Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Oriented Assembly of Copper Metal-Organic Frameworks Membranes as Tandem Catalysts to Enhance C-H Hydroxyalkynylation Reactions with Regiocontrol

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Contents

1. General Method. H_2BBDC (4'-benzoyl-(1,1'-biphenyl)-3,5-dicarboxylic acid) ligand was synthesized with the procedure modified from the literature.[1] Cu foam was treated by 2M HCl, and then dried under vacuum oven overnight. Other reagents and solvents were supplied by commercially available and utilized as received without further purification. Powder X-ray diffraction (PXRD) patterns were collected with a PANalyticalX'Pert PRO diffractometer on monochromated Cu Kα_1 radiation. Elemental analyses (C, H, and N) were recorded using a FLASH EA 1112 elemental analyzer. FT-IR spectra were tested on a Bruker-ALPHA spectrophotometer with KBr pellets in 400-4000 cm^{-1} region. ^{1}H spectra were recorded with Bruker Avance-400 spectrometers. Inductively coupled plasma atomic emission spectrometry (ICP-AES) analyses were carried out using a Thermo Scientific ICP 6000 spectrometry. The gas sorption isotherms of coordination polymers **1-1a** was collected on a Micromeritics ASAP 2420 surface area and pore size analyzer under ultrahigh vacuum in a clean system, with a diaphragm and turbo pumping system. Ultrahigh-purity-grade (> 99.999%) N_2 gas was applied in all adsorption measurements. The experimental temperature was maintained by liquid nitrogen (77 K). Prior to measurement, bulk sample of **1** was washed thoroughly with EtOH three times, and placed under vacuum. The samples were placed in a DB-80 simplex pump and purged 10 times with CO_2 about 30 min. After that period of time the pressure and temperature was raised over the arrest point of CO_2, forming supercritical CO_2 (SC-CO_2). The resulting SC-CO_2 in the column was gradually released within a time frame of 12 h.

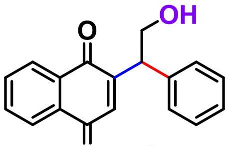
2. Synthesis

Synthesis of [Cu(BBDC)(azobpy)(H_2O)]$_n$ (1). H_2BBDC (0.05 mmol, 0.017 g), CuCN (0.2 mmol, 0.018 g), azobpy (0.03 mmol, 0.006g, azobpy = 4,4′-azopyridine), 3 mL DMF, 4 mL H_2O, and HNO_3 (3 drops) were placed in a bottle (10 mL). The bottle was heated at 100 °C for 2 days, the yellow green crystals of **1** were provided with 51 % yield (depended on Cu). Analysis calculated (%) for $C_{31}H_{22}CuN_4O_6$: C, 61.03 %; H, 3.63 %; N, 9.18 %. Found: C, 61.05 %; H, 3.59 %; N, 9.22 %. IR: 3426 (s)， 2930 (vw), 1605 (vs), 1510 (vw), 1472 (m), 1386 (vs), 1293 (w), 1127 (m), 1023 (vw), 919 (vw), 845 (w), 780 (m), 726 (w).

Synthesis of MOFs-based membranes 1a on Cu foam. In a typical synthesis, Cu foam and PVA poly(vinyl alcohol) (PVA, 1788, 0.1 g) were mixed in 1 mL DMF and sonicated for 30 min in a 10 mL vial. Then the solution of CuCN (0.2 mmol, 0.018 g, 1 mL) was added into the above solution and sonicated for 20 min. Subsequently, the H_2BBDC (0.05 mmol, 0.017 g), azobpy (0.03 mmol, 0.006 g), and HNO_3 (3 drops) in 1 mL DMF and 4 mL H_2O were added and further sonicated for 30 min. Finally, the mixture solution in the bottle heated at 100 °C for 2 days. The Cu foam was extracted, washed (H_2O and EtOH), and dried under vacuum oven overnight.

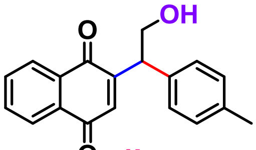
3. Procedure for the 1 or 1a-catalyzed three-component C-H hydroxyalkynylation tandem reactions.

General procedure for the 1a-catalyzed three-component C-H hydroxyalkynylation tandem reactions. To a mixture of H_2O (2 mL), acetone (2 mL) and acetonitrile (2 mL) in a seal tube was added naphthoquinone (**2**, 1.0 mmol), $(NH_4)_2S_2O_8$ (2.0 mmol), alkenes (**3a-g**, 2.0 mmol), and catalysts **1a** (0.1 mmol, 0.1 equiv based on copper ions) at room temperature. Then, the mixture was heated at 110 ºC for 4 h. The reactions were cooled to room temperature and extracted with ethyl acetate. Organic layers were combined, dried with $MgSO_4$, and concentrated under reduced pressure to remove the solvent. The residue was purified by flash chromatography using ethyl acetate/petroleum ether as eluent to provide the desired products.



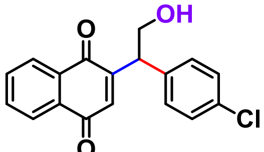
4a

2-(2-Hydroxy-1-phenylethyl)naphthalene-1,4-dione. After column chromatography (PE/EtOAc = 4/1) 253 mg (91%) of a light yellow oil were obtained. This compound had been reported.[2] ^1H NMR (400 MHz, $CDCl_3$) δ: 8.03-8.10 (m, 2H), 7.70-7.74 (m, 2H), 7.30-7.36 (m, 4H), 6.93 (d, *J* = 1.0 Hz, 1H), 4.57 (t, *J* = 4.0 Hz, 1H), 4.13 (d, *J* = 8.0 Hz, 2H), 1.65 (s, 1H).



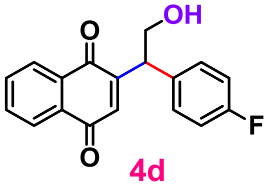
4b

2-(2-Hydroxy-1-(p-tolyl)ethyl)naphthalene-1,4-dione. After column chromatography (PE/EtOAc = 4/1) 264.8 mg (91%) of a light yellow oil were obtained. This compound had been reported.[2] ^1H NMR (400 MHz, $CDCl_3$) δ: 8.03-8.11 (m, 2H), 7.64-7.77 (m, 2H), 7.12-7.22 (m, 4H), 6.92 (d, *J* = 8.0 Hz, 1H), 4.53 (t, *J* = 4.0 Hz, 1H), 4.10 (d, *J* = 1.0 Hz, 2H), 2.32 (s, 1H), 1.83 (s, 1H).



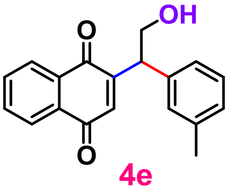
4c

2-(1-(4-Chlorophenyl)-2-hydroxyethyl)naphthalene-1,4-dione. After column chromatography (PE/EtOAc = 3/1) 277.7 mg (89%) of a light yellow oil were obtained. This compound had been reported.[2] ^{1}H NMR (400 MHz, CDCl$_3$) δ: 8.02-8.07 (m, 2H), 7.68-7.76 (m, 2H), 7.27-7.33 (m, 4H), 6.91 (d, *J* = 1.0 Hz, 1H), 4.52 (t, *J* = 4.0 Hz, 1H), 4.09-4.12 (m, 2H), 1.80 (s, 1H).



