Electronic Supplementary Information

Construction of defected MOF-74 with preserved crystallinity for efficient catalytic cyanosilylation of benzaldehyde

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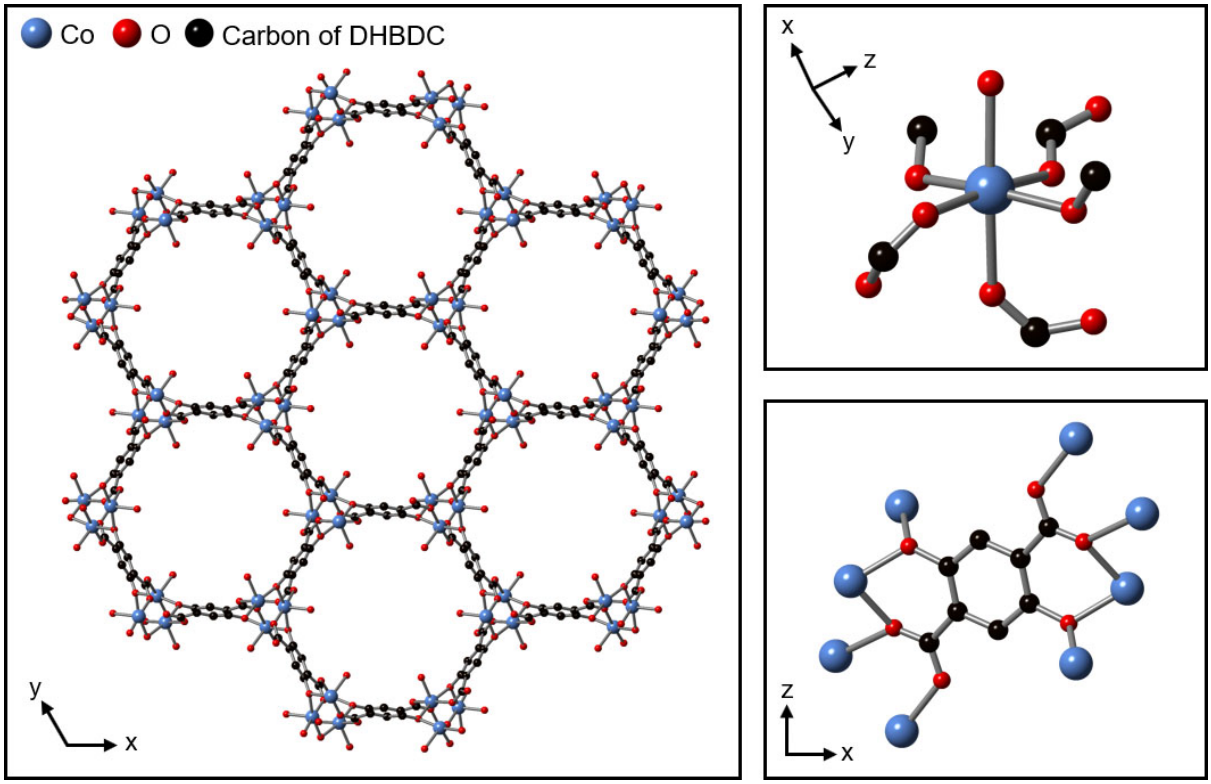

Fig. S1 Ball-and-stick representations of MOF-74. Co: sky blue; C: black; O: red. H atoms are omitted for clarity.

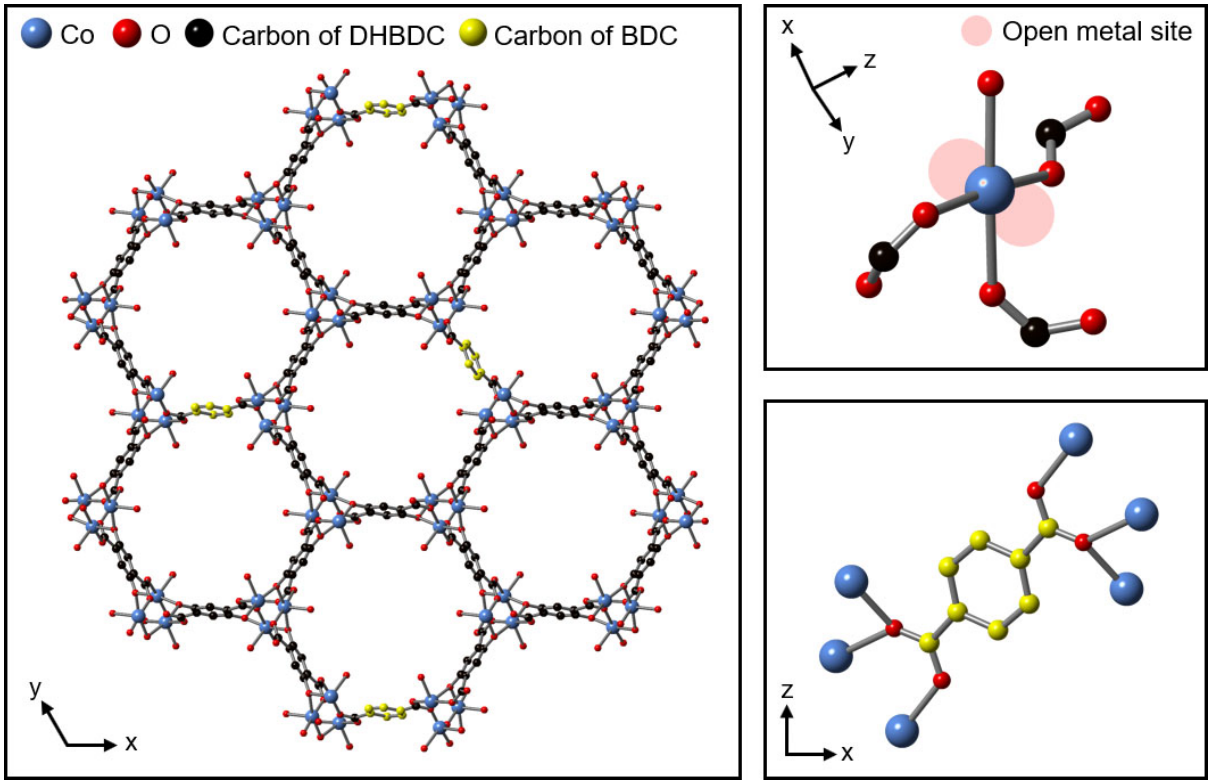

Fig. S2 Ball-and-stick representations of D-MOF-74. Co: sky blue; C: black or yellow; O: red. H atoms are omitted for clarity.

