SUPPORTING INFORMATION

PEG₁₀₀₀-based dicationic acidic ionic liquid as an efficient catalyst for Mannich-type reaction in water

Yi-Ming Ren*, Juan-Juan Shao, Zhi-Chuan Wu, Ren-Chun Yang, Ze Zhang and Ting-Xian Tao

Department of Biochemical Engineering, Anhui Polytechnic University, Wuhu, Anhui 241000, China

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General information:

The PEG₁₀₀₀-DAIL was prepared by the procedure given in the literature.^[10a] All the other chemicals and reagents are obtained from commercial resource. Commercially available reagents were used without further purification. ¹H NMR spectra were measured on Bruker Advance RX500. All products were known compounds and were identified by their Mp and ¹H NMR.^[8] All melting points were uncorrected.

Analytic data for PEG₁₀₀₀-DAIL:

PEG₁₀₀₀-DAIL: ¹H NMR (500 MHz, D₂O) δ = 2.14 (t, 4H, J = 7 Hz, 4H), 2.76 (m, 4H), 3.46-3.67 (m, 90H), 3.76 (s, 4H), 4.22-4.30 (m, 8H), 7.42 (s, 4H), 8.72 (s, 2H); IR (cm⁻¹): 3847, 3402, 3022, 2881, 1731, 1593, 1454, 1435, 1375, 1121, 1107, 976, 881, 796, 675, 574;

Synthetic procedure and analytic data for Table 2:

Typical procedure for the Mannich reaction of aldehydes, ketones, and amines: To a solution of aldehydes (1 mmol), ketones (1 mmol) and amines (1 mmol) in H₂O (2 mL) was added PEG₁₀₀₀-DAIL (0.05 mmol). The reaction mixture was vigorously stirred at room temperature for the period of time and monitored by TLC. Then the reaction mixture was extracted with diethyl ether or EtOAc. The combined organic extracts were dried over anhydrous Na₂SO₄ and concentrated to generate the crude product. The crude products were purified by column chromatography on silica-gel using ethyl acetate/hexane as eluent. The resultant residues H₂O containing ionic liquid were reused directly without further treatment for the next run after being charged with fresh starting materials.

Characterization Data for compounds Table 2:

1,3-Diphenyl-3-phenylamino-1-propanone (Table 2, entry 1): White solid (yield 94%); mp 169-171 °C (literature^[8] 169-170 °C); ¹H NMR (500 MHz, CDCl₃) δ = 3.48 (d, J = 4.8 Hz, 2H), 5.01 (t, J = 6.1 Hz, 1H), 6.57 (s, 2H), 6.68 (s, 1H), 7.11 (s, 2H), 7.22 (s, 2H), 7.34 (s, 2H), 7.45 (s, 4H), 7.58 (s, 1H), 7.95 (d, 2H).

1,3-Diphenyl-3-(*p*-nitrophenylamino)-1-propanone (Table 2, entry 2): Yellow solid (yield 96%); mp 184-186 °C (literature^[8] 183-185 °C); ¹H NMR (500 MHz, CDCl₃) δ = 3.58 (d, J = 5.0 Hz, 2H), 5.11 (t, J = 6.2 Hz, 1H), 5.58 (brs, 2H), 6.58 (d, 2H), 7.24 (t, 2H), 7.28 (t, 2H), 7.40 (d, 2H), 7.45 (t, 2H), 7.58 (t, 1H), 7.86 (d, 2H), 7.97-8.09 (m, 2H).

1,3-Diphenyl-3-(*p*-methylphenylamino)-1-propanone (Table 2, entry 3): White solid (yield 89%); mp 169-171 °C (literature^[8] 168-170 °C); ¹H NMR (500 MHz, CDCl₃) δ = 2.40 (s, 3H), 3.51 (d, J = 5.0 Hz, 2H), 5.04 (t, J = 5.3 Hz, 1H), 6.68 (d, 2H), 6.80 (d, 2H), 7.25 (t, 1H), 7.33 (t, 2H), 7.45 (t, 4H), 7.58 (t, 1H), 7.91 (d, 2H).

