Electronic Supplementary Material (ESI) for ChemComm.

Electronic supplementary information

Synthesis of a crystallochromic indolizine dye by a base- and catalyst-free photochemical route

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1. Experimental

1.1 Equipment

Photoreactions were carried out with a high-pressure Hg-lamp (Heraeus TQ150) with direct irradiation. Structures in the solid state were determined by X-ray diffraction analysis with a Bruker APEX DUO with Mo–Kα (**2a^{c}**) or Cu-Kα (**2a^{n}**) radiation. Data for both crystals were collected at 90(2) K and integrated using the Bruker SAINT[1] software package. Data were corrected for absorption effects using a multi-scan technique (SADABS[2]), structures were solved and refined using XT[3] and XL,[4] respectively. All non-hydrogen atom were refined anisotropically, while all hydrogen atoms were placed in calculated positions. IR spectra were recorded at room temperature on a Bruker Tensor 27 FT-IR spectrometer with 32 scans for each measurement. NMR spectra were recorded on a Bruker AV-400 spectrometer (^{1}H: 400 MHz, ^{13}C: 100 MHz, 22 °C) equipped with a 5 mm dual probe or on a Varian VNMR-S 600 spectrometer (^{1}H: 600 MHz, ^{13}C: 150 MHz, 25 °C) equipped with 3 mm triple resonance inverse and 3 mm dual broadband probes. Pulse sequences are taken from Bruker and Varian pulse sequence libraries. Spectra were analyzed manually with the software ACD/NMR Processor Academic Edition 12.02 and were referenced to the solvent signals (CD_3CN: δ_H = 1.94 ppm, δ_C = 118.69 ppm; DMSO-d_6: δ_H = 2.50 ppm, δ_C = 39.51 ppm; MeOD-d_4: δ_H = 3.31 ppm; $CDCl_3$: δ_H = 7.27 ppm, δ_C = 77.00 ppm). The signals were assigned with 2D-NMR techniques, namely H,H-COSY, HSQC and HMBC. Absorption spectra were collected in Hellma quartz glass cuvettes 110-QS (d = 10 mm) with a Cary 100 Bio spectrophotometer equipped with a thermostat. Emission spectra were recorded at 20 °C in Hellma quartz glass cuvettes 110-QS (d = 10 mm) with a Cary Eclipse spectrophotometer equipped with a thermostat. Mass spectra (ESI) were recorded on a Finnigan LCQ Deca (U = 6 kV; working gas: Argon; auxiliary gas: Nitrogen; temperature of the capillary: 200 °C). Elemental analysis data were determined by Rochus Breuer (Organische Chemie I, Universität Siegen) on a HEKAtech EUROEA combustion analyzer. Melting points were determined with a BÜCHI 545 (Büchi, Flawil, CH) and are uncorrected. Pictures of the polymorphs were taken with a Canon EOS 200D equipped with a macro lens from SIGMA (18–250 mm, 1:3.5–6.3) at daylight using the following parameters: 250 mm, f/6.3; 1/60; ISO 400.

1.2 Reagents and solvents

All commercially available chemicals were used without further purification unless stated otherwise.

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[1] SAINT. Version 8.34A. Bruker AXS Inc., Madison, Wisconsin, USA. (1997-2013).
[2] L. Krause, R. Herbst-Irmer, G. M. Sheldrick and D. Stalke, *J. Appl. Crystallogr.,* 2015*,* **48**, 3–10.
[3] G. M.Sheldrick, *Acta Cryst*., 2015, **A71**, 3–8.
[4] G. M.Sheldrick, *Acta Cryst*., 2015, **C71**, 3–8.

THF was freshly distilled from sodium wire before use. CH_2Cl_2 was dried 3 h with P_2O_5 under reflux with stirring and was distilled.

Chemicals were obtained from the following companies: MeI, Acros Organics N.V. (Geel, BE): Dimethylacetylene dicarboxylate (DMAD).

1.3 Methods

General remarks

Photoreactions were carried out in quartz glassware. Reaction solutions were stirred with a magnetic stirring bar. Reaction temperatures refer to the medium that surrounded the reaction vessel. Solvents were usually removed under reduced pressure at 40–50 °C with a rotatory evaporator, if necessary, at reduced pressure. The room temperature was approximately 21 °C.

Determination of fluorescence quantum yields

Solutions were prepared from stock solutions of the derivatives **2a**–**c** in MeCN (*c* = 1.0 mM). Aliquots of the stock solutions were evaporated under a stream of nitrogen and redissolved in the respective solvent. In general, absorption spectra were determined with a scan rate of 120 nm min^{-1} from 240 to 550 nm and subsequently smoothed in the Origin software with the adjacent-averaging function (factor 10). For the detection of emission spectra, the excitation and emission slits were adjusted to 5 nm. The scan rate was 120 nm min^{-1} and the detector voltage was adjusted to 500 V. The spectra were smoothed with the implemented moving-average function (factor 5). Due to the low emission intensity of derivitave **2b** the emission spectrum was recorded at 30 nm min^{-1} and smoothed in the Origin software with the adjacent-averaging function (factor 10). The relative fluorescence quantum yields of **2a**–**c** were determined under identical conditions, i.e. the same cuvettes were used and the measurements were performed at a constant temperature with the same settings on the spectrometer (detection wavelength, excitation wavelength, detector voltage, slit bandwidths, collection rate). Coumarin 153 (Φ_{fl} = 0.31 in EtOH[5]) was used as standard. The emission spectra were collected from solutions with Abs. = 0.10 at the excitation wavelength. After integration of the fluorescence band, the relative fluorescence quantum yields were calculated according to eq. 1.

$$\phi_F = \frac{J_x(1-T_s)\,n_x^2}{J_s(1-T_x)\,n_s^2} \cdot \phi_{F,S} \qquad \text{(eq. 1)}$$

The subscripts “x” and “s” refer to the substance under investigation and the reference compound, respectively; $J = \int_F(\lambda)\mathrm{d}\lambda$ is the integral of the emission band; T is the optical transmittance of the sample solution at the excitation wavelength λ_{ex}; n is the refractive index of the sample or standard solution.

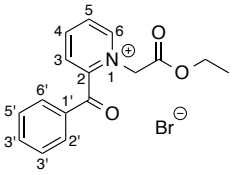
[5] G. Jones, W. R. Jackson, C. Y. Choi and W. R. Bergmark, *J. Phys. Chem*., 1985, **89**, 294–300.

1.4 Syntheses

Synthesis of 2-benzoylpyridinium salts

2-Benzoyl-1-benzylpyridinium bromide (**1a**),[6] 2-benzoyl-1-methylpyridinium tetrafluoroborate (**1c**),[7] and 1-benzylpyridinium bromide (**1d**)[8] were prepared according to literature procedures.

2-Benzoyl-1-ethyloxycarbonylmethylpyridinium bromide (**1b**)



A solution of 2-benzoylpyridine (7.7 g, 42 mmol) with ethyl bromoacetate (7.1 g, 42 mmol, 4.7 mL) in anhydrous DMF (5 mL) was stirred for 8 d at 60 °C. After cooling to room temperature the solution was poured into EtOAc (500 mL) with vigorous stirring, and the precipitate was collected by filtration and washed with EtOAc (3 × 20 mL). The crude was recrystallized from MeOH/EtOAc and dried in *vacuo* with $CaCl_2$. The product **1b** was obtained as a brownish crystalline solid in 70% yield (10 g, 30 mmol); mp 152–155 °C (dec.). – ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.07 (t, ^3J = 7.0 Hz, 3 H, CH_3), 4.04 (q, ^3J = 7.2 Hz, 2 H, -O-CH_2), 6.01 (s, 2 H, CH_2, N^+-CH_2), 7.46 (t, ^3J = 7.8 Hz, 2 H, 5'-H, 3'-H), 7.64 (t,^3J = 7.4 Hz, 1 H, 4'-H), 7.81 (d, ^3J = 7.6 Hz, 2 H, 2'-H, 6'-H), 8.06 (d, ^3J = 7.6 Hz, 1 H, 3-H), 8.35 (t, ^3J = 7.0 Hz, 1 H, 5-H), 9.02 (t,^3J = 7.8 Hz, 1 H, 4-H), 10.16 (d, ^3J = 6.0 Hz, 1 H, 6-H). – ^{13}C NMR (150 MHz, $CDCl_3$): δ 13.5 (CH_3), 59.0 (O-CH_2), 63.0 (N^+-CH_2), 129.0 (C3'), 128.9 (C3), 129.6 (C6), 130.9 (C2', C6'), 132.8 (C1'), 135.6 (C4'), 147.7 (C2), 148.0 (C4), 150.5 (C5), 165.1 (ester-C=O, ester), 187.1 (C=O, ketone). – El. Anal. (%) for $C_{16}H_{16}NO_3Br$, calc.: C 54.87; H 4.61; N 4.00, found: C 54.85, H 4.57, N 4.04. – MS (ESI^+): *m*/*z* (rel. Int.) = 270 (100) [M^+].

