Electronic Supplementary Material (ESI) for Chemical Science.

Supporting information for

Cobalt-Copper Dual Light-Driven Catalytic Reduction of Aldehydes and Aromatic Ketones in Aqueous Media

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SI.1. Catalysis and experimental procedures

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EXPERIMENTAL SECTION

1. Material and Reagents

Reagents and solvents were purchased from commercial sources and used as received unless otherwise stated. Triethylamine and *di*-isopropylethylamine were distilled over potassium hydroxide and stored under argon. Ascorbic acid (AscH) (≥ 99 %) was purchased from Sigma-Aldrich® and used without further purification. Photosensitizers $[Ir(bpy)(ppy)_2]PF_6$ (**PS_{Ir}**)[1] and $[Cu(bathocuproine)(Xantphos)]PF_6$ (**PS_{Cu}**),[2] complexes [Co(OTf)(Py2Tstacn)](OTf) (**1**)[3] and $[Co(OTf)_2(TPA)]$ (**6**),[4] and ligands N4Py,[5] DPA-Bpy,[6] BpcMe,[7] H-$CDPy_3$[8] and (*S,S*)-PDP[9] were synthesized according to the literature procedures.

Anhydrous acetonitrile was purchased from Sigma-Aldrich® Water (18.2 MΩ·cm) was purified with a Milli-Q Millipore Gradient AIS system. All solvents were degassed by the freeze-pump-thaw method and stored under argon.

2. Instrumentation

Nuclear magnetic resonance (NMR) spectra were recorded on Bruker Fourier300, AV400, AV500 and AVIII500 spectrometers using standard conditions (300 K). All ^1H chemical shifts are reported in ppm and have been internally calibrated to the residual protons of the deuterated solvent. The ^{13}C chemical shifts have been internally calibrated to the carbon atoms of the deuterated solvent. The coupling constants were measured in Hz.

Elemental analyses were performed using a CHNS-O EA-1108 elemental analyzer from Fisons.

Mass Spectrometry. Electrospray ionization mass spectrometry (ESI-MS) experiments were performed on a Bruker Daltonics Esquire 3000 Spectrometer using a 1 mM solution of the analyzed compound, by introducing the sample directly into the ESI-source using a syringe. High resolution mass spectra (HRMS) were recorded on a Bruker MicroTOF-Q IITM instrument with an ESI source at Serveis Tècnics of the University of Girona. Samples were introduced into the mass spectrometer ion source by direct infusion through a syringe pump and were externally calibrated using sodium formate.

Electrochemistry. A standard three-electrode configuration was employed in conjunction with CHI Instruments potentiostat interfaced to a computer with CHI Instruments 600D software. Using one-compartment cell, all cyclic voltammetry experiments were recorded using glassy carbon working electrode which was treated between experiments by means of a sequence of polishing with MicroPolish Powder (0.05 micron) before washing and sonification. Saturated calomel electrode (SCE) and Pt wire were used as reference and counter electrodes respectively.

Gas chromatography analysis. The analysis and quantification of the starting materials and products were carried out on an Agilent 7820A gas chromatograph (HP5 column, 30m or Cyclosil-B column, 30m) and a flame ionization detector. The enantioselectivity was determined by comparison with the pure samples synthesized by the reported procedures.[10]

GC-MS spectral analyses were performed on an Agilent 7890A gas chromatograph interfaced with an Agilent 5975c MS mass spectrometer.

Parallel Pressure Transducer Hardware. The parallel pressure transducer sensors that we used for these studies is the same that was previuosly reported for the water oxidation studies in our group.[11] This is composed by 8 differential pressure transducers (Honeywell-ASCX15DN, ± 15 psi) connected to a hardware data-acquisition system (base on Atmega microcontroller) controlled by a home-developed software program. The differential pressure transducer Honeywell-ASCX15DN is a 100 microseconds response, signal-conditioned (high level span, 4.5 V) output, calibrated and temperature compensated (0 ºC to 70 ºC) sensor. The differential sensor has two sensing ports that can be used for differential pressure measurements. The pressure calibrated devices to within ± 0.5 matm was offset and span calibrated *via* software with a high precision pressure transducer (PX409-030GUSB, 0.08 % Accuracy). Each of the 8 differential

pressure transducers (Honeywell-ASCX15DN, ±15 psi) produce a voltage outputs that can be directly transformed to a pressure difference between the two measuring ports. The voltage outputs were digitalized with a resolution of 0.25 matm from 0 to 175 matm and 1 matm from 176 to 1000 matm using an Atmega microcontroller with an independent voltage auto-calibration. Firmware Atmega microcontroller and control software were home-developed. The sensitivity of H_2 analytics allows for quantification of the gas formed when low H_2 volumes are generated. However, it could not be discarded that small amounts of H_2 were produced by inactive complexes.

Gas chromatography identification and quantification of gases. Gases at the headspace were analyzed with an Agilent 7820A GC System equipped with columns Washed Molecular Sieve 5A, 2m x 1/8'' OD, Mesh 60/80 SS and Porapak Q, 4m x 1/8'' OD, SS. Mesh: 80/100 SS and a Thermal Conductivity Detector. The quantification of the H_2 obtained was measured through the interpolation of a previous calibration using different H_2/N_2 mixtures.

In-house developed parallel photoreactor

Light source: The reactions were performed using Royal-Blue (λ = 447±20 nm) LUXEON Rebel ES LED, mounted on a 10mm Square Saber - 1030 mW @ 700mA (Datasheet: https://www.luxeonstar.com/assets/downloads/ds68.pdf) as a light source.

Temperature Control: Reaction temperature was controlled by a high precision thermoregulation Hubber K6 cryostat. Likewise, to guarantee a stable irradiation the temperature of the LEDs was also controlled and set up at 22 ºC.

Figure SI.1.1. In-house developed parallel photoreactor.

3. Experimental Procedures

General procedure employed in the reaction screening conditions for the light-driven reduction of aromatic ketones (9a-z) and aromatic aldehydes (11a-c). All catalytic reactions were conducted in a 20 mL septum-capped vial under vigorous stirring using an orbital stirrer and irradiating at 447 nm for 5h under nitrogen atmosphere at 30 ºC, unless otherwise indicated. The catalytic assays performed using $\mathbf{PS_{Ir}}$ (247.5 μM, 1.5 mol%) as photoredox catalyst in

H_2O:CH_3CN:Et_3N (8:2:0.2 mL) or (3:7:0.2 mL) reaction mixture, together with the corresponding substrate (16.5 mM) and complex **1** (495 μM, 3% mol). Similarly, catalytic reactions carried out using $\mathbf{PS_{cu}}$ (247.5 μM, 1.5% mol) as photoredox catalyst were performed in a H_2O:CH_3CN:Et_3N (6:4:0.2 mL) reaction mixture that contained the substrate (16.5 mM) and complex **1** (165 μM, 1% mol). After reaction completion, biphenyl was added as internal standard and the crude was quenched by adding 2 mL of CH_2Cl_2. The crude was purified by extraction with CH_2Cl_2 (3 x 3 mL), an aliquote of the organic phase was passed through a plug of $MgSO_4$ which was eluted with AcOEt. This sample was subjected to GC analysis to determine the conversion of **9a-z or 11a-c$_x$** and the yield of the desired product **10a-z** or **12a-c**. All GC yields reported are an average of at least two runs.

General procedure for the reduction of aliphatic aldehydes (11d-f). All catalytic reactions were conducted in a 20 mL septum-capped vial under vigorous stirring using an orbital stirrer and irradiating at 447 nm for 24h under nitrogen atmosphere at -3ºC, unless otherwise indicated. Catalytic photoreductions were performed in H_2O:CH_3CN:$^iPr_2EtN$ (6:4:0.2 mL) reaction solvent mixture, substrate (4.4 mM), $\mathbf{PS_{Cu}}$ (261 μM, 6% mol), **1** (261 μM, 6% mol), unless otherwise indicated. A 447 nm LED was employed as light source. Biphenyl was added as internal standard after the reaction and the reaction was quenched by adding 2 mL of AcOEt. The crude reaction mixtures were purified by extraction with AcOEt (1 x 3 mL), the organic layer was passed through a $MgSO_4$ plug which was eluded with more AcOEt. The resulting organic solution was subjected to GC analysis to determine the conversion of **11d-f** and the yield of the desired products **12d-f** respectively. All GC yields reported are an average of at least two runs.

General procedure for product isolation. The light-driven photocatalytic reductions of a targeted substrates were carried out under the optimized conditions described above. The crude mixtures of at least 16 independent reactions (equally prepared) for each compound were combined and extracted with CH_2Cl_2 (3 x 40 mL). Organic fractions were combined, dried over $MgSO_4$ and the solvent removed under reduced pressure. The resulting crude oil was purified by silica gel column chromatography with Hexane/AcOEt (9:1) to obtain the desired reduced product and the isolated yields reported are an average of at least 16 reactions.

General procedure for the competition studies between acetophenone (9a) and aliphatic aldehydes (11d-e) following the Luche reaction reported copnditions.[12] Catalytic reductions were performed in H_2O:EtOH (6:4 mL) reaction solvent mixture, equimolar amounts of both substrates A:B were used (8.7 mM each, total concentration 16.5 mM), $CeCl_3{\cdot}7H_2O$ (1 equivalent) and $NaBH_4$ (1.5 equivalents), unless otherwise indicated. All catalytic reactions were conducted in a 15 mL capped-vial under vigorous stirring for 15 minutes at 0ºC, unless otherwise indicated. To the equimolar mixture of substrates (ketone + aliphatic aldehyde) in H_2O:EtOH (6:4 mL), 1 equivalent of $CeCl_3{\cdot}7H_2O$ was added at r.t. and the reaction mixture was cooled down to 0 ºC. Then, 1.5 equivalents of $NaBH_4$ were added and the reaction was left stirring for 15 min at 0 ºC. Biphenyl was added as internal standard after the reaction and the reaction was quenched by adding 2 mL of acetone. Dilution with 2 ml of Brine solution and extractions with Et_2O, afforded the reaction products after the organic layer was passed through a $MgSO_4$ plug which was eluded with more Et_2O. The resulting organic solution was subjected to GC analysis to determine the conversion of **9a** and **11d/e** and the yield of the desired products **10a** and **12d/f** respectively. All GC yields reported are an average of at least two runs.

Gas-evolution monitoring studies. Each experiment was conducted in a 20 mL volume-calibrated-vial caped with a septa equipped with stir-bars and containing the solvent mixture and reagents. Each reaction vial was connected to one of the ports of a differential pressure transducer sensor (Honeywell-ASCX15DN) and the other port to a reference reaction. Reference reactions, have all components of the reaction except the catalyst. The reaction and reference vials are kept under the same experimental conditions to compensate the noise due to temperature-pressure fluctuations. In order to ensure a constant and stable irradiation, the LED sources were equipped with a water refrigeration system. This is composed for a refrigerated aluminum block by a Huber cryothermostat (refrigeration system, Minichiller -40ºC-20ºC). This block is shaken by an Orbital Shaker (IKA KS 260 Basic Package) which provides the agitation

of the reaction vessels during the irradiation time. The aluminum block accommodates 16 vials (20 mL) capped with septum in which the reaction takes place. Each vial is submitted and located over a LED irradiation source (Royal-Blue Rebel LEDs (λ = 447±20 nm). The reaction began when the LEDs were turned on. At this point, the hydrogen evolved from the reactions was monitored by recording the increase in pressure of the headspace (1 second interval). The pressure increment is the result of the difference in pressure between the reaction and reference vials. After the hydrogen evolution reached a plateau the amount of the gas formed was measured equilibrating the pressure between reaction and reference vials. The gases at the headspace of the reaction vials and references in each of the reactions were quantified by the analysis of an aliquot of gas at the headspace (0.2 mL) by gas chromatography.

Procedure for the reduction of acetophenone (9a) in presence of O_2. All catalytic reactions were conducted in a 20 mL septum-capped vial under vigorous stirring using an orbital stirrer and irradiating at 447 nm for 5 h at 30ºC under an atmosphere of N_2:O_2 of known ratio. The reactions contained **PS_{cu}** (247.5 μM, 1.5% mol), **1** (165 μM, 1% mol) and **9a** (16.5 mM) in H_2O:CH_3CN:Et_3N (6:4:0.2 mL) solvent mixture and were prepared under N_2 atmosphere. Before irradiation, a known O_2 aliquot was introduced into the head space of the reaction vial with a Hamilton gas-tight syringe through the septa. The mixture was vigorously shaken during 5 min to dissolve the O_2 into the solution. Then, after 5 h of irradiation, biphenyl (16 μmol) was added as internal standard and the reaction crude was quenched with 2 mL of CH_2Cl_2. The crude was purified by extraction with CH_2Cl_2 (3 x 3 mL). An aliquot of the organic phase was passed through a plug of $MgSO_4$ and eluted with AcOEt. The conversion and yield were determined with GC analysis. All GC yields reported are an average of at least two runs.

When using **PS_{Ir}** (247.5 μM, 1.5 mol%) as photoredox catalyst, the reactions were performed like in the case of **PS_{Cu}** but with the following modification in the reaction mixture: H_2O:CH_3CN:Et_3N (8:2:0.2 mL) reaction mixture, together with substrate **9a** (16.5 mM) and complex **1** (495 μM, 3% mol).

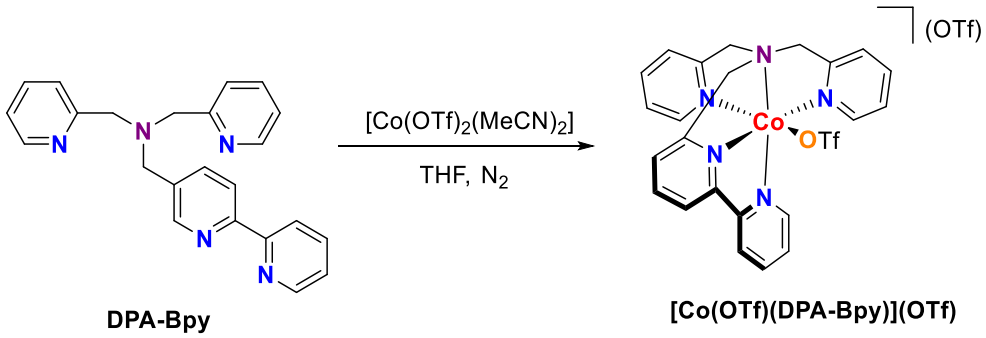
Procedure for the reduction of acetophenone (9a) with non-degassed solvents prepared outside the glovebox under air exposition. All catalytic reactions were conducted in a 10 mL septum-capped vial with negligible head space under vigorous stirring using an orbital stirrer and irradiating at 447 nm for 24 h under air atmosphere at 30ºC. The reactions were carried out in a non-degased H_2O:CH_3CN:Et_3N (3.6:2.4:0.12 mL) reaction mixture containing **9a** (16.5 mM), **1** (165 μM, 1% mol) and **PS_{cu}** (247.5 μM, 1.5% mol). The reaction vials were fully filled minimizing the head space of the reaction mixture. After reaction completion, biphenyl (16 μmol) was added as internal standard and the crude was quenched by adding 2 mL of CH_2Cl_2. The crude was purified by extraction with CH_2Cl_2 (3 x 3 mL), an aliquot of the organic phase was passed through a plug of $MgSO_4$ which was eluted with AcOEt. The conversion and yield were determined with GC analysis. All GC yields reported are an average of at least two runs. The estimated concentration of O_2 in solution is about 1 mM (6 eq. regarding **1**).

When using **PS_{Ir}** (247.5 μM, 1.5 mol%), the reactions were performed like in the case of **PS_{Cu}** but with the following modification in the reaction mixture: H_2O:CH_3CN:Et_3N (4.8:1.2:0.12 mL) reaction mixture, together with substrate **9a** (16.5 mM) and complex **1** (495 μM, 3% mol). The estimated concentration of O_2 in solution is about 1 mM (2 eq. regarding **1**).

4. Synthesis of complexes

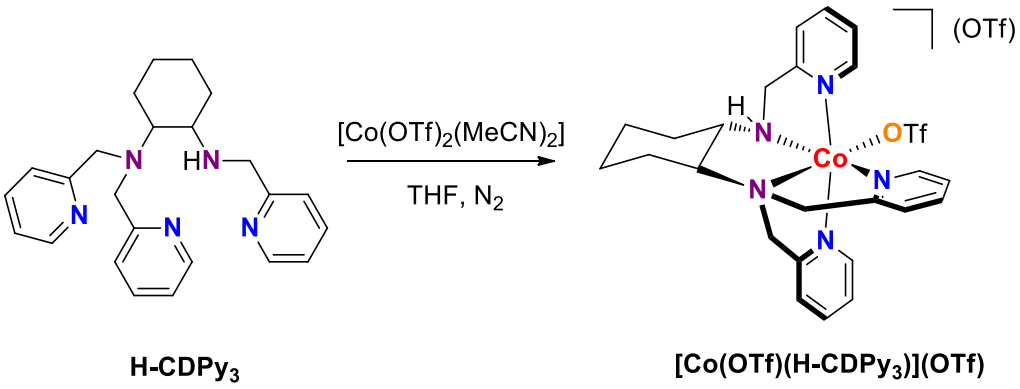
[Co(OTf)(DPA-Bpy)](OTf) (2). Inside a glovebox, a vial was charged with $[Co(OTf)_2(MeCN)_2]$ (131 mg, 0.300 mmol) and anhydrous THF (2 mL). Then a solution of ligand DPA-Bpy (110 mg, 0.300 mmol) in THF (2 mL) was added dropwise to the vigorously stirred suspension of cobalt salt in THF, which caused the formation of a brown precipitate after few minutes. The resulting mixture was stirred for additional 5 hours, then Et_2O (3 mL) was added and the resulting brown solid was filtered off and dried under vacuum. This solid was dissolved in CH_2Cl_2 and filtered

through Celite. Finally, slow diffusion of diethyl ether into the clear solution produced a pale brown solid. The solution was siphoned off by cannula and the solid material that corresponds to the targeted complex **2** was dried under vacuum (174 mg, 0.240 mmol, 80 %). ^{1}H-NMR (CD_3CN, 400 MHz, 260K) δ, ppm: 224.52, 208.60, 166.72, 121.28, 83.00, 80.43, 70.16. HR-ESI-MS (m/z): 575.0649 $[M - OTf]^+$, 213.0561 $[M\text{-}2\cdot OTf]^{2+}$.



