Click chemistry promoted by graphene supported copper nanoparticles

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Supporting information

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1. Materials

All chemicals and solvents, which were used for the synthesis were purchased from Sigma-Aldrich and used as received unless otherwise stated. Deutrated tetrahydrofuran (THF-d_8, 95%) was purchased from AMAR chemicals and phenyl acetylene from MERK. Graphite flakes (KFL 99.5, min 20% > 100 μm) was recieved from Kropfmühl AG. Tetrahydrofurane (THF) for recycling experiment was pre-dried over potassium hydroxide for several days, refluxed over sodium/benzophenone and freshly distilled under an argon atmosphere before use.

2. Methods

TEM, STEM and EDXS

The high-resolution transmission electron microscopy (HRTEM) analyses were performed on a FEI Titan^3 80-300 electron microscope with a c_s-image aberration corrector (FEI Company) at 300 kV acceleration voltage. Using the same instrument, scanning TEM (STEM) employing a high-angle annular dark field (HAADF) detector (Fischione Model 3000, camera length: 145 mm) was accomplished. STEM in combination with energy-dispersive X-ray spectroscopy (EDXS), performed with a dedicated, high-solid angle (0.7 sr) detector system (Super-X EDX analysis system, FEI Company) allowed to achieve distribution mappings of different elements of chosen samples, using the commercially available software Esprit (Bruker Company). Element distribution mappings were derived by evaluating the lateral distribution of the peak intensity, i.e., the area underlying the K_α edges of the analyzed elements, with an automatic routine provided by the software. In an attempt to evaluate the oxidation state of Cu in the copper-oxide nanoparticles, an EDXS quantification was also performed with the help of the same software, evaluating the peaks of the K-lines of the respective elements Cu and O. Since only the element ratio of Cu and O was of interest for this specific question, all other peaks in the respective EDX spectra, which originate from other elements of the sample (e.g., Cl, B and S) were only deconvoluted, but disregarded for quantification. A special Ni grid instead of a standard Cu grid was used for sample preparation to keep Cu quantification errors as low as possible.

XPS

XPS analysis was performed using a XPS PHI Versa Probe 5000 spectrometer. The pressure in the analysis chamber was typically 1.10^{-9} Torr. The XPS measurements were performed using a monochromatic AlK α radiation at 1486.6 eV. An neutralizer with a Ar gun was used during the XPS analysis to compensate charging effects. The analysis of the TRGO-Cu sample show the presence of C1s (88.78 atom %), O1s(9.3 atom%), Cu(0.34 atom%), Si(1.58 atom%) (pass energy: 187.85eV). Also the high resolution XPS spectra of each element recorded with a pass energy of 23.5 eV and an energy step 0.2eV.

NMR

All NMR spectra were recorded on a Varian spectrometer (Gemini 400) at 400 MHz at 27 °C. THF-d_8 and DMSO-d_6 (Armar AG, 99.8 Atom%D) was used as solvent and tetramethylsilane as internal standard. The coupling constants were given in Hz and the chemical shifts in ppm and referred to the solvent residue peak [THF-d_8 1.72 and 3.58 ppm and DMSO-d_6 2.5 ppm (^{1}H)]. For the interpretation of the spectra, MestReNova v. 6.0.2–5475 was used.

Rheology

Rheological measurements were performed on an oscillatory plate rheometer MCR 501/SN 80753612 from Anton Paar (Physica). For all measurements a PP08 measuring system (parallel plated, diameter 8 mm) was used. Measurements were performed at 20 °C and the sample temperature was regulated

by thermoelectric heating and cooling. For evaluation of data the RheoPlus/32 software (V 3.40) and OriginPro7 was used. For sample preparation a 1: 1 mixture of an azido-functionalized polymer and an alkyne-functionalized polymer was placed in a flask (ca. 100.0 mg) and was dissolved in THF (approximately 3.0 mL). The solvent was removed and the sample was dried in high vacuo. TRGO-Cu catalyst (0.02 equiv per functional group) was suspended in $CHCl_3$ (40.0 μL) and was added to the polymer mixture. Subsequently, the reaction mixture was mixed with a spatula and was immediately put on the rheometer plate. Measurements were performed with a strain γ of 0.1% and with an angular frequency ω ranging from 100 to 1 rad/s. A frequency sweep was performed every 10 minutes. All samples were measured at 20 °C. The gelation time was determined as crossover of the storage (G′) and loss modulus (G″) at 10 rad/s. Measurements were stopped after a total time (26.7 h) when the values of the storage and the loss modulus stayed constant (second decimal place) for at least 60 min.