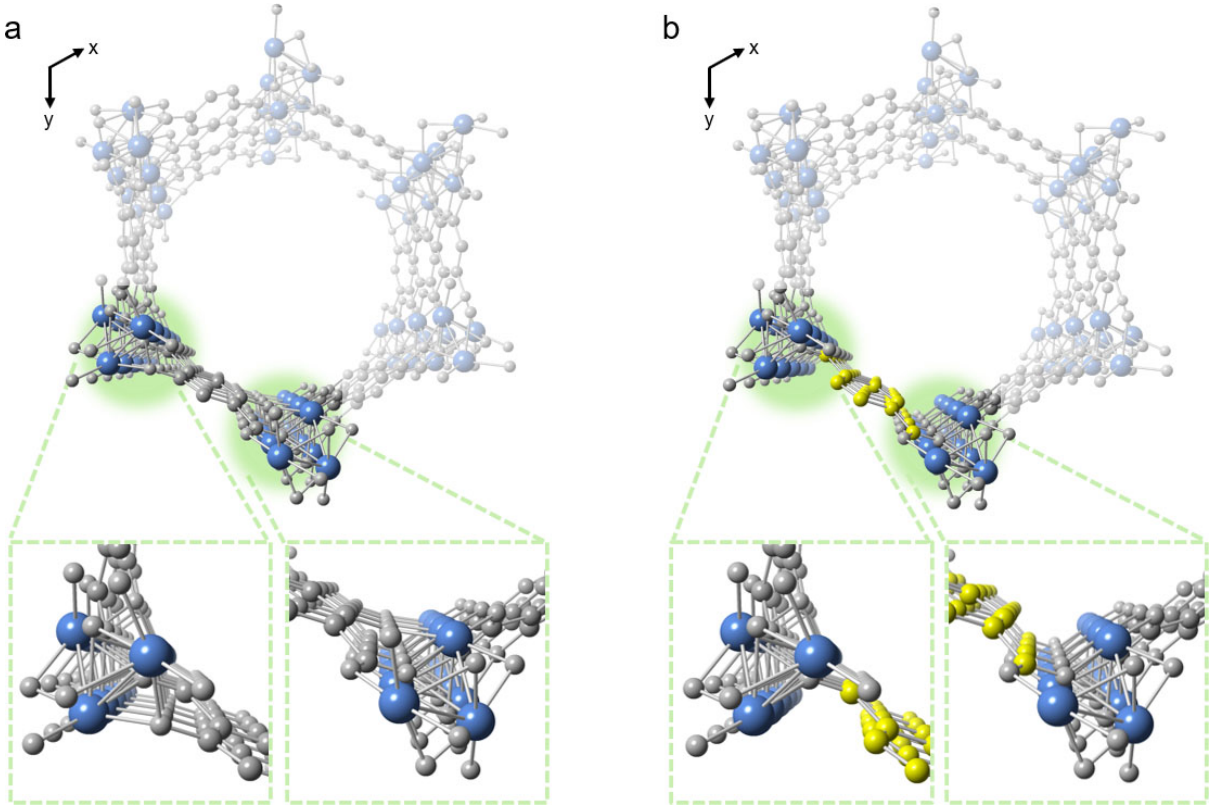

Fig. S3 Ball-and-stick representations of MOF-74 (left) and D-MOF-74 (right) showing the open metal sites generated due to the missing bridged hydroxyl groups. The reactants during the catalytic reaction can interact with these open metal sites through the hexagonal channels. Co: sky blue; C: grey; O: grey. H atoms and H_2O are omitted for clarity.

