**Supporting Information**

Key Laboratory of Applied Surface and Colloid Chemistry (Ministry of Education), School of Chemistry and Chemical Engineering, Shaanxi Normal University, Xi’an 710062, P. R. China
E-mail: zwgao@snnu.edu.cn; Fax: +86-029-81530821

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1. General Information

Reagents were purchased from commercial sources and were used as received unless mentioned otherwise. Reactions were monitored by thin layer chromatography using silica gel. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker EQUINX55 (400 MHz for $^1$H; 101 MHz for $^{13}$C) spectrometer by using DMSO-d$_6$ as a solvent. For $^1$H NMR, tetramethylsilane (TMS) served as internal standard ($\delta = 0$) and $^1$H NMR chemical shifts are reported in ppm downfield of tetramethylsilane and referenced to residual solvent peak (DMSO-d$_6$ at 2.5 ppm and 3.33 ppm) unless otherwise noted. The data are reported as follows: chemical shift, integration, multiplicity ($s$ = singlet, $d$ = doublet, $t$ = triplet, $q$ = quartet and $m$ = multiplet), and coupling constant in Hz. For $^{13}$C NMR, DMSO-d$_6$ was used as internal standard ($\delta = 39.52$) and spectra were obtained with complete proton decoupling.

ESI-MS and ESI-MS/MS measurements were performed in the positive-ion mode (m/z 50–2500 range) on an MAXIS instrument from Bruker. This instrument has a hybrid quadrupole/ion mobility/orthogonal acceleration time-of-flight (oa-TOF) geometry and was used in the TOF V+ mode. All samples were dissolved in methanol and were directly infused into the ESI source at a flow rate of 4.0L/min after 1 min at 180 °C. ESI source conditions were as follows: capillary voltage 4.0 kV, nebulizer 0.4 bar, scan begin 100m/z, scan end 1300m/z, collision cell RF 200.0 Vpp, end plate offset -500V.
2. General Procedure for Synthesis of 3,4-dihydropyrimidin-2(1H)-ones

A representative example for preparation of 4i is as following: a mixture of p-Bromo Benzaldehyde (185 g, 1 mmol), 1,3-dicarbonyl compound (128 µL, 1 mmol), urea (0.120 g, 2 mmol), and Cp₂TiCl₂ (0.0248 g, 10 mol % to all of the reactants) was charged into a 50 mL pressure flask with a magnetic stirring bar. EtOH (4 mL) was subsequent added by syringe. Then the reaction system was placed in an oil-bath (70 °C) with magnetic stirring. After completion of the reaction, as indicated by TLC analysis, the reaction mixture was carried out via Silica gel flask column chromatography (eluent: petroleum ether: EtOAc = 1:1) to give the desired product 4i 304.2 mg as white solid. Yield: 90%.
3. Experimental and Characterization Data

5-Ethoxycarbonyl-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1H)-one (4a, 93%)

$^{1}$H NMR (400 MHz, DMSO) $\delta$ 9.19 (s, 1H), 7.74 (s, 1H), 7.34 – 7.29 (m, 2H), 7.24 (d, $J = 6.9$ Hz, 3H), 5.15 (d, $J = 3.1$ 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 (101 MHz, DMSO) $\delta$ 165.4, 152.3, 148.4, 144.9, 128.4, 127.3, 126.3, 99.4, 59.3, 54.1, 17.8, 14.1.

4-(4-tert-butyl)-5-ethoxycarbonyl-6-methyl-3,4-dihydropyrimidin-2(1H)-one (4b, 88%)

$^{1}$H NMR (400 MHz, DMSO) $\delta$ 9.18 (s, 1H), 7.70 (s, 1H), 7.33 (d, $J = 8.3$ Hz, 2H), 7.17 (d, $J = 7.9$ Hz, 2H), 5.14 (d, 1H), 3.99 (q, $J = 7.1$ Hz, 2H), 2.25 (s, 3H), 1.25 (s, 9H), 1.11 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (101 MHz, DMSO) $\delta$ 165.4, 152.4, 149.6, 148.2, 142.0, 125.9, 125.1, 99.5, 59.2, 53.5, 34.2, 31.1, 17.8, 14.1.

