Supporting Information

Cu(I) Coordination Polymers (CPs) as Tandem Catalysts for Three-component sequential Click/Alkynylation Cycloaddition Reaction in Regiocontrol

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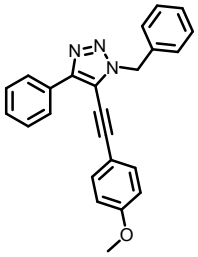
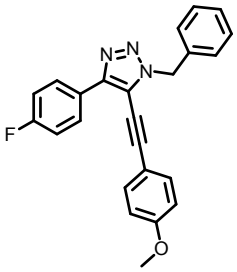
Contents

1. General Method. TPB and bromoalkyne were prepared with the procedure modified from the literature.[1] Other chemical reagents were supplied by business purchase and utilized without further purification. ^{1}H NMR was studied by the Bruker Avance-400 spectrometers. Powder X-ray diffraction (PXRD) was studied by the PANalyticalX'Pert PRO diffractometer on monochromated with Cu $K\alpha_1$. X-ray photoelectron spectroscopy (XPS) determination was measured in an ESCALAB 250Xi-type instrument. The FLASH EA 1112 elemental analyzer was used to record C, H, and N. Thermal analyse (TGA) was carried out under air atmosphere utilizing the Netzsch STA 449C thermal analyzer. Atomic absorption spectrum (AAS) was studied by the Z28000 atomic absorption Spectrophotometer.

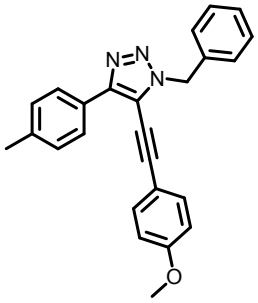
2. Synthesis



1-benzyl-5-((4-methoxyphenyl)ethynyl)-4-phenyl-1H-1,2,3-triazole. After column chromatography (PE/EtOAc = 10/1) 241.1 mg (91%) of a white solid were obtained. This compound had been reported.[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.15-8.21 (m, 2H), 7.32-7.48 (m, 10H), 6.90-6.92 (m, 2H), 5.67 (s, 2H), 3.86 (s, 3H). IR (KBr, cm^{-1}): 3394(w), 2919(m), 2215(m), 1727(w), 1605(s), 1497(s), 1254(s), 1026(s), 824(s), 727(m), 590(w).

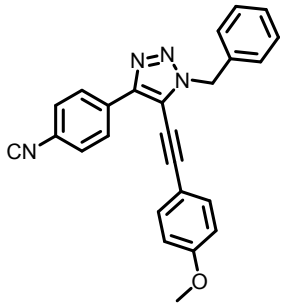


1-benzyl-4-(4-fluorophenyl)-5-((4-methoxyphenyl)ethynyl)-1H-1,2,3-triazole. After column chromatography (PE/EtOAc = 10/1) 348.5 mg (91%) of a white solid were obtained. This compound had been reported.[2] ^{1}H NMR (400 MHz, CDCl3) δ: 8.15-8.22 (m, 2H), 7.32-7.51 (m, 9H), 6.90-6.92 (m, 2H), 5.66 (s, 2H), 3.86 (s, 3H). IR (KBr, cm^{-1}): 3382(w), 3057(m), 2217(s), 1886(w), 1745(w), 1605(s), 1494(s), 908(w), 830(s), 734(s), 596(m).

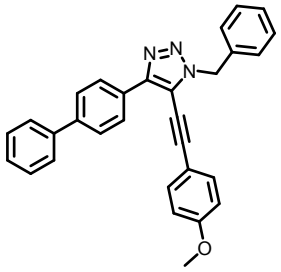


1-benzyl-5-((4-methoxyphenyl)ethynyl)-4-(p-tolyl)-1H-1,2,3-triazole. After column chromatography (PE/EtOAc = 10/1) 341.1 mg (90%) of a colorless oil obtained. This compound had been reported.[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.05-8.09 (m, 2H), 7.30-7.48 (m, 9H), 6.85-

6.94 (m, 2H), 5.65 (s, 2H), 3.86 (s, 3H), 2.38 (s, 3H). IR (KBr, cm^{-1}): 3423(m), 2917(s), 2214(s), 1801(w), 1605(s), 1456(s), 1100(m), 951(w), 824(s), 643(w), 470(w).



1-benzyl-4-(4-isocyanophenyl)-5-((4-methoxyphenyl)ethynyl)-1H-1,2,3-triazole. After column chromatography (PE/EtOAc = 8/1) 343.2 mg (88%) of a white solid were obtained. This compound had been reported.[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.26-8.33 (m, 2H), 7.68-7.74 (m, 9H), 7.33-7.46 (m, 7H), 6.93-6.97 (m, 2H), 5.67 (s, 2H), 3.87 (s, 3H). IR (KBr, cm^{-1}): 3342(m), 2924(s), 2221(s), 1890(w), 1550(m), 1439(m), 1250(s), 1161(s), 1130(w), 999(s), 827(s).



