

“Clickable” Metal-Organic Framework

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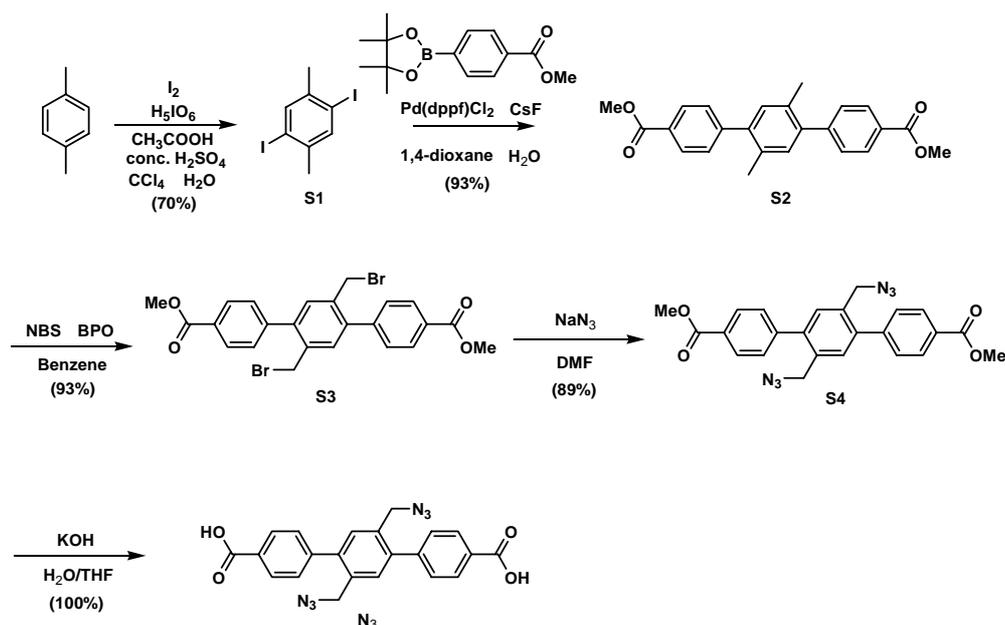
1. General

Compound **S1**, **S2**, **S3**, **S4** and **N3** were synthesized by following scheme S1. ^1H NMR spectra were recorded on a Bruker Biospin 300 MHz NMR, and Bruker 600 MHz NMR. IR spectra were collected on a PerkinElmer ATR-FT-IR spectrometer. Powder X-ray diffractions were measured on a Rigaku R-AXIS RAPID diffractometer with a 2D area detector using graphite-monochromatized Cu-K α radiation ($\lambda = 1.54178 \text{ \AA}$). Trials for X-ray structural analysis was also done by the same apparatus. Lattice parameters were obtained by a least-squares analysis from the reflections for three oscillation images.

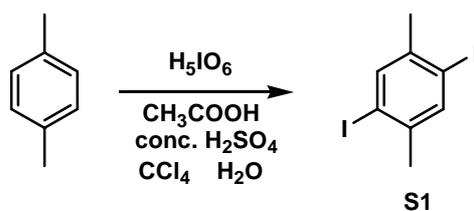
2. Preparation of N3

N3 was prepared according to Scheme S1.

