Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

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Published online: 29 Oct 2009.

Synthetic Communications®, 39: 4180–4198, 2009

ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397910902898528

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Abstract: Metal triflates have been used to catalyze synthesis of β-enamino ketones or pyrroles from amines and 1,3-dicarbonyl or 1,4-dicarbonyl compounds under solvent-free conditions, respectively. Among different metal triflates screened, 0.5 mol% $Ga(OTf)_3$ efficiently promoted the reactions to give excellent yields. In addition, the catalyst could be recovered easily after the reactions and reused without evident loss in activity.

Keywords: β-Enamino ketones, gallium(III) triflate, pyrroles, solvent-free conditions

INTRODUCTION

A variety of reactions using Lewis acids have been developed in organic synthesis.[1] The majority of the strong and efficient Lewis acids such as $AlCl_3$, BF_3, $TiCl_4$, and $SnCl_4$ used in various organic transformations are prone to fast hydrolysis and deactivate readily in the presence of even a

Received March 9, 2008.
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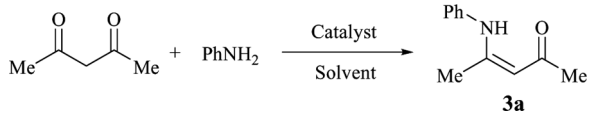
small amount of water. Generally, stoichiometric or even excess amounts of conventional Lewis acids are needed, and the catalyst cannot be recovered and reused after the reactions are completed. In recent decades, as consciousness of protecting the environment has strengthened, methods that are cheap or environmentally friendly have been advocated. Metal triflates have advantages of being water tolerant, air stable, recoverable from water, operationally simple (not requiring anhydrous treatment), strongly tolerant of oxygen, nitrogen, phosphorus, and sulfur-containing reaction substrates and functional groups, and reusable, showing their significant potential as safe and environmentally benign catalysts.[2] Thus, metal triflates as new versatile Lewis acids have been widely used in organic synthesis, such as formation of the C−C bond or C−X (X=N, O, P, etc.) bond, oxidation and reduction, rearrangement, protection and deprotection, polymerization, and miscellaneous reactions.[2] They can be easily synthesized by reacting metallic oxides with trifluoromethanesulfonic acid.[3]

β-Enamino ketones are the most important intermediates, having become increasingly important in medicinal chemistry and organic synthesis.[4] Consequently, an enormous number of procedures have been developed for the construction of β-enamino ketones.[5] The direct condensation of 1,3-dicarbonyl compounds with amines is the most straightforward method for the synthesis of β-enamino ketones in the presence of various promoting agents.[6] Recently, this condensation reaction has also been performed in water[6l,6o] and ionic liquid medium.[6i,6m]

Pyrroles are important heterocyclic compounds, having become increasingly important in medicinal chemistry and organic synthesis.[7] From the extensive work on the synthesis of pyrroles,[8] the Paal–Knorr reaction is one of the most common approaches in which γ-diketones are converted to pyrroles from 1,4-ketones and primary amines (or ammonia) in the presence of various promoting agents[9] and microwave irradiation.[10]

Although these methods are suitable for certain synthetic conditions, some of these methods often involve the use of stoichiometric and even excess amounts of acids because they can be trapped by nitrogen in this condensation, hazardous organic solvents, tedious workup, and unsatisfactory yield. Thus, they may not be preferred choices in view of green chemistry. Therefore, the development of facile and environmentally friendly methods for the synthesis of β-enamino ketones and pyrroles that can overcome the shortcomings of the previous methods is necessary.

On the other hand, the absence of solvent in organic synthesis and the employment of a small excess of reagent make procedures simpler, saves energy, and prevents solvent waste, hazards, and toxicity. To the



Scheme 1. The model reaction of acetylacetone with aniline under difference conditions.

best of our knowledge, $Ga(OTf)_3$-promoted[11] syntheses of β-enamino ketones and pyrroles have not been reported.

Recently, we have successfully applied metal triflates in several reactions.[12a–13i] In continuation of our interest in solvent-free organic synthesis,[12a,13d,12l] green chemistry, and Lewis acid–catalyzed organic reactions,[12] we herein developed green, simple, and practical methods for the synthesis of β-enamino ketones from 1,3-dicarbonyl compounds with amines and the synthesis of pyrroles from 1,4-dicarbonyl compounds with amines using a catalytic amount of $Ga(OTf)_3$ under solvent-free conditions.

