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Silica supported $Fe(HSO_4)_3$ as an efficient, heterogeneous and recyclable catalyst for synthesis of β-enaminones and β-enamino esters

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This paper is dedicated to Professor Sayyed Faramarz Tayyari on the occasion of his 65th birthday and his ongoing 35 years research in the field of β-dicarbonyl hydrogen bonding.

Keywords:
Amine
β-Dicarbonyl compounds
β-Enaminones
Silica ferric hydrogensulfate

ABSTRACT

A series of β-substituted enaminones were prepared through the one-pot reaction of β-dicarbonyl compounds with various amines in the presence of silica ferric hydrogensulfate under solvent free conditions at room temperature. The reactions proceed smoothly in excellent yield, high chemoselectivity and with an easy work-up. Catalytic amount of $Fe(HSO_4)_3{\cdot}SiO_2$ catalyzed one-pot reaction of linear and cyclic β-diketones and β-keto esters with aromatic and aliphatic amines. The B3LYP/6-31G** full optimizations were carried out for enol-enamine tautomers of enaminones.

1. Introduction

The enaminones and enamino esters are very stable structural motifs which are prepared by inexpensive raw materials. Hence they are considered as excellent starting materials in organic synthesis. Enaminones and enamino esters are used as versatile building blocks for synthesis of important heterocyclic compounds, nitrogen containing compounds, naturally occurring alkaloids, pharmaceutical drugs with antiepileptic, anticonvulsant and antitumor properties [1–8]. They even served as synthons for γ-aminoalcohol, β-aminoacids which are a class of very stable compounds useful in asymmetric catalysis as a chelating agent [9]. Condensation reactions of carbonyl compounds with amines in the presence of various acid catalysts like $Yb(OTf)_3$ [10], $Zn(O_4Cl)_2$ [11,12], $InBr_3$ [13], $CoCl_2$ [14], and $LiHSO_4{\cdot}SiO_2$ [15] are well reported for the synthesis of β-enaminones and enamino esters. Additionally, non-conventional techniques such as microwave and ultrasound are also reported [16–18]. However, these methods are associated with certain drawbacks like use of moisture sensitive metal triflates and tedious workup [10], requirement of drastic conditions and use of harmful reagents [11], use of homogenous and non recyclable catalyst [12–14]. Hence there is sufficient scope for the development of heterogeneous, reusable catalytic system, which could catalyze the synthesis of enaminones and enamino esters at milder operating conditions.

In this paper, we report a fast, clean and highly efficient method for the synthesis of β-enaminones and β-enamino esters *via* condensation of β-dicarbonyl compounds with amines using $Fe(HSO_4)_3{\cdot}SiO_2$ as a non-toxic, readily producible, heterogeneous and reusable catalytic system (Scheme 1).

2. Experimental

2.1. General

Chemicals were either prepared in our laboratories or purchased from Merck, Fluka and Aldrich Chemical Companies. All yields refer to the isolated products. Melting points were recorded on an Electro thermal type 9100 melting point apparatus. IR spectra were recorded on a Thermo Nicolet AVATAR-370-FTIR spectrophotometer. The ^1H and ^{13}C NMR spectra were recorded on a Bruker AC 100 and Bruker DRX-400 Avance spectrometers at 400 and 100.65 MHz,

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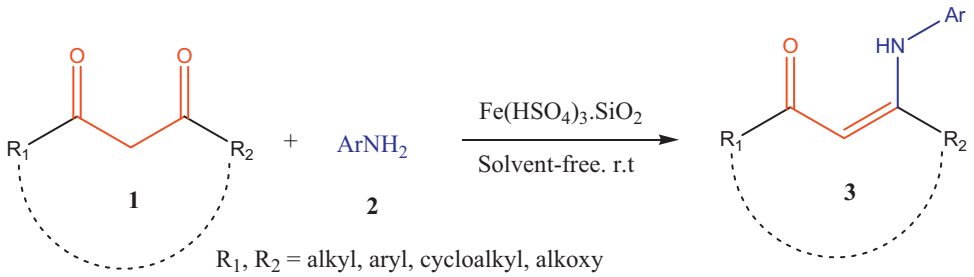


Scheme 1. Synthesis of β-enaminones and β-enamino esters in the presence of $Fe(HSO_4)_3{\cdot}SiO_2$.

