Supplementary Data

Three thiacalix[4]arene-based Cu(I) coordination polymers: catalytic activities for azide-alkyne cycloaddition reaction and luminescent properties

Jian-Fang Li,[a] Peng Du,[b] Ying-Ying Liu,[a,*] Guo-Hai Xu,[c,*] and Jian-Fang Ma[a,*]

[a]*Key Lab of Polyoxometalate Science, Department of Chemistry, Northeast Normal University, Changchun 130024, P. R. China*

[b]*College of Chemistry and Chemical Engineering, Dezhou University, Dezhou 253023, China*

[c]*Key Laboratory of Jiangxi University for Functional Materials Chemistry, School of Chemistry and Chemical Engineering, Gannan Normal University, Ganzhou, Jiangxi 341000, China*

Materials and Instrumentation. All chemicals we used were purchased from commercial suppliers and not purification. The C, H and N elemental analyses were determined on a Perkin-Elmer 240C elemental analyzer. IR spectra were collected on an Alpha Centaurt FT/IR spectrophotometer. PXRD patterns were performed on a Rigaku Dmax 2000 X-ray diffractometer with Cu-Kα radiation (λ = 0.154 nm). TGA was recorded on a DTG-60H under N_2 atmosphere. The yields of catalytic reaction were calculated by GC equipment which consists of a FID detector (GC-2014C, Shimadzu, Japan) and a capillary (30 m × 0.25 mm, WondaCAP 17). ^{1}H NMR spectra were collected on a Bruker 600 MHz. Solid state UV–vis absorption spectra were gained on a Cary 500 spectrophotometer.

X-ray crystallography. Crystallographic data of **1-3** was obtained on an Oxford Diffraction Gemini R CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 298K. The refinement of the structures was resolved by means of

SHELXL-2018/3 procedure. Non-hydrogen atoms were refined anisotropically. The SQUEEZE program in PLATON was utilized because there are the highly disordered solvents in **1** and **3**. The disordered atoms in **1** and **3** were treated using a split-atom model with a total occupancy of 0.5 or 1. Bond distances and angles are given in Tables S3.

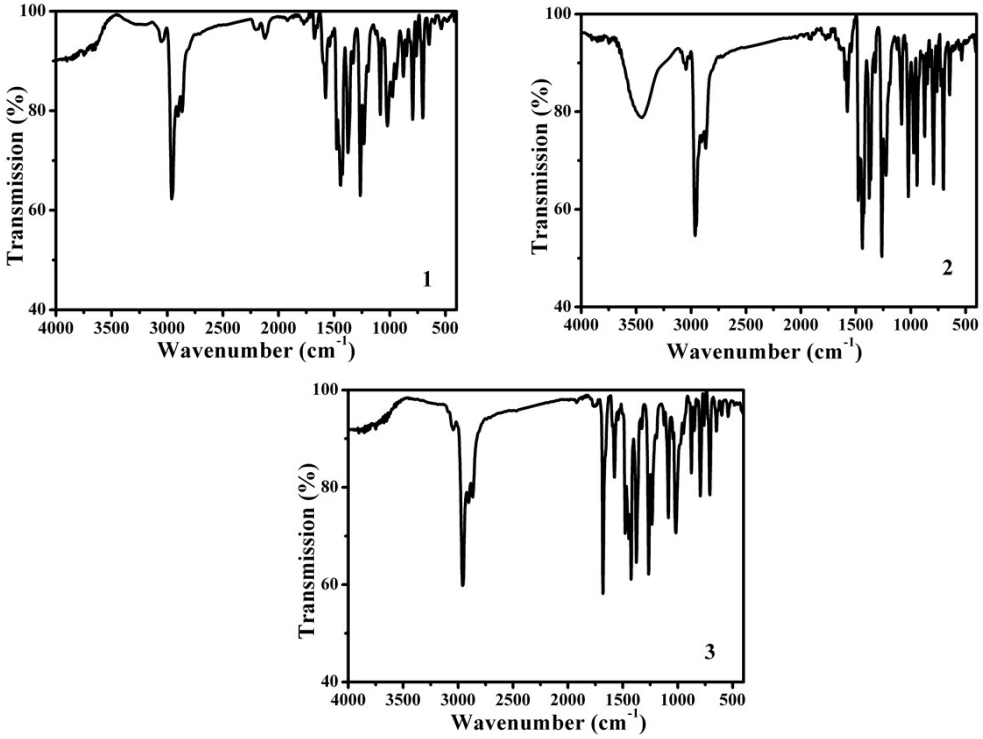


Fig. S1 IR spectra of **1-3**.

Azide-Alkyne Cycloaddition (AAC) Measurements. Catalyst (10 mg), benzyl azide (1 mmol), phenylacetylene (2 mmol) and amyl acetate (0.92 mmol) were added in MeOH (4 mL). Then the mixture was added in a 38 mL pressure tube. Amyl acetate acts as an internal standard to calculate the yields. The product yields were measured via GC and further verified by 1H NMR.

Table S1 Cu···Cu Distances (Å) of CPs **2** and **3**

	Cu(1)···Cu(3)$^{\#2}$	Cu(2)···Cu(3)	Cu(1)···Cu(1)$^{\#2}$
2	2.8041(11)	2.7977(11)	
3			2.6714(17)

Symmetry codes: for 2: $^{\#2}$ –x+1, –y–1, –z. For 3: $^{\#2}$ –x+1, –y, –z.

Table S2 Hydrogen-Bond Geometry for **3** in (Å) and (°)

	D-H···A	d(D-H)	d(D···A)	(D-H···A)
C(57)-H(57)···N(3)	2.64	0.93	3.467(7)	149.2

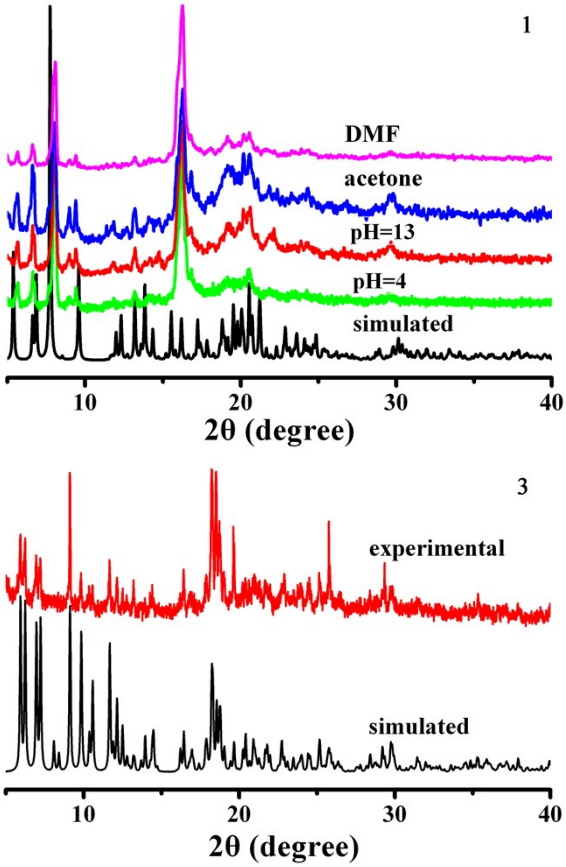


Fig. S2 PXRD patterns of **1** immersed in organic solvents and aqueous solutions with various pH values as well as **3**.

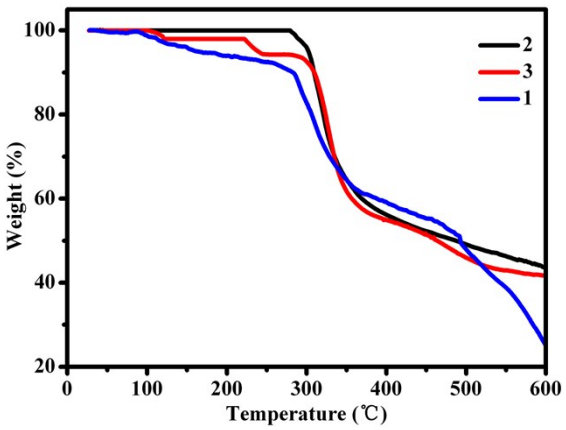
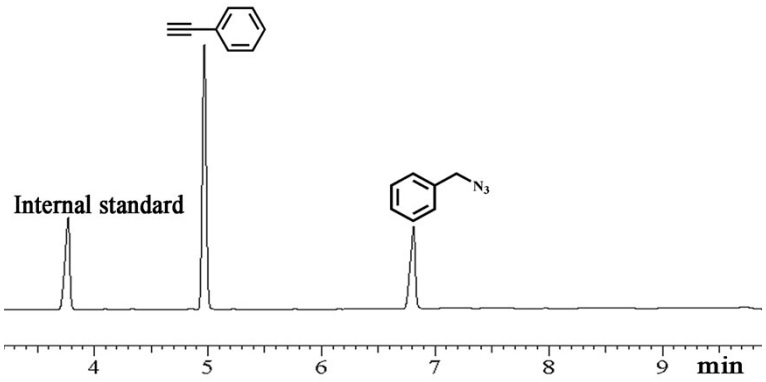
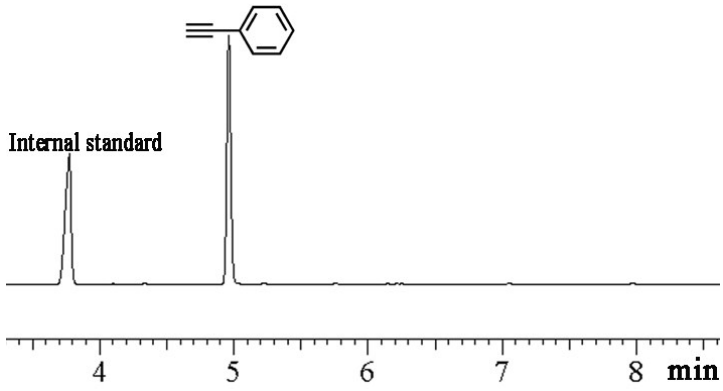


Fig. S3 TG curve of **1-3**.


