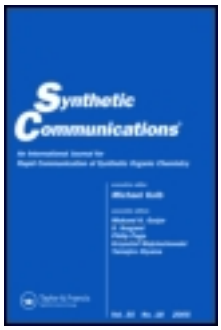

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Formic Acid: A Low-Cost, Mild, Ecofriendly and Highly Efficient Catalyst for the Rapid Synthesis of *β*-Enaminones

Siddappa A. Patil[1], Phillip A. Medina[1], Diego Gonzalez-Flores[2], Jason K. Vohs[3], Seth Dever[1], Leslie W. Pineda[2], Mavis L.Montero[2], Bradley D. Fahlman[1,]

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Abstract

β-Enaminones have been synthesized by the condensation reaction of β-diketones with various anilines in the presence of a catalytic amount of formic acid, a mild and ahighly efficient acid catalyst in methanol. These condensation reactionsproceed smoothly in short reaction times withnear-quantitative yields.

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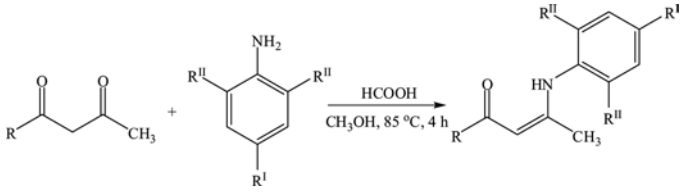

KEYWORDS: *β*-enaminone; formic acid; synthesis; crystal structure

INTRODUCTION

β-Enaminones have been widely used as key precursors in organic synthesis,[1–3] as well as synthons for different important heterocycles,[4–6] antibacterial,[7] anticonvulsant, anti-

inflammatory,[8] or antitumour agents,[9] and naturally occurring alkaloids.[10] Therefore, development of new synthetic methods has received considerable attention. In 1961, Martin[11] reported one of the most important ways to prepare *β*-enaminones, *via* the direct condensation of *β*-dicarbonyl compounds with amines in a refluxing aromatic solvent. In recent years, this reaction was investigated in depth and detail, mainly focusing on improving the reaction conditions. This has led to the development of interesting reaction systems, such as those catalyzed by K-10 clay,[12] $NaAuCl_4$,[13] $Zn(ClO_4)_2 \cdot 6H_2O$,[14] ionic liquids,[15] $CeCl_3 \cdot 7H_2O$,[16] $ZrCl_4$,[17] ytterbium triflate,[18] $KHSO_4$ and SiO_2.[19] Nevertheless, the application of these systems suffers from one or more disadvantages, such as using expensive or less readily available reagents, toxic solvents, drastic reaction conditions, long reaction times, unsatisfactory yields and/or low selectivity. Therefore, the development of facile and green synthetic methods is still in high demand.

Formic acid (HCOOH), a major product formed during biomass processing, is widely used as acid catalyst in organic synthesis since it is relatively inexpensive, and merits high volatility and easy work-up. Accordingly, it has emerged as a key replacement for conventional acidic catalysts in organic synthesis. Here in this paper, we report the synthesis and spectroscopic characterization of various*β*-enaminones derived from 1:1 condensation of *β*-diketones with various anilinesusing formic acid as a catalyst. In addition, the crystal structure of one of these compounds, (*Z*)-4-(4-methoxyphenylamino)pent-3-en-2-one is presented.

RESULTS AND DISCUSSION

To optimize the reaction conditions, we carried out the condensation of acetylacetone with aniline. To study the effect of different heterogeneous catalysts, the reaction was carried out in methanol at 85 °C in the presence of different acids catalysts (Table 1). The reaction was catalyzed by all the acid catalysts; however, formic acid was found to be the best. In order to understand the effect of solvents, the condensation reaction of acetylacetone with aniline was performed in $CHCl_3$, $CHCl_2$, CH_3OH, CH_3CH_2OH, $C_6H_5CH_3$, and C_6H_6, generatingrespective yields of 54%, 55%, ***98%***, 87%, 70%, and 76% (Table 2). Hence, methanol represents the best solvent for our reaction system relative to theother possible options. To evaluate the effect of amount of catalyst, 0.5, 1.0, and 2.0 mol% formic acid were used for the reaction, with 1.0 mol% formic acid the best choice.

The condensation reaction of acetylacetone with aniline was conducted under the above optimized conditions at 25 °C for 4 hrs. A new product, (Z)-4-(phenylamino)pent-3-en-one (**3a**), was detected by TLC,and isolated in 20% yield. To shorten the reaction time and increase the yield, the same reaction was carried out at different temperatures, and it was found that the reaction worked better at 85 °C. Further increases of temperature did not improve the yield. Based on the above experiments, the optimized reaction conditions were: 85 °Cfor 4 h in the presence of 1.0 mol% formic acid. This optimized reaction condition was applied to the condensation reaction of *β*-diketones (acetylacetone and benzoylacetone) with various anilines (Scheme 1), and the results are summarized in Table 3.