1,3-Diphenyl-3-(*p*-chlorophenylamino)-1-propanone (Table 2, entry 4): White solid (yield 92%); mp 170-171 °C (literature^[8] 170-171 °C); ¹H NMR (500 MHz, CDCl₃) δ = 3.45-3.47 (m, 2H), 4.91 (t, J = 6.4 Hz, 1H), 6.47 (d, 2H), 7.01 (d, 2H), 7.28 (t, 1H), 7.30 (t, 2H), 7.39-7.49 (m, 4H), 7.58 (t, 1H), 7.89 (d, 2H).

1,3-Diphenyl-3-(*p*-methoxyphenylamino)-1-propanone (Table 2, entry 5): Yellowish solid (yield 85%); mp 163-164 °C (literature^[8] 166-167 °C); ¹H NMR (500 MHz, CDCl₃) δ = 3.38-3.52 (m, 2H), 3.80 (s, 3H), 4.92 (t, J = 6.4 Hz, 1H), 6.47 (d, 2H), 6.84 (d, 2H), 7.22 (t, 1H), 7.32 (t, 2H), 7.41-7.45 (m, 4H), 7.53 (t, 1H), 7.90 (d, 2H).

1,3-Diphenyl-3-(*m*-nitrophenylamino)-1-propanone (Table 2, entry 6): Yellow solid

(yield 95%); mp 139-140 °C (literature^[8] 140-142 °C); ¹H NMR (500 MHz, CDCl₃) δ = 3.42-3.55 (m, 2H), 5.08 (s, 1H), 6.79-6.82 (m, 1H), 7.20 (t, 1H), 7.26 (t, 2H), 7.31-7.36 (m, 3H), 7.40-7.45 (m, 5H), 7.61 (t, 1H), 7.90 (d, 2H).

1-Phenyl-3-(*p*-nitrophenyl)-3-phenylamino-1-propanone (Table 2, entry 10): White solid (yield 82%); mp 107-109 °C (literature^[8] 107-110 °C); ¹H NMR (500 MHz, CDCl₃) δ = 3.51 (d, *J* = 6.1 Hz, 2H), 5.12 (t, *J* = 6.1 Hz, 1H), 6.70 (t, 1H), 6.72 (d, 2H), 7.10 (t, 2H), 7.51 (t, 2H), 7.58 (t, 1H), 7.63 (d, 2H), 7.85 (d, 2H), 8.18 (d, 2H).

1-Phenyl-3-(*p*-chlorophenyl)-3-phenylamino-1-propanone (Table 2, entry 11): White solid (yield 91%); mp 118-119 °C (literature^[8] 117-119 °C); ¹H NMR (500 MHz, CDCl₃) δ = 3.46 (d, *J* = 5.8 Hz, 2H), 5.16 (t, *J* = 5.9 Hz, 1H), 6.61 (d, 2H), 6.69 (t, 1H), 7.11 (t, 2H), 7.51 (t, 2H), 7.52 (t, 1H), 7.61 (d, 2H), 7.81 (d, 2H), 7.89 (d, 2H).

1-Phenyl-3-(*p*-methylphenyl)-3-phenylamino-1-propanone (Table 2, entry 12): White solid (yield 97%); mp 131-132 °C (literature^[8] 131-132 °C); ¹H NMR (500 MHz, CDCl₃) δ = 2.24 (s, 3H), 3.46-3.58 (m, 2H), 5.76 (t, *J* = 6.8 Hz, 1H), 6.51 (d, 2H), 6.69 (t, 1H), 6.86 (d, 2H), 7.08 (t, 2H), 7.40 (d, 2H), 7.46 (t, 2H), 7.58 (t, 1H), 7.90 (d, 2H).

1-Phenyl-3-(*p*-methoxyphenyl)-3-phenylamino-1-propanone (Table 2, entry 13): White solid (yield 90%); mp 151-152 °C (literature^[8] 151-152 °C); ¹H NMR (500 MHz, CDCl₃) δ = 3.36-3.51 (m, 2H), 3.71 (s, 3H), 5.01 (t, *J* = 6.7 Hz, 1H), 6.58 (d, 2H), 6.69 (t, 1H), 6.84 (d, 2H), 7.11 (t, 2H), 7.37 (d, 2H), 7.41 (t, 2H), 7.55 (t, 1H), 7.89 (d, 2H).

