Electronic Supplementary Information for

Bisindole Caulerpin Analogues as Nature-Inspired Photoresponsive Molecules

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Content

Detailed Synthetic Procedures

Synthesis of Methyl 2-(ethoxythiocarbonylthio)acetate *3*.

A solution of methyl 2-chloroacetate (1.0 mmol) in dry acetonitrile (2 mL/mmol) was cooled at 0 °C, and potassium O-ethyl dithiocarbonate (0.19 g, 1.2 mmol) was added portion-wise. The suspension was warmed to room temperature and stirred for 2 h. The solvent was removed under reduced pressure, and the crude residue was diluted with CH_2Cl_2 and washed several times with H_2O and brine. The organic layer was dried over anhydrous Na_2SO_4 then concentrated in vacuo. The residue was purified by flash column chromatography on silica gel (hexane to hexane: EtOAc 95:5), to give the desired xanthate as a yellow oil, yield 98%.

^{1}H-NMR (200 MHz, $CDCl_3$) δ: 1.30 (t, J = 7.2 Hz, 3H), 1.43 (t, J = 7.2 Hz, 3H), 3.92 (s, 2H), 4.22 (q, J = 7.2 Hz, 2H), 4.65 (q, J = 7.2 Hz, 2H).[1]

General Procedure for Synthesizing the Methyl 2-(1H-indol-2-yl)acetate Derivatives (*4a, 4c*)

To a refluxing solution of the xanthate **3** (2.5 mmol) and the corresponding 5-substituted indole (**2a**, **2c**) (1.0 mmol) in degassed 1,2-dichloroethane (4 mL), solid DLP was added portion wise (1.8 mmol of DLP). The reaction was monitored by TLC. The solvent was removed under reduced pressure and the crude residue was purified by flash column chromatography on silica gel (hexane, hexane: EtOAc 90:10 to 80:20), to furnish the desired C-2 alkylated indole derivatives **4a** and **4c**.[2]

Methyl 2-(1H-indol-2-yl)acetate *4a*

Orange solid; yield 46%; mp 67–68 °C. **IR** (ATR) (ν_{max}/cm^{-1}) 3352, 2952, 1717, 750. **^{1}H NMR** (300 MHz, $CDCl_3$) δ : 8.68 (bs, 1H, NH), 7.57 (d, J= 7.5 Hz, 1H, CH-C-CH=C), 7.10 (t, J= 7.5 Hz, 1H, CH=CH-C-CH), 7.17 (t, J= 6.9 Hz, 1H, CH=CH-C-NH), 7.35 (d, J= 7.8 Hz, 1H, CH=CH-C-NH), 6.37 (s, 1H, C-CH=C-NH), 3.85 (s, 2H, CH_2), 3.77 (s, 3H, O-CH3). **^{13}C NMR** (75 MHz, $CDCl_3$) δ: 171.0 (C=O), 136.3 (CH_2-C-NH), 130.3 (CH=CH-C-NH), 128.1 (C-CH=C-NH), 121.7

(CH=CH-C-NH), 120.1 (CH-C-CH=C), 119.8 (CH=CH- C-CH), 110.8 (CH=CH-C-NH), 101.8 (C-CH=C-NH), 52.3 (O-CH3), 33.7 (CH2). DART$^+$−HRMS calculated for $C_{11}H_{11}NO_2$ [M + H] 190.08680, found 190.08738.[3]

2-(2-Methoxy-2-oxoethyl)-1H-indole-5-carboxylic Acid *4c*

Yellow solid; yield 24%; mp 224–226 °C. **IR** (ATR) (ν_{max}/cm^{-1}) 3336, 2955, 2913, 2636, 2549, 1730, 1663. **^{1}H NMR** (400 MHz, DMSO-*d$_6$*) δ: 12.34 (bs, 1H, OH), 11.39 (bs, 1H, NH), 8.14 (s, 1H, CH-C=C-NH), 7.68 (dd, J= 8.8, 1.6 Hz, 1H, CH=CH-C-NH), 7.37 (d, J= 8.4 Hz, 1H, CH=CH-C-NH), 6.42 (s, 1H, C-CH=C-NH), 3.88 (s, 2H, CH_2), 3.66 (s, 3H, O-CH_3). **^{13}C NMR** (100 MHz, DMSO-*d$_6$*) δ: 170.2 (O=C-OCH_3), 168.4 (O=C-OH), 138.7 (CH=CH-C-NH), 133.5 (CH_2-C-NH), 127.5 (C-CH=C-NH), 122.2 (CH-C=C-NH), 122.1 (CH=CH-C-NH), 121.4 (C=CH-C-CH), 110.6 (CH=CH-C-NH), 102.0 (C-CH=C-NH), 51.9 (O-CH3), 33.4 (CH_2). DART$^+$−HRMS calculated for $C_{12}H_{11}NO_4$ [M + H] 234.07663; found 234.07614.

Synthesis of methyl 2-(2-methoxy-2-oxoethyl)-1H-indole-5-carboxylate *6c*

A solution of **4c** 0.59 mmol) and 0.030 mL of H_2SO_4 in anhydrous methanol (2 mL) was refluxed for 14 hours. After consumption of starting material (monitored using TLC), the reaction mixture was neutralized with a saturated $NaHCO_3$ solution (2 × 5 mL) and extracted with AcOEt (3 × 10 mL). The organic extracts were combined, dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure to give **6c** as a pink solid, yield 80 %; mp 140-142 °C. **IR** (ATR) (ν_{max}/cm^{-1}) 3341, 2958, 2917, 1717, 1204, 749. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 9.06 (bs, 1H, NH), 8.31 (s, 1H, CH-C=C-NH), 7.86 (dd, J= 8.8, 1.6 Hz, 1H, CH=CH-C-NH), 7.32 (d, J= 8.8 Hz, 1H, CH=CH-C-NH), 6.43 (s, 1H, C-CH=C-NH), 3.92 (s, 3H, C-CO_2-CH_3), 3.84 (s, 2H, CH_2), 3.75 (s, 3H, CH_2-CO_2-CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 170.8 (CH_2-CO_2), 168.2 (C-CO_2), 138.9 (CH2-C-NH), 131.9 (CH=CH-C-NH), 127.7 (C-CH=C-NH), 123.1 (CH-C=C-NH),

123.0 (CH=CH-C-NH), 121.8 (C=CH-C-CH), 110.5 (CH=CH-C-NH), 103.0 (C-CH=C-NH), 52.4 (CH_2-CO_2-CH_3), 51.8 (C-CO2-CH3), 33.5 (CH_2). DART$^+$−HRMS calculated for $C_{13}H_{13}NO_4$ [M + H] 248.09228; found 248.09192.

General Procedure for Synthesizing the Methyl (E)-2-(1H-indol-2-yl)-3-(1H-indol-3-yl)acrylates Derivatives (*1a*, *1b*, *1c*)

To a solution of the corresponding indole ester (**4a**, **6c**) (0.53 mmol) and 1H-indole-3-carbaldehyde in anhydrous xylene, **5a** or **5b**, (0.56 mmol) in anhydrous toluene (5.3 mL) were added piperidine (0.052 mL, 0.052 mmol) and acetic acid (0.034 mL), and the mixture was refluxed during the removal of water using a Dean-Stark separator. After the starting material had been consumed, as indicated by TLC analysis, the solvent was concentrated in vacuum. The residue was purified by column chromatography using silica gel and a mixture of hexane-ethyl acetate as the eluent to obtain **1a**, **1b** and **1c**.

Methyl (E)-2-(1H-indol-2-yl)-3-(1H-indol-3-yl)acrylate *1a*

Yellow solid; yield 49%; mp 239–240 °C. **IR** (ATR) (ν_{max}/cm^{-1}) 3378, 3340, 3053, 2951, 1658, 1231, 736. **^{1}H NMR** (400 MHz, DMSO-*d$_6$*) δ: 11.54 (bs, 1H, CH-NH-C), 11.39 (bs, 1H, C-NH-C), 8.27 (s, 1H, CH=C-CO_2), 7.61 (d, J= 7.6 Hz, 1H, CH-NH-C=C-CH), 7.57 (d, J= 7.6 Hz, 1H, C=CH-C-CH), 7.40 (d, J= 3.2 Hz, 1H, CH-NH-C-CH), 7.38 (d, J= 3.2 Hz, 1H, C-NH-C-CH), 7.16 (td, J= 7.6, 1.2 Hz, 1H, CH-NH-C-CH=CH), 7.11 (td, J= 7.6, 1.2 Hz, 1H, C-NH-C-CH=CH), 7.08 (td, J= 7.6, 1.2 Hz, 1H, CH=C-C-CH=CH), 7.03 (td, J= 7.6, 1.2 Hz, 1H, C=CH-C-CH=CH), 6.50 (s, 1H, C=CH-NH), 6.40 (s, 1H, NH-C=CH-C), 3.73 (s, 3H, O-CH_3). **^{13}C NMR** (100 MHz, DMSO-*d$_6$)* δ: 167.3 (C=O), 136.2 (C-CO_2-CH_3), 135.6 (CH-C-CO_2-CH_3), 135.5 (CH-NH-C),

133.3 (C-NH-C-CH), 128.3 (NH-C=CH-C), 128.2 (C=CH-NH), 127.2 (C=C-NH-CH), 122.3 (CH-NH-C-CH=CH), 121.0 (C-NH-C-CH=CH), 120.6 (CH=C-C-CH=CH), 120.0 (C=CH-C-CH), 118.9 (C=CH-C-CH=CH), 118.0 (CH-NH-C=C-CH), 117.0 (NH-C=CH-C), 112.1 (CH-NH-C-CH), 111.4 (C-NH-C-CH), 110.2 (C=CH-NH), 101.1 (NH-C=CH-C), 51.8 (O-CH_3). DART$^+$−RMS calculated for $C_{20}H_{16}N_2O_2$ [M + H] 317.12900; found 317.12907.

Methyl (E)-3-(5-bromo-1H-indol-3-yl)-2-(1H-indol-2-yl)acrylate *1b*

Yellow solid; yield 49%; mp 256–257 °C. **IR** (ATR) (ν_{max}/cm^{-1}) 3336, 3047, 2951, 1658, 1234, 740. **^{1}H NMR** (400 MHz, DMSO-*d$_6$*) δ: 11.61 (bs, 1H, CH-NH-C), 11.14 (bs, 1H, C-NH-C), 8.20 (s, 1H, CH=C-CO_2), 7.56-7.54 (m, 2H, CH-C=C-NH-C, C-CH=CBr), 7.38 (d, J= 8.0 Hz, 1H, C-NH-C-CH), 7.34 (d, J= 8.8 Hz, 1H, CH=CH-CBr), 7.23 (dd, J= 8.8, 1.6 Hz, 1H, C-CH=CH-CBr), 7.11 (t, J= 7.2 Hz, 1H, C-NH-C-CH=CH), 7.02 (t, J= 7.2 Hz, 1H, CH=CH-C=C-NH), 6.69 (s, 1H, C=CH-NH), 6.38 (s, 1H, NH-C=CH-C), 3.73 (s, 3H, O-CH_3). **^{13}C NMR** (100 MHz, DMSO-*d$_6$*) δ: 167.2 (C=O), 136.2 (C-CO_2-CH_3), 135.3 (CH-C-CO_2-CH_3), 134.5 (C-CH=CH-CBr), 133.0 (C-NH-C-C), 130.1 (C=CH-NH), 128.5 (C-CH=CBr), 128.2 (C=C-NH-C), 124.8 (C-CH=CH-CBr), 121.1 (C-NH-C-CH=CH), 121.0 (C-CH=CBr), 120.0 (CH-C=C-NH-C), 119.0 (CH=CH-C=C-NH), 117.6 (NH-C=CH-C), 114.0 (CH=CH-CBr), 113.4 (C-Br), 111.4 (C-NH-C-CH), 110.2 (C=CH-NH), 101.5 (NH-C=CH-C), 51.8 (O-CH_3). DART$^+$−HRMS calculated for $C_{20}H_{15}BrN_2O_2$ [M + H] 395.03952; found 395.03946.

