Supporting Information

Co/Mn-Mediated Oxygenative Cross-Coupling of Indoles with β-Keto Esters via Dioxygen Activation: An Efficient Access to Ketonization-Olefination of Indoles

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General

All reactions were carried out under dry O₂ with dry solvents under anhydrous conditions. Co(OAc)₂·4H₂O was purchased from Alfa Aesar and converted to the anhydrous salt by drying at 80 °C/1 mmHg for 60 h. Ethyl 3-cyano-benzoyl-acetate,¹ Methyl benzoylacetate,² ethyl 3-(naphthalen-3-yl)-3-oxopropanoate¹ 2b, isopropyl benzoylacetate² 2c, benzyl benzoyletacetate³ and Deuterioindoles⁴ were prepared according to the reported procedures. All other reagents were purchased from TCI, Sigma-Aldrich, Alfa Aesar, Acros, and Meryer and used without further purification. DMSO and DMF were distilled from CaH₂ under nitrogen and stored under nitrogen.¹ H NMR(400 MHz),¹³C NMR (100 MHz) and¹⁹F NMR (377 MHz) spectra were recorded in CDCl₃ solutions using a Burker AVANCE 400 spectrometer. Single-crystal X-ray diffraction data were collected on Rigaku Mercury CCD with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) in the ω scanning mode at room temperature. The structure were solved by direct methods and refined by full-matrix least squares on F² with the SHELXTL-97 program. CCDC reference number 763658. Elemental analyses were performed on a Vario EL III elemental analyzer.
Table S1 Screening Results for Co/Mn-Mediated Oxidative Coupling of Indole with Ethyl Benzoyleacetate

[a] 0.125 mmol scale, Co(OAc)₂ (1.0 equiv), DMF (1 mL, 0.125 M), 1 atm of O₂. [b] Isolated yields. [c] Co(OAc)₂ (0.15 equiv). [d] In the absence of Co(OAc)₂. [e] N₂ atmosphere.

**General procedure**

In a glove box, a 30 mL of Schlenk tube equipped with a stir bar was charged with indole 1, Co(OAc)₂ (1 equiv), Mn(OAc)₂ (0.25 equiv),
NHPI (0.15 equiv), pivalic acid (30 equiv), DMSO (0.1 mL), and DMF (1 mL, 0.125 M). The tube was fitted with a rubber septum and removed out of the glove box. Then, the tube was evacuated and refilled with O₂ for three times. Subsequently, ethyl benzoylacetae 2a (5 equiv) was added to the Schlenk tube through the rubber septum using syringes, and then the septum was replaced by a Teflon screwcap under an oxygen flow. The reaction mixture was stirred at 75 °C for 24 h. Upon completion, the reaction mixture was diluted with 10 mL of ethyl ether, filtered through a pad of silica gel, followed by washing the pad of the silica gel with the ethyl ether (30 mL). The filtrate was washed with water (3×15 mL). The organic phase was dried over Na₂SO₄, filtered, concentrated under reduced pressure. The residue was then purified by flash chromatography on silica gel to provide the corresponding product 3a.

**Experimental data**

Ethyl 3-(naphthal-3-yl)-3-oxopropanoate 2b, was prepared according to the reported procedures¹, afforded an oil (65% yield). ¹H NMR [shows a 18:82 enol/ketone ratio] (400 MHz, CDCl₃): δ [keto form] 8.44 (s, 1 H), 8.01 (d, J = 8.6 Hz, 1 H), 7.96 (d, J = 8.0 Hz, 1 H), 7.90 – 7.83 (m, 2 H), 7.63 – 7.51 (m, 2 H), 4.23 (q, J = 7.1 Hz, 2 H), 4.12 (s, 2 H), 1.26 (t, J = 7.1 Hz, 3 H); [enol form] 12.70 (s, 1 H), 8.35 (s, 1 H), 7.77 – 7.75 (m, 1 H), 5.81 (s, 1 H), 4.29 (q, J = 7.1 Hz, 2 H), 1.35 (t, J = 7.1 Hz, 3 H).
**Isopropyl benzoylacetate 2c**, was prepared according to the reported procedures\(^2\), afforded an oil (35% yield). \(^1\)H NMR [shows a 16:84 enol/ketone ratio] (400 MHz, CDCl\(_3\)): \(\delta\) [keto form] 7.93 (d, \(J = 7.4\) Hz, 2 H), 7.58 (t, \(J = 7.5\) Hz, 1 H), 7.47 (t, \(J = 7.7\) Hz, 2 H), 5.10 – 5.04 (m, 1 H), 3.95 (s, 2 H), 1.22 (d, \(J = 6.2\) Hz, 6 H); [enol form] 12.65 (s, 1 H), 7.77 (d, \(J = 7.6\) Hz, 2 H), 7.43 – 7.40 (m, 3 H), 5.63 (s, 1 H), 5.16 – 5.13 (m, 1 H), 1.31 (d, \(J = 6.3\) Hz, 6 H).

