Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information for

Synthesis, structure and multifunctional catalytic properties of Cu(I)-coordination polymer with outer-hanging $CuBr_2$

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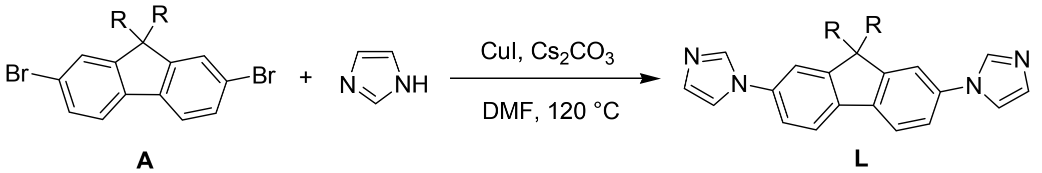
I. Synthesis of ligands L1 and L2



Under N_2, a mixture of **A** (10 mmol), imidazole (22 mmol), Cs_2CO_3 (40 mmol) and CuI (2 mmol) in fresh DMF (10 mL) was heated at 120°C for 8 hours (monitored by TLC). Then the reaction system was poured to large amounts of water. The crude product was purified by column chromatography using dichloromethane : ethyl acetate = 1 : 1 (v/v) as eluent. All the ligands were obtained as light yellow crystalline solids. The detailed characterized data were given as following.

For **L1** (R = methyl) Yield: 76%. IR (KBr pellet cm^{-1}): 3087(w), 2945(w), 2917(w), 2852(w), 1613(w), 1584(s), 1490(s), 1312(m), 1250(m), 1089(w), 1052(s), 976(w), 903(w), 813 (s), 763(m), 732(s), 655(s), 627(m). ^1H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ = 8.05 (s, 2H, $-C_3H_3N_2$), 7.83 (d, J = 8.0 Hz, 2H, $-C_6H_3-$), 7.46 (d, J = 1.7 Hz, 2H, $-C_3H_3N_2$), 7.43 (d, J = 1.9 Hz, 2H, $-C_3H_3N_2$), 7.40 (d, J = 1.9 Hz, 2H, $-C_6H_3-$), 7.36 (s, 2H, $-C_6H_3-$), 1.58 (s, 6H, $-CH_3$). Elemental analysis (%) calcd for $C_{21}H_{18}N_4$: C 77.27, H 5.56, N 17.17; Found: C 77.61, H 5.47, N 17.11.

For **L2** (R = ethyl) Yield: 68%. IR (KBr pellet cm^{-1}): 3107(w), 2957(w), 2924(w), 2867(w), 1674(w), 1613(m), 1498(s), 1370(m), 1255(s), 1104(m), 1056(s), 982(w), 900(m), 812 (s), 732(s), 653(s), 615(m), 533(m), 494(m). ^1H NMR (300 MHz, $CDCl_3$, 25°C, TMS): δ = 8.18 (s, 2H, $-C_3H_3N_2$), 7.83 (d, J = 7.2 Hz, 2H, $-C_6H_3-$), 7.46 (d, J = 2.0 Hz, 2H, $-C_3H_3N_2$), 7.43 (d, J = 2.0 Hz, 2H, $-C_3H_3N_2$), 7.42 (d, J = 1.4 Hz, 2H, $-C_6H_3-$), 7.31 (s, 2H, $-C_6H_3-$), 2.13 (q, 4H, J = 7.3 Hz, $-CH_2-$), 0.40 (t, J = 7.3 Hz, 6H, $-CH_3$). Elemental analysis (%) calcd for $C_{23}H_{22}N_4$: C 77.94, H 6.26, N 15.81; Found: C 78.31, H 6.09, N 16.23.

II. Stability of 1 in various organic solvents

1 is stable in common organic solvent systems, such as toluene, $CHCl_3$, THF, cyclohexane, CH_3CN and acetone (Fig. S1).

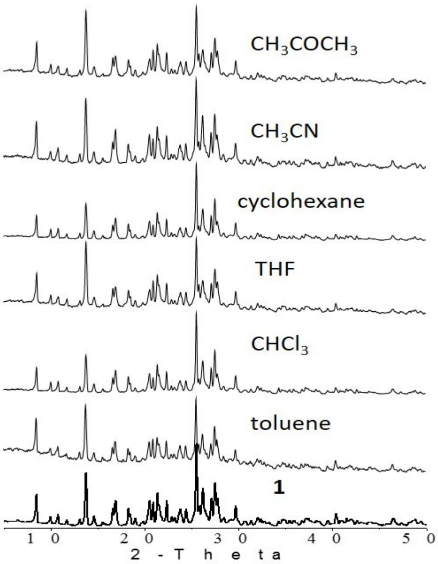


Fig. S1 The XRPD patterns of **1** after it was stirred in toluene, $CHCl_3$, THF, cyclohexane, CH_3CN and acetone for 10 h at room temperature.

