Electronic Supplementary Information (ESI)

Six metal-organic architectures from 5-methoxyisophthalate linker: assembly, structural variety and catalytic features

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Electronic Supplementary Information (ESI) contains: analytical data and synthesis for **1**−**6**, FTIR spectra (Fig. S1), PXRD patterns (Fig. S2), temperature dependence of $\chi_M T$ vs. T for compounds **1**–**5** (Fig. S3), additional catalysis data (Figs. S4−S7), structural parameters (Tables S1 and S2), the magmetic moments of compounds **1**–**5** (Table S3), and comparison of catalytic activity (Table S4). CCDC-2269625–2269630.

Synthesis and analytical data for 1–6

Synthesis of $[Cu_2(\mu\text{-mia})_2(phen)_2(H_2O)_2]\cdot 2H_2O$ **(1).** A mixture of $CuCl_2\cdot 2H_2O$ (34.1 mg, 0.2 mmol), H_2mia (38.4 mg, 0.2 mmol), phen (40.0 mg, 0.2 mmol), NaOH (16.0 mg, 0.4 mmol), and H_2O (10 mL) was stirred at room temperature for 15 min, then sealed in a 25 mL Teflon-lined stainless steel vessel, and heated at 160 °C for 3 days, followed by cooling to room temperature at a rate of 10 °C/h. Green needle-shaped crystals were isolated manually, washed with distilled water, and dried to furnish compound **1**. Yield: 52% (based on H_2mia). Calcd for $C_{42}H_{36}Cu_2N_4O_{14}$: C 53.22, H 3.83, N 5.91%. Found: C 52.97, H 3.84, N 5.95%. IR (KBr, cm^{-1}): 3414 w, 3060 w, 1704 w, 1627 m, 1583 s, 1519 m, 1426 s, 1382 s, 1221 w, 1145 w, 1044 w, 907 w, 855 w, 775 w, 730 m, 674 w, 642 w.

Synthesis of $[Mn(\mu_3\text{-mia})(phen)]_n$ **(2).** A mixture of $MnCl_2\cdot 4H_2O$ (40.0 mg, 0.2 mmol), H_2mia (38.4 mg, 0.2 mmol), phen (40.0 mg, 0.2 mmol), NaOH (16.0 mg, 0.4 mmol), and H_2O (10 mL) was stirred at room temperature for 15 min, then sealed in a 25 mL Teflon-lined stainless steel vessel, and heated at 160 °C for 3 days, followed by cooling to room temperature at a rate of 10 $°C\cdot h^{-1}$. Yellow block-shaped crystals were isolated manually, washed with distilled water and dried to give compound 2 (yield 53% based on H_2mia). Anal. Calcd for $C_{42}H_{28}Mn_2N_4O_{10}$: C, 58.75; H, 3.29; N, 6.53. Found: C, 58.97; H, 3.31; N, 6.55%. IR (KBr, cm^{-1}): 1613 w, 1584 s, 1547 s, 1514 w, 1452 w, 1402 m, 1381 s, 1320 w, 1226 w, 1187 w, 1125 w, 976 w, 923 w, 893 w, 844 w, 782 w, 724 m, 641 w.

Synthesis of $[Co(\mu_2\text{-mia})(2,2'\text{-bipy})(H_2O)]_n\cdot nH_2O$ **(3).** A mixture of $CoCl_2\cdot 6H_2O$ (47.6 mg, 0.2 mmol), H_2mia (38.4 mg, 0.2 mmol), 2,2'-bipy (31.2 mg, 0.2 mmol), NaOH (16.0 mg, 0.4 mmol), and H_2O (10 mL) was stirred at room temperature for 15 min, then sealed in a 25 mL Teflon-lined stainless steel vessel, and heated at 160 °C for 3 days, followed by cooling to room temperature at a rate of 10 $°C\cdot h^{-1}$. Pink block-shaped crystals were isolated manually, washed with distilled water and dried (yield 47% based on H_2mia) to give compound **3**. Anal. Calcd for $C_{19}H_{18}CoN_2O_7$: C, 51.25; H, 4.07; N, 6.29. Found: C, 51.13; H, 4.05; N, 6.33%. IR (KBr, cm^{-1}): 3268 w, 3120 w, 3004 w, 1609 w, 1572 s, 1547 s, 1473 w, 1457 w, 1440 s, 1398 s, 1328 w, 1266 w, 1191 w, 1130 w, 1105 w, 1055 w, 1026 w, 976 w,

931 w, 893 w, 798 w, 778 m, 732 w, 653 w.

