

Supporting Information

**Tailoring the electron density of cobalt oxide clusters
to provide high selective superoxide and peroxide
species for aerobic cyclohexane oxidation**

Silvia Gutiérrez-Tarriño,^[a] José Gaona-Miguélez^[a] and Pascual Oña-
Burgos*^[a,b]

[a] Instituto de Tecnología Química, Universitat Politècnica de València-Consejo Superior de Investigaciones Científicas (UPV-CSIC), Avda. de los Naranjos s/n, 46022 Valencia, Spain.

[b] Department of Chemistry and Physics, Research Centre CLAIMBITAL, University of Almería, Ctra. Sacramento, s/n, 04120 Almería, Spain.

Table of contents

I.	General information.....	S3
II.	Detailed Experimental procedures.....	S5
	A. Synthesis of catalysts	S5
	Preparation of $[\text{Co}_4\text{O}_4(\text{OAc})_4\text{py}_4]$ (1).....	S5
	Preparation of $[\text{Co}_4\text{O}_4(\text{OAc})_4(\text{p-COOEt-py})_4]$ (2).....	S5
	Preparation of $[\text{Co}_4\text{O}_4(\text{OAc})_4(\text{p-OMe-py})_4]$ (3)	S5
	Preparation of $[\text{Co}_4\text{O}_4(\text{OBz})_4\text{py}_4]$ (4)	S6
	Preparation of $[\text{Co}_4\text{O}_4(\text{OBz})_4(\text{p-COOEt-py})_4]$ (5).....	S6
	Preparation of $[\text{Co}_4\text{O}_4(\text{OBz})_4(\text{p-OMe-py})_4]$ (6).....	S6
	B. Catalytic Experiments.....	S7
	Cyclohexane oxidation.	S7
	Cyclohexyl hydroperoxide decomposition	S7
III.	Characterization Data of oxo cubane complexes	S8
	A. Crystallographic Description and Parameters for 2, 5 and 6	S8
	B. Cyclic voltammograms	S10
	C. NMR Spectra	S12
	D. ESI Spectra.....	S18
IV.	Catalytic study on cyclohexane oxidation.	S21
	A. Kinetics experiments on cyclohexane oxidation at 150 °C.....	S21
	B. Kinetics experiments on cyclohexane oxidation at 130 °C.....	S23
	C. Comparison with reported catalysts for cyclohexane oxidation	S26
V.	Mechanistic studies.....	S27
	A. EPR Spectra	S27
	B. CHHP decomposition	S30
	C. In situ Raman Spectroscopy.....	S32
VI.	References	S34

I. General information

All reagents and solvents were purchased from commercial suppliers and used without further purification.

Isolated catalysts were characterized by elemental analysis, ^1H -NMR, ^{13}C -NMR, ESI-MS, ICP, EPR, cyclic voltammetry and monocrystal X-Ray Diffraction. When available, characterization given in the literature was used for comparison.

ESI-MS: Exact mass values were determined by using a Waters ACQUITY™ XevoQToF spectrometer (Waters Corp.) connected to the UPLC system via electrospray ionization (ESI) interface. The ESI source was operated in positive ionization mode with the capillary voltage at 3.0 kV. The temperature of the source and desolvation was set at 120 °C and 400 °C, respectively. The cone and desolvation gas flows were 10 L h⁻¹ and 800 L h⁻¹, respectively. All data collected in Centroid mode were acquired using Masslynx™ software (Waters Corp.). Leucine-enkephalin was used as the lock mass generating an $[\text{M}+\text{H}]^+$ ion (m/z 556.2771) at a concentration of 500 pg/mL and a flow rate of 20 $\mu\text{L}/\text{min}$ to ensure accuracy during the MS analysis.

EPR: EPR spectra were recorded at 100K on a Bruker EMX-12 instrument operating in X band at 9.5 GHz, modulation amplitude of 1 G and modulation frequency of 100 KHz.

NMR: ^1H and ^{13}C NMR were recorded on a Bruker 300 spectrometer and the chemical shifts are reported in ppm relative to residual proton solvents signals. Data for ^1H NMR spectra are reported as follows: chemical shift (δ , ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = double doublets, bs = broad signal), coupling constant and integration. Data for ^{13}C NMR spectra are reported in chemical shift (δ , ppm).

Elemental analysis and ICP: C, N and H contents of isolated catalysts were determined with a Carlo Erba 1106 elemental analyzer and cobalt content of isolated catalysts were determined with a Varian 715-ES by inductively coupled plasma spectroscopy.

Cyclic voltammetry: CV was conducted using a three-electrode cell assembly consisting of a platinum disc as a working electrode, a platinum-wire as auxiliary electrode and Ag/AgCl as the reference electrode. All electrochemical studies were carried out at room temperature. Ferrocene was used in order to calibrate before the measurements. Sample solutions were 1 mM of catalyst in acetonitrile and 0.01 M in tetrabutylammonium perchlorate, which was used as an electrolyte. All the solutions were purged with and kept under an atmosphere of Ar.

Raman Spectroscopy: In situ Raman spectroscopy was carried out in a Linkam 600 cell. The spectra were recorded with 514 nm laser excitation on a Renishaw in via Raman Spectrometer (“Refelx”) equipped with a CCD detector. The laser power on the sample was between 5-50% and a total of 30 acquisitions were taken for each spectrum.

For carried out the in situ experiments, first, an Ar flow was passed through the sample during 24 hours in order to remove any species which can be adsorbed (the samples are store without inert atmosphere). After these 24 hours, the samples were characterized maintaining the Ar flow. After that, an oxygen flow was passed through the sample in order to observe the new bands, which can be assigned to Co-O species.

X-ray diffraction: Single crystals suitable for X-ray diffraction were coated with polyisobutylene oil. Crystals were measured on a κ -geometry diffractometer system, Bruker X8 APEXII CCD, equipped with a molybdenum graphite monochromator and a MoK α sealed x-ray tube ($\lambda = 0.71073 \text{ \AA}$) at 100 K. Preliminary data revealed the crystal system. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The space group was identified, and data were corrected for absorption effects using the Multi-Scan method (SADABS). The structures were solved using direct methods (SHELXT2014), completed by subsequent Fourier synthesis and refined by full-matrix least-squares procedures using SHELXL2016/6.

On the other hand, analyses of results for catalytic experiments were carried out by Gas Chromatography (GC).

Gas Chromatography: GC analyses were acquired on Varian CP-3800 gas chromatograph equipped with an HP5 capillary column (30 m x 250 μm). The instrument was set to an injection volume of 1 μL , an inlet split ratio of 50:1, and inlet and detector temperatures of 250 $^{\circ}\text{C}$ and 300 $^{\circ}\text{C}$, respectively. Helium was used as carrier gas with a constant flow rate of 2 mL/min. The temperature program used for all the analyses is as follows: 80.0 $^{\circ}\text{C}$, 3 min; 30 $^{\circ}\text{C}/\text{min}$ to 300 $^{\circ}\text{C}$, 5 min.

II. Detailed Experimental procedures

A. Synthesis of catalysts

Preparation of [Co₄O₄(OAc)₄py₄] (1)

Cobalt(II) nitrate hexahydrate (10.00 g, 34.3 mmol) and sodium acetate trihydrate (9.35 g, 68.6 mmol) were dissolved in 100 mL of methanol, and then pyridine (2.8 mL, 34 mmol) was added. Hydrogen peroxide (34-37% w/w in water, 17.1 mL, 170 mmol) was added dropwise to this solution, and then the reaction mixture was refluxed for 2 h. The dark brown-green solution was dried *in vacuo*, and the solid was partitioned between 20 mL of water and 100 mL of dichloromethane. The organic layer was collected, and the aqueous layer was extracted with 2 x 100 mL of dichloromethane. The combined extracts were dried with MgSO₄ and concentrated to ~50 mL, to which 500 mL of hexane were added to induce crystallization. The solid was dry-loaded onto a silica column and eluted with 5% methanol in acetone. The fractions were dried to give a dark-green solid (6.2 g, 85.6%), which was pure by ¹H NMR spectroscopy. ¹H NMR (300 MHz, DMSO-d₆): δ = 8.34 (d, *J* = 6.5, 8H), 7.66-7.61 (t, *J* = 6.6 Hz, 4H), 7.15-7.11 (m, 8H), 1.92 (s, 12H). ¹³C NMR (75 MHz, DMSO-d₆): δ = 183.97, 152.11, 136.92, 123.36, 26.08. Anal. Calcd for C₂₈H₃₂Co₄N₄O₁₂: C, 39.422; H, 3.754; N, 6.570; Co, 27.70. Found: C, 39.720; H, 3.978; N, 6.388; Co, 26.91.

Preparation of [Co₄O₄(OAc)₄(p-COOEt-py)₄] (2)

To prepare Co₄O₄(OAc)₄(p-COOEt-py)₄ it was followed the same method as in the case of complex **1**, using ethyl isonicotinate (5.14 g, 34 mmol) instead of pyridine. ¹H NMR (300 MHz, DMSO-d₆): δ = 8.53 (d, *J* = 6.5 Hz, 8H), 7.55 (d, *J* = 6.6 Hz, 8H), 4.35 (q, *J* = 7.1 Hz, 8H), 1.95 (s, 12H), 1.37 (t, *J* = 7.2 Hz, 12H). ¹³C NMR (75 MHz, DMSO-d₆): δ = 184.58, 163.82, 153.59, 137.41, 122.22, 61.79, 26.11, 13.94. Anal. Calcd for C_{40.74}H_{49.49}Cl_{1.49}Co₄N₄O₂₀: C, 41.660; H, 4.145; N, 4.655; Co, 20.70. Found: C, 41.720; H, 4.136; N, 4.955; Co, 20.28.

Preparation of [Co₄O₄(OAc)₄(p-OMe-py)₄] (3)

To prepare Co₄O₄(OAc)₄(p-OMe-py)₄ it was followed the same method as in the case of complex **1**, using 4-methoxypyridine (3.71 g, 34 mmol) instead of pyridine. ¹H NMR (300 MHz, DMSO-d₆): δ = 8.07-8.05 (d, *J* = 6.6 Hz, 8H), 6.76-6.74 (d, *J* = 6.7 Hz, 8H), 3.83 (s, 12H), 1.90 (s, 12H). ¹³C NMR (75 MHz, DMSO-d₆): δ = 183.75, 165.92, 152.80, 109.88, 64.87, 26.08. Anal. Calcd for C₃₂H₄₀Co₄N₄O₁₆: C, 39.332; H, 4.097; N, 5.736; Co, 24.14. Found: C, 38.947; H, 4.275; N, 6.006; Co, 23.35.

Preparation of [Co₄O₄(OBz)₄py₄] (4)

To prepare Co₄O₄(OBz)₄py₄ it was followed the same methodology as in the case of complex **1**, using sodium benzoate (9.89 g, 68.6 mmol) instead of sodium acetate. Besides, Co₄O₄(OBz)₄py₄ could be synthesized by an exchanging method using **1** as a precursor. For that, Co₄O₄(OAc)₄py₄ (2 g, 2.35 mmol) was dissolved in methanol and 8 equivalents of benzoic acid (2.29 g, 18.8 mmol) were added. The mixture was stirred at 50 °C for 4 hours. The solid was collected by filtration and washed with 3 x 50 mL diethyl ether. ¹H NMR (300 MHz, DMSO-d₆): δ = 8.49-8.46 (d, *J* = 6.5 Hz, 8H), 7.81-7.77 (d, *J* = 7.4 Hz, 8H), 7.73-7.68 (t, *J* = 6.7 Hz, 4H), 7.48-7.43 (t, *J* = 7.4 Hz, 4H), 7.37-7.32 (m, 8H), 7.24-7.20 (m, 8H). ¹³C NMR (75 MHz, DMSO-d₆): δ = 179.06, 152.10, 137.35, 135.69, 130.97, 128.29, 127.84, 123.86. Anal. Calcd for C₄₈H₄₀Co₄N₄O₁₂: C, 52.364; H, 3.636; N, 5.091; Co, 21.43. Found: C, 52.618; H, 3.869; N, 4.685; Co, 22.13.

Preparation of [Co₄O₄(OBz)₄(p-COOEt-py)₄] (5)

To prepare Co₄O₄(OBz)₄(p-COOEt-py)₄ it was followed the same method as in the case of complex **1**, using sodium benzoate (9.89 g, 68.6 mmol) instead of sodium acetate and ethyl isonicotinate (5.14 g, 34 mmol) instead of pyridine. Besides, Co₄O₄(OBz)₄(p-COOEt-py)₄ could be synthesized by an exchanging method using **2** as a precursor. For that, Co₄O₄(OAc)₄(p-COOEt-py)₄ (3.26 g, 2.35 mmol) was dissolved in methanol and 8 equivalents of benzoic acid (2.29 g, 18.8 mmol) were added. The mixture was stirred at 50 °C for 4 hours. The solid was collected by filtration and washed with 3 x 50 mL diethyl ether. ¹H NMR (300 MHz, DMSO-d₆): δ = 8.70-8.68 (d, *J* = 6.4, 8H), 7.82-7.80 (d, *J* = 7.2 Hz, 8H), 7.65-7.63 (d, *J* = 6.5 Hz, 8H), 7.49-7.44 (t, *J* = 7.2 Hz, 4H), 7.37-7.32 (m, 8H), 4.36 (q, *J* = 7.2 Hz, 8H), 1.36 (t, *J* = 7.1 Hz 12H). ¹³C NMR (75 MHz, DMSO-d₆): δ = 179.51, 163.78, 153.58, 137.72, 135.44, 131.14, 128.44, 127.88, 122.76, 61.81, 30.66, 13.96. Anal. Calcd for C₆₀H₅₆Co₄N₄O₂₀: C, 51.891; H, 4.064; N, 4.034; Co, 17.00. Found: C, 52.275; H, 4.351; N, 3.619; Co, 16.89.

Preparation of [Co₄O₄(OBz)₄(p-OMe-py)₄] (6)

To prepare Co₄O₄(OBz)₄(p-OMe-py)₄ it was followed the same method as in the case of complex **1**, using sodium benzoate (9.89 g, 68.6 mmol) instead of sodium acetate and 4-methoxypyridine (3.71 g, 34 mmol) instead of pyridine. Besides, Co₄O₄(OBz)₄(p-OMe-py)₄ could be synthesized by an exchanging method using **3** as a precursor. For that, Co₄O₄(OAc)₄(p-OMe-py)₄ (2.87 g, 2.35 mmol) was dissolved in methanol and 8 equivalents of benzoic acid (2.29 g, 18.8 mmol) were added. The mixture was stirred at 50 °C for 4 hours. The solid was collected by

filtration and washed with 3 x 50 mL diethyl ether. ^1H NMR (300 MHz, DMSO- d_6): δ = 8.19 (d, J = 6.4 Hz, 8H), 7.81-7.78 (m, 8H), 7.46-7.43 (t, J = 7.2 Hz, 4H), 7.37-7.32 (m, 8H), 6.85 (d, J = 7.3 Hz, 8H), 3.85 (s, 12H). ^{13}C NMR (75 MHz, DMSO- d_6): δ = 178.8, 167.5, 153.0, 139.9, 128.6, 128.4, 128.1 110.7, 56.0. Anal. Calcd for $\text{C}_{52.77}\text{H}_{54.41}\text{Cl}_{1.53}\text{Co}_4\text{N}_4\text{O}_{18.44}$: C, 49.667; H, 4.125; N, 4.214; Co, 19.32. Found: C, 50.627; H, 3.675; N, 4.552; Co, 19.91.

