

Supplementary Materials for

An Unusual Zig-zag 2D Copper(I) Coordination Polymer as an Outstanding Catalyst for Azide-Alkyne “Click” Chemistry at Room Temperature

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1. Materials and Methods

Copper sulphate pentahydrate (Merck, 98%), benzophenone-4,4'-dicarboxylic acid (Sigma, 95%), benzyl bromide (Merck, 98%), phenyl acetylene (Sigma, 98%), propargyl amine (Sigma, 98%), propargyl alcohol (Sigma, 95%), 3-ethynylthiophene (Sigma, 98%), propargyl acrylate (Sigma, 98%), ethyl 2-bromopropionate (Sigma, 98%), 4'-Methoxy-2-chloroacetophenone (Sigma, 97%), glacial acetic acid (Merck, 100%), d-dimethyl sulfoxide, (DMSO-d₆, Merck), sodium azide (NaN₃, Panreac), were used as received. Propargyl acrylate (Sigma, 98%), was purified before using by basic alumina column to remove inhibitor.

2. Instrumentation

Three-dimensional electron diffraction (3DED) data. Samples were prepared by dispersing Cu(bzpd) which was then gently mortared in ethanol and drop-cast onto a copper grid covered in a holey carbon film. Three-dimensional electron diffraction (3DED) data were collected using a JEOL JEM-2100 TEM at room temperature, equipped with a Timepix detector from Amsterdam Scientific Instruments, while continuously rotating the crystal at 0.45° s⁻¹. The experiment was carried out using Instamatic,¹ with data reduction performed in XDS.² The acquired intensities were then used to solve the structure with SHELXT,³ and refined using SHELXL,⁴ with previously determined electron scattering factors.⁵ From the 3DED data, all non-hydrogen atoms could be located in the initial structure solution. The positions of hydrogen atoms were inferred on a geometrical basis.

Powder X-ray diffraction measurements. The sample was prepared by drop-cast on a zero-background Si disc using isopropanol and PXRD measurements were carried out using a Panalytical X'pert Pro diffractometer (Cu K α 1,2, λ 1 = 1.540598 Å, λ 2 = 1.544426 Å) set up in a Bragg–Brentano geometry. A Pawley refinement against of the PXRD data was carried out using TOPAS-Academic V6.6.

Fourier-transform infrared (FTIR). spectra were recorded on Perkin–Elmer Spectrum One spectrometer with an ATR Accessory (ZnSe, Pike Miracle Accessory) and mercury cadmium telluride (MCT) detector. Sixteen scans were averaged.

TGA. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer Diamond TA/TGA with a heating rate of 10 K min⁻¹ under nitrogen flow (200 mL min⁻¹).

SEM Measurements. Scanning electron microscopic measurements were performed by using a Zeiss Ultra Plus field emission scanning electron microscope with EHT = 10.00 kV and probe at 200 nA. Imaging was performed using an in-lens detector for surface structure and an SE2 (Everhart-Thornley) detector for topography (Zeiss, Germany). SEM-EDX analyses were performed using the AZtecEnergy) software (Oxford Instruments, UK) linked to an Oxford detector (Oxford Instruments, UK) with an 80 mm² detection window.

TEM Measurements. High-angle annular dark-field (HAADF) images and corresponding energy dispersive X-ray spectroscopy with EDS mapping collected in STEM mode were collected on a JEOL-2100F.

Liquid State NMR. ¹H-NMR (500 MHz) spectra was recorded in deuterated dimethylsulfoxide (DMSO-d₆) with tetramethylsilane as an internal standard on Agilent VNMRS500 spectrometer at 25 °C.

3. Experimental Section

Synthesis of Azide Compounds

Benzyl azide

Benzyl azide was synthesized according to the literature¹. Product was obtained pale yellow oil, yield 96%. ¹H-NMR (500 MHz, DMSO-d₆) δ 7.43–7.34 (m, 5H, -C₆H₅), 4.43 (s, 2H, CH₂-N₃). FTIR: 2108 cm⁻¹.

2-Azido-1-[4-(methoxy)phenyl] ethanone

2-azido-1-[4-(methoxy)phenyl] ethanone was synthesized according to the literature.² 2-chloro-1-phenylethan-1-one (6.5 mmol) and NaN₃ (10 mmol) were dissolved in 3 ml water and 9 ml acetonitrile solution. After adding KI (0.33 mmol) to the solution it was stirred for 3 hours at room temperature. The reaction mixture was extracted with 50 mL EtOAc. The organic phase was wash with 2 x 30 mL of brine and lastly dried over MgSO₄ and evaporated to obtain yellowish solid compounds. Considering the click reactions selectivity, the material was used without further purification.

¹H-NMR (500 MHz, CDCl₃) δ 7.89 (d, 2H), 6.97 (d, 2H), 4.51 (s, 2H), 3.89 (d, 3H).

¹³C-NMR (500 MHz, CDCl₃) δ 191.6, 164.2, 130.2, 127.3, 114.1, 55.5, 54.4

FT-IR (cm⁻¹): 2898, 2121, 1681, 1593, 1512, 1452, 1242, 1167, 1025, 937, 815, 771, 624

Ethyl-2-azidopropionate

Ethyl-2- bromopropionate (0.015 mmol, 1 eq.) was dissolved in 200 mL DMSO and NaN₃ (1.5 eq.) was added in small portions to the reaction media. The solution was stirred for 3 hours at room temperature. 200 mL water was added to the reaction mixture and let down cool to room temperature. After cooling down the aqueous solution was extracted with 3 x 100 mL Et₂O. The organic layers were merged and washed with 2 x 100 mL water and 100 mL brine and lastly dried over MgSO₄ and evaporated to yield an azide compound.

¹H-NMR (500 MHz, CDCl₃) δ 4.07 (m, 2H), 3.91 (m, 1H), 1.29 (d, 3H), 1.15 (t, 3H)

¹³C-NMR (500 MHz, CDCl₃) δ 170.7, 61.4, 57.0, 16.3, 13.7

FT-IR (cm⁻¹): 2985, 2115, 1732, 1259, 1184

Synthesis of 1,2,3-triazoles

Azide compound (1 mmol) and Cu(bzpdC) were placed 0.5 mL MeCN in a Pyrex tube with a magnetic stir bar, after a while alkyne compound was slowly added to the solution. The tube was placed on a magnetic stirrer for different reaction times. Reactions were followed by ¹H-NMR measurements for each entry and all yields were calculated according to the recorded ¹H-NMR spectrum.

