General

Commercial chemicals were used as obtained from Sigma-Aldrich or Fisher. Solvents were used without further purification. DMSO was dried over molecular sieves (certified <0.005% water content, Sigma-Aldrich). TLC was performed using commercial silica gel coated aluminium plates (DC60 F254, Merck). Visualization was done by UV light. Product yields were determined as isolated by column chromatography using silica gel (Acros Organics, mesh 35-70). Purity and structure confirmation was done by ^{1}H NMR, ^{13}C NMR, GC-MS, and ^{19}F NMR (where appropriate). NMR spectral data were collected on a Bruker Avance 300 (300 MHz for ^{1}H spectra; 75 MHz for ^{13}C spectra) spectrometer and a Bruker Avance 400 (400 MHz for ^{1}H spectra; 100 MHz for ^{13}C spectra; 376 MHz for ^{19}F spectra) spectrometer at 25 °C. Chemical shifts are reported in δ/ppm, and coupling constant *J* given in Hertz. Solvent residual peak were used as internal referecnce for all NMR measurements. The number of protons was obtained by integration of appropriate signals. Abbreviations used in NMR spectra: s – singlet, d – doublet, t – triplet, q – quartet, m – multiplet, bs – broad singlet, dd – doublet of doublet, ddd – doublet of doublet of doublet.

General Procedure for the Synthesis of Arenediazonium salts

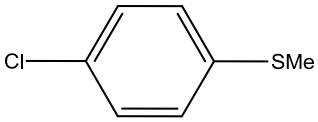
The parent aniline (4.5 mmol) was dissolved in glacial acetic acid (3 mL) and 48 % aqueous solution of tetrafluoroboric acid (1.3 mL). Then, an isoamylnitrite (1 mL) solution in glacial acetic acid (2 mL) was slowly added at room temperature during 5 min. Diethylether (15 mL) was added, and reaction mixture was cooled down to -30 °C in order to induce crystallization of the product. Crystals were filtered off *in vacuo*, washed with diethylether (2 x 10 mL) and dried on air to furnish the corresponding diazonium salts.

General Procedure for Photo-Catalytic Thiolation

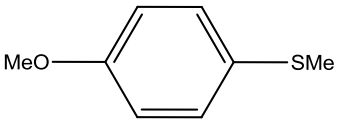
A 10 mL Schlenk flask was charged with the arenediazonium salt (0.5 mmol) and eosin Y (0.01 mmol). Dry DMSO (2 mL) was added under a stream of nitrogen. Then, nitrogen was bubbled through the solution during vigorous stirring for 15 min. Dimethyldisulfide (67 µL, 0.75 mmol) was added and the reaction vessel was sealed with a rubber septum. The reaction mixture was irradiated with green light (LED, λ_{max} = 525 nm, 3.8 W) for 12 h at 18°C (= r.t.). Deionized water (3 mL) was added to the reaction mixture, and the resulting emulsion was extracted with diethylether (2 x 5 mL). The combined organic extracts were washed with brine (5 mL) and dried over $MgSO_4$. The solvent was evaporated *in vacuo*, and the residue was purified by flash column chromatography (silica gel) using pentane/diethylether mixtures (from 100/0 to 80/20) as eluent to obtain pure product.

Products

4-Chlorothioanisole

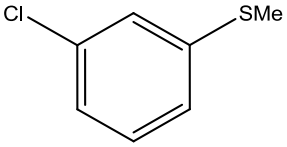


^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.26 (d, *J* = 8.7 Hz, 2H), 7.18 (d, *J* = 8.7 Hz, 2H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 137.3 (C), 131.0 (C), 128.9 (CH), 128.0 (CH), 16.2 (CH_3). GC-MS (EI) *m/z* (relative intensity): 160.0 (35) [M^+], 158.0 (100), 145.0 (22), 143.0 (55).



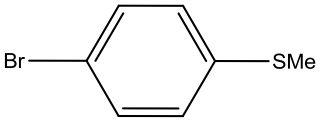
4-(Methylthio)anisole

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.28 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 3.79 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 157.3 (C), 129.2 (CH), 128.0 (C), 113.7 (CH), 54.3 (CH_3), 17.2 (CH_3). GC-MS (EI) *m/z* (relative intensity): 154.0 (94) [M^+], 139.0 (100), 111.0 (23), 96.0 (19).



