Electronic supplementary information for:
Tailoring flavins for visible light photocatalysis: Organocatalytic [2+2] cycloaddition mediated by flavin derivative and visible light

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1 Synthetic procedures and characterizations

1.1 General procedures

NMR spectra were recorded with an Agilent 400-MR DDR2 (399.94 MHz for $^1$H and 100.58 MHz for $^{13}$C), a Varian Mercury Plus 300 (299.97 MHz for $^1$H, 75.44 MHz for $^{13}$C and 282.23 MHz for $^{19}$F), a Bruker Avance III 600 MHz (600.13 MHz for $^1$H and 150.92 MHz for $^{13}$C) and a Bruker Avance III 500 MHz (500.13 MHz for $^1$H, 470.39 MHz for $^{19}$F and 125.77 MHz for $^{13}$C) at 298 K. Chemical shifts $\delta$ are given in ppm using residual solvent or tetramethylsilane as an internal standard for $^1$H and $^{13}$C NMR and CFC-11 for $^{19}$F NMR. High-resolution mass spectra were obtained on an LTQ Orbitrap Velos (Thermo Fisher Scientific), equipped with an orbitrap mass analyzer. The mass spectrometer was operated in ESI mode (ESI source temperature 250 °C, potential 3000 V) and in APCI mode (APCI source temperature 250 °C, spray current 4.0 μA) with a mass range from 200 to 2000 a.m.u. UV-VIS spectra were measured in quartz cuvettes (d = 1 cm) on a Varian Cary 50 spectrophotometer against a pure solvent. TLC analyses were carried out on a DC Alufolien Kieselgel 60 F254 (Merck). Preparative column chromatography separations were performed on a silica gel Kieselgel 60 (0.040–0.063 mm) (Merck). Melting points were measured on a Boetius melting point apparatus and are uncorrected. Starting materials, reagents and substrates were obtained from commercial suppliers and used without further purification. The solvents were purified and dried using standard procedures. 6-Chloro-3-methyluracil 13 was prepared according to the known procedure.1

1.2 Synthesis of catalyst 2

6-(3,4-Dimethoxyphenylamino)-3-methyluracil (14)$^2$

A mixture of 6-chloro-3-methyluracil 13 (0.35 g, 2.18 mmol) and 3,4-dimethoxyaniline (1.0 g, 6.54 mmol) was stirred and heated at 120 °C for 3 h. After cooling, the mixture was treated with ether. Crude product was filtered and washed with methanol and acetone to obtain white powder (0.50 g, 83 %, m.p. 304–306 °C). $^1$H NMR (300 MHz, DMSO-$d_6$) $\delta$ 10.47 (brs, 1H), 7.98 (s, 1H), 6.95 (d, $J = 8.5$ Hz, 1H), 6.81 (d, $J = 2.3$ Hz, 1H), 6.75 (dd, $J = 8.5, 2.4$ Hz, 1H), 4.65 (d, $J = 1.9$ Hz, 1H), 3.75 (s, 3H), 3.74 (s, 3H), 3.05 (s, 3H). $^{13}$C NMR (75 MHz, DMSO-$d_6$) $\delta$ 163.9,
HR-MS (ESI+): For C_{13}H_{16}N_{3}O_{4}^{+} [M+H]^{+} calculated 278.11353, found 278.11362, for C_{13}H_{15}N_{3}O_{4}Na^{+} [M+Na]^{+} calculated 300.09548, found 300.09583.

1-Butyl-7,8-dimethoxy-3-methylalloxizin (2)^{3}

Into the vigorously stirred suspension of uracil 14 (0.45 g, 1.6 mmol) in 4 mL of acetic acid, sodium nitrite (0.55 g, 8.0 mmol) was added by small portions. After 10 min, mixture was diluted by water (30 mL). Crude product was isolated by filtration and washed with water, acetone, and ether. Yellow–green very fine powder (0.42 g, m. p. > 300 °C decomp.), containing 7,8-dimethoxy-3-methylalloxazin and 7,8-dimethoxy-3-methylalloxazin-5-oxide (cca 7 : 4), as unseparable products was used for further synthesis without purification. ^{1}H NMR (300 MHz, DMSO-d_{6}) alloxazine set of signals: δ 12.05 (s, 1H), 7.51 (s, 1H), 7.21 (s, 1H), 4.00 (s, 3H), 3.96 (s, 3H), 3.30 (s, 3H); alloxazine-5-oxide set of signals: δ 12.01 (s, 1H), 7.61 (s, 1H), 7.14 (s, 1H), 3.98 (s, 3H), 3.95 (s, 3H), 3.21 (s, 3H). MS (ESI, DMSO): m/z (%): 287.1 (65) [M_{A} - H]^ {+}, 303.1 (100) [M_{B} - H]^ {+}.

The mixture of alloxazine and alloxazine-5-oxide (0.30 g) was suspended in dry DMSO (15 mL). After addition of finely powdered dry potassium carbonate (0.86 g, 6.2 mmol), flavin compounds dissolved into dark yellow solution. Then butyl bromide (450 µL, 4.2 mmol) was added
and the reaction mixture was stirred under argon for 3 days. Reaction was monitored by TLC. The mixture was acidified with acetic acid (5 mL), diluted with water (100 mL) and extracted with ethyl acetate (2×125 mL). Collected organic layers were dried over MgSO₄ and evaporated. Light yellow solid was diluted in acetic acid (100 mL), palladium on charcoal (10%, 15 mg, 14μmol) was added and the reaction mixture was stirred in autoclave under hydrogen (10 BAR) overnight. Hydrogenation catalyst was removed from the mixture by filtration through funnel with celite. Acetic acid was evaporated, light yellow solid was dried in vacuo. Product was purified by flash column chromatography (hexane/ethyl acetate ~ 1:1) and recrystallized from acetic acid/water. Obtained very fine light yellow needles still contained acetic acid. Short treatment in boiling ether resulted pure product (0.32 g, 0.93 mmol, 80% over 3 steps), m. p. 257–261 °C. ¹H NMR (300 MHz, CDCl₃) δ 7.57 (s, 1H), 7.24 (s, 1H), 4.46–4.38 (m, 2H), 4.12 (s, 3H), 4.04 (s, 3H), 3.58 (s, 3H), 1.84–1.71 (m, 2H), 1.57–1.37 (m, 2H), 1.00 (t, J = 7.3 Hz, 3H).¹³C NMR (101 MHz, CDCl₃) δ 160.4, 156.5, 152.5, 150.5, 144.4, 141.9, 137.4, 126.4, 107.4, 105.0, 56.7, 56.5, 42.4, 29.8, 29.0, 20.1, 13.9. HR-MS (ESI⁺): For C₁₇H₂₁N₄O₄ [M+H]⁺ calculated 345.15573, found 345.15586, for C₁₇H₂₀N₄O₄Na⁺ [M+Na]⁺ calculated 367.13768, found 367.13795, for C₁₇H₂₀N₄O₄K⁺ [M+K]⁺ calculated 383.11161, found 383.11163.

1.3 Syntheses of substrates

(E)-3-(4-Methoxyphenyl)prop-2-en-1-ol (15)₄

(E)-3-(4-Methoxyphenyl)prop-2-enal (23 g, 0.14 mol) was dissolved in dry methanol (230 mL) under argon. The solution was cooled to 0 °C, then sodium borohydride was added (3.9 g, 0.10 mol). The reaction mixture was stirred at room temperature for 1 h, then water was added dropwise for quenching. The mixture was extracted with ether (3×200 mL). Collected organic phases were washed with brine, dried over MgSO₄ and evaporated. By recrystallization from toluene/hexane, white flakes (20.4 g, 87%) were obtained, m. p. 76–78 °C (lit.⁵ 72–75 °C). ¹H NMR (300 MHz, CDCl₃) δ 7.36–7.30 (m, 2H), 6.89–6.83 (m, 2H), 6.56 (d, J = 15.9 Hz, 1H), 6.24 (dt, J = 15.8, 5.9 Hz, 1H), 4.30 (d, J = 4.8 Hz, 2H), 3.81 (s, J = 2.5 Hz, 3H), 1.40 (s, 1H).
\[(E)-3-(4-Methoxyphenyl)prop-2-en-1-yl 3-methylbut-2-en-1-yl ether (3a)^6\]

\[\begin{align*}
\text{MeO} & \quad \text{OH} & \quad \text{NaH} & \quad \text{THF} & \quad \text{MeO} \\
& \quad \text{Br} & \quad \text{MeO} & \quad \text{O}
\end{align*}\]

