

## SUPPORTING INFORMATION

### **Unveiling Non-Covalent Interactions in Novel Cooperative Photoredox Systems for Efficient Alkene Oxidation in Water**

*Isabel Guerrero,<sup>a</sup> Clara Viñas,<sup>a</sup> Francesc Teixidor<sup>a\*</sup> and Isabel Romero,<sup>b\*</sup>*

<sup>a</sup>Institut de Ciència de Materials de Barcelona, ICMA-B-CSIC, Campus UAB, E-08193 Bellaterra, Spain.  
and Serveis Tècnics de Recerca, Universitat de Girona, C/ M. Aurèlia Campmany, 69, E-17003 Girona, Spain.

<sup>b</sup>Departament de Química and Serveis Tècnics de Recerca, Universitat de Girona, C/ M. Aurèlia Campmany, 69, E-17003 Girona, Spain.

\*Correspondence to: marisa.romero@udg.edu; teixidor@icmab.es;

## TABLE OF CONTENTS

**Figure S1.** IR spectrum of **Ag[Cl<sub>6</sub>-1]**.

**Figure S2.** IR spectrum of **5**.

**Figure S3.** a) <sup>1</sup>H{<sup>11</sup>B}-NMR and b) <sup>11</sup>B{<sup>1</sup>H}-NMR spectra of **Ag[Cl<sub>6</sub>-1]** compound in acetone-d<sub>6</sub>.

**Figure S4.** a) <sup>1</sup>H-NMR; b) <sup>1</sup>H{<sup>11</sup>B}-NMR; c) <sup>11</sup>B{<sup>1</sup>H}-NMR d) <sup>11</sup>B-NMR and e) COSY NMR spectra of **5**. compound in acetone-d<sub>6</sub>.

**Figure S5.** UV-visible of **Ag[Cl<sub>6</sub>-1]** compound in CH<sub>2</sub>Cl<sub>2</sub>.

**Figure S6.** CV of a) **Ag[Cl<sub>6</sub>-1]** compound in CH<sub>3</sub>CN + 0.1 M TBAH vs Ag/AgCl; b) **5** in CH<sub>3</sub>CN + 0.1 M TBAH vs Ag/AgCl; and c) **5** in a phosphate buffer (pH = 7.12) vs Ag/AgCl; scan rate V= 100 mV/s.

**Figure S7.** Plot of conversion as a function of time for the photoredox catalysis of styrene. Conditions: **4** (0.01 mM), styrene (20 mM), Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (26 mM), 5 ml aqueous solution at pH=7, light irradiation (2.2 W, λ~300 nm).

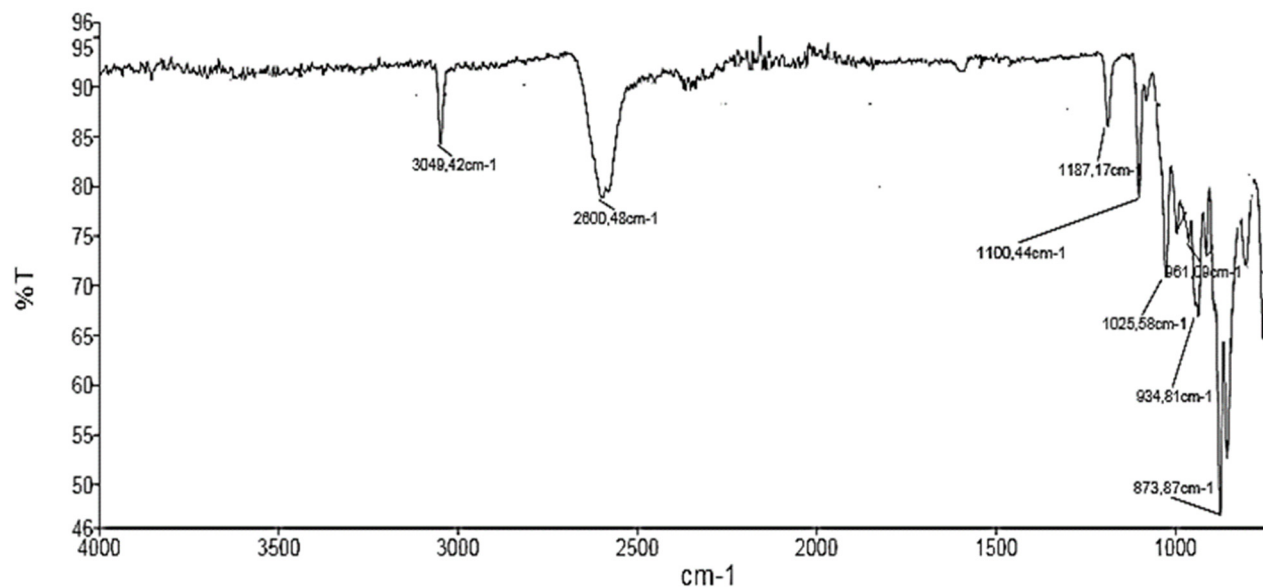
**Figure S8.** ESI-MS spectra of **5**.

**Table S1.** Photooxidation tests performed with complex **4**. Conditions: **4** (0.01 mM), substrate (20 mM), Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (26 mM), 5 mL aqueous solution at pH=7.

