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Glycerine-$CeCl_3 \cdot 7H_2O$: An Efficient Recyclable Reaction Medium for the Synthesis of Hantzsch Pyridines

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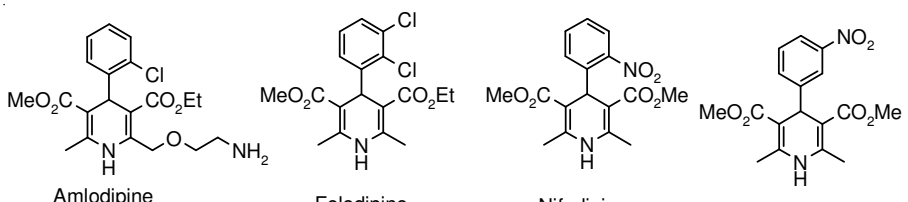
1,4-Dihydropyridine synthesis has been carried out using glycerine-$CeCl_3 \cdot 7H_2O$ as a recyclable reaction medium. A variety of aldehydes undergo smooth condensation reaction with β-ketoester and ammonium acetate to afford the corresponding 1,4-dihydro pyridines in one-pot reaction in excellent yields.

Key Words: Aldehydes, Diketones, Ammonium acetate, Glycerine, 1,4-Dihydropyridine.

INTRODUCTION

Multicomponent condensation strategies offer significant advantages over conventional linear type synthesis to provide products with the diversity needed for the discovery of new lead compounds or lead optimization employing combinatorial chemistry[1-3]. In 1882, Arthur Rudolf Hantzsch, a German chemist reported a cyclocondensation between ethyl acetoacetate, aldehyde and aqueous ammonium hydroxide to afford a heterocyclic system of 1,4-dihydropyridine, since then it became familiar as Hantzsch reaction[4,5]. The dihydropyridine derivatives exhibits a large range of biological activities such as anticonvulsant, antitumor, antianxiety, vasodilator, bronchodilator, antidepressive, analgesic, hypnotic, antiinflammatory and neuroprotectants as well as platelet antiaggregatory agents[6-9].



The dihydropyridines derivatives are commercially used as calcium channel blockers (amlodipine, felodipine, nifedipine, nitrendipine, *etc.*) for the treatment of cardiovascular diseases. The tremendous biological activity of Hantzsch pyridines, attracted many researchers and academicians. Hence, several attempts have been made to synthesize the 1,4-dihydro pyridine derivatives under mild reaction conditions[10-17]. Therefore, the development of an efficient and environmental friendly

green protocol is still in demand. The use of solvents like water, supercritical fluids, ionic liquids and solvent-free conditions under microwave irradiation has received much attention in recent years in the area of green synthesis[18-22]. In this respect, glycerine have emerged as a green solvent with unique prosperities such as high polarity, thermal stability and immiscibility with a number of organic solvents, negligible vapour pressure, low-toxic and recyclability. Accordingly, the glycerine occupies a novel replacement for volatile solvents in organic transformations[23-25]. Moreover, the glycerine is inexpensive and available in plenty. Recently, Silvera *et al.*[26] reported glycerine and $CeCl_3 \cdot 7H_2O$ as a new and efficient recyclable reaction medium for the synthesis of *bis* (indole) methanes. Herein we report a highly efficient and environmentally green protocol for the synthesis of 1,4-dihydropyrimidine derivatives using glycerine-$CeCl_3 \cdot 7H_2O$ as a recyclable reaction medium.

EXPERIMENTAL

Melting points were recorded on Buchi R-535 apparatus. IR spectra were recorded on a Perkin-Elmer FT-IR 240-c spectrophotometer. ^{1}H NMR spectra were recorded on Gemini-200 spectrometer in $CDCl_3$ using TMS as internal standard. Mass spectra were recorded on a Finnigan MAT 1020 mass spectrometer operating at 70 eV.

General procedure for the synthesis of 1,5-benzodiazepines: A stirred mixture of aldehyde (1 mmol), ethyl acetoacetate (2.2 mmol) and ammonium acetate (1.1 mmol) were stirred in glycerine (2 mL) in presence of $CeCl_3 \cdot 7H_2O$ (0.1 mol %) at 75-80 ºC for a period of appropriate time (Table-1). The progress of the reaction was monitored by thin layer chromatography (TLC). After completion of the reaction as indicated by TLC, the reaction mixture was extracted with ethyl acetate (2 mL × 10 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure to obtain the crude products, which were purified by column chromatography using 60-120 mesh. All the products were confirmed by their spectral data and compared with literature reports.