Scheme SI.1.1. Synthesis of [Co(OTf)(DPA-Bpy)](OTf).

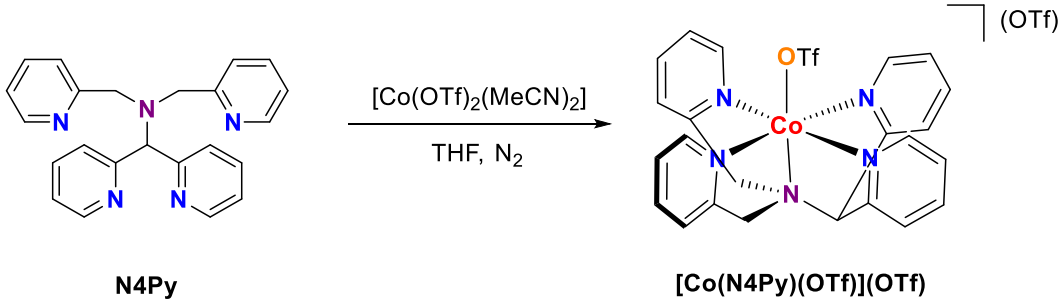
[Co(OTf)(H-CDPy$_3$)](OTf) (3). Inside a glovebox, a vial was charged with $[Co(OTf)_2(MeCN)_2]$ (0.259 g, 0.590 mmol) and anhydrous THF (2 mL). Then a solution of ligand H-CDPy$_3$ (0.229 g, 0.590 mmol) in THF (2 mL) was added dropwise to the vigorously stirred suspension of cobalt salt in THF, which caused the formation of a brown precipitate after few minutes. The resulting mixture was stirred for additional 2 hours, then Et_2O (3 mL) was added and the resulting brown solid was filtered off and dried under vacuum. This solid was dissolved in CH_2Cl_2 and filtered through Celite. Finally, slow diffusion of diethyl ether into the clear solution produced a brown solid. The solution was siphoned off by cannula and the solid material that corresponds to the targeted complex **3** was dried under vacuum (0.329 g, 0.442 mmol, 75 %). ^{1}H-NMR (CD_3CN, 500 MHz, 260K) δ, ppm: 99.84, 88.77, 83.14, 78.36, 69.73, 66.33, 59.08, 43.04, 40.23, 34.19, 33.29, 29.70, 26.35, 24.85, 16.65, 12.94, 11.45, -1.63. HR-ESI-MS (m/z): 595.1266 $[M - OTf]^+$, 223.0895 $[M\text{-}2\cdot OTf]^{2+}$.



Scheme SI.1.2. Synthesis of [Co(OTf)(H-CDPy$_3$)](OTf).

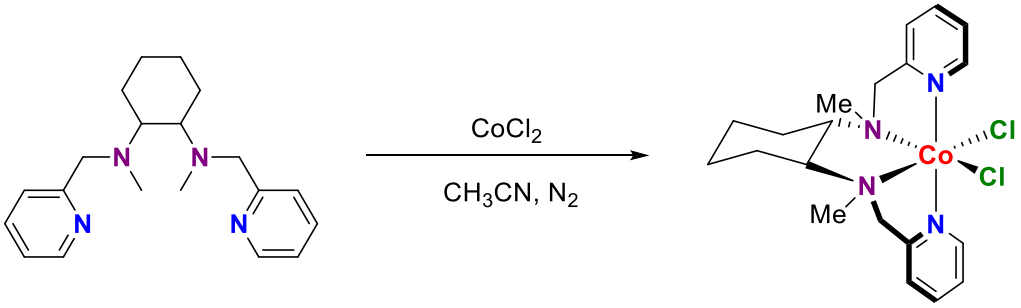
[Co(OTf)(N4Py)](OTf) (4). Inside a glovebox, a vial was charged with $[Co(OTf)_2(MeCN)_2]$ (191 mg, 0.434 mmol) and anhydrous THF (2 mL). Then a solution of N_4Py ligand (160 mg, 0.434 mmol) in THF (2 mL) was added dropwise to the vigorously stirred suspension of cobalt salt in THF, which caused the formation of a brown precipitate after few minutes. The resulting mixture was stirred for additional 5 hours, then Et_2O (3 mL) was added and the resulting solid was filtered off and dried under vacuum. This solid was dissolved in CH_2Cl_2 and filtered through Celite. Finally, slow diffusion of diethyl ether into the clear solution produced a pale brown solid. The solution

was siphoned off by cannula and the solid material that corresponds to the targeted complex **4** was dried under vacuum (0.325 mmol, 75 %). ^{1}H-NMR (CD_3CN, 400 MHz, 400K) δ, ppm: 171.33, 131.77, 86.12, 69.18, 67.92, 57.95, 48.33, 15.47, 9.62, -23.86. Anal. Calcd for $C_{25}H_{21}CoF_6N_5O_6S_2$: C, 41.44; N, 9.67; H, 2.92 %. Found: C, 41.52; N, 9.74; H, 2.99 %. HR-ESI-MS (m/z): 575.0645 [M - OTf]$^+$, 213.0560 [M-2·OTf]$^{2+}$.



Scheme SI.1.3. Synthesis of [Co(OTf)(N4Py)](OTf).

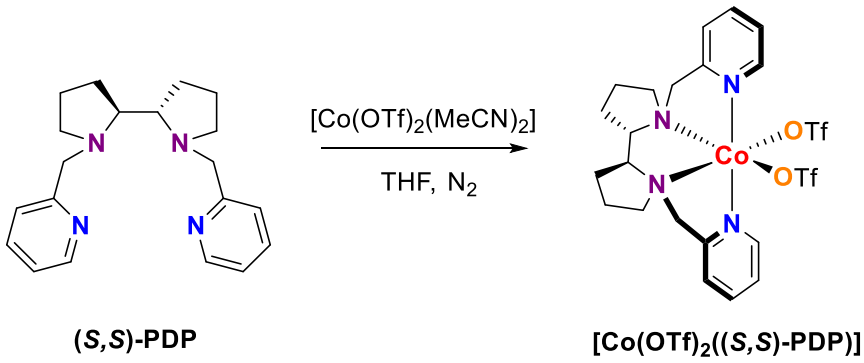
[Co(Cl)$_2$(mcp)] (5). Inside a glovebox, a vial was charged with $CoCl_2$ (115 mg, 0.886 mmol) and anhydrous THF (2 mL). Then a solution of BpcMe ligand (287 mg, 0.886 mmol) in THF (2 mL) was added dropwise to the vigorously stirred suspension of cobalt salt in THF, which caused the formation of a purple precipitate after few minutes. The resulting mixture was stirred for additional 2 hours, the resulting solid was filtered off, washed with CH_3CN (3x 2 mL) and dried under vacuum. This solid was dissolved in CH_2Cl_2 and filtered through Celite. Finally, slow diffusion of diethyl ether into the clear solution produced a purple solid. The solution was siphoned off by cannula and the solid material that corresponds to the targeted complex **5** was dried under vacuum (293 mg, 0.645 mmol, 73 %). ^{1}H-NMR (CD_3CN, 500 MHz, 260K) δ, ppm: 83.55, 74.16, 68.23, 51.15, 45.68, 43.85, 39.94, 22.63, 20.21, 18.74, 15.74, 39.94, 22.63, 20.21, 18.74, 15.74, 12.40, 8.22, -9.12, -33.38, -69.69. HR-ESI-MS (m/z): 418.3121 [M - Cl]$^+$.



Scheme SI.1.4. Synthesis of [Co(Cl)$_2$(mcp)].

[Co(OTf)$_2$((*S,S*)-PDP)] (6). Inside a glovebox, a vial was charged with [Co(OTf)$_2$(MeCN)$_2$] (0.483 g, 1.10 mmol) and anhydrous THF (2 mL). Then a solution of ligand (*S,S*)-PDP (0.355 g, 1.10 mmol) in THF (2 mL) was added dropwise to the vigorously stirred suspension of cobalt salt in THF, which caused the formation of a pink-red precipitate after few minutes. The resulting mixture was stirred for additional 2 hours, then Et_2O (3 mL) was added and the resulting pink solid was filtered off and dried under vacuum. This solid was dissolved in CH_2Cl_2 and filtered through Celite. Finally, slow diffusion of diethyl ether into the clear solution produced a pink solid. The solution was siphoned off by cannula and the solid material that corresponds to the targeted complex **6**

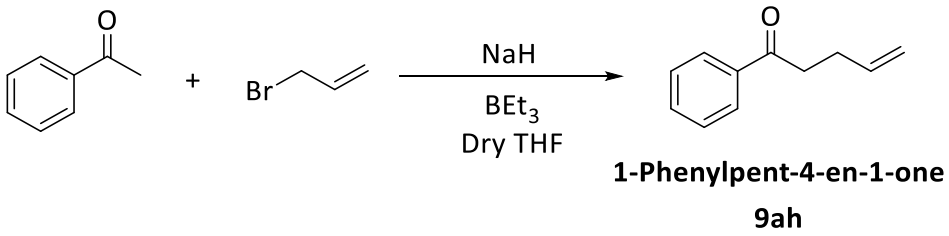
was dried under vacuum (0.669 g, 0.984 mmol, 90 %). ^{1}H-NMR (CD_3CN, 500 MHz, 260K) δ, ppm: 283.60, 107.68, 102.66, 73.13, 52.52, 34.40, 23.80, 20.16, -6.18, -21.19, -98.76. HR-ESI-MS (m/z): $[M - OTf]^+$, $[M\text{-}2\cdot OTf]^{2+}$.



Scheme SI.1.5. Synthesis of [Co(OTf)$_2$((*S,S*)-PDP)].

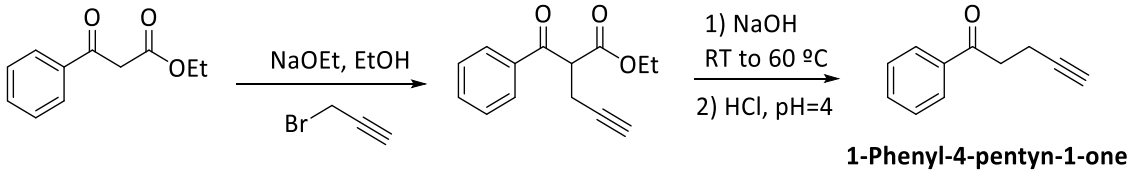
5. Synthesis of substrates

-Synthesis of 1-Phenylpent-4-en-1-one (9ah)



An oven-dried two-neck round-bottomed flask equipped with a stirring bar and a dropping funnel and connected to a nitrogen inlet was charged with sodium hydride (2.11 g, 52.8 mmol, 1.2 eq.) and anhydrous THF (100 mL). Then a solution of acetophenone (5.2 mL, 44 mmol, 1.0 eq.) in 20 mL of dry THF was added over the grey suspension during 20 min at 0ºC under nitrogen atmosphere. The yellow suspension formed was stirred at room temperature for 30 min and BEt_3 (56 mL 1M in THF, 56 mmol, 1.2 eq.) was added dropwise for 20 min. The resulting yellow solution was further stirred for 30 min and allyl bromide (5.8 mL, 68 mmol, 1.5 eq.) was added dropwise for 15 min and the resulting solution was left stirring overnight at room temperature. The reaction mixture was quenched by the addition of 50 mL of 1:1 mixture of 30 % NaOH and 30 % H_2O_2 at 0 ºC over 30 min and finally diluted with H_2O (100 mL). The organic layer was extracted, diluted with Et_2O (100 mL) and washed with H_2O (2 x 50 mL). All aqueous phases were combined and extracted with CH_2Cl_2 (3 x 40mL). The combined organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The resulting oil product was purified by column chromatography in silica gel using hexane:AcOEt (30:1) as eluent that gave the desired product as a colorless oil (65 % yield). ^{1}H-NMR ($CDCl_3$, 300 MHz, 300 K) δ, ppm: 8.00-7.97 (m, 2H, $\mathbf{H_{arom}}$), 7.61-7.55 (m, 1H, $\mathbf{H_{arom}}$), 7.51-7.46 (m, 2H, $\mathbf{H_{arom}}$), 5.97-5.86 (m, 1H, C**H**=CH_2), 5.13-5.02 (m, 2H, CH=C$\mathbf{H_2}$), 3.10 (t, 2H, *J* = 7.2 Hz), 2.51 (q, 2H, *J* = 6.6 Hz).

-**Synthesis of 1-Phenyl-4-pentyn-1-one (9ai)**

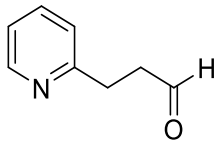


1-Phenyl-4-pentyn-1-one

9ai

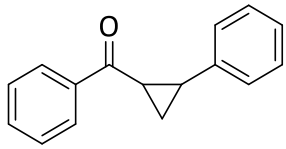
In a mixture of ethyl benzoylacetate (5.76 g, 30 mmol, 1.0 eq.) in a 50 mL of anhydrous ethanol were added 2.25 g of NaOEt (33 mmol, 1.1 eq.). After stirring the mixture for 15 min, propargyl bromide (3.76 mL, 80 % wt solution in toluene, 33 mmol, 1.1 eq.) was added dropwise at 0 ºC within 30 minutes. The resulting orange solution was stirred at room temperature for 1 day. After that, the sodium bromide was filtered off, and the solvent removed under vacuum in a rotary evaporator. To the residue was added 24 mL (60 mmol) of 10 % aq. NaOH, and the mixture was stirred 3 hour at room temperature and at 60 ºC for another 3 hours. Then, the crude mixture was cooled to ambient temperature, acidified with conc. HCl to a pH of 4 and extracted with CH_2Cl_2 (3x 50 mL). The combined organic layers were dried over $MgSO_4$ and the solvent were removed under reduced pressure. The resulting oil product was purified by silica column cromatography (Hexane:AcOEt 30:1) to afford the desired alkyne product (75 % yield) as a pale yellow solid. 1H-NMR ($CDCl_3$, 300 MHz, 300 K) δ, ppm: 8.01-7.98 (m, 2H, $\mathbf{H_{arom}}$), 7.62-7.57 (m, 1H, $\mathbf{H_{arom}}$), 7.52-7.46 (m, 2H, $\mathbf{H_{arom}}$), 3.27 (t, 2H, J = 7.1 Hz, C$\mathbf{H_2}$CH_2C≡CH), 2.68 (td, 2H, J = 7.1 Hz, J' = 2.7 Hz, CH_2C$\mathbf{H_2}$C≡CH), 2.00 (t, 1H, J = 2.7 Hz, C≡C**H**).

-Synthesis of 3-(pyridin-2-yl)propanal (11f)



3-(pyridin-2-yl)propanal (11f) was prepared by Swern oxidation of the corresponding comercially available alcohol according to previously reported procedure.[13] ^{1}H-NMR ($CDCl_3$, 400 MHz, 300 K) δ, ppm: 9.87 (s, 1H), 8.51 (d, *J* = 3.9 Hz, 1H), 7.59 (td, *J* = 7.7, 1.9 Hz, 1H), 7.19 (d, *J* = 7.8 Hz, 1H), 7.12 (dd, *J* = 7.2, 4 Hz, 1H), 3.14 (t, *J* = 7.1 Hz, 3H), 2.95 (tt, *J* = 6.4, 0.6 Hz, 2H). ^{13}C{^{1}H}-NMR ($CDCl_3$, 100.6 MHz, 300 K) δ, ppm: 201.7, 159.9, 149.4, 136.7, 123.2, 121.5, 42.8, 30,5. MS (GC): 135.1 [M].

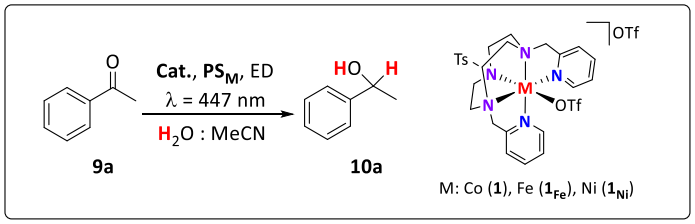
-Synthesis of phenyl(2-phenylcyclopropyl)methanone (9aj)



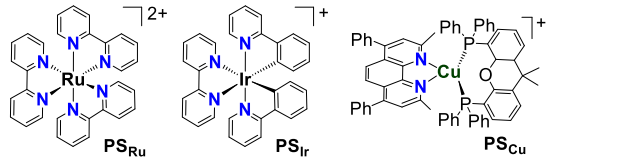
Phenyl(2-phenylcyclopropyl)methanone (9aj) was prepared according to previously reported procedure through a Corey-Chaykovsky reaction.[14] ^{1}H-NMR ($CDCl_3$, 300 MHz, 300 K) δ, ppm: 7.92 (d, *J* = 7.7 Hz, 2H), 7.48-7.35 (m, 3H), 7.26-7.09 (m, 5H), 2.83 (ddd, *J* = 8.0, 4.2, 4.0 Hz, 1H), 2.63 (m, *J* = 6.9 Hz, 1H), 1.84 (ddd, *J* = 9.0, 4.2, 4.1 Hz, 1H), 1.48 (ddd, *J* = 8.0, 6.9, 4.1 Hz, 1H).

