Application of novel multi-cationic ionic liquids in microwave assisted 2-amino-4H-chromene synthesis

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Supporting Information

Experimental

General Remarks

\textsuperscript{1}H NMR and \textsuperscript{13}C NMR spectra were recorded on a Brucker AC (300 MHz for \textsuperscript{1}H NMR and 75 MHz for \textsuperscript{13}C NMR) spectrometer using D\textsubscript{2}O and MSO-d\textsubscript{6} as solvent and tetramethylsilane (TMS) as an internal standard. IR spectra were recorded on a PerkinElmer FTIR spectrometer. The samples were examined as KBr discs ~5\% w/w. Melting points were determined with a DBK melting point apparatus and are uncorrected. All the chemicals were obtained from Spectrochem, Sigma Aldrich and were used without further purification. The compounds Ia, IIa and IIIa were prepared following the literature procedure.\textsuperscript{1} Microwave irradiation was made using a Samsung domestic Microwave oven with adjustable 0-300 W output power.

Typical procedure for synthesis of bromide salts (Ib, IIb and II Ib):

A solution of 1-methyl imidazole (30 mmol) in MeCN (10mL) was added dropwise to
slurry of mono (bromomethyl) mesitylene (30 mmol) or bis (bromomethyl) mesitylene (15 mmol) or tris (bromomethyl) mesitylene (10 mmol) in MeCN (20 mL). The reaction mixture was stirred at room temperature for 24 h. A white precipitate formed was filtered, washed with MeCN (3 × 10 mL) and dried in vacuum to afford Ib, IIb and IIIb as white solids.

Typical procedure for synthesis of hydroxide salts Ic, IIc and IIIc.

Aqueous solution of hydroxide salts (Ic, IIc and IIIc) were prepared from corresponding bromide salts (Ib, IIb and IIIb) by anion metathesis reaction over anion exchange resin AMBERLYST A26 OH. In typical experiment corresponding bromide salts (25 g, Ib, IIb and IIIb) were dissolved in deionized water (200 mL) and passed over anion exchange resin (250 g) slowly. The absence of any bromide ions in aqueous ILs solution was tested by AgNO3 test. The amount of hydroxide ILs in aqueous solution was determined by titrating the aqueous ILs solution with standard HCl (0.1 N) conductometrically.

Typical procedure for synthesis of acetate (Id, IID and IIID) and methane sulfonate salts (Ie, Ile and Ile).

To an aqueous solution of hydroxide salts Ic, IIc and IIIc were added a equimolar amount of acetic acid /methane sulphonic acid in water. The reaction mixture was stirred at room temperature for 12 hrs. The solvent was removed on a rotary evaporator and the resultant oily compound was dried in vacuum at 80°C affording the corresponding ILs.

Typical procedure for synthesis of 2-amino-4H-chromene.

A mixture of an aromatic aldehyde (1 mmol), malononitrile (1.2 mmol), α/β-Naphthol (1 mmol) and 20 mol % IL was irradiated in microwave oven under solvent-free condition for appropriate time. After completion of the reaction (as monitored by TLC)
water was added and the solid product obtained was filtered, washed with water and recrystallized from hot ethanol.

**Spectral of Compounds:**

3[(2, 4, 6-trimethyl-1-phenylene) mono (methylene)] mono (1-methyl-1H-imidazol-3-ium) monobromide (Ib);

![Chemical structure of Ib]

Yield- 95 %; IR (KBr): \( \nu = 3480, 3407, 3135, 3098, 3060, 2968, 2868, 1612, 1569, 1463, 1274, 1159, 1094, 1028, 871, 842, 798, 765 \text{ cm}^{-1} \); \(^1\)H NMR (300 MHz, D\(_2\)O): \( \delta \) 2.05 (s, 6H), 2.08 (s, 3H), 3.64 (3H), 5.17 (s, 2H), 6.84 (s, 2H), 7.13(d, 1H), 7.24(d, 1H), 8.23 (s, 1H); \(^{13}\)C NMR (75MHz, D\(_2\)O): 18.5, 20.0, 35.8, 47.1, 121.8, 123.6, 125.8, 129.3, 135.3, 138.6, 140.1

