

# Supporting Information

## **With or without a co-solvent? Highly efficient ultrafast Phenanthrenequinone-Electron Rich Alkene (PQ-ERA) photoclick reactions**

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## 1. General information

**Synthesis and isolation.** Compounds were synthesized and characterized as reported previously.<sup>[1]</sup>

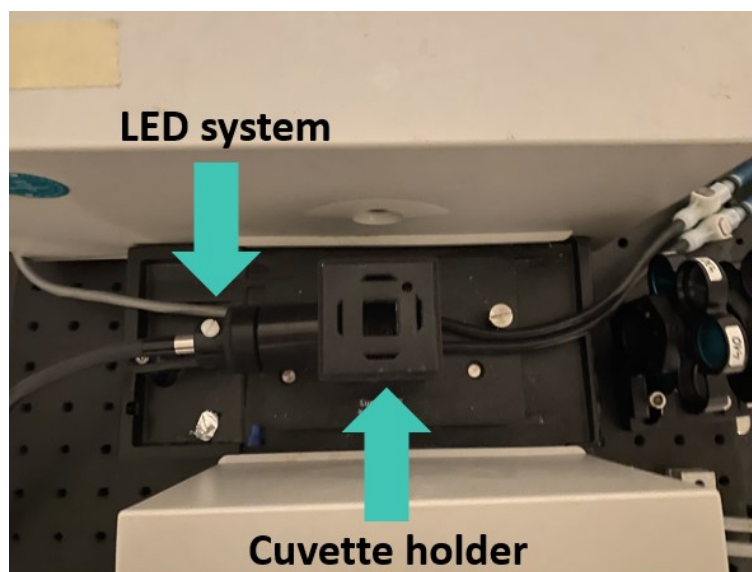
**Analysis.** UV-Vis spectra were recorded on a Hewlett-Packard HP 8543 Diode Array, an Agilent 8453 UV-Visible spectrophotometer in a quartz cuvette with 1 cm pathlength at 20 °C. The Agilent 8453 UV-Visible spectrometer was equipped with a custom-built (Prizmatix/Mountain Photonics) multi-wavelength fiber coupled LED-system (FC6-LED-WL) including the following LEDs: 365A, 390B, 420Z, 445B, 535R, 630CA. A detailed description of the setup was published earlier by our group (see Figure S1).<sup>[2]</sup> A Quantum Northwest TC1 temperature controller was used to maintain the temperature at 20 °C during photochemical studies.

**Femtosecond transient absorption spectroscopy.** The apparatus used for the transient absorption spectroscopy (TAS) measurements has been described in detail before. Briefly, 40 fs pulses centred at 800 nm, were produced by an integrated Ti: sapphire oscillator (Mira-Coherent) coupled with a regenerative amplifier system (Legend-Coherent). The excitation wavelength was set at 400 nm and excitation power was set at about 200 nJ for all measurements. The pump pulses were generated by second harmonic generation of the fundamental laser radiation using a 2 mm thick BBO crystal. The pump beam polarization has been set to magic angle with respect to the probe beam by rotating a  $\lambda/2$  plate, to exclude rotational contributions. The white light probe pulse was generated by focusing a small portion of the fundamental laser radiation on a 3 mm thick CaF<sub>2</sub> window. A portion of the generated white light was sent to the sample through a different path and used as a reference signal. After passing through the sample the white light probe and reference pulses were both directed to a flat field monochromator coupled to a home-made detector. Transient signals were acquired in a time interval spanning up to 1500 ps. The sample was contained in a 2 mm quartz cuvette, mounted on a movable holder to minimize photodegradation. Measurements were performed

at room temperature. Concentrations were adjusted to an absorbance of 0.9 – 1.0 OD (for the respective optical path) at the absorption maximum which amounted to about 0.3 – 0.5 OD at excitation wavelength. Before and after the measurements, the integrity of the sample was checked on a PerkinElmer LAMBDA 950 spectrophotometer.

**Nanosecond transient absorption spectroscopy.** Nanosecond transient absorption spectra were recorded with an in-house assembled setup with 400 nm used as the excitation wavelength for all of the samples. The excitation wavelength was generated using a tunable Nd:YAG-laser system (NT342B, Ekspla) comprising the pump laser (NL300) with harmonic spot generators (SHG, THG) producing 355 nm to pump an optical parametric oscillator (OPO) with SHG connected in a single device. The laser system was operated at a repetition rate of 10 Hz with a pulse length of 5 ns. The probe light running at 20 Hz was generated by a high-stability short arc xenon flash lamp (FX-1160, Excelitas Technologies) using a modified PS302 controller (EG&G). Using a 50/50 beam splitter, the probe light was split equally into a signal beam and a reference beam and focused (bi-convex lens 75 mm) on the entrance slit of a spectrograph (SpectraPro-150, Princeton Instruments) with a grating of 150 ln/mm, blaze at 500 nm. The probe beam ( $A = 1 \text{ mm}^2$ ) was passed through the sample cell and orthogonally overlapped with the excitation beam on a  $1 \text{ mm} \times 1 \text{ cm}$  area. The excitation energy was recorded by measuring the excitation power at the back of an empty sample holder. In order to correct for fluctuations in the flash lamp spectral intensity, the reference was used to normalize the signal. Both beams were recorded simultaneously using a gated intensified CCD camera (PI-MAX3, Princeton Instruments) which has an adjustable gate of minimal 2.9 ns, normally a gate of 20 ns and software binning is used to improve the dynamic range and signal to noise ratio. Two delay generators (DG535 and DG645, Stanford Research Systems, Inc.) were used to trigger the excitation and to change the delay of the flash lamp together with the gate of the camera during the experiment. The setup was controlled by an in-house written Labview program.

**Photocycloaddition of PQs with traps in solution.** Stock solutions of **PQs** and *N*-*boc*-2,3-dihydro-1*H*-pyrrole (**PY**) in MeCN were prepared. From them, a solution of **PQs/PY** (50  $\mu$ M/500  $\mu$ M) was prepared in MeCN (2.5 mL) in a quartz cuvette and degassed by N<sub>2</sub> for 3 min. The 390 nm LED was used as light source for photoclick reactions and positioned at a fixed distance to the cuvette. Changes in the absorption were monitored every 0.5 or 1 s. See Figure S1 for a photograph of the LED-system (FC6-LED-WL).



**Figure S1. Photograph of LED-system.** The custom-built FC6-LED-WL system used for irradiation during UV-Vis absorption spectroscopy.

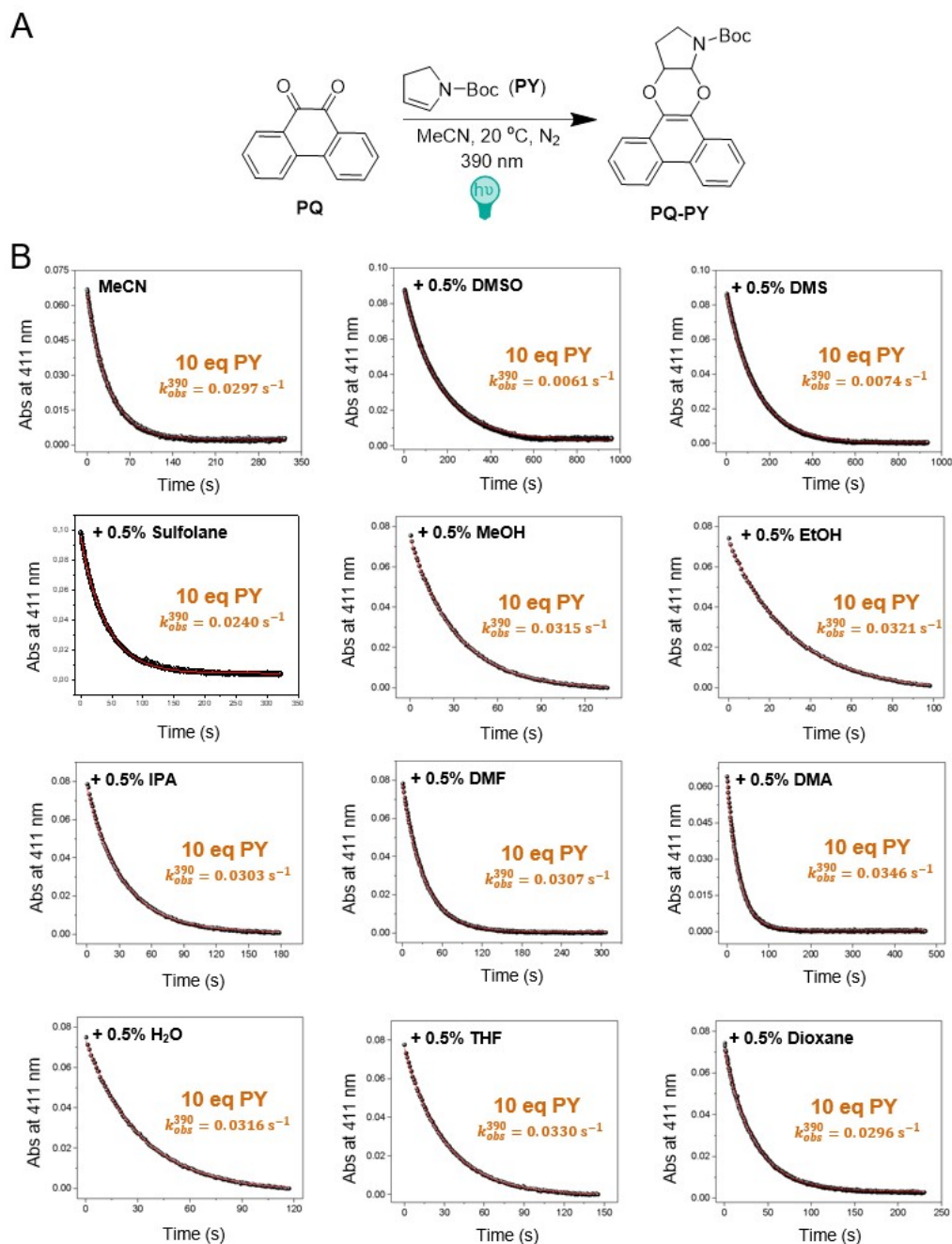
## 2. Photophysical and photochemical studies by UV-Vis spectroscopy

### 2.1. Analysis of reactions rates

To assess the different reaction rates of the photo-induced [4+2] cycloaddition of the phenanthrenequinone (**PQ**) and *N*-*tert*-butyloxycarbonyl-2,3-dihydro-1*H*-pyrrole (**PY**), we adapted procedures previously published for the evaluation of the kinetics of chemical<sup>[3]</sup> and photochemical click reactions.<sup>[4]</sup> Photochemical transformations are strongly depended on the used light source and setup, *etc.*, as shown *e.g.* for photocatalytic transformations<sup>[5]</sup> and photoclick reactions.<sup>[2,6]</sup> Therefore, we determined the respective rate constants *via* UV-Vis absorption spectroscopy using the fixed LED setup, described above, to achieve reliable comparability of the individual substrates. All reactions were performed at the same concentration (**PQ**s: 50  $\mu$ M, **PY**: 500  $\mu$ M) and under irradiation with the same light source and intensity, independently from the molar attenuation coefficient of the respective **PQ**s at this wavelength. Both the wavelength of irradiation ( $\lambda_{\text{exc}}=390$  nm) and  $\lambda_{\text{obs}}$  were chosen in the spectral regions where only the starting materials, **PQ**, and the photoclick product, absorb. Rate constants  $k_{\text{obs}}$  for the different **PQ**s (50  $\mu$ M) were measured under *pseudo*-first-order conditions with a 10-fold excess of **PY** in MeCN ( $\text{N}_2$  atmosphere) by time-dependent analysis. Mixing the appropriate volume of the prepared stock solutions to derive the desired final concentration in sample vials, and the mixture was transferred into a 1 cm optical path quartz optical cuvette, degassed by  $\text{N}_2$ . Signals were read out by monitoring the absorption signal of the **PQ**s. The kinetic traces were recorded using the following instrumental parameters: 1 or 2 data points per second over the recorded time range. The data was analyzed using single-exponential fits. All data processing was performed using Origin-pro software.

