Supporting Information

DMAP-Catalyzed alkylation of Isatin N,N'-Cyclic Azomethine Imine 1,3-Dipole with Morita–Baylis–Hillman Carbonates

Shihe Hu\textsuperscript{a,b}, Jian Zhang\textsuperscript{a,b}, and Qiaomei Jin\textsuperscript{*}, a,b

\textsuperscript{a} Affiliated Hospital of Integrated Traditional Chinese and Western Medicine, Nanjing University of Chinese Medicine, Nanjing 210028, Jiangsu, China

\textsuperscript{b} Laboratories of Translational Medicine, Jiangsu Province Academy of Traditional Chinese Medicine, Nanjing 210028, Jiangsu, China

\*E-mail: jqmxv@163.com

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1. General information
All reactions were performed in anhydrous solvents under an argon atmosphere and were monitored by thin-layer chromatography carried out on silica gel aluminum sheets (60F-254) and spots were visualized with UV light. All solvents were purchased from commercial suppliers and were purified according to standard procedures. Acrylates was obtained from commercial source without further purification prior to use. 1,3-dipoles 1 and MBH carbonates 2 can be prepared according to known procedures. 

1H NMR and 13C NMR spectra were recorded at room temperature on BRUKER Avance 400 spectrometers. Chemical shifts were reported in parts per million (ppm, δ units), and tetramethylsilane (TMS) was used as an internal reference. Coupling constants (J) were expressed in hertz. High-resolution mass spectra (HRMS) were recorded on a ZAB-HS instrument using an electrospray source (ESI).

2. General procedure for the C(sp3)-H alkylation of isatin N,N’-cyclic azomethine imine 1,3-dipoles 1 with MBH carbonates 2

\[
\begin{align*}
\text{N=NC(=O)R}_1 & \quad \text{+ BOcCOOR}_3 \\
\text{CH}_2\text{Cl}_2, \text{reflux, Ar} & \quad \text{DMAP (20 mol %)}
\end{align*}
\]

To the solution of isatin N,N’-cyclic azomethine imine 1,3-dipole 1 (0.2 mmol) and MBH carbonates 2 (0.25 mmol) in CH2Cl2 (2 mL), DMAP (20 mol %) was added. The resulting mixture was stirred and heated to reflux under argon atmosphere for the required period of time. After completion of the reaction as monitored by TLC, the solvents were evaporated under reduced pressure and the residue was purified by silica gel chromatography (PE/EtOAc, 3:1) to afford α-alkylated-isatin N,N’-cyclic azomethine imine 1,3-dipoles 3 or 4.

3. Procedure for the synthesis of Methyl 2-((2-(1-benzyl-2-oxoindolin-3-yl)-5-
oxo-2,5-dihydro-1H-pyrazol-3-yl)methyl)acrylate 5

![Chemical Structure]

Product 3b (100.0 mg, 0.25 mmol) was dissolved in CH$_2$Cl$_2$ (5 mL) at 0 °C. Then Et$_3$SiH (29.0 mg, 0.25 mmol) and BF$_3$·Et$_2$O (35.5 mg, 0.25 mmol) was added. The mixture was stirred at rt for 5 h. Then the mixture was quenched by saturated NaHCO$_3$ solution (10.0 mL) and extracted with CH$_2$Cl$_2$ (3 × 5 mL). The organic phase was dried and concentrated. Then the crude product was purified by flash chromatography on silica gel (PE/EtOAc, 5:1) to afford the product 5 as a white solid (79.0 mg, 79 % yield).

4. Characterization Data

2-(1-benzyl-2-oxoindolin-3-ylidene)-3-(2-(ethoxycarbonyl)allyl)-5-oxopyrazolidin-2-ium-1-ide (3a)

Red solid (90.7 mg, 92 % yield), MP: 154-155°C. $^1$H NMR (400 MHz, CDCl$_3$) δ8.48 (d, $J$ = 7.5 Hz, 1H), 7.45-7.34 (m, 6H), 7.12 (t, $J$ = 7.6 Hz, 1H), 6.78 (d, $J$ = 7.8 Hz, 1H), 6.39 (s, 1H), 6.19-6.12 (m, 1H), 5.76 (s, 1H), 5.01 (s, 2H), 4.20-4.13 (m, 2H), 3.01 (ddd, $J$ = 24.6, 15.1, 8.0 Hz, 3H), 2.71 (d, $J$ = 16.9 Hz, 1H), 1.28 (t, $J$ = 7.0 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ185.24, 166.09, 160.46, 142.04, 135.15, 132.76, 129.24, 128.96, 128.47, 127.98, 127.22, 123.46, 117.36, 109.17, 68.34, 61.33, 43.85, 37.42, 34.65, 14.12. HRMS calcd for C$_{24}$H$_{23}$N$_3$O$_4$Na[M+23]$^+$ 440.1586, found 440.1594.

