Supplementary Information

Cu(II) immobilized on aminated epichlorohydrin activated silica (CAES): as a new, green and efficient nanocatalyst for preparation of 5-substituted-1H-tetrazoles

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Experimental

General

The purity determinations of the products were accomplished by TLC on silica gel polygram STL G/UV 254 plates. The melting points of products were determined with an Electrothermal Type 9100 melting point apparatus. The FT-IR spectra were recorded on an Avatar 370 FT-IR Therma Nicolet spectrometer. The NMR spectra were provided on Brucker Avance 100 and 400 MHz instruments in acetone-\(d_6\), DMSO-\(d_6\) and CD\(_3\)CN. Mass spectra were recorded with Agilent Technologies (HP) 5973 Network Mass Selective Detector and Shimadzu GC-MS-QP5050 instruments at 70 eV. Thermogravimetric analysis (TGA) was performed on a Shimadzu Thermogravimetric Analyzer (TG-50) under air atmosphere. BET surface area and pore size distribution were measured on a Belsorp mini II system at −196 °C using N\(_2\) as adsorbate. Inductively coupled plasma (ICP) was carried out on a Varian, VISTA-PRO, CCD, Australia. All of the products were known compounds and characterized by the FT-IR and comparison of their melting points with known compounds. The structure of selected products was further confirmed by \(^1\)HNMR, \(^{13}\)CNMR spectroscopy, and mass spectrometry.
Figure 1: FT-IR (KBr) of activated silica with HCl.

Figure 2: Adsorption/desorption isotherm of activated silica with HCl.
Figure 3: BET-Plot of activated silica with HCl.

Figure 4: FT-IR (KBr) of activated silica with NaOH solution.
Figure 5: FT-IR (KBr) of epichlorohydrin-SiO$_2$.

Figure 6: FT-IR (KBr) of aminated epichlorohydrin-SiO$_2$. 
Figure 7: Adsorption/desorption isotherm of aminated epichlorohydrin-SiO$_2$.

Figure 8: BET-Plot of aminated epichlorohydrin-SiO$_2$. 
Figure 9: Thermogravimetric analysis (TGA) of aminated epichlorohydrin-SiO$_2$.

Figure 10: FT-IR (KBr) of Cu supported on aminated epichlorohydrin-SiO$_2$. 
Figure 11: Adsorption/desorption isotherm of Cu supported on aminated epichlorohydrin-SiO$_2$.

Figure 12: BET-Plot of Cu supported on aminated epichlorohydrin-SiO$_2$. 
Figure 13: ICP of Cu supported on aminated epichlorohydrin-SiO$_2$.

![Table](https://example.com/table.png)

Figure 14: ICP of fifth reused Cu supported on aminated epichlorohydrin-SiO$_2$.

![Table](https://example.com/table.png)
Figure 15: $^1$H NMR (400 MHz, DMSO-$d_6$) of 5-Phenyl-$1H$-tetrazole (Table 2, entry 1).

Figure 16: $^{13}$C NMR (100 MHz, DMSO-$d_6$) of 5-Phenyl-$1H$-tetrazole (Table 2, entry 1).
Figure 17: $^{13}$C NMR (100 MHz, DMSO-$d_6$) of 5-Phenyl-1H-tetrazole (Table 2, entry 1) expanded.

Figure 18: FT-IR (KBr) of 5-Phenyl-1H-tetrazole (Table 2, entry 1).
Figure 19: $^1$H NMR (100 MHz, DMSO-$d_6$) of 5-(4-Boromophenyl)-1$H$-tetrazole (Table 2, entry 2).

Figure 20: FT-IR (KBr) of 5-(4-Boromophenyl)-1$H$-tetrazole (Table 2, entry 2).
Figure 21: Mass spectrum of 5-(4-Boromophenyl)-1H-tetrazole (Table 2, entry 2).

Figure 22: $^1$H NMR (400 MHz, DMSO-d$_6$) of 5-(4-Chlorophenyl)-1H-tetrazole (Table 2, entry 3).
Figure 23: $^{13}$C NMR (100 MHz, DMSO-d$_6$) of 5-(4-Chlorophenyl)-1H-tetrazole (Table 2, entry 3).

Figure 24: FT-IR (KBr) of 5-(4-Chlorophenyl)-1H-tetrazole (Table 2, entry 3).
Figure 25: $^1$H NMR (100 MHz, CD$_3$CN) of 4-(1H-tetrazol-5-yl)benzonitrile (Table 2, entry 4).

Figure 26: $^{13}$C NMR (400 MHz, DMSO-$d_6$) of 4-(1H-tetrazol-5-yl)benzonitrile (Table 2, entry 4).
**Figure 27:** FT-IR (KBr) of 4-(1H-tetrazol-5-yl)benzonitrile (Table 2, entry 4).

**Figure 28:** Mass spectrum of 4-(1H-tetrazol-5-yl)benzonitrile (Table 2, entry 4).
Figure 29: $^1$H NMR (400 MHz, DMSO-d$_6$) of 5-(4-Nitrophenyl)-1H-tetrazole (Table 2, entry 5).

Figure 30: $^1$H NMR (400 MHz, DMSO-d$_6$) of 5-(4-Nitrophenyl)-1H-tetrazole (Table 2, entry 5) expanded.
Figure 31: $^{13}$C NMR (100 MHz, DMSO-d$_6$) of 5-(4-Nitrophenyl)-1$H$-tetrazole (Table 2, entry 5).