6. Screening of the catalysts developed for water reduction for the reduction of 9a

Table SI.1.1. Screening conditions for the light-driven acetophenone reduction.



Photoredox catalysts

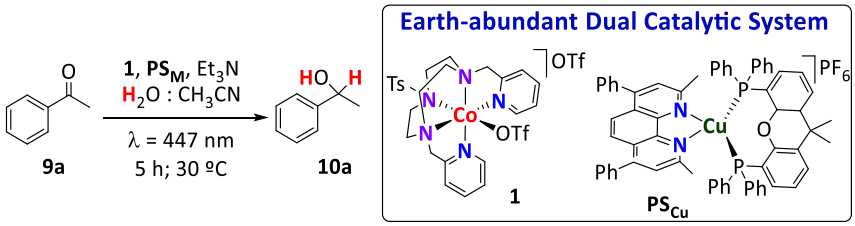


[Ru(bpy)$_3$](PF$_6$)$_2$ [Ir(ppy)$_2$(bpy)](PF$_6$) [Cu(bathocuproine)(Xantphos)](PF$_6$)

Entry	Cat.	PS$_M$	H$_2$O:CH$_3$CN (mL)	ED (eq.)	Yield 10a (%)
1[a]	**1**	**PS$_{Ir}$**	3.5:1.5	Et$_3$N (2.1)	23
2[a]	**1$_{Fe}$**	**PS$_{Ir}$**	3.5:1.5	Et$_3$N (2.1)	n.d. [b]
3[a]	**1$_{Ni}$**	**PS$_{Ir}$**	3.5:1.5	Et$_3$N (2.1)	n.d.
4	**1**	**PS$_{Ir}$**	3.5:1.5	Et$_3$N (8.5)	30
5	**1**	**PS$_{Ir}$**	8:2	Et$_3$N (8.5)	65
6	**1**	**PS$_{Ir}$**	8:2	TEOA (8.5)	17
7	**1**	**PS$_{Ir}$**	8:2	AscH (6)	4
8	**1**	**PS$_{Ru}$**	8:2	AscH (6)	11
9	**1**	**PS$_{Ru}$**	8:2	Et$_3$N (8.5)	3
10[c]	**1**	**PS$_{Ir}$**	8:2	Et$_3$N (8.5)	n.d.
11[d]	**1**	**PS$_{Ir}$**	8:2	Et$_3$N (8.5)	n.d.
12	**1**	**PS$_{Ir}$**	8:2	no ED	n.d.
13	**1**	**no PS**	8:2	Et$_3$N (8.5)	n.d.
14	**No cat.**	**PS$_{Ir}$**	8:2	Et$_3$N (8.5)	< 1[b]
15	**1**	**PS$_{Ir}$**	10:0	Et$_3$N (8.5)	n.d.
16	**1**	**PS$_{Ir}$**	0:10	Et$_3$N (8.5)	< 1
17	**Co(OTf)$_2$**[e]	**PS$_{Ir}$**	8:2	Et$_3$N (8.5)	4[b]
18	**Py$_2$^{Ts}tacn**	**PS$_{Ir}$**	8:2	Et$_3$N (8.5)	n.d. [b]
19	**Co(OTf)$_2$,**[e]**bpy**	**PS$_{Ir}$**	8:2	Et$_3$N (8.5)	<1
20	**Co(OTf)$_2$,**[e]**2·bpy**	**PS$_{Ir}$**	8:2	Et$_3$N (8.5)	6
21	**[Co(bpy)$_3$]$^{2+}$**	**PS$_{Ir}$**	8:2	Et$_3$N (8.5)	5

Reaction conditions: [**9a**] = 16.5 mM, Cat = 3 mol%, PS = 1.5 mol%, ED (electron donor), irradiation 5 h at λ = 447±20 nm and 30 ºC under N_2.[a] [**9a**] = 66 mM, Cat = 1 mol%, PS = 0.5 mol% in H$_2$O:CH$_3$CN:Et$_3$N (3.5:1.5:0.1 mL) at 30 ºC. **PS$_{Ir}$** = [Ir(bpy)(ppy)$_2$](PF$_6$), **PS$_{Ru}$** = [Ru(bpy)$_3$](PF$_6$)$_2$. [b] 22 % yield of 2,3-diphenyl-2,3-butanediol (14 % isolated yield). [c] In the dark. [d] In the dark under H_2 atmosphere. [e] Co(OTf)$_2$ stands for Co(OTf)$_2$(CH$_3$CN)$_2$, TEOA: triethanolamine. AscH: Ascorbic acid. n.d.= not detected. Yields determined by GC analysis after workup and relative to a calibrated internal standard given as averages of at least two runs.

Table SI.1.2. Screening conditions for the light-driven acetophenone reduction with **PS_{Cu}**.



Entry[a]	Catalyst	PS	H_2O:CH_3CN (mL)	ED (eq.)	Yield (%)
1	**1**	**PS_{Ir}**	8:2	Et_3N (8.5)	65
2	**1**	**PS_{Cu}**	6:4	Et_3N (8.5)	92
3	**no Co cat.**	**PS_{Cu}**	6:4	Et_3N (8.5)	n.d.[b]
4	**1**	**no PS**	6:4	Et_3N (8.5)	n.d.
5	**1**	**PS_{Cu}**	10:0	Et_3N (8.5)	n.d.
6	**1**	**PS_{Cu}**	0:10	Et_3N (8.5)	2
7	**1**	**PS_{Cu}**	6:4	no ED	n.d.
8[c]	**1**	**PS_{Cu}**	6:4	Et_3N (8.5)	n.d.
9[e]	**1**	**PS_{Cu}**	6:4	Et_3N (8.5)	n.d.
10	**$Co(OTf)_2$[e]**	**PS_{Cu}**	6:4	Et_3N (8.5)	n.d.[b]
11[f]	**$Co(OTf)_2$[e] +** Bathocuproine	**PS_{Cu}**	6:4	Et_3N (8.5)	n.d.
12[g]	**$Co(OTf)_2$[e] +** Xantphos	**PS_{Cu}**	6:4	Et_3N (8.5)	n.d.[b]

[a]Reaction conditions: [**9a**] = 16.5 mM, Cat = 3 mol%, PS = 1.5 mol% in a H_2O:CH_3CN:Et_3N mixture, irradiation 5 h at λ = 447±20 nm and 30 ºC under N_2. [b] 12 % yield of 2,3-diphenyl-2,3-butanediol [c] In the dark. [d] In the dark under H_2 atmosphere. [e] **$Co(OTf)_2$** stands for $Co(OTf)_2(CH_3CN)_2$. [f] $Co(OTf)_2(CH_3CN)_2$:Bathocuproine (1:1). [g] $Co(OTf)_2(CH_3CN)_2$: Xantphos (1:1). ED = Electron donor, n.d.= not detected. Yields determined by GC analysis after workup and relative to a calibrated internal standard given as averages of at least two runs.

7. Screening of cobalt catalysts in H_2 and 10a formation.

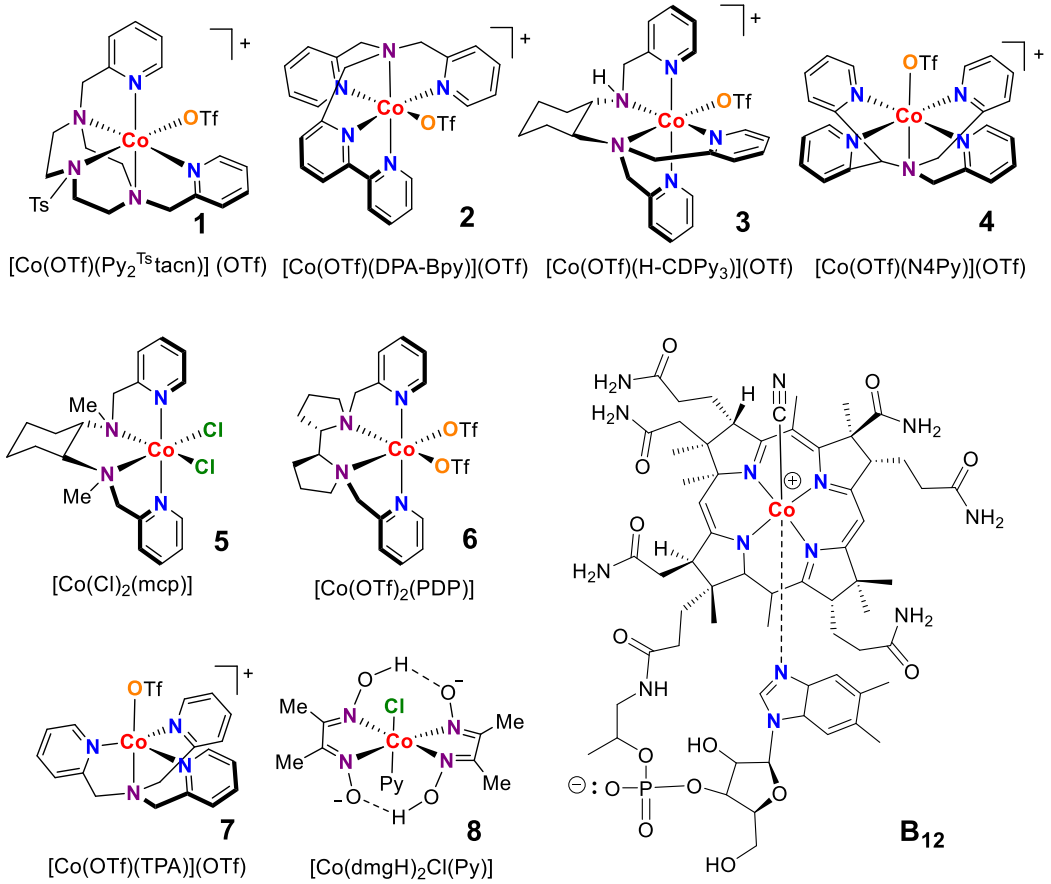


Figure SI.1.2. Selected cobalt complexes for the study.

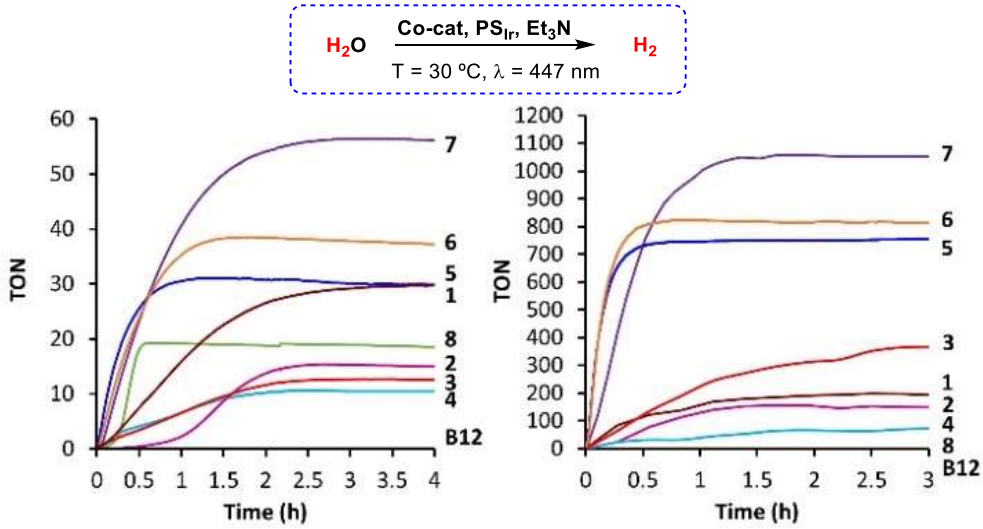


Figure SI.1.3. Photocatalytic activity in H_2 evolution under Left) optimized conditions for **9a** reduction: Co-cat. (0.49 mM) and $\mathbf{PS_{Ir}}$ (0.25 mM) in H_2O:CH_3CN:Et_3N (8:2:0.2 mL) at 30 ºC and Right) typical conditions for H_2 evolution: Co-cat. (5 μM) and $\mathbf{PS_{Ir}}$ (150 μM) in H_2O:CH_3CN:Et_3N (6:4:0.2 mL) at 30 ºC for the studied cobalt catalysts (Co-cat.): [Co(OTf)(Py_2Tstacn)](OTf) (**1**), [Co(OTf)(DPA-py)](OTf) (**2**), [Co(OTf)(H-$CDPy_3$)](OTf) (**3**), [Co(OTf)(N_4Py)](OTf) (**4**), [$Co(Cl)_2$(mcp)] (**5**), [$Co(OTf)_2$(PDP)] (**6**), [Co(OTf)(TPA)](OTf) (**7**), [$Co(dmgH)_2$Cl(Py)] (**8**) and B_{12}.

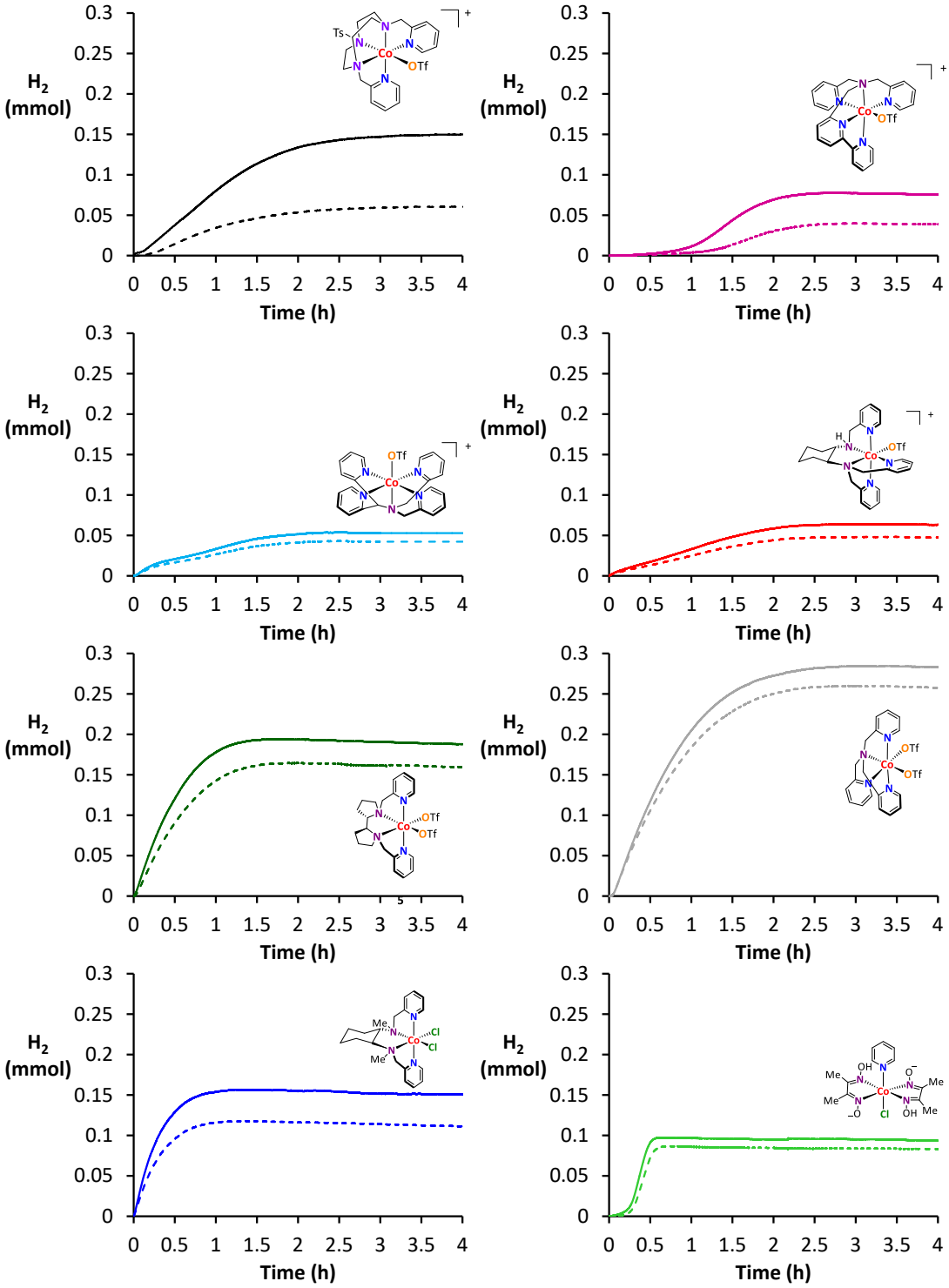
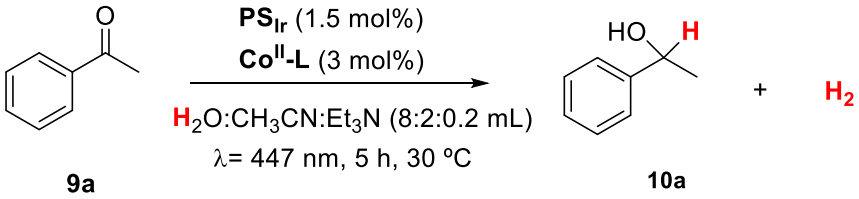


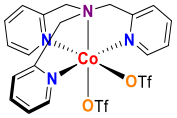
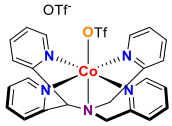
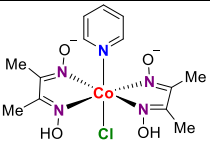
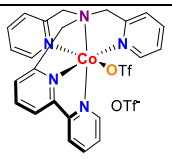
Figure SI.1.4. On-line monitoring of the photochemical H_2 production in the absence (solid line) and presence of **9a** (dashed line) for complexes **1-8**. Reaction conditions in the absence of substrate: **PS_{Ir}** (2.5 μmol), **cobalt catalyst** (5 μmol). Reaction conditions in the presence of substrate: [**9a**] (0.168 mmol, 16.5 mM), **PS_{Ir}** (2.5 μmol, 1.5 mol%), **cobalt catalyst** (5.04 μmol, 3 mol%). In samples were irradiated (λ = 447 nm) at 30ºC under N_2 in a H_2O:CH_3CN:Et_3N (8:2:0.2 mL).. The activity of **B_{12}** has not been included since it was not found to be active in H_2 formation. The amount of H_2 was quantified by GC analysis when the hydrogen evolved reached a plateau.

