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Tetracopper(I) thiolate- and amido-(SNS) complexes and copper-catalyzed azide-alkyne cycloaddition in water

Atousa Khanzadeh,[†] Saeed Ataie,[†] and R. Tom Baker*,[†]

[†] Department of Chemistry and Biomolecular Sciences and Centre for Catalysis Research and Innovation, University of Ottawa, Ottawa, Ontario K1N 6N5, Canada

rbaker@uottawa.ca

Electronic Supplementary Information:

Table of Contents:

I. Experimental

General considerations

Synthesis of the complexes (**1** and **2**) were carried out under dinitrogen, using a MBraun glovebox and stored in the glovebox. THF, DCM and hexane were dried on columns of activated alumina using a J. C. Meyer (formerly Glass Contour) solvent purification system. Anhydrous C_6D_6 were dried with activated alumina (ca. 10 wt %) overnight, followed by filtration. SNS ligands synthesized in the lab based on previous publications in our group.[1,2] All substrates were purchased from commercial suppliers. ^1H and ^{13}C NMR spectra were recorded on a 300 MHz Bruker Avance or Avance II instrument. Solid state ^{13}C NMR spectra recorded as the low solubility of the **1** on the Bruker 200 Avance III. For characterization of compound **3** the DEPT 135, HSQC and HMBC NMR spectra recorded on the 300 MHz Bruker Avance II instrument. ^1H NMR spectra were referenced respectively to solvent residual protons (C_6D_6, δ 7.15; $CDCl_3$, δ 7.26) and all the NMR spectra recorded at room temperature (21−25 °C). Mass spectra were recorded on an AB Sciex Q1MS mass spectrometer with electrospray ionization (ESIMS) in positive mode (ion spray voltage, 5000.0 V; TEM, 400 °C; declustering potential, 11.00 V; focusing potential, 300.0 V) with samples prepared to ca. 0.05 mg/mL in acetonitrile or dichloromethane. For electron impact (EI), solid samples were prepared by drying products under vacuum, and spectra obtained using a Kratos Concept S1 instrument (Hres 7000−10000). X-ray diffraction data were collected on a Bruker Smart or Kappa diffractometer equipped with an ApexII CCD detector and a sealed-tube Mo K source (□ = 0.71073 Å). EPR spectra recorded on a Bruker EMX plus 10/12 X-band spectrometer at room temperature.

Synthesis of complex 1, $(CuL^1)_4$

A vial was charged with 200 mg H**L¹** (0.77 mmol) and 129 mg of LiHMDS (0.77 mmol) in 5 mL of THF and the mixture was stirred for 15 min. In a second vial 76 mg of CuCl (0.77 mmol) was dissolved in 5 mL of THF and the mixture from the first vial was added dropwise with stirring. After stirring the resulting mixture for 24 h at room temperature, complex **1** was collected by filtration, washed two times with 5 mL of THF and dried under vacuum to give a dark powder (240 mg, 97% yield). $^{13}C\{^1H\}$ MAS NMR (200 MHz): 115-163 (aromatic) 15.5-19.5 ppm (S-Me), ESI-MS: $[(CuL^1)_2H^+]$ 642.9457, Calcd. 642.9492 and $[(CuL^1)H]^+$ 321.9736 Calcd 321.98 (Fig. S1).

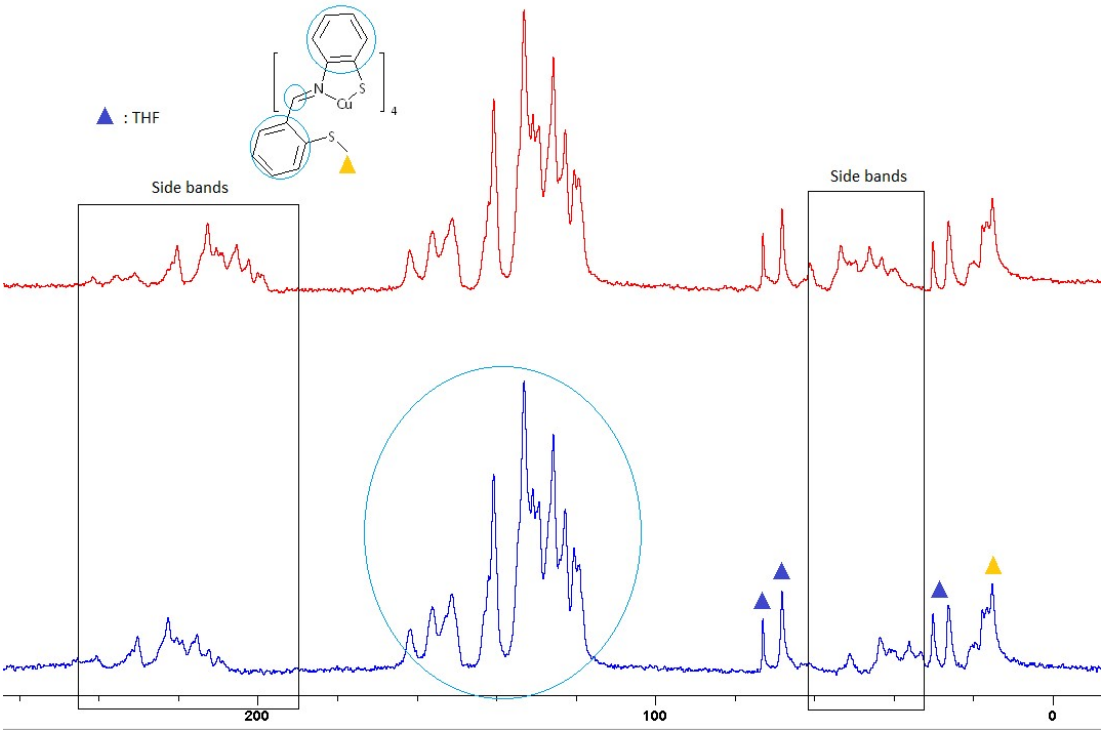
Synthesis of complex 2, $(CuL^2)_4$

A vial was charged with 200 mg H**L²** (0.727 mmol) and 121 mg of LiHMDS (0.727 mmol) in 5 mL of THF and the mixture was stirred for 30 min. In a second vial 71 mg of CuCl (0.727 mmol) was dissolved in 5 mL of THF and the mixture from the first vial was added dropwise with stirring. After stirring the resulting mixture for 24 h the solvent was removed in vacuo. The residue was extracted with 5 mL of DCM, filtered and evaporated under vacuum to give a light brown powder (203 mg, 83% yield). ^1H NMR (300 MHz, C_6D_6): δ 7.45 (d, 1H, aromatic), 7.20 (d, 1H, aromatic), 6.96 (t, 3H, aromatic), 6.87 (t, 1H, aromatic), 6.56 (t, 1H, aromatic), 6.49 (d, 1H, aromatic), 4.26 (d, 2H, N-CH_2), 1.97 (s, 3H, S-CH_3) 1.93 (s, 3H, S-CH_3). ESI-MS: $[(CuL^2)H]^+$ 338.0061, Calcd. 338.0098 (Fig. S2).

Catalysis protocol

A 15 mL vial was charged with 1-5 mol% **1** or **2** in the glovebox. The vial was then taken out and the organohalide substrate (0.5 mmol), NaN_3 (0.5 mmol), terminal alkyne substrate (0.5 mmol) and 4 ml of distilled water were added to the vial along with a small stir bar. The vial was then left to stir at the desired temperature from 1-24 h. The resulting product was then isolated by extracting three times with 4 mL of ethyl acetate. The extract was evaporated under vacuum and the collected triazole product was dried and weighed to calculate the yield. ^1H NMR spectra were then recorded to characterize the known triazole products.

II. Spectroscopic Data



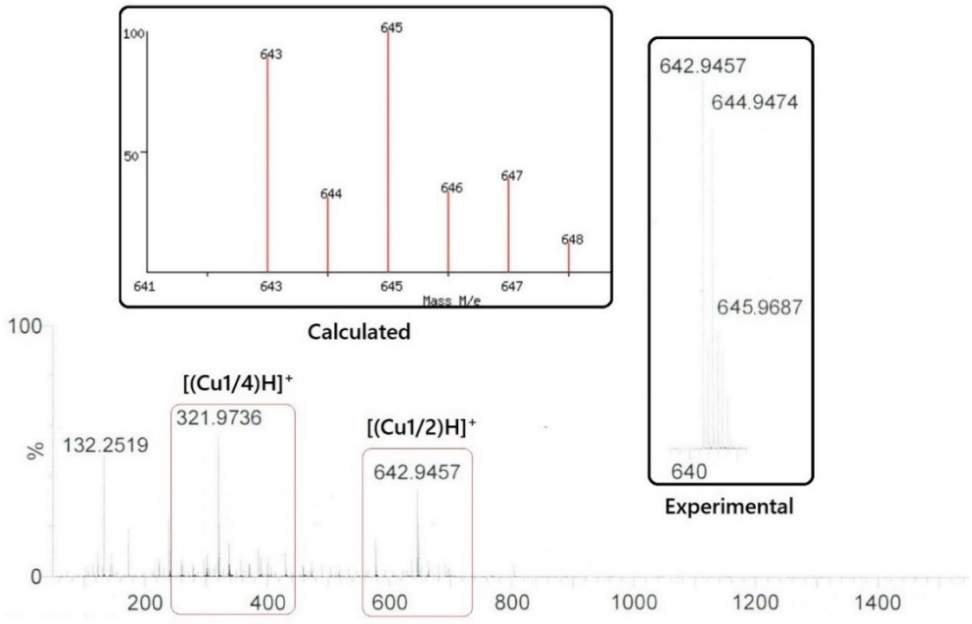


Figure S1. $^{13}C\{^{1}H\}$ MAS NMR spectrum (200MHz, solid) of complex **1** (top)[3]. ESI-mass spectrum of **1** (bottom) showing monomer $[(CuL^1)H]^+$ (Calcd 321.98, found 321.9736) and dimer $[(CuL^1)_2H^+]$ (Calcd 642.95, found 642.9492).

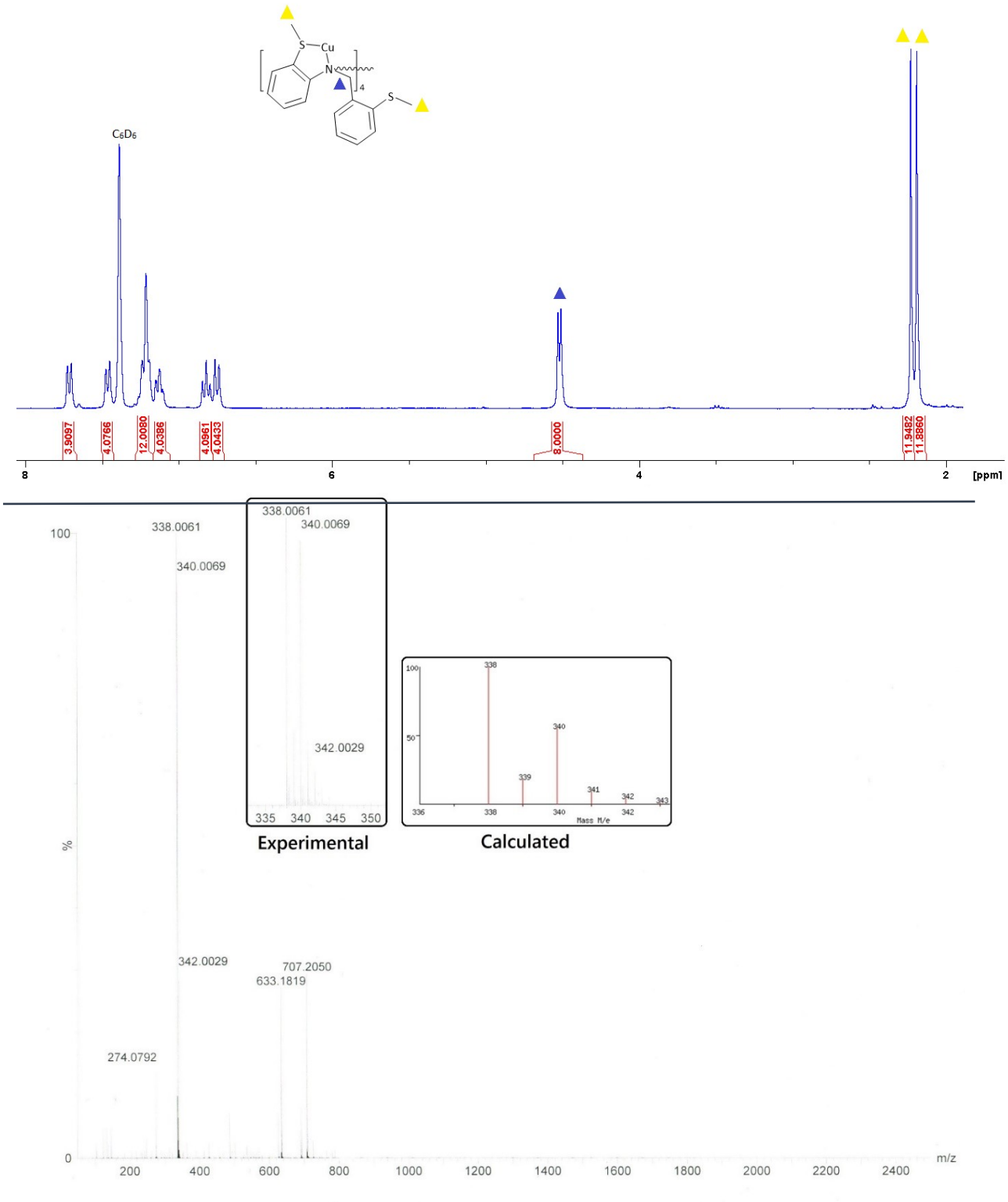


Figure S2. ^{1}H NMR spectrum of **2** (top). ESI-mass spectrum of **2** (bottom) showing monomer $[CuL^{2}]^{+}$ (Calcd 338.0098, found 338.0061).

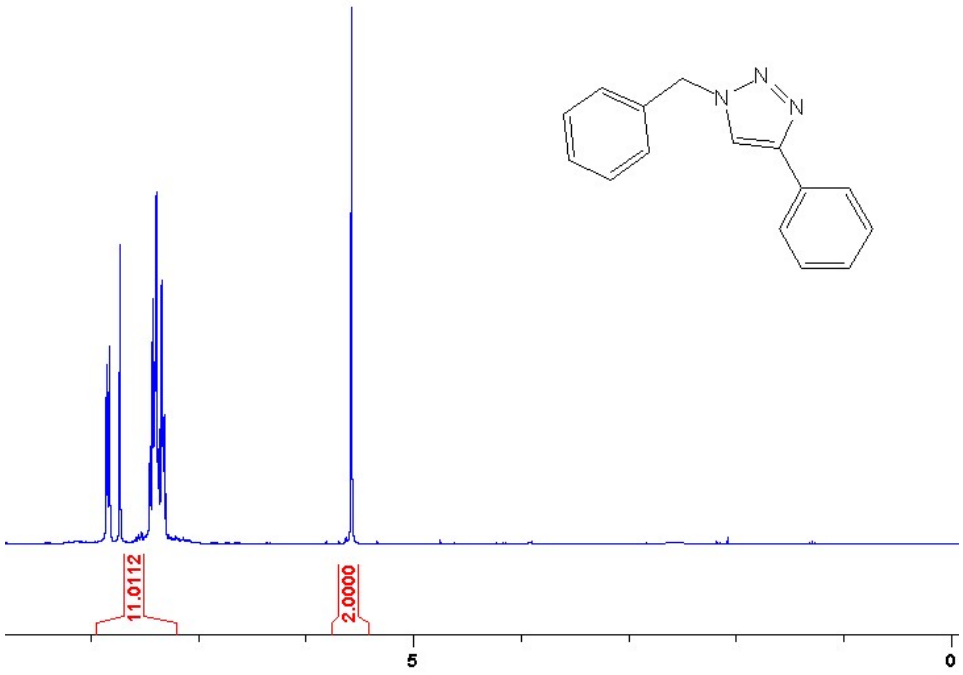


Figure S3. ^{1}H NMR spectrum of triazole product **3** from the catalytic reaction in $CDCl_3$.

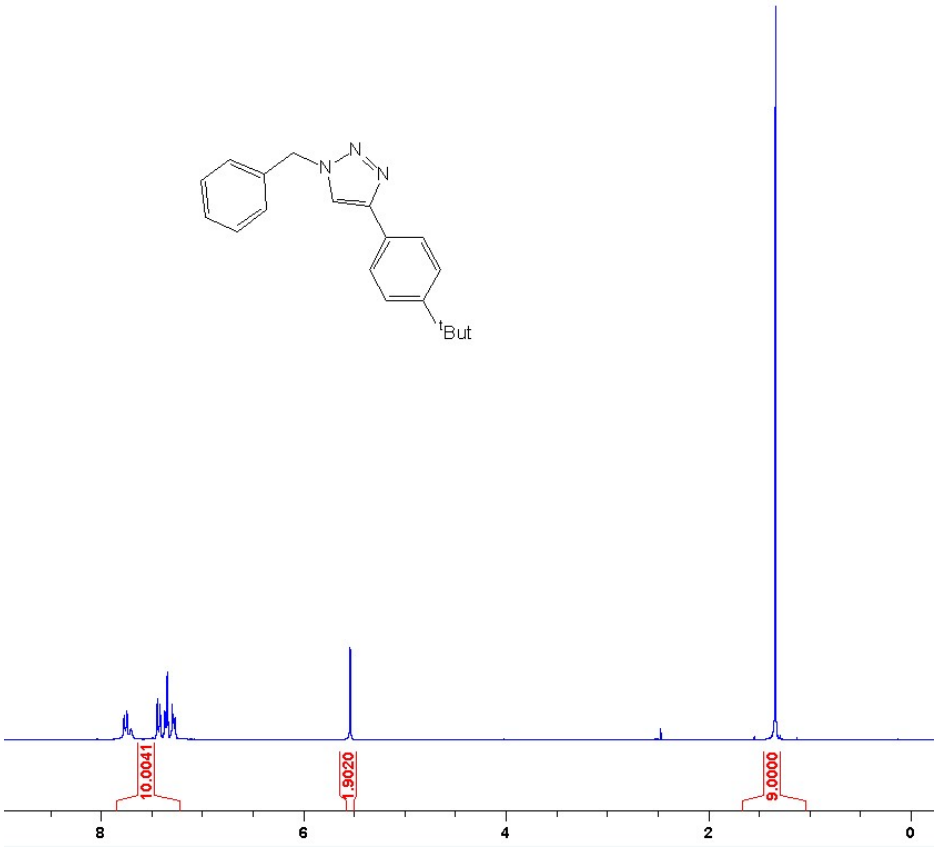


Figure S4. ^{1}H NMR spectrum of triazole product **4** from the catalytic reaction in $CDCl_3$.