III. ORTEP figures of 1-2

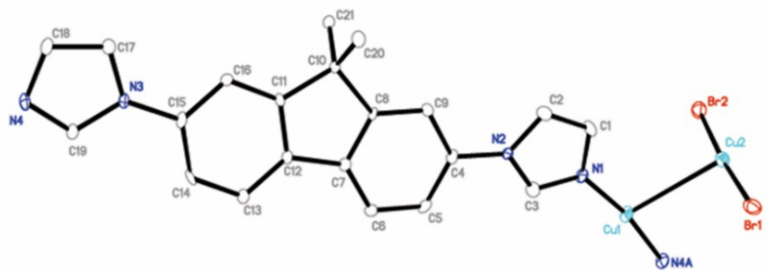


Fig. S2 The ORTEP figure of **[(CuL$_1$)(CuBr$_2$)] (1)**.

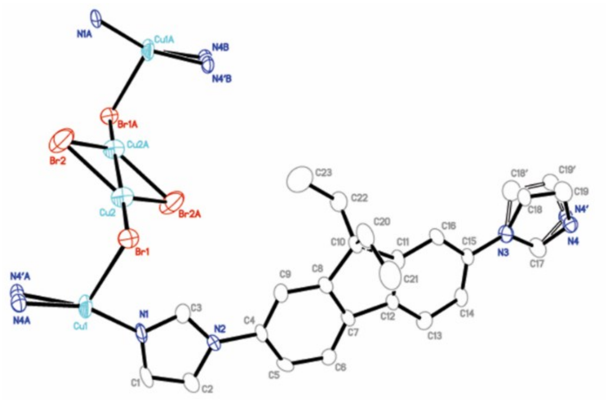


Fig. S3 The ORTEP figure of **[(CuL$_2$)$_2$(Cu$_2$Br$_4$)] (2)**.

IV. XRPD patterns of the as-synthesized and recovered 1.

1. XRPD patterns for as-synthesized and simulated 1 and its XPS spectrum

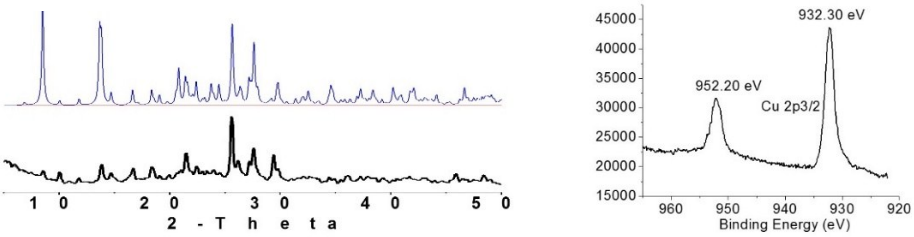


Fig. S4 Left: XRPD patterns of as-synthesized and simulated **1**. Right: XPS spectrum of **1**.

2. XRPD patterns of 1 for phenol acetylation

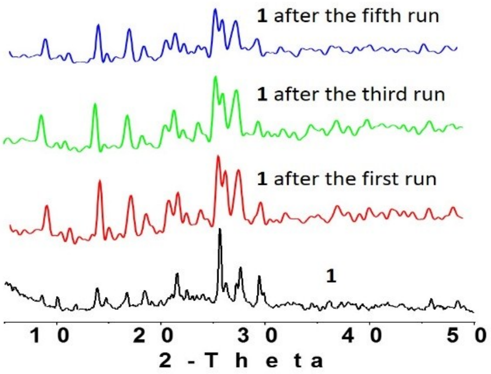


Fig. S5 XRPD patterns of as-synthesized and recovered **1**.

3. XRPD patterns of 1 for A^3-coupling (aldehyde-alkyne-amine)

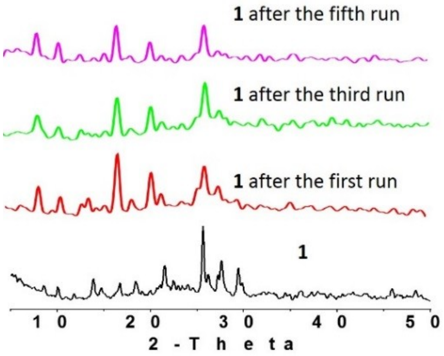


Fig. S6 XRPD patterns of as-synthesized and recovered **1**.

