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Supporting information for

Photocatalytic benzylic C–H bond oxidation with a Flavin scandium complex

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General considerations

Materials

Most starting materials were purchased from commercial suppliers and freshly distilled or used as received. RFT was synthesized by esterification of commercial available riboflavin.¹

Representative procedure: Oxidation of Ethylbenzene

Ethylbenzene (0.02 mmol) was added to RFT (10 mol%), Sc(OTf)₃ (20 mol% unless indicated otherwise) and hydrochloric acid (37%, 0.8 μ L) in 1 mL acetonitrile. The reaction vial was placed in a cooling block to maintain a constant temperature and the vials were irradiated with blue LEDs (440 nm, 6 W LED unless indicated otherwise) while stirring with a magnetic stirring bar. After 2.5 h of irradiation, *n*-pentadecane or cyclooctanone (internal standard), saturated Na₂CO₃ and brine were added. The organic phase was extracted with ethylacetate and subjected to GC-FID analysis. The retention time was verified with authentic samples.

The formation of H₂O₂ was monitored by a standard method.² A diluted acetonitrile solution was treated with an excess amount of NaI. The concentration of I₃⁻ formed was determined by UV-Vis spectroscopy (λ_{max} = 362 nm, ϵ = 13000 M⁻¹cm⁻¹).

ESR spectroscopy

RFT (3 mM), ethylbenzene (10 mM), Sc(OTf)₃ (10 mM) and HCI (10 mM) were dissolved in degassed MeCN (1 mL). An aliquot was placed in a closed glas tube, irradiated and introduced into the ESR apparatus (Magnettech miniscope MS400). Simulations of the ESR spectra were performed with the Easyspin software 4.5.5 implemented in MATLAB R2012a.³ Labelling scheme for the simulated hfc couplings:

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 $R = CH_2CH(OAc)CH(OAc)CH(OAc)CH_2(OAc)$

| Entry | Lewis acid | Conv. [%] ^[b] | Yield [%] ^[b] |
|-------|----------------------|--------------------------|--------------------------|
| 1 | Sc(OTf) ₃ | 81 | 38 |
| 2 | Mg(OTf) ₂ | 19 | 1 |
| 3 | La(OTf) ₃ | 25 | 2 |
| 4 | Zn(OTf) ₂ | 30 | 3 |
| 5 | AICI ₃ | 31 | 6 |

Table S1. Photocatalytic oxidation of ethylbenzene – influence of the Lewis acid.

[a] All reactions were performed with ethylbenzene (0.02 mmol), RFT (10 mol%), and Lewis acid (4.6 mM) in 1 mL MeCN and irradiated for 2.5 h with blue light (440 nm). [b] Conversion of 1 and yield of 2 determined by GC-FID.

| Entry ^[a] | MeCN/Solvent | Conv. [%] ^[b] | Yield [%] ^[b] |
|----------------------|------------------------|--------------------------|--------------------------|
| 1 | MeCN | 89 | 45 |
| 2 | MeCN/H ₂ O | 96 | 15 |
| 3 | MeCN/EtOH | 25 | 3 |
| 4 | MeCN/EtOAc | 61 | 24 |
| 5 | MeCN/Acetone | 70 | 27 |
| 6 | MeCN/CHCI ₃ | 86 | 41 |
| 7 | MeCN/isoprop. | 23 | 1 |
| 8 | MeCN/DMSO | 18 | 0 |
| 9 | MeCN/DMF | 20 | 0 |

Table S2. Photocatalytic oxidation of ethylbenzene – influence of the solvent.

[a] All Reactions were performed with ethylbenzene (0.02 mmol), RFT (10 mol%) and Sc(OTf)₃ (4.6 mM) in 1 mL MeCN/solvent=1:1 (v/v %) The samples were exposed to atmospheric oxygen and placed in a cooling block during irradiation (2.5 h) with blue light (440 nm). [b] Conversion and yield determined by GC-FID integration.



Figure S1. Hydrogen peroxide formation (•) in the photocatalytic oxidation of ethylbenzene (0.02 mmol) in the presence of RFT (10 mol%) and Sc(OTf)₃ (38 mol%) in MeCN at room temperature.



Figure S2. Photocatalyic aerobic oxidation of ethylbenzene (0.02 mmol) in presence of RFT (10 mol%) and various concentrations of $Sc(OTf)_3$ in 1 mL MeCN under irradiation (2.5 h) with blue light at 440 nm.

| Entry ^[a] | Additive | Conv. [%] ^[b] | Yield [%] ^[b] |
|----------------------|----------------------------|--------------------------|--------------------------|
| 1 | none | 89 | 45 |
| 2 | thiourea (30 mol%) | 70 | 31 |
| 3 | NaAc(aq) (30 mol%) | 27 | 1 |
| 4 | NaOH(aq) (30 mol%) | 25 | 2 |
| 5 | HCI (37%, 0.8 µL, 32 mol%) | 100 | 59 |
| 6 | HAc (30 mol%) | 82 | 39 |
| 7 | benzoic acid (30 mol%) | 87 | 41 |
| 8 | H ₂ O | 40 | 10 |

Table S3. Photocatalytic oxidation of ethylbenzene – Influence of various additives.