IR

ATR-IR spectra were performed on a Bruker Tensor VERTEX 70 equipped with a Golden Gate Heated Diamond ATR Top-plate. Opus 6.5 was used for analyzing data.

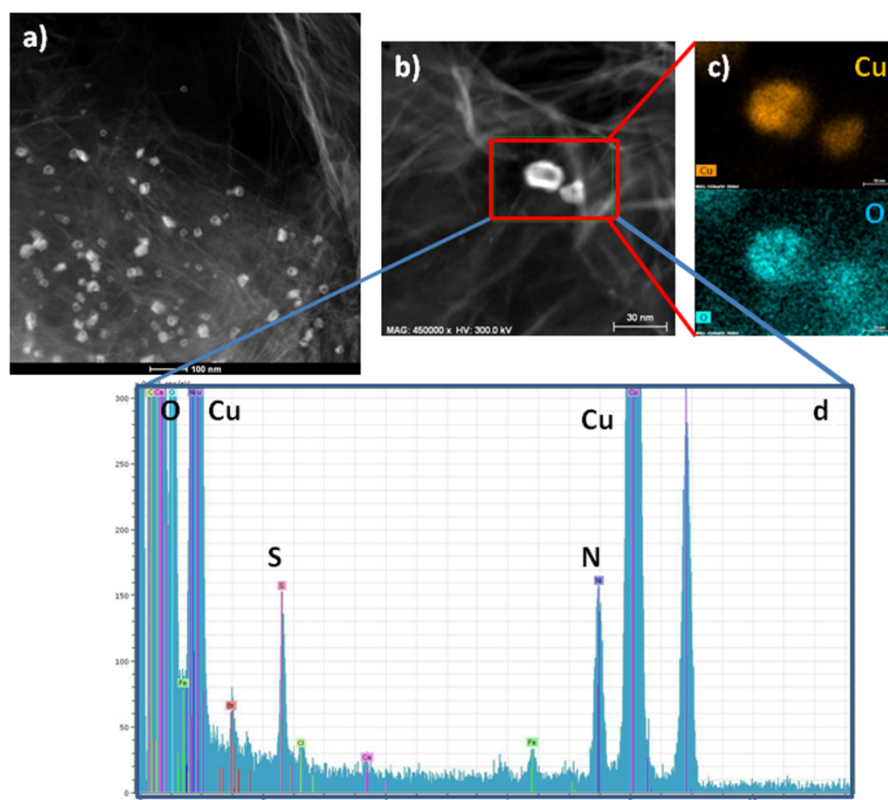## 3. Charatization

3.1-STEM-EDXS

Fig. S1 a) STEM-EDXS spectrum of TRGO/Cu(I), b) selected particle area for STEM-EDXS analysis, c) STEM spectrum of selected particle, d) EDXS spectrum of selected particle.

3.2- Kinetic study

In a 10 ml schlenk flask, benzyl azide (0.0751 mmol), phenyl acetylene (0.0826 mmol, 1.1eq) and TRGO-Cu (1.8 mg, 2mol%) were dissolved in 1.5 ml of deutrated THF. Afterwards the mixture was degassed by freeze-thaw cycle (2 times). Then the mixture was sonicated (bath sonicator) for some seconds to disperse the catalyst, and the reaction was run at 40°C. The aliquots taken at different intervals from the reaction, filtered to remove the catalyst and ^{1}H NMR study was performed to calculate the conversion according to equation S1(figure S2a,b). The equation (1) which was evaluated by Fokin and Finn et al.[1] was used for calculation of k' as below:

$$rate = k' \, [alkyne]^{1.3}[azide]^1 \quad (k' = k[Cu]^2)$$ equation 1

$$Conversion = \frac{intregration_{CH2-moiety\ of\ click\ product}}{integration_{CH2-moiety\ of\ click\ product} + integration_{CH2-moiety\ of\ benzyl\ azide}}$$

equation S1

1- [Cu]=constant. As the catalyst was highly dispersible in the reaction mixture, so we assumed that the catalyst concentration did not change while taking the aliquots.
2- [alkyne]=[azide]=C,
3- C_0= concentration of azide in the beginning $\quad C_0=0.0534$ M
4- C_t= concentration of azide at time t $\quad C_t=0.0524\times(1-Conversion)$ M

