Supporting Information

Rh-catalyzed C–H bond alkylation of indoles with α,α-difluorovinyl tosylate via indolyl group migration

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Table of Contents

General Information S2

Procedure for the synthesis of 1k, 1x and D1-1a S3

Unsuccessful substrates S6

General procedure for the Rh(III)-catalyzed alkylation reaction S6

Removal of the directing group S8

Mechanistic study S9

Characterization of products S15

References S28

1H and 13C NMR spectra for products S29
General Information

All reactions were carried out under nitrogen atmosphere unless otherwise stated. Reactions were monitored through thin layer chromatography. Flash chromatography was performed using silica gel with distilled solvents. HRMS spectra were recorded on a Waters Q-Tof Permier Spectrometer. $^1$H NMR and $^{13}$C NMR spectra were recorded using Bruker Avance 400 MHz spectrometers. Chemical shifts for $^1$H NMR spectra are reported as δ in units of parts per million (ppm) downfield from SiMe₄ (δ 0.0) and relative to the signal of SiMe₄ (δ 0.00, singlet). Multiplicities were given as: s (singlet), brs (broad singlet), d (doublet), t (triplet), q (quartet), dd (doublets of doublet), m (multiplets) and etc. Coupling constants are reported as a J value in Hz. Carbon nuclear magnetic resonance spectra ($^{13}$C NMR) are reported as δ in units of parts per million (ppm) downfield from CHCl₃ (δ 7.26) and relative to the signal of chloroform-d (δ 77.00, triplet). Unless otherwise noted, commercial reagents were used as received. Compounds 1a–1j, 1l–1w, 1y–1z,1-4 D₁-1a⁵ and 2⁶ were prepared according to literature methods.
**Procedure for synthesis of 1k**

To a solution of 5-nitro-1-(pyrimidin-2-yl)-1H-indole 1y (480 mg, 2 mmol, 1.0 equiv) in CH$_3$OH (10 mL) was added hydrazine hydrate (375 mg, 6 mmol, 3.0 equiv), Raney Ni (20 mg) at 0 °C, and the mixture was stirred for 2 h at room temperature. After the consumption of starting material, the mixture was filtered through celite and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 10 : 1 v/v) to give S1 (282 mg, 1.3 mmol) as a pale yellow oil in 67% yield.

A solution of S1 (244 mg, 1.2 mmol, 1.0 equiv), phthalicanhydride (151 mg, 1.0 mmol, 0.85 equiv) in glacial acetic acid (10 mL) was stirred at 120 °C for 2 h. After the mixture was cooled 30 mL of cold water was added, a white colour solid precipitated out. The precipitate was filtered, washed with cold water and dried under vacuum to afford 1k (245 mg, 0.72 mmol) as an off-white solid in 60% yield. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.96 (d, $J$ = 8.9 Hz, 1H), 8.73 (d, $J$ = 4.8 Hz, 2H), 8.36 (d, $J$ = 3.6 Hz, 1H), 7.99 (dd, $J$ = 5.4, 3.0 Hz, 2H), 7.81 (dd, $J$ = 5.4, 3.0 Hz, 2H), 7.67 (d, $J$ = 2.1 Hz, 1H), 7.37 (dd, $J$ = 8.9, 2.1 Hz, 1H), 7.10 (t, $J$ = 4.8 Hz, 1H), 6.76 (d, $J$ = 3.7 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 167.9, 158.2, 157.5, 134.7, 134.3, 131.9, 131.7, 126.9, 125.7, 123.7, 122.2, 119.3, 116.9, 116.5, 107.0; HRMS (ESI, m/z): calcd. for C$_{20}$H$_{13}$N$_4$O$_2$ [M+H$^+$]: 341.1039, found: 341.1036.
Procedure for the synthesis of 1x

To a solution of in 50 mL of CH₂Cl₂ was added 1H-indole-5-carboxylic acid (806 mg, 5.0 mmol, 1.0 equiv), DIPEA (4.5 mL, 25.0 mmol, 5.0 equiv) and pyrrolidine (3.8 mL, 50.0 mmol, 10.0 equiv). HBTU (280 mg, 7.5 mmol, 1.5 equiv) was added at 0 °C. The resulting mixture was stirred at room temperature for 18 h. The mixture was diluted with CH₂Cl₂ and washed with water. The organic layer was separated, dried over Na₂SO₄ and concentrated under reduced pressure. The crude residue was purified by column chromatography (eluent = petroleum ether/ethyl acetate = 10 : 1 v/v) to afford S₂ (900 mg, 4.2 mmol) as a pale yellow solid in 84% yield.

Following a procedure from Ackermann et al.,¹ to a stirred solution of S₂ (2.0 mmol, 1.0 equiv) in DMF (50 mL) was added NaH (88 mg, 2.2 mmol, 1.1 equiv) by portions at 0 °C. After stirring for 30 min at 0 °C, 2-chloropyrimidine (274 mg, 2.4 mmol, 1.2 equiv) was added and the mixture was heated to 130 °C and stirred for 24 h. Then the mixture was cooled to room temperature, poured into water and extracted with ethyl acetate. The combined organic phase was dried over Na₂SO₄, concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 10 : 1) to afford 1x (537 mg, 1.8 mmol) as a gray solid in 92% yield. ¹H NMR (400 MHz, CDCl₃): δ = 8.81 (dt, J = 8.6, 0.8 Hz, 1H), 8.71 (d, J = 4.8 Hz, 2H), 8.32 (d, J = 3.6 Hz, 1H), 7.82 (dd, J = 1.7, 0.7 Hz, 1H), 7.53
(dd, $J = 8.7$, 1.7 Hz, 1H), 7.08 (t, $J = 4.8$ Hz, 1H), 6.73 (dd, $J = 3.7$, 0.8 Hz, 1H), 3.70 (t, $J = 7.0$ Hz, 2H), 3.52 (t, $J = 6.6$ Hz, 2H), 2.03–1.93, (m, 2H), 1.91–1.83 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 170.5$, 158.2, 157.5, 135.9, 131.0, 130.8, 126.8, 122.9, 120.2, 116.5, 115.8, 107.1, 49.9, 46.3, 26.5, 24.5; HRMS (ESI, m/z): calcd. for C$_{17}$H$_{17}$N$_4$O [M+H]$^+$: 293.1402, found: 293.1405.