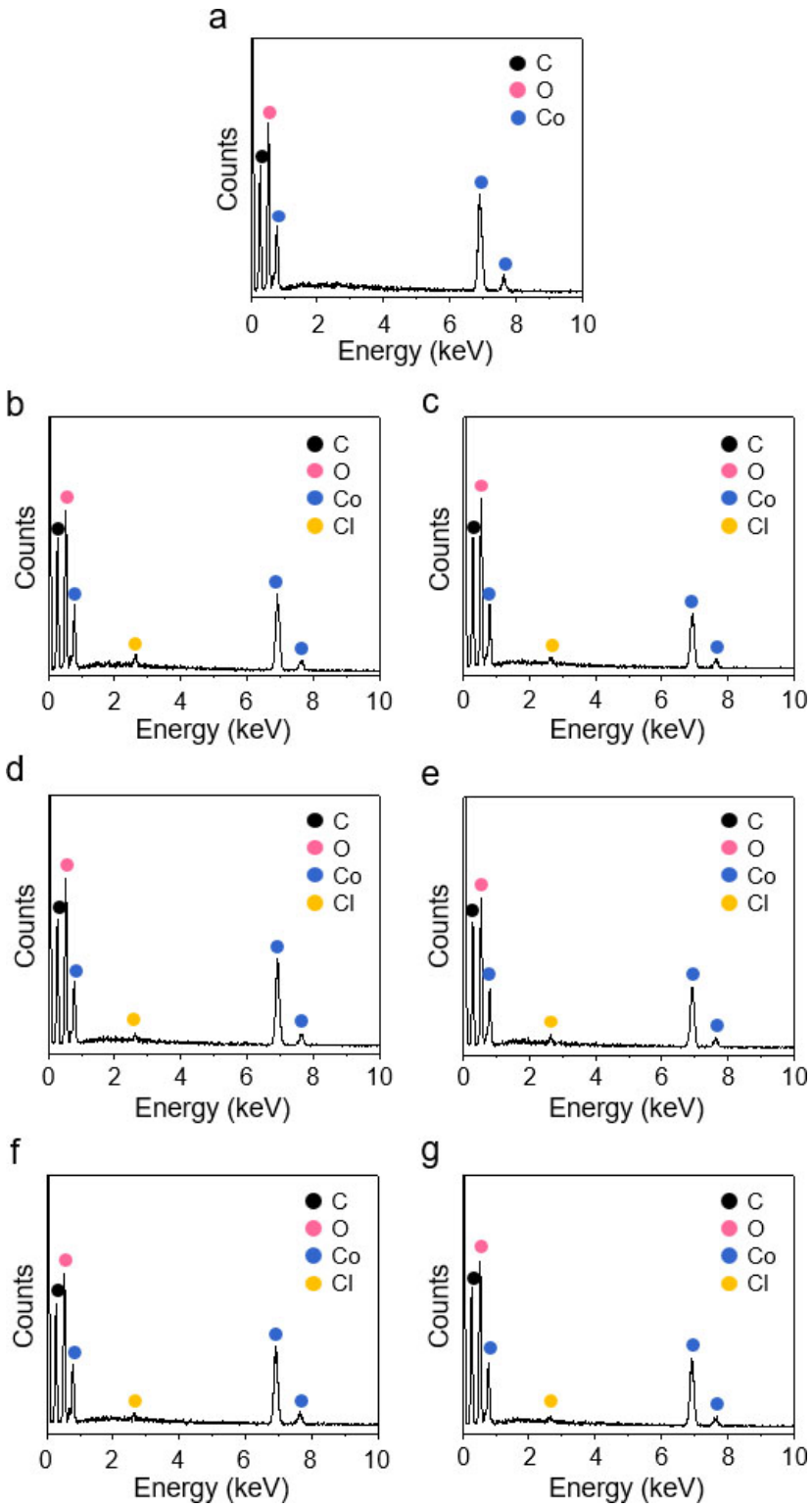

Fig. S4 EDX spectra of (a) pure MOF-74, (b) D3-MOF-74, (c) D4-MOF-74, (d) MOF-74@D1-MOF-74, (e) MOF-74@D2-MOF-74, (f) MOF-74@D3-MOF-74, and (g) MOF-74@D4-MOF-74.

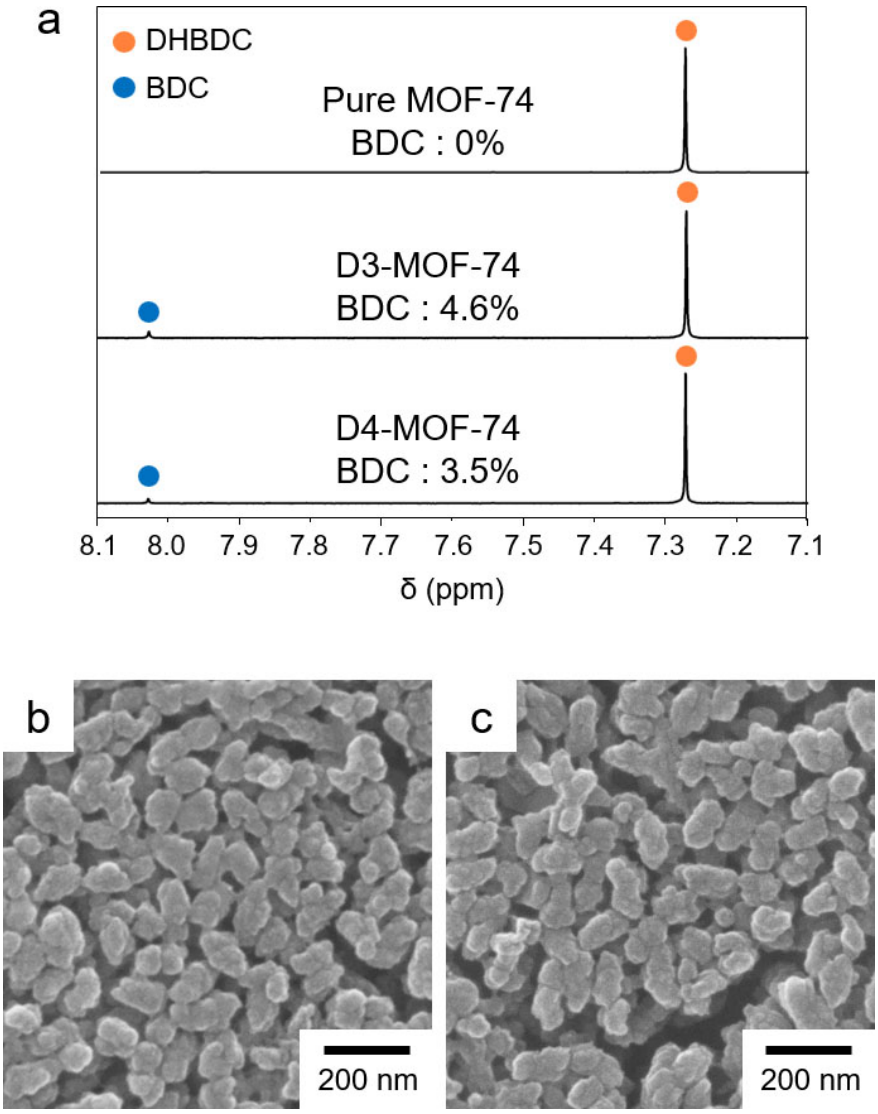

Fig. S5 (a) ^{1}H NMR spectra of pure MOF-74, D3-MOF-74, and D4-MOF-74 showing the incorporated ratios of DHBDC and BDC. The integrations of peaks corresponding to both DHBDC and BDC were used to determine the relative amounts of the two organic linkers. ^{1}H NMR spectra of D1-MOF-74 and D2-MOF-74 could not be measured because trace amounts of D1-MOF-74 and D2-MOF-74 were produced during these reactions at relatively dilute concentrations. SEM images of D1-MOF-74 and D2-MOF-74 are shown in (b) and (c), respectively.

