Supplementary Information for CrystEngComm

Highly thermally stable heterogeneous catalysts: study of 0D and 3D porphyrinic MOFs

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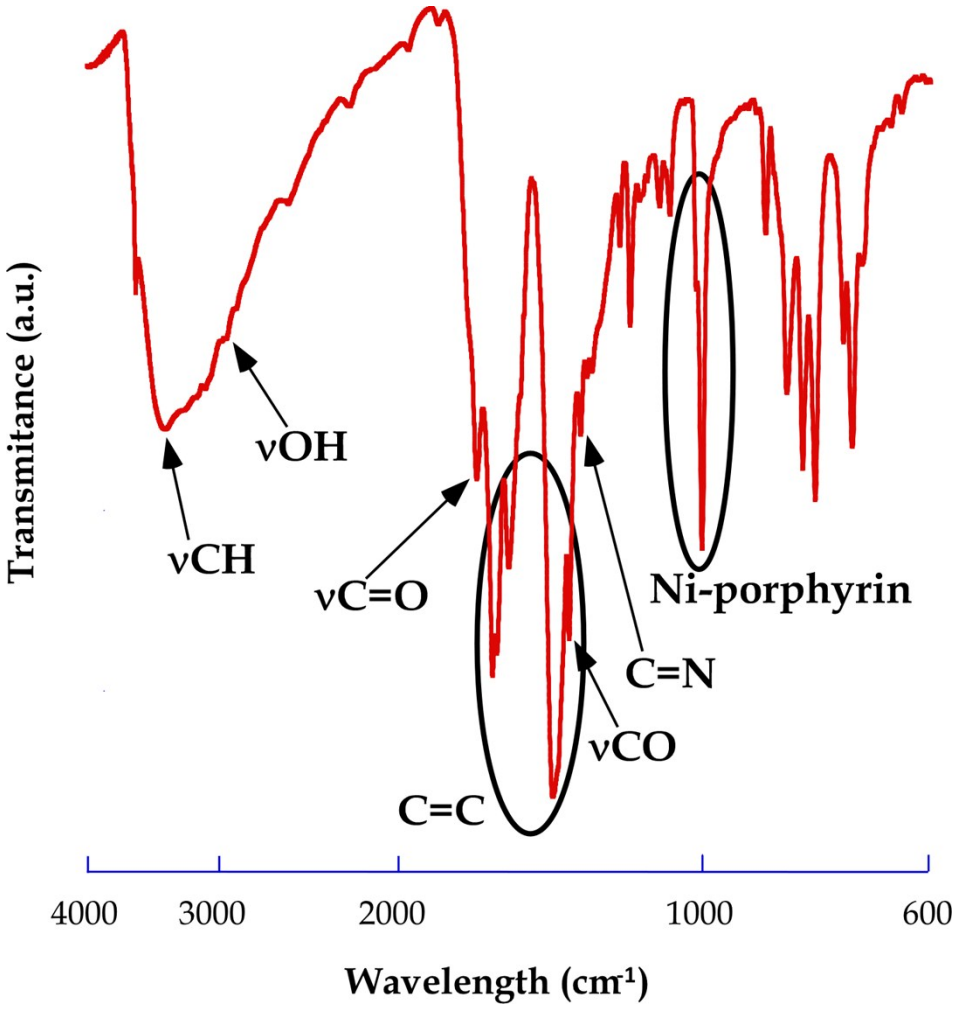

Figure S1. IR Spectra of compound **1.**

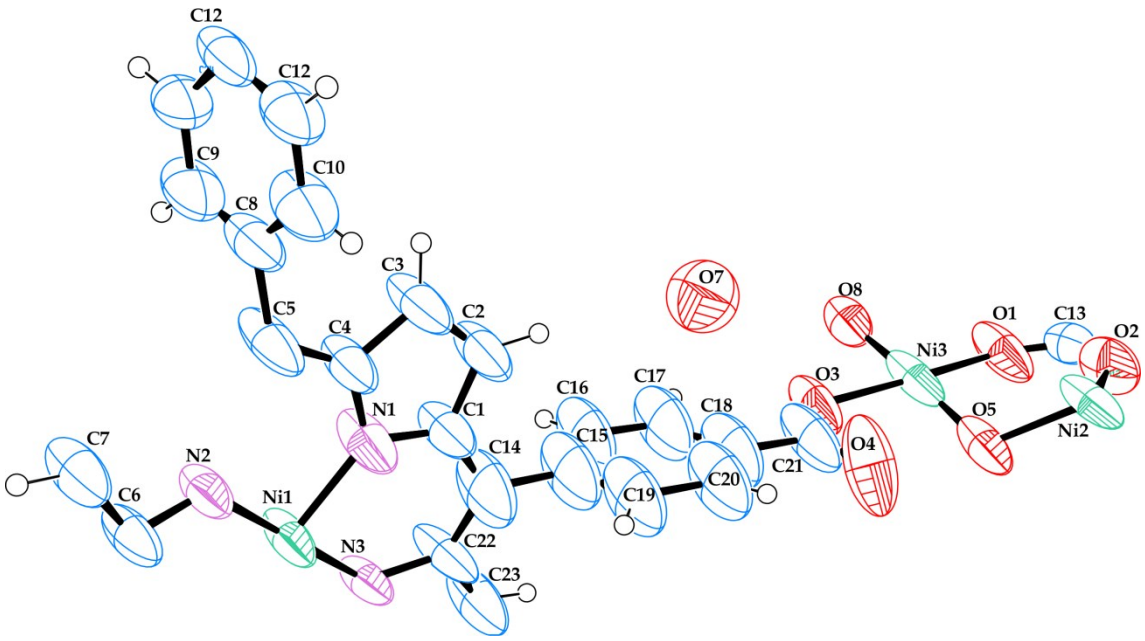

Figure S2. ORTEP[1] detail for compound **1**. The thermal ellipsoids correspond to 50% probability.

[1] Farrugia, L. J., *J. Appl. Crystallogr.,* 1997, **30**, 565.

