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FeF_3 as a novel catalyst for the synthesis of polyhydroquinoline derivatives via unsymmetrical Hantzsch reaction

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ABSTRACT

A facile and highly efficient one-pot synthesis of polyhydroquinoline derivatives is reported via four-component condensation reaction of aldehydes, β-keto compounds, active methylene compounds and ammonium acetate in the presence of FeF_3 as a catalyst in ethanol at 75–80 °C. The method offers several advantages including high yields, short reaction time, simple work-up procedure and catalyst reusability for several runs. The higher catalytic activity of FeF_3 ascribed due to its high acidity, thermal stability and water tolerance. The superiority of use of FeF_3 to the current process is compared with other Lewis acids, Fe-salts, fluoride sources and insights of the origin of the efficiency are discussed.

1. Introduction

In recent years, much attention has been devoted to the synthesis of polyhydroquinoline compounds due to their diverse therapeutic and pharmacological properties, such as vasodilator, antitumor, bronchodilator, antiartherosclerotic, geroprotective and hepatoprotective activity [1,2]. Particularly, 4-substituteted 1,4-dihydropyridines (1,4-DHPs) are well known as Ca^{2+} channel blockers and have emerged as one of the most important class of drugs for the treatment of cardiovascular diseases [3]. Despite their importance from a pharmacological, industrial and synthetic point of view, comparatively very few methods for their preparation have been reported. Generally, 1,4-DHPs are synthesized by the Hantszch condensation method, which involves cyclocondensation of aldehyde, β-ketoester and ammonia either in acetic acid at room temperature or refluxing in alcohol for a long time [3]. However, this method involves long reaction times, harsh reaction conditions and generally gives low yields of the products. Recently much effort has been expended to develop more efficient methods for the preparation of polyhydroquinoline derivatives such as using solar thermal energy [4], ionic liquid [5], TMSCl–NaI [6], metal triflates [7], grinding [8], Hy-Zeolite [9], montmorillonite K-10 [10], cerium(IV) ammonium nitrate [11], $HClO_4$–SiO_2 [12], molecular iodine [13], PTSA [14], L-proline and derivatives [15], nickel nano particle [16], polymers [17], Baker's yeast [18], glycine [19] and hafnium(IV) bis(perfluorooctanesulfonyl)imide complex in fluorous media [20]. Most of these processes, however, suffer from drawbacks such as unsatisfactory yields, high temperatures, long reaction times and the use of stoichiometric and/or relatively expensive reagents. Moreover, after completion of the reaction, the excess Lewis acids/catalyst are destroyed in the aqueous quench, liberating large amounts of harmful mixtures containing metal ions and organic wastes that are detrimental to our delicate ecosystem [4–20]. Furthermore, the use of soluble metal catalysts in these systems often necessitates a tedious catalyst separation step. Consequently, there is a need for a greater catalytically efficient method for these transformations which might work under mild and more economical and environmental benign conditions. For reasons of safety and health hazards especially in large-scale preparation of polyhydroquinoline derivatives an alternative method was sought and we found that use of FeF_3 led to better selectivity, highest yield, ease of catalyst recovery and reuse.

The use of iron as a catalyst has significant practical advantages since it is inexpensive and non toxic. In particular, FeF_3 is the most widely known fluoride of iron. It is white in color and the crystals have a rhombic structure. The most important industrial application of the FeF_3 is in the manufacture of Fe–Co–Nd magnets [21a], hydro-cracking [21b], preparation of perfluoroacyl fluorides [21c], hydrorefining of lubricating oils [21d], fluorinating agent [21e], pin-hole prevention in cast iron [21f], for xenon-fluorine com-

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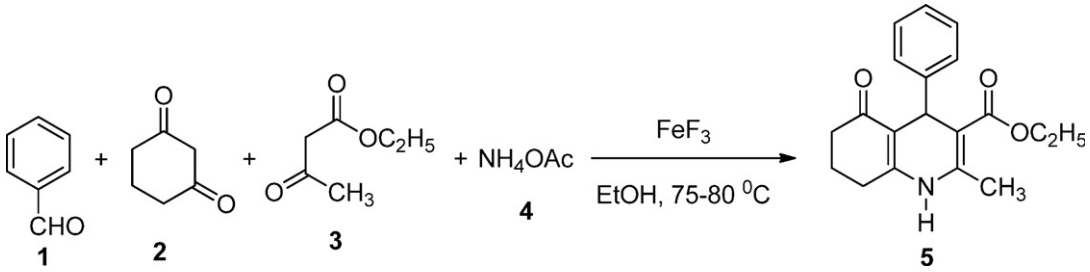


Scheme 1. Synthesis of polyhydroquinoline derivative from benzaldehyde, dimedone, ethyl acetoacetate and ammonium acetate in the presence of FeF_3 catalyst.

pounds [21g], and as a catalyst for aromatization, dealkylation, polymerization and conversion of vinylidene chloride to the fluoride [21h]. The chemistry of FeF_3 in organic synthesis has recently received increasing attention over its companion reagents like $FeCl_3$, $FeBr_3$, and FeI_3 owing to its stability in water and air actively utilized as a catalyst for various types of organic syntheses [22]. FeF_3 has been utilized as an effective catalyst for bis-indolylmethanes [22a], chemoselective addition of cyanotrimethylsilane to aldehydes [21b], cross-coupling reactions [22c and d] sulenylation and selenation reaction [22d and e], etc.

In addition the growing concern for the influence of the chemical reagents on the environment as well as on human body, recovery and reusability of the chemical reagents has attracted the attention of synthetic organic chemists. More importantly pharmaceutical industry has given more importance towards recovery and reuse of chemical reagents to reduce the cost of a product as well as the environmental burden. As part of continuing effort in our laboratory towards the development of new methods in organic synthesis, we became interested in the possibility of developing a one-pot synthesis of polyhydroquinoline derivatives catalyzed by FeF_3. We present our results about a FeF_3 catalyzed four-component Hantzsch reaction in ethanol.

