Supplementary Information

Fast and mild palladium(II)-catalyzed 1,4-oxidation of 1,3-dienes via activation of molecular oxygen with a designed cobalt(II) porphyrin

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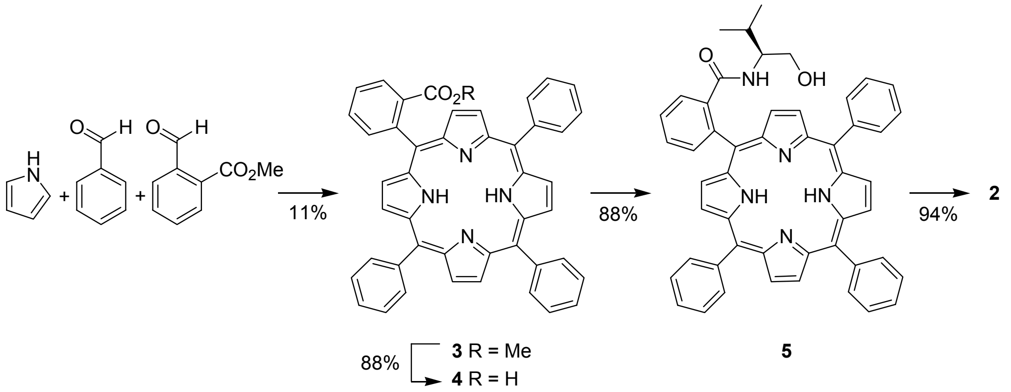
Synthesis of Co(II) porphyrin 2. Co(II) porphyrin **2** was synthesized from *L*-valinol and 5-(2-carboxyphenyl)-10,15,20-triphenyl porphyrin **4**,[1] as outlined in Scheme 1. For practical reasons, the corresponding 2-(10,15,20-triphenyl-porphyrin-5-yl)benzoic acid methyl ester (**3**)[2] was prepared by the method of Lindsey,[3] using a 4:3:1 mixture of pyrrole, benzaldehyde and methyl 2-formylbenzoate. 5-(2-carboxyphenyl)-10,15,20-triphenyl porphyrin (**4**) was prepared by hydrolysis of 3 using a slightly different procedure as reported previously. Treatment of **4** with thionyl chloride followed by condensation with *L*-valinol afforded amide **5**, which after insertion of cobalt gave Co(porphyrin)-amide **2** (83% from **4**).



Scheme 1 Synthesis of Co(II) porphyrin **2**.

General. ^{1}H (400 or 300 MHz) and ^{13}C (100 or 75 MHz) NMR spectra were recorded on a Varian Mercury spectrometer. Chemical shifts (δ) are reported in ppm, using residual solvent

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[1] (a) Peng, X.-B.; Huang, J. W.; Li, T.; Ji, L.-N. *Inorg. Chim. Acta* **2000**, *305*, 111. (b) Peng, X.-B.; Huang, J. W.; Ji, L.-N. *Chem. J. Chin. Univ. 1* **1999**, 19.

[2] Cho, H. S.; Jeong, D. H.; Yoon, M.-C.; Kim, Y. H.; Kim, Y.-R.; Kim, D.; Jeong, S. C.; Kim, S. K.; Aratani, N.; Shinmori, H.; Osuka, A. *J. Phys. Chem. A* **2001**, *105*, 4200.

[3] Lee, C. H.; Lindsey, J. S. *Tetrahedron* **1994**, *50*, 11427.

proton resonance or tetramethylsilane as internal standard. UV-vis spectra were were recorded on a Varian Cary 50 spectrometer. MALDI-TOF spectra were recorded on a Bruker Biflex III instrument. Merck silica gel 60 (240-400 mesh) was used for flash chromatography and analytical thin-layer chromatography was performed on Merck precoated silica gel 60-F_{254} plates. Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl prior to use. Dichloromethane (CH_2Cl_2) was distilled from calcium hydride. Solvents for extraction and chromatography (pentane and diethyl ether) were technical grade and distilled.

5-(2-carboxyphenyl)-10,15,20-triphenyl porphyrin (4). Methyl ester **3** (347 mg, 0.52 mmol) was dissolved in 300 mL THF, 60 mL of a 15N KOH solution was added and the mixture was refluxed overnight. The reaction mixture was cooled and the THF was evaporated *in vacuo*. 60 mL CH_2Cl_2 was added to redissolve the porphyrin and the organic layer was washed with water (× 2), dried over Na_2SO_4 and evaporated to dryness. Column chromatography (gradient $CH_2Cl_2 \rightarrow CH_2Cl_2$/MeOH 95:5) gave 299 mg (88%) of carboxy porphyrin **3** as a purple solid.