B. Catalytic Experiments

Cyclohexane oxidation.

To a 12 mL reactor equipped with a stir bar, pressure gauge, sample extraction probe, gas bubbling probe and gas outlet on the benchtop was added the corresponding amount of catalyst (% mol of cobalt) followed by cyclohexane (3 g). It was purged several times with N_2 to remove oxygen and it was pressurized to 4 bar with N_2 . The reactor was heated to a 130 °C on a heated plate. The total pressure of the reaction at the reaction temperature was 6 bar. At this moment (time = 0h) a mixture of depleted air ($\text{N}_2:\text{O}_2$ 95:5) was bubbled, maintaining the pressure constant at 6 bar with a pressure controller. Samples (25 μL) were taken at different times and were introduced in vials previously prepared with 1 mL of acetone, 10 μL of dodecane as internal standard and 100 μL of TFF to decompose the CHHP formed in the reaction (TFF 10% in acetone), which will be agitated in a vortex for analyzing them by GC. To analyze the formation of adipic acid and others, a sample was drawn (25 μL) and 100 μL of boron trifluoride in methanol (10%) was attached. This mixture was heated at 90 °C for 2 h. Then it was left to cool and 1 mL of distilled water was added and it was stirred vigorously. After that, 1 ml of dichloromethane was added and the organic phase was analyzed by GC.

If the reaction is done with pure oxygen, the reactor is pressurized to 4 bar with oxygen and placed on the heated stirring plate. The final pressure is 6 bar at 130 °C, maintaining the O_2 pressure with a pressure controller. All catalytic experiments have been carried out in triplicate to check the accuracy of the obtained results.

Cyclohexyl hydroperoxide decomposition

In the same previous reactor, 3 g of a mixture containing CHHP (3 mol %) in cyclohexane and the catalyst were introduced. It was purged with N_2 several times and pressurized to 5 bar with N_2 . Finally, it was placed on the stirring plate with heating at a temperature of 100 °C. Samples were taken at different times and the procedure to analyze them was the same as for the quantification of CHHP in the previous reaction. All catalytic experiments have been carried out in triplicate to check the accuracy of the obtained results.

For EPR experiments, several solutions were prepared. DMPO in cyclohexane (1% p/p), cyclohexyl hydroperoxide (CHHP) in cyclohexane and a mixture of them were measured as a blank. After that, one solution for each catalyst were prepared as follows: to 100 μ L of CHHP in cyclohexane, 200 μ L of a solution of catalyst (1 mg/5 mL of cyclohexane) were added and stirred during 5 minutes. After this time 100 μ L of DMPO in cyclohexane were put in. All solutions were purged with Ar before been measured.

III. Characterization Data of oxo cubane complexes

A. Crystallographic Description and Parameters for **2**, **5** and **6**

Table S1. Average Interatomic Bond Distances (\AA) and angles (deg) for **2**, **5** and **6** complexes compared with **1** and **4**.

Bond Distances (\AA) and angles (deg)	2	5	6	1 ²⁷	4 ³⁰
Co – N (py) (\AA)	1.964	1.957	1.958	1.962	1.968
Co – (μ_3 -O) (\AA)	1.867	1.865	1.868	1.865	1.879
Co – O _{carbox} (\AA)	1.949	1.954	1.956	1.953	1.967
Co \cdots Co ^[a] (\AA)	2.835	2.826	2.824	2.815	2.856
Co \cdots Co ^[b] (\AA)	2.701	2.697	2.701	2.702	2.725
O – Co – O ^[c] (deg)	84.83	84.99	85.10	85.21	84.80
Co – O – Co ^[c] (deg)	94.71	94.58	94.50	94.97	94.69

^[a]Bridged by two oxo ligands only. ^[b]Bridged by two oxo ligands and a bidentate carboxylate. ^[c]Only oxygen atoms of the Co₄O₄ core are consider.

The oxo cubanes **2**, **5** and **6** have been characterized from a single-crystal X-ray diffraction study. The compounds **2** and **5** crystallized in a triclinic space group with two and four unit included in the asymmetric unit, respectively, and could be formulated as [Co₄O₄(RCOO)₄(p-COOMe-py)₄] (R = Me for **2** and R = Ph for **5**). The compound **6** crystallize in monoclinic space group with four unit included in the asymmetric unit and could be formulated as [Co₄O₄(OPh)₄(p-OMe-py)₄]. Each oxo-cubane consists of four Co(III) ions, each in a pseudo-octahedral ligand environment at the four corners of the [Co₄O₄]⁴⁺ core with four μ_2 -acetate ligands bridging the Co³⁺ ions along four face diagonals of the cube. Finally, four pyridine ligands on the axial faces of the cubane complete the coordination spheres of the four Co(III) ions. All four cobalt atoms are thus in the +3 oxidation state and as expected for d⁶-Co³⁺ ions, the metal centers adopt nearly octahedral six-coordinate geometries.

Table S2. Crystal data and structure refinement details for **2**, **5** and **6**. The atomic coordinates, equivalent isotropic displacements parameters, bond length, angles and anisotropic displacement parameters are given in the CIF (CCDC 1874019, CCDC 1874000 and CCDC 1873998, respectively).

Identification Code	2	5	6
Empirical formula	C _{40.74} H _{49.49} Cl _{1.49} Co ₄ N ₄ O ₂₀	C ₆₀ H ₅₆ Co ₄ N ₄ O ₂₀	C _{52.77} H _{54.41} Cl _{1.53} Co ₄ N ₄ O _{18.44}
Formula weight	1203.47	1388.80	1329.69
Temperature (K)	100	100	100
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	-P1	-P1	P2 ₁ /m
Unit cell dimensions			
a (Å)	11.7374 (4)	17.5804 (4)	13.1722
b (Å)	13.1866 (4)	19.7199 (4)	22.6021
c (Å)	18.5347 (6)	21.5426 (5)	19.3273
α (deg)	103.879 (2)	70.454 (1)	90
β (deg)	103.877 (2)	80.365 (2)	105.554 (1)
γ (deg)	100.988 (2)	70.777 (1)	90
Volume (Å³)	2608.30 (15)	6631.9 (3)	5543.4 (2)
Z	2	4	4
Density (calc)	1.533	1.391	1.593
Absorption coef.	1.401	1.055	1.328
F (000)	1230	2848	2722
Crystal size	0.342 x 0.203 x 0.074	0.420 x 0.398 x 0.054	0.421 x 0.141 x 0.114
Theta range for data collection	1.85 – 27.55°	1.54 – 22.05°	1.80 – 27.51
Index ranges	-15 ≤ h ≤ 15, -16 ≤ k ≤ 17, -24 ≤ l ≤ 24	-18 ≤ h ≤ 18, -19 ≤ k ≤ 20, 0 ≤ l ≤ 22	-17 ≤ h ≤ 17, -29 ≤ k ≤ 29, -25 ≤ l ≤ 25
Reflections collected	11957	16234	12704
Independent	8814	10805	9452

reflections			
Goodness of fit on F2	1.027	1.012	1.059
Final R indices [I > 2 σ (I)]	R ₁ = 0.0483 wR ₂ = 0.1093	R ₁ = 0.0508 wR ₂ = 0.1087	R ₁ = 0.0416 wR ₂ = 0.1026
R indices (all data)	R ₁ = 0.0725 wR ₂ = 0.1188	R ₁ = 0.1002 wR ₂ = 0.1307	R ₁ = 0.0632 wR ₂ = 0.1115

B. Cyclic voltammograms

A nearly reversible oxidation process is observed in all these systems, where the CV scans show well-shaped reverse waves in the 25-250 mV/s scan rate range explored.

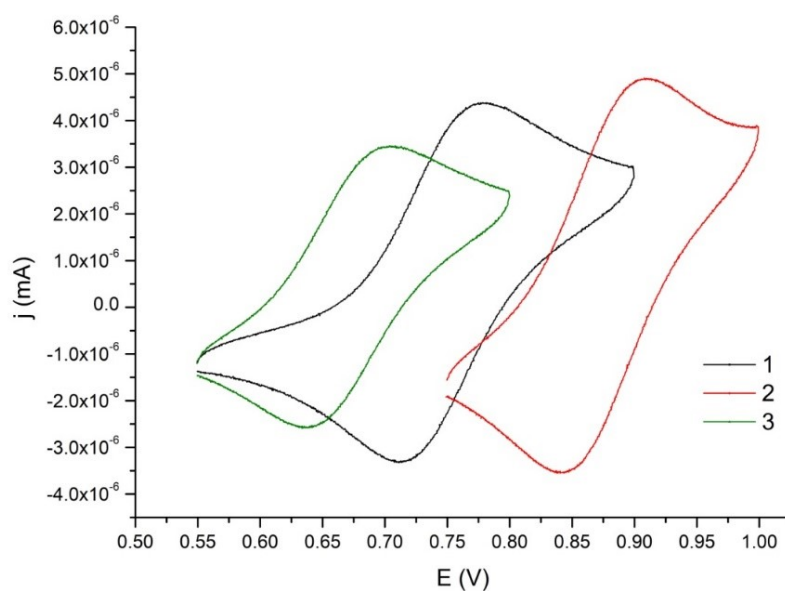


Figure S1. Cyclic voltammograms at 100 mV/s of 1 mM of **1** (black), **2** (red) and **3** (green) in AcN with 0.01M TBAP electrolyte.

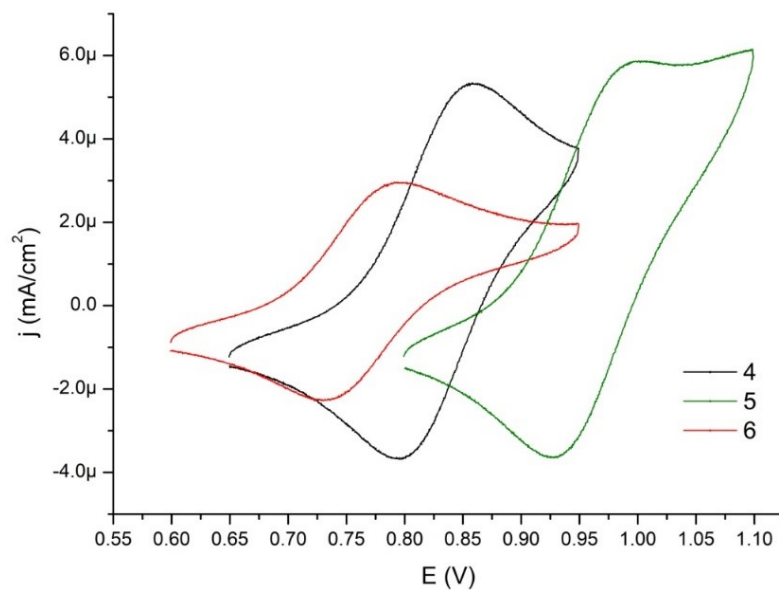


Figure S2. Cyclic voltammograms at 100 mV/s of 1mM of **4** (black), **5** (red) and **6** (green) in AcN with 0.01 M TBAP electrolyte.

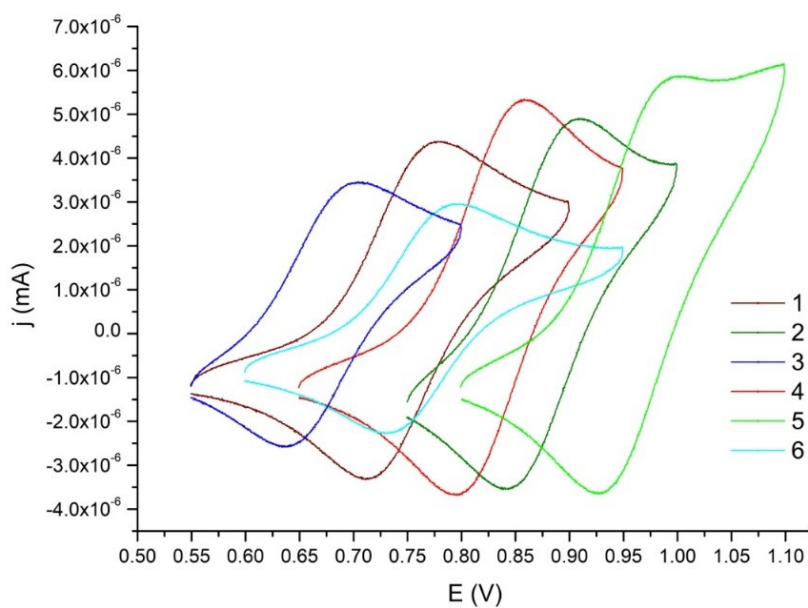


Figure S3. Comparison of cyclic voltammograms at 100 mV/s of 1mM of **1** (E = 0.704V), **2** (E = 0.857V), **3** (E = 0.670 V), **4** (E = 0.783V), **5** (E = 0.956V) and **6** (E = 0.743V) in AcN with 0.01 M TBAP electrolyte.

