## Supporting Information

## For

An Efficient Synthesis of Hydropyrido[1,2-a]indole-6(7H)-ones via an $\operatorname{In}$ (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 $\mathrm{N}_{2}$ prior to use. Acetonitrile was dried by fractional distillation over $\mathrm{CaH}_{2}$. Benzene was purified by drying with $\mathrm{CaH}_{2}$. 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$63 \mu \mathrm{~m})$ 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 $60 \mathrm{~F}_{254}$ TLC glass plates. Visualization was accomplished with UV light, aqueous basic potassium permanganate $\left(\mathrm{KMnO}_{4}\right)$ 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 ( ${ }^{1} \mathrm{H}$ NMR and ${ }^{13} \mathrm{C}$ NMR) were recorded on a Varian Mercury Vx 300 spectrometer or a Varian Mercury Vx 400 spectrometer with solvent resonances as the internal standard ( ${ }^{1} \mathrm{H} \mathrm{NMR}: \mathrm{CDCl}_{3}$ at $7.26 \mathrm{ppm} ;{ }^{13} \mathrm{C} \mathrm{NMR:} \mathrm{CDCl}_{3}$ at 77.0 ppm ). ${ }^{1} \mathrm{H}$ NMR data are reported as follows: chemical shift (ppm), multiplicity ( $s=$ singlet, $d=$ doublet, dd = doublet of doublets, $\mathrm{dt}=$ doublet of triplets, $\mathrm{ddd}=$ doublet of doublet of doublets, $\mathrm{t}=$ triplet, $\mathrm{m}=$ multiplet), coupling constants $(\mathrm{Hz})$, and integration. Mass spectra were obtained using a VG-70SE instrument.

Diastereomeric ratios for cyclized products 4 were determined by ${ }^{1} \mathrm{H}$ NMR based on comparing the integral ratios of the benzylic protons ( $\sim 4.0-5.0 \mathrm{ppm}$ ) 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 ${ }^{1} \mathrm{H}$ 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 $0{ }^{\circ} \mathrm{C}$. 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-1H-indol-1-yl)-3-oxopropanoate (5a): The general procedure was followed using sodium hydride ( $1.90 \mathrm{~g}, 47.7 \mathrm{mmol}$ ), 3-methyl-1H-indole ( $5.00 \mathrm{~g}, 38.1 \mathrm{mmol}$ ), methyl-3-chloro-3oxopropanoate ( $4.9 \mathrm{~mL}, 45.7 \mathrm{mmol}$ ), and THF ( 50 mL ). After 14 h , the reaction was quenched, and column chromatography ( $20 \% \mathrm{EtOAc} / \mathrm{Hex}, \mathrm{R}_{f} 0.26$ and $\mathrm{R}_{f} 0.15$ for keto and enol tautomers) afforded 5a as a light brown solid ( $6.44 \mathrm{~g}, 73 \%$ ). [m.p. $\left.49-51^{\circ} \mathrm{C}\right]{ }^{1} \mathrm{H} \operatorname{NMR}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.43(\mathrm{~d}, \mathrm{~J}=7.1 \mathrm{~Hz}, 1 \mathrm{H})$,
$7.52-7.47(\mathrm{~m}, 1 \mathrm{H}), 7.41-7.28(\mathrm{~m}, 2 \mathrm{H}), 7.10(\mathrm{~s}, 1 \mathrm{H}), 3.92(\mathrm{~s}, 2 \mathrm{H}), 3.79(\mathrm{~s}, 3 \mathrm{H}), 2.27(\mathrm{~s}, \mathrm{~J}=1.3 \mathrm{~Hz}, 3 \mathrm{H})$. ${ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 166.8,163.4,136.0,131.5,125.5,124.0,121.4,119.7,118.9,116.7,52.9$, 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) $\mathrm{cm}^{-1}$. HRMS (ESI) M/Z+ Calc. 231.0895, Obs. 231.0895.


Methyl 3-(3-(2-bromoethyl)-1H-indol-1-yl)-3-oxopropanoate (5b): ${ }^{1}$ A mixture of potassium carbonate $(0.100 \mathrm{~g}, 0.724 \mathrm{mmol})$ and 3 -(2-bromoethyl)-1H-indole $(0.250 \mathrm{~g}, 1.1 \mathrm{mmol})$, methyl-3-chloro-3oxopropanoate $(0.21 \mathrm{~mL}, 1.95 \mathrm{mmol})$ and acetonitrile $(13 \mathrm{~mL})$ 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, $\mathrm{R}_{f} 0.35$ ) afforded 5b as a yellow-brown solid ( $0.290 \mathrm{~g}, 81 \%$ ). [m.p. 68$\left.70^{\circ} \mathrm{C}\right]^{1} \mathrm{H}$ NMR $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.41(\mathrm{~d}, \mathrm{~J}=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.47(\mathrm{~d}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.40-7.24(\mathrm{~m}, 2 \mathrm{H})$, $7.22(\mathrm{~s}, 1 \mathrm{H}), 3.92(\mathrm{~s}, 2 \mathrm{H}), 3.76(\mathrm{~s}, 3 \mathrm{H}), 3.61(\mathrm{t}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 3.22(\mathrm{t}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (75 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 166.5,163.5,135.7,129.8,125.6,123.9,122.1,120.4,118.4,116.7,52.7,43.3,31.1$, 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)-1H-indol-1-yl)-3-oxopropanoate (5c): The general procedure was followed using sodium hydride ( $0.459 \mathrm{~g}, 11.5 \mathrm{mmol}$ ), 2-(2-(1H-indol-3-yl)ethyl)isoindoline-1,3-dione ${ }^{2}$ ( $3.01 \mathrm{~g}, 10.4 \mathrm{mmol}$ ), methyl-3-chloro-3-oxopropanoate ( $1.4 \mathrm{~mL}, 13.0 \mathrm{mmol}$ ), and THF ( 90 mL ). After 16 h , the reaction was quenched, and column chromatography ( $30 \% \mathrm{EtOAc} / \mathrm{Hex}, \mathrm{R}_{f} 0.17$ ) afforded 5c as a white solid ( $1.69 \mathrm{~g}, 42 \%$ ). [m.p. $\left.138-140^{\circ} \mathrm{C}\right]^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.41(\mathrm{~d}, \mathrm{~J}=7.7 \mathrm{~Hz}, 1 \mathrm{H})$, $7.88-7.77(\mathrm{~m}, 2 \mathrm{H}), 7.75-7.67(\mathrm{~m}, 2 \mathrm{H}), 7.64(\mathrm{~d}, \mathrm{~J}=7.7 \mathrm{~Hz}, 1 \mathrm{H}), 7.40-7.27(\mathrm{~m}, 3 \mathrm{H}), 4.04(\mathrm{t}, \mathrm{J}=7.2 \mathrm{~Hz}$, 2 H ), $3.96(\mathrm{~s}, 2 \mathrm{H}), 3.78(\mathrm{~s}, 3 \mathrm{H}), 3.10(\mathrm{t}, \mathrm{J}=7.4 \mathrm{~Hz}, 2 \mathrm{H}) .{ }^{13} \mathrm{C} \operatorname{NMR}\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 171.0,168.3,167.2$, 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) $\mathrm{cm}^{-1}$. HRMS (ESI) M/Z+ Calc. 390.1216, Obs. 390.1213.


Methyl 3-(3-(2-methoxy-2-oxoethyl)-1H-indol-1-yl)-3-oxopropanoate (5d): The general procedure was followed using sodium hydride ( $0.702 \mathrm{~g}, 17.6 \mathrm{mmol}$ ), methyl $2-(1 \mathrm{H}$-indol-3-yl)acetate ( $3.00 \mathrm{~g}, 15.9 \mathrm{mmol}$ ), methyl-3-chloro-3-oxopropanoate ( $2.0 \mathrm{~mL}, 18.6 \mathrm{mmol}$ ), and THF ( 60 mL ). After 16 h , the reaction was quenched, and column chromatography ( $30 \% \mathrm{EtOAc} / \mathrm{Hex}, \mathrm{R}_{f} 0.24$ ) afforded $5 \mathbf{d}$ as a dark brown oil (3.55 $\mathrm{g}, 77 \%) .{ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.43(\mathrm{~d}, \mathrm{~J}=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.57-7.49(\mathrm{~m}, 1 \mathrm{H}), 7.43-7.27(\mathrm{~m}, 3 \mathrm{H})$, $3.96(\mathrm{~s}, 2 \mathrm{H}), 3.79(\mathrm{~s}, 3 \mathrm{H}), 3.73(\mathrm{~s}, 2 \mathrm{H}), 3.72(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 171.0,166.6,163.6$, 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) $\mathrm{cm}^{-1}$. HRMS (ESI) M/Z+ Calc. 289.0950, Obs. 289.0945.


Methyl 3-(1H-indol-1-yl)-3-oxopropanoate (5e): Following a modification of Kerr's reported procedure, ${ }^{3}$ indoline ( $4.0 \mathrm{~g}, 33.56 \mathrm{mmol}$ ) was dissolved in THF ( 70 mL ) in a round bottom flask equipped with a magnetic stir bar. $\mathrm{K}_{2} \mathrm{CO}_{3}(9.28 \mathrm{~g}, 67.14 \mathrm{mmol})$ was added and the mixture was cooled to $0^{\circ} \mathrm{C}$. Methyl malonyl chloride ( $3.977 \mathrm{~mL}, 37.09 \mathrm{mmol}$ ) 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 $\beta$-amide ester, which was used without purification.

In a dry round bottom flask equipped with a reflux condenser, the resulting $\beta$-amide ester ( $4.26 \mathrm{~g}, 19.43$ mmol ) was dissolved in dry toluene ( 55 mL ), and DDQ ( $5.28 \mathrm{~g}, 23.26 \mathrm{mmol}$ ) 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 $\mathrm{MgSO}_{4}$. The solvent was removed in vacuo and purification of the crude reaction mixture by flash column chromatography ( $15 \% \mathrm{EtOAc} / \mathrm{Hex}, \mathrm{R}_{\mathrm{f}}$ 0.35 ) yielded 5 e as a yellow-brown oil ( $2.72 \mathrm{~g}, 37.3 \%$ over the two steps). ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 8.44 (d, $J=8.1 \mathrm{~Hz}, 1 \mathrm{H}), 7.56-7.51(\mathrm{~m}, 1 \mathrm{H}), 7.38-7.23(\mathrm{~m}, 3 \mathrm{H}), 6.61$ (dd, $J=3.8,0.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.91(\mathrm{~s}$, 2 H ), 3.74 (s, 3H). ${ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 166.5,163.8,135.4,130.2,125.1,124.5,123.9,120.7$, 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), $1529.04(\mathrm{w}), 1472.2$ (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), $689.3(\mathrm{~m}) \mathrm{cm}^{-1}$. HRMS (ESI) M/Z+ Calc. 217.0739, Obs. 217.0738.

## B. Formation of the Diazo Compounds

The $\beta$-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-1H-indol-1-yl)-3-oxopropanoate (6a): The general procedure was followed using methyl 3 -(3-methyl-1H-indol-1-yl)-3-oxopropanoate ( $2.71 \mathrm{~g}, 11.7 \mathrm{mmol}$ ), triethylamine ( $2.0 \mathrm{~mL}, 14.4$ 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, $\mathrm{R}_{f} 0.41$ ) afforded $\mathbf{6 a}$ as a yellow solid ( 2.79 g, 93\%). [m.p. $\left.74-76^{\circ} \mathrm{C}\right]^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.17$ (d, J=8.6 Hz, 1H), 7.51 - 7.47 (m, 1H), 7.39 $7.26(\mathrm{~m}, 2 \mathrm{H}), 7.11(\mathrm{~s}, 1 \mathrm{H}), 3.85(\mathrm{~s}, 3 \mathrm{H}), 2.28(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) ס 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) $\mathrm{cm}^{-1}$. HRMS (ESI) M/Z+ Calc. 257.0800, Obs. 257.0805.


Methyl 3-(3-(2-bromoethyl)-1H-indol-1-yl)-2-diazo-3-oxopropanoate (6b): The general procedure was followed using methyl 3 -(3-(2-bromoethyl)-1H-indol-1-yl)-3-oxopropanoate ( $0.110 \mathrm{~g}, 0.339 \mathrm{mmol}$ ), triethylamine ( $0.0412 \mathrm{~g}, 0.407 \mathrm{mmol}$ ), tosyl azide ( $0.080 \mathrm{~g}, 0.407 \mathrm{mmol}$ ), and acetonitrile ( 10 mL ). After 16 $h$, the reaction mixture was concentrated, and column chromatography ( $20 \% \mathrm{EtOAc} / \mathrm{Hex}, \mathrm{R}_{f} 0.50$ ) afforded 6 b as a yellow oil ( $0.104 \mathrm{~g}, 88 \%$ ). ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.15$ ( $\mathrm{d}, \mathrm{J}=8.0 \mathrm{~Hz}, 1 \mathrm{H}$ ), 7.47 (d, $J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.36-7.23(\mathrm{~m}, 2 \mathrm{H}), 7.22(\mathrm{~s}, 1 \mathrm{H}), 3.81(\mathrm{~s}, 3 \mathrm{H}), 3.61(\mathrm{t}, \mathrm{J}=7.3 \mathrm{~Hz}, 2 \mathrm{H}), 3.23(\mathrm{t}, \mathrm{J}=7.2$ $\mathrm{Hz}, 2 \mathrm{H}$ ). ${ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 161.2,159.1,136.0,130.1,125.0,124.2,123.8,118.7,118.5$, 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) $\mathrm{cm}^{-1}$. HRMS (ESI) M/Z+ Calc. 349.0062, Obs. 349.0061.


Methyl 2-diazo-3-(3-(2-(1,3-dioxoisoindolin-2-yl)ethyl)-1H-indol-1-yl)-3- oxo propanoate (6c): The general procedure was followed using methyl 3 -(3-(2-(1,3-dioxoisoindolin-2-yl)ethyl)-1H-indol-1-yl)-3oxopropanoate ( $1.48 \mathrm{~g}, 3.78 \mathrm{mmol}$ ), triethylamine ( $700 \mu \mathrm{~L}, 5.02 \mathrm{mmol}$ ), tosyl azide ( $0.896 \mathrm{~g}, 4.54 \mathrm{mmol}$ ), and acetonitrile ( 20 mL ). After 18 h , the reaction mixture was concentrated, and column chromatography ( $40 \% \mathrm{EtOAc} / \mathrm{Hex}, \mathrm{R}_{f} 0.44$ ) afforded $\mathbf{6 c}$ as a yellow-brown solid ( $1.49 \mathrm{~g}, 95 \%$ ). [m.p. $\left.98-100^{\circ} \mathrm{C}\right]{ }^{1} \mathrm{H}$ NMR $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.18-8.13(\mathrm{~m}, 1 \mathrm{H}), 7.86-7.80(\mathrm{~m}, 2 \mathrm{H}), 7.74-7.64(\mathrm{~m}, 3 \mathrm{H}), 7.37-7.27(\mathrm{~m}, 2 \mathrm{H})$, $7.23(\mathrm{~s}, 1 \mathrm{H}), 4.00(\mathrm{t}, \mathrm{J}=6.0 \mathrm{~Hz}, 2 \mathrm{H}), 3.81(\mathrm{~s}, 3 \mathrm{H}), 3.10(\mathrm{t}, \mathrm{J}=6.0 \mathrm{~Hz}, 2 \mathrm{H}) .{ }^{13} \mathrm{C} \mathrm{NMR}\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$ (Rotamers!!!) $\delta 168.2,161.2,159.2,136.1,133.9,133.8,132.1,130.5,125.0,124.1,123.9,123.2,123.1$, 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), $1256.4(\mathrm{~m}), 1170.7(\mathrm{~m}), 1095.3(\mathrm{~m}), 1004.0(\mathrm{w}), 861.2(\mathrm{~m}), 732.4(\mathrm{~s}) \mathrm{cm}^{-1}$. HRMS (ESI) M/Z+Calc. 416.1121, Obs. 416.1105.


Methyl 2-diazo-3-(3-(2-methoxy-2-oxoethyl)-1H-indol-1-yl)-3-oxopropanoate (6d): The general procedure was followed using methyl 3 -(3-(2-methoxy-2-oxoethyl)-1H-indol-1-yl)-3-oxopropanoate (1.49 $\mathrm{g}, 5.16 \mathrm{mmol}$ ), triethylamine ( $880 \mu \mathrm{~L}, 6.31 \mathrm{mmol}$ ), tosyl azide ( $1.22 \mathrm{~g}, 6.19 \mathrm{mmol}$ ), and acetonitrile ( 20 mL ). After 18 h , the reaction mixture was concentrated, and column chromatography ( $40 \% \mathrm{EtOAc} / \mathrm{Hex}$, $\mathrm{R}_{f} 0.43$ ) afforded $\mathbf{6 d}$ as a brown solid ( $1.36 \mathrm{~g}, 83 \%$ ). [m.p. $\left.77-79^{\circ} \mathrm{C}\right]^{1} \mathrm{H} \mathbf{N M R}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.17$ (d, $J=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.52(\mathrm{~d}, J=7.7 \mathrm{~Hz}, 1 \mathrm{H}), 7.41-7.26(\mathrm{~m}, 3 \mathrm{H}), 3.84(\mathrm{~s}, 3 \mathrm{H}), 3.73(\mathrm{~s}, 2 \mathrm{H}), 3.72(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 171.1,161.3,159.2,135.9,130.3,125.2,125.1,123.9,118.9,115.8,114.1$, 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) $\mathrm{cm}^{-1}$. HRMS (ESI) M/Z+ Calc. 315.0855, Obs. 315.0860.


