Electronic Supplementary Information (ESI)

Two metal-organic frameworks based on pyridyl–tricarboxylate ligand as size-selective catalysts for solvent-free cyanosilylation reaction

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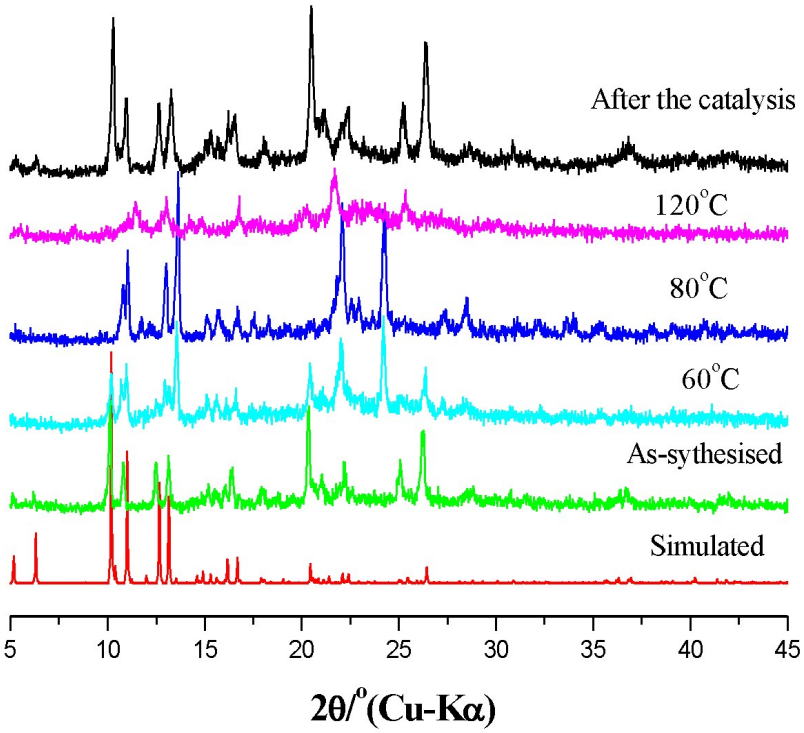

Fig. S1 Simulated and experimental X-ray powder diffraction patterns for **FJI-Y7**.

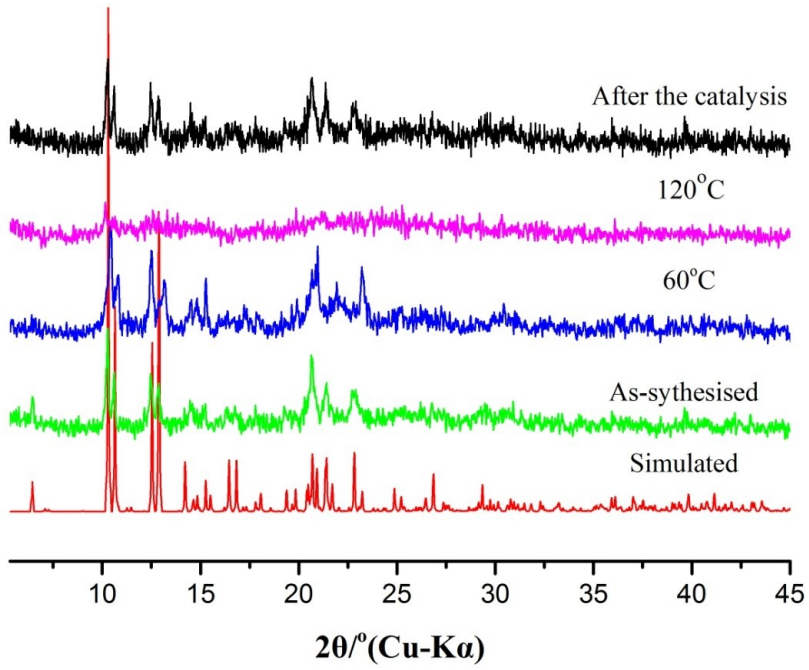

Fig. S2 Simulated and experimental X-ray powder diffraction patterns for **FJI-Y8**.

