Supporting Information

Cycloaddition of Huisgen 1,4-dipoles: synthesis and rapid epimerization of functionalized spiropyrido[2,1-b][1,3]oxazine-pyrroles and related products

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1. General information

1.1. General analytical methods:

$^1$H and $^{13}$C NMR spectra were recorded on a Bruker Avance III HD spectrometer (at 400, 101 MHz, respectively) at 40 °C (313K) or 30 °C (303K) in CDCl$_3$, DMSO-$d_6$, C$_6$D$_6$ or acetone-$d_6$ using the residual solvent peak (CDCl$_3$: $\delta_H$ = 7.26 ppm, $\delta_C$ = 77.16 ppm; DMSO-$d_6$: $\delta_H$ = 2.50 ppm; $\delta_C$ = 39.52 ppm; C$_6$D$_6$: $\delta_H$ = 7.16 ppm, $\delta_C$ = 128.06 ppm; acetone-$d_6$: $\delta_H$ = 2.05 ppm) as internal standards. Splitting patterns of apparent multiplets were designated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broadened).

CDCl$_3$ was stored over Ag-foil and was protected from light. K$_2$CO$_3$-treated CDCl$_3$ was prepared by addition of K$_2$CO$_3$ to bulk CDCl$_3$ solution (significant D/H exchange was observed after 1 month). Note: for NMR analyses of compounds 5a–c, 8a–c, 10a, b, CDCl$_3$ and K$_2$CO$_3$-treated CDCl$_3$ were used from the same stock. Spectra of all compounds 3, 5, 8, 10 were recorded right after complete dissolution.

FT-IR spectra were recorded on a Perkin–Elmer Spectrum Two spectrometer from mulls in mineral oil. Melting points were measured with Mettler Toledo MP70 Melting Point apparatus or Khimlabpribor PTP apparatus. Thin-layer chromatography (TLC) was performed on silica gel 60 F$_{254}$ plates (Merck); spots were visualized with UV light (254 nm) or iodine vapors.

HPLC analyses were performed on Hitachi Chromaster equipped with PDA detector Hitachi Chromaster 5430. The HPLC-UV conditions were as follows: wavelength 254 nm; solvent A, H$_2$O; solvent B, acetonitrile; NUCLEODUR C18 Gravity column 3 µm, 4 × 150 mm; column temperature, 35 °C; flow rate, 1.5 mL·min$^{-1}$; gradient program: 0–8.0 min, %B = 30–100% gradient, 8.0–9.5 min, %B = 100%, 9.5–11.0 min, %B = 100–30% gradient, 11.0–11.7 min, %B = 30%.

X-ray structural analyses were performed on an Xcalibur Ruby diffractometer using a Mo X-ray source (MoKα 0.71073 Å), by scanning at 295(2) K.

HRMS were recorded on Bruker MicroTOF (ESI+).

1.2. Starting materials:

$1H$-pyrrole-2,3-diones 3 [1–4], N-allyl isatine [5], 11$H$-indeno[1,2-b]quinoxalin-11-one (6) [6] and 2-(1-benzyl-2-oxoindolin-3-ylidene)malononitrile (9) [7] were synthesized according to the literature methods. Other reagents were purchased from commercial vendors (Acros, Alfa Aesar, TCI).

1.3. General remarks:

Reactions were carried out in oven-dried (120 °C) glassware, anhydrous solvent was stored under 4Å molecular sieves. All reactions were performed under ambient atmosphere, unless otherwise noted. The term room temperature (RT) refers to 23–27 °C, the term concentrated refers to solvent evaporation under vacuum on a rotary evaporator (bath temperature 40 °C), EtOH refers to 95%-solution of ethyl alcohol.
2. X-ray analysis

Single crystals of 3a (C_{27}H_{22}N_{2}O_{6}) and 3f (C_{31}H_{28}N_{2}O_{6}) were obtained from EtOH via slow evaporation. Single crystals of 8b (C_{30}H_{21}N_{3}O_{5}) were obtained from hexane/dichloromethane mixture via slow evaporation. Single crystals of 8c (C_{30}H_{21}N_{3}O_{5}) were obtained from acetonitrile via slow evaporation.

Crystal structure determination

The unit cell parameters and the X-ray diffraction intensities were measured on a Xcalibur Ruby diffractometer (Agilent Technologies). The empirical absorption correction was introduced by multi-scan method using SCALE3 ABSPACK algorithm[8]. Using OLEX2[9], the structures were solved with the SHELXS[10] program using Direct Methods and refined by the full-matrix least-squares minimization in the anisotropic approximation for all non-hydrogen atoms with the SHELXL[11] program. Hydrogen atoms were positioned geometrically and refined using a riding model.
Fig. S1. Structure of compound 3a showing 30% probability amplitude displacement ellipsoids (CCDC 2119396).

Table S1. Crystal data and structure refinement for 3a.

| Property                        | Value                        |
|---------------------------------|------------------------------|
| Empirical formula               | C_{27}H_{22}N_{2}O_{6}       |
| Formula weight                  | 470.46                       |
| Temperature, K                  | 295.15                       |
| Crystal system                  | triclinic                    |
| Space group                     | P-1                          |
| a, Å                            | 9.838(2)                     |
| b, Å                            | 10.401(2)                    |
| c, Å                            | 12.2553(17)                  |
| α, °                            | 102.291(17)                  |
| β, °                            | 100.426(16)                  |
| γ, °                            | 103.17(2)                    |
| Volume, Å³                      | 1157.9(4)                    |
| Z                               | 2                            |
| Density (calculated), g·cm⁻³    | 1.349                        |
| Absorption coefficient, mm⁻¹    | 0.096                        |
| F(000)                          | 492.0                        |
| Crystal size, mm³               | 0.35 × 0.2 × 0.12            |
| Radiation                       | Mo Kα (λ = 0.71073)          |
| 2Θ range for data collection, ° | 6.12 to 58.944               |
| Index ranges                    | -10 ≤ h ≤ 12, -14 ≤ k ≤ 11, -13 ≤ l ≤ 15 |
| Reflections collected           | 9360                         |
| Independent reflections         | 5376 [R_{int} = 0.0542, R_{sigma} = 0.0838] |
| Data/restraints/parameters      | 5376/0/319                   |
| Goodness-of-fit on F²           | 1.067                        |
| Final R indexes [I>2σ(I)]       | R₁ = 0.0672, wR₂ = 0.1540    |
| Final R indexes [all data]      | R₁ = 0.1247, wR₂ = 0.2013    |
| Largest diff. peak/hole, eÅ⁻³   | 0.24/-0.22                   |
**Fig. S2.** Structure of compound 3f showing 30% probability amplitude displacement ellipsoids (CCDC 2119397).

**Table S2.** Crystal data and structure refinement for 3f.

| Property                        | Value                                      |
|---------------------------------|--------------------------------------------|
| Empirical formula               | C$_{31}$H$_{28}$N$_2$O$_8$                  |
| Formula weight                  | 556.55                                     |
| Temperature, K                  | 295.15                                     |
| Crystal system                  | triclinic                                  |
| Space group                     | P-1                                        |
| a, Å                            | 11.1868(16)                                |
| b, Å                            | 11.4255(18)                                |
| c, Å                            | 12.2739(16)                                |
| α, °                            | 95.263(12)                                 |
| β, °                            | 107.966(12)                                |
| γ, °                            | 103.507(13)                                |
| Volume, Å$^3$                   | 1428.1(4)                                  |
| Z                               | 2                                          |
| Density (calculated), g·cm$^{-3}$| 1.294                                      |
| Absorption coefficient, mm$^{-1}$| 0.094                                      |
| F(000)                          | 584.0                                      |
| Crystal size, mm$^3$            | 0.6 × 0.5 × 0.4                            |
| Radiation                       | Mo Kα (λ = 0.71073)                        |
| 2Θ range for data collection, ° | 6.85 to 58.718                             |
| Index ranges                    | -14 ≤ h ≤ 13, -15 ≤ k ≤ 15, -16 ≤ l ≤ 15 |
| Reflections collected           | 10695                                      |
| Independent reflections         | 6592 [R$_{int}$ = 0.0308, R$_{sigma}$ = 0.0530] |
| Data/restraints/parameters      | 6592/0/375                                 |
| Goodness-of-fit on F$^2$        | 1.045                                      |
| Final R indexes [I$>2σ$(I)]    | R$_1$ = 0.0592, wR$_2$ = 0.1542             |
| Final R indexes [all data]     | R$_1$ = 0.0870, wR$_2$ = 0.1804             |
| Largest diff. peak/hole, eÅ$^{-3}$ | 0.24/-0.22                              |
**Table S3.** Crystal data and structure refinement for 8b.

