1. General Experimental Details

All reactions were conducted under an argon atmosphere unless otherwise indicated. Flasks were oven dried and cooled in a desiccator prior to use. All chemicals were of reagent quality and used as obtained from commercial sources with the exception of the Mn(OAc)$_2$$\cdot$2H$_2$O, which was prepared by literature procedure. High resolution mass spectra (HRMS) were obtained on a Thermo Scientific DFS mass spectrometer using electron impact ionization. Dichloromethane (DCM), acetonitrile (MeCN), toluene, benzene and THF were dried and deoxygenated by passing the nitrogen purged solvents through activated alumina columns. All other reagents and solvents were used as purchased from Aldrich, Alfa Aesar (VWR), or Caledon. Reaction progress was followed by thin layer chromatography (TLC) (Merck, TLC Silica gel 60 F254) visualizing with UV light, and the plates were developed using acidic p-anisaldehyde or vanillin. Column chromatography was performed using silica gel purchased from Silicycle Chemical Division Inc. (230-400 mesh). All columns were performed using Still's procedure for flash chromatography. IR spectra were acquired using a PerkinElmer Spectrum Two FT-IR. Melting points were determined using a Gallenkamp melting point apparatus and are uncorrected.

NMR experiments were performed on either a Bruker AvIII 400, Varian Inova 400 or Inova 600 instrument and samples were obtained in CDCl$_3$ (referenced to 7.25 ppm for $^1$H and 77.0 ppm for $^{13}$C). Coupling constants (J) are in Hz. The multiplicities of the signals are described using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet, br = broad.
2. Experimental Procedure A: Synthesis of Acryloyl Indoles (14a-14j)

A modified procedure from the literature.³ To a round-bottom charged with DCM (0.1M) was added indole (1 equiv.), powdered NaOH (5 equiv.) and tetrabutylammonium hydrogensulfate (Bu₄NHSO₄) (0.1 equiv.). The mixture was stirred for 30 minutes, at which point desired acid chloride (2.5 equiv.) was added to the reaction dropwise. The reaction was monitored by TLC until complete consumption of starting materials was observed. To the flask was added water and the mixture moved to a separatory funnel. The aqueous layer was extracted 3 times with DCM, and the organic layers combined and washed with brine. The collected organic fraction was dried with MgSO₄, filtered and concentrated in vacuo. The crude product was purified by flash column chromatography (Ethyl acetate: Hexanes).

2-methyl-1-(3-methyl-1H-indol-1-yl)prop-2-en-1-one (14a-c)

Following Experimental Procedure A compound 14a was obtained from commercially available 3-methylindole (skatole) (3 g, 22.9 mmol), Bu₄NHSO₄ (0.78 g, 2.29 mmol), NaOH (4.58 g, 114 mmol), methacryloyl chloride (5.98 g, 57.2 mmol, 5.6 mL) in 229 mL DCM. Stirred at rt for 2 h, the reaction was complete. 14a was acquired as a yellow oil (2.81 g, 62 %). Rf = 0.38 (10% EtOAc in hexanes)

¹H NMR (400 MHz, Chloroform-d) δ 8.41 (d, J = 7.7 Hz, 1H), 7.51 (d, J = 6.9 Hz, 1H), 7.41 – 7.27 (m, 2H), 7.24 (s, 1H), 5.68 – 5.59 (m, 1H), 5.47 – 5.40 (m, 1H), 2.27 (s,3H), 2.19 – 2.11 (m, 3H). Spectral data matched literature report of this compound.³

1-(indolin-1-yl)-2-methylprop-2-en-1-one (20)

Indoline 14z was synthesized following literature procedure.⁴ All spectral data matched. Crude product was used and pushed directly to product 14d.
1-(1H-indol-1-yl)-2-methylprop-2-en-1-one (14d)
Indoline 20 (1.59 g, 8.49 mmol) was dissolved in toluene (34 mL) and DDQ (2.32 g, 10.2 mmol) was added. The reaction was refluxed overnight for 16 h, at which point TLC confirmed consumption of starting material. The solvent was removed from the crude mixture in vacuo and then re-dissolved in DCM with 6g of silica added. The DCM was removed under pressure to give the crude material adsorbed to silica. Dry loaded flash column chromatography (5% EtOAc in hexanes) yielded pure acylated indole product 14d as an orange oil (0.93 g, 59% over 2-steps). Rf = 0.28 (5% EtOAc in hexanes)

$^1$H NMR (400 MHz, Chloroform-d) $\delta = 8.42$ (d, $J = 8.2$ Hz, 1H), 7.57 (d, $J = 7.6$ Hz, 1H), 7.47 (d, $J = 3.8$ Hz, 1H), 7.36 (td, $J = 8.3$, 7.9, 1.3 Hz, 1H), 7.29 (td, $J = 7.6$, 1.1 Hz, 1H), 6.60 (d, $J = 3.8$ Hz, 1H), 5.68 (d, $J = 1.0$ Hz, 1H), 5.46 (s, 1H), 2.16 (s, 3H)