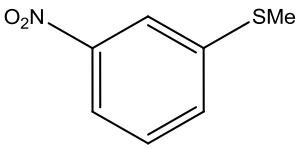
3-Chlorothioanisole

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.21 (t, *J* = 1.9 Hz, 1H), 7.19 (d, *J* = 7.8 Hz, 1H), 7.13 – 7.08 (m, 2H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 140.7 (C), 134.8 (C), 129.8 (CH), 125.8 (CH), 125.1 (CH), 124.5 (CH), 15.6 (CH_3). GC-MS (EI) *m/z* (relative intensity): 160.0 (36) [M^+], 158.0 (100), 127.0 (18), 125.0 (27).



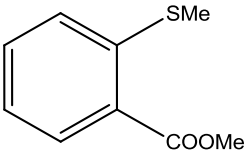
4-Bromothioanisole

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.39 (d, *J* = 8.6 Hz, 2H), 7.11 (d, *J* = 8.6 Hz, 2H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 137.8 (C), 131.8 (CH), 128.2 (CH), 118.7 (C), 19.9 (CH_3), 16.0 (CH_3). GC-MS (EI) *m/z* (relative intensity): 204.0 (100) [M^+], 202.0 (98), 188.9 (34), 186.9 (34), 108.0 (99).



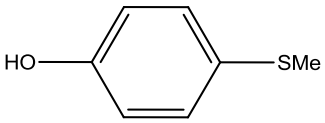
3-Nitrothioanisole

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.00 (t, *J* = 2.0 Hz, 1H), 7.91 (ddd, *J* = 8.1 Hz, *J* = 2.0 Hz, *J* = 1.0 Hz, 1H), 7.48 (ddd, *J* = 7.9 Hz, *J* = 1.8 Hz, *J* = 1.0 Hz, 1H), 7.39 (t, *J* = 8.0 Hz, 1H), 2.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 147.8 (C), 140.6 (C), 130.9 (CH), 128.4 (CH), 119.2 (CH), 118.7 (CH), 14.4 (CH_3). GC-MS (EI) *m/z* (relative intensity): 169.0 (100) [M^+], 123.0 (36), 108.0 (41).



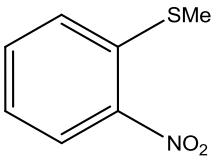
Methyl *S*-methylthiosalicylate

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.00 (dd, *J* = 7.8 Hz, *J* = 1.5 Hz, 1H), 7.91 (ddd, *J* = 8.2 Hz, *J* = 7.4 Hz, *J* = 1.5 Hz, 1H), 7.27 (d, *J* = 8.2 Hz, 1H), 7.15 (ddd, *J* = 8.0 Hz, *J* = 7.8 Hz, *J* = 1.0 Hz, 1H), 3.92 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 167.0 (C), 143.5 (C), 132.5 (CH), 131.4 (CH), 126.9 (C), 124.3 (CH), 123.6 (CH), 52.1 (CH_3), 15.6 (CH_3). GC-MS (EI) *m/z* (relative intensity): 182.0 (89) [M^+], 167.0 (32), 151.0 (100).



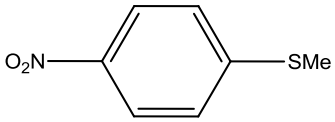
4-Hydroxythioanisole

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.23 (d, *J* = 8.8 Hz, 2H), 6.79 (d, *J* = 8.8 Hz, 2H), 4.88 (bs, 1H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 153.1 (C), 129.4 (CH), 128.0 (C), 115.1 (CH), 17.1 (CH_3). GC-MS (EI) *m/z* (relative intensity): 140.0 (97) [M^+], 125.0 (100), 97.0 (33).



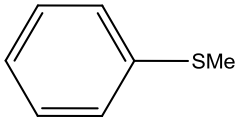
2-Nitrothioanisole

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.26 (dd, *J* = 8.3 Hz, *J* = 1.5 Hz, 1H), 7.59 (ddd, *J* = 8.6 Hz, *J* = 7.3 Hz, *J* = 1.5 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.26 (ddd, *J* = 8.0 Hz, *J* = 7.3 Hz, *J* = 1.3 Hz, 1H), 2.50 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 145.4 (C), 139.4 (C), 133.7 (CH), 126.3 (CH), 125.7 (CH), 124.2 (CH), 16.1 (CH_3). GC-MS (EI) *m/z* (relative intensity): 169.0 (39) [M^+], 108.0 (35), 96.0 (33), 78.0 (100).



