

## Supporting Information

Copper(I) Complexes Bearing Mesoionic Carbene Ligands:  
Influencing the Activity in Halo-Click Reactions

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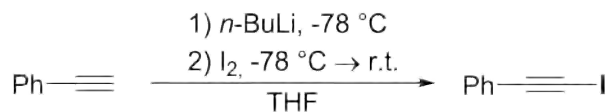
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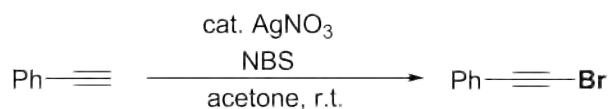
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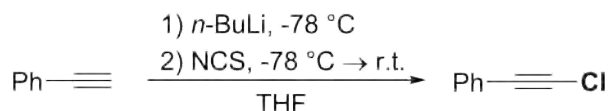
## 1 Synthesis of substrates used in catalysis



**(Iodoethynyl)benzene.**<sup>1</sup> In a 100 mL-Schlenk flask, a solution of phenylacetylene (10 mmol, 1.10 mL, 1.00 equiv.) in THF (10 mL) was cooled to  $-78\text{ }^\circ\text{C}$  before *n*-butyllithium (10.5 mmol, 2.5 M in hexanes, 4.2 mL, 1.05 equiv.) was added dropwise via syringe. The yellow solution was stirred for 1 hour before a solution of  $\text{I}_2$  in THF (10 mL) was added quickly to give a light brown solution. The mixture was stirred for 30 minutes before it was allowed to warm to room temperature. The reaction was quenched with  $\text{H}_2\text{O}$  (20 mL) and extracted with *n*-hexane (3 x 50 mL). The combined organic phases were washed with aq.  $\text{Na}_2\text{S}_2\text{O}_3$ -solution, dried with  $\text{Na}_2\text{SO}_4$  and filtered. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography ( $\text{SiO}_2$ , *n*-hexane) to give the product as a light-yellow oil (2.05 g, 8.90 mmol, 89%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.46–7.41 (m, 2H, phenyl-H), 7.35–7.28 (m, 3H, phenyl-H).



**(Bromoethynyl)benzene.**<sup>2</sup> In a 100 mL-Schlenk flask, phenylacetylene (10.0 mmol, 1.10 mL, 1.00 equiv.), *N*-bromosuccinimide (12.0 mmol, 2.12 g, 1.20 equiv.) and  $\text{AgNO}_3$  (1.00 mmol, 170 mg, 0.10 equiv.) were dissolved in acetone and stirred overnight under the exclusion of light. The mixture was passed through a plug of silica using pentanes as eluent, and the solvent was removed under reduced pressure to give the product as a light yellow oil (1.13 g, 6.21 mmol, 62%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.47–7.44 (m, 2H, phenyl-H), 7.37–7.29 (m, 3H, phenyl-H).



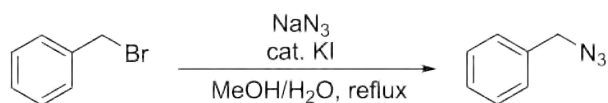
**(Chloroethynyl)benzene.**<sup>3</sup> In a 100 mL-Schlenk flask, phenylacetylene (9.80 mmol, 1.00 g, 1.00 equiv.) was dissolved in dry and degassed THF (20 mL) and cooled to  $-78\text{ }^\circ\text{C}$ . Slowly *n*-butyllithium (10.8 mmol, 2.5 M in hexanes, 4.3 mL, 1.05 equiv.) was added dropwise and the reaction mixture stirred at  $-78\text{ }^\circ\text{C}$  for 30 min. A suspension of *N*-chlorosuccinimide (10.8 mmol, 1.44 g, 1.10 equiv.) in THF (10 mL) was added and stirred for 1 hour. The reaction mixture was slowly warmed to room temperature and stirred for 4 days. After quenching with saturated ammonia chloride solution (15 mL), the aqueous layer was separated and extracted with diethyl ether (3 x 50 mL). The combined organic layers were dried with  $\text{Na}_2\text{SO}_4$ , filtered and the solvent

<sup>1</sup>D. L. Usanov, H. Yamamoto, *J. Am. Chem. Soc.* **2011**, *133*, 1286–1289.

<sup>2</sup>J. P. Marino, H. N. Nguyen, *J. Org. Chem.* **2002**, *67*, 6841–6844.

<sup>3</sup>D. Sud, T. J. Wigglesworth, N. R. Branda, *Angew. Chem. Int. Ed.* **2007**, *46*, 8017–8019.

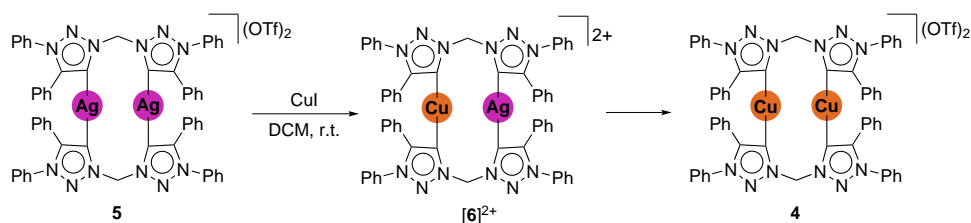
evaporated. After purification through flash column chromatography ( $\text{SiO}_2$ , *n*-hexane) the product was obtained as a clear oil (923 mg, 6.76 mmol, 69%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.46–7.43 (m, 2H, phenyl-H), 7.36–7.29 (m, 3H, phenyl-H).



**Benzyl azide.**<sup>4</sup> In a 500 mL round-bottomed flask, benzyl bromide (120 mmol, 14.3 mL, 1.00 equiv.), sodium azide (240 mmol, 15.6 g, 2.00 equiv.) and potassium iodide (2.40 mmol, 398 mg, 0.02 equiv.) were dissolved in MeOH/ $\text{H}_2\text{O}$  (200 mL, v/v 1:1) and refluxed for 24 hours. After cooling to room temperature,  $\text{H}_2\text{O}$  (200 mL) was added and the mixture was extracted with diethyl ether (2 x 200 mL). The combined organic phases were dried with  $\text{Na}_2\text{SO}_4$  and the solvent removed under reduced pressure to give benzyl azide as a colourless oil (117 mmol, 15.6 g, 98%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.42–7.30 (m, 5H, phenyl-H), 4.34 (s, 2H,  $\text{CH}_2$ ).

<sup>4</sup>similar procedure by: S. Wang, K. Jia, J. Cheng, Y. Chen, Y. Yuan, *Tetrahedron Lett.* **2017**, 58, 3717–3721.