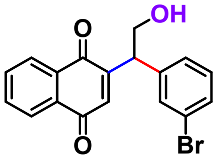
4d

2-(1-(4-Fluorophenyl)-2-hydroxyethyl)naphthalene-1,4-dione. After column chromatography (PE/EtOAc = 3/1) 260.5 mg (88%) of a light yellow oil were obtained. This compound had been reported.[2] ^{1}H NMR (400 MHz, CDCl$_3$) δ: 7.99-8.06 (m, 2H), 7.68-7.76 (m, 2H), 7.28-7.32 (m, 2H), 7.00-7.05 (m, 2H), 6.90 (d, *J* = 1.0 Hz, 1H), 4.54 (t, *J* = 4.0 Hz, 1H), 4.06-4.13 (m, 2H), 1.85 (s, 1H).



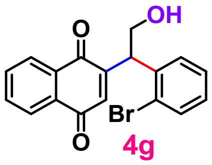
4e

2-(2-Hydroxy-1-(m-tolyl)ethyl)naphthalene-1,4-dione. After column chromatography (PE/EtOAc = 5/1) 257 mg (88%) of a light yellow oil were obtained. This compound had been reported.[2] ^{1}H NMR (400 MHz, CDCl$_3$) δ: 8.09-8.03 (m, 2H), 7.74-7.69 (m, 2H), 7.25-7.21 (m, 1H), 7.14-7.10 (m, 2H), 7.08 (d, *J* = 8.0 Hz, 1H), 6.93 (d, *J* = 1.0 Hz, 1H), 4.53 (t, *J* = 8.0 Hz, 1H), 4.10 (d, *J* = 8.0 Hz, 2H), 2.32 (s, 3H), 1.69 (s, 1H).



4f

2-(1-(3-Bromophenyl)-2-hydroxyethyl)naphthalene-1,4-dione. After column chromatography (PE/EtOAc = 4/1) 306.2 mg (86%) of a light yellow oil were obtained. This compound had been reported.[2] ^{1}H NMR (400 MHz, CDCl$_3$) δ: 8.08-8.03 (m, 2H), 7.75-7.70 (m, 2H), 7.46 (t, *J* = 4.0 Hz, 1H), 7.41-7.38 (m, 1H), 7.29-7.27 (m, 1H), 7.21 (t, *J* = 4.0 Hz, 1H), 6.92 (d, *J* = 1.0 Hz, 1H), 4.52 (t, *J* = 8.0 Hz, 1H), 4.14-4.07 (m, 2H), 1.82 (s, 1H).



4g

2-(1-(2-Bromophenyl)-2-hydroxyethyl)naphthalene-1,4-dione. After column chromatography (PE/EtOAc = 4/1) 306.2 mg (86%) of a light yellow oil were obtained. This compound had been reported.[2] ^{1}H NMR (400 MHz, CDCl$_3$) δ: 8.07-8.11 (m, 1H), 8.04-8.06 (m, 1H), 7.71-7.74 (m, 2H), 7.59-7.62 (m, 1H), 7.40-7.42 (m, 1H), 7.30-7.42 (m, 1H), 7.13-7.18 (m, 1H), 6.75 (s, 1H), 4.98 (t, J = 4.0 Hz, 1H),4.10-4.14 (m, 2H), 1.83 (s, 1H).

4. Crystal Data Collection and Refinement. The data of **1** was tested on a Bruker D8 VENTURE diffractometer (Mo-*K*α, λ = 0.71073 Å). The integration of the diffraction data, as well as the intensity corrections for the Lorentz and polarization effects, were performed using the SAINT program.[3] SADABS program was used to performed the semiempirical absorption correction.[4] The structure was solved by immediate methods and refined with a fullmatrix least-squares technique depended on F^2 with the SHELXL crystallographic software package.[5] All H atoms expect for those of H_2O molecules were defined at calculated positions and refined isotropic displacement parameters with riding model. Crystallographic data for **1** have been deposited at the Cambridge Crystallographic Data Centre with CCDC reference number 1953571.

Table S1. Crystallographic data and structure refinement details for complex**1**[a,b]

Complex	**1**	**1** in $(NH_4)_2S_2O_8$ solution
Formula	$C_{31}H_{22}CuN_4O_6$	$C_{31}H_{22}CuN_4O_6$
fw	610.07	610.07
T/K	293(2)	293(2)
λ (Mo K), Å	0.71073	0.71073
Crystsyst	monoclinic	monoclinic
Space group	*P2₁/c*	*P2₁/c*
a (Å)	11.8376(2)	11.8362(4)
b (Å)	19.0862(4)	19.8015(8)
c (Å)	11.5994(3)	11.5974(4)
β(°)	93.465(10)	93.475(2)
V (Å^3)	2714.6.4(10)	2713.14(17)
Z	4	
D_{calcd}.(g·cm^{-3})	1.493	
Reflections collected /unique	30714 / 5032	
abs coeff/mm^{-1}	0.858	
F(000)	1252	
θ (°)	2.60-25.50	
GOF	1.054	
R_1(I>2sigma(I))[a]	0.0697	
wR_2(I>2sigma(I))[b]	0.1191	

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

Table S2. Selected Bond Lengths (Å) and Bond Angles (deg) for **1**.

Complex **1**			
Cu(1)-O(2)#1	1.951(3)	Cu(1)-N(1)	2.028(4)
Cu(1)-O(5)	1.997(3)	Cu(1)-N(4)	2.033(4)
Cu(1)-O(6)	2.291(3)	O(5)-Cu(1)-N(1)	89.40(17)
O(2)#1-Cu(1)-O(5)	163.65(15)	O(5)-Cu(1)-N(4)	88.16(16)
O(2)#1-Cu(1)-O(6)	101.03(14)	N(1)-Cu(1)-O(6)	94.75(17)
O(2)#1-Cu(1)-N(1)	90.03(17)	N(1)-Cu(1)- N(4)	174.94(18)
O(2)#1-Cu(1)-N(4)	91.06(16)	N(4)-Cu(1)-O(6)	89.89(16)
O(5)-Cu(1)-O(6)	9530(14)		
Symmetry codes: #1 = 1-x, 1/2+y, 3/2-z			

