

## Electronic Supplementary Material

### **Reaction of sodium 2-(2-(2,4-dioxopentan-3-ylidene)hydrazinyl) benzenesulfonate with ethylenediamine on Cu(II) and Ni(II) centres: efficient Cu(II) homogeneous catalysts for cyanosilylation of aldehydes**

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## 1. X-ray analyses

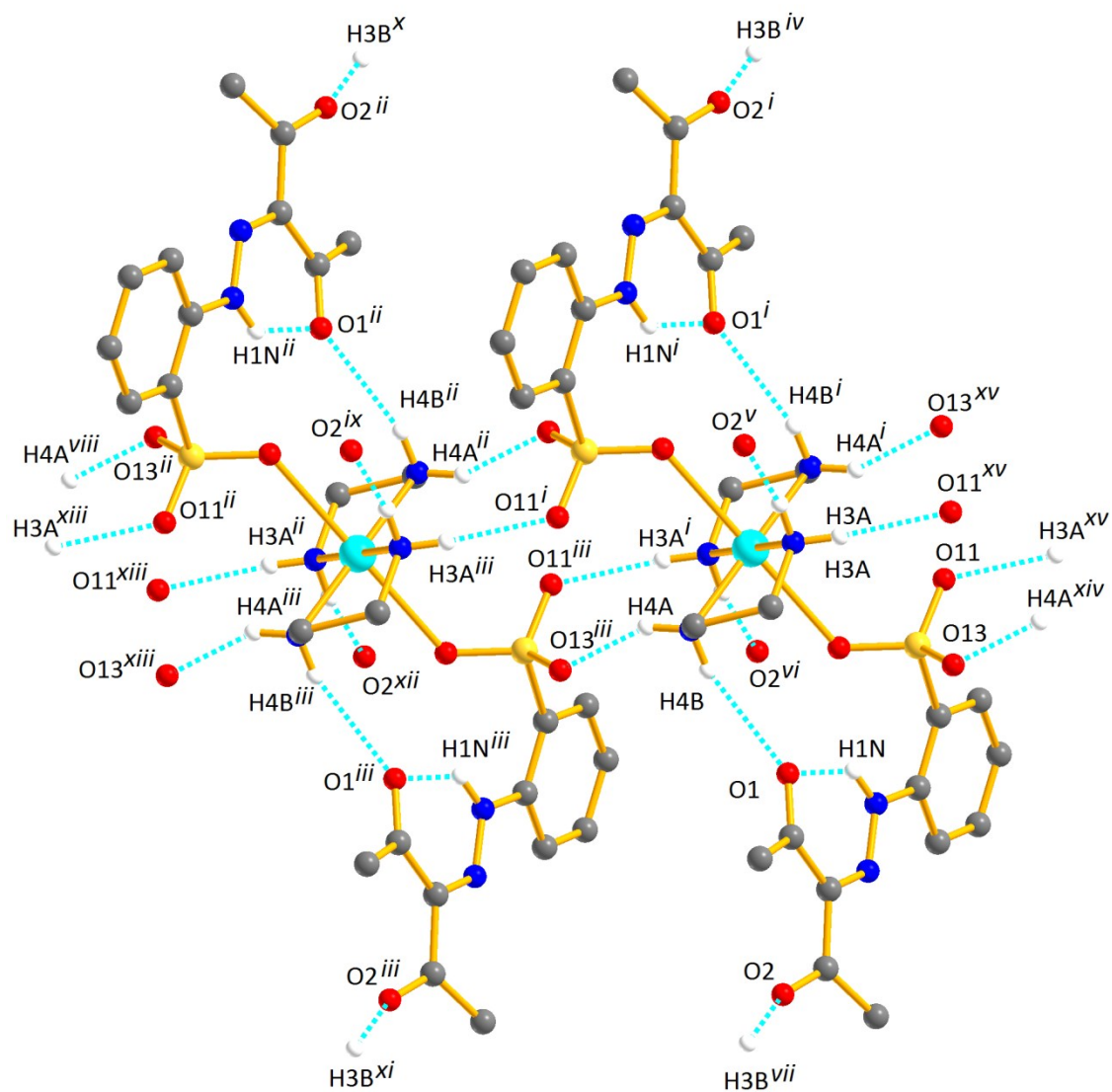
**Table S1.** Crystallographic data and structure refinement details for **1–3**.

