Supporting information for

Cu_3L_2 metal-organic cage for A^3-couping reaction: reversible coordination interaction triggered homogeneous catalysis and heterogeneous recovery

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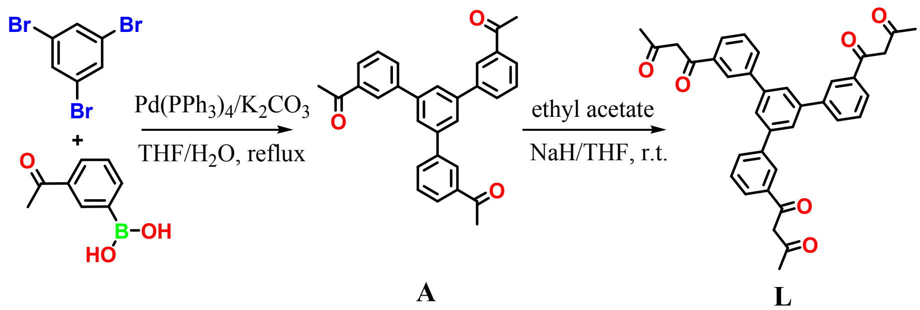
Content

1. Materials and instruments.

All chemicals and solvents were at least of analytic grade and employed as received without further purification. Elemental analyses for C and H were obtained on a Perkin-Elmer analyser model 240. The powder diffractometer (XRD) patterns were collected by a D8 ADVANCEX-ray with Cu Kα radiation (λ = 1.5405 Å). Infrared (IR) samples were prepared as KBr pellets, and spectra were obtained in the 400-4000cm^{-1} range using a Perkin-Elmer 1600 FTIR spectrometer. ^{1}H NMR spectra were obtained on a Bruker AVANCE-400 spectrometer, and the chemical shifts are reported in δ relative to TMS. High-resolution ESI data were obtained using a Bruker Daltonics Inc. instrument. The N_2 adsorption–desorption isotherms were performed on an ASAP 2020/TriStar 3000 (Micromeritics). HRTEM (High resolution transmission electron microscopy) analysis was performed on a JEOL 2100 Electron Microscope at an operating voltage of 200 kV. Thermogravimetric analyses (TGA) curves were obtained on a TA Instrument Q5 simultaneous TGA at a heating rate of 10°C/min from room temperature to 600°C under flowing nitrogen. X-ray photoelectron spectroscopy (XPS) was performed with a PHI 5000 Versaprobe II (VP-II) electron spectrometer (ULVAC-PHI) using 300 W Al Kα radiation with a base pressure of 3 × 10^{-9} mbar. The binding energies of the elements present in the air-facing side of the specimen perpendicular to the electron beam were calculated according to that of the C 1s line at 284.8 eV from adventitious carbon. Gas chromatography (GC) analysis was performed on an Agilent 7890B GC.

2. Synthesis and characterization of L, 1 and 2.



Scheme S1. Synthesis of **L**.

Synthesis and characterization of A

Under nitrogen, A mixture of 1, 3, 5-tribromobenzene (1.00 g, 3.17 mmol), 3-acetylbenzeneboronic acid (1.56 g, 9.52 mmol), K_2CO_3 (4 g, 29 mmol) $Pd(PPh_3)_4$ (250 mg, 0.032 mmol) in THF (100 mL) and H_2O (50 mL) was refluxed for 24 h. After the mixture was allowed to cool to room temperature, the solvent was removed under reduced pressure and the residue was re-dissolved in dichloromethane. The organic phase was dried over $MgSO_4$. The solvent was removed under reduced pressure to afford a crude product. The crude product was purified by the column on silica gel using dichloromethane/petroleum ether (2:1, v/v) as eluent to give white solid of **A** (6,6'-dichloro-2,2'-diethoxyl-1,1'-binaphthyl-4,4'-bis(p-ethynylpyridine)). Yield: 95%. ^{1}H NMR ($CDCl_3$): 8.28 (1H), 8.01 (1H), 7.92 (1H), 7.85 (1H), 7.62 (1H), 2.70 (3H). IR (KBr pellet, cm^{-1}): 1683 (s), 1600 (m), 1454 (w), 1398 (w), 1354 (w), 1273 (s), 1222 (m), 792 (w), 699 (w), 589 (w). Elemental analysis (%) calcd for $C_{30}H_{24}O_3$: C, 83.31, H, 5.59; Found: C, 83.15, H 5.63. ESI-MS: calcd for $C_{30}H_{24}O_3Na^+$, M+Na$^+$, 455.1623; found, m/z 455.1644.

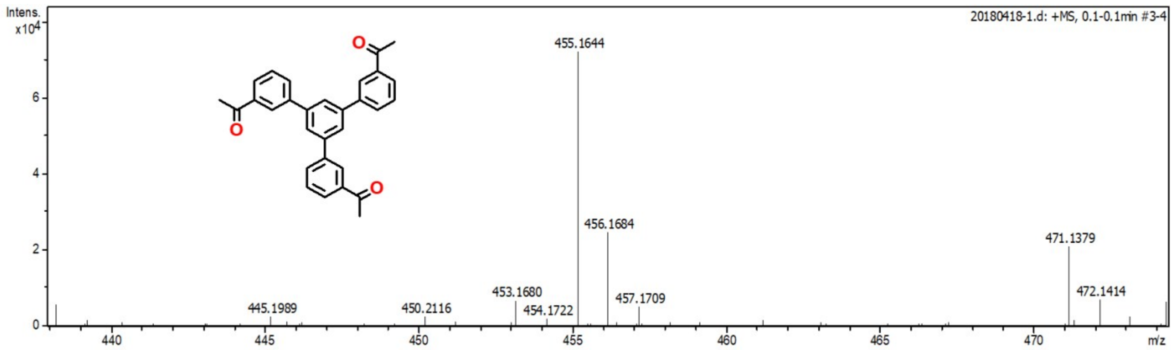


Fig. S1 ESI-MS spectrum of **A**.

Synthesis and characterization of L

Ethyl acetate (30 mL) was added dropwise to a vigorously stirred solution of **A** (1 g, 2.31 mmol), NaH (1 g, 41.67 mmol) in THF (40 mL). The resulting mixture was stirred at ambient temperature for 24 h. After removal of the solvent under reduced pressure, the residue was dissolved in H_2O and the pH value was adjusted to 5.0 with glacial acetic. The crude product was purified by column on silica gel using dichloromethane/ethyl acetate (1:1% v/v) as eluent to give **L** in 79% yield. ^{1}H NMR ($CDCl_3$): 8.19 (1H), 7.91 (1H), 7.86 (1H), 7.84 (1H), 7.59 (1H), 6.27 (1H). 2.23 (3H). IR (KBr pellet, cm^{-1}): 1575 (s), 1429 (w), 1363 (m), 1265 (w), 1193 (w), 767 (s), 701 (w). Elemental analysis (%) calcd for $C_{36}H_{30}O_6$ (desolvated): C, 77.40, H, 5.41; Found: C, 77.13, H 5.52. ESI-MS: calcd for $C_{36}H_{29}O_6^-$, M$^-$, 557.1965; found, m/z 557.2048.

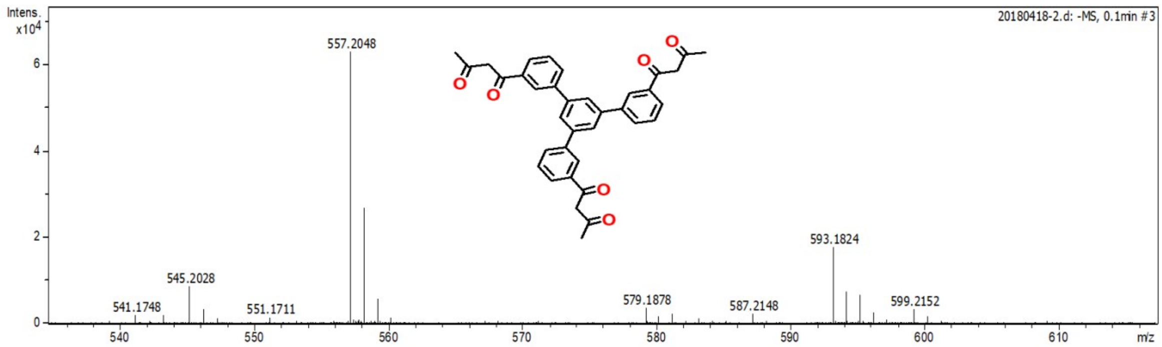


Fig. S2 ESI-MS spectrum of **L**.

Synthesis and characterization of Cu(II)-MOC (1)

A solution of $Cu(OAc)_2$ (5.46 mg, 0.03 mmol) in MeOH (2 mL) was carefully layered over a solution of **L** (5.58 mg, 0.01 mmol) in CH_2Cl_2 (2 mL). The solution were left for about 5 days at room temperature, and **1** was obtained as green crystals. Yield 88% (based on Cu). IR (KBr pellet, cm^{-1}): 3539 (w), 1558 (m), 1488 (s), 1410 (s), 1385 (s),1298 (w),1203 (w), 1093 (w), 1012 (w), 875 (m), 764 (w), 697 (w), 623 (w). Elemental analysis (%) calcd for $C_{150}H_{115}Cl_{12}Cu_6O_{24}$ (desolvated): C, 57.96, H, 3.73; Found: C, 57.09, H 3.42. ESI-MS: calcd for $C_{72}H_{54}O_{12}Cu_3Na$, M+Na$^+$; found, m/z 1324.1137.

