Electronic Supplementary Information for

Highly efficient and reusable CNT supported iron(II) catalyst for microwave assisted alcohol oxidation

L.M.D.R.S. Martins,*[a,b] A.P.C. Ribeiro,[a] S.A.C. Carabineiro,[c] J.L. Figueiredo,[c] A.J.L. Pombeiro[a]

[a] Centro de Química Estrutural, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001Lisboa, Portugal.
[b] Chemical Engineering Department, Instituto Superior de Engenharia de Lisboa, Instituto Politécnico de Lisboa, Rua Conselheiro Emídio Navarro, 1959-007 Lisboa, Portugal.
[c] LCM - Laboratory of Catalysis and Materials, Associate Laboratory LSRE-LCM, Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal
*Corresponding author e-mail address: *lmartins@deq.isel.ipl.pt*

CONTENTS

Experimental Details

Materials and Equipment

All the reagents and solvents were purchased from commercial sources and used as received. The water used for all preparations and analyses was double distilled and de-ionised.

The multi-walled carbon nanotubes (CNT) NC3100 from Nanocyl^{TM} were functionalized by treatment with 5 M nitric acid solution and subsequently treated with 20 mM sodium hydroxide aqueous solution, as previously reported by some of us[6c,7].

The catalytic tests under microwave (MW) irradiation were performed in a focused Anton Paar Monowave 300 microwave reactor using a sealed 10 mL capacity cylindrical Pyrex reaction tube with a 10 mm internal diameter, fitted with a rotational system and an IR temperature detector. Chromatographic analyses were undertaken by using a Fisons Instruments GC 8000 series gas chromatograph with a DB-624 (J&W) capillary column (DB-WAX, column length: 30 m; internal diameter: 0.32 mm), FID detector, and the Jasco-Borwin v.1.50 software. The temperature of injection was 240 ºC. The initial temperature was maintained at 140 ºC for 1 min, then raised 10 ºC/min to 220 ºC and held at this temperature for 1 min. Helium was used as the carrier gas. The products were identified by comparison of their retention times with known reference compounds. The internal standard method was used to quantify the organic products. GC-MS analyses were performed using a Perkin Elmer Clarus 600 C instrument (Helium as the carrier gas), equipped with two capillary columns (SGE BPX5; 30 m x 0.32 mm x 25 mm), one having an EI-MS (electron impact) detector and the other one with a FID detector. Reaction products were identified by comparison of their retention times with known reference compounds, and by comparing their mass spectra to fragmentation patterns obtained from the NIST spectral library stored in the computer software of the mass spectrometer.

The inductively coupled plasma (ICP) analyses were carried out by the Analytical Services of the Instituto Superior Técnico.

TEM measurements were performed on a Transmission Electron Microscope Hitachi 8100 with ThermoNoran light elements EDS detector and digital image acquisition. SEM analyses were carried out on a scanning electron microscope JEOL 7001F with Oxford light elements EDS detector and EBSD detector.

Far infrared spectrum FIR (400 – 200 cm^{-1}) was recorded on a Vertex 70 spectrophotometer in CsI pellets.

XPS were performed at CEMUP on a Kratos AXIS Ultra HAS equipment, with VISION software for data acquisition and CASAXPS software for data analysis. The effect of the electric charge was corrected by reference to the carbon peak (284.6 eV).

General procedure for the peroxidative microwave-assisted oxidation of alcohols

In a typical experiment, alcohol substrate (5.00 mmol), TBHP (70% aqueous solution, 10.0 mmol) and **1** or **1**@MWCNT (5 µmol based on the iron complex, 0.1 mol% *vs*. substrate) were introduced into a 10 mL cylindrical Pyrex tube, which was then placed in the microwave reactor. The system was stirred and irradiated at 80 °C (25 W power) for different times (0.1 – 1 h). After the reaction, the mixture was allowed to cool down to room temperature, and 300 µL of benzaldehyde were added as internal standard. Then 5 mL of NCMe were used to extract the substrate and the organic products from the reaction mixture. The obtained mixture was stirred for 10 min and then a sample (4 µL) was taken from the organic phase and analysed by GC (or GC–MS) using the internal standard method.

