

Supplementary Material

Hydrothermal Generation, Crystal Structures, and Catalytic Performance of Mn(II), Cu(II) and Ni(II) Coordination Polymers Based on a Pyridine-Tetracarboxylate Ligand

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Supplementary material contains:

Figure S1. FT-IR spectra of compounds **1–3**.

Figure S2. Powder X-ray diffraction for **1–3**.

Figure S3. Example of integration in the ¹H-NMR spectrum for the determination of the Henry reaction products (Table 2, Entry 7).

Figure S4. Accumulation of 2-nitro-1-(pyridin-3-yl)ethan-1-ol vs. time in the Henry reaction catalysed by **2**. Reaction conditions are those of Table 2, entries 1–8.

Figure S5. Catalyst recycling experiments in the Henry reaction catalyzed by **2** (conditions of Table 2, Entry 7).

Figure S6. PXRD patterns for **2**: simulated (red), before (black) and after (blue) catalysis.

Table S1. Selected bond lengths (Å) and bond angles (°) for **1–3**.

Table S2 Hydrogen bonds in crystal packing [Å, °] for **1–3**.

Table S3. Substrate scope for Cu-catalyzed the Henry reaction of substituted benzaldehydes with nitromethane.

Table S4. Comparison of various catalysts for the Henry reaction between pyridine-3-aldehyde with nitromethane.