**(Z)-ethyl 3-oxo-2-(3-oxoindolin-2-ylidene)-3-phenylpropanoate**

![Chemical structure of 3a](image)

Following the general procedure, using 20% ether in petroleum ether as the eluant afforded a red solid (70% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 9.28 (s, 1 H), 7.96 (d, \(J = 7.8\) Hz, 2 H), 7.58 – 7.42 (m, 5 H), 6.96 – 6.93 (m, 2 H), 4.22 (q, \(J = 7.1\) Hz, 2 H), 1.16 (t, \(J = 7.1\) Hz, 3 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\), 192.3, 186.1, 166.8, 152.6, 142.9, 137.6, 137.3, 133.4, 128.8, 128.5, 125.6, 122.0, 119.8, 111.9, 107.8, 61.6, 14.0. Anal. Calcd. for C\(_{19}\)H\(_{15}\)NO\(_4\): C, 71.02; H, 4.71; N, 4.36; Found: C, 70.97; H, 4.50; N, 4.31.

**(Z)-ethyl 3-oxo-2-(3-oxoindolin-2-ylidene)-3-p-tolylpropanoate**
Following the general procedure, using 20% ether in petroleum ether as the eluant afforded a red solid (69% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.29 (s, 1 H), 7.87 (d, $J = 8.2$ Hz, 2 H), 7.52 – 7.45 (m, 2 H), 7.23 (d, $J = 8.1$ Hz, 2 H), 6.95 – 6.91 (m, 2 H), 4.21 (q, $J = 7.1$ Hz, 2 H), 2.39 (s, 3 H), 1.16 (t, $J = 7.1$ Hz, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 191.9, 186.1, 166.9, 152.5, 144.3, 142.8, 137.5, 134.9, 129.3, 128.9, 125.6, 121.9, 119.9, 111.9, 108.1, 61.6, 21.8, 14.0. Anal. Calcd. for C$_{20}$H$_{17}$NO$_4$: C, 71.63; H, 5.11; N, 4.18; Found: C, 71.31; H, 4.95; N, 4.05.

(Z)-ethyl 3-oxo-2-(3-oxoindolin-2-ylidene)-3-m-tolylpropanoate

Following the general procedure, using 20% ether in petroleum ether as the eluant afforded a red solid (68% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.29 (s, 1 H), 7.81 (s, 1 H), 7.73 (d, $J = 7.6$ Hz, 1 H), 7.53 – 7.46 (m, 2 H), 7.38 – 7.29 (m, 2 H), 6.96 – 6.92 (m, 2 H), 4.22 (q, $J = 7.1$ Hz, 2 H), 2.39 (s, 3 H), 1.16 (t, $J = 7.1$ Hz, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$
192.4, 186.1, 166.8, 152.6, 142.8, 138.4, 137.5, 137.3, 134.3, 129.2, 128.4, 126.2, 125.6, 122.0, 119.9, 111.9, 108.1, 61.6, 21.4, 14.0. Anal. Calcd. for C$_{20}$H$_{17}$NO$_4$: C, 71.63; H, 5.11; N, 4.18; Found: C, 71.52; H, 4.90; N, 4.10.

(Z/E)-ethyl 3-oxo-2-(3-oxoindolin-2-ylidene)-3-o-tolylpropanoate

Following the general procedure, using 20% ether in petroleum ether as the eluant afforded a red solid (61% yield). $^1$H NMR [Z/E = 4:1] (400 MHz, CDCl$_3$): δ Z: 9.28 (s, 1 H), 7.67 – 6.91 (m, 8 H), 4.24 (q, $J = 7.1$ Hz, 2 H), 2.78 (s, 3 H), 1.20 (t, $J = 7.1$ Hz, 3 H). E: 10.59 (s, 1 H), 4.09 (q, $J = 7.1$ Hz, 2 H), 2.36 (s, 3 H), 1.06 (t, $J = 7.1$ Hz, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ Z: 193.8, 186.3, 167.0, 152.6, 142.4, 140.8, 137.5, 134.3, 132.0, 132.0, 130.7, 125.5, 125.2, 121.9, 119.9, 111.9, 110.1, 61.6, 21.6, 14.0. E: 197.3, 187.0, 167.9, 152.1, 139.5, 137.5, 136.6, 135.3, 132.7, 129.9, 125.9, 125.1, 123.6, 123.0, 119.7, 112.4, 109.0, 67.7, 19.3, 13.5. Anal. Calcd. for C$_{20}$H$_{17}$NO$_4$: C, 71.63; H, 5.11; N, 4.18; Found: C, 71.49; H, 5.10; N, 4.15.

