Electronic Supplementary Material (ESI) for ChemComm.

Electronic supplementary information (ESI)

for

A Tris(benzyltriazolemethyl)amine-based Cage as CuAAC Ligand Tolerant to Exogeneous Bulky Nucleophiles.

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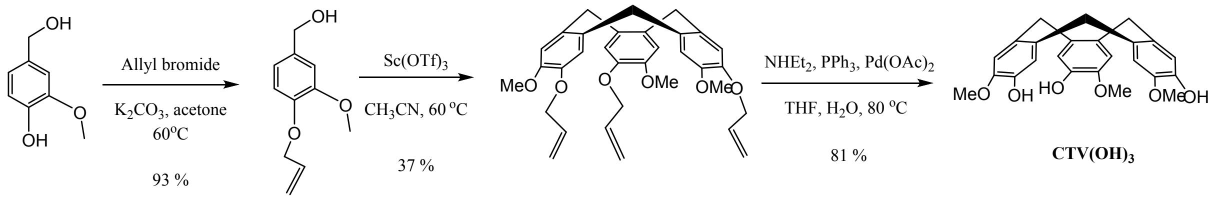
Table of contents :

1. Chemical and instrumentation

All reagents were commercial reagent grade and were used without further purification.
1-(azidomethyl)-4(bromomethyl)benzene **1**,[S1] tris(benzyltriazolemethyl)amine **TBTA**,[S2] and **CTV(OH)$_3$**,[S3] were obtained according to reported protocols.



Scheme S1. Three steps synthesis of **CTV(OH)$_3$**. [S3]

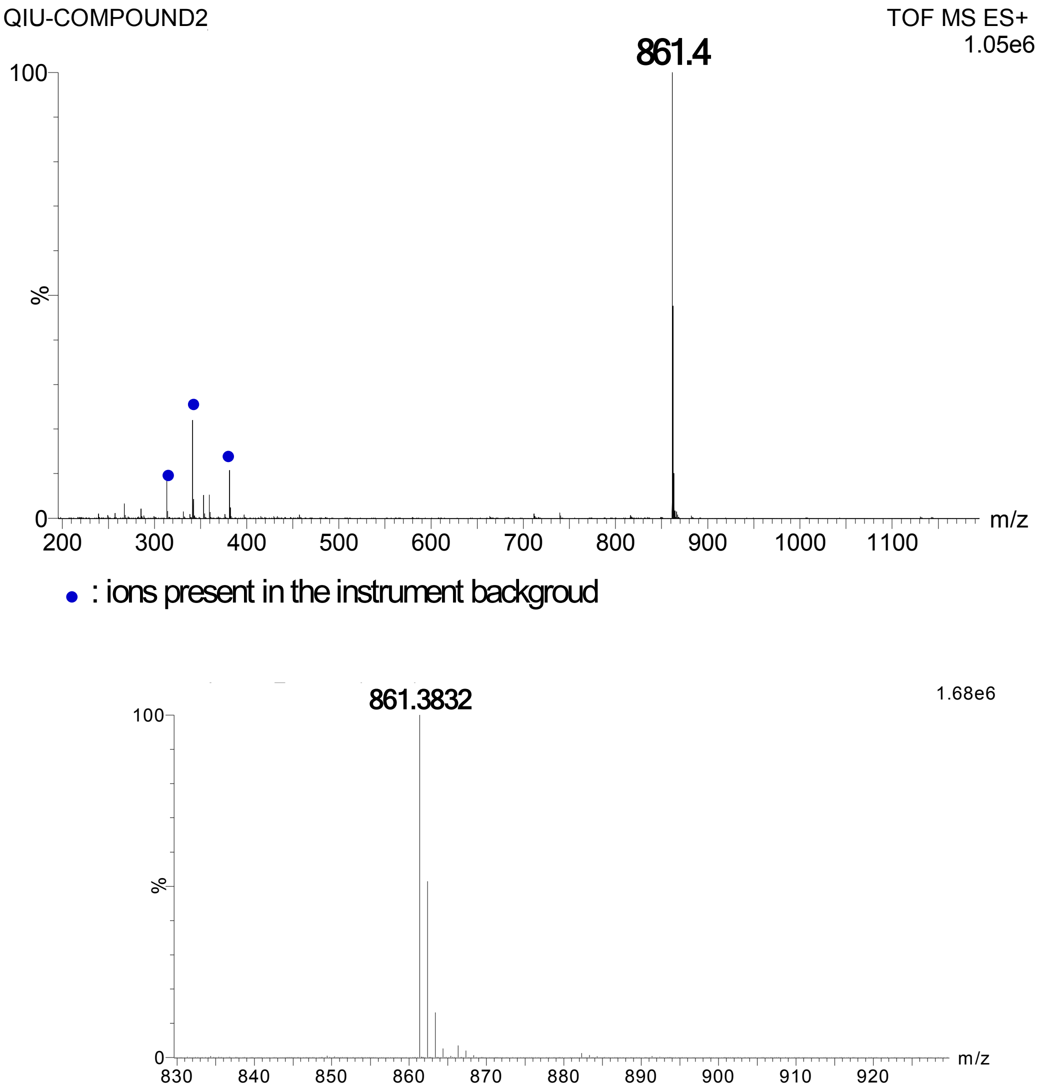
Instrumentation

^{1}H NMR and ^{13}C NMR were recorded on a Bruker Avance III HD 300 MHz and 500MHz spectrometers. ^{1}H NMR and ^{13}C NMR chemical shifts δ are reported in ppm referenced to the protonated residual solvent signal. ESI-HRMS were performed on a SYNAPT G2 HDMS (Waters) mass spectrometer with API and spectra were obtained with TOF analysis. Measurements were realized with two internal standards.

2. Experimental procedure and characterisation

Synthetic procedure for 2.

To a solution of **CTV(OH)$_3$** (408 mg, 1 mmol) and **1** (230 mg, 1.03 mmol) in DMF (50 mL), was added Cs_2CO_3 (500 mg) in one portion. Then the solution was stirred overnight at 90°C under argon. The mixture was then allowed to return to room temperature, evaporated and water was added (200 mL). The aqueous mixture was extracted with CH_2Cl_2 (3x 100 mL). The combined organic phases were washed with 1M aqueous NaOH (100 mL), washed with brine (100 mL), dried over Na_2SO_4, filtered and evaporated to dryness. The residue was purified by column chromatography on silica (eluent : CH_2Cl_2 / EtOAc; 2:1) to afford a white solid. Yield: 92%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.45(s, 3H), 7.32(s, 3H), 7.30(s, 3H), 7.26(s, 3H), 6.85(s, 3H), 6.72(s, 3H), 5.09(s, 6H), 4.73 (d, 3H), 4.34(s, 6H), 3.75(s, 9H), 3.49(d, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 147.5, 137.5, 133.4, 131.5, 129.2, 127.0, 116.8, 113.3, 71.1, 56.2, 55.4, 33.8. **HRMS (ESI)**: Calcd for $C_{48}H_{45}N_9O_6$ $[M + NH_4]^+$: 861.3831. Found: 861.3832



Spectra S1. ESI-HRMS spectra of **2** in a 3mM MeOH solution of ammonium acetate, along with the zoom on the isotopic pattern at 861.3832 that can be attributed to **2**.NH_4^+ ($m/z_{calculated}$ = 861.3831).

Synthetic procedure for Hm-TBTA.

