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$Ga(OTf)_3$ CATALYZED SYNTHESIS OF 1,4-DIHYDROPYRIMIDIN-2(1*H*)-ONES

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Abstract – Gallium(III) triflate was used to catalyze Biginelli-like reactions under solvent-free condition to obtain dihydropyrimidinone derivatives in good to excellent yields and short reaction time.

Dihydropyrimidinones (DHPMs) has attracted increasing attentions in organic and medicinal chemistry due to their versatile pharmacological and therapeutic properties, such as calcium channel modulators, α_{1a} adrenoaceptor-selective antagonists,[1-3] anticancer drugs to inhibit kinesin motor proteins,[4,5] Rho-kinase inhibitors,[6] anti-HIV activity[7] and so on.

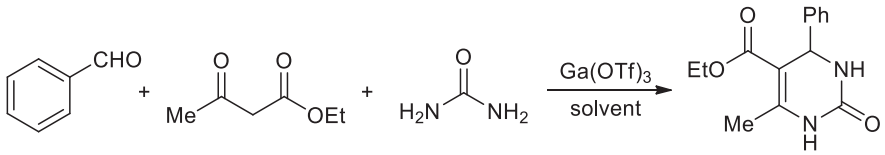
The first synthesis of DHPMs was reported by an Italian chemist, Pietro Biginelli, in 1893 through a simple one-pot, three-component condensation reaction of urea, ethyl acetoacetate and an aromatic aldehyde.[8] The Biginelli reaction was not widely applied until the early 1990s as the increasing requirement of biological active compounds, which made this multicomponent reaction attractive. In the past years, this reaction has gained much more attention and several modified procedures have been reported in order to improve its efficiency. Lewis acids catalyzed DHPMs synthesis is one of the most widely used methods, such as $BF_3{\cdot}OEt_2$,[9] $FeCl_3{\cdot}6H_2O$,[10] $LaCl_3$,[11] $Yb(OTf)_3$,[12] $Cu(OTf)_2$,[13] $InBr_3$,[14] $Zr(NO_3)_3$,[15] $BiCl_3$,[16] $Mn(OAc)_3$,[17] $CaCl_2$,[18] I_2,[19] $ZrOCl_2$,[20] montmorillonite KSF,[21] LiBr[22] etc. Although extensive investigations have devoted to improve the efficiency of Biginelli reaction, we, here, provide a relatively simple operation and environmental friendly reaction condition to carry out Biginelli reaction.

As a water-compatible strong Lewis acid, $Ga(OTf)_3$ has been widely used to catalyze organic reactions,[23] such as Beckmann rearrangements,[24] Friedel–Crafts reactions,[25,26] aldoxime dehydration,[27,28] regioselective rearrangements of 2-substituted vinylepoxides,[29] asymmetric Mukaiyama aldol reactions,[30] constructions of fused-bicyclolactones,[31] and so on. Herein, we report a new utility of gallium(III) triflate catalyzed neat Biginelli reaction. Compared to other methods reported in the literature, gallium(III)-promoted reactions are straightforward, giving good to excellent yields. Moreover, this

reaction condition can also expand to cycloketones, giving a novel transformation for the synthesis of dihydropyrimidinones.

Initially, the reaction conditions were screened by exploring a typical Biginelli reaction of ethyl acetoacetate, benzaldehyde and urea with catalyzed $Ga(OTf)_3$ in various solvents, as collected in Table 1. 10 mol% $Ga(OTf)_3$ was employed to catalyze this reaction under various solvents, such as THF, DCM, acetonitrile, ethanol and toluene. THF and DCM gave trace amount of the desired product after refluxing for 12 hours, which might be attributed to the low boiling points of the solvents (Table 1, entries 1 and 3). Low yields were also obtained in toluene and acetonitrile solutions (Table 1, entries 2 and 4). Ethanol can give a relatively better yield of 88% (Table 1, entry 5). However, when this reaction was carried out without solvent at 90 °C, 98% yield product can be obtained within 0.5 h (Table 1, entry 6). The yield was a little bit lower (90%) when the catalyst amount was reduced to 5 mol% (Table 1, entry 7).