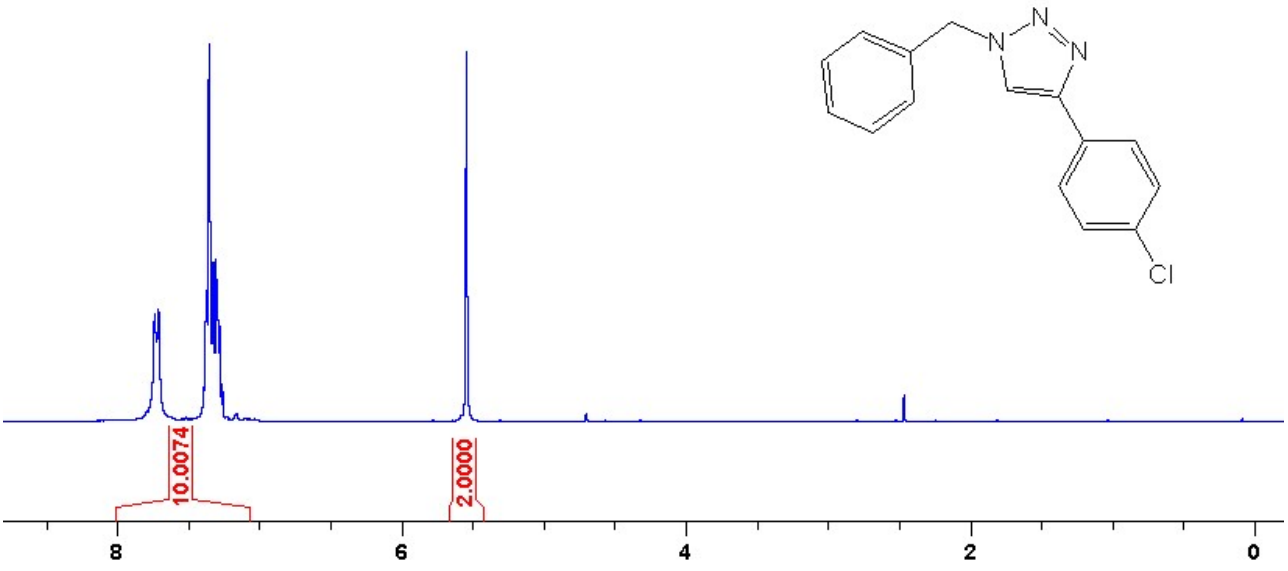


Figure S5. ^{1}H NMR spectrum of triazole product **5** from the catalytic reaction in $CDCl_3$.

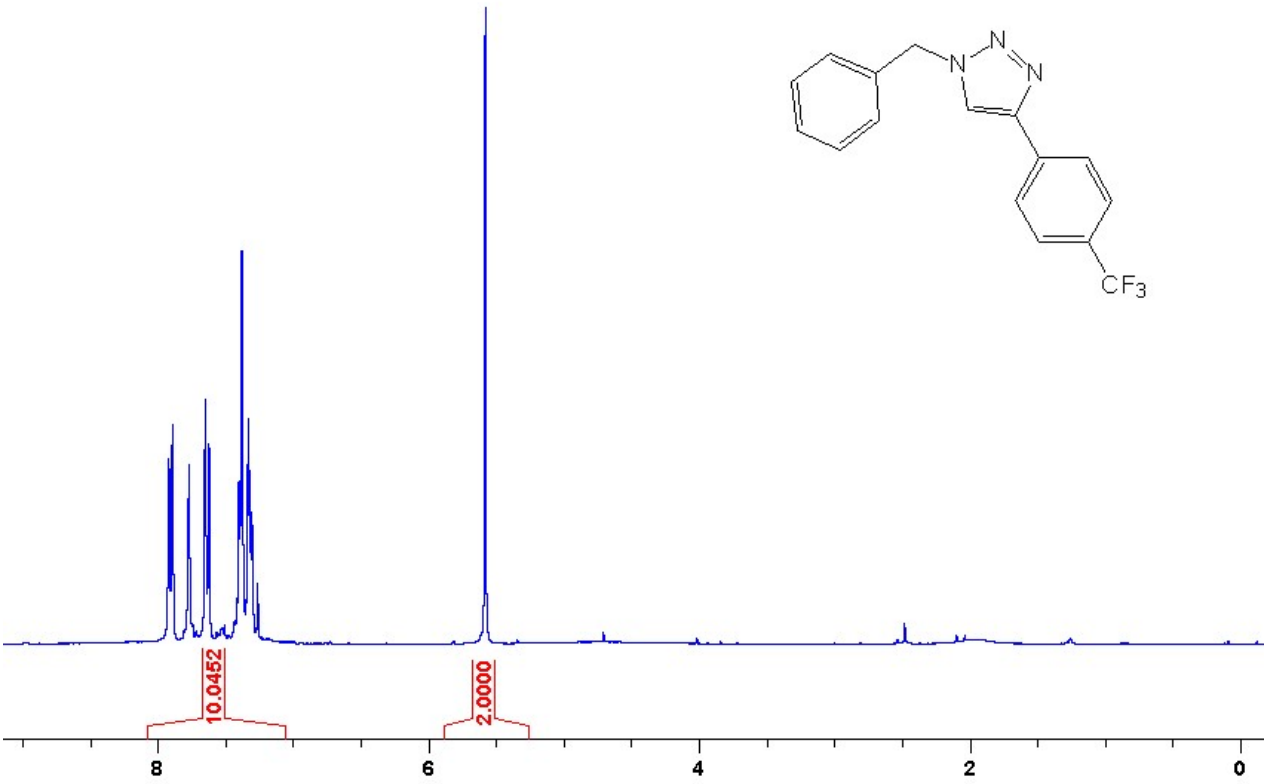


Figure S6. ^{1}H NMR spectrum of triazole product **6** from the catalytic reaction in $CDCl_3$.

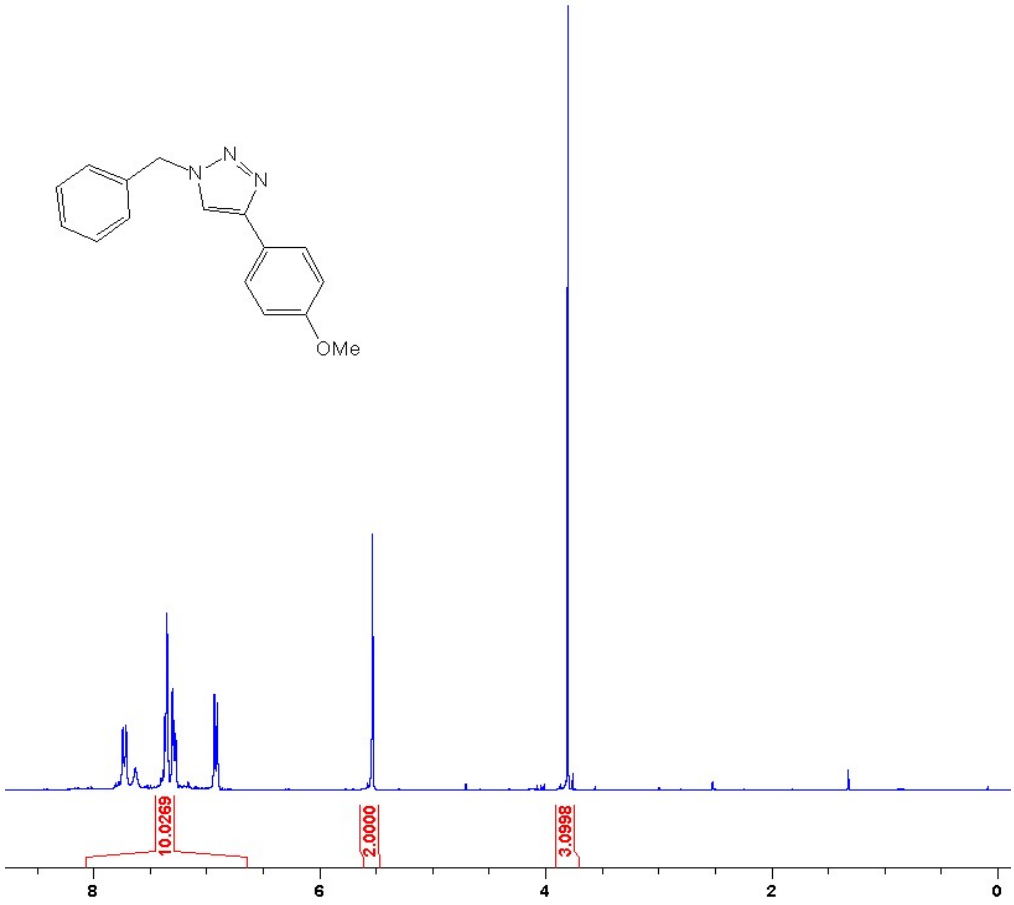


Figure S7. ^{1}H NMR spectrum of triazole product **7** from the catalytic reaction in $CDCl_3$.

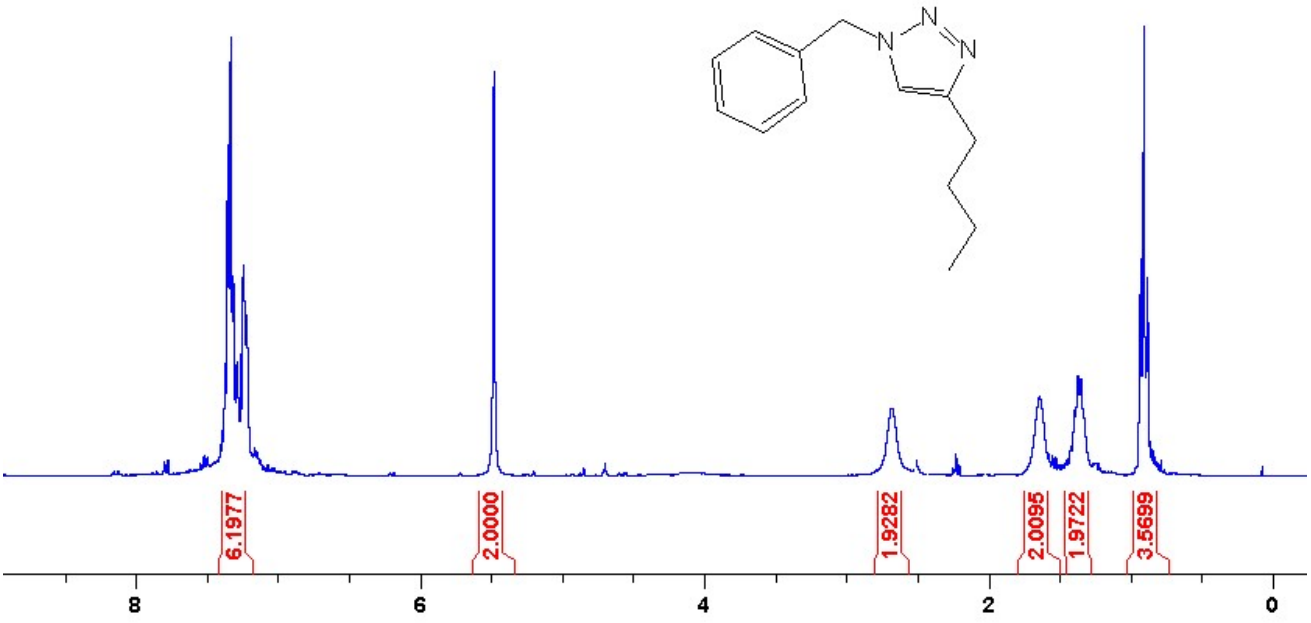


Figure S8. ^{1}H NMR spectrum of triazole product **8** from the catalytic reaction in $CDCl_3$.

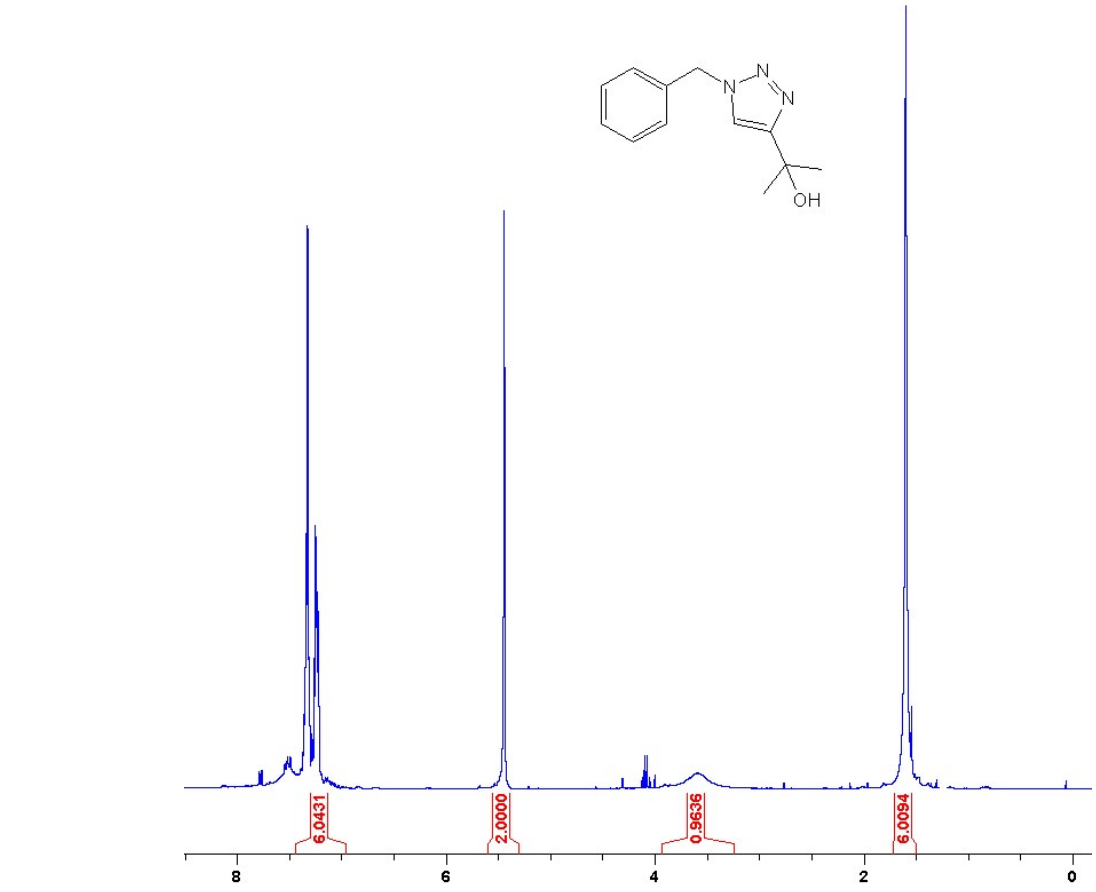


Figure S9. ^{1}H NMR spectrum of triazole product **9** from the catalytic reaction in $CDCl_3$.

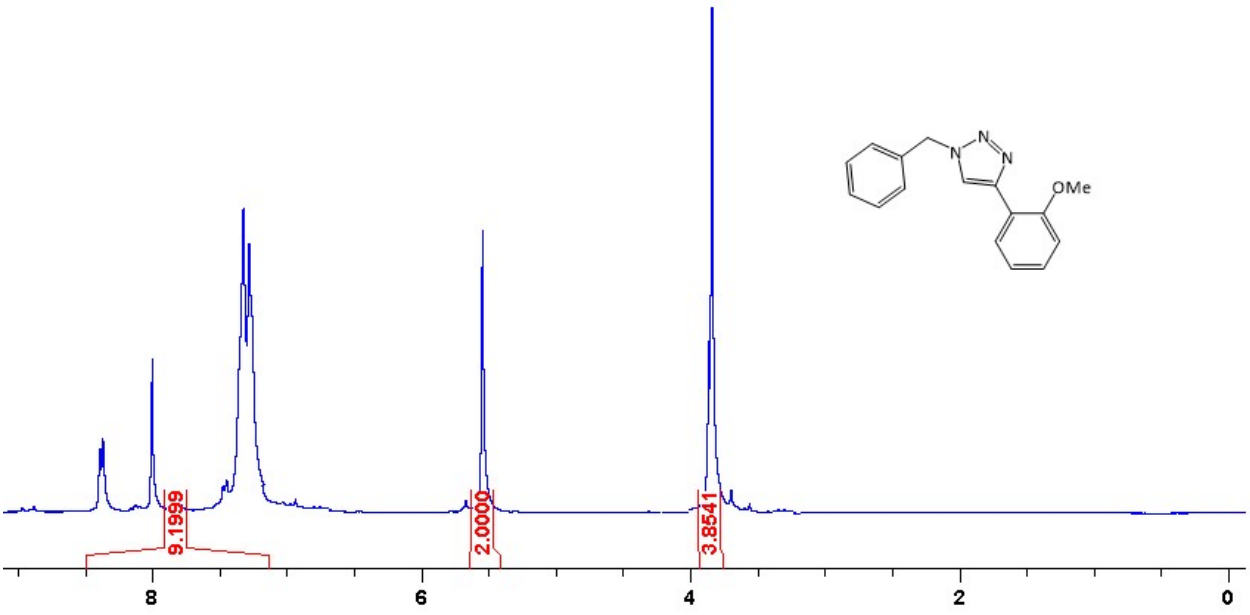


Figure S10. ^{1}H NMR spectrum of triazole product **10** from the catalytic reaction in $CDCl_3$.