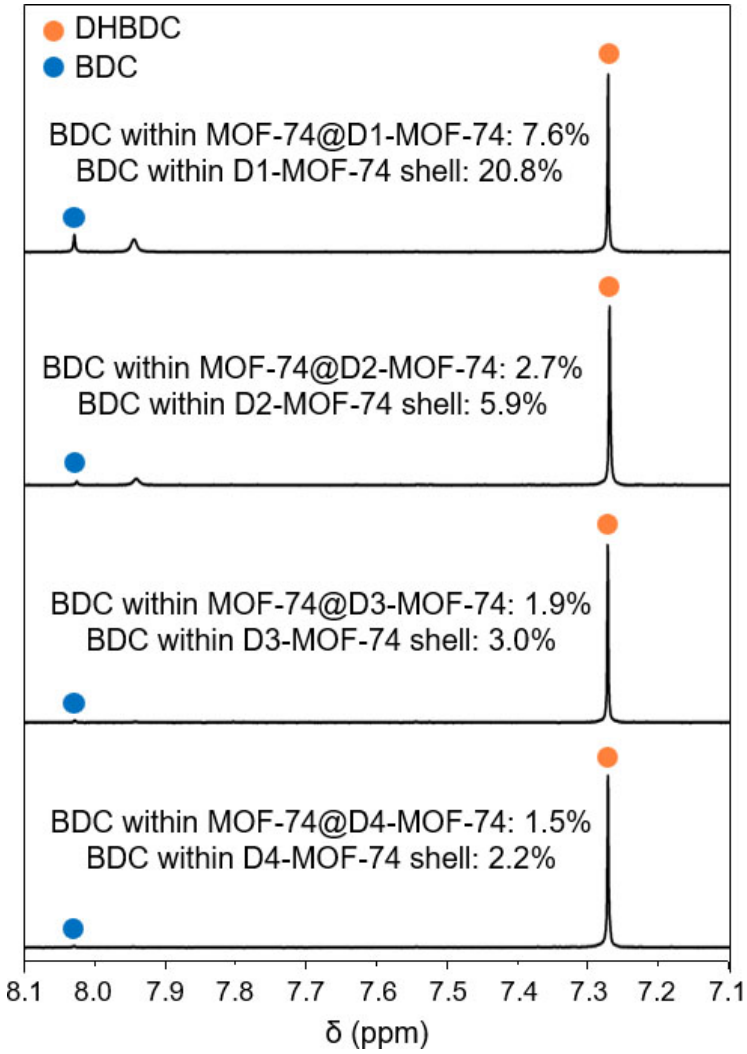

Fig. S6 ^{1}H NMR spectra of a series of MOF-74@D-MOF-74 showing the incorporated ratios of DHBDC and BDC. The integrations of peaks corresponding to both DHBDC and BDC were used to determine the relative amounts of the two organic linkers.

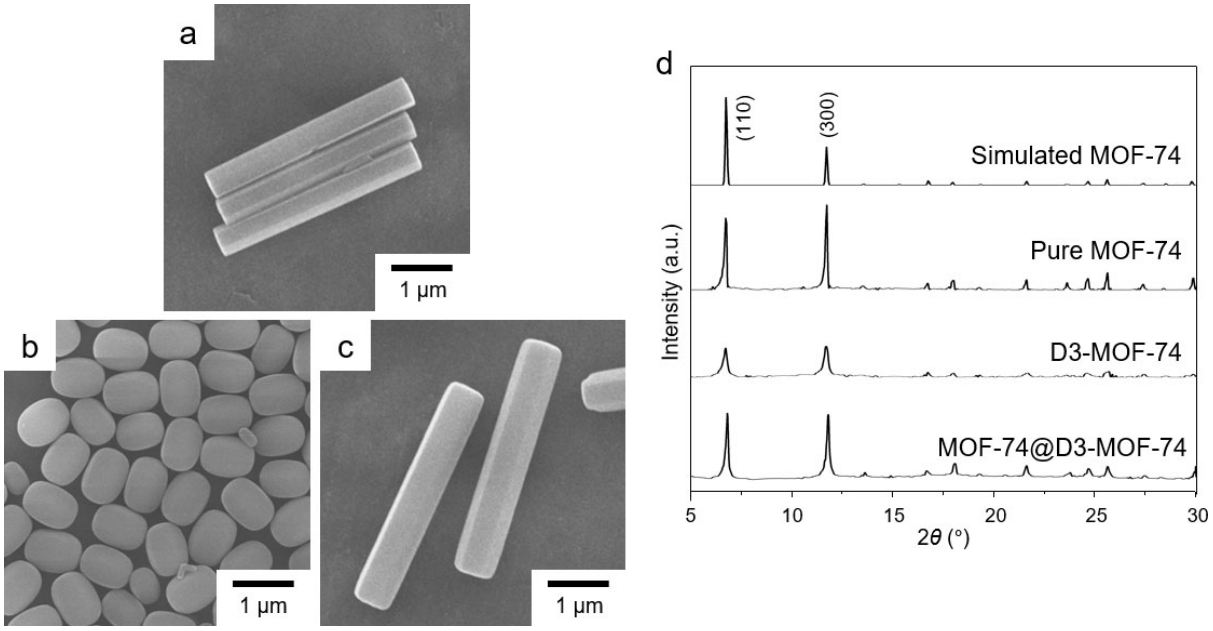

Fig. S7 Large scale productions of MOF-74, D3-MOF-74, and MOF-74@D3-MOF-74. SEM images of (a) MOF-74, (b) D3-MOF-74, and (c) MOF-74@D3-MOF-74. (d) PXRD patterns of MOF-74, D3-MOF-74, and MOF-74@D3-MOF-74. The simulated PXRD pattern of MOF-74 is also shown.