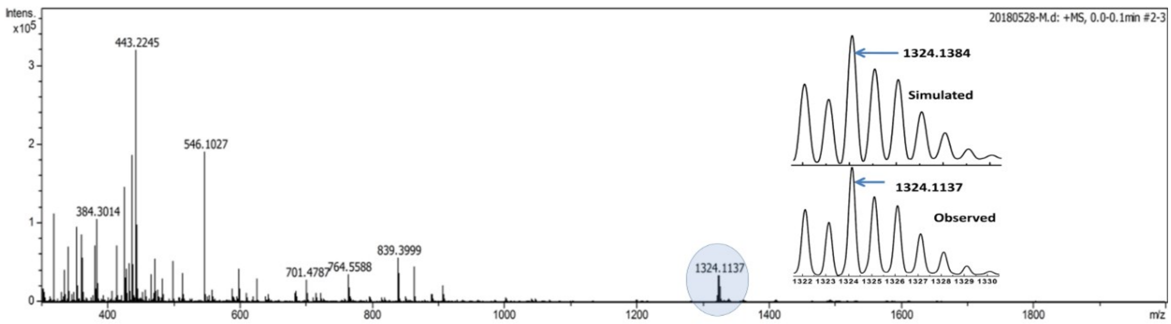


Fig. S3 ESI-MS spectrum of **1**.

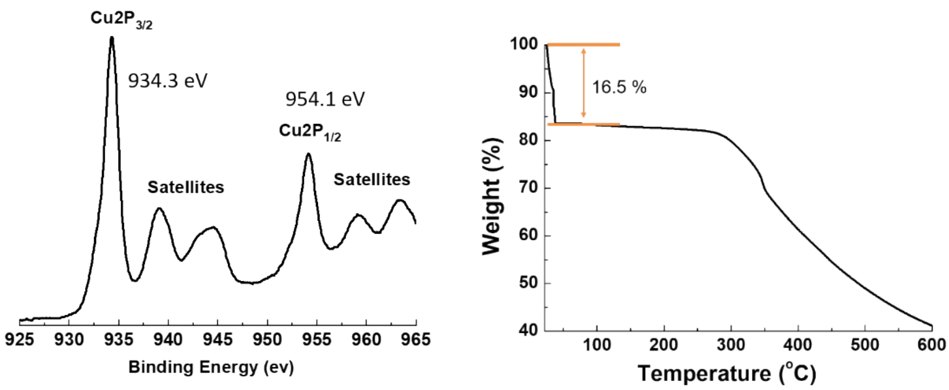


Fig. S4 Left: XPS spectrum of **1**. Right: TGA trace of **1**. The result revealed that the observed solvent molecule weight loss is 16.5% (calculated 16.5% based on $Cu_3L_2{\cdot}3CH_2Cl_2$).

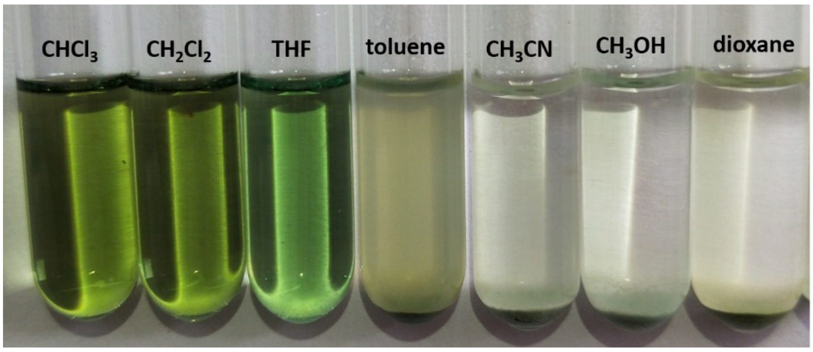


Fig. S5 **1** was soluble in $CHCl_3$, CH_2Cl_2 and THF, and it was poor soluble in toluene, CH_3CN, CH_3OH and dioxane.

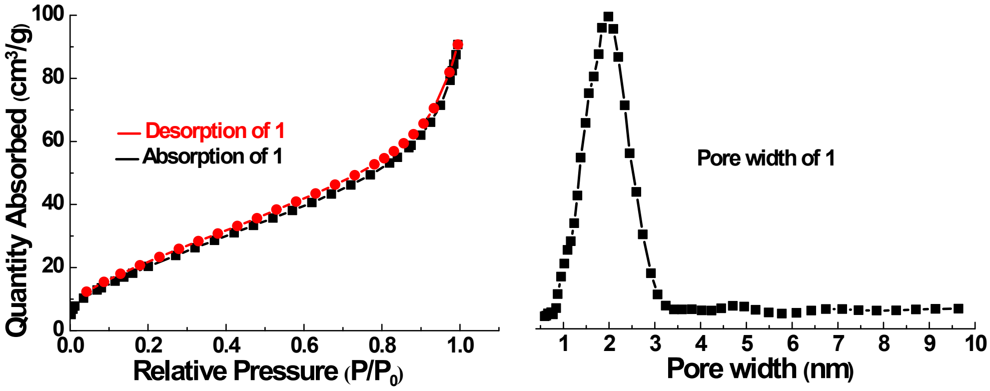


Fig. S6 Left: N_2 adsorption isotherm of **1** at 77 K. Right: the pore width of **1** is centered at ca. 1.98 nm.

Synthesis and characterization of Cu(II)-MOF (2)

2 was obtained in quantitative yield by stirring a solution of **1** (5.46 mg, 0.03 mmol) in $CHCl_3$/1, 4-dioxane (2 mL/5 mL) at room temperature for 8 h. The single crystals of **2** were obtained as following methods:

Method I: 1, 4-dioxane (5 mL) was layered over a solution of solution of **1** (5.46 mg, 0.03 mmol) in CH_2Cl_2 (2 mL). The solution were left for about 7 days at room temperature, and **2** was obtained as green block crystals. Yield 64% (based on Cu).

Method II: a mixture of $Cu(OAc)_2$ (12.0 mg, 0.05 mmol) and **L** (24.0 mg, 0.10 mmol) in methol/1, 4-dioxane (5 mL/5 mL) was transferred into a 25 mL Teflon-lined stainless steel autoclave and kept at 90 °C for 72 h. After slowly cooling to room temperature, green block crystals were generated. Yield, 75% (based on Cu). The PXRD patterns for the samples of **2** generated by different methods are the same. IR (KBr pellet, cm^{-1}): 3517 (w), 1562 (m), 1521 (s), 1417 (s), 1204 (w), 1117 (m), 1082 (w), 873 (m), 773 (w), 695 (w), 695 (w). Elemental analysis (%) calcd for $C_{78}H_{66}Cu_3O_{15}$ (desolvated): C, 65.33, H, 4.64; Found: C, 65.09, H 4.71.

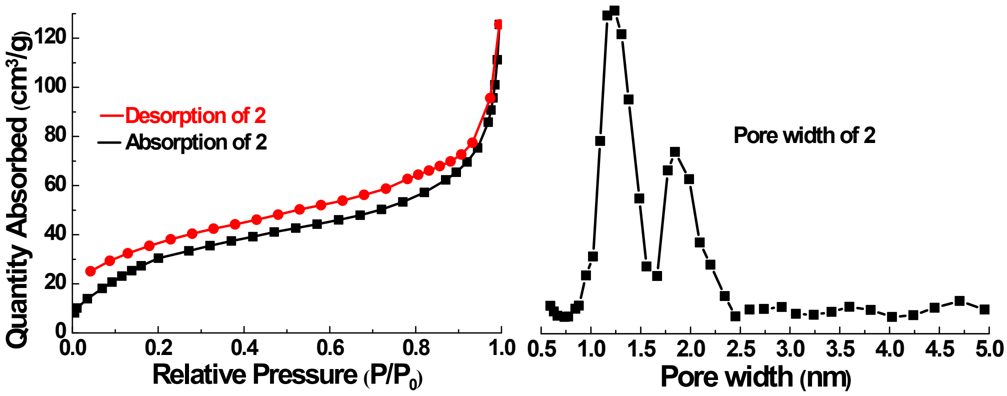


Fig. S7 Left: N_2 adsorption isotherm of **2** at 77 K. Right: the pore widths of **2** are centered at ca. 1.22 and 1.85 nm, respectively.

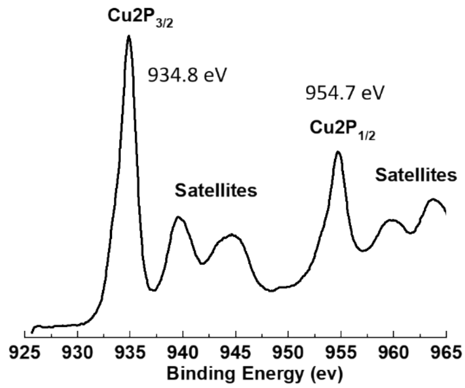


Fig. S8 XPS spectrum of **2**. Compared to **1**, no valence change for Cu(II) was found during the formation of **2** from **1**.

3. Single-crystal data of 1 and 2.

Diffraction data for single crystals of **1** and **2** were collected at 293 (2) K, with a Bruker Smart 1000 CCD diffractometer using Mo-Kα radiation (λ = 0.71073 Å) with the ω-2θ scan technique. An empirical absorption correction was applied to raw intensities.[1] The structures were solved by direct methods (SHELX-97) and refined with full-matrix least-squares technique on F^2 using the SHELX-97.[2] The hydrogen atoms were added theoretically, and riding on the concerned atoms and refined with fixed thermal factors. The details of crystallographic data and structure refinement parameters are summarized in Table S1. The selected bonds lengths and angles for **1** and **2** were shown in Table S2. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no CCDC 1848381 and 1842443. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Table S1. Crystal data and structure refinement for **1** and **2**.

