Supporting Information

For

An Efficient Synthesis of Hydropyrido[1,2-a]indole-6(7*H*)-ones via an In(III)-catalyzed Tandem Cyclopropane Ring-opening/Friedel-Crafts Alkylation Sequence

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1. General Methods

All reactions were carried out in pre-dried glassware from the oven where additional moisture was removed by flame-drying the reaction vessel. Each reaction proceeded under a nitrogen atmosphere, and dry solvents were used, unless stated otherwise. Tetrahydrofuran and diethyl ether were distilled from a sodium/benzophenone ketyl under nitrogen and stored in a Schlenk flask. 1,2-Dichloroethane and dichloromethane were purified by distillation from calcium hydride under N₂ prior to use. Acetonitrile was dried by fractional distillation over CaH₂. Benzene was purified by drying with CaH₂. All other reagents were purchased from Acros, Sigma-Aldrich, Fluka, VWR, Merck, Alfa Aesar, TCI and Strem (for metal catalysts) and used without further purification.

Chromatographic purification was performed as flash chromatography with Silicycle silica gel (40-63 μ m) and solvents indicated as eluent with 0.1-0.5 bar pressure. For quantitative flash chromatography, technical grade solvents were utilized. Analytical thin-layer chromatography (TLC) was performed on EMD silica gel 60 F₂₅₄ TLC glass plates. Visualization was accomplished with UV light, aqueous basic potassium permanganate (KMnO₄) solution, iodine, aqueous acidic dinitrophenylhydrazine (DNP) solution, aqueous acidic *p*-anisaldehyde (PAA) solution, and ethanol solution of phosphomolybdic acid (PMA) followed by heating. Each yield refers to isolated analytically pure material.

Infrared (IR) spectra were obtained using a Nicolet 4700 FTIR with an ATR attachment from SmartOrbit Thermoelectronic Corp. The IR bands are characterized as broad (br), weak (w), medium (m), and strong (s). Proton and carbon nuclear magnetic resonance spectra (¹H NMR and ¹³C NMR) were recorded on a Varian Mercury Vx 300 spectrometer or a Varian Mercury Vx 400 spectrometer with solvent resonances as the internal standard (¹H NMR: CDCl₃ at 7.26 ppm; ¹³C NMR: CDCl₃ at 77.0 ppm). ¹H NMR data are reported as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, dd = doublet of doublets, dt = doublet of triplets, ddd = doublet of doublets, t = triplet, m = multiplet), coupling constants (Hz), and integration. Mass spectra were obtained using a VG-70SE instrument.

Diastereomeric ratios for cyclized products **4** were determined by ¹H NMR based on comparing the integral ratios of the benzylic protons (~4.0-5.0 ppm) for the two diastereomeric protons. The first signal represents the *trans* isomer and the second signal represents the *cis* isomer. This assignment is based on the coupling constants assigned from ¹H NMR in conjunction with decoupling experiments to assign all the coupled proton signals.

2. Experimental Procedures

A. N-Acylation of Indole Compounds

Sodium hydride (1.1 equiv.) was suspended in THF (20 mL) and cooled to 0 °C. In a separate flask, the desired indole (1.0 equiv.) was dissolved in 30 mL of THF and syringed into the reaction vessel. After 30 min, methyl-3-chloro-3-oxopropanoate (1.1 equiv.) was slowly added. The reaction was stirred for 14 h at room temperature. The reaction mixture was quenched with water. The organic layer was separated, and the aqueous layer was extracted three times with EtOAc. The combined organic layers were washed with brine, dried with anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by silica gel flash chromatography for product isolation.



Methyl 3-(3-methyl-1*H***-indol-1-yl)-3-oxopropanoate (5a)**: The general procedure was followed using sodium hydride (1.90 g, 47.7 mmol), 3-methyl-1H-indole (5.00 g, 38.1 mmol), methyl-3-chloro-3-oxopropanoate (4.9 mL, 45.7 mmol), and THF (50 mL). After 14 h, the reaction was quenched, and column chromatography (20% EtOAc/Hex, R_f 0.26 and R_f 0.15 for keto and enol tautomers) afforded **5a** as a light brown solid (6.44 g, 73%). [**m.p.** 49-51°C] ¹**H NMR** (300 MHz, CDCl₃) δ 8.43 (d, *J* = 7.1 Hz, 1H),

7.52 – 7.47 (m, 1H), 7.41 – 7.28 (m, 2H), 7.10 (s, 1H), 3.92 (s, 2H), 3.79 (s, 3H), 2.27 (s, J = 1.3 Hz, 3H). ¹³**C NMR** (75 MHz, CDCl₃) δ 166.8, 163.4, 136.0, 131.5, 125.5, 124.0, 121.4, 119.7, 118.9, 116.7, 52.9, 43.6, 9.7. **IR**: 3051.9 (w), 2937.6 (w), 1747.0 (s), 1685.1 (s), 1604.1 (w), 1447.0 (s), 1375.5 (s), 1232.6 (m), 1070.7 (m), 913.5 (m), 732.6 (s) cm⁻¹. **HRMS (ESI)** M/Z+ Calc. 231.0895, Obs. 231.0895.



Methyl 3-(3-(2-bromoethyl)-1*H***-indol-1-yl)-3-oxopropanoate (5b):¹** A mixture of potassium carbonate (0.100 g, 0.724 mmol) and 3-(2-bromoethyl)-1*H*-indole (0.250 g, 1.1 mmol), methyl-3-chloro-3-oxopropanoate (0.21 mL, 1.95 mmol) and acetonitrile (13 mL) were heated to reflux. After 16 h, the reaction mixture was cooled, filtered and dried *in vacuo*. The residue was dissolved in EtOAc/Hex (1:2.5). The organic layer was separated, and the aqueous layer was extracted three times with EtOAc. The combined organic layers were dried with anhydrous sodium sulfate, filtered, and concentrated. Column chromatography (20% EtOAc/Hex, R_f 0.35) afforded **5b** as a yellow-brown solid (0.290 g, 81%). [**m.p.** 68-70°C] ¹**H NMR** (300 MHz, CDCl₃) δ 8.41 (d, *J* = 7.8 Hz, 1H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.40 – 7.24 (m, 2H), 7.22 (s, 1H), 3.92 (s, 2H), 3.76 (s, 3H), 3.61 (t, *J* = 7.2 Hz, 2H), 3.22 (t, *J* = 7.2 Hz, 2H). ¹³**C NMR** (75 MHz, CDCl₃) δ 166.5, 163.5, 135.7, 129.8, 125.6, 123.9, 122.1, 120.4, 118.4, 116.7, 52.7, 43.3, 31.1, 28.5. **IR**: 3091.7 (w), 2940.7 (w), 2878.8 (w), 1760.1 (s), 1657.8 (s), 1615.6 (s), 1535.5 (s), 1440.9 (s), 1239.4 (s), 1191.4 (s), 1040.8 (m), 820.8 (m), 777.4 (m) cm⁻¹. **HRMS (ESI)** M/Z+ Calc. 323.0157, Obs. 323.0162.



Methyl 3-(3-(2-(1,3-dioxoisoindolin-2-yl)ethyl)-1*H*-indol-1-yl)-3-oxopropanoate (5c): The general procedure was followed using sodium hydride (0.459 g, 11.5 mmol), 2-(2-(1*H*-indol-3-yl)ethyl)isoindoline-1,3-dione² (3.01 g, 10.4 mmol), methyl-3-chloro-3-oxopropanoate (1.4 mL, 13.0 mmol), and THF (90 mL). After 16 h, the reaction was quenched, and column chromatography (30% EtOAc/Hex, R_f 0.17) afforded **5c** as a white solid (1.69 g, 42%). [**m.p.** 138-140°C] ¹**H NMR** (300 MHz, CDCl₃) δ 8.41 (d, *J* = 7.7 Hz, 1H), 7.88 – 7.77 (m, 2H), 7.75 – 7.67 (m, 2H), 7.64 (d, *J* = 7.7 Hz, 1H), 7.40 – 7.27 (m, 3H), 4.04 (t, *J* = 7.2 Hz, 2H), 3.96 (s, 2H), 3.78 (s, 3H), 3.10 (t, *J* = 7.4 Hz, 2H). ¹³**C NMR** (75 MHz, CDCl₃) δ 171.0, 168.3, 167.2, 166.7, 163.7, 136.0, 134.1, 131.9, 130.4, 125.7, 124.2, 123.3, 121.9, 120.0, 118.9, 116.8, 52.9, 52.8, 43.4, 40.5, 37.2, 24.1. **IR**: 2937.6 (w), 1742.2 (s), 1703.2 (s), 1691.8 (s), 1599.3 (w), 1456.5 (m), 1383.6 (m), 1329.9 (m), 1210.0 (m), 1153.5 (s), 1008.8 (m), 923.1 (w), 719.7 (s) cm⁻¹. **HRMS (ESI)** M/Z+ Calc. 390.1216, Obs. 390.1213.



Methyl 3-(3-(2-methoxy-2-oxoethyl)-1*H***-indol-1-yl)-3-oxopropanoate (5d):** The general procedure was followed using sodium hydride (0.702 g, 17.6 mmol), methyl 2-(1*H*-indol-3-yl)acetate (3.00 g, 15.9 mmol), methyl-3-chloro-3-oxopropanoate (2.0 mL, 18.6 mmol), and THF (60 mL). After 16 h, the reaction was quenched, and column chromatography (30% EtOAc/Hex, R_f 0.24) afforded 5d as a dark brown oil (3.55 g, 77%). ¹**H NMR** (300 MHz, CDCl₃) δ 8.43 (d, *J* = 8.0 Hz, 1H), 7.57 – 7.49 (m, 1H), 7.43 – 7.27 (m, 3H), 3.96 (s, 2H), 3.79 (s, 3H), 3.73 (s, 2H), 3.72 (s, 3H). ¹³**C NMR** (75 MHz, CDCl₃) δ 171.0, 166.6, 163.6, 135.8, 130.1, 125.8, 124.2, 123.1, 118.9, 116.8, 116.0, 52.8, 52.2, 43.4, 30.6. **IR**: 3009.3 (w), 2952.1 (w),

1737.4 (s), 1703.2 (s), 1595.1 (m), 1366.0 (s), 1265.7 (m), 1204.7 (s), 1148.4 (s), 1015.7 (m), 909.4 (m), 728.3 (s) cm⁻¹. **HRMS (ESI)** M/Z+ Calc. 289.0950, Obs. 289.0945.



Methyl 3-(1*H***-indol-1-yl)-3-oxopropanoate (5e):** Following a modification of Kerr's reported procedure,³ indoline (4.0 g, 33.56 mmol) was dissolved in THF (70 mL) in a round bottom flask equipped with a magnetic stir bar. K_2CO_3 (9.28 g, 67.14 mmol) was added and the mixture was cooled to 0°C. Methyl malonyl chloride (3.977mL, 37.09 mmol) was added dropwise with rapid stirring. Formation of white precipitate was immediately observed. After 30 min, the reaction mixture was filtered, and the solvent was removed under reduced pressure to yield the indoline β -amide ester, which was used without purification.

In a dry round bottom flask equipped with a reflux condenser, the resulting β -amide ester (4.26 g, 19.43 mmol) was dissolved in dry toluene (55 mL), and DDQ (5.28 g, 23.26 mmol) was added. The reaction mixture was heated to a reflux for 12 hours. The reaction was cooled to room temperature, diluted with EtOAc, washed with water and brine and dried over anhydrous MgSO₄. The solvent was removed *in vacuo* and purification of the crude reaction mixture by flash column chromatography (15% EtOAc/Hex, R_f 0.35) yielded **5e** as a yellow-brown oil (2.72 g, 37.3% over the two steps). ¹**H NMR** (300 MHz, CDCl₃) δ 8.44 (d, *J* = 8.1 Hz, 1H), 7.56 – 7.51 (m, 1H), 7.38 – 7.23 (m, 3H), 6.61 (dd, *J* = 3.8, 0.8 Hz, 1H), 3.91 (s, 2H), 3.74 (s, 3H). ¹³**C NMR** (75 MHz, CDCl₃) δ 166.5, 163.8, 135.4, 130.2, 125.1, 124.5, 123.9, 120.7, 116.3, 109.8, 52.6, 43.1. **IR**: 3109.7 (w), 3152.9 (w), 3036.6 (w), 2953.6 (w), 2850.7 (w), 1737.9 (m), 1703.1 (s), 1691.8 (m), 1529.04 (w), 1472.2 (w), 1450.6 (m), 1383.1 (m), 1346.9 (s), 1261.2 (m), 1204.9 (s), 1150.2 (s), 1015.7 (m), 925.7 (m), 747.3 (s), 715.2 (m), 689.3 (m) cm⁻¹. **HRMS (ESI)** M/Z+ Calc. 217.0739, Obs. 217.0738.

B. Formation of the Diazo Compounds

The β -amide ester (1.0 equiv.) was dissolved in acetonitrile. Triethylamine (1.2 equiv.) was added to the reaction mixture and stirred for 10 min. Tosyl azide (1.2 equiv) was placed in the reaction flask. The mixture was stirred at room temperature for 12 h and concentrated under reduced pressure. The resulting residue was purified by silica gel flash chromatography to afford the diazo compound.



