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低共熔溶剂/苯磺酸: 通过 Biginelli 反应合成二氢嘧啶酮类化合物的环境友好催化体系

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摘要 在氯化胆碱和乙二醇组成的低共熔溶剂中, 苯磺酸催化下的 Biginelli 反应合成二氢嘧啶酮类化合物, 反应选择性高、产物易于分离、反应条件温和. 在较低温度下(50 ℃), 反应 10.0 h, 得到 94%的收率, 通过简单过滤产物即可分离, 且纯度较高. 该催化体系可以循环利用, 在此反应过程中催化剂、溶剂和没有反应的原料, 不需要进一步分离就可以进入下一次反应过程. 实验结果表明, 该催化体系循环利用 8 次后催化性能没有明显降低. 该反应体系对 F、Cl、OMe、CH_3 和 CH_3CONH 基团具有较好的容忍性, 共合成了 20 个产物, 收率 79%～99%.

关键词 低共融溶剂; Biginelli 反应; 二氢嘧啶酮; 对甲苯磺酸

Deep Eutectic Solvent/Benzenesulfonic Acid: An Environmental Friendly Catalyst System towards the Synthesis of Dihydropyrimidinones via Biginelli Reaction

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Abstract In a deep eutectic solvent (DES) that composed of choline chloride and ethylene glycol, 3,4-dihydropyrimidin-2(1*H*)-ones were synthesized via Biginelli reaction catalyzed by *p*-toluenesulfonic acid (*p*-TSA). 3,4-Dihydropyrimidin-2(1*H*)-ones were synthesized under mild conditions with high yield. High purity products were obtained by direct filtration without further purification. This catalytic system can be recycled, and the catalysts, solvents and remaining reactants can be directly recycled without separation. The results showed that the catalyst can be recycled up to 8 times. A wide variety of groups such as F, Cl, OMe, NO_2, CH_3, and CH_3CONH were tolerated in this procedure, and 20 products were obtained in high yields (79%～99%).

Keywords deep eutectic solvent (DES); Biginelli reaction; dihypyrimidinone; *p*-toluenesulfonic acid (*p*-TSA)

1 Introduction

Deep eutectic solvents (DESs), as an less expensive, more synthetically accessible, nontoxic and biodegradable room-temperature ionic liquids,[1] attracted much attentions in recent years. DESs were prepared from two or more components via hydrogen-bond interactions (Scheme 1). One component acted as a hydrogen-bond donor, and the other acted as a hydrogen-bond acceptor. The hydrogen-bond interactions played an important role in stabilizing the liquid configurations. DESs were considered to be an environmentally benign sustainable alternative to the conventional organic solvents.[2] Since it was firstly reported by Abbott and coworkers[3] that choline chloride (ChCl) and urea could form a DES by hydrogen bonding interaction, DESs have been widely used in diverse fields of research.[4-12] DESs have been used in traditional organic synthesis reaction as novel reactional media or catalyst, such as Friedel-crafts alkylation,[13] Diels-Alder reaction,[14] Knoevenagel condensation[15] and Clauson-Kaas reaction.[16] It was reported that the hydrogen-bonding interactions in the DESs enhances the electrophilicity of the carbonyl groups, thus surprisingly results were obtained when DESs were used as a solvent or catalyst.[17]

DES formed by ChCl and urea shows high viscosity,[1] which may cause troubles such as low mass transfer rate,

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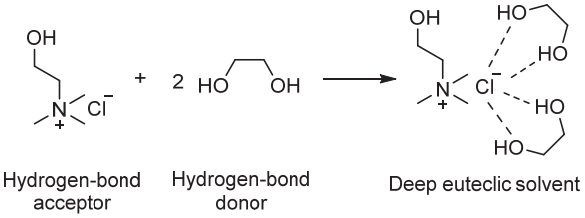


Scheme 1 Preparation of DES from chloline chloride and ethylene glycol

post-processing difficulty, besides, the DES remained the low melting point not longer because of decomposing of urea at high temperature which gives a great inconvenience to the reusing of DESs. ChCl and ethylene glycol (EG) with stable chemical properties were reported to form stable DES, which has the lower viscosity than others. In the past several years, the DES formed by ChCl and EG drew much more attentions, and it was widely used in many fields.[18-20]