$^{13}$C NMR (101 MHz, Chloroform-d) $\delta = 169.8$, 140.0, 135.7, 131.1, 127.1, 125.0, 124.0, 122.0, 120.9, 116.6, 108.6, 20.1 IR (cm$^{-1}$) 2922, 1683, 1534 1449, 1378, 1343, 1200, 1154, 1075, 888 HRMS m/z [M$^+$]
185.083877 (calcd for C$_{12}$H$_{11}$NO, 185.08406)

1-(1H-indol-1-yl)prop-2-en-1-one (14e)
Acylated indole was synthesized following literature procedure.$^4$ The title product was acquired as an orange solid (0.79 g, 53 % yield over 2-steps). Spectral data matched reported literature. MP = 44 - 47°C

$^1$H NMR (400 MHz, Chloroform-d) $\delta = 8.51$ (d, $J = 8.3$ Hz, 1H), 7.58 (d, $J = 7.7$ Hz, 1H), 7.51 (d, $J = 3.7$ Hz, 1H), 7.37 (t, $J = 7.7$ Hz, 1H), 7.30 (t, $J = 7.2$ Hz, 1H), 6.97 (dd, $J = 16.7$, 10.4 Hz, 1H), 6.73 – 6.60 (m, 2H), 6.04 (d, $J = 10.4$ Hz, 1H)

(E)-1-(1H-indol-1-yl)-3-phenylprop-2-en-1-one (14f)
Indoline (1.50 g, 12.6 mmol) was dissolved in THF (25 mL) followed by the addition of K$_2$CO$_3$ (3.48g, 25.2 mmol) to the round bottom. The mixture was cooled to 0 °C and cinnamoyl chloride (2.31 g, 13.9 mmol dissolved in 4 mL THF) was added via syringe to the mixture dropwise. The reaction was allowed to warm to rt and stirred for 6 h. The mixture was quenched with H$_2$O and the aqueous layer extracted 3 times with EtOAc. The combined organic layers were washed with brine once, dried with MgSO$_4$ and concentrated under pressure. The crude mixture (3.09 g, 12.4 mmol, yellow solid) obtained was immediately
pushed forward and dissolved in toluene (50 mL) followed by the addition of DDQ (3.38 g, 14.9 mmol) and refluxed for 12 h. The toluene was removed from the crude mixture in vacuo and then the crude re-dissolved in DCM with 6g of silica added. The DCM was removed under pressure to give the crude material adsorbed to silica. Dry loaded flash column chromatography (10% EtOAc in hexanes) was performed to collect acylated indole 14f as a yellow solid (1.30 g, 42% over 2-steps). Rf = 0.42 (50% EtOAc in hexanes) MP = 110 - 112°C

^1H NMR (400 MHz, Chloroform-d) δ = 8.54 (d, J = 8.8 Hz, 1H), 8.00 (d, J = 15.4 Hz, 1H), 7.64 (m 3H), 7.59 (d, J = 7.7 Hz, 1H), 7.46 – 7.42 (m, 3H), 7.38 (t, J = 7.7 Hz, 1H), 7.34 – 7.19 (m, 2H), 6.70 (d, J = 4.2 Hz, 1H) ^13C NMR (101 MHz, Chloroform-d) δ = 164.4, 146.7, 136.0, 134.6, 130.9, 129.2, 128.5, 125.2, 124.7, 123.9, 121.0, 117.4, 117.0, 109.3 IR (cm⁻¹) 3157, 3054, 1665, 1609, 1536, 1447, 1346, 1297, 1225, 1143, 709 HRMS m/z [M⁺] 247.09952 (calcd for C_{17}H_{13}NO, 247.09971)

1-(5-bromo-1H-indol-1-yl)-2-methylprop-2-en-1-one (14g)

Following Experimental Procedure A compound 14g was obtained from commercially available 5-bromoindole (2 g, 10.2 mmol), Bu₄NHSO₄ (0.35 g, 1.02 mmol), NaOH (2.04 g, 52 mmol), methacryloyl chloride (2.67 g, 25.5 mmol, 2.5 mL) in 100 mL DCM. The reaction was stirred for 20 h. 14g was obtained as a white solid (1.94 g, 72%). Rf= 0.38 (10% EtOAc in hexanes). MP = 32 - 34°C NOTE: 5-bromoindole and its acylated derivative will decompose in light over time.