Into the suspension of sodium hydride (60% w/w in mineral oil, 0.59 g, 14.6 mmol) in dry THF (20 mL), a solution of alcohol \(15\) (2.00 g, 12.2 mmol) in dry THF (25 mL) was added dropwise under argon. The reaction mixture was cooled to 0 °C and a solution of 1-bromo-3-methylbut-2-ene (90%, 2.47 g, 14.9 mmol) in dry THF (22 mL) was added slowly by a syringe. Mixture was stirred at r.t. for 3 days and the reaction was quenched by adding aqueous solution of ammonium chloride. Phases were separated and the water phase was extracted with ether. Combined organic phases were washed with brine, dried over MgSO\(_4\) and evaporated. Crude product was purified by flash column chromatography (hexane/ethyl acetate). Clear oil (1.83 g, 65 %) was obtained. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.38–7.28 (m, 2H), 6.92–6.79 (m, 2H), 6.55 (dt, \(J = 15.9, 1.4\) Hz, 1H), 6.18 (dtd, \(J = 15.9, 6.2, 0.5\) Hz, 1H), 5.39 (dddt, \(J = 7.6, 7.0, 2.8, 1.4\) Hz, 1H), 4.11 (dd, \(J = 6.2, 1.4\) Hz, 2H), 4.01 (dddd, \(J = 7.7, 1.9, 1.2, 0.7\) Hz, 2H), 3.81 (s, 3H), 1.76 (d, \(J = 1.2\) Hz, 3H), 1.69 (dd, \(J = 1.2, 0.6\) Hz, 3H).

\[(E)-3-Phenylprop-2-en-1-yl 3-methylbut-2-en-1-yl ether (3b)^6\]

\[\begin{align*}
\text{MeO} & \quad \text{OH} & \quad \text{NaH} & \quad \text{THF} & \quad \text{MeO} \\
& \quad \text{Br} & \quad \text{MeO} & \quad \text{O}
\end{align*}\]

\((E)-3\)-Phenylprop-2-en-1-ol (1.68 g, 12.5 mmol) was dissolved in dry THF (10 mL). Sodium hydride (60% w/w in mineral oil, 0.64 g, 16.0 mmol) was added and the reaction mixture was stirred under argon for 10 min. Then a solution of 1-bromo-3-methylbut-2-ene (90%, 2.25 g, 13.6 mmol) in dry THF (10 mL) was added dropwise. Reaction was quenched after 2 days by addition of water (20 mL). Phases were separated, water phase was extracted with ether (\(3 \times 30\) mL), collected organic phases were washed with brine, dried over MgSO\(_4\) and evaporated. Crude product was purified by vacuum distillation resulting colorless oil (1.72 g, 68 %). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.41–7.20 (m, 5H), 6.61 (d, \(J = 16.0\) Hz, 1H), 6.31 (dt, \(J = 15.9, 6.0\) Hz, 1H), 5.44–5.36 (m, 1H), 4.14 (dd, \(J = 6.1, 1.4\) Hz, 2H), 4.02 (d, \(J = 7.0\) Hz, 2H), 1.77 (s, 3H), 1.69 (s, 3H).
The solution of ethyl \((E)-3-(4\text{-bromophenyl})\text{prop-2-en-1-oate}\) (2.0 g, 98%, 7.7 mmol) in dry dichloromethane (23 mL) was cooled to -78 °C under argon. In cca 40 min, 1M solution of diisobutylaluminium hydride (16.5 mL, 16.5 mmol) in toluene was added dropwise into the solution. Reaction was monitored by TLC. The reaction was quenched after 30 min by adding 10% solution of sodium hydroxide in water (30 mL) and the reaction mixture was stirred until room temperature was achieved. Phases were separated, water phase was extracted with dichloromethane (3 × 30 mL), collected organic phases were dried over MgSO₄ and evaporated. White crystals (1.63 g, 99%) were pure enough for further synthesis, m. p. 64–67 °C (lit. 63–65 °C). \(^1\)H NMR (300 MHz, CDCl₃) \(\delta 7.47–7.42 \text{ (m, 2H)}, 7.28–7.22 \text{ (m, 2H)}, 6.57 \text{ (d, } J = 15.9 \text{ Hz, 1H)}, 6.36 \text{ (dt, } J = 15.9, 5.5 \text{ Hz, 1H}), 4.32 \text{ (dd, } J = 5.5, 1.5 \text{ Hz, 2H}).

\(\text{(E)-3-(4-Bromophenyl)prop-2-en-1-yl 3-methylbut-2-en-1-yl ether (3c)}\)

Into the cooled (-78 °C) mixture of alcohol 16 (1.48 g, 6.9 mmol), 1-bromo-3-methylbut-2-ene (90%, 2.29 g, 13.9 mmol) and DMPU (4.2 mL, 34.7 mmol) in dry THF (30 mL), sodium hydride (60% w/w in mineral oil, 0.39 g, 8.3 mmol) was added under argon. The cooling bath was removed and the reaction mixture was stirred at r. t. for 2.5 h. Reaction was quenched by adding saturated aqueous solution of ammonium chloride. Phases were separated and the water phase was extracted with ether. Combined organic phases were washed with brine, dried over MgSO₄ and evaporated. Crude product was purified by flash column chromatography (hexane/ethyl acetate). Clear oil (1.66 g, 85%) was obtained. \(^1\)H NMR (400 MHz, CDCl₃) \(\delta 7.46–7.40 \text{ (m, 2H)}, 7.28–7.20 \text{ (m, 2H)}, 6.55 \text{ (dt, } J = 15.9, 1.4 \text{ Hz, 1H)}, 6.30 \text{ (dt, } J = 15.9, 5.9 \text{ Hz, 1H}), 5.39 \text{ (tdt, } J = 7.0, 2.8, 1.4 \text{ Hz, 1H)}, 4.11 \text{ (dd, } J = 5.9, 1.5 \text{ Hz, 2H)}, 4.02 \text{ (dt, } J = 7.0, 0.9 \text{ Hz, 2H)}, 1.76 \text{ (d, } J = 1.2 \text{ Hz, 3H)}, 1.69 \text{ (d, } J = 1.4 \text{ Hz, 3H}). \(^{13}\)C NMR (101 MHz, CDCl₃) \(\delta 137.44, 135.90, 131.76, 131.03, 128.09, 127.40, 121.46, 121.06, 70.50, 66.90, 25.96, 18.20.\) HR-MS (APCI⁺): For C₁₄H₁₈BrO⁺ [M+H]⁺ calculated 281.05355, found 281.05341.
To the mixture of tetrakis(triphenylphosphine) palladium(0) (0.30 g, 0.3 mmol), copper(I) iodide (0.31 g, 1.6 mmol), 4-(trifluoromethyl)iodobenzene (2.28 g, 8.4 mmol) and dry triethylamine (45 mL), propargyl alcohol (0.58 g, 10.3 mmol) was added under nitrogen. After stirring overnight, the reaction was quenched by adding of ammonium chloride (aqueous solution) and extracted with dichloromethane (3×30 mL). Combined organic layers were dried over Na₂SO₄ and solvents were evaporated. Column chromatography (dichloromethane/MeOH from 100 : 1 to 10 : 1) gave alkyne 17 (1.57 g, 94%).

(E)-3-(4-Trifluoromethylphenyl)prop-2-en-1-ol (18)¹¹

Into the cooled (0 °C) mixture of LiAlH₄ (125 mg, 3.3 mmol) and dry diethyl ether (5 mL), the solution of alkyne 17 (505 mg, 2.5 mmol) in dry diethyl ether (10 mL) was added dropwise under nitrogen. Reaction mixture was stirred for 3 hours at 0 °C and after reaching room temperature overnight. Reaction was quenched by adding water and aqueous solution of HCl. Mixture was extracted with ether (3×30 mL), organic phase was dried over MgSO₄ and evaporated. Column chromatography (dichloromethane/MeOH 100 : 3) gave alkene 18 (320 mg, 63 %).
(E)-3-(4-Trifluoromethylphenyl)prop-2-en-1-yl 3-methylbut-2-en-1-yl ether (3d)

Into the cooled (-78 °C) solution of alcohol 18 (265 mg, 1.3 mmol) and 1-bromo-3-methylbut-2-ene (90%, 400 mg, 2.9 mmol) in dry THF (12 mL), sodium hydride (60% w/w in mineral oil, 70 mg, 1.75 mmol) and DMPU (800 mg, 6.2 mmol) were carefully added under nitrogen. The reaction mixture was stirred for 3 hours and after reaching the room temperature overnight. The reaction was quenched by adding ammonium chloride (aqueous solution), the product was isolated by extraction with dichloromethane (3 × 25 mL), organic phase was dried over MgSO₄ and evaporated. Column chromatography (hexane/ethyl acetate 25 : 1) gave 270 mg (77 %) of ether 3d. H NMR (400 MHz, CDCl₃) δ 7.56 (d, J = 8.3 Hz, 2H), 7.47 (d, J = 8.2 Hz, 2H), 6.65 (dt, J = 15.9, 1.5 Hz, 1H), 6.40 (dt, J = 16.0, 5.7 Hz, 1H), 5.40 (ddq, J = 8.4, 5.6, 1.4 Hz, 1H), 4.16 (dd, J = 5.8, 1.5 Hz, 2H), 4.07–3.99 (m, 2H), 1.77 (q, J = 1.1 Hz, 3H), 1.70 (d, J = 1.4 Hz, 3H). C NMR (101 MHz, CDCl₃) δ 140.47 (q, J = 1.6 Hz), 137.59, 130.60, 129.49 (q, J = 32.0), 129.40, 126.70, 125.64 (q, J = 3.8), 124.33 (q, J = 271.8 Hz), 121.00, 70.32, 67.06, 25.98, 18.22. F NMR (282 MHz, CDCl₃) δ -62.96. HR-MS (APCI⁺): For C₁₅H₁₈F₃O⁺ calculated 271.13043, found 271.13031.

