Electronic Supplementary Information

Simple pyrazoles as efficient organocatalysts for alkyne-CO$_2$ carboxylation and one-pot construction of heterocycles

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## Contents

S1 General information ....................................................................................................................... 3  
S2 Experimental section ..................................................................................................................... 4  
S3 Catalytic carboxylation of phenylacetylene (1a) with CO₂.......................................................... 5  
S4 Comparison of Me₂Pz with the reported catalysts ........................................................................ 7  
S5 Mechanism exploration ................................................................................................................ 8  
  S5.1 Interactions between azoles and Cs₂CO₃ ................................................................................. 8  
  S5.2 Formation of the Pz-CO₂ adduct ............................................................................................... 10  
  S5.3 Carboxylation of 1a with Cs(PzCO₂) ...................................................................................... 11  
  S5.4 Interaction between 1a and Cs₂CO₃ ......................................................................................... 12  
  S5.5 Interaction between 1a and Cs(PzCO₂) ................................................................................ 12  
S6 Synthesis and characterization for propiolic acids (2) ................................................................. 14  
S7 Synthesis and characterization for propiolic acid esters (3) ......................................................... 18  
S8 Synthesis and characterization for 4H-quinazin-4-ones (4) ......................................................... 20  
S9 Synthesis and characterization for 2H-pyran-2-one (5) ............................................................... 22  
S10 Synthesis and characterization for 3-cyano-6-hydroxy-2-pyridones (6) ................................. 24  
S11 Synthesis and characterization for 3a-hydroxyisoxazolo[3,2-a]isoindol-8(3aH)-ones (7) .......... 25  
S12 Synthesis and characterization for imidazole-4-carboxylic derivatives (9) ............................ 27  
S13 X-ray crystallographic study ..................................................................................................... 28  
S14 References .................................................................................................................................. 29  
S15 Copies of ′H NMR spectra of products ...................................................................................... 31
S1 General information

\(^1\)H and \(^{13}\)C spectra were collected on 300 MHz, 400 MHz or 500 MHz NMR spectrometers (Bruker AVANCE) using CDCl\(_3\), DMSO-\(d_6\) solution. For mechanism studies, NMR spectra were recorded in anhydrous DMSO, with positioning of a glass capillary filled with D\(_2\)O inside the NMR tube for magnetic field locking. \(^1\)H chemical shifts (\(\delta_H\)) are expressed in parts per million (ppm) and reported relative to the internal standard CDCl\(_3\) (\(\delta_H = 7.26\) ppm) or DMSO-\(d_6\) (\(\delta_H = 2.50\) ppm), or relative to the external standard DMSO (\(\delta_H = 2.50\) ppm) in a D\(_2\)O capillary. \(^{13}\)C chemical shifts (\(\delta_C\)) are expressed in ppm and reported relative to the internal standard DMSO-\(d_6\) (\(\delta_C = 39.6\) ppm), or relative to the external standard DMSO (\(\delta_C = 39.4\) ppm) in a D\(_2\)O capillary. Silica gel (300 - 400 mesh) was used for flash column chromatograph, eluting with ethyl acetate/petroleum ether (60 - 90 °C) mixture. Unless otherwise noted, the chemicals and reagents were purchased in analytical purity from commercial sources and used directly without further purification. Anhydrous DMSO was further dried over molecular sieve.
S2 Experimental section

**General procedure for catalytic carboxylation.** The catalyst and base were added to a Schlenk tube. After three times of atmosphere exchange with CO\(_2\), the reactor was equipped with a CO\(_2\) balloon and heated in an oil bath. Then 1.0 mmol terminal alkyne dissolved in 3 mL solution was injected under stirring to start the reaction. After stirring at required temperature for specified time, the reaction was quenched with water (15 mL). The resultant solution was washed with CH\(_2\)Cl\(_2\) to separate the catalyst and any unreacted alkyne. The aqueous phase was acidified with 1 M HCl to pH = 1 and then extracted with ethyl acetate (15 mL \(\times\) 3). The combined organic phase was washed with saturated NaCl solution and dried over anhydrous MgSO\(_4\). The solvent was removed under vacuum to obtain the product, which was weighed for yield calculations.

**Catalyst recovery.** A scale-up catalytic reaction was performed in a 250 mL flask by following the typical procedure with 10 mmol 1a, 1.0 mmol Me\(_2\)Pz and 15 mmol Cs\(_2\)CO\(_3\) in 20 mL DMSO. The reaction was performed at 80 °C until the alkyne was completely consumed as indicated by TLC. After addition of 100 mL water, the solution was extracted with CH\(_2\)Cl\(_2\) (3 \(\times\) 100 mL). The combined extracts were washed with aqueous NaHCO\(_3\), dried over MgSO\(_4\) and evaporated in vacuo. The solid thus obtained was confirmed by NMR to be Me\(_2\)Pz with satisfactory purity. The recovery rate is 95%. The aqueous phase after above extraction was treated by typical procedures to give 2a in a yield of about 99%.
S3 Catalytic carboxylation of phenylacetylene (1a) with CO$_2$