Table 1. Condensation of acetylacetone with aniline under different reaction conditions[a]

Entry	Solvent	Catalyst (mol%)	Time (min)	Yields (%)[b]
1	None	$Cu(OTf)_2$ (5)	60	78
2	None	$Mg(OTf)_2$ (5)	80	47
3	None	$Bi(OTf)_3$ (5)	60	79
4	None	$Yb(OTf)_3$ (5)	60	76
5	None	$Sc(OTf)_3$ (5)	60	83
6	None	$Y(OTf)_3$ (5)	60	81
7	None	$La(OTf)_3$ (5)	60	77
8	None	$Sm(OTf)_3$ (5)	60	82
9	None	$Eu(OTf)_3$ (5)	60	84
10	None	$Ga(OTf)_3$ (5)	25	93
11[c]	None	$Ga(OTf)_3$ (1)	30	92
12	None	$Ga(OTf)_3$ (0.5)	30	92, 90, 89
13	None	$Ga(OTf)_3$ (0.1)	35	82
14	H_2O	$Ga(OTf)_3$ (0.5)	40	72
15	CH_2Cl_2	$Ga(OTf)_3$ (0.5)	30	82
16	CH_3NO_2	$Ga(OTf)_3$ (0.5)	30	86
17	None	None	100	14 (22)[d]

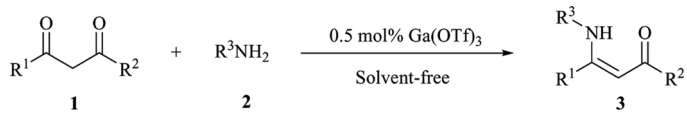
[a]30°C for 25 min.
[b]Isolated yield.
[c]Catalyst was reused three times.
[d]Reaction was run at 50°C for 12 h.

RESULTS AND DISCUSSION

Initially, we investigated the model reaction from acetylacetone with aniline using various metal triflates as catalysts (Scheme 1), and the results are summarized in Table 1. Most of the metal triflates bring out this reaction efficiently under solvent-free conditions. However, $Ga(OTf)_3$ was particularly effective for this reaction in the shortest time (Table 1, entries 10–13). It was observed that **3a** was obtained in only poor yield in the absence of $Ga(OTf)_3$ even after a long reaction time in higher temperature, which also further proved that $Ga(OTf)_3$ does play an important role in the condensation reaction (Table 1, entry 17). Moreover, we also examined the activity of the recycled catalyst; $Ga(OTf)_3$ could be reused three times without any loss of activity (Table 1, entry 12). In addition, we studied the influence of solvent and the amount of catalyst on the catalytic property of the reaction: 0.5 mol% of $Ga(OTf)_3$ was enough, and excessive amount of catalyst did not increase the yield (Table 1, entries 10–13). Obviously, the additional solvent does not make the reaction rate faster. Therefore, we achieved an optimized condition using 0.5 mol% of $Ga(OTf)_3$ as the catalyst under solvent-free conditions.

Because of the good results obtained, we expanded our methodology to synthesize other β-enamino ketones (Scheme 2, Table 2). In all cases, the condensation reactions proceeded smoothly and gave the corresponding products in good to excellent yield in the present protocol.

As shown in Table 2, aromatic amines bearing either electron-donating or electron-withdrawing groups on the aromatic ring were investigated. The substitution groups on the aromatic ring have no obvious effect on the yield and reaction time under the optimal conditions. However, amines with strongly electron-withdrawing groups on the aromatic ring such as *p*-nitroaniline gave the product of **3e** with good yield in a long reaction time (Table 2, entry 5). When an unsymmetrical β-dicarbonyl compound such as benzoylacetone was used as a substrate, the regiochemistry was controlled by the more reactive carbonyl group, which underwent the attack by the amine (Table 2, entries 11–13).



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Scheme 2. The reaction of amines with acetylacetone under solvent-free conditions.

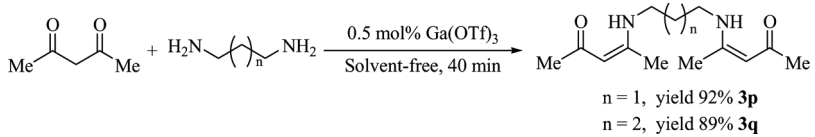
Table 2. Synthesis of β-enamino ketones by catalyzed $Ga(OTf)_3$[a]

Entry	R^1	R^2	R^3	Time (min)	Product	Yield[b](%)
1	Me	Me	C_6H_5	30	**3a**	92
2	Me	Me	*p*-$(CH_3)C_6H_4$	30	**3b**	94
3	Me	Me	*p*-$(OCH_3)C_6H_4$	30	**3c**	91
4	Me	Me	*p*-$(Cl)C_6H_4$	35	**3d**	90
5	Me	Me	*p*-$(NO_2)C_6H_4$	35	**3e**	65 (84)[c]
6	Me	Me	$CH_3CH_2CH_2CH_2$	30	**3f**	91
7	Me	Me	$C_6H_5CH_2$	30	**3g**	92
8	Ph	Ph	C_6H_5	45	**3h**	83
9	Ph	Ph	$C_6H_5CH_2$	50	**3i**	87
10	Ph	Ph	*o*-$(OCH_3)C_6H_4$	45	**3j**	85
11	Me	Ph	C_6H_5	30	**3k**	90
12	Me	Ph	$C_6H_5CH_2$	40	**3l**	90
13	Me	Ph	*o*-$(OCH_3)C_6H_4$	30	**3m**	89
14	Me	Me	*R*-(+)-$C_6H_5CH(CH_3)$	35	**3n**	91
15	Me	Me	*S*-(−)-$C_6H_5CH(CH_3)$	35	**3o**	88

