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Mn(II) acetate: An efficient and versatile oxidation catalyst for alcohols

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Electronic supplementary information (ESI)

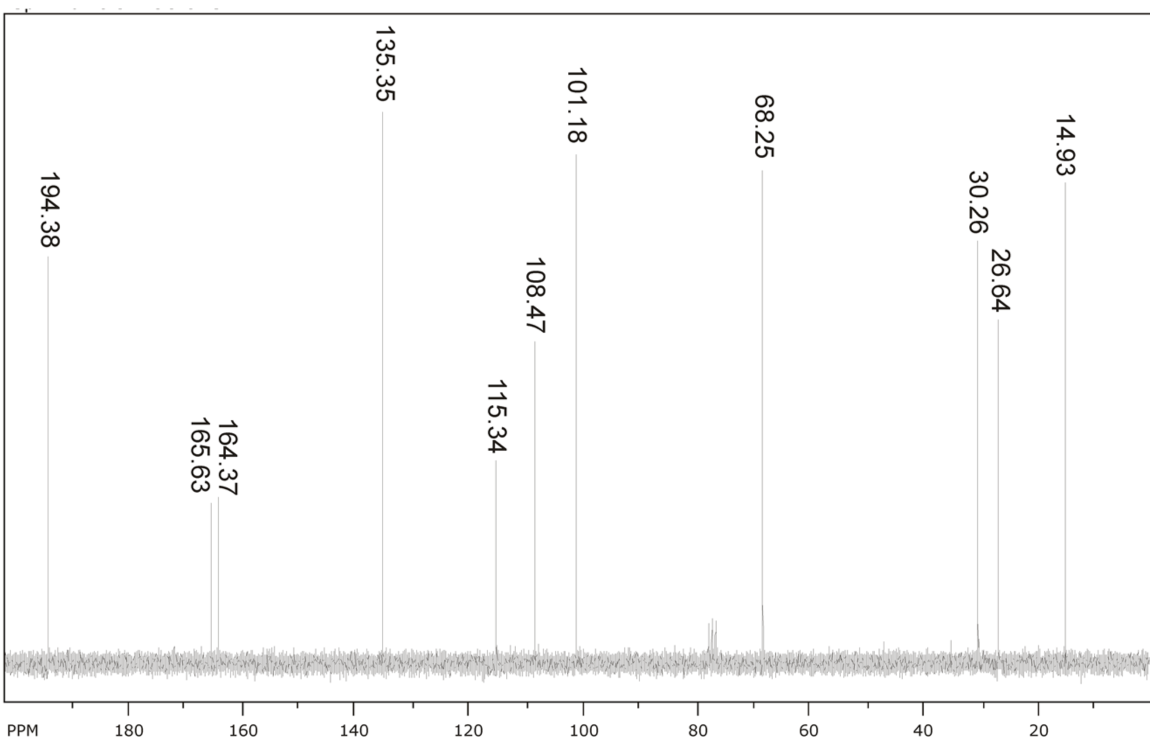

Fig. S1 ^{13}C NMR spectrum of 2-hydroxy-4-[2-(ethylthio)ethoxy]benzaldehyde measured in $CDCl_3$.

Table S1

Effect of TFA amount on the oxidation of 1-octanol and 2-octanol by a system based on $Mn(OAc)_2$/tBuOOH.[a]

Entry	Substrate	Main product	TFA amount (µL)	Alcohol conversion (%)	Selectivity (%)
1	2-octanol	2-octanone	0	46	>99.9
2			7	87	>99.9
3			25	67[b]	78
4			50	59[c]	74
5	1-octanol	1-octanoic acid	0	25	92
6			7	60	>99.9
7			25	42[d]	67
8			50	34[e]	50

[a] Reaction conditions: 1 mmol substrate, 1.8 mol% $Mn(OAc)_2$, 313 µL tBuOOH (2.5 equiv.), 7 µL TFA, 1.5 mL CH_3CN, 80 °C, 21 h. [b] 19% of side products (hexanoic acid, heptanoic acid, 2,5-hexanedione, octan-2-yl 2,2,2-trifluoroacetate). [c] 21% of side products (hexanoic acid, heptanoic acid, octan-2-yl 2,2,2-trifluoroacetate). [d] 21% of octyl 2,2,2-trifluoroacetate and 5% of octyl acetate formed. [e] 34% of octyl 2,2,2-trifluoroacetate and 8% of octyl acetate formed.

