Electronic Supplementary Information

Catalytic stereoselective total synthesis of (+)-3'-(4-oxoquinazolin-3yl)spiro[1H-indole-3,5'-oxolane]-2,2'-dione, and pentacyclic core of tryptoquivalines

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1. General information

All reagents bought from commercial sources were used as received. Organic solvents were evaporated under reduced pressure using a Büchi rotary evaporator. All solvents were commercially supplied or dried by filtration through activated alumina (powder ~150 mesh, pore size 58 Å, basic, Sigma-Aldrich) columns. Petrol ether (PE) refers to distilled light petroleum of fraction 30 - 40 °C. Toluene was distilled twice over calcium hydride. All reactions were followed by thin-layer chromatography (TLC) when practical, using Merck Kieselgel 60 F254 fluorescent treated silica. Visualisation was accomplished under UV light ($\lambda_{\text{max}}$= 254 nm) and by staining with KMnO4 staining dip. Chromatographic purification was performed on VWR 60 silica gel 40-63 μm using HPLC grade solvents that were used as supplied. High resolution mass spectra (HRMS) were recorded on a Bruker Daltonics MicroTOF mass spectrometer equipped with an ESI source or on a Micromass GCT equipped with an EI source unless otherwise specified. Infrared absorption spectra (IR) were recorded on a Bruker Tensor 27 FT-IR spectrometer from a thin film on a diamond ATR module. Only selected bands ($\nu_{\text{max}}$) are reported in wavenumbers (cm$^{-1}$). NMR spectra were recorded on Bruker spectrometers operating at 400 or 500 MHz ($^1$H resonance). Proton chemical shifts ($\delta$) are given in parts per million (ppm) relative to tetramethylsilane (TMS) with the solvent resonance (CDCl$_3$, $\delta$ = 7.26 ppm) as internal standard. The following abbreviations are used to describe spin multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet, br = broad signal. Coupling constants ($J$) are given in Hertz (Hz). $^{13}$C-NMR spectra were recorded with complete proton decoupling. Carbon chemical shifts are reported in ppm ($\delta$) relative to TMS with the solvent resonance (CDCl$_3$, $\delta$ = 77.16 ppm) as internal standard.
2. Synthetic procedures

**Compound 2**

![Chemical structure of Compound 2]

\(\beta\)-Tryptophan methyl ester hydrochloride (10 g, 39 mmol, 1.0 eq) and sodium hydrogen carbonate (13 g, 156 mmol, 4.0 eq) was dissolved in 130 mL of water and 130 mL of CH\(_2\)Cl\(_2\); while stirring 2-nitrobenzoyl chloride (7.2 g, 39 mmol, 1.0 eq) was added into the reaction mixture dropwise. After stirring for 15 min, the bi-phase reaction mixture was separated, and the aqueous phase was extract with CH\(_2\)Cl\(_2\), combined organic parts, washed with 1 N HCl, brine and dried with MgSO\(_4\), filtered and concentrated under vacuum. The residue was purified with FCC CH\(_2\)Cl\(_2\)/Et\(_2\)O (from 100/1 to 8/1) to give a light yellow foam 14.28 g (99%).

**m.p.** 50 – 55 °C; \([\alpha]_D^{25}\) –58.4 (c 0.48, CHCl\(_3\));

**IR** (film) \(\nu_{\text{max}}/\text{cm}^{-1}\): 3405, 3346, 1738, 1652, 1528, 1458, 1439, 1349, 1311, 1253, 1217, 1101, 1011, 910, 850, 789, 735, 699, 648;

\(^1\text{H NMR}\) (CDCl\(_3\), 400 MHz) \(\delta\) (ppm): 8.19 (s, 1H, Indole), 7.98 (dd, \(J = 7.9, 1.4\) Hz, 1H, C\(_{[ar]}\)H), 7.68 – 7.44 (m, 3H, C\(_{[ar]}\)H), 7.36 – 7.27 (m, 2H, C\(_{[ar]}\)H), 7.15 (ddd, \(J = 8.1, 7.0, 1.2\) Hz, 1H, C\(_{[ar]}\)H), 7.09 – 7.03 (m, 2H, C\(_{[ar]}\)H), 6.43 (d, \(J = 8.0\) Hz, 1H, CON\(_H\)), 5.15 (dt, \(J = 8.0, 5.2\) Hz, 1H, C\(_{[2]}\)H), 3.70 (s, 3H, C\(_{[5]}\)H), 3.45 (d, \(J = 5.3\) Hz, 2H, C\(_{[3]}\)H);
**1³C NMR** (CDCl₃, 100 MHz) δ (ppm): 172.2 (C₁₁), 166.0 (C₄₄), 146.8 (C₁₆₃), 136.3 (C₃₄), 133.8 (C₃₃), 132.5 (C₃₂), 130.8 (C₃₁), 128.9 (C₂₃), 127.8 (C₂₂), 124.7 (C₂₃), 123.4 (C₂₃), 122.4 (C₂₃), 119.9 (C₂₃), 118.7 (C₂₃), 111.5 (C₂₃), 109.8 (C₂₃), 53.5 (C₂₃), 52.8 (C₂₃), 27.6 (C₂₃);

**HRMS** (ESI) [C₁₉H₁₇N₃O₅+H]⁺ requires m/z 368.1241, found m/z 368.1238.

**Compound 3**

Compound 2 (3.67 g, 10.0 mmol, 1.0 eq) was dissolved in a mixture of 250 mL methanol and 100 mL of water. Sodium periodate (8.6 g, 40.0 mmol, 4.0 eq) was added in one portion at room temperature. The reaction was stirred at r.t. for 3 days before 300 mL of water was added, then extracted with chloroform three times, washed with sat. NaHCO₃, brine, and dried with MgSO₄. The organic layers were concentrated and the residue was dissolved in 150 mL methanol and 100 mL of water, sodium periodate (6.45 g, 30 mmol) was added. The reaction was stirred at room temperature for another 3 days, before 300 mL water was added, then extracted with chloroform three times, washed with sat. NaHCO₃, brine, and dried with MgSO₄. The organic layers were concentrated and the residue which was dissolved in 240 mL methanol and 80 mL of dioxane, and 20 mL of 4 M HCl was added. Then the reaction was stirred for 1 h at room temperature, before basified with saturated NaHCO₃, and extracted with CH₂Cl₂ for three times, washed with brine and dried over MgSO₄, concentrated, the residue was purified with FCC (methanol / CH₂Cl₂ from 1/200 to 1/50) to give the yellow thick oil 3.12 g (84 %).

[α]D²⁵ − 62.6 (c 1.01, CHCl₃);
**IR (film)** $v_{\text{max/cm}}$: 3470, 3350, 1742, 1648, 1616, 1584, 1529, 1485, 1451, 1349, 1313, 1216, 1162, 1114, 1042, 980, 905, 856, 790, 735, 700;

![Chemical Structure](image)

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ (ppm): 7.99 (dd, $J = 8.1$, 1.2 Hz, 1H, C$_{[ar]}$H), 7.70 (dd, $J = 8.2$, 1.5 Hz, 1H, C$_{[ar]}$H), 7.63 (td, $J = 7.5$, 1.2 Hz, 1H, C$_{[ar]}$H), 7.59 – 7.47 (m, 2H, C$_{[ar]}$H), 7.25 (ddd, $J = 8.4$, 7.0, 1.5 Hz, 1H, C$_{[ar]}$H), 7.04 (d, $J = 8.5$ Hz, 1H, CON$_2$H), 6.65 (ddd, $J = 8.2$, 7.1, 1.2 Hz, 1H, C$_{[ar]}$H), 6.60 (dd, $J = 8.4$, 1.1 Hz, 1H, C$_{[ar]}$H), 6.19 (s, 2H, N$_2$H$_2$), 5.13 (dt, $J = 8.1$, 3.9 Hz, 1H, C$_{[2]}$H), 3.87 – 3.68 (m, 5H, C$_{[11]}$H+C$_{[3]}$H);

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ (ppm): 199.6 (C$_{[4]}$), 171.8 (C$_{[1]}$), 166.2 (C$_{[12]}$), 150.7 (C$_{[ar]}$), 146.7 (C$_{[ar]}$), 135.3 (C$_{[ar]}$), 133.9 (C$_{[ar]}$), 132.6 (C$_{[ar]}$), 131.3 (C$_{[ar]}$), 130.8 (C$_{[ar]}$), 128.9 (C$_{[ar]}$), 124.7 (C$_{[ar]}$), 117.6 (C$_{[ar]}$), 117.2 (C$_{[ar]}$), 116.3 (C$_{[ar]}$), 53.0 (C$_{[11]}$), 48.9 (C$_{[2]}$), 40.7 (C$_{[3]}$);

HRMS (ESI) [C$_{18}$H$_{17}$N$_3$O$_6$+H]$^+$ requires $m/z$ 372.1190, found $m/z$ 372.1184.