Synthesis of [Co(μ$_3$-mia)(4,4'-bipy)]$_n$·nH$_2$O (4). A mixture of $CoCl_2·6H_2O$ (47.6 mg, 0.2 mmol), H_2mia (38.4 mg, 0.2 mmol), 4,4'-bipy (31.2 mg, 0.20 mmol), NaOH (16.0 mg, 0.40 mmol), and H_2O (10 mL) was stirred at room temperature for 15 min, then sealed in a 25 mL Teflon-lined stainless steel vessel, and heated at 160 °C for 3 days, followed by cooling to room temperature at a rate of 10 °C·h^{-1}. Pink block-shaped crystals were isolated manually, washed with distilled water and dried to give compound **4** (yield 45% based on H_2mia). Anal. Calcd for $C_{19}H_{16}CoN_2O_6$: C, 53.41; H, 3.77; N, 6.56. Found: C, 53.68; H, 3.80; N, 6.54%. IR (KBr, cm^{-1}): 3074 w, 3049 w, 2941 w, 1605 w, 1589 m, 1551 w, 1452 w, 1398 s, 1324 w, 1266 w, 1220 w, 1130 w, 1055 w, 1005 w, 930 w, 886 w, 823 w, 782 w, 728 m, 678 w, 633 w.

Synthesis of [Co(μ$_3$-mia)(py)$_2$]$_n$ (5). A mixture of $CoCl_2·6H_2O$ (47.6 mg, 0.2 mmol), H_2mia (38.4 mg, 0.2 mmol), py (0.5 mL, 6.05 mmol), and H_2O (10 mL) was stirred at room temperature for 15 min, then sealed in a 25 mL Teflon-lined stainless steel vessel, and heated at 160 °C for 3 days, followed by cooling to room temperature at a rate of 10 °C·h^{-1}. Pink block-shaped crystals were isolated manually, washed with distilled water and dried to give compound **5** (yield 52% based on H_2mia). Anal. Calcd for $C_{19}H_{16}CoN_2O_5$: C, 55.49; H, 3.92; N, 6.81. Found: C, 55.74; H, 3.94; N, 6.77%. IR (KBr, cm^{-1}): 1620 w, 1585 s, 1549 s, 1449 s, 1397 s, 1325 w, 1265 w, 1217 w, 1129 w, 1109 w, 1057 w, 1009 w, 945 w, 926 w, 889 w, 786 m, 757 w, 725 m, 698 m, 626 w.

Synthesis of [Cd(μ-mia)(py)(H$_2$O)$_2$]$_n$·nH$_2$O (6). A mixture of $CdCl_2·H_2O$ (40.2 mg, 0.2 mmol), H_2mia (38.4 mg, 0.2 mmol), py (0.5 mL, 6.05 mmol), and H_2O (10 mL) was stirred at room temperature for 15 min, then sealed in a 25 mL Teflon-lined stainless steel vessel, and heated at 160 °C for 3 days, followed by cooling to room temperature at a rate of 10 °C·h^{-1}. Yellow block-shaped crystals were isolated manually, washed with distilled water and dried to give compound **6** (yield 51% based on H_2mia). Anal. Calcd for $C_{14}H_{17}CdNO_8$: C, 38.24; H, 3.90; N, 3.19. Found: C, 38.44; H, 3.88; N, 3.17%. IR (KBr, cm^{-1}): 3547 w, 3352 m, 2944 w, 1608 w, 1565 s, 1449 m, 1381 s, 1317 w, 1261 w, 1221 w, 1157 w, 1129 w, 1049 w, 1009 w, 931 w, 889 w, 810 w, 781 w, 738 m, 698 w, 629 w.

