Gallium(III) Iodide-catalyzed Biginelli-type Reaction Under Solvent-free Conditions: Efficient Synthesis of Dihydropyrimidine-2(1*H*)-one Derivatives

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The Biginelli-type condensation of ethyl acetoacetate/cycloketone, aldehyde and urea/thiourea under solvent-free condition catalyzed by 10% gallium(III) iodide to form dihydropyrimidine-2(1*H*)-one derivatives was described. This process offered one way to constructing dihydropyrimidine-2(1*H*)-ones in good to excellent yields with simple procedure and short reaction time.

Keywords Biginelli reaction, gallium(III) iodide, dihydropyrimidine-2(1*H*)-one, solvent-free, multicomponent reaction, homogeneous catalysis

Introduction

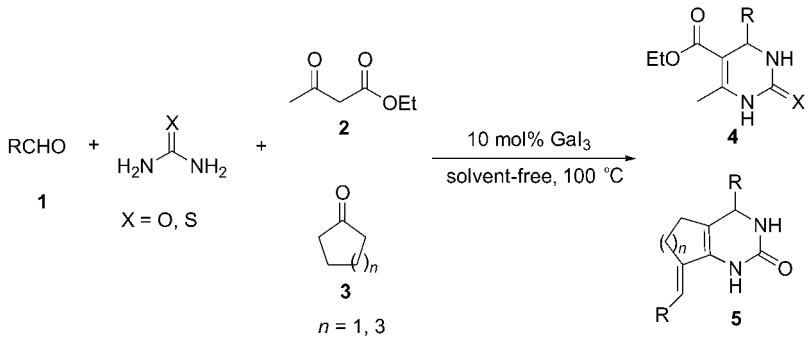
Organic reaction under solvent-free conditions has gained in popularity in recent years.[1] This is because solvent free reaction has the advantages of short reaction time, simple workup procedure, low cost and environment friendly.

Dihydropyrimidinone is an important class of compounds, which have interesting pharmacological properties used for calcium channel modulators, α_{1a}-antagonists, anticancer drugs, Rho-kinase inhibitors, and anti-HIV marine natural products.[2-4] Therefore, developing efficient synthetic methods for such compounds are much required.

The dihydropyrimidinone was first prepared by Biginelli in 1893 from the reaction of ethyl acetoacetate, aldehyde and urea in the presence of a catalytic amount of HCl, however, the yields were low (20%—50%).[5] Therefore, many chemists made many improvements in the last decade, and developed some efficient Lewis acid catalysts for Biginelli reaction, such as BF_3•Et_2O, $Yb(OTf)_3$, InX_3, $CeCl_3$.[6-22] In course of our study on the gallium salts, we found they were able to efficiently catalyze the C—C and C—N bond formations.[23] In this paper, we wish to report the Biginelli-type reaction efficiently catalyzed by gallium(III) iodide.

Experimental

^1H and ^{13}C NMR spectra were determined in $CDCl_3$ on an Inova-400 MHz spectrometer and chemical



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shifts (δ) reported relative to internal TMS. Melting points were determined on an XT-4 melting point apparatus and uncorrected. High resolution mass spectra were recorded on a Micromass OA-TOF (EI) mass spectrometer. All of the reagents were used directly as obtained commercially unless otherwise noted.

General procedure for gallium(III) iodide-catalyzed Biginelli-type reaction under solvent-free conditions

Typical experimental procedure for preparation of **4a**—**4k**: GaI_3 was prepared by stirring a mixture of Ga metal (0.1 mmol) and I_2 (0.15 mmol) in 2 mL CH_2Cl_2 (dried with P_2O_5) in flame-dried glassware. After stirring the mixture of Ga and I_2 for several hours, the red color disappeared and the mixture became a transparent liquid. To this solution aldehyde **1** (1 mmol), ethyl acetoacetate **2** (or cycloketone **3**) (1 mmol), and urea (1.2 mmol) were added, the mixture was heated to 100 ℃ and stirred for 20 min. After the reaction was completed (TLC analysis), the mixture was cooled to room temperature, added with water, extracted with ethyl acetate, and the organic layer was dried with anhydrous Na_2SO_4. The solvent was removed in reduced pressure and the residue was recrystallized from methanol or ethanol to afford the pure products **4** or **5** in good to excellent yields.

