

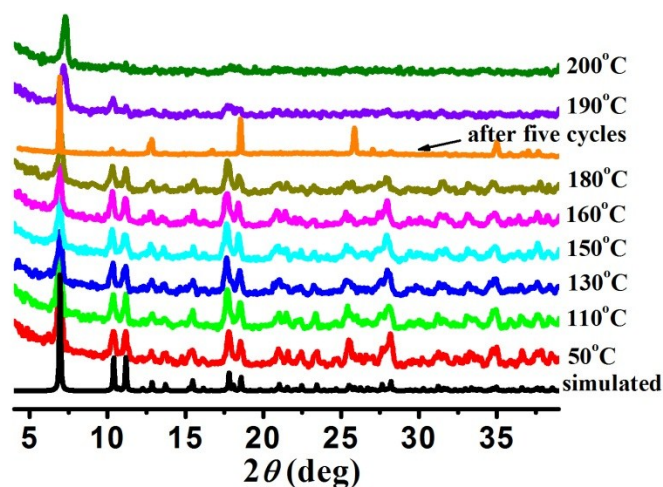
Electronic Supporting Information (ESI) for *Dalton Transactions*

## Solvent-Free Heterogeneous Catalysis for Cyanosilylation in a Dynamic Cobalt-MOF

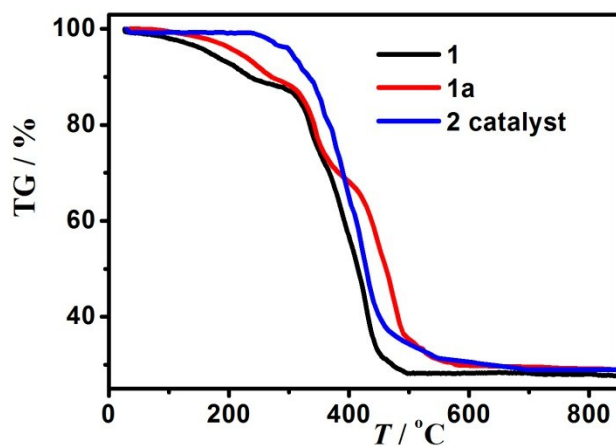
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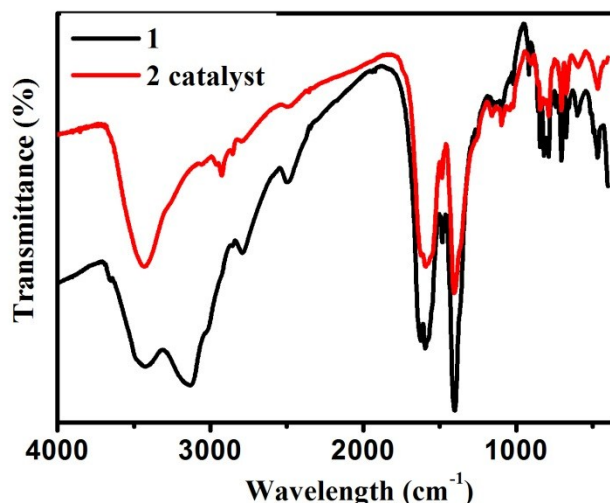
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**Figure S1.** The *in situ* temperature-dependent PXRD patterns plots of **1** and that of after five catalytic cycles for catalyst **2**.



**Figure S2.** TGA plots of **1**, **1a** and catalyst **2**.



**Figure S3.** IR spectra plots of the pristine complex **1** and catalyst **2**.

**Table S1.** Bond lengths [ $\text{\AA}$ ] and bond angles [deg] for **1**, **1a** and **2**.

Compound	<b>1</b>	<b>1a</b>	<b>2</b>
Co(1)-O(9)	2.0386(14)	2.0222(13)	2.023(4)
Co(1)-O(8b)	2.0503(15)	2.0171(15)	2.003(4)
Co(1)-O(5a)	2.0952(15)	2.0982(13)	2.056(4)
Co(1)-O(9c)	2.1072(14)	2.0689(12)	2.058(4)
Co(1)-O(1)	2.1075(15)	2.0643(13)	2.039(4)
Co(1)-O(1W)	2.2670(19)		
Co(2)-O(9)	2.0243(14)	2.0466(12)	2.046(4)
Co(2)-O(2)	2.0753(15)	2.0761(14)	2.047(4)
Co(2)-O(3d)	2.0795(16)	2.0737(16)	2.050(4)
Co(2)-O(7e)	2.1071(15)	2.0985(14)	2.081(4)
Co(2)-O(6a)	2.1435(15)	2.1529(12)	2.129(4)
Co(2)-O(2W)	2.1837(17)	2.1617(16)	2.210(6)
O(9)-Co(1)-O(8c)	176.63(6)	168.89(5)	165.1(2)
O(9)-Co(1)-O(5a)	92.03(6)	90.27(5)	90.10(17)
O(8c)-Co(1)-O(5a)	90.51(6)	87.98(6)	87.70(18)
O(9)-Co(1)-O(9b)	81.77(6)	81.69(6)	81.08(18)
O(8c)-Co(1)-O(9b)	95.83(6)	99.50(5)	100.17(18)
O(5a)-Co(1)-O(9b)	172.86(6)	171.66(5)	170.80(16)

