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Electronic Supporting Information for:

Tuning the Adsorption Behaviors of Water, Methanol, and Ethanol in a Porous Material by Varying the Flexibility of the Substituted Groups

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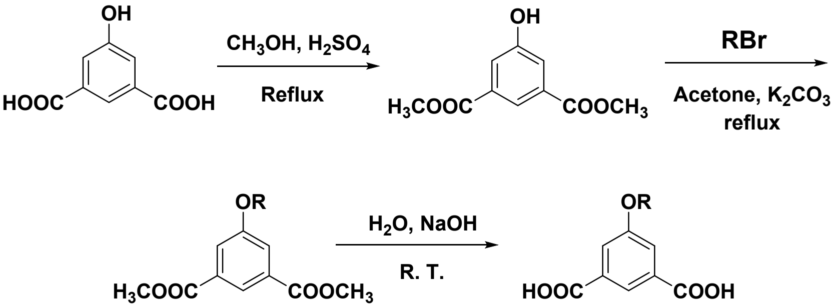
1. Materials and General Procedures.

All reagents were purchased from commercial sources and used without further purification. Thermogravimetric (TGA) analyses were investigated with a Mettler Tolepo TGA/SDTA851 analyzer under N_2 flow from 30 to 800 °C with a heating rate of 10 K min^{-1}. Elemental analysis was measured on an Elementar Vario EL III microanalyzer. To eliminate the adsorbed guest molecules, the samples for EA studying were vacuumed at 100 °C overnight. FT-IR spectra were measured from a KBr pellets on a Nicolet Nexus 470 FT-IR spectrometer in the range of 4000-400 cm^{-1}. Powder X-ray diffraction (XRD) patterns were measured using a Bruker D4 powder diffractometer at 40 kV, 40 mA for Cu Kα radiation (λ = 1.5406 Å), with a scan speed of 0.2 s/step and a step size of 0.05 °(2θ). ^{1}H NMR spectra in solution were recorded on a JEOL ECA 400 nuclear magnetic resonance spectrometer. Chemical shifts are given in ppm. Water, methanol and ethanol sorption isotherms at 298 K were carried out on IGA 002. Before gas sorption, the as-made crystal samples (about 100 mg) were degassed at 100 °C overnight.

2. Synthesis of the ligands

The three ligands ware synthesized according to the route shown in below, which was modified according to a reported method [1].



Synthesis of 5-(prop-2-yn-1-yloxy)isophthalic acid (H_2L1）(R = -$CH_2C{\equiv}CH$)： A 250 mL round-bottom flask was charged with 5-hydroxyisophthalate (3.65 g, 20 mmol), methanol (80 mL) and concentrated sulfuric acid (10 ml). The reaction was stirred at reflux overnight. Then the reaction solution was poured into 500 mL water, followed by adjusting pH value to about 7 by adding $NaHCO_3$. White solid dimethyl 5-hydroxyisophthalate was obtained by filtration, with isolated yield 3.5 g (83%), based on 5-hydroxyisophthalate.Then, a two-neck 250 mL round-bottom flask was charged with dimethyl 5-hydroxyisophthalate (2.1 g, 10 mmol), acetone (60 mL), K_2CO_3 (1.4 g, 10 mmol) and propargyl bromide (1.79 g, 15 mmol). The reaction was allowed to stir at reflux overnight. Upon cooling to RT, the reaction mixture was filtered, the filter cake was washed 3 times with acetone, and the filtrate was concentrated by rotary evaporation. White solid, crude product of dimethyl 5-(prop-2-yn-1-yloxy)isophthalate, was collected for further use. The crude product was then stirred in 50 mL water at RT. To this suspension, 4g NaOH was added. The solution became clear and was allowed to stir for 24 hours at room temperature. The aqueous solution was then cooled and acidified with 2M HCl solution until the pH reached about 7 where a white precipitate formed.

This suspension was then vacuum filtered and washed with water (3 × 5 mL). The product was obtained as white powder: Isolated yield 1.43 g (65%), based on dimethyl 5-hydroxyisophthalate). ^1H NMR (400 MHz, d_6-DMSO) δ ppm: 13.41 (br, 2H), 8.11 (s, 1H), 7.72 (s, 2H), 4.95 (s, 2H), 3.65 (s, 1H).