(Z)-ethyl 3-(4-chlorophenyl)-3-oxo-2-(3-oxoindolin-2-ylidene)propanoate
Following the general procedure, using 20% ether in petroleum ether as the eluant afforded a red solid (66% yield). $^1$H NMR (400 MHz, CDCl$_3$): δ 9.28 (s, 1 H), 7.90 (d, $J = 8.6$ Hz, 2 H), 7.53 – 7.47 (m, 2 H), 7.42 (d, $J = 8.6$ Hz, 2 H), 6.97 – 6.94 (m, 2 H), 4.22 (q, $J = 7.1$ Hz, 2 H), 1.17 (t, $J = 7.1$ Hz, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 191.1, 186.1, 166.5, 152.5, 143.1, 139.8, 137.7, 135.7, 130.2, 128.9, 125.7, 122.2, 119.8, 112.0, 107.2, 61.7, 14.0. Anal. Calcd. for C$_{19}$H$_{14}$ClNO$_4$: C, 64.14; H, 3.97; N, 3.94; Found: C, 64.15; H, 3.87; N, 3.87.

(Z)-ethyl 3-(3-chlorophenyl)-3-oxo-2-(3-oxoindolin-2-ylidene)propanoate

Following the general procedure, using 20% ether in petroleum ether as the eluant afforded a red solid (65% yield). $^1$H NMR (400 MHz, CDCl$_3$): δ 9.27 (s, 1 H), 7.93 (t, $J = 1.8$ Hz, 1 H), 7.84 (dt, $J = 7.8$ Hz, $J = 1.2$ Hz, 1 H), 7.55 – 7.49 (m, 3 H), 7.39 (t, $J = 7.8$ Hz, 1 H), 6.99 – 6.95 (m, 2
H), 4.24 (q, J = 7.1 Hz, 2 H), 1.18 (t, J = 7.1 Hz, 3 H); 13C NMR (100 MHz, CDCl3): δ 191.1, 186.1, 166.5, 152.5, 143.2, 138.9, 137.8, 134.9, 133.3, 129.9, 128.7, 126.9, 125.8, 122.2, 119.7, 111.9, 107.0, 61.8, 14.0. Anal. Calcd. for C19H14ClNO4: C, 64.14; H, 3.97; N, 3.94; Found: C, 64.15; H, 4.01; N, 3.91.

(Z)-ethyl 3-(4-bromophenyl)-3-oxo-2-(3-oxoindolin-2-ylidene)propanoate

Following the general procedure, using 20% ether in petroleum ether as the eluant afforded a red solid (65% yield). 1H NMR (400 MHz, CDCl3): δ 9.28 (s, 1 H), 7.83 (d, J = 8.8 Hz, 2 H), 7.58 (d, J = 8.6 Hz, 2 H), 7.53 – 7.47 (m, 2 H), 6.97 – 6.93 (m, 2 H), 4.21 (q, J = 7.1 Hz, 2 H), 1.16 (t, J = 7.1 Hz, 3 H); 13C NMR (100 MHz, CDCl3): δ 191.3, 186.1, 166.5, 152.5, 143.1, 137.7, 136.1, 131.9, 130.2, 128.6, 125.7, 122.2, 119.8, 112.0, 107.1, 61.7, 14.0. Anal. Calcd. for C19H14BrNO4: C, 57.02; H, 3.53; N, 3.50; Found: C, 56.61; H, 3.54; N, 3.33.

(Z)-ethyl 3-(4-fluorophenyl)-3-oxo-2-(3-oxoindolin-2-ylidene)propanoate
Following the general procedure, using 20% ether in petroleum ether as the eluant afforded a red solid (68% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.30 (s, 1 H), 8.00 – 7.97 (m, 2 H), 7.52 – 7.46 (m, 2 H), 7.12 – 7.08 (m, 2 H), 6.95 – 6.92 (m, 2 H), 4.20 (q, $J = 7.1$ Hz, 2 H), 1.15 (t, $J = 7.1$ Hz, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 192.1, 186.1, 166.6, 165.9 (d, $J = 254.8$ Hz), 152.6, 142.9, 137.7, 133.9 (d, $J = 2.8$ Hz), 131.4 (d, $J = 9.5$ Hz), 125.6, 122.1, 119.8, 115.7 (d, $J = 21.9$ Hz), 112.0, 107.4, 61.6, 14.0; $^{19}$F NMR (377 MHz, CDCl$_3$): $\delta$ -104.79. Anal. Calcd. for C$_{19}$H$_{14}$FNO$_4$: C, 67.25; H, 4.16; N, 4.13; Found: C, 66.68; H, 4.73; N, 4.01.