2-(1-benzyl-2-oxoindolin-3-ylidene)-3-(2-(methoxycarbonyl)allyl)-5-oxopyrazolidin-2-ium-1-ide (3b)

Red solid (76.7 mg, 95 % yield), MP: 137-139°C. $^1$H NMR (400 MHz, CDCl$_3$) δ8.45 (d, $J$ = 7.6 Hz, 1H), 7.37-7.28 (m, 6H), 7.10 (t, $J$ = 7.6 Hz, 1H), 6.76 (d, $J$ = 7.8 Hz, 7.2 Hz, 1H), 5.76 (s, 1H), 5.01 (s, 2H), 4.20-4.13 (m, 2H), 3.01 (ddd, $J$ = 24.6, 15.1, 8.0 Hz, 3H), 2.71 (d, $J$ = 16.9 Hz, 1H), 1.28 (t, $J$ = 7.0 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ185.24, 166.09, 160.46, 142.04, 135.15, 132.76, 129.24, 128.96, 128.47, 127.98, 127.22, 123.46, 117.36, 109.17, 68.34, 61.33, 43.85, 37.42, 34.65, 14.12. HRMS calcd for C$_{24}$H$_{23}$N$_3$O$_4$Na[M+23]$^+$ 440.1586, found 440.1594.
1H), 6.36 (s, 1H), 6.12 (dd, $J = 12.3, 7.3$ Hz, 1H), 5.75 (s, 1H), 4.98 (s, 2H), 3.69 (s, 3H), 3.07-2.88 (m, 3H), 2.68 (d, $J = 16.9$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ185.21, 166.53, 160.48, 142.05, 135.15, 134.82, 132.80, 129.63, 128.96, 128.49, 127.99, 127.20, 123.50, 117.34, 109.18, 68.24, 52.30, 43.86, 37.49, 34.68. HRMS calcd for C$_{23}$H$_{21}$N$_3$O$_4$Na[M+23]$^+$ 426.1430, found 426.1434.

2-(1-benzyl-2-oxoindolin-3-ylidene)-3-(2-((benzyloxy)carbonyl)allyl)-5-oxopyrazolidin-2-iium-1-ide (3c)

Red solid (85.4 mg, 89 % yield), MP: 155-156°C. $^1$H NMR (400 MHz, CDCl$_3$) δ8.45 (d, $J = 7.3$ Hz, 1H), 7.37-7.31 (m, 6H), 7.28-7.27 (m, 5H), 7.10 (t, $J = 7.5$ Hz, 1H), 6.74 (d, $J = 7.9$ Hz, 1H), 6.41 (s, 1H), 6.13 (dd, $J = 11.8, 7.7$ Hz, 1H), 5.77 (s, 1H), 5.15 (q, $J = 12.4$ Hz, 2H), 4.94 (q, $J = 15.8$ Hz, 2H), 3.06 (dd, $J = 14.1, 7.8$ Hz, 1H), 3.00-2.88 (m, 2H), 2.69 (dd, $J = 16.9, 1.4$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ185.13, 165.86, 160.42, 142.00, 135.56, 135.08, 134.88, 132.75, 129.74, 128.92, 128.54, 128.45, 128.27, 128.21, 127.94, 127.16, 123.46, 117.30, 109.16, 68.21, 67.00, 43.80, 37.49, 34.69, 29.68. HRMS calcd for C$_{29}$H$_{25}$N$_3$O$_4$Na[M+23]$^+$ 502.1743, found 502.1750.