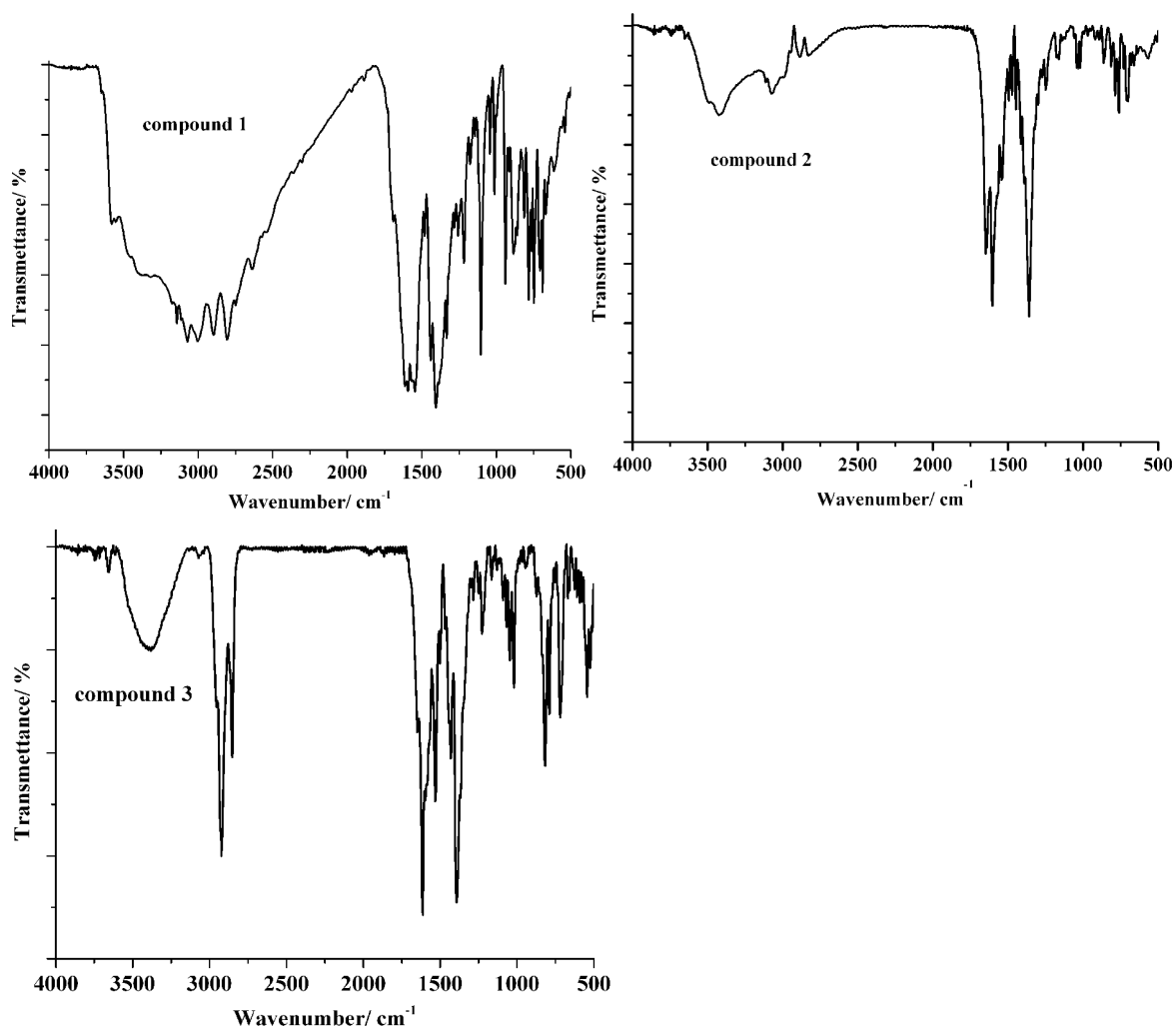
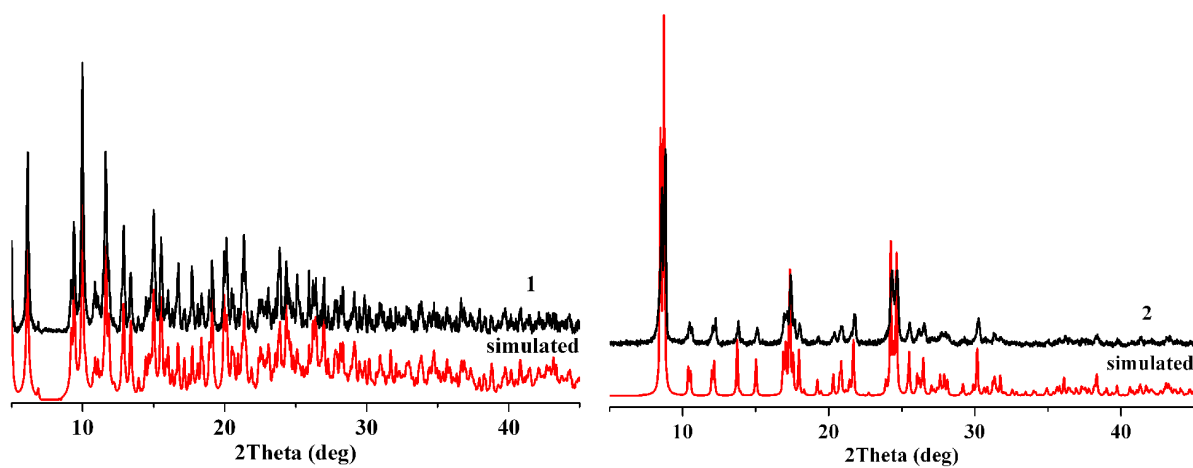


Figure S1. FT-IR spectra of compounds 1–3.



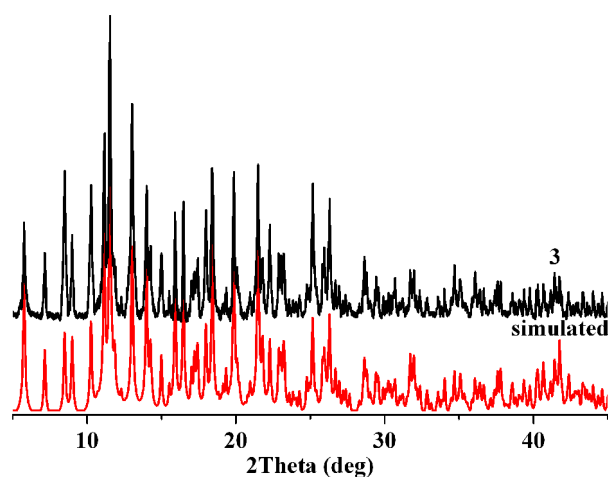


Figure S2. PXRD patterns of compounds **1–3** at room temperature.