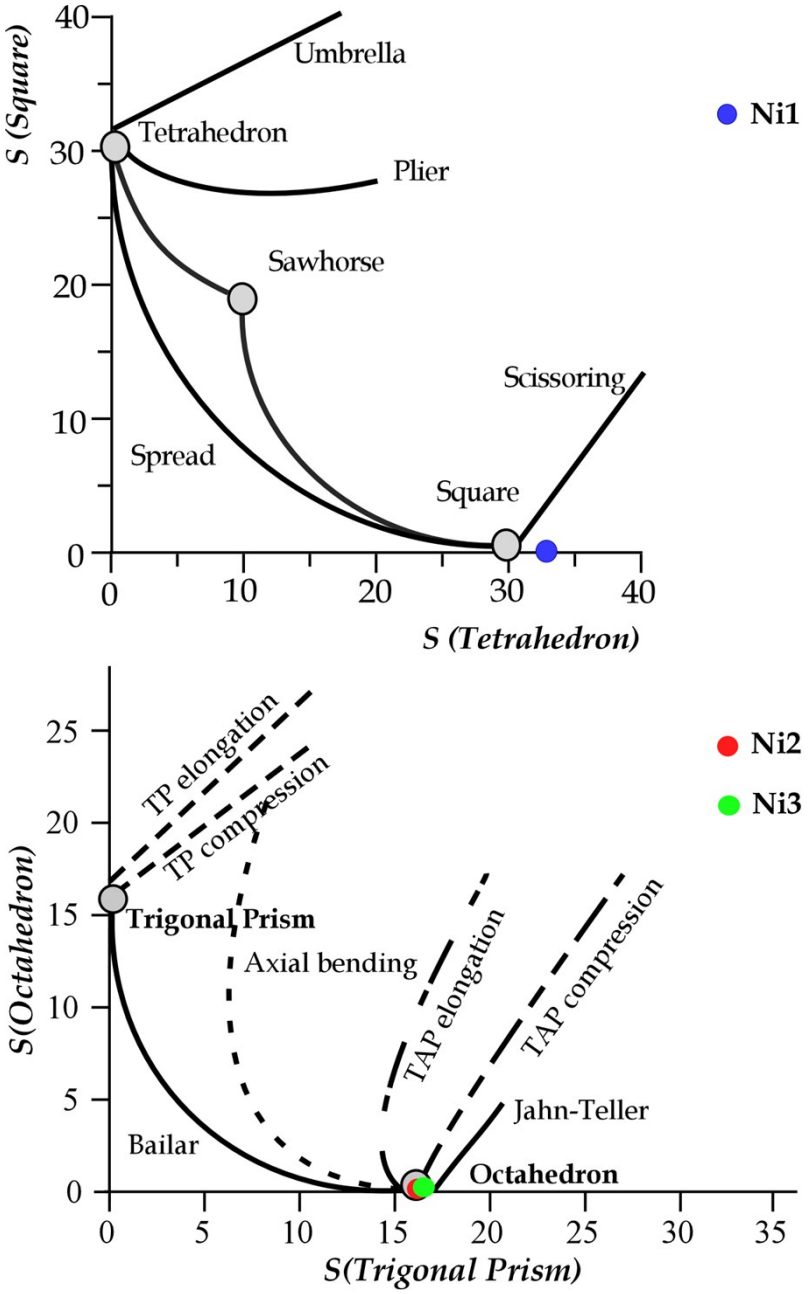

Figure S3. Projection of the calculated values on the distortion diagram for tetrahedral coordinated of Ni1 (blue) and octahedral coordination of Ni2 (red) and Ni3 (green) in compound **1**.

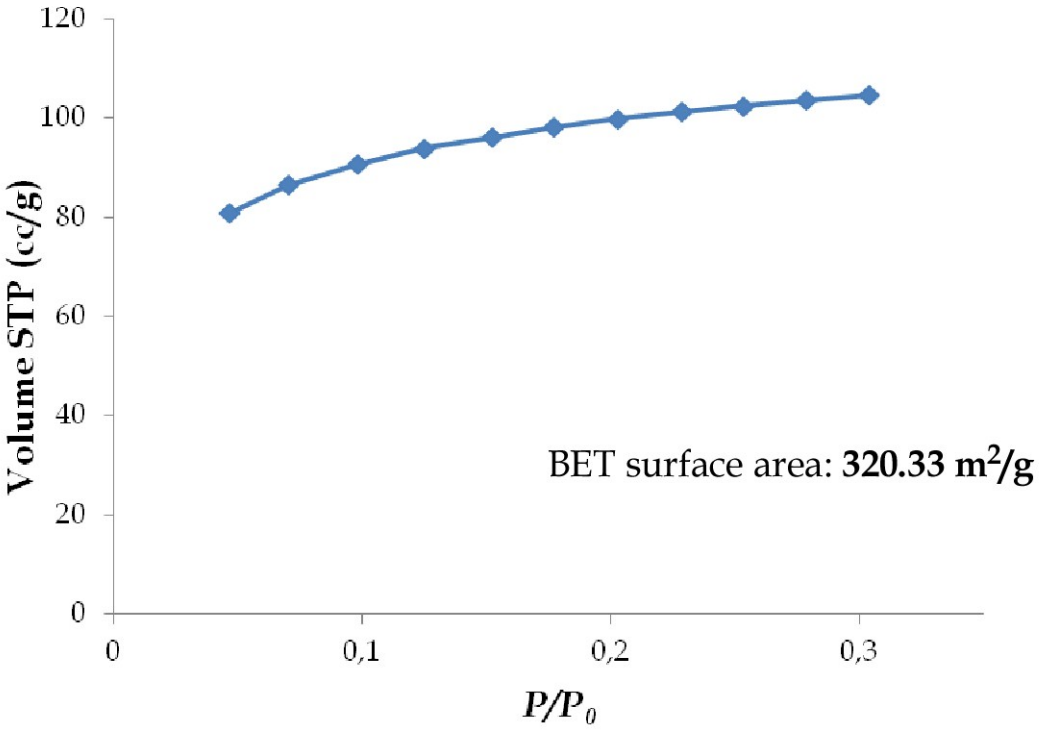

Figure S4. N_2 physisorption at 77 K and low pressure for compound **1**.

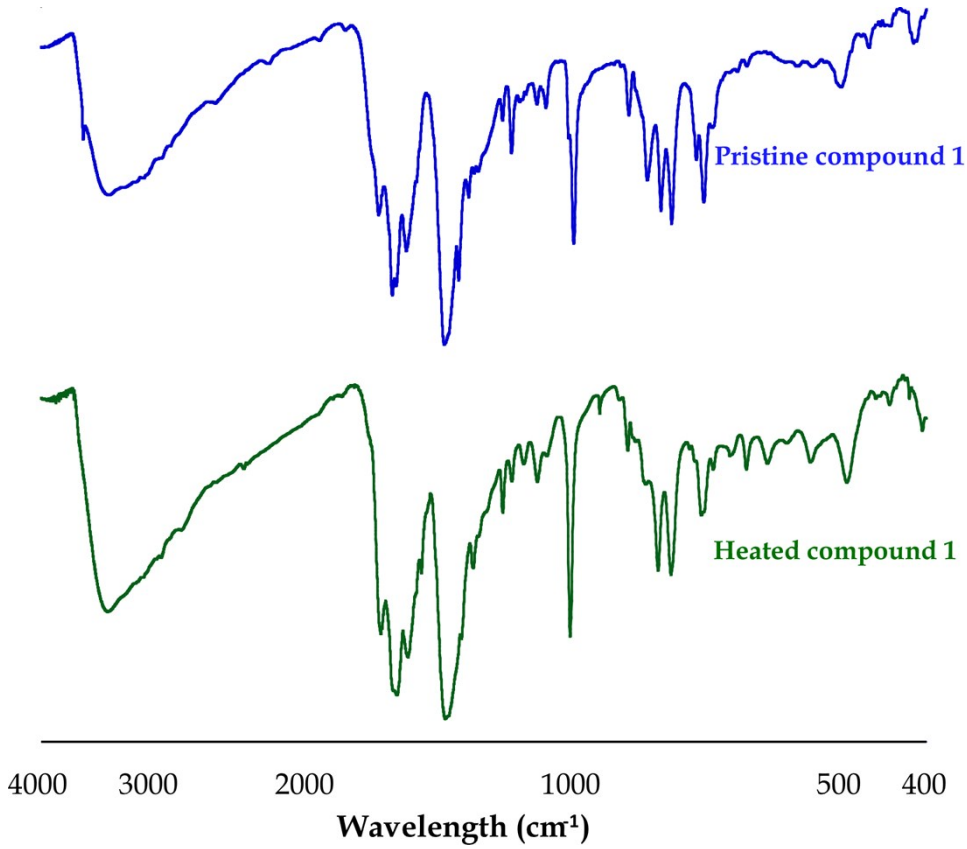

Figure S5. IR spectroscopy of pristine and heated over 150 °C compound **1**.