Synthesis of indolizine derivatives

Photochemical synthesis of indolizine derivatives

General procedure for the photochemical conversion of 2-benzoylpyridinium salts with dimethylacetylenedicarboxylate (DMAD) to indolizine derivatives (GP 1).

In a quartz tube equipped with a rubber septum a solution of the pyridinium derivative (1.00 mmol) and DMAD (2.00 mmol) in MeCN (12 mL) was purged with argon gas for 30 min and subsequently irradiated for 15.5 h with stirring. The photolysate was poured into a mixture of H_2O (50 mL) and EtOAc (50 mL) and the organic layer was washed with H_2O (2 x 30 mL). The organic layer was dried with Na_2SO_4, filtered from the desiccant, and the solvent was removed under reduced pressure. The residual oil was purified by column chromatography and crystallization.

[6] C. K. Bradsher and T. W. G. Solomons, *J. Am. Chem. Soc.*, 1959, **81**, 2550–2552.
[7] E. M. Kosower and L. Lindqvist, *Tetrahedron Lett.*, 1965, **6**, 4481–4485.
[8] K. Kang, H. Jang and Y.-K. Kim, *Analyst*, 2017, **142**, 2372–2377.

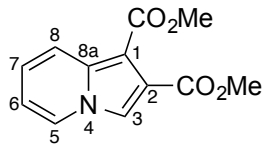


Chart S1. General numbering of indolizine-1,2-dicarboxylate derivatives (specific numbering see Figures S6–S14).

Dimethyl-5-benzoyl-3-phenylindolizine-1,2-dicarboxylate (**2a**)

According to GP 1 **1a** (200 mg, 565 µmol) and DMAD (160 mg, 1.12 mmol, 140 µmL) were irradiated in MeCN (6 mL), and the crude was purified by flash column chromatography (SiO_2; cyclohexane/EtOAc = 4/1, R_f = 0.26). The product was crystallized from hexane/CH_2Cl_2 and dried in *vacuo* with $CaCl_2$ to give **2a** as a fluorescent, orange, crystalline solid (43 mg, 104 µmol, 18%); mp 159–160 °C. – ^{1}H NMR (600 MHz, CD_3OD): δ = 3.68 (s, 3 H, 2-CO_2CH_3), 3.91 (s, 3 H, 1-CO_2CH_3), 6.99 (d, 2 H, ^3J = 7 Hz, 2',6'-H), 7.07 (dd, 2 H, 2 x ^3J = 8 Hz, 3',5'-H), 7.09 (dd, 1 H, ^3J = 7 Hz, ^4J = 1 Hz, 6-H), 7.17 (dddd, 1 H, 2 x ^3J = 8 Hz, 2 x ^4J = 1 Hz, 4'-H), 7.27 (dd, 2 H, ^3J = 8 Hz, ^4J = 1 Hz, 2'',6''-H), 7.31–7.34 (m, 2 H, 3'',5''-H), 7.34 (dd, 1 H, ^3J = 7 Hz, ^3J = 9 Hz, 7-H), 7.54 (dddd, 1 H, 2 x ^3J = 7 Hz, 2 x ^4J = 1 Hz, 4''-H), 8.45 (dd, 1 H, ^3J = 9 Hz, ^4J = 1 Hz, 8-H. – ^{13}C NMR (150 MHz, CD_3OD): 52.1 (1-CO_2**C**H_3), 53.1 (2-CO_2**C**H_3), 105.2 (C1), 120.3 (C6), 123.9 (C8), 124.1 (C7), 125.3 (C2), 128.7 (C3), 129.8 (C4'), 129.9 (C3', C5', C3'', C5''), 130.1 (C2'', C6''), 130.2 (C2', C6'), 132.0 (C1'), 135.0 (C4''), 136.8 (C5), 136.9 (C1'), 137.3 (C8a), 165.6 (1-CO_2), 168.4 (2-CO_2), 190.1 (5-COPh). – El. Anal. (%) for $C_{25}H_{19}NO_5$, calc.: C 72.63, H 4.63, N 3.39; found: C 72.65, H 4.56, N 3.34 – MS (ESI+): *m*/*z* (rel. intensity) = 849 (100) [2M + Na], 436 (16) [M + Na], 414 (10) [M$^+$].

3-Ethyl-1,2-dimethyl-5-benzoylindolizine-1,2,3-tricarboxylate (**2b**)

According to GP 1 **1b** (200 mg, 571 µmol) and DMAD (162 mg, 1.14 mmol, 140 µmL) were irradiated in MeCN (6 mL), and the crude was purified by flash column chromatography (Al_2O_3 neutral; hexane/EtOAc = 2/1, R_f = 0.45). The product was crystallized from hexane/CH_2Cl_2 and dried in *vacuo* with $CaCl_2$ to give **2b** as a fluorescent, yellow, crystalline solid (108 mg, 264 µmol, 46%). mp 147–149 °C. – ^{1}H NMR (600 MHz, CDCl3): = 1.18 (t, 3 H, ^3J = 7 Hz, CH_3), 3.93 (s, 3 H, 1-CO_2CH_3), 3.97 (s, 3 H, 2-CO_2CH_3), 4.15 (q, 2 H, ^3J = 7 Hz, CH_2), 7.11 (dd, 1 H, ^4J = 1 Hz, ^3J = 7 Hz, 6-H), 7.35 (dd, ^3J = 7 Hz, ^3J = 9 Hz, 7-H), 7.53 (2 x ddd, 2 H, ^4J = 1 Hz, ^4J = 2 Hz, 2 x 3J = 8 Hz, 3',5'-H), 7.65 (dddd, 1 H, 4J = 1 Hz, 4J = 2 Hz, 2 x ^3J = 8 Hz, 4'-H), 7.98 (ddd, 2 H, ^4J = 1 Hz, ^4J = 2 Hz, ^3J = 8 Hz, 2',6'-H), 8.52 (dd, 1 H, ^4J = 1 Hz, ^3J = 9 Hz, 8-H) – ^{13}C NMR (150 MHz, $CDCl_3$): = 13.9 (CH_3), 51.8 (1-CO_2CH$_3$), 52.7 (2-CO2*C*H$_3$), 61.2 (CH_2), 104.4 (C1), 116.2 (C3), 119.6 (C6), 122.8 (C8), 124.8 (C7), 128.6 (C3', C5'), 130.0 (C2', C6'), 130.1 (C2), 133.7 (C4'), 135.4 (C1'), 136.4 (C8a), 138.1 (C5), 159.9 (3-CO_2), 163.2 (2-CO_2), 165.8 (1-CO_2), 188.2 (5-COPh) – El. Anal. (%) for $C_{22}H_{19}NO_7$ x 0.5 H_2O, calc.: C 63.16, H 4.82, N 3.35; found: C 63.25, H 4.57, N 3.45 – MS (ESI+): m/z (rel. intensity) = 841 (100) [2M + Na], 432 (22) [M + Na], 410 (1) [M+].

Dimethyl-5-benzoylindolizine-1,2-dicarboxylate (**2c**)

According to GP 1 **1c** (570 mg, 2.00 mmol) and DMAD (568 mg, 4.00 mmol, 0.50 mL) were irradiated in MeCN (8.0 mL) for 14.5 h. The crude was purified by column chromatography (Al_2O_3 neutral; cyclohexane/EtOAc = 4/1; R_f = 0.28). The residue was crystallized from

cyclohexane/EtOAc and dried in *vacuo* with $CaCl_2$ to afford **2c** as fluorescent, yellow needles (24.3 mg, 72.0 µmol, 4%); mp 139–140 °C. – ^{1}H NMR (600 MHz, $CDCl_3$): δ = 3.93 (s, 3 H, 2-CO_2CH_3), 3.95 (s, 3 H, 1-CO_2CH_3), 7.10 (dd, 1 H, ^3J = 7 Hz, ^3J = 9 Hz, 7-H), 7.28 (dd, 1 H, ^3J = 7 Hz, ^4J = 1 Hz, 6-H), 7.55 (dd, 2 H, 2 x ^3J = 7 Hz, 3'-H, 5'-H), 7.67 (dd, 1 H, 2 x ^3J = 7 Hz, 4'-H), 7.81 (dd, 2 H, ^3J = 7 Hz, ^4J = 1 Hz, 2'-H, 6'-H), 8.45 (dd, 1 H, ^3J = 9 Hz, ^4J = 1 Hz, 8-H), 8.91 (s, 1 H, 3-H). – ^{13}C NMR (150 MHz, $CDCl_3$): δ = 51.6 (1-CO_2**C**H_3), 52.2 (2-CO_2**C**H_3), 105.0 (C1), 119.5 (C3), 120.7 (C7), 122.2 (C2), 123.7 (C6), 125.5 (C8), 128.6 (C3', C5'), 129.8 (C2', C6') 131.3 (C5), 133.1 (C4'), 136.6 (C8a), 137.3 (C1'), 164.1 (1-CO_2), 164.8 (2-CO_2), 190.2 (5-COPh). – El. Anal. (%) for $C_{19}H_{15}NO_5$, calc.: C 67.65, H 4.48, N 4.15; found: C 67.45, H 4.27, N 4.04 – MS (ESI$^+$): *m*/*z* (rel. intensity) = 697 (24) [2M + Na], 338 (93) [M^+], 360 (32) [M + Na], 306 (100) [$M^+ - CH_3O^-$].