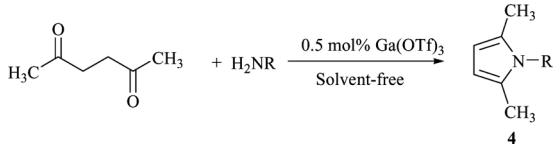
[a]Reaction conditions: amine (5 mmol), acetylacetone (5 mmol), and $Ga(OTf)_3$ (0.5 mol%), 30°C.
[b]Isolated total yield.
[c]Reaction was run for 2 h.

Next, we investigated the reaction of diamines and acetylacetone (Scheme 3). In this reaction, 2 equivalents of acetylacetone are required in the presence of diamines. When diamines such as 1,3-propanediamine and 1,4-butanediamine were examined, the products of **3p**–**3q** with two enaminone groups were obtained in excellent yields.

However, when 1,3-dicarbonyl compound was replaced with 1,4-dicarbonyl compound such as acetonylacetone, the Paal–knorr condensation product pyrrole was obtained under the same conditions (Scheme 4). Therefore, we also investigated the synthesis of pyrroles in the presence of $Ga(OTf)_3$, and similar results are shown in Table 3.



Scheme 3. The reaction of diamines with acetylacetone under solvent-free conditions.



Scheme 4. The reaction of amines with acetonylacetone under solvent-free conditions.

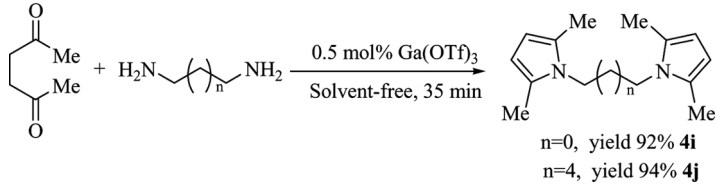
Table 3. Condensation of acetonylacetone with amines in the presence of $Ga(OTf)_3$[a]

Entry	R	Time (min)	Product	Yield (%)[b]
1	C_6H_5	30	**4a**	91
2	*p*-$(CH_3)C_6H_4$	40	**4b**	89
3	2,6-$(^iPr)_2C_6H_3$	35	**4c**	87
4	*p*-$(F)C_6H_4CH_2$	30	**4d**	91
5	$C_6H_5CH_2CH_2$	40	**4e**	88
6	*p*-$(Cl)C_6H_4$	30	**4f**	95
7	*p*-$(NO_2)C_6H_4$	40	**4g**	86
8	*p*-$(OCH_3)C_6H_4CH_2$	35	**4h**	90

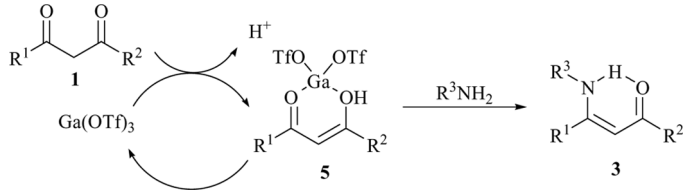
[a]Reaction conditions: amine (5 mmol), acetonylacetone (5 mmol), and $Ga(OTf)_3$ (0.5 mol%), 30°C.
[b]Isolated total yield.

In addition, we also investigated the reaction from diamines with acetonylacetone, and similar results were observed (Scheme 5).

A tentative mechanism for the formation of β-enamino ketones is proposed in Scheme 6. Species **5** is very prone to react immediately with amine by attack of the nitrogen nucleophile at the carbonyl carbon, which is activated by $Ga(OTf)_3$ to produce the product of **3**. The catalyst is regenerated for further reaction. The (*Z*)-selectivity in the product of **3** derived from 1,3-dicarbonyl compound was stabilized by intramolecular



Scheme 5. The reaction of diamines with acetonylacetone under solvent-free conditions.



