

## Electronic Supplementary Information

### Photooxygenation Mechanisms in Naproxen-Amino Acid

#### Linked Systems

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**S1.** This page.

**S2. Figure S1.** X-ray structures of (*R,S*)-**2**, (*R,S*)-**3** and (*R,S*)-**4**.

**S3. Figure S2.** Photodegradation of (*S*)-**1** under N<sub>2</sub> (solid circles), air (half solid circles) and O<sub>2</sub> (open circles).

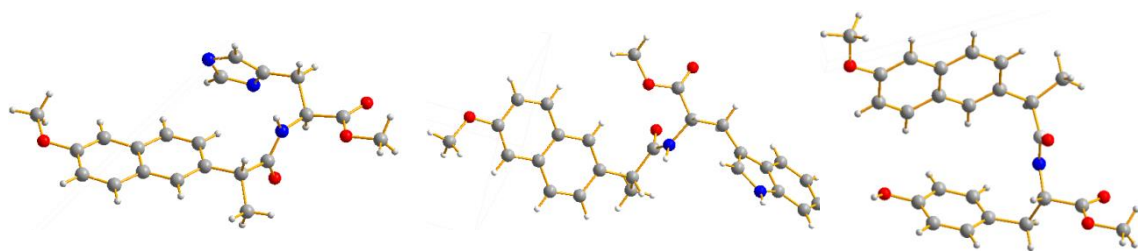
**S4. Figure S3.** Top: photoreactivity of (*R*)-**1** (black), (*R,S*)-**2** (blue), (*R,S*)-**3** (green) and (*R,S*)-**4** (red). Middle: oxygen-mediated photoreactivity of the same compounds (values under air – values under nitrogen). Bottom: photoreactivity of (*R,S*)-**2** under different conditions. Codes: solid circles (N<sub>2</sub>), half solid circles (air) and open circles (O<sub>2</sub>).

**S5. Figure S4.** Photodegradation of (*S,S*)-**4** under N<sub>2</sub> (solid circles), air (half solid circles) and O<sub>2</sub> (open circles).

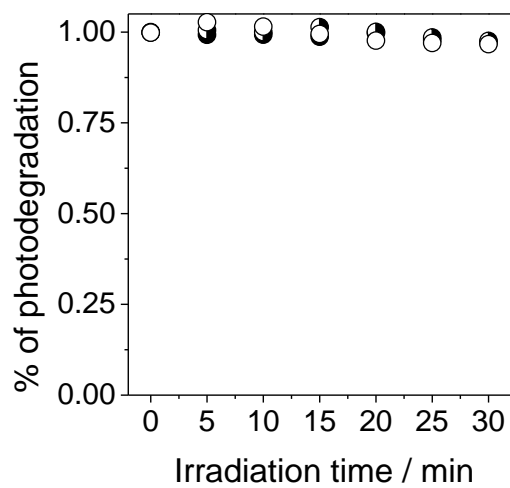
**S6. Figure S5.** Absorption spectra of A) (*S*)-NPX (violet), (*S*)-GlyMe ester (dash black) and (*S*)-**1** (solid black); B) (*S*)-NPX (violet), (*S*)-HisMe ester (dash blue) and (*S,S*)-**2** (solid blue); C) (*S*)-NPX (violet), (*S*)-TrpMe ester (dash green) and (*S,S*)-**3** (solid green); D) (*S*)-NPX (violet), (*S*)-TyrMe ester (dash red) and (*S,S*)-**4** (solid green). The intensity of NPX absorption in A and B has been slightly reduced in order to be distinguishable.

**S7. Figure S6.** Fluorescence spectra of (*S*)-**1** (black), (*S,S*)-**2** (blue line) and (*R,S*)-**2** (blue dot) in deaerated MeCN solutions ( $\lambda_{\text{exc}} = 266 \text{ nm}$ ).