3, 3'[(2, 4, 6-trimethyl-1, 3-phenylene) bis (methylene)] bis(1-methyl-1H-imidazol-3-ium) dibromide (IIb);

![Chemical structure of IIb]

Yield- 96 %; IR (KBr): \( \nu = 3438, 3350, 3140, 3073, 2952, 2887, 1601, 1567, 1454, 1333, 1157, 1019, 883, 811, 749, 614 \text{ cm}^{-1} \); \(^1\)H NMR(300MHz, D\(_2\)O): \( \delta \) 2.02 (s, 3H), 2.15 (s, 6H), 3.64 (s, 6H), 5.30 (s, 4H), 7.08 (s, 1H), 7.18 (s, 2H), 7.25 (d, 1H), 7.26 (d, 1H), 8.25 (s, 1H); \(^{13}\)C NMR (75MHz, D\(_2\)O):16.4, 18.8, 35.7, 47.5, 121.8, 123.7, 127.6, 131.2, 135.3, 139.0, 140.7
3, 3′,3″[(2, 4, 6-trimethyl-1,3,5-phenylene) tris (methylene)] tris (1-methyl-1H-imidazol-3-ium) tribromide (IIIb);

\[
\text{\begin{center}
\begin{tikzpicture}
\path
(0,0) node[draw,circle,inner sep=1.5pt] (a) {};
(1,0) node[draw,circle,inner sep=1.5pt] (b) {};
(2,0) node[draw,circle,inner sep=1.5pt] (c) {};
(0,-1) node[draw,circle,inner sep=1.5pt] (d) {};
(1,-1) node[draw,circle,inner sep=1.5pt] (e) {};
(2,-1) node[draw,circle,inner sep=1.5pt] (f) {};
\end{tikzpicture}
\end{center}}\]

Yield- 95 %; (KBr): \(\nu = 3435, 3144, 3078, 1630, 1570, 1489, 1333, 1158, 830, 762, 619\) cm\(^{-1}\); \(\text{\(1\)}\text{H NMR (300 MHz, D}_2\text{O): } \delta 2.22 (s, 9H), 3.73 (s, 9H), 5.48 (s, 6H), 7.27 (d, 3H), 7.29 (d, 3H), 8.34 (s, 3H); \(\text{\(13\)}\text{C NMR (75MHz, D}_2\text{O): } 15.2, 15.6, 35.9, 48.0, 121.8, 124.0, 129.0, 135.4, 140.6, 141.6.\)

3[(2, 4, 6-trimethyl-1-phenylene) mono (methylene)] mono (1-methyl-1H-imidazol-3-ium) monoacetate (Id)

\[
\text{\begin{center}
\begin{tikzpicture}
\path
(0,0) node[draw,circle,inner sep=1.5pt] (a) {};
(1,0) node[draw,circle,inner sep=1.5pt] (b) {};
(2,0) node[draw,circle,inner sep=1.5pt] (c) {};
(0,-1) node[draw,circle,inner sep=1.5pt] (d) {};
(1,-1) node[draw,circle,inner sep=1.5pt] (e) {};
(2,-1) node[draw,circle,inner sep=1.5pt] (f) {};
\end{tikzpicture}
\end{center}}\]

Yield 97 %; IR (thin film): \(\nu = 3479, 3411, 3140, 3094, 1571, 1408, 1160, 1017, 839, 763, 663\) cm\(^{-1}\); \(\text{\(1\)}\text{H NMR (300 MHz, D}_2\text{O): } \delta 1.72 (s, 3H), 2.10 (s, 9H), 3.62 (s, 3H), 5.19 (s, 2H), 6.88 (s, 2H), 7.15 (d, 1H), 7.23 (d, 1H), 8.19 (s, 1H); \(\text{\(13\)}\text{C NMR (75MHz, D}_2\text{O): } 18.3, 19.9, 23.0, 35.5, 47.0, 121.8, 123.6, 125.7, 129.2, 135.2, 138.6, 140.2, 181.1.\)