## 2 ESI Mass Spectrometry

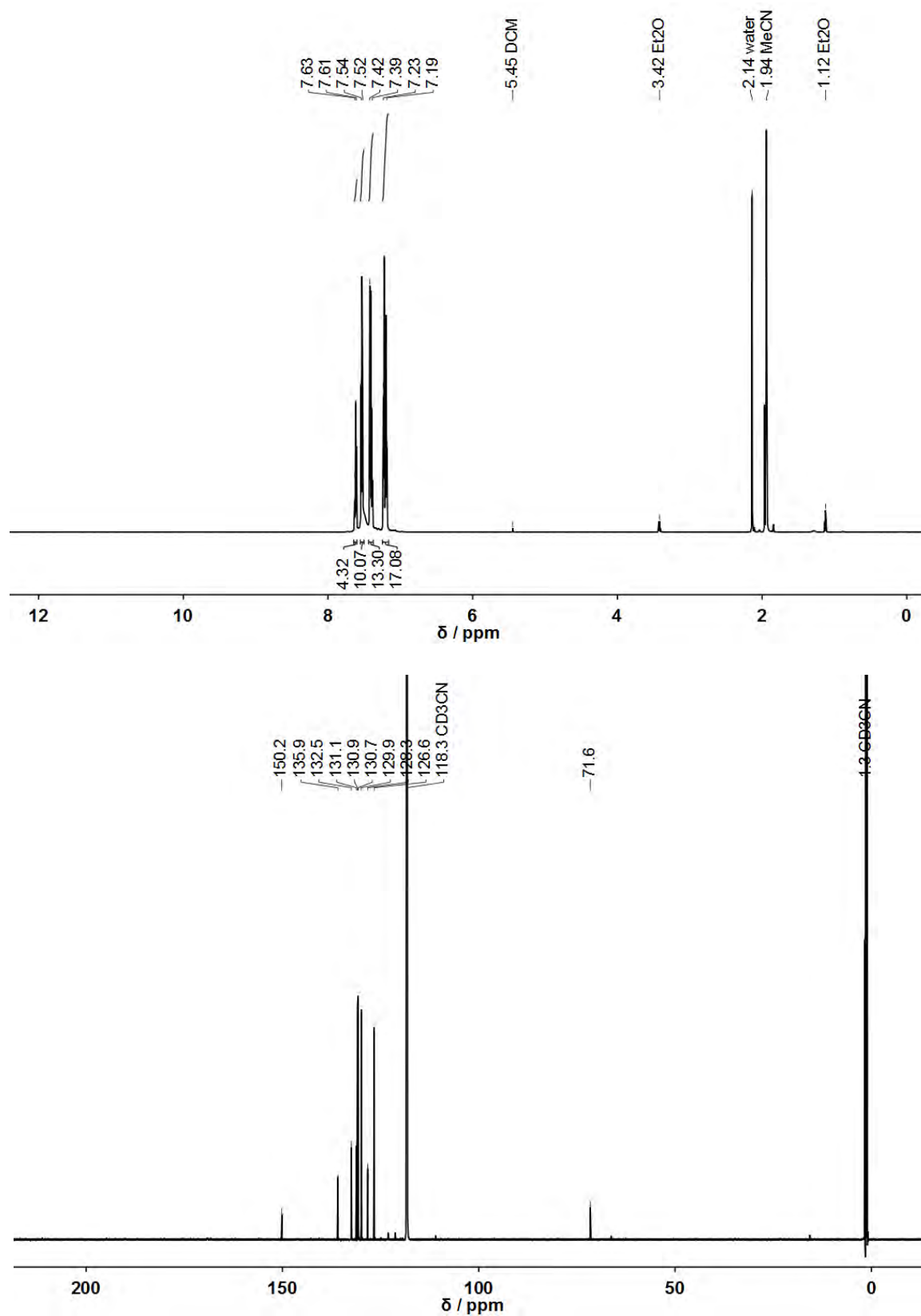


Species	$m/z$ (%)	
	experimental	simulated
Cu-Cu [4] <sup>2+</sup>	517.1185 (88.9)	517.1196 (89.5)
	517.6153 (60.8)	517.6221 (60.5)
	518.1123 (100)	518.1196 (100)
	518.6096 (56.4)	518.6196 (58.4)
	519.1202 (35.2)	519.1196 (36.5)
	519.6179 (16.5)	519.6196 (16.0)
	520.1159 (6.1)	520.1221 (4.6)
	520.6141 (0.4)	520.6196 (0.9)
Ag-Ag [5] <sup>2+</sup>	561.0950 (46.0)	561.0951 (48.0)
	561.5852 (31.1)	561.5976 (32.4)
	562.0893 (100)	562.0951 (100)
	562.5936 (62.3)	562.5976 (62.6)
	563.0845 (59.9)	563.0951 (61.9)
	563.5892 (31.7)	563.5976 (32.4)
	564.0942 (10.0)	564.0951 (10.0)
	564.5994 (2.3)	564.6001 (2.1)
Cu-Ag [6] <sup>2+</sup>	539.0959 (61.1)	539.1074 (62.5)
	539.6032 (41.8)	539.6099 (42.2)
	540.0973 (100)	540.1074 (100)
	540.6050 (61.4)	540.6099 (61.1)
	541.0996 (45.0)	541.1074 (45.7)
	541.6077 (21.2)	541.6099 (21.8)
	542.1028 (6.7)	542.1099 (6.5)
	542.6114 (1.7)	542.6124 (1.4)
	543.1203 (0.5)	543.1124 (0.2)

Table S1. Conclusive list of experimental and simulated mass peaks for the dinuclear species.

### 3 NMR Spectra

#### 3.1 Complex Characterization & Substrates



**Figure S1.** <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of di-silver complex **5** (measured in MeCN-d<sub>3</sub>).