5. Additional structure figures and characterizations of Cu-complexes 1-1a.

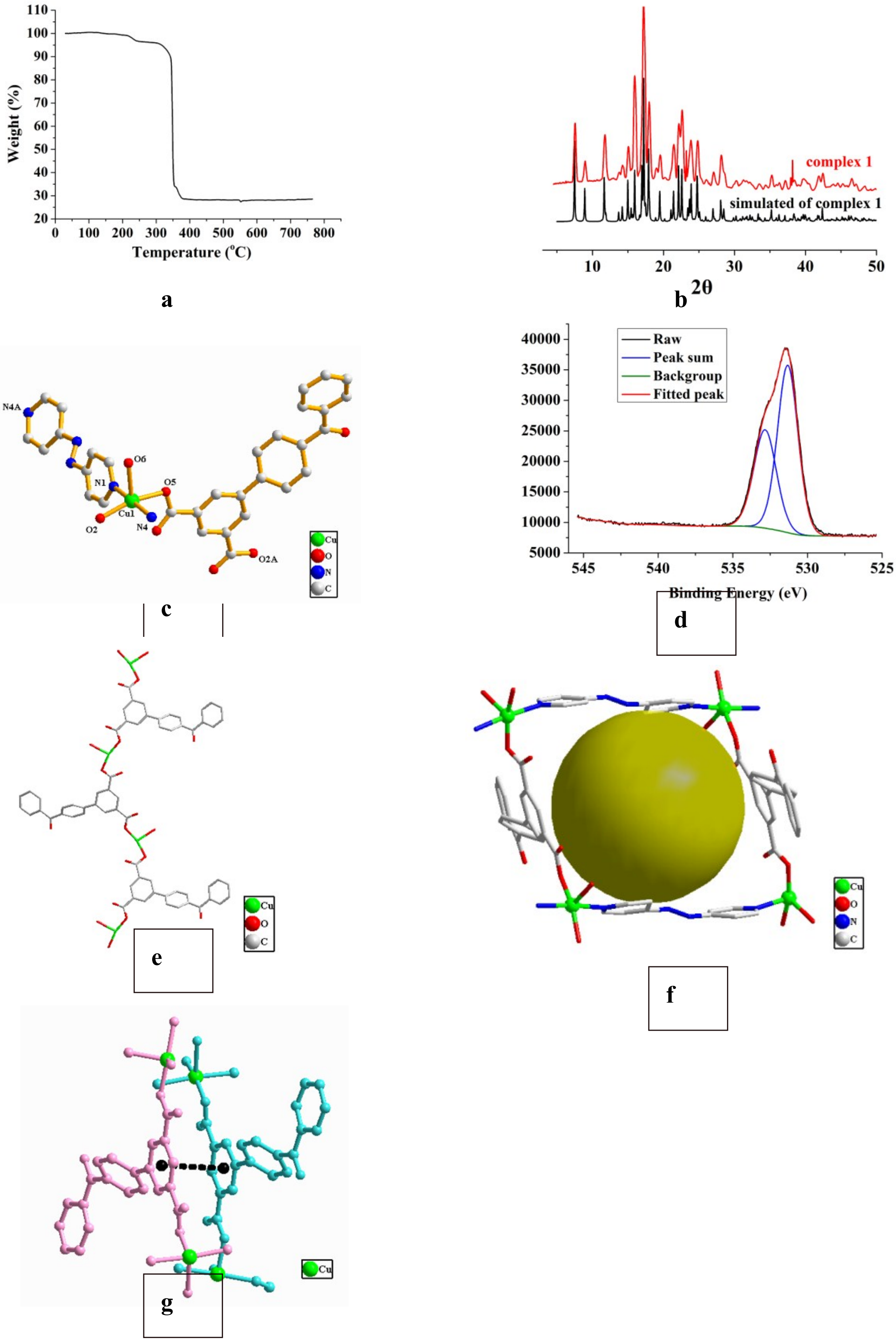


Figure S1. Crystal structure of **1**: (a) The TG curve of **1**. (b) PXRD patterns of **1**. (c) Coordination environments of the Cu^{II} ions. Hydrogen atoms are omitted for clarity. (d) The XPS of O atom in **1**. (e) The monodetate coordination mode to connect the Cu ions, producing a 1D chain structure. (f) Rhombus windows of **1**. (g) The π···π interactions between the adjacent carbxoyl benzene.

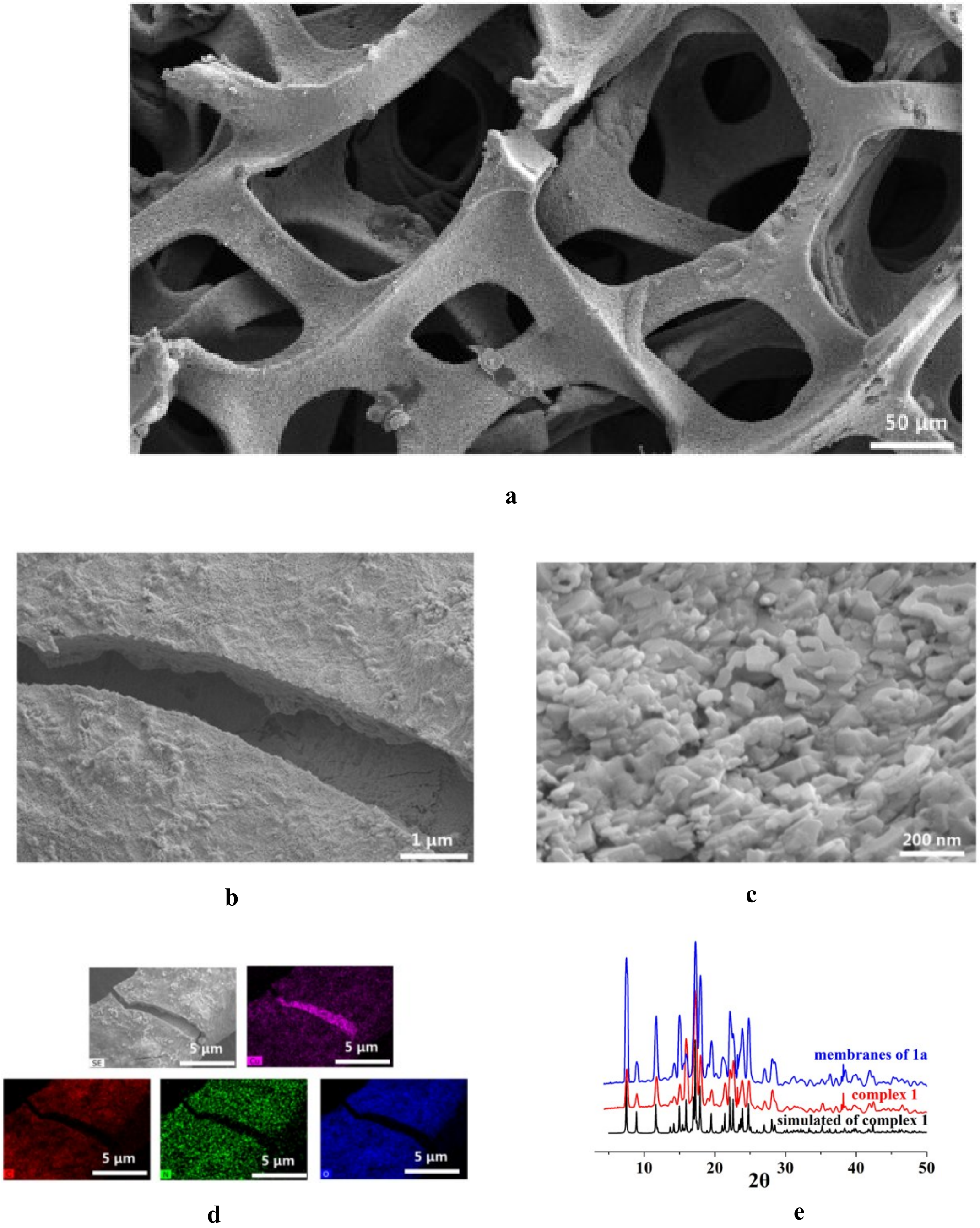


Figure S2. MOF-based membranes of **1a**: (a, b) SEM images of MOFs-based membranes **1a** on Cu foam with various magnifications. (c) Surface SEM images of membranes **1a** on Cu foam with various magnifications. (d) Elemental mappings of the related elements (Cu, O, N, and C) in **1a**. (e) PXRD patterns of **1a.**