2-(1-benzyl-2-oxoindolin-3-ylidene)-3-(2-(isopropoxycarbonyl)allyl)-5-oxopyrazolidin-2-iium-1-ide (3d)

Red solid (74.2 mg, 86 % yield), MP: 134-135°C. $^1$H NMR (400 MHz, CDCl$_3$) δ8.45 (d, $J = 7.6$ Hz, 1H), 7.37-7.27 (m, 6H), 7.08 (t, $J = 7.6$ Hz, 1H), 6.75 (d, $J = 7.8$ Hz, 1H), 6.33 (s, 1H), 6.09 (dd, $J = 12.2, 7.5$ Hz, 1H), 5.71 (s, 1H), 5.07-4.94 (m, 3H), 3.08-2.87 (m, 3H), 2.69 (d, $J = 16.8$ Hz, 1H), 1.24 (dd, $J = 9.3, 6.3$ Hz, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ185.25, 165.57, 160.43, 142.03, 135.51, 135.13, 132.74, 128.94, 128.86, 128.48, 127.96, 127.19, 123.43, 117.35, 109.15, 68.92, 68.39, 43.82, 37.35, 34.65, 21.72. HRMS calcd for C$_{23}$H$_{25}$N$_3$O$_4$Na[M+23]$^+$ 454.1743, found 454.1748.

2-(1-benzyl-2-oxoindolin-3-ylidene)-3-(2-(tert-butoxycarbonyl)allyl)-5-oxopyrazolidin-2-iium-1-ide (3e)
**oxopyrazolidin-2-ium-1-ide (3e)**

Red solid (83.8 mg, 94 % yield), MP: 143-144°C. 

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.45 (d, $J = 7.5$ Hz, 1H), 7.36-7.27 (m, 6H), 7.08 (t, $J = 7.6$ Hz, 1H), 6.74 (d, $J = 7.8$ Hz, 1H), 6.26 (s, 1H), 6.08 (d, $J = 4.0$ Hz, 1H), 5.68 (s, 1H), 4.99 (d, $J = 5.4$ Hz, 2H), 3.10 (dd, $J = 14.1$, 7.8 Hz, 1H), 2.95 (dd, $J = 16.9$, 8.4 Hz, 1H), 2.84 (dd, $J = 14.2$, 4.2 Hz, 1H), 2.70 (d, $J = 16.9$ Hz, 1H), 1.41 (s, 9H). 

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 185.12, 165.55, 165.28, 160.50, 142.02, 136.30, 135.15, 132.65, 128.93, 128.51, 128.41, 127.92, 127.14, 123.35, 117.38, 109.11, 81.52, 68.46, 43.79, 36.84, 34.60, 27.93. HRMS calcd for C$_{26}$H$_{27}$N$_3$O$_4$Na [M+23]$^+$ 468.1899, found 468.1906.

**2-(1-benzyl-2-oxoindolin-3-ylidene)-3-(2-(sec-butoxycarbonyl)allyl)-5-oxopyrazolidin-2-ium-1-ide (3f)**

Red solid (75.7 mg, 85 % yield), MP: 106-107°C. 

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.45 (d, $J = 7.6$ Hz, 1H), 7.37-7.27 (m, 6H), 7.09 (t, $J = 7.7$ Hz, 1H), 6.76 (d, $J = 7.8$ Hz, 1H), 6.35 (d, $J = 6.5$ Hz, 1H), 6.15-6.05 (m, 1H), 5.73 (d, $J = 8.5$ Hz, 1H), 5.07-4.93 (m, 2H), 4.91-4.80 (m, 1H), 3.10-2.99 (m, 1H), 3.00-2.87 (m, 2H), 2.70 (d, $J = 16.9$ Hz, 1H), 1.65-1.50 (m, 2H), 1.26-1.18 (m, 3H), 0.88 (dd, $J = 13.7$, 7.2 Hz, 3H). 

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 185.20, 165.71, 160.41, 142.01, 135.48, 135.40, 135.12, 132.71, 128.91, 128.72, 128.44, 127.93, 127.17, 123.39, 117.35, 109.13, 73.44, 68.42, 68.33, 43.81, 37.34, 37.14, 34.64, 34.51, 28.71, 28.67, 19.28, 19.26, 9.70. HRMS calcd for C$_{26}$H$_{27}$N$_3$O$_4$Na [M+23]$^+$ 468.1899, found 468.1903.

**2-(1-benzyl-5-methyl-2-oxoindolin-3-ylidene)-3-(2-(ethoxycarbonyl)allyl)-5-oxopyrazolidin-2-ium-1-ide (3g)**

Red solid (80.3 mg, 93 % yield), MP: 121-122°C. 