Figure 32: FT-IR (KBr) of 5-(4-Nitrophenyl)-1$H$-tetrazole (Table 2, entry 5).
**Figure 33:** $^1$H NMR (400 MHz, DMSO-$d_6$) of 4-Nitro-2-(1H-tetrazol-5-yl)benzenamine (Table 2, entry 6).

**Figure 34:** $^1$H NMR (400 MHz, DMSO-$d_6$) of 4-Nitro-2-(1H-tetrazol-5-yl)benzenamine (Table 2, entry 6) expanded.
Figure 35: $^{13}$C NMR (100 MHz, DMSO-$_d_6$) of 4-Nitro-2-(1H-tetrazol-5-yl)benzenamine (Table 2, entry 6).

Figure 36: $^{13}$C NMR (100 MHz, DMSO-$_d_6$) of 4-Nitro-2-(1H-tetrazol-5-yl)benzenamine (Table 2, entry 6) expanded.
Figure 37: FT-IR (KBr) of 4-Nitro-2-(1H-tetrazol-5-yl)benzenamine (Table 2, entry 6).

Figure 38: $^1$H NMR (100 MHz, acetone-$d_6$) of 5-(4-Ethoxyphenyl)-1H-tetrazole (Table 2, entry 7).
Figure 39: FT-IR (KBr) of 5-(4-Ethoxyphenyl)-1H-tetrazole (Table 2, entry 7).

Figure 40: $^1$H NMR (400 MHz, DMSO-d$_6$) of 5-(3, 5-Dimethoxyphenyl)-1H-tetrazole (Table 2, entry 8).
Figure 41: $^{13}$C NMR (100 MHz, DMSO-d$_6$) of 5-(3,5-Dimethoxyphenyl)-1$H$-tetrazole (Table 2, entry 8).

Figure 42: FT-IR (KBr) of 5-(3,5-Dimethoxyphenyl)-1$H$-tetrazole (Table 2, entry 8).
Figure 43: Mass spectrum of 5-(3, 5-Dimethoxyphenyl)-1H-tetrazole (Table 2, entry 8).

Figure 44: $^1$H NMR (100 MHz, CD$_3$CN) of 5-$m$-Tolyl-1H-tetrazole (Table 2, entry 9).
Figure 45: FT-IR (KBr) of 5-<i>m</i>-Tolyl-1<i>H</i>-tetrazole (Table 2, entry 9).

Figure 46: <sup>1</sup>H NMR (400 MHz, DMSO-<i>d</i><sub>6</sub>) of 4-<i>H</i>-tetrazol-5-yl phenol (Table 2, entry 10).
**Figure 47**: $^1$H NMR (400 MHz, DMSO-$d_6$) of 4-(1H-tetrazol-5-yl)phenol (Table 2, entry 10) expanded.

**Figure 48**: $^{13}$C NMR (100 MHz, DMSO-$d_6$) of 4-(1H-tetrazol-5-yl) phenol (Table 2, entry 10).
Figure 49: FT-IR (KBr) of 4-(1H-tetrazol-5-yl) phenol (Table 2, entry 10).

Figure 50: $^1$H NMR (100 MHz, DMSO-$d_6$) of 5-(Phenanthren-9-yl)-1H-tetrazole (Table 2, entry 11).
Figure 51: FT-IR (KBr) of 5-(Phenanthren-9-yl)-1\textit{H}-tetrazole (Table 2, entry 11).

Figure 52: Mass spectrum of 5-(Phenanthren-9-yl)-1\textit{H}-tetrazole (Table 2, entry 11).
Figure 53: $^1$H NMR (100 MHz, CD$_3$CN) of 5-(Thiophen-2-yl)-1H-tetrazole (Table 2, entry 12).

Figure 54: FT-IR (KBr) of 5-(Thiophen-2-yl)-1H-tetrazole (Table 2, entry 12).
Figure 55: Mass spectrum of 5-(Thiophen-2-yl)-1H-tetrazole (Table 2, entry 12).

Figure 56: FT-IR (KBr) of 4-(1H-tetrazol-5-yl) pyridine (Table 2, entry 13).
Figure 57: $^1$H NMR (400 MHz, DMSO-d$_6$) of 2-(1H-tetrazol-5-yl)pyridine (Table 2, entry 14).

Figure 58: $^{13}$C NMR (100 MHz, DMSO-d$_6$) of 2-(1H-tetrazol-5-yl)pyridine (Table 2, entry 14).
Figure 59: FT-IR of 2-(1H-tetrazol-5-yl) pyridine (Table 2, entry 14).

Figure 60: $^1$H NMR (100 MHz, CD$_3$CN) of 5-Benzyl-1H-tetrazole (Table 2, entry 15).
Figure 61: FT-IR of 5-Benzyl-1H-tetrazole (Table 2, entry 15).

Figure 62: FT-IR of 5-Isobutyl-1H-tetrazole (Table 2, entry 16).
Figure 63: $^1$H NMR (100 MHz, CDCl$_3$) of 5-Isopentyl-1H-tetrazole (Table 2, entry 17).

Figure 64: FT-IR of 5-Isopentyl-1H-tetrazole (Table 2, entry 17).