Scheme S1

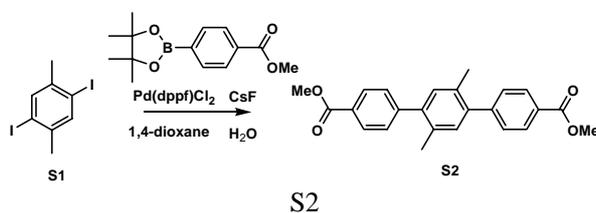


Preparation of S1



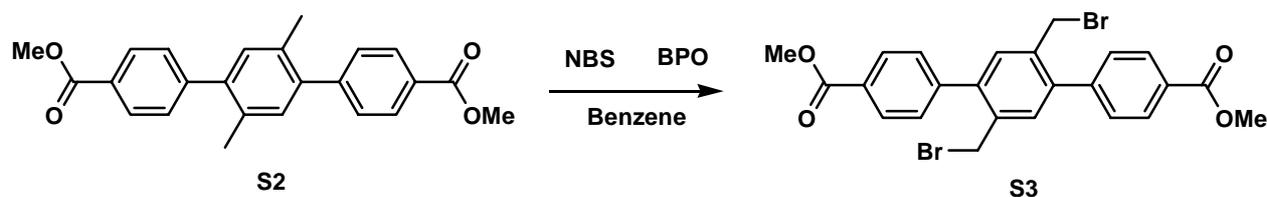
Iodine (28.7 g, 0.11 mol), orthoperiodic acid (10 g, 0.044 mol) and *p*-xylene (15 g, 0.14 mol) were dissolved in a mixed solvent (acetic acid (94 mL) and tetra chloromethane (30 mL) and 30% sulfuric acid (17 mL)) and the mixture was followed to reflux 18 h. After cooling to r.t., a large amount of H_2O and MeOH were added to the reaction mixture, then resulted in a white precipitation. The precipitate was filtered and washed by MeOH . (29 g, 70%). ^1H NMR (300 MHz, CDCl_3 , TMS, r.t.) δ 7.65 (s, 2H, ArH), 2.34 (s, 6H, Me).

Preparation of S2:



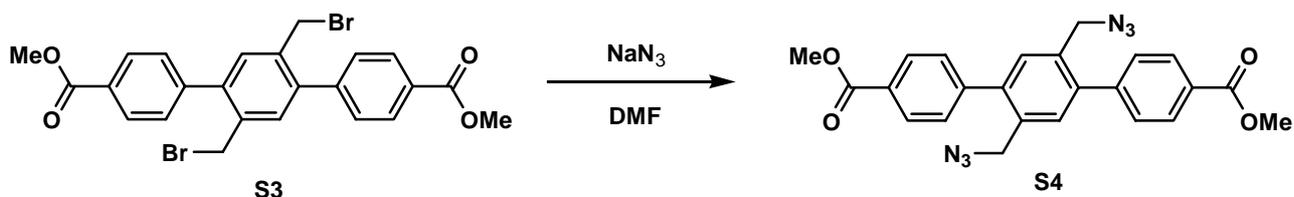
Compound **S1** (2.4 g, 6.6 mmol) and cesium fluoride (6.0 g, 40 mmol) were dissolved in a mixed solvent (1,4-dioxane (30 mL), H₂O (15 mL)). After argon bubbling for 30 min., 1,1'-bis(diphenylphosphino)ferrocenedichloropalladium(II) (0.29 g, 0.36 mmol) and methyl 4-(4,4,5,5-tetramethyl 1,3,2-dioxaborolan-2-yl) benzoate (4.0 g, 15 mmol) were added, and the mixture was followed to reflux 5 hours. After cooling to r.t., the solvent was evaporated to dryness. The residue was extracted with toluene and washed by saturated saline and separated organic layer was dried over anhydrous Na₂CO₃. After removing the solvent, the residue was purified with column chromatography (silica gel, chloroform) to give **2** as a white solid. (1.6 g, 65%). ¹H NMR (300 MHz, CDCl₃, TMS, r.t.) δ 8.11 (d, *J* = 7.5 Hz, 4H, ArH), 7.45 (d, *J* = 8.4, 4H, ArH), 7.16 (s, 2H, ArH), 3.96 (s, 6H, OMe), 2.27 (s, 6H, ArMe).