Methyl 2-diazo-3-(3-methyl-1*H***-indol-1-yl)-3-oxopropanoate (6a)**: The general procedure was followed using methyl 3-(3-methyl-1*H*-indol-1-yl)-3-oxopropanoate (2.71 g, 11.7 mmol), triethylamine (2.0 mL, 14.4 mmol), tosyl azide (2.81 g. 14.2 mmol), and acetonitrile (30 mL). After 12 h, the reaction mixture was concentrated, and column chromatography (20% EtOAc/Hex, R_f 0.41) afforded **6a** as a yellow solid (2.79 g, 93%). [**m.p.** 74-76°C] ¹**H NMR** (300 MHz, CDCl₃) δ 8.17 (d, *J* = 8.6 Hz, 1H), 7.51 – 7.47 (m, 1H), 7.39 – 7.26 (m, 2H), 7.11 (s, 1H), 3.85 (s, 3H), 2.28 (s, 3H). ¹³**C NMR** (75 MHz, CDCl₃) δ 161.5, 158.9, 136.0, 131.7, 124.8, 123.7, 123.3, 118.9, 117.7, 115.7, 69.7, 52.6, 9.7. **IR**: 3047.1 (w), 2956.6 (w), 2918.5 (w), 2132.7 (s), 1708.9 (s), 1651.7 (s), 1601.0 (m), 1466.0 (s), 1349.6 (s), 1302.9 (s), 1254.3(s), 1127.9(s), 1046.9 (s), 865.9 (m), 732.7 (s) cm⁻¹. **HRMS (ESI)** M/Z+ Calc. 257.0800, Obs. 257.0805.



Methyl 3-(3-(2-bromoethyl)-1*H***-indol-1-yl)-2-diazo-3-oxopropanoate (6b):** The general procedure was followed using methyl 3-(3-(2-bromoethyl)-1*H*-indol-1-yl)-3-oxopropanoate (0.110 g, 0.339 mmol), triethylamine (0.0412 g, 0.407 mmol), tosyl azide (0.080 g, 0.407 mmol), and acetonitrile (10 mL). After 16 h, the reaction mixture was concentrated, and column chromatography (20% EtOAc/Hex, R_f 0.50) afforded **6b** as a yellow oil (0.104 g, 88%). ¹**H NMR** (300 MHz, CDCl₃) δ 8.15 (d, *J* = 8.0 Hz, 1H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.36 – 7.23 (m, 2H), 7.22 (s, 1H), 3.81 (s, 3H), 3.61 (t, *J* = 7.3 Hz, 2H), 3.23 (t, *J* = 7.2 Hz, 2H). ¹³**C NMR** (75 MHz, CDCl₃) δ 161.2, 159.1, 136.0, 130.1, 125.0, 124.2, 123.8, 118.7, 118.5, 115.8, 70.1, 52.7, 31.2, 28.7. **IR**: 3018.6 (w), 2947.1, (w), 2142.0 (s), 1732.7 (s), 1656.5 (s), 1604.1 (w), 1451.7 (s), 1380.4 (s), 1306.8 (s), 1251.7 (m), 1056.4 (m), 861.2 (w), 734.3 (s), 708.8 (m) cm⁻¹. **HRMS (ESI)** M/Z+ Calc. 349.0062, Obs. 349.0061.



Methyl 2-diazo-3-(3-(2-(1,3-dioxoisoindolin-2-yl)ethyl)-1*H*-indol-1-yl)-3- oxo propanoate (6c): The general procedure was followed using methyl 3-(3-(2-(1,3-dioxoisoindolin-2-yl)ethyl)-1*H*-indol-1-yl)-3-oxopropanoate (1.48 g, 3.78 mmol), triethylamine (700 μL, 5.02 mmol), tosyl azide (0.896 g, 4.54 mmol), and acetonitrile (20 mL). After 18 h, the reaction mixture was concentrated, and column chromatography (40% EtOAc/Hex, R_f 0.44) afforded **6c** as a yellow-brown solid (1.49 g, 95%). [m.p. 98-100°C] ¹H NMR (300 MHz, CDCl₃) δ 8.18 – 8.13 (m, 1H), 7.86 – 7.80 (m, 2H), 7.74 – 7.64 (m, 3H), 7.37 – 7.27 (m, 2H), 7.23 (s, 1H), 4.00 (t, J = 6.0 Hz, 2H), 3.81 (s, 3H), 3.10 (t, J = 6.0 Hz, 2H). ¹³C NMR (75 MHz, CDCl₃) (Rotamers!!!) δ 168.2, 161.2, 159.2, 136.1, 133.9, 133.8, 132.1, 130.5, 125.0, 124.1, 123.9, 123.2, 123.1, 122.1, 122.0, 119.4, 119.0, 118.8, 118.0, 115.8, 112.4, 111.1, 69.8, 52.7, 38.5, 37.4, 24.4, 24.2. **IR**: 3032.8 (s), 2942.4 (w), 2137.5 (s), 1708.4 (s), 1642.2 (m), 1604.1 (w), 1451.7 (w), 1379.6 (s), 1306.8 (s), 1256.4 (m), 1170.7 (m), 1095.3 (m), 1004.0 (w), 861.2 (m), 732.4 (s) cm⁻¹. **HRMS (ESI)** M/Z+ Calc. 416.1121, Obs. 416.1105.



Methyl 2-diazo-3-(3-(2-methoxy-2-oxoethyl)-1*H***-indol-1-yl)-3-oxopropanoate (6d):** The general procedure was followed using methyl 3-(3-(2-methoxy-2-oxoethyl)-1*H*-indol-1-yl)-3-oxopropanoate (1.49 g, 5.16 mmol), triethylamine (880 µL, 6.31 mmol), tosyl azide (1.22 g, 6.19 mmol), and acetonitrile (20 mL). After 18 h, the reaction mixture was concentrated, and column chromatography (40% EtOAc/Hex, R_f 0.43) afforded **6d** as a brown solid (1.36 g, 83%). [**m.p.** 77-79°C] ¹**H NMR** (300 MHz, CDCl₃) δ 8.17 (d, J = 7.8 Hz, 1H), 7.52 (d, J = 7.7 Hz, 1H), 7.41 – 7.26 (m, 3H), 3.84 (s, 3H), 3.73 (s, 2H), 3.72 (s, 3H). ¹³**C NMR** (75 MHz, CDCl₃) δ 171.1, 161.3, 159.2, 135.9, 130.3, 125.2, 125.1, 123.9, 118.9, 115.8, 114.1, 70.1, 52.7, 52.1, 30.7. **IR**: 2999.5 (w), 2961.4 (w), 2137.5 (s), 1721.8 (s), 1637.44 (s), 1599.3 (w), 1446.9 (s), 1364.2 (s), 1305.1 (s), 1253.8 (s), 1139.6 (s), 1051.6 (w), 870.7 (m), 747.9 (s) cm⁻¹. **HRMS (ESI)** M/Z+ Calc. 315.0855, Obs. 315.0860.



Methyl 2-diazo-3-(1*H***-indol-1-yl)-3-oxopropanoate (6e):** The general procedure was followed using methyl 3-(1*H*-indol-1-yl)-3-oxopropanoate (1.42 g, 6.54 mmol), triethylamine (1.82 mL, 13.07 mmol), tosyl azide (1.547 g, 7.845 mmol), and acetonitrile (30 mL). After 12 h, the reaction mixture was concentrated, and column chromatography (10% EtOAc/Hex, R_f 0.35) afforded **6e** as a yellow oil (1.49 g, 93.7%). ¹H

NMR (300 MHz, CDCl₃) δ 8.22 – 8.16 (m, 1H), 7.59 – 7.53 (m, 1H), 7.40 – 7.23 (m, 3H), 6.61 (dd, *J* = 3.8, 0.7 Hz, 1H), 3.83 (s, 3H). ¹³**C NMR** (75 MHz, CDCl₃) δ 161.3, 159.5, 135.7, 130.6, 127.4, 126.7, 124.7, 123.8, 120.9, 115.5, 108.2, 52.7. IR: 3162.8 (w), 3053.2 (w), 2953.6 (w), 2140.3 (s), 1710.8 (s), 1721.3 (s), 1657.8 (s), 1649.7 (s), 1529.0 (w), 1451.1 (s), 1380.5 (s), 1342.4 (s), 1298.4 (s), 1244.9 (m), 1139.5 (m), 1121.6 (m), 1090.6 (m), 1067.0 (m), 945.5 (w), 883.1 (m), 859.7 (m), 746.5 (s), 640.3 (w) cm⁻¹. **HRMS (ESI)** M/Z+ Calc. 243.0644, Obs. 243.0640.

C. Synthesis of the Cyclopropanes

The cyclopropanes were prepared using a modified version of Gonzalez-Bobes' protocol:⁴ A round bottom flask was charged with Rh_2esp_2 (0.1 mol%) and a magnetic stir bar. DCM (2.0 mL) was added to the flask. The reaction vessel was cooled to 0 °C, and the corresponding alkene (1.0 equiv) was added. After 10 min, the diazo reagent (1.3 equiv.) was dissolved in DCM (5 mL) and syringed into the reaction mixture. After 10 min, the ice bath was removed and the reaction proceeded at room temperature. Upon completion (monitored by TLC) or 12 h of reactivity, the reaction was quenched with saturated thiourea and stirred for 30 min. The organic layer was separated, and the aqueous layer extracted three times with DCM. The combined organic layers were washed with brine, dried with anhydrous sodium sulfate, filtered, concentrated under reduced pressure. The residue was purified by silica gel flash chromatography.



Methyl 2-(4-methoxyphenyl)-1-(3-methyl-1*H***-indole-1-carbonyl) cyclopropane carboxylate (3a):** The general procedure was followed using 4-methoxystyrene (0.201 g, 1.49 mmol), methyl 2-diazo-3-(3-methyl-1*H*-indol-1-yl)-3-oxopropanoate (0.500 g, 1.94 mmol), Rh₂esp₂ (1.5 mg, 1.98 µmol) and DCM (8 mL). After 12 h, the reaction was quenched, and column chromatography (20% EtOAc/Hex, R_f 0.52) afforded **3a** as a pale yellow solid (0.328 g, 60%). [**m.p.** 110-112°C] ¹**H NMR** (300 MHz, CDCl₃) δ 8.45 (d, *J* = 8.0 Hz, 1H), 7.61-7.45 (m, 1H), 7.44 – 7.26 (m, 5H), 6.90 – 6.83 (m, 2H), 3.81 (s, 3H), 3.41 (t, *J* = 4Hz, 1H), 3.41 (s, 3H), 2.40 (dd, *J* = 8.3, 5.2 Hz, 1H), 2.28 (s, 3H), 1.82 (dd, *J* = 9.3, 5.2 Hz, 1H). ¹³**C NMR** (75 MHz, CDCl₃) δ 168.0, 165.8, 158.9, 136.0, 131.5, 130.2, 126.1, 125.4, 123.8, 121.5, 119.2, 118.9, 116.5, 113.6, 55.2, 52.8, 39.5, 31.1, 18.8, 9.8. **IR**: 3050.0 (w), 2914.3 (m), 1742.9 (m), 1681.0 (s), 1600.0 (m), 1514.29 (m), 1450.0 (s), 1346.3 (s), 1246.8 (s), 1176.5 (s), 1028.6 (s), 838.1 (s), 748.2 (s) cm⁻¹. **HRMS (ESI)** M/Z+ Calc. 363.1471, Obs. 363.1471.



Methyl 2-(2-methoxyphenyl)-1-(3-methyl-1H-indole-1-carbonyl)cyclopropane carboxylate (3b): The general procdure was followed using 1-methoxy-2-vinylbenzene (0.095 g, 0.709 mmol), methyl 2-diazo-3-(3-methyl-1*H*-indol-1-yl)-3-oxopropanoate (0.210 g, 0.816 mmol), Rh₂esp₂ (1.0 mg, 1.31 µmol), and DCM (10 mL). After 12 h, the reaction was quenched, and column chromatography (20% EtOAc/Hex, R_f 0.35) afforded **3b** as a pale yellow solid (0.196 g, 76%). [**m.p.** 106-108°C] ¹**H NMR** (300 MHz, CDCl₃) δ 8.54 (d, J = 7.9 Hz, 1H), 7.57 – 7.27 (m, 6H), 7.04 – 6.95 (m, 1H), 6.91 (d, J = 8.2 Hz, 1H), 3.88 (s, 3H), 3.45 (s, 3H), 3.45 (t, 1H), 2.35 (dd, J = 7.9, 4.5 Hz, 1H), 2.32 (d, J = 1.3 Hz, 3H), 1.97 (dd, J = 9.3, 5.0 Hz, 1H). ¹³**C NMR** (75 MHz, CDCl₃) δ 168.4, 165.9, 158.5, 136.0, 131.4, 130.0, 129.7, 128.7, 127.7, 125.0, 123.5, 122.8, 122.2, 120.0, 118.6, 118.1, 116.5, 109.9, 66.7, 55.2, 52.4, 38.0, 28.3, 21.5, 19.0, 14.6, 9.7. **IR**: 3059.9 (w), 2983.6 (w), 1720.3 (s), 1658.0 (s), 1441.1 (s), 1338.7 (s), 1233.7 (m), 712.5 (s), 674.4 (m) cm⁻¹. **HRMS (ESI)** M/Z+ Calc. 363.1471, Obs. 363.1471.



Methyl 1-(3-methyl-1*H***-indole-1-carbonyl)-2-phenylcyclopropanecarboxylate (3c):** The general procedure was followed using styrene (0.100 g, 0.960 mmol), methyl 2-diazo-3-(3-methyl-1*H*-indol-1-yl)-3-oxopropanoate (0.329 g, 1.28 mmol), Rh_2esp_2 (1.0 mg, 1.32 µmol), and DCM (13 mL). After 12 h, the reaction was quenched, and column chromatography (20% EtOAc/Hex, R_f 0.60) afforded **3c** as a white solid (0.273 g, 85%). [**m.p.** 130-132°C] ¹**H NMR** (300 MHz, CDCl₃) δ 8.46 (d, *J* = 8.0 Hz, 1H), 7.55 – 7.48 (m, 1H), 7.45 – 7.26 (m, 8H), 3.48 (t, *J* = 8.8 Hz, 1H), 3.40 (s, 3H), 2.46 (dd, *J* = 8.3, 5.2 Hz, 1H), 2.29 (s, 3H), 1.84 (dd, *J* = 9.3, 5.2 Hz, 1H). ¹³**C NMR** (75 MHz, CDCl₃) δ 167.9, 165.6, 136.0, 134.2, 131.5, 129.1, 128.2, 127.4, 125.4, 123.8, 121.4, 119.2, 118.9, 116.5, 52.8, 39.5, 31.5, 18.5, 9.8. **IR**: 3037.6 (w), 2951.9 (w), 2918.5 (w), 1732.7 (s), 1692.0 (s), 1446.9 (s), 1390.8 (s), 1348.3 (s), 1208.8 (m), 1051.6 (m), 742.1 (m), 684.9 (m) cm⁻¹. **HRMS (ESI)** M/Z+ Calc. 333.1365, Obs. 333.1367.