3-(4-Methoxyphenyl)prop-2-yn-1-ol (19)

To the mixture of tetrakis(triphenylphosphine) palladium(0) (1.48 g, 1.3 mmol), copper(I) iodide (0.40 g, 2.1 mmol), 4-iodoanisole (6.24 g, 25.7 mmol) and dry triethylamine (50 mL), propargyl alcohol (1.75 g, 31.2 mmol) was added under nitrogen. After stirring overnight, the reaction was quenched by adding ammonium chloride (aqueous solution) and the mixture was extracted with dichloromethane (5 × 50 mL). Combined organic layers were dried over MgSO₄ and solvents were evaporated. Column chromatography (dichloromethane) and crystallization (toluene/hexane) gave alkyne 19 (2.56 g, 61 %) as a white solid, m.p. 62–65 °C (lit. 62.5–64.5 °C). H NMR (400 MHz, CDCl₃) δ 7.42–7.34 (m, 2H), 6.84 (d, J = 8.9 Hz, 2H), 4.48 (d, J = 6.1 Hz, 2H), 3.81 (s, 3H), 1.68 (t, J = 6.1 Hz, 1H). C NMR (101 MHz, CDCl₃) δ
HR-MS (APCI\(^+\)): For \(\text{C}_{11}\text{H}_{13}\text{O}_2^+\) [M+MeOH\(^+\)] calculated 177.09101, found 177.09105.

\((Z)-3-(4\text{-Methoxyphenyl})\text{prop-2-en-1-ol (20)}\)\(^{13}\)

![Chemical structure](image)

Into the solution of alkyne 19 (500 mg, 3 mmol) in dry methanol (20 mL), Lindlar catalyst (110 mg) and Lindlar catalyst poison (3,6-dithiaoctane-1,8-diol, 30 mg, 0.16 mmol) were added. The reaction mixture was stirred in autoclave under hydrogen (3 BAR) for 3 days. After filtration through celite and evaporation of solvent, 480 mg (97\%\) of alkene 20 was obtained, m.p. 37–40 °C (lit.\(^{14}\) 45–50 °C). Product contained cca 10\% of \((E)\)-isomer and was without any purification used for preparation of ether \((Z)-3\text{a}\). \(^1\text{H}\) NMR (300 MHz, CDCl\(_3\)) \(\delta 7.15\) (d, \(J = 8.6\) Hz, 2H), 6.87 (d, \(J = 9.1\) Hz, 2H), 6.51 (d, \(J = 11.7\) Hz, 1H), 5.78 (dt, \(J = 11.7, 6.5\) Hz, 1H), 4.43 (dd, \(J = 6.3, 1.4\) Hz, 2H), 3.81 (s, 3H), 1.56 (t, \(J = 5.3\) Hz, 1H). \(^{13}\text{C}\) NMR (101 MHz, CDCl\(_3\)) \(\delta 158.94, 130.78, 130.23, 129.53, 129.32, 113.83, 59.91, 55.42\). HR-MS (APCI\(^+\)): For \(\text{C}_{10}\text{H}_{13}\text{O}^+\) calculated 165.09101, found 165.09073.

\((Z)-3-(4\text{-Methoxyphenyl})\text{prop-2-en-1-yl 3-methylbut-2-en-1-yl ether ((Z)-3a)}\)

![Chemical structure](image)

The solution of alcohol 20 (150 mg, 0.90 mmol) and 1-bromo-3-methylbut-2-ene (90\%, 300 mg, 2.00 mmol) in dry THF (10 mL) was cooled to -78 °C under nitrogen. Sodium hydride (60\% w/w in mineral oil, 45 mg, 1.13 mmol) and DMPU (480 mg, 3.75 mmol) were carefully added and the reaction mixture was stirred for 2 hours at -78 °C and after reaching the room temperature overnight. The reaction was quenched by adding of ammonium chloride (aqueous solution). The mixture was extracted with dichloromethane (3 \times 10 mL). Organic phase was dried over \(\text{Na}_2\text{SO}_4\) and evaporated. Column chromatography (hexane/ethyl acetate from 20 : 1 to 10 : 1) gave 160 mg (74\%) of ether \((Z)-3\text{a}\). \(^1\text{H}\) NMR (300 MHz, CDCl\(_3\)) \(\delta 7.23–7.10\) (m, 2H), 6.94–6.80 (m, 2H), 6.53 (dt, \(J = 11.8, 1.8\) Hz, 1H), 5.78 (dt, \(J = 11.8, 6.4\) Hz, 1H), 5.38 (ddq, \(J = 8.4, 5.6, 1.4\) Hz, 1H), 4.24 (dd, \(J = 6.4, 1.7\) Hz, 2H), 3.99 (dt, \(J = 7.2, 0.8\) Hz, 2H), 3.82 (s, 3H), 1.74 (q, \(J = 0.9\) Hz, 3H), 1.70–1.59 (m, 3H). \(^{13}\text{C}\) NMR (101 MHz, CDCl\(_3\)) \(\delta 158.82,\)
HR-MS (APCI\textsuperscript{+}): For C\textsubscript{15}H\textsubscript{20}O\textsubscript{2}Na\textsuperscript{+} [M+Na\textsuperscript{+}] calculated 255.13555, found 255.13547.

Cinnamyl (E)-3-(4-methoxyphenyl)prop-2-en-1-yl ether (5a)\textsuperscript{15, 16}

![Chemical structure of 5a]  

The solution of (E)-3-(4-methoxyphenyl)prop-2-en-1-ol 15 (1.05 g, 6.4 mmol) and cinnamyl bromide (1.25 g, 6.3 mmol) in dry THF (50 mL) was cooled to -78 °C under nitrogen. Sodium hydride (60\% w/w in mineral oil, 0.27 g, 6.7 mmol) and DMPU (1.26 g, 9.8 mmol) were carefully added and the reaction mixture was stirred for 3 hours at -78 °C and after reaching the room temperature overnight. The reaction was quenched by adding of ammonium chloride (aqueous solution). The mixture was extracted with dichloromethane (4×30 mL). Organic phase was dried over Na\textsubscript{2}SO\textsubscript{4} and evaporated. Column chromatography (hexane/ethyl acetate 10 : 1) gave 1.43 g (80 \%) of slightly yellow solid ether 5a, m.p. 33–34 °C. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.43 (dt, \(J = 7.8, 1.5\) Hz, 2H), 7.40–7.30 (m, 4H), 7.27 (dd, \(J = 7.2, 1.6\) Hz, 1H), 6.92–6.85 (m, 2H), 6.70–6.64 (m, 1H), 6.64–6.58 (m, 1H), 6.36 (dt, \(J = 15.9, 6.0, 1.7\) Hz, 1H), 6.28–6.17 (m, 1H), 4.25–4.19 (m, 4H), 3.82 (s, 3H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 159.41, 136.85, 132.57, 132.43, 129.58, 128.65, 127.80, 127.75, 126.59, 126.22, 123.81, 114.08, 71.06, 70.72, 55.35. HR-MS (ESI\textsuperscript{+}): For C\textsubscript{19}H\textsubscript{20}O\textsubscript{2}Na\textsuperscript{+} [M+Na\textsuperscript{+}] calculated 303.13555, found 303.13574.

(E)-3-(4-(Trifluoromethyl)phenyl)prop-2-en-1-yl bromide (21)\textsuperscript{17}

![Chemical structure of 21]  

The solution of alcohol 18 (115 mg, 0.55 mmol) in dry diethyl ether (3 mL) was cooled to 0 °C under nitrogen. At this temperature, phosphorus tribromide (170 mg, 0.60 mmol) in diethyl ether (1 mL) was added dropwise and the reaction mixture was stirred for 1 h. Then the reaction mixture was diluted with diethyl ether (10 mL) and sodium hydrogen carbonate (saturated aqueous solution) was added. Phases were separated and the product was isolated by extraction with diethyl ether (3×10 mL), combined organic layers were washed with brine, dried over MgSO\textsubscript{4} and evaporated. Bromide 21 (120 mg, 80 \%) was used for preparation of ether.
5b without any purification. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.65–7.53 (m, 2H), 7.53–7.43 (m, 2H), 6.67 (d, $J$ = 15.7 Hz, 1H), 6.48 (dt, $J$ = 15.5, 7.6 Hz, 1H), 4.15 (d, $J$ = 7.6 Hz, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 139.39, 133.06, 130.21 (q, $J$ = 32.7 Hz), 127.98, 127.03, 125.76 (q, $J$ = 3.8 Hz), 124.18 (q, $J$ = 272.1 Hz), 32.57. $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -63.09.

