Supporting Information

Visible Light Induced Redox Neutral Fragmentation of Diol Derivatives

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1. General information

Commercially available reagents and solvents were used without further purification. Dry solvents were used for all photoreactions. Industrial grade of solvents was used for automated flash column chromatography. All NMR spectra were measured at room temperature using a Bruker Avance 300 (300 MHz for $^1$H, 75 MHz for $^{13}$C) or a Bruker Avance 400 (400 MHz for $^1$H, 101 MHz for $^{13}$C)

NMR spectrometer. All chemical shifts are reported in δ-scale as parts per million [ppm] (multiplicity, coupling constant $J$, number of protons) relative to the solvent residual peaks as the internal standard. The spectra were analyzed by first order and coupling constants $J$ are given in Hertz [Hz]. Abbreviations used for signal multiplicity: $^1$H-NMR: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets and m = multiplet; $^{13}$C-NMR: (+) = primary/tertiary, (–) = secondary, (C$_q$) = quaternary carbon.

The mass spectrometrical measurements were performed at the Central Analytical Laboratory of the University of Regensburg. All mass spectra were recorded on a Finnigan MAT 95, ThermoQuest Finnigan TSQ 7000, Finnigan MAT SSQ 710 A or an Agilent Q-TOF 6540 UHD instrument. GC measurements were performed on a GC 7890 from Agilent Technologies. Data acquisition and evaluation was done with Agilent ChemStation Rev.C.01.04. GC-MS measurements were performed on a 7890A GC system from Agilent Technologies with an Agilent 5975 MSD Detector. Data acquisition and evaluation was done with MSD ChemStation E.02.02.1431. A capillary column HP-5MS/30 m x 0.25 mm/0.25 µM film and helium as carrier gas (flow rate of 1 mL/min) were used. The injector temperature (split injection: 40:1 split) was 280 °C, detection temperature 300 °C (FID). GC measurements were performed and investigated via integration of the signal obtained. The GC oven temperature program was adjusted as follows: initial temperature 40 °C was kept for 3 min, the temperature was increased at a rate of 15 °C/min over a period of 16 min until 280 °C was reached and kept for 5 min, the temperature was again increased at a rate of 25 °C/min over a period of 48 seconds until the final temperature (300 °C) was reached and kept for 5 min. Naphthalene was chosen as internal standard.

Analytical TLC was performed on silica gel coated alumina plates (MN TLC sheets ALUGRAM® Xtra SIL G/UV254). UV light (254 or 366 nm) was used for visualization. If necessary, potassium permanganate was used for chemical staining. Purification by column chromatography was performed with silica gel 60 M (40-63 µm, 230-440 mesh, Merck) or pre-packed Biotage® SNAP Ultra HP-Sphere columns (25 µm spherical silica gel) on a Biotage® Isolera™ Spektra One device.

UV-vis absorption spectroscopy was performed on a Varian Cary BIO 50 UV-vis/NIR spectrometer with a 10 mm Hellma® quartz fluorescence cuvette at room temperature. Fluorescence spectra were recorded on a HORIBA FluoroMax®-4 Spectrofluorometer with a 10 mm Hellma® quartz fluorescence cuvette at room temperature. FluorEssence Version 3.5.1.20 was used as software. Fluorescence measurements were performed under nitrogen atmosphere.

For irradiation with blue light, OSRAM Oslon SSL 80 LDCQ7P-1U3U (blue, $\lambda_{max} = 455$ nm, $I_{max} = 1000$ mA, 1.12 W) was used.
2. Synthesis and characterization of starting materials

Compound 1p is commercially available.

2.1. General procedure for the synthesis of unbranched lignin model substrates

1.)

\[
\begin{align*}
\text{R}_1, \text{R}_2, \text{R}_3 = \text{H} \text{ or OMe} & \quad \text{R}_4, \text{R}_5 = \text{H} \text{ or OMe or Me} \\
& \\
\text{[R1-O-Br]} & \quad \text{[O-H]} & \quad \text{[K}_2\text{CO}_3] & \quad \text{[acetone, reflux]} & \quad \text{[R1-O-R4]} & \quad \text{[R2-O-R5]} \\
\end{align*}
\]

A 250 mL round-bottom flask was equipped with a reflux condenser and charged with the respective phenol (16.5 mmol, 1.1 equiv.), K$_2$CO$_3$ (22.5 mmol, 1.5 equiv.) and acetone (150 mL). The mixture was stirred at rt and the corresponding aromatic 2-bromo-ketone (15.0 mmol, 1.0 equiv.) was added in portions. The resulting suspension was stirred at reflux for 4 h. Then, the suspension was filtered and concentrated in vacuo. If necessary, the crude product was purified by column chromatography.

2.)

\[
\begin{align*}
& \quad \text{[NaBH}_4] & \quad \text{[THF/H}_2\text{O, rt]} & \quad \text{[R1-O-R4]} & \quad \text{[R2-O-R5]} \\
\end{align*}
\]

In a 100 mL round-bottom flask, the ketone from step 1 (5.0 mmol, 1.0 equiv.) and a THF/water mixture (25 mL, v/v = 4/1) were mixed. NaBH$_4$ (6.0 mmol, 1.2 equiv.) was added in one portion and the reaction mixture was stirred at rt for 2 h. Then, an aqueous saturated NH$_4$Cl solution (30 mL) was added. The crude product was extracted with EA (3 × 20 mL) and the combined organic extracts were dried over anhydrous Na$_2$SO$_4$. The organic solvent was evaporated in vacuo and the residue was purified by automated column chromatography on flash silica gel (PE/EA = 9:1 to 1:1) to obtain the desired product.

2.2. Characterization of unbranched lignin model substrates

1-(4-Methoxyphenyl)-2-phenoxyethan-1-ol (1a)

\[
\begin{align*}
& \quad \text{Yield: step 1: 99%, step 2: 80%} \\
& \quad \text{MF: C}_{15}\text{H}_{16}\text{O}_{3} \\
& \quad \text{MW: 244.29 g/mol} \\
\end{align*}
\]

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ [ppm] = 7.43 – 7.35 (m, 2H), 7.35 – 7.26 (m, 2H), 7.04 – 6.88 (m, 5H), 5.08 (dd, $J = 8.6$ Hz, 3.4 Hz, 1H), 4.12 – 3.96 (m, 2H), 3.83 (s, 3H), 2.80 (brs, 1H).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ [ppm] = 159.6, 158.5, 131.9, 129.7, 127.7, 121.4, 114.7, 114.1, 73.4, 72.3, 55.4.
HRMS (APCI) (m/z): [M+H-H₂O]+ (C₁₅H₁₅O₂) calc.: 227.1072, found: 227.1092.

**2-(2-Methoxyphenoxy)-1-(4-methoxyphenyl)ethan-1-ol (1b)**[^5]

![Structural formula of 2-(2-Methoxyphenoxy)-1-(4-methoxyphenyl)ethan-1-ol (1b)](image)

Yield: step 1: 89%, step 2: 99%

MF: C₁₅H₁₅O₄

MW: 274.32 g/mol

[^5]: ¹H NMR (300 MHz, CDCl₃): δ [ppm] = 7.41 – 7.32 (m, 2H), 7.04 – 6.85 (m, 6H), 5.07 (dd, J = 9.4 Hz, 2.9 Hz, 1H), 4.18 – 4.10 (m, 1H), 4.02 – 3.92 (m, 1H), 3.87 (s, 3H), 3.81 (s, 3H), 3.40 (brs, 1H).

[^5]: ¹³C NMR (75 MHz, CDCl₃): δ [ppm] = 159.5, 150.1, 148.1, 131.8, 127.7, 122.5, 121.1, 115.8, 114.0, 112.0, 76.2, 72.0, 55.9, 55.4.

HRMS (APCI) (m/z): [M+H-H₂O]+ (C₁₆H₁₇O₃) calc.: 257.1178, found: 257.1221.