4. XRPD patterns of 1 for styrene oxide methanolysis

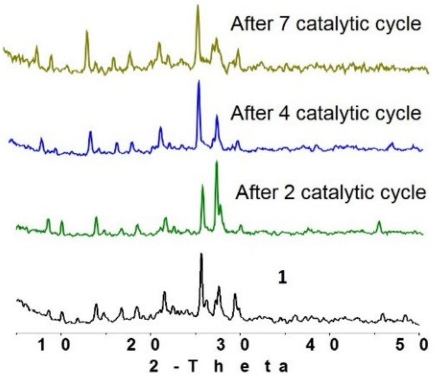
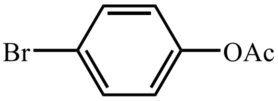


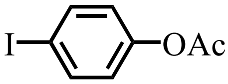
Fig. S7 XRPD patterns of as-synthesized and recovered **1**.

V. Characterization of the products of the catalytic reactions

1. Phenol acetylation

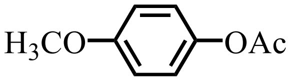


^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.51 (d, *J* = 11.7 Hz, 2H), 7.00 (d, *J* = 8.7 Hz, 2H), 2.31 (s, 3H). ^{13}C NMR (75MHZ, $CDCl_3$): δ = 21.02, 118.87, 123.37, 132.45, 149.73, 169.02. MS-EI, m/z, Anal. Calcd: 236.95, Exp: 236.97, $[M+Na]^+$.

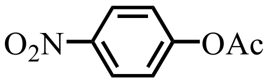


^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.70 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 2.31 (s, 3H). ^{13}C NMR (75MHZ, $CDCl_3$): δ = 21.08, 89.82, 123.78, 138.47, 150.55, 168.98. MS-EI, m/z, Anal. Calcd: 284.94, Exp: 284.93, $[M+Na]^+$.

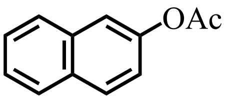
^{1}H NMR (300 MHz, DMSO-*d*^{6}): δ = 7.04 (d, *J* = 9.0 Hz, 2H), 6.95 (d, *J* = 11.7 Hz, 2H), 3.75 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (75MHZ, DMSO-*d*^{6}): δ = 20.78, 21.23, 121.90, 130.22, 135.30, 148.81, 169.68. MS-EI, m/z, Anal. Calcd: 173.06, Exp: 173.05, $[M+Na]^+$.



^{1}H NMR (300 MHz, DMSO-*d*^{6}): δ = 7.20 (d, *J* = 8.3 Hz, 2H), 6.99 (d, *J* = 8.3 Hz, 2H), 2.30 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (75MHZ, DMSO-*d*^{6}): δ = 21.12, 55.82, 114.82, 123.00, 144.43, 157.30, 169.88. MS-EI, m/z, Anal. Calcd: 189.05, Exp: 189.05, $[M+Na]^+$.

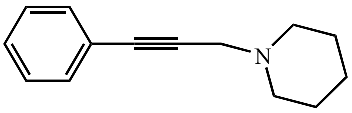


^{1}H NMR (300 MHz, CDCl$_3$): δ = 8.29 (d, *J* = 7.3 Hz, 2H), 7.30 (d, *J* = 9.1 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (75MHZ, CDCl$_3$): δ = 21.07, 122.43, 125.18, 145.34, 155.39, 168.34. MS-EI, m/z, Anal. Calcd: 204.03, Exp: 204.02, [M+Na]$^+$.

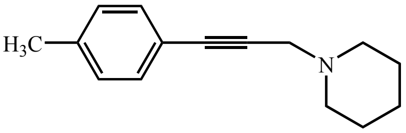


^{1}H NMR (300 MHz, DMSO-d^6): δ = 8.05-7.82 (m, 3H), 7.67 (s, 1H), 7.53 (s, 2H), 7.31 (d, *J* = 8.9 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (75MHZ, DMSO-d^6): δ = 21.30, 118.97, 122.09, 126.21, 127.10, 127.92, 128.13, 129.73, 131.49, 133.86, 148.74, 169.82. MS-EI, m/z, Anal. Calcd: 209.06, Exp: 209.05, [M+Na]$^+$.