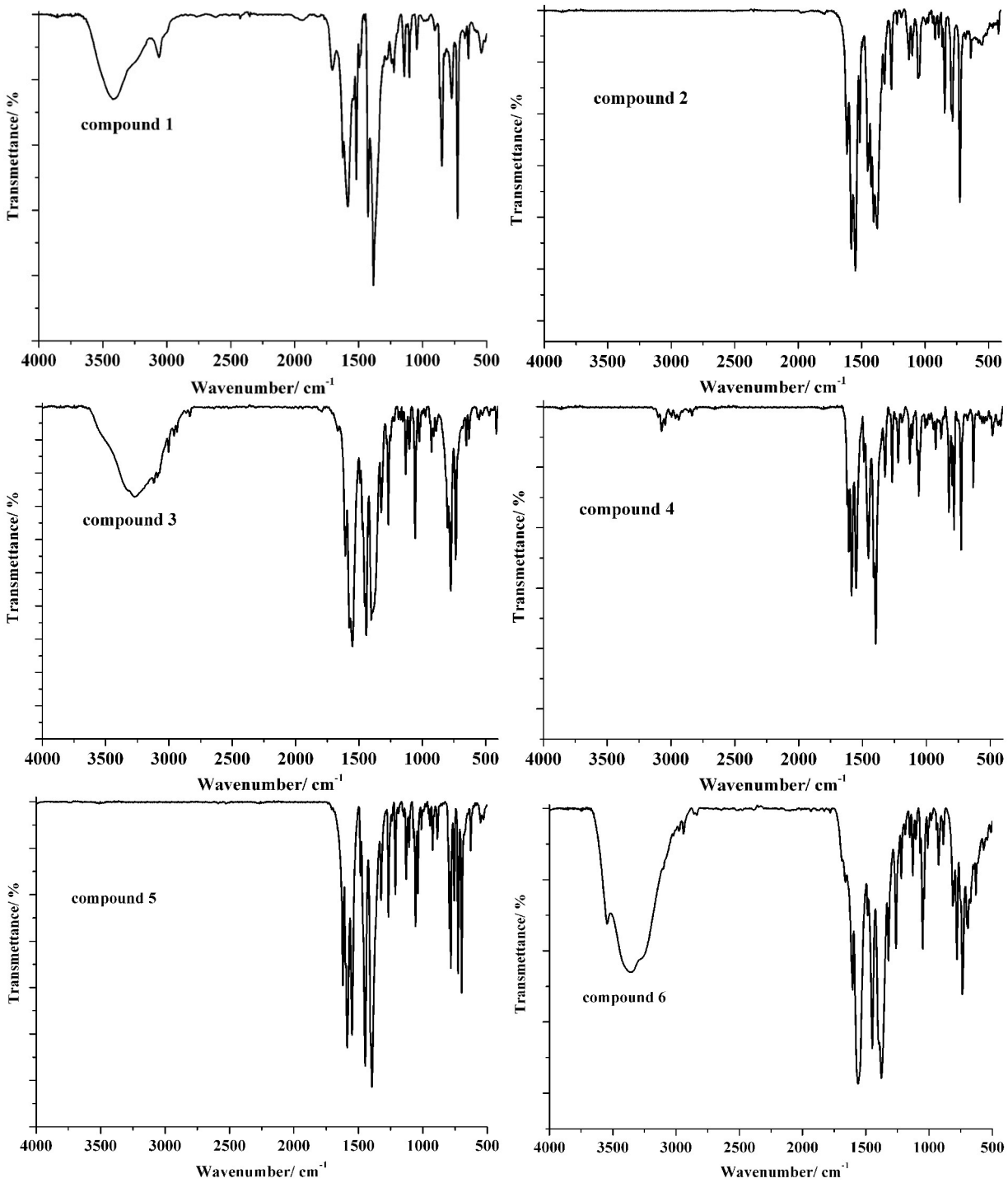

Fig. S1. FTIR spectra of compounds **1**–**6**.

