Transition Met Chem (2013) 38:93–103
DOI 10.1007/s11243-012-9665-5

Glycerin and [Iron(III)(salen)]Cl as an efficient catalytic medium for multicomponent reactions

Neda Seyedi

Received: 16 September 2012 / Accepted: 18 October 2012 / Published online: 7 November 2012

Abstract In this investigation, glycerol and [Fe(III)-(salen)]Cl as a green catalyst system were used in multicomponent reactions for the synthesis of bis(indolyl)methanes, 3,4-dihydropyrimidinones, and 1,4-dihydropyridines, respectively. Excellent product yields and short reaction times were achieved.

Introduction

Recently, glycerin, which is easily available as a co-product in biodiesel production, has attracted attention as it is a versatile, cheap, and renewable feedstock in synthetic organic chemistry [1]. In addition, glycerol has also promising physical and chemical properties. It has a very high boiling point and negligible vapor pressure; it is compatible with most organic and inorganic compounds, and does not require special handling or storage.

Metal heterocyclic compounds stand as a significant target for synthetic methodology and biological applications, mainly as a consequence of the abundance of interesting natural products that contain similar structural units [2]. Among many potential materials, Schiff base metal complexes have been the subject of extensive and continuous studies.

Transition metal complexes bearing the salen ligand or its derivatives have been one of the highlights in coordination chemistry and homogeneous catalysis, being used as catalysts for organic reactions [3], models of reaction centers of metalloenzymes [4], and nonlinear optical materials [5]. Some of these complexes possess interesting magnetic properties [6].

Indoles and their derivatives are widely present in bioactive metabolites of compounds of both terrestrial and marine origin [7]. Because of their versatile biological activities, in particular the pharmacological activity, various methods are mentioned for the preparation of bis(indolyl) methanes. The most common protocol involves the Lewis or protic acid-promoted electrophilic substitution reaction of indoles with carbonyl compounds [8, 9].

It is well known that 1,4-dihydropyridines (DHPs) exhibit a wide range of biological activities, acting as potent vasodilators, antihypertensives, bronchodilators, antiatherosclerotics, hepatoprotectants, and antitumor, antimutagenic, geroprotective, and antidiabetic agents [10]. DHPs are commercially used as calcium channel blockers for treatment of cardiovascular disease [11]. DHPs are generally synthesized by the Hantzsch method, which involves cyclocondensation of an aldehyde, β-ketoester, and ammonia either in acetic acid or by refluxing in alcohols for long reaction times, leading to low yields in general [12, 13].