**1-(4-Methoxyphenyl)-2-(p-tolyloxy)ethan-1-ol (1c)**[^6]

![Structural formula of 1-(4-Methoxyphenyl)-2-(p-tolyloxy)ethan-1-ol (1c)](image)

Yield: step 1: 100%, step 2: 97%

MF: C₁₆H₁₈O₃

MW: 258.32 g/mol

[^6]: ¹H NMR (300 MHz, CDCl₃): δ [ppm] = 7.46 – 7.35 (m, 2H), 7.14 (d, J = 8.2 Hz, 2H), 7.02 – 6.93 (m, 2H), 6.92 – 6.83 (m, 2H), 5.09 (dd, J = 8.1 Hz, 3.9 Hz, 1H), 4.12 – 3.96 (m, 2H), 3.84 (s, 3H), 3.32 (brs, 1H), 2.36 (s, 3H).

[^6]: ¹³C NMR (75 MHz, CDCl₃): δ [ppm] = 159.3, 156.3, 132.1, 130.3, 129.9, 127.5, 114.5, 113.8, 73.4, 72.0, 55.2, 20.4.

HRMS (APCI) (m/z): [M+H-H₂O]+ (C₁₆H₁₇O₂) calc.: 241.1229, found: 241.1290.

**2-Phenoxy-1-phenylethan-1-ol (1d)**[^7]

![Structural formula of 2-Phenoxy-1-phenylethan-1-ol (1d)](image)

Yield: step 1: 94%, step 2: 86%

MF: C₁₄H₁₄O₂

MW: 214.26 g/mol

[^7]: ¹H NMR (300 MHz, CDCl₃): δ [ppm] = 7.50 – 7.26 (m, 7H), 7.03 – 6.89 (m, 3H), 5.14 (dd, J = 8.8 Hz, 3.2 Hz, 1H), 4.12 (dd, J = 9.6 Hz, 3.2 Hz, 1H), 4.08 – 3.96 (m, 1H), 2.76 (brs, 1H).

[^7]: ¹³C NMR (75 MHz, CDCl₃): δ [ppm] = 158.5 (C₉), 139.7 (C₉), 128.7 (+), 128.7 (+), 128.3 (+), 126.4 (+), 121.4 (+), 114.7 (+), 73.4 (+), 72.7 (+).

HRMS (EI) (m/z): [M⁺]+ (C₁₄H₁₄O₂) calc.: 214.0994, found: 214.0993.

**1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)ethan-1-ol (1e)**[^8]

![Structural formula of 1-(3,4-Dimethoxyphenyl)-2-(2-methoxyphenoxy)ethan-1-ol (1e)](image)

Yield: step 1: 99%, step 2: 71%

MF: C₁₇H₂₀O₅

MW: 304.34 g/mol

[^8]: ¹H NMR (300 MHz, CDCl₃): δ [ppm] = 7.48 – 6.83 (m, 8H), 5.57 – 5.30 (m, 4H), 4.30 – 4.12 (m, 1H), 3.84 (s, 3H), 3.50 (s, 3H), 3.00 (brs, 1H).
1H NMR (300 MHz, CDCl₃): δ [ppm] = 7.04 – 6.81 (m, 7H), 5.05 (dd, J = 9.3 Hz, 3.0 Hz, 1H), 4.15 (dd, J = 10.0 Hz, 3.0 Hz, 1H), 4.03 – 3.93 (m, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 3.86 (s, 3H).

13C NMR (75 MHz, CDCl₃): δ [ppm] = 150.1, 149.1, 148.8, 148.1, 132.3, 122.5, 121.1, 118.7, 115.9, 112.0, 111.0, 109.4, 76.3, 72.2, 56.0, 55.93, 55.88.

HRMS (APCI) (m/z): [M+H-H₂O]+ (C₁₇H₁₉O₄) calc.: 287.1283, found: 287.1283.

2-(2,6-Dimethoxyphenoxy)-1-(3,4-dimethoxyphenyl)ethan-1-ol (1f) [5]
Yield: step 1: 83%, step 2: 88%
MF: C₁₈H₂₂O₆
MW: 334.37 g/mol

1H NMR (300 MHz, CDCl₃): δ [ppm] = 6.96 (dd, J = 14.9 Hz, 4.8 Hz, 2H), 6.85 (d, J = 8.3 Hz, 1H), 6.77 (d, J = 8.2 Hz, 1H), 6.55 (d, J = 8.4 Hz, 2H), 4.87 (dd, J = 9.9 Hz, 2.4 Hz, 1H), 4.51 (s, 1H), 4.35 (dd, J = 10.9 Hz, 2.3 Hz, 1H), 3.81 (m, 9H), 3.78 (s, 3H), 3.67 (t, J = 10.4 Hz, 1H).

13C NMR (75 MHz, CDCl₃): δ [ppm] = 153.0, 148.8, 148.3, 136.5, 131.9, 123.9, 118.5, 110.8, 109.2, 104.9, 79.9, 72.0, 55.8, 55.7, 55.6.

HRMS (APCI) (m/z): [M+H-H₂O]+ (C₁₈H₂₁O₅) calc.: 317.1389, found: 317.1388.

2-(3,5-Dimethoxyphenoxy)-1-(3,4-dimethoxyphenyl)ethan-1-ol (1g) [5]
Yield: step 1: 100%, step 2: 94%
MF: C₁₈H₂₂O₆
MW: 334.37 g/mol

1H NMR (300 MHz, CDCl₃): δ [ppm] = 7.03 – 6.94 (m, 2H), 6.87 (d, J = 8.2 Hz, 1H), 6.10 (s, 3H), 5.06 (dd, J = 8.7 Hz, 3.3 Hz, 1H), 4.07 – 3.95 (m, 2H), 3.91 (s, 3H), 3.89 (s, 3H), 3.76 (s, 6H), 2.74 (brs, 1H).

13C NMR (75 MHz, CDCl₃): δ [ppm] = 161.7, 160.4, 149.3, 149.0, 132.3, 118.7, 111.2, 109.4, 93.7, 93.6, 73.5, 72.5, 56.1, 56.0, 55.7, 55.6.

HRMS (ESI) (m/z): [M+H]+ = (C₁₈H₂₃O₆) calc.: 335.1495; found: 335.1493.

2-(2-Methoxyphenoxy)-1-(3,4,5-trimethoxyphenyl)ethan-1-ol (1h) [5]

2-Bromo-1-(3,4,5-trimethoxyphenyl)ethan-1-one which was necessary for the first step of the synthesis of 1h was prepared according to a previously reported procedure (10 mmol scale, 46% yield).[8]

Yield: step 1: 52%, step 2: 88%
MF: C₁₈H₂₂O₆
MW: 334.37 g/mol
1H NMR (300 MHz, CDCl₃): δ [ppm] = 7.05 – 6.84 (m, 4H), 6.66 (s, 2H), 5.03 (dd, J = 9.2 Hz, 2.9 Hz, 1H), 4.17 (dd, J = 10.0 Hz, 3.0 Hz, 1H), 4.02 – 3.92 (m, 1H), 3.87 (s, 3H), 3.86 (s, 6H), 3.83 (s, 3H).

13C NMR (75 MHz, CDCl₃): δ [ppm] = 153.4, 150.2, 148.0, 137.6, 135.4, 122.7, 121.2, 116.1, 112.0, 103.2, 76.4, 72.5, 60.9, 56.2, 55.9.

HRMS (APCI) (m/z): [M+H-H₂O]+ (C₁₈H₂₁O₅) calc.: 317.1389, found: 317.1398.

2.3. Synthesis and characterization of substrate 1i[3b]

1.)

To a suspension of K₂CO₃ (0.6 g, 4.3 mmol, 1.0 equiv.) in ethanol/aceton (v/v = 1/1, 20 mL), 2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)ethan-1-one (1.2 g, 4.4 mmol, 1.0 equiv.) and a solution of formaldehyde in water (37%) (0.6 mL, 7.3 mmol, 1.7 equiv.) was added. The reaction mixture was stirred for 4 h at rt under N₂ atmosphere, then it was filtered to remove K₂CO₃ and concentrated in vacuo. The residue was purified by column chromatography and used directly for the next step, although containing impurities.

2.)

In a 100 mL round-bottom flask, the ketone from step 1 (2.0 mmol, 1.0 equiv.) and a THF/water mixture (12 mL, v/v = 4/1) were mixed. NaBH₄ (2.4 mmol, 1.2 equiv.) was added in one portion and the reaction mixture was stirred at rt for 2 h. Then, an aqueous saturated NH₄Cl solution (15 mL) was added. The crude product was extracted with EA (3 × 10 mL) and the combined organic extracts were dried over anhydrous Na₂SO₄. The organic solvent was evaporated in vacuo and the residue was purified by automated column chromatography on flash silica gel (PE/EA = 9:1 to 1:1) to obtain the desired product.