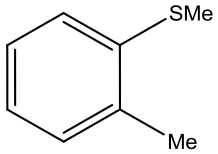
4-Nitrothioanisole

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.08 (d, *J* = 9.0 Hz, 2H), 7.24 (d, *J* = 9.0 Hz, 2H), 2.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 147.9 (C), 143.8 (C), 124.0 (CH), 122.9 (CH), 13.9 (CH_3). GC-MS (EI) *m/z* (relative intensity): 169.0 (100) [M^+], 139.0 (72), 123.0 (14), 108.0 (38).



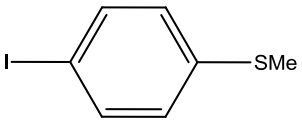
Thioanisole

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.32 – 7.25 (m, 4H), 7.17 – 7.11 (m, 1H), 2.49 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 138.4 (C), 128.9 (CH), 126.7 (CH), 125.1 (CH), 15.9 (CH_3). GC-MS (EI) *m/z* (relative intensity): 124.0 (100) [M^+], 109.0 (56), 91.0 (40), 78.0 (48).



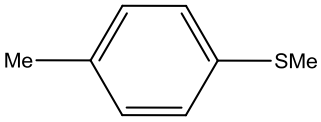
2-Methylthioanisole

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.23 – 7.13 (m, 3H), 7.09 – 7.04 (m, 1H), 2.47 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 137.6 (C), 135.8 (C), 129.8 (CH), 126.3 (CH), 124.6 (2x CH), 20.0 (CH_3), 15.3 (CH_3). GC-MS (EI) *m/z* (relative intensity): 138.1 (100) [M^+], 123.0 (65), 91.0 (70).



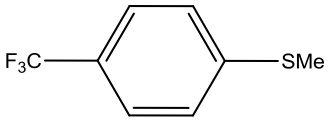
4-Iodothioanisole

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.58 (d, *J* = 8.6 Hz, 2H), 6.99 (d, *J* = 8.6 Hz, 2H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 138.7 (C), 137.7 (CH), 128.3 (CH), 89.3 (C), 15.7 (CH_3). GC-MS (EI) *m/z* (relative intensity): 249.9 (100) [M^+], 234.9 (22), 126.9 (20), 108.0 (41).



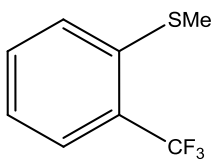
4-Methylthioanisole

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.19 (d, *J* = 8.2 Hz, 2H), 7.10 (d, *J* = 8.2 Hz, 2H), 2.47 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 134.1 (C), 133.7 (C), 128.6 (CH), 126.3 (CH), 19.9 (CH_3), 15.6 (CH_3). GC-MS (EI) *m/z* (relative intensity): 138.0 (100) [M^+], 123.0 (37), 91.0 (85).



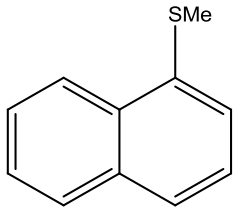
4-(Trifluoromethyl)thioanisole

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.52 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 2.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 143.9 (C), 126.8 (q, *J* = 32.7 Hz, C), 125.6 (CH), 125.5 (q, *J* = 3.8 Hz, C), 124.4 (q, *J* = 271.6 Hz, CF_3), 15.1 (CH_3). ^{19}F NMR (376 MHz, $CDCl_3$, ppm) -62.3 (s, CF_3). GC-MS (EI) *m/z* (relative intensity): 192.0 (100) [M^+], 173.0 (16), 159.1 (36).



