SUPPORTING INFORMATION

A Stand-Alone Cobalt bis(dicarbollide) Photoredox Catalyst Epoxidates Alkenes in Water at Extremely Low Catalyst Load

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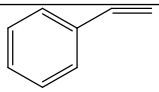
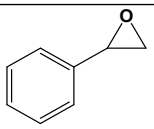
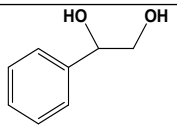
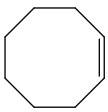
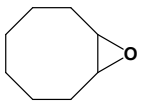
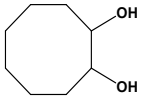
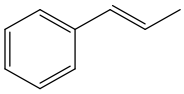
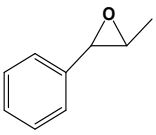
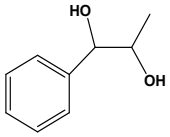
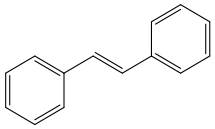
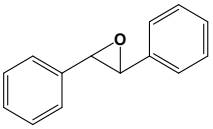
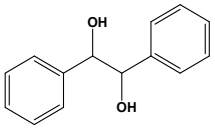
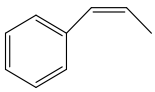
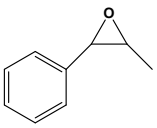
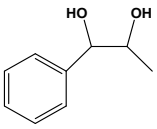
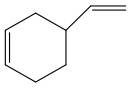
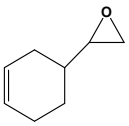
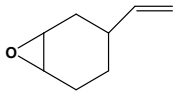
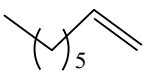
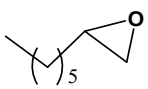
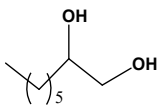
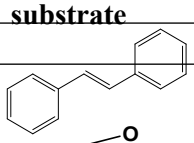
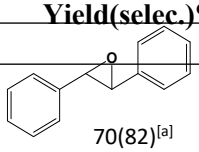
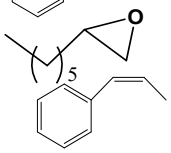
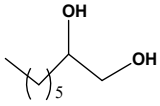
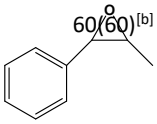
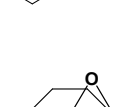
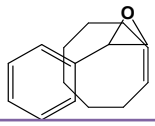
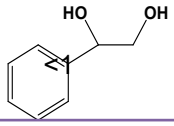
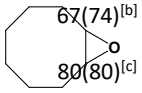
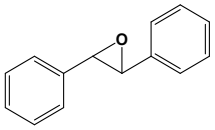
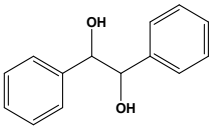
Entry	substrate	Conv.%	Yield(selec.)%		Yield.(selec.)%			
1		78[a] 80[b] 96 [c]		37(47)[a] 27(34)[b] 25(26)[c]		23(29)[a] 35(44)[b] 50(52)[c	Other products	18(23)[a]1 18(23)[b]1 21(22)[c]1
2		91[b] ≥99[c]		47(47)[b] 38(42)[c]		53(58)[b] 53(53)[c]		
3		85[b] 91[c]		44(52)[b] 20(22)[c]		41(48)[b] 71(78)[c]		
4		66[b] 95[c]		39(44)[b] 29(41)[c]		37(56)[b] 56(59)[c]		
5		92[b] ≥99 [c]		75[73/2, cis/trans](82[1])[b] 33[16/17, cis/trans](33[1])[c]			17(19)[b] 67(67)[c]	
6		97[b] ≥99 [c]		70(72)[b] 37(37)[c]		8(8)[b] 6(6)[c]	Other products	19[2](19)[b] 57[2](57)[c]
7		81[b] ≥99 [c]		58(72)[b] 16(16)[c]		9(11)[b] 44(44)[c]	Other products	14[3](17)[b] 39[3](39)[c]

Ratio 1:1000:1300: [a] 5 min of reaction [b] 15 min of reaction. [c] 30 min of reaction. [d] 60 min of reaction. [1]selectivity with respect the overall epoxide produced.[2]yield with diol and benzoic acid from vinyl produced. [3]octanal and octanoic produced.