Table S1. Additional control tests with potential catalysts

<table>
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<tr>
<th>Cat.</th>
<th>Yield</th>
<th>Me-N=NH</th>
<th>NH</th>
<th>nBu$_4$NOAc</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>30%</td>
<td>96%</td>
<td>36%</td>
<td>30%</td>
</tr>
<tr>
<td>DBU</td>
<td>28%</td>
<td>36%</td>
<td></td>
<td>34%</td>
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</table>

* Reaction conditions: 1a (1.0 mmol), catalyst (0.1 mmol, 10 mol%), Cs$_2$CO$_3$ (1.5 mmol, 1.5 eq.), CO$_2$ (balloon), DMSO (3 mL), 60 °C, 6 h; isolated yield.
Table S2. Optimization of carboxylation of 1a with CO$_2$ *a*

![Diagram](https://via.placeholder.com/150)

<table>
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<tr>
<th>Entry</th>
<th>Catalyst (mol%)</th>
<th>Base</th>
<th>Solvent</th>
<th>T/°C</th>
<th>Yield/%</th>
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</thead>
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<td>1</td>
<td>Me$_2$Pz (10)</td>
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<td>96</td>
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<td>&gt;99</td>
</tr>
</tbody>
</table>

*a* Reaction conditions: 1a (1.0 mmol), catalyst, base (1.5 mmol, 1.5 eq.), CO$_2$ (balloon), solvent (3 mL), 6 h; isolated yield. $^b$ PC: propylene carbonate.
S4 Comparison of Me₂Pz with the reported catalysts

Table S3. Carboxylation of 1a using various metal and organic catalysts at ambient CO₂ pressure. a

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Base</th>
<th>T/°C</th>
<th>t/h</th>
<th>Yield/%</th>
<th>Ref.</th>
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<tr>
<td>1</td>
<td>Cu(BPhen)(4-F-PPh₃)₂(NO₃)²</td>
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<td>35</td>
<td>16</td>
<td>98 b</td>
<td>1</td>
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<td>CuCl-TMEDA</td>
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<td>16</td>
<td>90 b</td>
<td>2</td>
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<tr>
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<td>Cu(dibpf)</td>
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<td>24</td>
<td>94 b</td>
<td>3</td>
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<tr>
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<td>16</td>
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<td>60</td>
<td>6</td>
<td>96</td>
<td>This work</td>
</tr>
</tbody>
</table>

a The solvent is DMSO unless otherwise specified. For a more complete collection, see ref. 30. b The solvent is DMF. c The CO₂ pressure is 5 atm. d n-Bu₄NOAc (1.5 mmol, 1.5 eq.), the solvent is MeCN. e The reaction performs ethylene carbonate (EC) as the solvent in the presence of n-butyl iodide.
S5 Mechanism exploration

S5.1 Interactions between azoles and Cs$_2$CO$_3$

Fig. S1. $^1$H NMR spectra of 1,2,3-triazole with/without Cs$_2$CO$_3$ in DMSO-$d_6$ at room temperature (*: DMSO-$d_6$; ❤: H$_2$O). The red dashed box shows the magnification in the 16 - 12 ppm range.

Fig. S2. $^1$H NMR spectra of 1,2,4-triazole with/without Cs$_2$CO$_3$ in DMSO-$d_6$ at room temperature (*: DMSO-$d_6$; ❤: H$_2$O). The red dashed box shows the magnification in the 16 - 11 ppm range.
Fig. S3. $^1$H NMR spectra of pyrazole (Pz) with/without Cs$_2$CO$_3$ in DMSO-$d_6$ at RT or 60 °C (*: DMSO-$d_6$; ❤: H$_2$O). The red dashed box shows the magnification in the 14 - 11 ppm range.

Fig. S4. $^1$H NMR spectra of 3,5-dimethylpyrazole (Me$_2$Pz) with/without Cs$_2$CO$_3$ in DMSO-$d_6$ at RT or 60 °C (*: DMSO-$d_6$; ❤: H$_2$O). The red dashed box shows the magnification in the 13 - 9 ppm range.
S5.2 Formation of the Pz-CO$_2$ adduct

Cs(PzCO$_2$). A mixture of Pz (10 mmol) and Cs$_2$CO$_3$ (1.5 eq.) in anhydrous DMSO was placed in a sealed round bottom flask. The resulting mixture was stirred for 2 h at 60 °C and then filtered. The filtrate, which contains CsPz, was stirred under CO$_2$ or $^{13}$CO$_2$ (balloon) for another 2 h. The solutions before and after reacting with CO$_2$ were tested by $^1$H NMR and $^{13}$C NMR.

Fig. S5. $^1$H NMR spectra (300 MHz, DMSO, 298 K, locked to a D$_2$O capillary) of Pz (A), CsPz (B) and Cs(PzCO$_2$) (C).