3-Methoxy-2-(2-methoxyphenoxy)-1-(4-methoxyphenyl)propan-1-ol (1i)[5]

Yield: 73%
MF: C₁₇H₂₀O₅
MW: 304.34 g/mol

1H NMR (300 MHz, CDCl₃): δ [ppm] = 7.40 – 7.28 (m, 2H), 7.16 – 6.86 (m, 6H), 5.03 – 4.95 (m, 1H), 4.18 – 4.07 (m, 1H), 4.07 – 3.99 (m, 1H), 3.92 – 3.86 (m, 3H), 3.81 – 3.78 (m, 3H), 3.69 – 3.57 (m, 1H), 3.50 – 3.40 (m, 1H), 2.95 (brs, 1H).

Spectral data are consistent with those reported in the literature.

HRMS (APCI) (m/z): [M+H-H₂O]+ (C₁₇H₂₀O₄) calc.: 287.1283, found: 287.1282.
2.4. General procedures for the synthesis of acetylated aromatic substrates

**General procedure for the synthesis of diols via reduction (step 1)**

![Chemical structure image]

In a 100 mL round-bottom flask, the respective ketone (5.0 mmol, 1.0 equiv.) and a THF/water mixture (25 mL, v/v = 4/1) were mixed. NaBH₄ (6.0 mmol, 1.2 equiv.) was added in one portion and the reaction mixture was stirred at rt for 2 h. Then, an aqueous saturated NH₄Cl solution (30 mL) was added. The crude product was extracted with EA (3 × 20 mL) and the combined organic extracts were dried over anhydrous Na₂SO₄. The organic solvent was evaporated in vacuo and the residue was purified by automated column chromatography on flash silica gel (PE/EA = 9:1 to 1:1) to obtain the desired diol.

**General procedure for the synthesis of diols via ring opening of epoxides (step 1)**

![Chemical structure image]

To the respective epoxide (5.0 mmol, 1.0 equiv.) was added distilled water (30 mL) and the reaction mixture was stirred for 3 h at 60 °C. The reaction mixture was extracted with EA (3 x 15 mL) and brine (2 x 15 mL). The combined organic phases were dried over Na₂SO₄, concentrated in vacuo and purified by flash column chromatography (PE/EA = 9:1 to 1:1).

**General procedure for the acetylation of diols (step 2)**

![Chemical structure image]

To a solution of diol (3.0 mmol) in DCM (12 mL) was added Ac₂O (4.5 mmol) and pyridine (1 mL) and the mixture was stirred for 3 h at rt. Then it was diluted with DCM to 30 mL and washed with 1M HCl (2 x 15 mL), saturated NaHCO₃ (aq.) (15 mL) and brine (15 mL). The organic phase was dried over anhydrous Na₂SO₄ and concentrated in vacuo. The crude product was purified by flash column chromatography (PE/EA = 9:1 to 2:1).
2.5. Characterization of acetylated aromatic substrates

2-Hydroxy-2-(4-methoxyphenyl)ethyl acetate (1j)[6]

\[
\text{Yield: step 1 (reduction): 56%, step 2: 61%}
\]

\[
\text{MF: C}_{11}\text{H}_{14}\text{O}_{4}
\]

\[
\text{MW: 210.23 g/mol}
\]

\[
^1\text{H NMR (300 MHz, CDCl}_3\text{)}: \delta [ppm] = 7.32 – 7.25 (m, 2H), 6.91 – 6.84 (m, 2H), 4.88 (dd, J = 8.4 Hz, 3.5 Hz, 1H), 4.26 – 4.07 (m, 2H), 3.79 (s, 3H), 2.67 (brs, 1H), 2.08 (s, 3H).
\]

\[
^{13}\text{C NMR (75 MHz, CDCl}_3\text{)}: \delta [ppm] = 171.3 (C_q), 159.6 (C_q), 132.0 (C_q), 127.5 (+), 114.0 (+), 72.0 (+), 69.4 (–), 55.4 (+), 21.0 (+).
\]

HRMS (APCI) (m/z): [M+NH\textsubscript{4}]\textsuperscript{+} (C\textsubscript{13}H\textsubscript{18}O\textsubscript{4}) calc.: 228.1230, found: 228.1230.

2-Hydroxy-2-phenylethyl acetate (1k)[10]

\[
\text{Yield: 52%}
\]

\[
\text{MF: C}_{10}\text{H}_{12}\text{O}_3
\]

\[
\text{MW: 180.20 g/mol}
\]

\[
^1\text{H NMR (300 MHz, CDCl}_3\text{)}: \delta [ppm] = 7.37 – 7.25 (m, 5H), 4.89 (dd, J = 8.3 Hz, 3.5 Hz, 1H), 4.26 – 4.06 (m, 2H), 3.09 (brs, 1H), 2.05 (s, 3H).
\]

\[
^{13}\text{C NMR (75 MHz, CDCl}_3\text{)}: \delta [ppm] = 171.3, 140.0, 128.5, 128.1, 126.2, 72.2, 69.3, 20.9.
\]

HRMS (APCI) (m/z): [M+H-H\textsubscript{2}O]\textsuperscript{+} (C\textsubscript{10}H\textsubscript{11}O\textsubscript{2}) calc.: 163.0759, found: 163.0755.

2-(4-Chlorophenyl)-2-hydroxyethyl acetate (1l)[10]

\[
\text{Yield: step 1 (epoxide opening): 95%, step 2: 45%}
\]

\[
\text{MF: C}_{10}\text{H}_{12}\text{ClO}_3
\]

\[
\text{MW: 214.65 g/mol}
\]

\[
^1\text{H NMR (300 MHz, CDCl}_3\text{)}: \delta [ppm] 7.40 – 7.14 (m, 4H), 4.98 – 4.76 (m, 1H), 4.29 – 3.95 (m, 2H), 3.07 (brs, 1H), 2.07 (s, 3H).
\]

\[
^{13}\text{C NMR (75 MHz, CDCl}_3\text{)}: \delta [ppm] = 171.4, 138.5, 133.9, 128.7, 127.6, 71.6, 69.1, 20.9.
\]

HRMS (APCI) (m/z): [M+H]\textsuperscript{+} (C\textsubscript{10}H\textsubscript{12}ClO\textsubscript{3}) calc.: 215.0475, found: 215.0469.

2-(4-Fluorophenyl)-2-hydroxyethyl acetate (1m)[10]

\[
\text{Yield: step 1 (epoxide opening): 68%, step 2: 38%}
\]

\[
\text{MF: C}_{10}\text{H}_{12}\text{FO}_3
\]

\[
\text{MW: 198.19 g/mol}
\]

\[
^1\text{H NMR (300 MHz, CDCl}_3\text{)}: \delta [ppm] = 7.38 – 7.21 (m, 2H), 7.00 (td, J = 8.6 Hz, 1.9 Hz, 2H), 4.92 – 4.78 (m, 1H), 4.23 – 3.99 (m, 2H), 3.09 (brs, 1H), 2.03 (s, 3H).
\]
$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ [ppm] = 171.4, 162.5 (d, $J = 246.1$ Hz), 135.8, 127.9 (d, $J = 8.2$ Hz), 115.4 (d, $J = 21.5$ Hz), 71.5, 69.2, 20.8.

HRMS (APCI) (m/z): [M+H]$^+$ (C$_{10}$H$_{12}$FO$_3$) calc.: 199.0770, found: 199.0766.

2.6. Synthesis and characterization of aromatic substrates with other leaving groups

**Synthesis and characterization of substrate with benzyl leaving group (1n)**

\[
\begin{align*}
\text{MeO} & \quad \text{OH} \\
| & | \\
| & | \\
\text{O} & \quad \text{MeO}
\end{align*}
\]

\[
\begin{align*}
\text{OH} & \quad \text{OBz} \\
| & | \\
| & | \\
\text{O} & \quad \text{MeO}
\end{align*}
\]

To a stirred solution of 1-(4-methoxyphenyl)-1,2-ethanediol (0.34 g, 2.0 mmol, 1.0 equiv.) in pyridine (4 mL) at 0 °C, benzoylchloride (0.25 mL, 2.2 mmol, 1.1 equiv.) was added dropwise. The mixture was allowed to warm to rt over night before ice water (4 mL) was added. After stirring for 30 minutes, the mixture was extracted with DCM (3 x 15 mL) and the combined organic phase was dried over sodium sulfate. Purification by column chromatography (PE/EA = 7:3) gave the product as colorless solid.