Methyl (E)-2-(1-(1H-indol-3-yl)-3-methoxy-3-oxoprop-1-en-2-yl)-1H-indole-5-carboxylate ***1c***

Yellow solid; yield 78%; mp 192–194°C. **IR** (ATR) (ν_{max}/cm^{-1}) 3320, 2848, 2920, 1679, 1229, 737. **^{1}H NMR** (400 MHz, DMSO-*d$_6$*) δ: 11.72 (bs, 1H, CH-NH-C), 11.60 (bs, 1H, C-NH-C), 8.27 (s, 2H, CH-C=CH-NH), 7.75 (dd, J= 8.7, 1.5 Hz, 2H, CH=CH-C-CO_2), 7.52 (d, J= 7.8 Hz, 1H, CH=CH-C=C-NH), 7.45 (d, J= 8.7 Hz, 1H, CH=CH-C-CO_2), 7.38 (d, J= 7.8 Hz, 1H, CH-NH-C-CH), 7.14 (t, J= 6.9 Hz, 1H, CH-NH-C-CH=CH), 7.04 (t, J= 7.2 Hz, 1H, CH=CH-C=C-NH), 6.59 (s, 1H, C=CH-NH), 6.58 (s, 1H, NH-C=CH-C), 3.86 (s, 1H, CO_2-CH_3), 3.73 (s, 3H, C-CO_2-CH_3). **^{13}C NMR** (100 MHz, DMSO-*d$_6$*) δ: 167.3 (CH-C-CO_2), 167.1 (C-C-CO_2) 138.8 (C-CO_2-CH_3), 136.1 (CH-C-CO_2-CH_3), 135.7 (CH-NH-C), 135.3 (C-NH-C-C-C), 128.5 (C=CH-NH), 127.8 (C=C-NH-CH), 127.0 (C-CH=C-CO_2), 122.7 (C-CH=C-CO_2), 122.4 (CH-NH-C-CH=CH), 122.1 (CH=CH-C-CO_2), 120.7 (CH=CH-C=C-NH), 120.5 (C-CO_2), 118.1 (CH=CH-C=C-NH), 116.1 (NH-C=CH-C), 112.2 (CH-NH-C-CH), 111.3 (CH=CH-C-CO_2), 110. 1 (C=CH-NH), 103.0 (NH-C=CH-C), 51.9 (C-C-CO_2-CH_3), 51.7 (CH-C-CO_2-CH_3). DART$^+$–HRMS calculated for $C_{22}H_{18}N_2O_4$ [M + H] 375.13448; found 375.13448.

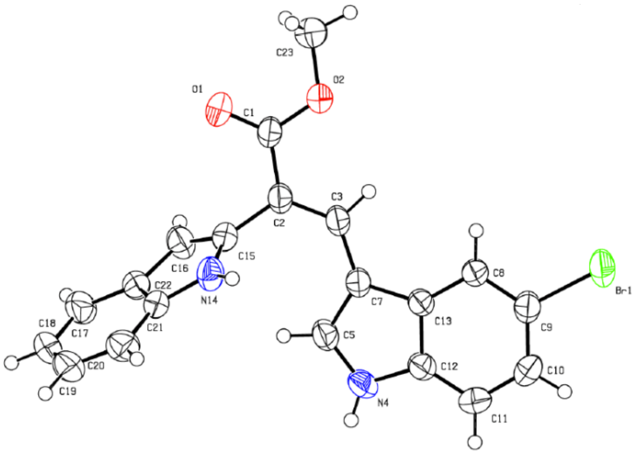


Figure S1. X-ray structure of **1b**.

Absorption and Emission Spectra for bisindole derivates

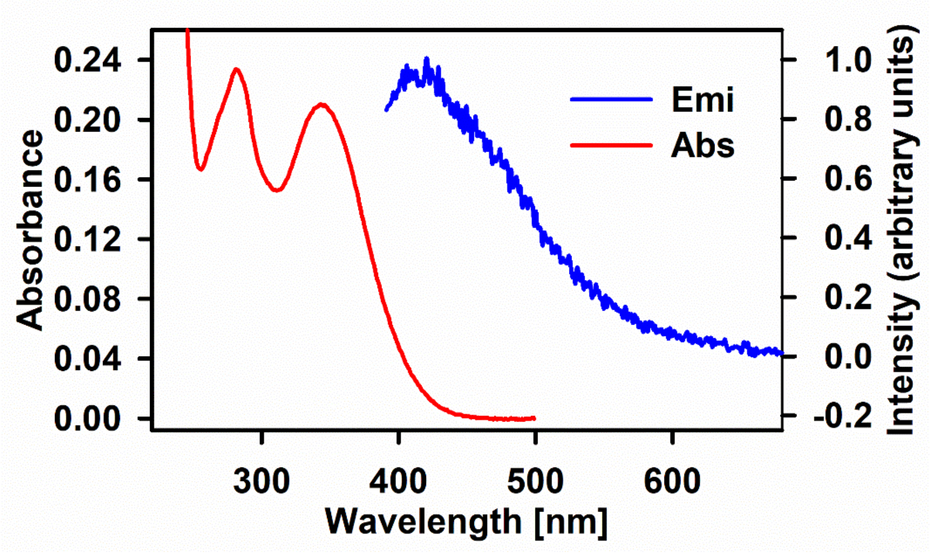


Figure S2. Absorption and emission spectra for bI-Br in methanol. λ_{exc} = 350 nm.

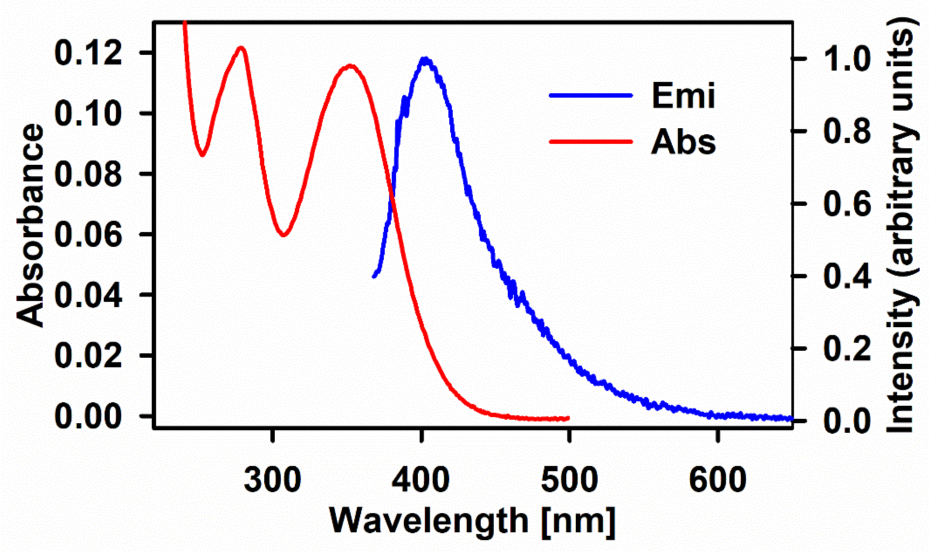


Figure S3. Absorption and emission spectra for bI-AcOMe in methanol. λ_{exc} = 350 nm.

Fit Parameters for Fluorescence Up-Conversion Experiments

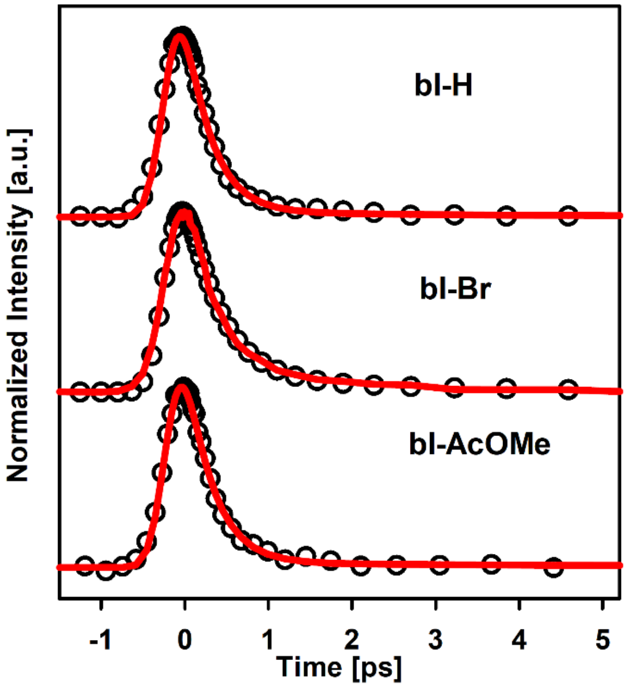


Figure S4. Fluorescence up-conversion results for bisindole derivates in methanol. The pump beam was set at 380 nm, and the emission was monitored at 510 nm. Solid lines indicate fits for bi-exponential decays.

Table S1. Fitting parameters for fluorescence up-conversion traces of bisindoles bI-H, bI-Br, and bI-AcOMe in methanol at 510 nm. The excitation wavelength was set at 385 nm.

λ_{det} = 510 nm	α_1 (%)	τ_1 (fs)	α_2 (%)	τ_2 (ps)
bI-H	98.6	310 ± 15	1.4	4.1 ± 0.2
bI-Br	95.2	390 ± 20	4.8	2.6 ± 0.2
bI-AcOMe	98.7	310 ± 16	1.3	6.6 ± 0.3

Photoisomerization Experiments

With the aim to demonstrate the bisindole photoisomerization and its use as photoresponsive molecules, the bI-H molecule was irradiated with 5.2 mW of a 405 nm CW laser from PicoQuant (LDH-DC-405) in a 1 cm quartz cell. The changes in the absorption spectrum were monitored as a function of irradiation time. Spectra were recorded before and during irradiation to notice the changes in absorbance values due to *E*-*Z* isomerization.

Absorption Spectra of the Isomers

The method used to obtain an estimation of the absorption spectra for each isomer is based on the one proposed by Calbo and coworkers.[4] Starting from the Lambert-Beer law:

$$A(t,\lambda) = l\big(\varepsilon_E(\lambda)C_E(t) + \varepsilon_Z(\lambda)C_Z(t)\big) \tag{S1}$$

Where $A(t,\lambda)$ is the total absorbance as a function of time (t) and wavelength (λ), l is the path length (in cm^{-1}), $\varepsilon_E(\lambda)$ and $\varepsilon_Z(\lambda)$ (in L mol^{-1} cm^{-1}) are the molar extinction coefficients as a function of the wavelength of the *E*- and *Z*- isomer respectively; and $C_E(t)$ and $C_Z(t)$ are the concentrations of the *E*- and *Z*-isomer as a function of time (in mol L^{-1}).

Rearranging for $\varepsilon_E(t)$ from Equation S1:

$$\varepsilon_Z(\lambda) = \frac{\frac{A(\lambda)}{l} - \varepsilon_E(\lambda)C_E(t)}{C_Z(t)} \tag{S2}$$

It is known that the initial concentration C_0 remains constant throughout the isomerization process and is also the sum of the concentration of both isomers.

$$C_0 = C_E(t) + C_Z(t) \tag{S3}$$

The fraction $f(t)$ could be expressed as the ratio of the *Z*- isomer concentration respect to the *E*- isomer. Furthermore, with the results from NMR experiments, the value of this fraction could be known.

$$f(t) = \frac{C_Z(t)}{C_E(t)} \tag{S4}$$

Using Equations S3 and S4, the concentrations of both isomers could be expressed in terms of the initial concentration C_0 and the fraction $f(t)$.

$$C_E(t) = \frac{C_0}{\left(1 + f(t)\right)} \tag{S5}$$

$$C_Z(t) = C_0\left(\frac{f(t)}{1 + f(t)}\right) \tag{S6}$$

Expressing Equation S2 at the time when the photostationary state, t_{pss}, was reached:

$$\varepsilon_Z\,(\lambda) = \frac{\frac{A(\lambda)}{l} - \varepsilon_E(\lambda)C_E\left(t_{pss}\right)}{C_Z\left(t_{pss}\right)} \tag{S7}$$

Finally, the Equations S5 and S6 are substituted in the last equation:

$$\varepsilon_Z\,(\lambda) = \frac{\frac{A(\lambda)}{l} - \varepsilon_E(\lambda)\left(\frac{C_0}{1 + f\left(t_{pss}\right)}\right)}{\left(C_0\frac{f\left(t_{pss}\right)}{1 + f\left(t_{pss}\right)}\right)} \tag{S8}$$

Using the method above, and relative concentrations obtained by NMR experiments as a guess, the isolated spectra obtained for both isomers are shown in Figure S6. The *Z*-bIH isomer exhibits a more significant molar extinction coefficient compared to the *E*-form, and the less energetic band is redshifted by around 15 nm.