Fig. S6. $^{13}$C NMR spectra (400 MHz, DMSO, 298 K, locked to a D$_2$O capillary) of CsPz (A, 1024 scans), Cs(PzCO$_2$) (B, 1024 scans) and Cs(Pz$^{13}$CO$_2$) (C, 8 scans).
S5.3 Carboxylation of 1a with Cs(Pz$^{13}$CO$_3$)

**Synthetic procedure**: The reactor with or without Cs$_2$CO$_3$ was equipped with a N$_2$/CO$_2$ balloon and heated in an oil bath. Then 1a (1.0 mmol) and Cs(Pz$^{13}$CO$_3$) (1 mmol in 3 mL DMSO) were injected under stirring to start the reaction. After stirring at 60 °C for 6 h, the reaction was quenched with water (15 mL). The resultant solution was washed with CH$_2$Cl$_2$, acidified with 1 M HCl to pH = 1 and then extracted with ethyl acetate (15 mL × 3). The combined organic phase was washed with saturated NaCl solution and dried over anhydrous MgSO$_4$. The solvent was removed under vacuum to obtain product, which was weighed for yield calculations.

![13C NMR spectra](image)

Fig. S7. $^{13}$C NMR spectra (400 MHz, DMSO-$d_6$) of $^{13}$C-carboxyl-labeled 2a with 8 scans.
S5.4 Interaction between 1a and Cs$_2$CO$_3$

![H NMR spectra of 1a (A), 1a with Cs$_2$CO$_3$ (B) and variable-temperature NMR spectra of 1a with Cs$_2$CO$_3$ at 40 °C (C) and at 60 °C (D) in DMSO-d$_6$ (*: DMSO-d$_6$; ❤: H$_2$O).](image)

Fig. S8. $^1$H NMR spectra of 1a (A), 1a with Cs$_2$CO$_3$ (B) and variable-temperature NMR spectra of 1a with Cs$_2$CO$_3$ at 40 °C (C) and at 60 °C (D) in DMSO-d$_6$ (*: DMSO-d$_6$; ❤: H$_2$O).

S5.5 Interaction between 1a and Cs(PzCO$_2$)

![H NMR spectra (300 MHz, DMSO, 298 K, locked to a D$_2$O capillary) of 1a (A), 1a with Cs(PzCO$_2$) (B) and Cs(PzCO$_2$) (C).](image)

Fig. S9. $^1$H NMR spectra (300 MHz, DMSO, 298 K, locked to a D$_2$O capillary) of 1a (A), 1a with Cs(PzCO$_2$) (B) and Cs(PzCO$_2$) (C).
Fig S10. Experimental and simulated XRD patterns of 4d.

Fig S11. $^1$H NMR spectrum of 4d synthesized from 1a (A) or 3c (B), the products obtained by these two methods are mixed for (C).
S6 Synthesis and characterization for propiolic acids (2)

\[
\text{R} \equiv \text{CO}_2 \xrightarrow{\text{Me}_2\text{Pz}, \text{Cs}_2\text{CO}_3, \text{DMSO} \atop 60^\circ \text{C}, 6 \text{ h}} \xrightarrow{\text{HCl}} \text{R} \equiv \text{COOH}
\]

**General synthetic procedure:** The catalyst (Me₂Pz, 10 mol%) and Cs₂CO₃ (1.5 mmol) were added to a Schlenk tube. After three times of atmosphere exchange with CO₂, the reactor was equipped with a CO₂ balloon and heated to 60 °C in an oil bath. Then 1.0 mmol terminal alkyne dissolved in 3 mL dry DMSO was injected under stirring to start the reaction. After stirring at 60 °C for 6 h, the reaction was quenched with water (15 mL). The resultant solution was washed with CH₂Cl₂, acidified with 1 M HCl to pH = 1 and then extracted with ethyl acetate (15 mL × 3). The combined organic phase was washed with saturated NaCl solution and dried over anhydrous MgSO₄. The solvent was removed under vacuum to obtain the propiolic acid, which was weighed for yield calculations.

**Characterization data**

3-Phenylpropiolic acid (2a)

![3-Phenylpropiolic acid](image)

White solid; 140.3 mg, yield: 96%

\[^1\text{H NMR (400 MHz, DMSO-d}_6\text{) } \delta 13.58 (s, 1\text{H}), 7.64 - 7.61 (m, 2\text{H}), 7.57 - 7.52 (m, 1\text{H}), 7.49 - 7.45 (m, 2\text{H}).\]

4-Methoxylphenylpropiolic acid (2b)

![4-Methoxylphenylpropiolic acid](image)

Yellow solid; 134 mg, yield: 76%

\[^1\text{H NMR (500 MHz, DMSO-d}_6\text{) } \delta 13.59 (s, 1\text{H}), 7.59 (d, J = 7.8 \text{ Hz}, 2\text{H}), 7.03 (d, J = 7.8 \text{ Hz}, 2\text{H}), 3.80 (s, 3\text{H}).\]

4-Methylphenylpropiolic acid (2c)

![4-Methylphenylpropiolic acid](image)

White solid; 128.4 mg, yield: 80%

\[^1\text{H NMR (500 MHz, DMSO-d}_6\text{) } \delta 7.49 (d, J = 8.1 \text{ Hz}, 2\text{H}), 7.26 (d, J = 8.1 \text{ Hz}, 2\text{H}), 2.33 (s, 3\text{H}).\]
4-Pentylphenylpropionic acid (2d)

C₄H₉-\(\equiv\)-COOH

White solid; 121.4 mg, yield: 60%

\(^1\)H NMR (300 MHz, DMSO-\(d_6\)) \(\delta\) 7.55 (d, \(J = 7.4\) Hz, 2H), 7.49 (d, \(J = 8.0\) Hz, 2H), 1.28 (s, 9H).