Table 1
Conditions optimization of the reaction between aniline and acetylacetone.

Entry	Solvent	Catalyst	Mol (%)	Condition	Yield (%)
1	CH_3OH	$Fe(HSO_4)_3$	10	Reflux, 1 h	50
2	CH_3OH	$Fe(HSO_4)_3$	10	r.t, 1 h	50
3	Solvent free	$Fe(HSO_4)_3/SiO_2$	10	r.t, 20 min	80
4[a]	Solvent free	$Fe(HSO_4)_3/SiO_2$	25	r.t, 7 min	89
5	Solvent free	$Fe(HSO_4)_3/SiO_2$	50	r.t, 7 min	89
6[b]	Solvent free	$Fe(HSO_4)_3/SiO_2$	25	r.t, 7 min	89
7[c]	Solvent free	$Fe(HSO_4)_3/SiO_2$	25	r.t, 7 min	87
8[d]	Solvent free	$Fe(HSO_4)_3/SiO_2$	25	r.t, 7 min	85
9[e]	Solvent free	$Fe(HSO_4)_3/SiO_2$	25	r.t, 7 min	85
10[f]	Solvent free	$Fe(HSO_4)_3/SiO_2$	25	r.t, 7 min	84

[a] Optimum conditions.
[b–f] Reusability of the catalyst in the new runs.

respectively. Chemical shifts are reported in ppm downfield from TMS as internal standard; coupling constants *J* are given in Hertz. Elemental analyses were obtained on a Thermo Finnigan Flash EA micro-analyzer. Silica supported ferric hydrogensulfate prepared as we previously reported [19].

2.2. General procedure for the synthesis of compounds 3a–3t

A mixture of the β-dicarbonyl compound (2 mmol), the amine (2 mmol) and $Fe(HSO_4)_3{\cdot}SiO_2$ [0.22 g containing 0.25 mmol of $Fe(HSO_4)_3$] was stirred in solvent free condition at room temperature for the appropriate time (Table 1). After completion of the reaction as indicated by TLC, the mixture was diluted by ethyl acetate (20 ml). The insoluble catalyst was separated by filtration and rinsed with ethyl acetate, dried and re-used. The solvent of the filtrate was evaporated and the crude product was purified by recrystallization from $EtOH/H_2O$ (1/1).

Spectral data of the prepared compounds:

(Z)-4-Anilino-3-penten-2-one (***3a***): yield 89%; m.p = 45–47 °C, lit. [15] m.p 47–49 °C; ^{1}H NMR ($CDCl_3$, 100 MHz) δ: 12.5 (b, 1H), 6.9–7.3 (m, 5H), 5.15 (s, 1H), 2.1 (s, 3H), 1.95 (s, 3H). IR (KBr, cm^{-1}) ν: 3435, 3051, 2994, 2924, 1614, 1596, 1282, 764, 696.

(Z)-4-(4-Methoxyanilino)-3-penten-2-one (***3b***): yield 91%; m.p = 45–47 °C, lit. [13] m.p 41–43 °C; ^{1}H NMR ($CDCl_3$, 100 MHz) δ: 12.3 (b, 1H), 6.9 (AB-q, 4H), 5.1 (s, 1H), 3.7 (s, 3H), 2.07 (s, 3H), 1.88 (s, 3H). IR (KBr, cm^{-1}) ν: 3447, 3358, 3219, 2990, 2916, 1617, 1567, 1494, 1277, 1091.

(Z)-4-(4-Toluidino)-3-penten-2-one (***3c***): yield 90%; m.p = 63–65 °C, lit. [15] m.p 66–68 °C; ^{1}H NMR ($CDCl_3$, 100 MHz) δ: 12.4 (b, 1H), 7.1 (m, 4H), 5.15 (s, 1H), 2.4 (s, 3H) 2.1 (s, 3H), 1.9 (s, 3H). IR (KBr, cm^{-1}) ν: 3440, 3031, 2994, 2921, 2855, 1610, 1567, 1276, 808.

(Z)-4-(4-Choloroanilino)-3-penten-2-one (***3d***): yield 85%; m.p = 59–60 °C, lit. [13] m.p 61–62 °C; ^{1}H NMR ($CDCl_3$, 100 MHz) δ: 12.45 (b, 1H), 7.2 (m, 4H), 5.25 (s, 1H), 2.15 (s, 3H), 2.0 (s, 3H). IR (KBr, cm^{-1}) ν: 3448, 3354, 3219, 3060, 2990, 2921, 1617, 1567, 1494, 1276.