(Z)-ethyl 3-(3-methoxyphenyl)-3-oxo-2-(3-oxoindolin-2-ylidene)propanoate

Following the general procedure, using 30% ether in petroleum ether as the eluant afforded a red solid (67% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.27 (s, 1 H), 7.58 (t, $J = 2.0$ Hz, 1 H), 7.52 (d, $J = 7.7$ Hz, 1 H), 7.50 –
7.46 (m, 2 H), 7.32 (t, J = 7.9 Hz, 1 H), 7.11 (dd, J = 8.3 Hz, J = 2.7 Hz, 1 H), 6.96 – 6.93 (m, 2 H), 4.22 (q, J = 7.1 Hz, 2 H), 3.86 (s, 3 H), 1.17 (t, J = 7.1 Hz, 3 H); 13C NMR (100 MHz, CDCl₃): δ 192.0, 186.0, 166.8, 159.9, 152.5, 142.9, 138.7, 137.5, 129.5, 125.6, 122.0, 121.8, 120.1, 120.0, 112.6, 111.9, 107.9, 61.6, 55.4, 14.0; Anal. Calcd. for C₂₀H₁₇NO₅: C, 68.37; H, 4.88; N, 3.99; Found: C, 67.87; H, 5.09; N, 3.65.

(Z)-ethyl 3-(3-cyanophenyl)-3-oxo-2-(3-oxoindolin-2-ylidene)propanoate

Following the general procedure, using 30% ether in petroleum ether as the eluant afforded a red solid (62% yield). 1H NMR (400 MHz, CDCl₃): δ 9.30 (s, 1 H), 8.22 – 8.20 (m, 2 H), 7.83 (d, J = 7.7 Hz, 1 H), 7.60 (t, J = 7.7 Hz, 1 H), 7.53 – 7.50 (m, 2 H), 6.99 – 6.96 (m, 2 H), 4.23 (q, J = 7.1 Hz, 2 H), 1.17 (t, J = 7.1 Hz, 3 H); 13C NMR (100 MHz, CDCl₃): δ 190.5, 186.2, 166.2, 152.6, 143.5, 138.2, 138.0, 136.1, 132.6, 132.4, 129.7, 125.8, 122.4, 119.6, 119.6, 118.1, 113.1, 112.1, 106.1, 61.8, 14.0. Anal. Calcd. for C₂₀H₁₄NO₄: C, 69.36; H, 4.07; N, 8.09; Found: C, 68.96; H, 4.39; N, 7.85.

(Z)-ethyl 3-(naphthalen-2-yl)-3-oxo-2-(3-oxoindolin-2-ylidene)propanoate

S11
Following the general procedure, using 20% ether in petroleum ether as the eluant afforded a red solid (64% yield). $^1$H NMR (400 MHz, CDCl$_3$): \( \delta \) 9.35 (s, 1 H), 8.39 (s, 1 H), 8.14 (dd, \( J = 8.6 \) Hz, \( J = 1.6 \) Hz, 1 H), 7.93 – 7.86 (m, 3 H), 7.60 – 7.47 (m, 4 H), 6.98 – 6.92 (m, 2 H), 4.23 (q, \( J = 7.1 \) Hz, 2 H), 1.15 (t, \( J = 7.1 \) Hz, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$): \( \delta \) 192.2, 186.1, 166.9, 152.5, 143.1, 137.6, 136.0, 134.9, 132.6, 130.8, 129.6, 128.6, 128.5, 127.9, 126.6, 125.7, 124.3, 122.0, 119.9, 111.9, 107.9, 61.7, 14.0. Anal. Calcd. for C$_{23}$H$_{17}$NO$_4$: C, 74.38; H, 4.61; N, 3.77; Found: C, 74.20; H, 4.71; N, 3.73.

(Z)-propyl 3-oxo-2-(3-oxoindolin-2-ylidene)-3-phenylpropanoate

Following the general procedure, using 20% ether in petroleum ether as the eluant afforded a red solid (61% yield). $^1$H NMR (400 MHz, CDCl$_3$): \( \delta \) 9.28 (s, 1 H), 7.95 (d, \( J = 7.8 \) Hz, 2 H), 7.57 – 7.42 (m, 5 H), 6.96 –
6.93 (m, 2 H), 5.12 (m, 1 H), 1.16 (d, J = 6.3 Hz, 6 H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 192.2, 186.0, 166.4, 152.5, 142.8, 137.5, 137.4, 133.2, 128.8, 128.5, 125.6, 121.9, 119.9, 111.8, 108.5, 69.5, 21.5. Anal. Calcd. for C\(_{20}\)H\(_{17}\)NO\(_4\): C, 71.63; H, 5.11; N, 4.18; Found: C, 71.55; H, 5.06; N, 4.09.