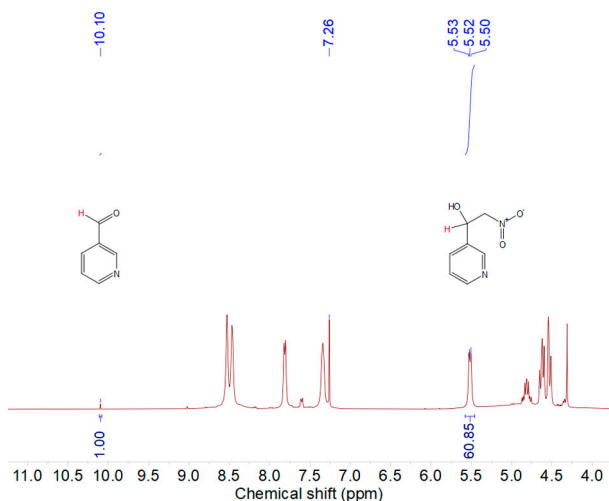


Figure S3. Example of the integration in the ^1H NMR spectrum of the reaction mixture for the determination of Henry reaction product (conditions of Table 2, Entry 7).

Product yield calculation in the Henry reaction. The $\text{C}(=\text{O})\text{H}$ signal of pyridine-3-aldehyde (substrate) appears at δ 10.10 ppm, while 2-nitro-1-(pyridin-3-yl)ethan-1-ol (product) shows a characteristic signal at δ 5.50–5.53 ppm.

Total integration of both signals: unreacted pyridine-3-aldehyde + product = 1 + 60.85 = 61.85.

Percentage of the unreacted substrate: $1/61.85 = 1.62\%$

Conversion of 4-nitrobenzaldehyde = yield of product = $100 - 1.62 = 98.38\%$

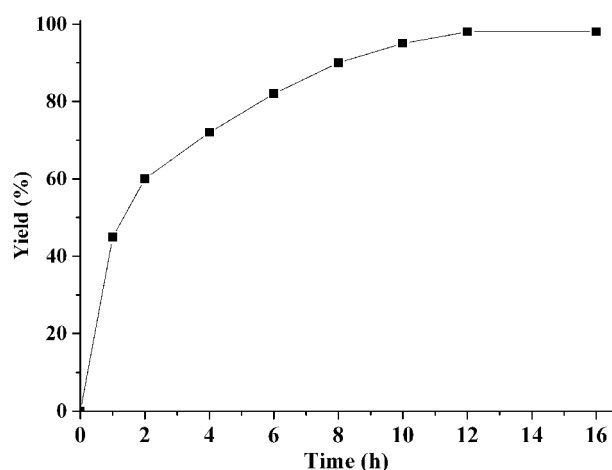


Figure S4. Accumulation of 2-nitro-1-(pyridin-3-yl)ethan-1-ol vs. time in the Henry reaction of pyridine-3-aldehyde with nitromethane catalysed by **2**. Reaction conditions are those of Table 2, entries 1–7.