**2-Hydroxy-2-(4-methoxyphenyl)ethyl benzoate (1n)**

Yield: 73%

MF: C$_{16}$H$_{16}$O$_4$

MW: 272.30 g/mol

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ [ppm] = 7.29 (m, 2H), 7.78 – 7.51 (m, 2H), 7.48 – 7.27 (m, 4H), 6.97 – 6.83 (m, 2H), 5.06 (dd, $J = 3.6$ Hz, 1H), 4.55 – 4.24 (m, 2H), 3.81 (s, 3H).

HRMS (ES) (m/z): [M+NH$_4$]$^+$ (C$_{16}$NH$_2$O$_4$) calc.: 290.1392, found: 290.1388.

**Synthesis and characterization of intramolecular substrate (1o)**

\[
\begin{align*}
\text{OH} & \quad \text{OH} \\
| & | \\
| & | \\
\text{NaBH}_4 & \quad \text{MeOH, 0°C to rt} \\
\text{MeOH} & \quad \text{MeOH, 0°C to rt}
\end{align*}
\]

To a stirred solution of 3-coumaranone (0.50 g, 3.7 mmol, 1.0 equiv.) in methanol (10 mL) at 0°C, sodium borohydride (1.6 g, 42 mmol, 11.4 equiv.) was added in portions within 1 hour. The reaction mixture was stirred for additional 30 minutes at 0 °C to complete conversion, monitored by TLC. The mixture was allowed to warm to rt and HCl (15 mL, 0.2 M) was added. After extraction with chloroform (3 x 15 mL), the combined organic phases were dried over sodium sulfate. The crude product was purified by column chromatography with tert-butyl methyl ether.

**2,3-Dihydrobenzofuran-3-ol (1o)**

Yield: 99%

MF: C$_8$H$_8$O$_2$

MW: 136.15 g/mol
\[ ^1H \text{NMR (300 MHz, CDCl}_3\]:} \( \delta \text{ [ppm]} = 7.40 (dd, J = 7.4 Hz, 0.6 Hz, 1H), 7.26 (td, J = 7.6 Hz, 1.3 Hz, 1H), 6.94 (td, J = 7.4 Hz, 0.9 Hz, 1H), 6.87 (d, J = 8.1 Hz, 1H), 5.29 (brs, 1H), 4.50 (dd, J = 10.7 Hz, 6.5 Hz, 1H), 4.39 (dd, J = 10.7 Hz, 2.2 Hz, 1H), 2.42 \text{ – 2.24 (m, 1H).} \]

\[ ^{13}C \text{NMR (75 MHz, CDCl}_3\]:} \( \delta \text{ [ppm]} = 160.3, 130.9, 128.3, 125.6, 121.1, 110.7, 79.2, 72.2. \]

HRMS (El) (m/z): [M\textsuperscript{+}] (C\textsubscript{8}H\textsubscript{8}O\textsubscript{2}) calc.: 136.0524, found: 136.0515.

2.7. Synthesis and characterization of unprotected and full protected diol derivatives

**1-(4-Methoxyphenyl)ethane-1,2-diol (4)[14]**

![OH](MeO)

Yield: (by reduction with NaBH\textsubscript{4}, see 2.4, step 1) 56%

MF: C\textsubscript{9}H\textsubscript{12}O\textsubscript{3}

MW: 168.19 g/mol

\[ ^1H \text{NMR (300 MHz, CDCl}_3\]:} \( \delta \text{ [ppm]} = 7.34 \text{ – 7.26 (m, 2H), 6.93 \text{ – 6.87 (m, 2H), 4.78 (dd, J = 8.0 Hz, 3.8 Hz, 1H), 3.81 (s, 3H), 3.76 \text{ – 3.62 (m, 2H), 2.01 (brs, 2H).} \]

HRMS (APCI) (m/z): [M+H-H\textsubscript{2}O]\textsuperscript{+} (C\textsubscript{9}H\textsubscript{11}O\textsubscript{2}) calc.: 151.0759, found: 151.0785.

**Synthesis and characterization of compound 5[15]**

![OH](MeO)

A solution of 1-(4-methoxyphenyl)ethane-1,2-diol (5 mmol, 1.0 equiv.) in 2 mL pyridine/acetic anhydride (1:1, v/v) was stirred at rt for 2 h. Then, the reaction mixture was diluted with EA (5 mL) and washed with a solution of NaHCO\textsubscript{3} (5%, 5 mL), water and brine. The organic phases were dried over anhydrous Na\textsubscript{2}SO\textsubscript{4} and concentrated in vacuo. The resulting crude product was purified by flash column chromatography (PE/EA = 9:1) to give compound 5.

**1-(4-Methoxyphenyl)ethane-1,2-diyl diacetate (5)**

![OH](MeO)

Yield: 58%

MF: C\textsubscript{13}H\textsubscript{16}O\textsubscript{5}

MW: 252.27 g/mol

\[ ^1H \text{NMR (300 MHz, CDCl}_3\]:} \( \delta \text{ [ppm]} = 7.33 \text{ – 7.26 (m, 2H), 6.92 \text{ – 6.85 (m, 2H), 5.96 (t, J = 6.1 Hz, 1H), 4.29 (d, J = 6.0 Hz, 2H), 3.80 (s, 3H), 2.09 (s, 3H), 2.05 (s, 3H).} \]

\[ ^{13}C \text{NMR (75 MHz, CDCl}_3\]:} \( \delta \text{ [ppm]} = 170.8 (C\textsubscript{q}), 170.2 (C\textsubscript{q}), 159.9 (C\textsubscript{q}), 128.7 (C\textsubscript{q}), 128.3 (+), 114.1 (+), 73.1 (+), 66.2 (–), 55.4 (+), 21.3 (+), 21.0 (+). \]

HRMS (APCI) (m/z): [M+H]\textsuperscript{+} (C\textsubscript{13}H\textsubscript{17}O\textsubscript{5}) calc.: 253.1071, found: 253.1068.
2.8. Procedure for the preparation of NaOP(O)(OBu)$_2$

To a solution of dibutylphosphate (10 mmol, 2.102 g) in 10 mL deionized water, NaHCO$_3$ (10 mmol, 0.840 g) was added in portions. After the addition was completed, the reaction mixture was stirred at rt for another 1 h. Then water was removed under reduced pressure. The resulting residue was further dried under vacuum for one week to afford the desired product in quantitative yield.
3. Optimization of reaction conditions for photocatalytic C–O cleavage

Table S1: Screening of photocatalysts.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Photocatalyst</th>
<th>Yield of ketone[a]</th>
<th>Yield of phenol[a]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ru(ppy)$_3$·6H$_2$O</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>2</td>
<td>fac-Ir(ppy)$_2$</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>3</td>
<td>Ir[dFCF$_3$(ppy)$_2$(dtbpy)]PF$_6$</td>
<td>3%</td>
<td>4%</td>
</tr>
<tr>
<td>4</td>
<td>Ir[FCF$_3$(ppy)$_2$(dtbpy)]PF$_6$</td>
<td>72%</td>
<td>57%</td>
</tr>
<tr>
<td>5</td>
<td>[Ir(ppy)$_2$(dtbpy)]PF$_6$</td>
<td>91%</td>
<td>81%</td>
</tr>
<tr>
<td>6</td>
<td>Eosin Y (5 mol%)</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>7</td>
<td>Perylene (5 mol%)</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>8</td>
<td>4CzIPN (5 mol%)</td>
<td>26%</td>
<td>26%</td>
</tr>
<tr>
<td>9</td>
<td>4CzIPN (5 mol%), air</td>
<td>59%</td>
<td>48%</td>
</tr>
</tbody>
</table>

[a] Determined by GC analysis using naphthalene as an internal standard.