**Procedure for synthesis of D$_1$-2**

To a solution of 2,2,2-trifluoroethyl sulfonate (1.27 g, 5.0 mmol, 1.0 equiv) in THF (29 mL) at -78 °C was added dropwise 2.5 M n-BuLi in hexanes (4.6 mL, 11.5 mmol, 2.3 equiv). After stirring at -78°C for 1 h, the solution was quenched with a mixture of THF/D$_2$O (1:1, 5 mL) at -78 °C. Water (~10 mL) was added, and the organic phase was extracted with ethyl acetate, dried over Na$_2$SO$_4$, filtered, and evaporated. The crude product was purified by column chromatography on silica gel (eluent = petroleum ether / ethyl acetate v/v = 50:1) to give product (1.04 g, 4.4 mmol, 88%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.82$ (d, $J = 8.2$ Hz, 2H), 7.39 (d, $J = 7.9$ Hz, 2H), 2.48 (s, 3H). $^{19}$F NMR (396 MHz, CDCl$_3$): $\delta = -90.70$ (dt, $J = 51.2$, 2.2 Hz), -109.19 (d, $J = 51.2$ Hz). $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta = 156.9$ (ddt, $J = 294.7$, 284.5, 2.1 Hz), 146.1, 131.0, 130.0 , 128.3, 100.5 (dtd, $J = 59.5$, 31.2, 15.3 Hz), 21.6.
Unsuccessful substrates

General procedure for the Rh(III)-catalyzed alkylation reaction

To an oven-dried Schlenk tube was added RhCp*(CH₃CN)₃(SbF₆)₂ (2.1 mg, 0.0025 mmol, 2.5 mol %), substrate 1 (0.1 mmol, 1.0 equiv), gem-difluoroalkene 2 (28 mg, 0.12 mmol, 1.2 equiv) and CH₃OH (1 mL) and sealed with a teflon cap. After stirring at 70 °C for 12 h or more (monitored by TLC), the reaction mixture was cooled to room temperature and put through a celite plug. The filtrate was concentrated under reduced pressure and the residual mixture was purified by silica gel column chromatography (eluent = petroleum ether/ethyl acetate = 9:1 v/v) to afford the product 3.

Procedure for synthesis of 3b

[IrCp*Cl₂]₂(4.0 mg, 0.0050 mmol, 5 mol %), AgSbF₆ (7.0 mg, 0.02 mmol, 20 mol %), substrate 1b (21 mg, 0.1 mmol, 1 equiv), gem-difluoroalkene 2 (28 mg, 0.12 mmol, 1.2 equiv) and in CH₃OH (1 mL) were stirred at
100 °C for 12 h under N₂ in a closed Schlenk tube. The reaction mixture was cooled to room temperature and put through a celite plug. The solvent was removed under reduced pressure and the residual mixture was purified by silica gel column chromatography (eluent = petroleum ether/ethyl acetate = 9:1 v/v) to afford the product 3b (12 mg, 0.044 mmol) as a white solid in 44%.

Procedure for synthesis of 3x

RhCp*(CH₃CN)₃(SbF₆)₂ (2.1 mg, 0.0025 mmol, 2.5 mol %), substrate 1x (29 mg, 0.1 mmol, 1.0 equiv), gem-difluoroalkene 2 (28 mg, 0.12 mmol, 1.2 equiv) and CH₃OH (32 mg, 1.0 mmol, 10.0 equiv) in DCE (1 mL) were stirred at 70 °C for 12 h under air in a closed Schlenk tube. The reaction mixture was cooled to room temperature and put through a celite plug. The solvent was removed under reduced pressure and the residual mixture was purified by silica gel column chromatography (eluent = petroleum ether/ethyl acetate = 9:1 v/v) to afford the product 3x (34 mg, 0.094 mmol) in 94% yield.

Reaction of 1a on 4.0 mmol scale:

An oven-dried Schlenk tube was added 1a (781 mg, 4.0 mmol, 1.0 equiv), RhCp*(MeCN)₃(SbF₆)₂ (86 mg, 0.1 mmol, 0.025 equiv), 2 (112 mg, 4.8 mmol, 1.2 equiv) and solvent CH₃OH (40 mL). Then the tube was sealed with a teflon cap. After stirring at 70 °C for 12 h, the mixture was put through a celite plug. The solvent was removed in vacuo and the residual
mixture was purified by silica gel column chromatography (eluent = petroleum ether/ethyl acetate = 10:1 v/v) to afford the product 3a (786.9 mg, 2.94 mmol) in 74% yield.

**Removal of the directing group**

An oven-dried Schlenk tube was added 3a (781 mg, 0.2 mmol, 1.0 equiv), NaOEt (68 mg, 1.0 mmol, 5.0 equiv) and DMSO (1 mL). Then the tube was sealed with a teflon cap. After stirring at 80 °C for 19 h, the mixture was cooled to room temperature and then quenched with 2 M HCl (5 mL). The aqueous layer was extracted with Et₂O (5 × 5 mL) and the combined organic layers was dried over Na₂SO₄, filtered and concentrated under vacuum. The crude product was purified by silica gel column chromatography (eluent = dichloromethane/MeOH/acetic acid = 10:1:0.01 v/v/v) to afford the product 4 (22 mg, 0.13 mmol, 65%).

**¹H NMR (400 MHz, acetone-d₆):** δ = 10.15 (brs, 1H), 7.47 (d, J = 7.8 Hz, 1H), 7.37 (d, J = 8.1 Hz, 1H), 7.07-7.02 (m, 1H), 6.99-6.94 (m, 1H), 6.34 (s, 1H), 3.84 (s, 2H); **¹³C NMR (101 MHz, acetone-d₆) δ =** 172.4, 138.4, 133.7, 130.2, 122.5, 121.2, 120.6, 112.4, 102.7, 35.0.; **HRMS (ESI, m/z):** calcd. for C₁₀H₁₀NO₂ [M+H]⁺: 176.0712, found: 176.0707.
Mechanistic study

Deuterium labeled experiment

To an oven-dried Schlenk tube was added 1a (20 mg, 0.1 mmol, 1.0 equiv), RhCp*(MeCN)₃SbF₆ (2.1 mg, 0.0025 mmol, 0.025 equiv), D₂-2 (28 mg, 0.12 mmol, 1.2 equiv) and CH₃OH (1 mL) under air and the tube was sealed with a teflon cap. After stirring at 70 °C for 0.5 h, the mixture was put through a celite plug. The solvent was removed under reduced pressure and the crude residue was purified by silica gel column chromatography (eluent = petroleum ether/ethyl acetate = 10:1 v/v) to afford the product D₁-3a (1.4 mg, 0.005 mmol) in 5.2% yield.
Preparation of 1-(pyrimidin-2-yl)-2-(2,2,2-trifluoroethyl)-1H-indole

![Chemical Structures]

