

## Supplementary Materials for

# Electrochemical conversion of 5-hydroxymethylfurfural to 2,5-furandicarboxaldehyde using Mn(III)-Schiff base catalysts

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CheckCIF (a service of International Union of Crystallography) for **1a**

CheckCIF (a service of International Union of Crystallography) for **2**

**Table S1.** Selected bond lengths (Å) and angles (°) for **1a**.

Mn1-O2	1.892(4)	Mn1-O24	1.879(4)
Mn1-N16	1.99(3)	Mn(1)-N(12)	1.977(5)
N(16A)-C(17)	1.33(4)	C11-N12	1.285(8)
C(28)-N(29)	1.268(11)	O(27A)-C(28)	1.134(12)
Mn1-O27	2.138(10)	Mn1-O30	2.367(4)
O2-Mn1-N12	92.6(2)	N16-Mn1-O24	94.7(9)
O2-Mn1-N16	163.8(8)	N12-Mn1-O24	172.0(2)
N12-Mn1-N16	79.0(9)	Mn1-N12-C11	125.1(4)
C8-C11-N12	126.9(5)	Mn1-N16A-C17	121.1(15)
O2-Mn1-O24	92.3(2)	N16A-C17-C18	126.9(12)
Mn1-O2-C3	128.7(3)		

**Table S2.** Hydrogen bond scheme showing distances (Å) and angles (°) for **1a**.

D ... H ... A	D - H	H ... A	D ... A	D - H ... A
O30-H30 ... O32	0.78(3)	1.92(4)	2.689(5)	167(5)
O32-H32A ... O2*	0.70(5)	2.47(5)	2.999(6)	134(5)
O32-H32A ... O9*	0.70(5)	2.23(4)	2.887(6)	157(5)
O32-H32B ... O24*	0.70(6)	2.42(6)	2.988(6)	139(6)
O32-H32B ... O25*	0.70(6)	2.25(6)	2.893(6)	153(6)
C10-H10C ... N29B**	0.98	2.46	3.387(11)	158
C19-H19 ... N29***	0.95	2.52	3.457(12)	167

Symmetry operations: \* = x, 1/2-y, 1/2+y ; \*\* = 1-x, 1/2+y, -1/2-z ; \*\*\* = 1-x, -y, -z

**Table S3.** Selected bond lengths (Å) and angles (°) for **2**.

O171-Mn1	1.8749(12)	O271-Mn1	1.8922(12)
N11-Mn1	1.9814(15)	N21-Mn1	1.9875(15)
O1-Mn1	2.3407(13)	N1-Mn1	2.1876(15)
N21-C21	1.288(2)	C17-O171	1.327(2)
C27-O271	1.321(2)	C16-O161	1.379(2)
C26-O261	1.367(2)	O161-C18	1.420(2)
O261-C28	1.445(2)	C2-N21	1.476(2)
N11-C11	1.288(2)	C1-N11	1.474(2)
O171-Mn1-O271	92.84(5)	O271-Mn1-N1	95.21(6)
O171-Mn1-N11	92.26(6)	O271-Mn1-O1	90.96(5)
O171-Mn1-N21	171.20(6)	N11-Mn1-N21	82.67(6)
O171-Mn1-N1	97.45(6)	N11-Mn1-N1	88.66(6)
O171-Mn1-O1	90.73(5)	N11-Mn1-O1	84.40(5)
O271-Mn1-N11	173.15(6)	N21-Mn1-N1	89.65(6)
O271-Mn1-N21	91.68(6)	N21-Mn1-O1	81.64(6)
N1-Mn1-O1	169.48(6)		