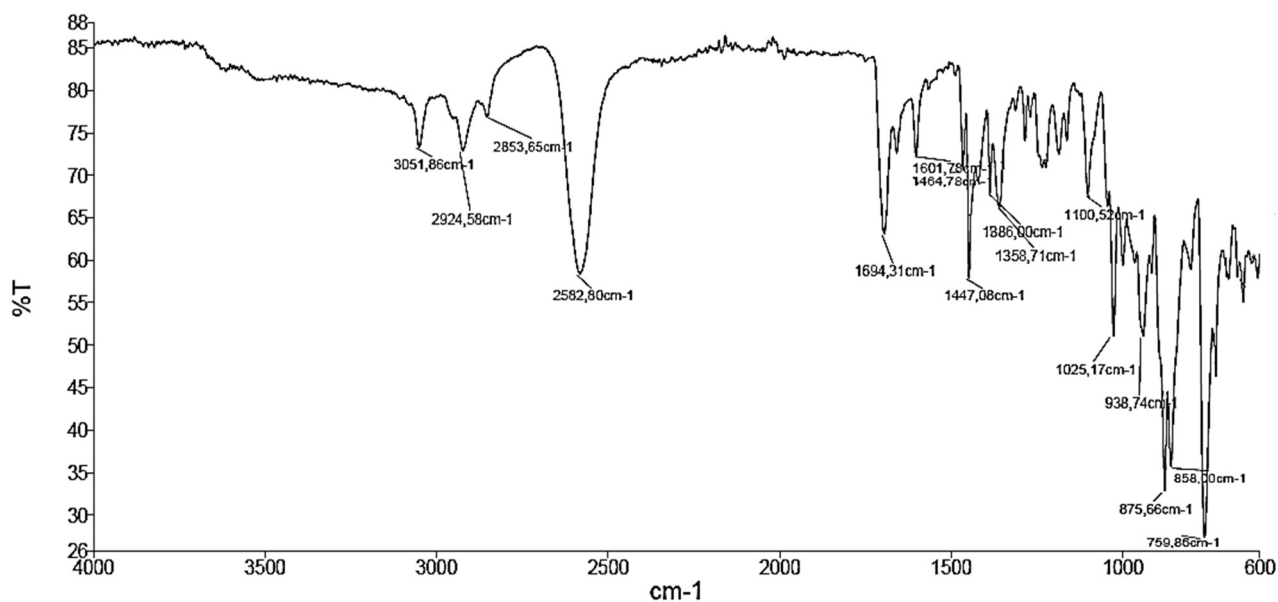
**Table S2.** Photooxidation of epoxides performed with complex **4**. Conditions: **4** (0.01 mM), epoxide (20 mM), Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (26 mM), 5 mL aqueous solution at pH=7.

**Table S3.** Photooxidation tests performed with **5** complex. Conditions: **5** (0.001 mM), substrate (20 mM), Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (26 mM), 5 mL aqueous solution at pH=7.