5-Ethoxycarbonyl-4-(4-methoxyphenyl)-6-methyl-3,4-dihydropyrimidin-2(1H)-one (4c, 90%)

$^{1}$H NMR (400 MHz, DMSO) $\delta$ 9.19 (s, 1H), 7.70 (s, 1H), 7.17 (d, $J = 8.7$ Hz, 2H), 6.88 (d, $J = 8.7$ Hz, 2H), 5.13 (d, $J = 3.2$ Hz, 1H), 3.98 (q, $J = 7.1$ Hz, 2H), 3.71 (s, 3H), 2.26 (s, 3H), 1.10 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (101 MHz, DMSO) $\delta$ 165.5, 152.4, 148.6, 148.2, 142.0, 125.9, 125.1, 99.7, 59.2, 55.1, 53.5, 17.8, 14.1.

4-(3,4-dimethoxyphenyl)-5-ethoxycarbonyl-6-methyl-3,4-dihydropyrimidin-2(1H)-one (4d, 86%)

$^{1}$H NMR (400 MHz, DMSO) $\delta$ 9.18 (s, 1H), 7.70 (s, 1H), 6.91 – 6.85 (m, 2H), 6.75 (d, $J = 9.6$ Hz, 1H), 5.13 (d, $J = 3.0$ Hz, 1H), 4.01 (q, $J = 7.0$ Hz, 2H), 3.72 (d, $J = 3.4$ Hz, 6H), 2.27 (s, 3H), 1.12 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (101 MHz, DMSO) $\delta$ 165.5, 152.4, 148.6, 148.2 (d, $J = 4.9$ Hz), 137.4, 118.0, 111.8, 110.6, 99.5, 59.3, 55.5 (d, $J = 10.0$ Hz), 53.6, 17.8, 14.2.
5-Ethoxycarbonyl-4-(4-methylphenyl)-6-methyl-3,4-dihydropyrimidin-2(1H)-one(4e,82%)

\[
\begin{align*}
\text{H NMR (400 MHz, DMSO)} & \delta 9.16 (s, 1H), 7.69 (s, 1H), 7.12 (s, 4H), 5.12 (d, J = 3.2 Hz, 1H), 3.98 (q, J = 7.0 Hz, 2H), 2.25 (d, J = 5.7 Hz, 6H), 1.10 (t, J = 7.1 Hz, 3H). \\
\text{C NMR (101 MHz, DMSO)} & \delta 165.4, 152.2, 148.2, 142.0, 136.4, 128.9, 126.2, 99.4, 59.2, 53.7, 20.7, 17.8, 14.1.
\end{align*}
\]

5-Ethoxycarbonyl-4-(3-methoxyphenyl)-6-methyl-3,4-dihydropyrimidin-2(1H)-one(4f,67%)

\[
\begin{align*}
\text{H NMR (400 MHz, DMSO)} & \delta 9.21 (s, 1H), 7.75 (s, 1H), 7.24 (t, J = 7.7 Hz, 1H), 6.86 – 6.78 (m, 3H), 5.15 (d, J = 2.5 Hz, 1H), 4.00 (q, J = 7.0 Hz, 2H), 3.72 (s, 3H), 2.26 (s, 3H), 1.11 (t, J = 7.0 Hz, 3H). \\
\text{C NMR (101 MHz, DMSO)} & \delta 165.4, 159.3, 152.4, 148.5, 146.4, 129.6, 118.3, 112.5, 112.2, 99.3, 59.3, 55.0, 53.9, 17.8, 14.2.
\end{align*}
\]

