

Green approach for Synthesizing Copper-containing ZIFs as efficient catalysts for Green Click chemistry

Alireza Pourvahabi Anbari ^{1,2}, Shima Rahmdel Delcheh ³, Philippe M. Heynderickx^{2,6}, Somboon Chaemcheun ⁵, Serge Zhuiykov ^{2,4}, Francis Verpoort ^{5,7,*}

¹ Department of Chemistry, Faculty of Science, Ghent University, 9000 Ghent, Belgium

² Center for Environmental and Energy Research (CEER), Ghent University Global Campus, Incheon, 406-840, South Korea

³ Department of Chemistry, Guilan University, Rasht, Iran

⁴ Department of Solid-State Sciences, Faculty of Science, Ghent University, 9000 Ghent, Belgium

⁵ State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, China

⁶ Department of Green Chemistry and Technology, Faculty of Bioscience Engineering, Ghent University, Coupure Links 653, Ghent, B-9000, Belgium

⁷ National Research Tomsk Polytechnic University, Lenin Avenue 30, 634050 Tomsk, Russian Federation

Corresponding author: Francis Verpoort; email: francis@whut.edu.cn

Contents

Figure S1: IR pattern for Cu _{10%} -ZIF-8.....	3
Figure S2: IR pattern for Cu _{20%} -ZIF-67.....	3
Figure S3: ¹ H NMR of 1-benzyl-4-phenyl-1H-1,2,3-triazole (product) from reaction catalyst by Cu _{10%} -ZIF-8.....	4
Figure S4: ¹³ C NMR of 1-benzyl-4-phenyl-1H-1,2,3-triazole (product) from reaction catalyst by Cu _{10%} -ZIF-8.....	5

Figure S5: ^1H NMR of 1-benzyl-4-phenyl-1H-1,2,3-triazole (product) from reaction catalyst by $\text{Cu}_{20\%}\text{-ZIF-67}$	6
Figure S6: ^{13}C NMR of 1-benzyl-4-phenyl-1H-1,2,3-triazole (product) from reaction catalyst by $\text{Cu}_{10\%}\text{-ZIF-67}$	7
Table S1: Applying different types of Organic halides and Azides to achieve 1,2,3 triazoles and its derivatives.....	8
Figure S7. The color change with different percentage of Cu (a) ZIF-67 (b) $\text{Cu}_{10}\text{ZIF-67}$ (c) $\text{Cu}_{20}\text{ZIF-67}$ (d) $\text{Cu}_{30}\text{ZIF-67}$ (e) $\text{Cu}_{40}\text{ZIF-67}$ (f) $\text{Cu}_{50}\text{ZIF-67}$ (g) ZIF-8 (h) $\text{Cu}_{10}\text{ZIF-8}$ (i) $\text{Cu}_{20}\text{ZIF-8}$ (j) $\text{Cu}_{30}\text{ZIF-8}$ (k) $\text{Cu}_{40}\text{ZIF-8}$ (l) $\text{Cu}_{50}\text{ZIF-8}$	10
Figure S 8. N_2 adsorption/desorption curves for Cu-ZIF-8 and Cu-ZIF-67 materials with different amount of copper (b) $\text{Cu}_{20}\text{ZIF-8}$, (c) $\text{Cu}_{30}\text{ZIF-8}$, (d) $\text{Cu}_{40}\text{ZIF-8}$, (e) $\text{Cu}_{50}\text{ZIF-8}$, (f) $\text{Cu}_{10}\text{ZIF-67}$, (h) $\text{Cu}_{30}\text{ZIF-67}$, (i) $\text{Cu}_{40}\text{ZIF-67}$, (j) $\text{Cu}_{50}\text{ZIF-67}$	11
Table S2: Porosity and surface area of $\text{Cu}_x\text{ZIF-8}$ and $\text{Cu}_x\text{ZIF-67}$ samples.....	Error! Bookmark not defined.
Figure S9. Energy dispersive spectrometry (EDS) mapping of $\text{Cu}_{20}\text{ZIF-67}$ obtained by the IST approach.....	13
Figure S10. Graphical abstract.....	14