Complexes	**1**	**2**
Empirical formula	$C_{150}H_{103}Cl_{12}Cu_6O_{24}$	$C_{78}H_{66}Cu_3O_{15}$
Formula weight	3096.03	1430.94
Temperature	293(2) K	293(2) K
Wavelength	1.54178 A	1.54178 Å
Crystal system, space group	Triclinic, *P-1*	Monoclinic, *C2/c*
Unit cell dimensions	a = 19.5003(10) Å alpha = 62.026(6) deg.	a = 36.2950(19) Å alpha = 90 deg.
	b = 22.2603(15) Å beta = 88.050(4) deg.	b = 25.3040(8) Å beta = 116.080(4) deg.
	c = 22.4658(13) Å gamma = 65.547(6) deg.	c = 20.4575(6) Å gamma = 90 deg.
Volume	7682.9(8) Å ^3	16875.3(11) Å ^3
Z, Calculated density	2, 1.339 Mg/m^3	8, 1.127 Mg/m^3
Absorption coefficient	3.346 mm^-1	1.328mm^-1
F(000)	3146	5904
Crystal size	0.3 x 0.25 x 0.2 mm	0.2 x 0.2 x 0.2 mm
Theta range for data collection	3.73 to 70.94 deg.	3.68 to 71.496 deg.
Limiting indices	-23<=h<=23, -26<=k<=26, -19<=l<=27	-38<=h<=44, -30<=k<=16, -24<=l<=24
Reflections collected / unique	56498/28938 [R(int) = 0.0649]	31467/16452 [R(int) = 0.0465]
Completeness to theta = 71.06	97.6 %	96.6 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	28938 / 0 / 1741	15895 / 0 / 870
Goodness-of-fit on F^2	1.625	1.728
Final R indices [I>2sigma(I)]	R1 = 0.1700, wR2 = 0.4702	R1 = 0.1469, wR2 = 0.4056
R indices (all data)	R1 = 0.2475, wR2 = 0.3176	R1 = 0.1860, wR2 = 0.4506
Largest diff. peak and hole	4.136 and -1.363 e. Å^-3	3.773 and -1.262 e. Å^-3

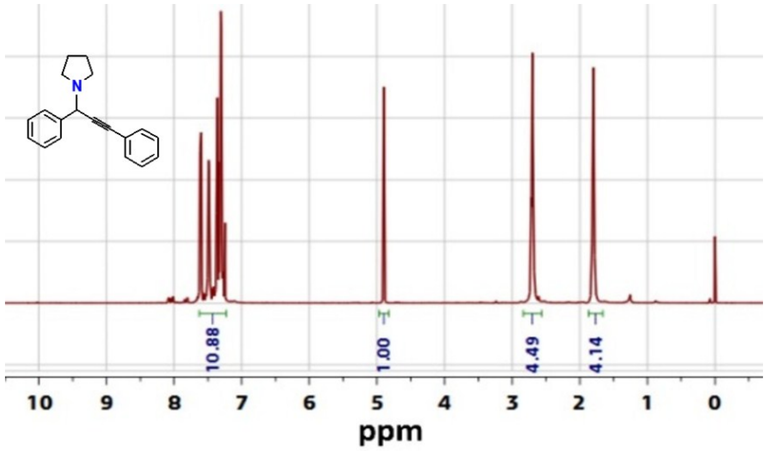
Table S2. Selected bonds lengths and angles for **1** and **2**

1	Cu(1)-O(2)	1.913(8)	Cu(1)-O(4)	1.922(8)
	Cu(1)-O(3)	1.924(9)	Cu(1)-O(1)	1.929(8)
	Cu(3)-O(9)	1.913(9)	Cu(3)-O(10)	1.896(10)
	Cu(3)-O(12)	1.892(9)	Cu(3)-O(11)	1.906(10)
	Cu(2)-O(6)	1.887(10)	Cu(2)-O(8)	1.906(10)
	Cu(2)-O(5)	1.932(9)	Cu(2)-O(7)	1.932(9)
	O(2)-Cu(1)-O(4)	88.3(4)	O(2)-Cu(1)-O(3)	178.2(4)
	O(4)-Cu(1)-O(3)	93.5(4)	O(2)-Cu(1)-O(1)	93.7(4)
	O(4)-Cu(1)-O(1)	177.9(4)	O(3)-Cu(1)-O(1)	84.5(4)
	O(9)-Cu(3)-O(10)	94.5(4)	O(9)-Cu(3)-O(12)	87.5(4)
	O(10)-Cu(3)-O(12)	169.9(4)	O(9)-Cu(3)-O(11)	172.5(4)
	O(10)-Cu(3)-O(11)	85.8(5)	O(12)-Cu(3)-O(11)	93.5(4)
	O(6)-Cu(2)-O(8)	175.5(5)	O(6)-Cu(2)-O(5)	94.1(4)
	O(8)-Cu(2)-O(5)	88.8(4)	O(6)-Cu(2)-O(7)	83.9(4)
	O(8)-Cu(2)-O(7)	93.2(4)	O(5)-Cu(2)-O(7)	177.2(4)
2	Cu(1)-O(8)	1.926(5)	Cu(1)-O(7)	1.924(6)
	Cu(1)-O(5)	1.926(6)	Cu(1)-O(6)	1.930(5)
	Cu(1)-O(14)	2.53(0)	Cu(2)-O(15)	2.62(3)
	Cu(2)-O(4)	1.909(5)	Cu(2)-O(3)	1.927(6)
	Cu(2)-O(1)	1.923(6)	Cu(2)-O(2)	1.930(6)
	Cu(3)-O(10)	1.920(6)	Cu(3)-O(12)	1.920(6)
	Cu(3)-O(9)	1.922(5)	Cu(3)-O(11)	1.927(6)
	Cu(3)-O(13)	2.48(3)		
	O(8)-Cu(1)-O(7)	93.7(2)	O(8)-Cu(1)-O(5)	177.3(2)
	O(7)-Cu(1)-O(5)	86.0(3)	O(8)-Cu(1)-O(6)	86.7(2)
	O(7)-Cu(1)-O(6)	169.6(2)	O(5)-Cu(1)-O(6)	94.2(2)
	O(4)-Cu(2)-O(3)	93.9(3)	O(4)-Cu(2)-O(1)	177.2(3)
	O(3)-Cu(2)-O(1)	84.4(3)	O(4)-Cu(2)-O(2)	88.0(2)
	O(3)-Cu(2)-O(2)	175.2(3)	O(1)-Cu(2)-O(2)	93.5(2)
	O(10)-Cu(3)-O(12)	83.7(3)	O(10)-Cu(3)-O(9)	93.6(3)
	O(12)-Cu(3)-O(9)	174.3(3)	O(10)-Cu(3)-O(11)	175.1(3)
	O(12)-Cu(3)-O(11)	93.9(2)	O(9)-Cu(3)-O(11)	88.5(2)

4. General procedure for the A^3-coupling model reaction catalyzed by 1

Under nitrogen, a mixture of benzaldehyde (0.5 mmol, 51 μL), phenylacetylene (0.75mmol, 83 μL), pyrrolidine (0.60 mmol, 50 μL) and **1** (6.5 mg, 3 mol %) in chloroform (1 mL) was stirred 60°C for 2 h to afford the corresponding products. Yield was determined by the GC.

5. Product characterization of the model A^3-coupling reaction



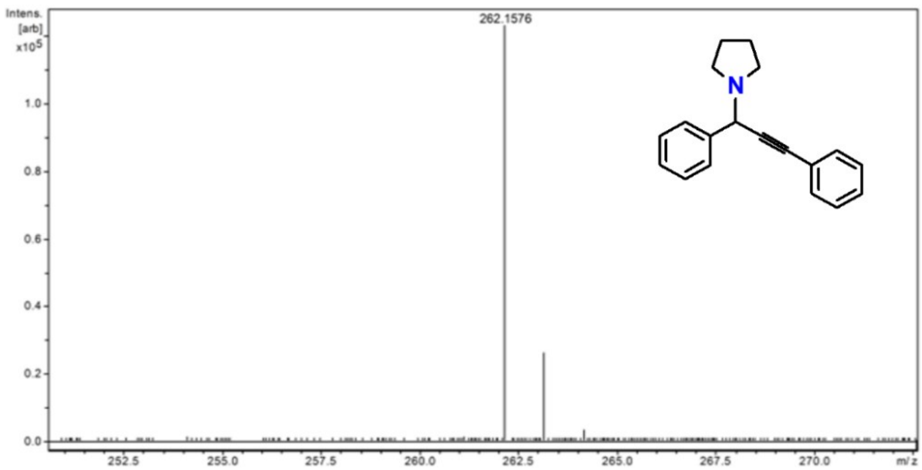
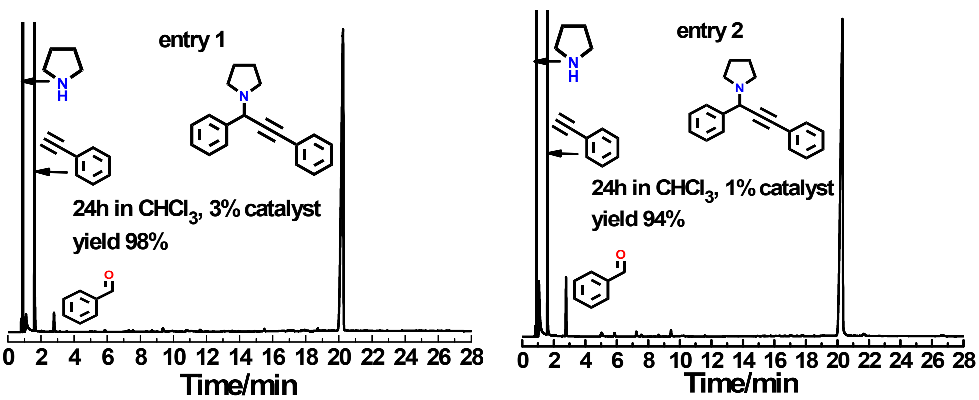
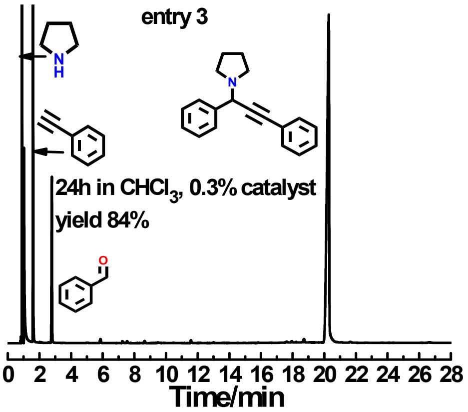


Fig. S9 ^{1}H NMR ($CDCl_3$, δ = 7.25-7.60 (10H), 4.89 (1H), 2.69 (4H), 1.80 (4H)), and ESI-MS (ESI-MS: calcd for $C_{19}H_{19}N$, 262.3688 ([M+H$^+$]); found: *m/z* 262.1576) spectra for the product generated from A^3-coupling model reaction.

