

Supplementary Material

Mechanosynthesis of *N*-methyl imines using recyclable imidazole-based acid-scavenger: *In situ* formed ionic liquid as catalyst and dehydrating agent

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Experiment

General

All chemicals were purchased from either Merck or Fluka Chemical Companies. All of the quoted yields refer to the yields of the isolated products unless otherwise stated. Known products were characterized by their melting point and FTIR, NMR spectral data, and comparison with the literature. The purity determination of the substrates and reaction monitoring was accompanied by TLC using silica gel SILG/UV254 plates. The infrared (IR) spectra were acquired on a Perkin–Elmer 781 spectrophotometer using KBr pellets as the diluent for solid and neat for liquid samples in the range of 4000–500 cm⁻¹. The reaction conversions were measured by GC–MS on an Agilent GC-Mass-6890 instrument under 70eV conditions. The ¹H and ¹³C NMR spectra were recorded on a Bruker Avance 300 or 400 MHz instrument (δ in ppm). Melting points were recorded on a Büchi B-545 apparatus. Ball-milling was performed in a Retsch PM100 planetary ball mill using a 25 mL stainless steel chamber and two or four stainless steel balls (diameter: 5 or 7 mm) with 300–600 revolution per minute (rpm).

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The modified method of the synthesis of 1,1'-(1,4-Butanediyl)bis(imidazole) [1,4-(Im)₂Bu]

A solution of sodium methoxide 30% in methanol (18 mL, 0.10 mol) was slowly added to a solution of imidazole (6.8 g, 0.10 mol) in methanol (100 mL) and stirred under reflux condition for 2 h. 1,4-Dichlorobutane (5.5 mL, 0.05 mol) was added, and the mixture was stirred under reflux condition overnight. Then the mixture was poured into 100 mL of water. A white solid formed immediately which separated and weighed 9.4g (98%) after drying. The reaction product was identified by comparing melting point and spectral data (i.e., FTIR, ¹H and ¹³C NMR, and MS) with that reported in the literature [50].

General procedure for *N*-methyl imines formation

1,4-(Im)₂Bu (0.5 g, 2.6 mmol) was ground with a mixture of methylamine hydrochloride (0.34 g, 5.0 mmol) and appropriate aldehydes (5.0 mmol) in a planetary ball mill at room temperature. After completion of the reaction (monitored by TLC), the product was extracted by EtOAc (5 × 5 mL). The combined organic extracts was washed with deionized water (3 × 5 mL), then dried over anhydrous sodium sulfate and the solvent was evaporated at room temperature on a rotary evaporator to obtain the enough pure oil products (Screen by ¹H NMR). The solid product **2v** was purified by recrystallization from hot ethanol. The FTIR and ¹H NMR spectra of known compounds were in agreement with those reported in the literature [33, 42-44 and 46].

In another experiment, the combined extracts were concentrated in vacuum and examined by GC-MS which no signal of the 1,4-(Im)₂Bu was detected.

Regeneration of 1,4-(Im)₂Bu

After each run, 1,1'-(1,4-butanediyl)bis(imidazolium) chloride 1,4-(Im)₂Bu•HCl was isolated and neutralized by the incremental addition of sodium hydrogen carbonate until pH 6. The residue solid was filtrated and washed several times with deionized water, then dried overnight at 50 °C under vacuum. The FT-IR spectra of fresh and recycled 1,4-(Im)₂Bu were identical in all aspects.