**Figure S1.** IR spectrum of Ag[Cl<sub>6</sub>-1].

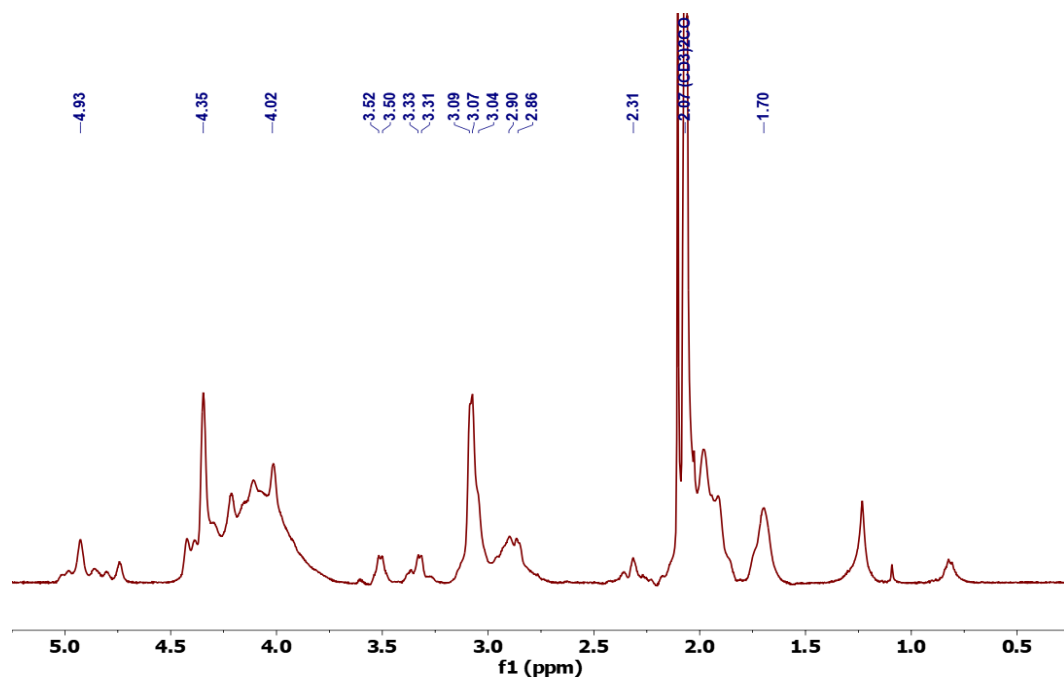


**Figure S2.** IR spectrum of **5**.

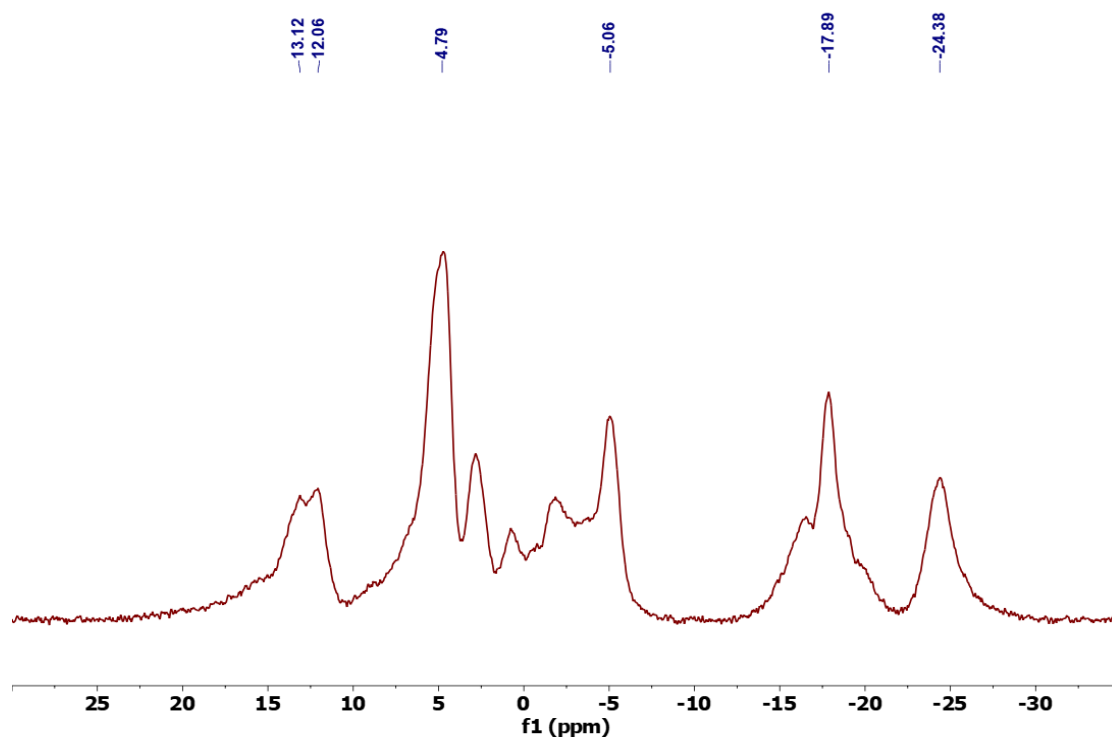


**Figure S3.** a)  $^1\text{H}\{^{11}\text{B}\}$ -NMR and b)  $^{11}\text{B}\{^1\text{H}\}$ -NMR spectra of  $\text{Ag}[\text{Cl}_6\text{-1}]$  compound in acetone- $\text{d}_6$ .

a)

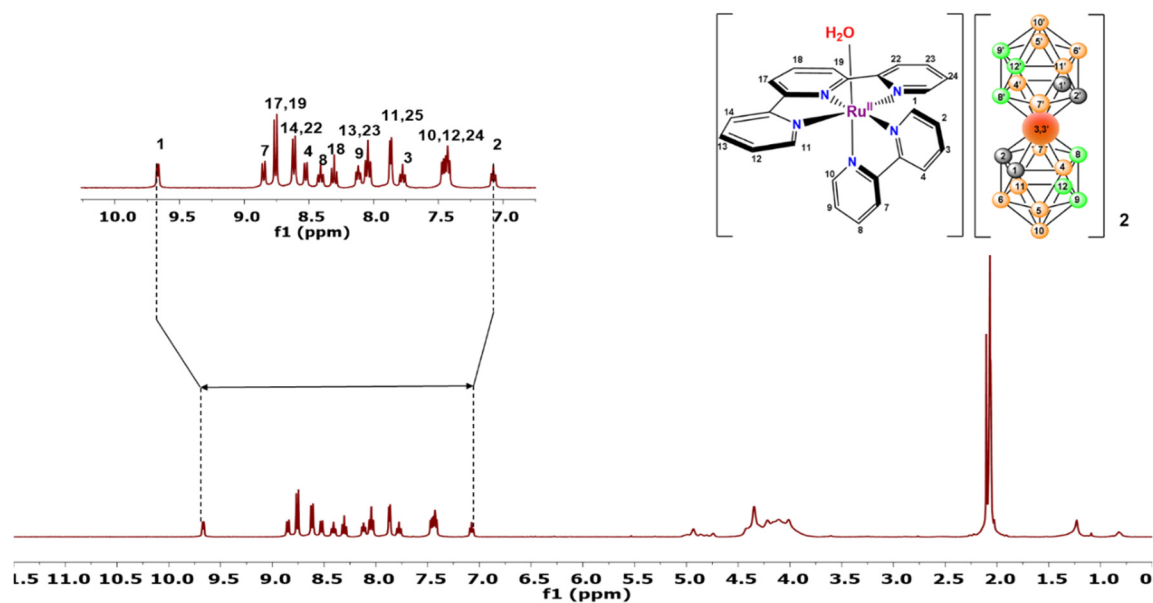


b)

