

Supporting Information for

## A Library of Cationic Organic Dyes for Visible-Light Driven Photoredox Transformations

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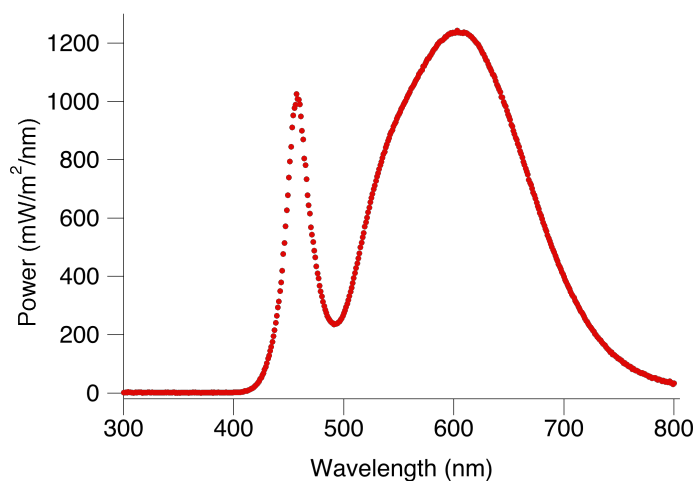
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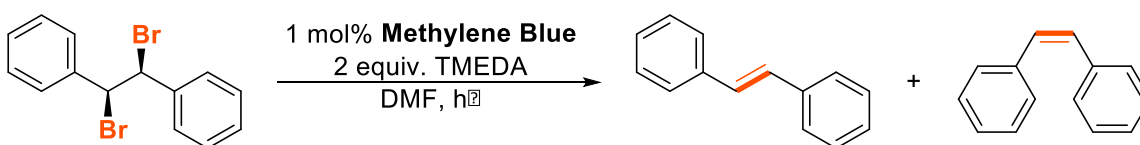
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### A. Power spectrum for LedEngin 90 W warm-white LEDs



**Figure S1.** Power spectrum for one LedEngin 90 W warm-white LED used in a typical photochemical reaction recorded with a Luzchem SPR-4001 spectroradiometer.

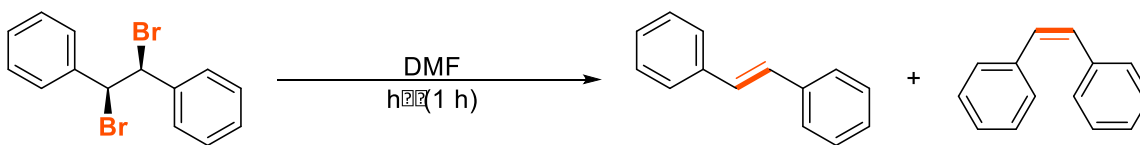
### B. Dehalogenation of *meso*-1,2-dibromo-1,2-diphenylethane using Methylene Blue



Irradiation Time	Percent Conversion	<i>E:Z</i> Ratios
18 h	Quantitative	13:1
1 h	96%	99:1
30 min.	92%	99:1
10 min.	83%	99:1
5 min.	66%	99:1

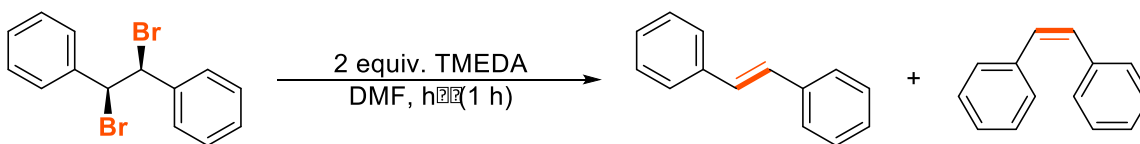
**Reaction Conditions:** An oven dried 10 mL schlenk tube was charged with *meso*-1,2-dibromo-1,2-diphenylethane (0.3 mmol, 102 mg) and Methylene Blue (0.003 mmol, 1.1 mg). The contents were dissolved in 5 mL of dry DMF, followed by the addition of TMEDA (0.6 mmol, 90  $\mu$ L). The reaction was purged with argon for 15 minutes, followed by irradiation with 2 warm white LEDs. The reaction mixture was extracted with ether (x3) and washed with brine (x5). The organic phase was dried with  $\text{MgSO}_4$ , and concentrated via rotary evaporation. Percent conversion and selectivity were determined by  $^1\text{H}$  NMR analysis.

### C. Dehalogenation of *meso*-1,2-dibromo-1,2-diphenylethane control reactions



Irradiation Source	Percent Conversion	<i>E</i> : <i>Z</i> Ratios
Warm-White LEDs	No Reaction	N. A.
UVA	No Reaction	N. A.
UVB	No Reaction	N. A.
UVC	No Reaction	N. A.

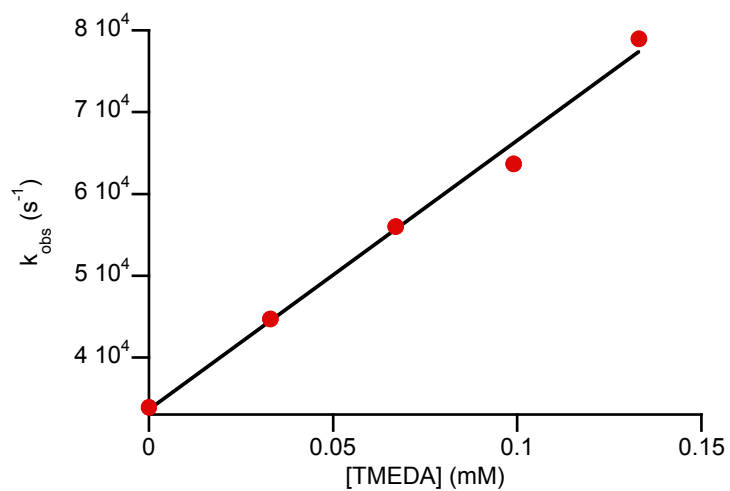
**Reaction Conditions:** An oven dried 10 mL schlenk tube was charged with *meso*-1,2-dibromo-1,2-diphenylethane, which was dissolved in 5 mL of dry DMF. The reaction was purged with argon for 15 minutes, followed by irradiation with 2 warm white LEDs or a Luzchem photoreactor with the corresponding UV-bulbs. The reaction mixture was extracted with ether (x3) and washed with brine (x5). The organic phase was dried with  $MgSO_4$ , and concentrated via rotary evaporation. Percent conversion and *E*:*Z* ratios were determined by  $^1H$  NMR analysis.



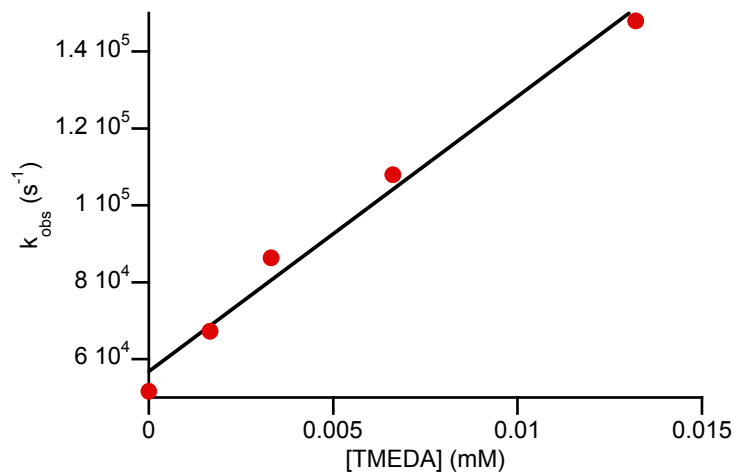
Irradiation Source	Percent Conversion	<i>E</i> : <i>Z</i> Ratio
Warm-White LEDs (5 min.)	No Reaction	N. A.
Warm-White LEDs	Trace	N. A.
UVA	96%	5.4:1
UVB	91%	1.5:1

**Reaction Conditions:** An oven dried 10 mL schlenk tube was charged with *meso*-1,2-dibromo-1,2-diphenylethane (0.3 mmol, 102 mg), which was dissolved in 5 mL of dry DMF, followed by the addition of TMEDA (0.6 mmol, 90  $\mu$ L). The reaction was purged with argon for 15 minutes, followed by irradiation with 2 warm white LEDs. The reaction mixture was extracted with ether (x3) and washed with brine (x5). The organic phase was dried with  $MgSO_4$ , and concentrated via rotary evaporation. Percent conversion and *E*:*Z* ratios were determined by  $^1H$  NMR analysis.

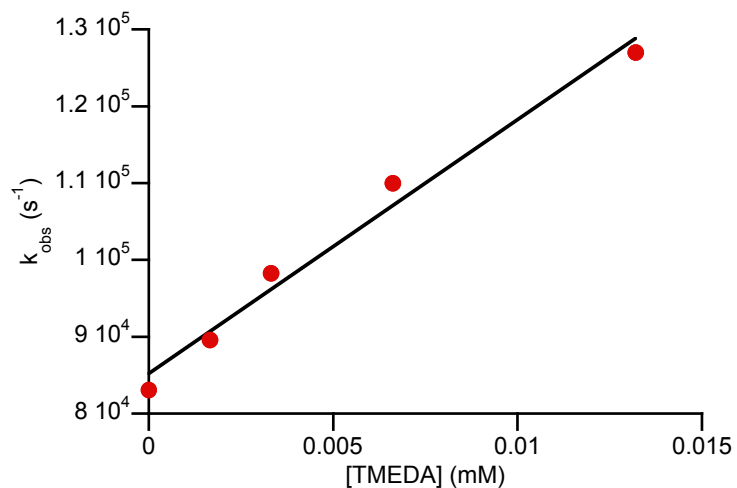
#### D. Excited Dye quenching by *N,N,N',N'*-tetramethylethylenediamine (TMEDA)



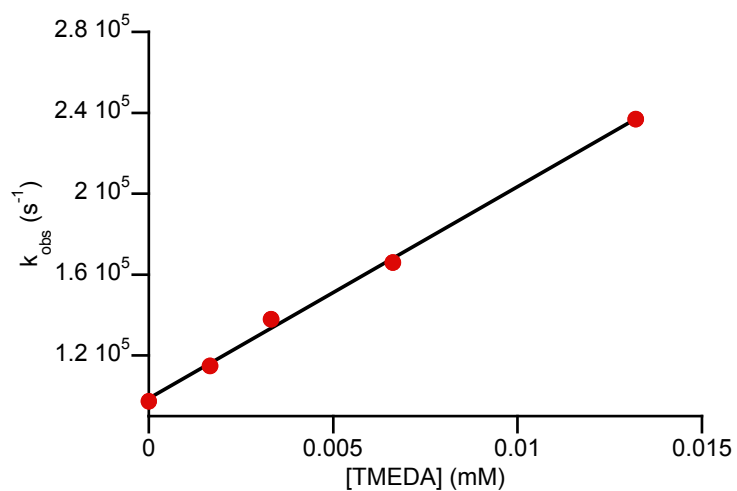
**Figure S2.** Representative kinetic bimolecular quenching plot for  $^3$ Methylene Blue and TMEDA.



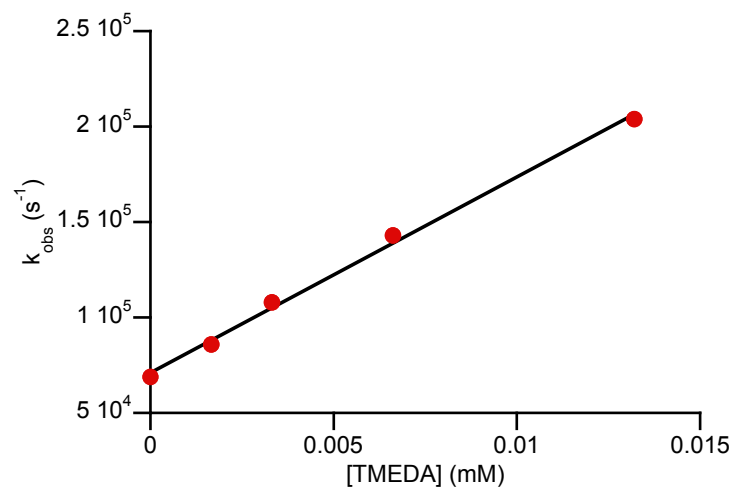
**Figure S3.** Representative kinetic bimolecular quenching plot for  $^3$ Thionin and TMEDA.



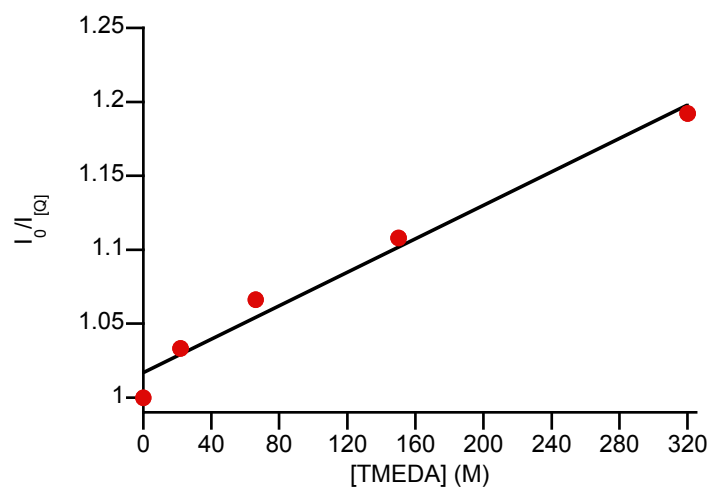
**Figure S4.** Representative kinetic bimolecular quenching plot for <sup>3</sup>New Methylene Blue N and TMEDA.



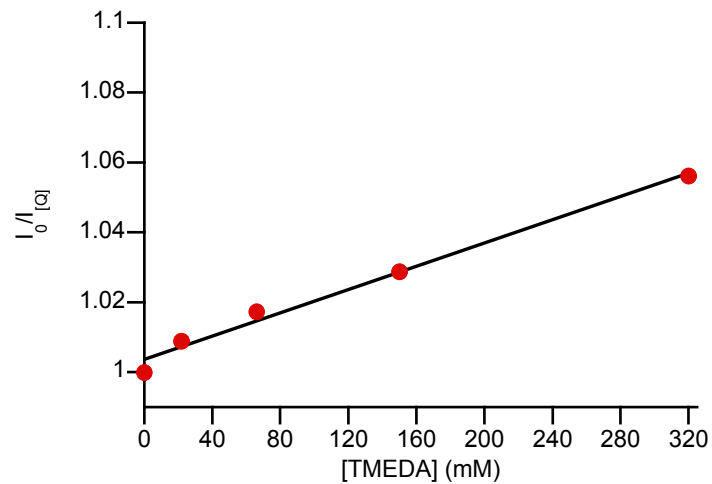
**Figure S5.** Representative kinetic bimolecular quenching plot for <sup>3</sup>1,9-dimethyl Methylene Blue and TMEDA.



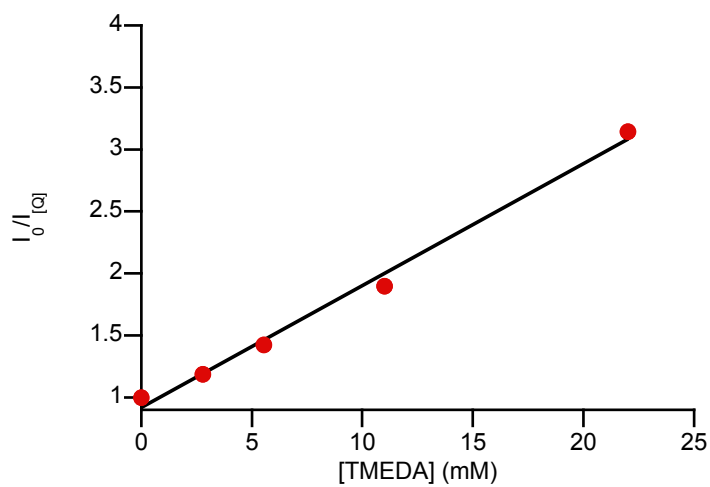
**Figure S6.** Representative kinetic bimolecular quenching plot for <sup>3</sup>Methylene Green and TMEDA.