Methyl (Z)-3-aniline-2-butenoate (***3e***): yield 90%; m.p = 48–49 °C, lit. [13] m.p 46–47 °C; ^{1}H NMR ($CDCl_3$, 100 MHz) δ: 10.3 (b, 1H), 7.0–7.3 (m, 5H), 4.7 (s, 1H), 3.67 (s, 3H), 2.0 (s, 3H(. IR (KBr, cm^{-1}) ν: 3248, 1651, 1606, 1590, 1262, 786.

Methyl(Z)-3-(4-methoxy aniline)-2-butenoate (***3f***): yield 93%; m.p = 65–67 °C, lit. [13] oil; ^{1}H NMR ($CDCl_3$, 100 MHz) δ:10.2 (b, 1H), 7.0 (AB-q, 4H), 4.8 (s, 1H), 3.75 (s, 3H), 3.06 (s, 3H), 2.0 (s, 3H). IR (KBr, cm^{-1}) ν: 3264, 1651, 1613, 1513, 1246, 788.

Methyl (Z)-3-(4-toluidino)-2-butenoate (***3g***): yield 91%; m.p = 58–60 °C, lit. [13] m.p 57–58 °C; ^{1}H NMR ($CDCl_3$, 100 MHz) δ: 10.3 (b, 1H), 7.1 (AB-q, 4H), 4.3 (s, 1H), 3.65 (s, 3H), 2.4 (s, 3H), 1.95 (s, 3H). IR (KBr, cm^{-1}) ν: 3264, 1651, 1598, 1275, 1163.

Methyl (Z)-3-(4-choloroaniline)-2-butenoate (***3h***): yield 85%; m.p = 61–62 °C, lit. [13] m.p 60–61 °C; ^{1}H NMR($CDCl_3$, 100 MHz) δ: 10.4 (b, 1H), 7.2 (AB-q, 4H), 6.6 (b, 1H), 4.85 (s, 1H), 3.7 (s, 3H), 2.1 (s, 3H). IR (KBr, cm^{-1}) ν: 3374, 1652, 7618, 1271, 1167.

(Z)-3-Anilino-1-phenyl-2-buten-1-one (***3i***): yield 93%; m.p = 108–110 °C, lit. [15] m.p 109–111 °C; ^{1}H NMR ($CDCl_3$, 100 MHz) δ: 13.1 (b, 1H), 8.0 (m, 2H), 7.1–7.5 (m, 8H), 5.95 (s, 1H), 2.3 (s, 3H). IR (KBr, cm^{-1}) ν: 3435, 1621, 1589, 1547, 1325, 752.

(Z)-3-(4-Methoxyaniline)-1-phenyl-2-buten-1-one (***3j***): yield 95%; m.p = 103–105 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 13.99 (b, OH, 0.083H), 12.96 (b, NH, 0.917H), 7.95 (d, 2H, *J* = 6.4 Hz), 7.47 (m, 3H), 7.14 (d, 2H, *J* = 7.6 Hz), 6.93 (d, 2H, *J* = 8.0 Hz), 5.90 (s, 1H), 3.85 (s, 3H), 2.10 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 188.4, 163.2, 157.9, 140.2, 131.5, 130.8, 128.3, 127.1, 126.6, 93.6, 55.5, 20.3. IR (KBr, cm^{-1}) ν: 3051, 3010, 2949, 2830, 1623, 1607, 1587, 1508, 1330, 768.

(Z)-1-Phenyl-3-(4-toluidino)-2-buten-1-one (***3k***): yield 91%; m.p = 90–92 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 13.96 (b, OH, 0.246H), 12.95 (b, NH, 0.754H), 7.96 (m, 2H), 7.47 (m, 3H), 7.20 (m, 2H), 7.11 (m, 2H), 5.91 (s, 1H), 2.34 (s, 3H), 2.15(s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 188.5, 162.6, 140.1, 136.0, 135.7, 130.8, 129.8, 128.3, 127.1, 124.9, 93.9, 21.0, 20.4. IR (KBr, cm^{-1}) ν: 3047, 2912, 1993, 1899, 1821, 1622, 1572, 754, 506.