To show the efficacy of this method, variousanilines containing electron-withdrawing groups (such as chloro, nitro and nitrile groups) and electron-donating groups (such as aryl, methyl and methoxy groups) were treated with *β*-diketones to afford the corresponding *β*-enaminones in good to excellent yields. This clearly demonstrates that the electronic nature of substituents of the aromatic ring did not show any obvious effects in terms of yields under these reaction conditions. Also, this method offers several advantages such as better yields, shorter reaction times, cleaner reaction profiles, and simple experimental and workup procedures. The additional advantage of this method is the survival of various functional groups such as halo, nitrile, and nitro, thus allowing a wide range of substitution patterns in the substrates. All reactions were clean and highly efficient, and the products were obtained in good to excellent yields. All the products were purified by general recrystallization method without column chromatography on silica gel and characterized by ^{1}H NMR, ^{13}C NMR, mass spectrometry, infrared (IR) spectroscopy, and elemental analysis. The compound (*Z*)-4-(4-methoxyphenylamino)pent-3-en-2-one was also analyzed by single crystal X-ray diffraction.

All ^{1}H NMR spectra of the *β*-enaminones present a broad signal, which corresponds to the protons of the amine group (N-H). The chemical shift of this proton appears between 11.93 -13.07 ppm, and is generally very sensitive to concentration, solvent, and temperature. The protons of the methyl carried by the amino group appear between 1.15 - 2.13 ppm. The vinylic protons appear in the form of singlet between 4.98 -5.92 ppm. The ^{13}C NMR spectra of *β*-enaminones present a signal characteristic of the sp^{2} carbon of the

ketone function between 188.40 -199.45 ppm, whereas the sp^3 carbon of the amine function appears around 157.21 - 165.72 ppm. Vinylic carbons appear between 101.40 and 92.39 ppm. The IR spectra of all β-enaminones showν(C=O) stretching frequencies around 1600-1650 cm^{-1}, which correspond to the ketone. The wide broad ν(N-H) stretching frequencies around 3420-3410 cm^{-1} are more significant and confirm well the obtention of β-ketoamine and not of β-ketoimine.

Description Of The Crystal Structure

Crystals suitable for single crystal X-ray diffraction were grown from slow evaporation from a methanol solution at room temperature. Crystallographic data for the compound (*Z*)-4-(4-methoxyphenylamino)pent-3-en-2-one is shown in Table 4. Selected bond lengths, bond angles and torsion angles are listed in Tables 5 and 6 respectively. Complete bond lengths and bond angles, anisotropic thermal parameters, and calculated hydrogen coordinates are deposited as supplementary materials. The structures were solved by direct methods using the SHELXS-97 program.[20] A perspective view of (*Z*)-4-(4-methoxyphenylamino)pent-3-en-2-one showing the atomic numbering scheme, is depicted in Figure 1. Compound (*Z*)-4-(4-methoxyphenylamino)pent-3-en-2-one has been shown by ^{1}H NMR spectroscopy to exist in solution in the enaminone and not the enol-imine form. IR spectroscopy shows only the enaminone form in the solid state and this has been further confirmed by its crystal structure. Compound (*Z*)-4-(4-methoxyphenylamino)pent-3-en-2-onecrystallized in the monoclinic space group $P2_1/c$, with four molecules in the unit cell. In this compound,there is an absence of any lattice held water molecules or organic solvent molecules in the unit cell of the determined

structure. The O1=C2 and C3-C2 bond distances [1.2467(13) and 1.4200(15) Å, respectively] further confirm the existence of the enamino-ketone. The bond distances in the C3=C4-N1 chain indicate greater electron delocalization [C3=C4=1.3781(15) Å and N1-C4=1.3509(13) Å]. The C-C bond distances in aromatic rings are in the normal range of 1.37-1.50 Å, which is characteristic of delocalized aromatic rings. The C-C-C bond angles in aromatic rings are around 120° with the variation being less than 2°, which is characteristic of sp^2-hybridized carbons. The title compound lies in two planes with plane I [O1, C2, C3, C4 and N1] making a dihedral angle of 35.76 with plane II [C6, C7, C8, C9, C11 and C12]. The methoxy group is slightly twisted away from the aniline ring, with a C8-C9-O2-C10 torsion angle of 4.3(2)°. The molecular packing diagram (Figure 2) shows four layers of molecules, which are independently arranged in the unit cell. Molecules forming each layer are connected through intermolecular hydrogen bonding. In each layer, the molecules are alternatively parallel. The molecular packing diagram also shows the presence of one intra-molecular hydrogen bond. One of the hydrogens, H1 of the NH group, is involved in intra-molecular hydrogen bonding with the O1 of the C=O entity. This hydrogen bonding stabilizes the crystal packing.

CONCLUSION

In conclusion, we have presented an efficient and environmentally benign protocol for the synthesis of *β*-enaminones from the reaction of *β*-diketones with various anilines in the presence of 1.0 mol% formic acid. The simple work-up, mild reaction conditions, and high yields make our methodology a valid contribution to the existing processes for *β*-enaminone syntheses.