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.30 (s, 1H), 7.35-7.27 (m, 5H), 7.10 (d, $J = 8.0$ Hz, 1H), 6.64 (d, $J = 8.0$ Hz, 1H), 6.36 (s, 1H), 6.17-6.06 (m, 1H), 5.73 (s, 1H), 4.95 (s, 1H), 3.96 (dd, $J = 14.0$, 7.8 Hz, 2H), 3.18 (dd, $J = 14.3$, 4.7 Hz, 2H), 2.68 (d, $J = 16.9$ Hz, 1H), 1.41 (s, 9H). 

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 185.05, 165.37, 160.39, 142.01, 135.48, 135.40, 135.12, 132.71, 128.91, 128.72, 128.44, 127.93, 127.17, 123.39, 117.35, 109.13, 73.44, 68.42, 68.33, 43.81, 37.34, 37.14, 34.64, 34.51, 28.71, 28.67, 19.28, 19.26, 9.70. HRMS calcd for C$_{26}$H$_{27}$N$_3$O$_4$Na [M+23]$^+$ 468.1899, found 468.1903.
2H), 4.25-4.09 (m, 2H), 3.07-2.91 (m, 3H), 2.69 (dd, \( J = 16.9, 1.4 \) Hz, 1H), 2.32 (s, 3H), 1.26 (t, \( J = 7.1 \) Hz, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \)185.25, 166.04, 160.44, 139.92, 135.20, 133.29, 129.11, 128.88, 127.88, 127.15, 117.29, 108.94, 68.21, 61.27, 43.81, 37.44, 34.68, 20.90, 14.08. HRMS calcd for C\(_{25}\)H\(_{25}\)N\(_3\)O\(_4\)Na [M+23]\(^+\) 454.1743, found 454.1752.

2-(1-benzyl-5-chloro-2-oxoindolin-3-ylidene)-3-(2-(ethoxycarbonyl)allyl)-5-oxopyrazolidin-2-ium-1-ide (3h)

Red solid (74.0 mg, 82 % yield), MP: 127-128°C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \)8.48 (d, \( J = 2.1 \) Hz, 1H), 7.40-7.29 (m, 5H), 7.27 (d, \( J = 2.1 \) Hz, 1H), 6.70 (d, \( J = 8.4 \) Hz, 1H), 6.39 (s, 1H), 6.19-6.10 (m, 1H), 5.77 (s, 1H), 5.06-4.93 (m, 2H), 4.24-4.16 (m, 2H), 3.12-3.05 (m, 1H), 3.03-2.90 (m, 2H), 2.74 (dd, \( J = 17.0, 1.4 \) Hz, 1H), 1.29 (t, \( J = 7.1 \) Hz, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \)185.17, 166.05, 160.20, 140.16, 134.92, 134.78, 132.12, 129.46, 129.04, 128.12, 127.74, 127.16, 124.19, 118.44, 110.12, 68.77, 61.39, 43.95, 37.34, 34.46, 14.11. HRMS calcd for C\(_{24}\)H\(_{22}\)ClN\(_3\)O\(_4\)Na [M+23]\(^+\) 474.1197, found 474.1208.

2-(1-benzyl-5-methoxy-2-oxoindolin-3-ylidene)-3-(2-(ethoxycarbonyl)allyl)-5-oxopyrazolidin-2-ium-1-ide (3i)

Red solid (86.8 mg, 97 % yield), MP: 137-138°C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \)8.07 (d, \( J = 2.6 \) Hz, 1H), 7.37-7.29 (m, 5H), 6.87 (dd, \( J = 8.6, 2.6 \) Hz, 1H), 6.66 (d, \( J = 8.6 \) Hz, 1H), 6.38 (s, 1H), 6.18-6.09 (m, 1H), 5.75 (s, 1H), 4.96 (s, 2H), 4.25-4.12 (m, 2H), 3.81 (s, 3H), 3.09-2.92 (m, 3H), 2.70 (dd, \( J = 16.9, 1.2 \) Hz, 1H), 1.28 (t, \( J = 7.1 \) Hz, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \)185.14, 166.00, 160.32, 156.20, 135.90, 135.16, 135.09, 129.13, 128.86, 127.86, 127.12, 125.92, 119.40, 117.77, 113.04, 109.89, 68.28, 61.23, 56.08, 43.80, 37.35, 34.59, 14.05. HRMS calcd for C\(_{25}\)H\(_{25}\)N\(_3\)O\(_5\)Na [M+23]\(^+\) 470.1692, found 470.1697.