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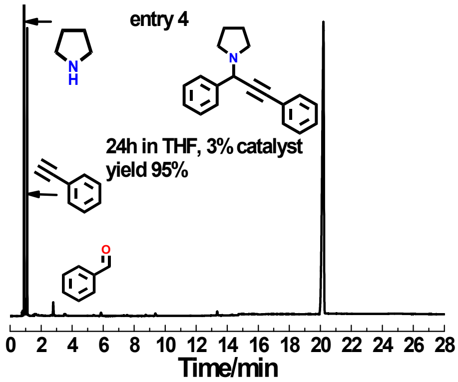
24h in $CHCl_3$, 0.3% catalyst
yield 84%
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28
Time/min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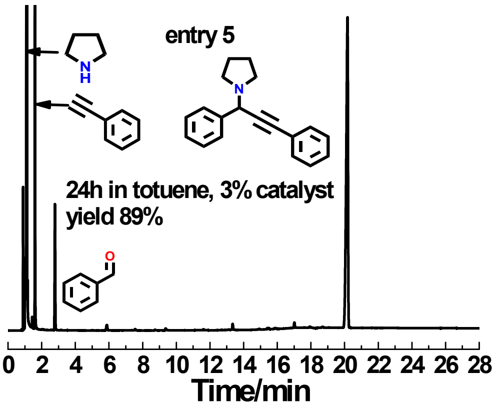
24h in THF, 3% catalyst
yield 95%
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28
Time/min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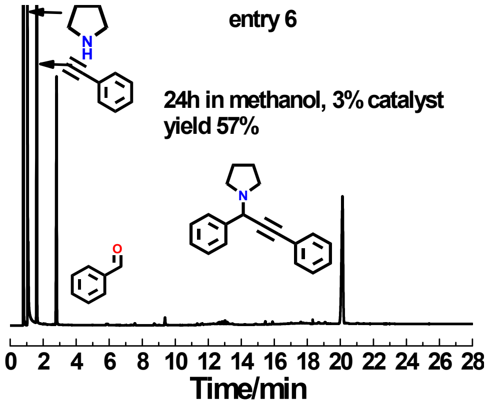
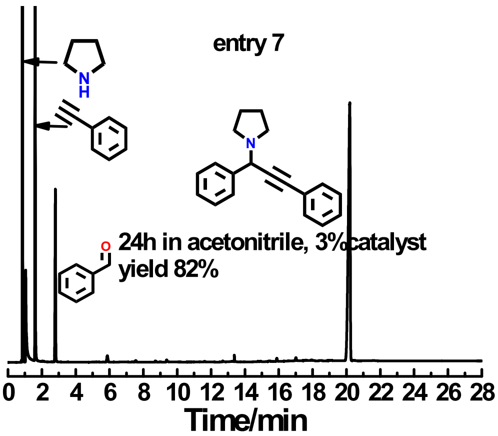
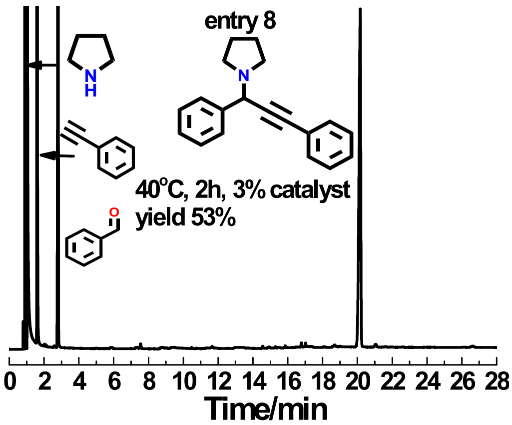
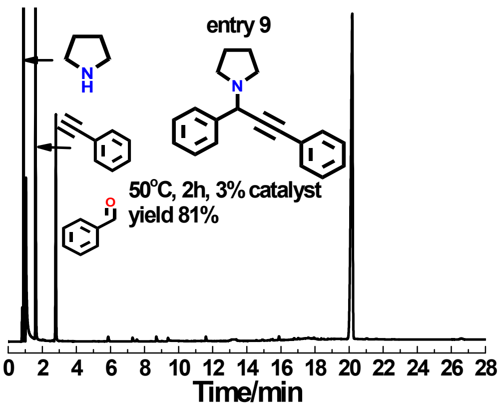
24h in totuene, 3% catalyst
yield 89%
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28
Time/min


entry 6
24h in methanol, 3% catalyst
yield 57%
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28
Time/min


entry 7
24h in acetonitrile, 3% catalyst
yield 82%
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28
Time/min


entry 8
40°C, 2h, 3% catalyst
yield 53%
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28
Time/min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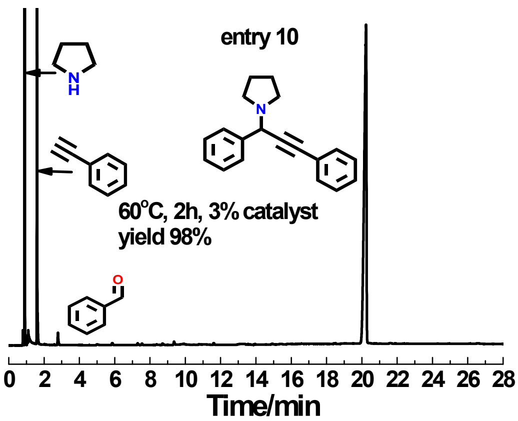
50°C, 2h, 3% catalyst
yield 81%
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28
Time/min


entry 10
60°C, 2h, 3% catalyst
yield 98%
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28
Time/min

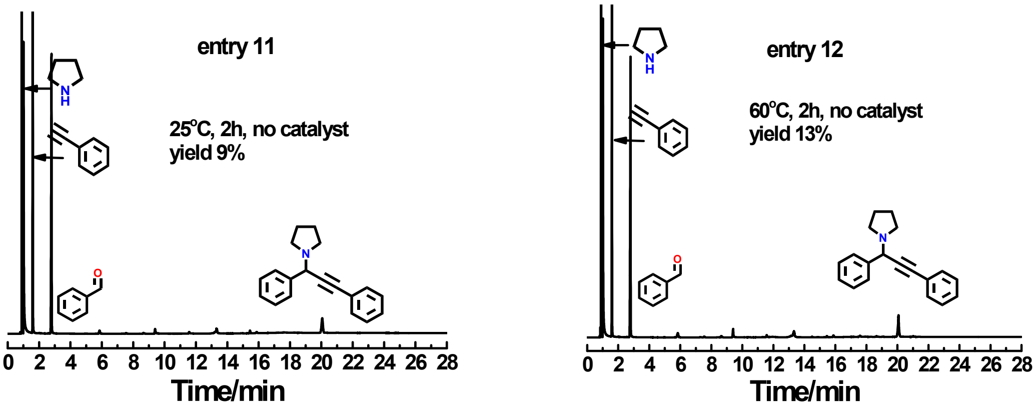
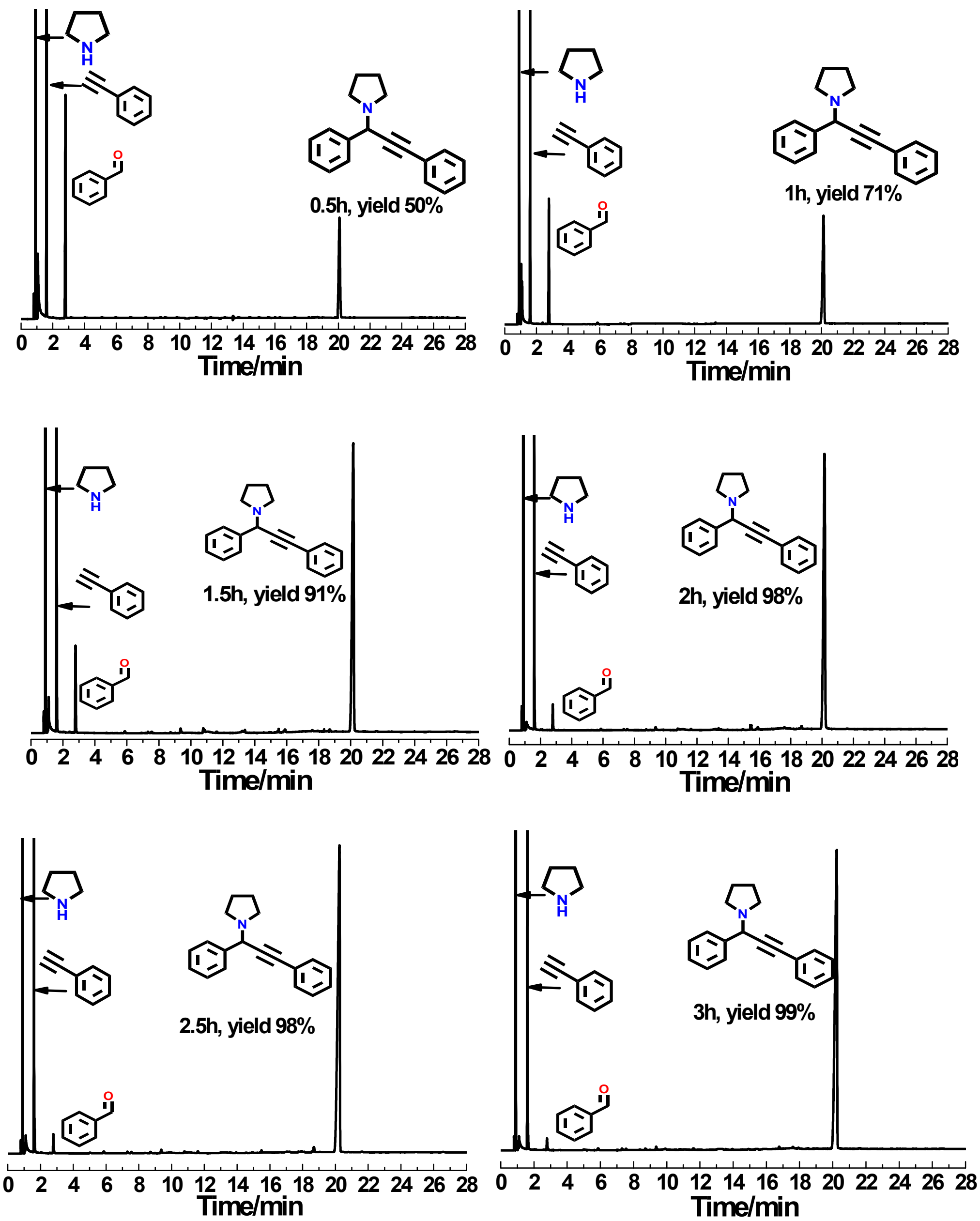


Fig. S10 GC analysis of the model A^3-coupling reaction catalyzed by **1** in different solvents and at different temperatures (For Table 1).



