Supporting Information
For
A General Intramolecular Friedel-Crafts Approach to Functionalized
Pyrrlo[3,2,1-ij]quinolin-4-ones

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1. General Methods

All reactions were carried out in pre-dried glassware from the oven and any additional moisture was removed by flame-drying the reaction vessel. Each reaction proceeded under a nitrogen atmosphere with anhydrous solvents, unless stated otherwise. Tetrahydrofuran and diethyl ether were distilled from a sodium/benzophenone ketyl under nitrogen and stored in a Schlenk flask. Benzene, toluene, 1,2-dichloroethane and dichloromethane were purified by distillation from calcium hydride. 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. Compounds 9 were synthesized according to our reported protocol. 1

Chromatographic purification was performed as flash chromatography with Silicycle silica gel (40-65μm). For quantitative flash chromatography, technical grades solvents were utilized. Analytical thin-layer chromatography (TLC) was performed on Dynamic Absorbents, Inc. silica gel 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 an ethanol solution of phosphomolybdic acid (PMA) followed by heating. Each yield refers to an 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 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 MHz spectrometer, Varian Mercury Vx 400 MHz spectrometer or Bruker 400 MHz 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 doublet of doublets, t = triplet, m = multiplet, br = broad), coupling constants (Hz), and integration. Mass spectra
were obtained using a MicroMass Autospec M. The accurate mass analyses were run in EI mode at a mass resolution of 10,000 using PFK (perfluorokerosene) as an internal calibrant.

Diastereomeric ratios for cyclized products 11 were determined by $^1$H NMR based on comparing the signal ratios of the benzylic protons (~4.0-5.0 ppm) for the two diastereomeric protons. These assignments are based on the coupling constants. A single observable diastereomer corresponds to >99:1 $dr$.

2. Experimental Procedures

A. Synthesis of β-amide esters

Sodium hydride (1.2 equiv.) was suspended in THF and cooled to 0 °C. In a separate flask, the desired N-heterocycle (1.0 equiv.) was dissolved in THF and syringed into the reaction vessel. After 30 min, methyl-3-chloro-3-oxopropanoate (1.25 equiv.) was added quickly. 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 Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. The residue was purified by silica gel flash chromatography for product isolation.

Methyl 3-(2-methyl-1H-indol-1-yl)-3-oxopropanoate (9a): The general procedure was followed using sodium hydride (1.91 g, 47.7 mmol), 2-methyl-1H-indole (5.00 g, 38.2 mmol), methyl-3-chloro-3-oxopropanoate (4.91 mL, 45.7 mmol), and THF (125 mL). After 14 h, the reaction was quenched, and column chromatography afforded 9a as a brick red solid (6.05 g, 69%). (R$_f$ 0.40, 30% EtOAc/Hex) [m.p. 74-76°C] $^1$H NMR (400 MHz, CDCl$_3$) δ ppm 7.87 - 7.92 (m, 1H), 7.43 - 7.48 (m, 1H), 7.21 - 7.28 (m, 2H), 6.39 (s, 1H), 4.07 (s, 2H), 3.81 (s, 3H), 2.61 (d, $J = 1.12$ Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ ppm 166.9, 165.9, 137.0, 136.3, 129.8, 123.9, 123.6, 120.0, 114.9, 110.6, 52.7, 45.6, 17.3. IR: 3022.4 (w), 2953.1 (w), 1733.8 (s), 1700.1 (s), 1684.4 (s), 1606.3 (m), 1588.1 (m), 1526.9 (m), 1450.5 (m), 1374.4 (m), 1300.3 (m), 1235.7 (s), 1162.5 (m), 1085.2 (w), 758.3 (s), 668.5 (w), 649.4 (w) cm$^{-1}$. HRMS (ESI) M/Z+ Calc. 231.0895, Obs. 231.0894.

Methyl 3-oxo-3-(2-phenyl-1H-indol-1-yl)propanoate (9b): The general procedure was followed using sodium hydride (0.414 g, 17.3 mmol), 2-phenyl-1H-indole (3.00 g, 15.5 mmol), methyl-3-chloro-3-oxopropanoate (2.0 mL, 18.7 mmol), and THF (140 mL). After 5 h, the reaction was quenched, and column chromatography afforded 9b as a orange oil (1.28 g, 28%). (R$_f$ 0.48, 30% EtOAc/Hex) $^1$H NMR (400 MHz, CDCl$_3$) δ ppm 8.40 (qd, $J = 0.84$, 8.28 Hz, 1H), 7.55 - 7.59 (m, 1H), 7.44 - 7.49 (m, 5H), 7.36 -
Methyl 3-(2,3-dimethyl-1H-indol-1-yl)-3-oxopropanoate (9c): The general procedure was followed using sodium hydride (0.330 g, 8.26 mmol), 2,3-dimethyl-1H-indole (1.00 g, 6.89 mmol), methyl-3-chloro-3-oxopropanoate (0.921 mL, 8.61 mmol), and THF (35 mL). After 14 h, the reaction was quenched, and column chromatography afforded 9c as a pale yellow solid (1.05 g, 62%). (R, 0.26, 20% EtOAc/Hex) [m.p. 75-77°C] \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) ppm 7.77-7.84 (m, 1H), 7.26-7.32 (m, 1H), 7.17 (m, 2H), 3.88 (s, 2H), 3.72 (s, 3H), 2.34 (s, 3H), 2.03 (s, 3H). \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) ppm 135.0, 128.3, 126.9, 124.7, 124.2, 123.9, 118.5, 117.3, 114.5, 115.8, 117.7, 122.9, 123.6, 130.8, 131.6, 135.0, 165.3, 166.7. IR: 2989.2 (w), 2959.3 (w), 2925.6 (w), 2852.3 (s), 1745.4 (s), 1715.4 (s), 1604.8 (w). HRMS (ESI) M/Z+ Calc. 293.1052, Obs. 293.1053.

Methyl 3-(2,3-dihydrocyclopenta[b]indol-4(1H)-yl)-3-oxopropanoate (9d): The general procedure was followed using sodium hydride (0.764 g, 19.1 mmol), 1,2,3,4-tetrahydrocyclopenta[b]indole (2.5 g, 15.9 mmol), methyl-3-chloro-3-oxopropanoate (2.1 mL, 19.1 mmol), and THF (45 mL). After 16 h, the reaction was quenched, and column chromatography afforded 9d as a brick red solid (3.47 g, 85%). (R, 0.30, 25% EtOAc/Hex) [m.p. 120-122°C] \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) ppm 8.41 (d, \(J = 5.46\) Hz, 1H), 7.31 - 7.37 (m, 1H), 7.21 - 7.30 (m, 2H), 3.86 (s, 2H), 3.79 (s, 3H), 2.92 - 3.00 (m, 2H), 2.70 - 2.78 (m, 2H), 2.45 - 2.57 (m, 2H). \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) ppm 167.0, 164.3, 140.9, 128.3, 126.9, 124.7, 124.2, 123.9, 118.5, 117.3, 114.5, 115.8, 117.7, 122.9, 123.6, 130.8, 131.6, 135.0, 165.3, 166.7. IR: 3116.2 (w), 2988.6 (w), 2947.9 (w), 2928.3 (w), 2869.6 (w), 1752.8 (s), 1693.5 (s), 1608.7 (m), 1447.9 (m), 1344.9 (s), 1379.7 (m), 1346.6 (w), 1325.2 (w), 1260.4 (s), 1161.9 (m), 1122.1 (m), 1074.0 (m), 1029.6 (m), 768.6 (s), 749.6 (m), 686.1 (m) cm\(^{-1}\). HRMS (ESI) M/Z+ Calc. 257.1052, Obs. 257.1045.
Methyl 3-(5-fluoro-2-methyl-1H-indol-1-yl)-3-oxopropanoate (9e): The general procedure was followed using potassium hydride (0.711 g, 17.7 mmol), 5-fluoro-2-methyl-1H-indole (2.03 g, 13.6 mmol), methyl-3-chloro-3-oxopropanoate (1.9 mL, 17.7 mmol), and THF (18 mL). After 14 h, the reaction was quenched, and column chromatography afforded 9e as a red solid (0.805 g, 24%). (R; 0.20, 20% EtOAc/Hex) [m.p. 80-82°C] ¹H NMR (300 MHz, CDCl₃) δ ppm 7.96 (dd, J = 4.45, 9.11 Hz, 1H), 7.08 (dd, J = 2.60, 8.54 Hz, 1H), 6.95 (dt, J = 2.64, 9.09 Hz, 1H), 6.35 (s, 1H), 4.03 (s, 2H), 3.80 (s, 3H), 2.59 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ ppm 168.4, 165.6, 161.2, 158.0, 138.1, 133.0, 130.9, 116.5 and 116.4 (doublet), 111.6, 110.6 and 110.5 (doublet), 105.8, 105.4, 52.8, 45.4, 17.3. IR: 3013.0 (w), 2956.9 (w), 1752.2 (s), 1682.4 (s), 1603.6 (m), 1476.2 (m), 1376.3 (m), 1301.9 (w), 1259.5 (w), 1187.8 (m), 1157.8 (s), 1129.8 (m), 1000.5 (m), 958.5 (m), 870.7 (m), 797.1 (m), 780.4 (m), 668.4 (m) cm⁻¹. HRMS (ESI) M/Z+ Calc. 249.0809, Obs. 249.0809.

Methyl 3-(5-chloro-2-methyl-1H-indol-1-yl)-3-oxopropanoate (9f): The general procedure was followed using sodium hydride (0.2908 g, 7.27 mmol), 5-chloro-2-methyl-1H-indole (1.00 g, 6.06 mmol), methyl-3-chloro-3-oxopropanoate (0.811 mL, 7.57 mmol), and THF (30 mL). After 16 h, the reaction was quenched, and column chromatography afforded 9f as a reddish brown solid (0.114 g, 11%). (R; 0.25, 20% EtOAc/Hex) [m.p. 46-48°C] ¹H NMR (300 MHz, CDCl₃) δ ppm 7.88 (dd, J = 0.44, 8.90 Hz, 1H), 7.35 (d, J = 2.05 Hz, 1H), 7.16 (dd, J = 2.09, 8.90 Hz, 1H), 6.27 (d, J = 0.62 Hz, 1H), 3.99 (s, 2H), 3.79 (s, 3H), 2.55 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ ppm 166.6, 165.6, 137.8, 134.9, 130.9, 129.1, 123.9, 119.4, 116.3, 109.9, 52.7, 45.3, 17.2. IR: 2993.0 (w), 2953.8 (w), 1746.0 (s), 1697.9 (s), 1594.7 (m), 1446.3 (s), 1362.6 (s), 1334.8 (m), 1309.2 (m), 1254.0 (s), 1159.8 (s), 1075.0 (w), 1041.4 (w), 1000.9 (w), 919.6 (w), 807.6 (w), 723.6 (w) cm⁻¹. HRMS (ESI) M/Z+ Calc. 265.0501, Obs. 265.0499.