(Z)-3-(4-Choloroanilino)-1-phenyl-2-buten-1-one (***3l***): yield 81%; m.p = 126–128 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 14.05 (b, OH, 0.242H), 13.10 (b, NH, 0.758H), 7.94 (d, 2H, *J* = 6.8 Hz), 7.47 (m, 3H), 7.37 (d, 2H, *J* = 7.2 Hz), 7.14 (d, 2H, *J* = 7.6 Hz), 5.95 (s, 1H), 2.17 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 189.0, 161.8, 139.8, 137.3, 131.3, 131.1, 129.4, 128.4, 127.1, 125.9, 94.7, 20.5. IR (KBr, cm^{-1}) ν: 3411, 3080, 3051, 1623, 1588, 1549, 1326, 766.

3-Anilino-5,5-dimethyl-2-cyclohexen-1-one (***3m***): yield 86%; m.p = 184–185 °C, lit. [15] m.p 184–186 °C; ^{1}H NMR ($CDCl_3$, 100 MHz) δ: 7.1–7.4 (m, 5H), 6.4 (b, 1H), 5.6 (s, 1H), 2.25 (m, 4H), 2.25 (m, 4H), 1.1(s, 6H). IR (KBr, cm^{-1}) ν: 3231, 1597, 1573, 1244, 705.

3-(4-Methoxy aniline)-5,5-dimethyl-2-cyclohexen-1-one (***3n***): yield 91%; m.p = 193–195 °C, lit. [15] m.p 192–194 °C; ^{1}H NMR ($CDCl_3$, 100 MHz) δ: 7.1 (b, 1H), 6.9 (AB-q, 4H), 5.3 (s, 1H), 3.75 (s, 3H), 2.25 (AB-q, 4H), 1.05 (s, 6H). IR (KBr, cm^{-1}) ν: 3206, 1607, 1568, 1536, 1509, 1243.

Table 2
Enamination of β-dicarbonyl compounds in the presence of $Fe(HSO_4)_3{\cdot}SiO_2$.

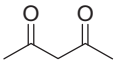
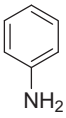
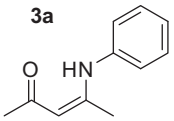
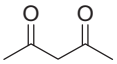
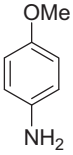
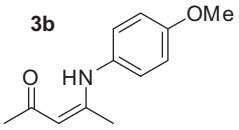
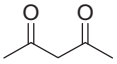
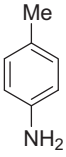
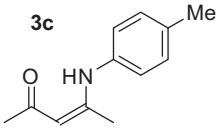
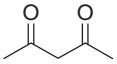
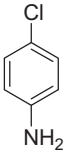
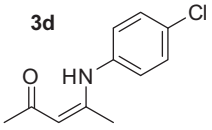
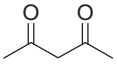
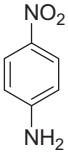
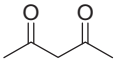
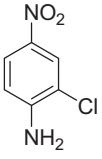
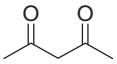
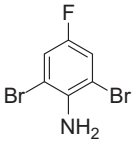
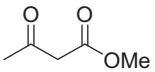
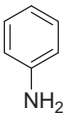
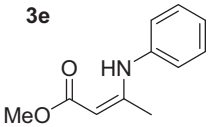
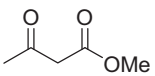
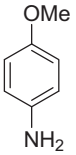
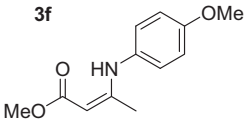
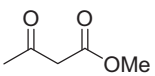
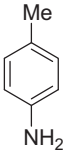
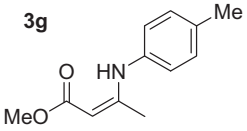
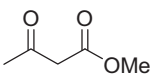
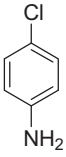
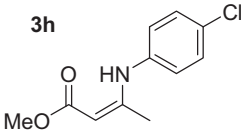
Entry	Dicarbonyl compound	Amine	Product	Time (min)	Yield (%)[a]
1			**3a** 	7	89
2			**3b** 	12	91
3			**3c** 	12	90
4			**3d** 	16	85
5			No reaction	40	–
6			No reaction	40	–
7			No reaction	40	–
8			**3e** 	12	90
9			**3f** 	16	93
10			**3g** 	16	91
11			**3h** 	16	85