Table SI.1.3. Photocatalytic reduction of acetophenone and water to 1-phenylethanol (**10a**) and H_2 respectively mediated by the studied cobalt complexes.

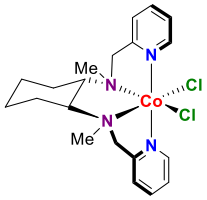
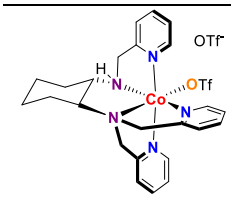
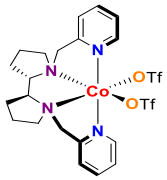
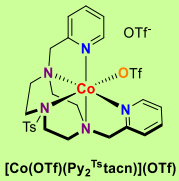


9a **10a**

L= TPA, N_4Py, glioxim, DPA-Bpy, BpcMe, H-CDPy$_3$, PDP, Py$_2^{Ts}$tacn

CATALYST	Presence of 9a ([16.5 mM])	Yield 10a (%)	9a (mmol)	ν_{10a} (mmol 10a·h^{-1})	H_2 (mL)	H_2 (mmol)	ν_{H2} (mmol H_2·h^{-1})	ν_{H2} (mL H_2·h^{-1})	Total mmol (10a + H_2)
 [Co(TPA)(OTf)$_2$]	**NO**	-	-	-	7.0	0.288	0.274	6.680	0.288
	YES	11	0.019	0.019	6.5	0.264	0.220	5.360	0.283
 [Co(N4Py)(OTf)](OTf)	**NO**	-	-	-	1.3	0.054	0.056	1.360	0.054
	YES	6	0.009	0.013	1.1	0.043	0.045	1.088	0.053
 [Co(Cl)(Py)(glioxim)]	**NO**	-	-	-	2.4	0.097	0.047	1.139	0.097
	YES	6	0.009	0.018	2.1	0.087	0.030	0.732	0.096
 [Co(DPA-Bpy)(OTf)] (OTf)	**NO**	-	-	-	1.9	0.078	0.004	0.108	0.078
	YES	20	0.034	0.037	1.0	0.040	0.003	0.064	0.074

Reaction conditions: **9a** (0.168 mmol, 16.5 mM), **PS$_{Ir}$** (2.5 μmol, 1.5 mol%), **cobalt catalyst** (5 μmol, 3 mol%), H_2O:CH_3CN:Et_3N (8:2:0.2 mL), irradiation at λ= 447 nm for 5 h at 30 ºC under N_2. Yields and rates of **10a** were determined by GC after workup of the reaction and they are relative to the calibrated internal standard. Total amounts and rates of H_2 were determined by monitoring the increase of pressure and quantified by GC analysis. ν_{10a}: Formation rate of **10a** (mmol h^{-1}), ν_{H2}: Formation rate of H_2 (mmol H_2 h^{-1}).

CATALYST	Presence of 9a ([16.5 mM])	Yield 10a (%)	9a (mmol)	ν_{10a} (mmol 10a·h^{-1})	H_2 (mL)	H_2 (mmol)	ν_{H2} (mmol H_2·h^{-1})	ν_{H2} (mL H_2·h^{-1})	Total mmol (10a + H_2)
 [Co(mpc)(Cl)$_2$]	**NO**	-	-	-	3.8	0.156	0.350	8.528	0.156
	YES	19	0.033	0.034	2.9	0.118	0.257	6.258	0.150
 [Co(H-CDPy$_3$)(OTf)](OTf)	**NO**	-	-	-	1.6	0.064	0.041	1.002	0.064
	YES	8	0.014	0.018	1.2	0.048	0.031	0.748	0.062
 [Co(PDP)(OTf)$_2$]	**NO**	-	-	-	4.7	0.194	0.273	6.655	0.194
	YES	16	0.028	0.030	4.0	0.165	0.192	4.678	0.192
 [Co(OTf)(Py$_2$^{Ts}tacn)](OTf)	**NO**	-	-	-	3.7	0.153	0.064	1.567	0.153
	YES	65	0.109	0.065	1.5	0.060	0.015	0.362	0.160

Reaction conditions: **9a** (0.168 mmol, 16.5 mM), **PS$_{Ir}$** (2.5 μmol, 1.5 mol%), **cobalt catalyst** (5 μmol, 3 mol%), H_2O:CH_3CN:Et_3N (8:2:0.2 mL), irradiation at λ= 447 nm for 5 h at 30 ºC under N_2. Yields and rates of **10a** were determined by GC after the workup of the reaction and they are relative to the calibrated internal standard. Total amounts and rates of H_2 were determined by monitoring the increase of pressure and quantified by GC analysis. ν_{10a}: Formation rate of **10a** (mmol h^{-1}), ν_{H2}: Formation rate of H_2 (mmol H_2 h^{-1}).

8. Optimization of 9a reduction using PS_{Cu}

Acetophenone (**9a**) was used as a model substrate for the optimization of the catalytic conditions when using PS_{Cu} as photoredox catalyst and **1** as catalyst.

8.1. Optimization of the H_2O:CH_3CN ratio

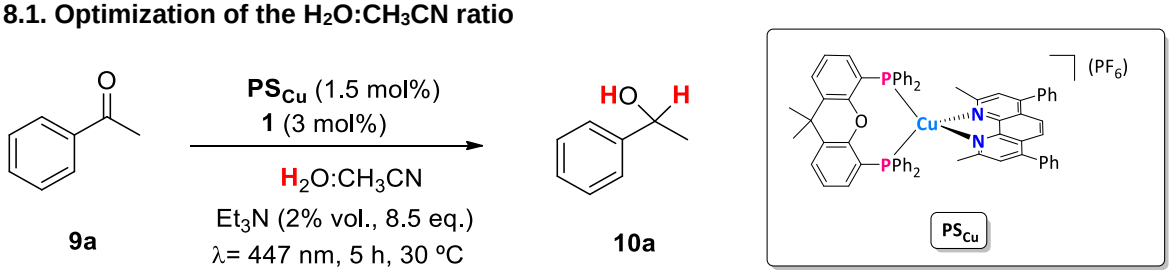


Table SI.1.4. Photocatalytic reduction of **9a** with PS_{Cu} at different ratios of H_2O:MeCN.

Entry	Solvent mixture (H_2O:MeCN)	Subs (%)	Yield **10a** (%)
1	8:2	93	<1
2	7:3	5	93
3	6.5:3.5	0	90
4	6:4	0	92
5	5.5:4.5	0	92
6	5:5	5	92
7	4:6	28	63
8	3:7	52	38

Reaction conditions: [**9a**] (0.168 mmol, 16.5 mM), **1** (5 μmol, 3 mol%), PS_{Cu} (2.5 μmol, 1.5 mol%), 0.2 mL Et_3N (8.5 eq.) irradiation at λ = 447 nm for 5 h at 30 ºC under N_2. Total volume mixture: 10 mL. Conversions of **9a** and yields of **10a** were determined by GC after the workup of the reaction and they are relative to a calibrated internal standard. Subs = recovered substrate. PS_{Cu} = [Cu(bathocuproine)(Xantphos)]PF_6.

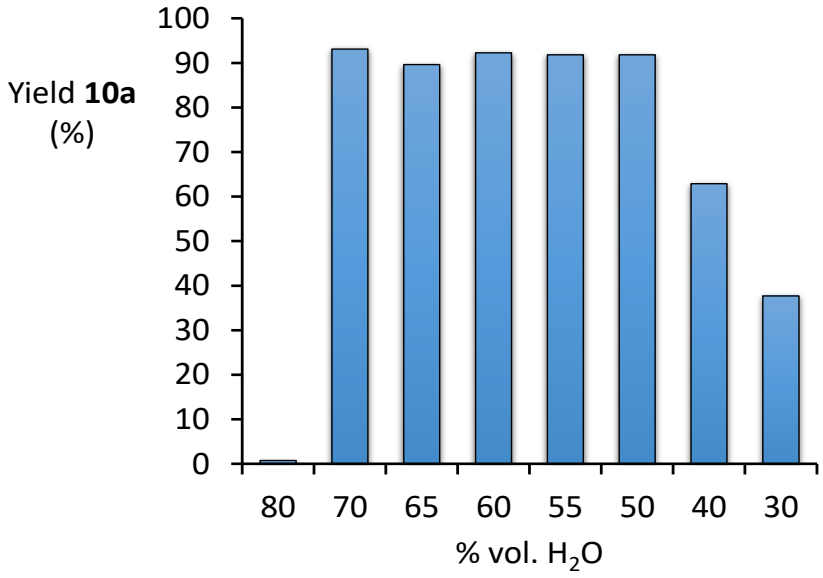


Figure SI.1.5. Photocatalytic reduction of **9a** into **10a** with PS_{Cu} at different ratios of H_2O:MeCN.

8.2. Optimization of the PS_{Cu} loading

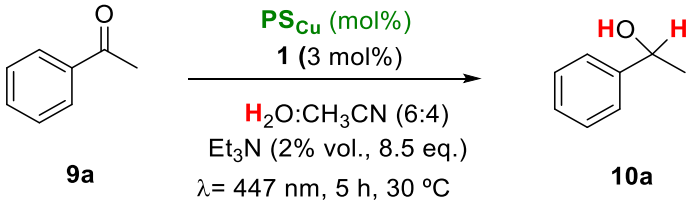


Table SI.1.5. Photocatalytic reduction of **9a** using different PS_{Cu} loadings.

Entry	PS_{Cu} (%mol)	Subs (%)	Yield **10a** (%)
1	0	90	0
2	0.3	70	20
3	0.6	53	36
4	0.9	28	62
5	1.2	0	92
6	1.5	0	92
7	1.8	0	93
8	2.1	0	92
9	2.4	0	91

Reaction conditions: [**9a**] (0.168 mmol, 16.5 mM), $\mathbf{1}_{Co}$ (5 μmol, 3 mol%), PS_{Cu} (0-2.4 mol%), 0.2 mL Et_3N (8.5 eq.) irradiation at λ = 447 nm for 5 h at 30 ºC under N_2. Total volume mixture: 10 mL. Conversions of **9a** and yields of **10a** were determined by GC after the workup of the reaction and they are relative to the calibrated internal standard. Subs = substrate unreacted.

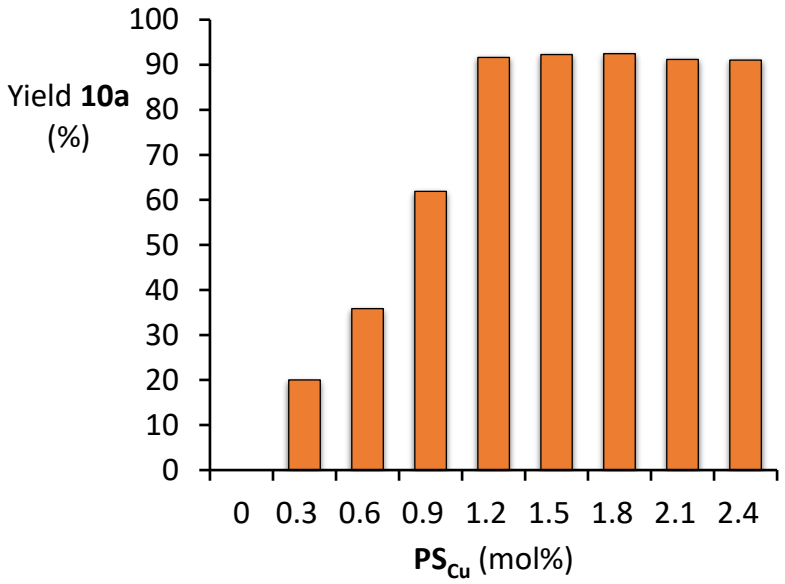


Figure SI.1.6. Photocatalytic reduction of **9a** into **10a** with PS_{Cu} at different photoredox catalyst loading.

8.3. Optimization of the cobalt catalyst 1 loading

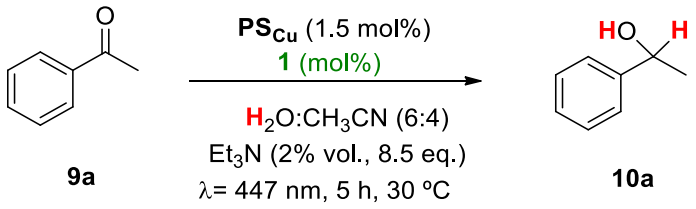


Table SI.1.6. Photocatalytic reduction of **9a** using different **1** loadings.

Entry	**1** (mol%)	Subs (%)	Yield **10a** (%)	TON $_{cat}$
1	5	0	93	18
2	4	0	92	22
3	3.5	0	92	27
4	3	0	91	31
5	2.5	0	92	36
6	2	0	93	44
7	1	0	92	88
8	0.5	0	91	173
9	0.25	0	90	353
10	0.1	44	45	449
11	0.05	54	35	700
12	0.03	67	23	900
13	0.01	80	11	1100
14	0.005	85	7	1400
15	0	92	n.d.	-

Reaction conditions: [**9a**] (0.168 mmol, 16.5 mM), **PS$_{Cu}$** (2.5 μmol, 1.5 mol%), **1** (0.005-5 mol%), 0.2 mL Et$_3$N (8.5 eq.) irradiation at λ = 447 nm for 5 h at 30 ºC under N_2. Total volume mixture: 10 mL. The amount of the starting material **9a** and the yields of **10a** were determined by GC after workup of the reaction and they are relative to the calibrated internal standard. Subs = substrate unreacted. TON$_{cat}$= mol **10a** / mol **1**.

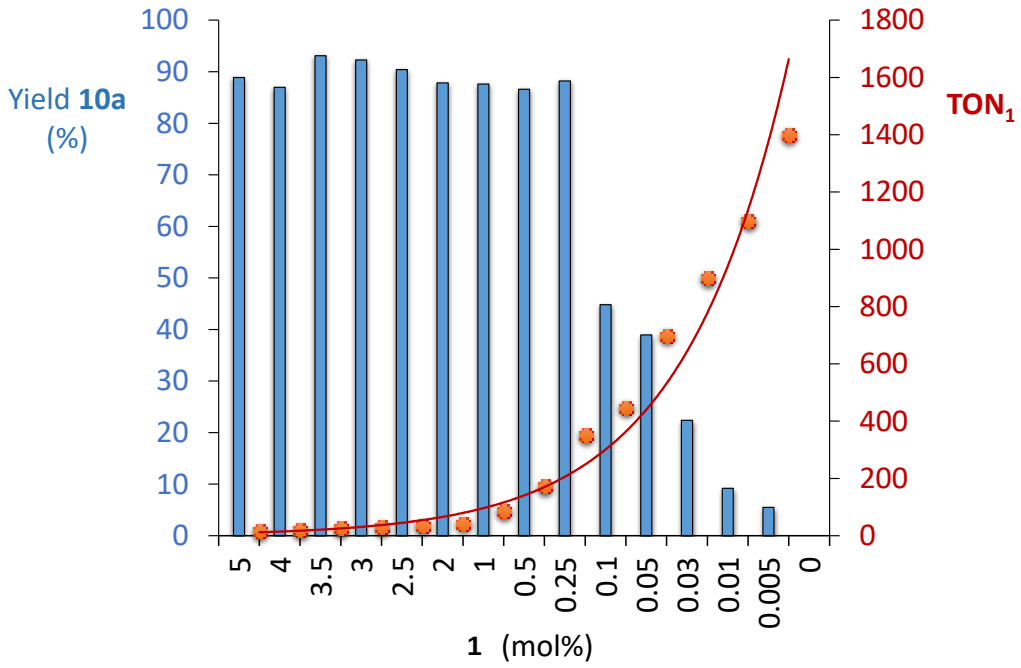


Figure SI.1.7. Optimization of the loading of complex **1** in the photocatalytic reduction of **9a** using $\mathbf{PS_{Cu}}$ as photoredox catalyst

8.4. Optimization of the Et_3N loading

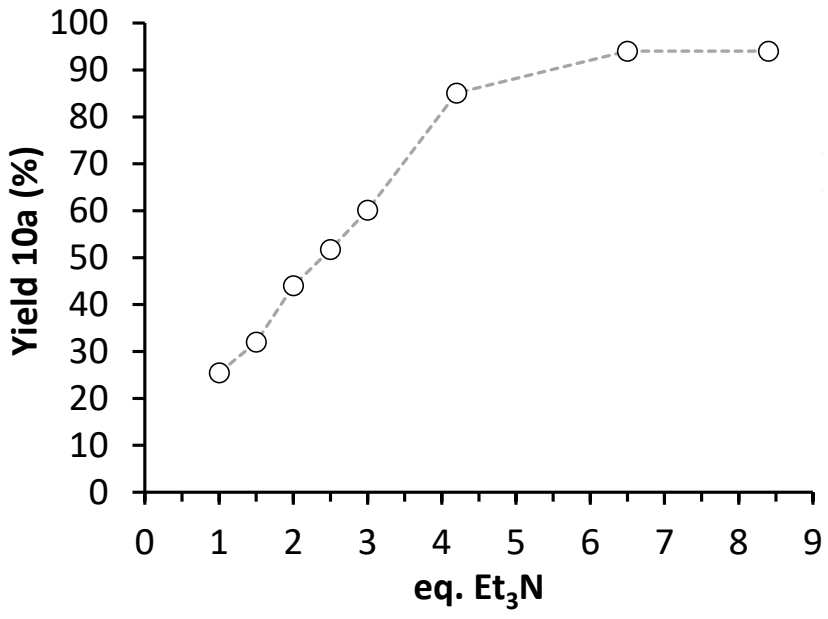


Figure SI.1.8. Optimization of the Et_3N loading in the photocatalytic reduction of **9a** using $\mathbf{PS_{Cu}}$ (1.5 mol%) as photoredox catalyst and complex **1** (1 mol%).