Table 1. Reaction condition optimization on the $Ga(OTf)_3$ catalyzed Biginelli reaction[a]



Entry	Solvent	$Ga(OTf)_3$/(mol%)	Reflux time/h	Yield/%
1	THF	10	12	trace
2	toluene	10	12	30
3	DCM	10	12	trace
4	MeCN	10	12	50
5	EtOH	10	12	88
6[b]	**solvent-free**	**10**	**0.5**	**98**
7[b]	solvent-free	5	12	90

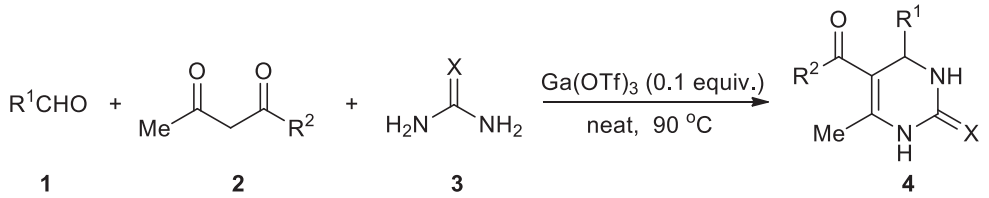
[a]: The reactant condition: benzaldehyde (1.0 mmol), ethyl acetoacetate (1.0 mmol), urea (1.2 mmol) in 10 mL solvent;

[b]: Reaction temperature: 90 °C.

With the best reaction condition (Table 1, entry 6) in hand; the reaction scope was explored to different aldehydes, alkyl acetoacetates and urea or thiourea. The collected results were presented in Table 2. First of all, different benzaldehydes with both electron donating (–OMe) and electron withdrawing ($–NO_2$ and –F) groups were investigated, giving high yield (> 90%) within less than one hour (Table 2, entries 1–5 and

9–11). Alkyl aldehydes were also explored (Table 2, entries 7 and 8), but with relatively low yields of 84% and 82%, respectively. Thioureas can also be applied in this reaction condition (Table 2, entries 12 and 13) with good yields.

Table 2. $Ga(OTf)_3$ catalyzed Biginelli reaction of aldehydes, alkyl acetoacetates and urea under solvent-free condition[a]



1 2 3 4

Entry	R^1	R^2	X	Time (h)	Product	Yield (%)
1	C_6H_5	OEt	O	0.5	**4a**	98
2	4-MeO-C_6H_4	OEt	O	0.5	**4b**	93
3	4-Cl-C_6H_4	OEt	O	0.5	**4c**	95
4	4-F-C_6H_4	OEt	O	0.25	**4d**	94
5	4-NO_2-C_6H_4	OEt	O	0.25	**4e**	96
6		OEt	O	0.75	**4f**	90
7	Me [b]	OEt	O	0.5	**4g**	84
8	n-C_6H_{13}	OEt	O	1.0	**4h**	82
9	C_6H_5	OMe	O	0.5	**4i**	94
10	4-MeO-C_6H_4	OMe	O	0.5	**4j**	90
11	4-Cl-C_6H_4	OMe	O	0.5	**4k**	92
12	C_6H_5	OEt	S	0.5	**4l**	91
13	C_6H_5	OMe	S	0.5	**4m**	85

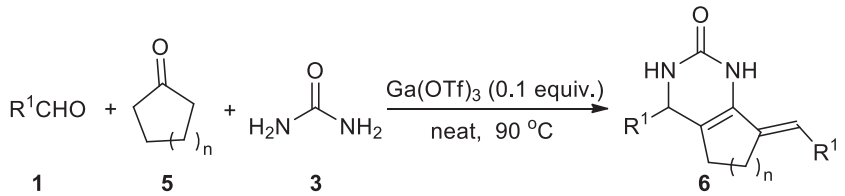
[a]: The reactant condition: aldehyde (1.0 mmol), alkyl acetoacetate (1.0 mmol) and urea (1.2 mmol);

[b]: From 40% acetaldehyde solution.

The successful scope investigation mentioned above (Table 2) prompted us to further expand the versatility of Biginelli reaction by replacing alkyl acetoacetate to cycloketones. Although Pan group has reported the one-pot multicomponent Biginelli reactions between cycloalkanones, urea or thiourea, and aldehydes catalyzed by TMSCl,[32] a combination solvent of DMF/MeCN was used. Liu group mentioned a solvent and catalyst free reaction condition, but the aldehydes were only restricted for aromatic aldehydes and no cycloketones were investigated.[33] In this reaction, $Ga(OTf)_3$ catalyzed cycloketones, urea and aldehydes

were also succeeded under solvent-free conditions with moderate to high yields (Table 3). Benzaldehydes with both electron donating (–Me and –OMe) and electron withdrawing (–NO_2) groups were tested with good yields (Table 3, entries 1–5 and 7). A seven-membered ring ketone, cycloheptanone, was also tried with a 83% yield (Table 3, entry 6).