Table 2 (*Continued*)

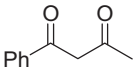
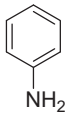
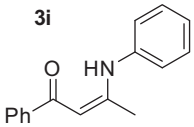
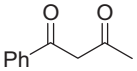
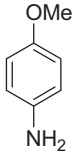
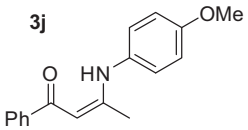
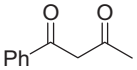
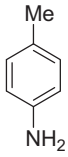
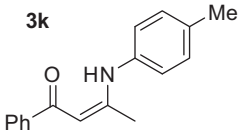
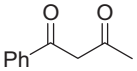
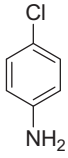
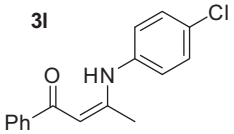
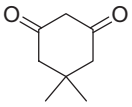
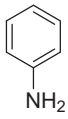
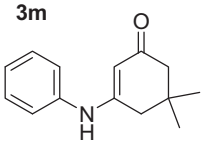
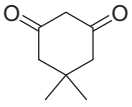
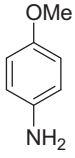
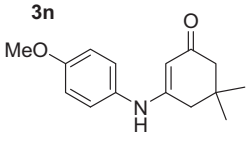
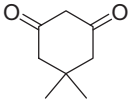
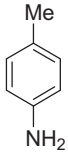
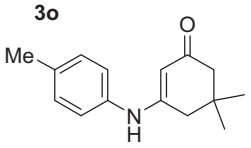
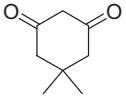
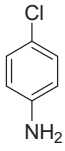
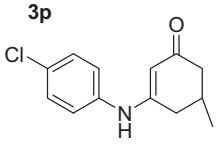
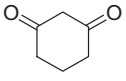
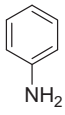
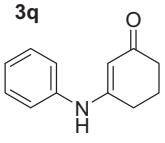
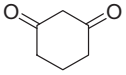
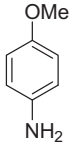
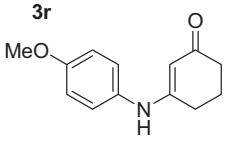
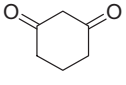
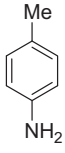
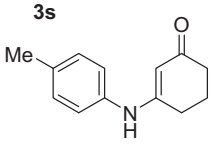
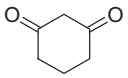
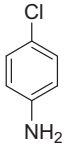
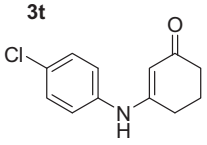
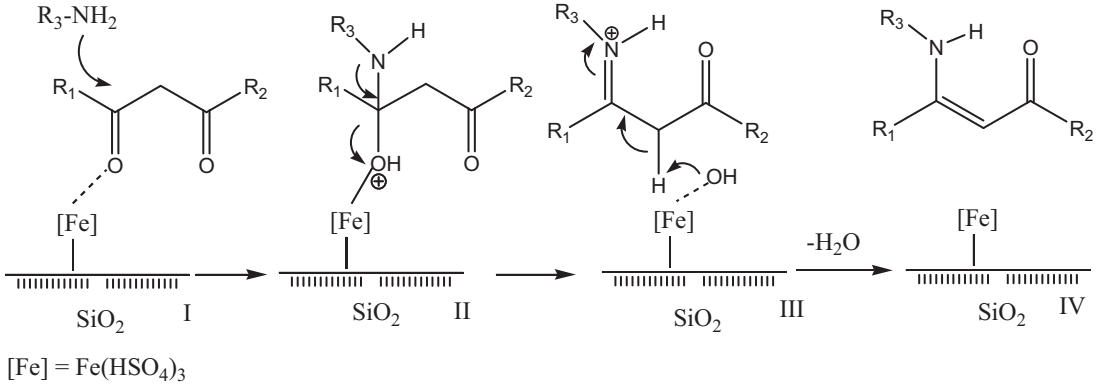
Entry	Dicarbonyl compound	Amine	Product	Time (min)	Yield (%)[a]
12			**3i** 	12	93
13			**3j** 	16	95
14			**3k** 	16	91
15			**3l** 	25	81
16			**3m** 	25	86
17			**3n** 	20	91
18			**3o** 	20	90
19			**3p** 	30	60
20			**3q** 	15	90
21			**3r** 	10	92
22			**3s** 	13	91

Table 2 (*Continued*)

Entry	Dicarbonyl compound	Amine	Product	Time (min)	Yield (%)[a]
23			**3t** 	20	87

[a] Isolated yields.