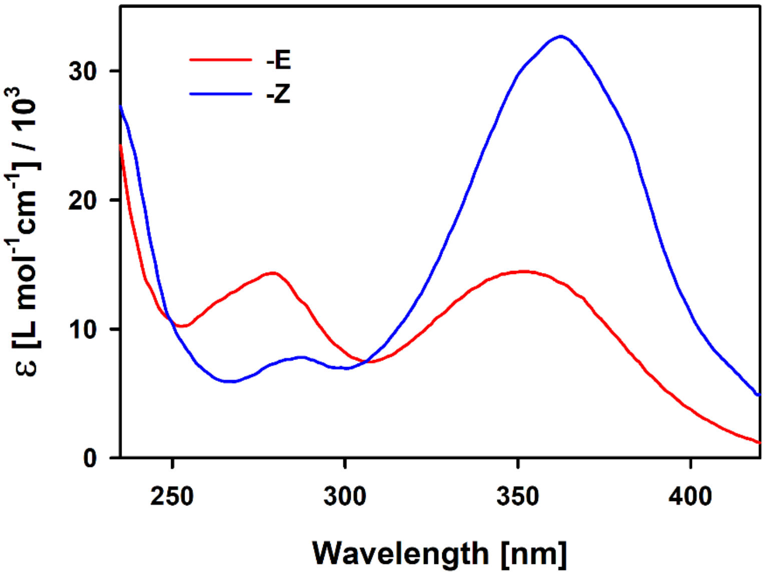


Figure S5. Absorption spectrum for E- bI-H and Z- bI-H in MeOH in terms of molar extinction coefficients.

Changes in Concentration

Once the absorption spectra from both isomers were obtained, the concentrations for *E*- and *Z*-isomers as a function of irradiation time could be determined with the following method:

Starting from Equation S3, the *Z*- isomer concentration can be expressed as a function of the *E*-isomer concentration and the initial concentration C_0.

$$C_Z(t) = C_0 - C_E(t) \tag{S9}$$

The last equation is replaced in the expression for the Beer-Lambert law described in Equation S1 and by factorizing $C_E(t)$, the following is obtained:

$$\frac{A(t,\lambda)}{l} = C_E(t)[\varepsilon_E(\lambda) - \varepsilon_Z(\lambda)] + \varepsilon_Z(\lambda)C_0 \qquad \text{(S10)}$$

By rearranging the *E*- isomer concentration from Equation S10 and replacing it in Equation S9, expressions for both isomers concentrations are obtained as a function of time.

$$C_E(t) = \frac{\frac{A(t,\lambda)}{l} - \epsilon_Z(\lambda)C_0}{\epsilon_E(\lambda) - \epsilon_Z(\lambda)} \qquad \text{(S11)}$$

$$C_Z(t) = C_0 - \frac{\frac{A(t,\lambda)}{l} - \epsilon_Z(\lambda)C_0}{\epsilon_E(\lambda) - \epsilon_Z(\lambda)} \qquad \text{(S12)}$$

From the results for the changes in concentrations as a function of irradiation time shown in Figure S6, it can be seen that the photostationary state is reached after 400 min of irradiation. At this particular photostationary state, the maximum amount of *Z*-isomer produced is 20 %.

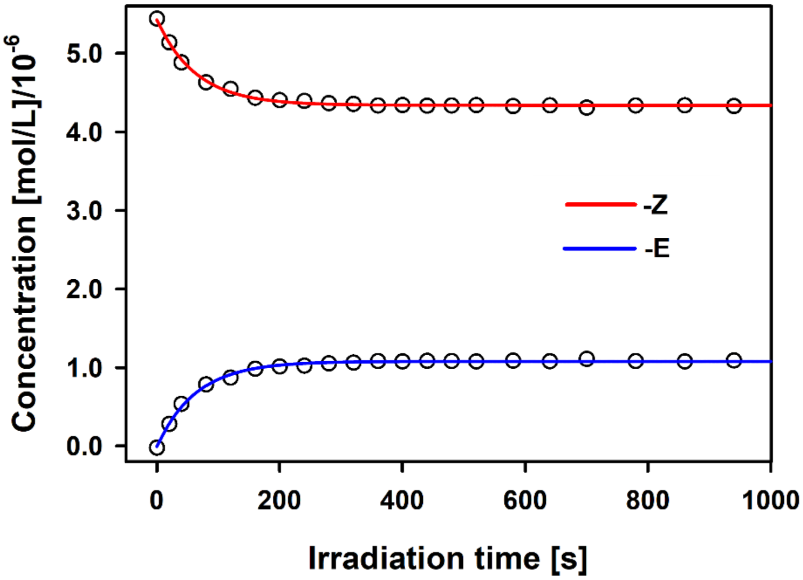


Figure S6. Concentrations of *E*-bI-H and *Z*-bI-H in MeOH solution as a function of irradiation time.

Photoisomerization Quantum Yield

With the data of the previous section, the efficiency of the photoisomerization process can be known using the methodology described by Stranius and Börjesson.[5]

As seen in Figure S6, both the *E*-isomer and the *Z*-isomer absorb at the wavelength at which the irradiation was carried out (405 nm). During the experiments, no spontaneous transformation of the *Z*-isomer to the *E*-isomer was observed. Thus, the photoisomerization kinetic system is described by the following equations:

$$E \overset{h\nu}{\rightarrow} Z \tag{S13}$$

$$Z \overset{h\nu}{\rightarrow} E \tag{S14}$$

The kinetic rate equation that describes these processes is:

$$\frac{d[E]}{dt} = \frac{-\Phi_{E\rightarrow Z}\, I\, \beta_E(t)}{N_A\, V} + \frac{\Phi_{Z\rightarrow E}\, I\, \beta_Z(t)}{N_A\, V} \qquad \text{(S16)}$$

Where N_A is Avogadro's number, V the volume, and I is the photon flux which was calculated as the irradiation power P_0 by the photon energy at wavelength λ.

$$I = \frac{P_0 \lambda}{hc} \qquad \text{(S16)}$$

Furthermore, $\beta_E(t)$ and $\beta_Z(t)$ are fractions of photons absorbed by both isomers respectively and $\Phi_{E\rightarrow Z}$ and $\Phi_{Z\rightarrow E}$ are the photoisomerization quantum yields.

The fractions of absorbed photons $\beta_E(t)$ and $\beta_Z(t)$, could be expressed in terms of the amount of total absorbed photons $\left(1-10^{-A(t)}\right)$ and the absorbance ratio between an isomer with respect to the total absorbance.

$$\beta_E(t)=\frac{C_E(t)\varepsilon_E}{C_E(t)\varepsilon_E+C_Z(t)\varepsilon_z}\left(1-10^{-A(t)}\right) \tag{S17}$$

$$\beta_Z(t)=\frac{C_Z(t)\varepsilon_Z}{C_E(t)\varepsilon_E+C_Z(t)\varepsilon_z}\left(1-10^{-A(t)}\right) \tag{S18}$$

When the system is at the photostationary state, the changes in the concentration of both isomers are zero. Therefore, Equation S16 can be expressed as follows:

$$\frac{d[E]}{dt}=\frac{-\Phi_{E\rightarrow Z}I\beta_E\left(t_{pss}\right)}{N_a\,V}+\frac{\Phi_{Z\rightarrow E}I\beta_Z\left(t_{pss}\right)}{N_a\,V}=0 \tag{S19}$$

Rearranging Equation S19 the following expression is obtained:

$$\Phi_{E\rightarrow Z}\beta_E\left(t_{pss}\right)=\Phi_{Z\rightarrow E}\beta_Z\left(t_{pss}\right) \tag{S20}$$

Substituting Equations S17 and S18 in the last equation,

$$\begin{aligned}\Phi_{E\rightarrow Z}\frac{C_E\left(t_{pss}\right)\varepsilon_E}{C_E\left(t_{pss}\right)\varepsilon_E+C_Z\left(t_{pss}\right)\varepsilon_z}&\left(1-10^{A\left(t_{pss}\right)}\right)\\&=\Phi_{Z\rightarrow E}\frac{C_Z\left(t_{pss}\right)\varepsilon_Z}{C_E\left(t_{pss}\right)\varepsilon_E+C_Z\left(t_{pss}\right)\varepsilon_z}\left(1-10^{-A\left(t_{pss}\right)}\right)\end{aligned} \tag{S21}$$

For $\Phi_{Z\rightarrow E}$, the following equation is obtained:

$$\Phi_{Z\rightarrow E}=\Phi_{E\rightarrow Z}\frac{C_E\left(t_{pss}\right)\varepsilon_E}{C_Z\left(t_{pss}\right)\varepsilon_Z} \tag{S22}$$

Substituting the last equation in the Equation S16 and factorizing, the following equation is obtained:

$$\frac{d[E]}{dt} = \frac{\Phi_{E\to Z}\, I}{N_A\, V}\left(\beta_Z(t)\,\frac{C_E(t_{pss})\,\varepsilon_E}{C_Z(t_{pss})\,\varepsilon_Z} - \beta_E(t)\right) \tag{S23}$$

The Equation S23 was solved using the program QYmain developed by Stranius and Börjesson[4]. The results for the isomerization quantum yields for a set of wavelengths are presented in Table S2.

Table S2. Isomerization Quantum Yield values for bI-H upon 405 nm laser irradiation monitoring several wavelengths.

λ_{det} [nm]	$\Phi_{E\to Z}$	$\Phi_{Z\to E}$
240	0.045	0.039
260	0.013	0.114
280	0.014	0.124
300	0.011	0.120
320	0.065	0.091
340	0.037	0.052
380	0.034	0.040
400	0.070	0.085

NMR Characterization of the Photoinduced Isomer

Light-induced changes were also monitored by NMR spectroscopy to study the structural changes, and to discard molecular photocleavage fragments or other photochemical changes. NMR spectra were acquired on an Avance III HD 700 spectrometer operating at a 1H frequency of 699.95 MHz (Bruker, Billerica, MA, USA) equipped with a 5-mm z-axis gradient TCI cryoprobe. NMR experiments were recorded using standard Bruker pulse sequences in solutions of bI-H in 5 mm NMR tubes at 298 K. The chemical shifts (δ) are reported in ppm relative to the solvent resonance as the internal standard (CD_3OD: $\delta_H = 3.310$ (q), $\delta_C = 49.00$). Coupling constants (*J*) are given in Hertz.