Internal standard
N3
4
5
6
7
8
9
min

(a)


Internal standard
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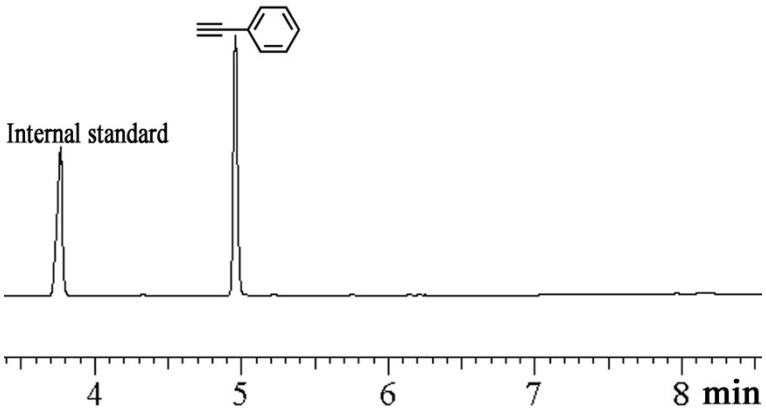
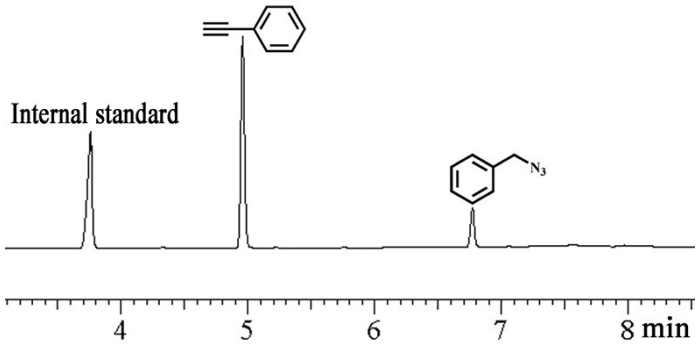
5
6
7
8
min

(b)


Internal standard
4
5
6
7
8 min

(c)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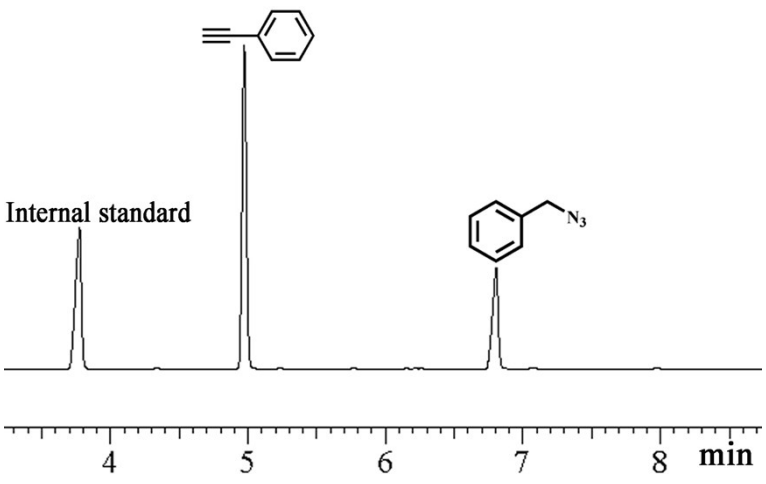
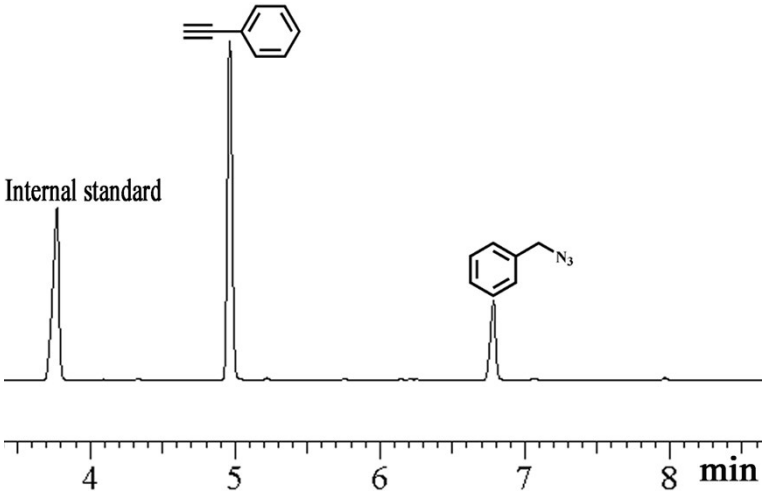
7
8 min

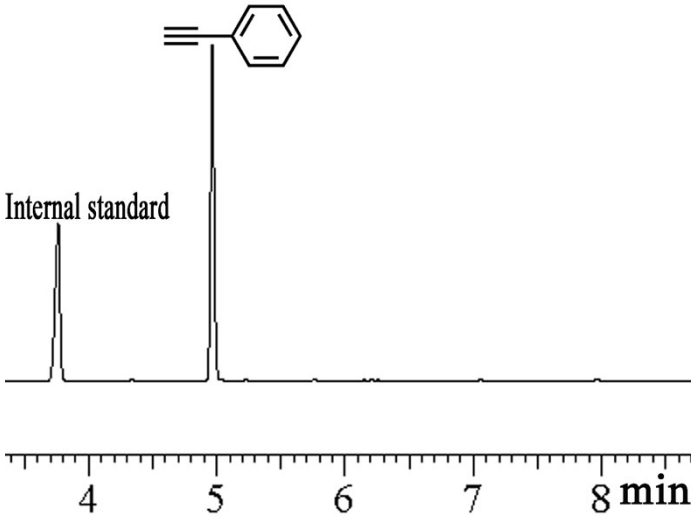
(d)


Internal standard
N3
4
5
6
7
8
min

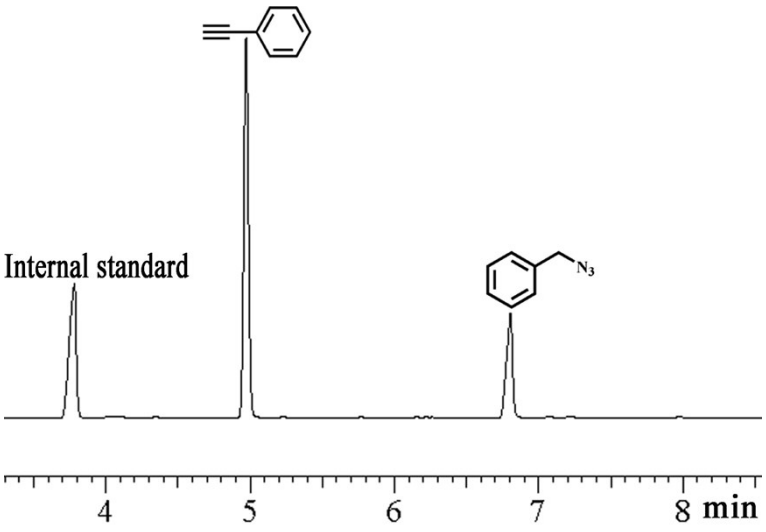
(e)