Methyl 3-(3,4-dihydroquinolin-1(2H)-yl)-3-oxopropanoate (9g): A mixture of potassium carbonate (6.23 g, 44.0 mmol) and 1,2,3,4-tetrahydroquinoline (3.0 g, 22.5 mmol), methyl-3-chloro-3-oxopropanoate (2.7 mL, 24.8 mmol) and acetonitrile (60 mL) were heated to reflux. After 14 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 afforded 9g as a reddish orange oil (3.76 g, 72%). (Rf 0.30, 25% EtOAc/Hex) $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ ppm 7.07 - 7.19 (m, 4H), 3.74 - 3.83 (m, 2H), 3.65 (s, 3H), 3.58 (s, 2H), 2.69 (t, J=6.49 Hz, 2H), 1.94 (quin, J=6.65 Hz, 2H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ ppm 168.1, 165.5, 128.4, 126.3, 125.8, 123.9, 52.2, 42.7, 41.4, 26.4, 23.7. IR: 3004.1 (w), 2951.0 (w), 2889.1 (w), 1739.3 (s), 1651.4 (s), 1603.6 (w), 1580.9 (w), 1491.8 (s), 1435.5 (w), 1386.9 (m), 1326.1 (w), 1201.5 (m), 1155.7 (m), 1074.0 (w), 1019.9 (m), 949.0 (w), 763.0 (s) cm$^{-1}$. HRMS (ESI) M/Z Calc. 233.1052, Obs. 233.1031.

B. Preparation of Acrylates

General Method A:$^1$ The β-amide ester (1.0 equiv.), aldehyde (1.3 equiv.), glacial acetic acid (0.5 equiv.), and piperidine (0.1 equiv.) were heated to a reflux in benzene using a Dean-Stark trap for 14 h. After cooling the reaction mixture to room temperature, water was added to the reaction vessel, and the organic layer was collected. Subsequently, the aqueous phase was extracted with EtOAc three times. The combined organic layers were washed with 1M HCl and saturated sodium bicarbonate. The combined organic layers were dried with Na$_2$SO$_4$, filtered, concentrated, and purified by silica gel column chromatography (gradient EtOAc/Hex).

General Method B:$^1$ A round bottom flask was charged with the β-amide ester (1.0 equiv.) and THF (25 mL). After cooling the solution to 0 °C, titanium(IV) chloride tetrahydrofuran complex (2.0 equiv.) and CCl$_4$ (2.0 equiv.) were added to the reaction vessel. After 1 h at 0 °C, the aldehyde (1.0 equiv.) was added slowly, and the reaction was stirred for an hour. Then, pyridine (4.0 equiv.) was added to the solution dropwise. The reaction mixture was warmed to room temperature and allowed to stir for 14 h. The reaction was quenched with water and the organic layer was collected. The aqueous layer was extracted with ether, and the combined organic layers were washed with saturated NaHCO$_3$ and brine. The organic layer was dried with MgSO$_4$, filtered, concentrated, and purified by silica gel column chromatography (gradient EtOAc/Hex).

(Z)-Methyl 3-(4-methoxyphenyl)-2-(2-methyl-1H-indol-1-yl)-3-oxopropanoate (10a): Methyl 3-(2-methyl-1H-indol-1-yl)-3-oxopropanoate (1.80 g, 7.78 mmol), 4-methoxybenzaldehyde (1.2 mL, 10.1 mmol), glacial acetic acid (0.262 g, 4.37 mmol), piperidine (80 µL, 0.810 mmol) and benzene (120 mL) were mixed according to general method A to afford 10a as an orange oil (2.50 g, 92%) after 18 h. (Rf 0.24, 20% EtOAc/Hex) (Diastereomer!) $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ ppm 8.43 (br. s., 0.81), 7.87 (s, 1.13), 7.72 (s, 0.15), 7.33 - 7.47 (m, 3.50), 7.21 - 7.30 (m, 2.08), 6.89 (d, J = 8.79 Hz, 0.27), 6.75 (d, J = 8.76 Hz, 2.10), 6.35 (s, 1.00), 3.87 (d, J = 0.70 Hz, 0.25), 3.83 (s, 0.26), 3.81 (s, 0.31), 3.77 (s, 2.63), 3.72 (s, 2.94), 2.48 (br. s., 2.87). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ ppm 166.3, 165.1, 161.8, 142.9, 142.5, 131.9, 131.4, 129.8, 125.6, 124.7, 119.6, 114.5, 114.3, 55.2, 52.7, 16.7. IR: 3065.3 (w), 2951.7 (w), 2939.1 (w), 1720.6 (s), 1682.4 (s), 1600.9 (s), 1511.8 (s), 1452.5 (s), 1385.8 (m), 1321.3 (m), 1290.4 (m), 1258.9 (s), 1203.7 (m), 1168.3 (w), 1148.6 (m), 1119.7 (w), 1084.9 (m), 1061.2 (w), 1025.3 (w), 994.5 (w), 986.0 (w), 958.8 (w), 949.0 (w), 887.3 (w), 861.1 (w), 837.9 (w), 785.2 (w), 763.0 (s), 741.3 (w), 714.0 (w), 691.8 (w), 674.1 (w), 618.7 (w), 571.6 (w), 551.8 (w), 539.9 (w), 514.5 (w), 498.6 (w), 475.7 (w), 455.7 (w), 433.8 (w), 413.8 (w), 393.9 (w), 373.9 (w), 354.0 (w), 333.9 (w), 314.0 (w), 294.0 (w), 274.0 (w), 254.0 (w), 234.0 (w), 214.0 (w), 194.0 (w), 174.0 (w), 154.0 (w), 134.0 (w), 114.0 (w), 94.0 (w), 84.0 (w), 74.0 (w), 64.0 (w), 54.0 (w), 44.0 (w), 34.0 (w), 24.0 (w), 14.0 (w).
1172.3 (s), 1123.0 (m), 1056.1 (w), 1027.6 (m), 917.2 (w), 831.4 (m), 763.9 (s), 751.0 (s), 700.6 (m) cm\(^{-1}\).

HRMS (ESI) M/Z+ Calc. 349.1314, Obs. 349.1319.

(Z)-Methyl 3-{(2-methoxyphenyl)-2-(2-methyl-1H-indole-1-carbonyl)acrylate (10b): Methyl 3-{(2-methyl-1H-indol-1-yl)-3-oxopropanoate (0.200 g, 0.865 mmol), 2-methoxybenzaldehyde (0.153 g, 1.12 mmol), glacial acetic acid (0.026 g, 0.433 mmol), piperidine (0.0147 g, 0.173 mmol) and benzene (20 mL) were mixed according to general method A to afford 10b as a yellow solid (0.231 g, 75%) after 16 h. (R, 0.69, 30% EtOAc/Hex) [m.p. 102-104 °C] (Temperature for the \(^1\)H NMR and \(^13\)C NMR = 70 °C) \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ ppm 8.30 (s, 1H), 8.22 (d, J = 7.28 Hz, 1H), 7.43 - 7.48 (m, 1H), 7.36 - 7.42 (m, 1H), 7.28 - 7.34 (m, 1H), 7.22 - 7.28 (m, 2H), 6.87 (d, J = 8.34 Hz, 1H), 6.82 (t, J = 7.84 Hz, 1H), 6.36 (s, 1H), 3.83 (s, 3H), 3.74 (s, 3H), 2.60 (d, J = 0.94 Hz, 3H). \(^13\)C NMR (101 MHz, CDCl\(_3\)) δ ppm 165.9, 165.2, 158.3, 139.7, 139.1, 132.2, 130.2, 129.9, 129.2, 123.8, 123.5, 122.2, 120.9, 119.6, 115.6, 111.2, 110.0, 55.3, 52.4, 16.5. IR: 3051.9 (w), 3003.8 (w), 2951.9 (m), 2840.2 (m), 1713.4 (s), 1680.3 (s), 1618.7 (m), 1596.8 (s), 1574.7 (-M/Z+ Calc. 349.1314, Obs. 349.1319.}