EXPERIMENTAL

General Procedure For The Synthesis Of *B*-Enaminones From The Condensation Reaction Of *B*-Diketones With Primary Amines

A mixture of *β*-diketone (10 mmol), aniline (10 mmol), and formic acid (1.0 mol%) were heated at 85 °Cin 40 mL methanol for 4 hours. On cooling, the precipitated product was filtered and recrystallized from a mixture of methanol and ether to afford *β*-enaminones. All compounds are stable in air and light over a period of several months. The synthetic pathway described in this work is outlined in Scheme 1.

Characterization Dataof *B*-Enaminones

(Z)-4-(Phenylamino)Pent-3-En-One (3a)

[211]H NMR (300MHz, $CDCl_3$) δ (ppm): 1.97 (s, 3H, CH_3), 2.09 (s, 3H, CH_3), 5.18 (s, 1H, CH), 7.10-7.07 (m, 2H, ArH), 7.19-7.15 (m, 1H, ArH), 7.34-7.28 (m, 2H, ArH), 12.49 (s, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$) δ19.61 (CH_3), 28.96 (CH_3), 97.41 (CH), 124.46, 125.31, 128.87, 138.50 (ArC), 159.98 (C-N), 195.86 (C=O).

(Z)-4-(*P*-Tolylamino)Pent-3-En-One (3b)

[221]H NMR (300MHz, $CDCl_3$) δ (ppm): 1.91 (s, 3H, CH_3), 2.05 (s, 3H, CH_3), 2.29 (s, 3H, CH_3), 5.13 (s, 1H, CH), 6.95 (d, J=10.0Hz, 2H, Ph), 7.09 (d, J=10.0 Hz, 2H, Ph), 12.38 (s, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$) δ19.52 (CH_3), 20.67 (CH_3), 28.84 (CH_3), 97.00 (CH), 124.57, 129.44, 135.24, 135.78 (ArC), 160.53 (C-N), 195.60 (C=O).

(Z)-4-(4-Methoxyphenylamino)Pent-3-En-One (3c)

[231]H NMR (300MHz, $CDCl_3$) δ (ppm): 1.77 (s, 3H, CH_3); 1.96 (s, 3H, CH_3); 3.65 (s, 3H, OCH_3); 5.03 (s, 1H, CH); 6.75-6.72 (m, 2H, ArH); 6.91-6.88 (m, 2H, ArH); 12.21 (s, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$) δ19.13 (CH_3), 28.55 (CH_3), 54.90 (OCH_3), 96.42 (CH), 113.80, 126.08, 130.96, 157.27 (ArC), 160.82 (C-N), 195.17 (C=O).

(Z)-4-(4-Chlorophenylamino)Pent-3-En-One (3d)

[221]H NMR (300MHz, $CDCl_3$) δ (ppm): 1.97 (s, 3H, CH_3), 2.09 (s, 3H, CH_3), 5.20 (s, 1H, CH), 7.03 (d, J = 8.4 Hz, 2H, ArH), 7.29 (d, J = 8.4 Hz, 2H, ArH), 12.44 (s, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$) δ19.59 (CH_3), 29.02 (CH_3), 97.95 (CH), 125.61, 129.01, 130.75, 137.16 (ArC), 159.53 (C-N), 196.29 (C=O).

(Z)-4-(4-Nitrophenylamino)Pent-3-En-One (3e)

[241]H NMR (300MHz, $CDCl_3$) δ (ppm):2.13 (s, 3H, CH_3), 2.18 (s, 3H, CH_3), 5.32 (s, 1H, CH), 7.16 (d, J=9 Hz, 2H, ArH), 8.18 (d, J=9 Hz, 2H, ArH), 12.76 (s, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$) δ20.81 (CH_3), 29.86 (CH_3), 101.40 (CH), 122.14, 125.40, 143.77, 145.53 (ArC), 157.21 (C-N), 198.11 (C=O).

(Z)-4-(4-Oxopent-2-En-2-Ylamino)Benzonitrile (3f)

[241]H NMR (300MHz, $CDCl_3$) δ (ppm): 2.11 (s, 3H, CH_3), 2.12 (s, 3H, CH_3), 5.28 (s, 1H, CH), 7.14 (d, J=8 Hz, 2H, ArH), 7.59 (d, J=8 Hz, 2H, ArH), 12.67 (s, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$) δ20.36 (CH_3), 29.50 (CH_3), 100.41 (CH), 107.27, 118.66, 122.83, 133.25 (ArC), 143.26 (C-N), 157.47 (C-N), 197.55 (C=O).

(Z)-4-(2,6-Dimethylphenylamino)Pent-3-En-One (3g)

^{251}H NMR (300MHz, $CDCl_3$) δ (ppm): 1.60 (s, 3H, CH_3), 2.08 (s, 3H, CH_3), 2.17 (s, 6H, $(CH_3)_2$), 5.19(s, 1H, CH), 7.11-7.04 (m, 3H, ArH), 11.91(1H, s, NH). ^{13}C NMR (100 MHz, $CDCl_3$) δ18.08 (CH_3), 18.72 (CH_3), 28.85 (CH_3), 95.64 (CH), 127.29, 128.05, 135.93, 136.33 (ArC), 162.80 (C-N), 195.85 (C=O).