Methyl 2-(4-fluorophenyl)-1-(3-methyl-1*H***-indole-1-carbonyl)cyclopropane carboxylate (3d)**: The general procedure was followed using 4-fluorostyrene (0.146 g, 1.19 mmol), methyl 2-diazo-3-(3-methyl-1*H*-indol-1-yl)-3-oxopropanoate (0.356 g, 1.38 mmol), Rh_2esp_2 (1.6 mg, 2.10 µmol), and DCM (8 mL). After 10 h, the reaction was quenched, and column chromatography (20% EtOAc/Hex, R_f 0.64) afforded **3d** as a pale green solid (0.273 g, 65%). [**m.p.** 120-122°C] ¹**H NMR** (300 MHz, CDCl₃) δ 8.45 (d, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 8.3 Hz, 1H), 7.44 – 7.29 (m, 4H), 7.25 (s, 1H), 7.07 – 6.98 (m, 2H), 3.46 (t, *J* = 8.5 Hz, 1H), 3.42 (s, 3H), 2.42 (dd, *J* = 8.2, 5.3 Hz, 1H), 2.29 (s, 3H), 1.84 (dd, *J* = 9.3, 5.3 Hz, 1H). ¹³**C NMR** (75 MHz, CDCl₃) δ 167.8, 165.4, 163.8, 160.5, 136.0, 131.5, 130.7, 130.0, 125.4, 123.9, 121.3, 119.4, 118.9, 116.5, 115.3, 115.0, 52.9, 39.5, 30.8, 18.7, 9.8. **IR**: 3010.0 (w), 2947.1 (w), 2904.3 (w), 1727.9 (m), 1685.1 (s), 1518.4 (s), 1456.5 (s), 1399.3 (s), 1337.4 (s), 1215.2 (s), 1146.9 (s), 1051.7 (m), 846.9 (m), 723.1 (s), 608.7 (m) cm⁻¹. **HRMS (ESI)** M/Z+ Calc. 351.1271, Obs. 351.1268.



Methyl 2-(4-chlorophenyl)-1-(3-methyl-1*H***-indole-1-carbonyl)cyclopropane carboxylate (3e): The general procedure was followed using 4-chlorostyrene (0.124 g, 0.898 mmol), methyl 2-diazo-3-(3-methyl-1***H***-indol-1-yl)-3-oxopropanoate (0.250 g, 0.973 mmol), Rh₂esp₂ (1.5 mg, 1.71 µmol), and DCM (8 mL). After 12 h, the reaction was quenched, and column chromatography (20% EtOAc/Hex, R_f 0.64) afforded 3e** as a white solid (0.275 g, 83%). [**m.p.** 129-131°C] ¹**H NMR** (300 MHz, CDCl₃) δ 8.46 (d, *J* = 8.0 Hz, 1H), 7.55 – 7.50 (m, 1H), 7.45 – 7.29 (m, 6H), 7.26 (d, *J* = 1.3 Hz, 1H), 3.44 (t, J = 6.8 Hz, 1H), 3.44 (s, 3H), 2.43 (dd, *J* = 8.3, 5.3 Hz, 1H), 2.30 (s, 3H), 1.86 (dd, *J* = 9.3, 5.3 Hz, 1H). ¹³**C NMR** (75 MHz, CDCl₃) δ 167.7, 165.3, 136.0, 133.3, 132.8, 131.5, 130.4, 128.3, 125.4, 123.9, 121.2, 119.4, 118.9, 116.5, 52.9, 39.5, 30.8, 18.6, 9.7. **IR**: 3010.0 (w), 2951.9 (w), 2913.8 (w), 1727.9 (s), 1691.9 (s), 1485.0 (m), 1451.0 (s), 1389.9 (s), 1347.9 (s), 1218.3 (m), 1156.4 (m), 1080.2 (m), 842.1 (m), 742.1 (m) 708.7 (w) cm⁻¹. **HRMS (ESI)** M/Z+ Calc. 367.0975, Obs. 367.0981.



Methyl 1-(3-methyl-1*H***-indole-1-carbonyl)-2-(4-nitrophenyl)cyclopropane carboxylate (3f):** The general procedure was followed using 4-nitrostyrene (0.252 g, 1.69 mmol), methyl 2-diazo-3-(3-methyl-1*H*-indol-1-yl)-3-oxopropanoate (0.505 g, 1.97 mmol), Rh_2esp_2 (1.2 mg, 1.98 µmol), and DCM (8 mL). After 10 h, the reaction was quenched, and column chromatography (20% EtOAc/Hex, R_f 0.69) afforded **3f** as a yellow solid (0.325 g, 51%). [**m.p.** 163-165°C] ¹**H NMR** (300 MHz, CDCl₃) δ 8.43 (d, *J* = 7.9 Hz, 1H), 8.24 – 8.17 (m, 2H), 7.58 – 7.50 (m, 3H), 7.45 – 7.30 (m, 2H), 7.21 (s, 1H), 3.54 (t, *J* = 8.8 Hz, 1H), 3.43 (s, 3H), 2.51 (dd, *J* = 8.3, 5.4 Hz, 1H), 2.29 (s, 3H), 1.94 (dd, *J* = 9.2, 5.4 Hz, 1H). ¹³**C NMR** (75 MHz, CDCl₃) δ 167.5, 164.8, 147.3, 142.0, 136.0, 131.5, 130.0, 125.6, 124.1, 123.4, 120.9, 119.8, 119.0, 116.5, 53.1, 40.0, 30.9, 18.9, 9.8. **IR:** 3000.0 (w), 2913.8 (w), 2851.9 (w), 1727.9 (m), 1691.2 (s), 1599.3 (m), 1508.9 (s), 1449.8 (s), 1390.3 (s), 1342.9 (s), 1216.9 (s), 1142.1 (m), 1046.9 (m), 856.4 (m), 736.7 (s), 699.2 (m) cm⁻¹. **HRMS (ESI)** M/Z+ Calc. 378.1216, Obs. 378.1208.



Methyl 2-(furan-2-yl)-1-(3-methyl-1H-indole-1-carbonyl)cyclopropanecarboxylate (3g): The general procedure was followed using 2-vinylfuran (0.059 g, 0.627 mmol), methyl 2-diazo-3-(3-methyl-1*H*-indol-1-yl)-3-oxopropanoate (0.210 g, 0.816 mmol), Rh₂esp₂ (1.0 mg, 1.31 µmol), and DCM (10 mL). After 12 h, the reaction was quenched, and column chromatography (15% EtOAc/Hex, R_f 0.35) afforded **3g** as a white solid (0.084 g, 41%). [**m.p.** 95-97°C] ¹**H NMR** (300 MHz, CDCl₃) δ 8.45 (d, *J* = 7.9 Hz, 1H), 7.56 – 7.50 (m, 1H), 7.44 – 7.30 (m, 4H), 6.41 – 6.35 (m, 1H), 6.32 – 6.28 (m, 1H), 3.54 (s, 3H), 3.25 (t, *J* = 8.7 Hz, 1H), 2.34 (dd, *J* = 6.9, 4.2 Hz, 1H), 2.31 (d, *J* = 1.3 Hz, 3H), 1.96 (dd, *J* = 9.5, 5.2 Hz, 1H). ¹³C **NMR** (75 MHz, CDCl₃) 167.6, 164.9, 149.1, 142.3, 136.0, 131.5, 125.3, 123.9, 121.7, 119.3, 118.8, 116.5, 110.5, 108.8, 52.9, 38.2, 24.7, 18.7, 9.8. **IR**: 3086.97 (w), 2972.5 (w), 1726.4 (m), 1711.4 (m), 1441.3 (m), 1382.7 (m), 759.9 (s), 663.0 (s) cm⁻¹. **HRMS (ESI)** M/Z+ Calc. 323.1158, Obs. 323.1159.



Methyl 2-methyl-1-(3-methyl-1H-indole-1-carbonyl)-2 phenylcyclopropane carboxylate (3h): The general procedure was followed using prop-1-en-2-ylbenzene (0.123 g, 1.046 mmol), methyl 2-diazo-3-(3-methyl-1*H*-indol-1-yl)-3-oxopropanoate (0.350 g, 1.360 mmol), Rh₂esp₂ (1.0 mg, 1.31 µmol), and DCM (10 mL). After 12 h, the reaction was quenched, and column chromatography (20% EtOAc/Hex, R_f 0.38) afforded **3h** as a colorless oil (0.225 g, 62%). ¹**H NMR** (300 MHz, CDCl₃) δ 8.61 (d, *J* = 7.8 Hz, 0.90), 7.88 – 7.80 (m, 0.16), 7.63 – 7.55 (m, 1.05), 7.54 – 7.28 (m, 8.37), 7.24 – 7.20 (m, 0.51), 3.69 (s, 0.40), 3.46 (d, *J* = 0.8 Hz, 3), 2.67 (d, *J* = 5.5 Hz, 0.14), 2.53 (d, *J* = 5.1 Hz, 1.33), 2.39 (s, 2.99), 2.26 (d, *J* = 1.3 Hz, 0.42), 1.96 (d, *J* = 6.6 Hz, 0.55) 1.85 (d, *J* = 5.1 Hz, 1.03), 1.64 (s, 0.27), 1.55 (s, 2.91). ¹³**C NMR** (75 MHz, CDCl₃) δ 168.4, 164.9, 140.6, 136.0, 131.5, 128.4, 128.0, 127.8, 127.2, 125.3, 123.8, 122.3, 118.8, 118.7, 116.8, 52.6, 41.9, 38.4, 26.0, 25.7, 9.8. **IR**: 3080.6 (w), 2939.6 (w), 2896.9 (w), 1724.3 (s), 1657.6 (s), 1421.8 (s), 1382.7 (s), 1267.7 (s), 789.5 (s), 664.3 (s) cm⁻¹. **HRMS (ESI)** M/Z+ Calc. 347.1521, Obs. 347.1516.



Methyl 2,2-diethyl-1-(3-methyl-1H-indole-1-carbonyl)cyclopropanecarboxylate (3i): The general procedure was followed using 3-methylenepentane (0.062 g, 0.747 mmol), methyl 2-diazo-3-(3-methyl-1*H*-indol-1-yl)-3-oxopropanoate (0.250 g, 0.971 mmol), Rh₂esp₂ (1.0 mg, 1.31 µmol), and DCM (10 mL). After 12 h, the reaction was quenched, and column chromatography (15% EtOAc/Hex, R_f 0.35) afforded **3i** as a white solid (0.117 g, 50%). [**m.p.** 78–80°C] ¹**H NMR** (300 MHz, CDCl₃) δ 8.40 (d, *J* = 8.0 Hz, 1H), 7.45 – 7.39 (m, 1H), 7.33 – 7.21 (m, 3H), 3.58 (s, 3H), 2.21 (d, *J* = 1.3 Hz, 3H), 1.97 – 1.73 (m, 3H), 1.62 (dd, *J* = 4.8, 1.2 Hz, 1H), 1.51 (d, *J* = 4.8 Hz, 1H), 0.99 (t, *J* = 7.5 Hz, 3H), 0.91 – 0.71 (m, 4H). ¹³**C NMR**

 $\begin{array}{l} (75 \text{ MHz, CDCI}_3) \ \bar{\delta} \ 169.7, \ 165.7, \ 135.9, \ 131.4, \ 125.0, \ 123.6, \ 122.7, \ 118.6, \ 118.0, \ 116.7, \ 52.6, \ 41.4, \ 40.1, \\ 27.4, \ 26.2, \ 21.5, \ 10.7, \ 10.6, \ 9.7. \ \textbf{IR}: \ 3059.7 \ (w), \ 2946.2 \ (m), \ 1714.5 \ (s), \ 1657.6 \ (s), \ 1414.8 \ (s), \ 1381.3 \ (s), \\ 1292.4 \ (s), \ 1081.2 \ (s), \ 728.5 \ (s), \ 663.3 \ (m) \ cm^{-1}. \ \textbf{HRMS (ESI)} \ M/Z + \ Calc. \ 313.1678, \ Obs. \ 313.1683. \end{array}$



Methyl 1-(3-methyl-1H-indole-1-carbonyl)spiro[2.4]heptane-1-carboxylate (3j): The general procedure was followed using methylenecyclopentane (0.098 g, 1.20 mmol), methyl 2-diazo-3-(3-methyl-1*H*-indol-1-yl)-3-oxopropanoate (0.400 g, 1.55 mmol), Rh₂esp₂ (1.0 mg, 1.31 µmol), and DCM (10 mL). After 4 h, the reaction was quenched, and column chromatography (15% EtOAc/Hex, R_f 0.35) afforded **3j** as a colorless oil (0.342 g, 92%). ¹H NMR (300 MHz, CDCl₃) δ 8.52 (s, 1H), 7.55 – 7.48 (m, 1H), 7.43 – 7.27 (m, 2H), 7.10 (s, 1H), 3.65 (s, 3H), 2.31 (s, 3H), 2.24 – 1.98 (m, 2H), 1.90 – 1.62 (m, 7H), 1.46 – 1.33 (m, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 170.1, 165.6, 135.7, 131.2, 124.9, 123.4, 121.9, 118.5, 118.3, 116.3, 52.2, 40.0, 39.2, 34.4, 34.2, 33.6, 31.6, 31.3, 29.0, 25.5, 25.5, 25.0, 22.4, 20.4, 13.9, 9.5. **IR**: 3040.0 (w), 2892.6 (w), 1765.3 (s), 1711.65 (s), 1439.1 (s), 1359.7 (s), 715.5 (s), 662.9 (m) cm⁻¹. **HRMS (ESI)** M/Z+ Calc. 311.1521, Obs. 311.1515.