| Property                                      | Value                                      |
|-----------------------------------------------|--------------------------------------------|
| Empirical formula                             | C_{30}H_{21}N_{3}O_{5}                      |
| Formula weight                                | 503.50                                     |
| Temperature, K                                 | 295.15                                     |
| Crystal system                                | triclinic                                  |
| Space group                                   | P-1                                        |
| a, Å                                          | 11.4672(12)                                |
| b, Å                                          | 14.0604(14)                                |
| c, Å                                          | 15.6426(15)                                |
| α, °                                          | 99.666(8)                                  |
| β, °                                          | 96.992(8)                                  |
| γ, °                                          | 94.581(8)                                  |
| Volume, Å³                                    | 2454.8(4)                                  |
| Z                                             | 4                                          |
| Density (calculated), g·cm⁻³                  | 1.362                                      |
| Absorption coefficient, mm⁻¹                  | 0.094                                      |
| F(000)                                        | 1048.0                                     |
| Crystal size, mm³                             | 0.55 × 0.3 × 0.12                          |
| Radiation                                     | Mo Kα (λ = 0.71073)                        |
| 2θ range for data collection, °              | 4.32 to 58.972                             |
| Index ranges                                  | -12 ≤ h ≤ 15, -16 ≤ k ≤ 18, -20 ≤ l ≤ 20  |
| Reflections collected                         | 22145                                      |
| Independent reflections                      | 11448 [R_{int} = 0.0398, R_{sigma} = 0.0583]|
| Data/restraints/parameters                    | 11448/0/701                                |
| Goodness-of-fit on F²                         | 1.020                                      |
| Final R indexes [l>=2σ (I)]                  | R₁ = 0.0558, wR₂ = 0.1314                  |
| Final R indexes [all data]                   | R₁ = 0.0984, wR₂ = 0.1688                  |
| Largest diff. peak/hole, eÅ⁻³                 | 0.20/-0.24                                 |
Fig. S4. Structure of compound 8c showing 30% probability amplitude displacement ellipsoids (CCDC 2119398).

Table S4. Crystal data and structure refinement for 8c.

| Property                        | Value                          |
|---------------------------------|--------------------------------|
| Empirical formula               | C$_{30}$H$_{21}$N$_{3}$O$_{5}$  |
| Formula weight                  | 503.50                         |
| Temperature, K                  | 295.15                         |
| Crystal system                  | monoclinic                     |
| Space group                     | P2$_{1}$/n                      |
| a, Å                            | 8.7697(18)                     |
| b, Å                            | 19.206(5)                      |
| c, Å                            | 14.480(3)                      |
| α, °                            | 90                             |
| β, °                            | 94.70(2)                       |
| γ, °                            | 90                             |
| Volume, Å$^3$                   | 2430.7(10)                     |
| Z                               | 4                              |
| Density (calculated), g·cm$^{-3}$ | 1.376                          |
| Absorption coefficient, mm$^{-1}$ | 0.095                          |
| F(000)                          | 1048.0                         |
| Crystal size, mm$^3$            | 0.5 × 0.25 × 0.12              |
| Radiation                       | Mo Kα (λ = 0.71073)            |
| 2Θ range for data collection, ° | 5.644 to 58.886                |
| Index ranges                    | -11 ≤ h ≤ 8, -24 ≤ k ≤ 26, -18 ≤ l ≤ 15 |
| Reflections collected           | 16407                          |
| Independent reflections         | 5791 [R$_{int}$ = 0.0548, R$_{sigma}$ = 0.0666] |
| Data/restraints/parameters      | 5791/0/346                     |
| Goodness-of-fit on F$^2$        | 1.019                          |
| Final R indexes [I>=2σ(I)]      | R$_1$ = 0.0652, wR$_2$ = 0.1616 |
| Final R indexes [all data]      | R$_1$ = 0.1360, wR$_2$ = 0.2173 |
| Largest diff. peak/hole, eÅ$^{-3}$ | 0.21/0.18                  |
3. NMR spectra of products 3a–k

3.1. Copies of NMR spectra for product 3a

$^1$H NMR of 3a, CDCl$_3$, 313 K

$^{13}$C NMR of 3a, CDCl$_3$, 313 K
$^1$H NMR of 3a, DMSO-$d_6$, 313 K

$^{13}$C NMR of 3a, DMSO-$d_6$, 313 K
$^1$H NMR of 3a, C$_5$D$_5$, 313 K

$^1$H NMR of 3a, Acetone-$d_6$, 313 K
3.2. Copies of NMR spectra for product 3b

$^1$H NMR of 3b, DMSO-$d_6$, 313 K

$^{13}$C NMR of 3b, DMSO-$d_6$, 313 K
3.3. Copies of NMR spectra for product 3c
3.4. Copies of NMR spectra for product 3d

$^1$H NMR of 3d, DMSO-$d_6$, 313 K

$^{13}$C NMR of 3d, DMSO-$d_6$, 313 K
3.5. Copies of NMR spectra for product 3e

$^{1}$H NMR of 3e, CDCl$_3$, 313 K

$^{13}$C NMR of 3e, CDCl$_3$, 313 K
$^1$H NMR of 3e, DMSO-$d_6$, 313 K

$^{13}$C NMR of 3e, DMSO-$d_6$, 313 K
3.6. Copies of NMR spectra for product 3f

$^1$H NMR of 3f, CDCl$_3$, 313 K

$^{13}$C NMR of 3f, CDCl$_3$, 313 K
3.7. Copies of NMR spectra for product 3g

$^1$H NMR of 3g, DMSO-$d_6$, 313 K

$^{13}$C NMR of 3g, DMSO-$d_6$, 313 K
3.8. Copies of NMR spectra for product 3h

$^1$H NMR of 3h, CDCl$_3$, 313 K

$^{13}$C NMR of 3h, CDCl$_3$, 313 K
3.9. Copies of NMR spectra for product 3i

^1H NMR of 3i, DMSO-d_6, 313 K

^13C NMR of 3i, DMSO-d_6, 313 K
3.10. Copies of NMR spectra for product 3j

^1^H NMR of 3j, CDCl₃, 313 K

^1^C NMR of 3j, CDCl₃, 313 K
3.11. Copies of NMR spectra for product 3k

**$^1$H NMR of 3k, CDCl$_3$, 313 K**

![NMR spectrum image]

**$^{13}$C NMR of 3k, CDCl$_3$, 313 K**

![NMR spectrum image]
4. Synthesis, HPLC and NMR spectra of compounds 5a-c

4.1. Synthesis of product 5a

Dimethyl 1-benzyl-2-oxo-9a’H-spiro[indoline-3,2’-pyrido[2,1-b][1,3]oxazine]-3’,4’-dicarboxylate (5a): The compound was prepared according to the modified (1.2 equiv. of DMAD and pyridine instead of 1.0 equiv.) reported procedure [12]: DMAD (78 µL, 0.64 mmol, 1.2 equiv.) and pyridine (64 µL, 0.64 mmol, 1.2 equiv.) were added to a solution of N-benzylisatin (126 mg, 0.53 mmol, 1 equiv.) in 1,2-dimethoxyethane (DME, 10 mL) under Ar atmosphere. The reaction mixture was stirred at RT for 1d. The reaction mixture was concentrated, the residue was triturated with EtOH, filtered and washed with EtOH and hexane, affording a mixture of inseparable diastereomers as a pale-yellow solid (222 mg, 70% yield); \( R_t = 0.59 \) (Hex/EA 1:1); m.p. 179–181 °C (decomp.) [lit. not reported].

NMR spectra of 5a in CDCl3: mixture of inseparable diastereomers, \( \text{dr} = \sim 4.8 : 1 \) (A : B) (the same \( \text{dr} \) was observed in K₂CO₃-treated-CDCl₃). \(^1\text{H NMR (400 MHz, CDCl₃)}: \delta = 7.43–7.38 \) (m, 2H, A + B), 7.36–7.13 (m, 5H, A + B), 7.01–6.89 (m, 1H, A + B), 6.76–6.68 (m, 1.83H, A + B), 6.40 (d[A], \( J = 7.5 \), 1H, A + B), 6.26 (dd, \( J = 10.0 \), 6.0 Hz, 1H, A + B), 6.07 (dd, \( J = 3.2 \), 1.3 Hz, 0.17H, B), 5.65 (dd, \( J = 10.0 \), 3.3 Hz, 0.83H, A), 5.53 (dd, \( J = 9.9 \), 3.3 Hz, 0.17H, B), 5.37–5.28 (m, 1H, A + B), 5.06 (d[A], \( J = 15.6 \) Hz, 1H, A + B), 4.80 (d, \( J = 15.6 \) Hz, 0.17H, B), 4.75 (d, \( J = 15.7 \) Hz, 0.83H, A), 3.97 (s, 2.48H, A), 3.95 (s, 0.52H, B), 3.33 (s, 0.52H, B), 3.31 (s, 2.48H, A). \(^{13}\text{C NMR (101 MHz, CDCl₃)}:
$\delta$ (A, major) = 174.2, 163.63, 163.56, 145.6, 144.6, 135.9, 130.2, 128.9 (2C), 128.6, 127.8 (2C), 127.8, 125.4, 124.7, 123.3, 123.1, 116.6, 109.5, 106.2, 101.9, 79.0, 76.9, 53.5, 51.8, 44.1.