Dimethyl-3-phenylindolizine-1,2-dicarboxylate (**2d**)

According to GP 1 DMAD (269 mg, 1.90 mmol, 0.23 mL) was added to a solution of **1d** (237 mg, 948 µmol) in MeCN (4.0 mL), and solution turned dark red immediately. The reaction mixture was irradiated for 19.5 h, and TLC analysis of the mixture showed the appearance of a blue fluorescent spot. The crude was purified by flash column chromatography (SiO_2 neutral; cyclohexane/EtOAc = 4/1; R_f = 0.32) to afford **2d** as a fluorescent, colorless solid (0.8 mg, 2.6 µmol, < 1%). – ^{1}H NMR (600 MHz, DMSO-d_6): δ = 3.71 (s, 3 H, 2-CO_2CH_3), 3.81 (s, 3 H, 1-CO_2CH_3), 6.95 (ddd, 1 H, 2 x ^3J = 7 Hz, ^4J = 1 Hz, 6-H), 7.32 (ddd, 1 H, ^3J = 7 Hz, ^3J = 9 Hz, ^4J = 1 Hz, 7-H), 7.51–7.52 (m, 1 H, 4'-H), 7.52–7.53 (m, 2 H, 2'-H,6'-H), 7.55–7.58 (m, 2 H, 3'-H, 5'-H), 8.12 (ddd, 1 H, ^3J = 9 Hz, 2 x ^4J = 1 Hz, 8-H), 8.23 (ddd, 1 H, ^3J = 8 Hz, 2 x ^4J = 1 Hz, 5-H). – ^{13}C NMR (150 MHz, $CDCl_3$): δ = 51.2 (1-CO_2*C*H_3), 52.2 (2-CO_2*C*H_3), 100.8 (C1), 114.2 (C6), 119.2 (C8), 121.3 (C2), 124.2 (C5), 124.4 (C3), 124.8 (C7), 128.2 (C1'), 129.1 (C4'), 129.2 (C3', C5'), 129.6 (C2', C6'), 134.4 (C8a), 163.2 (1-*C*O_2CH_3), 166.0 (2-*C*O_2CH_3). – MS (ESI$^+$): *m*/*z* (rel. intensity) = 332 (100) [M^+ + Na].

Base-induced synthesis of indolizine derivatives

General procedure for the synthesis of indolizine derivatives by the reaction of 2-benzoyl-pyridinium salts with alkynes under alkaline conditions (GP 2)[9]

A suspension of the pyridinium derivative (1.00 mmol), the alkyne (2 mol. eq.) and the base (3 mol. eq.) in the respective solvent (10 mL) was stirred at r.t. or with heating for 16–24 h. The solvent was removed under reduced pressure and the residue was dissolved in a mixture of EtOAc (100 mL) and H_2O (100 mL). The organic layer was washed with H_2O (3 x 100 mL), dried with Na_2SO_4, filtered from the desiccant, and the solvent was removed at reduced pressure. The residual oil was purified by column chromatography.

Dimethyl-5-benzoyl-3-phenylindolizine-1,2-dicarboxylate (**2a**)

According to GP 2 **1a** (1.64 g, 4.63 mmol) was made to react with DMAD (1.32 g, 9.27 mmol, 1.10 mL) and K_2CO_3 (1.92 g, 13.9 mmol) in THF (50 mL). The crude was purified by flash column chromatography (SiO_2 neutral; cyclohexane/EtOAc = 4/1, R_f = 0.26). The product was crystallized from hexane/CH_2Cl_2 and dried in *vacuo* with $CaCl_2$ to give **2a** as a fluorescent, orange-colored, crystalline solid (138 mg, 29.3 mmol, 11%). The product was identified by TLC analysis and ^{1}H-NMR spectroscopy.

[9] Y. Miki, H. Kinoshitam Toshihiko Yoshimaru, S. Takemura and M. Ikeda, *Heterocycles*, 1987, **26**, 199–204.

3-Ethyl-1,2-dimethyl-5-benzoylindolizine-1,2,3-tricarboxylate (**2b**).

According to GP 2 **1b** (0.70 g, 2.00 mmol) was made to react with DMAD (0.57 g, 4.00 mmol, 0.50 mL) and K_2CO_3 (830 mg, 6.00 mmol) in THF (20 mL). The crude was purified by flash column chromatography (SiO_2 neutral; cyclohexane/EtOAc = 4/1, R_f = 0.26). The product was crystallized from hexane/CH_2Cl_2 and dried in *vacuo* with $CaCl_2$ to give **2b** as a fluorescent, yellow, crystalline solid (415 mg, 1.01 mmol, 51%). The product was identified by TLC analysis and ^{1}H-NMR spectroscopy.

Dimethyl-5-benzoylindolizine-1,2-dicarboxylate (**2c**)

According to GP 2 **1c** (0.65 g, 2.00 mmol) was made to react with DMAD (0.57 g, 4.00 mmol, 0.50 mL) and Et_3N (0.61 g, 6.00 mmol, 0.85 mL) in MeCN (40 mL). The crude was purified by column chromatography (Al_2O_3 neutral; cyclohexane/EtOAc = 4/1; R_f = 0.28). The residue was crystallized from cyclohexane/EtOAc and dried in *vacuo* with $CaCl_2$ to afford **2c** as fluorescent, yellow needles (15 mg, 44.5 µmol, < 5%). The product was identified by TLC analysis and ^{1}H-NMR spectroscopy.

2. Absorption and emission spectra

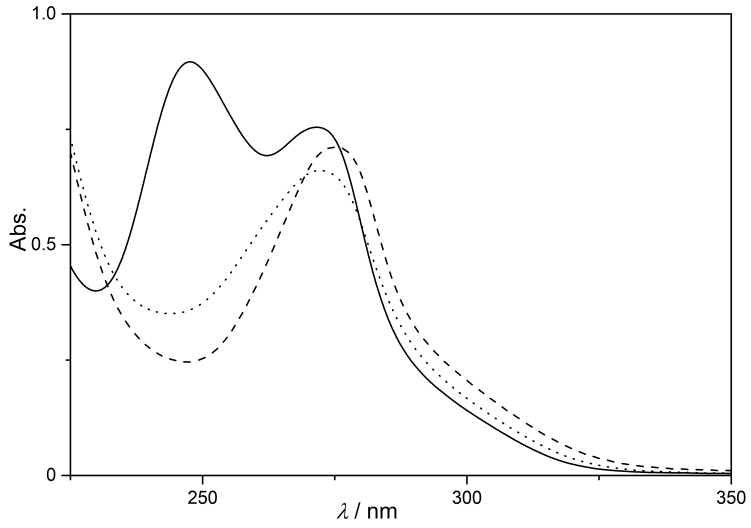


Figure S1. Absorption spectra of **1a** (solid line), **1b** (dashed line) and **1c** (dotted line) in MeCN; *c* = 50 µM.

