# Zinc triflate catalysed synthesis of β-enamino ketones(esters) under solvent-free conditions

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An efficient and mild procedure is described for the synthesis of a series of β-enamino ketones(esters) from 1,3-dicarbonyl compounds and aliphatic and aromatic amines using zinc triflate as the catalyst.

**Keywords:** zinc triflate, β-enamino ketones(esters), solvent-free conditions

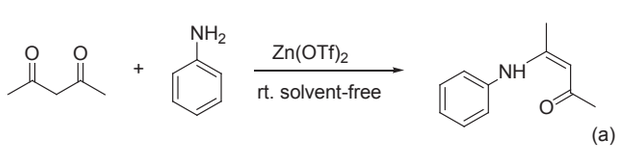
Enamination of 1,3-dicarbonyl compounds (β-diketones and β-ketoesters) to form β-enamino ketones (esters) is an important and widely used organic reaction.[1] β-Enamino ketones and esters have served as versatile intermediates for the synthesis of some biologically important natural products such as alkaloids, spiropyrrolines[2] and some compounds with anti-bacterial,[3] anti-convulsant,[4] anti-inflammatory,[5] and anti-tumour activities.[6] As a result, much effect has been devoted to the development of effective methods for the synthesis of β-enamino ketones and esters.

*Synthesis of β-enamino ketones (esters); general procedure*

Enamination of 1,3-dicarbonyls with amines using various of catalysts including $BF_3.OEt_2$,[7] $Mg(ClO_4)_2$,[8] $Bi(OTf)_3$,[9] $Sc(OTf)_3$,[10] $Yb(OTf)_3$,[11] $NaHSO_4$,[12] $InBr_3$,[13] $CoCl_2{\cdot}6H_2O$,[14] $CeCl_3{\cdot}7H_2O$,[15] $ZrOCl_2{\cdot}8H_2O$,[16] $Zn(ClO_4)_2{\cdot}6H_2O$,[17] $Zn(OAc)_2{\cdot}2H_2O$,[18] $ZrCl_4$,[19] $NaAuCl_4$,[20] $SnCl_4$,[21] $I_2$,[22] silica-supported $H_2SO_4$,[23] silica-supported $SbCl_3$,[24] phosphotungstic acid,[25] $SO_2$-$4ZrO_2$,[26] copper nanoparticles,[27] Ag nanoparticles,[28] $Cu(NO_3)_2$ $3(H_2O)$,[29] Silica-Supported $LiHSO_4$,[30] $Fe(HSO_4)_3$,[31] trimethylsilyl trifluoromethanesulfonate (TMSTf),[32] montmorillonite K10,[33] nano ZnO,[34] $VO(acac)_2$),[35] $KH_2PO_4$ [36] and Ag nanoparticles in hollow magnetic mesoporous spheres.[37]

Many of the reported catalysts for this transformation have some drawbacks such as long reaction times, high catalyst loading, low yields, use of solvents, and deactivation of catalyst on repeated use. Thus, there is a need to develop a new catalyst for synthesis of β-enamino ketones and esters.

Zinc triflate [$Zn(OTf)_2$)] is an important Lewis acid catalyst that has been used to catalyse many organic reactions, *e.g.* cascade reaction of anilines with aromatic aldehydes and carbonyl compounds,[38] Mannich-type reaction of the electron-deficient aromatic amines with the electron-deficient aromatic aldehydes and diethyl malonic ester[39] and intermolecular hydroamination of vinylarenes and anilines.[40] To the best of our knowledge, the synthesis of β-enamino ketones (esters) by the enamination of 1,3-dicarbonyls using catalysis with $Zn(OTf)_2$ has not yet been reported. Herein, we report an easy and mild procedure for the $Zn(OTf)_2$-catalysed enamination of 1,3-dicarbonyls with amines at room temperature.