**Compound 4**
The aniline compound 3 (1.6 g, 4.3 mmol, 1.0 eq) was dissolved in EtOH 15 mL and 48% HBF$_4$ (1.13 mL, 8.6 mmol, 2.0 eq), which was stirred for 30 min before at 0 °C 2-methyl-2-nitropropane (1.0 mL, 9.5 mmol, 2.2 eq) was added dropwise. Then at the same temperature, 50 mL of acetone was added to dissolve the participation, which solution was kept stirring for another 1 hour. At 0 °C, the above solution was added into a potassium iodide (9.7 g, 58.6 mmol, 14 eq) in 50 mL of acetone, and the reaction was kept stirring at the same temperature for another 1 hours. Then the reaction was exacted with ethyl acetate for three times, washed with sat. Na$_2$S$_2$O$_3$ and brine, dried with MgSO$_4$, filtered and concentrated under vacuum, and the residue was purified with FCC ethyl acetate / petrol ether (from 1/2 to 1/1) to give light yellow foam 1.30 g (63%).

m.p. 46 – 47 °C; $[\alpha]_D^{25}$ –9.9 (c 0.95, CHCl$_3$);

IR (film) $\nu_{\text{max}}$/cm$^{-1}$: 1745, 1690, 1653, 1615, 1578, 1530, 1437, 1349, 1312, 1220, 1219, 1041, 990, 963, 911, 854, 760, 733, 698;

$^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ (ppm): 8.07 (dd, $J = 8.6$, 1.2 Hz, 1H, C$_{[ar]}$H), 7.93 (dd, $J = 7.9$, 1.1 Hz, 1H, C$_{[ar]}$H), 7.74 – 7.65 (m, 1H, C$_{[ar]}$H), 7.63 – 7.53 (m, 3H, C$_{[ar]}$H), 7.44 (td, $J = 7.6$, 1.1 Hz, 1H, C$_{[ar]}$H), 7.20 – 7.10 (m, 1H, C$_{[ar]}$H), 7.01 (d, $J = 8.1$ Hz, 1H, CONH$^+$), 5.09 (dt, $J = 7.9$, 3.9 Hz, 1H, C$_{[1]}$H), 3.82 (s, 3H, C$_{[11]}$H), 3.76 (dd, $J = 3.9$, 2.8 Hz, 2H, C$_{[2]}$H);
\textbf{13C NMR} (CDCl$_3$, 125 MHz) $\delta$ (ppm): 202.2 (C$_{[3]}$), 171.0 (C$_{[10]}$), 166.3 (C$_{[12]}$), 146.6 (C$_{[ar]}$), 142.2 (C$_{[ar]}$), 141.3 (C$_{[ar]}$), 134.1 (C$_{[ar]}$), 132.7 (C$_{[ar]}$), 132.5 (C$_{[ar]}$), 131.0 (C$_{[ar]}$), 128.9 (C$_{[ar]}$), 128.9 (C$_{[ar]}$), 128.5 (C$_{[ar]}$), 124.9 (C$_{[ar]}$), 91.3 (C$_{[5]}$), 53.3 (C$_{[11]}$), 49.2 (C$_{[1]}$), 43.0 (C$_{[2]}$);

\textbf{HRMS} (ESI) [C$_{18}$H$_{15}$N$_2$O$_6$I+Na]$^+$ requires $m/z$ 504.9867, found $m/z$ 504.9866.

\textbf{Compound 5}

Fe powder (2.3 g, 41 mmol, 10.0 eq) and NH$_4$Cl (4.4 g, 82 mmol, 20.0 eq) was suspended in 40 mL of ethanol and 40 mL of water, which was heated at 70 °C for 15 min; then at the same temperature the iodide compound 4 (2.0 g, 4.1 mmol, 1.0 eq) in 40 mL of ethanol was added. After 60 min, the reaction is finished. The mixture was filtered through Celite, washed with methanol, and the solid residue was reflux in ethyl acetate / methanol for 60 min and filtered through Celite again. The combined solution was extracted with ethyl acetate and washed with brine, dried with MgSO$_4$, filtered and concentrated to give a light yellow foam 1.85 g, which was used directly without further purification.

The aniline from above, yellow foam, (1.85 g) and p-toluenesulfonic acid monohydrate (450 mg) was dissolved in 30 mL of methanol and 30 mL trimethyl orthoformate. The mixture was stirred at 70 °C for 2.5 hours. The volatiles were removed and the residue was dissolved in CH$_2$Cl$_2$, washed with sat. NaHCO$_3$, brine, dried with MgSO$_4$, filtered and concentrated under
vacuum. The residue was purified with FCC ethyl acetate / petrol ether (from 1/2 to 1/1) to give colorless solid 1.56 g (82%).

**m.p.** 137 – 140 °C; [α]_D^{2} +115.8 (c 0.67, CHCl₃);

**IR** (film) ν_{max}/cm⁻¹: 1747, 1674, 1608, 1581, 1564, 1473, 1434, 1382, 1354, 1287, 1232, 1213, 1196, 1163, 1108, 1084, 1015, 998, 978, 913, 776, 760, 731, 701, 675, 644;

![Chemical Structure](attachment:structure.png)

**¹H NMR** (CDCl₃, 500 MHz) δ (ppm): 8.29 (s, 1H, C_{[18]}H), 8.24 (dd, J = 8.0, 1.4 Hz, 1H, C_{[ar]}H), 7.88 (dd, J = 8.0, 1.1 Hz, 1H, C_{[ar]}H), 7.80 – 7.69 (m, 2H, C_{[ar]}H), 7.54 – 7.44 (m, 2H, C_{[ar]}H), 7.38 (td, J = 7.6, 1.1 Hz, 1H, C_{[ar]}H), 7.11 (td, J = 7.7, 1.7 Hz, 1H, C_{[ar]}H), 5.35 (dd, J = 8.0, 4.3 Hz, 1H, C_{[2]}H), 4.06 (dd, J = 19.1, 4.3 Hz, 1H, C_{[3]}H’), 3.86 (dd, J = 19.1, 8.0 Hz, 1H, C_{[3]}H’’), 3.76 (s, 3H, C_{[19]}H);

**¹³C NMR** (CDCl₃, 125 MHz) δ (ppm): 200.7 (C_{[4]}), 168.8 (C_{[1]}), 161.2 (C_{[11]}), 148.2 (C_{[ar]}), 147.2 (C_{[18]}), 142.5 (C_{[ar]}), 141.2 (C_{[ar]}), 134.9 (C_{[ar]}), 132.6 (C_{[ar]}), 128.6 (C_{[ar]}), 128.4 (C_{[ar]}), 127.9 (C_{[ar]}), 127.7 (C_{[ar]}), 126.8 (C_{[ar]}), 122.2 (C_{[ar]}), 91.3 (C_{[6]}), 57.4 (C_{[2]}), 53.5 (C_{[19]}), 41.8 (C_{[3]});

**HRMS** (ESI) [C_{19}H_{15}N_{2}O_{4}I+H]^+ requires m/z 463.0149, found m/z 463.0149.
Compound 9

The ketone compound 5 (950 mg, 2.06 mmol, 1.0 eq), Ligand-1 (63 mg, 0.1 mmol, 5% eq), silver acetate (16.6 mg, 0.1 mmol, 5% eq), 4A molecular sieve (950 mg) was dissolved in 60 mL of ethyl acetate. The mixture was stirred at room temperature for 20 min, and at 0 °C, tert-butyl isocyanatoacetate (435 mg, 3.1 mmol, 1.5 eq) in 3.5 mL of ethyl acetate was injected into the reaction, which was stirred at the same temperature for 48 h., before filtered through celite, concentrated and purified with FCC petrol ether / ethyl acetate (from 60/40 to 30/70, then 100% ethyl acetate) to give colorless foam 1.12 g (91%, dr = 14:1), which is unstable in solvents.