C. NMR Spectra

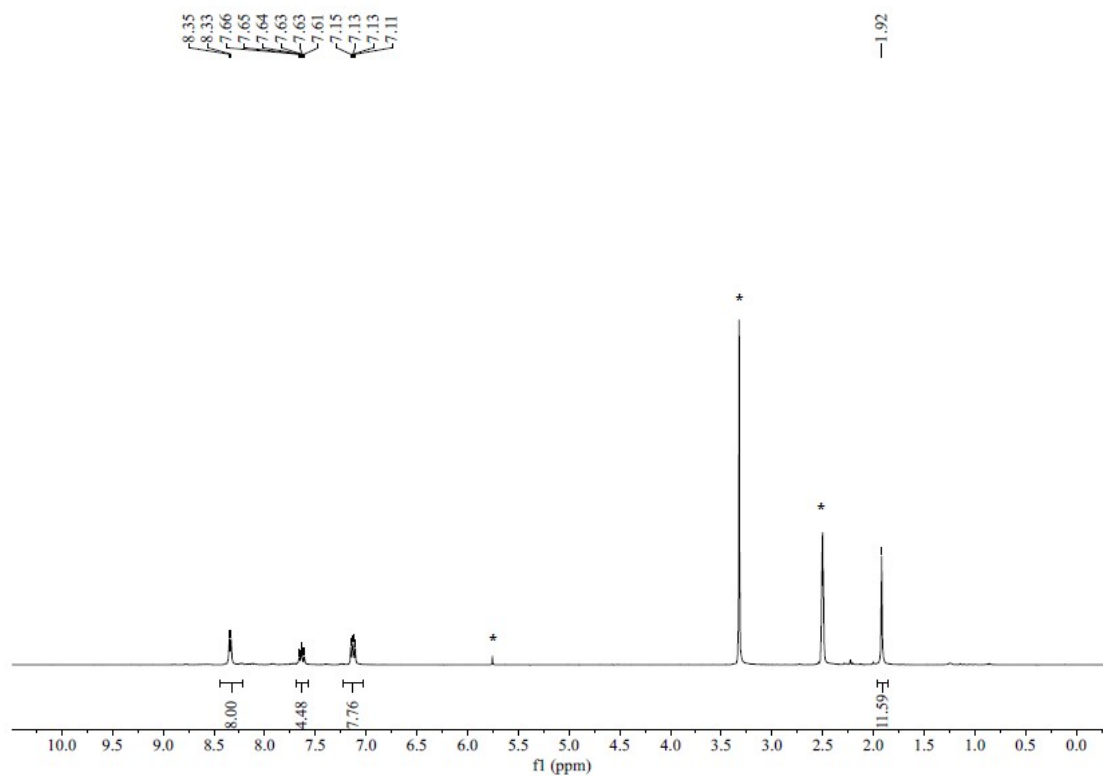


Figure S4. ^1H NMR Spectrum of oxo cubane **1**. * CH_2Cl_2 , water and DMSO-d_6 signals respectively.

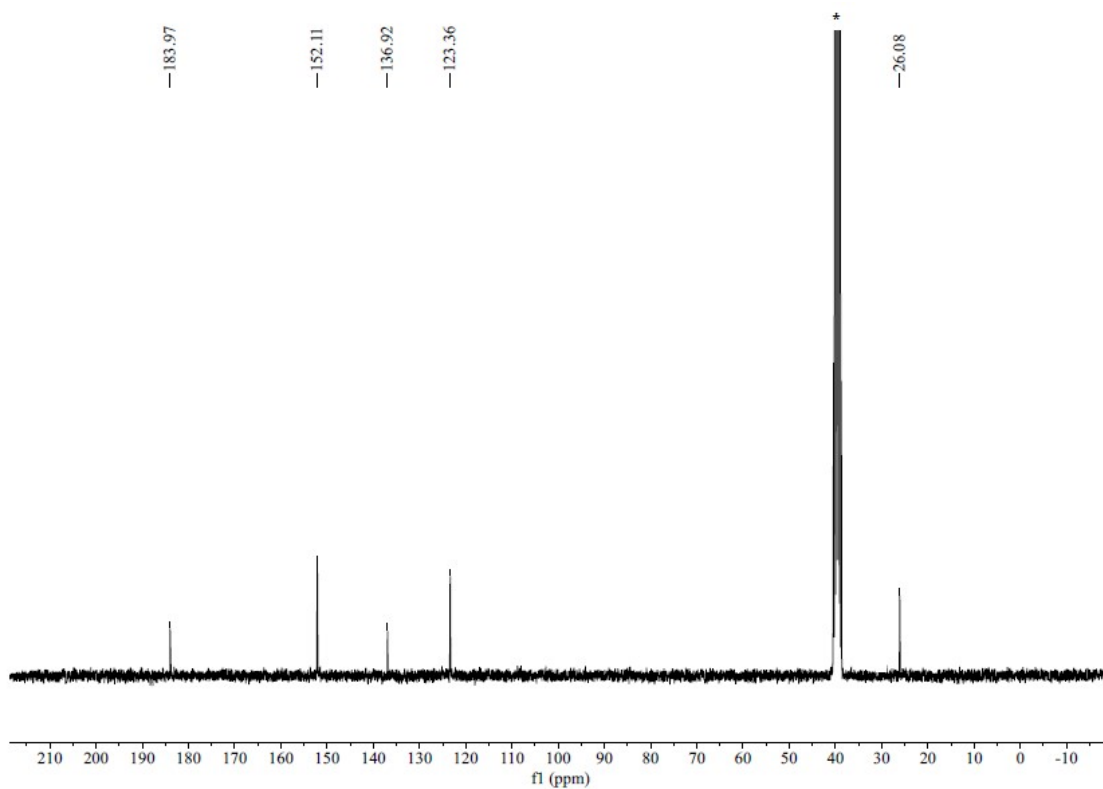


Figure S5. ^{13}C NMR Spectrum of oxo cubane **1**. * DMSO-d_6 signal.

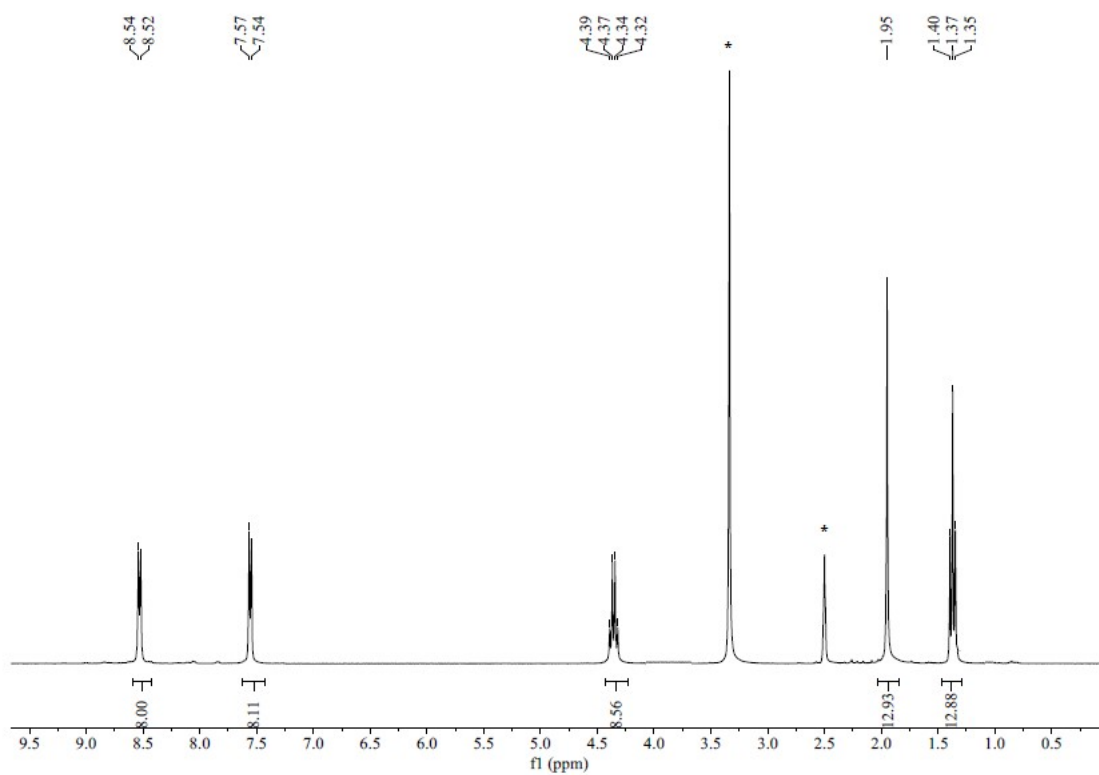


Figure S6. ^1H NMR Spectrum of oxo cubane **2**. *Water and DMSO- d_6 signals, respectively.

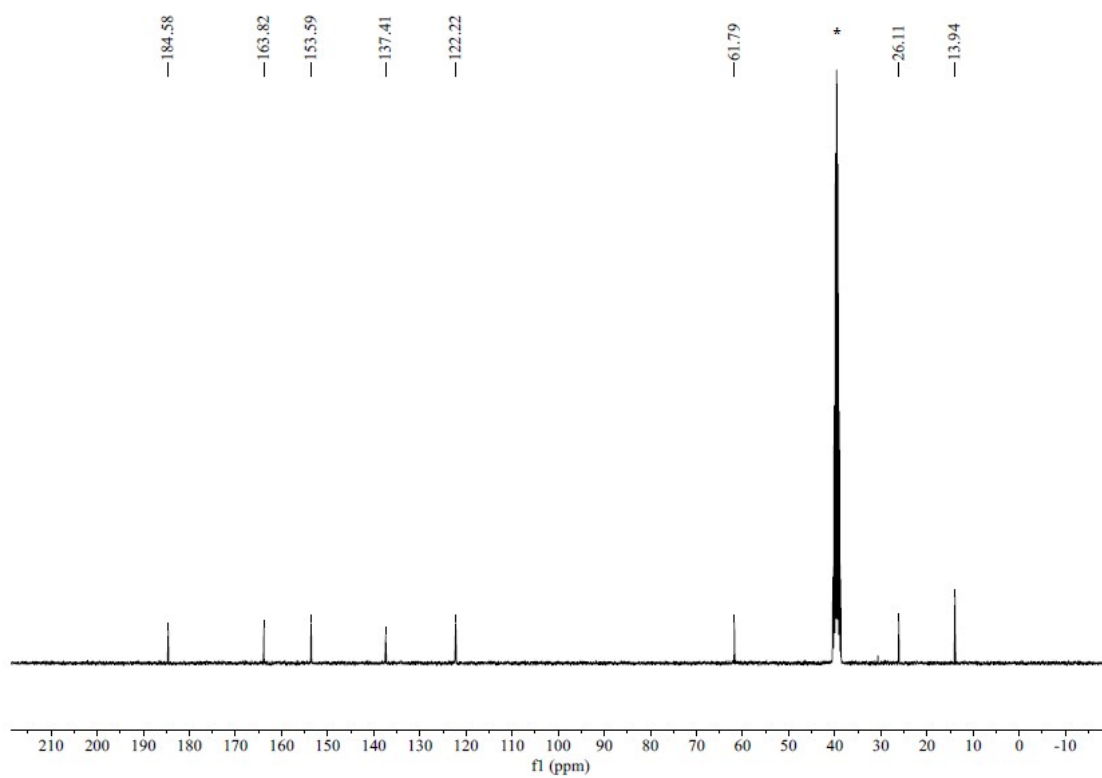


Figure S7. ^{13}C NMR Spectrum of oxo cubane **2**. *DMSO- d_6 signal.

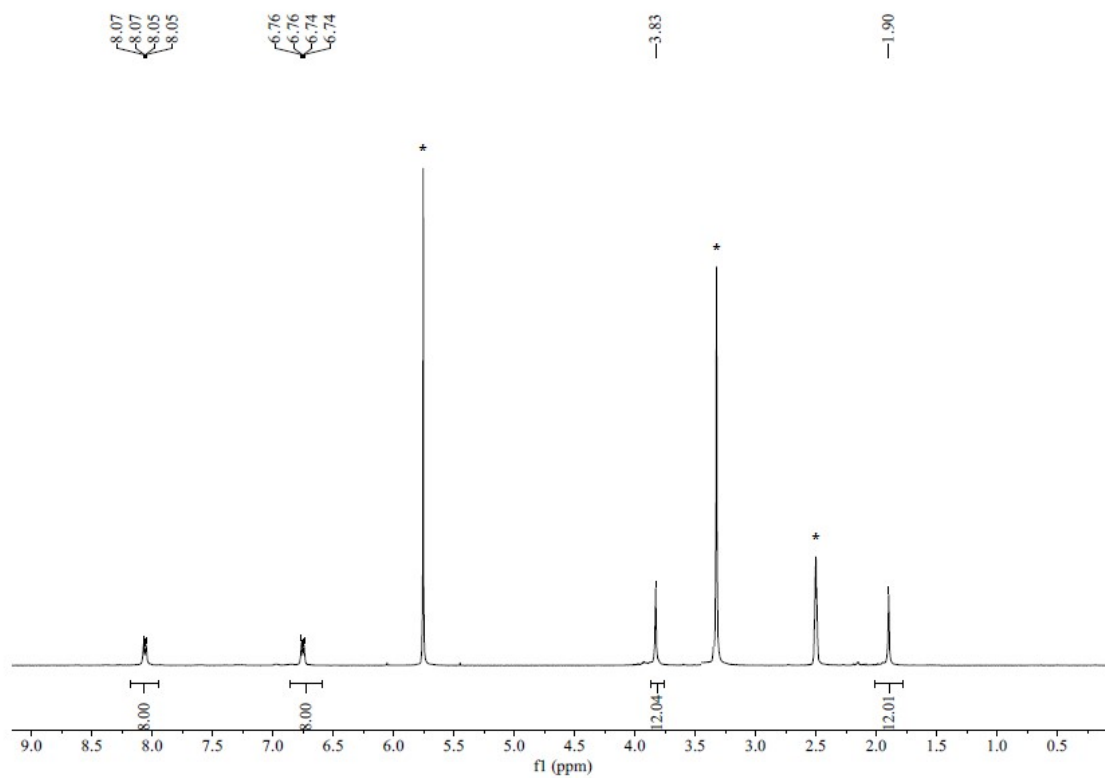


Figure S8. ^1H NMR Spectrum of oxo cubane **3**. *Water and DMSO- d_6 signals, respectively.

