Supporting information for

Copper based pillared-bilayer metal organic framework: synthesis, sorption property and catalytic performance

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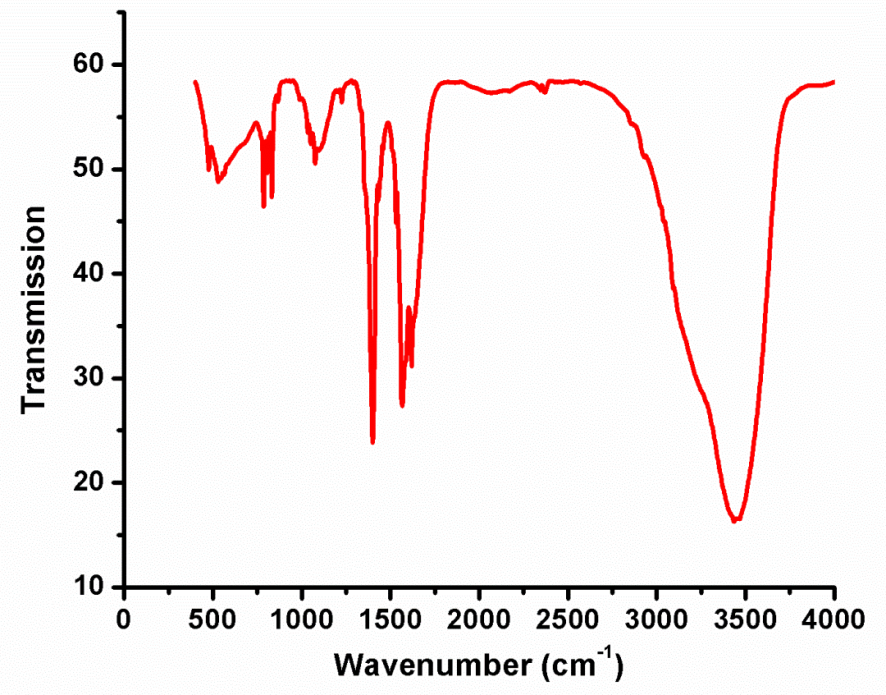


Fig. S1. IR Spectrum of compound **1**.

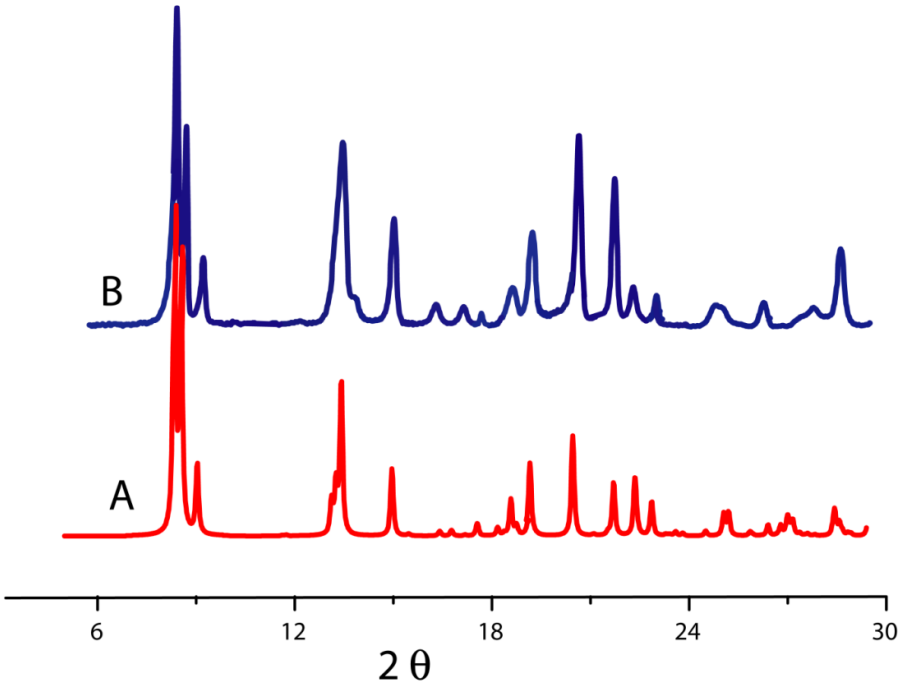


Fig. S2. PXRD patterns of compound **1**, (A) Simulated (magenta) and (B) Assynthesized (navy) sample in bulk amount.

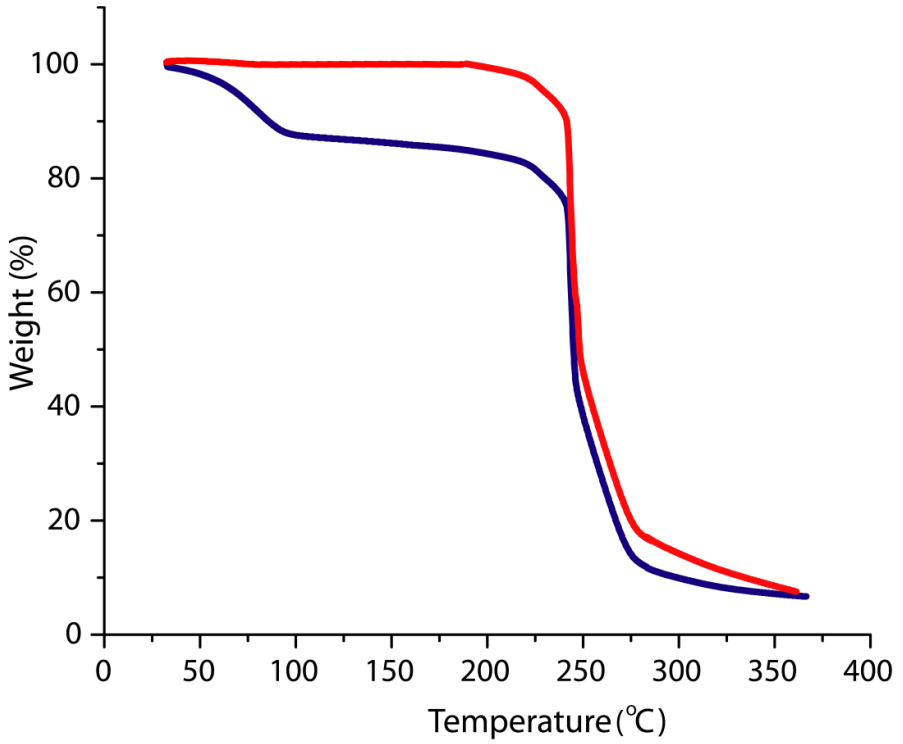


Fig. S3. TGA Plot of compound **1,** assynthesized (navy) and desolvated (red).