NMR spectra of 5a in DMSO-$d_6$: mixture of inseparable diastereomers, dr = ~ 1.2 : 1 (A : B). 

$^1$H NMR (400 MHz, DMSO-$d_6$): $\delta$ = 7.62 (dd, $J = 7.4, 1.2$ Hz, 0.55H, A), 7.43–7.39 (m, 2H, A + B), 7.38–7.32 (m, 2H, A + B), 7.31–7.22 (m, 2H, A + B), 7.05–6.85 (m, 2.45H, A + B), 6.70–6.58 (m, 1H, A + B), 6.48 (dd, $J = 3.3, 1.3$ Hz, 0.45H, B), 6.41–6.25 (m, 1H, A + B), 6.16 (dd, $J = 3.4, 1.2$ Hz, 0.55H, A), 5.67 (dd, $J = 9.9, 3.2$ Hz, 0.45H, B), 5.58 (dd, $J = 9.9, 3.4$ Hz, 0.55H, A), 5.50–5.35 (m, 1H, A + B), 5.03–4.73 (m, 2H, A + B), 3.92 (s, 1.36H, B), 3.90 (s, 1.64H, A), 3.29 (s, 1.64H, A), 3.27 (s, 1.36H, B). 

$^{13}$C NMR (101 MHz, DMSO-$d_6$): $\delta$ (A + B) = 173.33, 173.31, 163.3, 162.8, 162.6, 162.5, 145.3, 144.4, 144.2, 142.4, 136.02, 136.01, 130.12, 130.08, 128.57 (2C), 128.52 (2C), 128.07, 127.50 (2C), 127.46, 127.42 (4C), 125.9, 125.5, 125.3, 125.1, 124.5, 122.7, 122.6, 122.4, 116.1, 116.0, 109.7, 109.2, 106.8, 105.5, 101.9, 101.3, 78.9, 78.2, 76.8, 76.0, 53.6, 53.5, 51.8, 51.7, 43.2, 42.9.
4.1.1. Copies of NMR spectra for product 5a

$^1$H NMR of 5a, CDCl$_3$, 303 K

$^{13}$C NMR of 5a, CDCl$_3$, 303 K
4.2. Synthesis of product 5b

Dimethyl 1-benzyl-2-oxo-11b’H-spiro[indoline-3,2’-[1,3]oxazino[2,3-a]isoquinoline]-3’,4’-dicarboxylate (5b): The compound was prepared according to the reported procedure [13]: DMAD (125 µL, 1 mmol, 1.0 equiv.) and isoquinoline (120 µL, 1 mmol, 1.0 equiv.) were added to a solution of N-benzylisatin (237 mg, 1.0 mmol, 1 equiv.) in dichloromethane (DCM, 15 mL). The reaction was stirred at RT for 2d. The reaction mixture was concentrated, the residue was triturated with EtOH, filtered and washed with EtOH and hexane, affording a mixture of inseparable* diastereomers as a pale-yellow solid (436 mg, 86% yield); Rf = 0.57 + 0.66 (Hex/EA 1:1); m.p. 217–219 °C (decomp.) [lit. 235–237 °C].

* inseparable by crystallization, however separation via column chromatography is possible

NMR spectra of 5b in CDCl3: mixture of inseparable diastereomers, dr = ~ 4.8 : 1 (A : B). $^1$H NMR (400 MHz, CDCl3): δ = 7.47–7.4 (m, 2.17H, A + B), 7.38–7.25 (m, 5H, A + B), 7.24–6.99 (m, 4.83H, A + B), 6.94 (t, J = 7.5 Hz, 0.83H, A), 6.79 (d, J = 7.9 Hz, 0.17H, B), 6.74 (d, J = 7.8 Hz, 0.83H, A), 6.53 (s, 0.17H, B), 6.43 (d[A], J = 7.7 Hz, 1H, A + B), 5.84 (d, J = 7.7 Hz, 0.83H, A), 5.83 (d, J = 7.7 Hz, 0.17H, B), 5.09 (d, J = 15.6 Hz, 1H, A + B), 4.87 (d, J = 15.6 Hz, 0.83H, A), 4.78 (d, J = 15.7 Hz, 0.17H, B), 4.00 (s, 2.48H, A), 3.98 (s, 0.52H, B), 3.35 (s, 0.52H, B), 3.33 (s, 2.48H, A). $^{13}$C NMR (101 MHz, CDCl3): δ (A, major) = 174.8, 163.8, 163.7, 145.6, 144.4, 135.9, 130.2, 129.9, 129.7,
NMR spectra of 5b in K$_2$CO$_3$-treated-CDCl$_3$: mixture of inseparable diastereomers, $\text{dr} = \sim 1:1$ (A*: B).  $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.46$–7.40 (m, 2.5H, A + B), 7.39–7.26 (m, 5H, A + B), 7.24–7.01 (m, 4.5H, A + B), 6.94 (t, $J = 7.5$ Hz, 0.5H, A), 6.79 (d, $J = 7.8$ Hz, 0.5H, B), 6.74 (d, $J = 7.8$ Hz, 0.5H, A), 6.53 (s, 0.5H, B), 6.43 (d, $J = 7.7$ Hz, 0.5H, A), 6.43 (d, $J = 7.8$ Hz, 0.5H, B), 5.84 (d, $J = 7.7$ Hz, 0.5H, A), 5.83 (d, $J = 7.8$ Hz, 0.5H, B), 5.10 (d, $J = 15.7$ Hz, 0.5H, B), 5.09 (d, $J = 15.6$ Hz, 0.5H, A), 4.87 (d, $J = 15.6$ Hz, 0.5H, B), 4.78 (d, $J = 15.6$ Hz, 0.5H, A), 4.00 (s, 1.5H, A), 3.98 (s, 1.5H, B), 3.35 (s, 1.5H, B), 3.33 (s, 1.5H, A).  $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$(A, major) = 174.8, 163.78, 163.74, 145.6, 144.4, 135.94, 130.2, 129.9, 129.7, 128.9 (2C), 128.7, 128.2, 127.8, 127.7 (2C), 127.3, 126.3, 125.4, 123.5, 123.3, 123.2, 109.4, 105.4, 105.1, 79.7, 77.6, 53.6, 51.8, 44.1.  
$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$(B, minor) = 173.8, 164.0, 163.66, 145.2, 143.2, 135.87, 131.1, 130.4, 130.1, 129.8, 128.8 (2C), 127.9 (2C), 127.79, 127.1, 126.3, 126.0, 125.37, 124.3, 123.9, 122.8, 109.6, 105.2, 105.0, 80.3, 78.3, 53.6, 52.0, 44.6. 
*“A” denotes major diastereomer in acidic CDCl$_3$

NMR spectra of 5b in DMSO-d$_6$: mixture of inseparable diastereomers, $\text{dr} = \sim 1:1$ (A : B).  $^1$H NMR (400 MHz, DMSO-d$_6$): $\delta = 7.81$ (d, $J = 7.2$ Hz, 0.5H, A / B), 7.50–7.24 (m, 8.5H, A + B), 7.23–7.16 (m, 1H, A + B), 7.10–6.94 (m, 3H, A + B), 6.93–6.86 (m, 0.5H, A), 6.71 (d, $J = 5.2$ Hz, 0.5H, A / B), 6.69 (d, $J = 5.2$ Hz, 0.5H, A / B), 6.67 (s, 0.5H, A / B), 6.01 (d, $J = 7.8$ Hz, 0.5H, A / B), 6.00 (d, $J = 7.7$ Hz, 0.5H, A / B), 5.09–4.75 (m, 2H, A + B), 3.96 (s, 1.5H, A / B), 3.93 (s, 1.5H, A / B), 3.31 (s, 1.5H, A / B), 3.30 (s, 1.5H, A / B).  $^{13}$C NMR (101 MHz, DMSO-d$_6$): $\delta$(A + B) = 173.9, 173.0, 163.4, 162.9, 162.7, 162.6, 145.3, 144.5, 144.0, 142.5, 136.1, 136.0, 130.2 (2C), 129.8, 129.7, 129.6, 129.5, 128.6 (2C), 128.5 (2C), 128.0, 127.7, 127.5, 127.45 (5C), 127.4, 127.35, 127.2, 126.9, 125.5, 125.38, 125.36, 125.1, 124.7, 124.5, 123.9, 122.8, 122.7, 122.6, 109.7, 109.4, 105.8, 104.8, 104.3, 104.2, 79.4, 78.6, 77.7, 76.8, 53.6, 53.5, 51.72, 51.65, 43.3, 42.8.
4.2.1. Copies of NMR spectra for product 5b