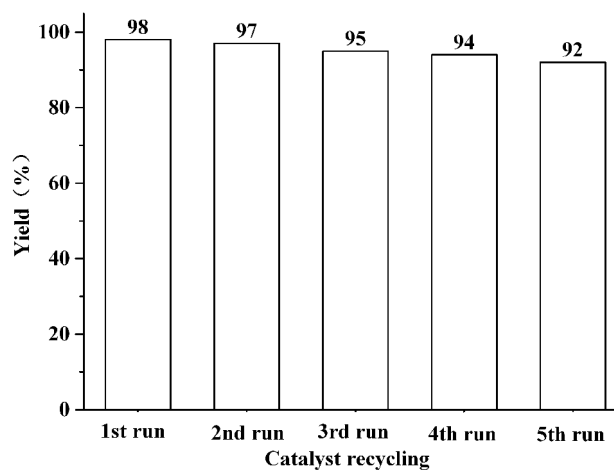


Figure S5. Catalyst recycling experiments in the Henry reaction of pyridine-3-aldehyde with nitromethane catalysed by **2**. Reaction conditions are those of Table 2, entry 7.

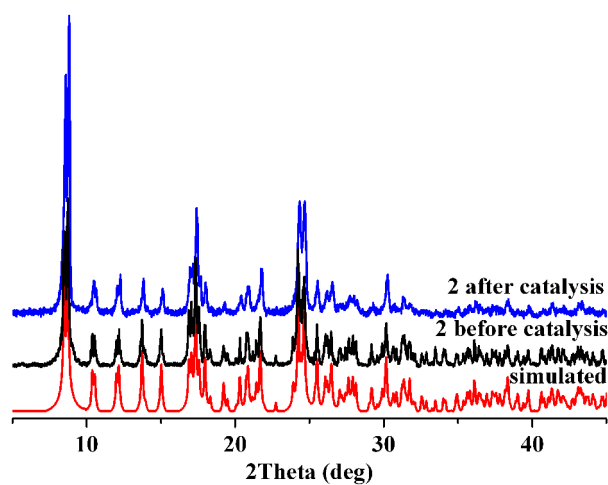


Figure S6. PXRD patterns **2**: simulated (red), before (black) and after (blue) catalysis.

Table S1. Selected bond distances (Å) and bond angles (°) for compounds **1–3**.