3.1. Optimization for [Ir(ppy)$_2$(dtbpy)]PF$_6$ system

Table S2: Screening of bases for the iridium system.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Base</th>
<th>Yield of ketone[a]</th>
<th>Yield of phenol[a]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>K$_2$CO$_3$</td>
<td>21%</td>
<td>14%</td>
</tr>
<tr>
<td>2</td>
<td>NaOAc</td>
<td>53%</td>
<td>54%</td>
</tr>
<tr>
<td>3</td>
<td>NaOPiv</td>
<td>23%</td>
<td>9%</td>
</tr>
<tr>
<td>4</td>
<td>NaHCO$_3$</td>
<td>29%</td>
<td>24%</td>
</tr>
<tr>
<td>5</td>
<td>NaHPO$_4$</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>6</td>
<td>2,4,6-collidine</td>
<td>traces</td>
<td>traces</td>
</tr>
<tr>
<td>7</td>
<td>NaOP(O)(OBu)$_2$</td>
<td>91%</td>
<td>81%</td>
</tr>
<tr>
<td>8</td>
<td>NaOP(O)(OBu)$_2$ (50 mol%)</td>
<td>40%</td>
<td>30%</td>
</tr>
</tbody>
</table>

[a] Determined by GC analysis using naphthalene as an internal standard.
Table S3: Screening of solvents for the iridium system.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Yield of ketone&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Yield of phenol&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DCM</td>
<td>28%</td>
<td>traces</td>
</tr>
<tr>
<td>2</td>
<td>DCE</td>
<td>9%</td>
<td>traces</td>
</tr>
<tr>
<td>3</td>
<td>1,4-Dioxane</td>
<td>12%</td>
<td>traces</td>
</tr>
<tr>
<td>4</td>
<td>Acetone</td>
<td>16%</td>
<td>13%</td>
</tr>
<tr>
<td>5</td>
<td>MeCN</td>
<td>11%</td>
<td>0%</td>
</tr>
<tr>
<td>6</td>
<td>EA</td>
<td>7%</td>
<td>22%</td>
</tr>
<tr>
<td>7</td>
<td>DMSO</td>
<td>46%</td>
<td>45%</td>
</tr>
<tr>
<td>8</td>
<td>DMF</td>
<td>23%</td>
<td>24%</td>
</tr>
</tbody>
</table>

<sup>a</sup>Determined by GC analysis using naphthalene as an internal standard.

Table S4: Screening of thiols for the iridium system.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Thiol</th>
<th>Yield of ketone&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Yield of phenol&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PhSH</td>
<td>22%</td>
<td>13%</td>
</tr>
<tr>
<td>2</td>
<td>PhSSPh</td>
<td>17%</td>
<td>8%</td>
</tr>
<tr>
<td>3</td>
<td>BnSH</td>
<td>58%</td>
<td>52%</td>
</tr>
<tr>
<td>4</td>
<td>CH₃CH(SH)COCH₃</td>
<td>71%</td>
<td>49%</td>
</tr>
<tr>
<td>5</td>
<td>CH₃CH(SH)CO₂Et</td>
<td>40%</td>
<td>33%</td>
</tr>
</tbody>
</table>

<sup>a</sup>Determined by GC analysis using naphthalene as an internal standard.

Table S5: Control reactions for the iridium system.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Deviation from standard conditions</th>
<th>Yield of ketone&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Yield of phenol&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>no light</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>2</td>
<td>no photocatalyst</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>3</td>
<td>no thiol</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>4</td>
<td>no base</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>5</td>
<td>under air</td>
<td>16%</td>
<td>trace</td>
</tr>
</tbody>
</table>

<sup>a</sup>Determined by GC analysis using naphthalene as an internal standard.
3.2. Optimization for 4CzIPN system

Table S6: Screening of bases for the 4CzIPN system.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Base</th>
<th>Yield of ketone$^a$</th>
<th>Yield of phenol$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$K_2CO_3$</td>
<td>20%</td>
<td>28%</td>
</tr>
<tr>
<td>2</td>
<td>NaOAc</td>
<td>31%</td>
<td>42%</td>
</tr>
<tr>
<td>3</td>
<td>NaHCO$_3$</td>
<td>32%</td>
<td>72%</td>
</tr>
<tr>
<td>4</td>
<td>NaOP(O)(OBu)$_2$</td>
<td>72%</td>
<td>44%</td>
</tr>
</tbody>
</table>

$^a$ Determined by GC analysis using naphthalene as an internal standard.

Table S7: Screening of solvents for the 4CzIPN system.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Yield of ketone$^a$</th>
<th>Yield of phenol$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DCM</td>
<td>63%</td>
<td>traces</td>
</tr>
<tr>
<td>2</td>
<td>DCE</td>
<td>62%</td>
<td>traces</td>
</tr>
<tr>
<td>3</td>
<td>1,4-Dioxane</td>
<td>21%</td>
<td>15%</td>
</tr>
<tr>
<td>4</td>
<td>Acetone</td>
<td>35%</td>
<td>traces</td>
</tr>
<tr>
<td>5</td>
<td>MeCN</td>
<td>39%</td>
<td>7%</td>
</tr>
<tr>
<td>6</td>
<td>DMSO</td>
<td>73%</td>
<td>54%</td>
</tr>
<tr>
<td>7</td>
<td>DMF</td>
<td>71%</td>
<td>41%</td>
</tr>
<tr>
<td>8</td>
<td>THF</td>
<td>50%</td>
<td>25%</td>
</tr>
</tbody>
</table>

$^a$ Determined by GC analysis using naphthalene as an internal standard.

Table S8: Screening of different amounts of catalyst and thiol.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Yield of ketone$^a$</th>
<th>Yield of phenol$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8 mol% 4CzIPN, 20 mol% thiol</td>
<td>80%</td>
<td>41%</td>
</tr>
<tr>
<td>2</td>
<td>8 mol% 4CzIPN, 40 mol% thiol</td>
<td>76%</td>
<td>58%</td>
</tr>
<tr>
<td>3</td>
<td>8 mol% 4CzIPN, 60 mol% thiol</td>
<td>71%</td>
<td>58%</td>
</tr>
<tr>
<td>4</td>
<td>8 mol% 4CzIPN, 80 mol% thiol</td>
<td>57%</td>
<td>55%</td>
</tr>
<tr>
<td>5</td>
<td>4 mol% 4CzIPN, 40 mol% thiol</td>
<td>82%</td>
<td>57%</td>
</tr>
</tbody>
</table>

$^a$ Determined by GC analysis using naphthalene as an internal standard.
<table>
<thead>
<tr>
<th>Entry</th>
<th>Thiol</th>
<th>Yield of ketone</th>
<th>Yield of phenol</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PhSH</td>
<td>40%</td>
<td>19%</td>
</tr>
<tr>
<td>2</td>
<td>PhSSPh</td>
<td>41%</td>
<td>19%</td>
</tr>
<tr>
<td>3</td>
<td>BnSH</td>
<td>56%</td>
<td>32%</td>
</tr>
<tr>
<td>4</td>
<td>CH₃CH(SH)COCH₃</td>
<td>80%</td>
<td>36%</td>
</tr>
<tr>
<td>5</td>
<td>CH₃CH(SH)CO₂Et</td>
<td>77%</td>
<td>38%</td>
</tr>
<tr>
<td>6</td>
<td>(iPr)₂SiSH</td>
<td>81%</td>
<td>52%</td>
</tr>
</tbody>
</table>

Table S9: Screening of thiols for the 4CzIPN system.

Table S10: Control reactions for the 4CzIPN system.

**Determined by GC analysis using naphthalene as an internal standard.**
Table S11: Further screening reactions for the 4CzIPN system.

\[
\begin{array}{ccc}
\text{Entry} & \text{Deviation from standard conditions} & \text{Yield of ketone$^a$} & \text{Yield of phenol$^a$} \\
1 & 0.2 \text{ mmol in 1 mL DMSO} & 64\% & 58\% \\
2 & 0.2 \text{ mmol in 2 mL DMSO} & 56\% & 54\% \\
3 & 0.1 \text{ mmol in 2 mL DMSO} & 67\% & 32\% \\
4 & \text{0.5 equiv. base} & 80\% & 57\% \\
\end{array}
\]

$^a$ Determined by GC analysis using naphthalene as an internal standard. Standard conditions: 0.1 mmol substrate in 1 mL DMSO.