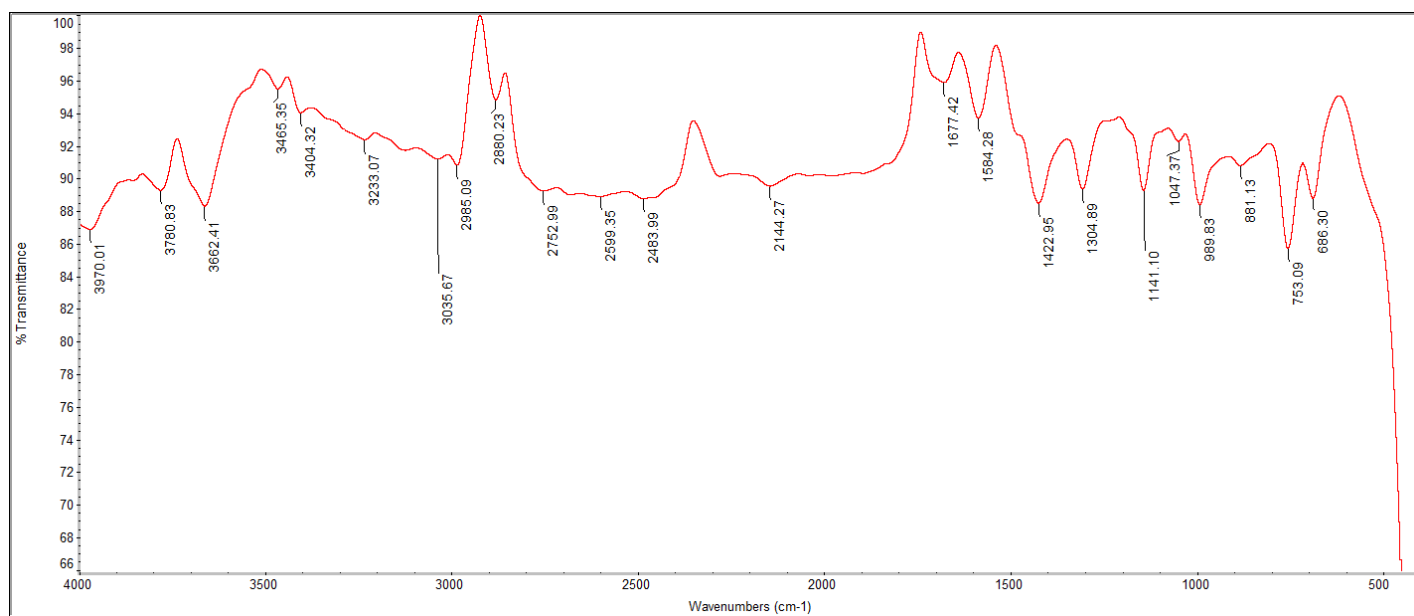


Figure S1: IR pattern for Cu₁₀-ZIF-8

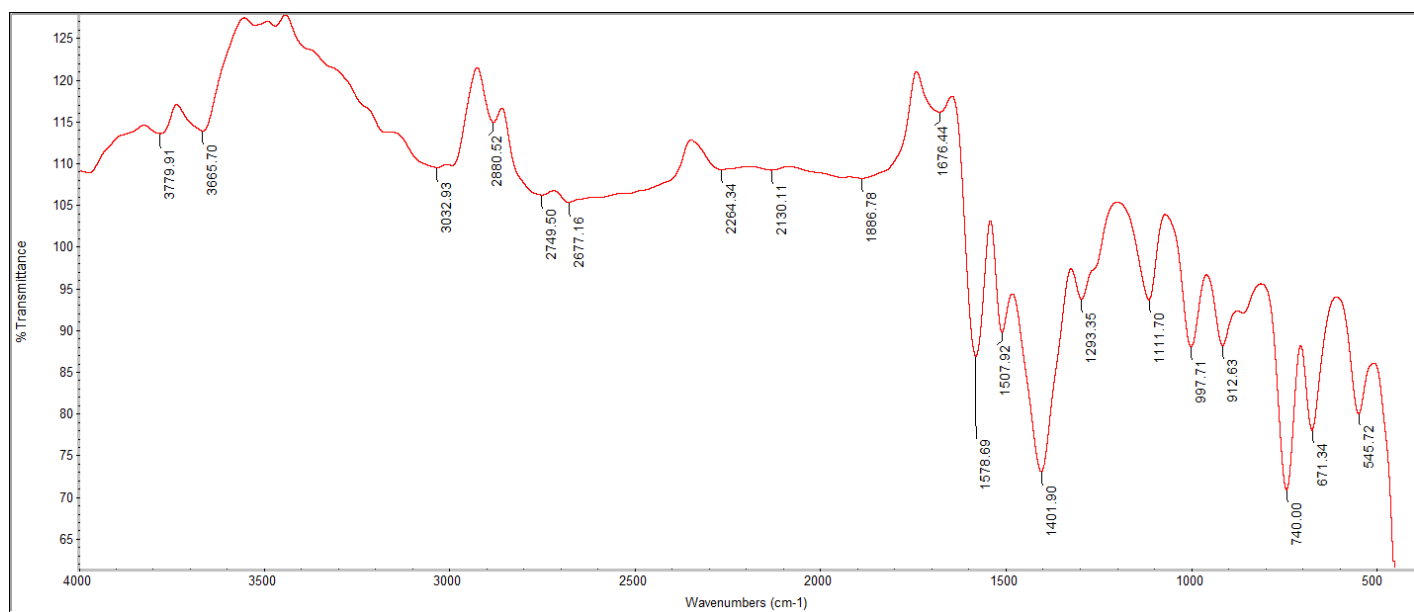


Figure S2: IR pattern for Cu₂₀-ZIF-67

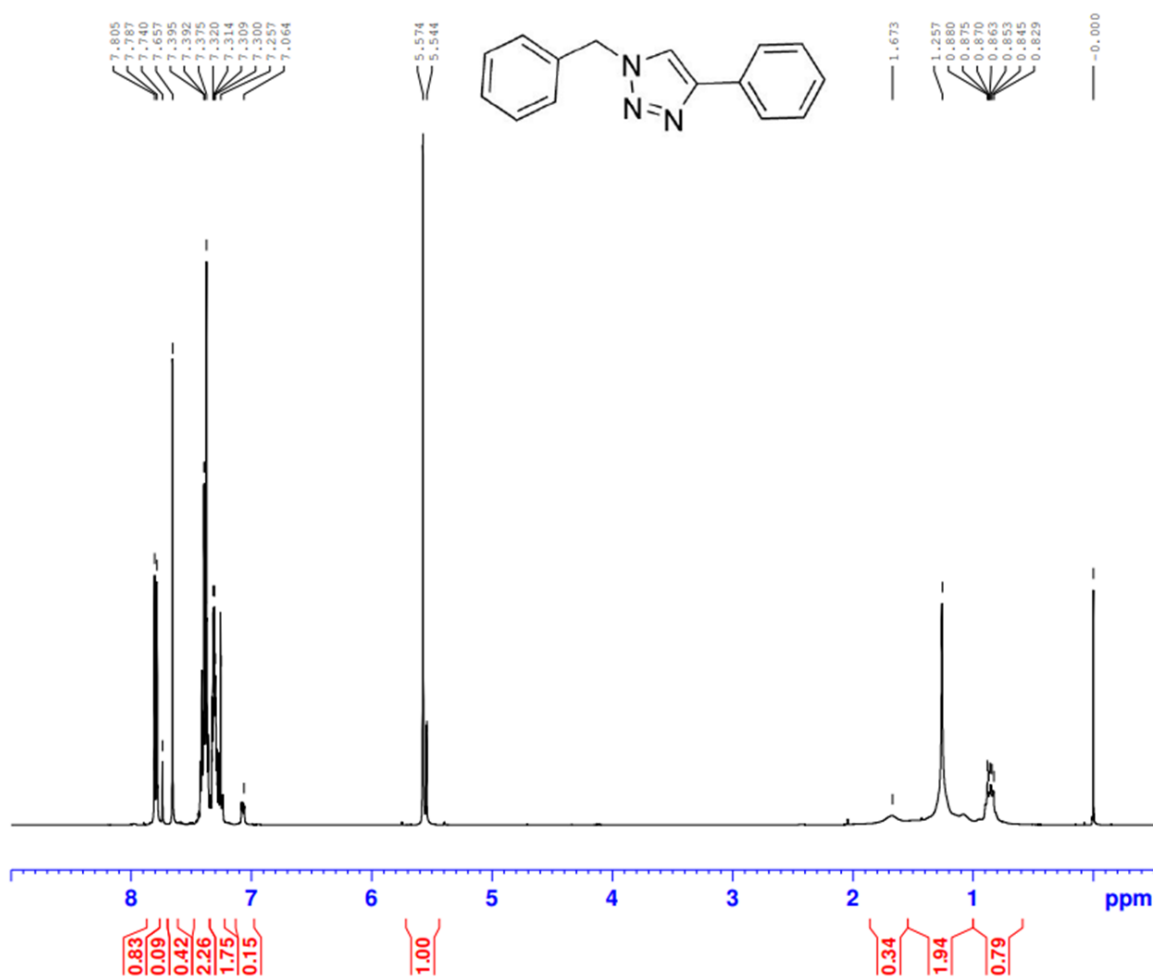