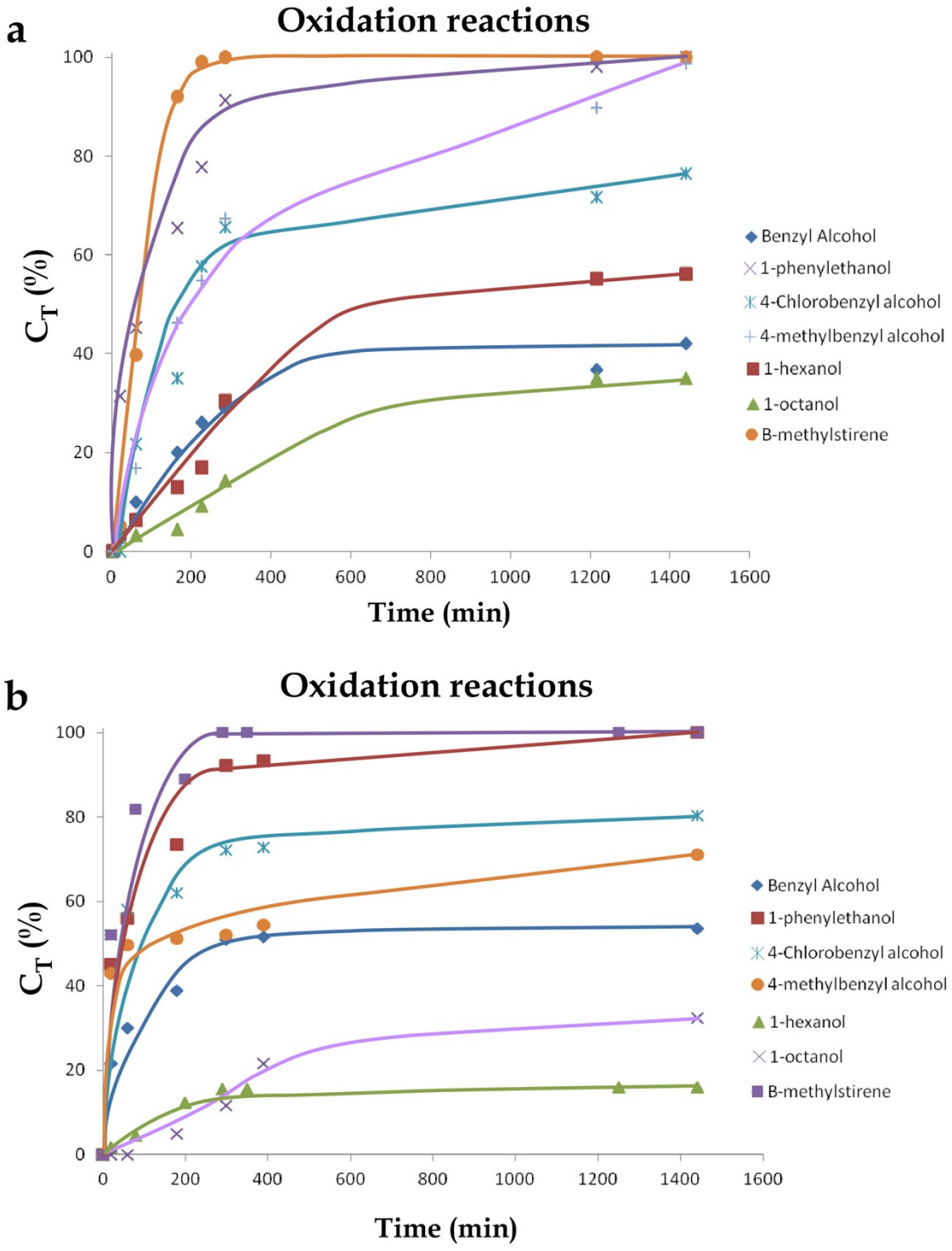

Figure S6. Kinetic profiles of alcohols and alkenes oxidation for (a) compound **1** and (b) compound **2** as catalysts.

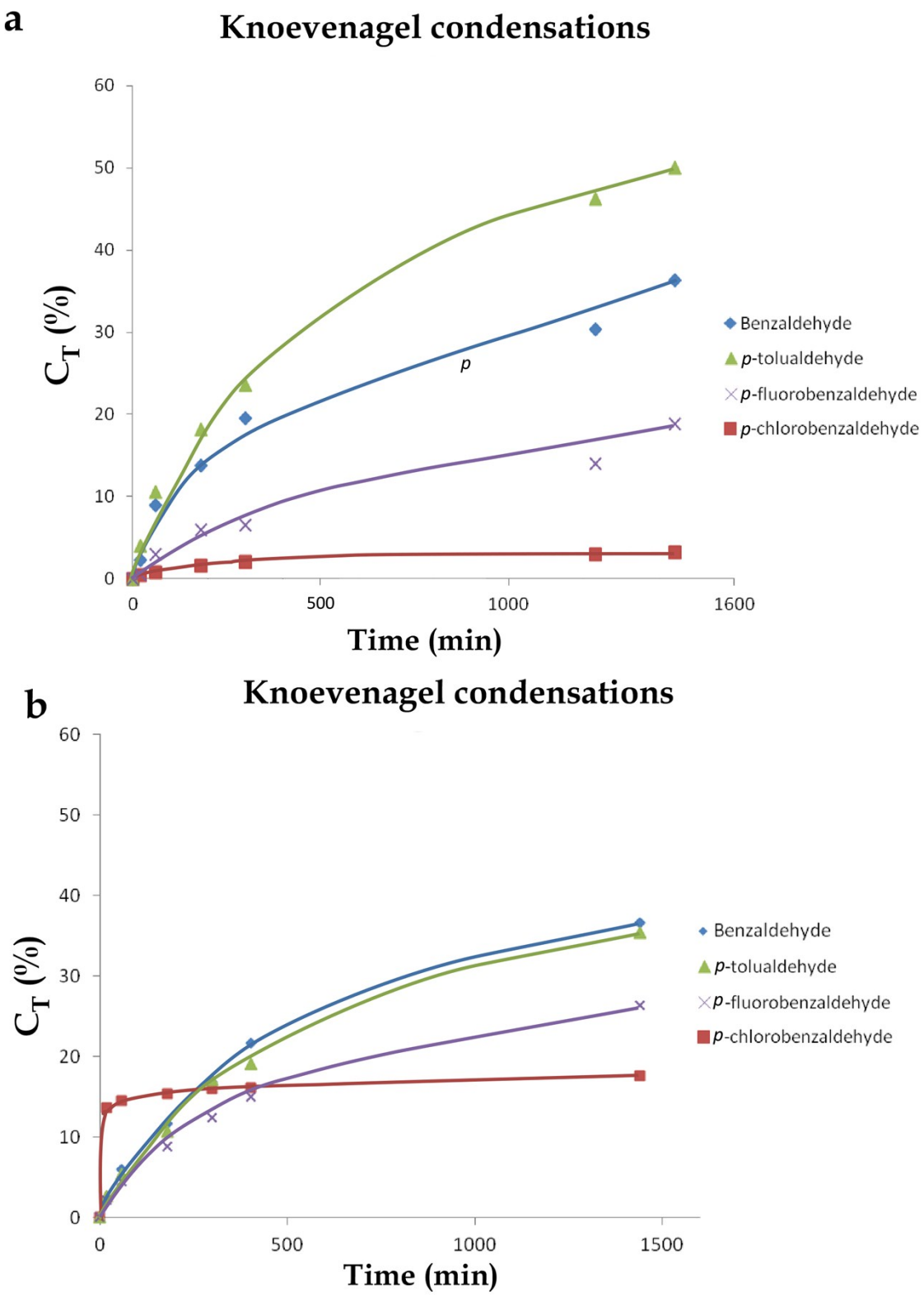

Figure S7. Kinetic profiles of Knoevenagel condensations using (a) compound **1** and (b) compound **2** as catalyst.