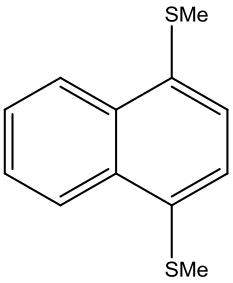
2-(Trifluoromethyl)thioanisole

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.63 (d, *J* = 7.8 Hz, 1H), 7.48 (t, *J* = 7.3 Hz, 1H), 7.38 (d, *J* = 7.9 Hz, 1H), 7.23 (t, *J* = 6.7 Hz, 1H), 2.52 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 137.3 (C), 130.1 (CH), 127.2 (q, *J* = 30.3 Hz, C), 126.5 (CH), 125.6 (q, *J* = 5.7 Hz, CH), 123.0 (q, *J* = 273.8 Hz, CF_3), 123.7 (CH), 15.4 (CH_3). ^{19}F NMR (376 MHz, $CDCl_3$, ppm) -61.5 (s, CF_3). GC-MS (EI) *m/z* (relative intensity): 192.0 (100) [M^+], 177.0 (14), 171.0 (15), 159.1 (33).



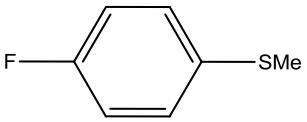
1-Methylthionaphthalene

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.28 (d, *J* = 8.3 Hz, 1H), 7.84 (d, *J* = 7.6 Hz, 1H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.57 – 7.49 (m, 2H), 7.45 – 7.37 (m, 2H), 2.58 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 135.8 (C), 133.7 (C), 131.7 (C), 128.6 (CH), 126.2 (CH), 126.1 (CH), 125.9 (CH), 125.7 (CH), 124.3 (CH), 123.7 (CH), 16.3 (CH_3). GC-MS (EI) *m/z* (relative intensity): 174.1 (100) [M^+], 159.0 (53), 128.1 (25), 115.1 (92).



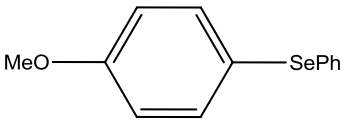
1,4-Bis(methylthio)naphthalene

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.36 – 8.31 (m, 2H), 7.61 – 7.56 (m, 2H), 7.38 (s, 2H), 2.55 (s, 6H).^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 133.8 (2 x C), 132.1 (2 x C), 126.6 (2 x CH), 125.1 (2 x CH), 124.5 (2 x CH), 16.8 (2 x CH_3). GC-MS (EI) *m/z* (relative intensity): 220.0 (100) [M^+], 205.0 (95), 190.0 (21), 171.1 (23), 158.0 (35).



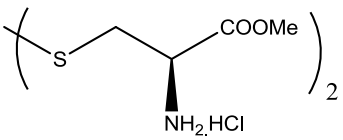
4-Fluorothioanisole

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.29 – 7.22 (m, 2H), 7.04 - 6.98 (m, 2H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 160.1 (d, *J* = 246.6 Hz, C), 132.3 (C), 128.2 (d, *J* = 7.9 Hz, CH), 114.9 (d, *J* = 21.9 Hz, CH), 16.2 (CH_3). ^{19}F NMR (376 MHz, $CDCl_3$, ppm) -117.3 (s, F). GC-MS (EI) *m/z* (relative intensity): 142.0 (100) [M^+], 127.0 (19), 109.0 (18), 96.0 (21), 83.0 (37).



(4-Methoxyphenyl)(phenyl)selane

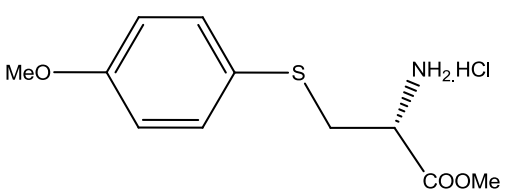
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.51 (d, *J* = 8.8 Hz, 2H), 7.37 – 7.19 (m, 5H), 6.86 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 158.9 (C), 135.5 (CH), 132.2 (C), 129.9 (CH), 128.0 (CH), 125.4 (CH), 118.9 (C), 114.2 (CH), 54.2 (CH_3). GC-MS (EI) *m/z* (relative intensity): 263.9 (44) [M^+], 184.0 (100), 169.0 (46), 141.0 (38).