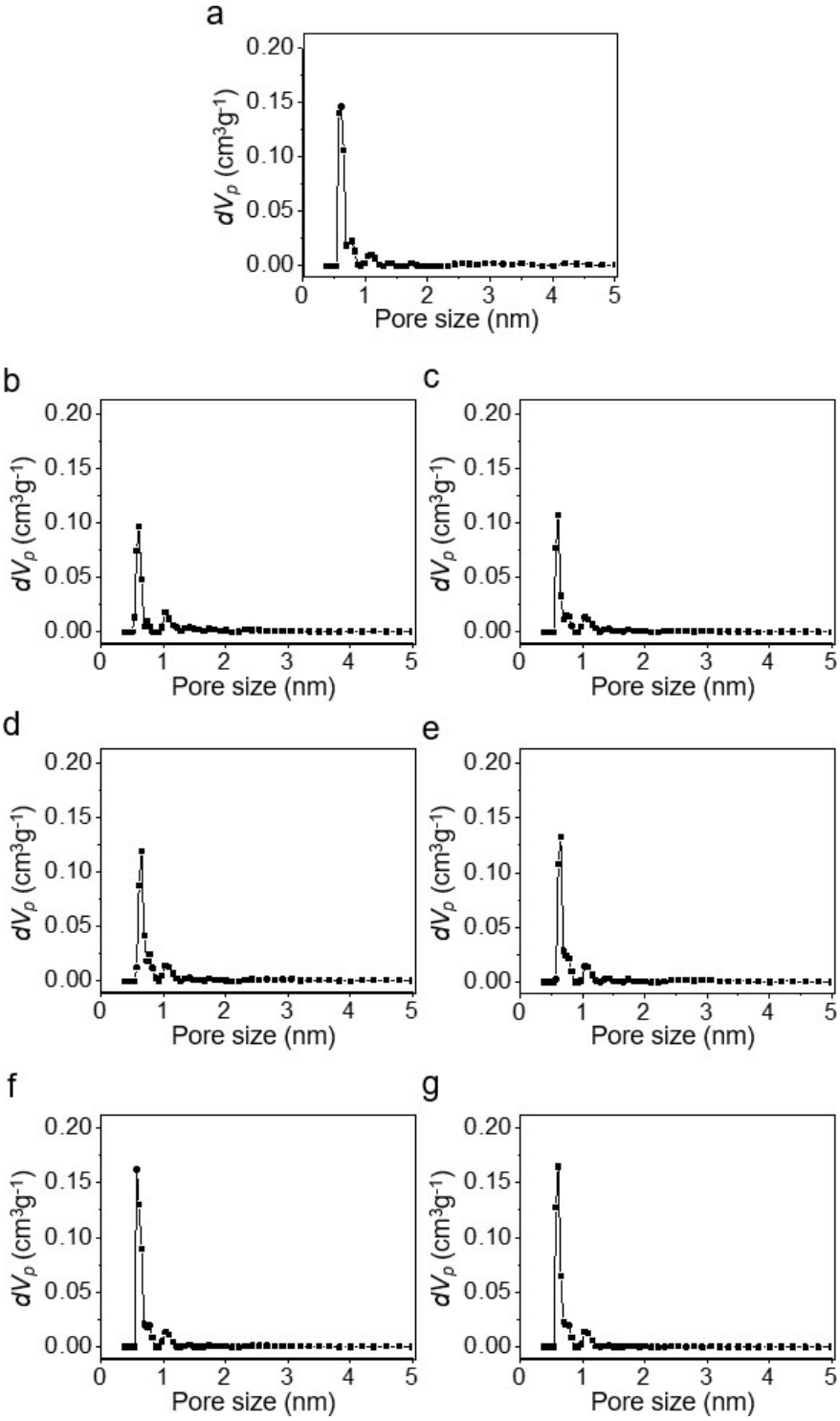

Fig. S8 Pore size distributions of (a) pure MOF-74, (b) D3-MOF-74, (c) D4-MOF-74, (d) MOF-74@D1-MOF-74, (e) MOF-74@D2-MOF-74, (f) MOF-74@D3-MOF-74, and (g) MOF-74@D4-MOF-74 calculated using the NLDFT method.