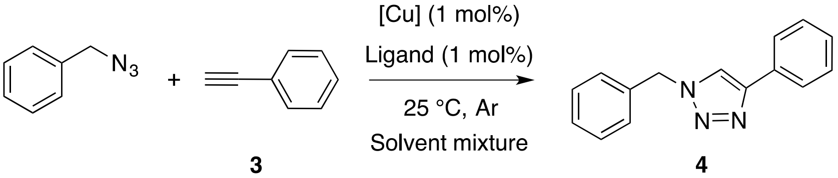
In a 500 mL round-bottom flask, compound **2** (422 mg, 0.5 mmol) and tripropargylamine (66 mg, 0.5 mmol) were suspended in a mixture of THF (300 mL) and *tert*-butyl alcohol (50 mL). Sodium ascorbate (0.1 mmol, 20 mg), $CuSO_4 \cdot 5H_2O$ (6.25 mg, 0.025 mmol, in 20 mL of water), and **TBTA** (26.5 mg, 0.05 mol) were then added. The reaction was stirred at 68°C for 16h. After concentration under reduced pressure, the residue was triturated with $CHCl_3$ (300 mL), washed with water (2 x100 mL) and brine (50 mL), and dried over Na_2SO_4. After removal of the solvent, the crude product was purified by column chromatography (CH_2Cl_2/MeOH from 50:1 to 20 :1) to give **Hm-TBTA** as a white solid (260 mg, 22%). ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.45(s, 3H), 7.28(d, 6H), 7.07(d, 6H), 6.87(s, 3H), 6.71(s, 3H), 5.56(d, 3H), 5.35(d, 3H), 5.30(d, 3H), 5.22(d, 3H), 5.10(d, 3H), 4.67(d, 3H), 3.76(s, 9H), 3.58(d, 6H), 3.50(d, 3H). ^{13}**C NMR** (101 MHz, Chloroform-d) δ 147.83, 145.69, 142.93, 132.24, 130.88, 125.24, 113.44, 113.12, 67.12, 56.10, 51.13, 36.46, 30.88. **HRMS (ESI)**: Calcd for C57H54N10O6 [M + H]+ : 975.4301. Found: 975.4301 (Figure S1).
For ^{1}H NMR; ^{13}C NMR and 2D-NMR spectra, see Figure 2 (main text), and supplementary Figures S1, S3 and S4 respectively.

Synthetic procedure for Cu^I(Hm-TBTA)(PF$_6$).

A solution of $Cu^I(CH_3CN)_4(PF_6)$ (4.7 mg, 12.5 µmol, 1.0 equiv.) in CH_3CN (0.5 mL) was added at room temperature to a stirred solution of **Hm-TBTA** (12 mg, 12.5 µmol, 1.0 equiv.) in CD_3CN (1 mL) under argon atmosphere. The pale yellow solution mixture was stirred at room temperature for 1 hour and an excess of Et_2O was added. A pale yellow precipitate was formed, isolated by filtration, washed with Et_2O, and dried in vacuo to give **Cu^I(Hm-TBTA)(PF$_6$)** in a 81% yield. ^{1}**H NMR** (400 MHz, Acetonitrile-*d*$_3$) δ 7.56 (s, 1H), 7.29 (d, *J* = 7.9 Hz, 2H), 7.09 – 7.01 (m, 3H), 6.89 (s, 1H), 5.58 (d, *J* = 15.5 Hz, 1H), 5.47 (d, *J* = 15.8 Hz, 1H), 5.27 (d, *J* = 13.7 Hz, 1H), 5.16 (d, *J* = 13.6 Hz, 1H), 4.68 (d, *J* = 13.7 Hz, 1H), 3.50 (d, *J* = 13.7 Hz, 1H). **HRMS (ESI)**: Calcd for C57H54N10O6Cu [M + H]+ : 1037.3524 Found: 1037.3533 (Figure S5). For ^{1}H NMR and 2D-NMR spectra, see supplementary Figures S6, S7, S8 and S9.

Typical procedure for model CuAAC reactions.

The model CuAAC reaction between benzyl azide and phenylacetylene, catalyzed by 1.0 mol% of a Cu-source in the presence of tris(triazole)-based ligands, was adapted from reported protocols.[S2]



In an oven-dried 5 mL Schlenk tube ligand **TBTA** or **Hm-TBTA**, (2.0 μmol, 1 mol%), $Cu^I(CH_3CN)_4(PF_6)$ (2.0 μmol, 1 mol%), and the internal standard 2,4-dibromomesitylene (66.7 μmol, 0.33 equiv), were dissolved in a 10:1 CH_2Cl_2 / MeOH solvent mixture (2 mL) under an argon atmosphere, at room temperature. The mixture was stirred for 5 minutes at room temperature and phenylacetylene (20.4 mg, 200 μmol, 1.0 equiv.) and benzyl azide (26.6 mg, 200 μmol, 1.0 equiv.) were subsequently added. The mixture was then stirred at room temperature, under argon atmosphere, for the desired reaction time. At the end of the reaction, the mixture was diluted with 20 mL of CH_2Cl_2 and the reaction was quenched by the addition of 2 mg of KCN dissolved in 20 mL of a 10% sodium hydroxide aqueous solution. The mixture was extracted with CH_2Cl_2 and organic residue were combined and dried over Na_2SO_4, filtered, and evaporated to dryness to give a copper-free crude mixture, which was analysed by ^1H NMR technique.

The appearance of the triazole product was determined by ^1H NMR spectroscopy using the 2,4-dibromomesitylene as an internal standard. The product **4** yield was determined by the integration of signals at 5.58 ppm corresponding to the methylene N-$\mathbf{CH_2}$-Ph protons.

In some cases the copper-free crude mixture was purified by column chromatography on silica (Eluent: pure CH_2Cl_2 to CH_2Cl_2: ethyl acetate=10:1) to afford the pure product **4** and determined isolated yields.

For reaction involving commercial phenylacetylene substrates **5**, **6**, **7**, **8** and **9**, formation of product $\mathbf{P_{5\text{-}9}}$ have been quantified by ^1H-NMR spectroscopy (using the 2,4-dibromomesitylene as internal standard) by comparison with samples of corresponding authentic products prepared separately and characterized by comparison to the spectral data reported in the literature. [S4]

3. Supplementary figures

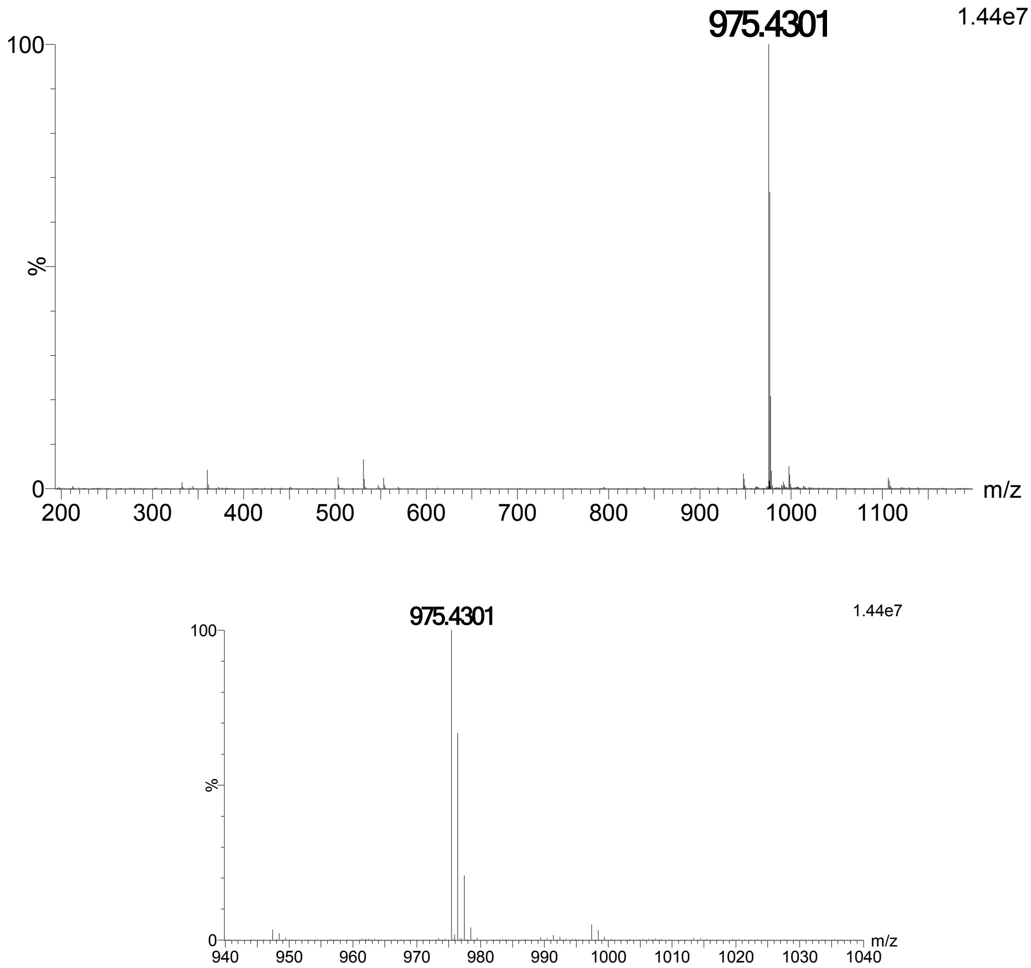


Figure S1. ESI-HRMS spectra of **Hm-TBTA** in CH_2Cl_2 along with the zoom on the isotopic pattern at m/z = 975.4301 that can be attributed to **Hm-TBTA**.H+ (m/z $_{calculated}$ = 975.4301).