(\textit{E})-3-(4-Methoxyphenyl)prop-2-en-1-yl (E)-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-yl ether (5b)

\begin{align*}
\text{O} & \quad \text{+} \quad \text{Br} \\
\text{OH} & \quad \text{NaH, DMPU} \\
\text{THF} & \quad \text{MeO} \\
\text{CF}_3 & \quad \text{5b}
\end{align*}

The solution of alcohol 15 (80 mg, 0.45 mmol) and bromide 21 (120 mg, 0.45 mmol) in dry THF (10 mL) was cooled to -78 °C under nitrogen. At this temperature, sodium hydride (60% w/w in mineral oil, 20 mg, 0.50 mmol) and DMPU (260 mg, 2.00 mmol) were carefully added and the reaction mixture was stirred for 3 hours and after reaching the room temperature overnight. The reaction was quenched by adding of ammonium chloride (aqueous solution). Mixture was extracted with dichloromethane (3×15 mL). Organic phase was dried over MgSO$_4$ and evaporated. Column chromatography (hexane/ethyl acetate 10:1) gave 95 mg (60 %) of ether 5b. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.62–7.54 (m, 2H), 7.53–7.45 (m, 2H), 7.39–7.31 (m, 2H), 6.91–6.82 (m, 2H), 6.68 (d, $J$ = 16.0 Hz, 1H), 6.59 (d, $J$ = 15.9 Hz, 1H), 6.42 (dt, $J$ = 16.0, 5.7 Hz, 1H), 6.20 (dt, $J$ = 15.9, 6.3 Hz, 1H), 4.25–4.17 (m, 4H), 3.81 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 159.49, 140.38, 132.73, 130.77, 129.52 (q, $J$ = 32.5), 129.47, 129.07, 127.86, 126.73, 125.66 (q, $J$ = 3.9), 123.55, 114.12, 71.44, 70.34, 55.43. $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -62.96. HR-MS (APCI-): For C$_{20}$H$_{18}$F$_3$O$_2$ [M-H]$^-$ calculated 347.12644, found 347.12622.

Pimelic dichloride (22)$^{18}$

\begin{align*}
\text{SOCl}_2 & \quad \text{Cl} \\
\text{Cl} & \quad \text{22}
\end{align*}

To the suspension of pimelic acid (2.40 g, 0.015 mol) in thionyl chloride (5.95 g, 0.05 mol), droplet of dimethyl formamide was added. Mixture was refluxed for 3 h. Colorless liquid (2.37 g, 80 %) was obtained by fractional distillation (86–88 °C, 0.25 Torr). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 2.91 (t, $J$ = 7.2 Hz, 4H), 1.81–1.67 (m, 4H), 1.50–1.36 (m, 2H).
1,7-Diphenylhept-1,7-dione (23)\textsuperscript{19, 20}

\[
\text{Cl} \quad \text{Cl} \quad \xrightarrow{\text{AlCl}_3, \text{benzene}} \quad \text{Ph} \quad \text{Ph}
\]

To the suspension of dry aluminium chloride (5.00 g, 37.5 mmol) in benzene (25 mL), pimelic dichloride 22 (2.37 g, 12.0 mmol) was added dropwise. Reaction mixture was refluxed for 3 h, then cooled and poured over slush of ice (100 g) with concentrated sulphuric acid (10 mL). Phases were separated, water phase was extracted with dichloromethane (3×50 mL). Combined organic phases were dried over MgSO\textsubscript{4} and evaporated. Raw product was dissolved in acetone (50 mL) and refluxed with activated carbon, then filtered and evaporated. After recrystallization from isopropyl alcohol, dione 23 (2.34 g, 69\%) was obtained. \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}) \(\delta\)

- 8.00–7.93 (m, 4H),
- 7.60–7.52 (m, 2H),
- 7.50–7.42 (m, 4H),
- 3.13–2.85 (m, 4H),
- 1.95–1.67 (m, 4H),
- 1.56–1.43 (m, 2H).

(\textbf{1E,6E})-1,7-Diphenylhepta-1,6-diene (7)\textsuperscript{21}

\[
\text{Ph} \quad \text{Ph} 
\quad \xrightarrow{1. \text{LiAlH}_4, \text{THF}} \quad \text{OH} \quad \text{OH}
\]

To the suspension of lithium aluminium hydride (0.76 g, 0.02 mol) in dry THF (20 mL), solution of dione 23 (1.41 g, 0.05 mol) in dry THF (10 mL) was added. The mixture was refluxed for 1 h, then cooled and quenched with ethanol, poured over slush of crushed ice (100 g) with sulfuric acid (10 mL). Phases were separated, water phase was extracted with dichloromethane (3×50 mL). Combined organic phases were dried over MgSO\textsubscript{4} and evaporated. Raw product 24 (1.37 g, 96\%) was used for further synthesis without purification.

To the solution of diol 24 (0.28 g, 1 mmol) in dichloromethane (10 mL), phosphorus tribromide (0.32 g, 1.2 mmol) was added while cooling in crushed ice and salt bath (approx. -17 °C). After 30 min, water (40 mL) was added and organic layer was separated. Water phase was extracted with dichloromethane (20 mL). Organic phases were combined, dried over MgSO\textsubscript{4}, and evaporated. Resulting dibromide was dissolved in dry THF (20 mL) under nitrogen and potassium tert-butoxide (0.50 g, 4.45 mmol) was added. The reaction mixture was stirred for 2 h at room
temperature, then quenched with water (100 mL). Phases were separated, water phase was extracted with dichloromethane (3 × 50 mL). Organic phases were combined, dried over MgSO₄ and evaporated. Crude product was purified by column chromatography (hexane/ethyl acetate ~ 50:1). Clear oil (60 mg, 24%) was obtained. ¹H NMR (300 MHz, CDCl₃) δ 7.41–7.14 (m, 10H), 6.41 (d, J = 15.8 Hz, 2H), 6.25 (dt, J = 15.8, 6.9 Hz, 2H), 2.28 (qd, J = 7.0, 1.4 Hz, 4H), 1.67 (p, J = 7.4 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 137.94, 130.74, 130.30, 128.62, 126.99, 126.06, 32.65, 29.13.

1,5-Diphenylpentane-1,5-dione (25)²²

![Chemical structure of 1,5-Diphenylpentane-1,5-dione (25)](image)

The glutaryl dichloride (3.38 g, 0.02 mol) was added dropwise to the solution of aluminium chloride (6.67 g, 0.05 mol) in benzene (25 mL). Resulting mixture was refluxed for 3 hours. The mixture was cooled and poured over slush of ice (100 g) with concentrated sulphuric acid (10 mL). Water phase was extracted with dichloromethane (3 × 50 mL). Collected organic layers were dried over MgSO₄ and evaporated. Crude product was dissolved in acetone (50 mL) and refluxed with activated carbon, then filtered and evaporated. Column chromatography (hexane/ethyl acetate 5:1) gave diketone 25 (2.81 g, 56%). ¹H NMR (300 MHz, CDCl₃) δ 8.00–7.96 (m, 4H), 7.59–7.52 (m, 2H), 7.46 (ddt, J = 8.3, 6.7, 1.2 Hz, 4H), 3.13 (t, J = 6.9 Hz, 4H), 2.21 (p, J = 6.9 Hz, 2H).

2,6-Diphenylhepta-1,6-diene (9)²³

![Chemical structure of 2,6-Diphenylhepta-1,6-diene (9)](image)

The potassium tert-butoxide (1.40 g, 12.5 mmol) was added to the suspension of methyltriphenylphosphonium bromide (4.46 g, 12.5 mmol) in dry THF (15 mL). The mixture was stirred under nitrogen for 2 hours. A solution of dione 25 (1.75 g, 5 mmol) in dry THF (10 mL) was added, and the reaction mixture was stirred vigorously for 5 days. After that, the mixture was poured into water (100 mL) and extracted with dichloromethane (3 × 50 mL). Organic layer was dried over MgSO₄ and evaporated. The column chromatography (hexane/ethyl acetate 50:1) gave 2,6-diphenylhepta-1,6-diene 9 (344 mg, 20%). ¹H NMR (300 MHz, CDCl₃) δ 7.39–7.24
(m, 10H), 5.27 (d, J = 1.5 Hz, 2H), 5.05 (q, J = 1.4 Hz, 2H), 2.54 (ddd, J = 8.5, 7.4, 1.3 Hz, 4H), 1.69–1.55 (m, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 148.20, 141.15, 128.23, 127.27, 126.10, 112.45, 34.79, 26.61.

($2E,7E$)-1,9-Diphenylnona-2,7-diene-1,9-dione (11a)$^{24,25}$

$\begin{array}{c}
\text{[Ph]}_3\text{P}^+\text{Br}^- \\
\text{CH}_2\text{Cl}_2
\end{array}$

Into the solution of (2-oxo-2-phenylethyl)triphenylphosphonium bromide (2.06 g, 4.5 mmol) in methanol (50 mL) and water (50 mL) sodium hydroxide (in the form of 1.5M aqueous solution) was added until the pH value of the reaction mixture reached 8. The mixture was stirred vigorously overnight. After evaporation of methanol, dichloromethane (80 mL) and water (20 mL) were added to the residue and water phase was extracted with dichloromethane (3×40 mL). Combined organic layers were dried over MgSO$_4$ and evaporated to obtain crude ylide 26 (1.70 g, 99%). The solution of ylide 26 (1.00 g, 2.6 mmol) and glutaraldehyde (50% solution in water, 1.20 g, 1.0 mmol) in dichloromethane (3 mL) was vigorously stirred at r.t. for 5 days. The column chromatography (dichloromethane/ethyl acetate from 100 : 1 to 100 : 4) gave the product 11a (0.10 g, 33%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.93 (d, 4H), 7.60–7.51 (m, 2H), 7.51–7.42 (m, 4H), 7.06 (dt, J = 15.3, 6.8 Hz, 2H), 6.92 (d, J = 15.4 Hz, 2H), 2.40 (q, J = 7.1 Hz, 4H), 1.79 (p, J = 7.4 Hz, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 190.59, 148.48, 137.82, 132.70, 128.53, 128.50, 126.47, 32.15, 26.68. HR-MS (APCI$^+$): For C$_{21}$H$_{21}$O$_2$ $^+[M+H]^+$ calculated 305.15361, found 305.15385.