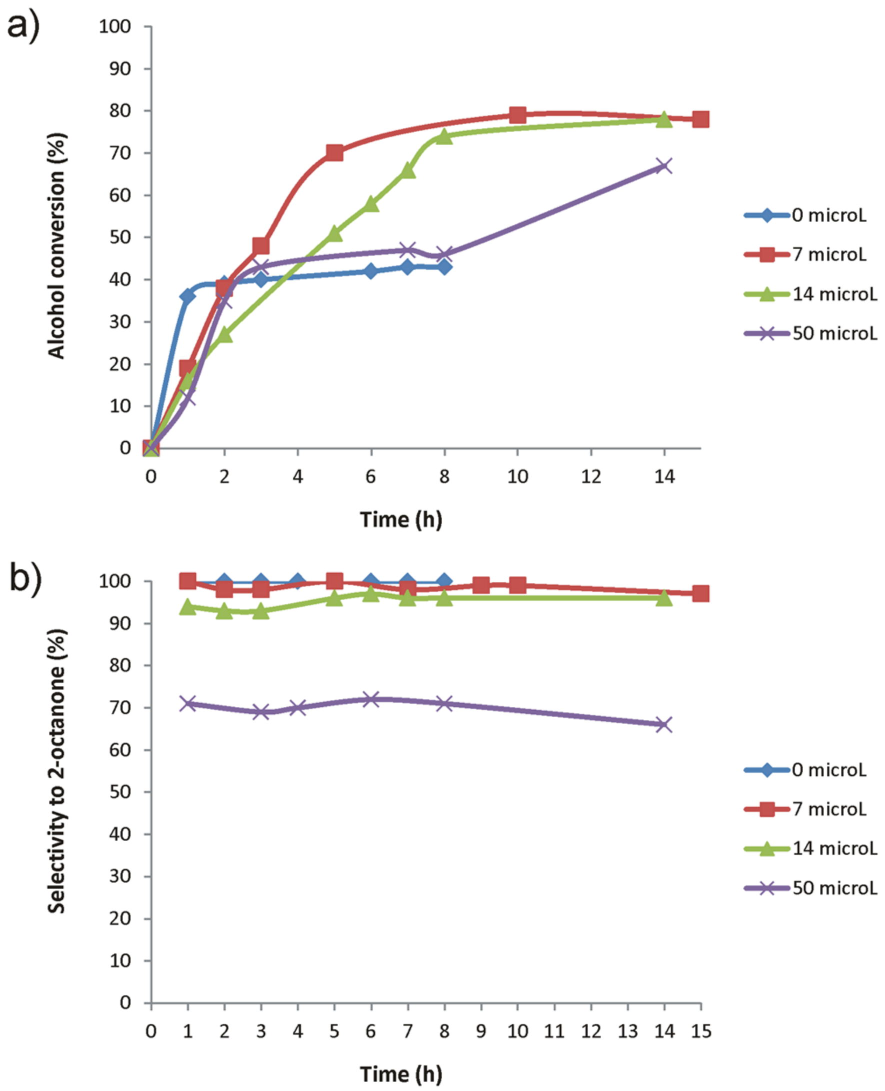

Fig. S2 a) Conversion and b) selectivity of the oxidation reaction of 2-octanol with different TFA amounts (from 0 to 50 µl). Reaction conditions: 1 mmol of 2-octanol, 1.8 mol% of $Mn(OAc)_2$, 1.5 mL of CH_3CN, 313 µL of *t*BuOOH, 80 °C.

Table S2

Effect of carboxylic acid additive on the oxidation of 2-octanol by a system based on $Mn(OAc)_2$/tBuOOH.[a]

Entry	Acid additive	Alcohol conversion (%)	Selectivity to 2-octanone
1	TFA, 7 µL	87	>99.9
2	acetic acid, 400 µL	66[b]	87

[a] Reaction conditions: 1 mmol 2-octanol, 1.8 mol% $Mn(OAc)_2$, 313 µL tBuOOH (2.5 equiv.), 1.5 mL CH_3CN, 80 °C, 21 h. [b] Side products: 7% hexanoic acid, 3% octan-2-yl acetate.