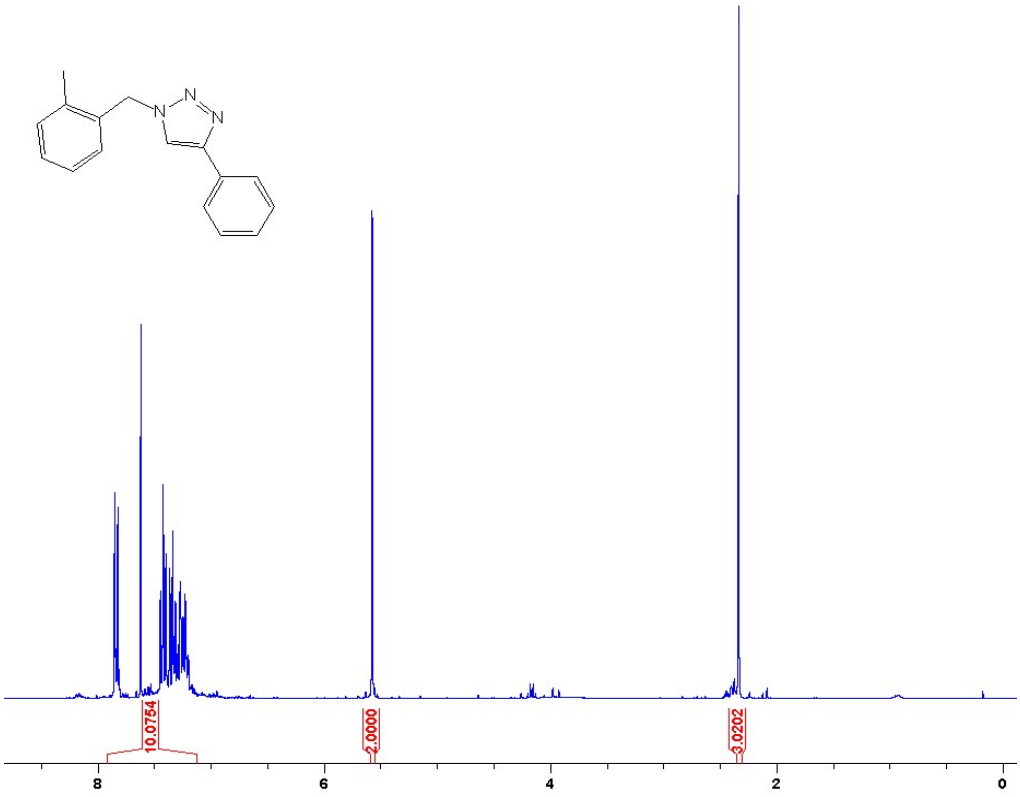


Figure S11. ^{1}H NMR spectrum of triazole product **11** from the catalytic reaction in $CDCl_3$.

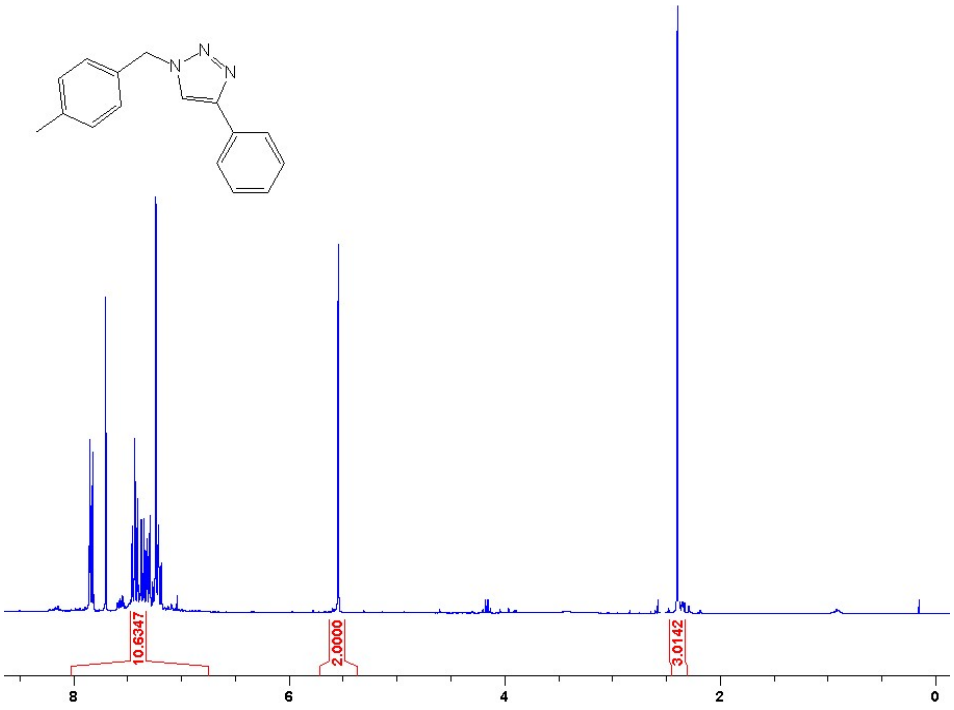


Figure S12. ^{1}H NMR spectrum of triazole product **12** from the catalytic reaction in $CDCl_3$.

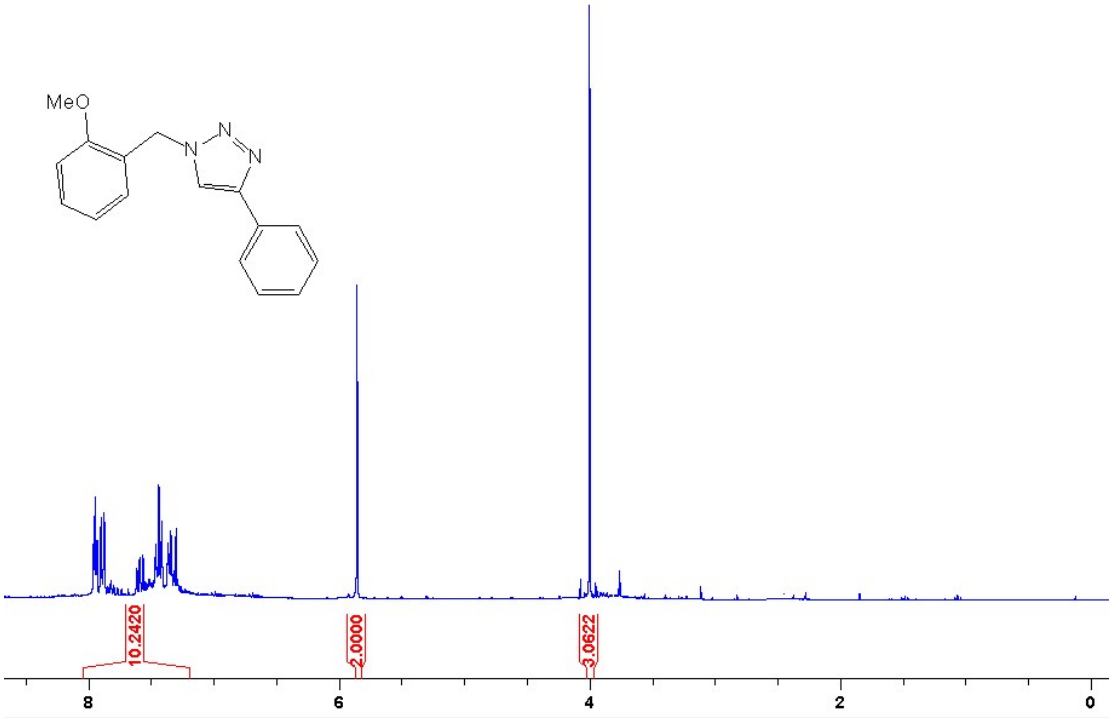


Figure S13. ^{1}H NMR spectrum of triazole product **13** from the catalytic reaction in $CDCl_3$.

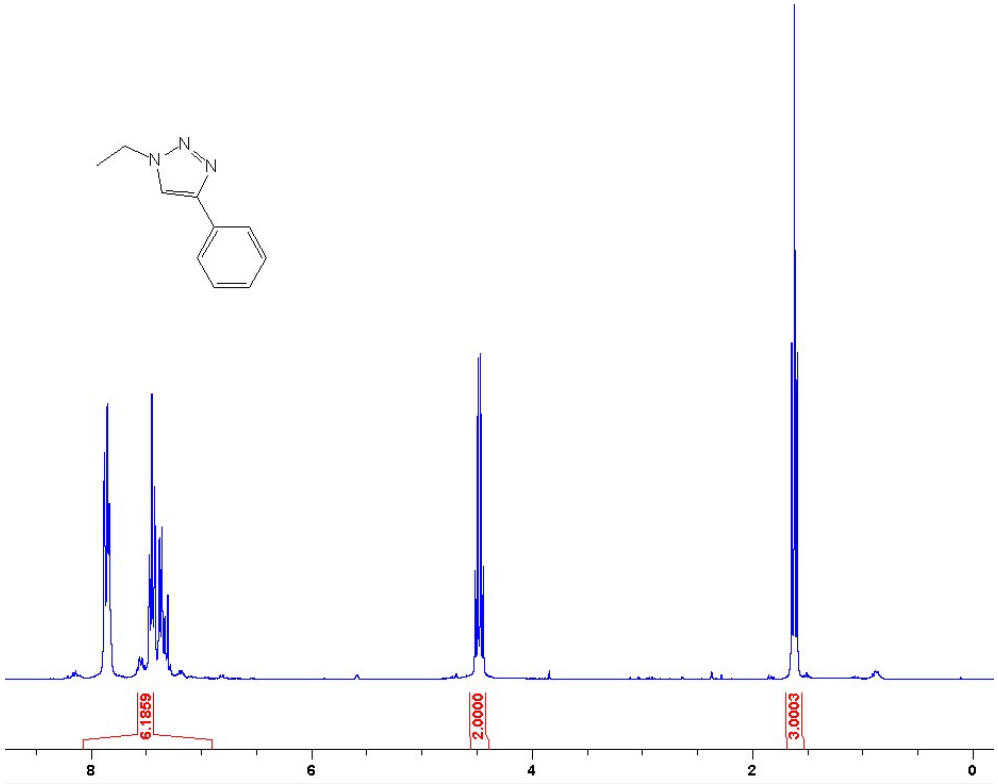


Figure S14. ^{1}H NMR spectrum of triazole product **14** from the catalytic reaction in $CDCl_3$.

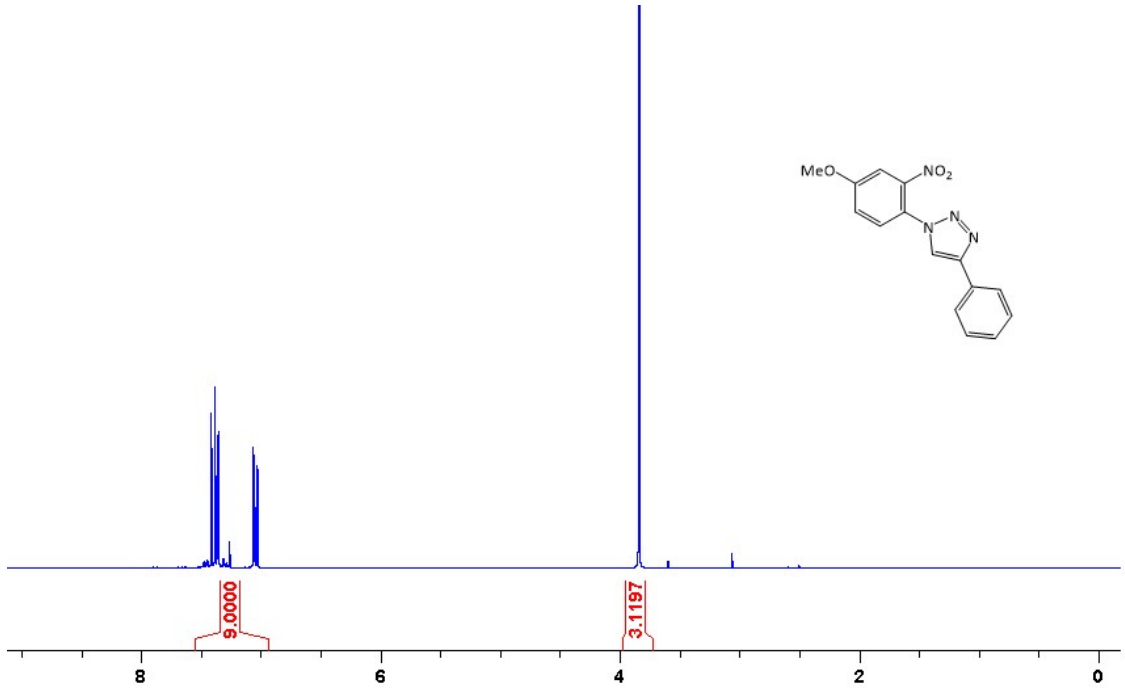


Figure S15. ^{1}H NMR spectrum of triazole product **15** from the catalytic reaction in $CDCl_3$.

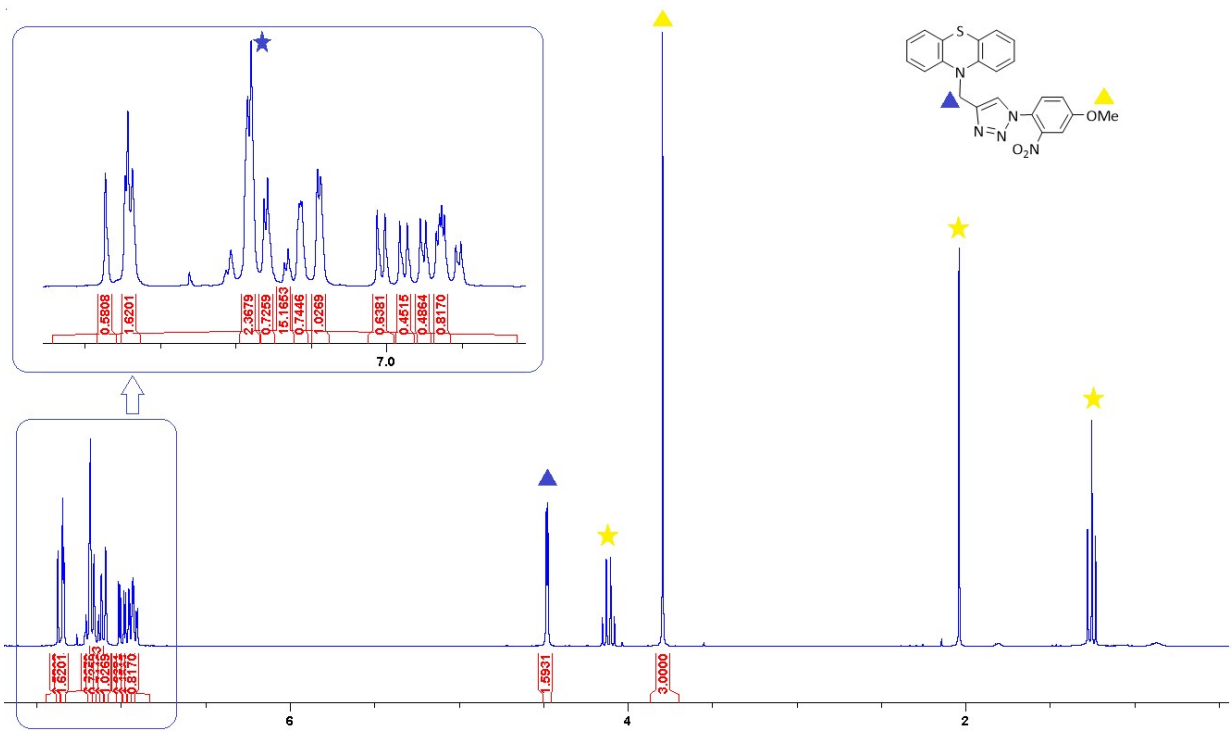


Figure S16. ^{1}H NMR spectrum of triazole product **16** from the catalytic reaction in $CDCl_3$. The ^{1}H NMR of the compound **16** in DMSO is available in literature.[4] Peaks with yellow star are due to ethyl acetate and peak with blue star is protic impurity in $CDCl_3$.

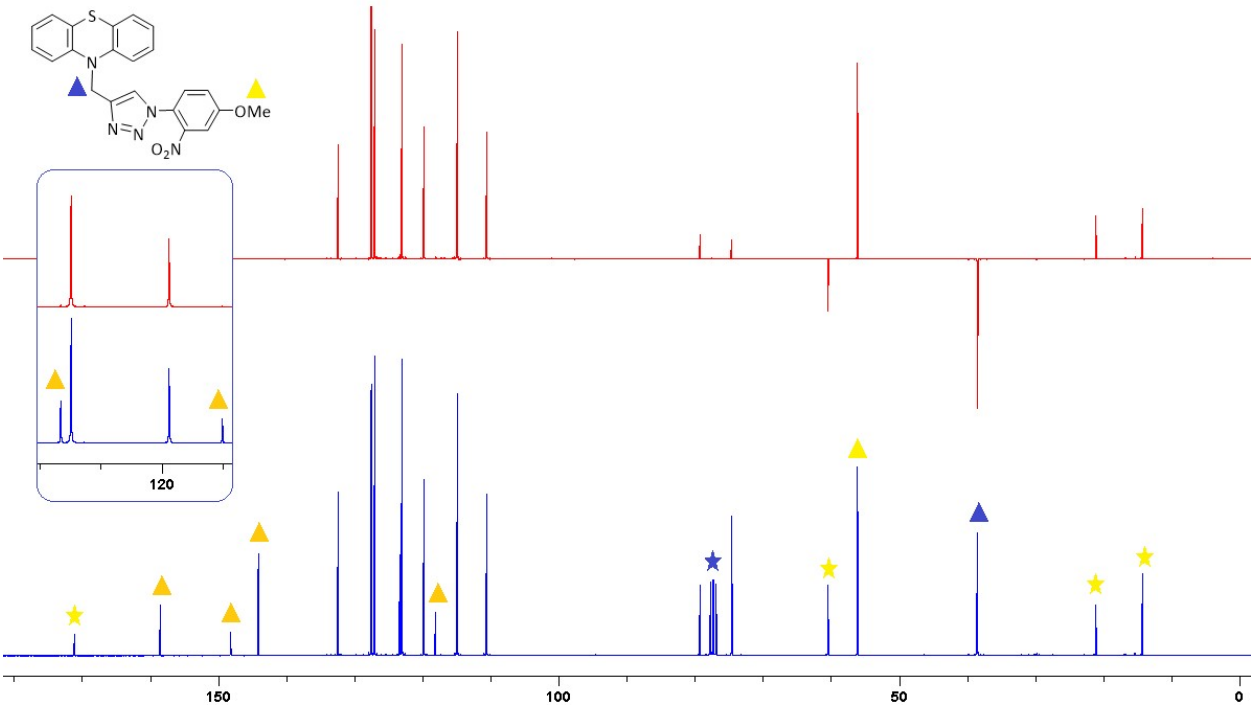


Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum (blue on the bottom) and DEPT 135 spectrum (red on top) of triazole product **16** from the catalytic reaction in $CDCl_3$. The peaks with yellow stars are ethyl acetate and the triplet assigned with blue star is $CDCl_3$.