Blank tests were performed, in a Fe-free system, for the different substrates. In the experiment with the radical trap, $NHPh_2$ (5.00 mmol) was added to the reaction mixture. Catalyst **1**@MWCNT recyclability was investigated, for up to nineteen consecutive cycles. Each cycle was initiated after the preceding one upon addition of new typical portions of all other reagents. After completion of each run, the products were analysed as above-mentioned and the catalyst was recovered by filtration, thoroughly washed with acetonitrile, and dried in oven at 80 ºC.

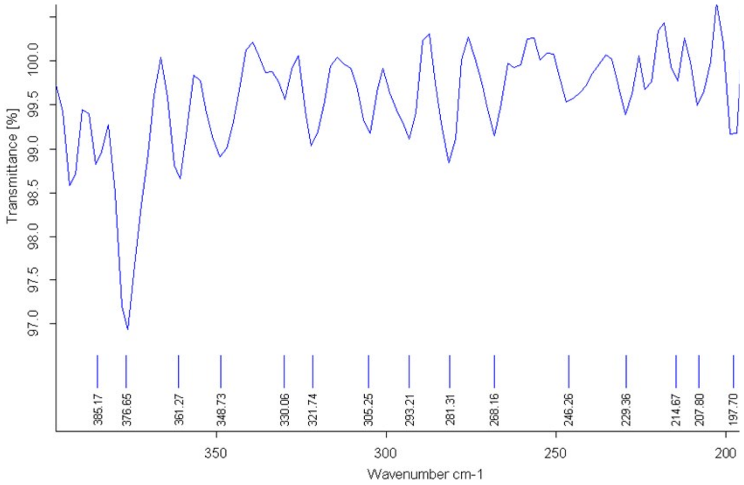
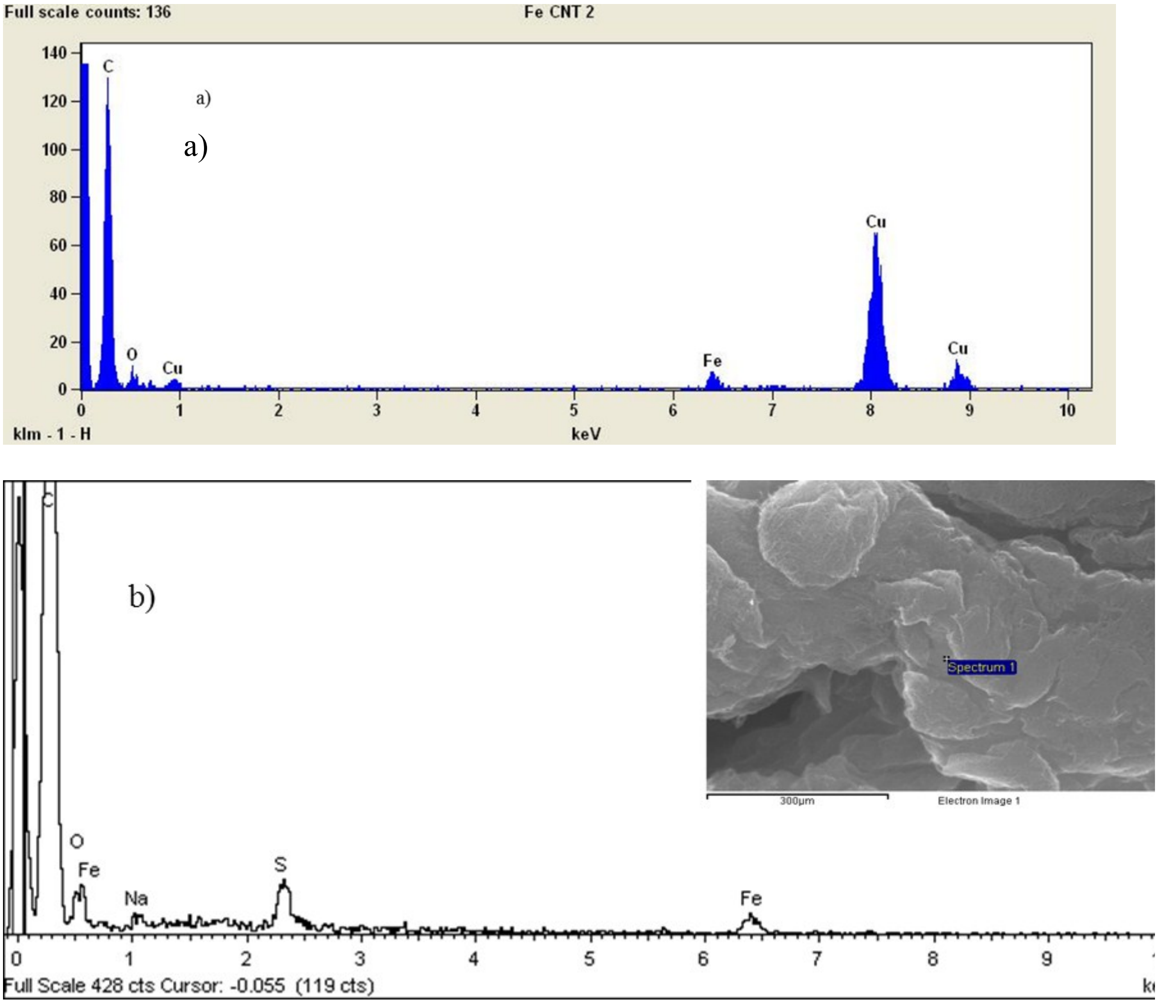