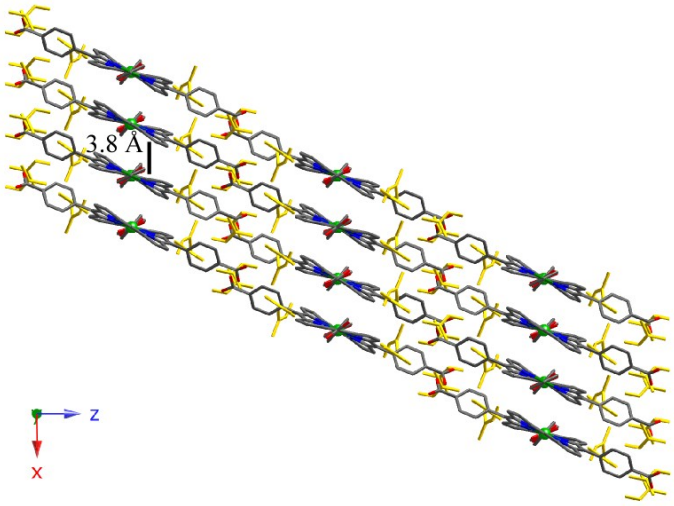

Figure S8. Distance between Cu centers in crystal structure of compound **2**.

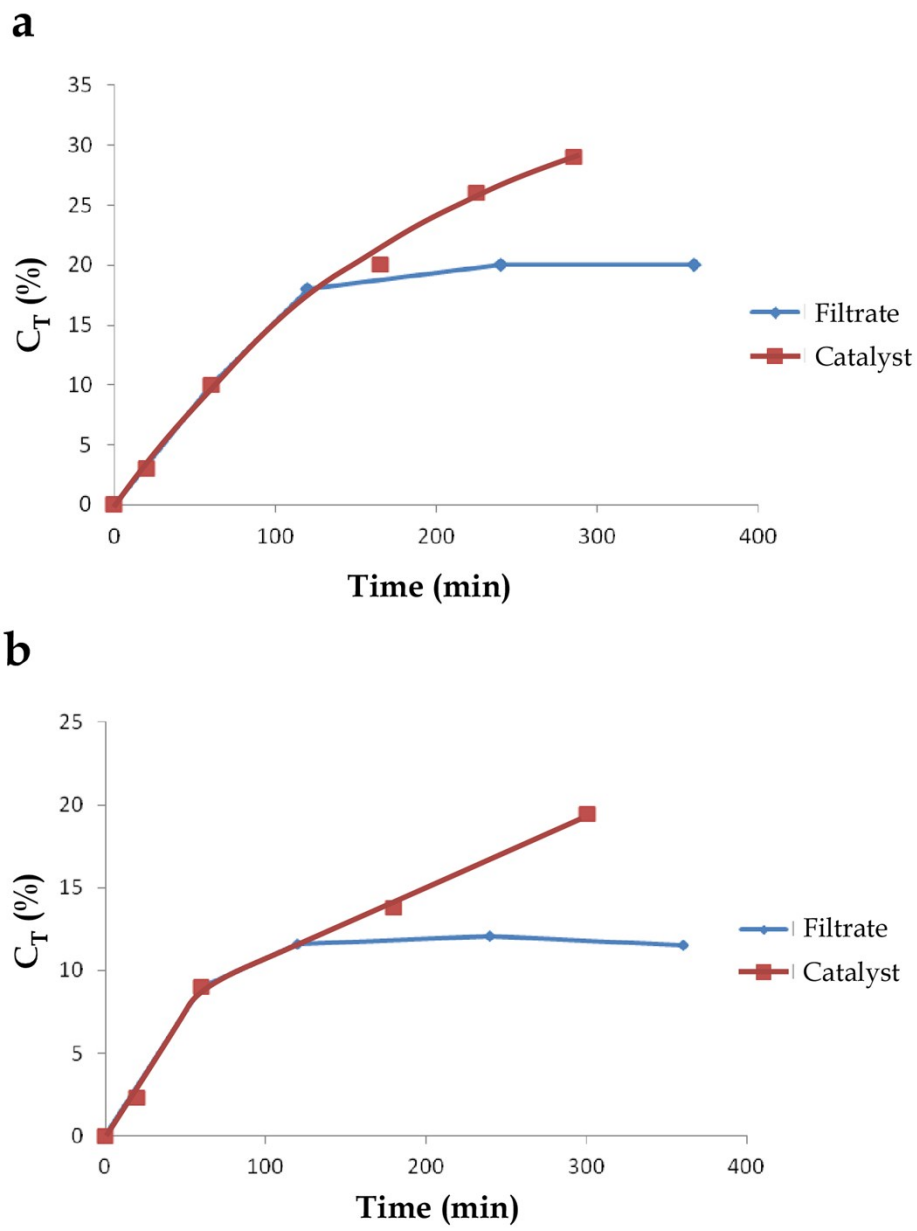

Figure S9. Kinetic profile of the (a) oxidation of benzyl alcohol with TBHP and (b) the condensation of benzaldehyde with malononitrile over compound **1** and after hot filtering.

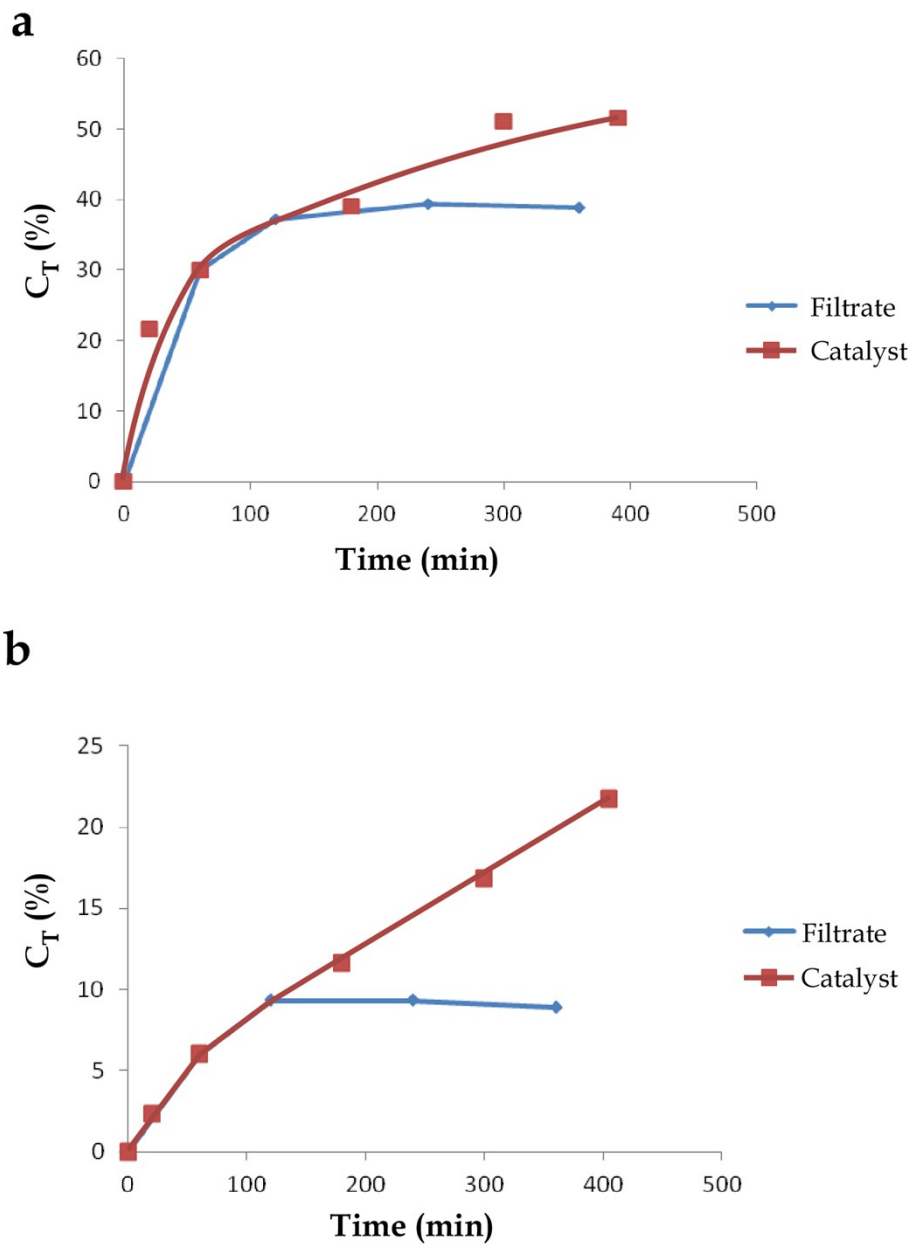

Figure S10. Kinetic profile of the (a) oxidation of benzyl alcohol with TBHP and (b) the condensation of benzaldehyde with malononitrile over compound **2** and after hot filtering.

