = 6 2H); 8.83–8.85 (d, *J* = 6.8 2H) | 14.3 ($CH_3$); 21.0 ($CH_3$); 21.6 ($CH_2$); 30.1 ($CH_2$); 32.9 ($CH_2$); 59.9 ($CH_2$); 60.2 ($CH_2$); 128.7 (CH); 143.8 (CH); 159.3(C); 172.9 (C) | 1730 ($CO_2Et$) | (M-$BF_4$) 222 found for $C_{13}H_{20}NO_2^+$ |
| **18** | 1.16–1.19 (t, *J* = 7.2, 3H); 1.49–1.52 (quint, *J* = 7.2, 2H); 1.91–1.94 (quint, *J* = 7.2, 2H); 2.33–2.37 (t, *J* = 7.2, 2H); 2.61 (s, 3H); 4.01–4.07 (q, *J* = 7.2, 2H); 4.52–4.55 (t, *J* = 7.2, 2H); 7.97–7.98 (d, *J* = 6 2H); 8.89–8.90 (d, *J* = 6.8 2H). | 14.0 ($CH_3$); 20.8 ($CH_3$); 21.3 ($CH_2$); 29.8 ($CH_2$); 32.6 ($CH_2$); 59.6 ($CH_2$); 59.8 ($CH_2$); 128.4 (CH); 143.6 (CH); 159.9(C); 172.4 (C) | 1730 ($CO_2Et$) | (M-$PF_6$) 222 found for $C_{13}H_{20}NO_2^+$ |

salt was finally dried at a reduced pressure to get rid of all the volatile organic compounds.

### 2.2.2. General procedure for the synthesis of picolinium tetrafluoroborates or hexafluorophosphates (2, 3, 5, 6, 8, 9, 11, 12, 14, 15, 17 and 18) using conventional method

The quaternary salt (1 eq) was dissolved in acetonitrile to obtain a clear solution. To this solution of quaternary halide was added solution of sodium tetrafluoroborate or potassium hexafluorophosphate (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 leaded quantitatively to the desired ionic liquids.

### 2.2.3. General procedures for the synthesis of picolinium halides (1, 4, 7, 10, 13 and 16) under microwave irradiation

Picoline (1 eq) and the appropriate alkyls halides (1 eq) were placed in a microwave reactor vessel and irradiated for 15 min at 80 °C the product is collected as described in conventional procedures.

### 2.2.4. General procedure for the synthesis of picolinium tetrafluoroborate hexafluorophosphates (2, 3, 5, 6, 8, 9, 11, 12, 14, 15, 17 and 18) under microwave irradiation

Picolinium-halides salts (1 eq) were placed in a microwave reactor vessel, 1 eq of $NaBF_4$ or $KPF_6$ in a small amount of acetonitrile was added. The reaction was carried out for 10 min at 70 °C the product is collected as described in conventional procedures.

## 3. Results and discussion

In continuation of our previous work dealing with the developing of novel functionalized ionic liquids (Messali, 2011), in this paper we aimed to synthesize a new variety of picolinium-based ionic liquids under both conventional and microwave irradiation methods. To the best of our knowledge, only compound **16** has been previously reported by conventional methods (Krieg et al., 2007), its preparation under microwave irradiation has never been disclosed.

Initially, by using conventional preparation ($CP_1$: toluene, 80 °C, 18 h), the alkylation of different picolines with different functionalized alkyl halides afforded the corresponding picolinium halides in 64–81% yield as liquids (Scheme 1).

It is noticeable that the reactivity trend of halides is found to be in the order Br > Cl as expected for an $S_N2$ reaction, i.e. higher temperatures and longer reaction times are required with poorer leaving groups ($Cl^- < Br^-$).

Alternative anions were subsequently introduced by a metathesis reaction ($CP_2$: acetonitrile, 70 °C, 3 h) (Huddleston et al., 2001), with slightly excess of anions namely, tetrafluoroborate and/or hexafluorophosphate (Scheme 1). The pure metathesis products 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 ($NaBF_4$, $KPF_6$). Finally, evaporation of the filtrate afforded the desired ionic liquids in good yields.

On the other hand, the microwave–assisted preparation of picolinium-based ionic liquids, already synthesized by conventional methods, was explored further with the objective of shortening the reaction time. The reaction conditions were optimized by using the CEM Discover monomode system with a strict control of power and 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.

The preparation of picolinium tetrafluoroborate and hexafluorophosphate salts was easily carried out under microwave irradiation. The data in Table 1 indicated that very good yields were obtained within very short reaction times. As observed, the anion nature of exchange agents did not affect the yields.

The structures of all the newly synthesized room temperature ionic liquids were confirmed by $^1H$ NMR, $^{13}C$ NMR, $^{11}B$ NMR, $^{19}F$ NMR, $^{31}P$ NMR, FT-IR, and LCMS. All spectroscopic data are summarized in Table 2.

## 4. Conclusion

In conclusion, new environmentally friendly functionalized picolinium-based ionic liquids were prepared by using microwave irradiation. Comparison of CP and MW methods afforded a lot of advantages and recommendations for the use of the green microwave assisted reactions. Further investigations on these new synthesized ionic-liquids as corrosion inhibitors will be discussed in details in the forthcoming paper.

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.arabjc.2011.06.030.

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