9. Control experiments in the photoreduction of acetophenone (9a)

9.1. Effect of the presence of O_2 in the photocatalytic reduction of acetophenone (9a)

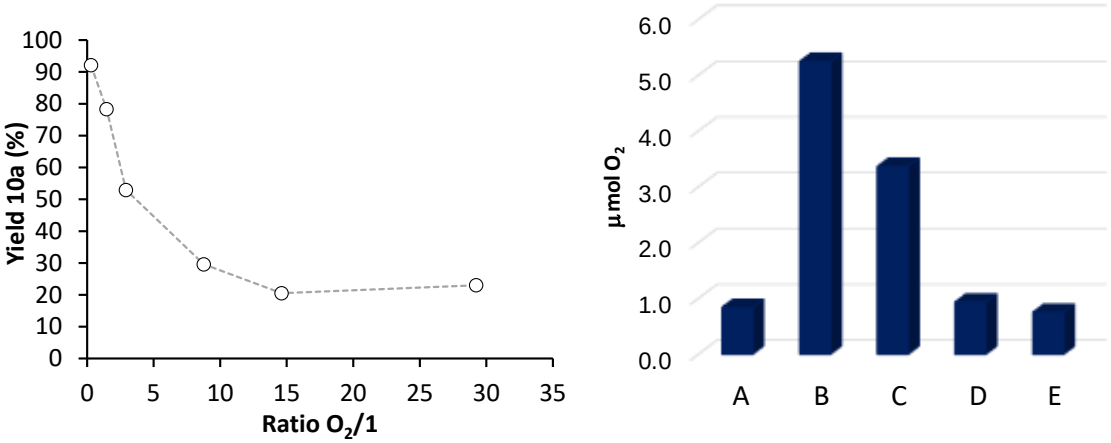


Figure SI.1.9. Right) Plot of the O_2/**1** stoichiometric ratio. O_2/**1** = (mmol O_2 added to the headspace versus the amount of **1** in solution. **Left)** n(O_2) measured in the headspace by CG-TDC **A)** under pure N_2, **B)** A + addition of 5 μmol O_2 (3 eq. respect the catalyst) after 1 min without shaking, **C)** B + after 5 min shaking, **D)** C + after 5 h of irradiation and **E)** C + after 24 h of irradiation. Conditions: **1** (1 mol%), $\mathbf{PS_{Cu}}$ (1.5 mol%), **9a** (16.5 mM) in H_2O:CH_3CN:Et_3N (6:4:0.2 mL) irradiation (447 nm) for 5 h at 30 ºC.

Quantification of the O_2 in the headspace after the reaction. The O_2 content in the headspace of reactions vials **(A-E)** prepared as described in the ***Procedure for the reduction of acetophenone (9a) in presence of O_2*** was quantified.

A) Reaction under pure N_2, before irradiation.
B) A + addition of 5 μmol O_2 (2 and 3 eq. respect the copper and cobalt catalysts, respectively) O_2 measured after 1 min without shaking.
C) B + O_2 measured after 5 min shaking.
D) C + O_2 measured after 5 h of irradiation.
E) C + O_2 measured after 24 h of irradiation (Figure SI.1.9, right).

For reactions **B**, **C**, **D** and **E** the 5 μmol of O_2 (from Air) were introduced into the reaction vial headspace using a Hamilton gas-tight syringe through the septa. The O_2 content was measured by GC-TDC.

The O_2 measured after 1 min of the O_2 addition (5.2 mmol) indicates that negligible amount of O_2 was introduced into the solution. After 5 min shaking, the O_2 level at the headspace of the reaction vial dropped about 40%. After 5h irradiation the headspace O_2 level found was equivalent to the measured in pure N_2. These results support the hypothesis that when using an over stoichiometry of O_2 respect the dual catalytic system (in this experiment, 2 and 3 eq. regarding the copper and cobalt catalysts, respectively) the O_2 is being consumed during the reaction.

Table SI.1.7. O_2 introduced and **10a** yields of experiments in Figure SI.1.9

O_2 (mmol)	n(O_2) / n(1)	n(O_2) / n(9a)	n(O_2) / n(PS_{Cu})	Yield 10a[a] (%)
0.0005	0.3	0.003	0.2	92
0.0025	1.5	0.02	1	78
0.005	3	0.03	2	53
0.015	9	0.09	6	30
0.025	15	0.15	10	21
0.049	30	0.30	20	23

[a] Conditions: **1** (1 mol%), **PS_{Cu}** (1.5 mol%), **9a** (16.5 mM) in H_2O:CH_3CN:Et_3N (6:4:0.2 mL) irradiation (447 nm) for 5 h at 30 ºC.

In the experiments carried out with the **procedure for the reduction of acetophenone (9a) with non-degassed solvents prepared outside the glovebox under air exposition** we have estimated the oxygen content of the solutions by **1)** employing the O_2 reported concentration for pure water and acetonitrile at the reaction temperature and 1 atm of pressure.

Estimation of the oxygen content using reported concentration values in water and acetonitrile. Data extracted from *Journal of Physical and Chemical Reference Data* **2014***, 43*, 033102; doi: 10.1063/1.4883876. Solubility of O_2 at 30ºC and 1 atm:

[H_2O]: 1 mM and [CH3CN]: 1.7 mM

*Estimation of n(O_2) in the reaction mixtures with **PS_{Cu}*** taking into account the solubility in both solvents employed: *V(MeCN) = 2.4 mL; V(H_2O) = 3.6 mL*

$$n(O_2\ in\ MeCN) = M(M) * V(L) = 1.7 \cdot 10^{-3} * \ 2.4 \cdot 10^{-3} = 4.1 \cdot 10^{-6}\ mol$$

$$n(O_2\ in\ H2O) = 1 \cdot 10^{-3} * \ 3.6 \cdot 10^{-3} = 3.6 \cdot 10^{-6}\ mol$$

$$n(O_2\ Reac.mix.) = \mathbf{7.7} * \ \mathbf{10^{-3}}\ \boldsymbol{mmol}\ \textit{and}\ [O_2\ Reac.mix.] \approx \mathbf{1}\ \boldsymbol{mM}$$

*Estimation of n(O_2) in the reaction mixtures with **PS_{Ir}*** taking into account the solubility in both solvents employed: *V(MeCN) = 1.2 mL; V(H_2O) = 4.8 mL*

$$n(O_2\ in\ MeCN) = M(M) * V(L) = 1.7 \cdot 10^{-3} * \ 1.2 \cdot 10^{-3} = 2 \cdot 10^{-6}\ mol$$

$$n(O_2\ in\ H2O) = 1 \cdot 10^{-3} * \ 4.8 \cdot 10^{-3} = 4.8 \cdot 10^{-6}\ mol$$

$$n(O_2\ Reac.mix.) = \mathbf{6.8} * \ \mathbf{10^{-3}}\ \boldsymbol{mmol}\ \textit{and}\ [O_2\ Reac.mix.] \approx \mathbf{1}\ \boldsymbol{mM}$$

In the case of **PS_{Cu}** we estimate about 1 mM of O_2 in solution, which represents 6 equivalents regarding complex **1** .(165 μM) and 4 equivalents regarding **PS_{Cu}**.(247.5 μM). When using **PS_{Ir}** we estimate 2 equivalents of O_2 regarding complex **1** .(495 μM) and 4 equivalents regarding **PS_{Ir}**.(247.5 μM).

9.2. Effect of the redox photocatalyst in the photocatalytic reduction of acetophenone (9a)

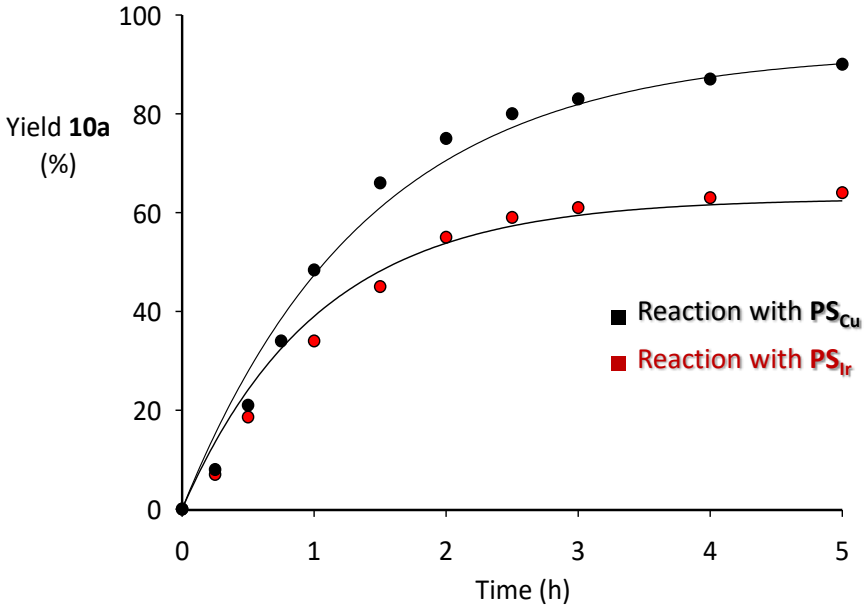


Figure SI.1.10. Photocatalytic conversion of **9a** into **10a** catalyzed by catalytic systems **1** /PS_{Cu} (black dots) and catalytic system **1**/ PS_{Ir} (red dots) versus the reaction time (h). Conditions: **9a** (0.168 mmol, 16.5 mM), PS_x (2.5 μmol, 1.5 mol%) (X = Cu, Ir), **1** (5 μmol, 3 mol%) in H_2O:CH_3CN:Et_3N (6:4:0.2 mL) irradiation at λ = 447 nm at 30 ºC under N_2. Each data point corresponds to a different reaction experiment.

10. Optimization of aliphatic aldehydes reduction

Hydrocinnamaldehyde (**11e**) was used as a model substrate for the optimization of the catalytic conditions when using $\mathbf{PS_{Cu}}$ as photoredox catalyst and **1** as catalyst.

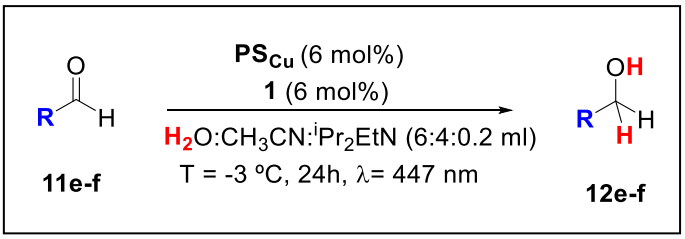


Table SI.1.8. Optimization of the catalytic conditions for the photoreduction of **11e**.

Entry	[Substrate] (mM)	[PS_{Cu}] (mol%)	[1] (mol%)	ED	T (ºC)	% Conv.	% alcohol	% dimer	Mass loss
1	16.5	1.5	1	TEA	30	90	23	2	65
2	16.5	1.5	1	DIPEA	30	96	44	2	50
3	8.7	1.5	1	TEA	30	82	23	3	55
4	8.7	1.5	1	DIPEA	30	93	44	3	46
5	16.5	1.5	1	TEA	15	69	13	2	54
6	16.5	1.5	1	DIPEA	15	92	45	2	45
7	8.7	1.5	1	TEA	15	61	11	3	46
8	8.7	1.5	1	DIPEA	15	86	37	2	47
9	16.5	3	3	TEA	30	97	37	2	59
10	16.5	3	3	DIPEA	30	96	47	2	47
11	8.7	3	3	TEA	30	96	36	2	57
12	8.7	3	3	DIPEA	30	97	60	3	34
13	16.5	3	3	TEA	15	79	22	2	55
14	16.5	3	3	DIPEA	15	94	52	1	41
15	8.7	3	3	TEA	15	50	12	3	35
16	8.7	3	3	DIPEA	15	95	57	2	36
17	16.5	6	6	TEA	30	98	46	2	50
18	16.5	6	6	DIPEA	30	96	48	2	47
19	8.7	6	6	TEA	30	97	45	2	50
20	8.7	6	6	DIPEA	30	97	64	2	30
21	16.5	6	6	TEA	15	87	34	1	51
22	16.5	6	6	DIPEA	15	89	38	1	49
23	8.7	6	6	TEA	15	76	30	2	44
24	**8.7**	**6**	**6**	**DIPEA**	**15**	**95**	**64**	**0**	**31**
25	4.4	6	6	DIPEA	15	99	54	0	46
26	8.7	3	3	DIPEA	-3	89	57	0	32
27	8.7	6	6	DIPEA	-3	89	57	0	31
28	4.4	3	3	DIPEA	-3	89	57	0	32
29	4.4	6	6	DIPEA	-3	91	54	0	37

Conditions: **1** (% mol), $\mathbf{PS_{Cu}}$ (% mol), substrate (mM) as indicated in the table in H_2O:CH_3CN:Et_3N or H_2O:CH_3CN:$^iPr_2EtN$ (6:4:0.2 mL) irradiated at λ= 447 nm for 5 h at 30 and 15 or for 24 h at -3 ºC under N_2. Yields were determined by GC analysis after reaction workup and they are relative to a calibrated internal standard. Values are average of triplicates.

Table SI.1.9. Optimization of the catalytic conditions for the photoreduction of **11f**.

Entry	[Substrate] (mM)	[cat] (mol %)	[PS_{Cu}] (mol %)	ED	T (ºC)	% Conv.	% alcohol	% dimer	Mass loss
1	8.7	3	3	TEA	15	96	50	0	46
2	4.4	6	6	TEA	15	98	70	0	28
3	**4.4**	**6**	**6**	**DIPEA**	**15**	**98**	**93**	**0**	**0**

Conditions: **1** (% mol), **PS_{Cu}** (% mol), substrate (mM) as indicated in the table in H_2O:CH_3CN:Et_3N or H_2O:CH_3CN:$^iPr_2EtN$ (6:4:0.2 mL) irradiation at λ= 447 nm for 5 h at 15 ºC under N_2. Yields were determined by GC analysis after workup of the reaction and they are relative to a calibrated internal standard. Values were average of triplicates.

11. Mechanical probes

11.1. ^{1}H-NMR monitoring of the 9a reduction in a NMR tube.