Internal standard
N3
4
5
6
7
8
min

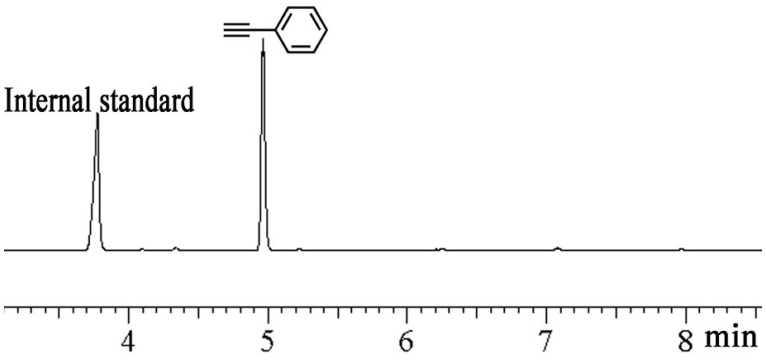
(f)


Internal standard
4
5
6
7
8 min

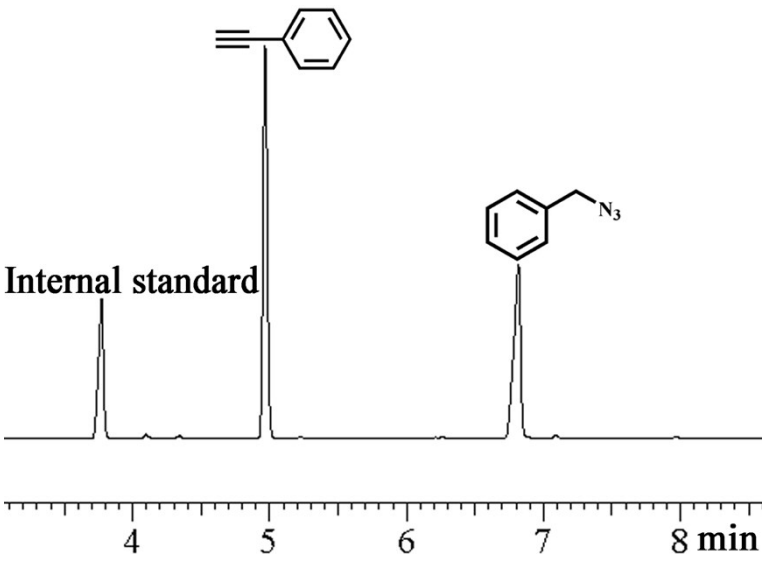
(g)



(h)



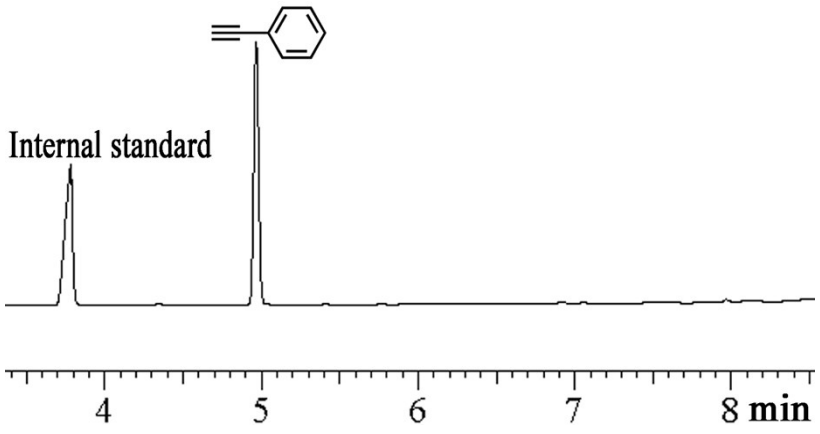
(i)



(j)

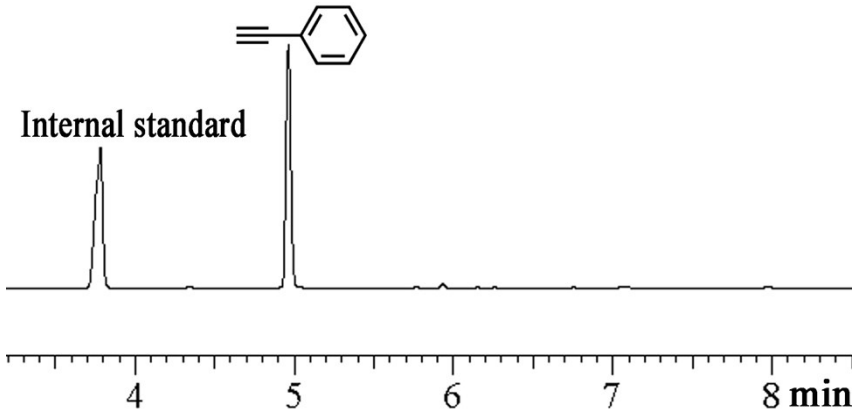
Fig. S4 GC spectra of AAC reaction for optimizing conditions. (a) Catalytic reaction in MeOH at 70°C for 8 h without catalyst. (b) Catalytic reaction in MeOH at 70°C for 8 h

with **2** (10 mg). (c) Catalytic reaction in EtOH at 70°C for 8 h with **2** (10 mg). (d) Catalytic reaction in DMC at 70°C for 8 h with **2** (10 mg). (e) Catalytic reaction in MeOH at 70°C for 2 h with **2** (10 mg). (f) Catalytic reaction in MeOH at 70°C for 4 h with **2** (10 mg). (g) Catalytic reaction in MeOH at 70°C for 6 h with **2** (10 mg). (h) Catalytic reaction in MeOH at 50°C for 8 h with **2** (10 mg). (i) Catalytic reaction in MeOH at 70°C for 8 h with **1** (10 mg). (j) Catalytic reaction in MeOH at 70°C for 8 h with **3** (10 mg).

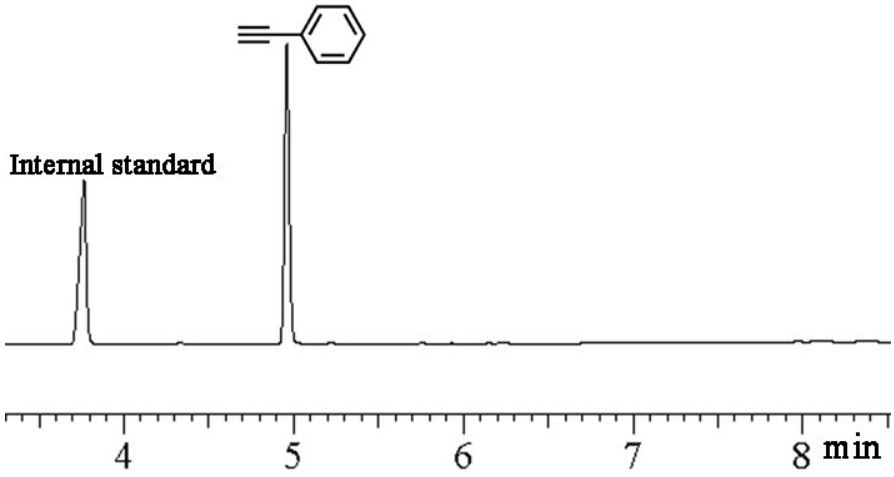


(a)

(b)


Internal standard
4
5
6
7
8 min

(c)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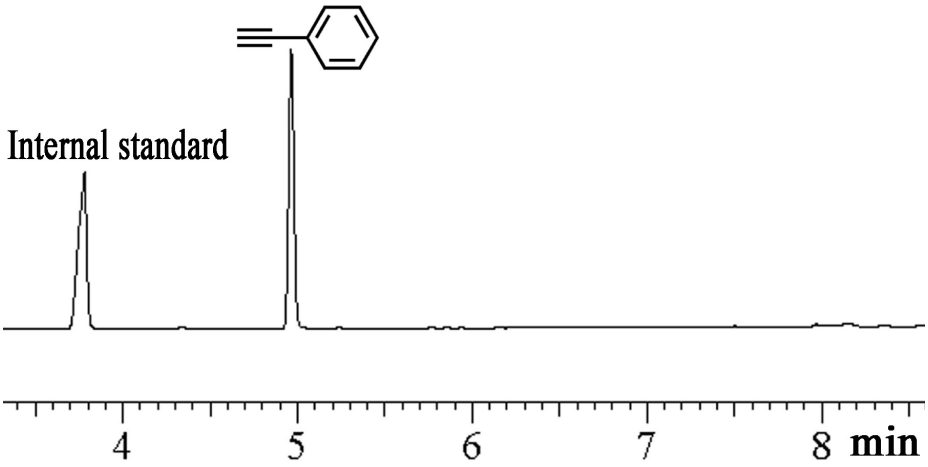
4
5
6
7
8 min