	<b>1</b>	<b>2</b>	<b>3</b>
Empirical formula	C <sub>26</sub> H <sub>38</sub> CuN <sub>8</sub> O <sub>10</sub> S <sub>2</sub>	C <sub>30</sub> H <sub>64</sub> N <sub>10</sub> NiO <sub>17</sub> S <sub>2</sub>	C <sub>13</sub> H <sub>16</sub> CuN <sub>4</sub> O <sub>4</sub> S
fw	750.30	959.74	387.90
Temperature (K)	296(2)	293(2)	150(2)
Cryst. Syst.	Monoclinic	Triclinic	Triclinic
Space group	<i>P</i> 21/ <i>c</i>	<i>P</i> -1	<i>P</i> -1
<i>a</i> (Å)	7.4179(4)	11.5824(7)	5.1923(10)
<i>b</i> (Å)	20.0875(12)	13.5921(7)	8.6543(16)
<i>c</i> (Å)	11.2037(7)	14.6115(9)	16.704(3)
$\alpha$ , °	90	72.171(3)	81.729(5)
$\beta$ , °	106.071(2)	75.626(4)	88.354(6)
$\gamma$ , °	90	85.530(3)	78.606(6)
<i>V</i> (Å <sup>3</sup> )	1604.19(16)	2121.3(2)	728.2(2)
<i>Z</i>	2	2	2
$\rho_{\text{calc}}$ (g cm <sup>-3</sup> )	1.553	1.503	1.769
$\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )	1.465	0.638	1.670
<i>F</i> (000)	782	1020	398
Rfl.total /ind./unique	16062/ 3597/ 3035	39682/ 7996/ 4331	20570/ 3657/ 2708
<i>R</i> <sub>int</sub>	0.0299	0.1097	0.0749
<i>R</i> 1 <sup>a</sup> ( <i>I</i> ≥ 2 $\sigma$ )	0.0372	0.0604	0.0407
w <i>R</i> 2 <sup>b</sup> ( <i>I</i> ≥ 2 $\sigma$ )	0.0971	0.1469	0.0826
GOOF	1.059	1.033	0.995

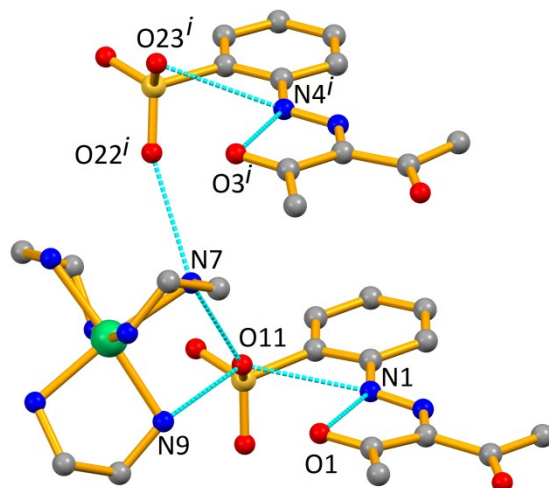
$$^a RI = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}.$$

