Visible-Light-Mediated Dearomatisation of Indoles and Pyrroles to Pharmaceuticals and Pesticides

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Supporting Information

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1. Materials, methods

Commercial reagents were used without purification and reactions were run under O\textsubscript{2} atmosphere with exclusion of moisture from reagents using standard techniques for manipulating air-sensitive compounds. \textsuperscript{1}H NMR spectra (300, 400 and 500 MHz) and \textsuperscript{13}C NMR spectra (75.58, 100.62 and 125.71 MHz) were recorded using Bruker spectrometers AVANCE III 300, AVANCE III HD 400, AVANCE III 400, AVANCE III HD 500 and Varian spectrometers Mercury VX 300, VNMRS 300 and Inova 500 with CDCl\textsubscript{3} and DMSO-d\textsubscript{6} as solvent. NMR spectra were calibrated using the solvent residual signals (CDCl\textsubscript{3}: $\delta$ \textsuperscript{1}H = 7.26, $\delta$ \textsuperscript{13}C = 77.16). ESI mass spectra were recorded on Bruker Daltonic spectrometers maXis (ESI-QTOF-MS) and micrOTOF (ESI-TOF-MS). GC-MS mass spectra were recorded on Thermo Finnigan spectrometers TRACE (Varian GC Capillary Column; wcot fused silica coated CP-SIL 8CB for amines; 30 m x 0.25 mm x 0.25 µm) and DSQ (Varian FactorFour Capillary Column; VF-5ms 30 m x 0.25 mm x 0.25 µm). Gas chromatography was performed on an Agilent Technologies chromatograph 7890A GC System (Supelcowax 10 Fused Silica Capillary Column; 30 m x 0.32 mm x 0.25 µm). GC calibrations were carried out with authentic samples and n-dodecane as an internal standard. Absorption-emission spectra were recorded on a Jasco FP-8500 Spectrofluorometer and UV/Vis spectra were recorded on a Jasco V-770 Spectrophotometer. Reference for reported products is given after the name of the product.
2. Setup for photocatalytic reactions

The reaction setup is depicted in Figure S1. The reaction setup consists of a self-constructed light source configuration, made up of a crystallizing dish with a diameter of 140 mm. Inside of the crystallizing dish, commercially available 5 m LED-Strip is glued with separable LED elements. In total, 3 m LED strip is used in a crystallizing dish, with a total power of 24 W. Light intensity of the light source can be adjusted by a self-constructed dimmer. Construction of the reaction setup and the dimmer was performed by the electronic services of the faculty for chemistry of the Georg-August-Universität Göttingen. Cooling of the setup is performed by a commercially available 120 mm computer fan. To ensure the constant room temperature, the dimmer setting was used at 50% (12 W). During the first experiment the temperature was monitored inside the crystallizing dish and did not exceed room temperature (25–30 °C). Magnetic stirring was performed with 250 rpm. The wavelength of the LED setup is ranging from 404 nm to 553 nm with a maximum at 456 nm.

![Figure S1: LED reaction setup.](image)
3. General procedure for the oxidation of indoles/pyrroles to isatines and imidazoles under air/oxygen

10 mL two-necked flask containing a stirring bar was charged with substrate (0.25 mmol), Rose bengal (0.0075 mmol), DMF (0.9 mL) and H₂O (0.1 mL). After purging the flask three times with vacuum and two times with nitrogen, O₂ atmosphere was incorporated through an O₂-filled balloon. Afterwards, dry DMF (0.9 mL) and degassed Milli-Q water (0.1 mL) were added. The resulting mixture was stirred for 16–48 h under blue LED irradiation (the progress can be monitored via TLC). Then, the resulting mixture underwent an aqueous workup (using distilled water; or saturated LiCl solution in case of slurry phase separation) and was extracted three times with ethyl acetate (in several cases extraction was performed with benzene). The combined organic layers were dried over anhydrous Na₂SO₄, filtered and concentrated in vacuo. Products were purified using silica gel chromatography with ethyl acetate and n-pentane as solvents (typically 50:50 ethyl acetate:n-pentane). In case of imidazoles, decomposition of the products was observed over time, therefore fast purification was necessary.
4. Optimization table

Table S1: Optimization table for the oxygenation of 1H indole\(^{[a]}\)

| Catalyst         | Solvent | Water content / Vol% | Yield / % |
|------------------|---------|----------------------|-----------|
| Rose bengal      | DMSO    | 0                    | 12        |
| Fluorenone       | DMSO    | 0                    | 3         |
| Eosin Y          | DMSO    | 0                    | 8         |
| Xanthone         | DMSO    | 0                    | 4         |
| Riboflavine      | DMSO    | 0                    | 7         |
| Rhodamine 6G     | DMSO    | 0                    | 2         |
| Rose bengal      | DMSO    | 20                   | 23        |
| Rose bengal      | DMA     | 20                   | 15        |
| Rose bengal      | THF     | 20                   | 7         |
| Rose bengal      | ACN     | 20                   | 9         |
| Rose bengal      | DMF     | 20                   | 30        |
| Rose bengal      | DMF     | 50                   | 12        |
| Rose bengal      | DMF     | 15                   | 40        |
| Rose bengal      | DMF     | 10                   | 52        |
| Rose bengal\(^{[b]}\) | DMF    | 10                   | 93        |

\(^{[a]}\) Reaction conditions: 1H indole (0.25 mmol), catalyst amount (3.0 mol%), reaction volume (1.0 ml), 18 h reaction time, 12 W blue LED, yield determined by GC calibration with biphenyl as internal standard; \(^{[b]}\) 24 h reaction time.
5. Mechanistic experiments

Summary of labelling experiments

Oxygenation under $^{18}\text{O}_2$ atmosphere

$^{1}H$ Indole was oxidized by the procedure described in section 4. with a 97 atom% $^{18}\text{O}_2$ atmosphere. After 18 h the resulting products were characterized by GC-MS, HRMS and ESI.

**MS (ESI):** calcd. for $\text{C}_8\text{H}_5\text{N}^{18}\text{O}_2 [\text{M+H}^+]$: 148.0393, found: 148.0401.

**MS (ESI):** calcd. for $\text{C}_8\text{H}_5\text{N}^{18}\text{O}_{16}\text{O} [\text{M+H}^+]$: 150.0441, found: 150.0431.