**m.p.** 42 – 45 °C; [α]D²⁵ +0.6 (c 0.83, CHCl₃);

**IR (film)** νₘₐₓ/cm⁻¹: 1735, 1678, 1636, 1609, 1565, 1473, 1435, 1389, 1370, 1326, 1265, 1213, 1153, 1106, 1073, 1037, 1005, 949, 904, 848, 755, 700, 669, 643;

**¹H NMR** (CDCl₃, 400 MHz) δ (ppm): 8.01 (d, J = 7.7 Hz, 1H, C[ar]H), 7.65 (t, J = 7.6 Hz, 1H, C[ar]H), 7.45 – 7.54 (m, 3H, C[ar]H), 7.37 (t, J = 7.6 Hz, 1H, C[ar]H), 7.30 (d, J = 7.7 Hz, 1H, C[ar]H), 7.22 (s, 1H, C[24]H), 6.91 (t, J = 7.7 Hz, 1H, C[ar]H), 6.37 (t, J = 7.6 Hz, 1H, C[6]H), 5.10
(d, J = 10.1 Hz, 1H, C[2]H), 4.80 (s, 1H, C[5]H), 3.98 (t, J = 13.0 Hz, 1H, C[3]H'), 3.69 (s, 3H, C[16]H), 3.16 (d, J = 15.9 Hz, 1H, C[3]H’’), 1.57 (s, 9H, C[9]H);

$^{13}$C NMR (CDCl$_3$, 100 MHz) δ (ppm): 170.8 (C[1]), 169.3 (C[7]), 167.4 (C[17]), 160.3 (C[ar]), 155.3 (C[24]), 147.4 (C[ar]), 145.6 (C[ar]), 142.9 (C[ar]), 140.6 (C[ar]), 134.0 (C[ar]), 129.5 (C[6]), 128.2 (C[ar]), 127.2 (C[ar]), 126.7 (C[ar]), 121.6 (C[ar]), 92.7 (C[11]), 89.7 (C[4]), 83.5 (C[8]), 77.4 (C[5]), 56.8 (C[2]), 53.4 (C[16]), 32.8 (C[3]), 28.3 (C[9]);

HRMS (ESI) [C$_{26}$H$_{26}$N$_3$O$_6$I+H]$^+$ requires m/z 604.0939, found m/z 604.0935.

**Compound 10**

The oxazoline compound 9 (710 mg, 1.17 mmol) was dissolved in 30 mL of THF, and 3 mL of 1 N HCl was added. The reaction was stirred at room temperature for 5 min. The reaction was extract with ethyl acetate, washed with brine, dried with MgSO$_4$, concentrated and purified with FCC CH$_2$Cl$_2$ / methanol (from 200/1 to 200/6) to give a white solid 728 mg (99%).

**m.p.** 88 – 92 °C; [α]$_{b}^{25}$ = +62.7 (c 0.51, CHCl$_3$);

**IR** (film) $\nu_{\text{max}}$/cm$^{-1}$: 3417, 2979, 2922, 1743, 1678, 1610, 1505, 1474, 1457, 1437, 1374, 1346, 1325, 1266, 1234, 1154, 1037, 1104, 912, 841, 774, 732, 700, 646;
**1H NMR** (Acetone-d$_6$, 400 MHz) δ (ppm): 8.02 (dd, $J = 8.0$, 1.5 Hz, 1H, C$_{[ar]}$H), 7.84 – 7.70 (m, 3H, NHCHO, C$_{[ar]}$H), 7.56 (s, 1H, C$_{[24]}$H), 7.52 (d, $J = 8.1$ Hz, 2H, C$_{[ar]}$H), 7.46 (t, $J = 7.6$ Hz, 1H, C$_{[ar]}$H), 7.38 (d, $J = 8.4$ Hz, 1H, NHCHO), 7.08 (t, $J = 7.7$ Hz, 1H, C$_{[ar]}$H), 6.53 (t, $J = 7.6$ Hz, 1H, C$_{[ar]}$H), 5.68 (s, 1H, C$_{[5]}$H), 5.08 (d, $J = 5.8$ Hz, 1H, C$_{[2]}$H), 4.14 – 3.89 (m, 1H, C$_{[3]}$H), 3.65 (s, 3H, C$_{[9]}$H), 3.30 (dd, $J = 15.7$, 3.0 Hz, 1H, C$_{[3]}$H$'$), 1.59 (s, 9H, C$_{[8]}$H);

**13C NMR** (Acetone-d$_6$, 125 MHz) δ (ppm): 171.2 (C$_{[1]}$), 169.4 (C$_{[6]}$), 161.9 (C$_{[16]}$), 161.0 (C$_{[17]}$), 148.9 (C$_{[ar]}$), 147.8 (C$_{[24]}$), 143.2 (C$_{[ar]}$), 143.0 (C$_{[ar]}$), 134.9 (C$_{[ar]}$), 130.4 (C$_{[ar]}$), 129.7 (C$_{[ar]}$), 128.6 (C$_{[ar]}$), 128.1 (C$_{[ar]}$), 127.6 (C$_{[ar]}$), 127.0 (C$_{[ar]}$), 122.8 (C$_{[ar]}$), 94.5 (C$_{[11]}$), 83.3 (C$_{[7]}$), 77.8 (C$_{[4]}$), 59.0 (C$_{[5]}$), 57.9 (C$_{[2]}$), 53.2 (C$_{[9]}$), 35.5 (C$_{[3]}$), 28.3 (C$_{[8]}$);

**HRMS** (ESI) [C$_{26}$H$_{28}$N$_3$O$_7$I+H]$^+$ requires $m/z$ 622.1045, found $m/z$ 622.1042.

**Compound 11**

The ester-formamide compound 10 (730 mg, 1.18 mmol) was dissolved in 50 mL of toluene and 2.3 mL of acetic acid, which was stirred at 75 °C for 3 days until all starting material is
consumed. The reaction was concentrated under vacuum and re-dissolved in ethyl acetate, washed with sat. NaHCO₃, brine, dried with MgSO₄, filtered and concentrated again. The residue was purified with FCC CH₂Cl₂ / methanol (from 200:1 to 200:4) to give product as white solid 485 mg (70%).

**m.p.** 100 – 112 °C; [α]D<sup>25</sup> –34.0 (c 1.33, CHCl₃);

**IR** (film) ν<sub>max</sub>/cm<sup>-1</sup>: 2925, 1796, 1723, 1682, 1610, 1517, 1475, 1460, 1424, 1386, 1370, 1324, 1298, 1252, 1200, 1187, 1153, 1108, 1029, 1005, 967, 929, 892, 774, 753, 699;

![Chemical Structure](image)

**<sup>1</sup>H NMR** (Acetone-d₆, 500 MHz) δ (ppm): 8.24 (s, 1H, C₂₂H), 8.20 (dd, J = 8.1, 1.4 Hz, 1H, C<sub>ar</sub>H), 8.09 (dd, J = 7.9, 1.3 Hz, 1H, C<sub>ar</sub>H), 7.96 (d, J = 1.0 Hz, 1H, C₂₃H), 7.87 (ddd, J = 8.5, 7.1, 1.6 Hz, 1H, C<sub>ar</sub>H), 7.70 (d, J = 8.1 Hz, 1H, C<sub>ar</sub>H), 7.68 (s, 1H, NHCHO), 7.61 – 7.55 (m, 2H, C<sub>ar</sub>H), 7.53 – 7.49 (m, 1H, C<sub>ar</sub>H), 7.15 (td, J = 7.5, 1.7 Hz, 1H, C<sub>ar</sub>H), 6.03 (d, J = 9.5 Hz, 1H, C₅H), 5.16 (dd, J = 11.3, 9.0 Hz, 1H, C₂H), 3.81 – 3.71 (m, 2H, C₃H), 1.56 (s, 9H, C₈H);

**<sup>13</sup>C NMR** (Acetone-d₆, 125 MHz) δ (ppm): 170.7 (C₁₁), 167.6 (C₆), 161.1 (C₂₃), 160.6 (C₁₅), 149.0 (C<sub>ar</sub>), 147.7 (C₂₂), 144.1 (C<sub>ar</sub>), 140.9 (C<sub>ar</sub>), 135.6 (C<sub>ar</sub>), 131.4 (C<sub>ar</sub>), 129.2 (C<sub>ar</sub>), 129.0 (C<sub>ar</sub>), 128.6 (C<sub>ar</sub>), 128.4 (C<sub>ar</sub>), 127.2 (C<sub>ar</sub>), 122.9 (C<sub>ar</sub>), 94.9 (C₁₀), 87.8 (C₄), 83.9 (C₇), 57.3 (C₂), 56.6 (C₅), 34.5 (C₃), 28.4 (C₈);
HRMS (ESI) [C_{25}H_{24}N_{3}O_{6}I+H]^+ requires m/z 590.0783, found m/z 590.0783.

**Compound 12**

![Compound 12 structure](image)

The formamide compound 11 (75 mg, 0.13 mmol, 1.0 eq) was dissolved in 7 mL of methanol, and 0.5 mL of thionyl chloride was added dropwise at 0 °C, the reaction was stirred for 2 h at r.t. before all volatiles were removed under vacuum and residue was dried overnight under high vacuum; then the solid was suspended in 10 mL of sat. NaHCO₃ and 10 mL of CH₂Cl₂ was added, after stirring for 1 min at r.t. the organic phase was collected and the aqueous phase was exacted with CH₂Cl₂ and ethyl acetate. The combined organic phase washed with brine and was dried with Na₂SO₄, filtered and concentrated; then 5 mL of CH₂Cl₂ and 2-iodoxybenzoic acid (42 mg, 0.15 mmol, 1.2 eq), then DMSO (1.0 mL) was added at 0 °C. The reaction was stirred at 0°C overnight before diluted with CH₂Cl₂ and washed with water and brine, dried with Na₂SO₄, filtered and concentrated under vacuum. The residue was purified with FCC methanol / CH₂Cl₂ (from 1/200 to 2.5/200) to give a white solid 55 mg (77%).