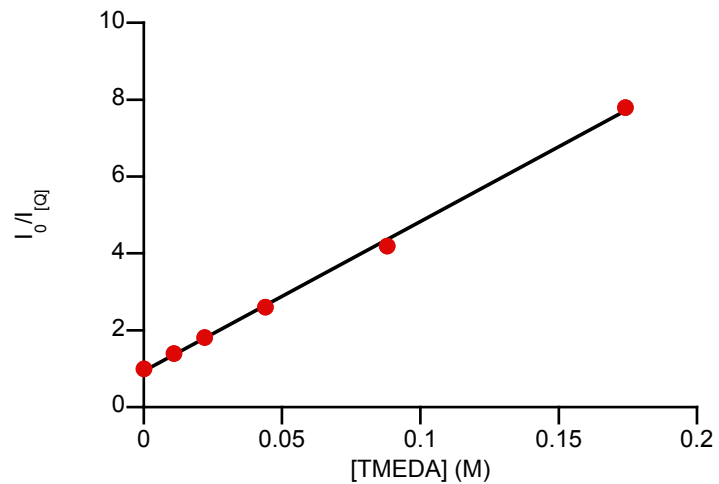
**Figure S7.** Representative Stern-Volmer quenching plot for <sup>1</sup>Brilliant Cresyl Blue and TMEDA.



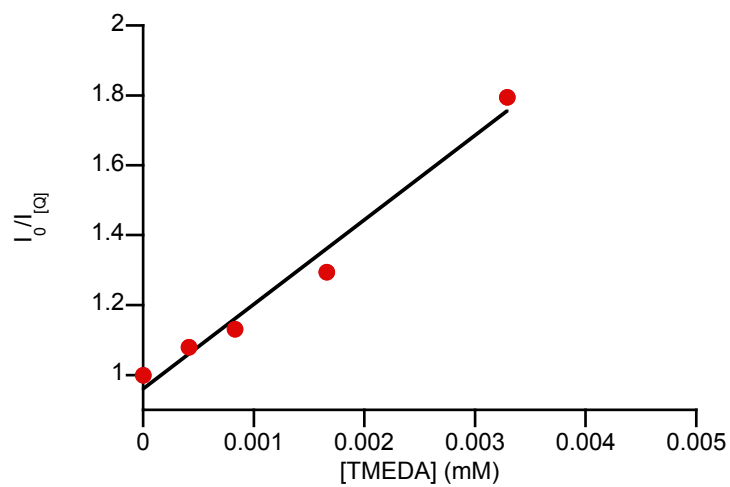
**Figure S8.** Representative Stern-Volmer quenching plot for <sup>1</sup>Nile Blue and TMEDA.



**Figure S9.** Representative Stern-Volmer quenching plot for <sup>1</sup>Pyronin Y and TMEDA.

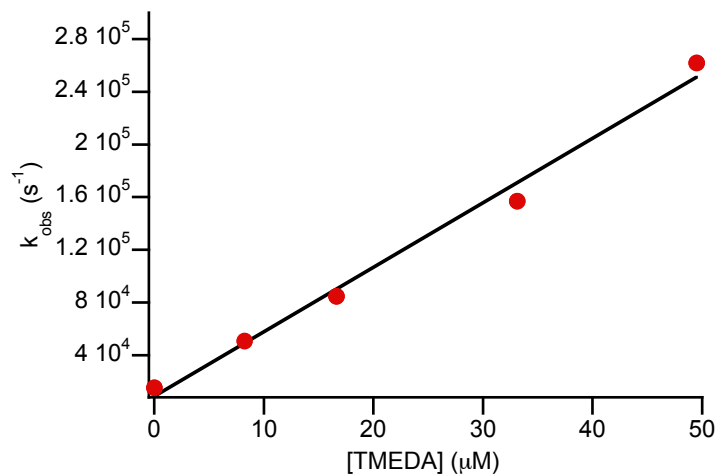


**Figure S10.** Representative Stern-Volmer quenching plot for <sup>1</sup>Rhodamine 6G and TMEDA.

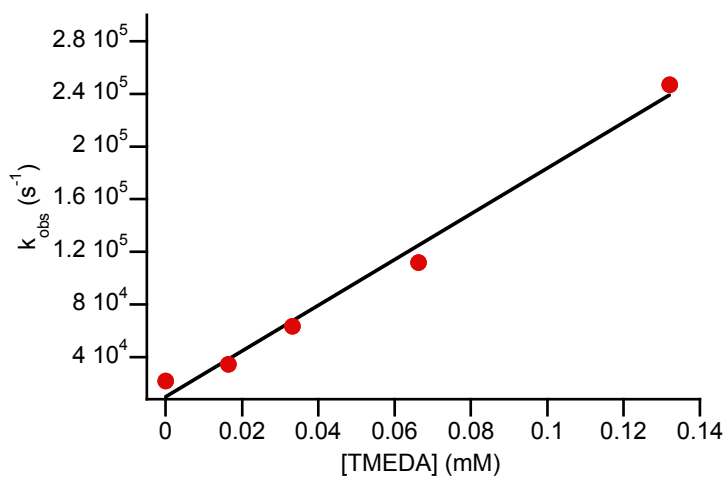


**Figure S11.** Representative Stern-Volmer quenching plot for <sup>1</sup>Rhodamine B and TMEDA.

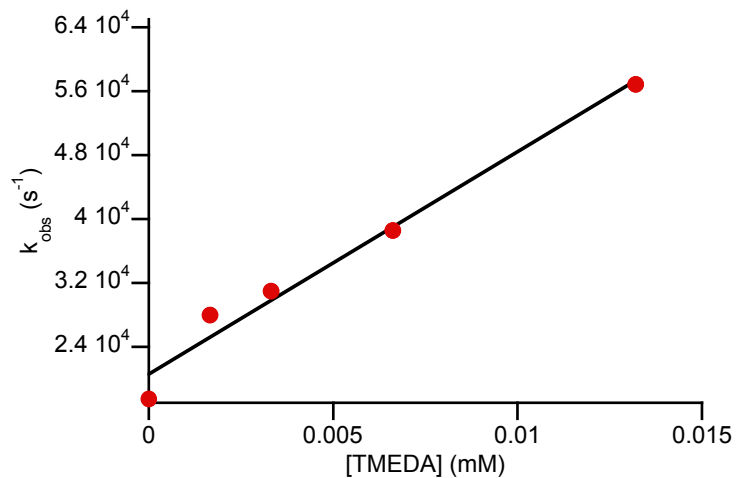




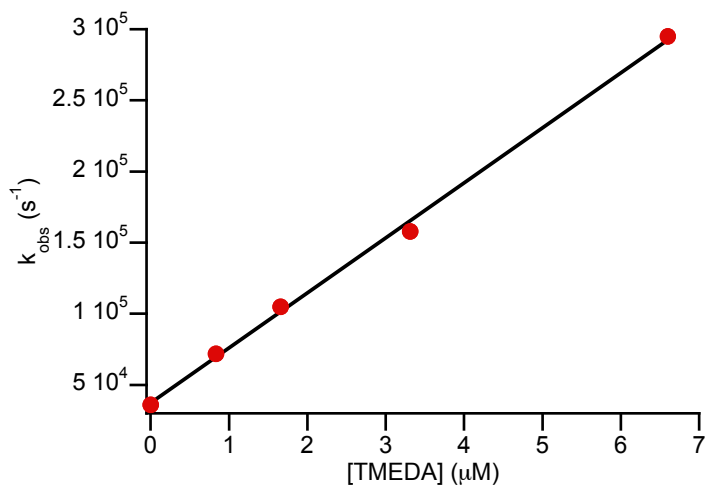
**Figure S12.** Representative kinetic bimolecular quenching plot for <sup>3</sup>Phenosafranin and TMEDA.



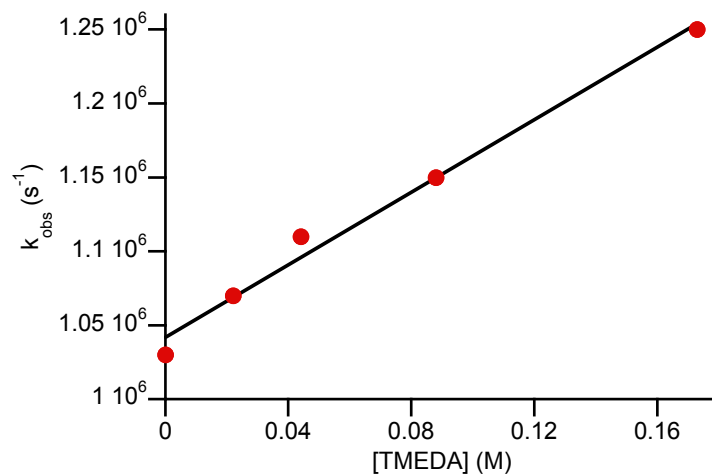
**Figure S13.** Representative kinetic bimolecular quenching plot for <sup>3</sup>Safranin O and TMEDA.



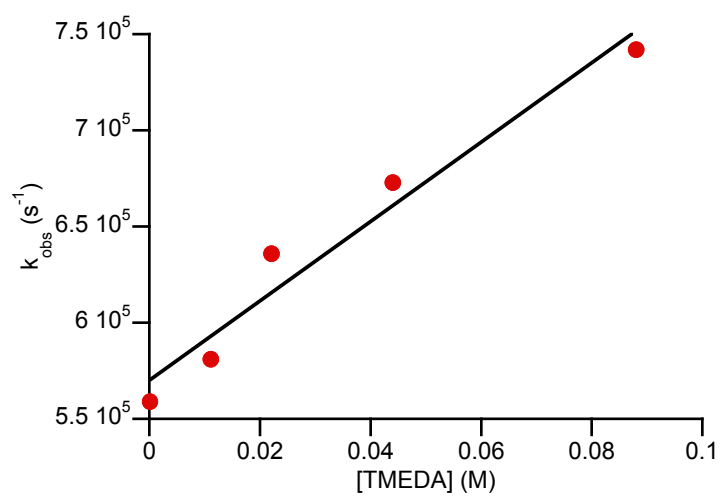
**Figure S14.** Representative kinetic bimolecular quenching plot for <sup>3</sup>Methylene Violet 3RAX and TMEDA.



**Figure S15.** Representative kinetic bimolecular quenching plot for <sup>3</sup>9-mesityl-10-methylacridinium perchlorate and TMEDA.

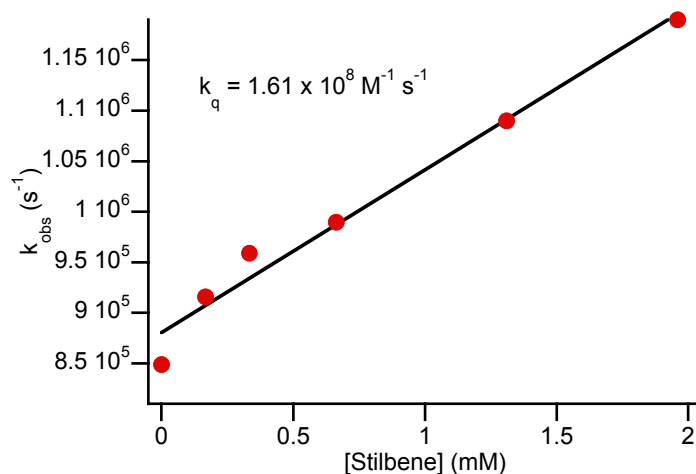


**Figure S16.** Representative kinetic bimolecular quenching plot for  $^3\text{Ru}(\text{bpy})_3\text{Cl}_2$  and TMEDA.



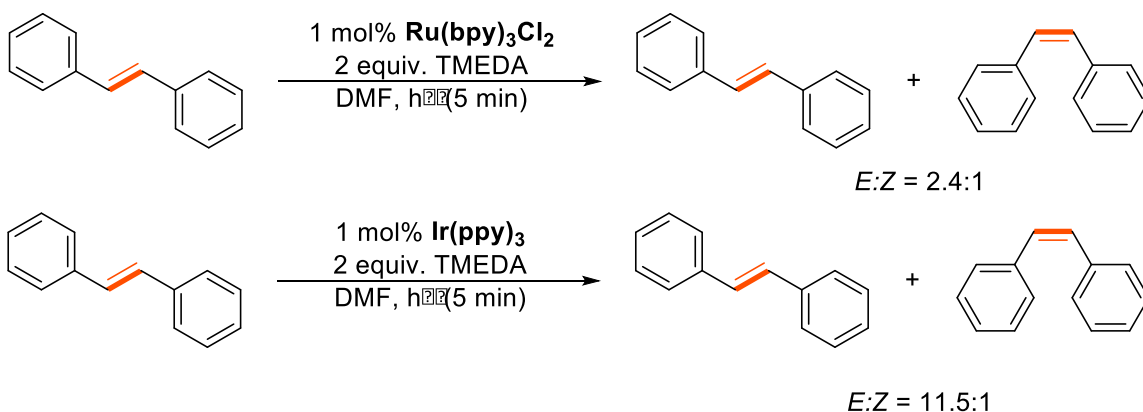
**Figure S17.** Representative kinetic bimolecular quenching plot for  $^3\text{fac-Ir}(\text{ppy})_3$  and TMEDA.

### E. Quenching of $^3\text{Ru}(\text{bpy})_3\text{Cl}_2$ by *trans*-Stilbene



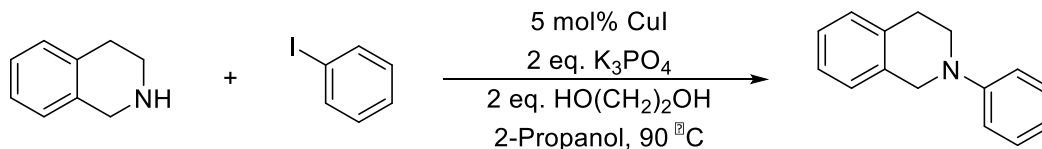
**Figure S18.** Representative kinetic bimolecular quenching plot for  $^3\text{Ru}(\text{bpy})_3\text{Cl}_2$  and *trans*-stilbene.

### F. *trans*-Stilbene control reactions with $\text{Ru}(\text{bpy})_3\text{Cl}_2$ and *fac*- $\text{Ir}(\text{ppy})_3$



**Reaction Conditions:** An oven dried 10 mL schlenk tube was charged with *meso*-1,2-dibromo-1,2-diphenylethane (0.3 mmol, 102 mg) and  $\text{Ru}(\text{bpy})_3\text{Cl}_2$  or *fac*- $\text{Ir}(\text{ppy})_3$  (0.003 mmol). The contents were dissolved in 5 mL of dry DMF, followed by the addition of TMEDA (0.6 mmol, 90  $\mu\text{L}$ ). The reaction was purged with argon for 15 minutes, followed by irradiation with 2 warm white LEDs. The reaction mixture was extracted with ether (x3) and washed with brine (x5). The organic phase was dried with  $\text{MgSO}_4$ , and concentrated via rotary evaporation. *E:Z* ratios were determined by  $^1\text{H}$  NMR analysis.

## G. Synthesis of 1-phenyl-1,2,3,4-tetrahydroisoquinoline



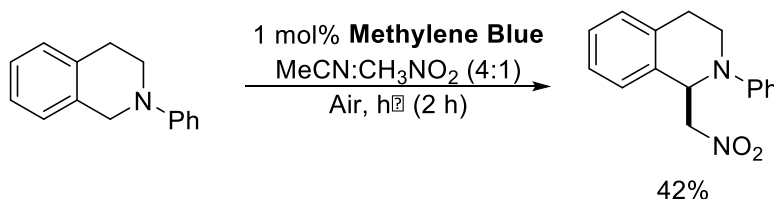
A 250 mL three-neck round bottom flask was charged with CuI (600 mg, 3.0 mmol) and K<sub>3</sub>PO<sub>4</sub> (12.75 g, 60 mmol), and was evacuated and back-filled with argon. 2-Propanol (30 mL), ethylene glycol (3.33 mL, 30 mmol), 1,2,3,4-tetrahydroisoquinoline (6.0 mL, 45 mmol), and iodobenzene (3.36 mL, 30 mmol) were then added by syringe at room temperature. The reaction mixture was heated to 90 °C for 24 hours and then allowed to cool to room temperature. The reaction mixture was then diluted with diethyl ether (60 mL) and water (60 mL), and the organic layer was extracted with diethyl ether (x2). The organic phase was dried with MgSO<sub>4</sub>, and the solvent was removed by rotary evaporation. The crude mixture was purified by flash column chromatography (20:1 Hexanes:EtOAc) to give the final product as an off-white solid (3.66 g, 58% isolated yield).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.34-7.27 (m, 2 H), 7.23-7.15 (m, 4 H), 7.00 (d, *J*=7.84 Hz, 2 H), 6.84 (t, *J*=7.25 Hz, 1 H), 4.43 (s, 2 H), 3.58 (t, *J*= 5.88 Hz, 2 H), 3.00 (t, *J*=5.78 Hz, 2 H)

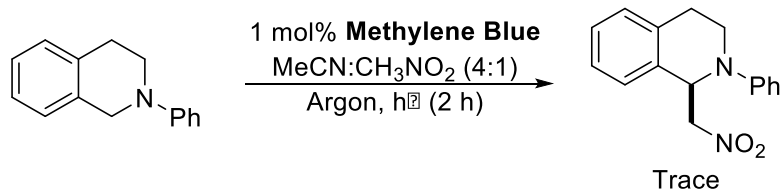
Reference: *Org. Biomol. Chem.* **2010**, *8*, 4077.