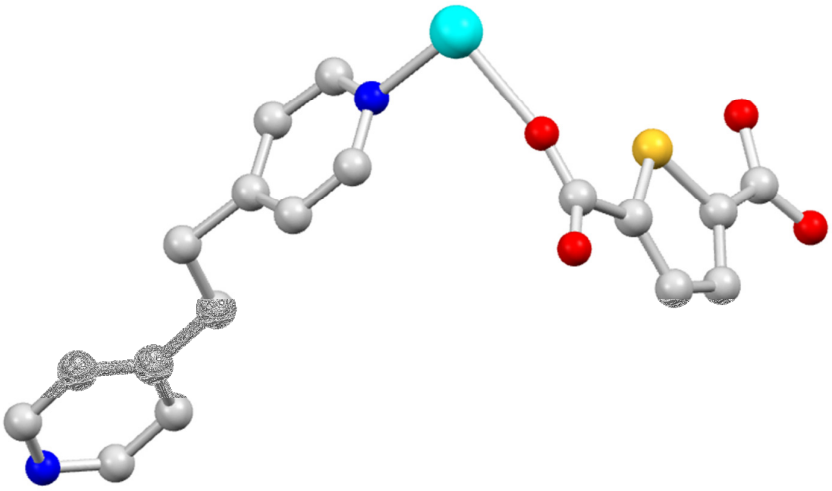


Fig. S4. Asymmetric unit of compond **1**. Colour code oxygen (red), nitrogen (blue), sulpher (yellow), carbon (light gray) and copper (cyan). (Hydrogen atoms and solvated water molecules omitted for clarity).

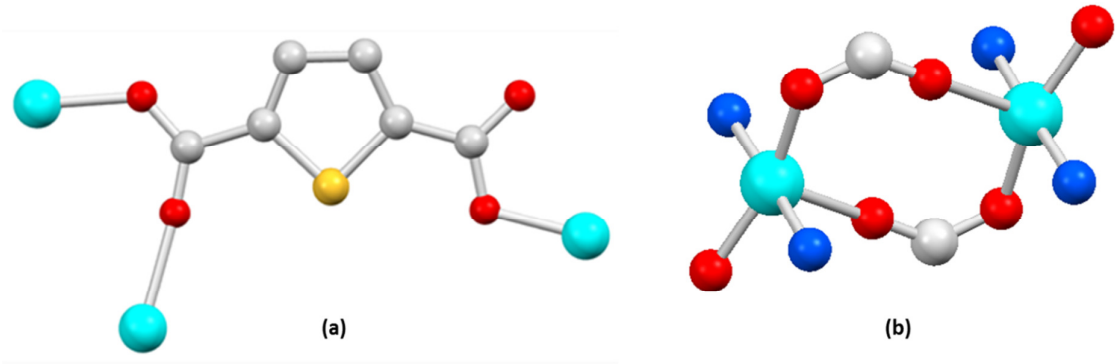


Fig. S5. (a) Cordination modes ((κ^1)-$(\kappa^1$-$\kappa^1)$-μ_3-TDC^{2-}) of tdc ligand with Cu(II) atom. (b) Di nuclear unit of compound **1**. Colour code; same as in Fig. S4.

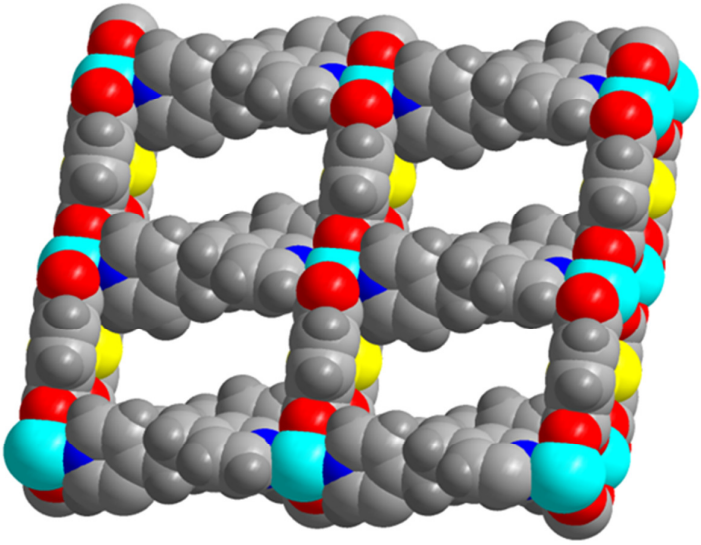


Fig. S6. Space-filling diagram of compound **1** along *bc*-plane**.** Colour code; same as in Fig. S4.

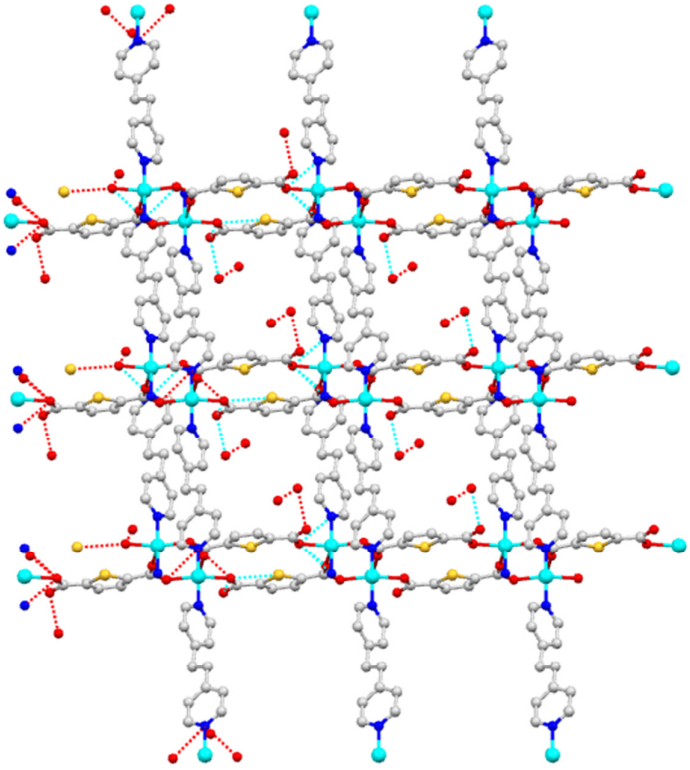


Fig. S7. View along the *a*-axis, showing H-bonding between H_2O and un-coordinate oxygen atom of tdc ligand. Colour code; same as in Fig. S4.