Spectral data of 4a—4k

4a Yield 95%, m.p. 202—203 ℃ (Lit.[6] 202—204 ℃). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.04 (s, 1H, NH), 7.32—7.26 (m, 5H, ArH), 5.73 (s, 1H, NH), 5.04 (s, 1H, CH), 4.07 (q, J=7.2 Hz, 2H, CH_2O), 2.35 (s, 3H, CH_3), 1.17 (t, J = 7.2 Hz, 3H, CH_3). HRMS calcd for $C_{14}H_{16}N_2O_3$ (M^+) 260.1161, found 260.1188 (M^+, 23.30).

4b Yield 90%, m.p. 211—212 ℃ (Lit.[6] 213—215 ℃). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.40 (s, 1H, NH), 7.30—7.24 (m, 4H, ArH), 5.58 (s, 1H, NH), 5.38 (s, 1H, CH), 4.09 (q, J=7.1 Hz, 2H, CH_2O), 2.34 (s, 3H, CH_3), 1.17 (t, J = 7.1 Hz, 3H, CH_3). HRMS calcd for $C_{14}H_{15}N_2O_3Cl$ (M^+) 294.0771, found 294.0779 (M^+, 27.76).

4c Yield 91%, m.p. 219—220 ℃ (Lit.[6] 219—222 ℃). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.07 (s, 1H, NH), 7.62—7.43 (m, 4H, ArH), 5.95 (s, 1H, NH), 5.46—5.45 (m, 1H, CH), 4.10 (q, J=7.2 Hz, 2H, CH_2O), 2.36 (s, 3H, CH_3), 1.18 (t, J=7.1 Hz, 3H, CH_3). HRMS calcd for $C_{15}H_{15}N_3O_3$ (M^+) 285.1131, found 285.1145 (M^+, 26.31).

4d Yield 90%, m.p. 206—207 ℃ (Lit.[6] 208—211 ℃). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.19—8.17 (m, 2H, ArH), 8.06 (s, 1H, NH), 7.52—7.49 (m, 2H, ArH), 5.00 (s, 1H, NH), 5.52 (s, 1H, CH), 4.11 (q, J=7.0 Hz, 2H, CH_2O), 2.36 (s, 3H, CH_3), 1.19 (t, J=7.0 Hz, 3H, CH_3). HRMS calcd for $C_{14}H_{15}N_3O_5$ (M^+) 305.1012, found 305.1023 (M^+, 19.25).

4e Yield 85%, m.p. 207—209 ℃ (Lit.[11b] 209—211 ℃). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.88 (s, 1H, NH), 7.32 (d, J=6.0 Hz, 1H, furan-H), 6.30—6.25 (m, 1H, furan-H), 6.12 (d, J=6.1 Hz, 1H, furan-H), 5.76 (s, 1H, NH), 5.49 (s, 1H, CH), 4.15 (q, J=7.2 Hz, 2H, CH_2O), 2.36 (s, 3H, CH_3), 1.22 (t, J=7.2 Hz, 3H, CH_3). HRMS calcd for $C_{12}H_{14}N_2O_4$ (M^+) 250.0954, found 250.0945 (M^+, 54.48).

4f Yield 92%, m.p. 174—177 ℃ (Lit.[9] 175—177 ℃). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.15 (s, 1H, NH), 7.28—6.99 (m, 4H, ArH), 6.05 (s, 1H, NH), 5.39 (s, 1H, CH), 4.09 (q, J=7.2 Hz, 2H, CH_2O), 2.33 (s, 3H, CH_3), 1.17 (t, J = 7.2 Hz, 3H, CH_3). HRMS calcd for $C_{14}H_{15}N_2O_3F$ (M^+) 278.1067, found 278.1083 (M^+, 17.20).