^1H NMR (400 MHz, Chloroform-d) δ = 8.28 (d, J = 8.8 Hz, 1H), 7.70 (d, J = 1.8 Hz, 1H), 7.48 (d, J = 3.6 Hz, 1H), 7.44 (dd, J = 8.8, 1.9 Hz, 1H), 6.53 (d, J = 3.7 Hz, 1H), 5.70 (s, 1H), 5.47 (s, 1H), 2.15 (s, 3H) ^13C NMR (101 MHz, CDCl₃) δ = 169.6, 134.4, 132.8, 128.3, 127.8, 123.6, 122.6, 118.0, 117.3, 107.7, 20.1 IR (cm⁻¹) 3019, 2400, 1691, 1445, 1366, 1340, 1216, 813, 778, 669 HRMS m/z [M⁺] 262.99414 (262.99458 calcd for C_{12}H_{10}BrNO)

2-methyl-1-(5-nitro-1H-indol-1-yl)prop-2-en-1-one (14h)

Following Experimental Procedure A compound 14h was synthesized from
5-nitroindole (1 g, 6.17 mmol), Bu$_4$NHSO$_4$ (0.21 g, 0.62 mmol), NaOH (1.23 g, 30.9 mmol) and methacryloyl chloride (1.61 g, 15.4 mmol, 1.5 mL) in 62 DCM. The reaction was stirred for 2.5 h at which point TLC confirmed consumption of starting material. **NOTE: 5-nitroindole will decompose over time in light.** 14h was obtained as a white powder (0.76 g, 53%). Rf = 0.21 (15% EtOAc in hexanes). MP = 125 – 126°C

$^1$H NMR (400 MHz, Chloroform-d) δ = 8.54 – 8.41 (m, 1H), 8.23 (dd, J = 9.2, 2.2 Hz, 1H), 7.64 (d, J = 3.8 Hz, 1H), 6.77 – 6.69 (m, 1H), 5.80 (s, 1H), 5.55 (s, 1H), 2.18 (s, 3H)

$^{13}$C NMR (101 MHz, CDCl$_3$) δ = 169.5, 144.5, 139.3, 138.8, 130.9, 130.0, 123.8, 120.2, 117.2, 116.7, 108.8, 19.9 IR (cm$^{-1}$) 1695, 1517, 1536, 1442, 1333, 1193, 884, 828, 777, 745 HRMS m/z [M$^+$] 230.06912 (calcd for C$_{12}$H$_{10}$N$_2$O$_3$, 230.0691)

1-(5-methoxy-1H-indol-1-yl)-2-methylprop-2-en-1-one (14i)

Following **Experimental Procedure A** compound 14i was synthesized from 5-methoxyindole (2 g, 13.6 mmol), Bu$_4$NHSO$_4$ (0.46 g, 1.36 mmol), NaOH (2.72 g, 68.0 mmol) and methacryloyl chloride (3.55 g, 34.0 mmol, 3.3 mL) in 140 mL DCM. Reaction was stirred overnight for 18 h. 14i was obtained as a yellow oil (2.39 g, 82%). Rf = 0.33 (15% EtOAc in hexanes).

$^1$H NMR (400 MHz, Chloroform-d) δ = 8.32 (d, J = 9.0 Hz, 1H), 7.44 (d, J = 3.7 Hz, 1H), 7.03 (s, 1H), 6.96 (dd, J = 9.0, 2.4 Hz, 1H), 6.53 (d, J = 3.7 Hz, 1H), 5.65 (s, 1H), 5.44 (s, 1H), 3.85 (s, 3H), 2.15 (s, 3H) $^{13}$C NMR (101 MHz, Chloroform-d) δ = 169.5, 156.8, 139.9, 132.1, 130.4, 127.8, 121.8, 117.4, 113.4, 108.5, 103.7, 55.8, 20.2 IR (cm$^{-1}$) 1682, 1534, 1472, 1371, 1201, 1158, 1033, 909, 722 HRMS m/z [M$^+$] 215.09440 (calcd for C$_{13}$H$_{13}$NO$_2$, 215.0946)

tert-butyl (2-(1-(2-methylenehex-5-enoyl)-1H-indol-3-yl)ethyl)carbamate (14j)