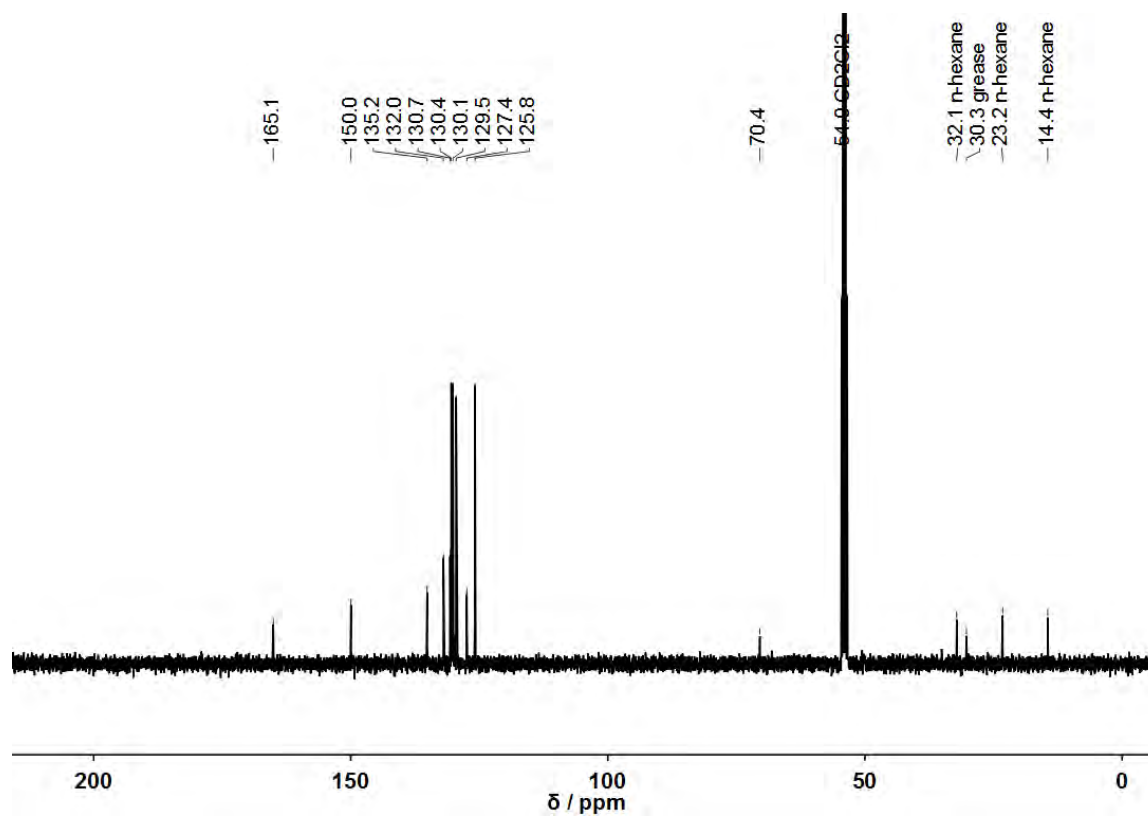
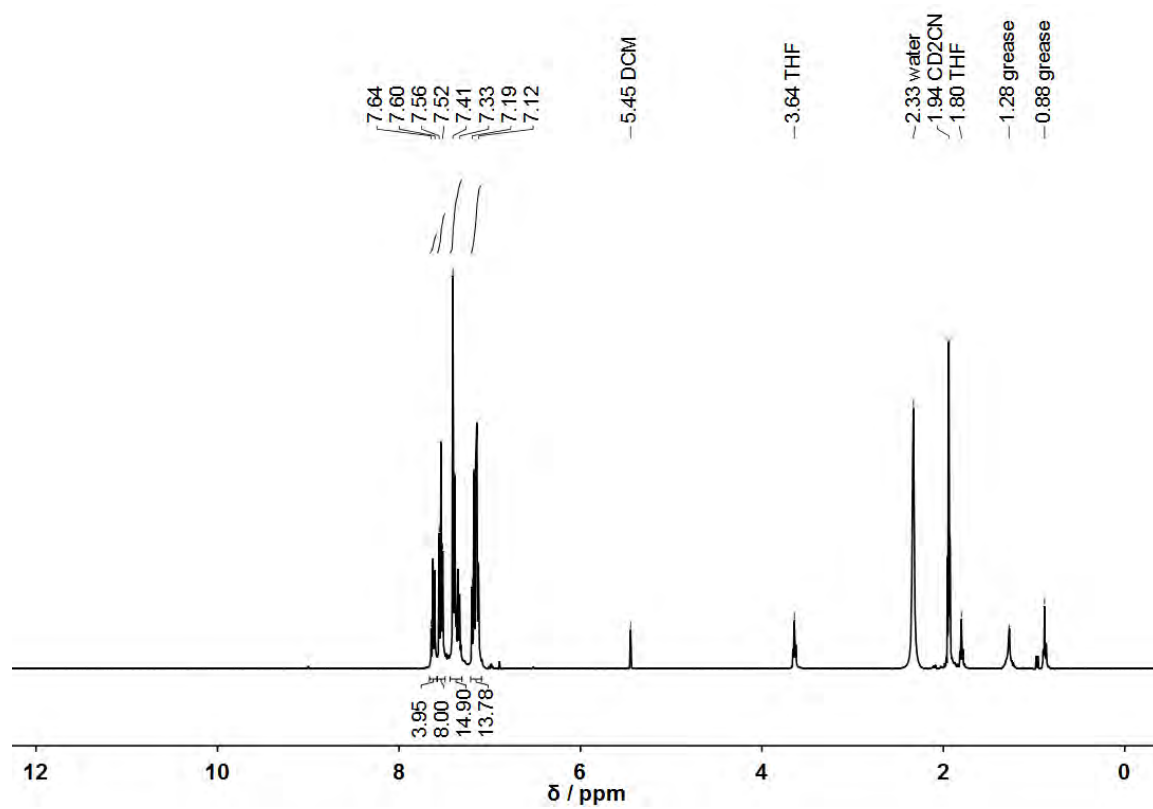
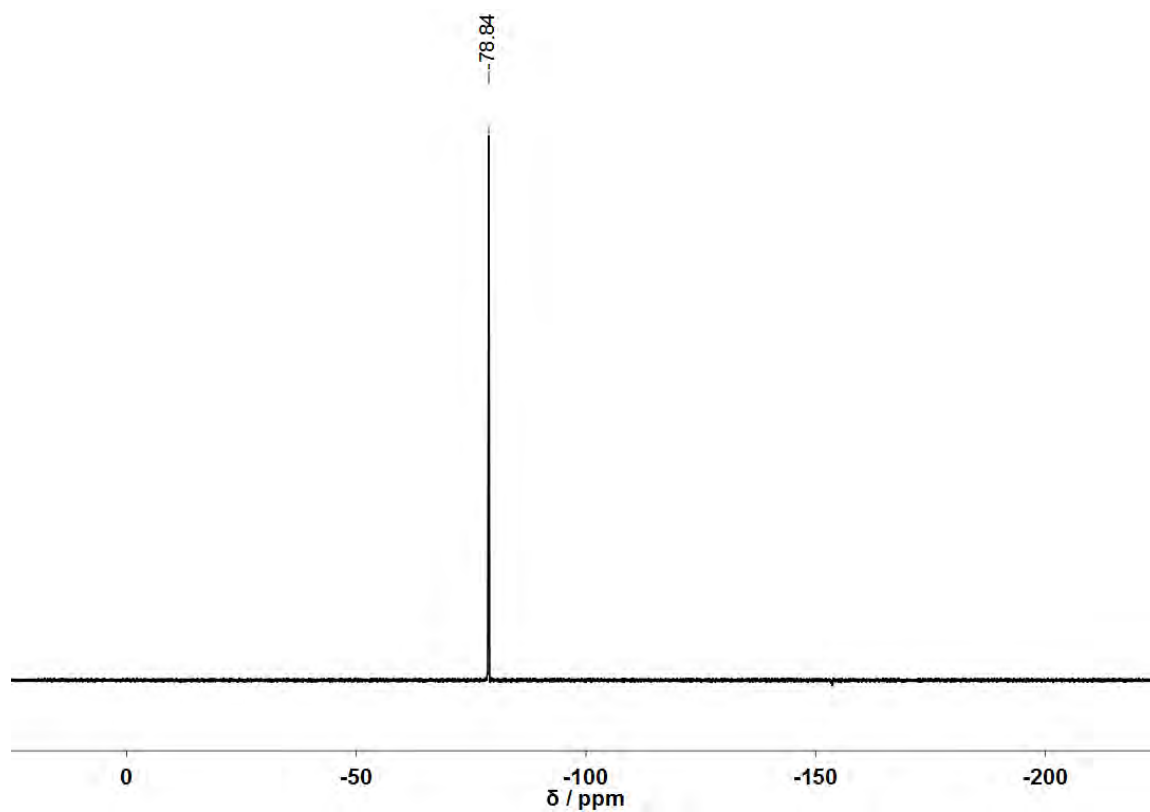
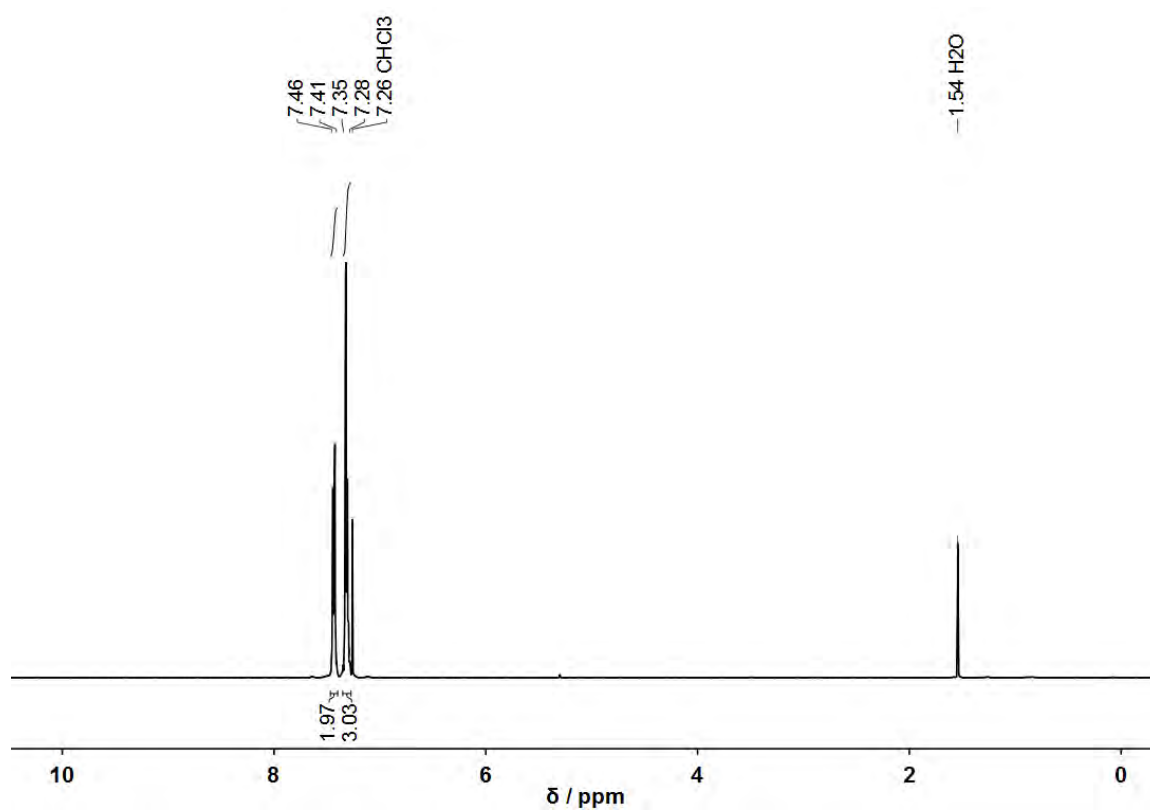