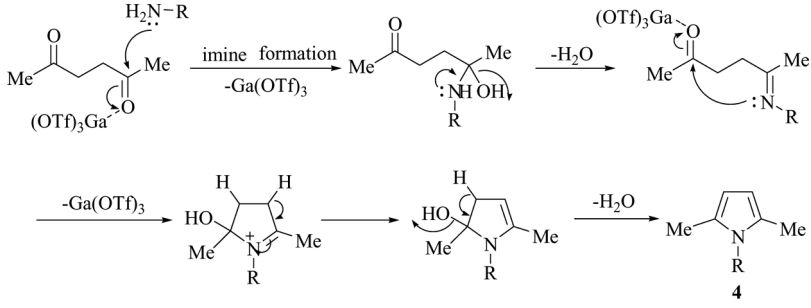
Scheme 6. A tentative mechanism for the formation of β-enamino ketones.

hydrogen bonding. A tentative mechanism for the formation of pyrroles is proposed in Scheme 7.

To sum up, a new catalytic protocol for the regioselectivity synthesis of β-enamino ketones from 1,3-dicarbonyl compounds and amines and the facile synthesis of pyrroles from 1,4-dicarbonyl compounds and amines have been developed. Compared with previously reported methodologies, the present method has the following noteworthy features: simple workup, the shorter reaction times, environmental friendliness, recovery and reuse of metal triflates, and mild reaction conditions with excellent yield. A wide range of β-enamino ketones and pyrroles were synthesized successfully by employing this present reaction system. Currently, studies on the extension of this protocol are ongoing in our laboratory.

EXPERIMENTAL

All the melting points were uncorrected and determined on digital melting-point apparatus WRS-1B. Infrared (IR) spectra were recorded on an Avatar 370 FI-IR spectrophotometer. Mass spectra were measured with a Thermo Finnigan LCQ-Advantage. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Mercury Plus-400 or Bruer-300



Scheme 7. A tentative mechanism for the formation of pyrroles.

instrument using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as an internal standard at room temperature. Chemical shifts are given in δ relative to TMS; coupling constants (J) values are given in hertz. All reagents used are commercially available. Silica gel 60 GF254 was used for analytical and preparative thin-layer chromatography (TLC).

General Procedure for the Synthesis of β-Enamino Ketones

$Ga(OTf)_3$ (0.025 mmol, 0.5 mol%) was added to a mixture of 1,3-dicarbonyl compound (5 mmol) and amines (5 mmol) or diamines (10 mmol). The mixture was stirred at 30°C for the appropriate time. After completion of the reaction as indicated by TLC, the reaction mixture was diluted with water, and the product was extracted with ethyl acetate (3×10 mL). The combined organic layer was dried ($MgSO_4$) and evaporated; the crude product was purified by flash-column chromatography to provide the desired product. The catalyst in the aqueous phase was concentrated in vacuo to give a crystalline residue, which was finally heated at 180°C for 48 h in vacuo. The recovered $Ga(OTf)_3$ could be reused in another reaction.

Characterization Data of All the Products

(Z)-4-(Phenylamino)pent-3-en-2-one (**3a**)

Yield: 92%; mp 47–48°C (lit.[6o] 47°C). IR (KBr), (ν/cm^{-1}): 3439 (NH), 1625 (CO). ^{1}H NMR (300 MHz, $CDCl_3$) ppm δ: 1.99 (s, 3H), 2.10 (s, 3H), 5.19 (s, 1H), 7.11 (d, $J = 8.4$ Hz, 2H), 7.17–7.21 (m, 1H), 7.34 (t, $J = 7.6$ Hz, 2H), 12.48 (br s, 1H, NH). ^{13}C NMR (75 MHz, $CDCl_3$) ppm δ: 19.8, 29.1, 97.6, 124.7, 125.5, 129.1, 138.8, 160.2, 196.1.

(Z)-4-(p-Toluidino)pent-3-en-2-one (**3b**)

Yield: 94%; mp 67–68°C (lit.[6n] 65–67°C). IR (KBr), (ν_{max}/cm^{-1}): 3414 (NH), 1631 (CO). ^{1}H NMR (300 MHz, $CDCl_3$) ppm δ: 1.97 (s, 3H), 2.09 (s, 3H), 2.33 (s, 3H), 5.16 (s, 1H), 7.00 (d, $J = 8.4$ Hz, 2H), 7.14 (d, $J = 8.4$ Hz, 2H), 12.37 (br s, 1H, NH).

(Z)-4-(4-Methoxyphenylamino)pent-3-en-2-one (**3c**)

Yield: 91%; mp 42°C (lit.[6r] 40.5–42.1°C). IR (KBr), ν_{max}/cm^{-1}: 3430 (NH), 1621 (CO). ^{1}H NMR (300 MHz, $CDCl_3$) ppm δ: 1.90 (s, 3H),

2.09 (s, 3H), 3.80 (s, 3H), 5.16 (s, 1H), 6.86 (d, $J = 7.6$ Hz, 2H), 7.04 (d, $J = 7.6$ Hz, 2H), 12.30 (br s, 1H, NH). ^{13}C NMR (75 MHz, $CDCl_3$) ppm δ: 119.5, 28.9, 55.3, 96.7, 114.1, 126.5, 131.3, 157.6, 161.1, 195.6.

