

# **Photochemical H<sub>2</sub> production with noble-metal-free molecular devices comprising a porphyrin photosensitizer and a cobaloxime catalyst**

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## Experimental Section.

**Reagents and instruments:** All reactions were carried out under N<sub>2</sub> atmosphere with standard Schlenk techniques. Solvents were dried and distilled prior to use according to the standard methods. *p*-Tert-butylbenzaldehyde, zinc acetate and magnesium acetate were purchased from Aldrich and used as received. Triethylamine (TEA) and pyrrole were freshly distilled before use. [Co(dmgh)(dmgh<sub>2</sub>)Cl<sub>2</sub>],<sup>[1]</sup> [Co(dmgh)<sub>2</sub>(Py)Cl] (dmgh = dimethylglyoxime),<sup>[2]</sup> 5-(4-pyridyl)-10,15,20-tri(*p*-tert-butylphenyl)porphyrin (H<sub>2</sub>PyTPP)<sup>[3]</sup>, Zinc 5-(4-pyridyl)-10,15,20-tri(*p*-tert-butylphenyl)porphyrin [Zn(PyTPP)],<sup>[3]</sup> and Magnesium 5-(4-pyridyl)-10,15,20-tri(*p*-tert-butylphenyl)porphyrin [Mg(PyTPP)],<sup>[4]</sup> were synthesized according to the literature procedures with little modification.

<sup>1</sup>H NMR spectra were collected on a Varian INOVA 400NMR spectrometer. Mass spectra were performed by electrospray ionization (ESI) on an HP 1100 MSD instrument.

### Synthesis of {{Co(dmgh)<sub>2</sub>Cl}{Zn(PyTPP)}} (1)

*Method A:*<sup>[2]</sup> Compound Zn(PyTPP) (170 mg, 0.2 mmol) was added to a solution of CoCl<sub>2</sub>·6H<sub>2</sub>O (47.5 mg, 0.2 mmol), dimethylglyoxime (52.5 mg, 0.45 mmol) and NaOH (8 mg, 0.2 mmol) in 10 mL 95% ethanol and the mixture was stirred at 70 °C for 1 h. After cooling to room temperature, a stream of air was blown through the solution for 2 h. The resulting purple precipitate was then filtered and washed successively with water, ethanol and diethyl ether. The product was dried under vacuum and obtained in a yield of 15% (36 mg).

**Method B:**<sup>[5]</sup> An equiv of TEA was added to a suspension of [Co(dmgh)(dmgh<sub>2</sub>)Cl<sub>2</sub>] (40 mg, 0.11 mmol) in methanol (10 mL). The complex was completely dissolved in methanol after stirring for 5 min. The mixture turned from a green suspension to a clear brown solution. Compound Zn(PyTPP) (85 mg, 0.1 mmol) was added to the solution and the mixture was stirred at room temperature for 4 h. The precipitate was collected by filtration, followed by washing with water, ethanol, and diethyl ether. The red-purple product was dried under vacuum and obtained in a yield of 28% (33 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 18.63 (br, 2H, OHO), 9.02 (d, 2H,  $\beta$ -H), 8.99–8.96 (m, 4H,  $\beta$ -H), 8.64–8.62 (m, 4H,  $\beta$ -H and Py-H), 8.14–8.09 (m, 8H, Py-H and phen-H), 7.76 (d, 6H, phen-H), 2.60 (s, 12H, CH<sub>3</sub>), 1.63 (s, 27H, C(CH<sub>3</sub>)<sub>3</sub>). UV-vis (THF):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 427 (368,760 M<sup>-1</sup>cm<sup>-1</sup>), 558 (17,406 M<sup>-1</sup>cm<sup>-1</sup>), 602 nm (8,560 M<sup>-1</sup>cm<sup>-1</sup>). MS (API-ES):  $m/z$  = 1170.2, calcd. for [M + H]<sup>+</sup>: 1170.4. Anal. calcd. For: C<sub>63</sub>H<sub>65</sub>N<sub>9</sub>O<sub>4</sub>ClCoZn: C, 64.56; H, 5.59; N, 10.76; Found: C, 64.91; H, 5.71; N, 10.92.