To an oven-dried Schlenk tube was added 1a (40 mg, 0.2 mmol, 1.0 equiv), RhCp*(MeCN)3(SbF6)2 (8.4 mg, 0.01 mmol, 0.05 equiv), 2 (28 mg, 0.24 mmol, 1.2 equiv) and DCE (1 mL) under air and the tube was sealed with a teflon cap. After stirring at 50 °C for 12 h, the mixture was put through a silica gel plug. The solvent was removed under reduced pressure and the crude residue was purified by silica gel column chromatography (eluent = petroleum ether/ethyl acetate = 10:1 v/v) to afford the product 5 (10 mg, 0.036 mmol) as a pale yellow oil in 18% yield. $^1$H NMR (400 MHz, CDCl3): $\delta = 8.81$ (d, $J = 4.8$ Hz, 2H), 8.34 (d, $J = 8.3$ Hz, 1H), 7.60 (d, $J = 7.7$ Hz, 1H), 7.30 (ddd, $J = 8.5$, 7.1, 1.4 Hz, 1H), 7.26-7.20 (m, 1H), 7.19 (t, $J = 4.8$ Hz, 1H), 6.76 (s, 1H), 4.30 (q, $J = 10.4$ Hz, 2H); $^{19}$F NMR (376 MHz, CDCl3) $\delta = -65.02$ (t, $J = 10.5$ Hz); $^{13}$C NMR (101 MHz, CDCl3): $\delta = 158.2$, 158.1, 137.2, 129.1 (q, $J = 3.5$ Hz), 128.5, 125.3 (q, $J = 277.4$ Hz), 123.8, 122.2, 120.4, 117.4, 114.2, 110.2, 33.9 (q, $J = 31.0$ Hz). All the data is in accordance with the literature values.7

Investigation of the intermediacy of 6

Procedure for the synthesis of 6
Following a procedure from Ackermann et al.,\textsuperscript{1-4} to a stirred solution of 1-(pyrimidin-2-yl)-1H-indole-2-carbaldehyde (1.60 g, 11.0 mmol, 1.0 equiv) in DMF (50 mL) was added NaH (484 mg, 12.1 mmol, 1.1 equiv) by portions at 0 °C. After stirring for 30 min at 0 °C, 2-chloropyrimidine (1.37 g, 12 mmol, 1.2 equiv) was added and the mixture was heated to 130 °C and stirred for 24 h. Then the mixture was cooled to room temperature, poured into water and extracted with ethyl acetate. The combined organic phase was dried over Na\textsubscript{2}SO\textsubscript{4}, concentrated under reduced pressure. The crude residue was purified by column chromatography on silica gel (eluent = petroleum ether/ethyl acetate = 10:1 v/v) to afford S3 (490 mg, 2.2 mmol) as a gray solid in 20% yield. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \( \delta = 10.39 \, (s, \, 1H)\), 8.83 (d, \( J = 4.8 \) Hz, 2H), 8.54 (dd, \( J = 8.6, 0.9 \) Hz, 1H), 7.76 (dt, \( J = 7.9, 1.0 \) Hz, 1H), 7.54-7.46 (m, 2H), 7.32 (ddd, \( J = 8.0, 7.1, 0.9 \) Hz, 1H), 7.24 (t, \( J = 4.8 \) Hz, 1H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}): \( \delta = 183.6, 158.3, 157.4, 138.3, 137.6, 127.7, 127.5, 123.2, 123.1, 117.5, 115.5, 115.3. \) HRMS (ESI, m/z): calcd. for C\textsubscript{13}H\textsubscript{10}N\textsubscript{3}O [M+H]\textsuperscript{+}: 224.0824, found: 224.0821. A solution of S3 (223 mg, 1.0 mmol, 1.0 equiv) and PPh\textsubscript{3} (524 mg, 2.0 mmol, 2.0 equiv) in DMF (5 mL) was heated to 100 °C. To the reaction mixture at 100 °C was added F\textsubscript{2}ClCOCONA (305 mg, 2.0 mmol, 2.0 equiv) slowly. After the reaction finished according to the TLC (about 3 min), the reaction mixture was cooled to room temperature, quenched with water and extracted with ethyl acetate. The combined organic layers were washed with H\textsubscript{2}O\textsubscript{2} (30 wt% in water, 5 mL), brine and dried over Na\textsubscript{2}SO\textsubscript{4}. After solvent was removed under reduced pressure, the residual mixture was purified by silica gel column chromatography (eluent = petroleum ether/ethyl acetate = 10:1 v/v) to afford 6 (62 mg, 0.24 mmol) as a pale yellow solid in 24% yield. \textsuperscript{1}H NMR
(400 MHz, CDCl₃): δ = 8.83 (d, J = 4.8 Hz, 2H), 8.28 (dt, J = 8.3, 0.9 Hz, 1H), 7.62 – 7.57 (m, 1H), 7.28 (dd, J = 7.1, 1.4 Hz, 1H), 7.24 (dd, J = 4.5, 1.5 Hz, 1H), 7.21 (d, J = 4.8 Hz, 1H), 6.86 (d, J = 2.5 Hz, 1H), 6.35 (dd, J = 25.2, 3.0 Hz, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ = -79.96 (t, J = 24.0 Hz), -83.14 (d, J = 23.2 Hz); ¹³C NMR (101 MHz, CDCl₃): δ = 158.2, 157.7, 156.5 (dd, J = 297.7, 286.1 Hz), 136.4, 129.2, 128.9 (dd, J = 10.0, 7.9 Hz), 123.5, 122.3, 120.2, 117.3, 114.0, 107.7(d, J = 9.9 Hz), 75.7(dd, J = 36.8, 12.2 Hz).

HRMS (ESI, m/z): calcd. for C₁₄H₁₀F₂N₃ [M+H]^+: 258.0843, found: 258.0846.

Procedure for the control reaction with 5

To an oven-dried Schlenk tube was added RhCp*(CH₃CN)₃(SbF₆)₂ (2.1 mg, 0.0025 mol, 2.5 mol%), gem-difluoroalkene 6 (25.7 mg, 0.1 mmol, 1.0 equiv) and CH₃OH (1 mL) and sealed with a teflon cap. After stirring at 70 °C for 4.5 h, the mixture was put through a celite plug. The solvent was removed under reduced pressure and the residual mixture was purified by silica gel column chromatography (eluent = petroleum ether/ethyl acetate = 9:1 v/v) to afford the product 3a (2.0 mg, 0.08 mmol) as a white solid in 8% yield.
**Kinetic isotope effect study**

To an oven-dried Schlenk tube was added 1a or D$_1$-1a (0.1 mmol, 1.0 equiv), RhCp*(MeCN)$_3$(SbF$_6$)$_2$ (2.1 mg, 0.0025 mmol, 0.025 equiv), 2 (28 mg, 0.12 mmol, 1.2 equiv) and CH$_3$OH (1 mL) under air and the tube was sealed with a teflon cap. The reaction mixtures were stirred side-by-side in a preheated oil bath at 70 °C for 30 min. Then the mixture were put through a celite plug and concentrated under reduced pressure separately. The crude residue were purified by silica gel column chromatography (eluent = petroleum ether/ethyl acetate = 10:1 v/v) to afford the product 3a (2.3 mg from 1a, 2.3 mg from D$_1$-1a).