\((Z)\)-benzyl 3-oxo-2-(3-oxoindolin-2-ylidene)-3-phenylpropanoate

\[\text{N} \quad \text{O} \quad \text{O}\]
\[\text{O} \quad \text{OBn}\]

\(3\text{m}\)

Following the general procedure, using 30\% ether in petroleum ether as the eluant afforded a red solid (68\% yield). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 9.30 (s, 1 H), 7.99 (d, \(J = 7.6\) Hz, 2 H), 7.61 – 7.44 (m, 5 H), 7.28 – 7.26 (m, 3 H), 7.14 – 7.12 (m, 2 H), 6.99 – 6.94 (m, 2 H), 5.22 (s, 2 H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 192.1, 186.0, 166.5, 152.4, 143.2, 137.6, 137.3, 135.4, 133.4, 128.9, 128.6, 128.4, 128.1, 127.3, 125.7, 122.1, 119.8, 111.9, 107.4, 66.8. Anal. Calcd. for C\(_{24}\)H\(_{17}\)NO\(_4\): C, 75.19; H, 4.47; N, 3.65; Found: C, 75.58; H, 4.55; N, 3.39.

\((Z)\)-methyl 3-oxo-2-(3-oxoindolin-2-ylidene)-3-phenylpropanoate

\[\text{N} \quad \text{O} \quad \text{O}\]
\[\text{O} \quad \text{OMe}\]

\(3\text{n}\)
Following the general procedure, using 20% ether in petroleum ether as the eluant afforded a red solid (69% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.28 (s, 1 H), 7.98 (d, $J = 7.8$ Hz, 2 H), 7.59 – 7.43 (m, 5 H), 6.98 – 6.94 (m, 2 H), 3.75 (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 192.2, 186.0, 167.2, 152.5, 143.0, 137.6, 137.2, 133.5, 128.9, 128.6, 125.7, 122.1, 119.9, 111.9, 107.3, 52.6. Anal. Calcd. for C$_{18}$H$_{13}$NO$_4$: C, 70.35; H, 4.26; N, 4.56; Found: C, 70.09; H, 4.25; N, 4.40.

(Z)-methyl 2-(1-(ethoxycarbonyl)-2-oxo-2-phenylethylidene)-3-oxoindoline-5-carboxylate

Following the general procedure, using 30% ether in petroleum ether as the eluant afforded a red solid (45% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.56 (s, 1 H), 8.25 – 8.23 (m, 2 H), 7.98 (d, $J = 7.6$ Hz, 2 H), 7.60 (t, $J = 7.4$ Hz, 1 H), 7.48 (t, $J = 7.7$ Hz, 2 H), 7.03 (d, $J = 8.9$ Hz, 1 H), 4.25 (q, $J = 7.1$ Hz, 2 H), 3.90 (s, 3 H), 1.18 (t, $J = 7.1$ Hz, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 191.6, 185.0, 166.5, 165.8, 155.1, 142.6, 139.0, 137.0, 133.6, 128.8, 128.6, 127.5, 124.2, 119.7, 111.6, 109.7, 61.9, 52.2, 13.9. Anal. Calcd. for C$_{21}$H$_{17}$NO$_6$: C, 66.49; H, 4.52; N, 3.69; Found: C, 66.38; H, 4.28; N, 3.62.

(Z)-methyl 2-(1-(ethoxycarbonyl)-2-oxo-2-phenylethylidene)-3-oxoindoline-5-carboxylate
oxoindoline-4-carboxylate

Following the general procedure, using 30% ether in petroleum ether as the eluant afforded a red solid (50% yield). $^1$H NMR (400 MHz, CDCl$_3$): δ 9.42 (s, 1 H), 7.95 (d, $J = 7.6$ Hz, 2 H), 7.57 – 7.51 (m, 2 H), 7.44 (d, $J = 7.6$ Hz, 2 H), 7.26 (d, $J = 7.0$ Hz, 1 H), 7.07 (d, $J = 8.0$ Hz, 1 H), 4.21 (q, $J = 7.1$ Hz, 2 H), 3.83(s, 3 H), 1.14 (t, $J = 7.1$ Hz, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 191.9, 183.1, 166.8, 165.9, 153.0, 142.3, 137.1, 136.8, 133.4, 131.3, 128.9, 128.5, 122.7, 116.9, 114.8, 108.7, 61.7, 52.6, 13.9. Anal. Calcd. for C$_{21}$H$_{17}$NO$_6$: C, 66.49; H, 4.52; N, 3.69; Found: C, 66.43; H, 4.61; N, 3.46.