3,4-Dihydropyrimidin-2(1*H*)-one and their derivatives have received great attentions due to their diverse therapeutic and pharmacological properties.[21] Biginelli reaction was one of the most elegant methods for preparing dihydropyrimidinones, which was one-pot but low yielding (20%～50%) condensation of *β*-dicarbonyl compounds with aldehydes and urea catalyzed by acid.[22] Since then, lots of protocols utilizing Lewis acids or metal-based as homogeneous catalyst (such as $FeCl_3$,[23] BF_3•OEt_2,[24] $Cu(OTf)_2$,[25] $Yb(PFO)_3$,[26] $LaCl_3$,[27] $PhB(OH)_2$[28]) to enhance the yield of products were reported. However, harsh reaction conditions such as high reaction temperature, expensive and highly acidic catalysts were necessary for the synthesis of dihydropyrimidinones. In these protocols, catalysts and solvents were difficult to be recovered. Heterogeneous catalyst such as niobium oxide supported in magnetite (Fe_3O_4@Nb_2O_5) was used to catalyze the Biginelli reaction under solvent free condition reported by Lima and co-workers.[29] In this case, 98% yield was obtained after 2 h at 80 ℃ when benzaldehydes/ethylacetoacetate/urea in a molar ratio of 1∶2∶2 was used. In order to separate the catalysts, additional organic solvent was added. As a common protonic acid, *p*-toluenesulfonic acid (*p*-TSA) is cheap and easy to available, usually used as a catalyst to get dihydropyrimidinones in the two-steps condensation reaction, and middle yield (40%～56%) can be obtained.[30] Simeonova *et al.*[31] carried out classical Biginelli reaction between ethyl acetoacetate and *p*-tolyl aldehyde catalyzed by *p*-TSA at 90 ℃ in sorbitol/urea (47 mol%/53 mol%) DES. The resulting dihydropyrimidone was obtained in 94% yield after 12 h. Because the decomposing of urea at high temperature, the catalytic system was hard to be reused. Therefore, recyclable DES and catalyst are still in demand. DES (ChCl/EG) as an environmental benign reaction solvent in combination with organic compound (benzenesulfonic acid) was used to catalyze the Biginelli reaction, and the resulting products were achieved under mild conditions.

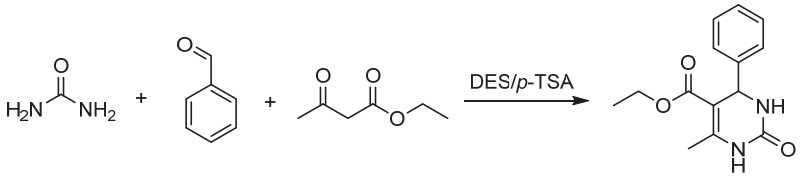
2 Results and discussion

In preliminary studies, the condensation of benzaldehyde, ethyl acetoacetate, and urea was studied as a model reaction to optimize the reaction conditions (Table 1). The condensation of the model substrates was investigated in diverse solvents at 50 ℃ for 2.0 h catalyzed by 10 mol% *p*-TSA. Solvent selection had a significant impact in the product yields. A satisfied yield (83%) of the expected dihydropyrimidinone was obtained when the reaction mixture was stirred in DES (Table 1, Entry 3). When the DES was replaced by ethanol or EG, there was a significant decrease in product yield (Table 1, Entry 1, 62% and Entry 2, 55%). Catalyst was critical, and only low yield (11%) was obtained in the absence of catalyst. Different benzenesulfonic acids showed similarly effective catalytic activity for the reaction (Table 1, Entries 5～8). And then the influence of reaction time, the mount of catalyst and temperature was examined. The reaction time extended to 6.0 h at 50 ℃, and the yield of the product increased to 93% (Table 1, Entry 8). But the yield of product shows a minor change with the increasing reaction time (Table 1, Entry 9). 5 mol% *p*-TSA was used to catalyze the reaction, and 72% yield of product was gained. When the amount of catalyst exceeded 20%, the yield varied a little (Table 1, Entries 9, 10). Experiment results showed that the yield of product increased with the increasing of reaction temperature, but it can't be improved remarkably when temperature exceeded 50 ℃ (Table 1, Entries 8, 13, 14, 15). It was worth to mention that high purity product was obtained by filtration without further operation.

The scope of this methodology was studied with the optimized condition in hand. Various aromatic aldehydes were used, and almost equivalent corresponding products were obtained. The experimental results were listed in Table 2. Various aromatic aldehydes (**1a**～**1j**) bearing either electron-rich or electron-deficient groups, such as NO_2, Cl, Br, Me, OMe, CN and CH_3CONH, were proved to be suitable substrates with the current conditions, when they reacted with ethyl acetoacetate. And the corresponding products (**3a**～**3j**) were obtained in good yields (Tabel 2, Entries 1～10, 90%～97%). The products from acetylacetone were also obtained in good yield (Table 2, Entries 11～20, 72%～97%). The electron-deficient substituent groups affected the reactivity of the aldehyde. Low reactivities were observed for 4-NO_2 and 4-CN benzaldehydes (Table 2, Entries 16, 19, 79%, 95%). 4-CH_3CONH benzaldehydes showed low reactivity because the solubility of the corresponding product in water (Table 2, Entry 18, 72%).

