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SUPPORTING INFORMATION

Title: A Basic Ionic Liquid as Catalyst and Reaction Medium: A Rapid and Simple Procedure for Aza-Michael Addition Reactions

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General procedure for the synthesis of basic ionic liquid. [BMIM]OH was prepared by passing the corresponding imidazolium halide ([BMIM]Cl) through a column filled with anion exchange resin, as described in the literature.[5] The ionic liquid was characterized by IR, ^{1}H-NMR and ^{13}C-NMR. IR(neat): 3422, 3079, 1571, 1169 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$, δ, ppm): 0.96 (t, *J*=7.4 Hz, 3 H), 1.36-1.40 (m, 2 H), 1.87-1.93 (m, 2 H), 3.25-3.32 (bs, 1 H), 4.12 (s, 3 H), 4.34 (t, *J*=7.4 Hz, 2H), 7.50 (t, *J*=1.7, 1 H), 7.62 (t, *J*=1.7 Hz, 1 H), 10.24 (s, 1 H); ^{13}C-NMR (125 MHz, $CDCl_3$, δ, ppm): 13.4, 19.4, 32.1, 36.7, 49.7, 122.1, 123.8, 137.2. These values were in good agreement with the reported ones.[10].

Typical Procedure. Amines (1 mmol) and α,β-unsaturated carbonyl compounds (1.2 mmol) were added to a 10 mL conical flask containing 1 ml [bmIm]OH and the mixture was shaken at ambient temperature for 10 min. The reaction mixture was extracted from the ionic liquid phase with ethyl ether (10.0 mL×3). The organic layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure. The residue was purified by flash column chromatography (silica gel，petroleum ether/ethyl acetate=1/1, v/v) to obtain the corresponding Michael adduct as a colorless oil. The ionic liquid left in the conical flask was further washed with ether, dried under vacuum at 90˚C for 2 h to eliminate any water trapped from moisture and reused for subsequent reactions.

Largle-scaled synthesis of 3a. piperidine (200 mmol) and methyl acrylate (240 mmol) were added to a 100 mL of rounded flask containing 5 mL [bmIm]OH and the mixture was stirred at ambient temperature for 15 min. The excess methyl acrylate was recycled. The product was distilled directly from the reaction flask to obtain 8.5g. The remained [bmIm]OH was reused without any additional operation. The reaction was repeated 8 times without significant loss of activity.

3-(1-piperidinyl)-propionic acid methyl ester (3a): colorless oil; IR (neat): 2935, 1742, 1170 cm^{-1} ; ^{1}H NMR ($CDCl_3$, 500 MHz, δ, ppm): 3.64 (s, 3H, -OC$\underline{H}_3$), 2.62 (t, 2H, *J*=7.40, N-C$\underline{H}_2$-CH_2-C=O), 2.47 (t, 2H, *J*=7.40, N-CH_2-C$\underline{H}_2$-C=O), 2.35 (bs, 4H, N-C$\underline{H}_2CH_2CH_2$), 1.53 (m, 4H, N-CH_2C$\underline{H}_2CH_2$), 1.38 (m, 2H, N-CH_2CH_2C$\underline{H}_2$). ^{13}C NMR ($CDCl_3$, 125 MHz, δ, ppm): 173.3 (-O-$\underline{C}$=O), 54.4 (N-$\underline{C}H_2CH_2CH_2$), 51.7 (-O$\underline{C}H_3$, N-$\underline{C}H_2CH_2C$=O), 32.1 (N-$CH_2\underline{C}H_2C$=O), 26.0 (N-$CH_2\underline{C}H_2CH_2$), 24.4 (N-$CH_2CH_2\underline{C}H_2$).

3-(1-piperidinyl)-propionic acid ethyl ester (3b): colorless oil; IR (neat): 2936, 1737, 1173 cm^{-1} ; ^{1}H NMR ($CDCl_3$, 500 MHz, δ, ppm): 4.07 (q, 2H, *J*=7.1, -OC$\underline{H}_2CH_3$), 2.60 (t, 2H, *J*=7.77, N-C$\underline{H}_2$-CH_2-C=O), 2.43 (t, 2H, *J*=7.77, N-CH_2-C$\underline{H}_2$-C=O), 2.33 (bs, 4H, N-C$\underline{H}_2CH_2CH_2$), 1.51 (m, 4H, N-CH_2C$\underline{H}_2CH_2$), 1.36 (m, 2H, N-CH_2CH_2C$\underline{H}_2$), 1.18 (t, 3H, *J*=7.1, -OCH_2C$\underline{H}_3$). ^{13}C NMR ($CDCl_3$, 125 MHz, δ, ppm): 172.8 (-O-$\underline{C}$=O), 60.4 (-O$\underline{C}H_2CH_3$), 54.3 (N-$\underline{C}H_2CH_2C$=O, N-$\underline{C}H_2CH_2CH_2$), 32.3 (N-$CH_2\underline{C}H_2C$=O), 26.0 (N-$CH_2\underline{C}H_2CH_2$), 24.3 (N-$CH_2CH_2\underline{C}H_2$), 14.3 (-O$CH_2\underline{C}H_3$).

