Supporting Information

for

A facile approach to spiro[dihydrofuran-2,3'-oxindoles] via formal [4 + 1] annulation reaction of fused 1H-pyrrole-2,3-diones with diazooxindoles

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General information

$^1$H and $^{13}$C NMR spectra were acquired on a Bruker Avance-III spectrometer (400 and 100 MHz, respectively) in DMSO-$d_6$ using the residual solvent signals (in $^1$H NMR 2.50 ppm for DMSO-$d_6$; in $^{13}$C NMR 39.51 ppm for DMSO-$d_6$) as internal standards. Melting points were measured on a Khimlabpribor PTP apparatus or a Mettler Toledo MP70 apparatus. The reaction conditions were optimized using UPLC–UV–MS [Waters ACQUITY UPLC I-Class system; Acquity UPLC BEH C18 column, grain size of 1.7 μm; acetonitrile/water as eluents; flow rate of 0.6 mL/min; ACQUITY UPLC PDA eλ Detector (wavelength range of 230–780 nm); Xevo TQD mass detector; electrospray ionization; positive and negative ion detection; ion source temperature of 150 °C; capillary voltage of 3500–4000 V; cone voltage of 20–70 V; vaporizer temperature of 200 °C]. Thin-layer chromatography (TLC) was performed on Merck silica gel 60 F254 plates using EtOAc/toluene 1:3 (v/v), acetic acid/EtOAc/toluene 1:8:24 (v/v) acetic acid, toluene, EtOAc as eluents, and the spots were visualized with UV light (254 and 365 nm) or by treating the plate with iodine vapor. HRMS were recorded on Bruker MicroTOF (ESI+), acetonitrile and methanol were used as solvents. The single crystal X-ray analyses of compounds 3aa, 3ab, and 3ha were performed on an Xcalibur Ruby diffractometer (Agilent Technologies). The empirical absorption correction was introduced by multi-scan method using SCALE3 ABSPACK algorithm. Using OLEX2, the structures were solved with the SUPERFLIP program or with the olex2.solve program and refined by the full-matrix least-squares minimization in the anisotropic approximation for all non-hydrogen atoms with the SHELXL program. Hydrogen atoms bound to carbon were positioned geometrically and refined using a riding model. The hydrogen atoms of NH groups were refined freely with isotropic displacement parameters.

Starting FPDs 1a–k were obtained according to reported procedures from oxalyl chloride (purchased from commercial vendors) and heterocyclic enamines (obtained according to reported procedures from commercially available reagents).

Diazooxindoles 2a–d and 3-bromooxindole (4) were obtained according to reported procedures from commercially available reagents.

Toluene, and 1,4-dioxane were distilled over Na before use. Ethyl acetate, chloroform, and acetone were distilled over P₂O₅ before the use. Acetonitrile, DMSO, DMF were dried over molecular sieves 4 Å before use. All other solvents and reagents were purchased from commercial vendors and were used as received.

Procedures involving FPDs 1a–k were carried out in oven-dried glassware.
General procedure to compounds 3aa–ka

A suspension of the corresponding FPD 1 (500 µmol) and diazooxindole 2 (500 µmol) in 3 mL of acetonitrile was vigorously stirred at room temperature for 24 hours or at 83 °C for 3–5 hours (for FPDs 1h–j) (until the disappearance of the dark violet color of FPD 1). Then, the resulting yellow or pale-yellow precipitate was filtered off and washed with acetonitrile (2 × 1 mL) to afford the desired compounds 3. Product 3ja was additionally recrystallized from 1,4-dioxane.

Control experiment:

A suspension of the FPD 1i (500 µmol) and 3-bromoxindole (4, 500 µmol) in 3 mL of acetonitrile was stirred at room temperature for 2 minutes and then 1.1 equiv of TEA was added in one portion. The mixture was stirred for 5 minutes (until the disappearance of the dark violet color of FPD 1i). Then, the resulting yellow precipitate was filtered off and washed with acetonitrile (2 × 1 mL) to afford the desired compound 3ia.

\((5R^*,5aR^*)-3\text{-Phenyl}-6H\text{-spiro[benzo}[b]furo}[3',4':2,3]\text{pyrrolo}[1,2-d][1,4]\text{oxazine}-5,3'\text{-indoline}]\text{-}1,2,2',6\text{-tetraone} \ (3aa)\)

Yield: 165 mg (73%); yellow solid; mp 246–247°C (decomp.).

\(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 10.83 (s, 1H), 8.24 (d, \(J = 7.3\) Hz, 2H), 7.86 (t, \(J = 7.5\) Hz, 1H), 7.72 (t, \(J = 7.7\) Hz, 2H), 7.30 (qd, \(J = 5.3, 4.8, 2.2\) Hz, 3H), 7.06 (ddd, \(J = 8.6, 6.1, 2.7\) Hz, 1H), 7.00 – 6.90 (m, 3H), 6.65 (d, \(J = 7.8\) Hz, 1H).