**m.p.** 95 – 105 °C; [α]D²⁵ – 76.2 (c 0.83, CHCl₃);

**IR** (film) νmax/cm⁻¹: 2980, 2931, 1797, 1725, 1679, 1610, 1565, 1474, 1425, 1370, 1325, 1251, 1203, 1187, 1154, 1103, 1029, 1006, 963, 909, 840, 760, 699;
$^1$H NMR (Acetone-d$_6$, 400 MHz) δ (ppm): 12.36 (s, 1H, NH), 8.32 (s, 1H, C$_{[22]}$), 8.22 (ddd, $J$ = 8.0, 1.6, 0.6 Hz, 1H, C$_{[ar]}$H), 8.06 (ddd, $J$ = 7.9, 1.3 Hz, 1H, C$_{[ar]}$H), 7.87 (ddd, $J$ = 8.2, 7.2, 1.6 Hz, 1H, C$_{[ar]}$H), 7.75 – 7.68 (m, 2H, C$_{[ar]}$H), 7.65 – 7.54 (m, 2H, C$_{[ar]}$H), 7.20 (td, $J$ = 7.6, 1.7 Hz, 1H, C$_{[ar]}$H), 5.35 (dd, $J$ = 11.3, 9.3 Hz, 1H, C$_{[2]}$H), 4.53 (dd, $J$ = 12.8, 11.3 Hz, 1H, C$_{[3]}$H’), 3.17 (dd, $J$ = 12.8, 9.3 Hz, 1H, C$_{[3]}$H’’), 1.25 (s, 9H, C$_{[8]}$H);

$^{13}$C NMR (Acetone-d$_6$, 125 MHz) δ (ppm): 171.6 (C$_{[1]}$), 168.0 (C$_{[6]}$), 160.6 (C$_{[15]}$), 159.9 (C$_{[5]}$), 149.1 (C$_{[ar]}$), 148.0* (C$_{[22]}$), 143.6 (C$_{[ar]}$H), 143.2* (C$_{[ar]}$H), 135.5* (C$_{[ar]}$H), 131.0 (C$_{[ar]}$H), 129.5 (C$_{[ar]}$H), 128.6 (C$_{[ar]}$H), 128.3 (C$_{[ar]}$H), 128.3 (C$_{[ar]}$H), 127.3* (C$_{[ar]}$H), 123.0 (C$_{[ar]}$H), 93.2 (C$_{[10]}$), 86.9 (C$_{[4]}$), 84.5 (C$_{[7]}$), 57.1 (C$_{[2]}$), 35.1 (C$_{[3]}$), 27.7 (C$_{[8]}$), * peak splits;

HRMS (ESI) [C$_{24}$H$_{22}$N$_{3}$O$_{5}$I+H]$^+$ requires m/z 560.0677, found m/z 560.0654.

**Compound 13**

The imine compound 12 (11 mg, 0.02 mmol, 1.0 eq), copper(I) iodide (4.6 mg, 0.024 mmol, 1.2 eq) and magnesium acetate tetrahydrate (6.4 mg, 0.03 mmol, 1.5 eq) was put in a dry flask and
charged with argon. Then 1.2 mL of dry DMSO was injected. The solution was stirred in the r.t. for 5 hours before quenched with sat. NH₄Cl and exacted with CH₂Cl₂, washed with water and dried with MgSO₄, filtered and concentrated under vacuum. The residue was purified with FCC diethyl ether / CH₂Cl₂ (1 / 10) to give the cyclized product as white solid 4.5 mg (52%).

**m.p.** T<sub>dec</sub> >210 °C; [α]<sub>D</sub><sup>25</sup> + 175.5 (c 0.38, CHCl₃);

**IR** (film) ν<sub>max</sub>/cm<sup>-1</sup>: 2979, 2922, 2852, 1795, 1730, 1677, 1610, 1567, 1472, 1370, 1326, 1254, 1196, 1135, 1059, 1033, 971, 910, 841, 773, 698;

**¹H NMR** (Acetone-d₆, 500 MHz) δ (ppm): 8.61 (s, 1H, C<sub>22</sub>H), 8.34 (dd, J = 8.0, 1.5 Hz, 1H, C<sub>ar</sub>H), 8.27 – 8.11 (m, 1H, C<sub>ar</sub>H), 7.91 (ddd, J = 8.5, 7.1, 1.6 Hz, 1H, C<sub>ar</sub>H), 7.76 (dt, J = 8.1, 1.0 Hz, 1H, C<sub>ar</sub>H), 7.75 – 7.68 (m, 1H, C<sub>ar</sub>H), 7.65 (ddd, J = 8.2, 7.1, 1.2 Hz, 1H, C<sub>ar</sub>H), 7.60 – 7.54 (m, 2H, C<sub>ar</sub>H), 5.78 (dd, J = 10.7, 8.5 Hz, 1H, C<sub>2</sub>H), 3.33 (dd, J = 14.0, 10.7 Hz, 1H, C<sub>3</sub>H<sup>+</sup>), 3.17 (dd, J = 14.0, 8.6 Hz, 1H, C<sub>[3]H</sub><sup>+</sup>), 1.65 (s, 9H, C<sub>8</sub>H);

**¹³C NMR** (Acetone-d₆, 125 MHz) δ (ppm): 173.1 (C<sub>11</sub>), 170.7 (C<sub>6</sub>), 161.6 (C<sub>5</sub>), 161.4 (C<sub>15</sub>), 152.8 (C<sub>ar</sub>), 149.4 (C<sub>ar</sub>), 148.5 (C<sub>22</sub>), 139.9 (C<sub>ar</sub>), 135.8 (C<sub>ar</sub>), 132.3 (C<sub>ar</sub>), 131.0 (C<sub>ar</sub>), 128.7 (C<sub>ar</sub>), 128.4 (C<sub>ar</sub>), 127.2 (C<sub>ar</sub>), 125.8 (C<sub>ar</sub>), 124.3 (C<sub>ar</sub>), 123.0 (C<sub>ar</sub>), 89.8 (C<sub>14</sub>), 84.8 (C<sub>7</sub>), 59.3 (C<sub>2</sub>), 32.6 (C<sub>3</sub>), 28.3 (C<sub>8</sub>);

**HRMS** (ESI) [C<sub>24</sub>H<sub>21</sub>N<sub>3</sub>O<sub>5</sub>+H]+ requires m/z 432.1554, found m/z 432.1555.
Compound 14

The imine compound 12 (70 mg, 0.13 mmol) was dissolved in 4 mL of THF and 3 mL of H2O, 0.15 mL of acetic acid was added, and the reaction was stirred at 50 °C for 5 hours. The reaction was extracted with ethyl acetate and washed with brine and dried with Na2SO4, filtered and concentrated under vacuum, the residue was purified with FCC methanol / CH2Cl2 (1/70 to 1/50) to give white solid 55 mg (73%).

**m.p.** 105 – 108 °C; [α]D25 –77.4 (c 0.65, CHCl3);

**IR** (film) νmax/cm⁻¹: 3063, 2981, 2926, 2853, 2362, 2335, 1802, 1742, 1680, 1609, 1565, 1469, 1428, 1372, 1296, 1252, 1196, 1162, 1108, 964, 904, 837, 757, 697, 662;

**1H NMR** (CD3CN-d3, 500 MHz) δ (ppm): 8.22 (dd, J = 8.0, 1.6 Hz, 1H, C[ar]H), 8.04 (dd, J = 7.9, 1.3 Hz, 1H, C[ar]H), 8.01 (s, 1H, C[22]H), 7.85 (ddd, J = 8.6, 7.2, 1.6 Hz, 1H, C[ar]H), 7.72 (dt, J = 8.3, 0.8 Hz, 1H, C[ar]H), 7.67 (dd, J = 8.0, 1.6 Hz, 1H, C[ar]H), 7.62 – 7.53 (m, 2H, C[ar]H), 7.21
(td, $J = 7.7, 1.7$ Hz, 1H, C$_{[ar]}$H), 5.04 (dd, $J = 10.4, 9.6$ Hz, 1H, C$_{[2]}$H), 3.83 (dd, $J = 13.3, 10.5$ Hz, 1H, C$_{[3]}$H’), 3.13 (dd, $J = 13.3, 9.6$ Hz, 1H, C$_{[3]}$H’’), 1.30 (s, 9H, C$_{[8]}$H);

$^{13}$C NMR (CD$_3$CN-d$_3$, 125 MHz) δ (ppm): 187.5 (C$_{[5]}$), 171.2 (C$_{[1]}$), 161.0 (C$_{[15]}$), 160.4 (C$_{[6]}$), 149.0 (C$_{[ar]}$), 147.6 (C$_{[22]}$), 142.9 (C$_{[ar]}$), 140.9 (C$_{[ar]}$), 136.0 (C$_{[ar]}$), 132.0 (C$_{[ar]}$), 129.9 (C$_{[ar]}$), 128.8 (C$_{[ar]}$), 128.7 (C$_{[ar]}$), 128.7 (C$_{[ar]}$), 127.2 (C$_{[ar]}$), 122.9 (C$_{[ar]}$), 94.0 (C$_{[10]}$), 88.0 (C$_{[4]}$), 86.3 (C$_{[7]}$), 57.5 (C$_{[2]}$), 34.1 (C$_{[3]}$), 27.8 (C$_{[8]}$);

HRMS (ESI) [C$_{24}$H$_{21}$N$_2$O$_6$I]+ requires m/z 561.0517, found m/z 561.0516.

