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# **Metal-Free Amination of Alkenes Based on Maleimides**

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# **Supporting Information**

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#### 1. General experimental information

Reagents were purchased from commercial sources and were used as received unless mentioned otherwise. Reactions were monitored by TLC. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> or DMSO- $d_6$ . <sup>1</sup>H NMR chemical shifts are reported in ppm relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard (CDCl<sub>3</sub> at 7.26 ppm, DMSO- $d_6$  at 2.50 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. <sup>13</sup>C NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard (CDCl<sub>3</sub> at 77.16 ppm, DMSO- $d_6$  at 39.52 ppm). Melting points products were recorded on a Büchi Melting Point B-545. The HRMS were recorded by Thermo Scientific LTQ Orbitrap XL.

#### 2. General experimental procedures for synthesis of compounds 3 and 5.



In an ordinary vial charged with a magnetic stirring bar, maleimides **1** (0.1 mmol, 1.0 equiv), *N*-tosyloxycarbamates **2 or 4** (0.15 mmol, 1.5 equiv), DIPEA (0.15 mmol, 1.5 equiv) and Acetone (1.0 mL) was added, and then the mixture was stirred at 25 °C for 2 h. the products **3 and 5** were isolated by flash chromatography on silica gel.

## benzyl (2,5-dioxo-1-phenyl-2,5-dihydro-1H-pyrrol-3-yl)carbamate (3a)



It was purified by flash chromatography (petroleum ether /EtOAc, 7:1) to afford white solid (32.0 mg, 99% yield); m.p. 110.1-113.0 °C.

<sup>1</sup>**H NMR (600 MHz, CDCl**<sub>3</sub>) δ 7.60 (s, 1H), 7.48 – 7.43 (m, 2H), 7.43 – 7.37 (m, 5H), 7.37 – 7.32 (m, 3H), 6.41 (s, 1H), 5.28 (s, 2H).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 170.4, 166.3, 152.1, 139.4, 134.7, 131.2, 129.2, 129.1, 128.9, 128.7, 128.0, 125.9, 102.6, 68.9.

**HRMS (ESI)** Calcd. for  $C_{18}H_{15}N_2O_4^+$  (M+H)<sup>+</sup> 323.10263, found 323.10266.

## benzyl (2,5-dioxo-1-(p-tolyl)-2,5-dihydro-1H-pyrrol-3-yl)carbamate (3b)



It was purified by flash chromatography (petroleum ether /EtOAc, 7:1) to afford white solid (27.6 mg, 82% yield); m.p. 108.7-111.3 °C.

<sup>1</sup>**H NMR (600 MHz, CDCl**<sub>3</sub>) δ 7.58 (s, 1H), 7.45 – 7.34 (m, 5H), 7.27 – 7.19 (m, 4H), 6.40 (s, 1H), 5.28 (s, 2H), 2.38 (s, 3H).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 170.6, 166.4, 152.1, 139.4, 138.1, 134.7, 129.9, 129.0, 128.9, 128.6, 128.5, 125.9, 102.6, 68.8, 21.3.

HRMS (ESI) Calcd. for C<sub>19</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub>Na<sup>+</sup> (M+Na)<sup>+</sup> 359.10023, found 359.10031.

benzyl (1-(4-(tert-butyl)phenyl)-2,5-dioxo-2,5-dihydro-1H-pyrrol-3-yl)carbamate (3c)



It was purified by flash chromatography (petroleum ether /EtOAc, 7:1) to afford white solid (33.4 mg, 88% yield); m.p. 105.5-108.8 °C.

<sup>1</sup>**H NMR (600 MHz, CDCl<sub>3</sub>)** δ 7.60 (s, 1H), 7.47 – 7.44 (m, 2H), 7.42 – 7.33 (m, 5H), 7.27 – 7.21 (m, 2H), 6.39 (s, 1H), 5.26 (s, 2H), 1.32 (s, 9H).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 170.6, 166.5, 152.1, 151.1, 139.4, 134.7, 129.0, 128.9, 128.6, 128.4, 126.2, 125.5, 102.6, 68.8, 34.8, 31.4.