4g Yield 79%, m.p. 215—216 ℃ (Lit.[11d] 216—217 ℃). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 9.15 (s, 1H, CHO), 8.31 (s, 2H, ArH+NH), 7.67 (s, 1H, ArH), 7.17 (s, 2H, ArH), 5.13 (s, 1H, NH), 3.97 (q, J=7.0 Hz, 2H, CH_2O), 2.29 (s, J=7.0 Hz, 3H, CH_3), 1.09 (t, J=7.2 Hz, 3H, CH_3).

4h Yield 84%, m.p. 194—195 ℃ (Lit.[11b] 194—195 ℃). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.12 (s, 1H, NH), 5.71 (s, 1H, NH), 4.44—4.42 (m, 1H, CH), 4.19 (q, J= 7.2 Hz, 2H, CH_2O), 2.29 (s, 3H, CH_3), 1.30—1.26 (m, 6H, 2 × CH_3). HRMS calcd for $C_8H_{11}N_2O_3$ (M^+) 183.0743, found 183.0740 (M^+, 100.00).

4i Yield 82%, m.p. 205—206 ℃ (Lit.[9] 208—210 ℃). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.12 (brs, 1H, NH), 5.85 (brs, 1H, NH), 4.34—4.28 (m, 1H, CH), 4.19 (q, J=7.1 Hz, 2H, CH_2O), 2.29 (s, 3H, CH_3), 1.56—1.52 (m, 2H, CH_2), 1.35—1.15 (m, 4×CH_2, 11H, CH_3), 0.88 (t, J=7.6 Hz, 3H, CH_3).

4j Yield 87%, m.p. 225—227 ℃ (Lit.[27] 225 ℃). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.71 (s, 1H, NH), 7.24—7.35 (m, 5H, ArH), 6.55—6.49 (m, 1H, CH), 6.24—6.18 (m, 1H, CH), 5.58 (m, 1H, NH), 5.01—4.99 (m, 1H, CH), 4.19 (q, J=7.1 Hz, 2H, CH_2O), 2.32 (s, 3H, CH_3), 1.28 (t, J=7.1 Hz, 3H, CH_3). HRMS calcd for $C_{16}H_{18}N_2O_3$ (M^+) 286.1317, found 286.1314 (M^+, 100.00).

4k Yield 90%, m.p. 232—234 ℃ (Lit.[11b] 232—234 ℃). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.86 (s, 1H, NH), 7.27—7.25 (m, 5H, ArH), 5.37 (s, 1H, NH), 4.06 (q, J= 7.2 Hz, 2H, CH_2O), 2.34 (s, 3H, CH_3), 1.14 (t, J=7.2 Hz, 3H, CH_3). HRMS calcd for $C_{14}H_{16}N_2O_2S$ (M^+) 276.0932, found 276.0940 (M^+, 84.33).

Spectral data of 5a—5g

5a Yield 90%, m.p. 236—238 ℃ (Lit.[22a] 236—239 ℃). ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 8.77 (s, 1H, NH), 7.40—7.21 (m, 11H, ArH+CH), 6.63 (s, 1H, NH), 5.15 (s, 1H, CH), 2.83—2.79 (m, 2H, CH_2), 2.38—2.37 (m, 1H, CH), 2.03—1.97 (m, 1H, CH). HRMS calcd for $C_{20}H_{18}N_2O$ (M^+) 302.1419, found 302.1418 (M^+, 100).

5b Yield 83%, m.p. 224—225 ℃ (Lit.[22a] 226—228 ℃). ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 8.83 (s, 1H, NH), 7.46—7.27 (m, 9H, ArH+CH), 6.63 (s, 1H, NH), 5.19 (s, 1H, CH), 2.81—2.77 (m, 2H, CH_2), 2.43—2.37 (m, 1H, CH), 2.02 — 1.96 (m, 1H, CH). ^{13}C NMR

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(DMSO-d_6, 100 MHz) δ: 28.1, 28.2, 56.6, 79.1, 115.6, 118.6, 128.3, 128.4, 128.5, 129.4, 130.3, 131.9, 135.9, 136.5, 139.9, 142.1, 152.9.