**$^1$H NMR of 5b, CDCl$_3$, 303 K**

**$^{13}$C NMR of 5b, CDCl$_3$, 303 K**
$^1$H NMR of 5b, $\text{K}_2\text{CO}_3$-treated-CDCl$_3$, 303 K

$^{13}$C NMR of 5b, $\text{K}_2\text{CO}_3$-treated-CDCl$_3$, 303 K
$^1$H NMR of 5b, DMSO-$d_6$, 303 K

$^{13}$C NMR of 5b, DMSO-$d_6$, 303 K
4.3. Synthesis of product 5c

Dimethyl 1-allyl-2-oxo-4a'-H-spiro[indoline-3,3'-[1,3]oxazino[3,2-a]quinoline]-1',2'-dicarboxylate (5c): The compound was prepared according to the reported procedure [14]: DMAD (65 µL, 0.53 mmol, 1.2 equiv.) and quinoline (63 µL, 0.53 mmol, 1.2 equiv.) were added to a solution of N-allylisatin (82 mg, 0.44 mmol, 1 equiv.) in toluene (3 mL). The reaction mixture was heated at 110 °C for 12h. The reaction mixture was concentrated, the residue was triturated with EtOH, filtered and washed with EtOH and hexane, affording a mixture of inseparable diastereomers as an off-white solid (156 mg, 77% yield); $R_f = 0.57 + 0.61$ (Hex/EA 1:1)**; m.p. 185–188 °C (decomp.) [lit. 164–166 °C].

* reaction was performed in a screw capped reaction vial placed in a preheated heating block
** inseparable by crystallization, however separation via column chromatography is possible
*** in original report, compound was purified by column chromatography (Hex/EA 90:10), however $R_f$ in this system is around zero

** NMR spectra of 5c in CDCl3: mixture of inseparable diastereomers, $d_r = \sim 1 : 1$ (A : B) (the same $d_r$ was observed in K₂CO₃-treated-CDCl₃). **¹H NMR (400 MHz, CDCl₃): $\delta = 7.38–7.17$ (m, 3.5H, A + B), 7.07–6.98 (m, 2.5H, A + B), 6.97–6.87 (m, 1H, A + B), 6.86–6.74 (m, 2H, A + B), 6.15 (d, $J = 4.3$ Hz, 0.5H, A / B), 5.99 (dd, $J = 9.9, 4.3$ Hz, 0.5H, A / B), 5.92–5.77 (m, 1.5H, A + B), 5.67 (d, $J = 4.3$ Hz, 0.5H, A / B), 5.41–5.32 (m, 1H, A + B), 5.29–5.19 (m, 1H, A + B), 4.47–4.35 (m, 1H, A + B), 4.31–4.16 (m, 1H, A + B), 3.90 (s, 1.5H, A / B), 3.88 (s, 1.5H, A / B), 3.59 (s, 1.5H, A / B), 3.44 (s,
$^{13}$C NMR (101 MHz, CDCl$_3$): $\delta (A + B) = 173.7, 172.2, 164.6, 164.4, 163.8, 163.7, 144.7, 144.6, 143.3, 142.2, 135.8, 135.6, 131.3, 131.2, 130.6, 130.3, 130.0, 129.9 (2C), 129.7, 129.3, 128.8, 128.5, 128.1, 123.7, 123.2, 123.1, 123.0, 122.7, 122.5, 122.0, 121.9, 121.4, 119.8, 118.7, 118.2, 118.0, 117.8, 115.4, 114.4, 109.6, 109.6, 79.64, 79.62, 78.9, 78.6, 53.4, 53.3, 52.4, 52.3, 43.2, 42.6.

Note: no change in dr was observed after 12d.

NMR spectra of 5c in DMSO-$d_6$: mixture of inseparable diastereomers, dr = ~ 1 : 1 (A : B). $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta = 7.68 (d, J = 7.0 Hz, 0.5H, A / B), 7.44–7.22 (m, 3H, A + B), 7.15–7.02 (m, 1.5H, A + B), 7.01–6.91 (m, 3H, A + B), 6.87 (d, J = 6.9 Hz, 0.5H, A / B), 6.74 (d, J = 8.2 Hz, 0.5H, A / B), 6.06 (dd, J = 9.8, 4.3 Hz, 0.5H, A / B), 5.99 (dd, J = 9.8, 4.4 Hz, 0.5H, A / B), 5.92 (d, J = 4.4 Hz, 0.5H, A / B), 5.89–5.74 (m, 1.5H, A + B), 5.35–5.25 (m, 1H, A + B), 5.24–5.10 (m, 1H, A + B), 4.41–4.12 (m, 2H, A + B), 3.88 (s, 1.5H, A / B), 3.84 (s, 1.5H, A / B), 3.54 (s, 1.5H, A / B), 3.40 (s, 1.5H, A / B). $^{13}$C NMR (101 MHz, DMSO-$d_6$): $\delta (A + B) = 172.6, 171.3, 164.1, 163.4, 163.2, 163.1, 144.2, 143.9, 142.5, 140.8, 135.3, 134.6, 131.4, 131.3, 130.4, 130.3, 130.2, 129.8, 128.84, 128.77, 128.7, 128.6, 128.4, 127.5, 124.1, 122.80, 122.75, 122.7, 122.4, 122.3, 122.1, 121.1, 120.9, 119.8, 118.7, 118.5, 117.4, 117.2, 114.4, 114.0, 109.9, 109.4, 78.9, 78.7, 78.3, 77.7, 53.5, 53.3, 52.4, 52.2, 42.1, 41.6.

Additional experiments on acid-catalyzed isomerization.

Compound 5c (0.05 mmol) was treated with $p$-TSA (20 mol%) or HCl$_{conc}$ (60 mol%) in 1 mL of DCM at RT, after 6h reaction mixtures were analyzed by LC. No significant dr change was observed in either case.
4.3.1. Copies of NMR spectra for product 5c

\[\text{\textsuperscript{1}H NMR of 5c, CDCl}_3, 303 \text{ K}\]

\[\text{\textsuperscript{13}C NMR of 5c, CDCl}_3, 303 \text{ K}\]
$^1$H NMR of 5c, DMSO-$d_6$, 303 K

$^{13}$C NMR of 5c, DMSO-$d_6$, 303 K
5. Synthesis, HPLC and NMR spectra of compounds 8a-c

5.1. Synthesis of product 8a

Dimethyl 9a’H-spiro[inden[1,2-b]quinoxaline-11,2’-pyrido[2,1-b][1,3]oxazine]-3’,4’-dicarboxylate (8a): The compound was prepared according to the modified (1.5 equiv. of DMAD and pyridine instead of 1.0 equiv.) reported procedure [15]: a solution of DMAD (185 µL, 1.5 mmol, 1.5 equiv.) in 2 mL of DCM was added to a solution of 6 (232 mg, 1.0 mmol, 1 equiv.) and pyridine (120 µL, 1.5 mmol, 1.5 equiv.) in dichloromethane (DCM, 10 mL) over 15 min (via syringe). The reaction mixture was stirred at RT for 1d. The reaction mixture was concentrated, the residue was triturated with EtOH, filtered and washed with EtOH affording a mixture of inseparable diastereomers as a yellow solid (240 mg, 53% yield); \( R_f = 0.53 \) (Hex/EA 1:1) [lit. 0.54 (Hex/EA 1:1)]; m.p. 168–170 °C (decomp.) [lit. 167–169 °C]. HRMS (ESI): \( m/z \) calcd for C26H19N3O5: 454.1397 [M+H]+; found: 454.1397.