## H. Light mediated Aza-Henry and control reactions using Methylene Blue

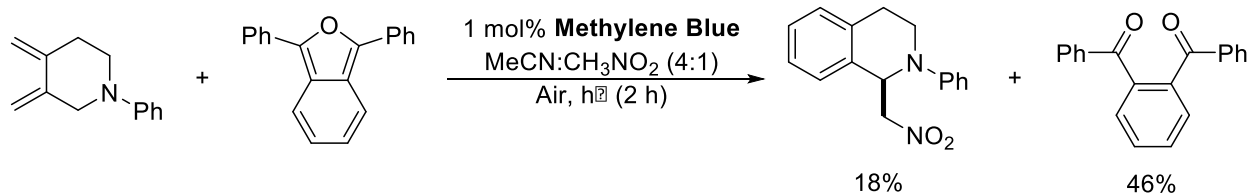
Note: For the following experiments, a 10 W 660 nm LED from LedEngin was used as the irradiation source to avoid any direct excitation of 1,3-diphenylisobenzofuran (DPBF).



**Reaction Conditions:** An oven dried 10 mL schlenk flask was charged with 2-phenyl-1,2,3,4-tetrahydroisoquinoline (0.3 mmol, 63 mg) and Methylene Blue (0.003 mmol, 1.1 mg). The contents were dissolved in 5 mL of a 4:1 mixture of MeCN:MeNO<sub>2</sub>. The reaction was then irradiated for 2 h with a 10 W 660 nm LED. The reaction was then diluted with ether (20 mL) and H<sub>2</sub>O (20 mL). The aqueous phase was extracted with ether (x2), and the combined organic phases were washed with brine, dried with MgSO<sub>4</sub>, and concentrated by rotary evaporation. Yield reported as isolated yield.



**Reaction Conditions:** An oven dried 10 mL schlenk flask was charged with 2-phenyl-1,2,3,4-tetrahydroisoquinoline (0.3 mmol, 63 mg) and Methylene Blue (0.003 mmol, 1.1 mg). The contents were dissolved in 5 mL of a 4:1 mixture of MeCN:MeNO<sub>2</sub>, and was purged with argon for roughly 15 minutes. The reaction was then irradiated for 2 h with a 10 W 660 nm LED. The reaction was then diluted with ether (20 mL) and H<sub>2</sub>O (20 mL). The aqueous phase was extracted with ether (x2), and the combined organic phases were washed with brine, dried with MgSO<sub>4</sub>, and concentrated by rotary evaporation. Yield reported as isolated yield.



**Reaction Conditions:** An oven dried 10 mL schlenk flask was charged with 2-phenyl-1,2,3,4-tetrahydroisoquinoline (0.3 mmol, 63 mg), 1,3-diphenylisobenzofuran (0.05 mmol, 14 mg) and Methylene Blue (0.003 mmol, 1.1 mg). The contents were dissolved in 5 mL of a 4:1 mixture of MeCN:MeNO<sub>2</sub>. The reaction was then irradiated for 2 h with a 10 W 660 nm LED. The reaction was then diluted with ether (20 mL) and H<sub>2</sub>O (20 mL). The aqueous phase was extracted with ether (x2), and the combined organic phases were washed with brine, dried with MgSO<sub>4</sub>, and concentrated by rotary evaporation. Yields reported as isolated yield averaged over two experiments.

### I. Kinetic analysis of the Aza-Henry reaction with Methylene Blue

As shown in Section H, addition of 1,3-diphenylisobenzofuran (DPBF) to the reaction mixture results in a decrease in yield of the Aza-Henry product, and formation of 1,2-phenylenebis(phenylmethanone) is observed as a result of the oxidation of DPBF. However, this information alone is not enough to rule out that the decrease in yield of the Aza-Henry product could also stem from DPBF outcompeting 2-phenyl-1,2,3,4-tetrahydroisoquinoline in the bimolecular quenching of Methylene Blue's triplet. In order to rule out this possibility, the excited-state kinetics of Methylene Blue and all the reaction substrates were examined, and are summarized in Table S1.

**Table S1.** Bimolecular quenching data for <sup>3</sup>Methylene Blue and the reaction substrates.

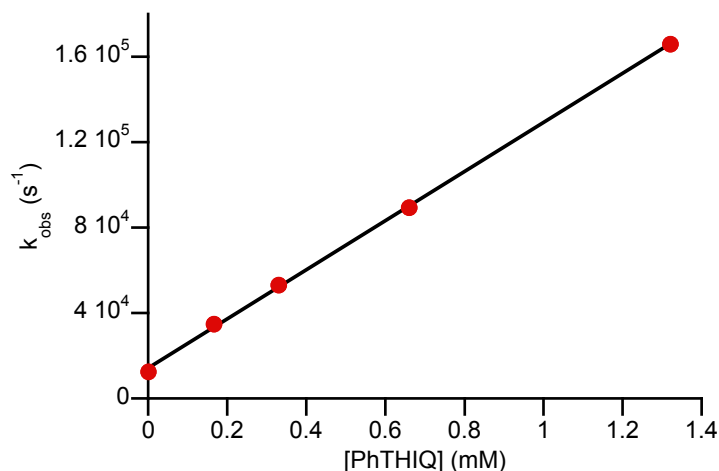
Substrate	<sup>3</sup> MB k <sub>q</sub> (M <sup>-1</sup> s <sup>-1</sup> )
O <sub>2</sub>	2.49 × 10 <sup>9</sup>
2-phenyl-1,2,3,4-tetrahydroisoquinoline	1.05 × 10 <sup>9</sup>
DPBF	< 10 <sup>6</sup>
MeNO <sub>2</sub>	< 10 <sup>6</sup>

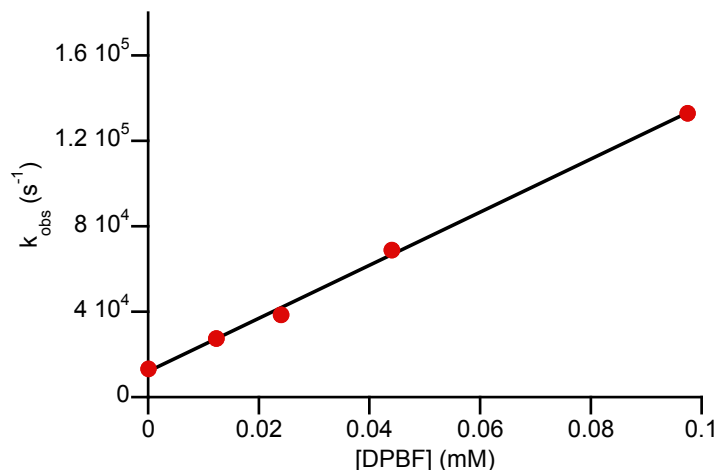
Since we could not detect any bimolecular quenching of <sup>3</sup>Methylene Blue by DPBF, we can assume that the observed decrease in reactivity observed is due to DPBF trapping reactive oxygen species, and not from DPBF outcompeting 2-phenyl-1,2,3,4-tetrahydroisoquinoline for Methylene Blue's triplet.

Since it is well known that Methylene Blue is an excellent sensitizer of singlet oxygen (<sup>1</sup>O<sub>2</sub>), we decided to examine the bimolecular quenching of <sup>1</sup>O<sub>2</sub> by the reaction substrates to determine the role of <sup>1</sup>O<sub>2</sub> in the overall reaction mechanism. Moreover, it is well known that <sup>1</sup>O<sub>2</sub> is capable of oxidizing amines<sup>1</sup>, an important step in the proposed mechanism for the Aza-Henry reaction.<sup>2,3</sup> The results of this kinetic investigation are summarized in Table S2 (see Figures S19 and S20 for the corresponding bimolecular quenching plots).

**Table S2.** Bimolecular quenching data for <sup>1</sup>O<sub>2</sub> and the reaction substrates.

Substrate	<sup>1</sup> O <sub>2</sub> k <sub>q</sub> (M <sup>-1</sup> s <sup>-1</sup> )
2-phenyl-1,2,3,4-tetrahydroisoquinoline	1.13 × 10 <sup>8</sup>
DPBF	1.19 × 10 <sup>9</sup>
MeNO <sub>2</sub>	< 10 <sup>6</sup>

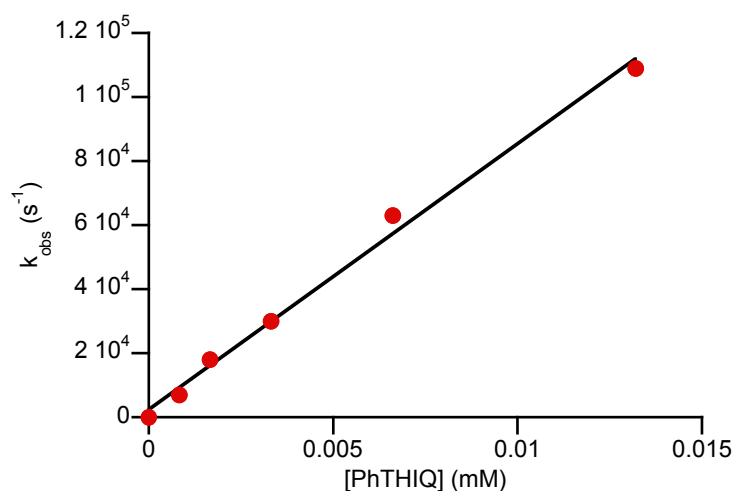
**Figure S19.** Representative kinetic bimolecular quenching plot for <sup>1</sup>O<sub>2</sub> and 2-phenyl-1,2,3,4-tetrahydroisoquinoline.



**Figure S20.** Representative kinetic bimolecular quenching plot for  $^1\text{O}_2$  and 1,3-diphenylisobenzofuran.

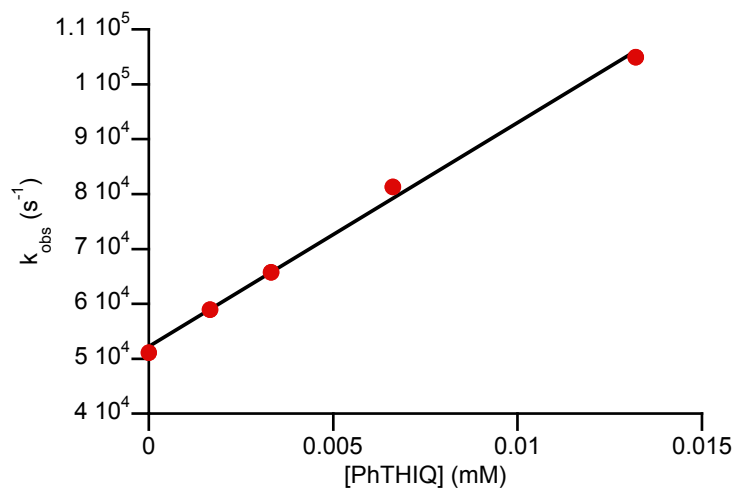
From these data, we can conclude that any  $^1\text{O}_2$  produced by Methylene Blue can indeed be trapped by 2-phenyl-1,2,3,4-tetrahydroisoquinoline. In good agreement, we also obtain a value approaching diffusion control for DPBF, a known excellent  $^1\text{O}_2$  quencher. Therefore, it is possible that  $^1\text{O}_2$  is indeed playing a role in the mechanism, as the addition of another potent  $^1\text{O}_2$  quencher (DPBF) significantly impacts the yield. However, DPBF is not solely specific to  $^1\text{O}_2$ , as it can also trap other reactive oxygen species, such as superoxide ( $\text{O}_2^{\bullet-}$ ).<sup>4</sup> Therefore, we cannot conclude from these data alone that the trapping of  $^1\text{O}_2$  is what is responsible for the decrease in the yield, but can only say that the decrease is due to the trapping of reactive oxygen species.

#### J. Excited Dye quenching by 2-phenyl-1,2,3,4-tetrahydroisoquinoline

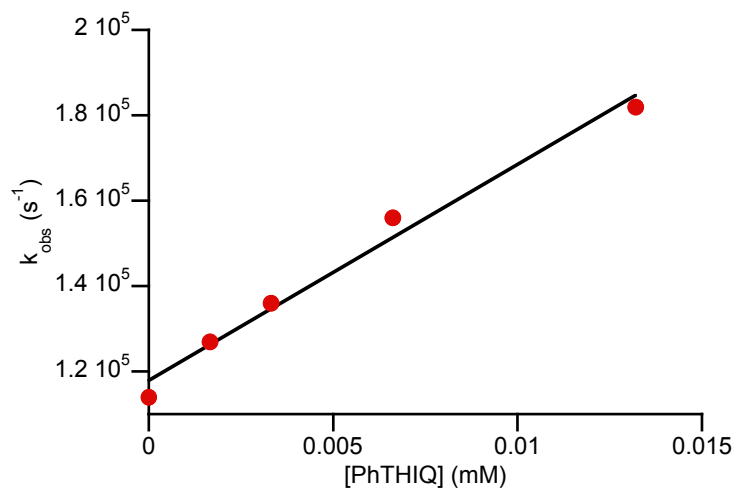


**Figure S21.** Representative kinetic bimolecular quenching plot for  $^3\text{Methylene Blue}$  and 2-phenyl-1,2,3,4-tetrahydroisoquinoline.

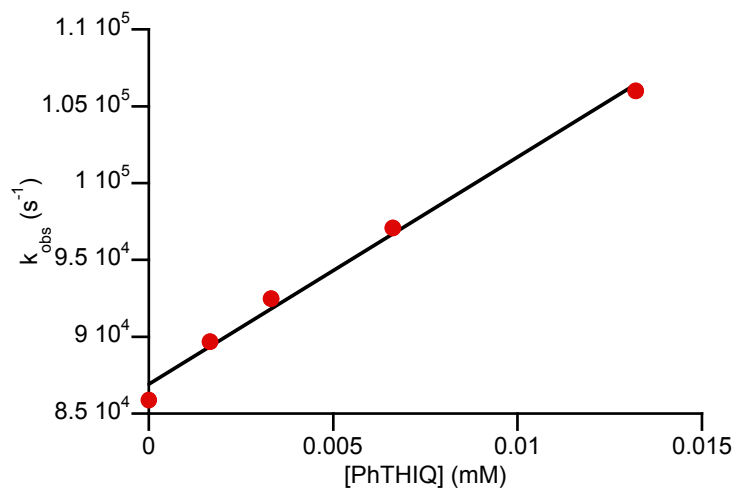




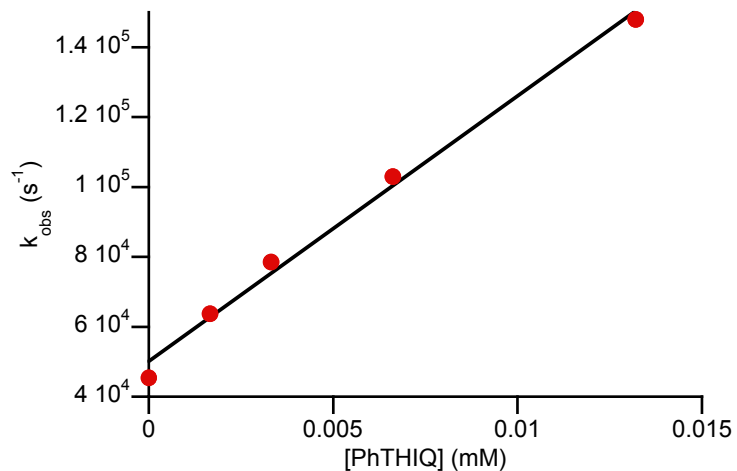
**Figure S22.** Representative kinetic bimolecular quenching plot for <sup>3</sup>Thionin and 2-phenyl-1,2,3,4-tetrahydroisoquinoline.