5c Yield 85%, m.p. 280—283 ℃ (Lit.[22b] 281—282 ℃). ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 8.87 (s, 1H, NH), 8.35—8.19 (m, 4H, ArH), 7.65—7.39 (m, 4H, ArH), 6.89—6.77 (m, 2H, NH+CH), 5.39 (s, 1H, CH), 2.91—2.86 (m, 2H, CH_2), 2.26—2.18 (m, 1H, CH), 2.05—2.01 (m, 1H, CH). HRMS calcd for $C_{20}H_{16}N_4O_5$ (M^+) 392.1121, found 392.1121 (M^+, 83.64).

5d Yield 81%, m.p. 238—240 ℃ (Lit.[22a] 238—241 ℃). ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 9.00 (s, 1H, NH), 7.41—7.26 (m, 9H, ArH+CH), 6.92 (s, 1H, NH), 5.20 (s, 1H, CH), 2.84—2.83 (m, 2H, CH_2), 2.45—2.37 (m, 1H, CH), 2.09 (s, 7H, 2×CH_3+CH). HRMS calcd for $C_{22}H_{22}N_2O$ (M^+) 330.1732, found 330.1723 (M^+, 57.81).

5e Yield 88%, m.p. 250—252 ℃ (Lit.[22a] 250—252 ℃). ^{1}H NMR (DMSO-d_6, 300 MHz) δ: 8.64 (s, 1H, NH), 7.30—7.22 (m, 2H, ArH), 7.20—7.14 (m, 2H, ArH), 7.06 (s, 1H, ArH), 6.96—6.88 (m, 4H, ArH), 6.56 (s, 1H, NH), 5.08 (s, 1H, CH), 3.75 (s, 6H, 2×OCH_3), 2.77 (s, 2H, CH_2), 2.38—2.33 (m, 1H, CH), 2.02—1.96 (m, 1H, CH). HRMS calcd for $C_{22}H_{22}N_2O_3$ (M^+) 362.1630, found 362.1626 (M^+, 100).

5f Yield 86%, m.p. 260—264 ℃. ^{1}H NMR (DMSO-d_6, 300 MHz) δ: 9.19 (s, 1H, NH), 8.38—6.74 (m, 15H, ArH+CH), 6.04 (s, 1H, NH), 5.28 (s, 1H, CH), 2.79—2.71 (m, 2H, CH_2), 2.43—2.41 (m, 1H, CH), 1.81—1.73 (m, 1H, CH). ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 27.6, 27.7, 55.87, 112.2, 118.7, 121.9, 122.7, 123.8, 124.0, 124.5, 124.8, 125.1, 125.6, 125.9, 127.2, 127.7, 127.9, 128.0, 129.6, 130.8, 132.8, 133.5, 135.5, 137.4, 138.4, 140.1, 153.0, 156.7. HRMS calcd for $C_{28}H_{22}N_2O$ (M^+) 402.1732, found 402.1737 (M^+, 10.60).

5g Yield 89%, m.p. 286—288 ℃. ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 9.01 (s, 1H, NH), 7.41—7.24 (m, 11H, ArH+CH), 6.92 (s, 1H, NH), 5.21 (s, 1H, CH), 2.84—2.83 (m, 2H, CH_2), 2.43—2.42 (m, 1H, CH), 2.10—2.06 (m, 5H, CH + 2CH_2). HRMS calcd for $C_{22}H_{22}N_2O$ (M^+) 330.1732, found 330.1736 (M^+, 15.30).

Results and discussion

Initially, we explored the typical Biginelli reaction of ethyl acetoacetate, benzaldehyde and urea in DCM or THF in the presence of 10 mol% GaI_3, unfortunately, trace product was obtained (Table 1, Entries 1, 2). Then, the different solvents such as CH_3CN, benzene, toluene and EtOH were scanned (Table 1, Entries 3—6), in which EtOH gave the 82% yield in 12 h (Table 1, Entry 6). Furthermore, the same reaction was conducted under the solvent free condition, interestingly, its yield reached to 95% and the reaction was completed in 0.5 h (Table 1, Entry 7), which might be attributed to the high concentration effect.[24,25] Finally, the effect of catalyst loading on the reaction was also investigated, showing that 10 mol% GaI_3 was the best choice (Scheme 1, Table 1, Entries 7—9).