1					
Mn(1)-O(1)	2.173(3)	Mn(1)-O(7)	2.259(3)	Mn(1)-O(9)i	2.166(3)
Mn(1)-O(13)	2.126(3)	Mn(1)-O(19)	2.138(3)	Mn(1)-N(2)	2.294(4)
Mn(2)-O(6)	2.260(3)	Mn(2)-O(7)ii	2.194(3)	Mn(2)-O(10)	2.159(3)
Mn(2)-O(14)ii	2.077(4)	Mn(2)-O(37)	2.273(3)	Mn(2)-N(1)	2.271(4)
Mn(3)-O(3)	2.122(3)	Mn(3)-O(16)	2.216(3)	Mn(3)-O(28)ii	2.136(4)
Mn(3)-O(25)	2.235(3)	Mn(3)-O(32)	2.108(3)	Mn(3)-N(5)	2.337(4)
Mn(4)-O(4)	2.075(4)	Mn(4)-O(17)ii	2.214(3)	Mn(4)-O(25)	2.201(3)
Mn(4)-O(27)ii	2.157(3)	Mn(4)-O(38)	2.250(4)	Mn(4)-N(3)ii	2.288(4)
Mn(5)-O(12)iii	2.126(3)	Mn(5)-O(17)ii	2.165(3)	Mn(5)-O(23)iii	2.160(3)
Mn(5)-O(26)	2.140(3)	Mn(5)-O(39)	2.288(3)	Mn(5)-N(4)iii	2.262(4)
Mn(6)-O(6)iv	2.163(3)	Mn(6)-O(8)iii	2.121(3)	Mn(6)-O(30)	2.144(3)
Mn(6)-O(36)	2.167(3)	Mn(6)-O(40)	2.322(4)	Mn(6)-N(6)	2.227(4)
Mn(7)-O(2)	2.069(3)	Mn(7)-O(20)	2.079(4)	Mn(7)-O(41)	2.193(4)
Mn(7)-N(7)	2.263(5)	Mn(7)-N(10)	2.206(4)	Mn(8)-O(15)	2.037(3)
Mn(8)-O(31)	2.044(4)	Mn(8)-O(42)	2.245(4)	Mn(8)-N(11)	2.243(5)
Mn(8)-N(14)	2.169(4)				
O(13)-Mn(1)-O(19)	101.40(14)	O(9)i-Mn(1)-O(13)	90.21(14)	O(9)i-Mn(1)-O(19)	80.38(13)
O(13)-Mn(1)-O(1)	88.83(13)	O(19)-Mn(1)-O(1)	90.97(12)	O(9)i-Mn(1)-O(1)	170.93(12)
O(13)-Mn(1)-O(7)	103.84(12)	O(7)-Mn(1)-O(19)	148.86(13)	O(9)i-Mn(1)-O(7)	81.58(12)
O(7)-Mn(1)-O(1)	107.40(12)	O(13)-Mn(1)-N(2)	168.48(14)	O(19)-Mn(1)-N(2)	86.54(13)
O(9)i-Mn(1)-N(2)	99.41(14)	O(1)-Mn(1)-N(2)	82.65(14)	O(7)-Mn(1)-N(2)	71.64(12)
O(14)ii-Mn(2)-O(10)	97.30(15)	O(14)ii-Mn(2)-O(7)ii	92.00(13)	O(10)-Mn(2)-O(7)ii	89.72(12)
O(14)ii-Mn(2)-O(6)	166.83(12)	O(10)-Mn(2)-O(6)	87.35(13)	O(7)ii-Mn(2)-O(6)	100.38(12)
O(14)ii-Mn(2)-O(37)	95.92(15)	O(10)-Mn(2)-O(37)	166.64(15)	O(7)ii-Mn(2)-O(37)	91.70(12)
O(6)-Mn(2)-O(37)	79.33(13)	O(14)ii-Mn(2)-N(1)	94.90(14)	O(10)-Mn(2)-N(1)	90.46(13)
O(7)ii-Mn(2)-N(1)	173.02(14)	O(6)-Mn(2)-N(1)	72.67(13)	O(37)-Mn(2)-N(1)	86.53(13)
O(3)-Mn(3)-O(32)	104.82(14)	O(32)-Mn(3)-O(28)ii	84.22(14)	O(3)-Mn(3)-O(28)ii	92.69(16)
O(16)-Mn(3)-O(32)	95.60(13)	O(16)-Mn(3)-O(3)	86.08(13)	O(16)-Mn(3)-O(28)ii	178.66(17)
O(25)-Mn(3)-O(32)	151.07(14)	O(3)-Mn(3)-O(25)	102.07(13)	O(25)-Mn(3)-O(28)ii	84.06(14)
O(16)-Mn(3)-O(25)	96.69(13)	O(32)-Mn(3)-N(5)	85.37(14)	O(3)-Mn(3)-N(5)	163.37(14)
O(28)ii-Mn(3)-N(5)	101.52(16)	O(16)-Mn(3)-N(5)	79.78(13)	O(25)-Mn(3)-N(5)	71.24(12)
O(4)-Mn(4)-O(27)ii	97.58(16)	O(25)-Mn(4)-O(4)	91.64(14)	O(25)-Mn(4)-O(27)ii	89.65(12)
O(4)-Mn(4)-O(17)ii	163.95(13)	O(27)ii-Mn(4)-O(17)	92.08(13)	O(25)-Mn(4)-O(17)ii	101.25(12)
O(4)-Mn(4)-O(38)	84.62(16)	O(27)ii-Mn(4)-O(38)	177.29(15)	O(25)-Mn(4)-O(38)	88.71(13)
O(17)ii-Mn(4)-O(38)	86.13(14)	O(4)-Mn(4)-N(3)ii	93.41(15)	O(27)ii-Mn(4)-N(3)ii	94.80(13)
O(25)-Mn(4)-N(3)ii	172.78(14)	O(17)ii-Mn(4)-N(3)ii	72.94(13)	O(38)-Mn(4)-N(3)ii	86.63(13)
O(12)iii-Mn(5)-O(2)	88.81(13)	O(12)iii-Mn(5)-O(23)	166.83(14)	O(26)-Mn(5)-O(23)iii	92.93(13)
O(12)iii-Mn(5)-O(1)	98.65(13)	O(26)-Mn(5)-O(17)ii	91.00(13)	O(23)iii-Mn(5)-O(17)	94.38(12)
O(12)iii-Mn(5)-N(4)	93.42(14)	N(4)iii-Mn(5)-O(26)	87.51(14)	N(4)iii-Mn(5)-O(23)i	73.63(13)