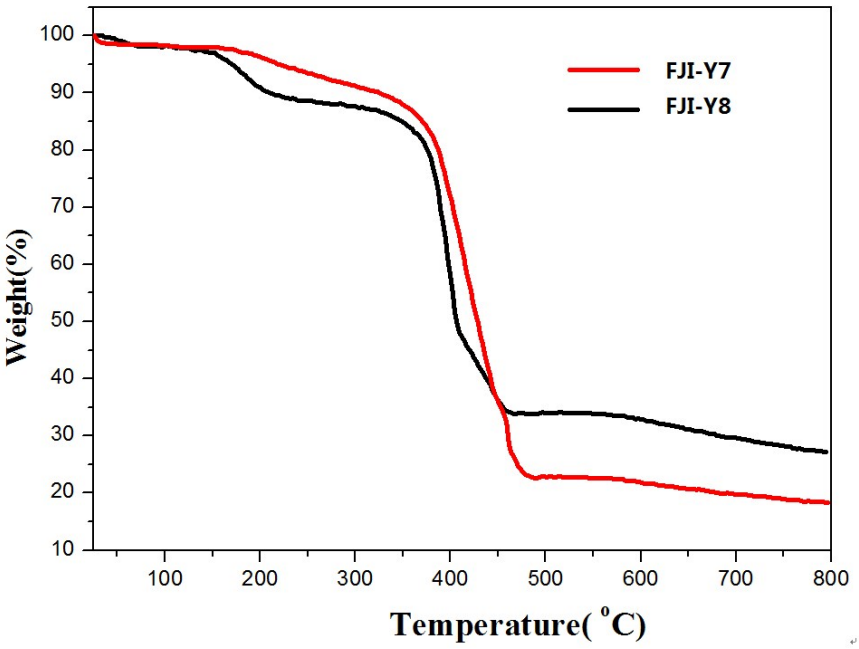

Fig. S3 TGA curves of **FJI-Y7** and **FJI-Y8**.