Methyl 2-((*tert***-butyldiphenylsilyl)methyl)-1-(3-methyl-1***H***-indole-1-carbonyl) cyclopropanecarboxylate (3I): The general procedure was followed using allyl(***tert***-butyl)diphenylsilane (0.294 g, 1.05 mmol), methyl 2-diazo-3-(3-methyl-1***H***-indol-1-yl)-3-oxopropanoate (0.350 g, 1.36 mmol), Rh₂esp₂ (1.0 mg, 1.31 µmol), and DCM (8 mL). After 6 h, the reaction was quenched, and column chromatography (20% EtOAc/Hex, R_f 0.45) afforded 3I** as a white solid (0.332 g, 62%). [m.p. 127 – 129°C] ¹H NMR (300 MHz, CDCl₃) δ 8.39 (d, *J* = 7.9 Hz, 1H), 7.76 – 7.64 (m, 4H), 7.57 – 7.23 (m, 9H), 7.17 (s, 1H), 3.69 (s, 3H), 2.28 (s, 3H), 1.74 – 1.66 (m, 1H), 1.57 – 1.40 (m, 2H), 1.31 (dd, *J* = 8.5, 5.5 Hz, 2H), 1.13 (s, 9H). ¹³C NMR (75 MHz, CDCl₃) δ 169.6, 166.3, 136.0, 136.9, 135.8, 134.1, 133.8, 131.4, 129.3, 129.2, 127.7, 127.6, 125.1, 123.6, 121.6, 118.7, 118.6, 116.4, 52.7, 37.3, 27.8, 25.7, 23.0, 18.1, 9.7, 8.0. IR: 3066.2 (w), 2932.8 (m), 2842.4 (m), 1728.1 (s), 1692.7 (s), 1451.6 (s), 1389.5 (m), 1348.5 (s), 1213.1 (m), 1153.3 (m), 1106.0 (m), 818.3 (w), 749.1 (m), 701.5 (s) cm⁻¹. HRMS (ESI) M/Z+ Calc. 509.2386, Obs. 509.2388.



Methyl 2-(1,3-dioxoisoindolin-2-yl)-1-(3-methyl-1*H***-indole-1-carbonyl)cyclopropane carboxylate (3m): The general procedure was followed using N-vinyl-phthalimide (0.155 g, 897 µmol), methyl 2-diazo-3-(3-methyl-1***H***-indol-1-yl)-3-oxopropanoate (0.300 g, 1.17 mmol), Rh₂esp₂ (1.1 mg, 1.45 µmol), and DCM (8 mL). After 12 h, the reaction was quenched, and column chromatography (20% EtOAc/Hex, R_f 0.20) afforded 3m** as a white solid (0.247 g, 68%). [**m.p.** 88-90°C] *Diastereomeric Ratio*: (2.5:1). ¹**H NMR** (300 MHz, CDCl₃) δ 8.43 (d, *J* = 7.4 Hz, 0.83), 8.22 (d, *J* = 6.1 Hz, 0.27), 7.98 (s, 1.00), 7.83 (dt, *J* = 6.9, 3.5 Hz, 2.19), 7.76 – 7.66 (m, 2.80), 7.66 – 7.58 (m, 1.00), 7.51 – 7.45 (m, 1.16), 7.42 – 7.18 (m, 3.88), 4.16 (dd, *J* = 9.2, 6.8 Hz, 0.23), 3.71 (s, 1.11), 3.67 (dd, *J* = 8.0, 6.5 Hz, 1.18), 3.57 (s, 3.00), 3.47 (t, *J* = 6.5 Hz, 0.63), 2.59 (t, *J* = 6.4 Hz, 1.00), 2.35 – 2.27 (m, 4.00), 2.23 (s, 1.45), 2.17 (dd, *J* = 9.2, 6.2 Hz, 0.60). ¹³C NMR (75 MHz, CDCl₃) δ 169.7, 168.2, 168.0, 167.8, 164.0, 136.0, 134.3, 134.2, 134.2, 131.8, 131.4, 131.3, 125.3, 125.1, 124.0, 123.8, 123.6, 123.4, 122.5, 122.1, 119.0, 118.9, 118.8, 118.7, 116.5, 116.3, 53.4, 53.3, 48.8, 35.9, 33.9, 20.6, 17.4, 9.8, 9.6. IR: 3056.7 (w), 2951.9 (w), 1770.8 (w), 1720.5 (s), 1680.3 (s), 1604.1 (w), 1442.2 (m), 1389.3 (s), 1308.8 (s), 1223.1 (s), 1070.7 (m), 970.7 (w), 865.9 (w), 714.8 (s) cm⁻¹ HRMS (ESI) M/Z+ Calc. 402.1216, Obs. 402.1213.



Methyl 1-(3-methyl-1H-indole-1-carbonyl)-2-(phenylthio)cyclopropanecarboxylate (3n): The general procedure was followed using phenyl(vinyl)sulfane (0.311 g, 2.29 mmol), methyl 2-diazo-3-(3-methyl-1*H*-indol-1-yl)-3-oxopropanoate (0.722 g, 2.81 mmol), Rh₂esp₂ (1.8 mg, 2.4 µmol), and DCM (13 mL). After 12 h, the reaction was quenched, and column chromatography (20% EtOAc/Hex, R_f 0.40) afforded **3n** as a colorless oil (0.125 g, 15%). ¹H NMR (300 MHz, CDCl₃) δ 8.44 (d, *J* = 7.9 Hz, 1H), 7.55 – 7.47 (m, 3H), 7.43 – 7.28 (m, 4H), 7.23 – 7.16 (m, 2H), 3.56 (dd, *J* = 7.5, 5.6 Hz, 1H), 3.52 (s, 3H), 2.25 (d, *J* = 1.3 Hz, 3H), 2.15 (dd, *J* = 7.3, 5.7 Hz, 1H), 1.92 (dd, *J* = 9.2, 5.7 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 167.3, 164.6, 135.9, 135.4, 131.6, 129.0, 127.7, 126.0, 125.7, 124.0, 121.1, 119.7, 119.0, 116.6, 53.1, 39.8, 28.2, 20.0, 9.7. IR: 3080.6 (w), 2939.6 (w), 2896.9 (w), 1724.3 (s), 1657.6 (s), 1421.8 (s), 1382.7 (s), 1267.7 (s), 789.5 (s), 664.3 (s) cm⁻¹. HRMS (ESI) M/Z+ Calc. 365.1079, Obs. 365.1083.



Methyl 6-(3-methyl-1*H***-indole-1-carbonyl)-2-oxabicyclo[3.1.0]hexane-6-carboxylate (30):** The general procedure was followed using 2,3-dihydrofuran (0.073 g, 1.05 mmol), methyl 2-diazo-3-(3-methyl-1*H*-indol-1-yl)-3-oxopropanoate (0.350 g, 1.36 mmol), Rh₂esp₂ (1.0 mg, 1.31 µmol), and DCM (9 mL). After 10 h, the reaction was quenched and column chromatography (20% EtOAc/Hex, R_f 0.30) afforded **3o** as a brown solid (0.235 g, 75%). [**m.p.** 83-85°C] ¹**H NMR** (300 MHz, CDCl₃) δ 7.72 – 7.63 (m, 1H), 7.56 – 7.49 (m, 2H), 7.31 – 7.17 (m, 2H), 6.27 (d, *J* = 6.2 Hz, 1H), 4.19 – 4.10 (m, 1H), 4.05 – 3.97 (m, 1H), 3.96 – 3.85 (m, 1H), 3.72 (s, 3H), 2.35 (s, 3H), 2.25 – 2.16 (m, 2H). ¹³**C NMR** (75 MHz, CDCl₃) δ 164.1, 156.4, 135.8, 130.3, 125.0, 123.2, 121.7, 118.8, 115.2, 114.2, 108.3, 89.2, 67.1, 50.9, 47.3, 32.0, 9.5. **IR**: 2951.9 (w), 2880.5 (w), 1740.9 (s), 1691.3 (s), 1599.3 (w), 1449.2 (s), 1348.9 (s), 1105.2 (s), 1064.3 (s), 995.6 (s), 734.8 (s) cm⁻¹. **HRMS (ESI)** M/Z+ Calc. 299.1158, Obs. 299.1155.



Methyl 7-(3-methyl-1*H***-indole-1-carbonyl)-2-oxabicyclo[4.1.0]heptane-7-carboxylate (3p):** The general procedure was followed using 2,3-dihydropyran (95 μL, 1.04 mmol), methyl 2-diazo-3-(3-methyl-1*H*-indol-1-yl)-3-oxopropanoate (0.350 g, 1.36 mmol), Rh₂esp₂ (1.0 mg, 1.31 μmol), and DCM (8 mL). After 12 h, the reaction was quenched, and column chromatography (20% EtOAc/Hex, R_f 0.40) afforded **3p** as a pale red solid (0.142 g, 43%). [**m.p.**123-125°C]. ¹**H NMR** (300 MHz, CDCl₃) δ 8.45 (d, *J* = 8.1 Hz, 1H), 7.51 – 7.43 (m, 1H), 7.42 – 7.22 (m, 2H), 7.17 (s, 1H), 6.54 (s, 1H), 4.60 (s, 1H), 4.00 – 3.87 (m, 2H), 3.77 (s, 3H), 2.39 – 2.27 (m, 1H), 2.26 (s, 3H), 2.14 – 2.02 (m, 1H), 1.97 – 1.77 (m, 2H). ¹³**C NMR** (75 MHz, CDCl₃) δ 168.8, 165.6, 144.5, 136.0, 131.2, 125.3, 123.8, 121.1, 119.2, 118.7, 116.7, 106.4, 80.7, 65.6, 56.0, 52.6, 21.8, 21.5, 9.6. **IR**: 2942.4 (w), 2866.2 (w), 1756.5 (s), 1694.6 (s), 1651.7 (s), 1608.9 (w), 1451.7 (s), 1385.0 (s), 1349.3 (s), 1140.7 (s), 1065.9 (s), 1018.3 (m), 937.4 (m), 745.4 9 (s) cm⁻¹. **HRMS** (**ESI**) M/Z+ Calc. 313.1314, Obs. 313.1312.



2-benzyl 7-methyl 7-(3-methyl-1*H***-indole-1-carbonyl)-2-azabicyclo[4.1.0]heptane-2,7-dicarboxylate (3q).** The general procedure was followed using benzyl 3,4-dihydropyridine-1(2*H*)-carboxylate (0.179 g, 0.897 mmol), methyl 2-diazo-3-(3-methyl-1*H*-indol-1-yl)-3-oxopropanoate (0.300 g, 1.17 mmol), Rh₂esp₂ (1.3 mg, 1.79 µmol), and DCM (9 mL). After 12 h, the reaction was quenched, and column chromatography (20% EtOAc/Hex, R_f 0.25) afforded **3q** as a colorless oil (0.295 g, 74%). ¹**H NMR** (300 MHz, CDCl₃) δ 8.48 (d, *J* = 7.9 Hz, 1H), 7.49 (d, *J* = 7.5 Hz, 1H), 7.42 – 7.26 (m, 6H), 7.13 (t, *J* = 32.4 Hz, 2H), 5.20 (s, 2H), 4.77 (d, *J* = 26.5 Hz, 1H), 3.76 (d, *J* = 11.9 Hz, 3H), 3.71 – 3.44 (m, 2H), 2.27 (s, 3H), 2.51 – 2.02 (m, 2H), 1.96 – 1.74 (m, 2H). ¹³C NMR (75 MHz,CDCl₃) δ 168.5, 165.4, 153.4, 152.6, 135.9, 135.8, 131.2, 128.4, 128.1, 128.0, 126.2, 125.7, 125.4, 123.8, 121.1, 119.3, 118.7, 116.7, 111.5, 110.8, 67.6, 57.5, 52.7, 41.9, 41.7, 23.5, 22.8, 21.1, 14.5, 9.6. IR: 2942.4 (w), 2880.5 (w), 1751.6 (w), 1703.3 (s), 1691.6 (s), 1449.2 (m), 1406.5 (m), 1319.9 (m), 1260.5 (m), 1172.1 (m), 747.1 (m) cm⁻¹. HRMS (ESI) M/Z+ Calc. 446.1842, Obs. 446.1840.

Methyl 1-(1*H***-indole4-1-carbonyl)-2-(4-methoxyphenyl)cyclopropanecarboxylate (3r):** The general procedure was followed using 4-methoxystyrene (0.061 g, 0.459 mmol) methyl 2-diazo-3-(5-methyl-1*H*-indol-1-yl)-3-oxopropanoate (0.331 g, 2.466 mmol), Rh₂esp₂ (1.87 mg, 2.4 µmol), and DCM (20 mL). After 12 h, the reaction was quenched, and column chromatography (20% EtOAc/Hex, R_f 0.30) afforded **3r** as a white solid (0.625 g, 72.8%). [**m.p.** 83-85°C] ¹**H NMR** (300 MHz, CDCl₃) δ 8.44 (d, J = 8.2 Hz, 1H), 7.56 – 7.46 (m, 2H), 7.39 – 7.19 (m, 4H), 6.86 – 6.80 (m, 2H), 6.63 – 6.60 (m, 1H), 3.76 (s, 3H), 3.44 – 3.34 (m, 4H), 2.38 (dd, J = 8.3, 5.3 Hz, 1H), 1.82 (dd, J = 9.7, 5.6, 0.7 Hz, 1H). ¹³**C NMR** (75 MHz, CDCl₃) δ 167.8, 166.2, 158.9, 135.7, 130.4, 130.1, 125.8, 125.2, 124.7, 124.0, 120.9, 116.4, 113.5, 109.7, 55.1, 52.7, 39.3, 31.2, 18.8 **IR**: 3109.7 (w), 3010.1 (w), 2947.0 (w), 2827.4 (w), 1741.56 (m), 1715.0 (s), 1685.1 (s), 1615.4 (m), 1505.8 (m), 1450.0 (s), 1376.29 (m), 1333.4 (s), 1306.6 (s), 1246.1 (s), 1160.6 (s), 1149.4 (s), 1123.91 (m), 1074.1 (m), 1030.9 (m), 951.2 (m), 841.7(m), 747.6 (s), 629.1 (m) cm⁻¹. **HRMS (ESI)** M/Z+ Calc. 349.1314, Obs. 349.1310.