Cystine dimethylester dihydrochloride

To a suspension of cystine (0.8 g, 3.33 mmol) in dry methanol (20 mL), thionyl chloride (0.6 mL, 8.27 mmol) was added slowly at room temperature. The temperature was increased to 80 °C over period of 15 min, and the reaction mixture was stirred at this temperature for 3 h, then left to cool down and stirred overnight at room temperature. The volatiles were evaporated *in vacuo*, and the residue was dissolved in a minimal amount of methanol. Crystals of crude product crashed out from the solution by addition of diethylether. The product was filtered *in vacuo*, washed two times with diethylether and dried on air to obtain white crystals of cystine dimethylester dihydrochloride (1.04 g, 3.05 mmol, 92 %).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.98 (bs, 6H), 4.34 (t, *J* = 5.7 Hz, 2H), 3.75 (s, 6H), 3.43 - 3.26 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 172.0 (C), 56.8 (CH_3), 54.2 (CH), 38.5 (CH_2).

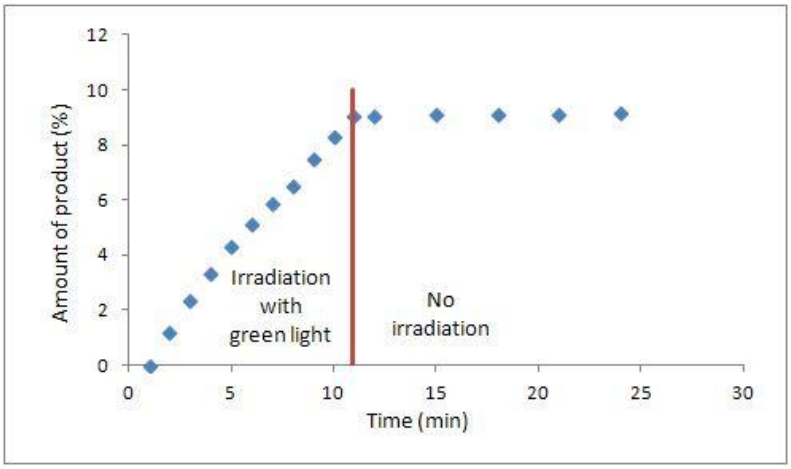


(*R*)-Methyl 2-amino-3-((4-methoxyphenyl)thio)propanoate hydrochloride

A dry Schlenk flask was charged with *p*-methoxyphenyldiazonium tetrafluoroborate (111 mg, 0.5 mmol), eosin Y (6 mg, 0.01 mmol) and cystine dimethylester dihydrochloride (205 mg, 0.6 mmol). Dry DMSO (4 mL) was added under a stream of nitrogen, and nitrogen was bubbled through reaction solution during vigorous stirring for 15 min, after which the reaction vessel was sealed. The mixture was irradiated with green light for 12 h at r.t. Then, water (5 mL) was added to the reaction mixture, and aqueous NaOH solution was added until pH 12. The mixture was extracted with ethyl acetate (2 x 7 mL), the combined organic extracts were washed with brine (5 mL) and dried over $MgSO_4$. The solvent was evaporated *in vacuo*, and the residue was dissolved in a minimal amount of diethyl ether. A stream of dry HCl gas was introduced into solution. The crystals that have crashed out were filtered *in vacuo*, washed with diethyl ether and dried in high vacuum to obtain (*R*)-methyl 2-amino-3-((4-methoxyphenyl)thio)propanoate hydrochloride (98 mg, 0.35 mmol, 71 %) as tan crystals, that turn blue on prolonged exposure on air.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.99 (bs, 3H), 7.53 (d, *J* = 8.8 Hz, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 4.37 – 4.25 (m, 1H), 3.86 – 3.76 (m, 2H), 3.75 (s, 3H), 3.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 168.2 (C), 159.9 (C), 135.5 (CH), 122.9 (C), 114.8 (CH), 55.4 (CH_3), 53.2 (CH), 52.3 (CH_3), 36.4 (CH_2). GC-MS (EI) (after neutralization of HCl salt with Na_2CO_3) *m/z* (relative intensity): 241.0 (51) [M^+], 193.9 (15), 153.0 (50), 139.0 (81), 124.9 (60), 108.0 (100).