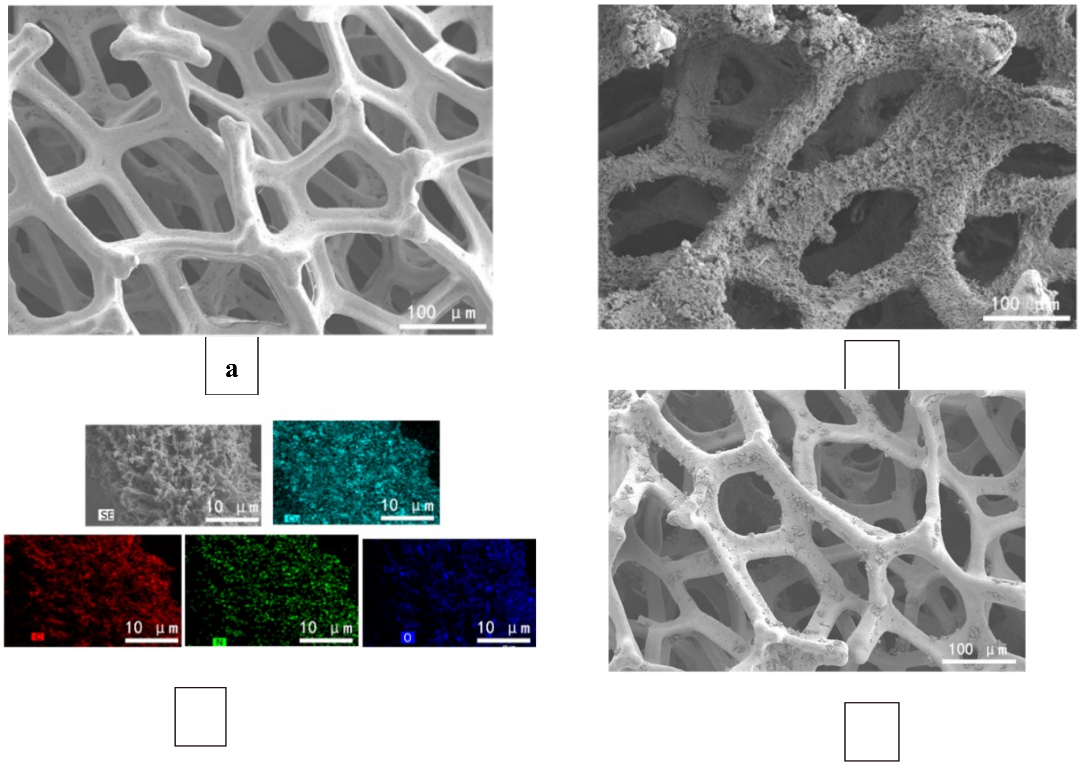


Figure S3. The influence of PVA on Cu foam: (a) SEM image of Cu foam in PVA after reaction 2 days under 100 ºC. (b) SEM image of Cu foam in PVA/CuCN after reaction 2 days under 100 ºC. (c) Elemental mappings of the related elements (Cu, O, N, and C) on Cu foam in PVA/CuCN after reaction 2 days under 100 ºC. (d) SEM image of Cu foam in CuCN/Cu foam after reaction 2 days under 100 ºC.

