Electronic Supplementary Material (ESI) for Dalton Transactions.

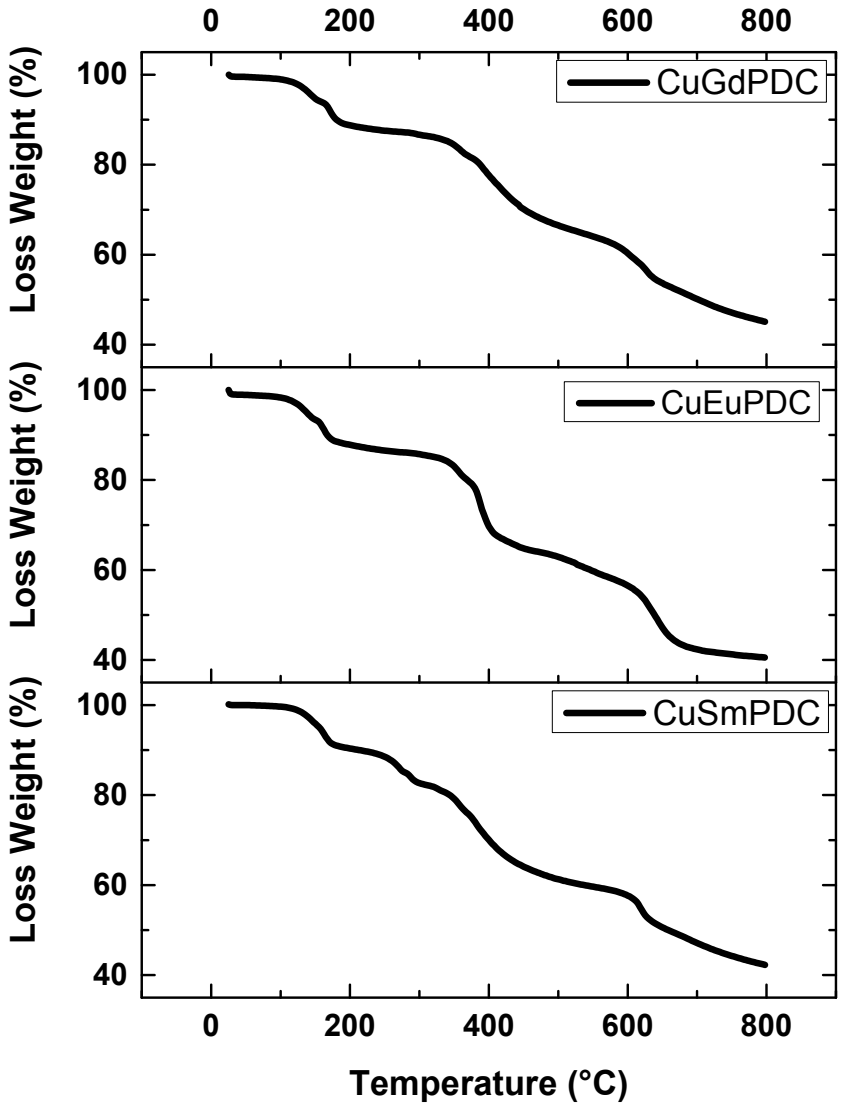
Heterometallic Cu^{II}/Ln^{III} Polymers Active in the Catalytic Aerobic Oxidation of Cycloalkenes in Solvent-Free Conditions.

Supplementary Material

P. Cancino[a,b], L. Santibañez[a], P. Fuentealba[a,b], C. Olea[a], A. Vega[b,c], E. Spodine[a,b]*.

[a] *Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile, Santiago, Chile.*
[b] *Centro para el Desarrollo de la Nanociencia y la Nanotecnología, CEDENNA, Santiago, Chile*
[c] *Facultad de Ciencias Exactas, Dpto. de Ciencias Químicas, Universidad Andrés Bello, Viña del Mar, Chile.*

e-mail: espodine@uchile.cl



FigureS1.Ther

mal analysis for $\{[CuLn_2(PDC)_2(SO_4)_2(H_2O)_6]\cdot H_2O\}_n$ (Ln^{III}: Sm, Eu or Gd)

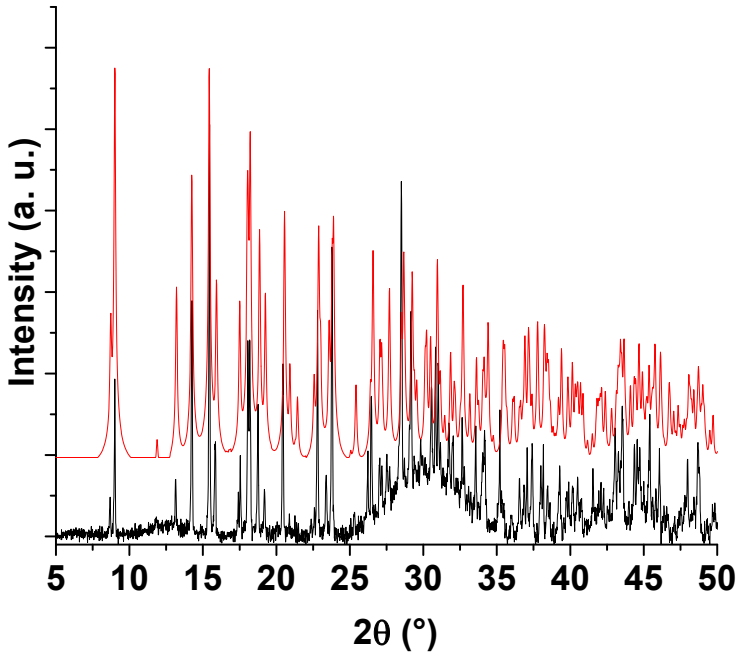


Figure S2. Comparison between de experimental powder diffraction patterns of CuSmPDC (**----**) with simulated diffractogram from single crystal parameters (**----**).