(Z)-4-(4-Chlorophenylamino)pent-3-en-2-one (**3d**)

Yield: 90%; mp 60–61°C (lit.[6n] 60–62°C). IR (KBr), (ν_{max}/cm^{-1}): 3456 (NH), 1619 (CO). ^{1}H NMR (300 MHz, $CDCl_3$) ppm δ: 1.97 (s, 3H), 2.11 (s, 3H), 5.20 (s, 1H), 7.03 (d, $J = 8.4$ Hz, 2H), 7.30 (d, $J = 8.4$ Hz, 2H), 12.41 (br s, 1H, NH).

(Z)-4-(4-Nitrophenylamino)pent-3-en-2-one (**3e**)

Yield: 84%; mp 142–143°C (lit.[13] 143.6–144.1°C). IR (KBr), (ν_{max}/cm^{-1}): 3405 (NH) 1634 (CO). ^{1}H NMR (300 MHz, $CDCl_3$) ppm δ: 2.06 (s, 3H), 2.19 (s, 3H), 5.34 (s, 1H), 7.18 (d, $J = 8.8$ Hz, 2H), 8.21 (d, $J = 8.8$ Hz, 2H), 12.72 (br s, 1H, NH).

(Z)-4-(Butylamino)pent-3-en-2-one (**3f**)

Yield: 91%; oil (lit.[6r]). IR (neat), (ν_{max}/cm^{-1}): 3378 (NH), 1617 (CO). ^{1}H NMR (300 MHz, $CDCl_3$) ppm δ: 0.96 (t, $J = 7.2$ Hz, 3H), 1.36–1.46 (m, 2H), 1.54–1.61 (m, 2H), 1.92 (s, 3H), 2.07 (s, 3H), 3.18–3.26 (m, 2H), 4.94 (s, 1H), 11.03 (br s, 1H, NH).

(Z)-4-(Benzylamino)pent-3-en-2-one (**3g**)

Yield: 92%; oil (lit.[6r]). IR (KBr), (ν_{max}/cm^{-1}): 3431 (NH), 1622 (CO). ^{1}H NMR (300 MHz, $CDCl_3$) ppm δ: 1.90 (s, 3H), 2.04 (s, 3H), 4.45 (d, $J = 6.4$ Hz, 2H), 5.02 (s, 1H), 7.29–7.33 (m, 5H), 11.13 (br s, 1H, NH).

(Z)-1,3-Diphenyl-3-(phenylamino)prop-2-en-1-one (**3h**)

Yield: 83%; mp 96–97°C (lit.[14] 103°C). IR (KBr), (ν_{max}/cm^{-1}): 3353 (NH), 1617 (CO). ^{1}H NMR (300 MHz, $CDCl_3$) ppm δ: 6.11 (s, 1H), 6.76 (d, $J = 7.6$ Hz, 2H), 6.96–7.01 (m, 1H), 7.08–7.12 (m, 2H), 7.24–7.49 (m, 8H), 7.96 (d, $J = 6.9$ Hz, 2H), 12.87 (br s, 1H, NH). ^{13}C NMR (75 MHz, $CDCl_3$) ppm δ: 97.0, 123.1, 124.2, 127.2, 127.9, 128.5, 128.6, 128.9, 131.4, 135.8, 139.4, 140.1, 161.3, 189.5.

(Z)-3-(Benzylamino)-1,3-diphenylprop-2-en-1-one (**3i**)

Yield: 87%; mp 100–101°C (lit.[14] 100°C). IR (KBr), (ν_{max}/cm^{-1}): 3351 (NH), 1624 (CO). ^1H NMR (300 MHz, $CDCl_3$) ppm δ: 4.41 (d, $J = 6.8$ Hz, 2H), 5.83 (s, 1H), 7.21–7.26 (m, 3H), 7.27–7.45 (m, 10H), 7.90 (t, $J = 7.6$, 2H), 11.68 (br s, 1H, NH). ^{13}C NMR (75 MHz, $CDCl_3$) ppm δ: 48.3, 93.9, 127.0, 127.2, 127.5, 127.9, 128.4, 128.7, 129.1, 129.6, 130.8, 135.4, 138.4, 140.2, 166.8, 188.6.

(Z)-3-(4-Methoxyphenylamino)-1,3-diphenylprop-2-en-1-one (**3j**)

Yield: 85%; mp 102°C (lit.[6r] 100–101°C). IR (KBr), (ν_{max}/cm^{-1}): 3452 (NH), 1626 (CO). ^1H NMR (300 MHz, $CDCl_3$) ppm δ: 3.90 (s, 3H), 6.07 (s, 1H), 6.37 (t, $J = 8.4$ Hz, 1H), 6.53–6.56 (m, 1H), 6.86 (t, $J = 8.4$ Hz, 1H), 6.91–6.94 (m, 1H), 7.30–7.51 (m, 8H), 7.99 (dd, $J = 7.8$, 1.5 Hz, 2H), 12.72 (br s, 1H, NH).