Synthesis of 5-(allyloxy)isophthalic acid (H_2L2）(R = $-CH_2CH=CH_2$): The procedure for preparation of H_2L2 is similar to that for H_2L1 except replacing propargyl bromide by allyl bromide. Yields: 1.58 g (71%), based on dimethyl 5-hydroxyisophthalate. ^1H NMR (400 MHz, d_6-DMSO) δ ppm: 13.35 (br, 2H), 8.07 (s, 1H), 7.66 (s, 2H), 6.05 (t, 1H), 5.40 (d, 2H), 4.69 (d, 2H).

Synthesis of 5-propoxyisophthalic acid (H_2L3）(R = $-CH_2CH_2CH_3$): The procedure for preparation of H_2L3 is similar to that for H_2L1 except replacing propargyl bromide by propyl bromide. Yields: 1.74 g (78%), based on dimethyl 5-hydroxyisophthalate. ^1H NMR (400 MHz, d_6-DMSO) δ ppm: 13.31 (br, 2H), 8.06 (s, 1H), 7.63 (s, 2H), 4.03 (t, 2H), 1.74 (t, 2H), 1.00 (t, 3H).

3. Synthesis of MOFs

Synthesis of $[Cu(H_2O)(L1)]_n$ (Cu-L1). A mixture of H_2L1 (0.110 g, 0.5 mmol), $Cu(NO_3)_2{\cdot}6H_2O$ (0.121 g, 0.5 mmol), ethanol (2 mL), and H_2O (8 mL) were placed in a 15 mL teflon-lined stainless steel autoclave and stirred for 10 min. Then, it was sealed and heated at 90 °C for 3 days, followed by slowly cooling down to room temperature. Blue hexagonal crystals of Cu-L1 were collected by filtration (yield: 32% based on H_2L1). Elemental analysis calcd. for **Cu-L1** ($C_{11}H_8O_6Cu$, 299.73): C, 44.04; H, 2.67 %.; Found: C, 43.48; H, 2.73 %.

Synthesis of Cu-L2: The procedure is similar to **Cu-L1** except replacing H_2L1 by H_2L2. Blue powders were obtained by filtration (yield: 40% based on H_2L2). Elemental analysis calcd. for **Cu-L2** ($C_{11}H_{10}O_6Cu$, 301.75): C, 43.75; H, 3.29 %; Found: C, 43.54; H, 3.35 %.

Synthesis of Cu-L3: The procedure is similar to **Cu-L1** except replacing H_2L1 by H_2L3. Blue powders were obtained by filtration (yield: 53% based on H_2L2). Elemental analysis calcd for **Cu-L2** ($C_{11}H_{12}O_6Cu$, 303.76): C, 43.45; H, 3.95 %.; Found: C, 43.18; H, 4.03 %.

Synthesis of $Cu\text{-}(L3)_{0.75}(L1)_{0.25}$: The procedure is similar to **Cu-L1** except replacing H_2L1 by a mixture of H_2L3 and H_2L1 in molar ratio ranging from 4:1 ~ 1:4. Blue powders were obtained by filtration. Elemental analysis calcd for **$Cu\text{-}(L3)_{0.75}(L1)_{0.25}$** ($C_{11}H_{11}O_6Cu$, 302.75): C, 43.64; H, 3.66 %.; Found: C, 43.56; H, 3.85 %.

4. X-ray Crystallographic Study

Data collection for Cu-L1 was carried out on a Bruker Apex Duo diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at 293 K. Data reduction was performed with SAINT, and empirical absorption corrections were applied by SADABS program.[2] Structures were solved by direct method using SHELXS program and refined with SHELXL program. [3] Heavy atoms and other non-hydrogen atoms were directly obtained from difference Fourier map. Final refinements were performed by full-matrix least-squares methods with anisotropic thermal parameters for all non-hydrogen atoms on F_2. C-bonded H atoms were placed geometrically and refined as riding modes. The H atoms of coordinated water molecules were obtained from Fourier map and then refined as rigid modes. While the H atoms of guest water molecules were not added because of their severe disorder. Crystallographic data are listed in Table S1, selected bond length and angles are given in Table S2. CCDC 1452219 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystal structural parameter and refinement data of Cu-L1.