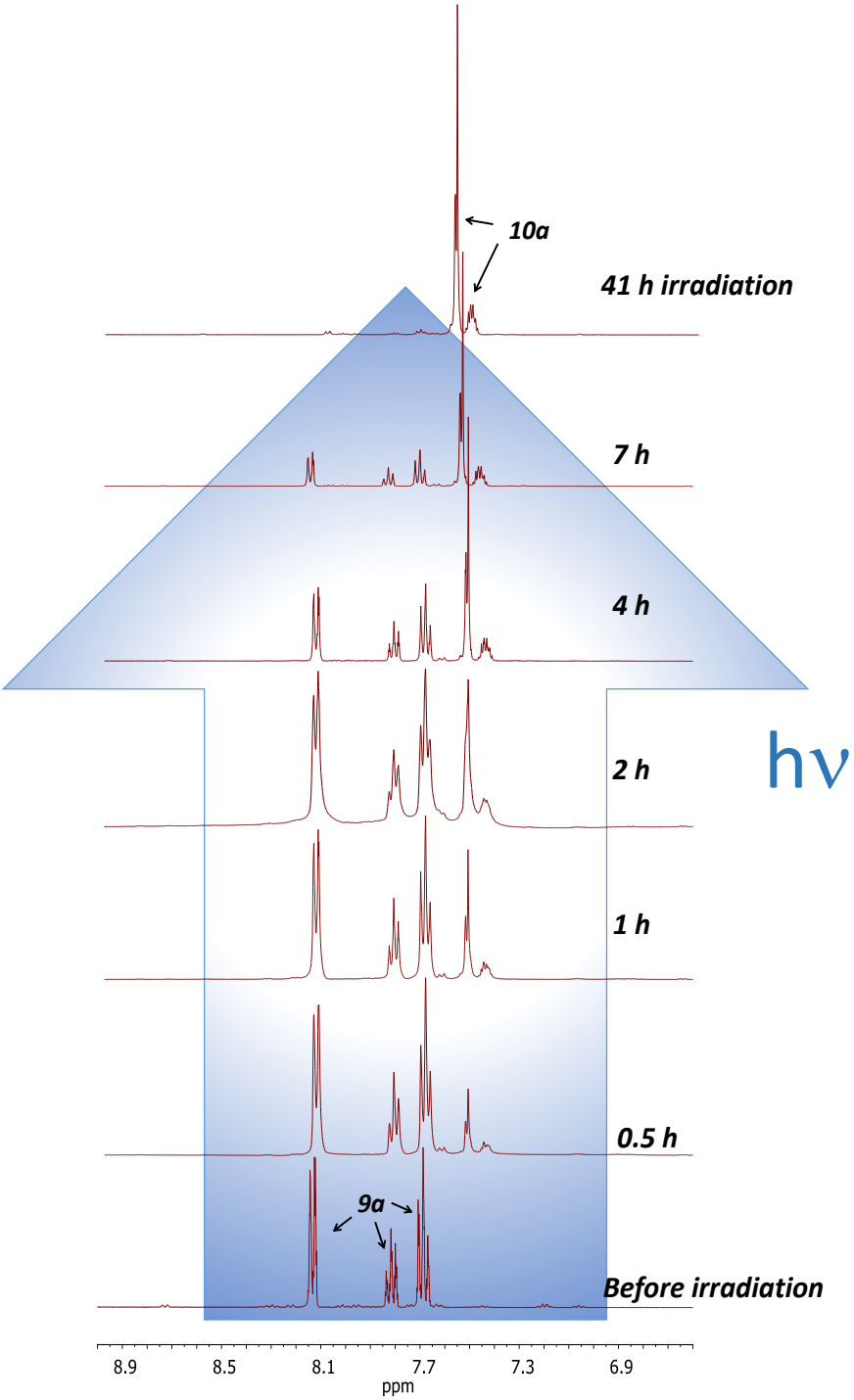


Figure SI.1.11. ^{1}H-NMR (400 MHz, 300 K) spectra recorded at different irradiation times. Conditions: **1** (0.32 μmol, 3 mol%), **PS_{Ir}** (1.2 μmol, 1.14 mol%), **9a** (10.5 μmol, 20.6 mM) in D_2O:CD_3CN:Et_3N (0.35:0.15: 0.01 mL) irradiation (λ = 447 nm) at 30 ºC, under N_2. The amount of **PS_{Ir}** was reduced to 1.14 mol% in order to ensure its solubilization in deuterated solvents. Each ^{1}H-NMR spectrum corresponds to a different reaction in order to have continued irradiation.

11.2. Effect of the reaction atmosphere in the reaction rate

11.2.1. Photocatalytic reduction of acetophenone under H_2 atmosphere

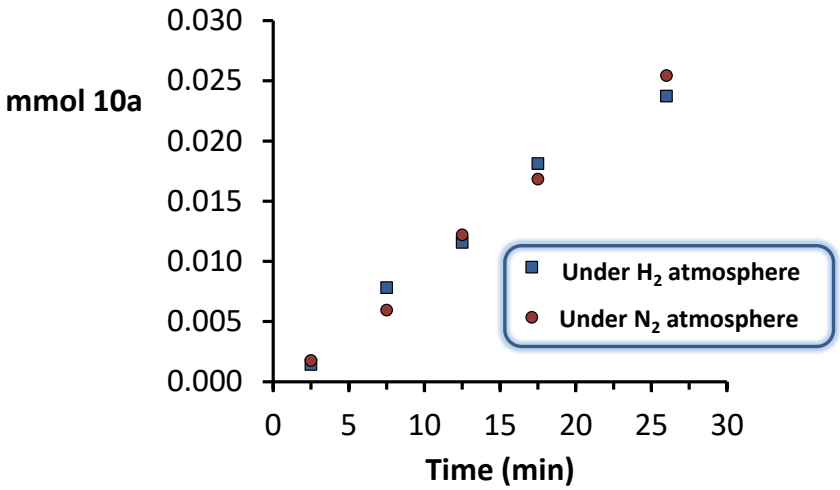


Figure SI.1.12. Formation of **10a** catalyzed by cobalt complex **1** under H_2 (blue squares) or N_2 (red cycles) atmosphere. Conditions: **1** (3.8 μmol, 3 mol%), **PS_{Ir}** (2.5 μmol, 2 mol%), substrate (0.126 mmol, 12.4 mM) in H_2O:CH_3CN:Et_3N (7:3:0.2 mL) irradiation at λ = 447 nm and 30 ºC. Each value of **10a** yield corresponds to an individual experiment. The yield of **10a** was determined by GC analysis after the workup of the reaction and using a calibrated internal standard. Reaction rate for **9a→10a** under N_2 atmosphere 0.061 mmol·h^{-1} and under H_2 atmosphere 0.060 mmol·h^{-1}.

12. Electrochemical studies

12.1. Redox potentials in acetonitrile

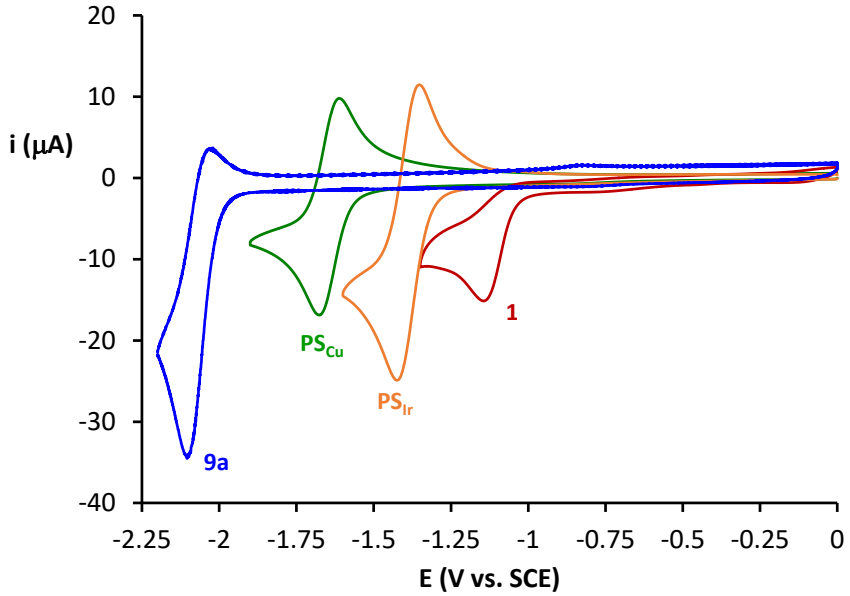


Figure SI.1.13. Cyclic voltammograms of **1** (1 mM, red), **PS_{Ir}** (1 mM, o) and **PS_{Cu}** (1 mM, green) and acetophenone (**9a**) (1 mM, blue). CV were recorded using Bu_4NPF_6 (0.1 M) as a supporting electrolyte in dry acetonitrile. Scan rate = 100 mV/s, glassy carbon working electrode. Potentials are referenced versus SCE. $E_1^{II/I}$= -1.10 V vs SCE; $E_{PSIr}^{III/II}$= -1.38 V vs SCE; $E_{1/2\ PSCu}^{I/0}$= -1.64 V vs SCE; E_{9a} = -2.05 V vs SCE. The redox potentials of **1** and **9a** have been determined at the half wave intensity.

12.2. Redox potentials of 1, PS_{Cu} and 9a under reaction conditions

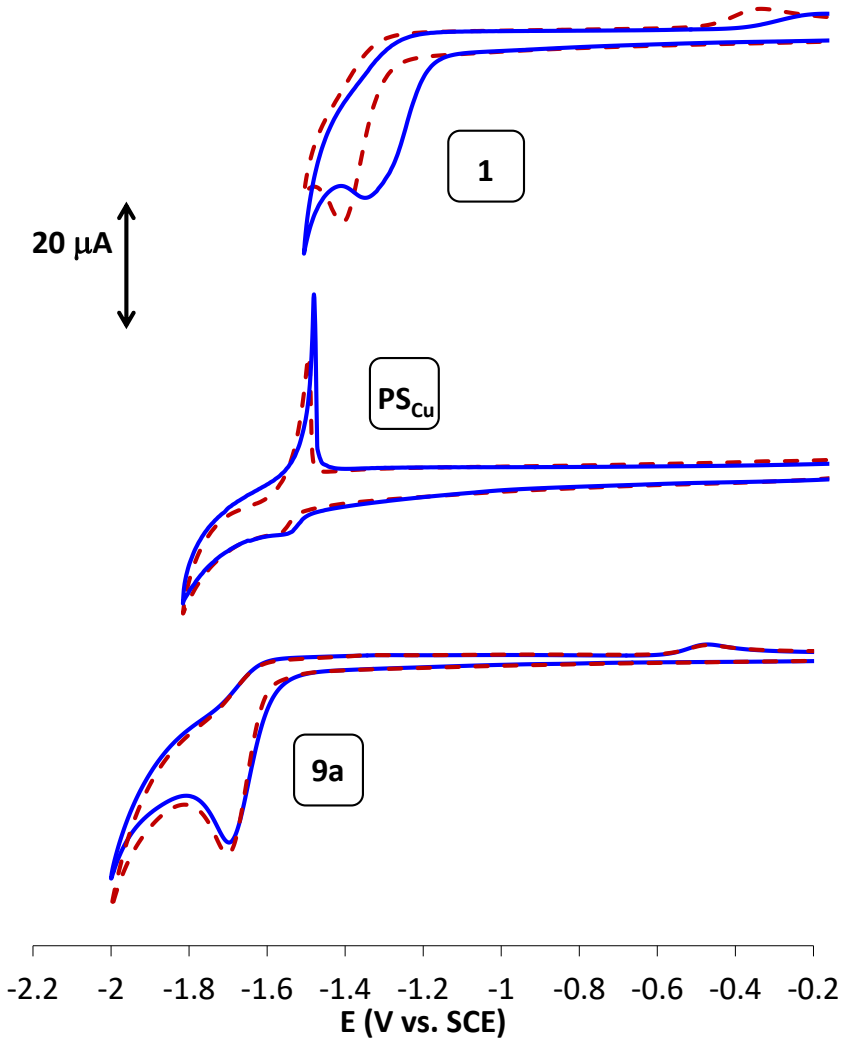
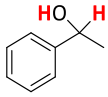


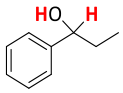
Figure SI.1.14. Cyclic voltammograms of 1mM of **1**, **PS_{Cu}** and acetophenone (**9a**) in the solvent mixture H_2O:MeCN (6:4) (blue CV) and H_2O:MeCN:Et_3N (6:4:0.2) (red dashed CV) using KNO_3 (0.1 M) as a supporting electrolyte. Scan rate = 100 mV/s, glassy carbon working electrode. Potentials are referenced versus SCE.

13. NMR data of the isolated products

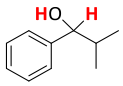
13.1. Isolated alcohols



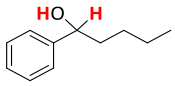
1-Phenylethanol (10a) (90%)**.** ^{1}H-NMR ($CDCl_3$, 300 MHz, 300 K) δ, ppm: 7.38-7.28 (m, 5H, **H$_{arom}$**), 4.90 (q, *J* = 6.6 Hz, 1H, C**H**), 1.84 (br, 1H, O**H**). 1.50 (d, *J* = 6.6 Hz, 3H, C**H$_3$**). ^{13}C{^{1}H}-NMR ($CDCl_3$, 75.4 MHz, 300 K) δ, ppm: 145.9, 128.6, 127.5, 125.5, 70.5, 25.3.



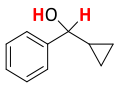
1-Phenyl-1-propanol (10b) (89%)**.** ^{1}H-NMR ($CDCl_3$, 300 MHz, 300 K) δ, ppm: 7.35-7.28 (m, 5H, **H$_{arom}$**), 4.60 (t, *J* = 6.6 Hz, 1H, C**H**), 1.80 (m, 2H, CH-C**H$_2$**-CH_3). 0.92 (t, *J* = 7.2 Hz, 3H, C**H$_3$**). ^{13}C{^{1}H}-NMR ($CDCl_3$, 75.4 MHz, 300 K) δ, ppm: 144.9, 128.7, 127.8, 126.3, 76.3, 32.2, 10.5.



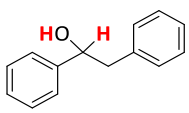
2-Methyl-1-phenylpropan-1-ol (10c) (77%)**.** ^{1}H-NMR ($CDCl_3$, 300 MHz, 300 K) δ, ppm: 7.35-7.26 (m, 5H, **H$_{arom}$**), 4.36 (d, *J* = 6.6 Hz, 1H, C**H**-CH-$(CH_3)_2$), 1.95 (m, 1H, CH-C**H**-$(CH_3)_2$). 1.85 (br, 1H, O**H**), 1.00 (d, *J* = 6.9 Hz, 3H, CH-CH-(C**H$_3$**)$_2$), 0.80 (d, *J* = 6.9 Hz, 3H, CH-CH-(C**H$_3$**)$_2$). ^{13}C{^{1}H}-NMR ($CDCl_3$, 75.4 MHz, 300 K) δ, ppm: 143.9, 128.4, 127.6, 126.8, 80.3, 35.5, 19.2, 18.5.



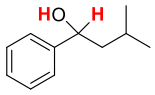
1-Phenyl-pentanol (10d) (90%)**.** ^{1}H-NMR ($CDCl_3$, 300 MHz, 300 K) δ, ppm: 7.36-7.26 (m, 5H, **H$_{arom}$**), 4.66 (t, *J* = 6.0 Hz, 1H, C**H**-$(CH_2)_3$-CH_3), 1.89 (br, 1H, O**H**). 1.79-1.71 (m, 2H, CH-C**H$_2$**-$(CH_2)_2$-CH_3), 1.39-1.28 (m, 4H, CH-CH_2-(C**H$_2$**)$_2$-CH_3), 0.89 (t, *J* = 6.9 Hz, 3H, CH-CH_2-$(CH_2)_2$-C**H$_3$**). ^{13}C{^{1}H}-NMR ($CDCl_3$, 75.4 MHz, 300 K) δ, ppm: 145.2, 128.6, 127.7, 126.2, 74.9, 39.0, 28.2, 22.9, 14.3.



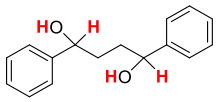
Cyclopropyl phenylmethanol (10e) (78%)**.** ^{1}H-NMR ($CDCl_3$, 400 MHz, 300 K) δ, ppm: 7.42-7.40 (m, 2H, **H$_{arom}$**), 7.36-7.32 (m, 2H, **H$_{arom}$**), 7.29-7.24 (m, 1H, **H$_{arom}$**), 3.99 (d, *J* = 8.28 Hz, 1H, C**H**-CH-$(CH_2)_2$), 2.12 (br, 1H, O**H**), 1.20 (m, 1H, CH-C**H**-$(CH_2)_2$), 0.63-0.59 (m, 1H, CH-CH-(C**H$_2$**)$_2$), 0.57-0.50 (m, 1H, CH-CH-(C**H$_2$**)$_2$), 0.49-043 (m, 1H, CH-CH-(C**H$_2$**)$_2$), 0.39-0.34 (m, 1H, CH-CH-(C**H$_2$**)$_2$). ^{13}C{^{1}H}-NMR ($CDCl_3$, 100.6 MHz, 300 K) δ, ppm: 144.0, 128.5, 127.6, 126.1, 78.6, 19.3, 3.7, 2.9.



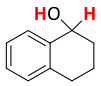
1,2,-diphenylethan-1-ol (10f) (90%)**.** ^{1}H-NMR ($CDCl_3$, 300 MHz, 300 K) δ, ppm: 7.39-7.22 (m, 10H, **H$_{arom}$**), 3.92 (dd, *J* = 5.16, 8.13 Hz, 1H, C**H**), 3.05 (m, 2H, C**H$_2$**), 1.99 (br, 1H, O**H**). ^{13}C{^{1}H}-NMR ($CDCl_3$, 75.4 MHz, 300 K) δ, ppm: 143.8, 138.1, 129.6, 128.5, 128.4, 127.6, 126.6, 125.9, 75.4, 46.1.



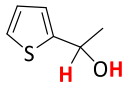
3-methyl-1-phenylbutan-1-ol (**10g**) (91%)**.** ^{1}H-NMR ($CDCl_3$, 400 MHz, 300 K) δ, ppm: 7.38-7.29 (m, 5H, **H$_{arom}$**), 4.77-4.74 (m, 1H, C**H**-CH_2-CH-$(CH_3)_3$), 2.05 (br, 1H, O**H**), 1.80-1.70 (m, 1H, CH-C**H$_2$**-CH-$(CH_3)_3$), 1.57-1.52 (m, 1H, CH-CH_2-C**H**-$(CH_2)_3$), 0.992 (d, *J* = 2.4 Hz, CH-CH_2-CH-(C**H$_3$**)$_3$), 0.976 (d, *J* = 2.4 Hz, CH-CH_2-CH-(C**H$_3$**)$_3$). ^{13}C{^{1}H}-NMR ($CDCl_3$, 100.6 MHz, 300 K) δ, ppm: 145.3, 128.5, 127.5, 125.9, 72.8, 48.4, 24.8, 23.1, 22.3.