3-(Biphenyl-4-yl)propionic acid (2e)

\(\equiv\)-COOH

Yellow solid; 210.5 mg, yield: 95%

\(^1\)H NMR (500 MHz, DMSO-\(d_6\)) \(\delta\) 7.77 (d, \(J = 8.0\) Hz, 2H), 7.72 - 7.69 (m, 4H), 7.49 (t, \(J = 7.5\) Hz, 2H), 7.41 (t, \(J = 7.3\) Hz, 1H).

4-Chlorophenylpropionic acid (2f)

Cl-\(\equiv\)-COOH

Yellow solid; 173 mg, yield: 96%

\(^1\)H NMR (500 MHz, DMSO-\(d_6\)) \(\delta\) 7.63 (d, \(J = 8.5\) Hz, 2H), 7.52 (d, \(J = 8.5\) Hz, 2H).

4-Trifluoromethylphenylpropionic acid (2g)

F₃C-\(\equiv\)-COOH

White solid; 211.5 mg, yield: 99%

\(^1\)H NMR (500 MHz, DMSO-\(d_6\)) \(\delta\) 7.85 (d, \(J = 8.5\) Hz, 2H), 7.82 (d, \(J = 8.5\) Hz, 2H).

4-Formylphenylpropionic acid (2h)

OHC-\(\equiv\)-COOH

White solid; 169 mg, yield: 97%

\(^1\)H NMR (300 MHz, DMSO-\(d_6\)) \(\delta\) 13.36 (br), 10.06 (s, 1H), 7.98 (d, \(J = 8.2\) Hz, 2H), 7.82 (d, \(J = 8.2\) Hz, 2H).
4-Cyanophenylpropionic acid (2i)

\[
\text{NC} \equiv \text{COOH}
\]

White solid; 167.8 mg, yield: 98%

\(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta 7.91 (d, J = 8.0 \text{ Hz}, 2\text{H}), 7.79 (d, J = 8.0 \text{ Hz}, 2\text{H}).

4-Nitrophenylpropionic acid (2j)

\[
\text{O}_2\text{N} \equiv \text{COOH}
\]

Yellow solid; 189 mg, yield: 99%

\(^1\)H NMR (500 MHz, DMSO-\(d_6\)) \(\delta 8.29 (d, J = 7.7 \text{ Hz}, 2\text{H}), 7.91 (d, J = 7.8 \text{ Hz}, 2\text{H}).

3-(Thiophen-3-yl)propionic acid (2k)

\[
\text{S} \equiv \text{COOH}
\]

White solid; 150 mg, yield: 99%

\(^1\)H NMR (500 MHz, DMSO-\(d_6\)) \(\delta 7.89 (dd, J = 5.1, 1.2 \text{ Hz}, 1\text{H}), 7.67 (dd, J = 3.7, 1.2 \text{ Hz}, 1\text{H}), 7.20 (dd, J = 5.1, 3.7 \text{ Hz}, 1\text{H}).

(Pyridin-2-yl)propynoic acid (2l)

\[
\text{N} \equiv \text{COOH}
\]

Dark red solid; 73 mg, yield: 50%

\(^1\)H NMR (500 MHz, DMSO-\(d_6\)) \(\delta 8.65 (dt, J = 4.8, 1.4 \text{ Hz}, 1\text{H}), 7.90 (td, J = 7.7, 1.8 \text{ Hz}, 1\text{H}), 7.73 (dt, J = 7.9, 1.2 \text{ Hz}, 1\text{H}), 7.52 (ddd, J = 7.7, 1.2 \text{ Hz}, 1\text{H}).

4-Amino-2-butynoic acid (2m)

\[
\text{H}_2\text{N} \equiv \text{COOH}
\]

Colorless oil; 66 mg, yield: 67%

\(^1\)H NMR (300 MHz, DMSO-\(d_6\)) \(\delta 3.79 (s, 2\text{H}).

16
4-Bromo-2-butynoic acid (2n)

$\text{Br}\overset{\equiv}{\text{C}}\overset{\equiv}{\text{O}}\text{H}$

Brown oil; 113 mg, yield: 70%

$^1\text{H NMR (300 MHz, DMSO-$d_6$)} \delta 4.23$ (s, 2H).

3,3′-(1,4-Phenylene)dipropiolic acid (2q)

\[ \text{HOOC-} \overset{\equiv}{\text{C}}\overset{\equiv}{\text{C}}\overset{\equiv}{\text{C}}\overset{\equiv}{\text{C}}\overset{\equiv}{\text{C}}\overset{\equiv}{\text{COOH}} \]

White solid; 197 mg, yield: 92%

$^1\text{H NMR (300 MHz, DMSO-$d_6$)} \delta 13.85$ (br), 7.70 (s, 4H).