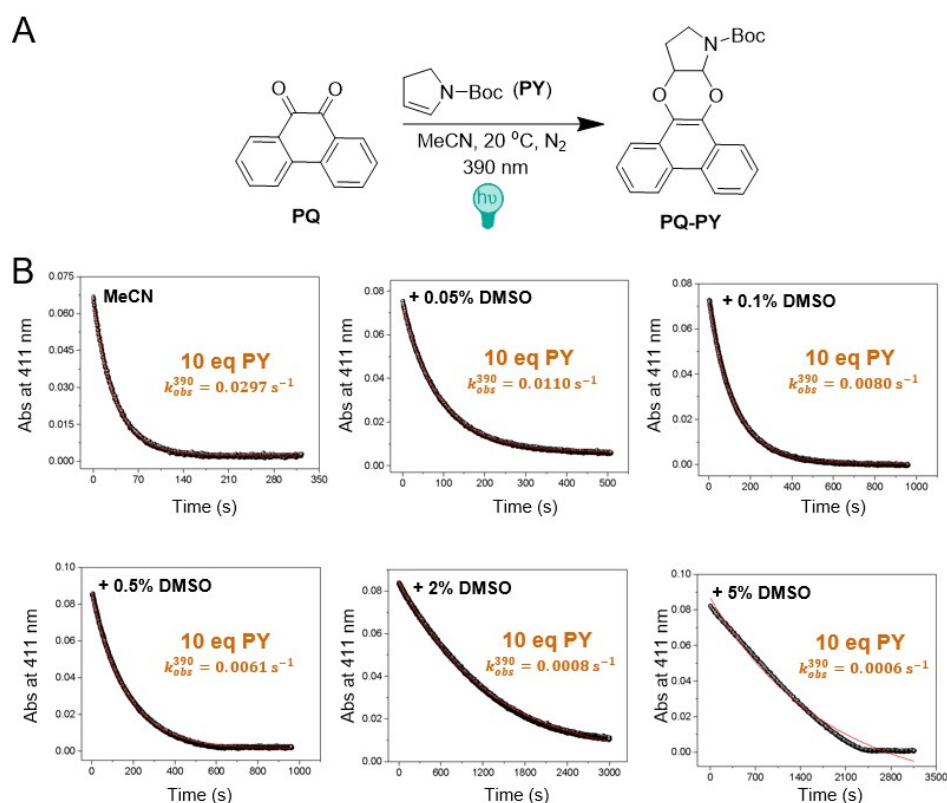
While this procedure does not lead to the best performance of all systems at the applied irradiation wavelength (due to different molar attenuation coefficient at that wavelength), it

does (i) facilitate rapid screening of PQs and (ii) give a good impression of the relative reaction rates between individual PQs-PY systems.



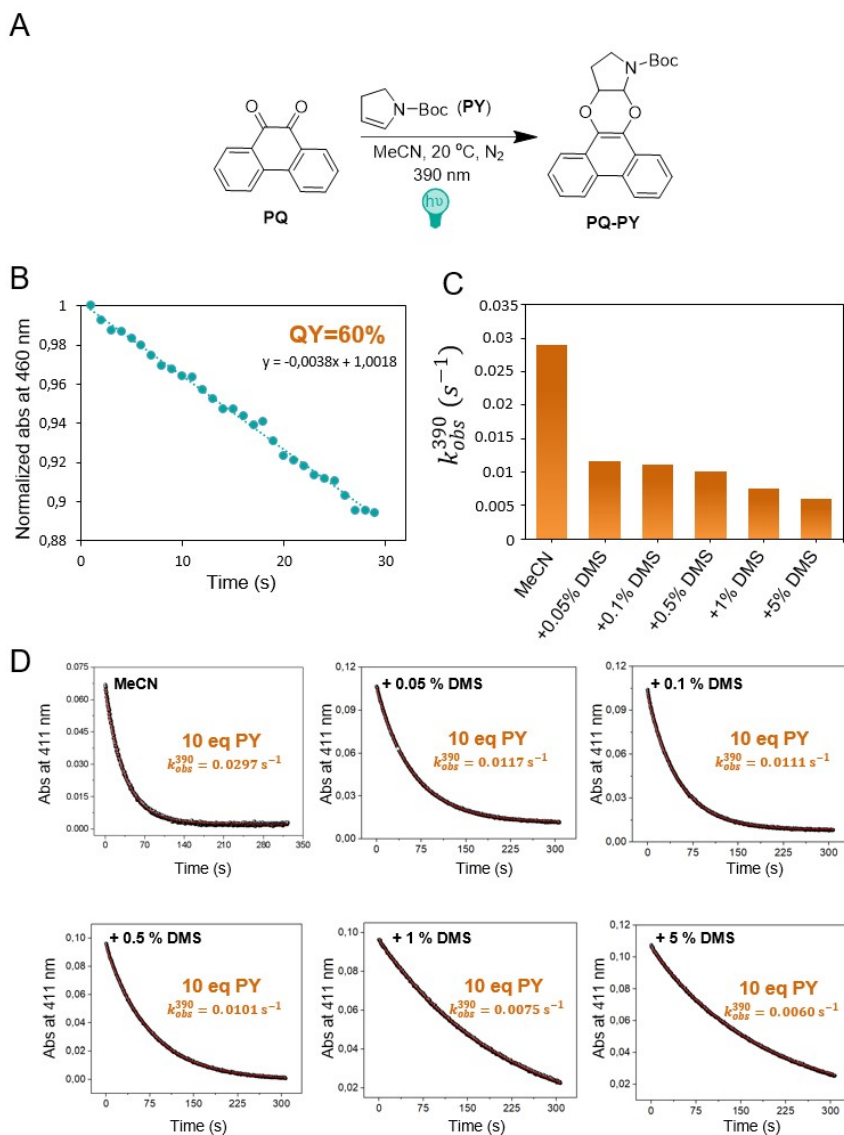
**Figure S2. Kinetic study of photo-induced [4+2] cycloaddition of PQ with PY with the addition of different co-solvents.** A) Reaction scheme. B) Kinetic traces of the photocycloaddition between PQ (50  $\mu$ M) and PY (500  $\mu$ M) in 2.5 mL MeCN ( $N_2$  atmosphere) including 0.5% (v/v) of co-solvent. The solution was irradiated with a 390 nm LED at 20  $^{\circ}$ C.

The reaction was monitored by UV-Vis absorption spectroscopy (1 cm cuvette, sample interval 1 s). **PQ-PY** formation was fitted to an exponential rise to the maximum equation,  $y = (y_0 - a) e^{-k_{obs} * t} + b$ , to give  $k_{obs}$ .



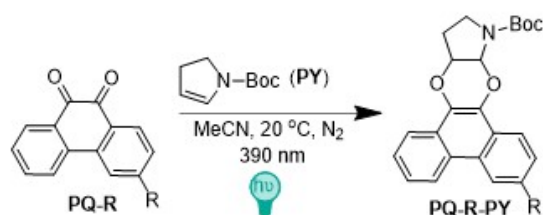
**Figure S3. Kinetic study of photo-induced [4+2] cycloaddition of PQ with PY with the addition of different amounts of DMSO co-solvent. A) Reaction scheme. B) Kinetic traces of the photocycloaddition between PQ (50  $\mu$ M) and PY (500  $\mu$ M) in 2.5 mL MeCN ( $N_2$  atmosphere) including various amounts of DMSO co-solvent. The solution was irradiated with a 390 nm LED at 20  $^{\circ}$ C. The reaction was monitored by UV-Vis absorption spectroscopy (1 cm cuvette, sample interval 1 s). **PQ-PY** formation was fitted to an exponential rise to the maximum equation,  $y = (y_0 - a) e^{-k_{obs} * t} + b$ , to give  $k_{obs}$ .**