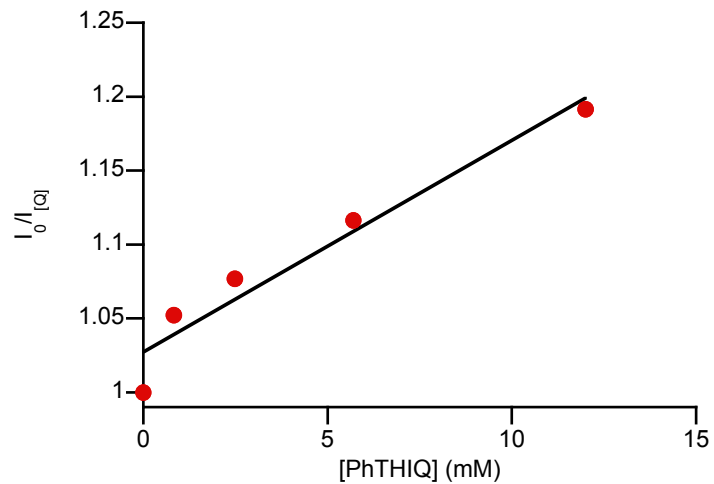
**Figure S23.** Representative kinetic bimolecular quenching plot for <sup>3</sup>New Methylene Blue N and 2-phenyl-1,2,3,4-tetrahydroisoquinoline.



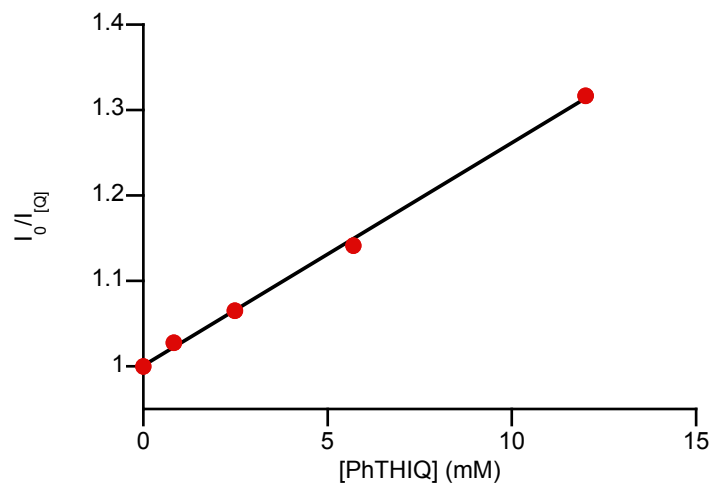
**Figure S24.** Representative kinetic bimolecular quenching plot for <sup>3</sup>1,9-dimethyl Methylene Blue and 2-phenyl-1,2,3,4-tetrahydroisoquinoline.



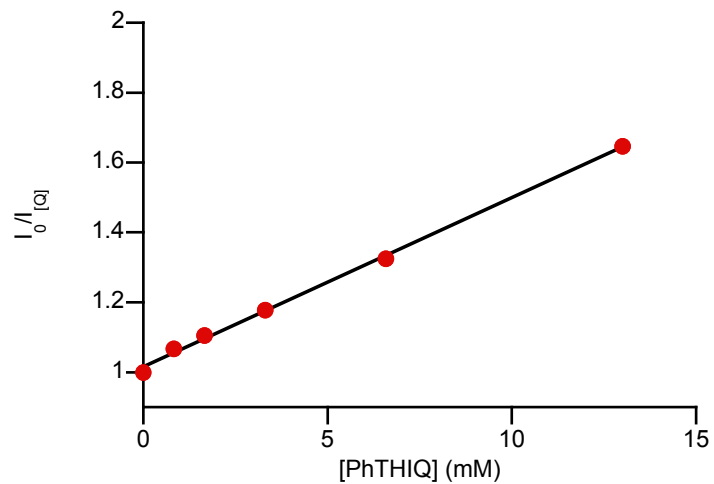
**Figure S25.** Representative kinetic bimolecular quenching plot for <sup>3</sup>Methylene Green and 2-phenyl-1,2,3,4-tetrahydroisoquinoline.



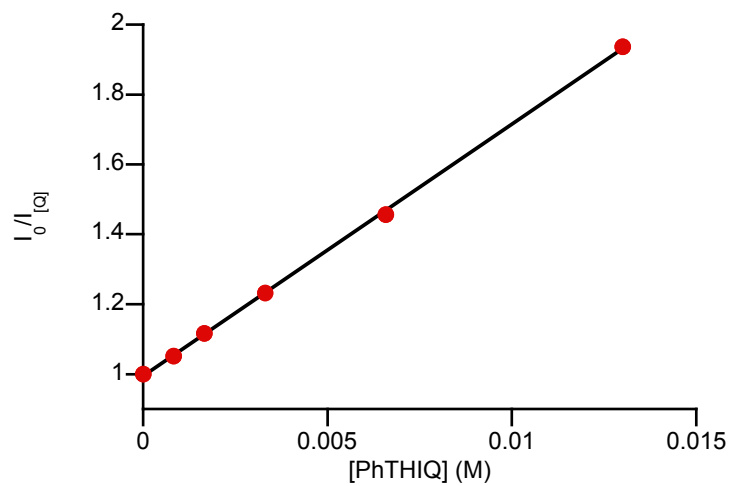
**Figure S26.** Representative Stern-Volmer quenching plot for <sup>1</sup>Brilliant Cresyl Blue and 2-phenyl-1,2,3,4-tetrahydroisoquinoline.



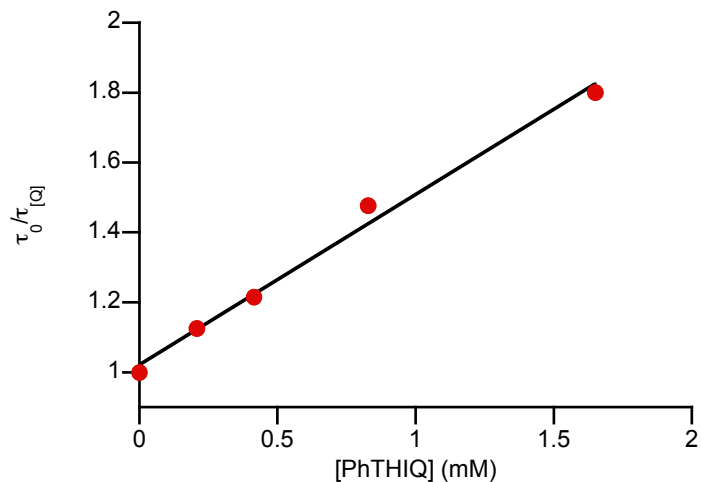
**Figure S27.** Representative Stern-Volmer quenching plot for <sup>1</sup>Nile Blue and 2-phenyl-1,2,3,4-tetrahydroisoquinoline.



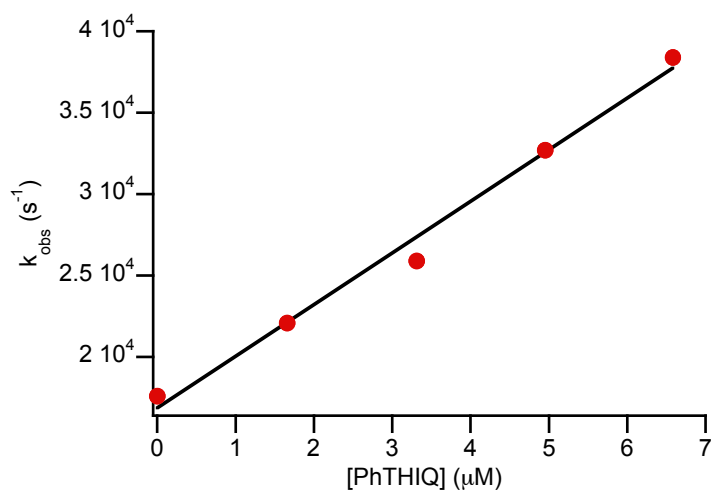
**Figure S28.** Representative Stern-Volmer quenching plot for <sup>1</sup>Pyronin Y and 2-phenyl-1,2,3,4-tetrahydroisoquinoline.



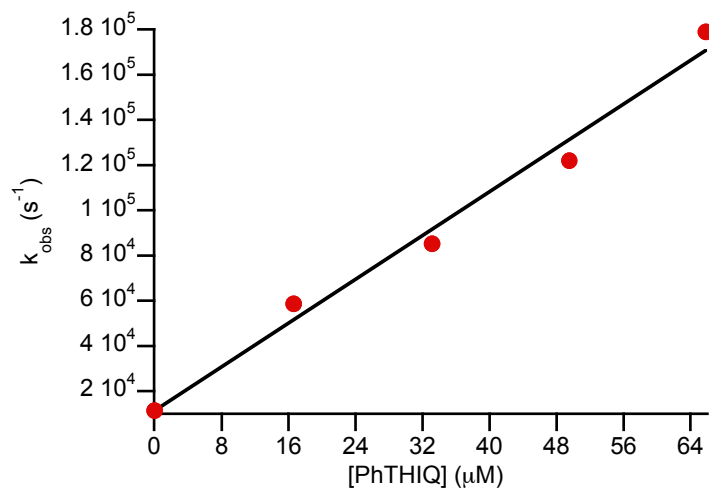
**Figure S29.** Representative Stern-Volmer quenching plot for <sup>1</sup>Rhodamine 6G and 2-phenyl-1,2,3,4-tetrahydroisoquinoline.



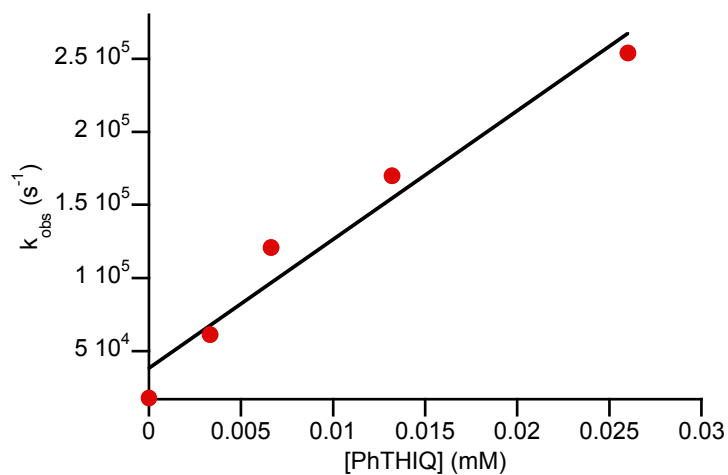
**Figure S30.** Representative Stern-Volmer quenching plot for <sup>1</sup>Rhodamine B and 2-phenyl-1,2,3,4-tetrahydroisoquinoline.



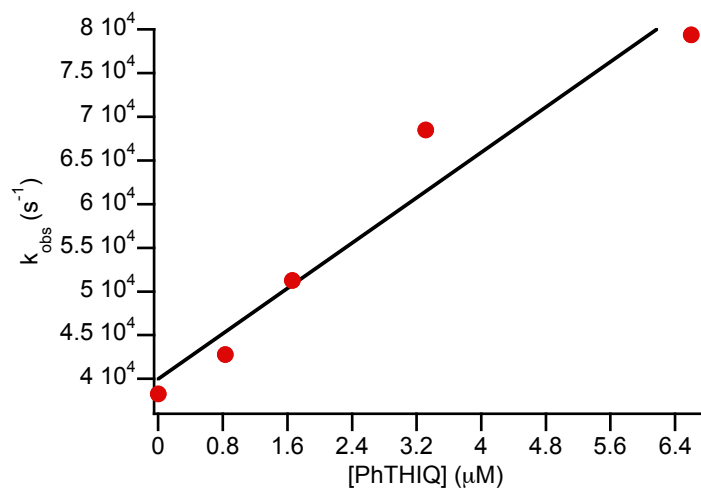
**Figure S31.** Representative kinetic bimolecular quenching plot for <sup>3</sup>Phenosafranin and 2-phenyl-1,2,3,4-tetrahydroisoquinoline.



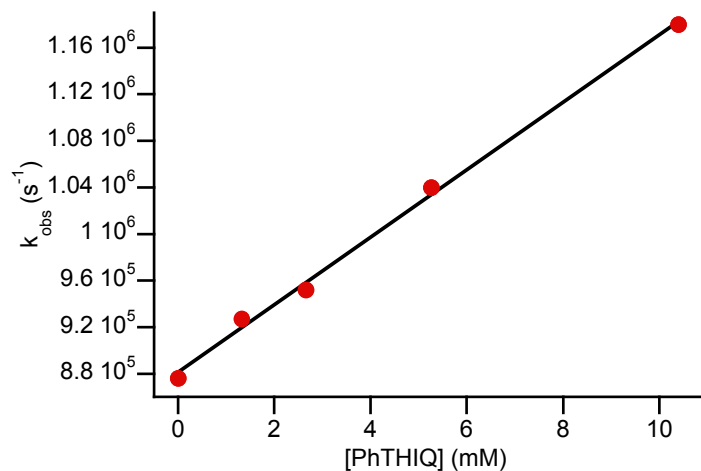
**Figure S32.** Representative kinetic bimolecular quenching plot for  $^3\text{Safranin O}$  and 2-phenyl-1,2,3,4-tetrahydroisoquinoline.



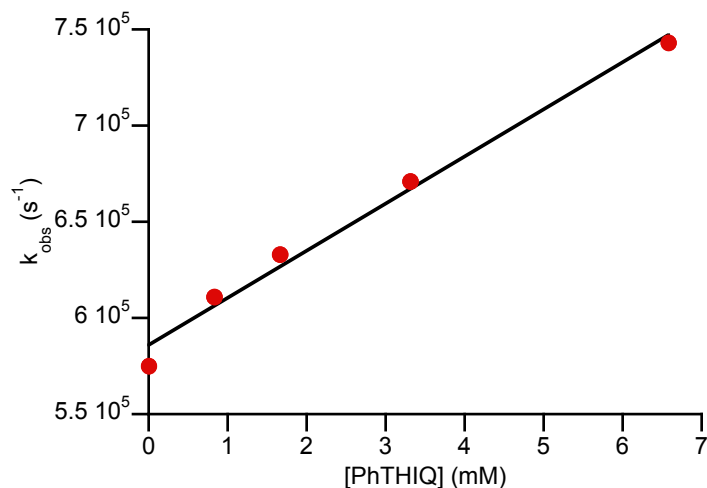
**Figure S33.** Representative kinetic bimolecular quenching plot for  $^3\text{Methylene Violet 3RAX}$  and 2-phenyl-1,2,3,4-tetrahydroisoquinoline.



**Figure S34.** Representative kinetic bimolecular quenching plot for  $^3\text{9-mesityl-10-methylacridinium perchlorate}$  and 2-phenyl-1,2,3,4-tetrahydroisoquinoline.



**Figure S35.** Representative kinetic bimolecular quenching plot for  $^3\text{Ru}(\text{bpy})_3\text{Cl}_2$  and 1-phenyl-2,2,3,4-tetrahydroisoquinoline.



**Figure S36.** Representative kinetic bimolecular quenching plot for  $^3fac\text{-Ir}(\text{ppy})_3$  and 2-phenyl-1,2,3,4-tetrahydroisoquinoline.