**Compound 15**

![Compound 15](image)

The ketone ester compound 14 (55 mg) was dissolved in 1.5 mL of CH$_2$Cl$_2$ and 3.0 mL of trifluoroacetic acid, the reaction was stirred at r.t. for 2 hours, and then all volatiles was removed, the residue was dried under high vacuum overnight to give light yellow solid 50 mg (quant.) which is used for next reaction without further purification.

**m.p.** 178 – 184 °C; $[^{25}$C$_{D}]-66.2$ (c 1.21, CHCl$_3$);

**IR** (film) ν$_{max}$/cm$^{-1}$: 3065, 2973, 2923, 2853, 2362, 2335, 1799, 1727, 1680, 1612, 1470, 1429, 1389, 1322, 1251, 1198, 1114, 1073, 1030, 961, 760, 698;
\[ \text{1H NMR (CDCl}_3, \text{ with one drop D}_2\text{O, 400 MHz) } \delta (\text{ppm}): 8.76 (s, 1H, C}[20]\text{H}, 8.45 – 8.23 (m, 1H, C}[\text{ar}]\text{H}, 8.04 (dd, } J = 7.9, 1.3 \text{ Hz, 1H, C}[\text{ar}]\text{H}, 7.91 – 7.78 (m, 2H, C}[\text{ar}]\text{H}, 7.70 – 7.56 (m, 2H, C}[\text{ar}]\text{H}, 7.51 (td, } J = 7.6, 1.3 \text{ Hz, 1H, C}[\text{ar}]\text{H}, 7.18 (td, } J = 7.6, 1.7 \text{ Hz, 1H}, 5.88 (t, } J = 10.6 \text{ Hz, 1H, C}[2\text{H}], 3.64 (d, } J = 10.6 \text{ Hz, 2H, C}[3\text{H}];\]

\[ \text{13C NMR (CDCl}_3, \text{ with one drop of D}_2\text{O, 125 MHz) } \delta (\text{ppm}): 186.7 (C}[5]\text{), 170.6 (C}[11]\text{), 162.4 (C}[6]\text{), 160.3 (C}[13]\text{), 146.1 (C}[20]\text{), 145.0 (C}[\text{ar}]\text{), 142.3 (C}[\text{ar}]\text{), 139.0 (C}[\text{ar}]\text{), 136.1 (C}[\text{ar}]\text{), 131.4 (C}[\text{ar}]\text{), 129.1 (C}[\text{ar}]\text{), 128.8 (C}[\text{ar}]\text{), 127.7 (C}[\text{ar}]\text{), 127.6 (C}[\text{ar}]\text{), 125.9 (C}[\text{ar}]\text{), 120.7 (C}[\text{ar}]\text{), 96.0 (C}[8]\text{), 87.7 (C}[4]\text{), 52.3 (C}[3]\text{), 37.5 (C}[3]\text{);}\]

\[ \text{HRMS (ESI) [C}_{20}\text{H}_{13}\text{N}_2\text{O}_6\text{I}+\text{H}^+ \text{ requires } m/z 504.9891, \text{ found } m/z 504.9889.\]

\[ \text{Compound 16}\]

The \(\alpha\)-ketone acid compound 15 (50 mg, 0.1 mmol, 1.0 eq) and (diacetoxyiodo)benzene (50 mg, 0.15 mmol, 1.5 eq) was dissolved in 3.6 mL of acetic acid and 0.4 mL of water, the reaction was stirred for 20 hours at r.t., before all volatiles was removed under vacuum and the residue was
purified with FCC methanol / CH₂Cl₂ (1 / 100 to 1 / 9 with acetic acid) to give a white solid 39 mg (80%).

**m.p.** 183 – 187 °C; [α]D²⁵ +45.6 (c 0.54, Acetone);

**IR** (film) νmax/cm⁻¹: 2979, 2362, 2335, 1799, 1728, 1681, 1614, 1567, 1476, 1429, 1393, 1318, 1275, 1239, 1201, 1083, 1003, 978, 927, 769, 733, 693;

**1H NMR** (Acetone-d₆, 500 MHz) δ (ppm): 8.31 (s, 1H, C[19]H), 8.23 (dd, J = 8.1, 1.5 Hz, 1H, C[ar]H), 8.07 (dd, J = 7.8, 1.2 Hz, 1H, C[ar]H), 7.87 (ddd, J = 8.5, 7.2, 1.5 Hz, 1H, C[ar]H), 7.72 (dd, J = 8.3, 1.2 Hz, 1H, C[ar]H), 7.65 – 7.53 (m, 3H, C[ar]H), 7.22 (td, J = 7.5, 1.9 Hz, 1H, C[ar]H), 5.30 (dd, J = 10.9, 9.3 Hz, 1H, C[2]H), 4.06 (dd, J = 12.9, 10.9 Hz, 1H, C[3]H’’), 3.28 (dd, J = 12.9, 9.4 Hz, 1H, C[3]H’’’), COOH does not appear;

**13C NMR** (Acetone-d₆, 125 MHz) δ (ppm): 171.3 (C[1]), 168.4 (C[5]), 160.7 (C[12]), 149.1 (C[ar]), 148.0 (C[19]), 142.7 (C[ar]), 142.3 (C[ar]), 135.6 (C[ar]), 131.3 (C[ar]), 129.4 (C[ar]), 128.6 (C[ar]), 128.4 (C[ar]), 127.6 (C[ar]), 127.2 (C[ar]), 123.0 (C[ar]), 95.1 (C[7]), 87.6 (C[4]), 57.3 (C[2]), 35.4 (C[3]);

**HRMS** (ESI) [C₁₉H₁₅O₅N₂I+H]+ requires m/z 476.9942, found m/z 476.9942.

**Compound 17**
The acid compound 16 (9.5 mg, 0.02 mmol, 1.0 eq), 4-methoxybenzylamine (4.11 mg, 0.03 mmol, 1.5 eq), HATU (11.4 mg, 0.03 mmol, 1.5 eq) and N,N-diisopropylethylamine (6.45 mg, 0.05 mmol, 2.5 eq) was dissolved in 1.8 mL of CH₂Cl₂ and 0.2 mL of DMF. The reaction was stirred for 40 min at r.t. before quenched with 1 N HCl, exacted with CH₂Cl₂ and ethyl acetate, washed with brine and dried with Na₂SO₄, filtered and concentrated under vacuum. The residue was purified with FCC methanol / CH₂Cl₂ (1 / 100 to 1 / 50) to give white solid 8.5 mg (70%).

**m.p.** 90 – 95 °C; [α]D²⁵ –39.1 (c 0.54, CHCl₃);

**IR** (film) ν_max/cm⁻¹: 3027, 2878, 2802, 1746, 1679, 1610, 1520, 1495, 1471, 1451, 1348, 1262, 1203, 1074, 1049, 1035, 996, 880, 794, 756, 726, 699;

**¹H NMR** (CDCl₃, 500 MHz) δ (ppm): 8.26 (dd, J = 8.0, 1.5 Hz, 1H, C[ar]H), 8.08 (s, 1H, C[25]H), 8.01 (dd, J = 7.9, 1.3 Hz, 1H, C[ar]H), 7.79 (ddd, J = 8.5, 7.1, 1.5 Hz, 1H, C[ar]H), 7.74 (dd, J = 8.2, 1.2 Hz, 1H, C[ar]H), 7.58 (dd, J = 7.9, 1.6 Hz, 1H, C[ar]H), 7.52 (ddd, J = 8.2, 7.0, 1.3 Hz, 1H, C[ar]H), 7.43 (td, J = 7.7, 1.3 Hz, 1H, C[ar]H), 7.24 – 7.26 (d, J = 8.4 Hz, 2H, C[ar]H), 7.10 (td, J = 7.6, 1.6 Hz, 1H, C[ar]H), 6.84 (d, J = 8.6 Hz, 2H, C[ar]H), 6.39 (t, J = 5.6 Hz, 1H, CONH), 5.23

$^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ (ppm): 170.9 (C[1]), 167.4 (C[5]), 160.6 (C[18]), 159.4 (C[10]), 148.0 (C[ar]), 144.9 (C[25]), 142.8 (C[ar]), 139.7 (C[ar]), 135.2 (C[ar]), 131.2 (C[ar]), 129.7 (C[ar]), 129.4 (C[ar]), 129.0 (C[ar]), 128.1 (C[ar]), 128.0 (C[ar]), 128.0 (C[ar]), 127.2 (C[ar]), 121.7 (C[ar]), 114.3 (C[ar]), 94.8 (C[13]), 87.9 (C[4]), 55.5 (C[2] & C[11]), 44.4 (C[6]), 36.4 (C[3]);

HRMS (ESI) [C$_{27}$H$_{22}$O$_5$N$_3$I+H]$^+$ requires m/z 596.0677, found m/z 596.0676.