N(4)iii-Mn(5)-O(17)	167.81(13)	O(12)iii-Mn(5)-O(39)	86.50(13)	O(26)-Mn(5)-O(39)	175.11(12)
O(23)iii-Mn(5)-O(3)	91.34(13)	O(17)ii-Mn(5)-O(39)	91.05(12)	N(4)iii-Mn(5)-O(39)	91.41(14)
O(8)iii-Mn(6)-O(30)	87.57(13)	O(6)iv-Mn(6)-O(8)iii	90.19(13)	O(6)iv-Mn(6)-O(30)	97.17(13)
O(8)iii-Mn(6)-O(30)	97.83(14)	O(30)-Mn(6)-O(36)	165.92(15)	O(6)iv-Mn(6)-O(36)	95.81(13)
O(8)iii-Mn(6)-N(6)	92.02(14)	O(30)-Mn(6)-N(6)	92.07(14)	O(6)iv-Mn(6)-N(6)	170.58(13)
O(36)-Mn(6)-N(6)	74.82(14)	O(8)iii-Mn(6)-O(40)	172.84(12)	O(30)-Mn(6)-O(40)	85.57(13)
O(6)iv-Mn(6)-O(40)	92.69(12)	O(36)-Mn(6)-O(40)	88.41(14)	N(6)-Mn(6)-O(40)	86.20(14)
O(2)-Mn(7)-O(20)	115.68(13)	O(2)-Mn(7)-O(41)	95.09(14)	O(20)-Mn(7)-O(41)	95.08(16)
O(2)-Mn(7)-N(10)	147.69(16)	O(20)-Mn(7)-N(10)	95.22(15)	O(41)-Mn(7)-N(10)	91.11(15)
O(2)-Mn(7)-N(7)	89.46(15)	O(20)-Mn(7)-N(7)	97.93(16)	O(41)-Mn(7)-N(7)	162.74(15)
N(10)-Mn(7)-N(7)	76.47(16)	O(15)-Mn(8)-O(31)	109.87(15)	O(15)-Mn(8)-N(14)	146.97(17)
O(31)-Mn(8)-N(14)	103.01(15)	O(15)-Mn(8)-O(42)	90.11(15)	O(31)-Mn(8)-O(42)	94.54(16)
O(42)-Mn(8)-N(14)	90.31(19)	O(15)-Mn(8)-N(11)	95.02(15)	O(31)-Mn(8)-N(11)	98.18(16)
N(14)-Mn(8)-N(11)	77.01(18)	O(42)-Mn(8)-N(11)	163.74(17)		

2

Cu(1)-O(1)	1.948(3)	Cu(1)-O(4)i	2.126(3)	Cu(1)-O(7)	1.989(3)
Cu(1)-N(2)	1.983(4)	Cu(1)-N(3)	1.998(4)	Cu(2)-O(5)	1.935(3)
Cu(2)-O(5)ii	1.935(3)	Cu(2)-N(1)	1.981(3)	Cu(2)-N(1)ii	1.980(3)
O(1)-Cu(1)-N(2)	170.61(14)	O(1)-Cu(1)-O(7)	93.08(12)	O(7)-Cu(1)-N(2)	90.84(13)
O(1)-Cu(1)-N(3)	90.83(15)	N(2)-Cu(1)-N(3)	80.90(15)	O(7)-Cu(1)-N(3)	142.50(15)
O(1)-Cu(1)-O(4)i	93.43(13)	N(2)-Cu(1)-O(4)i	94.38(14)	O(7)-Cu(1)-O(4)i	98.97(12)
N(3)-Cu(1)-O(4)i	118.00(13)	N(1)-Cu(2)-O(5)	84.09(12)	N(1)-Cu(2)-O(5)ii	95.91(12)