3-(2-(ethoxycarbonyl)allyl)-2-(1-methyl-2-oxoindolin-3-ylidene)-5-
oxopyrazolidin-2-ium-1-ide (3k)

Red solid (67.6 mg, 99 % yield), MP: 149-150°C. \( ^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.41 (d, \( J = 7.4 \text{ Hz}, \text{ 1H} \)), 7.40 (t, \( J = 7.5 \text{ Hz}, \text{ 1H} \)), 7.11 (t, \( J = 7.5 \text{ Hz}, \text{ 1H} \)), 6.84 (d, \( J = 7.6 \text{ Hz}, \text{ 1H} \)), 6.35 (s, 1H), 6.10-5.94 (m, 1H), 5.74 (s, 1H), 4.28-4.04 (m, 2H), 3.28 (s, 3H), 3.00-2.85 (m, 3H), 2.66 (d, \( J = 16.7 \text{ Hz}, \text{ 1H} \)), 1.27 (t, \( J = 6.9 \text{ Hz}, \text{ 3H} \)). \( ^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 185.15, 166.06, 160.24, 142.78, 135.02, 132.73, 129.18, 128.29, 123.36, 117.16, 108.15, 68.24, 61.25, 37.12, 34.35, 26.23, 14.06. HRMS calcd for C\(_{18}\)H\(_{19}\)N\(_3\)O\(_4\)Na [M+23]\(^+\) 364.1273, found 364.1275.

3-(2-(ethoxycarbonyl)allyl)-2-(1-isopropyl-2-oxoindolin-3-ylidene)-5-oxopyrazolidin-2-ium-1-ide (3l)

Red solid (71.0 mg, 96 % yield), MP: 133-134°C. \( ^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.49 (d, \( J = 7.6 \text{ Hz}, \text{ 1H} \)), 7.38 (t, \( J = 7.8 \text{ Hz}, \text{ 1H} \)), 7.09 (t, \( J = 7.7 \text{ Hz}, \text{ 1H} \)), 7.00 (d, \( J = 8.0 \text{ Hz}, \text{ 1H} \)), 6.34 (s, 1H), 5.70 (s, 1H), 5.31-5.17 (m, 1H), 4.65 (dt, \( J = 14.0, 7.0 \text{ Hz}, \text{ 1H} \)), 4.24-4.11 (m, 2H), 3.02-2.85 (m, 3H), 2.65 (dd, \( J = 16.8, 11.1 \text{ Hz}, \text{ 1H} \)), 1.51 (dd, \( J = 6.9, 4.4 \text{ Hz}, \text{ 6H} \)), 1.27 (t, \( J = 7.1 \text{ Hz}, \text{ 3H} \)). \( ^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 185.16, 166.02, 159.88, 141.62, 135.26, 132.59, 128.96, 128.78, 126.00, 122.83, 117.48, 109.65, 68.02, 61.22, 44.36, 37.40, 34.61, 19.61, 19.50, 14.06. HRMS calcd for C\(_{20}\)H\(_{23}\)N\(_3\)O\(_4\)Na [M+23]\(^+\) 392.1586, found 392.1591.

2-(1-allyl-2-oxoindolin-3-ylidene)-3-(2-(ethoxycarbonyl)allyl)-5-oxopyrazolidin-2-ium-1-ide (3m)