3, 3′[(2, 4, 6-trimethyl-1, 3-phenylene) bis (methylene)] bis (1-methyl-1H-imidazol-3-ium) diacetate (IId)
Yield 96%; IR (thin film): $\nu = 3438, 3354, 3147, 3075, 1649, 1573, 1408, 1158, 1018, 805, 702, 614 \text{ cm}^{-1}$; $^1$H NMR (300 MHz, D$_2$O): $\delta$ 1.64 (s, 6H), 1.19 (s, 3H), 2.11 (s, 6H), 3.64 (s, 6H), 5.38 (s, 4H), 7.03 (s, 1H), 7.24 (d, 2H), 7.26 (d, 2H), 8.33 (s, 2H); $^{13}$C NMR (75MHz, D$_2$O): 14.5, 18.3, 23.1, 35.6, 47.4, 121.7, 123.7, 127.6, 131.3, 135.3, 138.9, 140.7, 180.8.

$3, 3', 3''[(2, 4, 6$-trimethyl-1,3,5-phenylene) tris (methylene)] tris(1-methyl-1$H$-imidazol-3-ium) triacetate (IIId)

Yield 96%; IR (thin film): $\nu = 3444, 3354, 3151, 3101, 1642, 1574, 1410, 1336, 1160, 1019, 843, 763, 621 \text{ cm}^{-1}$; $^1$H NMR (300 MHz, D$_2$O): $\delta$ 1.68 (s, 9H), 2.13 (s, 9H), 3.65 (s, 9H), 5.39 (s, 6H), 7.17 (d, 3H), 7.28 (d, 3H), 8.32 (s, 3H); $^{13}$C NMR (75MHz, D$_2$O): 15.4, 23.1, 35.7, 47.8, 121.6, 123.8, 128.9, 135.5, 141.5, 181.1.

$3,[(2, 4, 6$-trimethyl-1-phenylene) mono (methylene)] mono (1-methyl-1$H$-imidazol-3-ium) mono methane sulphonate (Ie)
Yield 96 %; IR (thin film): $\nu = 3482, 3136, 3095, 3061, 2968, 1613, 1570, 1463, 1194, 1058, 785, 700 \text{ cm}^{-1}$; $^1$H NMR (300 MHz, D$_2$O): $\delta$ 2.00 (s, 9H), 2.56 (s, 3H), 3.63 (s, 3H), 5.11 (s, 2H), 6.75 (s, 2H), 7.05 (d, 1H), 7.21 (d, 1H), 8.22 (s, 1H); $^{13}$C NMR (75 MHz, D$_2$O): 18.9, 20.0, 35.6, 38.4, 47.0, 121.7, 123.7, 125.8, 129.3, 135.3, 138.5, 139.9.

3, 3’[(2, 4, 6-trimethyl-1, 3-phenylene) bis (methylene)] bis(1-methyl-1H-imidazol-3-ium) di methanesulphonate (IIe)

\[
\begin{align*}
\text{ Yield 97 %; IR (thin film): } & \nu = 3420, 3140, 3079, 3014, 2979, 1615, 1571, 1460, 1330, 1194, 1058, 785, 616 \text{ cm}^{-1}; \quad & ^1\text{H NMR (300 MHz, D}_2\text{O): } \delta 2.05 (s, 3H), 2.17 (s, 6H), 3.05 (s, 6H), 3.67 (s, 6H), 5.31 (s, 4H), 7.08 (s, 1H), 7.20 (d, 2H), 7.29 (d, 2H), 8.29 (s, 2H); \quad & ^{13}\text{C NMR (75 MHz, D}_2\text{O): } 14.6, 18.9, 35.7, 44.0, 47.5, 121.7, 123.8, 127.7, 131.3, 135.3, 139.0, 140.7.
\end{align*}
\]

3, 3’, 3”[(2, 4, 6-trimethyl-1,3,5-phenylene) tris (methylene)] tris(1-methyl-1H-imidazol-3-ium) tri methane sulphonate (IIle)

\[
\begin{align*}
\text{ Yield 96 %; IR (thin film): } & \nu = 3452, 3155, 3103, 2933, 1634, 1574, 1455, 1333, 1193, 1058, 784, 621 \text{ cm}^{-1}; \quad & ^1\text{H NMR (300 MHz, D}_2\text{O): } \delta 2.12(s, 9H), 2.57(s, 9H), 3.65(s, 9H),
\end{align*}
\]
5.38 (s, 6H), 7.19 (d, 3H), 7.27 (d, 3H), 8.30 (s, 3H); $^{13}$C NMR(75MHz, D$_2$O): 15.5, 35.7, 38.3, 47.9, 121.7, 123.9, 128.9, 135.3, 141.5.