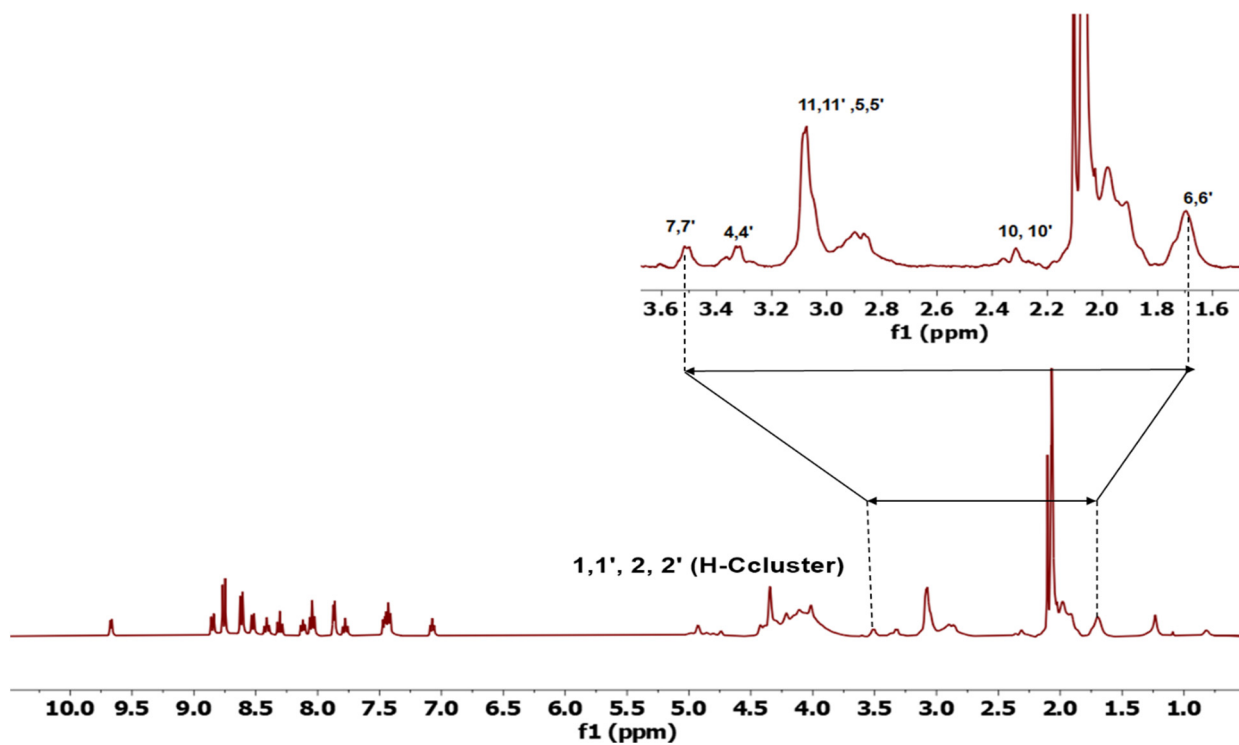


**Figure S4.** a)  $^1\text{H}$ -NMR; b)  $^1\text{H}\{^{11}\text{B}\}$ -NMR; c)  $^{11}\text{B}\{^1\text{H}\}$ -NMR d)  $^{11}\text{B}$ -NMR and e) COSY NMR spectra of **5**. compound in acetone- $\text{d}_6$ .

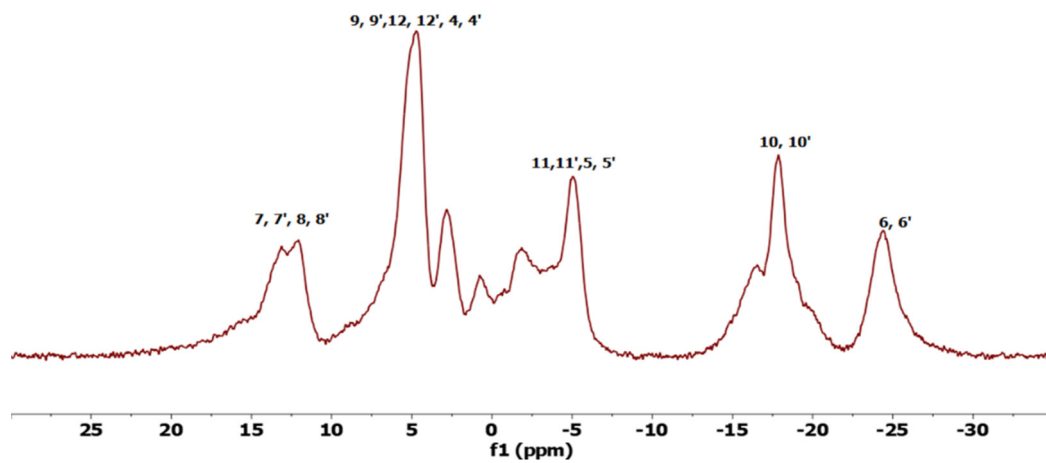
a)



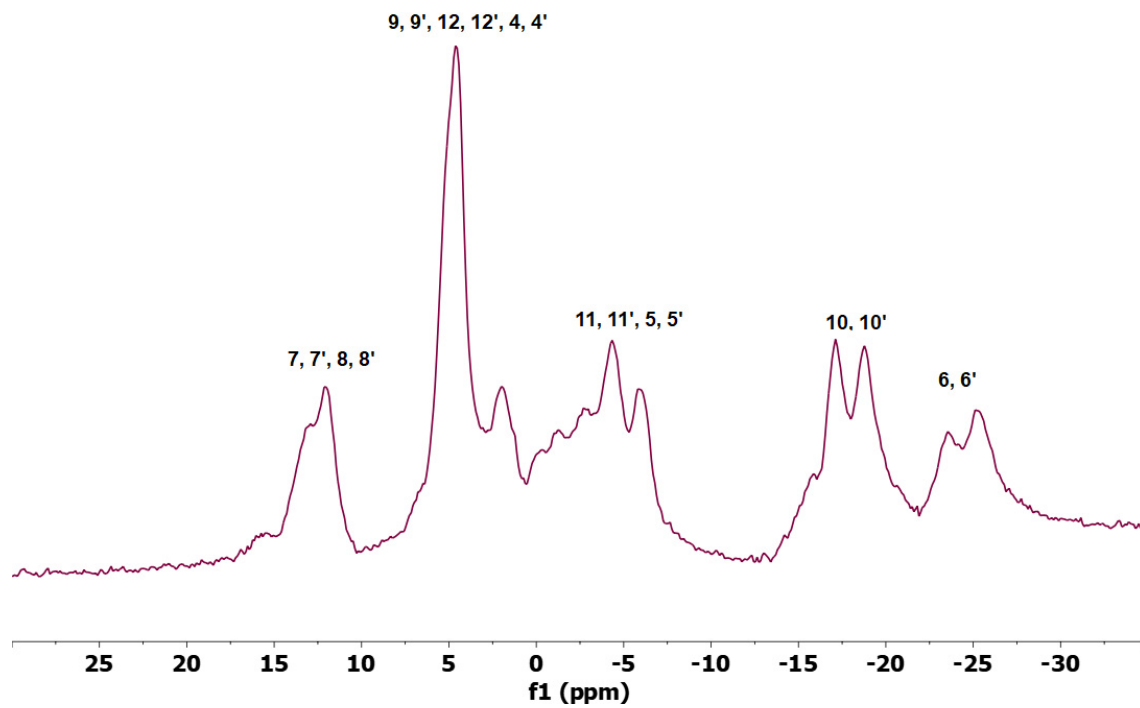
b)



c)



d)



e)