HRMS (ESI) Calcd. for C<sub>22</sub>H<sub>22</sub>N<sub>2</sub>O<sub>4</sub>Na<sup>+</sup> (M+Na)<sup>+</sup> 401.14718, found 401.14725.

benzyl (1-(4-chlorophenyl)-2,5-dioxo-2,5-dihydro-1H-pyrrol-3-yl)carbamate (3d)



It was purified by flash chromatography (petroleum ether /EtOAc, 7:1) to afford white solid (30.7 mg, 86% yield); m.p. 142.8-148.5 °C.

<sup>1</sup>**H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.60 (s, 1H), 7.44 – 7.37 (m, 7H), 7.34 – 7.29 (m, 2H), 6.41 (s, 1H), 5.28 (s, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 170.0, 166.1, 152.1, 139.6, 134.7, 133.6, 129.8, 129.4, 129.1, 129.0, 128.7, 126.9, 102.7, 69.0.

**HRMS (ESI)** Calcd. for  $C_{18}H_{13}ClN_2O_4Na^+$  (M+Na)<sup>+</sup> 379.04561, 381.04265, found 379.04568, 381.04257.

benzyl (2,5-dioxo-1-(m-tolyl)-2,5-dihydro-1H-pyrrol-3-yl)carbamate (3e)



It was purified by flash chromatography (petroleum ether /EtOAc, 7:1) to afford white solid (30.0 mg, 89% yield); m.p. 121.5-123.6 °C.

<sup>1</sup>**H NMR (600 MHz, CDCl<sub>3</sub>)** δ 7.58 (s, 1H), 7.44 – 7.36 (m, 5H), 7.36 – 7.31 (m, 1H), 7.17 (d, *J* = 7.7 Hz, 1H), 7.13 (dd, *J* = 10.6, 2.8 Hz, 2H), 6.40 (s, 1H), 5.28 (s, 2H), 2.39 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 170.5, 166.4, 152.1, 139.4, 139.3, 134.7, 134.3, 131.0, 129.1, 129.0, 129.0, 128.7, 126.7, 123.2, 102.7, 68.9, 21.5.

HRMS (ESI) Calcd. for C<sub>19</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub>Na<sup>+</sup> (M+Na)<sup>+</sup> 359.10023, found 359.10022.

benzyl (1-(3-chlorophenyl)-2,5-dioxo-2,5-dihydro-1H-pyrrol-3-yl)carbamate (3f)



It was purified by flash chromatography (petroleum ether /EtOAc, 7:1) to afford white solid (37.1 mg, 99% yield); m.p. 131.6-135.7 °C.

<sup>1</sup>**H NMR (600 MHz, CDCl<sub>3</sub>)** δ 7.59 (s, 1H), 7.44 – 7.38 (m, 6H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.34 – 7.31 (m, 1H), 7.31 – 7.28 (m, 1H), 6.42 (s, 1H), 5.28 (s, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 169.9, 166.0, 152.1, 139.6, 134.8, 132.4, 130.2, 129.1, 129.0, 128.8, 128.7, 128.1, 125.9, 123.8, 102.7, 69.0.

**HRMS (ESI)** Calcd. for  $C_{18}H_{13}ClN_2O_4Na^+$  (M+Na)<sup>+</sup> 379.04561, 381.04265, found 379.04553, 381.04242.

benzyl (1-(3-bromophenyl)-2,5-dioxo-2,5-dihydro-1H-pyrrol-3-yl)carbamate (3g)



It was purified by flash chromatography (petroleum ether /EtOAc, 7:1) to afford white solid (39.6 mg, 99% yield); m.p. 138.7-140.9 °C.

<sup>1</sup>**H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.59 (s, 1H), 7.57 – 7.56 (m, 1H), 7.50 – 7.46 (m, 1H), 7.42 – 7.39 (m, 5H), 7.34 – 7.30 (m, 2H), 6.41 (s, 1H), 5.28 (s, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 169.8, 165.9, 152.1, 139.6, 134.7, 132.5, 131.0, 130.4, 129.1, 129.0, 128.7, 124.3, 122.6, 102.7, 69.0.