O(9)-Co(1)-O(1)	97.79(6)	103.53(5)	105.11(18)
O(8c)-Co(1)-O(1)	84.46(6)	87.48(6)	89.7(2)
O(5a)-Co(1)-O(1)	89.08(6)	91.25(5)	91.94(18)
O(9b)-Co(1)-O(1)	88.26(6)	92.75(5)	92.85(18)
O(1w)-Co(1)-O(9b)	102.39(6)		
O(1w)-Co(1)-O(8c)	87.67(7)		
O(1w)-Co(1)-O(9)	90.54(7)		
O(1w)-Co(1)-O(5a)	81.10(6)		
O(1w)-Co(1)-O(1)	167.36(7)		
O(9)-Co(2)-O(2)	95.10(6)	96.56(6)	99.69(19)
O(9)-Co(2)-O(3d)	98.37(6)	95.43(5)	96.71(18)
O(2)-Co(2)-O(3d)	166.28(7)	167.18(6)	162.95(19)
O(9)-Co(2)-O(7e)	88.01(6)	89.45(5)	90.39(17)
O(2)-Co(2)-O(7e)	91.03(7)	89.04(18)	87.11(19)
O(3d)-Co(2)-O(7e)	86.86(7)	87.77(6)	88.15(19)
O(9)-Co(2)-O(6a)	100.89(6)	98.73(5)	99.80(16)
O(2)-Co(2)-O(6a)	82.43(6)	84.00(5)	84.41(17)
O(3d)-Co(2)-O(6a)	97.51(6)	98.66(5)	97.40(17)
O(7e)-Co(2)-O(6a)	169.35(6)	168.99(5)	167.70(17)
O(2w)-Co(2)-O(2)	82.31(7)	82.76(6)	80.3(2)
O(2w)-Co(2)-O(3d)	83.97(7)	84.81(6)	82.9(2)
O(2w)-Co(2)-O(6a)	88.30(6)	87.61(5)	85.9(2)
O(2w)-Co(2)-O(7e)	82.48(6)	84.10(6)	83.9(2)
O(2w)-Co(2)-O(9)	170.08(7)	173.53(5)	174.3(2)
Co(2)-O(9)-Co(1)	112.60(6)	109.62(5)	107.2(2)
Co(2)-O(9)-Co(1b)	116.94(7)	115.66(6)	114.8(2)
Co(1)-O(9)-Co(1b)	98.23(6)	98.31(6)	98.92(17)

Symmetry codes: (a)  $-x, -1/2+y, 1/2-z$ ; (b)  $1-x, 2-y, 1-z$ ; (c)  $-x, 2-y, 1-z$ ; (d)  $1-x, -1/2+y, 1/2-z$ ; (e)  $1+x, y, z$ .

**Table S2.** Optimization of conditions for catalyst **2** and contrast test of **1** and **1a**.

Entry	Cat.(mol %)	TMSCN	Temp.(°C)	Conv.(%) <sup>a</sup>
1	0	2eq	40	36.6
2	1	2eq	40	65.2
3	1	2eq	r.t.	76.6
4	0.5	2eq	r.t.	96.5
<b>5</b>	<b>0.1</b>	<b>2eq</b>	<b>r.t.</b>	<b>98.5</b>
6	0.1(hydrated <b>1</b> )	2eq	r.t.	38.2
7	0.1 ( <b>1a</b> )	2eq	r.t.	40.3

<sup>a</sup> Determined by GC based on the carbonyl substrate.

**Table S3.** Bond lengths [Å] and angles [deg] of cobalt cluster for **1**, **1a** and **2**.

bond / angle	<b>1</b>	<b>1a</b>	<b>2</b>
Co(1)-Co(1b)	3.1350(1)	3.1279(1)	3.1005(3)
Co(1)-Co(2)	3.3803(1)	3.3296(2)	3.2751(2)
Co(1)-Co(2a)	3.5218(1)	3.5051(2)	3.4578(3)
Co(1)-O(9)-Co(1b)	98.46(6)	98.79(17)	99.14(19)
Co(2)-O(9)-Co(1)	112.92(6)	109.93(19)	107.1(2)
Co(2)-O(9)-Co(1b)	117.27(7)	116.8(2)	115.1(2)