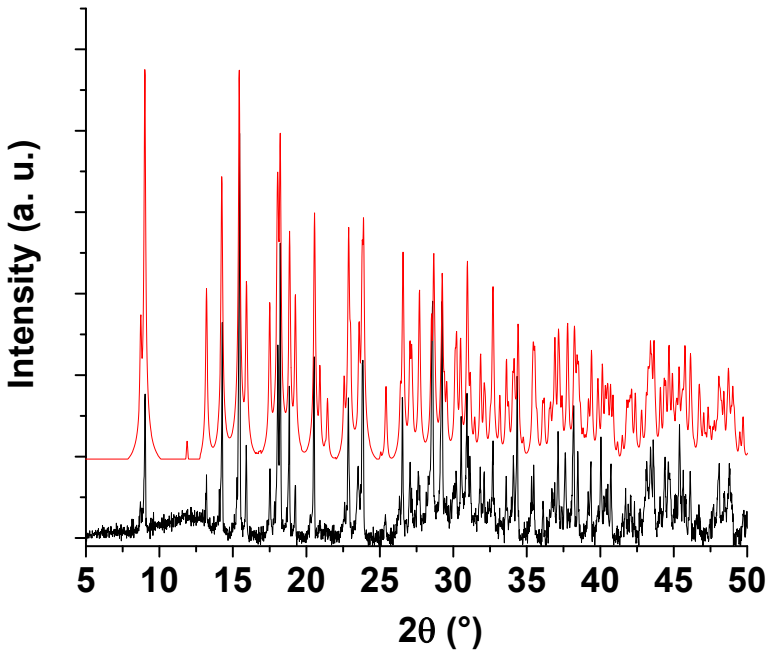


Figure S3. Comparison between de experimental powder diffraction pattern of CuEuPDC (**----**) with simulated diffractogram from single crystal parameters (**----**).

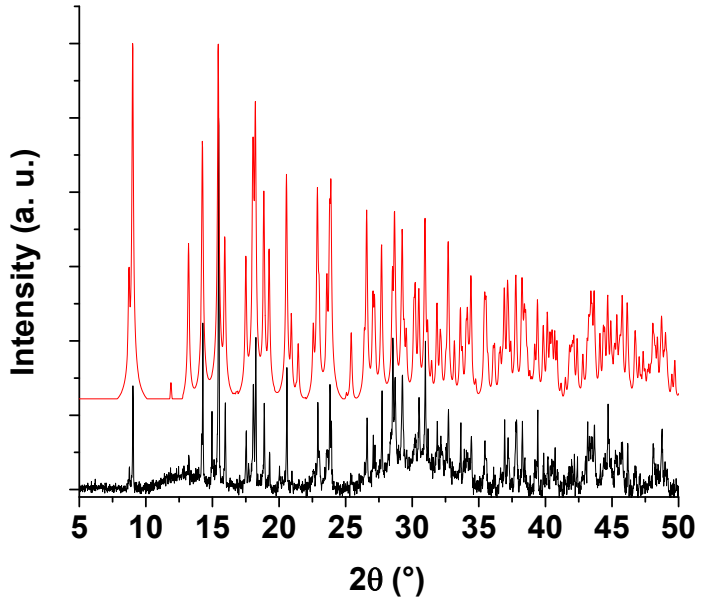


Figure S4. Comparison between de experimental powder diffraction pattern of CuGdPDC (**----**) with simulated diffractogram from single crystal parameters (**----**).

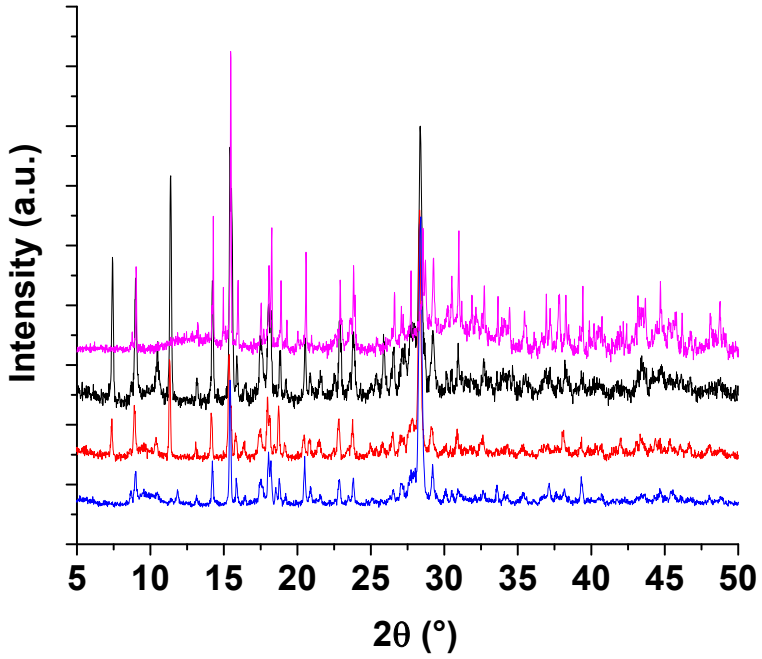


Figure S5. Powder X-ray diffraction pattern of CuSmPDC after different catalytic cycles. **----** pristine catalyst, **----** after first cycle, **----** after second cycle, **----** after fourth cycle.