Figure S2.  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of di-copper complex 4 (measured in  $\text{CDCl}_2$ ).



**Figure S3.**  $^{19}\text{F}$  NMR spectrum of di-copper complex **4** (measured in  $\text{CD}_2\text{Cl}_2$ ).



**Figure S4.**  $^1\text{H}$  NMR spectrum of (iodoethynyl)benzene (measured in  $\text{CDCl}_3$ ).



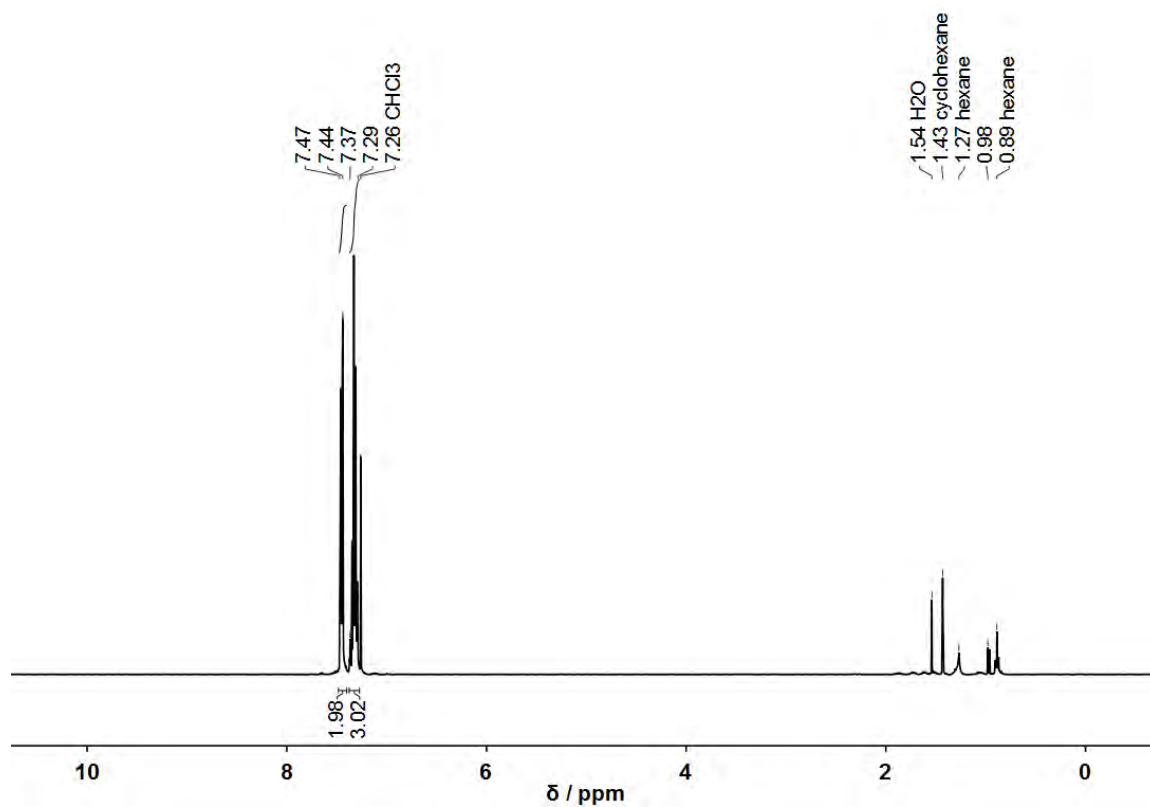


Figure S5.  $^1\text{H}$  NMR spectrum of (bromoethynyl)benzene (measured in  $\text{CDCl}_3$ ).