**Scheme 1**

## Results and discussion

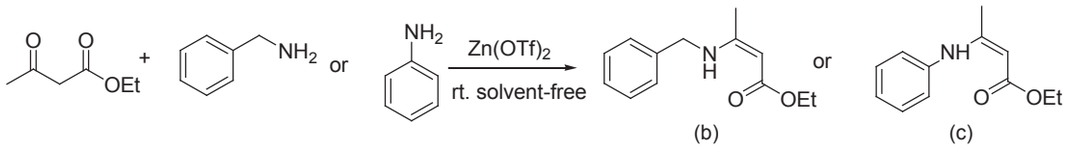
In our initial study, the reaction of acetylacetone (β-diketone) with aniline was chosen as a model substrate for optimisation of the reaction conditions (Scheme 1) using the following procedures: a mixture of acetylacetone (1.1 mmol), aniline (1 mmol) and $Zn(OTF)_2$ (0.5 mol%–10 mol%) was stirred at room temperature for certain times. As shown in Table 1, the mixture was stirred in the presence of 0.5 mol%, 1 mol% and 2 mol% of $Zn(OTf)_2$ and the product **a** was isolated in 78, 85 and 96% yield (Table 1, entries 1, 2, 3), respectively. The reaction was then examined with 5 mol% and 10 mol% of catalyst and the product was obtained in 94 and 96% yield, respectively. Consequently 2 mol% of catalyst was sufficient to obtain the best yield. The reaction conditions were used to check the reaction of ethyl acetoacetate (β-ketoesters) with benzylamine and aniline (Scheme 2). The reactions proceeded well and excellent yields were obtained (Table 1, entries 6, 7).

Then a variety of 1,3-dicarbonyl compounds and aliphatic and aromatic amines (primary and secondary amine) were examined under our reaction conditions. The results are summarised in Table 2, from which it can be seen that the majority of 1,3-dicarbonyl compounds could have reacted with primary amines (Table 2, entries 1–21) and afforded good yields. The reaction with aliphatic amines proceeded easily in a shorter time than those with aromatic amines. The reaction with

**Table 1** Optimisation of reaction condition using $Zn(OTf)_2$ catalyst[a]

| Entry | Catalyst[$Zn(OTf)_2$] /mol% | Times /min | Product | Yields/%[b] |
|---|---|---|---|---|
| 1 | 0.5 | 30 | a | 78 |
| 2 | 1 | 20 | a | 85 |
| 3 | 2 | 10 | a | 96 |
| 4 | 5 | 10 | 3 | 94 |
| 5 | 10 | 10 | a | 95 |
| 6 | 2 | 5 | b | 96 |
| 7 | 2 | 12 | c | 95 |

[a]Acetylacetone (1.1 mmol), aniline (1 mmol), ethyl acetoacetate (1.1 mmol).
[b]Isolated yields.




**Scheme 2**

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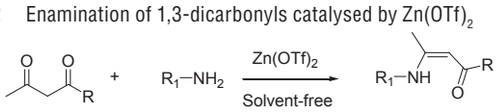
**Table 2** Enamination of 1,3-dicarbonyls catalysed by $Zn(OTf)_2$




| Entry | R | $R_1$ | Times/min | Yields/% |
|---|---|---|---|---|
| **1** | $CH_3$ | Ph | 10 | 96 |
| **2** | Ph | Ph | 8 | 92 |
| **3** | OMe | Ph | 12 | 94 |
| **4** | OEt | Ph- | 12 | 94 |
| **5** | OEt | 1-Np-$(CH_3)$CH- | 5 | 97 |
| **6** | OEt | 2-Cl-6-$MeC_6H_4$- | 15 | 94 |
| **7** | $CH_3$ | 2-Cl-6-$MeC_6H_4$- | 12 | 96 |
| **8** | OMe | $C_6H_5CH_2$- | 4 | 90 |
| **9** | OMe | 4-$MeC_6H_4$- | 2 | 95 |
| **10** | OEt | $C_6H_{11}$- | 3 | 94 |
| **11** | OEt | $(CH_3)_2CH$- | 2 | 96 |
| **12** | OEt | 4-$MeOC_6H_4$- | 6 | 97 |
| **13** | $CH_3$ | 4-$MeC_6H_4$- | 2 | 95 |
| **14** | $CH_3$ | 4-$ClC_6H_4$- | 15 | 94 |
| **15** | $CH_3$ | 4-$MeOC_6H_4$- | 3 | 97 |
| **16** | OMe | 4-$ClC_6H_4$- | 15 | 92 |
| **17** | OEt | 4-$NO_2C_6H_4$- | 20 | 53 |
| **18** | Ph | 4-$MeOC_6H_4$- | 4 | 96 |
| **19** | Ph | 4-$MeC_6H_4$- | 6 | 97 |
| **20** | Ph | 4-$ClC_6H_4$- | 10 | 95 |
| **21** | OEt | $C_6H_{11}CH_2$- | 5 | 96 |
| **22** | OEt | Piperidine | 60 | |
| **23** | OMe | Piperidine | 60 | |