Table S3

Effect of solvent on the oxidation of 2-octanol by a system based on $Mn(OAc)_2$/tBuOOH.[a]

Entry	Solvent	Alcohol conversion (%)	Selectivity to 2-octanone
1	CH_3CN	87	>99.9
2	EtOAc	38[b]	43
3	toluene	38[c]	70

[a] Reaction conditions: 1 mmol substrate, 1.8 mol% $Mn(OAc)_2$, 313 µL tBuOOH (2.5 equiv.), 7 µL TFA, 1.5 mL solvent, 80 °C, 21 h. [b] Side products: 23% octan-2-yl 2,2,2-trifluoroacetate, 13% hexanoic acid, 5% heptanoic acid, 10% octanediones. [c] Side products: 8% heptanoic acid, 8% octan-2-yl 2,2,2-trifluoroacetate. Also formed large amounts of benzaldehyde and benzoic acid as well as traces of benzyl alcohol from the oxidation of toluene (2-octanone/benzaldehyde/benzoic acid/benzyl alcohol ratio 1:1.7:2.4:0.4).

Table S4

Reaction rate constants (*k*) obtained with different concentrations of 2-octanol. See Fig. 3 for the experimental conditions.

2-octanol (mmol)	[2-octanol] (M)	*k* (M/min)	R^2
0.5	0.263158	0.0006	0.97
1.5	0.728509	0.0012	0.99
2.0	0.935454	0.0014	0.99

Table S5

Reaction rate constants (*k*) obtained with different concentrations of $Mn(OAc)_2$. See Fig. 3 for the experimental conditions.

$Mn(OAc)_2$ (mol%)	$[Mn(OAc)_2]$ (M)	*k* (M/min)	R^2
0.45	0.002276	0.0006	0.99
0.90	0.004552	0.0007	0.98
3.60	0.018207	0.0012	0.99