2. Results and discussions

We report herein an efficient one-pot synthesis of polyhydroquinoline derivatives from four components coupling of aromatic aldehydes, alkyl acetoacetate, β-keto compounds and ammonium acetate in the presence of a catalytic amount of FeF_3 in ethanol at 75–80 °C in excellent yield in short reaction time 1 h.

In an initial endeavor (Scheme 1), 1.0 equiv each of benzaldehyde **1**, dimedone **2**, ethyl acetoacetate **3** and ammonium acetate **4** were heated under reflux in ethanol without any catalyst. No reaction was observed even after 12 h, only dimedone/aldehyde adduct was isolated. However, addition of a catalytic amount of FeF_3 to this mixture has rapidly induced four component condensations in 1 h (Table 1). Hantzsch condensation of dimedone, benzaldehyde, ethylacetoacetate and ammonium acetate in the presence of catalytic amount of FeF_3 (5 mol%) at 75–80 °C in ethanol results in the formation of ethyl 2-methyl-5-oxo-4-phenyl-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (Table 1, entry 8) in 92% yield. To the best of our knowledge this is the first report for the polyhydroquinoline synthesis using FeF_3 as a homogeneous catalyst. We have not observed any fluorination while FeF_3 is used in the one-pot synthesis. In an attempt to improve the catalytic activity of the reactions we have examined other Lewis acids and iron salts such as $FeBr_3$, $FeCl_3$, FeI_3, $Fe_2(NO_3).9H_2O$, $Fe(SO_4)_3{\cdot}nH_2O$ for the synthesis of polyhydroquinolines (Table 1, entries 4, 5, 11, 12). It was found that conventional Lewis acids such as $AlCl_3$ (Table 1, entry 2), $ZnCl_2$ (Table 1, entry 3), and $FeCl_3$ (Table 1, entry 5) showed poor effect to the yield and reaction time. This probably due to their poor water tolerance of the reagents under the reaction condition we studied. Even large amount of catalysts was used, the results were still unsatisfactory and many side reactions were observed. When 5 mol% of $FeBr_3$, $FeCl_3$, FeI_3, $Fe_2(NO_3){\cdot}9H_2O$ and $Fe(SO_4)_3{\cdot}nH_2O$ (Table 1, entries 4, 5, 11, 12) was used for the synthesis of polyhydroquinolines, only 45, 60, 50 and 0% yield of the corresponding product were obtained. FeF_3 emerged as the best catalyst in terms of conversion and reaction rates (Table 1, entries 6–10). While adding 100 mol% of FeF_3 into the system under similar reaction conditions, the speed of the reaction was obviously accelerated, but the yield was not yet satisfactory (Table 1, entry 6). Further studies showed that decreasing the amount of FeF_3 improve the reaction significantly. Inspired by the results, we have changed the amount from 100 mol% to 10 mol% and 5 mol%, finding that 5 mol% of FeF_3 was good enough (Table 1, entry 8) to obtained very high yield of the product in shorter reaction time.

FeF_3 showed higher catalytic activity than other Fe-catalyst due to the high acidity, high thermal stability and high water tolerance. The acidity of 5 mol% FeF_3 measured in water and found the pH ~2.7. The catalytic process of FeF_3 using different solvents was also investigated. The reaction of benzaldehyde **1**, dimedone **2**, ethyl acetoacetate **3** and ammonium acetate **4** was chosen as a model reaction for comparison of solvents, the results are shown in Table

Table 1
The reaction of benzaldehyde, ethylacetoacetate, dimedone and ammonium acetate: effect of catalyst.[a]

Entry	Catalyst	Amount of catalyst (mol%)	Time (h)	Yield[b] (%)
1	None	–	12	None[c]
2	$AlCl_3$	5	24	40
3	$ZnCl_2$	5	24	36
4	$FeBr_3$	5	24	45
5	$FeCl_3$	5	24	60
6	FeF_3	100	1	80
7	FeF_3[c]	10	1	90
8	FeF_3[c]	5	1	92
9	FeF_3	2.5	2	75
10	FeI_3	5	24	50
11	$Fe_2(NO_3){\cdot}9H_2O$	5	24	None
12	$Fe(SO_4)_3{\cdot}nH_2O$	5		None

[a] All reactions were carried out in ethanol at 75–80 °C.
[b] Isolated yield.
[c] Major product isolated was dimedone/aldehyde adduct.

Table 2
The reaction of benzaldehyde, ethylacetoacetate, dimedone and ammonium acetate: effect of solvents and temperature.[a]

Entry	Solvent	Temp. (°C)	Time (h)	Yield (%)[b]
1	Ethanol	80	1	90
2	Methanol	60	4	65
3	Acetonitrile	80	3	85
4	H_2O	Reflux	3	43
5	Dichloromethane	Reflux	5	24
6	Toluene	Reflux	4	55
7	Cyclohexane	Reflux	4	40

[a] All reactions were carried out using 5 mol% of FeF_3.
[b] Isolated yield.

Table 3
The reaction of benzaldehyde, ethylacetoacetate, dimedone and ammonium acetate: screening of fluoride sources and temperature.[a]

Entry	Catalyst (Fluoride source)	Temp. (°C)	Time (h)	Yield (%)[b]
1	CaF_2	80	12	20
2	CsF	80	12	30
3	FeF_3	80	1	92
4	KF	80	12	35
5	NH_4F	80	12	15
6	TBAF	Reflux	12	30

[a] Conditions: benzaldehyde (1 mmol), ethylacetoacetate (1 mmol), dimedone (1 mmol), and ammonium acetate (1 mmol), catalyst (5 mol%), ethanol (5 mL), heating.
[b] Isolated yield.