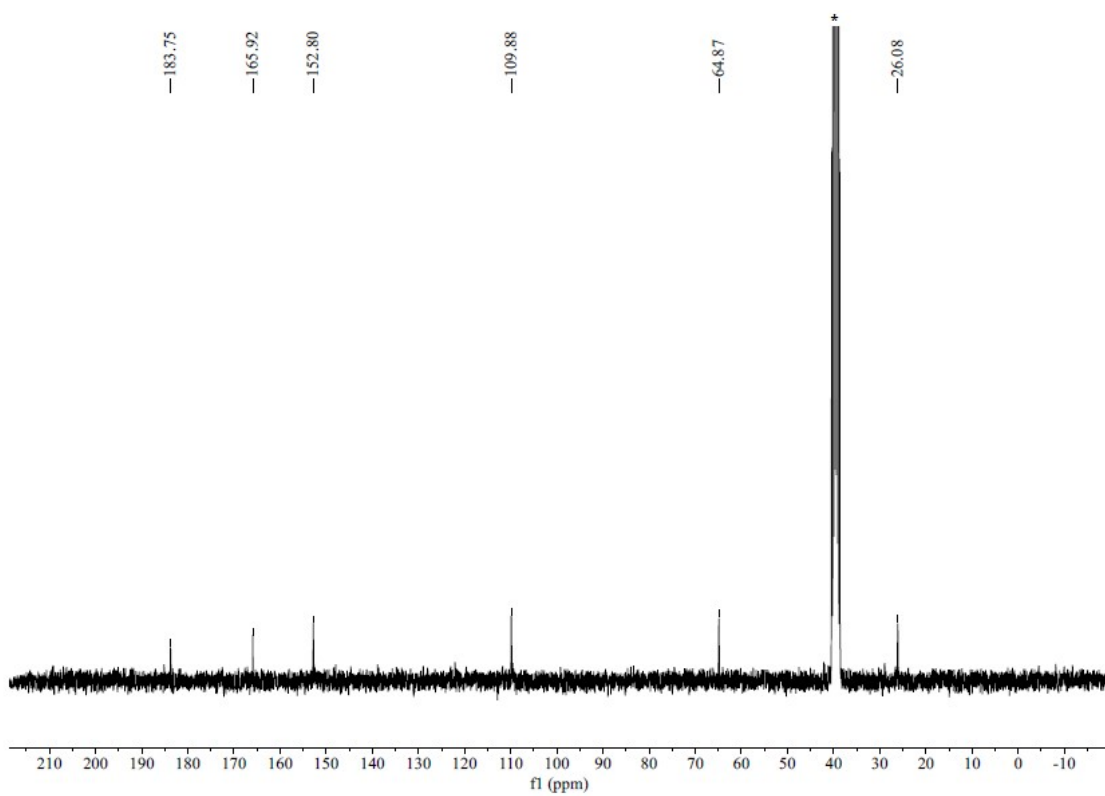


Figure S9. ^{13}C NMR Spectrum of oxo cubane **3**. DMSO- d_6 signal.

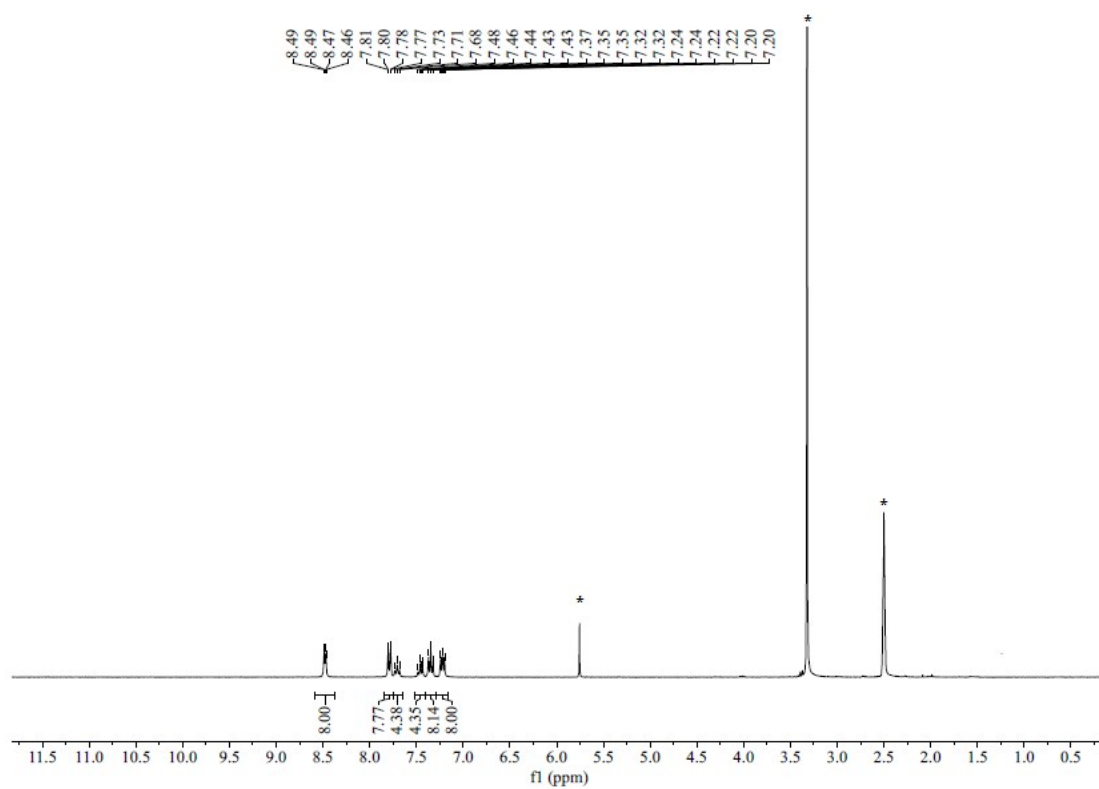


Figure S10. ^1H NMR Spectrum of oxo cubane **4**. * CH_2Cl_2 , water and DMSO-d_6 signals respectively.

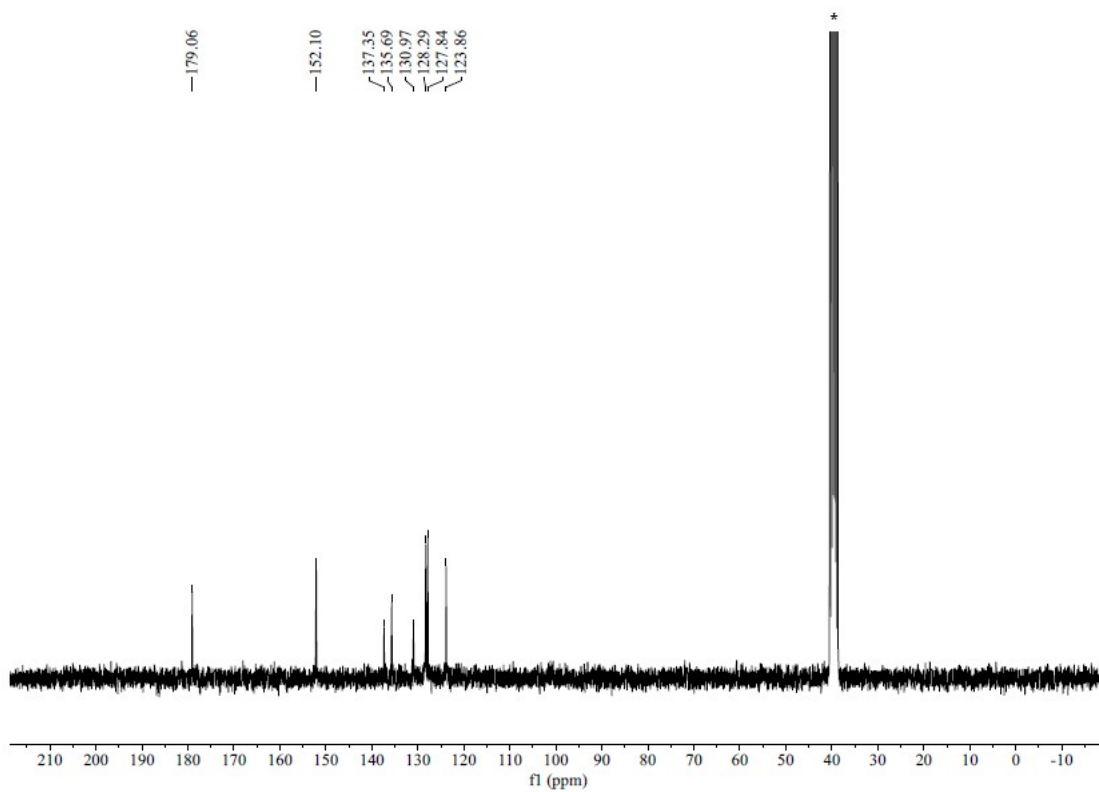


Figure S11. ^{13}C NMR Spectrum of oxo cubane **4**. * DMSO-d_6 signal.

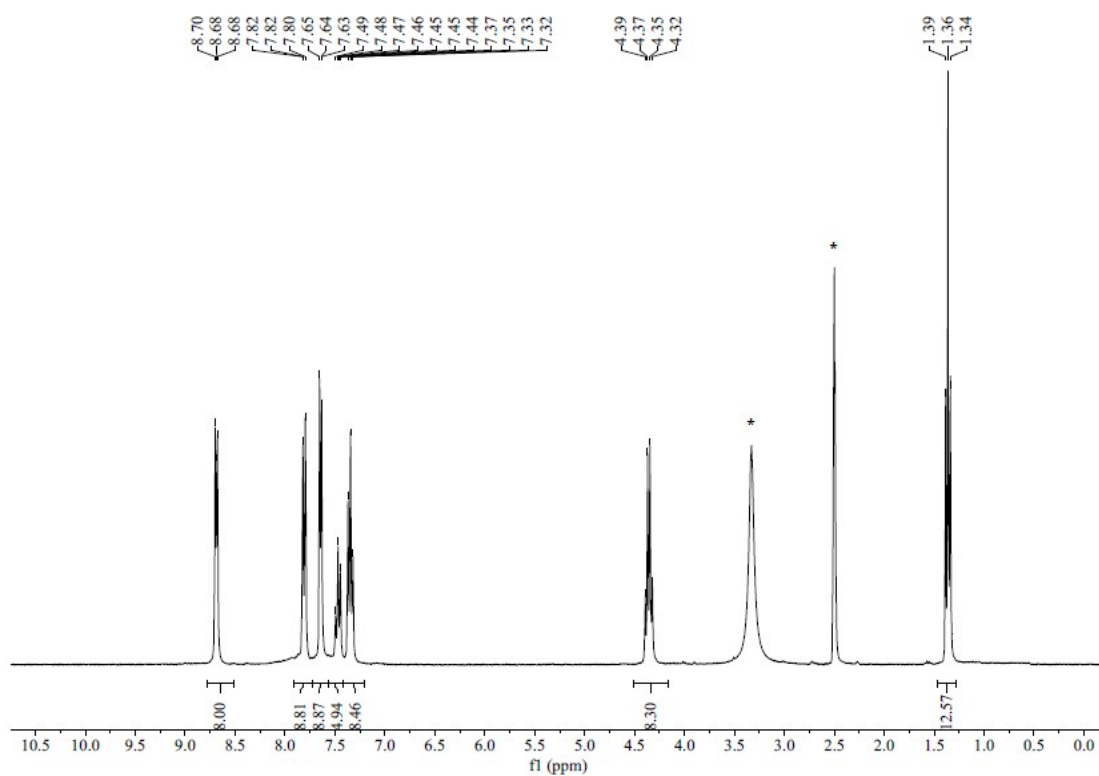


Figure S12. ^1H NMR Spectrum of oxo cubane **5**. *Water and DMSO-d_6 signals respectively.

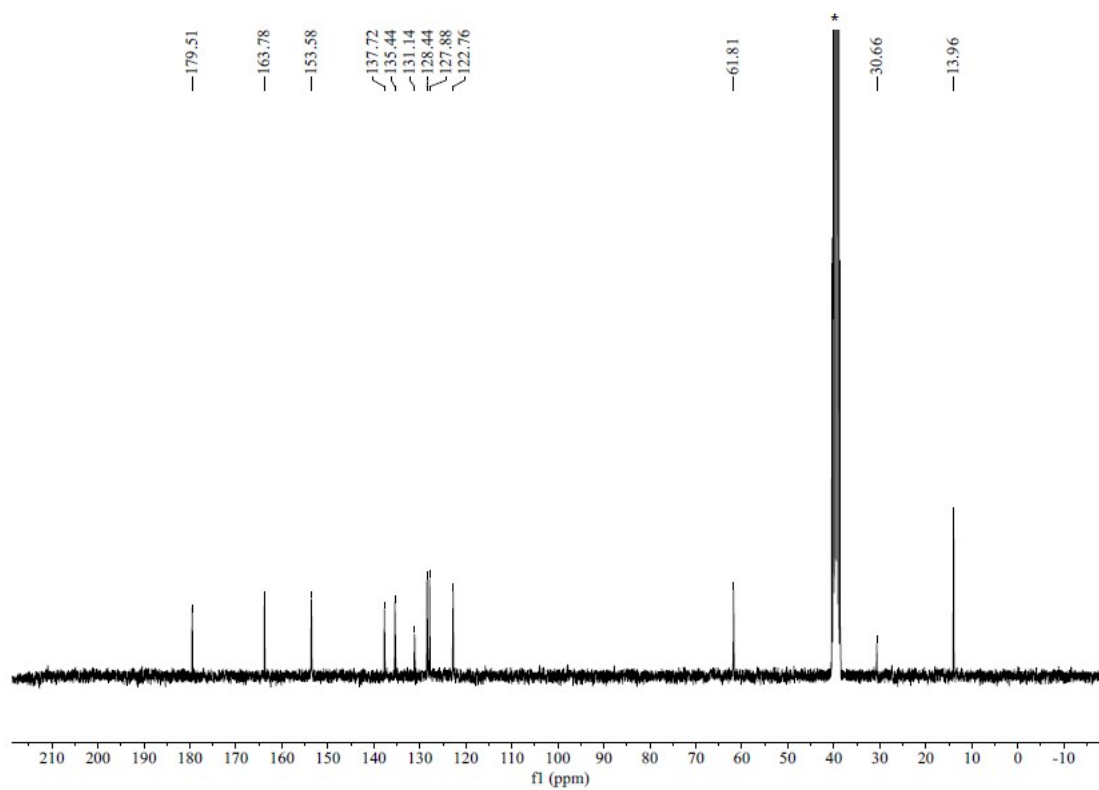


Figure S13. ^{13}C NMR Spectrum of oxo cubane **5**. * CH_2Cl_2 , water and DMSO-d_6 signal.

