A simple, efficient and green procedure for Knoevenagel condensation catalyzed by $[C_4 dabco][BF_4]$ ionic liquid in water

Supporting Information

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Experimental Section

1.0 General Information

The ¹H NMR and spectra was recorded at 300MHz or 400MHz, ¹³C NMR was recorded at 75MHz or 100MHz. ¹H and ¹³C NMR Chemical shifts were calibrated to tetramethylsilane as an external reference. Coupling constants are given in Hz. The following abbreviations are used to indicate the multiplicity: s, singlet; d, doublet: t, triplet; m, multiplet;

The chemicals were purchased from commercial suppliers (Aldrich, USA and Shanghai Chemical Company, China) and were used without purification prior to use. All reactions unless otherwise noted were carried out directly under air.

2.0 General Procedure and data for synthesis of catalysts



Ethyl-4-aza-1-azoniabicyclo[2.2.2]octane bromide ([C2dabco]Br)^[1]



A mixture of 1, 4-diazabicyclo[2.2.2]octane (dabco, 98% pure, 2.0 g, 17.8 mmol), bromoethane (1.4 ml, 18.7 mmol), and AcOEt (50 mL) was stirred at room temperature for 24 h. The white solid, isolated by decanting off the solvent, was suspended in anhydrous THF (20 mL) and stirred at room temperature for 1 h, then the THF was decanted off. The treatment was repeated twice, then the solid was dried under vacuum at 40 °C to give the title compound (3.8 g, 94%). Mp 68-70 °C. ¹H NMR (400 MHz, D₂O): δ 1.26-1.31 (m, 3H), 3.15 (t, 6H, J= 7.6 Hz), 3.28-3.36 (m, 8H); ¹³C NMR (100 MHz, D₂O): δ 6.97 (CH₃), 44.26 (CH₂), 51.61 (NCH₂), 60.06 (N⁺CH₂).

$Ethyl-4-aza-1-azoniabicyclo [2.2.2] octane \ tetrafluoroborate \ (\ [C_2 dabco] [BF_4] \)$



To a solution of 1-ethyl-4-aza-1-azoniabicyclo[2.2.2]octane bromide (1.78 g, 8.1 mmol) in ethanol (50 mL) was added freshly prepared silver tetrafluoroborate (1.57 g, 8.1 mmol). The mixture was stirred at room temperature for 30 min, then the precipitate was removed by filtration, and the resulting colourless solution was evaporated at reduced pressure (50 °C) to give [C₂dabco][BF₄] (1.72 g, 93%). ¹H NMR (300 MHz, D₂O): δ 1.19-1.26 (m, 3H), 3.1 (t, 6H, J= 7.6 Hz), 3.19-3.29 (m, 8H); ¹³C NMR (75 MHz, D₂O): δ 6.75 (CH₃), 44.20 (CH₂), 51.56 (NCH₂), 60.03 (N⁺CH₂); Anal. Calcd. for C₈H₁₇BF₄N₂: C, 42.14; H, 7.51; N, 12.28. Found C, 42.23; H, 7.48; N, 12.34.

 $Butyl-4-aza-1-azoniabicyclo [2.2.2] octane \ bromide \ ([C_4 dabco] Br \)$

This was prepared as per our general procedure to afford the product [C₄dabco]Br; yield 89%; ¹H

NMR (400 MHz, D₂O): δ 0.87 (t, 3H, J = 7.2 Hz), 1.23-1.35 (m, 2H), 1.63-1.69 (m , 2H), 3.12 (t, 6H, J = 6.8 Hz), 3.17-3.21 (m, 2H), 3.32 (t, 6H, J = 7.6 Hz); ¹³C NMR (100 MHz, D₂O): δ 12.83 (CH₃), 19.17 (CH₂), 23.17 (CH₂), 44.20 (CH₂), 52.06(NCH₂), 64.46 (N⁺CH₂).

 $Butyl-4-aza-1-azoniabicyclo [2.2.2] octane \ tetrafluoroborate \ ([C_4 dabco][BF_4])$

$$N^{-N}_{-N}$$
 BF_{4}^{-}

This was prepared as per our general procedure to afford the product [**C**₄**dabco**] [**BF**₄]; yield 95% ¹**H NMR** (300 MHz, D₂O): δ 0.82 (t, 3H, J = 7.5 Hz), 1.21-1.38 (m, 2H), 1.55-1.66 (m , 2H), 3.05-3.15 (m, 8H), 3.27 (t, 6H, J = 7.6 Hz); ¹³**C NMR** (75 MHz, D₂O): δ 12.76 (CH₃), 19.14 (CH₂), 23.12 (CH₂), 44.18 (CH₂), 52.03(NCH₂), 64.48 (N⁺CH₂); Anal. Calcd. for C₁₀H₂₁BF₄N₂: C, 46.90; H, 8.27; N, 10.94. Found C, 47.17; H, 8.12; N, 10.98.

Octyl-4-aza-1-azoniabicyclo[2.2.2]octane bromide ([C₈dabco]Br)

$$N$$
 N Br

This was prepared as per our general procedure to afford the product [C_8 dabco]Br; yield 91% NMR (400 MHz, D₂O): δ 0.80 (t, 3H, J = 6.8 Hz), 1.18-1.29 (m, 10H), 1.67-1.71 (m, 3H), 3.13 (t, 6H, J = 7.6 Hz), 3.18-3.22 (m, 2H), 3.35 (t, 6H, J = 7.2 Hz); ¹³C NMR (100 MHz, D₂O): δ 13.61 (CH₃), 21.25 (CH₂), 22.13 (CH₂), 25.70 (CH₂), 28.27 (CH₂), 28.33 (CH₂), 31.12 (CH₂), 44.23 (N⁺CH₂CH₂CH₂), 52.07 (NCH₂), 64.65 (N⁺CH₂CH₂N).

Benzyl-4-aza-1-azoniabicyclo[2.2.2]octane bromide ([Bndabco]Br)^[2]

$$N^{-N}$$
 Ph Br

This was prepared as per our general procedure to afford the product [**Bndabco]Br**; yield 98% **NMR** (400 MHz, D₂O): δ 3.07 (t, 6H, J = 7.6 Hz), 3.36 (t, 6H, J = 7.2 Hz), 4.41 (s, 2H), 7.40-7.52 (m, 5H); ¹³C NMR (100 MHz, D₂O): δ 44.23 (CH₂), 51.96 (NCH₂), 68.35 (N⁺CH₂), 125.96 (Ar), 129.22 (Ar), 130.77 (Ar), 133.02 (Ar).







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4.0 References

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