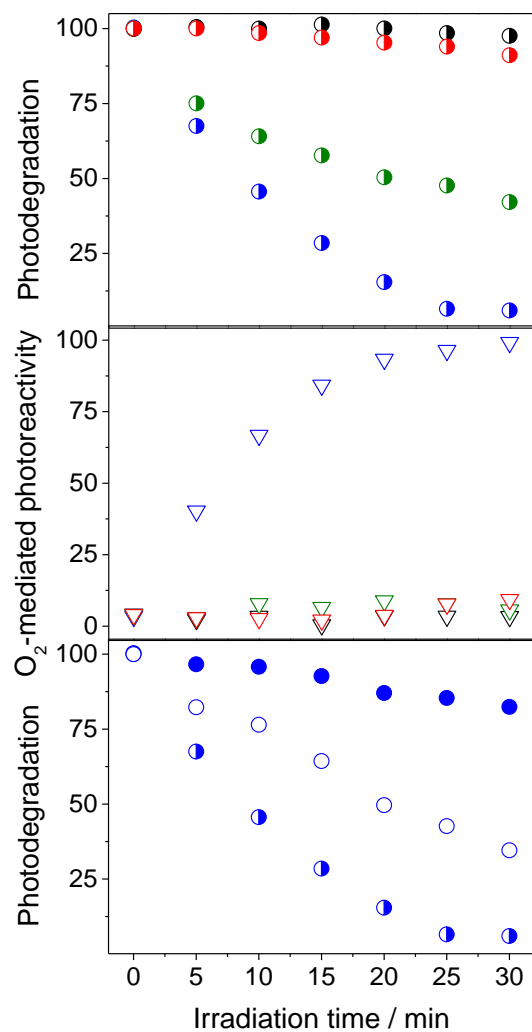
**S8. Figure S7.** A) Fluorescence spectra and B) triplet excited state decays of (*S*)-**1** (black), (*S,S*)-**4** (red line) and (*R,S*)-**4** (red dot) in deaerated MeCN solutions ( $\lambda_{\text{exc}} = 266 \text{ nm}$ ).



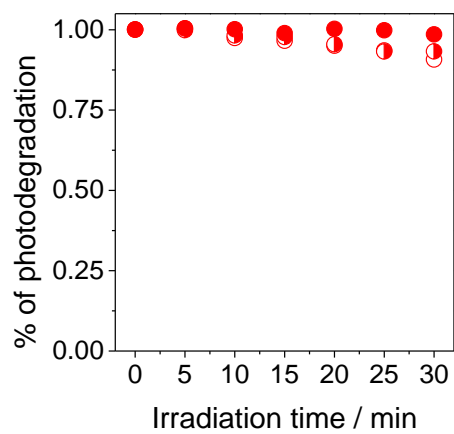
**Figure S1.** X-ray structures of (*R,S*)-**2**, (*R,S*)-**3** and (*R,S*)-**4**.



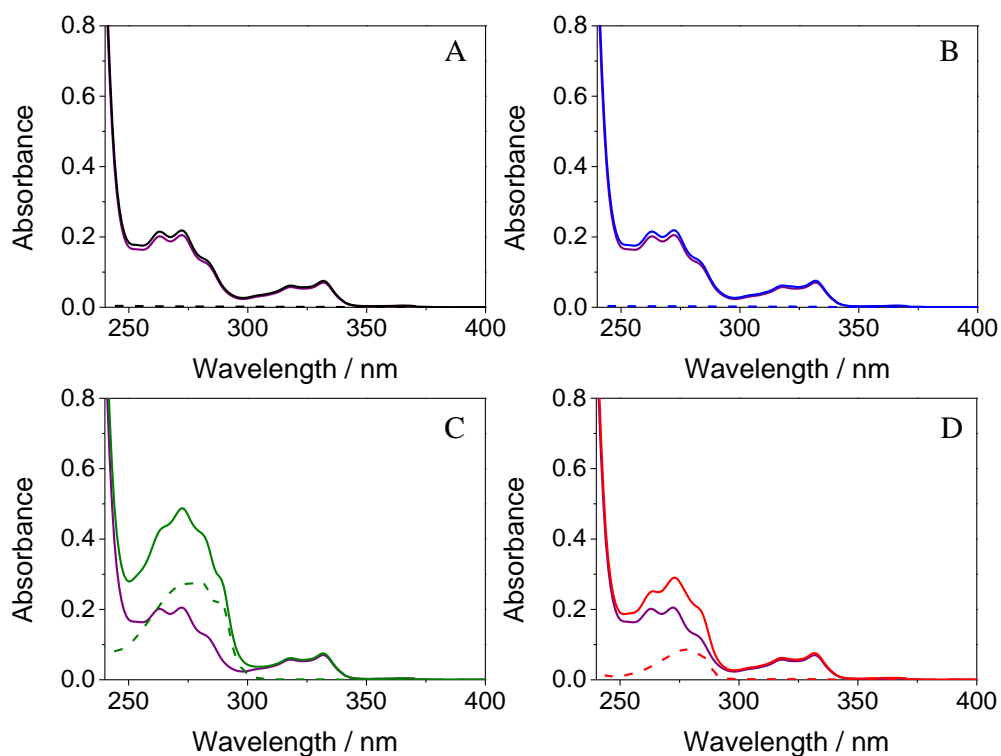
**Figure S2.** Photodegradation of (*S*)-**1** under N<sub>2</sub> (solid circles), air (half solid circles) and O<sub>2</sub> (open circles).



