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Electronic Supplementary Information for

N_2O-free single-pot conversion of cyclohexane to adipic acid catalysed by an iron(II) scorpionate complex

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Experimental Details

Materials and Equipment

All the reagents and solvents were purchased from commercial sources and used as received. [$FeCl_2\{\kappa^3\text{-}HC(pz)_3\}$] was prepared according to the literature [11]. The water used for all preparations and analyses was double distilled and de-ionised.

Ozone was generated by an ozone generator (Pacific Ozone, model L22) using pure oxygen gas (99%) from Air Liquide.

GC-MS analyses were performed using a Perkin Elmer Clarus 600 C instrument (Helium as the carrier gas), equipped with two capillary columns (SGE BPX5; 30 m x 0.32 mm x 25 mm), one having an EI-MS (electron impact) detector and the other one with a FID detector. The temperature of injection was 330 ºC. The initial temperature (50 ºC) was raised at 5 ºC/min to 330 ºC. Reaction products were identified by comparison of their retention times with known reference compounds, and by comparing their mass spectra to fragmentation patterns obtained from the NIST spectral library stored in the computer software of the mass spectrometer.

The ^1H and ^{13}C NMR spectra were recorded at ambient temperature on a Bruker Advance II + 300 (UltraShield^{TM} Magnet) spectrometer operating at 300.130 and 75.468 MHz for proton and carbon-13, respectively. The chemical shifts are reported in ppm using tetramethylsilane as an internal reference.

Infrared spectra (4000–400 cm^{-1}) were recorded on a Vertex 70 (Bruker) instrument in KBr pellets.

Elemental analyses were carried out by the Microanalytical Service of the Instituto Superior Técnico.

General procedure for the oxidation of cyclohexane by ozone

All reactions were conducted under an ozone atmosphere using oven-dried glassware. A Schlenk flask of 35 mL capacity was charged with cyclohexane (5 mL, 46 mmol), [$FeCl_2\{\kappa^3\text{-}HC(pz)_3\}$] (25 - 250 µmol, 0.05-0.5 mol% *vs*. cyclohexane), and equipped with a Teflon septum and a magnetic stirrer bar. In the experiments with additives, n(additive)/n(catalyst) = 50 of pyrazine carboxylic acid (Hpca), HNO_3 or K_2CO_3 was added to the reaction mixture. Ozone gas (flow rate = 0.67 g h^{-1}) was bubbled into the cyclohexane solution for 1 - 16 h at room temperature. The reaction vessel was connected to a cold trap immersed in a 70% water-methanol bath (0 to -20 ºC) to trap eventual evaporating reactants/intermediates. After 6 h, a white solid precipitates. The solid was dispersed in an ethyl acetate-hexane (20:80) solution, stirred for 30 min at room temperature, removed by filtration and dried under vacuum for 2 h at room temperature. Blank tests were performed, in a Fe-free system.