(Z)-Methyl 2-{(2-methyl-1H-indole-1-carbonyl)-3-(4-nitrophenyl)acrylate (10c): Methyl 3-{(2-methyl-1H-indol-1-yl)-3-oxopropanoate (0.300 g, 1.30 mmol), 4-nitrobenzaldehyde (0.255 mg, 1.69 mmol), glacial acetic acid (14.0 µL, 0.130 mmol) and benzene (25 mL) were mixed according to general method A to afford 10c as an orange solid (0.300 g, 64%) after 18 h. (R, 0.45, 20% EtOAc/Hex) [m.p. 109-111 °C] (Temperature for the \(^1\)H NMR and \(^13\)C NMR = 70 °C) \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ ppm 8.03 - 8.09 (m, 3H), 7.94 (s, 1H), 7.49 - 7.54 (m, 2H), 7.38 - 7.42 (m, 1H), 7.20 - 7.25 (m, 2H), 6.34 (d, J = 0.94 Hz, 1H), 3.85 (s, 3H), 2.51 (s, 3H). \(^13\)C NMR (101 MHz, CDCl\(_3\)) δ ppm 164.4, 164.0, 148.8, 139.9, 138.5, 136.7, 132.8, 130.0, 129.9, 124.3, 124.1, 123.9, 120.0, 115.0, 111.2, 52.9, 16.4. IR: 3108.3 (w), 2953.4 (w), 2929.6 (w), 1726.0 (s), 1678.5 (s), 1596.9 (m), 1521.3 (s), 1456.1 (s), 1436.1 (m), 1384.8 (s), 1291.1 (s), 1256.0 (s), 1200.9 (s), 1111.8 (w), 1083.9 (w), 1027.5 (w), 992.3 (w), 852.1 (w), 825.8 (w), 749.1 (s), 691.0 (w) cm\(^{-1}\). HRMS (ESI) M/Z+ Calc. 364.1059, Obs. 364.1076.
(Z)-Methyl 2-(2-methyl-1H-indole-1-carbonyl)-3-(3-nitrophenyl)acrylate (10d): Methyl 3-(2-methyl-1H-indol-1-yl)-3-oxopropanoate (0.350 g, 1.51 mmol), 3-nitrobenzaldehyde (0.297 mg, 1.97 mmol), glacial acetic acid (0.0417 g, 0.696 mmol), piperidine (15 µL, 0.151 mmol) and benzene (20 mL) were mixed according to general method A to afford 10d as a pale yellow solid (0.220 g, 40 %) after 20 h. (R_, 0.40, 20% EtOAc/Hex) [m.p. 112-114 °C] (Temperature for the ¹H NMR and ¹³C NMR = 60 °C) ¹H NMR (400 MHz, CDCl₃) δ ppm 8.21 - 8.24 (m, 1H), 8.10 (ddd, J = 1.00, 2.16, 8.25 Hz, 1H), 8.03 (br. s., 1H), 7.94 (s, 1H), 7.63 - 7.67 (m, 1H), 7.35 - 7.41 (m, 2H), 7.18 - 7.25 (m, 2H), 6.33 (d, J = 0.88 Hz, 1H), 3.86 (s, 3H), 2.54 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ ppm 164.6, 164.2, 148.7, 139.9, 136.7, 134.4, 134.2, 132.1, 130.1, 130.0, 124.9, 124.3, 124.2, 124.2, 120.0, 115.1, 111.3, 53.1, 16.7. IR: 3083.4 (w), 2954.9 (w), 2928.5 (w), 1727.7 (s), 1678.7 (s), 1603.1 (w), 1597.5 (w), 1576.9 (w), 1532.1 (s), 1456.4 (s), 1437.6 (m), 1386.4 (s), 1351.2 (s), 1308.8 (s), 1203.4 (s), 1086.2 (w), 1027.7 (w), 992.8 (w), 824.9 (w), 808.9 (w), 751.6 (m), 736.8 (m), 676.3 (w) cm⁻¹. HRMS (ESI) M/Z+ Calc. 364.1059, Obs. 364.1065.

(Z)-Methyl 3-(4-cyanophenyl)-2-(2-methyl-1H-indole-1-carbonyl)acrylate (10e): Methyl 3-(2-methyl-1H-indol-1-yl)-3-oxopropanoate (0.350 g, 1.51 mmol), 4-cyanobenzaldehyde (0.258 mg, 1.97 mmol), glacial acetic acid (0.0417 g, 0.696 mmol), piperidine (15 µL, 0.151 mmol) and benzene (20 mL) were mixed according to general method A to afford 10e as an off-white solid (0.325 g, 62%) after 18 h. (R_, 0.35, 20% EtOAc/Hex) [m.p. 122-124 °C] ¹H NMR (300 MHz, CDCl₃) δ ppm 8.81 - 8.05 (br. s., 1H), 7.38 - 7.53 (m, 6H), 7.20 - 7.28 (m, 2H), 6.35 (s, 1H), 3.82 (s, 3H), 2.46 (br. s., 3H). ¹³C NMR (75 MHz, CDCl₃) δ ppm 164.6, 164.0, 140.4, 136.4, 132.5, 131.5, 129.6, 124.2, 119.9, 117.7, 113.8, 111.2, 53.1, 16.7. IR: 3056.6 (w), 2954.9 (w), 2928.2 (w), 2229.5 (m), 1725.7 (s), 1677.7 (s), 1627.5 (m), 1596.9 (m), 1576.6 (m), 1504.2 (w), 1456.0 (s), 1435.5 (s), 1384.3 (s), 1303.3 (s), 1256.1 (s), 1201.7 (s), 1152.5 (w), 1117.1 (w), 1084.3 (m), 1027.4 (m), 992.3 (m), 936.0 (w), 830.2 (m), 750.5 (s) cm⁻¹. HRMS (ESI) M/Z+ Calc. 344.1161, Obs. 344.1169.
(Z)-Methyl 3-(4-fluorophenyl)-2-(2-methyl-1H-indole-1-carbonyl)acrylate (10f): Methyl 3-(2-methyl-1H-indol-1-yl)-3-oxopropanoate (0.350 g, 1.51 mmol), 4-fluorobenzaldehyde (0.210 mL, 2.00 mmol), glacial acetic acid (0.0417 g, 0.695 mmol), piperidine (15 µL, 0.151 mmol) and benzene (25 mL) were mixed according to general method A to afford 10f as a yellow solid (0.293 g, 57%) after 18 h. (Rf 0.40, 20% EtOAc/Hex) [m.p. 76-78 °C] (Temperature for the 1H NMR and 13C NMR = 60 °C) 1H NMR (300 MHz, CDCl3) δ ppm 8.20 (br. s., 1H), 7.89 (s, 1H), 7.34 - 7.45 (m, 3H), 7.17 - 7.30 (m, 2H), 6.92 (t, J = 8.59 Hz, 2H), 6.34 (s, 1H), 3.80 (s, 3H), 2.50 (s, 3H). 13C NMR (75 MHz, CDCl3) δ ppm 165.7, 165.5, 164.7, 162.4, 141.8, 136.9, 131.9 and 131.7 (doublet), 129.9, 124.2 and 124.0 (doublet), 119.8, 116.4, 116.1, 115.5, 110.9, 52.7, 16.6. IR: 3076.2 (w), 2951.8 (s), 1724.8 (s), 1683.9 (s), 1627.8 (w), 1598.7 (s), 1508.9 (s), 1456.5 (s), 1436.7 (m), 1386.76 (s), 1301.0 (m), 1260.4 (s), 1197.7 (s), 1162.4 (s), 834.7 (m), 750.5 (s), 668.5 (m) cm⁻¹. HRMS (ESI) M/Z+ Calc. 337.1114, Obs. 349.1107.

(Z)-Methyl 3-(3-bromophenyl)-2-(2-methyl-1H-indole-1-carbonyl)acrylate (10g): Methyl 3-(2-methyl-1H-indol-1-yl)-3-oxopropanoate (0.350 g, 1.51 mmol), 3-bromobenzaldehyde (0.230 mL, 1.97 mmol), glacial acetic acid (0.0417 g, 0.696 mmol), piperidine (15 µL, 0.151 mmol) and benzene (20 mL) were mixed according to general method A to afford 10g as a pale gray solid (0.430 g, 72 %) after 18 h. (Rf 0.40, 20% EtOAc/Hex) [m.p. 107-109 °C] (Temperature for the 1H NMR and 13C NMR = 60 °C) 1H NMR (400 MHz, CDCl3) δ ppm 8.08 - 8.19 (m, 1H), 7.86 (s, 1H), 7.52 - 7.56 (m, 1H), 7.39 - 7.44 (m, 2H), 7.27 - 7.33 (m, 1H), 7.21 - 7.27 (m, 2H), 7.05 - 7.11 (m, 1H), 6.35 (d, J = 0.75 Hz, 1H), 3.85 (s, 3H), 2.54 (s, 3H). 13C NMR (101 MHz, CDCl3) δ ppm 165.0, 164.4, 141.2, 136.8, 136.5, 134.5, 133.5, 132.5, 130.5, 130.3, 130.0, 127.5, 124.2, 124.0, 123.0, 119.8, 115.3, 111.0, 52.8, 16.6. IR: 2962.5 (w), 2926.4 (w), 1726.6 (s), 1681.3 (s), 1625.7 (m), 1596.8 (w), 1561.3 (w), 1456.4 (s), 1435.7 (m), 1384.9 (s), 1311.0 (s), 1258.9 (s), 1198.1 (s), 1076.9 (w), 1027.7 (w), 994.3 (w), 786.6 (w), 750.3 (s), 680.8 (w) cm⁻¹. HRMS (ESI) M/Z+ Calc. 397.0314, Obs. 397.0316.

(Z)-Methyl 2-(2-methyl-1H-indole-1-carbonyl)-3-(thiophen-2-yl)acrylate (10h): Methyl 3-(2-methyl-1H-indol-1-yl)-3-oxopropanoate (0.350 g, 1.51 mmol), thiophene-2-carbaldehyde (0.220 mg, 1.97 mmol), glacial acetic acid (0.0417 g, 0.696 mmol), piperidine (15 µL, 0.150 mmol) and benzene (20 mL) were mixed according to general method A to afford 10h as an off-white solid (0.396 g, 81%) after 18 h. (Rf 0.45, 20% EtOAc/Hex) [m.p. 153-155 °C] 1H NMR (300 MHz, CDCl3) δ ppm 8.28 (br. s., 1H), 8.04 (d, J = 0.37 Hz, 1H), 7.42 - 7.48 (m, 1H), 7.36 (d, J = 5.06 Hz, 1H), 7.29 - 7.33 (m, 1H), 7.23 - 7.29 (m, 2H), 6.95 - 7.00 (m, 1H), 6.39 (s, 1H), 3.79 (s, 3H), 2.50 (s, 3H). 13C NMR (75 MHz, CDCl3) δ ppm 165.3, 164.9, 136.9,
135.7, 135.1, 134.6, 132.5, 129.9, 128.0, 124.9, 124.2, 124.0, 119.7, 115.9, 111.0, 108.0, 52.8, 16.8. IR: 3104.8 (w), 2952.1 (w), 2927.5 (w), 1719.0 (s), 1675.8 (s), 1611.7 (s), 1455.9 (s), 1385.9 (s), 1342.5 (m), 1303.5 (s), 1253.5 (s), 1202.6 (s), 1086.3 (w), 1051.6 (w), 1027.9 (w), 992.9 (w), 858.1 (w), 750.5 (s), 717.4 (m) cm⁻¹. HRMS (ESI) M/Z+ Calc. 325.0773, Obs. 325.0780.

