Supporting Information

Cu(II) complexes of *N*-rich aroylhydrazone: magnetism and catalytic activity towards microwave-assisted oxidation of xylenes

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Table S1. Selected bond distances (Å) and angles (º) in complexes **1-3**.

1

Cu1—N3	1.9824 (16)
Cu1—N1	2.0171 (19)
Cu1—O1	2.0921 (16)
Cu1—Cl2	2.2255 (7)
Cu1—Cl1	2.4606 (11)
Cu2—N4	1.9376 (16)
Cu2—N2	2.0300 (18)
Cu2—N5	2.0369 (19)
Cu2—Cl3	2.2260 (7)
Cu2—O2	2.318 (2)

N3—Cu1—N1	78.13 (6)	N4—Cu2—N2	89.60 (6)
N3—Cu1—O1	77.71 (6)	N4—Cu2—N5	79.77 (6)
N1—Cu1—O1	154.62 (6)	N2—Cu2—N5	165.69 (7)
N3—Cu1—Cl2	153.85 (5)	N4—Cu2—Cl3	151.23 (5)
N1—Cu1—Cl2	99.57 (5)	N2—Cu2—Cl3	99.29 (5)
O1—Cu1—Cl2	98.68 (5)	N5—Cu2—Cl3	94.60 (5)
N3—Cu1—Cl1	102.23 (5)	N4—Cu2—O2	101.40 (7)
N1—Cu1—Cl1	94.79 (7)	N2—Cu2—O2	88.26 (8)
O1—Cu1—Cl1	97.77 (6)	N5—Cu2—O2	84.53 (8)
Cl2—Cu1—Cl1	103.92 (3)	Cl3—Cu2—O2	106.15 (5)

2

N1—Cu1	1.981 (11)	N10—Cu4	2.065 (15)
N2—Cu3	2.013 (11)	O1—Cu3	2.025 (9)
N3—Cu1	2.063 (11)	O4—Cu2	2.008 (9)
N4—Cu1	2.043 (9)	Cl1—Cu1	2.238 (3)
N5—Cu3	2.014 (10)	Cl2—Cu2	2.237 (3)
N6—N7	1.302 (14)	Cl3—Cu3	2.279 (3)
N6—Cu2	1.956 (12)	Cl3—Cu4	2.693 (3)
N7—Cu4	1.985 (11)	Cl4—Cu4	2.205 (3)
N8—Cu2	2.028 (10)	Cl5—Cu2	2.424 (3)
N9—Cu4	1.981 (16)	Cl6—Cu3	2.373 (3)

N1—Cu1—N4	90.8 (4)	N5—Cu3—O1	155.4 (4)
N1—Cu1—N3	78.5 (4)	N2—Cu3—Cl3	141.2 (3)
N4—Cu1—N3	168.9 (4)	N5—Cu3—Cl3	100.2 (3)
N1—Cu1—Cl1	168.3 (3)	O1—Cu3—Cl3	98.6 (3)
N4—Cu1—Cl1	97.8 (3)	N2—Cu3—Cl6	114.6 (3)
N3—Cu1—Cl1	93.2 (3)	N5—Cu3—Cl6	95.2 (3)
N6—Cu2—O4	80.8 (5)	O1—Cu3—Cl6	95.4 (3)
N6—Cu2—N8	76.4 (4)	Cl3—Cu3—Cl6	104.15 (12)
O4—Cu2—N8	156.0 (4)	N9—Cu4—N7	91.4 (4)
N6—Cu2—Cl2	150.4 (3)	N9—Cu4—N10	166.6 (5)
O4—Cu2—Cl2	96.2 (3)	N7—Cu4—N10	76.9 (5)
N8—Cu2—Cl2	99.8 (3)	N9—Cu4—Cl4	98.9 (3)
N6—Cu2—Cl5	104.9 (3)	N7—Cu4—Cl4	158.0 (3)
O4—Cu2—Cl5	100.4 (3)	N10—Cu4—Cl4	94.3 (4)
N8—Cu2—Cl5	92.8 (3)	N9—Cu4—Cl3	87.5 (3)
Cl2—Cu2—Cl5	104.65 (13)	N7—Cu4—Cl3	100.0 (3)
N2—Cu3—N5	76.6 (4)	N10—Cu4—Cl3	88.2 (4)
N2—Cu3—O1	78.8 (4)	Cl4—Cu4—Cl3	99.83 (13)