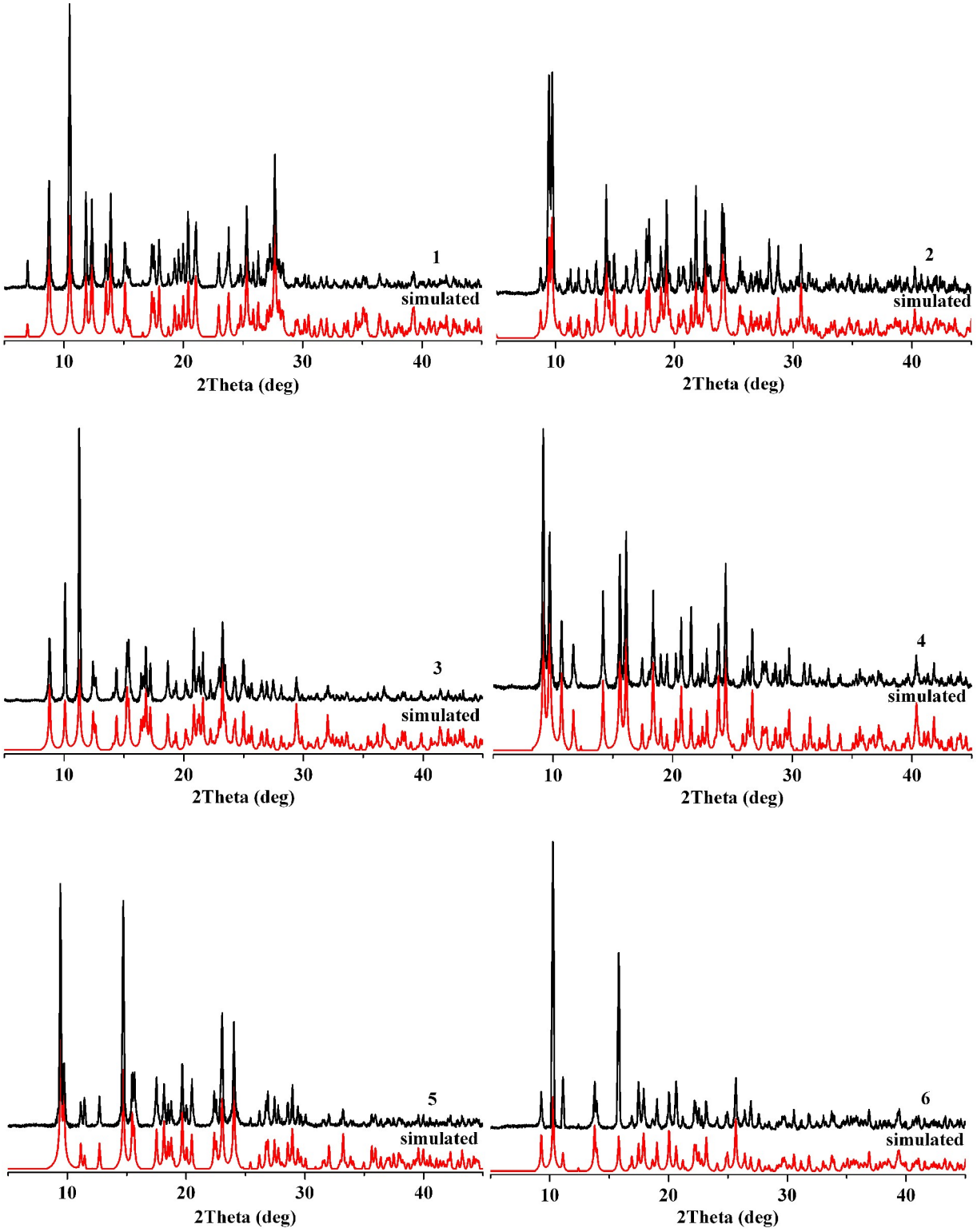

Fig. S2. PXRD patterns of compounds **1**–**6** at room temperature. Black paterns correspnond to the experimental data obtained using the as-synthesized bulk samples. Red patterns were simulated from the single crystal X-ray data.

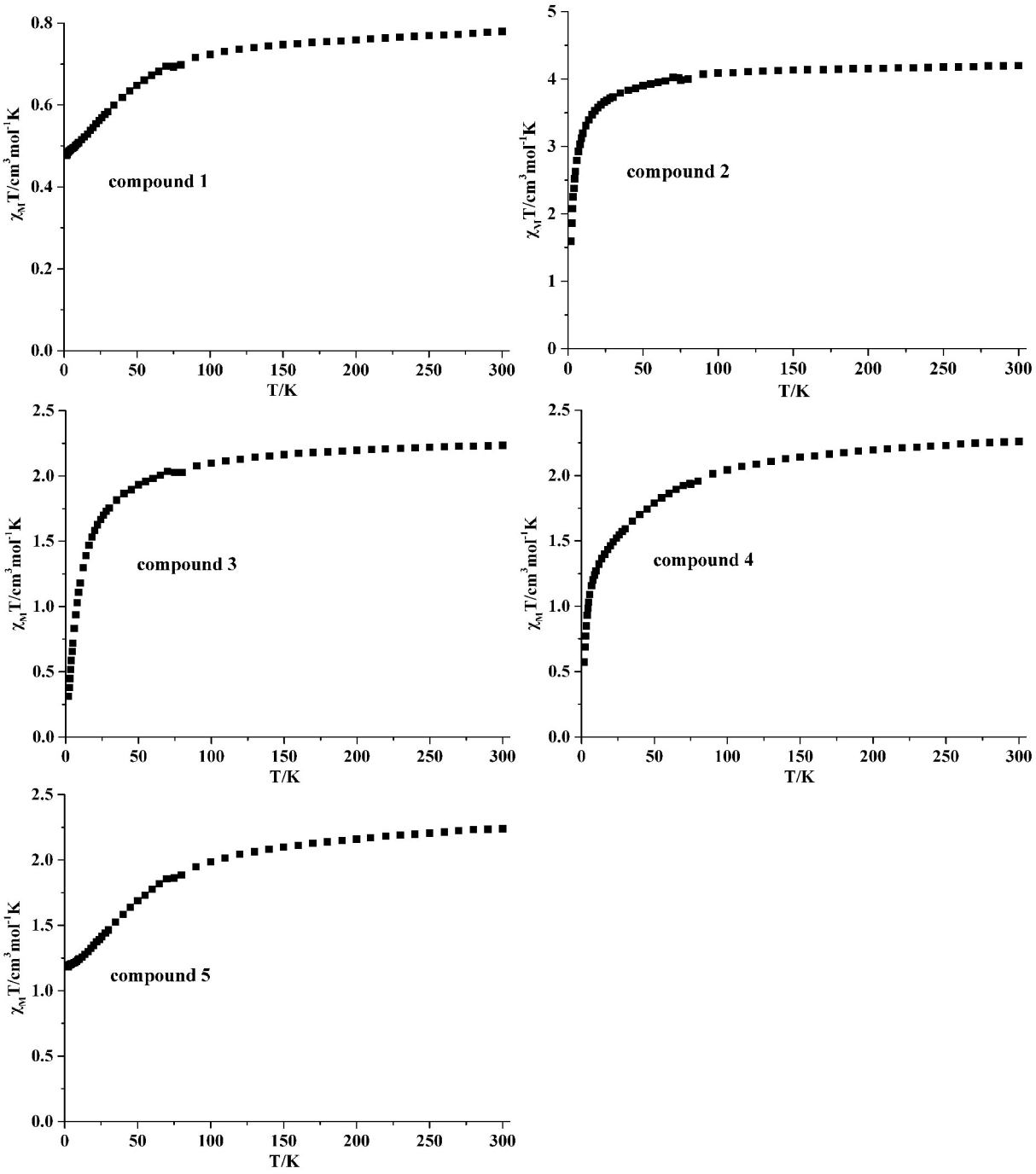

Fig. S3. Temperature dependence of $\chi_M T$ vs. T for compounds **1**–**5**.