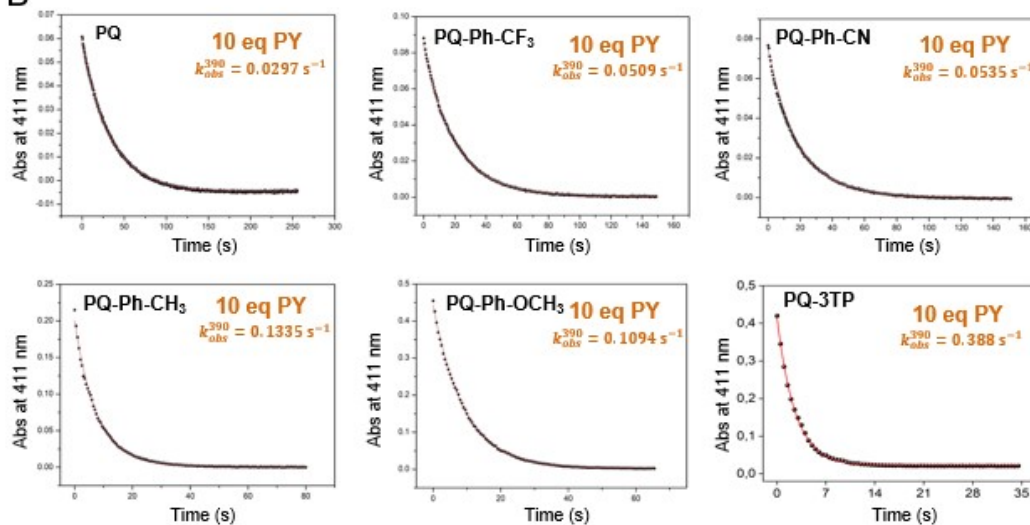


**Figure S4. Kinetic studies of photo-induced [4+2] cycloaddition of PQ with PY with the addition of different amounts of DMS co-solvent. A) Reaction scheme. B) Determination of photoreaction quantum yield for PQ (2 mM) with 10 eq PY (20 mM) in 2.5 mL MeCN (N<sub>2</sub> atmosphere). The measurement was performed in a 1 cm quartz cuvette with 390 nm LED irradiation at 20 °C, followed by UV-Vis absorption spectroscopy. C) The  $k_{obs}(390)$  upon addition of various amounts of DMS. D) Kinetic traces of the photocycloaddition between PQ (50  $\mu$ M) and PY (500  $\mu$ M) in 2.5 mL MeCN (N<sub>2</sub> atmosphere). The solution was irradiated with a 390 nm LED at 20 °C. The reaction was monitored by UV-Vis absorption spectroscopy (1 cm cuvette, sample interval 1 s). PQ-PY formation was fitted to an exponential rise to the maximum equation,  $y = (y_0 - a) e^{k_{obs} \cdot t} + a$ , to give  $k_{obs}$ .**

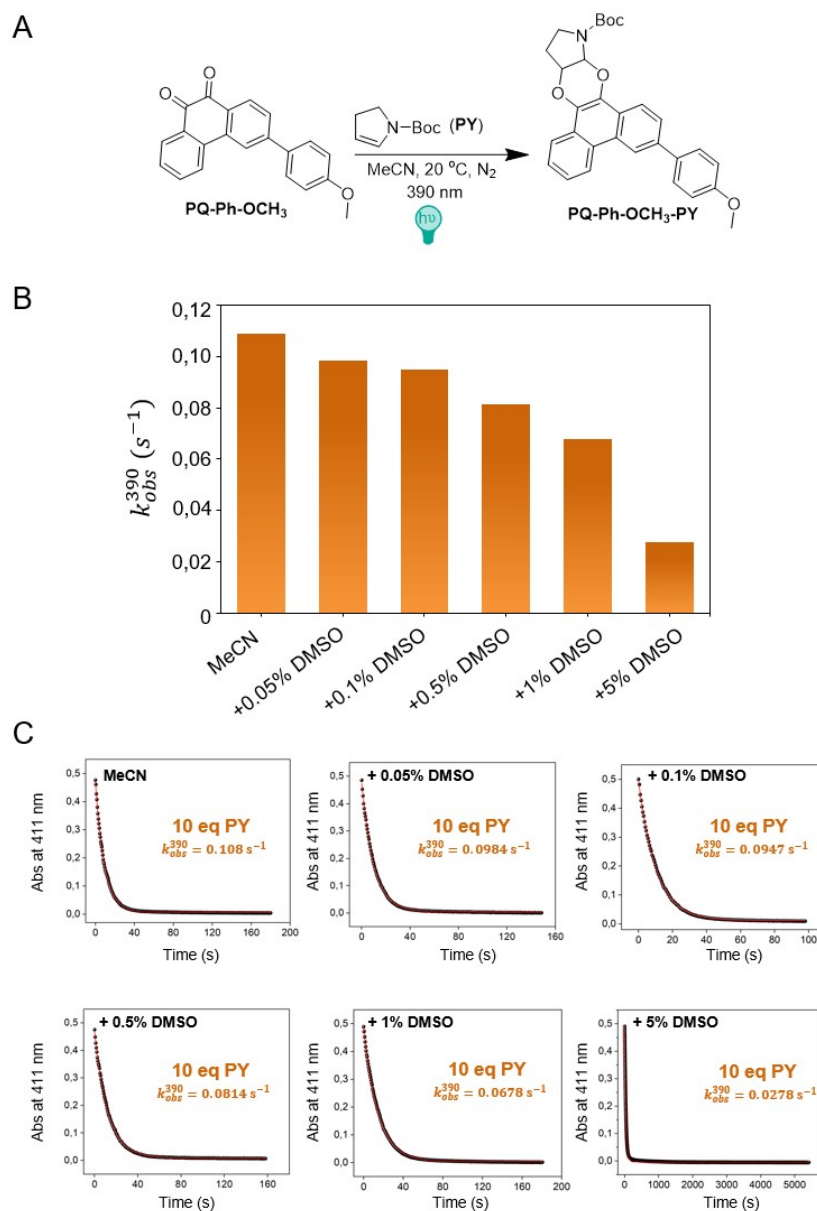
A



B



**Figure S5. Kinetic study of photo-induced [4+2] cycloaddition of various substituted PQs with PY without the addition of DMSO co-solvent. A) Reaction scheme. B) Kinetic traces of the photocycloaddition between PQs (50  $\mu$ M) and PY (500  $\mu$ M) in 2.5 mL MeCN (N<sub>2</sub> atmosphere). The solution was irradiated with a 390 nm LED at 20 °C. The reaction was monitored by UV-Vis absorption spectroscopy (1 cm cuvette, sample interval 1 s). PQ-PY formation was fitted to an exponential rise to the maximum equation,  $y = (y_0 - a) e^{-k_{obs}t} + a$ , to give  $k_{obs}$ .**



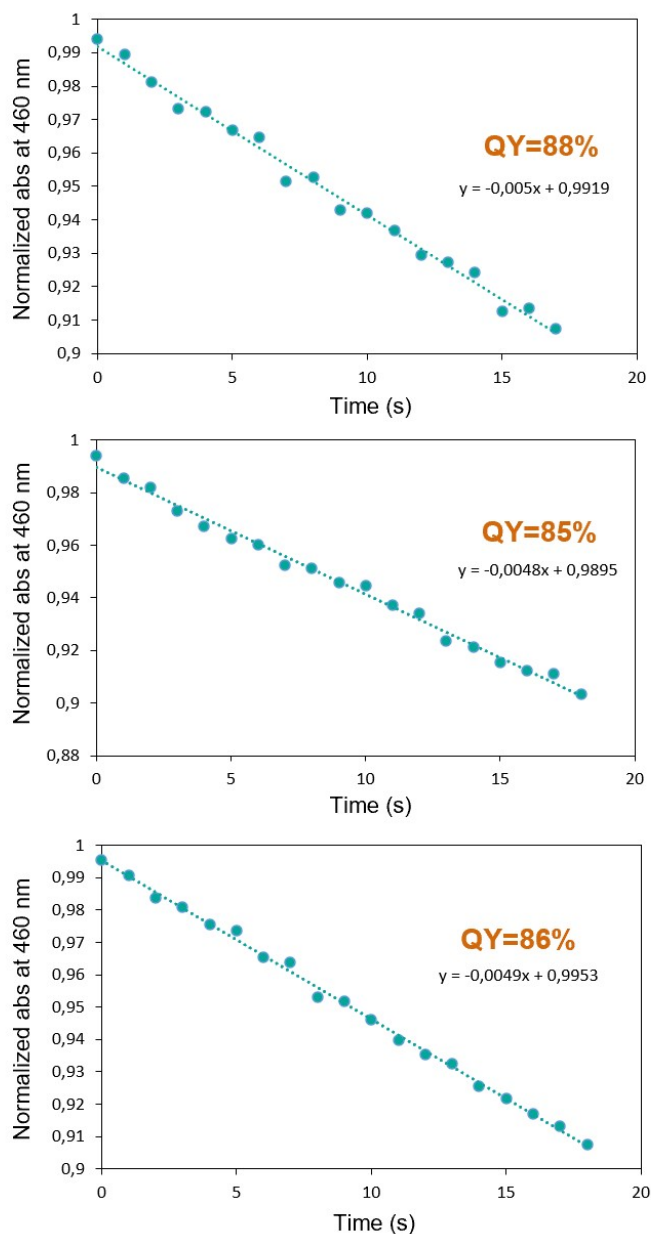
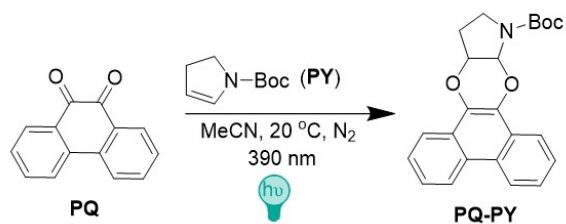
**Figure S6. Kinetic studies of photo-induced [4+2] cycloaddition of PQ-Ph-OCH<sub>3</sub> with PY with the addition of various amounts of DMSO co-solvent. A) Reaction scheme. B) The  $k_{obs}(390)$  upon addition of various amounts of DMSO. D) Kinetic traces of the photocycloaddition between PQ-Ph-OCH<sub>3</sub> (50  $\mu$ M) and PY (500  $\mu$ M) in 2.5 mL MeCN (N<sub>2</sub> atmosphere). The solution was irradiated with a 390 nm LED at 20 °C. The reaction was monitored by UV-Vis absorption spectroscopy (1 cm cuvette, sample interval 1 s). PQ-Ph-OCH<sub>3</sub>-PY formation was fitted to an exponential rise to the maximum equation,  $y = (y_0 - a) e^{-k_{obs} \cdot t} + a$ , to give  $k_{obs}$ .**