Scheme 1

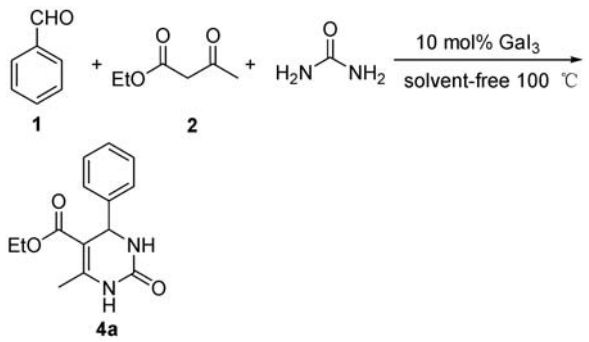


Table 1 Effects of reaction conditions on the typical Biginelli reaction catalyzed by GaI_3

Entry[a]	Solvent	GaI_3/mol%	Time/h	Yield[d]/%
1	THF	10	12[b]	trace
2	CH_2Cl_2	10	12[b]	trace
3	CH_3CN	10	12[b]	56
4	C_6H_6	10	12[b]	31
5	Toluene	10	12[b]	29
6	EtOH	10	12[b]	82
7	—	10	0.5[c]	95
8	—	5	1[c]	72
9	—	15	0.5[c]	94

[a] Benzaldehyde (1 mmol), ethyl acetoacetate (1 mmol), urea (1.2 mmol), GaI_3 (10 mol%) were used in 3 mL mentioned solvent. [b] Reflux. [c] 100 ℃. [d] Isolated yield.

The reactions of a series of aryl and alkyl aldehydes, ethyl acetoacetate and urea were performed under the optimized conditions (Table 1, Entry 7). As seen in the Table 2 and Scheme 2, all the reactions were finished in 1 h, and gave the good to excellent yields (79%—95%). The results showed that the different aromatic aldehydes (Table 2, Entries 1—7), aliphatic aldehydes (Table 2, Entries 8—9), α,β-unsaturated aldehyde (Table 2, Entry 10) were all good substrates for the Biginelli reaction catalyzed by 10 mol% GaI_3. When thiourea was used instead of urea, the expected product **4k** was obtained in 90% yield (Table 2, Entry 11).

Scheme 2

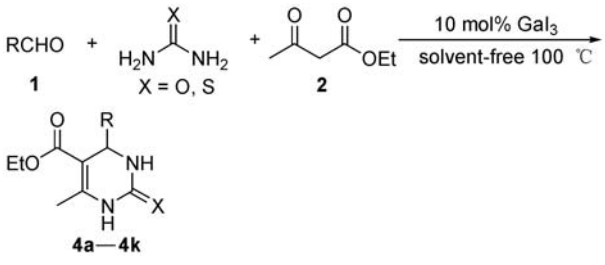
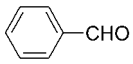
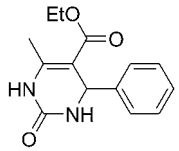
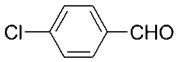
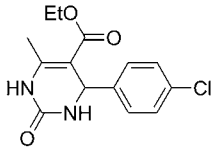
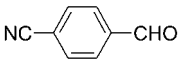
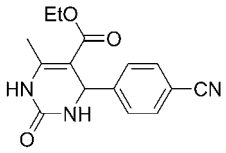
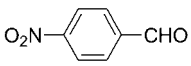
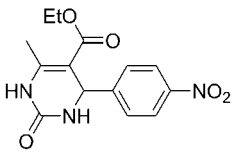
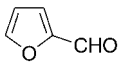
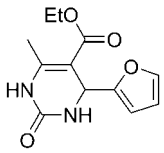
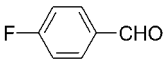
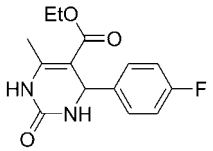
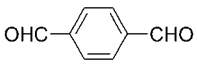
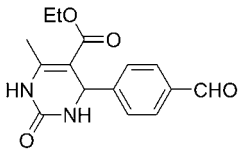
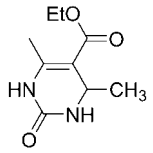