1,9-Diphenynona-2,7-diyne-1,9-diol (27)

To a solution of hepta-1,6-diyne (350 mg, 3.8 mmol) in anhydrous THF (10 mL) at -78 °C under nitrogen atmosphere, $n$-BuLi (2.5M solution in hexanes, 3 mL, 7.5 mmol) was added. The reaction mixture was stirred at this temperature for 1 h and then at r.t. for 1.5 h. After cooling to -78 °C, the benzaldehyde (800 mg, 7.5 mmol) in anhydrous THF (5 mL) was added to the reaction mixture and was left at -78 °C for 1 h and after reaching the room temperature for
3h. Reaction was quenched by adding of aqueous NH₄Cl and extracted with Et₂O (3×30 mL). Combined organic layers were dried over MgSO₄ and evaporated. The column chromatography (dichloromethane/ethyl acetate ~ 100:5) gave the product 27 (810 mg, 70%). ¹H NMR (400 MHz, CDCl₃) δ 7.53 (d, J = 7.8 Hz, 4H), 7.41–7.30 (m, 6H), 5.45 (s, 2H), 2.42 (td, J = 7.0, 1.9 Hz, 4H), 2.28 (s, 2H), 1.79 (p, J = 7.0 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 141.21, 128.71, 126.72, 86.48, 80.89, 64.93, 27.49, 18.25 (d, J = 0.8 Hz). HR-MS (ESI⁺): For C₂₁H₁₈O₂Na⁺ [M+Na]⁺ calculated 325.11990, found 325.12009.

(2Z,7Z)-1,9-Diphenylnona-2,7-diene-1,9-dione ((Z,Z)-11a)

To a solution of diyne 27 (800 mg, 2.6 mmol) in anhydrous methanol (60 mL), Lindlar catalyst (250 mg) and Lindlar catalyst poison (3,6-dithiaoctane-1,8-diol, 40 mg, 0.2 mmol) were added. Hydrogen was bubbled through the reaction mixture for 5 hours. After filtration through celite and evaporation of solvent, 800 mg (99%) of alkene was obtained as a (2Z,7Z) isomer, which was used without any purification for preparation of diketone (Z,Z)-11a. ¹H NMR (300 MHz, CDCl₃) of 1,9-diphenylnona-2,7-diene-1,9-diol: δ 7.41–7.22 (m, 10H), 5.66 (dd, J = 11.1, 8.1 Hz, 2H), 5.57 (t, J = 7.1 Hz, 2H), 2.82–2.70 (m, 4H), 2.03 (d, J = 3.5 Hz, 2H), 1.62–1.41 (m, 2H). To a solution of alcohol (620 mg, 2 mmol) in anhydrous THF (50 mL) and Et₂O (25 mL) MnO₂ (10 g, 115 mmol) was added and the reaction mixture was stirred for 4 days vigorously. Excess of MnO₂ was removed by filtration through celite, washed with Et₂O and solvents were evaporated. The column chromatography (dichloromethane) gave (Z,Z)-11a (210 mg, 35%). ¹H NMR (400 MHz, CDCl₃) δ 7.95–7.89 (m, 4H), 7.57–7.49 (m, 2H), 7.44 (td, J = 6.8, 1.5 Hz, 4H), 6.82 (dt, J = 11.6, 1.7 Hz, 2H), 6.35 (dt, J = 11.6, 7.4 Hz, 2H), 2.69 (qd, J = 7.5, 1.7 Hz, 2H), 1.70 (p, J = 7.5 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 192.12, 148.87, 138.64, 132.80, 128.66, 128.47, 124.92, 29.52, 28.80. HR-MS (ESI⁺): For C₂₁H₁₈O₂Na⁺ [M+Na]⁺ calculated 329.15120, found 329.15155.

(2E,7E)-1,9-Bis(4-methoxyphenyl)nona-2,7-diene-1,9-dione (11b)

1. NaOH / MeOH, H₂O

2. CH₂Cl₂

11b
Into the solution of (2-(4-methoxyphenyl)-2-oxoethyl)triphenylphosphonium bromide (1.47 g, 3.0 mmol) in methanol (50 mL) and water (50 mL) sodium hydroxide (in the form of 1.5M aqueous solution) was added until the pH value of the reaction mixture reached 10. The mixture was stirred vigorously overnight. After evaporation of methanol, dichloromethane (80 mL) and water (20 mL) were added to the residue and water phase was extracted with dichloromethane (3×30 mL). Combined organic layers were dried over MgSO$_4$ and evaporated to obtain the ylide 28 (1.14 g, 98%). The solution of ylide 28 (1.13 g, 2.7 mmol) and glutaraldehyde (50% solution in water, 275 mg, 1.4 mmol) in dichloromethane (5 mL) was vigorously stirred at r.t. for 10 days. The column chromatography (dichloromethane/ethyl acetate from 100:1 to 100:5) gave the product 11b (340 mg, 68%). \(^1\)H NMR (400 MHz, CDCl$_3$) δ 7.94 (d, \(J = 7.7\) Hz, 4H), 7.04 (dt, \(J = 15.2, 6.8\) Hz, 2H), 6.98–6.88 (m, 6H), 3.87 (s, 6H), 2.38 (q, \(J = 7.0\) Hz, 4H), 1.77 (p, \(J = 7.5\) Hz, 2H). \(^13\)C NMR (101 MHz, CDCl$_3$) δ 188.83, 163.34, 147.49, 130.80, 130.70, 126.11, 113.76, 55.45, 32.11, 26.79. HR-MS (APCI$^+$): For C$_{23}$H$_{25}$O$_4$ + [M+H]$^+$ calculated 365.17474, found 365.17459.

\((2E,7E)-1,9\)-Bis(4-(trifluoromethyl)phenyl)nona-2,7-diene-1,9-dione (11c)

\[
\begin{align*}
\text{F}_3\text{C} & \quad \text{Br} \\
\text{P}^+(\text{Ph})_3 & \quad \text{O} \\
\text{O} & \quad \text{CF}_3 \\
\text{CF}_3 & \\
\text{CH}_2\text{Cl}_2 & \\
\text{O} & \\
\text{O} & \\
\end{align*}
\]

Into the solution of (2-oxo-2-(4-(trifluoromethyl)phenyl)ethyl)triphenylphosphonium bromide (1.27 g, 2.4 mmol) in methanol (50 mL) and water (50 mL) sodium hydroxide (in the form of 1.5M aqueous solution) was added until the pH value of the reaction mixture reached 8. The mixture was stirred vigorously overnight. After evaporation of methanol, dichloromethane (100 mL) was added to the residue and water phase was extracted with dichloromethane (3×30 mL). Organic layers were dried over Na$_2$SO$_4$ and evaporated to obtain the ylide 29 (1.00 g, 93%). The solution of ylide 29 (975 mg, 2.2 mmol) and glutaraldehyde (50% solution in water, 200 mg, 1.0 mmol) in dichloromethane (3 mL) was vigorously stirred at r.t. for 3 days. The column chromatography (dichloromethane) gave the product 11c (108 mg, 25%), m.p. 66–70 °C. \(^1\)H NMR (300 MHz, CDCl$_3$) δ 8.01 (d, \(J = 8.7\) Hz, 4H), 7.74 (d, \(J = 8.5\) Hz, 2H), 7.10 (dt, \(J = 15.4, 6.9\) Hz, 2H), 6.89 (dt, \(J = 15.4, 1.4\) Hz, 2H), 2.53–2.32 (m, 4H), 1.80 (p, \(J = 7.5\) Hz, 2H). \(^13\)C NMR (126 MHz, CDCl$_3$) δ 189.77, 149.98, 140.79, 134.22 (q, \(J = 32.8\) Hz), 129.01, 126.38, 125.77 (q, \(J = 3.7\) Hz), 123.77 (q, \(J = 272.7\) Hz), 32.41, 26.74. \(^{19}\)F NMR (470 MHz, CDCl$_3$) δ -63.08. HR-MS (ESI$^+$): For C$_{23}$H$_{18}$F$_6$O$_2$Na$^+$ [M+Na]$^+$ calculated 463.11032, found 463.11057.
2 [2+2] Photocycloadditions

2.1 General procedures

For all photocatalytic experiments, Schlenck technique was used. Oxygen was removed from the solutions by three freeze-pump-thaw cycles using argon as an inert gas.

2.2 Experiments on analytical scale

Reactions were performed in Schlenck tube with inner diameter at 5 mm mounted on an optical bench with high power LED emitter LED Engin LZC-70UA00 as a light source. A solution of flavin catalyst 2 in CDCl$_3$ (0.02 M, 25 μL, 5×10$^{-7}$ mol) was added to the Schlenck tube and the solvent was evaporated by blowing a moderate stream of air into the tube for 5 min. Then the solution of corresponding substrate (0.1 M, 200 μL, 2×10$^{-5}$ mol) in deuterated solvent and 800 μL of the same deuterated solvent was added. Reaction tube was sealed with magnetic stirring bar inside and the oxygen was removed. Schlenck tube was irradiated for an appropriate time and then the reaction mixture was transferred to the NMR cuvette.