Figure S3: ¹H NMR of 1-benzyl-4-phenyl-1H-1,2,3-triazole (product) from reaction catalyst by Cu₁₀-ZIF-8

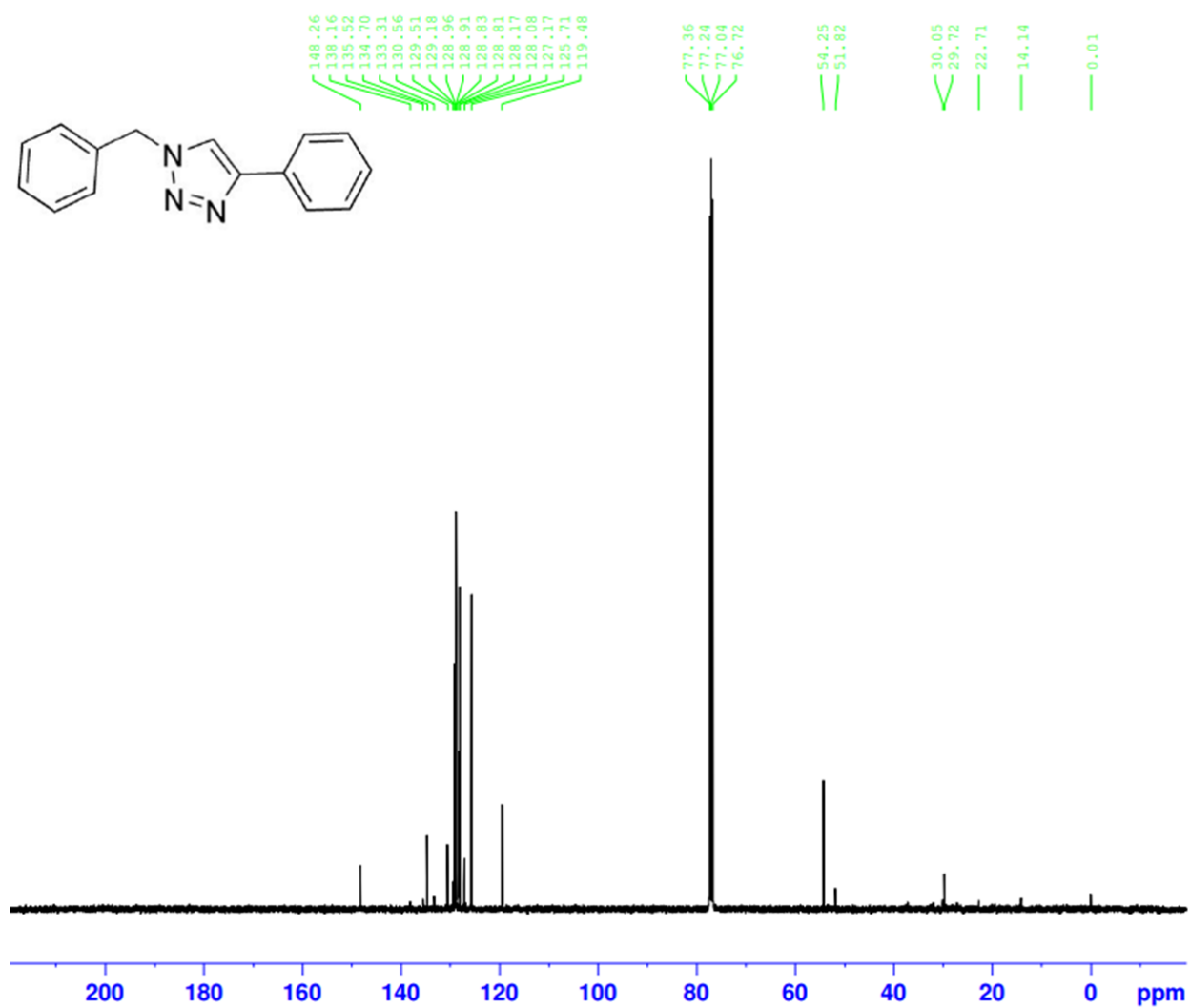


Figure S4: ¹³C NMR of 1-benzyl-4-phenyl-1H-1,2,3-triazole (product) from reaction catalyst by Cu₁₀-ZIF-8