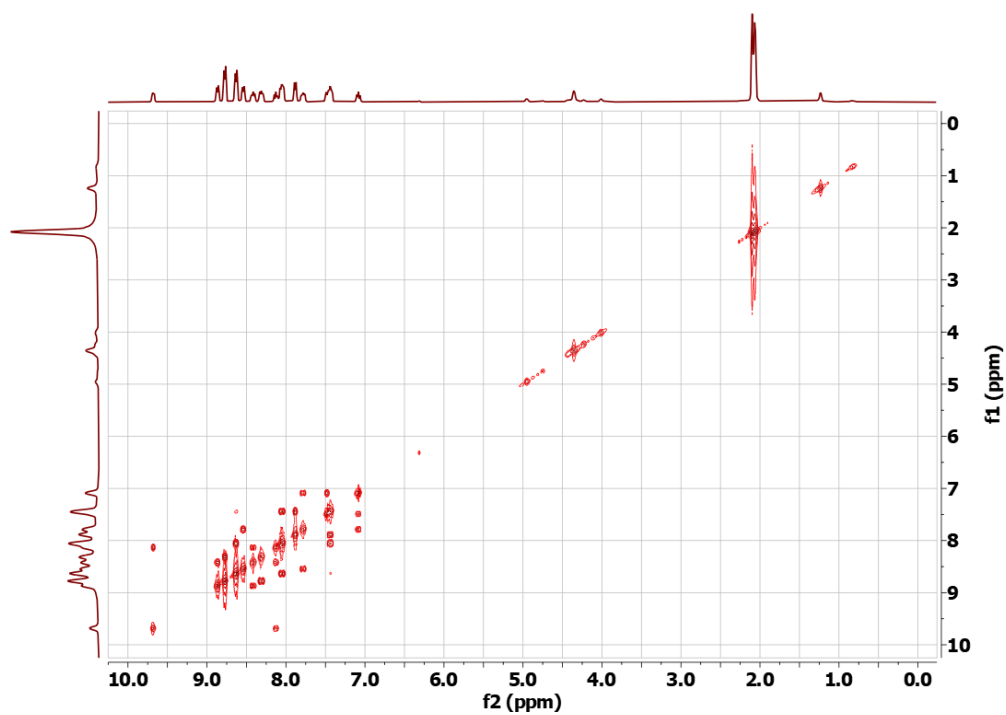
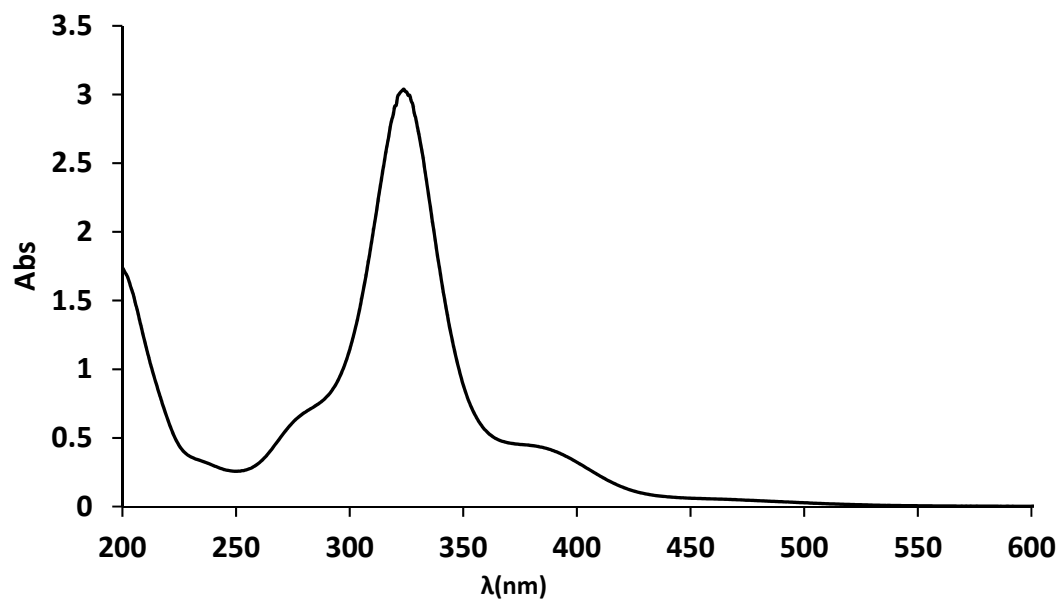
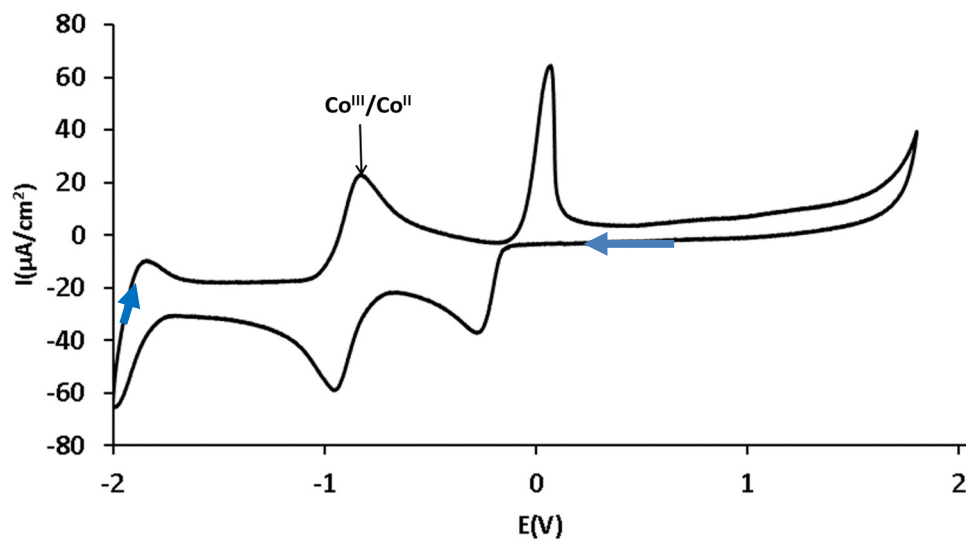


Figure S5. UV-visible of  $\text{Ag}[\text{Cl}_6\text{-1}]$  compound in  $\text{CH}_2\text{Cl}_2$ .