(Z)-10i

(Z)-methyl 2-(2-methyl-1H-indole-1-carbonyl)penta-2-enoate (10i): Methyl 3-(2-methyl-1H-indol-1-yl)-3-oxopropanoate (0.500 g, 2.16 mmol), propanaldehyde (0.155 mL, 2.16 mmol), TiCl₄•THF (1.44 g, 4.32 mmol), CCl₄ (0.418 mL, 4.32 mmol), pyridine (0.699 mL, 8.65 mmol) and THF (35 mL) were combined according to general method B to yield 10i as a clear oil (0.421 g, 72%) after 14 h. (Rf 0.55, 20% EtOAc/Hex) ¹H NMR (300 MHz, CDCl₃) δ ppm 8.13 (br. s., 1H), 7.50 - 7.58 (m, 1H), 7.27 - 7.36 (m, 3H), 6.48 (d, J = 0.77 Hz, 1H), 3.82 (s, 3H), 2.60 (s, 3H), 2.28 (quin, J = 7.63 Hz, 2H), 1.13 (t, J = 7.53 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ ppm 165.1, 164.2, 150.7, 136.8, 136.5, 131.5, 129.8, 123.8, 123.7, 119.8, 115.2, 110.4, 52.5, 23.1, 16.9, 12.3. IR: 2973.6 (w), 2936.1 (w), 1726.6 (s), 1685.9 (s), 1643.0 (w), 1596.5 (w), 1575.5 (w), 1456.3 (s), 1436.9 (m), 1384.1 (s), 1310.8 (s), 1289.7 (s), 1243.9 (s), 1205.4 (w), 1036.7 (w), 989.8 (w), 783.4 (w), 750.3 (s) cm⁻¹. HRMS (ESI) M/Z+ Calc. 271.1208, Obs. 271.1218.

(Z)-10j

(2Z, 4E)-Methyl 2-(2-methyl-1H-indole-1-carbonyl)-5-phenylpenta-2,4-dienoate (10j): Methyl 3-(2-methyl-1H-indol-1-yl)-3-oxopropanoate (0.300 g, 1.30 mmol), cinnamaldehyde (0.21 mL, 1.69 mmol), glacial acetic acid (0.0357 g, 0.596 mmol), piperidine (13.97 µL, 0.1297 mmol) and benzene (25 mL) were mixed according to general method A to afford 10j as a reddish orange oil (0.256 g, 57%) after 20 h. (Rf 0.48, 20% EtOAc/Hex) ¹H NMR (300 MHz, CDCl₃) δ ppm 8.10 - 8.18 (m, 1H), 7.76 (d, J = 11.73 Hz, 1H), 7.45 - 7.51 (m, 1H), 7.34 - 7.42 (m, 2H), 7.23 - 7.34 (m, 5H), 7.12 (d, J = 15.39 Hz, 1H), 6.82 - 6.95 (m, 1H), 6.42 (s, 1H), 3.74 (s, 3H), 2.54 (d, J = 0.99 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ ppm 165.1, 164.8, 145.4, 145.0, 136.7, 136.6, 135.1, 130.0, 129.7, 129.7, 129.0, 128.8, 128.5, 127.8, 123.9, 123.7, 122.2, 119.8, 115.3, 110.4, 52.6, 16.7. IR: 3030.0 (w), 2949.9 (w), 1721.0 (s), 1682.4 (s), 1614.7 (m), 1590.8 (m), 1456.2 (s), 1435.3 (m), 1384.9 (s), 1308.3 (s), 1278.6 (s), 1237.6 (s), 1202.0 (w), 1077.2 (w), 993.8 (w), 836.1 (w), 750.7 (s), 691.5 (w) cm⁻¹. HRMS (ESI) M/Z+ Calc. 345.1365, Obs. 345.1383.
(Z)-Methyl 3-(4-methoxyphenyl)-2-(2-phenyl-1H-indole-1-carbonyl)acrylate (10k): Methyl 3-oxo-3-(2-phenyl-1H-indol-1-yl)propanoate (1.28 g, 4.36 mmol), 4-methoxybenzaldehyde (0.70 mL, 5.75 mmol), glacial acetic acid (0.131 g, 2.18 mmol), piperidine (50 µL, 0.506 mmol) and benzene (120 mL) were mixed according to general method A to afford 10k as a dark brown solid (0.456 g, 25%) after 18 h. (Rf 0.37, 20% EtOAc/Hex) [m.p. 105-107 °C] \(^1\)H NMR (300 MHz, CDCl₃) δ ppm 8.63 (d, J = 8.17 Hz, 1H), 7.40 - 7.51 (m, 2H), 7.29 - 7.38 (m, 2H), 7.19 - 7.27 (m, 2H), 7.16 (s, 1H), 7.00 - 7.13 (m, 4H), 6.54 - 6.61 (m, 2H), 6.34 (s, 1H), 3.73 (s, 3H), 3.71 (s, 3H). \(^13\)C NMR (75 MHz, CDCl₃) δ ppm 166.8, 164.4, 161.5, 143.1, 139.8, 138.2, 133.4, 131.6, 129.6, 128.6, 127.8, 125.4, 125.2, 125.0, 124.3, 120.2, 116.6, 114.0, 111.9, 55.3, 52.3. IR: 3065.3 (w), 2951.7 (w), 2939.1 (w), 1720.6 (s), 1682.4 (s), 1600.9 (s), 1511.8 (s), 1452.5 (s), 1385.8 (m), 1321.3 (m), 1290.4 (m), 1203.7 (m), 1172.3 (s), 1123.0 (m), 1056.1 (w), 1027.6 (m), 917.2 (w), 831.4 (m), 763.9 (s), 751.0 (s), 700.6 (m) cm⁻¹. HRMS (ESI) M/Z+ Calc. 411.1471, Obs. 411.1480.

(Z)-Methyl 2-(2,3-dimethyl-1H-indole-1-carbonyl)-3-(4-methoxyphenyl)acrylate (10l): Methyl 3-(2,3-dimethyl-1H-indol-1-yl)-3-oxopropanoate (1.00 g, 4.08 mmol), 4-methoxybenzaldehyde (0.617 mL, 5.10 mmol), glacial acetic acid (0.112 g, 1.88 mmol), piperidine (0.0340 g, 0.407 mmol) and benzene (35 mL) were mixed according to general method A to afford 10l as a yellow solid (1.080 g, 73%) after 18 h. (Rf 0.25, 20% EtOAc/Hex) [m.p. 94-96°C] \(^1\)H NMR (300 MHz, CDCl₃) δ ppm 8.63 (br. s, 1H), 7.87 (br. s., 1H), 7.33 - 7.48 (m, 3H), 7.28 (br. s., 2H), 6.73 (d, J = 8.50 Hz, 2H), 3.77 (s, 3H), 3.67 (d, J = 1.21 Hz, 3H), 2.25 - 2.53 (s, 3H), 2.15 (s, 3H). \(^13\)C NMR (75 MHz, CDCl₃) δ ppm 165.9, 165.2, 161.9, 142.5, 136.1, 131.8, 131.5, 126.6, 125.3, 124.3, 123.6, 117.9, 116.5, 114.6, 55.2, 52.4, 13.4, 8.6. IR: 3008.4 (w), 2933.3 (w), 2839.7 (w), 1721.5 (s), 1675.4 (s), 1601.6 (s), 1513.5 (s), 1458.5 (s), 1396.3 (m), 1306.8 (s), 1258.4 (s), 1203.4 (m), 1174.8 (s), 1133.5 (w), 1028.0 (w), 907.9 (w), 832.0 (w), 750.0 (s) cm⁻¹. HRMS (ESI) M/Z+ Calc. 363.1471, Obs. 363.1470.
(Z)-Methyl 3-(4-methoxyphenyl)-2-(1,2,3,4-tetrahydrocyclopenta[b]indole-4-carbonyl)acrylate (10m): Methyl 3-(2,3-dihydrocyclopenta[b]indol-4(1H)-yl)-3-oxopropanoate (0.175 g, 0.681 mmol), 4-methoxybenzaldehyde (0.107 mL, 0.885 mmol), glacial acetic acid (0.0187 g, 0.313 mmol), piperidine (6.8 µL, 0.0680 mmol) and benzene (15 mL) were mixed according to general method A to afford 10m as a white solid (0.052 g, 20%) after 18 h. (Rf 0.40, 20% EtOAc/Hex) [m.p. 156-158 °C] 1H NMR (300 MHz, CDCl₃) δ ppm 8.64 - 8.72 (m, 1H), 7.82 (s, 1H), 7.24 - 7.44 (m, 5H), 6.75 - 6.82 (m, 2H), 3.80 (s, 3H), 3.75 (s, 3H), 2.60 - 2.80 (m, 4H), 2.25 - 2.50 (m, 2H). 13C NMR (75 MHz, CDCl₃) δ ppm 165.5, 165.3, 161.8, 142.9, 141.7, 140.9, 132.0, 128.1, 127.4, 124.9, 124.5, 124.3, 124.2, 118.5, 115.7, 114.7, 55.3, 52.7, 28.9, 27.5, 23.8. IR: 2950.7 (w), 2857.5 (w), 1720.8 (m), 1681.7 (s), 1602.0 (s), 1513.5 (s), 1450.13 (m), 1392.8 (m), 1258.2 (s), 1173.02 (s), 1103.5 (w), 1043.3 (w), 983.9 (w), 831.7 (w), 751.0 (m) cm⁻¹. HRMS (ESI) M/Z+ Calc. 375.1471, Obs. 375.1474.

(Z)-10n

(Z)-Methyl 2-(5-fluoro-2-methyl-1H-indole-1-carbonyl)-3-(4-methoxyphenyl)acrylate (10n): Methyl 3-(5-fluoro-2-methyl-1H-indol-1-yl)-3-oxopropanoate (0.301 g, 1.21 mmol), 4-methoxybenzaldehyde (0.180 mL, 1.48 mmol), glacial acetic acid (0.0520 g, 0.873 mmol), piperidine (25 µL, 0.253 mmol) and benzene (30 mL) were mixed according to general method A to afford 10n as a pale brick solid (0.382 g, 86%) after 18 h. (Rf 0.43, 30% EtOAc/Hex) [m.p. 95-97 °C] (Temperature for the 1H NMR and 13C NMR = 60 °C) 1H NMR (300 MHz, CDCl₃) δ ppm 8.25 (brs, 1H), 7.85 (s, 1H), 7.28 - 7.39 (m, 2H), 7.05 (dd, J = 2.57, 8.61 Hz, 1H), 6.95 (dt, J = 2.58, 9.12 Hz, 1H), 6.70 - 6.79 (m, 2H), 6.27 (s, 1H), 3.78 (s, 3H), 3.71 (s, 3H). 13C NMR (75 MHz, CDCl₃) δ ppm 166.0, 165.0, 162.1, 161.5, 158.3, 143.0, 133.3, 131.8, 131.1 and 131.0 (doublet), 125.8, 124.9, 116.9, 114.6, 111.5, 111.2, 110.3, 105.5, 105.2, 55.2, 52.5, 16.5. IR: 2948.8 (w), 2903.6 (w), 1720.7 (m), 1685.4 (m), 1602.5 (s), 1513.7 (s), 1472.7 (m), 1448.5 (m), 1389.2 (m), 1301.5 (m), 1274.6 (s), 1260.5 (s), 1176.5 (s), 995.0 (w), 957.3 (w), 832.8 (w), 764.3 (s), 750.0 (s) cm⁻¹. HRMS (ESI) M/Z+ Calc. 367.1220, Obs. 367.1226.