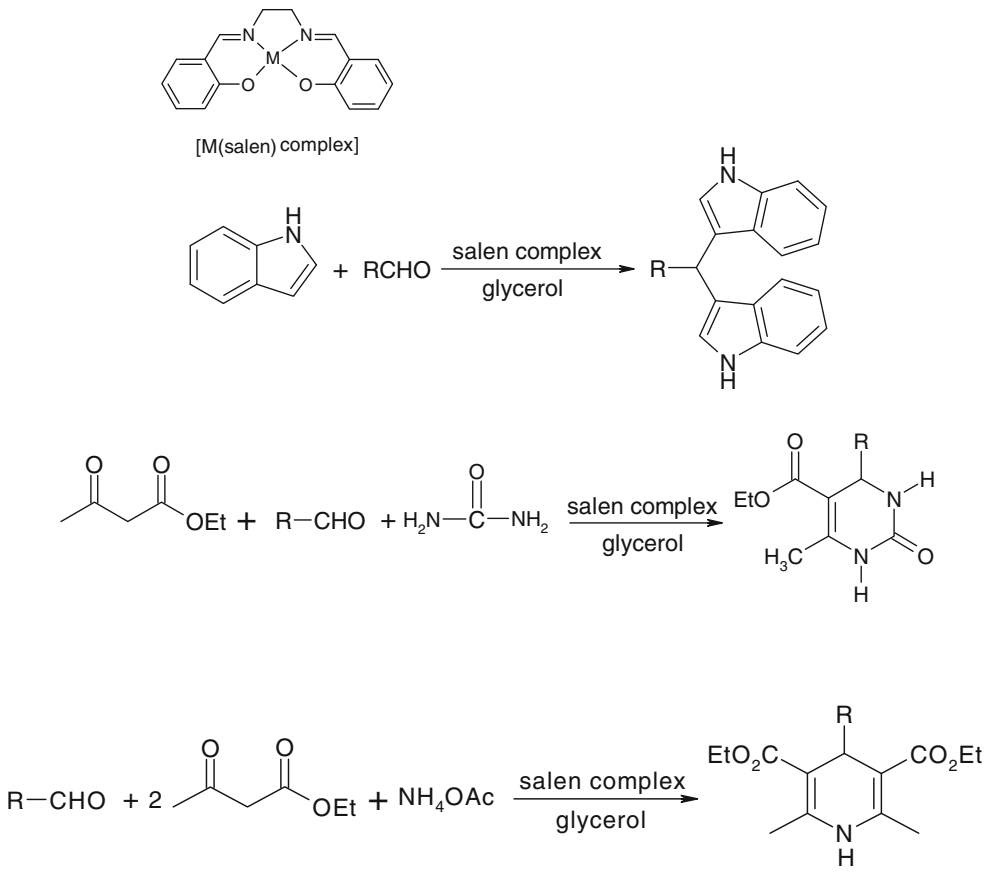
Dihydropyrimidinones (DHPMs), named Biginelli compounds, are known to exhibit a wide range of biological activities such as antiviral, antitumour, antibacterial, and anti-inflammatory actions [14, 15].

In recent years, new methods for the synthesis of 3,4-dihydropyrimidin-2-(1H)-ones have been developed by different groups.

In order to improve the efficiency of the Biginelli reaction, different Lewis catalysts such as $FeCl_3.6H_2O$ [16], $Cu(OTf)_2$ [17], and chloroacetic acid [18] have been reported.

N. Seyedi (✉)
Department of Chemistry, University of Jiroft, Jiroft, Iran
e-mail: nedaseyedi@ujiroft.ac.ir

Scheme 1 Salen complex-catalyzed synthesis of bis(indolyl)methanes, DHPs, and DHMPs in glycerol



It was of interest, therefore, to investigate the catalytic effect of some of transition metal salen complexes on the synthesis of the foregoing compounds in glycerol as a green solvent under microwave irradiation (Scheme 1).

Experimental

All chemicals used in the syntheses were purchased from Merck chemical company and were used without further purification.

All products are known and were identified by comparing their spectroscopic data and physical properties with those of the authentic samples. Melting points were obtained on an Electrothermal-9100 melting point apparatus and were uncorrected. IR spectra were recorded on a Bruker Tensor 27 FTIR spectrometer. NMR spectra were recorded on a BRUKER DRX-500 AVANCE NMR spectrometer using $CDCl_3$ and DMSO-d_6 as solvent. [Fe(III)(salen)]Cl was synthesized according to the literature, and its spectroscopic data were essentially identical to those reported [19].

General procedure for preparation of bis-indolylmethanes

A mixture of indole (2 mmol), aldehyde (1 mmol), and [Fe(III)(salen)]Cl (5 mol %) in glycerol (4 ml) was placed

Table 1 Catalytic effect of 1 mol % of different salen catalysts on the reaction of indole with benzaldehyde

Entry	Catalyst	Time (min)	Yield (%)
1	[Mn(III)(salen)]Cl	12	90
2	[Fe(III)(salen)]Cl	8	90
3	Ni(II)(salen)	15	85
4	Cu(II)(salen)	10	88
5	None	50	15

Table 2 Effects of different amounts of [Fe(III)(salen)]Cl on the reaction of benzaldehyde and indol

Entry	[Fe(III)(salen)]Cl mol %	Time (min)	Yield (%)
1	1	8	90
2	3	6	92
3	5	4	95
4	10	4	95

Table 3 Synthesis of bis(indolyl)methanes using the glycerin/[Fe(III)(salen)]Cl catalytic system