**Table S2.** Selected bond distances (Å) and angles (°) for **1–3**.

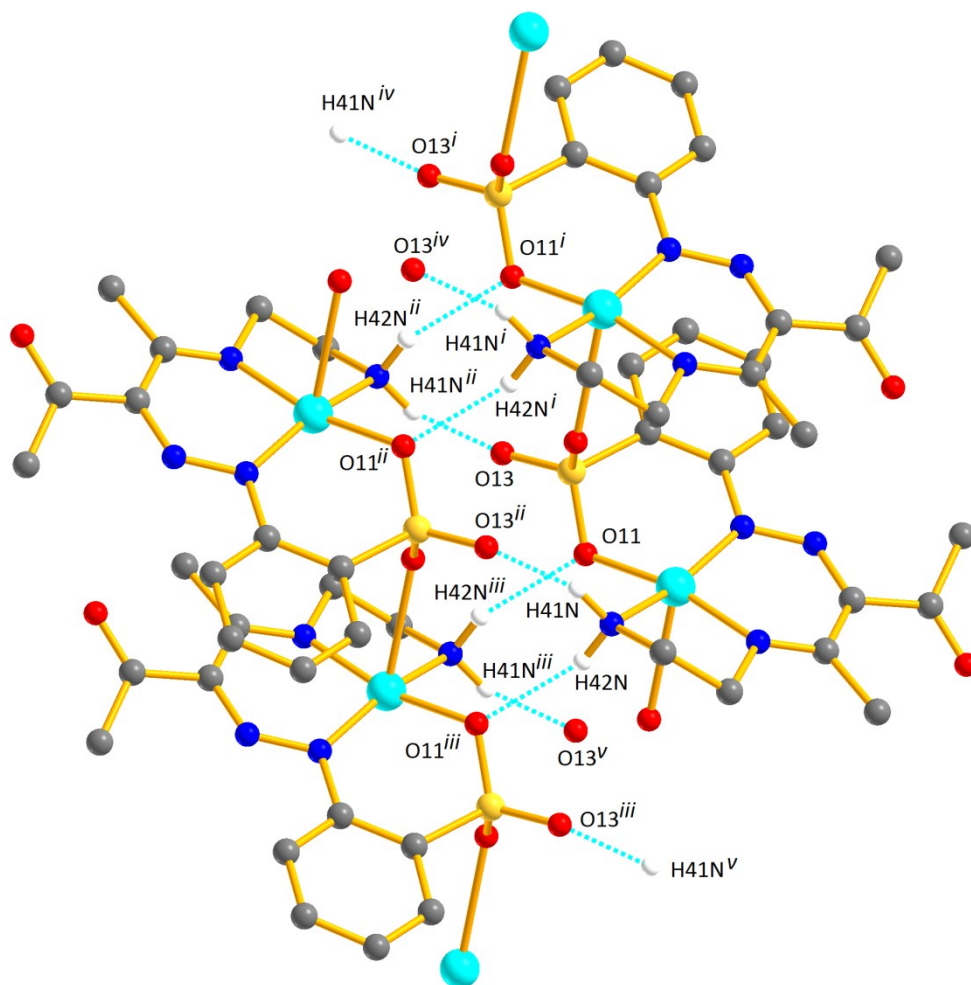
<b>1</b>		<b>2</b>		<b>3</b>	
C8 O1	1.228(3)	C6 N1	1.388(8)	C6 N1	1.435(3)
C10 O2	1.212(3)	C7 N2	1.318(8)	C7 N2	1.321(4)
C12 N4	1.466(4)	C8 O1	1.233(10)	C8 O1	1.223(4)
C13 N3	1.480(4)	C10 O2	1.200(9)	C10 N3	1.294(4)
N1 N2	1.301(3)	C17 N4	1.406(7)	C12 N3	1.477(3)
N3 Cu1	2.011(2)	C18 N3	1.308(8)	C13 N4	1.481(4)
N4 Cu1	2.012(2)	C19 O3	1.235(8)	N1 N2	1.316(3)
Cu1 N3	2.011(2)	C21 O4	1.222(8)	N1 Cu1	1.928(2)
Cu1 N4	2.013(2)	N1 N2	1.308(7)	N3 Cu1	1.933(2)
N2 N1 H1N	119(2)	N3 N4	1.315(7)	N4 Cu1	1.986(2)
N3 Cu1 N3	180.00(11)	N5 Ni1	2.140(8)	O11 Cu1	1.9671(18)
N3 Cu1 N4	85.00(9)	N6 Ni1	2.125(9)	O12Cu1	2.528
N3 Cu1 N4	95.00(9)	N7 Ni1	2.137(7)	N1 Cu1 N3	93.65(10)
N3 Cu1 N4	95.00(9)	N8 Ni1	2.135(8)	N1Cu1 O11	92.05(9)
N3 Cu1 N4	85.00(9)	N9 Ni1	2.146(8)	N3Cu1 O11	166.71(9)
N4 Cu1 N4	180.0	N10 Ni1	2.122(8)	N1 Cu1 N4	163.76(10)
		N10Ni1 N6	92.2(4)	N3 Cu1 N4	86.25(10)
		N10Ni1 N8	94.6(4)	O11Cu1 N4	91.61(9)
		N6 Ni1 N8	171.5(3)		
		N10Ni1 N7	172.8(4)		
		N6 Ni1 N7	91.9(3)		
		N8 Ni1 N7	82.0(3)		
		N10Ni1 N5	94.4(4)		
		N6 Ni1 N5	81.2(4)		
		N8 Ni1 N5	93.1(3)		
		N7 Ni1 N5	92.1(3)		
		N10Ni1 N9	82.7(4)		
		N6 Ni1 N9	94.7(4)		
		N8 Ni1 N9	91.3(3)		
		N7 Ni1 N9	91.0(3)		
		N5 Ni1 N9	175.0(3)		