Acrylic acid (2-methylenehex-5-enoic acid) (6.20 g, 49.1 mmol, 1 equiv) was added to a 25 mL round-bottom and put under and inert atmosphere of argon. Oxalyl chloride (4.45 mL, 51.0 mmol, 1.05 equiv.) was added slowly to the flask followed by a single catalytic drop of DMF. This reaction mixture was stirred two hours. To a 500 mL round-bottom was added boc-protected tryptamine (6.39 g, 24.5 mmol, 1 equiv) in 250 mL of DCM. Bu$_4$NHSO$_4$ (0.83 g, 2.45 mmol, 0.1 equiv) was added to the tryptamine followed by
powdered NaOH (4.91 g, 122.7 mmol, 5 equiv.). The reaction was put under and inert atmosphere of argon and allowed to stir for a minimum of 15 min. At this point the acid chloride generated in the 25 mL round bottom was cannula transferred over in its entirety (~7.10 g, 49.1 mmol, 2 equiv). The mixture was allowed to stir under argon for 1 hr at which point TLC confirmed complete consumption of starting material. The reaction was quenched with water, and extraction with DCM 3 times was performed. The combined organic extracts were washed with water once, followed by brine and then dried with MgSO₄. The solvent was removed in vacuo to yield the crude material. Purification of the crude compound by flash column chromatography was performed using 30% EtOAc:Hexanes to yield the product as a slightly yellow oil (8.81 g, 83%). $R_f = 0.46$ (30% EtOAc:Hexanes) $^1$H NMR (400 MHz, CDCl₃) $\delta = 8.43$ (d, $J = 8.2$ Hz, 1H), 7.54 (d, $J = 7.8$ Hz, 1H), 7.37 (t, $J = 7.7$ Hz, 1H), 7.33 – 7.27 (m, 2H), 5.81 (ddt, $J = 16.9$, 10.2, 6.6 Hz, 1H), 5.65 (s, 1H), 5.45 (s, 1H), 5.08 – 4.96 (m, 2H), 4.63 (br, s, 1H), 3.44 (q, $J = 6.6$ Hz, 2H), 2.88 (t, $J = 6.9$ Hz, 2H), 2.62 (t, $J = 7.4$ Hz, 2H), 2.34 – 2.26 (m, 2H), 1.43 (s, 9H) $^{13}$C NMR (101 MHz, CDCl₃) $\delta = 169.3$, 156.0, 143.9, 137.2, 136.2, 131.1, 125.3, 123.9, 121.2, 119.0, 116.9, 116.0, 40.17, 32.0, 33.2, 28.5, 25.7 IR (cm⁻¹) 3356, 2976, 2928, 1684, 1630, 1510, 1451, 1356, 1248, 1170 HRMS m/z [M⁺] 368.20938 (calcd for C$_{22}$H$_{28}$N$_2$O$_3$, 368.20999)

3. Experimental Procedure B: One-Pot Michael Addition, Oxidative Radical Cyclization (15a-j, 16)

To an argon flushed round-bottom was added half of the total THF (0.15M) required followed by NaH (60% dispersed in mineral oil, 1.5 equiv.). 1, 3-dicarbonyl species (1.5 equiv.) was added dropwise via syringe with stirring. The resultant mixture was stirred for 15 mins at which point the desired indole (1 equiv.) dissolved in the other half-volume of THF was added via syringe. The Michael addition was monitored by TLC. Once TLC confirmed complete consumption of starting indole, Mn(OAc)$_3$ (7 equiv.) was added to the round bottom flask followed by AcOH (0.12M). The flask was equipped with a reflux condenser and put back under an argon
atmosphere. The reaction was brought to 110 °C and refluxed until the mixture changed colour from dark brown mixture to containing obvious white solid with yellow/orange solution. At this point TLC analysis always indicated complete consumption of starting materials. The crude reaction mixture was allowed to cool to rt and then diluted with a large excess of EtOAc. The solution was filtered through a thick pad of celite and then flushed with even more EtOAc. The solvent was removed under reduced pressure with added toluene to aid in the removal of acetic acid. Obtained dried crude was purified with flash column chromatography (EtOAc in hexanes). The desired fractions of the column were collected to a separatory funnel and washed twice with 1 M NaOH solution and then followed with a brine wash. The organic layer was collected, dried with MgSO₄ and concentrated in vacuo to yield product.

**dimethyl 7,10-dimethyl-6-oxo-7,8-dihydropyrido[1,2-a]indole-9,9(6H)-dicarboxylate (15a)**

Following **Experimental Procedure B** 15a was synthesized from acyl-indole 14a (0.30 g, 1.51 mmol), NaH (0.091 g, 2.27 mmol), dimethyl malonate (0.30 g, 2.27 mmol, 0.26 mL) in 10 mL of THF then Mn(OAc)₃ (2.80 g, 10.6 mmol) in acetic acid (13 mL). 15a was isolated as a yellow solid (0.33 g, 65%) Rf = 0.40 (20% EtOAc in hexanes) MP = 126 – 129 °C

\[ ^1H \text{NMR (400 MHz, CDCl}_3 \] \( \delta = 8.50 \text{ (d, } J = 8.2 \text{ Hz, 1H), 7.50 \text{ (d, } J = 7.7 \text{ Hz, 1H), 7.35 \text{ (t, } J = 7.7 \text{ Hz, 1H), 7.30 \text{ (t, } J = 7.5 \text{ Hz, 1H), 3.83 \text{ (s, 3H), 3.79 \text{ (s, 3H), 2.90 \text{ (ddq, } J = 12.6, 6.5, 6.3 \text{ Hz, 1H), 2.84 \text{ (dd, } J = 13.0, 4.4 \text{ Hz, 1H), 2.39 \text{ (t, } J = 13.0 \text{ Hz, 1H), 2.16 \text{ (s, 3H), 1.42 \text{ (d, } J = 6.8 \text{ Hz, 3H) }} \]