\(^{13}\)C NMR (101 MHz, DMSO-\(d_6\)) \(\delta\) 173.28, 169.07, 166.82, 160.47, 158.64, 143.17, 141.48, 135.55, 132.61, 129.99 (2C), 129.34 (2C), 127.89, 125.69, 124.60, 124.11, 122.77, 121.81, 121.44, 121.28, 116.67, 110.77, 105.02, 91.14, 70.63.

MS (ESI+): m/z calcd for C\(_{26}\)H\(_{14}\)N\(_2\)O\(_6\)\(+\)MeOH\(+\)Na\(^+\): 505.1006 [M+ MeOH+Na\(^+\)]; found: 505.1011.

\((5R^*,5aR^*)-5'\text{-Bromo}-3\text{-Phenyl}-6H\text{-spiro[benzo}[b]furo}[3',4':2,3]\text{pyrrolo}[1,2-d][1,4]\text{oxazine}-5,3'\text{-indoline}]\text{-}1,2,2',6\text{-tetraone} \ (3ab)\)

Yield: 159 mg (60%); yellow solid; mp 225–226 °C (decomp.).

\(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) 11.00 (s, 1H), 8.23 (d, \(J = 7.5\) Hz, 2H), 7.85 (t, \(J = 7.4\) Hz, 1H), 7.72 (t, \(J = 7.7\) Hz, 2H), 7.50 – 7.44 (m, 1H), 7.36 (d, \(J = 1.5\) Hz, 1H), 7.29 (d, \(J = 5.4\) Hz, 2H), 7.12 – 7.06 (m, 1H), 6.98 (d, \(J = 7.8\) Hz, 1H), 6.59 (d, \(J = 8.4\) Hz, 1H).

\(^{13}\)C NMR (101 MHz, DMSO-\(d_6\)) \(\delta\) 173.14, 169.01, 166.82, 160.44, 158.35, 143.16, 140.82, 135.44, 135.27, 130.09 (2C), 129.25 (2C), 127.92, 127.27, 125.73, 124.75, 123.40, 121.88, 121.44, 116.72, 114.04, 112.63, 104.46, 90.51, 71.18.

MS (ESI+): m/z calcd for C\(_{26}\)H\(_{13}\)BrN\(_2\)O\(_6\)+MeOH+Na\(^+\): 583.0111 [M+ MeOH+Na\(^+\)]; found: 583.0117.
(5R*,5aR*)-5'-Methoxy-3-phenyl-6H-spiro[benzo[b]furo[3',4':2,3]pyrrolo[1,2-d][1,4]oxazine-5,3'-indoline]-1,2,2',6-tetraone (3ac)

Yield: 146 mg (61%); yellow solid; mp 255–256°C (decomp.).

1H NMR (400 MHz, DMSO-d6) δ 10.67 (s, 1H), 8.23 (d, J = 7.5 Hz, 2H), 7.86 (t, J = 7.4 Hz, 1H), 7.73 (t, J = 7.7 Hz, 2H), 7.33–7.23 (m, 2H), 7.10–7.05 (m, 1H), 7.00 (d, J = 7.6 Hz, 1H), 6.90 (dd, J = 8.6, 2.4 Hz, 1H), 6.58 (d, J = 8.6 Hz, 1H), 6.51 (d, J = 2.3 Hz, 1H), 3.60 (s, 3H).

13C NMR (101 MHz, DMSO-d6) δ 173.28, 168.96, 167.20, 160.49, 158.59, 155.09, 143.15, 135.54, 134.73, 130.06 (2C), 129.32 (2C), 127.85, 125.71, 124.64, 122.26, 121.77, 121.45, 117.35, 116.66, 111.50, 110.93, 104.85, 91.27, 70.68, 55.79.

MS (ESI+): m/z calcd for C27H16N2O7+Na+: 503.0850 [M+Na+]; found: 503.0860.

(5R*,5aR*)-1'-Benzy1-3-phenyl-6H-spiro[benzo[b]furo[3',4':2,3]pyrrolo[1,2-d][1,4]oxazine-5,3'-indoline]-1,2,2',6-tetraone (3ad)

Yield: 157 mg (58%); yellow solid; mp 240–241°C (decomp.).

1H NMR (400 MHz, DMSO-d6) δ 8.28–8.22 (m, 2H), 7.89–7.82 (m, 1H), 7.72 (t, J = 7.8 Hz, 2H), 7.36–7.23 (m, 5H), 7.18 (dd, J = 8.3, 1.3 Hz, 1H), 7.05 (dt, J = 21.0, 7.6, 1.1 Hz, 3H), 6.97 (dd, J = 8.0, 1.6 Hz, 1H), 6.92–6.86 (m, 2H), 6.75 (d, J = 7.9 Hz, 1H), 4.80 (d, J = 15.9 Hz, 1H), 4.64 (d, J = 15.9 Hz, 1H), minor product: 5.00 (d, J = 15.8 Hz, 1H).