2-[1'-(*N*-phenylamino)-1'-phenyl]methylcyclohexane (Table 2, entry 14): White solid (yield 89%); mp 139-140 °C (literature^[8] 139-140 °C); ¹H NMR (500 MHz, CDCl₃) δ = 1.61-1.87 (m, 6H), 2.30-2.45 (m, 2H), 2.72 (m, 1H), 4.53 (br, 1H), 4.65 (d, *J* = 7.3 Hz, 5H),

6.48 (m, 2H), 6.62 (m, 2H), 7.18-7.40 (m, 5H).

2-[1'-(*N*-*p*-methylphenylamino)-1'-phenyl]methylcyclohexane (Table 2, entry 15): White solid (yield 92%); mp 116-118 °C (literature^[8] 116-118 °C); ¹H NMR (500 MHz, CDCl₃) δ = 1.61-1.90 (m, 6H), 2.28-2.41 (m, 2H), 2.71 (m, 1H), 3.62 (s, 3H), 4.51 (br, 1H), 4.67 (d, *J* = 5.2 Hz, 5H), 6.51 (m, 2H), 6.62 (m, 2H), 7.18-7.36 (m, 5H).

2-[1'-(*N*-*p*-chlorophenylamino)-1'-phenyl]methylcyclohexane (Table 2, entry 16): Yellowish solid (yield 93%); mp 136-138 °C (literature^[8] 136-138 °C); ¹H NMR (500 MHz, CDCl₃) δ = 1.60-1.91 (m, 6H), 2.28-2.32 (m, 2H), 2.65 (m, 1H), 3.54 (s, 3H), 4.58 (br, 1H), 4.66 (d, *J* = 5.5 Hz, 5H), 6.50 (m, 2H), 6.61 (m, 2H), 7.20-7.55 (m, 5H).

2-[1'-(*N*-*p*-chlorophenylamino)-1'-(*p*-methoxyphenyl)]methylcyclohexane (Table 2, entry 17): Yellowish solid (yield 85%); mp 132-133 °C (literature^[8] 133-134 °C); ¹H NMR (500 MHz, CDCl₃) δ = 1.15-2.64 (m, 9H), 3.07 (s, 1H), 3.61 (s, 3H), 4.63 (d, *J* = 4.9 Hz, 1H), 6.30-6.82 (m, 3H), 7.07-7.36 (m, 5H).

2-[1'-(*N*-phenylamino)-1'-phenyl]methylcyclopentanone (Table 2, entry 18): White solid (yield 83%); mp 164-165 °C (literature^[8] 164-165 °C); ¹H NMR (500 MHz, CDCl₃) δ = 1.60-2.42 (m, 7H), 3.64 (s, 1H), 4.40 (d, *J* = 4.8 Hz, 1H), 6.49-6.64 (m, 3H), 6.81-7.18 (m, 7H).

2-[1'-(*N*-*p*-chlorophenylamino)-1'-phenyl]methylcyclopentanone (Table 2, entry 19): Yellow solid (yield 85%); mp 144-146 °C (literature^[8] 144-147 °C); ¹H NMR (500 MHz, CDCl₃) δ = 1.61-2.44 (m, 7H), 3.67 (s, 1H), 4.42 (d, *J* = 5.2 Hz, 1H), 6.57-6.76 (m, 3H), 6.92-7.31 (m, 6H).

2-[1'-(*N*-*p*-nitrophenylamino)-1'-(*p*-methoxyphenyl)]methylcyclopentanone (Table 2,

entry 20): Yellow solid (yield 80%); mp 127-128 °C (literature^[8] 127-129 °C); ¹H NMR (500 MHz, CDCl₃) δ = 1.45-2.62 (m, 7H), 3.33 (s, 1H), 3.62 (s, 1H), 4.43 (d, *J* = 4.9 Hz, 1H), 6.38-6.66 (m, 2H), 6.90-7.41 (m, 6H).