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

NMR (300 MHz, $\left.\mathrm{CDCl}_{3}\right) ~ \delta 8.22-8.16(\mathrm{~m}, 1 \mathrm{H}), 7.59-7.53(\mathrm{~m}, 1 \mathrm{H}), 7.40-7.23(\mathrm{~m}, 3 \mathrm{H}), 6.61(\mathrm{dd}, \mathrm{J}=3.8$, $0.7 \mathrm{~Hz}, 1 \mathrm{H}), 3.83(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 161.3,159.5,135.7,130.6,127.4,126.7,124.7$, 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 $\mathrm{Rh}_{2} \operatorname{esp}_{2}(0.1 \mathrm{~mol} \%$ ) and a magnetic stir bar. $\mathrm{DCM}(2.0 \mathrm{~mL})$ was added to the flask. The reaction vessel was cooled to $0^{\circ} \mathrm{C}$, 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-1H-indole-1-carbonyl) cyclopropane carboxylate (3a): The general procedure was followed using 4-methoxystyrene ( $0.201 \mathrm{~g}, 1.49 \mathrm{mmol}$ ), methyl 2-diazo-3-(3-methyl-1H-indol-1-yl)-3-oxopropanoate ( $0.500 \mathrm{~g}, 1.94 \mathrm{mmol}$ ), $\mathrm{Rh}_{2} \mathrm{esp}_{2}(1.5 \mathrm{mg}, 1.98 \mu \mathrm{~mol}$ ) and DCM (8 mL ). After 12 h , the reaction was quenched, and column chromatography ( $20 \% \mathrm{EtOAc} / \mathrm{Hex}, \mathrm{R}_{f} 0.52$ ) afforded 3 a as a pale yellow solid $(0.328 \mathrm{~g}, 60 \%)$. [m.p. $\left.110-112^{\circ} \mathrm{C}\right]^{1} \mathrm{H} \mathbf{N M R}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.45(\mathrm{~d}$, $J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.61-7.45(\mathrm{~m}, 1 \mathrm{H}), 7.44-7.26(\mathrm{~m}, 5 \mathrm{H}), 6.90-6.83(\mathrm{~m}, 2 \mathrm{H}), 3.81(\mathrm{~s}, 3 \mathrm{H}), 3.41(\mathrm{t}, \mathrm{J}=$ $4 \mathrm{~Hz}, 1 \mathrm{H}), 3.41(\mathrm{~s}, 3 \mathrm{H}), 2.40(\mathrm{dd}, J=8.3,5.2 \mathrm{~Hz}, 1 \mathrm{H}), 2.28(\mathrm{~s}, 3 \mathrm{H}), 1.82(\mathrm{dd}, \mathrm{J}=9.3,5.2 \mathrm{~Hz}, 1 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (75 MHz, $\mathrm{CDCl}_{3}$ ) $\delta 168.0$, 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) $\mathrm{cm}^{-1}$. 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 ( $0.095 \mathrm{~g}, 0.709 \mathrm{mmol}$ ), methyl 2-diazo-3-(3-methyl-1H-indol-1-yl)-3-oxopropanoate ( $0.210 \mathrm{~g}, 0.816 \mathrm{mmol}$ ), $\mathrm{Rh}_{2} \mathrm{esp}_{2}(1.0 \mathrm{mg}, 1.31 \mu \mathrm{~mol})$, and DCM $(10 \mathrm{~mL})$. After 12 h , the reaction was quenched, and column chromatography ( $20 \% \mathrm{EtOAc} / \mathrm{Hex}, \mathrm{R}_{f} 0.35$ ) afforded 3 b as a pale yellow solid ( $0.196 \mathrm{~g}, 76 \%$ ). [m.p. $\left.106-108^{\circ} \mathrm{C}\right]^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.54$ (d, $J=7.9 \mathrm{~Hz}, 1 \mathrm{H}), 7.57-7.27(\mathrm{~m}, 6 \mathrm{H}), 7.04-6.95(\mathrm{~m}, 1 \mathrm{H}), 6.91(\mathrm{~d}, \mathrm{~J}=8.2 \mathrm{~Hz}, 1 \mathrm{H}), 3.88(\mathrm{~s}, 3 \mathrm{H}), 3.45(\mathrm{~s}$, $3 \mathrm{H}), 3.45(\mathrm{t}, 1 \mathrm{H}), 2.35(\mathrm{dd}, J=7.9,4.5 \mathrm{~Hz}, 1 \mathrm{H}), 2.32(\mathrm{~d}, J=1.3 \mathrm{~Hz}, 3 \mathrm{H}), 1.97(\mathrm{dd}, J=9.3,5.0 \mathrm{~Hz}, 1 \mathrm{H})$. ${ }^{13} \mathrm{C}$ NMR $\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 168.4,165.9,158.5,136.0,131.4,130.0,129.7,128.7,127.7,125.0,123.5$, 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-1H-indole-1-carbonyl)-2-phenylcyclopropanecarboxylate (3c): The general procedure was followed using styrene ( $0.100 \mathrm{~g}, 0.960 \mathrm{mmol}$ ), methyl 2-diazo-3-(3-methyl-1 H -indol-1-yl)-3-oxopropanoate ( $0.329 \mathrm{~g}, 1.28 \mathrm{mmol}$ ), $\mathrm{Rh}_{2} \mathrm{esp}_{2}(1.0 \mathrm{mg}, 1.32 \mu \mathrm{~mol})$, and $\mathrm{DCM}(13 \mathrm{~mL})$. After 12 h , the reaction was quenched, and column chromatography ( $20 \% \mathrm{EtOAc} / \mathrm{Hex}, \mathrm{R}_{f} 0.60$ ) afforded 3 c as a white solid ( $0.273 \mathrm{~g}, 85 \%$ ). [m.p. $\left.130-132^{\circ} \mathrm{C}\right]^{1} \mathrm{H}$ NMR $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.46(\mathrm{~d}, \mathrm{~J}=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.55-7.48$ $(\mathrm{m}, 1 \mathrm{H}), 7.45-7.26(\mathrm{~m}, 8 \mathrm{H}), 3.48(\mathrm{t}, \mathrm{J}=8.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.40(\mathrm{~s}, 3 \mathrm{H}), 2.46(\mathrm{dd}, \mathrm{J}=8.3,5.2 \mathrm{~Hz}, 1 \mathrm{H}), 2.29(\mathrm{~s}$, $3 \mathrm{H}), 1.84(\mathrm{dd}, \mathrm{J}=9.3,5.2 \mathrm{~Hz}, 1 \mathrm{H}) .{ }^{13} \mathrm{C} \operatorname{NMR}\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 167.9,165.6,136.0,134.2,131.5,129.1$, 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) $\mathrm{cm}^{-1}$. HRMS (ESI) M/Z+ Calc. 333.1365, Obs. 333.1367.


Methyl 2-(4-fluorophenyl)-1-(3-methyl-1H-indole-1-carbonyl)cyclopropane carboxylate (3d): The general procedure was followed using 4-fluorostyrene ( $0.146 \mathrm{~g}, 1.19 \mathrm{mmol}$ ), methyl 2-diazo-3-(3-methyl1 H -indol-1-yl)-3-oxopropanoate ( $0.356 \mathrm{~g}, 1.38 \mathrm{mmol}$ ), $\mathrm{Rh}_{2} \mathrm{esp}_{2}$ ( $1.6 \mathrm{mg}, 2.10 \mu \mathrm{~mol}$ ), and DCM ( 8 mL ). After 10 h , the reaction was quenched, and column chromatography ( $20 \% \mathrm{EtOAc} / \mathrm{Hex}, \mathrm{R}_{f} 0.64$ ) afforded 3d as a pale green solid $(0.273 \mathrm{~g}, 65 \%)$. [m.p. $\left.120-122^{\circ} \mathrm{C}\right]^{1} \mathrm{H}$ NMR $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.45(\mathrm{~d}, \mathrm{~J}=8.0$ $\mathrm{Hz}, 1 \mathrm{H}), 7.52(\mathrm{~d}, \mathrm{~J}=8.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.44-7.29(\mathrm{~m}, 4 \mathrm{H}), 7.25(\mathrm{~s}, 1 \mathrm{H}), 7.07-6.98(\mathrm{~m}, 2 \mathrm{H}), 3.46(\mathrm{t}, \mathrm{J}=8.5$ $\mathrm{Hz}, 1 \mathrm{H}), 3.42(\mathrm{~s}, 3 \mathrm{H}), 2.42(\mathrm{dd}, J=8.2,5.3 \mathrm{~Hz}, 1 \mathrm{H}), 2.29(\mathrm{~s}, 3 \mathrm{H}), 1.84(\mathrm{dd}, J=9.3,5.3 \mathrm{~Hz}, 1 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (75 MHz, $\mathrm{CDCl}_{3}$ ) $\delta 167.8,165.4,163.8,160.5,136.0,131.5,130.7,130.0,125.4,123.9,121.3,119.4$, 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-1H-indole-1-carbonyl)cyclopropane carboxylate (3e): The general procedure was followed using 4-chlorostyrene ( $0.124 \mathrm{~g}, 0.898 \mathrm{mmol}$ ), methyl 2-diazo-3-(3-methyl-1 H -indol-1-yl)-3-oxopropanoate ( $0.250 \mathrm{~g}, 0.973 \mathrm{mmol}$ ), $\mathrm{Rh}_{2} \mathrm{esp}_{2}(1.5 \mathrm{mg}, 1.71 \mu \mathrm{~mol}$ ), and DCM (8 mL ). After 12 h , the reaction was quenched, and column chromatography ( $20 \% \mathrm{EtOAc} / \mathrm{Hex}, \mathrm{R}_{f} 0.64$ ) afforded 3 e as a white solid ( $0.275 \mathrm{~g}, 83 \%$ ). [m.p. $\left.129-131^{\circ} \mathrm{C}\right]^{1} \mathrm{H} \mathbf{N M R}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.46(\mathrm{~d}, \mathrm{~J}=$ $8.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.55-7.50(\mathrm{~m}, 1 \mathrm{H}), 7.45-7.29(\mathrm{~m}, 6 \mathrm{H}), 7.26(\mathrm{~d}, \mathrm{~J}=1.3 \mathrm{~Hz}, 1 \mathrm{H}), 3.44(\mathrm{t}, \mathrm{J}=6.8 \mathrm{~Hz}, 1 \mathrm{H})$, $3.44(\mathrm{~s}, 3 \mathrm{H}), 2.43(\mathrm{dd}, \mathrm{J}=8.3,5.3 \mathrm{~Hz}, 1 \mathrm{H}), 2.30(\mathrm{~s}, 3 \mathrm{H}), 1.86(\mathrm{dd}, J=9.3,5.3 \mathrm{~Hz}, 1 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( 75 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 167.7,165.3,136.0,133.3,132.8,131.5,130.4,128.3,125.4,123.9,121.2,119.4,118.9,116.5$, 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) $708.7(\mathrm{w}) \mathrm{cm}^{-}$ ${ }^{1}$. HRMS (ESI) M/Z+ Calc. 367.0975, Obs. 367.0981.


Methyl 1-(3-methyl-1H-indole-1-carbonyl)-2-(4-nitrophenyl)cyclopropane carboxylate (3f): The general procedure was followed using 4-nitrostyrene ( $0.252 \mathrm{~g}, 1.69 \mathrm{mmol}$ ), methyl 2-diazo-3-(3-methyl1 H -indol-1-yl)-3-oxopropanoate ( $0.505 \mathrm{~g}, 1.97 \mathrm{mmol}$ ), $\mathrm{Rh}_{2} \mathrm{esp}_{2}$ ( $1.2 \mathrm{mg}, 1.98 \mu \mathrm{~mol}$ ), and DCM ( 8 mL ). After 10 h , the reaction was quenched, and column chromatography ( $20 \% \mathrm{EtOAc} / \mathrm{Hex}, \mathrm{R}_{f} 0.69$ ) afforded $3 f$ as a yellow solid ( $0.325 \mathrm{~g}, 51 \%$ ). [m.p. $\left.163-165^{\circ} \mathrm{C}\right]^{1} \mathrm{H} \mathbf{N M R}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.43(\mathrm{~d}, \mathrm{~J}=7.9 \mathrm{~Hz}$, $1 \mathrm{H}), 8.24-8.17(\mathrm{~m}, 2 \mathrm{H}), 7.58-7.50(\mathrm{~m}, 3 \mathrm{H}), 7.45-7.30(\mathrm{~m}, 2 \mathrm{H}), 7.21(\mathrm{~s}, 1 \mathrm{H}), 3.54(\mathrm{t}, \mathrm{J}=8.8 \mathrm{~Hz}, 1 \mathrm{H})$, 3.43 (s, 3H), 2.51 (dd, $J=8.3,5.4 \mathrm{~Hz}, 1 \mathrm{H}), 2.29(\mathrm{~s}, 3 \mathrm{H}), 1.94$ (dd, $J=9.2,5.4 \mathrm{~Hz}, 1 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( 75 MHz , $\left.\mathrm{CDCl}_{3}\right)$ б 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 ( $0.059 \mathrm{~g}, 0.627 \mathrm{mmol}$ ), methyl 2-diazo-3-(3-methyl-1 H -indol-1-$\mathrm{yl})$-3-oxopropanoate ( $0.210 \mathrm{~g}, 0.816 \mathrm{mmol}$ ), $\mathrm{Rh}_{2} \operatorname{esp}_{2}(1.0 \mathrm{mg}, 1.31 \mu \mathrm{~mol})$, and DCM ( 10 mL ). After 12 h , the reaction was quenched, and column chromatography ( $15 \% \mathrm{EtOAc} / \mathrm{Hex}, \mathrm{R}_{f} 0.35$ ) afforded 3 g as a white solid ( $0.084 \mathrm{~g}, 41 \%$ ). [m.p. $95-97^{\circ} \mathrm{C}{ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.45(\mathrm{~d}, \mathrm{~J}=7.9 \mathrm{~Hz}, 1 \mathrm{H}), 7.56-$ $7.50(\mathrm{~m}, 1 \mathrm{H}), 7.44-7.30(\mathrm{~m}, 4 \mathrm{H}), 6.41-6.35(\mathrm{~m}, 1 \mathrm{H}), 6.32-6.28(\mathrm{~m}, 1 \mathrm{H}), 3.54(\mathrm{~s}, 3 \mathrm{H}), 3.25(\mathrm{t}, \mathrm{J}=8.7$ $\mathrm{Hz}, 1 \mathrm{H}), 2.34(\mathrm{dd}, J=6.9,4.2 \mathrm{~Hz}, 1 \mathrm{H}), 2.31(\mathrm{~d}, \mathrm{~J}=1.3 \mathrm{~Hz}, 3 \mathrm{H}), 1.96(\mathrm{dd}, J=9.5,5.2 \mathrm{~Hz}, 1 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) 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) $\mathrm{cm}^{-1}$. 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 ( $0.123 \mathrm{~g}, 1.046 \mathrm{mmol}$ ), methyl 2-diazo-3-(3-methyl-1H-indol-1-yl)-3-oxopropanoate ( $0.350 \mathrm{~g}, 1.360 \mathrm{mmol}$ ), $\mathrm{Rh}_{2} \mathrm{esp}_{2}(1.0 \mathrm{mg}, 1.31 \mu \mathrm{~mol}$ ), and DCM (10 mL ). After 12 h , the reaction was quenched, and column chromatography ( $20 \% \mathrm{EtOAc} / \mathrm{Hex}, \mathrm{R}_{f} 0.38$ ) afforded 3 h as a colorless oil $(0.225 \mathrm{~g}, 62 \%){ }^{1} \mathrm{H} \operatorname{NMR}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.61(\mathrm{~d}, J=7.8 \mathrm{~Hz}, 0.90), 7.88$ $-7.80(\mathrm{~m}, 0.16), 7.63-7.55(\mathrm{~m}, 1.05), 7.54-7.28(\mathrm{~m}, 8.37), 7.24-7.20(\mathrm{~m}, 0.51), 3.69(\mathrm{~s}, 0.40), 3.46$ (d, $J=0.8 \mathrm{~Hz}, 3$ ), $2.67(\mathrm{~d}, J=5.5 \mathrm{~Hz}, 0.14), 2.53(\mathrm{~d}, J=5.1 \mathrm{~Hz}, 1.33), 2.39(\mathrm{~s}, 2.99), 2.26(\mathrm{~d}, J=1.3 \mathrm{~Hz}$, 0.42 ), 1.96 ( $\mathrm{d}, J=6.6 \mathrm{~Hz}, 0.55$ ) $1.85(\mathrm{~d}, J=5.1 \mathrm{~Hz}, 1.03), 1.64(\mathrm{~s}, 0.27), 1.55(\mathrm{~s}, 2.91) .{ }^{13} \mathrm{C}$ NMR (75 $\mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 168.4,164.9,140.6,136.0,131.5,128.4,128.0,127.8,127.2,125.3,123.8,122.3,118.8$, 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 ( $0.062 \mathrm{~g}, 0.747 \mathrm{mmol}$ ), methyl 2-diazo-3-(3-methyl1 H -indol-1-yl)-3-oxopropanoate ( $0.250 \mathrm{~g}, 0.971 \mathrm{mmol}$ ), $\mathrm{Rh}_{2} \mathrm{esp}_{2}$ ( $1.0 \mathrm{mg}, 1.31 \mu \mathrm{~mol}$ ), and DCM ( 10 mL ). After 12 h , the reaction was quenched, and column chromatography ( $15 \% \mathrm{EtOAc} / \mathrm{Hex}, \mathrm{R}_{f} 0.35$ ) afforded 3 i as a white solid $(0.117 \mathrm{~g}, 50 \%)$. [m.p. $\left.78-80^{\circ} \mathrm{C}\right]{ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.40(\mathrm{~d}, \mathrm{~J}=8.0 \mathrm{~Hz}, 1 \mathrm{H})$, $7.45-7.39(\mathrm{~m}, 1 \mathrm{H}), 7.33-7.21(\mathrm{~m}, 3 \mathrm{H}), 3.58(\mathrm{~s}, 3 \mathrm{H}), 2.21(\mathrm{~d}, \mathrm{~J}=1.3 \mathrm{~Hz}, 3 \mathrm{H}), 1.97-1.73(\mathrm{~m}, 3 \mathrm{H}), 1.62$ (dd, $J=4.8,1.2 \mathrm{~Hz}, 1 \mathrm{H}), 1.51(\mathrm{~d}, J=4.8 \mathrm{~Hz}, 1 \mathrm{H}), 0.99(\mathrm{t}, J=7.5 \mathrm{~Hz}, 3 \mathrm{H}), 0.91-0.71(\mathrm{~m}, 4 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR
( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 169.7,165.7$, 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. 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 ${ }^{-1}$. HRMS (ESI) M/Z+ Calc. 313.1678, Obs. 313.1683.


