ESI for

Poly(N-isopropylacrylamide-co-L-proline)-catalyzed Claisen-Schmidt and Knoevenagel condensations: unexpected enhanced catalytic activity of the polymer catalyst

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**S1 Condition optimizations**

**Table S1.** Screenings of the catalyst and additive.\(^a\)

\[
\begin{array}{cccc}
\text{Entry} & \text{Catalyst} & \text{Additive} & \text{Yield} \\
\hline
1 & L-Proline & - & 44 \\
2 & L-Proline & 1-Methylpiperazine & 55 \\
3 & L-Proline & Morpholine & 61 \\
4 & L-Proline & Pyrrolidine & 49 \\
5 & L-Proline & Piperazine & 70 \\
6 & L-Proline & Et₂NH & 36 \\
7 & L-Proline & (i-Pr)₂NH & 34 \\
8 & L-Proline & Pyridine & 32 \\
9 & L-Proline & Et₃N & 28 \\
10 & L-Proline & 1-Methylpiperidine & 43 \\
11 & L-Proline & PhNH₂ & 48 \\
12 & - & Piperazine & 15 \\
13 & L-Cysteine & Piperazine & 29 \\
14 & L-Histidine & Piperazine & 22 \\
15 & L-Arginine & Piperazine & 12 \\
16 & L-Norvaline & Piperazine & 52 \\
\end{array}
\]

\(^{a}\) Yields are reported as average of three independent experiments. 

\(^{b}\) Reaction conditions: \(1\)a + \(2\) \(\xrightarrow{\text{catalyst (5 mol %)}}\) \(3\)a. Reaction carried out in EtOH, 20 °C, 48 h, \(N₂\).
17 5-Aminopentanoic acid  Piperazine  17
18 Piperidine-2-carboxylic acid  Piperazine  25
19 Pyrrolidine-3-carboxylic acid  Piperazine  32

\(^a\)1 mmol of \(1a\), 3 mmol of acetone and 1 mL of EtOH were employed.

\(^b\)Isolated yields of \(3a\) based on \(1a\).

### Table S2. Condition optimizations.\(^a\)


<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>(2/1a^b)</th>
<th>Cat(^c)</th>
<th>(T)</th>
<th>Yield (^e)</th>
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<tr>
<td>1</td>
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<td>20</td>
<td>70</td>
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<tr>
<td>2</td>
<td>EtOH/H(_2)O (4:1)</td>
<td>3</td>
<td>5</td>
<td>20</td>
<td>64</td>
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<tr>
<td>3</td>
<td>EtOH/H(_2)O (1:1)</td>
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<td>5</td>
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<tr>
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<td>MeOH</td>
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<td>(i)-PrOH</td>
<td>3</td>
<td>5</td>
<td>20</td>
<td>66</td>
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<td>6</td>
<td>(t)-BuOH</td>
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<td>7</td>
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<td>20</td>
<td>64</td>
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\(^a\) 1 mmol of 1a, and 1 mL of solvent were employed.

\(^b\) Molar ratio of acetone vs. 1a.

\(^c\) Catalyst amount (mol %) based on 1a.

\(^d\) Reaction temperature.

\(^e\) Isolated yields of 3a based on 1a.
S2 Original $^1$H NMR spectra of benzaldehyde in mechanism study experiments

**Instruction:** The original spectra were given here to confirm that the chemical shifts of aldehyde-H were referred to the internal standard Me$_4$Si at 0 ppm. Although the solubility of L-proline was low in CDCl$_3$, it obviously affected the chemical shift of the aldehyde-H, which moved to the low field region (from 10.028 ppm to 10.030 ppm).