(Z)-10o

(Z)-Methyl 2-(5-chloro-2-methyl-1H-indole-1-carbonyl)-3-(4-methoxyphenyl)acrylate (10o): Methyl 3-(5-chloro-2-methyl-1H-indol-1-yl)-3-oxopropanoate (0.565 g, 2.14 mmol), 4-methoxybenzaldehyde (0.337 mL, 2.77 mmol), glacial acetic acid (0.0589 g, 0.982 mmol), piperidine (21 µL, 0.214 mmol) and benzene (30 mL) were mixed according to general method A to afford 10o as an off-white solid (0.300 g, 37%) after 20 h. (Rf 0.40, 20% EtOAc/Hex) [m.p. 111-113 °C] (Temperature for the 1H NMR and 13C NMR = 60 °C) 1H NMR (300 MHz, CDCl₃) δ ppm 8.20 (d, J = 8.54 Hz, 1H), 7.86 (s, 1H), 7.30 - 7.40 (m, 3H), 7.20 (dd, J = 2.11, 8.85 Hz, 1H), 6.72 - 6.79 (m, 2H), 6.26 (s, 1H), 3.78 (s, 3H), 3.72 (s, 3H), 2.47 (s, 3H). 13C
NMR (75 MHz, CDCl₃) δ ppm 166.1, 164.9, 162.1, 143.2, 138.0, 135.4, 131.8, 131.2, 129.5, 125.8, 124.9, 124.1, 119.3, 116.7, 114.7, 109.8, 55.2, 52.5, 16.5. IR: 2952.3 (w), 2839.8 (w), 2360.1 (m), 2342.4 (m), 1718.7 (s), 1683.4 (s), 1597.9 (s), 1512.5 (s), 1442.9 (s), 1385.6 (s), 1345.9 (m), 1294.5 (m), 1255.6 (s), 1201.3 (m), 1171.5 (s), 1124.2 (w), 1072.5 (w), 1021.4 (w), 995.1 (w), 914.0 (w), 829.9 (m), 800.5 (w). HRMS (ESI) M/Z+ Calc. 337.1314, Obs. 337.1319.

Methyl 2-(indoline-1-carbonyl)-3-(4-methoxyphenyl)acrylate (12a): Methyl 3-(indolin-1-yl)-3-oxopropanoate (0.350 g, 1.60 mmol), 4-methoxyphenylacrylate (0.3500 g, 1.5010 mmol) and benzene (30 mL) were mixed according to general method A to afford 12a as an orange oil (0.390 g, 72%) after 20 h. (Rr 0.35, 20% EtOAc/Hex) (Diastereomers) ¹H NMR (300 MHz, CDCl₃) δ ppm 8.41 (d, J = 8.03 Hz, 1.00), 7.82 (s, 0.20), 7.70 (s, 1.14), 7.43 - 7.54 (m, 2.47), 7.28 - 7.33 (m, 0.81), 7.16 - 7.22 (m, 1.27), 7.01 - 7.13 (m, 1.44), 6.80 - 6.88 (m, 2.53), 4.36 - 4.50 (m, 0.18), 4.18 - 4.31 (m, 0.20), 3.94 (br.s., 1.16), 3.83 (s, 3.16), 3.61 - 3.80 (m, 3.87), 3.71 - 3.76 (m, 1.78), 2.92 - 3.22 (m, 2.49). ¹³C NMR (101 MHz, CDCl₃) δ ppm 165.4, 165.0, 161.9, 142.6, 142.4, 140.6, 132.0, 131.8, 127.7, 126.0, 125.8, 124.6, 124.4, 117.5, 114.8, 114.5, 55.3, 52.4, 48.4, 28.0. IR: 3004.8 (w), 2951.7 (w), 2839.7 (w), 1716.9 (s), 1645.7 (s), 1598.9 (s), 1512.6 (s), 1482.3 (s), 1413.3 (m), 1255.3 (s), 1174.5 (s), 1126.4 (m), 1057.9 (m), 1027.4 (m), 832.3 (m), 755.8 (s), 668.5 (m) cm⁻¹. HRMS (ESI) M/Z+ Calc. 337.1314, Obs. 337.1319.

(Z)-Methyl 3-(4-methoxyphenyl)-2-(1,2,3,4-tetrahydroquinoline-1-carbonyl)acrylate (12b): Methyl 3-(3,4-dihydroquinolin-1(2H)-yl)-3-oxopropanoate (0.3500 g, 1.5010 mmol), 4-methoxybenzaldehyde (0.2370 mL, 1.9510 mmol), glacial acetic acid (0.0414 g, 0.6900 mmol), piperidine (14.80 µL, 0.1501 mmol) and benzene (30 mL) were mixed according to general method A to afford 12b as a orange oil (0.4230 g, Crude = 80%) after 15 h. (Rr 0.35, 20% EtOAc/Hex) HRMS (ESI) M/Z+ Calc. 351.1471, Obs. 351.1499.
C. In(OTf)₃-Catalyzed Cyclizations

**General Procedure**: To a mixture of In(OTf)₃ (0.10-0.15 equiv.) in 1,2-DCE (or toluene) heated to a reflux, dissolved 10 (or 12) (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 DCM. The combined organic layers were washed with brine, dried over MgSO₄, filtered, and concentrated for column chromatography using silica gel.

![11a](image)

**Methyl 6-(4-methoxyphenyl)-2-methyl-4-oxo-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinoline-5-carboxylic acid (11a)**: Methyl 3-(4-methoxyphenyl)-2-(2-methyl-1H-indole-1-carbonyl)acrylate (0.258 g, 0.739 mmol), In(OTf)₃ (0.0428 g, 0.0760 mmol) and 1,2-DCE (13 mL) were combined according to the general procedure to afford 11a as a brown solid (0.161 g, 63%) after 3 h. (Rf 0.35, 20% EtOAc/Hex) [m.p. 122-124 °C] *Diastereomeric ratio*: (50:1). ¹H NMR (300 MHz, CDCl₃) δ ppm 7.31 - 7.37 (m, 1H), 7.14 - 7.20 (m, 2H), 7.08 - 7.13 (m, 1H), 6.84 - 6.92 (m, 2H), 6.71 (d, J = 7.48 Hz, 1H), 6.41 (d, J = 1.25 Hz, 1H), 4.96 (d, J = 10.85 Hz, 1H), 4.19 (d, J = 10.88 Hz, 1H), 3.81 (s, 3H), 3.68 (s, 3H), 2.71 (d, J = 1.03 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ ppm 169.0, 164.0, 158.3, 137.2, 134.9, 130.9, 129.6, 127.4, 124.0, 122.7, 121.0, 118.4, 114.3, 109.4, 58.8, 55.2, 52.6, 45.3, 15.2. IR: 2954.7 (w), 2922.5 (w), 2850.5 (w), 1749.6 (s), 1709.3 (s), 1611.6 (w), 1531.5 (s), 1443.5 (s), 1381.8 (s), 1340.9 (s), 1252.6 (s), 1178.9 (w), 1153.2 (m), 1032.8 (m), 818.6 (m), 764.7 (m), 749.1 (s) cm⁻¹. HRMS (ESI) M/Z+ Calc. 349.1314, Obs. 349.1310.

![11b](image)

**Methyl 6-(2-methoxyphenyl)-2-methyl-4-oxo-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinoline-5-carboxylic acid (11b)**: Methyl 3-(2-methoxyphenyl)-2-(2-methyl-1H-indole-1-carbonyl)acrylate (0.060 g, 0.172 mmol), In(OTf)₃ (0.0145 g, 0.0250 mmol) and toluene (4 mL) were combined according to the general procedure to afford 11b as a clear oil (0.0522 g, 87% for combined cis and trans isomers) after 3 h. (Rf 0.35, 20% EtOAc/Hex) *Diastereomeric ratio*: (3:7:1). (trans-Diastereomer chemical shifts reported) ¹H NMR (400 MHz, CDCl₃) δ ppm 7.33 (d, J = 7.72 Hz, 1H), 7.23 - 7.29 (m, 1H), 7.11 (t, J = 7.62 Hz, 1H), 6.83 - 6.94 (m, 3H), 6.76 (d, J = 7.47 Hz, 1H), 6.40 (d, J = 1.13 Hz, 1H), 5.26 (d, J = 7.72 Hz, 1H), 4.41 (d, J = 7.65 Hz, 1H), 3.75 (s, 3H), 3.67 (s, 3H), 2.72 (d, J = 0.94 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ ppm 169.4, 164.4, 157.3, 137.2, 135.1, 129.7, 129.0, 127.7, 127.4, 124.0, 121.8, 120.9, 120.6, 118.1, 111.2, 109.2, 56.2, 55.4, 52.7, 41.8, 15.2. IR: 3065.0 (w), 3032.3 (w), 3003.1 (m), 2954.0 (m), 2839.0 (m), 1745.7 (s), 1707.2 (s), 1627.5 (w), 1600.6 (w), 1586.6 (w), 1573.3 (w), 1493.3 (m), 1443.7 (m), 1380.9 (m), 1338.7 (m), 1287.0 (m), 1210.6 (s), 1154.0 (m), 1119.0 (m), 1047.7 (w), 1026.1 (m), 967.6 (m), 911.8 (m), 820.2 (w), 748.8 (m), 732.9 (m) cm⁻¹. HRMS (ESI) M/Z+ Calc. 349.1314, Obs. 349.1328.
trans-Methyl 2-methyl-6-(4-nitrophenyl)-4-oxo-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinoline-5-carboxylate (11c): Methyl 2-(2-methyl-1H-indole-1-carbonyl)-3-(4-nitrophenyl)acrylate (0.070 g, 0.1922 mmol), In(OTf)₃ (0.0162 g, 0.0288 mmol) and toluene (4 mL) were combined according to the general procedure to afford 11c as an orange oil (0.0548 g, 78% for combined cis and trans isomers) after 14 h. (Rₚ 0.40, 20% EtOAc/Hex) Diastereomeric ratio: (2.4:1) (trans-Diastereomer chemical shifts reported) ¹H NMR (300 MHz, CDCl₃) δ ppm 8.19 - 8.28 (m, 2H), 7.42 - 7.50 (m, 2H), 7.39 (d, J = 7.77 Hz, 1H), 7.15 (t, J = 7.64 Hz, 1H), 6.64 (d, J = 7.48 Hz, 1H), 6.45 (d, J = 1.21 Hz, 1H), 5.16 (d, J = 10.44 Hz, 1H), 4.21 (d, J = 10.44 Hz, 1H), 3.69 (s, 3H), 2.71 (d, J = 1.17 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ ppm 168.4, 163.0, 147.6, 146.8, 137.6, 129.6, 127.8, 124.3, 124.2, 120.8, 120.6, 119.2, 109.6, 58.0, 53.0, 45.8, 15.2. IR: 3066.3 (w), 2955.2 (w), 2923.9 (w), 2850.9 (w), 168.4, 163.0, 147.6, 146.8, 137.6, 129.6, 127.8, 124.3, 124.2, 120.8, 120.6, 119.2, 109.6, 58.0, 53.0, 45.8, 15.2. HRMS (ESI) M/Z+ Calc. 364.1059, Obs. 364.1048.