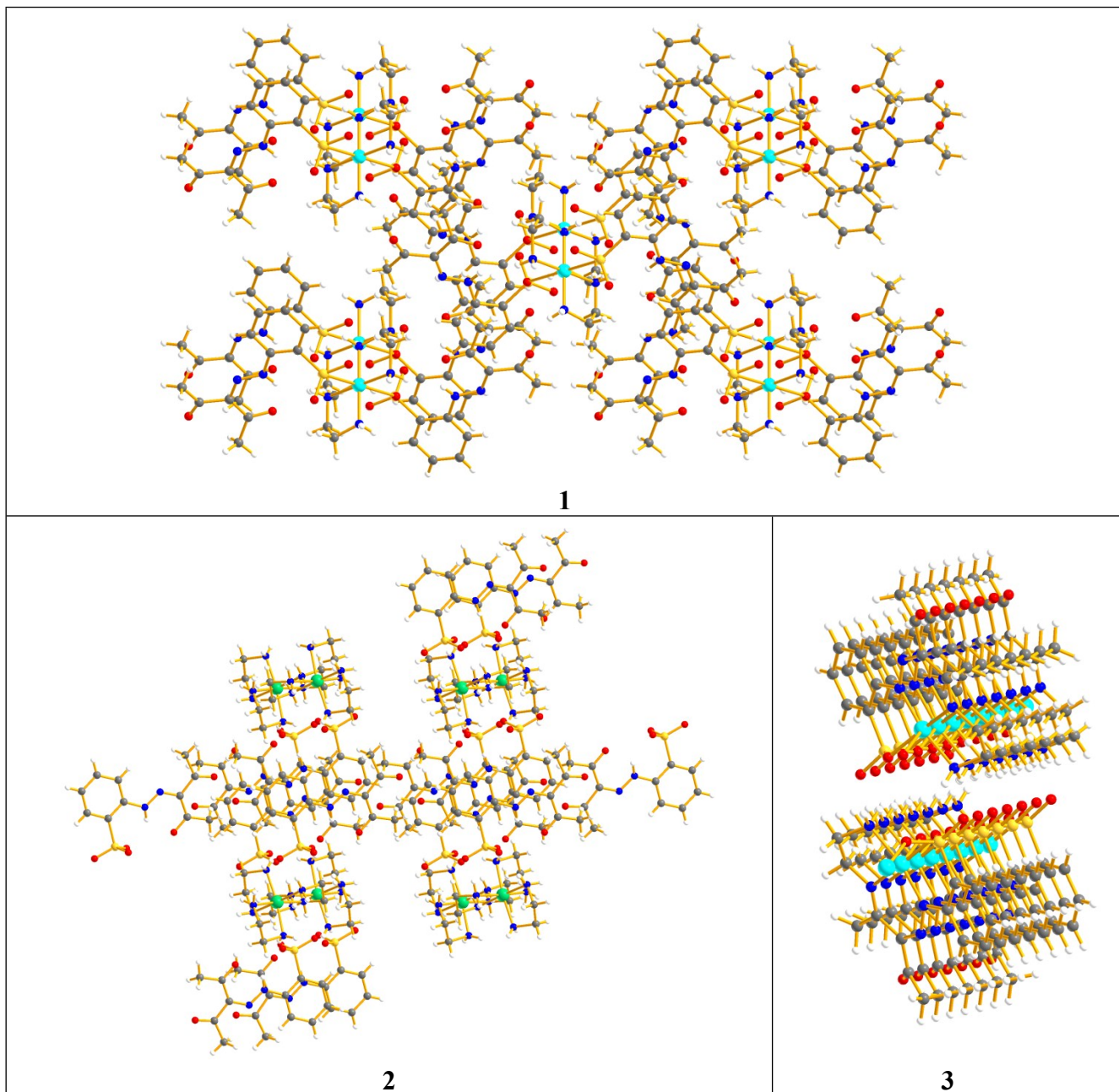
**Figure S1.** H-bond interactions (in dash light blue colour) in compound **1**. H-atoms not involved in contact interactions were omitted for clarity. Symmetry codes to generate equivalent atoms: *i*)  $-x, -y, -z$ ; *ii*)  $-1-x, -y, -z$ ; *iii*)  $-1+x, y, z$ ; *iv*)  $x, -1/2-y, 1/2+z$ ; *v*)  $-x, -1/2+y, -1/2-z$ ; *vi*)  $x, 1/2-y, 1/2+z$ ; *vii*)  $-x, 1/2+y, -1/2-z$ ; *viii*)  $-2-x, -y, -z$ ; *ix*)  $-1-x, -1/2+y, -1/2-z$ ; *x*)  $-1+x, -1/2-y, 1/2+z$ ; *xi*)  $-1-x, 1/2+y, -1/2-z$ ; *xii*)  $-1+x, 1/2-y, 1/2+z$ ; *xiii*)  $-2+x, y, z$ ; *xiv*)  $1+x, y, z$ ; *xv*)  $1-x, -y, -z$ . Hydrogen bonding distances (Å) and angles (°) [d(D...A), ∠(D–H...A)]: N1–H1N...O1 2.579(3), 133(2); N1–H1N...O12 2.970(3), 128.6(19); N3–H3A...O11 3.099(3), 158(3); N3–H3B...O2 2.953(3), 153(2); N4–H4A...O13 3.044(3), 147(3); N4–H4B...O1 2.61(3), 136(2).