**HRMS (ESI)** Calcd. for C<sub>18</sub>H<sub>13</sub>BrN<sub>2</sub>O<sub>4</sub>Na<sup>+</sup> (M+Na)<sup>+</sup> 422.99509, 424.99304, found 422.99527, 424.99323.

benzyl (2,5-dioxo-1-(o-tolyl)-2,5-dihydro-1H-pyrrol-3-yl)carbamate (3h)



It was purified by flash chromatography (petroleum ether /EtOAc, 7:1) to afford white solid (29.5 mg, 88% yield); m.p. 105.7-108.3 °C.

<sup>1</sup>**H NMR (600 MHz, CDCl<sub>3</sub>)** δ 7.56 (s, 1H), 7.46 – 7.35 (m, 5H), 7.35 – 7.29 (m, 2H), 7.29 – 7.25 (m, 1H), 7.09 (dd, *J* = 7.8, 1.3 Hz, 1H), 6.42 (s, 1H), 5.27 (s, 2H), 2.15 (s, 3H).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 170.6, 166.4, 152.1, 139.6, 136.7, 134.7, 131.3, 129.9, 129.6, 129.1, 129.0, 128.8, 128.7, 127.0, 102.9, 68.9, 18.1.

HRMS (ESI) Calcd. for C<sub>19</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub>Na<sup>+</sup> (M+Na)<sup>+</sup> 359.10023, found 359.10043.

### benzyl (1-(2,6-dimethylphenyl)-2,5-dioxo-2,5-dihydro-1H-pyrrol-3-yl)carbamate (3i)



It was purified by flash chromatography (petroleum ether /EtOAc, 7:1) to afford white solid (30.5 mg, 87% yield); m.p. 120.7-125.1 °C.

<sup>1</sup>**H NMR (600 MHz, CDCl<sub>3</sub>)** δ 7.54 (s, 1H), 7.44 – 7.35 (m, 5H), 7.25 – 7.21 (m, 1H), 7.13 (d, *J* = 7.6 Hz, 2H), 6.43 (s, 1H), 5.28 (s, 2H), 2.11 (s, 6H).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 170.5, 166.3, 152.2, 139.4, 137.2, 134.8, 134.5, 129.6, 129.1, 128.9, 128.7, 128.6, 102.8, 68.9, 18.1.

HRMS (ESI) Calcd. for C<sub>20</sub>H<sub>18</sub>N<sub>2</sub>O<sub>4</sub>Na<sup>+</sup> (M+Na)<sup>+</sup> 373.11588, found 373.11581.

#### benzyl (1-ethyl-2,5-dioxo-2,5-dihydro-1H-pyrrol-3-yl)carbamate (3j)



It was purified by flash chromatography (petroleum ether /EtOAc, 7:1) to afford White solid (14.5 mg, 53% yield); m.p. 109.3-111.5 °C.

<sup>1</sup>**H NMR (600 MHz, CDCl<sub>3</sub>)**  $\delta$  7.54 (s, 1H), 7.47 – 7.30 (m, 5H), 6.22 (s, 1H), 5.24 (s, 2H), 3.53 (q, J = 7.2 Hz, 2H), 1.16 (t, J = 7.2 Hz, 3H).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 171.6, 167.3, 152.2, 139.4, 134.8, 129.0, 128.9, 128.6, 102.6, 68.7, 33.0, 14.0.

**HRMS (ESI)** Calcd. for C<sub>14</sub>H<sub>14</sub>N<sub>2</sub>O<sub>4</sub>Na<sup>+</sup> (M+Na)<sup>+</sup> 297.08458, found 297.08472.

## benzyl (2,5-dioxo-1-propyl-2,5-dihydro-1H-pyrrol-3-yl)carbamate (3k)



It was purified by flash chromatography (petroleum ether /EtOAc, 7:1) to afford White solid (14.4 mg, 50% yield); m.p. 107.5-110.3 °C.

<sup>1</sup>**H NMR (600 MHz, CDCl**<sub>3</sub>) δ 7.48 (s, 1H), 7.42 – 7.33 (m, 5H), 6.23 (s, 1H), 5.24 (s, 2H), 3.54 – 3.37 (m, 2H), 1.66 – 1.53 (m, 2H), 0.93 – 0.81 (m, 3H).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 171.8, 167.6, 152.2, 139.3, 134.8, 129.0, 128.9, 128.6, 102.5, 68.7, 39.7, 22.0, 11.3.

