

[Bmim]N₃ as an efficient reagent for the Schmidt reactions of ketones, arylaldehydes and aromatic carboxylic acids

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Abstract Schmidt reaction of arylaldehydes, ketones and aromatic carboxylic acids using task-specific ionic liquid, [bmim]N₃ in the presence of AcOH/H₂SO₄ proceeds at 50–60 °C within 2–4 h to give the corresponding products. Benzaldehydes containing electron releasing groups afforded to the related benzamide derivatives. Benzonitrile derivatives were formed from the reaction of benzaldehydes containing electron withdrawing groups under these conditions. High yields of the related amides and anilines were obtained from the reaction of a variety of ketones and aromatic carboxylic acids, respectively, utilizing this procedure.

Keywords Aldehydes · Carboxylic acids · Ketones · Schmidt reaction

Introduction

The reaction of carbonyl compounds, such as carboxylic acids, ketones and aldehydes, with hydrazoic acid under acidic conditions is known as Schmidt reaction or Schmidt rearrangement [1–3]. Thus, aldehydes are converted into formamides and nitriles, ketones into amides, and carboxylic acids into amines [2]. The mechanism of the reaction was proposed in the literature [3]. One of the disadvantages in the classical Schmidt reaction realizing is the use of highly toxic and explosive reagent NaN₃.

Ionic liquids (ILs), due to their considerable advantages over routine organic solvents, have been widely employed

over the past years [4–6]. Many organic reactions such as Wittig, diazotization, Mannich and oxidation reactions have already been reported in ILs [7–10]. Verevkin et al. [11] studied the thermochemistry of ionic liquid-catalyzed Beckmann rearrangements reaction. Horvath and co-workers used imidazolium-based ionic liquids as catalysts in Wagner–Meerwein rearrangement of 16 α ,17 α -epoxy-androstanes and 16 α ,17 α -epoxyestrans [12]. The task-specific ionic liquid consisting sulfonyl chloride was used as efficient catalyst for the Beckmann rearrangement [13]. In connection with our interest to use ionic liquids [14–18], we wish to report here the clean and efficient method of the Schmidt reaction of ketones, aldehydes and carboxylic acids using a task-specific azide ionic liquid [bmim]N₃. Mild reaction conditions and high yields of benzonitriles, benzamides, amides and anilines make this transformation as an attractive alternative for the reported methods.

Experimental

All reagents were purchased from Merck and used without further purification. Infrared spectra were recorded in KBr and were determined on a Perkin Elmer FT-IR spectrometer. ¹H NMR spectra were recorded on Bruker Avance AC-300 MHz and 400 MHz using CDCl₃ as the deuterated solvent and TMS as an internal standard. All melting points are uncorrected and measured in open glass capillaries using Stuart melting point apparatus.

General procedure for the Schmidt reaction of aldehydes, ketones and carboxylic acids

The aldehyde/ketone/carboxylic acid (10 mmol) was dissolved in glacial acetic acid (10 mmol) containing

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concentrated sulfuric acid (2 mmol). To the stirred solution at 54 °C on a water bath, [bmim]N₃ (20 mmol) was added in small portions over 1 h. The mixture was stirred with heating for 2–4 h and was then allowed to stand overnight at room temperature. The reaction mixture was then poured onto ice and water. In some cases, solid products were obtained that filtered off, washed with water, dried and recrystallized from appropriate solvent/solvents. In other cases, the solution was alkalized (pH = 12–13) with sodium hydroxide and the resulting solution was extracted 4 times with 15 mL portions of chloroform. The resulting organic layer was dried over anhydrous Na₂SO₄, filtered and evaporated to yield crude product. The crude product was recrystallized from appropriate solvent/solvents.

Selected spectroscopic data

Benzamide (2a)

Crude product was extracted from reaction mixture and recrystallized from chloroform/*n*-hexane; IR (KBr): $\bar{\nu}$ = 3,368, 3,174, 1,656 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): δ = 7.81–7.84 (d, *J* = 7.2 Hz, 2H, Ar-H), 7.47–7.53 (m, 3H, Ar-H), 5.60–5.90 (br., 2H, NH₂) ppm.

