Electronic supplementary information

Mn^{II} and Cu^{II} complexes with arylhydrazones of active methylene compounds as effective heterogeneous catalysts for solvent- and additive-free microwave-assisted peroxidative oxidation of alcohols

Kamran T. Mahmudov,[a,b,*] Manas Sutradhar,[a] Luísa M. D. R. S. Martins,[a,c,*]
M. Fátima C. Guedes da Silva,[a,*] Alice Ribera,[a,d] Ana V. M. Nunes,[e]
Shahnaz I. Gahramanova,[f] Fabio Marchetti,[d] Armando J. L. Pombeiro[a,*]

[a] Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049–001 Lisbon, Portugal
[b] Baku State University, Department of Chemistry, Z. Xalilov Str. 23, Az 1148 Baku, Azerbaijan
[c] Chemical Engineering Department, ISEL, R. Conselheiro Emídio Navarro, 1959-007 Lisboa, Portugal
[d] School of Pharmacy, University of Camerino, via S. Agostino 1, 62032 Camerino, Italy
[e] Requimte/CQFB, Departamento de Química, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Campus de Caparica, Caparica 2829-516, Portugal.
[f] Institute of Catalysis and Inorganic Chemistry named after acad. M.F. Nagiyev, H. Cavid 113, Az 1143 Baku, Azerbaijan

*Corresponding authors:

E-mail addresses:

kamran_chem@yahoo.com, kamran_chem@mail.ru (K.T. Mahmudov),
fatima.guedes@tecnico.ulisboa.pt (M. Fátima C. Guedes da Silva)
lmartins@deq.isel.ipl.pt (Luísa M. D. R. S. Martins)
pombeiro@tecnico.ulisboa.pt (Armando J. L. Pombeiro)

Analytical data for compounds $NaHL^1$ and $Na_2H_2L^2$.

$NaHL^1$:[7b,12a] Yield 90 % (based on malononitrile), yellow-orange crystals are soluble in methanol, ethanol, water. Anal. Calcd for $C_9H_{13}N_4NaO_7S$ (M = 344.28): C, 31.40; H, 3.81; N, 16.27. Found: C, 31.25; H, 3.75; N, 16.13. IR (KBr, selected bands, cm^{-1}): 3436, 3146 and 3100 ν(OH), 3014 ν(NH), 2218 and 2227 ν(C≡N) and 1599 ν(C=N). ^{1}H NMR (300.13 MHz, [D_6]DMSO, 25°C, TMS), δ: 7.13−7.85 (4H, Ar−H), 13.25 (1H, NH). $^{13}C\{^1H\}$ NMR (75.468 MHz, [D_6]DMSO, 25°C, TMS), 87.1 (C=N), 110.0 (CN), 114.1 (C≡N), 115.6, 125.3, 127.3 and 131.3 (Ar−H), 134.2 (Ar−SO_3Na), 136.2 (Ar−NH−N).

$Na_2H_2L^2$:[12b] Yield 74.00 % (based on 5,5-dimethylcyclohexane-1,3-dione), red brown powder, soluble in water, DMSO, methanol and insoluble in chloroform. Anal. Calcd for $C_{14}H_{30}N_2Na_2O_{17}S_2$ (M=608): C, 27.63; H, 4.97; N, 4.60. Found: C, 27.36; H, 4.88; N, 4.65 %. IR, cm^{-1}: 3287, 3203 and 3105 ν(OH), 2965 ν(NH), 1648 and 1622 ν(C=O), 1576 ν(C=N). ^{1}H NMR (DMSO): δ = 0.98 (s, 3H, CH_3), 1.29 (s, 3H, CH_3), 2.55 (s, 2H, CH_2), 2.54 (s, 2H, CH_2), 7.72-7.79 (s, 2H, Ar-H), 11.81 (s, 1H, OH), 14.45 (s, 1H, NH). $^{13}C\{^1H\}$ (DMSO): δ = 28.14 (CH_3), 30.75 (CH_3), 51.87 ($2CH_2$), 114.36 (Ar-H), 114.57 (Ar-H), 125.30 (Ar-SO_3Na), 124.68 (Ar-SO_3Na), 128.43 (Ar-OH), 133.49 (Ar-NH-N), 175.61 (C=N), 206.61 (C=O), 206.94 (C=O).