aromatic amines with electron-donating (p-OMe) substituents proceeded more easily and gave better yields than those with electron-withdrawing substituents (p-$NO_2$). For example, the yield of compound **15** is higher than compound **17**.

However, it was noted that 1,3-dicarbonyl compounds could not react with any secondary amines (**22** and **23**). For example, the mixture of ethyl acetolacetate or methyl acetolacetate/piperidine (**22** and **23**) and $Zn(OTf)_2$ was stirred at 1 h, no products were obtained. The reaction still did not occur on increasing the catalyst (10, 20, 30 50 mol%) and raising the temperature (40, 60, 80 °C).

Additionally, we found that all 1,3-dicarbonyl compounds including β-diketones and β-ketoesters reacted with primary amines to give the Z-β-enaminones and Z-β-enaminoesters with 100% stereoselectivity, respectively. The Z-form configuration of the products was confirmed by $^1$HNMR analysis and NOE experiments. The proton of the –NH-group appearing at a lower field ($\delta < 8.0$) indicated the formation of an intramolecular hydrogen bond, which stabilised the products. Therefore this reaction was stereospecific.

This method was successfully applied to enamination of 1,3-dicarbonyls. In all cases, we found that amine attack took place only at the methyl ketone carbonyl for 1,3-dicarbonyls. The use of $Zn(OTf)_2$ as a heterogeneous catalyst showed short reaction times, high yields and mild reaction conditions. The other advantage of the use of this catalyst for this reaction, is the recyclability. Since $Zn(OTf)_2$ is not soluble in organic solvents, it could be separated by simple filtration, washed with ethyl acetate and dried.

In conclusion, we report an efficient catalyst for chemo-and regioselective synthesis β-enamino ketones and esters using primary amines and 1,3-dicarbonyl compounds. The reaction was catalysed by $Zn(OTf)_2$ at room temperature under solvent-free conditions. All the products were identified by $^1$H NMR, $^{13}$C NMR, MS, HRMS, and IR.

## Experimental

All reagents were purchased from commercial sources and used without further purification. Melting points were determined on a RY-1 hot stage microscope and are uncorrected. IR spectra were determined as KBr pellets on a Thermo–Nicolet 6700 spectrophotometer. $^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker Avance DPX-300 MHz/500 MHz instrument in $CDCl_3$, chemical shifts (δ) were given in part per million (ppm) relative to TMS as an internal standard. The HRMS spectra were obtained on a Thermo Finnigan spectrometer, model MAT 95XP. All reactions were monitored by TLC on silica gel GF-254 glass plates (E. Merck) and viewed under UV light at 254 nm.

*Synthesis of β-enamino ketones and esters; general procedure*

$Zn(OTf)_2$ (0.05 mmol) was added into a mixture of primary amines (1 mmol) and the 1,3-dicarbonyl compounds (1.1 mmol) in a 50 mL round bottomed flask and it was kept stirring at room temperature. The completion of the reaction was monitored by TLC. The product was dissolved in ethyl acetate (50 mL) and filtered. The pure product was obtained by directly passing through a silica gel (200–300 mesh) column using petroleum ether/ethyl acetate and identified by IR, $^1$H NMR, $^{13}$C NMR, MS, and HRMS.