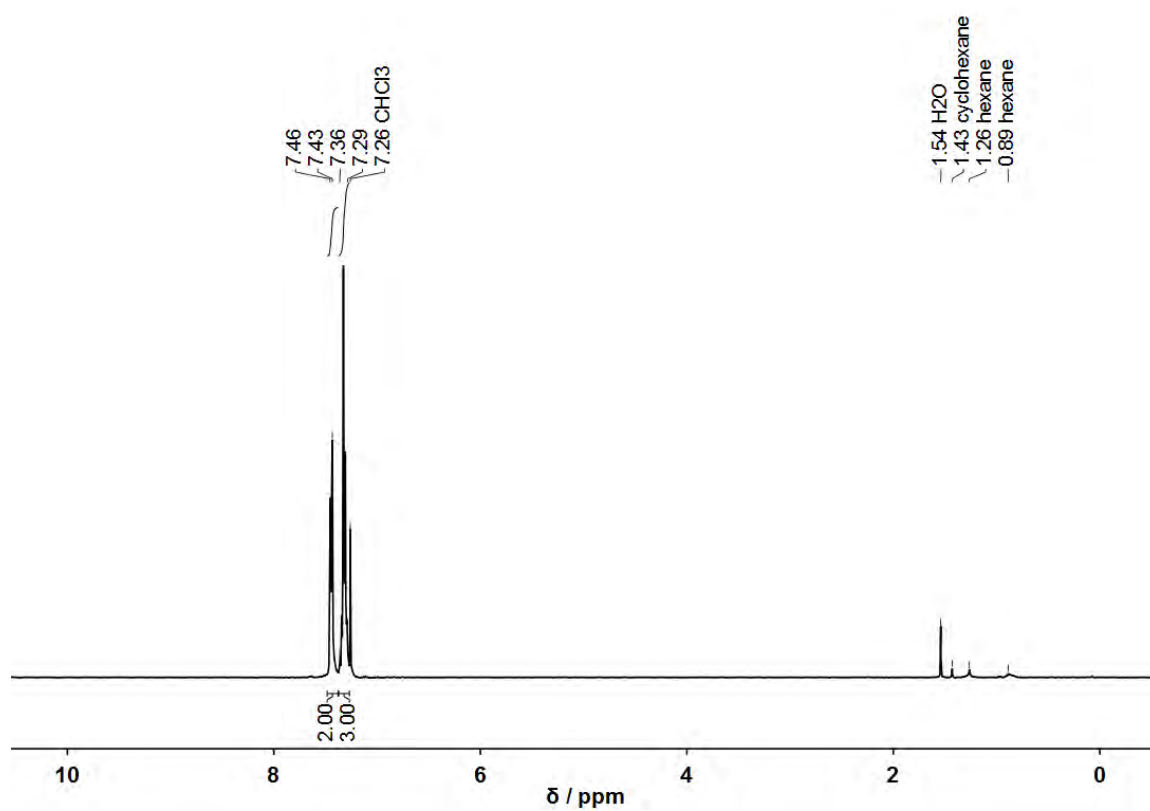
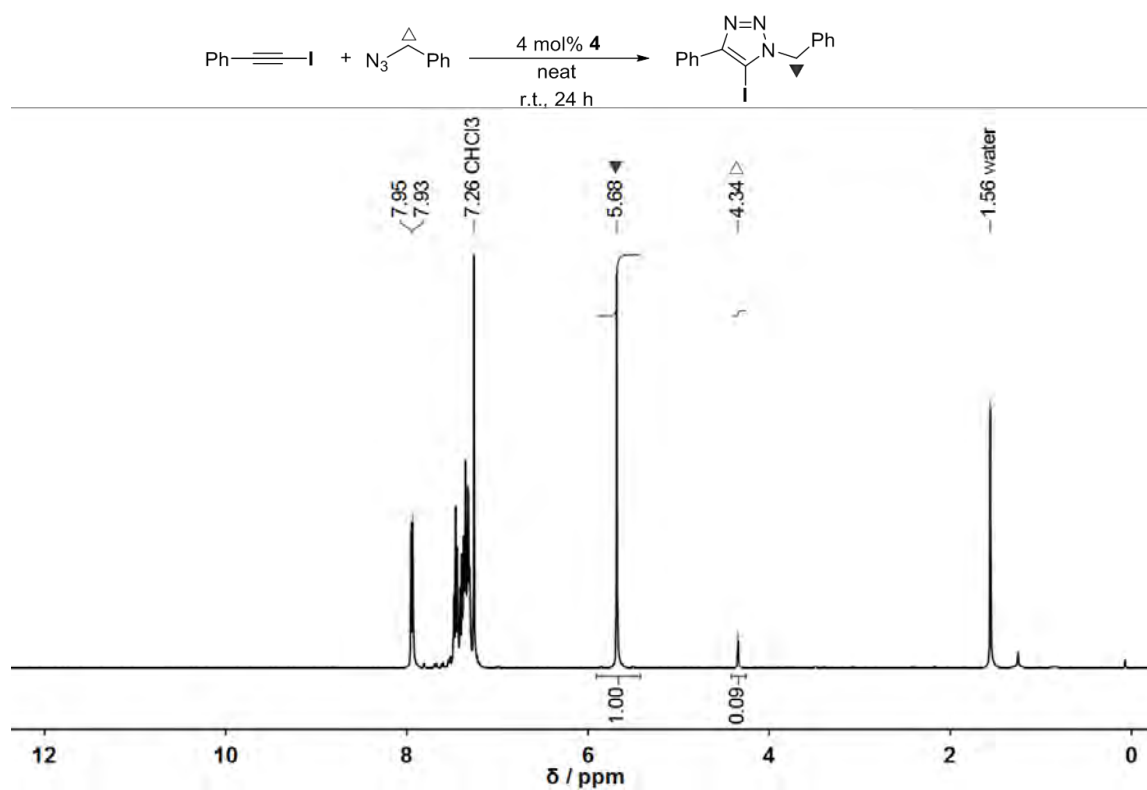
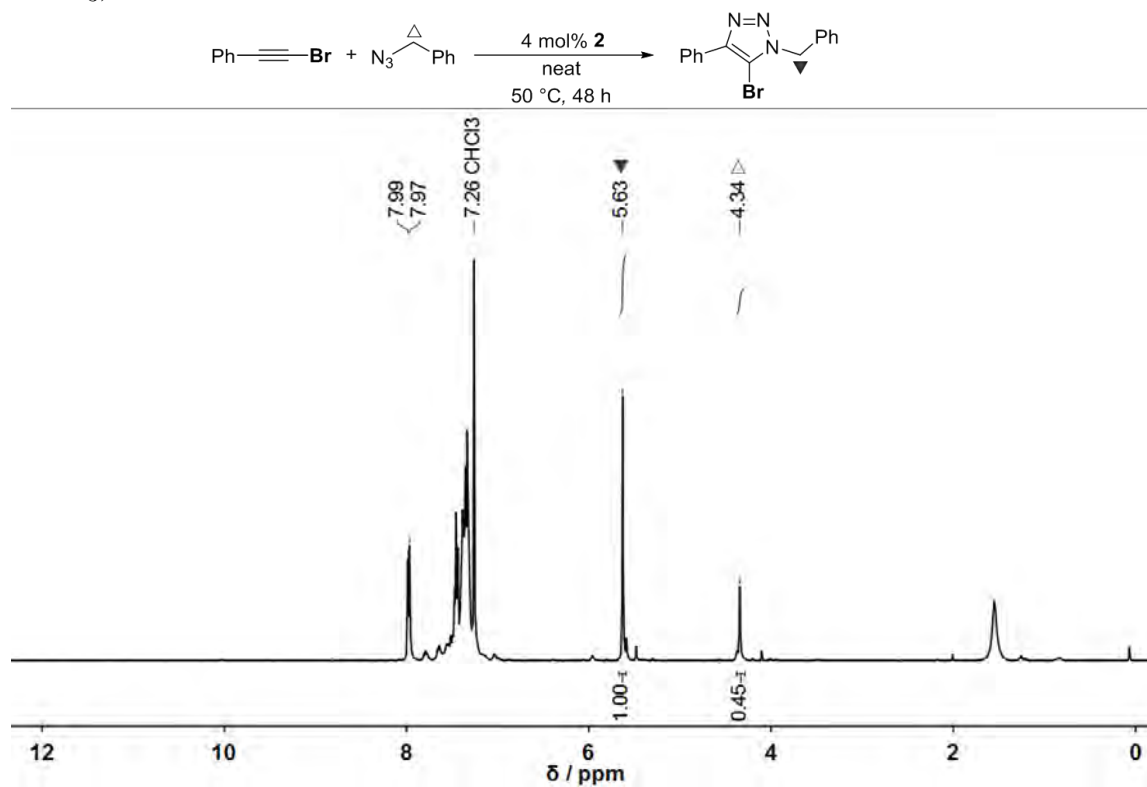


Figure S6.  $^1\text{H}$  NMR spectrum of (chloroethynyl)benzene (measured in  $\text{CDCl}_3$ ).