4-(4-Fluorophenyl)-5-ethoxycarbonyl-6-methyl-3,4-dihydropyrimidin-2(1H)-one(4g,87%)

\[
\begin{align*}
\text{H NMR (400 MHz, DMSO)} & \delta 9.23 (s, 1H), 7.75 (s, 1H), 7.30 – 7.23 (m, 2H), 7.18 – 7.11 (m, 2H), 5.16 (d, J = 3.2 Hz, 1H), 4.03 – 3.93 (m, 2H), 2.26 (s, 3H), 1.09 (t, J = 7.1 Hz, 3H). \\
\text{C NMR (101 MHz, DMSO)} & \delta 165.3, 162.6, 160.2, 152.1 (d, J = 9.3 Hz), 148.5 (d, J = 3.9 Hz), 141.2 (d, J = 3.0 Hz), 128.3 (d, J = 8.2 Hz), 115.1 (d, J = 21.1 Hz), 115.0 – 114.7 (m, 99.2 (d, J = 4.3 Hz), 59.2, 53.4, 17.8, 14.0.
\end{align*}
\]

4-(4-Chlorophenyl)-5-ethoxycarbonyl-6-methyl-3,4-dihydropyrimidin-2(1H)-one(4h,81%)

\[
\begin{align*}
\text{H NMR (400 MHz, DMSO)} & \delta 9.29 (s, 1H), 7.81 (s, 1H), 7.37 (d, J = 8.3 Hz, 2H), 7.28 (d, J = 8.3 Hz, 2H), 5.19 (d, J = 2.4 Hz, 1H), 3.98 (dd, J = 12.4, 6.5 Hz, 2H), 2.28 (s, 3H), 1.08 (t, J = 7.0 Hz, 3H). \\
\text{C NMR (101 MHz, DMSO)} & \delta 165.3, 152.2, 148.8, 143.9, 132.0, 128.4 (d, J = 14.7 Hz), 99.0, 59.4, 53.6, 17.9, 14.1.
\end{align*}
\]

4-(4-Bromophenyl)-5-ethoxycarbonyl-6-methyl-3,4-dihydropyrimidin-2(1H)-one(4i,90%)
$^1$H NMR (400 MHz, DMSO) δ 9.30 (s, 1H), 7.81 (s, 1H), 7.51 (d, $J$ = 8.0 Hz, 2H), 7.23 (d, $J$ = 8.2 Hz, 2H), 5.17 (d, $J$ = 12.4 Hz, 1H), 3.98 (dd, $J$ = 13.2, 6.4 Hz, 2H), 2.28 (s, 3H), 1.08 (t, $J$ = 6.9 Hz, 3H). $^{13}$C NMR (101 MHz, DMSO) δ 165.3, 152.2, 148.8, 144.3, 131.4, 128.7, 120.5, 99.0, 59.4, 53.7, 17.9, 14.1.

4-(2-Bromophenyl)-5-ethoxycarbonyl-6-methyl-3,4-dihydropyrimidin-2(1H)-one (4j, 67%)

$^1$H NMR (400 MHz, DMSO) δ 9.32 (s, 1H), 7.74 (s, 1H), 7.32 (dt, $J$ = 28.2, 8.3 Hz, 4H), 5.67 (d, 1H), 3.90 (q, $J$ = 7.1 Hz, 2H), 2.32 (s, 3H), 0.99 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (101 MHz, DMSO) δ 165.0, 151.6, 149.3, 141.8, 132.7, 129.4, 128.8, 127.8, 98.5, 59.1, 54.1, 17.7, 14.0.

4-(2-Chlorophenyl)-5-ethoxycarbonyl-6-methyl-3,4-dihydropyrimidin-2(1H)-one (4k, 75%)

$^1$H NMR (400 MHz, DMSO) δ 9.33 (s, 1H), 7.72 (s, 1H), 7.56 (d, $J$ = 7.9 Hz, 1H), 7.33 (s, 2H), 7.17 (s, 1H), 5.65 (d, $J$ = 2.0 Hz, 1H), 3.90 (q, $J$ = 7.0 Hz, 2H), 2.33 (s, 3H), 0.99 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (101 MHz, DMSO) δ 165.0, 151.5, 149.3, 143.4, 132.7, 129.4, 128.5, 122.4, 98.5, 59.1, 54.1, 17.7, 14.0.