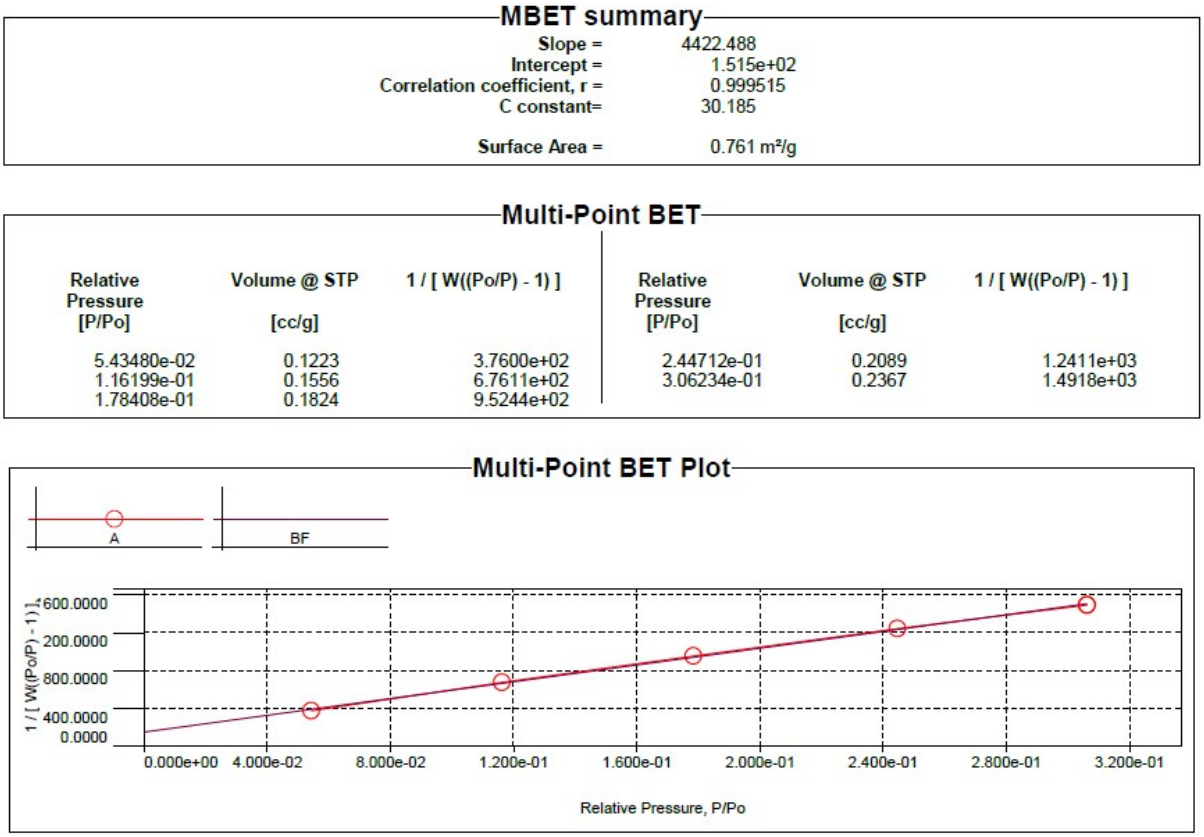


Figure S6. Nitrogen sorptometry for CuGdPDC.

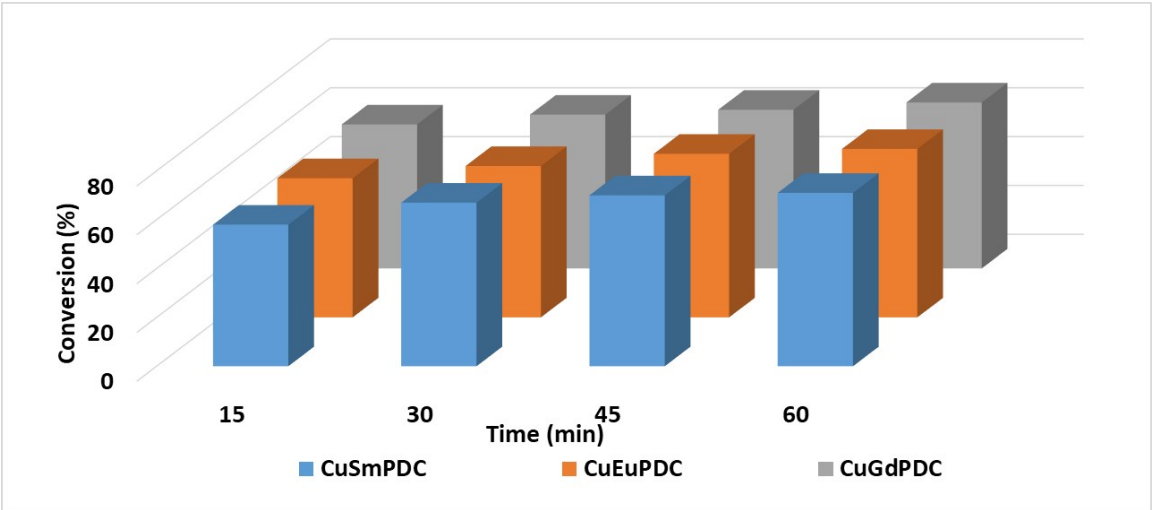


Figure S7. Temporal evolution of the conversion for the oxidation of cyclohexene using the different catalysts.