(Z)-4-(2,6-Diisopropylphenylamino)Pent-3-En-One (3h)

^{251}H NMR (300MHz, $CDCl_3$) δ (ppm): 1.14 (d, J = 6.6 Hz, 1H, $CH(CH_3))_2$, 1.21 (d, J = 7.2 Hz, 1H, $CH(CH_3))_2$, 1.63 (1H, s, CH_3CNHAr), 2.12 (1H, s, CH_3COC), 3.02 (sept, J = 6.8 Hz, 1H, $CHMe_2$), 5.21 (s, 1H, CH), 7.18-7.15 (2H, m, ArH), 7.32-7.27 (1H, m, ArH), 12.04 (1H, s, NH). ^{13}C NMR (100 MHz, $CDCl_3$) δ19.14 (CH_3CNHAr), 22.63, 24.54 ($CH(CH_3)_2$), 28.43 ($CHMe_2$), 28.98 ($CH_3C=O$), 95.55 (CH), 123.52, 128.23, 133.42, 146.22(ArC), 163.39(HC(CNHAr), 195.81 (C=O).

(Z)-1-Phenyl-3-(Phenylamino)But-2-En-1-One (3i)

^{261}H NMR (300MHz, $CDCl_3$) δ (ppm): 2.13 (s, 3H, CH_3), 5.89 (s, 1H, CH), 7.22-7.16 (m, 3H,ArH), 7.37-7.34 (m, 2H,ArH), 7.45-7.40 (m, 3H,ArH); 7.93-7.91 (m, 2H,ArH); 13.11 (s, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$) δ20.39 (CH_3), 94.18 (CH), 124.69, 125.70, 126.99, 128.22, 129.10, 130.84, 138.56, 139.93 (ArC), 162.16 (C-N), 188.59 (C=O).

(Z)-1-Phenyl-3-(P-Tolylamino)But-2-En-1-One (3j)

^{271}H NMR (300MHz, $CDCl_3$) δ (ppm): 2.11 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 5.87 (s, 1H, CH), 7.09-7.05 (m, 2H,ArH), 7.18-7.14 (m, 2H,ArH), 7.46-7.40 (m, 3H,ArH), 7.93-7.89 (m, 2H,ArH), 13.02 (s, 1H, NH).^{13}C NMR (100 MHz, $CDCl_3$) δ20.34 (CH_3), 20.91 (CH_3), 93.87 (CH), 124.80, 126.99, 128.23, 129.71, 130.77, 135.70, 135.90, 140.03 (ArC), 162.65 (C-N), 188.43 (C=O).

(Z)-3-(4-Methoxyphenylamino)-1-Phenylbut-2-En-1-One (3k)

^{281}H NMR (300MHz, $CDCl_3$) δ (ppm): 2.06(s, 3H, CH_3), 3.80 (s, 3H, OCH_3), 5.86 (s, 1H, CH), 6.90-6.87 (m, 2H,ArH), 7.11-7.08 (m, 2H,ArH), 7.45-7.40 (m, 3H,ArH), 7.93-7.91 (m, 2H,ArH), 12.94 (s, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$) δ20.17 (CH_3), 55.38 (OCH_3), 93.45 (CH), 114.24, 126.50, 126.93, 128.17, 130.69, 131.33, 140.04, 157.74 (ArC), 163.06 (C-NH), 188.28 (C=O).

(Z)-3-(4-Chlorophenylamino)-1-Phenylbut-2-En-1-One (3l)

^{291}H NMR (300MHz, $CDCl_3$) δ (ppm): 2.13 (s, 3H, CH_3), 5.91 (s, 1H, CH), 7.12-7.08 (m, 2H, ArH), 7.35-7.32 (m, 2H, ArH), 7.46-7.43 (m, 3H, ArH), 7.92-7.89 (m, 2H, ArH), 13.07 (s, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$) δ20.38 (CH_3), 94.65 (CH), 125.89, 127.06, 128.30, 129.29, 131.06, 137.25, 139.74 (ArC), 161.69 (C-NH), 188.95 (C=O).

(Z)-3-(2,6-Dimethylphenylamino)-1-Phenylbut-2-En-1-One (3m)

^{291}H NMR (300MHz, $CDCl_3$) δ (ppm): 1.74(s, 3H, CH_3), 2.22 (s, 6H, $2CH_3$), 5.96 (s, 1H, CH), 7.13-7.07 (m, 3H,ArH), 7.43-7.41 (m, 3H,ArH), 8.00-7.99 (m, 2H,ArH), 12.64 (s, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$) δ17.79 (2,6-$(CH_3)_2$-C6H_3), 18.90 (CH_3), 91.87

(CH), 126.63, 127.07, 127.76, 127.82, 130.29, 135.33, 136.00, 139.57 (ArC), 164.21 (CN), 187.93 (C=O).

Supplementary Material

Crystallographic data for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Center with the deposition number 831504. A copy of the data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 1223 336-033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk].