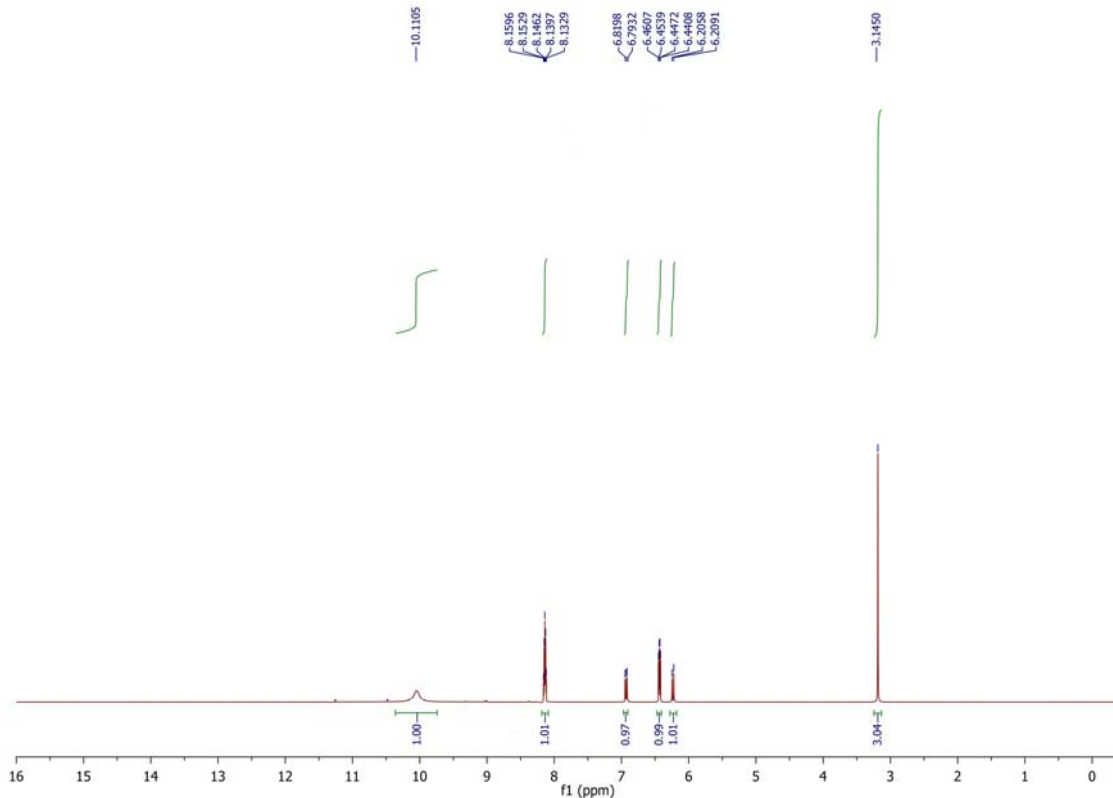
Physical and spectral data of new products