Table 2 GaI_3 catalyzed the Biginelli-type reaction under solvent-free condition[a]

Entry	Aldehyde	Time/h	Yield[b]/%	Product[c]
1		0.3	95	 **4a**
2		0.5	90	 **4b**
3		0.3	91	 **4c**
4		0.25	90	 **4d**
5		0.75	85	 **4e**
6		0.5	92	 **4f**
7		0.5	79	 **4g**
8	CH_3CHO	0.5	84	 **4h**

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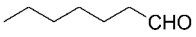
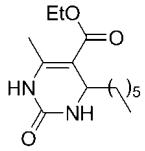
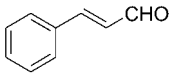
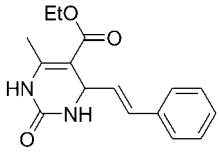
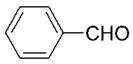
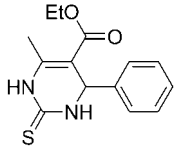
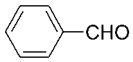
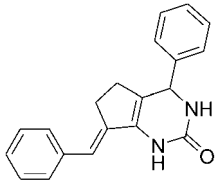
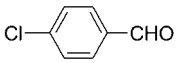
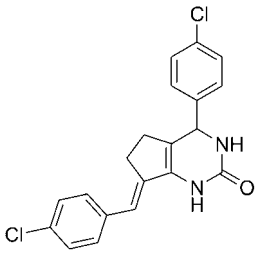
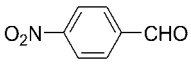
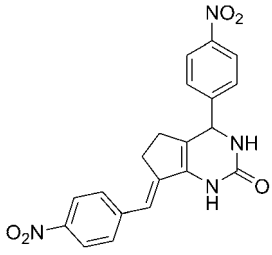
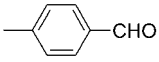
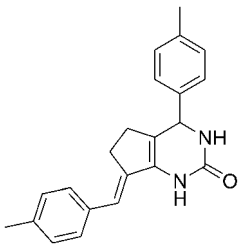
Continued

Entry	Aldehyde	Time/h	Yield[b]/%	Product[c]
9		1	82	 **4i**
10		0.5	87	 **4j**
11		0.5	90	 **4k**
12		0.5	90	 **5a**
13		0.75	83	 **5b**
14		0.25	85	 **5c**
15		0.75	81	 **5d**

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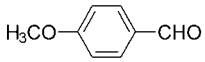
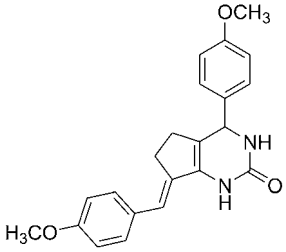
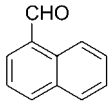
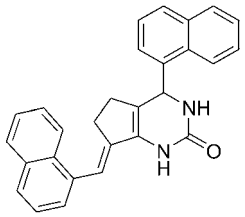
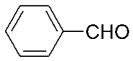
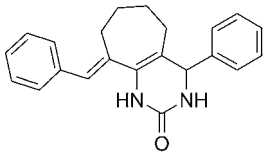
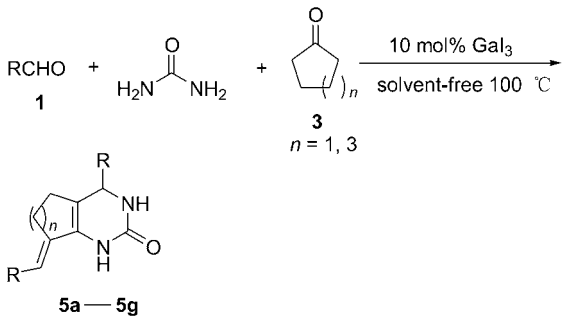
Entry	Aldehyde	Time/h	Yield[b]/%	Product[c]
16		0.5	88	 **5e**
17		1	86	 **5f**
18		1	89	 **5g**