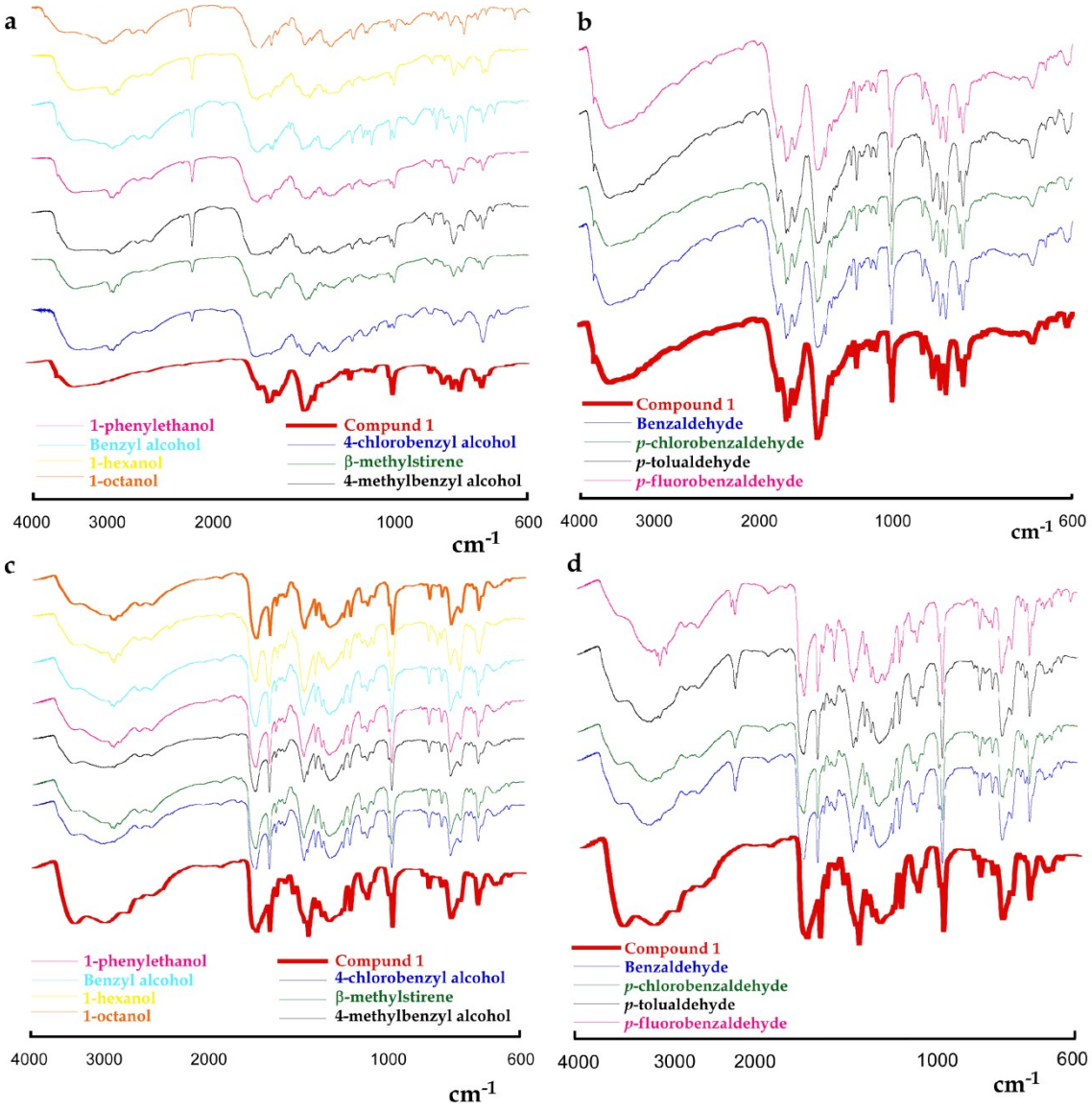

Figure S11. Infrared spectra of the recovered residues after oxidation reactions (a) and Knoevenagel condensations (b) for compound **1** and of the recovered residues after oxidation reactions (c) and Knoevenagel condensations (d), for compound **2**.

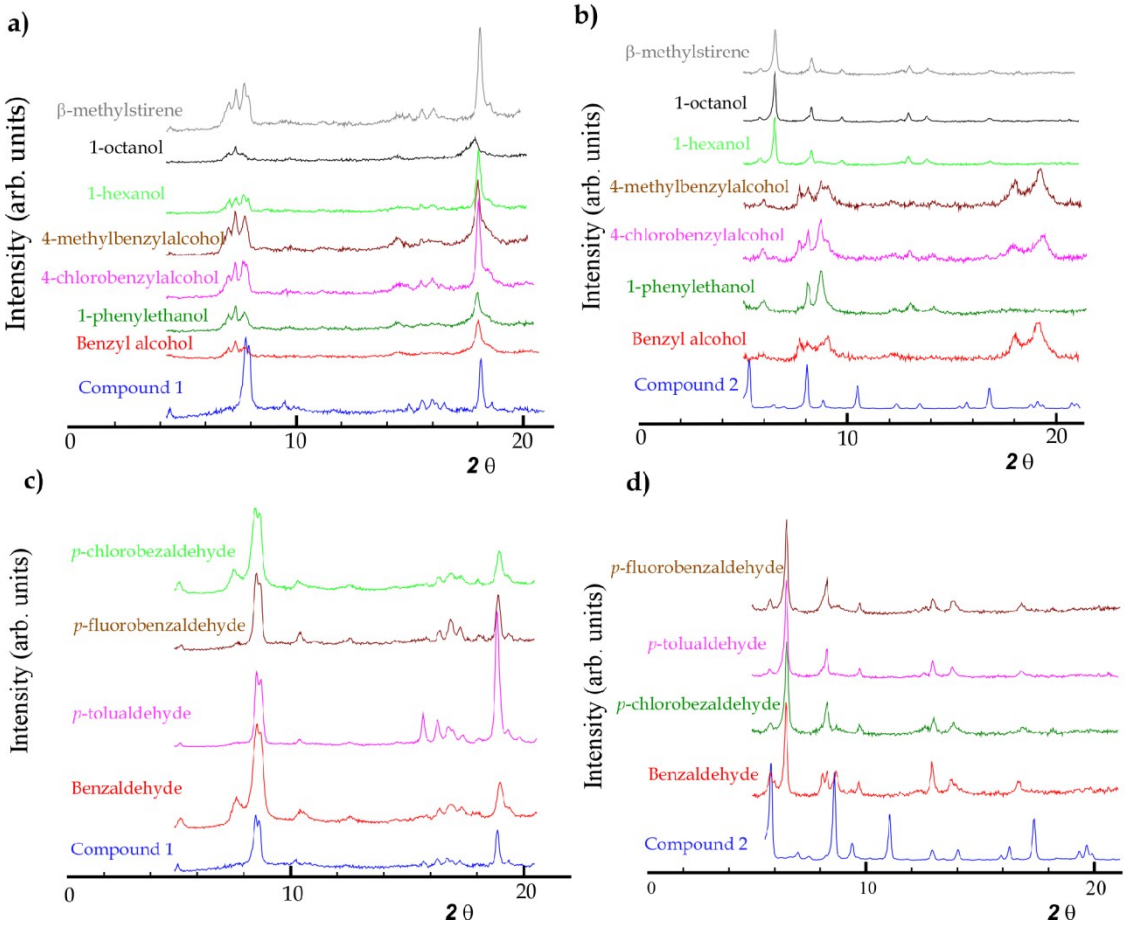

Figure S12. XRD patterns of the recovered residues after oxidation reactions (a) and Knoevenagel condensations (c) for compound **1** and of the recovered residues after oxidation reactions (b) and Knoevenagel condensations (d), for compound **2**.