4. Figures and Tables

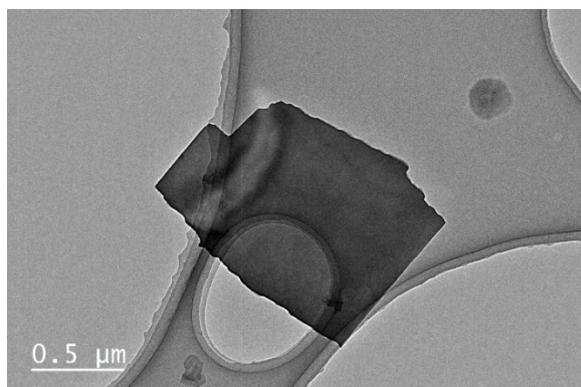


Figure S1. One of the six crystals studied by 3DED measurements.

Table S1. Crystallographic data and refinement details of Cu(bzpdC), as determined from 3DED data through a merging of 6 individual datasets.

Empirical formula	C ₁₅ H ₈ Cu ₂ O ₅
Formula weight	395.32 g mol ⁻¹
Temperature	293(2) K
Wavelength	0.0251 Å
Crystal system	Monoclinic
Space group	P21/n (No. 14)
Unit cell dimensions	a = 3.950(8) Å b = 29.930(6) Å c = 12.040(2) Å β = 92.96(3)°
Volume	1421(1) Å ³
Z	4
Density (calc.)	1.847 g cm ⁻³
Index ranges	-4 ≤ h ≤ 4 -34 ≤ k ≤ 34 -14 ≤ l ≤ 14
Reflections collected	25475
Completeness (0.80 Å)	86.7 %
Independent reflections	2486 [R(int) = 0.1992]
Data / restr. / param.	2486/160/199
Goodness-of-fit on F ²	1.098
Final R index [I > 2σ(I)]	R1 = 0.1854

Table S2. Crystallographic table for the Pawley refinement of Cu(bpzdc) against PXRD data.

Crystal system	Monoclinic
Space group	P21/n (No. 14)
Unit cell dimensions	a = 3.650(8) Å b = 28.754(3) Å c = 11.469(4) Å $\beta = 94.9(2)^\circ$
Volume (Å ³)	1199(3) Å ³
Wavelength	$\lambda_1 = 1.540598$ Å $\lambda_2 = 1.544426$ Å
Refinement method	Pawley
Refinement statistics	Rwp = 4.27 % GOF = 1.16

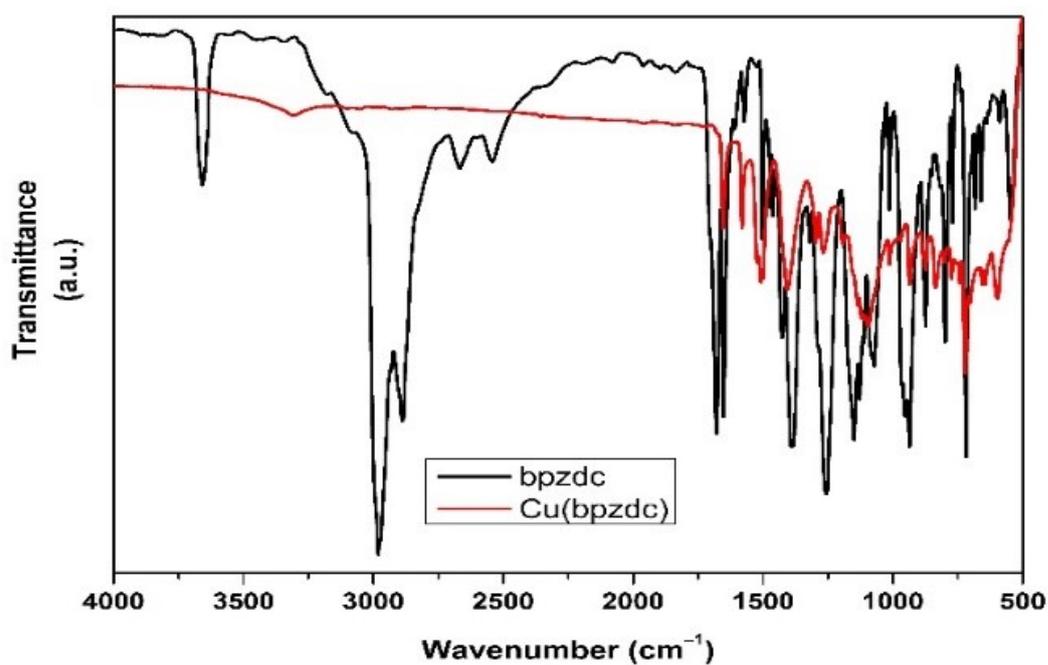


Figure S2. IR spectra of bpzdc (black) and Cu(bpzdc) (red).