Table S12: Screening of C–O cleavage of alkyl substrates.

\[
\begin{array}{ccc}
\text{Entry} & \text{Deviation from standard conditions} & \text{Conversion} & \text{Yield of phenol$^a$} \\
1 & \text{no change} & 44\% & 39\% \\
2 & 72 \text{ h} & 62\% & 49\% \\
3 & \text{2.0 mol\% Ir-cat, 40 mol\% thiol, 72 h} & 80\% & 72\% \\
4 & \text{same as entry 3, 0.2 mmol in 1 mL DMA} & 79\% & 66\% \\
5 & \text{4.0 mol\% 4CzIPN, 40 mol\% thiol, 48 h, under air} & 41\% & \text{nd} \\
\end{array}
\]

$^a$ Determined by GC analysis using naphthalene as an internal standard.
4. General procedures for photocatalytic reactions

4.1. Visible light-induced C–O cleavage of benzylic diol derivatives via 4CzIPN catalysis

The substrate (0.1 mmol, 1.0 equiv.), 4CzIPN (3.2 mg, 0.004 mmol, 4 mol%) and NaOP(O)(OBu)\(_2\) (11.6 mg, 0.05 mmol, 0.5 equiv.) were weighed into a 5 mL crimp cap vial equipped with a stirring bar. Dry DMSO (1.0 mL) and methyl thioglycolate (4 μL, 0.04 mmol, 40 mol%) were added via syringe and the vial was capped. The yellow reaction mixture was irradiated using a blue LED for 24 h at 25 °C. Then four vials with the same content were combined and the reaction mixture was diluted with EA (40 mL) and washed with water (2 x 15 mL). The organic layer was dried over Na\(_2\)SO\(_4\) and the solvent was removed under reduced pressure. Purification of the crude product was performed by flash column chromatography (PE/EA = 9:1 up to 1:1).

4.2. Visible light-induced C–O cleavage of benzylic diol derivatives via [Ir(ppy)\(_2\)(dtbpy)]PF\(_6\) catalysis

The substrate (0.2 mmol, 1.0 equiv.), [Ir(ppy)\(_2\)(dtbpy)]PF\(_6\) (1.8 mg, 0.002 mmol, 1 mol%) and NaOP(O)(OBu)\(_2\) (46.4 mg, 0.2 mmol, 1.0 equiv.) were weighed into a 5 mL crimp cap vial equipped with a stirring bar. Dry DMA (2.0 mL) and methyl thioglycolate (4 μL, 0.04 mmol, 20 mol%) were added via syringe. Nitrogen atmosphere was then introduced via three cycles of freeze-pump-thaw (10 minutes vacuum at 1 mbar). The yellow reaction mixture was irradiated using a blue LED for 24 h at 25 °C. Then two vials with the same content were combined and the reaction mixture was diluted with EA (40 mL) and extracted with water (2 x 15 mL). The organic layer was dried over Na\(_2\)SO\(_4\) and the solvent was removed under reduced pressure. Purification of the crude product was performed by flash column chromatography (PE/EA = 9:1 up to 1:1).

Following the general procedure 4.1. with substrate 1a (24.4 mg, 0.1 mmol) and 4CzIPN. Four reactions were carried out in parallel and then combined for isolation by column chromatography to obtain ketone 2a (47.6 mg, 79%) and phenol 3a (23.9 mg, 63%).

Following the general procedure 4.2. with substrate 1a (48.9 mg, 0.2 mmol) and 1 mol% Ir catalyst. Two reactions were carried out in parallel and then combined for isolation by column chromatography to obtain ketone 2a (51.8 mg, 86%) and phenol 3a (26.8 mg, 71%).
Following the general procedure 4.1. with substrate 1b (27.4 mg, 0.1 mmol) and 4CzIPN. Four reactions were carried out in parallel and then combined for isolation by column chromatography to obtain ketone 2a (41.3 mg, 69%) and phenol 3b (25.4 mg, 51%).

Following the general procedure 4.1. with substrate 1c (25.8 mg, 0.1 mmol) and 4CzIPN. Four reactions were carried out in parallel and then combined for isolation by column chromatography to obtain ketone 2a (54.2 mg, 90%) and phenol 3c (26.4 mg, 61%).

Following the general procedure 4.1. with substrate 1d (21.4 mg, 0.1 mmol) and 4CzIPN. Four reactions were carried out in parallel and then combined for isolation by column chromatography to obtain ketone 2b (33.0 mg, 69%) and phenol 3a (18.9 mg, 50%).

Following the general procedure 4.1. with substrate 1e (30.4 mg, 0.1 mmol) and 4CzIPN. Four reactions were carried out in parallel and then combined for isolation by column chromatography to obtain ketone 2c (54.0 mg, 75%) and phenol 3b (30.1 mg, 61%).

Following the general procedure 4.1. with substrate 1f (33.4 mg, 0.1 mmol) and 4CzIPN. Four reactions were carried out in parallel and then combined for isolation by column chromatography to obtain ketone 2c (60.1 mg, 83%) and phenol 3d (46.6 mg, 76%).
Following the general procedure 4.1. with substrate 1g (33.4 mg, 0.1 mmol) and 4CzIPN. Four reactions were carried out in parallel and then combined for isolation by column chromatography to obtain ketone 2c (72.0 mg, 100%) and phenol 3e (51.8 mg, 84%).

Following the general procedure 4.1. with substrate 1h (33.4 mg, 0.1 mmol) and 4CzIPN. Two reactions were carried out in parallel and then combined for isolation by column chromatography to obtain ketone 2d (28.6 mg, 68%) and phenol 3b (8.3 mg, 33%).

Following the general procedure 4.1. with substrate 1i (30.4 mg, 0.1 mmol) and 4CzIPN. Four reactions were carried out in parallel and then combined for isolation by column chromatography to obtain phenol 3b (10.0 mg, 20%), but no ketone could be isolated. Ketone 2e was detected by GC-MS analysis.

Following the general procedure 4.2. with substrate 1i (60.9 mg, 0.2 mmol) and 1 mol% Ir catalyst. Two reactions were carried out in parallel and then combined for isolation by column chromatography, but no ketone 2e nor phenol 3b could be isolated. Ketone 2e was detected by GC-MS analysis.

Following the general procedure 4.1. with substrate 1j (21.0 mg, 0.1 mmol) and 4CzIPN. Four reactions were carried out in parallel and then combined for isolation by column chromatography to obtain ketone 2a (41.9 mg, 70%).
Following the general procedure 4.1. with substrate 1k (18.0 mg, 0.1 mmol) and 4CzIPN. Four reactions were carried out in parallel and then combined for isolation by column chromatography to obtain ketone 2b (35.6 mg, 74%).

Following the general procedure 4.1. with substrate 1l (21.5 mg, 0.1 mmol) and 4CzIPN. Four reactions were carried out in parallel and then combined for isolation by column chromatography to obtain ketone 2f (37.6 mg, 61%).

Following the general procedure 4.1. with substrate 1m (19.8 mg, 0.1 mmol) and 4CzIPN. Four reactions were carried out in parallel and then combined for isolation by column chromatography to obtain ketone 2g (41.6 mg, 75%).

Following the general procedure 4.1. with substrate 1n (27.2 mg, 0.1 mmol) and 4CzIPN. Four reactions were carried out in parallel and then combined for isolation by column chromatography to obtain ketone 2a (43.8 mg, 73%) and benzoic acid 3f (34.1 mg, 70%).

Following the general procedure 4.1. with substrate 1o (13.4 mg, 0.1 mmol) and 4CzIPN. Four reactions were carried out in parallel and then combined for isolation by column chromatography to obtain ketone 2h (24.5 mg, 45%).
5. Mechanistic investigations

5.1. Control experiments for clarification of the mechanism

Following the general procedure 4.1. with substrate 4 (16.8 mg, 0.1 mmol) and 4CzIPN. The yield of ketone 2a (5%) was determined by GC-analysis with the internal standard naphthalene.

Following the general procedure 4.1. with substrate 5 (25.2 mg, 0.1 mmol) and 4CzIPN. Four reactions were carried out in parallel and then combined for isolation by column chromatography, but ketone 2a could not be obtained and no conversion was observed.