3

Ni(1)-O(1)	2.131(6)	Ni(1)-O(1)i	2.131(6)	Ni(1)-O(2)	2.068(5)
Ni(1)-O(2)i	2.068(5)	Ni(1)-N(2)	2.061(6)	Ni(1)-N(2)i	2.061(6)
Ni(2)-O(3)ii	2.094(5)	Ni(2)-O(5)	2.039(5)	Ni(2)-O(7)	2.188(5)
Ni(2)-N(1)	2.082(6)	Ni(2)-N(3)	2.083(6)	Ni(2)-N(4)	2.084(7)
N(2)-Ni(1)-N(2)	89.2(3)	O(2)-Ni(1)-N(2)	97.5(2)	O(2)-Ni(1)-N(2)i	97.7(2)
O(2)-Ni(1)-O(2)i	158.6(3)	O(1)-Ni(1)-N(2)	95.7(2)	O(1)-Ni(1)-N(2)i	160.4(2)
O(2)-Ni(1)-O(1)	62.9(2)	O(2)-Ni(1)-O(1)i	100.7(2)	O(1)-Ni(1)-O(1)	86.1(3)
O(5)-Ni(2)-N(1)	80.3(2)	O(5)-Ni(2)-N(3)	93.3(2)	N(3)-Ni(2)-N(1)	172.9(3)
O(5)-Ni(2)-N(4)	93.2(2)	N(4)-Ni(2)-N(1)	90.3(3)	N(3)-Ni(2)-N(4)	93.2(3)
O(5)-Ni(2)-O(3)ii	169.1(2)	N(1)-Ni(2)-O(3)ii	89.5(2)	N(3)-Ni(2)-O(3)ii	96.6(2)
N(4)-Ni(2)-O(3)ii	90.6(2)	O(5)-Ni(2)-O(7)	87.8(2)	O(7)-Ni(2)-N(1)	89.4(2)
O(7)-Ni(2)-N(3)	87.2(2)	O(7)-Ni(2)-N(4)	178.9(2)	O(7)-Ni(2)-O(3)ii	88.3(2)

Symmetry transformations used to generate equivalent atoms: i: $x - 1, y, z$; ii: $x + 1, y, z$; iii: $x - 1, y + 1, z$; iv: $x - 2, y + 1, z$ for **1**; i: $-x + 1, -y + 1, -z + 1$; ii: $-x, -y + 1, -z$ for **2**; i: $-x + 2, y, -z + 3/2$; ii: $-x + 2, -y + 1, -z + 1$ for **3**.

Table S2. Hydrogen bond lengths (Å) and angles (°) of compounds **1–3**.

Compound	D-H...A	$d(\text{D-H})$	$d(\text{H}\cdots\text{A})$	$d(\text{D}\cdots\text{A})$	$\angle\text{DHA}$	Symmetry code
1	N(8)-H(1)···O(18)	0.860	2.451	3.134	136.80	$-x+1, -y+2, -z$