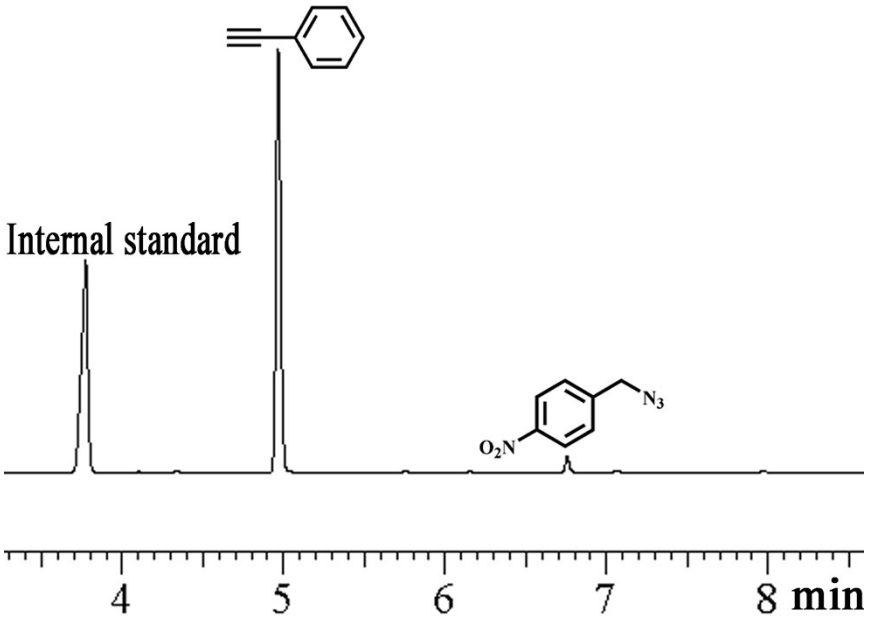
(d)


Internal standard
4
5
6
7
8 min

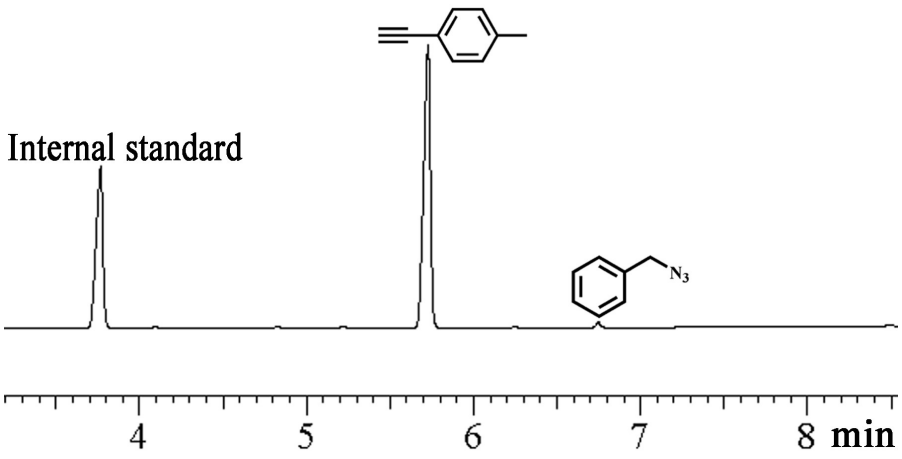
(e)

(f)

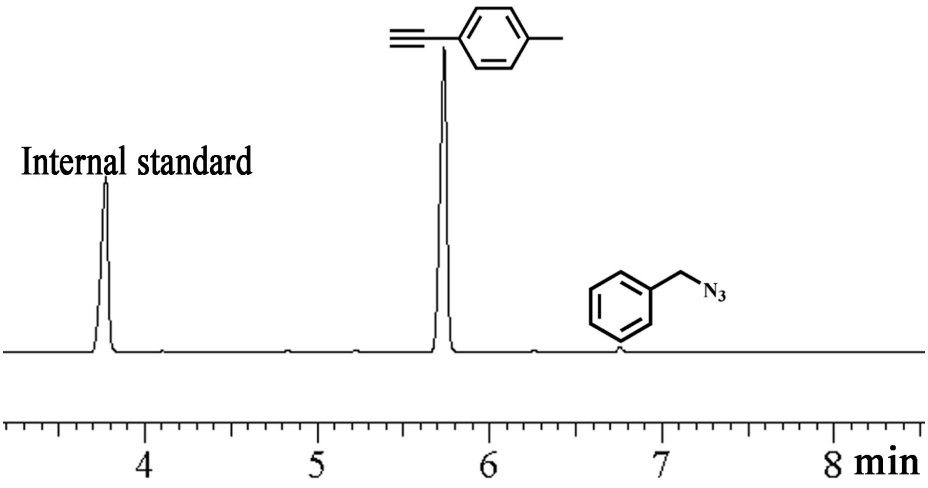
(g)



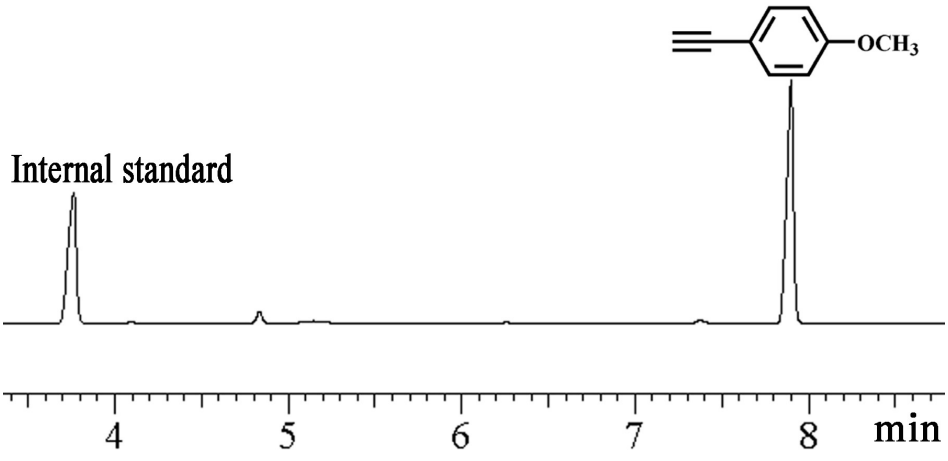
(h)


Internal standard
N3
4
5
6
7
8 min

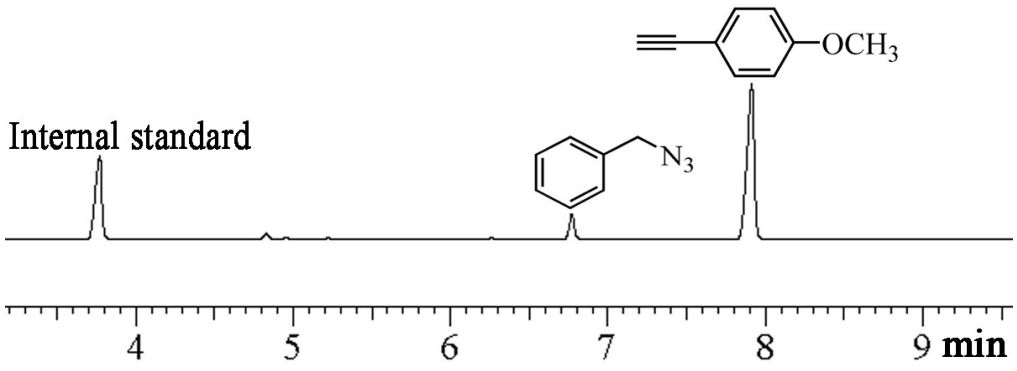
(i)


Internal standard
N3
4
5
6
7
8 min

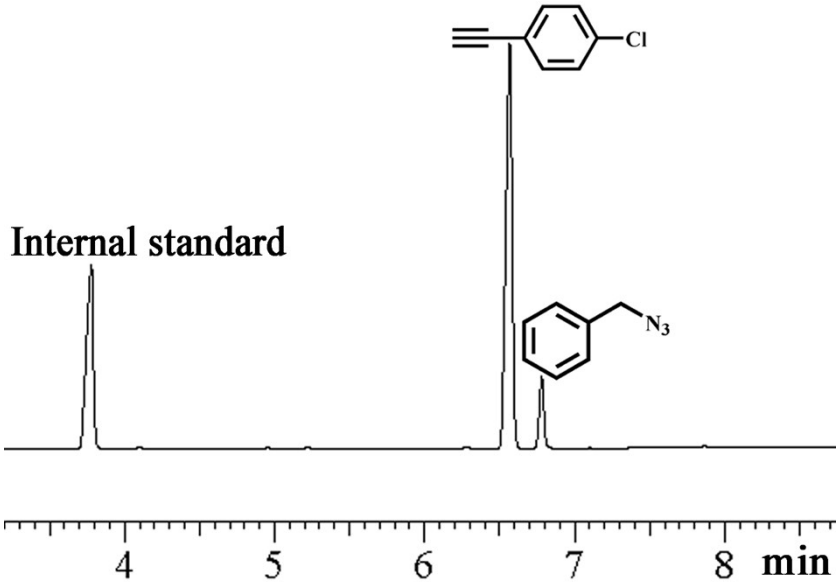
(j)