Fig. S1- Far infrared spectrum (400 – 200 cm^{-1}) of **1**@MWCNT.



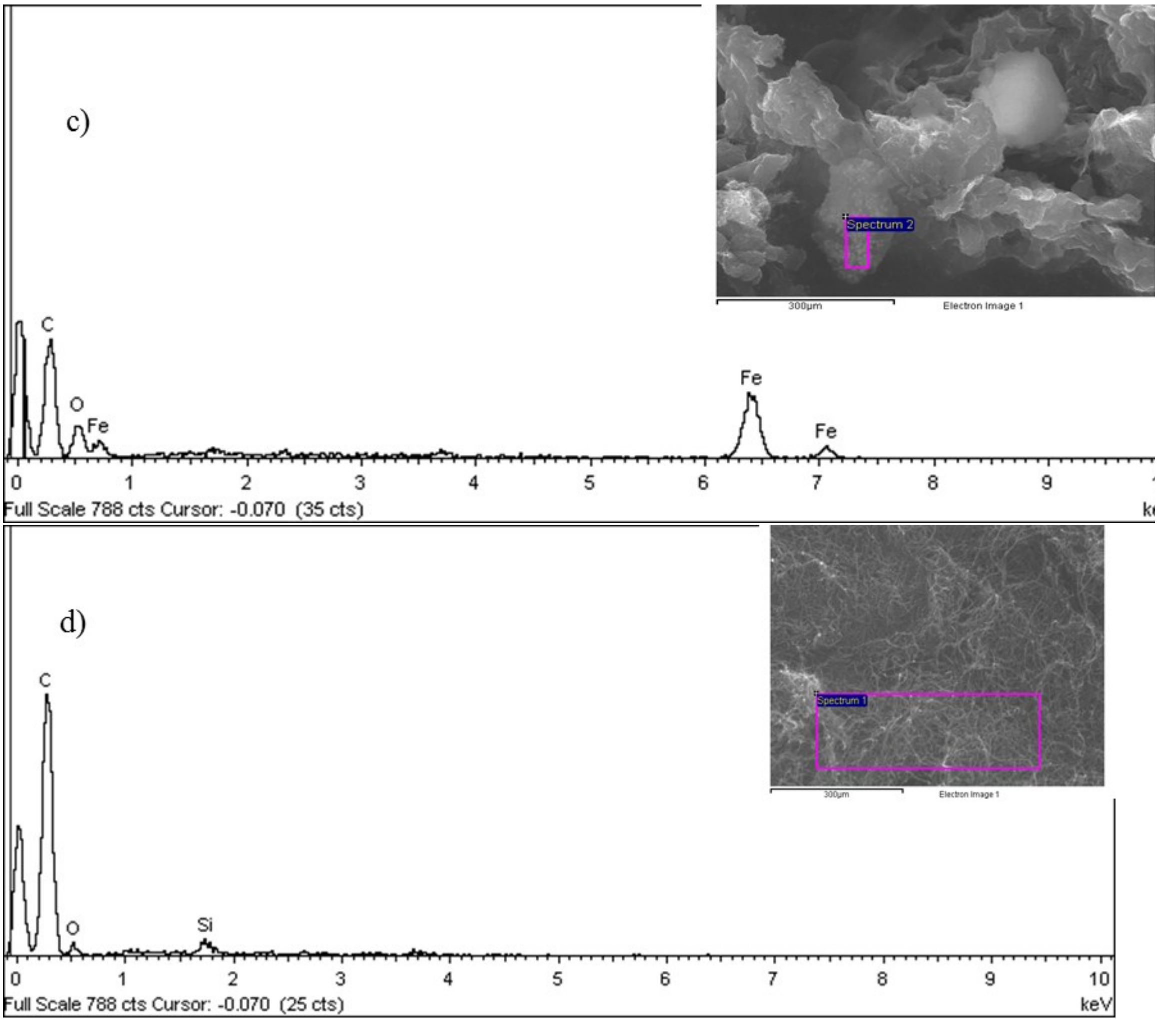


Fig. S2- EDS results for **1**@MWCNT: from TEM, before the catalytic oxidation reaction, a); from SEM, before the catalytic oxidation reaction, b); from SEM, after the 5th run, c); from SEM, after the 19th run, d).