**MS (ESI):** calcd. for $\text{C}_8\text{H}_5\text{N}^{18}\text{O}_2 [\text{M+H}^+]$: 152.0478, found: 152.0471.

**Ratio:** 5 : 10 : 1
Oxidation with $H_2^{18}O$

$1H$ Indole was oxidized by the procedure described in section 4. with $H_2^{18}O$, and an $^{16}O_2$-atmosphere. After 18 h the resulting products were characterized by GC-MS, HRMS and ESI.

**MS (ESI):** calcd. for $C_8H_8N^{16}O_2 [M+H^+]$: 148.0393, found: 148.0401.

**MS (ESI):** calcd. for $C_8H_8N^{18}O^{16}O [M+H^+]$: 150.0441, found: 150.0431.

**MS (ESI):** calcd. for $C_8H_8N^{18}O_2 [M+H^+]$: 152.0478, found: 152.0471.

Ratio: 10 : 5 : 1.5

Oxidation with $H_2^{18}O$ under $^{18}O_2$ atmosphere

$1H$ Indole was oxidized by the procedure described in section 4. with $H_2^{18}O$ and an 97 atom% $^{18}O_2$ atmosphere. After 18 h the resulting products were characterized by GC-MS, HRMS and ESI.

**MS (ESI):** calcd. for $C_8H_8N^{18}O_2 [M+H^+]$: 152.0478, found: 152.0471.
**Test for hydrogen peroxide**

To test the formation of hydrogen peroxide as side product, the reaction was performed according to the procedure described in section 2.

The resulting reaction mixture was extracted with ethyl acetate (5 mL), water (5 mL), aqueous and organic phase were tested for hydrogen peroxide with literature-known reactions.

**H$_2$O$_2$ glowing splint test**

![Chemical Reaction](image)

**Procedure:** 1 mL solution was taken, was transferred to a snap cap vial and MnO$_2$ (~5 mg) was added, the forming gas was tested with a glowing splint:

**Results:**
- Aqueous phase tested positive: production of flammable gas (oxygen) after addition of MnO$_2$.
- Organic phase tested negative.
- Control aqueous phase tested negative.
- Control organic phase tested negative.

**H$_2$O$_2$ luminol test**

![Chemical Reaction](image)

**Procedure:** Luminol (10 mg) was dissolved in H$_2$O (5 mL) and NaHCO$_3$ (100 mg) was added to adjust the pH value. The resulting mixture was divided between 5 vials. For each vial, one drop of a 1 M $K_3[Fe(CN)_6]$ solution was added shortly before the test. 1 mL of the corresponding phases of the reaction mixture were added to the luminol solution. In case of peroxides, a luminescence was observed. Afterwards all samples were controlled by the addition of hydrogen peroxide solution (30 V%) for luminescence.

**Results:**
- Aqueous phase tested positive with luminescence for over 2 minutes.
- Organic phase tested negative.
- Control aqueous phase tested negative.
- Control organic phase tested negative.
**Stern-Volmer plot**

To determine the reactive species, in the beginning of the photocatalytic reaction absorption-emission spectra for a Stern-Volmer plot were acquired. Firstly, a 3D spectrum for excitation and emission of rose bengal in DMF was recorded in order to detect the maxima of absorption and emission. The resulting spectrum is depicted in **Figure S3** with 3 absorption bands. The excitation maximum was measured at 565 nm and the emission maximum at 575 nm. These wavelengths were used for further measurements.

![Figure S2: 3D absorption-emission spectrum of Rose Bengal in DMF.](image)

A blank sample was recorded under N\textsubscript{2} atmosphere without substrate, water, oxygen and the received intensity was set as I\textsubscript{0}. The effect of varied amounts of substrate was investigated, as also the saturation of the solution with air and oxygen. The effect of varied amounts of water was investigated. **Figures S4–S6** show the results for each parameter separately. Depending on the concentration of oxygen and water, the emission decreases significantly. The amount of substrate had no effect on the emission of Rose Bengal.

Based in the mechanistic investigation the 3D spectrum for excitation and emission of 1\textsubscript{H} indole was recorded additionally, which shows an absorption band at blue light.
**Figure S3:** 3D absorption-emission spectrum of $1H$ indole in DMF.

**Figure S4:** Stern-Volmer plot for different concentration of $1H$ indole.
Figure S5: Stern-Volmer plot for different concentration of oxygen in % used to saturate the solution.

Figure S6: Stern-Volmer plot for different amount of water.
6. Procedure for synthesis of products 34b–38b

Synthesis of 5'-chloro-spiro[benzothiazole-2(3H),3'-[3H]indol]-2'(1'H)-one (34b):

5-Chloroindole (37.8 mg, 0.25 mmol) and rose bengal (7.3 mg, 0.0075 mmol) were prepared in a 10 mL two-necked flask. After purging the flask three times with vacuum and two times with nitrogen, O₂ atmosphere was incorporated through an O₂-filled balloon. Afterwards dry DMF (0.9 mL) and degassed Milli-Q water (0.1 mL) were added. The resulting mixture was stirred for 24 h under blue LED irradiation (the progress can be monitored via TLC). After completion of the oxygenation reaction 2-amino-benzenethiol (37.5 mg, 0.3 mmol) in DMF (0.2 mL), was added and the LED setup replaced by an oil bath. The reaction was stirred for further 24 h at 85 °C. Then, the resulting mixture underwent an aqueous workup and was extracted three times with ethyl acetate. The combined organic layers were dried over anhydrous Na₂SO₄, filtered and concentrated in vacuo. The product mixture was purified using silica gel chromatography with ethyl acetate and n-pentane as solvents (50:50 ethyl acetate:n-pentane).
Synthesis of $2'$-amino-5-chloro-1,2-dihydro-6'-$\{[3\beta,17\beta]-3$-hydroxyandrost-5-en-17-yl$\}$-2-oxo$\{3H$-indole-3,4'$\{1'H$-pyridine$\}$-3'$-carbonitrile (35b)

**Step 1:** 5-Chloroindole (75.6 mg, 0.5 mmol) and rose bengal (14.6 mg, 0.015 mmol) were prepared in a 10 mL two-necked flask. After purging the flask three times with vacuum and two times with nitrogen, O$_2$ atmosphere was incorporated through an O$_2$-filled balloon. Afterwards dry DMF (1.8 mL) and degassed Milli-Q water (0.2 mL) were added. The resulting mixture was stirred for 24 h under blue LED irradiation (the progress can be monitored via TLC). After completion of the oxygenation reaction the resulting mixture underwent an aqueous workup and was extracted three times with ethyl acetate. The combined organic layers were dried over anhydrous Na$_2$SO$_4$, filtered and concentrated in vacuo. The product mixture was purified using silica gel chromatography with ethyl acetate and $n$-pentane as solvents (ratio 50:50 ethyl acetate:$n$-pentane).