**Compound 18**

The amide compound 17 (7.5 mg, 0.013 mmol, 1.0 eq), Copper(I) iodide (2.9 mg, 0.015 mmol, 1.2 eq) and magnesium acetate tetrahydrate (4.1 mg, 0.019 mmol, 1.5 eq) was put in a dry flask and charged with argon, then 0.76 mL of dry DMSO was injected. The solution was stirred at r.t. for 3 hours before being quenched with sat. NH$_4$Cl and exacted with CH$_2$Cl$_2$ and ethyl acetate, washed with water and dried with Na$_2$SO$_4$, filtered and concentrated under vacuum. The residue was purified with FCC methanol / CH$_2$Cl$_2$ (1 / 150) to give the protected oxindole product as white solid 4.2 mg (70%).

**m.p.** 204 – 210 °C; $[\alpha]_D^{25}$ –33.9 (c 0.23, CHCl$_3$);
IR (film) $\nu_{\text{max}}$/cm$^{-1}$: 2926, 1779, 1731, 1673, 1611, 1469, 1373, 1322, 1300, 1256, 1191, 1109, 1047, 977, 908, 839, 812, 774, 748, 690;

$^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ (ppm): 8.38 (d, $J = 1.6$ Hz, 1H, C$_{[ar]}$H), 8.37 (d, $J = 1.4$ Hz, 1H, C$_{[ar]}$H), 7.89 – 7.78 (m, 2H, C$_{[ar]}$H), 7.58 (ddd, $J = 8.2$, 6.9, 1.5 Hz, 1H, C$_{[ar]}$H), 7.47 (dd, $J = 7.5$, 1.2 Hz, 1H, C$_{[ar]}$H), 7.37 (td, $J = 7.8$, 1.2 Hz, 1H, C$_{[ar]}$H), 7.27 (d, $J = 8.7$ Hz, 2H, C$_{[ar]}$H), 7.18 (td, $J = 7.6$, 0.9 Hz, 1H, C$_{[ar]}$H), 6.92 – 6.84 (m, 3H, C$_{[ar]}$H), 6.18 (t, $J = 10.1$ Hz, 1H, C$_{[2]}$H), 4.94 (d, $J = 15.4$ Hz, 1H, C$_{[6]}$H$''$), 4.84 (d, $J = 15.4$ Hz, 1H, C$_{[6]}$H$'$$'$$) 3.80 (s, 3H, C$_{[11]}$H), 3.08 (dd, $J = 13.6$, 10.4 Hz, 1H, C$_{[3]}$H$'$$) 3.00 (dd, $J = 13.6$, 9.8 Hz, 1H, C$_{[3]}$H$''$$);

$^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ (ppm): 172.7 (C$_{[5]}$), 171.2 (C$_{[1]}$), 160.9 (C$_{[18]}$), 159.6 (C$_{[10]}$), 147.9 (C$_{[ar]}$), 144.2 (C$_{[25]}$), 143.2 (C$_{[ar]}$), 135.2 (C$_{[ar]}$), 131.9 (C$_{[ar]}$), 129.0 (C$_{[ar]}$), 128.2 (C$_{[ar]}$), 128.1 (C$_{[ar]}$), 127.3 (C$_{[ar]}$), 126.8 (C$_{[ar]}$), 126.4 (C$_{[ar]}$), 124.3 (C$_{[ar]}$), 124.1 (C$_{[ar]}$), 121.6 (C$_{[ar]}$), 114.6 (C$_{[ar]}$), 110.7 (C$_{[ar]}$), 80.7 (C$_{[4]}$), 55.5 (C$_{[11]}$), 52.9 (C$_{[2]}$), 44.1 (C$_{[6]}$), 36.5 (C$_{[3]}$);

HRMS (ESI) [C$_{27}$H$_{21}$O$_{5}$N$_{3}$+H]$^+$ requires $m/z$ 468.1554, found $m/z$ 468.1555.

**Compound 1**
The protected cyclic amide compound 18 (2.5 mg) was dissolved in 1.5 mL of CH$_2$Cl$_2$, and trifluoromethanesulfonic acid (15 µL) was added at r.t., the reaction was stirred at r.t. for another 5 min until the starting material disappeared completely on TLC. After quench with aq. NaHCO$_3$, the mixture was extracted with chloroform and ethyl acetate, washed with brine and dried with Na$_2$SO$_4$, filtered and concentrated under vacuum, the residue was purified with FCC methanol / CH$_2$Cl$_2$ (1 / 100 to 1 / 30) to give a white solid 1.3 mg (64%).

m.p. 271 – 276 °C; [α]$^\text{D}_{25}$ +278.6 (c 0.03, MeOH);

IR (film) $\nu_{\text{max}}$/cm$^{-1}$: 2920, 2851, 1787, 1743, 1673, 1612, 1563, 1473, 1439, 1387, 1327, 1280, 1251, 1207, 1186, 1112, 1058, 776, 752, 700;

$^1$H NMR (DMSO, 500 MHz) $\delta$ (ppm): 10.90 (s, 1H, CON$_2$), 8.64 (s, 1H, C$_{[19]}$H), 8.24 (dd, $J =$ 7.9, 1.5 Hz, 1H, C$_{[14]}$H), 7.93 (ddd, $J =$ 8.4, 7.1, 1.6 Hz, 1H, C$_{[16]}$H), 7.76 (d, $J =$ 8.2 Hz, 1H, C$_{[17]}$H), 7.68 – 7.62 (m, 2H, C$_{[10]}$H & C$_{[15]}$H), 7.42 (td, $J =$ 7.7, 1.3 Hz, 1H, C$_{[8]}$H), 7.18 (td, $J =$ 7.6, 1.0 Hz, 1H, C$_{[9]}$H), 6.96 (d, $J =$ 7.8 Hz, 1H, C$_{[7]}$H), 5.86 (t, $J =$ 10.0 Hz, 1H, C$_{[2]}$H), 3.01 (dd, $J =$ 10.1, 3.1 Hz, 2H, C$_{[3]}$H);

$^{13}$C NMR (DMSO, 125 MHz) $\delta$ (ppm): 175.4 (C$_{[5]}$), 171.9 (C$_{[11]}$), 159.9 (C$_{[12]}$), 147.8 (C$_{[19]}$), 147.7 (C$_{[18]}$), 142.8 (C$_{[6]}$), 135.1 (C$_{[16]}$), 131.7 (C$_{[8]}$), 127.7 (C$_{[15]}$), 127.5 (C$_{[17]}$), 126.4 (C$_{[11]}$), 126.1 (C$_{[14]}$), 125.3 (C$_{[10]}$), 123.1 (C$_{[9]}$), 121.4 (C$_{[13]}$), 110.7 (C$_{[7]}$), 80.9 (C$_{[4]}$), 56.5 (C$_{[2]}$), 33.4 (C$_{[3]}$);
**HRMS** (ESI) [C\textsubscript{19}H\textsubscript{13}O\textsubscript{4}N\textsubscript{3}+H]\textsuperscript{+} requires \textit{m/z} 348.0979, found \textit{m/z} 348.0979.

Spectroscopic and other data for synthetic compound 1 are in good agreement with reported data\textsuperscript{1}, where compound 1’s melting point was 267 – 269 °C and [\textit{\textalpha}]	extsubscript{\textit{\textbeta}}\textsubscript{20} was +250 (c 0.3, MeOH).

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<td>125.3</td>
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<tr>
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<tr>
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<tr>
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</table>
Compound S1

\[
\text{BnO}^+\text{CN}^- (\text{NH}_2\text{HCl})
\]

Compound S1 was synthesized from \(\delta\)-Asparagine following the same procedure as described by Rapoport \textit{et al}^2.