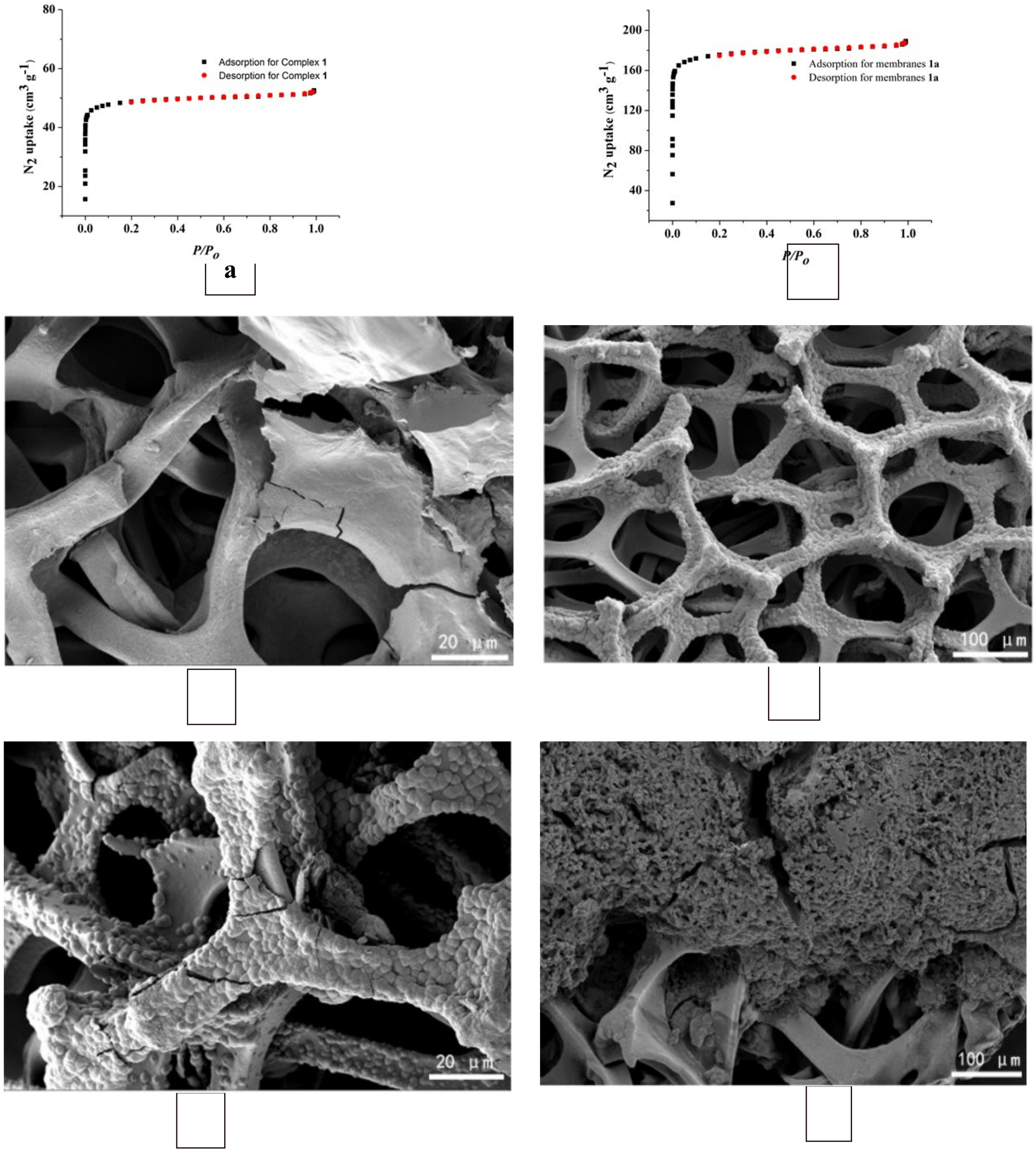


Figure S4. MOF-based membranes of **1a**: (a, b) N_2 adsorption isotherm of **1** and **1a** at 77 K. (c) SEM images of MOFs-based membranes **1a** on Cu foam with PVA was 0.05 g. (d) SEM images of MOFs-based membranes **1a** on Cu foam with PVA was 0.15 g. (e) SEM images of MOFs-based membranes **1a** on Cu foam with PVA was 0.20 g. (f) SEM images of MOFs-based membranes **1a** on Cu foam with PVA was 0.30 g.

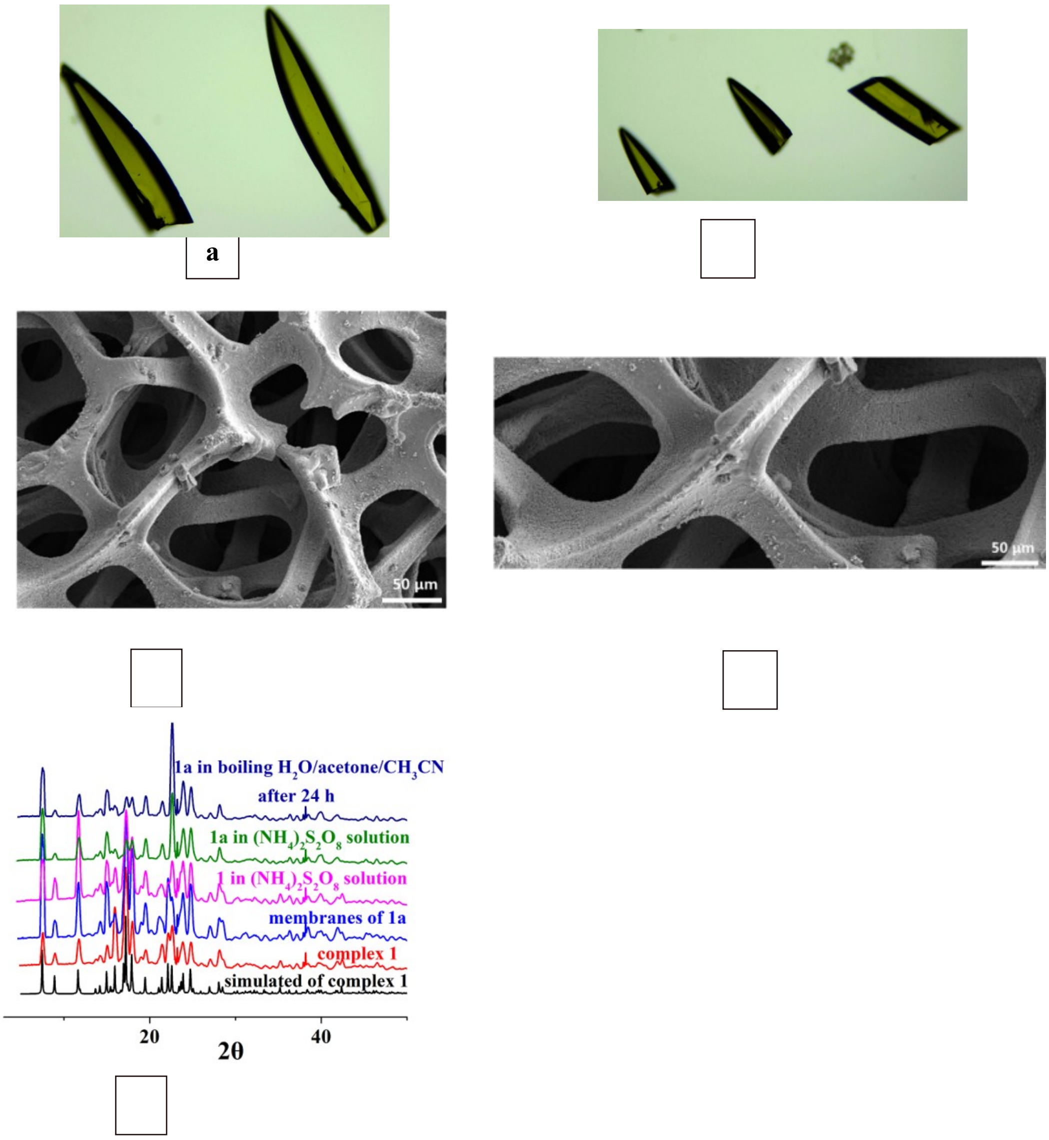
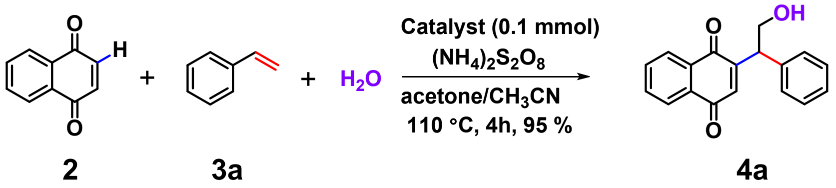


Figure S5. (a, b) The samples of **1** in H_2O/acetone/CH_3CN and $(NH_4)_2S_2O_8$ aqueous solution after 24 h, respectively. (c, d) SEM images of MOFs-based membranes **1a** in H_2O/acetone/CH_3CN and $(NH_4)_2S_2O_8$ aqueous solution after 24 h, respectively. (e) PXRD patterns of **1** and **1a** in H_2O/acetone/CH_3CN and $(NH_4)_2S_2O_8$ aqueous solution after 24 h, respectively.