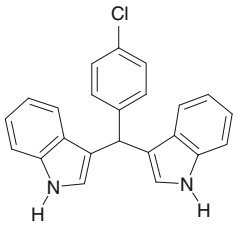
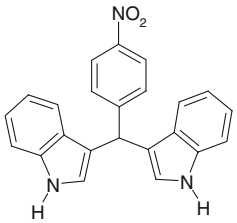
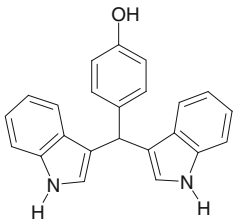
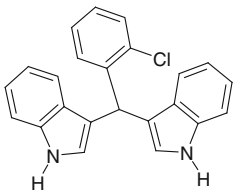
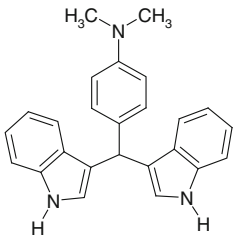
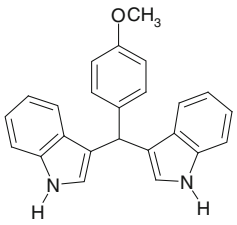
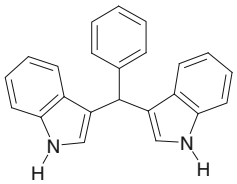
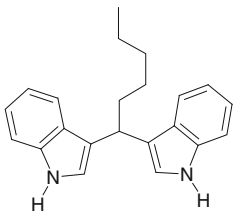
Entry	Product	Yield (%)	MP (°C) (observed)	MP (°C) (reported) [Ref.]
1		94	83–85	78–80 [20]
2		90	223–226	221–223 [21]
3		88	127–129	123–125 [21]
4		86	76–78	74–76 [22]
5		85	167–170	170–172 [20]
6		87	191–193	191–193 [21]

Table 3 continued

Entry	Product	Yield (%)	MP (°C) (observed)	MP (°C) (reported) [Ref.]
7		95	142–145	140–142 [22]
8		70	72–75	71–73 [22]

in a microwave oven and irradiated at 300 watts of microwave power for a period of 1 min at a time. After each irradiation, the reaction mixture was removed from the microwave oven for shaking. The total period of microwave irradiation was 4 min. The progress of the reaction was monitored by TLC. After completion of the reaction, as indicated by TLC, the reaction mixture was dissolved in 10 ml ethanol and poured into 50 ml water. The resulting precipitate was filtered off and purified by silica gel column chromatography using chloroform as eluent, to afford the desired bis(indolyl)methane in pure form.

Spectral data of selected compounds

4-Chlorophenyl-3,3′-bis(indolyl)methane (Table 1, entry 1)

IR (KBr): 1,217, 1,420, 1,456, 1,525, 1,600, 2,927, 3,021, 3,478. ^{1}HNMR: δ (ppm) 5.90 (1H, s, CH aliphatic), 6.66 (2H, d, $J = 1.35$ Hz, 2CH indole ring), 7.05 (2H, t, $J = 7.3$ Hz, arom), 7.18 (2H, t, $J = 8.2$ Hz, arom), 7.21–7.42 (8H, m, arom), 7.90 (2H, s, br, 2NH). ^{13}CNMR: δ (ppm) 40.1, 111.5, 119.6, 119.8, 120.3, 122.5, 124.0, 127.3, 128.8, 130.2, 130.5, 137.1, 142.9.

3,3′-Bis(indolyl)phenylmethane (Table 1, entry 7)

IR (KBr): 1,205, 1,424, 1,460, 1,522, 1,606, 2,920, 3,015, 3,470. ^{1}HNMR: δ (ppm) 5.93 (1H, s, CH aliphatic), 6.67 (2H, s, 2CH indole ring), 7.05 (2H, t, $J = 7.4$ Hz, arom), 7.22 (2H, t, $J = 7.4$ Hz, arom), 7.26 (1H, t, $J = 7.2$ Hz, arom), 7.33 (2H, t, $J = 7.2$ Hz, arom), 7.39 (4H, t, $J = 7.1$ Hz, arom), 7.44 (2H, d, $J = 7.9$ Hz, arom), 7.87 (2H, s, br, 2NH). ^{13}CNMR: δ (ppm) 40.6, 111.4, 119.7, 120.2, 120.4, 122.4, 124.0, 126.6, 127.5, 128.6, 129.2, 137.1, 144.4.