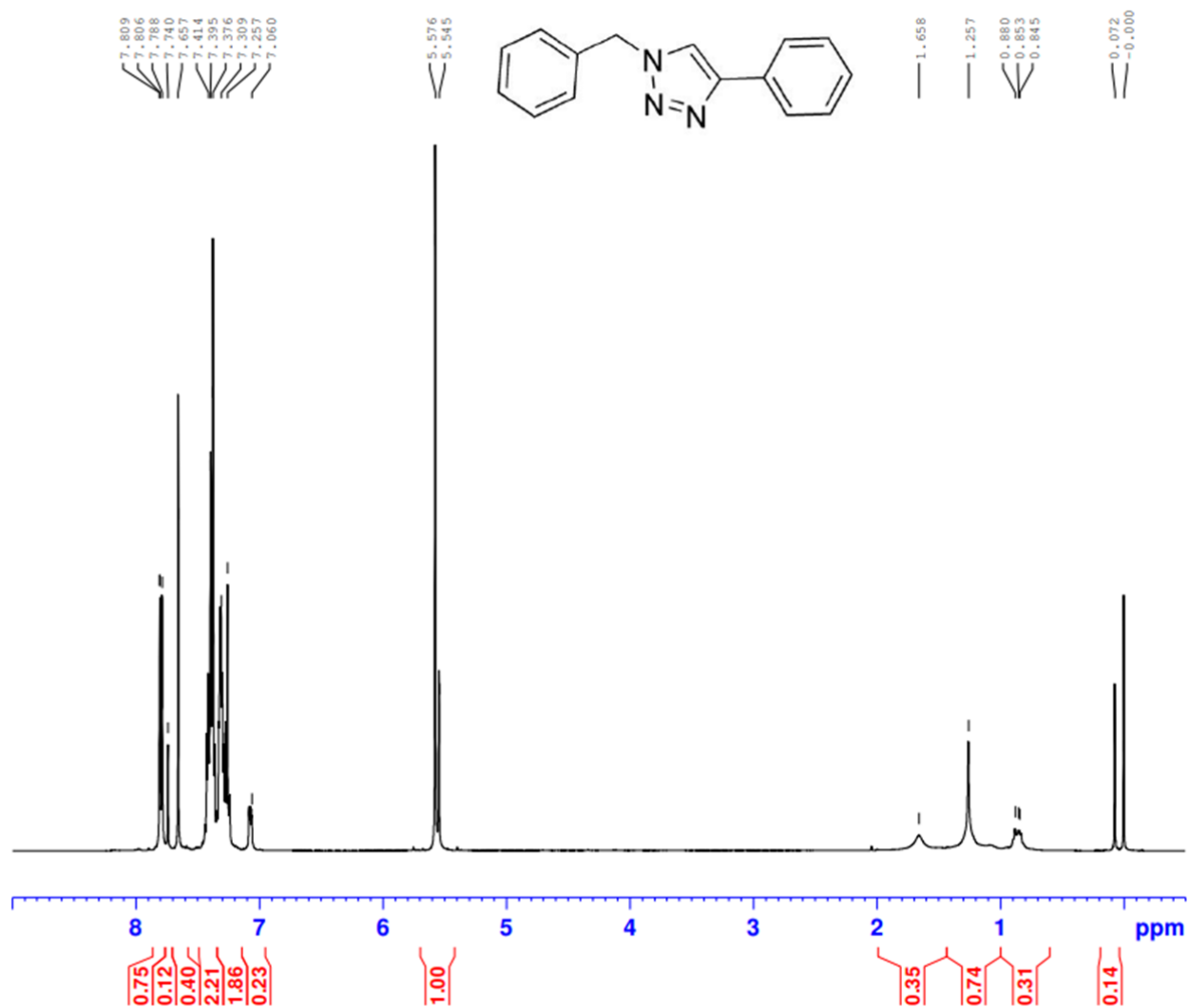


Figure S5: ¹H NMR of 1-benzyl-4-phenyl-1H-1,2,3-triazole (product) from reaction catalyst by Cu₂₀-ZIF-67

