Supplementary Material

Design and synthesis of piperazine–based ionic liquids for liquid–liquid extraction of Cu(II), Ni(II) and Co(II) from water

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**Synthesis of piperazine functional groups**

Two N–heteroalkyl–N′–tosylpiperazines were synthesized according to protocols published in the literature (Huang JY, Xu WY, Xie HJ and Li SJ, One-Step Cyclization: Synthesis of N–Heteroalkyl–N′–tosylpiperazines. *J Org Chem* **77**: 7506–7511 (2012)). Subsequently, tosyl group was removed by sulfuric acid (98 v/v%, 10 mL) with stirring at 120 °C for 24 h under N₂ atmosphere. The mixture was cooled and adjusted pH to 10 with aq. NaOH. The resulting solution was extracted with CHCl₃ (10 mL ×3). The combined organic phases were concentrated under reduced pressure and the residue was dried under vacuum to give mono-substituted piperazines.

![Scheme S1](image)

**Scheme S1.** Synthetic route of mono-substituted piperazines. Reaction Conditions: (a, b) K₂CO₃, MeCN, reflux under N₂ atmosphere, 12 h; (c, d) H₂SO₄, N₂ atmosphere, 120°C, 24 h.
Compound 1

$^1$H NMR

$^{13}$C NMR
Compound 2

$^1$H NMR

$^{13}$C NMR
Compound 3a

$^1$H NMR

$^{13}$C NMR
Compound 3b

$^1$H NMR

$^{13}$C NMR