Methyl 1-(3-(2-bromoethyl)-1H-indole-1-carbonyl)-2-(4-methoxyphenyl) cyclopropanecarboxylate (3s): The general procedure was followed using 4-methoxy styrene (0.073 g, 0.549 mmol), methyl 3-(3-(2-bromoethyl)-1*H*-indol-1-yl)-2-diazo-3-oxopropanoate (0.250 g, 0.713 mmol), Rh₂esp₂ (1.0 mg, 1.31 µmol), and DCM (15 mL). After 12 h, the reaction was quenched, and column chromatography (20% EtOAc/Hex, R_f 0.35) afforded **3s** as a white solid (0.188 g, 75%). [**m.p.** 122-124°C]. ¹**H NMR** (300 MHz, CDCl₃) δ 8.43 (d, *J* = 8.1 Hz, 1H), 7.51 – 7.45 (m, 1H), 7.41 – 7.19 (m, 5H), 6.86 – 6.79 (m, 2H), 3.76 (s, 3H), 3.61 (t, *J* = 7.0 Hz, 2H), 3.42 – 3.34 (m, 4H), 3.23 (t, *J* = 7.3, 4.4 Hz, 2H), 2.38 (dd, *J* = 8.3, 5.3 Hz, 1H), 1.82 (dd, *J* = 9.4, 5.2 Hz, 1H). ¹³**C NMR** (75 MHz, CDCl₃) δ 167.8, 166.0, 158.9, 136.0, 130.1, 130.0, 126.0, 125.6, 124.0, 122.4, 120.1, 119.3, 118.5, 116.7, 113.6, 55.2, 52.8, 43.4, 39.3, 31.4, 31.3, 28.7, 18.9. **IR**: 2982.4 (w), 2917.1 (w), 1722.1 (s), 1658.4 (s), 1441.3 (s), 1375.7 (s), 934.5 (s), 700.5 (s), 662.9 (m) cm⁻¹. **HRMS (ESI) M/Z+** Calc. 455.0708, Obs. 455.0732.



Methyl 1-(3-(2-(1,3-dioxoisoindolin-2-yl)ethyl)-1*H*-indole-1-carbonyl)-2-(4-methoxy phenyl)cyclopropanecarboxylate (3t): The general procedure was followed using 4-methoxystyrene (0.208 g, 1.55 mmol), methyl 3-(3-(2-(1,3-dioxoisoindolin-2-yl)ethyl)-1*H*-indol-1-yl)-3-oxopropanoate (0.810 g, 1.95 mmol), Rh₂esp₂ (1.3 mg, 1.71 µmol), and DCM (8 mL). After 12 h, the reaction was quenched, and column chromatography (40% EtOAc/Hex, R_f 0.38) afforded **3t** as a pale brown solid (0.182 g, 23%). [m.p. 158-160°C] ¹H NMR (300 MHz, CDCl₃) δ 8.44 (d, *J* = 7.9 Hz, 1H), 7.88 – 7.81 (m, 2H), 7.78 – 7.65 (m, 3H), 7.44 – 7.24 (m, 5H), 6.92 – 6.83 (m, 2H), 4.02 (t, *J* = 7.2 Hz, 2H), 3.81 (s, 3H), 3.39 (t, J = 9.0, 1H), 3.38 (s, 3H), 3.11 (t, *J* = 7.7 Hz, 2H), 2.41 (dd, *J* = 8.3, 5.3 Hz, 1H), 1.79 (dd, *J* = 9.4, 5.3 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃) (Rotamers!!) δ 168.2, 167.7, 166.0, 158.9, 136.1, 134.0, 133.8, 132.0, 130.4, 130.2, 126.0, 125.6, 124.0, 123.3, 123.2, 122.1, 122.0, 119.6, 119.5, 119.0, 118.9, 116.6, 113.6, 55.2, 53.4, 52.7, 39.6, 38.5, 37.4, 31.3, 24.3, 18.9. IR: 3051.9 (w), 2942.4 (w), 1760.0 (w), 1708.8 (s), 1685.1 (s), 1594.6 (m), 1513.6 (m), 1442.2 (m), 1375.5 (m), 1242.2 (m), 1104.0 (w), 832.6 (m), 732.8 (s), cm⁻¹. HRMS (ESI) M/Z+ Calc. 522.1791, Obs. 522.1777.



Methyl 1-(3-(2-methoxy-2-oxoethyl)-1*H*-indole-1-carbonyl)-2-(4-methoxyphenyl) cyclopropanecarboxylate (3u): The general procedure was followed using 4-methoxystyrene (0.211 g, 1.57 mmol), methyl 2-diazo-3-(3-(2-methoxy-2-oxoethyl)-1*H*-indol-1-yl)-3-oxopropanoate (0.611 g, 1.94 mmol,), Rh₂esp₂ (1.5 mg, 1.98 µmol), and DCM (8 mL). After 14 h, the reaction was quenched, and column chromatography (EtOAc/Hex, R_f 0.21) afforded **3u** as a yellow solid (0.312 g, 47%). [m.p. 82 – 84 $^{\circ}$ C]. ¹H NMR (300 MHz, CDCl₃) δ 8.46 (d, *J* = 8.1 Hz, 1H), 7.58 – 7.49 (m, 2H), 7.46 – 7.26 (m, 4H), 6.92 – 6.82 (m, 2H), 3.81 (s, 3H), 3.73 (s, 2H), 3.73 (s, 3H), 3.43 (s, 3H), 3.43 (t, J = 4.5 Hz, 1H), 2.42 (dd, *J* = 8.3, 5.3 Hz, 1H), 1.86 (dd, *J* = 9.4, 5.2 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 171.0, 167.8, 166.0, 158.9, 135.9, 130.2, 130.1, 125.9, 125.6, 124.0, 123.3, 119.0, 116.6, 115.7, 113.6, 55.2, 52.8, 52.2, 39.3, 31.3, 30.8, 18.9. IR: 3009.0 (w), 2947.1 (w), 1742.2 9 (s), 1694.6 (s), 1608.9 (m), 1504.1 (m), 1446.9 (s), 1356.5 (s), 1246.9 (s), 1032.6 (m), 827.8 (m), 732.8 (s) cm⁻¹. HRMS (ESI) M/Z+ Calc. 421.1525, Obs. 421.1519.



Methyl 2-bromo-1-(3-methyl-1*H***-indole-1-carbonyl)-2-phenylcyclopropanecarboxylate(3v):** The general procedure was followed using (1-bromovinyl)benzene (0.150 g, 0.819 mmol), methyl 2-diazo-3-(3-methyl-1*H*-indol-1-yl)-3-oxopropanoate (0.274 g, 1.065 mmol), Rh_2esp_2 (1.0 mg, 1.319 µmol), and DCM (12 mL). After 12 h, the reaction was quenched, and column chromatography (20% EtOAc/Hex, R_f 0.40) afforded **3v** as a white solid (0.075 g, 22.2%). [**m.p.** 132-134°C] ¹**H NMR** (300 MHz, CDCl₃) δ 8.12 – 8.04 (m, 1H), 7.48 – 7.37 (m, 3H), 7.27 – 7.18 (m, 3H), 7.17 – 7.04 (m, 3H), 3.80 (s, 3H), 2.86 (d, *J* = 7.3 Hz, 1H), 2.27 (d, *J* = 1.3 Hz, 3H). ¹³**C NMR** (75 MHz, CDCl₃) δ 166.76, 161.38, 136.52, 135.61, 131.27, 128.86, 128.57, 127.85, 125.06, 123.77, 122.47, 118.71, 118.60, 116.25, 53.54, 43.79, 40.49, 26.14, 9.70. **IR**: 3066.5 (w), 2960.3 (w), 2920.4 (w), 2867.3 (w), 1737.9 (m), 1691.2 (m), 1678.5 (m), 1612.1 (w), 1448.6 (m), 1388.6 (m), 1346.9 (s), 1238.1 (s), 1218.1 (m), 1146.1 (m), 1120.2 (s), 1063.0 (m), 1018.9 (m), 914.7 (w), 749.3 (s), 693.5 (s), 632.5 (w) cm⁻¹. **HRMS (ESI)** M/Z+Calc. 411.0470, Obs. 411.0461.

D. In(OTf)₃-Catalyzed Homo-Nazarov Cyclizations

General Method A: The cyclopropyl β -amide ester **3** (1.0 equiv) was added to a solution of In(OTf)₃ (0.30 equiv) in anhydrous dichloromethane (2 mL) at room temperature. Upon completion, the reaction mixture was quenched with water and the product was extracted from the aqueous phase with dichloromethane. The combined organic layers were washed with brine and dried over MgSO₄. The organic layers were concentrated for silica gel flash column chromatography.

General Method B: To a mixture of $In(OTf)_3$ (0.30 equiv) in anhydrous 1,2-dichloroethane heated to a reflux, dissolved cyclopropyl β -amide ester **3** (1.0 equiv) was syringed into the reaction vessel. The reaction was monitored by TLC and quenched with water. The phases were separated, and the product was extracted from the aqueous phase with dichloromethane. The combined organic layers were washed with brine, dried over MgSO₄, filtered, and concentrated for silica gel flash column chromatography.



Methyl 9-(4-methoxyphenyl)-10-methyl-6-oxo-6,7,8,9-tetrahydropyrido[1,2-a]indole-7carboxylate(4a): Methyl 2-(4-methoxyphenyl)-1-(3-methyl-1*H*-indole-1-carbonyl)cyclopropanecarboxylate (0.100 g, 0.275 mmol), ln(OTf)₃ (0.046 g, 0.082 mmol) and DCM (4 mL) were combined according to general method A to afford **4a** as a pale brown oil (0.099 g, 99%) after 2 h. R_f 0.35 (20% EtOAc/Hex). *Diastereomeric ratio*: (2.6:1). ¹**H NMR** (300 MHz, CDCl₃) δ 8.55 – 8.47 (m, 1.34), 7.50 – 7.28 (m, 4.53), 7.15 – 7.09 (m, 0.86), 7.01 – 6.95 (m, 2.09), 6.88 – 6.80 (m, 3.05), 4.59 (t, *J* = 4.3 Hz, 0.94), 4.34 (dd, *J* = 8.5, 5.1 Hz, 0.36), 3.81 – 3.78 (m, 8.28), 3.69 (d, *J* = 4.5 Hz, 0.56), 3.65 (d, *J* = 4.5 Hz, 0.56), 3.56 (d, *J* = 1.1 Hz, 1.37), 2.92 – 2.68 (m, 1.40), 2.59 – 2.34 (m, 1.39), 2.00 (s, 3.0), 1.75 (s, 1.26). ¹³**C NMR** (75 MHz, CDCl₃) δ 169.6, 169.2, 165.0, 164.9, 158.5, 158.5, 134.5, 134.4, 133.7, 133.5, 132.8, 132.3, 131.3, 131.0, 128.9, 128.3, 124.8, 124.1, 124.0, 118.1, 118.0, 116.5, 115.2, 114.8, 114.1, 113.9, 55.1, 52.5, 52.4, 49.7, 47.1, 43.4, 37.9, 35.2, 33.8, 33.0, 8.7, 8.3. **IR**: 3051.9 (w), 2932.8 (w), 1747.0 (s), 1685.1 (s), 1618.4 9 (w), 1451.7 (s), 1366.0 (s), 1242.2 (s), 1170.7 (s), 1156.4 (s), 1023.1 (s), 899.2 (m), 729.0 (s) cm⁻¹. **HRMS (ESI)** M/Z+ Calc. 363.1471, Obs. 363.1475.



Methyl 9-(2-methoxyphenyl)-10-methyl-6-oxo-6,7,8,9-tetrahydropyrido[1,2-a] indole-7-carboxylate (4b): Methyl 2-(2-methoxyphenyl)-1-(3-methyl-1H-indole-1-carbonyl)cyclopropanecarboxylate (0.070 g,

0.192 mmol), $\ln(OTf)_3$ (0.032 g, 0.057 mmol) and DCM (3 mL) were mixed according to general method A to afford a pale yellow oil (0.066 g, 95.0%) after 3 h. R_f 0.37 (20% EtOAc/Hex). *Diastereomeric ratio*: (3.2:1). ¹H NMR (300 MHz, CDCl₃) δ 8.59 – 8.48 (m, 1.32), 7.50 – 7.29 (m, 4.33), 7.28 – 7.19 (m, 1.66), 6.93 (dd, *J* = 8.3, 3.2 Hz, 1.57), 6.84 – 6.74 (m, 1.84), 6.57 (dd, *J* = 7.5, 1.6 Hz, 1.12), 4.95 (dd, *J* = 4.9, 3.0 Hz, 1.03), 4.80 (t, *J* = 6.1 Hz, 0.32), 3.97 – 3.88 (m, 4.23), 3.83 – 3.75 (m, 3.52), 3.74 – 3.62 (m, 1.07), 3.45 (s, 0.94), 2.95 (dt, *J* = 13.8, 7.0 Hz, 0.37), 2.81 – 2.66 (m, 1.36), 2.61 – 2.44 (m, 1.44), 2.31 (q, *J* = 7.8 Hz, 0.37), 2.00 (s, 2.89), 1.81 (s, 0.94). ¹³C NMR (75 MHz, CDCl₃) δ 169.9, 169.4, 165.5, 156.8, 156.5, 134.6, 134.0, 131.2, 129.0, 128.6, 128.5, 128.4, 128.3, 124.7, 124.66, 124.15, 124.0, 122.1, 120.5, 120.4, 118.2, 117.9, 116.7, 116.6, 114.4, 110.5, 110.3, 55.4, 55.3, 52.5, 52.3, 49.5, 47.6, 31.0, 30.7, 30.1, 8.3, 8.3. IR: 3097.4 (w), 2986.9 (w), 2854.2 (w), 1724.1 (s), 1711.7 (m), 1657.3 (s), 1591.8 (m), 1440.0(s), 1374.7(s), 1221.0(s), 1044.7(s), 784.2 (s), 674.3 (m) cm⁻¹. HRMS (ESI) M/Z+ Calc. 363.1471, Obs. 363.1472.