\[ ^{13}C \text{NMR (101 MHz, CDCl}_3 \] \( \delta = 170.9, 170.4, 169.0, 134.5, 131.1, 128.2, 125.7, 124.0, 118.6, 117.9, 116.8, 55.7, 53.6, 37.5, 35.4, 15.7, 9.2 \text{ IR 3027, 2954, 1785, 1702, 1456, 1386, 1385, 1308, 1245, 751 HRMS } m/z [M'] 329.12682 \text{ (calcd for } C_{18}H_{19}NO_5, 329.1263) \]

**1,1'-(7,10-dimethyl-6-oxo-6,7,8,9-tetrahydropyrido[1,2-a]indole-9,9-diyl)diethanone (15b)**

To an oven-dried round bottom was added acylated indole 14b (0.20 g, 1.00 mmol), acetylacetone (0.50 g, 5.00 mmol, 0.51 mL), K₂CO₃ (0.14 g, 1 mmol), 6 mL of THF and one drop of water. The flask was equipped with reflux condenser and the mixture heated at 55 °C for 24 h at which point starting materials had been consumed. To the reaction was then added Mn(OAc)₃ (1.87 g, 7 mmol) and acetic acid (8 mL) and refluxed at 110 °C for 3 h. The mixture was then worked up as described in **Experimental Procedure B** from
this point onwards. Product 15b was obtained as an orange solid (0.17g, 59%). Rf = 0.33 (20 % EtOAc in hexanes) MP = 158 – 161°C

\[ \text{1H NMR (400 MHz, CDCl}_3\text{)} \delta = 8.52 \text{ (d, } J = 8.1 \text{ Hz, 1H), 7.52 \text{ (d, } J = 7.1 \text{ Hz, 1H), 7.40 \text{ (t, } J = 7.0 \text{ Hz, 1H), 7.34 \text{ (t, } J = 7.4 \text{ Hz, 1H), 2.85 – 2.69 \text{ (m, 2H), 2.26 \text{ (s, 3H), 2.24 \text{ (s, 3H), 2.22 \text{ (s, 3H), 1.42 \text{ (d, } J = 6.6 \text{ Hz, 3H)}}}} \text{]} \]

\[ \text{13C NMR (101 MHz, CDCl}_3\text{)} \delta = 205.5, 204.0, 171.2, 134.9, 130.9, 129.0, 126.2, 124.3, 118.7, 116.9, 67.1, 35.4, 28.8, 26.2, 16.0, 10.1 \text{ IR } 2936, 1708, 1607, 1455, 1364, 1305, 1190, 1153, 1128, 1080, 754 \text{ HRMS m/z [M}^+\text{]} 297.136556 \text{ (calcd for } C_{18}H_{19}NO_3, 297.1365) \]

methyl 9-acetyl-7,10-dimethyl-6-oxo-6,7,8,9-tetrahydropyrido[1,2-a]indole-9-carboxylate (15c)

To an oven-dried round bottom was added acylated indole 14c (0.25 g, 1.25 mmol), methyl acetoacetate (0.73 g, 6.25 mmol, 0.67 mL), K$_2$CO$_3$ (0.09 g, 0.63 mmol), 8 mL of THF and one drop of water. The flask was equipped with reflux condenser and the mixture heated at 55 °C for 24 h at which point starting materials had been consumed. To the reaction was then added Mn(OAc)$_3$ (2.35 g, 8.75 mmol) and acetic acid (10 mL) and reacted at 110 °C for 6 h. The mixture was then worked up as described in Experimental Procedure B from this point onwards. Product 15c was obtained as a yellow solid (0.21g, 54%). Rf = 0.34 (20% EtOAc in hexanes) MP = 107 – 111 °C

\[ \text{1H NMR (400 MHz, CDCl}_3\text{)} \text{ diastereomers } \delta = 8.50 \text{ (d, } J = 8.0 \text{ Hz, 1H), 7.51 \text{ (d, } J = 7.7 \text{ Hz, 1H), 7.41 – 7.27 \text{ (m, 2H), 3.84 (diastereomer a) and 3.78 (diastereomer b) (s, 3H), 2.97 – 2.66 \text{ (m, 2H), 2.45 – 2.31 \text{ (m, 1H), 2.27 (diastereomer a) and 2.23 (diastereomer b) (s, 3H), 2.20 (diastereomer a) and 2.17 (diastereomer b) (s, 3H), 1.44 (diastereomer b) (d, } J = 6.8 \text{ Hz, 3H), and 1.38 (diastereomer a) (d, } J = 6.7 \text{ Hz, 3H)}} \text{]} \]