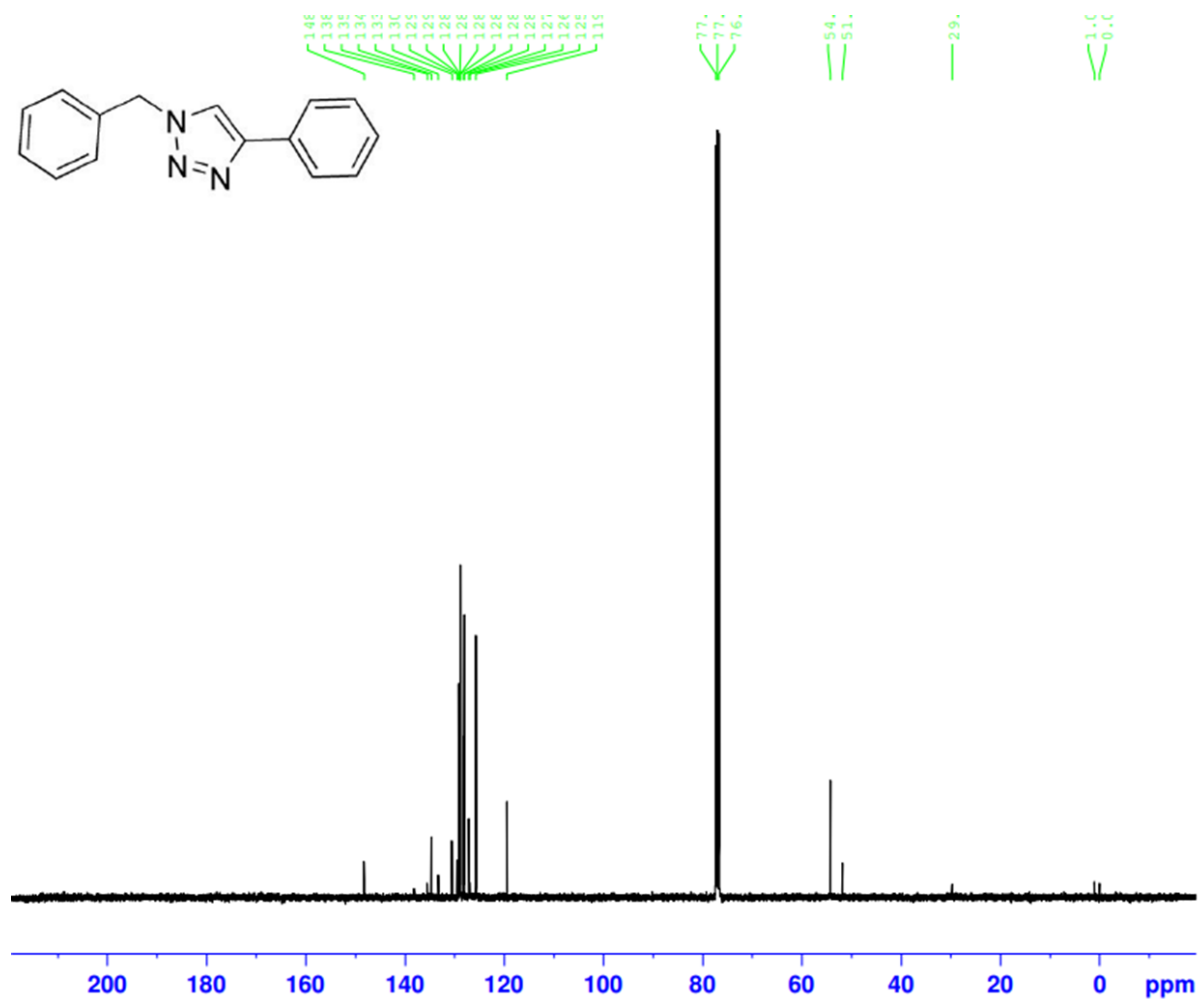
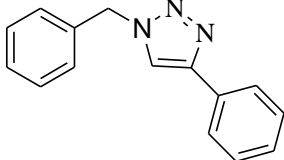
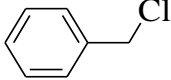
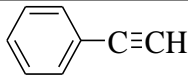
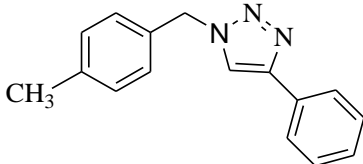
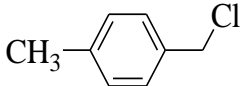
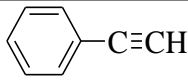
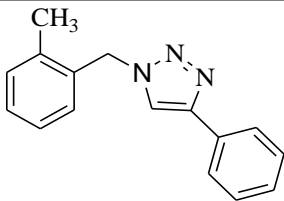
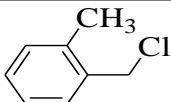
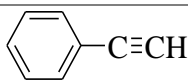
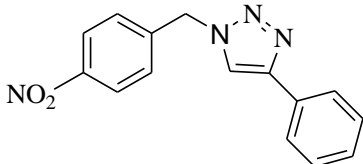
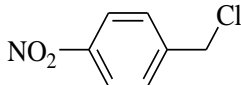
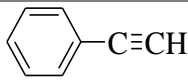
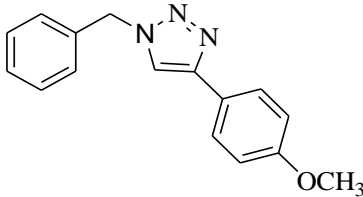
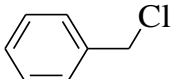
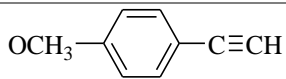
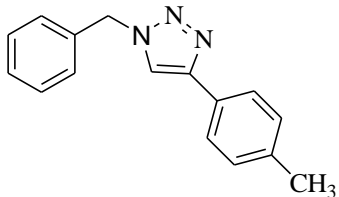
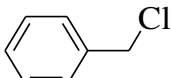
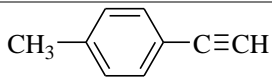
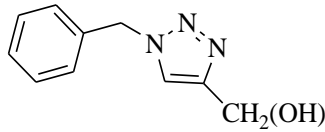
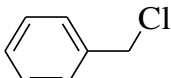
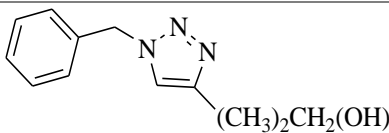
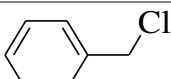


Figure S6: ¹³C NMR of 1-benzyl-4-phenyl-1H-1,2,3-triazole (product) from reaction catalyst by Cu₁₀-ZIF-67

	product	Organic halides	Alkynes	Yield
1				99
2				94
3				83
4				91
5				96
6				96
7			$(\text{HO})\text{CH}_2-\text{C}\equiv\text{CH}$	55
8			$(\text{HO})\text{CH}_2(\text{CH}_3)-\text{C}\equiv\text{CH}$	67

9				97
10				95
11				96
12				81
13				65
14				59
15				63
16				74

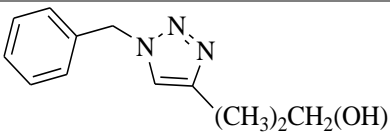
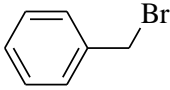
17			$(\text{HO})(\text{CH}_3)_2\text{CH}_2-\text{C}\equiv\text{CH}$	78
----	---	---	---	----

Table S1: Applying different types of Organic halides and Azides to achieve 1,2,3 triazoles and its derivatives.