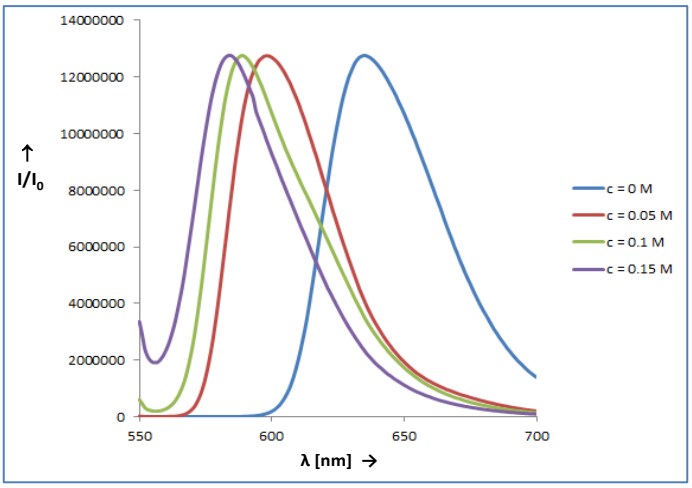
NMR Monitoring of Reaction Progress: Irradiation vs. Dark reaction



A dry Schlenk flask was charged with *p*-methoxyphenyldiazonium tetrafluoroborate (0.1 mmol) and eosin Y (0.005 mmol). Dry DMSO-d_6 (0.7 mL) was added under a stream of nitrogen. Then, nitrogen was bubbled through the solution during vigorous stirring for 15 min. Dimethyldisulfide (16 µL, 0.18 mmol) was added and the reaction mixture was transferred to a dry, argon-purged NMR tube and sealed. The NMR tube was irradiated with green light for 30 sec, and a ^{1}H NMR spectrum was immediately recorded. This routine was repeated another 10 times, after which the irradiation was stopped. Then, another five ^{1}H NMR spectra were measured over 12 minutes. The amount of product formed was determined by comparing integral intensities of protons of product vs. the parent diazonium salt.

Fluorescence Quenching

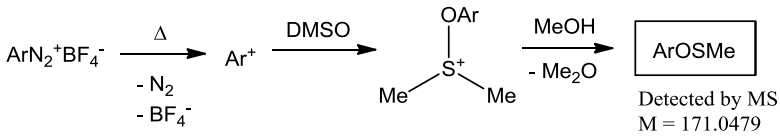
Fluorescence spectra of solutions of *para*-methoxyphenyldiazonium tetrafluoroborate (0, 0.05, 0.1, 0.15 M) and eosin Y disodium salt ($2 \cdot 10^{-6}$ M) in dry DMSO-d_6 were recorded (λ_{ex} = 525 nm, absorbance A_{525} = 0.27). No quenching of fluorescence was observed, but blue-shifted emission maxima (635 nm → 584 nm). This hypsochromic shift could be a consequence of H-aggregates or π-stacking. The lack of fluorescence quenching is indicative of reaction pathways involving eosin Y in the triplet-state. See also ref. 21b in manuscript.



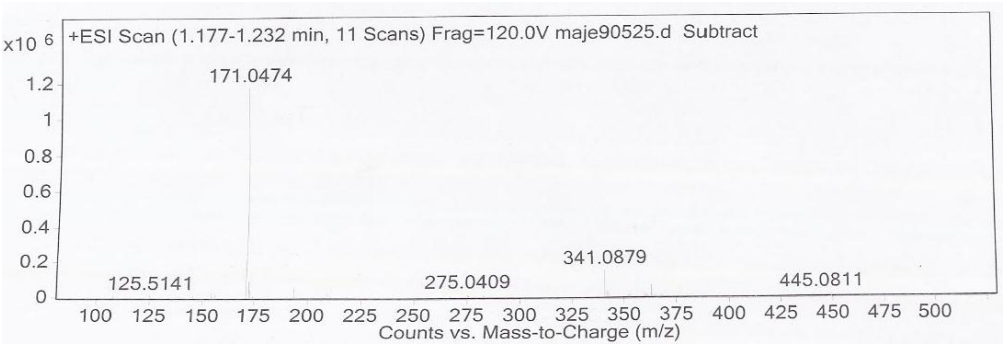
By-Product from Thermal Decomposition of Arenediazonium Salt

A reaction was performed under standard reaction conditions, using *p*-methoxyphenyldiazonium tetrafluoroborate and dimethyl disulfide. After the termination of irradiation, a high vacuum was applied to the flask, and all volatiles were distilled off at 130 °C. The residue was dissolved in

methanol and subjected to MS analysis. The major by-product detected by MS was $[Ar\text{-}OSMe]^+$ with Ar = 4-MeOPh and could have formed via the following mechanism:



Detected by MS
M = 171.0479



Selected Spectra of Synthesized Compounds