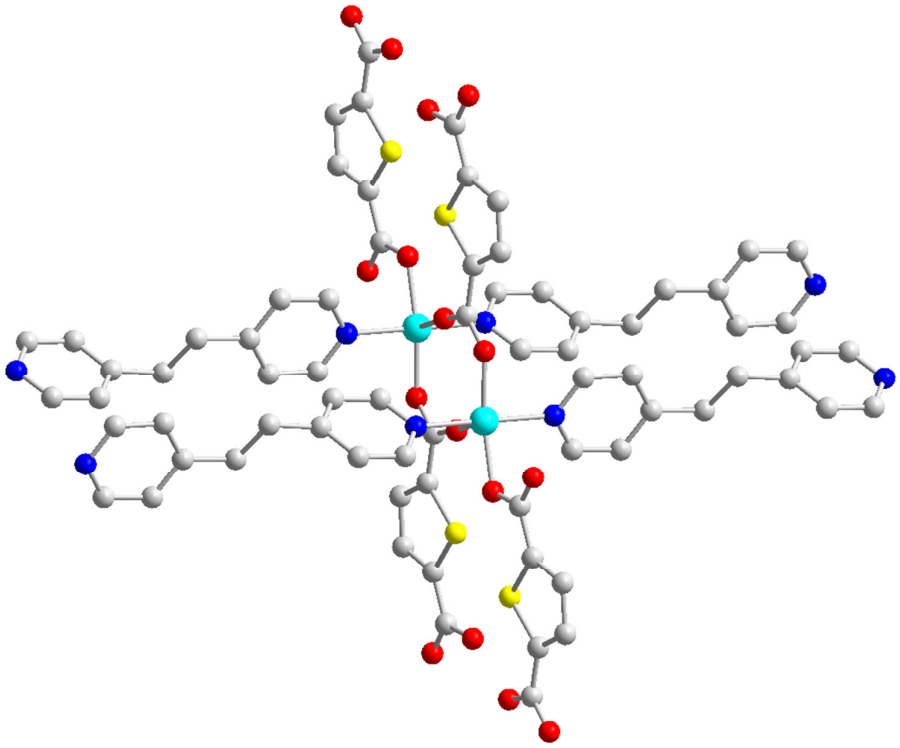


Fig S8. Secondary building unit (SBUs) of compound **1**. Colour code; same as in Fig. S4.

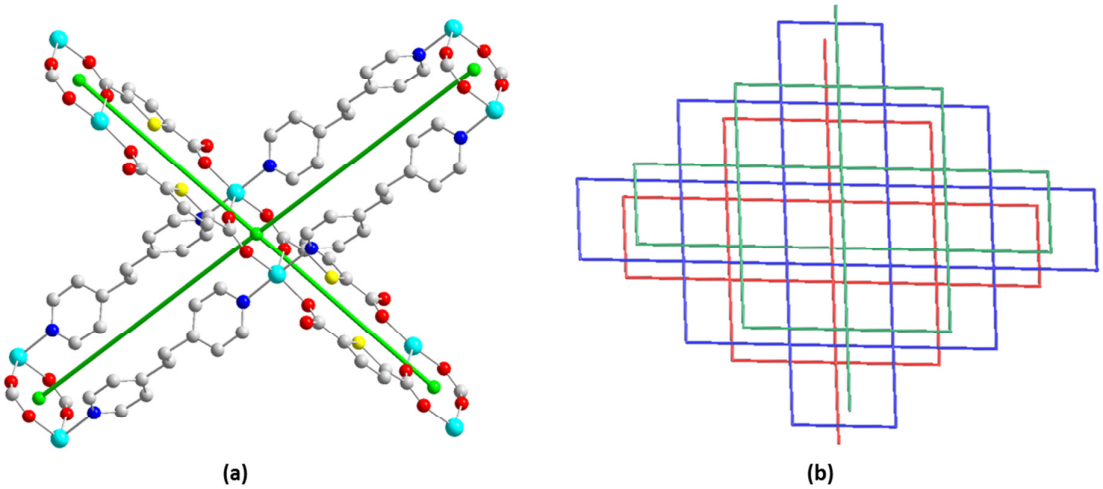


Fig. S9. (a) View of the 4-connected uninodal net (b) topological view ($\{4^4.6^2\}$ sq1/Shubnikob tetragonal plane) of compound **1**. Colour code; same as in Fig. S4.

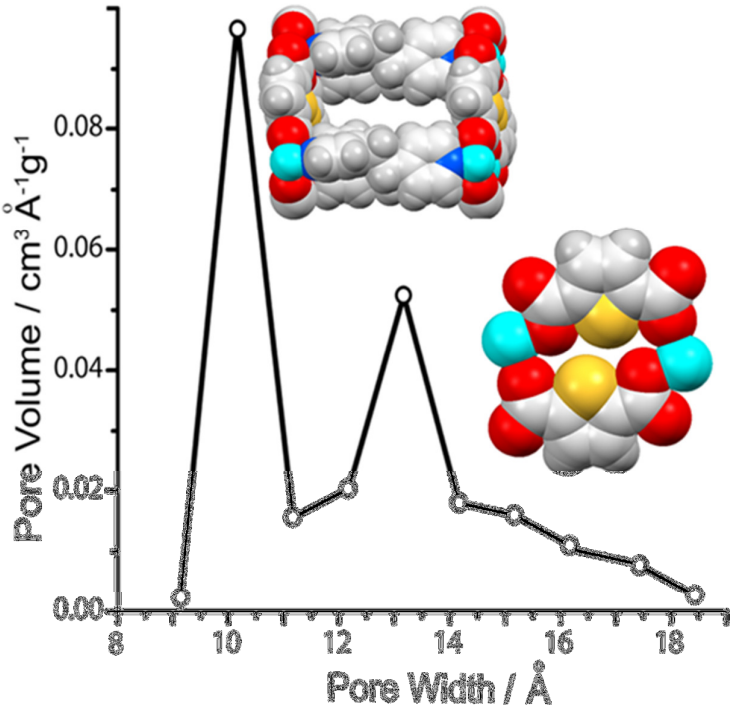


Fig. S10. Pore distribution analysis curve of compound **1** calculated from N_2 adsorption isotherm using the nonlocal density functional theory (NLDFT).