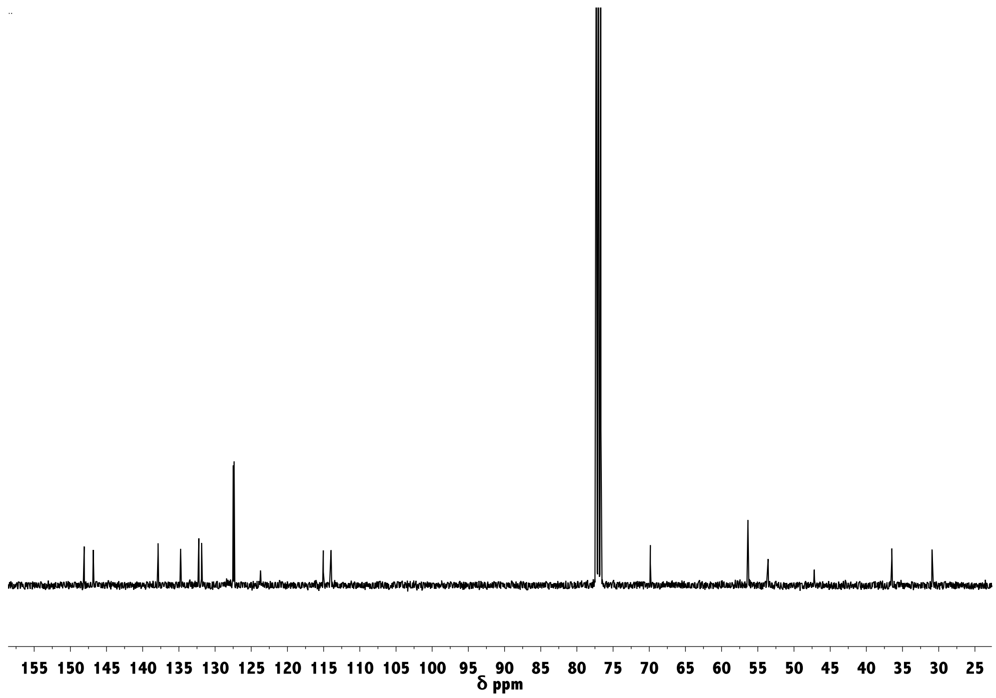


Figure S2. ^{13}C-NMR spectra spectra ($CDCl_3$, 400 MHz) of hemicryptophane **Hm-TBTA**, at 298K.