**Synthesis of [{Co(dmgh)<sub>2</sub>Cl}]{Mg(PyTPP)} (2):** The red-purple product was prepared using *method B* in 25% (28 mg) yield. The <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectra is the same as **1**. UV-vis (THF):  $\lambda_{\text{max}}$  ( $\epsilon$ ) = 431 (362,496 M<sup>-1</sup>cm<sup>-1</sup>), 571 (14,174 M<sup>-1</sup>cm<sup>-1</sup>), 618 nm (11,115 M<sup>-1</sup>cm<sup>-1</sup>). MS (API-ES):  $m/z$  = 1130.2, calcd. for [M + H]<sup>+</sup>: 1130.4. Anal. calcd. for C<sub>63</sub>H<sub>65</sub>N<sub>9</sub>O<sub>4</sub>ClCoMg: C, 66.91; H, 5.79; N, 11.15; Found: C, 67.14; H, 5.88; N, 11.03.

**Synthesis of [{Co(dmgh)<sub>2</sub>Cl}]{H<sub>2</sub>PyTPP} (3):** An equiv of TEA was added to a suspension of [Co(dmgh)(dmgh<sub>2</sub>)Cl<sub>2</sub>] (58 mg, 0.15 mmol) in methanol (15 mL). The

complex was completely dissolved in methanol after stirring for 5 min. The mixture turned from a green suspension to a clear brown solution. A solution of compound H<sub>2</sub>TPP (78 mg, 0.1 mmol) in 10 mL CHCl<sub>3</sub> was added to the solution and the mixture was stirred at room temperature overnight. After removal of solvent, the residue washed with water, ethanol, and diethyl ether. The red purple product was obtained after removal the solvent in 26% (29 mg) yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 18.58 (br, 2H, OHO), 8.93(d, 2H, β-H), 8.89(s, 4H, β-H), 8.76 (d, 2H, β-H), 8.58 (d, 2H, Py-H), 8.17–8.13 (m, 8H, Py-H and phen-H), 7.76 (d, 6H, phen-H), 2.61 (s, 12H, CH<sub>3</sub>), 1.61 (s, 27H, C(CH<sub>3</sub>)<sub>3</sub>), -2.79 (s, 2H, NH). UV-vis (THF): λ<sub>max</sub> (ε) = 421 (362,260 M<sup>-1</sup>cm<sup>-1</sup>), 517 (23,228 M<sup>-1</sup>cm<sup>-1</sup>), 553 (15,073 M<sup>-1</sup>cm<sup>-1</sup>), 594 (7,438 M<sup>-1</sup>cm<sup>-1</sup>), 650 nm (6,775 M<sup>-1</sup>cm<sup>-1</sup>). MS (API-ES): *m/z* = 1107.4, calcd. for [M + H]<sup>+</sup>: 1107.4. Anal. calcd. for C<sub>63</sub>H<sub>67</sub>ClCoN<sub>9</sub>O<sub>4</sub>: C, 68.25; H, 6.09; N, 11.37; Found: C, 68.49; H, 6.18; N, 11.23.

**Steady-state absorption and fluorescence emission:** UV-vis absorption measurements were carried out on a Jasco-V-530 spectrophotometer. Photoluminescence spectra were recorded using a Spex Fluorolog fluorimeter by exciting the sample at 420 nm.

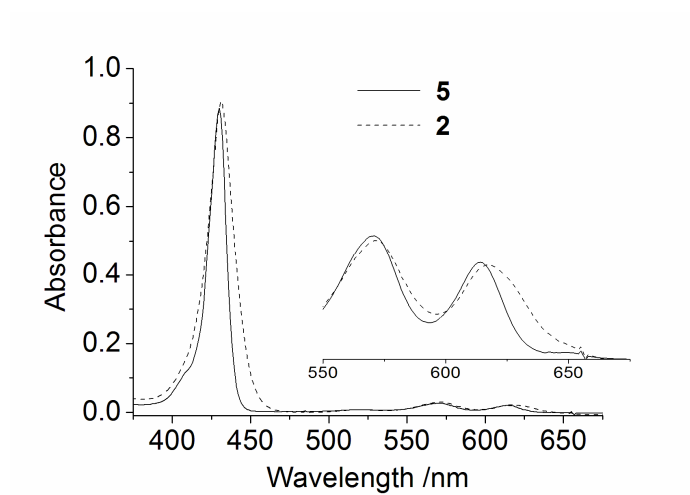
**Photoinduced H<sub>2</sub> production:** In a typical photochemical hydrogen evolution experiment, the photocatalyst (0.5 mL, 1 × 10<sup>-3</sup> M in THF) and THF (3.5 mL) were added to a Schlenk tube. To this solution was added 1 mL of water and 35 μL of TEA. The mixture was magnetically stirred under N<sub>2</sub> atmosphere for 10 min. The solution was freeze-pump-thaw degassed for three times and then warmed to room