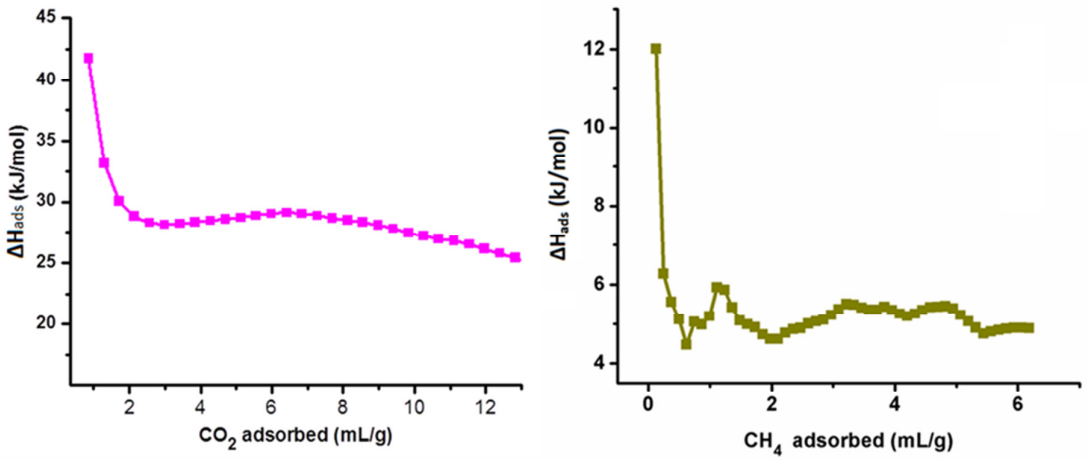


Fig. S11. The adsorption enthalpies of CO_2 and CH_4 calculated at 273 K by using Clausius-Clapeyron equation.

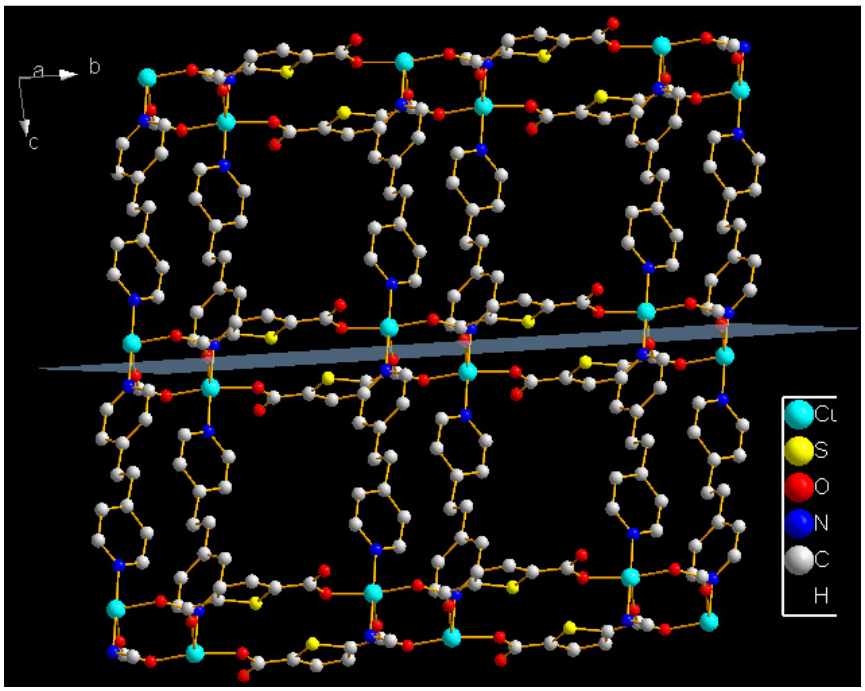


Fig. S12. View along the (001) plane that contains the {Cu-O(tdc) bond} in compound **1.** Colour code; same as in Fig. S4.

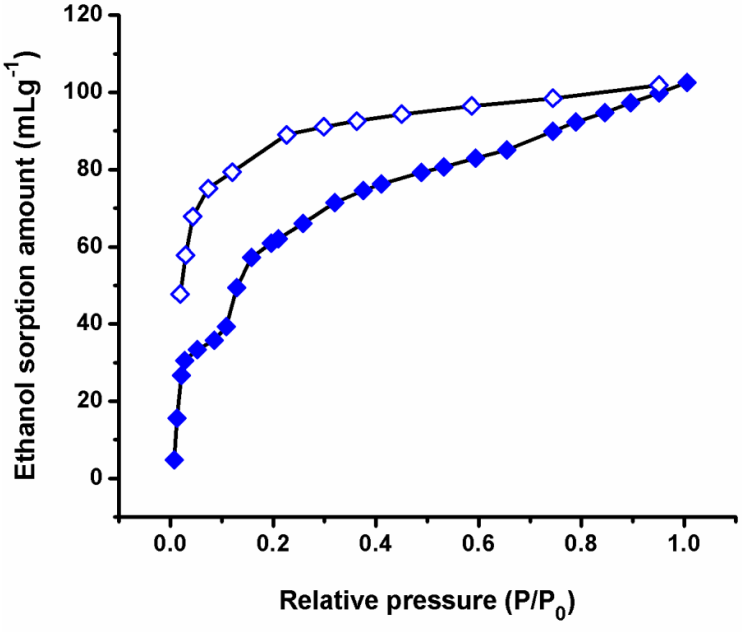


Fig. S13. Vapour sorption isotherms of EtOH.

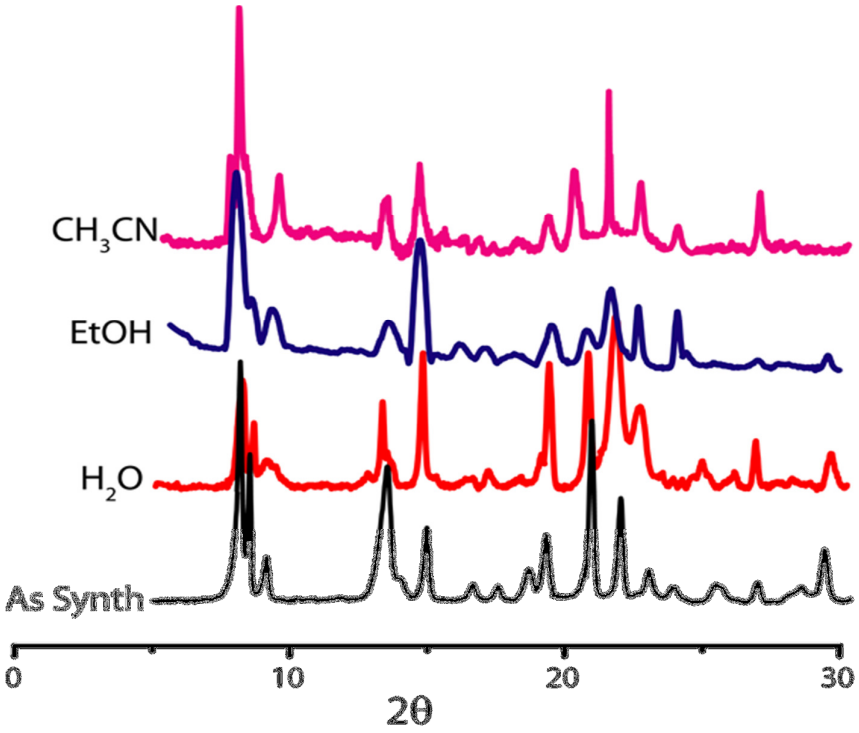


Fig. S14. PXRD patterns of different organic solvents exposed samples after complete adsorption steps.