**Step 2:** 5-Chloroisatin (45.4 mg, 0.25 mmol), Pregnenolone (79.1 mg, 0.25 mmol), Malononitrile (16.5 mg, 0.25 mmol) and freshly dried ammonium acetate (38.5 mg, 0.5 mmol) were dissolved in ethanol (5 mL). The resulting mixture was refluxed for 18 h. After cooling, the solvent was removed under reduced pressure. The product mixture was purified using silica gel chromatography with acetone and $n$-pentane as solvents (with increasing amount of acetone).
Synthesis of 1,3-dihydro-3-(phenylimino)-2H-indol-2-one (36b)

\[
\begin{align*}
\text{1H Indole (29.3 mg, 0.25 mmol) and rose bengal (7.3 mg, 0.0075 mmol) were prepared in a 10 mL two-necked flask. After purging the flask three times with vacuum and two times with nitrogen, O}_2 \text{ atmosphere was incorporated through an O}_2\text{-filled balloon. Afterwards, dry DMF (0.9 mL) and degassed Milli-Q water (0.1 mL) was added. The resulting mixture was stirred for 24 h under blue LED irradiation (the progress can be monitored via TLC). After completion of the oxygenation reaction aniline (27.9 mg, 0.3 mmol) was added and the reaction was stirred for further 24 h at room temperature. Then, the resulting mixture underwent an aqueous workup and was extracted three times with ethyl acetate. The combined organic layers were dried over anhydrous Na}_2\text{SO}_4, \text{ filtered and concentrated in vacuo. The product mixture was purified using silica gel chromatography with ethyl acetate and n-pentane as solvents (20:80 ethyl acetate:n-pentane).}
\end{align*}
\]
1,3-Dihydro-3-(phenylimino)-2H-indol-2-one (57.0 mg, 0.25 mmol), TsOH (4.3 mg, 0.025 mmol) and 1H indole (58.6 mg, 0.5 mmol) were dissolved in ethanol (5.0 mL) and refluxed 18 h under stirring. Then, the resulting mixture underwent an aqueous workup and was extracted three times with ethyl acetate. The combined organic layers were dried over anhydrous Na₂SO₄, filtered and concentrated in vacuo. The product mixture was purified using silica gel chromatography with ethyl acetate and n-pentane as solvents (20:80 ethyl acetate:n-pentane).
2-Phenyl-1H-indole (48.3 mg, 0.25 mmol) and rose bengal (7.3 mg, 0.0075 mmol) were prepared in a 10 mL two-necked flask. After purging the flask three times with vacuum and two times with nitrogen, O\textsubscript{2} atmosphere was incorporated through an O\textsubscript{2}-filled balloon. Afterwards, dry DMF (0.9 mL) and degassed Milli-Q water (0.1 mL) were added. After completion of the oxygenation reaction the resulting mixture underwent an aqueous workup and was extracted three times with ethyl acetate. The combined organic layers were dried over anhydrous Na\textsubscript{2}SO\textsubscript{4}, filtered and concentrated in vacuo. The product 27b (29.1 mg) was purified using silica gel chromatography with ethyl acetate and n-pentane as solvents. Then, 27b and CoCl\textsubscript{2} (0.1 eq.) were added into 10 mL flask with MeCN as solvent (3 mL). Then, TBHP (5 eq.) was added dropwise at room temperature over a period of 30 min. The reaction mixture was then heated to reflux and kept at that temperature until TLC analysis indicated full conversion. The solvent was evaporated under reduced pressure. The residue was mixed with water (10 mL), and the resulting solution was extracted with ethyl acetate (3 × 10 mL). The combined organic phases were washed with brine (1 × 10 mL) and dried with anhydrous Na\textsubscript{2}SO\textsubscript{4}. The solvent was removed by rotary evaporation to give the crude residue, which was purified by flash column chromatography on silica to afford the desired compound 38b (23.6 mg).
7. Characterization of products

3 mol% Rose Bengal, O₂, 24 h, Isatin\(^{[1]}\) (1b): \(^1\)H NMR (300 MHz, DMSO-\(d_6\)): \(\delta\) 11.03 (s, 1H), 7.73 – 7.30 (m, 2H), 7.22 – 6.72 (m, 2H); \(^{13}\)C NMR (75 MHz, DMSO-\(d_6\)): \(\delta\) 184.4, 159.4, 150.8, 138.4, 124.7, 122.8, 117.8, 112.3; MS (GC-MS): \(m/z\) 147 (M\(^+\)); 93% yield.

3 mol% Rose Bengal, O₂, 36 h, 4-Methylisatin\(^{[2]}\) (2b): \(^1\)H NMR (300 MHz, DMSO-\(d_6\)): \(\delta\) 11.00 (s, 1H), 7.44 (t, \(J = 8\) Hz, 1H), 6.86 (dt, \(J = 8\) Hz, 1H), 6.71 (dt, \(J = 7.8\) Hz, 1H), 2.44 (s, 3H); \(^{13}\)C NMR (75 MHz, DMSO-\(d_6\)): \(\delta\) 184.4, 159.4, 150.8, 138.6, 137.6, 124.5, 115.6, 109.2, 17.2; MS (GC-MS): \(m/z\) 161 (M\(^+\)); 78% yield.

3 mol% Rose Bengal, O₂, 18 h, 5-Methylisatin\(^{[2]}\) (3b): \(^1\)H NMR (300 MHz, DMSO-\(d_6\)): \(\delta\) 10.94 (s, 1H), 7.46 – 7.37 (m, 1H), 7.34 – 7.30 (m, 1H), 6.81 (d, \(J = 8\) Hz, 1H), 2.26 (s, 3H); \(^{13}\)C NMR (75 MHz, DMSO-\(d_6\)): \(\delta\) 185.0, 159.9, 149.0, 139.2, 132.4, 125.2, 118.2, 112.5, 20.5; MS (GC-MS): \(m/z\) 161 (M\(^+\)); 86% yield.