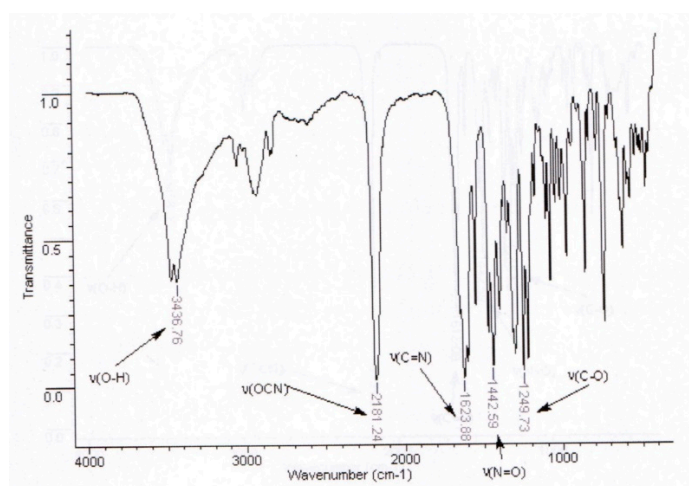
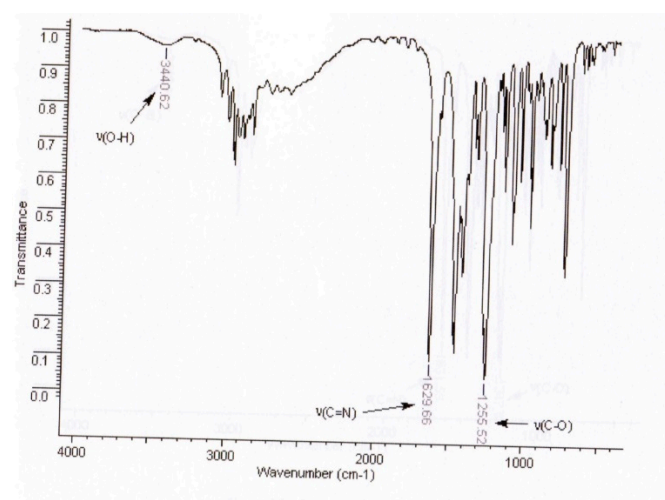
**Table S4.** Hydrogen bond scheme showing distances (Å) and angles (°) for **2**.

D ... H ... A	D-H	H...A	D...A	D-H...A
O3-H3A...O561*	0.78(3)	2.28(2)	2.988(2)	151(2)
O3-H3A...O571*	0.78(3)	2.22(3)	2.852(2)	139(2)
O3-H3B...O461*	0.80(2)	2.47(2)	3.1628(19)	145(2)
O3-H3B...O471*	0.80(2)	2.32(2)	3.0269(19)	148(2)
O1-H11A...O261**	0.77(2)	2.37(2)	3.0544(19)	150(2)
O1-H11A...O271**	0.77(2)	2.26(3)	2.903(2)	142(2)
O1-H11B...O161**	0.81(2)	2.25(2)	2.949(2)	146(2)
O1-H11B...O171**	0.81(2)	2.28(2)	2.9789(18)	145(2)
C2-H2A...O2***	0.99	2.41	3.314(3)	152
C4-H4B...N1	0.99	2.51	3.467(2)	162
C13-H13...N2 <sup>+</sup>	0.95	2.42	3.334(3)	161
C51-H51...O4 <sup>++</sup>	0.952	2.34	3.252(3)	160

Symmetry operations: \* : 1-x; -y; 1-z; \*\* : 1-x; 1-y; -z; \*\*\* : 2-x; -y; -z; + : x; y; -1+z; ++ : 2-x; -y; 1-z

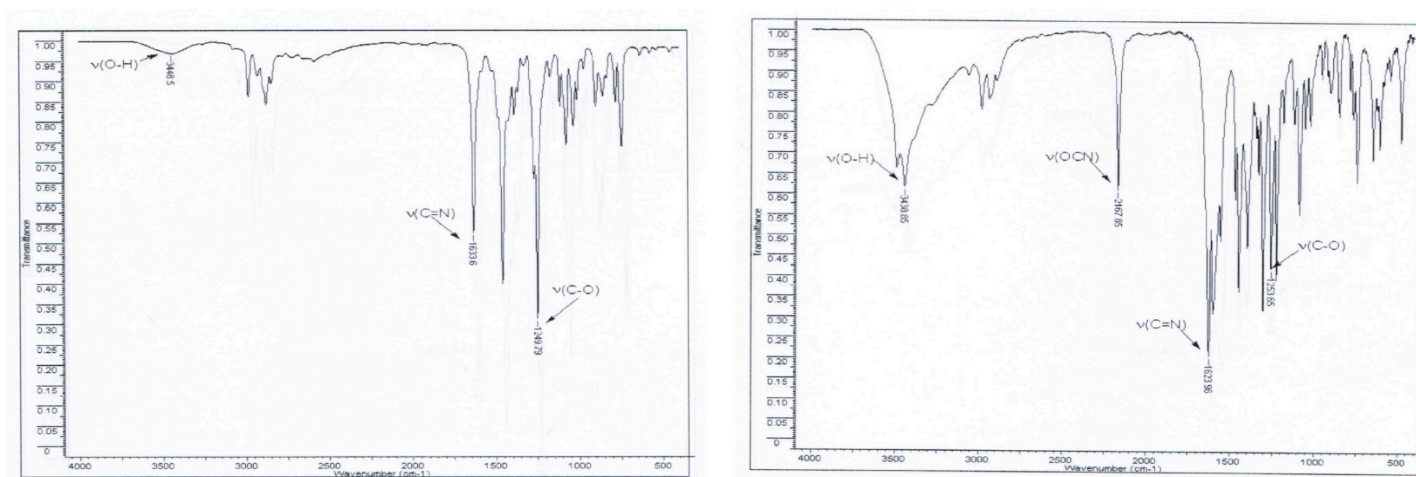
**Table S5.** Physical measurements details.