2.3 Experiments on preparative scale

Reactions were performed in Schlenck tube with inner diameter at 22 mm. A solution of flavin catalyst 2 in CDCl$_3$ (0.02 M, 250 μL, 5×10$^{-6}$ mol) was added to the Schlenck tube and the solvent was evaporated by blowing a moderate stream of air into the tube for 10 min. Substrate (2×10$^{-4}$ mol) and acetonitrile (20 mL) were added. Reaction tube was sealed with magnetic stirring bar inside and the oxygen was removed. Schlenck tube was irradiated on laboratory apparatus with six high power LED emitters LED Engin LZ4-00UA00 directly shining on the tube from three directions at distance of 5 mm from the tube wall. The apparatus including the reaction tube is actively air-cooled by 120mm fan from the bottom (see A.10 for apparatus picture). After evaporation of solvents, the crude product was purified by chromatography or sublimation (see below for details). NMR spectra of known products corresponded to those already published (references given at the name of the cycloadduct).
After 10 min of irradiation, water (30 mL) was added and the product was extracted with ether (2 × 30 mL), organic layers were combined, washed twice with water, dried over MgSO₄ and evaporated. Crude product was purified by flash column chromatography (hexane/ethyl acetate). Clear oil was isolated (38 mg, 82 %, dr > 10 : 1). ¹H NMR (400 MHz, CDCl₃) δ 7.09–7.03 (m, 2H), 6.88–6.83 (m, 2H), 4.22–4.10 (m, 1H), 3.80 (s, 3H), 3.78 (d, J = 8.7 Hz, 1H), 3.56–3.47 (m, 1H), 3.47–3.37 (m, 1H), 3.21 (td, J = 7.7, 4.5 Hz, 1H), 2.92 (d, J = 7.4 Hz, 1H), 2.43–2.35 (m, 1H), 1.08 (s, 3H), 0.74 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 157.87, 132.75, 128.58, 113.41, 72.04, 69.10, 55.21, 51.24, 46.53, 38.44, 37.18, 26.17, 24.15. HR-MS (APCI⁺): For C₁₅H₂₁O₂⁺ [M+H]⁺ calculated 233.15361, found 233.15348.

(1R*,5R*,7R*)-6,6-Dimethyl-7-phenyl-3-oxabicyclo[3.2.0]heptane (4b)⁶

After 10 min of irradiation, water (30 mL) was added and the product was extracted with ether (2 × 30 mL), organic layers were combined, washed twice with water, dried over MgSO₄ and evaporated. Crude product was purified by flash column chromatography (hexane/ethyl acetate). Clear oil was isolated (35 mg, 87 %, dr > 10 : 1). ¹H NMR (400 MHz, CDCl₃) δ 7.35–7.11 (m, 5H), 4.18 (ddd, J = 10.0, 0.6 Hz, 1H), 3.80 (dd, J = 9.1, 0.8 Hz, 1H), 3.52 (dd, J = 10.1, 6.7 Hz, 1H), 3.45 (ddt, J = 9.0, 4.5, 0.5 Hz, 1H), 3.28 (td, J = 7.7, 4.5 Hz, 1H), 3.00 (d, J = 7.3 Hz, 1H), 2.41 (ddt, J = 8.1, 6.7, 0.7 Hz, 1H), 1.12 (s, 3H), 0.75 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 140.73, 128.11, 127.77, 126.04, 72.20, 69.25, 52.03, 46.72, 38.10, 26.35, 24.36. HR-MS (APCI⁺): For C₁₄H₁₉O⁺ [M+H]⁺ calculated 203.14304, found 203.14301.
(1R*,5R*,7R*)-7-(4-Bromophenyl)-6,6-dimethyl-3-oxabicyclo[3.2.0]heptane (4c)

![Chemical structure of 4c]

After 45 min of irradiation, acetonitrile was evaporated. Crude product was purified by flash column chromatography (hexane/ethyl acetate). Slightly yellow oil was isolated (42 mg, 76%, dr > 10 : 1). 1H NMR (400 MHz, CDCl3) δ 7.54–7.36 (m, 2H), 7.08–6.90 (m, 2H), 4.16 (dd, J = 10.1, 1.1 Hz, 1H), 3.77 (d, J = 9.0 Hz, 1H), 3.50 (dd, J = 10.1, 6.7 Hz, 1H), 3.43 (dd, J = 9.0, 4.5 Hz, 1H), 3.21 (td, J = 7.7, 4.5 Hz, 1H), 2.93 (d, J = 7.3 Hz, 1H), 2.44–2.36 (m, 1H), 1.09 (s, 3H), 0.73 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 139.59, 131.06, 129.30, 119.69, 71.93, 69.05, 51.37, 46.55, 38.06, 37.23, 26.17, 24.16. HR-MS (ESI+): For C14H18BrO+ [M+H]+ calculated 281.05355, found 281.05347. For structure assignment by NMR see Section A.4.

(1R*,5R*,7R*)-6,6-Dimethyl-7-[4-(trifluoromethyl)phenyl]-3-oxabicyclo[3.2.0]heptane (4d)

![Chemical structure of 4d]

After 30 min of irradiation, acetonitrile was evaporated. Crude product was purified by preparative TLC (dichloromethane). Clear oil was isolated (44 mg, 81%, dr > 10 : 1). 1H NMR (400 MHz, CDCl3) δ 7.59–7.51 (m, 2H), 7.27–7.22 (m, 2H), 4.18 (dt, J = 10.3, 0.7 Hz, 1H), 3.79 (d, J = 9.1 Hz, 1H), 3.52 (dd, J = 10.1, 6.7 Hz, 1H), 3.45 (dd, J = 9.1, 4.4 Hz, 1H), 3.29 (td, J = 7.7, 4.4 Hz, 1H), 3.04 (d, J = 7.3 Hz, 1H), 2.43 (ddt, J = 7.5, 5.6, 1.2 Hz, 1H), 1.13 (s, 3H), 0.74 (s, 3H). 13C NMR (101 MHz, CDCl3) δ 144.76, 128.20 (q, J = 32.3 Hz), 127.82, 124.92 (q, J = 3.8 Hz), 124.33 (q, J = 271.7 Hz), 71.90, 69.04, 51.69, 46.58, 37.90, 37.51, 26.19, 24.18. 19F NMR (282 MHz, CDCl3) δ -62.79. HR-MS (APCI+): For C15H18F3O+ [M+H]+ calculated 271.13043, found 271.13045.
(1R*,5S*,6R*,7S*)-6-(4-Methoxyphenyl)-7-phenyl-3-oxabicyclo[3.2.0]heptane (6a)

After 10 min of irradiation, acetonitrile was evaporated. Crude product was purified by preparative TLC (hexane/ethyl acetate ~ 10:1). White solid was isolated (34 mg, 61%, dr ~ 7:3). For $^1$H NMR and $^{13}$C NMR, see Section A.4. HR-MS (APCI$^+$): For C$_{19}$H$_{21}$O$_2$ [M+H]$^+$ calculated 281.15361, found 281.15353.

(1R*,5S*,6R*,7S*)-6-(4-Methoxyphenyl)-7-[4-(trifluoromethyl)phenyl]-3-oxabicyclo[3.2.0]heptane (6b)

After 10 min of irradiation, acetonitrile was evaporated. Crude product was purified by sublimation. Slightly yellow grease was obtained (68 mg, 97%, dr ~ 5:1). For $^1$H NMR and $^{13}$C NMR, see Section A.4. $^{19}$F NMR (282 MHz, CDCl$_3$) δ -62.74. HR-MS (APCI$^-$): For C$_{20}$H$_{18}$F$_3$O$_2$ [M-H]$^-$ calculated 347.12644, found 347.12620.

(1R,5S,6R,7S)-6,7-Diphenylbicyclo[3.2.0]heptane (8)

After 90 min of irradiation, acetonitrile was evaporated. Crude product was purified by preparative TLC (hexane/ethyl acetate ~ 10:1). Clear oil was isolated (18 mg, 42%, dr ~ 7:1).
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.10–7.02 (m, 4H), 7.00–6.92 (m, 6H), 3.50 (d, \(J = 4.1\) Hz, 2H), 3.16–3.06 (m, 2H), 2.20–2.03 (m, 1H), 2.02–1.92 (m, 1H), 1.85–1.70 (m, 4H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 142.05, 128.24, 127.48, 125.14, 47.63, 41.57, 32.94, 25.73. HR-MS (APCI\(^+\)): For C\(_{19}\)H\(_{21}\) \([M+H]\)^+ calculated 249.16378, found 249.16328.

**cis-1,5-Diphenylbicyclo[3.2.0]heptane (10)**

![cis-1,5-Diphenylbicyclo[3.2.0]heptane (10)](image)

After 25 min of irradiation, acetonitrile was evaporated. Crude product was purified by sublimation. White solid was isolated (40 mg, 80 %). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.16–7.07 (m, 4H), 7.08–6.99 (m, 2H), 6.98–6.90 (m, 4H), 2.63–2.48 (m, 2H), 2.37–2.19 (m, 1H), 2.19–2.03 (m, 7H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 147.18, 127.49, 127.23, 125.05, 56.95, 42.67, 29.91, 25.04. HR-MS (APCI\(^+\)): For C\(_{19}\)H\(_{21}\) \([M+H]\)^+ calculated 249.16378, found 249.15380.