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Table 1 Condensation reaction of acetylacetone with aniline in the presence of different liquid acid catalysts[a]

Entry	Solvent	Catalyst	Time (h)	Temperature/°C	Yields[b] (%)
1	CH_3OH	H_2SO_4	4	85	58
2	CH_3OH	HCl	4	85	54
3	CH_3OH	$CH_3C_6H_4SO_3H$	4	85	61
4	CH_3OH	HCOOH	4	85	98
5	CH_3OH	CH_3COOH	4	85	53

[a]Reaction conditions: acetylacetone (1.03 g, 10 mmol), aniline (0.91 g, 10 mmol), acid catalyst (1.0 mol%). [b]Isolated yields.

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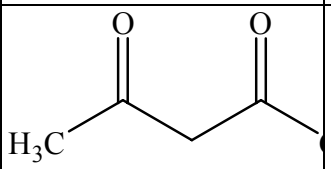
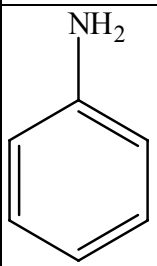
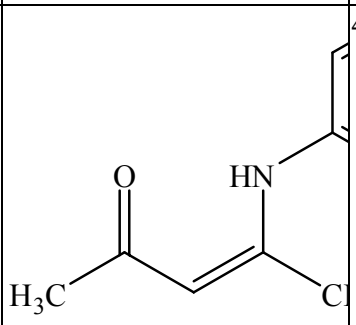
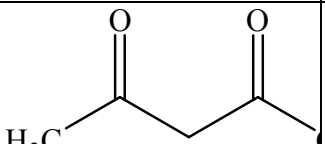
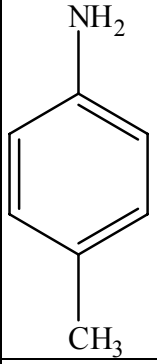
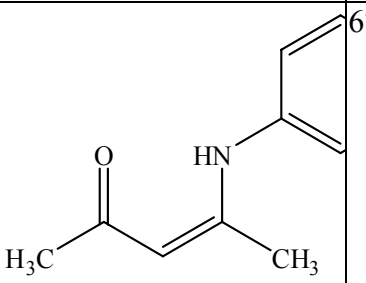
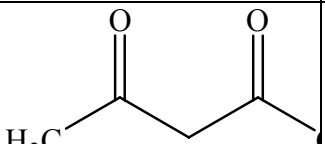
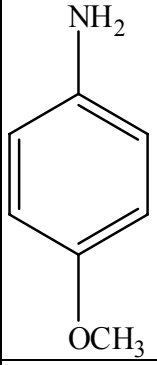
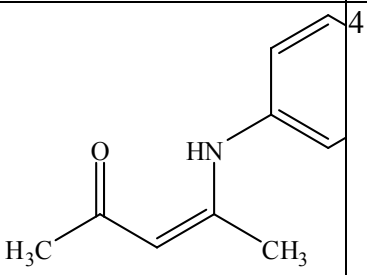
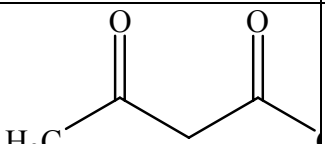
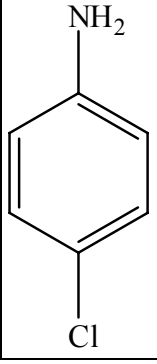
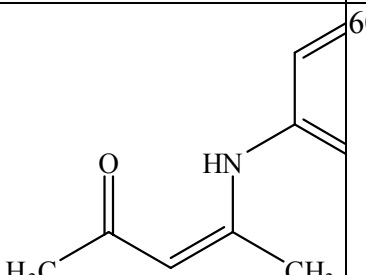
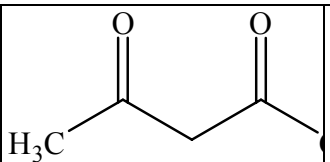
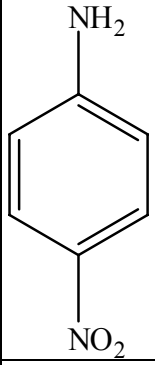
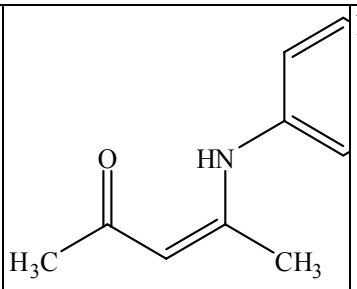
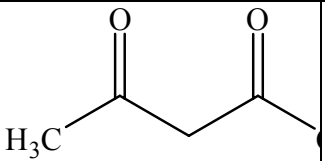
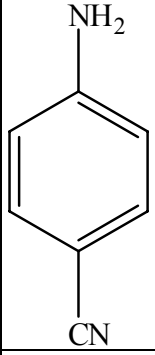
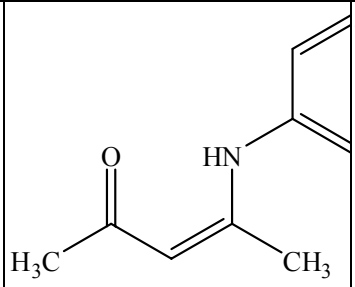
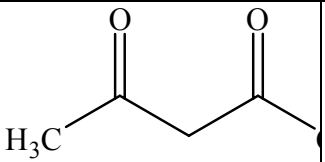
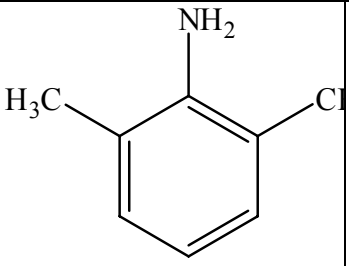
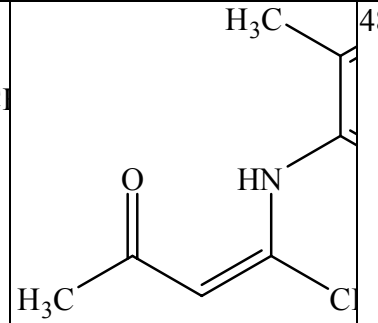
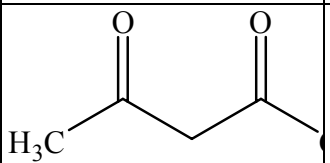
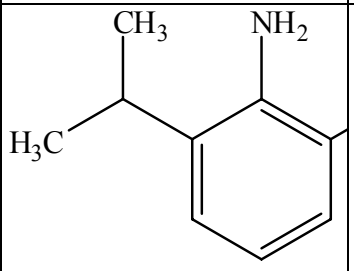
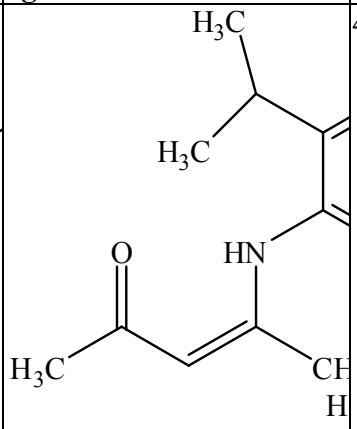
Table 2. Condensation reaction of acetylacetone with aniline in the presence of different organic solvents[a]