III. Mechanistic Studies

*Catalysis using amido complex **1***

After the catalytic run using complex **2** in dry DMF, the solvent was removed, the residue dissolved in 0.5 mL of $CDCl_3$ and the ^1H NMR spectrum recorded (Fig. S18).

In another experiment, 4 equiv of water were added to a solution of complex **2** in C_6D_6. The ^1H NMR spectrum is compared with that of **2** in Fig. S19.

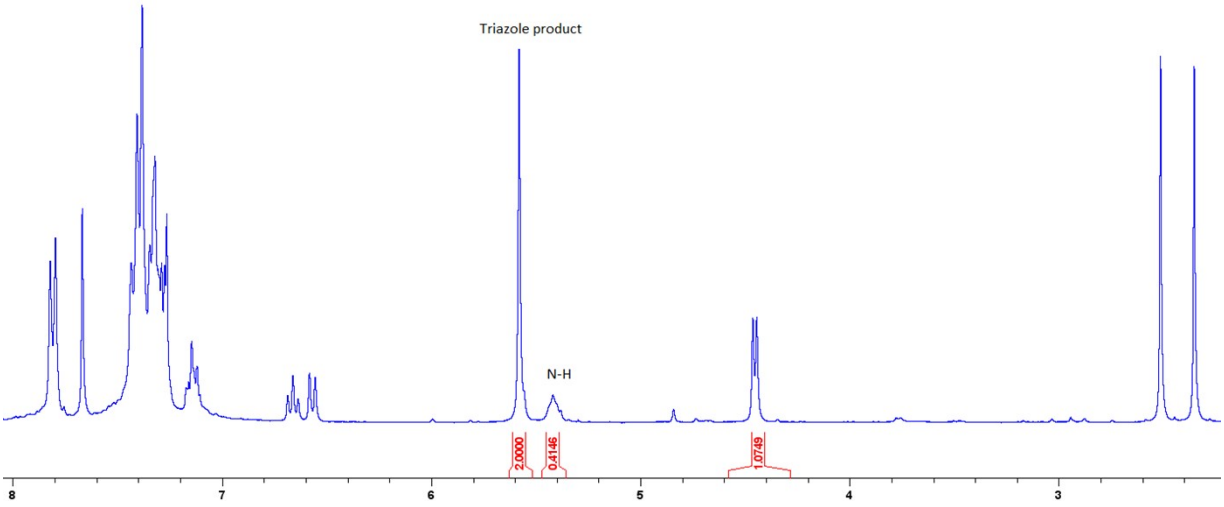


Figure S18. ^1H NMR spectrum (300 MZ, D_2O) of CuAAC reaction using complex **2** resulting in 7.5% yield of the triazole product and formation of protonated amido-SNS ligand.

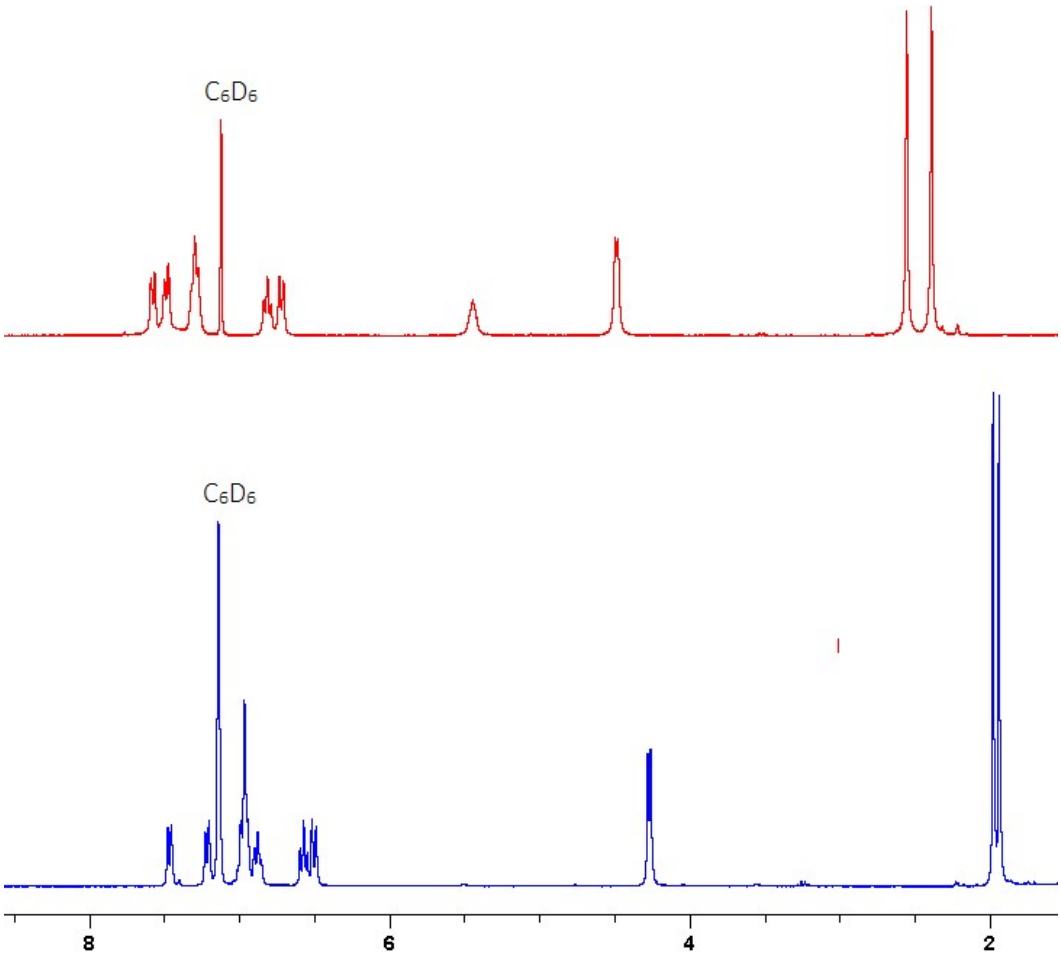


Figure S19. ^{1}H NMR spectrum of the Complex **2** before (bottom) and after (top) adding water.

*Catalysis using thiolate complex **2***

Using the above catalysis protocol, one reaction on a higher scale (23 mmol benzyl chloride, 23 mmol sodium azide and 21.9 mmol of phenylacetylene) with 1 mol% of complex **1** was conducted. After extraction of the product, the insoluble used catalyst was dried and characterized by ^{1}H NMR (Fig. S20), UV/Vis (Fig. S21), ESI-MS (Fig. S22), and EPR spectroscopy (Fig. S23). In another experiment, the used catalyst was filtered off, dried and then reused in the same protocol to give the triazole product in 90% yield.

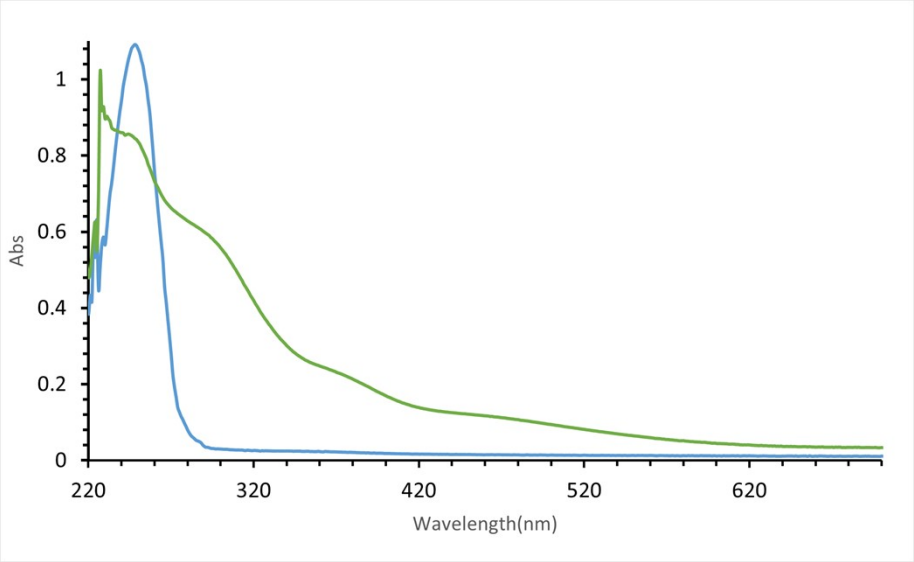


Figure S20. UV-Vis spectrum comparison of the initial catalyst **1** (green spectra) and the resting state catalyst (blue spectra).

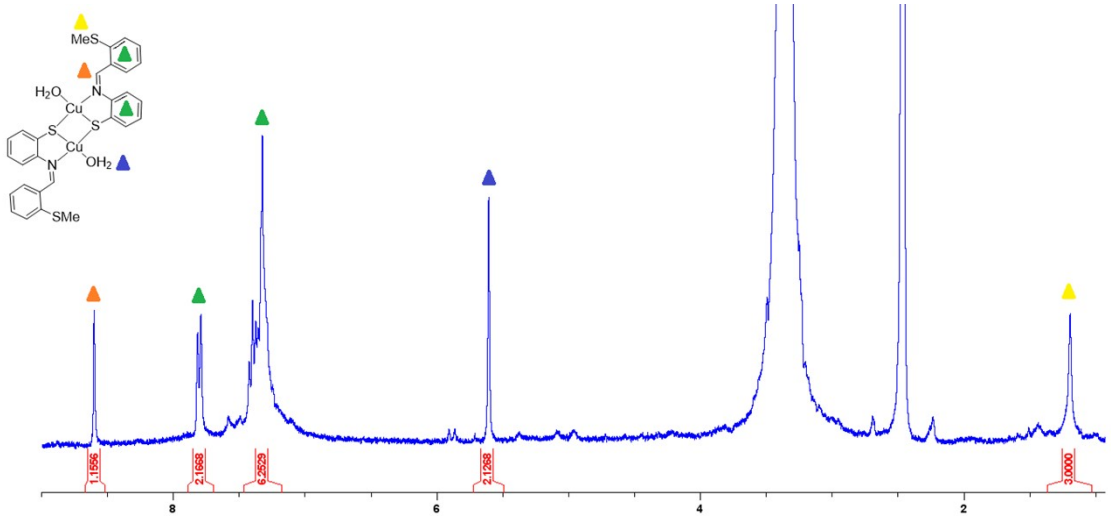


Figure 21. ^{1}H NMR spectrum of the used catalyst from **1**-catalysed CuAAC. The singlet peak at δ 8.59 is due to the ligand imine hydrogen which shows that the ligand is still coordinated to a copper(I) center.

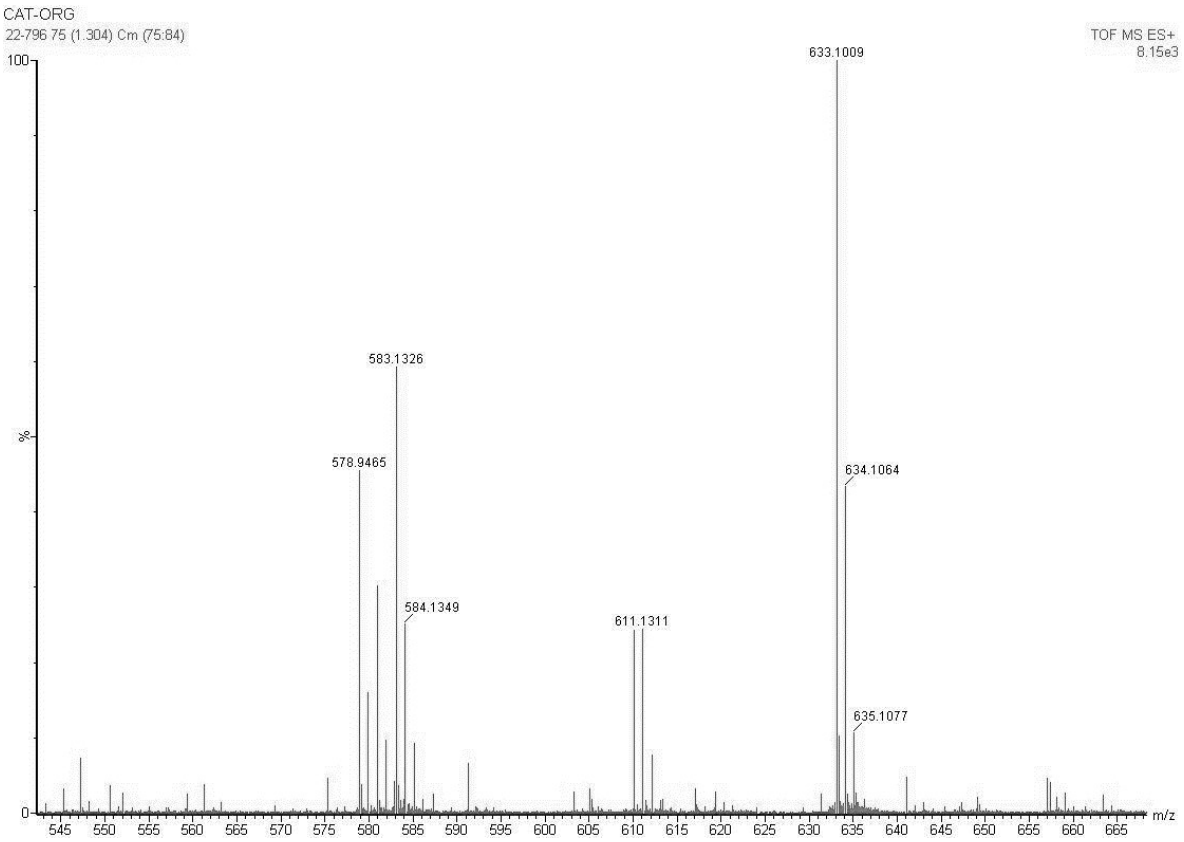


Figure S22. ESI-MS spectrum of recovered catalyst from **1**-catalysed CuAAC showing $[Cu(L^1)_2H]^+$ (Calcd 579.01, found 578.9465) and accumulation of the thiolate ligand (peaks at 583.1 and 633.1).

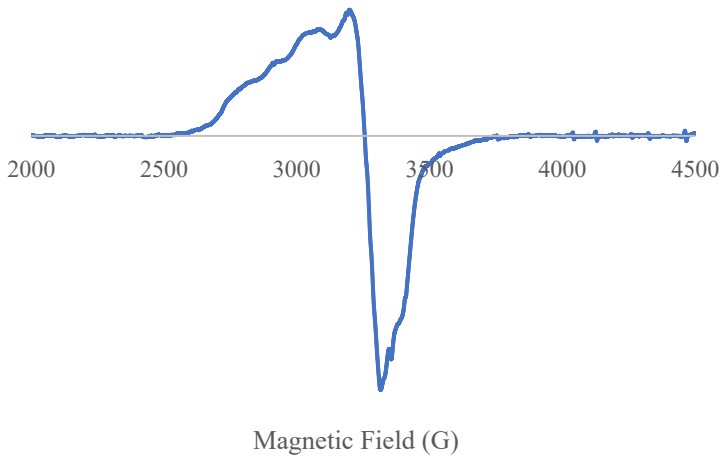


Figure S23. EPR spectrum of the solid resting state catalyst at room temperature [g_x, $g_y=g_\perp$= 2.061, $g_z=g_\parallel$= 2.324, A(Cu) = 101.7G].

IV. Crystallographic Details

Crystallographic data were collected from single crystals mounted on MiTeGen dual thickness MicroMounts using Parabar oil. Data were collected on a Bruker Smart (**Cu1**) or Kappa (**Cu2**) ApexII single crystal diffractometer equipped with a graphite monochromator. The instrument was equipped with a sealed tube Mo Kα source ($\lambda =$ 0.71073 Å), an ApexII CCD detector and a dry compressed air-cooling system. The samples were cooled to 203 K. Raw data collection and processing were performed with the Apex3 software package from Bruker.[5] Initial unit cell parameters were determined from 36 data frames from select ω scans. Semi-empirical absorption corrections based on equivalent reflections were applied.[6] Systematic absences in the diffraction data-set and unit-cell parameters were consistent with the assigned space group. The initial structural solutions were determined using ShelxT direct methods[7] , and refined with full-matrix least-squares procedures based on F^2 using ShelXL or ShelXle.[8] Hydrogen atoms were placed geometrically and refined using a riding model. Deposition Numbers: 2232759-2232760.