Methyl 2-methyl-6-(3-nitrophenyl)-4-oxo-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinoline-5-carboxylate (11d): Methyl 2-(2-methyl-1H-indole-1-carbonyl)-3-(3-nitrophenyl)acrylate (0.100 g, 0.275 mmol), In(OTf)₃ (0.0231 g, 0.0411 mmol) and 1,2-DCE (4 mL) were combined according to the general procedure to afford 11d as an off-white solid (0.0861 g, 86% for combined cis and trans isomers) after 13 h. (Rₚ 0.35, 20% EtOAc/Hex) [m.p. 106-108 °C] Diastereomeric ratio: (2.2:1) (trans-Diastereomer chemical shifts reported) ¹H NMR (300 MHz, CDCl₃) δ ppm 8.19 - 8.28 (m, 2H), 7.42 - 7.50 (m, 2H), 7.39 (d, J = 7.77 Hz, 1H), 7.15 (t, J = 7.64 Hz, 1H), 6.64 (d, J = 7.48 Hz, 1H), 6.43 - 6.46 (m, 1H), 5.16 (d, J = 10.44 Hz, 1H), 4.21 (d, J = 10.44 Hz, 1H), 3.69 (s, 3H), 2.71 (d, J = 1.17 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ ppm 168.4, 163.0, 147.6, 146.8, 137.6, 129.6, 127.8, 125.0, 124.3, 124.2, 120.8, 120.6, 119.2, 109.6, 58.0, 53.0, 45.8, 15.2. IR: 3066.6 (w), 2955.3 (w), 2923.4 (w), 1746.0 (s), 1708.6 (s), 1530.3 (s), 1444.0 (s), 1380.6 (s), 1346.0 (s), 1286.5 (m), 1267.1 (m), 1154.2 (s), 1052.1 (w), 1003.0 (w), 966.4 (w), 904.1 (w), 817.3 (m), 738.9 (s), 709.5 (m), 613.4 (m) cm⁻¹. HRMS (ESI) M/Z+ Calc. 364.1059, Obs. 364.1055.
Methyl 6-(cyanophenyl)-2-methyl-4-oxo-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinoline-5-carboxylate (11e): Methyl 3-(cyanophenyl)-2-(2-methyl-1H-indole-1-carbonyl)acrylate (0.0900 g, 0.263 mmol), {\(\text{In(OTf)}_3\)} (0.0220 g, 0.0392 mmol) and 1,2-DCE (4 mL) were combined according to the general procedure to afford 11e as a pale orange solid (0.0704 g, 78% for combined cis and trans isomers) after 14 h. (Rf 0.35, 20% EtOAc/Hex) [m.p. 155-157 °C] Diastereomeric ratio: (1.85:1). (trans-diastereomer chemical shifts reported) \(^{1}H\) NMR (300 MHz, CDCl\(_3\)) \(\delta\) ppm 7.66 (d, \(J = 8.25\) Hz, 2H), 7.38 (d, \(J = 7.88\) Hz, 3H), 7.14 (t, \(J = 7.62\) Hz, 1H), 6.64 (d, \(J = 7.44\) Hz, 1H), 6.44 (d, \(J = 0.92\) Hz, 1H), 5.09 (d, \(J = 10.30\) Hz, 1H), 4.18 (d, \(J = 10.85\) Hz, 1H), 3.69 (s, 3H), 2.71 (s, 3H). \(^{13}C\) NMR (75 MHz, CDCl\(_3\)) \(\delta\) ppm 168.4, 163.1, 144.8, 137.5, 132.8, 129.4, 127.7, 124.3, 120.8, 119.1, 118.4, 112.0, 109.6, 52.8, 52.9, 46.0, 15.2. IR: 2955.3 (w), 2922.9 (w), 2229.2 (w), 1748.4 (s), 1712.4 (s), 1532.6 (w), 1445.2 (s), 1383.0 (s), 1344.2 (m), 1275.0 (s), 1262.2 (s), 1156.3 (m), 819.0 (w), 749.7 (s) cm\(^{-1}\). HRMS (ESI) M/Z+ Calc. 344.1161, Obs. 344.1172.

Methyl 6-(fluorophenyl)-2-methyl-4-oxo-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinoline-5-carboxylate (11f): Methyl 3-(fluorophenyl)-2-(2-methyl-1H-indole-1-carbonyl)acrylate (0.0760 g, 0.225 mmol), {\(\text{In(OTf)}_3\)} (0.0188 g, 0.0330 mmol) and 1,2-DCE (8 mL) were combined according to the general procedure to afford 11f as a yellow solid (0.0716 g, 94% for combined cis and trans isomers) after 1 h. (Rf 0.68, 30% EtOAc/Hex) [m.p. 153-155 °C] Diastereomeric ratio: (2.6:1) (trans-Diastereomer chemical shifts reported) \(^{1}H\) NMR (300 MHz, CDCl\(_3\)) \(\delta\) ppm 7.36 (d, \(J = 7.77\) Hz, 1H), 7.19 - 7.25 (m, 2H), 7.13 (t, \(J = 7.62\) Hz, 1H), 7.00 - 7.09 (m, 2H), 6.68 (d, \(J = 7.44\) Hz, 1H), 6.42 (d, \(J = 1.17\) Hz, 1H), 5.01 (d, \(J = 10.85\) Hz, 1H), 4.18 (d, \(J = 10.85\) Hz, 1H), 3.68 (s, 3H), 2.71 (s, 3H). \(^{13}C\) NMR (75 MHz, CDCl\(_3\)) \(\delta\) ppm 168.8, 163.7, 137.3, 134.8, 130.2 and 130.1 (doublet), 127.5, 124.2, 122.1, 120.9, 118.7, 116.1, 115.8, 109.5, 77.2, 58.7, 52.7, 45.4, 15.2. IR: 3058.4 (w), 2954.5 (w), 2923.0 (w), 1746.8 (s), 1708.7 (s), 1605.3 (w), 1509.8 (s), 1443.8 (s), 1380.9 (s), 1340.0 (s), 1267.9 (m), 1224.3 (s), 1159.1 (s), 1097.6 (w), 1051.5 (w), 1010.0 (w), 967.1 (w), 818.5 (m), 748.7 (s) cm\(^{-1}\). HRMS (ESI) M/Z+ Calc. 337.1114, Obs. 337.1115.
Methyl 6-{3-bromophenyl}-2-methyl-4-oxo-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinoline-5-carboxylate (11g): Methyl 3-{3-bromophenyl}-2-(2-methyl-1H-indole-1-carbonyl)acrylate (0.100 g, 0.252 mmol), In(OTf)₃ (0.0213 g, 0.0377 mmol) and 1,2-DCE (4 mL) were combined according to the general procedure to afford 11g as a pale yellow solid (0.0614 g, 61%) after 14 h. (Rₛ, 0.40, 20% EtOAc/Hex) [m.p. 123-125 °C] Diastereomeric ratio: (8:3:1). (trans-Diastereomer chemical shifts reported) ¹H NMR (300 MHz, CDCl₃) δ ppm 7.41 - 7.49 (m, 2H), 7.33 - 7.39 (m, 1H), 7.10 - 7.27 (m, 3H), 6.69 (d, J = 7.48 Hz, 1H), 6.43 (d, J = 0.92 Hz, 1H), 4.98 (d, J = 10.59 Hz, 1H), 4.19 (d, J = 10.63 Hz, 1H), 3.70 (s, 3H), 2.71 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ ppm 169.0, 163.8, 142.6, 137.8, 134.8, 128.0, 127.4, 127.0, 125.7, 124.6, 122.2, 121.3, 119.4, 109.9, 59.7, 53.3, 41.7, 15.6. IR: 2961.2 (w), 2927.0 (w), 1751.0 (s), 1712.1 (s), 1445.7 (s), 128.0, 127.4, 127.0, 125.7, 124.6, 122.2, 121.3, 119.4, 109.9, 59.7, 53.3, 41.7, 15.6. HRMS (ESI) M/Z+ Calc. 397.0314, Obs. 397.0315.