13C NMR (101 MHz, DMSO-d6) δ 173.13, 168.96, 167.70, 166.87, 160.49, 158.40, 142.95, 142.02, 135.62, 134.60, 132.70, 130.01 (2C), 129.36 (2C), 127.85, 125.71, 124.64, 122.26, 121.77, 121.45, 117.35, 116.66, 111.50, 110.93, 104.85, 91.27, 70.68, 55.79.

MS (ESI+): m/z calcd for C33H20N2O6+Na+: 563.1213 [M+Na+]; found: 563.1215.

(5R*,5aR*)-3-(4-Chlorophenyl)-6H-spiro[benzo[b]furo[3',4':2,3]pyrrolo[1,2-d][1,4]oxazine-5,3'-indoline]-1,2,2',6-tetraone (3ba)

Yield: 172 mg (71%); yellow solid; mp 225–226 °C (decomp.).

1H NMR (400 MHz, DMSO-d6) δ 10.83 (s, 1H), 8.23 (d, J = 8.6 Hz, 2H), 7.81 (d, J = 8.6 Hz, 2H), 7.28 (q, J = 6.0, 5.1 Hz, 3H), 7.04 (dd, J = 18.3, 10.1, 4.8 Hz, 2H), 6.97–6.89 (m, 2H), 6.64 (d, J = 7.8 Hz, 1H).

13C NMR (101 MHz, DMSO-d6) δ 173.38, 168.98, 165.68, 160.31, 158.53, 143.17, 141.46, 140.43, 132.66, 131.49 (2C), 129.65 (2C), 127.95, 124.64, 124.50, 124.24, 122.78, 121.84, 121.40, 121.21, 116.69, 110.75, 105.40, 91.34, 70.65.

MS (ESI+): m/z calcd for C26H16ClN2O6+MeOH+Na+: 539.0616 [M+ MeOH+Na+]; found: 539.0638.
(5R*,5aR*)-3-(4-Bromophenyl)-6H-spiro[benzo[b]furo[3',4':2,3]pyrrolo[1,2-d][1,4]oxazine-5,3'-indoline]-1,2,2',6-tetraone (3ca)

Yield: 159 mg (62%); yellow solid; mp 230–231 °C (decomp.).

1H NMR (400 MHz, DMSO-d$_6$) δ 10.83 (s, 1H), 8.14 (d, J = 8.5 Hz, 2H), 7.95 (d, J = 8.5 Hz, 2H), 7.29 (q, J = 7.3, 5.2 Hz, 3H), 7.04 (dd, J = 18.9, 10.4, 4.8 Hz, 2H), 6.98 – 6.88 (m, 2H), 6.64 (d, J = 7.8 Hz, 1H).

13C NMR (101 MHz, DMSO-d$_6$) δ 173.38, 168.97, 165.81, 160.29, 158.49, 143.16, 141.45, 132.65, 132.60 (2C), 131.44 (2C), 129.77, 127.94, 124.80, 124.63, 124.24, 122.77, 121.83, 121.39, 121.20, 116.69, 110.74, 105.46, 91.33, 70.65.

MS (ESI+): m/z calcd for C$_{26}$H$_{13}$BrN$_2$O$_6$: 583,0111 [M+Na$^+$]; found: 583.0126.

(5R*,5aR*)-3-(4-Methylphenyl)-6H-spiro[benzo[b]furo[3',4':2,3]pyrrolo[1,2-d][1,4]oxazine-5,3'-indoline]-1,2,2',6-tetraone (3da)

Yield: 170 mg (73%); yellow solid; mp 247–248°C (decomp.).

1H NMR (400 MHz, DMSO-d$_6$) δ 10.82 (s, 1H), 8.14 (d, J = 8.1 Hz, 2H), 7.54 (d, J = 8.1 Hz, 2H), 7.31 – 7.27 (m, 3H), 7.05 (td, J = 7.0, 6.1, 2.6 Hz, 1H), 7.00 – 6.88 (m, 3H), 6.65 (d, J = 7.8 Hz, 1H), 2.48 (s, 3H).

13C NMR (101 MHz, DMSO-d$_6$) δ 173.15, 169.11, 167.41, 160.65, 158.76, 147.02, 143.17, 141.50, 132.59, 130.10 (2C), 129.98 (2C), 127.86, 124.59, 123.95, 123.08, 122.76, 121.77, 121.48, 121.31, 116.67, 110.80, 104.33, 91.02, 70.58, 21.56.