TABLE-1
OPTIMIZATION OF REACTION CONDITIONS FOR
THE SYNTHESIS OF 1,4-DIHYDROPYRIDINES

Entry	Solvent	$CeCl_3 \cdot 7H_2O$	Temp. (ºC)	Time (h)	Yield (%)
1	Glycerine	1.0	r.t	24.0	60
2	Glycerine	1.0	75-80	3.0	95
3	Glycerine	0.5	75-80	3.0	93
4	Glycerine	0.1	75-80	3.0	93
5	Glycerine	0.1	90-95	3.0	90
6.	CH_3CN	0.1	80-85	4.0	79
7	CH_3OH	0.1	60-65	5.0	75
8	THF	0.1	60-65	6.0	71

Diethyl-2,6-dimethyl-4-phenyl-1, 4-dihydropyrimidine-3,5-dicarboxylate (3a): Solid, m.p. 155-156 ºC. IR (KBr, ν_{max}, cm^{-1}): 3342, 3061, 2978, 2931, 1690, 1651, 1489, 1453, 1375, 1300, 1248, 1212, 1121, 1091, 1024, 825, 767, 701; ^1H NMR ($CDCl_3$): δ 1.25 (t, 6H, *J* = 6.0 Hz), 2.35 (s, 6H), 4.10 (q, 4H, *J* = 6.0 Hz), 4.90 (s, 1H), 5.52 (brs, 1H, NH), 7.08-7.25 (m, 5H); ^{13}C NMR (75, MHz, $CDCl_3$): δ: 168.3, 146.1, 143.9, 136.1, 129.2, 126.8, 103.9, 60.1, 40.0, 20.5, 14.3; EIMS m/z (%): 328 (m^+ 95), 284 (100), 256 (25), 252 (35), 225 (15), 219 (10), 195 (10), 181 (12), 173 (25), 131 (15), 107 (20).

Diethyl-2,6-dimethyl-4-(3,4,5-trimethoxyphenyl)-1,4-dihydropyrimidine-3,5-dicarboxylate (3b): IR (KBr, ν_{max}, cm^{-1}): 3357, 2928, 2853, 1696, 1636, 1593, 1497, 1460, 1378, 1317, 1273, 1205, 1127, 1092, 1001, 864, 803, 748, 627; ^1H NMR ($CDCl_3$): δ 1.28 (t, 6H, *J* = 6.0 Hz), 2.35 (s, 6H), 3.78 (s, 6H), 3.80 (s, 3H), 4.12 (q, 4H, *J* = 6.0 Hz), 4.90 (s, 1H), 5.52 (brs, 1H, NH), 6.45 (s, 2H); EIMS m/z (%): 420 (m^{+1} 30), 374 (25), 346 (20), 328 (10), 252 (100), 227 (10), 170 (10), 121 (10).

Diethyl-2,6-dimethyl-4-(4-nitrophenyl)-1,4-dihydropyrimidine-3,5-dicarboxylate (3c): Solid, m.p. 130-131 ºC. IR (KBr, ν_{max}, cm^{-1}): 3341, 3084, 2979, 2927, 2855, 1683, 1518, 1484, 1344, 1301, 1213, 1101, 1020, 828, 754, 706; ^1H NMR ($CDCl_3$): δ 1.25 (t, 6H, *J* = 6.0 Hz), 2.35 (s, 6H), 4.10 (q, 4H, *J* = 6.0 Hz), 5.05 (s, 1H), 5.70 (brs, 1H, NH), 7.41 (d, 2H, *J* = 6.5 Hz), 8.06 (d, 2H, *J* = 6.5 Hz); ^{13}C NMR (75, MHz, $CDCl_3$): δ 166.9, 156.0, 145.9, 144.7, 128.3, 123.5, 103.4, 60.1, 40.2, 20.3, 14.2; EIMS m/z (%): 375 (m^{+1} 45), 348 (10), 329 (100), 320 (10), 301 (25), 102 (10).