The recycling reactions were carried out with the model reaction of 20.0 mmol urea, 20.0 mmol ethyl acetoacetate, and 20.0 mmol benzaldehyde in 10.0 mL DES at 50 ℃ for 12.0 h. The product precipitated from the reaction mixture, so that it could be easily separated by filtration

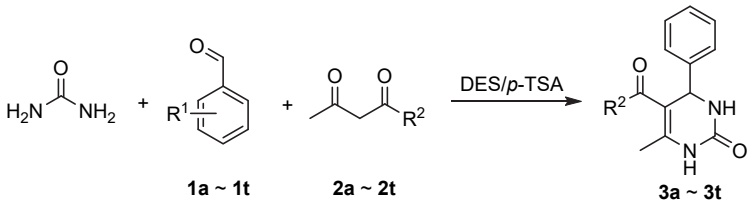
Table 1 Optimization of reaction conditions



Entry[a]	Temperature/℃	Solution (mL)	Time/h	Catalyst (mol%)	Yield[b]/%
1	50	EtOH (2.5)	2.0	*p*-TSA (10)	62
2	50	EG (2.5)	2.0	*p*-TSA (10)	55
3	50	DES (2.5)	2.0	*p*-TSA (10)	83
4	50	DES (2.5)	2.0	—	6
5	50	DES (2.5)	2.0	$C_6H_5SO_2OH$ (10)	80
6	50	DES (2.5)	2.0	3-$O_2NC_6H_4SO_2OH$ (10)	82
7	50	DES (2.5)	4.0	*p*-TSA (10)	90
8	50	DES (2.5)	6.0	*p*-TSA (10)	93
9	50	DES (2.5)	10.0	*p*-TSA (10)	94
10	50	DES (2.5)	6.0	*p*-TSA (5)	72
11	50	DES (2.5)	6.0	*p*-TSA (20)	91
12	50	DES (2.5)	6.0	*p*-TSA (30)	89
13	70	DES (2.5)	6.0	*p*-TSA (10)	91
14	40	DES (2.5)	6.0	*p*-TSA (10)	74
15	30	DES (2.5)	6.0	*p*-TSA (10)	27

[a] Condition: 5.0 mmol of urea, 5.0 mmol of ethyl acetoacetate, 5.0 mmol of benzaldehyde. [b] Isolated yield.

Table 2 Reaction scope for the Biginelli reaction

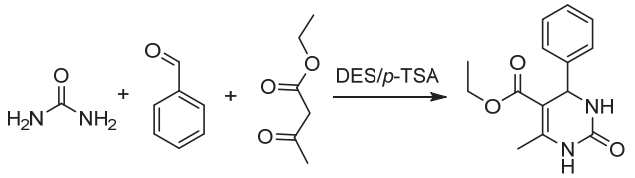


Entry[a]	R^1 (**1**)	R^2 (**2**)	R^1/R^2 (**3**)	Yield[b]/%
1	H (**1a**)	C_2H_5O (**2a**)	H/C_2H_5O (**3a**)	94
2	Cl (**1b**)	C_2H_5O (**2b**)	Cl/C_2H_5O (**3b**)	91
3	F (**1c**)	C_2H_5O (**2c**)	F/C_2H_5O (**3c**)	97
4	2,4-F_2 (**1d**)	C_2H_5O (**2d**)	2,4-F_2/C_2H_5O (**3d**)	97
5	CH_3O (**1e**)	C_2H_5O (**2e**)	CH_3O/C_2H_5O (**3e**)	96
6	NO_2 (**1f**)	C_2H_5O (**2f**)	NO_2/C_2H_5O (**3f**)	93
7	CH_3 (**1g**)	C_2H_5O (**2g**)	CH_3/C_2H_5O (**3g**)	97
8	CH_3CONH (**1h**)	C_2H_5O (**2h**)	CH_3CONH/C_2H_5O (**3h**)	90
9	CN (**1i**)	C_2H_5O (**2i**)	CN/C_2H_5O (**3i**)	95
10	Br (**1j**)	C_2H_5O (**2j**)	Br/C_2H_5O (**3j**)	97
11	H (**1k**)	CH_3 (**2k**)	H/CH_3 (**3k**)	86
12	Cl (**1l**)	CH_3 (**2l**)	Cl/CH_3 (**3l**)	94
13	F (**1m**)	CH_3 (**2m**)	F/CH_3 (**3m**)	89
14	2,4-F_2 (**1n**)	CH_3 (**2n**)	2,4-F_2/CH_3 (**3n**)	96
15	CH_3O (**1o**)	CH_3 (**2o**)	CH_3O/CH_3 (**3o**)	95
16	NO_2 (**1p**)	CH_3 (**2p**)	NO_2/CH_3 (**3p**)	79
17	CH_3 (**1q**)	CH_3 (**2q**)	CH_3/CH_3 (**3q**)	97
18	CH_3CONH (**1r**)	CH_3 (**2r**)	CH_3CONH/CH_3 (**3r**)	72
19	CN (**1s**)	CH_3 (**2s**)	CN/CH_3 (**3s**)	85
20	Br (**1t**)	CH_3 (**2t**)	Br/CH_3 (**3t**)	84

[a] Condition: 5.0 mmol of urea, 5.0 mmol of ethyl acetoacetate/acetylacetone, 5.0 mmol of benzaldehyde, 10 mol% *p*-TSA, 50 ℃, 10.0 h.. [b] Isolated yield.