**\(1R,5S,6R,7S\)-6,7-Dibenzoylbicyclo[3.2.0]heptane (12a)**

![\(1R,5S,6R,7S\)-6,7-Dibenzoylbicyclo[3.2.0]heptane (12a)](image)

After 40 min of irradiation, acetonitrile was evaporated. Crude product was purified by preparative TLC (dichloromethane). Slightly yellow solid was isolated (40 mg, 70 %, \(dr \approx 5 : 1\)). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.79–7.73 (m, 4H), 7.48–7.41 (m, 2H), 7.39–7.31 (m, 4H), 3.89–3.83 (m, 2H), 3.25–3.15 (m, 2H), 2.09–1.96 (m, 2H), 1.90–1.80 (m, 2H), 1.76–1.60 (m, 2H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 198.61, 136.35, 132.50, 128.45, 127.77, 48.30, 39.10, 32.47, 25.23. HR-MS (APCI\(^+\)): For C\(_{21}\)H\(_{21}\)O\(_2\) \([M+H]\)^+ calculated 305.15361, found 305.15396.

**\(1R,5S,6R,7S\)-6,7-Bis-(4-methoxybenzoyl)bicyclo[3.2.0]heptane (12b)**

![\(1R,5S,6R,7S\)-6,7-Bis-(4-methoxybenzoyl)bicyclo[3.2.0]heptane (12b)](image)
After 45 min of irradiation, acetonitrile was evaporated. Crude product was purified by preparative TLC (hexane/ethyl acetate ~ 10:1). Isolated in two fractions as a white solid (49 mg, 67%, dr ~ 4:1). Analysis for major isomer: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.84–7.67 \text{ (m, 4H), 6.92–6.72 \text{ (m, 4H), 3.80 (s, 6H), 3.22–3.16 \text{ (m, 2H), 2.05–1.97 \text{ (m, 2H), 1.86–1.78 \text{ (m, 2H), 1.73–1.61 \text{ (m, 2H).}}}}\) \(^1\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 197.41, 163.04, 130.08, 129.67, 113.73, 55.49, 48.19, 39.21, 32.62, 25.42.\) HR-MS (APCI\(^+\)): For C\(_{23}\)H\(_{25}\)O\(_4\) \([\text{M+H}]^+\) calculated 365.17474, found 365.17535.

6,7-Bis-[4-(trifluoromethyl)benzoyl]bicyclo[3.2.0]heptane (12c)

After 40 min of irradiation, acetonitrile was evaporated. Crude product was purified by preparative TLC (dichloromethane). (\(1R*,5S*,6R*,7R*\)-12c (26 mg) and (\(1R,5S,6R,7S\)-12c (25 mg) isolated as white solids (overall yield 58%, \(dr \sim 1:1\)). (\(1R*,5S*,6R*,7R*\)-12c: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 8.14–8.02 \text{ (m, 4H), 7.79–7.70 \text{ (m, 4H), 4.57 (dd, } J = 10.3, 7.8 \text{ Hz, 1H), 4.27 (dd, } J = 7.6, 6.3 \text{ Hz, 1H), 3.34–3.22 \text{ (m, 1H), 3.12–3.01 \text{ (m, 1H), 1.93–1.75 \text{ (m, 3H), 1.62–1.50 \text{ (m, 1H), 1.49–1.32 \text{ (m, 2H)}}.}}\) \(^1\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 199.15, 197.19, 138.52 \text{ (d, } J = 32.2 \text{ Hz), 134.71 (d, } J = 32.6 \text{ Hz), 129.09, 128.81, 126.05 \text{ (q, } J = 3.6 \text{ Hz), 125.90 (q, } J = 3.5 \text{ Hz), 125.05 (q, } J = 3.9 \text{ Hz), 122.34 (q, } J = 4.0 \text{ Hz), 43.39, 43.11, 40.71, 40.45, 32.19, 28.55, 25.59.\) \(^1\)F NMR (282 MHz, CDCl\(_3\)) \(\delta -63.57, -63.58.\) \((1R,5S,6R,7S\)-12c: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.89–7.82 \text{ (m, 4H), 7.66–7.61 \text{ (m, 4H), 3.96–3.83 \text{ (m, 2H), 3.21 (dq, } J = 4.1, 2.4 \text{ Hz, 2H), 2.13–1.99 \text{ (m, 2H), 1.93–1.82 \text{ (m, 2H), 1.80–1.64 \text{ (m, 2H)}}.}}\) \(^1\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 197.73, 138.98, 134.20 \text{ (q, } J = 32.8 \text{ Hz), 128.23, 125.80 \text{ (q, } J = 3.7 \text{ Hz), 123.66 (q, } J = 27.25 \text{ Hz), 48.55, 39.26, 32.55, 25.31.\) \(^1\)F NMR (282 MHz, CDCl\(_3\)) \(\delta -63.62.\) HR-MS (ESI\(^-\)): For C\(_{23}\)H\(_{17}\)F\(_6\)O\(_2\) \([\text{M}]^-\) calculated 439.11382, found 439.11282.
References


A Appendix

A.1 NMR Spectra of catalyst 2

Figure S1: $^1$H NMR Spectrum of catalyst 2
Figure S2: $^{13}$C NMR Spectrum of catalyst 2
A.2 NMR Spectra of substrates

Figure S3: $^1$H NMR Spectrum of substrate 3a.
Figure S4: $^1$H NMR Spectrum of substrate 3b.
Figure S5: $^1$H NMR Spectrum of substrate 3c.
Figure S6: $^{13}$C NMR Spectrum of substrate 3c.
Figure S7: $^1$H NMR Spectrum of substrate 3d.
Figure S8: $^{13}$C NMR Spectrum of substrate 3d.
Figure S9: $^1$H NMR Spectrum of substrate (Z)-3a.
Figure S10: $^{13}$C NMR Spectrum of substrate (Z)-3a.
Figure S11: $^1$H NMR Spectrum of substrate 5a.
Figure S12: $^{13}$C NMR Spectrum of substrate 5a.
Figure S13: $^1$H NMR Spectrum of substrate 5b.
Figure S14: $^{13}$C NMR Spectrum of substrate 5b.
Figure S15: $^1$H NMR Spectrum of substrate 7.
Figure S16: $^{13}$C NMR Spectrum of substrate 7.
Figure S17: $^1$H NMR Spectrum of substrate 9.
Figure S18: $^{13}$C NMR Spectrum of substrate 9.
Figure S19: $^1$H NMR Spectrum of substrate 11a.
Figure S20: $^{13}$C NMR Spectrum of substrate 11a.
Figure S21: $^1$H NMR Spectrum of substrate (Z,Z)-11a.
Figure S22: $^{13}$C NMR Spectrum of substrate (Z,Z)-11a.
Figure S23: $^1$H NMR Spectrum of substrate 11b.
Figure S24: $^{13}$C NMR Spectrum of substrate 11b.
Figure S25: $^1$H NMR Spectrum of substrate 11c.
Figure S26: $^{13}$C NMR Spectrum of substrate 11c.
A.3 NMR Spectra of cycloadducts

Figure S27: $^1$H NMR Spectrum of cycloadduct 4a.
Figure S28: $^{13}$C NMR Spectrum of cycloadduct 4a.
Figure S29: $^1$H NMR Spectrum of cycloadduct 4b.
Figure S30: $^{13}$C NMR Spectrum of cycloadduct 4b.
Figure S31: $^1$H NMR Spectrum of cycloadduct 4e.
Figure S32: $^{13}$C NMR Spectrum of cycloadduct 4c.
Figure S33: $^1$H NMR Spectrum of cycloadduct 4d.
Figure S34: $^{13}$C NMR Spectrum of cycloadduct 4d.
Figure S35: $^1$H NMR Spectrum of cycloadduct 8.
Figure S36. $^{13}$C NMR Spectrum of cycloadduct 8.
Figure S37: $^1$H NMR Spectrum of cycloadduct 10.
Figure S38: $^{13}$C NMR Spectrum of cycloadduct 10.
Figure S39: $^1$H NMR Spectrum of cycloadduct 12a (with minor trans-isomer).
Figure S40: $^{13}$C NMR Spectrum of cycloadduct 12a.
Figure S41: $^1$H NMR Spectrum of cycloadduct 12b.
Figure S42: $^{13}$C NMR Spectrum of cycloadduct 12b.
Figure S43: $^1$H NMR Spectrum of cycloadduct ($1R^*,5S^*,6R^*,7R^*$)-12c.
Figure S44: $^{13}$C NMR Spectrum of cycloadduct (1$R^*$,5$S^*$,6$R^*$,7$R^*$)-12c.
Figure S45: $^1$H NMR Spectrum of cycloadduct (1R,5S,6R,7S)-12c.
Figure S46: $^{13}$C NMR Spectrum of cycloadduct (1R,5S,6R,7S)-12c.
A.4 Examples of signals assignment of cycloadducts