Table 3. $Ga(OTf)_3$ catalyzed Biginelli reaction of cycloketone, aldehyde, and urea under solvent-free condition[a]



Entry	R^1	n	Time (h)	Product	Yield (%)[a]
1	C_6H_5	1	0.5	**6a**	94
2	4-NO_2-C_6H_4	1	0.25	**6b**	86
3	4-Cl-C_6H_4	1	0.75	**6c**	88
4	4-MeO-C_6H_4	1	0.5	**6d**	89
5	4-Me-C_6H_4	1	0.75	**6e**	88
6	C_6H_5	3	1.0	**6f**	83
7		1	1.0	**6g**	82

[a]: The reactant condition: benzaldehyde (2.0 mmol), cycloketone (1.0 mmol) and urea (1.2 mmol).

In conclusion, $Ga(OTf)_3$ can effectively catalyze Biginelli reaction of alkyl acetoacetates (or cycloketones), aldehydes and urea or thiourea under solvent-free conditions. The functional group diversity, environmental friendly condition, high yield and mild reactions conditions will promote this reaction with wide applications.

EXPERIMENTAL

All chemicals (AR grade) were obtained from commercial resources and used without further purification. ^1H NMR (400 MHz) spectra were recorded on a Varian Mercury MHz spectrometer in $CDCl_3$ with TMS as the internal standard. All products are known and they were also identified by melting point, which were determined using XT-4 apparatus and are not corrected. High-resolution mass spectra (HRMS) were obtained using a GCT-TOF instrument.

General procedure for the synthesis of DHPMs

To a mixture of alkyl acetoacetate (or cycloketone) (1.0 mmol), aldehyde (1.0 mmol, for cycloketones: 2.0 mmol) and urea (or thiourea) (1.2 mmol), 0.1 equivalent $Ga(OTf)_3$ was added. The mixture was stirred at 90 °C for appropriate time. After reaction completed by TLC analysis, water was added and the product was extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4 and evaporated. The residue was recrystallized from methanol or ethanol to obtain pure products.

NMR and HR-MS for part of the compounds:

Ethyl 6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4a). mp 202–203 °C (Lit.[9] 202–204 °C). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.04 (br, 1H, NH), 7.33–7.25 (m, 5H, ArH), 5.74 (br, 1H, NH), 5.05 (s, 1H, CH), 4.08 (q, J = 7.2 Hz, 2H, CH_2O), 2.36 (s, 3H, CH_3), 1.18 (t, J = 7.2 Hz, 3H, CH_3).

Ethyl 4-(4-methoxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4b). mp 201–202 °C (Lit.[9] 201–203 °C). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 9.14 (br, 1H, NH), 7.70 (br, 1H, NH), 7.15 (d, J = 8.6 Hz, 2H), 6.88 (d, J = 8.6 Hz, 2H), 5.10 (d, J = 3.4 Hz, 1H), 3.98 (q, J = 7.2 Hz, 2H, CH_2O), 3.72 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 1.11 (t, J = 7.2 Hz, 3H, CH_3). HR-MS(EI): calcd for $C_{15}H_{18}N_2O_4$: 290.1267, found: 290.1271.

Ethyl 4-(4-chlorophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4c). mp 214–216 °C (Lit.[9] 213–215 °C). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 9.25 (br, 1H, NH), 7.78 (br, 1H, NH), 7.39 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 8.4 Hz, 2H), 5.14 (d, J = 3.0 Hz, 1H), 3.98 (q, J = 7.1 Hz, 2H, CH_2O), 2.26 (s, 3H), 1.10 (t, J = 7.1 Hz, 3H, CH_3).

Ethyl 4-(4-fluorophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4d). mp 176–178 °C (Lit.[34] 175–177 °C). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.13 (br, 1H, NH), 7.26 (d, J = 8.4 Hz, 2H), 7.01 (d, J = 8.4 Hz, 2H), 5.40 (d, J = 3.2 Hz, 1H), 4.08 (q, J = 7.2 Hz, 2H, CH_2O), 2.33 (s, 3H), 1.18 (t, J = 7.2 Hz, 3H, CH_3).