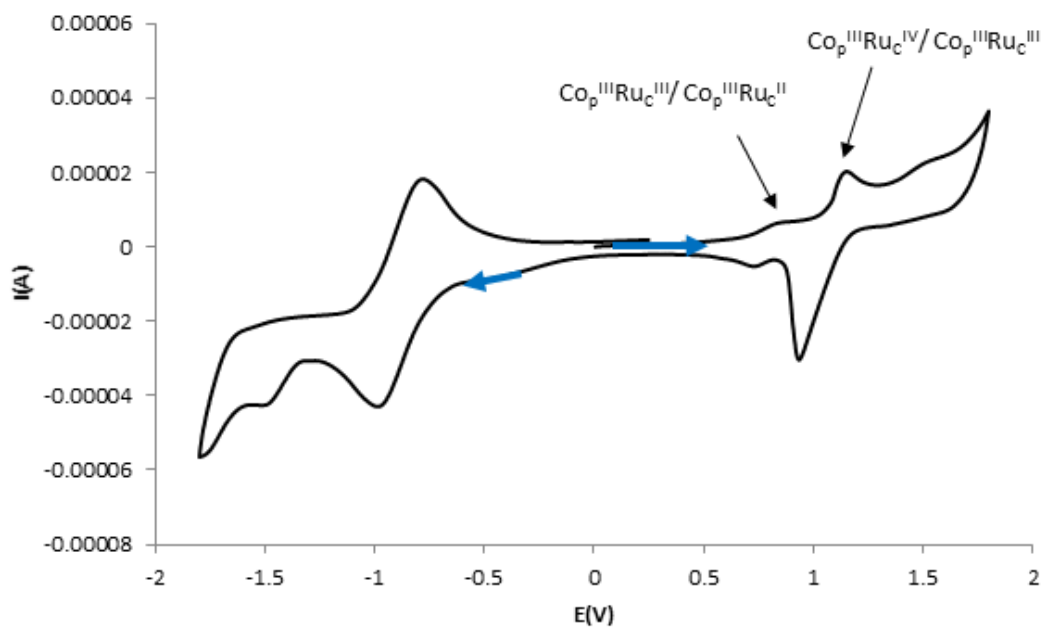


**Figure S6.** CV of a) **Ag[Cl<sub>6</sub>-1]** compound in CH<sub>3</sub>CN + 0.1 M TBAH vs Ag/AgCl; b) **5** in CH<sub>3</sub>CN + 0.1 M TBAH vs Ag/AgCl; and c) **5** in a phosphate buffer (pH = 7.12) vs Ag/AgCl; scan rate V= 100 mV/s.

a)

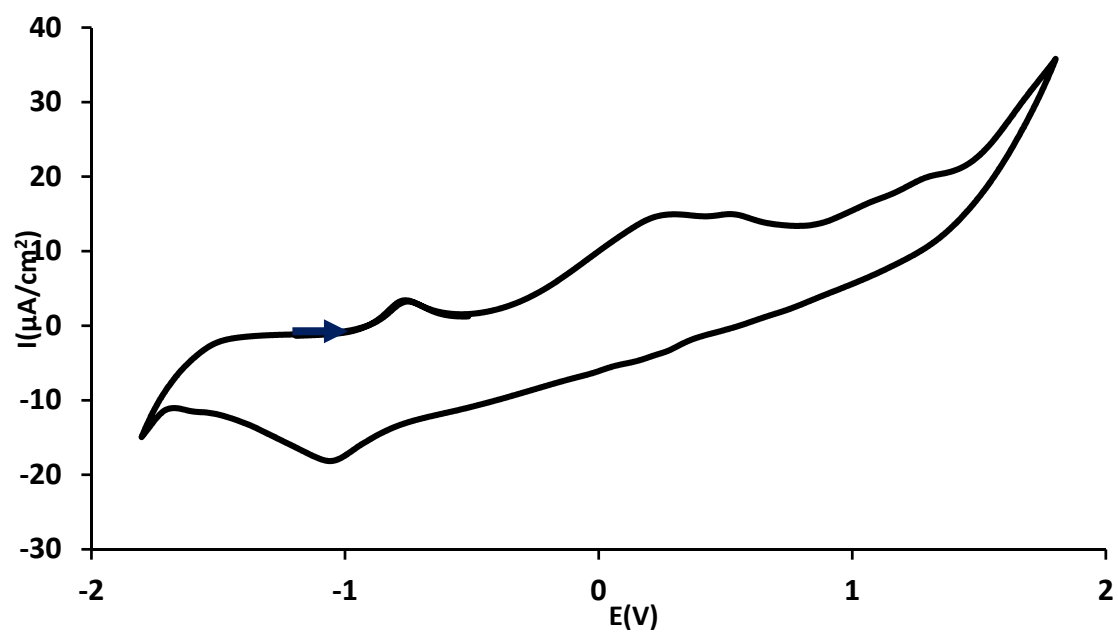


b)