Most of the products are known, except for entries 5, 6, 7 in Table **2**. All new compounds were characterised by IR, $^1$H NMR, $^{13}$C NMR and HRMS. All known products were characterised by IR, $^1$H NMR and $^{13}$C NMR.

*(Z)-4-(Phenylamino)pent-3-en-2-one* (**1**): Yellow solid, m.p. 46–48 °C, (lit.[13] 45–47 °C). IR (KBr, $cm^{-1}$): 3443, 3348, 3234, 2988, 2916, 1632, 1558, 1510, 1287, 1088. $^1$H NMR ($CDCl_3$, 300 MHz) δ 12.42(s, 1H), 7.03–7.46(m, 5H), 5.16(s, 1H), 2.12 (s, 3H), 2.01(s, 3H). $^{13}$C NMR ($CDCl_3$, 75 MHz) δ 19.82, 29.20, 97.68, 124.63, 124.63, 125.54, 129.08, 129.08, 138.68, 160.31, 196.07.

*(Z)-1-Phenyl-3-(phenylamino)but-2-en-1-one* (**2**): Yellow solid, m.p. 108–109 °C, (lit.[30] 109–111 °C). IR (KBr, $cm^{-1}$): 3435, 1621, 1589, 1547, 1325, 1267. $^1$H NMR (CDCl3, 300 MHz) δ 13.14(s, 1H), 7.21–7.96(m, 10H), 5.93(s, 1H), 2.18(s, 3H). $^{13}$C NMR ($CDCl_3$, 75 MHz) δ 21.03, 94.71, 125.24, 125.24, 126.17, 127.53, 127.53, 128.66, 129.12, 129.12, 129.64, 129.64, 131.44, 139.02, 162.67, 189.12.

*(Z)-Methyl 3-(phenylamino)but-2-enoate* (**3**): Yellow oil;[13] IR (KBr, $cm^{-1}$): 3244, 2992, 1651, 1589, 1467, 1423, 1321, 1267, 1165. $^1$H NMR ($CDCl_3$, 300 MHz) δ 10.37(s, 1H), 7.34(m, 2H), 7.12(m, 3H), 4.69(s, 1H), 3.68(s, 3H), 1.98(s, 3H). $^{13}$C NMR ($CDCl_3$, 75 MHz) δ 20.20, 50.19, 85.63, 124.44, 124.44, 125.03, 128.98, 128.98, 139.31, 159.04, 170.02.

*(Z)-Ethyl 3-(phenylamino)but-2-enoate* (**4**): Yellow oil;[13] IR (KBr, $cm^{-1}$): 3256, 2979, 1651, 1596, 1503, 1440, 1359, 1272, 1164. $^1$H NMR ($CDCl_3$, 300 MHz) δ 10.38(s, 1H), 7.30–7.34(m, 2H), 7.07–7.17(m, 3H), 4.70(s, 1H), 4.11–4.18(m, 2H), 1.99(s, 3H), 1.28(m, 3H). $^{13}$C NMR ($CDCl_3$, 75 MHz) δ 14.48, 20.16, 58.63, 85.94, 124.26, 124.78, 128.93, 139.23, 158.81, 170.25.

*(Z)-Ethyl 3-(1-(naphthalen-1-yl)ethylamino)but-2-enoate* (**5**): Yellow oil. IR (KBr, $cm^{-1}$):3279, 3061, 1650, 1607, 1493, 1443, 1266, 1170. $^1$H NMR ($CDCl_3$, 300 MHz) δ 8.47(b, 1H), 7.02–7.71(m, 7H), 4.64(s, 1H), 4.06–4.17(m, 3H), 1.92(s, 3H), 1.48(s, 3H), 1.15(m, 3H). $^{13}$C NMR ($CDCl_3$, 75 MHz) δ 13.68, 21.46, 22.52, 51.23, 62.05, 82.79, 122.36, 123.69, 124.76, 124.85, 126.88, 127.13, 128.42, 134.53, 134.69, 166.46, 168.59. HRMS calcd for $C_{18}H_{22}NO_2$ $[M+H]^+$: 284.1651, found: 284.1653.