after cooling the reaction mixture to room temperature. The reaction flask and the product were washed with 10 mL of ethanol. Before the solvent and catalyst were recharged to the next cycle, ethanol was easily removed under vacuum. The experimental results showed that 4.17 g of product was obtained in the first run. Partial products dissolved in the DES and ethanol used to wash product may be the main reason leading to the low yield. 5.12～5.32 g of product was obtained in the flowing 7 cycles. The total recovery of the product was 98%. In this process, the unreacted substrates don't need to be separated from the DES. The unreacted substrates continued to react in the next circle, so the product was obtained with high yield. During the repeat process, water was substituted by ethanol, and it brought great convenience for post-processing. Generally, this is a green synthetic method, and almost no byproducts will be obtained in any cycles.

Table 3 Rcycling reaction in DES catalyzed by *p*-TSA



Entry[a]	Yield[b]/g	Total yield/%
1	4.17	
2	5.12	
3	5.25	
4	5.30	
5	5.31	98
6	5.32	
7	5.28	
8	5.32	

[a] Conditions: 1.20 g (20.0 mmol) of urea, 2.60 g (20.0 mmol) of ethyl acetoacetate, 2.12 g (20.0 mmol) of benzaldehyde, 10 mol% *p*-TSA, 50 ℃, 10.0 h. [b] Isolated yield.

3 Conclusions

In summary, an efficient and practical method for the synthesis of dihydropyrimidinones in deep eutectic solvent has been discovered, and it has the ability to tolerate a wide variety of substitutions. Metal-free catalyst system (*p*-TSA/DES) was applied for the reaction, which can be reused for 8 cycles without obvious decreasing in catalytic performance. unreacted substrates don't need to be separated from the DES, and almost equivalent amount of product can be obtained with almost no waste produced.

4 Experimental section

4.1 Instruments and reagents

^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra were recorded on a Bruker ASCEND 400 (400 MHz for ^{1}H NMR; 100 MHz for ^{13}C NMR, 376 MHz for ^{19}F NMR) spectrometer by using DMSO-d_6 as a solvent. HRMS (ESI) measurements were performed in the positive-ion mode (*m*/*z* 50～800 range) on an Aglilent 6545 LC/Q-TOF. All samples were dissolved in methanol and were directly infused into the ESI source at a flow rate of 3.0 L/min after 1 min at 320 ℃. ESI source conditions were as follows: scan begin *m*/*z* 50, scan end *m*/*z* 800, during gas 8 L/min, nebulizer 0.24 MPa, sheath gas flow 11 L/min. A Nicolet iS50 FT-IR spectrophotometer was used for recording the IR spectra using potassium bromide pellets in the range of 400～4000 cm^{-1}. Melting points (℃) were determined in an open-glass capillary on an electrothermal X-5 apparatus and without correction. Reagents were purchased from commercial sources and were used as received unless mentioned otherwise.

4.2 Preparation of DES (ChCl/EG)

This DES was prepared in a round-bottomed flask, ChCl and EG were mixed at a molar ratio of 1∶2. The two raw composites were stirred vigorously in an oil bath with a magnetic stirrer at a temperature of 80 ℃ for 2 h. The as-prepared DESs were homogeneous liquid.

4.3 General procedure for the synthesis of dihydropyrimidinone derivatives to optimize the reaction condition

A mixture of benzaldehyde (0.51 mL, 5.0 mmol), urea (0.30 g, 5.0 mmol), ethyl acetoacetate (0.63 mL, 5.0 mmol), *p*-TSA (0.19 g, 1.0 mmol), and DES (2.5 mL) was added into a tube with a magnetic stirring bar under N_2 atmosphere. The reaction mixture was stirred at 50 ℃ for 10.0 h, and a solid product gradually precipitated. At the terminal of reaction, ice water (90 mL) was added slowly, the mixture was filtered and washed with lots of water and 50% ethanol. The crude product obtained was dried under vacuum.

5-Ethoxycarbonyl-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1*H*)-one (**3a**): A white solid, yield 94%. m.p. 206～210 ℃ (Lit.[24] 202～204 ℃); ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.21 (brs, 1H), 7.76 (brs, 1H), 7.41～7.29 (m, 2H), 7.29～7.15 (m, 3H), 5.16 (d, J=3.3 Hz, 1H), 3.99 (q, J=7.1 Hz, 2H), 2.26 (s, 3H), 1.10 (t, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 165.8, 152.6, 148.8, 145.3, 128.9, 127.7, 126.7, 99.7, 59.7, 54.5, 18.3, 14.5; IR (KBr) v: 3245, 3116, 2992, 1724, 1700, 1645, 1600 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{17}N_2O_3$ $[M+H]^+$ 261.1234, found 261.1248.