2-Bromobenzamide (2b)

Crude product was extracted from reaction mixture and recrystallized from chloroform/*n*-hexane; IR (KBr): $\bar{\nu}$ = 3,364, 3,182, 1,648 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz): δ = 7.82–7.85 (dd, ⁴*J* = 1.6 Hz, ³*J* = 6.0 Hz, 1H, Ar-H), 7.38–7.47 (m, 3H, Ar-H), 5.89 (br., 1H, N-H), 6.80 (br., 1H, N-H) ppm.

4-Methylbenzamide (2c)

Crude product was extracted from reaction mixture and recrystallized from chloroform/*n*-hexane; IR (KBr): $\bar{\nu}$ = 3,384, 3,169, 2,852–2,960, 1,669 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz): δ = 7.27–7.29 (d, *J* = 7.2 Hz, 2H, Ar-H), 7.57–7.59 (d, *J* = 8.4 Hz, 2H, Ar-H), 5.64 (br., 1H, N-H), 6.04 (br., 1H, N-H), 2.44 (s, 3H, CH₃) ppm.

2-Methoxybenzamide (2d)

Crude product was extracted from reaction mixture and recrystallized from chloroform/*n*-hexane; IR (KBr): $\bar{\nu}$ = 3,415, 3,175, 2,946–2,980, 1,638 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz): δ = 8.23–8.26 (d, *J* = 6.0 Hz, 1H, Ar-H), 7.75 (br., 1H, N-H), 7.42–7.53 (t, *J* = 7.2 Hz, 1H, Ar-H), 7.10–7.13 (t, *J* = 7.2 Hz, 1H, Ar-H), 7.01–7.03 (d, *J* = 8.4 Hz, 1H, Ar-H), 5.86 (br., 1H, N-H), 4.00 (s, 3H, OCH₃) ppm.

4-Methoxybenzamide (2e)

Crude product was extracted from reaction mixture and recrystallized from chloroform/*n*-hexane; IR (KBr): $\bar{\nu}$ = 3,392, 3,170, 2,941–2,995, 1,643 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz): δ = 7.80–7.82 (d, *J* = 8.8 Hz, 2H, Ar-H), 6.96–6.98 (d, *J* = 8.8 Hz, 2H, Ar-H), 5.65–5.93 (br., 2H, N-H), 3.89 (s, 3H, OCH₃) ppm.

2,5-Dimethoxybenzamide (2f)

Crude product was extracted from reaction mixture and recrystallized from chloroform/*n*-hexane; IR (KBr): $\bar{\nu}$ = 3,378, 3,170, 2,946–2,970, 1,646 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz): δ = 7.87 (broad, 1H, N-H), 7.78 (d, *J* = 3.2 Hz, 1H, Ar-H), 7.05–7.08 (dd, ⁴*J* = 3.2 Hz, ³*J* = 6.0 Hz, 1H, Ar-H), 6.95–6.97 (d, *J* = 9.2 Hz, 1H, Ar-H), 5.80 (br., 1H, N-H), 3.85 (s, 3H, OCH₃), 3.96 (s, 3H, OCH₃) ppm.

2-Nitrobenzonitrile (3a)

Crude product was filtered off from aqueous reaction mixture and recrystallized from chloroform/*n*-hexane; IR (KBr): $\bar{\nu}$ = 3,063–3,111, 2,232, 1,534, 1,356 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz): δ = 8.36–8.40 (m, 1H, Ar-H), 7.94–7.98 (m, 1H, Ar-H), 7.84–7.89 (m, 2H, Ar-H) ppm.

3-Nitrobenzonitrile (3b)

Crude product was filtered off from aqueous reaction mixture and recrystallized from chloroform/*n*-hexane; IR (KBr): $\bar{\nu}$ = 3,079–3,111, 2,237, 1,527, 1,343 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz): δ = 8.57 (m, 1H, Ar-H), 8.50 (d, *J* = 5.2 Hz, 1H, Ar-H), 8.00 (d, *J* = 5.2 Hz, 1H, Ar-H), 7.75–7.79 (t, *J* = 8.0 Hz, 1H, Ar-H) ppm.