2-amino-4-(2-chlorophenyl)-3,4-dihydro-2H-benzo[h]chromene-3-carbonitrile

(Table 2, entry 1): IR (KBr) $\nu = 3479, 3327, 3192, 3056, 2199, 1661, 1407, 1185, 1102, 1049, 751$ cm$^{-1}$ $^1$H NMR (300 MHz, DMSO-d$_6$): $\delta$ 5.30 (s, 1H), 6.90 (d, 1H, $J$=8.4), 7.15-7.16 (m, 5H), 7.35 (d, 1H, $J$= 6.9), 7.47-7.56 (m, 3H), 7.77 (d, 1H, $J$ = 7.5), 8.14 (d, 1H, $J$=8.1) $^{13}$C NMR (75 MHz, DMSO-d$_6$): $\delta$ 55.29, 117.01, 120.62, 121.18, 123.09, 124.54, 125.88, 127.21, 127.36, 128.14, 128.40, 129.32, 130.26, 131.66, 132.45, 133.27, 142.63, 143.43, 160.82.

References:
IR and NMR Spectra of compounds:

Spectra 1. IR spectrum of compound 1a
Spectra 2. $^1$H NMR spectrum of compound Ia
Spectra 3. $^{13}$C NMR spectrum of compound Ia

Spectra 4. IR spectrum of compound IIa
Spectra 5. $^1$H NMR spectrum of compound IIa

Spectra 6. $^{13}$C NMR spectrum of compound IIa
Spectra 7. IR spectrum of compound IIIa

Spectra 8. $^1$H NMR spectrum of compound IIIa
Spectra 9. $^{13}$C NMR spectrum of compound IIIa

Spectra 10. IR spectrum of compound Ib
Spectra 11. $^1$H NMR spectrum of compound Ib

Spectra 12. $^{13}$C NMR spectrum of compound Ib
Spectra 13. IR spectrum of compound IIb

Spectra 14. $^1$H NMR spectrum of compound IIb
Spectra 15. $^{13}$C NMR spectrum of compound IIb

Spectra 16. IR spectrum of compound IIIb
Spectra 17. $^1$H NMR spectrum of compound IIIb

Spectra 18. $^{13}$C NMR spectrum of compound IIIb
Spectra 19. IR spectrum of compound 1d

Spectra 20. $^1$H NMR spectrum of compound 1d
Spectra 21. $^{13}$C NMR spectrum of compound Id

Spectra 22. IR spectrum of compound IId
Spectra 23. $^1$H NMR spectrum of compound IId

Spectra 24. $^{13}$C NMR spectrum of compound IId
Spectra 25. IR spectrum of compound IIId

Spectra 26. $^1$H NMR spectrum of compound IIId
Spectra 27. $^{13}$C NMR spectrum of compound IIId

Spectra 28. IR spectrum of compound Ie
Spectra 29. $^1$H NMR spectrum of compound Ie

Spectra 30. $^{13}$C NMR spectrum of compound Ie
Spectra 31. IR spectrum of compound IIe

Spectra 32. $^1$H NMR spectrum of compound IIe
Spectra 33. $^{13}$C NMR spectrum of compound IIe

Spectra 34. IR spectrum of compound IIIe
Spectra 35. $^1$H NMR spectrum of compound IIIe

Spectra 36. $^{13}$C NMR spectrum of compound IIIe
Spectra 37. IR spectrum of compound chromene

Spectra 38. $^1$H NMR spectrum of compound chromene
Spectra 39. $13^c$ NMR spectrum of compound chromene