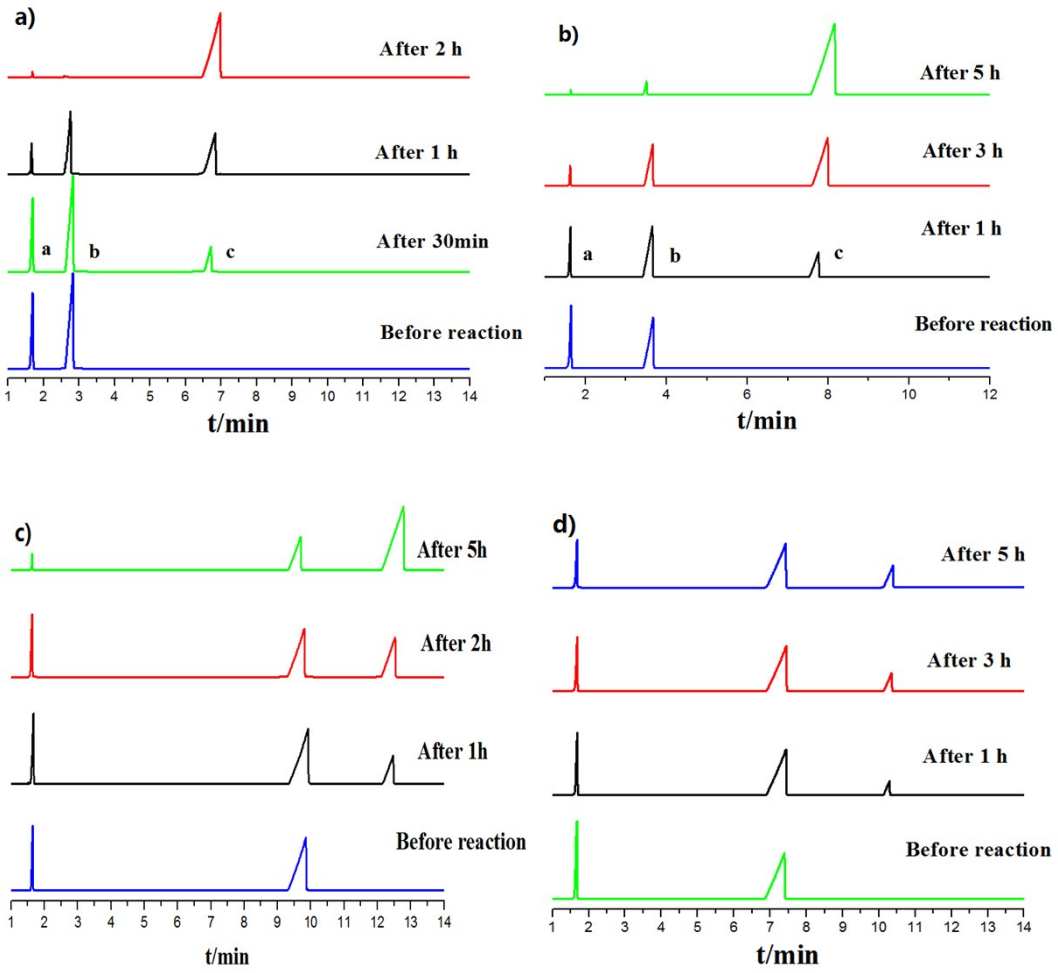

Fig. S4 The GC of the reactions of **(a)** n-Heptaldehyde and Cyanotrimethylsilane **(b)** Benzaldehyde and Cyanotrimethylsilane, **(c)** 1-Naphthaldehyde and Cyanotrimethylsilane, **(d)** p-anisaldehyde and Cyanotrimethylsilane, catalyzed by **FJI-Y7**.