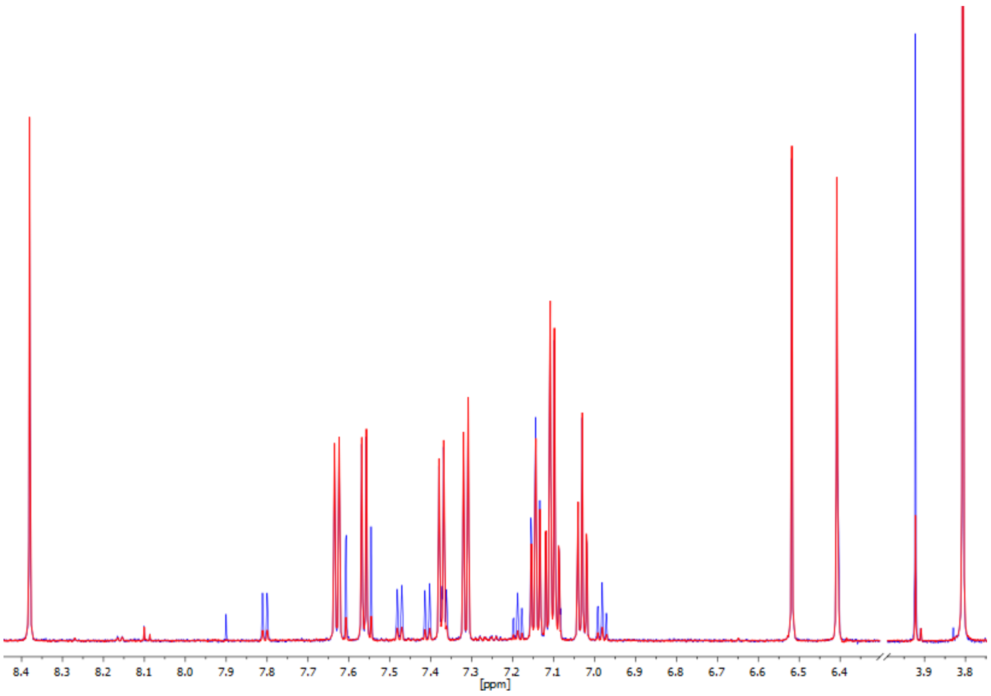


Figure S7. ^{1}H NMR spectra (700 MHz, methanol-*d*$_4$, 298 K) of the bI-H solution before (red line) and after (blue line) irradiation. The *E*:*Z* ratio in the mixture was 20.8:1.0 before and 4.1:1.0 after irradiation.

Table S3. DFT calculated relative Gibbs free energies, equilibrium constants, and ratios for *E* and *Z* isomers for the bisindole derivatives. Level of theory CAM-B3LYP/cc-PVTZ/PCM: Methanol.

Molecule	$\Delta G^0_{E\rightarrow Z}$ [kCal/mol]	K_{eq}	$E{:}Z$ ratio
bI-H	1.91	0.0397	25.2:1
bI-Br	2.47	0.0144	69.3:1
bI-AcOMe	1.59	0.0657	15.2:1

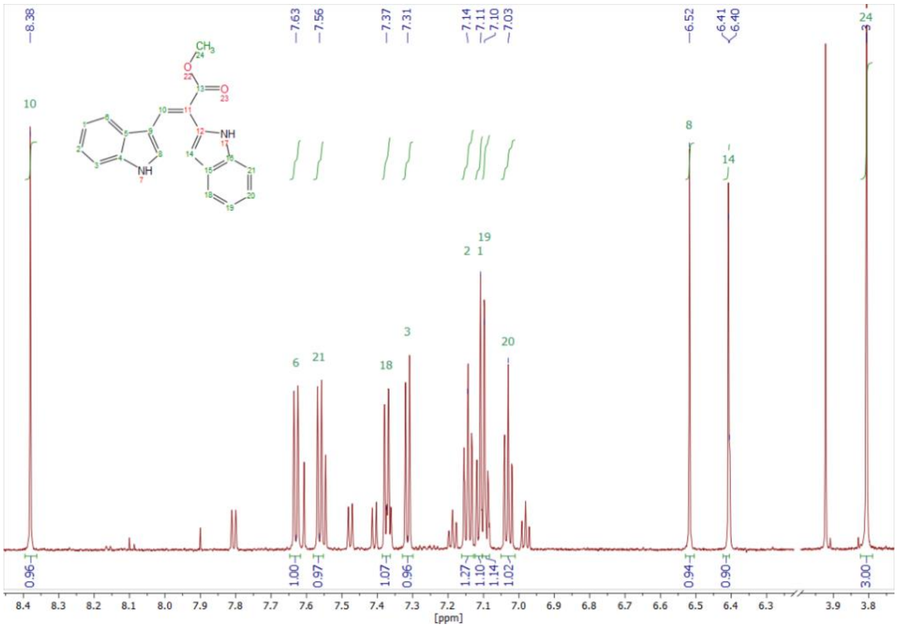


Figure S8. ^{1}H NMR spectrum (700 MHz, methanol-d_4, 298 K) of the irradiated solution (*E*:*Z* ratio 4.1:1.0) with the principal isomer *E*-bI-H signals assignment.

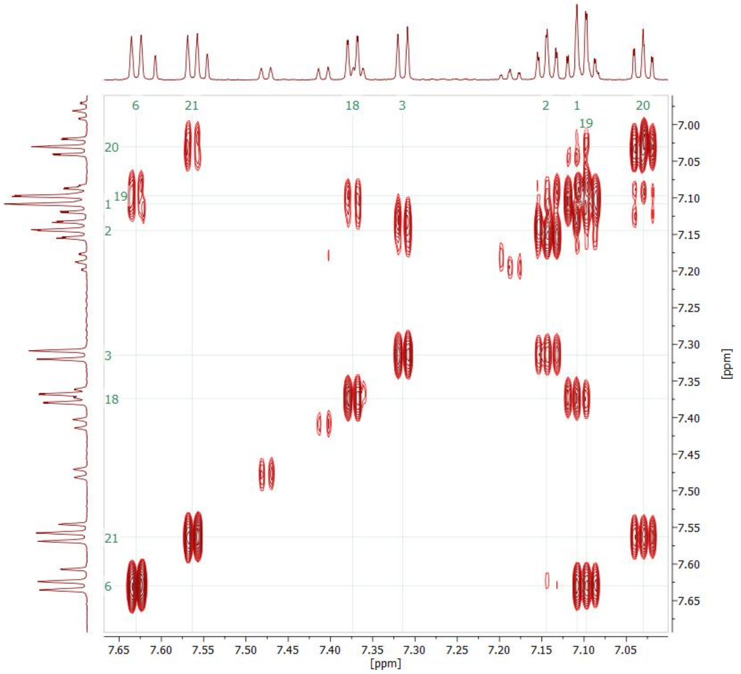


Figure S9. ^{1}H -^{1}H COSY spectrum of the irradiated solution (*E*:*Z* ratio 4.1:1.0) with the major isomer *E*-bI-H signals assignment.

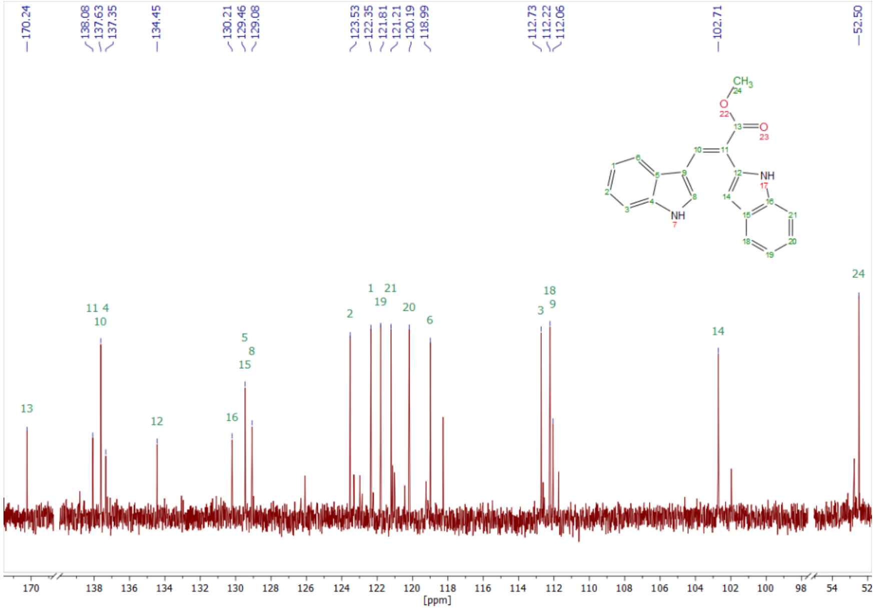


Figure S10. ^{13}C NMR spectrum (175 MHz, methanol-*d*$_4$, 298 K) of the irradiated solution (*E*:*Z* ratio 4.1:1.0) with the major isomer *E*-bI-H signals assignment.

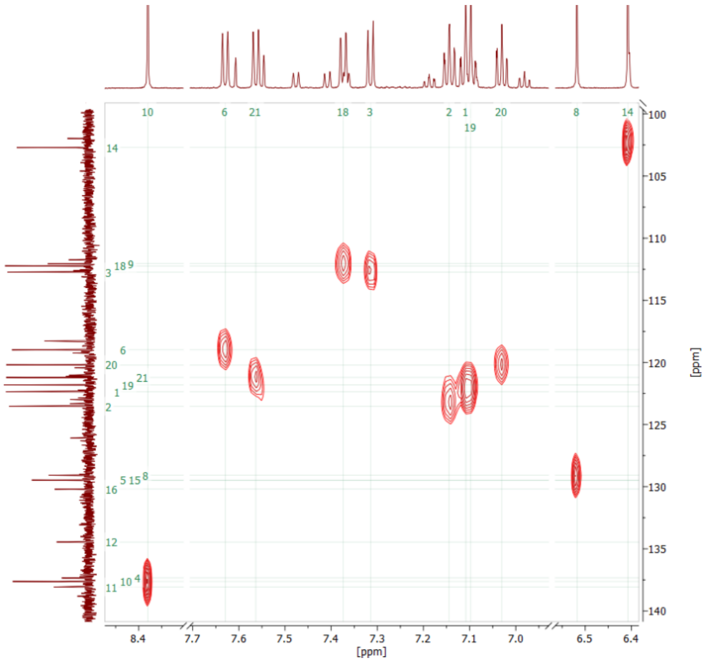


Figure S11. ^{1}H -^{13}C HSQC NMR spectrum of the irradiated solution (*E*:*Z* ratio 4.1:1.0) with the major isomer *E*-bI-H signals assignment.

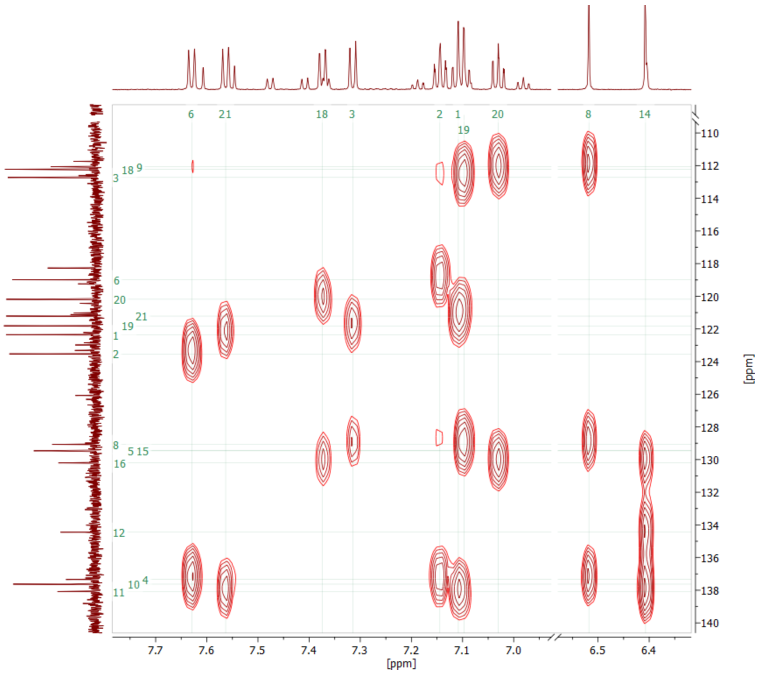


Figure S12. ^{1}H -^{13}C HMBC NMR spectrum of the irradiated solution (*E*:*Z* ratio 4.1:1.0) with the major isomer *E*-bI-H signals assignment.