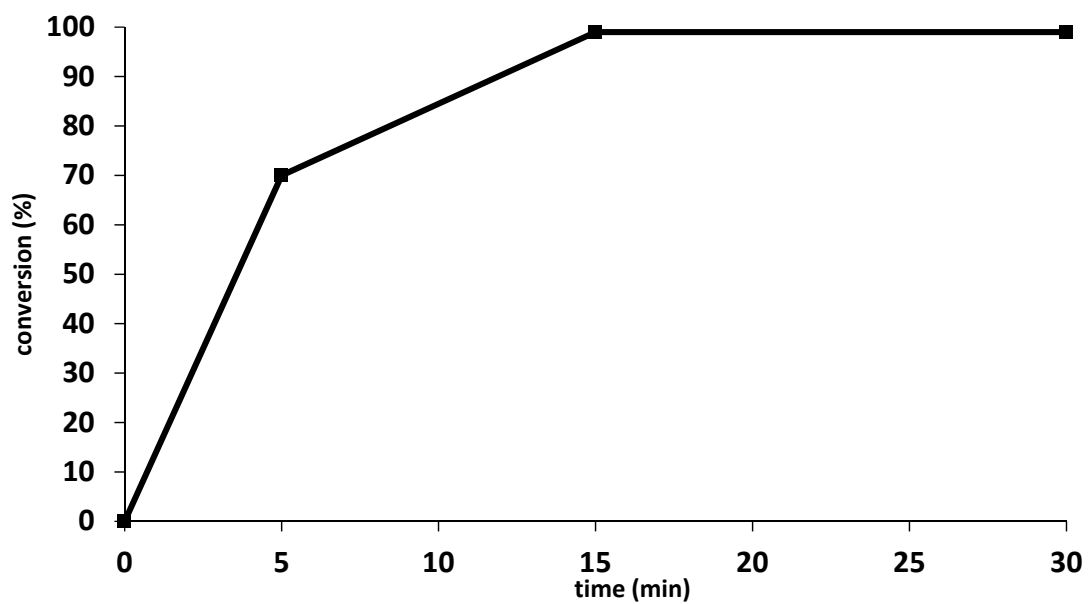




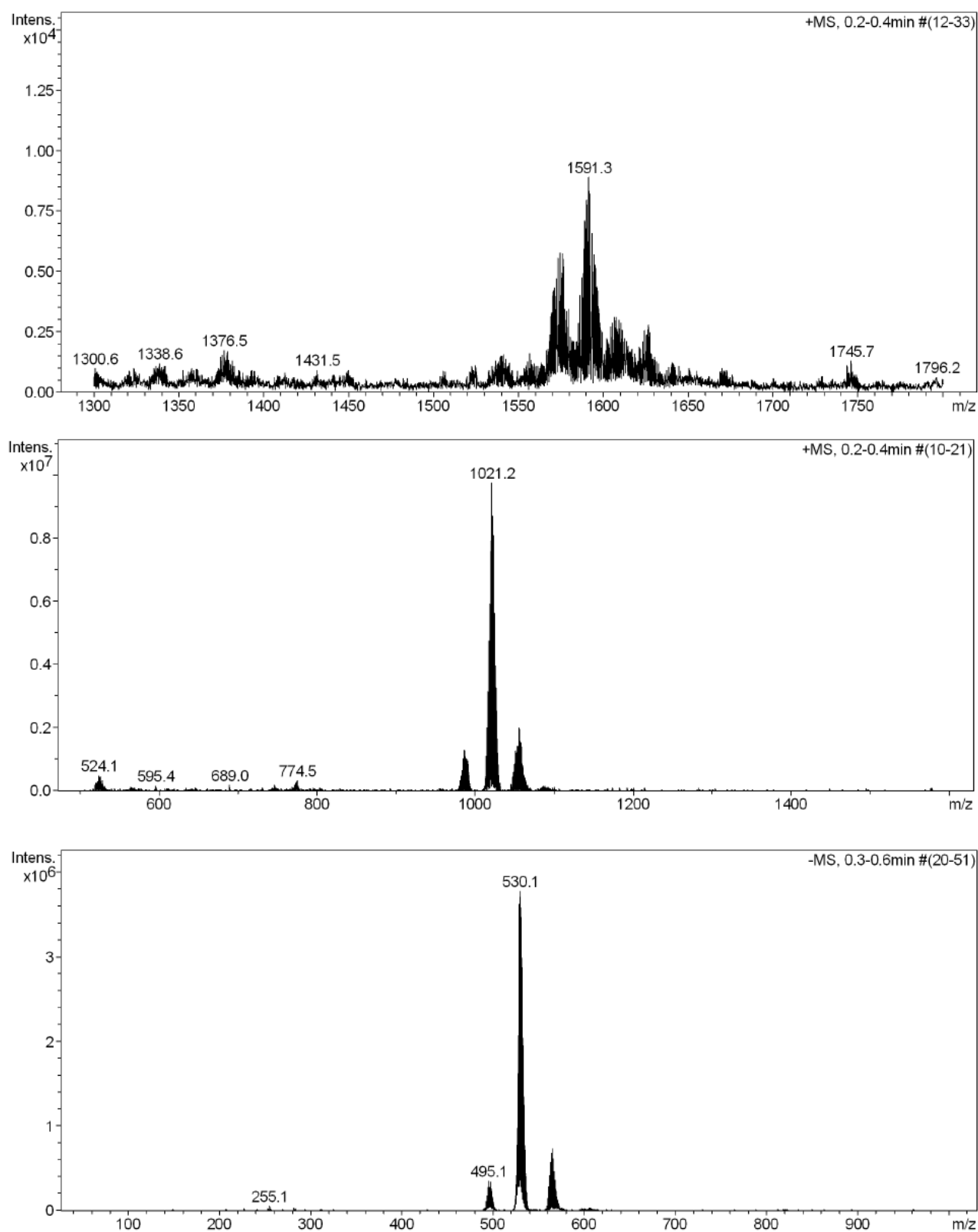
c)



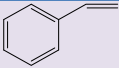
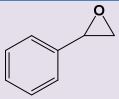
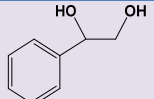

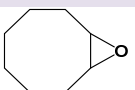
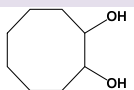
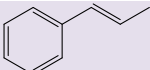
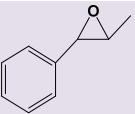
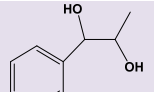
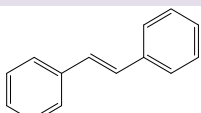
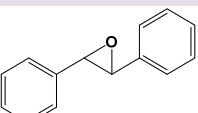
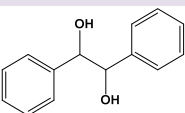
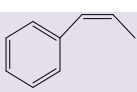
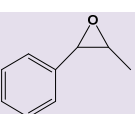
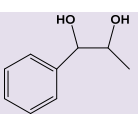
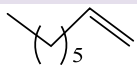

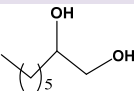
**Figure S7.** Plot of conversion as a function of time for the photoredox catalysis of styrene. Conditions: **4** (0.01 mM), styrene (20 mM), Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (26 mM), 5 ml aqueous solution at pH=7, light irradiation (2.2 W,  $\lambda$  ~300 nm).