Methyl 10-methyl-6-oxo-9-phenyl-6,7,8,9-tetrahydropyrido[1,2-a]indole-7-carboxylate (4c): Methyl 1-(3-methyl-1*H*-indole-1-carbonyl)-2-phenylcyclopropane carboxylate (0.100 g, 0.300 mmol), $In(OTf)_3$ (0.050 g, 0.090 mmol) and DCE (4 mL) were combined according to general method B to afford 4c as a brown oil (0.051 g, 52%) after 8 h. R_f 0.25 (20% EtOAc/Hex). *Diastereomeric ratio*: (2.6:1). ¹H NMR (300 MHz, CDCl₃) δ 8.57 – 8.47 (m, 1.37), 7.53 – 7.27 (m, 10.63), 7.07 (d, *J* = 7.4 Hz, 2.24), 4.64 (t, *J* = 4.3 Hz, 1.00), 4.40 (dd, *J* = 8.2, 5.7 Hz, 0.39), 3.80 (dd, *J* = 9.4, 3.3 Hz, 3.61), 3.75 – 3.63 (m, 1.46), 3.53 (d, *J* = 1.1 Hz, 1.28), 2.95 – 2.74 (m, 2.28), 2.64 – 2.42 (m, 2.12), 2.00 (s, 3.13), 1.74 (s, 1.24). ¹³C NMR (75 MHz, CDCl₃) δ 169.6, 169.2, 165.0, 164.9, 140.8, 140.5, 134.6, 133.3, 133.2, 131.3, 131.1, 128.9, 128.7, 128.6, 128.3, 128.0, 127.6, 127.3, 127.2, 127.2, 125.7, 125.0, 124.2, 124.1, 118.2, 118.0, 116.7, 116.6, 115.47, 115.12, 52.6, 52.4, 49.8, 47.1, 38.7, 36.1, 33.8, 32.9, 8.8, 8.4. IR: 3032.9 (w), 2961.4 (w), 2904.3 (w), 1744.6 (s), 1699.4 (s), 1537.4 (w), 1457.6 (s), 1382.5 (s), 1242.2 (m), 1018.3 (w), 749.9 (s) cm⁻¹. HRMS (ESI) M/Z+ Calc. 333.1365, Obs. 333.1367.



Methyl 9-(4-fluorophenyl)-10-methyl-6-oxo-6,7,8,9-tetrahydropyrido[1,2-a]indole-7-carboxylate (4d): Methyl 2-(4-fluorophenyl)-1-(3-methyl-1*H*-indole-1-carbonyl) cyclopropanecarboxylate (0.100 g, 0.285 mmol), $\ln(OTf)_3$ (0.047 g, 0.085 mmol, 30 mol%) and DCE (4 mL) were combined according to general method B to afford a brown oil (0.048 g, 48%) after 8 h. R_f 0.28 (20% EtOAc/Hex). *Diastereomeric ratio*: (2.6:1). ¹H NMR (300 MHz, CDCI3) δ 8.57 – 8.46 (m, 1.37), 7.76 (d, *J* = 8.1 Hz, 0.68), 7.53 – 7.29 (m, 5.16), 7.26 – 6.77 (m, 12.82), 5.75 (s, 0.62), 4.62 (t, *J* = 4.4 Hz, 1.00), 4.39 (dd, *J* = 8.2, 5.3 Hz, 0.35), 3.80 (s, 3.03), 3.65 (dd, *J* = 11.8, 4.5 Hz, 1.24), 3.55 (s, 1.24), 2.93 – 2.79 (m, 2.17), 2.61 – 2.38 (m, 1.87), 2.00 (s, 3.18), 1.76 (s, 1.43). ¹³C NMR (75 MHz, CDCI₃) δ 169.5, 169.2, 164.8, 160.2, 136.2, 134.6, 132.9, 131.0, 129.6, 129.4, 128.9, 128.8, 125.1, 124.3, 124.2, 118.3, 118.1, 116.6, 115.9, 115.6, 115.4, 115.2, 52.7, 52.5, 49.6, 47.8, 47.1, 35.9, 35.4, 33.8, 33.0, 33.1, 8.4. IR: 3051.9 (w), 2932.8 (w), 2861.4 (w), 1738.3 (m), 1664.6 (m), 1604.1 (m), 1535.1 (m), 1508.3 (m), 1314.8 (m), 1250.8 (s), 1209.5 (s), 1097.4 (m), 989.0 (w), 832.4 (m), 736.0 (s) cm⁻¹. HRMS (ESI) M/Z+ Calc. 351.1271, Obs. 351.1272.



Methyl 9-(4-chlorophenyl)-10-methyl-6-oxo-6,7,8,9-tetrahydropyrido[1,2-a]indole-7-carboxylate (4e): Methyl 2-(4-chlorophenyl)-1-(3-methyl-1*H*-indole-1-carbonyl) cyclopropanecarboxylate (0.100 g, 0.272 mmol), $\ln(OTf)_3$ (0.045 g, 0.081 mmol) and DCE (4 mL) were mixed according to general method B to yield a brown oil (0.049 g, 49.7%) after 12 h. R_f 0.43 (15% EtOAc/Hex). *Diastereomeric ratio*: (1.9:1). ¹H NMR (300 MHz, CDCl₃) δ 8.55 – 8.46 (m, 1.38), 7.50 – 7.27 (m, 8.02), 7.17 – 7.13 (m, 1.05), 7.04 – 6.98 (m, 2.15), 6.81 – 6.77 (m, 0.45), 4.61 (t, *J* = 4.6 Hz, 1.00), 4.40 (dd, *J* = 7.6, 5.8 Hz, 0.52), 3.80 (s, 3.14), 3.65 (d, *J* = 4.5 Hz, 0.55), 3.61 (d, *J* = 4.5 Hz, 0.55), 3.54 (s, 1.24), 2.93 – 2.70 (m, 2.53), 2.62 – 2.37 (m, 2.54), 1.99 (s, 2.80), 1.77 (s, 1.20). ¹³C NMR (75 MHz, CDCl₃) δ 169.4, 164.7, 139.1, 134.6, 133.2, 132.6, 131.0, 129.3, 129.1, 129.0, 128.8, 128.7, 127.1, 125.2, 124.4, 124.3, 118.3, 118.2, 116.7, 115.3, 77.4, 77.2, 77.0, 76.5, 52.7, 52.5, 49.6, 47.1, 38.0, 35.6, 33.6, 32.9, 8.9, 8.5. IR: 3051.9 (w), 2956.6 (m), 2918.6 (m), 2847.1 (m), 1747.0 (m), 1699.4 (m), 1613.6 (m), 1542.2 (s), 1313.6 (m), 1251.5 (m), 1208.8 (m), 1094.5 (w), 1004.0 (w), 832.6 (w), 737.7 (s) cm⁻¹. HRMS (ESI) M/Z+ Calc. 367.0975, Obs. 367.0988.



Methyl 10-methyl-9-(4-nitrophenyl)-6-oxo-6,7,8,9-tetrahydropyrido[1,2-*a*]indole-7-carboxylate (4f): Methyl 1-(3-methyl-1*H*-indole-1-carbonyl)-2-(4-nitrophenyl) cyclopropanecarboxylate (0.100 g, 0.264 mmol), $\ln(OTf)_3$ (0.044 g, 0.079 mmol) and DCE (4 mL) were mixed according to general method B to yield a brown oil after 20 h. The reaction afforded an inseparable mixture of trace amounts of **4f** and other by-products as observed by crude ¹H NMR. $R_f 0.35$ (15% EtOAc/Hex).



Methyl 9-(furan-2-yl)-10-methyl-6-oxo-6,7,8,9-tetrahydropyrido[1,2-a]indole-7-carboxylate (4g): Methyl 2-(furan-2-yl)-1-(3-methyl-1H-indole-1-carbonyl)cyclopropane carboxylate (0.050 g, 0.154 mmol), $\ln(OTf)_3$ (0.026 g, 0.046 mmol) and DCM (3 mL) were mixed according to general method A to afford a colorless oil (0.049 g, 99.0%) after 2 h. R_f 0.40 (20% EtOAc/Hex). *Diastereomeric ratio*: (4.5:1). ¹H NMR (300 MHz, CDCl₃) δ 8.57 – 8.51 (m, 0.37), 8.50 – 8.42 (m, 0.97), 7.53 – 7.46 (m, 1.50), 7.42 – 7.29 (m, 3.77), 6.30 – 6.25 (m, 1.21), 5.91 – 5.87 (m, 1.16), 4.65 (t, *J* = 3.9 Hz, 1), 4.52 (t, *J* = 5.2 Hz, 0.22), 3.84 (d, *J* = 1.0 Hz, 3.24), 3.81 – 3.72 (m, 1.42), 3.51 (d, *J* = 0.8 Hz, 0.69), 3.08 (dt, *J* = 13.8, 5.6 Hz, 0.25), 2.72 (dt, *J* = 4.4, 3.6 Hz, 2.07), 2.53 (dt, *J* = 13.8, 5.3 Hz, 0.27), 2.15 (d, *J*= 0.3 Hz, 3.09), 2.00 (d, *J* = 0.9 Hz, 0.67). ¹³C NMR (75 MHz, CDCl₃) δ 169.6, 164.8, 152.4, 142.4, 142.1, 134.6, 131.1, 130.8, 125.1, 124.2, 118.3, 116.6, 115.3, 110.3, 110.2, 108.1, 107.6, 52.7, 47.7, 31.3, 30.7, 29.3, 8.3. IR: 3090.2 (w), 2936.8 (w), 1767.1 (s), 1725.6 (s), 1469.4(s), 1376.2(m), 1269.5(m), 785.4 (s), 663.0 (m) cm⁻¹. HRMS (ESI) M/Z+ Calc. 323.1158, Obs. 323.1159.



Methyl 9,10-dimethyl-6-oxo-9-phenyl-6,7,8,9-tetrahydropyrido[1,2-a]indole-7-carboxylate (4h): Methyl 2-methyl-1-(3-methyl-1H-indole-1-carbonyl)-2-phenyl cyclopropanecarboxylate (0.070 g, 0.201 mmol), $\ln(OTf)_3$ (0.033 g, 0.060 mmol) and DCM (3 mL) were combined according to general Method A to afford a **4h** as a white solid (0.065 g, 94.14%) after 2 h. R_f 0.28 (20% EtOAc/Hex). [**m.p.** 139-141°C] *Diastereomeric ratio*: (1.1:1). ¹**H NMR** (300 MHz, CDCl₃) δ 8.58 – 8.50 (m, 1.81), 7.54 (ddt, *J* = 7.6, 4.3, 2.2 Hz, 1.0), 7.45 – 7.25 (m, 13.52), 7.13 – 7.08 (m, 2.11), 3.99 (dd, *J* = 12.2, 5.0 Hz, 0.80), 3.80 (s, 3.0), 3.72 (s, 2.71), 3.43 (dd, *J* = 13.2, 4.4 Hz, 0.99), 2.84 (dt, *J* = 26.7, 13.4 Hz, 1.88), 2.50 – 2.41 (m, 1.35), 2.26 – 2.18 (m, 4.15), 1.99 (s, 2.99), 1.85 (s, 2.62), 1.65 (s, 2.68). ¹³C NMR (75 MHz, CDCl₃) δ 169.5, 169.4, 165.3, 164.9, 145.9, 143.8, 138.5, 136.9, 134.3, 134.2, 131.6, 131.9, 128.9, 128.5, 127.1, 126.8, 126.4, 125.9, 125.1, 124.9, 124.1, 124.1, 118.0, 117.9, 116.7, 115.6, 114.6, 52.6, 48.5, 47.9, 42.1, 41.23, 40.74, 39.56, 29.4, 24.6, 10.0, 9.2. **IR**: 3040.9 (w), 2963.4 (w), 2890.4 (w), 1722.2 (s), 1640.6 (s), 1483.9 (s), 1383.5 (s), 1270.4 (m), 1182.4 (m), 1134.3 (w), 740.1 (s), 640.4 (s) cm⁻¹. **HRMS (ESI)** M/Z+ Calc. 347.1521, Obs. 347.1516.



Methyl 9,9-diethyl-10-methyl-6-oxo-6,7,8,9-tetrahydropyrido[1,2-*a*]indole-7-carboxylate (4i): Methyl 2,2-diethyl-1-(3-methyl-1H-indole-1-carbonyl)cyclopropane carboxylate (0.055 g, 0.175 mmol), $ln(OTf)_3$ (0.029 g, 0.052 mmol) and DCE (3 mL) were mixed according to general method B to yield a colorless oil (0.046 g, 84.8%) after 6 h. R_f 0.38 (20% EtOAc/Hex). ¹H NMR (300 MHz, CDCl₃) δ 8.51 – 8.44 (m, 1H), 7.44 (ddd, J = 6.7, 4.5, 2.6 Hz, 1H), 7.34 – 7.28 (m, 2H), 3.94 – 3.83 (m, 4H), 2.58 (t, J = 13.5 Hz, 1H), 2.30 (d, J = 0.7 Hz, 3H), 2.21 (dt, J = 14.6, 7.4 Hz, 1H), 1.95 (dd, J = 13.7, 5.0 Hz, 1H), 1.87 – 1.65 (m, 3H), 0.93 (dt, J = 10.0, 7.4 Hz, 6H). ¹³C NMR (75 MHz, CDCl₃) δ 170.2, 165.3, 136.9, 134.4, 131.7, 124.7, 123.9, 117.6, 116.6, 113.7, 77.4, 76.9, 76.5, 52.7, 47.4, 39.3, 32.3, 31.6, 29.1, 9.7, 8.5, 8.3. IR: 3025.9 (w), 2894.8 (w), 1786.6 (s), 1725.4 (s), 1484.2 (s), 1383.2 (m), 1283.0 (m), 1180.6 (m), 713.41 (s), 662.9 (m) cm⁻¹. HRMS (ESI) M/Z+ Calc. 313.1678, Obs. 313.1678.