Table S1. Data collection and refinement metrics for **Cu-1** and **Cu-2.**

	Cu-1 (K0590)	**Cu-2** (S0726)
empirical formula	$C_{56}H_{48}Cu_4N_4S_8$	$C_{60}H_{64}Cu_4N_4S_8$
formula weight (g · mol^{-1})	1287.62	1351.79
crystal system	Tetragonal	Tetragonal
space group	*P*-42$_1$*c*	*I* 4$_1$/*acd*
a (A)	24.1902(11)	14.4406(12)
b (A)	24.1902(11)	14.4406(12)
c (A)	22.8468(12)	14.0771(12)
α (deg)	90	90
β (deg)	90	90
γ (deg)	90	90
V (A^3)	13369.2(14)	2935.5(5)
Z	8	2
T (K)	203(2)	203(2)
ρ_{calcd} (g · cm^{-3})	1.279	1.529
μ (mm^{-1})	1.540	1.757
$2^{\theta}_{\max}$ (deg)	50.162	61.042
total/unique reflections	8977/3088	12226/4484
Reflections [$I_o \geq 2\sigma(I_o)$]	2317	3550
R_1, wR_2 [$I_o \geq 2\sigma(I_o)$]	0.2109, 0.0724	0.0373, 0.0942
goodness of fit	1.134	1.039
CCDC number	2232759	2232760

Table S2. Bond lengths for complex **1**

Atom1	**Atom2**	**Length Å**
Cu1	S1	2.247(5)

Cu1	N1	2.08(1)
Cu1	S1	2.181(5)
S1	C1	1.77(1)
S1	Cu1	2.181(5)
S2	C13	1.71(2)
S2	C14A	1.83(6)
N1	C6	1.41(2)
N1	C7	1.30(2)
C1	C2	1.34(3)
C1	C6	1.45(2)
C2	H2	0.94
C2	C3	1.41(3)
C3	H3	0.94
C3	C4	1.38(3)
C4	H4	0.94
C4	C5	1.40(2)
C5	H5	0.94
C5	C6	1.40(2)
C7	H7	0.94
C7	C8	1.46(2)
C8	C9	1.40(3)
C8	C13	1.44(2)
C9	H9	0.94
C9	C10	1.37(3)
C10	H10	0.94
C10	C11	1.43(3)
C11	H11	0.94
C11	C12	1.32(3)
C12	H12	0.94
C12	C13	1.41(3)
C14A	H14A	1
C14A	H14B	0.98
C14A	H14C	1
Cu1	S1	2.247(5)
Cu1	N1	2.08(1)
Cu1	S1	2.181(5)
S1	C1	1.77(1)
S2	C13	1.71(2)
S2	C14A	1.83(6)
N1	C6	1.41(2)
N1	C7	1.30(2)
C1	C2	1.34(3)
C1	C6	1.45(2)

C2	H2	0.94
C2	C3	1.41(3)
C3	H3	0.94
C3	C4	1.38(3)
C4	H4	0.94
C4	C5	1.40(2)
C5	H5	0.94
C5	C6	1.40(2)
C7	H7	0.94
C7	C8	1.46(2)
C8	C9	1.40(3)
C8	C13	1.44(2)
C9	H9	0.94
C9	C10	1.37(3)
C10	H10	0.94
C10	C11	1.43(3)
C11	H11	0.94
C11	C12	1.32(3)
C12	H12	0.94
C12	C13	1.41(3)
C14A	H14A	1
C14A	H14B	0.98
C14A	H14C	1
Cu1	S1	2.247(5)
Cu1	N1	2.08(1)
S1	C1	1.77(1)
S1	Cu1	2.181(5)
S2	C13	1.71(2)
S2	C14A	1.83(6)
N1	C6	1.41(2)
N1	C7	1.30(2)
C1	C2	1.34(3)
C1	C6	1.45(2)
C2	H2	0.94
C2	C3	1.41(3)
C3	H3	0.94
C3	C4	1.38(3)
C4	H4	0.94
C4	C5	1.40(2)
C5	H5	0.94
C5	C6	1.40(2)
C7	H7	0.94
C7	C8	1.46(2)

C8	C9	1.40(3)
C8	C13	1.44(2)
C9	H9	0.94
C9	C10	1.37(3)
C10	H10	0.94
C10	C11	1.43(3)
C11	H11	0.94
C11	C12	1.32(3)
C12	H12	0.94
C12	C13	1.41(3)
C14A	H14A	1
C14A	H14B	0.98
C14A	H14C	1
Cu1	S1	2.247(5)
Cu1	N1	2.08(1)
S1	C1	1.77(1)
S2	C13	1.71(2)
S2	C14A	1.83(6)
N1	C6	1.41(2)
N1	C7	1.30(2)
C1	C2	1.34(3)
C1	C6	1.45(2)
C2	H2	0.94
C2	C3	1.41(3)
C3	H3	0.94
C3	C4	1.38(3)
C4	H4	0.94
C4	C5	1.40(2)
C5	H5	0.94
C5	C6	1.40(2)
C7	H7	0.94
C7	C8	1.46(2)
C8	C9	1.40(3)
C8	C13	1.44(2)
C9	H9	0.94
C9	C10	1.37(3)
C10	H10	0.94
C10	C11	1.43(3)
C11	H11	0.94
C11	C12	1.32(3)
C12	H12	0.94
C12	C13	1.41(3)
C14A	H14A	1

C14A	H14B	0.98
C14A	H14C	1

Table S3. All angles for complex **1**

Atom1	**Atom2**	**Atom3**	**Angle**
S1	Cu1	N1	88.3(3)
S1	Cu1	S1	140.1(2)
N1	Cu1	S1	128.9(4)
Cu1	S1	C1	96.3(5)
Cu1	S1	Cu1	82.6(2)
C1	S1	Cu1	104.3(5)
C13	S2	C14A	132(3)
Cu1	N1	C6	112.1(9)
Cu1	N1	C7	126(1)
C6	N1	C7	115(1)
S1	C1	C2	122(1)
S1	C1	C6	119(1)
C2	C1	C6	119(1)
C1	C2	H2	119
C1	C2	C3	122(2)
H2	C2	C3	119
C2	C3	H3	119
C2	C3	C4	121(2)
H3	C3	C4	119
C3	C4	H4	122
C3	C4	C5	117(2)
H4	C4	C5	122
C4	C5	H5	118
C4	C5	C6	123(1)
H5	C5	C6	118
N1	C6	C1	119(1)
N1	C6	C5	123(1)
C1	C6	C5	117(1)
N1	C7	H7	118
N1	C7	C8	125(1)
H7	C7	C8	118
C7	C8	C9	122(1)
C7	C8	C13	118(1)
C9	C8	C13	119(2)
C8	C9	H9	119
C8	C9	C10	122(2)

H9	C9	C10	119
C9	C10	H10	121
C9	C10	C11	117(2)
H10	C10	C11	122
C10	C11	H11	119
C10	C11	C12	122(2)
H11	C11	C12	119
C11	C12	H12	119
C11	C12	C13	122(2)
H12	C12	C13	119
S2	C13	C8	121(1)
S2	C13	C12	123(1)
C8	C13	C12	117(2)
S2	C14A	H14A	110
S2	C14A	H14B	110
S2	C14A	H14C	110
H14A	C14A	H14B	109
H14A	C14A	H14C	110
H14B	C14A	H14C	109
S1	Cu1	N1	88.3(3)
S1	Cu1	S1	140.1(2)
N1	Cu1	S1	128.9(4)
Cu1	S1	Cu1	82.6(2)
Cu1	S1	C1	104.3(5)
Cu1	S1	C1	96.3(5)
C13	S2	C14A	132(3)
Cu1	N1	C6	112.1(9)
Cu1	N1	C7	126(1)
C6	N1	C7	115(1)
S1	C1	C2	122(1)
S1	C1	C6	119(1)
C2	C1	C6	119(1)
C1	C2	H2	119
C1	C2	C3	122(2)
H2	C2	C3	119
C2	C3	H3	119
C2	C3	C4	121(2)
H3	C3	C4	119
C3	C4	H4	122
C3	C4	C5	117(2)
H4	C4	C5	122
C4	C5	H5	118
C4	C5	C6	123(1)

H5	C5	C6	118
N1	C6	C1	119(1)
N1	C6	C5	123(1)
C1	C6	C5	117(1)
N1	C7	H7	118
N1	C7	C8	125(1)
H7	C7	C8	118
C7	C8	C9	122(1)
C7	C8	C13	118(1)
C9	C8	C13	119(2)
C8	C9	H9	119
C8	C9	C10	122(2)
H9	C9	C10	119
C9	C10	H10	121
C9	C10	C11	117(2)
H10	C10	C11	122
C10	C11	H11	119
C10	C11	C12	122(2)
H11	C11	C12	119
C11	C12	H12	119
C11	C12	C13	122(2)
H12	C12	C13	119
S2	C13	C8	121(1)
S2	C13	C12	123(1)
C8	C13	C12	117(2)
S2	C14A	H14A	110
S2	C14A	H14B	110
S2	C14A	H14C	110
H14A	C14A	H14B	109
H14A	C14A	H14C	110
H14B	C14A	H14C	109
S1	Cu1	S1	140.1(2)
S1	Cu1	N1	128.9(4)
S1	Cu1	N1	88.3(3)
Cu1	S1	C1	96.3(5)
Cu1	S1	Cu1	82.6(2)
C1	S1	Cu1	104.3(5)
C13	S2	C14A	132(3)
Cu1	N1	C6	112.1(9)
Cu1	N1	C7	126(1)
C6	N1	C7	115(1)
S1	C1	C2	122(1)
S1	C1	C6	119(1)

C2	C1	C6	119(1)
C1	C2	H2	119
C1	C2	C3	122(2)
H2	C2	C3	119
C2	C3	H3	119
C2	C3	C4	121(2)
H3	C3	C4	119
C3	C4	H4	122
C3	C4	C5	117(2)
H4	C4	C5	122
C4	C5	H5	118
C4	C5	C6	123(1)
H5	C5	C6	118
N1	C6	C1	119(1)
N1	C6	C5	123(1)
C1	C6	C5	117(1)
N1	C7	H7	118
N1	C7	C8	125(1)
H7	C7	C8	118
C7	C8	C9	122(1)
C7	C8	C13	118(1)
C9	C8	C13	119(2)
C8	C9	H9	119
C8	C9	C10	122(2)
H9	C9	C10	119
C9	C10	H10	121
C9	C10	C11	117(2)
H10	C10	C11	122
C10	C11	H11	119
C10	C11	C12	122(2)
H11	C11	C12	119
C11	C12	H12	119
C11	C12	C13	122(2)
H12	C12	C13	119
S2	C13	C8	121(1)
S2	C13	C12	123(1)
C8	C13	C12	117(2)
S2	C14A	H14A	110
S2	C14A	H14B	110
S2	C14A	H14C	110
H14A	C14A	H14B	109
H14A	C14A	H14C	110
H14B	C14A	H14C	109

S1	Cu1	S1	140.1(2)
S1	Cu1	N1	128.9(4)
S1	Cu1	N1	88.3(3)
Cu1	S1	Cu1	82.6(2)
Cu1	S1	C1	104.3(5)
Cu1	S1	C1	96.3(5)
C13	S2	C14A	132(3)
Cu1	N1	C6	112.1(9)
Cu1	N1	C7	126(1)
C6	N1	C7	115(1)
S1	C1	C2	122(1)
S1	C1	C6	119(1)
C2	C1	C6	119(1)
C1	C2	H2	119
C1	C2	C3	122(2)
H2	C2	C3	119
C2	C3	H3	119
C2	C3	C4	121(2)
H3	C3	C4	119
C3	C4	H4	122
C3	C4	C5	117(2)
H4	C4	C5	122
C4	C5	H5	118
C4	C5	C6	123(1)
H5	C5	C6	118
N1	C6	C1	119(1)
N1	C6	C5	123(1)
C1	C6	C5	117(1)
N1	C7	H7	118
N1	C7	C8	125(1)
H7	C7	C8	118
C7	C8	C9	122(1)
C7	C8	C13	118(1)
C9	C8	C13	119(2)
C8	C9	H9	119
C8	C9	C10	122(2)
H9	C9	C10	119
C9	C10	H10	121
C9	C10	C11	117(2)
H10	C10	C11	122
C10	C11	H11	119
C10	C11	C12	122(2)
H11	C11	C12	119

C11	C12	H12	119
C11	C12	C13	122(2)
H12	C12	C13	119
S2	C13	C8	121(1)
S2	C13	C12	123(1)
C8	C13	C12	117(2)
S2	C14A	H14A	110
S2	C14A	H14B	110
S2	C14A	H14C	110
H14A	C14A	H14B	109
H14A	C14A	H14C	110
H14B	C14A	H14C	109

Table S4. Bond lengths for complex **2**

Atom1	**Atom2**	**Length**
Cu1	S1	2.535(1)
Cu1	N1	1.934(3)
Cu1	Cu1	2.5666(6)
Cu1	Cu1	2.5666(6)
Cu1	N1	1.953(3)
S1	C1	1.785(5)
S1	C2	1.763(4)
S2	C14	1.753(6)
S2	C15	1.808(6)
N1	C7	1.417(5)
N1	C8	1.474(5)
N1	Cu1	1.953(3)
C1	H1A	0.97
C1	H1B	0.97
C1	H1C	0.97
C2	C3	1.391(7)
C2	C7	1.421(6)
C3	H3	0.941
C3	C4	1.380(9)
C4	H4	0.94
C4	C5	1.36(1)
C5	H5	0.94
C5	C6	1.387(7)
C6	H6	0.941
C6	C7	1.393(6)
C8	H8A	0.98

C8	H8AB	0.98
C8	C9	1.522(6)
C9	C10	1.371(6)
C9	C14	1.413(6)
C10	H10	0.939
C10	C11	1.402(8)
C11	H11	0.94
C11	C12	1.37(1)
C12	H12	0.94
C12	C13	1.365(9)
C13	H13	0.94
C13	C14	1.400(8)
C15	H15A	0.97
C15	H15B	0.971
C15	H15C	0.97
Cu1	S1	2.535(1)
Cu1	N1	1.934(3)
Cu1	Cu1	2.5666(6)
S1	C1	1.785(5)
S1	C2	1.763(4)
S2	C14	1.753(6)
S2	C15	1.808(6)
N1	C7	1.417(5)
N1	C8	1.474(5)
N1	Cu1	1.953(3)
C1	H1A	0.97
C1	H1B	0.97
C1	H1C	0.97
C2	C3	1.391(7)
C2	C7	1.421(6)
C3	H3	0.941
C3	C4	1.380(9)
C4	H4	0.94
C4	C5	1.36(1)
C5	H5	0.94
C5	C6	1.387(7)
C6	H6	0.941
C6	C7	1.393(6)
C8	H8A	0.98
C8	H8AB	0.98
C8	C9	1.522(6)
C9	C10	1.371(6)
C9	C14	1.413(6)

C10	H10	0.939
C10	C11	1.402(8)
C11	H11	0.94
C11	C12	1.37(1)
C12	H12	0.94
C12	C13	1.365(9)
C13	H13	0.94
C13	C14	1.400(8)
C15	H15A	0.97
C15	H15B	0.971
C15	H15C	0.97
Cu1	S1	2.535(1)
Cu1	N1	1.934(3)
Cu1	Cu1	2.5666(6)
Cu1	N1	1.953(3)
S1	C1	1.785(5)
S1	C2	1.763(4)
S2	C14	1.753(6)
S2	C15	1.808(6)
N1	C7	1.417(5)
N1	C8	1.474(5)
C1	H1A	0.97
C1	H1B	0.97
C1	H1C	0.97
C2	C3	1.391(7)
C2	C7	1.421(6)
C3	H3	0.941
C3	C4	1.380(9)
C4	H4	0.94
C4	C5	1.36(1)
C5	H5	0.94
C5	C6	1.387(7)
C6	H6	0.941
C6	C7	1.393(6)
C8	H8A	0.98
C8	H8AB	0.98
C8	C9	1.522(6)
C9	C10	1.371(6)
C9	C14	1.413(6)
C10	H10	0.939
C10	C11	1.402(8)
C11	H11	0.94
C11	C12	1.37(1)

C12	H12	0.94
C12	C13	1.365(9)
C13	H13	0.94
C13	C14	1.400(8)
C15	H15A	0.97
C15	H15B	0.971
C15	H15C	0.97
Cu1	S1	2.535(1)
Cu1	N1	1.934(3)
S1	C1	1.785(5)
S1	C2	1.763(4)
S2	C14	1.753(6)
S2	C15	1.808(6)
N1	C7	1.417(5)
N1	C8	1.474(5)
C1	H1A	0.97
C1	H1B	0.97
C1	H1C	0.97
C2	C3	1.391(7)
C2	C7	1.421(6)
C3	H3	0.941
C3	C4	1.380(9)
C4	H4	0.94
C4	C5	1.36(1)
C5	H5	0.94
C5	C6	1.387(7)
C6	H6	0.941
C6	C7	1.393(6)
C8	H8A	0.98
C8	H8AB	0.98
C8	C9	1.522(6)
C9	C10	1.371(6)
C9	C14	1.413(6)
C10	H10	0.939
C10	C11	1.402(8)
C11	H11	0.94
C11	C12	1.37(1)
C12	H12	0.94
C12	C13	1.365(9)
C13	H13	0.94
C13	C14	1.400(8)
C15	H15A	0.97
C15	H15B	0.971

C15	H15C	0.97

Table S5. All angles for complex **2**

Atom1	Atom2	Atom3	Angle
S1	Cu1	N1	79.58(9)
S1	Cu1	Cu1	73.87(3)
S1	Cu1	Cu1	130.89(3)
S1	Cu1	N1	110.71(9)
N1	Cu1	Cu1	49.00(9)
N1	Cu1	Cu1	122.71(9)
N1	Cu1	N1	169.3(1)
Cu1	Cu1	Cu1	89.28(2)
Cu1	Cu1	N1	129.43(9)
Cu1	Cu1	N1	48.35(9)
Cu1	S1	C1	157.1(2)
Cu1	S1	C2	95.3(1)
C1	S1	C2	103.9(3)
C14	S2	C15	103.4(3)
Cu1	N1	C7	122.1(2)
Cu1	N1	C8	112.9(2)
Cu1	N1	Cu1	82.7(1)
C7	N1	C8	115.0(3)
C7	N1	Cu1	107.4(2)
C8	N1	Cu1	111.5(2)
S1	C1	H1A	109.5
S1	C1	H1B	109.5
S1	C1	H1C	109.4
H1A	C1	H1B	109.5
H1A	C1	H1C	109.5
H1B	C1	H1C	109.5
S1	C2	C3	123.7(4)
S1	C2	C7	116.3(3)
C3	C2	C7	120.0(4)
C2	C3	H3	120
C2	C3	C4	120.1(5)
H3	C3	C4	119.9
C3	C4	H4	119.6
C3	C4	C5	120.7(6)
H4	C4	C5	119.7

C4	C5	H5	119.9
C4	C5	C6	120.2(6)
H5	C5	C6	120
C5	C6	H6	119.4
C5	C6	C7	121.2(5)
H6	C6	C7	119.4
N1	C7	C2	118.4(4)
N1	C7	C6	123.9(4)
C2	C7	C6	117.7(4)
N1	C8	H8A	108.3
N1	C8	H8AB	108.3
N1	C8	C9	115.8(3)
H8A	C8	H8AB	107.4
H8A	C8	C9	108.4
H8AB	C8	C9	108.4
C8	C9	C10	122.3(4)
C8	C9	C14	118.4(4)
C10	C9	C14	119.2(4)
C9	C10	H10	119.5
C9	C10	C11	121.0(5)
H10	C10	C11	119.5
C10	C11	H11	120.7
C10	C11	C12	118.7(6)
H11	C11	C12	120.6
C11	C12	H12	118.8
C11	C12	C13	122.3(6)
H12	C12	C13	118.9
C12	C13	H13	120.3
C12	C13	C14	119.3(6)
H13	C13	C14	120.4
S2	C14	C9	118.0(4)
S2	C14	C13	122.5(4)
C9	C14	C13	119.5(5)
S2	C15	H15A	109.5
S2	C15	H15B	109.5
S2	C15	H15C	109.5
H15A	C15	H15B	109.4
H15A	C15	H15C	109.5
H15B	C15	H15C	109.4
Cu1	Cu1	N1	48.35(9)
Cu1	Cu1	S1	130.89(3)
Cu1	Cu1	N1	122.71(9)
Cu1	Cu1	Cu1	89.28(2)