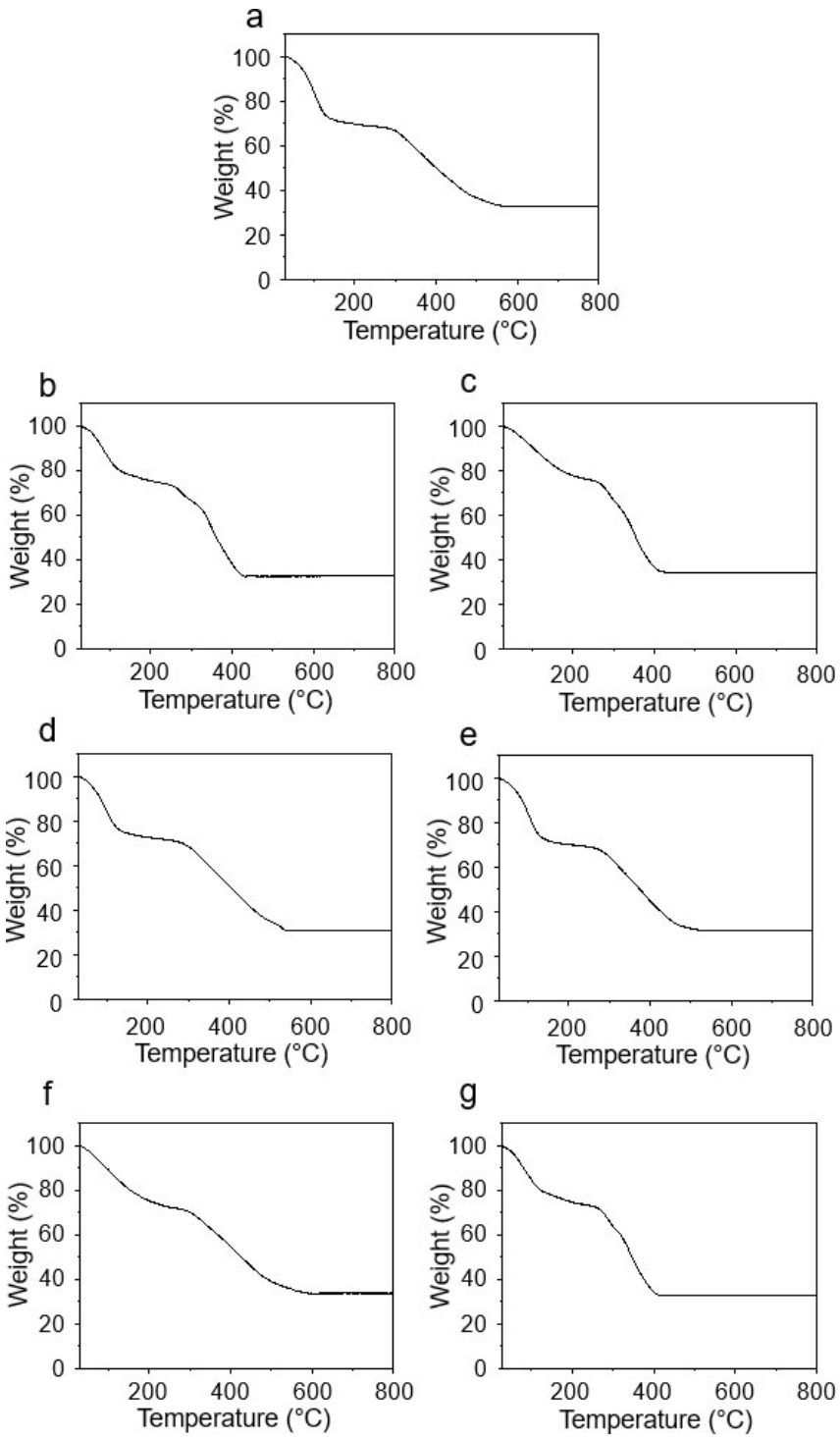

Fig. S9 TGA curves of (a) pure MOF-74, (b) D3-MOF-74, (c) D4-MOF-74, (d) MOF-74@D1-MOF-74, (e) MOF-74@D2-MOF-74, (f) MOF-74@D3-MOF-74, and (g) MOF-74@D4-MOF-74.

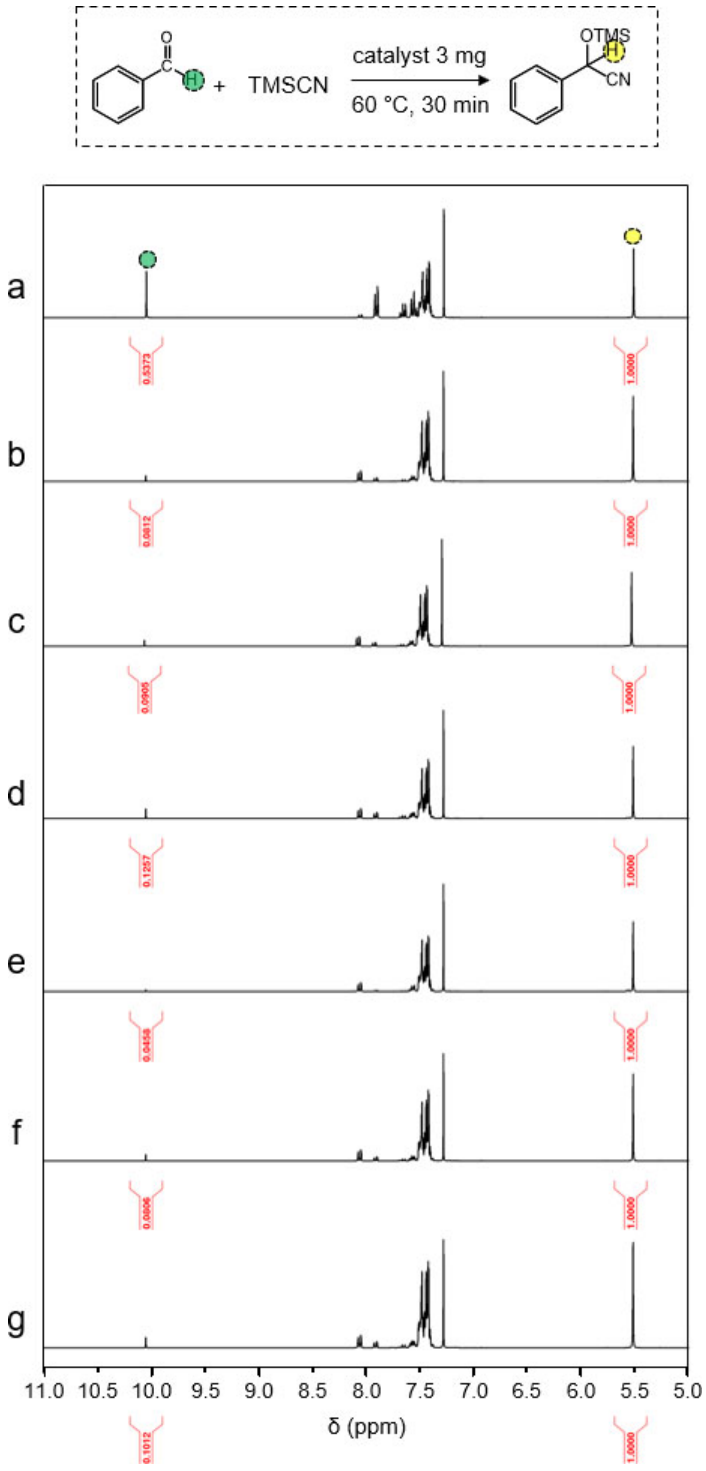

Fig. S10 ^{1}H NMR spectra showing the conversions of benzaldehyde to 2-phenyl-2-[(trimethylsilyl)oxy] acetonitrile in the presence of a catalytic amount of (a) pure MOF-74, (b) D3-MOF-74, (c) D4-MOF-74, (d) MOF-74@D1-MOF-74, (e) MOF-74@D2-MOF-74, (f) MOF-74@D3-MOF-74, and (g) MOF-74@D4-MOF-74 after 30 min of reaction.