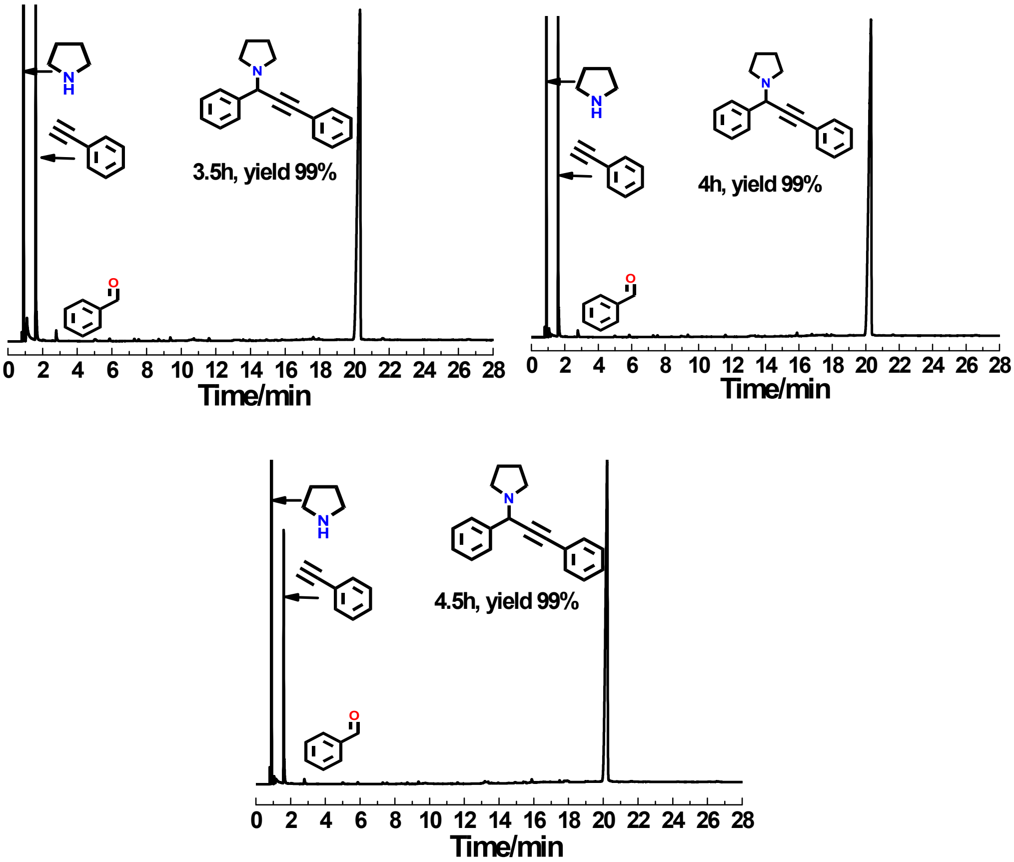


Fig. S11 GC analysis of the model A^3-coupling reaction catalyzed by **1** ($CHCl_3$, 60°C): the relationship between time and yield.

6. Recycle of 1

After addition of 1, 4-dioxane (2 mL) to the reaction solution ($CHCl_3$, 1 mL) containing **1**. **2** was precipitaed completely from solution after 8 h. The regenerated **2** was obtained by centrifugation, and was directly redissolved in $CHCl_3$ for the next catalytic run.

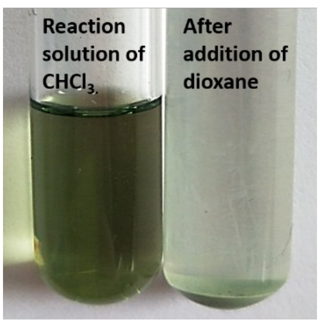
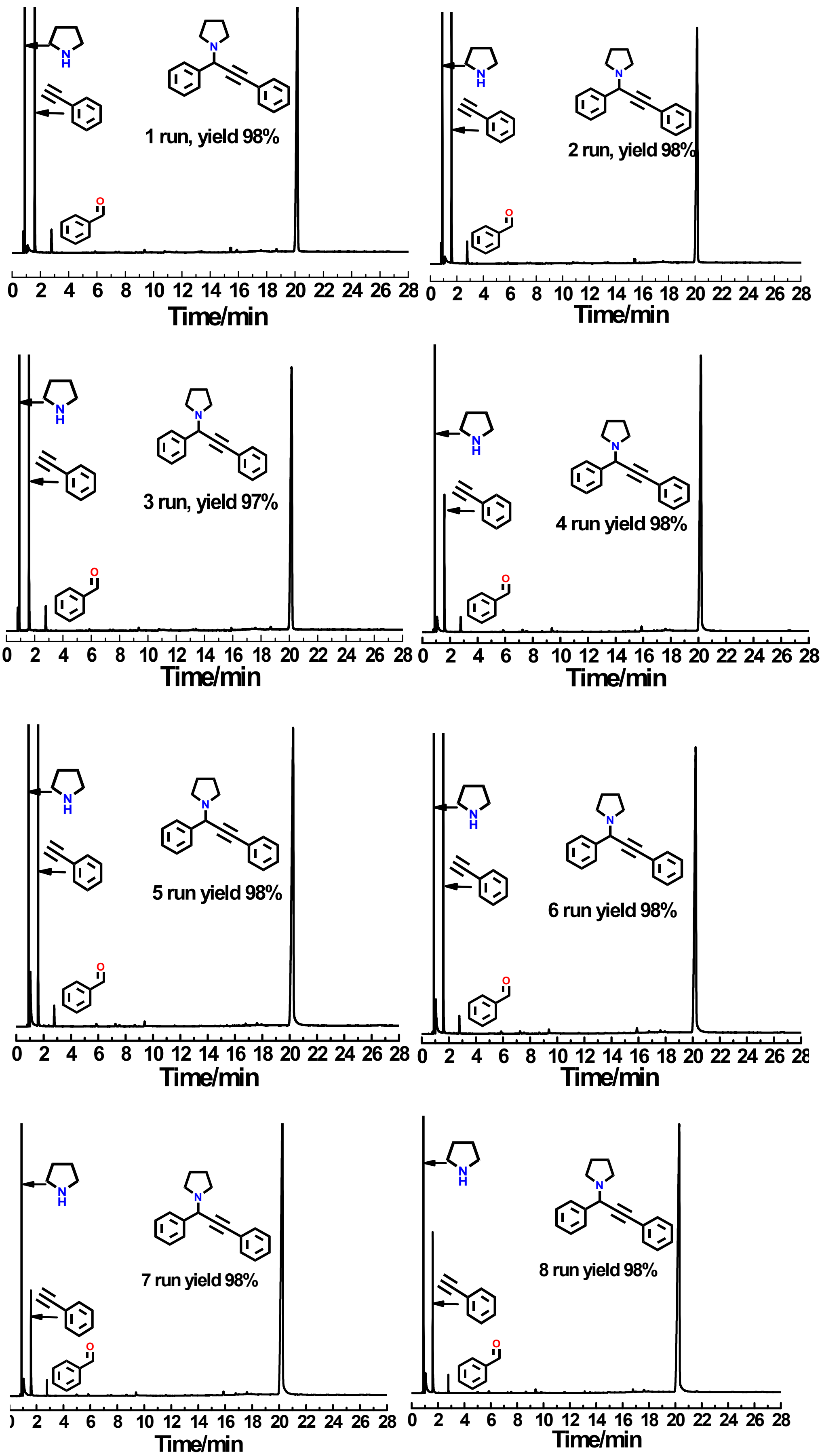


Fig. S12 Recation solution of $CHCl_3$ and it after addition of dioxane.