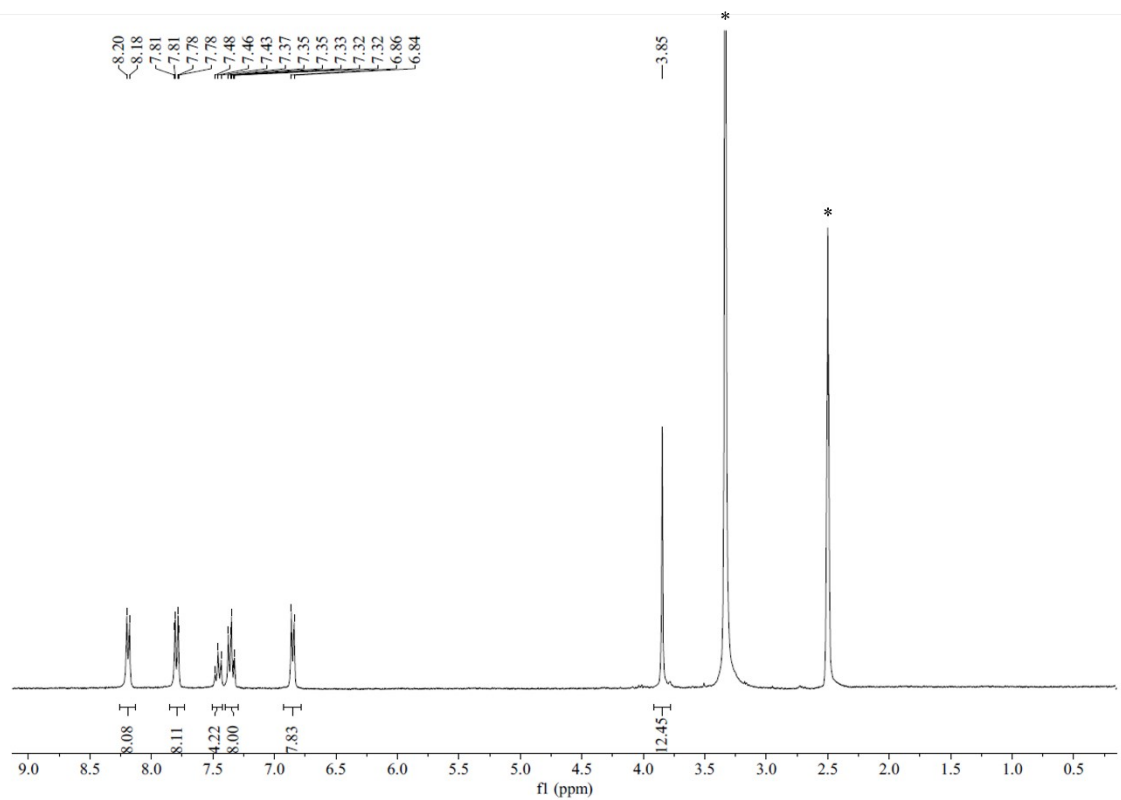


Figure S14. ^1H NMR Spectrum of oxo cubane **6**. * water and DMSO- d_6 signals respectively.

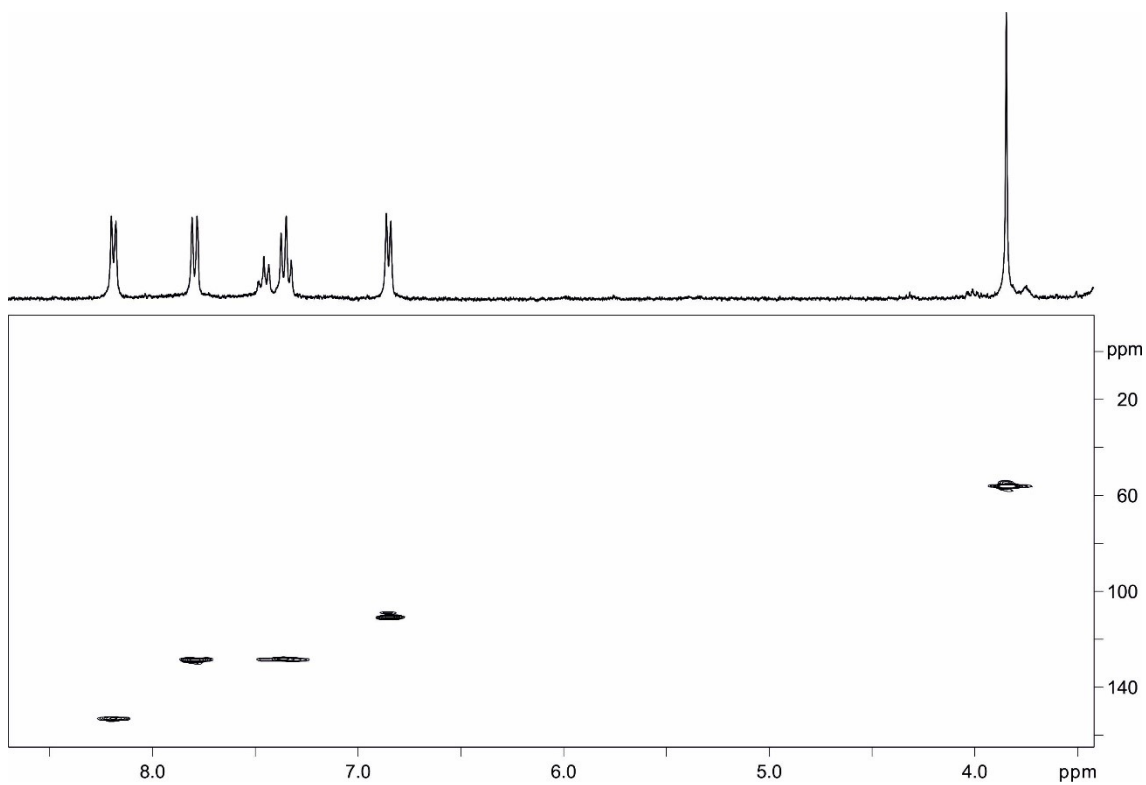


Figure S15. ^1H , ^{13}C gHMBC NMR spectrum of oxo cubane **6**.

D. ESI Spectra.

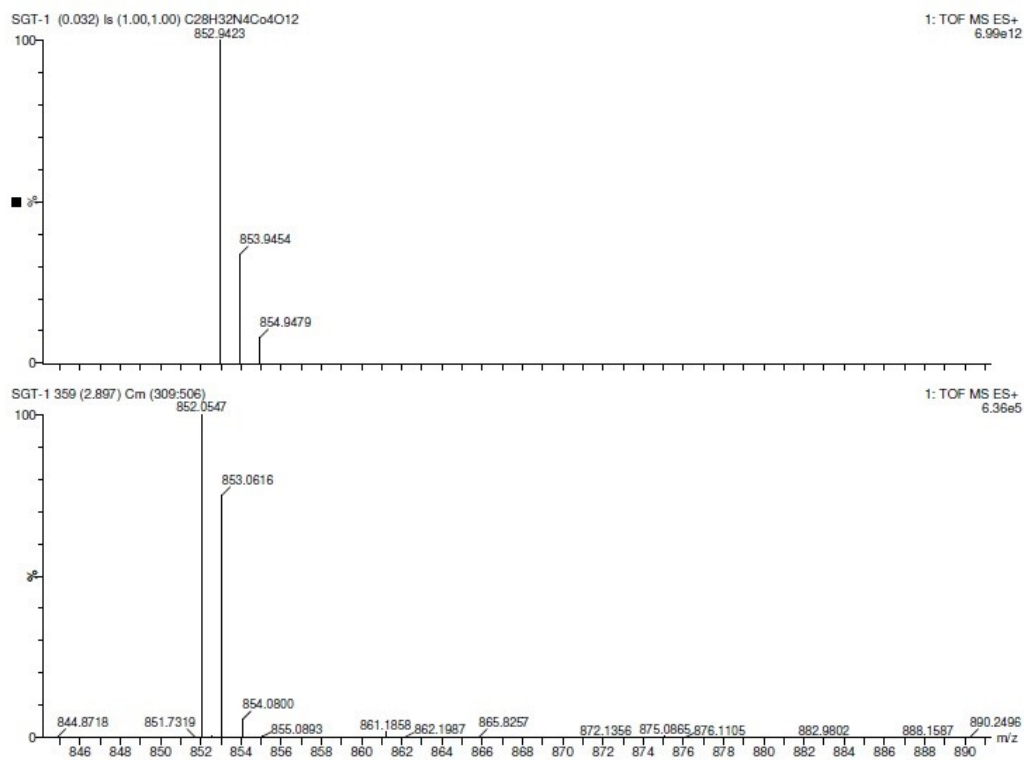


Figure S16. ESI Spectra of complex 1 which correspond with the formula $C_{28}H_{32}Co_4N_4O_{12}$.

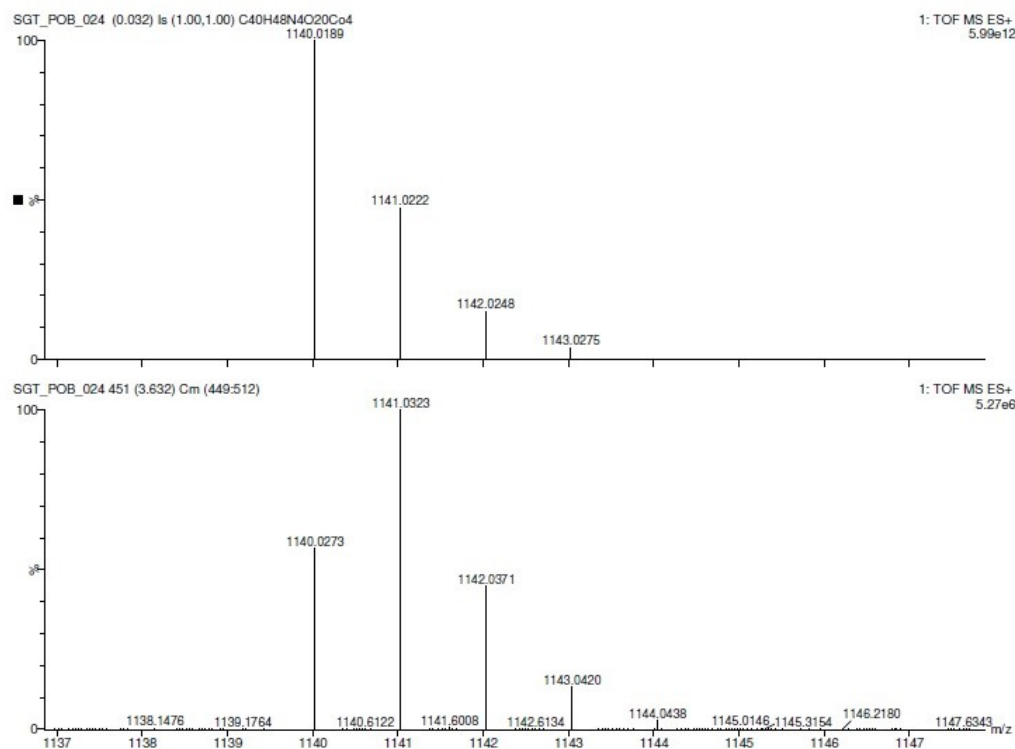


Figure S17. ESI Spectra of complex 2 which correspond with the formula $C_{40}H_{48}Co_4N_4O_{20}$.

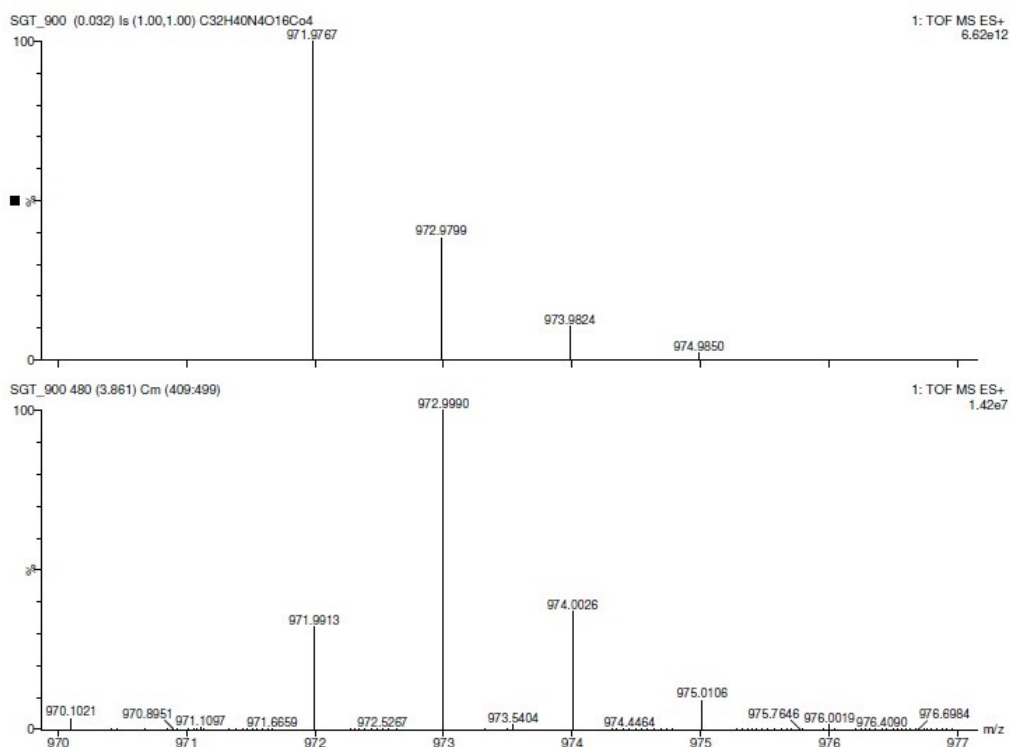


Figure S18. ESI Spectra of complex **3** which correspond with the formula C₃₂H₄₀Co₄N₄O₁₆.

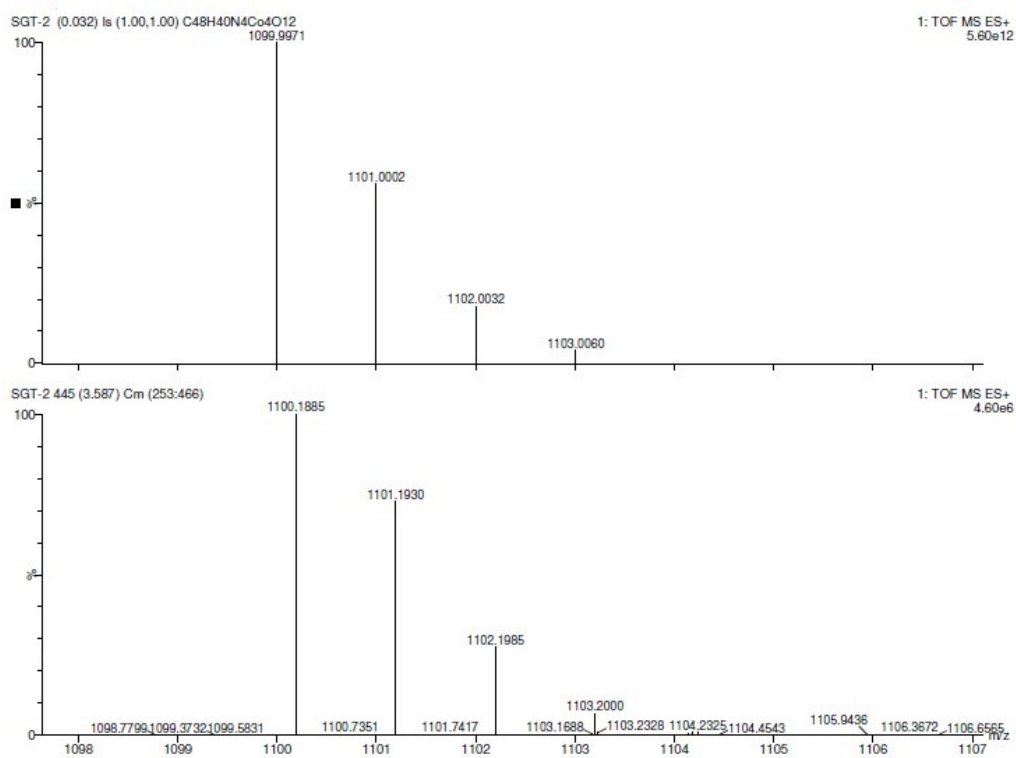


Figure S19. ESI Spectra of complex **4**, which correspond with the formula C₄₈H₄₀Co₄N₄O₁₂.