**Figure S2.** The asymmetric unit of **2** showing the H-bond interactions in dash light blue colour. Symmetry codes to generate equivalent atoms: *i*) 2-x,1-y,1-z. Hydrogen bonding distances (Å) and angles (°) [d(D...A), ∠(D-H...A)]: N1-H1N...O1 2.583(6), 136(5); N1-H1N...O11 2.825(5), 126(5); N4-H4N...O3 2.566(5), 134(5); N4-H4N...O23 2.924(4), 124(5); N7-H7A...O11 3.039(6), 152; N7-H7B...O22 2.975(7), 157; N9-H9D...O11 3.027(7), 150.



**Figure S3.** H-bond interactions (in dash light blue colour) in compound **3**. H-atoms not involved in contact interactions were omitted for clarity. Symmetry codes to generate equivalent atoms: *i*) - 1+x,y,z; *ii*) -x,1-y,1-z; *iii*) 1-x,1-y,1-z; *iv*) -1-x,1-y,1-z; *v*) 1+x,y,z. Hydrogen bonding distances (Å) and angles (°) [d(D...A), ∠(D-H...A)]: N4-H41N...O13 3.002(3), 161(3); N4-H42N...O11 2.975(3), 151(2).



**Figure S4.** Packing diagrams for compounds 1–3, viewed perpendicular to the bc plane (1), down the crystallographic *c* axis (2), or in a general scenery (3).