**11h**

trans-Methyl 2-methyl-4-oxo-6-(thiophen-2-yl)-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinoline-5-carboxylate (11h): Methyl 2-(2-methyl-1H-indole-1-carbonyl)-3-(thiophen-2-yl)acrylate (0.090 g, 0.277 mmol), In(OTf)₃ (0.0233 g, 0.0415 mmol) and 1,2-DCE (4 mL) were combined according to the general procedure to afford 11h as an off-white solid (0.0459 g, 51%) after 14 h. (Rₛ, 0.40, 20% EtOAc/Hex) [m.p. 153-155 °C] Diastereomeric ratio: (Single Diastereomer) ¹H NMR (300 MHz, CDCl₃) δ ppm 7.37 (d, J = 7.70 Hz, 1H), 7.23 - 7.28 (m, 1H), 7.17 (t, J = 7.62 Hz, 1H), 6.91 - 6.99 (m, 3H), 6.42 (s, 1H), 5.32 (d, J = 9.45 Hz, 1H), 4.25 (d, J = 9.45 Hz, 1H), 3.72 (s, 3H), 2.70 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ ppm 169.0, 163.8, 142.6, 137.8, 134.8, 128.0, 127.4, 127.0, 125.7, 124.6, 122.2, 121.3, 119.4, 109.9, 59.7, 53.3, 41.7, 15.6. IR: 2961.2 (w), 2927.0 (w), 1751.0 (s), 1712.1 (s), 1445.7 (s), 1382.5 (s), 1341.1 (s), 1275.5 (s), 1267.3 (m), 1156.4 (m), 1042.5 (w), 1004.0 (w), 748.9 (s), 702.5 (w) cm⁻¹. HRMS (ESI) M/Z+ Calc. 325.0773, Obs. 325.0754.

**11i**

Methyl 6-ethyl-2-methyl-4-oxo-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinoline-5-carboxylate (11i): Methyl 2-(2-methyl-1H-indole-1-carbonyl)pent-2-enoate (0.090 g, 0.332 mmol), In(OTf)₃ (0.0559 g, 0.0959 mmol) and toluene (5 mL) were combined according to the general procedure to afford 11i as a clear oil (0.0754 g, 84%) after 12 h. (Rₛ, 0.40, 20% EtOAc/Hex) [m.p. 108-110 °C] Diastereomeric ratio: (25:1). (trans-Diastereomer chemical shifts reported) ¹H NMR (300 MHz, CDCl₃) δ ppm 7.33 (d, J = 7.48 Hz, 1H), 7.18 (t, J = 7.55 Hz, 1H), 7.06 (d, J = 6.00 Hz, 1H), 6.35 - 6.39 (m, 1H), 3.86 (d, J = 4.69 Hz, 1H), 3.61 - 3.71 (m, 4H), 2.66 - 2.73 (m, 3H), 1.78 - 1.95 (m, 1H), 1.61 - 1.77 (m, 1H), 0.95 (t, J = 7.40 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ ppm 169.6, 164.3, 136.9, 134.6, 127.5, 123.7, 121.7, 120.6, 118.1, 109.2, 55.8, 52.8, 41.5, 27.2, 15.1, 10.6. IR: 2963.1 (w), 2927.6 (w) 1743.0 (w), 1715.0 (s), 1629.2 (s), 1573.2 (w), 1447.6 (w),
1381.4 (s), 1328.6 (m), 1274.9 (m), 1259.8 (m), 1194.6 (w), 1160.3 (w), 821.1 (w), 763.4 (m), 750.0 (s) cm\(^{-1}\). **HRMS (ESI)** M/Z+ Calc. 271.1208, Obs. 271.1208.

(\(E\))-methyl 2-methyl-4-oxo-6-styryl-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinoline-5-carboxylate (11j): Methyl 2-(2-methyl-1H-indole-1-carbonyl)-5-phenylpenta-2,4-dieneoate (0.0700 g, 0.203 mmol), In(OTf)\(_3\) (0.0341 g, 0.0608 mmol) and toluene (4 ml) were combined according to the general procedure to afford 11j as a pale yellow solid (0.0457 g, 65%) after 14 h. \((R, R)\) 0.35, 20% EtOAc/Hex) [m.p. 98-100 °C]**

**Diastereomeric ratio:** (20:1). \((trans\)-Diastereomer chemical shifts reported)** ¹H NMR (300 MHz, CDCl\(_3\)) δ ppm 7.26 (0.0223 g, 0.0400 mmol) and 1,2-DCE (13 ml) were combined according to the general procedure to afford 11k as a reddish orange solid (0.160 g, 0.390 mmol), In(OTf)\(_3\) (0.0223 g, 0.0400 mmol) and 1,2-DCE (13 ml) were combined according to the general procedure to afford 11k as a reddish orange solid (0.155 g, 97%) after 3 h. \((R, R)\) 0.33, 20% EtOAc/Hex) [m.p. 108-110 °C]**

**Diastereomeric ratio:** (17.3:1). \((trans\)-Diastereomer chemical shifts reported)** ¹H NMR (300 MHz, CDCl\(_3\)) δ ppm 8.16 - 8.22 (m, 1H), 7.71 - 7.76 (m, 1H), 7.16 - 7.45 (m, 7H), 7.02 - 7.09 (m, 2H), 6.71 - 6.77 (m, 2H), 5.19 (d, J = 4.40 Hz, 1H), 4.05 (d, J = 4.43 Hz, 1H), 3.86 (s, 3H), 3.73 (s, 3H). ¹³C NMR (75 MHz, CDCl\(_3\)) δ ppm 168.0, 164.9, 158.9, 139.4, 134.4, 132.0, 131.7, 130.5, 128.4, 128.4, 128.4, 127.0, 124.9, 124.5, 120.2, 116.7, 114.3, 114.1, 63.0, 55.2, 53.3, 42.7. IR: 3056.9 (w), 2953.2 (w), 2837.9 (w), 1730.5 (s), 1610.2 (s), 1511.9 (s), 1454.6 (s), 1392.4 (s), 1345.1 (m), 1305.2 (m), 1246.7 (s), 1145.4 (s), 1103.0 (w), 1029.6 (s), 830.8 (m), 748.6 (s), 699.8 (s), 628.6 (m) cm\(^{-1}\). **HRMS (ESI)** M/Z+ Calc. 411.1471, Obs. 411.1470.
**11l**

Trans-Methyl 6-(4-methoxyphenyl)-1,2-dimethyl-4-oxo-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinoline-5-carboxylate (11l): Methyl 2-(2,3-dimethyl-1H-indole-1-carbonyl)-3-(4-methoxyphenyl)acrylate (0.090 g, 0.2476 mmol), In(OTf)$_3$ (0.0208 g, 0.0371 mmol) and DCE (5 mL) were combined according to the general procedure to afford 11l as a clear oil (0.7740 g, 86%) after 4 h. R$_f$ 0.40 (20% EtOAc/Hex).

**Diastereomic ratio:** (Single Diastereomer observed) $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ ppm 7.31 (d, $J$ = 7.72 Hz, 1H), 7.12 - 7.19 (m, 3H), 6.85 - 6.89 (m, 2H), 6.72 (d, $J$ = 7.47 Hz, 1H), 4.94 (d, $J$ = 10.60 Hz, 1H), 4.17 (d, $J$ = 10.60 Hz, 1H), 3.81 (s, 3H), 3.68 (s, 3H), 2.64 (d, $J$ = 0.82 Hz, 3H), 2.22 (d, $J$ = 0.88 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ ppm 169.2, 163.6, 159.0, 134.0, 132.3, 131.2, 129.5, 129.1, 123.9, 122.5, 121.1, 116.9, 116.7, 114.3, 58.9, 55.2, 52.6, 45.2, 12.4, 8.6. IR: 3035.9 (w), 2999.5 (w), 2953.5 (m), 2924.2 (m), 2837.8 (m), 1747.0 (s), 1700.9 (s), 1627.9 (w), 1610.8 (w), 1512.4 (s), 1434.8 (s), 1378.4 (s), 1353.9 (s), 1338.2 (s), 1286.7 (m), 1250.0 (s), 1211.6 (m), 1178.1 (m), 1155.5 (s), 1136.1 (w), 1112.2 (w), 1030.9 (m), 980.7 (w), 912.6 (w), 850.7 (w), 822.5 (w), 792.4 (w), 768.1 (w), 746.4 (m), 731.9 (m), 610.7 (w) cm$^{-1}$. HRMS (ESI) M/Z+ Calc. 363.1471, Obs. 363.1465.

**11m**

Methyl 4-(4-methoxyphenyl)-6-oxo-4,5,6,8,9,10-hexahydrocyclopenta[4,5]pyrrolo[3,2,1-ij]quinoline-5-carboxylate (11m): Methyl 3-(4-methoxyphenyl)-2-(1,2,3,4-tetrahydrocyclopenta[b]indole-4-carbonyl)acrylate (0.0450 g, 0.120 mmol), In(OTf)$_3$ (0.0101 g, 0.0178 mmol) and toluene (3 mL) were combined according to the general procedure to afford 11m as a white solid (0.0369 g, 82%) after 12 h. R$_f$ 0.40 (20% EtOAc/Hex) [m.p. 140-142 °C] (Single Diastereomer observed) $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ ppm 7.39 - 7.47 (m, 2H), 7.13 - 7.29 (m, 2H), 7.03 - 7.09 (m, 1H), 6.76 - 6.82 (m, 2H), 3.91 (s, 1H), 3.89 (d, $J$ = 0.40 Hz, 3H), 3.75 (s, 3H), 3.74 (s, 1H), 2.49 (td, $J$ = 5.46, 13.07 Hz, 1H), 2.29 - 2.41 (m, 1H), 2.03 - 2.27 (m, 2H), 1.75 - 1.87 (m, 2H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ ppm 170.4, 169.2, 160.6, 147.1, 141.0, 140.0, 133.9, 128.1, 126.3, 125.9, 123.3, 117.4, 114.6, 109.6, 91.5, 67.9, 59.9, 55.5, 53.0, 51.7, 37.7, 36.3, 26.3. IR: 3059.4 (w), 2953.0 (w), 2867.2 (w), 1737.7 (s), 1708.1 (s), 1601.1 (m), 1579.5 (w), 1487.4 (m), 1474.2 (m), 1480.2 (m), 1352.9 (m), 1331.6 (m), 1304.1 (m), 1272.9 (s), 1227.6 (s), 1174.0 (m), 1156.2 (m), 1111.4 (w), 1096.0 (w), 1029.9 (s), 863.2 (w), 844.6 (w), 821.6 (w), 752.2 (s), 734.8 (s), 727.2 (m) cm$^{-1}$. HRMS (ESI) M/Z+ Calc. 375.1471, Obs. 375.1476.
**trans-Methyl 8-fluoro-6-(4-methoxyphenyl)-2-methyl-4-oxo-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinoline-5-carboxylate (11n):** Methyl 2-(5-fluoro-2-methyl-1H-indole-1-carbonyl)-3-(4-methoxyphenyl)acrylate (0.0750 g, 0.204 mmol), In(OTf)$_3$ (0.0180 g, 0.0320 mmol) and 1,2-DCE (7 mL) were combined according to the general procedure to afford 11n as a yellow solid (0.660 g, 88%) after 12 h. (R$_f$ 0.40, 20% EtOAc/Hex) [m.p. 106-108 °C] (Single Diastereomer Observed) $^1$H NMR (400 MHz, CDCl$_3$) δ ppm 7.13 - 7.18 (m, 2H), 7.01 (ddd, $J$ = 6.3, 2.21, 8.96 Hz, 1H), 6.86 - 6.91 (m, 2H), 6.43 - 6.48 (m, 1H), 6.37 - 6.39 (m, 1H), 4.92 (d, $J$ = 10.79 Hz, 1H), 4.17 (d, $J$ = 10.85 Hz, 1H), 3.81 (s, 3H), 3.68 (s, 3H), 2.70 (d, $J$ = 1.19 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ ppm 168.8, 163.7, 161.7, 159.3, 159.2, 138.7, 131.1, 130.3, 129.5, 128.1 and 128.0 (doublet), 124.0 and 123.9 (doublet), 114.4, 109.2, 109.2, 109.1, 108.9, 104.7, 104.4, 58.5, 55.2, 52.7, 45.3, 15.2. IR: 3001.9 (w), 2954.8 (w), 2838.9 (w), 1747.7 (s), 1710.5 (s), 1611.3 (m), 1597.4 (s), 1593.0 (s), 1581.8 (m), 1473.7 (s), 1435.4 (s), 1381.4 (s), 1327.8 (s), 1294.9 (s), 1258.0 (s), 1210.5 (s), 1156.7 (s), 1112.8 (s), 1031.8 (s), 961.2 (m), 852.7 (s), 832.2 (s), 741.1 (s), 714.0 (m), 619.6 (m) cm$^{-1}$. HRMS (ESI) M/Z+ Calc. 367.1220, Obs. 367.1227.