General procedure for the preparation of 3,4-dihydropyrimidin-2(1H)-ones

A mixture of the appropriate aldehyde (1 mmol), ethylacetoacetate (1.2 mmol), urea (1.5 mmol), and [Fe(III)(salen)]Cl (5 mol %) in glycerol (4 ml) was placed in a microwave oven and irradiated for a period of 1 min at a time. After each irradiation, the reaction mixture was removed from the microwave oven for shaking. The total period of microwave irradiation was 7 min. The progress of the reaction was monitored by TLC. The resulting mixture was dissolved in 10 ml ethanol and poured into 50 ml water. The resulting precipitate was filtered off and purified by silica gel column chromatography using ethylacetate:chloroform 50:50 as eluent, to afford the desired 3,4-dihydropyrimidin-2(1H)-one in pure form.

Spectral data of selected compounds

6-Methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydro-pyrimidine-5-carboxylic acid ethyl ester (Table 2, entry 1)

White powder, IR (KBr): 1,650, 1,699, 2,982, 3,131, 3,230 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ = 1.10 (t, $J = 7.1$ Hz, 3H, CH_3), 2.25 (s, 3H, CH_3), 3.99 (q, $J = 7.1$ Hz, 2H, CH_2), 5.15 (d, $J = 3.2$ Hz, 1H, CH), 7.23–7.34 (m, 5H, arom CH), 7.73 (s, 1H, NH), 9.18 (s, 1H, NH). ^{13}C NMR (DMSO-d_6) δ = 14.9, 18.6, 54.8, 60.0, 100.1, 127.1, 128.1, 129.2, 145.7, 149.2, 152.9, 166.2.

Table 4 Synthesis of 3,4-dihydropyrimidin-2(1H)-ones using the glycerin/[Fe(III)(salen)]Cl catalytic system

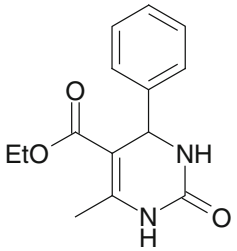
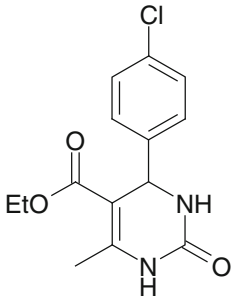
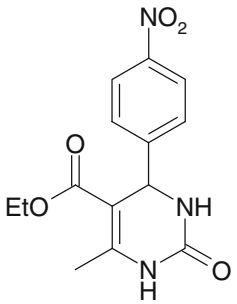
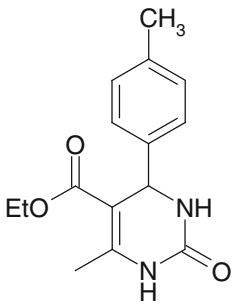
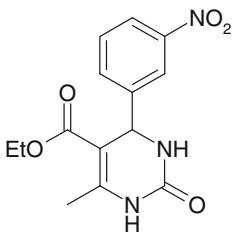
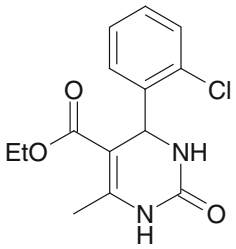
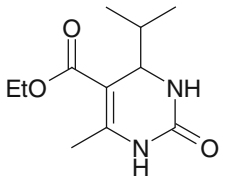
Entry	Product	Yield (%)	MP (°C) (observed)	MP (°C) (reported) [Ref.]
1		94	199–202	198–200 [18]
2		93	212–215	211–213 [18]
3		90	207–209	205–207 [23]
4		85	215–218	213–216 [18]
5		93	231–235	229–230 [24]