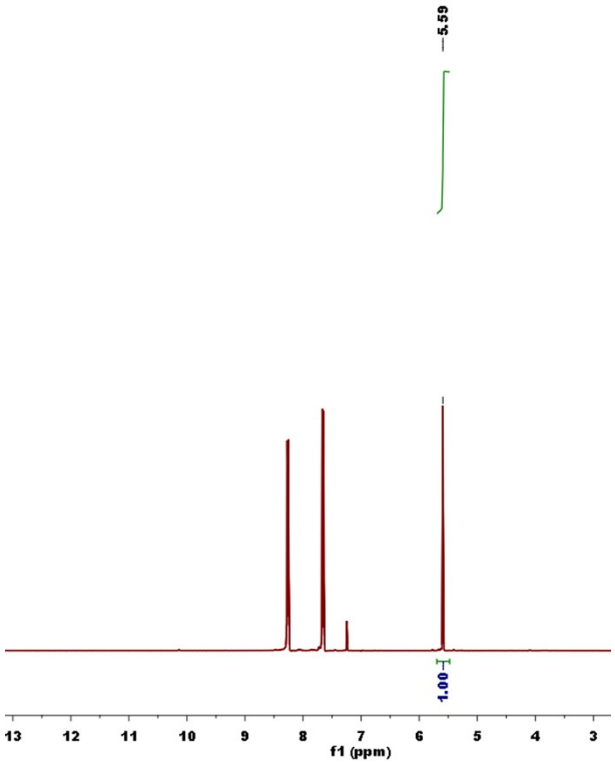

Fig. S4. Example of the integration in the ^{1}H NMR spectrum of the reaction mixture for the determination of the cyanosilylation product (conditions of Table 3, Entry 6).

Examples of product yield calculation in the cyanosilylation reaction. The C(=O) *H* signal of 4-nitrobenzaldehyde (substrate) appears at δ10.15 ppm, while 2-(4-nitrophenyl)-2-((trimethylsilyl)oxy)acetonitrile (product) shows a characteristic signal at δ5.59 ppm.
Total integration of both signals: unreacted 4-nitrobenzaldehyde + 2-(4-nitrophenyl)-2-((trimethylsilyl)oxy)acetonitrile = 0 + 1 = 1.
Percentage of the unreacted substrate: 0/1 = 0
Conversion of 4-nitrobenzaldehyde = yield of 2-(4-nitrophenyl)-2-((trimethylsilyl)oxy)acetonitrile = 100−0 = 100%.

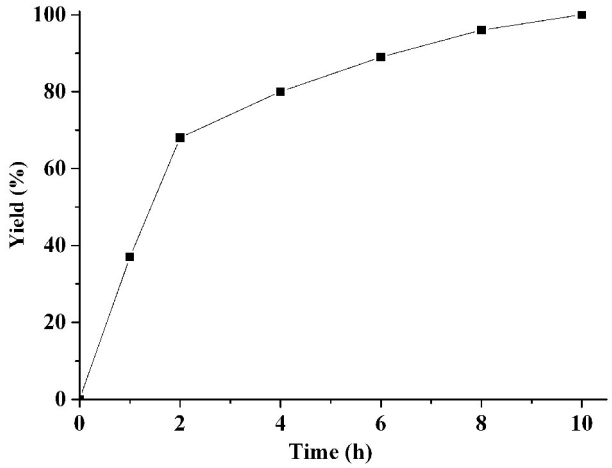

Fig. S5. Accumulation of 2-(4-nitrophenyl)-2-[(trimethylsilyl)oxy]acetonitrile vs. time in the cyanosilylation of 4-nitrobenzaldehyde with TMSCN catalysed by **1**. Reaction conditions are those of Table 3, entries 1−6.

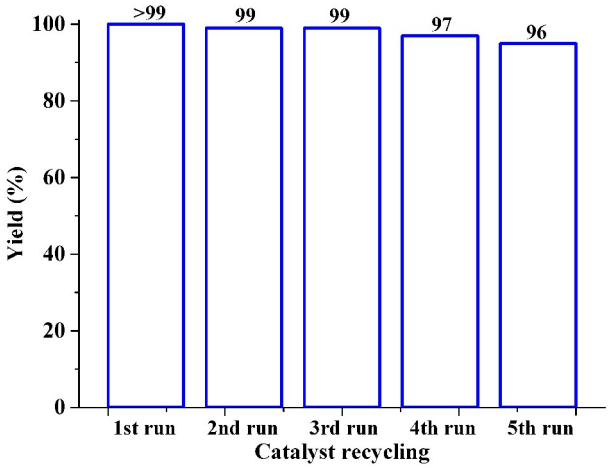

Fig. S6. Catalyst recycling experiments in the cyanosilylation of 4-nitrobenzaldehyde with TMSCN catalysed by **1**. Reaction conditions are those of Table 3, entry 6.