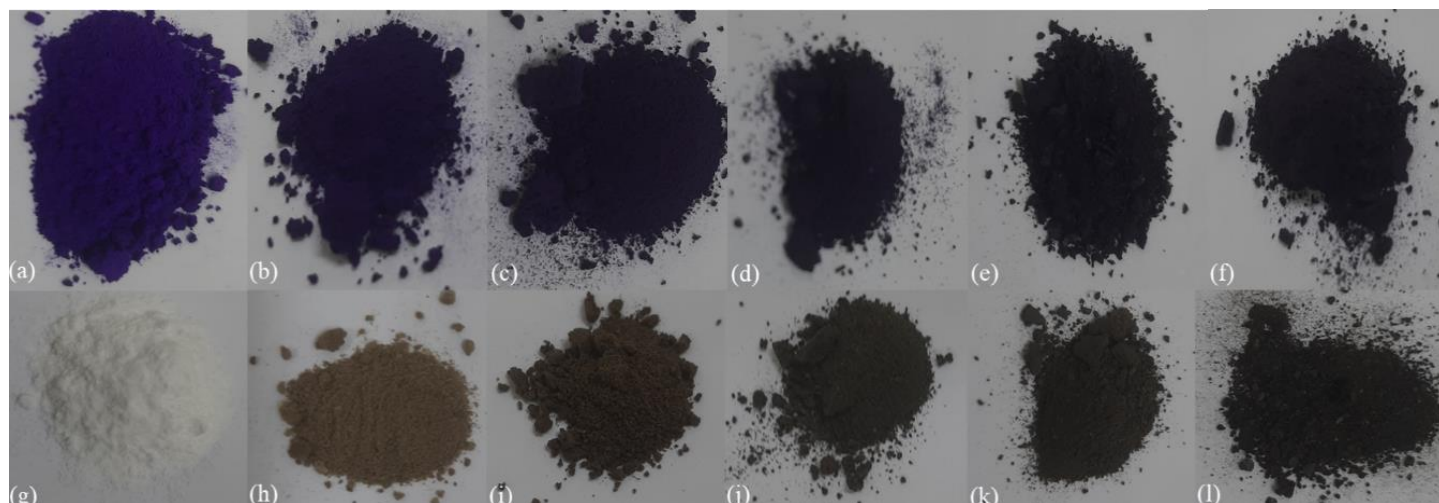
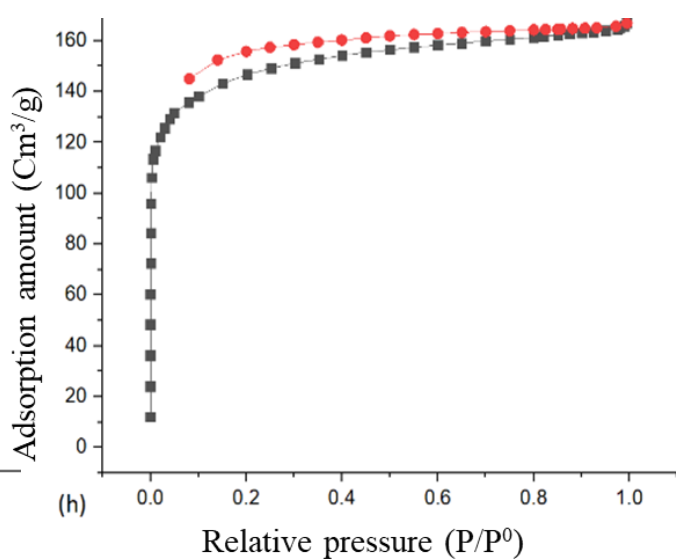
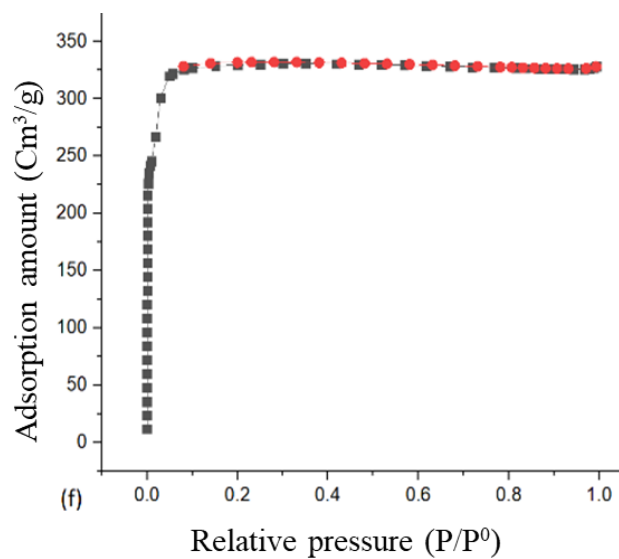
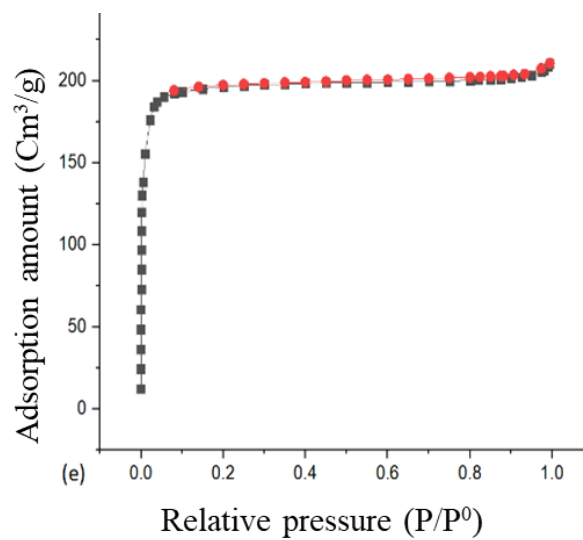