Preparation of S3



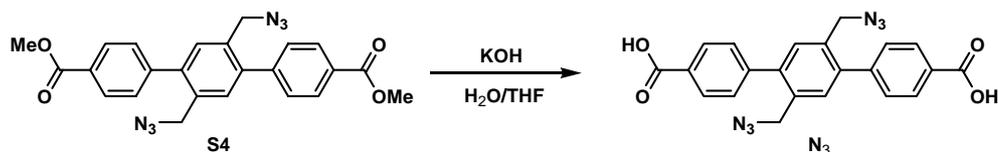
Compound **S2** (1.5 g, 4.0 mmol) and *N*-bromosuccinimide (1.7 g, 6.8 mmol) were dissolved in 10 mL benzene. After argon bubbling for 30 min., benzoyl peroxide was added to the solution and the mixture was followed to reflux 12 h. After cooling to r.t., the solvent was removed. The residue was washed with MeOH to give **3** as a white solid. (1.8 g, 86%). ¹H NMR (600 MHz, CDCl₃, TMS, r.t.) δ 8.17 (d, *J* = 8.2 Hz, 4H, ArH), 7.58 (d, *J* = 8.1, 4H, ArH), 7.43 (s, 2H, ArH), 4.42 (s, 4H, CH₂Br), 3.97 (s, 6H, OMe). Anal. Calcd for C₂₄H₂₀Br₂O₄: C, 54.16 ; H, 3.79. Found: C, 54.14; H, 3.79.

Preparation of S4



Compound **S3** (1.8 g, 3.4 mmol) was dissolved in dry DMF, then sodium azide (0.44 g, 6.8 mmol) was added. The mixture was stirring at 60°C for 4 h. After cooling to r.t., reaction mixture was diluted with a large amount of ethyl acetate and washed with firstly saturated saline, then water. The separated organic layer was dried over anhydrous Na₂CO₃. To remove the solvent, **S4** was given as a white solid. (1.4 g, 89%). ¹H NMR (300 MHz, CDCl₃, TMS, r.t.) δ 8.15 (d, *J* = 8.1 Hz, 4H, ArH), 7.49 (d, *J* = 8.1, 4H, ArH), 7.43 (s, 2H, ArH), 4.33 (s, 4H, CH₂N₃), 3.97 (s, 6H, OMe). IR(ATR) : 2089, 1718 cm⁻¹. Anal. Calcd for C₂₄H₂₀N₆O₄: C, 63.15 ; H, 4.42; N, 18.41. Found: C, 63.15; H, 4.42; N, 18.41.