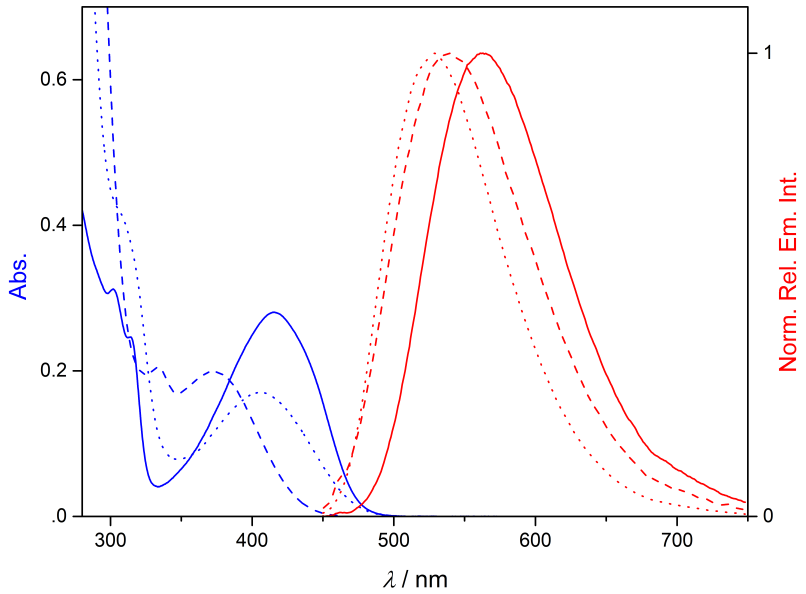


Figure S2. Absorption spectra (left; blue; c = 40 µM) and emission spectra (right; red; Abs. = 0.10 at λ_{ex} = 405 nm) of **2a** (solid line), **2b** (dashed line) and **2c** (dotted line) in MeCN.

3. Crystallographic data

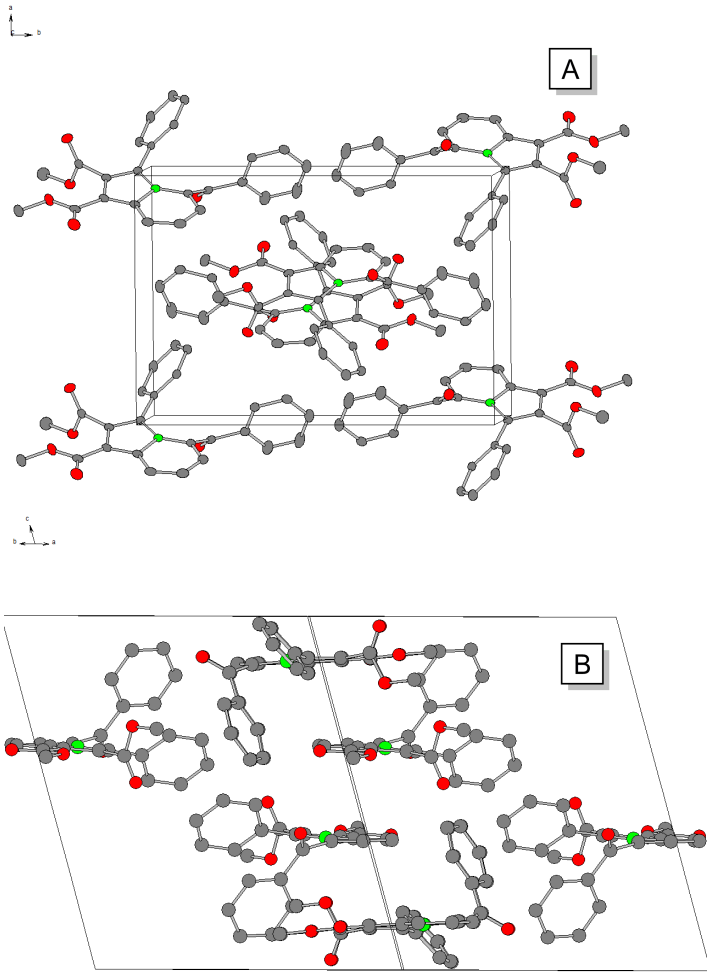


Figure S3. Unit cells of the polymorphs **2a**^{c} (A) and **2a**^{n} (B).

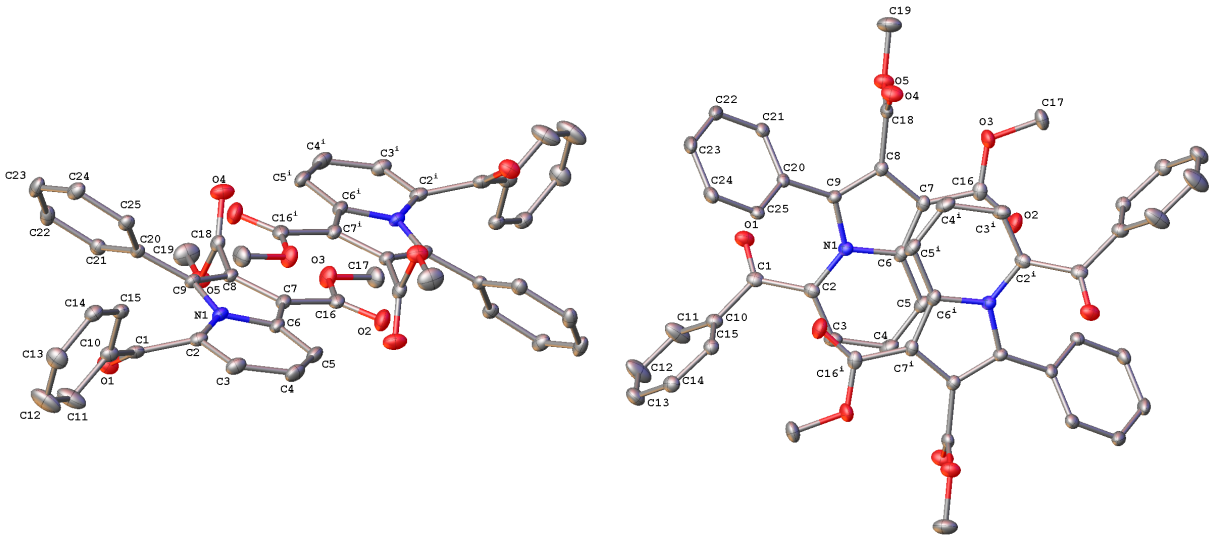


Figure S4. Structure of **2a**^{c} in the solid state showing the closest pair of coplanar indolizine units (50% probability ellipsoids). Atoms with same number, but with and without superscript, are related by the symmetry operation 1-X, 1-Y, 1-Z.

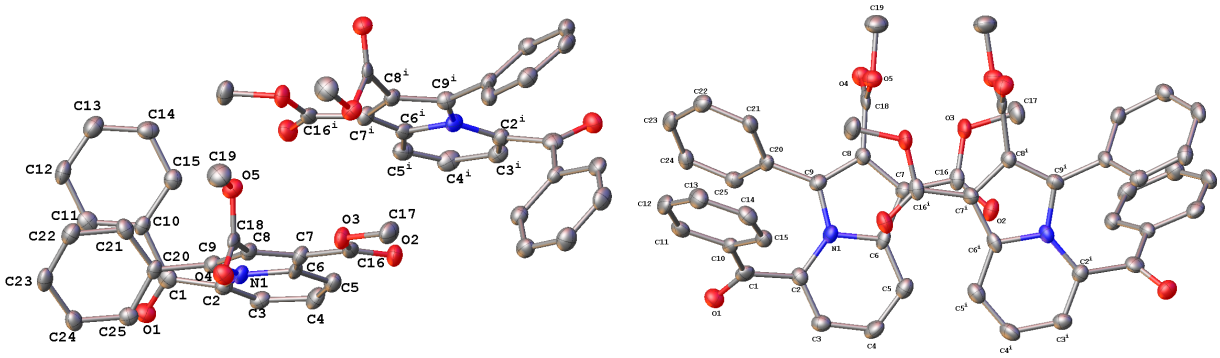


Figure S5. Structure of **2a^{n}** in the solid state showing the closest pair of coplanar indolizine units (50% probability ellipsoids). Atoms with same number, but with and without superscript, are related by the symmetry operation 1-X, +Y, ½-Z.