**Intermolecular competition experiments**

To an oven-dried Schlenk tube was added 1h (22.5 mg, 0.1 mmol, 1.0 equiv), 1v (25.3 mg, 0.1 mmol, 1.0 equiv), RhCp*(MeCN)$_3$(SbF$_6$)$_2$ (2.1 mg, 0.0025 mmol, 0.025 equiv), 2 (28 mg, 0.12 mmol, 1.2 equiv) and CH$_3$OH (1 mL) under air and the tube was sealed with a teflon cap. The reaction
mixtures were stirred side-by-side in a preheated oil bath at 70 °C for 12 h. Then the mixture were put through a celite plug and concentrated under reduced pressure separately. The crude residue were purified by silica gel column chromatography (eluent = petroleum ether/ethyl acetate = 10:1 v/v) to afford the product 3h (15.4 mg, 0.05 mmol, 52%) and 3v (8.8 mg, 0.03 mmol, 27%).
Characterization of products

Methyl 2-(1-(pyrimidin-2-yl)-1H-indol-2-yl)acetate 3a

Following the general procedure, 3a was obtained as a white solid (25 mg, 0.095 mmol, 95%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.70 (d, $J$ = 4.8 Hz, 2H), 8.58 (d, $J$ = 8.3 Hz, 1H), 7.57 (d, $J$ = 7.6 Hz, 1H), 7.34-7.27 (m, 1H), 7.25-7.19 (m, 1H), 7.09 (t, $J$ = 4.8 Hz, 1H), 6.60 (s, 1H), 4.18 (s, 2H), 3.62 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 171.1, 158.0, 157.6, 136.7, 133.2, 128.9, 123.3, 122.0, 120.0, 116.5, 115.31, 109.6, 51.8, 36.9; HRMS (ESI, m/z): calcd. for C$_{15}$H$_{14}$N$_3$O$_2$ [M+H]$^+$: 268.1086, found: 268.1087. The spectral data were in accordance with those reported in the literature.$^8$

Ethyl 2-(1-(pyrimidin-2-yl)-1H-indol-2-yl)acetate 3a’

Following the general procedure, 3a’ was obtained as a colorless oil (22 mg, 0.078 mmol, 78%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.70 (d, $J$ = 4.8 Hz, 2H), 8.57 (d, $J$ = 8.4 Hz, 1H), 7.57 (dd, $J$ = 7.6, 1.2 Hz, 1H), 7.33-7.27 (m, 1H), 7.25-7.19 (m, 1H), 7.08 (t, $J$ = 4.8 Hz, 1H), 6.60 (s, 1H), 4.20 (s, 2H), 4.09 (q, $J$ = 7.1 Hz, 2H), 1.13 (t, $J$ = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 170.7, 158.2, 157.7, 136.8, 133.5, 129.0, 123.3, 122.0, 120.1, 116.5, 115.3, 109.6, 60.5, 37.1, 14.1; HRMS (ESI, m/z): calcd. for C$_{16}$H$_{16}$N$_3$O$_2$ [M+H]$^+$: 282.1243, found: 282.1247.
Isopropyl 2-(1-(pyrimidin-2-yl)-1H-indol-2-yl)acetate 3a”

Following the general procedure, 3a” was obtained as a colorless oil (17 mg, 0.058 mmol, 58%). $^1\text{H} \text{NMR (400 MHz, CDCl}_3\text{): } \delta = 8.71 (d, J = 4.8 \text{ Hz, 2H}), 8.56 (d, J = 8.3 \text{ Hz, 1H}), 7.56 (dt, J = 7.5, 1.1 \text{ Hz, 1H}), 7.29 (td, J = 7.4, 1.1Hz, 1H), 7.22 (td, J = 7.4, 1.1 Hz, 1H), 7.08 (t, J = 4.8 Hz, 1H), 6.62-6.56 (m, 1H), 4.96 (hept, J = 6.2 Hz, 1H), 4.18 (s, 2H), 1.12 (d, J = 6.3 Hz, 6H); $^{13}\text{C NMR (100 MHz, CDCl}_3\text{): } \delta = 170.3, 158.3, 157.7, 136.8, 133.6, 129.0, 123.2, 122.0, 120.1, 116.5, 115.3, 109.6, 67.9, 37.4, 21.7; \text{ HRMS (ESI, m/z): } \text{calcd. for C}_{17}\text{H}_{18}\text{N}_3\text{O}_2 [M+H]^+: 296.1399, \text{ found: 296.1399.}$

Methyl 2-(3-methyl-1-(pyrimidin-2-yl)-1H-indol-2-yl)acetate 3b

3b was obtained as a colorless oil (12 mg, 0.044 mmol, 44%). $^1\text{H} \text{NMR (400 MHz, CDCl}_3\text{): } \delta = 8.68 (d, J = 4.8 \text{ Hz, 2H}), 8.55 (d, J = 8.2 \text{ Hz, 1H}), 7.55 (dd, J = 7.5, 1.4 \text{ Hz, 1H}), 7.34-7.27 (m, 1H), 7.26 – 7.22 (m, 1H), 7.05 (t, J = 4.8 \text{ Hz, 1H}), 4.14 (s, 2H), 3.63 (s, 3H), 2.32 (s, 3H); $^{13}\text{C NMR (100 MHz, CDCl}_3\text{): } \delta = 171.4, 158.2, 157.7, 136.0, 130.3, 128.9, 123.6, 121.8, 118.3, 116.2, 115.9, 115.0, 51.9, 33.9, 8.9; \text{ HRMS (ESI, m/z): } \text{calcd. for C}_{16}\text{H}_{16}\text{N}_3\text{O}_2 [M+H]^+: 282.1243, \text{ found: 282.1242.}$ The spectral data were in accordance with those reported in the literature.8

Methyl 2-(4-methyl-1-(pyrimidin-2-yl)-1H-indol-2-yl)acetate 3c

Following the general procedure, 3c was obtained as a white solid (23 mg, 0.082 mmol, 82%). $^1\text{H} \text{NMR (400 MHz, CDCl}_3\text{): } \delta = 8.70 (d, J = 4.8 \text{ Hz, 2H}), 8.41 (d, J = 8.4 \text{ Hz, 1H}), 7.20 (dd, J = 8.5, 7.2 Hz, 1H), 7.08 (t, J = 4.8 \text{ Hz,
1H), 7.03 (d, J = 7.2 Hz, 1H), 6.64 (s, 1H), 4.19 (s, 2H), 3.62 (s, 3H), 2.55 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 171.3, 158.2, 157.7, 136.6, 132.7, 129.4, 128.6, 123.5, 122.5, 116.5, 112.9, 108.2, 51.9, 37.1, 18.5; HRMS (ESI, m/z): calcd. for C$_{16}$H$_{16}$N$_3$O$_2$ [M+H]$^+$: 282.1243, found: 282.1241.