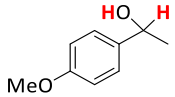
1,4-diphenylbutane-1,4-diol (10i) (89%)**.** ^{1}H-NMR ($CDCl_3$, 400 MHz, 300 K) δ, ppm: 7.37-7.27 (m, 10H, **H$_{arom}$**), 4.73-4.68 (m, 2H, C**H**-CH_2), 3.12 (br, 1H, O**H**), 2.87 (br, 1H, O**H**), 1.94-1.81 (m, 4H, CH-C**H$_2$**). ^{13}C{^{1}H}-NMR ($CDCl_3$, 100.6 MHz, 300 K) δ, ppm: 144.7, 144.6, 128.4, 128.4, 127.5, 127.4, 125.8, 74.6, 74.2, 35.9, 35.1, 35.9, 35.1.



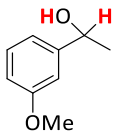
1,2,3,4-tetrahydro-1-naphthol (10j) (91%)**.** ^{1}H-NMR ($CDCl_3$, 300 MHz, 300 K) δ, ppm: 7.45-7.42 (m, 1H, **H$_{arom}$**), 7.22-7.19 (m, 2H, **H$_{arom}$**), 7.12-7.09 (m, 1H, **H$_{arom}$**), 4.78 (t, *J* = 5.07 MHz, 1H, C**H**), 2.89-2.68 (m, 2H, C**H$_2$**), 2.05-1.88 (m, 2H, C**H$_2$**), 1.84-1.73 (m, 2H, C**H$_2$**). ^{13}C{^{1}H}-NMR ($CDCl_3$, 75.4 MHz, 300 K) δ, ppm: 139.1, 137.4, 129.2, 128.9, 127.8, 126.4, 68.3, 32.5, 29.5, 19.1.



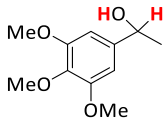
1-(thiophen-2-yl)ethan-1-ol (10k) (40%)**.** ^{1}H-NMR ($CDCl_3$, 400 MHz, 300 K) δ, ppm: 7.28-7.25 (m, 1H, **H$_{arom}$**), 7.01-6.97 (m, 2H, **H$_{arom}$**), 5.15 (q, *J* = 6.4 MHz, 1H, C**H**), 2.16 (br, 1H, O**H**), 1.62 (d, *J* = 6.4 Hz, 3H, C**H$_3$**). ^{13}C{^{1}H}-NMR ($CDCl_3$, 100.6 MHz, 300 K) δ, ppm: 149.9, 126.7, 124.4, 123.2, 66.3, 25.3.



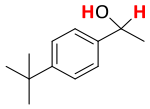
1-(4-methoxyphenyl)ethan-1-ol (10l) (42%)**.** ^{1}H-NMR ($CDCl_3$, 300 MHz, 300 K) δ, ppm: 7.32-7.29 (m, 2H, **H$_{arom}$**), 6.90-6.87 (m, 2H, **H$_{arom}$**), 4.86 (q, *J* = 6.6 MHz, 1H, C**H**), 3.81 (s, 3H, OC**H$_3$**), 1.74 (br, 1H, O**H**), 1.48 (d, *J* = 6.6 MHz, 3H, C**H$_3$**,). ^{13}C{^{1}H}-NMR ($CDCl_3$, 75.4 MHz, 300 K) δ, ppm: 158.9, 138.0, 126.7, 113.8, 69.9, 55.3, 25.0.



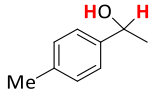
1-(3-methoxyphenyl)ethan-1-ol (10m) (93%)**.** ^{1}H-NMR ($CDCl_3$, 300 MHz, 300 K) δ, ppm: 7.31-7.26 (m, 1H, **H$_{arom}$**), 6.98-6.96 (m, 2H, **H$_{arom}$**), 6.85-6.82 (m, 1H, **H$_{arom}$**), 4.89 (q, *J* = 6.4 MHz 1H, C**H**), 3.84 (s, 3H, OC**H$_3$**), 1.92 (br, 1H, O**H**), 1.51 (d, 3H, C**H$_3$**, *J* = 6.4 MHz). ^{13}C{^{1}H}-NMR ($CDCl_3$, 75.4 MHz, 300 K) δ, ppm: 159.7, 147.6, 129.5, 117.7, 112.9, 110.9, 70.3, 55.2, 25.2.



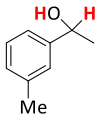
1-(3,4,5-trimethoxyphenyl)ethan-1-ol (10n) (90%)**.** ^{1}H-NMR ($CDCl_3$, 400 MHz, 300 K) δ, ppm: 6.58 (s, 2H, **H$_{arom}$**), 4.81 (q, *J* = 6.4 MHz, 1H, C**H**), 3.85 (s, 6H, *3*-OC**H$_3$**), 3.82 (s, 3H, *4*-OC**H$_3$**), 2.31 (br, 1H, O**H**), 1.47 (d, , *J* = 6.4 MHz, 3H, C**H$_3$**). ^{13}C{^{1}H}-NMR ($CDCl_3$, 100.6 MHz, 300 K) δ, ppm: 153.2, 141.8, 137.0, 102.2, 70.4, 60.8, 56.0,25.2.



1-(4-(tert-butyl)phenyl)ethan-1-ol (10o) (92%)**.** ^{1}H-NMR ($CDCl_3$, 400 MHz, 300 K) δ, ppm: 7.43-7.33 (m, 4H, **H$_{arom}$**), 5.89 (q, *J* = 6.4 MHz, 1H, C**H**), 2.01 (br, 1H, O**H**), 1.52 (d, *J* = 6.4 MHz, 3H, C**H$_3$**), 1.36 (s, 9H, (C**H$_3$**)$_3$). ^{13}C{^{1}H}-NMR ($CDCl_3$, 100.6 MHz, 300 K) δ, ppm: 150.4, 142.8, 125.4, 125.2, 70.2, 34.5, 31.4, 24.9.

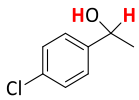


1-(4-methylphenyl)ethanol (10p) (89%)**.** ^{1}H-NMR ($CDCl_3$, 300 MHz, 300 K) δ, ppm: 7.28-7.25 (m, 2H, **H$_{arom}$**), 7.17-7.15 (m, 2H, **H$_{arom}$**), 4.87 (q, *J* = 6.4 MHz, 1H, C**H**), 2.34 (s, 3H, C**H$_3$**), 1.82 (br, 1H, O**H**), 1.48 (d, *J* = 6.4 MHz, 3H, C**H$_3$**). ^{13}C{^{1}H}-NMR ($CDCl_3$, 75.4 MHz, 300 K) δ, ppm: 143.1, 137.3, 129.4, 125.6, 70.4, 25.3, 21.3.

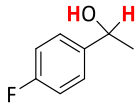


1-(3-methylphenyl)ethanol (10q) (88%)**.** ^{1}H-NMR ($CDCl_3$, 300 MHz, 300 K) δ, ppm: 7.27-7.07 (m, 4H, **H$_{arom}$**), 4.86 (q, *J* = 6.4 MHz, 1H, C**H**), 2.36 (s, 3H, C**H$_3$**), 1.85 (br, 1H, O**H**), 1.48 (d, *J* = 6.4 MHz, 3H, C**H$_3$**). ^{13}C{^{1}H}-NMR ($CDCl_3$, 75.4 MHz, 300 K) δ, ppm: 145.8, 138.2, 128.4, 128.2, 126.1, 122.5, 70.4, 25.1, 21.5.

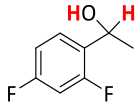
1-(2-methylphenyl)ethanol (10r) (31%)**.** ^{1}H-NMR ($CDCl_3$, 300 MHz, 300 K) δ, ppm: 7.53-7.50 (m, 1H, **H$_{arom}$**), 7.25-7.12 (m, 3H, **H$_{arom}$**), 5.13 (q, *J* = 6.4 MHz, 1H, C**H**), 2.35 (s, 3H, C**H$_3$**), 1.74 (br, 1H, O**H**), 1.46 (d, *J* = 6.4 MHz, 3H, C**H$_3$**). ^{13}C{^{1}H}-NMR ($CDCl_3$, 75.4 MHz, 300 K) δ, ppm: 143.8, 134.2, 130.4, 127.2, 126.4, 124.5, 66.8, 23.9, 18.9.



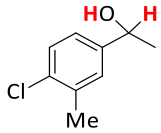
1-(4-chlorophenyl)ethanol (10s) (91%)**.** ^{1}H-NMR ($CDCl_3$, 400 MHz, 300 K) δ, ppm: 7.34.7.29 (m, 4H, **H$_{arom}$**), 4.88 (q, *J* = 6.4 MHz, 1H, C**H**), 2.18 (br, 1H, O**H**), 1.48 (d, *J* = 6.4 MHz, 3H, C**H$_3$**). ^{13}C{^{1}H}-NMR ($CDCl_3$, 100.6 MHz, 300 K) δ, ppm: 144.3, 133.0, 128.6, 126.8, 69.7, 25.2.



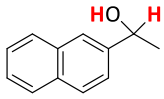
1-(4-fluorophenyl)ethan-1-ol (10t) (94%)**.** ^{1}H-NMR ($CDCl_3$, 400 MHz, 300 K) δ, ppm: 7.35-7.31 (m, 2H, **H$_{arom}$**), 7.05-7.00 (m, 2H, **H$_{arom}$**), 4.86 (q, 1H, C**H**, *J* = 6.4 MHz), 2.44 (br, 1H, O**H**), 1.46 (d, 3H, C**H$_3$**, *J* = 6.4 MHz). ^{19}F{^{1}H}-NMR ($CDCl_3$, 376 MHz, 300 K) δ, ppm: -115.5 (s, 1F, *4*-**F**). ^{13}C{^{1}H}-NMR ($CDCl_3$, 100.6 MHz, 300 K) δ, ppm: 162.1 (d, $J_{C,F}$ = 245.9 MHz), 141.5 (d, $J_{C,F}$ = 3.1 MHz), 127.03 (d, $J_{C,F}$ = 8.1 MHz), 115.18 (d, $J_{C,F}$ = 21.4 MHz), 69.7, 25.2.



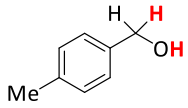
1-(2,4-difluorophenyl)ethan-1-ol (10u) (96%)**.** ^{1}H-NMR ($CDCl_3$, 400 MHz, 300 K) δ, ppm: 7.49-7.43 (m, 1H, **H$_{arom}$**), 6.91-6.86 (m, 1H, **H$_{arom}$**), 6.80-6.75 (m, 1H, **H$_{arom}$**), 5.16 (q, 1H, C**H**, *J* = 6.4 MHz), 2.33 (br, 1H, O**H**), 1.49 (d, 3H, C**H$_3$**, *J* = 6.4 MHz). ^{19}F{^{1}H}-NMR ($CDCl_3$, 376 MHz, 300 K) δ, ppm: -112.2 (d, 1F, *4*-**F**, $J_{F,F}$ = 7.1 MHz), -116.2 (d, 1F, *2*-**F**, $J_{F,F}$ = 7.1 MHz). ^{13}C{^{1}H}-NMR ($CDCl_3$, 100.6 MHz, 300 K) δ, ppm: 162.1 (dd, $J_{C,F}$ = 248.6 MHz, $J_{C,F}$' = 12.2 MHz), 159.5 (dd, $J_{C,F}$ = 248.6 MHz, $J_{C,F}$' = 12.2 MHz), 128.6 (dd, $J_{C,F}$ = 13.7 MHz, $J_{C,F}$' = 3.7 MHz), 127.5 (dd, $J_{C,F}$ = 9.6 MHz, $J_{C,F}$' = 6.2 MHz), 111.2 (dd, $J_{C,F}$ = 21.0 MHz, $J_{C,F}$' = 3.7 MHz), 103.6 (t, $J_{C,F}$ = 25.7 MHz), 63.9 (d, $J_{C,F}$ = 2.6 MHz), 24.1.



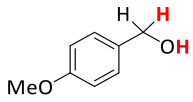
1-(3-chloro-4-methylphenyl)ethanol (10v) (94%)**.** ^{1}H-NMR ($CDCl_3$, 500 MHz, 300 K) δ, ppm: 7.32-7.13 (m, 3H, **H$_{arom}$**), 4.86 (q, 1H, C**H**, *J* = 6.4 MHz), 2.40 (s, 3H, C**H$_3$**), 1.95 (br, 1H, O**H**), 1.49 (d, 3H, C**H$_3$**, *J* = 6.4 MHz). ^{13}C{^{1}H}-NMR ($CDCl_3$, 125.8 MHz, 300 K) δ, ppm: 144.3, 136.1, 133.2, 129.1, 128.0, 124.1, 69.8, 25.2, 20.1.



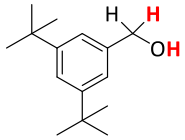
1-(2-napthyl)ethanol (10w) (90%)**.** ^{1}H-NMR ($CDCl_3$, 300 MHz, 300 K) δ, ppm: 7.86-7.82 (m, 4H, **H$_{arom}$**), 7.53-7.44 (m, 4H, **H$_{arom}$**), 5.08 (q, 1H, C**H**, *J* = 6.0 MHz), 1.58 (d, 3H, C**H$_3$**, *J* = 6.0 MHz). ^{13}C{^{1}H}-NMR ($CDCl_3$, 75.4 MHz, 300 K) δ, ppm: 134.5, 138.8, 133.6, 133.2, 128.6, 128.3, 128.0, 126.5, 126.1, 124.1, 124.0, 70.8, 25.5.



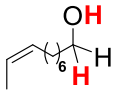
1-(4-methylphenyl)methanol (12a) (90%)**.** ^{1}H-NMR ($CDCl_3$, 300 MHz, 300 K) δ, ppm: 7.28-7.16 (m, 2H, **H$_{arom}$**), 4.65 (s, 2H, C**H$_2$**), 2.35 (s, 3H, C**H$_3$**), 1.62 (br, 1H, O**H**). ^{13}C{^{1}H}-NMR ($CDCl_3$, 75.4 MHz, 300 K) δ, ppm: 138.2, 137.6, 129.5, 127.4, 65.4, 21.4.



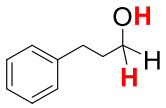
1-(4-methoxyphenyl)methanol (12b) (91%)**.** ^{1}H-NMR ($CDCl_3$, 300 MHz, 300 K) δ, ppm: 7.30 (m, 2H, **H$_{arom}$**), 6.90 (m, 2H, **H$_{arom}$**), 4.62 (d, 2H, C**H$_2$**, *J* = 4.9 MHz), 3.81 (s, 3H, OC**H$_3$**), 1.59 (br, 1H, O**H**). ^{13}C{^{1}H}-NMR ($CDCl_3$, 75.4 MHz, 300 K) δ, ppm: 159.2, 133.2, 128.7, 113.9, 65.0, 55.4.



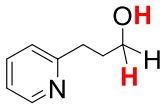
(3,5-di-*tert*-butylphenyl)methanol (12c) (91%)**.** ^{1}H-NMR ($CDCl_3$, 400 MHz, 300 K) δ, ppm: 7.41 (s, 1H, **H$_{arom}$**), 7.25 (s, 2H, **H$_{arom}$**), 4.71 (s, 2H, C**H$_2$**), 1.76 (br, 1H, O**H**), 1.37 (s, 9H, (C**H$_3$**)$_3$). ^{13}C{^{1}H}-NMR ($CDCl_3$, 100.6 MHz, 300 K) δ, ppm: 151.1, 140.0, 121.8, 121.4, 66.2, 31.5.



(*Z*)-pent-3-en-1-ol (12d) (82%). ^{1}H-NMR ($CDCl_3$, 500 MHz, 300 K) δ, ppm: 5.41-5.27 (m, 2H), 3.64 (q, *J* = 6.3 Hz, 2H), 2.08-1.98 (m, 4H), 1.61-1.53 (m, 2H), 1.41-1.28 (m, 6H), 1.25-1.20 (m, 1H), 0.95 (t, *J* = 7.5 Hz, 3H). ^{13}C{^{1}H}-NMR ($CDCl_3$, 125.8 MHz, 300 K) δ, ppm: 131.8, 129.3, 63.2, 32.9, 29.9, 29.2, 27.1, 25.8, 20.7, 14.5. MS (GC): 156.0 [M].



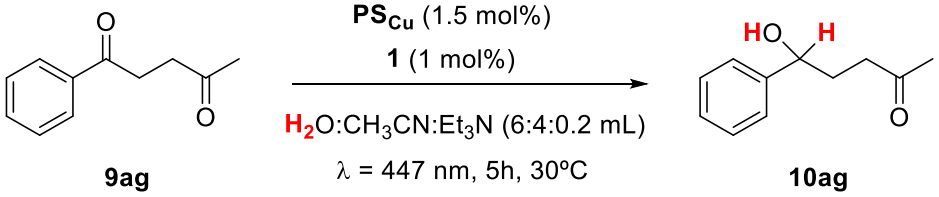
3-phenylpropan-1-ol 12e (67%). ^{1}H-NMR ($CDCl_3$, 400 MHz, 300 K) δ, ppm: 7.32-7.26 (m, 2H), 7.23-7.16 (m, 3H), 3,69 (t, *J* = 6.3 Hz, 3H), 2.72 (t, *J* = 7.7 Hz, 2H), 1.96-1.86 (m, 2H), 1.32-1.24 (m, 1H). ^{13}C{^{1}H}-NMR ($CDCl_3$, 100.6 MHz, 300 K) δ, ppm: 142.0, 128.6, 128.5, 126.0, 62.5, 34.4, 32.2. MS (GC): 136.0 [M].



