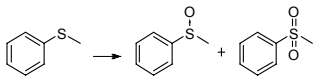
Suplementary Material

ATOMS	x	y	z	U(eq)	Ocupac. F
As	0.1916 (1)	0.1877(1)	0.2305(1)	15(1)	1
V	0.1806(1)	0.1848(1)	0.5335(1)	16(1)	1
F	0.2820(2)	0.1015(5)	0.5358(4)	21(1)	1
O(1)	0.1596(2)	0.0920(8)	0.3451(4)	20(1)	1
O(2)	0.1528(2)	0.3951(6)	0.1865(5)	25(1)	1
O(3)	0.1727(2)	0.0720(7)	0.0889(4)	20(1)	1
O(4)	0.2725(2)	0.2240(6)	0.2811(4)	21(1)	1
O(5)	0.1112(2)	0.2650(8)	0.5409(5)	26(1)	1
N(1)	0.1167(3)	0.2913(10)	-0.1463(7)	30(1)	1
C(1)	0.0478(3)	0.2891(11)	-0.1201(8)	30(1)	1
C(2)	0.0114(4)	0.1156(11)	-0.1724(9)	33(1)	1
C(3)	0.0116(4)	0.4596(11)	-0.1764(8)	35(1)	1
H(I)	0.1672	0.4433	0.1283	38	1
H(1A)	0.1134	0.2752	-0.2325	45	1
H(1B)	0.1407	0.2011	-0.1006	45	1
H(1C)	0.1358	0.3989	-0.1208	45	1
H(1)	0.0532	0.2915	-0.0327	36	1
H(2A)	-0.0266	0.1037	-0.1360	40	1
H(2B)	0.0396	0.0104	-0.1433	40	1
H(3A)	-0.0260	0.4741	-0.1389	42	1
H(3B)	0.0400	0.5649	-0.1492	42	1

Table S1. Fractional atomic coordinates and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **1**.

ATOMS	x	y	z	U(eq)	Ocupac. F
As	0.1958 (1)	0.1878(1)	0.2199(1)	13(1)	1
V	0.1842(1)	0.1839(1)	0.5201(1)	12(1)	1
F	0.2808(1)	0.1037(3)	0.5410(2)	18(1)	1
O(1)	0.1656(1)	0.0912(4)	0.3283(2)	18(1)	1
O(2)	0.1593(1)	0.3927(4)	0.1646(3)	21(1)	1
O(3)	0.1787(1)	0.0714(4)	0.0744(3)	18(1)	1
O(4)	0.2717(1)	0.2252(4)	0.2851(3)	19(1)	1
O(5)	0.1183(1)	0.2580(4)	0.5157(3)	25(1)	1
N(1)	0.1317(1)	0.3021(5)	-0.1583(4)	24(1)	1
C(1)	0.0646(2)	0.3025(7)	-0.1773(6)	42(1)	1
C(2)	0.0344(2)	0.1241(8)	-0.2422(8)	73(1)	1
C(3)	0.0343(2)	0.4709(8)	-0.2472(7)	62(1)	1
H(I)	0.1733	0.4391	0.1089	31	1
H(1A)	0.1370	0.2823	-0.2386	37	1
H(1B)	0.1501	0.2141	-0.0999	37	1
H(1C)	0.1479	0.4096	-0.1252	37	1
H(1)	0.0612	0.3050	-0.0853	63	1
H(2A)	-0.0543	0.0302	-0.1871	109	1
H(2B)	0.0390	0.1218	-0.3317	109	1
H(3A)	0.0364	0.4754	-0.3393	92	1
H(3B)	0.0552	0.5775	-0.1978	92	1

Table S2. Fractional atomic coordinates and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **2**.



Conditions	Catalyst	Conv. (%) (h.)	Select. (%)[a]
1% cat., r.t., H_2O_2 (2.5 mmol)	Phase 1	100 (4.5)	18
1% cat., r.t., H_2O_2 (1.1 + 1 mmol)	Phase 1	90 (2)	90
1% cat., r.t., H_2O_2 (2.5 mmol)	Phase 2	90 (6)	0

*Blank tests achieved conversions lower than 3 per cent with H_2O_2.[a]Selectivity referred to the sulfoxides.