3-(1-piperidinyl)-propionic acid butyl ester (3c): colorless oil; IR (neat): 2935, 1737, 1171 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz, δ, ppm): 4.08 (t, 2H, -OC$\underline{H}_2CH_2$), 2.67 (t, 2H, *J*=7.27, N-C$\underline{H}_2$-CH_2-C=O), 2.51 (t, 2H, *J*=7.27, N-CH_2-C$\underline{H}_2$-C=O), 2.40 (bs, 4H, N-C$\underline{H}_2CH_2CH_2$), 1.63-1.55 (m, 6H, -OCH_2C$\underline{H}_2CH_2CH_3$, N-

$CH_2C\underline{H}_2CH_2$), 1.43-1.36 (m, 4H, -$OCH_2CH_2C\underline{H}_2CH_3$, N-$CH_2CH_2C\underline{H}_2$), 0.93 (t, 3H, -$OCH_2CH_2CH_2C\underline{H}_3$). ^{13}C NMR ($CDCl_3$, 125 MHz, δ, ppm): 172.9 (-O-$\underline{C}$=O), 64.4 (-$O\underline{C}H_2CH_3$), 54.4, 54.3 (N-$\underline{C}H_2CH_2C$=O, N-$\underline{C}H_2CH_2CH_2$), 32.4 (N-$CH_2\underline{C}H_2C$=O), 30.8 (-$OCH_2\underline{C}H_2CH_2CH_3$), 26.0 (N-$CH_2\underline{C}H_2CH_2$), 24.4 (N-$CH_2CH_2\underline{C}H_2$), 19.2 (-$OCH_2CH_2\underline{C}H_2CH_3$), 13.8 (-$OCH_2CH_2CH_2\underline{C}H_3$).

3-(1-piperidinyl)-propionitrile (3d): colorless oil; IR (neat): 2936, 2248, 1678, 1117 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz, δ, ppm): 2.66 (t, 2H, *J*=7.16, N-CH_2-$C\underline{H}_2$-CN), 2.49 (t, 2H, *J*=7.16, N-$C\underline{H}_2$-CH_2-CN), 2.42 (bs, 4H, N-$C\underline{H}_2CH_2CH_2$), 1.58 (m, 4H, N-$CH_2C\underline{H}_2CH_2$), 1.43 (m, 2H, N-$CH_2CH_2C\underline{H}_2$). ^{13}C NMR ($CDCl_3$, 125 MHz, δ, ppm): 119.2 (-$\underline{C}$N), 54.3, 54.1 (N-$\underline{C}H_2CH_2C$=O, N-$\underline{C}H_2CH_2CH_2$), 25.9 (N-$CH_2\underline{C}H_2CH_2$), 24.2 (N-$CH_2CH_2\underline{C}H_2$), 15.8 (N-$CH_2\underline{C}H_2CN$).

4-Piperidin-1-yl-butan-2-one (3e): colorless oil; IR (neat): 2936, 1715, 1168 cm^{-1} ; ^{1}H NMR ($CDCl_3$, 500 MHz, δ, ppm): 2.76 (m, 4H, .N-CH_2-$C\underline{H}_2$-C=O, N-$C\underline{H}_2$-CH_2-C=O), 2.55 (bs, 4H, N-$C\underline{H}_2CH_2CH_2$), 2.14 (s, 3H, O=$CC\underline{H}_3$), 1.64 (m, 4H, N-$CH_2C\underline{H}_2CH_2$), 1.45 (m, 2H, N-$CH_2CH_2C\underline{H}_2$). ^{13}C NMR ($CDCl_3$, 125 MHz, δ, ppm): 207.3 (-O-$\underline{C}$=O), 54.0 (N-$\underline{C}H_2$-CH_2-CH_2), 52.4 (N-$\underline{C}H_2CH_2C$=O), 40.0 (N-$CH_2\underline{C}H_2C$=O), 30.3 (O=$C\underline{C}H_3$), 24.7 (N-$CH_2\underline{C}H_2CH_2$), 23.6 (N-$CH_2CH_2\underline{C}H_2$).