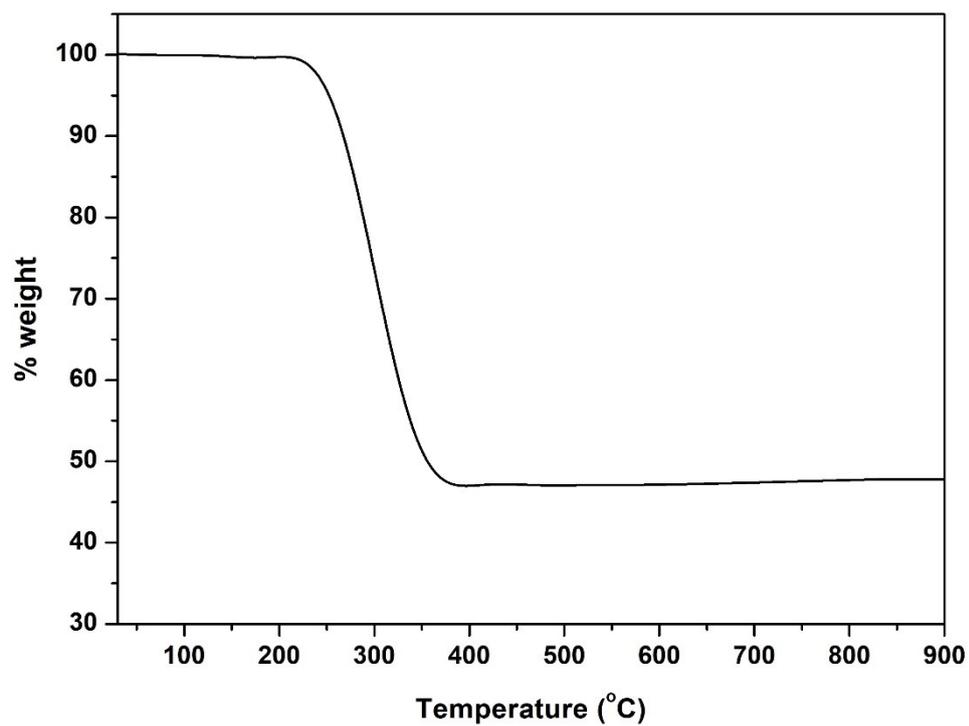


Figure S3. Thermogravimetric analysis of Cu(bzpdC).

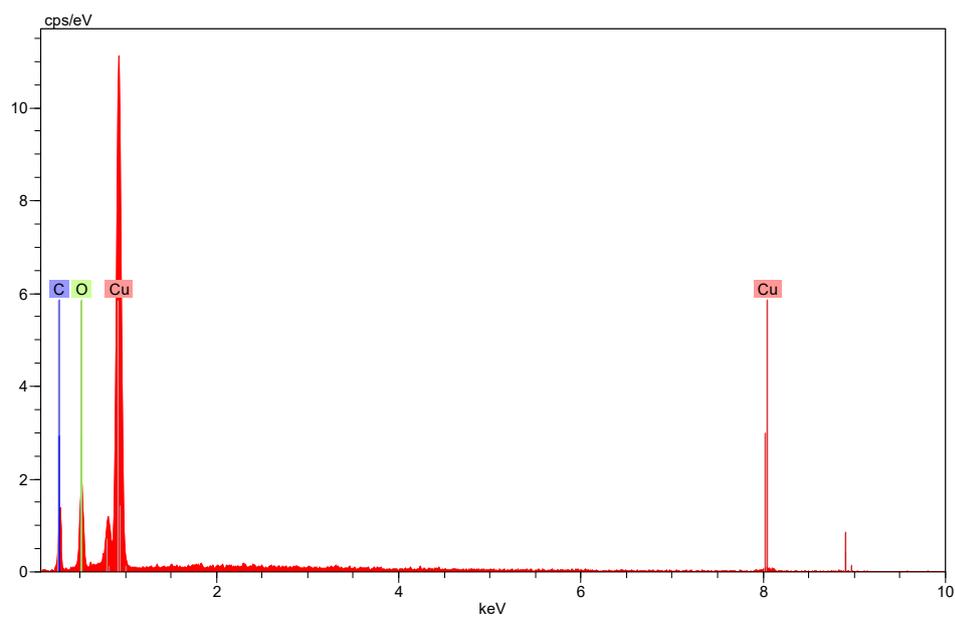


Figure S4. Qualitative SEM-EDX analysis of Cu(bzpdC).

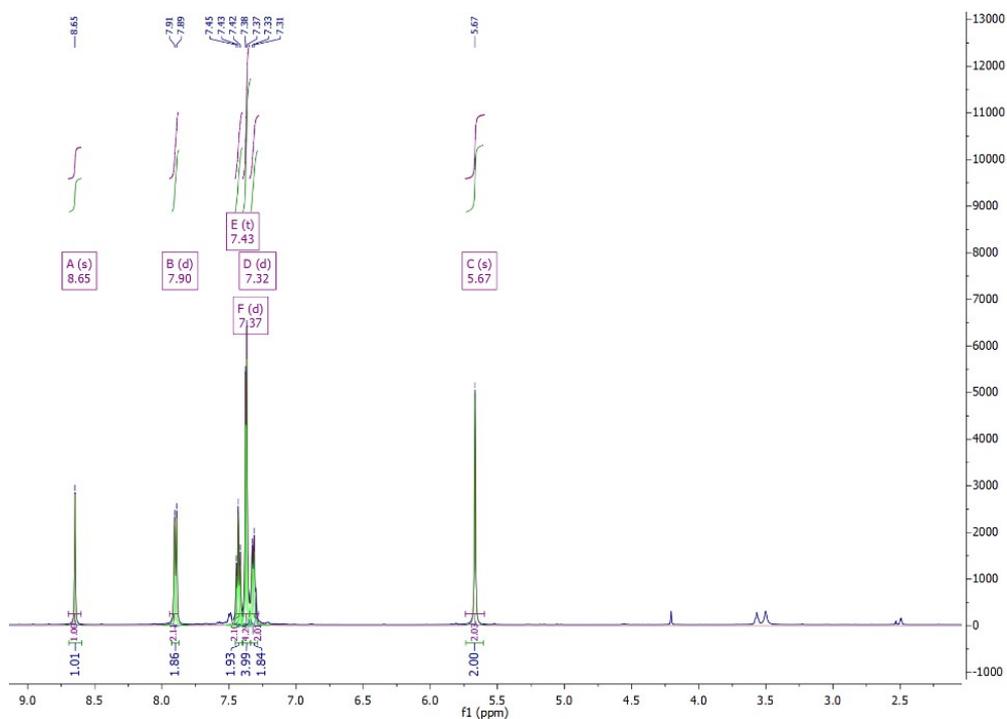


Figure S5. $^1\text{H-NMR}$ spectrum of 4-Benzyl-1-phenyl-1H-1,2,3-triazole.