Ethyl 4-(4-nitrophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4e). mp 207–211 °C (Lit.[9] 208–211 °C). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 9.38 (br, 1H, NH), 8.20 (d, J = 8.6 Hz, 2H), 7.50 (d, J = 8.6 Hz, 2H), 5.26 (d, J = 2.0 Hz, 1H), 3.97 (q, J = 7.2 Hz, 2H, CH_2O), 2.26 (s, 3H), 1.10 (t, J = 7.2 Hz, 3H, CH_3).

Ethyl 4-(2-furanyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4f). mp 209–212 °C (Lit.[34] 207–209 °C). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.86 (br, 1H, NH), 7.32 (d, J = 6.0 Hz, 1H), 6.29–6.24 (m, 2H), 6.13 (d, J = 6.2 Hz, 1H), 5.47 (s, 1H, CH), 4.15 (q, J = 7.2 Hz, 2H, CH_2O), 2.35 (s, 3H), 1.20 (t, J = 7.2 Hz, 3H, CH_3).

Ethyl 4,6-dimethyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4g). mp 194–196 °C (Lit.[14] 194–195 °C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.11 (br, 1H, NH), 5.70 (br, 1H, NH), 4.43–4.32 (m, 1H, CH), 4.20 (q, J = 7.2 Hz, 2H, CH_2O), 2.28 (s, 3H, CH_3), 1.29–1.26 (m, 6H, 2×CH_3). HR-MS(EI): calcd for $C_9H_{14}N_2O_3$: 198.1004, found: 198.1003.

Ethyl 4-hexyl-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4h). mp 208–210 °C (Lit.[12] 208–210 °C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.15 (br, 1H, NH), 5.87 (br, 1H, NH), 4.35–4.25 (m, 1H, CH), 4.19 (q, J = 7.2 Hz, 2H, CH_2O), 2.30 (s, 3H, CH_3), 1.55–1.52 (m, 2H, CH_2), 1.35–1.10 (m, 11H, CH_3 + 4×CH_2), 0.88 (t, J = 7.2 Hz, 3H, CH_3).

Methyl 6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4i). mp 210–212 °C (Lit.[9] 209–212 °C). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 8.10 (br, 1H, NH), 7.33–7.28 (m, 5H, ArH), 5.38 (d, J = 2.6 Hz, 1H), 3.61 (s, 3H), 2.35 (s, 3H).

Methyl 4-(4-methoxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4j). mp 193–194 °C

(Lit.[9] 192–194 °C). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 9.16 (br, 1H, NH), 7.71 (br, 1H, NH), 7.20(d, J = 8.4 Hz, 2H), 6.83 (d, J = 8.4 Hz, 2H), 5.30 (d, J = 2.2 Hz, 1H), 3.76 (s, 3H), 3.62 (s, 3H), 2.31 (s, 3H).

Methyl 4-(4-chlorophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4k). mp 205–207 °C (Lit.[12] 204–207 °C). ^{1}H NMR (DMSO-d_6, 400 MHz) δ 9.21 (br, 1H, NH), 7.71 (br, 1H, NH), 7.15 (d, J = 8.4 Hz, 2H), 6.88 (d, J = 8.4 Hz, 2H), 5.10 (d, J = 2.8 Hz, 1H), 3.54 (s, 3H), 2.27 (s, 3H).

Ethyl 6-methyl-4-phenyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4l). mp 231–234 °C (Lit.[14] 232–234 °C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.88 (br, 1H, NH), 7.28–7.26 (m, 5H, ArH), 5.39 (d, J = 3.4 Hz, 1H, CH), 4.05 (q, J = 7.2 Hz, 2H, CH_2O), 2.35 (s, 3H, CH_3), 1.16 (t, J = 7.2 Hz, 3H, CH_3). HR-MS(EI): calcd for $C_{14}H_{16}N_2O_2S$: 276.0932, found: 276.0940.

Methyl 6-methyl-4-phenyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4m). mp 220–222 °C (Lit.[35] 221–222 °C). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.90 (br, 1H, NH), 7.30–7.25 (m, 5H, ArH), 5.25 (d, J = 3.4 Hz, 1H, CH), 3.60 (s, 3H, CH_3), 2.27 (s, 3H, CH_3).

7-Benzylidene-4-phenyl-3,4,6,7-tetrahydro-1*H*-cyclopenta[*d*]pyrimidin-2(5*H*)-one (6a). mp 237–239 °C (Lit.[32] 236–239 °C). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 8.78 (s, 1H, NH), 7.41–7.23 (m, 11H, ArH, =CH), 6.64 (s, 1H, NH), 5.16 (s, 1H, CH), 2.84–2.80 (m, 2H, CH_2), 2.36–2.35 (m, 1H, CH), 2.04–1.98 (m, 1H, CH). HR-MS (EI): calcd for $C_{20}H_{18}N_2O$: 302.1419, found: 302.1418.