Crystallographic data	**Cu-L1**
Empirical formula	$C_{11}H_{10}CuO_7$
Formula weight	317.73
Temperature / K	293(2)
Wavelength / Å	0.71073
Crystal system	Trigonal
Space group	*P-3m1*
a / Å	18.4978(19)
b / Å	18.4978(19)
c / Å	6.7746(7)
Volume / Å^3	2007.5(5)
Z	6
D_{Calc} / g cm^{-3}	1.567
μ / mm^{-1}	1.655
F(000)	954
Tot., Uniq. Data, R_{int}	12430, 1331, 0.045
Observed data [$I > 2.0\ \sigma(I)$]	1142
R_1, wR_2 [$I > 2\sigma(I)$]	0.0438, 0.1368
R_1,[a] wR_2 [b] (all data)	0.0563, 0.1568
GOF on F^2	1.200
Max/min Δρ [e Å^{-3}]	1.167 / -1.297

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

Table S2. Selected bonds lengths (Å) and angles (º) for Cu-L1.

Cu-L1			
Cu(1)-O(1)	2.129(4)	Cu(1)-O(3)	1.947(4)
Cu(1)-O(2)$^{\#1}$	1.963(5)	C7-C8	1.21(3)
O(1)-Cu(1)-O(3)	96.57(15)	O(2)$^{\#1}$-Cu(1)-O(2)$^{\#2}$	88.09(18)
O(1)-Cu(1)-O(2)$^{\#1}$	94.56(15)	O(2)$^{\#2}$-Cu1-O(3)	168.82(14)
O(2)$^{\#1}$-Cu(1)-O(3)	90.02(18)		

Symmetry codes：#1: x-y, -y, 3-z; #2: 1-x, -y, 3-z

Figure S1. The asymmetric structure of Cu-L1 (Hydrogen atoms and guest molecules are omitted for clarity, the symmetry used: A: 1-y, 1-x, z; B: x-y, -y, 3-z; C: 1-x, -y, 3-z; D: 1-x+y, y, z.)

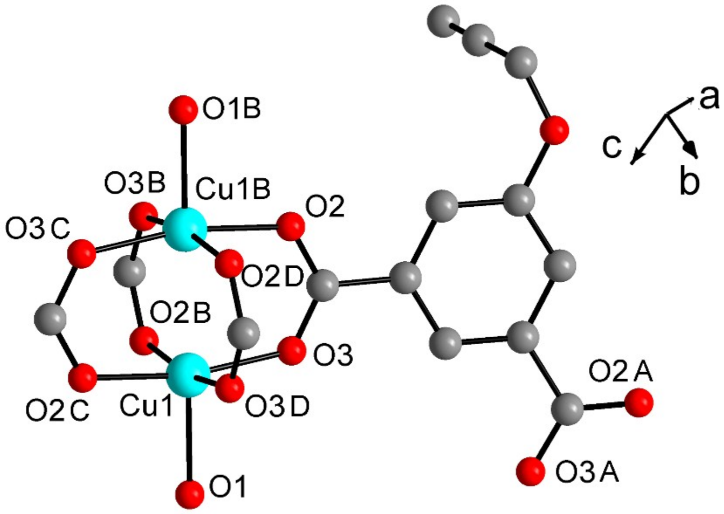


Figure S2. The TGA data of Cu-L1, Cu-L2 and Cu-L3.