Table S1. Crystal Data and Structure Refinement Details of the Polymorphs **2a^{n}** and **2a^{c}**.[a]

	2a^{n}	**2a^{c}**
source	Cu-Kα (1.54178 Å)	Mo- Kα (0.71073 Å)
Molecular formula	$C_{26}H_{19}NO_5$	$C_{26}H_{19}NO_5$
formula weight / g mol^{-1}	413.41	413.41
Space group	C2/c (#15)	P 21/n (#14)
Crystal system	monoclinic	monoclinic
Unit cell dimensions	a = 17.712 (14) Å	a = 10.7046 (8) Å
	b = 16.498 (16) Å	b = 15.0609 (11) Å
	c = 14.990 (14) Å	c = 12.5922 (10) Å
	β = 111.50 (7)°	β = 99.232 (2)°
d(max), Å	0.92	0.70
No.unique ref.	2727	6129
I>2σ(1)	1761	4218
R1 (I>2σ(1))	0.049	0.047
wR2 (all data)	0.109	0.120
Volume / Å	4075.4 (70)	2003.8 (30)
Z	8	4
calc. density / g cm^{-3}	1.347	1.370

[a] CCDC deposition number 1923161 (**2a^{n}**) and 1923160 (**2a^{c}**) contain the supplementary crystallographic data for these compounds. These data can be obtained at The Cambridge Crystallographic Data Centre at https://www.ccdc.cam.ac.uk

4. IR spectra

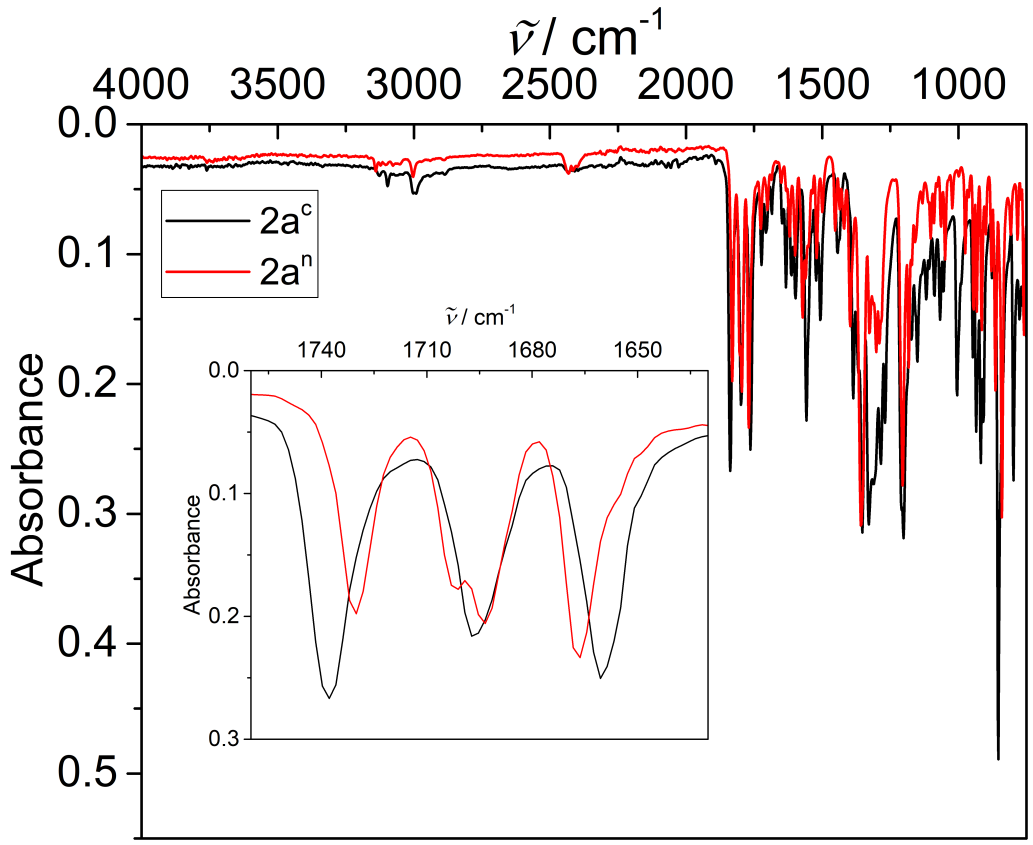


Figure S6. FT-IR spectra of the polymorphs **2a^{n}** (red line) and **2a^{c}** (black line).

5. NMR spectra

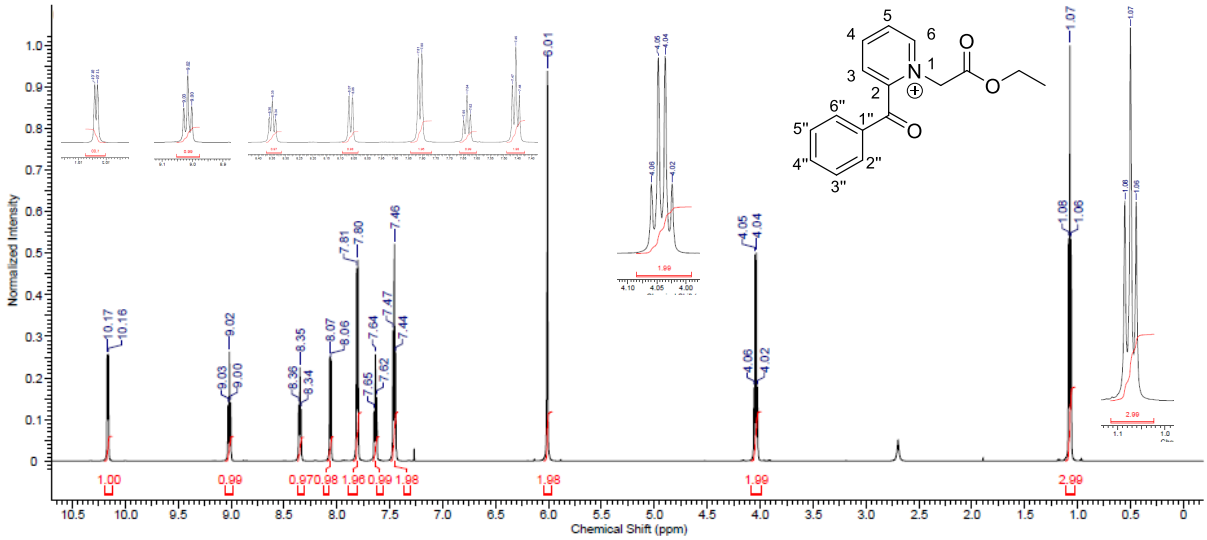


Figure S7. ^{1}H-NMR spectrum (400 MHz) of (**1b**) in $CDCl_3$.

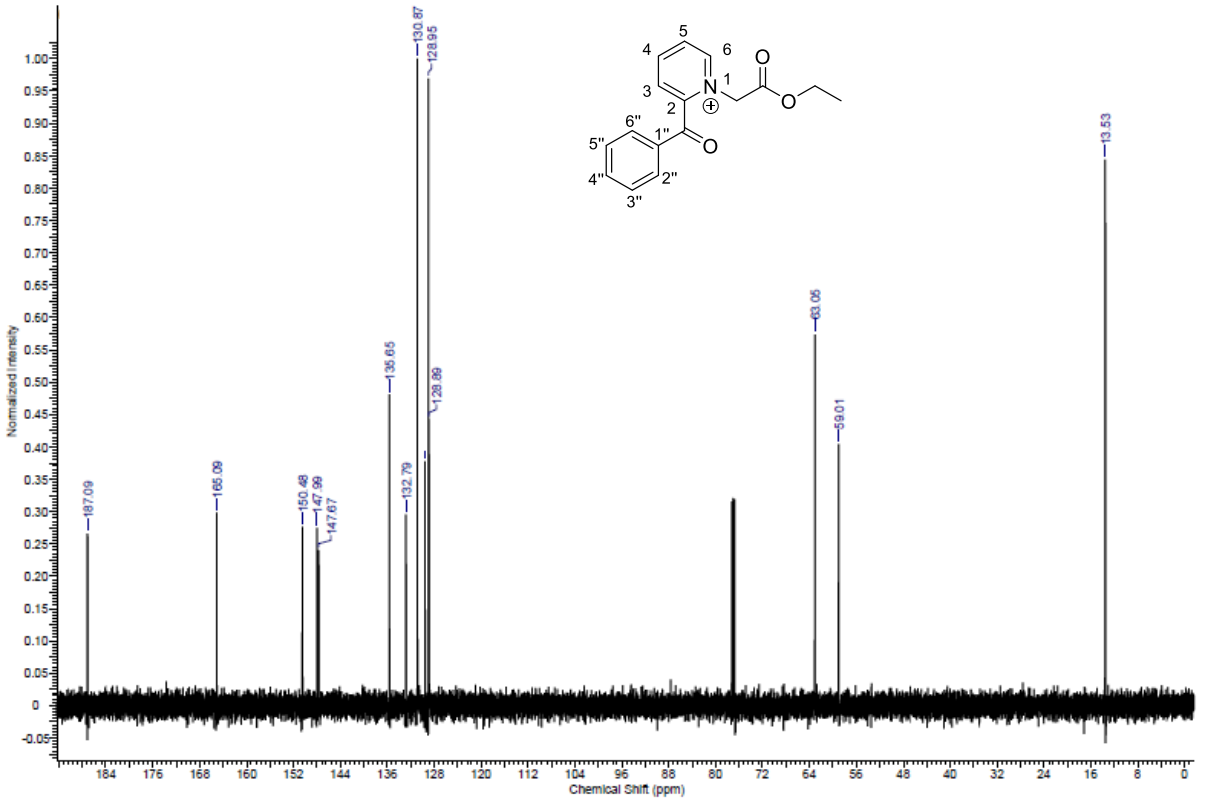


Figure S8. ^{13}C-NMR spectrum (150 MHz) of **1b** in $CDCl_3$.