Methyl 1-(3-methyl-1H-indole-1-carbonyl)spiro[2.4]heptane-1-carboxylate (3j): The general procedure was followed using methylenecyclopentane ( $0.098 \mathrm{~g}, 1.20 \mathrm{mmol}$ ), methyl 2-diazo-3-(3-methyl1 H -indol-1-yl)-3-oxopropanoate ( $0.400 \mathrm{~g}, 1.55 \mathrm{mmol}$ ), $\mathrm{Rh}_{2} \mathrm{esp}_{2}(1.0 \mathrm{mg}, 1.31 \mu \mathrm{~mol})$, and DCM ( 10 mL ). After 4 h , the reaction was quenched, and column chromatography ( $15 \% \mathrm{EtOAc} / \mathrm{Hex}, \mathrm{R}_{f} 0.35$ ) afforded $\mathbf{3 j}$ as a colorless oil $(0.342 \mathrm{~g}, 92 \%)$. ${ }^{1} \mathrm{H}$ NMR $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.52(\mathrm{~s}, 1 \mathrm{H}), 7.55-7.48(\mathrm{~m}, 1 \mathrm{H}), 7.43-$ $7.27(\mathrm{~m}, 2 \mathrm{H}), 7.10(\mathrm{~s}, 1 \mathrm{H}), 3.65(\mathrm{~s}, 3 \mathrm{H}), 2.31(\mathrm{~s}, 3 \mathrm{H}), 2.24-1.98(\mathrm{~m}, 2 \mathrm{H}), 1.90-1.62(\mathrm{~m}, 7 \mathrm{H}), 1.46-1.33$ (m, 1H). ${ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 170.1,165.6,135.7,131.2,124.9,123.4,121.9,118.5,118.3$, 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 1-(3-methyl-1H-indole-1-carbonyl)spiro[2.5]octane-1-carboxylate (3k): The general procedure was followed using methylenecyclohexane ( $0.068 \mathrm{~g}, 0.709 \mathrm{mmol}$ ), methyl 2-diazo-3-(3-methyl-1H-indol1 -yl)-3-oxopropanoate ( $0.210 \mathrm{~g}, 0.816 \mathrm{mmol}$ ), $\mathrm{Rh}_{2} \mathrm{esp}_{2}(1.0 \mathrm{mg}, 1.31 \mu \mathrm{~mol})$, and DCM ( 10 mL ). After 6 h , the reaction was quenched, and column chromatography ( $15 \% \mathrm{EtOAc} / \mathrm{Hex}, \mathrm{R}_{f} 0.40$ ) afforded $\mathbf{3 k}$ as a white solid ( $0.160 \mathrm{~g}, 69 \%$ ). [m.p. $\left.120-122^{\circ} \mathrm{C}\right]$. ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.49(\mathrm{~d}, \mathrm{~J}=5.7 \mathrm{~Hz}, 1 \mathrm{H}), 7.60$ $-7.48(\mathrm{~m}, 1 \mathrm{H}), 7.44-7.27(\mathrm{~m}, 2 \mathrm{H}), 7.14(\mathrm{~s}, 1 \mathrm{H}), 3.65(\mathrm{~s}, 3 \mathrm{H}), 2.32(\mathrm{~d}, \mathrm{~J}=1.2 \mathrm{~Hz}, 3 \mathrm{H}), 2.18(\mathrm{~d}, \mathrm{~J}=12.5$ $\mathrm{Hz}, 1 \mathrm{H}), 1.92-1.21(\mathrm{~m}, 10 \mathrm{H}), 1.05-0.94(\mathrm{~m}, 1 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 169.5,165.7,135.8$, 131.4, 125.0, 123.5, 122.5, 118.6, 118.2, 116.5, 52.5, 41.1, 37.5, 33.9, 28.7, 26.4, 25.8, 25.6, 25.5, 9.7. IR: 2998.1 (w), 2878.5 (w), 1720.8 (m), 1711.4 (m), 1439.8 (m), 1340.7 (m), 1138.1 (w), 759.5 (s), 674.3 (s) $\mathrm{cm}^{-1}$. HRMS (ESI) M/Z+ Calc. 325.1678, Obs. 325.1681.


Methyl
2-((tert-butyldiphenylsilyl)methyl)-1-(3-methyl-1H-indole-1-carbonyl) cyclopropanecarboxylate (3I): The general procedure was followed using allyl(tert-butyl)diphenylsilane ( $0.294 \mathrm{~g}, 1.05 \mathrm{mmol}$ ), methyl 2-diazo-3-(3-methyl-1H-indol-1-yl)-3-oxopropanoate ( $0.350 \mathrm{~g}, 1.36 \mathrm{mmol}$ ), $R h_{2} \operatorname{esp}_{2}(1.0 \mathrm{mg}, 1.31 \mu \mathrm{~mol})$, and $\mathrm{DCM}(8 \mathrm{~mL})$. After 6 h , the reaction was quenched, and column chromatography ( $20 \%$ EtOAc/Hex, $\mathrm{R}_{f} 0.45$ ) afforded 31 as a white solid ( $0.332 \mathrm{~g}, 62 \%$ ). [m.p. 127 $\left.129^{\circ} \mathrm{C}\right]{ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.39(\mathrm{~d}, \mathrm{~J}=7.9 \mathrm{~Hz}, 1 \mathrm{H}), 7.76-7.64(\mathrm{~m}, 4 \mathrm{H}), 7.57-7.23(\mathrm{~m}, 9 \mathrm{H})$, $7.17(\mathrm{~s}, 1 \mathrm{H}), 3.69(\mathrm{~s}, 3 \mathrm{H}), 2.28(\mathrm{~s}, 3 \mathrm{H}), 1.74-1.66(\mathrm{~m}, 1 \mathrm{H}), 1.57-1.40(\mathrm{~m}, 2 \mathrm{H}), 1.31(\mathrm{dd}, \mathrm{J}=8.5,5.5 \mathrm{~Hz}$, 2H), $1.13(\mathrm{~s}, 9 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 169.6,166.3,136.0,136.9,135.8,134.1,133.8,131.4$, 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), $1106.0(\mathrm{~m}), 818.3(\mathrm{w}), 749.1(\mathrm{~m}), 701.5(\mathrm{~s}) \mathrm{cm}^{-1}$. HRMS (ESI) M/Z+Calc. 509.2386, Obs. 509.2388.


Methyl 2-(1,3-dioxoisoindolin-2-yl)-1-(3-methyl-1H-indole-1-carbonyl)cyclopropane carboxylate (3m): The general procedure was followed using N -vinyl-phthalimide ( $0.155 \mathrm{~g}, 897 \mu \mathrm{~mol}$ ), methyl 2-diazo-3-(3-methyl-1H-indol-1-yl)-3-oxopropanoate ( $0.300 \mathrm{~g}, 1.17 \mathrm{mmol}$ ), $\mathrm{Rh}_{2} \mathrm{esp}_{2}$ ( $1.1 \mathrm{mg}, 1.45 \mu \mathrm{~mol}$ ), and DCM $(8 \mathrm{~mL})$. After 12 h , the reaction was quenched, and column chromatography ( $20 \% \mathrm{EtOAc} / \mathrm{Hex}, \mathrm{R}_{f} 0.20$ ) afforded 3 m as a white solid ( $0.247 \mathrm{~g}, 68 \%$ ). [m.p. $88-90^{\circ} \mathrm{C}$ ] Diastereomeric Ratio: (2.5:1). ${ }^{1} \mathrm{H}$ NMR (300 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right)^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.43(\mathrm{~d}, \mathrm{~J}=7.4 \mathrm{~Hz}, 0.83$ ), $8.22(\mathrm{~d}, \mathrm{~J}=6.1 \mathrm{~Hz}, 0.27$ ), 7.98 (s, 1.00), 7.83 ( $\mathrm{dt}, J=6.9,3.5 \mathrm{~Hz}, 2.19$ ), $7.76-7.66$ (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, $J=9.2,6.8 \mathrm{~Hz}, 0.23$ ), 3.71 (s, 1.11), 3.67 (dd, J = 8.0, $6.5 \mathrm{~Hz}, 1.18$ ), 3.57 ( $\mathrm{s}, 3.00$ ), 3.47 (t, $J=6.5 \mathrm{~Hz}, 0.63$ ), 2.59 (t, $J=6.4 \mathrm{~Hz}, 1.00$ ), $2.35-2.27$ (m, 4.00), 2.23 (s, 1.45), 2.17 (dd, $J=9.2,6.2 \mathrm{~Hz}, 0.60) .{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 169.7,168.2,168.0,167.8,164.0,136.0,134.3$, 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 ( $0.311 \mathrm{~g}, 2.29 \mathrm{mmol}$ ), methyl 2-diazo-3-(3-methyl-1H-indol-1-yl)-3-oxopropanoate ( $0.722 \mathrm{~g}, 2.81 \mathrm{mmol}$ ), $\mathrm{Rh}_{2} \mathrm{esp}_{2}(1.8 \mathrm{mg}, 2.4 \mu \mathrm{~mol})$, and DCM ( 13 mL ). After 12 h , the reaction was quenched, and column chromatography ( $20 \% \mathrm{EtOAc} / \mathrm{Hex}, \mathrm{R}_{f} 0.40$ ) afforded 3 n as a colorless oil $(0.125 \mathrm{~g}, 15 \%) .{ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.44(\mathrm{~d}, \mathrm{~J}=7.9 \mathrm{~Hz}, 1 \mathrm{H}), 7.55-7.47(\mathrm{~m}, 3 \mathrm{H})$, $7.43-7.28(\mathrm{~m}, 4 \mathrm{H}), 7.23-7.16(\mathrm{~m}, 2 \mathrm{H}), 3.56(\mathrm{dd}, \mathrm{J}=7.5,5.6 \mathrm{~Hz}, 1 \mathrm{H}), 3.52(\mathrm{~s}, 3 \mathrm{H}), 2.25(\mathrm{~d}, \mathrm{~J}=1.3 \mathrm{~Hz}$, 3 H ), $2.15\left(\mathrm{dd}, J=7.3,5.7 \mathrm{~Hz}, 1 \mathrm{H}\right.$ ), $1.92(\mathrm{dd}, J=9.2,5.7 \mathrm{~Hz}, 1 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 167.3$, 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) $\mathrm{cm}^{-1}$. HRMS (ESI) M/Z+ Calc. 365.1079, Obs. 365.1083.


Methyl 6-(3-methyl-1H-indole-1-carbonyl)-2-oxabicyclo[3.1.0]hexane-6-carboxylate (30): The general procedure was followed using 2,3-dihydrofuran ( $0.073 \mathrm{~g}, 1.05 \mathrm{mmol}$ ), methyl 2-diazo-3-(3-methyl1 H -indol-1-yl)-3-oxopropanoate ( $0.350 \mathrm{~g}, 1.36 \mathrm{mmol}$ ), $\mathrm{Rh}_{2} \mathrm{esp}_{2}$ ( $1.0 \mathrm{mg}, 1.31 \mu \mathrm{~mol}$ ), and DCM ( 9 mL ). After 10 h , the reaction was quenched and column chromatography ( $20 \% \mathrm{EtOAc} / \mathrm{Hex}, \mathrm{R}_{f} 0.30$ ) afforded 3o as a brown solid ( $0.235 \mathrm{~g}, 75 \%$ ). [m.p. $\left.83-85^{\circ} \mathrm{C}\right]{ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.72-7.63(\mathrm{~m}, 1 \mathrm{H})$, $7.56-7.49(\mathrm{~m}, 2 \mathrm{H}), 7.31-7.17(\mathrm{~m}, 2 \mathrm{H}), 6.27(\mathrm{~d}, \mathrm{~J}=6.2 \mathrm{~Hz}, 1 \mathrm{H}), 4.19-4.10(\mathrm{~m}, 1 \mathrm{H}), 4.05-3.97(\mathrm{~m}$, $1 \mathrm{H}), 3.96-3.85(\mathrm{~m}, 1 \mathrm{H}), 3.72(\mathrm{~s}, 3 \mathrm{H}), 2.35(\mathrm{~s}, 3 \mathrm{H}), 2.25-2.16(\mathrm{~m}, 2 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR $\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ 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-1H-indole-1-carbonyl)-2-oxabicyclo[4.1.0]heptane-7-carboxylate (3p): The general procedure was followed using 2,3-dihydropyran ( $95 \mu \mathrm{~L}, 1.04 \mathrm{mmol}$ ), methyl 2-diazo-3-(3-methyl1 H-indol-1-yl)-3-oxopropanoate ( $0.350 \mathrm{~g}, 1.36 \mathrm{mmol}$ ), $\mathrm{Rh}_{2} \mathrm{esp}_{2}(1.0 \mathrm{mg}, 1.31 \mu \mathrm{~mol})$, and DCM ( 8 mL ). After 12 h , the reaction was quenched, and column chromatography ( $20 \% \mathrm{EtOAc} / \mathrm{Hex}, \mathrm{R}_{f} 0.40$ ) afforded $3 p$ as a pale red solid ( $0.142 \mathrm{~g}, 43 \%$ ). [m.p. $\left.123-125^{\circ} \mathrm{C}\right] .{ }^{1} \mathrm{H} \operatorname{NMR}\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.45(\mathrm{~d}, \mathrm{~J}=8.1 \mathrm{~Hz}$, $1 \mathrm{H}), 7.51-7.43(\mathrm{~m}, 1 \mathrm{H}), 7.42-7.22(\mathrm{~m}, 2 \mathrm{H}), 7.17(\mathrm{~s}, 1 \mathrm{H}), 6.54(\mathrm{~s}, 1 \mathrm{H}), 4.60(\mathrm{~s}, 1 \mathrm{H}), 4.00-3.87(\mathrm{~m}, 2 \mathrm{H})$, $3.77(\mathrm{~s}, 3 \mathrm{H}), 2.39-2.27(\mathrm{~m}, 1 \mathrm{H}), 2.26(\mathrm{~s}, 3 \mathrm{H}), 2.14-2.02(\mathrm{~m}, 1 \mathrm{H}), 1.97-1.77(\mathrm{~m}, 2 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (75 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 168.8,165.6,144.5,136.0,131.2,125.3,123.8,121.1,119.2,118.7,116.7,106.4,80.7$, 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), 745.49 (s) $\mathrm{cm}^{-1}$. HRMS (ESI) M/Z+ Calc. 313.1314, Obs. 313.1312.