Table 4 continued

Entry	Product	Yield (%)	MP (°C) (observed)	MP (°C) (reported) [Ref.]
6		88	217–220	216–218 [23]
7		60	195–197	196–197 [18]

4-(4-Chloro-phenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydro-pyrimidine-5-carboxylic acid ethyl ester (Table 2, entry 2)

White powder, IR (KBr): 1,651, 1,711, 2,957, 3,106, 3,230 cm^{-1}. ^1H NMR (DMSO-d_6): $\delta = 1.10$ (t, $J = 7.1$ Hz, 3H, CH_3), 2.26 (s, 3H, CH_3), 3.99 (q, $J = 7.1$ Hz, 2H, CH_2), 5.14 (d, $J = 3.3$ Hz, 1H, CH), 7.25 (d, $J = 8.4$ Hz, 2H, arom CH), 7.40 (d, 8.4 Hz, 2H, arom CH), 7.77 (s, 1H, NH), 9.24 (s, 1H, NH). ^{13}C NMR (DMSO-d_6) $\delta = 14.9$, 18.6, 54.2, 60.1, 99.6, 129.0, 129.2, 132.6, 144.6, 149.6, 152.7, 166.0.

6-Methyl-4-(4-nitro-phenyl)-2-oxo-1,2,3,4-tetrahydro-pyrimidine-5-carboxylic acid ethyl ester (Table 2, entry 3)

Pale yellow powder, IR (KBr): 1,343, 1,520, 1,641, 1,702, 2,957, 3,007, 3,106, 3,230 cm^{-1}. ^1H NMR (DMSO-d_6): $\delta = 1.10$ (t, $J = 7.0$ Hz, 3H, CH_3), 2.28 (s, 3H, CH_3), 3.99 (q, $J = 7.0$ Hz, 2H, CH_2), 5.28 (d, $J = 2.7$ Hz, 1H, CH), 7.51 (t, $J = 8.5$ Hz, 1H, arom CH), 7.91 (s, 1H, NH), 8.22 (d, $J = 8.5$ Hz, 1H, arom CH), 9.36 (s, 1H, NH). ^{13}C NMR (DMSO-d_6) $\delta = 14.9$, 18.7, 54.5, 60.2, 99.0, 124.6, 128.5, 147.5, 150.2, 152.6, 152.8, 165.9.

General procedure for the synthesis of 1,4-dihydropyridines

A mixture of aldehyde (1 mmol), ethylacetoacetate (2 mmol), NH_4OAc (1 mmol), and [Fe(III)(salen)]Cl (5 mmol %) in glycerol (4 ml) was placed in a microwave oven and irradiated for a period of 1 min at a time. After each irradiation, the reaction mixture was removed from the microwave oven for shaking. The total period of microwave irradiation was 5 min. The progress of the reaction was monitored by TLC. After completion of reaction, the resulting mixture was dissolved in 10 ml ethanol and poured into 50 ml water. The resulting precipitate was filtered off and purified by silica gel column chromatography using chloroform as eluent, to afford the desired 1,4-dihydropyridine in pure form.

Spectral data of selected compounds

Diethyl 1,4-dihydro-2,6-dimethyl-4-phenylpyridine-3,5-dicarboxylate (Table 3, entry 1)

Yellow powder, IR (KBr): 1,703, 2,950, 3,100, 3,300 cm^{-1}.^1H NMR ($CDCl_3$, 500 MHz): δ (ppm) 1.24 (6H, t, $J = 7.0$ Hz, $2CH_3$), 3.37 (6H, s, CH_3), 4.13 (4H, m, $2CH_2$), 5.02 (1H, s, CH aliphatic), 5.72 (1H, s, NH), 7.12–7.35 (5H, m, arom). $^{13}CNMR$ ($CDCl_3$, 125 MHz): δ (ppm) 14.5, 20.4, 40.2, 60.6, 104.5, 126.8, 128.3, 128.8, 145.0, 148.3, 168.5.