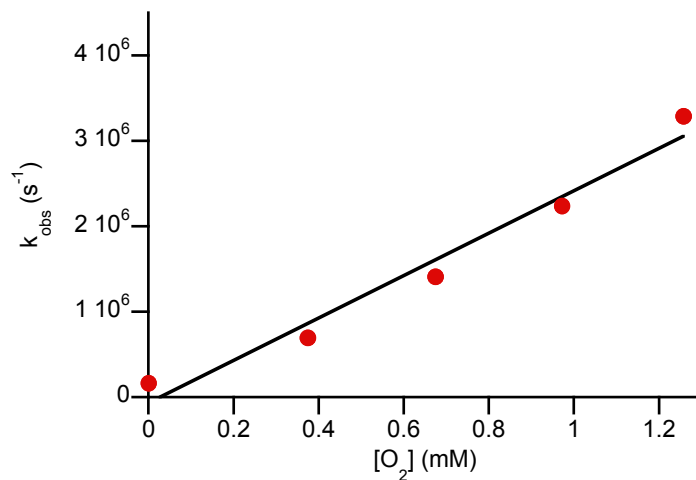
### K. Excited Dye quenching by molecular oxygen

**General Procedure:** Experiments at variable oxygen concentrations were carried out by using mixtures of oxygen and nitrogen prepared with a gas flow controller-mixer system. The concentration of oxygen was calculated using Henry's law:

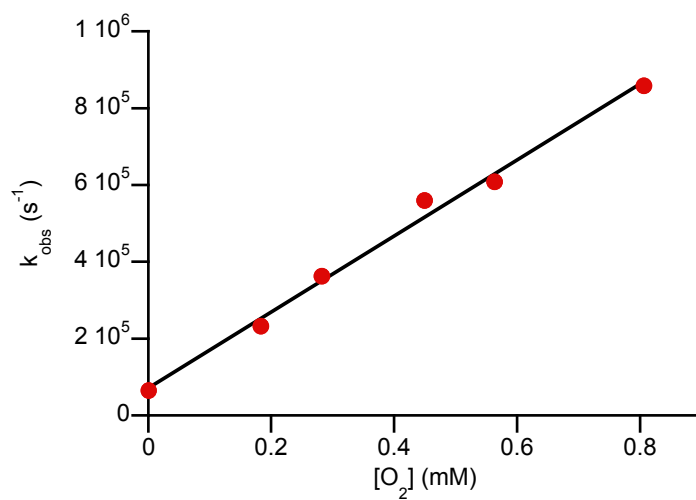
$$[\text{O}_2] = \rho / K_{\text{H}}$$

where  $K_{\text{H}}$  is the Henry's constant, and its value is  $769.23 \text{ L}\cdot\text{atm}/\text{mol}$  for water and  $131.25 \text{ L}\cdot\text{atm}/\text{mol}$  for acetonitrile,<sup>5</sup>  $\rho$  is the partial pressure of oxygen obtained from the mixer scale readings. Henry's constant for acetonitrile was calculated under the assumption that acetonitrile under an atmosphere of air ( $\rho_{\text{O}_2} = 0.21 \text{ atm}$ ) contains  $1.6 \times 10^{-3} \text{ mol/L O}_2$ .<sup>6</sup> In cases where the solutions were comprised of a mixture of acetonitrile and water it was necessary to determine the number of moles of  $\text{O}_2$  based on each of the components and then take into consideration the total volume of the mixed solution.

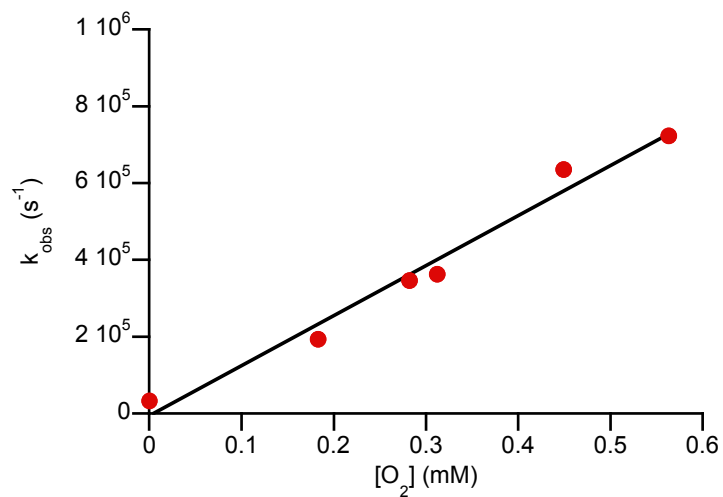




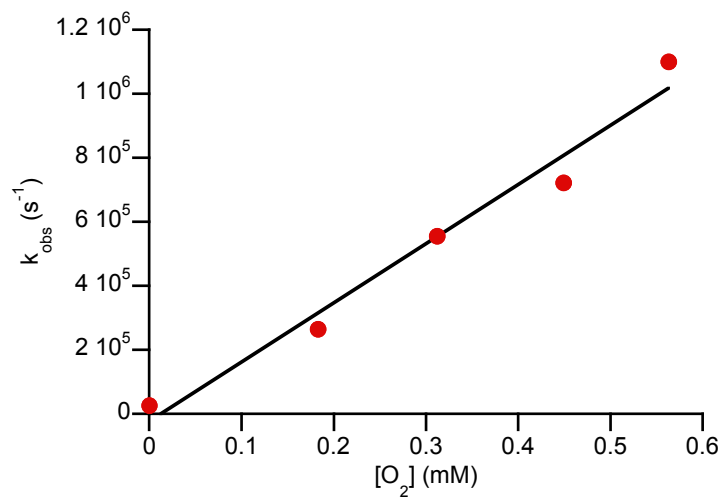
**Figure S37.** Representative kinetic bimolecular quenching plot for  $^3\text{Methylene Blue}$  and  $\text{O}_2$ .



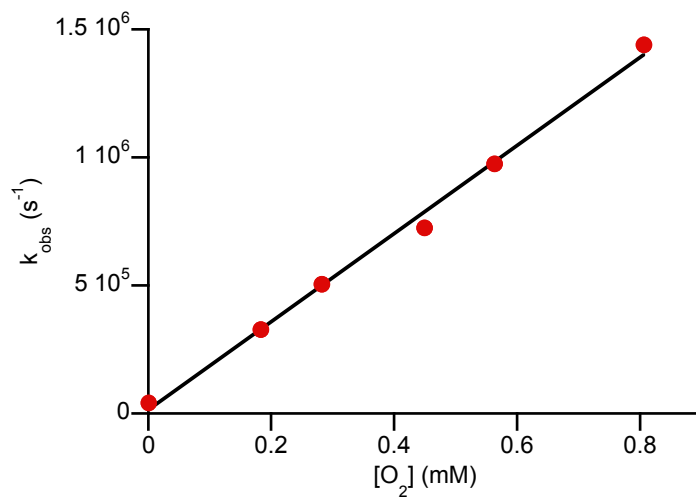
**Figure S38.** Representative kinetic bimolecular quenching plot for  $^3\text{New Methylene Blue N}$  and  $\text{O}_2$ .



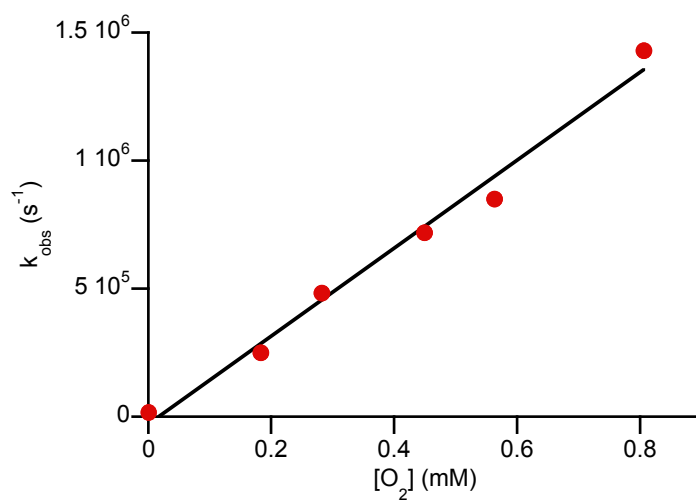
**Figure S39.** Representative kinetic bimolecular quenching plot for  $^3$ 1,9-dimethyl Methylene Blue and  $\text{O}_2$ .



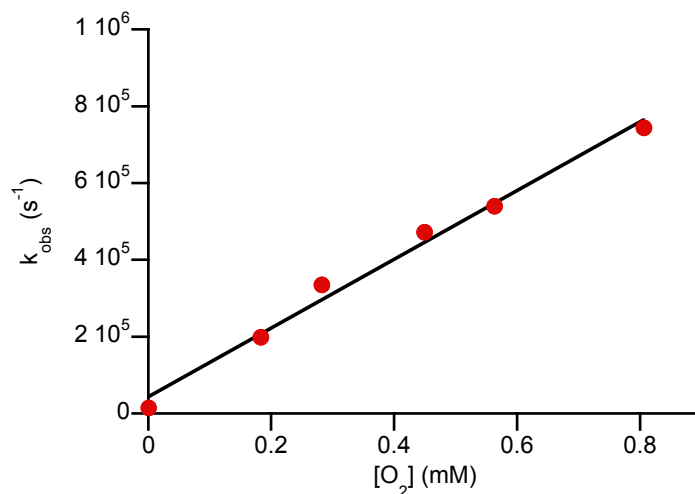
**Figure S40.** Representative kinetic bimolecular quenching plot for  $^3$ Methylene Green and  $\text{O}_2$ .



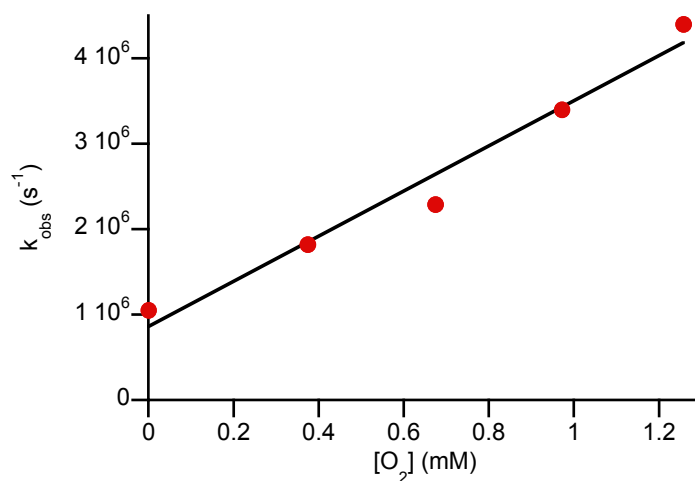
**Figure S41.** Representative kinetic bimolecular quenching plot for  $^3\text{Phenosafranin}$  and  $\text{O}_2$ .



**Figure S42.** Representative kinetic bimolecular quenching plot for  $^3\text{Safranin O}$  and  $\text{O}_2$ .

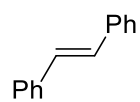


**Figure S43.** Representative kinetic bimolecular quenching plot for <sup>3</sup>Methylene Violet 3RAX and O<sub>2</sub>.



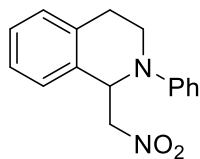
**Figure S44.** Representative kinetic bimolecular quenching plot for <sup>3</sup>Ru(bpy)<sub>3</sub>Cl<sub>2</sub> and O<sub>2</sub>.

#### L. Spectral data of reaction products


 According to the general procedure, *meso*-1,2-dibromo-1,2-diphenylethane (102 mg, 0.3 mmol), photosensitizer (0.003 mmol), and DMF (5 mL) were purged with argon and irradiated with two warm-white LEDs for 5 minutes. The reaction mixture was extracted with ether (x3) and washed with brine (x5) and concentrated to afford a crude product containing the title compound. Percent conversion was determined by <sup>1</sup>H NMR (10-94% conversion).

$^1\text{H}$  NMR: (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.55-7.50 (m, 4 H), 7.40-7.34 (m, 4 H), 7.29-7.24 (m, 2 H), 7.12 (s, 2 H)

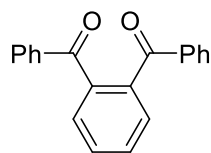
Reference: *J. Org. Chem.* **2015**, *80*, 6922.



According to the general procedure, 1-phenyl-1,2,3,4-tetrahydroisoquinoline (63 mg, 0.3 mmol), photosensitizer (0.003 mmol), and a mixture of  $\text{MeCN}:\text{MeNO}_2$  (4:1, 5 mL) were irradiated for 1 hour with two-warm white LEDs. The reaction was then diluted with ether (20 mL) and  $\text{H}_2\text{O}$  (20 mL). The aqueous phase was extracted with ether (x2), and the combined organic phases were washed with brine, dried and concentrated. The crude reaction mixture was purified by flash column chromatography (20:1 Hexanes:EtOAc) to afford the title compound as a yellow oil (9-66% isolated yield).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.36-7.09 (m, 5 H), 6.99 (d,  $J=8.03$  Hz, 2 H), 6.89-6.82 (m, 1 H), 5.56 (t,  $J=7.25$  Hz, 1 H), 4.88 (dd,  $J=11.76, 7.84$  Hz, 1 H), 4.57 (dd,  $J=11.76, 6.66$  Hz, 1 H), 3.73-3.55 (m, 2H), 3.18-3.01 (m, 1 H), 2.80 (dt,  $J=16.31, 4.97$  Hz, 1 H).

Reference: *J. Am. Chem. Soc.* **2010**, *132*, 1464.

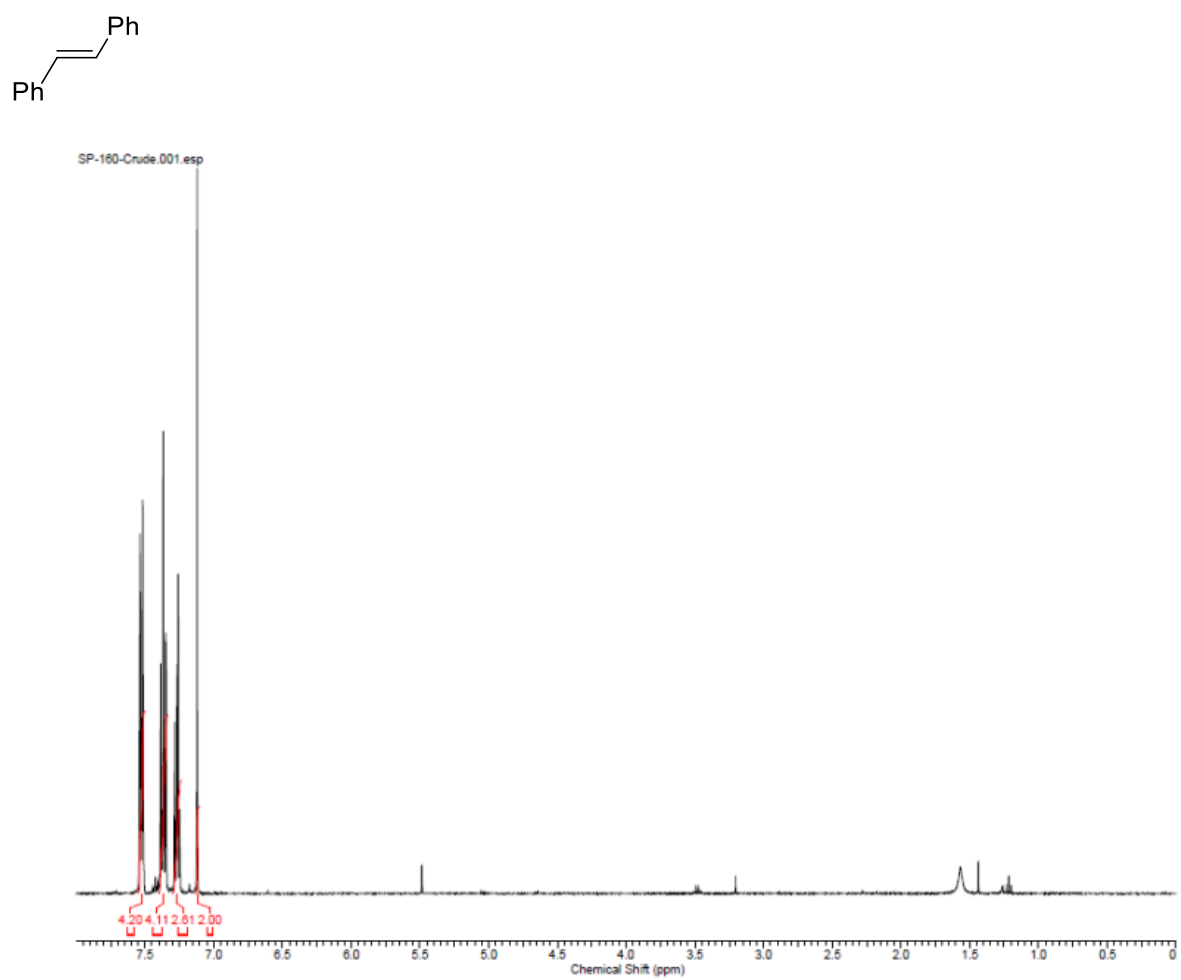


According to the procedure described in Section H of the ESI, 2-phenyl-1,2,3,4-tetrahydroisoquinoline (0.3 mmol, 63 mg), 1,3-diphenylisobenzofuran (0.05 mmol, 14 mg), Methylene Blue (0.003 mmol, 1.1 mg), and a mixture of  $\text{MeCN}:\text{MeNO}_2$  (4:1, 5 mL) was irradiated for 2 h with a 10 W 660 nm LED. The reaction was then diluted with ether (20 mL) and  $\text{H}_2\text{O}$  (20 mL). The aqueous phase was extracted with ether (x2), and the combined organic phases were washed with brine, dried and concentrated. The crude reaction mixture was purified by Prep TLC (20:1 Hexanes:EtOAc) to afford the final product as a white solid (6.5 mg, 46% isolated yield).