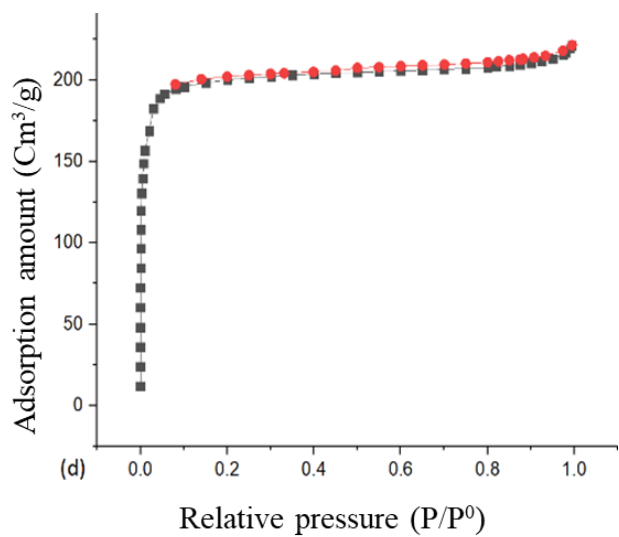
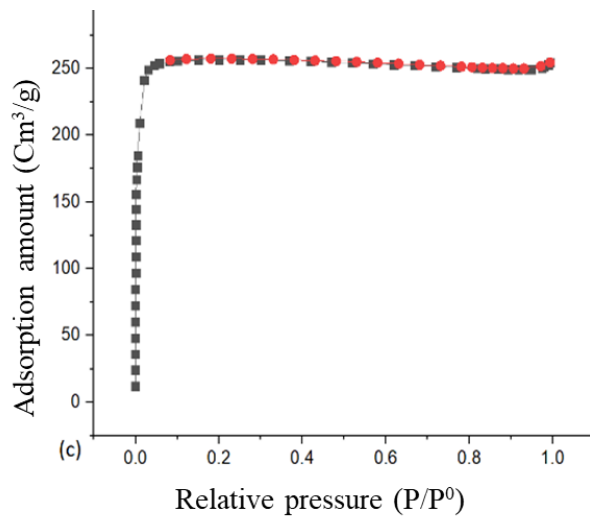
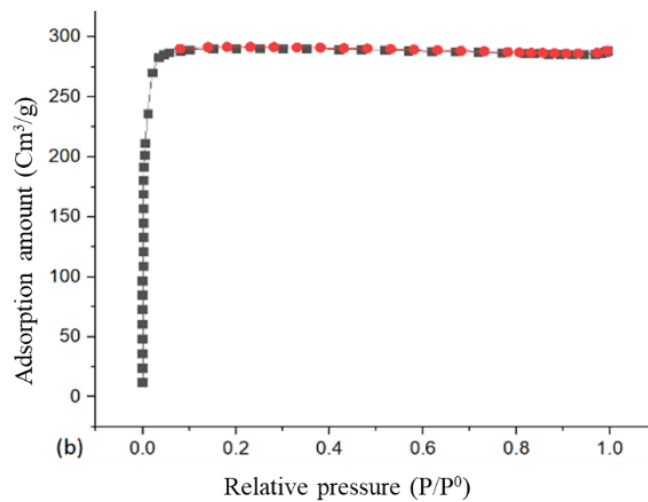