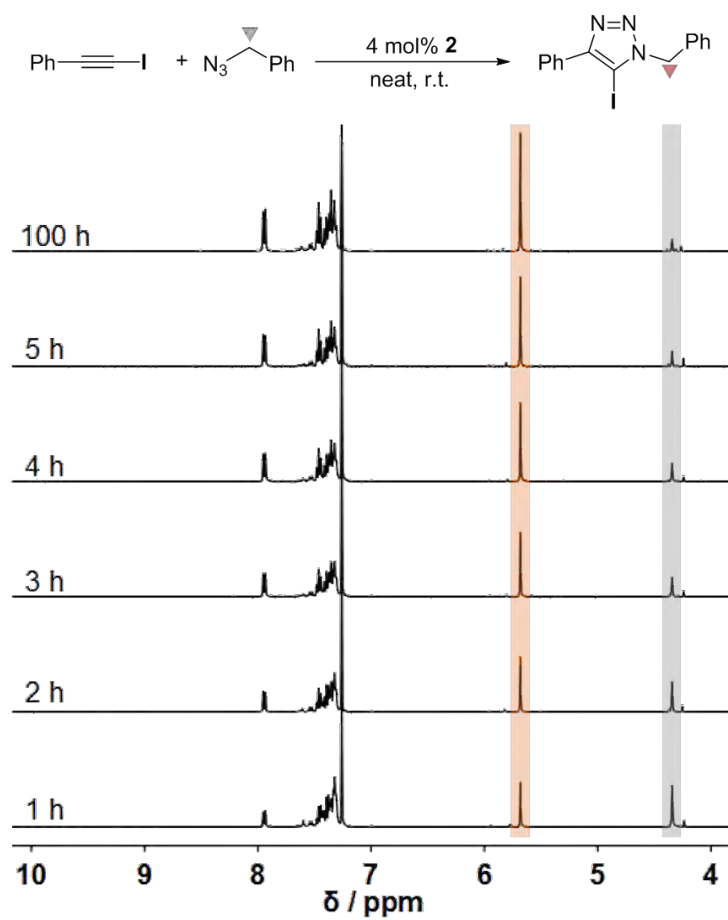
## 3.2 Catalysis



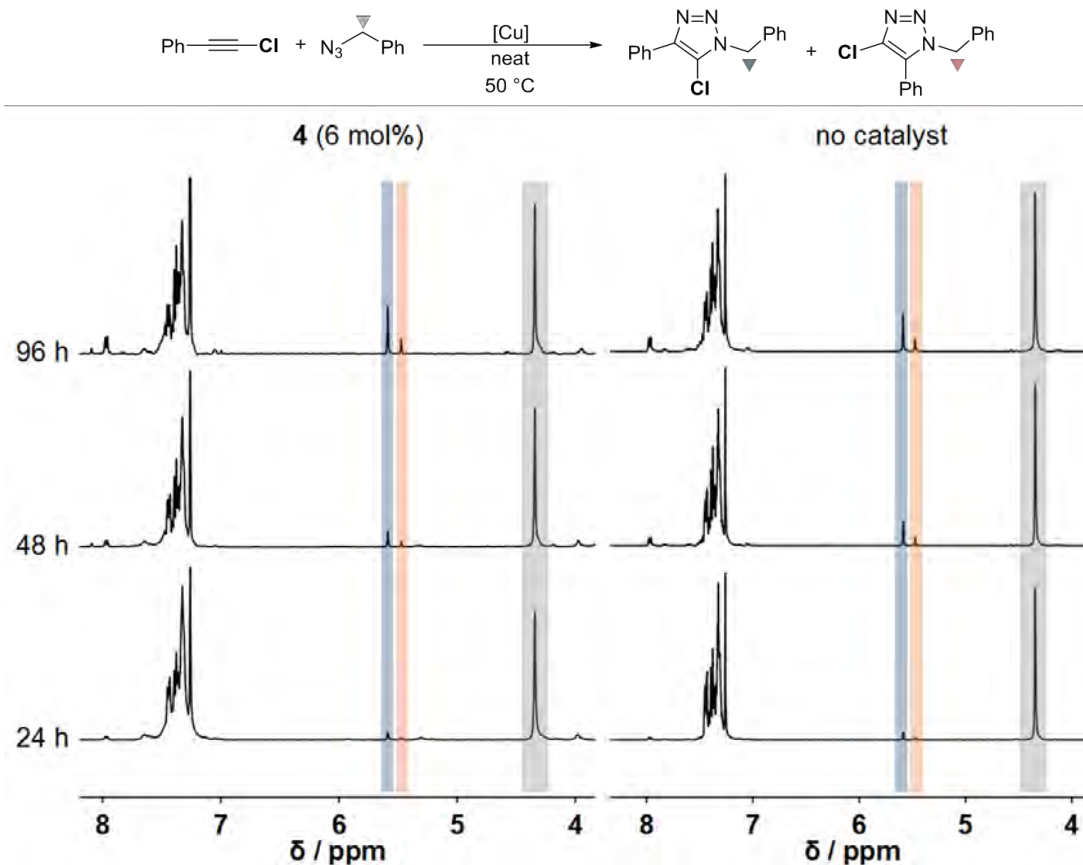
**Figure S7.** Exemplary  $^1\text{H}$  NMR spectrum of conversion of (iodoethynyl)benzene (measured in  $\text{CDCl}_3$ ).



**Figure S8.** Exemplary  $^1\text{H}$  NMR spectrum of conversion of (bromoethynyl)benzene (measured in  $\text{CDCl}_3$ ).



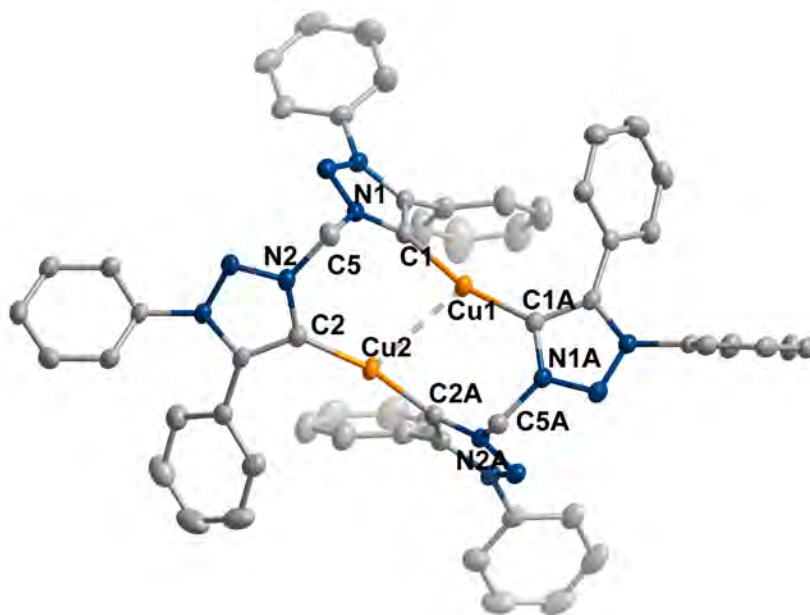
**Figure S9.**  $^1\text{H}$  NMR spectra of conversion of (iodoethynyl)benzene using **2** (4 mol%) at r.t. (measured in  $\text{CDCl}_3$ ).