(Z)-1-Phenyl-3-(phenylamino)but-2-en-1-one (**3k**)

Yield: 90%; mp 111–112°C (lit.[15] 110.5–111.5°C). IR (KBr), (ν_{max}/cm^{-1}): 3418 (NH), 1620 (CO). ^1H NMR (300 MHz, $CDCl_3$) ppm δ: 2.14 (s, 3H), 5.91 (s, 1H), 7.16–7.23 (m, 3H), 7.35–7.47 (m, 5H), 7.91–7.94 (m, 2H), 12.98 (br s, 1H, NH).

(Z)-3-(Benzylamino)-1-phenylbut-2-en-1-one (**3l**)

Yield: 90%; mp 61–62°C (lit.[6m]). IR (KBr), (ν_{max}/cm^{-1}): 3428 (NH), 1618 (CO). ^1H NMR (300 MHz, $CDCl_3$) ppm δ: 1.97 (s, 3H), 4.45 (d, $J = 6.4$ Hz, 2H), 5.71 (s, 1H), 7.28–7.41 (m, 3H), 7.81–7.94 (m, 2H), 11.70 (br, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) ppm δ: 19.2, 46.8, 92.4, 126.6, 127.3, 128.1, 128.7, 130.4, 137.6, 140.2, 164.6, 187.7.

(Z)-3-(4-Methoxyphenylamino)-1-phenylbut-2-en-1-one (**3m**)

Yield: 89%; mp 92°C (lit.[15] 92–93°C). IR (KBr), (ν_{max}/cm^{-1}): 3356 (NH), 1607 (CO). ^1H NMR (300 MHz, $CDCl_3$) ppm δ: 2.12 (s, 3H), 3.89 (s, 3H), 5.92 (s, 1H), 6.90–6.96 (m, 2H), 7.17–7.23 (m, 2H), 7.40–7.45 (m, 3H), 7.91–7.94 (m, 2H), 12.86 (br s, 1H, NH). ^{13}C NMR (75 MHz, $CDCl_3$) ppm δ: 20.3, 55.6, 94.3, 111.5, 120.6, 125.2, 126.8, 127.0, 128.0, 130.7, 140.2, 153.0, 162.5, 188.6.

(R, Z)-4-(1-Phenylethylamino)pent-3-en-2-one (**3n**)

Yield: 91%; oil (lit.[6r]); $[a]_D^{20.8}$, −847.55 (*c* 0.70, EtOH). IR (neat), (ν_{max}/cm^{-1}): 3443 (NH), 1613 (CO). ^1H NMR (300 MHz, $CDCl_3$) ppm δ: 1.52 (d, $J = 6.9$ Hz, 3H), 1.77 (s, 3H), 2.03 (s, 3H), 4.60–4.68 (m, 1H), 4.98 (s, 1H), 7.23–7.35 (m, 5H), 11.22 (br s, 1H, NH). ^{13}C NMR (75 MHz, $CDCl_3$) ppm δ: 18.7, 24.3, 28.5, 52.5, 95.6, 125.2, 127.1, 128.6, 143.9, 162.1, 194.5.

(S, Z)-4-(1-Phenylethylamino)pent-3-en-2-one (**3o**)

Yield: 88%; oil (lit.[6r]); $[a]_D^{20.4}$: +848.02 (*c* 0.70, EtOH). ^1H NMR (300 MHz, $CDCl_3$) ppm δ: 1.52 (d, $J = 6.9$ Hz, 3H), 1.77 (s, 3H), 2.03 (s, 3H), 4.60–4.68 (m, 1H), 4.98 (s, 1H), 7.23–7.35 (m, 5H), 11.22 (br s, 1H, NH). ^{13}C NMR (75 MHz, $CDCl_3$) ppm δ: 18.7, 24.3, 28.5, 52.5, 95.6, 125.2, 127.1, 128.6, 143.9, 162.1, 194.5; IR (neat), (ν_{max}/cm^{-1}): 3443 (NH), 1613 (CO).

(3Z, 3′Z)-4,4′-(Propane-1,3-diylbis(azanediyl))dipent-3-en-2-one (**3p**)

Yield: 92%; mp 50–51°C (lit.[16], 51°C). IR (KBr), (ν_{max}/cm^{-1}): 3442 (NH), 1606 (CO). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.86$ (t, $J = 6.4$ Hz, 2H), 1.92 (s, 6H), 1.99 (s, 6H), 3.32–3.38 (m, 4H), 4.98 (s, 2H), 10.87 (br s, 2H, NH). ^{13}C NMR (75 MHz, $CDCl_3$) ppm δ: 18.8, 28.8, 30.2, 39.6, 95.6, 163.2, 195.2.