[a] Aldehyde (1 mmol), ethyl acetoacetate (or cycloketone) (1 mmol), urea (1.2 mmol) and 10 mol% GaI_3 were used under solvent-free condition at 100 ℃. [b] Isolated yield. [c] All compounds were characterized by ^{1}H NMR and HRMS analyses.

The above good results prompted us to extend the substrates to cycloketones, fortunately, the reaction of cyclopentanone, benzaldehyde and urea catalyzed by 10 mol% GaI_3 yielded the expected product **5a** in 90% yield (Scheme 3, Table 2, Entry 12), which was characterized by ^{1}H NMR and HRMS analyses. Subsequently, other aromatic aldehydes bearing either electron-donating or electron-withdrawing substituents were used for the reaction, and it was found that the electron effect of substituents had little impact on the yield, all the reaction gave the good yields (81—90%, Scheme 3, Table 2, Entries 12—16) without any by-product observed. More hindered 1-naphthaldehyde was also conducted for the reaction, giving the expected product **5f** in 86% yield (Table 2, Entry 17). However, when using cyclohexanone instead of cyclopentanone, to our surprise, the resultant was complicated. Interestingly, in case of cyclohepanone the expected product **5g** was afforded in 89% yield (Table 2, Entry 18). The reason of the difference for cycloketones is unknown. As seen the plausible mechanism in Scheme 4, complex **6** added to imine **7** to form intermediate **8**, followed by cyclization and dehydration to yield product **4a**. Scheme 5 showed that two molecules of imine **7** reacted with complex **10** derived from cyclopentanone and GaI_3 *in situ*, to yield intermediate **11**, followed by cyclization and leaving one molecule of H_2O and urea to afford product **5a**.[26-28]