Methyl 2-(5-methyl-1-(pyrimidin-2-yl)-1H-indol-2-yl)acetate 3d

Following the general procedure, 3d was obtained as a white solid (26 mg, 0.092 mmol, 92%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.69 (d, $J$ = 4.8 Hz, 2H), 8.50 (d, $J$ = 8.6 Hz, 1H), 7.40-7.36 (m, 1H), 7.14 (dd, $J$ = 8.6, 1.7 Hz, 1H), 7.06 (t, $J$ = 4.8 Hz, 1H), 6.55 (s, 1H), 4.19 (s, 2H), 3.65 (s, 3H), 2.48 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 171.3, 158.1, 157.6, 135.0, 133.3, 131.4, 129.2, 124.7, 119.9, 116.2, 115.2, 109.5, 51.8, 37.1, 21.2; HRMS (ESI, m/z): calcd. for C$_{16}$H$_{16}$N$_3$O$_2$ [M+H]$^+$: 282.1243, found: 282.1242. The spectral data were in accordance with those reported in the literature.$^8$

Methyl 2-(6-methyl-1-(pyrimidin-2-yl)-1H-indol-2-yl)acetate 3e

Following the general procedure, 3e was obtained as a white solid (23 mg, 0.083 mmol, 83%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.71 (d, $J$ = 4.8 Hz, 2H), 8.38 (s, 1H), 7.44 (d, $J$ = 7.9 Hz, 1H), 7.08 (t, $J$ = 4.8, 1H), 7.06 (d, $J$ = 7.9 Hz, 1H) 6.55 (s, 1H), 4.16 (s, 2H), 3.61 (s, 3H), 2.51 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 171.3, 158.2, 157.7, 137.1, 133.2, 132.7, 126.7, 123.6, 119.7, 116.4, 115.3, 109.6, 51.8, 37.0, 22.1; HRMS (ESI, m/z): calcd. for C$_{16}$H$_{16}$N$_3$O$_2$ [M+H]$^+$: 282.1243, found: 282.1241. The spectral data were in accordance with those reported in the literature.$^8$
Methyl 2-(7-methyl-1-(pyrimidin-2-yl)-1H-indol-2-yl)acetate 3f

Following the general procedure, 3f was obtained as a white solid (11 mg, 0.039 mmol, 39%). ¹H NMR (400 MHz, CDCl₃): δ = 8.82 (d, J = 4.8 Hz, 2H), 7.45 (d, J = 7.7 Hz, 1H), 7.26 (t, J = 4.8 Hz, 1H), 7.11 (t, J = 7.5 Hz, 1H), 7.02 (d, J = 7.2 Hz, 1H), 6.59 (s, 1H), 3.94 (s, 2H), 3.52 (s, 3H), 2.06 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 170.5, 158.3, 158.2, 136.5, 133.6, 129.4, 126.0, 122.5, 121.7, 118.5, 118.3, 107.3, 52.0, 34.4, 20.7.; HRMS (ESI, m/z): calcd. for C₁₆H₁₆N₃O₂ [M+H]⁺: 282.1243, found: 282.1242. The spectral data were in accordance with those reported in the literature.⁸

Methyl 2-(4-methoxy-1-(pyrimidin-2-yl)-1H-indol-2-yl)acetate 3g

Following the general procedure, 3g was obtained as a white solid (24 mg, 0.082 mmol, 82%). ¹H NMR (400 MHz, CDCl₃): δ = 8.70 (d, J = 4.8 Hz, 2H), 8.16 (d, J = 8.4 Hz, 1H), 7.22 (t, J = 8.2 Hz, 1H), 7.09 (t, J = 4.8 Hz, 1H), 6.72 (s, 1H), 6.66 (d, J = 7.9 Hz, 1H), 4.16 (s, 2H), 3.95 (s, 3H), 3.60 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 171.3, 158.2, 157.7, 152.5, 138.1, 131.8, 124.1, 119.4, 116.6, 108.6, 106.6, 102.4, 55.4, 51.9, 37.0.; HRMS (ESI, m/z): calcd. for C₁₆H₁₆N₃O₃ [M+H]⁺: 298.1192, found: 298.1192. The spectral data were in accordance with those reported in the literature.⁸

Methyl 2-(5-methoxy-1-(pyrimidin-2-yl)-1H-indol-2-yl)acetate 3h

Following the general procedure, 3h was obtained as a white solid (21 mg, 0.07 mmol, 70%). ¹H NMR (400 MHz, CDCl₃): δ = 8.66 (d, J = 4.8 Hz, 2H), 8.52 (d, J = 9.1 Hz, 1H), 7.04 (t, J = 4.8 Hz, 1H), 7.03 (d, J = 2.6 Hz, 1H), 6.92 (dd, J = 9.1 Hz, 1H), 6.67 (t, J = 7.7 Hz, 1H), 6.57 (d, J = 8.4 Hz, 1H), 5.95 (s, 1H), 4.16 (s, 2H), 3.95 (s, 3H), 3.60 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 171.3, 158.2, 157.7, 152.5, 138.1, 131.8, 124.1, 119.4, 116.6, 108.6, 106.6, 102.4, 55.4, 51.9, 37.0.; HRMS (ESI, m/z): calcd. for C₁₆H₁₆N₃O₃ [M+H]⁺: 298.1192, found: 298.1192. The spectral data were in accordance with those reported in the literature.⁸
9.1, 2.7 Hz, 1H), 6.53 (s, 1H), 4.16 (s, 2H), 3.87 (s, 3H), 3.62 (s, 3H); \(^{13}\text{C NMR (100 MHz, CDCl}\text{)}_3\): \(\delta = 171.3, 158.1, 157.7, 155.5, 134.0, 131.7, 129.8, 116.6, 116.3, 112.4, 109.8, 102.5, 55.7, 51.9, 37.3;\) HRMS (ESI, m/z): calcd. for \(\text{C}_{16}\text{H}_{16}\text{N}_3\text{O}_3 [\text{M+H}]^+\): 298.1192, found: 298.1192. The spectral data were in accordance with those reported in the literature.\(^8\)

**Methyl 2-(6-methoxy-1-(pyrimidin-2-yl)-1H-indol-2-yl)acetate 3i**

Following the general procedure, 3i was obtained as a white solid (23 mg, 0.077 mmol, 77%). \(^1\text{H NMR (400 MHz, CDCl}\text{)}_3\): \(\delta = 8.70 (d, J = 4.8 \text{ Hz}, 2\text{H}), 8.23 (d, J = 2.3 \text{ Hz}, 1\text{H}), 7.43 (d, J = 8.5 \text{ Hz}, 1\text{H}), 7.08 (t, J = 4.8 \text{ Hz}, 1\text{H}), 6.88 (dd, J = 8.5, 2.4 \text{ Hz}, 1\text{H}), 6.52 (s, 1\text{H}), 4.14 (s, 2\text{H}), 3.89 (s, 3\text{H}), 3.61 (s, 3\text{H}); \(^{13}\text{C NMR (100 MHz, CDCl}\text{)}_3\): \(\delta = 171.4, 158.2, 157.6, 157.1, 137.6, 132.2, 123.0, 120.4, 116.4, 110.9, 109.6, 100.3, 55.7, 51.8, 37.1;\) HRMS (ESI, m/z): calcd. for \(\text{C}_{16}\text{H}_{16}\text{N}_3\text{O}_3 [\text{M+H}]^+\): 298.1192, found: 298.1189. The spectral data were in accordance with those reported in the literature.\(^8\)