3-(1-morpholinyl)-propionic acid methyl ester (3f): colorless oil; IR (neat): 2953, 1739, 1117 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz, δ, ppm): 3.64-3.66 (m, 7H, -$OC\underline{H}_3$, N-CH_2-$C\underline{H}_2$-O), 2.64 (t, 2H, *J*=7.2, N-$C\underline{H}_2$-CH_2-C=O), 2.47 (t, 2H, *J*=7.2, N-CH_2-$C\underline{H}_2$-C=O), 2.42 (bs, 4H, N-$C\underline{H}_2CH_2O$). ^{13}C NMR ($CDCl_3$, 125 MHz, δ, ppm): 173.0 (-O-$\underline{C}$=O), 67.1 (N-CH_2-$\underline{C}H_2$-O), 54.1 (-$O\underline{C}H_3$), 53.6 (N-$\underline{C}H_2CH_2$-O), 51.9 (N-$\underline{C}H_2CH_2C$=O), 32.1 (N-$CH_2\underline{C}H_2C$=O).

4-morpholin-4-yl-butan-2-one (3g): colorless oil; IR (neat): 2957, 1712, 1117 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz, δ, ppm): 3.69 (t, 4H, N-CH_2-$C\underline{H}_2$-O), 2.65 (t, 2H, *J*=6.3, N-$C\underline{H}_2$-CH_2-C=O), 2.63 (t, 2H, *J*=6.3, N-CH_2-$C\underline{H}_2$-C=O), 2.44 (bs, 4H, N-$C\underline{H}_2CH_2O$), 2.18 (s, 3H, O=CCH_3). ^{13}C NMR ($CDCl_3$, 125 MHz, δ, ppm): 207.9 (-O-$\underline{C}$=O), 67.0 (N-CH_2-$\underline{C}H_2$-O), 53.7 (N-$\underline{C}H_2CH_2$-O), 53.2 (N-$\underline{C}H_2CH_2C$=O), 41.1 (N-$CH_2\underline{C}H_2C$=O), 30.3 (O=$C\underline{C}H_3$).

3-(1-moroholinyl)-propionitrile (3h): colorless oil; IR (neat): 2957, 2248, 1675, 1116 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz, δ, ppm): 3.72 (t, 4H, N-CH_2-$C\underline{H}_2$-O), 2.68 (t, 2H, N-$C\underline{H}_2$-CH_2-CN), 2.2.54-2.50 (m, 6H, N-$C\underline{H}_2CH_2O$, N-$C\underline{H}_2CH_2CN$). ^{13}C NMR ($CDCl_3$, 125 MHz, δ, ppm): 118.8 (-$\underline{C}$N), 67.0 (N-$CH_2\underline{C}H_2O$), 53.9 (N-$\underline{C}H_2CH_2CN$), 53.3 (N-$\underline{C}H_2CH_2O$), 16.0 (N-$CH_2\underline{C}H_2CN$).

3-Diethylamino-propionic acid methyl ester (3i): colorless oil; IR (neat): 2968, 1741, 1202 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz, δ, ppm): 3.68 (s, 3H, -$OC\underline{H}_3$), 2.80 (t, 2H, *J*=7.30, N-CH_2-$C\underline{H}_2$C=O), 2.52 (q, 4H, *J*=7.

18, N-C$\underline{H}_2$-CH_3), 2.46 (t, 2H, *J*=7.30, N-C$\underline{H}_2$-CH_2C=O), 1.03 (t, 3H, *J*=7.18, N-CH_2-C$\underline{H}_3$). ^{13}C NMR ($CDCl_3$, 125 MHz, δ, ppm): 173.5 (-O-$\underline{C}$=O), 51.8 (-O$\underline{C}H_3$), 48.2 (N-$\underline{C}H_2CH_2$C=O), 47.1 (N-$\underline{C}H_2CH_3$), 32.1 (N-$CH_2\underline{C}H_2$C=O), 12.2 (N-$CH_2\underline{C}H_3$).