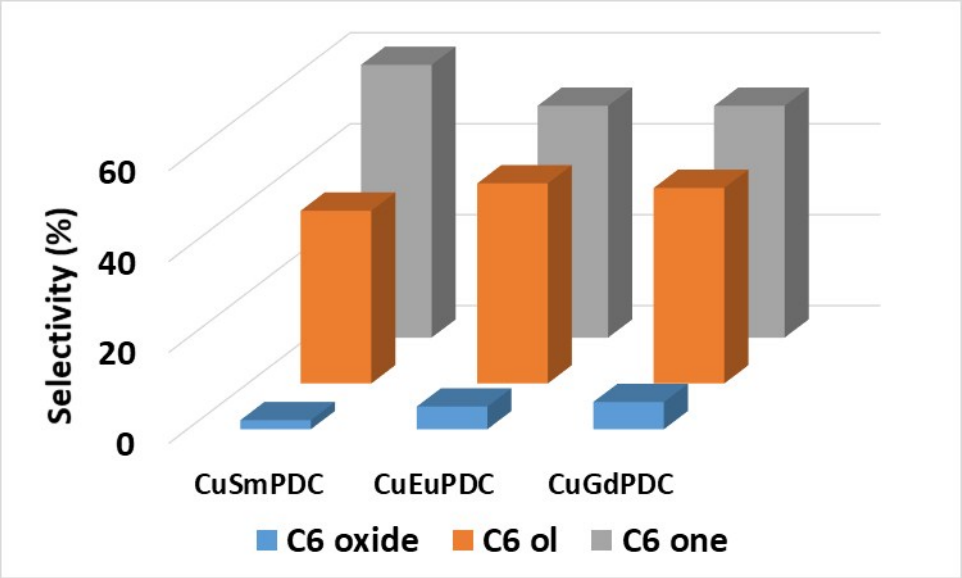


Figure S8. Selectivity after 1 h of reaction for the oxidation of cyclohexene using the different catalysts.

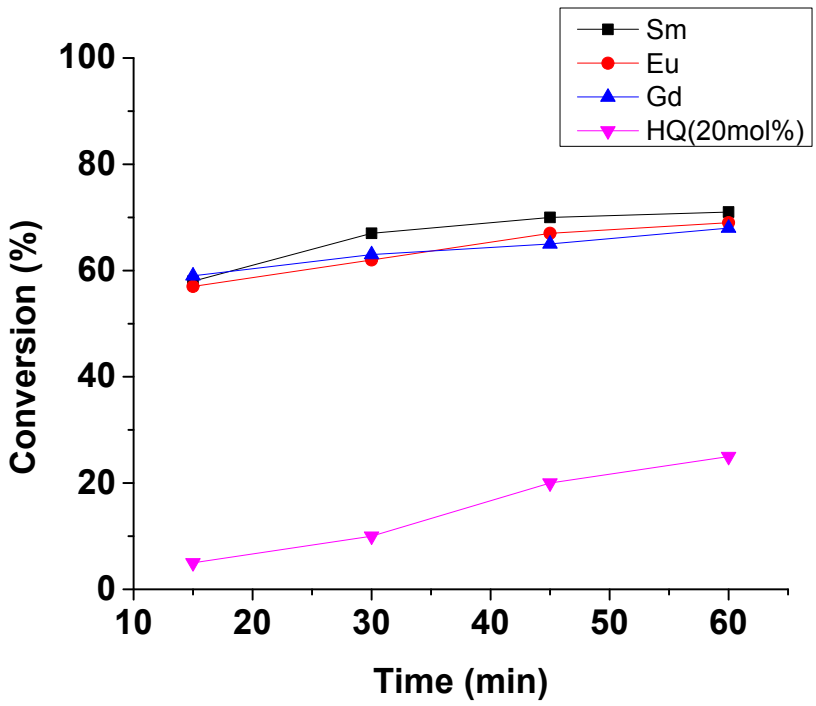


Figure S9. Temporal evolution of the conversion for the oxidation of cyclohexene using the different catalysts. (■) CuSmPDC; (●) CuEuPDC; (▲) CuSmPDC; (▼) Hydroquinone (20 mol% in relationship with substrate).

