Supporting Information

for

Brønsted Acid Catalyzed Selective Cyclization Reaction: An Efficient and Facile Synthesis of Polysubstituted Imidazole and Pyrrole Derivatives

Lei Dai, Ping Shu, Zhansheng Wang, Qingyang Li, Qiuyu Yu, Yanhui Shi, Liangce Rong*

Cw Chu college, College of Chemistry and Chemical Engineering, Jiangsu Normal University,
Xuzhou 221116, Jiangsu, People’s Republic of China
*Corresponding author: lcrong@jsnu.edu.cn

Table of contents

(A) General methods ...........................................................................................................S2
(B) X-ray diffraction of 3a ..................................................................................................S2-S3
(C) Copies of $^1$H NMR and $^{13}$C NMR spectra for the products ..............................S4-S35
(A) General methods:

1. Experimental section:

All reagents were purchased from the Merck and Sigma-Aldrich chemical companies and used without further purification. Melting points were determined on XT-5 microscopic melting-point apparatus and were uncorrected. IR spectra were recorded on a FT Bruker Tensor 27 spectrometer. $^1$H NMR and $^{13}$C NMR spectra of 3 were obtained from solution in DMSO-$d_6$ with Me$_4$Si as internal standard using a Bruker-400 spectrometer under 50 °C, $^1$H NMR and $^{13}$C NMR spectra of 5 were obtained from solution in DMSO-$d_6$ with Me$_4$Si as internal standard using a Bruker-400 spectrometer under 25 °C. HRMS spectra were obtained with a Bruker microTOF-Q 134 instrument. X-ray diffraction analysis was performed with a Siemens P4 diffractometer.

2. General procedures:

The mixture of substituted 3-(2-oxo-2-arylethylidene)-indolin-2-one 1 (1 mmol), 1,3-dimethylurea 2 (1.2 mmol) or 3-amino-1-phenyl-1H-pyrazol-5(4H)-one 4 (1 mmol), p-TSA•H$_2$O (0.3 mmol), and CH$_3$CN (5 mL) was put in a 25 mL flask and reacted under 80 °C (monitored by TLC) about 2 h. After completion, the reaction the mixture was cooled to room temperature and the precipitate obtained was isolated by filtration and dried. Compounds 3 or 5 were purified by recrystallization from DMF or EtOH.

(B) X-ray diffraction of 3a:

Figure 1.X-Ray crystal structure of 3a (CCDC 1469591)
<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C&lt;sub&gt;20&lt;/sub&gt;H&lt;sub&gt;18&lt;/sub&gt;ClN&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>Formula weight</td>
<td>367.82</td>
</tr>
<tr>
<td>Temperature</td>
<td>296(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Monoclinic, P2(1)/c</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 9.8551(14) Å, α = 90 deg.</td>
</tr>
<tr>
<td></td>
<td>b = 16.606(2) Å, β = 120.337(8) deg.</td>
</tr>
<tr>
<td></td>
<td>c = 13.4927(17) Å, γ = 90 deg.</td>
</tr>
<tr>
<td>Volume</td>
<td>1905.8(4) Å&lt;sup&gt;3&lt;/sup&gt;</td>
</tr>
<tr>
<td>Z, Calculated density</td>
<td>4, 1.282 Mg/m&lt;sup&gt;3&lt;/sup&gt;</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.096 mm&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>F(000)</td>
<td>1016</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>2.62 to 25.00 deg.</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>-12 ≤ h ≤ 11, -16 ≤ k ≤ 17, -19 ≤ l ≤ 19</td>
</tr>
<tr>
<td>Reflections collected / unique</td>
<td>18732 / 4217 [R(int) = 0.0253]</td>
</tr>
<tr>
<td>Completeness to theta = 25.00</td>
<td>99.8 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.7457 and 0.6804</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>4217 / 1 / 317</td>
</tr>
<tr>
<td>Goodness-of-fit on F&lt;sup&gt;2&lt;/sup&gt;</td>
<td>1.034</td>
</tr>
<tr>
<td>Final R indices [I&gt;2σ(I)]</td>
<td>R&lt;sub&gt;1&lt;/sub&gt; = 0.0803, wR&lt;sub&gt;2&lt;/sub&gt; = 0.1811</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R&lt;sub&gt;1&lt;/sub&gt; = 0.0588, wR&lt;sub&gt;2&lt;/sub&gt; = 0.1610</td>
</tr>
<tr>
<td>Extinction coefficient</td>
<td>0.0042(15)</td>
</tr>
<tr>
<td>Largest diff. peak and hole /e. Å&lt;sup&gt;3&lt;/sup&gt;</td>
<td>0.835 and -0.456</td>
</tr>
</tbody>
</table>