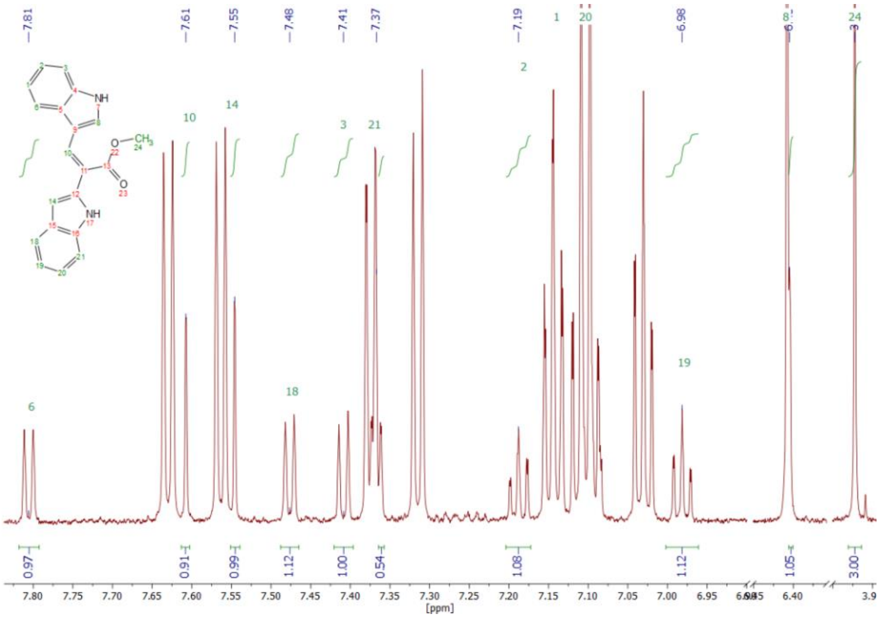


Figure S13. ^{1}H NMR spectrum (700 MHz, methanol-d_4, 298 K) of the irradiated solution (*E*:*Z* ratio 4.1:1.0) with the minor isomer *Z*-bI-H signals assignment.

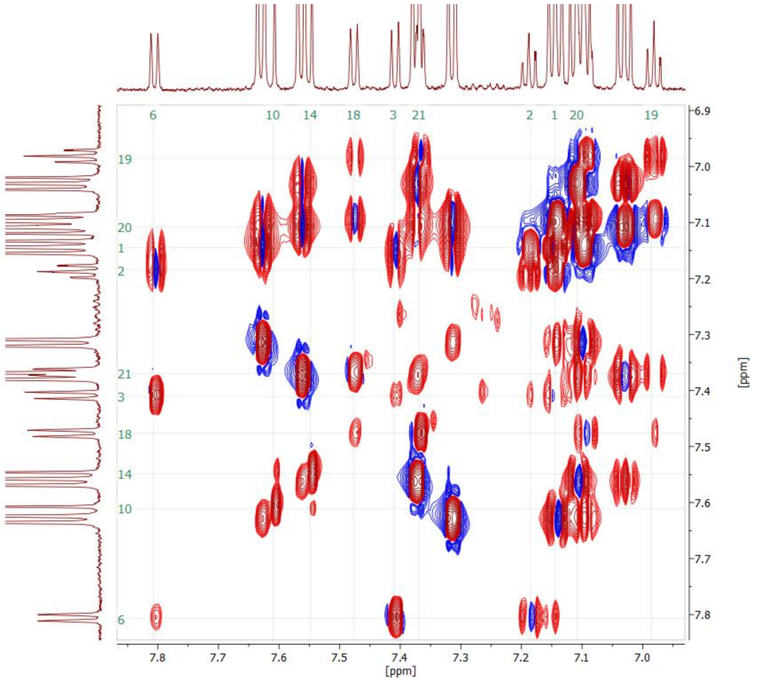


Figure S14. ^{1}H -^{1}H TOCSY spectrum of the irradiated solution (*E*:*Z* ratio 4.1:1.0) with the minor isomer *Z*-bI-H signals assignment.

Calculated Excited States for Bisindole Molecules

Table S4. Vertical electronic transition energies and oscillator strengths for *E*-bI-H and *Z*-bI-H singlet excited states. Level of theory CAM-B3LYP/cc-PVTZ/PCM: Methanol

E-bI-H			*Z*-bI-H		
State	Energy [eV]	Oscillator Strength	State	Energy [eV]	Oscillator Strength
S_1	3.46	0.093	S_1	2.90	0.5001
S_2	3.61	0.6338	S_2	3.60	0.2563
S_3	4.10	0.0630	S_3	4.03	0.0081
S_4	4.35	0.0433	S_4	4.15	0.0226
S_5	4.65	0.4578	S_5	4.29	0.1009
S_6	4.73	0.1337	S_6	4.42	0.3628
S_7	4.78	0.0443	S_7	4.95	0.0082
S_8	4.87	0.0090	S_8	4.98	0.1202
S_9	4.91	0.0553	S_9	5.02	0.0031
S_{10}	5.02	0.0866	S_{10}	5.07	0.0464

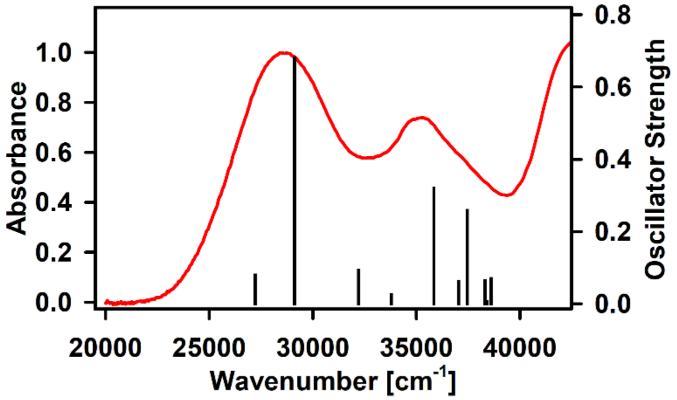


Figure S15. Experimental electronic absorption spectrum for bI-Br in methanol (red line) together with calculated oscillator strengths at CAM-B3LYP/cc-PVTZ/PCM: Methanol level of theory.

Table S5. Vertical electronic transition energies and oscillator strengths for *E*-bI-Br and *Z*-bI-Br singlet excited states. Level of theory CAM-B3LYP/cc-PVTZ/PCM: Methanol

E-bI-Br			*Z*-bI-Br		
State	Energy [eV]	Oscillator Strength	State	Energy [eV]	Oscillator Strength
S_1	3.42	0.0801	S_1	2.88	0.4316
S_2	3.66	0.6804	S_2	3.63	0.2107
S_3	4.06	0.0935	S_3	3.98	0.0100
S_4	4.26	0.0255	S_4	4.07	0.0402
S_5	4.52	0.3201	S_5	4.30	0.1835
S_6	4.68	0.0634	S_6	4.45	0.3420
S_7	4.73	0.2569	S_7	4.80	0.0362
S_8	4.85	0.0657	S_8	4.91	0.2512
S_9	4.86	0.0059	S_9	4.95	0.0002
S_{10}	4.88	0.0708	S_{10}	4.97	0.1398

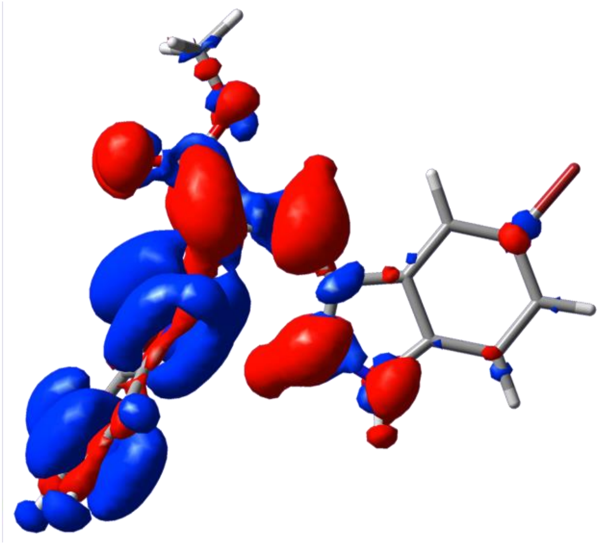


Figure S16. Electron density difference envelopes (Δρ(r)) for $S_0 \rightarrow S_1$ vertical excitation of *E*-bI-Br. The values correspond to +0.001 a.u. (red) and −0.001 a.u. (blue). The level of theory used was CAM-B3LYP/cc-PVTZ/PCM: Methanol.

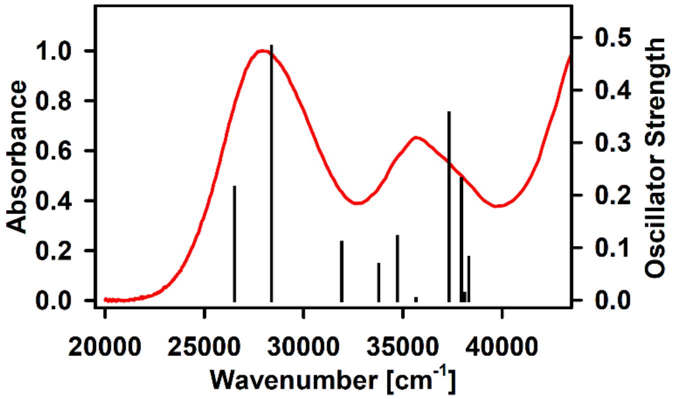


Figure S17. Experimental electronic absorption spectrum for bI-AcOMe in methanol (red line) together with calculated oscillator strengths at CAM-B3LYP/cc-PVTZ/PCM: Methanol level of theory.

Table S6. Vertical electronic transition energies and oscillator strengths for *E*-bI-AcOMe and *Z*-bI-AcOMe singlet excited states. Level of theory CAM-B3LYP/cc-PVTZ/PCM: Methanol

E-bI-AcOMe			*Z*-bI-AcOMe		
State	Energy [eV]	Oscillator Strength	State	Energy [eV]	Oscillator Strength
S_1	3.33	0.2151	S_1	2.90	0.4864
S_2	3.57	0.4836	S_2	3.61	0.2472
S_3	4.02	0.111	S_3	4.02	0.0085
S_4	4.26	0.0688	S_4	4.13	0.0261
S_5	4.38	0.1215	S_5	4.29	0.1174

S_6	4.50	0.0031	S_6	4.43	0.3586
S_7	4.71	0.3564	S_7	4.92	0.0138
S_8	4.80	0.2318	S_8	4.97	0.1464
S_9	4.82	0.0138	S_9	5.01	0.0025
S_{10}	4.85	0.0827	S_{10}	5.05	0.0651

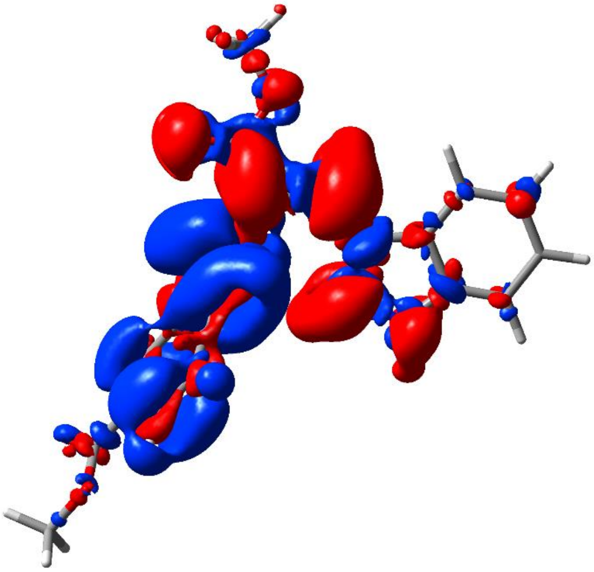


Figure S18. Electron density difference envelopes ($\Delta\rho(r)$) for $S_0 \rightarrow S_1$ vertical excitation of *E*-bI-AcOMe. The values correspond to +0.001 a.u. (red) and −0.001 a.u. (blue). The level of theory used was CAM-B3LYP/cc-PVTZ/PCM: Methanol.

