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SUPPLEMENTARY MATERIAL FOR

Titanium-(IV)-(R,R,R)-*tris*(2-phenylethoxy)amine-alkylperoxo complex Mediated Oxidations: The Biphilic Nature of the Oxygen Transfer to Organic Sulfur Compounds

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Table S1. $\log(k_X/k_H)$ for the oxidation of *p*-substituted thioanisoles and *p*-substituted phenylmethyl sulfoxides by **2**.

p-X	$\log(k_X/k_H)^b$	$\log(k_X/k_H)^c$	$\log(k_X/k_H)^d$	$\log(k_X/k_H)^e$	σ_p
NMe_2	-	0.12	0.10	0.10	-0.83
OMe	0.28	0.05	0.02	0.04	-0.28
Me	0.12	0.002	0.007	0.06	-0.14
Cl	0.03	0.16	0.13	0.12	+0.24
CN	-	0.30	0.30	0.06	+0.70
NO_2	0.44	-	-	-	+0.81

a) $\log(k_X/k_H)$ values were determined in competitive oxidations performed in the presence of equal amounts of the two substrates. Yields of final products were determined by quantitative G.C. analysis.

b) $[p\text{-X-}C_6H_4SMe]_o=[PhSMe]_o$ =0.1M, $[CumOOH]_o=5.4\times10^{-2}$ M, $[\mathbf{1}]_o=5.4\times10^{-3}$ M in DCE at -20°C, *rho*=-0.60, *r*=0.984.

c) $[p\text{-X-}C_6H_4SOMe]_o=[PhSOMe]_o$=0.5M, $[CumOOH]_o=5.4\times10^{-2}$ M, $[\mathbf{1}]_o=5.4\times10^{-3}$ M in DCE at -20°C, *rho* ($\sigma<0$) = -0.15, *r*=0.980, *rho* ($\sigma>0$) = +0.43, *r*=0.980.

d) $[p\text{-X-}C_6H_4SOMe]_o=[PhSOMe]_o$=0.5M, $[CumOOH]_o=[\mathbf{1}]_o=5.4\times10^{-2}$ M in DCE at -20°C. *rho* = +0.45, *r*=0.997

e) $[p\text{-X-}C_6H_4SOMe]_o=[PhSOMe]_o$=0.5M, $[CumOOH]_o=5.4\times10^{-2}$ M, $[\mathbf{1}]_o=5.4\times10^{-2}$ M in HMPA:DCE =1:1 at -20°C, *rho* ≈ 0.

Table S2. Kinetic data for the *mono*-oxidation of methyl *p*-tolyl sulfide by **2**.[a]

[Substate], M	Ro, M sec^{-1}
0.00[b]	0.00[b]
0.33	$4.7\ 10^{-5}$
0.55	$6.4\ 10^{-5}$
0.83	$1.20\ 10^{-4}$
1.10	$1.40\ 10^{-4}$

a. In all the experiments [CumOOH]=[**1**]=0.054M in DCE at -20°C.

b. The correlation was constrained to intercept the axes at R_o=0 and $[p\text{-TolSMe}]_o$=0, $k_{Sobs}=1.31\ 10^{-4}\ s^{-1}$, *r*= 0.994.