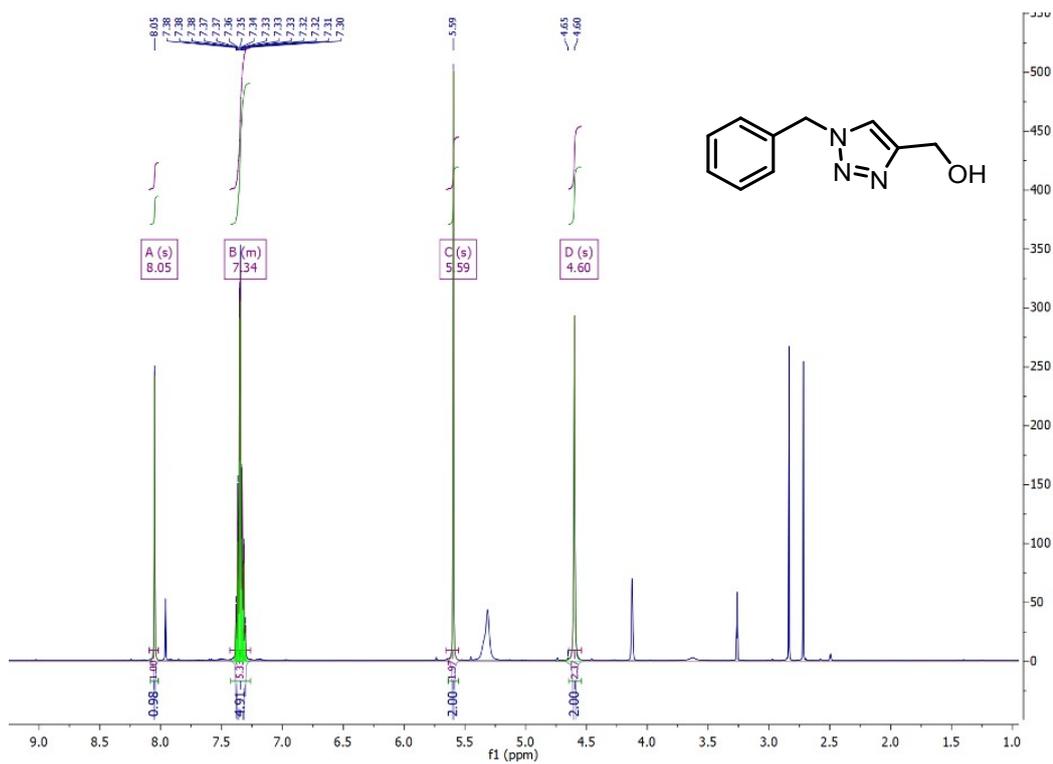


Figure S6. $^1\text{H-NMR}$ spectrum of (1-Benzyl-1H-1,2,3-triazol-4-yl)methanol.

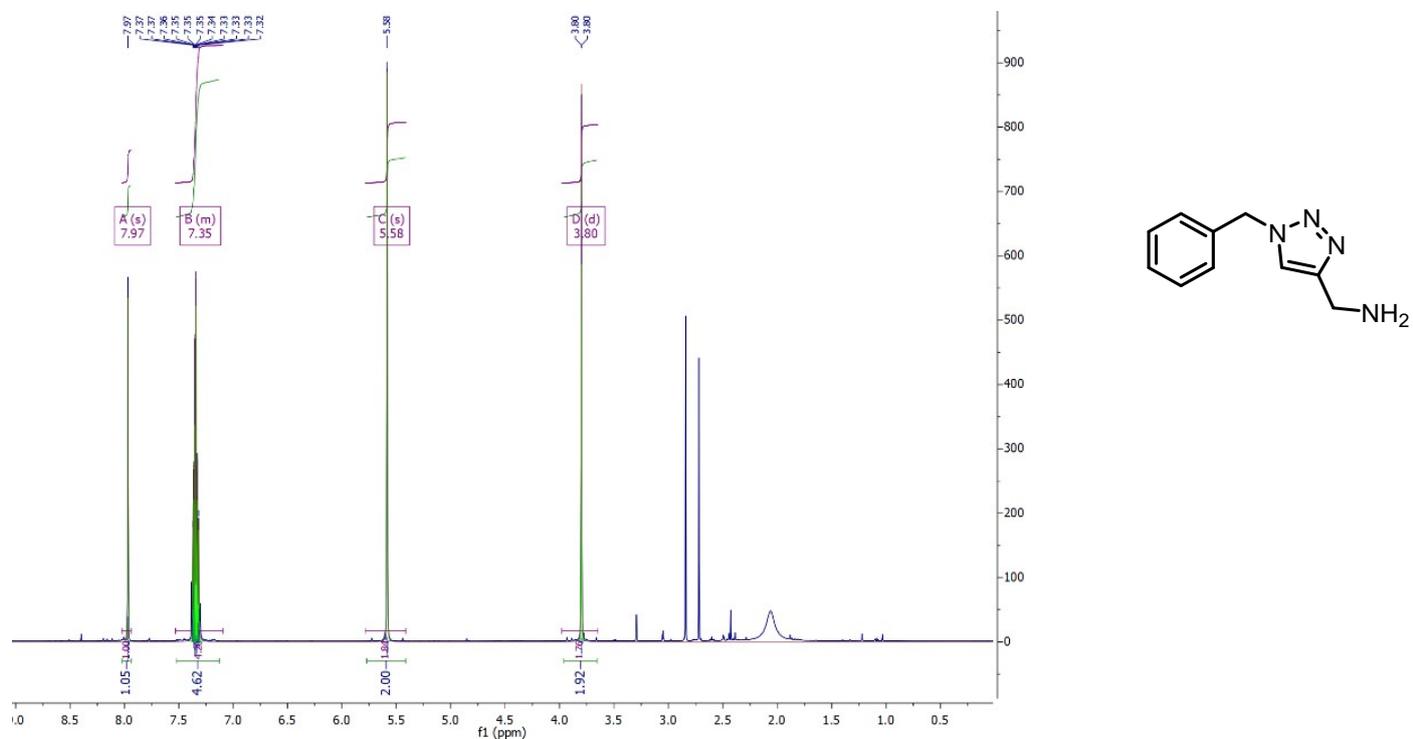


Figure S7. $^1\text{H-NMR}$ spectrum of (1-Benzyl-1H-1,2,3-triazol-4-yl)methanamine.