N1	Cu1	S1	110.71(9)
N1	Cu1	N1	169.3(1)
N1	Cu1	Cu1	129.43(9)
S1	Cu1	N1	79.58(9)
S1	Cu1	Cu1	73.87(3)
N1	Cu1	Cu1	49.00(9)
Cu1	S1	C1	157.1(2)
Cu1	S1	C2	95.3(1)
C1	S1	C2	103.9(3)
C14	S2	C15	103.4(3)
Cu1	N1	C7	122.1(2)
Cu1	N1	C8	112.9(2)
Cu1	N1	Cu1	82.7(1)
C7	N1	C8	115.0(3)
C7	N1	Cu1	107.4(2)
C8	N1	Cu1	111.5(2)
S1	C1	H1A	109.5
S1	C1	H1B	109.5
S1	C1	H1C	109.4
H1A	C1	H1B	109.5
H1A	C1	H1C	109.5
H1B	C1	H1C	109.5
S1	C2	C3	123.7(4)
S1	C2	C7	116.3(3)
C3	C2	C7	120.0(4)
C2	C3	H3	120
C2	C3	C4	120.1(5)
H3	C3	C4	119.9
C3	C4	H4	119.6
C3	C4	C5	120.7(6)
H4	C4	C5	119.7
C4	C5	H5	119.9
C4	C5	C6	120.2(6)
H5	C5	C6	120
C5	C6	H6	119.4
C5	C6	C7	121.2(5)
H6	C6	C7	119.4
N1	C7	C2	118.4(4)
N1	C7	C6	123.9(4)
C2	C7	C6	117.7(4)
N1	C8	H8A	108.3
N1	C8	H8AB	108.3
N1	C8	C9	115.8(3)

H8A	C8	H8AB	107.4
H8A	C8	C9	108.4
H8AB	C8	C9	108.4
C8	C9	C10	122.3(4)
C8	C9	C14	118.4(4)
C10	C9	C14	119.2(4)
C9	C10	H10	119.5
C9	C10	C11	121.0(5)
H10	C10	C11	119.5
C10	C11	H11	120.7
C10	C11	C12	118.7(6)
H11	C11	C12	120.6
C11	C12	H12	118.8
C11	C12	C13	122.3(6)
H12	C12	C13	118.9
C12	C13	H13	120.3
C12	C13	C14	119.3(6)
H13	C13	C14	120.4
S2	C14	C9	118.0(4)
S2	C14	C13	122.5(4)
C9	C14	C13	119.5(5)
S2	C15	H15A	109.5
S2	C15	H15B	109.5
S2	C15	H15C	109.5
H15A	C15	H15B	109.4
H15A	C15	H15C	109.5
H15B	C15	H15C	109.4
Cu1	Cu1	S1	73.87(3)
Cu1	Cu1	N1	49.00(9)
Cu1	Cu1	Cu1	89.28(2)
Cu1	Cu1	N1	129.43(9)
S1	Cu1	N1	79.58(9)
S1	Cu1	Cu1	130.89(3)
S1	Cu1	N1	110.71(9)
N1	Cu1	Cu1	122.71(9)
N1	Cu1	N1	169.3(1)
Cu1	Cu1	N1	48.35(9)
Cu1	S1	C1	157.1(2)
Cu1	S1	C2	95.3(1)
C1	S1	C2	103.9(3)
C14	S2	C15	103.4(3)
Cu1	N1	Cu1	82.7(1)
Cu1	N1	C7	107.4(2)

Cu1	N1	C8	111.5(2)
Cu1	N1	C7	122.1(2)
Cu1	N1	C8	112.9(2)
C7	N1	C8	115.0(3)
S1	C1	H1A	109.5
S1	C1	H1B	109.5
S1	C1	H1C	109.4
H1A	C1	H1B	109.5
H1A	C1	H1C	109.5
H1B	C1	H1C	109.5
S1	C2	C3	123.7(4)
S1	C2	C7	116.3(3)
C3	C2	C7	120.0(4)
C2	C3	H3	120
C2	C3	C4	120.1(5)
H3	C3	C4	119.9
C3	C4	H4	119.6
C3	C4	C5	120.7(6)
H4	C4	C5	119.7
C4	C5	H5	119.9
C4	C5	C6	120.2(6)
H5	C5	C6	120
C5	C6	H6	119.4
C5	C6	C7	121.2(5)
H6	C6	C7	119.4
N1	C7	C2	118.4(4)
N1	C7	C6	123.9(4)
C2	C7	C6	117.7(4)
N1	C8	H8A	108.3
N1	C8	H8AB	108.3
N1	C8	C9	115.8(3)
H8A	C8	H8AB	107.4
H8A	C8	C9	108.4
H8AB	C8	C9	108.4
C8	C9	C10	122.3(4)
C8	C9	C14	118.4(4)
C10	C9	C14	119.2(4)
C9	C10	H10	119.5
C9	C10	C11	121.0(5)
H10	C10	C11	119.5
C10	C11	H11	120.7
C10	C11	C12	118.7(6)
H11	C11	C12	120.6

C11	C12	H12	118.8
C11	C12	C13	122.3(6)
H12	C12	C13	118.9
C12	C13	H13	120.3
C12	C13	C14	119.3(6)
H13	C13	C14	120.4
S2	C14	C9	118.0(4)
S2	C14	C13	122.5(4)
C9	C14	C13	119.5(5)
S2	C15	H15A	109.5
S2	C15	H15B	109.5
S2	C15	H15C	109.5
H15A	C15	H15B	109.4
H15A	C15	H15C	109.5
H15B	C15	H15C	109.4
Cu1	Cu1	N1	48.35(9)
Cu1	Cu1	Cu1	89.28(2)
Cu1	Cu1	S1	130.89(3)
Cu1	Cu1	N1	122.71(9)
N1	Cu1	Cu1	129.43(9)
N1	Cu1	S1	110.71(9)
N1	Cu1	N1	169.3(1)
Cu1	Cu1	S1	73.87(3)
Cu1	Cu1	N1	49.00(9)
S1	Cu1	N1	79.58(9)
Cu1	S1	C1	157.1(2)
Cu1	S1	C2	95.3(1)
C1	S1	C2	103.9(3)
C14	S2	C15	103.4(3)
Cu1	N1	Cu1	82.7(1)
Cu1	N1	C7	107.4(2)
Cu1	N1	C8	111.5(2)
Cu1	N1	C7	122.1(2)
Cu1	N1	C8	112.9(2)
C7	N1	C8	115.0(3)
S1	C1	H1A	109.5
S1	C1	H1B	109.5
S1	C1	H1C	109.4
H1A	C1	H1B	109.5
H1A	C1	H1C	109.5
H1B	C1	H1C	109.5
S1	C2	C3	123.7(4)
S1	C2	C7	116.3(3)

C3	C2	C7	120.0(4)
C2	C3	H3	120
C2	C3	C4	120.1(5)
H3	C3	C4	119.9
C3	C4	H4	119.6
C3	C4	C5	120.7(6)
H4	C4	C5	119.7
C4	C5	H5	119.9
C4	C5	C6	120.2(6)
H5	C5	C6	120
C5	C6	H6	119.4
C5	C6	C7	121.2(5)
H6	C6	C7	119.4
N1	C7	C2	118.4(4)
N1	C7	C6	123.9(4)
C2	C7	C6	117.7(4)
N1	C8	H8A	108.3
N1	C8	H8AB	108.3
N1	C8	C9	115.8(3)
H8A	C8	H8AB	107.4
H8A	C8	C9	108.4
H8AB	C8	C9	108.4
C8	C9	C10	122.3(4)
C8	C9	C14	118.4(4)
C10	C9	C14	119.2(4)
C9	C10	H10	119.5
C9	C10	C11	121.0(5)
H10	C10	C11	119.5
C10	C11	H11	120.7
C10	C11	C12	118.7(6)
H11	C11	C12	120.6
C11	C12	H12	118.8
C11	C12	C13	122.3(6)
H12	C12	C13	118.9
C12	C13	H13	120.3
C12	C13	C14	119.3(6)
H13	C13	C14	120.4
S2	C14	C9	118.0(4)
S2	C14	C13	122.5(4)
C9	C14	C13	119.5(5)
S2	C15	H15A	109.5
S2	C15	H15B	109.5
S2	C15	H15C	109.5

H15A	C15	H15B	109.4
H15A	C15	H15C	109.5
H15B	C15	H15C	109.4

V. Details on DFT analysis

General information

All DFT calculations were performed using Gaussian 16 on Grex server from Westgrid (provided by Compute Canada/Calcul Canada). Geometry optimizations were carried out using the mixed basis set 6-31g** for all light atoms (C, H, O, S, N) and def2TZVP for copper atoms. The M06L functional was exploited in aqueous solvent using the CPCM model. Local minima were assessed by convergence and the absence of imaginary frequencies in the frequency calculation. The mechanism of the first step of the catalytic reaction was inspected by considering the different possible pathways of formation of the copper alkynyl intermediates in order to investigate the potential bifunctional ability of the thiolate ligand in complex **1**. The electronic energy, thermal enthalpy and free Gibbs energy were calculated for each intermediate and the other molecules in the equation regarding each pathways.

Path 1 - Protonation by the S group and formation of copper acetylide monomers (SMe group in trans position):

Complex **1** (Tetramer)			
Cu	-0.88736800	-0.44783400	-1.25121700
S	-0.82256900	1.79049700	-1.83844900
S	-5.52669300	-2.10159300	-4.16835300
N	-3.02090700	-0.20840100	-1.30365200
C	-2.45990100	2.15746300	-1.23937100
C	-2.85838000	3.48256100	-1.04094100
H	-2.12889400	4.27404000	-1.19220200
C	-4.15231900	3.79225900	-0.63336400
H	-4.42818500	4.82848800	-0.45942600
C	-5.07577100	2.77144500	-0.41821900
H	-6.07925700	2.99917800	-0.07087400
C	-4.70612600	1.44963300	-0.64188100
H	-5.41873900	0.64621000	-0.47082900
C	-3.40860200	1.12774800	-1.06461300
C	-3.89173200	-0.97483000	-1.88739100
H	-4.82439800	-0.52624000	-2.25544600
C	-3.74054600	-2.39796500	-2.09951700
C	-2.89194000	-3.14968700	-1.27509300
H	-2.35111600	-2.62806500	-0.48805800
C	-2.77939200	-4.52322100	-1.41238700
H	-2.12710600	-5.08339200	-0.74868900
C	-3.52815800	-5.17141800	-2.39345600
H	-3.45598400	-6.24841400	-2.51446600
C	-4.37877600	-4.45290000	-3.22869100

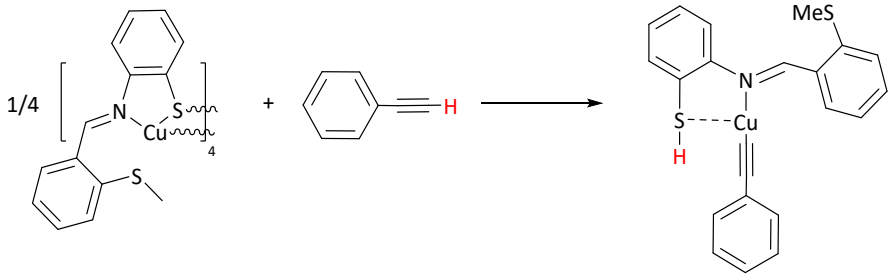
H	-4.94174000	-4.98357800	-3.98769900
C	-4.50062000	-3.06587600	-3.09784100
Cu	0.65916600	-1.75167900	0.40644500
S	0.22149600	-2.37882300	-1.77108400
S	6.21580800	-3.57308000	1.53390000
N	2.71773600	-1.73417700	-0.13156600
C	1.81237100	-1.87847100	-2.39374300
C	2.01603400	-1.81189600	-3.77682800
H	1.18685700	-2.05654900	-4.43560600
C	3.24035600	-1.42238000	-4.30828600
H	3.36580700	-1.36054900	-5.38540600
C	4.28352200	-1.06797600	-3.45456200
H	5.22872900	-0.71399300	-3.85471400
C	4.10597400	-1.15162700	-2.07969400
H	4.91009300	-0.85182900	-1.41227000
C	2.89188200	-1.58925500	-1.52825800
C	3.75999100	-2.10336300	0.55242200
H	4.67475100	-2.35346600	0.00194900
C	3.83692500	-2.25063500	1.98858900
C	2.84699400	-1.71988800	2.82719400
H	2.04537200	-1.14518500	2.36973100
C	2.89986500	-1.86320900	4.20345800
H	2.11905900	-1.43352300	4.82442900
C	3.98008000	-2.53384300	4.77261600
H	4.04451300	-2.65573400	5.85002500
C	4.99720800	-3.04679500	3.97204600
H	5.82714600	-3.55793200	4.44537900
C	4.94737800	-2.91738100	2.58071800
C	7.45978100	-4.14487700	2.70586800
H	8.29274700	-4.49624400	2.09675700
H	7.80779300	-3.33218700	3.34610700
H	7.09315600	-4.97549200	3.31169400
Cu	0.70638000	1.36716700	-0.20058100
S	1.08228500	1.88952800	2.03586700
S	4.49405900	4.77100800	-2.70466500
N	2.82232800	1.61633600	-0.41149300
C	2.81158600	1.47388100	2.01886900
C	3.51574900	1.31678500	3.21636600
H	2.97036300	1.38442200	4.15404300
C	4.88197400	1.05341300	3.21938900
H	5.39992400	0.90832400	4.16319900
C	5.57047600	0.94228400	2.01325500
H	6.63021800	0.70509800	2.00241600
C	4.89262000	1.12839400	0.81349400
H	5.42147600	1.03786900	-0.13236400
C	3.51909000	1.40978100	0.79944300
C	3.43965300	2.29289600	-1.33248400
H	4.40493300	2.75646200	-1.08772900
C	2.96102400	2.49067200	-2.68353000
C	2.08189500	1.56599800	-3.26388400
H	1.76323400	0.71662000	-2.66246800
C	1.66795800	1.68917400	-4.57993500
H	0.99968400	0.94873800	-5.00989200

C	2.13613900	2.75819000	-5.34228300
H	1.82542800	2.86961600	-6.37708000
C	3.00674700	3.69533600	-4.79330500
H	3.34544900	4.52129400	-5.40791500
C	3.43263700	3.57917500	-3.46644200
C	5.04235200	5.77630900	-4.09716700
H	5.78257200	6.46480800	-3.68933100
H	5.51438300	5.16303500	-4.86693000
H	4.22234600	6.35632100	-4.52433900
Cu	-0.38017300	0.13821100	1.81227200
S	-0.37770800	-2.10404800	2.42001400
S	-5.32951300	2.40793700	4.20283400
N	-2.50281300	0.04187400	2.01315600
C	-2.10470400	-2.36637100	2.09487100
C	-2.61225700	-3.67042800	2.07179300
H	-1.92698500	-4.49707200	2.24012300
C	-3.95710700	-3.91659200	1.81966200
H	-4.32192400	-4.93917800	1.78868500
C	-4.81836500	-2.85167800	1.56108200
H	-5.86003600	-3.03151200	1.31318200
C	-4.33589300	-1.55009200	1.60399300
H	-5.00132000	-0.72055000	1.37811200
C	-2.99163800	-1.28205000	1.90544500
C	-3.32866800	0.93177500	2.47830200
H	-4.30875200	0.59069300	2.83233100
C	-3.07988200	2.35002200	2.60643500
C	-2.00387900	2.95939500	1.94707900
H	-1.38952900	2.34317400	1.29450900
C	-1.74815200	4.31527700	2.06230900
H	-0.90880800	4.75606000	1.53216300
C	-2.59819500	5.10007900	2.83824400
H	-2.41937200	6.16651200	2.94098900
C	-3.69395200	4.53307500	3.48357900
H	-4.33925600	5.17142500	4.07525300
C	-3.95472400	3.16317000	3.38196900
C	-6.22650000	3.81665300	4.88078100
H	-7.12414000	3.39790900	5.33599900
H	-6.52102500	4.51650900	4.09654400
H	-5.64933700	4.33052100	5.65160900
C	-6.47405000	-3.35135700	-5.05740600
H	-7.19853200	-2.79989100	-5.65678400
H	-5.84147800	-3.93876900	-5.72542100
H	-7.00951200	-4.00699800	-4.36827300
$E_{electronic}$ (Ha) =	-12129.3573378		
H (Ha)=	-12128.383622		
G (Ha) =	-12128.572745		

Phenyl Acetylene			
C	3.23004200	0.00001300	-0.00001700
H	4.29617700	0.00005200	-0.00005100
C	2.01625200	-0.00004200	0.00002000

C	0.59324200	-0.00002900	0.00001200
C	-0.11975400	1.21186400	0.00000500
C	-0.11980100	-1.21188500	0.00000600
C	-1.50922900	1.20663500	-0.00000300
H	0.42758000	2.14970800	0.00000700
C	-1.50928300	-1.20660100	-0.00000400
H	0.42748100	-2.14975900	0.00000800
C	-2.20792100	0.00002800	-0.00000800
H	-2.04931700	2.14876000	-0.00000700
H	-2.04939500	-2.14871200	-0.00000800
H	-3.29381500	0.00005900	-0.00001600