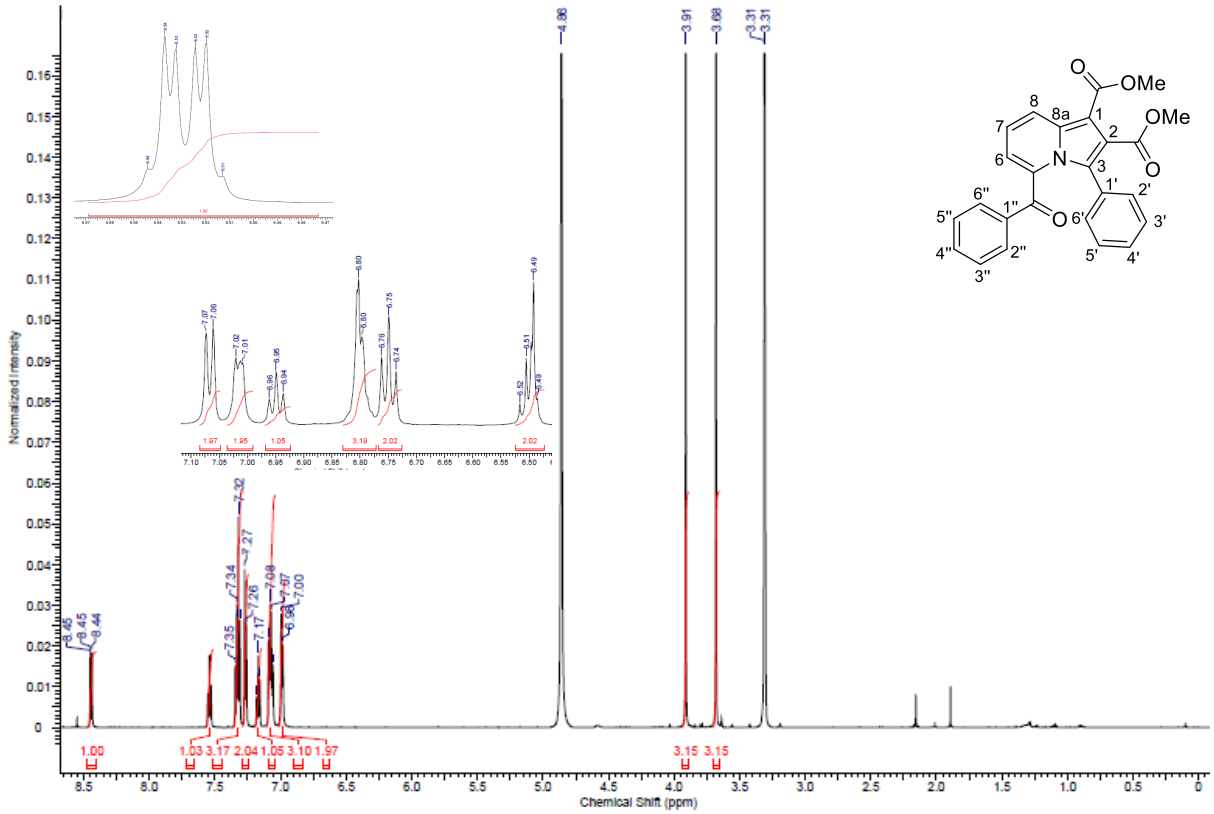


Figure S9. ^{1}H-NMR spectrum (400 MHz) of **2a** in CD_3OD.

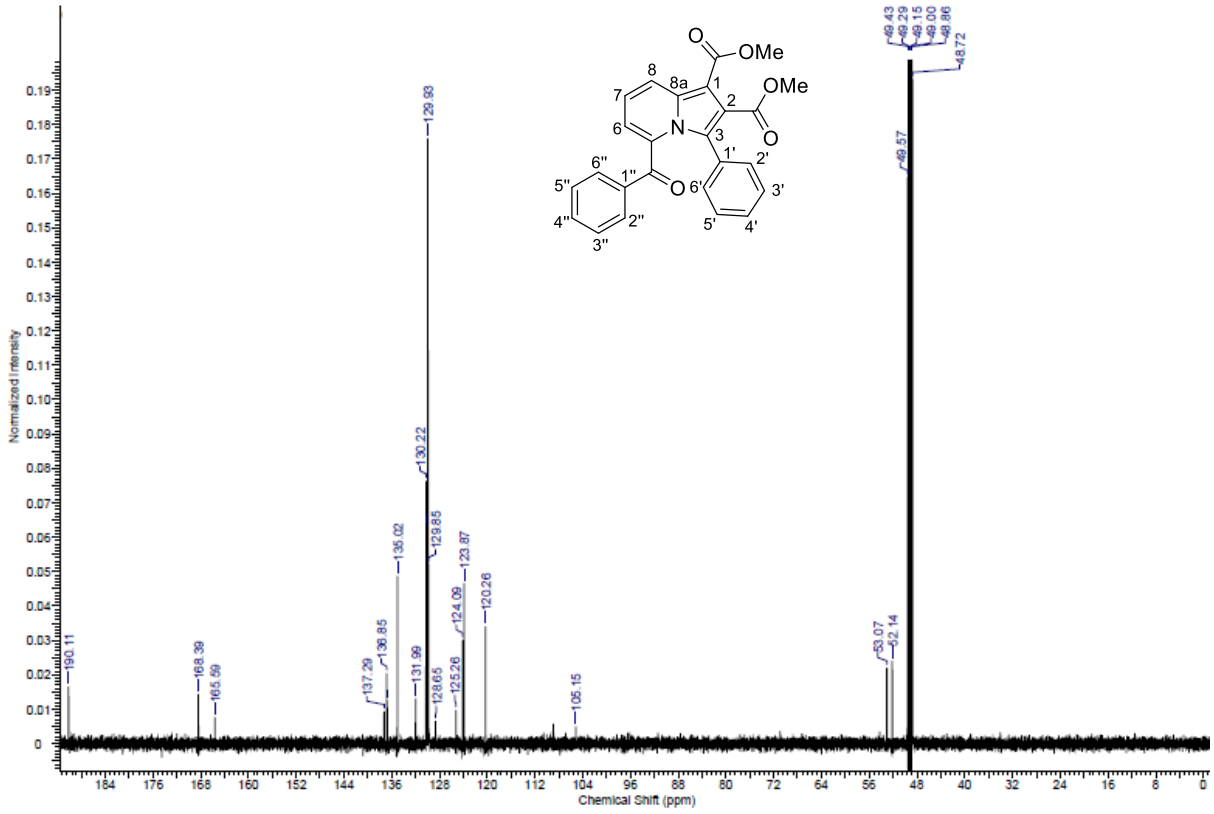


Figure S10. ^{13}C-NMR spectrum (100 MHz) of **2a** in CD_3OD.

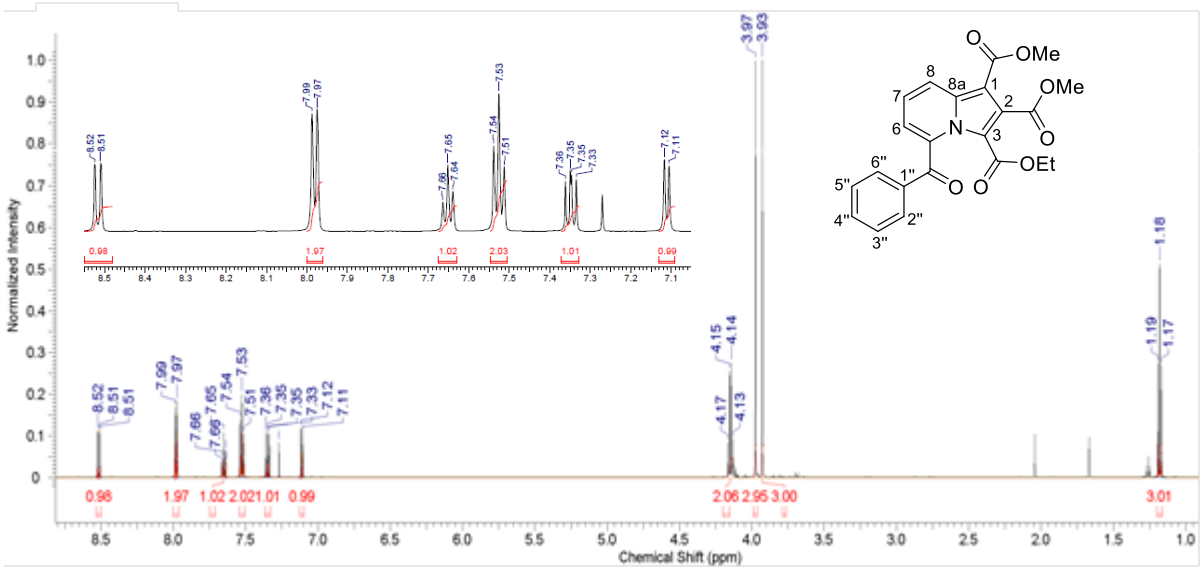


Figure S11. ^{1}H-NMR spectrum (600 MHz) of **2b** in$CDCl_3$.