4-(3-Bromophenyl)-5-ethoxycarbonyl-6-methyl-3,4-dihydropyrimidin-2(1H)-one (4l, 78%)

$^1$H NMR (400 MHz, DMSO) δ 9.29 (s, 1H), 7.81 (s, 1H), 7.47 – 7.39 (m, 2H), 7.28 (q, $J$ = 7.7 Hz, 2H), 5.18 (d, $J$ = 2.9 Hz, 1H), 4.01 (dd, $J$ = 14.9, 7.3 Hz, 2H), 2.28 (s, 3H), 1.10 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (101 MHz, DMSO) δ 165.2, 152.0, 149.0, 147.6, 130.8, 130.2, 129.3, 125.3, 121.6, 98.7, 59.4, 53.7, 17.9, 14.1.

5-Ethoxycarbonyl-6-methyl-4-(3-nitrophenyl)-3,4-dihydropyrimidin-2(1H)-one (4m, 67%)

$^1$H NMR (400 MHz, DMSO) δ 9.38 (s, 1H), 8.11 (s, 2H), 7.91 (s, 1H), 7.67 (dt, $J$ = 15.5, 7.7 Hz, 2H), 5.33 (d, $J$ = 3.1 Hz, 1H), 3.98 (dd, $J$ = 7.3, 7.7 Hz, 2H), 2.28 (s, 3H), 0.99 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (101 MHz, DMSO) δ 165.0, 151.6, 149.3, 143.4, 132.7, 129.4, 128.5, 122.4, 98.5, 59.1, 54.1, 17.7, 14.0.
13.5, 6.7 Hz, 2H), 3.40 (s, 1H), 2.28 (s, 3H), 1.09 (t, J = 7.1 Hz, 3H). 13C NMR (101 MHz, DMSO) δ 165.1, 152.0, 149.4, 147.8, 147.1, 133.1, 130.2, 122.4, 121.1, 98.5, 59.5, 53.7, 17.9, 14.0.

**5-Ethoxycarbonyl-6-methyl-4-isopropyl-3,4-dihydropyrimidin-2(1H)-one (4n, 12%)**

\[ \text{EtO} \quad \text{NH} \quad \text{NH} \quad \text{Me} \quad \text{C} \quad \text{H}_3 \]

\[ \begin{align*}
1^1H \text{ NMR (400 MHz, DMSO)} & \delta 8.89 (s, 1H), 7.28 (s, 1H), 4.11 - 4.01 (m, 2H), 3.95 (t, J = 3.4 Hz, 1H), 2.17 (s, 3H), 1.18 (t, J = 7.1 Hz, 4H), 0.82 (d, J = 6.9 Hz, 3H), 0.74 (d, J = 6.8 Hz, 3H). \\
13C \text{ NMR (101 MHz, DMSO)} & \delta 165.8, 153.2, 148.5, 98.2, 59.1, 55.5, 34.6, 18.5, 17.7, 16.0, 14.2.
\end{align*} \]

**5-Ethoxycarbonyl-6-methyl-4-propyl-3,4-dihydropyrimidin-2(1H)-one (4o, 50%)**

\[ \text{EtO} \quad \text{NH} \quad \text{NH} \quad \text{Me} \quad \text{C} \quad \text{H}_3 \]

\[ \begin{align*}
1^1H \text{ NMR (400 MHz, DMSO)} & \delta 8.93 (s, 1H), 7.32 (s, 1H), 4.10 - 4.01 (m, 3H), 2.16 (s, 3H), 1.43 - 1.30 (m, 3H), 1.18 (t, J = 7.1 Hz, 4H), 0.85 (t, J = 6.9 Hz, 3H). \\
13C \text{ NMR (101 MHz, DMSO)} & \delta 165.5, 152.9, 148.3, 99.5, 59.1, 49.8, 39.1, 17.7, 17.0, 14.2, 13.7.
\end{align*} \]