**Methyl 8-chloro-6-(4-methoxyphenyl)-2-methyl-4-oxo-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinoline-5-carboxylate (11o):** Methyl 2-(5-chloro-2-methyl-1H-indole-1-carbonyl)-3-(4-methoxyphenyl)acrylate (0.0100 g, 0.261 mmol), In(OTf)$_3$ (0.0220 g, 0.0391 mmol) and toluene (5 mL) were combined according to the general procedure to afford 11o as a white solid (0.0900 g, 90%) after 4 h. (R$_f$ 0.45, 20% EtOAc/Hex) [m.p. 132-134 °C] (Single Diastereomer observed) $^1$H NMR (300 MHz, CDCl$_3$) δ ppm 7.29 - 7.33 (m, 1H), 7.11 - 7.18 (m, 2H), 6.85 - 6.93 (m, 2H), 6.68 (d, $J$ = 1.10 Hz, 1H), 6.35 (d, $J$ = 1.14 Hz, 1H), 4.91 (d, $J$ = 10.74 Hz, 1H), 4.16 (d, $J$ = 10.77 Hz, 1H), 3.81 (s, 3H), 3.67 (s, 3H), 2.69 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ ppm 168.6, 163.7, 159.2, 138.5, 133.2, 130.1, 129.7, 129.5, 128.4, 123.9, 121.1, 118.3, 114.4, 108.6, 58.5, 55.2, 52.7, 45.2, 15.2. IR 2954.9 (w), 2838.0 (w), 1747.7 (s), 1710.5 (s), 1611.3 (m), 1513.0 (s) 1462.4 (m), 1427.7 (m), 1371.8 (s), 1251.1 (s), 1210.2 (m), 1178.1 (m), 1152.2 (s), 1031.1 (m), 886.2 (m), 858.6 (m), 829.4 (m), 763.7 (w), 737.9 (s), 701.6 (m) cm$^{-1}$. HRMS (ESI) M/Z+ Calc. 383.0924, Obs. 383.0923.
Methyl 6-(methoxyphenyl)-4-oxo-2,4,5,6-tetrahydro-1H-pyrrolo[3,2,1-ij]quinoline-5-carboxylate (12): Methyl 2-(indoline-1-carbonyl)-3-(methoxyphenyl)acrylate (0.075 g, 0.222 mmol), In(OTf)₃ (0.0187 g, 0.0333 mmol) and toluene (5 mL) were combined according to the general procedure to afford 12 as an off-white solid (0.0606 g, 81%) after 42 h. (Rf 0.40, 20% EtOAc/Hex) [m.p. 69-71 °C] (Mixture of Single Diastereomer and Decarboxylated Product) ¹H NMR (300 MHz, CDCl₃) δ ppm 7.06 - 7.17 (m, 7.16), 6.84 - 6.93 (m, 7.14), 6.64 - 6.75 (m, 2.38), 4.66 (d, J = 10.77 Hz, 1.00), 4.27 (dd, J = 7.05, 9.69 Hz, 1.36), 4.02 - 4.22 (m, 5.13), 3.77 - 3.87 (m, 8.16), 3.65 (s, 3.16), 3.17 - 3.33 (m, 5.05), 2.77 - 2.98 (m, 2.87). ¹³C NMR (75 MHz, CDCl₃) δ ppm 169.7, 166.9, 162.9, 158.9, 158.6, 141.0, 140.1, 133.7, 131.2, 129.3, 128.9, 128.8, 125.6, 125.4, 124.0, 123.9, 123.6, 123.5, 122.6, 114.3, 114.2, 57.0, 55.2, 55.2, 52.5, 45.5, 45.2, 45.0, 41.4, 40.2, 27.9. IR: 3035.8 (w), 2951.3 (w), 2837.7 (w), 1745.8 (m), 1668.2 (s), 1595.3 (m), 1512.9 (s), 1480.9 (s), 1468.7 (m), 1396.6 (m), 1353.3 (w), 1250.1 (s), 1178.6 (w), 1153.9 (w), 1031.8 (w), 834.7 (w), 764.9 (m), 747.5 (m) cm⁻¹. HRMS (ESI) M/Z+ Calc. 337.1314, Obs. 337.1313.

trans-Methyl 4-(methoxyphenyl)-3-oxo-1,2,3,5,6,7-hexahydropyrido[3,2,1-ij]quinoline-2-carboxylate (14): Methyl 3-(4-methoxyphenyl)-2-(1,2,3,4-tetrahydroquinoline-1-carbonyl)acrylate (0.075 g, 0.213 mmol), In(OTf)₃ (0.0179 g, 0.0320 mmol) and toluene (5 mL) were combined according to the general procedure to afford 14 as a colorless oil (0.0622 g, 83%) after 42 h. (Rf 0.40, 20% EtOAc/Hex) (Single Diastereomer Observed) ¹H NMR (400 MHz, CDCl₃) δ ppm 7.07 - 7.12 (m, 2H), 7.02 - 7.06 (m, 1H), 6.83 - 6.91 (m, 3H), 6.65 - 6.69 (m, 1H), 4.53 (d, J = 10.04 Hz, 1H), 3.96 - 4.04 (m, 1H), 3.82 - 3.91 (m, 2H), 3.79 (s, 3H), 3.62 (s, 3H), 2.85 (t, J = 6.27 Hz, 2H), 1.93 - 2.03 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ ppm 169.3, 165.0, 158.8, 134.9, 131.0, 129.3, 128.5, 127.1, 126.4, 125.4, 123.0, 114.3, 55.2, 55.0, 52.5, 43.9, 41.3, 27.3, 21.3. IR: 3003.2 (w), 2950.0 (w), 2886.7 (w), 1746.6 (s), 1666.8 (s), 1612.8 (w), 1592.4 (w), 1513.7 (s), 1469.9 (m), 1460.9 (w), 1383.3 (m), 1274.9 (m), 1251.2 (m), 1179.0 (w), 1154.0 (w), 1031.7 (w), 764.4 (s), 749.9 (s) cm⁻¹. HRMS (ESI) M/Z+ Calc. 351.1471, Obs. 351.1477.
3. Control Reactions

**TfOH Control Reaction:**
To a mixture of TfOH (0.0010 g, 0.0068 mmol) in 1,2-DCE heated to a reflux, dissolved (Z)-Methyl 2-(2-methyl-1H-indole-1-carbonyl)-3-(4-nitrophenyl)acrylate (0.250 g, 0.6866 mmol) was syringed into the reaction vessel. The reaction mixture was stirred at reflux for 16 h. The reaction afforded only starting material as observed by crude $^1$H NMR.

**DBU Epimerization Reaction:**
The diastereomeric mixture of Methyl 2-methyl-6-(4-nitrophenyl)-4-oxo-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinoline-5-carboxylate (0.06 g, 0.16478 mmol), DBU (0.0075 g, 0.0494 mmol) and 1,2-DCE (3 mL) were combined and stirred at room temperature for 14 h. The reaction afforded trans as a single observable diastereomer (>99:1 dr) from $^1$H NMR of the crude reaction mixture.

4. References

5. NMR Spectra ($^1$H and $^{13}$C)
1H NMR Spectra for Compound 49

Chemical Shifts (ppm):
- 10h: 18.771
- 135.019, 134.636, 124.192, 121.527
- 130.854, 128.661, 124.688, 124.200
- 115.651, 110.981
- 77.495
- 77.000, 76.393
- 52.781

Inorganic Compound: Me

This page contains a 1H NMR spectrum for Compound 49, showing the chemical shifts in ppm. The spectrum includes several peaks at different frequencies, indicating the presence of various types of hydrogen nuclei in the compound. The inorganic compound Me is also shown. This information is typically used in chemical analysis to identify and characterize compounds.
2-methoxy benzyl chloride derived

Sample: Me-1-pg-28-D-crude

Pulse sequences used: 1D, 2D, 3D, 4D

Ambient temperature: 298 K

Reference: 300 MHz

Total acquisition time: 15 hr, 51 min, 35 sec

11b (crude)
11a (crude)

- NO₂ benzidine derived
25:1 trans: cis diastereomeric mixture

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20:1 trans:cis diastereomeric mixture
20:1 trans:cis diastereomeric mixture
trans-12b

(crude mixture)
trans-12b

(crude mixture)
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