*(Z)-Ethyl 3-(2-chloro-6-methylphenylamino)but-2-enoate* (**6**): Yellow oil. IR (KBr, $cm^{-1}$): 3256, 3058, 1652, 1605, 1483, 1436, 1232, 1127. $^1$H NMR ($CDCl_3$, 500 MHz) δ 9.79(b, 1H), 6.58(m, 1H), 6.92(d, $J$=7.35, 1H), 7.27(m, 1H), 4.75(b, 1H), 4.17(m, 2H), 1.29(m, 3H), 1.65(s, 3H), 2.16(s, 3H). $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 14.45, 17.74, 18.43, 58.59, 84.86, 118.11, 123.36, 126.90, 127.92, 128.55, 141.08, 160.59, 170.45. HRMS calcd for $C_{13}H_{16}ClNO_2$ $[M+Na]^+$: 276.0767, found: 276.0769.

*(Z)-4-(2-Chloro-6-methylphenylamino)pent-3-en-2-one* (**7**): Yellow oil. IR (KBr, $cm^{-1}$): 3450, 3061, 2922, 1617, 1566, 1496, 1463, 1274, 1172. $^1$H NMR ($CDCl_3$, 500 MHz) δ 11.97(b, 1H), 7.12–7.29(m, 3H), 5.25(s, 1H), 2.25(s, 3H), 2.11(s, 3H), 1.68(s, 3H). $^{13}$C NMR ($CDCl_3$, 125 MHz) δ 14.76, 21.55, 28.79, 96.87, 118.43, 124.72, 126.85, 128.46, 131.68, 146.44,

160.58, 198.02. HRMS calcd for $C_{12}H_{14}ClNONa$ $[M+Na]^+$: 246.0662, found: 246.0665.

*(Z)-Methyl 3-(benzylamino)but-2-enoate* (**8**): Yellow oil, (lit.[35] Yellow oil). IR (KBr, $cm^{-1}$): 3446, 3133, 1646, 1605, 1451, 1400, 1316, 1284, 1238, 1172. $^1H$ NMR ($CDCl_3$, 300 MHz) δ 8.94(s, 1H), 7.26–7.32(m, 2H), 7.23(m, 3H), 4.53(s, 1H), 4.42(m, 2H), 3.63(s, 3H), 1.93(s, 3H). $^{13}C$ NMR ($CDCl_3$, 75 MHz) δ 19.43, 46.80, 50.01, 82.70, 126.51, 126.51, 127.18, 128.60, 128.60, 138.46, 161.69, 170.59.

*(Z)-Methyl 3-(p-toluidino)but-2-enoate* (**9**): Yellow solid, m.p. 56–57 °C, (lit.[31]. 57–58 °C). IR (KBr, $cm^{-1}$): 3246, 2992, 1652, 1602, 1489, 1364, 1277, 1167. $^1H$ NMR ($CDCl_3$, 300 MHz) δ 10.24(s, 1H), 6.96–7.13(m, 4H), 4.66(s, 1H), 3.68(s, 3H), 2.34(s, 3H), 1.96(s, 3H). $^{13}C$ NMR ($CDCl_3$, 75 MHz) δ 20.09, 20.81, 50.14, 85.02, 124.69, 124.69, 129.58, 130.83, 130.83, 136.57, 159.44, 170.71.

*(Z)-Ethyl 3-(cyclohexylamino)but-2-enoate* (**10**): Yellow oil,[13] IR (KBr, $cm^{-1}$): 3230, 2930, 1654, 1608, 1596, 1448, 1276, 1172. $^1H$ NMR (300 MHz, $CDCl_3$) δ 8.64 (s, 3H), 4.38(s, 1H), 4.10(m, 2H), 3.29–3.34(m, 1H), 1.92(s, 3H), 1.30–1.91(m, 10H), 1.24(m, 3H). $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 14.72, 19.14, 24.63, 25.41, 34.52, 51.40, 58.09, 60.38, 81.78, 160.80, 170.52.