5- rate= $\dfrac{-d[azide]}{dt} = \dfrac{-d[c]}{dt}$

$$\frac{-dC}{dt} = k'C^{2.3} \qquad \int_{C_0}^{C_t} \frac{-dC}{dt} = \int_0^t k't \qquad C_t^{-1.3} - C_0^{-1.3} = k't$$

6- The slope of ($C_t^{-1.3} - C_0^{-1.3}$) Vs. t is k' (Fig. S2c)

b)

Conversion = 0.16/(0.16+2)= 0.074
Or 7.4%

a)

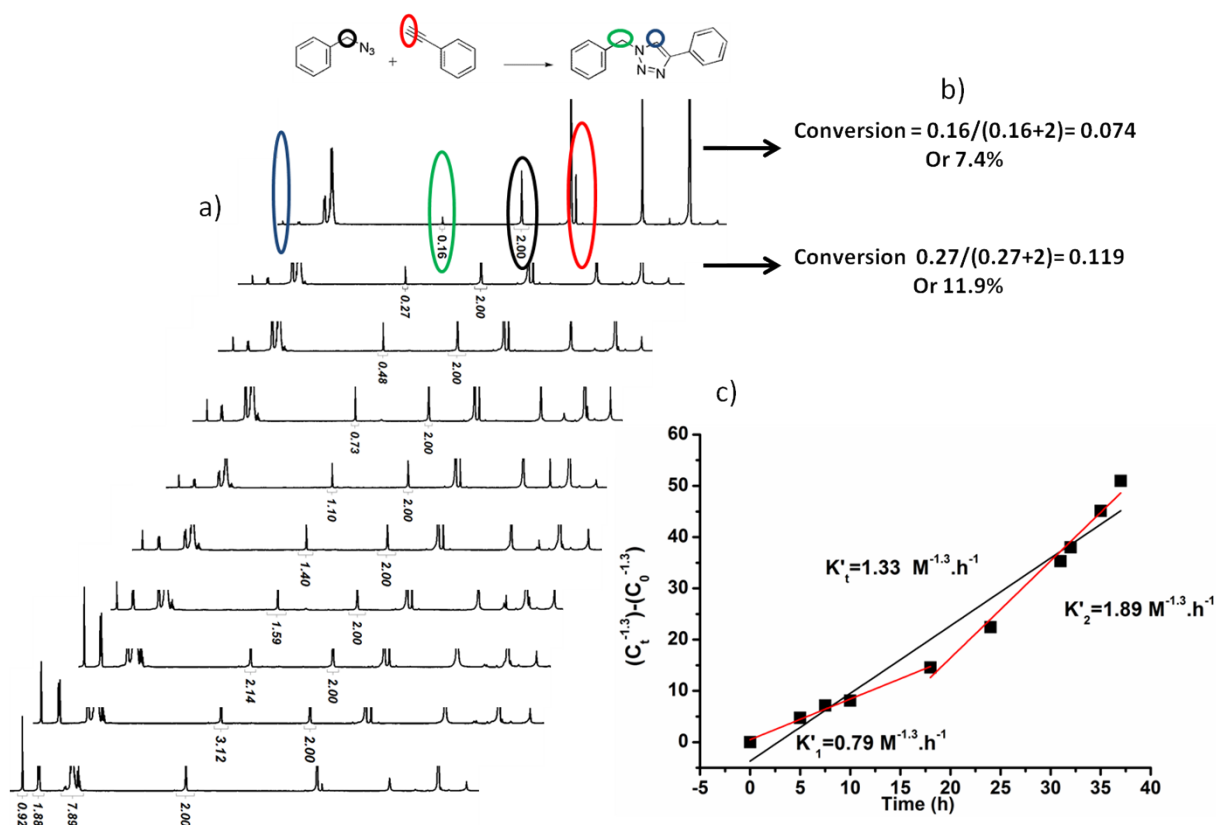Conversion 0.27/(0.27+2)= 0.119
Or 11.9%

c)

Fig. S2 Kinetic study of model click reaction with TRGO/Cu(I) as catalyst a) NMR measurements at different time intervals, b) calculation of % conversion c) different k' values of reaction derived from graph