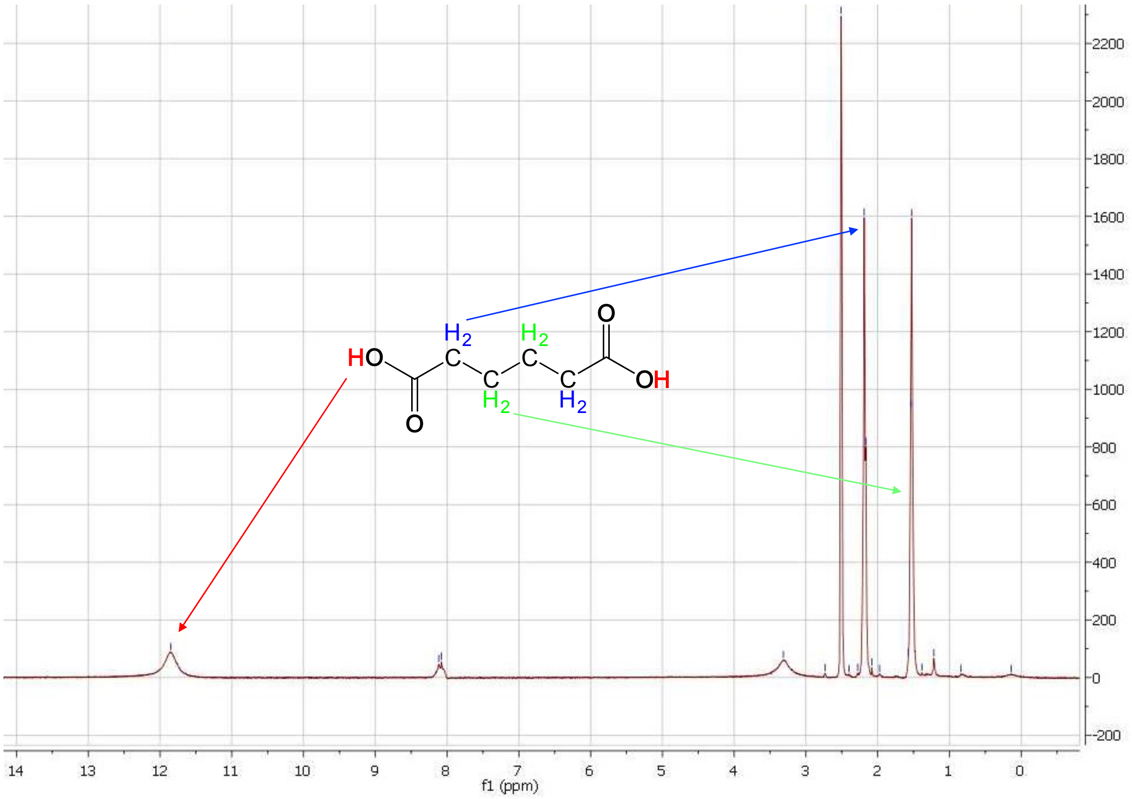


Figure S1 - ^{1}H NMR spectrum of isolated adipic acid in DMSO.

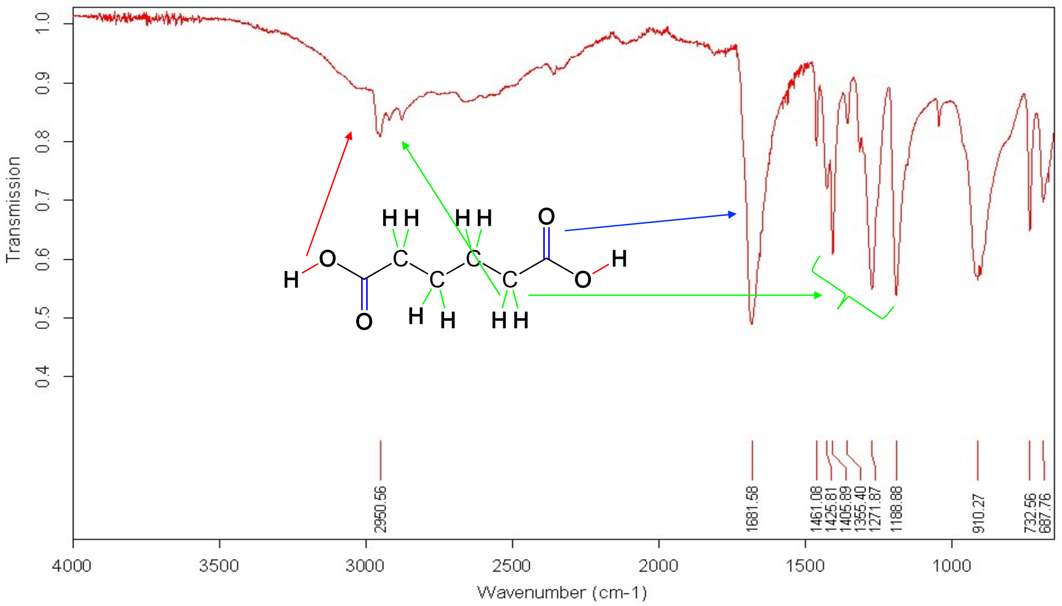
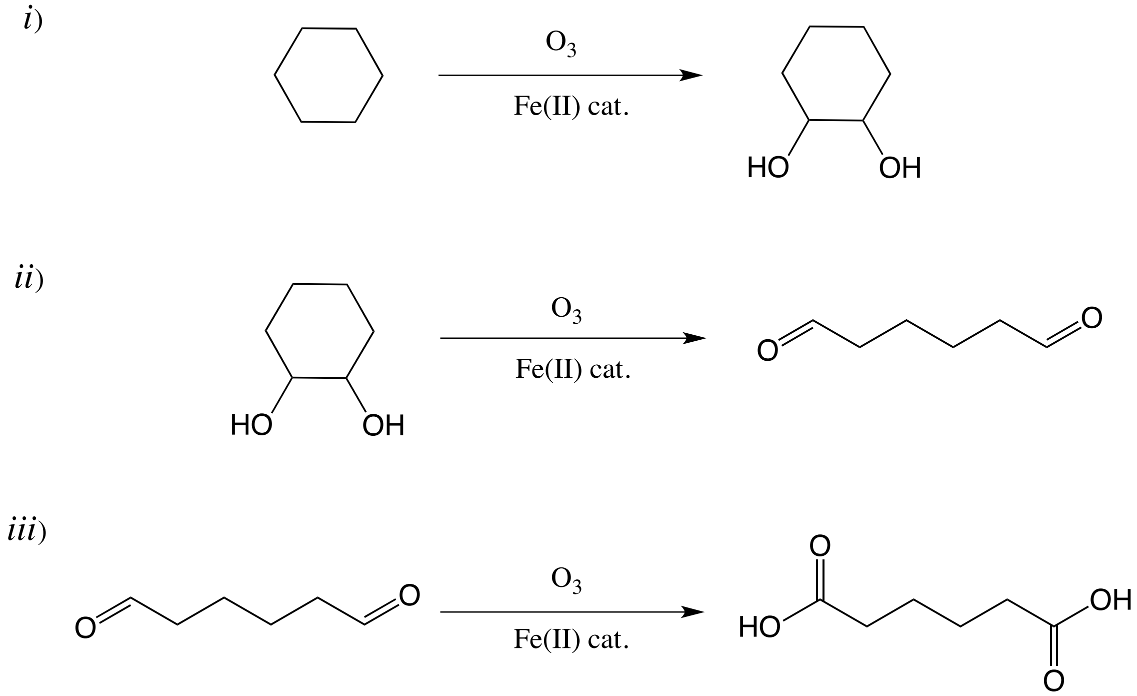