These data can be obtained free of charge from the Cambridge Crystallographic DataCentre via [www.ccdc.cam.ac.uk/data_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), the CCDC number is 1469591.
(C) Copies of $^1$H NMR and $^{13}$C NMR spectra for the products:

$^1$H NMR of compound 3a (50 °C)

$^{13}$C NMR of compound 3a (50 °C)
$^1$H NMR of compound 3b (50 °C)

$^{13}$C NMR of compound 3b (50 °C)
$^1$H NMR of compound 3c (50 °C)

$^{13}$C NMR of compound 3c (50 °C)
$^1$H NMR of compound 3d (50 °C)

$^{13}$C NMR of compound 3d (50 °C)
$^1$H NMR of compound 3e (25 °C)

$^1$H NMR of compound 3e (25 °C and 50 °C)
$^1$H NMR of compound 3e (50 °C)

$^{13}$C NMR of compound 3e (50 °C)
$^1$H NMR of compound $3g$ (50 °C)

$^{13}$C NMR of compound $3g$ (50 °C)
$^1$H NMR of compound 3h (50 °C)

$^{13}$C NMR of compound 3h (50 °C)
$^1$H NMR of compound 3i (50 °C)

$^{13}$C NMR of compound 3i (50 °C)
$^1$H NMR of compound 3j (50 °C)

$^{13}$C NMR of compound 3j (50 °C)
$^1$H NMR of compound 3k (50 °C)

$^{13}$C NMR of compound 3k (50 °C)
$^{1}H$ NMR of compound 31 (50 °C)

$^{13}C$ NMR of compound 31 (50 °C)
$^{1}$H NMR of compound 3m (50 °C)

$^{13}$C NMR of compound 3m (50 °C)
\[ {^1}H \text{NMR of compound 3n} \ (50 \ ^\circ \text{C}) \]

\[ {^{13}}C \text{NMR of compound 3n} \ (50 \ ^\circ \text{C}) \]
$^1$H NMR of compound 3o (50 °C)

$^{13}$C NMR of compound 3o (50 °C)
$^1$H NMR of compound 3p (50 °C)

$^{13}$C NMR of compound 3p (50 °C)
HNMR of compound 3r (50 °C)

\[ ^{13}\text{C NMR of compound 3r (50 °C)} \]
\( ^1H \text{ NMR of compound 5a} \)

\( ^{13}C \text{ NMR compound of 5a} \)
$^1$H NMR compound of 5b

$^{13}$C NMR compound of 5b
$^{13}$C NMR compound of 5c

$^1$H NMR compound of 5c
$^1$H NMR compound of 5d

$^{13}$C NMR compound of 5d
$^1$H NMR compound of 5e

$^{13}$C NMR compound of 5e
$^1$H NMR compound of 5f

$^{13}$C NMR compound of 5f
$^1$H NMR compound of 5g

$^{13}$C NMR compound of 5g
$^1$H NMR compound of 5i

$^{13}$C NMR compound of 5i
$^1$H NMR compound of 5j

$^{13}$C NMR compound of 5j
**H NMR compound of 5k**

**C NMR compound of 5k**
**H NMR compound of S1**

![H NMR spectrum of S1](image)

**C NMR compound of S1**

![C NMR spectrum of S1](image)
$^1$H NMR compound of 5m

$^{13}$C NMR compound of 5m