Following the general procedure 4.1. with the proposed ketone intermediate B (21.2 mg, 0.1 mmol) and 4CzIPN. Four reactions were carried out in parallel and then combined for isolation by column chromatography to obtain ketone 2b (28.6 mg, 60%) and phenol 3a (15.1 mg, 40%).
5.2. Cyclic voltammetry measurements

CV measurements were performed with the three-electrode potentiostat galvanostat PGSTAT302N from Metrohm Autolab using a glassy carbon working electrode, a platinum wire counter electrode, a silver wire as a reference electrode and TBATFB 0.1 M as supporting electrolyte. The potentials were achieved relative to the Fc/Fc⁺ redox couple with ferrocene as internal standard. The control of the measurement instrument, the acquisition and processing of the cyclic voltammetric data were performed with the software Metrohm Autolab NOVA 1.10.4. The measurements were carried out as follows: a 0.1 M solution of TBATFB in CH₃CN was added to the measuring cell and the solution was degassed by argon purge for 5 min. After recording the baseline, the electroactive compound was added (0.01 M) and the solution was again degassed a stream of argon for 5 min. The cyclic voltammogram was recorded with one to three scans with a scan rate of 50 mV/s. Afterwards ferrocene (2.20 mg, 12.0 μmol) was added to the solution which was again degassed by argon purge for 5 min and the final measurement was performed with three scans.

Figure S1: Cyclic voltammogram of 1d in DMSO under argon (scan direction indicated by black arrow). The peak at -1.93 V shows the reduction of 1d and corresponds to a potential of -2.52 V vs SCE; the reversible peaks at 1.00 and 0.90 V correspond to ferrocene, which was used as an internal standard.
Figure S2: Cyclic voltammogram of 2-phenoxy-1-phenylethan-1-one in DMSO under argon (scan direction indicated by black arrow). The peak at -1.43 V shows the reduction of 2-phenoxy-1-phenylethan-1-one and corresponds to a potential of -1.72 V vs SCE; the reversible peaks at 0.74 and 0.65 V correspond to ferrocene, which was used as an internal standard.
5.3. Fluorescence quenching experiments

For fluorescence quenching experiments, a 38 µM solution of the photocatalyst 4CzIPN in degassed DMF was prepared under nitrogen atmosphere in a gas-tight 10 mm quartz cuvette. The photocatalyst was irradiated with 390 nm and the change of the fluorescence emission upon addition of different potential quenchers was recorded.

Figure S3: Fluorescence quenching of 4CzIPN (38 µM in DMSO) upon titration with methylthioglycolate + base (1:1).

Figure S4: Fluorescence quenching of 4CzIPN (38 µM in DMSO) upon titration with methyl thioglycolate.
**Figure S5:** Fluorescence quenching of 4CzIPN (38 µM in DMSO) upon titration with 1d.

**Figure S6:** Corresponding Stern-Volmer plot at 554 nm.

\[
y = 0.0059x + 1.0584 \\
R^2 = 0.9224
\]
5.4. GC analysis of crude reaction mixture

To verify the formation of ketone intermediate using GC-FID and GC-MS analysis, 1d was subjected to General Procedure in DMSO and the reaction mixture was irradiated for 4 hours.

Figure S7: GC-FID of crude reaction mixture after 4-hour irradiation using starting material 1d. The presence of intermediate ketone is clearly visible.
6. Characterization of isolated products

6.1. Characterization of ketones

1-(4-Methoxyphenyl)ethan-1-one (2a)[17]

\[
\begin{align*}
\text{MF: } & C_9H_{10}O_2 \\
\text{MW: } & 150.18 \text{ g/mol}
\end{align*}
\]

\[^1H \text{ NMR (300 MHz, CDCl}_3): \delta [\text{ppm}] = 7.97 \text{– } 7.88 (m, 2H), 6.97 \text{– } 6.87 (m, 2H), 3.85 (s, 3H), 2.54 (s, 3H). \\
[^13C \text{ NMR (75 MHz, CDCl}_3): \delta [\text{ppm}] = 196.9 (C_q), 163.6 (C_q), 130.7 (+), 130.4 (C_q), 113.8 (+), 55.6 (+), 26.5 (+). \\
\text{HRMS (APCI) (m/z): [M+H]^+ (C}_9H_{11}O_2) \text{ calc.: } 151.0759, 151.0762.
\]

Acetophenone (2b)[18]

\[
\begin{align*}
\text{MF: } & C_8H_8O \\
\text{MW: } & 120.15 \text{ g/mol}
\end{align*}
\]

\[^1H \text{ NMR (300 MHz, CDCl}_3): \delta [\text{ppm}] = 8.02 \text{– } 7.91 (m, 2H), 7.60 \text{– } 7.53 (m, 1H), 7.49 \text{– } 7.43 (m, 2H), 2.61 (s, 3H). \\
[^13C \text{ NMR (75 MHz, CDCl}_3): \delta [\text{ppm}] = 198.5 (C_q), 137.2 (C_q), 133.3 (+), 128.7 (+), 128.5 (+), 26.7 (+). \\
\text{HRMS (EI) (m/z): [M]^+ (C}_8H_8O) \text{ calc.: } 120.0570, \text{ found: } 120.0572.
\]

1-(3,4-Dimethoxyphenyl)ethan-1-one (2c)[19]

\[
\begin{align*}
\text{MF: } & C_{10}H_{12}O_3 \\
\text{MW: } & 180.20 \text{ g/mol}
\end{align*}
\]

\[^1H \text{ NMR (300 MHz, CDCl}_3): \delta [\text{ppm}] = 7.54 (dd, J = 8.3 \text{ Hz, } 2.0 \text{ Hz, } 1H), 7.49 (d, J = 2.0 \text{ Hz, } 1H), 6.85 (d, J = 8.3 \text{ Hz, } 1H), 3.91 (s, 3H), 3.90 (s, 3H), 2.53 (s, 3H). \\
[^13C \text{ NMR (75 MHz, CDCl}_3): \delta [\text{ppm}] = 196.9 (C_q), 153.3 (C_q), 149.0 (C_q), 130.5 (C_q), 123.3 (+), 110.04 (+), 109.96 (+), 56.1 (+), 56.0 (+), 26.3 (+). \\
\text{HRMS (EI) (m/z): [M]^+ (C}_{10}H_{12}O_3) \text{ calc.: } 180.0781, \text{ found: } 180.0776.
\]

1-(3,4,5-Trimethoxyphenyl)ethan-1-one (2d)[20]

\[
\begin{align*}
\text{MF: } & C_{11}H_{14}O_4 \\
\text{MW: } & 210.23 \text{ g/mol}
\end{align*}
\]

\[^1H \text{ NMR (300 MHz, CDCl}_3): \delta [\text{ppm}] = 7.21 (s, 2H), 3.92 (s, 6H), 3.92 (s, 3H), 2.59 (s, 3H). \\
[^13C \text{ NMR (101 MHz, CDCl}_3): \delta [\text{ppm}] = 197.0 (C_q), 153.2 (C_q), 142.8 (C_q), 132.6 (C_q), 106.0 (+), 61.1 (+), 56.5 (+), 26.6 (+).
HRMS (El) (m/z): [M•]+ (C₁₁H₁₄O₄) calc.: 210.0887, found: 210.0884.

1-(4-Chlorophenyl)ethan-1-one (2f)[21]

\[
\text{MF: C₈H₇ClO} \\
\text{MW: 154.59 g/mol}
\]

\(^1\)H NMR (300 MHz, CDCl₃): δ [ppm] = 7.92 – 7.85 (m, 2H), 7.46 – 7.39 (m, 2H), 2.58 (s, 3H).

\(^1^3\)C NMR (75 MHz, CDCl₃): δ [ppm] = 197.1 (C₉), 139.7 (C₈), 135.5 (C₉), 129.9 (+), 129.0 (+), 26.7 (+).

HRMS (El) (m/z): [M•]+ (C₈H₇ClO) calc.: 154.0180, found: 154.0180.

1-(4-Fluorophenyl)ethan-1-one (2g)[22]

\[
\text{MF: C₈H₇FO} \\
\text{MW: 138.14 g/mol}
\]

\(^1\)H NMR (300 MHz, CDCl₃): δ [ppm] = 8.02 – 7.91 (m, 2H), 7.17 – 7.05 (m, 2H), 2.58 (s, 3H).

\(^1^3\)C NMR (75 MHz, CDCl₃): δ [ppm] = 196.7 (C₉), 165.9 (C₈, d, J = 254.7 Hz), 133.6 (C₉, d, J = 3.0 Hz), 131.1 (+, d, J = 9.3 Hz), 115.8 (+, d, J = 21.9 Hz), 26.6 (+).