Preparation of N3

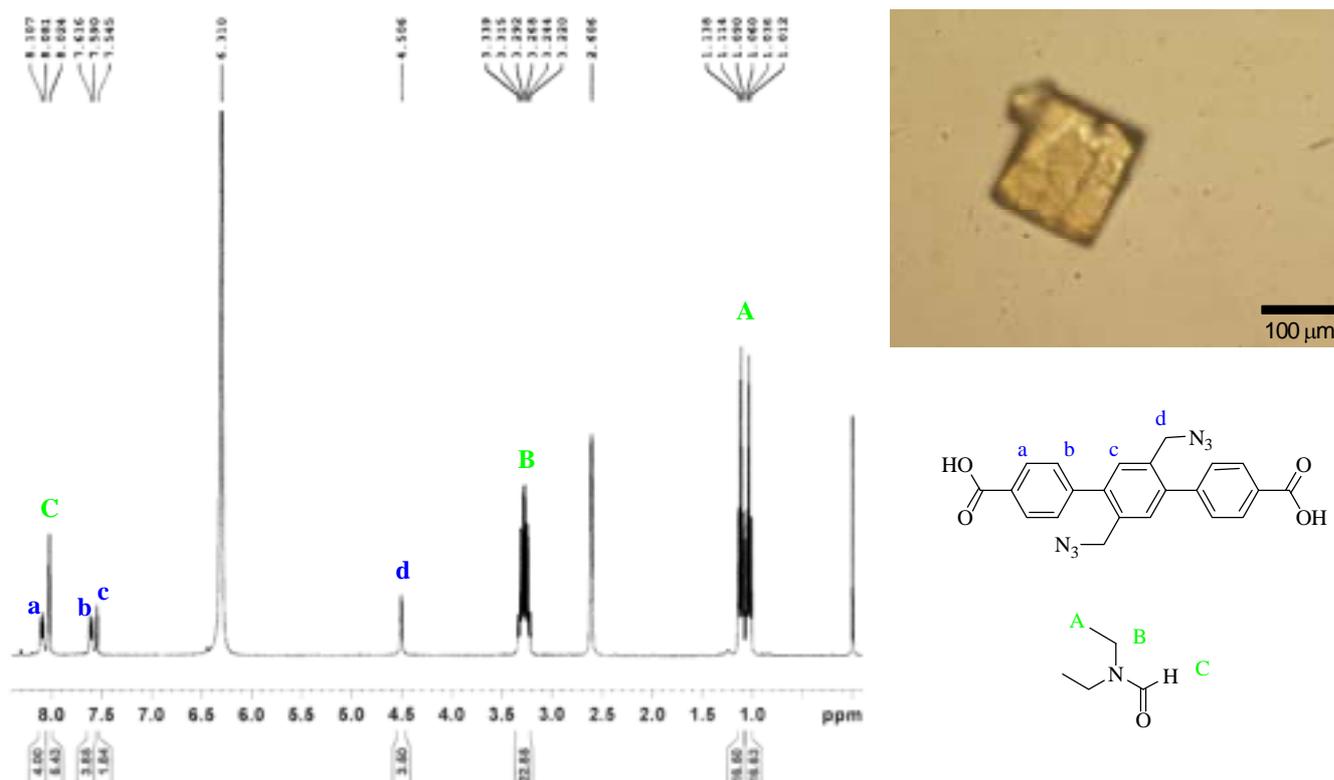


Compound **S4** (1.0 g, 2.2 mmol) and potassium hydrate were dissolved in mixed solvent (tetrahydrofuran / H₂O = 2 / 1(v/v)) and the mixture was stirred at r.t. for 72 h. After tetrahydrofuran was evaporated, 1N HCl was added to the reaction mixture up to pH 1. The reaction mixture was extracted with ethyl acetate several times and the separated organic layer was dried over anhydrous Na₂CO₃. To remove the solvent, ligand **N₃** was given as a pale brown solid. (0.94 g, >99%). ¹H NMR (300 MHz, DMSO-*d*₆, TMS, r.t.) δ 8.15 (d, *J* = 8.1 Hz, 4H, ArH), 7.49 (d, *J* = 8.1, 4H, ArH), 7.43 (s, 2H, ArH), 4.33 (s, 4H, CH₂N₃), 3.97 (s, 6H, OMe). IR(ATR) : 2089, 1683 cm⁻¹. Anal. Calcd for C₂₂H₁₆N₆O₄: C, 61.68; H, 3.76; N, 19.62. Found: C, 61.68; H, 3.76; N, 19.62.

3. Preparation of N₃-MOF-16

Compound **N₃** and zinc nitrate hexahydrate were dissolved in *N,N*-diethylformamide and the mixture was heated at 80°C for 18 hours without stirring, to yield pale yellow crystals **Figure S1**. **Figure S1** was depicted ¹H NMR spectrum after decomposition to soluble species by treatment of hydrochloric acid.

Figure S1 ¹H-NMR spectrum and photo of a crystal of DEF solvated N₃-MOF-16.