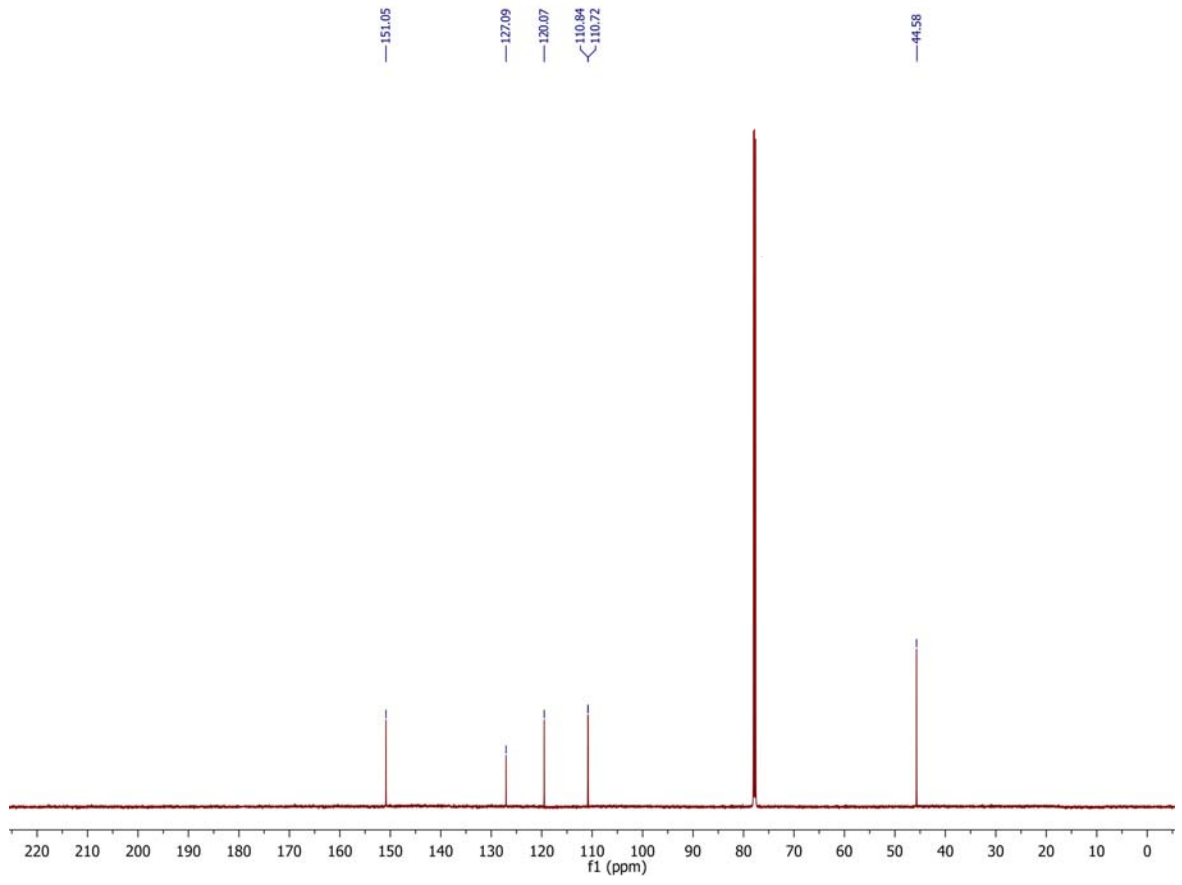
N-(1*H*-pyrrol-2-ylmethylene)-methyl-amine (Table 2, entry 21): colorless oil; IR (neat): ν_{\max} 3452, 2944, 1641 (C=N), 1572, 1551, 1445 (C=C), 1389, 1262, 1208, 1146, 1038 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): δ 3.14 (m, 3H, CH₃), 6.21 (d, *J* = 2.0 Hz, 1H, pyrrole), 6.45 (dd, *J* = 2.0 Hz, 1H, pyrrole), 6.80 (d, *J* = 0.8 Hz, 1H, pyrrole), 8.15 (q, *J* = 2.0 Hz, 1H, N=CH), 10.11 (br s, 1H, NH) ppm; ¹³C NMR (CDCl₃, 75 MHz): δ 44.6, 110.7, 110.8, 120.1, 127.1, 151.0 ppm; Anal. Calcd for C₆H₈N₂: C, 66.64; H, 7.46, N, 25.90. Found: C, 66.67; H, 7.43; N, 25.93.

N,N'-(*p*-Phenylenedimethyldiylidene)-bis(methyl-amine) (Table 2, entry 22): yellow powder; IR (neat): ν_{\max} 3005, 2805, 1645 (C=N), 995, 935, 805 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz): δ 3.50 (d, $J = 1.5$ Hz, 6H, $2 \times \text{CH}_3$), 7.66 (s, 4 H, Ar-H), 8.23 (m, 2H, N=CH) ppm; ^{13}C NMR (CDCl_3 , 75 MHz): δ 44.2, 127.1, 140.5, 159.8 ppm; Anal. Calcd for $\text{C}_{10}\text{H}_{12}\text{N}_2$: C, 74.97; H, 7.55; N, 17.48. Found: C, 74.92; H, 7.51; N, 17.43.

^1H NMR and ^{13}C NMR copies of 2u and 2v (The NMR spectra were recorded in 300 MHz Bruker instrument and CDCl_3 were used as NMR solvent).

N-(1*H*-pyrrol-2-ylmethylene)-methyl-amine (2u)





N,N'-(*p*-Phenylenedimethyldiylidene)-bis(methyl-amine) (**2v**)