*(Z)-Ethyl 3-(isopropylamino)but-2-enoate* (**11**): Yellow oil,[13] IR (KBr, $cm^{-1}$): 3274, 2972, 2933, 1656, 1601, 1498, 1444, 1276, 1157. $^1H$ NMR (300 MHz, $CDCl_3$) δ 8.48(s, 1H), 4.40 (s, 1H), 4.10(m, 2H), 3.62–3.73 (m, 1H), 1.92 (s, 3H), 1.21(m, 9H). $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 14.49, 19.12, 24.02, 44.28, 58.01, 81.59, 160.73, 170.54.

*(Z)-Ethyl 3-(4-methoxyphenylamino)but-2-enoate* (**12**): Yellow solid, m.p. 44–46, (lit.[30] 45–47). IR (KBr, $cm^{-1}$): 3260, 2948, 2835, 1650, 1616, 1514, 1478, 1424, 1247, 1211, 1164. $^1H$ NMR (300 MHz, $CDCl_3$) δ 10.16(s, 1H), 6.86–7.05(m, 4H), 4.65(s, 1H), 4.11–4.14(m, 2H), 3.80(s, 3H), 1.87(s, 3H), 1.28(m, 3H). $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 14.16, 19.72, 55.01, 58.17, 84.44, 113.82, 113.82, 126.39, 131.83, 131.83, 157.14, 159.58, 170.08.

*(Z)-4-(p-Toluidino)pent-3-en-2-one* (**13):** Yellow solid, m.p. 64–65 °C, (lit.[31] 66–68). IR (KBr, $cm^{-1}$): 3440, 3031, 2990, 2933, 2860, 1610, 1576, 1276. $^1H$ NMR (300 MHz, $CDCl_3$) δ 12.39(s, 1H), 7.06–7.24(m, 4H), 5.16(s, 1H), 2.38(s, 3H), 2.11(s, 3H), 1.94(s, 3H). $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 19.76, 20.93, 29.17, 97.07, 124.86, 124.86, 129.67, 129.67, 135.52, 136.02, 160.64, 195.91.

*(Z)-4-(4-Chlorophenylamino) pent-3-en-2-one* (**14**): Yellow solid, m.p. 58–60 °C, (lit.[31] 61–62). IR (KBr, $cm^{-1}$): 3444, 3350, 3220, 3058, 2990, 2921, 1618, 1562, 1494, 1272. $^1H$ NMR (300 MHz, $CDCl_3$) δ 12.45(s, 1H), 7.06–7.28(m, 4H), 5.24(s, 1H), 2.12(s, 3H), 1.98(s, 3H). $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 19.78, 29.26, 98.16, 125.85, 125.85, 129.28, 129.28, 130.94, 137.34, 160.13, 196.52.

*(Z)-4-(4-Methoxyphenylamino) pent-3-en-2-one* (**15**): Yellow solid, m.p. 40–42 °C, (lit.[31] 41–43). IR (KBr, $cm^{-1}$): 3443, 3352, 3220, 2991, 2916, 1620, 1567, 1487, 1243. $^1H$ NMR (300 MHz, $CDCl_3$) δ 12.34(s, 1H), 6.90–7.06(m, 4H), 5.15(s, 1H), 3.74(s, 3H), 2.03(s, 3H), 1.90(s, 3H). $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 19.63, 29.04, 55.44, 96.85, 114.28, 114.28, 126.65, 126.65, 131.46, 157.73, 161.32, 195.76.

*(Z)-Methyl 3-(4-chlorophenylamino)but-2-enoate* (**16**): Yellow solid, m.p. 62–63 °C, (lit.[31] 61–62). IR (KBr, $cm^{-1}$): 3276, 2944, 1652, 1598, 1487, 1352, 1277, 1167. $^1H$ NMR ($CDCl_3$, 300 MHz) δ 10.34(s, 1H), 7.01–7.28(m, 4H), 4.73(s, 1H), 3.68(s, 3H), 1.99(s, 3H). $^{13}C$ NMR ($CDCl_3$, 75 MHz) δ 20.09, 50.31, 86.42, 125.53, 125.53, 129.07, 137.94, 137.94, 158.52, 162.34, 170.62.