6. Optimization of reaction conditions for three-component C-H tandem hydroxyalkynylation reactions

Table S3. Optimization of reaction conditions for synthesizing of hydroxyalkynylation naphthoquinones skeletons via tandem reactions.[a]



Entry	Catalyst (mmol)	Temperature/°C	Solvent	Yield (%) of **4a**[b]
1	**1a** (0.1)	110	CH_3CN	41
2	**1a** (0.1)	110	acetone	46
3	**1a** (0.1)	110	THF	31
4	**1a** (0.1)	110	DCE	n.o.[c]
5	**1a** (0.1)	110	$CHCl_3$	n.o.[c]
6	**1a** (0.1)	110	Et_2O	36
7	**1a** (0.1)	110	DCM	n.o.[c]
8	**1a** (0.1)	110	acetone/CH_3CN	91
9	**1a** (0.01)	110	acetone/CH_3CN	47
10	**1a** (0.05)	110	acetone/CH_3CN	71
11	**1a** (0.15)	110	acetone/CH_3CN	94
12	**1a** (0.20)	110	acetone/CH_3CN	97
13	**1a** (0.1)	25	acetone/CH_3CN	< 10
14	**1a** (0.1)	60	acetone/CH_3CN	21
15	**1** (0.1)	110	acetone/CH_3CN	62
16	$Cu(NO_3)_2$	110	acetone/CH_3CN	23
17	Cu foam (0.1)	110	acetone/CH_3CN	n.o.

[a] Reaction conditions: naphthoquinone (1.0 mmol), styrene (2.0 mmol), catalyst (0.10 mmol), $(NH_4)_2S_2O_8$ (2.0 mmol), H_2O (2 mL), acetone (2 mL) and acetonitrile (2 mL), 110 ºC (4h). [b] Isolated yield of the product after 4h. [c] Not observed = n.o.

7. The change of 1a during the reaction process

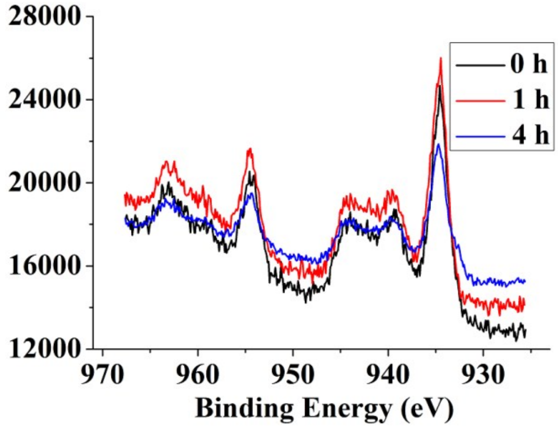
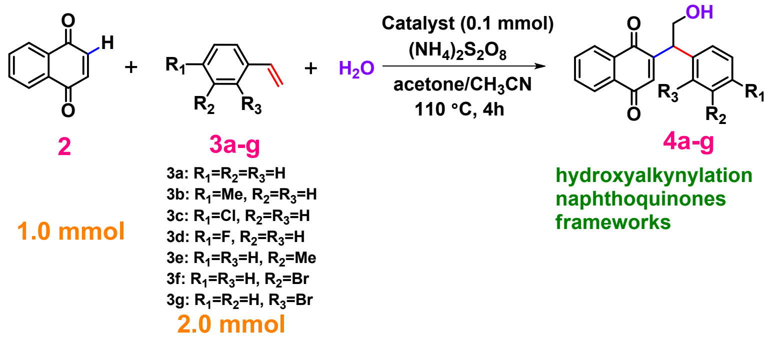
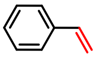
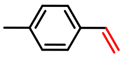
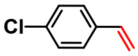
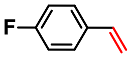
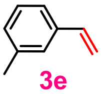


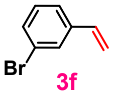
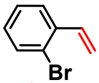
Figure S6. XPS spectrums of Cu-MOF membranes **1a** during the reaction process (0, 1, and 4 h).

8. The direct C-H hydroxyalkynylation tandem reaction catalyzed by $Cu(NO_3)_2/H_2BBDC$/azobpy or H_2BBDC/azobpy in H_2O.

Table S4. The direct C-H hydroxyalkynylation tandem reaction catalyzed by $Cu(NO_3)_2/H_2BBDC$/azobpy or H_2BBDC/azobpy in H_2O.[a]



Entry	Catalysts	Alkene	Yield % of **4a-i**[b]
1	$Cu(NO_3)_2/H_2BBDC$/azobpy	 **3a**	45
2	**1a**		91
3	H_2BBDC/azobpy		n.o.[c]
4	$Cu(NO_3)_2/H_2BBDC$/azobpy	 **3b**	45
5	**1a**		91
6	H_2BBDC/azobpy		n.o.
7	$Cu(NO_3)_2/H_2BBDC$/azobpy	 **3c**	41
8	**1a**		89
9	H_2BBDC/azobpy		n.o.
10	$Cu(NO_3)_2/H_2BBDC$/azobpy	 **3d**	39
11	**1a**		88
12	H_2BBDC/azobpy		n.o.
13	$Cu(NO_3)_2/H_2BBDC$/azobpy	 **3e**	37
14	**1a**		88

15	H_2BBDC/ azobpy		n.o.
16	$Cu(NO_3)_2$/ H_2BBDC/ azobpy	 **3f**	35
17	**1a**		86
18	H_2BBDC/ azobpy		n.o.
19	$Cu(NO_3)_2$/ H_2BBDC/ azobpy	 **3g**	31
20	**1a**		86
21	H_2BBDC/ azobpy		n.o.

[a] Reaction conditions: naphthoquinone (1.0 mmol), alkenes (**3a-g**, 2.0 mmol), catalyst (0.10 mmol), $(NH_4)_2S_2O_8$ (2.0 mmol), H_2O (2 mL), acetone (2 mL) and acetonitrile (2 mL), 110 ºC (4h). [b] Isolated yield of the product after 4h. [c] Not observed = n.o.