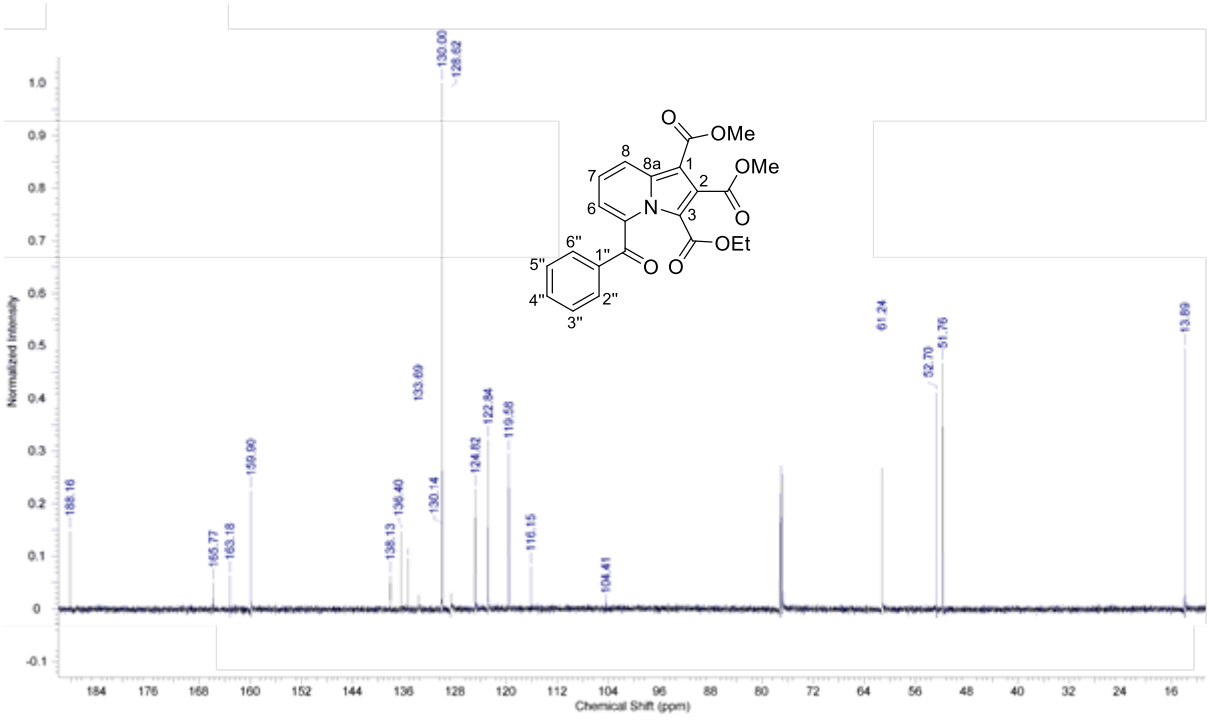


Figure S12. ^{13}C-NMR spectrum (150 MHz) of **2b** in $CDCl_3$.

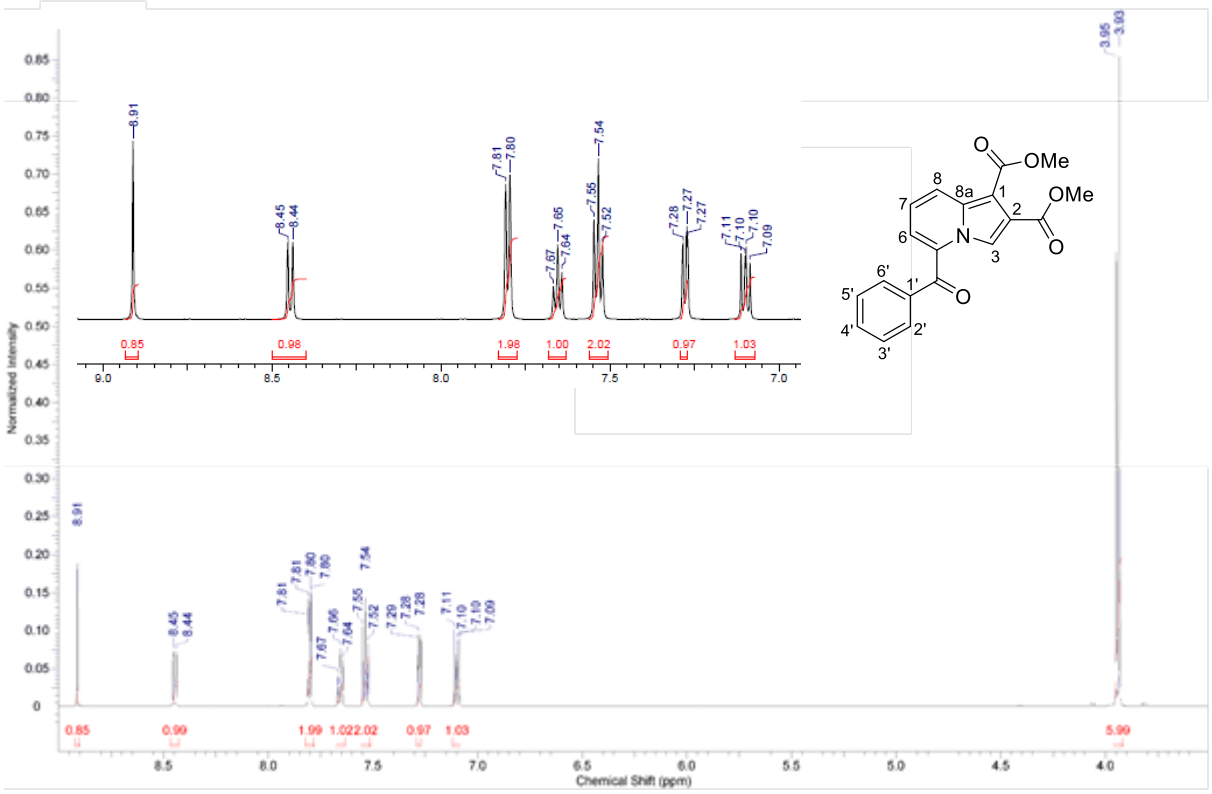


Figure S13. ^{1}H-NMR spectrum (400 MHz) of **2c** in $CDCl_3$.