**5-Methoxycarbonyl-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1H)-one (4p, 77%)**

\[ \text{MeO} \quad \text{NH} \quad \text{NH} \quad \text{Me} \quad \text{C} \quad \text{H}_3 \]

\[ \begin{align*}
1^1H \text{ NMR (400 MHz, DMSO)} & \delta 9.25 (s, 1H), 7.78 (s, 1H), 7.36 - 7.29 (m, 2H), 7.28 - 7.21 (m, 3H), 5.18 (d, J = 3.1 Hz, 1H), 3.54 (s, 3H), 2.27 (s, 3H). \\
13C \text{ NMR (101 MHz, DMSO)} & \delta 165.9, 152.3, 148.7, 144.7, 128.5, 127.3, 126.2, 99.1, 53.9, 50.8, 17.9.
\end{align*} \]

**5-Methoxycarbonyl-4-(4-methoxyphenyl)-6-methyl-3,4-dihydropyrimidin-2(1H)-one (4q, 90%)**

\[ \text{MeO} \quad \text{NH} \quad \text{NH} \quad \text{Me} \quad \text{C} \quad \text{H}_3 \]

\[ \begin{align*}
1^1H \text{ NMR (400 MHz, DMSO)} & \delta 9.21 (s, 1H), 7.71 (s, 1H), 7.17 (d, J = 8.6 Hz, 2H), 6.88 (d, J = 8.6 Hz, 2H), 5.12 (d, J = 3.1 Hz, 1H), 3.72 (s, 3H), 3.53 (s, 3H), 2.27 (s, 3H). \\
13C \text{ NMR (101 MHz, DMSO)} & \delta 165.9, 158.5, 152.3, 148.4, 136.9, 127.4, 113.8, 99.4, 55.1, 53.3, 50.8, 17.9.
\end{align*} \]
5,6-Dimethyl-4-phenyl-3,4-dihydropyrimidin-2(1H)-one (4R,3S,4%)}

$^1$H NMR (400 MHz, DMSO) $\delta$ 9.20 (s, 1H), 7.85 (s, 1H), 7.35 – 7.31 (m, 2H), 7.26 (d, $J$ = 4.8 Hz, 3H), 5.28 (d, $J$ = 3.3 Hz, 1H), 2.30 (s, 3H), 2.11 (s, 3H). $^{13}$C NMR (101 MHz, DMSO) $\delta$ 194.7, 152.6, 148.5, 144.7, 128.9, 127.8, 126.8, 110.0, 54.3, 30.7, 19.3.
4. $^1$H and $^{13}$C Spectra for 3,4-dihydropyrimidin-2(1H)-ones Products

![Diagram of 3,4-dihydropyrimidin-2(1H)-ones Products]
5. HR-ESI-MS studies for proposed mechanism.

![HR-ESI-MS spectra of intermediate I mode.](image)

**Figure S5-1.** ESI(+)–MS spectra of intermediate I mode.
Figure S5-2. ESI(+)‐MS spectra of intermediate III mode.

Figure S5-3. ESI(+)‐MS spectra of intermediate VI mode.

Figure S5-4. ESI(+)‐MS spectra of intermediate IV mode.
**Figure S5-5.** MS/MS spectrum and the fragment structures of intermediate I under positive ion mode.

**Figure S5-6.** MS/MS spectrum and the fragment structures of intermediate VI under positive ion mode.

**Figure S5-7.** MS/MS spectrum and the fragment structures of intermediate III under positive ion mode.
6. $^{13}$C NMR Spectra studies for proposed mechanism
D. $\text{O=O}$ + EtOH

E. $\text{Cp}_2\text{TiCl}_2$ + $\text{O=O}$ + EtOH

F. $\text{Cp}_2\text{TiCl}_2$ + $\text{CHO}$ + EtOH
G. $\text{Cp}_2\text{TiCl}_2 + \text{H}_2\text{N} = \text{NH}_2 + \text{EtOH}$

H. $\text{Cp}_2\text{TiCl}_2 + \text{CHO} + \text{H}_2\text{N} = \text{NH}_2 + \text{EtOH}$

I. $\text{Cp}_2\text{TiCl}_2 + \text{O} = \text{OEt} + \text{H}_2\text{N} = \text{NH}_2 + \text{EtOH}$