2-benzyl 7-methyl 7-(3-methyl-1H-indole-1-carbonyl)-2-azabicyclo[4.1.0]heptane-2,7-dicarboxylate (3q). The general procedure was followed using benzyl 3,4-dihydropyridine-1(2H)-carboxylate ( 0.179 g , 0.897 mmol ), methyl 2-diazo-3-(3-methyl-1H-indol-1-yl)-3-oxopropanoate ( $0.300 \mathrm{~g}, 1.17 \mathrm{mmol}$ ), $\mathrm{Rh}_{2} \mathrm{esp}_{2}$ (1.3 mg, $1.79 \mu \mathrm{~mol})$, and DCM ( 9 mL ). After 12 h , the reaction was quenched, and column chromatography ( $20 \%$ EtOAc/Hex, $\mathrm{R}_{f} 0.25$ ) afforded 3 q as a colorless oil ( $0.295 \mathrm{~g}, 74 \%$ ). ${ }^{1} \mathrm{H}$ NMR (300 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.48(\mathrm{~d}, \mathrm{~J}=7.9 \mathrm{~Hz}, 1 \mathrm{H}), 7.49(\mathrm{~d}, J=7.5 \mathrm{~Hz}, 1 \mathrm{H}), 7.42-7.26(\mathrm{~m}, 6 \mathrm{H}), 7.13(\mathrm{t}, \mathrm{J}=32.4 \mathrm{~Hz}$, $2 \mathrm{H}), 5.20(\mathrm{~s}, 2 \mathrm{H}), 4.77(\mathrm{~d}, J=26.5 \mathrm{~Hz}, 1 \mathrm{H}), 3.76(\mathrm{~d}, J=11.9 \mathrm{~Hz}, 3 \mathrm{H}), 3.71-3.44(\mathrm{~m}, 2 \mathrm{H}), 2.27(\mathrm{~s}, 3 \mathrm{H})$, $2.51-2.02(\mathrm{~m}, 2 \mathrm{H}), 1.96-1.74(\mathrm{~m}, 2 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (75 MHz, $\left.\mathrm{CDCl}_{3}\right) \delta 168.5,165.4,153.4,152.6,135.9$, 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), $1691.6(\mathrm{~s}), 1449.2(\mathrm{~m}), 1406.5(\mathrm{~m}), 1319.9(\mathrm{~m}), 1260.5(\mathrm{~m}), 1172.1(\mathrm{~m}), 747.1(\mathrm{~m}) \mathrm{cm}^{-1}$. HRMS (ESI) $\mathrm{M} / \mathrm{Z}+$ Calc. 446.1842 , Obs. 446.1840.


Methyl 1-(1H-indole4-1-carbonyl)-2-(4-methoxyphenyl)cyclopropanecarboxylate (3r): The general procedure was followed using 4-methoxystyrene ( $0.061 \mathrm{~g}, 0.459 \mathrm{mmol}$ ) methyl 2-diazo-3-(5-methyl-1H-indol-1-yl)-3-oxopropanoate ( $0.331 \mathrm{~g}, 2.466 \mathrm{mmol}$ ), $\mathrm{Rh}_{2} \operatorname{esp}_{2}(1.87 \mathrm{mg}, 2.4 \mu \mathrm{~mol})$, and DCM ( 20 mL ). After 12 h , the reaction was quenched, and column chromatography ( $20 \% \mathrm{EtOAc} / \mathrm{Hex}, \mathrm{R}_{f} 0.30$ ) afforded 3 r as a white solid ( $0.625 \mathrm{~g}, 72.8 \%$ ). [m.p. $\left.83-85^{\circ} \mathrm{C}\right]^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.44(\mathrm{~d}, \mathrm{~J}=8.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.56$ $-7.46(\mathrm{~m}, 2 \mathrm{H}), 7.39-7.19(\mathrm{~m}, 4 \mathrm{H}), 6.86-6.80(\mathrm{~m}, 2 \mathrm{H}), 6.63-6.60(\mathrm{~m}, 1 \mathrm{H}), 3.76(\mathrm{~s}, 3 \mathrm{H}), 3.44-3.34$ $(\mathrm{m}, 4 \mathrm{H}), 2.38(\mathrm{dd}, \mathrm{J}=8.3,5.3 \mathrm{~Hz}, 1 \mathrm{H}), 1.82(\mathrm{dd}, \mathrm{J}=9.7,5.6,0.7 \mathrm{~Hz}, 1 \mathrm{H}){ }^{13}{ }^{13} \mathrm{C}$ NMR $\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ $167.8,166.2,158.9,135.7,130.4,130.1,125.8,125.2,124.7,124.0,120.9,116.4,113.5,109.7,55.1$, 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), $841.7(\mathrm{~m}), 747.6$ (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 ( $0.073 \mathrm{~g}, 0.549 \mathrm{mmol}$ ), methyl 3-(3-(2-bromoethyl)-1H-indol-1-yl)-2-diazo-3-oxopropanoate ( $0.250 \mathrm{~g}, 0.713 \mathrm{mmol}$ ), $\mathrm{Rh}_{2} \mathrm{esp}_{2}$ ( $1.0 \mathrm{mg}, 1.31$ $\mu \mathrm{mol})$, and DCM ( 15 mL ). After 12 h , the reaction was quenched, and column chromatography ( $20 \%$ $\mathrm{EtOAc} / \mathrm{Hex}, \mathrm{R}_{f} 0.35$ ) afforded 3 s as a white solid ( $0.188 \mathrm{~g}, 75 \%$ ). [m.p. $\left.122-124^{\circ} \mathrm{C}\right] .{ }^{1} \mathrm{H}$ NMR ( 300 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 8.43(\mathrm{~d}, \mathrm{~J}=8.1 \mathrm{~Hz}, 1 \mathrm{H}), 7.51-7.45(\mathrm{~m}, 1 \mathrm{H}), 7.41-7.19(\mathrm{~m}, 5 \mathrm{H}), 6.86-6.79(\mathrm{~m}, 2 \mathrm{H}), 3.76(\mathrm{~s}$, $3 \mathrm{H}), 3.61(\mathrm{t}, J=7.0 \mathrm{~Hz}, 2 \mathrm{H}), 3.42-3.34(\mathrm{~m}, 4 \mathrm{H}), 3.23(\mathrm{t}, J=7.3,4.4 \mathrm{~Hz}, 2 \mathrm{H}), 2.38(\mathrm{dd}, J=8.3,5.3 \mathrm{~Hz}$, 1 H ), 1.82 (dd, $J=9.4,5.2 \mathrm{~Hz}, 1 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 167.8,166.0,158.9,136.0,130.1,130.0$, $126.0,125.6,124.0,122.4,120.1,119.3,118.5,116.7,113.6,55.2,52.8,43.4,39.3,31.4,31.3,28.7$, 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) $\mathrm{cm}^{-1}$. HRMS (ESI) M/Z+ Calc. 455.0708, Obs. 455.0732.


Methyl 1-(3-(2-(1,3-dioxoisoindolin-2-yl)ethyl)-1H-indole-1-carbonyl)-2-(4-methoxy phenyl)cyclopropanecarboxylate (3t): The general procedure was followed using 4-methoxystyrene ( $0.208 \mathrm{~g}, 1.55 \mathrm{mmol}$ ), methyl 3-(3-(2-(1,3-dioxoisoindolin-2-yl)ethyl)-1H-indol-1-yl)-3-oxopropanoate $(0.810 \mathrm{~g}, 1.95 \mathrm{mmol}), \mathrm{Rh}_{2} \operatorname{esp}_{2}(1.3 \mathrm{mg}, 1.71 \mu \mathrm{~mol})$, and $\mathrm{DCM}(8 \mathrm{~mL})$. After 12 h , the reaction was quenched, and column chromatography ( $40 \% \mathrm{EtOAc} / \mathrm{Hex}, \mathrm{R}_{f} 0.38$ ) afforded 3 t as a pale brown solid ( $0.182 \mathrm{~g}, 23 \%$ ). [m.p. $158-160^{\circ} \mathrm{C}{ }^{1}{ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.44(\mathrm{~d}, J=7.9 \mathrm{~Hz}, 1 \mathrm{H}), 7.88-7.81(\mathrm{~m}$, 2H), $7.78-7.65(\mathrm{~m}, 3 \mathrm{H}), 7.44-7.24(\mathrm{~m}, 5 \mathrm{H}), 6.92-6.83(\mathrm{~m}, 2 \mathrm{H}), 4.02(\mathrm{t}, \mathrm{J}=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 3.81(\mathrm{~s}, 3 \mathrm{H})$, $3.39(\mathrm{t}, \mathrm{J}=9.0,1 \mathrm{H}), 3.38(\mathrm{~s}, 3 \mathrm{H}), 3.11(\mathrm{t}, J=7.7 \mathrm{~Hz}, 2 \mathrm{H}), 2.41(\mathrm{dd}, J=8.3,5.3 \mathrm{~Hz}, 1 \mathrm{H}), 1.79$ (dd, $J=9.4$, $5.3 \mathrm{~Hz}, 1 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) (Rotamers!!) $\delta 168.2,167.7,166.0,158.9,136.1,134.0,133.8$, $132.0,130.4,130.2,126.0,125.6,124.0,123.3,123.2,122.1,122.0,119.6,119.5,119.0,118.9,116.6$, 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), $\mathrm{cm}^{-1}$. HRMS (ESI) M/Z+ Calc. 522.1791, Obs. 522.1777.


## Methyl

1-(3-(2-methoxy-2-oxoethyl)-1H-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)-1H-indol-1-yl)-3-oxopropanoate (0.611 g, 1.94 mmol,$), \mathrm{Rh}_{2} \mathrm{esp}_{2}(1.5 \mathrm{mg}, 1.98 \mu \mathrm{~mol})$, and $\mathrm{DCM}(8 \mathrm{~mL})$. After 14 h , the reaction was quenched, and column chromatography (EtOAc/Hex, $\mathrm{R}_{f} 0.21$ ) afforded 3 u as a yellow solid ( $0.312 \mathrm{~g}, 47 \%$ ). [m.p. $82-84$ $\left.{ }^{\circ} \mathrm{C}\right] .{ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.46(\mathrm{~d}, \mathrm{~J}=8.1 \mathrm{~Hz}, 1 \mathrm{H}), 7.58-7.49(\mathrm{~m}, 2 \mathrm{H}), 7.46-7.26(\mathrm{~m}, 4 \mathrm{H}), 6.92$ $-6.82(\mathrm{~m}, 2 \mathrm{H}), 3.81(\mathrm{~s}, 3 \mathrm{H}), 3.73(\mathrm{~s}, 2 \mathrm{H}), 3.73(\mathrm{~s}, 3 \mathrm{H}), 3.43(\mathrm{~s}, 3 \mathrm{H}), 3.43(\mathrm{t}, \mathrm{J}=4.5 \mathrm{~Hz}, 1 \mathrm{H}), 2.42(\mathrm{dd}, \mathrm{J}=$ $8.3,5.3 \mathrm{~Hz}, 1 \mathrm{H}), 1.86(\mathrm{dd}, \mathrm{J}=9.4,5.2 \mathrm{~Hz}, 1 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 171.0,167.8,166.0,158.9$, $135.9,130.2,130.1,125.9,125.6,124.0,123.3,119.0,116.6,115.7,113.6,55.2,52.8,52.2,39.3,31.3$, 30.8, 18.9. IR: 3009.0 (w), 2947.1 (w), 1742.29 (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 .



#### Abstract

Methyl 2-bromo-1-(3-methyl-1H-indole-1-carbonyl)-2-phenylcyclopropanecarboxylate(3v): The general procedure was followed using (1-bromovinyl)benzene ( $0.150 \mathrm{~g}, 0.819 \mathrm{mmol}$ ), methyl 2-diazo-3-(3-methyl-1H-indol-1-yl)-3-oxopropanoate ( $0.274 \mathrm{~g}, 1.065 \mathrm{mmol}$ ), $\mathrm{Rh}_{2} \mathrm{esp}_{2}(1.0 \mathrm{mg}, 1.319 \mu \mathrm{~mol})$, and DCM ( 12 mL ). After 12 h , the reaction was quenched, and column chromatography ( $20 \% \mathrm{EtOAc} / \mathrm{Hex}, \mathrm{R}_{f}$ 0.40 ) afforded $3 v$ as a white solid ( $0.075 \mathrm{~g}, 22.2 \%$ ). [m.p. $\left.132-134^{\circ} \mathrm{C}\right]{ }^{1} \mathrm{H}$ NMR ( 300 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 8.12-8.04(\mathrm{~m}, 1 \mathrm{H}), 7.48-7.37(\mathrm{~m}, 3 \mathrm{H}), 7.27-7.18(\mathrm{~m}, 3 \mathrm{H}), 7.17-7.04(\mathrm{~m}, 3 \mathrm{H}), 3.80(\mathrm{~s}, 3 \mathrm{H})$, $2.86(\mathrm{~d}, J=7.3 \mathrm{~Hz}, 1 \mathrm{H}), 2.56(\mathrm{~d}, J=7.3 \mathrm{~Hz}, 1 \mathrm{H}), 2.27(\mathrm{~d}, J=1.3 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (75 MHz, CDCl $\left.{ }_{3}\right) \delta$ $166.76,161.38,136.52,135.61,131.27,128.86,128.57,127.85,125.06,123.77,122.47,118.71,118.60$, 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) $\mathrm{cm}^{-1}$. HRMS (ESI) M/Z+ Calc. 411.0470, Obs. 411.0461.