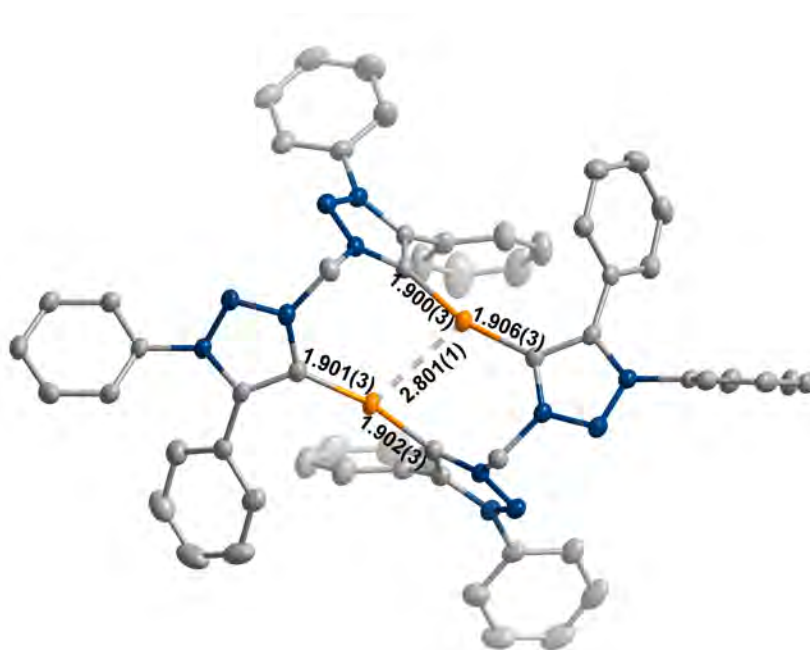
**Figure S10.**  $^1\text{H}$  NMR spectra of conversion of (chloroethynyl)benzene (measured in  $\text{CDCl}_3$ ). For the assignment of the NMR shift of the protons of the regioisomers in **Figure S10** we were not able to isolate and characterize the products. However, the proton shift for the 5-chloro-1,2,3-triazole was previously reported and was used to assign the methylene protons at 5.59 ppm in chloroform-d in the product mixture. The minor product, 4-chloro-1,2,3-triazole, has not been reported yet, and we were not able to isolate it in its pure form. However, based on the NMR shift of the methylene protons for the 5-iodo-/4-iodo-triazoles (5.68 and 5.56 ppm) and the 5-bromo-/4-bromo-triazole (5.63 and 5.49 ppm), we are reasonably confident to assign the singlet at 5.47 ppm to the methylene protons of the 4-chloro-derivative.<sup>5</sup>

<sup>5</sup>Y. Zhou, T. Lecourt and L. Micouin, *Angew. Chem. Int. Ed.*, **2010**, *49*, 2607–2610; J. Huang, S. J. F. Macdonald and J. P. A. Harrity, *Chem. Commun.*, **2009**, 436–438.

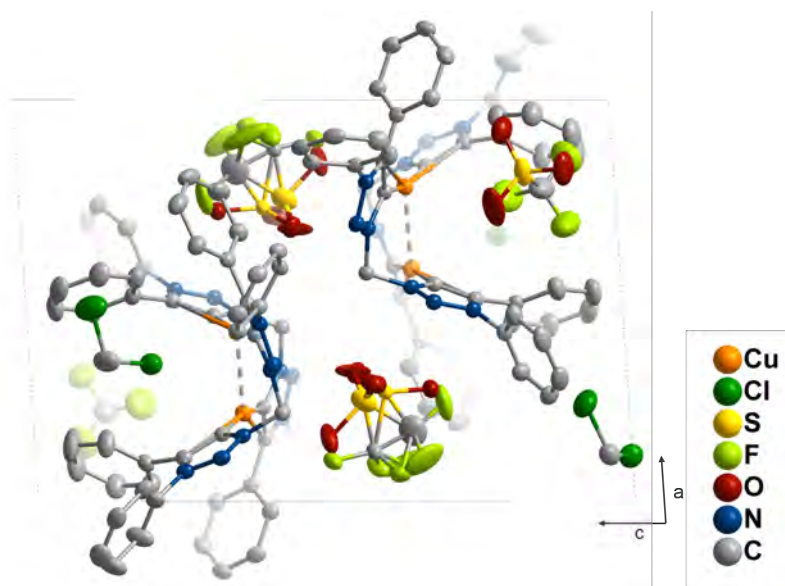
## 4 Single-Crystal X-Ray Diffraction Data &amp; Crystal Structures



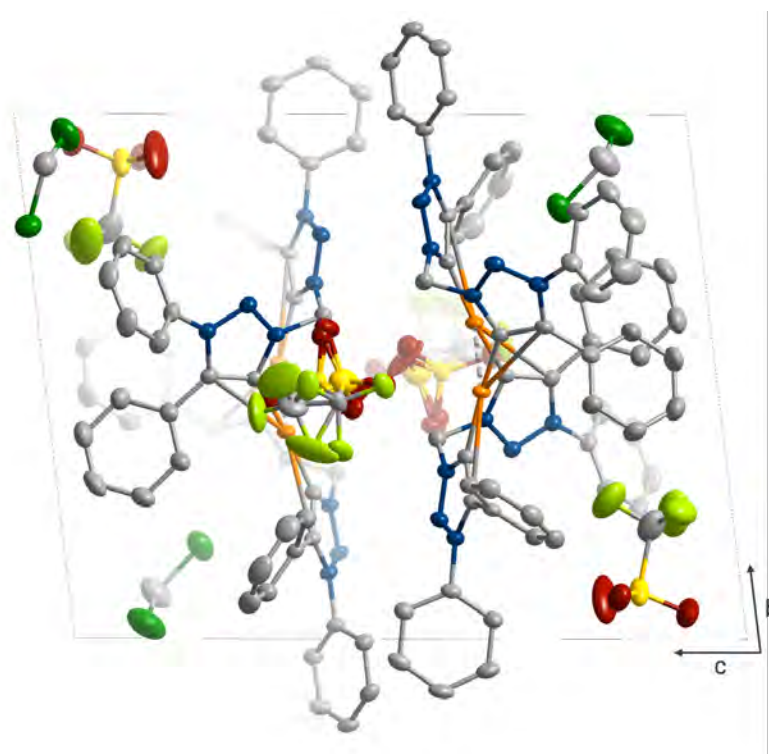
**Figure S11.** ORTEP representation of 4. Two solvent molecules ( $\text{CHCl}_3$ ) and protons omitted for clarity.