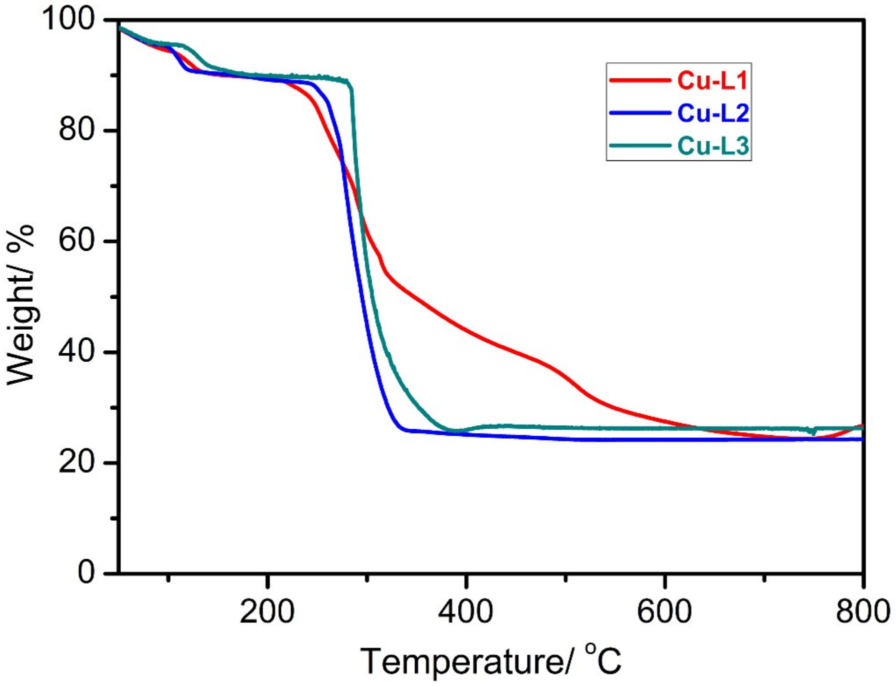


Figure S3. The various-temperature PXRD patterns in air of (a) Cu-L1, (b) Cu-L2 and (c) Cu-L3, indicating that the phase transformation at the temperature higher than 140 °C for Cu-L1, 180 °C for Cu-L2, 250 °C for Cu-L3.