## D. $\operatorname{In}(\mathrm{OTf})_{3}$-Catalyzed Homo-Nazarov Cyclizations

General Method A: The cyclopropyl $\beta$-amide ester 3 (1.0 equiv) was added to a solution of $\ln (\mathrm{OTf})_{3}(0.30$ 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 $\mathrm{MgSO}_{4}$. The organic layers were concentrated for silica gel flash column chromatography.
General Method B: To a mixture of $\ln (\mathrm{OTf})_{3}(0.30$ equiv) in anhydrous 1,2-dichloroethane heated to a reflux, dissolved cyclopropyl $\beta$-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 $\mathrm{MgSO}_{4}$, 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-1H-indole-1-carbonyl)cyclopropanecarboxylate $(0.100 \mathrm{~g}, 0.275 \mathrm{mmol}), \ln (\mathrm{OTf})_{3}(0.046 \mathrm{~g}, 0.082 \mathrm{mmol})$ and DCM $(4 \mathrm{~mL})$ were combined according to general method $A$ to afford 4a as a pale brown oil ( $0.099 \mathrm{~g}, 99 \%$ ) after $2 \mathrm{~h} . \mathrm{R}_{f} 0.35$ (20\% EtOAc/Hex). Diastereomeric ratio: (2.6:1). ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.55-8.47$ (m, 1.34), $7.50-7.28$ (m, 4.53), $7.15-7.09(\mathrm{~m}, 0.86), 7.01-6.95(\mathrm{~m}, 2.09), 6.88-6.80(\mathrm{~m}, 3.05), 4.59(\mathrm{t}, \mathrm{J}=4.3 \mathrm{~Hz}, 0.94), 4.34(\mathrm{dd}, \mathrm{J}=$ $8.5,5.1 \mathrm{~Hz}, 0.36$ ), $3.81-3.78(\mathrm{~m}, 8.28), 3.69(\mathrm{~d}, \mathrm{~J}=4.5 \mathrm{~Hz}, 0.56), 3.65(\mathrm{~d}, \mathrm{~J}=4.5 \mathrm{~Hz}, 0.56), 3.56(\mathrm{~d}, \mathrm{~J}=$ $1.1 \mathrm{~Hz}, 1.37$ ), $2.92-2.68(\mathrm{~m}, 1.40), 2.59-2.34(\mathrm{~m}, 1.39), 2.00(\mathrm{~s}, 3.0), 1.75(\mathrm{~s}, 1.26) .{ }^{13} \mathrm{C}$ NMR (75 MHz, $\left.\mathrm{CDCl}_{3}\right) \delta 169.6,169.2,165.0,164.9,158.5,158.5,134.5,134.4,133.7,133.5,132.8,132.3,131.3,131.0$, $128.9,128.3,124.8,124.8,124.1,124.0,118.1,118.0,116.5,115.2,114.8,114.1,113.9,55.1,52.5$, 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), 1618.49 (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) $\mathrm{cm}^{-1}$. 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,
$0.192 \mathrm{mmol}), \ln (\mathrm{OTf})_{3}(0.032 \mathrm{~g}, 0.057 \mathrm{mmol})$ and DCM $(3 \mathrm{~mL})$ were mixed according to general method A to afford a pale yellow oil ( $0.066 \mathrm{~g}, 95.0 \%$ ) after $3 \mathrm{~h} . \mathrm{R}_{f} 0.37$ ( $20 \% \mathrm{EtOAc} / \mathrm{Hex}$ ). Diastereomeric ratio: (3.2:1). ${ }^{1} \mathrm{H}$ NMR $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) ~ \delta 8.59-8.48(\mathrm{~m}, 1.32), 7.50-7.29$ ( $\mathrm{m}, 4.33$ ), $7.28-7.19$ (m, 1.66), 6.93 (dd, $J=8.3,3.2 \mathrm{~Hz}, 1.57$ ), $6.84-6.74$ (m, 1.84), 6.57 (dd, $J=7.5,1.6 \mathrm{~Hz}, 1.12$ ), 4.95 (dd, $J=4.9$, $3.0 \mathrm{~Hz}, 1.03$ ), $4.80(\mathrm{t}, \mathrm{J}=6.1 \mathrm{~Hz}, 0.32)$, $3.97-3.88(\mathrm{~m}, 4.23), 3.83-3.75(\mathrm{~m}, 3.52), 3.74-3.62(\mathrm{~m}$, 1.07 ), 3.45 ( $\mathrm{s}, 0.94$ ), 2.95 ( $\mathrm{dt}, J=13.8,7.0 \mathrm{~Hz}, 0.37$ ), $2.81-2.66$ ( $\mathrm{m}, 1.36$ ), $2.61-2.44$ ( $\mathrm{m}, 1.44$ ), 2.31 ( q , $J=7.8 \mathrm{~Hz}, 0.37$ ), $2.00(\mathrm{~s}, 2.89), 1.81(\mathrm{~s}, 0.94) .{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) ס 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), $1440.0(\mathrm{~s})$, 1374.7(s), 1221.0(s), 1044.7(s), 784.2 (s), $674.3(\mathrm{~m}) \mathrm{cm}^{-1}$. 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 ( $0.100 \mathrm{~g}, 0.300 \mathrm{mmol}$ ), $\ln (\mathrm{OTf})_{3}$ $(0.050 \mathrm{~g}, 0.090 \mathrm{mmol})$ and DCE $(4 \mathrm{~mL})$ were combined according to general method $B$ to afford 4 c as a brown oil ( $0.051 \mathrm{~g}, 52 \%$ ) after 8 h. $\mathrm{R}_{f} 0.25$ ( $20 \% \mathrm{EtOAc} / \mathrm{Hex}$ ). Diastereomeric ratio: (2.6:1). ${ }^{1} \mathrm{H}$ NMR (300 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.57-8.47(\mathrm{~m}, 1.37), 7.53-7.27(\mathrm{~m}, 10.63), 7.07(\mathrm{~d}, \mathrm{~J}=7.4 \mathrm{~Hz}, 2.24), 4.64(\mathrm{t}, \mathrm{J}=4.3$ $\mathrm{Hz}, 1.00$ ), 4.40 (dd, $J=8.2,5.7 \mathrm{~Hz}, 0.39$ ), 3.80 (dd, $J=9.4,3.3 \mathrm{~Hz}, 3.61$ ), $3.75-3.63$ ( $\mathrm{m}, 1.46$ ), 3.53 (d, $J=1.1 \mathrm{~Hz}, 1.28$ ), $2.95-2.74(\mathrm{~m}, 2.28), 2.64-2.42(\mathrm{~m}, 2.12), 2.00(\mathrm{~s}, 3.13), 1.74(\mathrm{~s}, 1.24) .{ }^{13} \mathrm{C}$ NMR ( 75 $\mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 169.6,169.2,165.0,164.9,140.8,140.5,134.6,133.3,133.2,131.3,131.1,128.9,128.7$, 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) $\mathrm{cm}^{-1}$. 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-1H-indole-1-carbonyl) cyclopropanecarboxylate ( $0.100 \mathrm{~g}, 0.285$ $\mathrm{mmol}), \operatorname{In}(\mathrm{OTf})_{3}(0.047 \mathrm{~g}, 0.085 \mathrm{mmol}, 30 \mathrm{~mol} \%)$ and DCE $(4 \mathrm{~mL})$ were combined according to general method B to afford a brown oil ( $0.048 \mathrm{~g}, 48 \%$ ) after $8 \mathrm{~h} . \mathrm{R}_{f} 0.28$ ( $20 \% \mathrm{EtOAc} / \mathrm{Hex}$ ). Diastereomeric ratio: (2.6:1). ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl} 3$ ) б $8.57-8.46(\mathrm{~m}, 1.37$ ), 7.76 ( $\mathrm{d}, \mathrm{J}=8.1 \mathrm{~Hz}, 0.68$ ), $7.53-7.29(\mathrm{~m}$, $5.16), 7.26-6.77(\mathrm{~m}, 12.82), 5.75(\mathrm{~s}, 0.62), 4.62(\mathrm{t}, \mathrm{J}=4.4 \mathrm{~Hz}, 1.00), 4.39$ (dd, $J=8.2,5.3 \mathrm{~Hz}, 0.35)$, 3.80 (s, 3.03), 3.65 (dd, J = 11.8, $4.5 \mathrm{~Hz}, 1.24$ ), 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). ${ }^{13}{ }^{5}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 169.5,169.2,164.8,160.2,136.2,134.6$, 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), $1314.8(\mathrm{~m}), 1250.8$ (s), $1209.5(\mathrm{~s})$, $1097.4(\mathrm{~m}), 989.0(\mathrm{w}), 832.4(\mathrm{~m}), 736.0(\mathrm{~s}) \mathrm{cm}^{-1}$. 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-1H-indole-1-carbonyl) cyclopropanecarboxylate ( 0.100 g , $0.272 \mathrm{mmol}), \ln (\mathrm{OTf})_{3}(0.045 \mathrm{~g}, 0.081 \mathrm{mmol})$ and DCE $(4 \mathrm{~mL})$ were mixed according to general method $B$ to yield a brown oil ( $0.049 \mathrm{~g}, 49.7 \%$ ) after $12 \mathrm{~h} . \mathrm{R}_{f} 0.43$ (15\% EtOAc/Hex). Diastereomeric ratio: (1.9:1). ${ }^{1} \mathrm{H}$ NMR $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.55-8.46(\mathrm{~m}, 1.38), 7.50-7.27(\mathrm{~m}, 8.02), 7.17-7.13(\mathrm{~m}, 1.05), 7.04-$ 6.98 (m, 2.15), $6.81-6.77(\mathrm{~m}, 0.45), 4.61(\mathrm{t}, \mathrm{J}=4.6 \mathrm{~Hz}, 1.00), 4.40$ (dd, $J=7.6,5.8 \mathrm{~Hz}, 0.52$ ), 3.80 (s, 3.14 ), 3.65 ( $\mathrm{d}, \mathrm{J}=4.5 \mathrm{~Hz}, 0.55$ ), 3.61 ( $\mathrm{d}, \mathrm{J}=4.5 \mathrm{~Hz}, 0.55$ ), 3.54 ( $\mathrm{s}, 1.24$ ), $2.93-2.70$ (m, 2.53), $2.62-$ 2.37 ( $\mathrm{m}, 2.54$ ), 1.99 ( $\mathrm{s}, 2.80$ ), 1.77 ( $\mathrm{s}, 1.20$ ). ${ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 169.4,164.7,139.1,134.6$, 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), $2956.6(\mathrm{~m}), 2918.6$ (m), 2847.1 (m), $1747.0(\mathrm{~m}), 1699.4(\mathrm{~m}), 1613.6$ (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-1H-indole-1-carbonyl)-2-(4-nitrophenyl) cyclopropanecarboxylate ( $0.100 \mathrm{~g}, 0.264$ $\mathrm{mmol}), \ln (\mathrm{OTf})_{3}(0.044 \mathrm{~g}, 0.079 \mathrm{mmol})$ and DCE $(4 \mathrm{~mL})$ 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 $\mathbf{4 f}$ and other by-products as observed by crude ${ }^{1} \mathrm{H}$ NMR. $\mathrm{R}_{f} 0.35$ (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 ( $0.050 \mathrm{~g}, 0.154 \mathrm{mmol}$ ), $\ln (\mathrm{OTf})_{3}(0.026 \mathrm{~g}, 0.046 \mathrm{mmol})$ and DCM $(3 \mathrm{~mL})$ were mixed according to general method $A$ to afford a colorless oil ( $0.049 \mathrm{~g}, 99.0 \%$ ) after $2 \mathrm{~h} . \mathrm{R}_{f} 0.40$ ( $20 \% \mathrm{EtOAc} / \mathrm{Hex}$ ). Diastereomeric ratio: (4.5:1). ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) ठ $8.57-8.51$ (m, 0.37), $8.50-8.42$ (m, 0.97), $7.53-7.46$ (m, 1.50), $7.42-7.29$ (m, 3.77 ), $6.30-6.25(\mathrm{~m}, 1.21), 5.91-5.87(\mathrm{~m}, 1.16), 4.65(\mathrm{t}, \mathrm{J}=3.9 \mathrm{~Hz}, 1), 4.52(\mathrm{t}, \mathrm{J}=5.2 \mathrm{~Hz}, 0.22), 3.84$ (d, $J=1.0 \mathrm{~Hz}, 3.24), 3.81-3.72(\mathrm{~m}, 1.42), 3.51(\mathrm{~d}, J=0.8 \mathrm{~Hz}, 0.69), 3.08(\mathrm{dt}, J=13.8,5.6 \mathrm{~Hz}, 0.25)$, 2.72 (dt, $J=4.4,3.6 \mathrm{~Hz}, 2.07$ ), $2.53(\mathrm{dt}, J=13.8,5.3 \mathrm{~Hz}, 0.27$ ), 2.15 (d, $J=0.3 \mathrm{~Hz}, 3.09$ ), $2.00(\mathrm{~d}, J=0.9$ $\mathrm{Hz}, 0.67$ ). ${ }^{13} \mathrm{C}$ NMR (75 MHz, $\mathrm{CDCl}_{3}$ ) $\delta 169.6,164.8,152.4,142.4,142.1,134.6,131.1,130.8,125.1$, 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 $\mathrm{mmol}), \ln (\mathrm{OTf})_{3}(0.033 \mathrm{~g}, 0.060 \mathrm{mmol})$ and DCM $(3 \mathrm{~mL})$ were combined according to general Method $A$ to afford a 4 h as a white solid ( $0.065 \mathrm{~g}, 94.14 \%$ ) after $2 \mathrm{~h} . \mathrm{R}_{f} 0.28(20 \% \mathrm{EtOAc} / \mathrm{Hex})$. [m.p. $139-141^{\circ} \mathrm{C}$ ] Diastereomeric ratio: (1.1:1). ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.58-8.50$ (m, 1.81), 7.54 (ddt, $J=7.6,4.3$, $2.2 \mathrm{~Hz}, 1.0$ ), $7.45-7.25$ (m, 13.52), $7.13-7.08$ ( $\mathrm{m}, 2.11$ ), 3.99 (dd, $J=12.2,5.0 \mathrm{~Hz}, 0.80$ ), 3.80 (s, 3.0), 3.72 (s, 2.71), 3.43 (dd, $J=13.2,4.4 \mathrm{~Hz}, 0.99$ ), 2.84 (dt, $J=26.7,13.4 \mathrm{~Hz}, 1.88$ ), $2.50-2.41$ (m, 1.35), $2.26-2.18$ ( $\mathrm{m}, 4.15$ ), 1.99 ( $\mathrm{s}, 2.99$ ), 1.85 ( $\mathrm{s}, 2.62$ ), 1.65 (s, 2.68). ${ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 169.5$, 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) $\mathrm{cm}^{-1}$. 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 ( $0.055 \mathrm{~g}, 0.175 \mathrm{mmol}$ ), $\operatorname{In}(\mathrm{OTf})_{3}$ ( $0.029 \mathrm{~g}, 0.052 \mathrm{mmol}$ ) and DCE ( 3 mL ) were mixed according to general method $B$ to yield a colorless oil ( $0.046 \mathrm{~g}, 84.8 \%$ ) after 6 h. $\mathrm{R}_{f} 0.38(20 \% \mathrm{EtOAc} / \mathrm{Hex}) .{ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.51-8.44(\mathrm{~m}, 1 \mathrm{H})$, 7.44 (ddd, $J=6.7,4.5,2.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.34-7.28(\mathrm{~m}, 2 \mathrm{H}), 3.94-3.83(\mathrm{~m}, 4 \mathrm{H}), 2.58(\mathrm{t}, J=13.5 \mathrm{~Hz}, 1 \mathrm{H})$, $2.30(\mathrm{~d}, J=0.7 \mathrm{~Hz}, 3 \mathrm{H}), 2.21(\mathrm{dt}, J=14.6,7.4 \mathrm{~Hz}, 1 \mathrm{H}), 1.95(\mathrm{dd}, J=13.7,5.0 \mathrm{~Hz}, 1 \mathrm{H}), 1.87-1.65(\mathrm{~m}$, $3 \mathrm{H}), 0.93(\mathrm{dt}, \mathrm{J}=10.0,7.4 \mathrm{~Hz}, 6 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR $\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 170.2,165.3,136.9,134.4,131.7,124.7$, 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) $\mathrm{cm}^{-1}$. 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, $0.160 \mathrm{mmol}), \ln (\mathrm{OTf})_{3}(0.027 \mathrm{~g}, 0.048 \mathrm{mmol})$ and DCE $(3 \mathrm{~mL})$ were mixed according to general method B to yield a colorless oil ( $0.044 \mathrm{~g}, 88.8 \%$ ) after $6 \mathrm{~h} . \mathrm{R}_{f} 0.35(20 \% \mathrm{EtOAc} / \mathrm{Hex}) .{ }^{1} \mathrm{H}$ NMR $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ $8.48-8.41(\mathrm{~m}, 1 \mathrm{H}), 7.47-7.41(\mathrm{~m}, 1 \mathrm{H}), 7.30(\mathrm{ddd}, J=4.6,4.2,2.9 \mathrm{~Hz}, 2 \mathrm{H}), 3.85(\mathrm{~d}, J=0.8 \mathrm{~Hz}, 3 \mathrm{H})$, $3.84-3.79(\mathrm{~m}, 1 \mathrm{H}), 2.69-2.54(\mathrm{~m}, 1 \mathrm{H}), 2.47(\mathrm{t}, \mathrm{J}=13.2 \mathrm{~Hz}, 1 \mathrm{H}), 2.30(\mathrm{~d}, \mathrm{~J}=0.7 \mathrm{~Hz}, 3 \mathrm{H}), 2.13(\mathrm{dd}, \mathrm{J}=$ $13.4,4.6 \mathrm{~Hz}, 1 \mathrm{H}), 2.02-1.83(\mathrm{~m}, 5 \mathrm{H}), 1.83-1.70(\mathrm{~m}, 2 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 169.9,165.4$, 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) $\mathrm{cm}^{-1}$. 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, $0.246 \mathrm{mmol}), \ln (\mathrm{OTf})_{3}(0.041 \mathrm{~g}, 0.073 \mathrm{mmol})$ and DCE $(3 \mathrm{~mL})$ were mixed according to general method $B$ to yield a colorless oil ( $0.062 \mathrm{~g}, 78.6 \%$ ) after $6 \mathrm{~h} . \mathrm{R}_{\mathrm{f}} 0.39$ (20\% EtOAc/Hex). (Conformers!!) ${ }^{1} \mathrm{H}$ NMR (300 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.49-8.41(\mathrm{~m}, 1 \mathrm{H}), 7.47-7.42(\mathrm{~m}, 1 \mathrm{H}), 7.36-7.27(\mathrm{~m}, 2 \mathrm{H}), 3.86(\mathrm{dd}, \mathrm{J}=2.9,0.6 \mathrm{~Hz}$, $3 \mathrm{H}), 3.76$ (dd, $J=13.1,4.6 \mathrm{~Hz}, 1 \mathrm{H}), 2.71-2.59(\mathrm{~m}, 3 \mathrm{H}), 2.54-2.39(\mathrm{~m}, 4 \mathrm{H}), 2.36-2.17(\mathrm{~m}, 2 \mathrm{H}), 1.91-$ $1.76(\mathrm{~m}, 4 \mathrm{H}), 1.70(\mathrm{~d}, \mathrm{~J}=11.9 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C} \operatorname{NMR}\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 170.2,165.5,139.5,134.0,132.1$, $125.1,124.8,123.9,121.7,119.4,117.7,116.6,114.4,113.1,58.6,52.7,47.2,36.1,35.6,33.9,33.7$, 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 ( $0.100 \mathrm{~g}, 0.196 \mathrm{mmol}$ ), $\operatorname{In}(\mathrm{OTf})_{3}(0.033 \mathrm{~g}, 0.058 \mathrm{mmol})$ and DCE (4 mL ) were combined according to general method $B$ to afford a colorless oil ( $0.082 \mathrm{~g}, 82 \%$ ) after 16 h . $\mathrm{R}_{f}$ 0.41 (20\% EtOAc/Hex). ${ }^{1} \mathrm{H}$ NMR $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.37$ (ddd, $\left.J=4.3,2.2,0.6 \mathrm{~Hz}, 1 \mathrm{H}\right), 7.72-7.66(\mathrm{~m}$, $4 \mathrm{H}), 7.45-7.32(\mathrm{~m}, 7 \mathrm{H}), 7.29-7.24(\mathrm{~m}, 2 \mathrm{H}), 3.89(\mathrm{dd}, \mathrm{J}=13.5,4.8 \mathrm{~Hz}, 1 \mathrm{H}), 3.72(\mathrm{~s}, 3 \mathrm{H}), 3.45-3.33$ ( $\mathrm{m}, 1 \mathrm{H}$ ), 2.19 (ddd, $J=18.1,8.8,3.1 \mathrm{~Hz}, 1 \mathrm{H}$ ), $1.99(\mathrm{~s}, 3 \mathrm{H}), 1.83$ (ddd, $J=13.5,4.8,2.5 \mathrm{~Hz}, 1 \mathrm{H}), 1.55$ (dd, $J=8.3,4.6 \mathrm{~Hz}, 2 \mathrm{H}), 1.06-1.00(\mathrm{~m}, 9 \mathrm{H}) .{ }^{13} \mathrm{C} \operatorname{NMR}\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 169.7,165.1,138.5,135.8,135.7$, $134.4,134.1,133.0,131.2,129.5,129.4,127.9,124.5,124.0,117.9,116.5,112.0,52.4,46.7,29.9,27.7$, 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) $\mathrm{cm}^{-1}$. 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 ( 4 m ): Methyl 2-(1,3-dioxoisoindolin-2-yl)-1-(3-methyl-1H-indole-1-carbonyl) cyclopropane carboxylate ( $0.090 \mathrm{~g}, 0.224 \mathrm{mmol}$ ), $\ln (\mathrm{OTf})_{3}(0.037 \mathrm{~g}, 0.067 \mathrm{mmol})$ and DCE ( 4 mL ) were mixed according to general method B to yield a yellow-green solid ( $0.049 \mathrm{~g}, 55 \%$ ) after $8 \mathrm{~h} . \mathrm{R}_{f} 0.38$ ( $20 \%$ $\mathrm{EtOAc} / \mathrm{Hex}$ ). [m.p. $\left.167-169^{\circ} \mathrm{C}\right]$ Diastereomeric ratio: (4.8:1). ${ }^{1} \mathrm{H}$ NMR (300 MHz, $\mathrm{CDCl}_{3}$ ) ठ $8.52-8.47$ (m, 1.27), $7.89-7.70(\mathrm{~m}, 5.64), 7.46-7.28(\mathrm{~m}, 4.18), 5.96(\mathrm{t}, \mathrm{J}=4.5 \mathrm{~Hz}, 1.00), 4.19(\mathrm{dt}, \mathrm{J}=12.5,6.3 \mathrm{~Hz}$, 0.70 ), $3.83-3.79(\mathrm{~m}, 3.92)$, 2.86 (ddd, $\mathrm{J}=14.1,11.8,5.3 \mathrm{~Hz}, 0.75$ ), 2.58 (ddd, $\mathrm{J}=14.3,4.9,4.0 \mathrm{~Hz}$, 0.75 ), $2.29-2.26(\mathrm{~m}, 0.22), 2.07$ ( $\mathrm{s}, 2.75$ ), 2.04 ( $\mathrm{s}, 0.38$ ). ${ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) ס 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) $\mathrm{cm}^{-1}$. 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 ( $0.018 \mathrm{~g}, 0.049 \mathrm{mmol}$ ), $\ln (\mathrm{OTf})_{3}(0.008 \mathrm{~g}, 0.014 \mathrm{mmol})$ and $\mathrm{DCE}(1 \mathrm{~mL})$ were mixed according to general method B to yield a colorless oil ( $0.014 \mathrm{~g}, 81 \%$ ) after $7 \mathrm{~h} . \mathrm{R}_{f} 0.30$ ( $20 \% \mathrm{EtOAc} / \mathrm{Hex}$ ). Diastereomeric ratio: ( $10: 1$ ). ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.54(\mathrm{~d}, \mathrm{~J}=8.6 \mathrm{~Hz}, 0.10$ ), $8.47-8.40(\mathrm{~m}, 1), 7.54-7.29(\mathrm{~m}, 9.0), 4.91-4.84(\mathrm{~m}$, 1.06), 4.48 (dd, $J=13.1,4.8 \mathrm{~Hz}, 1.04$ ), $3.94-3.76$ ( $\mathrm{m}, 3.80$ ), 2.72 (td, $J=13.6,3.9 \mathrm{~Hz}, 1.19$ ), $2.42-2.32$ (m, 1.42), 2.20 ( $\mathrm{s}, 0.31$ ), 2.04 ( $\mathrm{s}, 3.10$ ). ${ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 169.6,164.5,134.7,134.5,132.5$, 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) $\mathrm{cm}^{-1}$. 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 (4o): Methyl 6-(3-methyl-1 H-indole-1-carbonyl)-2-oxabicyclo[3.1.0] hexane-6-carboxylate ( $0.025 \mathrm{~g}, 0.083$ $\mathrm{mmol}), \operatorname{In}(\mathrm{OTf})_{3}(0.014 \mathrm{~g}, 0.025 \mathrm{mmol})$ and DCM $(2 \mathrm{~mL})$ were combined according to general method $A$ to afford a colorless oil ( $0.024 \mathrm{~g}, 97 \%$ ) after $2.5 \mathrm{~h} . \mathrm{R}_{f} 0.30(20 \% \mathrm{EtOAc} / \mathrm{Hex}) .{ }^{1} \mathrm{H}$ NMR $\left(300 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) ~ \delta$ $8.39(\mathrm{~d}, J=4.9,3.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.51(\mathrm{~d}, J=6.8,1.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.41-7.27(\mathrm{~m}, 2 \mathrm{H}), 5.05(\mathrm{~d}, J=4.5 \mathrm{~Hz}, 1 \mathrm{H})$, $4.17-3.99(\mathrm{~m}, 2 \mathrm{H}), 3.87(\mathrm{~s}, 3 \mathrm{H}), 3.78(\mathrm{~d}, \mathrm{~J}=10.7 \mathrm{~Hz}, 1 \mathrm{H}), 3.32-3.21(\mathrm{~m}, 1 \mathrm{H}), 2.47-2.22(\mathrm{~m}, 1 \mathrm{H}), 2.32$ (s, 3H), $1.96-1.82(\mathrm{~m}, 1 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 169.2,164.0,134.5,130.9,128.8,125.8,124.2$, 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 ), $1623.2(\mathrm{w}), 1459.5(\mathrm{~m}), 1382.2(\mathrm{~s}), 1265.2(\mathrm{~m}), 1035.5(\mathrm{~m}), 751.0(\mathrm{~s}) \mathrm{cm}^{-1}$. HRMS (ESI) M/Z+ Calc. 299.1158, Obs. 299.1158.