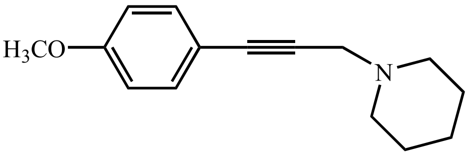
2. A^3-coupling (aldehyde-alkyne-amine)



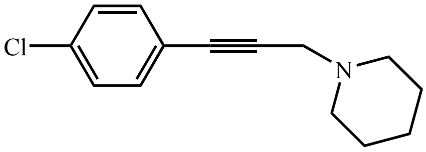
^{1}H NMR (400 MHz, DMSO-d^6): δ =7.49 – 7.39 (m, 2H), 7.39 – 7.30 (m, 3H), 3.45 (s, 2H), 2.49 (d, *J* = 15.5 Hz, 4H), 1.64 – 1.43 (m, 4H), 1.38 (d, *J* = 5.2 Hz, 2H). ^{13}C NMR (75MHz, DMSO-d^6): δ = 23.86, 25.63, 47.79, 52.79, 85.16, 86.32, 123.04, 128.56, 128.82, 131.36. MS-EI , m/z, Anal. Calcd: 199. 14, Exp: 200. 13, (M$^+$).



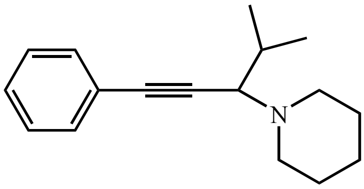
^{1}H NMR (300 MHz, DMSO-d^6): δ = 7.31 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 7. 9 Hz, 2H), 3. 43 (s, 2H), 2.47 (d, *J* = 13.5 Hz, 4H), 2.30 (s, 3H), 1.52 (d, *J* = 5.1 Hz, 4H), 1. 37 (s, 2H). ^{13}C NMR (75MHZ, DMSO-d^6): δ = 21.00, 23.75, 25.54, 48.09, 52.77, 84.71, 85.53, 119.99, 129.61, 131.68, 138.20. MS-EI, m/z, Anal. Calcd: 213.15, Exp: 214.15, (M$^+$).



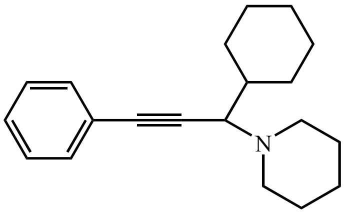
^{1}H NMR (300 MHz, DMSO-d^6): δ =7. 35 (d, *J* = 8.7 Hz, 2H), 6.91 (d, *J* = 8.7 Hz, 2H), 3.76 (s, 3H), 3.41 (s, 2H), 2.45-2.43 (d, *J* = 5.1 Hz, 4H), 1.52 (d, *J* = 10.6 Hz, 4H), 1.36 (d, *J* = 4.8Hz, 2H). ^{13}C NMR (75MHz, DMSO-d^6): δ = 24.00, 26.02, 47.91, 52.99, 55.26, 84.42, 84.66, 114.61, 115.22, 133.26, 159.56. MS-EI, m/z, Anal. Calcd: 229. 15, Exp: 230. 15, (M$^+$).



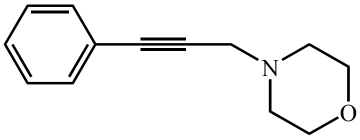
^{1}H NMR (300 MHz, DMSO-d^6): δ = 7.45-7.39 (m, 4H), 3.44 (s, 2H), 2.50-2.44 (m, 4H), 1.53-1.49 (m, 4H), 1.37 (d, J=5.1, 2H). ^{13}C NMR (75MHZ, DMSO-d^6): δ = 23.88, 25.52, 48.05, 53.11, 83.88, 87.29, 121.78, 129.01, 133.29. MS-EI, m/z, Anal. Calcd: 233. 10, Exp: 234. 10, (M$^+$).



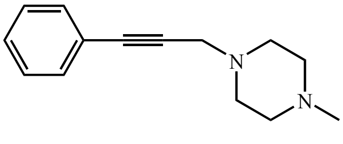
^{1}H NMR (300 MHz, DMSO-d^6): δ = 7.40 (s, 2H), 7.36 (d, *J* = 3.3Hz, 3H), 3.05 (d, *J* = 10.2Hz, 1H), 2.56-2.50 (m, 4H), 1.85(s, 1H), 1.54 (d, *J* = 4.8Hz, 4H), 1.41 (d, J=5.7Hz, 2H), 1.06 (d, *J* = 6.6Hz, 3H), 0.97 (d, *J* = 6.6Hz, 2H). ^{13}C NMR (75MHZ, DMSO-d^6): δ = 20.76, 24.57, 26.32, 30.03, 50.68, 64.98, 86.31, 87.97, 123.15, 128.38, 128.99, 131.63. MS-EI, m/z, Anal. Calcd: 242. 19, Exp: 242. 18, (M$^+$).