**Methyl 2-(4-(benzyloxy)-1-(pyrimidin-2-yl)-1H-indol-2-yl)acetate 3j**

Following the general procedure, 3j was obtained as a white solid (25 mg, 0.067 mmol, 67%). \(^1\text{H NMR (400 MHz, CDCl}\text{)}_3\): \(\delta = 8.70 (d, J = 4.8 \text{ Hz}, 2\text{H}), 8.18 (d, J = 8.5 \text{ Hz}, 1\text{H}), 7.55-7.46 (m, 2\text{H}), 7.45-7.37 (m, 2\text{H}), 7.37-7.29 (m, 1\text{H}), 7.20 (t, J = 8.2 \text{ Hz}, 1\text{H}), 7.09 (t, J = 4.8 \text{ Hz}, 1\text{H}), 6.80 (s, 1\text{H}), 6.72 (d, J = 7.9 \text{ Hz}, 1\text{H}), 5.22 (s, 2\text{H}), 4.17 (s, 2\text{H}), 3.61 (s, 3\text{H}); \(^{13}\text{C NMR (100 MHz, CDCl}\text{)}_3\): \(\delta = 171.3, 158.2, 157.7, 151.6, 138.2, 137.4, 131.9, 128.5, 127.8, 127.3, 124.1, 119.8, 116.6, 108.9, 106.9, 103.9, 70.0, 51.9, 37.0;\)
HRMS (ESI, m/z): calcd. for C_{22}H_{20}N_{3}O_{3} [M+H]^+: 374.1505, found: 374.1500.

Methyl 2-(5-(1,3-dioxoisindolin-2-yl)-1-(pyrimidin-2-yl)-1H-indol-2-yl)acetate 3k

Following the general procedure, 3k was obtained as a white solid (30 mg, 0.072 mmol, 72%). \(^1\)H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta = 8.83-8.65\) (m, 3H), 7.96 (dd, \(J = 5.4, 3.1\) Hz, 2H), 7.78 (dd, \(J = 5.5, 3.1\) Hz, 2H), 7.60 (d, \(J = 2.2\) Hz, 1H), 7.31 (dd, \(J = 8.9, 2.1\) Hz, 1H), 7.12 (t, \(J = 4.8\) Hz, 1H), 6.65 (s, 1H), 4.20 (s, 2H), 3.62 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta = 171.0, 167.8, 158.0, 157.8, 136.2, 134.7, 134.2, 131.9, 129.3, 125.8, 123.6, 122.0, 118.6, 116.9, 116.1, 109.8, 51.9, 37.1.

HRMS (ESI, m/z): calcd. for C_{23}H_{17}N_{4}O_{4} [M+H]^+: 413.1250, found: 413.1246.

Methyl 2-(4-phenyl-1-(pyrimidin-2-yl)-1H-indol-2-yl)acetate 3l

Following the general procedure, 3l was obtained as a white solid (30 mg, 0.087 mmol, 87%). \(^1\)H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta = 8.72\) (d, \(J = 4.8\) Hz, 2H), 8.59 (d, \(J = 8.4\), Hz, 1H), 7.70 – 7.63 (m, 2H), 7.52-7.46 (m, 2H), 7.42 – 7.35 (m, 2H), 7.30 (dd, \(J = 7.4, 1.0\) Hz, 1H), 7.11 (t, \(J = 4.8\) Hz, 1H), 6.78 (s, 1H), 4.18 (s, 2H), 3.62 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta = 171.2, 158.1, 157.7, 140.7, 137.2, 134.0, 133.6, 128.9, 128.4, 127.2, 127.0, 123.7, 122.2, 116.7, 114.3, 109.0, 51.9, 37.0; HRMS (ESI, m/z): calcd. for C_{21}H_{18}N_{3}O_{2} [M+H]^+: 344.1399, found: 344.1395.
Methyl 2-(5-phenyl-1-(pyrimidin-2-yl)-1H-indol-2-yl)acetate 3m

Following the general procedure, 3m was obtained as a white solid (24 mg, 0.069 mmol, 69%). ¹H NMR (400 MHz, CDCl₃): δ = 8.72 (d, J = 4.8 Hz, 2H), 8.65 (d, J = 8.7 Hz, 1H), 7.78 (d, J = 1.9 Hz, 1H), 7.71 – 7.64 (m, 2H), 7.55 (dd, J = 8.8, 1.9 Hz, 1H), 7.46 (t, J = 7.7 Hz, 2H), 7.38 – 7.30 (m, 1H), 7.10 (t, J = 4.8 Hz, 1H), 6.66 (s, 1H), 4.21 (s, 2H), 3.63 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 171.2, 158.1, 157.7, 141.9, 136.3, 135.4, 134.1, 129.5, 128.7, 127.3, 126.6, 123.0, 118.6, 116.6, 115.7, 110.0, 51.9, 37.2; HRMS (ESI, m/z): calcd. for C₂₁H₁₈N₃O₂ [M+H]⁺: 344.1399, found: 344.1397.

Methyl 2-(5-fluoro-1-(pyrimidin-2-yl)-1H-indol-2-yl)acetate 3n

Following the general procedure, 3n was obtained as a white solid (28 mg, 0.098 mmol, 98%). ¹H NMR (400 MHz, CDCl₃): δ = 8.69 (d, J = 4.8 Hz, 2H), 8.56 (dd, J = 9.2, 4.7 Hz, 1H), 7.20 (dd, J = 8.9, 2.6 Hz, 1H), 7.09 (t, J = 4.8 Hz, 1H), 7.01 (td, J = 9.2, 2.7 Hz, 1H), 6.55 (s, 1H), 4.17 (s, 2H), 3.63 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 171.0, 159.0 (d, J = 220.8 Hz), 157.8, 157.7, 135.0, 133.2, 129.7 (d, J = 10.2 Hz), 116.7, 116.6 (d, J = 8.9 Hz), 111.08 (d, J = 24.8 Hz), 109.5 (d, J = 4.0 Hz), 105.3 (d, J = 23.5 Hz), 51.9, 37.1; HRMS (ESI, m/z): calcd. for C₁₅H₁₃FN₃O₂ [M+H]⁺: 286.0992, found: 286.0992.