Scheme 2. Suggested mechanism for the synthesis of β-enaminones and β-enamino esters.

5,5-Dimethyl-3-(4-toluidino)-2-cyclohexen-1-one (***3o***): yield 90%; m.p = 199–201 °C, lit. [21] m.p 203–204 °C; ^{1}H NMR ($CDCl_3$, 100 MHz) δ: 7.5 (AB-q, 4H), 6.95 (b, 1H), 5.5 (s, 1H), 2.3 (AB-q, 4H), 1.1 (s, 6H). IR (KBr, cm^{-1}) ν: 3244, 1608, 1575, 1282, 1147,812.

3-(4-Choloroaniline)-5,5-dimethyl-2-cyclohexen-1-one (***3p***): yield 60%; m.p = 208–209 °C, lit. [21] m.p 208–210 °C; ^{1}H NMR ($CDCl_3$, 100 MHz) δ: 6.9–7.3 (m, 5H), 5.4 (s, 4H), 2.25 (AB-q, 4H), 1.1 (s, 3H), 1.05 (s, 3H). IR (KBr, cm^{-1}) ν: 3244, 1611, 1574, 1284, 1149.

3-Anilino-2-cyclohexen-1-one (***3q***): yield 90%; m.p = 179–180 °C, lit. [17] m.p 178–180 °C; ^{1}H NMR ($CDCl_3$, 100 MHz) δ: 6.6–7.4 (m, 6H), 5.5 (s, 1H), 2.2–2.5 (m, 4H), 1.9 (m, 2H). IR (KBr, cm^{-1}) ν: 3264, 1604, 1593, 1571, 1527, 1244.

3-(4-Methoxy aniline)-2-cyclohexen-1-one (***3r***): yield 92%; m.p = 163–164 °C, lit. [22] m.p 164–166 °C; ^{1}H NMR ($CDCl_3$, 100 MHz) δ: 6.95 (AB-q, 4H), 6.2 (b, 1H), 5.35 (S, 7H), 3.75 (S, 3H), 2.2–2.5 (m, 4H), 2.0 (m,2H). IR (KBr, cm^{-1}) ν: 3220, 1571, 1535, 1510, 1240, 1185.

3-(4-Toluidino)-2-cyclohexen-1-one (***3s***): yield 91%; m.p = 150–152 °C; ^{1}H NMR ($CDCl_3$, 100 MHz) δ: 7.1 (AB-q, 4H), 6.8 (b, 1H), 5.5 (s, 1H), 2.2–2.5 (m, 4H), 2.3 (s, 3H), 2.0 (m, 2H). IR (KBr, cm^{-1}) ν: 3214, 1572, 1535, 1512, 1243, 1184.

3-(4-Choloroaniline)-2-cyclohexen-1-one (***3t***): yield 87%; m.p = 191–192 °C, lit. [21] m.p 190–191.5 °C; ^{1}H NMR ($CDCl_3$, 100 MHz) δ: 7.4 (b, 1H), 7.1 (AB-q, 4H), 5.45 (s, 1H), 2.2–2.5 (m, 4H), 1.95 (m, 2H). IR (KBr, cm^{-1}) ν: 3250, 1602, 1569, 1520, 1245.

3. Results and discussion

Initially condensation of aniline and acetylacetone was selected as a model reaction, and the influence of various reaction parameters like catalyst, temperature and time was examined (Table 1). $Fe(HSO_4)_3{\cdot}SiO_2$ proved to be the most efficient because the reaction could be carried out in excellent yield and short reaction time. The best reaction conditions require the presence of a small amount of $Fe(HSO_4)_3{\cdot}SiO_2$ (25 mol%) under solvent-free condition at room temperature.