**HPLC of the reaction mixture**

**HPLC of the isolated product 8a**

NMR spectra of 8a in K2CO3-treated-CDCl3: (the same dr was observed in CDCl3) mixture of inseparable diastereomers, \( \text{dr} = \sim 16:1 \) (A : B). \( ^1H \text{ NMR (400 MHz, CDCl}_3\)): \( \delta = 8.21–8.10 \) (m, 2H, A + B), 8.09–8.02 (m, 1H, A + B), 7.78–7.65 (m, 2H, A + B), 7.59–7.46 (m, 3H, A + B), 7.02 (dd, \( J = 3.3, 1.3 \text{ Hz}, 0.94 \text{H, A} \)), 6.51 (d, \( J = 7.8 \text{ Hz}, 0.06 \text{H, B} \)), 6.47 (d, \( J = 7.6 \text{ Hz}, 0.94 \text{H, A} \)), 6.39 (dd, \( J = 3.2, 1.3 \text{ Hz}, 0.06 \text{H, B} \)), 6.24 (dd[A], \( J = 9.9, 6.1 \text{ Hz, 1H, A + B} \)), 5.53 (dd[A], \( J = 10.0, 3.3 \text{ Hz, 1H, A} \))...
NMR spectra of 8a in DMSO-\textit{d}_6: mixture of inseparable diastereomers, \textit{dr} = ~ 3.2 : 1 (A : B). \textbf{\textit{1H NMR (400 MHz, DMSO-\textit{d}_6)}}: \(\delta = 8.19–8.00\) (m, 3.24H, A + B), 7.90–7.73 (m, 2H, A + B), 7.68–7.55 (m, 2H, A + B), 7.42 (d, \(J = 6.7\) Hz, 0.76H, A), 6.79 (dd, \(J = 3.4, 1.3\) Hz, 0.76H, A), 6.76 (d, \(J = 7.6\) Hz, 0.24H, B), 6.73 (d, \(J = 7.6\) Hz, 0.76H, A), 6.47 (d, \(J = 2.7\) Hz, 0.24H, B), 6.36–6.24 (m, 1H, A + B), 5.66–5.51 (m, 1H, A + B), 5.51–5.40 (m, 1H, A + B), 3.95 (s, 2.29H, A), 3.92 (s, 0.71H, B), 3.20 (s, 0.71H, B), 3.19 (s, 2.29H, A). \textbf{\textit{13C NMR (101 MHz, DMSO-\textit{d}_6)}}: (A, major) \(\delta = 162.8, 162.7, 161.3, 153.4, 147.1, 145.3, 142.1, 140.4, 137.7, 132.4, 130.6, 130.5, 129.5, 129.5, 128.9, 125.4, 125.3, 123.3, 122.1, 116.1, 106.7, 101.9, 79.4, 78.8, 53.6, 51.6. \textbf{\textit{13C NMR (101 MHz, DMSO-\textit{d}_6)}}: (B, minor) \(\delta = 163.2, 162.7, 162.4, 154.5, 148.0, 144.6, 141.9, 140.8, 136.0, 132.4, 130.6, 130.2, 129.5, 129.3, 128.9, 126.2, 125.6, 125.2, 121.9, 116.2, 108.5, 101.2, 79.2, 79.0, 53.5, 51.6.
5.1.1. Comparison of NMR spectra of 8a and the reported structure

| 1H NMR | 13C NMR | **Difference, ppm** |
|--------|---------|---------------------|
| **Reported in [15], 4a** | **Observed, 8a*** | **Reported in [15], 4a** | **Observed, 8a** |  
| δ, ppm | int., mult. | J, Hz | δ, ppm | int., mult. | J, Hz | δ, ppm | δ, ppm |
| 3.16 | 3H, s | | 3.16 | 3H, s | | 51.4 | 51.4 | 0 |
| 4 | 3H, s | | 3.99 | 3H, s | | 53.3 | 53.3 | 0 |
| 5.36 | 1H, m | | 5.29–5.40 | 1H, m | | 79.4 | 79.3 | -0.1 |
| 5.53 | 1H, m | | 5.53 | 1H, dd | 10.0, 3.3 | | 80.0 | 79.9 | -0.1 |
| 6.24 | 1H, m | | 6.24 | 1H, dd | 9.9, 6.1 | | 101.6 | 101.5 | -0.1 |
| 6.46 | 1H, d | 7.5 | | 6.47 | 1H, d | 7.6 | | 107.4 | 107.4 | 0 |
| 7.01 | 1H, s | | 7.01 | 1H, dd | 3.3, 1.3 | | 116.5 | 116.5 | 0 |
| 7.46 | 5H, m | | 7.45–7.58 | 3H, m | | 123.3 | 122.3 | -1 |
| | | | 7.65–7.78 | 2H, m | | 123.6 | 123.6 | 0 |
| 8.07 | 1H, d | 7.5 | | 8.01–8.08 | 1H, m | | 124.8 | 124.8 | 0 |
| 8.16 | 2H, m | | 8.09–8.21 | 2H, m | | 125.0 | 125.0 | 0 |

* first proton signal was set to 3.16 ppm

** first carbon signal was set to 51.4 ppm
5.1.2. Copies of NMR spectra for product 8a

$^1$H NMR of 8a, $\text{K}_2\text{CO}_3$-treated-CDCl$_3$, 303 K

$^{13}$C NMR of 8a, $\text{K}_2\text{CO}_3$-treated-CDCl$_3$, 303 K
$^1$H NMR of 8a, DMSO-$d_6$, 303 K

$^{13}$C NMR of 8a, DMSO-$d_6$, 303 K
5.2. Synthesis of product 8b

Dimethyl 11b’H-spiro[indeno[1,2-b]quinoxaline-11,2’-[1,3]oxazino[2,3-a]isoquinoline]-3’,4’-dicarboxylate (8b): The compound was prepared according to the modified (1.5 equiv. of DMAD and pyridine instead of 1.0 equiv.) reported procedure [15]: a solution of DMAD (185 µL, 1.5 mmol, 1.5 equiv.) in 2 mL of dichloromethane (DCM) was added to a solution of 11H-indeno[1,2-b]quinoxalin-11-one 6 (232 mg, 1.0 mmol, 1 equiv.) and isoquinoline (180 µL, 1.5 mmol, 1.5 equiv.) in DCM (10 mL) over 15 min (via syringe). The reaction mixture was stirred at RT for 1 d. The reaction mixture was concentrated, the residue was triturated with EtOH, filtered and washed with EtOH affording a mixture of inseparable* diastereomers as a bright-yellow solid (414 mg, 82% yield); Rf = 0.49 + 0.59 (Hex/EA 1:1) [lit. 0.59 (Hex/EA 1:1)]**; m.p. 214–217 °C (decomp.) [lit. 190–193 °C].

HRMS (ESI): m/z calcd for C30H21N3O5: 504.1554 [M+H]+; found: 504.1554.

* inseparable by crystallization, however separation via column chromatography is possible
** in the original work, only one diastereomer was reported, see the manuscript

**HPLC of the reaction mixture**

**HPLC of the isolated product 8b**

NMR spectra of 8b in CDCl3: mixture of inseparable diastereomers, d.r. = ~ 2.6 : 1 → 12 : 1 (A : B; in 30–40 min). 1H NMR (400 MHz, CDCl3): (A, major) δ = 8.26–8.22 (m, 2H), 8.14–8.07 (m, 1H), 7.83–7.76 (m, 1H), 7.76–7.69 (m, 1H), 7.59–7.45 (m, 4H), 7.26–7.20 (m, 1H), 7.13–7.08 (m, 1H), 7.08–6.98 (m, 2H), 6.52 (d, J = 7.8 Hz, 1H), 5.87 (d, J = 7.8 Hz, 1H), 4.03 (s, 3H), 3.20 (s, 3H). 13C NMR (101 MHz, CDCl3): (A, major) δ = 164.1, 163.8, 162.5, 154.0, 147.7, 145.7, 142.2, 141.6,
NMR spectra of 8b in K$_2$CO$_3$-treated-CDCl$_3$: mixture of inseparable diastereomers, $\text{dr} = \sim 1.1 : 1$ (A : B).  $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 8.26$–8.23 (m, 0.53H, A), 8.19–8.14 (m, 1H, A + B), 8.13–8.07 (m, 1.47H, A + B), 7.84–7.75 (m, 1H, A + B), 7.74–7.67 (m, 1H, A + B), 7.67–7.44 (m, 3.47H, A + B), 7.26–7.18 (m, 1H, A + B), 7.13–6.98 (m, 3H, A + B), 6.84 (s, 0.53H, A), 6.52 (d, $J = 7.8$ Hz, 0.53H, A), 6.52 (d, $J = 7.8$ Hz, 0.47H, B), 5.94–5.75 (m, 1H, A + B), 4.03 (s, 1.47H, B), 4.02 (s, 1.53H, A), 3.19 (s, 1.47H, B), 3.18 (s, 1.53H, A).  $^{13}$C NMR (101 MHz, CDCl$_3$): $\delta$ (A + B) = 164.13, 164.11, 163.95, 163.87, 162.3, 162.1, 154.8, 154.4, 148.9, 147.5, 145.6, 145.4, 143.0, 142.9, 142.0, 141.5, 138.4, 137.4, 132.2, 131.9, 130.6, 130.5, 130.3, 130.1, 130.05, 130.02, 129.94, 129.89, 129.7, 129.6, 129.4, 129.2, 129.1, 128.9, 128.0, 127.6, 127.22, 127.19, 126.6, 126.4, 125.33, 125.29, 125.1, 124.14, 124.10, 123.6, 122.8, 122.5, 106.5, 106.2, 105.24, 105.18, 81.0, 80.8, 80.4, 80.2, 53.6, 53.6, 51.7, 51.6.