4-(4'-Chlorophenyl)phenyl-5-ethoxycarbonyl-6-methyl-3,4-dihydropyrimidin-2(1*H*)-one (**3b**): A white solid, yield 91%. m.p. 212～214 ℃ (Lit.[24] 213～215 ℃); ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.25 (brs, 1H), 7.78 (brs, 1H), 7.40 (d, J=8.5 Hz, 2H), 7.25 (d, J=8.5 Hz, 2H), 5.15 (d, J=3.3 Hz, 1H), 3.99 (q, J=7.0 Hz, 2H), 2.25 (s, 3H), 1.10 (t, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 165.7, 152.4, 149.2, 144.2, 132.2, 128.8, 128.6, 99.2, 59.7, 53.8, 18.2, 14.5; IR (KBr) v: 3244, 3117, 2980, 1727, 1702, 1647,1573, 1490 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{16}ClN_2O_3$ $[M+H]^+$ 295.0844, found 295.0842.

5-Ethoxycarbonyl-4-(4'-fluorophenyl)-6-methyl-3,4-dihydropyrimidin-2(1*H*)-one(**3c**): A white solid, yield

97%. m.p. 188～191 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.23 (brs, 1H), 7.76 (brs, 1H), 7.24～7.28 (m, 2H), 7.20～7.08 (m, 2H), 5.15 (d, J=3.3 Hz, 1H), 3.98 (q, J=7.1 Hz, 2H), 2.25 (s, 3H), 1.09 (t, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 165.7, 162.9, 161.8 (d, J=121.70 Hz), 152.4, 149.0, 141.6 (d, J=1.51 Hz), 128.7 (d, J=4.04 Hz), 115.6 (d, J=10.61 Hz), 99.6, 59.7, 53.8, 18.3, 4.5; ^{19}F NMR (376 MHz, DMSO-d_6) δ: −115.4; IR (KBr) ν: 3246, 3123, 2980, 1727, 1713, 1700, 1647, 1600, 1508 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{16}FN_2O_3$ $[M+H]^+$ 279.1139, found 279.1130.

4-(2',4'-Difluorophenyl)-5-ethoxycarbonyl-6-methyl-3,4-dihydropyrimidin-2(1*H*)-one (**3d**): A white solid, yield 97%. m.p. 186～188 ℃ (Lit.[24] 185～186 ℃); ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.29 (brs, 1H), 7.72 (brs, 1H), 7.30 (td, J=8.6, 6.5 Hz, 1H), 7.21～7.15 (m, 1H), 7.07～7.02 (m, 1H), 5.42 (d, J=3.0 Hz, 1H), 3.92 (q, J=7.1 Hz, 2H), 2.27 (s, 3H), 1.04 (t, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 165.34, 162.1 (dd, J=201.7, 12.4 Hz), 159.6 (dd, J=204.5, 12.4), 151.9, 149.6, 130.6 (dd, J=10.0, 5.7 Hz), 128.8 (dd, J=13.9, 3.7 Hz), 111.99 (dd, J=21.0, 3.1 Hz), 104.2 (t, J=25.8 Hz), 97.7, 59.6, 48.81 (d, J=2.7 Hz), 18.2, 14.4; ^{19}F NMR (376 MHz, DMSO-d_6) δ: −111.4, −114.8; IR (KBr) ν: 3352, 3230, 3119, 2984, 1697, 1645, 1609, 1504 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{15}F_2N_2O_3$ $[M+H]^+$ 297.1045, found 297.1048.

5-Ethoxycarbonyl-4-(4'-methoxyphenyl)-6-methyl-3,4-dihydropyrimidin-2(1*H*)-one (**3e**): A white solid, yield 96%. m.p. 202～204 ℃ (Lit.[24] 201～203 ℃); ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.16 (brs, 1H), 7.68 (brs, 1H), 7.15 (d, J=8.7 Hz, 2H), 6.88 (d, J=8.7 Hz, 2H), 5.10 (d, J=3.3 Hz, 1H), 3.98 (q, J=7.1 Hz, 2H), 3.72 (s, 3H), 2.24 (s, 3H), 1.11 (t, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 165.8, 158.9, 152.6, 148.5, 137.5, 127.9, 114.2, 100.1, 59.6, 55.5, 53.8, 18.2, 14.6; IR (KBr) ν: 3242, 3112, 2956, 2837, 1723, 1705, 1650, 1613, 1513 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{19}N_2O_4$ $[M+H]^+$ 291.1339, found 291.1340.

5-Ethoxycarbonyl-6-methyl-4-(4'-Nitrophenyl)-3,4-dihydropyrimidin-2(1*H*)-one (**3f**): A light yellow solid, yield 98%. m.p. 207～209 ℃ (Lit.[20] 208～211 ℃); ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.36 (brs, 1H), 8.22 (d, J=8.8 Hz, 2H), 7.90 (brs, 1H), 7.51 (d, J=8.8 Hz, 2H), 5.28 (d, J=3.4 Hz, 1H), 3.99 (q, J=7.1 Hz, 2H), 2.27 (s, 3H), 1.10 (t, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 165.5, 152.5, 152.2, 149.9, 147.2, 128.1, 124.3, 98.6, 59.9, 54.1, 18.3, 14.5; IR (KBr) ν: 3237, 3120, 2975, 1728, 1698, 1595, 1520 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{16}N_3O_5$ $[M+H]^+$ 306.1084, found 306.1083.