MS (ESI+): m/z calcd for C$_{27}$H$_{16}$N$_2$O$_6$+MeOH+Na$^+$: 519.1162 [M+Na$^+$]; found: 519.1173.

(5R*,5aR*)-3-(4-Methoxyphenyl)-6H-spiro[benzo[b]furo[3',4':2,3]pyrrolo[1,2-d][1,4]oxazine-5,3'-indoline]-1,2,2',6-tetraone (3ea)

Yield: 187 mg (78%); yellow solid; mp 247–248 °C (decomp.).

1H NMR (400 MHz, DMSO-d$_6$) δ 10.81 (s, 1H), 8.23 (d, J = 8.8 Hz, 2H), 7.34 – 7.22 (m, 5H), 7.05 (td, J = 7.0, 6.1, 2.6 Hz, 1H), 6.98 – 6.92 (m, 2H), 6.88 (d, J = 7.4 Hz, 1H), 6.65 (d, J = 7.8 Hz, 1H), 3.94 (s, 3H).

13C NMR (101 MHz, DMSO-d$_6$) δ 172.91, 169.17, 167.50, 165.47, 160.97, 158.95, 143.15, 141.51, 132.76 (2C), 132.53, 127.76, 124.56, 123.84, 122.73, 121.71, 121.55, 121.34, 118.13, 116.64, 115.10 (2C), 110.79, 103.00, 90.79, 70.56, 55.97.

MS (ESI+): m/z calcd for C$_{27}$H$_{16}$N$_2$O$_7$+Na$^+$: 503.0850 [M+Na$^+$]; found: 503.0850.

(5R*,5aR*)-3-(4-Nitrophenyl)-6H-spiro[benzo[b]furo[3',4':2,3]pyrrolo[1,2-d][1,4]oxazine-5,3'-indoline]-1,2,2',6-tetraone (3fa)

Yield: 119 mg (48%); yellow solid; mp 234–236°C (decomp.).
**1H NMR (400 MHz, DMSO-d$_6$)** $\delta$ 10.87 (s, 1H), 8.56 – 8.38 (m, 4H), 7.31 (q, $J = 7.8$ Hz, 3H), 7.12 (d, $J = 7.5$ Hz, 1H), 7.10 – 7.02 (m, 1H), 7.00 – 6.89 (m, 2H), 6.64 (d, $J = 7.8$ Hz, 1H).

**13C NMR (101 MHz, DMSO-d$_6$)** $\delta$ 173.60, 168.90, 163.84, 159.91, 158.26, 150.75, 143.19, 141.45, 132.77, 130.97 (2C), 130.79, 128.09, 124.72, 124.56, 124.30 (2C), 122.80, 121.94, 121.30, 121.16, 116.75, 110.75, 107.52, 91.72, 70.77.

MS (ESI+): m/z calcd for C$_{26}$H$_{13}$N$_3$O$_8$+MeOH+Na$^+$: 550.0857 [M+ MeOH+Na$^+$]; found: 550.0875.

(5R*,5aR*)-10-Chloro-3-phenyl-6H-spiro[benzo[b]furo[3',4':2,3]pyrrolo[1,2-d][1,4]oxazine-5,3'-indoline]-1,2,2',6-tetraone (3ga)

Yield: 208 mg (86%); yellow solid; mp 259–260°C (decomp.).

**1H NMR (400 MHz, DMSO-d$_6$)** $\delta$ 10.89 (s, 1H), 8.24 (d, $J = 7.6$ Hz, 2H), 7.86 (t, $J = 7.4$ Hz, 1H), 7.72 (t, $J = 7.6$ Hz, 2H), 7.35 (d, $J = 12.6$ Hz, 3H), 7.04 – 6.95 (m, 2H), 6.88 (s, 1H), 6.70 (d, $J = 7.8$ Hz, 1H).

**13C NMR (101 MHz, DMSO-d$_6$)** $\delta$ 172.79, 169.12, 167.57, 160.35, 158.06, 142.10, 141.42, 135.69, 132.67, 130.10 (2C), 129.36 (2C), 128.13, 127.74, 125.59, 124.33, 122.92, 122.45, 121.20, 121.07, 118.51, 110.83, 104.46, 91.20, 70.54.

MS (ESI+): m/z calcd for C$_{26}$H$_{14}$ClN$_2$O$_5$+MeOH+Na$^+$: 539.0616 [M+ MeOH+Na$^+$]; found: 539.0623.

(5R*,5aR*)-3-(4-Chlorophenyl)spiro[furo[3',4':2,3]pyrrolo[1,2-a]quinoxaline-5,3'-indoline]-1,2,2',6(7H)-tetraone ACN solvate 1:1 (3ha)

Yield: 184 mg (70%); yellow solid; mp 252–253°C (decomp.).