3,3′,3′′-(1,3,5-Phenylene)tripropiolic acid (2r)

\[ \text{HOOC-} \overset{\equiv}{\text{C}}\overset{\equiv}{\text{C}}\overset{\equiv}{\text{C}}\overset{\equiv}{\text{C}}\overset{\equiv}{\text{C}}\overset{\equiv}{\text{COOH}} \]

Yellow solid; 279 mg, yield: 99%

$^1\text{H NMR (300 MHz, DMSO-$d_6$)} \delta 7.96$ (s, 3H).
S7 Synthesis and characterization for propiolic acid esters (3)

General synthetic procedure: The catalyst (Me$_2$Pz, 10 mol%) and Cs$_2$CO$_3$ (1.5 mmol) were added to a Schlenk tube. After three times of atmosphere exchange with CO$_2$, the reactor was equipped with a CO$_2$ balloon and heated to 60 °C in an oil bath. Then 1a (1.0 mmol) dissolved in 3 mL dry DMSO was injected under stirring to start the reaction. After stirring at 60 °C for 6 h and cooling to room temperature, RX (1.2 eq.) was added and stirred for another 4 h. The reaction was quenched with water (15 mL) and the resultant solution was extracted with ethyl acetate (15 mL × 3). The combined organic phase was washed with saturated NaCl solution, dried over anhydrous MgSO$_4$ and the solvent was removed in vacuo. The crude product was purified by flash column chromatography.

Characterization data

Methyl 3-phenylpropiolate (3a)

\[ \text{Colorless oil; 155.4 mg, yield: 97%} \]

$^1$H NMR (300 MHz, DMSO-$d_6$) δ 7.69 - 7.66 (m, 2H), 7.62 - 7.56 (m, 1H), 7.53 - 7.47 (m, 2H), 3.79 (s, 3H).

Butyl 3-phenyl-2-propynoate (3b)

\[ \text{Colorless oil; 186 mg, yield: 92%} \]

$^1$H NMR (300 MHz, Chloroform-$d$) δ 7.57 - 7.54 (m, 2H), 7.44 - 7.38 (m, 1H), 7.36 - 7.31 (m, 2H), 4.21 (t, $J = 6.7$ Hz, 2H), 1.70 - 1.60 (m, 2H), 1.45 - 1.36 (m, 2H), 0.94 (t, $J = 7.4$ Hz, 3H).
Ethyl 3-phenylpropionate (3c)

Colorless oil; 163.5 mg, yield: 94%

$^1$H NMR (300 MHz, Chloroform-$d$) $\delta$ 7.60 - 7.57 (m, 2H), 7.48 - 7.42 (m, 1H), 7.40 - 7.34 (m, 2H), 4.30 (q, $J = 7.1$ Hz, 2H), 1.36 (t, $J = 7.2$ Hz, 3H).

2-Oxo-2-phenylethyl 3-phenylpropionate (3d)

Pale yellow solid; 250 mg, yield: 95%

$^1$H NMR (300 MHz, Chloroform-$d$) $\delta$ 7.94 (d, $J = 7.1$ Hz, 2H), 7.63 (dd, $J = 6.9$, 1.8 Hz, 3H), 7.54 - 7.45 (m, 3H), 7.39 (t, $J = 7.3$ Hz, 2H), 5.50 (s, 2H).

Cinnamyl 3-phenylpropionate (3e)

Colourless oil; 207 mg, yield: 79%

$^1$H NMR (300 MHz, Chloroform-$d$) $\delta$ 7.62 - 7.59 (m, 2H), 7.49 - 7.28 (m, 8H), 6.73 (d, $J = 15.9$ Hz, 1H), 6.35 (dt, $J = 15.9$, 6.6 Hz, 1H), 4.90 (dd, $J = 6.6$, 1.3 Hz, 2H).
S8 Synthesis and characterization for 4H-quinazin-4-ones (4)

General synthetic procedure: The catalyst (Me$_2$Pz, 10 mol%) and Cs$_2$CO$_3$ (1.5 mmol) were added to a Schlenk tube. After three times of atmosphere exchange with CO$_2$, the reactor was equipped with a CO$_2$ balloon and heated to 60 °C in an oil bath. Then 1a (1.0 mmol) dissolved in 3 mL dry DMSO was injected under stirring to start the reaction. After stirring at 60 °C for 6 h and cooling to room temperature, EtBr (1.2 eq.) and pyridine derivatives (2.0 eq.) were added and heated at 100 °C for another 8 h. The reaction was quenched with water (15 mL) and the resultant solution was extracted with ethyl acetate (15 mL x 3). The combined organic phase was washed with saturated NaCl solution, dried over anhydrous MgSO$_4$ and the solvent was removed in vacuo. The crude product was purified by flash column chromatography.

Characterization data

4-Oxo-2-phenyl-4H-quinolizine-1-carbonitrile (4a)

Yellow solid; 218 mg, yield: 89%

$^1$H NMR (300 MHz, Chloroform-$d$) δ 9.28 (d, $J$ = 7.0 Hz, 1H), 8.15 (d, $J$ = 9.0 Hz, 1H), 7.81 - 7.75 (m, 1H), 7.66 - 7.63 (m, 2H), 7.53 (dd, $J$ = 4.3, 2.4 Hz, 3H), 7.29 - 7.24 (m, 1H), 6.63 (s, 1H).