OCH3
Internal standard
4
5
6
7
8
min

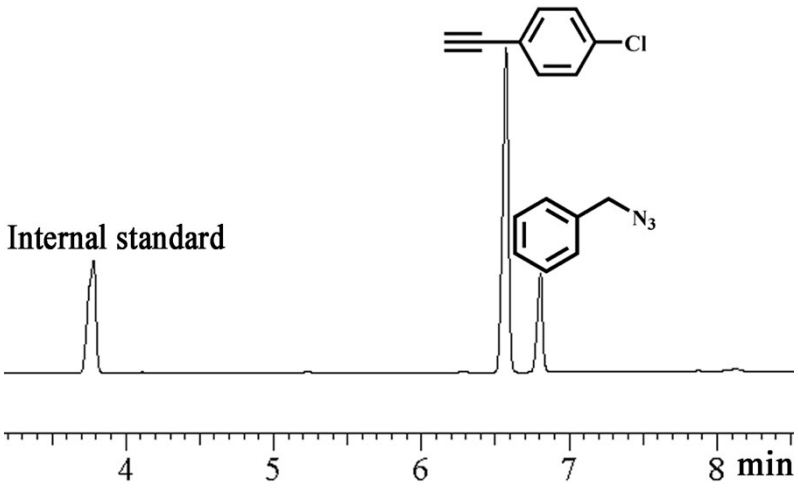
(k)


Internal standard
OCH3
N3
4
5
6
7
8
9 min

(l)


Internal standard
Cl
N3
4
5
6
7
8 min

(m)


Internal standard
Cl
N3
4
5
6
7
8 min

(n)

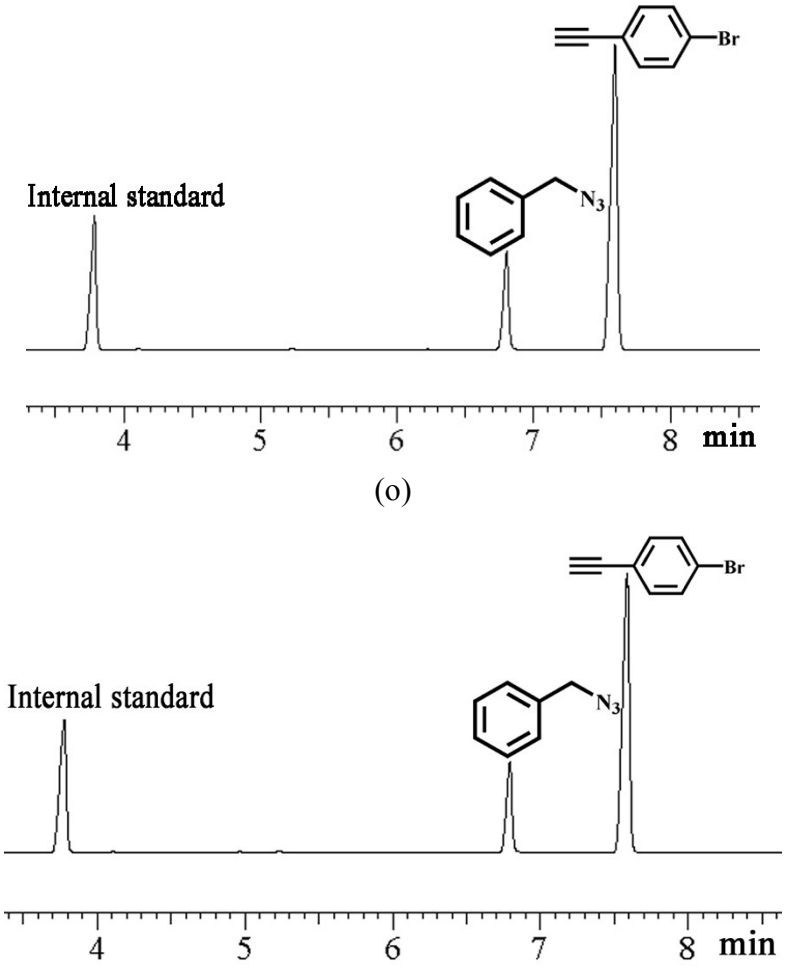


Fig. S5 GC spectra for the AAC reaction with various functional groups.

(a) 1-(azidomethyl)-4-methylbenzene and phenylacetylene catalyzed by **1**.

(b) 1-(azidomethyl)-4-methylbenzene and phenylacetylene catalyzed by **2**.

(c) 1-(azidomethyl)-3-methylbenzene and phenylacetylene catalyzed by **1**.

(d) 1-(azidomethyl)-3-methylbenzene and phenylacetylene catalyzed by **2**.

(e) 1-(azidomethyl)-2-fluorobenzene and phenylacetylene catalyzed by **1**.

(f) 1-(azidomethyl)-2-fluorobenzene and phenylacetylene catalyzed by **2**.

(g) 1-(azidomethyl)-4-nitrobenzene and phenylacetylene catalyzed by **1**.

(h) 1-(azidomethyl)-4-nitrobenzene and phenylacetylene catalyzed by **2**.

(i) 1-(azidomethyl)benzene and 1-ethynyl-4-methylbenzene catalyzed by **1**.

(j) 1-(azidomethyl)benzene and 1-ethynyl-4-methylbenzene catalyzed by **2**.

(k) 1-(azidomethyl)benzene and 1-ethynyl-4-methoxybenzene catalyzed by **1**.

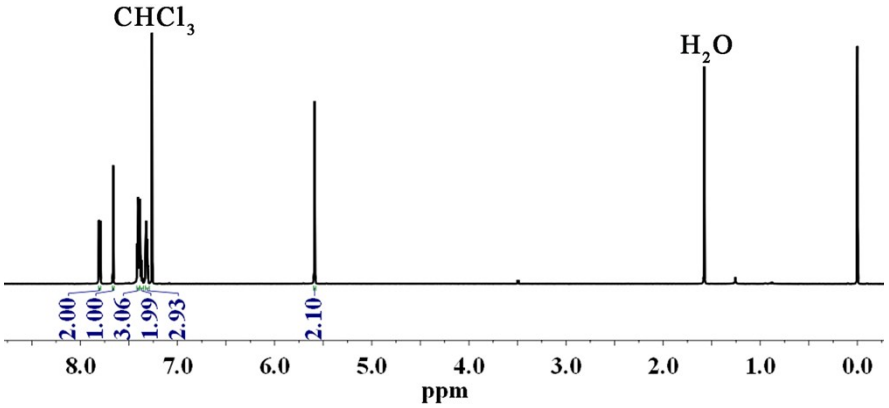
(l) 1-(azidomethyl)benzene and 1-ethynyl-4-methoxybenzene catalyzed by **2**.

(m) 1-(azidomethyl)benzene and 1-ethynyl-4-chlorobenzene catalyzed by **1**.

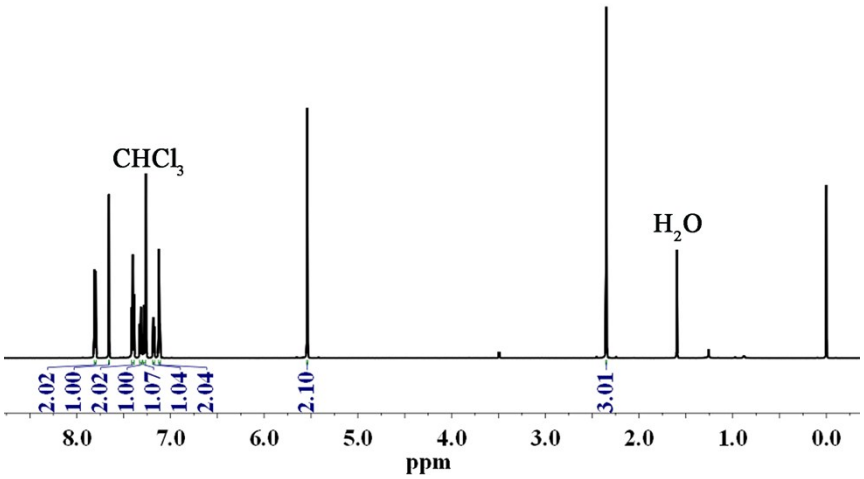
(n) 1-(azidomethyl)benzene and 1-ethynyl-4-chlorobenzene catalyzed by **2**.

(o) 1-(azidomethyl)benzene and 1-ethynyl-4-bromobenzene catalyzed by **1**.

(p) 1-(azidomethyl)benzene and 1-ethynyl-4-bromobenzene catalyzed by **2**.