\((1R^*,5R^*,7R^*)-7-(4\text{-Bromophenyl})-6,6\text{-dimethyl}3\text{-oxabicyclo[3.2.0]heptane (4c)}\)

Figure S47: 4c\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\ 7.54–7.36\) (m, 2H, H–A\(_3\)), 7.08–6.90 (m, 2H, H–A\(_2\)), 4.16 (dd, \(J = 10.1, 1.1\) Hz, 1H, H–G-down), 3.77 (d, \(J = 9.0\) Hz, 1H, H–F-down), 3.50 (dd, \(J = 10.1, 6.7\) Hz, 1H, H–G-up), 3.43 (dd, \(J = 9.0, 4.5\) Hz, 1H, H–F-up), 3.21 (td, \(J = 7.7, 4.5\) Hz, 1H, H–E), 2.93 (d, \(J = 7.3\) Hz, 1H, H–B), 2.44–2.36 (m, 1H, H–D), 1.09 (s, 3H, CH\(_3\)–H), 0.73 (s, 3H, CH\(_3\)–I).
Figure S48: $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 139.59 (4° C–A4), 131.06 (CH–A3), 129.30 (CH–A2), 119.69 (4° C–A1), 71.93 (CH$_2$–F), 69.05 (CH$_2$–G), 51.37 (CH–B), 46.55 (CH–D), 38.06 (CH–E), 37.23 (4° C–C), 26.17 (CH$_3$–I), 24.16 (CH$_3$–H).
Figure S49: 4c: COSY and HMQC spectra for assignement explanation.
Figure S50: 4c: NOE spectra for assignment explanation.
(1R*,5S*,6R*,7S*)-6-(4-Methoxyphenyl)-7-phenyl-3-oxabicyclo[3.2.0]heptane (6a)

Figure S51: 

\[ ^1H \text{NMR (600.13 MHz, CDCl}_3 \] \delta 7.13 (dd, 2H, \( J = 7.3, 7.3 \) Hz, H–B3), 7.04 (dd, 1H, \( J = 7.3, 7.3 \) Hz, H–B4), 6.98 (d, 2H, \( J = 7.3 \) Hz, H–B2), 6.89 (d, 2H, \( J = 6.9 \) Hz, H–A2), 6.66 (d, 2H, \( J = 6.9 \) Hz, H–A3), 4.13 (d, 2H, \( J = 9.5 \) Hz, H–G,H-down), 3.77–3.70 (overlapped m, 4H, H–C, H–D, H–G,H-up), 3.72 (s, 3H, OCH3), 3.36–3.30 (m, 1H, H–E), 3.30–3.25 (m, 1H, H–F).
Figure S52: 6a: $^{13}$C NMR (150.92 MHz, CDCl$_3$) $\delta$ 157.5 (4° C–A4), 140.9 (4° C–B1), 133.0 (4° C–A1), 129.1 (CH–A2), 128.1 (CH–B2), 127.8 (CH–B3), 125.6 (CH–B4), 113.2 (CH–A3), 74.0 (CH$_2$–G and CH$_2$–H), 55.1 (OCH$_3$), 47.2 and 46.5 (CH$_2$–D and CH$_2$–C), 42.7 and 42.0 (CH$_2$–E and CH$_2$–F).
Figure S53: 6a: COSY, HMQC and NOE spectra for assignment explanation.
(1R*,5S*,6R*,7S*)-6-(4-Methoxyphenyl)-7-[4-(trifluoromethyl)phenyl]-3-oxabicyclo[3.2.0]-heptane (6b)

Figure S54: 6b: $^1$H NMR (600.13 MHz, CD$_3$CN) $\delta$ 7.41 (d, 2H, $J = 8.1$ Hz, H–B3), 7.22 (d, 2H, $J = 8.1$ Hz, H–B2), 6.96 (d, 2H, $J = 8.7$ Hz, H–A2), 6.66 (d, 2H, $J = 8.7$ Hz, H–A3), 4.04 (d, 2H, $J = 9.4$ Hz, H–G,H-down), 3.79 (overlapped 1H, H–D), 3.72 (dd, 1H, $J = 5.1$, 10.1 Hz, H–C), 3.67 (s, 3H, OCH$_3$), 3.65 (dd, 2H, $J = 5.4$, 9.4 Hz, H–G,H-up), 3.38–3.32 (m, 1H, H–E), 3.32–3.25 (m, 1H, H–F).
Figure S55: $^{13}$C NMR (150.92 MHz, CD$_3$CN) $\delta$ 157.7 (4° C–A4), 146.4 (4° C–B1), 132.9 (4° C–A1), 129.2 (CH–A2), 128.9 (CH–B2), 126.8 (q, $J = 31.5$ Hz, kv. C–B4), 124.6 (q, $J = 273$ Hz, CF$_3$), 124.3 (q, $J = 3.7$ Hz, CH–B3), 113.1 (CH–A3), 73.3 and 73.2 (CH$_2$–G and CH$_2$–H), 54.7 (OCH$_3$), 46.9 (CH$_2$–D), 46.4 (CH$_2$–C), 42.2 (CH$_2$–F), 41.6 (CH$_2$–E).
Figure S56: 6b: COSY, HMQC and NOE spectra for assignment explanation.
A.5 UV-VIS spectra of substrates 3

Figure S57: Left: UV-VIS spectra of substrates 3a-d, including spectrum of 3e (R = NO$_2$). – 3a $c = 2.5 \times 10^{-5}$ mol L$^{-1}$, – 3b $c = 5.0 \times 10^{-5}$ mol L$^{-1}$, – 3e $c = 5.0 \times 10^{-5}$ mol L$^{-1}$, – 3d $c = 2.7 \times 10^{-5}$ mol L$^{-1}$, – 3e $c = 5.5 \times 10^{-5}$ mol L$^{-1}$. Right: Narrow band of higher concentrated spectrum of 3e $c = 2.0 \times 10^{-3}$ mol L$^{-1}$.

A.6 Intermolecular [2+2] cycloadditions

Scheme S1: Intermolecular [2+2] cycloaddition of trans-anethole or phenylpropene was not observed, only E/Z-isomerization occured (see main text).

A.7 E/Z Photoisomerization sensitized with flavin 2

Triplet E/Z photoisomerization sensitized with flavin 2 was observed in the case of trans-anethole (see A.6) and (E)-1-(4-methoxyphenyl)-but-2-en-1-one (Scheme S2) as examples of substituted styrenes and arylenones, respectively.
Scheme S2: \(E/Z\) Photoisomerization of \((E)-1-(4\text{-methoxyphenyl})\text{-but-2-en-1-one}\) sensitized with flavin 2.

**A.8 \(E/Z\) Photoisomerization of \((Z,Z)-11a\) followed by [2+2] cycloaddition sensitized with flavin 2**

Triplet \(E/Z\) photoisomerization producing mixture \((Z,Z)-11a : (E,E)-11a = 2 : 1\) was observed after short (2 min) irradiation of \((Z,Z)-11a\) in the presence of 2.5 mol% of 2. Only traces of cyclobutane \(12a\) were detected after this short irradiation. On the other hand, after 45 minutes, conversion of \((Z,Z)-11a\) to \(12a\) was completed. The product was the mixture of stereoisomers of similar composition (\(cis : trans = 4.5 : 1\)) as we observed starting from \((E,E)-11a\) (\(cis : trans = 5 : 1\)).

Scheme S3: \(E/Z\) Photoisomerization and [2+2] cycloaddition of \(11a\) sensitized with flavin 2.
A.9 Kinetic profile of 3a [2+2] cycloaddition to 4a on analytical scale

Figure S58: Time progress of reaction mixture composition during the cycloaddition of 3a on analytical scale.
A.10 Laboratory apparatus (illuminator) for preparative experiments

Figure S59: Front view of the switched on apparatus on magnetic stirrer with reaction mixture in Schlenk tube (cyan fluorescence of 2 occurs).

Figure S60: Top view of the apparatus with and without grating.
Figure S61: Detailed view of LEDs.
A.11 Estimated free-energy changes for electron transfer from dienes to alloxazine

The change in free Gibbs energy $\Delta G_{eT}$ of the electron transfer from the substituted methyl-styrene (see formula below) to the excited alloxazines (lumichrome was used as model compound with all characteristics known) in singlet state were calculated from the observed reduction potentials using the Rehm-Weller equation (1), \(^{31,32}\)

$$\Delta G_{eT} = 96.4 (E_{1/2}^{ox} - E_{1/2}^{red} - \frac{e^2}{\varepsilon a} - E_{0-0})$$

(1)

in which $E_{1/2}^{ox}$ and $E_{1/2}^{red}$ are the oxidation potential of the substrate and the reduction potential of alloxazine (-1.3 V, value for lumichrome), \(^{33}\) $\frac{e^2}{\varepsilon a}$ is the Coulomb term (-0.06 eV) \(^{33}\) and $E_{0-0}$ is the lumichrome excitation energy (2.92 eV). \(^{33}\)

<table>
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<th>R</th>
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<td>$\alpha$-methylstyrene</td>
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<td>22</td>
</tr>
</tbody>
</table>

[a] Values from the reference\(^{34-36}\) obtained in acetonitrile vs SCE. [b] Free energy changes calculated from equation (1) using $E_{1/2}^{red}$ (lumichrome) = -1.3 V vs SCE. \(^{33}\)