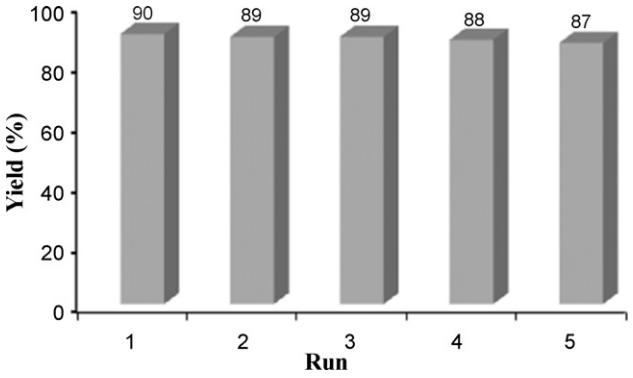


Fig. 2. Recycling and reuse of FeF_3 for polyhydroquinoline synthesis.

2. In each case, the reactants were mixed together with 5 mol% of FeF_3 stirred with 5 mL solvent. The polar solvents such as ethanol and acetonitrile were found to be better solvents than the non-polar solvents like toluene, dichloromethane, cyclohexane, etc. Obviously, the results could be attributed to the better solubility of the catalyst and the reagents in the polar solvents. Among the two solvents viz. ethanol and acetonitrile, ethanol stands out as the solvent of choice, with its fast conversion, high yield and low toxicity.

We have further compared the catalytic process of FeF_3 by screening other fluoride sources under the same reaction conditions (Table 3), it was found that FeF_3 is the most reactive than other fluoride sources (Table 3, entry 3). The corresponding product was obtained in low yield in the presence of CaF_2, CsF, KF, NH_4F and TBAF (Table 3, entries 1, 2, 4–6), respectively.

The powder X-ray diffraction pattern of FeF_3, recovered FeF_3 (after 5th run) and $FeCl_3$ (Fig. 1) were recorded on a Rigaku D/Max-2200 model diffractometer equipped with horizontal goniometer in $\theta/2\theta$ geometry. The Copper Kα (λ = 1.5418 Å) radiation was used and the sample was scanned between 3–45 degrees 2θ. The sharp peaks in the diffractogram indicate that the FeF_3 and recovered FeF_3 (after 5th run) are crystalline in nature. $FeCl_3$ showing absence of any sharp peak in XRD pattern confirms the amorphous nature.

After completion of the reaction (TLC), the product was extracted with ethyl acetate and the catalyst was recovered from the aqueous layer. FeF_3 is more soluble in water than that in organic solvents. The catalyst was recovered almost quantitatively from the aqueous layer, which was subsequently reused for several runs. As indicated in Fig. 2, it showed almost no loss of activity after five successive runs. The yields obtained were from 90, 89, 89, 88 and 87% in the first, second, third, fourth and fifth run respectively. In view of environment friendly methodologies, recovery and reuse of the catalyst is highly preferable. More importantly pharmaceutical industry has given more importance towards recovery and reuse of chemical reagents to reduce the cost of a product as well as the environmental burden.

Thus, we selected the optimized reaction condition to examine the universality of this catalyst's application with different electron rich and deficient substrates. Various substituted aromatic aldehydes, β-keto esters and dimedone undergo the Hantzsch reaction in the presence of catalytic amount of FeF_3 (5 mol%) in ethanol at 75–80 °C (Scheme 2). The results of this study are summarized in Table 4. It was indicated that both electron deficient (Table 4, entries 1, 2, 8, 10–13, 15, 16) and electron rich aromatic aldehydes (Table 4, entries 4–7, 9, 14) worked well, giving high yields of the product in shorter reaction time. Next we investigated the effect of substitution in 1,3-cyclohexadione (dimedone) system. Aromatic aldehydes such as 3-nitro benzaldehyde (Table 4, entry 1), 4-chloro benzaldehyde (Table 4, entry 2), 4-nitro benzaldehyde (Table 4, entry 3), 3,4-dimethoxy benzaldehyde (Table 4, entry 5), 4-trifluoro benzaldehyde (Table 4, entry 6), 3,4-dihydroxy benzaldehyde (Table 4, entry 7), etc., reacts with 5,5-dimethyl-1,3-cyclohexadione, ethyl acetoacetate and ammonium acetate in the presence of FeF_3 (5 mol%) in ethanol at 75–80 °C to afford the products in excellent yields. Interestingly, 1,3-cyclohexadione (dimedone) reacts with aromatic aldehyde (Table 4, entries 15 and 16), ethyl acetoacetate

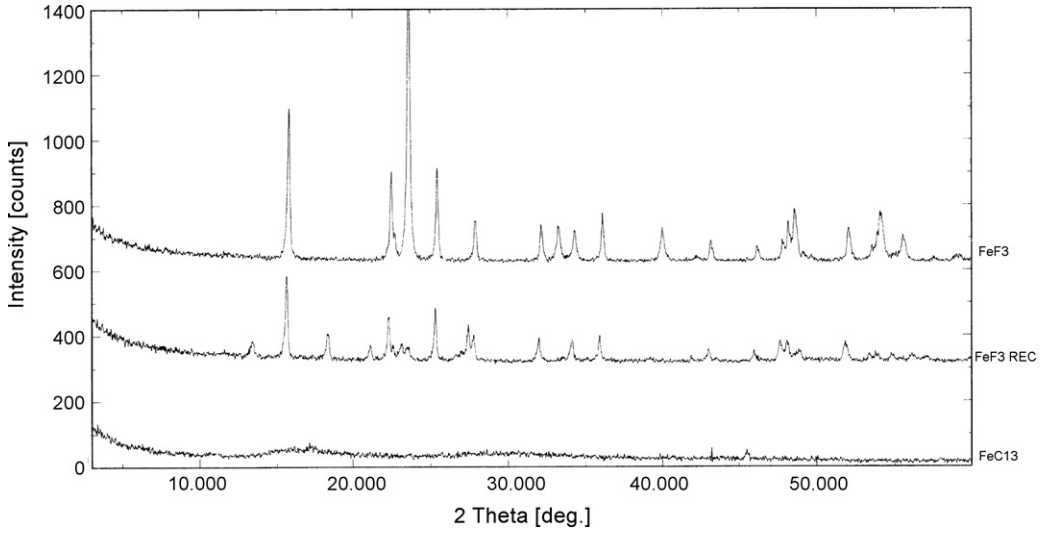
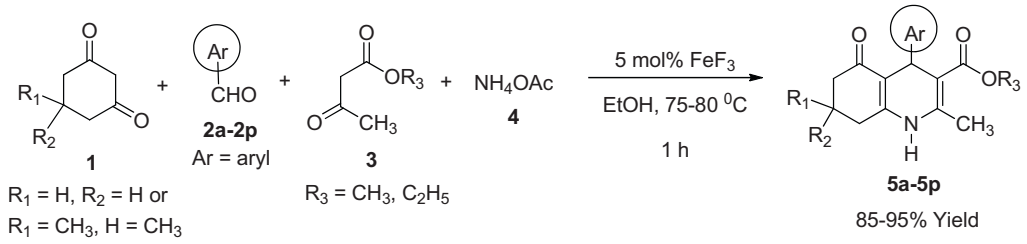