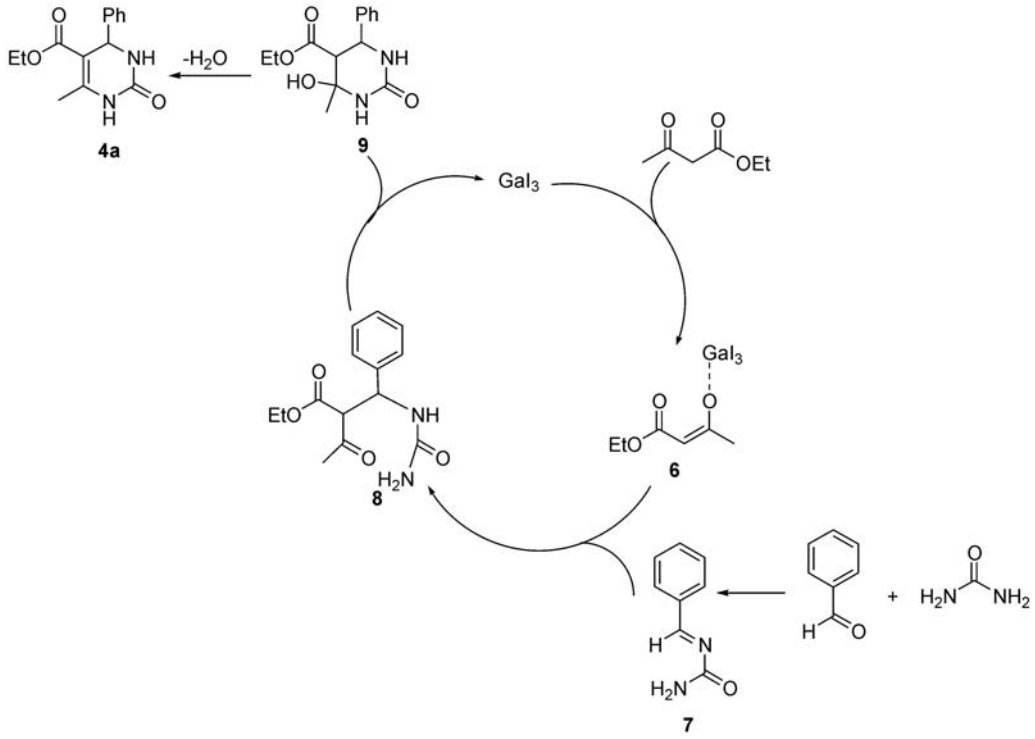
Scheme 3



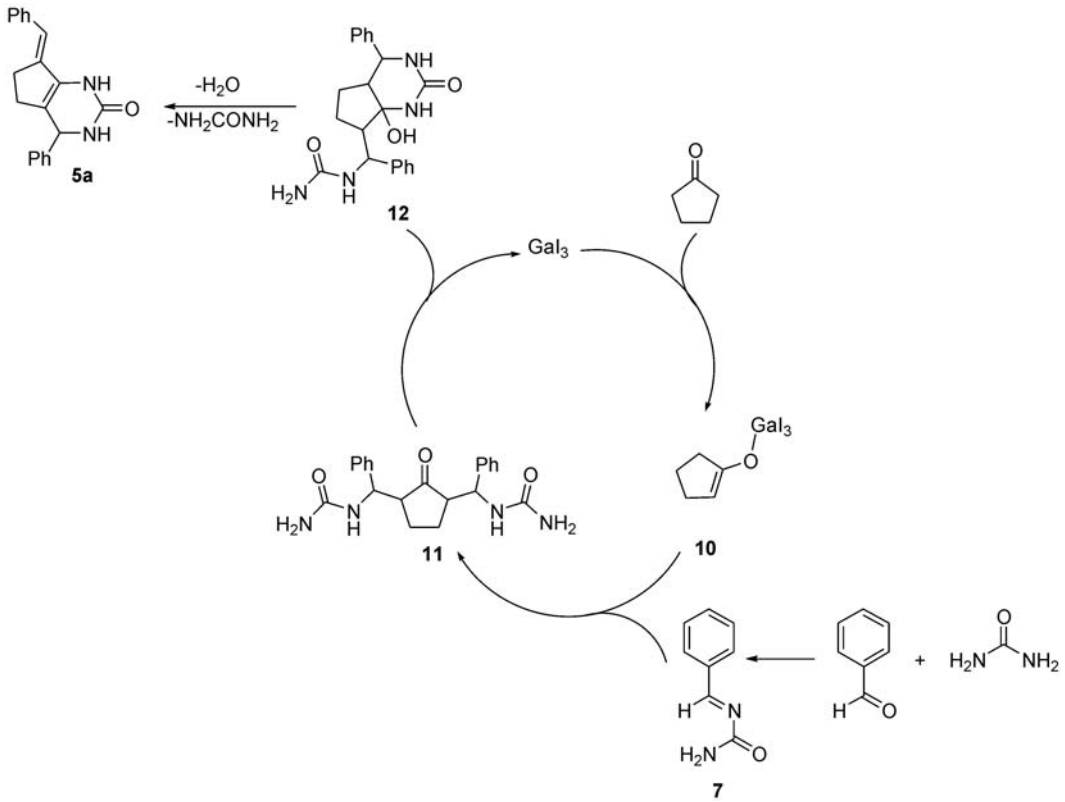
Conclusion

In conclusion, 10 mol% GaI_3 can effectively catalyze the Biginelli reaction of ethyl acetoacetate/cycloketone, aldehyde and urea/thiourea under solvent-free condition at 100 ℃. This work provided a new alternative way to dihydropyrimidine-2(1*H*)-ones in good to excellent yields, and our developed method has the advantages of environmental benignity, simple workup, and easy preparation of catalyst.

Scheme 4



Scheme 5



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