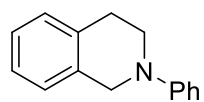
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.72-7.68 (m, 4 H), 7.62 (s, 4 H), 7.55-7.49 (m, 2 H), 7.41-7.34 (m, 4 H)

Reference: *Eur. J. Org. Chem.* **2015**, 775.

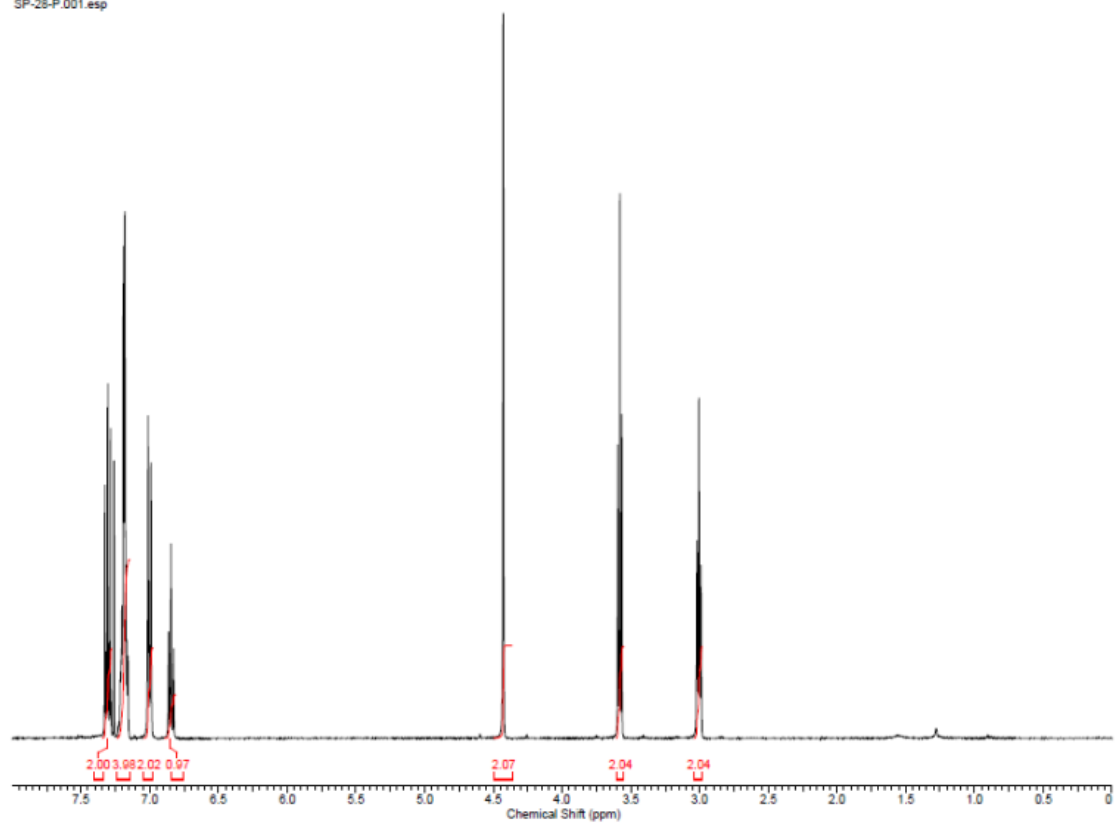
## M. NMR spectra



**Figure S45.**  $^1\text{H}$  NMR spectrum of a crude reaction mixture containing *trans*-stilbene used to calculate reaction conversion. (Photosensitizer: Methylene Blue, Conversion: 96%)



SP-28-P.001.esp



**Figure S46.**  $^1\text{H}$  NMR spectrum 1-phenyl-1,2,3,4-tetrahydroisoquinoline.

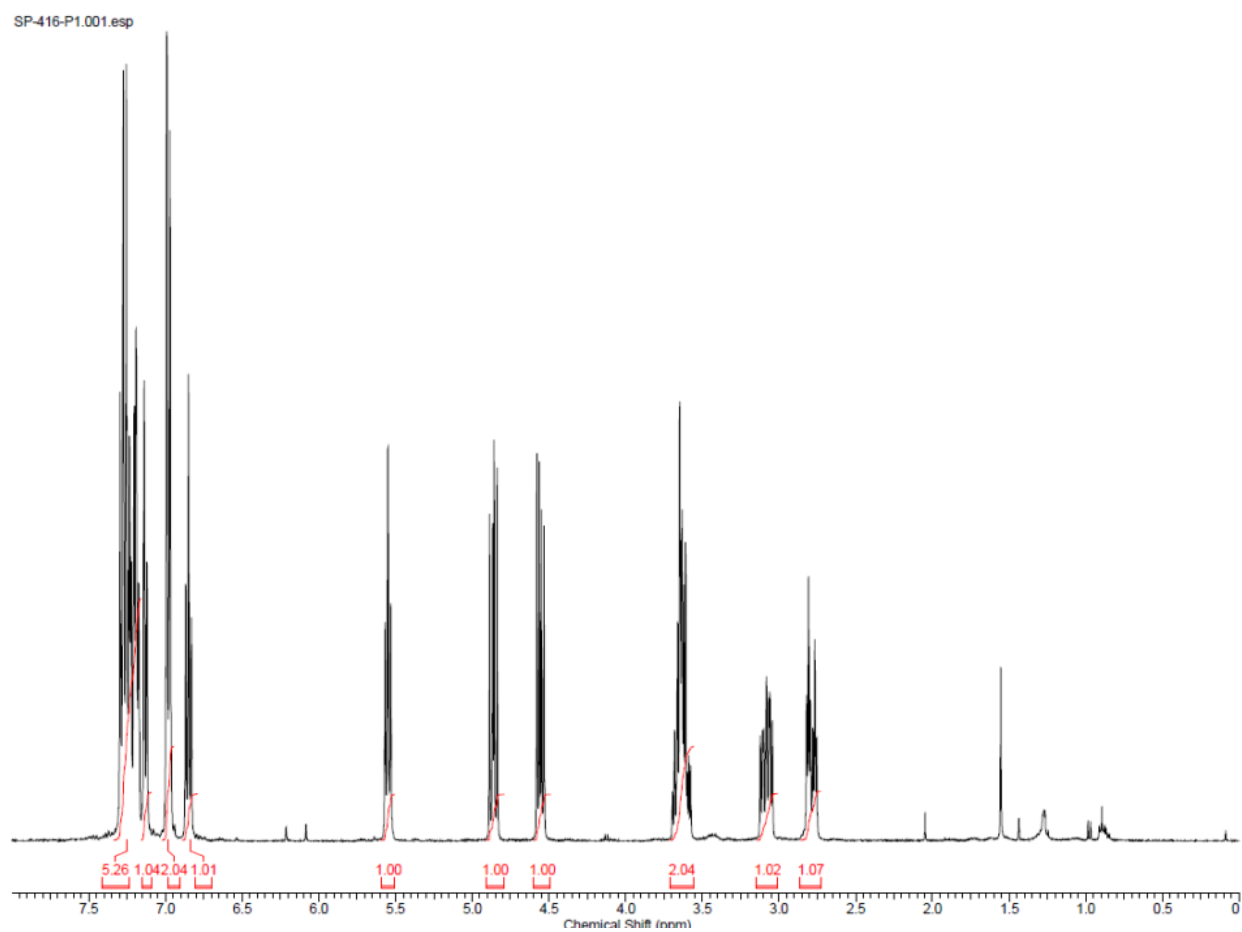
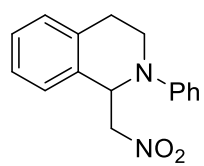
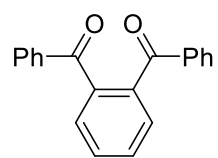
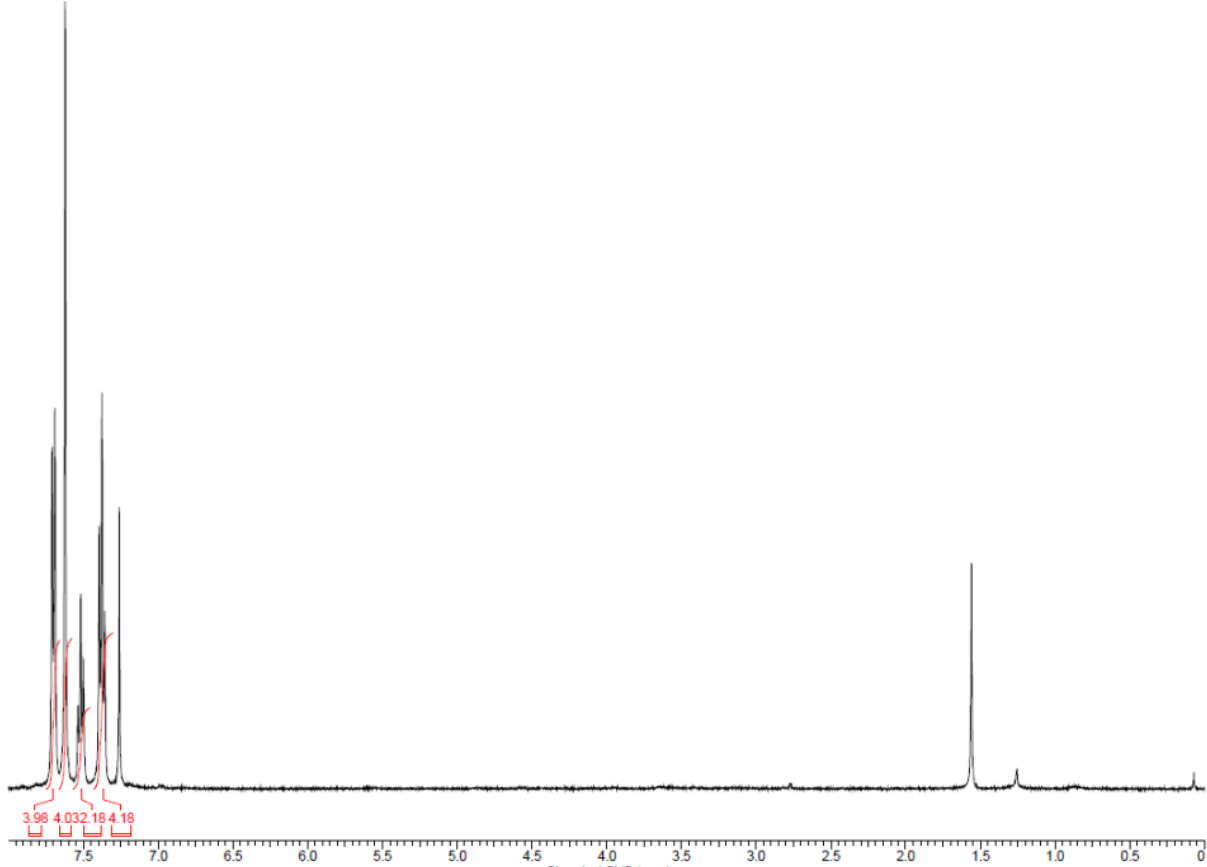


Figure S47.  $^1\text{H}$  NMR of Aza-Henry product.





SP-416-P2-Pure.001.esp



**Figure S48.** <sup>1</sup>H NMR of 1,2-dibenzoylbenzene.

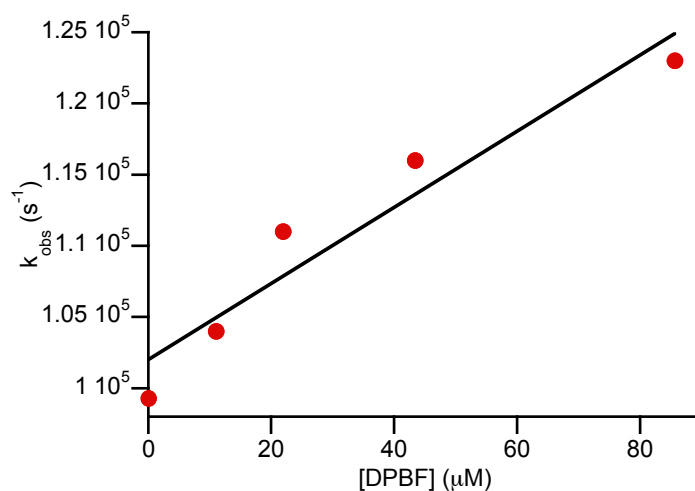
## N. Determination of triplet energies by laser flash photolysis

In order to determine the triplet energy of the newly characterized dyes, quenchers with known triplet energies were employed, and their bimolecular quenching constants were determined using laser flash photolysis. Once no bimolecular quenching between the dye excited-state and the quencher was observed ( $<10^6 \text{ M}^{-1} \text{ s}^{-1}$ ), the triplet energy was calculated to be the midpoint between the failed quencher and the last quencher employed. The data for the determination of the triplet energies are summarized in Tables S3-S6 followed by their corresponding bimolecular quenching plots. The triplet energies for the following compounds can be found in the appropriate section of the Appendix section. All measurements were performed in acetonitrile, unless otherwise noted, using the same general procedure previously described.

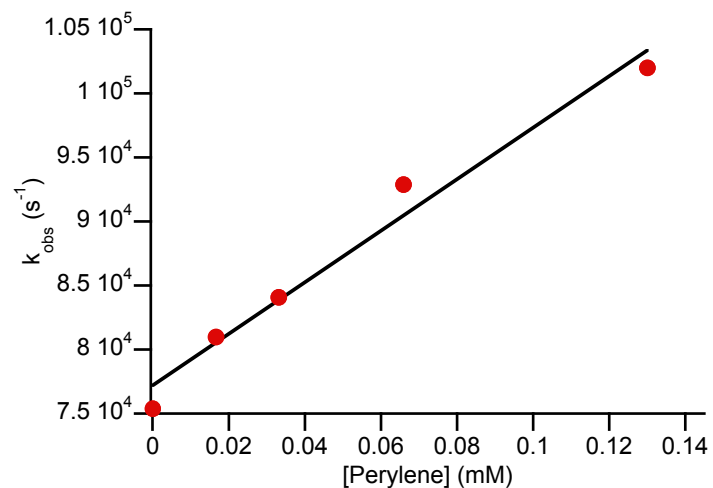
**Table S3.** Bimolecular quenching values for New Methylene Blue N and a series of quenchers.

Quencher	Quencher $E_T$ (eV)	$k_q$ ( $\text{M}^{-1} \text{ s}^{-1}$ )
$\text{O}_2$	0.91	$9.9 \times 10^8$
1,3-diphenylisobenzofuran	1.47	$2.9 \pm 0.5 \times 10^8$
Perylene <sup>1</sup>	1.53	$2.3 \pm 0.3 \times 10^8$
Azulene	1.69	$1.2 \pm 0.1 \times 10^8$
9,10-diphenylanthracene <sup>1</sup>	1.77	$< 10^6$

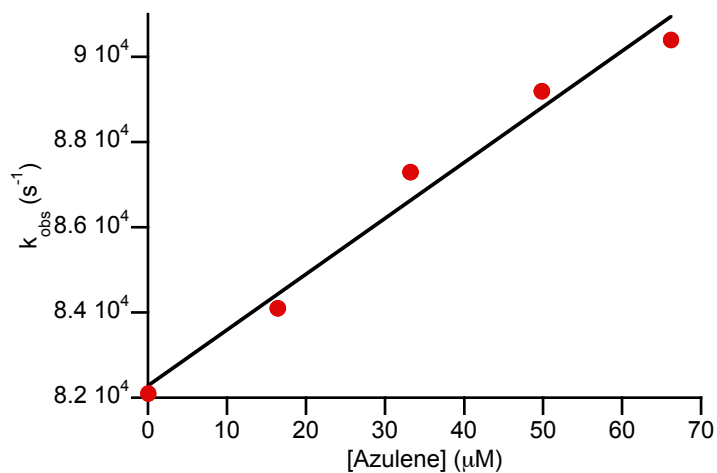
<sup>1</sup>Performed in  $\text{CH}_2\text{Cl}_2$



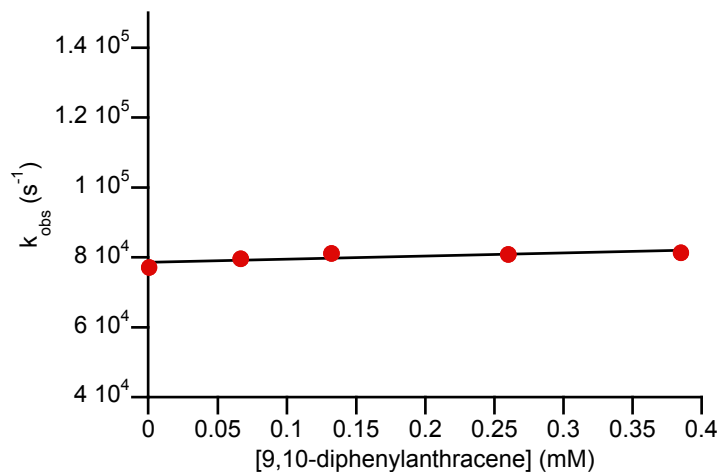
**Figure S49.** Representative kinetic bimolecular quenching plot for <sup>3</sup>New Methylene Blue N and 1,3-diphenylisobenzofuran.