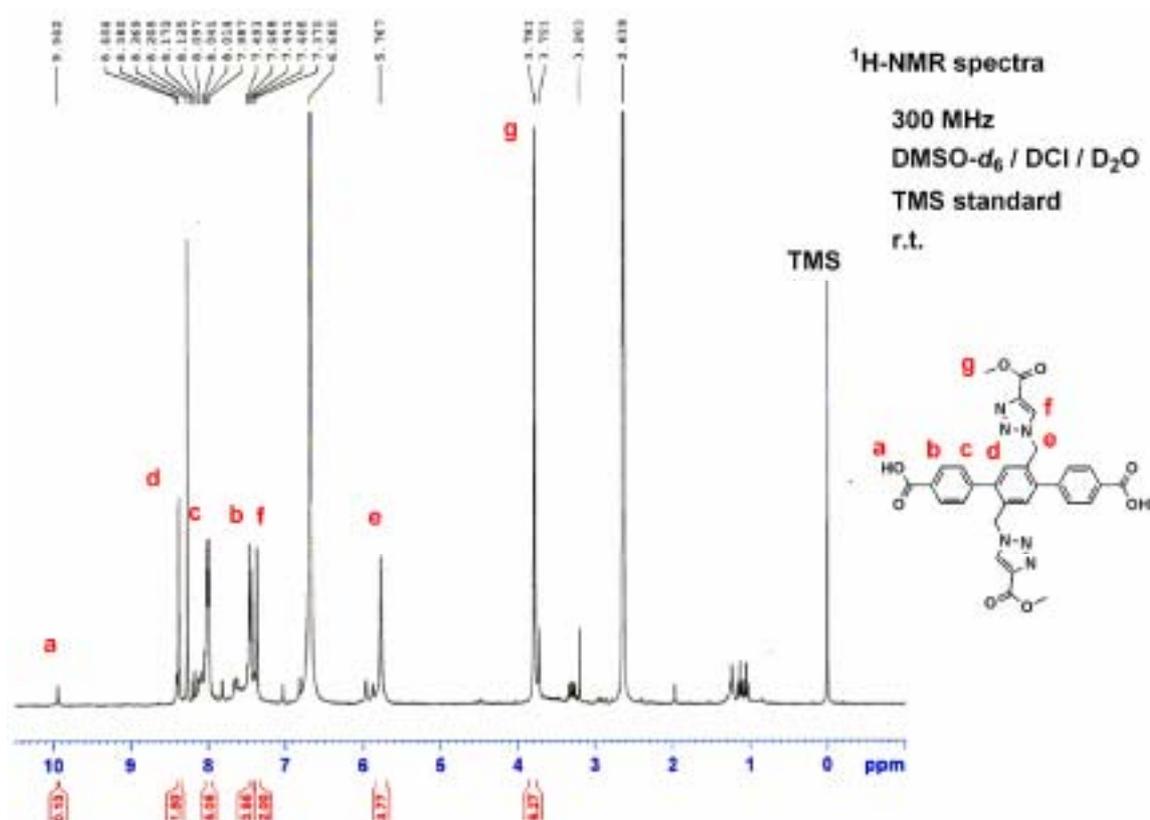
4. Click reaction of N₃-MOF-16 with 1

In 30 mL vial, N₃-MOF-16 was dispersed in ca. 10 mL of DEF. Then excess amount of alkyne and small amount of copper bromide were added, and the solution was kept at 80 °C for 24 hrs. The crystals were collected and transferred to chloroform. Figure S2 depicts the photo of the same crystal as that of Figure S1 after the click reaction. The crystals were collected and dried *in vacuo*. The IR spectra were measured in dried state and XRD patterns were measured as DEF solvated by immersion in DEF. ¹H-NMR of the clicked MOF was measured after decomposition to soluble species by treatment of deuterated hydrochloric acid in the mixture of DMSO-d₆ and D₂O.

Figure S2 Photo of the crystal (the same crystal of Figure S1) of N₃-MOF-16 after the click reaction with 1.



Figure S3 ¹H-NMR spectrum of clicked N₃-MOF-13 with 1 after decomposition.



