Supplementary Information (S1-S2)

V(IV), Fe(II), Ni(II) and Cu(II) complexes bearing 2,2,2-tris(pyrazol-1-yl)ethyl methanesulfonate: application as catalysts for the cyclooctane oxidation

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Table S1. Effect of the reduction with triphenylphosphine (PPh_3) of the reaction mixture of the oxidation of cyclooctane catalysed by **4**[a]: Total yield[b] (%) and ketone/alcohol molar ratio (in brackets)[c]

Entry	Time (h)	**Before PPh_3**	**After PPh_3**
1	1	3 (84:16)	4 (2:98)
2	4	11 (85: 15)	20 (8:92)
3	24	18 (82:18)	19 (34:66)

[a]Reaction conditions: cyclooctane (0.25 M), complex **4** (10^{-3} M), H_2O_2 (1.0 M) in acetonitrile at 60 °C; total volume of reaction mixture is 10 mL. [b]Amounts of cyclooctanone and cyclooctanol were determined after reduction of the aliquots with PPh_3. [c]Cyclooctanone/cyclooctanol molar ratio.

Table S2. Estimative[a] along the reaction time of the concentration of cyclooctyl hydroperoxide in the oxidation of cyclooctane reaction,[b] (alcohol + hydroperoxide)/ ketone ratio[c] and percentage of cyclooctyl hydroperoxide[d].

Entry	Time (h)	[ROOH] (M)	(A + H)/K	% of ROOH
1	1	1.60×10^{-2}	111.2	92%
2	4	2.83×10^{-2}	48.3	84%
3	24	2.36×10^{-2}	3.4	49%

[a] Calculations using conditions and values described in table S1. [b] [ROOH]=[Alcohol product after reduction with PPh_3]-[Alcohol product before reduction with PPh_3]. [c] ([Alcohol]–[ROOH]/[Ketone]. [d] % of ROOH = [ROOH]/ [Total]