Methyl 12-methyl-6-oxo-3,4,4a,5,6,12b-hexahydro-2H-pyrano[2',3':3,4]pyrido[1,2-a]indole-5carboxylate (4p): Methyl 7-(3-methyl-1H-indole-1-carbonyl)-2-oxabicyclo[4.1.0]heptane-7-carboxylate ( $0.025 \mathrm{~g}, 0.079 \mathrm{mmol}), \ln (\mathrm{OTf})_{3}(0.013 \mathrm{~g}, 0.023 \mathrm{mmol})$ and DCM $(2 \mathrm{~mL})$ were mixed according to general method A to yield a pale yellow solid ( $0.023 \mathrm{~g}, 92.9 \%$ ) after $2.5 \mathrm{~h} . \mathrm{R}_{f} 0.25$ ( $20 \% \mathrm{EtOAc} / \mathrm{Hex}$ ). [m.p. 128$\left.130^{\circ} \mathrm{C}\right]{ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.41(\mathrm{~d}, 1 \mathrm{H}), 7.50(\mathrm{~d}, 1 \mathrm{H}), 7.40-7.25(\mathrm{~m}, 2 \mathrm{H}), 4.81(\mathrm{~s}, 1 \mathrm{H}), 4.33(\mathrm{~d}$, $J=12.2 \mathrm{~Hz}, 1 \mathrm{H}), 4.08(\mathrm{~d}, 1 \mathrm{H}), 3.86(\mathrm{~s}, 3 \mathrm{H}), 3.71(\mathrm{t}, \mathrm{J}=11.6,2.4 \mathrm{~Hz}, 2 \mathrm{H}), 2.72(\mathrm{~d}, 1 \mathrm{H}), 2.30(\mathrm{~s}, 3 \mathrm{H}), 1.98$ $-1.73(\mathrm{~m}, 2 \mathrm{H}), 1.56-1.47(\mathrm{~m}, 1 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 169.5,165.2,134.3,130.8,125.8$, 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) $\mathrm{cm}^{-1}$. HRMS (ESI) M/Z+ Calc. 313.1314, Obs. 313.1315.


1-Benzyl 5-methyl 12-methyl-6-oxo-2,3,4,4a,5,6-hexahydroindolo[1,2-h][1,7] naphthyridine-1,5(12bH)-dicarboxylate (4q): 2-benzyl 7-methyl 7-(3-methyl-1H-indole-1-carbonyl)-2-azabicyclo[4.1.0]heptane-2,7-dicarboxylate ( $0.100 \mathrm{~g}, 0.223 \mathrm{mmol}$ ), $\ln (\mathrm{OTf})_{3}(0.037 \mathrm{~g}, 0.067 \mathrm{mmol})$ and DCM ( 4 mL ) were combined according to general method $A$ to afford 4 q as a colorless oil ( 0.098 g , 98.0\%) after 2 h. $\mathrm{R}_{f} 0.25$ ( $25 \%$ EtOAc/Hex). Diastereomeric ratio: (7.1:1). ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz} \mathrm{CDCl}_{3}$ ) $\delta$ $8.55-8.40$ (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 ( $\mathrm{m}, 1.20$ ), 3.95 (dd, $J=13.9,3.7 \mathrm{~Hz}, 0.23$ ), $3.85(\mathrm{~s}, 0.77), 3.74(\mathrm{~s}, 3), 3.68(\mathrm{~d}, J=1.7 \mathrm{~Hz} 1.41), 2.81-$ $2.50(\mathrm{~m}, 2.68), 2.35-2.20(\mathrm{~m}, 0.32), 2.08-2.03(\mathrm{~m}, 3.99), 1.79-1.85(\mathrm{~m}, 1.54), 1.58-1.70(\mathrm{~m}, 2.70)$, 1.51 - 1.33 (m, 1.42). ${ }^{13} \mathrm{C}$ NMR (75 MHz, $\mathrm{CDCl}_{3}$ ) $\delta 168.4,167.6,162.6,155.0,136.3,134.5,131.3$, $128.4,128.3,128.1,127.8,127.7,125.1,124.1,122.0,117.9,116.4,116.3,67.5,56.0,53.5,53.0,52.4$, 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-(1H-indole-1-carbonyl)-2-(4-methoxyphenyl)cyclopropanecarboxylate ( $0.75 \mathrm{~g}, 0.215 \mathrm{mmol})$, $\ln (\mathrm{OTf})_{3}$ $(0.036 \mathrm{~g}, 0.064 \mathrm{mmol})$ and DCM ( 4 mL ) were combined according to general method $A$ to afford 4 r as a colorless oil ( $0.742 \mathrm{~g}, 98.99 \%$ ) after 45 min . $\mathrm{R}_{f} 0.30$ ( $20 \% \mathrm{EtOAc} / \mathrm{Hex}$ ). Diastereomeric ratio: (1.1:1). ${ }^{1} \mathrm{H}$ NMR (300 MHz, $\mathrm{CDCl}_{3}$ ) ठ 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), $6.08(\mathrm{~s}, 0.78), 6.00-5.89(\mathrm{~m}, 1), 4.36(\mathrm{dd}, J=9.9,4.2 \mathrm{~Hz}, 0.76 \mathrm{H}), 4.13(\mathrm{dd}, J=13.0,2.6 \mathrm{~Hz}$, 1.09), $3.97-3.79(m, 13.94), 2.79-2.64(m, 1.92), 2.54-2.37(m, 1.88) .{ }^{3}{ }^{3} \mathrm{C} N \mathrm{NM}\left(75 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ $169.5,169.3,165.3,164.7,159.1,158.9,141.5,140.6,135.2,135.1,132.7,132.3,129.6,129.5,129.3$, $129.0,124.7,124.4,124.4,120.1,120.1,116.6,116.5,114.2,107.6,55.3,53.0,52.8,51.6,49.2,40.3$, 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) $\mathrm{cm}^{-1}$. 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-7carboxylate (4s): Methyl 1-(3-(2-bromoethyl)-1H-indole-1-carbonyl)-2-(4-methoxyphenyl)cyclopropane carboxylate $(0.050 \mathrm{~g}, 0.109 \mathrm{mmol})$, $\ln (\mathrm{OTf})_{3}(0.018 \mathrm{~g}, 0.032 \mathrm{mmol})$ and $\mathrm{DCM}(3 \mathrm{~mL})$ were mixed according to general method $A$ to afford 4 s as a colorless oil ( $0.049 \mathrm{~g}, 98.2 \%$ ) after $1 \mathrm{~h} . \mathrm{R}_{f} 0.35$ (20\% EtOAc/Hex). Diastereomeric ratio: (2.7:1). ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.54$ (ddd, $J=10.3,6.9,1.4 \mathrm{~Hz}$, 1.38), $7.53-7.29(\mathrm{~m}, 4.31), 7.16-7.11(\mathrm{~m}, 0.81), 6.95(\mathrm{dd}, J=6.9,4.7 \mathrm{~Hz}, 2.07), 6.89-6.80(\mathrm{~m}, 2.88)$, $4.68(\mathrm{t}, J=4.2 \mathrm{~Hz}, 1), 4.43(\mathrm{dd}, J=8.8,5.3 \mathrm{~Hz}, 0.37), 3.86-3.77(\mathrm{~m}, 7.57), 3.69(\mathrm{dd}, J=12.2,4.6 \mathrm{~Hz}$, 1.29), 3.57 ( $\mathrm{d}, \mathrm{J}=3.5 \mathrm{~Hz}, 1.28$ ), $3.53-3.05(\mathrm{~m}, 4.08), 3.03-2.73(\mathrm{~m}, 3.37), 2.66-2.37(\mathrm{~m}, 2.03) .{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 169.4,165.2,158.8,135.5,134.7,132.3,129.6,129.1,128.3,125.2,124.4$, 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), $993.6(\mathrm{~s}), 725.0 \mathrm{~s}), 663.0$ (m) $\mathrm{cm}^{-1}$. 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)-1H-indole-1-carbonyl)-2-(4-methoxyphenyl)cyclopropanecarboxylate ( $0.050 \mathrm{~g}, 0.096 \mathrm{mmol}$ ), $\ln (\mathrm{OTf})_{3}(0.016 \mathrm{~g}, 0.028$ mmol ) and DCM ( 3 mL ) were mixed according to general method A to yield a white solid ( $0.038 \mathrm{~g}, 76.0 \%$ ) after 2 h. [m.p. $\left.166-168^{\circ} \mathrm{C}\right] \mathrm{R}_{f} 0.38\left(40 \%\right.$ EtOAc/Hex). Diastereomeric ratio: (2.8:1). ${ }^{1} \mathrm{H}$ NMR (300 MHz, $\left.\mathrm{CDCl}_{3}\right) ~ \delta 8.52-8.46(\mathrm{~m}, 1.35), 7.79-7.58(\mathrm{~m}, 7.24), 7.41-7.26(\mathrm{~m}, 2.90), 7.18-7.13$ (m, 0.89), $7.00-$ $6.93(\mathrm{~m}, 2.37), 6.86-6.72(\mathrm{~m}, 2.97), 4.70(\mathrm{t}, \mathrm{J}=4.1 \mathrm{~Hz}, 1), 4.48(\mathrm{dd}, J=8.3,5.1 \mathrm{~Hz}, 0.35), 3.85-3.80$ ( $\mathrm{m}, 0.84$ ), 3.79-3.63 (m, 11.93), 3.54 (s, 1.09), $3.02-2.90(\mathrm{~m}, 1.23), 2.88-2.71$ (m, 3.21), $2.61-2.50$ ( $\mathrm{m}, 0.57$ ), $2.44-2.33(\mathrm{~m}, 1.73) .{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 169.6,169.2,168.0,165.3,165.1,158.8$, $158.7,135.5,135.3,134.7,134.6,133.8,132.5,131.9,131.9,130.4,130.0,129.1,128.3,125.1,125.0$, $124.5,124.4,123.1,123.0,118.4,118.2,116.8,116.7,115.7,115.2,114.2,114.1,55.2,55.2,52.7,52.5$, 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), $1618.4(\mathrm{~m}), 1504.1$ (m), 1451.7 (m), 1376.6 (s), 1245.9 (s), 1032.6 (s), $837.3(\mathrm{~m}), 715.9$ (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[1,2-a]indole-7-carboxylate (4u): Methyl 1-(3-(2-methoxy-2-oxoethyl)-1H-indole-1-carbonyl)-2-(4methoxyphenyl) cyclopropanecarboxylate ( $0.070 \mathrm{~g}, 0.167 \mathrm{mmol}$ ), $\ln (\mathrm{OTf})_{3}(0.028 \mathrm{~g}, 0.049 \mathrm{mmol})$ and DCM ( 3 mL ) were combined according to general method $A$ to afford 4 u as a brown oil ( $0.062 \mathrm{~g}, 88.0 \%$ ) after 3 h. $\mathrm{R}_{f} 0.45$ (40\% EtOAc/Hex). Diastereomeric ratio: (2.0:1). ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.56$ 8.47 ( $\mathrm{m}, 1.45$ ), $7.56-7.48$ (m, 1.05), $7.44-7.28$ (m, 3.67), $7.18-7.11$ (m, 1.06), $7.01-6.90$ (m, 2.29), $6.88-6.78(\mathrm{~m}, 3.02), 4.66(\mathrm{t}, \mathrm{J}=4.5 \mathrm{~Hz}, 1), 4.40(\mathrm{dd}, J=9.7,5.1 \mathrm{~Hz}, 0.48), 3.90-3.81(\mathrm{~m}, 1.32), 3.81-$ 3.78 (m, 7.54), $3.73-3.67(\mathrm{~m}, 1.32)$, 3.64 (s, 1.44), 3.55 (s, 1.42), 3.53 (s, 2.98), 3.52 (s, 0.31 ), 3.43 (d, J $=17.3 \mathrm{~Hz}, 1.59), 3.32(\mathrm{~d}, \mathrm{~J}=17.7 \mathrm{~Hz}, 0.85), 3.02-2.69(\mathrm{~m}, 2.34), 2.58-2.38(\mathrm{~m}, 1.62) .{ }^{13} \mathrm{C}$ NMR (75 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 170.8,170.6,169.4,169.1,165.2,158.9,158.8,136.3,135.8,134.6,134.5,132.3,131.9$, $130.3,129.9,129.2,128.5,125.2,125.2,124.5,124.4,118.4,118.0,116.7,114.2,114.1,112.3,112.0$, $55.3,52.7,52.6,52.0,51.9,50.1,47.2,38.5,35.4,34.0,33.2,29.7,29.4$. 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-1H-indole-1-carbonyl)-2-phenylcyclopropanecarboxylate ( $0.060 \mathrm{~g}, 0.145 \mathrm{mmol}$ ), $\mathrm{In}(\mathrm{OTf})_{3}(0.0245$ $\mathrm{g}, 0.043 \mathrm{mmol})$ and DCM ( 3 mL ) were combined according to general method A to afford 8 as a yellowgreen oil ( $0.013 \mathrm{~g}, 28.5 \%$ ) after $4 \mathrm{~h} . \mathrm{R}_{f} 0.55$ ( $20 \% \mathrm{EtOAc} / \mathrm{Hex}$ ). ${ }^{1} \mathrm{H}$ NMR ( $300 \mathrm{MHz}, \mathrm{CDCl} 3$ ) $\delta 12.12$ (s, $1 \mathrm{H}), 8.57-8.50(\mathrm{~m}, 1 \mathrm{H}), 7.86(\mathrm{~s}, 1 \mathrm{H}), 7.71-7.66(\mathrm{~m}, 1 \mathrm{H}), 7.63-7.46(\mathrm{~m}, 2 \mathrm{H}), 7.38-7.32(\mathrm{~m}, 1 \mathrm{H}), 7.23$ $-7.06(\mathrm{~m}, 3 \mathrm{H}), 6.95(\mathrm{~m}, 1 \mathrm{H}), 3.98(\mathrm{~s}, 3 \mathrm{H}), 2.45(\mathrm{~d}, \mathrm{~J}=1.1 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $75 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 170.9$, $160.7,138.5,134.6,130.3,128.7,127.4,126.5,125.4,124.3,123.7,123.4,122.1,119.4,119.0,112.0$,
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), 1255.49 s ), 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.