## 2. Calculation of aldehyde cyanosilylation conversion values by $^1\text{H}$ NMR analysis of crude products.

Two examples are provided for conversion calculation of cyanosilylation reaction of two different aldehydes:

a) Table1, entry 16

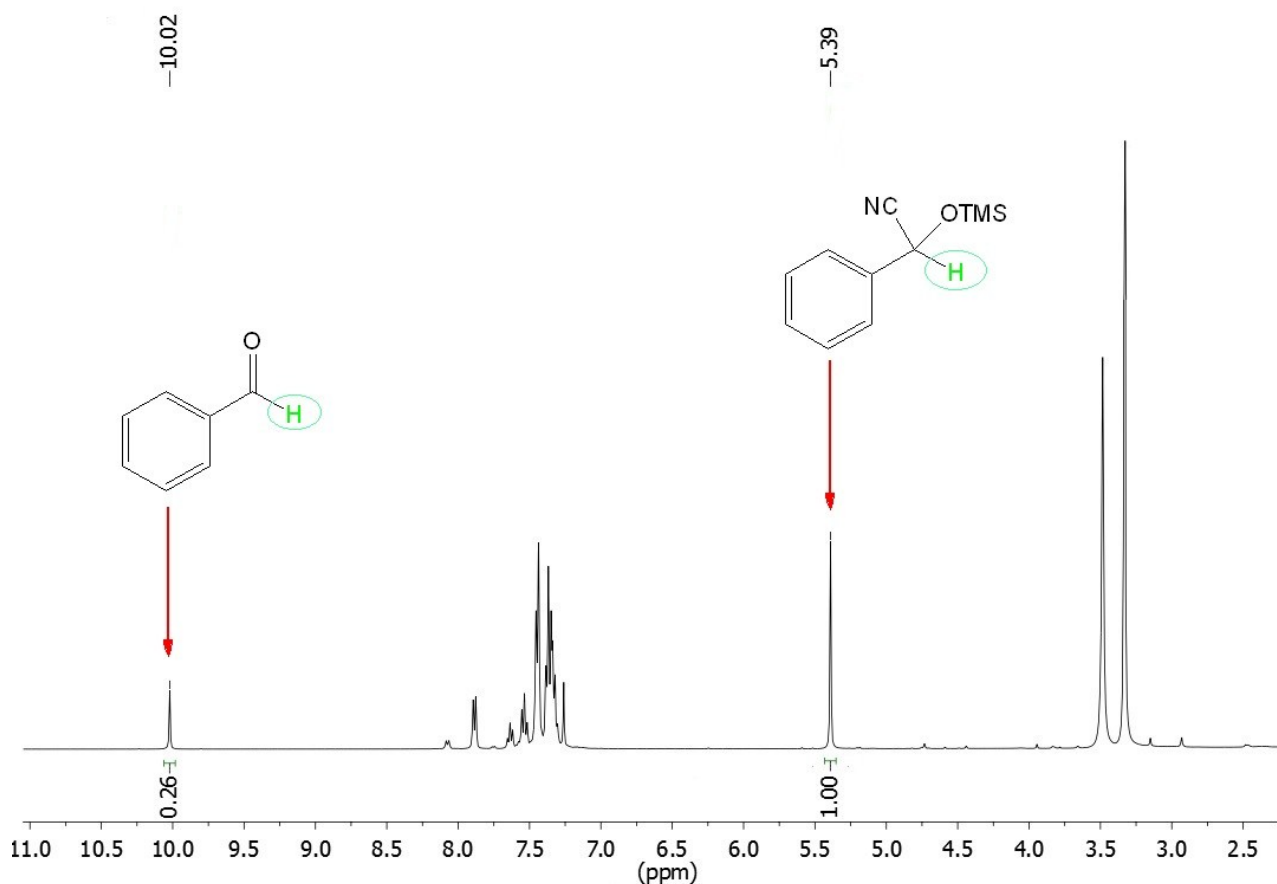
The  $^1\text{H}$  NMR spectrum of crude products from benzaldehyde cyanosilylation under the conditions described at Table1, entry 16, is displayed in Figure S5.