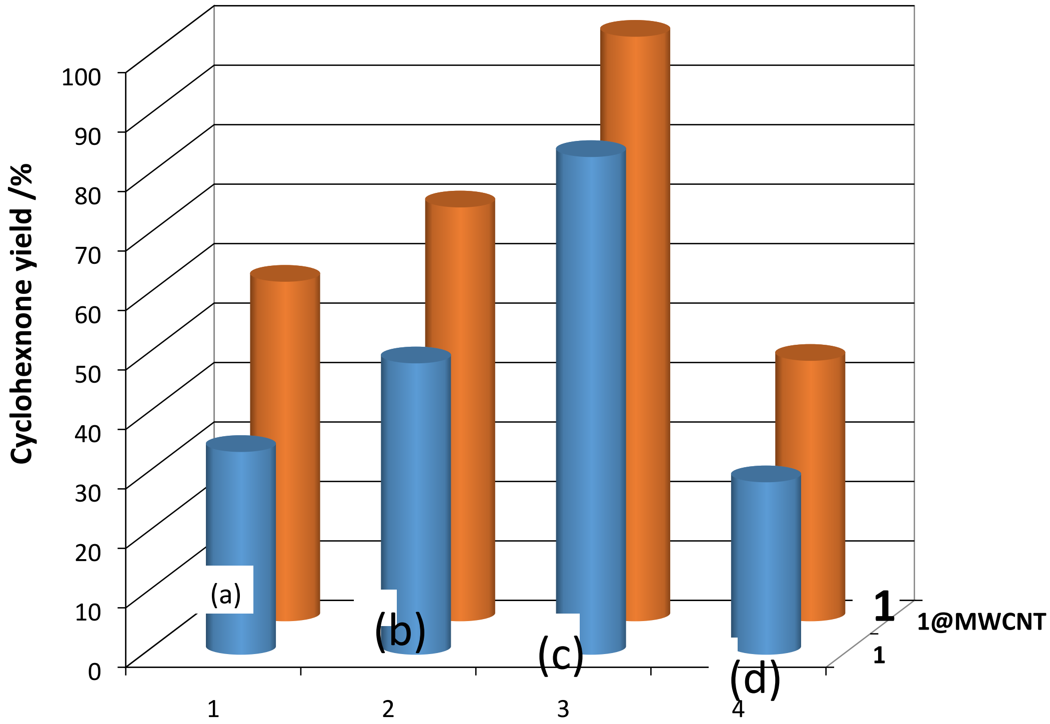


Fig. S3 - Cyclohexanone yield obtained by MW-assisted oxidation of cyclohexanol with H_2O_2 (30%), at 80 ºC, catalysed by **1** (🟦) or **1**@MWCNT (🟧): (a) 5 mmol H_2O_2; (b) 10 mmol H_2O_2; (c) 10 mmol H_2O_2 in the presence of TEMPO and (d) 50 mmol H_2O_2.