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## 4. Characterization/Spectra

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## Electronic Supplementary Material (ESI) for Chemical Communications

 This journal is © The Royal Society of Chemistry 2011Che: $x p^{\text {nh }}$-5-ONP-88-c-
Futse sequence: szmu:

operator, dpatin
mercury-30
r2as.



Total tiae $1=1510$, is sec



Std carbon expariment

rulse sequence: szpul





Nont
MAK proct mivinated



## Electronic Supplementary Material (ESI) for Chemical Communications

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| Inetx | Freputncy | PP\% | nesomy |
| :---: | :---: | :---: | :---: |
| 1 | 12542.1 | 157.724 | 5.7 |
| $\%$ | 12515.1 | 155.732 | 4.4 |
| 3 | 12333.2 | 158.465 | 6.5 |
| 1 | 10267.7 | 136.012 | 3.4 |
| 5 | 9920.4 | 134.523 | 5.6 |
| d | 9324.3 | 130.132 | 27.3 |
| 7 | 9318.6 | 126.035 | 7.9 |
| ${ }^{1}$ | 9452.4 | 125.341 | 11.7 |
| 3 | $9 \times 45.0$ | 123-735 | 10.6 |
| 10 | 5159.2 | 121.450 | 8.1 |
| 11 | 8336.2 | 119.168 | 5.7 |
| 12 | 8973.5 | 118.asa | 14.7 |
| 13 | 8783.8 | 110.517 | 5.5 |
| 14 | 8574.9 | 113.536 | 24.2 |
| 15 | 5844.9 | 77.425 | 34.4 |
| 15 | 5812 - ${ }^{\text {a }}$ | 17,090 | 36.3 |
| 17 | s780.8 | Fe.575 | 36.1 |
| 18 | 4165.3 | 55.176 | 14.1 |
| 18 | 3*82.1 | 52.753 | 10.2 |
| 20 | 2976.7 | 38.431 | 7.7 |
| 21 | 2348.6 | 31.118 | 3,8 |
| 22 | 1414.3 | 15.735 | a.8 |
| 23 | 737.1 | 8,764 | 9.7 |



## Electronic Supplementary Material (ESI) for Chemical Communications

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Sta Proton parawaters
Amples we-5-DVP-51-A-m
rurse sequtnce1 szpu1
Solvent: Escl3, 235,1 K
*porntor: dpati, 2*5*
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```
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Etd Carbon experimemt

pulse sequsncel szapul


Relax. de lay 1.000 sec



Dáta ploscessing mita

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Electronic Supplementary Material (ESI) for Chemical Communications
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II-MAC-34-8
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Anbleat seaperatur,
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Acgintig, 3, 5S0
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```
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pulse sequencat szpul
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    Pulse 20.0 degress
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M,
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| tmoex | Fkeouency | PPM | meriger |
| :---: | :---: | :---: | :---: |
| 1 | 12574.2 | 167, 833 | 6.5 |
| 2 | 12504.5 | 365,644 | a.? |
| 3 | 10268.2 | 136,020 | 0.1 |
| , | 10134.4 | 134.248 | 13.4 |
| 5 | \$326.7 | 131.524 | 1.7 |
| E | 5744.1 | 125.078 | 43.1 |
| 7 | 1576.1 | 128.177 | 37.3 |
| E | 5586.2 | 127,437 | 83.3 |
| ? | 2464.2 | 125.372 | 22.7 |
| 10 | 9347.1 | 123.815 | 13.7 |
| 11 | 5165.2 | 121.410 | 11.7 |
| 12 | 5061.5 | 113.242 | 11.8 |
| 13 | 8974.5 | 118.63 | 21.6 |
| 14 | s786.5 | 146.525 | 10.1 |
| 13 | 1884.6 | 77,425 | 57,1 |
| 16 | 5812.7 | 77.080 | 51.4 |
| 17 | 5780.7 | 76.575 | 58.2 |
| ${ }^{18}$ | 3**2,2 | 52.752 | 23.7 |
| ${ }^{17}$ | 2381.6 | 33.588 | 13,3 |
| 20 | 23860.1 | 31.528 | 15.4 |
| 21 | 13)p,6 | 10,543 | 15.2 |
| 12 | 137,0 | 3.763 | 20.1 |



```
1-m+C-151_t0p
Flle= hose/Trance/cavitt/1_mac_183_top.flet
Fu7se sequemet s2pul
    Solvemt: edel3
Amblent tewatrature
FH1t1r=*ack-15! tog
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I_mac_181_top_130
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| :---: | :---: | :---: | :---: |
| 1 | 12565, | 167,632 | 11.8 |
| 2 | 12485-6 | 165.444 | 9.1 |
| 3 | 12341.3 | 163.753 | 6.7 |
| 4 | 12115.9 | 160.434 | 5.8 |
| 5 | 10256.8 | 135.537 | 5.7 |
| 6 | 1328.a | 131.522 | 11.2 |
| 7 | 1866,5 | 130.724 | 27.6 |
| 0 | 3350.2 | 130,614 | 27.2 |
| 3 | 3936.4 | 130.006 | 5.6 |
| 10 | 8311.6 | 121.870 | 7.6 |
| 11 | 3468.3 | 125.428 | 25.6 |
| 12 | s3s 1.6 | 123.827 | 23.8 |
| 13 | 4153.7 | 121.255 | 15.1 |
| 14 | 9312.7 | 113.28) | 13.9 |
| 15 | 8377.3 | 113,*18 | 26.0 |
| 15 | 8736, | 116.502 | s. 4 |
| 17 | 6762,6 | 113.279 | 26.5 |
| 18 | 8531.0 | 114.8*3 | 20,5 |
| 13 | sa40.\% | 77.484 | 30.4 |
| 20 | 5312.8 | 76.78* | 50.8 |
| 21 | 57at.? | 76.575 | 52.8 |
| 22 | 3345.5 | 52.297 | 20.2 |
| 23 | 2974.4 | 34.467 | 10,2 |
| 24 | 2321.6 | 36.745 | 14.7 |
| 25 | 1413.2 | 14.720 | 17.6 |
| 26 | 737.0 | 1.763 | 21.5 |



## Electronic Supplementary Material (ESI) for Chemical Communications

 This journal is © The Royal Society of Chemistry 2011```
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fllet hges/rrance/cavitt/1 nar 183. fle
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Solyent:, cdcis
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&etak, delay 1,v40 sec
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Midin 4ats, ism
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I_ $\operatorname{mid}$ _163_13C
T17es hone/frane e/cavitt/1_men_183_120.+11
Fwise sequence: s2pul











| Inetx | trequeswer | Pren | herant |
| :---: | :---: | :---: | :---: |
| 1 | 12651.1 | 107.710 | 23.5 |
| 2 | 12475.1 | 185.232 | 21.5 |
| 3 | 16264.5 | 135.76 | 15.6 |
| 4 | 10040.3 | 133.318 | 22.1 |
| 5 | 19530.3 | 132.711 | 38.8 |
| 4 | 1326.7 | 131,456 | 24.1 |
| 7 | 3040.3 | 139.463 | 124.6 |
| s | 1545.5 | 123.358 | 126.1 |
| , | 3487.3 | 125.465 | 48.3 |
| 16 | 9331.2 | 123.871 | 46.4 |
| 11 | 5145.4 | 121.198 | 10.5 |
| 12 | 3013.9 | 114.463 | 31.5 |
| 13 | 8376.3 | 118.765 | 58.6 |
| 14 | 8732.2 | 116.49? | 19.3 |
| 15 | 5345.5 | 37,433 | 40.2 |
| 15 | 5313.4 | 37.485 | 43,3 |
| 17 | 5731.4 | 75.563 | 43.1 |
| 18 | 3356.7 | 52.463 | 44.4 |
| 13 | 2303.3 | 34.527 | 23.5 |
| 29 | 2324., | 30.737 | 23.8 |
| 21 | 1443.3 | 12.5as | 34.1 |
| 22 | 734.3 | 0.735 | 41.4 |




Pulsw sequence: 4 pul
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Operator, Cavity








Noz
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solvent: ede13

operator cavite
Nercury-300 -r2az"



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Data proce situlated


| Index | trequency | Pen | Hetiont |
| :---: | :---: | :---: | :---: |
| 1 | 12644.7 | 167.431 | 19.3 |
| 2 | 12433.4 | 164.758 | s.6 |
| 3 | 11110.6 | 147.248 | 7, |
| 4 | 10720.4 | 142.013 | 14.4 |
| 5 | 10264.? | 135.773 | 5.2 |
| 6 | 9323-1 | 135.526 | 7,6 |
| 7 | 8317.4 | 130.947 | 51.7 |
| 6 | \$473.6 | 125.572 | 16.4 |
| s | 8365.7 | 124.363 | 17.1 |
| 10 | $8316 . *$ | 133.444 | 52.6 |
| 11 | 8123.6 | 120.338 | 3.7 |
| 12 | \$046.2 | 113.839 | 23.7 |
| 13 | 6964.3 | 113.019 | 19.1 |
| 14 | 0782,4 | 116.469 | 4.8 |
| 15 | 5844.6 | 77.421 | 57.7 |
| 16 | 5612.5 | 76.136 | 83.3 |
| 17 | 5760.4 | 76.571 | ¢a.* |
| 16 | 4010.8 | \$3.123 | 21.8 |
| 15 | 2016.4 | 35.383 | 14.3 |
| 20 | 2332.6 | 30.302 | 19.2 |
| 21 | 2240.5 | 29.574 | 6.9 |
| 22 | 1424.6 | 15.862 | 12.1 |
| 23 | 738.4 | \$.781 | 13.1 |



## Electronic Supplementary Material (ESI) for Chemical Communications

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Bta Fcoton barameters
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Pulae Bequaces sरूpul
Solvent1, Edcl3,295.1 5
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Relax. delay 1.000 sec
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Std carbon expertimerts

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Totelike 10 min, 45 sec


## Electronic Supplementary Material (ESI) for Chemical Communications

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Sta Proton parazcter=
lum,
Pelse sequence: szpu!
M,
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lol
Molax. delay 1,000 sec
Pulve 30,0 14.0.000
```




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l
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3h
7.5:1 mixture of diastereomers


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ta carbon expariment
    Fl1e: kp
    Pulse sesuence: stpul
    Solventicidcl3, 205.1 k
```



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    ketax, detay l-600 sec
    poys tise 1.3%)
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    *)
    ovcoupte M1,
    ConTR-1% #odu lated
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    los
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## Electronic Supplementary Material (ESI) for Chemical Communications

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Rh esp CP z-vimylanisuth
sapplex
Puise Sequence: s2pul
Aoiventl cde 13
Teerion.0 C

Melak. gelay 1 -ppe sec




frotiritime $\begin{gathered}5535 \\ \text { Toln, is sec }\end{gathered}$


```
Stut Carbon experiment
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Mu'se sequencel szam!
    Solvent: edel3, 203,1 K
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    Ralax-delay 1,000 sec
    Rolaw, delawy 1,000
```



```
    *)
    Cont:muovily an
    0NTMPROCESINMated 
    TVI= brodsentmu e.5 nz
```



## Electronic Supplementary Material (ESI) for Chemical Communications

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Fed Fretom parametere
Sanple: NE-5-0yP-48-5
Pu)=0 secuencez &2pul
solveat! cotcis 2mul
Movent! cacl3
Mgeraton deatin)
Relax- tetay 1,000 vec
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M,
l
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```
sta Carben exper inernt
Tamplet wa-5-tive-4a-n
rulse sequencet szpol
    Solvent \(\mathrm{csc} 13,2,3.1 \mathrm{~K}\)
```



```
    Relax. de lay 1,040 ter
Rolse so degrees
```






```
    DATA P-16CESANated
```




## Electronic Supplementary Material (ESI) for Chemical Communications

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Ste Proton parameters
Finaplat NB-5-0VP-51-6-k
pules Bequencet szpuit

Operator: dinall1
Mercury-jee
"rzez"


Widet aits. 1 us
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onsropetitions
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5td Carben expertment
Gavple: NB-5-0vp-5I-B-H
Haple: *
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    $0.4Nmti, ceti3
    *)
    kephx-selay t.0bo =ne
    Relax Selay 1,006
    jain 1at1s.9 H7
    *)
    continuousix
    wh12-16 soourated
    tine broadening e.s mz
    Five 65536 0.3 Mz
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## Electronic Supplementary Material (ESI) for Chemical Communications

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Std Proton parametsers
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Masesequencel s2bu
Moivent, edels matura
Mperator, doat11 (ag*
Relax, detay 1,000 sec
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#
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Total time 1 min, 16 sec
```





```
sta carbon experiment
f110: xp wh-4-0vF-474-11
Pulse sesuencet szpul
    Solvents cdet, (
    daclent tesperature
Mperator:jpat11
    Relar, delay 1.000 =ec
```



```
%,
Mosenc c13: 75.4913137 nmz
manymu,byom
```



```
*)
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## Electronic Supplementary Material (ESI) for Chemical Communications

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11-MAC-53-B
f17e: xp
Fulve sequence: szpal
Solvant ticla
noblisint teeperater




Me $3 n$




```
#1-muc-53-c
F11*3 xp
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Solvent Caclu
Mmblent tenplratur
Kolax. de jay 1.000 see
```



```
lol
%awitom:
contlemousiy on
```



| index | Preputway | ppr | stiont |
| :---: | :---: | :---: | :---: |
| 1 | 12625.7 | 167,251 | 3.6 |
| 2 | 12423.? | 164,543 | 7,9 |
| 3 | 10263.5 | 135,329 | 5. |
| 4 | 10221.8 | 135,409 | c. |
| 5 | 3830.0 | 131.541 | 3,2 |
| 6 | 3734.2 | 128,099 | 41.2 |
| 7 | 3594 -2 | 127.623 | 38.6 |
| 5 | 3511.5 | 125.397 | 18.7 |
|  | 3471.7 | 125,479 | 17.7 |
| 10 | 3362.4 | 124.027 | 16.7 |
| 11 | 3137.a | 121.048 | 13.6 |
| 18 | 3036. ${ }^{\text {a }}$ | 145.768 | 10.5 |
| 13 | 5879.7 | 116. 352 | 15.6 |
| 14 | 8790.3 | 136-550 | 3.6 |
| 15 | 5844.4 | 77.420 | 83.1 |
| 16 | 5812.3 | 77.002 | 55.1 |
| 17 | 5780.8 | 76.578 | 56.7 |
| 18 | 3007.3 | 33.654 | 15.6 |
| 18 | 2898.4 | 35.733 | 8.8 |
| 20 | 2128.1 | 25.191 | 11.7 |
| 21 | 1507.8 | 15.974 | 14,0 |
| 22 | 734.4 | 1.728 | 12.1 |



## Electronic Supplementary Material (ESI) for Chemical Communications

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russe sequemes szpul
Solvent: escis


Petax. de asy 1.000 sec


gerepertions
OATA Processinc
Totatitime $8=\mathrm{mtm}$, 39 sec


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ample: Ws-4-tvp-1AC-pi
wise fequencet n2pu!
Wolvom cecly
*)
M=1ax, dolay 1.00e vec
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## Electronic Supplementary Material (ESI) for Chemical Communications

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DHP-CP
f1e: xp
Pulve Seqvence: s2pul
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Nnmblent, cacisecatur,
Mperatory cavllt
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Ste carbon experliment

ule sequence: slyut
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Operators dipat11
Nercury $3 p e$ "rav2.