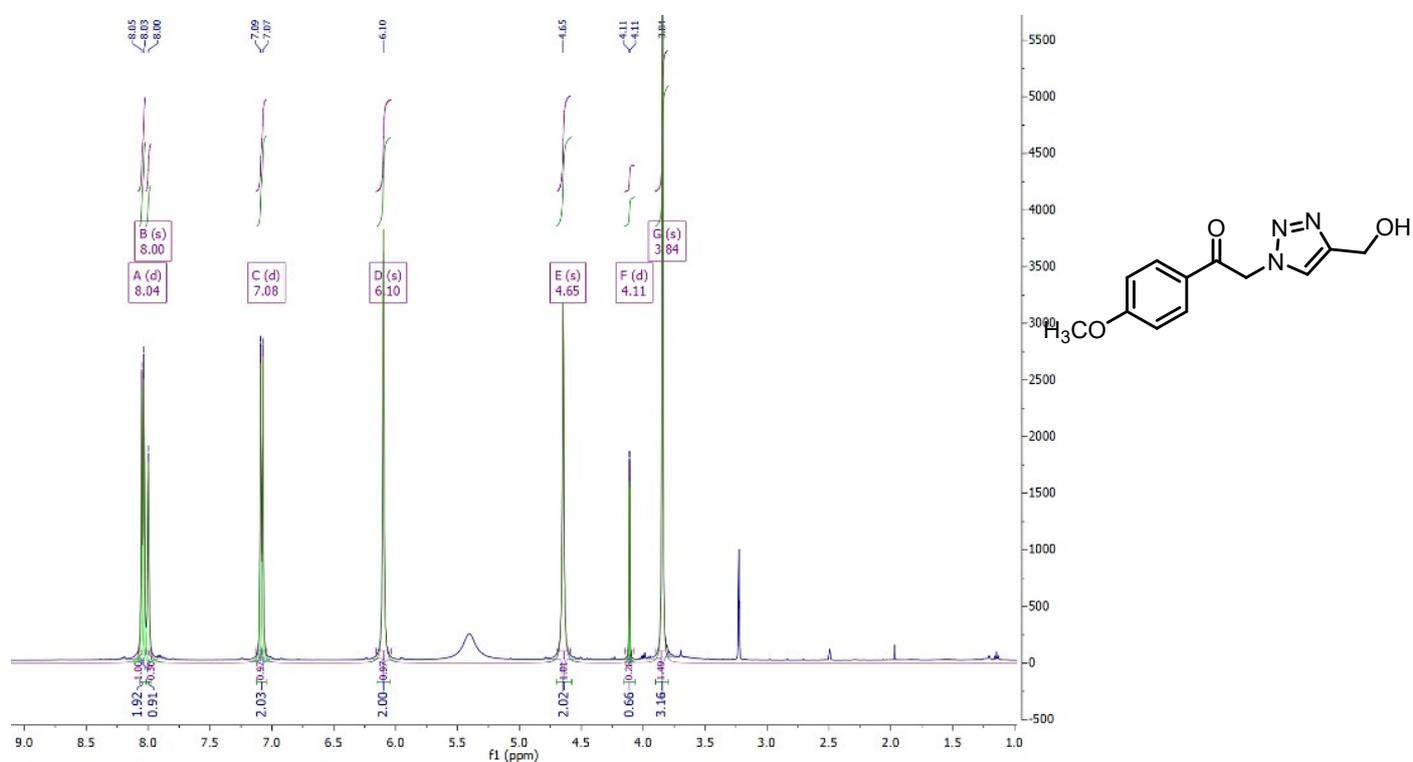


Figure S8. $^1\text{H-NMR}$ spectrum of 2-(4-(hydroxymethyl)-1H-1,2,3-triazol-1-yl)-1-(4-methoxyphenyl)ethan-1-one.

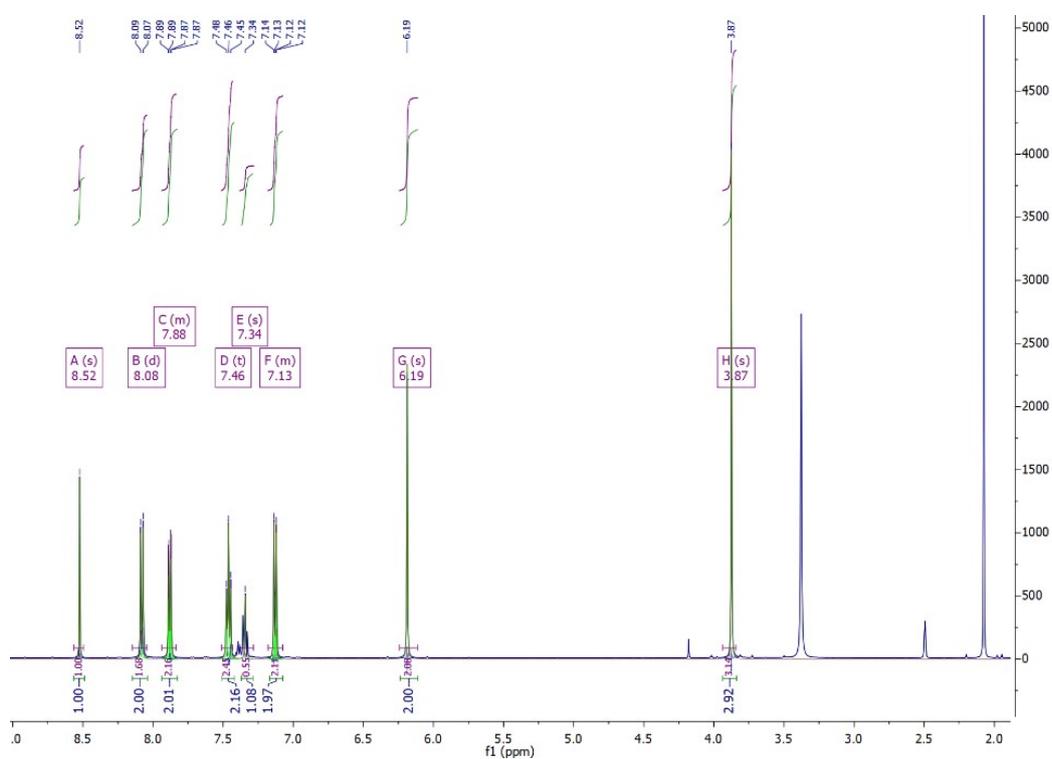


Figure S9. $^1\text{H-NMR}$ spectrum of 1-(4-methoxyphenyl)-2-(4-phenyl-1H-1,2,3-triazol-1-yl)ethan-1-one.