3 mol% Rose Bengal, O₂, 48 h, 6-Methylisatin\(^{[3]}\) (4b): \(^1\)H NMR (300 MHz, DMSO-\(d_6\)): \(\delta\) 11.00 (s, 1H), 7.40 (d, \(J = 7.7\) Hz, 1H), 6.97 – 6.84 (m, 1H), 6.78 – 6.69 (m, 1H), 2.35 (s, 3H); \(^{13}\)C NMR (75 MHz, DMSO-\(d_6\)): \(\delta\) 184.1, 160.4, 151.6, 150.6, 125.1, 124.0, 116.0, 113.1, 22.7; MS (GC-MS): \(m/z\) 161 (M\(^+\)); 82% yield.

3 mol% Rose Bengal, O₂, 18 h, 7-Methylisatin\(^{[4]}\) (5b): \(^1\)H NMR (300 MHz, DMSO-\(d_6\)): \(\delta\) 11.08 (s, 1H), 7.50 – 7.39 (m, 1H), 7.38 – 7.27 (m, 1H), 6.98 (t, \(J = 7.5\) Hz, 1H), 2.18 (s, 3H); \(^{13}\)C NMR (75 MHz, DMSO-\(d_6\)): \(\delta\) 184.8, 160.0, 149.3, 139.5, 122.6, 122.0, 121.6, 117.6, 15.4; MS (GC-MS): \(m/z\) 161 (M\(^+\)); 69% yield.

3 mol% Rose Bengal, O₂, 48 h, Methyl-5-carboxylateisatin\(^{[5]}\) (6b): \(^1\)H NMR (300 MHz, DMSO-\(d_6\)): \(\delta\) 11.40 (s, 1H), 8.16 (dd, \(J = 8.3, 1.8\) Hz, 1H), 7.93 (dd, \(J = 1.9, 0.6\) Hz, 1H), 7.02 (dd, \(J = 8.3, 0.6\) Hz, 1H), 3.85 (s, 3H); \(^{13}\)C NMR (75 MHz, DMSO-\(d_6\)): \(\delta\) 183.3, 165.2, 159.7, 154.1, 138.9, 124.9, 123.8, 118.0, 112.3, 52.2; MS (GC-MS): \(m/z\) 205 (M\(^+\)); 58% yield.
3 mol% Rose Bengal, O₂, 48 h, 4-Bromoisatin[6] (7b): ¹H NMR (300 MHz, DMSO-d₆): δ 11.18 (s, 1H), 7.45 (t, J = 8.0 Hz, 1H), 7.21 (dd, J = 8.1, 0.7 Hz, 1H), 6.88 (dd, J = 7.8, 0.8 Hz, 1H); ¹³C NMR (75 MHz, DMSO-d₆): δ 181.7, 158.6, 152.5, 138.9, 126.7, 119.4, 116.5, 111.4; MS (GC-MS): m/z 225 (M⁺); 71% yield.

3 mol% Rose Bengal, O₂, 48 h, 5-Bromoisatin[7] (8b): ¹H NMR (300 MHz, DMSO-d₆): δ 11.13 (s, 1H), 7.73 (dd, J = 8.3, 2.1 Hz, 1H), 7.65 (d, J = 2.0 Hz, 1H), 6.87 (dd, J = 8.3, 0.5 Hz, 1H); ¹³C NMR (75 MHz, DMSO-d₆): δ 183.6, 159.4, 150.0, 140.5, 131.1, 127.4, 120.4, 114.7; MS (GC-MS): m/z 225 (M⁺); 80% yield.

3 mol% Rose Bengal, O₂, 48 h, 5,6-Dichloroisatin[8] (9b): ¹H NMR (300 MHz, DMSO-d₆): δ 11.25 (s, 1H), 7.78 (s, 1H), 7.13 (s, 1H); ¹³C NMR (75 MHz, DMSO-d₆): δ 182.7, 159.6, 150.1, 140.1, 126.5, 125.5, 118.6, 114.4; MS (GC-MS): m/z 215 (M⁺); 65% yield.

3 mol% Rose Bengal, O₂, 48 h, 5-Chloroisatin[3] (10b): ¹H NMR (300 MHz, DMSO-d₆): δ 11.13 (s, 1H), 7.60 (dd, J = 8.4, 2.3 Hz, 1H), 7.53 (d, J = 2.2 Hz, 1H), 6.91 (d, J = 8.3 Hz, 1H); ¹³C NMR (75 MHz, DMSO-d₆): δ 182.3, 159.2, 149.2, 137.3, 126.8, 124.1, 119.1, 113.8; MS (GC-MS): m/z 181 (M⁺); 73% yield.

3 mol% Rose Bengal, O₂, 48 h, 0.1 mmol scale, 4,6-Dibromoisatin[9] (11b): ¹H NMR (300 MHz, DMSO-d₆): δ 11.27 (s, 1H), 7.51 (d, J = 1.5 Hz, 1H), 7.05 (d, J = 1.5 Hz, 1H); ¹³C NMR (75 MHz, DMSO-d₆): δ 180.7, 158.7, 153.0, 131.4, 128.6, 120.2, 116.0, 114.1; MS (GC-MS): m/z 303 (M⁺); 93% yield.

3 mol% Rose Bengal, O₂, 48 h, 1-Methylisatin[10] (12b): ¹H NMR (300 MHz, DMSO-d₆): δ 7.68 (dd, J = 7.8, 1.4 Hz, 1H), 7.59 – 7.46 (m, 1H), 7.17 – 7.05 (m, 2H), 3.13 (s, 3H); ¹³C NMR (75 MHz, DMSO-d₆): δ 183.4, 158.1, 151.3, 138.2, 124.2, 123.2, 117.2, 110.5, 26.0; MS (GC-MS): m/z 161 (M⁺); 84% yield.
3 mol% Rose Bengal, O₂, 48 h, 6-Methyl-1-ethylisatin[11] (13b): ¹H NMR (300 MHz, CDCl₃): δ 7.42 (t, J = 7.8 Hz, 1H), 6.87 (dd, J = 7.8, 1.0 Hz, 1H), 6.70 (d, J = 7.8 Hz, 1H), 3.77 (q, J = 7.2 Hz, 2H), 2.56 (s, 3H), 1.29 (t, J = 7.2 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 184.3, 157.9, 150.8, 141.5, 137.6, 126.1, 115.9, 107.4, 35.0, 18.2, 12.7; MS (GC-MS): m/z 189 (M⁺); 64% yield.