## 2.2. Photoclick reaction quantum yields

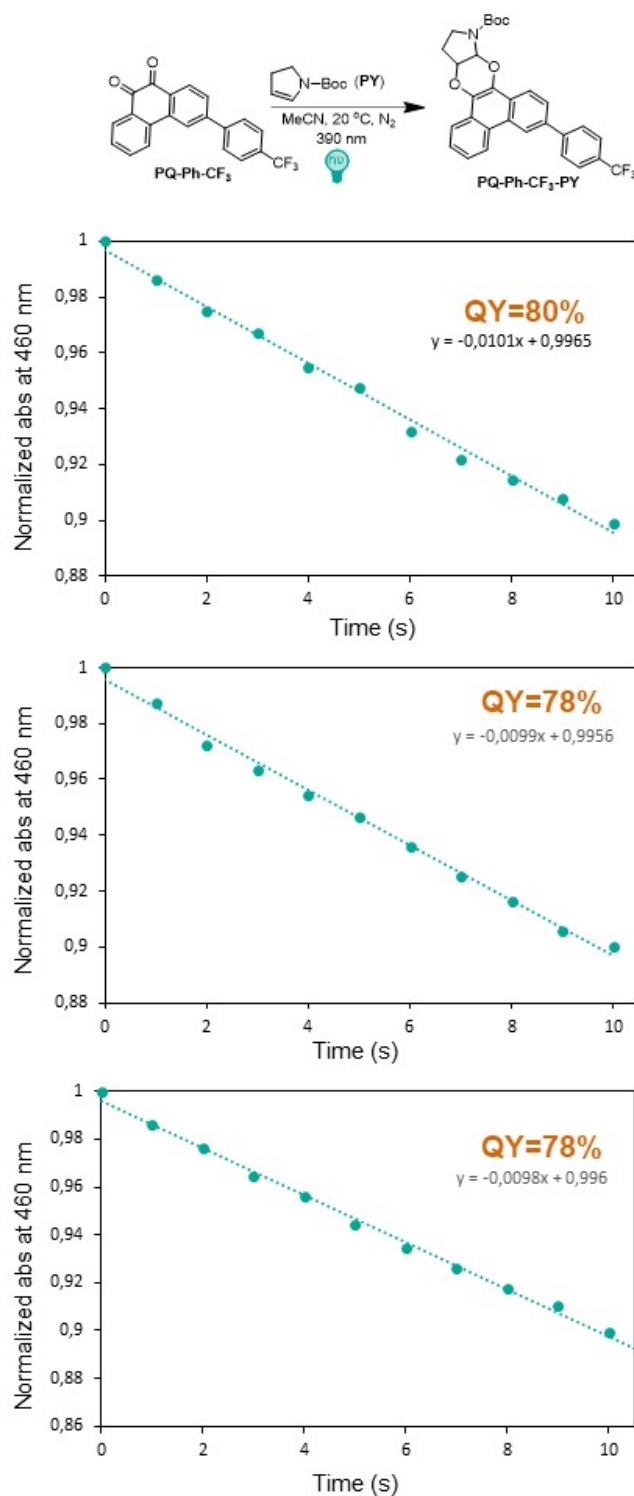
UV-Vis evolution spectra were recorded using the setup described above with the 390 nm LED. The photon flux was determined using standard ferrioxalate actinometry, which provided a value of  $3.1594 \times 10^{-5}$  mol photons  $s^{-1}$  for the 390B LED.<sup>[7]</sup> Spectra were collected over 10000 seconds, exported, and processed in SpectraGryph and OriginPro. Baseline corrections were carried out to correct for baseline drifting, after which the data was processed in QYMain (<https://www.nature.com/articles/srep41145#Sec14>) developed by Stranius & Börjesson.<sup>[8]</sup>

$$\frac{d[A]}{dt} = \frac{I * QY_{(A \rightarrow B)} * \beta_A}{N_a * V} + \frac{I * QY_{(B \rightarrow A)} * \beta_B}{N_a * V} + [A] * k_{(B \rightarrow A)}$$

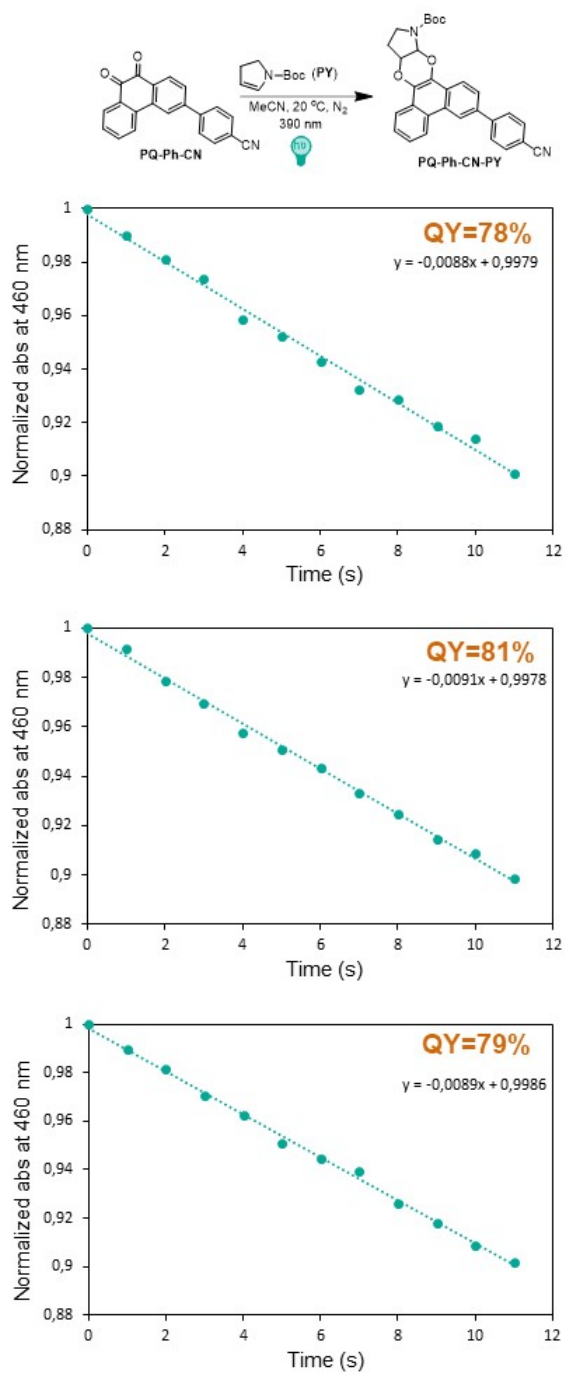
was used to fit the data collected in the first 10% reaction process using the following molar extinction coefficients and absorbance data at the irradiation wavelength (390 nm). Normalized absorbance ( $\lambda=460$  nm) fitting plot and  $\Phi_P$  are shown below:



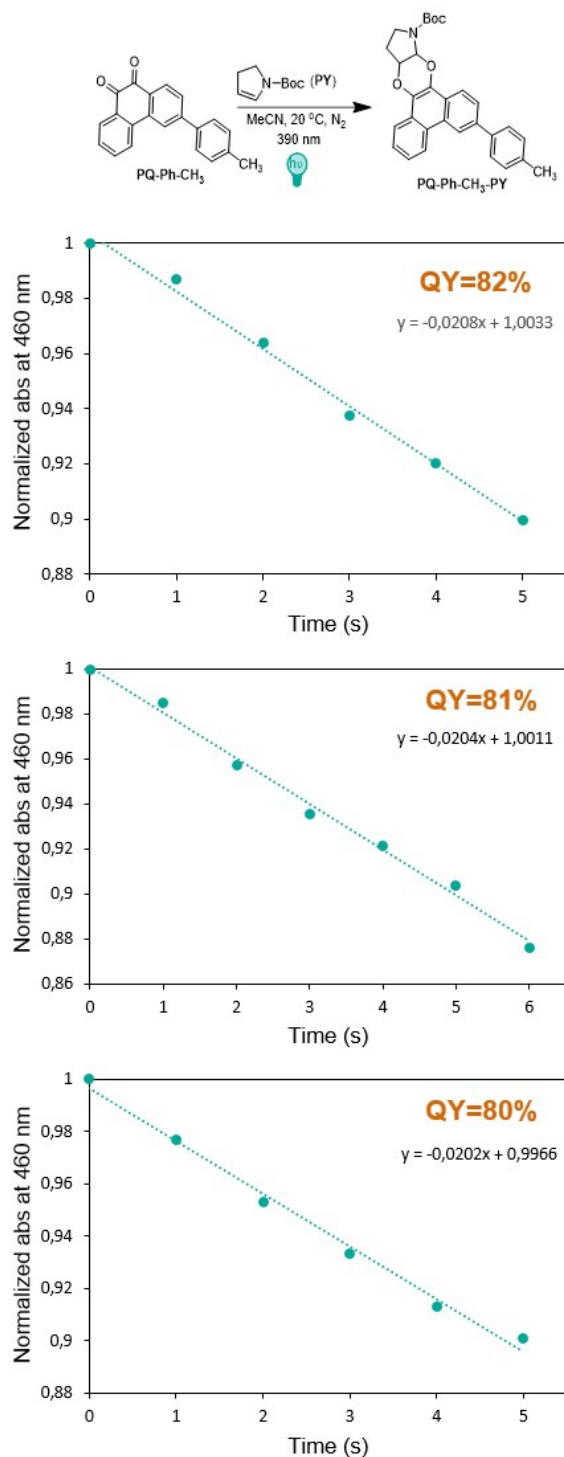
**Figure S7. Determination of photoreaction quantum yield for photo-induced [4+2] cycloaddition of PQ with PY without DMSO co-solvent.** Photoclick reaction of PQ (2 mM) with 10 eq PY (20 mM) in 2.5 mL MeCN (N<sub>2</sub> atmosphere). The measurement was performed in a 1 cm quartz cuvette with 390 nm LED irradiation at 20 °C, followed by UV-Vis absorption spectroscopy.



**Figure S8. Determination of photoreaction quantum yield for photo-induced [4+2] cycloaddition of PQ-Ph-CF<sub>3</sub> with PY without DMSO co-solvent.** Photoclick reaction of PQ-Ph-CF<sub>3</sub> (1 mM) with 10 eq PY (10 mM) in 2.5 mL MeCN (N<sub>2</sub> atmosphere). The measurement was performed in a 1 cm quartz cuvette with 390 nm LED irradiation at 20 °C, followed by UV-Vis absorption spectroscopy.