Potential Energy Curves

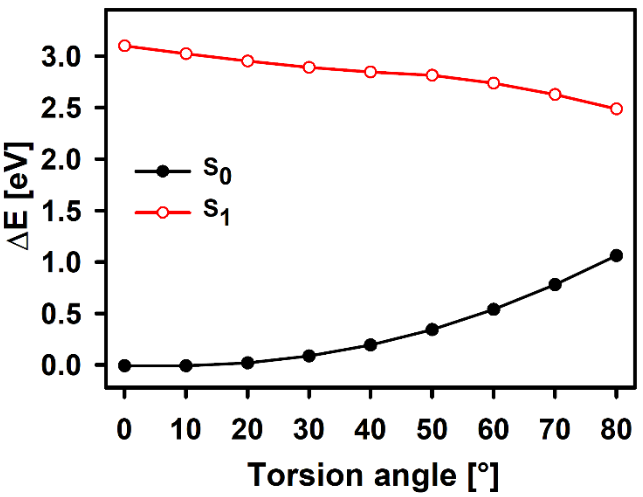


Figure S19. Potential energy curves for bI-Br ground (S_0) and first singlet excited (S_1) states along the cis-trans isomerization coordinate at CAM-B3LYP/cc-PVTZ/PCM: Methanol level of theory.

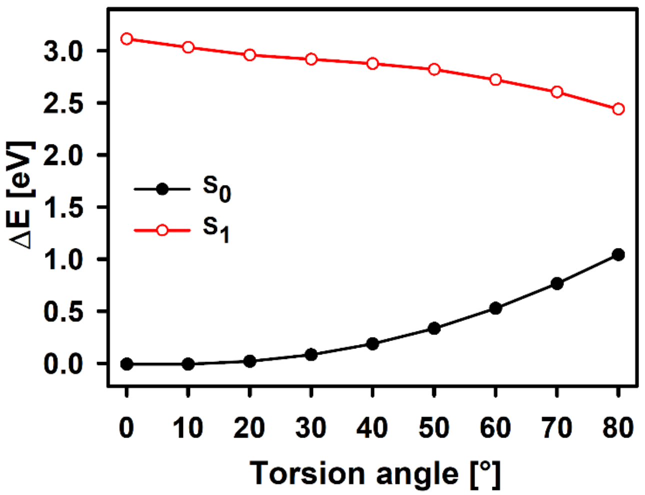


Figure S20. Potential energy curves for bI-AcOMe ground (S_0) and first singlet excited (S_1) states along the *cis-trans* isomerization coordinate at CAM-B3LYP/cc-PVTZ/PCM: Methanol level of theory.

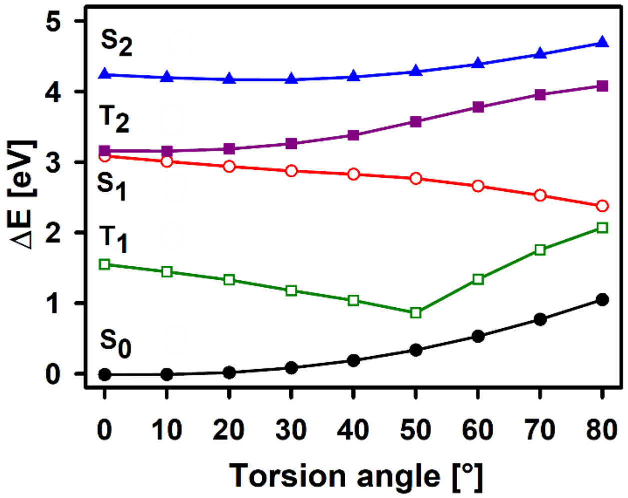
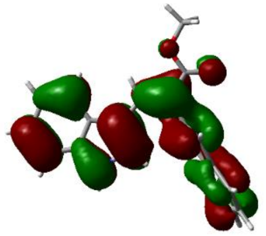
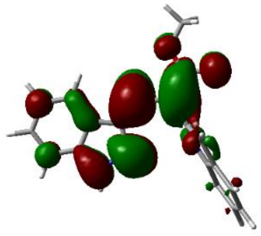
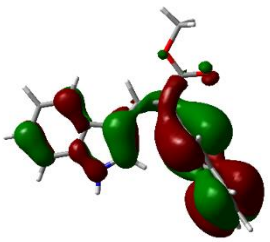


Figure S21. Potential energy curves for bI-H ground (S_0), first (S_1), and second singlet (S_2), first (T_1), and second triplet (T_2) excited states along the *cis-trans* isomerization coordinate. The level of theory used was CAM-B3LYP/cc-PVTZ/PCM: Methanol.

Table S7. Main molecular orbitals involved in relevant electronic vertical transitions for *E*-bI-H. Level of theory CAM-B3LYP/cc-PVTZ/PCM: Methanol.

State (Character)	Molecular Orbitals Involved		
S_1 (π-π^*)		→	
	HOMO	→	LUMO



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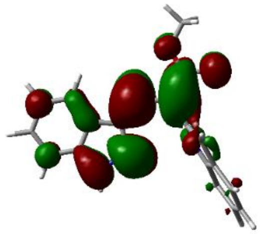
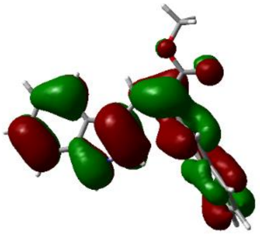


HOMO−1 → LUMO



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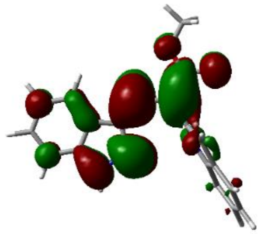
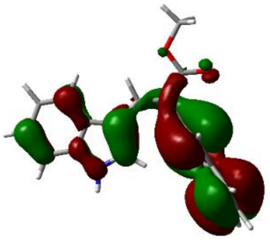


S_2

(π-π^{*})

HOMO → LUMO



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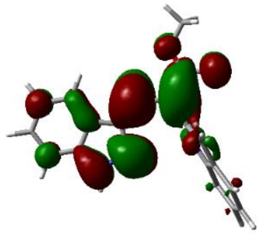
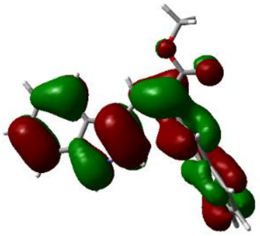


HOMO−1 → LUMO

T_1

(π-π^{*})



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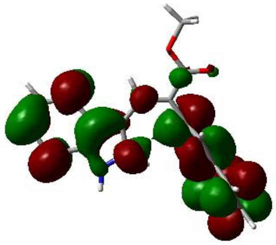
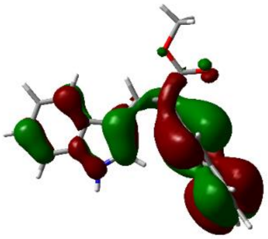


HOMO → LUMO+1



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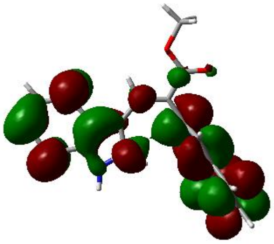
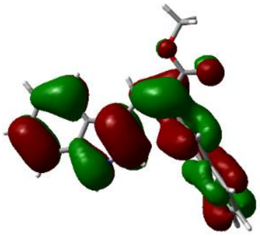


HOMO−1 → LUMO+1



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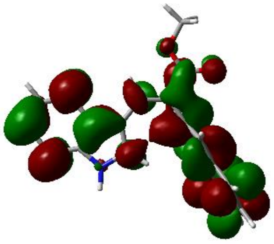
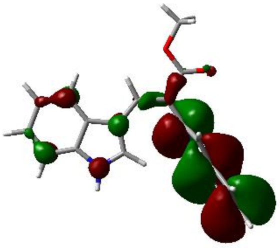


T_2 HOMO → LUMO+2

$(\pi\text{-}\pi^*)$



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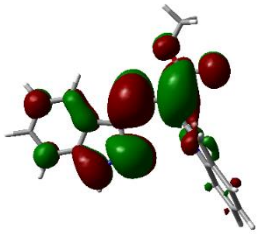

HOMO−2 → LUMO

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3. S. Mahboobi and K. Bernauer, *Helv. Chim. Acta*, 1988, **71**, 2034-2041.
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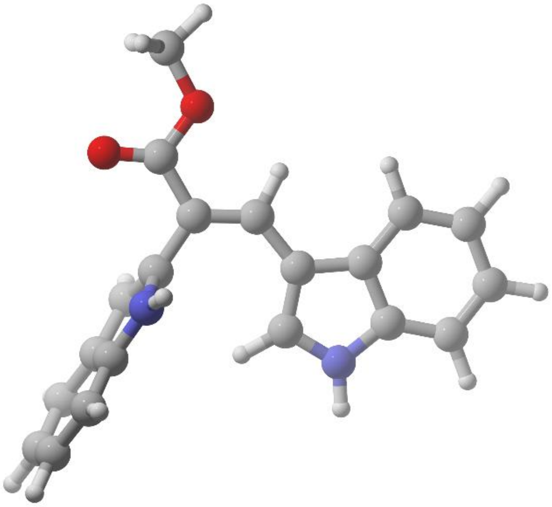
5. K. Stranius and K. Börjesson, *Scientific Reports*, 2017, **7**, 41145.

Relevant Geometries

bI-H *cis* isomer



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H	1.96577300	2.19329400	-0.53218800

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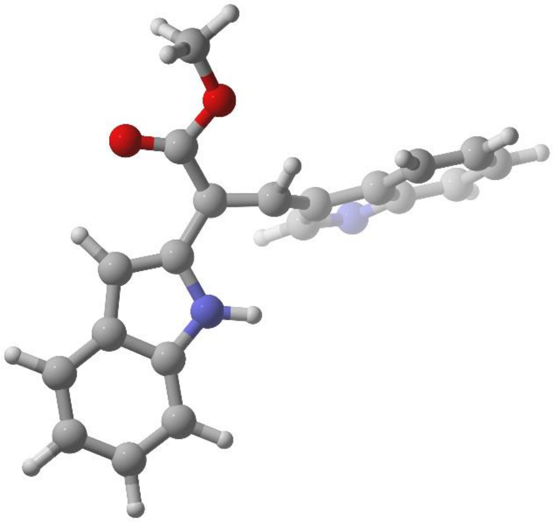
bI-H twisted geometry



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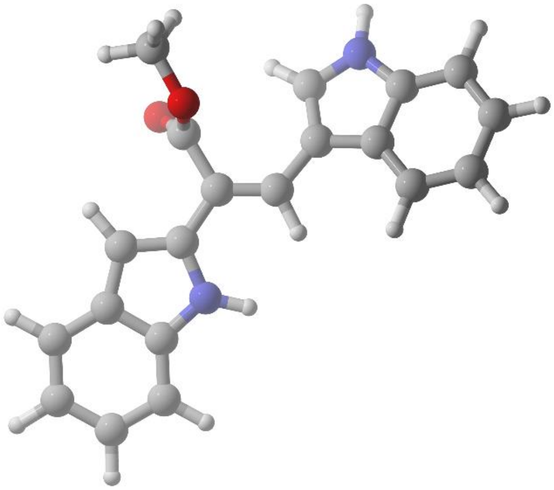
N	1.73741374	-0.28427204	0.83725743