HRMS (ESI) Calcd. for C<sub>15</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub>Na<sup>+</sup> (M+Na)<sup>+</sup> 311.10023, found 311.10007.

tert-butyl 3-(((benzyloxy)carbonyl)amino)-2,5-dioxo-2,5-dihydro-1H-pyrrole-1-carboxylate (3l)



It was purified by flash chromatography (petroleum ether /EtOAc, 7:1) to afford White solid (29.7 mg, 86% yield); m.p. 120.5-123.1 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.55 (s, 1H), 7.44 – 7.35 (m, 5H), 6.37 (s, 1H), 5.25 (s, 2H), 1.57 (s, 9H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 166.4, 163.9, 152.0, 145.9, 129.8, 129.6, 129.1, 128.9, 128.7, 104.2, 69.0, 58.5, 28.0.

HRMS (ESI) Calcd. for C<sub>17</sub>H<sub>18</sub>N<sub>2</sub>O<sub>6</sub>Na<sup>+</sup> (M+Na)<sup>+</sup> 369.10571, found 369.10577.

### cyclopentyl (2,5-dioxo-1-phenyl-2,5-dihydro-1H-pyrrol-3-yl)carbamate (3m)



It was purified by flash chromatography (petroleum ether /EtOAc, 7:1) to afford White solid (25.4 mg, 85% yield); m.p. 111.1-112.5 °C.

<sup>1</sup>**H NMR (400 MHz, CDCl**<sub>3</sub>) δ 7.52 (s, 1H), 7.47 – 7.40 (m, 2H), 7.37 – 7.32 (m, 3H), 6.35 (s, 1H), 5.26 (tt, *J* = 5.9, 2.5 Hz, 1H), 1.97 – 1.85 (m, 2H), 1.83 – 1.71 (m, 4H), 1.69 – 1.61 (m, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 170.5, 166.4, 152.0, 139.6, 131.2, 129.1, 127.8, 125.8, 102.0, 80.6, 32.7, 23.6.

HRMS (ESI) Calcd. for C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub>Na<sup>+</sup> (M+Na)<sup>+</sup> 323.10023, found 323.10095.

## butyl (2,5-dioxo-1-phenyl-2,5-dihydro-1H-pyrrol-3-yl)carbamate (3n)



It was purified by flash chromatography (petroleum ether /EtOAc, 7:1) to afford White solid (25.4 mg, 88% yield); m.p. 104.8-106.0 °C.

<sup>1</sup>**H NMR (600 MHz, CDCl**<sub>3</sub>)  $\delta$  7.51 (s, 1H), 7.48 – 7.43 (m, 2H), 7.39 – 7.31 (m, 3H), 6.38 (s, 1H), 4.26 (t, J = 6.7 Hz, 2H), 1.79 – 1.61 (m, 2H), 1.50 – 1.34 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H).

<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 170.5, 166.4, 152.4, 139.6, 131.3, 129.2, 128.0, 125.9, 102.3, 67.1, 30.7, 19.1, 13.7.
HRMS (ESI) Calcd. for C<sub>15</sub>H<sub>16</sub>N<sub>2</sub>O<sub>4</sub>Na<sup>+</sup> (M+Na)<sup>+</sup> 311.10023, found 311.10074.

### allyl (2,5-dioxo-1-phenyl-2,5-dihydro-1H-pyrrol-3-yl)carbamate (30)



It was purified by flash chromatography (petroleum ether /EtOAc, 7:1) to afford White solid (25.9 mg, 90% yield); m.p. 104.8-106.0 °C.

<sup>1</sup>**H NMR (400 MHz, CDCl**<sub>3</sub>) δ 7.52 (s, 1H), 7.49 – 7.43 (m, 2H), 7.39 – 7.33 (m, 3H), 6.41 (s, 1H), 5.96 (dt, *J* = 17.4, 10.4, 5.9 Hz, 1H), 5.46 – 5.27 (m, 2H), 4.75 (dt, *J* = 5.9, 1.4 Hz, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 170.4, 166.4, 152.0, 139.4, 131.2, 131.2, 129.3, 128.0, 125.9, 119.8, 102.6, 67.7.

HRMS (ESI) Calcd. for C<sub>14</sub>H<sub>12</sub>N<sub>2</sub>O<sub>4</sub>Na<sup>+</sup> (M+Na)<sup>+</sup> 295.06893, found 295.06897.