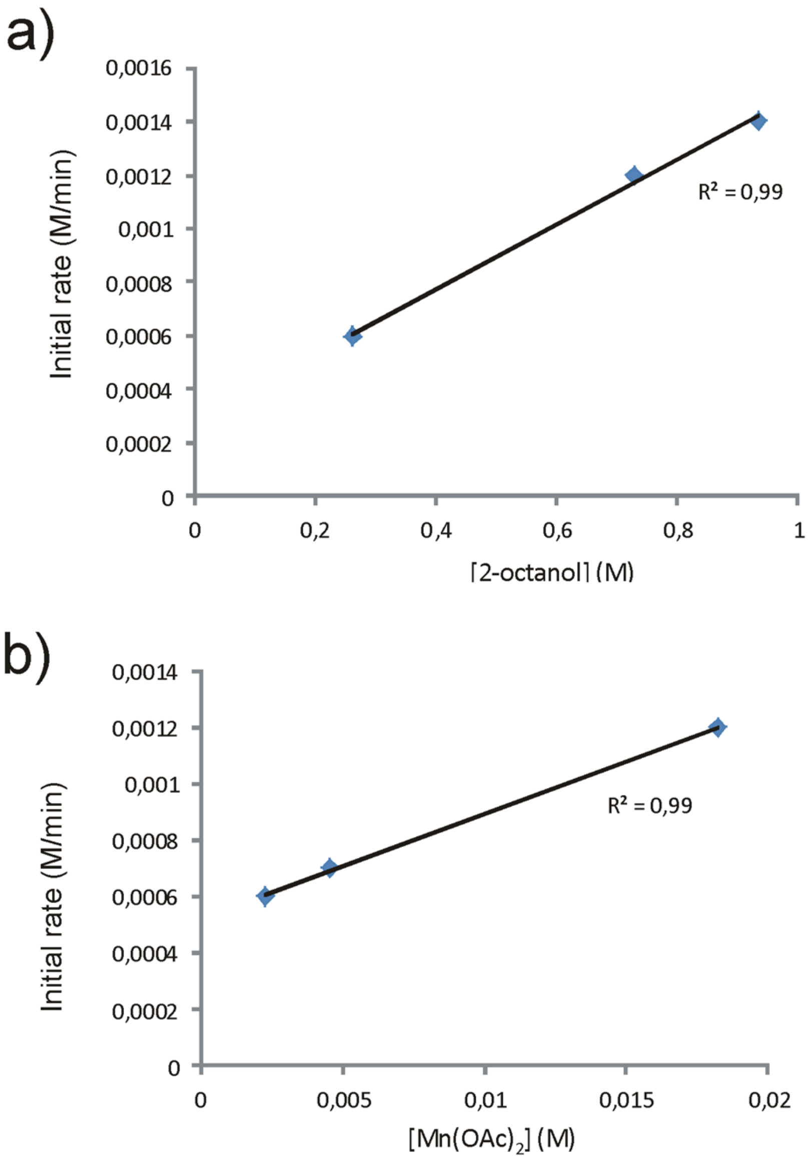

Fig. S3 The initial oxidation rate depends linearly on the concentration of (a) 2-octanol and (b) $Mn(OAc)_2$.

Table S6

Oxidation of various alcohols with a $Mn(OAc)_2$/tBuOOH system under argon.[a]

Entry	Substrate	Main product[b]	Time (h)	Alcohol conv. (%) [in air]	Select. (%) [in air]
1	2-octanol	2-octanone	1.5	12 [25]	>99.9 [>99.9]
2	1-phenyl-1-propanol	1-phenyl-1-propanone	2	39 [40]	>99.9 [>99.9]
3	benzyl alcohol	benzaldehyde	8	40 [67]	83 [52]
4	4-nitrobenzyl alcohol	4-nitrobenzaldehyde	4	29 [42]	>99.9 [>99.9]
5	1-naphthalenemethanol	1-naphthaldehyde (1-naphthoic acid for the reaction done in air)	8	35 [68]	80 [74]
6	4-chlorobenzyl alcohol	4-chlorobenzaldehyde	4	59 [62]	73 [74]
7	2-thiophenemethanol	2-thiophenecarboxaldehyde	15	93 [93]	70 [67]

[a] Reaction conditions: 1 mmol alcohol substrate, 18 µmol $Mn(OAc)_2$, 313 µL tBuOOH (2.5 equiv.), 7 µL TFA, 1.5 mL CH_3CN, 80 °C, Ar atmosphere. [b] Side products formed under Ar. Entry 3: 7% benzoic acid. Entry 5: 7% 1-naphthoic acid. Entry 6: 16% 4-chlorobenzoic acid. Entry 7: 13% 2-thiophenecarboxylic acid, 15% 2-methylthiophene.

Table S7

Oxidation of hydrocarbons with the $Mn(OAc)_2$/tBuOOH system under argon.[a]

Entry	**Substrate**	**Main product**[b]	**Substrate conversion (%)**	**Selectivity %)**
1	cyclooctane	cyclooctanone	32	44
2	isochroman	isochroman-1-one	47	>99.9
3	ethylbenzene	acetophenone	43	42

[a] Reaction conditions: 1 mmol hydrocarbon substrate, 18 µmol $Mn(OAc)_2$, 313 µL tBuOOH (2.5 equiv.), 7 µL TFA, 1.5 mL CH_3CN, 70 °C, 16 h, Ar atmosphere. [b] Side products formed. Entry 1: 7% cyclooctene, 2% cyclooctanol, 9% unidentified compound. Entry 3: 10% benzaldehyde, 15% 1,1'-(oxydiethylidene)bisbenzene.

Table S8

Oxidation of *N*,*N*-dimethylaniline (DMA) and *N*,*N*-dimethylaminopyridine (DMAP) in CH_3CN with the $Mn(OAc)_2$/tBuOOH system.[a]

Entry	**Substrate**	**Main product**[b]	**Substrate conversion (%)**	**Selectivity (%)**
1	DMA	4-(methylamino)benzaldehyde	100	42
2	DMAP	*N*-methyl-*N*-(pyridin-4-yl)formamide	92	49

[a] Reaction conditions: 1 mmol amine, 18 µmol $Mn(OAc)_2$, 313 µL tBuOOH (2.5 equiv.), 7 µL TFA, 1.5 mL CH_3CN, 70 °C, 16 h. [b] Side products. Entry 1: 40% 4-(dimethylamino)benzaldehyde, 4% *N*-(4-formylphenyl)-*N*-methylformamide, 7% *N*-methyl-*N*-phenylformamide, 7% *N*-methylaniline. Entry 2: 37% *N*-methylpyridin-4-amine, 5% 4-aminopyridine, 5% *N*-(pyridin-4-yl)formamide.