Conversion is calculated by dividing characteristic peak area of the corresponding product by sum of characteristic peak areas of substrate and corresponding product.

$$\text{Conversion (\%)} = [a/(a + b)] \times 100\%$$

a: characteristic peak area of the corresponding product.

b: characteristic peak area of substrate.



**Figure S5.** <sup>1</sup>H NMR spectrum of crude products from benzaldehyde cyanosilylation with TMSCN using 5 mol% of catalyst **3** (Table 1, Entry 16).

Characteristic peak area of 2-phenyl-2-((trimethylsilyloxy)acetonitrile) = 1

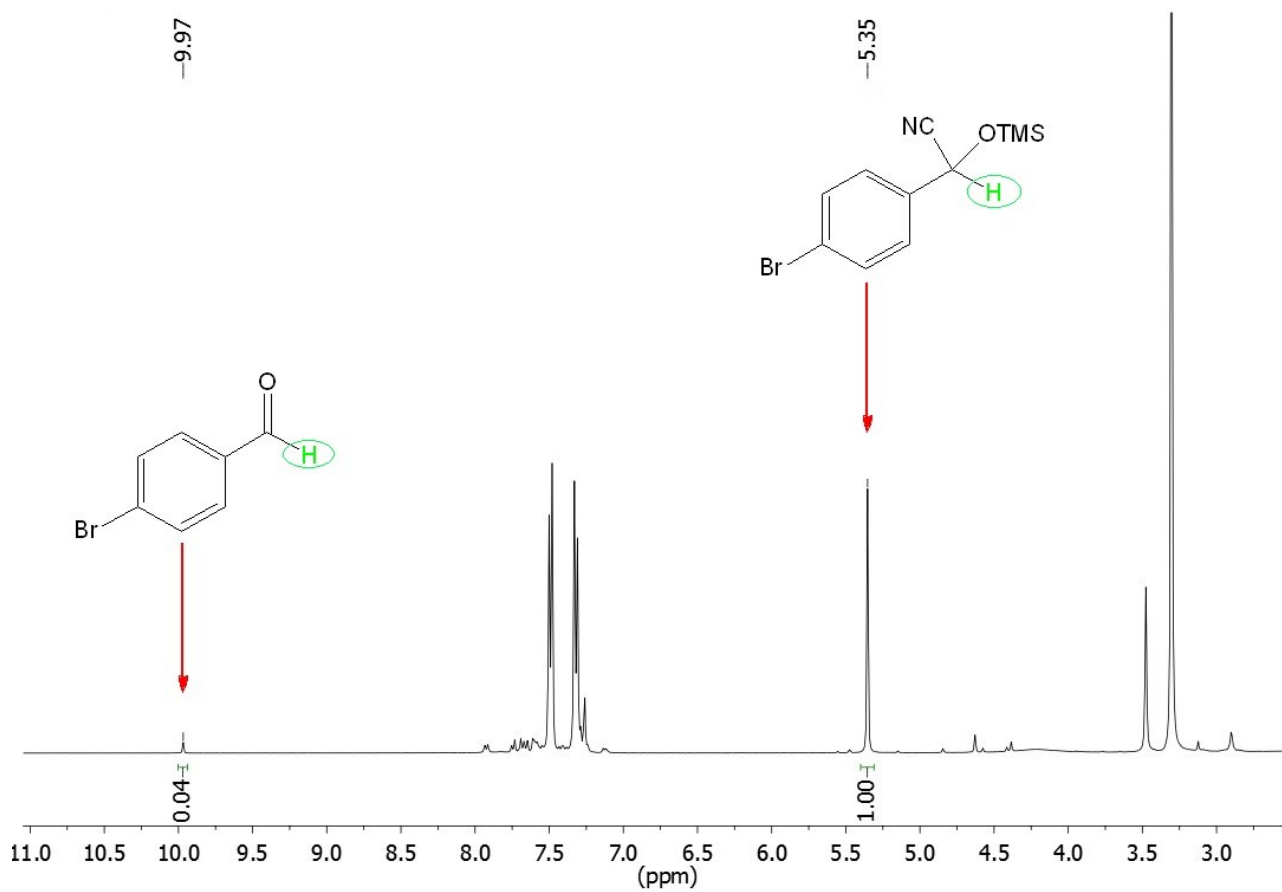
Characteristic peak area of benzaldehyde = 0.26