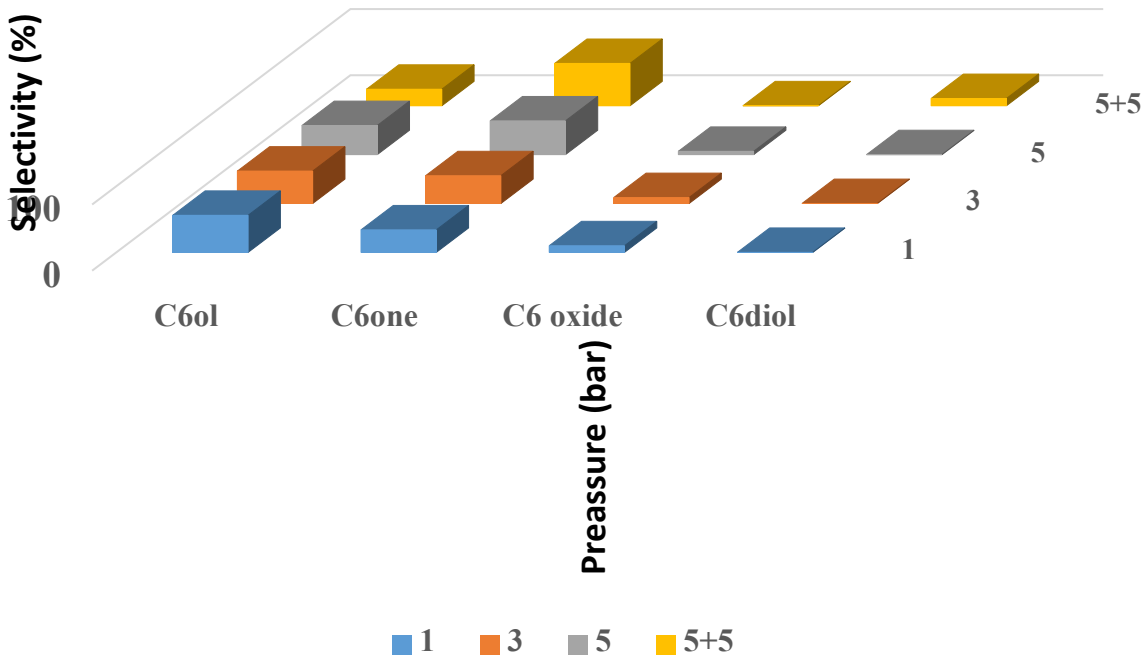
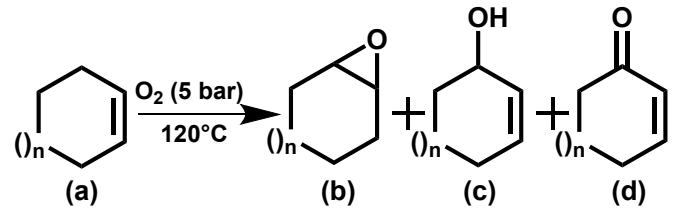
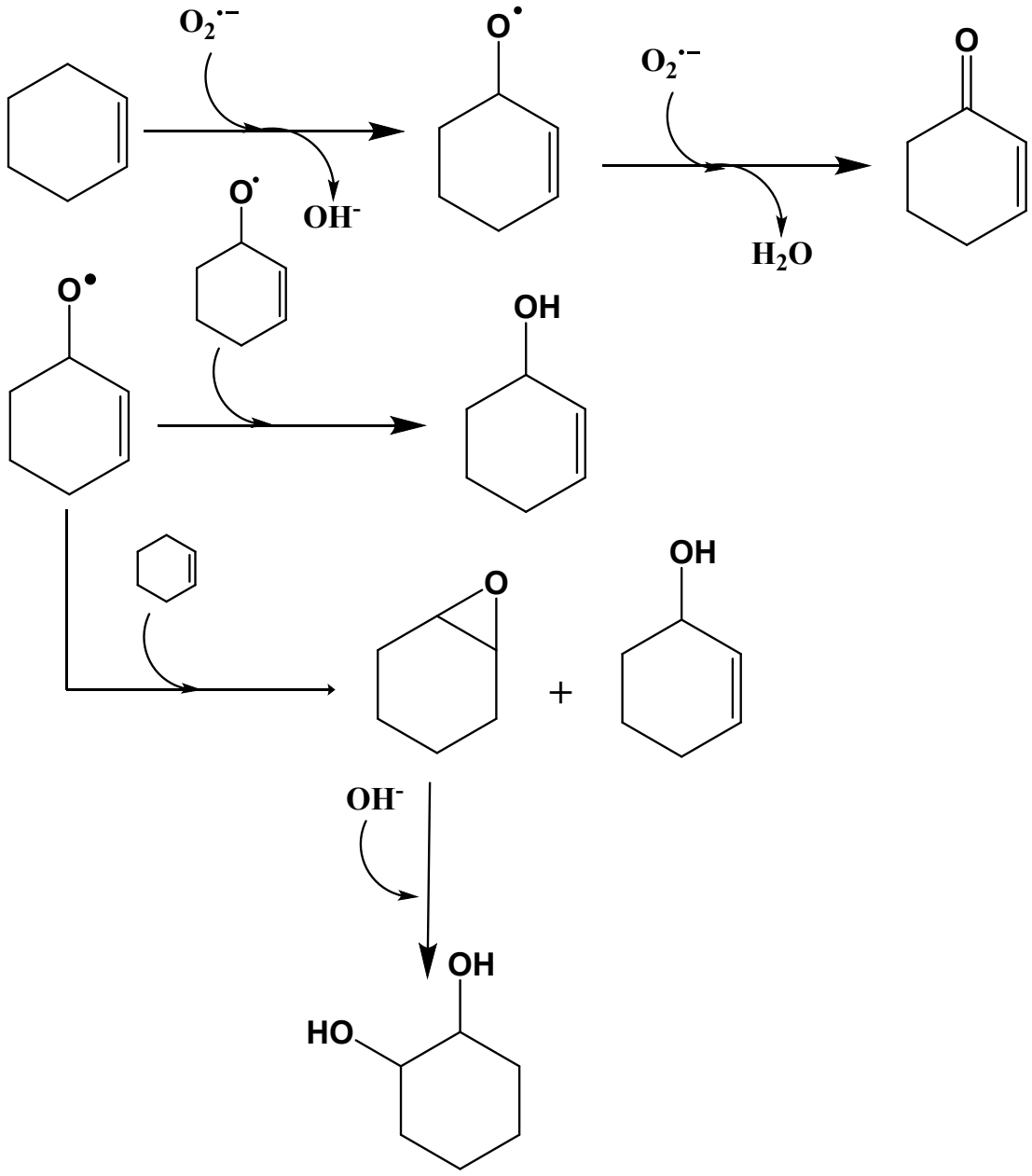