4-Nitrobenzonitrile (3c)

Crude product was filtered off from aqueous reaction mixture and recrystallized from chloroform/*n*-hexane; IR (KBr): $\bar{\nu}$ = 3,053–3,106, 2,233, 1,525, 1,348 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz): δ = 8.39 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.91 (d, *J* = 8.8 Hz, 2H, Ar-H) ppm.

Terephthalonitrile (4a)

Crude product was filtered off from aqueous reaction mixture and recrystallized from ethanol; IR (KBr): $\bar{\nu}$ = 3,051–3,097, 2,232 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz): δ = 7.82 (s, 4H, Ar-H) ppm.

Terephthalamide (4b)

Crude product was filtered off from aqueous reaction mixture and recrystallized from ethanol; IR (KBr): $\bar{\nu}$ = 3,365, 3,166, 1,660 cm^{-1} .

N-Phenylbenzamide (5a)

Crude product was filtered off from aqueous reaction mixture and recrystallized from ethanol; IR (KBr): $\bar{\nu}$ = 3,345, 3,051, 1,655 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz): δ = 7.90 (d, J = 7.6 Hz, 2H, Ar-H), 7.86 (br., 1H, N-H), 7.67 (d, J = 8.0 Hz, 2H, Ar-H), 7.58 (t, 1H, Ar-H), 7.52 (t, 2H, Ar-H), 7.41 (t, 2H, Ar-H), 7.19 (t, 1H, Ar-H) ppm.

N-(4-Bromophenyl)acetamide (5b)

Crude product was filtered off from aqueous reaction mixture and recrystallized from ethanol; IR (KBr): $\bar{\nu}$ = 3,363, 3,294, 3,053, 2,853–2,924, 1,668 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz): δ = 7.42 (s, 2H, Ar-H), 7.25 (s, 2H, Ar-H), 7.19 (br., 1H, N-H), 2.18 (s, 3H, CH_3) ppm.

4-Chloro-N-phenylbenzamide (5c)

Crude product was extracted from reaction mixture and recrystallized from ethylacetate/*n*-hexane; IR (KBr): $\bar{\nu}$ = 3,353, 3,051, 1,654 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz): δ = 7.81–7.84 (d, J = 8.4 Hz, 2H, Ar-H), 7.73 (br., 1H, N-H), 7.62–7.65 (d, J = 8.4 Hz, 2H, Ar-H), 7.47–7.50 (d, J = 8.4 Hz, 2H, Ar-H), 7.37–7.42 (t, 2H, Ar-H), 7.18–7.21 (m, 1H, Ar-H) ppm.

N-(4-Chlorophenyl)benzamide (5'c)

Crude product was extracted from reaction mixture and recrystallized from ethylacetate/*n*-hexane; IR (KBr): $\bar{\nu}$ = 3,349, 3,045, 1,655 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz): δ = 7.86–7.88 (d, J = 8.1 Hz, 2H, Ar-H), 7.79 (br., 1H, N-H), 7.49–7.63 (m, 5H, Ar-H), 7.34–7.37 (d, J = 8.7 Hz, 2H, Ar-H) ppm.

N-(4-Phenylphenyl)acetamide (5d)

Crude product was filtered off from aqueous reaction mixture and recrystallized from chloroform/*n*-hexane; IR (KBr): $\bar{\nu}$ = 3,303, 3,053–3,112, 2,928, 1,662 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz): δ = 7.57 (s, 6H, Ar-H), 7.41–7.46 (t, 2H, Ar-H), 7.33–7.36 (br., 1H, N-H and 1H, Ar-H), 2.22 (s, 3H, CH_3) ppm.

N-Phenylacetamide (5e)

Crude product was filtered off from aqueous reaction mixture and recrystallized from chloroform/*n*-hexane; IR (KBr): $\bar{\nu}$ = 3,295, 3,021–3,136, 2,801–2,927, 1,654 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz): δ = 7.51–7.53 (d, J = 8.0 Hz, 2H, Ar-H), 7.33–7.37 (t, 2H, Ar-H), 7.22 (br., 1H, N-H), 7.12–7.15 (t, 2H, Ar-H), 2.21 (s, 3H, CH_3) ppm.