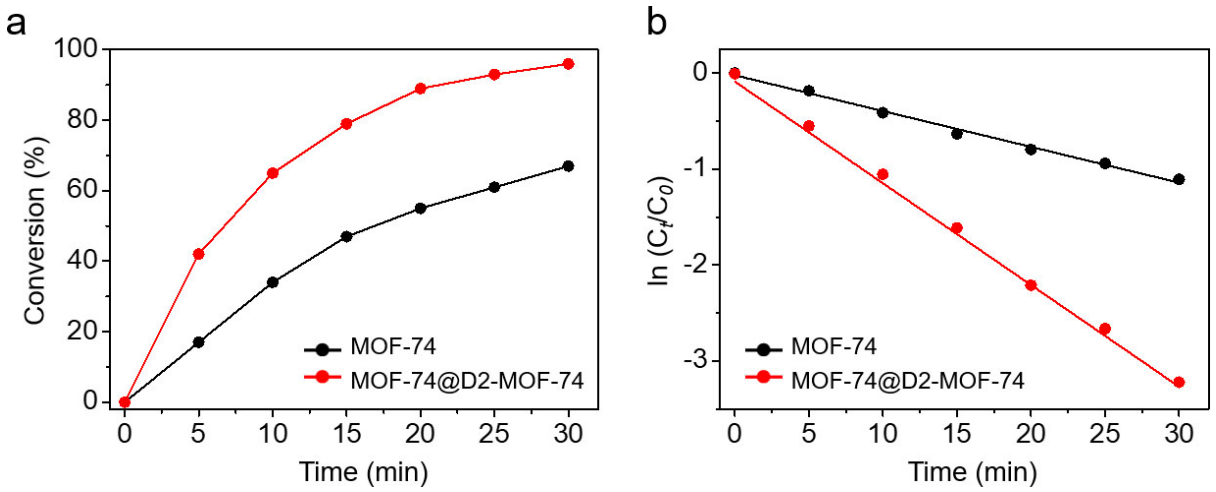

Fig. S11 The plots for the conversions of benzaldehyde to 2-phenyl-2-[(trimethylsilyl)oxy] acetonitrile by pure MOF-74 and MOF-74@D2-MOF-74 in varied time points. (b) Linear relationships between $\ln(C_t/C_0)$ and reaction time in the presence of pure MOF-74 and MOF-74@D2-MOF-74. C_0 and C_t represent the amounts of benzaldehyde at the initial stage and time t, respectively.

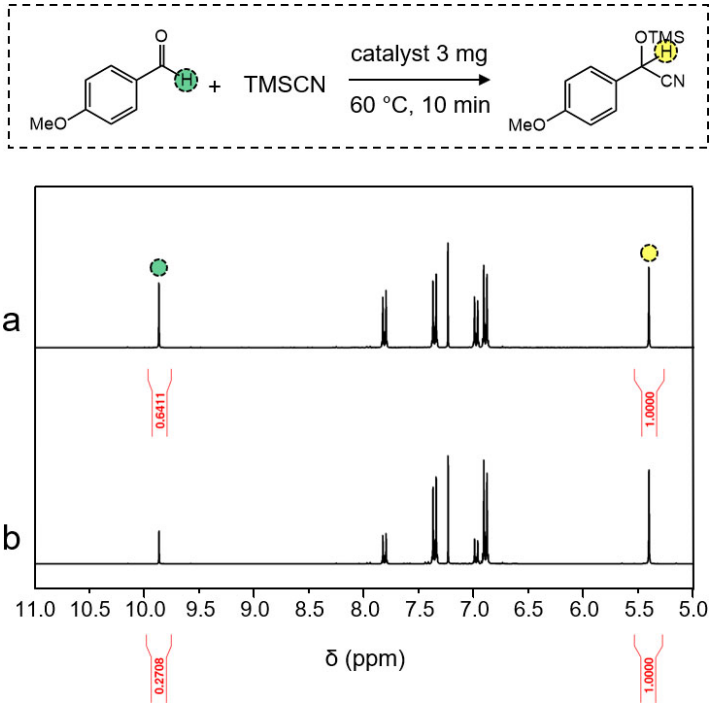

Fig. S12 ^{1}H NMR spectra showing the conversions of 4-methoxybenzaldehyde to 2-(4-methoxyphenyl)-2-[(trimethylsilyl)oxy] acetonitrile in the presence of a catalytic amount of (a) pure MOF-74 and (b) MOF-74@D2-MOF-74 after 10 min of reaction.

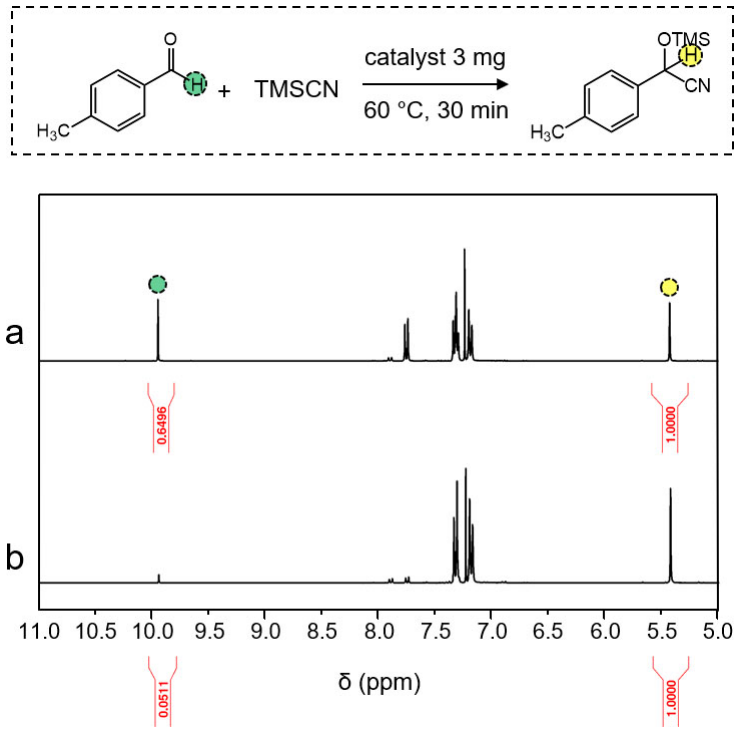

Fig. S13 ^{1}H NMR spectra showing the conversion of 4-methylbenzaldehyde to 2-(p-tolyl)-2-[(trimethylsilyl)oxy] acetonitrile in the presence of a catalytic amount of (a) pure MOF-74 and (b) MOF-74@D2-MOF-74 after 30 min of reaction.