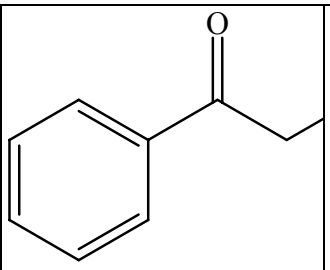
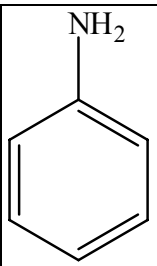
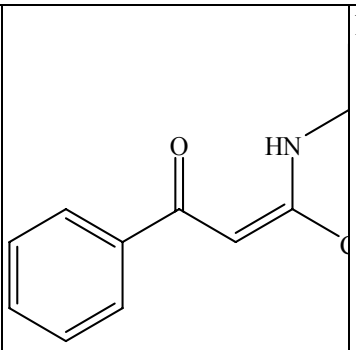
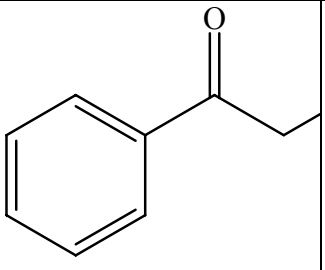
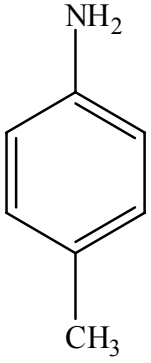
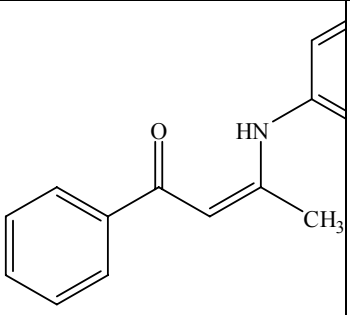
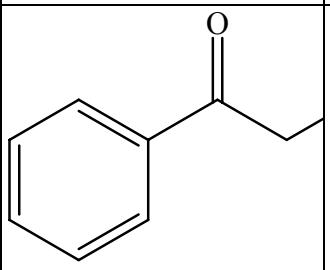
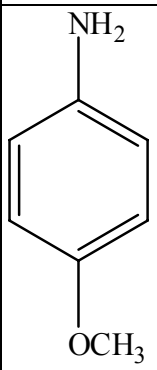
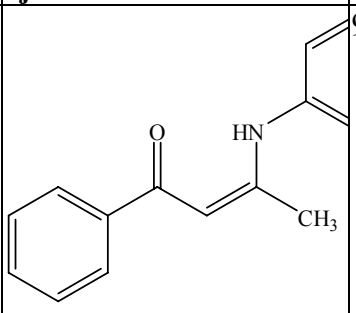
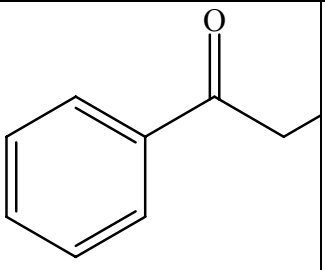
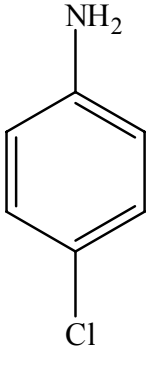
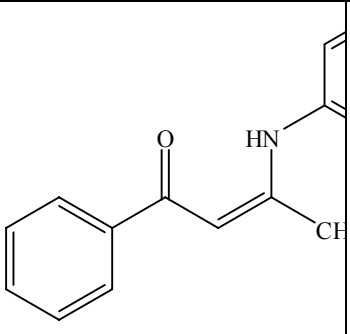
Entry	Solvent	Catalyst	Time (h)	Temperature/°C	Yields[b] (%)
1	$CHCl_3$	HCOOH	4	85	54
2	$CHCl_2$	HCOOH	4	85	55
3	CH_3OH	HCOOH	4	85	98
4	CH_3CH_2OH	HCOOH	4	85	87
5	$C_6H_5CH_3$	HCOOH	4	85	70
6	C_6H_6	HCOOH	4	85	76