The spectral data were in accordance with those reported in the literature.⁸

Methyl 2-(6-fluoro-1-(pyrimidin-2-yl)-1H-indol-2-yl)acetate 3o

Following the general procedure, 3o was obtained as a white solid (28 mg, 0.097 mmol, 97%). ¹H NMR
(400 MHz, CDCl$_3$): $\delta = 8.69$ (d, $J = 4.8$ Hz, 2H), 8.38 (dd, $J = 11.3$, 2.4 Hz, 1H), 7.46 (dd, $J = 8.5$, 5.6 Hz, 1H), 7.09 (t, $J = 4.8$ Hz, 1H), 6.98 (td, $J = 8.9$, 2.4 Hz, 1H), 6.56 (s, 1H), 4.16 (s, 2H), 3.63 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 171.2, 160.4 (d, $J = 237.6$ Hz), 158.0, 157.7, 136.8 (d, $J = 13.1$ Hz), 133.8 (d, $J = 4.0$ Hz), 125.3, 120.5 (d, $J = 9.9$ Hz), 116.7, 110.4 (d, $J = 24.3$ Hz), 109.5, 102.9 (d, $J = 29.3$ Hz), 51.9, 37.1; HRMS (ESI, m/z): calcd. for C$_{15}$H$_{13}$FN$_3$O$_2$ [M+H]$^+$: 286.0992, found: 286.0998.

Methyl 2-(4-chloro-1-(pyrimidin-2-yl)-1H-indol-2-yl)acetate 3p

Following the general procedure, 3p was obtained as a white solid (25 mg, 0.084 mmol, 84%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.72$ (d, $J = 4.8$ Hz, 2H), 8.58 – 8.39 (m, 1H), 7.25 – 7.17 (m, 2H), 6.73 (s, 1H), 7.13 (t, $J = 4.8$ Hz, 1H), 4.20 (s, 2H), 3.62 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 170.9, 157.9, 157.8, 137.4, 134.1, 127.7, 125.3, 124.0, 121.9, 117.0, 114.0, 107.8, 52.0, 37.0; HRMS (ESI, m/z): calcd. for C$_{15}$H$_{13}$ClN$_3$O$_2$ [M+H]$^+$: 302.0696, found: 302.0697.

Methyl 2-(5-chloro-1-(pyrimidin-2-yl)-1H-indol-2-yl)acetate 3q

Following the general procedure, 3q was obtained as a white solid (22 mg, 0.074 mmol, 74%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.69$ (d, $J = 4.8$ Hz, 2H), 8.52 (d, $J = 8.9$ Hz, 1H), 7.52 (d, $J = 2.2$ Hz, 1H), 7.23 (dd, $J = 8.9$, 2.2 Hz, 1H), 7.10 (t, $J = 4.8$ Hz, 1H), 6.53 (s, 1H), 4.17 (s, 2H), 3.62 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 171.0, 157.9, 157.7, 135.1, 134.8, 130.1, 127.6, 123.4, 119.5, 116.8, 116.7, 109.0, 51.9, 37.0; HRMS (ESI, m/z): calcd. for C$_{15}$H$_{13}$ClN$_3$O$_2$
[M+H]⁺: 302.0696, found: 302.0697. The spectral data were in accordance with those reported in the literature.⁸

**Methyl 2-(4-bromo-1-(pyrimidin-2-yl)-1H-indol-2-yl)acetate 3r**

Following the general procedure, 3r was obtained as a white solid (23 mg, 0.067 mmol, 67%). ¹H NMR (400 MHz, CDCl₃): δ = 8.73 (d, J = 4.8 Hz, 2H), 8.53 (d, J = 8.3 Hz, 1H), 7.39 (dd, J = 7.7, 0.8 Hz, 1H), 7.17 (d, J = 8.2 Hz, 1H), 7.14 (t, J = 4.8 Hz, 1H), 6.69 (s, 1H), 4.21 (s, 2H), 3.63 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 170.9, 158.0, 157.8, 137.1, 134.1, 129.5, 125.0, 124.3, 117.1, 114.5, 113.9, 109.5, 52.0, 37.0; HRMS (ESI, m/z): calcd. for C₁₅H₁₃BrN₃O₂ [M+H]⁺: 346.0191, found: 346.0193.

**Methyl 2-(5-bromo-1-(pyrimidin-2-yl)-1H-indol-2-yl)acetate 3s**

Following the general procedure, 3s was obtained as a white solid (28 mg, 0.082 mmol, 82%). ¹H NMR (400 MHz, CDCl₃): δ = 8.69 (d, J = 4.8 Hz, 2H), 8.47 (d, J = 8.9 Hz, 1H), 7.67 (d, J = 2.1 Hz, 1H), 7.36 (dd, J = 8.9, 2.1 Hz, 1H), 7.10 (t, J = 4.8 Hz, 1H), 6.52 (s, 1H), 4.17 (s, 2H), 3.62 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 171.0, 157.8, 157.7, 135.5, 134.6, 130.7, 126.1, 122.6, 117.1, 116.9, 115.3, 108.9, 52.0, 37.0; HRMS (ESI, m/z): calcd. for C₁₅H₁₃BrN₃O₂ [M+H]⁺: 346.0191, found: 346.0190. The spectral data were in accordance with those reported in the literature.⁸

**Methyl 2-(6-bromo-1-(pyrimidin-2-yl)-1H-indol-2-yl)acetate 3t**

Following the general procedure, 3t was obtained as a white solid (30 mg, 0.086 mmol, 86%). ¹H NMR
(400 MHz, CDCl₃): δ = 8.80 (d, J = 1.7 Hz, 1H), 8.70 (d, J = 4.8 Hz, 2H), 7.41 (d, J = 8.3 Hz, 1H), 7.33 (dd, J = 8.3, 1.8 Hz, 1H), 7.11 (t, J = 4.8 Hz, 1H), 6.56 (s, 1H), 4.16 (s, 2H), 3.62 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 171.0, 157.80, 157.78, 137.4, 134.0, 127.8, 125.3, 118.5, 118.1, 117.0, 116.9, 109.5, 51.9, 37.0; HRMS (ESI, m/z): calcd. for C₁₅H₁₃BrN₃O₂ [M+H]⁺: 346.0191, found: 346.0188.

Methyl 2-(5-ido-1-(pyrimidin-2-yl)-1H-indol-2-yl)acetate 3u

Following the general procedure, 3u was obtained as a white solid (31 mg, 0.079 mmol, 79%). ¹H NMR (400 MHz, CDCl₃): δ = 8.69 (d, J = 4.8 Hz, 2H), 8.36 (d, J = 8.9 Hz, 1H), 7.88 (d, J = 1.8 Hz, 1H), 7.53 (dd, J = 8.8, 1.8 Hz, 1H), 7.10 (t, J = 4.8 Hz, 1H), 6.51 (d, J = 0.8 Hz, 1H), 4.17 (s, 2H), 3.62 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 171.0, 157.9, 157.8, 136.0, 134.3, 131.7, 131.3, 128.8, 117.5, 116.9, 108.7, 86.0, 51.9, 36.9; HRMS (ESI, m/z): calcd. for C₁₅H₁₃IN₃O₂ [M+H]⁺: 394.0052, found: 394.0050.

