

Supporting Information

Table S1. Kinetic parameters of the reaction between **1** and O₂ in dichloromethane determined by the integral method

T, °C	k _{1(obs)} , ^a s ⁻¹	d(CH ₂ Cl ₂), g cm ⁻³	[O ₂], mM	k _{2(obs)} , M ⁻¹ s ⁻¹	α(2) ^b
-40	2.08(15) 10 ⁻³	1.442	3.14	0.66(6)	0.9
-50	1.47(10) 10 ⁻³	1.460	3.18	0.46(4)	0.95
-60	9.5(5) 10 ⁻⁴	1.478	3.22	0.30(3)	>0.95
-70	5.2(5) 10 ⁻⁴	1.496	3.25	0.16(2)	>0.95
-80	3.0(3) 10 ⁻⁴	1.514	3.29	0.091(9)	>0.95

a – average from the values determined at 640 nm and 420 nm

b – determined from the A_∞ and ε₆₄₀(**2**) = 1100 M⁻¹ cm⁻¹

Table S2. Kinetic parameters of the reaction between **1** and O₂ in dichloromethane determined by the method of initial rates in one series of stopped-flow experiments

T, °C	dA ₆₄₀ /dt ^a	[1] _o , mM	k ₁ , s ⁻¹	[O ₂], mM	k _{2(obs)} , M ⁻¹ s ⁻¹
-50	2.38 10 ⁻⁵	0.152	1.38 10 ⁻³	3.18	0.493
-52.9	1.94.10 ⁻⁴	0.153	1.16 10 ⁻³	3.19	0.399
-58.5	1.56 10 ⁻⁴	0.154	9.23 10 ⁻⁴	3.21	0.316
-63.2	1.29 10 ⁻⁴	0.155	7.59 10 ⁻⁴	3.23	0.258
-68.7	8.92 10 ⁻⁵	0.156	5.21 10 ⁻⁴	3.25	0.176
-73.4	6.72 10 ⁻⁵	0.157	3.91 10 ⁻⁴	3.27	0.131
-78.8	5.13 10 ⁻⁵	0.158	2.96 10 ⁻⁴	3.29	0.099
-80	5.05 10 ⁻⁵	0.158	2.91 10 ⁻⁴	3.29	0.097

a – determined at 640 nm using ε₆₄₀(**2**) = 1100 M⁻¹ cm⁻¹

Table S3. Kinetic parameters of the reaction between **1** and O₂ in different solvents at -40°C

Solvent	ϵ	$k_1(\text{obs}), \text{s}^{-1}$	[O ₂] ^b , mM	$k_2(\text{obs}), \text{M}^{-1} \text{s}^{-1}$	$\alpha(2)$
CH ₂ Cl ₂	10	0.0021	3.14	0.66	0.9
CH ₂ Cl ₂ satur. with H ₂ O at -40°C	-	0.0024	3.14	0.76	0.8
CH ₂ Cl ₂ satur. with D ₂ O at -40°C	-	0.0022	3.14	0.70	0.8
CH ₂ Cl ₂ -MeCN (9:1)	13 ^c	0.0020	3.3 ^c	0.61	0.6
CH ₂ Cl ₂ -MeCN (9:1) with 10 mM H ₂ O	-	0.0025	3.3 ^c	0.76	0.6
CH ₂ Cl ₂ -MeCN (9:1) with 10 mM D ₂ O	-	0.0022	3.3 ^c	0.67	0.6
Me ₂ CO	20	0.0035	6.0	0.6	0.2
MeCN	36	0.010	4.2	2.4	0.25

a – calculated from the rate of absorbance change at 640 nm using $\epsilon_{640}(2) = 1100 \text{ M}^{-1} \text{ cm}^{-1}$

b – corrected for the contraction of solvent from room temperature to -40°C (corrections for MeCN and Me₂CO are assumed to be 8%, the average value for other solvents; see text)

c – assuming linear behavior of the CH₂Cl₂ – MeCN mixture

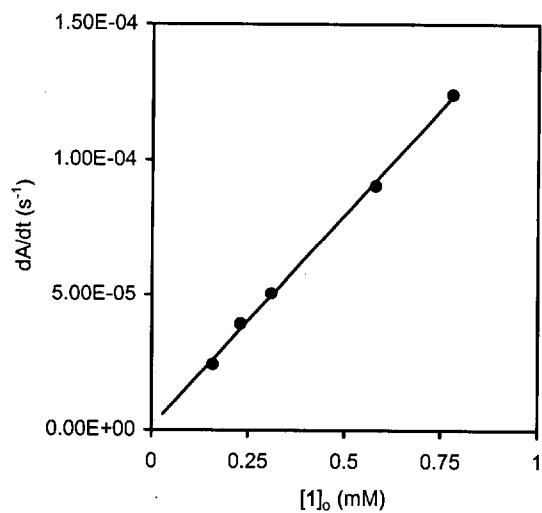


Fig. S1 Initial rate of optical absorbance increase at 640 nm vs the starting concentration of **1** during its oxygenation in dichloromethane at -50°C ; $[\text{O}_2]_o = 3.18 \text{ mM}$.