Two different k' are calculated (k'$_1$=0.79 **M$^{-1.3}$.h^{-1}** , k'$_2$= 1.89 **M$^{-1.3}$.h^{-1}**) by linear fit (Fig. S2c). Increment in k' value is explainable by autocatalytic effect caused by the formed triazole moieties and the subsequent complexation by the Cu(I) -ions.[1] However in order to compare the current work with Finn et al[2]., a single linear fit was used to calculate k'$_t$ = 1.33 **M$^{-1.3}$.h^{-1}**.
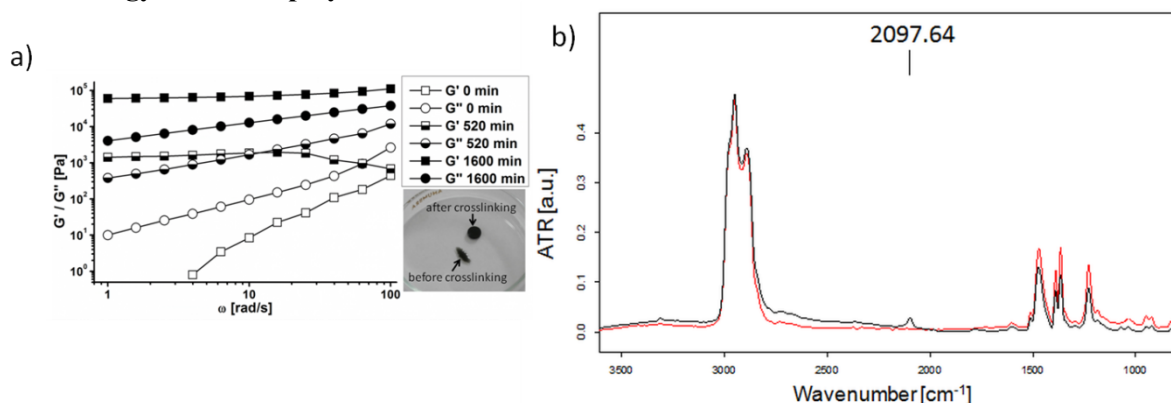
3.3-Rheology and IR of polymer mixture

Fig. S3 a) Typical graphs derived from an in-situ rheological measurement by reaction of PIB-azide and PIB-alkyne with TRGO/Cu(I) conjugate at 20 ^{0}C **b)** IR spectrum of polymer mixture with TRGO/Cu(I) before (black curve) and after crosslinking (red curve).

4. Recycling experiment

In a 10 ml schlenk flask, benzyl azide (0.0751 mmol), phenyl acetylene (0.0826 mmol, 1.1eq) and TRGO-Cu (1.8 mg, 2mol%) were dissolved in 1.5 ml of THF. Afterwards the mixture was degassed by freeze-thaw cycle (2 times). Then the mixture was sonicated (bath sonicator) for few seconds to disperse the catalyst and the reaction was run at 40°C for 55 h. Afterwards the reaction mixture was filtered and washed by 10-15 ml of THF. The solvent of the filtrate was evaporated under reduced pressure (200 mbar was used as the minimum pressure to avoid flashing of starting materials). The recovered catalyst was dried under high vacuum for 30 min and used for next cycle.

5. Synthesis

5.1-synthesis of graphene oxide (GO)