Table S3. Oxidation of methylphenyl sulphide by phases **1** and **2**.*

Conditions	Time (h)	Conv. (%)	Furanes	Pyranes	F/P
R.T.	24	45	33	12	2.7
60 ºC	24	63	47	16	2.9

Table S4. Oxidation of Linalool catalyzed by phase **1.**

	Phase 1	**Phase 2**
Empiric Formula	$C_3NH_9VOAsO_4F$	$C_3NH_9VOAsO_4$ F
Formula Weight (g/mol)	283.97	283.97
Crystal System	Monoclinic	Monoclinic
Space Group (Nº15)	C2/c	C2/c
a, Å	21.065(2)	23.025(1)
b, Å	7.2717(4)	7.322(1)
c, Å	10.396(1)	10.344(1)
β, º	104.290(8)	109.250(6)
V, Å^3	1543.2(2)	1646.5(2)
Z	8	8
ρ_{obs}, ρ_{calc}, gr/cm^3	2.40(3), 2.445	2.27(2), 2.29
F(000)	1112	1112
μ, mm^{-1}	5.54	5.19
Radiation, λ(Mo Kα), Å	0.71073	0.71073
Collected reflections	9114	7607
Independent reflections	1698	2710
Intervale h, k, l	h±27,k± 9, l±11	-33<h<30 ,k± 10, l±15
Completeness	θ=26, 0.966	θ=32.46, 0.913 θ=26, 0.997
R (int)	0.05	0.05
R [I>2σ(I)]	R1=0.0405 R2=0.0854	R1=0.0387 R2=0.0836
R [All data]	R1=0.0640 wR2=0.0898	R1=0.0781 wR2=0.0889
Δ_{pmax} y Δ_{pmin}, e.Å^{-3}	1.266, -0.980	1.779, -0.694
G. O. F	0.947	0.859

Table S5.- Crystal data, details of data collection, and structure refinement for $(C_6N_2H_{16})_{0.5}[(VO)(HAsO_4)F]$ **1** and **2**

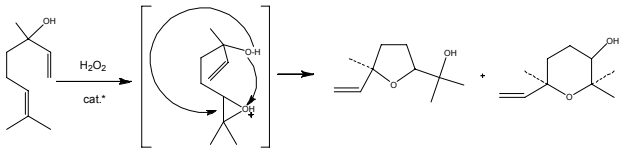


Fig. S1.- Schematically representation of linalool oxidation.

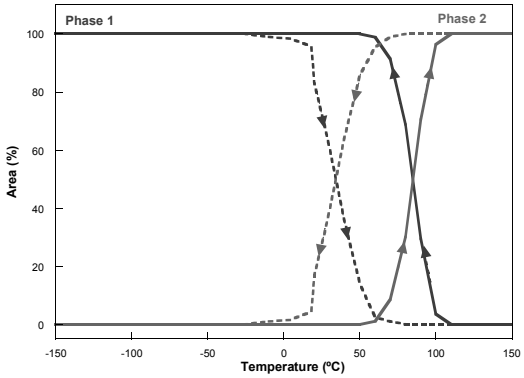


Fig. S2.- Stability diagram of **1** and **2,** as a function of the integrated area of the (200) reflection.

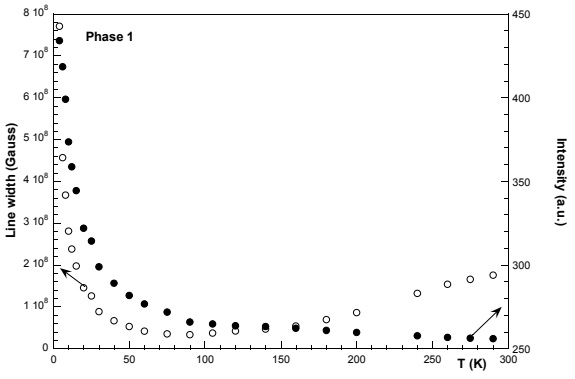


Fig. S3.- Thermal evolution of the line-width and the intensity of the ESR signals for **1**.