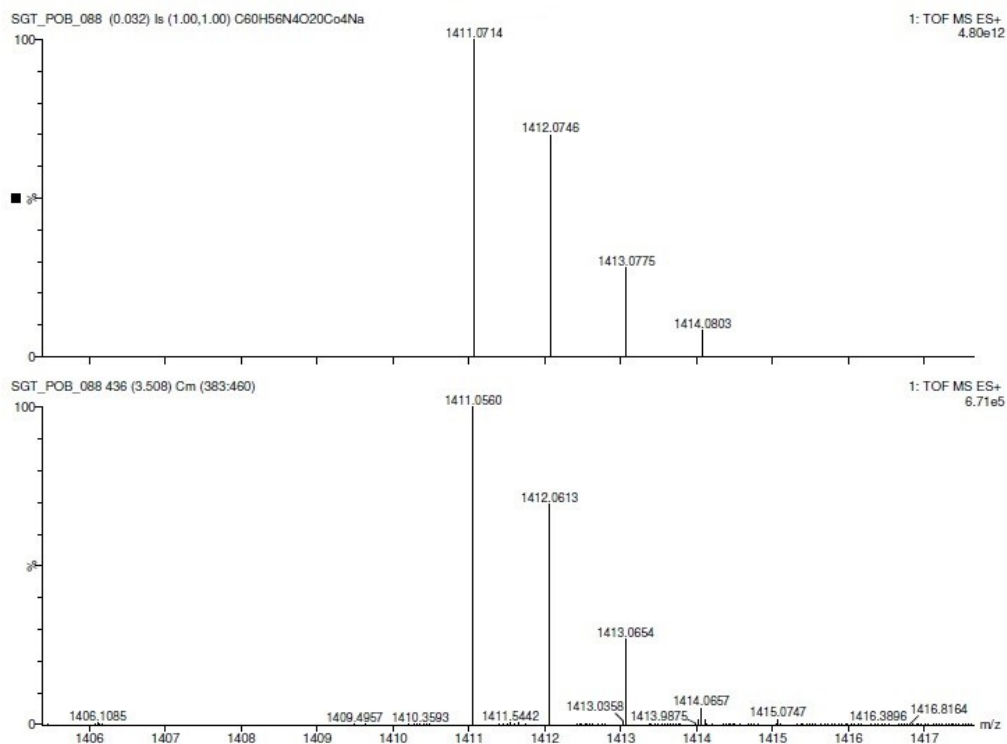


Figure S20. ESI Spectra of complex **5** which correspond with the formula C₆₀H₅₆Co₄N₄O₂₀.

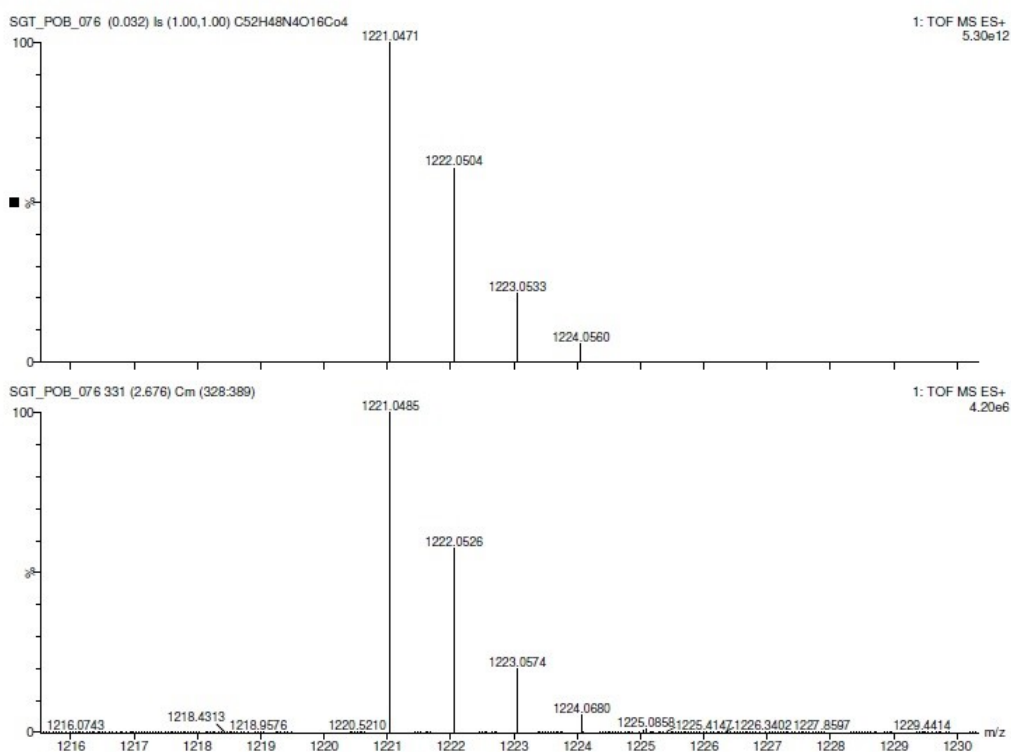


Figure S21. ESI Spectra of complex **6** which correspond with the formula C₅₂H₄₈Co₄N₄O₁₆.

IV. Catalytic study on cyclohexane oxidation.

A. Kinetics experiments on cyclohexane oxidation at 150 °C

Cobalt (II) acetate was initially tested as a benchmark for investigating the activity of cobalt (II) species (entry 2, Table S3). The cobalt clusters **1-6** show a high conversion of cyclohexane oxidation (entries 3-8, Table S3), but only clusters **4** and **5** are better than $\text{Co}(\text{OAc})_2$ under this reaction conditions. In the table S3 are indicated all these reactions at four reaction time 30, 60, 90 and 120 minutes.

Table S3. Summary of the catalytic activity (conversion and product distribution) of cobalt catalysts for cyclohexane oxidation. Reaction conditions: 3 g Cyclohexane (36 mmol); 0.14 ppm Co; T^a 150 °C; 10 bar ($\text{N}_2:\text{O}_2 = 80:20$); $Q = 10$ mL/min). [a] A = alcohol, cyclohexanol; [b] K = ketone, cyclohexanone; [c] CHHP = cyclohexyl hydroperoxide; [d] AA = adipic acid; [e] Total observed selectivity.

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Reaction time (min)	Conversion (%)	Selectivity (%)				
		A ^a	K ^b	CHHP ^c	AA ^d	Total ^e
30	0.1	6	21	73	0	100
60	0.3	7	6	86	0	99
90	1.2	8	10	80	0	98
120	3.4	33	18	45	0	96

$\text{Co}(\text{OAc})_2$.

Reaction time (min)	Conversion (%)	Selectivity (%)				
		A ^a	K ^b	CHHP ^c	AA ^d	Total ^e
30	1.1	17	10	72	0	99
60	4.3	44	22	30	0	96
90	7.1	50	35	8	1	94
120	9	47	41	4	2	94

Cluster 1.

Reaction time (min)	Conversion (%)	Selectivity (%)				
		A ^a	K ^b	CHHP ^c	AA ^d	Total ^e
30	0.4	8	10	82	0	100
60	2.7	35	18	42	1	96
90	4.7	38	26	29	1	94
120	6.8	41	35	17	1	94

Cluster 2.

Reaction time (min)	Conversion (%)	Selectivity (%)				
		A ^a	K ^b	CHHP ^c	AA ^d	Total ^e
30	0.9	8	15	76	0	99
60	3.6	40	24	32	0	96
90	6.5	41	35	17	1	95
120	8.3	40	41	11	2	94

Cluster 3.

Reaction time (min)	Conversion (%)	Selectivity (%)				
		A ^a	K ^b	CHHP ^c	AA ^d	Total ^e
30	0.2	5	10	84	0	99
60	2.2	14	20	62	0	96
90	3.8	21	24	47	1	93
120	4.5	25	25	40	2	92

Cluster 4.

Reaction time (min)	Conversion (%)	Selectivity (%)				
		A ^a	K ^b	CHHP ^c	AA ^d	Total ^e
30	1	27	13	59	0	99
60	4	41	24	32	0	97
90	7.1	43	39	14	1	97
120	8.6	40	45	10	1	96

Cluster 5.

Reaction time (min)	Conversion (%)	Selectivity (%)				
		A ^a	K ^b	CHHP ^c	AA ^d	Total ^e
30	2.2	36	18	45	0	99
60	5.8	45	30	21	0	96
90	8.2	41	37	14	1	93
120	10.8	36	43	13	2	94

Cluster 6.

Reaction time (min)	Conversion (%)	Selectivity (%)				
		A ^a	K ^b	CHHP ^c	AA ^d	Total ^e
30	0.7	25	10	63	0	98
60	2.8	33	18	44	0	95
90	5.1	21	24	46	1	92
120	6.2	39	32	19	2	92

B. Kinetics experiments on cyclohexane oxidation at 130 °C

Table S4. Summary of the catalytic activity (conversion and product distribution) of cobalt catalysts for cyclohexane oxidation. Reaction conditions: 3 g Cyclohexane (36 mmol); 0.14 ppm Co; T^a 130 °C; 6 bar (N₂:O₂ = 95:5); Q = 10 mL/min). [a] A = alcohol, cyclohexanol; [b] K = ketone, cyclohexanone; [c] CHHP = cyclohexyl hydroperoxide; [d] AA = adipic acid; [e] Total observed selectivity.

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Reaction time (h)	Conversion (%)	Selectivity (%)				
		A ^a	K ^b	CHHP ^c	AA ^d	Total ^e
2	0.1	1	2	97	0	100
4	0.2	30	12	58	0	100
6	0.4	25	6	58	1	90
7	0.6	20	10	58	1	89
8	0.8	30	15	54	1	100

Co(OAc)₂.

Reaction time (h)	Conversion (%)	Selectivity (%)				
		A ^a	K ^b	CHHP ^c	AA ^d	Total ^e
2	0.9	10	15	74	0	99
4	4.8	31	37	28	0	96
7	6.1	41	52	2	1	96
8	7.7	30	53	5	5	93

Cluster 1.

Reaction time (h)	Conversion (%)	Selectivity (%)				
		A ^a	K ^b	CHHP ^c	AA ^d	Total ^e
2	0.6	26	10	63	0	100
4	2.3	43	14	38	1	97
6	8.0	53	25	17	1	96
7	9.9	55	27	12	1	95
8	10.9	54	29	10	2	94

Cluster 2.

Reaction time (h)	Conversion (%)	Selectivity (%)				
		A ^a	K ^b	CHHP ^c	AA ^d	Total ^e
2	1.0	22	13	65	0	100
4	2.8	32	18	49	1	99
6	7.1	37	27	28	2	94
7	10.5	35	32	22	3	91
8	12.2	35	36	14	3	88

Cluster 3.

Reaction time (h)	Conversion (%)	Selectivity (%)				
		A ^a	K ^b	CHHP ^c	AA ^d	Total ^e
2	0.4	17	18	65	0	100
4	1.9	33	20	46	1	99
6	4.6	44	30	20	5	98
7	6.3	49	34	8	6	98
8	7.5	50	38	6	5	99

Cluster 4.

Reaction time (h)	Conversion (%)	Selectivity (%)				
		A ^a	K ^b	CHHP ^c	AA ^d	Total ^e
2	0.9	19	14	67	0	100
4	5.7	49	23	21	0	93
6	9.5	49	29	11	8	97
7	11.1	46	28	9	6	89
8	12.2	44	29	7	6	86

Cluster 5.

Reaction time (h)	Conversion (%)	Selectivity (%)				
		A ^a	K ^b	CHHP ^c	AA ^d	Total ^e
2	2.6	14	8	77	0	99
4	6.1	38	25	31	1	96
6	10.6	44	38	11	2	95
7	12.9	42	42	9	2	95
8	14.2	37	44	8	3	92

Cluster 6.

Reaction time (h)	Conversion (%)	Selectivity (%)				
		A ^a	K ^b	CHHP ^c	AA ^d	Total ^e
2	0.7	0	13	87	0	100
4	2.4	10	20	64	2	97
6	7.8	27	37	23	3	89
7	9.6	34	45	13	4	96
8	11.1	32	53	9	5	99

C. Comparison with reported catalysts for cyclohexane oxidation

Table S5. Comparison of the best cobalt cluster (5) with reported catalysts.