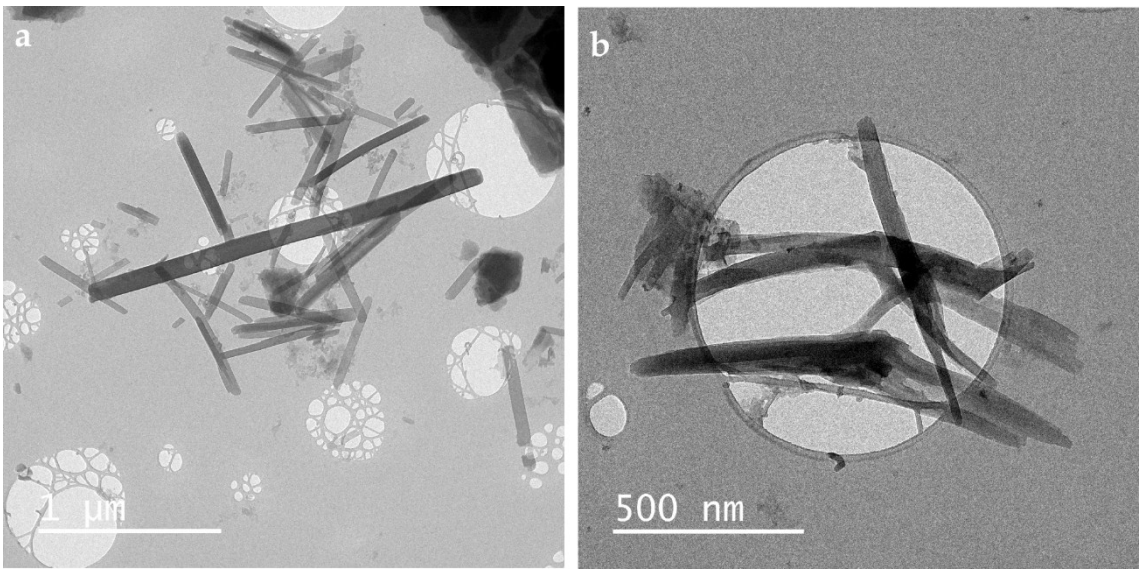

Figure S13. Particles of compound **2** (a) before and (b) after catalytic tests.

Table S1. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for compound **1**.

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.5918 (4)	0.27603 (14)	0.6625 (3)	0.097 (2)
C2	0.6283 (5)	0.26406 (17)	0.7434 (4)	0.122 (3)
H2	0.6606	0.2801	0.785	0.147*
C3	0.6088 (6)	0.22519 (15)	0.7509 (4)	0.136 (4)
H3	0.6183	0.2095	0.7999	0.164*
C4	0.5705 (4)	0.21305 (14)	0.6682 (3)	0.098 (2)
C5	0.5494 (6)	0.17315 (14)	0.6485 (4)	0.137 (4)
C6	0.4818 (5)	0.16213 (13)	0.4326 (3)	0.112 (3)
C7	0.4873 (5)	0.12057 (13)	0.4600 (4)	0.133 (4)
H7	0.4745	0.0977	0.4255	0.16*
C8	0.5595 (5)	0.14125 (15)	0.7182 (4)	0.106 (3)
C9	0.4939 (5)	0.12609 (19)	0.7419 (4)	0.120 (3)
H9	0.4424	0.1347	0.7167	0.144*
C10	0.6309 (6)	0.12942 (15)	0.7575 (4)	0.138 (4)
H10	0.6742	0.1417	0.7429	0.166*
C11	0.6456 (5)	0.10049 (17)	0.8179 (4)	0.101 (2)
H11	0.697	0.0911	0.8411	0.121*
C12	0.5787 (5)	0.08504 (14)	0.8444 (4)	0.106 (3)
C13	0.9064 (4)	0.55429 (15)	1.0924 (3)	0.0747 (15)
C14	0.5901 (6)	0.3152 (2)	0.6342 (5)	0.1399 (14)
C15	0.6343 (6)	0.3460 (2)	0.6910 (5)	0.1399 (14)
C16	0.6011 (6)	0.3699 (2)	0.7412 (5)	0.1399 (14)
H16	0.5475	0.3672	0.7416	0.168*
C17	0.6484 (6)	0.39828 (19)	0.7914 (5)	0.1399 (14)
H17	0.6272	0.414	0.8283	0.168*
C18	0.7294 (6)	0.4041 (2)	0.7882 (5)	0.1399 (14)
C19	0.7112 (6)	0.34974 (19)	0.6894 (5)	0.1399 (14)
H19	0.733	0.3336	0.6537	0.168*
C20	0.7596 (6)	0.37962 (19)	0.7445 (5)	0.1399 (14)
H20	0.8141	0.3808	0.7478	0.168*
C21	0.7737 (6)	0.43601 (17)	0.8425 (5)	0.121 (3)
C22	0.5424 (5)	0.32708 (12)	0.5606 (3)	0.125 (3)
C23	0.5256 (6)	0.36877 (15)	0.5371 (4)	0.155 (4)
H23	0.5469	0.3916	0.5684	0.186*

C24	0.5086 (5)	0.09860 (16)	0.8025 (4)	0.111 (3)
H24	0.4644	0.0875	0.8175	0.134*
N1	0.5583 (4)	0.24449 (10)	0.6149 (3)	0.119 (3)
N2	0.5	0.18703 (15)	0.5	0.085 (2)
N3	0.5	0.30178 (13)	0.5	0.088 (2)
O1	0.8415 (4)	0.54377 (10)	1.0561 (3)	0.127 (2)
O2	0.9672 (4)	0.54371 (12)	1.0716 (3)	0.1081 (16)
O3	0.7427 (3)	0.45606 (11)	0.8878 (3)	0.1148 (19)
O4	0.8431 (4)	0.43958 (18)	0.8346 (5)	0.170 (3)
O5	0.8939 (4)	0.5	0.9224 (3)	0.102 (2)
O6	0.6990 (4)	0.5	1.0164 (3)	0.0885 (18)
Ni1	0.5	0.24442 (3)	0.5	0.1003 (7)
Ni2	1	0.5	1	0.0996 (9)
Ni3	0.79685 (11)	0.5	0.97305 (8)	0.1135 (8)
O7	0.5	0.5	1	0.207 (7)*

$$U_{eq} = \frac{1}{3}\left[U_{11}\left(aa^*\right)^2 + U_{22}\left(bb^*\right)^2 + U_{33}\left(cc^*\right)^2 + 2U_{13}aca^*c^*\cos\beta\right]$$