3 mol% Rose Bengal, O₂, 48 h, 1-Benzylisatin[12] (14b): ¹H NMR (300 MHz, CDCl₃): δ 7.67 – 7.61 (m, 1H), 7.55 – 7.48 (m, 1H), 7.43 – 7.34 (m, 5H), 7.12 (t, J = 7.6 Hz, 1H), 6.80 (d, J = 8.0 Hz, 1H), 4.96 (s, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 189.94, 168.88, 154.62, 129.05, 128.17, 127.42, 125.43, 123.86, 110.98, 44.07; MS (GC-MS): m/z 237 (M⁺); 72% yield.

3 mol% Rose Bengal, O₂, 48 h, 1-Hexylisatin[13] (15b): ¹H NMR (300 MHz, CDCl₃): δ 7.64 – 7.52 (m, 2H), 7.10 (m, 1H), 6.89 (dd, J = 7.9, 0.8 Hz, 1H), 3.76 – 3.65 (m, 2H), 1.75 – 1.61 (m, 2H), 1.40 – 1.22 (m, 6H), 0.95 – 0.79 (m, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 183.7, 151.1, 138.3, 125.4, 123.6, 121.2, 117.6, 110.1, 40.3, 31.4, 27.2, 26.6, 22.5, 14.0; MS (GC-MS): m/z 231 (M⁺); 62% yield.

3 mol% Rose Bengal, O₂, 48 h, 5,6-Dihydro-[1,2-dione[3,2,1-i]quinoline-1,2-dione[14] (16b): ¹H NMR (300 MHz, DMSO-d₆): δ 7.43 (dd, J = 7.6, 1.0 Hz, 1H), 7.35 – 7.31 (m, 1H), 7.00 (t, J = 7.6 Hz, 1H), 3.70 – 3.55 (m, 2H), 2.72 (t, J = 6.1 Hz, 2H), 1.98 – 1.85 (m, 2H); ¹³C NMR (75 MHz, DMSO-d₆): δ 184.0, 156.6, 147.5, 136.9, 122.6, 122.1, 122.0, 115.5, 37.9, 23.2, 19.7; MS (GC-MS): m/z 187 (M⁺); 79% yield.
3 mol% Rose Bengal, O₂, 48 h, 7-Azaisatin[15] (20b): $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$ 11.61 (s, 1H), 8.40 (dd, $J = 5.2, 1.7$ Hz, 1H), 7.88 (dd, $J = 7.4, 1.7$ Hz, 1H), 7.11 (dd, $J = 7.4, 5.2$ Hz, 1H); $^{13}$C NMR (75 MHz, DMSO-$d_6$): $\delta$ 183.4, 164.5, 160.4, 155.7, 133.1, 119.4, 113.3; MS (GC-MS): $m/z$ 148 (M$^+$); yield: 84%; 3 mol% Rose Bengal, O₂, 5 mmol scale: 74% yield.

3 mol% Rose Bengal, O₂, 18 h, 3,4-Diethylmaleimide[16] (21b): $^1$H NMR (300 MHz, CDCl₃): $\delta$ 7.62 (bs, 1H) 2.40 (q, $J = 7.6$ Hz, 4H), 1.14 (t, $J = 7.6$ Hz, 6H); $^{13}$C NMR (75 MHz, CDCl₃): $\delta$ 172.0, 143.0, 17.0, 13.4; MS (GC-MS): $m/z$ 153 (M$^+$); 75% yield.

3 mol% Rose Bengal, O₂, 18 h, 3-[Ethyl ester]-4-phenyl-1H-pyrrole-2,5-dione (22b): $^1$H NMR (300 MHz, CDCl₃): $\delta$ 7.69 (dd, $J = 7.8, 1.7$ Hz, 2H), 7.55 – 7.41 (m, 3H), 4.37 (q, $J = 7.1$ Hz, 2H), 1.30 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl₃): $\delta$ 168.8, 166.4, 161.3, 143.0, 131.6, 130.1, 128.6, 127.0, 62.4, 13.9; ESI-HRMS: $m/z$ calcld. for C₁₃H₁₁NO₄ [M+H]$^+$: 245.0688 $m/z$, found 245.0697 $m/z$; 50% yield.

3 mol% Rose Bengal, O₂, 18 h, 2-Phenylmaleinimide[17] (23b): $^1$H NMR (300 MHz, CDCl₃): $\delta$ 7.94 (dd, $J = 7.5, 2.3$ Hz, 2H), 7.60 – 7.42 (m, 3H), 6.76 (s, 1H); $^{13}$C NMR (CDCl₃, 75 MHz): $\delta$ 170.4, 169.7, 144.7, 131.3, 129.0, 128.7, 128.5, 124.7; MS (GC-MS): $m/z$ 173 (M$^+$); yield 53%.

3 mol% Rose Bengal, O₂, 18 h, N-Phenylmaleimide[18] (24b): $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$ 7.51 (d, $J = 7.0$ Hz, 2H), 7.49-7.34 (m, 3H), 7.16 (d, $J = 0.8$ Hz, 2H); $^{13}$C NMR (75 MHz, DMSO-$d_6$): $\delta$ 169.9, 134.6, 131.6, 128.9, 127.7, 126.7; MS (GC-MS): $m/z$ 173 (M$^+$); 74% yield.
3 mol% Rose Bengal, O₂, 18 h, N-para-Iodophenylmaleimide[19] (25b): \(^1\)H NMR (300 MHz, DMSO-\(d_6\)): \(\delta\) 7.86 (d, \(J = 8.5\) Hz, 2H), 7.20 (s, 2H), 7.17 (d, \(J = 8.5\) Hz, 2H) \(^13\)C NMR (75 MHz, CDCl₃): \(\delta\) 161.78, 158.74, 138.76, 138.07, 121.70, 120.55, 88.11; MS (GC-MS): m/z 299 (M⁺); 69% yield.

3 mol% Rose Bengal, O₂, 18 h, N-para-Methoxyphenylmaleimide[20] (26b): \(^1\)H NMR (300 MHz, CDCl₃): \(\delta\) 7.54 (d, \(J = 9.0\) Hz, 2H), 7.10 (d, \(J = 8.8\) Hz, 2H), 6.81 (dd, \(J = 9.1, 7.1\) Hz, 2H), 3.80 (d, \(J = 3.2\) Hz, 3H); \(^13\)C NMR (75 MHz, CDCl₃): \(\delta\) 162.8, 158.7, 121.8, 121.7, 114.9, 114.3, 55.5; MS (GC-MS): 203 (M⁺); 77% yield.