Table S2. Photooxidation of epoxides performed with **Na[1]** complex. Conditions: **Na[1]** (0.02 mM), epoxide (20 mM), $Na_2S_2O_8$ (26 mM), 5 mL of a 0.4 μM in K_2CO_3 solution at pH=7. UV irradiation (2.2 W, λ 300 nm, 12 lamps in the walls of a box)

Entry	substrate	Conv.% Na[1]	Conv.% $[Ru(bpy)_3]^{2+}$	product Yield(selec.)%
1		95	10	 70(82)[a]
1		85[a] ≥99[b]		 60(60)[b]
2		≥99	3	
2		90[a] ≥99[c] ≥99[b]	 <1	 67(74)[b] 80(80)[c]
3		70[b] ≥99[c]		70(≥99)[b] ≥99(≥99)[c]

Ratio 1:1000:1300: [a]15 min of reaction [b]30 min of reaction. Yield and selectivity with respect the overall diol produced.

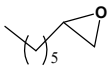
4		≥99[c]	<1		

Table S3. Photooxidation tests performed with **Na[1]** and $[Ru(bpy)_3]^{2+}$ complexes.

Conditions: **Na[1]** or $[Ru(bpy)_3]^{2+}$ (0.02 mM), substrate (20 mM), $Na_2S_2O_8$ (26 mM), 5 mL of a 0.4 μM in K_2CO_3 solution at pH=7. Ratio 1:1000:1300. After 30 min of reaction. UV irradiation (2.2 W, λ 300 nm, 12 lamps in the walls of a box)

Figure S1. Plot of conversion as a function of time for the photoredox catalysis of styrene. Conditions: $Na[3,3'\text{-}Co(1,2\text{-}C_2B_9H_{11})_2]$ (0.02 mM), styrene (20 mM), $Na_2S_2O_8$ (26 mM), 5 mL of water (0.4 μM in K_2CO_3 solution at pH=7), light irradiation (2.2 W, λ 300 nm, 12 lamps in the walls of a box)