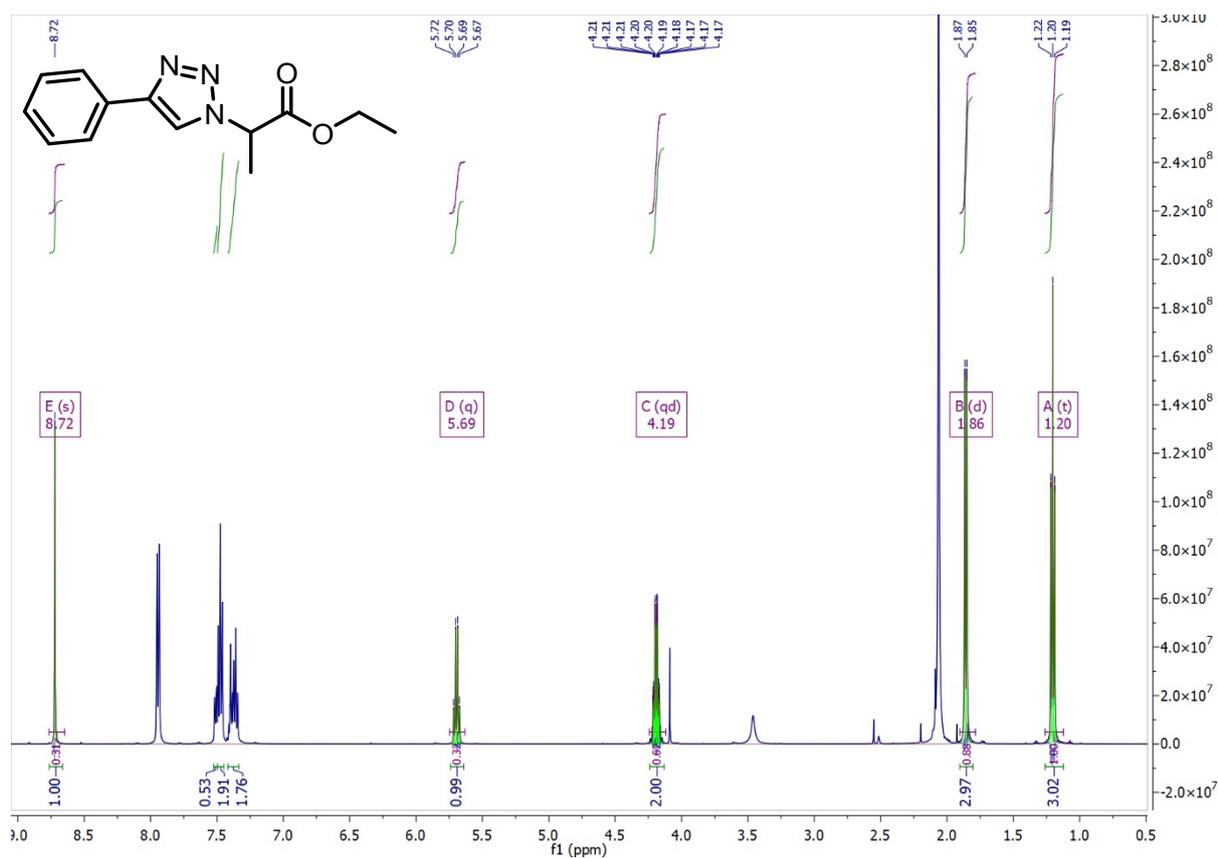


Figure S10. ¹H-NMR spectrum of Ethyl 2-(4-phenyl-1H-1,2,3-triazol-1-yl)propanoate

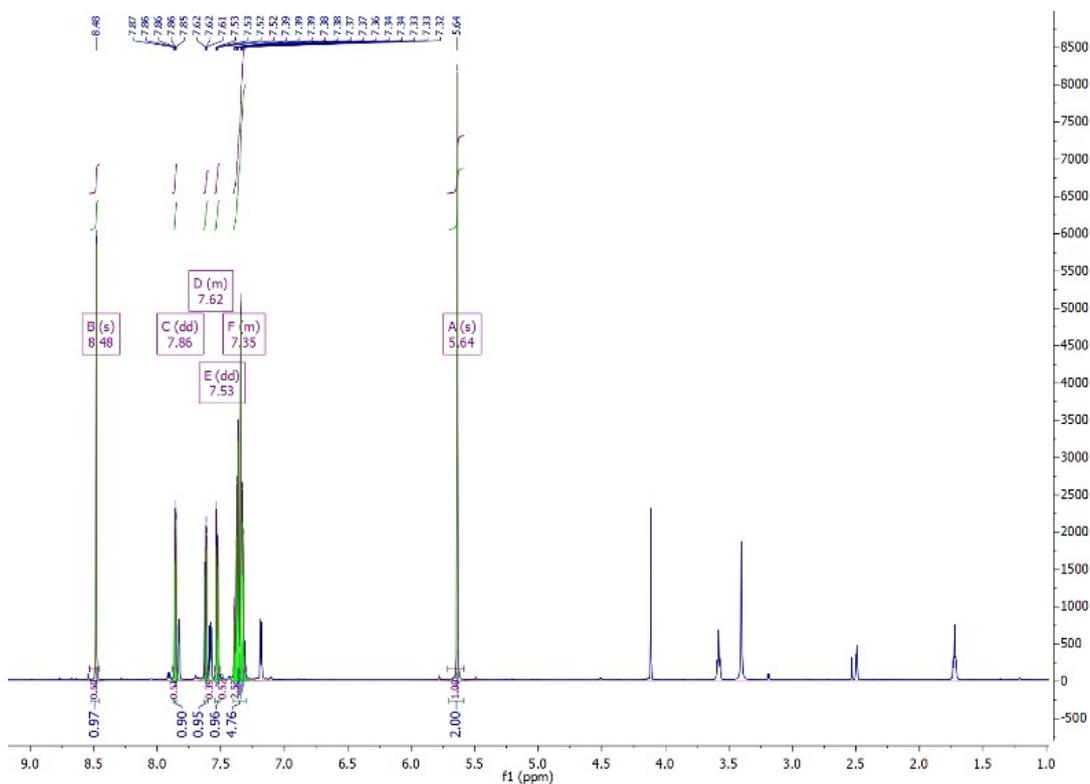


Figure S11. ¹H-NMR spectrum of 1-Benzyl-4-(thiophen-3-yl)-1H-1,2,3-triazole.