Diethyl 1,4-dihydro-2,6-dimethyl-4-(3-nitrophenyl) pyridine-3,5-dicarboxylate (Table 3, entry 4)

Yellow powder, IR (KBr): 1,695, 2,970, 3,080, 3,320 cm^{-1}. ^1H NMR ($CDCl_3$, 500 MHz): δ (ppm) 1.28 (6H, t, $J = 7.0$ Hz, $2CH_3$), 2.40 (6H, s, $2CH_3$), 4.15 (4H, m, $2OCH_2$), 5.12 (1H, s, CH), 5.85 (1H, s, NH), 7.44 (1H, t, $J = 7.5$ Hz, CH arom), 7.66 (1H, d, $J = 7.5$ Hz, CH arom), 8.03 (1H, d, $J = 7.6$ Hz, CH arom), 8.16 (1H, s, CH

Table 5 Synthesis of 1,4-dihydropyridines using the glycerin/[Fe(III)(salen)]Cl catalytic system

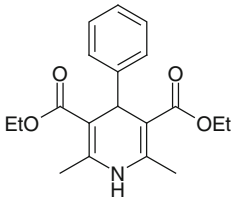
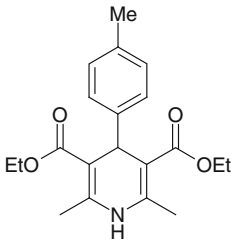
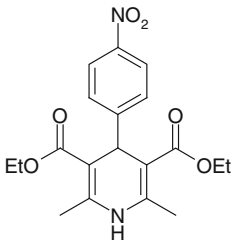
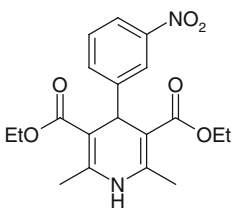
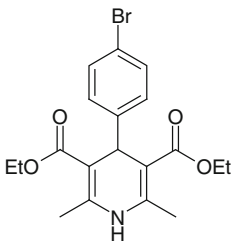
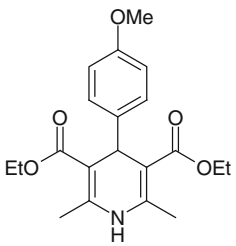
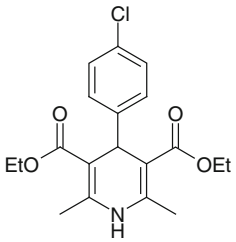
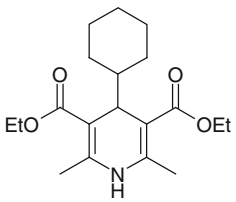
Entry	Product	Yield (%)	MP (°C) observed	MP (°C) reported [Ref.]
1		90	136–138	139–141 [25]
2		88	131–134	135–138 [25]
3		90	128–130	129–131 [25]
4		95	158–161	162–164 [25]
5		87	162–165	160–162 [26]
6		80	162–164	157–159 [25]

Table 5 continued

Entry	Product	Yield (%)	MP (°C) observed	MP (°C) reported [Ref.]
7		93	141–143	144–145 [27]
8		88	213–215	210–212 [26]

arom). ^{13}CNMR ($CDCl_3$, 125 MHz): δ (ppm) 14.7, 20.2, 41.4, 60.2, 104.2, 121.5, 123.7, 129.0, 135.0, 145.2, 148.7, 151.3, 167.3.

Results and discussion

At first, the catalytic ability of 1 mol % of different transition metal salen complexes in glycerol as a solvent was investigated on the reaction of indole with benzaldehyde. When the reaction was performed in glycerin, without salen complexes, incomplete consumption of the starting materials and poor yields were observed. The results are presented in Table 1.

As Table 1 shows, initial screening studies identified [Fe(III)(salen)]Cl as the more efficient catalyst. Encouraged by these results, [Fe(III)(salen)]Cl was chosen as the best catalyst for further work.