3-Benzylamino-propionic acid methyl ester (3j): yellow oil; IR (neat): 3327, 3026, 2951, 1736, 1172 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz, δ, ppm): 7.32-7.24 (m, 5H, -Phenyl), 3.80 (s, 2H, Ph-C$\underline{H}_2$NH), 3.67 (s, 3H, -OC$\underline{H}_3$), 2.90 (t, 2H, *J*=6.49, NH-C$\underline{H}_2$-CH_2C=O), 2.54 (t, 2H, *J*=6.49, NH-CH_2-C$\underline{H}_2$C=O). ^{13}C NMR ($CDCl_3$, 125 MHz, δ, ppm): 173.4 (-O-$\underline{C}$=O), 140.2, 128.6, 128.3, 127.2 (Phenyl), 53.9 (O$\underline{C}H_3$), 51.8 (Ph-$\underline{C}H_2$NH), 44.6 (NH-$\underline{C}H_2CH_2$C=O), 34.7 (N-$CH_2\underline{C}H_2$C=O).

3-Diisopropylamino-propionic acid methyl ester (3k): colorless oil; IR (neat): 2960, 1739, 1200 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz, δ, ppm): 3.64 (s, 3H, -OC$\underline{H}_3$), 3.05 (m, 2H, N-C$\underline{H}(CH_3)_2$), 2.54 (q, 4H, N-C$\underline{H}_2$-CH_3), 2.50 (t, 2H, N-C$\underline{H}_2$-CH_2C=O), 0.98 (d, 12H, N-CH(C$\underline{H}_3)_2$). ^{13}C NMR ($CDCl_3$, 125 MHz, δ, ppm): 174.0 (-O-$\underline{C}$=O), 51.6 (-O$\underline{C}H_3$), 48.9 (N-$\underline{C}H(CH_3)_2$), 48.0 (N-$\underline{C}H_2CH_2$C=O), 32.6 (N-$CH_2\underline{C}H_2$C=O), 21.6 (N-CH($\underline{C}H_3)_2$).

2-Methyl-3-(1-piperidinyl)-propionic acid methyl ester (3l): yellow oil; IR (neat): 2935, 1740, 1171 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz, δ, ppm): 3.67 (s, 3H, -OC$\underline{H}_3$), 2.70 (m, 1H, N-CH_2CH(CH_3)C=O), 2.62, 2.27 (m, 2H, N-CH_2CH(CH_3)C=O), 2.33, 2.31 (bs, 4H, N-C$\underline{H}_2CH_2CH_2$), 1.54 (m, 4H, N-CH_2C$\underline{H}_2CH_2$), 1.40 (bs, 2H, N-CH_2CH_2C$\underline{H}_2$), 1.13 (d, 3H, N-CH_2CH(C$\underline{H}_3$)C=O). ^{13}C NMR ($CDCl_3$, 125 MHz, δ, ppm): 177.1 (-O-$\underline{C}$=O), 62.6 (N-$\underline{C}H_2$CH(CH_3)C=O), 54.8 (N-$\underline{C}H_2CH_2CH_2$), 51.8 (-O$\underline{C}H_3$), 38.1 (N-$CH_2\underline{C}$H(CH_3)C=O), 26.2 (N-$CH_2\underline{C}H_2CH_2$), 24.5 (N-$CH_2CH_2\underline{C}H_2$), 16.0 (N-CH_2CH($\underline{C}H_3$)).

3-Piperidin-1-yl-butyric acid methyl ester (3m): yellow oil; IR (neat): 2933, 1740, 1170 cm^{-1}; ^{1}H NMR ($CDCl_3$, 500 MHz, δ, ppm): 3.67 (s, 3H, -OC$\underline{H}_3$), 3.12 (m, 1H, N-C$\underline{H}$(CH_3)CH_2C=O), 2.60, 2.23 (m, 2H, N-CH(CH_3)C$\underline{H}_2$C=O), 2.45 (m, 4H, N-C$\underline{H}_2CH_2CH_2$), 1.55 (m, 4H, N-CH_2C$\underline{H}_2CH_2$), 1.40 (t, 2H, N-CH_2CH_2C$\underline{H}_2$), 1.06 (d, 3H, N-CH(C$\underline{H}_3$)CH_2C=O). ^{13}C NMR ($CDCl_3$, 125 MHz, δ, ppm): 173.6 (-O-$\underline{C}$=O), 57.2 (N-$\underline{C}$H(CH_3)CH_2C=O), 51.7 (-O$\underline{C}H_3$), 49.6 (N-$\underline{C}H_2CH_2CH_2$), 38.0 (N-CH(CH_3)$\underline{C}H_2$C=O), 32.4 (N-$CH_2CH_2\underline{C}H_2$), 26.6 (N-$CH_2\underline{C}H_2CH_2$), 24.9 (N-CH($\underline{C}H_3$)CH_2C=O).