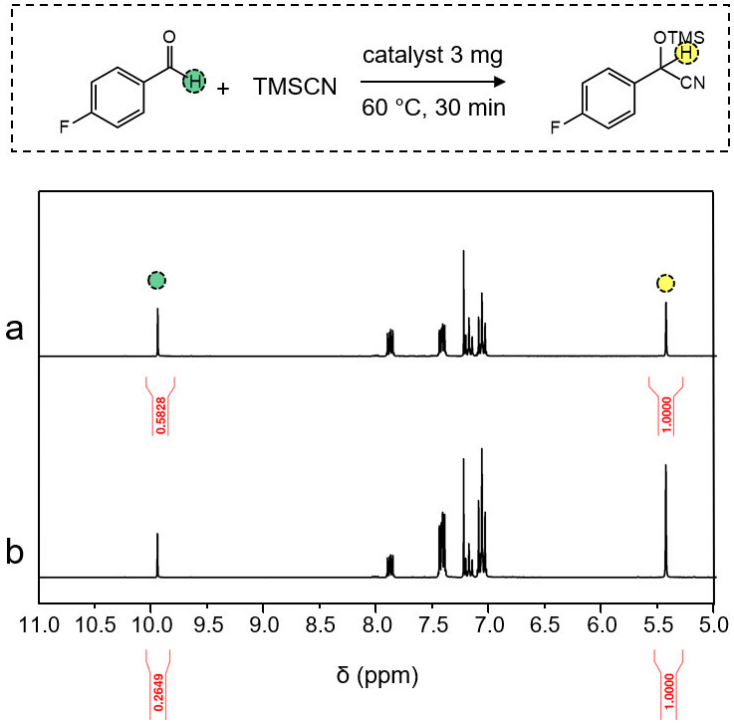

Fig. S14 ^{1}H NMR spectra showing the conversion of 4-fluorobenzaldehyde to 2-(4-fluorophenyl)-2-[(trimethylsilyl)oxy] acetonitrile in the presence of a catalytic amount of (a) pure MOF-74 and (b) MOF-74@D2-MOF-74 after 30 min of reaction.

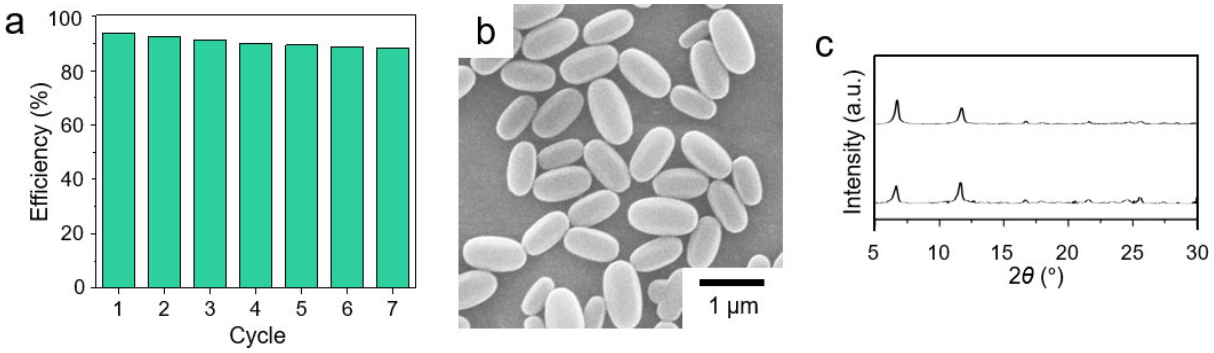

Fig. S15 (a) Recyclability of D3-MOF-74 over seven successive catalytic cycles. (b) SEM image and (c) PXRD patterns of D3-MOF-74 measured before (top) and after (bottom) seven successive catalytic reactions.

Table S1 BET surface areas and total pore volumes of pure MOF-74, a series of D-MOF-74, and a series of MOF-74@D-MOF-74

MOF	Surface area (m^2 g^{-1})	Total pore volume (cm^3 g^{-1})
MOF-74	1180.8	0.50
D3-MOF-74	925.7	0.43
D4-MOF-74	919.3	0.40
MOF-74@D1-MOF-74	1102.8	0.48
MOF-74@D2-MOF-74	1130.4	0.50
MOF-74@D3-MOF-74	1158.9	0.50
MOF-74@D4-MOF-74	1172.3	0.50

Table S2 Comparison of BET surface areas and total pore volumes between D-MOF-74 and D-MOF-74 shell within MOF-74@D-MOF-74

Entry	MOF	Surface area ($m^2\ g^{-1}$)	Total pore volume ($cm^3\ g^{-1}$)
1[a]	D3-MOF-74	925.7	0.43
2[b]	D3-MOF-74 within MOF-74@D3-MOF-74	1146.4	0.50
3[a]	D4-MOF-74	919.3	0.40
4[b]	D4-MOF-74 within MOF-74@D4-MOF-74	1167.9	0.50

[a] These values were obtained with N_2 sorption isotherms. [b] These values were estimated based on the relative amounts of the MOF-74 core and the D-MOF-74 shell within MOF-74@D-MOF-74.

Table S3 Cyanosilylation of benzaldehyde with TMSCN catalyzed by pure MOF-74, D3-MOF-74, and MOF-74@D2-MOF-74[a]

Entry	Catalyst	Conversion (%)[b]	Conversion (%)[c]
1	MOF-74	65	67
2	D3-MOF-74	93	92
3	MOF-74@D2-MOF-74	96	95

[a] Reaction conditions: benzaldehyde (1 mmol), MOF catalyst (3.0 mg, 1.7 mol% based on Co(II)), trimethylsilyl cyanide (TMSCN; 3 mmol). [b] Conversion determined by ^{1}H NMR based on the ratio between benzaldehyde and cyanosilylated product. [c] Conversion determined by ^{1}H NMR using dodecane as an internal standard.