**Figure S50.** Representative kinetic bimolecular quenching plot for  $^3\text{New}$  Methylene Blue N and Perylene.



**Figure S51.** Representative kinetic bimolecular quenching plot for  $^3\text{New}$  Methylene Blue N and Azulene.

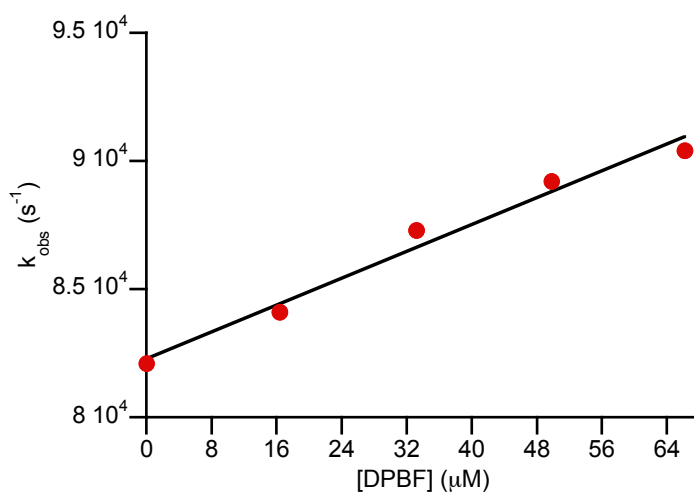


**Figure S52.** Representative kinetic bimolecular quenching plot for  $^3$ New Methylene Blue N and 9,10-diphenylanthracene.

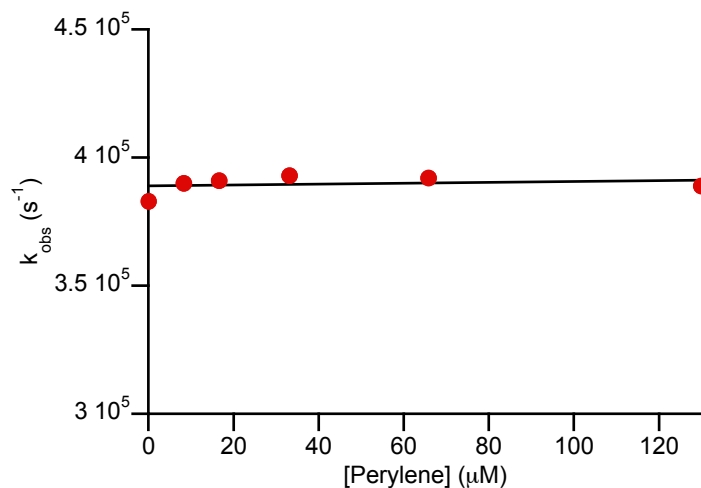
**Table S4.** Bimolecular quenching values for 1,9-dimethyl Methylene Blue and a series of quenchers.

Quencher	Quencher $E_T$ (eV)	$k_q$ ( $M^{-1} s^{-1}$ )
O <sub>2</sub>	0.91	$1.2 \times 10^9$
1,3-diphenylisobenzofuran	1.47	$1.2 \pm 0.4 \times 10^9$
Perylene <sup>1</sup>	1.53	$< 10^6$

<sup>1</sup>Performed in CH<sub>2</sub>Cl<sub>2</sub>.



**Figure S53.** Representative kinetic bimolecular quenching plot for  $^3$ 1,9-dimethyl Methylene Blue and 1,3-diphenylisobenzofuran.

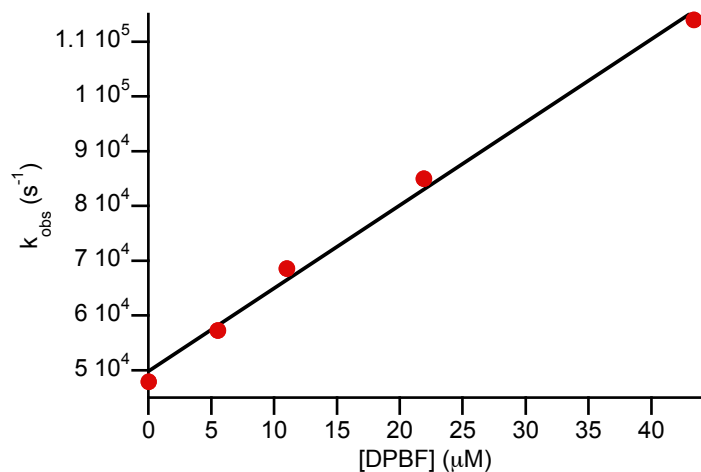


**Figure S54.** Representative kinetic bimolecular quenching plot for <sup>3</sup>1,9-dimethyl Methylene Blue and Perylene.

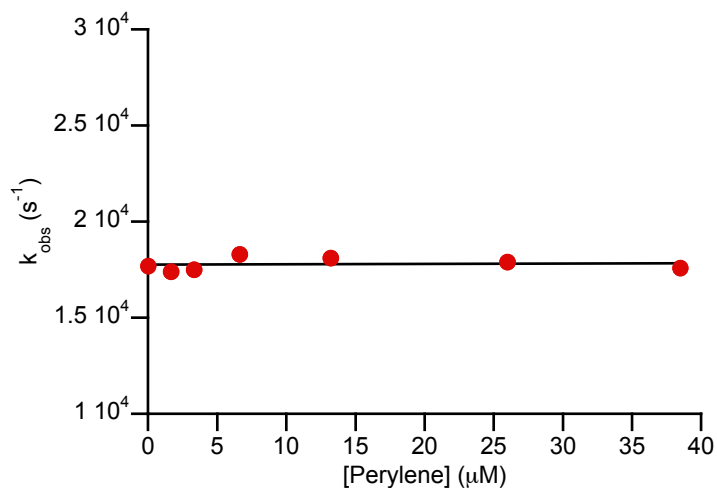
**Table S5.** Bimolecular quenching values for Methylene Green and a series of quenchers.

Quencher	Quencher E <sub>T</sub> (eV)	k <sub>q</sub> (M <sup>-1</sup> s <sup>-1</sup> )
O <sub>2</sub>	0.91	1.2 × 10 <sup>9</sup>
1,3-diphenylisobenzofuran	1.47	1.6 ± 0.1 × 10 <sup>9</sup>
Perylene <sup>1</sup>	1.53	< 10 <sup>6</sup>

<sup>1</sup>Performed in DMSO.



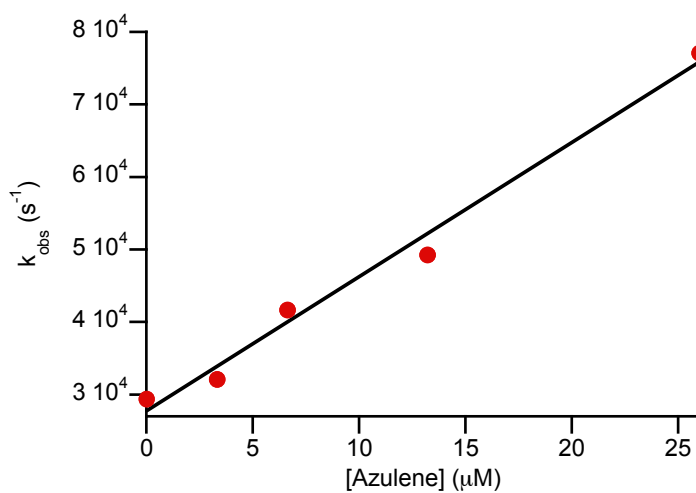
**Figure S55.** Representative kinetic bimolecular quenching plot for <sup>3</sup>Methylene Green and 1,3-diphenylisobenzofuran.



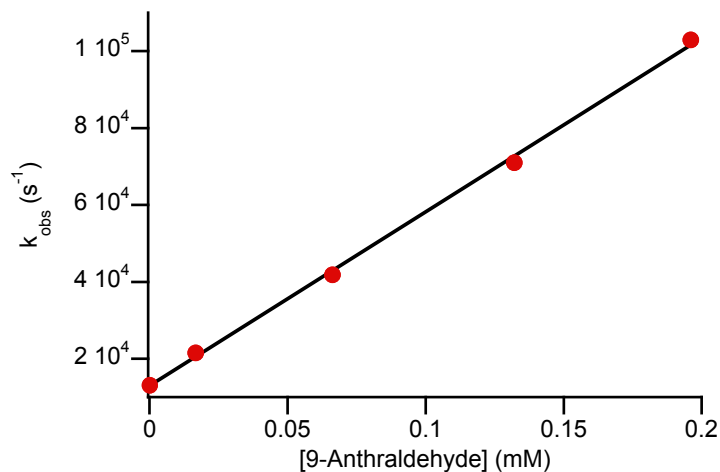
**Figure S56.** Representative kinetic bimolecular quenching plot for <sup>3</sup>Methylene Green and Perylene.

**Table S6.** Bimolecular quenching values for Methylene Violet 3RAX and a series of quenchers.

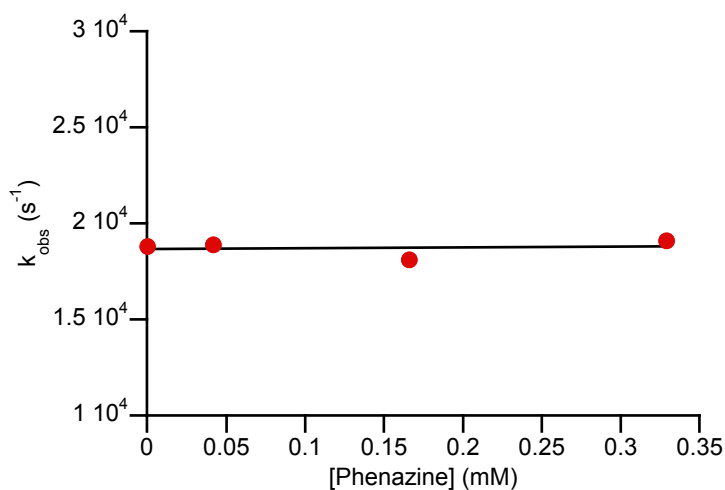
Quencher	Quencher $E_T$ (eV)	$k_q$ ( $M^{-1} s^{-1}$ )
O <sub>2</sub>	0.91	$1.2 \times 10^9$
Azulene	1.69	$1.8 \pm 0.2 \times 10^9$
9-Anthracenecarboxaldehyde	1.89	$4.1 \pm 0.4 \times 10^8$
Phenazine	1.92	$<10^6$



**Figure S57.** Representative kinetic bimolecular quenching plot for <sup>3</sup>Methylene Violet 3RAX and Azulene.



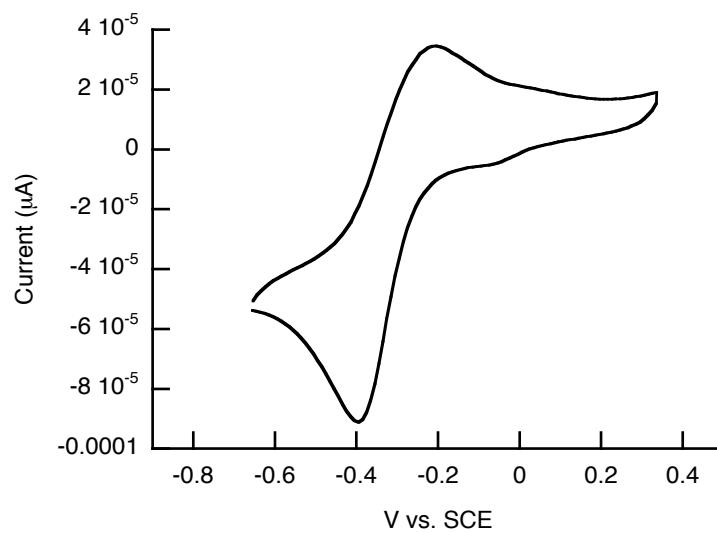
**Figure S58.** Representative kinetic bimolecular quenching plot for  $^3$ Methylene Violet 3RAX and 9-Anthracenecarboxaldehyde.



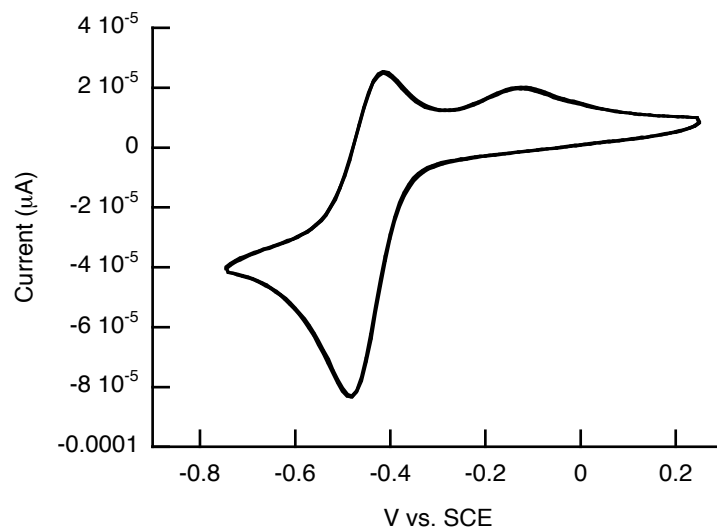
**Figure S59.** Representative kinetic bimolecular quenching plot for  $^3$ Methylene Violet 3RAX and Phenazine.

### O. Electrochemical determination of ground-state reduction potentials

**Conditions for cyclic voltammetry measurements:** scan rate =  $100 \text{ mV s}^{-1}$ ; 0.5-2.0 mM Dye in Ar degassed MeCN containing 100 mM  $\text{Bu}_4\text{NClO}_4$  supporting electrolyte; Pt wire working electrode; Pt wire counter electrode; Ag wire pseudo-reference electrode;  $\text{Fc}/\text{Fc}^+$  redox couple as internal reference (0.41 V vs. SCE); reduction potential reported as peak cathodic ( $E_{\text{pc}}$ ) potentials.