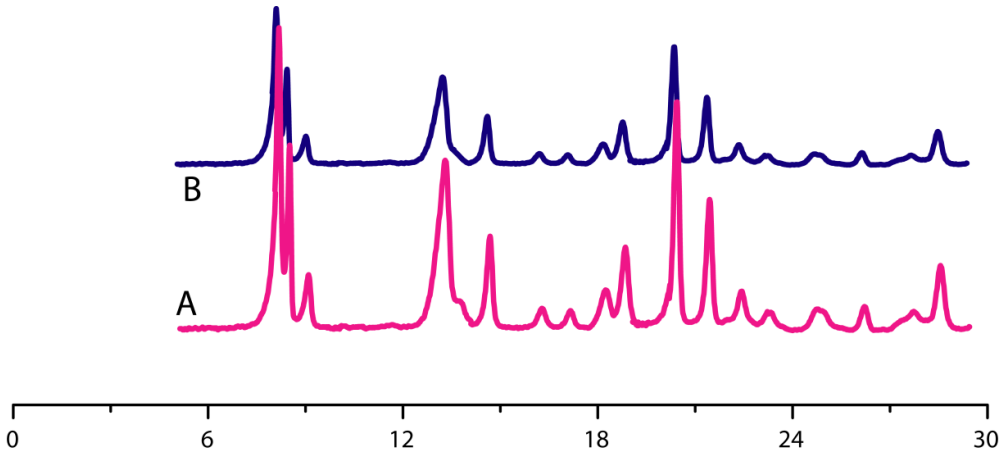


Fig. S15. Powder xrd patterns of compound **1**. The magenta and navy curves were taken, before and after reaction respectively.

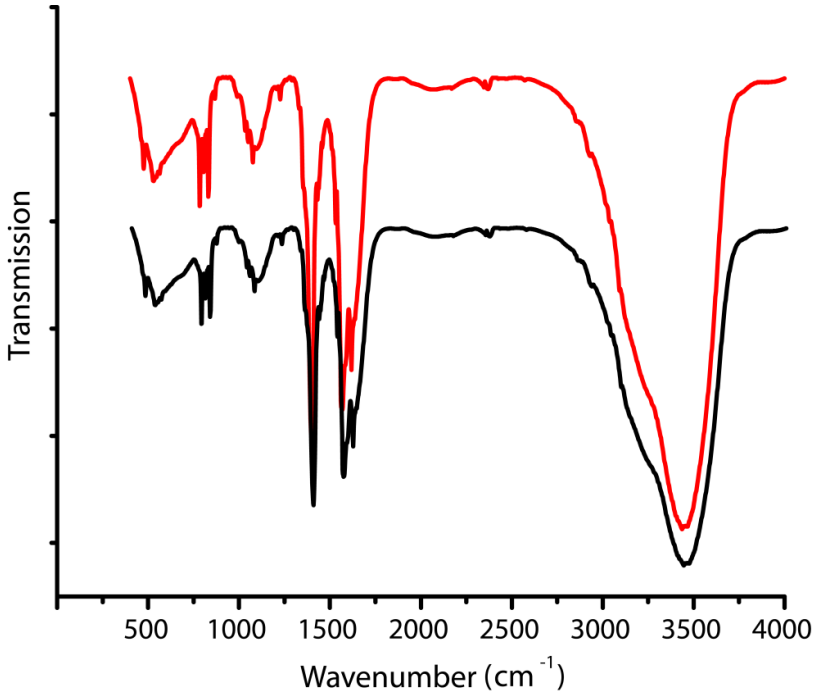
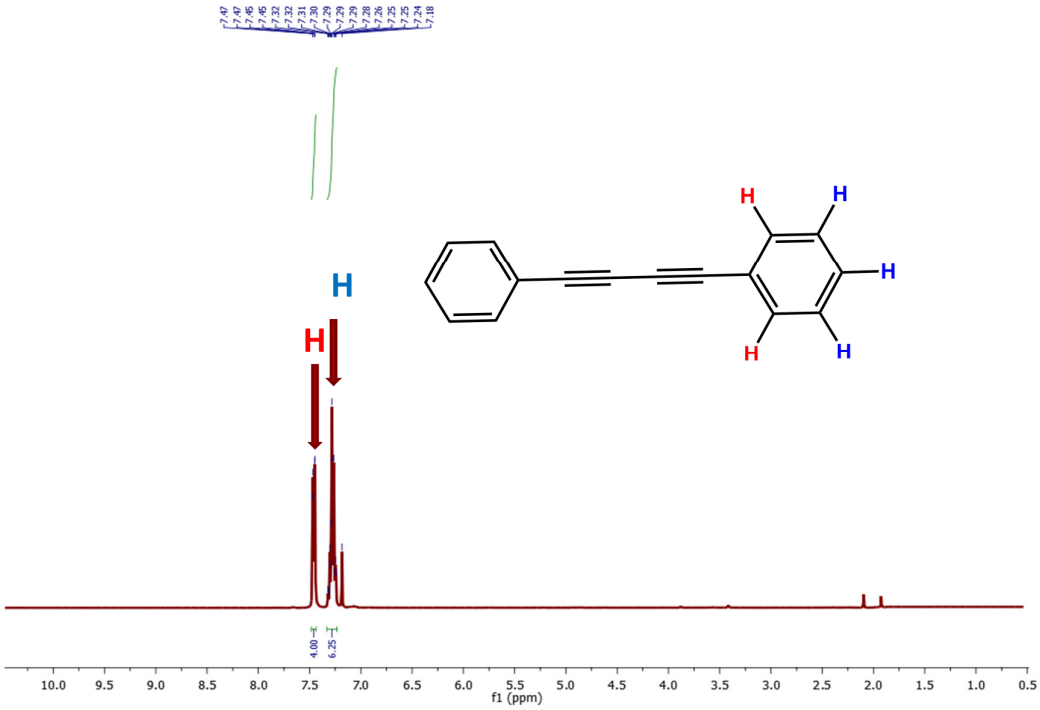
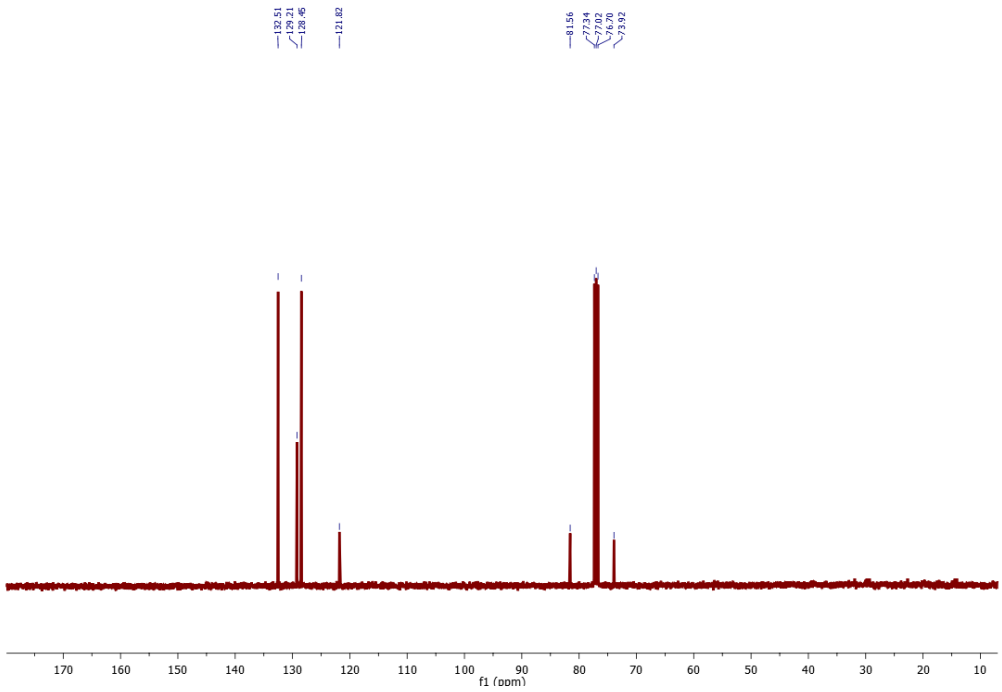