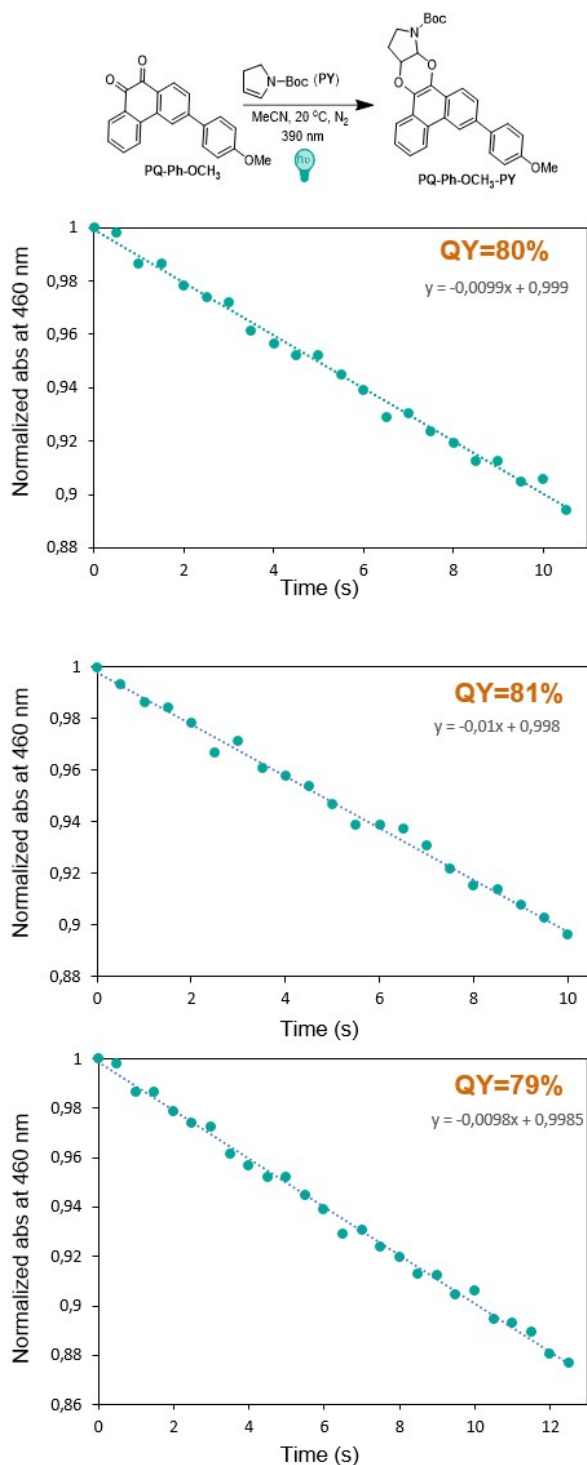


**Figure S9. Determination of photoreaction quantum yield for photo-induced [4+2] cycloaddition of PQ-Ph-CN with PY without DMSO co-solvent.** Photoclick reaction of PQ-Ph-CN (1.125 mM) with 10 eq PY (11.25 mM) in 2.5 mL MeCN (N<sub>2</sub> atmosphere). The measurement was performed in a 1 cm quartz cuvette with 390 nm LED irradiation at 20 °C, followed by UV-Vis absorption spectroscopy.

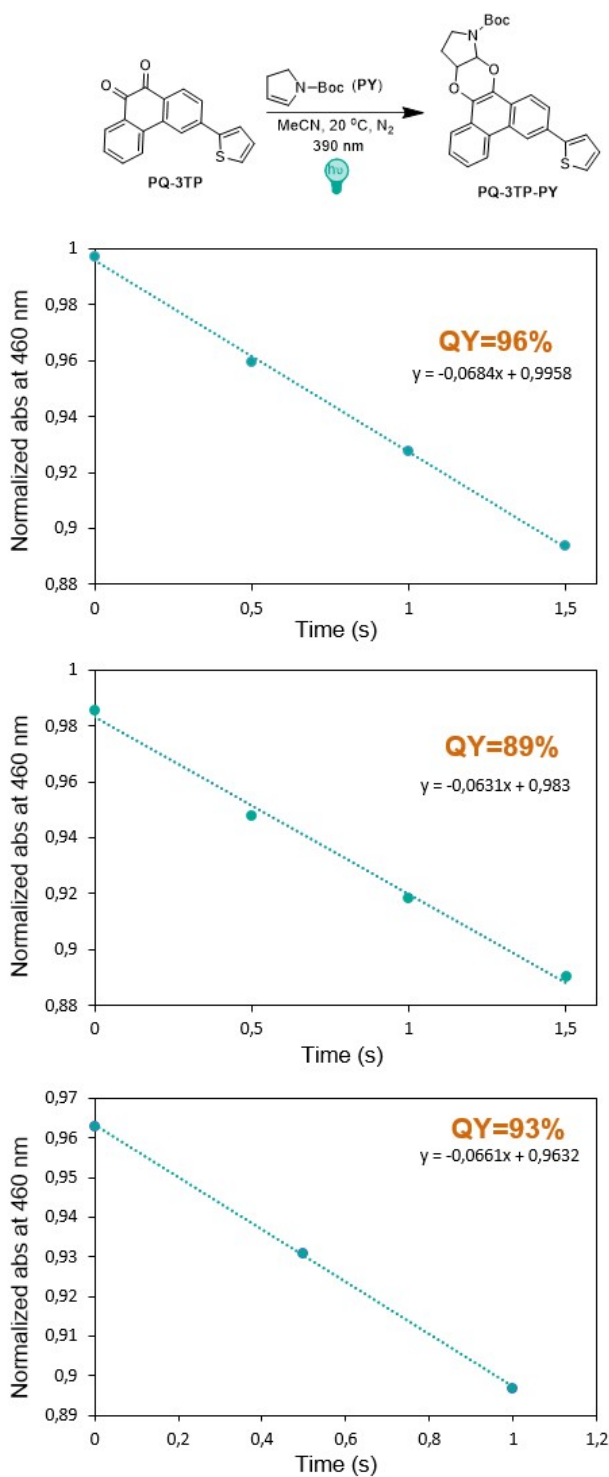


**Figure S10. Determination of photoreaction quantum yield for photo-induced [4+2] cycloaddition of PQ-Ph-CH<sub>3</sub> with PY without DMSO co-solvent.** Photoclick reaction of PQ-Ph-CH<sub>3</sub> (0.5 mM) with 10 eq PY (5 mM) in 2.5 mL MeCN (N<sub>2</sub> atmosphere). The measurement was performed in a 1 cm quartz cuvette with 390 nm LED irradiation at 20 °C, followed by UV-Vis absorption spectroscopy.





**Figure S11. Determination of photoreaction quantum yield for photo-induced [4+2] cycloaddition of PQ-Ph-OCH<sub>3</sub> with PY without DMSO co-solvent.** Photoclick reaction of PQ-Ph-OCH<sub>3</sub> (1 mM) with 10 eq PY (10 mM) in 2.5 mL MeCN (N<sub>2</sub> atmosphere). The measurement was performed in a 1 cm quartz cuvette with 390 nm LED irradiation at 20 °C, followed by UV-Vis absorption spectroscopy.



**Figure S12. Determination of photoreaction quantum yield for photo-induced [4+2] cycloaddition of PQ-Ph-3TP with PY without DMSO co-solvent.** Photoclick reaction of PQ-3TP (2 mM) with 1 eq PY (2 mM) in 2.5 mL MeCN (N<sub>2</sub> atmosphere). The measurement was performed in a 1 cm quartz cuvette with 390 nm LED irradiation at 20 °C, followed by UV-Vis absorption spectroscopy.

### 3. High performance liquid chromatography (HPLC) analysis

HPLC analysis of the photoclick reaction system with various co-solvents. **PQ** (50 $\mu$ M, 1 eq) and **PY** (500  $\mu$ M, 10 eq) were deoxygenated with N<sub>2</sub> and irradiated with the UV-Vis set up as described above. The samples were analyzed by HPLC. The corresponding HPLC traces are shown below:

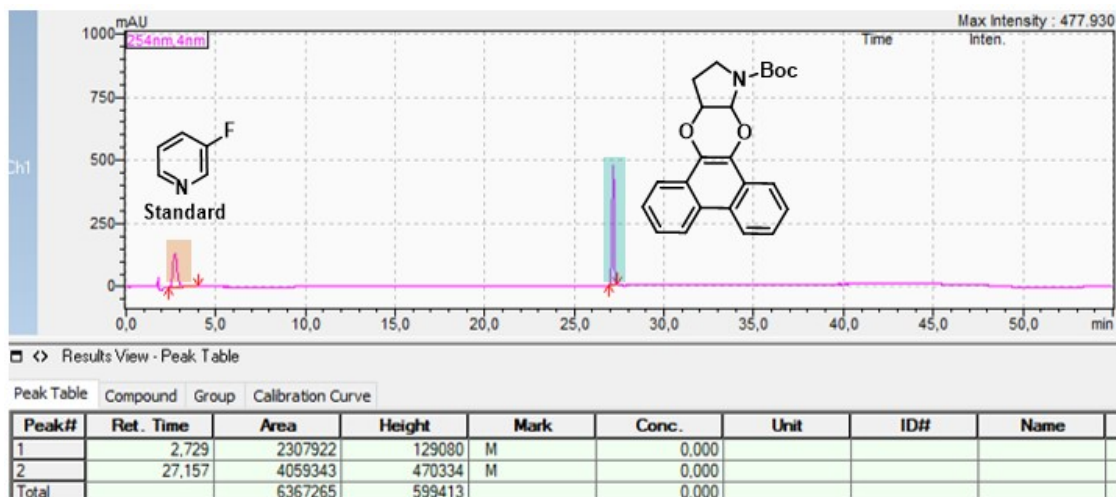


Figure S13. HPLC trace of **PQ-PY** photoclick product.