Technique	Instrument
Elemental analyses	Carlo Erba Model 1108 CHNS-O elemental analyzer (CE Instruments, Wigan, UK)
ESI mass spectra	Hewlett-Packard model LC-MSD 1100 instrument (positive-ion mode, 98:2 CH <sub>3</sub> OH/HCOOH as the mobile phase, 30–100 V; Hewlett-Packard, Palo Alto, CA, USA)
IR spectra	Bio-Rad FTS 135 spectrophotometer (Bio-Rad Laboratories, Hercules, CA, USA)
Conductivities	Crison microCM 2200 conductivity meter (Crison Instruments, Barcelona, Spain)
Room-temperature magnetic moments	MSB-MKI system (Sherwood Scientific, Cambridge, UK)
Electronic spectra	Cary 50 spectrometer (Agilent Technologies, Stockport, UK)
Electrochemical measurements	Autolab PGSTAT101 potentiostat (Metrohm Autolab, Utrecht, Netherlands) working with a three-electrode configuration. The working electrode was a glassy carbon disc (Metrohm 6.1204.300)
<sup>1</sup> H NMR spectra	Bruker Avance 300 MHz spectrometer (Bruker BioSpin, Rheinstetten, Germany)

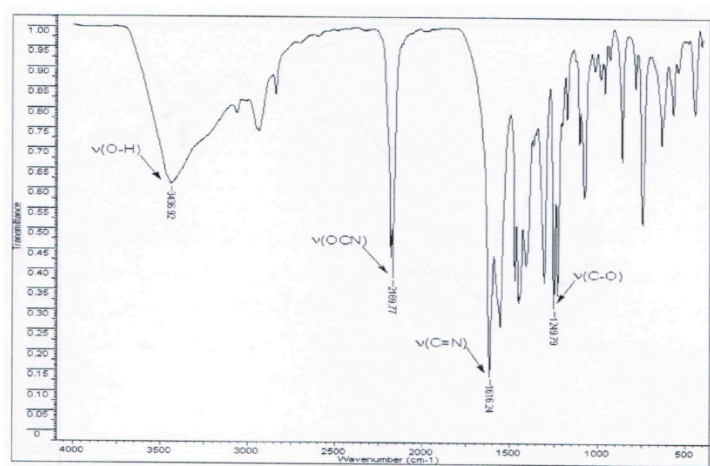
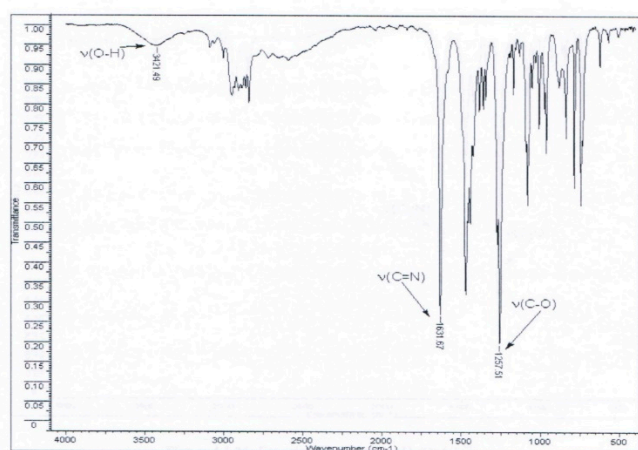