Red solid (72.7 mg, 99 % yield), MP: 124-125°C. \( ^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.44 (d, \( J = 7.6 \text{ Hz}, \text{ 1H} \)), 7.37 (t, \( J = 7.7 \text{ Hz}, \text{ 1H} \)), 7.11 (t, \( J = 7.7 \text{ Hz}, \text{ 1H} \)), 6.84 (d, \( J = 7.8 \text{ Hz}, \text{ 1H} \)), 6.34 (s, 1H), 6.10-6.02 (m, 1H), 5.84 (ddd, \( J = 22.4, 10.3, 5.2 \text{ Hz}, \text{ 1H} \)), 5.72 (s, 1H), 5.31-5.17 (m, 2H), 4.40 (d, \( J = 4.3 \text{ Hz}, \text{ 2H} \)), 4.23-4.08 (m, 2H), 3.02-2.85 (m, 3H), 2.66 (d, \( J = 16.8 \text{ Hz}, \text{ 1H} \)), 1.26
(t, J = 7.1 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 185.17, 166.01, 159.97, 142.01, 135.05, 132.68, 130.74, 129.13, 128.37, 123.33, 118.01, 117.21, 108.97, 68.23, 61.24, 42.34, 37.21, 34.48, 14.05. HRMS calcd for C$_{20}$H$_{21}$N$_3$O$_4$Na [M+23]$^+$ 390.1430, found 390.1433.

2-(1-benzyl-2-oxoindolin-3-ylidene)-3-(2-(ethoxycarbonyl)-1-phenylallyl)-5-oxopyrazolidin-2-ium-1-ide (4a)

Red solid (77.0 mg, 78 % yield), MP: 128-129°C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.39 (d, J = 7.6 Hz, 1H), 7.44-7.34 (m, 6H), 7.30-7.28 (m, 3H), 7.13 (t, J = 7.6 Hz, 1H), 7.01 (d, J = 6.6 Hz, 2H), 6.85 (d, J = 7.7 Hz, 1H), 6.58 (s, 1H), 6.50-6.43 (m, 1H), 5.70 (s, 1H), 5.15 (d, J = 15.8 Hz, 1H), 4.97 (d, J = 15.8 Hz, 1H), 4.78-4.74 (m, 1H), 4.10-4.00 (m, 2H), 2.93 (dd, J = 16.7, 8.7 Hz, 1H), 2.71 (d, J = 16.6 Hz, 1H), 1.08 (t, J = 7.1 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 184.44, 165.63, 160.80, 141.75, 139.87, 135.23, 134.00, 132.54, 128.98, 128.92, 128.60, 128.10, 128.01, 127.27, 125.74, 123.54, 117.45, 109.14, 71.25, 61.17, 50.83, 44.00, 32.66, 13.85. HRMS calcd for C$_{30}$H$_{27}$N$_3$O$_4$Na [M+23]$^+$ 516.1899, found 516.1906.

2-(1-benzyl-2-oxoindolin-3-ylidene)-3-(1-(4-cyanophenyl)-2-(ethoxycarbonyl)allyl)-5-oxopyrazolidin-2-ium-1-ide (4b)

Red solid (81.9 mg, 79 % yield), MP: 125-127°C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.35 (d, J = 7.6 Hz, 1H), 7.55 (d, J = 8.2 Hz, 2H), 7.40-7.30 (m, 6H), 7.17-7.08 (m, 3H), 6.86 (d, J = 7.9 Hz, 1H), 6.64 (s, 1H), 6.48-6.40 (m, 1H), 5.75 (s, 1H), 5.14 (d, J = 15.8 Hz, 1H), 4.92 (d, J = 15.8 Hz, 1H), 4.77 (s, 1H), 4.13-3.94 (m, 2H), 2.97 (dd, J = 16.8, 8.8 Hz, 1H), 2.59 (d, J = 16.8 Hz, 1H), 1.10 (t, J = 7.1 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 183.72, 165.07, 160.62, 141.90, 139.76, 138.74, 135.00, 133.04, 132.59, 129.29, 128.99, 128.21, 128.09, 127.27, 126.62, 123.74, 118.18, 117.13, 112.67, 109.33, 70.65, 61.44, 50.56, 44.05, 32.48, 13.85. HRMS calcd for C$_{31}$H$_{26}$N$_4$O$_4$Na [M+23]$^+$ 541.1852, found 541.1857.