9. Recycling test for the direct C-H hydroxyalkynylation tandem reaction catalyzed by 1a.

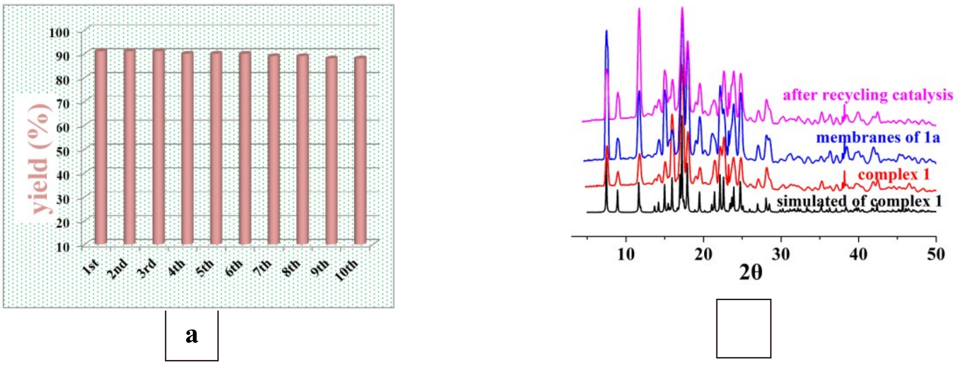
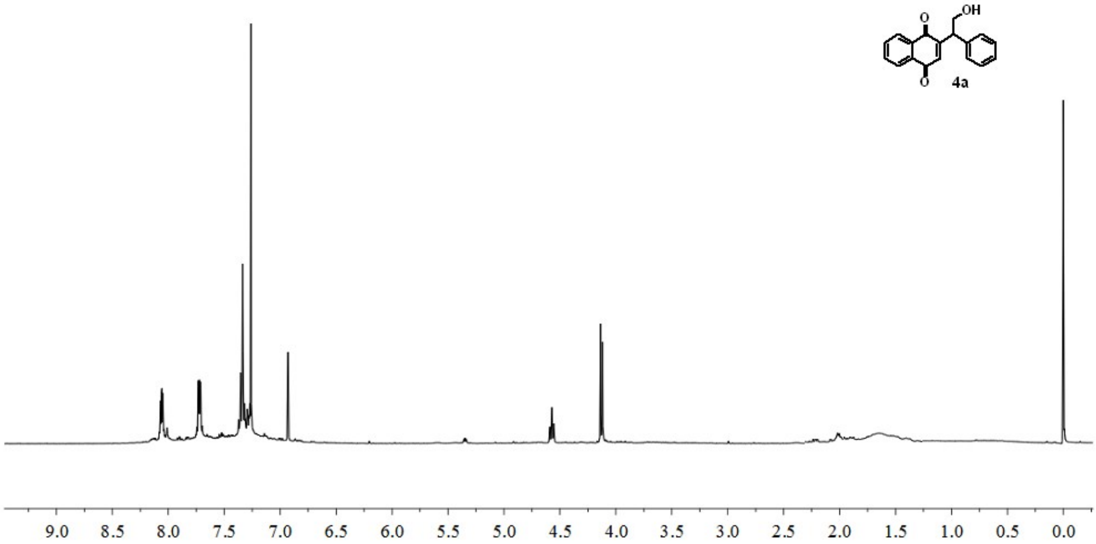
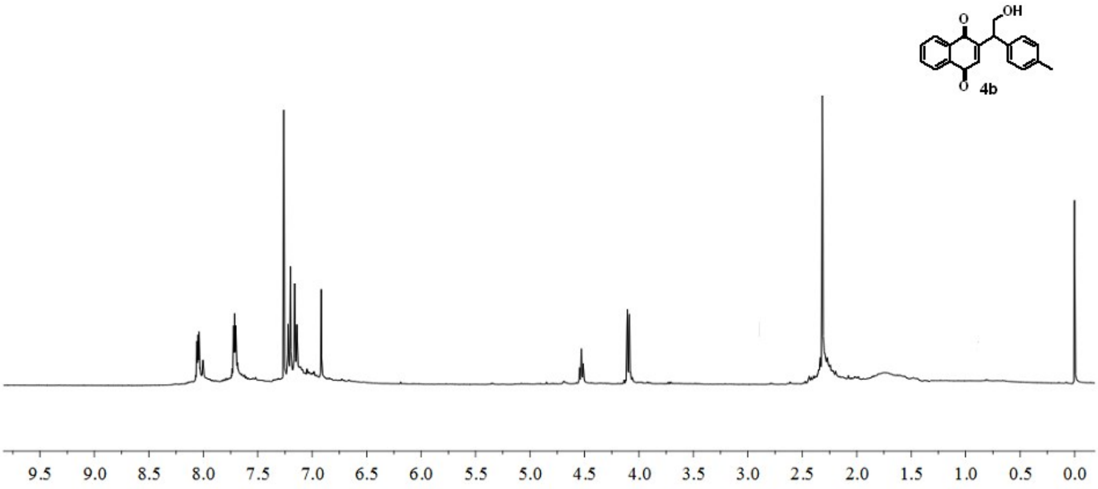
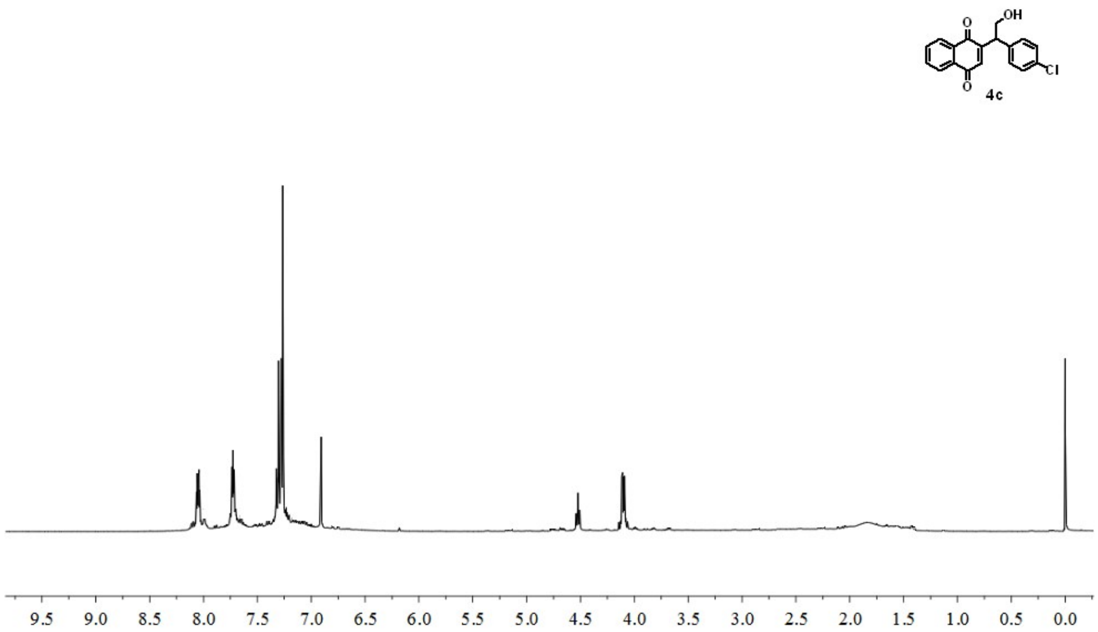


Figure S7. (a) Recycling test for the direct C-H hydroxyalkynylation tandem reaction catalyzed by **1a**. (b) Comparison of the PXRD patterns of **1a** before and after catalysis.