Figure S7. The color change with different percentage of Cu (a) ZIF-67 (b) $\text{Cu}_{10}\text{ZIF-67}$ (c) $\text{Cu}_{20}\text{ZIF-67}$ (d) $\text{Cu}_{30}\text{ZIF-67}$ (e) $\text{Cu}_{40}\text{ZIF-67}$ (f) $\text{Cu}_{50}\text{ZIF-67}$ (g) ZIF-8 (h) $\text{Cu}_{10}\text{ZIF-8}$ (i) $\text{Cu}_{20}\text{ZIF-8}$ (j) $\text{Cu}_{30}\text{ZIF-8}$ (k) $\text{Cu}_{40}\text{ZIF-8}$ (l) $\text{Cu}_{50}\text{ZIF-8}$



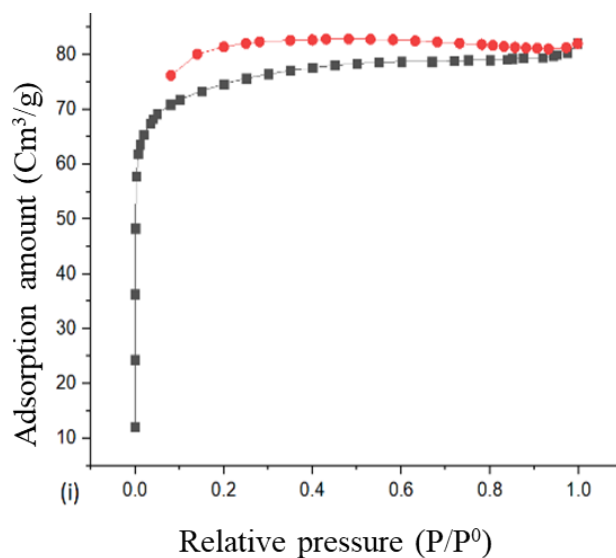


Figure S 8. N₂ adsorption/desorption curves for Cu-ZIF-8 and Cu-ZIF-67 materials with different amount of copper
 (b) Cu₂₀ZIF-8, (c) Cu₃₀ZIF-8, (d) Cu₄₀ZIF-8, (e) Cu₅₀ZIF-8, (f) Cu₁₀ZIF-67, (h) Cu₃₀ZIF-67, (i) Cu₄₀ZIF-67, (j) Cu₅₀ZIF-67

sample	BET	Langmuir	Pore size (nm)	Pore volume (cm ³ .g ⁻¹)
Cu ₂₀ ZIF-8	1248.80	1328.26	1.429	0.446
Cu ₃₀ ZIF-8	1102.68	1173.18	1.427	0.393
Cu ₄₀ ZIF-8	831.62	885.43	1.647	0.342
Cu ₅₀ ZIF-8	834.25	881.79	1.562	0.325
Cu ₁₀ ZIF-67	1429.04	1562.15	1.420	0.508
Cu ₃₀ ZIF-67	562.90	607.94	1.834	0.256
Cu ₄₀ ZIF-67	286.20	313.10	1.744	0.126
Cu ₅₀ ZIF-67	277.73	299.93	1.667	0.115

Table S2: Porosity and surface area of Cu_xZIF-8 and Cu_xZIF-67 samples

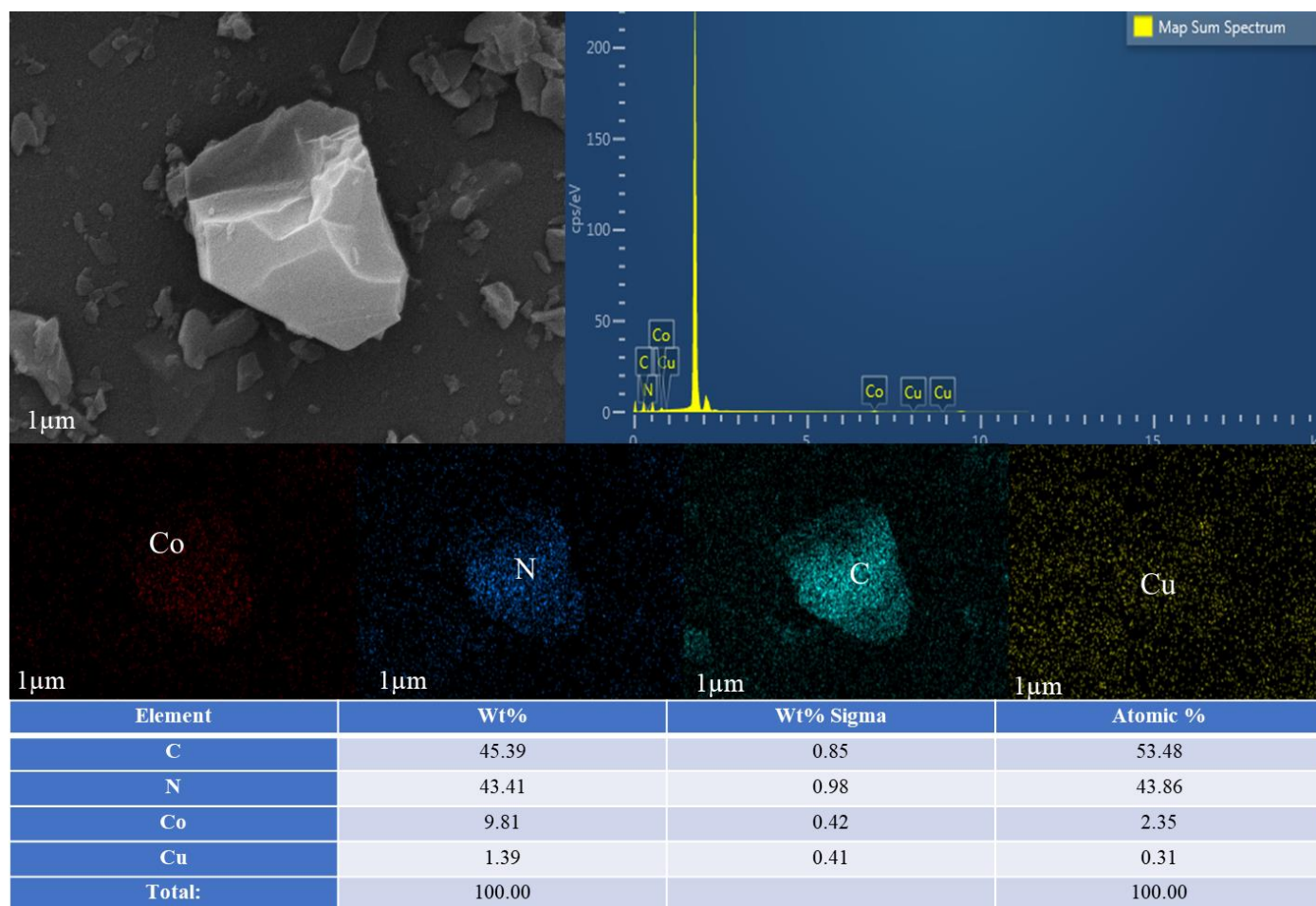


Figure S9. Energy dispersive spectrometry (EDS) mapping of $\text{Cu}_{20}\text{ZIF-67}$ obtained by the IST approach