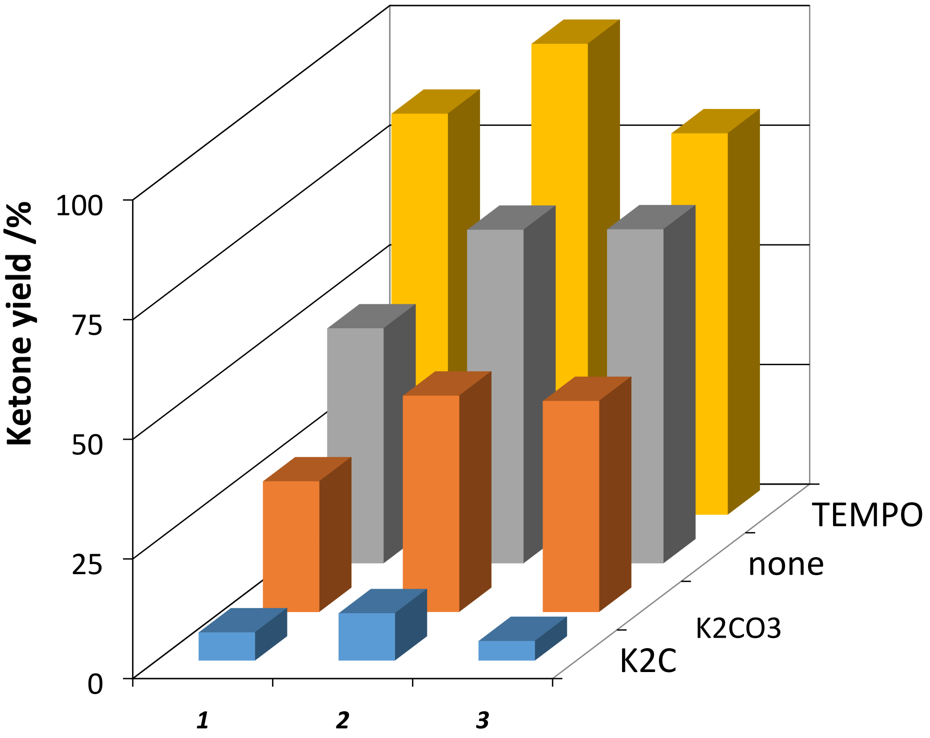


Fig. S4 - Effect of acidic (pyrazine carboxylic acid, Hpca), basic (1 M K_2CO_3) or TEMPO additives on the ketone yield obtained by MW-assisted oxidation of cyclohexanol (*1* and *2*) or 1-phenylethanol (*3*) with TBHP, at 80 ºC, catalysed by **1** (*1* or *3*) or **1**@MWCNT (*2*).