\[ \text{13C NMR (101 MHz, CDCl}_3\text{)} \text{ (both diastereomer a and b)} \delta = 202.8, 202.2, 171.0, 170.9, 169.4, 134.6, 130.9, 130.8, 129.1, 127.8, 124.0, 118.6, 118.4, 118.1, 116.8, 116.7, 116.5, 62.9, 59.9, 53.2, 53.2, 36.5, 35.7, 35.5, 35.0, 28.1, 25.4, 16.0, 15.5, 9.5, 9.3 \text{ IR (cm}^{-1}\text{)} 2952, 1716, 1456, 1365, 1307, 1239, 1153, 1130, 1084, 754 \text{ HRMS m/z [M}^+\text{]} 313.13116 \text{ (calcd for } C_{18}H_{19}NO_4, 313.1314) \]

dimethyl 7-methyl-6-oxo-7,8-dihydropyrido[1,2-a]indole-9,9(6H)-dicarboxylate (15d)
Following **Experimental Procedure B**, 15d was synthesized from acryloyl indole 14d (0.25 g, 1.35 mmol), dimethyl malonate (0.27 g, 2.02 mmol, 0.23 mL), NaH (0.081 g, 2.02 mmol) in 9 mL of THF. Following completion of the Michael addition was then added Mn(OAc)$_3$ (2.53 g, 9.40 mmol) and acetic acid (11 mL). 15d was isolated as a pale orange solid (0.18 g, 45%). Rf = 0.27 (20 % EtOAc in hexanes). MP = 109 – 113˚C

$^1$H NMR (400 MHz, CDCl$_3$) δ = 8.48 (d, $J$ = 8.2 Hz, 1H), 7.52 (d, $J$ = 8.4 Hz, 1H), 7.39 – 7.31 (m, 1H), 7.28 (m, 1H), 6.68 (s, 1H), 3.89 (s, 3H), 3.77 (s, 3H), 2.80 (ddd, $J$ = 13.3, 6.7, 4.5 Hz, 1H), 2.72 (dd, $J$ = 13.6, 4.5 Hz, 1H), 2.51 (t, $J$ = 13.5 Hz, 1H), 1.43 (d, $J$ = 6.8 Hz, 3H) $^{13}$C NMR (101 MHz, CDCl$_3$) δ = 171.0, 169.6, 168.8, 135.4, 133.0, 129.3, 125.5, 124.3, 120.8, 116.8, 109.2, 55.7, 53.7, 42.0, 36.4, 35.3, 15.9 IR (cm$^{-1}$) 2956, 2923, 2852, 1746, 1708, 1437, 1300, 1144, 1063, 836 HRMS m/z [M$^+$] 315.11120 (calcd for C$_{17}$H$_{17}$NO$_5$, 315.11067)

dimethyl 6-oxo-7,8-dihydropyrido[1,2-a]indole-9,9(6H)-dicarboxylate (15e)

Following **Experimental Procedure B**, 15e was synthesized from acryloyl indole 14e (0.30 g, 1.75 mmol), dimethyl malonate (0.27 g, 2.60 mmol, 0.30 mL), NaH (0.10 g, 2.60 mmol) in 12 mL of THF. Following the completion of the Michael addition, Mn(OAc)$_3$ (3.27 g, 12.2 mmol) was then added with 14 mL of acetic acid. 15e was isolated as an orange oil (0.20 g, 38%) Rf = 0.17 (20% EtOAc in hexanes).

**Or alternative procedure from indoline 16**: Acylated indoline 16 was synthesized following literature procedure.$^4$ To a round bottom under argon was added THF (6 mL) followed by NaH (0.10 g, 2.60 mmol) followed by dimethyl malonate (0.34 g, 2.6 mmol, 0.3 mL) dropwise via syringe and the mixture was allowed to stir for 15 min. Acylated indoline 16 (0.3 g, 1.70 mmol) dissolved in 5 mL THF was added to the reaction via syringe and the reaction was monitored by TLC for completion of the Michael addition. Upon completion, to the flask was added 17 mL acetic acid and Mn(OAc)$_3$ (4.02 g, 15.0 mmol) and the round bottom equipped with a reflux condenser. The mixture was heated to reflux for 22 h at which point TLC confirmed the reaction was complete. The mixture was cooled to room temperature and filtered through a pad of celite and rinsed thoroughly with ethyl acetate. The crude mixture was concentrated in vacuo and then subjected to flash column chromatography to isolate 15e as an orange oil (0.083 g, 16%) the collected fraction from the column were washed once with 1M NaOH to remove traces of dimethyl malonate. Rf = 0.17 (20% EtOAc in hexanes)
**1H NMR (400 MHz, CDCl₃)** \( \delta = 8.47 \) (d, \( J = 8.2 \) Hz, 1H), 7.52 (d, \( J = 7.7 \) Hz, 1H), 7.35 (t, \( J = 8.4 \) Hz, 1H), 7.30 – 7.26 (m, 1H), 6.69 (s, 1H), 3.84 (s, 6H), 2.85 – 2.78 (m, 2H), 2.68 (t, \( J = 6.6 \) Hz, 2H) **13C NMR (101 MHz, CDCl₃)** \( \delta = 168.0, 166.6, 134.3, 131.8, 128.0, 124.6, 123.4, 119.8, 115.8, 108.4, 54.4, 52.7, 29.9, 27.5 \)