Methyl 10'-methyl-6'-oxo-7',8'-dihydro-6'*H***-spiro[cyclopentane-1,9'-pyrido[1,2-a]indole]-7'carboxylate (4j):** Methyl 1-(3-methyl-1H-indole-1-carbonyl)spiro[2.4] heptane-1-carboxylate (0.050 g, 0.160 mmol), $\ln(OTf)_3$ (0.027 g, 0.048 mmol) and DCE (3 mL) were mixed according to general method B to yield a colorless oil (0.044 g, 88.8%) after 6 h. $R_f 0.35$ (20% EtOAc/Hex). ¹H NMR (300 MHz, CDCl₃) δ 8.48 – 8.41 (m, 1H), 7.47 – 7.41 (m, 1H), 7.30 (ddd, *J* = 4.6, 4.2, 2.9 Hz, 2H), 3.85 (d, *J* = 0.8 Hz, 3H), 3.84 – 3.79 (m, 1H), 2.69 – 2.54 (m, 1H), 2.47 (t, *J* = 13.2 Hz, 1H), 2.30 (d, *J* = 0.7 Hz, 3H), 2.13 (dd, *J* = 13.4, 4.6 Hz, 1H), 2.02 – 1.83 (m, 5H), 1.83 – 1.70 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 169.9, 165.4, 139.3, 134.0, 131.9, 124.7, 124.0, 117.6, 116.5, 112.6, 52.7, 48.8, 42.6, 39.0, 38.7, 37.8, 25.8, 25.3, 9.73. IR: 2998.5 (w), 2893.7 (w), 1786.8 (s), 1724.9 (s), 1470.0 (s), 1385.1 (m), 1269.5 (m), 1180.4 (m), 714.3 (s), 662.7 (m) cm⁻¹. HRMS (ESI) M/Z+ Calc. 311.1521, Obs. 311.1520.



Methyl 10'-methyl-6'-oxo-7',8'-dihydro-6'*H*-spiro[cyclohexane-1,9'-pyrido[1,2-a]indole]-7'carboxylate (4k): Methyl 1-(3-methyl-1H-indole-1-carbonyl)spiro[2.5]octane-1-carboxylate (0.080 g, 0.246 mmol), $In(OTf)_3$ (0.041 g, 0.073 mmol) and DCE (3 mL) were mixed according to general method B to yield a colorless oil (0.062 g, 78.6%) after 6 h. R_f 0.39 (20% EtOAc/Hex). (*Conformers!!*) ¹H NMR (300 MHz, CDCl₃) δ 8.49 – 8.41 (m, 1H), 7.47 – 7.42 (m, 1H), 7.36 – 7.27 (m, 2H), 3.86 (dd, *J* = 2.9, 0.6 Hz, 3H), 3.76 (dd, *J* = 13.1, 4.6 Hz, 1H), 2.71 – 2.59 (m, 3H), 2.54 – 2.39 (m, 4H), 2.36 – 2.17 (m, 2H), 1.91 – 1.76 (m, 4H), 1.70 (d, *J* = 11.9 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 170.2, 165.5, 139.5, 134.0, 132.1, 125.1, 124.8, 123.9, 121.7, 119.4, 117.7, 116.6, 114.4, 113.1, 58.6, 52.7, 47.2, 36.1, 35.6, 33.9, 33.7, 32.7, 31.2, 30.8, 25.6, 25.4, 23.1, 21.5, 21.3, 10.8, 10.2. IR: 2969.7 (w), 2890.9 (w), 1736.7 (m), 1689.1 (m), 1469.0 (m), 1382.7 (m), 1269.5 (s), 759.9 (s), 662.9 (s) cm⁻¹. HRMS (ESI) M/Z+ Calc. 325.1678, Obs. 325.1681.



Methyl 9-((tert-butyldiphenylsilyl)methyl)-10-methyl-6-oxo-6,7,8,9-tetrahydropyrido[1,2-a]indole-7carboxylate (4I): Methyl 2-((*tert*-butyldiphenylsilyl) methyl)-1-(3-methyl-1H-indole-1carbonyl)cyclopropanecarboxylate (0.100 g, 0.196 mmol), In(OTf)₃ (0.033 g, 0.058 mmol) and DCE (4 mL) were combined according to general method B to afford a colorless oil (0.082 g, 82%) after 16 h. R_f 0.41 (20% EtOAc/Hex). ¹H NMR (300 MHz, CDCl₃) δ 8.37 (ddd, J = 4.3, 2.2, 0.6 Hz, 1H), 7.72 – 7.66 (m, 4H), 7.45 – 7.32 (m, 7H), 7.29 – 7.24 (m, 2H), 3.89 (dd, J = 13.5, 4.8 Hz, 1H), 3.72 (s, 3H), 3.45 – 3.33 (m, 1H), 2.19 (ddd, J = 18.1, 8.8, 3.1 Hz, 1H), 1.99 (s, 3H), 1.83 (ddd, J = 13.5, 4.8, 2.5 Hz, 1H), 1.55 (dd, J = 8.3, 4.6 Hz, 2H), 1.06 – 1.00 (m, 9H). ¹³**C** NMR (75 MHz, CDCl₃) δ 169.7, 165.1, 138.5, 135.8, 135.7, 134.4, 134.1, 133.0, 131.2, 129.5, 129.4, 127.9, 124.5, 124.0, 117.9, 116.5, 112.0, 52.4, 46.7, 29.9, 27.7, 26.5, 18.3, 14.9, 8.5. IR: 3061.4 (w), 2951.9 (m), 2928.1 (m), 2851.9 (m), 1745.6 (s), 1692.0 (s), 1457.2 (s), 1381.4 (s), 1270.6 (m), 1103.8 (m), 740.4 (s), 702.1 (s) cm⁻¹. **HRMS (ESI)** M/Z+ Calc. 509.2386, Obs. 509.2383.



Methyl 9-(1,3-dioxoisoindolin-2-yl)-10-methyl-6-oxo-6,7,8,9-tetrahydropyrido[1,2-a]indole-7carboxylate (4m): Methyl 2-(1,3-dioxoisoindolin-2-yl)-1-(3-methyl-1*H*-indole-1-carbonyl) cyclopropane carboxylate (0.090 g, 0.224 mmol), $ln(OTf)_3$ (0.037 g, 0.067 mmol) and DCE (4 mL) were mixed according to general method B to yield a yellow-green solid (0.049 g, 55%) after 8 h. R_f 0.38 (20% EtOAc/Hex). [m.p. 167–169°C] *Diastereomeric ratio*: (4.8:1). ¹H NMR (300 MHz, CDCl₃) δ 8.52 – 8.47 (m, 1.27), 7.89 – 7.70 (m, 5.64), 7.46 – 7.28 (m, 4.18), 5.96 (t, J = 4.5 Hz, 1.00), 4.19 (dt, J = 12.5, 6.3 Hz, 0.70), 3.83 – 3.79 (m, 3.92), 2.86 (ddd, J = 14.1, 11.8, 5.3 Hz, 0.75), 2.58 (ddd, J = 14.3, 4.9, 4.0 Hz, 0.75), 2.29 – 2.26 (m, 0.22), 2.07 (s, 2.75), 2.04 (s, 0.38). ¹³C NMR (75 MHz, CDCl₃) δ 169.5, 167.6, 164.4, 134.8, 134.5, 131.3, 130.3, 128.2, 125.8, 124.1, 123.6, 118.5, 116.7, 116.3, 52.8, 48.2, 40.3, 30.7, 8.3. IR: 3061.6 (w), 2942.6 (w), 2928.32 (w), 1733.2 (m), 1708.2 (s), 1614.2 (w), 1452.3 (m), 1452.3 (m), 1383.6 (s), 1309.5 (s), 1261.0 (s), 1104.7 (m), 890.4 (m), 734.4 (s) cm⁻¹. HRMS (ESI) M/Z+ Calc. 402.1216, Obs. 402.1219.



Methyl 10-methyl-6-oxo-9-(phenylthio)-6,7,8,9-tetrahydropyrido[1,2-a]indole-7-carboxylate (4n): Methyl 1-(3-methyl-1H-indole-1-carbonyl)-2-(phenylthio)cyclopropane carboxylate (0.018 g, 0.049 mmol), In(OTf)₃ (0.008 g, 0.014 mmol) and DCE (1 mL) were mixed according to general method B to yield a colorless oil (0.014 g, 81%) after 7 h. R_f 0.30 (20% EtOAc/Hex). *Diastereomeric ratio*: (10:1). ¹H NMR (300 MHz, CDCl₃) δ 8.54 (d, J = 8.6 Hz, 0.10), 8.47 – 8.40 (m, 1), 7.54 – 7.29 (m, 9.0), 4.91 – 4.84 (m, 1.06), 4.48 (dd, J = 13.1, 4.8 Hz, 1.04), 3.94 – 3.76 (m, 3.80), 2.72 (td, J = 13.6, 3.9 Hz, 1.19), 2.42 – 2.32 (m, 1.42), 2.20 (s, 0.31), 2.04 (s, 3.10). ¹³C NMR (75 MHz, CDCl₃) δ 169.6, 164.5, 134.7, 134.5, 132.5, 130.5, 130.4, 129.3, 129.2, 128.8, 128.6, 125.6, 124.3, 118.5, 116.6, 52.8, 46.9, 40.0, 29.6, 8.3. IR: 2997.7 (w), 2890.9 (w), 1766.6 (m), 1711.7 (m), 1468.2 (m), 1269.7 (s), 760.1 (s), 663.0 (s) cm⁻¹. HRMS (ESI) M/Z+ Calc. 365.1119, Obs. 365.1089.



Methyl 11-methyl-5-oxo-2,3,3a,4,5,11b-hexahydrofuro[2',3':3,4]pyrido[1,2-a]indole-4-carboxylate (40): Methyl 6-(3-methyl-1*H*-indole-1-carbonyl)-2-oxabicyclo[3.1.0] hexane-6-carboxylate (0.025 g, 0.083 mmol), $\ln(OTf)_3$ (0.014 g, 0.025 mmol) and DCM (2 mL) were combined according to general method A to afford a colorless oil (0.024 g, 97%) after 2.5 h. R_f 0.30 (20% EtOAc/Hex). ¹H NMR (300 MHz, CDCl₃) δ 8.39 (d, *J* = 4.9, 3.3 Hz, 1H), 7.51 (d, *J* = 6.8, 1.3 Hz, 1H), 7.41 – 7.27 (m, 2H), 5.05 (d, *J* = 4.5 Hz, 1H), 4.17 – 3.99 (m, 2H), 3.87 (s, 3H), 3.78 (d, *J* = 10.7 Hz, 1H), 3.32 – 3.21 (m, 1H), 2.47 – 2.22 (m, 1H), 2.32 (s, 3H), 1.96 – 1.82 (m, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 169.2, 164.0, 134.5, 130.9, 128.8, 125.8, 124.2, 119.5, 118.8, 116.4, 69.9, 66.3, 52.8, 52.3, 40.7, 30.7, 8.5. **IR**: 2947.1 (w), 2923.3 (w), 2856.6 (w), 1744.8 (s), 1703.1 (s), 1623.2 (w), 1459.5 (m), 1382.2 (s), 1265.2 (m), 1035.5 (m), 751.0 (s) cm⁻¹. **HRMS (ESI)** M/Z+ Calc. 299.1158.



Methyl 12-methyl-6-oxo-3,4,4a,5,6,12b-hexahydro-2*H*-pyrano[2',3':3,4]pyrido[1,2-a]indole-5carboxylate (4p): Methyl 7-(3-methyl-1*H*-indole-1-carbonyl)-2-oxabicyclo[4.1.0]heptane-7-carboxylate (0.025 g, 0.079 mmol), $ln(OTf)_3$ (0.013 g, 0.023 mmol) and DCM (2 mL) were mixed according to general method A to yield a pale yellow solid (0.023 g, 92.9%) after 2.5 h. R_f 0.25 (20% EtOAc/Hex). [m.p. 128-130°C] ¹H NMR (300 MHz, CDCl₃) δ 8.41 (d, 1H), 7.50 (d, 1H), 7.40 – 7.25 (m, 2H), 4.81 (s, 1H), 4.33 (d, J = 12.2 Hz, 1H), 4.08 (d, 1H), 3.86 (s, 3H), 3.71 (t, J = 11.6, 2.4 Hz, 2H), 2.72 (d, 1H), 2.30 (s, 3H), 1.98 – 1.73 (m, 2H), 1.56 – 1.47 (m, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 169.5, 165.2, 134.3, 130.8, 125.8, 124.2, 122.2, 118.8, 117.7, 116.6, 68.3, 68.1, 52.6, 50.1, 35.7, 25.7, 20.4, 8.4. IR: 2737.5(w), 1746.9(m), 1632.6(w), 1532.6(m), 1056.8(w), 751.6(s), 680.1(s) cm⁻¹. HRMS (ESI) M/Z+ Calc. 313.1314, Obs. 313.1315.