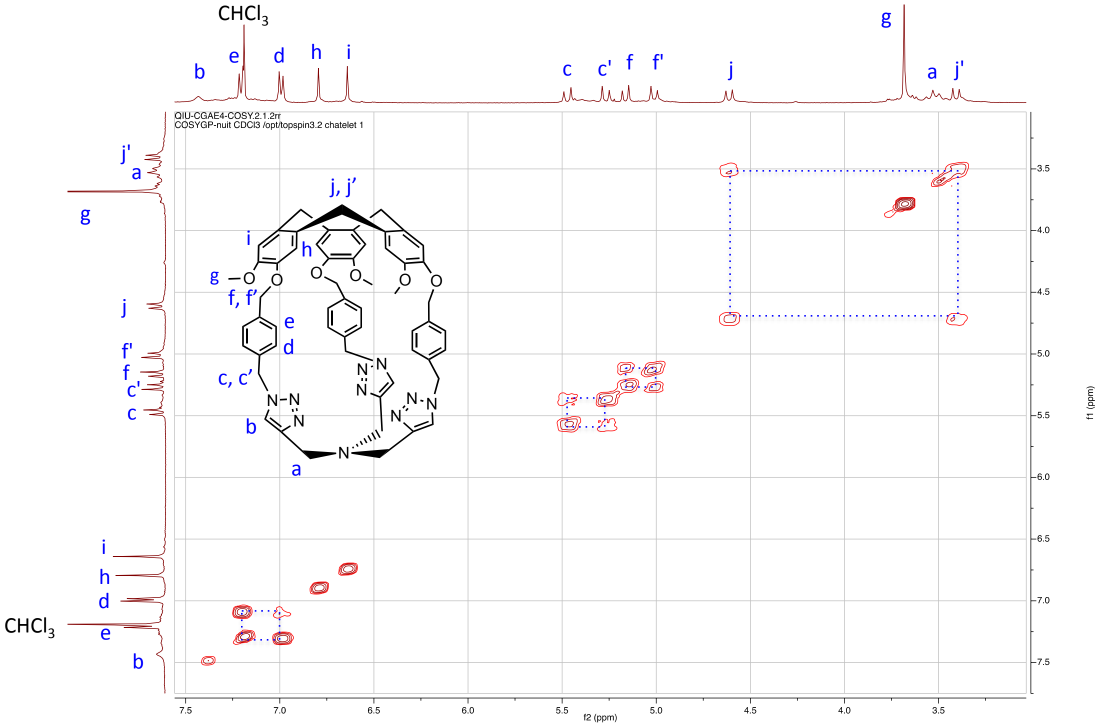


Figure S3. 2D COSY-NMR spectra ($CDCl_3$, 400MHz) of **Hm-TBTA**, at 298K

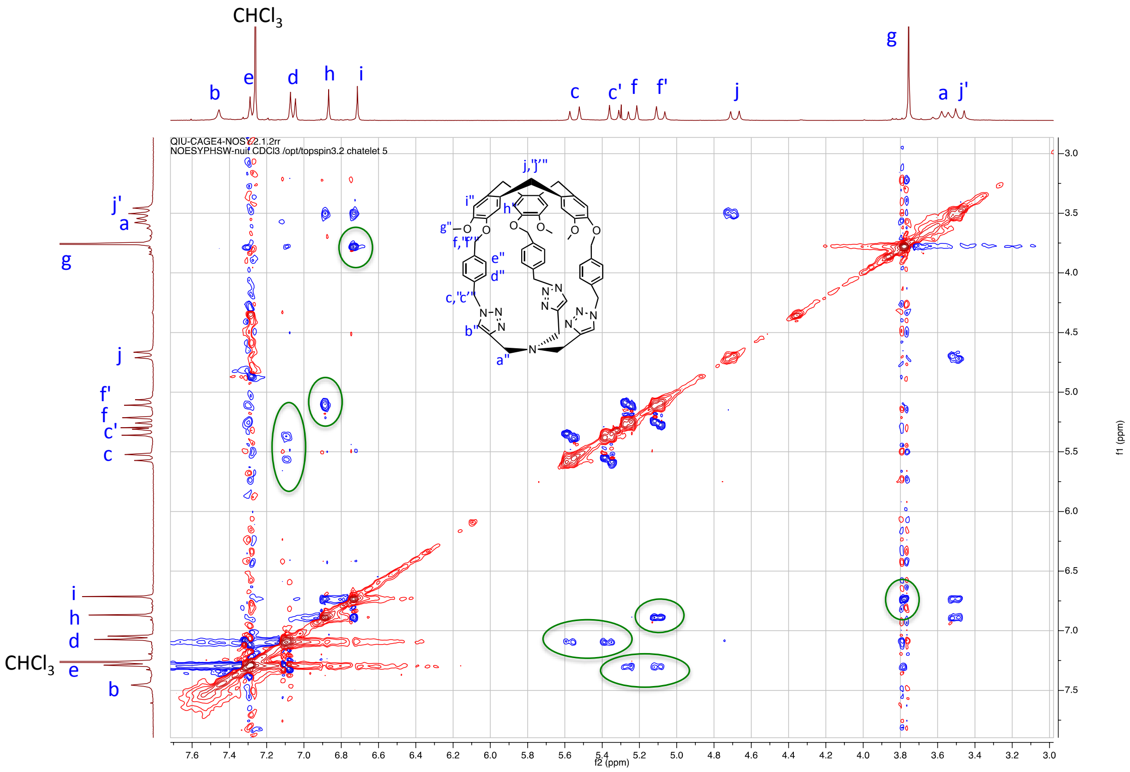


Figure S4. 2D NOESY-NMR spectra ($CDCl_3$, 300MHz) of **Hm-TBTA**, at 298K

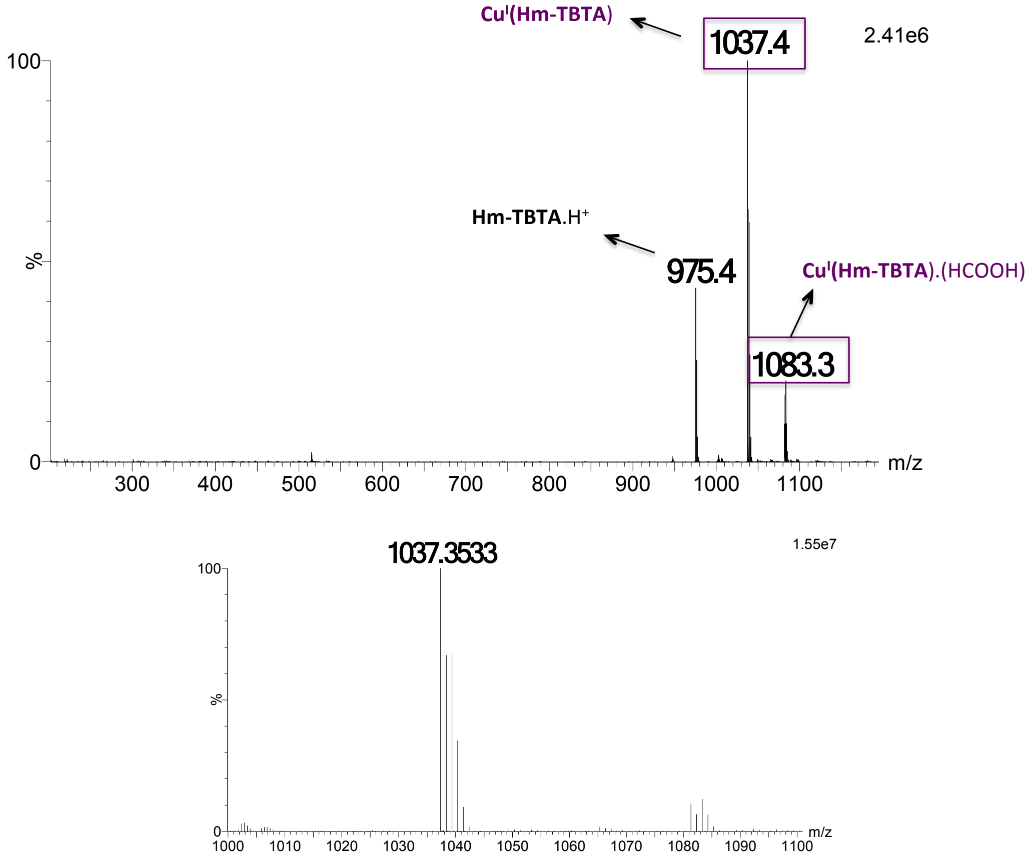


Figure S5. ESI-HRMS spectra of **Cu^{I}(Hm-TBTA)(PF$_6^-$)** in CH$_3$CN along with the zoom on the isotopic pattern at m/z = 1037.3533 that can be attributed to **Cu^{I}(Hm-TBTA)+** (m/z $_{\text{calculated}}$ = 1037.3524). Isotopic pattern at m/z = 975.4 could be attributed to the free ligand due to common partial metal-ion decomplexation in the condition of analysis (electrospray ionization). Isotopic pattern at m/z= 1083.3 could be attributed to adduct formation between **Cu^{I}(Hm-TBTA)** and formic acid.

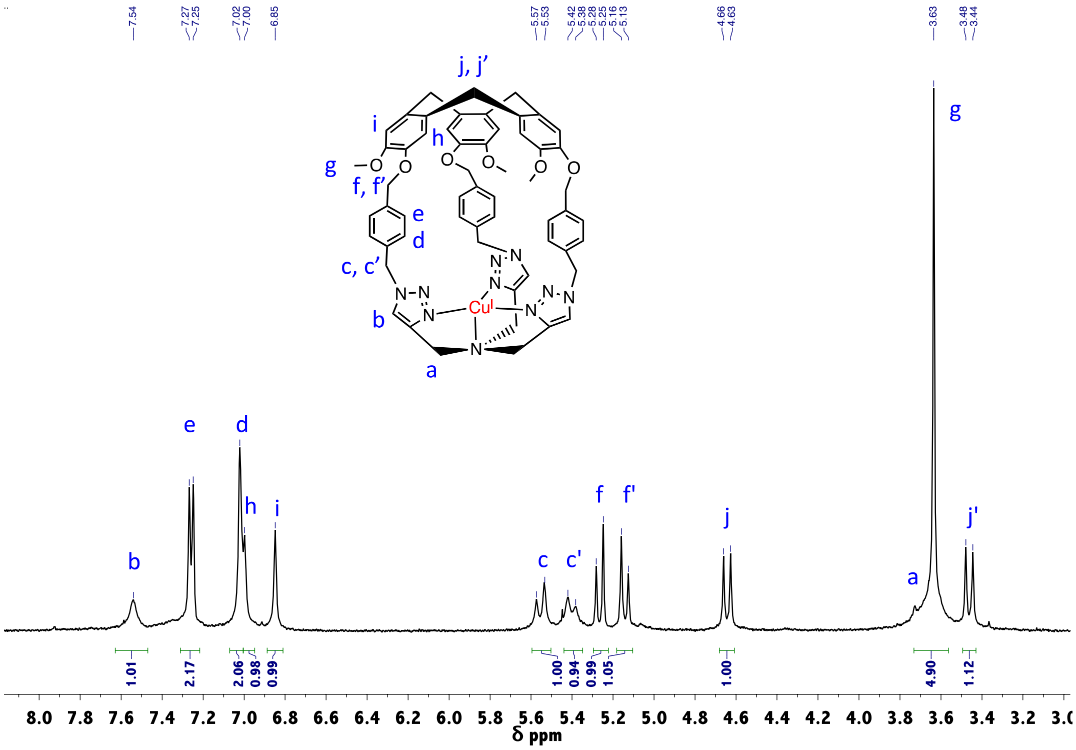


Figure S6. ^{1}H-NMR spectra (CD$_3$CN, 400 MHz) of **Cu^I(Hm-TBTA)(PF$_6^-$)** at 298K

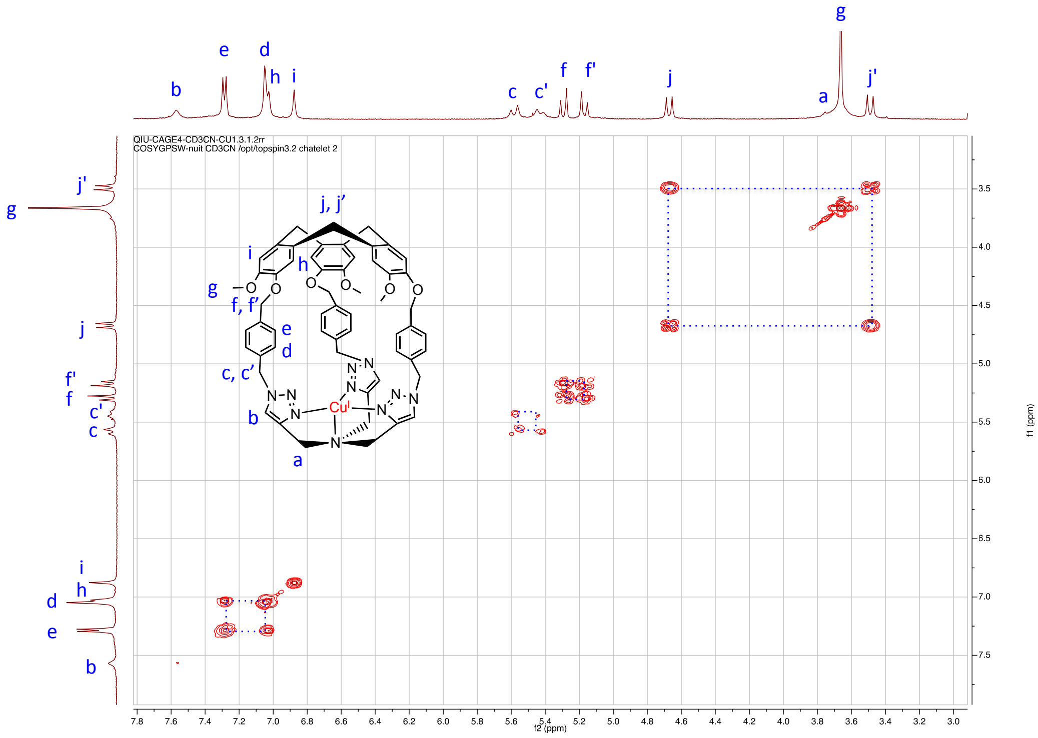


Figure S7. 2D COSY-NMR spectra (CD$_3$CN, 400MHz) of **Cu^I(Hm-TBTA)(PF$_6^-$)**, at 298K.