Fig. S16. FTIR spectra of compound **1**.The red and black curves were taken, before and after reaction respectively.

1) 1,4-diphenylbuta-1,3-diyne

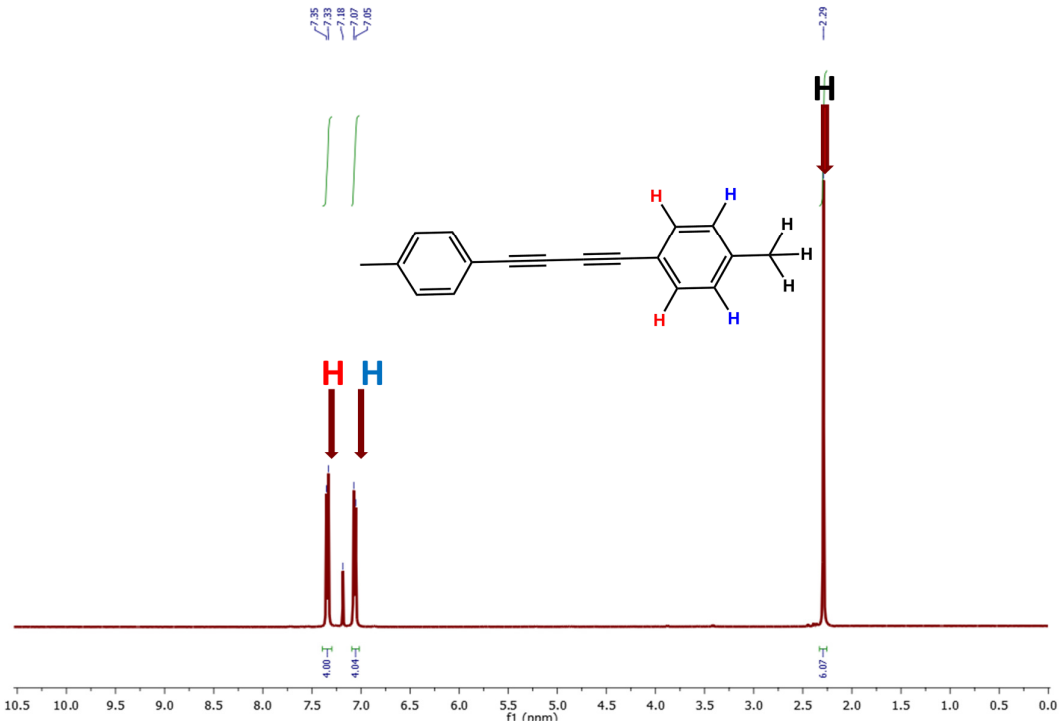


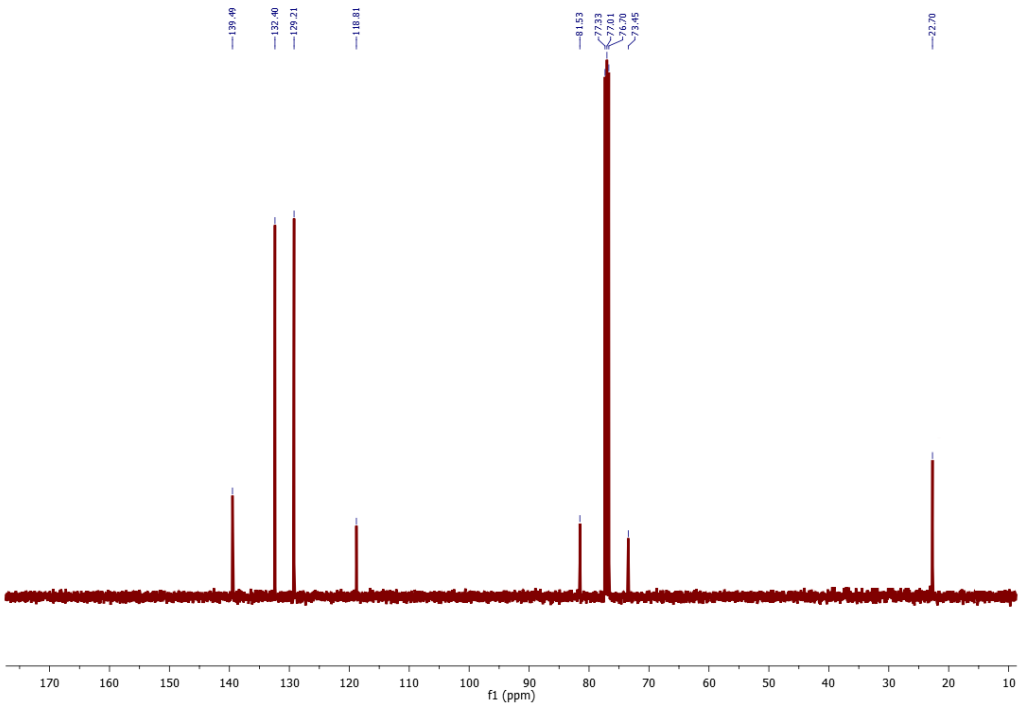


^{1}H NMR (400 MHz, $CDCl_3$): δ =7.46 (dd, 4H), 7.30 (m, 6H), ^{13}C NMR (100MHz, $CDCl_3$): δ = 132.51, 129.91, 128.45, 121.8, 81.56, 73.92.