1 run, yield 98%
Time/min
2 run, yield 98%
Time/min
3 run, yield 97%
Time/min
4 run yield 98%
Time/min
5 run yield 98%
Time/min
6 run yield 98%
Time/min
7 run yield 98%
Time/min
8 run yield 98%
Time/min

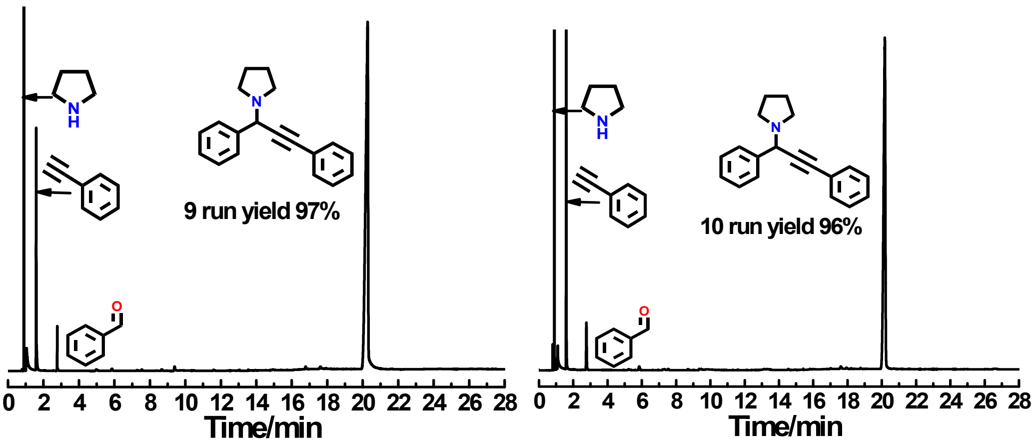
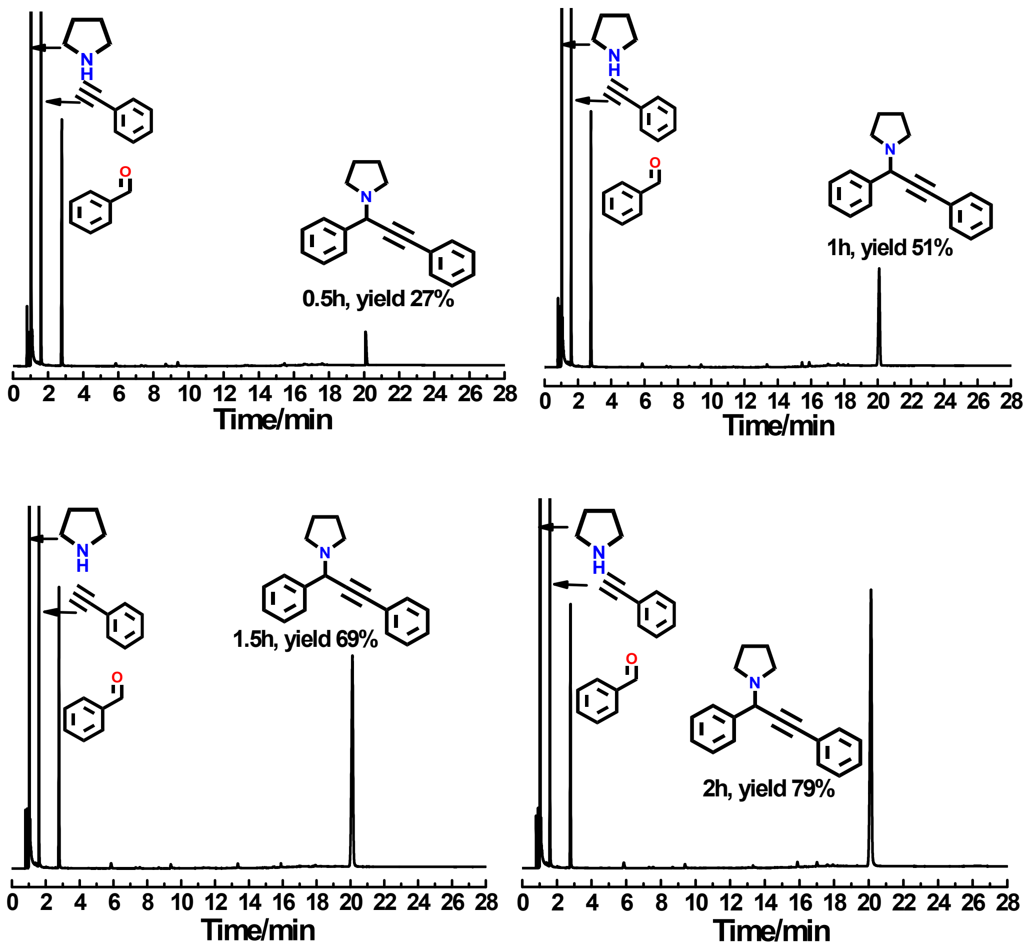


Fig. S13 GC analysis for the A^3-coupling model reaction catalyzed by **1** for 10 catalytic runs.

7. GC analysis of the model A^3-coupling reaction catalyzed by 2



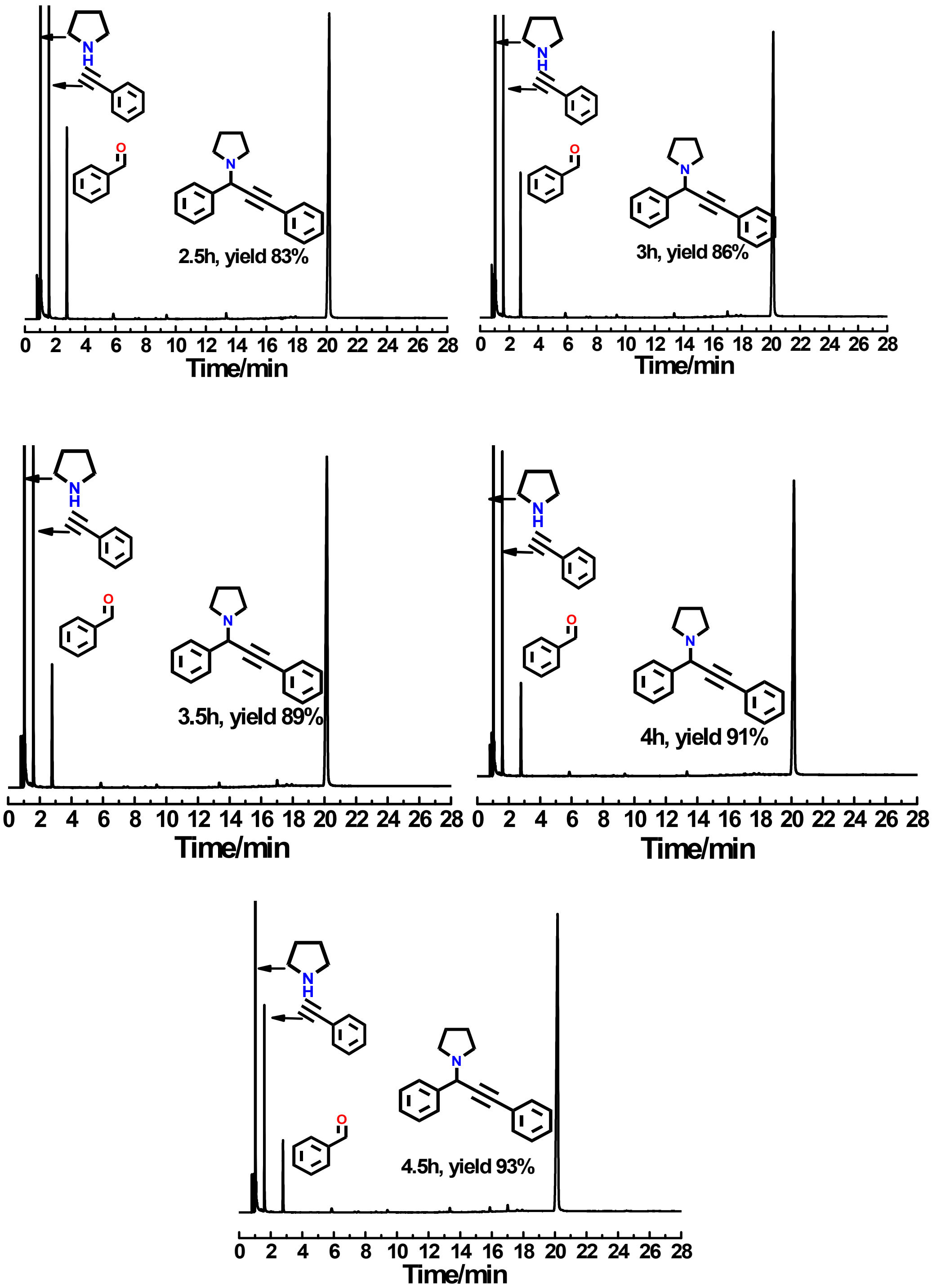
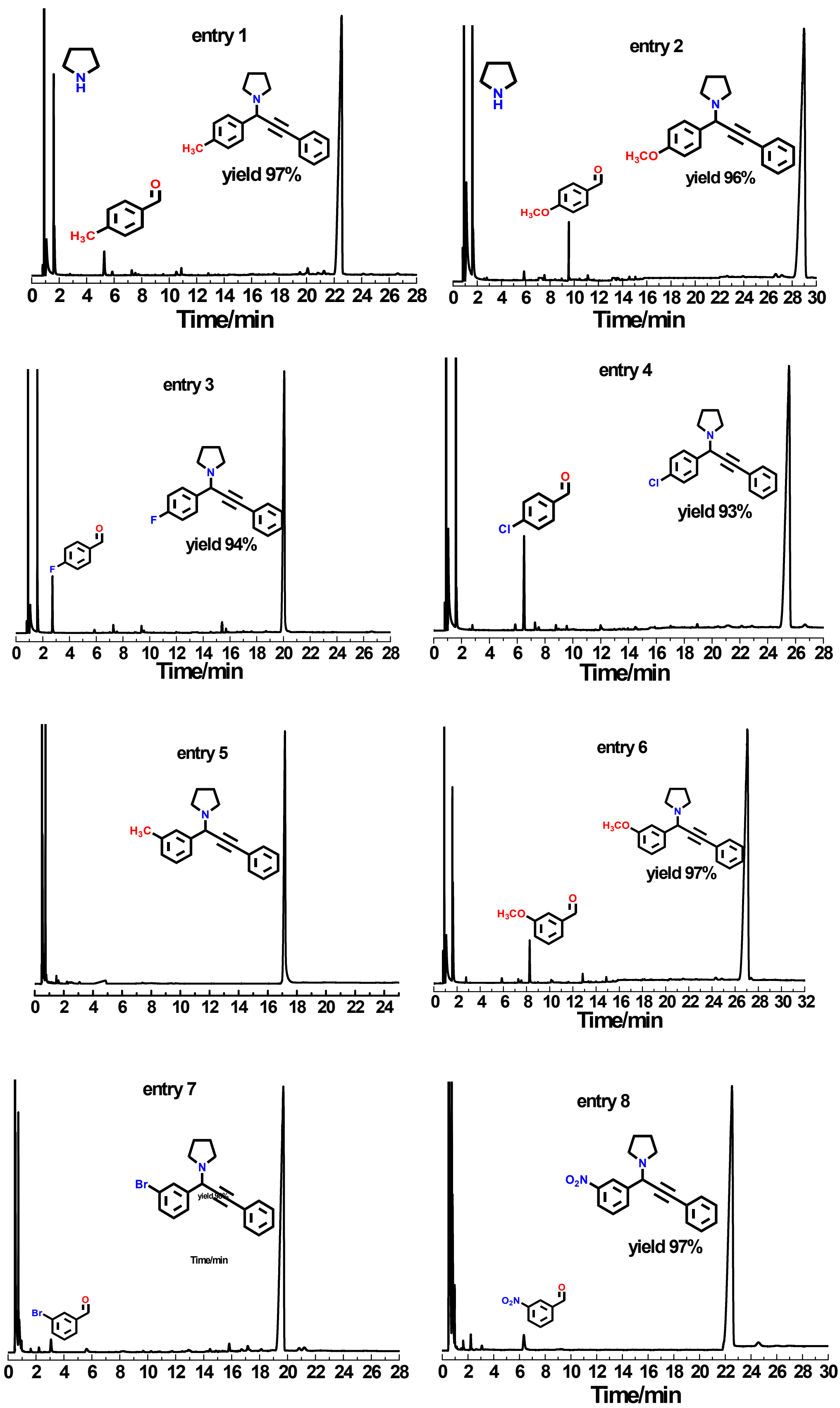
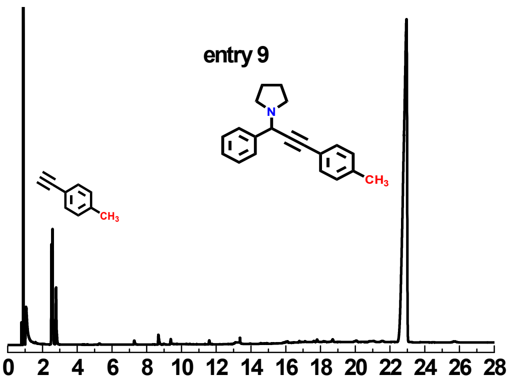
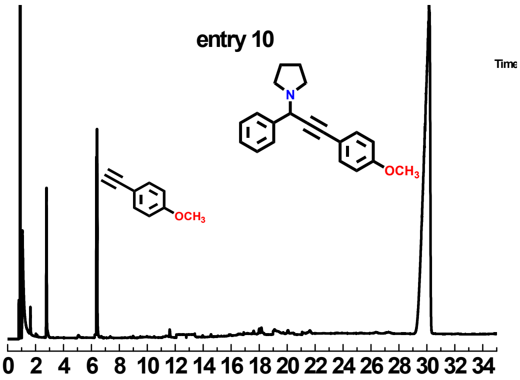