Diethyl-2,6-dimethyl-4-(3-chlorophenyl)-1,4-dihydropyrimidine-3,5-dicarboxylate (3d): Solid, m.p. 130-131 ºC. IR (KBr, ν_{max}, cm^{-1}): 3323, 3246, 3098, 2979, 2925, 1705, 1649, 1488, 1375, 1333, 1299, 1214, 1119, 1022, 869, 788, 751, 694; ^1H NMR ($CDCl_3$): δ 1.23 (t, 6H, *J* = 6 Hz), 2.36 (s, 6H), 4.10 (q, 4H, *J* = 6 Hz), 4.90 (s, 1H), 5.58 (brs, 1H, NH), 7.05-7.20 (m, 4H); ^{13}C NMR (75, MHz, $CDCl_3$): δ 167.9, 150.1, 144.1, 143.5, 132.6, 128.0, 127.6, 126.0, 103.6, 60.1, 40.2, 19.3, 14.8; EIMS m/z (%): 386 (m^{+1} 65), 364 (40), 318 (100), 292 (10), 251 (20), 201 (10), 171 (25).

(E)-Diethyl-2,6-dimethyl-4-styryl-1,4-dihydropyridine-3,5-dicarboxylate (3e): Solid, m.p. 148-150 ºC. IR (KBr, ν_{max}, cm^{-1}): 3334, 3095, 2924, 1690, 1644, 1490, 1375, 1326, 1296, 1219, 1161, 1116, 1025, 783, 755, 715; ^1H NMR ($CDCl_3$): δ 1.22 (t, 3H, *J* = 6.0 Hz), 2.38 (s, 6H), 3.92 (s, 3H), 4.18 (q, 2H, *J* = 6.0 Hz), 5.14 (d, 1H, *J* = 4.5 Hz), 5.6.0 (brs, 1H), 6.15 (dd, 1H, *J* = 4.5 and 14.8 Hz), 7.18 (d, 1H, *J* = 14.8 Hz), 7.22-7.34 (m, 5H); EIMS m/z (%): 341 (m^{+1} 20), 327 (10), 297 (100), 269 (10), 211 (15), 183 (20), 104 (18), 81 (25), 76 (35), 51 (22).

Diethyl-4-decyl-2,6-dimethyl-1,4-dihydropyrimidine-3,5-dicarboxylate(3f): IR (neat, ν_{max}, cm^{-1}): 3377, 2926, 2855, 1728, 1567, 1461, 1376, 1282, 1233, 1104, 1041, 860, 772; ^1H NMR ($CDCl_3$): δ 0.90 (t, 3H, *J* = 6.0 Hz), 1.20-1.36 (m, 24H), 2.29 (s, 6H), 3.85 (t, 1H, *J* = 6.0 Hz), 4.20 (q, 4H, *J* = 6.0 Hz), 5.48 (brs, 1H, NH); EIMS m/z (%): 393 (m^{-1} 100), 335 (10), 320 (10).

Diethyl-4-benzyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (3g): IR (neat, ν_{max}, cm^{-1}): 2978, 2927, 1719, 1592, 1443, 1369, 1289, 1252, 1222, 1105, 1043, 863, 769, 699; ^1H NMR ($CDCl_3$): δ 1.26 (t, 6H, *J* = 6.0 Hz), 2.15 (s, 6H), 2.55 (d, 2H, *J* = 5.0 Hz), 4.05 (q, 4H, *J* = 6.0 Hz), 4.97 (s, 1H), 5.45 (brs, 1H, NH), 6.98 (d, 2H, *J* = 7.0 Hz), 7.10-7.20 (m, 3H); EIMS m/z (%): 344 (m^{+1} 20), 342 (10), 318 (10), 250 (10), 298 (25), 252 (100), 224 (10).

Diethyl-2,6-dimethyl-4-(pyridin-2-yl)-1,4-dihydropyridine-3,5-dicarboxylate (3h): IR (KBr, ν_{max}, cm^{-1}): 3273, 3172, 3054, 2925, 1676, 1593, 1508, 1437, 1371, 1304, 1256, 1212, 1116, 1018, 751, 677; ^1H NMR ($CDCl_3$): δ 1.20 (t, 6H, *J* = 6.0 Hz), 2.25 (s, 6H), 4.05 (q, 4H, *J* = 6.0 Hz), 5.12 (s, 1H), 7.08-7.12 (m, 1H), 7.32-7.38 (m, 1H), 7.51-7.58 (m, 1H), 8.05 (brs, 1H), 8.48 (d, 1H, *J* = 6.0 Hz); EIMS m/z (%): 331 (m^{+1} 100), 308 (10), 286 (55), 292 (10), 262 (10).