(Z)-ethyl 2-(5-fluoro-3-oxoindolin-2-ylidene)-3-oxo-3-phenylpropanoate

Following the general procedure, using 20% ether in petroleum ether as the eluant afforded a red solid (57% yield). $^1$H NMR (400 MHz, CDCl$_3$): δ 9.25 (s, 1 H), 7.96 (d, $J = 7.4$ Hz, 2 H), 7.57 (t, $J = 7.4$ Hz, 1 H), 7.45 (t,
$J = 7.7$ Hz, 2 H), 7.25 – 7.19 (m, 2 H), 6.92 (dd, $J = 8.5$ Hz, $J = 3.6$ Hz, 1 H), 4.22 (q, $J = 7.1$ Hz, 2 H), 1.16 (t, $J = 7.1$ Hz, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 191.9, 185.4 (d, $J = 3.0$ Hz), 166.7, 158.2 (d, $J = 242.8$ Hz), 148.8, 143.2, 137.2, 133.5, 128.8, 128.6, 124.6 (d, $J = 24.9$ Hz), 120.5 (d, $J = 8.1$ Hz), 112.7 (d, $J = 8.1$ Hz), 111.7 (d, $J = 24.2$ Hz), 108.7, 61.7, 14.0; $^{19}$F NMR (377 MHz, CDCl$_3$): $\delta$ -121.1. Anal. Calcd. for C$_{19}$H$_{14}$FNO$_4$: C, 67.25; H, 4.16; N, 4.13; Found: C, 66.97; H, 4.37; N, 4.05.

(Z)-ethyl 2-(5-chloro-3-oxoindolin-2-ylidene)-3-oxo-3-phenylpropanoate

3r

Following the general procedure, using 20% ether in petroleum ether as the eluant afforded a red solid (56% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.33 (s, 1 H), 7.95 (d, $J = 7.6$ Hz, 2 H), 7.57 (t, $J = 7.5$ Hz, 1 H), 7.47 – 7.42 (m, 4 H), 6.91 (d, $J = 8.4$ Hz, 1 H), 4.21 (q, $J = 7.1$ Hz, 2 H), 1.15 (t, $J = 7.1$ Hz, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 191.8, 185.0, 166.6, 150.8, 142.6, 137.1, 137.0, 133.5, 128.8, 128.6, 127.5, 125.2, 120.9, 113.1, 108.9, 61.8, 14.0. Anal. Calcd. for C$_{19}$H$_{14}$ClNO$_4$: C, 64.14; H, 3.97; N, 3.94; Found: C, 64.10; H, 3.95; N, 3.67.

(Z)-ethyl 2-(5-bromo-3-oxoindolin-2-ylidene)-3-oxo-3-phenylpropanoate

S16
oxo-3-phenylpropanoate

Following the general procedure, using 20% ether in petroleum ether as the eluant afforded a red solid (60% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.32 (s, 1 H), 7.95 (d, $J = 7.4$ Hz, 2 H), 7.63 – 7.55 (m, 3 H), 7.45 (t, $J = 7.7$ Hz, 2 H), 6.87 (d, $J = 8.4$ Hz, 1 H), 4.22 (q, $J = 7.1$ Hz, 2 H), 1.16 (t, $J = 7.1$ Hz, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 191.7, 184.8, 166.6, 151.2, 142.4, 139.8, 137.1, 133.5, 128.8, 128.6, 128.2, 121.4, 114.5, 113.5, 109.0, 61.8, 14.0 Anal. Calcd. for C$_{19}$H$_{14}$BrNO$_4$: C, 57.02; H, 3.53; N, 3.50; Found: C, 56.77; H, 3.55; N, 3.49.

(Z)-ethyl 2-(5-iodo-3-oxoindolin-2-ylidene)-3-oxo-3-phenylpropanoate

Following the general procedure, using 20% ether in petroleum ether as the eluant afforded a red solid (51% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 9.32 (s, 1 H), 7.94 (d, $J = 7.8$ Hz, 2 H), 7.80 (s, 1 H), 7.75 (dd, $J = 8.5$ Hz, 2 H), 6.87 (d, $J = 8.4$ Hz, 1 H), 4.22 (q, $J = 7.1$ Hz, 2 H), 1.16 (t, $J = 7.1$ Hz, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 191.7, 184.8, 166.6, 151.2, 142.4, 139.8, 137.1, 133.5, 128.8, 128.6, 128.2, 121.4, 114.5, 113.5, 109.0, 61.8, 14.0 Anal. Calcd. for C$_{19}$H$_{14}$BrNO$_4$: C, 57.02; H, 3.53; N, 3.49.
Hz, \( J = 1.8 \text{ Hz, 1 H} \), 7.56 (t, \( J = 7.5 \text{ Hz, 1 H} \)), 7.44 (t, \( J = 7.7 \text{ Hz, 2 H} \)), 6.77 (d, \( J = 8.4 \text{ Hz, 1 H} \)), 4.21 (q, \( J = 7.1 \text{ Hz, 2 H} \)), 1.15 (t, \( J = 7.1 \text{ Hz, 3 H} \)); \(^{13}\text{C NMR (100 MHz, CDCl\textsubscript{3})}: \delta 191.8, 184.5, 166.6, 151.7, 145.5, 142.0, 137.1, 134.1, 133.5, 128.8, 128.6, 121.9, 113.9, 108.8, 83.7, 61.7, 13.9. Anal. Calcd. for C\textsubscript{19}H\textsubscript{14}INO\textsubscript{4}: C, 51.03; H, 3.16; N, 3.13; Found: C, 50.88; H, 3.01; N, 2.98.