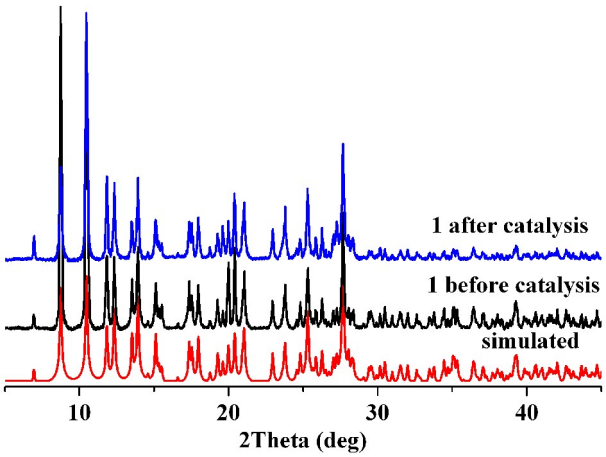

Fig. S7. PXRD patterns for **1**: simulated (red), before (black) and after (blue) catalytic experiments.

Table S1. Selected bond lengths [Å] and angles [°] for compounds **1**–**6**.[a]

1					
Cu(1)-O(1)	1.953(2)	Cu(1)-O(4)#1	2.250(2)	Cu(1)-O(6)	1.966(2)
Cu(1)-N(1)	2.001(3)	Cu(1)-N(2)	2.011(3)		
O(1)-Cu(1)-O(6)	94.73(9)	O(1)-Cu(1)-N(1)	169.99(11)	N(1)-Cu(1)-O(6)	91.95(10)
O(1)-Cu(1)-N(2)	89.45(10)	N(2)-Cu(1)-O(6)	163.28(10)	N(1)-Cu(1)-N(2)	82.08(11)
O(1)-Cu(1)-O(4)#1	95.03(10)	O(6)-Cu(1)-O(4)#1	96.12(9)	N(1)-Cu(1)-O(4)#1	91.65(10)
N(2)-Cu(1)-O(4)#1	99.64(10)				
2					
Mn(1)-O(1)	2.132(5)	Mn(1)-O(6)	2.291(5)	Mn(1)-O(7)	2.226(5)
Mn(1)-O(9)#1	2.110(5)	Mn(1)-N(1)	2.280(6)	Mn(1)-N(2)	2.278(7)
Mn(2)-O(2)#2	2.111(5)	Mn(2)-O(3)	2.230(5)	Mn(2)-O(4)	2.308(6)
Mn(2)-O(8)	2.105(5)	Mn(2)-N(3)	2.304(7)	Mn(2)-N(4)	2.263(7)
O(1)-Mn(1)-O(9)#1	96.3(2)	O(7)-Mn(1)-O(9)#1	109.1(2)	O(1)-Mn(1)-O(7)	90.2(2)
N(2)-Mn(1)-O(9)#1	155.6(2)	O(1)-Mn(1)-N(2)	80.9(2)	O(7)-Mn(1)-N(2)	95.1(2)
N(1)-Mn(1)-O(9)#1	89.5(2)	O(1)-Mn(1)-N(1)	124.0(2)	O(7)-Mn(1)-N(2)	139.6(2)
N(2)-Mn(1)-N(1)	72.7(2)	O(6)-Mn(1)-O(9)#1	97.1(2)	O(6)-Mn(1)-O(1)	147.21(19)
O(6)-Mn(1)-O(7)	57.11(18)	O(6)-Mn(1)-N(2)	98.0(2)	O(6)-Mn(1)-N(1)	85.91(19)
O(8)-Mn(2)-O(2)#2	98.0(2)	O(8)-Mn(2)-O(3)	91.5(2)	O(3)-Mn(2)-O(2)#2	102.7(2)