**1H NMR (400 MHz, DMSO-d$_6$)** $\delta$ 11.06 (s, 1H), 10.65 (s, 1H), 8.24 (d, $J = 8.7$ Hz, 2H), 7.80 (d, $J = 8.7$ Hz, 2H), 7.30 – 7.21 (m, 1H), 7.19 – 7.14 (m, 1H), 7.01 (d, $J = 8.0$ Hz, 1H), 6.98 – 6.90 (m, 2H), 6.86 – 6.81 (m, 1H), 6.77 (d, $J = 6.8$ Hz, 1H), 6.60 (d, $J = 7.8$ Hz, 1H), minor product: 10.98 (s, 1H), 10.76 (s, 1H), 7.92 – 7.86 (m, 2H).

**13C NMR (101 MHz, DMSO-d$_6$)** $\delta$ 173.81, 169.21, 167.57, 160.35, 158.06, 142.10, 141.42, 135.69, 132.67, 130.10 (2C), 129.36 (2C), 128.13, 127.74, 125.59, 124.33, 122.92, 122.45, 121.20, 121.07, 118.51, 110.83, 104.46, 91.20, 70.54.

MS (ESI+): m/z calcd for C$_{26}$H$_{14}$ClN$_2$O$_5$+MeOH+Na$^+$: 538,0776 [M+MeOH+Na$^+$]; found: 538.0764.

(5R*,5aR*)-3,7-Diphenyl-6H-spiro[benzo[b]furo[3',4':2,3]pyrrolo[1,2-d][1,4]oxazine-5,3'-indoline]-1,2,2',6-tetraone (3ia)

Yield: 223 mg (85%); yellow solid; mp 254–255°C (decomp.).

**1H NMR (400 MHz, DMSO-d$_6$)** $\delta$ 10.82 (s, 1H), 8.26 – 8.22 (m, 2H), 7.84 (tt, $J = 7.0$, 1.2 Hz, 1H), 7.72 (t, $J = 7.7$ Hz, 2H), 7.58 (t, $J = 7.4$ Hz, 2H), 7.52 – 7.47 (m, 1H), 7.39 (br s,
2H) 7.31 – 7.26 (m, 1H), 7.12 – 7.07 (m, 1H), 7.02 – 6.95 (m, 2H), 6.89 (td, \( J = 7.7, 1.2 \) Hz, 1H), 6.84 (dd, \( J = 7.9, 1.5 \) Hz, 1H), 6.62 (d, \( J = 7.8 \) Hz, 1H), 6.35 (dd, \( J = 8.3, 0.9 \) Hz, 1H).

\(^{13}\)C NMR (101 MHz, DMSO-\( d_6 \)) \( \delta \) 173.87, 169.50, 166.83, 160.51, 160.32, 141.45, 137.08, 135.35, 133.24, 132.31, 129.95 (2C), 129.56 (2C), 129.30 (2C), 128.74 (2C), 128.57, 127.17, 125.95, 123.77, 122.88, 122.63, 122.52, 122.17, 121.88, 116.72, 110.62, 105.87, 91.73, 71.06.

MS (ESI+): m/z calcd for C\(_{32}\)H\(_{19}\)N\(_3\)O\(_5\)+Na\(^+\): 548.1217 [M+Na\(^+\)]; found: 548.1208.

Control experiment:

Yield: 142 mg (54%); yellow solid; mp 254 – 255°C (decomp.).

\(^1\)H NMR (400 MHz, DMSO-\( d_6 \)) \( \delta \) 10.81 (s, 1H), 8.27 – 8.22 (m, 2H), 7.84 (tt, \( J = 7.0, 1.2 \) Hz, 1H), 7.72 (t, \( J = 7.7 \) Hz, 2H), 7.58 (t, \( J = 7.6 \) Hz, 2H), 7.52 – 7.47 (m, 1H), 7.39 (br s, 2H), 7.31 – 7.26 (m, 1H), 7.12 – 7.07 (m, 1H), 7.02 – 6.95 (m, 2H), 6.89 (dd, \( J = 15.3, 1.2 \) Hz, 1H), 6.83 (dd, \( J = 7.9, 1.5 \) Hz, 1H), 6.62 (d, \( J = 7.8 \) Hz, 1H), 6.34 (dd, \( J = 8.3, 0.9 \) Hz, 1H).

\(^{13}\)C NMR (101 MHz, DMSO-\( d_6 \)) \( \delta \) 173.85, 169.47, 166.80, 160.48, 160.29, 141.43, 137.06, 135.32, 133.23, 132.29, 129.93 (2C), 129.54 (2C), 129.28 (2C), 128.73 (2C), 128.54, 127.14, 125.94, 123.76, 122.86, 122.60, 122.51, 122.16, 121.85, 116.69, 110.59, 105.85, 91.71, 71.04.