12-methyl-6-oxo-2,3,4,4a,5,6-hexahydroindolo[1,2-*h*][1,7] 1-Benzyl 5-methyl naphthyridine-2-benzyl 1,5(12bH)-dicarboxylate (4q): 7-methyl 7-(3-methyl-1H-indole-1-carbonyl)-2azabicyclo[4.1.0]heptane-2,7-dicarboxylate (0.100 g, 0.223 mmol), In(OTf)₃ (0.037 g, 0.067 mmol) and DCM (4 mL) were combined according to general method A to afford 4q as a colorless oil (0.098 g, 98.0%) after 2 h. R_f 0.25 (25% EtOAc/Hex). Diastereomeric ratio: (7.1:1). ¹H NMR (300 MHz, CDCl₃) δ 8.55 - 8.40 (m, 1.22), 7.52 - 7.27 (m, 10.67), 5.98 (d, 1), 5.91 (d, 0.14), 5.38 - 5.16 (m, 2.64), 4.20 - 4.04 (m, 1.20), 3.95 (dd, J = 13.9, 3.7 Hz, 0.23), 3.85 (s, 0.77), 3.74 (s, 3), 3.68 (d, J = 1.7 Hz 1.41), 2.81 -2.50 (m, 2.68), 2.35 - 2.20 (m, 0.32), 2.08 - 2.03 (m, 3.99), 1.79 - 1.85 (m, 1.54), 1.58 - 1.70 (m, 2.70), 1.51 - 1.33 (m, 1.42). ¹³C NMR (75 MHz, CDCl₃) δ 168.4, 167.6, 162.6, 155.0, 136.3, 134.5, 131.3, 128.4, 128.3, 128.1, 127.8, 127.7, 125.1, 124.1, 122.0, 117.9, 116.4, 116.3, 67.5, 56.0, 53.5, 53.0, 52.4, 48.3, 39.4, 37.9, 34.5, 31.4, 26.5, 25.1, 24.6, 22.5, 14.6, 7.6. IR: 3042.4 (w), 2932.8 (w), 2861.4 (w), 1738.4 (s), 1702.9 (s), 1457.3 (m), 1373.1 (s), 1256.6 (m), 1201.5 (m), 1164.4 (m), 1113.6 (w), 761.1 (m), 689.7 (m) cm⁻¹. HRMS (ESI) M/Z+ Calc. 446.1842, Obs. 446.1840.



Methyl 9-(4-methoxyphenyl)-6-oxo-6,7,8,9-tetrahydropyrido[1,2-a]indole-7-carboxylate (4r): Methyl 1-(1*H*-indole-1-carbonyl)-2-(4-methoxyphenyl)cyclopropanecarboxylate (0.75 g, 0.215 mmol), In(OTf)₃ (0.036 g, 0.064 mmol) and DCM (4 mL) were combined according to general method A to afford **4r** as a colorless oil (0.742 g, 98.99%) after 45 min. R_f 0.30 (20% EtOAc/Hex). *Diastereomeric ratio*: (1.1:1). ¹**H NMR** (300 MHz, CDCl₃) δ 8.53 – 8.42 (m, 1.77), 7.45 – 7.20 (m, 8.18), 7.19-7.12 (m, 1.68), 6.96 – 6.85 (m, 3.86), 6.08 (s, 0.78), 6.00 – 5.89 (m, 1), 4.36 (dd, *J* = 9.9, 4.2 Hz, 0.76H), 4.13 (dd, *J* = 13.0, 2.6 Hz, 1.09), 3.97 – 3.79 (m, 13.94), 2.79 – 2.64 (m, 1.92), 2.54 – 2.37 (m, 1.88). ¹³**C NMR** (75 MHz, CDCl₃) δ 169.5, 169.3, 165.3, 164.7, 159.1, 158.9, 141.5, 140.6, 135.2, 135.1, 132.7, 132.3, 129.6, 129.5, 129.3, 129.0, 124.7, 124.4, 120.1, 120.1, 116.6, 116.5, 114.2, 107.6, 55.3, 53.0, 52.8, 51.6, 49.2, 40.3, 37.4, 33.6, 33.2. IR: 2997.1 (w), 2950.6 (w), 2834.32 (w), 1737.9 (s), 1703.3 (s), 1555.7 (w), 1512.5 (m), 1453.1 (s), 1379.0 (s), 13050.2 (s), 1247.2 (s), 1177.1 (s), 1034.6 (s), 838.4 (m), 798.5 (m), 752.0 (m), 688.9 (w) cm⁻¹. **HRMS (ESI)** M/Z+ Calc. 349.1314, Obs. 349.1307.



Methyl 10-(2-bromoethyl)-9-(4-methoxyphenyl)-6-oxo-6,7,8,9-tetrahydropyrido[1,2-a]indole-7-carboxylate (4s): Methyl 1-(3-(2-bromoethyl)-1H-indole-1-carbonyl)-2-(4-methoxyphenyl)cyclopropane carboxylate (0.050 g, 0.109 mmol), $\ln(OTf)_3$ (0.018 g, 0.032 mmol) and DCM (3 mL) were mixed according to general method A to afford **4s** as a colorless oil (0.049 g, 98.2%) after 1 h. R_f 0.35 (20% EtOAc/Hex). *Diastereomeric ratio*: (2.7:1). ¹H NMR (300 MHz, CDCl₃) δ 8.54 (ddd, *J* = 10.3, 6.9, 1.4 Hz, 1.38), 7.53 – 7.29 (m, 4.31), 7.16 – 7.11 (m, 0.81), 6.95 (dd, *J* = 6.9, 4.7 Hz, 2.07), 6.89 – 6.80 (m, 2.88), 4.68 (t, *J* = 4.2 Hz, 1), 4.43 (dd, *J* = 8.8, 5.3 Hz, 0.37), 3.86 – 3.77 (m, 7.57), 3.69 (dd, *J* = 12.2, 4.6 Hz, 1.29), 3.57 (d, *J* = 3.5 Hz, 1.28), 3.53 – 3.05 (m, 4.08), 3.03 – 2.73 (m, 3.37), 2.66 – 2.37 (m, 2.03). ¹³C NMR (75 MHz, CDCl₃) δ 169.4, 165.2, 158.8, 135.5, 134.7, 132.3, 129.6, 129.1, 128.3, 125.2, 124.4, 118.0, 116.9, 116.0, 114.3, 114.2, 55.3, 52.7, 47.1, 35.4, 33.0, 30.9, 27.7. IR: 3023.9 (w), 2918.9 (w), 1725.1 (s), 1658.6 (s), 1591.0 (m), 1493.2 (s), 1349.0 (m), 993.6(s), 725.0 s), 663.0 (m) cm⁻¹. HRMS (ESI) M/Z+ Calc. 455.0708, Obs. 455.0734.



Methyl 10-(2-(1,3-dioxoisoindolin-2-yl)ethyl)-9-(4-methoxyphenyl)-6-oxo-6,7,8,9-tetrahydro-pyrido[1,2-a]indole-7-carboxylate (4t): Methyl 1-(3-(2-(1,3-dioxoisoindolin-2-yl)ethyl)-1*H*-indole-1-carbonyl)-2-(4-methoxyphenyl)cyclopropanecarboxylate (0.050 g, 0.096 mmol), $ln(OTf)_3$ (0.016 g, 0.028 mmol) and DCM (3 mL) were mixed according to general method A to yield a white solid (0.038 g, 76.0%) after 2 h. [m.p. 166–168°C] R_f 0.38 (40% EtOAc/Hex). *Diastereomeric ratio*: (2.8:1). ¹H NMR (300 MHz, CDCl₃) δ 8.52 – 8.46 (m, 1.35), 7.79 – 7.58 (m, 7.24), 7.41 – 7.26 (m, 2.90), 7.18 – 7.13 (m, 0.89), 7.00 – 6.93 (m, 2.37), 6.86 - 6.72 (m, 2.97), 4.70 (t, *J* = 4.1 Hz, 1), 4.48 (dd, *J* = 8.3, 5.1 Hz, 0.35), 3.85 – 3.80 (m, 0.84), 3.79- 3.63 (m, 11.93), 3.54 (s, 1.09), 3.02 – 2.90 (m, 1.23), 2.88 – 2.71 (m, 3.21), 2.61 – 2.50 (m, 0.57), 2.44 – 2.33 (m, 1.73). ¹³C NMR (75 MHz, CDCl₃) δ 169.6, 169.2, 168.0, 165.3, 165.1, 158.8, 158.7, 135.5, 135.3, 134.7, 134.6, 133.8, 132.5, 131.9, 131.9, 130.4, 130.0, 129.1, 128.3, 125.1, 125.0, 124.5, 124.4, 123.1, 123.0, 118.4, 118.2, 116.8, 116.7, 115.7, 115.2, 114.2, 114.1, 55.2, 55.2, 52.7, 52.5, 49.6, 47.0, 37.7, 36.9, 36.8, 35.3, 33.7, 33.2, 23.1, 22.8. IR: 3047.1 (w), 2947.1 (w), 2847.1 (w), 1766.03 (w), 1751.74 (m), 1708.8 (s), 1618.4 (m), 1504.1 (m), 1451.7 (m), 1376.6 (s), 1245.9 (s), 1032.6 (s), 837.3 (m), 715.9 (s) cm⁻¹. HRMS (ESI) M/Z+ Calc. 522.1791, Obs. 522.1791.



Methyl 10-(2-methoxy-2-oxoethyl)-9-(4-methoxyphenyl)-6-oxo-6,7,8,9-tetrahydropyrido[1,2alindole-7-carboxvlate (4u): Methvl 1-(3-(2-methoxy-2-oxoethyl)-1H-indole-1-carbonyl)-2-(4methoxyphenyl) cyclopropanecarboxylate (0.070 g, 0.167 mmol), In(OTf)₃ (0.028 g, 0.049 mmol) and DCM (3 mL) were combined according to general method A to afford 4u as a brown oil (0.062 g, 88.0%) after 3 h. R_f 0.45 (40% EtOAc/Hex). Diastereomeric ratio: (2.0:1). ¹H NMR (300 MHz, CDCl₃) δ 8.56 -8.47 (m, 1.45), 7.56 - 7.48 (m, 1.05), 7.44 - 7.28 (m, 3.67), 7.18 - 7.11 (m, 1.06), 7.01 - 6.90 (m, 2.29), 6.88 - 6.78 (m, 3.02), 4.66 (t, J = 4.5 Hz, 1), 4.40 (dd, J = 9.7, 5.1 Hz, 0.48), 3.90 - 3.81 (m, 1.32), 3.81 -3.78 (m, 7.54), 3.73 – 3.67 (m, 1.32), 3.64 (s, 1.44), 3.55 (s, 1.42), 3.53 (s, 2.98), 3.52 (s, 0.31), 3.43 (d, J = 17.3 Hz, 1.59), 3.32 (d, J = 17.7 Hz, 0.85), 3.02 – 2.69 (m, 2.34), 2.58 – 2.38 (m, 1.62). ¹³C NMR (75 MHz, CDCl₃) δ 170.8, 170.6, 169.4, 169.1, 165.2, 158.9, 158.8, 136.3, 135.8, 134.6, 134.5, 132.3, 131.9, 130.3, 129.9, 129.2, 128.5, 125.2, 125.2, 124.5, 124.4, 118.4, 118.0, 116.7, 114.2, 114.1, 112.3, 112.0, 55.3, 52.7, 52.6, 52.0, 51.9, 50.1, 47.2, 38.5, 35.4, 34.0, 33.2, 29.7, 29.4. IR: 3013.8 (w), 2918.6 (w), 2832.8 (w), 1747.0 (s), 1737.7 (s), 1699.3 (s), 1613.6 (m), 1518.4 (m), 1456.5 (s), 1366.0 (s), 1245.6 (s), 1152.1 (s), 1032.6 (s), 837.3 (m), 731.8 (s) cm⁻¹. **HRMS (ESI)** M/Z+ Calc. 421.1525, Obs. 421.1522.



Methyl 6-hydroxy-10-methyl-9-phenylpyrido[1,2-*a*]indole-7-carboxylate (8): Methyl 2-bromo-1-(3-methyl-1*H*-indole-1-carbonyl)-2-phenylcyclopropanecarboxylate (0.060 g, 0.145 mmol), $In(OTf)_3$ (0.0245 g, 0.043 mmol) and DCM (3 mL) were combined according to general method A to afford **8** as a yellow-green oil (0.013 g, 28.5%) after 4 h. R_f 0.55 (20% EtOAc/Hex). ¹H NMR (300 MHz, CDCI3) δ 12.12 (s, 1H), 8.57 – 8.50 (m, 1H), 7.86 (s, 1H), 7.71 – 7.66 (m, 1H), 7.63 – 7.46 (m, 2H), 7.38 – 7.32 (m, 1H), 7.23 – 7.06 (m, 3H), 6.95 (m, 1H), 3.98 (s, 3H), 2.45 (d, *J* = 1.1 Hz, 3H). ¹³C NMR (75 MHz, CDCI₃) δ 170.9, 160.7, 138.5, 134.6, 130.3, 128.7, 127.4, 126.5, 125.4, 124.3, 123.7, 123.4, 122.1, 119.4, 119.0, 112.0,

110.5, 105.0, 52.5, 9.7. **IR**: 3600-2800 (br), 2960.3 (m), 2923.7 (m), 2847.4 (m), 1657.1 (s), 1649.7 (s), 1525.7 (m), 1449.7 (s), 1334.3 (m), 1321.1 (m), 1255.4 9s), 1226.3 (s), 1193.8 (w), 1122.6 (m), 1020 (m), 796.6 (s), 740.7 (s), 705.2 (m). **HRMS (ESI)** M/Z+ Calc. 331.1208, Obs. 331.1203.

3. References

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4. Characterization/Spectra






































































56



Std Proton parameters Sample: 2-OMestyrene-cycln-new-H File: xp Pulse Sequence: s2pel

Solvent: cdc13 Ambient temperature Operator: dpati1 Marcury-308 "r2d2"

Relax. delay 1,000 sac Palso 30.0 degres Ack. time 3.550 tec Vidth 4003.1 Nz 16 repellions 0355492 Histor 0355492 Histor 0355492 Histor 03556 Telse 65556 Total time 1 min, 16 sec



(3.2:1 trans:cis mixture of diastereomers)













5 - C









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220 200 180 160 140 120 100 80 60 40 20 0 ppm



71



72






75













2.7 0 ppm !!

NOE Spectra for **4q**