**Figure S12.** ORTEP representation of 4 with selected bond lengths (in Å).



**Figure S13.** ORTEP representation of the unit cell of 4, view along b axis, protons omitted for clarity.



**Figure S14.** ORTEP representation of the unit cell of 4, view along a axis, protons omitted for clarity.

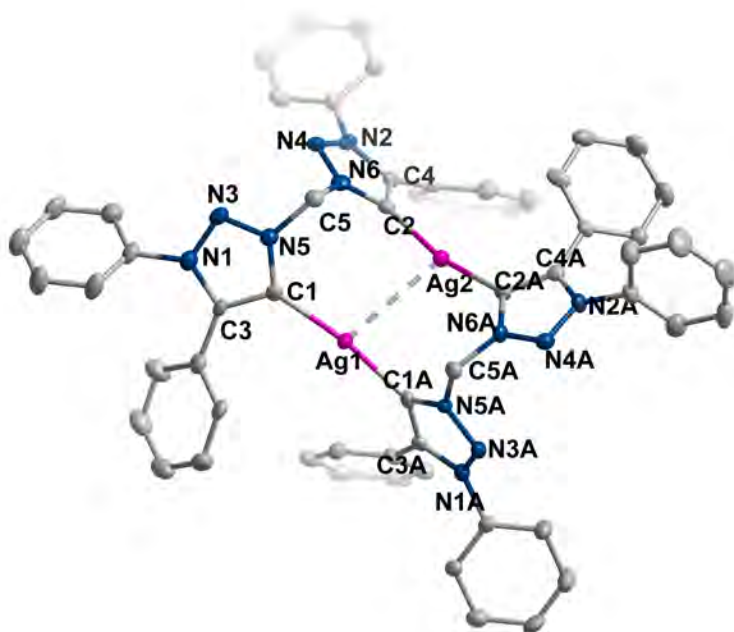
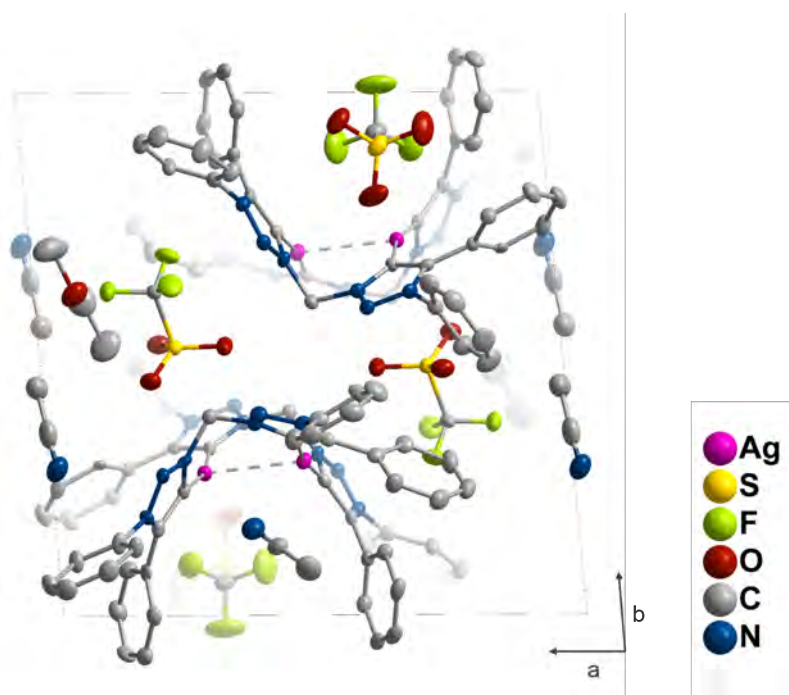


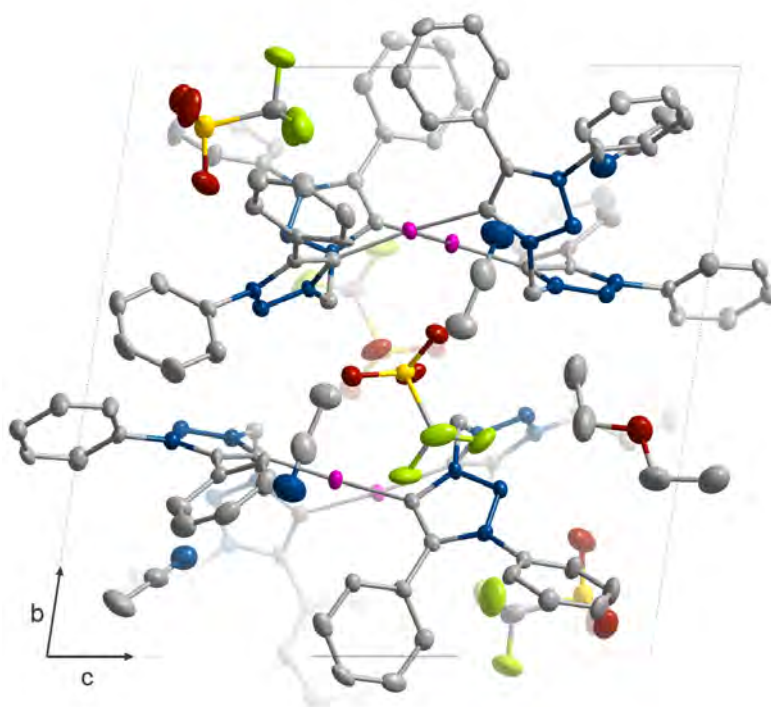
Figure S15. ORTEP representation of **5**. Protons omitted for clarity.



Figure S16. ORTEP representation of **5** with selected bond lengths (in Å).



**Figure S17.** ORTEP representation of the unit cell of **5**, view along *c* axis, protons omitted for clarity.



**Figure S18.** ORTEP representation of the unit cell of **5**, view along *a* axis, protons omitted for clarity.



**Table S2.** Crystallographic details for **4** and **5**.

	[ <b>4</b> • 2 DCM]	[ <b>5</b> • 2 MeCN, Et <sub>2</sub> O]
Chemical formula	C <sub>62</sub> H <sub>48</sub> Cl <sub>4</sub> Cu <sub>2</sub> F <sub>6</sub> N <sub>12</sub> O <sub>6</sub> S <sub>2</sub>	C <sub>68</sub> H <sub>60</sub> Ag <sub>2</sub> F <sub>6</sub> N <sub>14</sub> O <sub>7</sub> S <sub>2</sub>
M <sub>r</sub>	1504.12	1576.13
Crystal System	triclinic	triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
a (Å)	12.651(5)	14.906(5)
b (Å)	14.796(5)	15.174(5)
c (Å)	18.256(5)	15.306(5)
$\alpha$ (°)	81.941(5)	81.103(5)
$\beta$ (°)	84.184(5)	88.574(5)
$\gamma$ (°)	74.672(5)	84.738(5)
V (Å <sup>3</sup> )	3255.7(19)	3406(2)
Z	2	2
Density (g·cm <sup>-3</sup> )	1.534	1.540
F(000)	1528	1604
Radiation Type	MoK $\alpha$	MoK $\alpha$
$\mu$ (mm <sup>-1</sup> )	0.959	0.717
Crystal size	0.3 x 0.3 x 0.1	0.5 x 0.2 x 0.1
Meas. Refl.	30012	29995
Indep. Refl.	13309	12905
Observ. [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] relf.	10461	10034
R <sub>int</sub>	0.0201	0.0410
R [ <i>F</i> <sup>2</sup> > $\sigma$ ( <i>F</i> <sup>2</sup> )], wR( <i>F</i> <sup>2</sup> ), S	0.0393, 0.1212, 0.859	0.0735, 0.2213, 1.177
$\Delta\rho_{max}, \Delta\rho_{min}$ (e·Å <sup>-3</sup> )	0.864, -0.709	2.339, -0.998