NMR spectra of 8c in DMSO-$d_6$: mixture of inseparable diastereomers, $\text{dr} = \sim 1.3 : 1$ (A : B).  $^1$H NMR (400 MHz, DMSO-$d_6$): $\delta = 8.27$–8.10 (m, 3H, A + B), 8.08–8.03 (m, 0.43H, B), 7.90 (dd, $J = 8.3$, 7.0, 1.6 Hz, 0.57H, A), 7.86–7.80 (m, 1H, A + B), 7.76 (ddd, $J = 8.4$, 7.0, 1.5 Hz, 0.43H, B), 7.72–7.55 (m, 2H, A + B), 7.48–7.39 (m, 0.57H, A), 7.35–7.29 (m, 1.57H, A + B), 7.27–7.22 (m, 1H, A + B), 7.16–7.05 (m, 1H, A + B), 6.98 (s, 0.43H, B), 6.95–6.87 (m, 1H, A + B), 6.81 (d, $J = 7.8$ Hz, 0.43H, B), 6.78 (d, $J = 7.8$ Hz, 0.57H, A), 6.05 (d, $J = 7.9$ Hz, 0.57H, A), 6.02 (d, $J = 8.0$ Hz, 0.43H, B), 3.98 (s, 1.7H, A), 3.95 (s, 1.3H, B), 3.21 (s, 1.3H), 3.20 (s, 1.7H).  $^{13}$C NMR (101 MHz, DMSO-$d_6$): $\delta$ (A + B) = 163.4, 163.0, 162.8 (2C), 162.1, 161.7, 154.4, 153.6, 148.1, 146.9, 145.2, 144.6, 142.2, 141.9, 140.8, 140.6, 137.6, 136.1, 132.6, 132.4, 130.7 (2C), 130.5, 130.3, 129.7, 129.60 (2C), 129.58, 129.55, 129.5, 129.4, 129.3, 128.9, 128.8, 127.6, 127.5, 127.1, 126.9, 125.8, 125.6, 125.5, 125.2, 125.1, 125.0, 124.1, 123.5, 122.1, 122.0, 107.3, 105.7, 104.8, 104.2, 80.1, 80.0, 79.6, 79.4, 53.7, 53.5, 51.64, 51.58.
5.2.1. Comparison of NMR spectra of 8b and the reported structure

The proposed structure of compound 4c in original publication (ref. 15)

The revised structure (8b)

| H NMR | 13C NMR |
|---|---|
| Reported in [15], 4c | Observed, 8b* | Reported** in [15], 4c | Observed, 8b*** | Difference, ppm |
| δ, ppm | int., mult. | J, Hz | δ, ppm | int., mult. | J, Hz | δ, ppm | δ, ppm |
| 3.19 | 3H, s | 3.19 | 3H, s | 51.50 | 51.50 | 0 |
| 4.03 | 3H, s | 4.03 | 3H, s | 53.40 | 53.50 | -0.1 |
| 5.87 | 1H, d | 7.5 | 5.87 | 1H, d | 7.8 | 79.90 | 80.00 | -0.1 |
| 6.51 | 1H, d | 7.5 | 6.51 | 1H, d | 7.8 | 80.80 | 80.90 | -0.1 |
| 7.02 | 1H, s | 6.97–7.07 | 2H, m | 105.10 | 105.20 | -0.1 |
| 7.11 | 3H, m | 7.08–7.13 | 1H, m | 106.20 | | |
| 7.56 | 6H, m | 7.19–7.25 | 1H, m | 122.60 | 122.80 | -0.2 |
| | | 7.44–7.58 | 4H, m | 123.40 | 123.50 | -0.1 |
| | | 7.68–7.76 | 1H, m | 123.90 | 124.00 | -0.1 |
| 8.17 | 3H, m | 7.76–7.83 | 1H, m | 125.20 | 125.20 | 0 |
| | | 8.06–8.14 | 1H, m | 126.30 | 126.40 | -0.1 |
| | | 8.21–8.25 | 2H, m | 127.00 | 127.10 | -0.1 |

* first proton signal was set to 3.19 ppm

** 29 out of 30 signals were reported

*** first carbon signal was set to 51.5 ppm, data from spectra in CDCl₃ (non-treated with K₂CO₃) were used
5.2.2. Copies of NMR spectra for product 8b

$^1$H NMR of 8b, CDCl$_3$, 303 K

$^{13}$C NMR of 8b, CDCl$_3$, 303 K
$^1$H NMR of 8b, $K_2CO_3$-treated-CDCl$_3$, 303 K

$^{13}$C NMR of 8b, $K_2CO_3$-treated-CDCl$_3$, 303 K
$^1$H NMR of 8b, DMSO-$d_6$, 303 K

$^{13}$C NMR of 8b, DMSO-$d_6$, 303 K
5.3. Synthesis of product 8c

Dimethyl 4a’H-spiro[indenophenazine-11,3’-[1,3]oxazino[3,2-a]quinoline]-1’,2’-dicarboxylate (8c): The compound was prepared according to the modified (1.5 equiv. of DMAD and pyridine instead of 1.0 equiv.) reported procedure [15]: DMAD (185 µL, 1.5 mmol, 1.5 equiv.) was added to a solution of 11H-indeno[1,2-b]quinolin-11-one 6 (232 mg, 1.0 mmol, 1 equiv.) and quinoline (180 µL, 1.5 mmol, 1.5 equiv.) in acetonitrile* (5 mL). The reaction mixture was stirred at RT for 1d. The reaction mixture was concentrated, the residue was triturated with EtOH, filtered and washed with EtOH affording a mixture of inseparable** diastereomers as a pale-yellow solid (435 mg, 86% yield); $R_f = 0.54 + 0.69$ (Hex/EA 1:1) [lit. not reported]; m.p. 219–220 °C (decomp.) [lit. 216–220 °C]. HRMS (ESI): $m/z$ calcd for C₃₀H₂₁N₃O₅: 504.1554 [M+H]⁺; found: 504.1555.

* reaction in DCM, which was used in the original method, was slow (not full conversion after 6d)
** inseparable by crystallization, however separation via column chromatography is possible

NMR spectra of 8c in K₂CO₃-treated-CDCl₃: (the same dr was observed in CDCl₃) mixture of inseparable diastereomers, dr = ~ 1 : 1 (A : B). $^1$H NMR (400 MHz, CDCl₃): δ = 8.23–8.01 (m, 2.5H, A + B), 7.90 (dd, $J = 8.3$, 1.5 Hz, 0.5H, A / B), 7.79–7.64 (m, 2H, A + B), 7.62–7.55 (m, 1.5H, A + B), 7.52 (td, $J = 7.5$, 1.3 Hz, 0.5H, A /B), 7.45 (td, $J = 7.5$, 1.2 Hz, 0.5H, A / B), 7.40–7.30 (m, 1.5H, A + B), 7.25–7.21 (m, 1H, A + B), 7.13–7.02 (m, 2H, A + B), 6.87 (d, $J = 9.7$ Hz, 0.5H, A / B), 6.83
(d, J = 9.7 Hz, 0.5H, A / B), 6.51 (dd, J = 4.3, 1.0 Hz, 0.5H, A / B), 6.00 (d, J = 4.3 Hz, 0.5H, A / B), 6.02–5.90 (m, 1H, A + B), 3.92 (s, 1.5H, A / B), 3.88 (s, 1.5H, A / B), 3.27 (s, 1.5H, A / B), 3.24 (s, 1.5H, A / B). $^{13}$C NMR (101 MHz, CDCl$_3$): δ (A + B) = 164.8, 164.6, 164.1, 163.9, 161.4, 160.7, 154.5, 154.2, 147.3, 146.6, 143.8, 143.0, 142.8, 142.3, 142.1, 141.6, 138.4, 137.4, 136.4, 136.0, 132.3, 132.2, 130.7, 130.54, 130.46, 130.05, 129.98, 129.91 (2C), 129.89, 129.8, 129.4, 129.3, 129.1 (2C), 128.83, 128.78, 128.5, 124.8, 124.5, 123.9, 122.7, 122.6 (3C), 122.3, 121.9, 121.4, 118.7, 118.1, 115.5, 114.5, 81.3, 81.2, 80.1, 79.9, 53.4, 53.3, 52.14, 52.13.