$$U_{iso} = \exp\left[-8\pi^2 U\left(sen\theta/\lambda\right)^2\right]$$

Table S2. Atomic displacement parameters (Å^2) for compound **1**.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C1	0.151 (6)	0.056 (2)	0.058 (3)	0.006 (3)	-0.028 (3)	-0.004 (2)
C2	0.196 (8)	0.068 (3)	0.063 (4)	-0.019 (4)	-0.049 (4)	-0.001 (3)
C3	0.243 (10)	0.056 (3)	0.062 (4)	-0.005 (4)	-0.060 (5)	0.003 (2)
C4	0.147 (6)	0.057 (2)	0.059 (3)	0.003 (3)	-0.037 (3)	0.000 (2)
C5	0.242 (9)	0.042 (2)	0.071 (4)	0.009 (3)	-0.071 (5)	0.001 (2)
C6	0.213 (8)	0.037 (2)	0.052 (3)	0.000 (3)	-0.033 (4)	-0.005 (2)
C7	0.256 (10)	0.034 (2)	0.068 (4)	0.001 (3)	-0.042 (5)	-0.002 (2)
C8	0.177 (7)	0.053 (2)	0.057 (4)	0.002 (3)	-0.034 (4)	-0.001 (2)
C9	0.152 (7)	0.079 (4)	0.092 (5)	0.003 (4)	-0.046 (5)	0.022 (3)
C10	0.205 (9)	0.052 (3)	0.108 (5)	0.001 (4)	-0.058 (5)	0.020 (3)
C11	0.125 (6)	0.066 (3)	0.084 (4)	0.012 (3)	-0.028 (4)	0.010 (3)
C12	0.162 (7)	0.052 (2)	0.066 (4)	0.001 (3)	-0.048 (4)	0.003 (2)
C13	0.103 (4)	0.062 (2)	0.056 (3)	-0.001 (3)	0.012 (3)	0.000 (2)
C14	0.192 (3)	0.0772 (13)	0.118 (2)	-0.0068 (17)	-0.028 (2)	-0.0399 (14)
C15	0.192 (3)	0.0772 (13)	0.118 (2)	-0.0068 (17)	-0.028 (2)	-0.0399 (14)
C16	0.192 (3)	0.0772 (13)	0.118 (2)	-0.0068 (17)	-0.028 (2)	-0.0399 (14)
C17	0.192 (3)	0.0772 (13)	0.118 (2)	-0.0068 (17)	-0.028 (2)	-0.0399 (14)

C18	0.192 (3)	0.0772 (13)	0.118 (2)	-0.0068 (17)	-0.028 (2)	-0.0399 (14)
C19	0.192 (3)	0.0772 (13)	0.118 (2)	-0.0068 (17)	-0.028 (2)	-0.0399 (14)
C20	0.192 (3)	0.0772 (13)	0.118 (2)	-0.0068 (17)	-0.028 (2)	-0.0399 (14)
C21	0.175 (8)	0.064 (3)	0.085 (5)	0.010 (4)	-0.042 (5)	-0.034 (3)
C22	0.249 (9)	0.0321 (19)	0.050 (3)	0.010 (3)	-0.051 (4)	-0.0018 (18)
C23	0.278 (11)	0.036 (2)	0.092 (5)	-0.017 (3)	-0.069 (6)	-0.001 (2)
C24	0.163 (7)	0.067 (3)	0.078 (4)	-0.014 (3)	-0.023 (4)	0.021 (3)
N1	0.200 (6)	0.0396 (17)	0.074 (3)	0.005 (2)	-0.053 (4)	0.0029 (18)
N2	0.133 (6)	0.054 (3)	0.047 (3)	0	-0.023 (3)	0
N3	0.165 (7)	0.034 (2)	0.041 (3)	0	-0.021 (3)	0
O1	0.188 (5)	0.0561 (18)	0.091 (3)	0.002 (2)	-0.059 (3)	-0.0064 (18)
O2	0.156 (5)	0.079 (2)	0.077 (3)	-0.020 (3)	0.004 (3)	-0.030 (2)
O3	0.163 (4)	0.0635 (19)	0.081 (3)	-0.016 (2)	-0.044 (3)	-0.011 (2)
O4	0.136 (5)	0.131 (4)	0.207 (7)	-0.011 (4)	-0.026 (5)	-0.102 (5)
O5	0.138 (5)	0.055 (2)	0.076 (3)	0	-0.048 (3)	0
O6	0.112 (4)	0.052 (2)	0.080 (3)	0	-0.018 (3)	0
Ni1	0.1749 (16)	0.0369 (5)	0.0534 (8)	0	-0.0431 (9)	0
Ni2	0.168 (2)	0.0350 (6)	0.0594 (11)	0	-0.0456 (12)	0
Ni3	0.1863 (18)	0.0357 (5)	0.0710 (9)	0	-0.0630 (11)	0

$$U_{ij} = \exp(-2\pi^2[h^2(a^*)^2 U_{11} + k^2(b^*)^2 U_{22} + \ldots + 2hka^*b^* U_{12}])$$

Table S3. Geometric parameters (Å, °) for Compound **1**.

C1—N1	1.367 (6)	C16—H16	0.95
C1—C14	1.393 (9)	C17—C18	1.457 (14)
C1—C2	1.403 (7)	C17—H17	0.95
C2—C3	1.361 (8)	C18—C20	1.291 (12)
C2—H2	0.95	C18—C21	1.494 (8)
C3—C4	1.436 (7)	C19—C20	1.483 (9)
C3—H3	0.95	C19—H19	0.95
C4—N1	1.360 (7)	C20—H20	0.95
C4—C5	1.405 (7)	C21—O3	1.231 (10)
C5—C6^{i}	1.379 (7)	C21—O4	1.267 (12)
C5—C8	1.554 (8)	C22—N3	1.390 (6)
C6—N2	1.372 (6)	C22—C23	1.462 (6)
C6—C5^{i}	1.379 (7)	C23—C23^{i}	1.344 (11)
C6—C7	1.461 (6)	C23—H23	0.95
C7—C7^{i}	1.298 (11)	C24—H24	0.95
C7—H7	0.95	N1—Ni1	1.940 (4)
C8—C10	1.333 (11)	N2—C6^{i}	1.372 (6)

C8—C9	1.404 (12)	N2—Ni1	1.923 (5)
C9—C24	1.344 (8)	N3—C22^{i}	1.390 (6)
C9—H9	0.95	N3—Ni1	1.922 (5)
C10—C11	1.374 (8)	O1—Ni3	2.039 (4)
C10—H10	0.95	O2—Ni2	2.056 (5)
C11—C12	1.450 (11)	O3—Ni3	2.107 (4)
C11—H11	0.95	O5—Ni2	2.004 (5)
C12—C24	1.346 (10)	O5—Ni3	2.080 (8)
C12—C13^{ii}	1.450 (8)	O6—Ni3	2.022 (7)
C13—O1	1.212 (8)	Ni1—N1^{i}	1.940 (4)
C13—O2	1.252 (8)	Ni2—O5^{iv}	2.004 (5)
C13—C12^{iii}	1.450 (8)	Ni2—O2^{v}	2.056 (5)
C14—C22	1.368 (9)	Ni2—O2^{iv}	2.056 (5)
C14—C15	1.487 (9)	Ni2—O2^{vi}	2.056 (5)
C15—C19	1.369 (14)	Ni3—O1^{v}	2.039 (4)
C15—C16	1.384 (13)	Ni3—O3^{v}	2.107 (4)
C16—C17	1.402 (9)		
N1—C1—C14	124.2 (5)	O3—C21—C18	121.0 (10)
N1—C1—C2	111.7 (4)	O4—C21—C18	112.6 (9)
C14—C1—C2	124.1 (5)	C14—C22—N3	125.5 (4)
C3—C2—C1	107.0 (4)	C14—C22—C23	123.9 (5)
C3—C2—H2	126.5	N3—C22—C23	110.5 (4)
C1—C2—H2	126.5	C23^{i}—C23—C22	107.1 (3)
C2—C3—C4	104.8 (5)	C23^{i}—C23—H23	126.5
C2—C3—H3	127.6	C22—C23—H23	126.5
C4—C3—H3	127.6	C9—C24—C12	127.5 (9)
N1—C4—C5	126.4 (4)	C9—C24—H24	116.3
N1—C4—C3	111.6 (4)	C12—C24—H24	116.3
C5—C4—C3	122.0 (5)	C4—N1—C1	104.0 (4)
C6^{i}—C5—C4	120.3 (5)	C4—N1—Ni1	127.2 (3)
C6^{i}—C5—C8	119.4 (4)	C1—N1—Ni1	128.7 (3)
C4—C5—C8	120.3 (5)	C6^{i}—N2—C6	105.1 (5)
N2—C6—C5^{i}	126.6 (4)	C6^{i}—N2—Ni1	127.4 (3)
N2—C6—C7	109.9 (4)	C6—N2—Ni1	127.4 (3)
C5^{i}—C6—C7	122.7 (4)	C22—N3—C22^{i}	104.8 (5)
C7^{i}—C7—C6	107.5 (3)	C22—N3—Ni1	127.6 (2)
C7^{i}—C7—H7	126.3	C22^{i}—N3—Ni1	127.6 (2)