HRMS (El) (m/z): [M•]+ (C₈H₇FO) calc.: 138.0475, found: 138.0486.

1-(2-Hydroxyphenyl)ethan-1-one (2h)[18]

\[
\text{MF: C₈H₈O₂} \\
\text{MW: 136.15 g/mol}
\]

\(^1\)H NMR (300 MHz, CDCl₃): δ [ppm] = 12.26 (s, 1H), 7.74 (dd, J = 8.0 Hz, 1.7 Hz, 1H), 7.48 (ddd, J = 8.5 Hz, 7.2 Hz, 1.7 Hz, 1H), 6.98 (dd, J = 8.4 Hz, 1.1 Hz, 1H), 6.90 (ddd, J = 8.3 Hz, 7.2 Hz, 1.2 Hz, 1H), 2.64 (s, 3H).

\(^1^3\)C NMR (75 MHz, CDCl₃): δ [ppm] = 204.7 (C₉), 162.5 (C₈), 136.6 (+), 130.9 (+), 119.8 (C₉), 119.1 (+), 118.6 (+), 26.8 (+).
6.2. Characterization of phenols and other leaving fragments

**Phenol (3a)**

\[ \text{MF: C}_6\text{H}_6\text{O} \]
\[ \text{MW: 94.11 g/mol} \]

\[ ^1\text{H NMR (300 MHz, CDCl}_3\text{)}: \delta \text{ [ppm] = 7.29 – 7.22 (m, 2H), 6.98 – 6.90 (m, 1H), 6.90 – 6.77 (m, 2H), 5.31 (brs, 1H).} \]
\[ ^{13}\text{C NMR (75 MHz, CDCl}_3\text{)}: \delta \text{ [ppm] = 155.7 (C}_q\text{), 129.8 (+), 120.8 (+), 115.4 (+).} \]
\[ \text{HRMS (El) (m/z): [M}^+\text{] (C}_6\text{H}_6\text{O) calc.: 94.0413, found: 94.0422.} \]

**2-Methoxyphenol (3b)**

\[ \text{MF: C}_7\text{H}_8\text{O}_2 \]
\[ \text{MW: 124.14 g/mol} \]

\[ ^1\text{H NMR (300 MHz, CDCl}_3\text{)}: \delta \text{ [ppm] = 6.99 – 6.81 (m, 4H), 3.89 (s, 3H).} \]
\[ ^{13}\text{C NMR (75 MHz, CDCl}_3\text{)}: \delta \text{ [ppm] = 146.7 (C}_q\text{), 145.8 (C}_q\text{), 121.6 (+), 120.3 (+), 114.7 (+), 110.8 (+), 56.0 (+).} \]
\[ \text{HRMS (El) (m/z): [M}^+\text{] (C}_7\text{H}_8\text{O}_2\text{) calc.: 124.0524, found: 124.0534.} \]

**p-Cresol (3c)**

\[ \text{MF: C}_7\text{H}_8\text{O} \]
\[ \text{MW: 108.14 g/mol} \]

\[ ^1\text{H NMR (300 MHz, CDCl}_3\text{)}: \delta \text{ [ppm] = 7.10 – 6.99 (m, 2H), 6.81 – 6.70 (m, 2H), 5.07 (brs, 1H), 2.28 (s, 3H).} \]
\[ ^{13}\text{C NMR (75 MHz, CDCl}_3\text{)}: \delta \text{ [ppm] = 153.3 (C}_q\text{), 130.2 (+), 130.1 (C}_q\text{), 115.2 (+), 20.6 (+).} \]
\[ \text{HRMS (El) (m/z): [M}^+\text{] (C}_7\text{H}_8\text{O) calc.: 108.0570, found: 108.0566.} \]

**2,6-Dimethoxyphenol (3d)**

\[ \text{MF: C}_8\text{H}_{10}\text{O}_3 \]
\[ \text{MW: 154.17 g/mol} \]

\[ ^1\text{H NMR (300 MHz, CDCl}_3\text{)}: \delta \text{ [ppm] = 6.80 (dd, } J = 8.8 \text{ Hz, 7.8 Hz, 1H), 6.61 - 6.54 (m, 2H), 3.88 (s, 6H).} \]
\[ ^{13}\text{C NMR (75 MHz, CDCl}_3\text{)}: \delta \text{ [ppm] = 149.0 (C}_q\text{), 130.5 (C}_q\text{), 123.4 (+), 110.1 (+), 56.1 (+).} \]
\[ \text{HRMS (El) (m/z): [M}^+\text{] (C}_8\text{H}_{10}\text{O}_3\text{) calc.: 154.0630, found: 154.0638.} \]
3,5-Dimethoxyphenol (3e)[5]

\[
\text{MF: } C_8H_{10}O_3 \\
\text{MW: 154.17 g/mol}
\]

\[
\begin{align*}
\text{H NMR (300 MHz, CDCl}_3\text{): } & \delta \text{ [ppm] = 6.09 – 6.05 (m, 1H), 6.04 (d, } J = 2.1 \text{ Hz, 2H), 3.74 (s, 6H).} \\
\text{C NMR (75 MHz, CDCl}_3\text{): } & \delta \text{ [ppm] = 161.7 (C}_q\text{), 157.6 (C}_q\text{), 94.4 (+), 93.2 (+), 55.5 (+).} \\
\text{HRMS (El) (m/z): } [M^+ \text{]} & (C_8H_{10}O_3) \text{ calc.: 154.0630, found: 154.0638.}
\end{align*}
\]

Benzoic acid (3f)[24]

\[
\text{MF: } C_7H_6O_2 \\
\text{MW: 122.12 g/mol}
\]

\[
\begin{align*}
\text{H NMR (300 MHz, CDCl}_3\text{): } & \delta \text{ [ppm] = 12.45 (brs, 1H), 8.19 – 8.10 (m, 2H), 7.68 – 7.58 (m, 1H), 7.54 – 7.44 (m, 2H).} \\
\text{C NMR (75 MHz, CDCl}_3\text{): } & \delta \text{ [ppm] = 172.7 (C}_q\text{), 134.0 (+), 130.4 (+), 129.5 (C}_q\text{), 128.6 (+).} \\
\text{HRMS (El) (m/z): } [M^+ \text{]} & (C_7H_6O_2) \text{ calc.: 122.0368, found: 122.0357.}
\end{align*}
\]
7. $^1$H- and $^{13}$C-NMR spectra

$^1$H and $^{13}$C-NMR of compound 1a in CDCl$_3$: 

![NMR Spectra](image)
$^{1}$H and $^{13}$C-NMR of compound 1b in CDCl$_3$:
$^1$H and $^{13}$C-NMR of compound 1c in CDCl$_3$: 

![NMR spectra](image_url)
$^1$H and $^{13}$C-NMR of compound 1d in CDCl$_3$: 

![NMR Spectrum](image-url)
$^1$H and $^{13}$C-NMR of compound 1e in CDCl$_3$:
$^1$H and $^{13}$C-NMR of compound 1f in CDCl$_3$: 
\(^1\)H and \(^{13}\)C-NMR of compound 1g in CDCl\(_3\):
$^1\text{H}$ and $^{13}\text{C}$-NMR of compound 1h in CDCl$_3$:
\(^1\)H and \(^{13}\)C-NMR of compound 1j in CDCl\(_3\):
$^{1}$H and $^{13}$C-NMR of compound 1l in CDCl$_3$:
$^1$H and $^{13}$C-NMR of compound 1m in CDCl$_3$:
$^1$H and $^{13}$C-NMR of compound 1o in CDCl$_3$: 

![NMR Spectrum](image-url)
$^1$H-NMR of compound 4 in CDCl$_3$: 

$^1$H-NMR of compound 5 in CDCl$_3$: 

$^1$H and $^{13}$C-NMR of compound 2a in CDCl$_3$:
$^1$H and $^{13}$C-NMR of compound 2c in CDCl$_3$: 

![NMR spectrum image]
$^1$H and $^{13}$C-NMR of compound 2d in CDCl$_3$:
$^1$H-NMR of compound 2f in CDCl$_3$:

$^1$H-NMR of compound 2g in CDCl$_3$:
$^1$H and $^{13}$C-NMR of compound 2h in CDCl$_3$: 
$^1$H and $^{13}$C-NMR of compound 3e in CDCl$_3$: 

![NMR Spectra](image-url)
8. References