(a)



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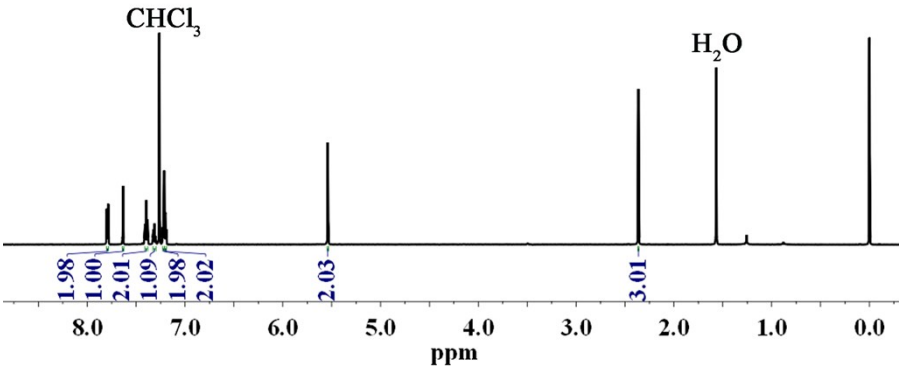
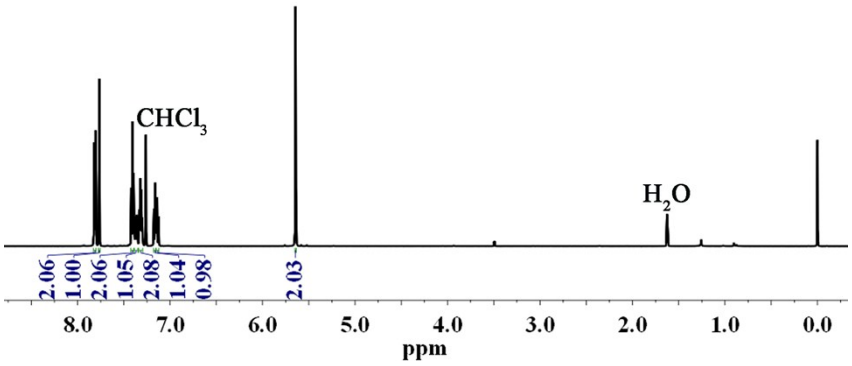


(c)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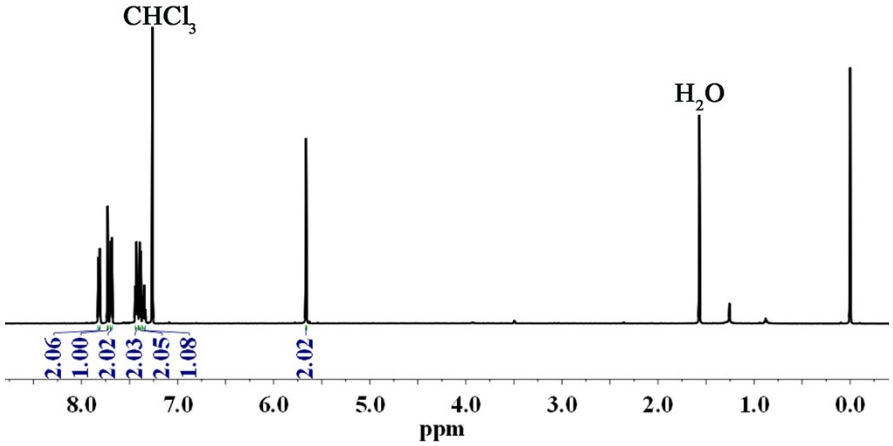
2.06
1.05
2.08
1.04
0.98
2.03
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm

(d)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H2O
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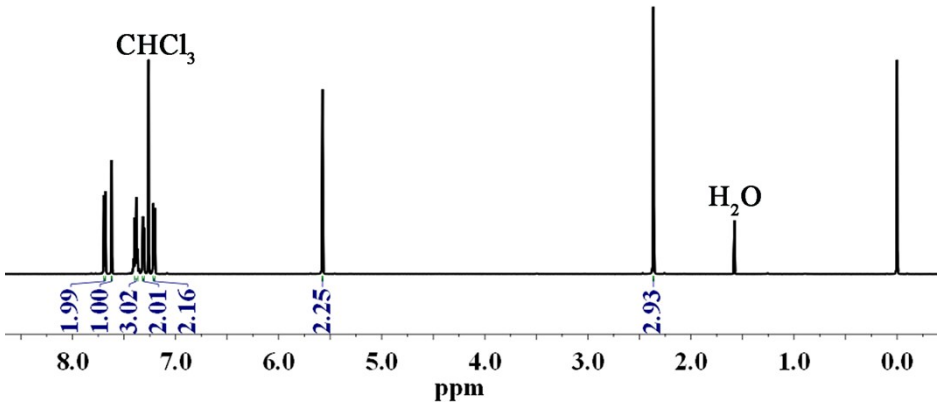
1.00
2.02
2.03
2.05
1.08
2.02
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm

(e)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3.02
2.01
2.16
2.25
2.93
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7.0
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5.0
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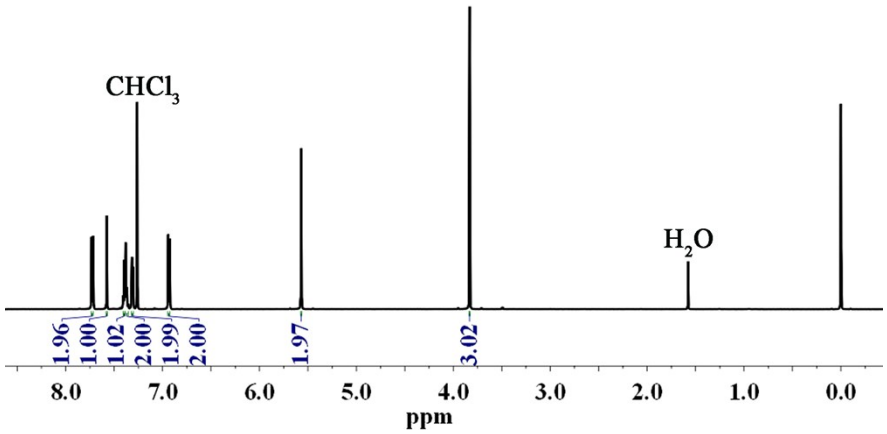
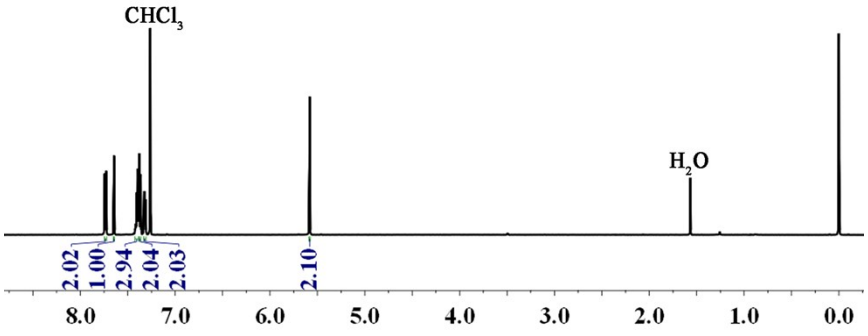
3.0
2.0
1.0
0.0
ppm

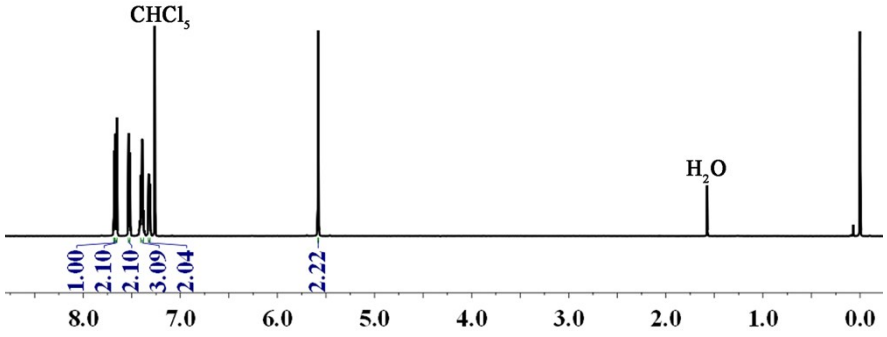
(f)



(g)



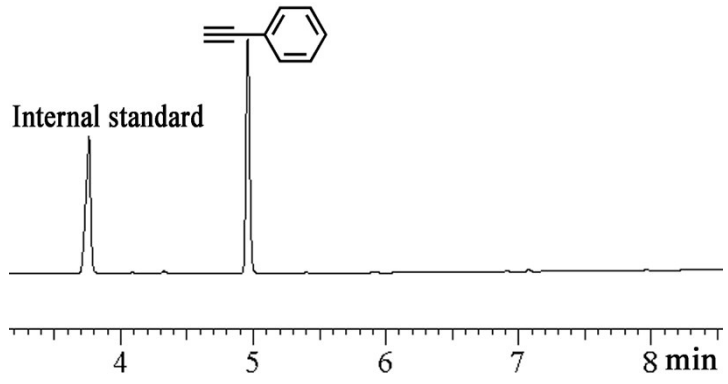
(h)