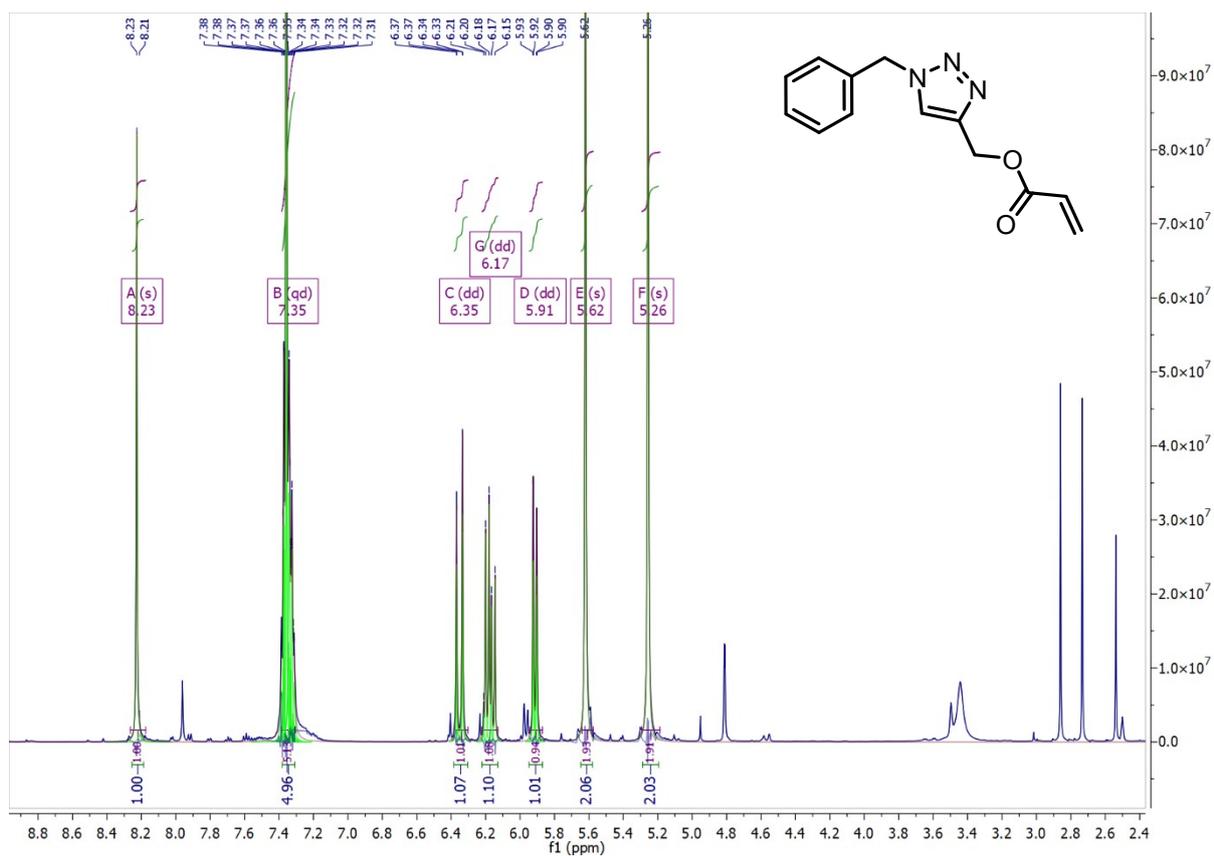


Figure S12. $^1\text{H-NMR}$ spectrum of (1-Benzyl-1H-1,2,3-triazol-4-yl)methyl acrylate.

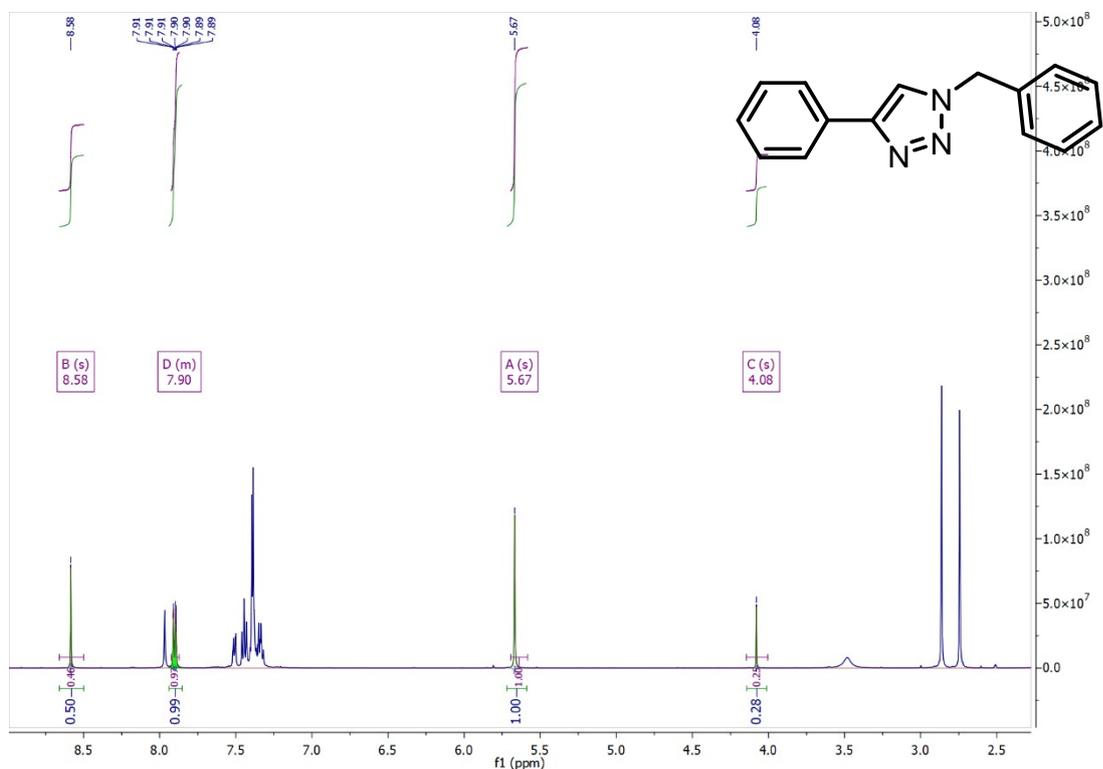


Figure S13. $^1\text{H-NMR}$ spectrum of click reaction between benzyl azide and phenyl acetylene catalyzed by $\text{Cu}(\text{OAc})_2$ in the presence of sodium ascorbate.