(Z)-ethyl 2-(5-methyl-3-oxoindolin-2-ylidene)-3-oxo-3-phenylpropanoate

Following the general procedure, using 20% ether in petroleum ether as the eluant afforded a red solid (64% yield). \(^{1}\text{H NMR (400 MHz, CDCl\textsubscript{3})}: \delta 9.19 (s, 1 H), 7.96 (d, \( J = 7.8 \text{ Hz, 2 H} \)), 7.56 (t, \( J = 7.4 \text{ Hz, 1 H} \)), 7.44 (t, \( J = 7.6 \text{ Hz, 2 H} \)), 7.31 – 7.29 (m, 2 H), 6.84 (d, \( J = 8.6 \text{ Hz, 1 H} \)), 4.21 (q, \( J = 7.1 \text{ Hz, 2 H} \)), 2.27 (s, 3 H), 1.16 (t, \( J = 7.1 \text{ Hz, 3 H} \)); \(^{13}\text{C NMR (100 MHz, CDCl\textsubscript{3})}: \delta 192.4, 186.2, 166.9, 150.6, 143.4, 138.4, 137.4, 133.3, 131.7, 128.8, 128.5, 125.5, 119.9, 111.6, 107.3, 61.5, 20.6, 14.0. Anal. Calcd. for C\textsubscript{20}H\textsubscript{17}NO\textsubscript{4}: C, 71.63; H, 5.11; N, 4.18; Found: C, 71.56; H, 5.15; N, 4.11.

(Z)-ethyl 2-(7-methyl-3-oxoindolin-2-ylidene)-3-oxo-3-phenylpropanoate

S18
Following the general procedure, using 20% ether in petroleum ether as the eluant afforded a red solid (50% yield). $^1$H NMR (400 MHz, CDCl$_3$): δ 9.20 (s, 1 H), 7.97 (d, $J = 7.8$ Hz, 2 H), 7.56 (t, $J = 7.4$ Hz, 1 H), 7.44 (t, $J = 7.7$ Hz, 2 H), 7.38 (d, $J = 7.6$ Hz, 1 H), 7.32 (d, $J = 7.4$ Hz, 1 H), 6.87 (t, $J = 7.5$ Hz, 1 H), 4.24 (q, $J = 7.1$ Hz, 2 H), 2.32 (s, 3 H), 1.18 (t, $J = 7.1$ Hz, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 192.2, 186.4, 167.0, 151.4, 143.2, 138.3, 133.3, 128.8, 128.5, 123.1, 121.9, 120.9, 119.5, 107.9, 61.6, 15.3, 14.0. Anal. Calcd. for C$_{20}$H$_{17}$NO$_4$: C, 71.63; H, 5.11; N, 4.18; Found: C, 71.45; H, 5.02; N, 4.15.

(Z)-ethyl 2-(5-methoxy-3-oxoindolin-2-ylidene)-3-oxo-3-phenylpropanoate

Following the general procedure, using 30% ether in petroleum ether as the eluant afforded a red solid (61% yield). $^1$H NMR (400 MHz, CDCl$_3$): δ 9.10 (s, 1 H), 7.97 (d, $J = 7.4$ Hz, 2 H), 7.56 (t, $J = 7.4$ Hz, 1 H), 7.44 (t, $J = 7.6$ Hz, 2 H), 7.10 (dd, $J = 8.6$ Hz, $J = 2.6$ Hz, 1 H), 7.00 (d, $J = 2.6$ Hz, 1 H), 6.50 (d, $J = 8.6$ Hz, 1 H), 4.24 (q, $J = 7.1$ Hz, 2 H), 2.32 (s, 3 H), 1.18 (t, $J = 7.1$ Hz, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 192.2, 186.4, 167.0, 151.4, 143.2, 138.3, 133.3, 128.8, 128.5, 123.1, 121.9, 120.9, 119.5, 107.9, 61.6, 15.3, 14.0. Anal. Calcd. for C$_{20}$H$_{17}$NO$_4$: C, 71.63; H, 5.11; N, 4.18; Found: C, 71.45; H, 5.02; N, 4.15.
Hz, 1 H), 6.87 (d, J = 8.6 Hz, 1 H), 4.22 (q, J = 7.1 Hz, 2 H), 3.73 (s, 3 H), 1.16 (t, J = 7.1 Hz, 3 H); $^{13}$C NMR (100 MHz, CDCl3): δ 192.4, 186.2, 166.8, 155.3, 147.2, 143.7, 137.4, 133.3, 128.8, 128.5, 125.8, 120.2, 112.8, 107.9, 107.6, 61.5, 55.9, 14.0. Anal. Calcd. for C$_{20}$H$_{17}$NO$_{5}$: C, 68.37; H, 4.88; N, 3.99; Found: C, 67.82; H, 4.84; N, 3.73.