Fig. 1. XRD profile of FeF_3, recovered FeF_3 (after 5th run) and $FeCl_3$.



Scheme 2. Synthesis of polyhydroquinoline derivative from aldehydes, alkylacetoacetate, β-keto compounds and ammonium acetate in the presence of a reusable FeF_3 (5 mol%) catalyst.

Table 4
FeF_3 catalyzed synthesis of polyhydroquinoline derivatives.[a]

Entry	R	R_1	R_2	R_3	Time (h)	Product	Yield[b] (%)	Mp (°C)	
								Observed	Reported
1	3-$NO_2C_6H_4$	CH_3	CH_3	C_2H_5	1.0	**5a**	92	176–177	177–178 [12]
2	4-ClC_6H_4	CH_3	CH_3	C_2H_5	1.0	**5b**	92[c]	233–235	232–234 [13]
3	4-$NO_2C_6H_4$	CH_3	CH_3	C_2H_5	1.0	**5c**	89	242–243	242–244 [12]
4	4-CNC_6H_4	CH_3	CH_3	C_2H_5	1.0	**5d**	95	140–142	–
5	3,4-$OCH_3C_6H_3$	CH_3	CH_3	C_2H_5	1.0	**5e**	95	204–206	198–199 [12]
6	4-$CF_3C_6H_4$	CH_3	CH_3	C_2H_5	1.0	**5f**	91	188–190	–
7	3,4-OHC_6H_3	CH_3	CH_3	C_2H_5	1.0	**5g**	92	216–218	–
8	5-OH_2–$NO_2C_6H_3$	CH_3	CH_3	C_2H_5	1.0	**5h**	90	167–169	–
9	4-$OCH_3C_6H_4$	CH_3	CH_3	C_2H_5	1.0	**5i**	95	250–252	256–257 [13]
10	2-Cl_4–$CF_3C_6H_3$	CH_3	CH_3	C_2H_5	1.0	**5j**	89	104–106	–
11	4-$NO_2C_6H_4$	CH_3	CH_3	CH_3	1.0	**5k**	88	250–252	252–254 [20]
12	4-ClC_6H_4	CH_3	CH_3	CH_3	1.0	**5l**	90	220–22	221–223 [13]
13	4-CNC_6H_4	CH_3	CH_3	CH_3	1.0	**5m**	94	220–222	–
14	3,4-$OCH_3C_6H_3$	CH_3	CH_3	CH_3	1.0	**5n**	94	209–211	–
15	3-$NO_2C_6H_4$	H	H	C_2H_5	1.0	**5o**	88	204–206	198–200
16	2-Cl_4–$CF_3C_6H_3$	H	H	C_2H_5	1.5	**5p**	85	92–94	–

[a] All reactions were carried out in ethanol at 75–80 °C using 5 mol% FeF_3.
[b] Yields refer to isolated pure products.
[c] Catalyst has been reused for 4 times.

and ammonium acetate in the presence of FeF_3 (5 mol%) with little lower yield. Aromatic aldehydes (Table 4, entries 11–14) reacts with 5,5-dimethyl-1,3-cyclohexadione, methyl acetoacetate and ammonium acetate in the presence of FeF_3 (5 mol%) in shorter reaction time with high yields. As seen from Table 4 the methodology tolerates most of the substrates.

3. Conclusions

In conclusion, we have developed an easy and efficient method to prepare a variety of polyhydroquinoline derivatives from the reaction of different aryl aldehydes, β-keto compounds, including 1,3-cyclohexanedione or 5,5-dimethyl-1,3-cyclohexanedione, alkyl acetoacetate and ammonium acetate in the presence of catalytic amount of FeF_3 at 75–80 °C. The higher catalytic activity of FeF_3 ascribed due to its high acidity, thermal stability and water tolerance. Also the superiority of use of FeF_3 towards the synthesis of polyhydroquinoline is compared with other Lewis acids, Fe-salts, fluoride sources and insights of the origin of the efficiency are discussed. The mildness of the conversion, experimental simplicity, compatibility with various functional groups, high yields of the reaction product, shorter reaction times and the easy workup procedure, etc., makes this procedure attractive to synthesize a variety of these derivatives. Moreover, FeF_3 can be recovered and reused for several times, which makes it a useful and attractive for synthesis of these classes of compounds for economic viability and greater selectivity. Based on all the results hitherto obtained it may be stated that FeF_3 is an important addition to the realm of Lewis acid to prepare verities of polyhydroquinoline derivatives. Further studies of utilization of FeF_3 in different organic syntheses are in progress in our laboratory.