**S3.1 Without L-proline (CDCl$_3$, 400 MHz; aldehyde-H at 10.028 ppm; Me$_4$Si at 0 ppm)**
S3.2 After adding L-proline (CDCl₃, 400 MHz; aldehyde-H at 10.030 ppm; Me₄Si at 0 ppm)
S3.3 Without L-proline (Methanol-D₄, 400 MHz; aldehyde-H at 9.989 ppm; Me₄Si at 0 ppm)
S3.4 After adding L-proline (Methanol-D$_4$, 400 MHz; aldehyde-H at 9.992 ppm; Me$_4$Si at 0 ppm)
S3 GC data and spectra of the polymer absorption test

S3.1 GC analysis data of the sample PhCHO/EtOH without polymer 8

1st time

<table>
<thead>
<tr>
<th>Compound</th>
<th>Retention time/min</th>
<th>Peak wide/min</th>
<th>Peak area</th>
<th>%</th>
<th>PhCHO / EtOH</th>
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</thead>
<tbody>
<tr>
<td>PhCHO</td>
<td>1.195</td>
<td>0.0399</td>
<td>792.13324</td>
<td>4.77030</td>
<td>0.05009</td>
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<tr>
<td>EtOH</td>
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<td>0.0318</td>
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<td>95.22970</td>
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</table>

2nd time

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<th>Retention time/min</th>
<th>Peak wide/min</th>
<th>Peak area</th>
<th>%</th>
<th>PhCHO / EtOH</th>
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3rd time

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<th>%</th>
<th>PhCHO / EtOH</th>
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</thead>
<tbody>
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Average: 0.05009
S3.2 GC analysis data of the sample PhCHO/EtOH after adding polymer 8

1st time

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<th>Compound</th>
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<th>Peak area</th>
<th>%</th>
<th>PhCHO / EtOH</th>
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<td>0.2125</td>
<td>9075.36621</td>
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<td>0.04539</td>
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2nd time

<table>
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<tr>
<th>Compound</th>
<th>Retention time/min</th>
<th>Peak wide/min</th>
<th>Peak area</th>
<th>%</th>
<th>PhCHO / EtOH</th>
</tr>
</thead>
<tbody>
<tr>
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3rd time

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<th>Compound</th>
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<th>Peak area</th>
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<th>PhCHO / EtOH</th>
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Average:          0.04496

S4 NMR Spectra of the products
3a, CDCl₃, 600 MHz
$3\text{a, CDCl}_3$, 150 MHz
3b, CDCl₃, 600 MHz
3b, CDCl$_3$, 150 MHz
$3c$, CDCl$_3$, 400 MHz
3c, CDCl$_3$, 100 MHz
3d, CDCl₃, 600 MHz
3d, CDCl₃, 150 MHz
3e, CDCl$_3$, 600 MHz
$3e$, CDCl$_3$, 150 MHz
3f, CDCl₃, 600 MHz
3f, CDCl$_3$, 150 MHz
3g, CDCl₃, 400 MHz
$3g$, CDCl$_3$, 100 MHz
$\text{Cl}$

$\text{Me}$

$3h$, CDCl$_3$, 400 MHz
3h, CDCl₃, 100 MHz
3i, CDCl₃, 400 MHz
3i, CDCl₃, 100 MHz
$3j$, CDCl$_3$, 400 MHz
3j, CDCl₃, 100 MHz
3k, CDCl₃, 600 MHz
3l, CDCl₃, 400 MHz
$\text{HO-CH=CH-Me}$

$\text{31, CDCl}_3, 100 \text{ MHz}$
$\text{3m, CDCl}_3, 400 \text{ MHz}$
$^{3}$m, CDCl$_3$, 100 MHz
$3n$, DMSO-$d_6$, 100 MHz
10a, CDCl$_3$, 400 MHz
10a, CDCl₃, 100 MHz
$^{10b}$, CDCl$_3$, 400 MHz
10b, CDCl₃, 100 MHz
10c, CDCl$_3$, 400 MHz
$10c$, CDCl$_3$, 100 MHz
10d, CDCl$_3$, 600 MHz
$10d$, CDCl$_3$, 150 MHz
10e, CDCl$_3$, 600 MHz
10e, CDCl₃, 100 MHz
10f, CDCl₃, 400 MHz
10f, CDCl₃, 100 MHz