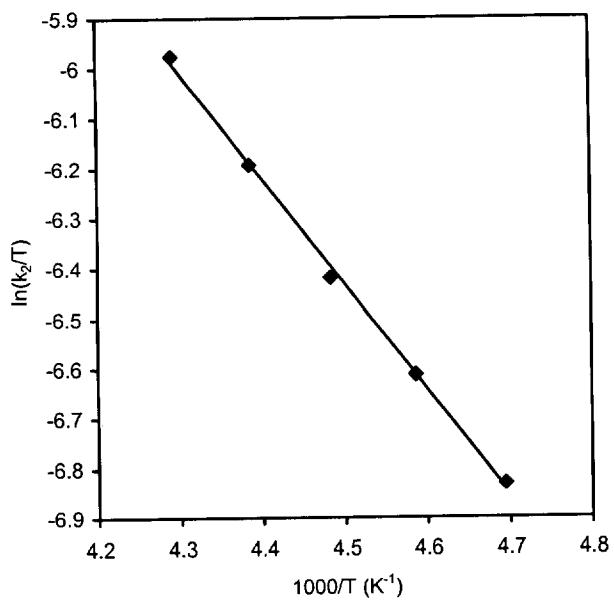


Fig. S2 Eyring plot for the reaction of **1** (0.2 mM) with excess O₂ (\approx 3.3 mM) in the dichloromethane – acetonitrile mixture (9:1 by volume) giving $\Delta H^\ddagger = 17.5 \pm 2$ kJ mol⁻¹ and $\Delta S^\ddagger = -172 \pm 20$ J mol⁻¹ K⁻¹.

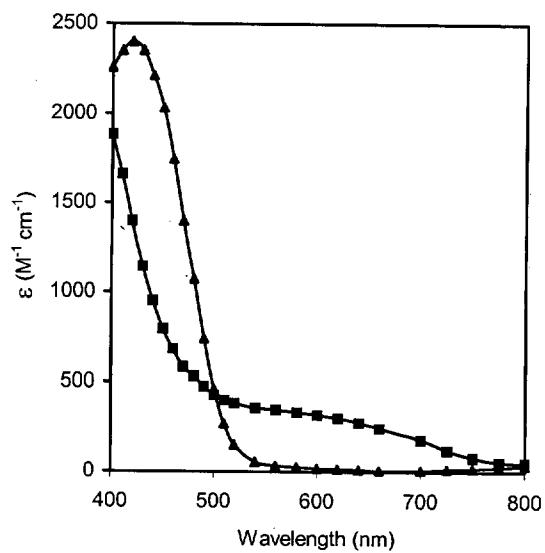


Fig. S3 Optical spectra of **1** (triangles) and the reaction mixture upon its oxygenation in acetone at -50°C (squares) obtained by stopped-flow spectrophotometry.

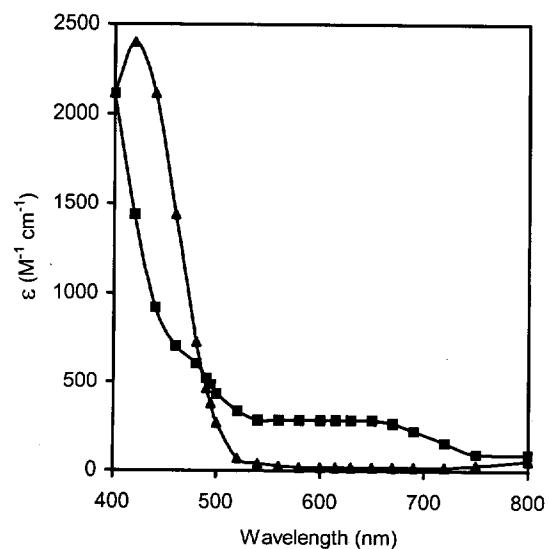


Fig. S4 Optical spectra of **1** (triangles) and the reaction mixture upon its oxygenation in acetonitrile at -40°C (squares) obtained by stopped-flow spectrophotometry.