## N-(2,5-dioxo-1-phenyl-2,5-dihydro-1H-pyrrol-3-yl)benzamide (5a)



It was purified by flash chromatography (petroleum ether /EtOAc, 8:1) to afford White solid (28.6 mg, 98% yield); m.p. 122.5-126.0°C.

<sup>1</sup>**H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.66 (s, 1H), 7.99 – 7.87 (m, 2H), 7.69 – 7.62 (m, 1H), 7.59 – 7.53 (m, 2H), 7.51 – 7.45 (m, 2H), 7.42 – 7.35 (m, 3H), 6.86 (s, 1H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 170.8, 167.1, 165.6, 138.5, 133.6, 132.1, 131.3, 129.3, 129.3, 128.1, 127.6, 126.0, 105.0.

HRMS (ESI) Calcd. for C<sub>17</sub>H<sub>12</sub>N<sub>2</sub>O<sub>3</sub>Na<sup>+</sup> (M+Na)<sup>+</sup> 315.07401, found 315.07361.

## N-(2,5-dioxo-1-(p-tolyl)-2,5-dihydro-1H-pyrrol-3-yl)benzamide (5b)



It was purified by flash chromatography (petroleum ether /EtOAc, 7:1) to afford White solid (29.1 mg, 95% yield); m.p. 114.8-117.0 °C.

<sup>1</sup>**H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.71 (s, 1H), 8.03 – 7.87 (m, 2H), 7.70 – 7.64 (m, 1H), 7.57 (dd, *J* = 8.5, 7.0 Hz, 2H), 7.33 – 7.27 (m, 4H), 6.86 (s, 1H), 2.42 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 171.0, 167.2, 165.6, 138.5, 138.1, 133.5, 132.1, 129.9, 129.3, 128.5, 127.6, 125.9, 104.9, 21.3.

**HRMS (ESI)** Calcd. for  $C_{18}H_{14}N_2O_3Na^+$  (M+Na)<sup>+</sup> 329.08966, found 329.08920.

## N-(1-(2,6-dimethylphenyl)-2,5-dioxo-2,5-dihydro-1H-pyrrol-3-yl)benzamide (5c)



It was purified by flash chromatography (petroleum ether /EtOAc, 7:1) to afford White solid (28.9 mg, 90% yield); m.p. 135.3-138.2 °C.

<sup>1</sup>**H NMR (400 MHz, CDCl**<sub>3</sub>) δ 8.70 (s, 1H), 8.05 – 7.91 (m, 2H), 7.72 – 7.65 (m, 1H), 7.59 (dd, *J* = 8.3, 6.9 Hz, 2H), 7.30 – 7.27 (m, 1H), 7.21 – 7.18 (m, 2H), 6.92 (s, 1H), 2.19 (s, 6H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 170.9, 167.1, 165.7, 138.5, 137.3, 133.6, 132.1, 129.7, 129.3, 129.1, 128.6, 127.6, 105.1, 18.1.

HRMS (ESI) Calcd. for C<sub>19</sub>H<sub>16</sub>N<sub>2</sub>O<sub>3</sub>Na<sup>+</sup> (M+Na)<sup>+</sup> 343.10531, found 343.10580.

## N-(1-(naphthalen-2-yl)-2,5-dioxo-2,5-dihydro-1H-pyrrol-3-yl)benzamide (5d)



It was purified by flash chromatography (petroleum ether /EtOAc, 7:1) to afford White solid (30.2 mg, 88% yield); m.p. 126.5-129.3 °C.

<sup>1</sup>**H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.69 (s, 1H), 7.94 (dd, *J* = 8.4, 1.3 Hz, 3H), 7.88 (dd, *J* = 6.1, 3.0 Hz, 3H), 7.69 – 7.63 (m, 1H), 7.58 – 7.49 (m, 5H), 6.90 (s, 1H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 171.0, 167.3, 165.6, 138.6, 133.7, 133.4, 132.6, 132.1, 129.3, 129.2, 128.7, 128.3, 127.9, 127.7, 126.8, 126.8, 124.9, 123.7, 105.0.