3

Cu1—N3	1.9443 (10)	Cu2—N5	2.0522 (10)
Cu1—O4	1.9496 (9)	Cu2—O16	2.2508 (9)
Cu1—N1	1.9997 (11)	Cu3—O11	1.9729 (9)
Cu1—O1	2.0371 (9)	Cu3—O12	1.9818 (9)
Cu1—O3	2.3442 (10)	Cu3—N6	2.0007 (10)
Cu2—N4	1.9153 (10)	Cu3—O10	2.0346 (10)

Cu2—O7	1.9932 (9)	Cu3—O15^{i}	2.2497 (10)
Cu2—N2	2.0166 (10)	O15—Cu3ii	2.2498 (10)

N3—Cu1—O4	176.85 (4)	N2—Cu2—N5	169.25 (4)
N3—Cu1—N1	79.65 (4)	N4—Cu2—O16	104.35 (4)
O4—Cu1—N1	99.44 (4)	O7—Cu2—O16	82.71 (3)
N3—Cu1—O1	79.85 (4)	N2—Cu2—O16	96.12 (4)
O4—Cu1—O1	101.40 (4)	N5—Cu2—O16	81.33 (4)
N1—Cu1—O1	158.32 (4)	O11—Cu3—O12	86.98 (4)
N3—Cu1—O3	87.66 (4)	O11—Cu3—N6	172.33 (4)
O4—Cu1—O3	89.40 (4)	O12—Cu3—N6	90.55 (4)
N1—Cu1—O3	93.80 (4)	O11—Cu3—O10	94.20 (4)
O1—Cu1—O3	92.36 (4)	O12—Cu3—O10	136.78 (4)
N4—Cu2—O7	167.41 (4)	N6—Cu3—O10	92.58 (4)
N4—Cu2—N2	90.35 (4)	O11—Cu3—O15^{i}	88.17 (4)
O7—Cu2—N2	99.36 (4)	O12—Cu3—O15^{i}	132.05 (4)
N4—Cu2—N5	80.24 (4)	N6—Cu3—O15^{i}	88.10 (4)
O7—Cu2—N5	90.71 (4)	O10—Cu3—O15^{i}	91.15 (4)

Symmetry codes: (i) *x*+1/2, -*y*+1/2, *z*-1/2; (ii) *x*-1/2, -*y*+1/2, *z*+1/2.

Table S2 - MW-assisted oxidation of xylene isomers by H_2O_2 (30% aq) at 50ºC in presence of HNO_3 using **1-3** as catalyst precursors.[a]

Entry	Catalyst	Substrate	Additve n(HNO_3)/n(cat)	Yield (%)			
				Alcohol	Aldehyde	Acid	Total[b]
1	**1**	*o*-xylene	10	0.5	3.5	0.4	4.4
2			25	0.9	0.8	1.3	3.0
3			50	1	1	1.2	3.2
4		*m*-xylene	10	1.2	3.4	0.9	6.0
5			25	3.1	2.5	1.8	7.4
6			50	3.1	3.3	2	8.4
7		*p*-xylene	10	2.9	3.4	3.4	9.7
8			25	3	3.4	2.9	9.3
9			50	3.1	2.5	1.8	9.1
10		*o*-xylene	10	0.3	2.3	0.3	2.9
11			25	0.9	1.5	0.8	3.2
12			50	0.4	1.1	0.6	2.1

13		*m*-xylene	10	2.3	3.3	1.5	7.1
14			25	2.4	5.6	3.8	11.9
15			50	4.5	2.3	3	9.7
16		*p*-xylene	10	1.6	2.7	1.5	5.9
17			25	2.4	1.6	2.5	6.5
18			50	2.8	1.6	2.6	7.0
19	**3**	*o*-xylene	10	1.1	4	0.6	5.7
20			25	1	3.2	0.6	4.8
21			50	1.1	5.1	0.7	6.8
23		*m*-xylene	10	3.5	5.5	2.4	11.4
24			25	6.9	3.9	4.2	15
25			50	4.5	3.2	3.1	10.8
26		*m*-xylene	10	3.1	3.1	2.7	8.9
27			25	3.4	2.2	3.4	8.9
28			50	3.2	2.4	3.3	8.8

[a]Reaction conditions: *o*-, *m*-, or *p*-xylene (5 mmol), catalyst precursor **1**, **2** or **3** (10 μmol), H_2O_2 (30% aq.) (10 mmol), NCMe (3 mL), additive HNO_3 (n/n= 10, 25 or 50), MW, 3 h, 50 ºC. [b]Moles of products [alcohol + aldehyde + acid]/100 mol of xylene isomer, determined by GC.