2-(3-Chlorophenyl)-4-oxo-4H-quinolizine-1-carbonitrile (4b)

Yellow solid; 257 mg, yield: 92%

$^1$H NMR (300 MHz, Chloroform-$d$) δ 9.28 (d, $J$ = 7.2 Hz, 1H), 8.13 (d, $J$ = 8.9 Hz, 1H), 7.83 - 7.77 (m, 1H), 7.61 - 7.56 (m, 2H), 7.53 - 7.48 (m, 2H), 7.31 - 7.28 (m, 1H), 6.58 (s, 1H).
Ethyl 4-oxo-2-phenyl-4H-quinolizine-1-carboxylate (4c)

Yellow solid; 220 mg, yield: 75%

$^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 9.25 (d, $J = 7.4$ Hz, 1H), 8.22 (d, $J = 9.2$ Hz, 1H), 7.58 - 7.52 (m, 1H), 7.45 - 7.36 (m, 5H), 7.15 - 7.10 (m, 1H), 6.59 (s, 1H), 3.96 (q, $J = 7.1$ Hz, 2H), 0.79 (t, $J = 7.1$ Hz, 3H).

3-Acetyl-2-phenyl-4H-quinolizin-4-one (4d)

Yellow solid; 238 mg, yield: 90%

$^1$H NMR (300 MHz, Chloroform-$d$) $\delta$ 9.21 (d, $J = 8.4$ Hz, 1H), 7.54 - 7.49 (m, 2H), 7.43 - 7.35 (m, 5H), 7.12 (ddd, $J = 7.4$, 5.5, 2.5 Hz, 1H), 6.64 (s, 1H), 2.50 (s, 3H).
Synthesis and characterization for 2H-pyran-2-one (5)

**General synthetic procedure:** The catalyst (Me₂Pz, 10 mol%) and Cs₂CO₃ (1.5 mmol) were added to a Schlenk tube. After three times of atmosphere exchange with CO₂, the reactor was equipped with a CO₂ balloon and heated to 60 °C in an oil bath. Then 1a (1.0 mmol) dissolved in 3 mL dry DMSO was injected under stirring to start the reaction. After stirring at 60 °C for 6 h and cooling to room temperature, EtBr (1.2 eq.) was added and stirred at RT for 4 h. Then, 1,3-dicarbonyl compound (1.0 eq.) was added at 100 °C and allowed to react for 4 h. The reaction was quenched with water (15 mL) and the resultant solution was extracted with ethyl acetate (15 mL × 3). The combined organic phase was washed with saturated NaCl solution, dried over anhydrous MgSO₄ and the solvent was removed in vacuo. The crude product was purified by flash column chromatography.

**Characterization date**

**Ethyl 6-methyl-2-oxo-4-phenyl-2H-pyran-5-carboxylate (5a)**

Pale yellow solid; 116 mg, yield: 45%

\[ ^1H \text{ NMR} (400 \text{ MHz, Chloroform}-d) \delta 7.42 - 7.40 \text{ (m, 3H)}, 7.28 \text{ (dt, } J = 7.6, 1.9 \text{ Hz, 2H)}, 6.15 \text{ (s, 1H)}, 3.97 \text{ (q, } J = 7.2 \text{ Hz, 2H)}, 2.45 \text{ (s, 3H)}, 0.86 \text{ (t, } J = 6.4 \text{ Hz, 3H}). \]

**5-Acetyl-6-methyl-4-phenyl-2H-pyran-2-one (5b)**

White solid; 86.8 mg, yield: 38%

\[ ^1H \text{ NMR} (400 \text{ MHz, Chloroform}-d) \delta 7.43 \text{ (d, } J = 6.3 \text{ Hz, 3H)}, 7.32 - 7.29 \text{ (m, 2H)}, 6.12 \text{ (s, 1H)}, 2.33 \text{ (s, 3H)}, 2.31 \text{ (s, 3H)}. \]
5-Benzoyl-4,6-diphenyl-2H-pyran-2-one (5c)

Yellow solid; 263 mg, yield: 75%

$^1$H NMR (300 MHz, Chloroform-$d$) $\delta$ 7.96 - 7.91 (m, 2H), 7.88 - 7.85 (m, 2H), 7.53 - 7.46 (m, 4H), 7.41 - 7.35 (m, 4H), 7.34 - 7.30 (m, 3H), 6.89 (s, 1H).
S10 Synthesis and characterization for 3-cyano-6-hydroxy-2-pyridones (6)

General synthetic procedure: The catalyst (Me$_2$Pz, 10 mol%) and Cs$_2$CO$_3$ (1.5 mmol) were added to a Schlenk tube. After three times of atmosphere exchange with CO$_2$, the reactor was equipped with a CO$_2$ balloon and heated to 60 °C in an oil bath. Then 1a (1.0 mmol) dissolved in 3 mL dry DMSO was injected under stirring to start the reaction. After stirring at 60 °C for 6 h and cooling to room temperature, CH$_3$I (1.2 eq.) was added and stirred at RT for 4 h. Then, cyanoacetamide or 2-cyano-N-methyl-acetamide (1.02 eq.) was added and heated to 100 °C for 12 h. The reaction was quenched with water (15 mL) and the resultant solution was acidified with 1M HCl to produce solid. The solid was filtered and dried in vacuum.

