

Electronic Supplementary Information (ESI)

A mechanistic glimpse on the oxidation of alcohols using TEMPO/NO_x catalytic systems: towards a greener bifunctional catalyst

Apparatus

Elemental analysis was performed on a EuroEA elemental analyzer. IR spectra were recorded using KBr disks on a Jasco FTIR 4100 apparatus. TGA and DTA analysis have been performed by heating the samples from room temperature up to 300 °C, with a temperature rate of 5 °C/min. ESR spectra were recorded on a Jeol JES FA100 apparatus (typical settings: frequency 8.99 GHz, field 3330 G, sweep width 100 G, sweep time 60 s, time constant 30 ms, gain 50, modulation frequency 100 kHz, modulation width 1 G, using 1 mm inner diameter plain glass tubes).

Materials and methods

All chemicals and materials were Sigma-Aldrich or VWR products. Silica supported TEMPO (*catalyst A*) was an Aldrich product with a loading of 0.70 mmol/g. *Catalyst B* has been obtained by passing gaseous nitrogen dioxide through a pad of *catalyst A*. Gaseous nitrogen dioxide has been prepared by thermal decomposition of lead (II) nitrate, according to the reaction:



Fig. S1. Left- *catalyst A* (silica supported TEMPO); Right- *catalyst B*

**Typical alcohol oxidation procedure using *catalyst A*, exemplified for benzylic alcohol
(molar ratio alcohol : *catalyst A* : sodium nitrite 1 : 0.1 : 0.1)**

The reaction vessel was loaded with 0.5 mmol benzylic alcohol (54 mg), 0.05 mmol *catalyst A* (71 mg), 0.05 mmol sodium nitrite (3.5 mg), 4.5 mL DCM and 0.5 mL acetic acid, and the mixture was stirred for 24 h under air or oxygen atmosphere (balloon). The reaction mixture was filtered off to separate the catalyst (which was washed three times with 1 mL DCM) and the combined solution was concentrated under vacuum to about 1 mL. Removal of the acetic acid prior to isolation of the benzaldehyde is necessary, and this can be achieved in two ways: *i*) the reaction mixture is loaded on a small pad of silica, and the product is eluted with DCM, or *ii*) the solution is stirred with water, and the organic phase is separated and dried over anhydrous sodium sulfate. After removal of the acetic acid, the product is further purified by column chromatography over silica gel using a mixture of DCM : hexane 1 : 1 (v/v) as eluent, affording the pure benzaldehyde.



Fig. S2. Experimental setup

**Typical alcohol oxidation procedure using *catalyst B*, exemplified for benzylic alcohol
(molar ratio alcohol : *catalyst B* 1 : 0.1)**

The reaction vessel was loaded with 0.5 mmol benzylic alcohol (54 mg), 0.05 mmol *catalyst B* (71 mg), 5 mL DCM, and the mixture was stirred for 24 h under air or oxygen atmosphere (balloon). The reaction mixture was filtered off to separate the catalyst (which was washed three times with 1 mL DCM) and the combined solution was concentrated under vacuum. The residue was purified by column chromatography over silica gel using a mixture of DCM : hexane 1 : 1 (v/v) as eluent, affording the pure benzaldehyde.

Solvent free system, exemplified for benzylic alcohol (this can be used only for liquid alcohols and *catalyst B*, molar ratio alcohol : *catalyst B* 1 : 0.1)

The reaction vessel was loaded with 0.5 mmol benzylic alcohol (54 mg) and 0.05 mmol *catalyst B* (71 mg), and left at room temperature under air or oxygen atmosphere (balloon) for 24 h. Next day to the reaction mixture was added 3 mL DCM, the mixture was stirred for 5 min, filtered off to separate the catalyst (which was washed three times with 1 mL DCM), and the combined solution was concentrated under vacuum. The residue was purified by column chromatography over silica gel using a mixture of DCM : hexane 1 : 1 (v/v) as eluent, affording the pure benzaldehyde.

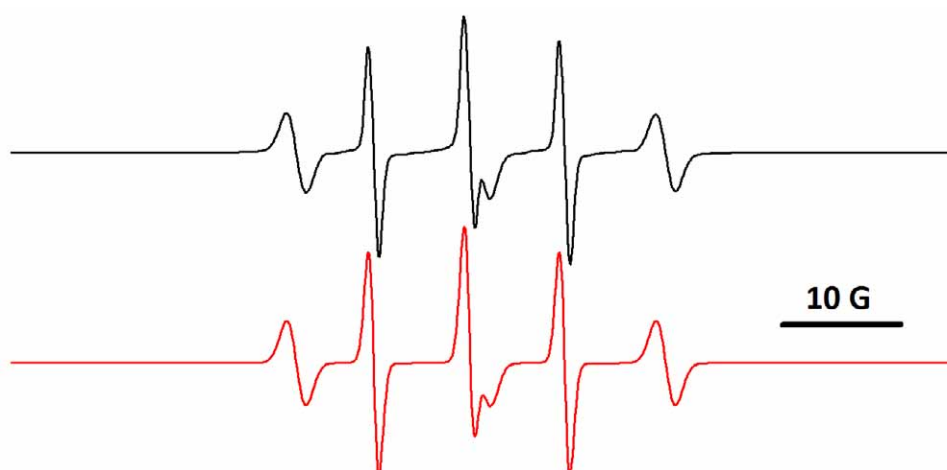


Fig. S3. Simulation of the ESR spectrum obtained in a system involving *catalyst B* and PBN: experimental spectrum in black and simulated one in red ($a_N=8.08$ G)

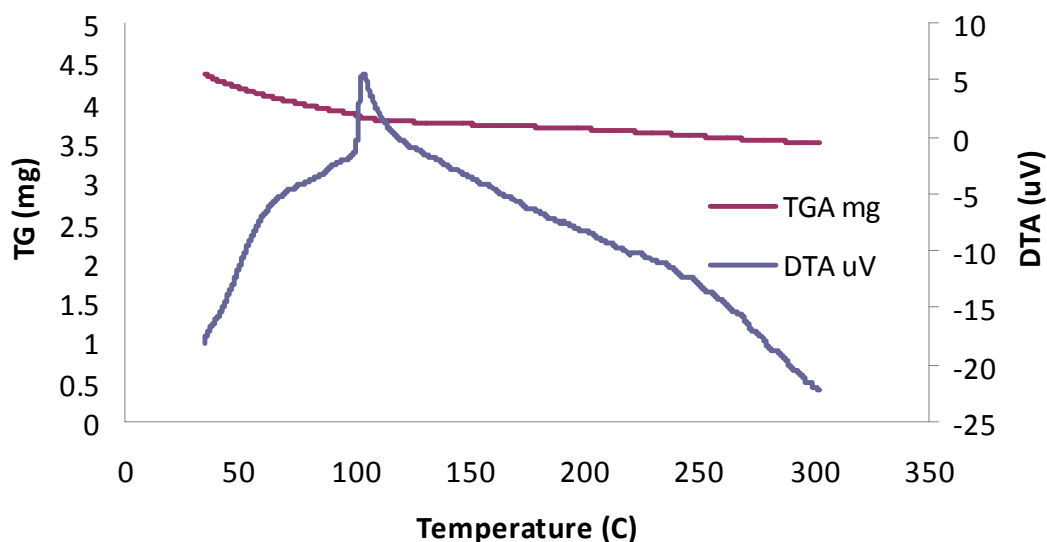


Fig. S4. TGA and DTA analysis of the *catalyst B*