Figure S10. Dependence of the selectivity with oxygen pressure, using CuSmPDC as catalyst and cyclohexene as substrate



Scheme S1. Products obtained from the oxidation of cycloalkenes. (a) alkene; (b) epoxide; (c) conjugated alcohol; (d) conjugated ketone.



Scheme S2. Radical mechanism proposed for aerobic oxidation of cyclohexene.

Table S1. Crystal data and structure refinement details for **CuSmPDC, CuEuPDC, CuGdPDC**

	CuSmPDC	**CuEuPDC**	**CuGdPDC**
FW/uma	1000.61	1015.93	1026.49
Crystal System	Triclinic	Triclinic	Triclinic
Space Group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	6.3502(16)	6.3414(14)	6.3399(9)
b (Å)	10.056(3)	10.023(2)	10.0110(14)
c (Å)	10.316(3)	10.260(2)	10.2144(14)
α (°)	95.008(3)	95.008(6)	95.020(2)
β (°)	95.640(3)	95.330(6)	95.038(2)
γ (°)	99.677(3)	99.785(6)	99.872(2)
V (Å ^{3})	642.6(3)	636.3(2)	636.3(2)
Z(Z')	1(2)	1(2)	1(2)
d (g cm^{-3})	2.586	2.651	2.694
μ (mm^{-1})	5.60	5.97	6.29
F(000)	475	489	491
θ range	2.3–29.9	2.3–29.2	2.7–30.1
hkl range	$-7 \le h \le 7$	$-7 \le h \le 7$	$-8 \le h \le 8$
	$-12 \le l \le 12$	$-12 \le l \le 12$	$-13 \le l \le 14$
	$-12 \le k \le 12$	$-12 \le k \le 12$	$-14 \le k \le 14$
N_{tot}, N_{uniq} (R_{int}), N_{obs}	4925, 2531 (0.044), 2348	4784, 2481 (0.021), 2328	6784, 3484 (0.024), 3341
Ref. Parameters	173	237	237
GOF	1.08	1.05	1.14
R1, wR2 (obs)	0.046, 0.126	0.020, 0.041	0.023, 0.055
Max. and min $\Delta\rho$ e Å^{-3}	2.47 and -3.39	0.53 and -0.62	0.77 and -1.68

Table S2. Selected bond distances (Å), angles (°) and torsion angles (°) for compounds **CuSmPDC, CuEuPDC,** and **CuGdPDC,** as determined by X-rays diffraction.

CuSmPDC			
O6—C1	1.261(8)	Sm1—O8	2.515(5)
O6—Sm1^{i}	2.400(4)	Sm1—O2	2.521(5)
O9—C1	1.259(9)	Cu1—N1^{vii}	1.990(6)
O9—Sm1^{ii}	2.331(5)	Cu1—N1	1.990(6)
O7—Sm1^{iii}	2.418(5)	Cu1—O10^{vii}	2.016(6)
Cu1—O3^{vii}	2.370(6)	Cu1—O10	2.016(6)
Cu1—O3	2.370(6)	O4—Sm1^{v}	2.396(5)
Sm1—O9^{iv}	2.331(5)	Sm1—O7^{vi}	2.418(5)
Sm1—O4^{v}	2.396(5)	Sm1—O5	2.449(5)
Sm1—O6^{i}	2.400(4)	Sm1—O1	2.458(6)
N1^{vii}—Cu1—N1	180.0	O9^{iv}—Sm1—O2	144.37(19)
N1^{vii}—Cu1—O10^{vii}	91.6(3)	O4^{v}—Sm1—O2	75.35(18)
N1—Cu1—O10^{vii}	88.4(3)	O6^{i}—Sm1—O2	80.08(17)
N1^{vii}—Cu1—O10	88.4(3)	O7^{vi}—Sm1—O2	129.41(17)
N1—Cu1—O10	91.6(3)	O5—Sm1—O2	70.01(18)
O10^{vii}—Cu1—O10	180.0	O1—Sm1—O2	56.18(17)
N1^{vii}—Cu1—O3^{vii}	86.4(2)	O8—Sm1—O2	116.75(19)
N1—Cu1—O3^{vii}	93.6(2)	O9^{iv}—Sm1—O4^{v}	87.18(18)
O10^{vii}—Cu1—O3^{vii}	93.3(3)	O9^{iv}—Sm1—O6^{i}	100.62(17)
O10—Cu1—O3^{vii}	86.7(3)	O4^{v}—Sm1—O6^{i}	146.87(18)
N1^{vii}—Cu1—O3	93.6(2)	O9^{iv}—Sm1—O7^{vi}	83.28(18)
N1—Cu1—O3	86.4(2)	O4^{v}—Sm1—O7^{vi}	140.24(17)
O10^{vii}—Cu1—O3	86.7(3)	O6^{i}—Sm1—O7^{vi}	72.89(16)
O10—Cu1—O3	93.3(3)	O9^{iv}—Sm1—O5	76.01(18)
O3^{vii}—Cu1—O3	180.0	O4^{v}—Sm1—O5	77.22(18)
O4^{v}—Sm1—O1	92.7(2)	O6^{i}—Sm1—O5	73.66(17)
O6^{i}—Sm1—O1	91.8(2)	O7^{vi}—Sm1—O5	136.23(18)
O7^{vi}—Sm1—O1	82.45(18)	O9^{iv}—Sm1—O1	157.4(2)
O5—Sm1—O1	125.98(18)	O7^{vi}—Sm1—O8	71.04(17)
O9^{iv}—Sm1—O8	84.3(2)	O5—Sm1—O8	142.09(18)
O4^{v}—Sm1—O8	69.65(19)	O1—Sm1—O8	74.5(2)