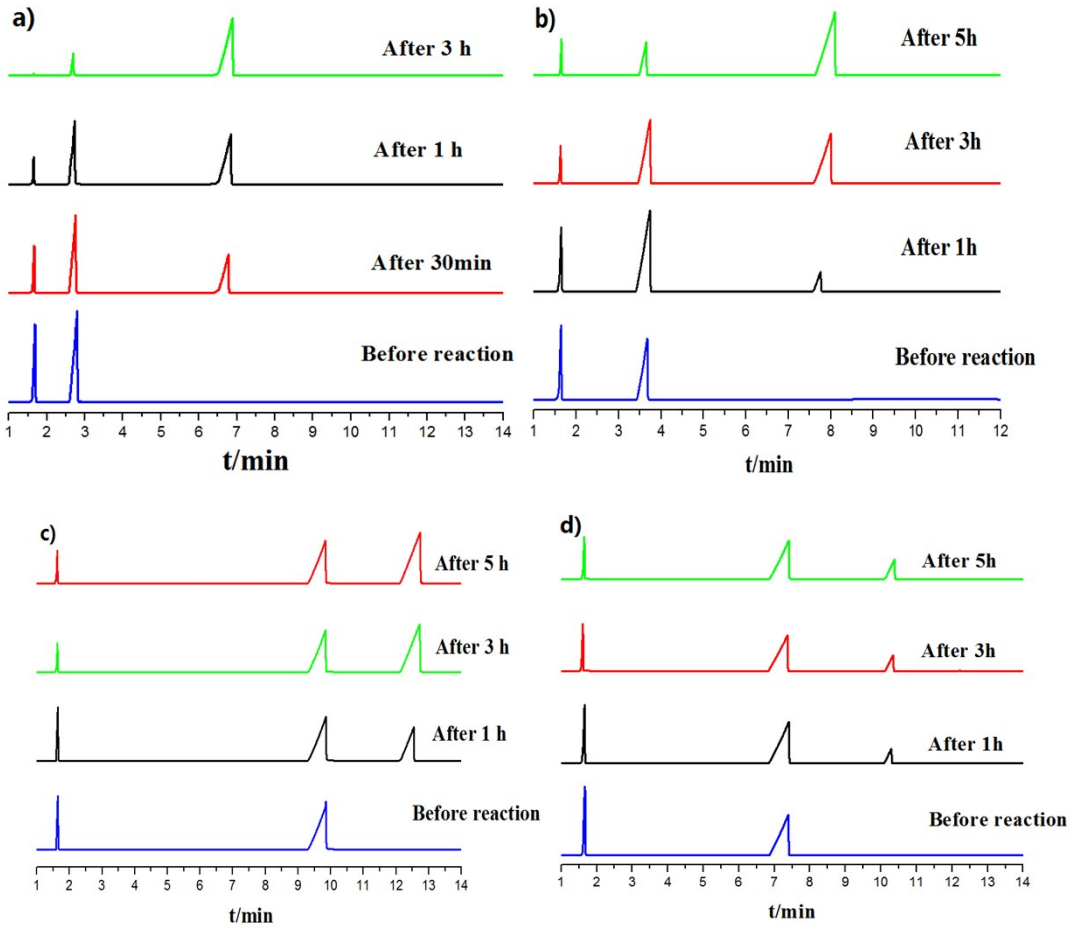

Fig. S5 The GC of the reactions of (a) n-Heptaldehyde and Cyanotrimethylsilane (b) Benzaldehyde and Cyanotrimethylsilane, (c) 1-Naphthaldehyde and Cyanotrimethylsilane, (d) p-anisaldehyde and Cyanotrimethylsilane, catalyzed by **FJI-Y8**.

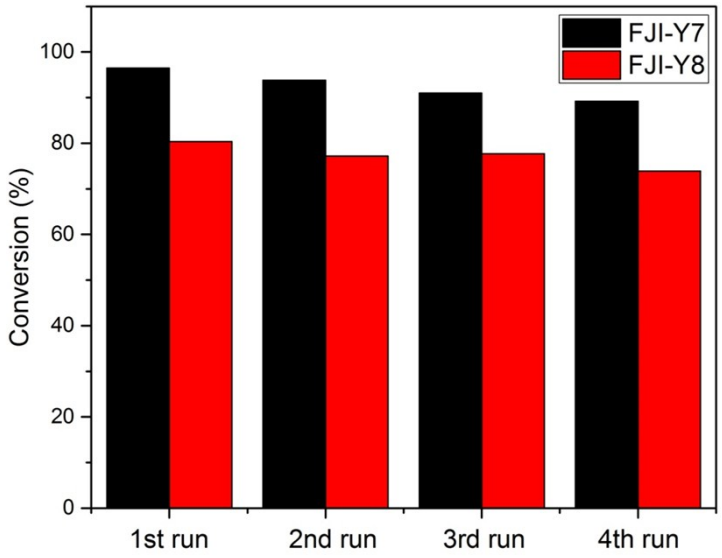

Fig. S6. Recycling experiments for cyanosilylation of benzaldehyde catalyzed by **FJI-Y7** and **FJI-Y8**. Reaction conditions: benzaldehyde (4 mmol), Trimethylsilyl cyanide (4 mmol), catalyst (0.05 mmol), 40 °C, N_2 atmosphere.