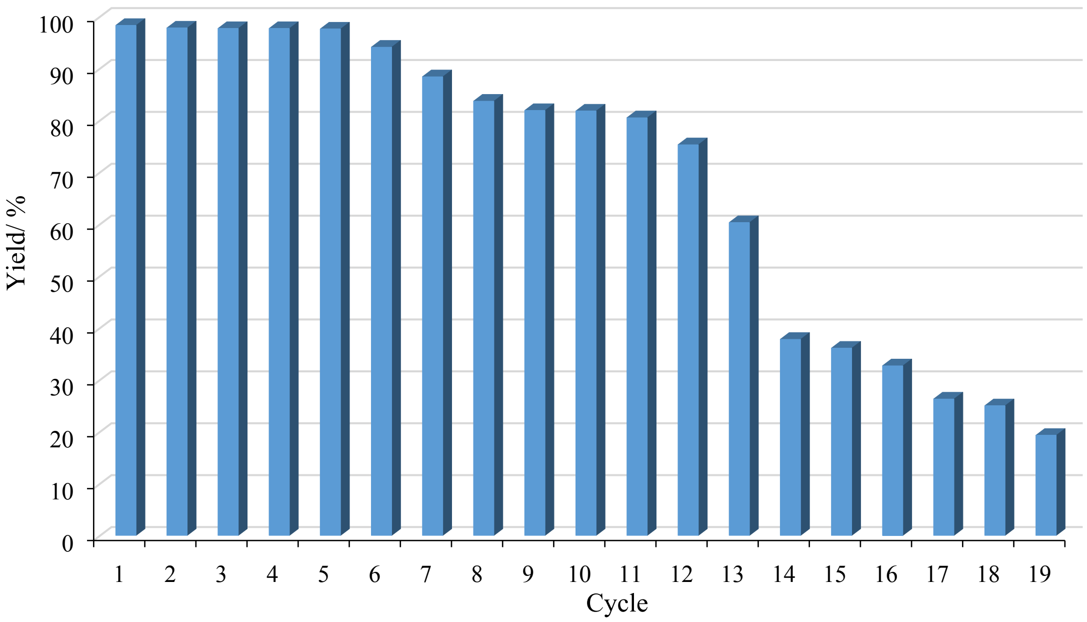


Fig. S5 – Effect of the catalyst recycling on the yield of cyclohexanone for the MW-assisted cyclohexanol oxidation (1 h) with TBHP in the presence of TEMPO, at 80 ºC, catalysed by **1**@MWCNT.

Table S1 - Solvent-free MW-assisted oxidation cyclohexanol catalysed by **1**@MWCNT.[a]

Entry	Catalyst amount /mol% *vs.* substrate	Reaction time /h	Additive (mol% *vs.* substrate)	Yield /%[b]	TOF /h^{-1} [c]	Selectivity /% [d]
1	0.1	0.1	–	4.0	400	80
2		0.25		18.0	720	81
3		0.5		53.2	1064	94
4		1		89.6	896	99
5	0.1	0.1	TEMPO (2.5)	10.0	1000	90
6		0.25		35.0	1400	95
7		0.5		62.4	1248	97
8		1		98.3	984	99
9	0.02	1	TEMPO (2.5)	36.3	1815	95
10[e]	0.1	1	TEMPO (2.5)	65.7	657	94
11[e]	0.1	1	-	20.1	201	95
12[f]				50.4	504	93
13[g]				43.8	438	97
14[h]				57.1	571	98
15	0.1	1	K_2CO_3 (2.5)	9.8	98	97
16			Hpca (2.5)	45.1	451	98
17			Ph_2NH (100)	1.3	13	65
18			$CBrCl_3$ (100)	5.2	52	57

[a] Reaction conditions unless stated otherwise: 5 mmol of cyclohexanol, 1 – 5 μmol (based on the iron complex; 0.02 – 0.1mol% *vs*. cyclohexanol) of **1**@MWCNT, 10 mmol of TBHP (2 eq., 70% in H_2O), 80 °C, MW irradiation (25 W). [b] Moles of cyclohexanone per 100 mol of cyclohexanol. [c] Turnover frequency (TOF) = number of moles of cyclohexanone per mol of **1**, per hour. [d] Moles of cyclohexanone per mole of converted cyclohexanol. [e] 10 mmol of H_2O_2 (30% aq. solution) instead of TBHP. [f] 50 mmol of H_2O_2 instead of TBHP. [g] 50 mmol of TBHP. [h] 5 mmol of TBHP.

Table S2 - Solvent-free MW-assisted oxidation of 1-phenylethanol catalysed by **1** or **1**@MWCNT.[a]

Entry	**Catalyst**	**Reaction time /h**	**Additive (mol% *vs.* substrate)**	**Yield /%**[b]	**TOF /h^{-1}** [c]	**Selectivity /%** [d]
1	**1**	0.5	–	33.4	668	88
2		1		69.7	697	97
3	**1**	0.5	TEMPO (2.5)	55.6	1112	98
4		1		79.6	796	99
5	**1**@MWCNT	0.5	–	59.1	1182	96
6		1		73.4	734	96
7	**1**@MWCNT	0.5	TEMPO (2.5)	69.1	1382	97
8		1		94.2	942	98
9	**1**	1	K_2CO_3 (2.5)	4.0	40	63
10			Hpca (2.5)	44.0	440	92
11			Ph_2NH (100)	2.3	23	77
12			$CBrCl_3$ (100)	3.6	36	64
13	-	1	TEMPO (2.5)	5	50	71

[a] Reaction conditions unless stated otherwise: 5 mmol of 1-phenylethanol, 5 μmol (based on the iron complex; 0.1 mol% *vs*. 1-phenylethanol) of catalyst, 10 mmol of TBHP (2 eq., 70% in H_2O), 80 °C, MW irradiation (25 W). [b] Moles of acetophenone per 100 mol of 1-phenylethanol. [c] Turnover frequency (TOF) = number of moles of acetophenone per mol of catalyst, per hour. [d] Moles of acetophenone per mole of converted 1-phenylethanol.