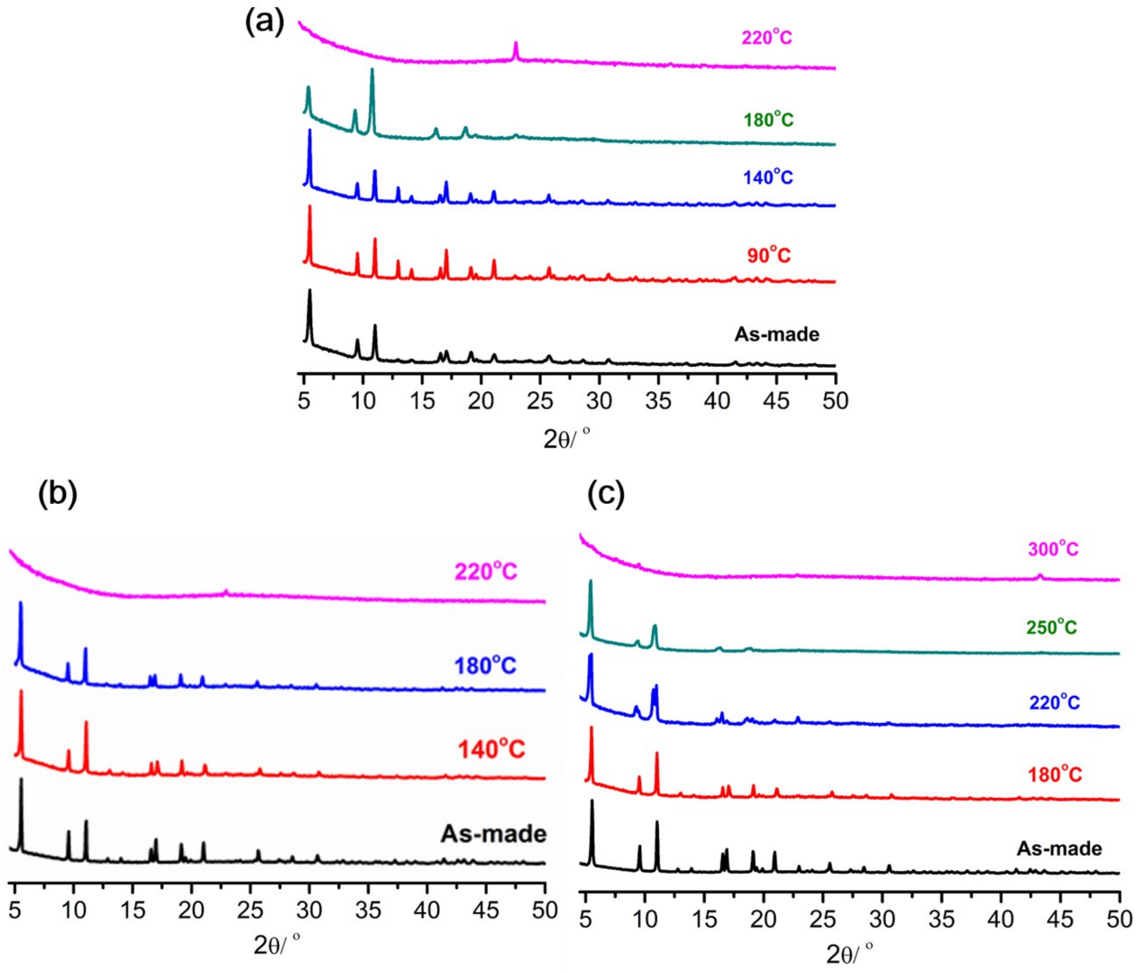


Figure S4. The adsorption isotherms of methanol, H_2O, and ethanol on Cu-L1 (a), Cu-L2 (b), and Cu-L3 (c) at 298 K.