In the next step, the influence of the amount of [Fe(III)(salen)]Cl on the reaction time and yield was studied. As shown in Table 2, the best results were obtained with 5 mol % of catalyst. So we inferred that 5 mol % of [Fe(III)(salen)]Cl was sufficient for this reaction.

Several types of aldehydes were examined to establish the scope and generality of the process; therefore, a series of aldehydes having electron-donating as well as electron-withdrawing substituents were used under the optimized reaction conditions.

In all cases, good yields of the expected bis(indolyl)methane derivatives were obtained. The results are summarized in Table 3.

After successfully synthesizing a series of bis(indolyl)-methanes, we turned our attention toward the synthesis of 3,4-dihydropyrimidin-2(1H)-one derivatives under similar conditions (Scheme 1), and then, the reactions of various aldehydes, ethyl acetoacetate and urea were investigated. In all cases, good yields of the expected 3,4-dihydropyrimidin-2(1H)-one were obtained. The results are summarized in Table 4.

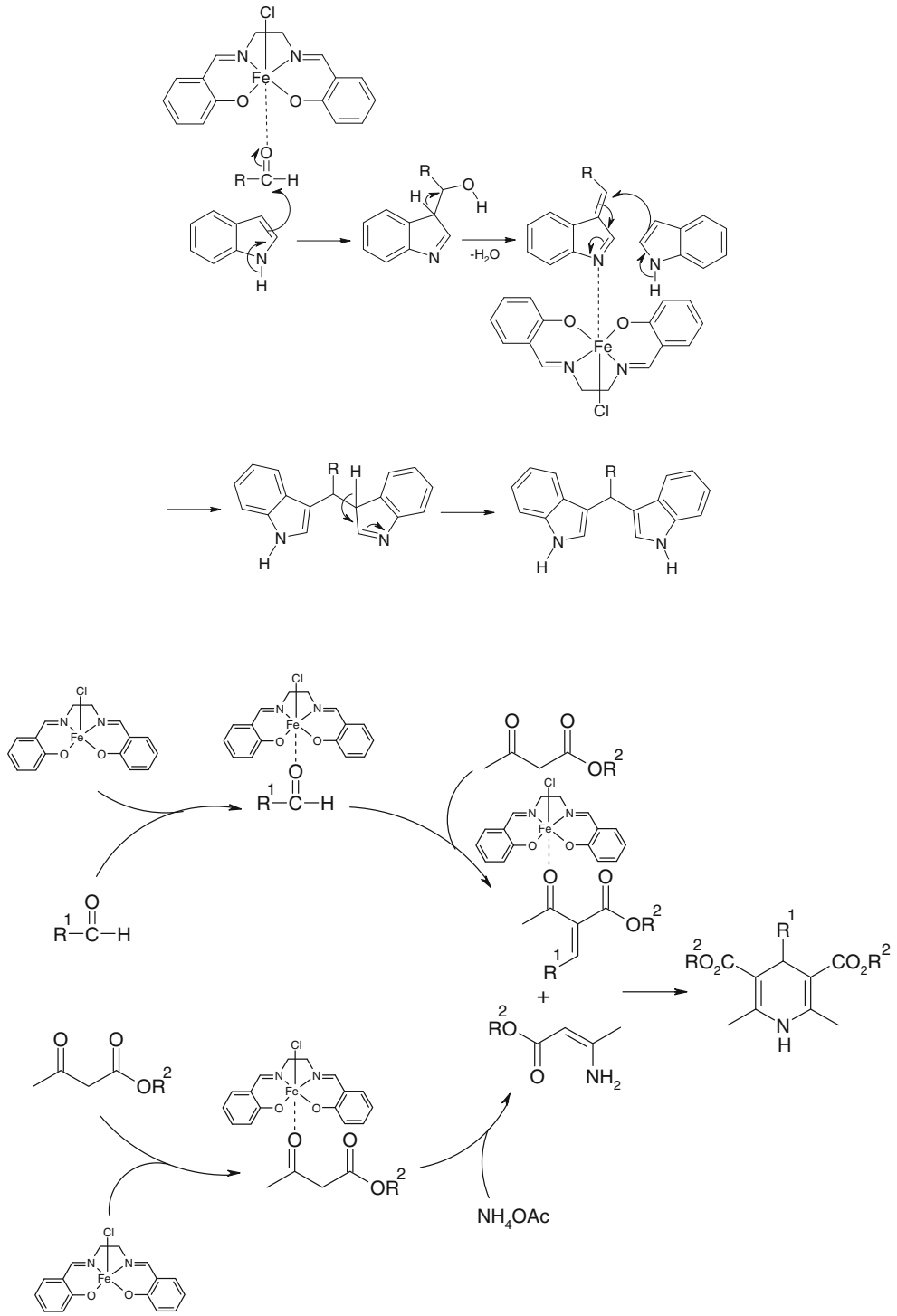
In the next step, we turned our attention toward the synthesis of 1,4-dihydropyridine derivatives in the presence of the glycerin/[Fe(III)(salen)]Cl catalytic system (Scheme 1), and then, the reactions of various aldehydes, ethyl acetoacetate, and ammonium acetate were investigated. In all cases, good yields of the expected 1,4-dihydropyridines were obtained. The results are summarized in Table 5.