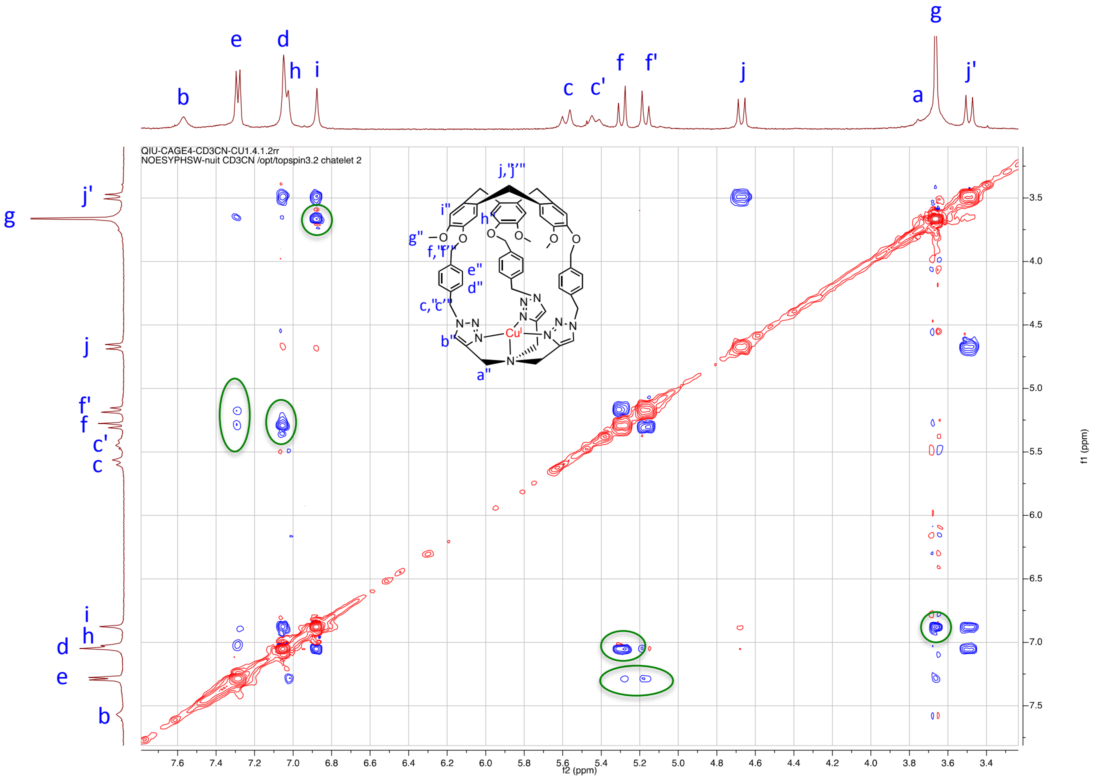


Figure S8. 2D NOESY-NMR spectra (CD$_3$CN, 400MHz) of **Cu^I(Hm-TBTA)(PF$_6^-$)**, at 298K

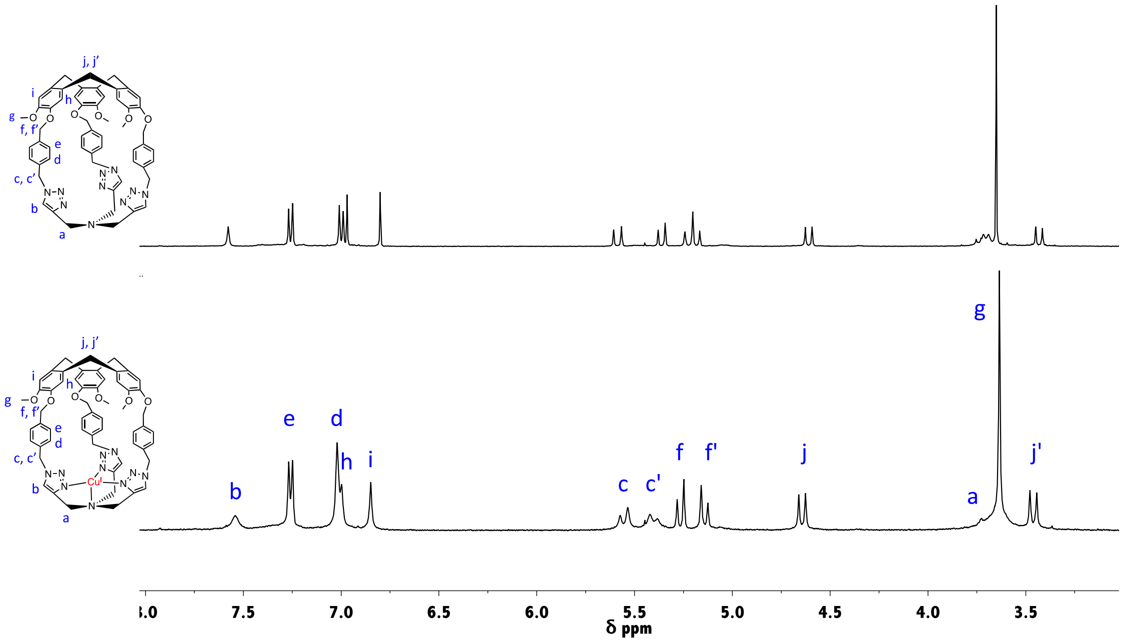


Figure S9. Comparison of the ^{1}H NMR spectra (CD$_3$CN, 400MHz) of **Hm-TBTA** (top) and **Cu^I(Hm-TBTA)(PF$_6^-$)** (bottom) at 298K.