4-([1,1'-biphenyl]-4-yl)-1-benzyl-5-((4-methoxyphenyl)ethynyl)-1H-1,2,3-triazole. After column chromatography ((PE/EtOAc = 8/1) 344.0 mg (78%) of a white solid were obtained. This compound had been reported.[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.27-8.31 (m, 2H), 7.65-7.73 (m, 4H), 7.34-7.50 (m, 10H), 6.94-6.98 (m, 2H), 5.68 (s, 2H), 3.89 (s, 3H). IR (KBr, cm^{-1}): 3440(m), 3030(w), 2215(m), 1604(s), 1556(w), 1480(m), 1252(s), 1027(s), 914(w), 724(s), 698(s).

3. Crystal Data Collection and Refinement. **1-2** were tested on a Rigaku Saturn 724 CCD diffractomer with Mo-*K*α (λ = 0.71073 Å), respectively. CrystalClear (Rigaku/MSC Inc., 2006) were utilized to perform the absorption corrections. The structure was worked out by immediate ways, and refined by a fullmatrix least-squares technique relied on F^2 with the SHELXL-1997.[3] The whole H atoms expect for those of H_2O molecules were established with calculated positions, and refined isotropic displacement parameters with riding model. The detailed crystallographic data is summarized in Table S1. Corresponding bond lengths (Å) and bond angles (°) are provided in Table S2. Crystallographic data of **1-2** have been deposited at the Cambridge Crystallographic Data Centre with CCDC reference number 1861698 and 1861697.

Table S1. Crystallographic data and structure refinement details for complex**1-2**[a,b]

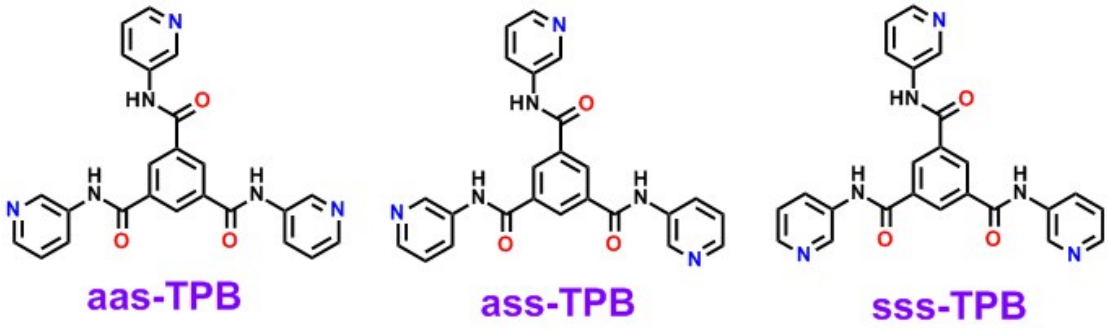
Complex	**1**	**2**
Formula	$C_{24}H_{18}BrCuN_6O_3$	$C_{48}H_{36}Cu_3I_3N_{12}O_6$
fw	581.89	1448.21
T/K	293(2)	293(2)
λ (Mo K), Å	0.71073	0.71073
Crystsyst	Monoclinic	Monoclinic
Space group	*C2/c*	*P2/c*
a (Å)	31.938(6)	14.770(3)
b (Å)	7.7414(15)	11.093(2)
c (Å)	20.506(4)	15.890(3)
β(°)	90	108.00(3)
V (Å^3)	4390.6(15)	2476.1(9)
Z	8	2
$D_{calcd.}$(g·cm^{-3})	1.761	1.942
Reflections collected /unique	15413 / 4076	25077 / 4618
abs coeff/mm^{-1}	2.857	3.209
F(000)	2336	1404
θ (º)	2.01-25.49	1.45-25.50
GOF	1.080	1.193
R_1(I>2sigma(I))[a]	0.0500	0.0682
wR_2(I>2sigma(I))[b]	0.1216	0.1491

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

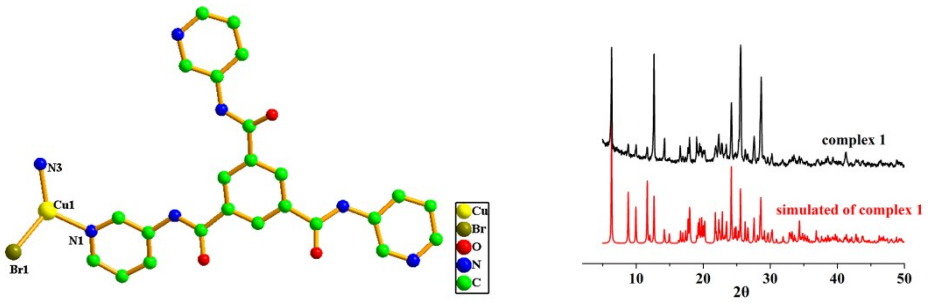
Table S2. Selected Bond Lengths (Å) and Bond Angles (deg) for **1**-**2**.