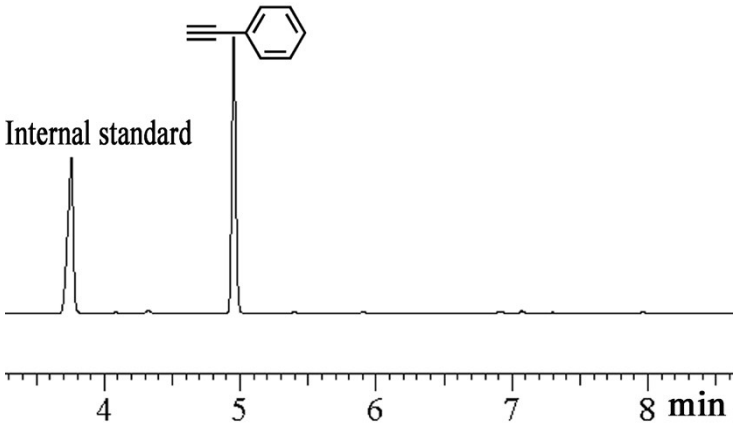
(i)

Fig. S6 [1]H NMR spectra of the products from AAC reaction. (a) 1-benzyl-4-phenyl-1H-1,2,3-triazole. (b) 1-(3-methyl-benzyl)-4-phenyl-1H-1,2,3-triazole. (c) 1-(4-methyl-benzyl) -4-phenyl-1H-1,2,3-triazole. (d) 1-(2-fluoro-benzyl)-4-phenyl-1H-1,2,3-triazole. (e) 1- (4-nitor-benzyl)-4-phenyl-1H-1,2,3-triazole. (f) 1-benzyl-4-(4-methyl-phenyl)-1H-1,2,3 – triazole. (g) 1-benzyl-4-(4-methoxy-phenyl)-1H-1,2,3-triazole. (h) 1-benzyl-4-(4-chloro-phenyl)-1H-1,2,3-triazole. (i) 1-benzyl -4-(4-bromo-phenyl)-1H-1,2,3-triazole.

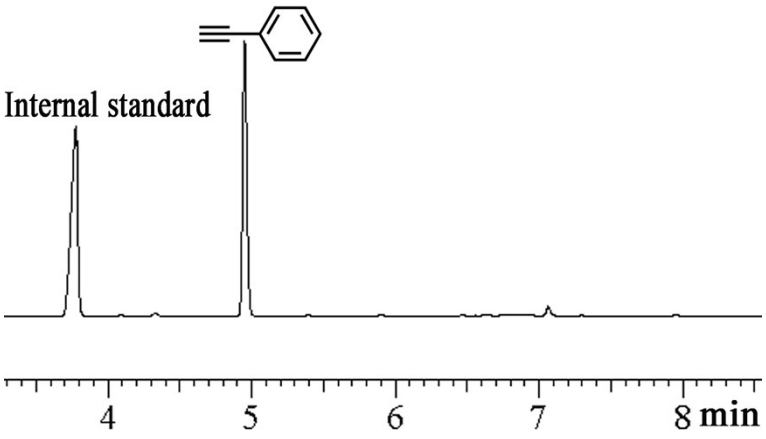
(a)



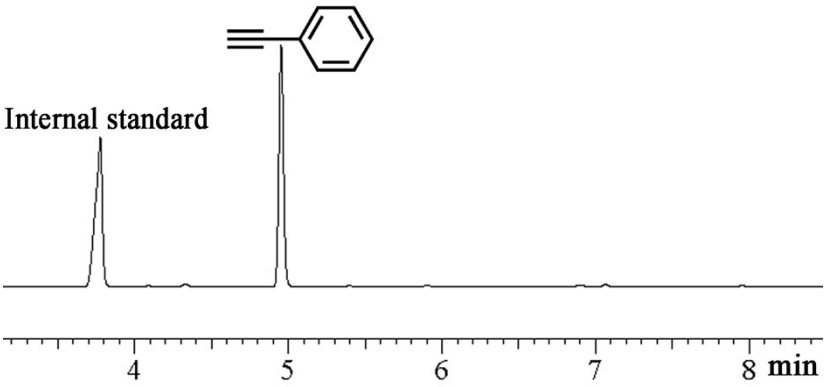
(b)



(c)



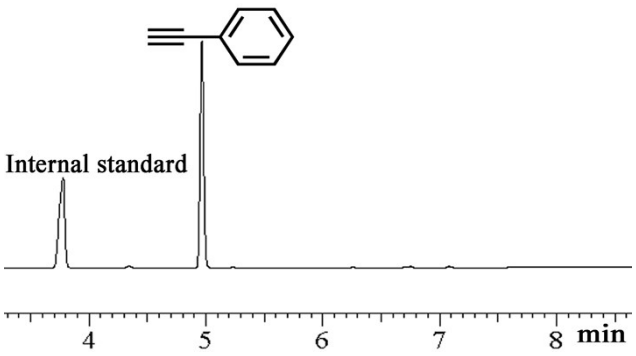
(d)



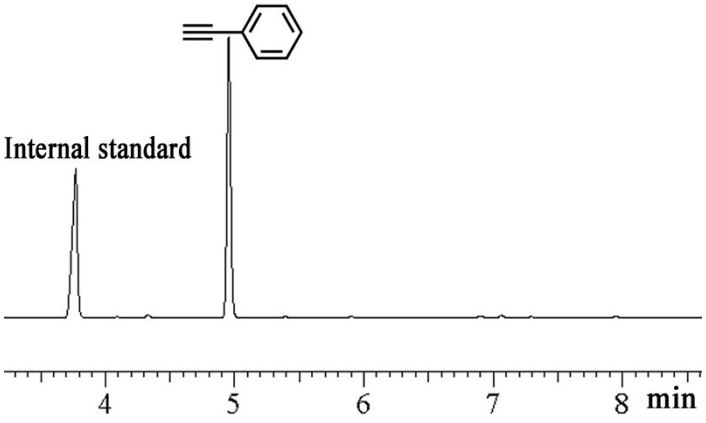
(e)

Fig. S7 GC spectra for the AAC reaction of cycle experiments with **1**. (a) After the first circle. (b) After the second circle. (c) After the third circle. (d) After the fourth circle. (e) After the fifth circle.

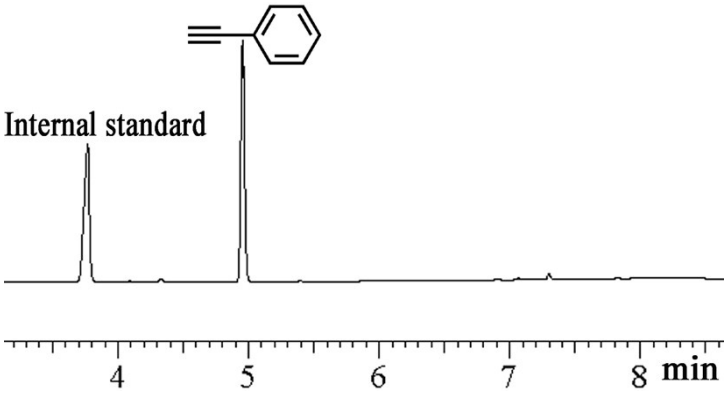
(a)


Internal standard
4
5
6
7
8
min

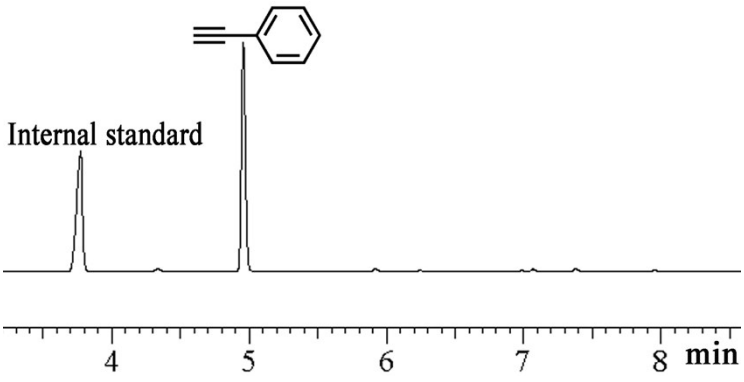
(b)


Internal standard
4
5
6
7
8
min

(c)


Internal standard
4
5
6
7
8
min

(d)


Internal standard
4
5
6
7
8
min

(e)

Fig. S8 GC spectra for the AAC reaction of cycle experiments with **2**. (a) After the first circle. (b) After the second circle. (c) After the third circle. (d) After the fourth circle. (e) After the fifth circle.