Methyl 2-(2-methoxy-2-oxoethyl)-1-(pyrimidin-2-yl)-1H-indole-4-carboxylate 3v

Following the general procedure, 3v was obtained as a white solid (26 mg, 0.081 mmol, 81%). ¹H NMR (400 MHz, CDCl₃): δ = 8.79 (d, J = 8.3 Hz, 1H), 8.72 (d, J = 4.7 Hz, 2H), 7.97 (d, J = 7.5 Hz, 1H), 7.33 (t, J = 8.0 Hz, 1H), 7.31 (s, 1H), 7.13 (t, J = 4.7 Hz, 1H), 4.23 (s, 2H), 3.98 (s, 3H), 3.61 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ = 170.9, 167.7, 157.9, 157.8, 137.5, 135.5, 128.9, 125.2, 122.7, 121.0, 120.0, 117.1, 110.4, 52.0, 51.8, 37.0; HRMS (ESI, m/z): calcd. for C₁₇H₁₆N₃O₄ [M+H]⁺: 326.1141, found: 326.1140.
Methyl 2-(2-methoxy-2-oxoethyl)-1-(pyrimidin-2-yl)-1H-indole-5-carboxylate 3w

Following the general procedure, 3w was obtained as a white solid (32 mg, 0.098 mmol, 98%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.73$ (d, $J = 4.8$ Hz, 2H), 8.56 (dt, $J = 8.8$, 0.7 Hz, 1H), 8.29 (d, $J = 1.4$ Hz, 1H), 7.98 (dd, $J = 8.8$, 1.8 Hz, 1H), 7.14 (t, $J = 4.8$ Hz, 1H), 6.67 (d, $J = 0.8$ Hz, 1H), 4.19 (s, 2H), 3.94 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 171.3$, 168.1, 158.3 (overlap), 139.8, 135.2, 129.0, 125.1, 124.3, 123.0, 117.6, 115.4, 110.5, 52.4, 52.3, 37.2; HRMS (ESI, m/z): calcd. for C$_{17}$H$_{16}$N$_3$O$_4$ [M+H]$^+$: 326.1141, found: 326.1141. The spectral data were in accordance with those reported in the literature.  

Methyl2-(1-(pyrimidin-2-yl)-5-(pyrrolidine-1-carbonyl)-1H-indol-2-yl)acetate 3x

3x was obtained as a white solid (34 mg, 0.094 mmol, 94%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.70$ (t, $J = 4.8$ Hz, 2H), 8.55 (d, $J = 8.7$ Hz, 1H), 7.73 (d, $J = 1.6$ Hz, 1H), 7.45 (dd, $J = 8.7$, 1.8 Hz, 1H), 7.11 (t, $J = 4.8$ Hz, 1H), 6.61 (s, 1H), 4.31 (s, 2H), 3.80 (t, $J = 7.0$ Hz, 2H), 3.75 (s, 3H), 3.62 (t, $J = 6.6$ Hz, 2H), 2.09 (m, 2H), 1.85 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 171.0$, 170.5, 157.9, 157.8, 137.4, 134.4, 130.7, 128.4, 122.6, 119.5, 116.9, 115.0, 109.9, 51.9, 49.9, 46.3, 36.9, 26.4, 24.4; HRMS (ESI, m/z): calcd. for C$_{20}$H$_{21}$N$_4$O$_3$ [M+H]$^+$: 365.1614, found: 365.1601.
Methyl 2-(5-nitro-1-(pyrimidin-2-yl)-1H-indol-2-yl)acetate 3y

Following the general procedure, 3y was obtained as a white solid (16 mg, 0.050 mmol, 50%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.77$ (d, $J = 4.8$ Hz, 2H), 8.63 (d, $J = 9.3$ Hz, 1H), 8.49 (d, $J = 2.3$ Hz, 1H), 8.17 (dd, $J = 9.3$, 2.4 Hz, 1H), 7.23 (t, $J = 4.8$ Hz, 1H), 6.75 (s, 1H), 4.22 (s, 2H), 3.64 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 170.6$, 158.1, 157.6, 143.2, 139.8, 136.7, 128.6, 118.7, 117.9, 116.6, 115.5, 110.3, 52.1, 36.8; HRMS (ESI, m/z): calcd. for C$_{15}$H$_{13}$N$_4$O$_4$ [M+H]$^+$: 313.0937, found: 313.0935.

Methyl 2-(1-(pyridin-2-yl)-1H-indol-2-yl)acetate 3z

Following the general procedure, 3z was obtained as a colorless oil (13 mg, 0.047 mmol, 47%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.58$ (ddd, $J = 4.9$, 2.0, 0.9 Hz, 1H), 7.89 (td, $J = 7.7$, 2.0 Hz, 1H), 7.63–7.59 (m, 1H), 7.55 (dt, $J = 8.0$, 1.0 Hz, 1H), 7.43 (ddd, $J = 7.1$, 2.2, 0.8 Hz, 1H), 7.29 (ddd, $J = 7.4$, 4.9, 1.0 Hz, 1H), 7.22-7.12 (m, 2H), 6.61 (d, $J = 0.9$ Hz, 1H), 4.04 (s, 2H), 3.56 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 170.7$, 151.3, 149.4, 138.4, 136.9, 133.0, 128.4, 122.5, 121.8, 121.0, 120.6, 120.2, 110.3, 105.7, 52.0, 34.1; HRMS (ESI, m/z): calcd. for C$_{16}$H$_{15}$N$_2$O$_2$ [M+H]$^+$: 267.1134, found: 267.1143.

Dimethyl 2,2'-(1-(pyrimidin-2-yl)-1H-pyrrole-2,5-diyl)diacetate 3aa

Following the general procedure, 3aa was obtained as a colorless oil (16 mg, 0.055 mmol, 55%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.60$ (d, $J = 4.8$ Hz, 2H), 7.08 (t, $J = 4.8$ Hz, 1H), 6.14 (s, 2H), 3.96 (s, 4H), 3.59 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 171.8$, 157.6, 127.6, 117.3, 112.4, 99.9,
51.8, 36.0; **HRMS (ESI, m/z):** calcd. for $\text{C}_{14}\text{H}_{16}\text{N}_{3}\text{O}_{4}$ $[\text{M}+\text{H}]^+$: 290.1141, found: 290.1147.
References

\textbf{$^1\text{H}, \, ^{13}\text{C} \text{NMR spectra of products}}$

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{nmr_spectra.png}
\caption{\textit{1H, 13C NMR spectra of products}}
\end{figure}

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