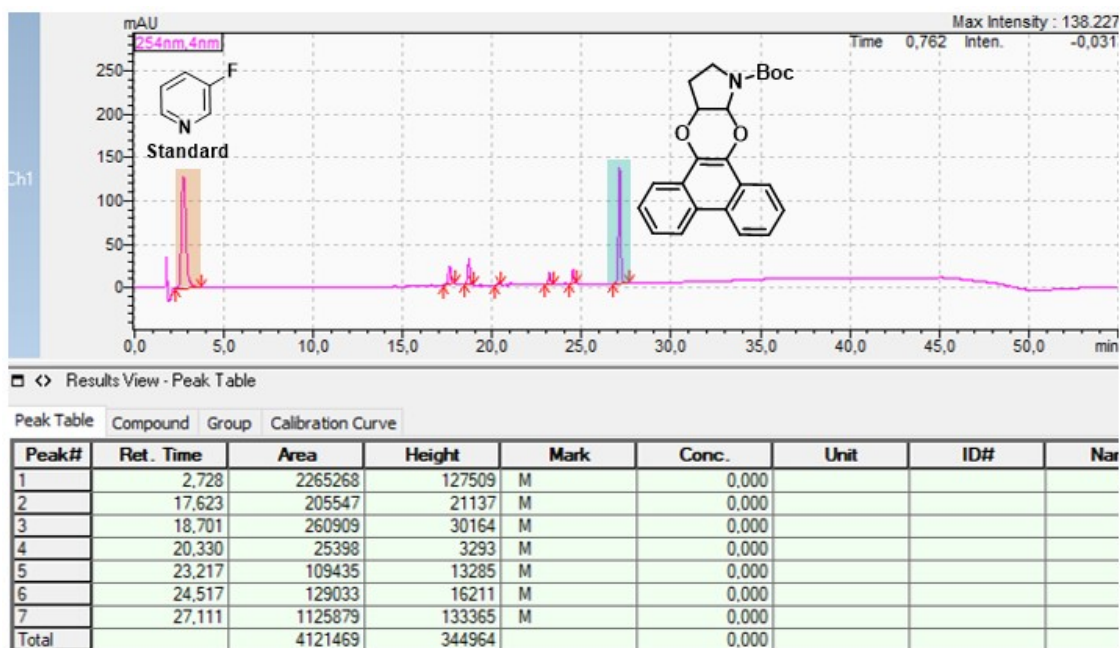
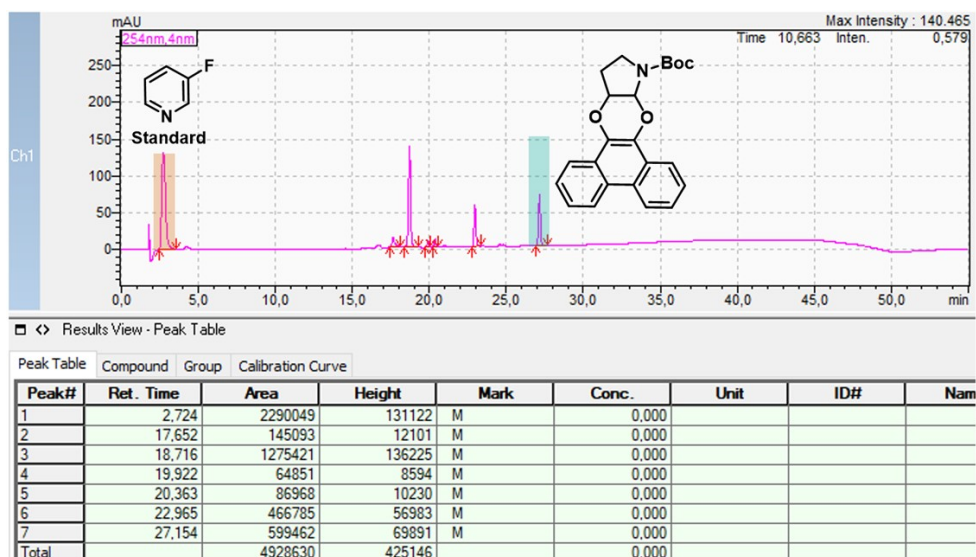
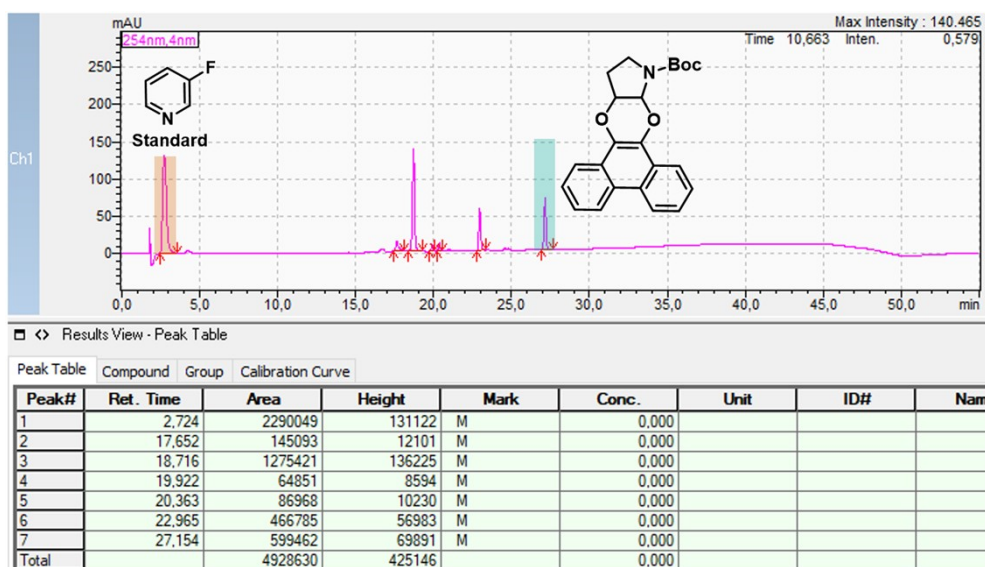


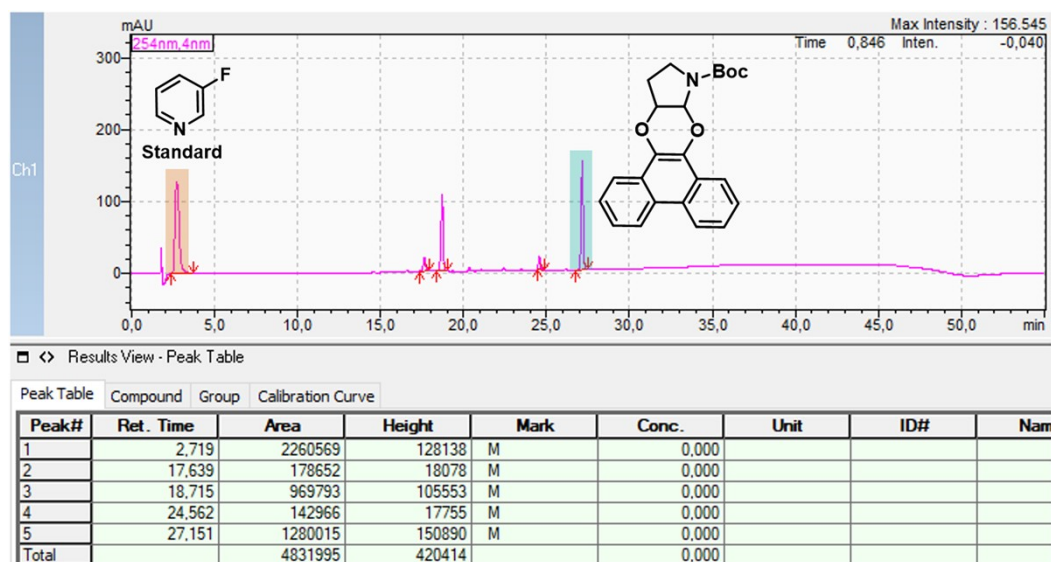
Figure S14. HPLC trace of the reaction mixture of **PQ-PY** photoclick reaction in MeCN.



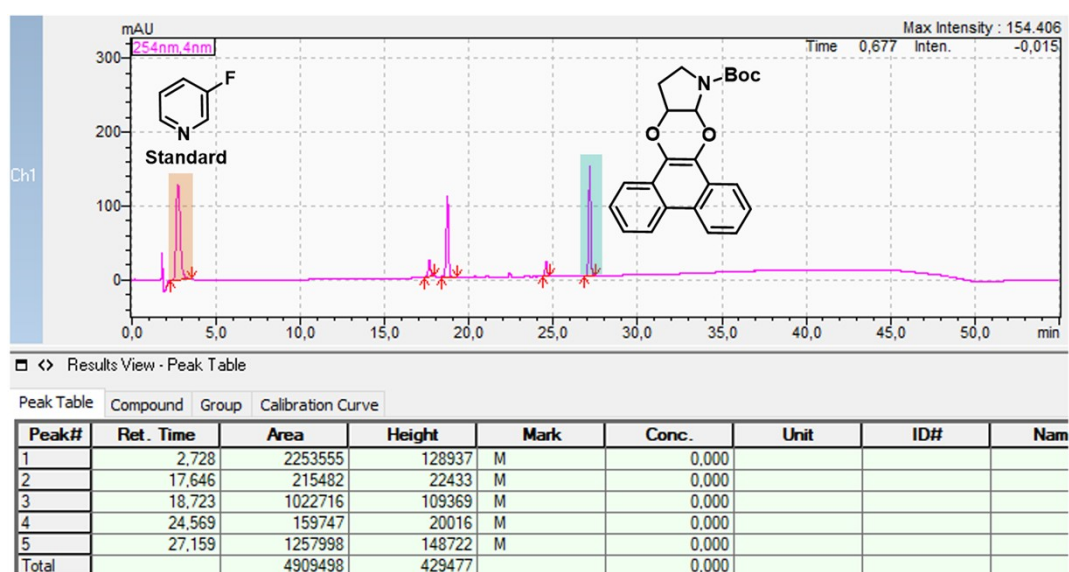
**Figure S15.** HPLC trace of the reaction mixture of **PQ-PY** photoclick reaction in MeCN with 0.5% (v/v) DMSO co-solvent.



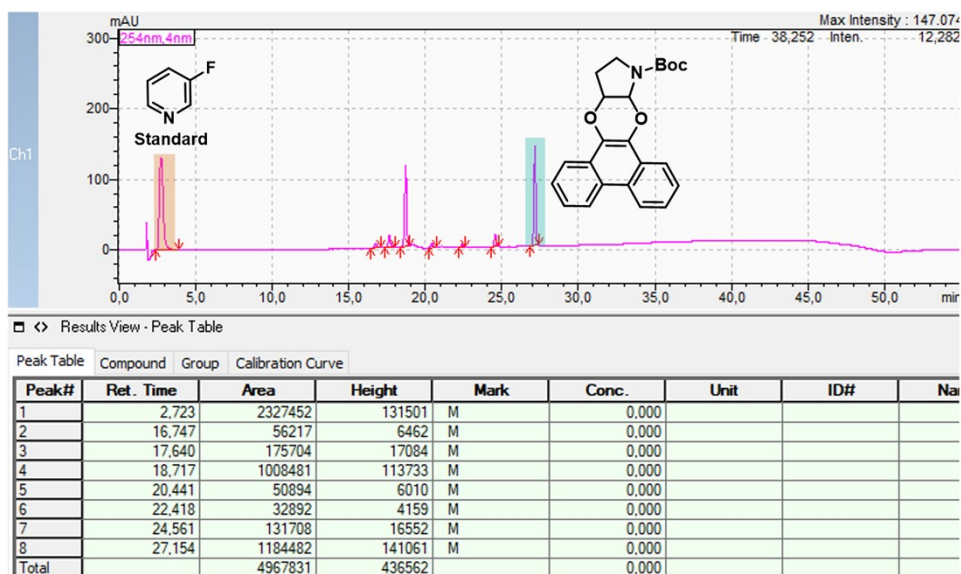
**Figure S16.** HPLC trace of the reaction mixture of **PQ-PY** photoclick reaction in MeCN with 0.5% (v/v) DMS co-solvent.