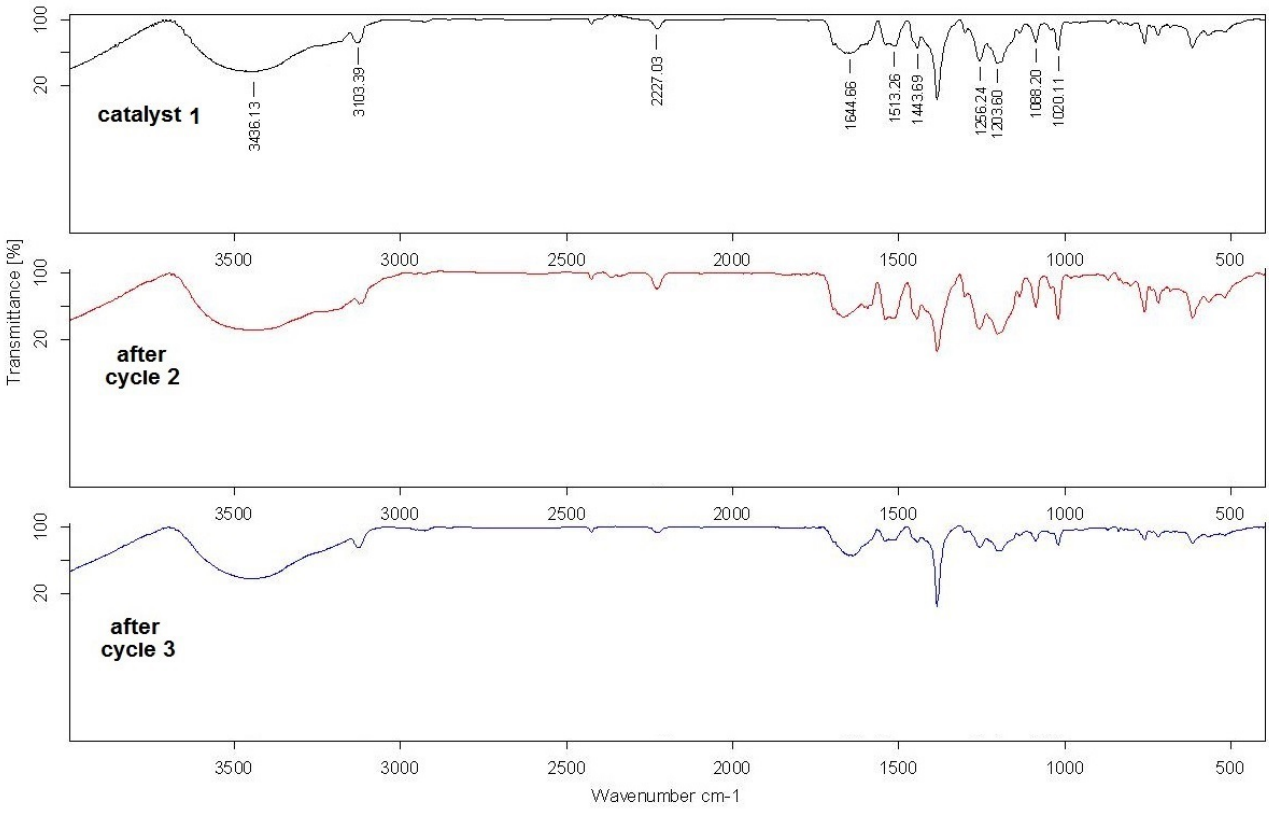

Figure S1. IR spectrum of catalyst **1** before and after catalytic cycles.