NMR spectra of 8c in DMSO-d$_6$: mixture of inseparable diastereomers, dr = ~ 1 : 1 (A : B). $^1$H NMR (400 MHz, DMSO-d$_6$): δ = 8.21–8.07 (m, 3H, A + B), 7.93–7.79 (m, 2H, A + B), 7.77–7.70 (m, 0.5H, A / B), 7.69–7.53 (m, 2H, A + B), 7.48–7.34 (m, 2H, A + B), 7.26 (d, J = 7.4 Hz, 0.5H, A / B), 7.15 (t, J = 6.2 Hz, 0.5H, A / B), 7.11 (t, J = 6.1 Hz, 0.5H, A / B), 7.06–6.95 (m, 1.5H, A + B), 6.91 (d, J = 8.1 Hz, 0.5H, A / B), 6.28 (d, J = 4.4 Hz, 0.5H, A / B), 6.21 (d, J = 4.3 Hz, 0.5H, A / B), 6.10–5.97 (m, 1H, A + B), 3.89 (s, 1.5H, A / B), 3.84 (s, 1.5H, A / B), 3.26 (s, 3H, A + B). $^{13}$C NMR (101 MHz, DMSO-d$_6$): δ (A + B) = 164.2, 163.6, 163.5, 163.2, 160.8, 160.7, 154.2, 153.3, 146.7, 146.1, 143.3, 142.2, 141.9, 141.2, 140.8, 140.6, 137.5, 136.1, 135.5, 134.9, 132.7, 132.6, 130.9, 130.8, 130.7, 130.4, 130.2, 129.9, 129.7, 129.54, 129.48, 129.3, 129.0, 128.9 (2C), 128.68, 128.66, 128.4, 125.3, 124.1, 123.3, 122.7, 122.2, 122.1, 121.9, 121.8, 121.2, 121.0, 118.9, 118.5, 114.6, 114.0, 80.7, 80.3, 79.5, 79.0, 53.5, 53.3, 52.2, 52.1.

Additional experiments on acid-catalyzed isomerization.

Compound 8c (0.1 mmol) was treated with p-TSA (20 mol%) or HCl$_{conc}$ (30 mol%) in 1 mL of DCM at RT, after 6h reaction mixtures were analyzed by LC. For conditions employing p-TSA, dr changed from ~ 1:1.05 to 1:1.16. Conditions employing HCl$_{conc}$ resulted in dr change from ~1:1.05 to 1:1.37.
5.3.1. Comparison of NMR spectra of 8c and the reported structure

|             | Reported in [15], 4e | Observed, 8c |
|-------------|----------------------|--------------|
| δ, ppm      | int., mult.          | J, Hz        | δ, ppm      | int., mult.          | J, Hz        |
| major       | minor                |              | major       | minor                |              |
| 3.26        | 3H, s                |              | 3.27        | 3H, s                |              |
| 3.24        | 3H, s                |              | 3.24        | 3H, s                |              |
| 3.92        | 3H, s                |              | 3.92        | 3H, s                |              |
| 3.89        | 3H, s                |              | 3.88        | 3H, s                |              |
| 5.94        | 1H, m                |              | 5.90–6.02   | 2H, m                |              |
| 5.94        | 1H, m                |              | 6.51        | 1H, dd               | 4.3, 1.0     |
| 6.5         | 1H, d                | 4.3          | 6.00        | 1H, d                | 4.3          |
| 5.99        | 1H, d                | 4.3          | 6.87        | 1H, d                | 9.7          |
| 6.87        | 1H, d                | 9.7          | 6.83        | 1H, d                | 9.7          |
| 7.08        | 2H, m                |              | 7.02–7.13   | 4H, m                |              |
| 7.08        | 2H, m                |              | 7.20–7.28   | 2H, m                |              |
| 7.26-8.24   | 7.26-8.24            | Σ20H, m      | 7.30–7.40   | 3H, m                |              |
|             |                      |              | 7.45        | 1H, td               | 7.5, 1.2     |
|             |                      |              | 7.52        | 1H, td               | 7.5, 1.3     |
|             |                      |              | 7.55–7.62   | 3H, m                |              |
|             |                      |              | 7.64–7.79   | 4H, m                |              |
|             |                      |              | 7.90        | 1H, dd               | 8.3, 1.5     |
|             |                      |              | 8.01–8.23   | 5H, m                |              |

The $^1$H NMR spectrum from the original work shows inconsistency with our data, at least 6 carbon signals do not match with literature data; for other signals, the difference with literature is 0–0.6 ppm. No copies of NMR spectra were provided in the original work, which complicated data analysis.
5.3.2. Copies of NMR spectra for product 8c

$^1$H NMR of 8c, $K_2CO_3$-treated-CDCl$_3$, 303 K

$^{13}$C NMR of 8c, $K_2CO_3$-treated-CDCl$_3$, 303 K
$^1$H NMR of 8c, DMSO-$d_6$, 303 K

$^{13}$C NMR of 8c, DMSO-$d_6$, 303 K
6. Synthesis, HPLC and NMR spectra of compounds 10a,b

6.1. Synthesis of product 10a

Dimethyl 1-benzyl-1′,1′′-dicyano-2-oxo-1′,9a′-dihydrospiro[indoline-3,2′-quinolizine]-3′,4′-dicarboxylate (10a): The compound was prepared according to the reported procedure [16]: DMAD (92 μL, 0.75 mmol, 1.5 equiv.) was added to a solution of 2-(1-benzyl-2-oxindolin-3-ylidene)malononitrile 9 (143 mg, 0.5 mmol, 1 equiv.) and pyridine (61 μL, 0.75 mmol, 1.5 equiv.) in tetrahydrofuran (THF, 12 mL). The reaction mixture was refluxed for 2h. The reaction mixture was concentrated, the residue was triturated with EtOH, filtered and washed with EtOH. Compound was additionally purified by recrystallization from hexane/DCM, affording a mixture of inseparable diastereomers as a pale-yellow solid (158 mg, 62% yield); $R_f = 0.63$ (Hex/EA 1:1); m.p. 183–185 °C (decomp.) [lit. 222–226 °C].

HPLC of the reaction mixture

HPLC of the isolated product 10a

NMR spectra of 10a in CDCl3: (the same dr was observed in K2CO3-treated-CDCl3) mixture of inseparable diastereomers, d.r. $\approx 9 : 1$ (A : B). $^1$H NMR (400 MHz, CDCl3): $\delta$ = 7.54–7.46 (m, 1.18H, A + B), 7.45–7.40 (m, 1.82H, 2×A), 7.37–7.27 (m, 4H, A + B), 7.15–7.05 (m, 1H, A + B), 6.92 (d, $J = 7.8$ Hz, 0.09H, B), 6.88 (d, $J = 7.9$ Hz, 0.91H, A), 6.32–6.20 (m, 3H, A + B), 5.75 (dd, $J = 10.0$, 3.3 Hz, 0.91H, A), 5.69 (d, $J = 10.5$ Hz, 0.09H, B), 5.31–5.21 (m, 1H, A + B), 5.16 (d, $J = 15.6$ Hz, 0.91H, A), 5.09 (d, $J = 15.5$ Hz, 0.09H, B), 5.00 (d, $J = 15.5$ Hz, 0.09H, B), 4.82 (d, $J = 15.5$ Hz,
0.91H, A), 3.96 (s, 3H, A + B), 3.26 (s, 0.27H, B), 3.14 (s, 2.73H, A). $^{13}$C NMR (101 MHz, CDCl$_3$): δ (A, major) = 173.5, 163.6, 163.4, 146.8, 143.7, 135.1, 130.7, 129.0 (2C), 128.1, 128.0 (2C), 126.8, 126.5, 125.2, 124.1, 123.7, 114.3, 110.9, 110.3, 110.2, 103.3, 100.4, 57.2, 53.7, 52.0, 51.9, 45.3, 44.9.

NMR spectra of 10a in DMSO-$d_6$: mixture of inseparable diastereomers, dr = ~ 1.5 : 1 (A : B). $^1$H NMR (400 MHz, DMSO-$d_6$): δ = 7.68–7.56 (br. m, 0.6H, A), 7.52–7.25 (br. m, 6.4H, A + B), 7.23–7.07 (br. m, 2H, A + B), 6.51 (br. s, 1H, A + B), 6.40 (t, J = 8.0 Hz, 1H, A + B), 6.13 (br. s, 0.4H, B), 5.78 (br. s, 1H, A + B), 5.70–5.59 (br. m, 0.6H, A), 5.37 (br. s, 1H, A + B), 5.16–4.89 (br. m, 2H, A + B), 3.92 (s, 3H, A + B), 3.26 (br. s, 1.8H, A), 3.08 (br. s, 1.2H, B).