**Figure S1.** IR spectra for  $H_2L^1$  (left) and **1** (right).

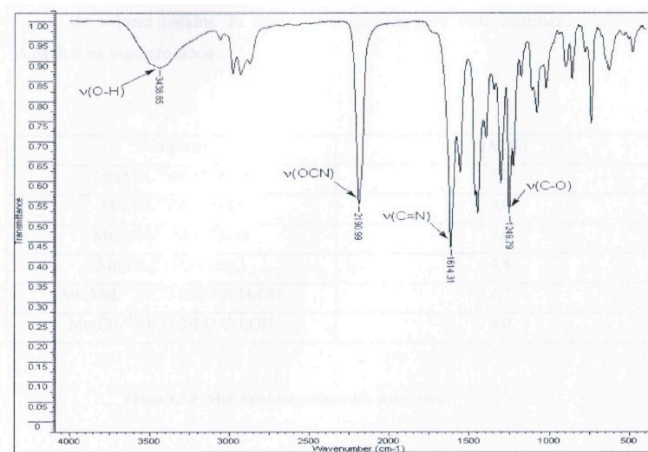
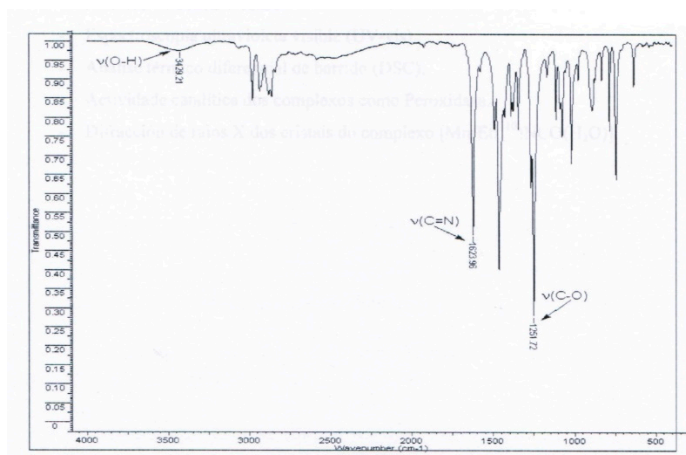




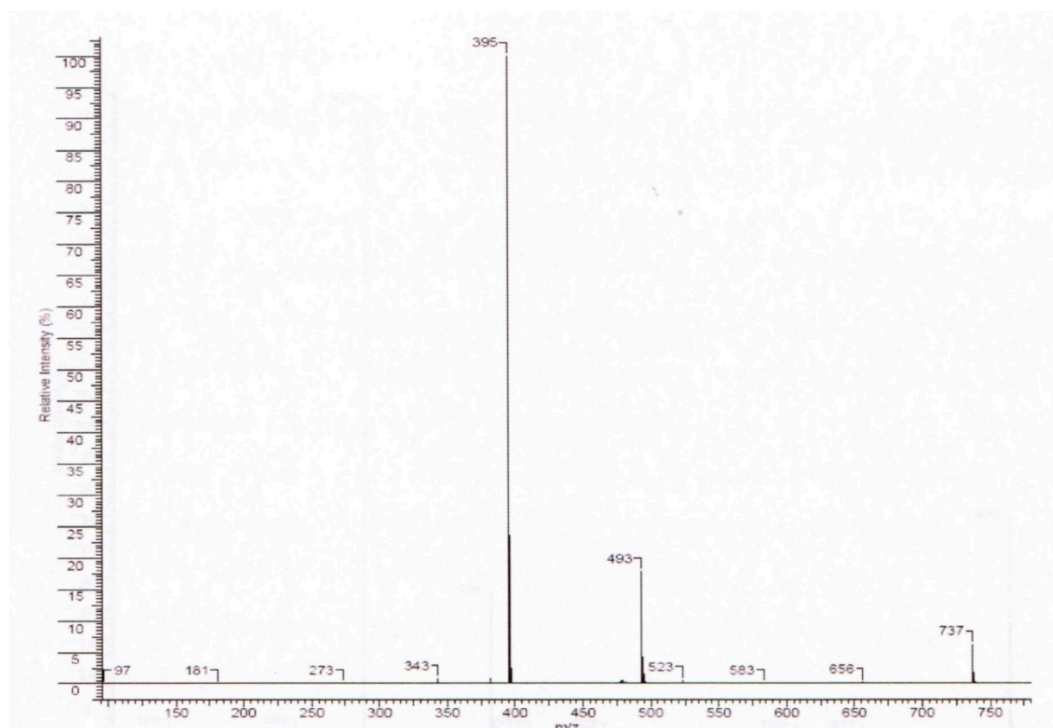
**Figure S2.** IR spectra for  $H_2L^2$  (left) and **2** (right).