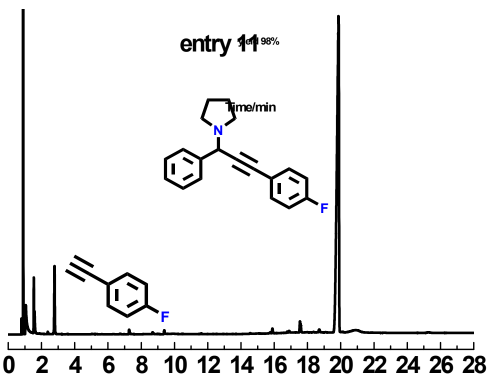
Fig. S14 GC analysis of the model A^3-coupling reaction catalyzed by **2** in a heterogeneous way (dioxane, 60^{o}C): the relationship between time and yield.

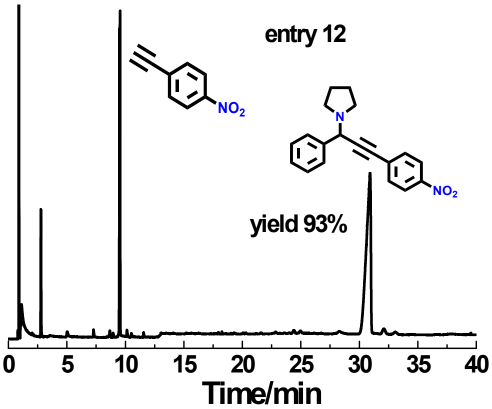
8. GC analysis of the expanded A^3-coupling reaction catalyzed by 1 (For Table 2)

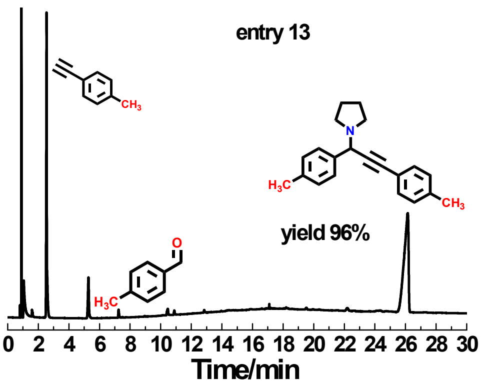

entry 1
yield 97%
Time/min
entry 2
yield 96%
Time/min
entry 3
yield 94%
Time/min
entry 4
yield 93%
Time/min
entry 5
entry 6
yield 97%
Time/min
entry 7
Time/min
entry 8
yield 97%
Time/min

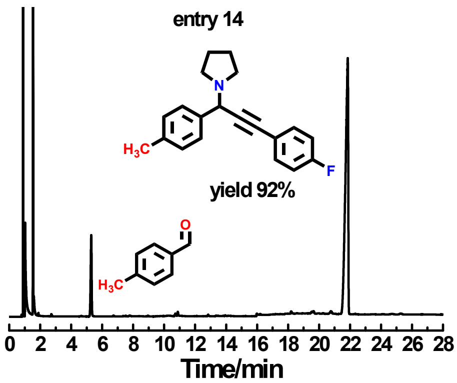

entry 9
CH3
CH3

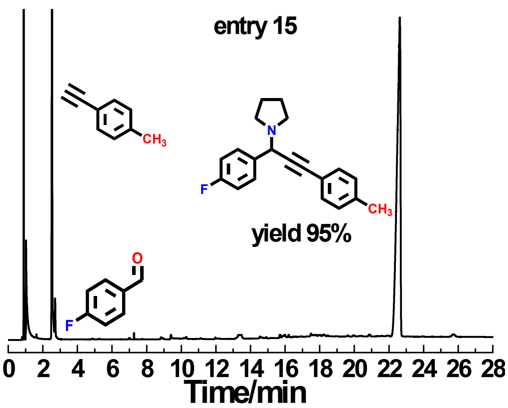

entry 10
N
OCH3
OCH3

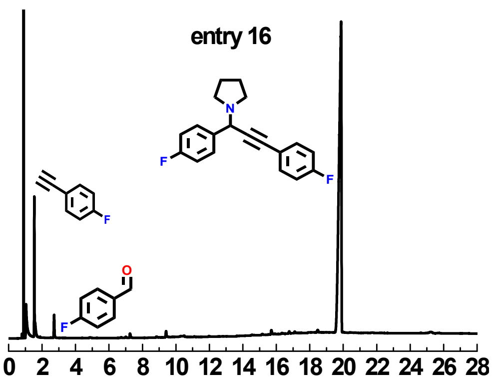

entry 11
N
F
F


entry 12
NO2
N
NO2
yield 93%
Time/min


entry 13
CH3
N
H3C
CH3
O
H3C
yield 96%
Time/min


entry 14
N
H3C
F
yield 92%
O
H3C
Time/min


entry 15
CH3
N
F
CH3
yield 95%
O
F
Time/min


entry 16
N
F
F
F
O
F

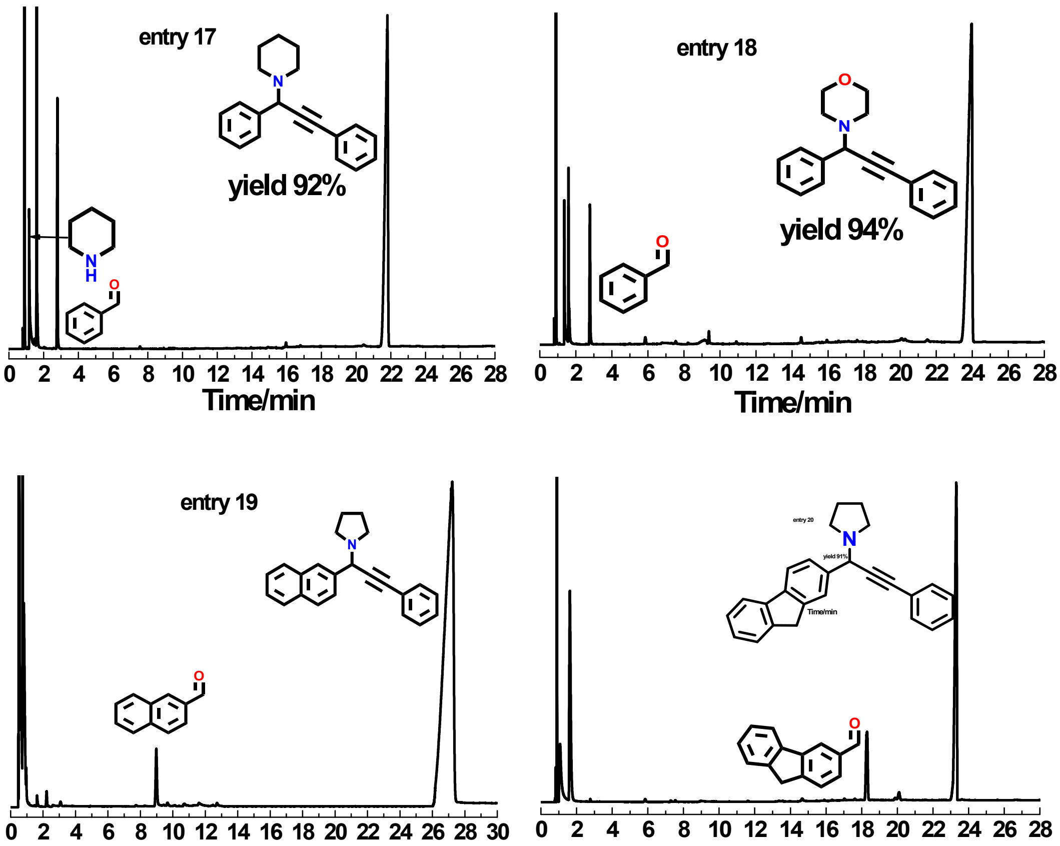


Fig. S15 GC results for the A^3-coupling reactions with various aldehydes, amines and alkynes substrates catalyzed by **1** in $CHCl_3$ (For Table 2).