After the above optimization, we chose a variety of structurally different amines including aliphatic and aromatic amines were condensed with various 1,3-diketones like methyl acetoacetate, acetyl acetone and 1,3-cyclohexanedione using $Fe(HSO_4)_3{\cdot}SiO_2$ as a heterogeneous catalyst at room temperature (Scheme 1). The results are shown in Table 2. All the isolated products were well characterized by their IR, ^{1}H NMR spectral analysis.

It was also found that amines containing electron donating groups gave better yield and showed good reactivity in comparison to amines having electron withdrawing groups, owing to the availability of the lone pair on nitrogen. However, electron withdrawing substituents were failed in this reaction. The condensation of aliphatic amines as well as diamines with β-dicarbonyl compounds was also efficiently performed and after further studies on ligand abilities and biological activities will be published.

Reusability of the catalyst is the most significant advantage of our method. For the reaction of aniline with acetylacetone no significant loss of the product yield was observed when $Fe(HSO_4)_3{\cdot}SiO_2$ was reused after five times of recycling (Table 1, entries 6–10).

It is clear from our results that the $Fe(HSO_4)_3{\cdot}SiO_2$ catalyzed condensation reaction of 1,3-dicarbonyls with the amines provides a remarkably rapid and viable alternative route for the synthesis of β-enaminones. This paper reports for the first time a regio- and chemoselective enamination of β-dicarbonyl compounds under mainly solvent free conditions using silica ferric hydrogensulphate at room temperature in excellent yields and purity.

Suggested mechanism for this reaction was shown in Scheme 2. According to, electron releasing substituted anilines which have nucleophilic identity carry on the first step of reaction and then by stabilizing the cationic intermediate III forwarded intermediate II to products and catalyst was regenerated. Electron releasing groups such as 4-methyl or 4-methoxy aniline reacted with all β-dicarbonyl compounds in high yields but 4-chloroaniline reacted in relatively longer reaction times and lower yields. Strong electron withdrawing groups such as nitro group (Table 2, entries 5–7) failed in this reaction because of low nucleophilic identity.

Fig. 1 shows two possible enol forms of compound **3a**. As it is cleared, one form is in enolic state (**3a**$_{enol}$) and another is in enamine

Table 3
Calculated energies (Hartrees), the energy differences between $\mathbf{3a}_{enamine}$ and $\mathbf{3a}_{enol}$ kcal/mol, and some selected parameters of the enamine and enol tautomers of **3a** in gas phase and in some solvents.[a]

Solution/parameters	$\mathbf{3a}_{enamine}$					$\mathbf{3a}_{enol}$					ΔE^{b}
	N—H (Å)	H···O (Å)	N···O (Å)	NHO (°)	*E*	N···H (Å)	O—H (Å)	N···O (Å)	NHO (°)	*E*	
Gas	1.033	1.749	2.637	141.6	−557.0012778	1.604	1.024	2.542	149.9	−556.9936801	4.8(4.5)
$CHCl_3$	1.032	1.741	2.646	141.3	−557.0064494	1.558	1.028	2.534	150.5	−556.9974235	5.7(4.9)
CH_3CN	1.031	1.769	2.651	141.1	−557.0085458	1.582	1.029	2.531	150.8	−556.9990001	6.0(5.2)
Ethanol	1.031	1.768	2.651	141.1	−557.0083881	1.583	1.023	2.531	150.8	−556.9988801	6.0(5.2)
Cyclohexane	1.032	1.755	2.642	141.4	−557.0040765	1.596	1.026	2.538	150.2	−556.9956836	5.3(4.5)
Water	1.031	1.769	2.652	141.1	−557.008747	1.583	1.029	2.531	150.8	−556.9991539	6.0(5.2)

[a] All calculated at B3LYP/6-31G**.
[b] ΔE, energy difference between $\mathbf{3a}_{enamine}$ and $\mathbf{3a}_{enol}$ in kcal/mol, the corrected value for the ZPE is given in parenthesis.

Table 4
Comparison of enamination of acetylacetone with aniline by $Fe(HSO_4)_3{\cdot}SiO_2$ with literature reported methods.