^{1}H NMR (400 MHz, DMSO-d^6): δ = 7.41-7.40 (m, 2H), 7.36-7.35 (m, 3H), 3.16 (d, *J* = 10.2 Hz, 1H), 2.54 (S, 2H), 2.36 (s, 2H), 2.02-1.96 (m, 2H), 1.73-1.67 (m, 2H), 1.61-1.51 (s, 6H), 1.39 (s, 2H), 1.27 – 1.1.23 (m, 3H), 1.20-1.15(m, 2H). ^{13}C NMR (75MHZ, DMSO-d^6): δ = 24.61, 25.83, 26.30, 26.75, 29.88, 31.15, 50.36, 63.76, 86.51, 88.05, 110.60, 123.56, 128.31, 129.07, 131.93. MS-EI, m/z, Anal. Calcd: 282.22, Exp: 282. 21, (M$^+$).

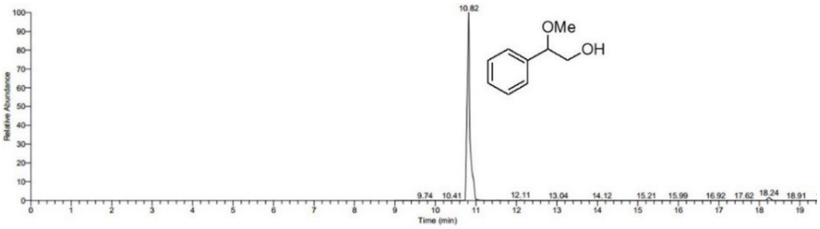


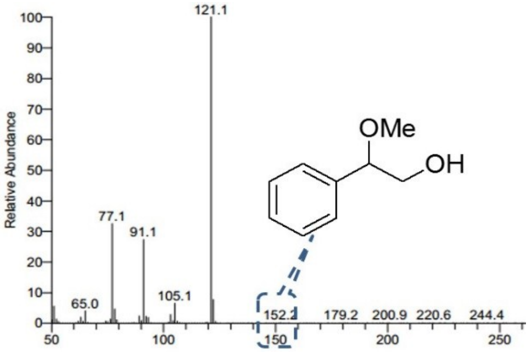
^{1}H NMR (400 MHz, DMSO-d^6): δ = 7.43 (s, 2H), 7.37 (d, *J* = 3.6 Hz, 3H), 3.70 – 3.55 (m, 4H), 3.51 (s, 2H), 2.58 – 2.46 (m, 4H). ^{13}C NMR (75MHZ, DMSO-d^6): δ = 47.29, 51.95, 63.41, 66.64, 85.05, 85.61, 122.85, 128.67, 129.06, 13.69. MS-EI, m/z, Anal. Calcd: 202. 12, Exp: 202. 12, (M$^+$).

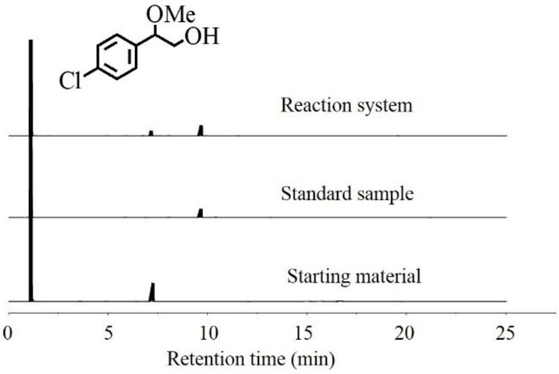


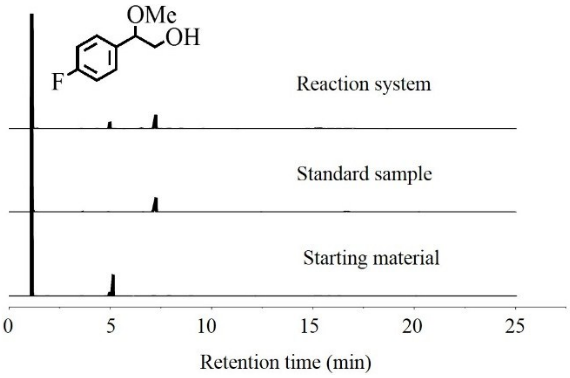
^{1}H NMR (400 MHz, DMSO-d^{6}): δ = 7.42 (s, 2H), 7.39 (d d, J = 22.0, 7.0 Hz, 2H), 7.36 (d, J = 3.5 Hz, 1H), 3.46 (d, J = 26.2 Hz, 2H), 2.59 – 2.50 (m, 4H), 2.35 (s, 4H), 2.16 (s, 3H). ^{13}C NMR (75MHZ, DMSO-d^{6}): δ = 46.19, 46.93, 51.77, 55.04, 85.22, 86.00, 123.13, 128.59, 128.59, 129.12, 131.63. MS-EI, m/z, Anal. Calcd: 215. 15, Exp: 215. 15, (M^{+}).