3-(pyridin-2-yl)propan-1-ol 12f (61%). ^{1}H-NMR ($CDCl_3$, 400 MHz, 300 K) δ, ppm: 8.49-8.47 (m, 1H), 7.64-7.59 (m, 1H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.14-7.11 (m, 1H), 3.71 (td, *J* = 6 Hz, *J* = 1.6 Hz, 2H), 2.96 (td, *J* = 6.8 Hz, *J* = 1.6 Hz, 2H), 1.98 (m, 2H).^{13}C{^{1}H}-NMR ($CDCl_3$, 100.6 MHz, 300 K) δ, ppm: 161.45, 148.63, 136.81, 123.18, 121.16, 62.13, 35.21, 31.71. MS (GC): 137.1 [M].

13.2. Characterization of 10ag, 10ah and 10ai

A) Reduction of 1-Phenyl-1,4-pentanedione (**9ag**)



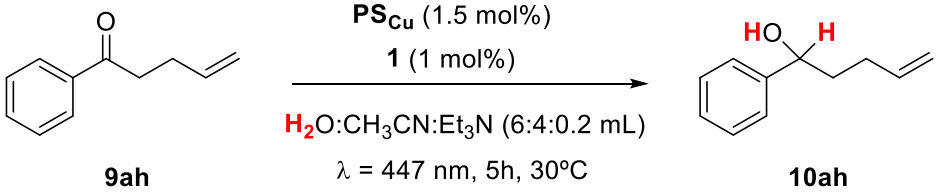
9ag → **10ag**

91% isolated yield

The only product formed

^{1}H-NMR ($CDCl_3$, 400 MHz, 300 K) δ, ppm: 7.39-7.28 (m, 5H, **H$_{arom}$**), 4.71 (t, *J* = 6.5 Hz, 1H, C**H**-CH_2-CH_2), 2.74 (br, 1H, O**H**), 2.55 (t, *J* = 6.5 Hz, 2H, CH-CH_2-C**H$_2$**), 2.14 (s, 1H, C**H$_3$**), 2.00 (m, 2H, CH-C**H$_2$**-CH_2). ^{13}C{^{1}H}-NMR ($CDCl_3$, 100.6 MHz, 300 K) δ, ppm: 209.5, 144.3, 128.4, 127.5, 125.7, 73.4, 39.8, 32.6, 29.9.

B) Reduction of 1-Phenyl-4-penten-1-one (**9ah**)



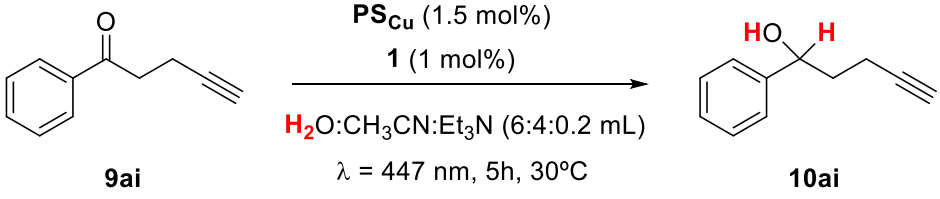
9ah → **10ah**

95% isolated yield

The only product formed

^{1}H-NMR ($CDCl_3$, 400 MHz, 300 K) δ, ppm: 7.39-7.30 (m, 5H, **H$_{arom}$**), 5.87 (ddt, 1H, CH_2-CH_2-C**H**=CH_2, *J* = 17.0 Hz, *J* = 10.0 Hz and *J* = 6.5 Hz), 5.09-5.05 (m, 1H, CH=C**H^e**H^f), 5.03-5.00 (m, 1H, CH=CH^e**H^f**), 4.73-4.69 (m, 1H, C**H**-CH_2-CH_2), 2.19-2.11 (m, 2H, CH-CH_2-C**H$_2$**), 1.94-1.81 (m, 2H, CH-C**H$_2$**-CH_2). ^{13}C{^{1}H}-NMR ($CDCl_3$, 100.6 MHz, 300 K) δ, ppm: 144.6, 138.2, 128.5, 127.6, 125.9, 114.9, 74.0, 38.1, 30.1.

C) Reduction of 1-Phenyl-4-pentyn-1-one (9**ai**)



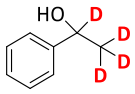
9ai → **10ai**

95% isolated yield

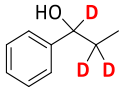
The only product formed

^{1}H-NMR ($CDCl_3$, 400 MHz, 300 K) δ, ppm: 7.39-7.28 (m, 5H, **H$_{arom}$**), 4.86 (dd, 1H, C**H**-CH_2-CH_2, *J* = 8.2 Hz, *J*' = 5.5 Hz), 2.41-2.22 (m, 2H, CH-CH_2-C**H$_2$**), 2.06-1.88 (m, 3H, CH-C**H$_2$**-CH_2≡-**H**).^{13}C{^{1}H}-NMR ($CDCl_3$, 400 MHz, 300 K) δ, ppm: 144.0, 128.5, 127.7, 125.8, 83.9, 73.1, 68.9, 37.3, 15.1.

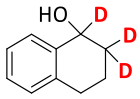
13.3. Characterization of the deuterated alcohols



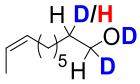
1-phenylethan-1,2,2,2-*d*$_4$-1-ol ([D]-10a). ^{1}H-NMR ($CDCl_3$, 300 MHz, 300 K) δ, ppm: 7.26-7.38 (m, 5H, **H$_{arom}$**), 2.12 (s, 1H, O**H**). $^{13}C\{^1H\}$-NMR ($CDCl_3$, 75.4 MHz, 300 K) δ, ppm: 145.9 (C_3), 128.6 (C_5), 127.5 (C_4), 125.5 (C_6), 69.9 (t, *J* = 21.2 Hz, C_2), 24.3 (m, C_1).



1-phenylpropan-1,2,2,-*d*$_3$-1-ol ([D]-10b). ^{1}H-NMR ($CDCl_3$, 500 MHz, 300 K) δ, ppm: 7.38-7.30 (m, 5H, **H$_{arom}$**), 1.99 (s, 1H, O**H**), 0.93 (s, 3H, C**H$_3$**). $^{13}C\{^1H\}$-NMR ($CDCl_3$, 125.8 MHz, 300 K) δ, ppm: 144.5 (C_4), 128.4 (C_6), 127.5 (C_7), 125.9 (C_5), 75.5 (t, *J* = 22.7 Hz, C_2), 31.1 (m, C_2), 9.9 (C_1).



1, 2,3,4-tetrahydronaphthalen-1,2,2,-*d*$_3$-1-ol ([D]-10j). ^{1}H-NMR ($CDCl_3$, 500 MHz, 300 K) δ, ppm: 7.45 (m, 1H, **H$_{arom}$**), 7.23 (m, 2H, **H$_{arom}$**), 7.13 (m, 1H, **H$_{arom}$**), 2.88-2.75 (m, 2H, **H$_c$**), 2.02-1.76 (m, 2H, **H$_b$**). $^{13}C\{^1H\}$-NMR ($CDCl_3$, 125.8 MHz, 300 K) δ, ppm: 138.7 (C_{10}), 137.2 (C_5), 129.0, 128.7, 127.56, 126.1, 67.6 (m, C_1), 31.6 (m, C_2), 29.2 (C_4), 18.6 (C_3).



(*Z*)-hex-4-en-1,2-*d*$_2$-1-ol-*d* ([D]-12d). ^{1}H-NMR ($CDCl_3$, 400 MHz, 300 K) δ, ppm: 5.41-5.27 (m, 2H), 3.64 (q, *J* = 6.3 Hz, 1H), 2.08-1.98 (m, 4H), 1.61-1.53 (m, mixture of 2H and 1H with ratio 1:0.8), 1.40-1.25 (m, 7H), 0.95 (t, *J* = 7.5 Hz, 3H). $^{13}C\{^1H\}$-NMR ($CDCl_3$, 125.8 MHz, 300 K) δ, ppm: 131.81, 129.38, 63.03-62.54 (m, **C**HD), 32.81, 32.41 (t, *J* = 19.1 Hz, **C**HD), 29.85, 29.19, 27.15, 25.76, 20.66, 14.52. MS (GC): 156.0 [M].

14. Competition experiments between acetophenone and aliphatic aldehydes

14.1. Selectivity studies using our dual catalytic system: Blank ^{1}H-NMR sutdy of the selectivity for acetophenone (9a) versus aliphatic aldehydes

Following the suggestion of a reviewer we have measured the ^{1}H-NMR spectrum of substrate **11d** with and without the presence of Et_3N (40 μl) under catalytic conditions to discard the possible formation of a hemiacetal, which could be responsible for the observed selectivity. Both spectra, before and after the addition of Et_3N (40 μl), are the same appart from the integration increase of the signals at 2.7 and 1.2 ppm, corresponding to the methyls and methylenes of Et_3N. The peak at 9.95 ppm corroborates the presence of the aldehyde under catalytic conditions, which rules out this possibility.

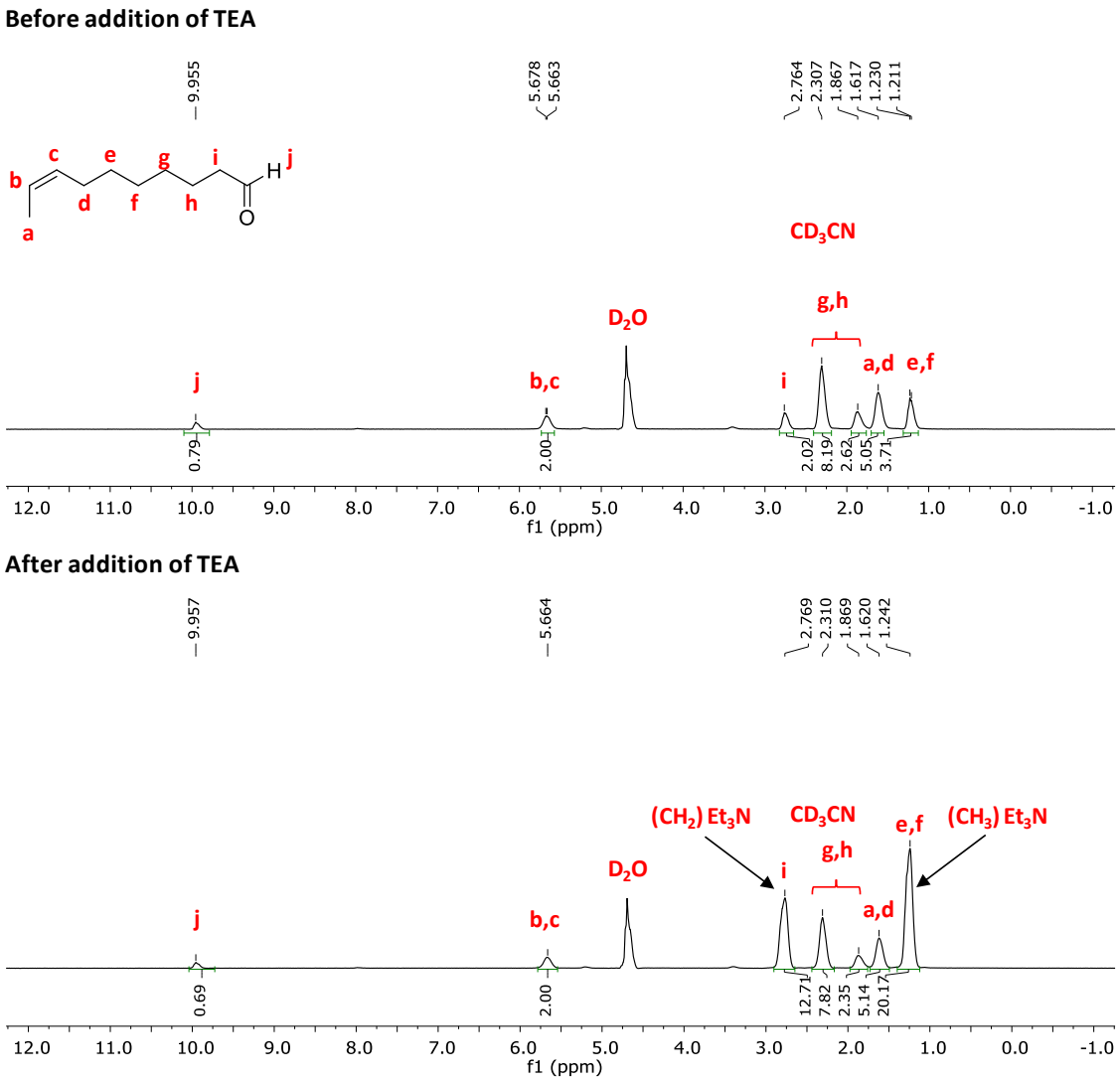
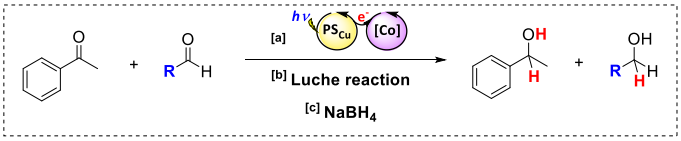
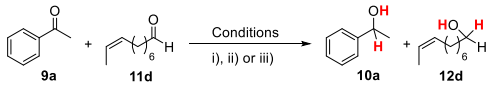


Figure SI.1.15. ^{1}H-NMR (D_2O:CD_3CN (1.2:0.8), 400 MHz, 300 K) spectrum of substrate **11d** before and after the addition of TEA (40 μl, 2 % volume). Conditions analogous to the photocatalytic competition experiments of scheme 3: **11d** (8.7 mM) in 2 ml solvent mixture of D_2O:CD_3CN (1.2:0.8) before the addition of Et_3N (40 μl), top, and after the addition of Et_3N (40 μl), bottom.

14.2. Comparison between different methodologies in the selectivity studies

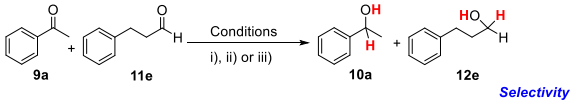


Ar-ketone-aliphatic aldehyde selectivity



				Selectivity
i)	[a],[d]Light-driven	100 % (100 %)	0 % (n.d.)	100 %
ii)	[b]Luche reaction	100 % (91 %)	58 % (49 %)	1.8:1
	1 eq $NaBH_4$	100 % (95 %)	39 % (30 %)	3.2:1
	0.5 eq $NaBH_4$	100 % (87 %)	39 % (8 %)	10.9:1
(acidic work-up)	0.5 eq $NaBH_4$	99 % (45 %)	45 % (0 %)	100 %
	0.25 eq $NaBH_4$	99 % (61 %)	52 % (0 %)	100 %
(acidic work-up)	0.25 eq $NaBH_4$	100 % (23 %)	50 % (0 %)	100 %
iii)	[c]$NaBH_4$	56 % (51 %)	100 % (94 %)	0.6:1

Ar-ketone-aliphatic aldehyde selectivity



				Selectivity
i)	[a],[e]Light-driven	100 % (94 %)	6 % (6 %)	16:1
ii)	[b]Luche reaction	96 % (86 %)	64 % (13 %)	6.6:1
	1 eq $NaBH_4$	100 % (95 %)	70 % (1 %)	95:1
	0.5 eq $NaBH_4$	99 % (78 %)	69 % (0 %)	100%
(acidic work-up)	0.5 eq $NaBH_4$	98 % (47 %)	71 % (0 %)	100%
	0.25 eq $NaBH_4$	96 % (43 %)	70 % (0 %)	100%
(acidic work-up)	0.25 eq $NaBH_4$	98 % (27 %)	74 % (0 %)	100%
iii)	[c]$NaBH_4$	93 % (93 %)	89 % (51 %)	1.8:1

Scheme SI.1.6. Competition experiments between aromatic ketones and aliphatic aldehydes. [a] Light-driven conditions: **1** (1 mol%), **PS_{Cu}** (1.5 mol%), Substrate A + B (16.5 mM), A:B (1:1), in H_2O:CH_3CN:Et_3N (6:4:0.2 mL)irradiated (447 nm) for 5 h at 30 ºC under N_2. [b]Luche reaction conditions: **$CeCl_3$·7 H_2O** (1 eq molar), **$NaBH_4$** (1.5, 1, 0.5 and 0.25 eq molar, subsequently), Substrate A + B (16.5 mM), A:B (1:1), in EtOH:H_2O (4:6 mL) for 15 min at 0 ºC under air. In two cases (shown in brackets) an acidic work.up was used in addition to the reported procedure to dissociate the possible formed B-(OR)x when using low equivalents of **$NaBH_4$**. [c]**$NaBH_4$** (1 eq molar), Substrate A + B (16.5 mM), A:B (1:1), in MeOH (10 mL) for 15 min at rt under air. The same conditions but with **$NaBH_4$** (0.5 eq molar) are also showed in the table [d]Analysis after 35 minutes of irradiation. [e]Analysis after 30 minutes of irradiation. Percentages show the conversions of the substrate from which the product derives, percentages in brakets show the yield of the reduced product.

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