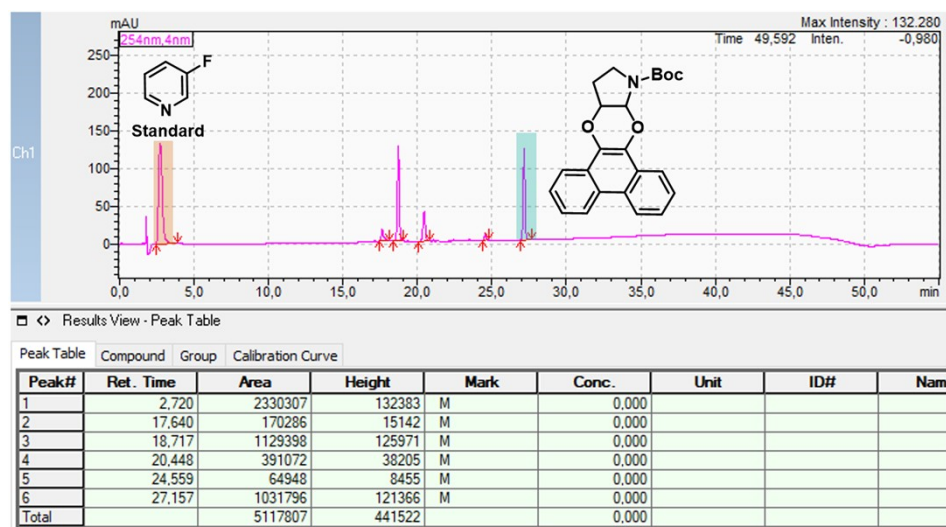
**Figure S17.** HPLC trace of the reaction mixture of PQ-PY photoclick reaction in MeCN with 0.5% (v/v) MeOH co-solvent.



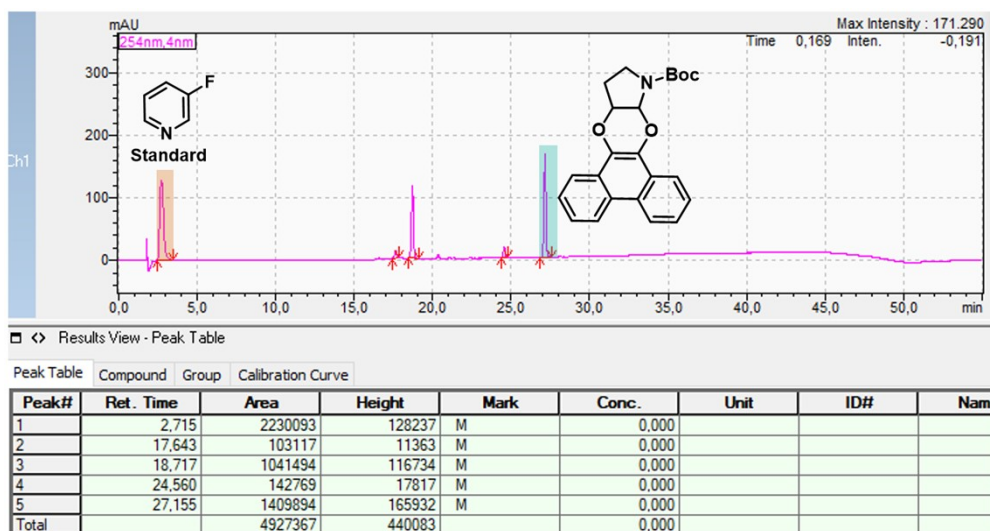
**Figure S18.** HPLC trace of the reaction mixture of PQ-PY photoclick reaction in MeCN with 0.5% (v/v) EtOH co-solvent.



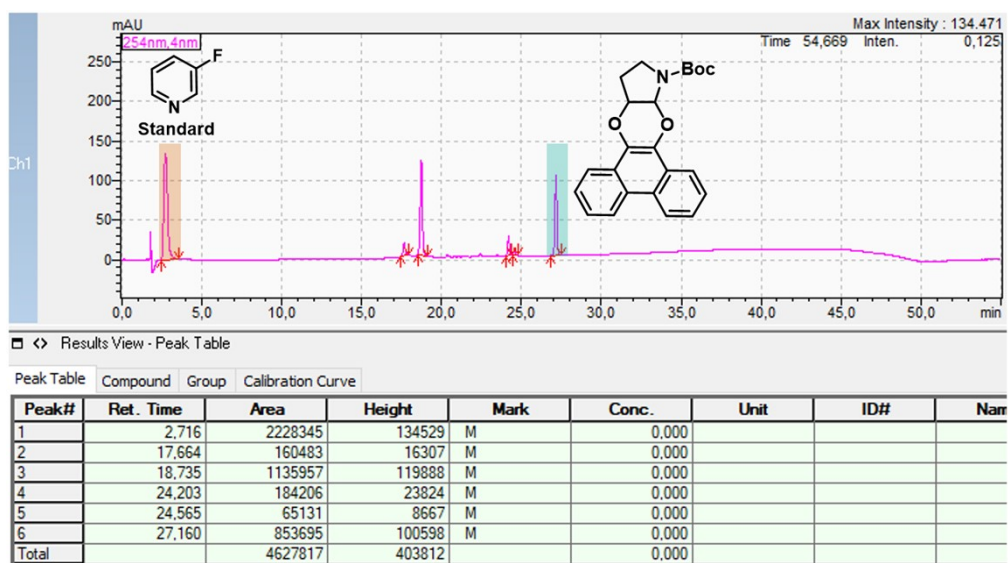
**Figure S19.** HPLC trace of the reaction mixture of PQ-PY photoclick reaction in MeCN with 0.5% (v/v) DMF co-solvent.



**Figure S20.** HPLC trace of the reaction mixture of PQ-PY photoclick reaction in MeCN with 0.5% (v/v) DMA co-solvent.



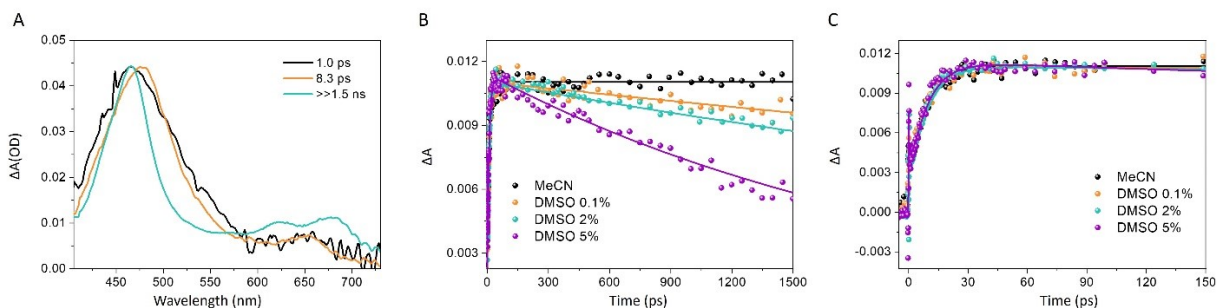
**Figure S21.** HPLC trace of the reaction mixture of PQ-PY photoclick reaction in MeCN with 0.5% (v/v) H<sub>2</sub>O co-solvent.



**Figure S22.** HPLC trace of the reaction mixture of PQ-PY photoclick reaction in MeCN with 0.5% (v/v) THF co-solvent.

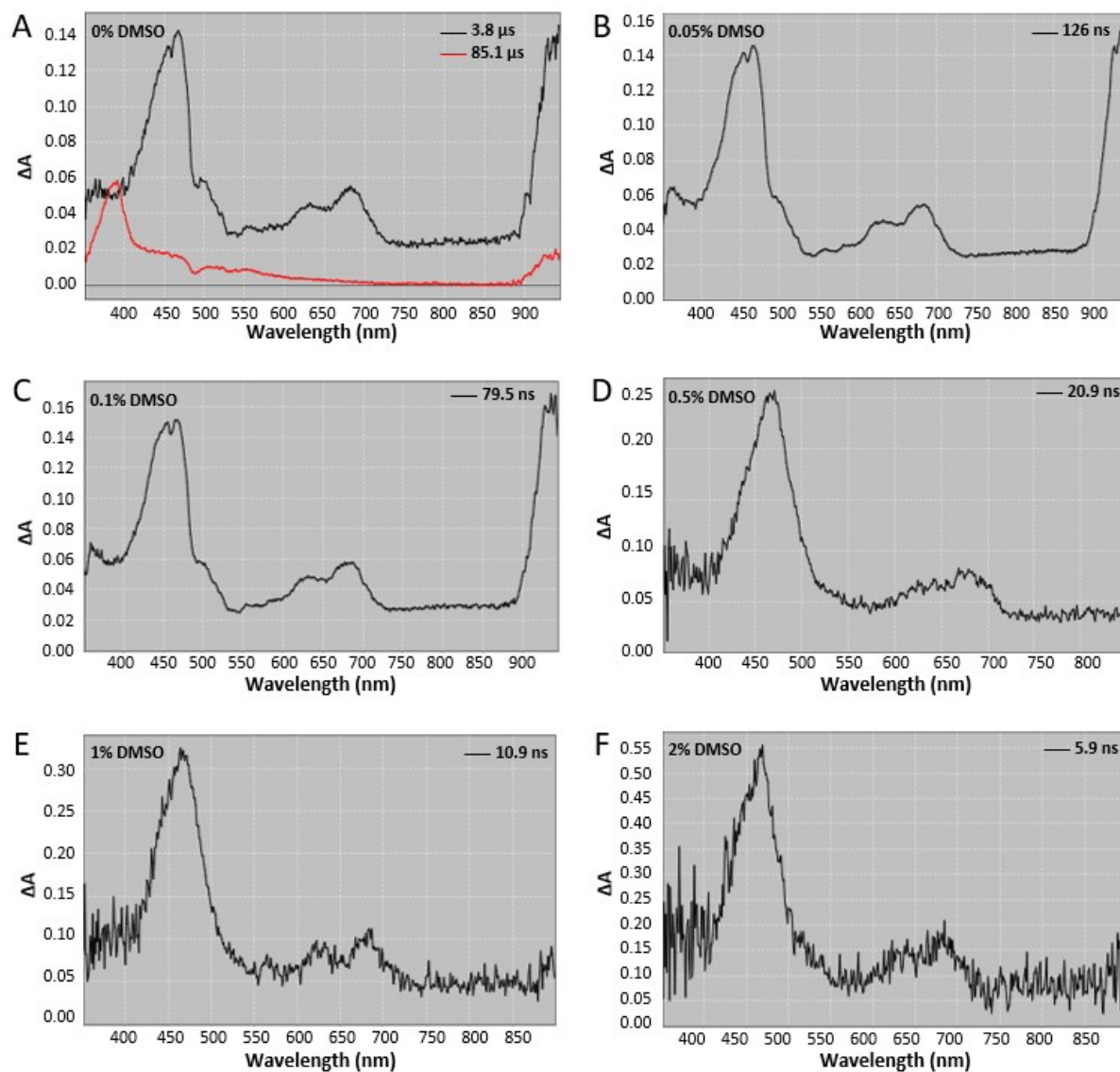
## 4. Photophysical and photochemical studies by transient absorption spectroscopy