3 mol% Rose Bengal, O₂, 46 h, N-(2-Formylphenyl)benzamide[21] (27b): \(^1\)H NMR (300 MHz, CDCl₃): \(\delta\) 12.12 (s, 1H), 10.03 (s, 1H), 8.99 (d, \(J = 8.4\) Hz, 1H), 8.11 - 8.09 (m, 2H), 7.79 - 7.68 (m, 2H), 7.63 - 7.53 (m, 3H), 7.39 - 7.34 (m, 1H); \(^13\)C NMR (CDCl₃, 75 MHz): \(\delta\) 195.9, 166.2, 141.3, 136.4, 136.2, 134.3, 132.2, 128.9, 127.5, 123.1, 122.0, 120.0; MS (GC-MS): m/z 225 (M⁺); 60% yield.

3 mol% Rose Bengal, O₂, 46 h, N-(1-Formylnapthalen-2-yl)acetamide (28b): \(^1\)H NMR (300 MHz, CDCl₃): \(\delta\) 9.11 (s, 1H), 8.21 - 8.17 (d, \(J = 9.0\) Hz, 1H), 7.88 - 7.83 (m, 2H), 7.79 - 7.76 (dd, \(J = 8.4, 1.2\) Hz, 1H), 7.56 - 7.45 (m, 2H), 2.72 (s, 3H), 2.22 (s, 3H); \(^13\)C NMR (CDCl₃, 75 MHz): \(\delta\) 206.2, 169.2, 133.3, 131.8, 130.7, 129.8, 128.7, 127.4, 126.9, 125.5, 124.7, 122.0, 32.8, 24.7; ESI-HRMS: m/z calcd. for C₁₄H₁₃NO₂ [M+H⁺]: 228.1025 m/z, found 228.1019 m/z; 73% yield.
3 mol% Rose Bengal, O₂, 46 h, \(N\)-(2-Acetylphenyl)acetamide\(^{[23]}\) (29b): \(^1\)H NMR (300 MHz, CDCl₃): δ 11.72 (s, 1H), 8.76 (d, \(J = 8.4\) Hz, 1H), 7.93 – 7.89 (m, 1H), 7.60 – 7.54 (m, 1H), 7.13 (t, \(J = 7.5\) Hz, 1H), 2.69 (s, 3H), 2.25 (s, 3H); \(^{13}\)C NMR (CDCl₃, 75 MHz): δ 202.8, 169.4, 141.0, 135.2, 131.6, 122.3, 121.7, 120.7, 28.6, 25.6; MS (GC-MS): \(m/z\) 177 (M⁺); 76% yield.

3 mol% Rose Bengal, O₂, 46 h, \(N\)-(2-Formylphenyl)formamide\(^{[23]}\) (30b): \(^1\)H NMR (300 MHz, CDCl₃): δ 11.62 (br-s, 1H), 8.79 – 8.76 (d, \(J = 8.8\) Hz, 1H), 8.52 (br-s, 1H), 7.95 – 7.92 (dd, \(J = 8.0, 1.6\) Hz, 1H), 7.61 – 7.56 (t, \(J = 8.8\), 1H), 7.21 – 7.17 (m, 1H), 2.70 (s, 3H); \(^{13}\)C NMR (CDCl₃, 75 MHz): δ 202.8, 159.9, 139.9, 135.2, 131.7, 123.1, 122.0, 121.6, 28.6; MS (GC-MS): \(m/z\) 163 (M⁺); 70% yield.

3 mol% Rose Bengal, O₂, 46 h, \(N\)-(1-acetylnaphthalene-2-yl)-N-methylacetamide (32b): \(^1\)H NMR (300 MHz, CDCl₃): δ 7.98 – 7.88 (m, 2H), 7.75 – 7.71 (m 1H), 7.60 – 7.55 (m, 2H), 7.27 – 7.22 (m, 1H), 3.24 (s, 3.0 H), 2.57 (s, 3.0 H), 1.86 (s, 3.0 H); \(^{13}\)C NMR (CDCl₃, 75 MHz): δ 204.2, 171.1, 137.5, 137.1, 132.7, 131.4, 129.4, 128.3, 127.2, 125.1, 124.7, 37.3, 32.2, 22.4; ESI-HRMS: \(m/z\) calcd. for C₁₅H₁₃NO₂ [M+H⁺]: 242.1181 \(m/z\), found 242.1176 \(m/z\); 84% yield.
3 mol% Rose Bengal, O$_2$, 46 h, N-(2-Formylphenyl)-N-methylbenzamide$^{[24]}$ (33b): $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 10.12 (s, 1 H), 7.77 (m, 1H), 7.52 (m, 1H), 7.36 (m, 1H), 7.20–7.10 (m, 6H), 3.48 (s, 3H); $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta$ 189.2, 171.0, 146.4, 135.2, 135.0, 131.9, 130.8, 130.0, 129.4, 128.4, 128.0, 127.9, 39.2; MS (GC-MS): m/z 239 (M$^+$); 92% yield.

3 mol% Rose Bengal, O$_2$, 24 h + 24h, 5'-chloro-spiro[benzothiazole-2(3H),3'-[3H]indol]-2'(1'H)-one$^{[25]}$ (34b): $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 10.53 (s, 1H), 7.55 (d, $J$ = 2.2 Hz, 1H), 7.41–7.28 (m, 2H), 7.06 (dd, $J$ = 7.6, 1.2 Hz, 1H), 6.95–6.85 (m, 2H), 6.63 (ddd, $J$ = 27.2, 7.6, 1.1 Hz, 2H); $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta$ 176.4, 147.4, 140.6, 132.5, 130.8, 126.8, 126.3, 125.9, 124.3, 121.6, 109.4, 112.2, 109.1, 74.7; MS (GC-MS): m/z 288 (M$^+$); 72% yield.

2'-Amino-5-chloro-1,2-dihydro-6'-(3β,17β)-3-hydroxyandrost-5-en-17-yl]-2-oxospiro[3H-indole-3,4'-(1'H)-pyridine]-3'-carbonitrile$^{[26]}$ (35b): $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ = 10.25 (s, 1H), 7.47–7.39 (m, 1H), 7.27–7.14 (m, 1H), 7.02 (d, $J$ = 2.2 Hz, 1H), 6.79 (d, $J$ = 8.2 Hz, 1H), 5.78 (s, 2H), 5.25 (d, $J$ = 4.7 Hz, 1H), 4.58 (d, $J$ = 4.4 Hz, 1H), 4.07 (s, 1H), 3.24 (s, 1H), 2.20–0.85 (m, 23 H) 0.56 (s, 3H); $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta$ 180.6, 153.7, 141.8, 139.9, 136.7, 128.5, 126.4, 125.2, 121.3, 120.7, 111.3, 96.6, 96.5, 70.5, 56.3, 56.3, 53.7, 52.5, 51.9, 50.3, 43.9, 43.7, 42.7, 37.4, 36.6, 31.9, 31.1, 30.1, 24.3, 23.6, 19.7, 13.4; ESI-HRMS: m/z calcd. for C$_{32}$H$_{37}$ClN$_3$O$_2$ 545.2678 (M+H) $^+$ found: 545.2689 (M+H) $^+$; 62% yield.