temperature prior to irradiation. The gas phase volume is ca. 65 cm<sup>3</sup>. The reaction solution was irradiated at 25 °C using an Xe lamp (300 W) with a cutoff filter ( $\lambda > 400$  nm). The gas phase of the reaction system was analyzed on a GC 7890T instrument with a 5 Å molecular sieve column, a thermal conductivity detector, and with N<sub>2</sub> as carrier gas. The amount of hydrogen generated was determined by the external standard method and the hydrogen dissolved in the solution was neglected.

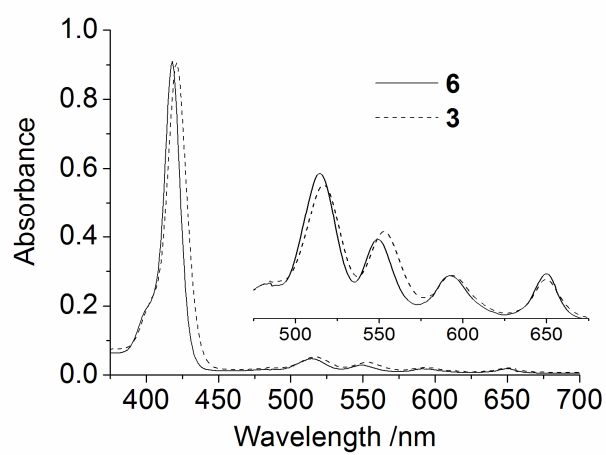
## References

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- [4] E. G. Azenha, A. C. Serra, M. Pineiro, M. M. Pereira, J. S. de Melo, L. G. Arnaut, S. J. Fonrmosinho, A.M.d'A. R. Gonsalves, *Chem. Phys.* **2002**, *280*, 177–190.
- [5] P. Du, J. Schneider, G. Luo, W. W. Brennessel, R. Eisenberg, *Inorg. Chem.* **2009**, *48*, 4952–4962.