Catalytic system	Reaction conditions	Conversion (%)	Selectivity (%)	Ref.
GOS	CH = 46.28 mmol, cat = 2mg, 1.5 MPa O ₂ , 150°C, 3h	3.8	92.4	2
Fe(TCPP)	CH = 1.85 mol, cat = 1 mg, 0.8 MPa O ₂ , 160°C, 4h	35.6	64	3
Fe(TCPP)/ZnS	CH = 1.85 mol, cat = 1 mg, 0.8 MPa O ₂ , 160°C, 4h	24.4	40	3
Fe(TPFPP)	CH = 1.85 mol, cat = 1·10 ⁻³ mmol, 0.7 MPa O ₂ , 150°C, 2.5h	15	64	4
Fe(TPFPP)/ZnO	CH = 1.85 mol, cat = 1·10 ⁻³ mmol, 0.7 MPa O ₂ , 150°C, 2.5h	22.5	56.5	4
Fe(TPPS)pd-CTS	CH = 1.85 mol, cat = 1.0753 g, 0.8 MPa O ₂ , 155°C, 4h	28.67	60	5
1.0Au/Al ₂ O ₃	CH = 185.1 mmol, cat = 50 mg, 1.5 MPa O ₂ , 150°C, 3h	10.9	84.3	6
Au@MCM-22-S	CH = 18.51 mmol, cat = 25 mg, 1 MPa O ₂ , 150°C, 2h	12	87	7
Au@MCM-22-L	CH = 18.51 mmol, cat = 25 mg, 1 MPa O ₂ , 150°C, 2h	16	80	7
2%Co-MgAlO	CH = 712.9 mmol, cat = 50 mg, 0.6 MPa O ₂ , 150°C, 2h	9.1	82	8
1%Pt/SiO ₂	CH = 185.1 mmol, cat = 50 mg, 1 MPa O ₂ , 140°C, 1h	9.9	89.4	9
1%Au/SiO ₂	CH = 185.1 mmol, cat = 50 mg, 1 MPa O ₂ , 140°C, 1h	8.9	94.6	9
Co(II) (DPDME) + L-cysteine	CH = --, cat = 2·10 ⁻⁵ mol/L, 0.8 MPa O ₂ , 150°C, 3.5h	24.8	85.8	10
Ag ₃ Pd ₁ /MgO	CH = 101 mmol, cat = 6 mg, 0.3 MPa O ₂ , 140°C, 17h	10	95	11
Industrial process, Co, Mn complexes	1.5 MPa O ₂ , 160°C	> 9	85	12
Co ₄ O ₄ (OBz) ₄ (p- COOEt-py) ₄ (5)	CH = 36 mmol, cat = 0.14 ppm Co, 0.6 MPa air (N ₂ :O ₂ = 95:5), 130°C, 7h	12.9	95	This work

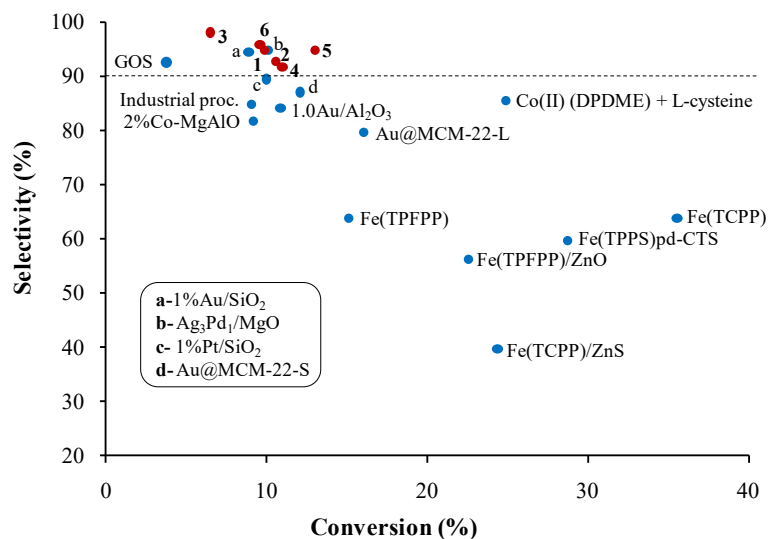


Chart S1. Comparison of **1-6** cobalt catalysts (red) with other reported catalysts (blue) for aerobic cyclohexane oxidation under similar reaction conditions.

V. Mechanistic studies.

A. EPR Spectra

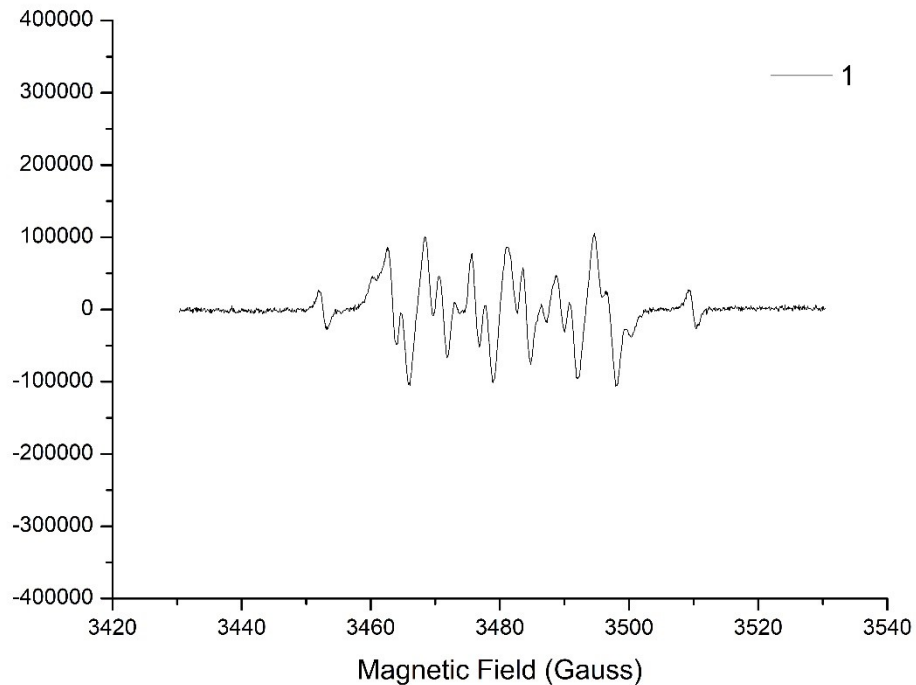


Figure S22. EPR spectra of spin trapping experiments for CHHP decomposition by **1**.

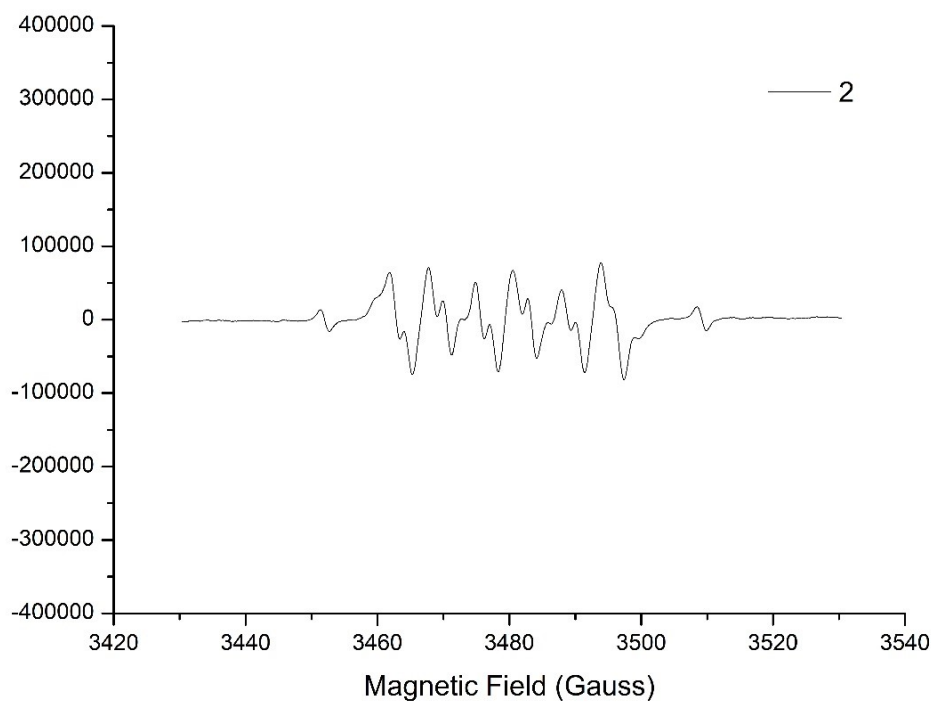


Figure S23. EPR spectra of spin trapping experiments for CHHP decomposition by **2**.

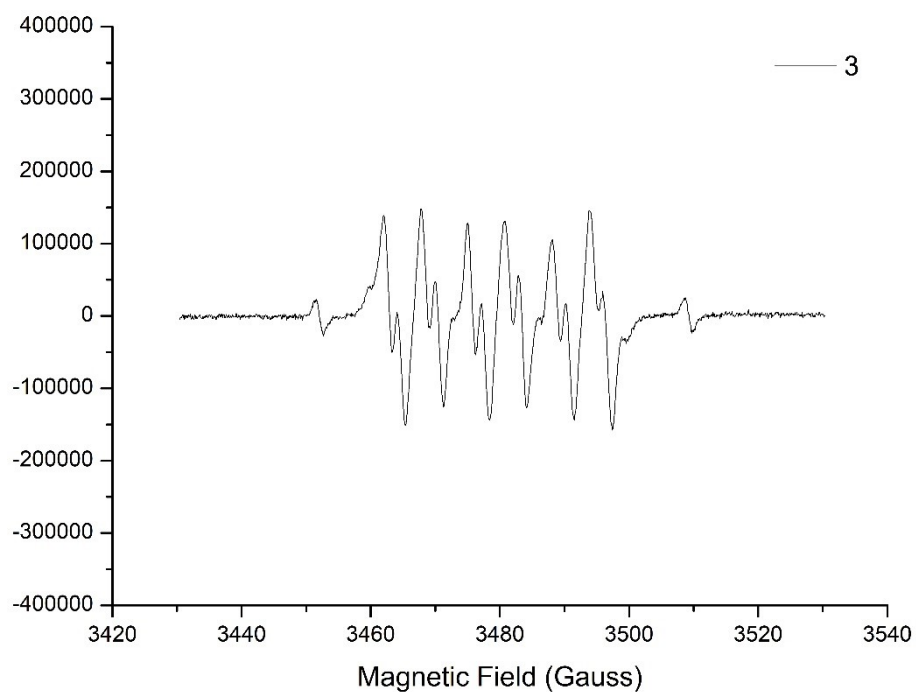


Figure S24. EPR spectra of spin trapping experiments for CHHP decomposition by **3**.

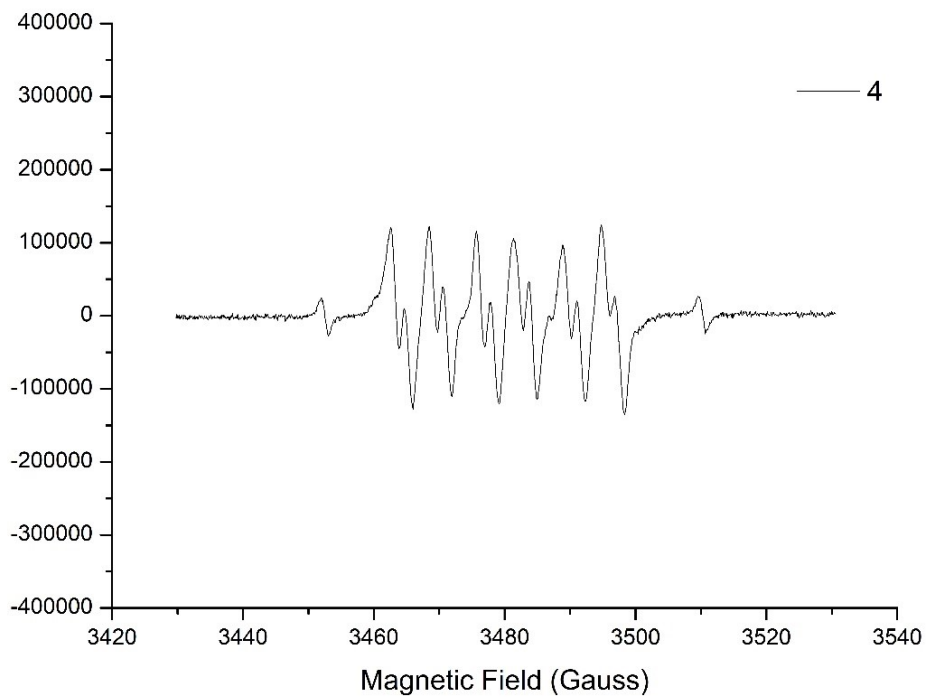


Figure S25. EPR spectra of spin trapping experiments for CHHP decomposition by **4**.

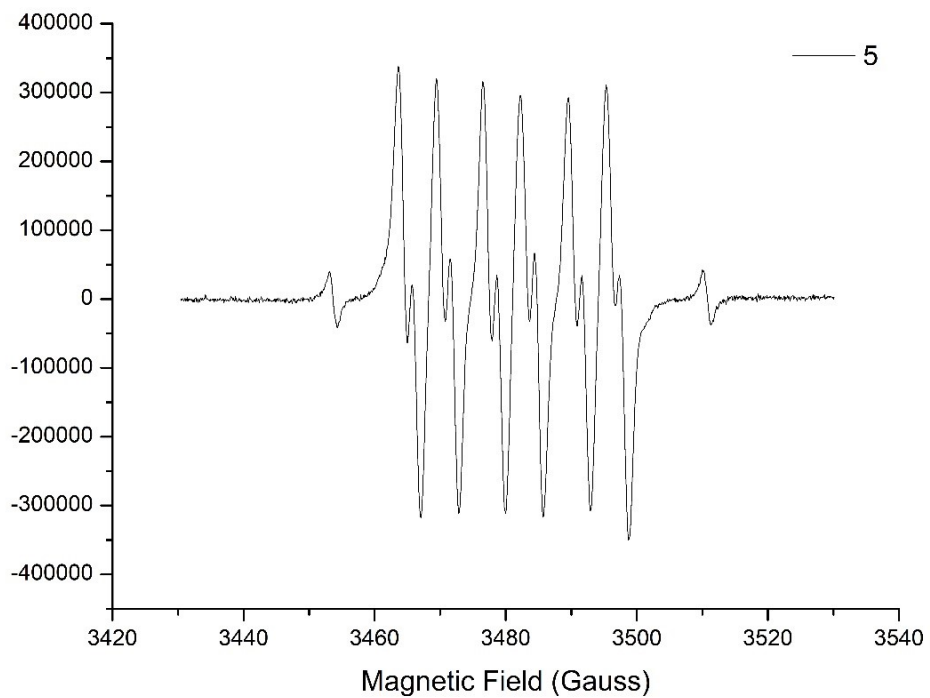


Figure S26. EPR spectra of spin trapping experiments for CHHP decomposition by **5**.

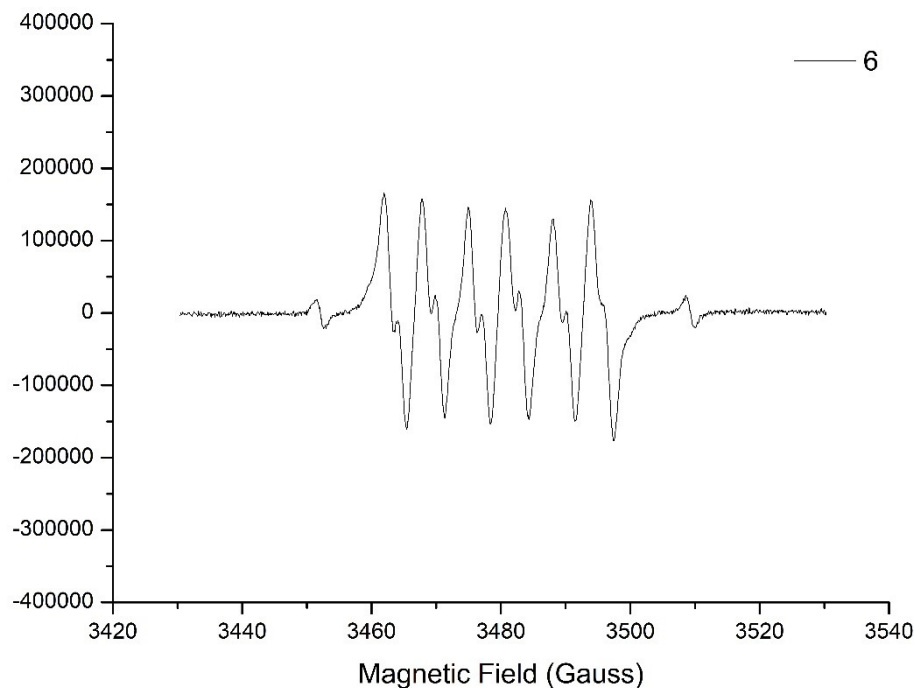


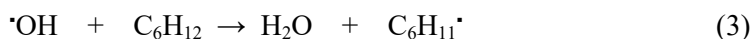
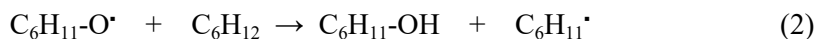
Figure S27. EPR spectra of spin trapping experiments for CHHP decomposition by **6**.

