Supplementary Information for

Poly(ethylene glycol)-Supported Tetrahydroxyphenyl Porphyrin : a Convenient, Recyclable Catalyst for Photooxidation Reactions.

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General. All PEG samples (Aldrich) ($MW > 2000$ daltons) were melted at 80°C in vacuum for 30 min before use to remove traces of moisture. After reaction, product purification involved evaporation of the reaction solvent in vacuum and addition of the residue dissolved in a few ml of CH_2Cl_2 to a stirred solution of Et_2O (50 mL/g of polymer) cooled at 0°C . After 20-30 min stirring at 0°C , the obtained suspension was filtered through a sintered glass filter and the solid repeatedly washed on the filter with Et_2O (up 100 mL of Et_2O /g of polymer, overall). ^1H NMR spectra were recorded at 300 MHz on CDCl_3 solutions at 25°C ; δ are in ppm downfield from TMS.

Yield and Purity Determination of PEG-Supported Compounds.

The yields of the PEG-supported compounds were determined by weight, assuming a MW of 750 or 2000 daltons for the PEG fragments. The indicated yields are for pure compounds. The purity of these compounds was determined by 300 MHz ^1H NMR analysis in CDCl_3 with pre-saturation of the methylene signals of the polymer at 3.63 ppm. In recording the NMR spectra, a relaxation delay of 6 sec and an acquisition time of 4 sec were used to ensure complete relaxation and accuracy of integration. The relaxation delay was selected after T_1 measurements. The integrations of the signals of the PEG CH_3OCH_2 fragment at 3.30 and 3.36 ppm were used as internal standards. The estimated integration error is $\pm 5\%$.

Synthesis of compound 5.

To a solution of mesylate **3** ¹ (1.50 g, previously dried under vacuum, 4.0 equiv) in dry DMF (8 mL), Cs₂CO₃ (0.3 g, 5.2 equiv) and 5,10,15,20-tetrakis-4-hydroxyphenyl)-porphyrin **1** (0.12 g, 1.0 equiv) were added. The mixture was stirred for 22 h at 110°C and the solvent evaporated under vacuum. Purification by addition of methylene chloride (3 mL) and precipitation by addition of Et₂O (70-80 mL) gave PEG **5** (1.39 g, 87%). ¹H NMR : δ 8.89 (m, 2H: H Porf), 8.13 (A part of AB system, ³J (H,H) = 8.5 Hz, 2H: H meta to O in O-Ar-Porf), 7.29 (B part of AB system, ³J (H,H) = 8.5 Hz, 2H: H ortho to O in O-Ar-Porf), 7.25 (A part of AB system, ³J (H,H) = 8.5 Hz, 2H: H meta to O in O-Ar-CH₂), 6.94 (B part of AB system, ³J (H,H) = 8.5 Hz, 2H: H ortho to O in O-Ar-CH₂), 4.28 (t, ³J (H,H) = 6.5 Hz, 2H: CH₂-O-Ar-Porf), 4.17 (t, ³J (H,H) = 5.1 Hz, 2H: PEGCH₂-CH₂-OAr), 3.87 (t, ³J (H,H) = 5.1 Hz, 2H: PEGCH₂-CH₂-O-Ar), 3.40 (s, 3H: CH₃O), 2.93 (t, ³J (H,H) = 6.5 Hz, 2H: ArCH₂), 2.28 (t, ³J (H,H) = 6.5 Hz, 2H: CH₂-CH₂-CH₂).

UV-VIS (CH₂Cl₂): λ_{max} = 421 nm.

Photooxidation Reactions.

Standard Photooxygenation Reaction. All reactions were carried in a water-cooled jacketed test tube capped with a rubber septum punctured with a syringe needle and a narrow Teflon[®] tubing in which oxygen was flushing (ca 10 mL/min). The well-stirred solutions were irradiated during bubbling with an halogen lamp of reported power placed at 10 cm from the test tube. The disappearance of the reagent was monitored by GC-MS, ¹H NMR or TLC. To the solution of the diene (0.15 mmol) in dichloromethane (14 mL) a solution of TPP or PEG-TPP (1.0 mL of 4.5x10⁻³ M) in dichloromethane was added; the reaction mixture was irradiated with a lamp of reported power (see text) until starting material was not observed. The solvent was evaporated under vacuum and diethyl ether (5-10 mL) was added; the PEG-TPP **5** was filtered and the organic solution evaporated under vacuum.

Analytical Data for:

Purified by flash-chromatography (eluant 1 : 1 dichloromethane/hexanes). Colorless oil, $[\alpha]_D^{22} = +4$ (c 0.4, CHCl_3). $^1\text{H-NMR}$ (CDCl_3 , 200 MHz) δ (ppm): 4.58 (1 H, d, $J = 4.8$ Hz), 3.95 (1 H, d, $J = 11.2$ Hz), 2.38 (2 H, m), 2.24 (2 H, m), 2.12 (2 H, hept, $J = 7.2$ Hz), 1.89-1.76 (4 H, series of m), 1.74-1.54 (2 H, series of m), 1.38 (2 H, m), 1.00 (3 H, d, $J = 7.2$ Hz), 0.98 (6 H, d, $J = 7.2$ Hz), 0.95 (3 H, d, $J = 7.2$ Hz), 0.94 (3 H, d, $J = 7.2$ Hz), 0.84 (3 H, d, $J = 7.2$ Hz). $^{13}\text{C-NMR}$ (CDCl_3 , 50 MHz) δ (ppm): 137.2, 133.8, 84.9, 79.9, 43.1, 35.1, 32.1, 31.8, 29.9, 29.6, 28.0, 26.7, 24.4, 22.9, 22.3, 21.7, 20.9, 20.4, 19.1, 13.5. IR (KBr) ν_{max} : 2966, 2940, 2874, 1459, 1380, 1261, 1169, 1038 cm^{-1} . Anal. calcd. for $\text{C}_{20}\text{H}_{34}\text{O}_2$: C, 78.38; H, 11.18. Found: C, 78.35; H, 11.20.

Large Scale Synthesis of Tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-one. A solution of dicyclopentadiene (13.0 mL, 98 mmol), acetic anhydride (10.0 mL, 100 mmol), pyridine (4.0 mL, 49 mmol), DMAP (240 mg, 2.0 mmol) and PEG-TPP (200 mg, 0.022 mmol) in CH_2Cl_2 (90 mL) was irradiated with a halogen lamp (500 Watt) for 5 h with O_2 bubbling and vigorous stirring. The mixture was diluted in CH_2Cl_2 (100 mL), washed in sequence with saturated aqueous NaHCO_3 (3x50 mL), 1 M HCl (3x50 mL), saturated aqueous CuSO_4 (3x20 mL), brine (100 mL), and dried over Na_2SO_4 . The volatile materials were removed in *vacuum*, Et_2O (100 mL) was added in order to precipitate PEG-TPP that was filtered off (190 mg, 85% recovery). The ethereal solution was concentrated to afford 10.9 g of tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-one (76% yield) as a pale yellow oil, that crystallised on standing.

References for Supplementary Information.

- 1) Annunziata, R.; Benaglia, M.; Cinquini, M.; Cozzi, F. *Chem. Eur. J.* **2000**, *6*, 133-138.