\textbf{m.p.} 157 – 160 °C; \([\alpha]_D^{25} +14.0 \ (c \ 1.00, \text{MeOH})

\textbf{IR} (neat) \(v_{\text{max}}/\text{cm}^{-1} \): 2830, 1743, 1486, 1413, 1223, 1152, 1069, 935, 753, 701;

\begin{align*}
\text{H NMR} \ (\text{DMSO-}d_6, \ 400 \text{ MHz}) \delta \ (\text{ppm}) : & 8.92 \ (s, \ 3\text{H, NH}_3), \ 7.34 - 7.50 \ (m, \ 5\text{H, C}[7][8][9]\text{H}), \ 5.29 \\
& (s, \ 2\text{H, C}[5]\text{H}), \ 4.60 \ (dd, \ J = 6.7, 5.3 \text{ Hz}, \ 1\text{H, C}[2]\text{H}), \ 3.14 - 3.31 \ (m, \ 2\text{H, C}[3]\text{H});
\end{align*}

\begin{align*}
\text{C NMR} \ (\text{DMSO-}d_6, \ 100 \text{ MHz}) \delta \ (\text{ppm}) : & 166.6 \ (C[1]), \ 134.3 \ (C[6]), \ 128.0 \ (C[7]), \ 127.9 \ (C[9]), \\
& 127.7 \ (C[8]), \ 115.8 \ (C[4]), \ 67.3 \ (C[5]), \ 47.7 \ (C[2]), \ 18.1 \ (C[3]).
\end{align*}

Compound S2
Compound **S1** (3.22 g, 13.4 mmol, 1.0 eq) was dissolved in H₂O 50 mL and CH₂Cl₂ 100 mL. To the heterogeneous mixture, NaHCO₃ (3.37 g, 40.1 mmol, 3.0 eq) was added portionwise, and 2-nitrobenzoyl chloride (2.98 g, 2.1 mL, 16.1 mmol, 1.2 eq) was added dropwise. After stirred at room temperature for 30 min, the mixture was separated, and the aqueous phase was extract by 20 mL of CH₂Cl₂ for twice. Combined organic phase was washed by 20 mL of 0.5 M NaOH and brine, dried with MgSO₄. The combined layers were filtered and the solvent removed under vacuum to give 4.70 g of crude product, which was recrystallized from PE/EA to give 4.18 g (88%) of white solid.

**m.p.** 162 – 164 °C; [α]D²⁵ −31.4 (c 1.00, CHCl₃)

**IR** (film) νₘₐₓ/cm⁻¹: 2922, 2852, 1742, 1669, 1532, 1349, 1214, 770, 630;

**¹H NMR** (DMSO-d₆, 400 MHz) δ (ppm): 9.61 (d, J = 7.8 Hz, 1H, CONH), 8.07 (dd, J = 8.1, 1.2 Hz, 1H, C[8]H), 7.70 – 7.85 (m, 2H, C[9][11]H), 7.52 (dd, J = 7.5, 1.5 Hz, 1H, C[10]H), 7.32 – 7.44 (m, 5H, C[14][15][16]H), 5.20 (d, J = 5.6 Hz, 2H, C[12]H), 4.86 (td, J = 8.1, 5.4 Hz, 1H, C[2]H), 3.13 (dd, J = 17.0, 5.5 Hz, 1H, C[3]H'), 3.05 (dd, J = 17.0, 8.4 Hz, 1H, C[3]H'');
**13C NMR** (DMSO-d$_6$, 100 MHz) $\delta$ (ppm): 168.2 (C$_{[1]}$), 165.2 (C$_{[5]}$), 146.4 (C$_{[7]}$), 135.0 (C$_{[ar]}$), 133.2 (C$_{[ar]}$), 130.8 (C$_{[ar]}$), 130.7 (C$_{[ar]}$), 128.5 (C$_{[ar]}$), 127.9 (C$_{[ar]}$), 127.7 (C$_{[ar]}$), 127.4 (C$_{[ar]}$), 123.8 (C$_{[ar]}$), 117.2 (C$_{[4]}$), 66.4 (C$_{[12]}$), 48.4 (C$_{[2]}$), 18.9 (C$_{[3]}$);

**HRMS** (ESI) [C$_{18}$H$_{15}$N$_3$O$_5$+Na]$^+$ requires $m/\text{z}$ 376.0915, found $m/\text{z}$ 376.0914.

**Compound 6**

![Compound 6](image)

**Compound 6** was synthesized following a modified procedure described by Wu *et al*.$^3$

**Compound S2** (3.25 g, 9.2 mmol, 1.0 eq), potassium phenyltrifluoroborate (3.38 g, 18.4 mmol, 2.0 eq), palladium(II) acetate (155 mg, 0.69 mmol, 0.075 eq) and 2,2’-Bipyridyl (215 mg, 1.38 mmol, 0.15 eq) were dissolved in the mixture of THF 69 mL and H$_2$O 13.8 mL. To this solution, TFA (10.5 g, 7.0 mL, 92.0 mmol, 10.0 eq) was added. Then the reaction was stirred at 70 °C under Argon atmosphere for 15 hours. Then the mixture was diluted with ethyl acetate 100 mL, washed with 1 M HCl, 0.5 M NaOH and brine, dried with MgSO$_4$, filtered and concentrated to give a dark yellow solid residue, which was purified by the first FCC Et$_2$O/CH$_2$Cl$_2$ (from 1/50 to 1/20) to give crude product 3.61 g. Recrystallization from EtOH/H$_2$O (70 mL / 35 mL) gave a yellow crystal 3.35 g, which was purified by the second FCC Et$_2$O / CH$_2$Cl$_2$ (1/20) to give a white solid 3.30 g (83%).
m.p. 121 – 122 °C; [α]_D^{25} +53.6 (c 1.00, CHCl₃);

IR (film) ν_{max}/cm⁻¹: 1742, 1674, 1529, 1451, 1348, 1215, 1111, 1039, 995, 909, 734, 696;

**1H NMR** (CDCl₃, 400 MHz) δ (ppm): 8.04 (dd, J = 8.1, 1.2 Hz, 1H, C₁₂H), 7.95 – 8.02 (m, 2H, C₁₀H), 7.58 – 7.72 (m, 3H, C₁₀H), 7.50 – 7.58 (m, 3H, C₁₂H), 7.37 (s, 5H, C₁₀H), 7.12 (d, J = 8.3 Hz, 1H, NHC=O), 5.23 (dd, J = 11.2, 5.1 Hz, 1H, C₁₆H), 3.95 (dd, J = 18.5, 4.0 Hz, 1H, C₃H’), 3.88 (dd, J = 18.4, 3.9 Hz, 1H, C₃H’’);

**13C NMR** (CDCl₃, 100 MHz) δ (ppm): 198.2 (C₄), 170.6 (C₁), 166.1 (C₉), 146.4 (C₁₁), 135.9 (C₁₀), 135.1 (C₁₀), 133.8 (C₁₀), 133.7 (C₁₂), 132.3 (C₁₂), 130.6 (C₁₀), 128.7 (C₁₀), 128.6 (C₁₂), 128.5 (C₁₀), 128.4 (C₁₀), 128.3 (C₁₀), 128.2 (C₁₀), 124.6 (C₁₀), 67.6 (C₁₆), 48.9 (C₂), 39.9 (C₃);

**HRMS** (ESI) [C_{24}H_{20}N_{2}O_{6}+Na]^+ requires m/z 455.1214, found m/z 455.1213.

**Compound 7**
The ketone compound 6, (432 mg, 1.0 mmol, 1.0 eq), Ligand-1 (30 mg, 0.05 mmol, 0.05 eq), AgOAc (8 mg, 0.05 mmol, 0.05 eq) and activated 4A molecular sieve 300 mg were dissolved in 18 mL ethyl acetate. After stirring at 0 °C for 30 min, tert-butyl isocyanocetate (216 mg, 1.5 mmol, 1.5 eq) in 2 mL of ethyl acetate was added into the reaction mixture. The reaction was stirring at 0 °C for 5 days. The reaction was filtered through the Celite, concentrated and purified by FCC Et₂O/CH₂Cl₂ (from 1/10 to 1/8) to give a colourless foam 410 mg (71%, d.r. = 12.5:1).