$E_{electronic}$ (Ha) =	-308.360964774
H (Ha)=	-308.244079
G (Ha) =	-308.281916



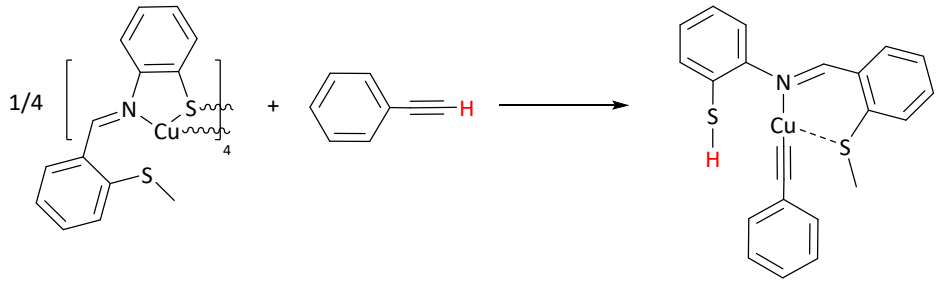
Complex **1** Int **1**

Int 1			
Cu	0.57073900	0.43609800	-0.05560800
S	-0.25517800	2.53320300	1.86497600
S	-4.63974800	-1.60927800	0.75610500
N	-1.33692400	0.79014900	-0.26425900
C	-1.17746400	3.11225100	0.46728100
C	-1.47876100	4.46195700	0.27141200
H	-1.10724300	5.20129700	0.97480300
C	-2.25571800	4.86053500	-0.81117100
H	-2.46785800	5.91541200	-0.95400900
C	-2.75850200	3.91502900	-1.70318000
H	-3.36184900	4.22385900	-2.55042700
C	-2.46970500	2.56954600	-1.51398300
H	-2.82055000	1.82084500	-2.21884400
C	-1.67559400	2.15832000	-0.43886900
C	-2.30434100	-0.07663000	-0.35246300
H	-3.32914900	0.30569100	-0.42029400
C	-2.13981400	-1.51230200	-0.37295900
C	-0.96686800	-2.09843700	-0.87977600
H	-0.17979600	-1.44703800	-1.25682300
C	-0.82340600	-3.47302700	-0.96018300
H	0.08381900	-3.90463900	-1.36916000
C	-1.86928300	-4.29203300	-0.53287600
H	-1.77533700	-5.37217500	-0.59344600
C	-3.04280100	-3.74271900	-0.02964600

H	-3.83361000	-4.40447000	0.30378700
C	-3.19967600	-2.35525900	0.05882100
C	-5.80818400	-2.98018800	0.83789800
H	-6.75708800	-2.53947300	1.14369800
H	-5.51007300	-3.72030600	1.58240800
H	-5.93329900	-3.45079300	-0.13881400
H	0.21226900	3.73895600	2.22511000
C	2.38418100	0.05389400	-0.03001300
C	3.59448700	-0.19818400	-0.01618100
C	4.98783000	-0.48185200	0.00200600
C	5.72849900	-0.55272300	-1.19505600
C	5.66854800	-0.69856500	1.21709900
C	7.09056100	-0.82749000	-1.17395400
H	5.21778500	-0.38824100	-2.13991300
C	7.03073100	-0.97345200	1.23030400
H	5.11134900	-0.64730700	2.14851900
C	7.74947000	-1.03939200	0.03689900
H	7.64199700	-0.87682200	-2.10898800
H	7.53530500	-1.13712100	2.17870000
H	8.81403700	-1.25404900	0.05036700

$E_{electronic}$ (Ha) =	-3340.65165842
H (Ha)=	-3340.292291
G (Ha) =	-3340.379605
ΔG (Path 1)	0.181989 Ha = 28.6 kcal/mol

Path 2 - Protonation by the S group and formation of copper acetylide monomers (SMe group in cis position):



Complex **1** Int **2**

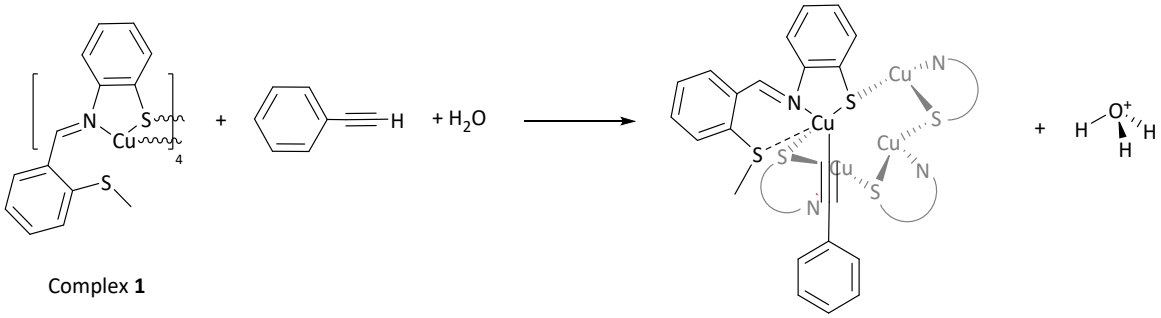
Int 2			
Cu	0.01979600	-0.09605800	0.49088000
S	0.77126900	2.14836200	2.13204000
S	1.79348000	-1.37306900	1.57820900
N	1.71682800	0.90131100	-0.28741300
C	0.91042900	2.99502600	0.57863800
C	0.57166500	4.33898000	0.41277400
H	0.18811100	4.90655200	1.25532900
C	0.72107700	4.94725500	-0.82906300
H	0.43923200	5.98852000	-0.94982700
C	1.21938600	4.22396600	-1.91270600

H	1.32042600	4.69468100	-2.88525000
C	1.56952100	2.89002100	-1.75269700
H	1.91899800	2.30945700	-2.60161100
C	1.42488700	2.26316600	-0.50917700
C	2.69705600	0.34820800	-0.93098800
H	3.29807300	0.95201600	-1.62192300
C	3.07589300	-1.04543100	-0.85334400
C	3.90165400	-1.51043600	-1.89323100
H	4.22184200	-0.79626100	-2.64769400
C	4.28140900	-2.83898300	-1.98879700
H	4.90762200	-3.17228400	-2.80918900
C	3.84636300	-3.73583600	-1.01621200
H	4.12787700	-4.78295100	-1.06989600
C	3.06336200	-3.30035200	0.04931400
H	2.76871300	-4.01704200	0.80629700
C	2.67480200	-1.96307400	0.15560300
C	1.30697100	-2.88900100	2.42606000
H	0.66541500	-2.56590800	3.24589700
H	2.17230400	-3.40939100	2.83880900
H	0.73961400	-3.54542400	1.76434600
C	-1.79578400	-0.33381400	0.15149100
C	-3.00331200	-0.51835600	-0.05531800
H	-0.06585000	3.03430000	2.69371800
C	-4.38936000	-0.72721300	-0.28905200
C	-4.83499300	-1.49773600	-1.38317700
C	-5.36334100	-0.17091700	0.56616800
C	-6.19121200	-1.70033600	-1.60791900
H	-4.09865600	-1.93410900	-2.05274900
C	-6.71778600	-0.37803700	0.33518000
H	-5.03834400	0.42574600	1.41430600
C	-7.14099000	-1.14302500	-0.75176500
H	-6.50981700	-2.29809400	-2.45782100
H	-7.44922700	0.06083000	1.00863900
H	-8.20035300	-1.30327400	-0.92972900
$E_{electronic}$ (Ha) =	-3340.65333949		
H (Ha)=	-3340.294076		
G (Ha) =	-3340.380696		
ΔG (Path 2)	0.177625 Ha = 27.86 kcal/mol		

Path 3 - Protonation by water formation of copper acetylide in tetranuclear complex:

H_2O			
O	0.00000000	0.00000000	0.11970300
H	0.00000000	0.75156000	-0.47881200
H	0.00000000	-0.75156000	-0.47881200
$E_{electronic}$ (Ha) =	-76.4174212		
H (Ha)=	-76.391862		
G (Ha) =	-76.413288		

H_3O^+			
H	0.24252300	-0.88916900	0.23457800
H	-0.89153400	0.23473900	0.23472300
H	0.64940900	0.65432100	0.23457900
O	-0.00005000	0.00001400	-0.08798500
$E_{electronic}$ (Ha) =	-76.81969281		
H (Ha)=	-76.780433		
G (Ha) =	-76.803371		



Complex **1**

Int **3**

Int 3			
Cu	-2.09206000	1.75176300	1.03782800
S	-0.99781300	1.12145900	2.92620900
S	-6.47380100	-0.33783200	-0.90612000
N	-2.64698500	-0.50503100	0.95694200
C	-1.76749200	-0.44457700	3.21066200
C	-1.66066800	-1.03757900	4.47827900
H	-1.06369400	-0.53570300	5.23613400
C	-2.31180600	-2.22720300	4.78062200
H	-2.20916200	-2.66100700	5.77162600
C	-3.06083700	-2.87960300	3.79969400
H	-3.54088100	-3.83034700	4.01349900
C	-3.16258000	-2.32273600	2.53296400
H	-3.71256400	-2.84752300	1.75521000
C	-2.54848600	-1.09710300	2.22005700
C	-3.66863700	-0.74891800	0.19516700
H	-4.53445700	-1.31045400	0.57631300
C	-3.74070200	-0.24116400	-1.15886100
C	-2.55723500	0.08626800	-1.83197200
H	-1.61431400	-0.11147100	-1.32509600
C	-2.57241200	0.61697200	-3.11308900
H	-1.63568600	0.85058900	-3.61291600
C	-3.79464000	0.82475000	-3.74676900
H	-3.83077500	1.23305800	-4.75342700
C	-4.98977600	0.51698300	-3.09781800
H	-5.92766900	0.71194800	-3.60587900

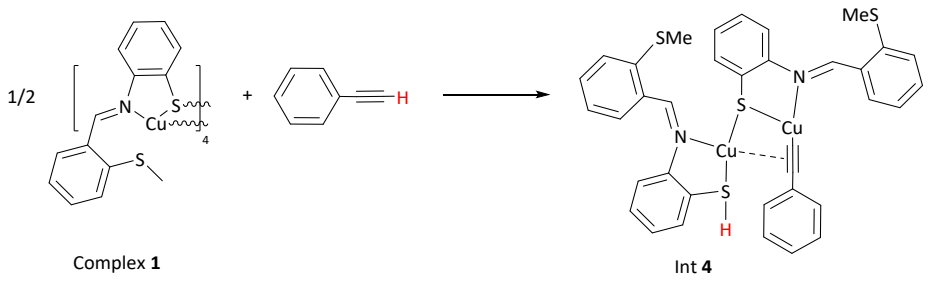
C	-4.98112500	-0.00928000	-1.80402400
Cu	1.12991200	-0.09525800	-1.42528000
S	0.18090400	1.93088900	-1.00606800
S	4.73945900	0.00380300	-5.66716300
N	2.92587400	0.98570600	-1.94010400
C	1.64853200	2.91261700	-1.18019300
C	1.59895200	4.28261700	-0.89822000
H	0.65366300	4.71155500	-0.57671200
C	2.73273000	5.08250900	-0.98860300
H	2.67021000	6.13618700	-0.72864200
C	3.94926900	4.52102600	-1.37573800
H	4.84981300	5.12675700	-1.41494500
C	4.00878600	3.17224800	-1.70444500
H	4.96091800	2.72258200	-1.97496200
C	2.86761200	2.35751400	-1.63374500
C	3.75517300	0.60237000	-2.86363300
H	4.25875200	1.35626700	-3.48443200
C	4.10697000	-0.77964600	-3.11476300
C	3.99154400	-1.72408600	-2.08362900
H	3.58684400	-1.38876900	-1.13119500
C	4.41322300	-3.03258000	-2.25028500
H	4.32553400	-3.74102900	-1.43136400
C	4.95825500	-3.42031800	-3.47421400
H	5.29755100	-4.44131800	-3.62353100
C	5.07521500	-2.50932600	-4.51999000
H	5.49105700	-2.84235200	-5.46405000
C	4.65779000	-1.18377900	-4.35928200
C	5.72343400	-0.83975800	-6.92065600
H	5.88779000	-0.10607500	-7.70996500
H	6.68961300	-1.15319600	-6.52078900
H	5.19269900	-1.69513300	-7.34270900
Cu	0.58930500	0.68260600	1.04624700
S	1.84495300	-1.12922100	2.03728500
S	4.31123100	5.34461800	3.32659300
N	2.64014700	1.76737900	1.60624100
C	3.43133800	-0.53399400	1.49201700
C	4.48207000	-1.43337500	1.27874400
H	4.28692000	-2.49606600	1.40207800
C	5.74230600	-0.99487300	0.88521500
H	6.53082100	-1.71855900	0.69795900
C	5.97322700	0.36716100	0.69925200
H	6.94193200	0.72150500	0.35902100
C	4.95216800	1.27756800	0.94229200
H	5.11764700	2.33786700	0.76821200
C	3.68044400	0.85147400	1.35885700
C	2.97095700	2.89478100	2.14819900
H	4.01546600	3.04280000	2.45439400
C	2.07695600	4.00501200	2.41259300
C	0.71386400	3.93070900	2.09187400
H	0.34730500	3.02743100	1.60733900
C	-0.15488200	4.97969000	2.34177600
H	-1.20593400	4.88749100	2.08081300
C	0.34148700	6.14981400	2.91418900

H	-0.32064200	6.98661200	3.11742900
C	1.69326200	6.26610200	3.22321300
H	2.05166300	7.19285200	3.65536100
C	2.57721000	5.20878800	2.98114900
C	4.46592800	7.00387300	4.01355100
H	5.52442100	7.12384500	4.24520100
H	4.17513200	7.76840600	3.29060600
H	3.88962300	7.11385400	4.93409100
Cu	0.76389400	-1.97005300	0.26863000
S	0.80928900	-2.25711200	-2.06145400
S	-0.33354400	-7.46521700	1.35055900
N	-0.78193600	-3.42636700	0.18980600
C	-0.91108600	-2.72213100	-2.12995900
C	-1.63993700	-2.62100200	-3.31762300
H	-1.16017300	-2.18263800	-4.18896600
C	-2.96217600	-3.05046300	-3.38835300
H	-3.51572700	-2.93612400	-4.31623900
C	-3.57901700	-3.59571100	-2.26442600
H	-4.61913800	-3.90664000	-2.30230700
C	-2.85982500	-3.73111700	-1.08145000
H	-3.33284800	-4.14593100	-0.19404600
C	-1.52859600	-3.30356700	-1.00297700
C	-0.89625300	-4.54452100	0.83910600
H	-1.48288100	-5.35552900	0.38638200
C	-0.28488400	-4.82724100	2.12101400
C	0.00012500	-3.78721100	3.01620900
H	-0.27779900	-2.77609400	2.72965000
C	0.55184400	-4.03898800	4.26280000
H	0.74418600	-3.21652600	4.94559200
C	0.82567900	-5.35381800	4.63356500
H	1.25528600	-5.56980200	5.60762300
C	0.54772000	-6.40878800	3.76792400
H	0.77632900	-7.42106300	4.08095000
C	-0.00928100	-6.16626200	2.50913800
C	-0.08220500	-8.95617100	2.33232800
H	-0.36458000	-9.78639900	1.68475400
H	-0.72294300	-8.96198800	3.21611000
H	0.96310700	-9.07792900	2.62212200
C	-7.73852900	0.40443700	-1.95687300
H	-8.66793700	0.34938600	-1.38882600
H	-7.50457900	1.45483100	-2.15288900
H	-7.86517700	-0.14111200	-2.89426000
C	-3.45459100	2.74381100	0.18176700
C	-4.49257700	3.16316300	-0.35301100
C	-5.69931400	3.56001400	-0.98955900
C	-5.73957600	3.84322100	-2.37168000
C	-6.90732700	3.65868400	-0.26641400
C	-6.92831700	4.20332500	-2.99563400
H	-4.82139100	3.76470900	-2.94807500
C	-8.09322300	4.01819000	-0.89603600
H	-6.89925000	3.43943000	0.79837900
C	-8.11319800	4.29326800	-2.26389700
H	-6.93114800	4.41280800	-4.06234300

H	-9.01006800	4.08184800	-0.31549600
H	-9.04120100	4.57301100	-2.75411900

$E_{electronic}$ (Ha) =	-12437.24494
H (Ha)=	-12436.16516
G (Ha) =	-12436.37455
ΔG (Path 2)	0.090025 Ha = 56.49 kcal/mol

Path 4 - Proton capture by S group and formation of dimer complex (proton and alkynyl group located on different monomers and SMe group located at trans position):



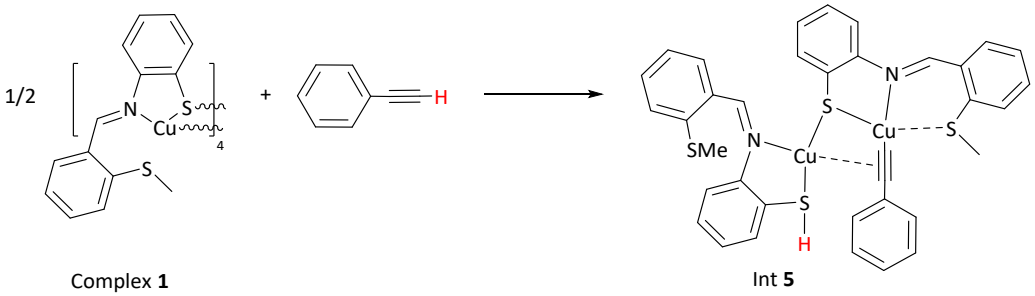
Complex **1** Int **4**

Int 4			
Cu	-0.27246600	-1.99400500	0.92166800
S	1.82088600	-1.91938900	2.07853300
S	-4.15283700	1.77391600	0.64099300
N	-0.58462900	-0.15207200	1.81694700
C	1.81009200	-0.12554500	2.10751200
C	3.02095000	0.55665200	2.22757200
H	3.94829100	-0.00838300	2.26597300
C	3.04099500	1.94488600	2.29283000
H	3.98853800	2.46874500	2.36911300
C	1.84007200	2.65419100	2.27455300
H	1.84446400	3.73842500	2.33749900
C	0.63239000	1.98335200	2.15929700
H	-0.28728000	2.55861900	2.11013100
C	0.59161700	0.58537500	2.04525800
C	-1.77231700	0.36743300	1.87597200
H	-1.92235400	1.43354600	2.08630800
C	-2.94790300	-0.45610700	1.67178400
C	-2.91014400	-1.81625600	2.03046900
H	-2.01716400	-2.19631900	2.52532000
C	-4.00579900	-2.64480000	1.84285000
H	-3.95922600	-3.68804800	2.13746200
C	-5.16931200	-2.11278000	1.29168200
H	-6.03756800	-2.74642700	1.13438800
C	-5.24190800	-0.76859500	0.93986200
H	-6.15805800	-0.38909900	0.50257900
C	-4.14471500	0.07708700	1.12555900
C	-5.79354600	1.98160800	-0.07158600
H	-5.83933900	3.01675400	-0.41025400
H	-5.92772000	1.31958100	-0.93093100