2-(1-benzyl-2-oxoindolin-3-ylidene)-3-(2-(ethoxycarbonyl)-1-(4-
(methoxycarbonyl)phenyl)(allyl)-5-oxopyrazolidin-2-ium-1-ide (4c)

Red solid (102.6 mg, 93 % yield), MP: 116-117°C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$8.35 (d, $J$ = 7.5 Hz, 1H), 7.91 (d, $J$ = 8.3 Hz, 2H), 7.43-7.27 (m, 6H), 7.16-7.01 (m, 3H), 6.84 (d, $J$ = 7.9 Hz, 1H), 6.60 (s, 1H), 6.53-6.40 (m, 1H), 5.71 (d, $J$ = 1.1 Hz, 1H), 5.13 (d, $J$ = 15.8 Hz, 1H), 4.93 (d, $J$ = 15.8 Hz, 1H), 4.78 (d, $J$ = 2.5 Hz, 1H), 4.13-3.91 (m, 2H), 3.86 (s, 3H), 2.95 (dd, $J$ = 16.8, 8.7 Hz, 1H), 2.65 (dd, $J$ = 16.8, 1.3 Hz, 1H), 1.06 (t, $J$ = 7.1 Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$184.05, 166.45, 165.32, 160.69, 141.80, 139.35, 139.22, 135.09, 132.78, 130.28, 130.12, 128.96, 128.57, 128.15, 128.01, 127.24, 126.21, 123.64, 117.25, 109.21, 70.85, 61.28, 52.07, 50.56, 44.00, 32.51, 13.81. HRMS calcd for C$_{32}$H$_{29}$N$_3$O$_6$Na [M+23]$^+$ 574.1954, found 574.1960.

2-(1-benzyl-2-oxoindolin-3-ylidene)-3-(2-(ethoxycarbonyl)-1-(pyridin-4-yl)allyl)-5-oxopyrazolidin-2-ium-1-ide (4d)

Red solid (82.1 mg, 83 % yield), MP: 130-131°C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$8.51 (d, $J$ = 5.3 Hz, 2H), 8.39 (d, $J$ = 7.7 Hz, 1H), 7.42-7.28 (m, 6H), 7.14 (t, $J$ = 7.7 Hz, 1H), 6.95 (d, $J$ = 5.6 Hz, 2H), 6.85 (d, $J$ = 8.0 Hz, 1H), 6.63 (s, 1H), 6.47-6.43 (m, 1H), 5.72 (s, 1H), 5.12 (d, $J$ = 15.8 Hz, 1H), 4.94 (d, $J$ = 15.9 Hz, 1H), 4.76-4.70 (m, 1H), 4.12-3.98 (m, 2H), 2.98 (dd, $J$ = 16.9, 8.8 Hz, 1H), 2.62 (d, $J$ = 16.8 Hz, 1H), 1.10 (t, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$183.85, 165.08, 160.66, 150.25, 149.41, 143.70, 141.91, 138.43, 135.02, 133.01, 128.99, 128.70, 128.29, 128.07, 127.24, 127.03, 123.74, 123.67, 122.69, 117.19, 109.30, 70.39, 61.47, 50.10, 44.03, 32.66, 13.83. HRMS calcd for C$_{29}$H$_{26}$N$_4$O$_4$Na [M+23]$^+$ 517.1852, found 517.1857.

Methyl 2-((2-(1-benzyl-2-oxoindolin-3-yl)-5-oxo-2,5-dihydro-1H-pyrazol-3-yl)methyl)acrylate (5)

Red solid (79.0 mg, 79 % yield), MP: 187-188°C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$10.34 (s, 1H), 7.40 (d, $J$ = 7.4
Hz, 1H), 7.35-7.25 (m, 6H), 7.21 (t, J = 7.9 Hz, 1H), 7.02 (t, J = 7.5 Hz, 1H), 6.71 (d, J = 7.8 Hz, 1H), 6.04 (s, 1H), 5.68-5.63 (m, 1H), 5.54 (s, 1H), 4.98 (d, J = 15.8 Hz, 1H), 4.84 (d, J = 15.8 Hz, 1H), 3.71 (d, J = 13.0 Hz, 1H), 3.52-3.44 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ172.68, 166.94, 162.98, 142.61, 135.22, 133.47, 130.53, 130.21, 130.07, 128.72, 127.67, 127.26, 126.18, 126.04, 122.78, 109.72, 92.24, 68.66, 51.77, 44.17, 36.16. HRMS calcd for C₂₃H₂₁N₃O₄Na [M+23]⁺ 426.1430, found 426.1439.

5. References

6. Copies of NMR spectra for products 3 and 4
3a
3e
3h
3k
4b
4d
7. Copie of NMR spectra for compound 5
8. ORTEP drawing of 3b with thermal ellipsoids at the 30% probability.
9. ESI-MS studies