HRMS (ESI) Calcd. for C<sub>21</sub>H<sub>14</sub>N<sub>2</sub>O<sub>3</sub>Na<sup>+</sup> (M+Na)<sup>+</sup> 365.08966, found 365.08954.

## N-(1-benzyl-2,5-dioxo-2,5-dihydro-1H-pyrrol-3-yl)benzamide (5e)



It was purified by flash chromatography (petroleum ether /EtOAc, 7:1) to afford White solid (28.4 mg, 93% yield); m.p. 115.7-117.9 °C.

<sup>1</sup>**H NMR (400 MHz, CDCl**<sub>3</sub>) δ 8.55 (s, 1H), 7.91 – 7.84 (m, 2H), 7.65 – 7.59 (m, 1H), 7.52 (dd, *J* = 8.4, 7.0 Hz, 2H), 7.37 – 7.27 (m, 5H), 6.70 (s, 1H), 4.70 (s, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 171.7, 167.9, 165.4, 138.4, 136.1, 133.4, 132.1, 129.2, 128.8, 128.4, 128.0, 127.5, 104.9, 41.6.

HRMS (ESI) Calcd. for C<sub>18</sub>H<sub>14</sub>N<sub>2</sub>O<sub>3</sub>Na<sup>+</sup> (M+Na)<sup>+</sup> 329.08966, found 329.08905.



It was purified by flash chromatography (petroleum ether /EtOAc, 7:1) to afford White solid (28.9 mg, 94% yield); m.p. 126.7-129.6 °C.

<sup>1</sup>**H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.63 (s, 1H), 7.85 – 7.79 (m, 2H), 7.52 – 7.44 (m, 2H), 7.42 – 7.36 (m, 3H), 7.34 (d, *J* = 8.1 Hz, 2H), 6.83 (s, 1H), 2.45 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 170.9, 167.2, 165.5, 144.6, 138.6, 131.3, 130.0, 129.3, 128.0, 127.7, 126.0, 104.6, 21.8.

**HRMS (ESI)** Calcd. for C<sub>18</sub>H<sub>14</sub>N<sub>2</sub>O<sub>3</sub>Na<sup>+</sup> (M+Na)<sup>+</sup> 329.08966, found 329.08908.

N-(2,5-dioxo-1-phenyl-2,5-dihydro-1H-pyrrol-3-yl)-3-methylbenzamide (5g)



It was purified by flash chromatography (petroleum ether /EtOAc, 7:1) to afford White solid (30.1 mg, 98% yield); m.p. 106.8-109.3 °C.

<sup>1</sup>**H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.64 (s, 1H), 7.75 – 7.68 (m, 2H), 7.50 – 7.42 (m, 4H), 7.41 – 7.36 (m, 3H), 6.84 (s, 1H), 2.46 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 170.8, 167.1, 165.7, 139.3, 138.5, 134.3, 132.0, 131.2, 129.2, 129.1, 128.2, 128.0, 125.9, 124.6, 104.7, 21.4.

HRMS (ESI) Calcd. for C<sub>18</sub>H<sub>14</sub>N<sub>2</sub>O<sub>3</sub>Na<sup>+</sup> (M+Na)<sup>+</sup> 329.08966, found 329.08923.

## N-(2,5-dioxo-1-phenyl-2,5-dihydro-1H-pyrrol-3-yl)-3-fluorobenzamide (5h)



It was purified by flash chromatography (petroleum ether /EtOAc, 7:1) to afford White solid (30.3 mg, 98% yield); m.p. 142.3-144.5 °C.

<sup>1</sup>**H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.62 (s, 1H), 7.71 – 7.63 (m, 2H), 7.58 – 7.51 (m, 1H), 7.50 – 7.44 (m, 2H), 7.41 – 7.32 (m, 4H), 6.86 (s, 1H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  170.6, 167.0, 164.3, 163.1 (d, J = 251.2 Hz), 138.2, 134.2 (d, J = 7.2 Hz), 131.2, 131.1 (d, J = 7.8 Hz), 129.3, 128.1, 126.0, 123.0 (d, J = 3.2 Hz), 120.8 (d, J = 21.2 Hz), 115.2 (d, J = 23.4 Hz), 105.5.

HRMS (ESI) Calcd. for  $C_{17}H_{11}FN_2O_3Na^+$  (M+Na)<sup>+</sup> 333.06459, found 333.06445.