Complex **1**			
Cu(1)-N(3)#1	1.973(3)	Cu(1)-Br(1)	2.4087(9)
Cu(1)-N(1)	2.031(3)	N(3)#1-Cu(1)-Br(1)	125.73(10)
N(3)#1-Cu(1)-N(1)	123.84(14)	N(1)-Cu(1)-Br(1)	106.56(10)
Symmetry codes: #1 = -x, y+1, -z+1/2			
Complex **2**			
Cu(1)-N(3)#1	2.075(6)	Cu(2)-N(1)	1.990(6)
Cu(1)-N(3)#2	2.075(6)	Cu(2)-I(2)	2.5746(15)
Cu(1)-I(1)#3	2.6406(12)	Cu(2)-I(1)	2.5745(14)
Cu(1)-I(1)	2.6406(12)	I(1)#3-Cu(1)-I(1)	116.23(6)
N(3)#1-Cu(1)-N(3)#2	97.9(3)	N(1)-Cu(2)-I(2)	121.90(18)
N(3)#1-Cu(1)-I(1)#3	109.97 (15)	N(1)-Cu(2)-I(1)	118.63(17)
N(3)#2-Cu(1)-I(1)#3	110.63(15)	I(2)-Cu(2)-I(1)	118.38(5)
N(3)#1-Cu(1)-I(1)	110.63(15)	Cu(2)-I(1)-Cu(1)	76.26(5)
N(3)#2-Cu(1)-I(1)	109.97 (15)	Cu(2)-I(2)-Cu(2)#3	58.71(6)
Symmetry codes: #1 = x-1, y, z; #2 -x+1, y, -z+1/2; #3 –x ,y, -z+1/2			

4. Additional structure figures and characterizations of Cu-complexes.



Scheme S1. The conformations of the ligand in crystal structures (a and s are defined based on the relative orientation of the amide oxygen and the pyridyl nitrogen. a-conformation means the two atoms are in the opposite side. s-conformation means that the pyridine nitrogen atom and the amide oxygen atom of the ligand are in the same side).



a **b**

Figure S1. Crystal structure of **1**: (a) coordination environments of the Cu^{I} ions. Hydrogen atoms are omitted for clarity. (b) PXRD patterns of **1**.

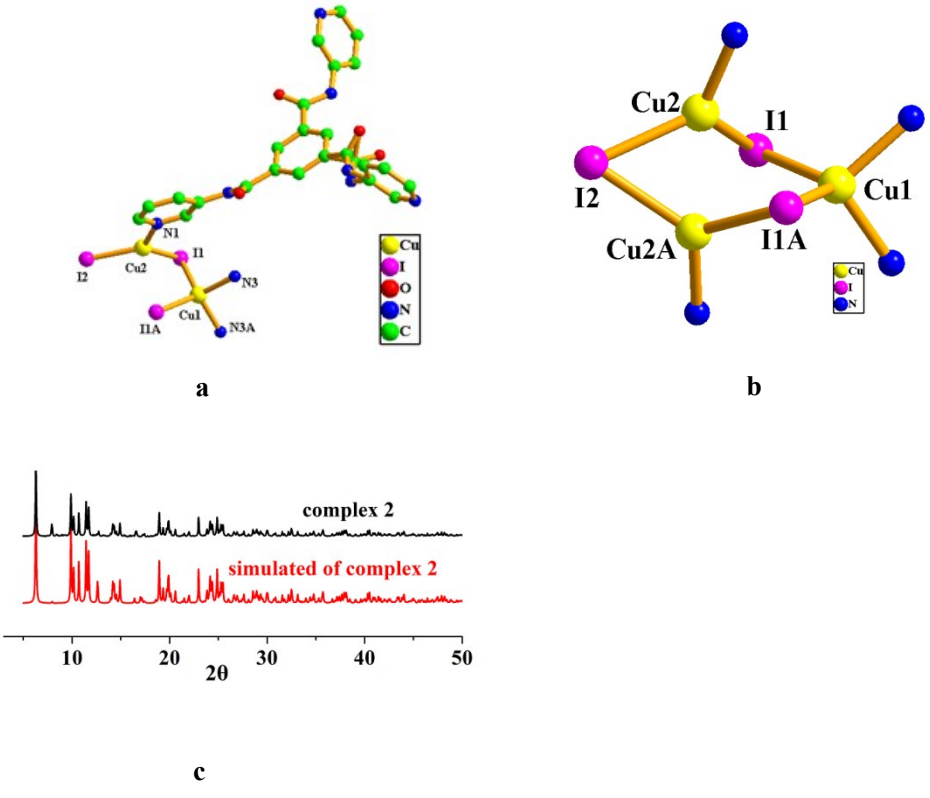
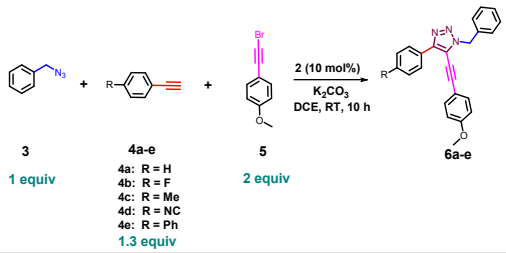
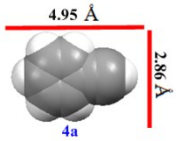
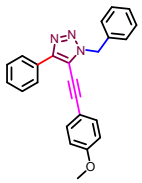
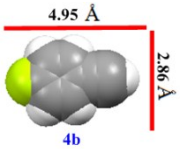
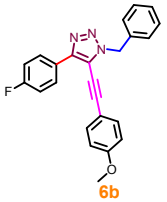
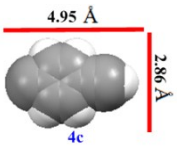
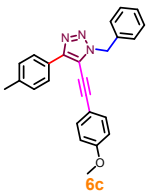
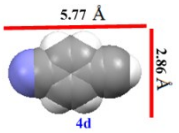
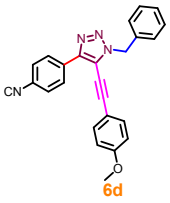
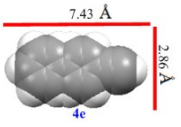
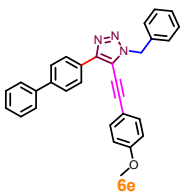