4. Experimental

4.1. General

All the reagents used are from commercial sources and used as such. Unless stated otherwise, reactions were monitored by thin layer chromatography (TLC) on silica gel plates (60 F_{254}), visualizing with ultraviolet light or iodine spray. Melting points are recorded in Buchi Mp apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ and DMSO-d_6 solution using 400 and 200 MHz spectrometers respectively. Proton chemical shifts (δ) are relative to tetramethylsilane (TMS, δ 0.0) as internal standard and expressed in parts per million. Spin multiplicities are given as s (singlet), d (doublet), t (triplet), and m (multiplet) as well as b (broad). Coupling constants (J) are given in Hertz. Infrared spectra were recorded on a Perkin Elmer FTIR spectrometer (Spectrum one). Mass spectra were recorded with PE Sciex model API 3000 instrument. HRMS spectra were recorded with Waters LCT Premier XE (Micro mass Qa-TOF) instrument. The X-ray powder diffraction pattern recorded on a Rigaku D/Max-2200 model diffractometer.

4.2. Typical procedure for the synthesis of polyhydroquinoline derivatives 5

In a typical experimental procedure, a mixture of aldehyde **1** (1 mmol), dimedone **2** (1 mmol), alkyl acetoacetate **3** (1 mmol),

ammonium acetate (1 mmol), FeF_3 (5 mol%) and ethanol (5 mL) was placed in a 25 mL round bottomed flask equipped with a cold water condenser and calcium chloride guard tube. The reaction mixture was slowly heated to 75–80 °C. Typically the reaction completed within one hour. After completion of the reaction (TLC), the mixture was cooled and 15 mL of ethyl acetate and 5 mL of water was added to the flask. The ethyl acetate layer was separated and washed with cold water (20 mL). The organic layer was then dried over anhydrous sodium sulfate, filtered and the solvent distilled under vacuum to afford the crude product. The crude product was finally recrystallized from ethanol to afford the pure products **5a**–**5p**. The aqueous layer containing the catalyst (FeF_3) was evaporated under reduced pressure to give a solid (slight pale pink in color). The IR spectrum of the recovered catalyst was identical to that of the commercially available catalyst (Aldrich), which was further reused for the next reaction without loss in activity. The catalyst has been recovered and reused five times (reaction yields: 90, 89, 89, 88% and 87%).

Ethyl 2,7,7-trimethyl-4-(3-nitrophenyl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (compound **5a***).* A pale yellow solid; IR (KBr) 3289, 2959, 1702, 1607, 1528, 1487, 1349, 1217, 1073, 683 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ 0.83 (s, 3H), 1.01 (s, 3H), 1.13 (t, J = 7.2 Hz, 3H), 2.00 (d, J = 16.4 Hz, 1H), 2.21 (d, J = 16.0 Hz, 1H), 2.38 (m, 4H), 2.48 (d, J = 17.2 Hz, 1H), 3.98 (q, J = 7.2 Hz, 2H), 4.96 (s, 1H), 7.62–7.50 (m, 2H), 7.98 (m, 2H), 9.24 (s, 1H, NH). ^{13}C NMR (50 MHz, DMSO-d_6) δ 14.0, 18.3, 26.3, 29.0, 32.2, 36.4, 50.0, 59.2, 102.6, 109.2, 120.8, 121.9, 129.3, 134.2, 146.0, 147.3, 149.6, 150.3, 166.3, 194.2. MS (ES) m/z 385.10 (M+1). HRMS (ESI) calculated for $C_{21}H_{25}N_2O_5$ $(M+H)^+$ 385.1763 found 385.1769.

Ethyl 4-(4-chlorophenyl)-2,7,7-trimethyl-5-oxo-1,4,5, 6,7,8-hexahydroquinoline-3-carboxylate (compound **5b***).* A off-white solid; IR (KBr) 3275, 2958, 1706, 1604, 1488, 1381, 1214, 1214, 1071, 844, 534 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ 0.83 (s, 3H), 1.00 (s, 3H), 1.13 (t, J = 7.2 Hz, 3H), 1.99 (d, J = 16.0 Hz, 1H), 2.19 (d, J = 16.0 Hz, 1H), 2.25–2.28 (m, 4H), 2.43 (d, J = 17.2 Hz, 1H), 3.99 (q, J = 7.2 Hz, 2H), 4.83 (s, 1H), 7.16 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 9.12 (s, 1H, NH). ^{13}C NMR (50 MHz, DMSO-d_6) δ 4.1, 18.3, 26.4, 29.0, 32.1, 35.6, 50.1, 59.0, 103.0, 109.6, 127.6, 129.2, 130.2, 145.3, 146.5, 149.5, 166.5, 194.1. MS (ES) m/z 374.00 (M+1). HRMS (ESI) calculated for $C_{21}H_{25}NO_3Cl$ $(M+H)^+$ 374.1763 found 374.1756

Ethyl 2,7,7-trimethyl-4-(4-nitrophenyl)-5-oxo-1,4,5, 6,7,8-hexahydroquinoline-3-carboxylate (compound **5c***).* A yellow solid; IR (KBr) 3295, 2959, 1699, 1605, 1517, 1482, 1345, 1218, 1073, 836, 694 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ 0.82 (s, 3H), 1.00 (s, 3H), 1.12 (t, J = 7.2 Hz, 3H), 1.99 (d, J = 16.0 Hz, 1H), 2.20 (d, J = 16.0 Hz, 1H), 2.27–2.31 (m, 4H), 2.45 (d, J = 16.4 Hz, 1H), 3.98 (q, J = 7.2 Hz, 2H), 4.96 (s, 1H), 7.42 (d, J = 8.8 Hz, 2H), 8.10 (d, J = 8.8 Hz, 2H), 9.23 (s, 1H, NH). ^{13}C NMR (50 MHz, DMSO-d_6) δ 14.0, 18.3, 26.4, 29.0, 32.1, 36.6, 50.0, 59.2, 102.3, 109.0, 123.0, 128.7, 145.6, 146.0, 150.0, 154.9, 166.3, 194.1. MS (ES) m/z 385.10 (M+1). HRMS (ESI) calculated for $C_{21}H_{25}N_2O_5$ $(M+H)^+$ 385.1763 found 385.1756.