O(8)-Mn(2)-N(4)	82.9(2)	N(4)-Mn(2)-O(2)#2	162.1(2)	N(4)-Mn(2)-O(3)	95.1(2)
O(8)-Mn(2)-N(3)	128.0(2)	N(3)-Mn(2)-O(2)#2	93.2(2)	O(3)-Mn(2)-N(3)	134.9(2)
N(4)-Mn(2)-N(3)	72.7(3)	O(8)-Mn(2)-O(4)	147.41(19)	O(2)-Mn(2)-O(4)	97.8(2)
O(3)-Mn(2)-O(4)	57.17(19)	N(4)-Mn(2)-O(4)	90.5(2)	N(3)-Mn(2)-O(4)	79.2(2)
3					
Co(1)-O(1)	2.335(2)	Co(1)-O(2)	2.162(2)	Co(1)-O(3)#1	2.0205(19)
Co(1)-O(6)	2.1028(19)	Co(1)-N(1)	2.127(2)	Co(1)-N(2)	2.102(2)
O(3)#1-Co(1)-N(2)	126.57(9)	O(3)#1-Co(1)-O(6)	97.18(8)	O(6)-Co(1)-N(2)	96.64(8)
O(3)#1-Co(1)-N(1)	89.57(9)	N(2)-Co(1)-N(1)	76.38(9)	O(6)-Co(1)-N(1)	172.36(8)
O(3)#1-Co(1)-O(2)	86.09(8)	O(2)-Co(1)-N(2)	144.26(9)	O(6)-Co(1)-O(2)	92.45(8)
O(2)-Co(1)-N(1)	91.58(9)	O(3)#1-Co(1)-O(1)	142.95(8)	O(1)-Co(1)-N(2)	88.33(8)
O(6)-Co(1)-O(1)	89.58(8)	O(1)-Co(1)-N(1)	87.16(9)	O(1)-Co(1)-O(2)	57.15(8)
4					
Co(1)-O(1)#1	2.029(3)	Co(1)-O(2)	2.041(3)	Co(1)-O(3)#2	2.235(3)
Co(1)-O(4)#2	2.136(3)	Co(1)-N(1)	2.132(3)	Co(1)-N(2)#3	2.150(3)
O(1)#1-Co(1)-O(2)	118.93(12)	O(1)#1-Co(1)-N(1)	91.38(12)	O(2)-Co(1)-N(1)	91.01(11)
O(1)#1-Co(1)-O(4)#2	90.83(11)	O(2)-Co(1)-O(4)#2	150.11(12)	O(4)#2-Co(1)-N(1)	91.02(13)
O(1)#1-Co(1)-N(2)#3	88.09(12)	O(2)-Co(1)-N(2)#3	86.51(12)	N(1)-Co(1)-N(2)#3	176.83(12)
O(4)#2-Co(1)-N(2)#3	92.11(13)	O(3)#2-Co(1)-O(1)#1	150.04(11)	O(3)#2-Co(1)-O(2)	90.47(11)
O(3)#2-Co(1)-N(1)	93.89(12)	O(3)#2-Co(1)-O(4)#2	59.64(11)	O(3)#2-Co(1)-N(2)#3	88.12(12)
5					
Co(1)-O(1)	2.1303(19)	Co(1)-O(2)	2.246(2)	Co(1)-O(3)#1	2.021(2)
Co(1)-O(4)#2	2.0450(19)	Co(1)-N(1)	2.170(3)	Co(1)-N(2)	2.158(3)
O(3)#1-Co(1)-O(4)#2	119.76(8)	O(3)#1-Co(1)-O(1)	91.62(8)	O(1)-Co(1)-O(4)#2	148.61(8)
O(3)#1-Co(1)-N(2)	90.47(10)	N(2)-Co(1)-O(4)#2	90.17(9)	O(1)-Co(1)-N(2)	90.46(9)
O(3)#1-Co(1)-N(1)	89.10(10)	O(4)#2-Co(1)-N(1)	87.73(9)	N(1)-Co(1)-O(1)	92.23(9)
N(1)-Co(1)-N(2)	177.29(9)	O(3)#1-Co(1)-O(2)	151.20(8)	O(4)#2-Co(1)-O(2)	88.90(7)
O(2)-Co(1)-O(1)	59.72(7)	O(2)-Co(1)-N(2)	92.39(9)	O(2)-Co(1)-N(1)	89.27(9)
6					
Cd(1)-O(1)	2.404(3)	Cd(1)-O(2)	2.413(3)	Cd(1)-O(4)#1	2.256(3)
Cd1)-O(6)	2.288(3)	Cd(1)-O(7)	2.360(3)	Cd(1)-N(1)	2.295(3)
O(4)#1-Cd(1)-O(6)	89.24(11)	O(4)#1-Cd(1)-N(1)	136.12(11)	O(6)-Cd(1)-N(1)	90.73(12)
O(8)#1-Cd(1)-N(1)	86.60(11)	O(6)-Cd(1)-O(7)	175.59(10)	N(1)-Cd(1)-O(7)	91.25(11)
O(4)#1-Cd(1)-O(1)	83.57(10)	O(6)-Cd(1)-O(1)	94.70(12)	N(1)-Cd(1)-O(1)	140.07(11)
O(7)-Cd(1)-O(1)	86.30(11)	O(4)#1-Cd(1)-O(2)	137.44(10)	O(2)-Cd(1)-O(6)	94.03(12)
O(2)-Cd(1)-N(1)	86.32(12)	O(7)-Cd(1)-O(2)	90.03(11)	O(1)-Cd(2)-O(2)	53.87(10)

[a] Symmetry transformations used to generate equivalent atoms: #1 –*x*+2, –*y*+2, –*z*+2 for **1** ; #1 *x*, –*y*+2, *z*–1/2; #2, *x*, –*y*+2, *z*+1/2 for **2**; #1 –*x*, *y*–1/2, –*z*+3/2 for **3**; #1 –*x*+1, –*y*+1, –*z*+1; #2 *x*, *y*+1, *z*; #3 *x*–1, *y*, *z*+1 for **4**; #1 –*x*+2, –*y*+1, –*z*+1; #2 *x*+1/2, *y*+1/2, *z* for **5**; #1 *x*, *y*, *z*–1 for **6**.