[a]Reaction conditions: acetylacetone (1.03 g, 10 mmol), aniline (0.91 g, 10 mmol), formic acid catalyst (1.0 mol%). [b]Isolated yields.

Table 3. Reaction of β-diketones with anilinescatalysed by formic acid in methanol[a]

Entry	Diketone	Primary Amine	Product	Mp (°C)	Time (h)	Yield[b](%)
1			 **3a**	47-48	4	98
2			 **3b**	67-68	4	96
3			 **3c**	41-42	4	97
4			 **3d**	60-62	4	98

5			 **3e**	142-143	4	95
6			 **3f**	86-88	4	94
7			 **3g**	48-49	4	95
8			 **3h**	45-47	4	93

9			 **3i**	108-110	4	97
10			 **3j**	88-89	4	96
11			 **3k**	92-93	4	96
12			 **3l**	128-129	4	94

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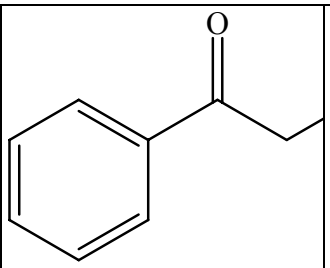
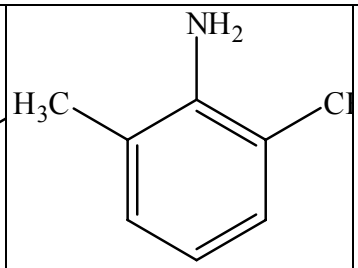
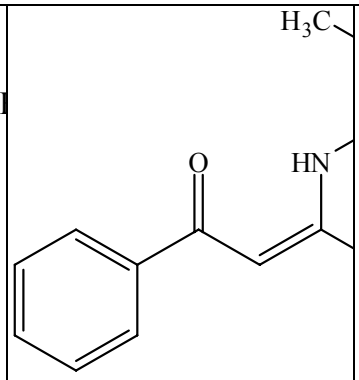
13			 **3m**	109-110	4	95

Table 4 Crystal data and the structure refinement of (*Z*)-4-(4-methoxyphenylamino)pent-3-en-2-one

Empirical formula	$C_{12}H_{15}NO_2$
Formula weight	205.25
Temperature (K)	296 (2) K
Wavelength (Å)	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	11.2440(4)
b (Å)	8.5311(3)
c (Å)	11.6168(4)
α (°)	90°
β (°)	102.163(2)°
γ (°)	90°
Volume ($Å^3$)	1089.31(7)$Å^3$
Z	4
Density (calculated) (Mg/m^3)	1.252 Mg/m^3
Absorption coefficient (mm^{-1})	0.085 mm^{-1}
F_{000}	440
Crystal size	0.45 x 0.18 x 0.14 mm^3
Theta range for data collection	1.85 to 30.93°
Index ranges	$-16 \le h \le 16$, $-12 \le k \le 12$, $-16 \le l \le 16$
Reflections collected	18529
Independent reflections	3448 [R(int) = 0.0218]
Refinement method	Full-matrix least-squares on F^2
Completeness to theta = 25.50°	99.6 %
Max. and min. Transmission	0.7461 and 0.6940
Data / restraints / parameters	3448 /0 /143
Goodness-of-fit on F^2	1.032
Final R indices [I>2sigma(I) = 2608 data]	R1 = 0.0437, wR2 = 0.1198
R indices (all data)	R1 = 0.0594, wR2 = 0.1329
Largest diff. peak and hole ($e.Å^{-3}$)	0.159 and -0.184 $e.Å^{-3}$

Table 5. Selected bond lengths(Å) and bond angles(°) of (*Z*)-4-(4-methoxyphenylamino)pent-3-en-2-one