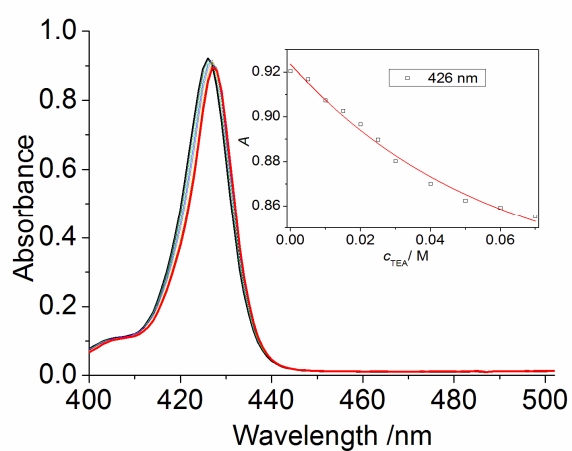
## Figures



**Fig. S1** A comparison of UV-vis spectra of **2** and **5** in THF at  $2.5 \times 10^{-6}$  M.

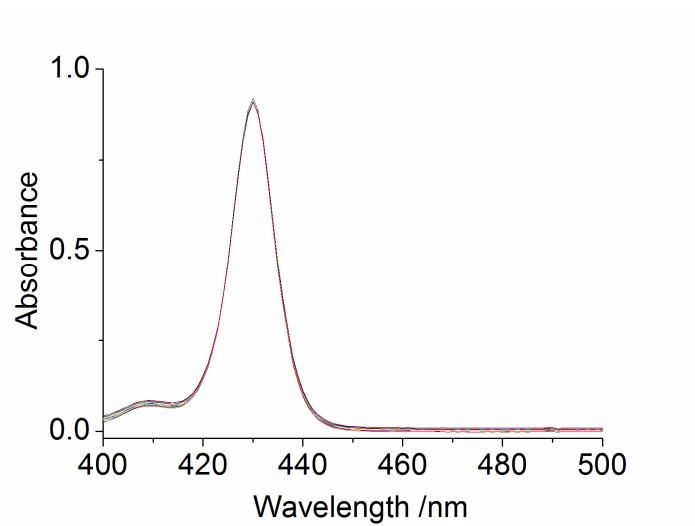


**Fig. S2** A comparison of UV-vis spectra of **3** and **6** in THF at  $2.5 \times 10^{-6}$  M.

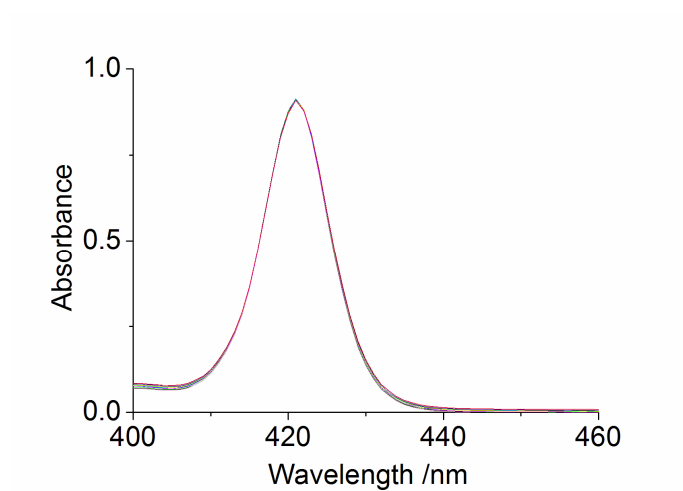


**Fig. S3** UV-Vis spectral changes observed upon addition of TEA (0–0.07 M) to the THF/H<sub>2</sub>O (8:2) solution of **1** ( $2.5 \times 10^{-6}$  M). Plots for the changes of absorptions at  $\lambda = 426$  nm.

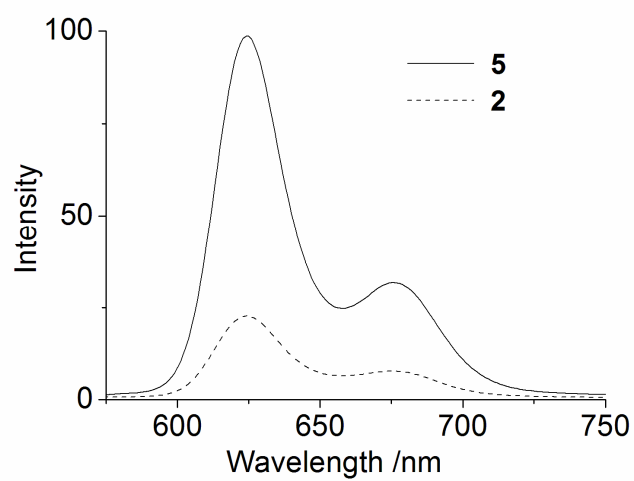




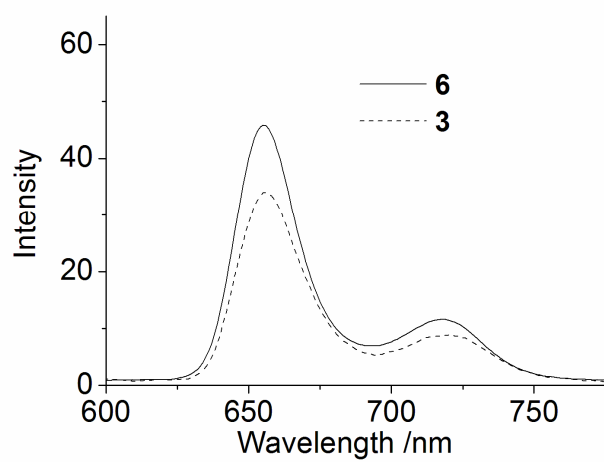
**Fig. S4** UV-Vis spectra observed upon addition of TEA (0–0.1 M) to the THF/H<sub>2</sub>O (8:2) solution of **2** ( $2.5 \times 10^{-6}$  M).