2-(10,15,20-triphenyl-porphyrin-5-yl)benzoyl-*L*-valinol (5). Acid **4** (299 mg, 0.46 mmol) was dissolved in 15 mL $SOCl_2$ and the solution was heated at reflux temperature for 2.5h. The solvent was evaporated *in vacuo* and coevaporated with toluene (× 3). The material was dissolved in 5 mL CH_2Cl_2, Et_3N (127 µL, 0.91 mmol) was added and the solution was cooled to 0 ° C. *L*-valinol (70.4 mg, 0.68 mmol), dissolved in 1 mL CH_2Cl_2, was added and the solution was stirred for 3h, during which it was allowed to reach rt. CH_2Cl_2 was added and the organic phase was washed with water, saturated aqueous $NaHCO_3$, and water. After drying over Na_2SO_4, the solvent was evaporated *in vacuo*. Column chromatography (gradient $CH_2Cl_2 \rightarrow CH_2Cl_2$/MeOH 95:5) gave 299 mg (88%) of amide **4** as a purple solid. ^{1}H NMR: δ 8.96-8.82 (m, 7H), 8.76-8.74 (d, J = 4.8 Hz, 1H), 8.34-8.29 (dd, J = 8.1, 1.5 Hz, 1H), 8.27-8.17 (m, 6H), 7.95-7.88 (dt, J = 7.8, 1.2 Hz, 1H), 7.84-7.72 (m, 11H), 4.92-4.87 (br d, J = 9.3 Hz, 1H), 2.84-2.75 (m, 1H), 1.35-1.28 (m, 2H), 0.25-0.15 (m, 1H), -0.42 (d, J = 6.9 Hz, 3H), -0.49 (d, J = 6.9 Hz, 3H), -1.70 (br s, 1H), -2.80 (s, 2H). ^{13}C NMR: δ 168.8, 142.1, 142.0, 141.9, 140.2, 139.0, 135.3, 135.0, 134.8-134.1, 129.1, 128.7, 128.0, 126.9-126.4, 121.2, 121.1, 120.9, 116.8, 61.5, 58.7, 56.3, 27.5, 18.6, 18.4, 17.5 (contains some traces of Et_3N). UV-VIS (CH_2Cl_2): λ = 419, 515, 551, 591, 657 nm. MALDI-TOF MS: Calc. for $C_{50}H_{41}N_5O_2$: 743.3259; Found 743.4592 $[M]^+$.

2-(10,15,20-triphenyl-cobalt(II)porphyrin-5-yl)benzoyl-*L*-valinol (Co(II) porphyrin 2). A solution of $Co(OAc)_2{\cdot}4H_2O$ (264 mg, 1.06 mmol), dissolved in 12.5 mL MeOH, was added to a solution of amide **5** (263 mg, 0.35 mmol) in 50 mL CH_2Cl_2, and the reaction was heated at reflux temperature for 4h. After cooling to rt, the solution was washed with water (× 4), dried (Na_2SO_4) and the solvent was evaporated. 267 mg (94%) of **2** was obtained as a purple-red solid. UV-VIS (CH_2Cl_2): λ = 412, 530 nm. MALDI-TOF MS: Calc. for $C_{50}H_{39}N_5O_2Co$: 800.2436; Found 800.3088 $[M]^+$.

General procedure for the aerobic 1,4-oxidation of 1,3-dienes. 1,3-Cyclohexadiene (95 µL, 1.0 mmol) was added to a solution of $Pd(OAc)_2$ (5.61 mg, 0.025 mmol) and Co(II) porphyrin **2** (22 mg, 0.0275 mmol) in 2 mL HOAc. The reaction was stirred under an oxygen atmosphere at room temperature for 16 h. The solution was diluted with saturated aqueous NaCl (5 mL) and extracted with pentane/Et_2O 1:1 (3 × 15 mL). The combined organic phases were washed with ice-cold 1M NaOH (3 × 10 mL) and the combined aqueous phases were back-extracted with pentane/Et_2O 1:1 (3 × 10 mL). The combined organic phases were washed with saturated aqueous NaCl (2 × 5 mL), dried ($MgSO_4$) and evaporated.