\((5S*,5aS*)-7-Benzyl-3-(4-chlorophenyl)spiro[furo[3',4':2,3]pyrrolo[1,2-a]quinoxaline-5,3'-indoline]-1,2,2',6(7H)-tetraone 1:1 dioxyane solvate (3ja)\)

Yield: 210 mg (63%); yellow solid; mp 258 – 260°C (decomp.).

\(^1\)H NMR (400 MHz, DMSO-\( d_6 \)) \( \delta \) 10.68 (s, 1H), 8.26 (d, \( J = 8.6 \) Hz, 2H), 7.81 (d, \( J = 8.6 \) Hz, 2H), 7.38 (d, \( J = 7.4 \) Hz, 2H), 7.27 (td, \( J = 7.3, 3.1 \) Hz, 3H), 7.22 (d, \( J = 7.2 \) Hz, 1H), 7.14 (d, \( J = 7.0 \) Hz, 2H), 6.96 (dt, \( J = 14.8, 7.1 \) Hz, 2H), 6.88 – 6.83 (m, 1H), 6.80 (d, \( J = 7.4 \) Hz, 1H), 6.60 (d, \( J = 7.8 \) Hz, 1H), 5.40 (d, \( J = 16.5 \) Hz, 1H), 4.93 (d, \( J = 16.4 \) Hz, 1H).

\(^{13}\)C NMR (101 MHz, DMSO-\( d_6 \)) \( \delta \) 173.83, 169.20, 165.44, 161.39, 160.28, 141.49, 140.20, 136.04, 132.31, 131.45 (2C), 130.85, 129.59 (2C), 128.19 (2C), 127.33, 127.21 (2C), 126.97, 124.78, 123.76, 122.74, 122.70, 122.53, 122.03, 121.80, 116.15, 110.57, 106.58, 91.80, 71.10, 45.63.

MS (ESI+): m/z calcd for C\(_{33}\)H\(_{20}\)ClN\(_3\)O\(_5\)+Na\(^+\): 596.0983 [M+Na\(^+\)]; found: 596.0986.

\((10R*,10aR*)-8-Phenyl-3,4-dihydro-1H-spiro[furo[3',4':2,3]pyrrolo[2,1-c][1,4]oxazine-10,3'-indoline]-1,2',6,7-tetraone (3ka)\)

Yield: 113 mg (56%); yellow solid; mp 217–218°C (decomp.).

\(^1\)H NMR (400 MHz, DMSO-\( d_6 \)) \( \delta \) 11.35 (s, 1H), 8.19 (d, \( J = 8.4 \) Hz, 2H), 7.82 (t, \( J = 7.5 \) Hz, 1H), 7.68 (t, \( J = 7.8 \) Hz, 2H), 7.48 – 7.42 (m, 1H), 7.09 – 6.94 (m, 3H), 4.61 (ddd, \( J = 12.9, 5.8, 2.0 \) Hz, 1H), 3.99 (td, \( J = 12.7, 12.3, 4.3 \) Hz, 1H), 3.74 (ddd, \( J = 13.2, 11.7, 6.0 \) Hz, 1H), 2.94 (ddd, \( J = 13.4, 4.1, 2.0 \) Hz, 1H).

S7
$^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 173.55, 169.72, 165.82, 164.54, 164.05, 141.81, 135.45, 132.93, 129.86 (2C), 129.29 (2C), 125.64, 125.01, 123.39, 121.98, 111.66, 108.44, 90.39, 72.14, 63.54 (2C).

MS (ESI+): m/z calcd for C$_{22}$H$_{14}$N$_2$O$_6$+Na$: 425.0744 [M+Na$^+$]; found: 425.0747.
NMR charts of compounds 3aa–ka

3aa $^1$H (400 MHz, DMSO-$d_6$)

[Graph of NMR chart for 3aa]
3aa $^{13}$C (101 MHz, DMSO-$d_6$)
3ab $^1$H (400 MHz, DMSO-$d_6$)
3ab $^{13}$C (101 MHz, DMSO-$d_6$)
3ac $^1$H (400 MHz, DMSO-$d_6$)
$^{13}$C (101 MHz, DMSO-$d_6$)
3ad $^1$H (400 MHz, DMSO-$d_6$)
$^{13}$C (101 MHz, DMSO-$d_6$)
$3ba \, ^1H \, (400 \, MHz, \, DMSO-d_6)$
$3ba^{13}C$ (101 MHz, DMSO-$d_6$)
3ca $^1$H (400 MHz, DMSO-$d_6$)
$3ca^{13}C$ (101 MHz, DMSO-$d_6$)
$3\text{da}^1\text{H (400 MHz, DMSO-}$d$\text{)}$
3da $^{13}$C (101 MHz, DMSO-$d_6$)
3ea $^1$H (400 MHz, DMSO-$d_6$)
3ea $^{13}$C (101 MHz, DMSO-$d_6$)
3fa $^1$H (400 MHz, DMSO-$d_6$)
3fa $^{13}$C (101 MHz, DMSO-$d_6$)
$^{1}$H (400 MHz, DMSO-$d_6$)
$3ga^{13}$C (101 MHz, DMSO-$d_6$)
$3\text{ha} \ ^1\text{H} \ (400 \ \text{MHz, DMSO-d}_6) \ \text{ACN solvate} \ 1:1$
$^{13}\text{C} \ (101 \text{ MHz, DMSO-d}_6) \ \text{ACN solvate } 1:1$