9. GC analysis of the fluorene-2-carboxaldehyde based A^3-coupling catalysed by 2

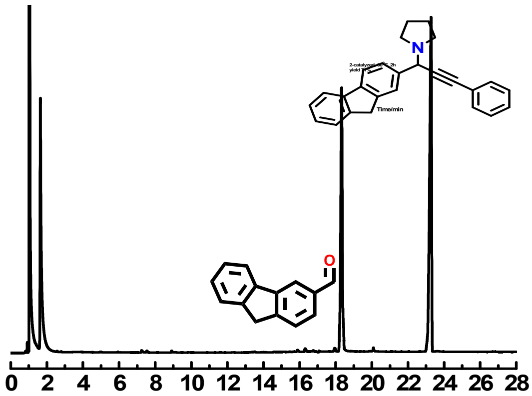


Fig. S16 GC analysis for the A^3-coupling reaction of fluorene-2-carboxaldehyde, pyrrolidine and phenylacetylene catalyzed by **2** in a heterogeneous way.

10. MS Spectra for the model reaction system

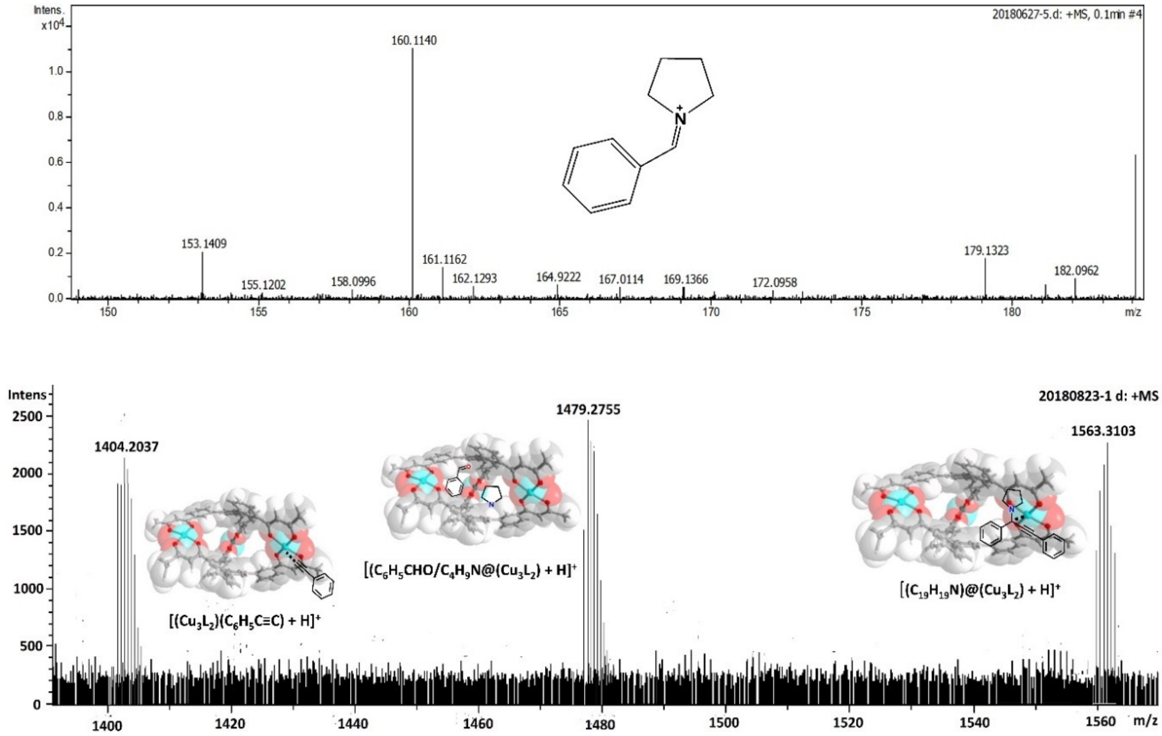


Fig. S17 ESI-MS spectra performed on the model reaction system.

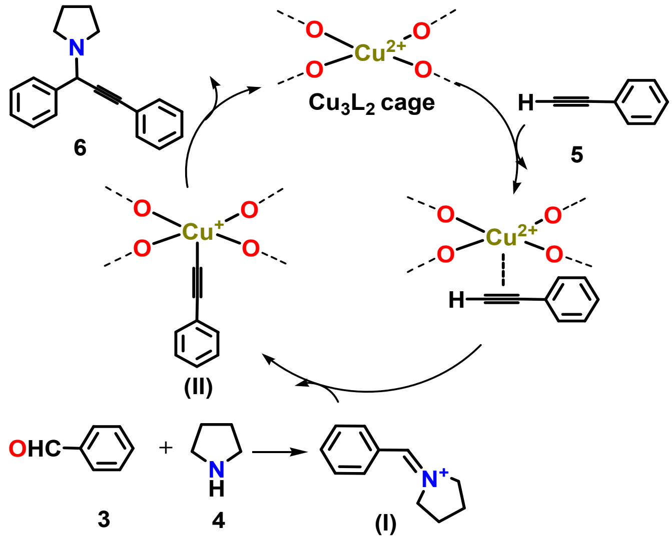


Fig. S18 The proposed mechanism based on the model A^3-coupling reaction.

11. Table S3. Comparison of 1 with the reported copper-based heterogeneous catalysts for pyrrolidine (piperidine)-benzaldehyde-phenylacetylene A^3-coupling reactions

catalyst (mol%)	conditions	recycle	yield (%)	ref.
Cu(0)-montmorylonit (0.5%) (pyrrolidine)	toluene, reflux, 3 h	3	94	3
Cu NPs on graphene (1%) (pyrrolidine)	toluene, 100°C, 24 h	4	96	4
Cu(I)-modified zeolites (7%) (pyrrolidine)	neat, 80°C, 15 h	5	95	5
Cu-(2-pymo)$_2$ (10%) (piperidine)	393 K, 21h	5	71	6
CuSBA-15 (1.8%) (piperidine)	toluene 110°C, 6h	several	80	7

Cu-MPTA (0.1%) (piperidine)	CH_2Cl_2, rt, 24h	6	93	8
IRMOF-3-Gl-Cu (3.3%) (pyrrolidine)	$CHCl_3$, 40^{o}C, 6 h	4	80	9
Cu/NCNTs (4%) (piperidine)	THF, 70^{o}C, 6 h	7	85	10
CuO NPs (8%) (piperidine)	toluene, 90^{o}C, 5h	5	85	11
CuNPs-1 (5 mg) (pyrrolidine)	solvent-free, 8h, 70^{o}C	4	80	12
CuO NPs (0.7%) (pyrrolidine)	acetonitrile, 4h, 82^{o}C	5	90	13
Cu(II)-MOC (3 %) (pyrrolidine)	$CHCl_3$, 60^{o}C, 2h or $CHCl_3$, r.t., 24h	10	98	**this work**

12. References

1. G. M. Sheldrick. SHELXS 97, Program for the Solution of Crystal Structures, University of Götingen, Germany, 1997.

2. G. M. Sheldrick. SHELXL 97, Program for the Refinement of Crystal Structures, University of Götingen: Germany, 1997.

3. B. J. Borah, S. J. Borah, L. Saikia, D. K. Dutta, *Catal. Sci. Technol*., 2014, **4**, 1047-1054.

4. S. Frindy, A. E Kadib, M. Lahcini, A. Primo, H. García, *Catal. Sci. Technol.*, 2016, **6**, 4306-4317.

5. M. K. Patil, M. Keller, B. M. Reddy, P. Pale, J. Sommer, *Eur. J. Org. Chem.*, 2008, **26**, 4440-4445.

6. I. Luz, F. X. L. Xamena, A. Corma, *J. Catal*., 2012, **285**, 285-291.

7. M. Srinivas, P. Srinivasu, S. K. Bhargava, M. L. Kantam, *Catal. Today*. 2013, **208**, 66-71.

8. N. Salam, S. K. Kundu, A. S. Roy, P. Mondal, S. Roy, A. Bhaumik, S. M. Islam, *Catal. Sci. Technol.*, 2013, **3**, 3303-3316.

9. J. Yang, P. Li, L. Wang, *Catal. Commun.*, 2012, **27**, 58-62.

10. V. G. Ramua, A. Bordoloi, T. C. Nagaiahc, W. Schuhmannc, M. Muhler, C. Cabrelea, *Appl. Catal. A: Gen*., 2012, **431–432**, 88–94.

11. M. Nasrollahzadeh, S. M. Sajadi, A. Rostami-Vartoonia, *J. Coll. Interf. Sci.*, 2015, **459**, 183–188.

12. V. V. Kumar, R. Rajmohan, P. Vairaprakash, M. Mariappan, S. P. Anthony, *Dalton Trans.*, 2017, **46**, 11704-11714.

13. M. Gopiraman, D. Deng, S. G. Babu, T. Hayashi, R. Karvembu, I. S. Kim, *ACS Sustainable Chem. Eng.*, 2015, **3**, 2478–2488.