3. Styrene oxide methanolysis









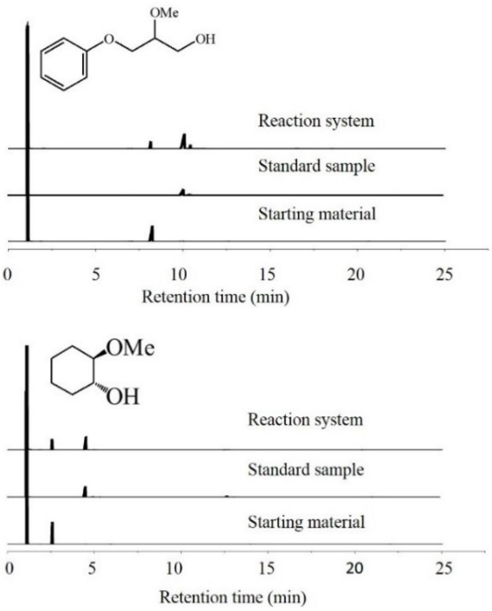
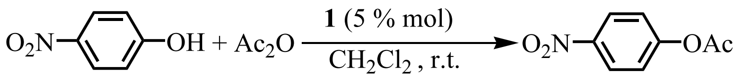


Fig. S8 GC-MS spectra for styrene oxide methanolysis and the product 2-methoxy-2-phenylethanol, and the GC spectra for methanolysis of the extended epoxide substrates (the conversion rate is determined by GC using nitrobenzene as the external standard).[1]

VI. XPS and ICP measurements for 1 after catalysis

1. XPS and ICP measurements for 1 after Phenol acetylation



The *p*-nitrophenol acetylation was chosen as the model reaction for examination the stability of **1** during phenol acetylation. Acetic anhydride (4 mmol) was added to a CH_2Cl_2 (1 mL) solution of *p*-nitrophenol (139 mg, 1 mmol). After addition of **1** (5 % mol), the mixture was stirred at room temperature for 3 h (monitored by TLC, petroleum/CH_2Cl_2 = 1 : 1). **1** was recovered by centrifugation, washed with MeOH and dried at 80°C. The recovered **1** was measured by ICP. The results indicated that the leaching loss of copper and Br is 0.16 and 0.78 %, respectively (Table S1). XPS spectra of **1** after the reaction indicated that no valence change occurred (Fig. S9).

Table S1. ICP results for **1** after *p*-nitrophenol acetylation

sample	type	Cu 324.754	Cu 224.700	Cu 327.396	Br 163.340
1 after Phenol acetylation	1	0.42477	0.40192	0.38598	2.84309
	2	0.42046	0.39523	0.39367	2.16295
	<x>	**0.42262**	**0.39858**	**0.38982**	**2.50302**
	sd	0.00305	0.00473	0.00544	0.48093
	rsd	0.721	1.187	1.395	19.214

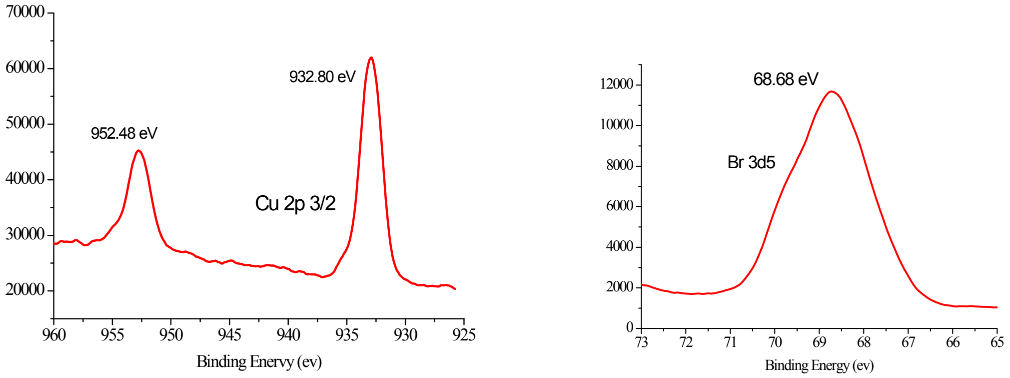
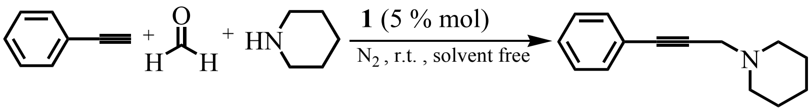