B. CHHP decomposition

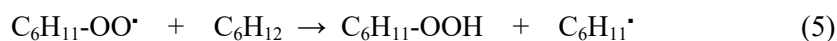
CHHP can decompose by cleavage of the O-O bond of the hydroperoxide group either through thermal decomposition or assisted by a metal centre.¹³ This reaction affords the formation of an alkoxy and a hydroxy radical (Equation 1):



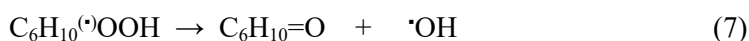
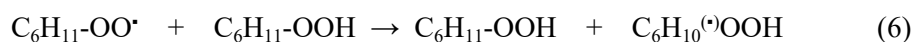
The alkoxy radical can react further with cyclohexane to give cyclohexanol and a $\text{C}_6\text{H}_{11}^\bullet$ radical (Equation 2), while the reaction between the hydroxy radical and cyclohexane provides water and another $\text{C}_6\text{H}_{11}^\bullet$ radical, respectively (Equation 3):



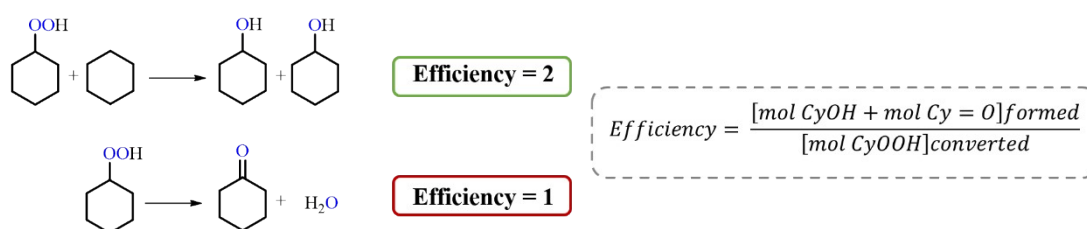
On the other hand, the $\text{C}_6\text{H}_{11}^\bullet$ radical reacts quickly with molecular oxygen, in a diffusion-limited reaction step¹³ affording to the formation of cyclohexyl peroxide ($\text{C}_6\text{H}_{11}\text{-OO}^\bullet$, abbreviated to CHP) (Equation 4). Then, CHP reacts with cyclohexane to provide cyclohexyl hydroperoxide ($\text{C}_6\text{H}_{11}\text{-OOH}$, CHHP) and $\text{C}_6\text{H}_{11}^\bullet$ radical (Equation 5):



The equations 6 and 7 show a series of reactions, involving H- α abstraction, where the CHP/CHHP molecules initiate the formation of cyclohexanol and cyclohexanone.¹⁴ Also, it is likely the CHP disproportionation, which is known as the termination reaction (Equation 8).¹⁵



Several studies support that a free radical pathway requires an initiation step, which involves the abstraction of a H atom from cyclohexane to form a cyclohexyl radical ($\text{C}_6\text{H}_{12} \rightarrow \text{C}_6\text{H}_{11}^\bullet$).¹⁶ So thus, no alkoxy radical ($\text{C}_6\text{H}_{11}\text{-O}^\bullet$) is needed to promote the reaction, and the cyclohexanone, will always be obtained as a consequence of the autoxidation pathway involving the CHP/CHHP pair (Equations 6-8). The conclusion will be if a pure radical pathway governs the reaction, the cyclohexanone will always be in excess with respect to the cyclohexanol. Current studies of the autoxidation reaction report a K/A ratio of about 1–1.5 when no selectivity control by the catalyst is occurring.¹⁷ These studies conclude that a fast cleavage of the O-O bond in CHHP (Equation 1) is the mainly way to obtain an excess of alcohol from the mentioned Equations (1–8).^{18,19}



Scheme S1. CCHP decomposition and efficiency calculation.

C. In situ Raman Spectroscopy

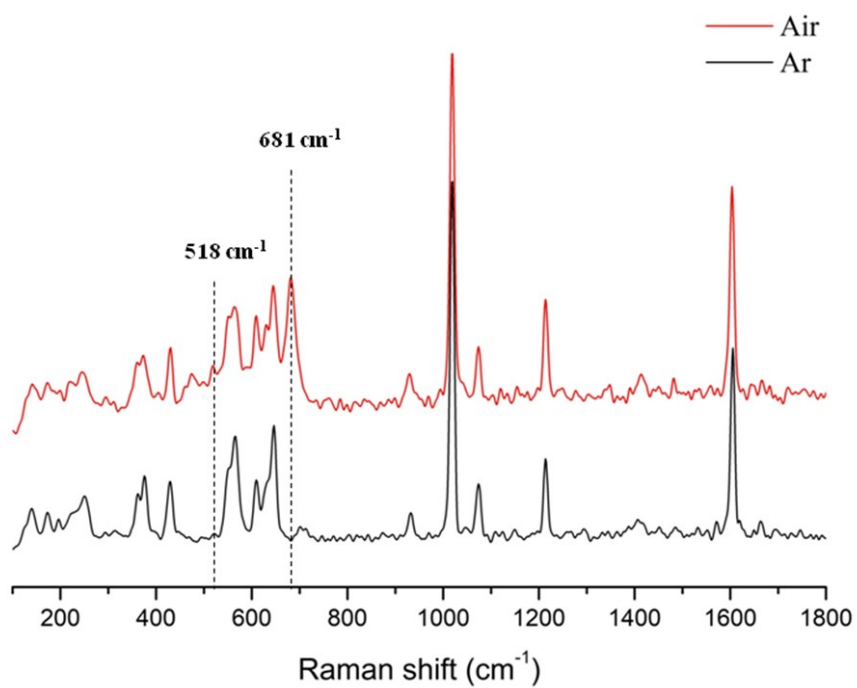


Figure S28. Raman spectra of complex **1** in Ar (black) and passing an O_2 flow.

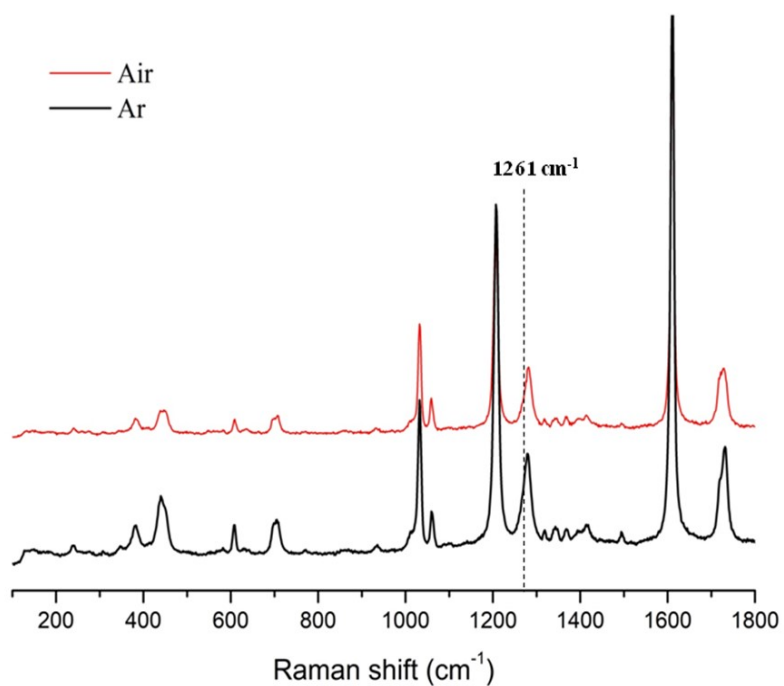


Figure S29. Raman spectra of complex **2** in Ar (black) and passing an O_2 flow.

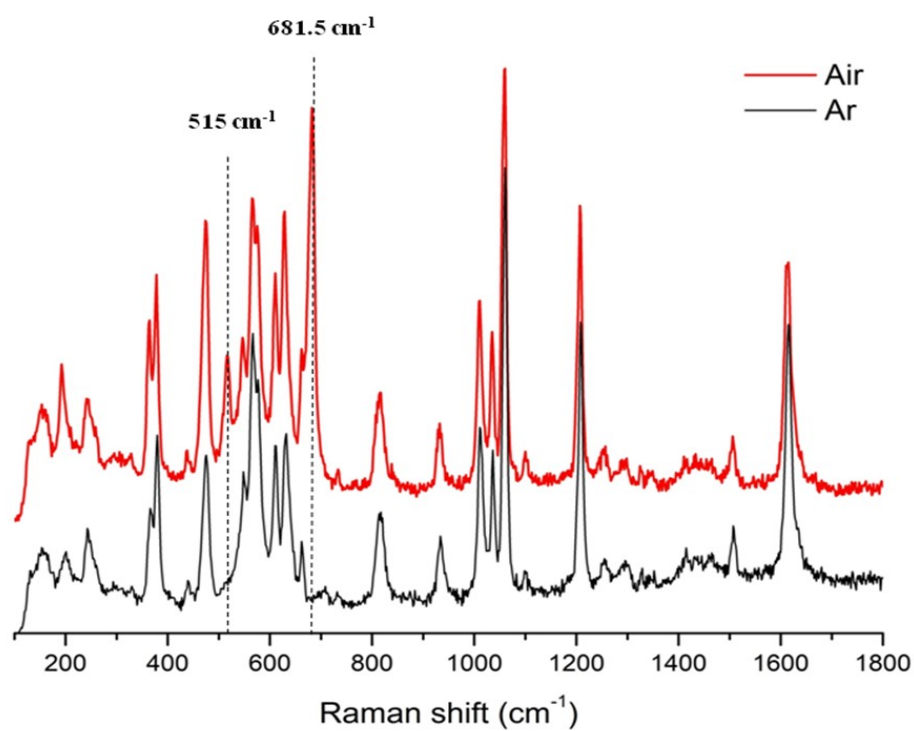


Figure S30. Raman spectra of complex 3 in Ar (black) and passing an O_2 flow.

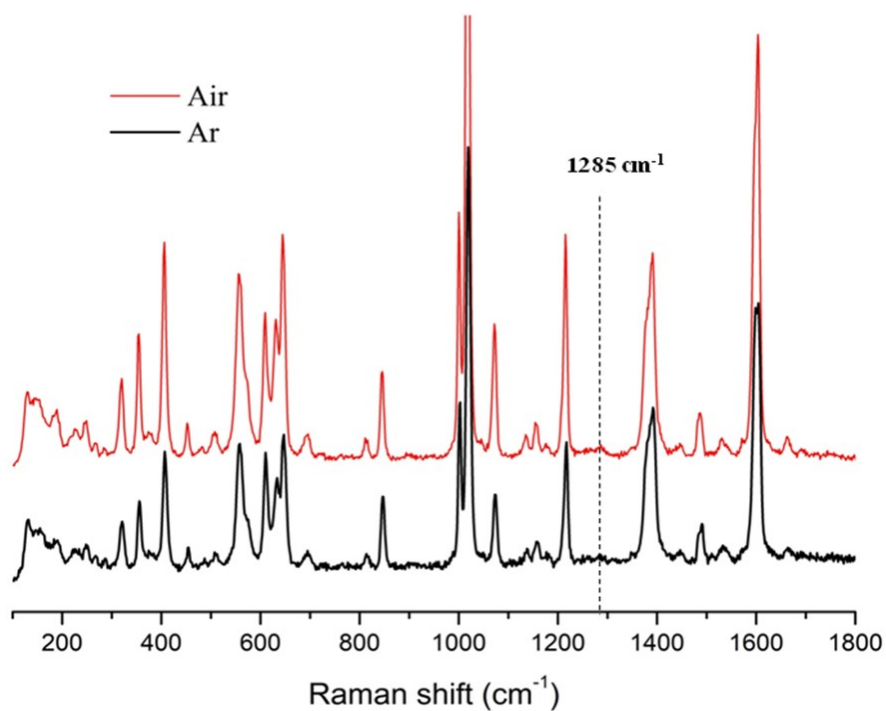


Figure S31. Raman spectra of complex 4 in Ar (black) and passing an O_2 flow.

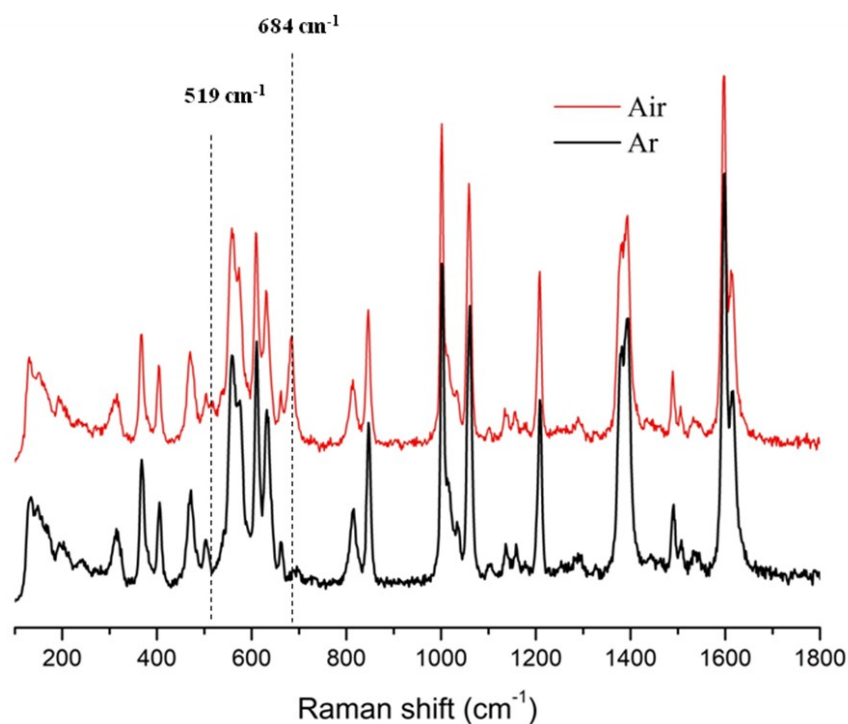


Figure S32. Raman spectra of complex **6** in Ar (black) and passing an O₂ flow (red).

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