Diethyl-4-isopropyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (3i): IR (KBr, ν_{max}, cm^{-1}): 3421, 2981, 2930, 1722, 1592, 1553, 1442, 1372, 1295, 1255, 1223, 1117, 1043, 865, 771, 699; ^1H NMR ($CDCl_3$): δ 0.72 (s, 3H), 0.74 (s, 3H), 1.31 (t, 6H, *J* = 6.0 Hz), 2.21 (s, 6H), 3.88 (d, 1H, *J* = 6.0 Hz), 4.20 (q, 4H, *J* = 6.0 Hz), 5.48 (brs, 1H, NH).; EIMS m/z (%): 296 (m^{+1} 30), 252 (55), 250 (100), 224 (10), 204 (10), 184 (10), 102 (12), 90 (10), 87 (10), 59 (15).

Diethyl-4-(furan-2-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (3j): Solid, m.p. 158-160 ºC. IR (KBr, ν_{max}, cm^{-1}): 3346, 2981, 1702, 1650, 1487, 1373, 1331, 1298, 1262, 1209, 1119, 1095, 1047, 1013, 807, 731, 687; ^1H NMR ($CDCl_3$): δ 1.28 (t, 6H, *J* = 6.0 Hz), 2.32 (s, 6H), 4.10-4.22 (m, 4H), 5.12 (s, 1H), 5.61 (brs, 1H), 5.90 (s, 1H), 6.20 (s, 1H), 7.18 (s, 1H); ^{13}C NMR (75, MHz, $CDCl_3$): δ 168.1, 159.0, 145.5, 141.2, 109.8, 104.9, 99.8, 60.2, 33.5, 20.1, 14.5; EIMS m/z (%): 320 (m^{+1} 45), 318 (25), 304 (40), 274 (10), 261 (10), 252 (100), 214 (15).

Diethyl-4-(2-chloro-6-methylquinolin-3-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (3k): IR (neat, ν_{max}, cm^{-1}): 3338, 2981, 1725, 1695, 1560, 1495, 1448, 1375, 1301, 1275, 1213, 1171, 1104, 1043, 925, 824, 755; ^1H NMR ($CDCl_3$): δ 1.19 (t, 6H, *J* = 6.0 Hz), 2.32 (s, 6H), 2.50 (s, 3H), 4.01-4.12 (m, 4H), 5.42 (s, 1H), 5.65 (brs, 1H), 7.40-7.50 (m, 2H), 7.82 (d, 1H, *J* = 7.0 Hz), 7.99 (s, 1H). EIMS m/z (%): 429 (m^{+1} 100), 393 (35), 251 (10), 178 (20).

Diethyl-4-(2,6-dimethylhept-5-enyl)-2, 6-dimethyl-1,4-dihydropyridine-3,5-dicarbo xylate (3l): IR (neat, ν_{max}, cm^{-1}): 3373, 2967, 2927, 1728, 1565, 1449, 1377, 1283, 1236, 1106, 1040, 859, 775; ^1H NMR ($CDCl_3$): δ 0.88 (s, 3H), 0.90 (s, 3H), 0.98-1.10 (m, 1H), 1.20-1.35 (m, 10H), 1.58 (s, 3H), 1.68 (s, 3H), 1.80-1.95 (m, 2H), 2.30 (s, 6H), 4.20 (q, 4H, *J* = 6.0 Hz), 5.48 (brs, 1H, NH); EIMS m/z (%): 378 (m^{+1} 40), 376 (50), 332 (20), 306 (10), 274 (15), 252 (100), 197 (10), 161 (10), 116 (10), 81 (10), 65 (18).

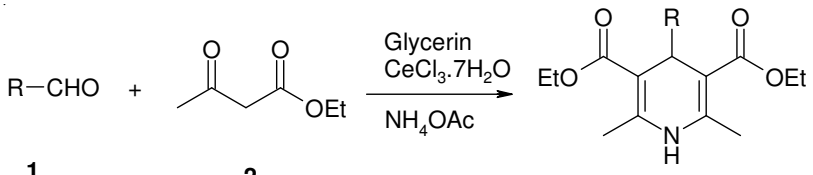
Diethyl-4-[4-(dimethylamino) phenyl]-2,6-dimethyl-1,4-dihydropyridine-3,5-dicar boxylate (3m): IR (KBr, ν_{max}, cm^{-1}): 3319, 3095, 2979, 2923, 2804, 1697, 1674, 1613, 1519, 1492, 1446, 1352, 1302, 1276, 1203, 1128, 1096, 1050, 1021, 945, 818, 785, 747, 683; ^1H NMR ($CDCl_3$): δ 1.26 (t, 6H, *J* = 6.0 Hz), 2.32 (s, 6H),