Characterization data

6-Hydroxy-2-oxo-4-phenyl-1,2-dihydropyridine-3-carbonitrile (6a)

![Structure of 6a]

White solid; 159.7 mg, yield: 75%

$^1$H NMR (300 MHz, DMSO-$_d_6$) δ 7.51 (s, 5H), 5.65 (s, 1H).

MS: [M+H]$^+$; 213.21, found: 213.2

6-Hydroxy-1-methyl-2-oxo-4-phenyl-1,2-dihydropyridine-3-carbonitrile (6b)

![Structure of 6b]

White solid; 162.5 mg, yield: 72%

$^1$H NMR (300 MHz, DMSO-$_d_6$) δ 7.51 - 7.50 (m, 5H), 5.63 (s, 1H), 3.31 (s, 3H).

MS: [M+H]$^+$; 227.24, found: 227.2
S11 Synthesis and characterization for 3a-hydroxyisoxazolo[3,2-a]isoindol-8(3aH)-ones (7)

**General synthetic procedure:** The catalyst (Me₂Pz, 10 mol%) and Cs₂CO₃ (1.5 mmol) were added to a Schlenk tube. After three times of atmosphere exchange with CO₂, the reactor was equipped with a CO₂ balloon and heated to 60 °C in an oil bath. Then 1a or 1o (1.0 mmol) dissolved in 3 mL dry DMSO was injected under stirring to start the reaction. After stirring at 60 °C for 6 h and cooling to room temperature, EtBr (1.2 eq.), NHPI (1.0 eq.) and PPh₃ (0.1 eq.) were added. The reaction system soon became reddish brown and was stirred at RT for 6 h. The reaction was quenched with water (15 mL) and the resultant solution was extracted with ethyl acetate (15 mL × 3). The combined organic phase was washed with saturated NaCl solution, dried over anhydrous MgSO₄ and the solvent was removed in vacuo. The crude product was purified by flash column chromatography.

**Characterization data**

Ethyl 3a-hydroxy-8-oxo-2-phenyl-3a,8-dihydroisoxazolo[3,2-a]-isoindole-3-carboxylate (7a)

![Chemical structure of 7a](image)

White solid; 327 mg, yield: 97%

$^1$H NMR (300 MHz, DMSO-$d_6$) δ 8.01 (d, $J = 7.7$ Hz, 1H), 7.98 (s, 1H), 7.90 - 7.83 (m, 2H), 7.72 - 7.63 (m, 3H), 7.61 - 7.48 (m, 3H), 4.11 - 4.00 (m, 2H), 1.10 (t, $J = 7.1$ Hz, 3H).

Diethyl 2,2′-(1,4-phenylene)bisis(3a-hydroxy-8-oxo-3a,8-dihydroisoxazolo[3,2-a]isoindole-3-carboxylate) (7b)

![Chemical structure of 7b](image)

Pale yellow solid; 378 mg, yield: 69%

$^1$H NMR (300 MHz, DMSO-$d_6$) δ 8.00 (d, $J = 6.8$ Hz, 4H), 7.92 - 7.83 (m, 8H), 7.68 (t, $J = 8.0$ Hz, 2H), 4.13 - 4.08 (m, 4H), 1.15 - 1.10 (m, 6H).
Ethyl 2-(4-ethynylphenyl)-3a-hydroxy-8-oxo-3a,8-dihydro-isoxazolo[3,2-a]isoindole-3-carboxylate (7b*)

White solid; 72 mg, yield: 22%

$^1$H NMR (300 MHz, DMSO-$d_6$) $\delta$ 8.01 - 7.96 (m, 2H), 7.90 - 7.83 (m, 2H), 7.73 - 7.61 (m, 5H), 4.43 (s, 1H), 4.12 - 4.07 (m, 2H), 1.13 (t, $J$ = 7.1 Hz, 3H).
Synthesis and characterization for imidazole-4-carboxylic derivatives (9)

General synthetic procedure: The catalyst (Me$_2$Pz, 10 mol%) and Cs$_2$CO$_3$ (1.5 mmol) were added to a Schlenk tube. After three times of atmosphere exchange with CO$_2$, the reactor was equipped with a CO$_2$ balloon and heated to 60 °C in an oil bath. Then 1a (1.0 mmol) dissolved in 3 mL dry DMSO was injected under stirring to start the reaction. After stirring at 60 °C for 6 h and cooling to room temperature, EtBr (1.2 eq.) was added and stirred for 4 h. Benzyamine (1.2 eq.) and Cs$_2$CO$_3$ (1.0 mmol) were addition to form intermediate products (8). KI (0.3 eq.) and tBuONO (2.0 eq.) were added and the reaction mixture was stirred at 80 °C for 18 h. The reaction was quenched with water (15 mL) and the resultant solution was extracted with ethyl acetate (15 mL × 3). The combined organic phase was washed with saturated NaCl solution, dried over anhydrous MgSO$_4$ and the solvent was removed in vacuo. The crude product was purified by flash column chromatography.