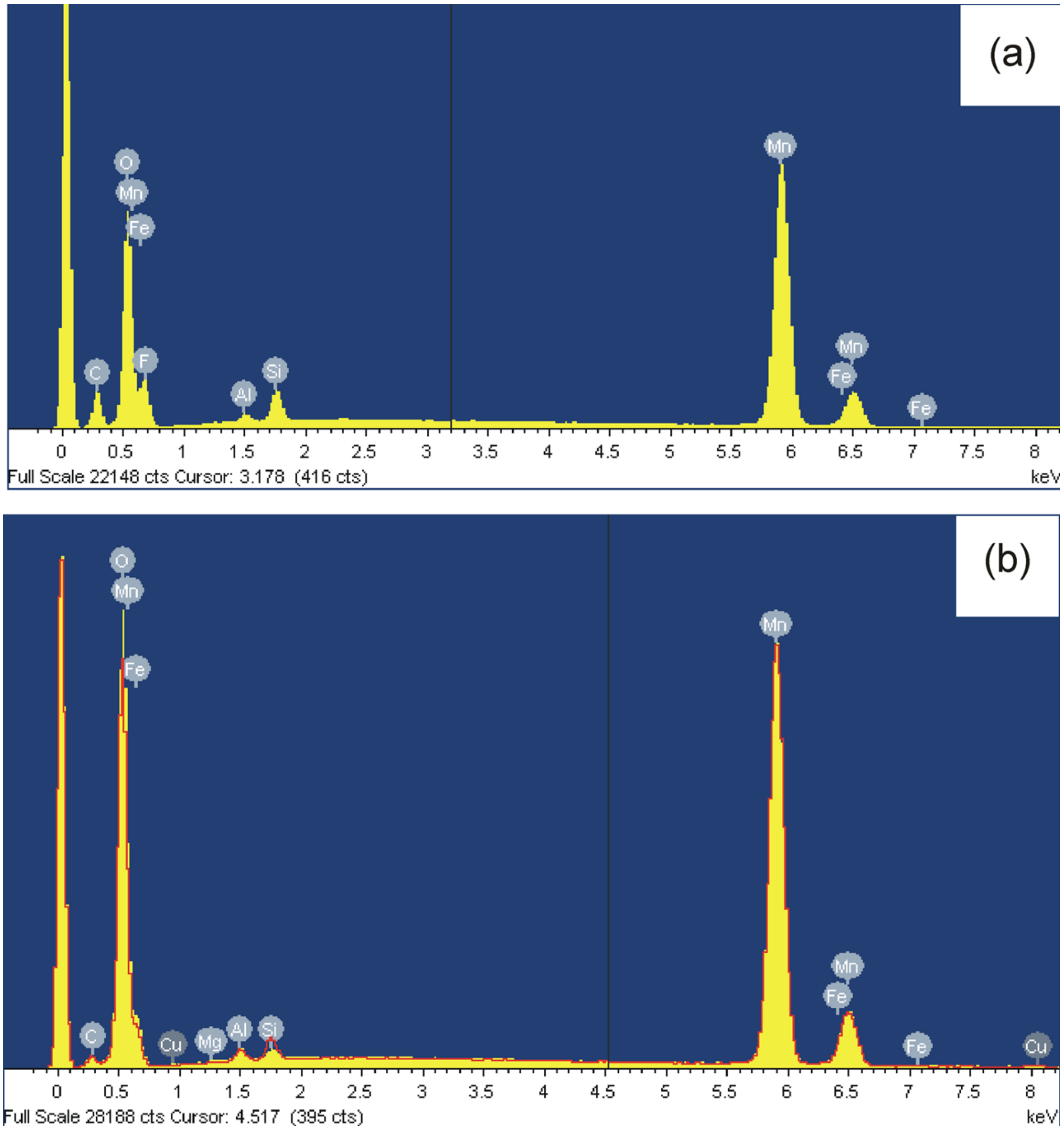

Fig. S4 EDS spectra of (a) the black precipitate formed during the alcohol oxidation reaction in the absence of TFA and of (b) commercial MnO_2 powder (Merck, 85-90%). The Mn/O Kα ratio for the powder isolated from the reaction mixture is 2.8. The theoretical Mn/O Kα ratio is 2.4 for MnO_2 and 3.3 for Mn_2O_3.