Ethyl 4-(4-cyanophenyl)-2,7,7-trimethyl-5-oxo-1,4,5, 6,7,8-hexahydroquinoline-3-carboxylate (compound **5d***).* A ash solid; IR (KBr) 3296, 2959, 2226, 1697, 1606, 1488, 1379, 1219, 1074, 845, 555 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ 0.81 (s, 3H), 1.00 (s, 3H), 1.12 (t, J = 7.2 Hz, 3H), 1.99 (d, J = 16.4 Hz, 1H), 2.19 (d, J = 16.4 Hz, 1H), 2.30–2.26 (m, 4H), 2.44 (d, J = 17.2 Hz, 1H), 3.98 (q, J = 7.2 Hz, 2H), 4.90 (s, 1H), 7.34 (d, J = 8.0 Hz, 2H), 7.68 (d, J = 8.0 Hz, 2H), 9.19 (s, 1H, NH). ^{13}C NMR (50 MHz, DMSO-d_6) δ 14.1, 18.3, 26.4, 29.0, 32.1, 36.7, 50.1, 59.1, 102.4, 108.5, 109.1, 119.0, 128.5, 131.8, 146.0, 149.9, 152.8, 166.3, 194.1. MS (ES) m/z 365.10 (M+1). HRMS (ESI) calculated for $C_{22}H_{25}N_2O_3$ $(M+H)^+$ 365.1865 found 365.1852.

Ethyl 4-(3,4-dimethoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (compound **5e***).* A white solid; IR (KBr) 3279, 2957, 1695, 1604, 1491, 1379, 1216, 1139, 1031, 788, 730 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ 0.88 (s, 3H), 1.01 (s, 3H), 1.17 (t, J = 7.2 Hz, 3H), 2.00 (d, J = 16.4 Hz, 1H), 2.19 (d, J = 16.4 Hz, 1H), 2.30–2.26 (m, 4H), 2.44 (d, J = 17.2 Hz, 1H), 3.65 (s, 3H, OCH_3), 3.66 (s, 3H, OCH_3), 4.02 (q, J = 7.2 Hz, 2H), 4.79 (s, 1H), 6.63 (dd, J = 2.0 & 8.4 Hz 1H), 6.77–6.74 (m, 2H), 9.02 (s, 1H, NH). ^{13}C NMR (50 MHz, DMSO-d_6) δ 14.2, 18.2, 26.4, 29.2, 32.1, 35.1, 50.3, 55.3, 55.4, 59.0, 103.8, 110.0, 111.4, 111.7, 119.2, 140.4, 144.5, 146.9, 147.9, 149.3, 166.8, 194.2. MS (ES) m/z 400.50 (M+1). HRMS (ESI) calculated for $C_{23}H_{30}NO_5$ $(M+H)^+$ 400.2124 found 400.2127.

Ethyl 2,7,7-trimethyl-5-oxo-4-(4-(trifluoromethyl) phenyl)-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (compound **5f***).* A yellow solid; IR (KBr) 3281, 2938, 1710, 1603, 1496, 1382, 1324, 1216, 1136, 1065, 862, 598, 531 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ 0.83 (s, 3H), 1.00 (s, 3H), 1.13 (t, J = 7.2 Hz, 3H), 2.00 (d, J = 16.0 Hz, 1H), 2.19 (d, J = 16.4 Hz, 1H), 2.32 (m, 4H), 2.45 (d, J = 16.4 Hz, 1H), 3.99 (q, J = 7.2 Hz, 2H), 4.93 (s, 1H), 7.37 (d, J = 8.0 Hz, 2H), 7.57 (d, J = 7.6 Hz, 2H), 9.17 (s, 1H, NH). ^{13}C NMR (50 MHz, DMSO-d_6) δ 14.1, 18.3, 26.5, 29.0, 32.1, 36.3, 50.1, 59.1, 102.8, 109.3, 124.6, 124.7, 128.2, 145.7, 149.8, 151.8, 166.6, 194.1. MS (ES) m/z 408.50 (M+1). HRMS (ESI) calculated for $C_{22}H_{25}NO_3F_3$ $(M+H)^+$ 408.1787 found 408.1786.

Ethyl 4-(3,4-dihydroxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (compound **5g***).* A brown solid; IR (KBr) 3504, 3276, 2960, 1681, 1603, 1487, 1380, 1286, 1217, 1074, 814, 659 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ 0.87 (s, 3H), 1.00 (s, 3H), 1.16 (t, J = 7.2 Hz, 3H), 1.99 (d, J = 16.0 Hz, 1H), 2.16 (d, J = 16.0 Hz, 1H), 2.27 (m, 4H), 2.40 (d, J = 17.2 Hz, 1H), 4.00 (q, J = 7.2 Hz, 2H), 4.68 (s, 1H), 6.39 (dd, J = 2.0 and 8.4 Hz, 1H), 6.51 (d, J = 8.0 Hz, 1H), 6.57 (d, J = 2.0 Hz, 1H), 8.45 (s, 1H, OH), 8.56 (s, 1H, OH), 8.94 (s, 1H, NH). ^{13}C NMR (100 MHz, DMSO-d_6) δ 14.2, 18.0, 26.6, 29.2, 32.1, 34.9, 50.4, 59.0, 104.1, 110.3, 114.8, 115.2, 118.1, 138.6, 143.1, 144.1, 144.6, 149.0, 167.1, 194.3. MS (ES) m/z 372.60 (M+1). HRMS (ESI) calculated for $C_{21}H_{26}NO_5$ $(M+H)^+$ 372.1811 found 372.1817.