O6^{i}—Sm1—O8	142.71(18)

Symmetry codes: (i) -*x*+1, -*y*, -*z*+1; (ii) *x*-1, *y*-1, *z*; (iii) *x*-1, *y*, *z*; (iv) *x*+1, *y*+1, *z*; (v) -*x*+2, -*y*+1, -*z*+2; (vi) *x*+1, *y*, *z*; (vii) -*x*+1, -*y*, -*z*+2.

CuEuPDC			
Eu1—O1	2.318(2)	O2—Eu1^{ii}	2.388(2)
Eu1—O8^{i}	2.374(2)	Eu1—O6	2.443(2)
Eu1—O2^{ii}	2.388(2)	Eu1—O10W	2.494(3)
Eu1—O3^{iii}	2.402(2)	Eu1—O5	2.511(2)
Eu1—O9W	2.436(3)	O3—Eu1^{vi}	2.402(2)
O7—Cu1^{vii}	2.363(3)	O8—Eu1^{i}	2.374(2)
Cu1—N1	1.986(3)	Cu1—O7^{i}	2.363(3)
Cu1—N1^{iv}	1.986(3)	Cu1—O7^{v}	2.363(3)
Cu1—O11W^{iv}	2.020(3)	Cu1—O11W	2.020(3)
O1—Eu1—O8^{i}	87.27(8)	O11W—Cu1—O7^{i}	86.67(13)
O1—Eu1—O2^{ii}	100.39(8)	N1—Cu1—O7^{v}	86.82(10)
O8^{i}—Eu1—O2^{ii}	146.67(9)	N1^{iv}—Cu1—O7^{v}	93.18(10)
O1—Eu1—O3^{iii}	83.39(8)	O11W^{iv}—Cu1—O7^{v}	86.67(13)
O8^{i}—Eu1—O3^{iii}	140.32(8)	O11W—Cu1—O7^{v}	93.33(13)
O2^{ii}—Eu1—O3^{iii}	73.00(8)	O7^{i}—Cu1—O7^{v}	180.0
O1—Eu1—O9W	76.11(9)	O1—Eu1—O6	157.25(9)
O8^{i}—Eu1—O9W	76.87(9)	O8^{i}—Eu1—O6	93.01(8)
O2^{ii}—Eu1—O9W	73.71(8)	O2^{ii}—Eu1—O6	91.83(8)
O3^{iii}—Eu1—O9W	136.63(8)	O3^{iii}—Eu1—O6	81.93(8)
O1—Eu1—O10W	84.42(10)	O9W—Eu1—O6	126.10(9)
O8^{i}—Eu1—O10W	69.80(9)	O3^{iii}—Eu1—O5	128.98(8)
O2^{ii}—Eu1—O10W	142.79(9)	O9W—Eu1—O5	70.07(8)
O3^{iii}—Eu1—O10W	70.95(9)	O6—Eu1—O5	56.23(8)
O9W—Eu1—O10W	141.99(9)	O10W—Eu1—O5	116.70(9)
O6—Eu1—O10W	74.40(10)	O8^{i}—Eu1—O5	75.51(8)
O1—Eu1—O5	144.65(9)	O2^{ii}—Eu1—O5	80.00(8)
N1—Cu1—N1^{iv}	180.0	O11W^{iv}—Cu1—O11W	180.0
N1—Cu1—O11W^{iv}	88.44(12)	N1—Cu1—O7^{i}	93.18(10)
N1^{iv}—Cu1—O11W^{iv}	91.56(12)	N1^{iv}—Cu1—O7^{i}	86.82(10)
N1—Cu1—O11W	91.56(12)	O11W^{iv}—Cu1—O7^{i}	93.33(13)
N1^{iv}—Cu1—O11W	88.44(12)		

Symmetry codes: (i) -*x*+1, -*y*+2, -*z*; (ii) -*x*+1, -*y*+2, -*z*+1; (iii) *x*, *y*+1, *z*; (iv) -*x*, -*y*+1, -*z*; (v) *x*-1, *y*-1, *z*; (vi) *x*, *y*-1, *z*; (vii) *x*+1, *y*+1, *z*.