H	-6.58182900	1.81456700	0.66488900
S	-0.93763000	-3.02636600	-0.95577000
S	-1.33252200	3.92502900	-0.19319100
N	-0.82984000	-0.07404900	-1.71726700
C	-2.28102400	-2.03424500	-1.56601300
C	-3.53245700	-2.62364000	-1.76810200
H	-3.66198500	-3.67178300	-1.51176600
C	-4.59835300	-1.89040600	-2.27757900
H	-5.56142900	-2.37028800	-2.42733100
C	-4.42223000	-0.54603900	-2.59967700
H	-5.23777200	0.02939500	-3.02881000
C	-3.18496200	0.05525500	-2.40357100
H	-3.03695700	1.09121000	-2.69691800
C	-2.10248600	-0.66726800	-1.87530800
C	-0.81797200	1.18484800	-1.38058500
H	-1.77166100	1.64542300	-1.08851900
C	0.33550200	2.06052700	-1.36312100
C	1.57172300	1.64759500	-1.88622600
H	1.64594000	0.64326300	-2.29105100
C	2.68049700	2.47664800	-1.87880200
H	3.62641900	2.12474700	-2.27953200
C	2.56237600	3.76611300	-1.36142500
H	3.41926400	4.43356900	-1.34840200
C	1.34538800	4.21720700	-0.86112200
H	1.28381300	5.22608800	-0.47065300
C	0.22212300	3.38446400	-0.85054000
C	-0.95788400	5.57161500	0.43717000
H	-1.88582500	5.92761300	0.88522500
H	-0.18483000	5.53721500	1.20823600
H	-0.66727800	6.25746600	-0.36073100
Cu	0.78574700	-1.53152000	-1.39506700
H	2.55921500	-2.01306500	0.93543300
C	3.86431900	-1.29560700	-0.98175300
C	2.65991800	-1.42319000	-1.25649700
C	5.23942900	-1.10973500	-0.67297500
C	6.10500900	-0.45185700	-1.57088600
C	5.77724800	-1.56806000	0.54781800
C	7.44509800	-0.26053100	-1.25686800
H	5.70805500	-0.09525300	-2.51761500
C	7.11737400	-1.36929300	0.85694600
H	5.12696800	-2.08711700	1.24898200
C	7.95908000	-0.71515000	-0.04244300
H	8.09343000	0.24899800	-1.96459400
H	7.50811500	-1.72982400	1.80459000
H	9.00644500	-0.56205400	0.20043100

$E_{electronic}$ (Ha) =	-6373.001616
H (Ha)=	-6372.399318
G (Ha) =	-6372.522937
ΔG (Path 2)	0.090703 Ha = 28.45 kcal/mol

Path 5 - Proton capture by S group and formation of dimer complex (proton and alkynyl group located on different monomers and SMe group located at cis position):



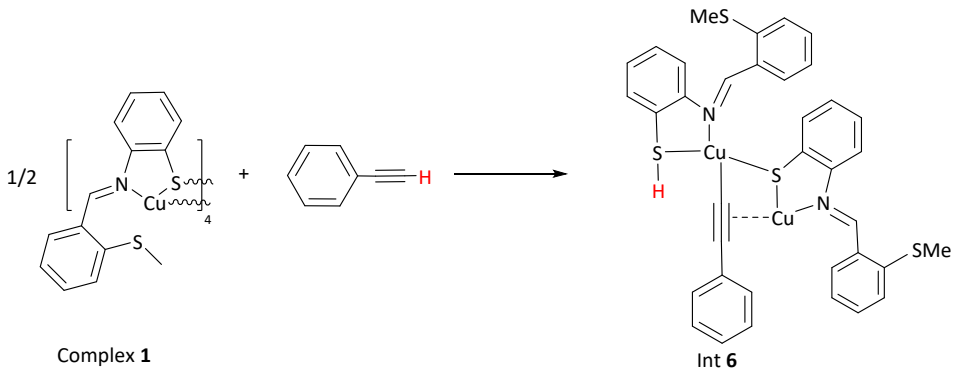
Complex **1** Int **5**

Int 5			
Cu	1.33659400	-0.34083800	0.20861000
S	2.33824800	0.79323900	-1.74045200
S	0.51183400	-2.46713800	0.75040500
N	3.29926900	-1.30706400	0.02073200
C	3.91037100	0.83999600	-0.89166100
C	4.79888000	1.90498000	-1.01834400
H	4.52751200	2.76235400	-1.62773500
C	6.01772800	1.87595200	-0.34660000
H	6.69458300	2.72064300	-0.42826400
C	6.36302800	0.76902900	0.42810200
H	7.31194800	0.74645600	0.95483800
C	5.49069600	-0.30764600	0.53885600
H	5.73786700	-1.16173100	1.16331200
C	4.25338800	-0.28214800	-0.11500300
C	3.69096400	-2.53199900	-0.10360900
H	4.74771900	-2.72453700	-0.33556900
C	2.87999800	-3.73386900	-0.06537200
C	3.58435100	-4.90937400	-0.39817600
H	4.65342900	-4.82450900	-0.57622400
C	2.96234000	-6.13856200	-0.52687500
H	3.53859200	-7.01990700	-0.78660700
C	1.58674100	-6.21886600	-0.32692200
H	1.06917100	-7.16791800	-0.42676700
C	0.86147900	-5.08485300	0.02075400
H	-0.20296900	-5.18268800	0.19839600
C	1.48141100	-3.83978300	0.16877700
C	-1.17142200	-2.90224900	0.25419400

H	-1.73872100	-1.96959400	0.34253000
H	-1.18190300	-3.26070600	-0.77655400
H	-1.60051600	-3.64809100	0.92516500
S	1.36523300	1.19349300	2.01091000
S	-1.11794400	0.25020000	-1.75630300
N	-0.39967300	2.48925600	-0.09352900
C	1.66957600	2.71526300	1.14970600
C	2.85602800	3.41577400	1.38774400
H	3.58032600	2.99271900	2.07998700
C	3.12334300	4.62120800	0.74585100
H	4.05993400	5.13698400	0.93829700
C	2.20341600	5.14447500	-0.16173600
H	2.41223200	6.07282200	-0.68478200
C	1.02181900	4.45833200	-0.41878800
H	0.32357900	4.83442800	-1.16225700
C	0.73039600	3.24812000	0.23307100
C	-1.50261400	3.08845500	-0.42209500
H	-1.61676100	4.17221700	-0.26709800
C	-2.66000100	2.41437800	-0.96189100
C	-3.87953300	3.11064300	-0.88343000
H	-3.86796800	4.10665300	-0.44639600
C	-5.07075000	2.55710200	-1.32270300
H	-6.00045400	3.10961200	-1.23470700
C	-5.05039700	1.27957100	-1.87890300
H	-5.97173500	0.81322200	-2.21811400
C	-3.85503800	0.58005800	-2.00523700
H	-3.88038300	-0.40849500	-2.44845300
C	-2.64555100	1.12102300	-1.55711200
C	-1.58008800	-1.10802200	-2.85447400
H	-0.64593200	-1.63378200	-3.06341200
H	-2.27142500	-1.80653400	-2.37648200
H	-2.00492700	-0.74734200	-3.79366800
Cu	-0.76469100	0.74631300	1.42473200
H	2.02946900	2.09258900	-1.56034100
C	-3.68036900	-0.31670200	1.39279700
C	-2.51599900	0.08477000	1.52839000
C	-5.00171600	-0.76437700	1.12893600
C	-6.12387800	-0.11999200	1.68821100
C	-5.23063400	-1.84829500	0.25529800
C	-7.41330500	-0.53554900	1.37771300
H	-5.96677000	0.72068900	2.35912800
C	-6.52210700	-2.26053600	-0.04859100
H	-4.37560500	-2.35284300	-0.18961800
C	-7.62157900	-1.60644500	0.50836400
H	-8.26305500	-0.01893900	1.81631300
H	-6.67282600	-3.09573700	-0.72760000
H	-8.63054500	-1.92801600	0.26694200

$E_{electronic}$ (Ha) =	-6372.995577
H (Ha)=	-6372.393296
G (Ha) =	-6372.519458
ΔG (Path 2)	0.097661 Ha = 30.64 kcal/mol

Path 6 - Proton capture by S group and formation of dimer complex (Proton and alkynyl group located on the same monomer and SMe group located at trans position):



Complex **1** Int **6**

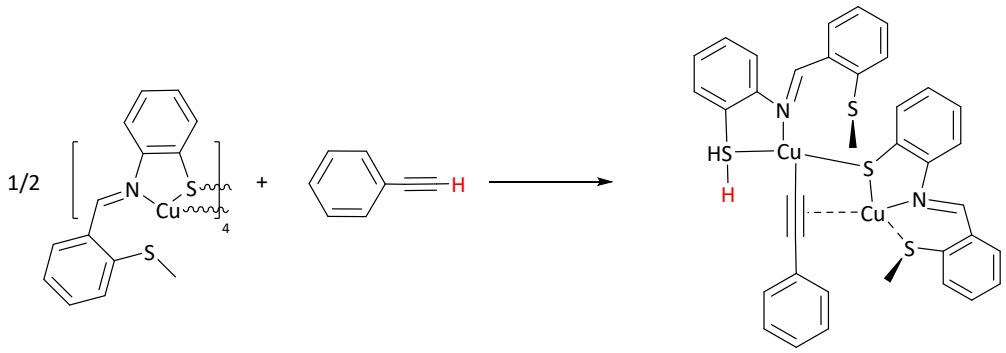
Int 6			
Cu	0.32013700	-0.33167600	-1.37411100
S	0.25439800	1.75633900	-2.67166000
S	6.17737700	-0.35599400	-1.20917800
N	2.06667400	0.56277700	-0.73063100
C	0.91128700	2.61720400	-1.25140100
C	0.59899600	3.94818900	-0.97575700
H	-0.08178400	4.48788200	-1.62724100
C	1.16457400	4.57644800	0.13021000
H	0.90248800	5.60624700	0.35218900
C	2.05804100	3.88665900	0.94928500
H	2.48230800	4.36977400	1.82363800
C	2.38216300	2.56579800	0.67174300
H	3.03261100	2.00466200	1.33719600
C	1.81613700	1.91768400	-0.43320600
C	3.26877300	0.10530200	-0.55428800
H	4.06384400	0.81803900	-0.30308600
C	3.65260100	-1.28542200	-0.64909200
C	2.70722100	-2.30382000	-0.43882000
H	1.68099300	-2.01657100	-0.21474400
C	3.07174000	-3.63954300	-0.45393800
H	2.32802800	-4.40954100	-0.27507000
C	4.40539100	-3.97965300	-0.68392900
H	4.70871200	-5.02243200	-0.69881800
C	5.36307100	-2.99430700	-0.89751100

H	6.38896000	-3.28963300	-1.08458300
C	5.00863500	-1.64081600	-0.88347100
C	7.76011400	-1.21602600	-1.13044200
H	8.52080700	-0.43937900	-1.20959700
H	7.88076700	-1.73541700	-0.17812000
H	7.88331800	-1.91242000	-1.96165900
S	0.88404200	-0.89170600	2.62199500
S	-2.96031800	3.31453900	-1.60498200
N	-1.37888900	0.89827500	1.61378100
C	0.56788800	0.78304900	3.06212000
C	1.40470000	1.42070400	3.99302000
H	2.22036200	0.84902700	4.42885700
C	1.21584000	2.74742200	4.35654400
H	1.88178700	3.20691600	5.08207000
C	0.16085800	3.47851800	3.80650500
H	-0.01263900	4.50868100	4.10364400
C	-0.68233300	2.87165900	2.88798100
H	-1.53043100	3.42409400	2.49145400
C	-0.49076300	1.53698100	2.48866600
C	-2.02763000	1.59989300	0.73196200
H	-1.74224100	2.64562500	0.54521400
C	-3.15096600	1.07337500	-0.01663200
C	-3.75333000	-0.13439200	0.37511300
H	-3.34732200	-0.64338900	1.24609600
C	-4.83486600	-0.66554600	-0.30811100
H	-5.27506200	-1.60423300	0.01610000
C	-5.34618100	0.01825900	-1.40935200
H	-6.19480800	-0.38022700	-1.95754400
C	-4.78402100	1.22608800	-1.81509300
H	-5.20749800	1.74023800	-2.66989300
C	-3.69476500	1.76910400	-1.12937500
C	-3.92090000	3.80597000	-3.04881700
H	-3.48660200	4.74950300	-3.37957300
H	-3.83478100	3.07409900	-3.85397300
H	-4.96884100	3.96993100	-2.79214500
Cu	-0.59385200	-1.13002100	0.97518700
H	-0.99861400	2.27469300	-2.56919700
C	-1.73503200	-2.44105900	-0.36959100
C	-0.93865100	-1.66885400	-0.96110200
C	-2.74961300	-3.35819200	0.03395800
C	-3.08618800	-3.50585200	1.39222100
C	-3.46042400	-4.10714100	-0.92345800
C	-4.10593600	-4.36664500	1.77910200
H	-2.53582800	-2.92703800	2.13339400
C	-4.47481800	-4.96963900	-0.52726700
H	-3.21073900	-3.99713500	-1.97483100
C	-4.80486300	-5.10177400	0.82198700
H	-4.35580700	-4.46483000	2.83157200
H	-5.01552500	-5.53978700	-1.27736900
H	-5.60171600	-5.77415900	1.12535900

$E_{electronic}$ (Ha) =	-6373.001786
H (Ha)=	-6372.399746

G (Ha) =	-6372.528031
ΔG (Path 6)	0.080515 Ha = 25.26 kcal/mol

Path 7 - Proton capture by S group and formation of dimer complex (Proton and alkynyl group located on the same monomer and SMe group located at cis position):



Complex **1** Int **7**

Int 7			
Cu	1.17551400	0.01116400	-0.28351400
S	-0.19779100	1.48872000	2.21249100
S	2.43471300	-2.41870800	-0.89654600
N	0.51766400	-1.22650200	1.30551500
C	-1.33733800	0.13287300	2.10924600
C	-2.67931900	0.24550200	2.48213600
H	-3.06359900	1.20639300	2.81688100
C	-3.51927300	-0.86454500	2.43930700
H	-4.56439400	-0.75074300	2.71329000
C	-3.02175700	-2.10465000	2.04835900
H	-3.67222700	-2.97329900	2.01355100
C	-1.68300500	-2.22961700	1.68856200
H	-1.27964000	-3.18178200	1.35152200
C	-0.83820900	-1.11862400	1.70048200
C	1.25640400	-2.02494700	2.00926400
H	0.81691100	-2.50583800	2.89330800
C	2.68728900	-2.23553000	1.82936100
C	3.42934400	-2.34054700	3.01756900
H	2.89070100	-2.35976100	3.96209000
C	4.81643500	-2.35650500	3.00711100
H	5.36990300	-2.41002800	3.93856100
C	5.48470900	-2.29575600	1.78552000
H	6.57034000	-2.29880600	1.75477700

C	4.77192900	-2.27022600	0.59086700
H	5.31348500	-2.27903100	-0.34899900
C	3.37371800	-2.25892700	0.59072300
C	3.57765500	-1.81191100	-2.15373700
H	2.98999100	-1.72594000	-3.06957300
H	3.93569400	-0.81824700	-1.86543700
H	4.40691600	-2.49875300	-2.33118500
S	-0.23437100	-0.23281800	-2.20824200
S	-2.82193500	2.57060700	-0.00417500
N	-2.98681700	-0.57718000	-0.94814100
C	-1.16782200	-1.74077500	-2.04725200
C	-0.62545800	-2.93681600	-2.53511700
H	0.36087500	-2.91353300	-2.99113500
C	-1.32173500	-4.13635200	-2.44529800
H	-0.86925000	-5.05035900	-2.81880300
C	-2.58983800	-4.16461100	-1.86280900
H	-3.13055400	-5.10087900	-1.76483800
C	-3.15312500	-2.98917900	-1.38758700
H	-4.12038300	-3.01619700	-0.89304600
C	-2.46519000	-1.76946600	-1.48033700
C	-4.26545100	-0.39459900	-0.90205000
H	-4.93120000	-1.14920600	-1.34116300
C	-4.98584100	0.70391300	-0.27568000
C	-6.35739800	0.43463000	-0.07823400
H	-6.73930900	-0.52361000	-0.42157100
C	-7.21270400	1.32625600	0.54623700
H	-8.25743500	1.06881700	0.68556100
C	-6.71705000	2.54831400	0.99325700
H	-7.36543100	3.26255000	1.49031700
C	-5.37471700	2.85301300	0.80112400
H	-4.98544300	3.80397900	1.15436700
C	-4.50648300	1.96325800	0.16305100
C	-3.08443100	3.94400000	-1.16857400
H	-2.11023200	4.40883700	-1.32076900
H	-3.47016600	3.57107600	-2.11697100
H	-3.77077500	4.67165700	-0.73386100
Cu	-1.58679200	0.95862500	-0.91483500
H	-1.12956800	2.39793900	2.54559300
C	3.77799600	1.76347500	-0.40089800
C	2.69752300	1.15738400	-0.32669600
C	5.02354300	2.44266600	-0.48059400
C	6.23182700	1.72759900	-0.62535200
C	5.09811900	3.85026200	-0.41795900
C	7.45067600	2.39019700	-0.70411900
H	6.19478900	0.64151700	-0.67346900
C	6.32060800	4.50643100	-0.49670800
H	4.17896900	4.41954700	-0.30643400
C	7.50454200	3.78296100	-0.64058000
H	8.36662500	1.81563000	-0.81580200
H	6.35008300	5.59185200	-0.44596000
H	8.45858600	4.29840200	-0.70229800

$E_{electronic}$ (Ha) =	-6372.981012
H (Ha)=	-6372.378685
G (Ha) =	-6372.506296
ΔG (Path 7)	0.123985 Ha = 38.9 kcal/mol

Calculation demonstrates Int **6** with the lowest ΔG (25.2 kcal/mol) as the most thermodynamically favorable copper alkynyl intermediate. In this pathway the acidic proton on the terminal alkyne is captured by the basic thiolate, resulting in formation of the dinuclear σ,π–alkynyl copper complex with the SMe group located on the trans position.

VI. References

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