2.90 (s, 6H), 4.02-4.15 (m, 4H), 4.81 (s, 1H), 5.50 (brs, 1H, NH), 6.60-6.70 (m, 2H), 7.10 (d, 2H, *J* = 7.0 Hz); EIMS m/z (%): 373 (m^{+1} 100), 252 (25), 227 (10), 205 (10), 116 (10), 65 (10), 55 (10).

Diethyl-4-[4-(benzyloxy)-3-methoxyphenyl]-2,6-dimethyl-1,4-dihydropyridine-3,5-di carboxylate (3n): IR (KBr, ν_{max}, cm^{-1}): 3365, 3063, 2926, 2853, 1693, 1642, 1621, 1511, 1484, 1422, 1380, 1270, 1201, 1161, 1093, 1049, 1007, 862, 812, 748, 703, 658; ^{1}H NMR ($CDCl_3$): δ 1.25 (t, 6H, *J* = 6.0 Hz), 2.32 (s, 6H), 3.82 (s, 3H), 4.06-4.15 (m, 4H), 4.85 (s, 1H), 5.05 (s, 2H), 5.42 (brs, 1H, NH), 6.62-6.70 (m, 2H), 6.82 (s, 1H), 7.28-7.42 (m, 5H).; EIMS m/z (%): 465 (m^+ 35), 464 (65), 420 (15), 392 (20), 367 (10), 322 (10), 252 (100), 152 (10), 115 (10), 102 (15), 75 (10).

RESULTS AND DISCUSSION

In order to evaluate the practicability of the reaction, preliminary experiments were carried out by reacting the benzaldehyde, β-ketoester and ammonium acetate in presence of a catalytic amount (10 mol %) of $CeCl_3 \cdot 7H_2O$ in glycerine at 75-80 ºC as shown in the **Scheme-I**. The reaction was completed within 3 h to afford the corresponding derivative of diethyl-2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (**3a**) in excellent yields. The product was confirmed by ^{1}H NMR, IR and mass spectroscopy.



1 **2** **3**

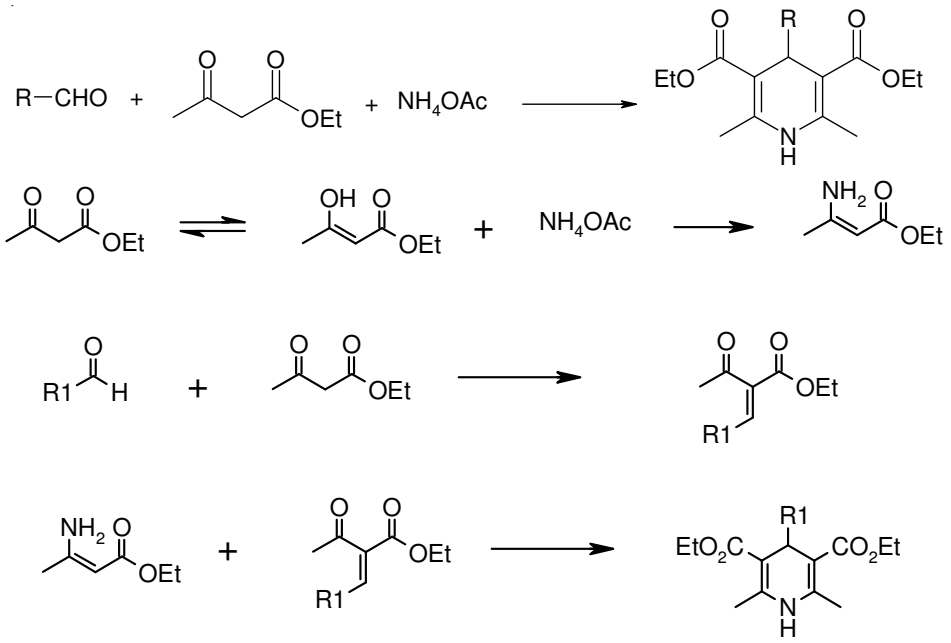
Scheme-1

After completion of the reaction as indicated by thin layer chromatography, the reaction mixture was extracted with ethyl acetate and the glycerine was used for further reactions up to five cycles with out any problem.