Bond length	(Å)
N(1)-C(4)	1.3509(13)
N(1)-C(6)	1.4203(13)
O(1)-C(2)	1.2467(13)
C(7)-C(6)	1.3862(15)
C(7)-C(8)	1.3896(16)
C(6)-C(12)	1.3923(15)
C(12)-C(11)	1.3774(15)
C(9)-O(2)	1.3736(14)
C(9)-C(8)	1.3823(16)
C(9)-C(11)	1.3900(16)
O(2)-C(10)	1.4139(18)
C(3)-C(4)	1.3781(15)
C(3)-C(2)	1.4200(15)
C(4)-C(5)	1.4968(15)
C(2)-C(1)	1.5090(16)
Bond angle	**(°)**
C(4)-N(1)-C(6)	128.05(9)
C(6)-C(7)-C(8)	120.79(10)
C(7)-C(6)-C(12)	118.36(10)
C(7)-C(6)-N(1)	124.26(9)
C(12)-C(6)-N(1)	117.36(9)
C(11)-C(12)-C(6)	120.89(10)
O(2)-C(9)-C(8)	124.93(11)
O(2)-C(9)-C(11)	116.03(10)
C(8)-C(9)-C(11)	119.04(10)
C(9)-O(2)-C(10)	117.52(11)
C(4)-C(3)-C(2)	125.19(9)
N(1)-C(4)-C(3)	121.11(10)
N(1)-C(4)-C(5)	119.89(10)
C(3)-C(4)-C(5)	118.98(10)
O(1)-C(2)-C(3)	123.38(10)
O(1)-C(2)-C(1)	118.95(10)
C(3)-C(2)-C(1)	117.64(10)
C(9)-C(8)-C(7)	120.32(10)
C(12)-C(11)-C(9)	120.48(10)

Table 6. Torsion angles [°] for (*Z*)-4-(4-methoxyphenylamino)pent-3-en-2-one

C(4)-N(1)-C(6)-C(7)	-44.9(2)
C(4)-N(1)-C(6)-C(12)	136.7(1)
C(6)-N(1)-C(4)-C(3)	-167.4(1)
C(6)-N(1)-C(4)-C(5)	10.9(2)
C(8)-C(7)-C(6)-N(1)	177.7(1)
C(8)-C(7)-C(6)-C(12)	-3.8(2)
C(6)-C(7)-C(8)-C(9)	1.7(2)
N(1)-C(6)-C(12)-C(11)	-178.6(1)
C(7)-C(6)-C(12)-C(11)	2.8(2)
C(6)-C(12)-C(11)-C(9)	0.3(2)
C(8)-C(9)-O(2)-C(10)	4.3(2)
C(11)-C(9)-O(2)-C(10)	-176.2(1)
O(2)-C(9)-C(8)-C(7)	-179.1(1)
C(11)-C(9)-C(8)-C(7)	1.5(2)
O(2)-C(9)-C(11)-C(12)	178.0(1)
C(8)-C(9)-C(11)-C(12)	-2.5(2)
C(2)-C(3)-C(4)-N(1)	5.2(2
C(2)-C(3)-C(4)-C(5)	-173.0(1)
C(4)-C(3)-C(2)-O(1)	-5.4(2)
C(4)-C(3)-C(2)-C(1)	172.5(1)

Scheme. 1. Synthesis of β-enaminonesby the condensation reaction of β-diketones with anilinesin the presence of formic acid.

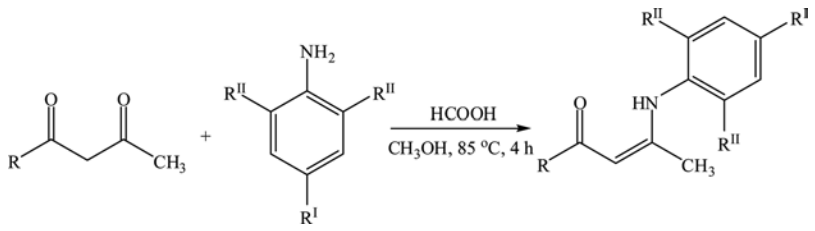


Figure 1. Molecular structure of (*Z*)-4-(4-methoxyphenylamino)pent-3-en-2-oneshowing 50% probability displacement ellipsoids.

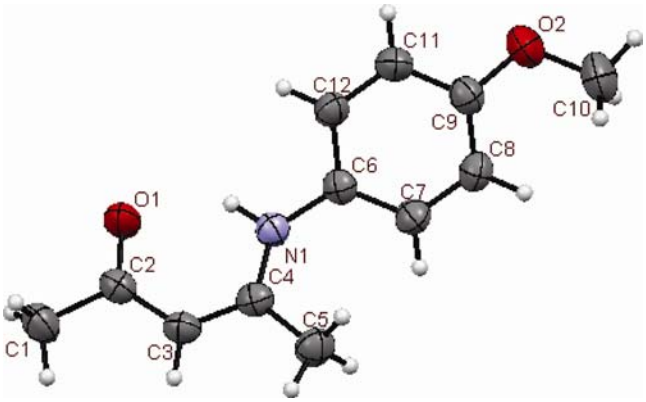


Figure 2. Packing diagram of (*Z*)-4-(4-methoxyphenylamino)pent-3-en-2-oneapproximately viewed along the *b* axis.