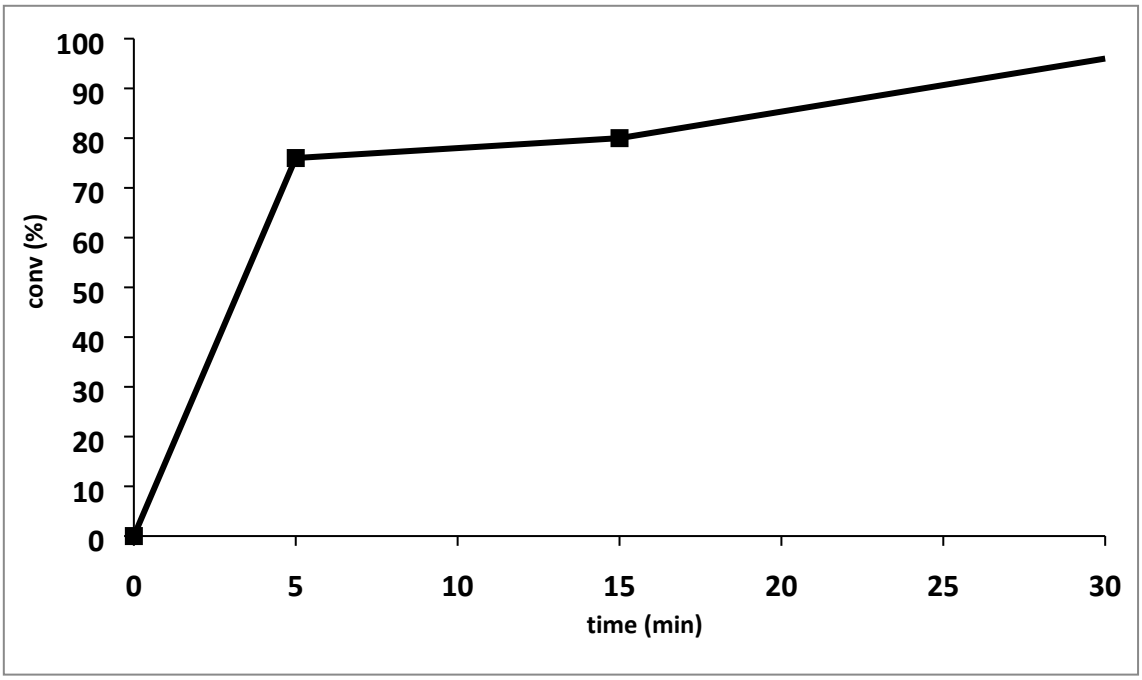


Figure S2. Plot of TON of styrene as a function of pH. Conditions: Na[3,3'-Co(1,2-$C_2B_9H_{11})_2$] (0.02 mM), styrene (20 mM), $Na_2S_2O_8$ (26 mM), 5 mL of water, light irradiation (2.2 W, λ 300 nm, 12 lamps in the walls of a box)

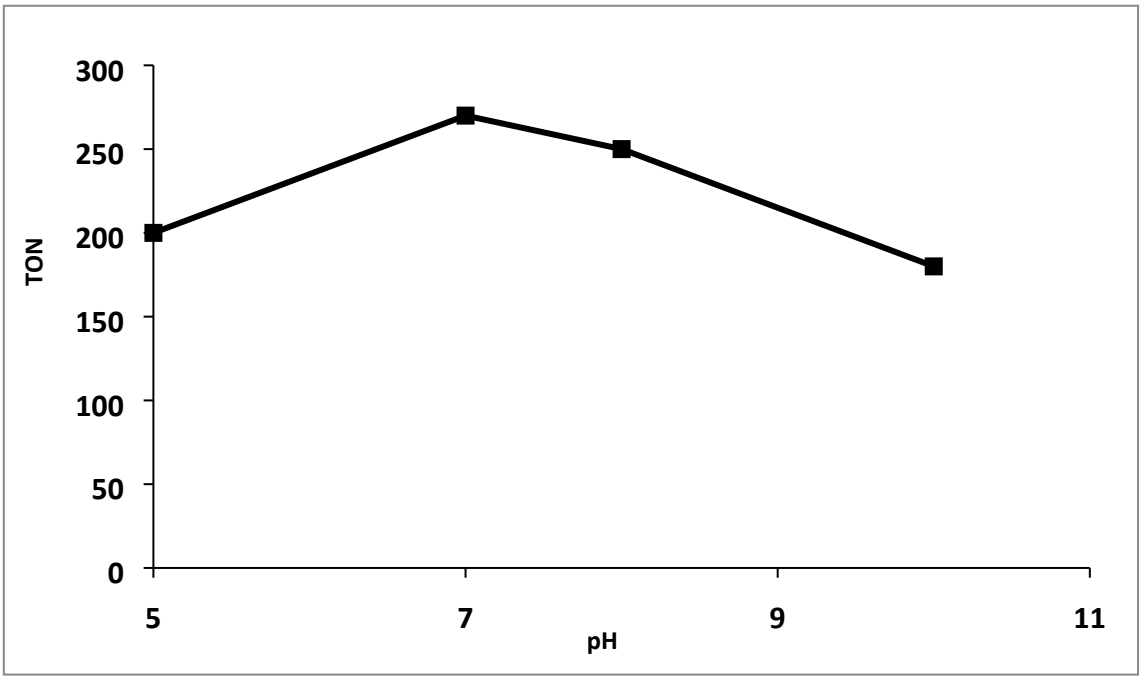


Figure S3. HPLC/ESI-MS resulting of the photooxidation of methyl oleate by **Na[1]** in water.