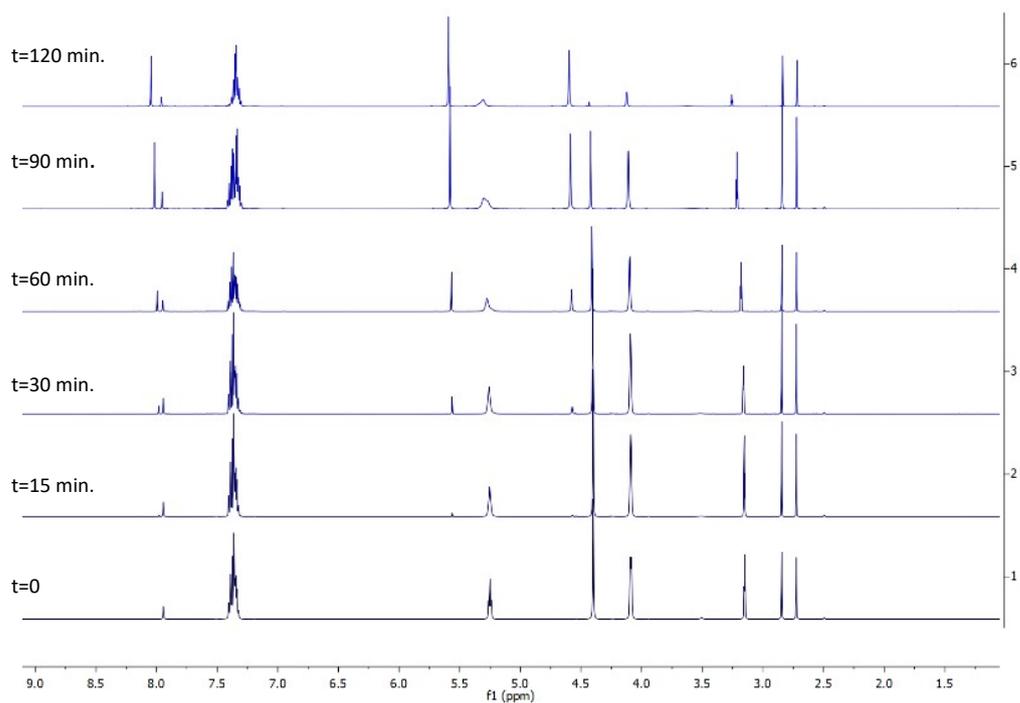


Figure S14. ¹H-NMR spectra of entry 4 with different time intervals.

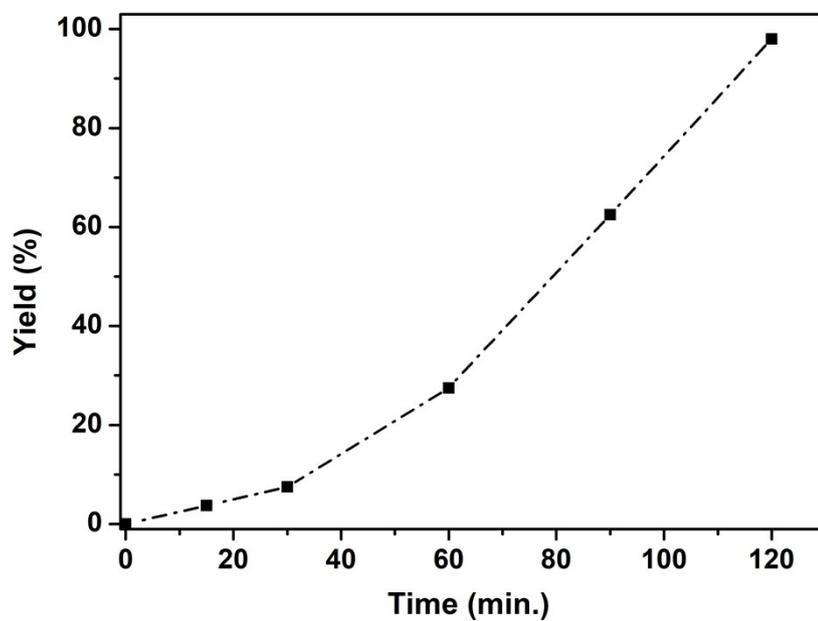


Figure S15. Kinetic investigation of click reaction (entry 4) catalyzed by Cu(bzpd).

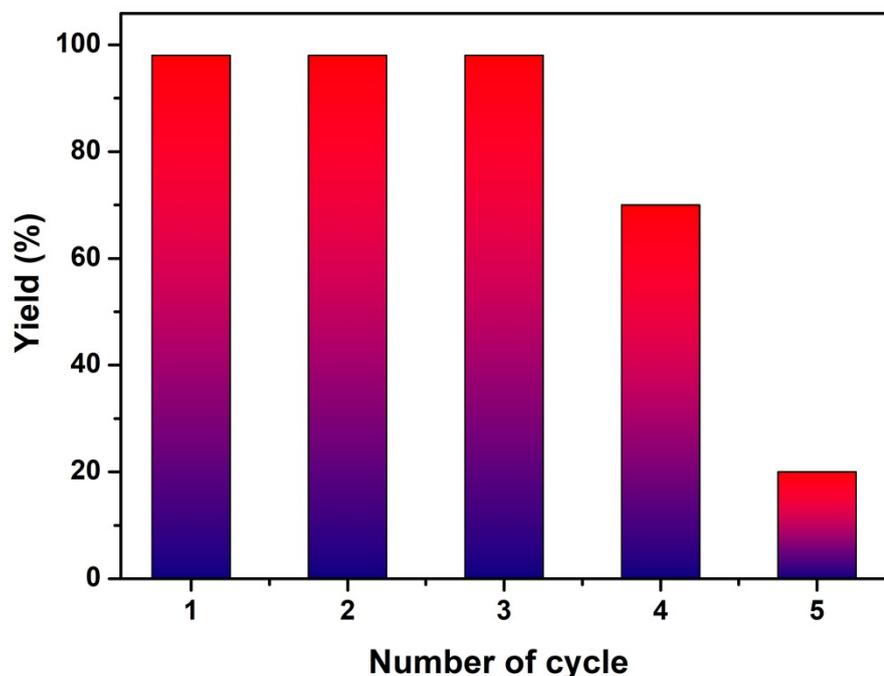


Figure S16. Recyclability of Cu(bzpdcc) for the catalyzed click chemistry (entry 4).

Supplementary References

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