Table 1. Aerobic 1,4-oxidation of 1,3-cyclohexadiene: variation of solvents[a]

entry	ligand	oxidant	solvent	yield (%)[b]	trans/cis[c]
1	**2**	O_2	CH_2Cl_2 / AcOH = (5/1)	32	83:17
2	**2**	O_2	Acetone / AcOH = (5/1)	17	76:24
3	**2**	O_2	CH_3CN / AcOH = (5/1)	18	18:82
4	**2**	O_2	DMSO / AcOH = (5/1)	19	2:98
5	**2**	O_2	DMF / AcOH = (5/1)	21	68:32
6	**2**	O_2	THF / AcOH = (5/1)	21	81:19
7	**2**	O_2	EtOAc / AcOH = (5/1)	26	81:19
8	**2**	O_2	AcOH	44	47:53
9[d]	**2**	O_2	AcOH	19	22:78
10[e]	-	O_2	DMSO / AcOH = (1/1)	20	5:95

[a] Reactions were performed on a 0.5 mmol scale. Reaction conditions: the diene was added to a solution of $Pd(OAc)_2$ (2.5 mol%), **2** (2.75 mol%) and LiOAc (30 mol%) in 1 mL solvent. The reaction was stirred at rt under an oxygen atmosphere for 16 h. [b] Isolated yields of 1,4-diacetoxy-2-cyclohexene. [c] Determined by ^1H NMR. [d] With 10 mol% LiCl. [e] Performed on a 1.0 mmol scale. Reaction conditions: the diene was added to a solution of $Pd(OAc)_2$ (2.5 mol%) and LiOAc (30 mol%) in 2 mL solvent. The reaction was stirred at rt under an oxygen atmosphere for 16 h.

UV-vis spectroscopy titration experiments. In a typical experiment the UV-vis cuvette was filled with 2.5 ml of $1.0*10^{-6}$ M Co(II) porphyrin **2** in acetic acid. In addition, a $2.5*10^{-3}$ M lithium acetate and a $1.0*10^{-6}$ M Co(II) porphyrin **2** solution in acetic acid was added stepwise. Measurements were performed at room temperature under air. In the UV-vis spectrum the typical decrease of the Q-bands of the porphyrin at 530 nm was followed (figure 1). We have analyzed the titration curves with a fitting program developed by Hunter.[4]

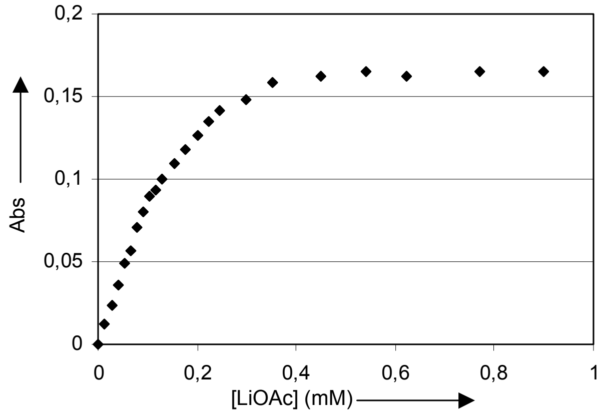

Figure 1. Plot of absorption at 530nm (Abs) versus the concentration of LiOAc (mM) taken from the spectroscopy titration experiments in acetic acid, $K_1 = 2.2 \times 10^3$ M^{-1} and $K_2 = 1.0 \times 10^4$ M^{-1}.

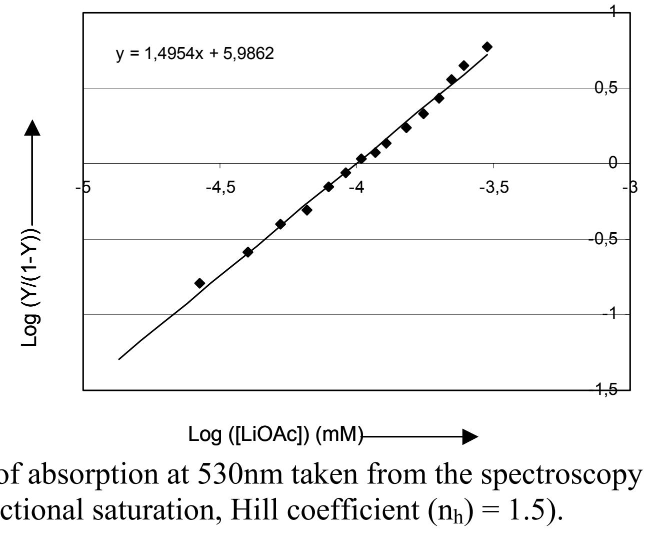

Figure 2. Hill-plot of absorption at 530nm taken from the spectroscopy titration experiments in acetic acid (Y = Fractional saturation, Hill coefficient (n_h) = 1.5).

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[4] Bisson, A. P.; Hunter, C. A.; Carlos, J.; Young, K. *Chem. Eur. J.* **1998**, *4*, 845.