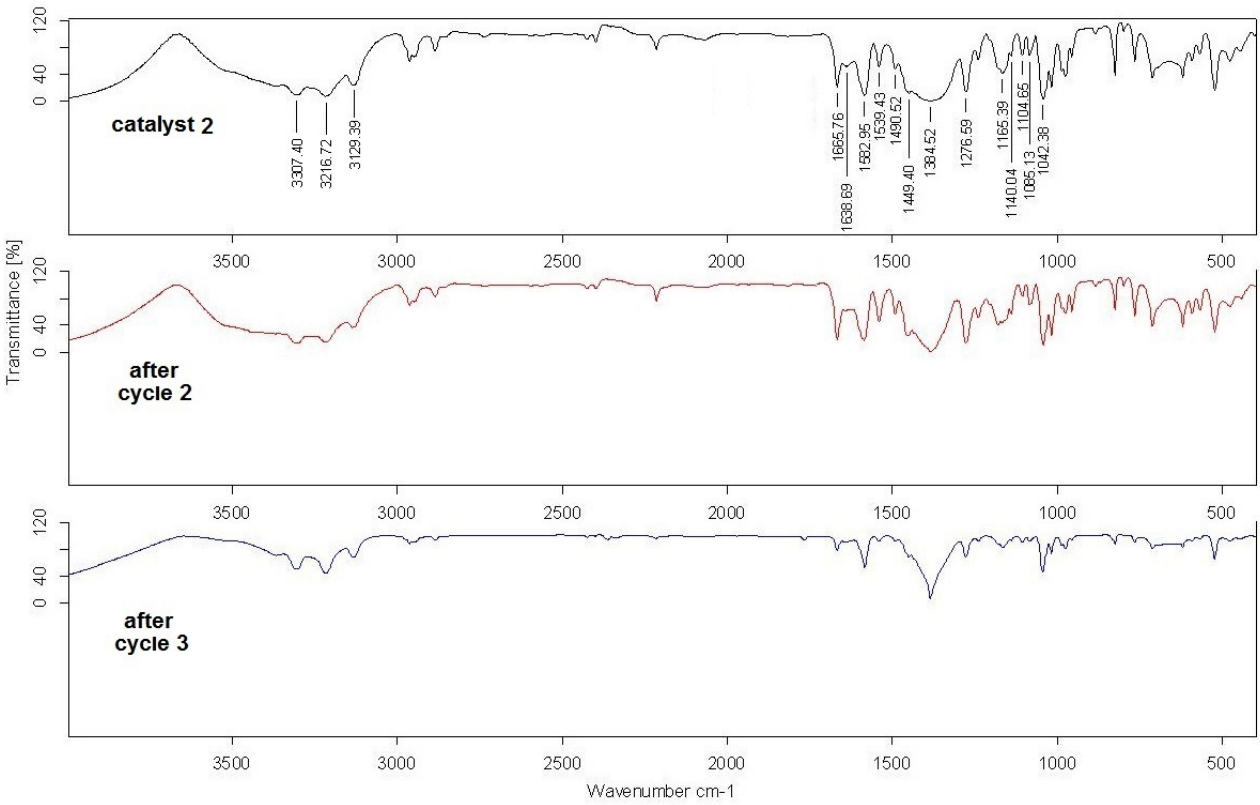

Figure S2. IR spectrum of catalyst **2** before and after catalytic cycles.

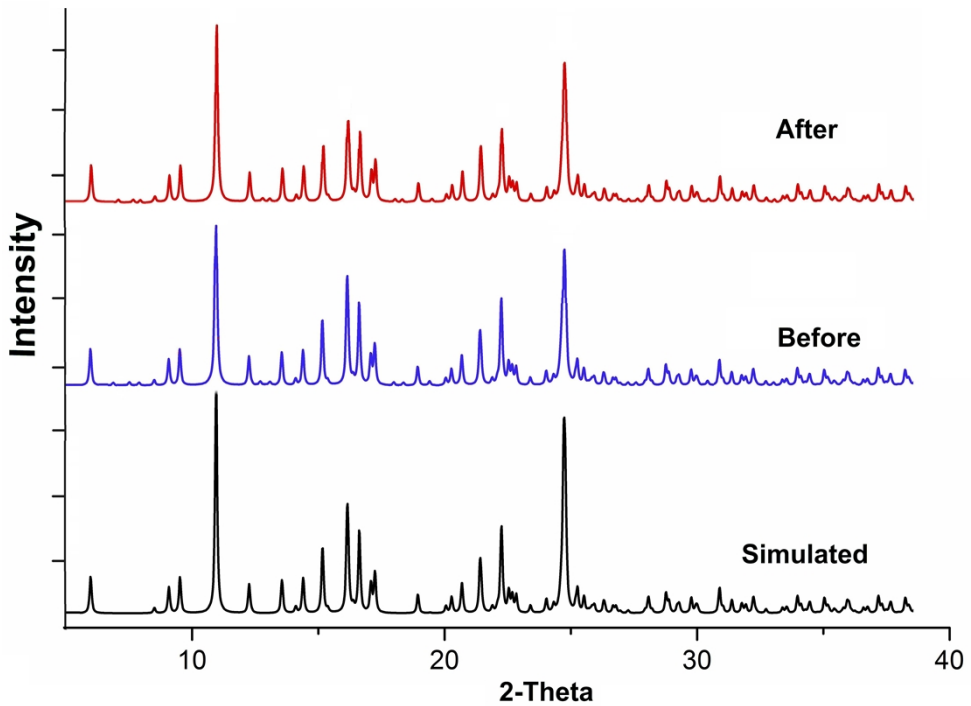

Figure S3. Powder XRD of **1** (before and after the catalytic reaction).