Figure S2. Crystal structure of **2**: (a) coordination environments of the Cu^{I} ions. Hydrogen atoms are omitted for clarity. (b) View the Cu_3I_3 clusters. (c) PXRD patterns of **2**.

5. Tandem for three-component click/alkynylation reactions with CuI, CuI/TPB and TPB as catalysts.

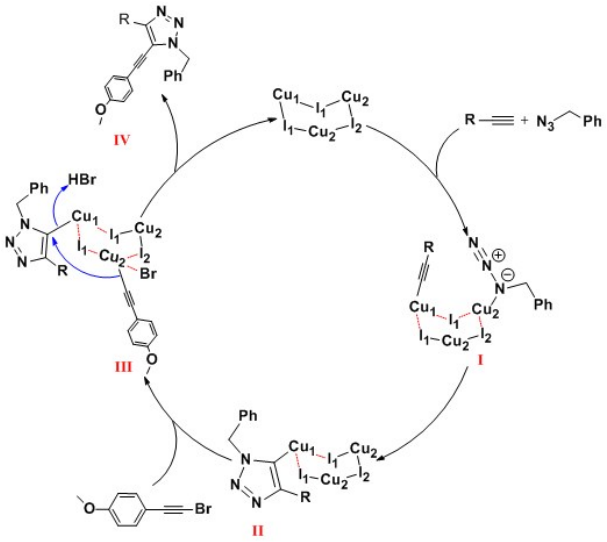
Table S3. Tandem for three-component click/alkynylation reactions with CuI, CuI/TPB and TPB as catalysts [a]



Entry	Catalysts	Alkynes	Products	Yield of **6a-e**[b]
1	CuI			15
2	CuI/TPB			29
3	TPB			n.o.[c]
4	$[Cu(CH_3CN)]PF_6$			19
5	CuI			15
6	CuI/TPB			26
7	TPB			n.o.[c]
8	$[Cu(CH_3CN)]PF_6$			19
9	CuI			13
10	CuI/TPB			25
11	TPB			n.o.[c]
12	$[Cu(CH_3CN)]PF_6$			17
13	CuI			11
14	CuI/TPB			19
15	TPB			n.o.[c]
16	$[Cu(CH_3CN)]PF_6$			16
17	CuI			10
18	CuI/TPB			17
19	TPB			n.o.[c]
20	$[Cu(CH_3CN)]PF_6$			13

[a]Reaction conditions: **3** (1.0 mmol), **4a-e** (1.3 mmol), **5** (2.0 mmol), catalyst (0.10 mmol), K_2CO_3 (2.0 mmol), DCE (10 mL), RT (10h). [b]Isolated yield of the product after 10h. [c]Not observed = n.o.

6. The plausible mechanism for the three-component tandam click/alkynylation reactions.



Scheme S2. The suggested mechanism for the three-component tandam click/alkynylation reactions.