CuGdPDC			
Gd1—O8^{i}	2.309(2)	O5—Gd1^{ii}	2.361(2)
Gd1—O5^{ii}	2.361(2)	O6—Gd1^{vi}	2.386(2)
Gd1—O7^{iii}	2.376(2)	O7—Gd1^{iii}	2.376(2)
Gd1—O6^{iv}	2.386(2)	O8—Gd1^{vii}	2.309(2)
Gd1—O10	2.429(2)	Cu2—N1	1.989(3)
Gd1—O3	2.432(3)	Cu2—O1^{v}	2.015(3)
Gd1—O11	2.484(3)	Cu2—O1	2.015(3)
Gd1—O4	2.500(2)	Cu2—O2	2.358(3)
Cu2—N1^{v}	1.989(3)	Cu2—O2^{v}	2.358(3)
O8^{i}—Gd1—O5^{ii}	87.09(8)	O5^{ii}—Gd1—O4	75.55(9)
O8^{i}—Gd1—O7^{iii}	100.49(8)	O7^{iii}—Gd1—O4	79.75(8)
O5^{ii}—Gd1—O7^{iii}	146.25(9)	O6^{iv}—Gd1—O4	129.10(8)
O8^{i}—Gd1—O6^{iv}	83.23(8)	O10—Gd1—O4	69.95(8)
O5^{ii}—Gd1—O6^{iv}	140.73(9)	O3—Gd1—O4	56.60(8)
O7^{iii}—Gd1—O6^{iv}	73.02(8)	O11—Gd1—O4	116.91(9)
O8^{i}—Gd1—O10	76.14(9)	N1^{v}—Cu2—N1	180.0
O5^{ii}—Gd1—O10	76.46(8)	N1^{v}—Cu2—O1^{v}	91.80(12)
O7^{iii}—Gd1—O10	73.65(8)	N1—Cu2—O1^{v}	88.20(12)
O6^{iv}—Gd1—O10	136.46(8)	N1^{v}—Cu2—O1	88.20(12)
O8^{i}—Gd1—O3	157.00(9)	N1—Cu2—O1	91.80(12)
O5^{ii}—Gd1—O3	93.52(9)	O1^{v}—Cu2—O1	180.0
O7^{iii}—Gd1—O3	91.72(9)	N1^{v}—Cu2—O2	92.89(11)
O6^{iv}—Gd1—O3	81.81(8)	N1—Cu2—O2	87.11(11)
O10—Gd1—O3	126.35(9)	O1^{v}—Cu2—O2	86.31(15)
O8^{i}—Gd1—O11	84.28(10)	O1—Cu2—O2	93.69(15)
O5^{ii}—Gd1—O11	70.09(9)	N1^{v}—Cu2—O2^{v}	87.11(11)
O7^{iii}—Gd1—O11	142.96(9)	N1—Cu2—O2^{v}	92.89(11)
O6^{iv}—Gd1—O11	71.12(9)	O1^{v}—Cu2—O2^{v}	93.69(15)
O10—Gd1—O11	141.87(9)	O1—Cu2—O2^{v}	86.31(15)
O3—Gd1—O11	74.40(11)	O2—Cu2—O2^{v}	180.0
O8^{i}—Gd1—O4	144.59(8)		

Symmetry codes: (i) *x*+1, *y*+1, *z*; (ii) -*x*+2, -*y*+1, -*z*+2; (iii) -*x*+1, -*y*, -*z*+1; (iv) *x*+1, *y*, *z*; (v) -*x*+1, -*y*, -*z*+2; (vi) *x*-1, *y*, *z*; (vii) *x*-1, *y*-1, *z*.

Table S3. Oxidation of cyclohexene at 1 hour using CuLnPDC (Ln: Sm^{III}, Eu^{III}, Gd^{III}) and homogeneous control $Cu(acac)_2$, $Eu(acac)_3(H_2O)_3$ and $Gd(acac)_3(H_2O)_3$ as catalysts.

Catalyst	Conv. (%)	Products	Selectivity (%)
CuSmPDC	71	Cyclohexenone Cyclohexenol Cyclohexene oxide	55 42 3
Cu(acac)$_2$	74	Cyclohexenone Cyclohexenol Cyclohexene oxide	56 41 4
CuEuPDC	69	Cyclohexenone Cyclohexenol Cyclohexene oxide	51 44 5
Eu(acac)$_3$ $(H_2O)_3$	70	Cyclohexenone Cyclohexenol Cyclohexene oxide	38 49 13
CuGdPDC	68	Cyclohexenone Cyclohexenol Cyclohexene oxide	51 43 6
Gd(acac)$_3$ $(H_2O)_3$	70	Cyclohexenone Cyclohexenol Cyclohexene oxide	39 47 14
Blank	30	Cyclohexenone Cyclohexenol Cyclohexene oxide	46 43 11

Reaction conditions: Catalyst (0.005 mmol, based on copper (0.00031 mmol)), substrate (10 mmol), 120 ºC. Ratio S/C = 32000/1 or 0.003mol% of copper per mole of substrate. The homogeneous control were done using the same amount of metal ions present in the CuLnPDC.

Table S4. Catalytic results for the oxidation of cyclooctene, using CuSmPDC.

Substrate	Consumption of O_2 (bar)	Time (h)	Conversion (%)	TOF (h^{-1})	Selectivity (%)
Cyclooctene	3.5	6	47	159	99 (epoxide)
Cyclooctene + Hydroquinone*	0	6	0	-	0
Blank	0	6	0		0

Reaction conditions: Catalyst (0.005 mmol, based on copper (0.00031 mmol)), substrate (10 mmol), 120 ºC. Ratio S/C = 32000/1 or 0.003mol% of copper per mole of substrate. Initial pressure 5 bar. TOF calculated as moles of products per mole of active site (Cu^{II} ions) per hour (TOF values were calculated using the time reported in the table).
*Hydroquinone was used in 20 mol% in relation to cyclooctene.