## N-(2,5-dioxo-1-phenyl-2,5-dihydro-1H-pyrrol-3-yl)-3,5-dimethylbenzamide (5i)



It was purified by flash chromatography (petroleum ether /EtOAc, 7:1) to afford White solid (31.8 mg, 99% yield); m.p. 104.8-106.0 °C.

<sup>1</sup>**H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.62 (s, 1H), 7.53 – 7.50 (m, 2H), 7.50 – 7.45 (m, 2H), 7.41 – 7.36 (m, 3H), 7.28 – 7.26 (m, 1H), 6.83 (s, 1H), 2.41 (s, 6H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 170.9, 167.2, 165.9, 139.2, 138.6, 135.3, 132.0, 131.3, 129.3, 128.0, 126.0, 125.4, 104.7, 21.4.

HRMS (ESI) Calcd. for C<sub>19</sub>H<sub>16</sub>N<sub>2</sub>O<sub>3</sub>Na<sup>+</sup> (M+Na)<sup>+</sup> 343.10531, found 343.10556.

#### N-(2,5-dioxo-1-phenyl-2,5-dihydro-1H-pyrrol-3-yl)thiophene-2-carboxamide (5j)



It was purified by flash chromatography (petroleum ether /EtOAc, 7:1) to afford White solid (26.1 mg, 87% yield); m.p. 109.2-111.3 °C.

<sup>1</sup>**H NMR (400 MHz, CDCl**<sub>3</sub>) δ 8.49 (s, 1H), 7.75 (dd, *J* = 3.9, 1.1 Hz, 1H), 7.69 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.50 – 7.44 (m, 2H), 7.40 – 7.34 (m, 3H), 7.17 (dd, *J* = 5.0, 3.8 Hz, 1H), 6.78 (s, 1H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 170.7, 166.9, 159.9, 138.3, 136.6, 133.7, 131.2, 130.6, 129.3, 128.5, 128.1, 126.0, 104.8.

HRMS (ESI) Calcd. for C<sub>15</sub>H<sub>10</sub>N<sub>2</sub>O<sub>3</sub>SNa<sup>+</sup> (M+Na)<sup>+</sup> 321.03043, found 321.03104.

## 3. The synthesis of compound compounds 6.



In an ordinary vial charged with a magnetic stirring bar, **5a** (0.2 mmol, 1.0 equiv), NaBH<sub>4</sub> (0.4 mmol, 2.0 equiv) and MeOH (2 mL) was added, and then the mixture was stirred at 25 °C for 4 h. After determining the complete disappearance of **5a** by TLC, quench the reaction with water, and extract with ethyl acetate (10 mL×3). Combine the organic phases, add anhydrous Na<sub>2</sub>SO<sub>4</sub> for drying, and concentrate under reduced pressure to obtain the crude solid product. Then, add an appropriate amount of DCM and stir for 1 h, followed by filtration to obtain product **6**.

## (Z)-3-benzamido-4-oxo-4-(phenylamino)but-2-enoic acid (6)



It was purified by DCM washing to afford white solid (52.9 mg, 90% yield); m.p. 167.7-170.2 °C.

<sup>1</sup>**H NMR (600 MHz, DMSO-***d*<sub>6</sub>) δ 10.93 (s, 1H), 8.01 (d, *J* = 7.6 Hz, 2H), 7.70 (d, *J* = 8.1 Hz, 2H), 7.67 – 7.63 (m, 1H), 7.60 – 7.54 (m, 2H), 7.43 – 7.32 (m, 2H), 7.17 – 7.07 (m, 1H), 6.79 (d, *J* = 9.9 Hz, 1H), 6.28 (d, *J* = 5.0 Hz, 1H), 6.08 (d, *J* = 9.0 Hz, 1H).

<sup>13</sup>C NMR (101 MHz, DMSO-*d*<sub>6</sub>) δ 169.3, 166.5, 153.0, 137.8, 133.0, 132.6, 128.6, 128.0, 123.3, 120.1, 104.0, 81.4.