C6—C7—H7	126.3	C13—O1—Ni3	135.4 (5)
C10—C8—C9	120.0 (6)	C13—O2—Ni2	137.6 (4)
C10—C8—C5	119.8 (9)	C21—O3—Ni3	126.6 (6)
C9—C8—C5	120.2 (7)	Ni2—O5—Ni3	118.2 (3)
C24—C9—C8	115.7 (7)	N3—Ni1—N2	180.0 (1)
C24—C9—H9	122.1	N3—Ni1—N1^{i}	89.93 (10)
C8—C9—H9	122.1	N2—Ni1—N1^{i}	90.07 (10)
C8—C10—C11	124.1 (9)	N3—Ni1—N1	89.93 (10)
C8—C10—H10	118	N2—Ni1—N1	90.07 (10)
C11—C10—H10	118	N1^{i}—Ni1—N1	179.9 (2)
C10—C11—C12	116.6 (7)	O5^{iv}—Ni2—O5	180.0 (1)
C10—C11—H11	121.7	O5^{iv}—Ni2—O2^{v}	88.6 (2)
C12—C11—H11	121.7	O5—Ni2—O2^{v}	91.4 (2)
C24—C12—C13^{ii}	126.9 (8)	O5^{iv}—Ni2—O2^{iv}	91.4 (2)
C24—C12—C11	115.9 (6)	O5—Ni2—O2^{iv}	88.6 (2)
C13^{ii}—C12—C11	117.0 (6)	O2^{v}—Ni2—O2^{iv}	89.1 (3)
O1—C13—O2	123.4 (6)	O5^{iv}—Ni2—O2	88.6 (2)
O1—C13—C12^{iii}	123.5 (8)	O5—Ni2—O2	91.4 (2)
O2—C13—C12^{iii}	112.4 (6)	O2^{v}—Ni2—O2	90.9 (3)
C22—C14—C1	122.3 (6)	O2^{iv}—Ni2—O2	180.0 (2)
C22—C14—C15	118.9 (6)	O5^{iv}—Ni2—O2^{vi}	91.4 (2)
C1—C14—C15	118.3 (7)	O5—Ni2—O2^{vi}	88.6 (2)
C19—C15—C16	121.6 (7)	O2^{v}—Ni2—O2^{vi}	180.0 (2)
C19—C15—C14	115.1 (9)	O2^{iv}—Ni2—O2^{vi}	90.9 (3)
C16—C15—C14	123.3 (10)	O2—Ni2—O2^{vi}	89.1 (3)
C15—C16—C17	118.3 (10)	O6—Ni3—O1	89.1 (2)
C15—C16—H16	120.9	O6—Ni3—O1^{v}	89.1 (2)
C17—C16—H16	120.9	O1—Ni3—O1^{v}	92.0 (2)
C16—C17—C18	121.2 (9)	O6—Ni3—O5	177.1 (2)
C16—C17—H17	119.4	O1—Ni3—O5	93.0 (2)
C18—C17—H17	119.4	O1^{v}—Ni3—O5	93.0 (2)
C20—C18—C17	118.5 (7)	O6—Ni3—O3	87.2 (2)
C20—C18—C21	124.6 (11)	O1—Ni3—O3	175.9 (3)
C17—C18—C21	116.7 (9)	O1^{v}—Ni3—O3	89.58 (14)
C15—C19—C20	118.5 (9)	O5—Ni3—O3	90.7 (2)
C15—C19—H19	120.7	O6—Ni3—O3^{v}	87.2 (2)
C20—C19—H19	120.7	O1—Ni3—O3^{v}	89.58 (14)
C18—C20—C19	121.4 (10)	O1^{v}—Ni3—O3^{v}	175.9 (3)

C18—C20—H20	119.3	O5—Ni3—O3^{v}	90.7 (2)
C19—C20—H20	119.3	O3—Ni3—O3^{v}	88.6 (2)
O3—C21—O4	126.3 (6)		

Symmetry codes: (i) -*x*+1, *y*, -*z*+1; (ii) -*x*+3/2, *y*-1/2, -*z*+2; (iii) -*x*+3/2, *y*+1/2, -*z*+2; (iv) -*x*+2, -*y*+1, -*z*+2; (v) *x*, -*y*+1, *z*; (vi) -*x*+2, *y*, -*z*+2.

Table S4. Angles (°) and distances (Å) for Ni1, Ni2 and Ni3 in compound **1** (distances in bold).

Compound **1**

Ni1	**N1^{i}**	**N3**	**N2**	**N1**
N1	179.9 (2)	89.9 (1)	90.1 (1)	**1.940 (4)**
N2	90.1 (1)	180.0 (1)	**1.923 (5)**	
N3	89.9 (1)	**1.922 (5)**		
N1^{i}	**1.940 (4)**			

Ni2. NiO_6 octahedra

Compound **1**

Ni2	**O2^{vi}**	**O2^{v}**	**O2^{iv}**	**O2**	**O5^{iV}**	**O5**
O5	88.6(2)	91.4(2)	88.6(2)	91.4(2)	180.0(10)	**2.004(5)**
O5^{iv}	91.4(2)	88.6(2)	91.4(2)	88.6(2)	**2.004(5)**	
O2	89.1(3)	90.9(3)	180.0(2)	**2.056(5)**		
O2^{iv}	90.9(3)	89.1(3)	**2.056(5)**			
O2^{v}	180.0(16)	**2.056(5)**				
O2^{vi}	**2.056(5)**					

Ni3. NiO_6 octahedra

Compound **1**

Ni3	**O6**	**O5**	**O1^{v}**	**O1**	**O3^{v}**	**O3**
O3	87.2(2)	90.7(2)	89.58(14)	175.9(3)	88.6(2)	**2.107(4)**
O3^{v}	87.2(2)	90.7(2)	175.9(3)	89.58(14)	**2.107(4)**	
O1	89.1(2)	93.0(2)	92.0(2)	**2.039(4)**		
O1^{v}	89.1(2)	93.0(2)	**2.039(4)**			
O5	177.07(19)	**2.080(8)**				
O6	**2.022(7)**					

Symetry codes: (i) −*x*+1, *y*, −*z*+1; (ii) −*x*+3/2, *y*−1/2, −*z*+2; (iii) −*x*+3/2, *y*+1/2, −*z*+2; (iv) −*x*+2, −*y*+1, −*z*+2; (v) *x*, −*y*+1, *z*; (vi) −*x*+2, *y*, −*z*+2.