Ethyl 4-(5-hydroxy-2-nitrophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (compound **5h***).* A yellow solid; IR (KBr) 3486, 3310, 2956, 1698, 1607, 1494, 1280, 1218, 1066, 856, 613 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ 0.79 (s, 3H), 0.98 (s, 3H), 1.00 (t, J = 7.2 Hz, 3H), 1.92 (d, J = 15.6 Hz, 1H), 2.13 (d, J = 15.6 Hz, 1H), 2.25 (d, J = 16.8 Hz, 1H), 2.29 (s, 3H), 2.42 (d, J = 16.8 Hz, 1H), 3.94 (q, J = 7.2 Hz, 2H), 5.77 (s, 1H), 6.62 (dd, J = 2.4 & 8.8 Hz, 1H), 6.75 (d, J = 2.4 Hz, 1H), 7.69 (d, J = 8.8 Hz, 1H), 9.06 (s, 1H, NH), 10.37 (s, 1H, OH). ^{13}C NMR (100 MHz, DMSO-d_6) δ 13.8, 18.2, 26.3, 28.8, 31.7, 32.0, 50.1, 59.0, 103.5, 100.3, 113.3, 166.5, 126.3, 140.1, 145.4, 145.8, 149.4, 161.5, 166.7, 193.9. MS (ES) m/z 401.50 (M+1). HRMS (ESI) calculated for $C_{21}H_{25}N_2O_6$ $(M+H)^+$ 401.1713 found 401.1721.

Ethyl 4-(4-methoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4, 5,6,7,8-hexahydroquinoline-3-carboxylate (compound **5i***).* A white solid; IR (KBr) 3279, 2958, 1699, 1605, 1492, 1380, 1214, 1072, 1031, 849, 762, 536 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ 0.85 (s, 3H), 1.00 (s, 3H), 1.15 (t, J = 7.2 Hz, 3H), 1.98 (d, J = 16.0 Hz, 1H), 2.17 (d, J = 16.0 Hz, 1H), 2.29 (m, 4H), 2.43 (d, J = 16.8 Hz, 1H), 3.67 (s, 3H, OCH_3), 3.99 (q, J = 7.2 Hz, 2H), 4.78 (s, 1H), 6.74 (d, J = 8.4 Hz, 2H), 7.05 (d, J = 8.4 Hz, 2H), 9.00 (s, 1H, NH). ^{13}C NMR (100 MHz, DMSO-d_6) δ 14.2, 18.2, 26.5, 29.1, 32.1, 34.9, 50.3, 54.8, 59.0, 103.9, 110.1, 113.1, 128.4, 140.0, 144.6, 149.2, 157.3, 166.9, 194.2, MS (ES) m/z 370.50 (M+1). HRMS (ESI) calculated for $C_{22}H_{28}NO_4$ $(M+H)^+$ 370.2018 found 370.2025.

Ethyl 4-(2-chloro-3-(trifluoromethyl)phenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (compound **5j***).* A white solid; IR (KBr) 3297, 2961, 1701, 1614, 1492, 1380, 1312, 1216, 1133, 803, 735, 597 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ 0.85 (s, 3H), 1.00 (s, 3H), 1.15 (t, J = 7.2 Hz, 3H), 1.98 (d, J = 16.0 Hz, 1H), 2.17 (d, J = 16.0 Hz, 1H), 2.29 (m, 4H), 2.43 (d, J = 16.8 Hz, 1H), 3.99 (q, J = 7.2 Hz, 2H), 5.31 (s, 1H), 7.40 (m, 1H), 7.59 (m, 2H), 9.17 (s, 1H, NH). ^{13}C NMR (50 MHz, DMSO-d_6) δ 13.9, 18.3, 26.4, 29.0,

31.4, 35.0, 50.1, 59.0, 102.9, 109.4, 125.4, 126.0, 126.7, 129.5, 135.3, 145.7, 148.0, 150.0, 166.4, 193.9. MS (ES) m/z 442.40 (M+1). HRMS (ESI) calculated for $C_{22}H_{24}NO_3F_3Cl$ $(M+H)^+$ 442.1397 found 442.1391.

Methyl 2,7,7-trimethyl-4-(4-nitrophenyl)-5-oxo-1,4, 5,6,7,8-hexahydroquinoline-3-carboxylate (compound **5k***).* A pale yellow solid; IR (KBr) 3277, 2959, 1709, 1605, 1491, 1345, 1217, 1075, 866, 833, 533 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ 0.81 (s, 3H), 1.00 (s, 3H), 2.00 (d, J = 16.4 Hz, 1H), 2.21 (d, J = 16.4 Hz, 1H), 2.32 (m, 4H), 2.46 (d, J = 17.2 Hz, 1H), 3.52 (s, 3H, OCH_3), 4.98 (s, 1H), 7.42 (d, J = 8.8 Hz, 2H), 8.10 (d, J = 8.8 Hz, 2H), 9.26 (s, 1H, NH). ^{13}C NMR (50 MHz, DMSO-d_6) δ 18.4, 26.4, 29.0, 32.1, 36.4, 50.0, 50.6, 102.0, 109.0, 123.2, 128.5, 145.6, 146.3, 150.0, 154.7, 166.8, 194.1. MS (ES) m/z 371.50 (M+1). HRMS (ESI) calculated for $C_{20}H_{23}N_2O_5$ $(M+H)^+$ 371.1607 found 371.1616.