N-(Naphthalen-5-yl)acetamide (5f)

Crude product was filtered off from aqueous reaction mixture and recrystallized from ethanol/water; IR (KBr): $\bar{\nu}$ = 3,270, 3,050, 2,925, 1,655 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz): δ = 7.4–8.0 (m, 7H, Ar-H and 1H, N-H), 2.35 (s, 3H, CH_3) ppm.

N-Phenylcyclohexanecarboxamide (5g)

Crude product was filtered off from aqueous reaction mixture and recrystallized from chloroform/*n*-hexane; IR (KBr): $\bar{\nu}$ = 3,313, 3,060, 2,851–2,947, 1,661 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz): δ = 7.07–7.12 (br., 1H, N-H and 1H, Ar-H), 7.29–7.35 (t, 2H, Ar-H), 7.52–7.54 (d, J = 7.8 Hz, 2H, Ar-H), 2.19–2.27 (m, 1H, aliphatic C-H), 1.27–1.99 (m, 10 H, aliphatic C-H) ppm.

N-Cyclohexylbenzamide (5'g)

Crude product was filtered off from aqueous reaction mixture and recrystallized from chloroform/*n*-hexane; IR (KBr): $\bar{\nu}$ = 3,330, 3,239, 3,080, 2,851–2,928, 1,627 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz): δ = 7.73–7.75 (d, J = 6.3 Hz, 2H, Ar-H), 7.42–7.44 (m, 3H, Ar-H), 5.94 (br., 1H, N-H), 1.2–2.0 (m, 10H, aliphatic C-H), 3.97 (m, 1H, aliphatic C-H) ppm.

Azepan-2-one (5h)

Crude product was extracted from reaction mixture and recrystallized from ethylacetate/*n*-hexane; IR (KBr): $\bar{\nu}$ = 3,213, 3,077, 2,856–2,929, 1,661 cm^{-1} ; ^1H NMR (CDCl_3 , 300 MHz): δ = 6.54 (br., 1H, N-H), 1.66–3.22 (m, 10H, aliphatic C-H) ppm.

Aniline (6a)

Liquid product was extracted from reaction mixture; IR (KBr): $\bar{\nu}$ = 3,356 and 3,431, 3,071–3,011, 1,277 cm^{-1} ; ^1H -NMR (400 MHz, CDCl_3): δ = 7.20–7.24 (m, 2H, Ar-H), 6.81–6.84 (t, 1H, Ar-H), 6.73–6.75 (dd, 2H, Ar-H), 3.68 (s, br., 2H, NH_2) ppm.

4-Nitroaniline (6b)

Crude product was extracted from reaction mixture and recrystallized from ethylacetate/*n*-hexane; IR (KBr): $\bar{\nu}$ = 3,361 and 3,482, 3,082, 3,108, 1,326, 1,505, 1,297 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ = 8.09–8.11 (d, J = 8.8 Hz, 2H, Ar-H), 6.64–6.66 (d, J = 8.8 Hz, 2H, Ar-H), 4.42 (s, br., 2H, NH_2) ppm.

4-Chloroaniline (6c)

Crude product was extracted from reaction mixture and recrystallized from ethylacetate/*n*-hexane; IR (KBr): $\bar{\nu}$ = 3,381 and 3,472, 1,288, 1,089 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ = 7.12–7.14 (d, J = 8 Hz, 2H, Ar-H), 6.62–6.64 (d, J = 8 Hz, 2H, Ar-H), 3.68 (s, br., 2H, NH_2) ppm.

4-Fluoroaniline (6d)

Liquid product was extracted from reaction mixture; IR (KBr): $\bar{\nu}$ = 3,363, 3,443, 3,023, 3,051, 1,273, 1,154 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ = 6.86–6.91 (m, 2H, Ar-H), 6.63–6.66 (m, 2H, Ar-H), 3.51 (s, br., 2H, NH_2) ppm.

4-Bromoaniline (6e)

Crude product was extracted from reaction mixture and recrystallized from ethylacetate/*n*-hexane; IR (KBr): $\bar{\nu}$ = 3,382, 3,473, 1,286 (C–N), 1,070 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ = 7.25–7.28 (dd, 2H, Ar-H), 6.58–6.60 (dd, 2H, Ar-H), 3.96 (s, br., 2H, NH_2) ppm.