Figure S2 - FTIR spectrum of isolated adipic acid in KBr pellet.

Table S1 - Solvent-, heating-, radiation- and N_2O-free oxidation of cyclohexane with O_3.[a]

Entry	Catalyst	Catalyst amount /mol L^{-1}	n(additive) / n(catalyst)	Time /h	Conversion /%	Yield /% [b]				Total TOF /h^{-1} [c]	Mass balance [d] /%	Carbon efficiency [e] /%	Atom economy [f] /%
						Cyclohexanol	Cyclohexanone	Cyclohexane-1,2-diol	Adipic acid				
1	$[FeCl_2\{HC(pz)_3\}]$	$5x10^{-3}$	0	6	20	0.0	3.0	2.4	14.6	61	88	14.6	81.1
2				16	29	0.0	1.5	6.4	21.2	33	85	21.2	81.1
3			Hpca, 50	1	18	13.0	4.9	0.0	0.0	329	89	0.0	48.0
4				1.5	28	18.6	8.7	0.0	0.4	340	88	0.4	48.0
5				3	47	30	16.5	0.0	0.7	298	90	0.7	48.0
6				4	58	24.3	13.4	1.2	18.7	265	90	18.7	48.0
7				5	78	14.7	6.1	1.7	55.2	286	91	55.2	48.0
8				6	98	0.0	0.0	2.0	96.0	301	98	96.0	48.0
9			HNO_3, 50	6	50	0.0	0.5	0.0	49.5	153	90	49.5	60.1
10			K_2CO_3, 50	6	32	0.0	1.0	0.0	31.0	98	91	31.0	45.9
11		$5x10^{-2}$	0	6	83	0.0	0.0	2.5	80.5	25	95	80.5	81.1
12			Hpca, 50	6	88	0.0	0.0	1.8	86.2	27	90	86.2	48.0
13	–	–	0	6	15	3.1	9.0	0.0	2.9	-	84	2.9	81.1
14	$FeCl_2.2H_2O$	$5x10^{-3}$	0	6	13	9.8	3.3	0.0	0.0	40	83	0.0	81.1
15			Hpca, 50	6	27	12.8	1.42	0.0	0.0	44	84	0.0	48.0
16	$FeCl_3.6H_2O$	$5x10^{-3}$	0	6	12	8.4	3.6	0.0	0.0	113	82	0.0	81.1
17			Hpca, 50	6	21	9.0	12.0	0.0	0.0	196	79	0.0	48.0

[a] Reaction conditions unless stated otherwise: 46 mmol of cyclohexane, 25 – 250 μmol (0.05 – 0.5 mol% *vs.* cyclohexane) of $[FeCl_2\{\kappa^3\text{-}HC(pz)_3\}]$, ozone (flow rate = 0.67 g h^{-1}), room temperature. [b] Moles of oxygenated product *per* 100 mol of cyclohexane. [c] Moles of oxygenated products *per* mol of $[FeCl_2\{\kappa^3\text{-}HC(pz)_3\}]$ *per* hour. [d] Sum of all products (in moles, including unreacted cyclohexane) divided by the initial mole number of cyclohexane. [e] Amount of carbon in adipic acid *per* total amount of carbon in reactants. [f] Molecular weight of adipic acid *per* combined molecular weight of starting materials.



Scheme S1 – The three major oxidative steps of the proposed reaction mechanism for the oxidation of cyclohexane with O_3.