### 4.1. Transient UV-Vis spectra

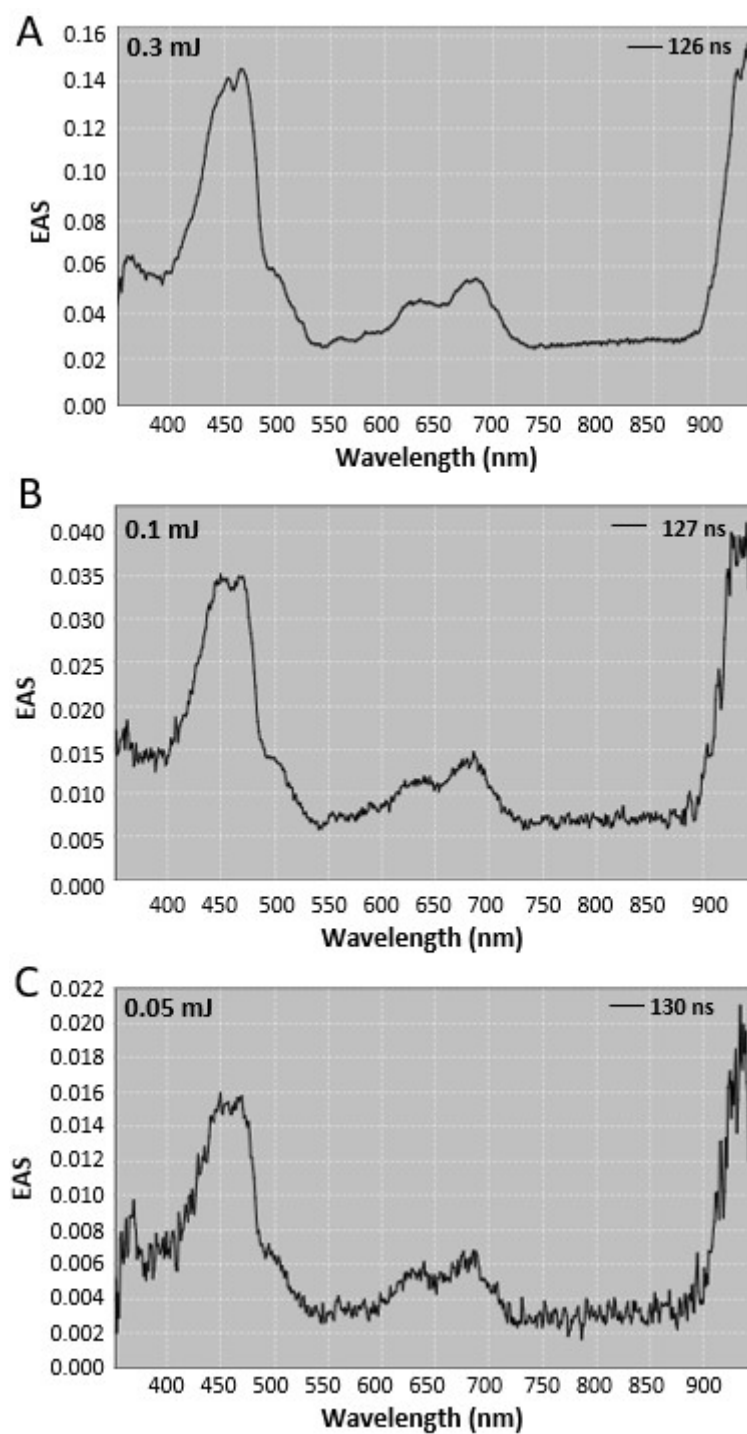


**Figure S23.** A) EADS obtained from global analysis of transient absorption data recorded in the time interval -5 to 1500 ps (ultrafast data) of **PQ** dissolved in MeCN. The spectral shape of the signal remains the same upon addition of DMSO, while the kinetic constant changes accordingly to the data in Table 1, main text. B) Effect of DMSO on the kinetic traces recorded at 680 nm with the ultrafast setup. C) Effect of DMSO on the short timescale (up to 150 ps), evidencing that rise time of the triplet state is not influenced by the addition of DMSO.

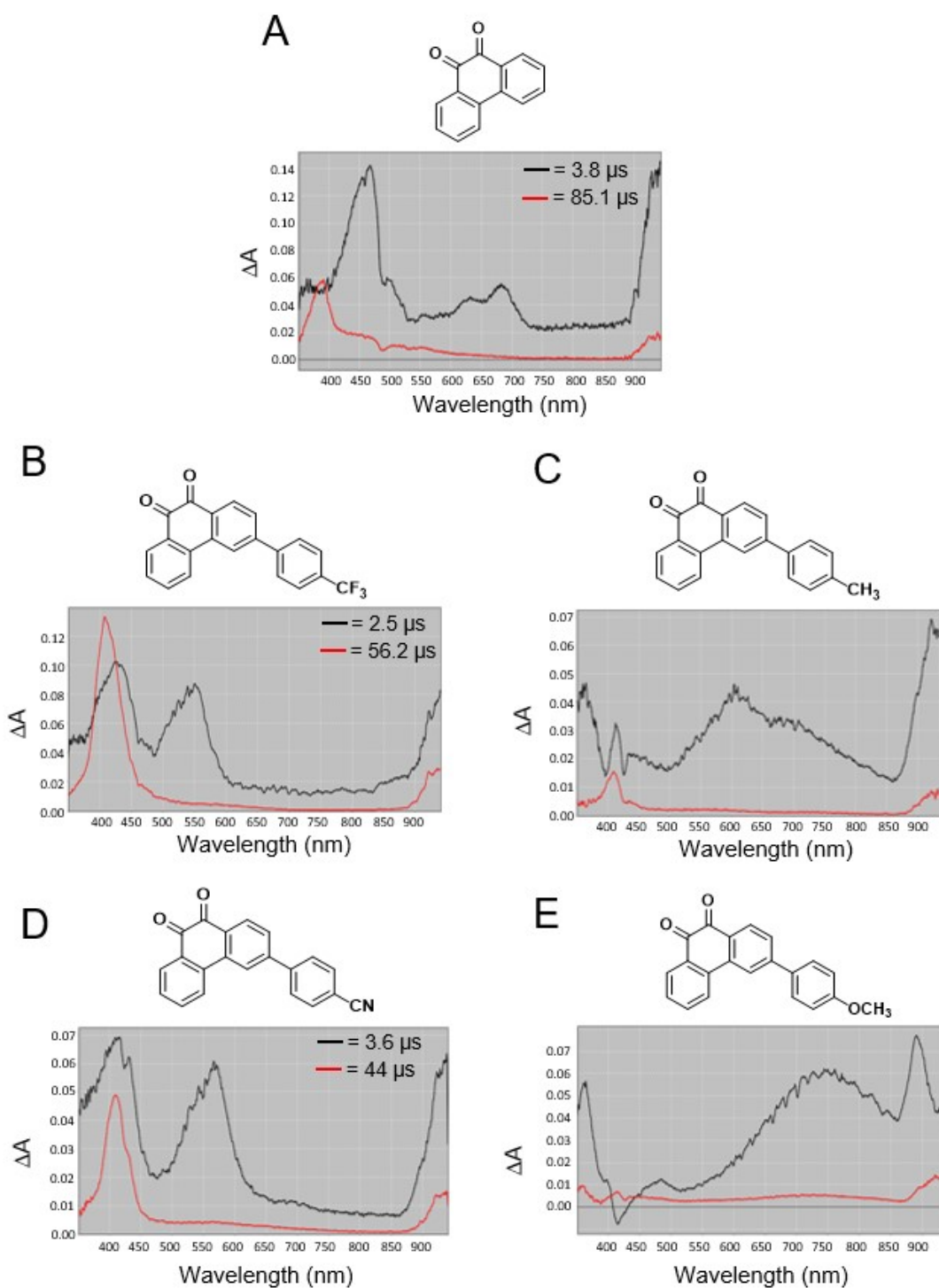




**Figure S24.** EADS obtained from global analysis of the nanosecond transient absorption spectra of PQ in MeCN with different amounts (v/v) of DMSO (0%, 0.05%, 0.1%, 0.5%, 1.0% and 2.0%, for **A**, **B**, **C**, **D**, **E** and **F**, respectively) at room temperature under a N<sub>2</sub> atmosphere, excited at 400 nm at 0.3 mJ excitation power.

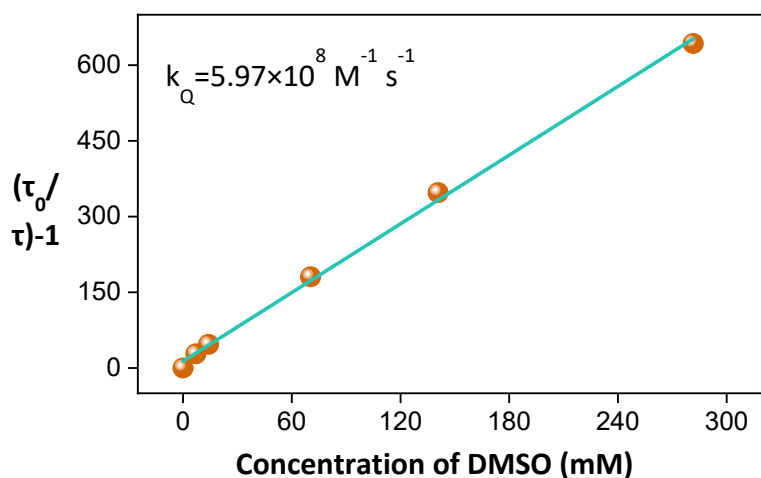


**Figure S25.** EADS obtained from global analysis of the nanosecond transient absorption spectra of PQ in MeCN with 0.05% (v/v) DMSO at room temperature under N<sub>2</sub> atmosphere, excited at 400 nm with different excitation powers (0.3 mJ, 0.1 mJ and 0.05 mJ, for A, B, and C, respectively).



**Figure S26.** EADS obtained from global analysis of the nanosecond transient absorption spectra of various PQs in MeCN at room temperature under  $N_2$  atmosphere, excited at 400 nm with 0.3 mJ excitation power. PQs measured are PQ, PQ-Ph- $CF_3$ , PQ-Ph- $CH_3$ , PQ-Ph-CN and PQ-Ph- $OCH_3$  (A, B, C, D and E, respectively).

## 4.2. Determination of quenching rate constant



**Figure S27.** Stern-Volmer plot of quenching kinetics of PQ with varying amounts of DMSO.

## 5. References

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