[a] All reactions were performed with ethylbenzene (0.02 mmol), additive, RFT (10 mol%) and Sc(OTf)₃ (4.6 mM) in 1 mL MeCN. For all entries except 3, 4 and 8 the solvent was neat MeCN. The solvent mixture was MeCN/water = 7/1 (v/v%) for entries 3 and 8, and MeCN/water = 22/1 for entry 4. The samples were exposed to atmospheric oxygen and placed in a cooling block irradiation (2.5 h) with blue light (440 nm). [b] Conversion and yield were determined by GC-FID integration.



Figure S3. Photocatalytic oxidation of ethylbenzene (0.02 mmol) with RFT (10 mol%) and Sc(OTf)₃ (38 mol%) in the absence of HCI (•) and in presence of 30 mol% HCI (•) during irradiation with blue light (440 nm, 3 W, 1 h).

| Entry | Conditions ^[a] Conv. [| | Yield [%] ^[b] |
|-------------------------|---|-----|--------------------------|
| 1 | standard cond. | 100 | 52 |
| 2 | no Sc ³⁺ | 33 | 8 |
| 3 | no RFT | 21 | 0 |
| 4 | no irradiation | 19 | 0 |
| 5 | no (atmospheric) O ₂ | 35 | traces |
| 6 ^[c] | O ₂ (100%) | 100 | 50 |
| 7 | CD₃CN | 100 | 44 |
| 8 ^[c] | CD ₃ CN, O ₂ (100%) | 100 | 44 |

Table S4. Photocatalytic oxidation of ethylbenzene – control experiments.

[a] All reactions were performed with ethylbenzene (0.02 mmol), RFT (10 mol%), HCl (37%, 0.8 μ L) and Sc(OTf)₃ (4.6 mM) in 1 mL MeCN. The samples were exposed to atmospheric oxygen and placed in a cooling block during irradiation (1 h) with blue light (440 nm). [b] Conversion and yield determined by GC-FID integration. [c] O₂: oxygen saturated solution.



Figure S4. Electronic absorption spectra of ethylbenzene (58 mM) and RFT (0.14 mM) in the presence of $Sc(OTf)_3$ (0.68mM) while irradiating with blue light under atmospheric oxygen (left) and in a solution purged with pure dioxygen (right) in MeCN at 298 K. The spectra were measured over 2 h (120 s between each spectrum displayed).



Figure S5. Electronic absorption spectra of ethylbenzene (5.8 mM) and RFT (0.07 mM) in the presence of $Sc(OTf)_3$ (0.34 mM) during irradiation with blue light under aerobic conditions in absence of HCI (black) and in presence of HCI (2.7 mM, red) in MeCN at room temperature.

Integral of the absorption spectrum (red) calculated numerically by OriginPro 8:

$$\int_{306}^{500} red \ curve \ dx = 111.67$$

Integral of the absorption spectrum (black) calculated numerically by OriginPro 8:

$$\int_{306}^{500} black \ curve \ dx = 111.72$$

Table S5. The v(C=O) frequencies of the C²- and C⁴-carbonyl groups of RFT in the absence of Sc³⁺, in the presence of Sc³⁺ and in the presence of Sc³⁺ and HCl in MeCN.

| additive | v(C²=O) | ∨(C4=O) | |
|---------------------------------------|---------|----------------|--|
| none ^[a] | 1689 | 1718 | |
| Sc ^{3+ [b]} | 1606 | 1677 | |
| Sc ³⁺ / HCl ^[c] | 1606 | 1660–1680 (br) | |

[a] In the absence of metal ions. [b] $c(Sc^{3+}) = 30 \text{ mM}$. [c] $c(Sc^{3+}) = 30 \text{ mM}$, c(HCI) = 10 mM, in this case the $v(C^4=O)$ frequency overlaps with the N-H out-of-plane frequency



Figure S6. ESR-spectrum generated in the photocatalytic reaction of RFT (3.0 mM) with ethylbenzene (10 mM), Sc(OTf)₃ (10 mM) and 10 mM HCl in deaerated MeCN at 298 K.



Figure S7. Electronic absorption spectra of ethylbenzene (58 mM) and RFT (0.14 mM) in the presence of Sc(OTf)₃ (0.68 mM) before irradiation (red), after 3 min of irradiation with blue light in deaterated MeCN (blue), after 3 min of irradiation with blue light in deaterated MeCN and purging the solution with dioxygen (black), after 3 min of irradiation with blue light in deaterated MeCN and purging the solution with dioxygen and 2 h exposing to atmospheric oxygen (green).



Figure S8. Electronic absorption spectra of ethylbenzene (58 mM) and RFT (0.14 mM) in the presence of $Sc(OTf)_3$ (0.68mM) while irradiating with blue light under atmospheric oxygen in MeCN at 298 K. The spectra were measured over 1 h (120 s between each spectrum displayed).

References

- 1. S. Alagaratnam, N. J. Meeuwenoord, J. A. Navarro, M. Hervás, M. A. De la Rosa, M. Hoffmann, O. Einsle, M. Ubbink and G. W. Canters, *FEBS J.*, 2011, **278**, 1506–1521.
- 2. R. D. Mair and A. J. Graupner, Anal Chem, 36, 194.
- 3. S. Stoll and A. Schweiger, J. Magn. Reson., 2006, 178, 42–55.