IR (cm⁻¹) HRMS \( m/z \) [M⁺] 301.09588 (calcd for C₁₆H₁₅NO₅, 301.09502)

Following **Experimental Procedure B** 15f was synthesized from acryloyl-indole 14f (0.30 g, 1.21 mmol), dimethyl malonate (0.24 g, 1.80 mmol, 0.21 mL), NaH (0.072 g, 1.80 mmol) in 8 mL of THF. Followed up with Mn(OAc)₃ (2.28 g, 8.50 mmol) and acetic acid (10 mL). 15f was isolated as a white solid (0.12 g, 27%) \( R_f = 0.25 \) (20% EtOAc in hexanes). MP = 54 – 57 °C

**1H NMR (400 MHz, CDCl₃)** \( \delta = 8.55 \) (d, \( J = 8.2 \) Hz, 1H), 7.60 (d, \( J = 8.3 \) Hz, 1H), 7.44 – 7.37 (m, 1H), 7.33 (td, \( J = 7.5, 1.1 \) Hz, 1H), 7.22 – 7.12 (m, 3H), 7.01 (s, 1H), 6.96 (dd, \( J = 7.5, 2.0 \) Hz, 2H), 4.26 (dd, \( J = 6.0, 4.3 \) Hz, 1H), 3.76 (s, 3H), 3.72 – 3.65 (m, 1H), 3.55 (s, 3H), 3.08 (dd, \( J = 17.7, 4.3 \) Hz, 1H) **13C NMR (101 MHz, CDCl₃)** \( \delta = 168.6, 167.5, 167.4, 138.8, 135.0, 131.3, 129.6, 128.9, 128.0, 125.7, 124.5, 121.0, 117.0, 112.9, 77.5, 58.7, 53.8, 44.7, 42.0, 38.2 \)

IR (cm⁻¹) 3034, 2953, 1736, 1696, 1452, 1371, 1323, 1234, 1202, 1167 HRMS \( m/z \) [M⁺] 377.126904 (calcd for C₂₂H₁₉NO₅, 377.12632)

Following **Experimental Procedure B** 15g was synthesized from acryloyl-indole 14g (0.30 g, 1.14 mmol), dimethyl malonate (0.22 g, 1.70 mmol, 0.19 mL), NaH (0.068 g, 1.70 mmol) in 8 mL THF, then followed with Mn(OAc)₃ (2.14 g, 8.00 mmol) and acetic acid (10 mL). 15g was isolated as a yellow solid (0.28 g, 63%) \( R_f = 0.29 \) (20% EtOAc in hexanes) MP = 118 – 122 °C

**1H NMR (400 MHz, CDCl₃)** \( \delta = 8.35 \) (d, \( J = 8.8 \) Hz, 1H), 7.65 (s, 1H), 7.44 (d, \( J = 10.7 \) Hz, 1H), 6.62 (s, 1H), 3.90 (s, 3H), 3.79 (s, 3H), 2.80 (ddd, \( J = 13.2, 6.7, 4.6 \) Hz, 1H), 2.73 (ddd, \( J = 13.6, 4.5 \) Hz, 1H), 2.51 (t, \( J = 13.5 \) Hz, 1H), 1.43 (d, \( J = 6.8 \) Hz, 3H) **13C NMR (101 MHz, CDCl₃)** \( \delta = 168.0, 166.6, 134.3, 131.8, 128.0, 124.6, 123.4, 119.8, 115.8, 108.4, 54.4, 52.7, 29.9, 27.5 \)

IR (cm⁻¹) 3034, 2953, 1736, 1696, 1452, 1371, 1323, 1234, 1202, 1167 HRMS \( m/z \) [M⁺] 377.126904 (calcd for C₂₂H₁₉NO₅, 377.12632)
Following Experimental Procedure B 15i was synthesized from acryloyl-indole 14i (0.30 g, 1.39 mmol), dimethyl malonate (0.28 g, 2.09 mmol, 0.24 mL), NaH (0.084 g, 2.09 mmol) in THF (9 mL) followed then by Mn(OAc)$_3$ (2.61 g, 9.70 mmol) and acetic acid (11 mL). 15i was isolated as a pale yellow solid (0.29 g, 61%). Rf = 0.24 (25% EtOAc in hexanes) MP = 117 – 120 °C