3ha
$3{i}^{1}H$ (400 MHz, DMSO-$d_6$)
$3\text{i}a^{13}\text{C} \ (101 \text{ MHz, DMSO-d}_6)$
3ia (control experiment) $^1$H (400 MHz, DMSO-$d_6$)
3ia (control experiment) $^{13}$C (101 MHz, DMSO-$d_6$)
$3ja$ $^1H$ (400 MHz, DMSO-$d_6$) 1,4-dioxane solvate 1:1
$3ja^{13}C$ (101 MHz, DMSO-$d_6$) 1,4-dioxane solvate 1:1

$3ja$
3ka $^1$H (400 MHz, DMSO-$d_6$)
$^{13}\text{C}$ (101 MHz, DMSO-$d_6$)

3ka
NMR charts of compound 3aa after dissolution and 24 h later
X-Ray crystal data of CCDC 2201614 (3aa)

Figure S1. Molecular structure of compound 3aa showing 30% probability amplitude displacement ellipsoids (CCDC 2201614).

Table S1. Crystal data and structure refinement for compound 3aa.

| Property                  | Value                           |
|---------------------------|---------------------------------|
| Empirical formula         | C_{26}H_{14}N_{2}O_{6}           |
| Formula weight            | 450.39                          |
| Temperature, K            | 295.15                          |
| Crystal system            | triclinic                       |
| Space group               | P-1                             |
| a, Å                      | 9.1925(12)                      |
| b, Å                      | 9.5653(12)                      |
| c, Å                      | 12.2709(16)                     |
| α, °                      | 79.986(11)                      |
| β, °                      | 82.628(10)                      |
| γ, °                      | 67.316(12)                      |
| Volume, Å³                | 978.1(2)                        |
| Z                         | 2                               |
| Density (calculated), g/cm³| 1.529                           |
| Absorption coefficient, mm⁻¹| 0.111                           |
| F(000)                    | 464.0                           |
| Crystal size, mm$^3$ | $0.56 \times 0.44 \times 0.19$ |
|---------------------|-------------------------------|
| Radiation           | MoKα ($\lambda = 0.71073$)   |
| 2Θ range for data collection, ° | 6.066 to 58.674 |
| Index ranges        | $-12 \leq h \leq 12$, $-8 \leq k \leq 13$, $-16 \leq l \leq 16$ |
| Reflections collected | 7645                        |
| Independent reflections | 4485 [$R_{\text{int}} = 0.0275$, $R_{\text{sigma}} = 0.0396$] |
| Data/restraints/parameters | 4485/0/311                  |
| Goodness-of-fit on $F^2$ | 1.040                       |
| Final R indexes [$I \geq 2\sigma (I)$] | $R_1 = 0.0457$, $wR_2 = 0.1113$ |
| Final R indexes [all data] | $R_1 = 0.0573$, $wR_2 = 0.1219$ |
| Largest diff. peak/hole, eÅ$^{-3}$ | 0.26/-0.23                |
X-Ray crystal data of CCDC 2201616 (3ab)

**Figure S2.** Molecular structure of compound 3ab showing 30% probability amplitude displacement ellipsoids (CCDC 2201616).

**Table S2.** Crystal data and structure refinement for compound 3ab.

| Property                          | Value                        |
|----------------------------------|------------------------------|
| Empirical formula                | C_{28}H_{16}BrN_{3}O_{6}     |
| Formula weight                   | 570.35                       |
| Temperature, K                   | 295.15                       |
| Crystal system                   | triclinic                    |
| Space group                      | P-1                          |
| a, Å                             | 8.9672(17)                   |
| b, Å                             | 11.983(3)                    |
| c, Å                             | 13.017(2)                    |
| α, °                             | 107.746(17)                  |
| β, °                             | 93.660(15)                   |
| γ, °                             | 109.614(18)                  |
| Volume, Å³                       | 1233.2(4)                    |
| Z                                | 2                            |
| Density (calculated), g/cm³      | 1.536                        |
| Absorption coefficient, mm⁻¹     | 1.717                        |
| F(000)                           | 576.0                        |
| Crystal size, mm³                | 0.55 × 0.5 × 0.4             |
| Radiation                        | Mo Kα (λ = 0.71073)          |
| 2Θ range for data collection, °  | 5.754 to 58.83               |
| Index ranges                     | -11 ≤ h ≤ 9, -15 ≤ k ≤ 16, -17 ≤ l ≤ 16 |
| Reflections collected | 10367 |
|-----------------------|-------|
| Independent reflections | 5707 [R_{int} = 0.0369, R_{sigma} = 0.0656] |
| Data/restraints/parameters | 5707/1/348 |
| Goodness-of-fit on F^2 | 1.021 |
| Final R indexes [I\geq 2\sigma (I)] | R_1 = 0.0576, wR_2 = 0.1315 |
| Final R indexes [all data] | R_1 = 0.0935, wR_2 = 0.1578 |
| Largest diff. peak/hole, eÅ^{-3} | 0.91/-1.23 |
**X-Ray crystal data of CCDC 2201615 (3ha)**