One of the possible reasons for broadening peaks in NMR spectra of 10a in DMSO-$d_6$ might be the presence of ring-chain equilibrium (see ref. [17] for related example on partial unsaturated [1,3]oxazine) depicted in A, scheme 1. In that case, $\alpha$–CH (shown in red) of the pyridinium fragment should have δ > 8.5 ppm (see B on scheme 1 for literature examples). However, no such signal can be seen in $^1$H NMR of 10a, indicating that two sets of signals are likely attributed to diastereomers.

A. The possible ring-chain equilibrium

B.

| Compound | δ (ppm) (DMSO-$d_6$) |
|----------|-----------------|
| Ref. 18  | 9.15 ppm        |
| Ref. 19  | 9.04 ppm        |
| Ref. 20  | 9.15 ppm        |

Scheme 1
6.1.1. Copies of NMR spectra for product 10a

**$^1$H NMR of 10a, K$_2$CO$_3$-treated-CDCl$_3$, 303 K**

![NMR spectrum of 10a](image)

**$^{13}$C NMR of 10a, K$_2$CO$_3$-treated-CDCl$_3$, 303 K**

![C NMR spectrum of 10a](image)
$^1$H NMR of 10a, DMSO-$d_6$, 303 K

\[
\text{H} \quad \text{N} \quad \text{COCH}_3
\]
\[
\text{NC} \quad \text{N} \quad \text{COCH}_3
\]
\[
\text{Ph}
\]
6.1.2. The NOESY/EXSY of compound 10a

The NOESY (EXSY) spectrum of compound 10a in DMSO-$d_6$ at 303K, acquired with standard Bruker program (NOESYPHSW), mixing time 0.700 sec; Off-diagonal cross-peaks in the same phase (red color) as the diagonal ones indicate chemical exchange between these peaks (protons).

The fragment of the NOESY spectrum (region of 4.80–6.80 ppm); cross peaks indicate exchange between $CH$ fragments of the dihydropyridine moiety.

The fragment of the NOESY spectrum (region of 2.85–3.50 ppm); cross-peaks indicate exchange between the methoxy groups.
6.2. Synthesis of product 10b

Dimethyl 1-benzyl-1',1'-dicyano-2-oxo-1',11b'-dihydrospiro[indoline-3,2'-pyrido[2,1-a][isoquinoline]-3',4'-dicarboxylate (10b): The compound was prepared according to the adopted reported procedure [16]: DMAD (92 µL, 0.75 mmol, 1.5 equiv.) was added to a solution of 2-(1-benzyl-2-oxoindolin-3-ylidene)malononitrile 9 (143 mg, 0.5 mmol, 1 equiv.) and isoquinoline (99 µL, 0.75 mmol, 1.5 equiv.) in tetrahydrofuran (THF, 12 mL). The reaction mixture was refluxed for 8h. The reaction mixture was concentrated, the residue was triturated with EtOH, filtered and washed with EtOH. Compound was additionally purified by recrystallization from hexane/DCM, affording a mixture of inseparable* diastereomers as a yellow solid (213 mg, 76% yield); \( R_I = 0.53 + 0.65 \) (Hex/EA 1:1); m.p. 180–183 °C (decomp.); HRMS (ESI): \( m/z \) calcd for C_{33}H_{24}N_{4}O_{5}: 579.1639 \([M+Na]^+\); found: 579.1652.

* inseparable by crystallization, however separation via column chromatography is possible

**HPLC of the reaction mixture**

| Peak | Retention (min) | Area (μA sec) | Area % | Component |
|------|----------------|---------------|--------|-----------|
| 1    | 6.83           | 966.900       | 51.85  |           |
| 2    | 7.65           | 897.942       | 48.15  |           |

**HPLC of the isolated product 10b**

| Peak | Retention (min) | Area (μA sec) | Area % | Component |
|------|----------------|---------------|--------|-----------|
| 1    | 6.85           | 5056.957      | 55.16  | Peak1     |
| 2    | 7.67           | 4193.616      | 44.84  |           |

NMR spectra of 10b in K_{2}CO_{3}-treated-CDCl_{3}: (the same dr was observed in CDCl_{3}) mixture of inseparable diastereomers, \( dr = 1.4 : 1 \) (A : B). \(^1\text{H NMR (400 MHz, CDCl}_3\)): \( \delta = 7.55–7.45 \) (m, 3H, A+B), 7.42–7.26 (m, 6H, A+B), 7.23–7.19 (m, 1H, A+B), 7.17–7.05 (m, 2H, A+B), 6.96 (d, \( J = 7.9 \) Hz, 0.58H, A), 6.89 (d, \( J = 7.9 \) Hz, 0.42H, B), 6.64 (s, 0.42H, B), 6.44 (d, \( J = 7.9 \) Hz, 0.42H, B), S57
6.38 (d, \(J = 7.9\) Hz, 0.58H, A), 5.82 (d, \(J = 7.9\) Hz, 0.58H, A), 5.81 (d, \(J = 7.9\) Hz, 0.42H, B), 5.67 (s, 0.58H, A), 5.24 (d, \(J = 15.5\) Hz, 0.42H, B), 5.12 (d, \(J = 15.6\) Hz, 0.58H, A), 5.00 (d, \(J = 15.6\) Hz, 0.58H, A), 4.87 (d, \(J = 15.5\) Hz, 0.42H, B), 3.98 (s, 1.25H, B), 3.97 (s, 1.75H, A), 3.31 (s, 1.75H, A), 3.21 (s, 1.25H, B). 13C NMR (101 MHz, CDCl3): \(\delta\) (A + B) = 173.7, 172.3, 163.8, 163.7, 163.6, 163.5, 146.8, 146.4, 144.1, 143.8, 135.2, 135.1, 131.3, 130.8, 130.7, 130.6, 130.4, 130.1, 129.3, 129.0 (2C), 128.9 (2C), 128.9, 128.3 (2C), 128.14, 128.09, 128.05 (2C), 128.0, 127.7, 127.5, 126.3, 126.0 (2C), 125.5, 125.3, 124.7, 124.4, 123.7, 123.2, 122.4, 121.7, 111.2, 111.1, 110.8, 110.5, 110.2, 109.6, 107.4, 107.1, 104.3, 103.9, 60.1, 58.1, 54.4, 53.8, 53.7, 53.5, 52.4, 52.0, 46.2, 45.8, 45.4, 45.3.

NMR spectra of 10b in DMSO-d6: mixture of inseparable diastereomers, dr = ~ 1.4 : 1 (A : B). 1H NMR (400 MHz, DMSO-d6): \(\delta\) = 7.94 (d, \(J = 7.5\) Hz, 0.6H, A), 7.54–7.41 (m, 3.8H, A + B), 7.41–7.25 (m, 6H, A + B), 7.23–7.12 (m, 2H, A + B), 7.09 (d, \(J = 7.7\) Hz, 0.6H, A), 6.68 (d, \(J = 7.9\) Hz, 0.4H, B), 6.64 (d, \(J = 7.9\) Hz, 0.6H, A), 6.53 (s, 0.4H, B), 6.14 (s, 0.6H, A), 6.01 (d, \(J = 7.9\) Hz, 0.4H, B), 5.96 (d, \(J = 7.9\) Hz, 0.6H, A), 5.20–4.94 (m, 2H, A + B), 3.95 (s, 1.25H, B), 3.94 (s, 1.75H, A), 3.31 (s, 1.75H, A), 3.15 (s, 1.25H, B). 13C NMR (101 MHz, DMSO-d6): \(\delta\) (A + B) = 172.9, 171.9, 163.3, 162.9, 162.8, 162.7, 146.4, 146.0, 143.4, 143.3, 135.6, 135.3, 131.0, 130.9, 130.7, 130.5, 130.2, 129.7, 129.0, 128.6 (2C), 128.5 (3C), 127.9 (2C), 127.7 (3C), 127.6, 127.5, 127.3, 126.9, 126.8, 126.0, 125.9, 125.7, 125.4, 124.6, 123.5, 123.2, 123.2, 121.9, 121.6, 111.0, 110.92, 110.90, 110.6, 110.02, 109.97, 106.7, 106.1, 103.8, 102.7, 59.3, 57.2, 53.9, 53.8, 53.7, 52.6, 52.2, 52.0, 45.9, 45.8, 44.2, 43.9.
6.2.1. Copies of NMR spectra for product 10b

$^1$H NMR of 10b, $K_2$CO$_3$-treated-CDCl$_3$, 303 K

$^{13}$C NMR of 10b, $K_2$CO$_3$-treated-CDCl$_3$, 303 K
$^1$H NMR of 10b, DMSO-$d_6$, 303 K

$^{13}$C NMR of 10b, DMSO-$d_6$, 303 K
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