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 8.36 (d, $J = 8.9$ Hz, 1H), 7.02 – 6.87 (m, 2H), 6.61 (s, 1H), 3.89 (s, 3H), 3.83 (s, 3H), 3.77 (s, 3H), 2.83 – 2.65 (m, 2H), 2.50 (t, $J = 13.4$ Hz, 1H), 1.42 (d, $J = 6.7$ Hz, 3H) $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 170.6, 169.6, 168.7, 156.9, 133.5, 130.3, 130.1, 117.5, 113.8, 109.1, 103.6, 55.8, 53.7, 36.4, 35.1, 15.9 IR (cm$^{-1}$) 2955, 2837, 1732, 1615, 1435, 1383, 1105, 1073, 1030, 912.9 HRMS m/z [M$^+$] 345.12214 (calcd for C$_{18}$H$_{19}$NO$_6$, 345.1212)

Following Experimental Procedure B 15h was synthesized from acryloyl-indole 14h (0.30 g, 1.30 mmol), dimethyl malonate (0.26 g, 1.95 mmol, 0.22 mL), NaH (0.078 g, 1.95 mmol) in 9 mL of THF, followed by Mn(OAc)$_3$ (2.44 g, 9.10 mmol) and acetic acid (11 mL). 15h was isolated as a white solid (0.17 g, 36%). Rf = 0.34 (30% EtOAc in hexanes). MP = 135 – 140 °C

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 8.58 (d, $J = 9.5$ Hz, 1H), 8.43 (d, $J = 2.3$ Hz, 1H), 8.22 (dd, $J = 9.1$, 2.3 Hz, 1H), 6.83 (s, 1H), 3.92 (s, 3H), 3.80 (s, 3H), 2.86 (dq, $J = 13.5$, 6.9, 4.6 Hz, 1H), 2.76 (dd, $J = 13.8$, 4.5 Hz, 1H), 2.53 (t, $J = 13.6$ Hz, 1H), 1.45 (d, $J = 6.8$ Hz, 3H) $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 171.1, 168.9, 168.2, 144.7, 138.3, 136.3, 129.3, 120.7, 117.0, 109.5, 55.6, 54.0, 36.0, 35.4, 15.7 IR (cm$^{-1}$) 3128, 2959, 1739, 1717, 1562, 1516, 1443, 1333, 1232, 1174 HRMS m/z [M$^+$] 360.09543 (calcd for C$_{18}$H$_{19}$NO$_7$, 360.09575)
dimethyl 7-(but-3-en-1-yl)-10-(3-((tert-butoxycarbonyl)amino)propyl)-6-oxo-7,8-dihydropyrido[1,2-a]indole-9,9(6H)-dicarboxylate (15j)

Following Experimental Procedure B, 15j was synthesized from acryloyl indole 14j (0.26 g, 0.69 mmol), dimethyl malonate (0.18 g, 1.39 mmol, 0.16 mL), NaH (0.06 g, 1.39 mmol) in 5 mL of THF. Upon the completion of the Michael addition, to the reaction mixture was added Mn(OAc)$_3$ (1.11 g, 4.14 mmol) and 10 mL of MeOH (instead of acetic acid). The mixture was heated under argon at 65 °C for a minimum of 20 h before proceeding with work-up as per Experimental Procedure B. 15j was isolated as a white solid (0.11 g, 30%) Rf = 0.27 (25% EtOAc in hexanes). MP = 106 – 110 °C

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 8.50 (d, $J$ = 8.0 Hz, 1H), 7.66 (d, $J$ = 7.6 Hz, 1H), 7.36 (t, $J$ = 7.1 Hz, 1H), 7.30 (t, $J$ = 7.5 Hz, 1H), 5.83 (ddt, $J$ = 17.2, 10.2, 6.3 Hz, 1H), 5.13 – 5.00 (m, 2H), 4.81 (br, s, 1H), 3.85 (s, 3H), 3.80 (s, 3H), 3.42 (dt, $J$ = 12.4, 6.0 Hz, 2H), 2.93 – 2.83 (m, 2H), 2.77 – 2.59 (m, 2H), 2.38 (t, $J$ = 13.1 Hz, 1H), 2.33 – 2.17 (m, 3H), 1.67 (q, $J$ = 8.3 Hz, 1H), 1.43 (s, 9H) $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ = 170.5, 170.4, 168.9, 156.0, 137.5, 134.8, 128.7, 125.9, 124.3, 119.5, 119.0, 116.9, 115.9, 55.9, 53.9, 53.7, 39.3, 35.0, 30.8, 28.9, 28.6 IR (cm$^{-1}$) 3272, 2956, 1736, 1697, 1456, 1377, 1242, 1167, 1075, 76 HRMS m/z [M$^+$] 498.23610 (calcld for C$_{27}$H$_{34}$N$_2$O$_7$, 498.23660)
4. $^1$H and $^{13}$C NMR
References