7. Recycling test for the three-component tandam click/alkynylation reactions.

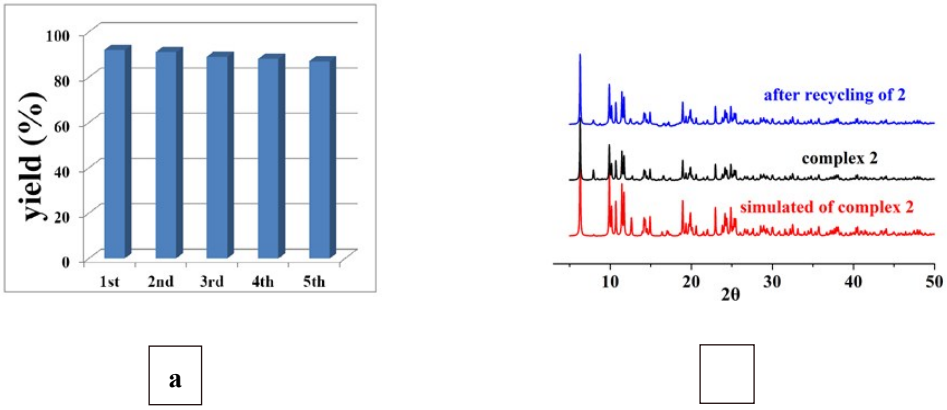