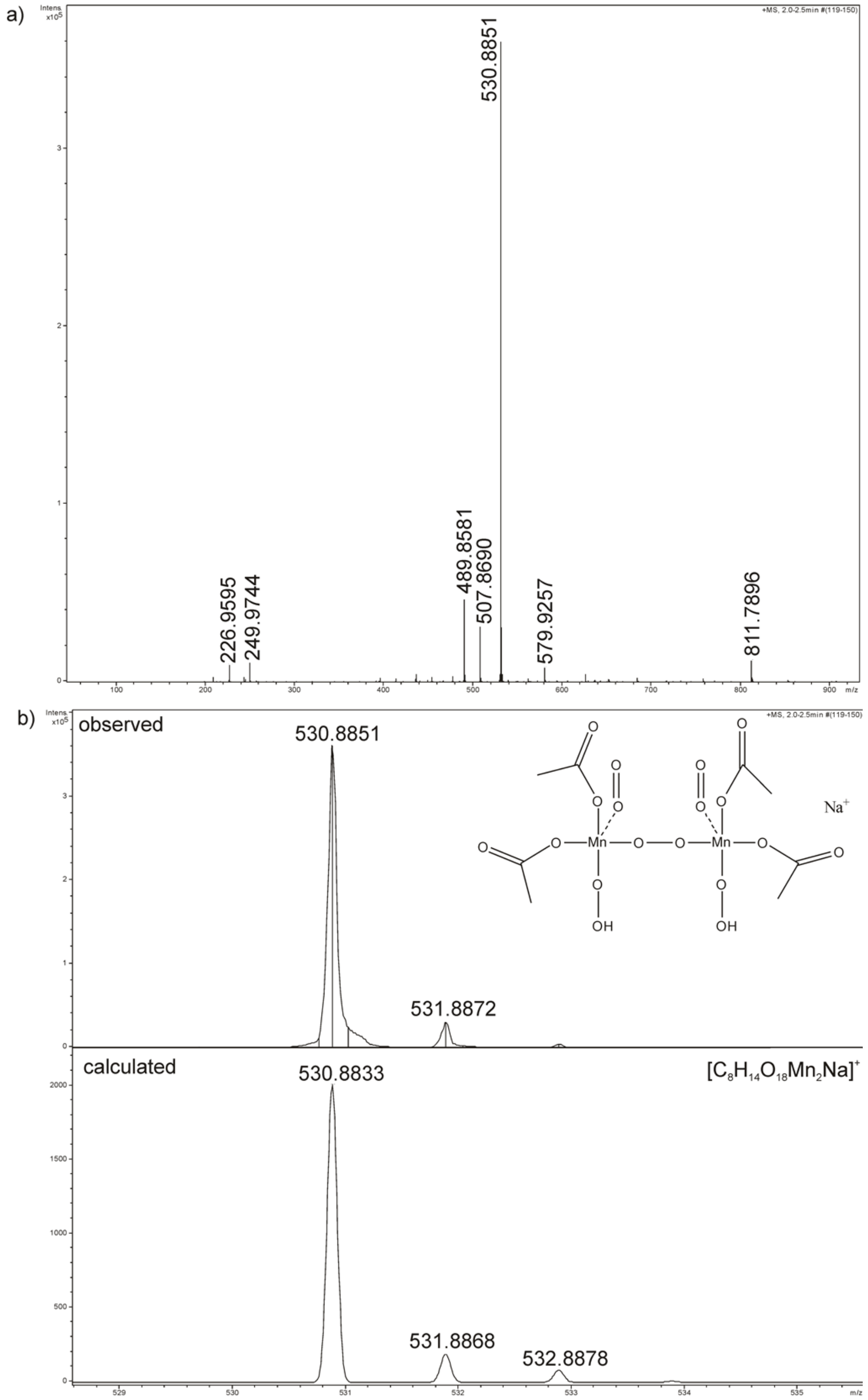

Fig. S5 a) HRMS (ESI$^+$-TOF) spectrum of acetonitrile solution of Mn(OAc)$_2$, TFA and *t*BuOOH measured ca. 5 min after mixing all the components at room temperature. b) Observed and calculated isotopic patterns of 530 *m/z* species (error -3.391 ppm). Acquisition parameters: capillary exit 120 V, hexapole RF 100 V, skimmer 1 40 V, hexapole 1 22.8 V.