N	-2.79423545	1.73221763	1.67612003
C	-0.68409300	-0.26381188	-4.59994468
H	-1.67418489	-0.60696364	-4.88899344
H	-0.49058140	0.72371818	-5.01876489
H	0.07522525	-0.95798982	-4.96055164
H	-5.61958283	-2.39926710	0.33117535

bI-H *trans* isomer

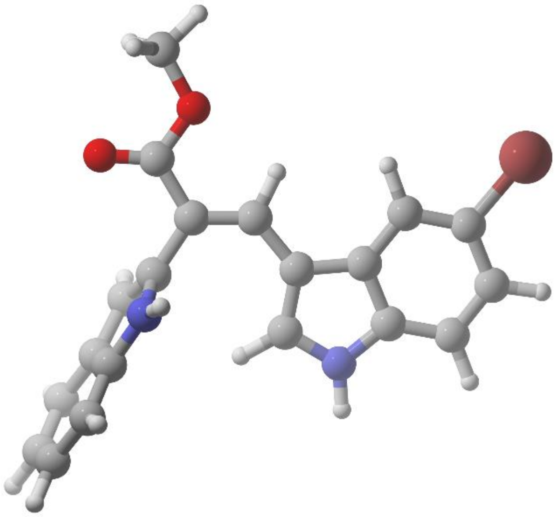


C	3.52178508	0.13002018	1.23618982
C	4.01984297	-0.07112091	-0.07393212
C	5.40034398	-0.21048797	-0.26035371
C	6.23269184	-0.14304571	0.83921050
C	5.71692310	0.06184445	2.12827509
C	4.35830851	0.20125559	2.34548054
C	1.76907518	0.10653770	-0.16658583
C	2.89301622	-0.08013139	-0.94207396

H	5.80758958	-0.36816335	-1.25239094
H	7.30312756	-0.24924954	0.70943866
H	6.39667892	0.11101988	2.97047355
H	3.96146977	0.35791973	3.34129590
H	1.55263955	0.43100160	1.91931369
H	2.90204511	-0.20616855	-2.01295560
C	0.38304087	0.14046884	-0.58049487
C	-0.65972110	0.19779068	0.27499299
H	-0.43434132	0.14973729	1.33667766
C	0.17494749	0.12029477	-2.06167254
O	-0.36328016	-1.02662401	-2.46740831
O	0.47163001	1.02201226	-2.80760207
C	-2.06288476	0.33322728	-0.01521862
C	-3.12875848	0.00871130	0.89957187
C	-2.67828264	0.82769509	-1.14727374
C	-4.34301334	0.31731617	0.25043110
C	-3.16915175	-0.52017841	2.19261433
H	-2.24665438	1.23108403	-2.04932241
C	-5.58234427	0.11943062	0.85020510
C	-4.39671187	-0.71348011	2.79610361
H	-2.25622248	-0.77853521	2.71661399
H	-4.68654188	1.14694832	-1.66832341
C	-5.59099106	-0.39766952	2.13147353

H	-6.50302168	0.36145340	0.33352886
H	-6.53745797	-0.56402126	2.63144839
N	2.16128238	0.22943023	1.14705015
N	-4.02672000	0.81081880	-0.98887359
C	-0.61884531	-1.13372891	-3.87039837
H	-1.03536345	-2.12574136	-4.01897622
H	-1.33152213	-0.37190589	-4.18650566
H	0.30501580	-1.01911786	-4.43617632
H	-4.44180040	-1.11960891	3.79943859

bI-Br *cis* isomer



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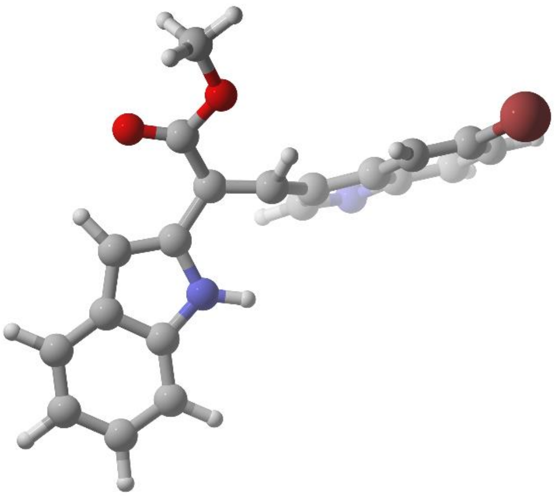
C	5.45925000	1.25198700	1.24633700

C	6.24892700	0.45905000	2.06179600
C	5.97929000	-0.91629700	2.22335000
C	4.91552200	-1.52089800	1.57361200
C	2.56172000	0.09931600	-0.65845500
C	3.36728000	1.15947500	-0.32895800
H	5.67602000	2.31537400	1.12580500
H	7.09581200	0.90103500	2.59002500
H	6.62072100	-1.51491100	2.87268100
H	4.70461800	-2.58457500	1.69704900
H	2.60210900	-1.94885300	-0.09349500
H	3.24760000	2.17829200	-0.68745800
C	1.35502100	0.04626900	-1.51120600
C	0.09288500	0.06498200	-1.02228600
H	-0.70273000	0.01463300	-1.76810700
C	1.59809600	-0.03209100	-2.97138200
O	0.47084400	-0.02555400	-3.70346300
O	2.70088900	-0.10072800	-3.47459400
C	-0.36143700	0.13579800	0.34629500
C	-1.75378300	0.13157500	0.74933800
C	0.36758200	0.23595100	1.52174200
C	-1.78091600	0.23103700	2.15738400
C	-2.96461900	0.05320200	0.04487100
H	1.44106500	0.27444700	1.67194600

C	-2.97300400	0.25462700	2.88471500
C	-4.13897600	0.07741700	0.77434200
H	-2.98615000	-0.02461900	-1.04168400
H	-0.17457800	0.36599100	3.55154900
C	-4.16097200	0.17653900	2.17733700
H	-2.97486100	0.33188100	3.97258500
H	-5.11411100	0.19164000	2.70414400
N	3.01511200	-1.03008400	-0.00448000
N	-0.47295500	0.29293100	2.58727900
C	0.65195000	-0.11734000	-5.11812400
H	-0.35439200	-0.09782400	-5.54964000
H	1.24407100	0.73060200	-5.48885300
H	1.16430500	-1.05238400	-5.38365400
Br	-5.80659000	-0.02849800	-0.15263200

bI-Br twisted geometry



C	4.28052900	-0.57076900	1.09757200
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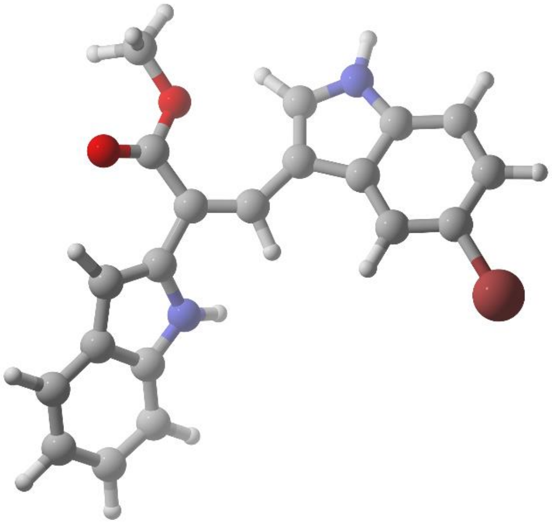
C	6.45629200	0.01059800	0.18059500
C	7.03911200	-0.63254900	1.26111000
C	6.24958000	-1.24844500	2.25328700
C	4.86381800	-1.22730300	2.18536200
C	2.85758700	0.29529700	-0.43262500
C	4.13449000	0.59983300	-0.86687100
H	7.07501300	0.48393700	-0.58471700
H	8.12672300	-0.66633100	1.34867000
H	6.73715900	-1.75048300	3.09100000
H	4.25058400	-1.70277200	2.95300800
H	2.17765500	-0.80033700	1.26093600
H	4.36869800	1.15661400	-1.76491600
C	1.52767400	0.55514500	-0.98957300
C	0.36886500	-0.02377400	-0.46546200
H	-0.23662800	-0.46607300	-1.26709400
C	1.54358000	0.72147500	-2.47621200
O	0.37233900	0.42886200	-3.07137000
O	2.47898400	1.16919500	-3.11051400
C	-0.53625300	0.41663200	0.55751000
C	-1.88843200	-0.06379900	0.76637100
C	-0.33451900	1.40274700	1.51853400

C	-2.43556100	0.69220200	1.82507600
C	-2.67093900	-1.04632400	0.14532500
H	0.54129700	2.02273400	1.68976600
C	-3.74226500	0.50726500	2.27827200
C	-3.96477600	-1.22323800	0.60307500
H	-2.27720800	-1.65658200	-0.66701100
H	-1.57963000	2.27318300	2.97386600
C	-4.50823700	-0.46441300	1.65440900
H	-4.15180000	1.10225200	3.09512800
H	-5.53259400	-0.64426800	1.97771400
N	2.96032700	-0.38785500	0.77121900
N	-1.45974000	1.57136900	2.25383700
C	0.33380600	0.61789500	-4.48713600
H	-0.67787300	0.33560300	-4.79740700
H	0.53417000	1.66772900	-4.74088000
H	1.07842500	-0.01724000	-4.98665400
Br	-5.06301100	-2.55328000	-0.21631000

bI-Br *trans* isomer



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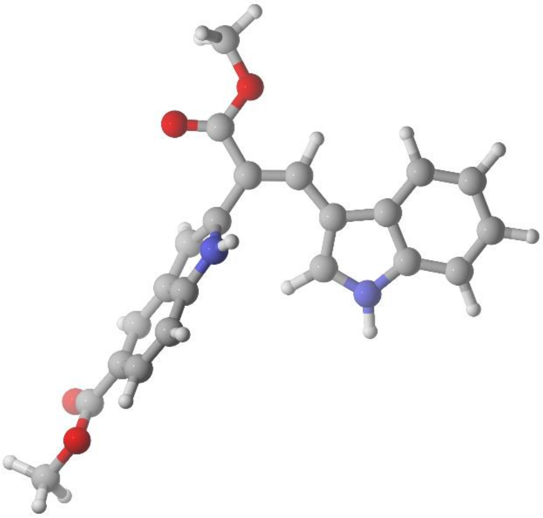
C	6.30169800	-1.33199400	-0.20529700
C	6.98445500	-1.69675900	0.94368500
C	6.39486100	-1.55479300	2.21669900
C	5.11073300	-1.05210500	2.36214900
C	2.91724100	0.05449900	-0.31088600
C	4.02954900	-0.32846100	-1.02769400
H	6.76611500	-1.44264500	-1.18740700
H	7.99608800	-2.09977900	0.86732400
H	6.95900500	-1.84792700	3.10398800
H	4.65176700	-0.94431100	3.34650900
H	2.57647500	0.15877400	1.78866300
H	4.11912300	-0.28338000	-2.10579800
C	1.61378200	0.59556800	-0.73967000

C	0.51515200	0.32190200	0.01701900
H	0.72950800	-0.35967100	0.84633900
C	1.61665400	1.31066400	-2.04308300
O	0.62657400	2.20256400	-2.17315300
O	2.42836400	1.12293900	-2.92497900
C	-0.89853500	0.63365300	-0.02654500
C	-1.87751700	-0.16897800	0.68791100
C	-1.61962700	1.67571400	-0.58724800
C	-3.13837400	0.43651600	0.49900700
C	-1.79169800	-1.34342300	1.45065800
H	-1.26573600	2.51872300	-1.16363700
C	-4.31198300	-0.08614000	1.04602800
C	-2.95887300	-1.85002100	1.99313300
H	-0.84084900	-1.85059000	1.61212800
H	-3.65590700	2.20945200	-0.56201300
C	-4.21237300	-1.24219200	1.80241700
H	-5.27707400	0.39617000	0.88688300
H	-5.10224300	-1.68351700	2.24933400
N	3.15854500	-0.18033500	1.03482700
N	-2.93787300	1.55615200	-0.27671000
C	0.56705200	2.87754300	-3.43681100
H	-0.30604700	3.53645800	-3.38185700
H	1.48051400	3.46475100	-3.59898600