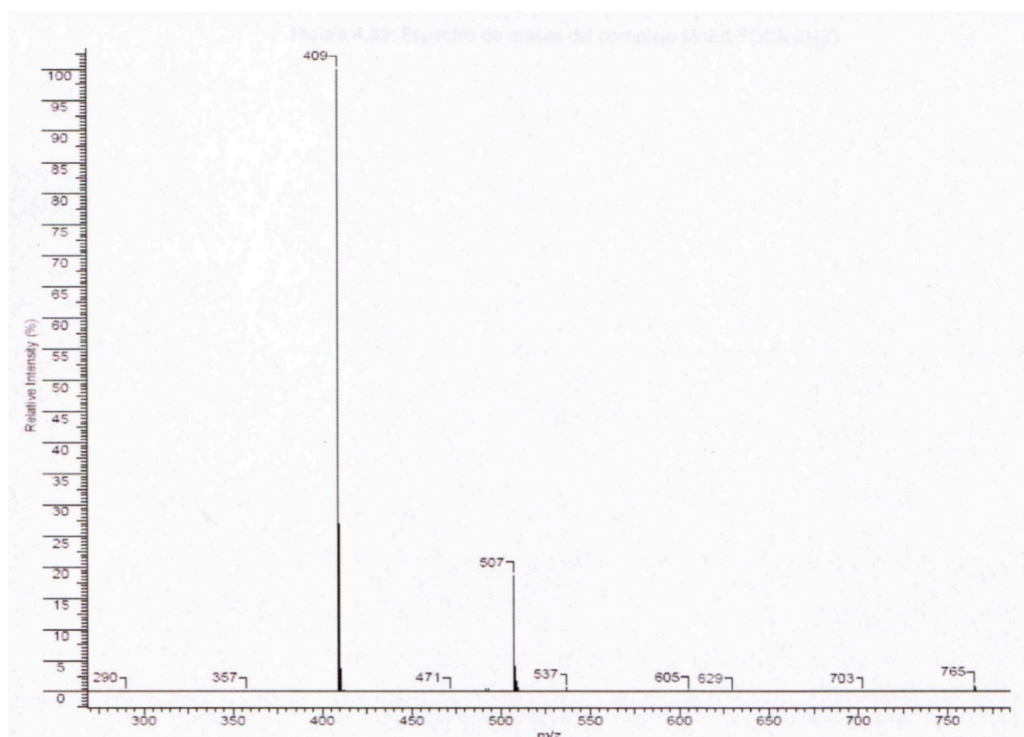
**Figure S3.** IR spectra for  $H_2L^3$  (left) and **3** (right).



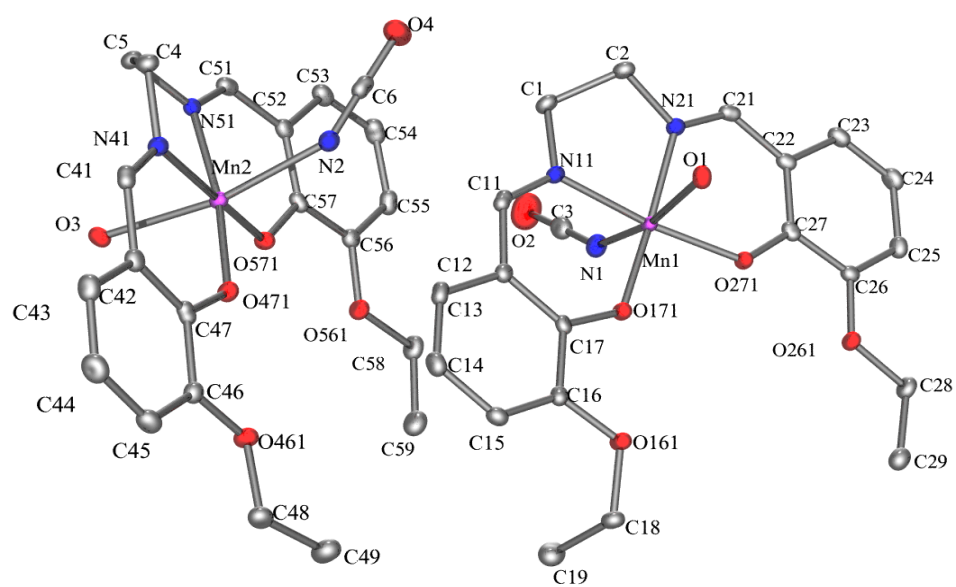
**Figure S4.** IR spectra for  $H_2L^4$  (left) and **4** (right).



**Figure S5.** ESI mass spectrum for **1**.



**Figure S6.** ESI mass spectrum for **2**.



**Figure S7.** ORTEP crystal structure view for **2** showing the two molecules in the unit cell.

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CheckCIF (a service of International  
Union of Crystallography) for **2**