HRMS (ESI): $C_{16}H_{20}$, $[M+Na]^+$ (202.10) found: 202,25.

2)1,4-di-p-tolylbuta-1,3-diyne

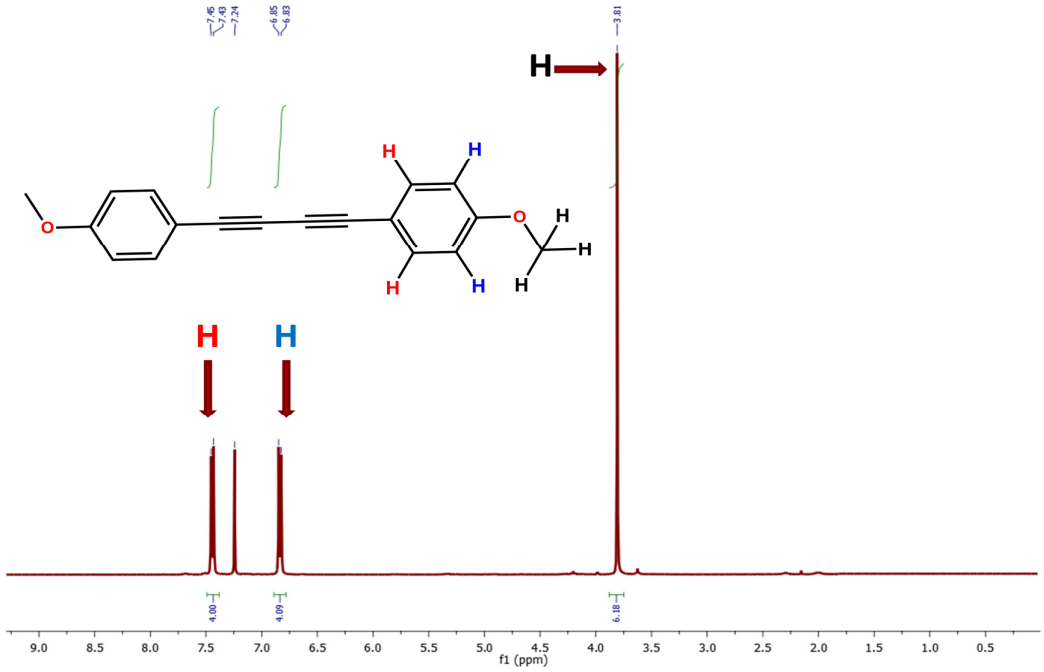


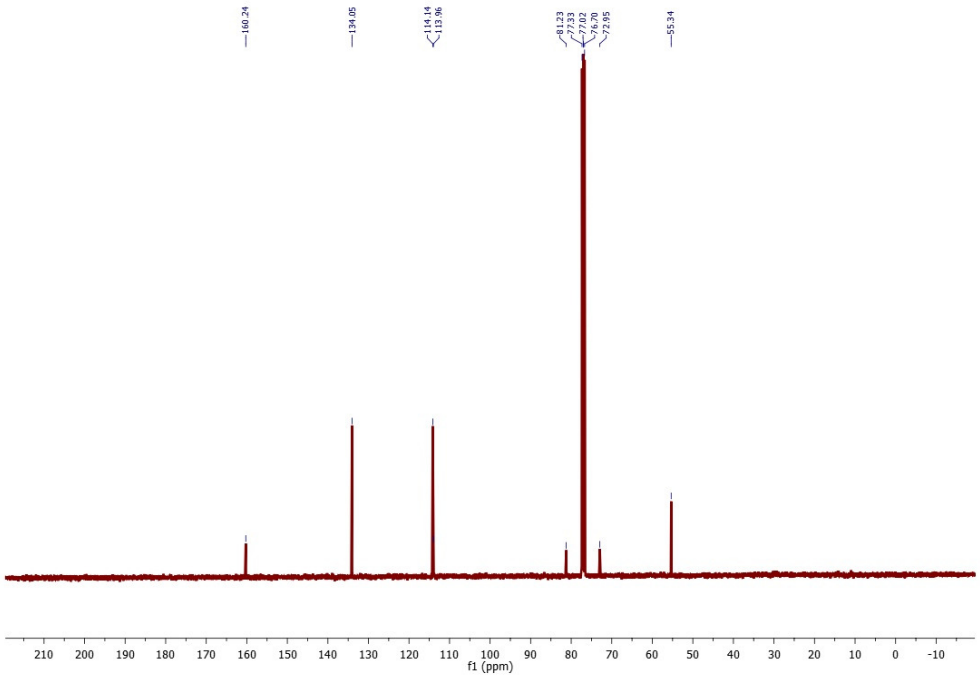


^{1}H NMR (400 MHz, $CDCl_3$): δ =7.34 (d, 4H), 7.06 (d, 4H), 2.29(s, 6H), ^{13}C NMR (100MHz, $CDCl_3$): δ = 139.49, 132.49, 129.21, 118.81, 81.45, 73.45, 22.70.

HRMS (ESI): $C_{18}H_{14}$, $[M+Na]^+$ (230.15) found: 230.30.