We have examined the effect of temperature, amount of the $CeCl_3 \cdot 7H_2O$ and solvents role on the condensation reaction and the results were summarized in the Table-1. The comparative study shows that the use of catalyst $CeCl_3 \cdot 7H_2O$ in 10 % mol and glycerine as solvent at 75-80 ºC reaction temperature were found to be ideal.

Encouraged by the results obtained with the above typical experiment, this methodology was extended to a variety of aldehydes such as aromatic, heteroaromatic and aliphatic, the different aldehydes were reacted smoothly with β-ketoester and ammonium acetate to give the corresponding 1,4-dihydropyridines in excellent yields. The reactions proceeded efficiently at 75-80 ºC with high selectivity. The acid sensitive aldehydes worked well under these reaction conditions. This

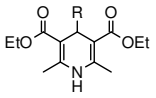
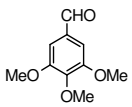
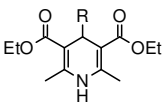
protocol is successfully applicable to both electron rich as well as electron deficient aldehydes (**Scheme-II**)

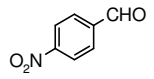
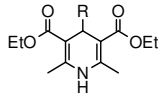
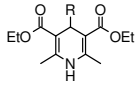
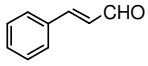
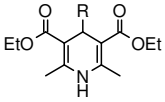
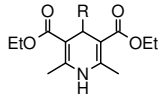
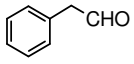
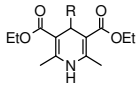
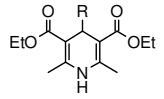
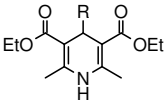
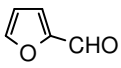
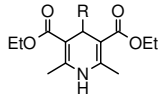
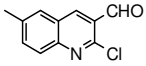
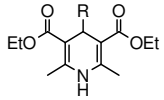
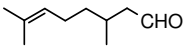
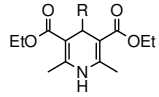
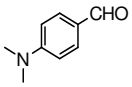
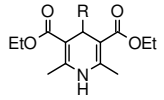
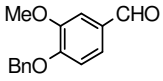
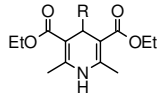


Scheme-II: Proposed reaction mechanism

The possible reaction mechanism can be explained by 3 steps. The first step involves the reaction of β-ketoester with ammonium acetate to form an enamine. The second step involves the reaction of aldehyde and β-ketoester by Knoevenagel condensation to form and olefin compound. The third step involves the condensation of enamine and olefin compound to form a 1,4-dihydropyridine derivatives. In general, all the reactions were completed within 3-5 h of reaction time at 75-80 ºC in glycerine solvent. The products of 1,4-dihydropyridine derivatives were obtained in 80-95 % yields (Table-2). All the products were confirmed by their ^{1}H NMR, IR and mass spectroscopy data.

TABLE-2
GLYCERINE-$CeCl_3 \cdot 7H_2O$: CATALYZED SYNTHESIS OF HANTZSCH PYRIDINES

Entry	Aldehyde (R)	Product (**3a-3n**)*	Reaction time (h)	Yield** (%)
a			3.0	93
b			3.0	95

c			5.0	87
d			4.0	90
e			4.0	80
f			5.0	86
g			4.0	90
h			4.0	85
i			5.0	84
j			3.0	93
k			4.0	85
l			5.0	87
m			4.0	90
n			3.0	91

*Products were confirmed by their ^{1}H NMR, IR and mass spectroscopy. **Yields were isolated by column chromatography and unoptimized.

Conclusion

In this paper, an efficient and environmentally friendly one-pot three-component process for the synthesis of 1,4-dihydropyridines by the condensation of aldehyde, β-ketoester and ammonium acetate using glycerine as novel reaction medium in

presence of a catalytic amount of $CeCl_3 \cdot 7H_2O$ is reported. The notable features of this protocol are mild reaction conditions, simplicity in operation, improved yields, cleaner reaction profiles and reusability of the glycerine make it a economic and eco-friendly process for the synthesis of 1,4-dihydropyridines.

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