5-Ethoxycarbonyl-6-methyl-4-(4'-methylphenyl)-3,4-dihydropyrimidin-2(1*H*)-one (**3g**): A white solid, yield 97%. m.p. 292～294 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.16 (brs, 1H), 7.69 (brs, 1H), 7.12 (s, 4H), 5.11 (d, J=3.5 Hz, 1H), 3.98 (q, J=7.0 Hz, 2H), 2.26 (s, 3H), 2.24 (s, 3H), 1.11 (t, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 165.8, 152.6, 148.6, 142.4, 136.8, 129.4, 126.6, 99.9, 59.6, 54.1, 21.1, 18.2, 14.6; IR (KBr) ν: 3246, 3116, 2985, 1723, 1703, 1649, 1577, 1495 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{19}N_2O_3$ $[M+H]^+$ 275.1390, found 275.1386.

4-(4'-Acetamidophenyl)-5-ethoxycarbonyl-6-methyl-3,4-dihydropyrimidin-2(1*H*)-one (**3h**): A white solid, yield 90%. m.p. 290～293 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.92 (brs, 1H), 9.16 (brs, 1H), 7.69 (s, 1H), 7.50 (d, J=8.6 Hz, 2H), 7.15 (d, J=8.6 Hz, 2H), 5.09 (d, J=3.3 Hz, 1H), 3.98 (q, J=7.1 Hz, 2H), 2.25 (s, 3H), 2.02 (s, 3H), 1.10 (t, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 168.7, 165.8, 152.5, 148.6, 140.0, 138.8, 127.1, 119.5, 99.8, 59.6, 54.0, 24.4, 18.3, 14.6; IR (KBr) ν: 3349, 3277, 3207, 3153, 2981, 1696, 1641, 1606, 1547, 1511 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{20}N_3O_4$ $[M+H]^+$ 318.1448, found 318.1445.

4-(4'-Cyanophenyl)-5-ethoxycarbonyl-6-methyl-3,4-dihydropyrimidin-2(1*H*)-one (**3i**): A white solid, yield 95%. m.p. 157～159 ℃ (Lit.[32] 154～156 ℃); ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.33 (brs, 1H), 7.86 (brs, 1H), 7.82 (d, J=8.4 Hz, 2H), 7.43 (d, J=8.3 Hz, 2H), 5.22 (d, J=3.3 Hz, 1H), 3.99 (q, J=7.1 Hz, 2H), 2.26 (s, 3H), 1.09 (t, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 165.6, 152.3, 150.5, 149.8, 133.0, 127.8, 119.2, 110.6, 98.68, 59.8, 54.3, 40.6, 40.4, 40.18, 40.0, 39.8, 39.6, 39.4, 18.3, 14.5; IR (KBr) ν: 3231, 3111, 2976, 2929, 1707, 1649, 1606, 1497 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{16}N_3O_4$ $[M+H]^+$ 286.1186, found 286.1181.

4-(4'-Bromophenyl)-5-ethoxycarbonyl-6-methyl-3,4-dihydropyrimidin-2(1*H*)-one (**3j**): A white solid, yield 97%. m.p. 200～203 ℃ (Lit.[34] 194～197 ℃); ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.25 (brs, 1H), 7.78 (brs, 1H), 7.53 (d, J=8.4 Hz, 2H), 7.19 (d, J=8.4 Hz, 2H), 5.13 (d, J=3.3 Hz, 1H), 3.99 (q, J=7.1 Hz, 2H), 2.25 (s, 3H), 1.10 (t, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 165.6, 152.4, 149.2, 144.7, 131.8, 129.0, 120.8, 99.2, 59.7, 54.0, 40.6, 40.4, 40.2, 40.0, 39.8, 39.6, 39.4, 18.3, 14.5; IR (KBr) ν: 3245, 3116, 2978, 1724, 1701, 1645, 1580, 1485 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{16}BrN_2O_3$ $[M+H]^+$ 339.0339, found 339.0334.

5-Acetyl-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1*H*)-one (**3k**): A red solid, yield 86%. m.p. 241～243 ℃ (Lit.[33] 233～236 ℃); ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.19 (brs, 1H), 7.84 (brs, 1H), 7.42～7.30 (m, 2H), 7.26 (d, J=6.0 Hz, 3H), 5.27 (d, J=3.5 Hz, 1H), 2.30 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 194.7, 152.6, 148.6, 144.7, 129.0, 127.8, 126.9, 110.0, 54.3, 30.8, 19.4; IR (KBr) ν: 3259, 3123, 2925, 1702, 1675, 1598, 1494 cm^{-1}; HRMS (ESI) calcd for $C_{13}H_{15}N_2O_2$ $[M+H]^+$ 231.1128, found 231.1122.