**Figure S8.** ESI-MS spectra of **5**.


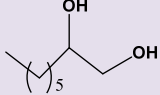
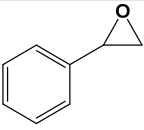
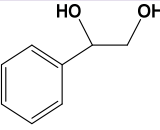
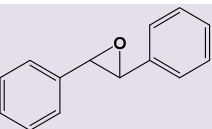
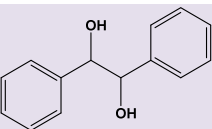


**Table S1.** Photooxidation tests performed with **4** complex.

Entry	substrate	Conv.%		Yield.(selec.)%		Yield(selec.)%	
1		70 <sup>[a]</sup> 1		67(96) <sup>[a]</sup>		1(1) <sup>[a]</sup>	
		≥99 <sup>[b]</sup> 1		57(57) <sup>[b]</sup>		35(35) <sup>[b]</sup>	
2		≥99 <sup>[b]</sup>		67(67) <sup>[b]</sup>		33(33) <sup>[b]</sup>	
		≥99 <sup>[c]</sup>		55(55) <sup>[c]</sup>		45(43) <sup>[c]</sup>	
3		96 <sup>[b]</sup>		76(79) <sup>[b]</sup>		20(21) <sup>[b]</sup>	
		≥99 <sup>[c]</sup>		69(69) <sup>[c]</sup>		31(31) <sup>[c]</sup>	
4		89 <sup>[b]</sup>		85(96) <sup>[b]</sup>		4(5) <sup>[b]</sup>	
		97 <sup>[c]</sup>		52(54) <sup>[c]</sup>		45(46) <sup>[c]</sup>	
5		≥99 <sup>[b]</sup>		91[59/32, cis/trans](91 <sup>2</sup> ) <sup>[b]</sup>		9(9) <sup>[b]</sup>	
		≥99 <sup>[c]</sup>		60[36/24, cis/trans](60 <sup>2</sup> ) <sup>[c]</sup>		40(40) <sup>[c]</sup>	
7		≥99 <sup>[b]</sup>		65(65) <sup>[b]</sup>		15(15) <sup>[b]</sup>	Other products
		≥99 <sup>[c]</sup>		39(39) <sup>[c]</sup>		24(24) <sup>[c]</sup>	20 <sup>4</sup> (20) <sup>[b]</sup>
							37 <sup>4</sup> (37) <sup>[c]</sup>

Conditions: **4** (0.01 mM), substrate (20 mM), Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (26 mM), 5 mL aqueous solution at pH=7. <sup>[a]</sup> 5 min of reaction <sup>[b]</sup> 15 min of reaction. <sup>[c]</sup> 30 min of reaction. <sup>1</sup> benzaldehyde and benzoic acid produced as another byproducts. <sup>2</sup>selectivity with respect the overall epoxide produced. <sup>3</sup>yield with diol and benzoic acid from vinyl produced. <sup>4</sup>octanal and octanoic produced.

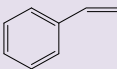
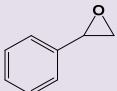
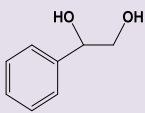

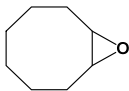
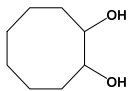
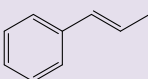
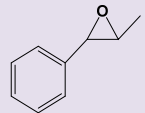
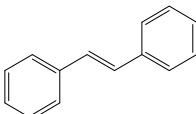
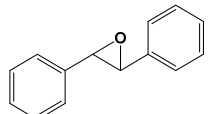
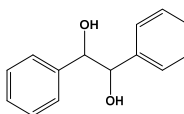
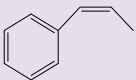
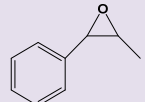
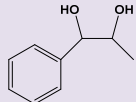
**Table S2.** Photooxidation of epoxides performed with complex **4**.

Entry	substrate	Conv.%	Product	Yield(select.)%
<b>1</b>		$\geq 99^{[a]}$		90(90) <sup>[a]</sup>
		$\geq 99^{[b]}$		60(60) <sup>[b]</sup>
<b>2</b>		$\geq 99^{[a]}$		55(55) <sup>[b]</sup>
		$\geq 99^{[b]}$		65(65) <sup>*[c]</sup>
<b>3</b>		97 <sup>[a]</sup>		97( $\geq 99$ ) <sup>[b]</sup>
		$\geq 99^{[b]}$		$\geq 99(\geq 99)^{[c]}$

Conditions: **4** (0.01 mM), substrate (20 mM), Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (26 mM), 5 mL aqueous solution at pH=7.

<sup>[a]</sup>15 min of reaction <sup>[b]</sup>30 min of reaction. Yield and selectivity with respect the overall diol produced.\* [ [yield (selectivity)] with respect the obtention of benzaldehyde and benzoic acid.

**Table S3.** Photooxidation tests performed with **5** complex.

Entry	substrate	Conv.%		Yield.(selec.)%		Yield(selec.)%
1		75 <sup>[a]</sup> <sup>1</sup>		23(31) <sup>[a]</sup>		38(51) <sup>[a]</sup>
2		92 <sup>[a]</sup> 96 <sup>[b]</sup>		92(>99) <sup>[a]</sup> 53(55) <sup>[b]</sup>		43(45) <sup>[b]</sup>
3		87 <sup>[b]</sup>		87(>99) <sup>[b]</sup>		
4		>99 <sup>[a]</sup> >99 <sup>[b]</sup>		86(86) <sup>[a]</sup> 83(83) <sup>[b]</sup>		14(14) <sup>[a]</sup> 17(17) <sup>[b]</sup>
5		88 <sup>[a]</sup> 89 <sup>[b]</sup>		50[50, trans](57) <sup>[a]</sup> 50[51, trans](57) <sup>[b]</sup>		38(43) <sup>[a]</sup> 37 (42) <sup>[b]</sup>

Conditions: **5** (0.001 mM), substrate (20 mM), Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (26 mM), 5 mL aqueous solution at pH=7. <sup>[a]</sup> 15 min of reaction. <sup>[b]</sup> 30 min of reaction. <sup>1</sup> benzaldehyde and benzoic acid produced as another byproducts.