Entry	Catalyst mole (%)	Solvent	Temperature (°C)	Reaction time	Isolated yield (%)	Ref.
1	$Yb(OTf)_3$, 5	–	r.t	12 h	99	[10]
2	$[Hbim]BF_4$	$[Hbim]BF_4$	28	25 min	91	[20]
3	$LiHSO_4{\cdot}SiO_2$, 20	–	80	10 min	91	[15]
4	$P_2O_5{\cdot}SiO_2$, 11.5	–	r.t	10 min	85	[23]
5	$Fe(HSO_4)_3{\cdot}SiO_2$, 12.5	–	r.t	7 min	89	Present work

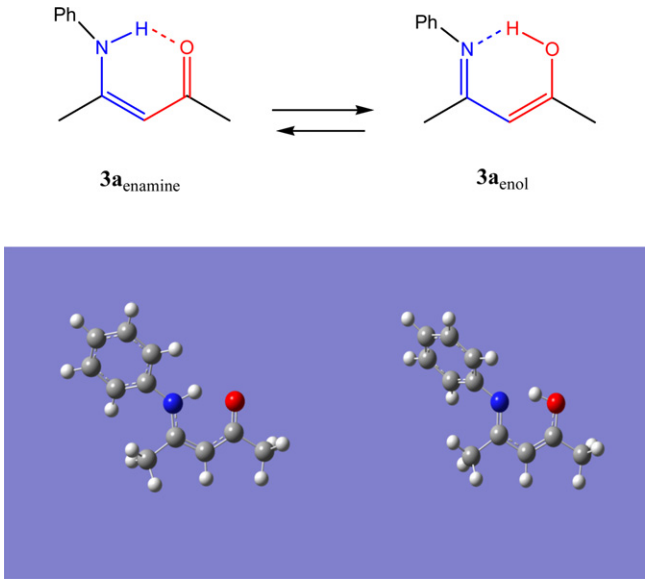


Fig. 1. Optimized structures of two possible enol forms of compound **3a**: ($\mathbf{3a}_{enol}$) right and ($\mathbf{3a}_{enamine}$) left.

state ($\mathbf{3a}_{enamine}$). The B3LYP/6-31G** full optimizations were carried out for each forms of **3a**. Table 3 reports the optimized energies and some selected parameters of these tautomers in gas phase and in some solvents. However, this calculation suggests that enamine form ($\mathbf{3a}_{enamine}$) is stable tautomer in gas and solution phases. In gas phase the energy differences is 4.8 kcal/mol, whereas in solution increased to 5.3–6.0 kcal/mol due to more stabilized $\mathbf{3a}_{enamine}$ with higher dipole moment in solvents.

In the ^1H NMR (100 MHz, $CDCl_3$) spectra of compounds **3m–3t** which exist in its enaminones form show a broad singlet in 6.2–7.4 region for NH group. However, this group can not form an intramolecular hydrogen bonding. This signal was shifted to 10.2–10.4 ppm for enamino esters **3e–3h** which includes an intramolecular hydrogen bonding of NH group with ester carbonyl group. Compounds **3a–3d** show a broad singlet in 12.2–12.5 ppm for NH group hydrogen bonded with ketone carbonyl group. In compounds **3i–3l**, this signal was shifted to 13–13.1 ppm which for accurate assignment to NH or OH group we prepared their (**3j–3l**) 400 MHz ^1H NMR spectra in $CDCl_3$ and observed NH group at 13 ppm (enaminones as major tautomers of **3j–3l**, 75.4–91.7%) and OH group at 14 ppm (enols as minor tautomers of **3j–3l**, 8.3–24.6%). Hydroxyl group is acidic than amine group and so, H···N hydrogen bonding of OH group with imine (14 ppm) is stronger than H···O hydrogen bonding of NH group with carbonyl group (13 ppm), respectively. However, experimental data showed enamino ketones and enamino esters exist usually as enamine form. The parent keto forms were not observed.

Table 4 shows efficiency of our catalyst compared to other catalysts reported in the literature. The results of enamination of acetylacetone with aniline by $Fe(HSO_4)_3{\cdot}SiO_2$ was compared with some reported methods. The results revealed that the reaction times and catalyst loading in our method were significantly lower than reported methods.

4. Conclusion

In conclusion, we have developed an efficient protocol for synthesis of β-enaminones and β-enamino esters using silica ferric hydrogensulfate as a heterogeneous, recyclable and stable catalyst. The reaction was optimized with respect to various parameters and could be employed for the condensation of different dicarbonyl compounds and amines. The advantages offered by this protocol include high yields of desired products, under ambient conditions with diverse substrate compatibility making it an important supplement to the existing methods.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2012.07.021.

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