Table S2. Hydrogen bonds in crystal packing [Å, °] of **1**, **3** and **6**.

Complexes	D-H…A	*d*(D-H)	*d*(H…A)	*d*(D…A)	∠DHA	Symmetry code
1	O(6)-H(1W)···O(3)	0.820	1.874	2.632	153.18	-*x*+1, -*y*+2, -*z*+2
	O(6)-H(2W)···O(2)	0.850	1.747	2.597	179.60	
	O(7)-H(3W)···O(3)	0.850	2.118	2.968	179.44	-*x*+1, -*y*+1, -*z*+2
	O(7)-H(4W)···O(4)	0.850	1.996	2.846	179.03	*x*-1, *y*-1, *z*-1
3	O(6)-H(1W)···O(4)	0.869	1.931	2.743	154.74	*x*, -*y*+1/2, *z*+1/2
	O(7)-H(3W)···O(6)	0.844	1.902	2.684	153.58	*x*+1, *y*, *z*-1
	O(7)-H(4W)···O(2)	0.829	1.892	2.721	178.85	*x*+1, -*y*+1/2, *z*-1/2
6	O(6)-H(1W)···O(8)	0.844	1.877	2.715	171.84	*x*, *y*+1, *z*-1
	O(6)-H(2W)···O(2)	0.841	1.912	2.750	173.76	-*x*+1, -*y*+2, -*z*
	O(7)-H(3W)···O(1)	0.853	2.006	2.778	152.00	-*x*+1, -*y*+1, -*z*
	O(7)-H(4W)···O(4)	0.852	2.006	2.797	154.05	-*x*+1, -*y*+1, -*z*+1
	O(8)-H(5W)···O(3)	0.830	1.942	2.760	168.66	-*x*+1, -*y*+1, -*z*+1
	O(8)-H(6W)···O(5)	0.850	2.098	2.948	179.31	-*x*, -*y*+1, -*z*+1

Table S3. The magmetic moments of compounds **1**–**5**.

Entry	Compound	Magnetic unit	$\chi_M T$ at 300 K ($cm^3 \cdot mol^{-1} \cdot K$)	μ (B.M.)[a]	Assigned to the metal centers[b]
1	**1**	Cu_2	0.78	Exptl, 1.77; Calcd,1.73	Two Cu(II), S = 1/2
2	**2**	Mn_2	4.40	Exptl, 5.94; Calcd, 5.92	One Mn(II), S = 5/2
3	**3**	Co chain	2.23	Exptl, 4.23; Calcd,3.87	One Co(II), S = 3/2
4	**4**	Co_2	2.26	Exptl, 4.25; Calcd, 3.87	One Co(II), S = 3/2
5	**5**	Co_2	2.24	Exptl, 4.24; Calcd, 3.87	One Co(II), S = 3/2

[a] $\mu = 2.83(\chi_M T)^{1/2}$, where χ_M is the molar magnetic susceptibility. [b] $\mu = [n(n+2)]^{1/2}$, where n is the number of unpaired electrons.

Table S4. Comparison of various catalysts for the cyanosilylation between 4-nitrobenzaldehyde with TMSCN.

Entry	Catalyst	Catalyst (mol%)	Solvent	Time (h)	Temp. (°C)	Conversion (%)	Ref.
1	$[Cu_2(\mu_2\text{-mia})_2(phen)_2(H_2O)_2]\cdot 2H_2O$	3	CH_2Cl_2	10	35	100	This work
2	$\{Mn_2(bdc)_2(DMF)_2\}_n$	2.5	CH_2Cl_2	19	30	100	62
3	$[Cd_3(tipp)(bpdc)_2]\cdot DMA\cdot 9H_2O$	0.6	Solvent free	18	RT	100	63
4	Zn-ADBA	0.3	CH_2Cl_2	12	25	92.3	64
5	$[Cu_3(OH)_2(L)_2]_n\cdot n(H_2O)$	2	CH_2Cl_2	10	25-30	65	65
6	[Zn(3,3′-TPDC)] ·DMF·$2H_2O$	0.8	toluene	24	50	77	66
7	BINAPDA-Zr-MOF	5	CH_3CN	5	0	85	67
8	Tb-TCA	2	CH_2Cl_2	4	RT	47	68
9	$[Sc(pydc)(H_2O)(NO_3)]$	10	CH_3CN	24	RT	85.2	69