H	0.45371900	2.15454800	-4.25520000
Br	-2.87542100	-3.44542100	3.04203300

bI-AcOMe *cis* isomer



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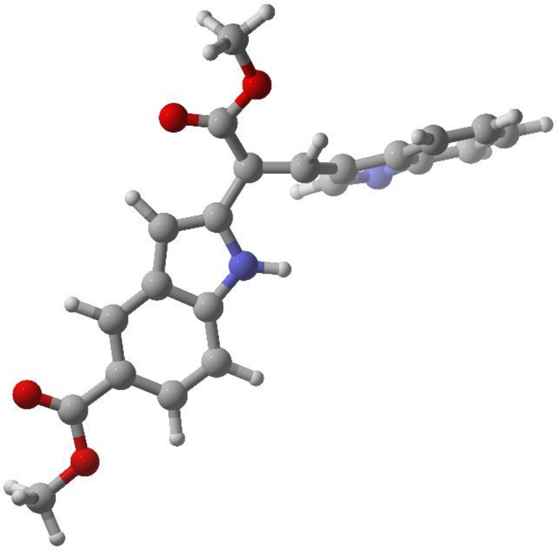
C	3.37575922	0.81914110	-0.32446182
C	4.27325819	-0.02642137	0.31768173
C	3.89827757	-1.34146649	0.68329375
C	2.63147308	-1.82279608	0.41552125
C	-0.05402994	-0.02061680	-1.22828312
C	0.93171445	0.93116952	-1.24279819
H	3.69405566	1.82596901	-0.59582206
H	4.62707811	-1.97676850	1.18372851

H	2.34180390	-2.83629767	0.69631382
H	-0.09309663	-2.01758086	-0.49334510
H	0.83964311	1.93107646	-1.65710813
C	-1.44898045	0.03211167	-1.71116146
C	-2.52615241	0.06857757	-0.88949630
H	-3.49712288	0.05707854	-1.38817795
C	-1.62482270	0.01418510	-3.18259255
O	-2.91067755	0.09150696	-3.56762044
O	-0.71163281	-0.06359120	-3.97890861
C	-2.58891227	0.13726470	0.54978596
C	-3.81773900	0.08503451	1.32005467
C	-1.56983014	0.29966299	1.47652148
C	-3.46126203	0.21785819	2.67937546
C	-5.17314933	-0.06195295	0.98616684
H	-0.50041767	0.39924869	1.32415064
C	-4.40484982	0.20757960	3.71056024
C	-6.11569979	-0.07082362	2.00187448
H	-5.48445140	-0.16885578	-0.05462303
H	-1.54121438	0.46784926	3.57403395
C	-5.73545686	0.06192253	3.35222147
H	-4.10330835	0.31090798	4.75402062
H	-6.50214503	0.04989837	4.12862239
N	0.43452762	-1.16298655	-0.61531194

N	-2.08797658	0.34795474	2.73104570
C	-3.13652245	0.05852858	-4.97825113
H	-4.22153992	0.13044633	-5.10839239
H	-2.63509402	0.90284015	-5.47102064
H	-2.76075986	-0.87951417	-5.40981905
H	-7.17267408	-0.18363336	1.75480900
C	5.63095559	0.50070857	0.60025025
O	6.41954720	-0.39286691	1.21700008
O	6.01144354	1.61766906	0.31349002
C	7.74459528	0.05201626	1.51733121
H	8.27863711	0.32612540	0.59714421
H	7.71817313	0.92313178	2.18639726
H	8.23916577	-0.79230052	2.00892753

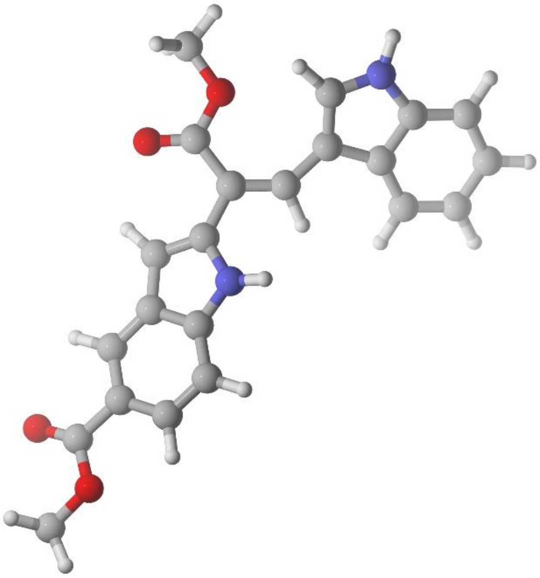
bI-AcOMe twisted geometry



C	1.91747044	-0.18984470	0.63945161
C	2.53930035	0.20179031	-0.57606850
C	3.93547988	0.24781577	-0.63358909
C	4.67598657	-0.09405333	0.49525121
C	4.03364869	-0.48902712	1.69103022
C	2.65336774	-0.54247903	1.77586105
C	0.29099961	0.23408371	-0.87571064
C	1.49114336	0.47756624	-1.51438416
H	4.45885864	0.54679708	-1.54216967
H	4.64249028	-0.75278994	2.55414726
H	2.15677086	-0.84674347	2.69832822
H	-0.13251170	-0.43609957	1.10462407
H	1.59447858	0.81253294	-2.53788113
C	-1.10381302	0.29580435	-1.31779360
C	-2.15018399	-0.25631612	-0.56646745
H	-2.77745835	-0.91297130	-1.18321114
C	-1.25063365	0.16776989	-2.79673991
O	-2.45772888	-0.28832893	-3.18491324
O	-0.41979443	0.52193435	-3.61169650
C	-2.97568945	0.30715111	0.45482985
C	-4.23706460	-0.22812110	0.93682841
C	-2.77106934	1.49174499	1.16143473
C	-4.73559358	0.69001956	1.88442749

C	-4.98289659	-1.37767878	0.64406367
H	-1.95571335	2.20552384	1.07948929
C	-5.95443248	0.50734761	2.53970722
C	-6.19472759	-1.56865729	1.29098531
H	-4.61751624	-2.11315173	-0.07480062
H	-3.92463310	2.54834330	2.56180830
C	-6.67579972	-0.63574023	2.22894802
H	-6.32229138	1.23368887	3.26553267
H	-7.63261865	-0.81574626	2.72147482
N	0.56719599	-0.14666740	0.43399482
N	-3.81349977	1.71920700	1.99066793
C	-2.65527755	-0.38987679	-4.59598934
H	-3.67380230	-0.77064458	-4.72726279
H	-2.54966895	0.59458049	-5.07187850
H	-1.92813352	-1.08111028	-5.04436185
H	-6.78710982	-2.45870749	1.07286852
C	6.15335439	-0.02826592	0.39342669
O	6.77224942	-0.37542617	1.53350729
O	6.76442320	0.30183862	-0.60317098
C	8.20040302	-0.33211467	1.50140218
H	8.59213839	-1.02141398	0.74067592
H	8.55226673	0.68385206	1.27510976
H	8.53155112	-0.63737106	2.49962526

bI-AcOMe *trans* isomer



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C	2.60576149	0.15829343	-0.52785413
C	3.97281111	0.44669482	-0.59372882
C	4.81463929	-0.01810462	0.41158458
C	4.30515754	-0.77605384	1.49218267
C	2.95762377	-1.07124329	1.58400871
C	0.36785224	-0.09939709	-0.77124725
C	1.47947579	0.45209435	-1.36583126
H	4.39479659	1.02512117	-1.41592348
H	4.99264677	-1.12700394	2.25986718
H	2.56318795	-1.65400932	2.41758365
H	0.17384191	-1.32060323	0.96792406
H	1.47959131	1.01089434	-2.29306451

C	-1.05847226	-0.08058341	-1.14980977
C	-1.98703297	-0.10620833	-0.14891513
H	-1.53243657	-0.04691813	0.84511629
C	-1.32726127	0.05226922	-2.60286817
O	-2.61841146	-0.08962771	-2.93058448
O	-0.48089015	0.28994638	-3.44047096
C	-3.42471424	-0.16129531	-0.02668492
C	-4.09166814	0.13609483	1.23360778
C	-4.43497386	-0.55342193	-0.89350633
C	-5.47121683	-0.08701510	1.04118380
C	-3.64928366	0.57799296	2.49005300
H	-4.36628117	-0.89113403	-1.91795789
C	-6.41762249	0.11224627	2.04939900
C	-4.57958269	0.77318867	3.49924409
H	-2.59140008	0.77240192	2.67670179
H	-6.51598442	-0.76504145	-0.69059844
C	-5.95194129	0.54377222	3.28154453
H	-7.47911470	-0.06608623	1.87140762
H	-6.65962886	0.70981320	4.09538551
N	0.76535377	-0.72278161	0.40644462
N	-5.63534734	-0.51076199	-0.26201072
C	-2.92957372	0.10071455	-4.31548584
H	-4.01348454	-0.03408086	-4.39764860

H	-2.64295096	1.11022444	-4.63895360
H	-2.40256004	-0.63783265	-4.93401417
H	-4.24521530	1.11477635	4.48032090
C	6.25743040	0.30814022	0.30402031
O	6.98224856	-0.18750246	1.31934088
O	6.75474167	0.95321163	-0.59688551
C	8.38340674	0.09183190	1.27540217
H	8.83424328	-0.33081173	0.36692423
H	8.56281194	1.17567438	1.29046520
H	8.81018666	-0.37836711	2.16758649

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) Compound_1b

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No syntax errors found.   CIF dictionary   Interpreting this report

Datablock: Compound_1b

```
Bond precision:  C-C = 0.0045 A           Wavelength=0.71073

Cell:            a=5.586(3)     b=26.400(12)         c=11.913(5)
                 alpha=90       beta=96.885(10)      gamma=90
Temperature:     298 K

                Calculated                 Reported
Volume          1744.2(14)                 1744.2(13)
Space group     P 21/c                     P 21/c
Hall group      -P 2ybc                    -P 2ybc
Moiety formula  C20 H15 Br N2 O2           C20 H15 Br N2 O2
Sum formula     C20 H15 Br N2 O2           C20 H15 Br N2 O2
Mr              395.24                     395.25
Dx,g cm-3       1.505                      1.505
Z               4                          4
Mu (mm-1)       2.372                      2.372
F000            800.0                      800.0
F000'           799.16
h,k,lmax        7,37,16                    7,37,16
Nref            5109                       5095
Tmin,Tmax       0.575,0.691                0.370,0.709
Tmin'           0.363

Correction method= # Reported T Limits: Tmin=0.370 Tmax=0.709
AbsCorr = MULTI-SCAN

Data completeness= 0.997           Theta(max)= 30.076

R(reflections)= 0.0521( 2781)      wR2(reflections)= 0.1286( 5095)

S = 1.026                  Npar= 233
```

The following ALERTS were generated. Each ALERT has the format
      test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

```
 Alert level C
PLAT431_ALERT_2_C Short Inter HL..A Contact  Br1      ..O2        .        3.24 Ang.
                                         -x,-y,1-z  =      3_556 Check
PLAT480_ALERT_4_C Long H...A H-Bond Reported H23A     ..BR1       .        3.11 Ang.
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ......       8.540 Check
PLAT906_ALERT_3_C Large K Value in the Analysis of Variance ......       2.756 Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.600          6 Report
```

```
 Alert level G
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).          2 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600          7 Note
PLAT933_ALERT_2_G Number of OMIT Records in Embedded .res File ...          7 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          9 Info
```

```
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
   5 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   4 ALERT level G = General information/check it is not something unexpected

   0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   3 ALERT type 2 Indicator that the structure model may be wrong or deficient
   4 ALERT type 3 Indicator that the structure quality may be low
   2 ALERT type 4 Improvement, methodology, query or suggestion
   0 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 07/08/2019; check.def file version of 30/07/2019

Datablock Compound_1b - ellipsoid plot