WIA pROCE BSilis
time brogsting 0.5 mp
Fotix)


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```
Std Proton paranaters
Uaple: 3-sethylindole-CBr-CP-N
Pu)se sequ*nces sipul
Solvent, cacls
Anblent temperature
M
Relax. welay 1.0nt sec
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## Electronic Supplementary Material (ESI) for Chemical Communications

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2, %-ponsubststuted inasolv GP
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Pulse sequancel szpu1
Molvent: edels szum
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l
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atd Carton experiment

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Solvente eser3
hetint






DiTh PRoce 3 Sintioted



# Electronic Supplementary Material (ESI) for Chemical Communications 

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Sumplet etBrindole=CP-H
) 又
Fure= seqwence: s2pul
Solventt cac 13
Moblent, temparature
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fovize s5s36min, is sec
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```
Sad Carlom experimem
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Mulse Svqu*nce: sipul
    Solyent: cdc13
    Ambisot taparaturn
    tle: f-0we-tter thiolo-CD-C
    Relax-delay 1,300 sec
    Mywe 3N=0 deg%oes
    *)
    otcoupt, 覓:; 300
    *)
    LIng broadentmg B.5. Hz
    *)
```



11-N0CO-55-H
F17en mp
(Flse sequsece: s2pul
solvent! edcis
Anbivent teegris
Aeprator, cavinture
Operator, ceasitatur
Mercury-joe







## Electronic Supplementary Material (ESI) for Chemical Communications

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The: thomertrance/cavith/1_nec_202.fle
pulse seguencer szau!
Solvent: edel3
Antient tomptrature







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I_*ac_20%_vac
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ITME brogognimg a.5 Mz
```

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| :---: | :---: | :---: | :---: |
| 1 | 12sen.z | 170.393 | 7,3 |
| 2 | 12660, | 167.810 | \%.\% |
| 3 | 12534.4 | 166.033 | 6.4 |
| 4 | 115se.d | $15 \mathrm{s.c55}$ | 0.2 |
| $\stackrel{1}{2}$ | 10260:0 | 135.810 | 5.4 |
| * | 9826.0 | 130.151 | 23.0 |
| 7 | 9823.a | 130.131 | a.2 |
| 8 | 3302.8 | 125.877 | a. 1 |
| , | 1483.6 | 125.528 | 11.5 |
| 10 | 9343.3 | 124.031 | 10.6 |
| 11 | 3307.4 | 123.291 | 3.3 |
| 12 | 8381. | 118.978 | 12.3 |
| 13 | 8340.5 | 116.976 | 7.8 |
| 14 | 8733.0 | 115.482 | 5.8 |
| 15 | 8574.9 | 113.548 | 25.5 |
| 16 | S344.) | 37.425 | 32.6 |
| 17 | 5812.8 | 33.486 | 33.8 |
| 15 | 5760.4 | 76.378 | 32.4 |
| 15 | 4164.6 | 55.161 | 17.2 |
| 20 | 3883.4 | 52.757 | 11.4 |
| 21 | 3*30.? | 52.174 | 12.3 |
| 22 | 2969.5 | 39.331 | 10.3 |
| 23 | 2359,7 | 31.250 | 10.4 |
| 24 | 2327.1 | 30.825 | 14.1 |
| 25 | 1425.4 | 15.881 | 8.1 |



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pu1se sequence: szpu!
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Melax. dolay 1,000
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TM=12t 65585
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## Electronic Supplementary Material (ESI) for Chemical Communications

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std Proton parameter:
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M,
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Pu1ve 30.0 deg%en
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(2.6:1 trans:cis mixture of diastereomers)


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te Carbon exper tment
```



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    \(\mathrm{Acg}^{2 / 120}\), 1
    vidih 18115 ; \({ }^{10} \mathrm{~Hz}\)
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    coit imouty
    nia ritasinice
    Thit
```



## Electronic Supplementary Material (ESI) for Chemical Communications

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0-ME cyclized


## 1H_1H COSY Spectrum of 4a



## 1H_1H COSY Spectrum of 4a



## 1H_13C HMBC Spectrum of 4a



1H_13C HMBC Spectrum of 4a


```
sti Provon parameters
Bample1 2-onestyrene-cycin-new-1%
Fulse sequence: srpu)
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*)
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(3.2:1 trans:cis mixture of diastereomers)


Sta carbon experiment

Pulse sequence: szpul

Oparators dpatis
Mersery- 300 "rzas"

| Gelas- delay 1.060 sec <br> pulse 30.0 degrees <br> nidin ibilis: 9 He <br> 132 repetitions <br> obathVe, <br> plcoupte ni, 300.225166 <br> cont tnapesily on <br> WALT $2=15$ moruiated <br> OATA PROCESSTMO <br> rTine brousenting 0.5 nz <br> Totel time 10 mln . 45 sec |
| :---: |

```
Etyrene-cyclized=now
flee: xp
plse Beqvence: s2pal
Solvent: cdc13
Operatort caveratmr
ercury-3*e "rzaz*
Rolax, 4elay 1,044 =ec
lol
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```
CT
```


(2.6:1 trans:cis mixture of diastereomers)


ahse Sequencet szpul
Solvant t cscls
Aoblom temperatur
operator
operatory itpat11



```
F1varo-cyellzed-H
FHe: howe/france/cav ite/f luoro-cyellzed-1%,F1d
Palse Sequence: s2pal
#Nolvent Escla
Motlent temperatur *
Fl163rflocro-cyel1zed-N
Melax.selay 1.000 vec
*)
#*)
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(2.8:1 trans:cis mixture of diastereomers)



|  |
| :---: |
|  <br>  <br>  |
|  <br>  |
|  |




(1.9:1 trans:cis mixture of diastereomers)



## Electronic Supplementary Material (ESI) for Chemical Communications

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Sotvent: edels 203,


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oferove ini 300.2237271 men
Totize

(4.5:1 trans:cis mixture of diastereomers)


Bed Carbor experimemt
3aple: wB-5-DVr-54-A-M
Folse Sequence: 32 pu
Solvent cicis, 293.1


Fagis 1 me 1.391
Ylatis $18115,9 \mathrm{~Hz}$
$128 \mathrm{tept1tions}$







```
std Proton paranater=
Amples Ftwrindole-diaxo-|
putse seqvencel szpu1
Sotvent: caci3, 233.2 K
Sotvent:. Caclu,233.2 K
&olax.sulay 4,044 sec
Mul6e si,6 deg%est
*)
```



```
MTA, PEDESSiNo 
```


(1.1:1 mixture of diastereomers)



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```
3ts Proton paraweters
FThele: NA-5-ovp-5a-A-M
Pulse sequencer szpw)
Mulse sequence, sipwl
Mospiz2,0 Ci!́!
Melak- delay 1,000 s*c
Mulce sio.0 segrest
```



```
lol
```



```
!T, &1ze 65535 min, 16 se%
```



```
sta carcon experjeont
Staple{ he-5-DNF-3A-A-H
Fu%se s+quenc51 szpul
    Solvent: ceclu
Operator: dpati, res
    Rolax, delay t,000 sec
    Accotinis,3D1,
```



```
*)
    \
ouTA Processimatated
n+1ne broadentng e.s nz
```



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```
Stut Carton experiment
Samplez ME-5-0VP-50-8-m
Puise sequencer: *2pul
    Solventy cdcls
    Amblent tomporatur
    Operator, mpat11 Maz*
    Relax., delay 1.00e swt
    Acgin $1me 1,381 se
    lol
    Decoupe, H1 :
    contimpusiy on 
    DATA procts51MG
    OTM% brotgentag e.5 N%
    Total thme 10 eln, 4s sec
```



## Electronic Supplementary Material（ESI）for Chemical Communications

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Molse Sequencet sipul
Solvent cdc 13
Timp．20． 20.1 f
Operotor，dpatil
Merctury＝300

AKg．IBe 3．55e tec






```
sta Cartion skeeriaent
samplen me-5-ovp-s3-e-m
lis: \(0 p\)
rulse seguence, stzout
solvent: Edc 13,
feas
0
perator: dpatín \({ }^{289+1} \mathrm{x}\)
"rcury-30の -rさtiz"
    Pulse solay do.000 \(=52\)
```



```
    s350 repetitiont
    pisenve c13: ? ?
    Conet 48 dis
    WALTZ-16 moulolated
    L'My brosioning e.5 mz
```


水
（180

## Electronic Supplementary Material (ESI) for Chemical Communications

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-

```
&ta Proton parawsters
STHyle: TMPPS-15eol-*/
Futse sequence: szmul
Molvent: cdel3 233.1,
M
&elax, detay 1,00# sec
Mulse 30.0 segrant
*)
```



```
los
```


Std Carbon experinent
Sumplet
Fiter
NR
Falbe sequerocel ${ }^{2}$
solyent: cac 13
Abbisht teptratur
perstor stoply
rcury-30



$\frac{180}{200}$

## Electronic Supplementary Material (ESI) for Chemical Communications

 This journal is © The Royal Society of Chemistry 2011Files xp
مulse sequence: $=2 p 01$


Relax, delay 1,000 sec
False 30.0 degrees







```
Itd Carbon experiment
Napplu= HE-4-UVP-205-A-N
*15e sequ*nce) szpal
    Solvent, ciccis
    Amblent temporaturn
    Relox, delas 1,04t sec
    Molse so,9 e6gres
    l
    lol
    col
Dath Frocrsinva
```



```
%1, Nire Es536 br, 41 mit, 3 sec
```



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```
std Proton parasetere
Fitel move/franca/cavite/thiontherbhamol.fid
Putse sequence, =2pal
Solvsat! cicl3
Pperatofl Sarits (hiostherphany)
Merarymbigetherphang
kelaw, idelay i,0acesec
Fulsersem,
```



```
M,
CT,11ze 65536 min, 34 wec
```



6.3:1 mixture of diastereomers
$\underbrace{10}_{10}$
thesthercyellizedi3t

File: xp
Pulse Beqvence: sYpul






Nover 40 de
cont muous 1 y


fotalize ifme assonz hr, S5 min. -s see

| Index | Preputher | PP\% | metant |
| :---: | :---: | :---: | :---: |
| 1 | 12806 -5 | 169.544 | 6.1 |
| 2 | 12813.8 | 164.817 | 5.4 |
| $y$ | 18109.9 | 134.764 | 5.9 |
| , | 10154.9 | 139,504 | 36.7 |
| \% | 10006.4 | 132.551 | 6.8 |
| 1 | 9857,? | 130.581 | 6.4 |
| \% | \$893.4 | 130,471 | 5.9 |
| s | 1764.5 | 126.350 | 36.2 |
| , | v757.1 | 128.243 | 4.5 |
| $1{ }^{10}$ | 1723.4 | 128.841 | 17.3 |
| 11 | sess. 1 | 125,445 | 14.6 |
| 12 | 9364.5 | 124.312 | 15.7 |
| 13 | 6*51,9 | 218,579 | 16.3 |
| 14 | 3805.6 | :516,644 | 19:3 |
| 15 | 58.64 .5 | 77,420 | 268.1 |
| 16 | 5ate.a | 27,209 | 15.2 |
| 17 | 5312.5 | 24.935 | 300 , 6 |
| 14 | 5731.0 | 76.578 | 193.6 |
| 13 | 3983.0 | 58.793 | 44.6 |
| 20 | 3543.6 | 45.540 | 15.4 |
| 21 | 3022.2 | 40.834 | 14.2 |
| 22 | 2238.6 | 29.657 | 13.4 |
| 2.3 | 626.1 | 8.234 | 10.7 |



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OHF-cycilized-H
fites xp
Pulve Sequente: $=2 \mathrm{pu} 1$





ossteve if1; 200.2504581 mitz



Dit -cycileed-C
riler xp
Putse setuencer szpul

operator, cavitt
nercury 300 "rzal




power 40 es
Whit $=15$ moralated




40

| inelx | Fregeumar | P9\% | MeICom |
| :---: | :---: | :---: | :---: |
| 1 | 12773.8 | 165.278 | 16.0 |
| 2 | 12387.4 | 164-634 | 5.5 |
| 3 | 10157.2 | 134.531 | 8.7 |
| 4 | 9303s.5 | 130.731 | 7.1 |
| 5 | 7731.0 | 125.104 | 8.1 |
| 4 | 3spl.s | 125 -485 | 18.3 |
| 7 | 9378.8 | 124.239 | 17.5 |
| $a$ | 1623.3 | 112.930 | 7.7 |
| 3 | 3974.1 | 118.818 | 22.1 |
| 19 | 5784.7 | 125.318 | 24.2 |
| 11 | 5844.4 | 73.420 | 37.2 |
| 12 | 5827.3 | 37.133 | 3.2 |
| 13 | 5812.3 | 95-139 | 34.4 |
| 14 | 5739.\% | 70.577 | 35.4 |
| 15 | 5232.? | 60.47) | 10.4 |
| 16 | Sess. 5 | 60.281 | 21.4 |
| 17 | 3931.2 | \$2.671 | 13.5 |
| 13 | $39.45 \cdot 2$ | \$2.315 | 22.2 |
| 13 | 3675.2 | 49.736 | 23.6 |
| 20 | 2317,4 | 30.703 | 13.1 |
| 21 | 642.0 | a. 505 | 13.4 |








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11-Mnc-63-15
Fthes кp
Pulse Sequance: $\quad$ s2pal
Solvent © edcia
Antient temperatur
Operator, cavizt
Mercury-30e "rzaz"





10 ,

```
sta Carbon experiment
Sample% NE-A-6VF-196-A-N
Futve sequence: 82pu!
Solvent cacl3
cychotet, capperater,
Moprater! dpat!}
```



```
Acg. Nim, 1,301,
*)
continuorly on
onTM phocezsimated
HThe broadening e.5 Az
```




```
Std Proton parmaster=
#amplun 3-xsctz-cycim-N
Fwise sequencet szpu1
solvent: cacle
Molvent: Cde13
*)
Relax, delay 2,000 osc
False, 30,0,$5y:000
```



```
lol
TTY&20.65536
```




(7.1:1 mixture of diastereomers)

$4 q$

(7.1:1 mixtue of diasteremes)



| Ste Carbon experiment. <br> Sanplez 3 -HeCbz-cyclin-C <br> fif: kp <br> Pylse seguepce: szpul <br> solvent edel3 <br> hasient temperature <br>  <br> Relax. delay 1.000 sec <br>  <br>  <br> 256 repetition <br> oeskeve c13: 5.4899093 moxz <br> DECOUNE H1; 300.2139481 MNF <br> power to de <br> contimoousiy oo <br> Vatriz-15 godyiated <br> pata proctssinc <br> tine brounention e.5 NF <br> Total time 10 <br> min. 4s sec |
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|  |  |
|  |  |



## 1H_1H COSY Spectra of 4q














NOE Spectra for 4q


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8td Proton paranster*
Maples NA-5-DVP-33-A-H
rulse soawencet szyal
Sise soquence: s7pul
Nablent eneperatura
```



```
Retan. delay 1,04t sec
```




```
lol
MTA PROCKSA No, %
```



(1.1:1 trans:cis mixture of diastereomers)


```
sta Carbon experiment
Nag1Ez 3n-5-OVF-B3-A-C
Pulse sequenc%1 szpu:
    Solvent. cdels
    natient temparatur
Merkwry-360% -r2az-
    Rulax, delay 1,000 sec
    *idin 1814,3614,
    *id! 18113, % Kz
#N
    Moner 40 a6 %
    Whtrz-16COD|Nate,
    H/ne brosient!y e.5 H2
```




```
Std Protom parameters
Sonp 1e: CtBr-40Ne-Cr-Cycin-H
Pulse Seqvence: s2pu)
Molvin
Molvant1 cacl3
mercury-300 "rzdz"
Ma|ak, deldy i, aed s*C
Pulve 3b-a aegreen
ACyin $100 3,5%0
```





(2.7:1 trans:cis mixture of diastereomers)


```
sad carlon emperimen
```



```
pulse sequencet szpul
    Solvantz cdc13
```



```
    kelaw.aelay, 1.000 sec
    064in tion 1,395,*
    *)
    obhtRVE M13: 30, 4313153 Mre
    cotvon
```



```
    In* brosiening 0.5 w%
```




(2.9:1 trans:cis mixture of diastereomers)


1_mac_ras_b
fllet homefrance/cavir1/1_mo_zos_b.fla
Putpe Seavencel szpus
Solymet celc 13
Sobitat teaper
habient teaperature
operator, cavilt




mixture of diastereomers)



## Electronic Supplementary Material (ESI) for Chemical Communications

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Id Proton parancter:
Aaple: NB-5-OVF-5z-A-E
u)se sequence: s2pu1
solugequenke: s2pul
Solvent! cacty
0perator, doath! dur
Relax- setay 1.600 vec
Mulve 3060, degreni
ACgin t10e 3, 550
```



```
aATA processino
```