(3Z, 3′Z)-4,4′-(Propane-1,3-diylbis(azanediyl))dipent-3-en-2-one (**3q**)

Yield: 94%; mp 61–62°C (lit.[17] not reported). IR (KBr), (ν_{max}/cm^{-1}): 3272 (NH), 1622 (CO). ^1H NMR (300 MHz, $CDCl_3$) ppm δ: 1.57–1.61 (m, 4H), 1.85 (s, 6H), 1.97 (s, 6H), 3.18–3.23 (m, 4H), 4.96 (s, 2H), 10.75 (br, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) ppm δ: 18.9, 28.6 29.8, 40.3, 95.6, 163.2, 195.1.

General Procedure for the Synthesis of Pyrroles

$Ga(OTf)_3$ (0.025 mmol, 0.5 mol%) was added to a mixture of 1,3-dicarbonyl compound (5 mmol) and amines (5 mmol) or diamines (10 mmol). The mixture was stirred at 30°C for the appropriate time. After completion of the reaction as indicated by TLC, water was added, and the product was

extracted with diethyl ether (3×10 mL). The organic layer was dried ($MgSO_4$) and evaporated; the crude product was purified by flash column chormatography to provide the corresponding product. The catalyst in the aqueous phase was concentrated in vacuo to give a crystalline residue, which was finally heated at 180°C for 48 h in vacuo. The recovered $Ga(OTf)_3$ could be reused in another reaction.

Data

2,5-Dimethyl-1-phenyl-1H-pyrrole (**4a**)

Yield: 91%; mp 50–51°C (lit.[9k]). IR (KBr), (ν_{max}/cm^{-1}): 3060, 2922, 1599, 1520, 1498, 1403, 1321. ^{1}H NMR (400 MHz, $CDCl_3$) ppm δ: 2.04 (s, 6H), 5.92 (s, 2H), 7.22–7.27 (m, 2H),7.41–7.49 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) ppm δ: 139.9, 129.0, 128.8, 127.6, 105.6, 13.0.

2,5-Dimethyl-1-p-tolyl-1H-pyrrole (**4b**)

Yield: 89%; mp 45–46°C (lit.[9k]). IR (KBr), (ν_{max}/cm^{-1}): 3033, 2923, 1549, 1515, 1409, 1384. ^{1}H NMR (400 MHz, $CDCl_3$) ppm δ: 2.02 (s, 6H), 2.41 (s, 3H), 5.89 (s, 2H), 7.09 (d, $J = 7.6$ Hz, 2H), 7.24 (d, $J = 7.6$ Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) ppm δ: 137.4, 136.3, 128.8, 127.9, 105.4, 21.1, 13.0.

1-(2,6-Diisopropylphenyl)-2,5-dimethyl-1H-pyrrole (**4c**)

Yield: 87%; mp 55–56°C. IR (KBr): 3070, 2965, 2927, 1580, 1473, 1459, 1398, 1382 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) ppm δ: 1.11 (d, $J = 6.8$ Hz, 12H, $CHCH_3$), 1.91 (s, 6H, CH_3), 2.39–2.32 (m, 2H, $CHCH_3$), 5.94 (s, 2H, pyrrole), 7.25 (d, $J = 8.0$ Hz, 2H, ArH), 7.41 (t, $J = 7.2$ Hz, 1H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$) ppm δ: 12.7, 24.1, 27.8, 105.1, 123.8, 128.6, 128.9, 133.8, 147.5. MS (EI): m/z (%) = 256 (22) $[M + 1]^+$, 255 (100), $[M^+]$, 240 (50). Anal. calcd. for $C_{18}H_{25}N$: C, 84.65; H, 9.87. Found: C, 84.73; H, 9.69.

1-(4-Fluorobenzyl)-2,5-dimethyl-1H-pyrrole (**4d**)

Yield: 91%; mp 56–57°C. IR (KBr): 3067, 2932, 1509, 1444, 1409, 1347, 1224, 1157 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) ppm δ: 2.13 (s, 6H, CH_3), 4.97 (s, 2H, CH_2), 5.85 (s, 2H, pyrrole), 6.98 (t, $J = 8.8$ Hz, 2H, ArH),

6.98 (m, 2H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$) ppm δ: 12.4, 46.0, 105.5, 115.6 (d, $^2J_{CCF} = 21.2$ Hz), 127.2 (d, $^3J_{CCCF} = 7.5$ Hz), 127.8, 134.1, 161.9 (d, $^1J_{CF} = 243.4$ Hz). MS (EI): m/z (%) = 203 (55) [M^+], 109 (100), 83 (40). Anal. calcd. for $C_{13}H_{14}FN$: C, 76.82; H, 6.94. Found: C, 76.90; H, 7.03.