3) 1,4-bis(4-methoxyphenyl)buta-1,3-diyne

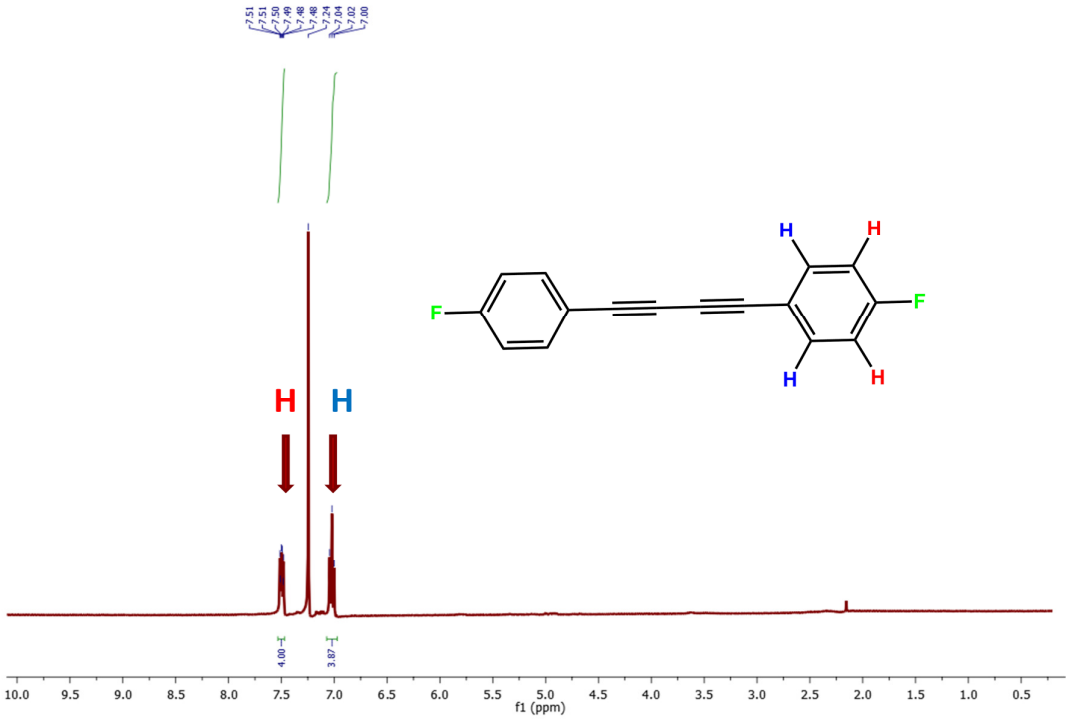


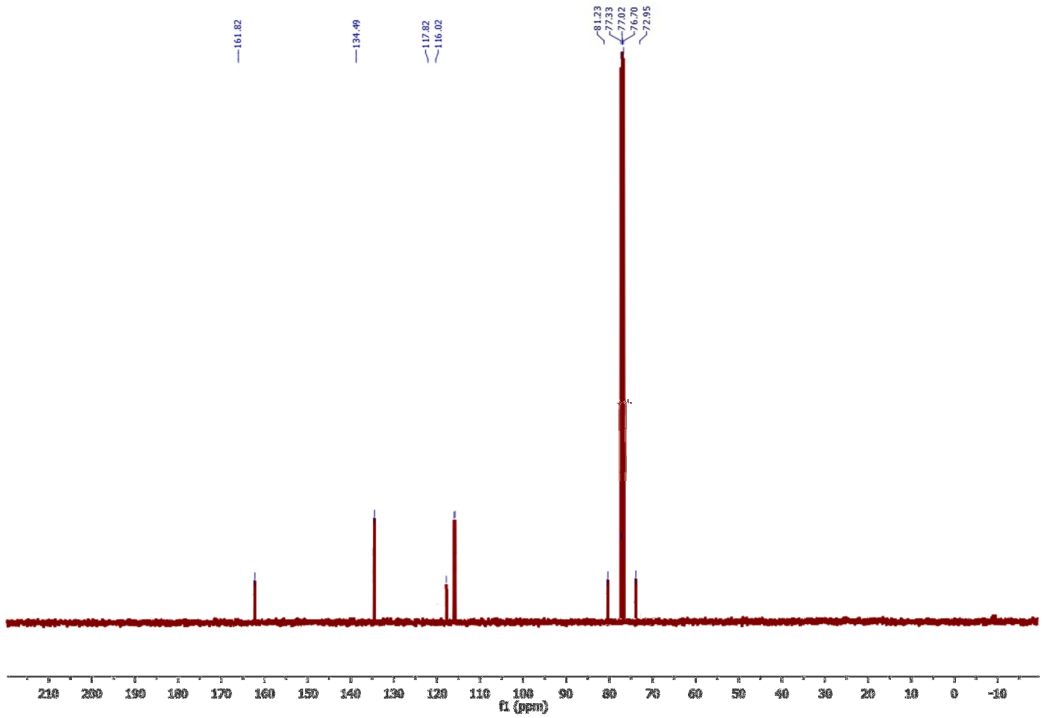


^{1}H NMR (400 MHz, $CDCl_3$): δ =7.44 (d, 4H), 6.84 (d, 4H), 3.86(s, 6H), ^{13}C NMR (100MHz, $CDCl_3$): δ = 160.24, 134.05, 114.14, 113.96, 81.23, 72.95, 55.34.

HRMS (ESI): $C_{18}H_{14}O_2$, $[M+H]^+$ (262.12) found: 262.30.

4) 1,4-bis(4-fluorophenyl)buta-1,3-diyne.





^{1}H NMR (400 MHz, $CDCl_3$): δ =7.50 (t, 4H), 7.03 (t, 4H), ^{13}C NMR (100MHz, $CDCl_3$): δ = 162.10, 134.58, 117.82, 116.02, 81.23, 72.95, 55.34.

HRMS (ESI): $C_{16}H_8F_2$, $[M+H]^+$ (238.12) found: 238.23.

Table S1. Virial graph analysis of compound 1

Temperature (K)	**adsorbate**	**A_0 ln(mol g^{-1} Pa^{-1})**	**Henry's const K_H (mol g^{-1} Pa^{-1})**	**R^2**	**S_{ij}**
273	CO_2	-15.9198	$12.1x10^{-8}$	0.9674	
273	CH_4	-19.40813	$3.7x10^{-9}$	0.8245	32
298	CO_2	-16.97815	$4.2x10^{-8}$	0.9901	
298	CH_4	-20.27246	$1.5x10^{-9}$	0.8153	28

Table S2. Comparison of compound 1 with reported Cu-MOF's.

S.No	**Cu-MOFs**	**CO_2/CH_4 Selectivity**	**Glaser Coupling**
1	[Cu3(BTB^{6-}), Cu3($TATB^{6-}$)][1]	8.6	NO
2	[$Cu_2(HBTB)^{2-}$][2]	12.4	NO
3	[NJU-Bai][3]	14.7	NO
4	[HKUST-1/PSf][4]	21.5	NO
5	[Cu-BPY-HFS][5]	22.5	NO
6	[HKUST-1/PI][6]	27.5	NO
7	[CuTPA MOF][7]	34.9	NO
8	[CuTPA][7]	40	NO
9	[NJU-Bai8][3]	40.8	NO
10	Compound **1**	32	YES

Table S3. Bases screening for the homocoupling of compound 1 with phenylacetylene.

S.No.	Base	Time(h)	(%) Yield(based on NMR analysis)
1	K_2CO_3	6	82
2	Na_2CO_3	8	52
3	$Ca(CO_3)_2$	8	58
4	KOH	7	62
5	NaOH	7	54

Table S4. Selected bond angles and bond lengths of compound 1

Bond angles (°)		Bond lengths. (Å)	
O1-Cu1-N2	93.5(2)	Cu1-O1	2.242(6)
O1-Cu-O2	108.8(2)	Cu1-O2	1.953(6)
O1-Cu1-O3	89.7(2)	Cu1-O3	1.945(6)
O1-Cu1-N1	89.4(2)	Cu1-N1	2.036(5)
N2-Cu1-O2	89.4(3)	Cu1-N2	2.018(6)
N2-Cu1-O3	90.7(3)		

References.

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