2-Chloroaniline (6f)

Liquid product was extracted from reaction mixture; IR (KBr): $\bar{\nu}$ = 3,382, 3,472, 3,026, 3,070, 1,262, 1,077 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ = 7.26–7.28 (dd, 1H, Ar-H), 7.08–7.12 (td, 1H, Ar-H), 6.78–6.80 (dd, 1H, Ar-H), 6.70–6.74 (td, 1H, Ar-H), 4.07 (s, br., 2H, NH_2) ppm.

2-Nitroaniline (6g)

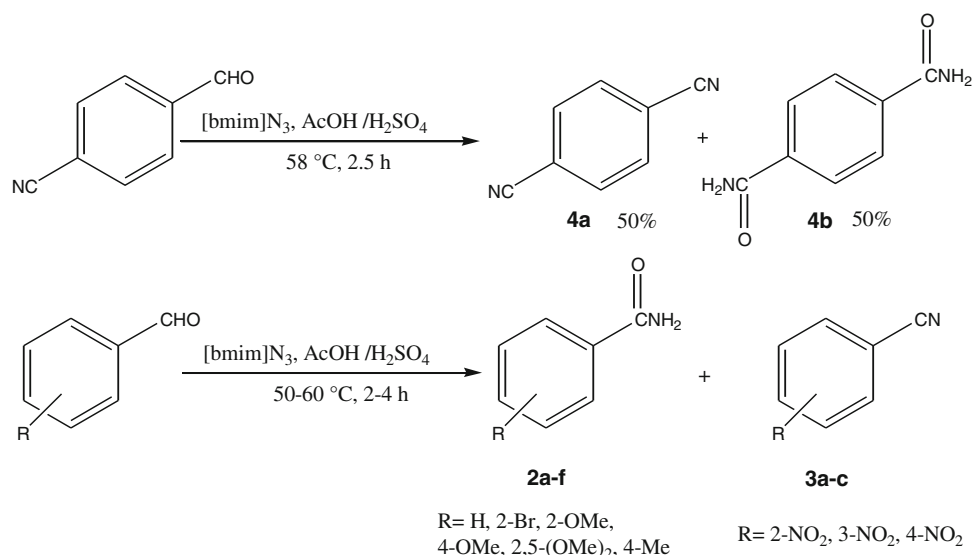
Crude product was extracted from reaction mixture and recrystallized from ethylacetate/*n*-hexane; IR (KBr): $\bar{\nu}$ = 3,356, 3,477, 3,082, 3,108, 1,348, 1,508, 1,261 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ = 8.12–8.15 (dd, 1H, Ar-H), 7.36–7.40 (td, 1H, Ar-H), 6.82–6.85 (dd, 1H, Ar-H), 6.70–6.75 (td, 1H, Ar-H), 6.11 (s, br., 2H, NH_2) ppm.

Results and discussion

[Bmim] N_3 was prepared according to the literature [15]. We examined the typical reaction under different conditions (Table 1). Schmidt reaction needs strongly acidic conditions [3]. Using a solvent such as CHCl_3 or CH_2Cl_2 caused a decrease in acid concentration and therefore the reaction rates were significantly reduced and low yields were obtained. Furthermore, best results will be obtained when aldehyde or ketone is completely dissolved. Considering these observations and reasons, we chose acetic acid as solvent. Results showed average reaction times and yields. As a typical reaction, we examined the reaction of benzaldehyde (2 equiv) and [bmim] N_3 (3 equiv) in the

Table 1 Various conditions tested for the Schmidt reactions of some aldehydes and ketones using [bmim] N_3