Table S3 – Recycling of **1**@MWCNT at the solvent-free MW-assisted oxidation cyclohexanol.[a]

Cycle	Yield /% [b]	Selectivity /% [c]
1	98.3	99
2	97.8	99
3	97.7	99
4	97.7	99
5	97.6	98
6	94.1	96
7	88.4	97
8	83.7	95
9	81.9	95
10	81.8	94
11	80.5	98
12	75.3	98
13	60.3	87
14	37.8	82
15	36.1	92
16	32.7	87
17	26.3	91
18	25.0	87
19	19.3	69

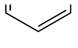
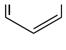
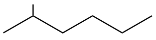
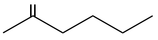
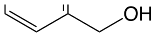
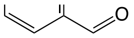
[a] Reaction conditions unless stated otherwise: 5 mmol of cyclohexanol, 5 μmol (based on the iron complex; 0.1 mol% *vs*. cyclohexanol) of **1**, 10 mmol of TBHP (2 eq., 70% in H_2O), TEMPO (2.5 mol% *vs*. substrate), 80 °C, 1 h of MW irradiation (25 W). [b] Moles of cyclohexanone per 100 mol of cyclohexanol. [c] Moles of cyclohexanone per mole of converted cyclohexanol.

Table S4 - Solvent-free MW-assisted oxidation of cyclohexanol catalysed by **1**.[a]

Entry	Catalyst amount /mol% *vs.* substrate	Reaction time /h	Additive (mol% *vs.* substrate)	Yield /% [b]	TOF /h^{-1} [c]	Selectivity /% [d]
1	0.1	0.1	–	2.4	240	56
2		0.25		10.0	400	83
3		0.5		21.7	434	97
4		1		49.0	490	96
5	0.1	0.1	TEMPO (2.5)	8.3	830	77
6		0.25		26.5	1060	94
7		0.5		48.4	968	95
8		1		83.7	838	100
9	0.02	1	TEMPO (2.5)	29.1	1455	91
10[e]	0.1	1	TEMPO (2.5)	52.3	523	97
11[e]	0.1	1	-	14.8	148	87
12[f]				38.3	383	93
13[g]				29.1	291	87
14[h]				34.1	341	96
15	0.1	1	K_2CO_3 (2.5)	5.8	58	83
16			Hpca (2.5)	27.2	272	97
17			Ph_2NH (100)	2	20	67
18			$CBrCl_3$ (100)	4	40	63
19	-	1	TEMPO (2.5)	3	-	77

[a] Reaction conditions unless stated otherwise: 5 mmol of cyclohexanol, 1 – 5 µmol (0.02 – 0.1 mol% *vs.* cyclohexanol) of **1**, 10 mmol of TBHP (2 eq., 70% in H_2O), 80 °C, MW irradiation (25 W). [b] Moles of cyclohexanone per 100 mol of cyclohexanol. [c] Turnover frequency (TOF) = number of moles of cyclohexanone per mol of **1**, per hour. [d] Moles of cyclohexanone per mole of converted cyclohexanol. [e] 10 mmol of H_2O_2 (30% aq. solution) instead of TBHP. [f] 50 mmol of H_2O_2 instead of TBHP. [g] 50 mmol of TBHP. [h] 5 mmol of TBHP.

Table S5 – Selected results for the solvent-free MW-assisted oxidation of primary and secondary alcohols catalysed by **1**@MWCNT.[a]

Entry	Substrate	Product	Yield /% [b]	TOF / h^{-1} [c]	Selectivity /% [d]
1			14	113	33
2			10	100	32
3			6	60	75
4			9	90	100
5			10	98	100

[a] Reaction conditions unless stated otherwise: 5 mmol of alcohol, 5 µmol (0.1 mol% *vs*. substrate) of **1**, 10 mmol of TBHP (2 eq., 70% in H_2O), 80 °C, 1 h of MW irradiation (25 W). [b] Moles of oxygenated product per 100 mol of alcohol. [c] Turnover frequency (TOF) = number of moles of oxygenated product per mol of **1**, per hour. [d] Moles of presented product per mole of converted alcohol.