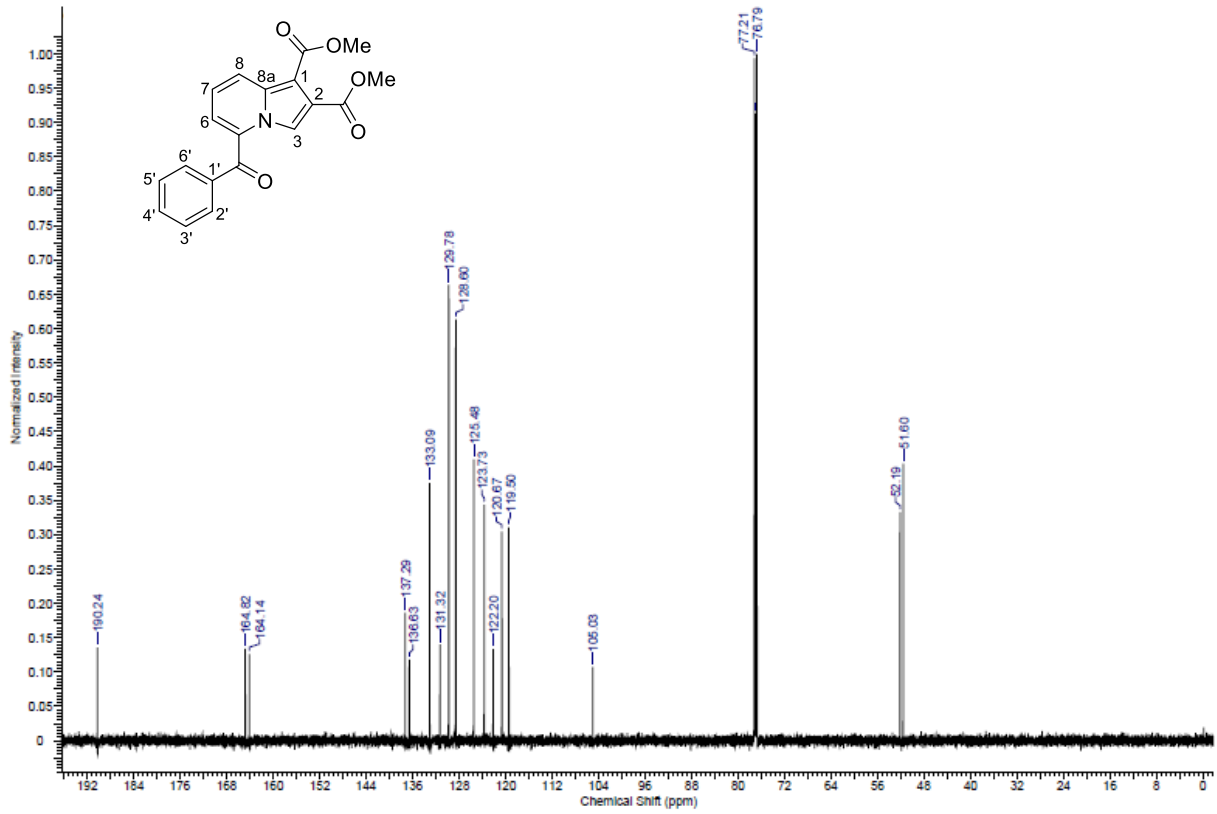


Figure S14. ^{13}C-NMR spectrum (150 MHz) of **2c** in $CDCl_3$.

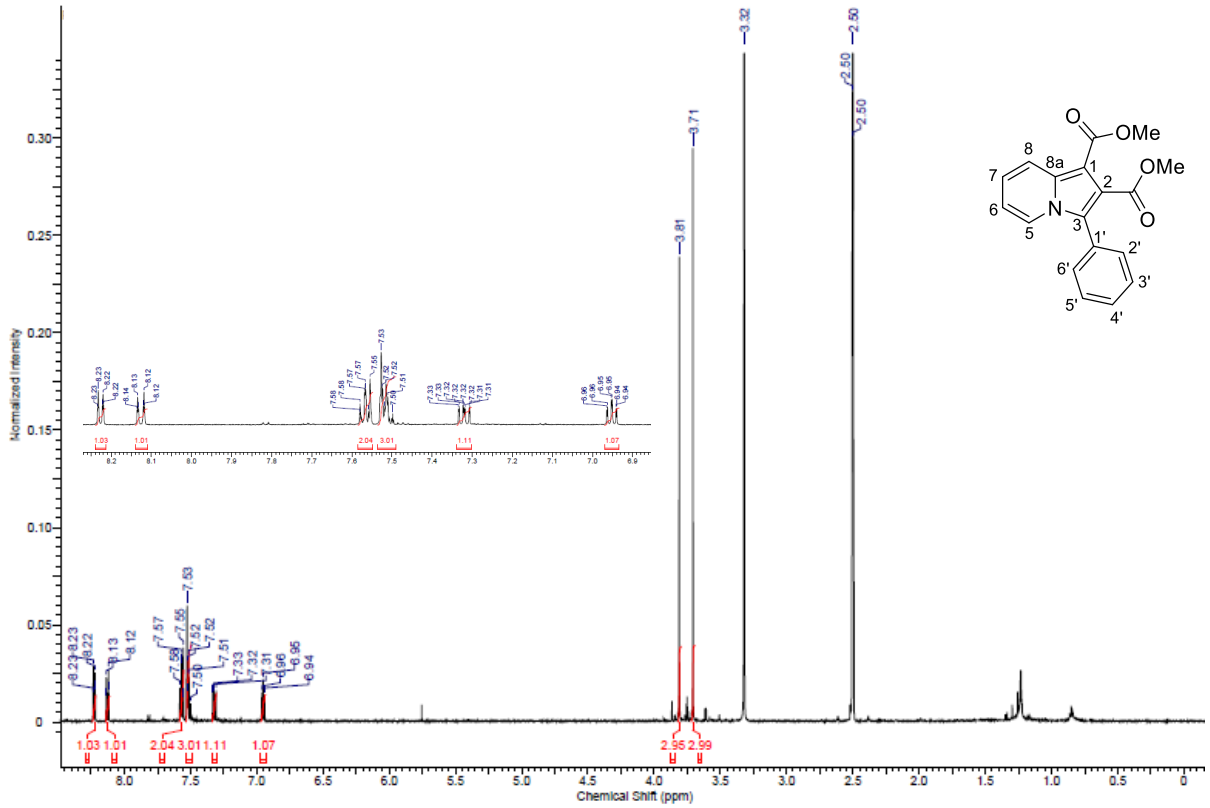


Figure S15. ^{1}H-NMR spectrum (400 MHz) of **2d** in DMSO-d_6.

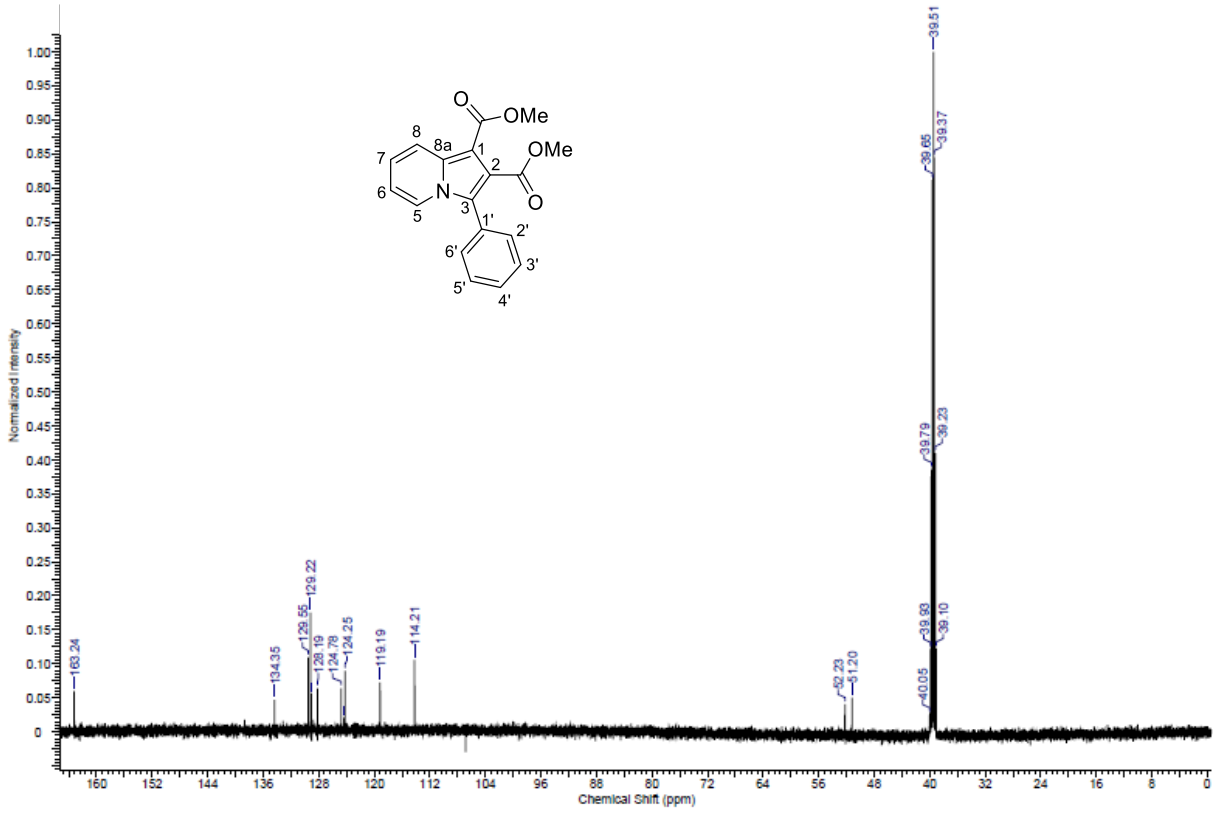


Figure S16. ^{13}C-NMR spectrum (150 MHz) of **2d** in DMSO-d_6.