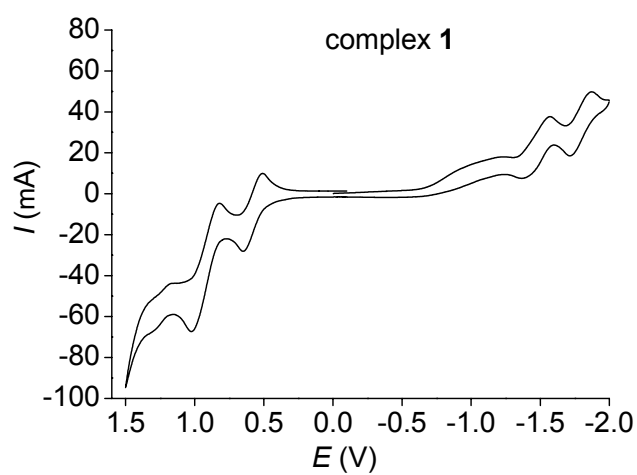
**Fig. S5** UV-Vis spectra observed upon addition of TEA (0–0.1 M) to the THF/H<sub>2</sub>O (8:2) solution of **3** ( $2.5 \times 10^{-6}$  M).



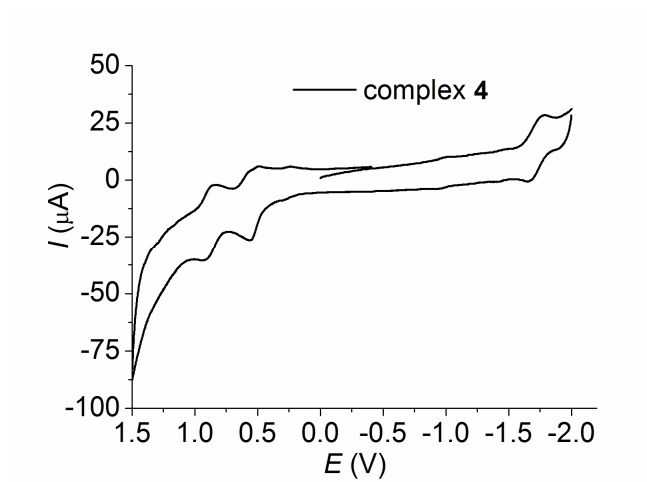
**Fig. S6** Fluorescence emission spectra of **2** and **5** ( $2.5 \times 10^{-6}$  M) in THF/H<sub>2</sub>O (8:2).



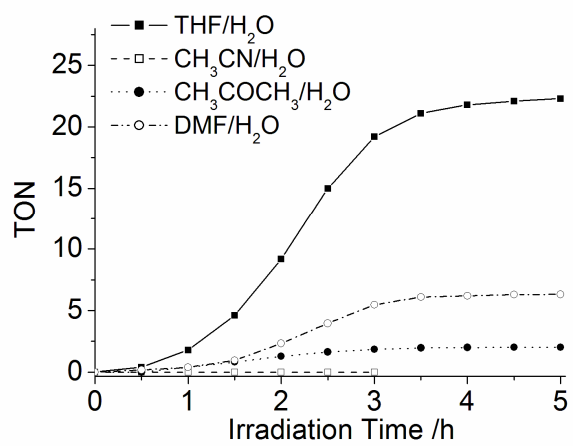
**Fig. S7** Fluorescence emission spectra of **3** and **6** ( $2.5 \times 10^{-6}$  M) in THF/H<sub>2</sub>O (8:2).



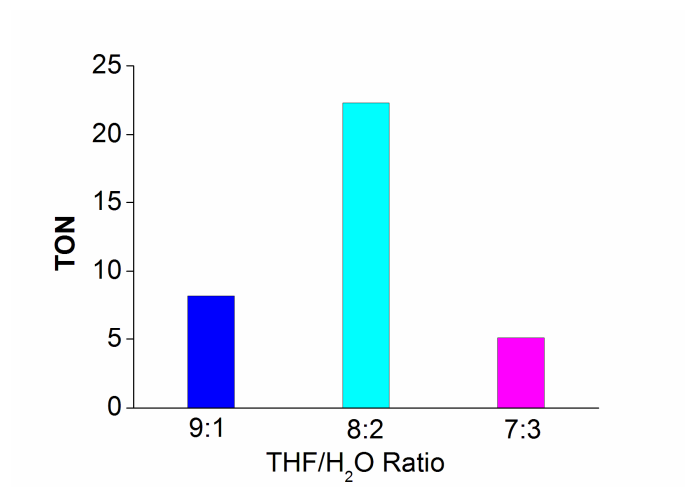
**Fig. S8** Cyclic voltammogram of complex **1** (1.0 mM) in THF with 0.05 M *n*-BuNPF<sub>6</sub> at a scan rate of 100 mV/s.