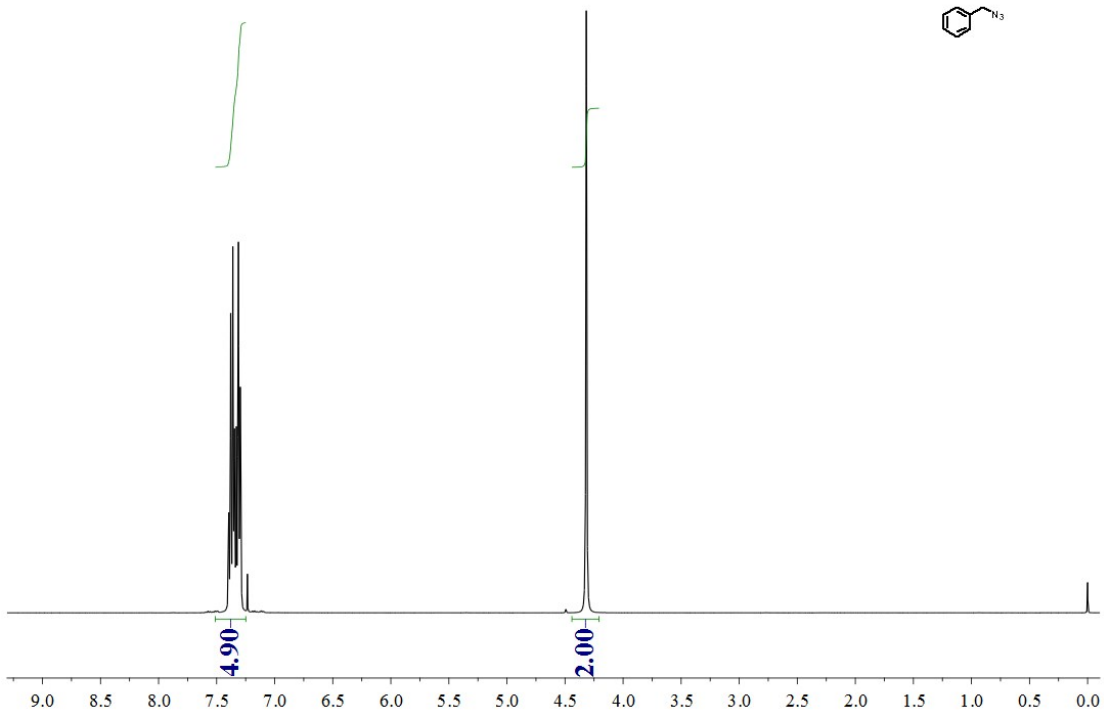
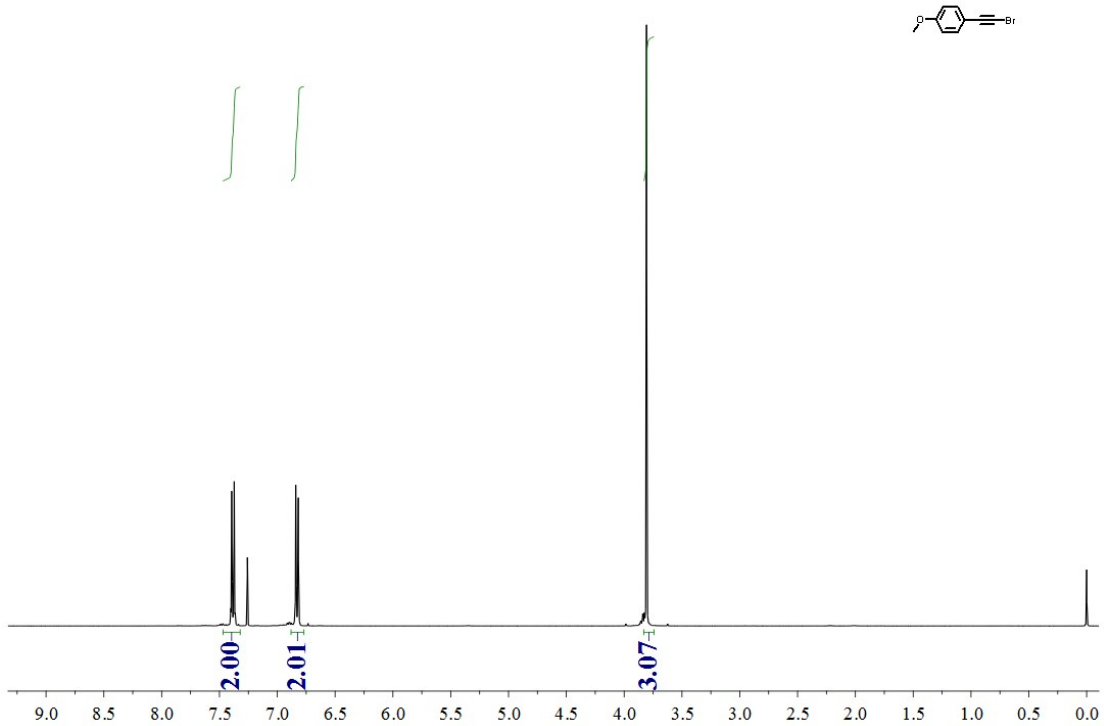
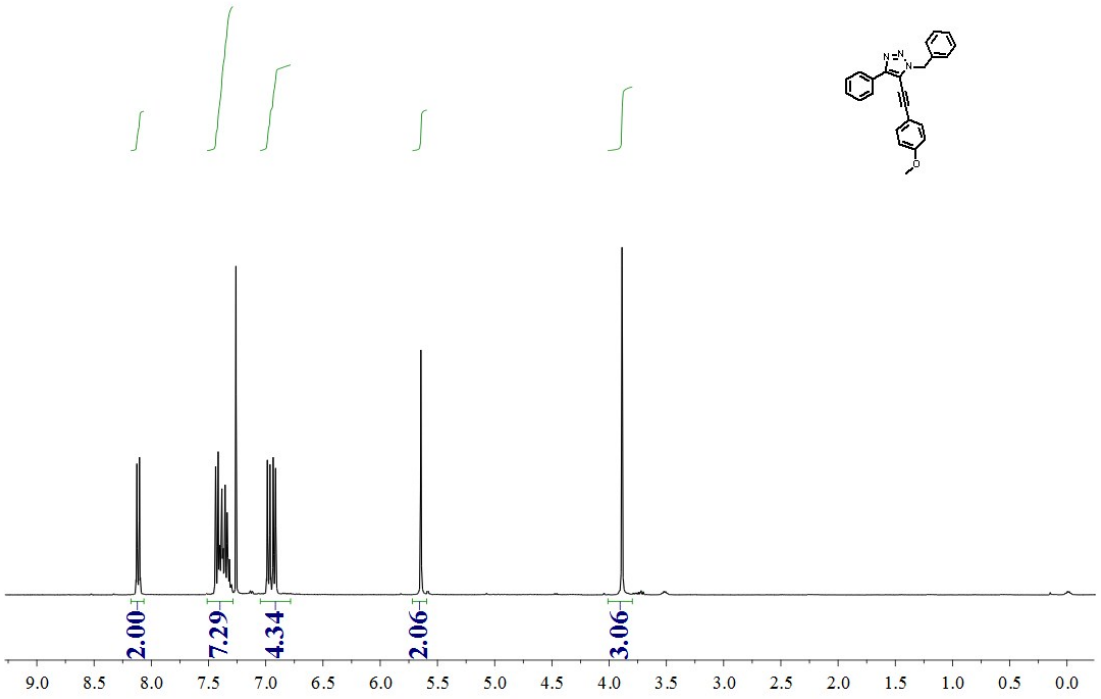