2,5-Dimethyl-1-phenethyl-1H-pyrrole (**4e**)

Yield: 88%; oil (lit.[18]). IR (neat): 3063, 2928, 1604, 1518, 1496, 1454, 1407, 1359, 1299 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) ppm δ: 2.15 (s, 6H, CH_3), 2.88 (t, $J = 7.8$ Hz, 2H, CH_2CH_2Ph), 3.94 (t, $J = 7.8$ Hz, 2H, CH_2CH_2Ph), 5.77 (s, 2H, pyrrole), 7.10 (d, $J = 7.2$ Hz, 2H, ArH), 7.26–7.22 (m, 1H, ArH), 7.30 (t, $J = 7.2$ Hz, 2H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$) ppm δ: 12.3, 37.5, 45.2, 105.2, 127.3, 128.6, 128.8, 138.5. MS (ESI): m/z (%) = 200.2 (100) [$M + 1$]$^+$.

1-(4-Chlorophenyl)-2,5-dimethyl-1H-pyrrole (**4f**)

Yield: 95%; mp 62–63°C (lit.[19]). IR (KBr), (ν_{max}/cm^{-1}): 3045, 2923, 1596, 1493, 1406. ^{1}H NMR (400 MHz, $CDCl_3$) ppm δ: 2.02 (s, 6H) 5.90 (s, 2H), 7.15 (d, $J = 8.4$ Hz, 2H), 7.43 (d, $J = 8.4$ Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) ppm δ: 13.0, 106.0, 128.7, 129.3, 129.5, 133.5, 137.5.

2,5-Dimethyl-1-(4-nitrophenyl)-1H-pyrrole (**4g**)

Yield: 86%; mp 143–144°C (lit.[9c]). IR (KBr), (ν_{max}/cm^{-1}): 3106, 3075, 2920, 1604, 1595, 1518, 1492, 1398, 1337, 1311. ^{1}H NMR (400 MHz, $CDCl_3$) ppm δ: 2.08 (s, 6H), 5.96 (s, 2H), 7.39 (d, $J = 8.8$ Hz, 2H), 8.35 (d, $J = 8.8$ Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) ppm δ: 146.8, 144.7, 128.8, 128.6, 124.6, 107.4, 13.1.

1-(4-Methoxybenzyl)-2,5-dimethyl-1H-pyrrole (**4h**)

Yield: 90%; mp 76–77°C. IR (KBr), (ν_{max}/cm^{-1}): 3028, 2958, 2931, 1584, 1513, 1443, 1409, 1353, 1304, 1291, 1250, 1170. ^{1}H NMR (400 MHz, $CDCl_3$) ppm δ: 2.14 (s, 6H), 3.77 (s, 3H), 4.94 (s, 2H), 5.84 (s, 2H), 6.82 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) ppm δ: 158.5, 130.5, 127.9, 126.7, 114.0, 105.3, 55.2, 46.1, 12.4. MS (EI): m/z (%) = 215 (10) [M^+],

121 (100). Anal. calcd. for $C_{14}H_{17}NO$: C, 78.10; H, 7.96. Found: C, 77.86; H, 8.02.

1,2-Bis(2,5-dimethyl-1H-pyrrol-1-yl)ethane (**4i**)

Yield: 92%; mp 136–137°C (lit.[20]). IR (KBr): 3101, 2970, 1607, 1575, 1520, 1474, 1405, 1301, 1224 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) ppm δ: 2.01 (s, 6H, CH_3), 3.93 (s, 4H, CH_2CH_2), 5.75 (s, 4H, pyrrole). ^{13}C NMR (100 MHz, $CDCl_3$) ppm δ: 127.9, 106.0, 44.1, 12.2. MS (EI): m/z (%) = 216 (100) [M^+], 201 (21), 122 (33), 108 (95), 106 (47), 94 (10), 79 (24), 67 (27).

1,6-Bis(2,5-dimethyl-1H-pyrrol-1-yl)hexane (**4j**)

Yield: 94%; mp 103–105°C (lit.[18]). IR (KBr): 3103, 3093, 2969, 2924, 1518, 1475, 1410, 1373, 1301 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) ppm δ: 1.38–1.34 (m, 4H), 1.65–1.58 (m, 4H), 2.20 (s, 12H, CH_3), 3.70 (t, $J = 7.6$ Hz, 4H), 5.76 (s, 4H, pyrrole). ^{13}C NMR (100 MHz, $CDCl_3$) ppm δ: 127.2, 105.0, 43.5, 30.9, 26.7, 12.5. MS (EI): m/z (%) = 272 (100) [M^+], 257 (8), 164 (38), 108 (30), 94 (18).

ACKNOWLEDGMENTS

We are grateful to the National Natural Science Foundation of China (No. 20676123 and 20476098) and Natural Science Foundation of Zhejiang Province (No. Y405015) for financial support.

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