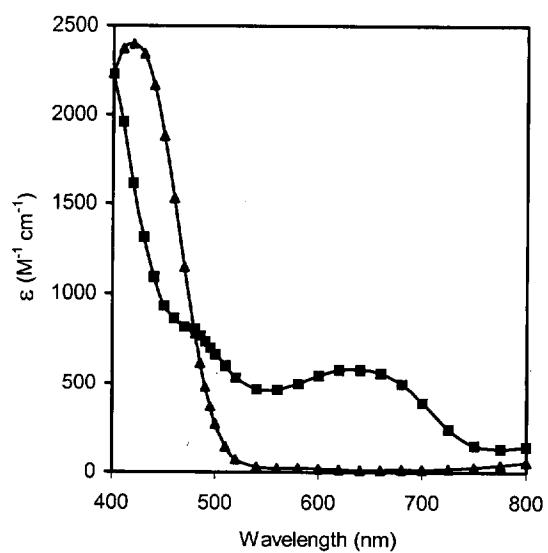


Fig. S5 Optical spectra of **1** (triangles) and the reaction mixture upon its oxygenation in dichloromethane – acetonitrile mixture (9:1 by volume) at -50°C (squares) obtained by stopped-flow spectrophotometry.

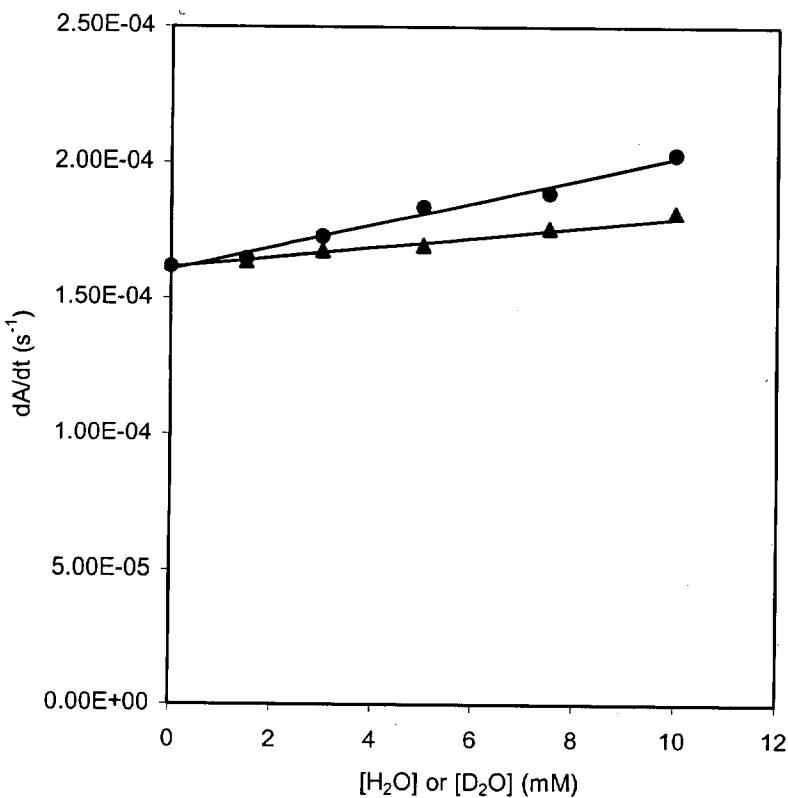


Fig. S6 Influence of H_2O (circles) and D_2O (triangles) on the rate of oxygenation of **1** in the dichloromethane – acetonitrile mixture (9:1 by volume) at $-50^\circ C$, measured as the rate of absorbance increase at 640 nm; $[1]_o = 0.20$ mM; $[O_2] \approx 3.3$ mM.

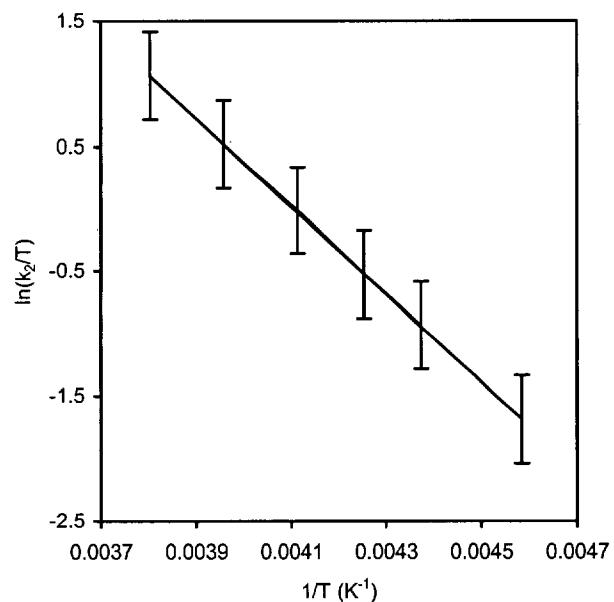


Fig. S7 Eyring plot for the reaction of ca 0.55 mM **1** with ca 2.5 - 5 mM NO in dichloromethane based on second-order rate constants calculated from integral kinetic data. The uncertainty in $[\text{NO}]_0$ is represented by vertical bars.