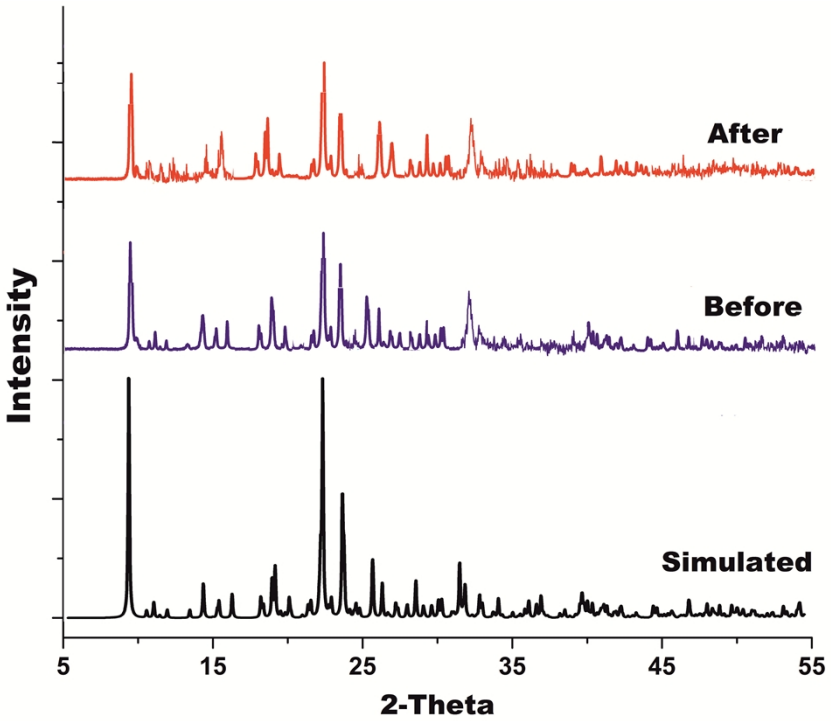

Figure S4. Powder XRD of **2** (before and after the catalytic reaction).

X-ray analyses

Table S1. Crystallographic data and structure refinement details for **1** and **2**.

	1	**2**
Empirical formula	$C_{18}H_{34}MnN_8O_{18}S_2$	$C_{28}H_{48}Cu_4N_4O_{30}S_4$
fw	769.59	1303.10
Temperature (K)	296(2)	296(2)
Cryst. Syst.	Triclinic	Monoclinic
Space group	*P -1*	*P 21/n*
a (Å)	7.2288(4)	9.9962(4)
b (Å)	9.9748(6)	17.2664(8)
c (Å)	11.5954(6)	13.1588(6)
α, °	85.652(3)	90
β, °	82.940(3)	107.705(2)
γ, °	76.401(3)	90
V (Å^3)	805.54(8)	2163.61(17)
Z	1	2
ρ_{calc} (g cm^{-3})	1.586	2.000
μ(Mo Kα) (mm^{-1})	0.627	2.242
F (000)	399	1328
R_{int}	0.0254	0.0962
Refl. Collected/unique	13853 / 4954	41836 / 4422
GOOF	1.058	1.024
R1[a] ($I \geq 2\sigma$)	0.0273	0.0445
wR2[b] ($I \geq 2\sigma$)	0.0739	0.1030

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

Table S2. Selected bond distances (Å) and angles (°) for **1** and **2**.

1		**2**	
N1-N2	1.3151(12)	N1-N2	1.265(5)
O5-Mn1	2.1890(8)	Cu1-O1	1.933(3)
O6-Mn1	2.1449(8)	Cu1-O2	1.938(3)
O7-Mn1	2.1752(9)	Cu1-N2	1.944(4)
O6-Mn1-O5	88.88(3)	Cu1-O4	1.987(3)
O6-Mn1-O7	90.23(4)	Cu1-O11^{i}	2.302(4)
O7-Mn1-O5	90.35(4)	Cu2-O3	1.955(3)
		Cu2-O8	1.960(3)
		Cu2-O5	1.959(4)
		Cu2-O6	1.966(4)
		Cu2-O7	2.270(4)
		O1-Cu1-O2	165.90(15)
		N2-Cu1-O4	174.51(15)
		O3-Cu2-O5	173.77(15)
		O8-Cu2-O6	175.48(17)