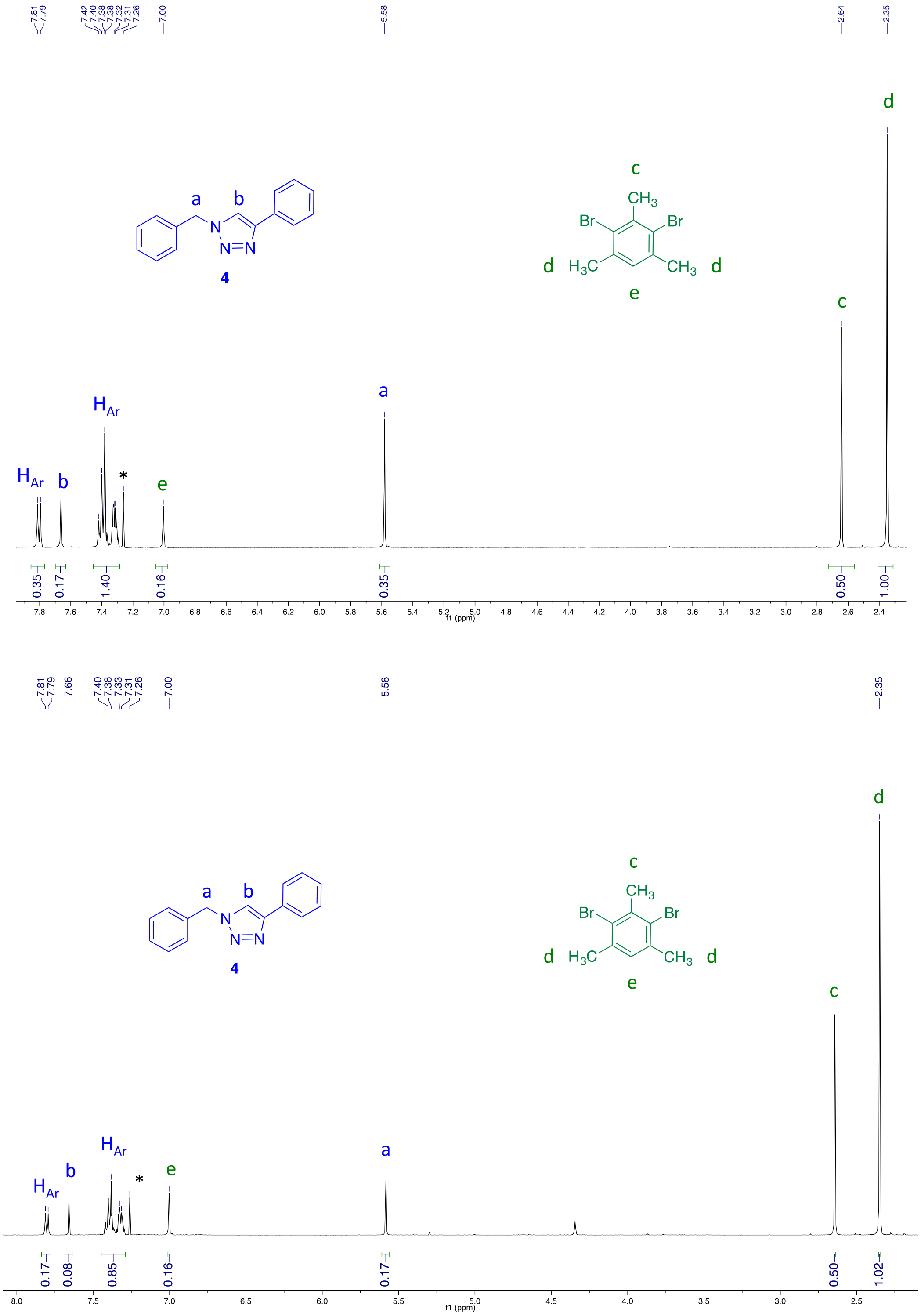


Figure S10. Typical ^{1}H NMR (CDCl$_3$, 400 MHz) analysis of the reaction mixture obtained after the model Cu^I-catalyzed cycloaddition reaction between phenylacetylene and benzyl-azide in the presence of **TBTA** (top) and **Hm-TBTA** (bottom) at 298K, after 2 hours (*=CHCl$_3$). KCN-based work-up was performed before analysis to remove the active copper ion. Yields were determined using 2,4-dibromomesitylene as internal standard (0.33 equiv. with respect to alkyne substrate). Signal corresponding to traces of unreacting phenylacetylene starting material are observed in the case of **Hm-TBTA** (4.34 ppm and 7.30-7.40 ppm).

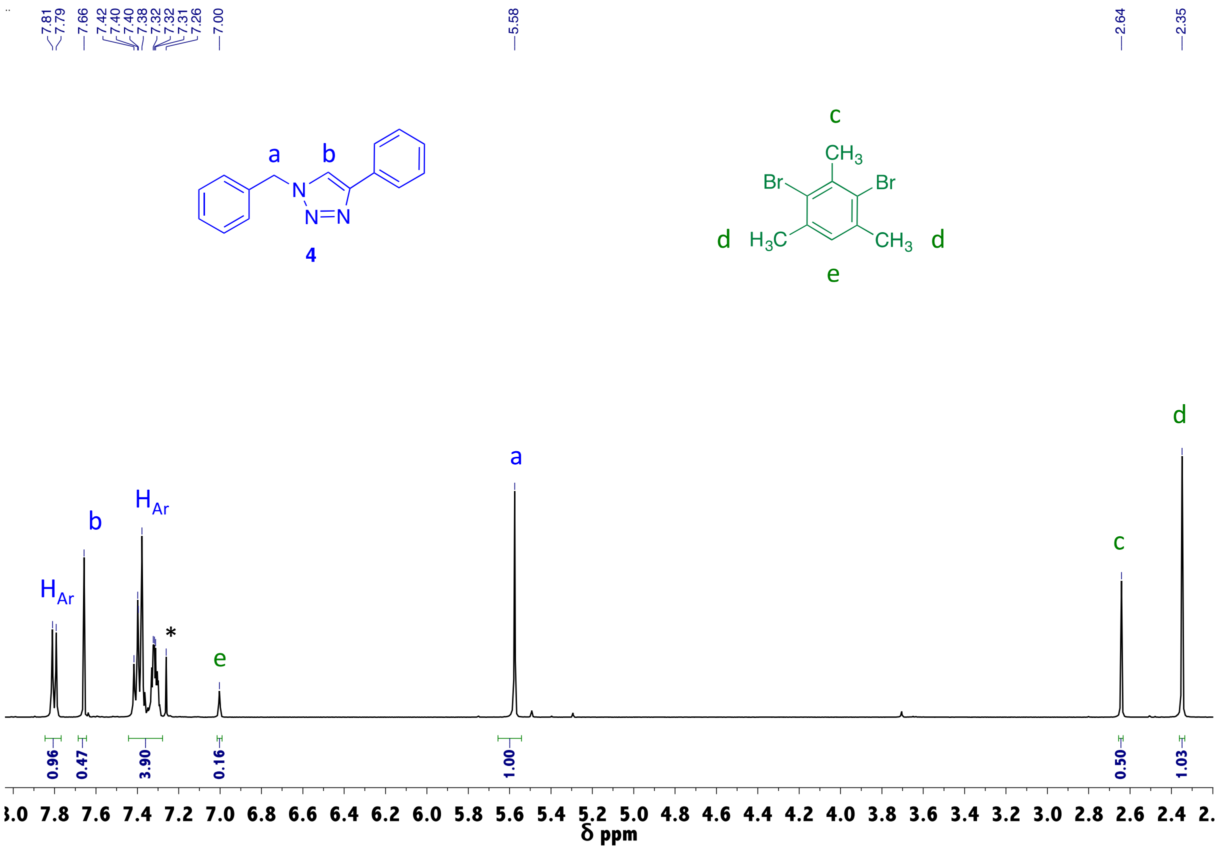
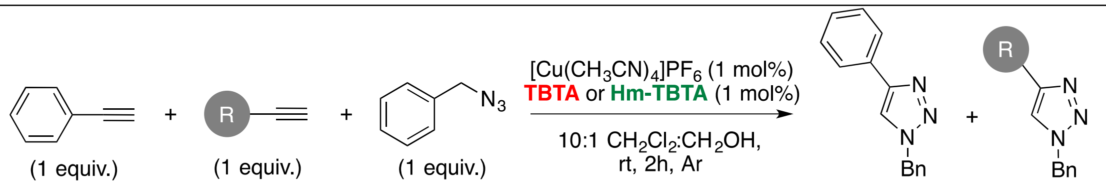


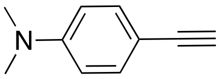
Figure S11. ^{1}H NMR (CDCl$_3$, 400 MHz) spectra of the authentic triazole product **4** (1 equiv.), in the presence of 0.33 equivalent of dibromomesithylene, at 298K (*=CHCl$_3$).



3 **n** **4** **P_n**

	Ratios of CuAAC products **4** and **P_n**			
	4 :**P_5**	**4** :**P_6**	**4** :**P_7**	**4** : **P_9**
TBTA	50 :50	25 :75	46 :54	86 : 14
Hm-TBTA	55 :45	27 :73	50 :50	98 : 02

n =



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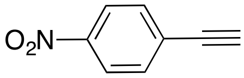

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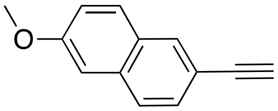

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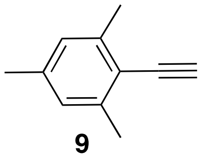

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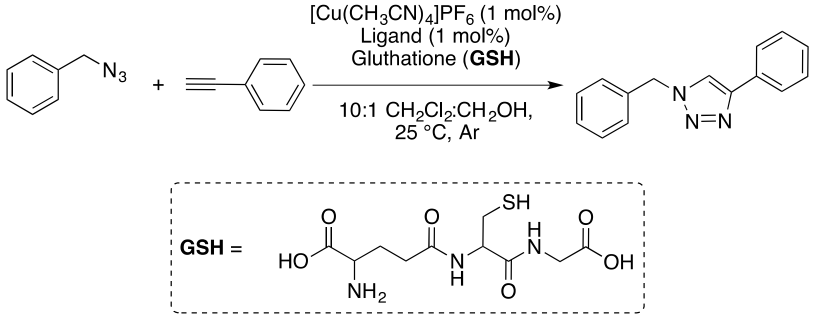
Figure S12. Competition CuAAC reactions of systems containing benzyl azide (0,2 mmol), phenylacetylene (1 equiv.), and another alkynes substrate (1 equiv.), along with products ratios determined by ^1H NMR using 2,4-dibromomesitylene as internal standard.