(E)-methyl 2-cyano-2-(3-oxoindolin-2-ylidene)acetate

Following the general procedure, using 40% ether in petroleum ether as the eluant afforded a red solid (50% yield). $^1$H NMR (400 MHz, (CD$_3$)$_2$SO): δ 11.37 (s, 1 H), 7.67 – 7.61 (m, 2 H), 7.35 (d, J = 8.0 Hz, 1 H), 7.13 (t, J = 7.4 Hz, 1 H), 3.85 (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 185.1, 165.4, 151.9, 149.9, 138.4, 125.8, 123.9, 119.5, 115.0, 114.3, 75.8, 53.1. Anal. Calcd. for C$_{12}$H$_8$N$_2$O$_3$: C, 63.16; H, 3.53; N, 12.28; Found: C, 63.07; H, 3.62; N, 12.11.

(E)-2-(1,3-dioxo-1-phenylbutan-2-ylidene)indolin-3-one

Following the general procedure, but in the absence of Mn(OAc)$_2$. Using 20% ether in petroleum ether as the eluant afforded a red solid (45%
yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 10.34 (s, 1 H), 8.01 (d, $J = 7.4$ Hz, 2 H), 7.58 (t, $J = 7.4$ Hz, 1 H), 7.50 – 7.44 (m, 4 H), 6.97 – 6.94 (m, 2 H), 2.20 (s, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 198.3, 195.5, 187.8, 152.9, 141.3, 137.6, 137.5, 133.8, 128.9, 125.6, 122.6, 119.4, 113.9, 112.2, 29.3. Anal. Calcd. for C$_{18}$H$_{13}$NO$_3$: C, 74.22; H, 4.50; N, 4.81; Found: C, 73.88; H, 4.52; N, 4.67.

(E/Z)-ethyl 3-oxo-2-(3-oxoindolin-2-ylidene)butanoate

Following the general procedure, using 20% ether in petroleum ether as the eluant afforded a red solid (40% yield). $^1$H NMR [E/Z = 3.6:1] (400 MHz, CDCl$_3$): $\delta$ E: 10.23 (s, 1 H), 7.64 – 7.62 (m, 1 H), 7.51 – 7.47 (m, 1 H), 7.02 (t, $J = 7.4$ Hz, 1 H), 6.98 – 6.90 (m, 1 H), 4.44 (q, $J = 7.2$ Hz, 2 H), 2.35 (s, 3 H), 1.40 (t, $J = 7.2$ Hz, 3 H). Z: 9.04 (s, 1 H), 4.29 (q, $J = 7.1$ Hz, 2 H), 2.50 (s, 3 H), 1.32 (t, $J = 7.1$ Hz, 3 H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ E: 197.6, 187.2, 167.1, 152.3, 141.2, 137.5, 125.6, 122.7, 119.6, 112.1, 108.2, 62.2, 28.5, 13.8. Z: 199.8, 186.6, 166.1, 152.6, 141.3, 137.6, 125.6, 122.0, 119.8, 111.8, 110.6, 61.6, 31.3, 14.1. Anal. Calcd. for C$_{20}$H$_{17}$NO$_4$: C, 64.86; H, 5.05; N, 5.40; Found: C, 64.67; H, 5.08; N, 5.21.
Labeling experiments:

The $^{18}\text{O}$ was determined by HRMS. It should be noted that the labeling product undergoes partial oxygen exchange during the purification process. When the reaction was carried out in the presence of 10 equiv of $\text{H}_2\text{O}_{18}$, only normal $^{16}\text{O}$-product was detected.

The HRMS spectra of 3a for the reaction in the presence of $\text{H}_2\text{O}_{18}$.
The HRMS spectra of 3a for the reaction under $^{18}\text{O}_2$ (97%).
References


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\(^a\) \(R\) defined as \(\Sigma |F_o| - |F_c|/\Sigma |F_o|\) and \(R_w\) defined as \(\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4)^{1/2}\).
**Table S3. Bond lengths [Å] and angles [deg] for compound 3a**

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Table S4. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{
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Figure 1. ORTEP diagram of compound 3a (ellipsoids at 30% probability.)