10. Spectral copies of ^{1}H NMR of compounds obtained in this study.



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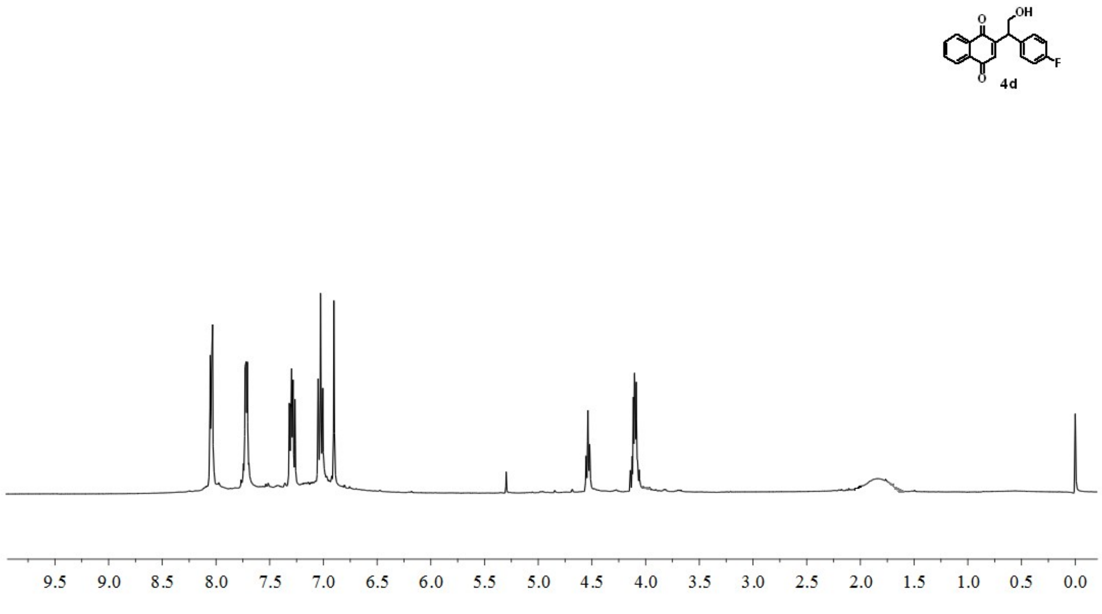
O
O
Cl
4c
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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O
O
F
4d
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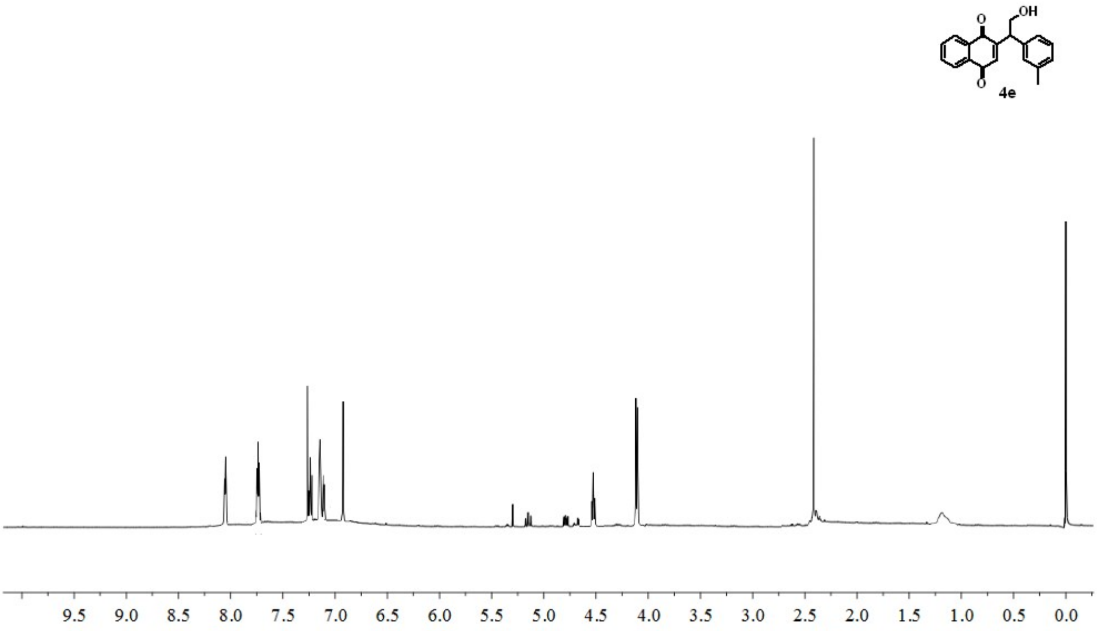
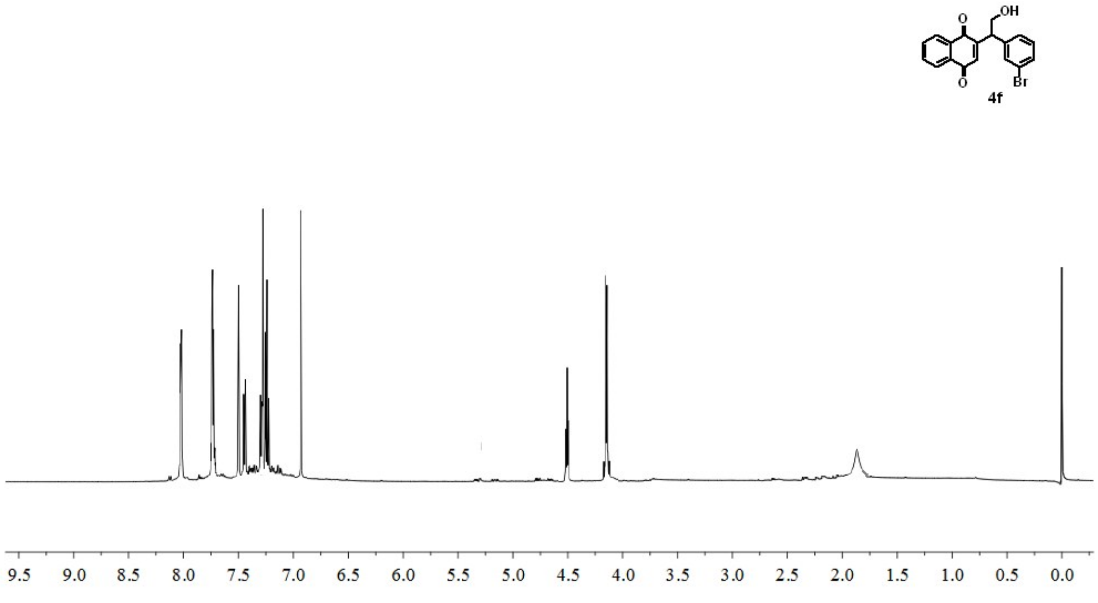

OH
O
O
4e
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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O
O
Br
4f
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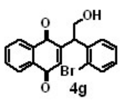
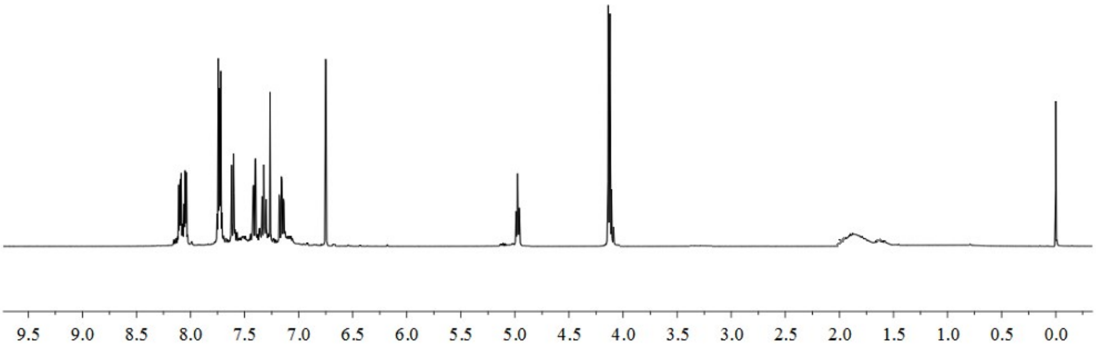


4g



11. References.

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