Figure S3. (a) Recycling test for the three-component tandam click/alkynylation reactions catalyzed by **2**. (b) Comparison of the PXRD patterns of **2** before and after catalysis.

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



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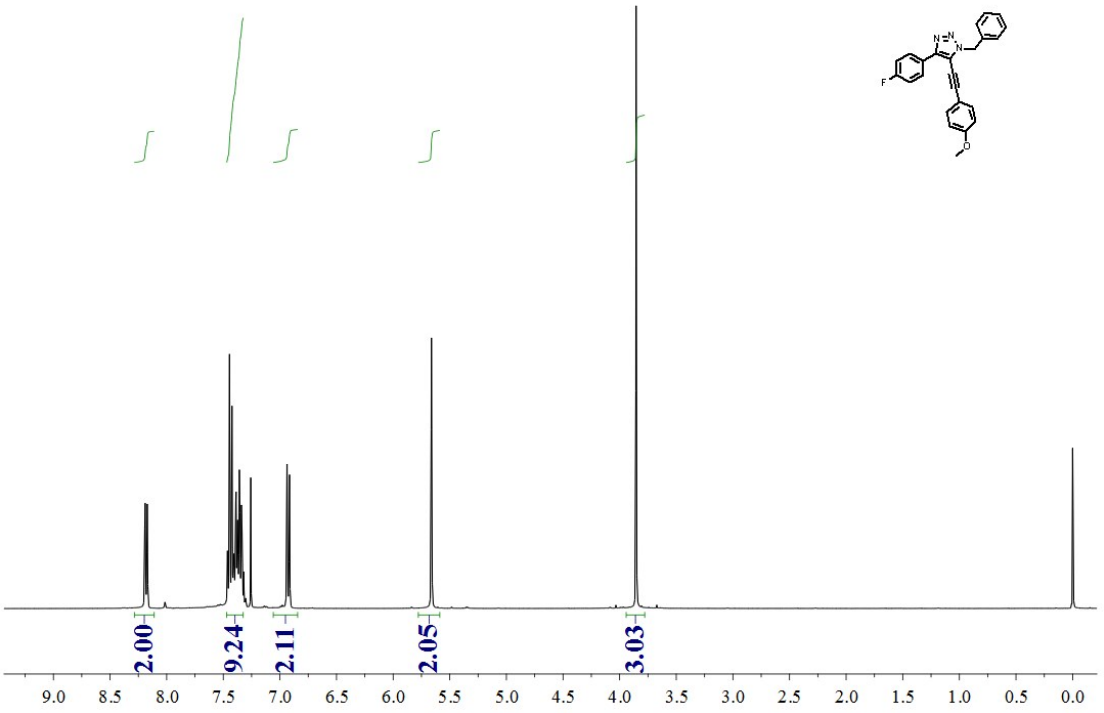
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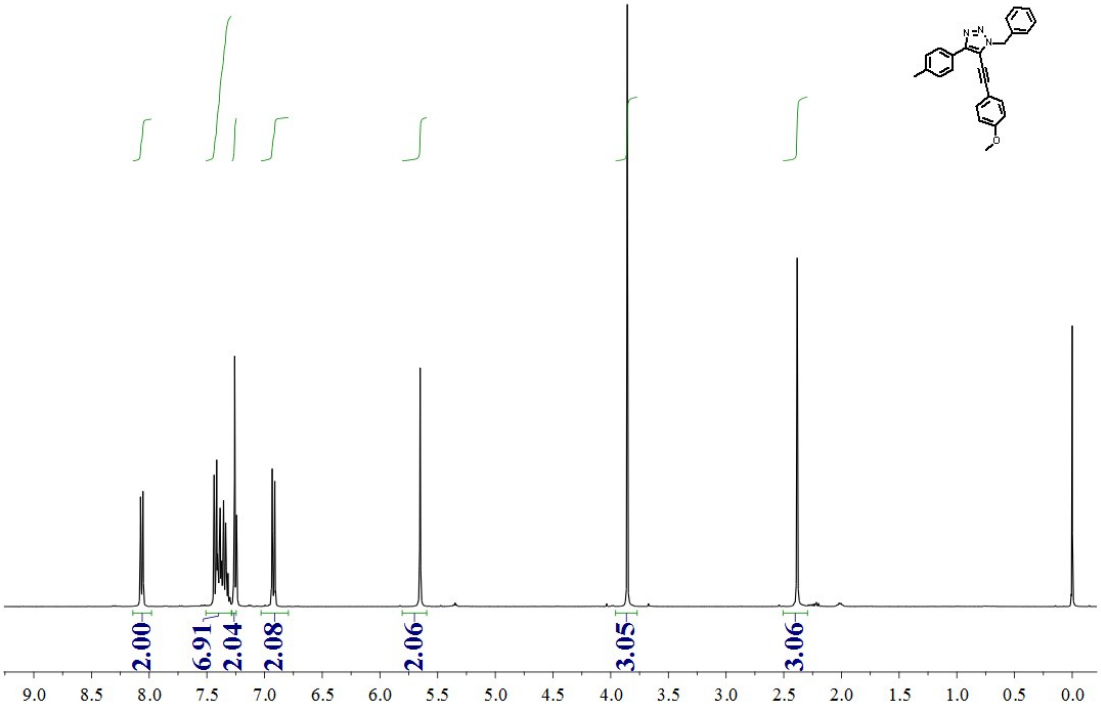
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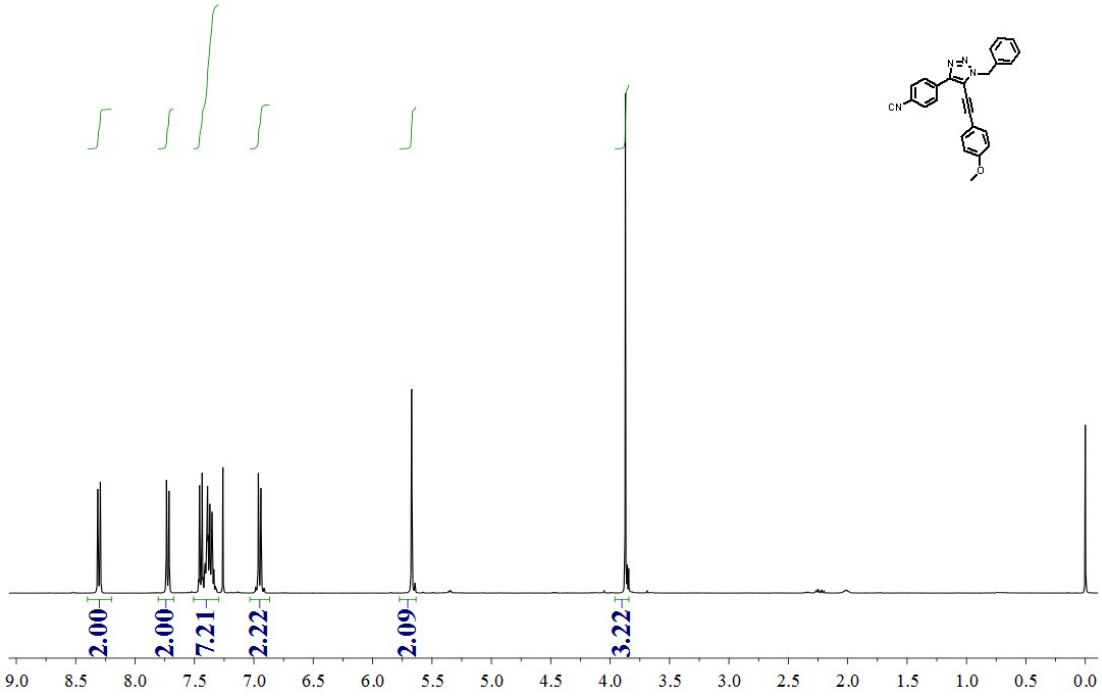
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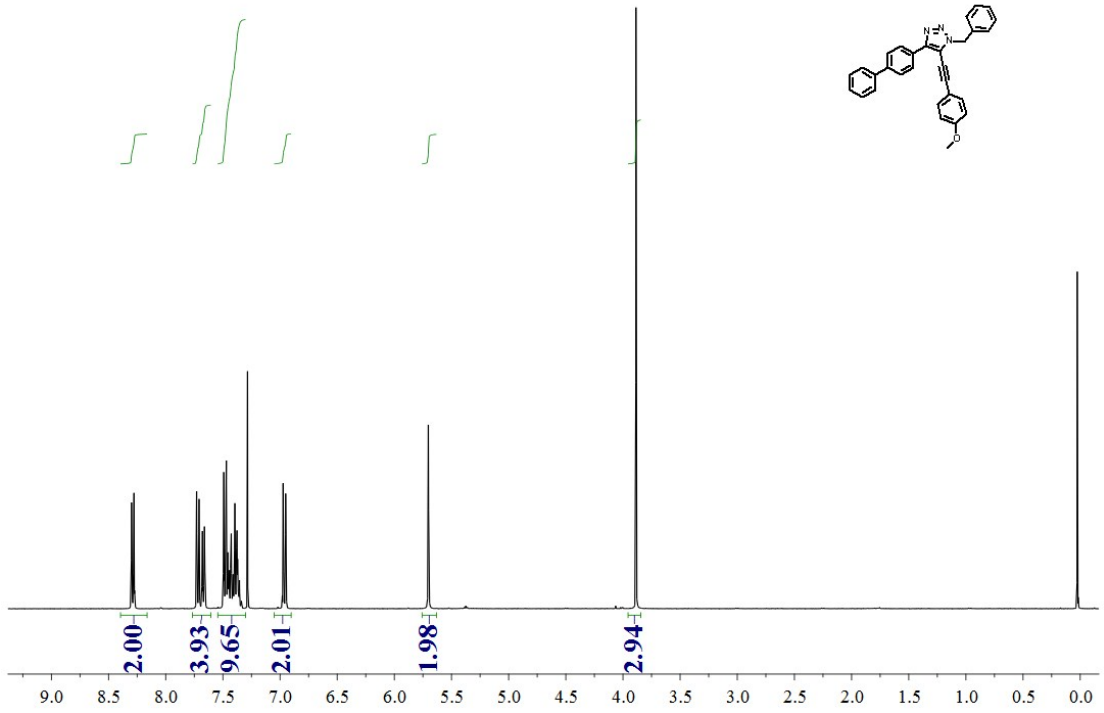
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3.0
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1.0
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0.0

8. References.

(1) (a) X. Wang, M. Liu, Y. Wang, H. Fan, J. Wu, C. Huang, H. Hou, *Inorg. Chem.,* 2017, **56**, 13329; (b) W. Song, N. Zheng, *Org. Lett.,* 2017, **19**, 6200.

(2) W. Wang, F. Wei, Y. Ma, C. Tung, Z. Xu, *Org. Lett.,* 2016, **18**, 4158.

(3) G. M. Sheldrick, SHELXS 97, Program for the Refinement of Crystal Structures; University of Göttingen, Germany, **1997**.