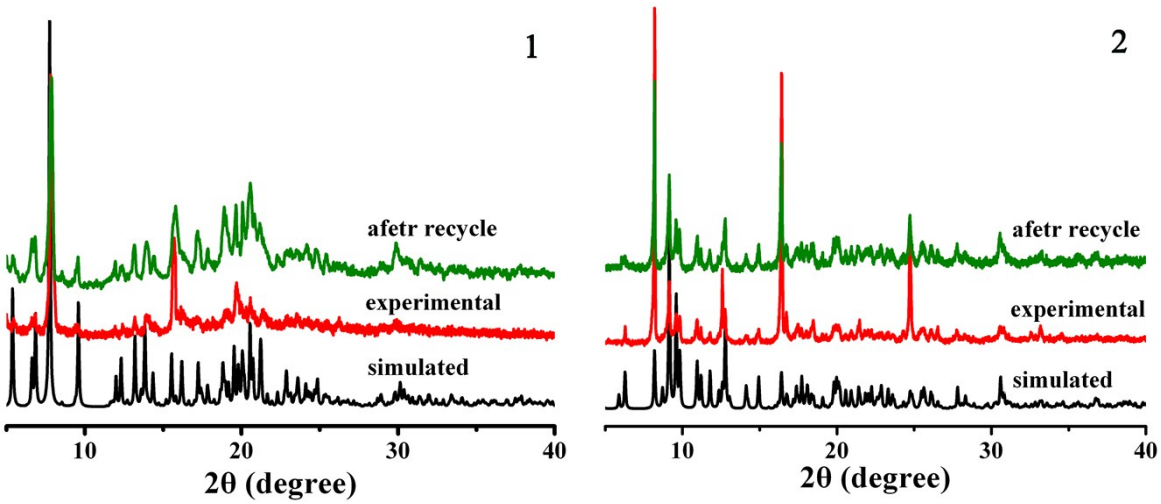


Fig. S9 PXRD patterns of **1** and **2** before and after five recycle experiments.

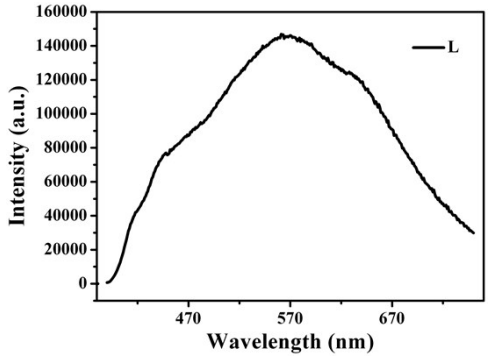
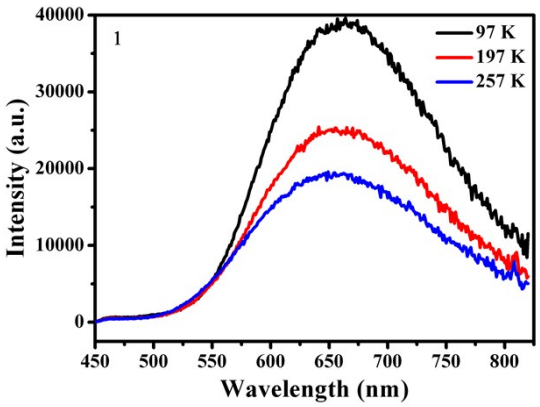


Fig. S10 Luminescence emission spectra of L at room temperature.



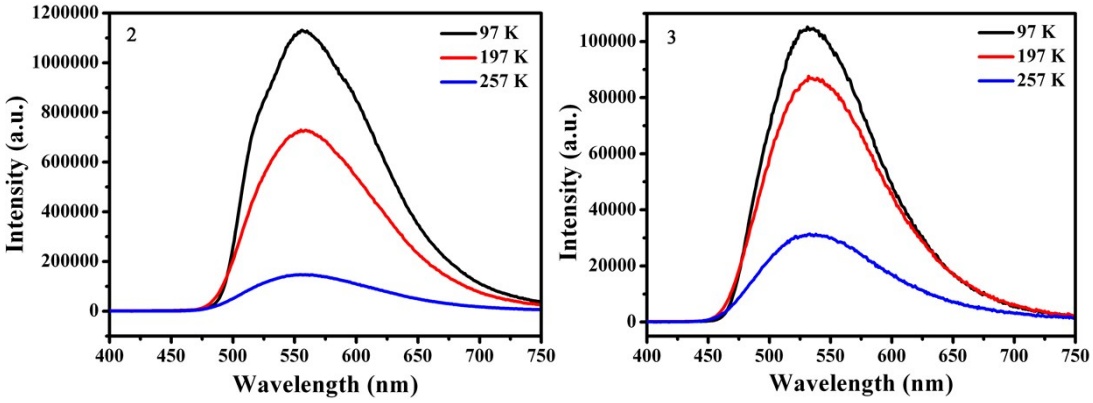


Fig. S11 Luminescence emission spectra of **1-3** at 97 K, 197 K and 257 K.

Table S3 Selected Bond Distances (Å) and Angles (°) for CPs **1-3**

		1	
Cu(1)-N(5)	1.957(9)	N(5)-Cu(1)-N(1)$^{\#1}$	103.1(3)
Cu(1)-N(2)	2.025(7)	N(2)-Cu(1)-N(1)$^{\#1}$	108.3(3)
Cu(1)-N(1)$^{\#1}$	2.092(8)	N(5)-Cu(1)-N(4)$^{\#2}$	102.9(3)
Cu(1)- N(4)$^{\#2}$	2.105(7)	N(2)-Cu(1)-N(4)$^{\#2}$	102.7(3)
Cu(2)-C(65)$^{\#3}$	1.799(9)	N(1)$^{\#1}$-Cu(1)- N(4)$^{\#2}$	112.6(3)
Cu(2)-N(3)	1.909(9)	C(65)$^{\#3}$-Cu(2)-N(3)	157.3(5)
Cu(2)-O(5)	2.354(6)	C(65)$^{\#3}$-Cu(2)-O(5)	103.3(4)
N(5)-Cu(1)-N(2)	127.3(4)	N(3)-Cu(2)-O(5)	98.1(3)
Symmetry codes: $^{\#1}$ –x+2, –y+1, –z; $^{\#2}$ –x+1, –y+2, –z; $^{\#3}$ x, y–1, z+1.			
		2	
Cu(1)-N(1)	2.028(4)	N(1)-Cu(1)-Br(1)	104.88(13)
Cu(1)-N(3)$^{\#1}$	2.100(5)	N(3)$^{\#1}$-Cu(1)-Br(3)$^{\#2}$	104.46(12)
Cu(1)-Br(3)$^{\#2}$	2.4408(9)	N(1)-Cu(1)-Br(1)	104.88(13)
Cu(1)-Br(1)	2.5436(10)	N(3)$^{\#1}$-Cu(1)-Br(1)	105.19(14)
Cu(2)-N(4)$^{\#3}$	2.027(4)	Br(3)$^{\#2}$-Cu(1)-Br(1)	109.82(4)
Cu(2)-N(2)	2.076(5)	N(4)$^{\#3}$-Cu(2)-N(2)	110.67(19)
Cu(2)-Br(3)	2.4475(10)	N(4)$^{\#3}$-Cu(2)-Br(3)	120.89(13)
Cu(2)-Br(2)	2.5943(10)	N(2)-Cu(2)-Br(3)	107.17(13)
Cu(3)-Br(1)$^{\#2}$	2.2703(10)	N(4)$^{\#3}$-Cu(2)-Br(2)	104.18(14)
Cu(3)-Br(2)	2.2761(10)	N(2)-Cu(2)-Br(2)	101.61(13)

N(1)-Cu(1)-N(3)$^{\#1}$	104.31(19)	Br(3)-Cu(2)-Br(2)	110.66(4)
N(1)-Cu(1)-Br(3)$^{\#2}$	126.36(13)	Br(1)$^{\#2}$-Cu(3)-Br(2)	165.47(4)

Symmetry codes: $^{\#1}$ –x+1, –y, –z; $^{\#2}$ –x+1, –y–1, –z; $^{\#3}$ –x+1, –y–1; –z+1.

3

Cu(1)-N(1)	2.062(4)	N(4)$^{\#1}$-Cu(1)-I(1)	111.02(11)
Cu(1)-N(4)$^{\#1}$	2.064(4)	N(1)-Cu(1)-I(1)$^{\#2}$	106.40(11)
Cu(1)-I(1)	2.6150(7)	N(4)$^{\#1}$-Cu(1)-I(1)$^{\#2}$	105.84(10)
Cu(1)-I(1)$^{\#2}$	2.6406(7)	I(1)-Cu(1)-I(1)$^{\#2}$	118.90(2)
N(1)-Cu(1)-N(4)$^{\#1}$	106.91(15)	N(1)-Cu(1)-I(1)	107.13(11)

Symmetry codes: $^{\#1}$ x, y, z+1; $^{\#2}$ –x+1, –y, –z.