5. Guest inclusion of clicked MOF with 1 and N3-MOF-13.

Figure S4 ¹H-NMR spectrum and TGA diagram of DEF solvated N3-MOF-13 with 1

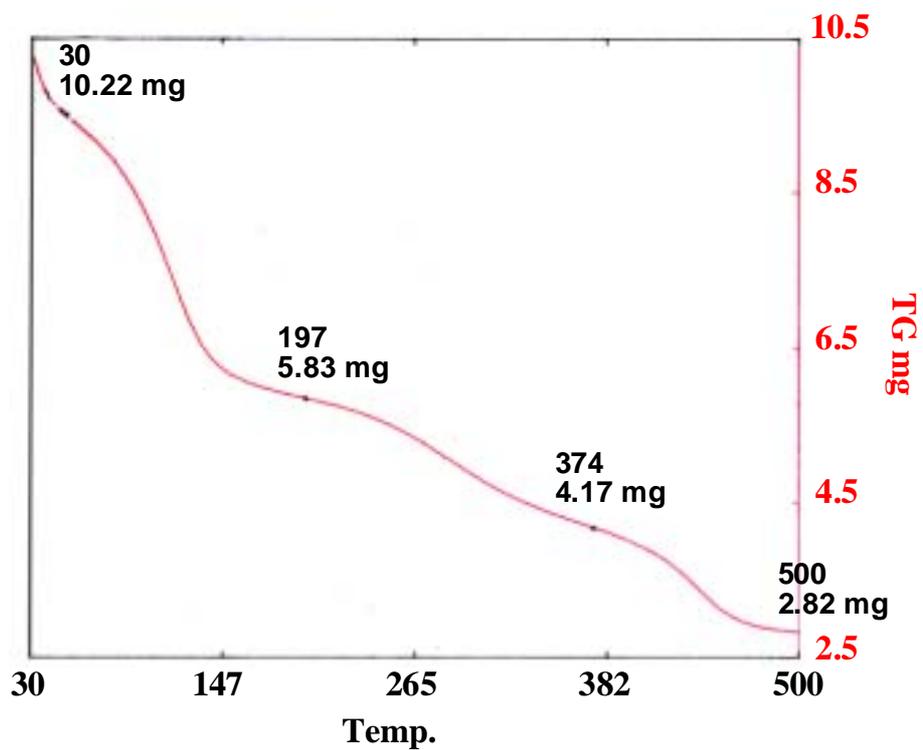
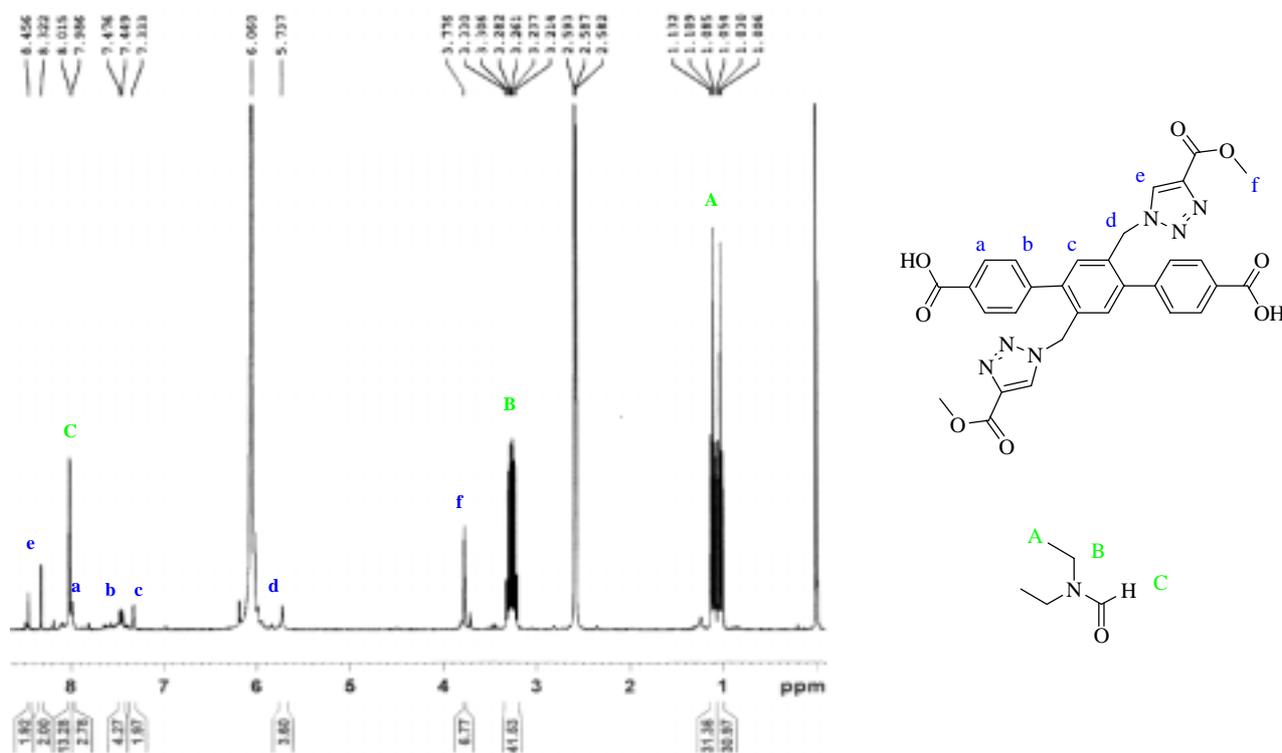
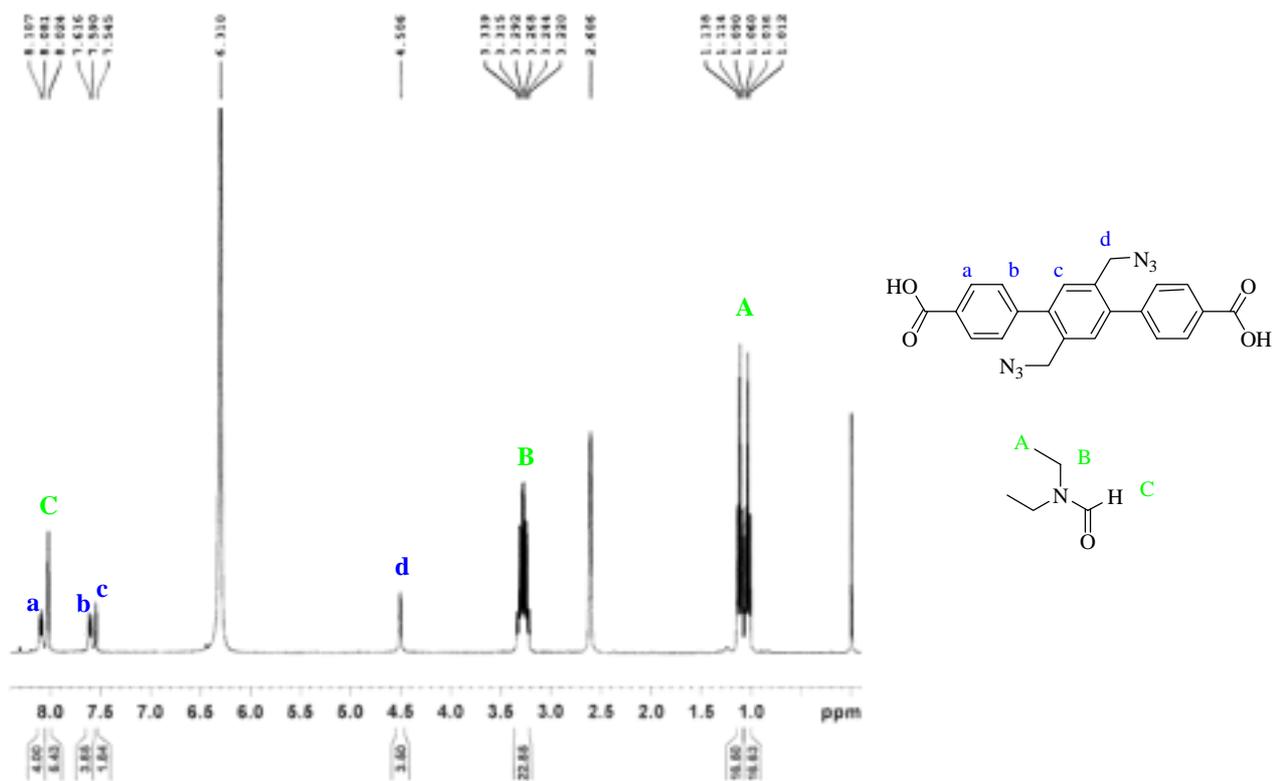


Figure S5 $^1\text{H-NMR}$ spectrum of DEF inclusion crystals of N3-MOF-13.



6. Model click reaction in solution

In 5 mL vial, N3 (10 mg) and 1 mL of alkyne **1** and small amount of copper bromide was dissolved in 1 mL DEF, and the solution was kept at 80 °C for 24 hrs. The insoluble part was removed by filtration and the solvent was removed *in vacuo*. The residue was washed repeatedly by chloroform.

Figure S6 ¹HNMR and IR spectra of the product.