Methyl 4-(4-chlorophenyl)-2,7,7-trimethyl-5-oxo-1,4, 5,6,7,8-hexahydroquinoline-3-carboxylate (compound **5l***).* A white solid; IR (KBr) 3288, 2959, 1682, 1606, 1489, 1381, 1226, 1074, 1013, 840, 776, 538 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ 0.82 (s, 3H), 1.00 (s, 3H), 1.99 (d, J = 16.0 Hz, 1H), 2.19 (d, J = 16.0 Hz, 1H), 2.29 (m, 4H), 2.44 (d, J = 17.2 Hz, 1H), 3.52 (s, 3H, OCH_3), 4.85 (s, 1H), 7.15 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 8.4 Hz, 2H), 9.14 (s, 1H, NH). ^{13}C NMR (50 MHz, DMSO-d_6) δ 18.3, 26.4, 29.0, 32.0, 35.4, 50.1, 50.6, 102.7, 109.6, 127.7, 129.1, 130.1, 145.6, 146.3, 149.5, 167.0, 194.1. MS (ES) m/z 360.50 (M+1). HRMS (ESI) calculated for $C_{20}H_{23}NO_3Cl$ $(M+H)^+$ 360.1366 found 360.1373.

Methyl 4-(4-cyanophenyl)-2,7,7-trimethyl-5-oxo-1,4, 5,6,7,8-hexahydroquinoline-3-carboxylate (compound **5m***).* A white solid; IR (KBr) 3276, 2960, 2226, 1708, 1607, 1493, 1379, 1217, 1074, 858, 553 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ 0.80 (s, 3H), 1.00 (s, 3H), 2.00 (d, J = 16.0 Hz, 1H), 2.20 (d, J = 16.0 Hz, 1H), 2.31 (m, 4H), 2.45 (d, J = 17.2 Hz, 1H), 3.51 (s, 3H, OCH_3), 4.92 (s, 1H), 7.33 (d, J = 8.0 Hz, 2H), 7.68 (d, J = 8.0 Hz, 2H), 9.22 (s, 1H, NH). ^{13}C NMR (50 MHz, DMSO-d_6) δ 18.3, 26.4, 29.0, 32.1, 36.4, 50.0, 50.7, 102.1, 108.5, 109.1, 118.9, 128.3, 131.8, 146.2, 149.9, 152.6, 166.8, 194.1. MS (ES) m/z 351.50 (M+1). HRMS (ESI) calculated for $C_{21}H_{23}N_2O_3$ $(M+H)^+$ 351.1709 found 351.1705.

Methyl 4-(3,4-dimethoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (compound **5n***).* A white solid; IR (KBr) 3276, 2945, 1699, 1602, 1492, 1379, 1217, 1137, 1030, 858, 788, 768, 733, 657 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6) δ 0.87 (s, 3H), 1.01 (s, 3H), 2.01 (d, J = 16.0 Hz, 1H), 2.20 (d, J = 16.0 Hz, 1H), 2.30 (m, 4H), 2.44 (d, J = 17.2 Hz, 1H), 3.55 (s, 3H, OCH_3), 3.65 (s, 3H, OCH_3), 3.67 (s, 3H, OCH_3), 4.80 (s, 1H), 6.61 (d, J = 8.0 Hz, 1H), 6.77 (m, 2H), 9.04 (s, 1H, NH). ^{13}C NMR (50 MHz, DMSO-d_6) δ 18.2, 26.4, 29.2, 32.1, 34.9, 50.2, 50.6, 55.3, 55.4, 103.4, 110.0, 111.6, 118.9, 140.2, 144.8, 146.9, 148.01, 149.3, 167.3, 194.3. MS (ES) m/z 386.50 (M+1). HRMS (ESI) calculated for $C_{22}H_{28}NO_5$ $(M+H)^+$ 386.1967 found 386.1971.

Ethyl 2-methyl-4-(3-nitrophenyl)-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (compound **5o***).* A yellow solid; IR (KBr) 3297, 2940, 1703, 1608, 1527, 1480, 1346, 1222, 1182, 1076, 718, 680, 525 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.19 (t, J = 7.2 Hz, 3H), 2.05–1.92 (m, 2H), 2.36–2.32 (m, 2H), 2.42 (s, 3H), 2.50–2.47 (m, 2H), 4.08 (q, J = 7.2 Hz, 2H), 5.18 (s, 1H), 6.06 (s, 1H, NH), 7.39 (m, 1H), 7.74 (d, J = 7.6 Hz, 1H), 7.99 (dd, J = 2.0 & 8.0 Hz, 1H), 8.09 (m, 1H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.2, 19.2, 21.0, 27.2, 36.8, 60.0, 104.9, 112.22, 121.2, 122.8, 128.5, 134.7, 144.5, 148.2, 149.3, 150.8, 166.9, 195.8. MS (ES) m/z 357.50 (M+1). HRMS (ESI) calculated for $C_{19}H_{21}N_2O_5$ $(M+H)^+$ 357.1450 found 357.1467.

Ethyl 4-(2-chloro-3-(trifluoromethyl)phenyl)-2-methyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3 carboxylate (compound **5p***).* A pale yellow solid; IR (KBr) 3295, 2979, 1698, 1614, 1490, 1315, 1225, 1184, 1130, 977, 736, 697, 530 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.16 (t, J = 7.2 Hz, 3H), 2.01–1.89 (m, 2H), 2.32–2.28 (m, 2H), 2.34 (s, 3H), 2.45–2.37 (m, 2H), 4.05 (q, J = 7.2 Hz, 2H), 5.51 (s, 1H), 6.00 (s, 1H, NH), 7.24 (t, J = 7.6 Hz, 1H), 7.49 (d, J = 7.6 Hz, 1H), 7.63 (d, J = 7.6 Hz, 1H). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 14.1, 19.2, 21.0, 27.3, 36.5, 37.0, 59.9, 104.7, 111.8, 125.5, 125.6, 125.8, 135.8, 144.3, 146.5, 151.2, 167.1, 195.7. MS (ES) m/z 414.40 (M+1). HRMS (ESI) calculated for $C_{20}H_{20}NO_3ClF_3$ $(M+H)^+$ 414.1084 found 414.1072.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jfluchem.2011.09.005.

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