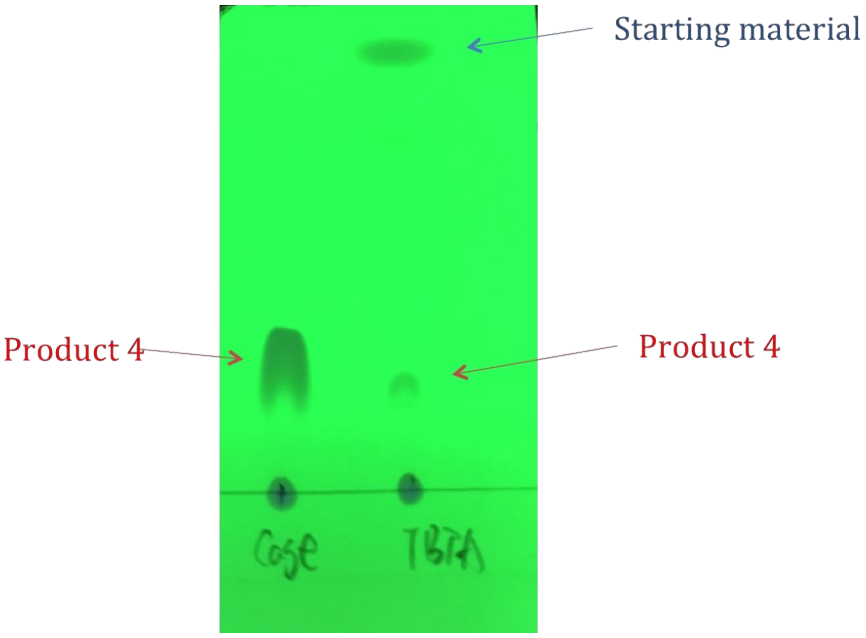
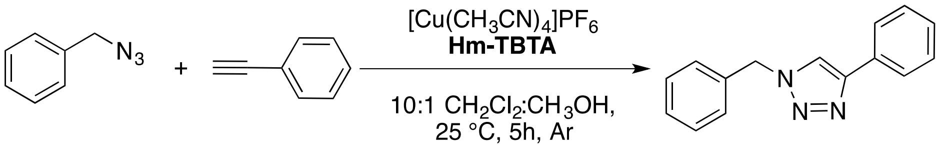


Figure S13. Photograph of the TLC analysis corresponding to the reaction mixture obtained after the model CuAAC reaction in the presence of gluthatione reduced (GSH, 20 mol%) using **Hm-TBTA** (1 mol%, left) and **TBTA** (1 mol% right), after 24h of reaction at room temperature, followed by a KCN-based work-up. Eluent: DCM: EtOAc 10:1)

4. Supplementary tables

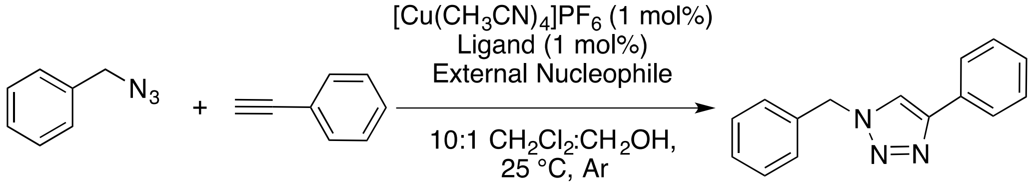
Table S1. Effect of the ligand :Cu^I ratio on the **Hm-TBTA**-assisted model CuAAC reaction.[a]



Entry	**Hm-TBTA**	**$[Cu^I(CH_3CN)_4]PF_6$**	**Yield** (%) [b]
1	1 mol%	1 mol%	32
2	1 mol%	2 mol%	85
3	2 mol%	1 mol%	30

[a] Reaction conditions: benzyl azide (0.2 mmol), phenylacetylene (1.0 equiv.), $[Cu^I(CH_3CN)_4]PF_6$ (1 mol% or 2 mol%), **Hm-TBTA** (1 mol% or 2 mol%) in a 1:10 MeOH/CH_2Cl_2 solvent mixture, at 25°C, for 5 hours, under an argon atmosphere. [b] Yields determined by ^{1}H NMR using 2,4-dibromomesitylene as internal standard.

Table S2. Effect of the addition of **K⁺Pic⁻** on the **TBTA**- and **Hm-TBTA**-assisted model CuAAC reaction.[a]



Entry	Ligand	External Nucleophile	Time (min)	Yield (%)
1	**TBTA**	none	30	12
2	**TBTA**	Picrate (7 mol%)	30	6
3	**Hm-TBTA**	none	30	6
4	**Hm-TBTA**	Picrate (7 mol%)	30	7
5	**TBTA**	none	120	35
6	**TBTA**	Picrate (7 mol%)	120	17
7	**TBTA**	Picrate (30 mol%)	120	9
8	**TBTA**	Picrate (70 mol%)	120	7
9	**Hm-TBTA**	None	120	17
10	**Hm-TBTA**	Picrate (7 mol%)	120	17
11	**Hm-TBTA**	Picrate (30 mol%)	120	17
12	**Hm-TBTA**	Picrate (70 mol%)	120	16

[a] CuAAC reaction between phenylacetylene (200 μM) and benzyl azide (1 equiv.), catalyzed by 1.0 mol% of $Cu^I(CH_3CN)_4(PF_6)$, in the presence of potassium picrate (**K⁺Pic⁻**), using 1.0 mol% of the accelerating-ligands **Hm-TBTA** or **TBTA**. Reaction conditions: 25°C, 10:1 CH_2Cl_2:MeOH solvent mixture.

5. Computational details

Calculations were performed with the TURBOMOLE program package,[S5] within the frame of the Density Functional Theory and the BP86-D3/def2-SV(P) level of computation.[S6,S7] The RI (Resolution of Identity) technique was employed.[S7] Coordinates of the optimized structures are reported here below in the xyz format.