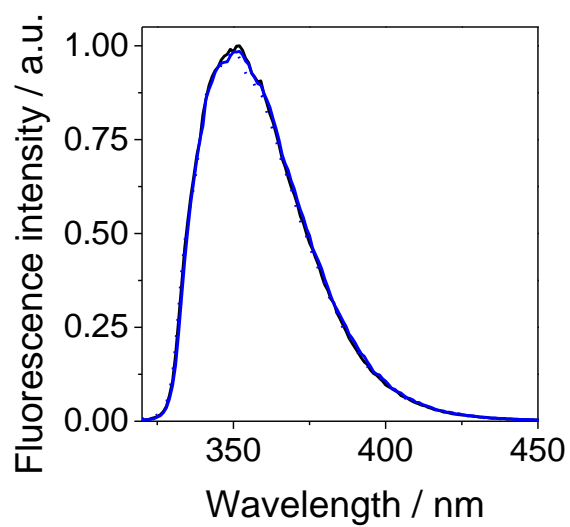
**Figure S3.** Top: photoreactivity of (*R*)-**1** (black), (*R,S*)-**2** (blue), (*R,S*)-**3** (green) and (*R,S*)-**4** (red). Middle: oxygen-mediated photoreactivity of the same compounds (values under air minus values under nitrogen). Bottom: photoreactivity of (*R,S*)-**2** under different conditions. Codes: solid circles (N<sub>2</sub>), half solid circles (air) and open circles (O<sub>2</sub>).



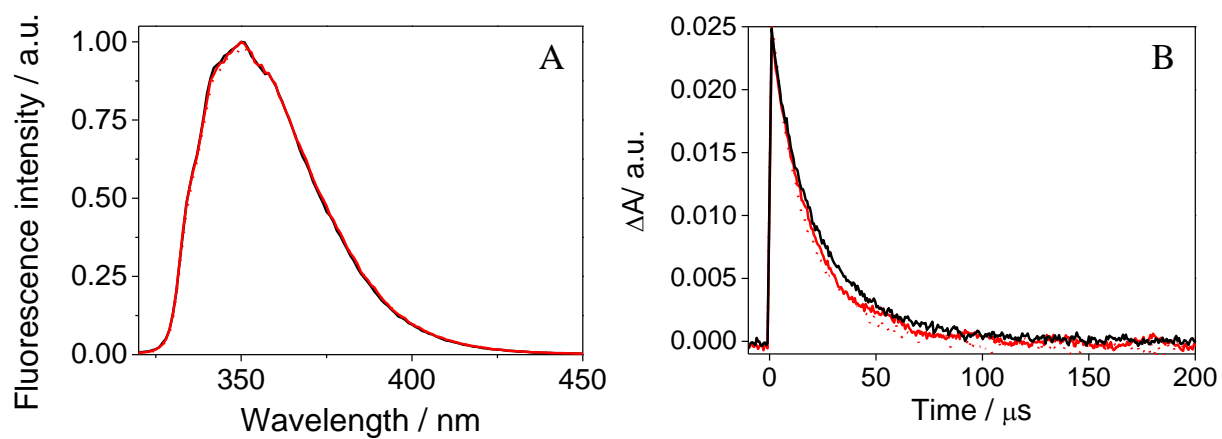
**Figure S4.** Photodegradation of (*S,S*)-**4** under N<sub>2</sub> (solid circles), air (half solid circles) and O<sub>2</sub> (open circles).



**Figure S5.** Absorption spectra of A) (*S*)-NPX (violet), (*S*)-GlyMe ester (dash black) and (*S*)-1 (solid black); B) (*S*)-NPX (violet), (*S*)-HisMe ester (dash blue) and (*S,S*)-2 (solid blue); C) (*S*)-NPX (violet), (*S*)-TrpMe ester (dash green) and (*S,S*)-3 (solid green); D) (*S*)-NPX (violet), (*S*)-TyrMe ester (dash red) and (*S,S*)-4 (solid green). The intensity of NPX absorption in A and B has been slightly reduced in order to be distinguishable.



**Figure S6.** Fluorescence spectra of (*S*)-**1** (black), (*S,S*)-**2** (blue line) and (*R,S*)-**2** (blue dot) in deaerated MeCN solutions ( $\lambda_{\text{exc}} = 266 \text{ nm}$ ).



**Figure S7.** A) Fluorescence spectra and B) triplet excited state decays of (*S*)-**1** (black), (*S,S*)-**4** (red line) and (*R,S*)-**4** (red dot) in deaerated MeCN solutions ( $\lambda_{\text{exc}} = 266$  nm).