3 mol% Rose Bengal, O$_2$, 24 h + 24h, Dianthalexin B/1,3-dihydro-3-(phenylimino)-2H-indol-2-one$^{[27]}$ (36b): $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 9.59 (s, 1H), 7.44 (t, $J$ = 7.8 Hz, 2H), 7.37–7.22 (m, 2H), 7.04 (dd, $J$ = 7.7, 1.2 Hz, 2H), 6.94 (d, $J$ = 7.9 Hz, 1H), 6.74 (td, $J$ = 7.6 Hz, 1H) 6.66 (dd, $J$ = 7.8 Hz, 1.2 Hz, 1H); $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta$ 165.6, 154.8, 150.2, 145.8, 134.5, 129.6, 126.5, 125.6, 122.9, 118.0, 116.3, 112.0; MS (GC-MS): m/z 222 (M$^+$); 92% yield.
Trisindoline\textsuperscript{[28]} (37b): \textsuperscript{1}H NMR (300 MHz, DMSO-\textit{d}_6): δ = 11.00 (d, \textit{J} = 2.6 Hz, 2H), 10.66 (s, 1H), 7.41 (d, \textit{J} = 8.2 Hz, 2H), 7.36 – 7.21 (m, 4H), 7.11 – 7.02 (m, 3H), 7.00 – 6.92 (m, 3H), 6.85 (ddd, \textit{J} = 8.0, 7.0, 1.0 Hz, 2H); \textsuperscript{13}C NMR (DMSO-\textit{d}_6, 75 MHz): δ 179.3, 170.8, 141.8, 137.5, 135.1, 128.3, 126.2, 125.4, 124.8, 121.9, 121.4, 121.3, 118.7, 114.9, 112.1, 110.1, 60.2, 53.1, 21.2, 14.5; MS (GC-MS): \textit{m/z} 363 (M\textsuperscript{+}); 74% yield.

2-Phenyl-4\textit{H}-benzo[d][1,3]oxazin-4-one\textsuperscript{[29]} (38b): \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): δ = 8.36-8.32 (m, 2H), 8.28 (dd, \textit{J} = 7.9, 1.5 Hz, 1H), 7.88-7.83 (m, 1H), 7.74-7.70 (d, \textit{J} = 8.0 Hz, 1H), 7.60-7.53 (m, 4H); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 75 MHz): δ 159.6, 157.1, 147.0, 136.5, 132.6, 130.2, 128.7, 128.6, 128.3, 128.2, 127.2, 117.0; MS (GC-MS): \textit{m/z} 223 (M\textsuperscript{+}); 81% yield.
8. References
(1) S. M. Huber, A. Henning, F. G. Pühlhofer, R. Weiss J. Heterocyclic Chem. 2009, 46, 421-427.
(2) B. C. G. Soederberg, S. P. Gorugantula, C. R. Howerton, J. L. Petersen, S. W. Dantale, Tetrahedron, 2009, 65, 7357-7363.
(3) H. A. Radhy, G. F. Fadhil, A. Perjessy, E. Kolehmainen, W. M. F. Fabian, M. Samalikova, K. Laihia, Z. Sustekova, Heterocycl. Commun. 2001, 7, 387-392.
(4) P. J. Montoya-Pelaez, Y.-S. Uh, C. Lata, M. P. Thompson, R. P. Lemieux, C. M. Crudgen, J. Org. Chem. 2006, 71, 7921-5929.
(5) J. S. Yadav, B. V. Subba Reddy, C. Suresh Reddy, A. D. Krishna, Synthesis 2007, 5, 693-696.
(6) M. E. Matheus, F. d. A. Violante, S. J. Garden, A. C. Pinto, P. D. Fernandes, Eur. J. Pharmacol. 2007, 556, 200-206.
(7) W.-B. Chen, X.-L. Du, L.-F. Cun, X.-M. W.-C. Zhang, Yuan, Tetrahedron 2010, 66, 1441-1446.
(8) E. Ziegler, R. Wolf, Th. Kappe, Monatsh. Chem. 1965, 96, 418-422.
(9) F. Ablondi, S. Gordon, J. II. Morton, J. H. Williams, J. Org. Chem. 1952, 17, 149-156.
(10) L. A. McAllister, R. A. McCormick, K. M. James, S. Brand, N. Willetts, D. J. Procter, Chem. Eur. J. 2007, 13, 1032-1046.
(11) Q. Gui, F. Dai, J. Liu, P. Chen, Z. Yang, X. Chen, Z. Tan, Org. Biomol. Chem. 2014, 12, 3349-3353.
(12) M. Akkurt, S. Tuerktekin, A. A. Jarrahpour, D. Khalili, O. Buyukgungor, Acta Cryst. Section E 2006, 62, 1575-1577.
(13) P. Diaz, J. Xu, F. Astruc-Diaz, H.-M. Pan, D. L. Brown, M. Naguib, J. Med. Chem. 2008, 51, 4932-4947.
(14) H. Wittmann, F. Guenzl, Z. Naturforsch. B, 1978, 33B, 1540-1546.
(15) M. Abass, A. S. Mayas, J. Chem. Res. 2009, 2, 93-94.
(16) M. Broering, F. Bregier, C. Kleeberg, Acta Cryst. Section C 2007, 63, 225-227.
(17) Z. Han, P. Li, Z. Zhang, C. Chen, Q. Wang, X.-Q. Dong, X. Zhang, ACS Catal. 2016, 6, 6214-6218.
(18) H. S. Lee, J. S. Yu, C. K. Lee, Magn. Reson. Chem. 2009, 47, 711-715.
(19) N. Matuszak, G. G. Muccioli, G. Labar, D. M. Lambert, J. Med. Chem. 2009, 52, 7410-7420.
(20) J. Trujillo-Ferrara, R. Santillan, H. I. Beltran, N. Farfan, H. Hopfl, Mag. Reson. Chem. 1999, 9, 682-686.
(21) L. Zhang, X. Zheng, J. Chen, K. Cheng, L. Jin, X. Jiang, C. Yu, Org. Chem. Front. 2018, 5, 2115-2119.
(22) A. Verma, S. Kumar, Org. Lett. 2016, 18, 4388-4391.
(23) M. R. Mutra, G. K. Dhandabani, J.-J. Wang, Adv. Synth. Catal. 2018, 360, 3960-3968.
(24) X. Ji, D. Li, Z. Wang, M. Tan, H. Huang, G.-J. Deng, Eur. J. Org. Chem. 2017, 45, 6652-6659.
(25) N. Karali, O. Guzel, N. Ozsoy, S. Ozbey, A. Salman, Eur. J. Med. Chem. 2010, 45, 1068-1077.
(26) Y.-L. Zhang, Y.-F. Li, J.-W. Wang, B. Yu, Y.-K. Shi, Liu, H.-M. Steroids 2016, 109, 22-28.
(27) M. Pandey, D. S. Raghuvanshi, K. N. J. Singh, Heterocyclic Chem. 2009, 46, 49-53.
(28) K. Rad-Moghadam, M. Sharifi-Kiasaraie, H. Taheri-Amlashi, Tetrahedron 2010, 13, 2316-2321.
(29) C. Zhang, S. Li, F. Bureš, R. Lee, X. Ye, Jiang, Z. ACS Catal. 2016, 6, 6853-6860.
9. NMR-Spectra
1b