*(Z)-4-(4-Nitrophenylamino)pent-3-en-2-one* (**17**): Yellow solid, m.p. 110–112 °C, (lit.[13] 111–112). IR (KBr, $cm^{-1}$): 3306, 3095, 2992, 1650, 1592, 1509, 1334, 1287, 1179. $^1H$ NMR (300 MHz, $CDCl_3$) δ 10.92(s, 1H), 8.20(d, $J$=9.0 Hz, 2H), 7.11(d, $J$=9.0 Hz, 2H), 4.86(s, 1H), 4.21(m, 2H), 2.21(s, 3H), 1.30(m, 3H). $^{13}C$ NMR (75 MHz, $CDCl_3$) δ 14.45, 21.26, 61.57, 84.46, 119.14, 119.14, 122.65, 122.65, 139.05, 152.25, 162.04, 167.23.

*(Z)-3-(4-Methoxyphenylamino)-1-phenylbut-2-en-1-one* (**18**): Yellow solid, m.p. 103–104 °C, (lit.[31] 103–105). IR (KBr, $cm^{-1}$): 3051, 3010, 2949, 2830, 1623, 1607, 1587, 1508, 1330. $^1H$ NMR ($CDCl_3$, 300 MHz) δ 12.96(s, 1H), 6.90–7.94(m, 9H), 5.90(s, 1H), 3.85(s, 3H), 2.10(s, 3H). $^{13}C$ NMR ($CDCl_3$, 75 MHz) δ 20.31, 55.54, 93.61, 126.59, 126.59, 127.14, 128.32, 128.32, 130.84, 131.49, 131.49, 140.18, 140.18, 157.90, 163.23, 188.41.

*(Z)-3-(p-Toluidino)-1-phenylbut-2-en-1-one* (**19**) Yellow solid, m.p. 83–85 °C, (lit.[31] 90–92). IR (KBr, $cm^{-1}$): 3446, 3047, 2912, 1993, 1899, 1622, 1572, 1446, 1377. $^1H$ NMR (CDCl3, 300 MHz) δ 13.03(s, 1H), 7.07–7.94(m, 9H), 5.88(s, 1H), 2.37(s, 3H), 2.12(s, 3H). $^{13}C$ NMR ($CDCl_3$, 75 MHz) δ 20.81, 21.43, 94.34, 125.31, 125.31, 127.52, 128.68, 128.68, 130.23, 131.27, 131.27, 136.17, 136.17, 140.48, 163.11, 190.02.

*(Z)-3-(4-Chlorophenylamino)-1-phenylbut-2-en-1-one* (**20**): Yellow solid, m.p. 126–127 °C, (lit.[31] 126–128). IR (KBr, $cm^{-1}$): 3411, 3080, 3051, 1623, 1588, 1549, 1446, 1326, 1247. $^1H$ NMR (CDCl3, 300 MHz) δ 13.10(s, 1H), 7.10–7.95(m, 9H), 5.91(s, 1H), 2.16(s, 3H). $^{13}C$ NMR ($CDCl_3$, 75 MHz) δ 20.51, 94.69, 125.93, 125.93, 127.06, 128.43, 128.43, 129.44, 131.11, 131.11, 131.28, 137.33, 137.33, 139.90, 161.84, 189.16.

*(Z)-Ethyl 3-(benzylamino)but-2-enoate* (**21**): Yellow oil,[35] IR (KBr, $cm^{-1}$): 3315, 2979, 1652, 1606, 1543, 1477, 1423, 1337, 1276. $^1H$ NMR (500 MHz, $CDCl_3$) δ 10.29(s, 1H), 7.11(m, 2H), 6.96(m, 3H), 4.66(s, 1H), 4.15(m, 4H), 1.91(s, 3H), 1.25(m, 3H). $^{13}C$ NMR (125 MHz, $CDCl_3$) δ 14.71, 19.52, 24.13, 46.84, 58.49, 83.18, 126.78, 127.44, 128.79, 138.83, 162.81, 170.60.

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