**Figure S3.** Molecular structure of compound 3ha showing 30% probability amplitude displacement ellipsoids (CCDC 2201615).

**Table S3.** Crystal data and structure refinement for compound 3ha.

| Property                        | Value                                      |
|---------------------------------|--------------------------------------------|
| Empirical formula               | C$_{26}$H$_{14}$ClN$_{3}$O$_{5}$          |
| Formula weight                  | 483.85                                     |
| Temperature, K                  | 295.15                                     |
| Crystal system                  | monoclinic                                 |
| Space group                     | C2/c                                       |
| a, Å                            | 22.204(3)                                  |
| b, Å                            | 11.7801(15)                                |
| c, Å                            | 17.325(2)                                  |
| α, °                            | 90                                         |
| β, °                            | 90.997(12)                                 |
| γ, °                            | 90                                         |
| Volume, Å$^3$                   | 4531.0(11)                                 |
| Z                               | 8                                          |
| Density (calculated), g/cm$^3$  | 1.419                                      |
| Absorption coefficient, mm$^{-1}$| 0.213                                      |
| F(000)                          | 1984.0                                     |
| Crystal size, mm$^3$            | 0.5 × 0.3 × 0.2                            |
| Radiation                       | Mo Kα ($λ = 0.71073$)                      |
| 2Θ range for data collection, ° | 6.016 to 58.588                            |
|                                |                             |
|--------------------------------|------------------------------|
| **Index ranges**               | -20 ≤ h ≤ 28, -10 ≤ k ≤ 16, -21 ≤ l ≤ 22 |
| **Reflections collected**      | 11513                        |
| **Independent reflections**    | 5313 \([R_{int} = 0.0414, R_{sigma} = 0.0537]\) |
| **Data/restraints/parameters** | 5313/84/384                  |
| **Goodness-of-fit on F^2**     | 1.032                        |
| **Final R indexes \([I>=2\sigma (I)]\)** | R_1 = 0.0509, wR_2 = 0.1263 |
| **Final R indexes [all data]** | R_1 = 0.0812, wR_2 = 0.1488  |
| **Largest diff. peak/hole, eÅ\(^{-3}\)** | 0.21/-0.26                |
References

1. CrysAlisPro, Agilent Technologies, Version 1.171.37.33 (release 27-03-2014 CrysAlis171 .NET).
2. Dolomanov O. V., Bourhis L. J., Gildea R. J, Howard J. A. K., Puschmann H. J. Appl. Cryst., 2009, 42, 339.
3. Palatinus L., Chapuis G. J. Appl. Cryst., 2007, 40, 786.
4. Bourhis L. J., Dolomanov O. V., Gildea R. J., Howard J. A. K., Puschmann H. Acta Crystallogr., Sect. A: Found. Adv., 2015, 71, 59.
5. Sheldrick G. M. Acta Crystallogr., Sect. C: Struct. Chem., 2015, 71, 3.
6. (a) Bozdyreva K. S., Smirnova I. V., Maslivets A. N. Russ. J. Org. Chem., 2005, 41, 1081; (b) Mashevskaya I. V., Mokrushin I. G., Bozdyreva K. S., Maslivets A. N. Russ. J. Org. Chem., 2011, 47, 253; (c) Maslivets A. N., Mashevskaya I. V., Smirnova L. I., Krasnykh O. P., Shurov S. N., Andreichikov Yu. S. Zh. Org. Khim., 1992, 28, 2545; (d) Stepanova E. E., Babenysheva A. V., Maslivets A. N. Russ. J. Org. Chem., 2011, 47, 937; (e) Mashevskaya I. V., Mokrushin I. G., Bozdyreva K. S., Maslivets A. N. Russ. J. Org. Chem., 2011, 47, 253, (a) Tret’yakov N. A., Dmitriev M. V., Maslivets A. N. Russ. J. Org. Chem., 2020, 56(8), 1367.
7. Marek L., Kolman L., Váňa J., Svoboda J., Hanusek J. Beilstein J. Org. Chem., 2021, 17(1), 527.