7-(4-Nitrobenzylidene)-4-(4-nitrophenyl)-3,4,6,7-tetrahydro-1*H*-cyclopenta[*d*]pyrimidin-2(5*H*)-one (6b). mp 280–282 °C (Lit.[34] 281–282 °C). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 8.88 (s, 1H, NH), 8.36–8.18 (m, 4H, ArH), 7.66–7.38 (m, 4H, ArH), 6.90–6.79 (m, 2H, NH+CH), 5.40 (s, 1H, CH), 2.93–2.89 (m, 2H, CH_2), 2.27–2.19 (m, 1H, CH), 2.04–2.02 (m, 1H, CH).

7-(4-Chlorobenzylidene)-4-(4-chlorophenyl)-3,4,6,7-tetrahydro-1*H*-cyclopenta[*d*]pyrimidin-2(5*H*)-one (6c). mp 227–228 °C (Lit.[32] 226–228 °C). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 8.84 (s, 1H, NH), 7.47–7.28 (m, 9H, ArH, =CH), 6.63 (s, 1H, NH), 5.18 (s, 1H, CH), 2.83–2.78 (m, 2H, CH_2), 2.44–2.38 (m, 1H, CH), 2.03–1.97 (m, 1H, CH).

7-(4-Methoxybenzylidene)-4-(4-methoxyphenyl)-3,4,6,7-tetrahydro-1*H*-cyclopenta[*d*]pyrimidin-2(5*H*)-one (6d). mp 250–252 °C (Lit.[32] 250–252 °C). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 8.65 (s, 1H, NH), 7.27 (d, 2H, J = 8.4Hz, ArH), 7.16 (d, 2H, J = 8.4Hz, ArH), 7.05 (s, 1H, ArH), 6.94 (d, 4H, J = 7.5Hz, ArH, =CH), 6.58 (s, 1H, NH), 5.10 (s, 1H, CH), 3.76 (s, 6H, 2×OCH_3), 2.79 (s, 2H, CH_2), 2.40–2.36 (m, 1H, CH), 2.01–1.94 (m, 1H, CH); HR-MS (EI): calcd for $C_{22}H_{22}N_2O_3$: 362.1630; found: 362.1626.

7-(4-Methylbenzylidene)-4-(*p*-tolyl)-3,4,6,7-tetrahydro-1*H*-cyclopenta[*d*]pyrimidin-2(5*H*)-one (6e). mp 239–241 °C (Lit.[32] 238–241 °C). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 8.99 (s, 1H, NH), 7.40–7.25 (m, 9H, ArH, =CH), 6.94 (s, 1H, NH), 5.20 (s, 1H, CH), 2.85–2.83 (m, 2H, CH_2), 2.44–2.36 (m, 1H, CH), 2.10 (s, 7H, 2 ×CH_3+CH). HR-MS (EI): calcd for $C_{22}H_{22}N_2O$: 330.1732; found: 330.1729.

9-Benzylidene-4-phenyl-3,4,6,7,8,9-hexahydro-1*H*-cyclohepta[*d*]pyrimidin-2(5*H*)-one (6f). mp 287–288 °C (Lit.[34] 286–288 °C). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.02 (s, 1H, NH), 7.43–7.22 (m, 11H, ArH, =CH), 6.93 (s, 1H, NH), 5.24 (s, 1H, CH), 2.85–2.83 (m, 2H, CH_2), 2.44–2.43 (m, 1H, CH), 2.09 (s, 5H, CH, $2CH_2$).

4-(Naphthalen-1-yl)-7-(naphthalen-1-ylmethylene)-3,4,6,7-tetrahydro-1*H*-cyclopenta[*d*]pyrimidin-2(5*H*)-one (6g). mp 262–264 °C (Lit.[34] 260–264 °C). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.20 (s, 1H, NH), 8.39–6.76 (m, 14H, ArH), 7.05 (s, 1H, =CH), 6.03 (s, 1H, NH), 5.29 (s, 1H, CH), 2.80–2.70 (m, 2H, CH_2), 2.45–2.41 (m, 1H, CH), 1.83–1.75 (m, 1H,

CH). HR-MS (EI): calcd for $C_{28}H_{22}N_2O$: 402.1732; found: 402.1725.

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