5-Acetyl-4-(4'-chlorophenyl)-6-methyl-3,4-dihydropyrimidin-2(1*H*)-one (**3l**): A light yellow solid, yield 94%. m.p. 213～215 ℃ (Lit.[35] 210～212 ℃); ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.24 (brs, 1H), 7.87 (brs, 1H), 7.40 (d, J=8.5 Hz, 2H), 7.26 (d, J=8.5 Hz, 2H), 5.26 (d, J=3.5 Hz, 1H), 2.29 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 194.6, 152.5, 149.0, 143.7, 132.3, 128.9, 128.8, 110.0, 53.5, 30.9, 19.5; IR (KBr) ν: 3288, 3107,

2921, 1701, 1640, 1618, 1490 cm^{-1}; HRMS (ESI) calcd for $C_{13}H_{14}ClN_2O_2$ $[M+H]^+$ 265.0738, found 275.0737.

5-Acetyl-4-(4'-fluorophenyl)-6-methyl-3,4-dihydropyrimidin-2(1*H*)-one (**3m**): A pink solid, yield 96%. m.p. 217～219 ℃ (Lit.[36] 217～218 ℃); ^1H NMR (400 MHz, DMSO-d_6) δ: 9.22 (brs, 1H), 7.85 (brs, 1H), 7.33～7.24 (m, 2H), 7.15 (t, J=8.8 Hz, 2H), 5.26 (d, J=3.4 Hz, 1H), 2.29 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 194.7, 161.8 (J=243.4Hz), 152.5, 148.8, 141.0 (J=2.0 Hz), 128.9, 128.9 (J=4.0 Hz), 115.7 (J=10.6 Hz), 110.1, 53.5, 30.8, 19.4; ^{19}F NMR (376 MHz, DMSO-d_6) δ: −115.3; IR (KBr) v: 3422, 1752, 1660, 1616, 1509 cm^{-1}; HRMS (ESI) calcd for $C_{13}H_{14}N_2O_2$ $[M+H]^+$ 249.1034, found 249.1035.

5-Acetyl-4-(2'4'-difluorophenyl)-6-methyl-3,4-dihydropyrimidin-2(1*H*)-one (**3n**): An orange solid, yield 95%. m.p. 222～224 ℃; ^1H NMR (400 MHz, DMSO-d_6) δ: 9.28 (brs, 1H), 7.80 (brs, 1H), 7.35～7.11 (m, 2H), 7.04 (tdd, J=8.5, 2.6, 1.0 Hz, 1H), 5.50 (d, J=3.2 Hz, 1H), 2.31 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ: 194.3, 162.0 (dd, J=244.1, 12.0 Hz), 160.0 (dd, J=247.8, 12.5 Hz), 152.1, 130.3 (dd, J=5.8, 9.8 Hz), 128.1 (dd, J=14.0, 3.6 Hz), 112.1 (dd, J=21.0, 3.6 Hz), 108.6, 104.4 (t, J=25.9 Hz), 48.6 (d, J=2.5 Hz), 30.8, 19.5; ^{19}F NMR (376 MHz, DMSO-d_6) δ: −111.2, −114.1; IR (KBr) v: 3340, 3277, 3048, 1708, 1672, 1600, 1503 cm^{-1}; HRMS (ESI) calcd for $C_{13}H_{14}N_2O_2$ $[M+H]^+$ 267.0940, found 267.0936.

5-Acetyl-4-(4'-methoxyphenyl)-6-methyl-3,4-dihydropyrimidin-2(1*H*)-one (**3o**): An orange solid, yield 95%. m.p. 170～172 ℃ (Lit.[33] 168～170 ℃); ^1H NMR (400 MHz, DMSO-d_6) δ: 9.16 (brs, 1H), 7.77 (brs, 1H), 7.17 (d, J=8.7 Hz, 2H), 6.89 (d, J=8.7 Hz, 2H), 5.21 (d, J=3.4 Hz, 1H), 3.72 (s, 3H), 2.28 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ: 194.8, 159.0, 152.6, 148.3, 136.8, 128.1, 114.3, 110.1, 55.5, 53.8, 30.6, 19.3; IR (KBr) v: 3422, 1654, 1612, 1560, 1513; HRMS (ESI) calcd for $C_{14}H_{17}N_2O_3$ $[M+H]^+$ 261.1234, found 261.1256.

5-Acetyl-6-methyl-4-(4'-nitrophenyl)-3,4-dihydropyrimidin-2(1*H*)-one (**3p**): A light yellow solid, yield 79%. m.p. 266～268 ℃ (Lit.[31] 268～270 ℃); ^1H NMR (400 MHz, DMSO-d_6) δ: 9.35 (brs, 1H), 8.21 (d, J=8.8 Hz, 2H), 7.99 (brs, 1H), 7.51 (d, J=8.8 Hz, 2H), 5.39 (d, J=3.6 Hz, 1H), 2.32 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 194.4, 152.4, 152.0, 149.6, 147.1, 128.1, 124.3, 109.9, 53.6, 31.1, 19.6; IR (KBr) v: 3242, 3107, 2938, 1705, 1629, 1512 cm^{-1}; HRMS (ESI) calcd for $C_{13}H_{14}N_3O_4$ $[M+H]^+$ 276.0979, found 276.0977.