STRUCTURE OF **[Cu(TBTA)](I)**

```
71
Energy = -3348.043873078 a.u.
C    1.1097754  -1.4020054  -1.1680570
H    0.4368977  -2.2787211  -1.0340249
H    1.7135494  -1.5973484  -2.0893704
C    0.9024029   1.0297240  -1.6658811
H    0.9087556   1.2006461  -2.7714640
H    1.9663698   0.9543454  -1.3470202
C   -1.1059135  -0.4391242  -1.7728710
H   -1.1390465  -0.9835130  -2.7496199
H   -1.5497518   0.5661644  -1.9513102
N    0.2519724  -0.2209367  -1.2725596
Cu  -0.1908936   0.2196768   1.0542412
C    0.2720361   2.2031628  -0.9565740
C    0.0296805   3.5146413  -1.3379799
N   -0.6286596   3.2299487   0.7857735
H    0.1835406   4.0584351  -2.2761123
N   -0.1529905   2.0819581   0.3511037
N   -0.5078484   4.1038121  -0.2282157
C   -1.0668429   5.4581844  -0.0994382
H   -1.1763062   5.6246987   0.9919244
H   -0.3149495   6.1762904  -0.4871153
C   -1.9446339  -1.1559272  -0.7431645
C   -2.9661604  -2.0888167  -0.8454678
N   -2.6449850  -1.5797569   1.3138116
H   -3.4203513  -2.6063927  -1.6971418
N   -3.3701561  -2.3018895   0.4425692
N   -1.7865705  -0.8817208   0.6003518
C   -4.3478106  -3.2831368   0.9372088
H   -4.5475690  -2.9888456   1.9880719
H   -5.2845747  -3.1551246   0.3562636
C    2.0107036  -1.3022099   0.0387331
C    3.3078318  -1.7292744   0.2822773
N    2.4791364  -0.7887742   2.1407715
H    4.0632420  -2.2142594  -0.3450898
N    3.5390600  -1.4044208   1.5894421
N    1.5514911  -0.7309611   1.2084168
C    4.7935950  -1.5275819   2.3472146
H    4.5117322  -1.3457005   3.4047104
H    5.1469663  -2.5758086   2.2572458
C   -3.8182313  -4.7011888   0.8351546
C   -2.6738869  -5.0740227   1.5718704
C   -4.4437145  -5.6469095   0.0006561
C   -2.1659064  -6.3782022   1.4741727
H   -2.1821910  -4.3338547   2.2265065
C   -3.9365760  -6.9551725  -0.0938159
H   -5.3423423  -5.3642351  -0.5745829
C   -2.7970365  -7.3213841   0.6412793
H   -1.2764582  -6.6656048   2.0587191
H   -4.4371096  -7.6913891  -0.7437349
H   -2.4006983  -8.3475229   0.5700032
C    5.8401657  -0.5431647   1.8602416
C    5.5981767   0.8430443   1.9663071
C    7.0440704  -0.9945272   1.2867890
C    6.5516713   1.7630927   1.5050179
H    4.6552227   1.1989483   2.4162408
C    8.0014852  -0.0719315   0.8286435
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H	7.2427594	-2.0772037	1.2053274
C	7.7555898	1.3068578	0.9357308
H	6.3600201	2.8447797	1.5979455
H	8.9448028	-0.4341479	0.3883139
H	8.5066090	2.0306342	0.5790310
C	-2.3906805	5.5884312	-0.8293789
C	-3.4923249	4.8060557	-0.4224708
C	-2.5302480	6.4678415	-1.9198345
C	-4.7173530	4.9066646	-1.0990039
H	-3.3845674	4.1158178	0.4320008
C	-3.7595579	6.5713961	-2.5949116
H	-1.6745875	7.0868591	-2.2407891
C	-4.8531772	5.7903628	-2.1862680
H	-5.5764984	4.2986048	-0.7710497
H	-3.8621925	7.2682233	-3.4427734
H	-5.8179594	5.8734098	-2.7129914

STRUCTURE OF **[Cu(Hm-TBTA)](I)**

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Energy = -4841.696021065 a.u.

O	4.8858247	-1.9269821	1.8298393
O	4.6803060	-2.7023770	-0.6952034
O	1.6706352	3.6383900	3.6823071
O	0.4185024	5.1774914	1.9297279
O	1.4442165	0.9734412	-5.2662240
O	0.1534731	3.1348005	-4.4443452
C	4.1069821	-1.6886186	2.9927684
H	3.6040041	-0.6924843	2.9329124
H	4.7761563	-1.6674029	3.8859697
C	4.9855422	-0.9536804	0.8719443
C	5.2025867	0.3986387	1.1559675
H	5.3052053	0.7000659	2.2108355
C	5.3220053	1.3790984	0.1430189
C	5.2638873	0.9633949	-1.2058571
C	5.0674889	-0.4089376	-1.4933040
H	5.0307262	-0.7184586	-2.5479457
C	4.9070910	-1.3717622	-0.4858460
C	4.5714552	-3.1629610	-2.0298260
H	3.7276657	-2.6679581	-2.5717917
H	4.3736789	-4.2524539	-1.9660681
H	5.5151090	-2.9994723	-2.6038851
C	5.4694972	2.8341378	0.5737500
H	6.0823064	2.8674677	1.5010021
H	6.0412579	3.4098888	-0.1800615
C	4.1289829	3.5066210	0.8577147
C	3.5510795	3.3017068	2.1338846
H	4.1079758	2.6979558	2.8652274
C	2.2990538	3.8279101	2.4844166
C	1.6086152	4.6295532	1.5328771
C	2.1896151	4.8506730	0.2799162
H	1.6636783	5.5089259	-0.4302591
C	3.4322812	4.2858408	-0.0924966
C	2.3075332	2.8280558	4.6533956
H	2.4738683	1.7870216	4.2801326
H	1.6243826	2.7967458	5.5266151
H	3.2867208	3.2574173	4.9751616
C	-0.6801388	5.1954900	1.0308390
H	-0.4243740	4.6568866	0.0856128
H	-0.9156122	6.2515075	0.7557337
C	1.4762346	-0.4378536	-5.1149913
H	1.9984152	-0.7207514	-4.1683200
H	2.0546568	-0.8864597	-5.9578782
C	2.0833916	1.7662960	-4.3511894
C	3.3638685	1.5043795	-3.8529614
H	3.8940747	0.6111397	-4.2207026
C	4.0071188	2.3552603	-2.9234563
C	3.3435954	3.5353953	-2.5202517

C	2.0568926	3.8118119	-3.0423207
H	1.5554999	4.7375564	-2.7244396
C	1.4052252	2.9447300	-3.9317797
C	-0.5704512	4.2825533	-4.0394303
H	-1.5505596	4.2283708	-4.5557967
H	-0.0547995	5.2262504	-4.3400139
H	-0.7385389	4.2981048	-2.9338821
C	5.3677609	1.9246533	-2.3870606
H	5.9242921	1.4165464	-3.2046070
H	5.9792976	2.8076075	-2.1167445
C	3.9257021	4.5258105	-1.5150038
H	3.6296239	5.5525240	-1.8224405
H	5.0325452	4.5127066	-1.5531614
C	-1.8950234	4.5324444	1.6596397
C	-1.7864974	3.8331444	2.8769751
C	-3.1396181	4.5775813	0.9999445
C	-2.9007026	3.1666846	3.4057900
H	-0.8117853	3.8085033	3.3892897
C	-4.2480501	3.8984399	1.5244502
H	-3.2424096	5.1395494	0.0553608
C	-4.1355746	3.1772072	2.7291356
H	-2.8003319	2.6043880	4.3500625
H	-5.2097616	3.9200879	0.9836729
C	0.0657390	-1.0042800	-5.0855305
C	-1.0527015	-0.1524642	-5.0070901
C	-0.1308412	-2.3998559	-5.0946903
C	-2.3422413	-0.6936787	-4.9097658
H	-0.8905724	0.9369543	-5.0069747
C	-1.4205433	-2.9375803	-4.9833022
H	0.7364544	-3.0779333	-5.1763680
C	-2.5390207	-2.0876400	-4.8796545
H	-3.2109000	-0.0177387	-4.8287662
H	-1.5577589	-4.0323931	-4.9649411
C	3.0460589	-2.7650115	3.1572100
C	2.2595897	-2.8022235	4.3262230
C	2.8080417	-3.7064174	2.1376851
C	1.2240308	-3.7376417	4.4578355
H	2.4493512	-2.0819972	5.1410761
C	1.7800203	-4.6492474	2.2784104
H	3.4311594	-3.6741226	1.2300672
C	0.9685018	-4.6652923	3.4290375
H	0.5993494	-3.7388454	5.3675182
H	1.5888081	-5.3705736	1.4652874
C	-3.9158153	-2.6552287	-4.6340559
H	-4.7028484	-2.0518161	-5.1358890
H	-3.9987425	-3.7017653	-4.9977035
C	-5.2860253	2.3413673	3.2350683
H	-5.3304483	2.3353309	4.3456307
H	-6.2610974	2.7117927	2.8525164
C	-0.2178364	-5.5949376	3.5096795
H	-0.0004018	-6.5771031	3.0370667
H	-0.5237451	-5.7784261	4.5618668
N	-1.3977869	-5.0290440	2.8017530
C	-2.6396590	-5.5861011	2.6518558
C	-3.3503670	-4.6661682	1.8910392
H	-2.9036613	-6.5609544	3.0766548
N	-4.2432862	-2.6671690	-3.1826396
C	-5.3958293	-3.0955091	-2.5800214
C	-5.1940878	-2.8627049	-1.2252363
H	-6.2385302	-3.5083320	-3.1456147
N	-5.1537940	0.9238484	2.8027126
C	-5.9877146	-0.1258663	3.0814752
C	-5.3939479	-1.2218251	2.4677270
H	-6.8984481	-0.0122436	3.6798400
N	-1.3195785	-3.8358104	2.1943917
N	-2.4917815	-3.6167967	1.6417823
N	-3.3623186	-2.2057400	-2.2827476

N	-3.9333912	-2.3181246	-1.1044439
N	-4.1098994	0.5350911	2.0557896
N	-4.2493655	-0.7564131	1.8564378
C	-4.7372057	-4.6750880	1.2867256
H	-4.6583038	-5.0631596	0.2462929
H	-5.3998310	-5.3850391	1.8425900
C	-5.7241520	-2.6979367	2.4413887
H	-5.1565256	-3.1939244	3.2606004
H	-6.8091935	-2.8586292	2.6625311
C	-6.0764302	-3.0165494	-0.0061218
H	-6.5787738	-2.0412306	0.1823643
H	-6.8883047	-3.7606414	-0.2040265
N	-5.2883796	-3.3217235	1.1900107
Cu	-3.2683740	-2.0476862	0.7330967

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