**m.p.** 64 – 66 °C; [α]D 25 –40.4 (c 1.27, CHCl₃);

**IR** (film) $\nu_{\text{max}}$/cm⁻¹: 1742, 1670, 1636, 1533, 1450, 1350, 1312, 1154, 1024, 960, 913, 846, 790, 735, 700;

$^1$H NMR (CDCl₃, 400 MHz) $\delta$ (ppm): 7.94 – 8.05 (m, 1H, C₁₁H), 7.50 – 7.60 (m, 2H, CᵦH), 7.41 – 7.48 (m, 2H, CᵦH), 7.32 – 7.40 (m, 7H, CᵦH), 7.27 – 7.32 (m, 1H, CᵦH), 7.07 – 7.12 (m, 1H, CᵦH), 6.87 (d, $J$ = 1.5 Hz, 1H, CONH), 6.09 (d, $J$ = 7.6 Hz, 1H, C₁₁H), 5.00 (d, $J$ = 3.4 Hz, 1H, C₁₁H), 2.76 (s, 3H, $CH₃$).
Hz, 2H, C_{[21]}H), 4.75 (q, J = 6.5 Hz, 1H, C_{[5]}H), 4.59 (s, 1H, C_{[2]}H), 2.77 (dd, J = 14.5, 6.2 Hz, 1H, C_{[4]}H’), 2.58 (dd, J = 14.4, 6.6 Hz, 1H, C_{[4]}H”), 1.54 (s, 9H, C_{[9]}H);

$^{13}$C NMR (CDCl$_3$, 100 MHz) δ (ppm): 170.7 (C$_{[6]}$), 167.7 (C$_{[7]}$), 165.3 (C$_{[14]}$), 154.7 (C$_{[1]}$), 146.5 (C$_{[16]}$), 142.1 (C$_{[10]}$), 134.9 (C$_{[ar]}$), 133.3 (C$_{[ar]}$), 131.8 (C$_{[ar]}$), 130.7 (C$_{[ar]}$), 128.9 (C$_{[ar]}$), 128.7 (C$_{[ar]}$), 128.6 (C$_{[ar]}$), 128.5 (C$_{[ar]}$), 128.5 (C$_{[ar]}$), 128.1 (C$_{[ar]}$), 124.6 (C$_{[ar]}$), 124.5 (C$_{[ar]}$), 87.9 (C$_{[3]}$), 83.3 (C$_{[8]}$), 80.4 (C$_{[2]}$), 67.5 (C$_{[21]}$), 50.2 (C$_{[5]}$), 38.0 (C$_{[4]}$), 28.0 (C$_{[9]}$);

HRMS (ESI) [C$_{31}$H$_{31}$N$_{3}$O$_{8}$+Na]$^+$ requires m/z 596.2003, found m/z 596.2000.

**Compound 8**

![Chemical structure of Compound 8](image)

The ketone compound 6 (432 mg, 1.0 mmol, 1.0 eq), Ligand-2 (30 mg, 0.05 mmol, 0.05 eq), AgOAc (8 mg, 0.05 mmol, 0.05 eq) and activated 4A molecular sieve 300 mg were dissolved in 18 mL ethyl acetate. After stirring at 0 °C for 30 min, tert-butyl isocyanatoacetate (216 mg, 1.5 mmol, 1.5 eq) in 2 mL of ethyl acetate was added into the reaction mixture. The reaction was stirring at 0 °C for 5 days, then filtered through the Celite, concentrated and purified by FCC Et$_2$O/CH$_2$Cl$_2$ (from 1/10 to 1/8) gave the colourless foam 430 mg (75%, d.r. > 20:1).

m.p. 55 – 58 °C; [α]$_D^{25}$ +10.7 (c 1.50, CHCl$_3$);
IR (film) $\nu_{\text{max}}$/cm$^{-1}$: 1739, 1672, 1635, 1531, 1456, 1369, 1349, 1214, 1153, 1019, 963, 912, 843, 791, 733, 700, 647;

![Chemical structure](attachment:image.png)

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ (ppm): 7.92 – 8.01 (m, 1H, C$_{[17]}$H), 7.50 – 7.60 (m, 2H, C$_{[ar]}$H), 7.45 (d, $J = 7.4$ Hz, 2H, C$_{[ar]}$H), 7.32 – 7.41 (m, 7H, C$_{[ar]}$H), 7.23 – 7.28 (m, 1H, C$_{[ar]}$H), 7.04 – 7.10 (m, 1H, C$_{[ar]}$H), 6.68 (d, $J = 1.9$ Hz, 1H, CONH), 6.21 (d, $J = 7.0$ Hz, 1H, C$_{[1]}$H), 5.22 (d, $J = 12.1$ Hz, 1H, C$_{[21]}$H$'$), 5.09 (d, $J = 12.1$ Hz, 1H, C$_{[21]}$H$''$), 4.63 (d, $J = 2.1$ Hz, 1H, C$_{[2]}$H), 4.60 (dt, $J = 7.6$, 3.9 Hz, 1H, C$_{[5]}$H), 2.81 (dd, $J = 14.8$, 3.8 Hz, 1H, C$_{[4]}$H$'$), 2.50 (dd, $J = 14.8$, 7.9 Hz, 1H, C$_{[4]}$H$''$), 1.51 (s, 9H, C$_{[9]}$H);

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ (ppm): 170.7 (C$_{[6]}$), 167.7 (C$_{[7]}$), 165.4 (C$_{[14]}$), 154.6 (C$_{[11]}$), 146.7 (C$_{[16]}$), 142.1 (C$_{[10]}$), 135.1 (C$_{[ar]}$), 133.2 (C$_{[ar]}$), 131.8 (C$_{[ar]}$), 130.6 (C$_{[ar]}$), 129.1 (C$_{[ar]}$), 128.8 (C$_{[ar]}$), 128.6 (C$_{[ar]}$), 128.6 (C$_{[ar]}$), 128.6 (C$_{[ar]}$), 128.2 (C$_{[ar]}$), 124.4 (C$_{[ar]}$), 88.5 (C$_{[3]}$), 83.3 (C$_{[8]}$), 80.3 (C$_{[2]}$), 67.5 (C$_{[21]}$), 50.3 (C$_{[5]}$), 37.4 (C$_{[4]}$), 28.0 (C$_{[9]}$);

HRMS (ESI) [C$_{31}$H$_{31}$N$_3$O$_8$+H]$^+$ requires $m/z$ 574.2184, found $m/z$ 574.2182.

Compound S3
The oxazoline Compound 7 (660 mg, 1.15 mmol) was dissolved in methanol 40 mL, and added 3.0 mL of thionyl chloride at −78 °C; removed the cold bath and stirred at r.t. for 90 min, the reaction was quenched by saturated NaHCO₃, exacted by Ethyl acetate 20 mL for three times, combined the organic phase, washed with brine 15 mL, dried with Magnesium sulfate, removed solvent and re-dissolved in Ethyl acetate 10 mL and 1 mL of Triethylamine; the mixture was stirred at 70 °C for 90 min. After cooling down, filtered the mixture and washed the solid with Ether to give white solid 430 mg (82%, single diastereomer).

**m.p.** 206 – 208 °C; [α]D²⁵ −101.3 (c 0.63, MeOH);

**IR** (neat) νmax/cm⁻¹: 3392, 1736, 78, 1658, 1640, 1541, 1482, 1410, 1356, 1325, 1273, 1223, 1157, 1094, 1068, 1046, 957, 943, 912, 899, 855, 790, 759, 733, 696, 643;

**¹H NMR** (MeOD-d₄, 500 MHz) δ (ppm): 8.14 (dd, J = 8.0, 0.9 Hz, 1H, C[16]H), 7.78 – 7.83 (m, 2H, C[ar]H), 7.70 (ddd, J = 8.2, 5.5, 3.5 Hz, 1H, C[ar]H), 7.51 – 7.56 (m, 2H, C[ar]H), 7.38 – 7.44 (m, 2H, C[ar]H), 7.33 – 7.38 (m, 1H, C[ar]H), 5.21 (dd, J = 12.0, 6.1 Hz, 1H, C[2]H), 4.17 (d, J = 1.6 Hz, 1H, C[5]H), 2.99 (dd, J = 12.9, 12.1 Hz, 1H, C[3]H⁺), 2.57 (ddd, J = 12.8, 6.2, 1.7 Hz, 1H, C[3]H⁺⁺), 1.03 (s, 9H, C[8]H);
\(^{13}\text{C NMR}\) (MeOD-d4, 125 MHz) \(\delta\) (ppm): 172.9 (C\(_6\)), 171.1 (C\(_{11}\)), 169.7 (C\(_{13}\)), 148.1 (C\(_{15}\)), 144.2 (C\(_9\)), 135.2 (C\(_{\text{ar}}\)), 134.1 (C\(_{\text{ar}}\)), 132.0 (C\(_{\text{ar}}\)), 130.6 (C\(_{\text{ar}}\)), 130.0 (C\(_{\text{ar}}\)), 127.7 (C\(_{\text{ar}}\)), 125.6 (C\(_{\text{ar}}\)), 83.2 (C\(_7\)), 72.9 (C\(_4\)), 67.4 (C\(_5\)), 48.6 (C\(_2\)), 35.6 (C\(_3\)), 27.8 (C\(_8\));

HRMS (ESI) \([\text{C}_{23}\text{H}_{25}\text{N}_3\text{O}_7\text{Na}]^+\) requires \(m/\text{z}\) 478.1585, found \(m/\text{z}\) 478.1581.
3. References


4. NMR spectra

Compound 2
Compound 3
Compound 4
Compound 5
Compound 9
Compound 10
Compound 11
Compound 12
Compound 13
Compound 14
Compound 15
Compound 16
Compound 17
Compound 18
Compound 1
Compound S1
Compound S2
Compound 6
Compound 7
Compound 8
Compound S3
Compound S3 nOe