Aldehyde/ketone	Acid	Solvent	Temp. ($^{\circ}\text{C}$)	Time (h)	Product	Yield (%)
Benzaldehyde	ZrCl_4	CHCl_3 , MeOH, CH_2Cl_2	r.t., 50, 70	3–8	Benzamide	20–35
	AcOH	CHCl_3 , H_2O	r.t., 50, 70			30–50
	H_2SO_4	CHCl_3 , H_2O	r.t., 50			35–50
4-Nitrobenzaldehyde	ZrCl_4	CHCl_3 , MeOH, CH_2Cl_2	r.t., 50, 70	3–8	4-Nitrobenzonitrile	15–20
	AcOH	CHCl_3 , H_2O	r.t., 50, 70			20–25
	H_2SO_4	CHCl_3 , H_2O	r.t., 50			20–30
Acetophenone	ZrCl_4	CHCl_3 , MeOH, CH_2Cl_2	r.t., 50, 70	3–8	<i>N</i> -phenylacetamide	20–30
	AcOH	CHCl_3 , H_2O	r.t., 50, 70			25–30
	H_2SO_4	CHCl_3 , H_2O	r.t., 50			30–40
Benzophenone	ZrCl_4	CHCl_3 , MeOH, CH_2Cl_2	r.t., 50, 70	3–8	<i>N</i> -phenylbenzamide	20–25
	AcOH	CHCl_3 , H_2O	r.t., 50, 70			35–40
	H_2SO_4	CHCl_3 , H_2O	r.t., 50			35–40

Scheme 1 Schmidt reaction of aldehydes using [bmim]N₃

presence of a stoichiometric amount of HOAc/H₂SO₄. The reaction proceeded rapidly at 50 °C and the product, benzamide **2a** was isolated in 80 % yield (Scheme 1). For optimizing the reaction conditions, sulfuric acid in various molar ratios was added to acetic acid and results were studied. It was found that the best results were obtained using 1:2:1:0.2 molar ratios of benzaldehyde/[bmim]N₃/HOAc/H₂SO₄ and the product **2a** was isolated in 95 % yield at 54 °C in this procedure. Encouraged by this result, we turned our attention to other benzaldehyde derivatives such as 2-bromobenzaldehyde and 4-methoxybenzaldehyde. These compounds were converted successfully into their corresponding benzamide derivatives in good yields in this procedure (Table 1, entries 2 and 5). Reactions of the other benzaldehydes containing electron donating groups were tested and good to high yields of benzamides were isolated under the above described optimized conditions (Table 2, entry 3, 4, 6, 7). It seems that in the case of benzaldehydes containing electron donating groups, first benzonitrile products were formed and then corresponding primary amides were formed under reaction conditions through a hydrolysis process (Scheme 2).

Next, we examined the reactivity of 4-nitrobenzaldehyde in this procedure and 4-nitrobenzonitrile **3c** was isolated instead of benzamide derivative in 94 % yield under optimized conditions (Table 2, entry 9). Similarly, benzaldehydes containing electron withdrawing groups such as 2-nitrobenzaldehyde, 3-nitrobenzaldehyde and 4-cyanobenzaldehyde, also gave the relative benzonitriles (Table 2, entries 7, 8 and 9). Two products, 1,4-dicyanobenzene, **4a** and 1,4-benzenedicarboxamide, **4b** were isolated from the Schmidt reaction of 4-cyanobenzaldehyde in 100 % total yield (1:1 ratio) in 2.5 h at 58 °C (Scheme 1; Table 2, entry 10). All synthesized

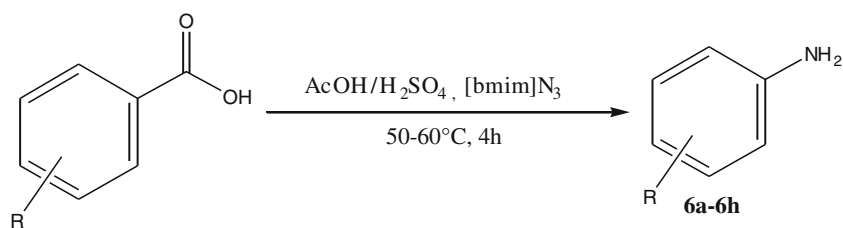
Table 2 Schmidt reaction of aldehydes using task-specific ionic liquid [bmim]N₃

Entry	R	Product	Yield ^a (%)	M.P (°C)	
				Found	Reported (lit. [references])
1	C ₆ H ₅	2a	95	125–127	127–128 [19]
2	2-Br-C ₆ H ₄	2b	85	157–159	160–162 [20]
3	4-Me-C ₆ H ₄	2c	90	155–157	155–156 [21]
4	2-OMe-C ₆ H ₄	2d	92	126–128	127–128 [22]
5	4-OMe-C ₆ H ₄	2e	93	167–169	164–167 [23]
6	2,5-(OMe) ₂ -C ₆ H ₃	2f	91	141–143	–
7	2-NO ₂ -C ₆ H ₄	3a	95	108–110	107–111 [24]
8	3-NO ₂ -C ₆ H ₄	3b	91	114–117	117–118 [25]
9	4-NO ₂ -C ₆ H ₄	3c	94	147–149	147–150 [26]
10	4-CN-C ₆ H ₄	4a	50	223–225	221–225 [27]
		4b	50	>340 (dec.)	>345 (dec.) [28]

^a Isolated yield

compounds have melting points and ¹HNMR and IR spectral characteristics identical to those described in the literature.