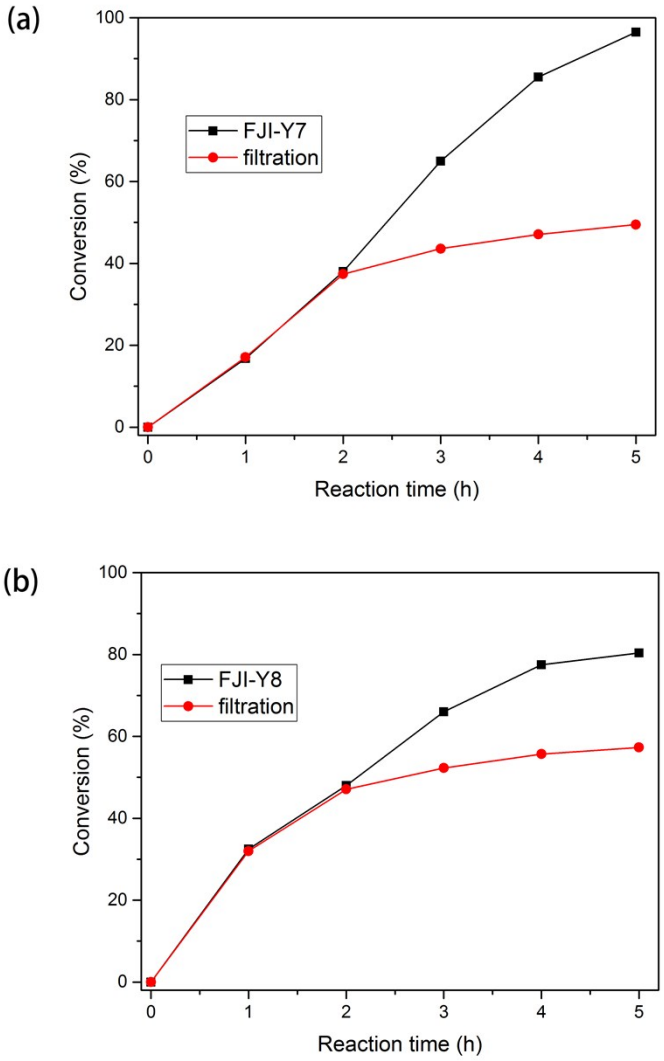

Fig. S7. Catalyst leaching tests for the cyanosilylation reaction of benzaldehyde and Trimethylsilyl cyanide catalyzed by **FJI-Y7** (a) and **FJI-Y8** (b).

The mixture of catalyst (0.05 mmol), aldehyde (4 mmol), TMSCN (4 mmol) was stirred at 40 °C under N_2 atmosphere. After 2h, the catalysts were isolated from the mixture *via* filtration, then the remaining filtrate react continually at 40 °C. As shown in Fig. S7, comparing with the reactions without removal of catalysts, the reaction rates of the leaching texts decrease dramatically after removal of catalysts, implying the loss of the main active species. GC analysis revealed that no dissolved ligand were existed in the filtrate.

Table S1. Cyanosilylation of benzaldehyde (comparison of yields)

Catalyst	Solvent	Temp. K	Time /h	Yield %	Ref
MIL-101(0.5 mol%)	heptane	313	3	98.5	S1
$Mn_3[(Mn_4Cl)_3(BTT)_8(CH_3OH)_{10}]_2$(11mol%)	CH_2Cl_2	298	9	98	S2

$Cu_3(BTC)_2$(5mol%)	CH_2Cl_2	313	48	50	S3
(O_2H_3)Sc-MOF(5 mol%)	ethanol	313	8	84	S4
(μ-OH)6Sc-MOF(5 mol%)	ethanol	313	8.5	77.3	S4
(Phen)Sc-MOF(5 mol%)	ethanol	313	7	55	S4
$[Cd_3(tipp)(bpdc)_2]\cdot DMA\cdot 9H_2O$(0.6mol%)	Solvent-Free	298	18	94	S5
[Me2NH2][Co2(bptc)(μ3-OH)(H2O)2] (0.1 mol %)	Solvent-Free	298	12	98	S6
$\{[Zn_3(4,4'\text{-bpy})_{3.5}(\square\text{-}O_2CH)_4(H_2O)_2](ClO_4)_2(H_2O)_2\}_n$ (5 mol %)	CH_2Cl_2	298	24	22	S7
$[Cu_2(bpy)(H_2O)_{5.5}]_2[H_2W_{11}O_{38}]\cdot 3H_2O\cdot 0.5CH_3CN$ (2 mol %)	CH_2Cl_2	313	24	98.1	S8
DUT-4 (4 mol%)	N-heptane	313	12	~100	S9
FJI-Y7 (1.25 mol%)	Solvent-Free	313	5	96.5	This work
FJI-Y8 (1.25 mol%)	Solvent-Free	313	5	80.4	This work

References

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