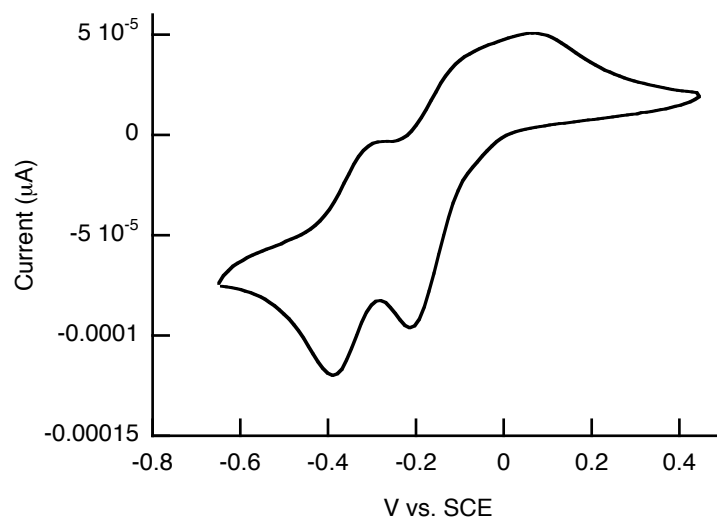


**Figure S60.** Cyclic voltammogram of New Methylene Blue [Cathodic Scan].

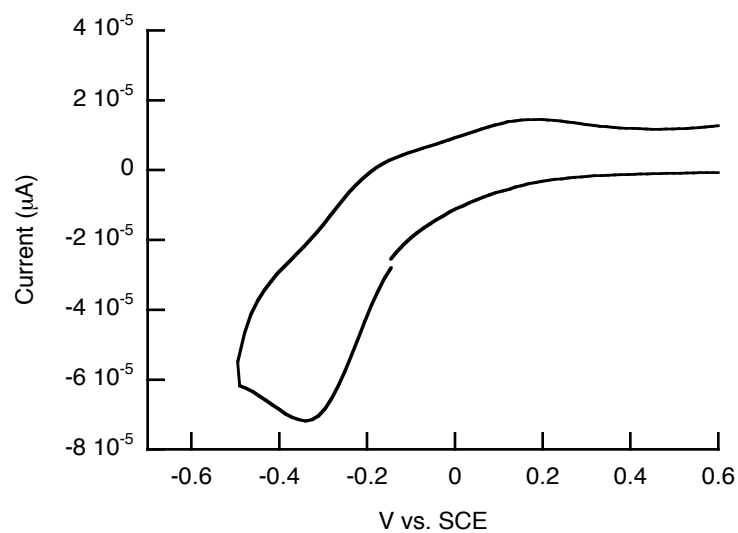


**Figure S61.** Cyclic voltammogram of 1,9-dimethyl Methylene Blue [Cathodic Scan].

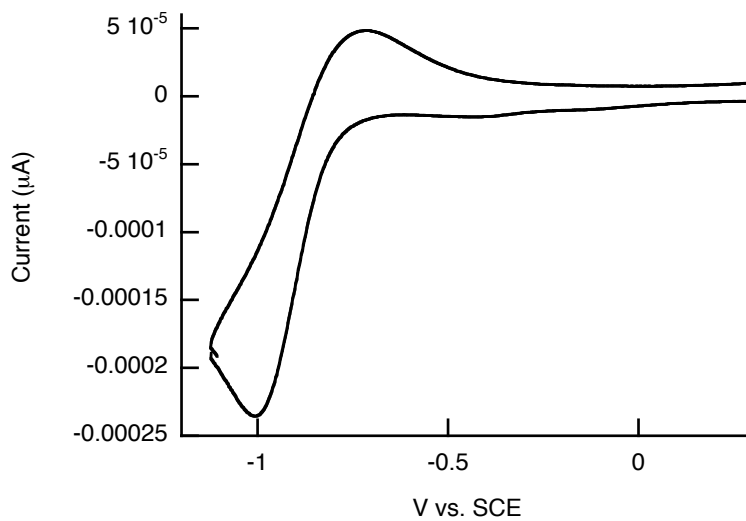




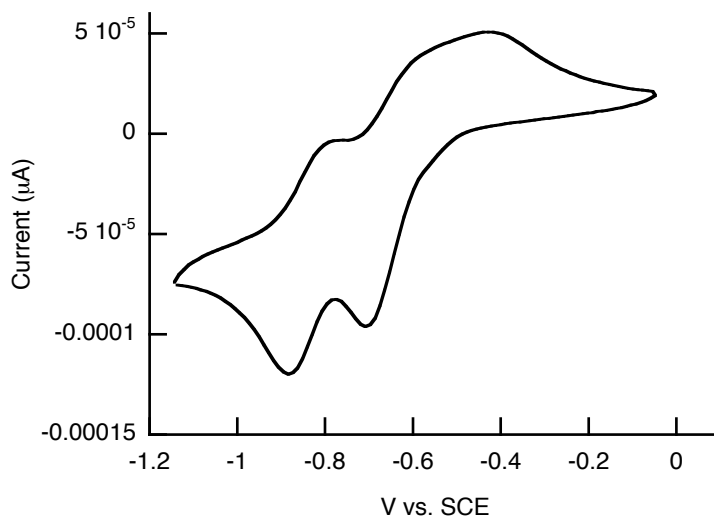
**Figure S62.** Cyclic voltammogram of Methylene Green [Cathodic Scan].



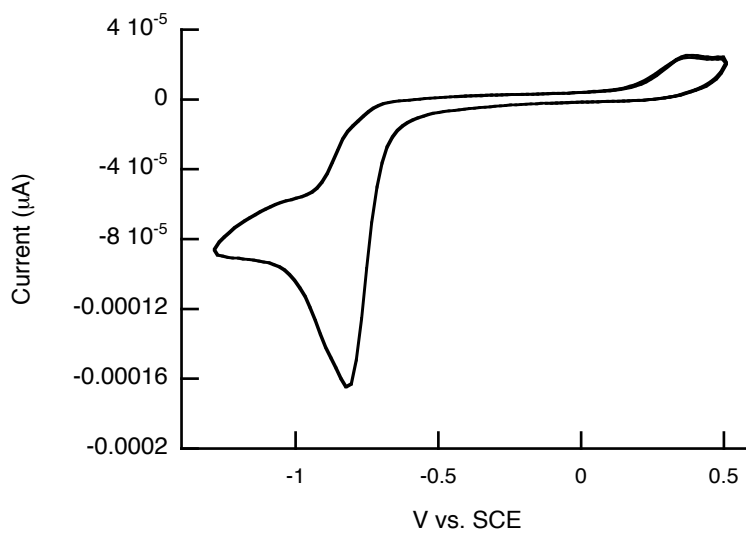
**Figure S63.** Cyclic voltammogram of Brilliant Cresyl Blue [Cathodic Scan].



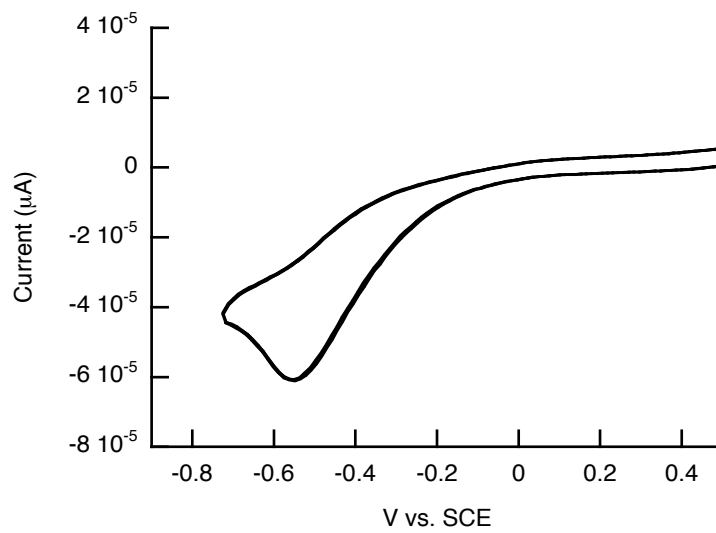
**Figure S64.** Cyclic voltammogram of Nile Blue [Cathodic Scan].



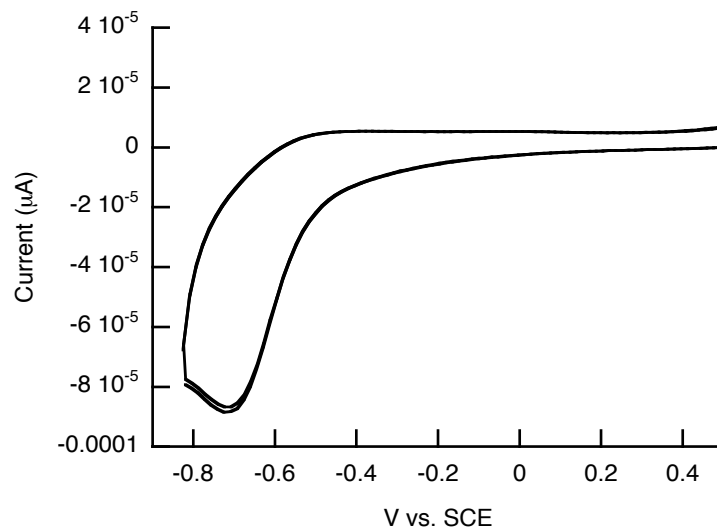
**Figure S65.** Cyclic voltammogram of Pyronin Y [Cathodic Scan].



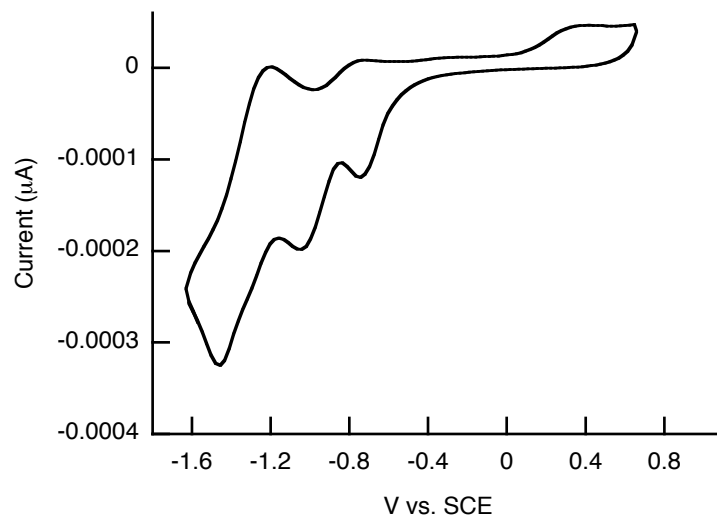
**Figure S66.** Cyclic voltammogram of Rhodamine 6G [Cathodic Scan].



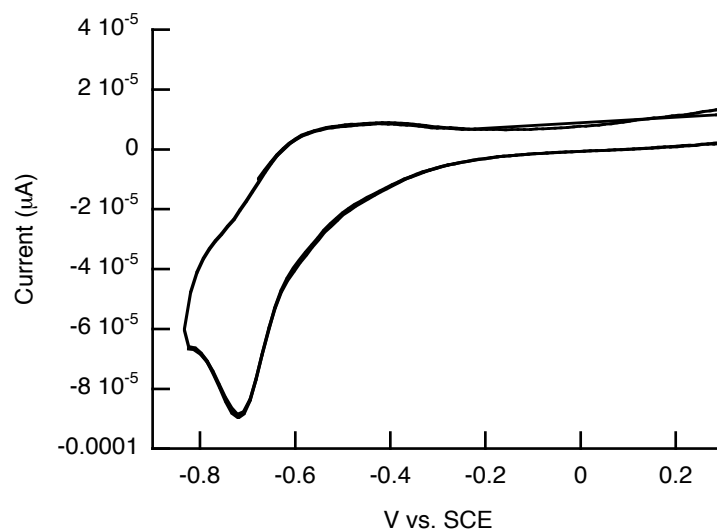
**Figure S67.** Cyclic voltammogram of Rhodamine B [Cathodic Scan].



**Figure S68.** Cyclic voltammogram of Phenosafranin [Cathodic Scan].



**Figure S69.** Cyclic voltammogram of Safranin O [Cathodic Scan].



**Figure S70.** Cyclic voltammogram of Methylene Violet 3RAX [Cathodic Scan].

**P. Concentration of quencher required to quench 50 % and 90 % of excited photocatalyst**

**Table S7.** Concentration of oxygen required to quench 50 % and 90 % of \*PC.

Photocatalyst	Quencher [O <sub>2</sub> ]	
	50 % quench of *PC	90 % quench of *PC
Methylene Blue	1.3x10 <sup>-2</sup> mM	1.1x10 <sup>-1</sup> mM
Thionin	1.1x10 <sup>-1</sup> mM	1.0 mM
New Methylene Blue N	9.2x10 <sup>-2</sup> mM	8.3x10 <sup>-1</sup> mM
1,9-Dimethyl Methylene Blue	6.9x10 <sup>-2</sup> mM	6.3x10 <sup>-1</sup> mM
Methylene Green	3.6x10 <sup>-2</sup> mM	3.2x10 <sup>-1</sup> mM
Brilliant Cresyl Blue	NA	NA
Nile Blue	NA	NA
Pyronin Y	NA	NA
Rhodamine 6G	NA	NA
Rhodamine B	NA	NA
Phenosafranin	9.3x10 <sup>-3</sup> mM	8.4x10 <sup>-2</sup> mM
Safranin O	8.8x10 <sup>-3</sup> mM	7.9x10 <sup>-2</sup> mM
Methylene Violet 3RAX	1.4x10 <sup>-2</sup> mM	1.3x10 <sup>-1</sup> mM
9-Mesityl-10-methylacridinium	5.4x10 <sup>-2</sup> mM	4.9x10 <sup>-1</sup> mM
Ru(bpy) <sub>3</sub> Cl <sub>2</sub>	3.0x10 <sup>-1</sup> mM	2.7 mM
<i>fac</i> -Ir(ppy) <sub>3</sub>	1.2x10 <sup>-2</sup> mM	1.2x10 <sup>-1</sup> mM

Calculation performed with O<sub>2</sub> as sole quencher of \*PC

**Table S8.** Concentration of TMEDA required to quench 50 % and 90 % of \*PC.

Photocatalyst	Quencher [TMEDA]	
	50 % quench of *PC	90 % quench of *PC
Methylene Blue	$9.1 \times 10^{-2}$ mM	$8.3 \times 10^{-1}$ mM
Thionin	$6.9 \times 10^{-3}$ mM	$6.3 \times 10^{-2}$ mM
New Methylene Blue N	$2.8 \times 10^{-2}$ mM	$2.5 \times 10^{-1}$ mM
1,9-Dimethyl Methylene Blue	$1.2 \times 10^{-2}$ mM	$1.0 \times 10^{-1}$ mM
Methylene Green	$7.1 \times 10^{-3}$ mM	$6.4 \times 10^{-2}$ mM
Brilliant Cresyl Blue	$2.0 \times 10^3$ mM	$1.7 \times 10^4$ mM
Nile Blue	$7.6 \times 10^3$ mM	$6.8 \times 10^4$ mM
Pyronin Y	10 mM	93 mM
Rhodamine 6G	27 mM	$2.4 \times 10^2$ mM
Rhodamine B	$2.5 \times 10^{-2}$ mM	$2.2 \times 10^{-1}$ mM
Phenosafranin	$3.3 \times 10^{-3}$ mM	$3.0 \times 10^{-2}$ mM
Safranin O	$7.5 \times 10^{-3}$ mM	$6.7 \times 10^{-2}$ mM
Methylene Violet 3RAX	$4.6 \times 10^{-2}$ mM	$4.1 \times 10^{-2}$ mM
9-Mesityl-10-methylacridinium	$9.9 \times 10^{-4}$ mM	$8.1 \times 10^{-3}$ mM
Ru(bpy) <sub>3</sub> Cl <sub>2</sub>	$7.6 \times 10^2$ mM	$6.8 \times 10^3$ mM
<i>fac</i> -Ir(ppy) <sub>3</sub>	$2.3 \times 10^2$ mM	$2.0 \times 10^3$ mM

Calculation performed with TMEDA as sole quencher of \*PC

**Table S8.** Concentration of PhTHIQ required to quench 50 % and 90 % of \*PC.

Photocatalyst	Quencher [PhTHIQ]	
	50 % quench of *PC	90 % quench of *PC
Methylene Blue	$3.8 \times 10^{-3}$ mM	$3.4 \times 10^{-2}$ mM
Thionin	$1.2 \times 10^{-2}$ mM	$1.0 \times 10^{-1}$ mM
New Methylene Blue N	$1.5 \times 10^{-2}$ mM	$1.4 \times 10^{-1}$ mM
1,9-Dimethyl Methylene Blue	$5.5 \times 10^{-1}$ mM	5.0 mM
Methylene Green	$1.2 \times 10^{-2}$ mM	$1.1 \times 10^{-1}$ mM
Brilliant Cresyl Blue	78 mM	$7.1 \times 10^2$ mM
Nile Blue	41 mM	$3.7 \times 10^2$ mM
Pyronin Y	17 mM	$1.5 \times 10^2$ mM
Rhodamine 6G	13 mM	$1.2 \times 10^2$ mM
Rhodamine B	20 mM	$1.8 \times 10^2$ mM
Phenosafranin	$6.3 \times 10^{-3}$ mM	$5.7 \times 10^{-2}$ mM
Safranin O	$5.5 \times 10^{-3}$ mM	$4.9 \times 10^{-2}$ mM
Methylene Violet 3RAX	$1.5 \times 10^{-3}$ mM	$1.4 \times 10^{-2}$ mM
9-Mesityl-10-methylacridinium	$5.2 \times 10^{-3}$ mM	$4.7 \times 10^{-2}$ mM
Ru(bpy) <sub>3</sub> Cl <sub>2</sub>	31 mM	$2.8 \times 10^2$ mM
<i>fac</i> -Ir(ppy) <sub>3</sub>	19 mM	$1.7 \times 10^2$ mM

Calculation performed with PhTHIQ as sole quencher of \*PC

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