**Fig. S9** Cyclic voltammogram of complex **4** (1.0 mM) in THF with 0.05 M *n*-BuNPF<sub>6</sub> at a scan rate of 100 mV/s.

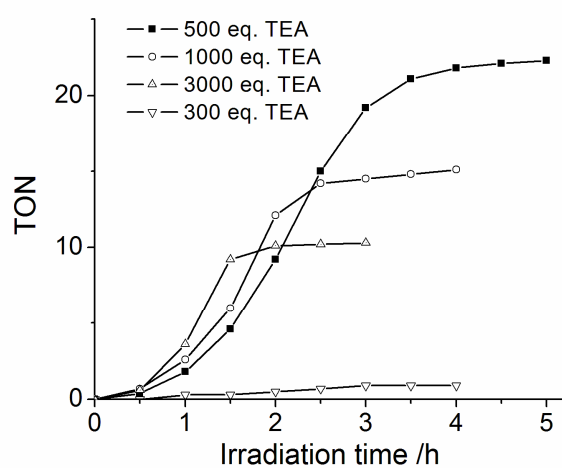


**Fig. S10** Influence of the solvent on H<sub>2</sub> evolution using **1** (0.1 mM) as photocatalyst in solvent/H<sub>2</sub>O (8:2) in 5 h irradiation.

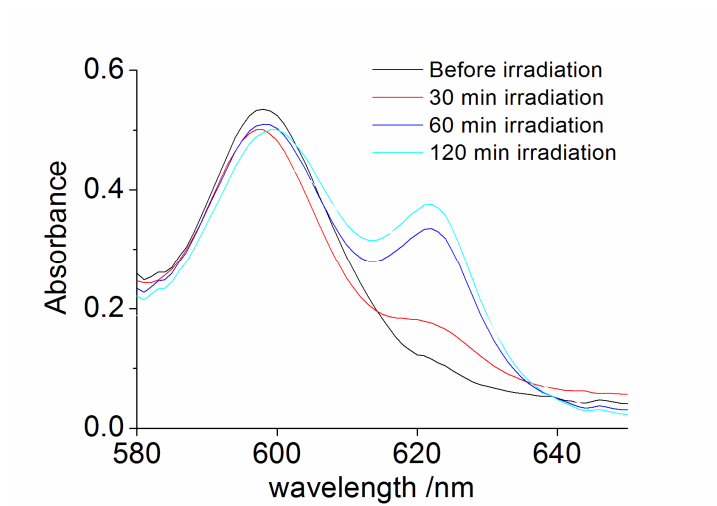


**Fig. S11** Influence of the THF/H<sub>2</sub>O ratio on H<sub>2</sub> evolution using **1** (0.1 mM) as photocatalyst in 5 h irradiation.





**Fig. S12** Influence of the loading amount of TEA on H<sub>2</sub> evolution using **1** (0.1 mM) as photocatalyst in THF/H<sub>2</sub>O (8:2) in 5 h irradiation.



**Fig. S13** The selected region of time-dependent UV-vis spectra of **1** (0.1 mM) and TEA (0.05 M) in THF/H<sub>2</sub>O (8:2).

**Table S1** Photoinduced H<sub>2</sub> generation catalyzed by **1–3** under optimal conditions

Entry <sup>a</sup>	Photocatalyst	TON
1	<b>1</b>	22
2	<b>2</b>	3 <sup>b</sup>
3	<b>3</b>	< 1 <sup>b</sup>
4	<b>4</b>	–
5	<b>4</b> + 0.4 mM [Co(dmgh) <sub>2</sub> PyCl]	–
6	<b>1</b> + 0.1 mM pyridine	–

<sup>a</sup> [TEA] = 0.05 M, [photocatalyst] = 0.2 mM, in THF/H<sub>2</sub>O (8/2, v/v), irradiation light  $\lambda > 400$  nm, irradiation time 5 h. <sup>b</sup> Irradiation time 3 h.