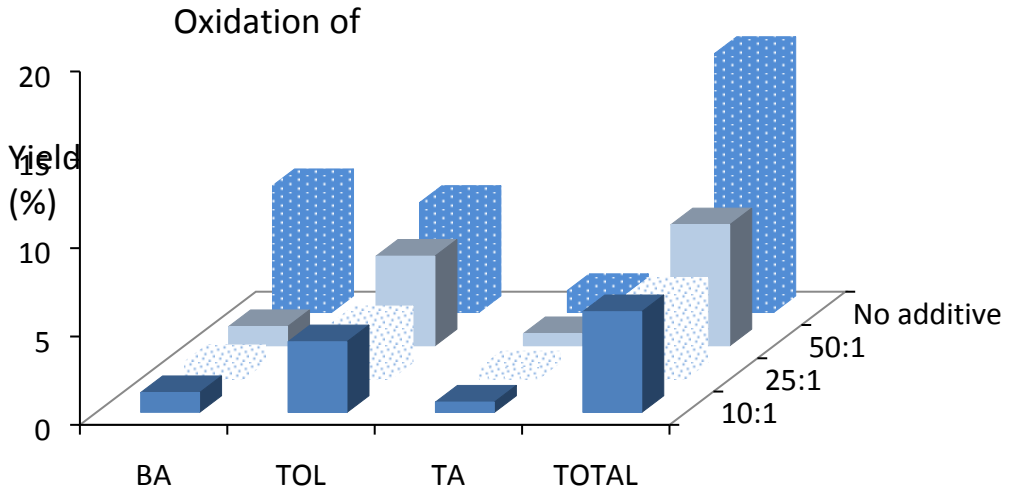

Fig. S1 Effect of HNO_3 additive on the peroxidative oxidation of *o*-xylene in presence of **3**. Reaction conditions: *o*-xylene (5 mmol), **3** (10 μmol), H_2O_2 30% aq. sol. (10 mmol), NCMe (3 mL), additive HNO_3 [n(HNO_3)/n(cat) = 10, 25 or 50], 50 ºC, 3 h under MW-irradiation (5 W).

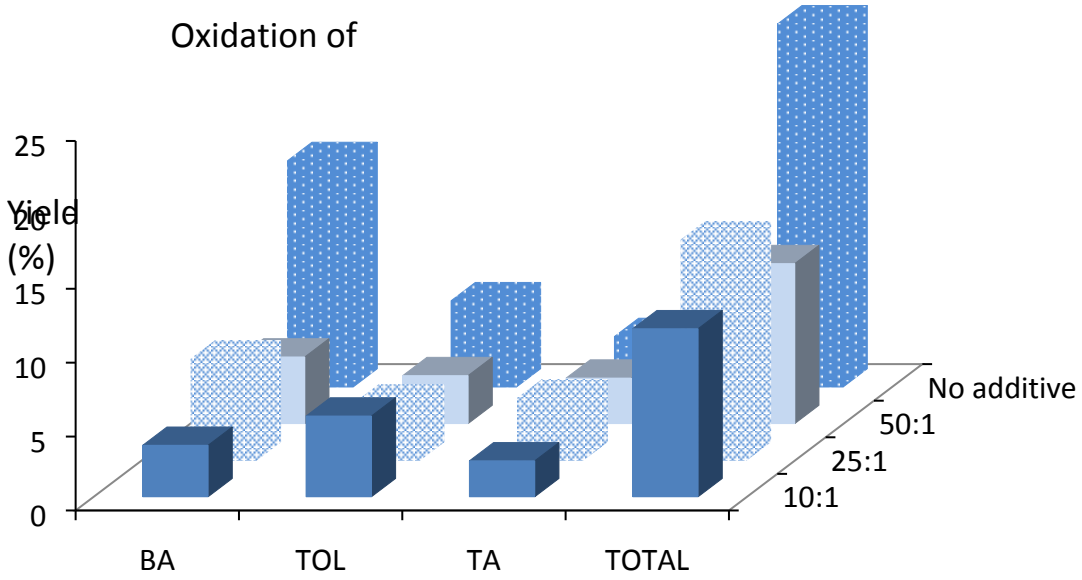

Fig. S2 Effect of HNO_3 additive on the peroxidative oxidation of *m*-xylene in presence of **3**. Reaction conditions: *m*-xylene (5 mmol), **3** (10 μmol), H_2O_2 30% aq. sol. (10 mmol), NCMe (3 mL), additive HNO_3 [n(HNO_3)/n(cat) = 10, 25 or 50], 50 ºC, 3 h under MW-irradiation (5 W).