A reasonable mechanistic interpretation to explain the formation of the observed bis(indolyl)methanes and 1,4-dihydropyridines might reasonably assume a reaction path as shown in Scheme 2.

In order to show the merits of [Fe(III)(salen)]Cl in glycerin as an efficient catalytic system in comparison with the other catalysts used for similar reactions, some of the previous literature results have been tabulated in Table 6 that shows [Fe(III)(salen)]Cl/glycerin is an effective catalyst and solvent system.

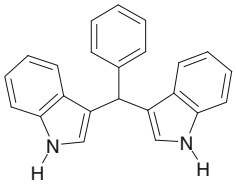
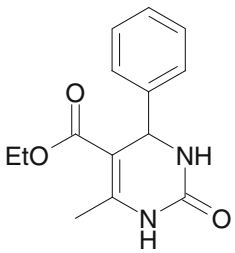
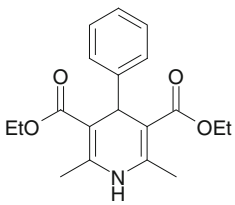
Conclusion

In conclusion, an efficient and green procedure has been established for the synthesis of bis(indolyl)methanes,



Scheme 2 A reasonable mechanism for [Fe(III)(salen)]Cl-catalyzed synthesis of bis(indolyl)methanes and 1,4-dihydropyridines

Table 6 Comparison [Fe(III)(salen)]Cl/glycerin catalytic system with the literatures

Entry	Product	Catalyst	Catalyst (mol %)	Solvent	Condition	Time (min)	Yield (%) [Ref.]
1		$ZrOCl_2{\cdot}8H_2O$	5	Solvent-free	50 °C	40	84 [28]
		$Sb_2(SO_4)_3$	5	CH_3OH	RT	90	96 [29]
		[Fe(III)(salen)]Cl	5	Glycerin	MW	4	95
2		$FeCl_3{\cdot}H_2O$	60	EtOH	Reflux	240	93.8 [16]
		$Y(NO_3)_3{\cdot}6H_2O$	5	Solvent-free	70 °C	20	97 [30]
		[Fe(III)(salen)]Cl	5	Glycerin	MW	7	94
3		PPh_3	20	EtOH	Reflux	300	72 [31]
		$[Fe(CF_3CO_2)_3]$	5	Solvent-free	70 °C	30	90 [32]
		[Fe(III)(salen)]Cl	5	Glycerin	MW	5	90

3,4-dihydropyrimidin-2(1H)-ones, and 1,4-dihydropyridines. This method has several advantages, such as high yields, very short reaction time, efficiency, generality, the use of cheap and non-toxic solvent and catalyst, and simplicity in operation.

Acknowledgments The author gratefully acknowledges the financial support from the Research Council of University of Jiroft.

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