	N(9)-H(2)···O(39)	0.860	1.945	2.780	163.50	-x+2, -y+2, -z
	N(12)-H(4)···O(5)	0.860	2.126	2.864	143.57	-x+1, -y+1, -z+1
	N(13)-H(5)···O(40)	0.860	2.049	2.891	165.95	-x-1, -y+2, -z+1
	O(22)-H(22)···O(44)	0.820	1.824	2.641	174.39	x+1, y, z-1
	O(33)-H(33)···O(47)	0.820	1.769	2.587	175.67	x-1, y, z
	O(37)-H(1W)···O(35)	0.849	1.909	2.758	179.13	-x+1, -y+2, -z+1
	O(38)-H(4W)···O(48)	0.820	1.884	2.689	166.84	
	O(39)-H(5W)···O(11)	0.850	1.788	2.638	179.47	x-1, y+1, z
	O(39)-H(6W)···O(18)	0.850	1.860	2.711	179.40	x+1, y, z
	O(40)-H(7W)···O(29)	0.820	1.901	2.633	147.99	
	O(40)-H(8W)···O(5)	0.850	1.850	2.700	179.31	x-2, y+1, z
	O(41)-H(9W)···O(43)	0.820	1.983	2.766	159.73	x+1, y, z
	O(42)-H(12W)···O(16)	0.820	2.161	2.806	135.60	
	O(43)-H(13W)···O(9)	0.850	1.962	2.812	179.33	x-1, y, z
	O(43)-H(14W)···O(44)	0.849	2.099	2.949	179.06	-x+1, -y+1, -z+1
	O(44)-H(15W)···O(11)	0.849	2.001	2.851	179.21	-x+2, -y+1, -z+1
	O(45)-H(17W)···O(43)	0.849	1.916	2.766	178.91	
	O(45)-H(18W)···O(21)	0.849	2.106	2.955	178.98	-x+2, -y+1, -z
	O(46)-H(19W)···O(37)	0.639	2.366	2.973	159.67	x-1, y, z
	O(46)-H(20W)···O(36)	0.850	2.093	2.943	178.97	x+1, y-1, z
	O(47)-H(21W)···O(34)	0.918	1.827	2.743	175.05	-x, -y+2, -z+1
	O(47)-H(22W)···O(29)	0.850	1.891	2.741	179.44	-x, -y+2, -z+1
	O(48)-H(23W)···O(23)	0.851	1.978	2.829	179.38	x-1, y+1, z
	O(48)-H(24W)···O(24)	0.975	1.898	2.810	154.63	-x+2, -y+1, -z
2	O(7)-H(1W)···O(4)	0.850	1.981	2.735	147.30	x, y, z+1
	O(7)-H(2W)···O(2)	0.820	1.891	2.630	149.40	
	O(8)-H(3W)···O(6)	0.850	2.032	2.882	178.89	x, y, z+1
	O(8)-H(4W)···O(9)	0.674	2.155	2.781	155.01	x, y+1, z
	O(9)-H(5W)···O(3)	0.837	1.886	2.723	178.08	
3	O(7)-H(1W)···O(4)	0.861	1.785	2.579	152.30	-x+2, -y+1, -z+1

Table S3 Substrate scope for Cu-catalyzed the Henry reaction of substituted benzaldehydes with nitromethane ^a

Entry	Substituted benzaldehyde substrate	Product Yield ^b , %
1	benzaldehyde	87
2	2-nitrobenzaldehyde	94
3	3-nitrobenzaldehyde	96
4	4-nitrobenzaldehyde	97
5	4-chlorobenzaldehyde	82
6	4-methylbenzaldehyde	47
7	4-methoxybenzaldehyde	25
8	4-hydroxybenzaldehyde	14
9	pyridine-3-aldehyde	98

^a Reaction conditions: aldehyde (0.5 mmol), nitromethane (2.0 mmol), catalyst **2** (4.0 mol-%), and CH₃OH (1.0 mL) at 70 °C. ^b Calculated by ¹H NMR spectroscopy.

Table S4. Comparison of various catalysts for the Henry reaction between pyridine-3-aldehyde with nitromethane.

Entry	Catalyst	Catalyst (mol%)	Solvent	Time (h)	Temp. (°C)	Conversion (%)	Ref.
1	[Cu ₃ (μ ₃ -cpia) ₂ (bipy) ₂ (H ₂ O) ₂] _n ·4nH ₂ O	4	MeOH	12	70	98	This work
2	Zn(proline) ₂	10	H ₂ O	8	25	95	40