Conversion =  $[1/(1+0.26)] \times 100 = 79.3\%$

b) Table 2, entry 4

The <sup>1</sup>H NMR spectrum of crude products from 4-bromobenzaldehyde cyanosilylation under the conditions described at Table 2, is displayed in Figure S6.





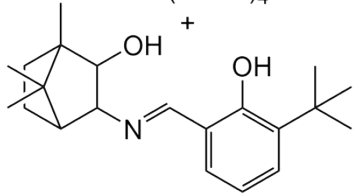
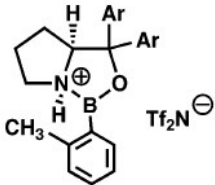
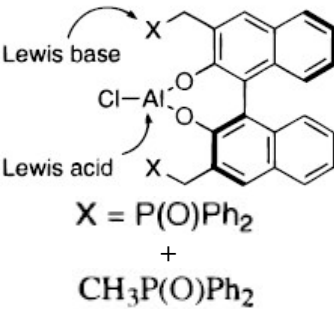
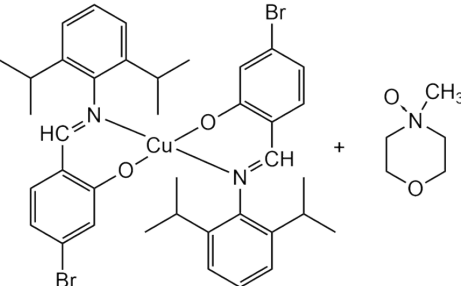
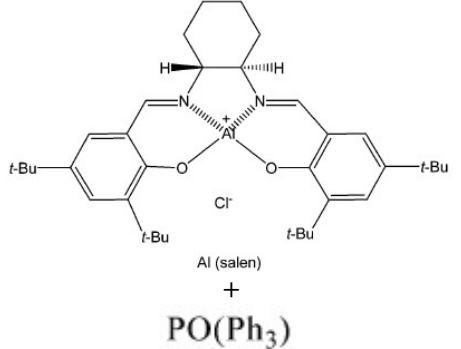
**Figure S6.**  $^1\text{H}$  NMR spectrum of crude products from 4-bromobenzaldehyde cyanosilylation with TMSCN using 5 mol% of catalyst **3** (Table 2, Entry 4).

Characteristic peak area of corresponding cyanohydrin trimethylsilyl ether = 1

Characteristic peak area of 4-bromobenzaldehyde = 0.04

Conversion =  $[1/(1+0.04)] \times 100 = 96.2\%$

**Table S3.** Comparison of various homogeneous catalysts in the cyanosilylation of benzaldehyde

Catalyst	Reaction Conditions			Conversion (%)	Ref.
	Solvent	Time (h)	Temperature °C		
<b>3</b>	MeOH	16	25	93	<b>This study</b>
$\text{Ti}(\text{O}-i\text{Pr})_4$ 	$\text{CH}_2\text{Cl}_2$	48	-20	86	9a
$\text{Cu}(\text{II})$ - <i>S</i> -4,4'-bis(4-carboxyphenyl)-2,2'-bis(diphenylphosphinoyl)-1,1'-binaphthyl	n-Pentane	48	40	27.1	9b
 Ar = 3,5-dimethylphenyl (mexyl)	Toluene	40	0	94	9c
 X = $\text{P}(\text{O})\text{Ph}_2$ + $\text{CH}_3\text{P}(\text{O})\text{Ph}_2$	$\text{CH}_2\text{Cl}_2$	96	-40	98	9d
	THF	2	25	80	9e
 Al (salen) + $\text{PO}(\text{Ph}_3)$	$\text{CH}_2\text{Cl}_2$	18	-50	95	6a