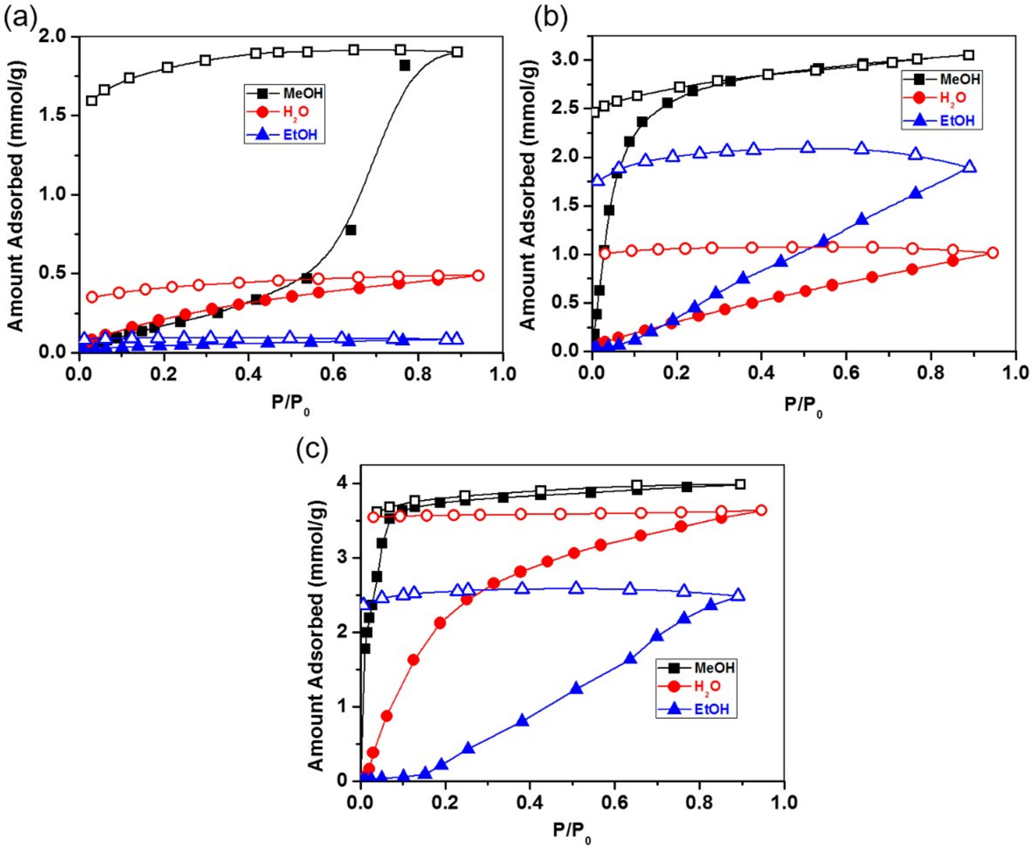


Figure S5. The ^{1}H NMR of Cu-$(L1)_{0.25}(L3)_{0.75}$

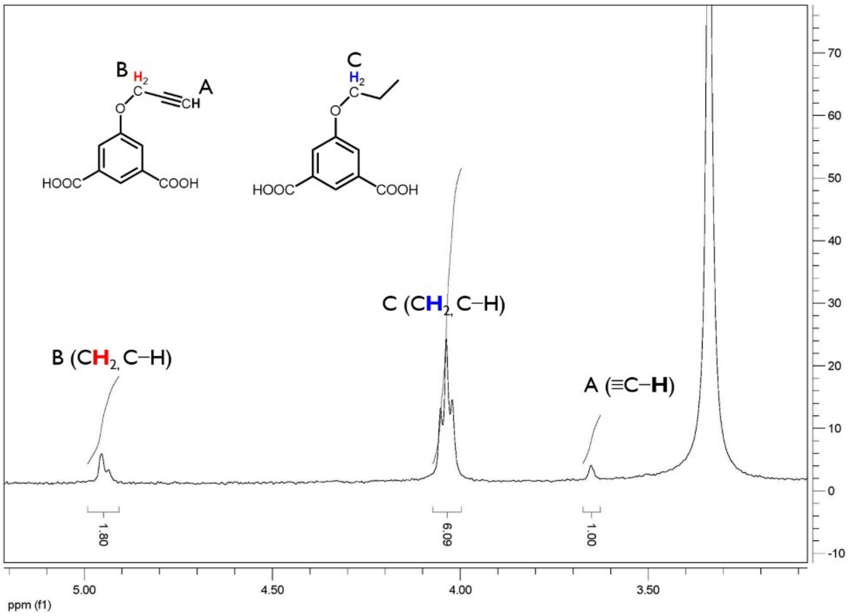
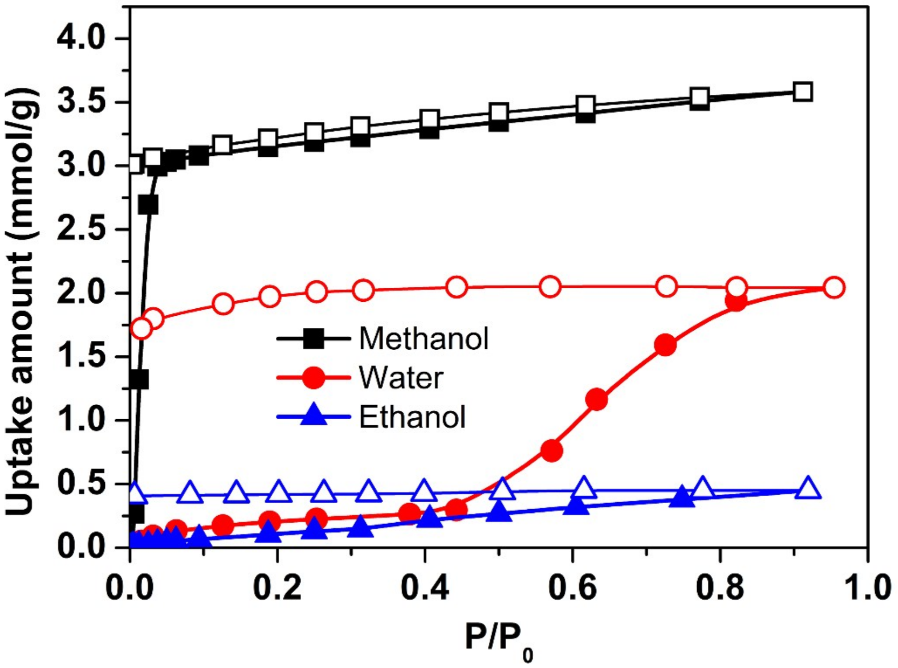


Figure S6. The sorption isotherm of methanol, water, ethanol on Cu(L1)$_{0.25}$(L3)$_{0.75}$ at 298 K



Reference

[1] M. J. Joralemon, R. K. O'Reilly, J. B. Matson, A. K. Nugent, C. J. Hawker and K. L. Wooley, *Macromolecules,* 2005, 38, 5436-5443.

[2] Sheldrick, G. M.; SADABS, Program for Empirical Absorption Correction of Area Detector Data; University of Göttingen: Göttingen, 1996.

[3] (a) Sheldrick, G. M.; SHELXS 97, Program for X-ray Crystal Structure Solution; University of Göttingen, 1997. (b) Sheldrick, G. M. SHELXL-97; Program for the Refinement of Crystal Structures, University of Göttingen, 1997. (c) Sheldrick, G. M. Acta Crystallogr., Sect. A: Found. Crystallogr. 2008, 64, 112-122.