$^1$H NMR spectrum in DMSO-$d_6$.

$^{13}$C NMR spectrum in DMSO-$d_6$. 
$^1$H NMR spectrum in DMSO-$d_6$.

$^{13}$C NMR spectrum in DMSO-$d_6$. 

![1H NMR spectrum in DMSO-d6.](image)

![13C NMR spectrum in DMSO-d6.](image)
$^1$H NMR spectrum in DMSO-$d_6$.

$^{13}$C NMR spectrum in DMSO-$d_6$. 

3b
$^1$H NMR spectrum in DMSO-$d_6$.

$^{13}$C NMR spectrum in DMSO-$d_6$. 
$^1$H NMR spectrum in DMSO-$d_6$.

$^{13}$C NMR spectrum in DMSO-$d_6$. 

5b
$^1$H NMR spectrum in DMSO-$d_6$.

$^{13}$C NMR spectrum in DMSO-$d_6$. 

![Chemical structure](image)
$^1$H NMR spectrum in DMSO-$d_6$.

$^{13}$C NMR spectrum in DMSO-$d_6$. 
8b

$^1$H NMR spectrum in DMSO-$d_6$.

$^{13}$C NMR spectrum in DMSO-$d_6$. 

![Chemical Structure](image)
$^1$H NMR spectrum in DMSO-$d_6$.

$^{13}$C NMR spectrum in DMSO-$d_6$. 
$^{1}H$ NMR spectrum in DMSO-$d_6$.

$^{13}C$ NMR spectrum in DMSO-$d_6$. 
1H NMR spectrum in DMSO-$d_6$.

13C NMR spectrum in DMSO-$d_6$. 
$^{1}H$ NMR spectrum in DMSO-$d_6$.

$^{13}C$ NMR spectrum in DMSO-$d_6$. 

[Image of NMR spectra]
$^{13}$C NMR spectrum in CDCl$_3$. 

$^1$H NMR spectrum in CDCl$_3$. 

[Chemical structures and spectra images are present, depicting the NMR analyses.]
$^{1}H$ NMR spectrum in CDCl$_3$.

$^{13}C$ NMR spectrum in CDCl$_3$. 
$^{1}H$ NMR spectrum in DMSO-$d_6$.

$^{13}C$ NMR spectrum in DMSO-$d_6$. 
$^{1}H$ NMR spectrum in DMSO-$d_{6}$.

$^{13}C$ NMR spectrum in DMSO-$d_{6}$.
$^{1}H$ NMR spectrum in DMSO-$d_6$.

$^{13}C$ NMR spectrum in DMSO-$d_6$. 
$^{1}H$ NMR spectrum in CDCl$_3$.

$^{13}$C NMR spectrum in CDCl$_3$. 
$^1$H NMR spectrum in CDCl$_3$.

$^{13}$C NMR spectrum in CDCl$_3$. 
$^{1}H$ NMR spectrum in CDCl$_3$.

$^{13}C$ NMR spectrum in CDCl$_3$. 
24b

$^1$H NMR spectrum in DMSO-$d_6$.

$^{13}$C NMR spectrum in DMSO-$d_6$. 

$^{1}H$ NMR spectrum in DMSO-$d_6$.

$^{13}C$ NMR spectrum in CDCl$_3$. 
$^1$H NMR spectrum in CDCl$_3$.

$^{13}$C NMR spectrum in CDCl$_3$. 
$^{1}H$ NMR spectrum in CDCl₃.

$^{13}C$ NMR spectrum in CDCl₃.
$^1$H NMR spectrum in CDCl$_3$.

$^{13}$C NMR spectrum in CDCl$_3$. 
$^{1}H$ NMR spectrum in CDCl$_3$.

$^{13}C$ NMR spectrum in CDCl$_3$. 
$^{1}H$ NMR spectrum in CDCl$_3$.

$^{13}C$ NMR spectrum in CDCl$_3$. 
**31b**

\[ \text{H NMR spectrum in CDCl}_3. \]

\[ \text{C NMR spectrum in CDCl}_3. \]
$^{13}$C NMR spectrum in CDCl$_3$. 

$^1$H NMR spectrum in CDCl$_3$. 

32b
$^1$H NMR spectrum in CDCl$_3$.

$^{13}$C NMR spectrum in CDCl$_3$. 
H NMR spectrum in DMSO-$d_6$.

$^1$H NMR spectrum in DMSO-$d_6$.

$^{13}$C NMR spectrum in DMSO-$d_6$. 
$^1$H NMR spectrum in DMSO-$d_6$.

$^{13}$C NMR spectrum in DMSO-$d_6$. 

$^1$H NMR spectrum in CDCl$_3$.

$^{13}$C NMR spectrum in CDCl$_3$. 
$^1$H NMR spectrum in DMSO-$d_6$.

$^{13}$C NMR spectrum in DMSO-$d_6$. 

37b
$^1$H NMR spectrum in CDCl$_3$.

$^{13}$C NMR spectrum in CDCl$_3$. 

[Diagram of the molecules and their NMR spectra]