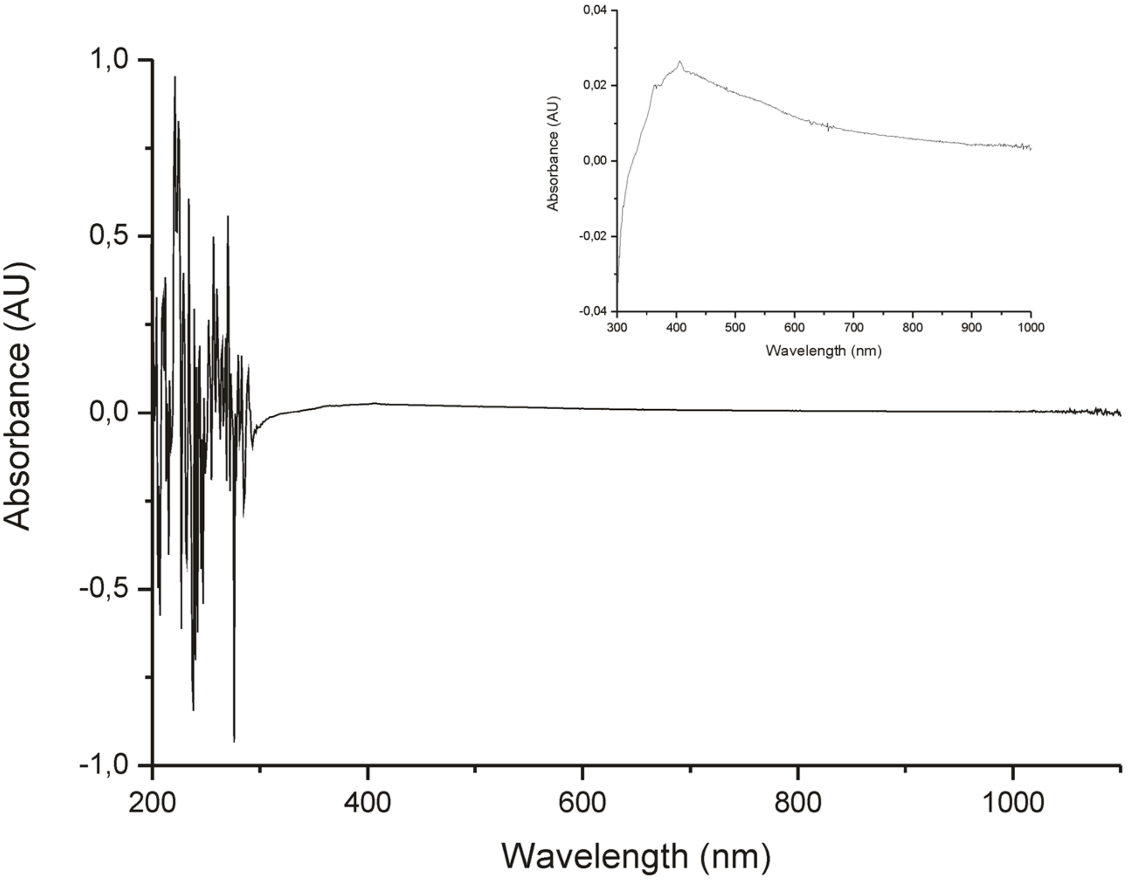

Fig. S6 UV-Vis spectrum of the concentrated acetonitrile (1.5 mL) solution of Mn(OAc)$_2$ (13.2 mg, 0.03 mol/L), TFA (21 µL, 0.15 mol/L) and *t*BuOOH (313 µL, 1.4 mol/L) measured ca. 15 min after mixing all the components at room temperature. In the inset is shown the 300-1000 nm region. UV-Vis spectrum was measured with a Hewlett Packard 8453 spectrophotometer.