Fig. S9 XPS spectra for copper and bromine in **1** after *p*-nitrophenol acetylation.

2. XPS and ICP measurements for 1 after A^3-coupling (aldehyde-alkyne-amine) reaction



Above A^3-coupling (aldehyde-alkyne-amine) reaction was chosen as the model reaction for examination the stability of **1** during phenol acetylation.

A mixture of phenylacetylene (120 mg, 1.2 mmol), paraformaldehyde (PFA, 30 mg, 1.0 mmol), piperidine (94 mg, 1.1 mmol) and **1** (5 % mol) was stirred at room temperature in nitrogen atmosphere for 6 h (monitored by TLC). After addition of ether, the product was purified by column chromatography on silica gel (hexane/ethyl acetate = 3 : 1). **1** was recovered by centrifugation and washed with ether and MeOH and dried at 80°C. The recovered **1** was measured by ICP. The results indicated that the leaching loss of copper and Br is 1.12 and 3.28 %, respectively (Table S2). XPS spectra of **1** after the reaction indicated that no valence change occurred (Fig. S10).

Table S2. ICP results for **1** after phenylacetylene, paraformaldehyde and piperidine A^3-coupling reaction

sample	type	Cu 324.754	Cu 224.700	Cu 327.396	Br 163.340
1 after A^3-coupling reaction	1	2.81692	2.88024	2.83875	9.95547
	2	2.82294	2.88681	2.78428	11.0601
	<x>	**2.81993**	**2.88353**	**2.81152**	**10.5078**
	sd	0.00426	0.00465	0.03852	0.78109
	rsd	0.151	0.161	1.37	7.433

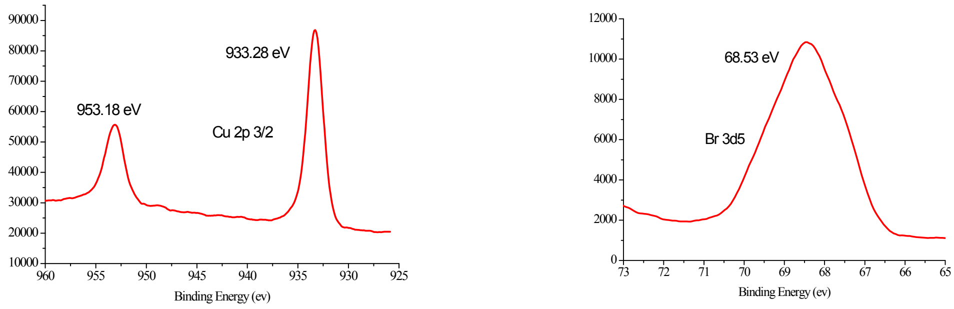
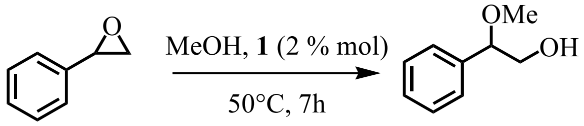


Fig. S10 XPS spectra for copper and bromine in **1** after phenylacetylene, paraformaldehyde and piperidine A^3-coupling reaction.

3. XPS and ICP measurements for 1 after styrene oxide methanolysis



Styrene oxide methanolysis was chosen as the model reaction for examination the stability of **1** during methanolysis.

A methanol (5 mL) solution of styrene oxide (1 mmol) and **1** (0.02 mmol, 2 mol %) was stirred at 50°C for 7 hours. The reaction was monitored by TLC. After that, the catalyst of **1** was recovered by centrifugation and washed by fresh methanol. After dried at 70°C for 1 hour, the recovered **1** was measured by ICP and XPS. The recovered **1** was measured by ICP. The results indicated that the leaching loss of copper and Br is 1.12 and 3.28 %, respectively (Table S3). XPS spectra of **1** after the reaction indicated that no valence change occurred (Fig. S11).