We have successfully employed a variety of ketones in the Schmidt reaction under the above described optimized conditions. The reaction time was varied in between 2–4 h depending on the nature of starting ketone (Scheme 3; Table 3). The corresponding amides **5a–h** were obtained in 90–100 % yields. Aryl methyl ketones in the Schmidt reaction under these optimized conditions afforded to corresponding acetanilides (Table 3, entries 2, 4–6). The reaction of *p*-chlorobenzophenone and cyclohexylphenyl ketone gave two isomeric products (**5c**, **5c'**

Scheme 4 Schmidt reaction of carboxylic acids using [bmim]N₃**Table 4** Schmidt reaction of aromatic carboxylic acids using task-specific ionic liquid [bmim]N₃

Entry	R	Product	Yield ^a (%)	M.P (°C)	
				Found	Reported [references]
1	H	6a	90	–	–
2	4-NO ₂	6b	85	146–147	147–151 [19]
3	4-Cl	6c	95	68–69	68–72 [19]
4	4-F	6d	85	–	–
5	4-Br	6e	80	59–61	66–66.5 [36]
6	2-Cl	6f	97	–	–
7	2-NO ₂	6g	97	69–71	70–75 [37]

^a Isolated yield after recrystallization**Table 5** Comparison of the times and isolated yields of the present method with reported methods

Product number	Time (h)		Yield ^a (%)	
	Found	Reported [references]	Found	Reported [references]
2a	2	15 [22]	95	98 [22]
2c	2.5	15 [22]	92	87 [22]
2d	2	23 [22]	90	73 [22]
2e	3	22 [29]	93	88 [29]
3b	2	2 [25]	91	88 [25]
3c	2	2 [26]	94	94 [26]
5c	2	4 [32]	50	98 [32]
5e	3	2 [30]	92	86 [30]
5'g	3	12 [34]	50	47 [34]
5h	3	3 [35]	89	70 [35]

^a Isolated yield after recrystallization

and **5g**, **5'g**) in 1:1 molar ratios, respectively, depending on the migration of the two substituents of carbonyl (Table 3, entries 3 and 7).

The Schmidt reaction for aromatic carboxylic acids was also investigated using [bmim]N₃ as an azide source and good to high yields of anilines were obtained under optimized conditions (Scheme 4; Table 4).

To recognize the efficiency and potency of our protocol, the reaction time and yield of the products are compared to other established methods and results are shown in Table 5.

In summary, the task-specific azide ionic liquid, [bmim]N₃, has proved to be a useful and highly efficient reagent for the Schmidt reaction of ketones, arylaldehydes and aromatic carboxylic acids under acidic conditions. Using [bmim]N₃ as an alternative for conventional very toxic and explosive reagent, NaN₃, provides some remarkable advantages for the present procedure. [Bmim]N₃ has notable preferences to NaN₃ in storage and usage. Due to less explosivity, converting NaN₃ to [bmim]N₃ provides a source of azide ion that is more storable and usable in more wide range of

temperatures and pressures. For example, as we see in the present procedure, Schmidt reaction of carboxylic acids and their conversion into corresponding amines, needs to relatively higher temperatures using [bmim] N_3 instead of NaN_3 , these temperatures would be easily accessible and therefore shorter reaction times and higher yields could be obtained.

In addition to its simplicity and efficiency, this method produces benzamides and amides in good to excellent yields in short reaction times. Benzaldehydes containing electron donating groups afforded to the corresponding benzamide derivatives. Benzonitrile derivatives were prepared from the reaction of benzaldehydes containing electron withdrawing groups in this procedure.

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