Characterization data

Ethyl-3-(benzylamino)-3-phenylacrylate (8)

\[
\begin{align*}
\text{HN} & \text{Ph} \\
Ph & \text{O} \text{Et} \\
\text{Ph} & \text{OEt}
\end{align*}
\]

$^1$H NMR (300 MHz, Chloroform-$d$) $\delta$ 9.02 (t, $J$ = 6.4 Hz, 1H), 7.40 - 7.37 (m, 5H), 7.34 - 7.31 (m, 2H), 7.29 - 7.21 (m, 3H), 4.76 (s, 1H), 4.31 (d, $J$ = 6.5 Hz, 2H), 4.21 (q, $J$ = 7.1 Hz, 2H), 1.32 (t, $J$ = 7.1 Hz, 3H).

Ethyl 2,5-diphenyl-1H-imidazole-4-carboxylate (9)

\[
\begin{align*}
\text{EtOOOC} & \text{N} \\
\text{Ph} & \text{Ph} \\
\text{N} & \text{H}
\end{align*}
\]

Yellow solid; 175 mg, yield: 60%

$^1$H NMR (300 MHz, Chloroform-$d$) $\delta$ 10.13 (br), 7.97 - 7.95 (m, 4H), 7.48 - 7.38 (m, 6H), 4.35 (q, $J$ = 7.1 Hz, 2H), 1.33 (t, $J$ = 7.1 Hz, 3H).

MS: [M+H]$^+$; 293.34 , found: 293.3
S13 X-ray crystallographic study

Crystal structure determination. The diffraction intensity data of 4b - d, 5a - c were collected at 173 K on a Rigaku XtaLAB PRO MM003-DS dual System with a Cu micro-focus source (Cu-Kα, λ = 1.54184 Å). The structure was refined by Olex2 program. The nonhydrogen atoms were refined anisotropically. The H atoms attached to carbons were added geometrically and refined isotropically with the riding model. The crystal data were collected in Table S4.

Table S4. Summary of single crystal X-ray diffraction analysis

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<tr>
<td>ρ calcd, g cm³</td>
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<td>1.357</td>
<td>1.340</td>
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<td>R₁ [I &gt; 2σ(I)]</td>
<td>0.0445</td>
<td>0.0405</td>
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<td>wR₂ (all data)</td>
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<td>0.1517</td>
<td>0.1305</td>
<td>0.1386</td>
<td>0.0826</td>
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S14 References


S15 Copies of $^1$H NMR spectra of products

$^1$H NMR (400 MHz) spectrum of 2a in DMSO-$d_6$

$^1$H NMR (500 MHz) spectrum of 2b in DMSO-$d_6$
$^1$H NMR (400 MHz) spectrum of 2c in DMSO-$d_6$

$^1$H NMR (300 MHz) spectrum of 2d in DMSO-$d_6$
$^1$H NMR (500 MHz) spectrum of 2e in DMSO-$d_6$

$^1$H NMR (500 MHz) spectrum of 2f in DMSO-$d_6$
$^1$H NMR (500 MHz) spectrum of 2g in DMSO-$d_6$

$^1$H NMR (300 MHz) spectrum of 2h in DMSO-$d_6$
$^1$H NMR (400 MHz) spectrum of $2i$ in DMSO-$d_6$

$^1$H NMR (500 MHz) spectrum of $2j$ in DMSO-$d_6$
$^1\text{H NMR (500 MHz) spectrum of 2k in DMSO-$d_6$}

$^1\text{H NMR (500 MHz) spectrum of 2l in DMSO-$d_6$}
$\ ^1\text{H NMR (300 MHz) spectrum of } 2n \text{ in DMSO-$d_6$}$

$\ ^1\text{H NMR (300 MHz) spectrum of } 2q \text{ in DMSO-$d_6$}$
$^1$H NMR (300 MHz) spectrum of 2r in DMSO-$d_6$
$^1$H NMR (300 MHz) spectrum of 3b in DMSO-$d_6$

$^1$H NMR (300 MHz) spectrum of 3c in Chloroform-$d$
$^1$H NMR (300 MHz) spectrum of 3d in Chloroform-$d$

$^1$H NMR (300 MHz) spectrum of 3e in Chloroform-$d$
$\text{H NMR (300 MHz) spectrum of 4a in Chloroform-d}$

$\text{H NMR (300 MHz) spectrum of 4b in Chloroform-d}$
$^1$H NMR (400 MHz) spectrum of 4c in Chloroform-$d$

$^1$H NMR (300 MHz) spectrum of 4d in Chloroform-$d$
$^1$H NMR (400 MHz) spectrum of 5a in Chloroform-$d$

$^1$H NMR (400 MHz) spectrum of 5b in Chloroform-$d$
$^1$H NMR (300 MHz) spectrum of 5c in Chloroform-$d$

$^1$H NMR (300 MHz) spectrum of 6a in DMSO-$d_6$
$^1$H NMR (300 MHz) spectrum of $6b$ in DMSO-$d_6$

$^1$H NMR (300 MHz) spectrum of $7a$ in DMSO-$d_6$
$^1$H NMR (300 MHz) spectrum of 7b in DMSO-d$_6$
$^1$H NMR (300 MHz) spectrum of 8 in Chloroform-$d$

$^1$H NMR (300 MHz) spectrum of 9 in Chloroform-$d$