5-Acetyl-6-methyl-4-(4'-methylphenyl)-3,4-dihydropyrimidin-2(1*H*)-one (**3q**): A pink solid, yield 97%. m.p. 208～210 ℃ (Lit.[35] 208～210 ℃); ^1H NMR (400 MHz, DMSO-d_6) δ: 9.16 (brs, 1H), 7.79 (brs, 1H), 7.13 (s, 4H), 5.22 (d, J=3.5 Hz, 1H), 2.28 (s, 3H), 2.26 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ: 194.8, 152.6, 148.4, 141.8, 137.0, 129.5, 126.8, 110.0, 54.0, 30.7, 21.1 19.3; IR (KBr) v: 3290, 3123, 2921, 1701, 1641, 1618, 1501 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{17}N_2O_2$ $[M+H]^+$ 245.1285, found 245.1287.

4-(4'-Acetamidophenyl)-5-acetyl-6-methyl-3,4-dihydropyrimidin-2(1*H*)-one (**3r**): A red solid, yield 72%. m.p. 241～243 ℃; ^1H NMR (400 MHz, DMSO-d_6) δ: 9.95 (brs, 1H), 9.16 (brs, 1H), 7.78 (s, 1H), 7.50 (d, J=8.6 Hz, 2H), 7.16 (d, J=8.6 Hz, 1H), 5.20 (d, J=3.4 Hz, 1H), 3.11 (s, 1H), 2.28 (s, 2H), 2.08 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 194.8, 168.7, 152.5, 148.4, 139.3, 138.9, 127.3, 119.6, 109.9, 53.9, 30.7, 24.4, 19.4; IR (KBr) v: 3273, 3118, 3060, 2925, 1744, 1685, 1604, 1577 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{18}N_3O_3$ $[M+H]^+$ 288.1343, found 288.1361.

5-Acetyl-4-(4'-cyanophenyl)-6-methyl-3,4-dihydropyrimidin-2(1*H*)-one (**3s**): A light yellow solid, yield 85%. m.p. 206～208 ℃; ^1H NMR (400 MHz, DMSO-d_6) δ: 9.32 (brs, 1H), 7.98 (brs, 1H), 7.81 (d, J=8.4 Hz, 2H), 7.43 (d, J=8.3 Hz, 2H), 5.34 (d, J=3.6 Hz, 1H), 2.31 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 194.4, 152.5, 150.0, 149.5, 133.1, 127.9, 119.2, 110.5, 109.8, 53.8, 40.6, 40.4, 40.2, 40.0, 39.6, 39.5, 39.3, 31.1, 19.6; IR (KBr) v: 3226, 3111, 2929, 1693, 1616, 1505 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{14}N_3O_2$ $[M+H]^+$ 256.1081, found 256.1078.

5-Acetyl-4-(4'-bromophenyl)-6-methyl-3,4-dihydropyrimidin-2(1*H*)-one (**3t**): A light yellow solid, yield 84%. m.p. 240～243 ℃ (Lit.[37] 238～241 ℃); ^1H NMR (400 MHz, DMSO-d_6) δ: 9.24 (brs, 1H), 7.87 (brs, 1H), 7.53 (d, J=8.5 Hz, 2H), 7.20 (d, J=8.4 Hz, 2H), 5.24 (d, J=3.5 Hz, 2H), 2.29 (s, 4H), 2.13 (s, 4H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 194.6, 152.5, 149.0, 144.1, 131.9, 129.1, 120.8, 109.9, 53.6, 40.6, 40.4, 40.3, 40.2, 40.0, 39.8, 39.6, 39.4, 30.9, 19.5; IR (KBr) v: 3290, 3127, 2921, 1700, 1640, 1617, 1488 cm^{-1}; HRMS (ESI) calcd for $C_{13}H_{14}BrN_2O_2$ $[M+H]^+$ 309.0233, found 309.0223.

4.4 General procedure for the repeated protocol

8.0 mL of DES was added into a mixture of benzaldehyde (0.51 mL, 5.0 mmol), urea (0.30 g, 5.0 mmol), ethyl acetoacetate (0.63 mL, 5.0 mmol), and *p*-TSA (0.19 g, 1.0 mmol) was put in a round bottom flask under N_2 atmosphere, and then the mixture was heated in an oil bath at 50 ℃ for 20.0 h. After the completion of reaction, the reaction mixture was allowed to cool to room temperature, and then filtered. Ethanol (10.0 mL) was used to wash the reaction bottom flask and crucial product. Removed ethanol by vacuum distillation, all the filtrates collected were used up to 8 cycles.

Supporting Information ^1H NMR and ^{13}C NMR spectra of compounds **3a**～**3t**. The Supporting Information is available free of charge *via* the Internet at http://sioc-journal.cn/.

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