Table S3. ICP results for **1** after styrene oxide methanolysis

sample	type	Cu 324.754	Cu 224.700	Cu 327.396	Br 163.340
		mg/l	mg/l	mg/l	mg/l
1 after styrene oxide methanolysis	1	0.06576	0.03852	0.03641	< 0.06448
	2	0.06217	0.03698	0.03356	< 0.07137
	<x>	**0.06397**	**0.03775**	**0.03498**	**< 0.06792**
	sd	0.00254	0.00109	0.00202	0.00487
	rsd	3.976	2.882	5.769	7.171

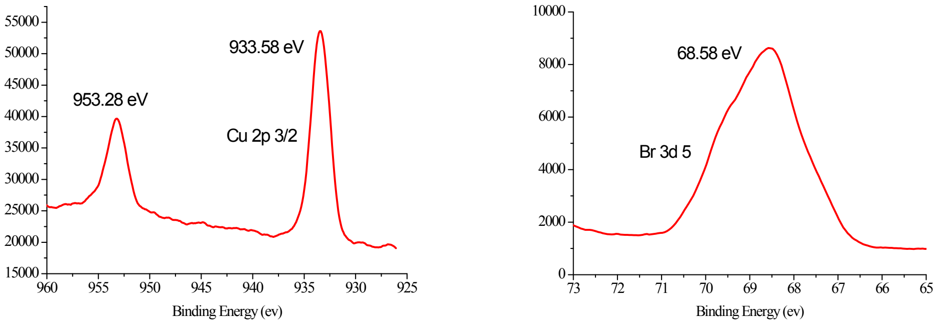


Fig. S11 XPS spectra for copper and bromine in **1** after styrene oxide methanolysis.

VII. Selected bond lengths and bond angles of 1-2

Table S4. Selected bond lengths [Å] and angles [°] for **1**

Br(1)-Cu(2)	2.2345(8)	Br(2)-Cu(2)	2.2292(8)
Cu(1)-N(4)#1	1.884(3)	Cu(1)-N(1)	1.885(3)
Cu(1)-Cu(2)	2.8717(8)	N(4)-Cu(1)#2	1.884(3)
N(4)#1-Cu(1)-N(1)	169.82(17)	N(4)#1-Cu(1)-Cu(2)	92.29(12)
N(1)-Cu(1)-Cu(2)	95.72(12)	Br(2)-Cu(2)-Br(1)	174.50(4)
Br(2)-Cu(2)-Cu(1)	85.52(3)	Br(1)-Cu(2)-Cu(1)	99.35(3)

Symmetry transformations used to generate equivalent atoms:
#1 x+1,-y+3/2,z+3/2 #2 x-1,-y+3/2,z-3/2

Table S5. Selected bond lengths [Å] and angles [°] for **2**

Br(1)-Cu(2)	2.3258(15)	Br(1)-Cu(1)	2.7581(14)
Br(2)-Cu(2)#1	2.4034(16)	Br(2)-Cu(2)	2.4171(14)
Cu(1)-N(4)#2	1.89(3)	Cu(1)-N(1)	1.906(5)
Cu(1)-N(4')#2	1.93(2)	Cu(2)-Br(2)#1	2.4034(16)
Cu(2)-Cu(2)#1	2.709(2)	N(4)-Cu(1)#3	1.89(3)
N(4')-Cu(1)#3	1.93(2)	Cu(2)-Br(1)-Cu(1)	80.56(4)
Cu(2)#1-Br(2)-Cu(2)	68.37(5)	N(4)#2-Cu(1)-N(1)	157.7(10)
N(4)#2-Cu(1)-N(4')#2	10.7(13)	N(1)-Cu(1)-N(4')#2	160.3(6)
N(4)#2-Cu(1)-Br(1)	101.3(9)	N(1)-Cu(1)-Br(1)	98.64(17)

N(4')#2-Cu(1)-Br(1)	101.0(6)	Br(1)-Cu(2)-Br(2)#1	127.51(5)
Br(1)-Cu(2)-Br(2)	120.81(6)	Br(2)#1-Cu(2)-Br(2)	111.63(5)
Br(1)-Cu(2)-Cu(2)#1	175.85(7)	Br(2)#1-Cu(2)-Cu(2)#1	56.05(5)
Br(2)-Cu(2)-Cu(2)#1	55.57(4)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+3,-z+1 #2 x+1,y+1,z #3 x-1,y-1,z

VIII. References

1. A. Dhakshinamoorthy, M. Alvaro, H. Garcia, Chem.-Eur. J. *2010*, **16**, 8530.