**HRMS (ESI)** Calcd. for  $C_{17}H_{14}N_2O_3Na^+$  (M+Na)<sup>+</sup>: 317.08966; found: 317.08972.

4. Scale-up experiment



In an ordinary vial charged with a magnetic stirring bar, maleimide **1a** (5.0 mmol, 1.0 equiv), *N*-tosyloxycarbamate **2a or 4a** (7.5 mmol, 1.5 equiv), DIPEA (7.5 mmol, 1.5 equiv) and Acetone (50 mL) was added, and then the mixture was stirred at 25 °C for 4 h. The products **3a or 5a** were isolated by flash chromatography on silica gel.

## 5. X-ray crystal data for compound 3a



Identification code	3a
Empirical formula	C18H14N2O4
Formula weight	322.31
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	Pbca
a/Å	12.3771(2)
b/Å	7.62053(17)
c/Å	33.9209(7)
$\alpha/^{\circ}$	90
β/°	90
$\gamma^{\prime \circ}$	90
Volume/Å <sup>3</sup>	3199.42(11)
Z	8
$\rho_{calc}g/cm^3$	1.338
$\mu/\text{mm}^{-1}$	0.797
F(000)	1344.0
Crystal size/mm <sup>3</sup>	0.14  imes 0.1  imes 0.08
Radiation	$CuK\alpha \ (\lambda = 1.54184)$
$2\Theta$ range for data collection/°	8.844 to 134.066
Index ranges	$-14 \le h \le 14, -7 \le k \le 9, -37 \le l \le 40$
Reflections collected	12816
Independent reflections	2847 [ $R_{int} = 0.0334, R_{sigma} = 0.0263$ ]
Data/restraints/parameters	2847/72/216
Goodness-of-fit on F <sup>2</sup>	1.047
Final R indexes [I>= $2\sigma$ (I)]	$R_1 = 0.0487, wR_2 = 0.1320$
Final R indexes [all data]	$R_1 = 0.0621, wR_2 = 0.1465$
Largest diff. peak/hole / e Å <sup>-3</sup>	0.21/-0.18

6. The copies of <sup>1</sup>H NMR and <sup>13</sup>C NMR for compounds 3a-3o, 5a-5j and 6

benzyl (2,5-dioxo-1-phenyl-2,5-dihydro-1H-pyrrol-3-yl)carbamate (3a)





benzyl (2,5-dioxo-1-(p-tolyl)-2,5-dihydro-1H-pyrrol-3-yl)carbamate (3b)



## benzyl (1-(4-(tert-butyl)phenyl)-2,5-dioxo-2,5-dihydro-1H-pyrrol-3-yl)carbamate (3c)



benzyl (1-(4-chlorophenyl)-2,5-dioxo-2,5-dihydro-1H-pyrrol-3-yl)carbamate (3d)







benzyl (1-(3-chlorophenyl)-2,5-dioxo-2,5-dihydro-1H-pyrrol-3-yl)carbamate (3f)



benzyl (1-(3-bromophenyl)-2,5-dioxo-2,5-dihydro-1H-pyrrol-3-yl)carbamate (3g)





benzyl (1-(2,6-dimethylphenyl)-2,5-dioxo-2,5-dihydro-1H-pyrrol-3-yl)carbamate (3i)





tert-butyl 3-(((benzyloxy)carbonyl)amino)-2,5-dioxo-2,5-dihydro-1H-pyrrole-1-carboxylate (3l)









allyl (2,5-dioxo-1-phenyl-2,5-dihydro-1H-pyrrol-3-yl)carbamate (30)





220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 f1 (ppm)



N-(1-(2,6-dimethylphenyl)-2,5-dioxo-2,5-dihydro-1H-pyrrol-3-yl)benzamide (5c)



f1 (ppm) 



N-(1-benzyl-2,5-dioxo-2,5-dihydro-1H-pyrrol-3-yl)benzamide (5e)



N-(2,5-dioxo-1-phenyl-2,5-dihydro-1H-pyrrol-3-yl)-4-methylbenzamide (5f)



N-(2,5-dioxo-1-phenyl-2,5-dihydro-1H-pyrrol-3-yl)-3-methylbenzamide (5g)



N-(2,5-dioxo-1-phenyl-2,5-dihydro-1H-pyrrol-3-yl)-3-fluorobenzamide (5h)







N-(2,5-dioxo-1-phenyl-2,5-dihydro-1H-pyrrol-3-yl)thiophene-2-carboxamide (5j)