Graphite (3g) was stirred in concentrated sulfuric acid (117 mL) at room temperature (rt), and sodium nitrate (1.5 g) was added, afterwards the mixture was cooled to 0 °C and potassium permanganate (9 g) was added during 30 min to 1 hour in order to avoid the increment in internal temperature of the reaction mixture. After 2 h, the green slurry was allowed to come to rt, and after being stirred for 3 h (during this time the viscosity of mixture was increased) the whole batch was carefully poured into a 700ml beaker filled with ice-cold water (distilled). Subsequently, hydrogen peroxide (3%) was added in excess and the mixture was stirred overnight and then filtered. Workup was accomplished by several washings with a mixture of HCl/H$_2$O$_2$ (1:1, 5%) and filtration was followed by several washings with water and centrifugation until the supernatant did not show anymore precipitation with AgNO$_3$ solution. The obtained GO carefully powdered in a ball mill, with pre cooling by liquid nitrogen.
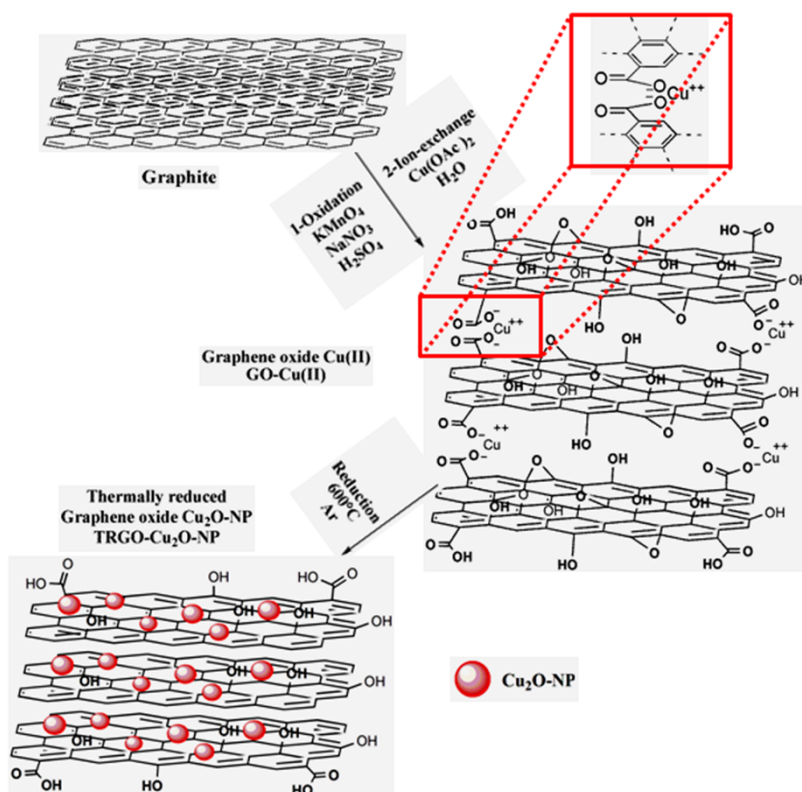
Fig. S4 Synthesis of Cu catalyst immobilized graphene nanosheets.

5.2-Synthesis of different click product

In a 10 ml schlenk flask, benzyl azide (0.0751 mmol), different alkynes (0.0826- 0.09763 mmol, 1.1-1.3eq) and TRGO-Cu (1.8 mg, 2mol%) were dissolved in 1.5 ml of deutrated THF. Afterwards the mixture was degassed by freeze-thaw cycle (2 times). Then the mixture was sonicated (bath sonicator) for some seconds to disperse the catalyst. The reaction was run at 40°C for 48 hours. Afterwards the reaction mixture was filtered and the ^{1}H NMR of filtrate showed the conversion of the like kinetic measurements. The ^{1}H NMR's of the products were measured without any purification and they just filter to remove the graphene catalyst. Therefore the traces of excess alkyne and unreacted azide are visible in some spectra (Figure S6-S9). Furthermore the ^{1}H NMRs of these products are in agreeing with the previous works.[3-6]

5.2.1- 1-benzyl-4-phenyl-1H-1,2,3-triazole

^{1}H NMR (400 MHz, *THF-d_8*) δ ppm 5.81 (s, 2H), 7.39-7.21 (m, 7H), 7.82 (m, 2H), 8.08 (s, 1H)

5.2.2- 1-benzyl-4-(4-chlorobutyl)-1H-1,2,3-triazole

^{1}H NMR (400 MHz, *THF-d_8*) δ ppm 1.84-1.74 (m, 3H), 2.67 (t, J = 6.87, 6.87 Hz, 2H), 3.56 (t, J = 9.10, 9.10 Hz, 2H), 5.49 (s, 2H), 7.39-7.21 (m, 5H), 7.49 (s, 1H)

5.2.3- 2-(1-benzyl-1H-1,2,3-triazol-4-yl)butan-2-ol
^{1}H NMR (400 MHz, *THF-d_8*) δ ppm 0.78 (t, J = 7.43, 7.43 Hz, 3H), 1.46 (s, 3H), 1.88-1.74 (m, 2H), 3.97 (s, 1H), 5.50 (s, 2H), 7.42-7.19 (m, 5H), 7.55 (s, 1H),

5.2.4- 1-(1-benzyl-1H-1,2,3-triazol-4-yl)pentan-1-ol

^{1}H NMR (400 MHz, *THF-d$_8$*) δ ppm 0.89 (t, *J* = 7.12, 7.12 Hz, 3H), 1.37 (m 4H), 2.58 (s, 2H), 4.23 (s, 1H), 4.70 (s, 1H), 5.50 (s, 2H), 7.46-7.18 (m, 5H), 7.59 (s, 1H)

5.2.5- 2-(1-benzyl-1H-1,2,3-triazol-4-yl)propan-2-ol

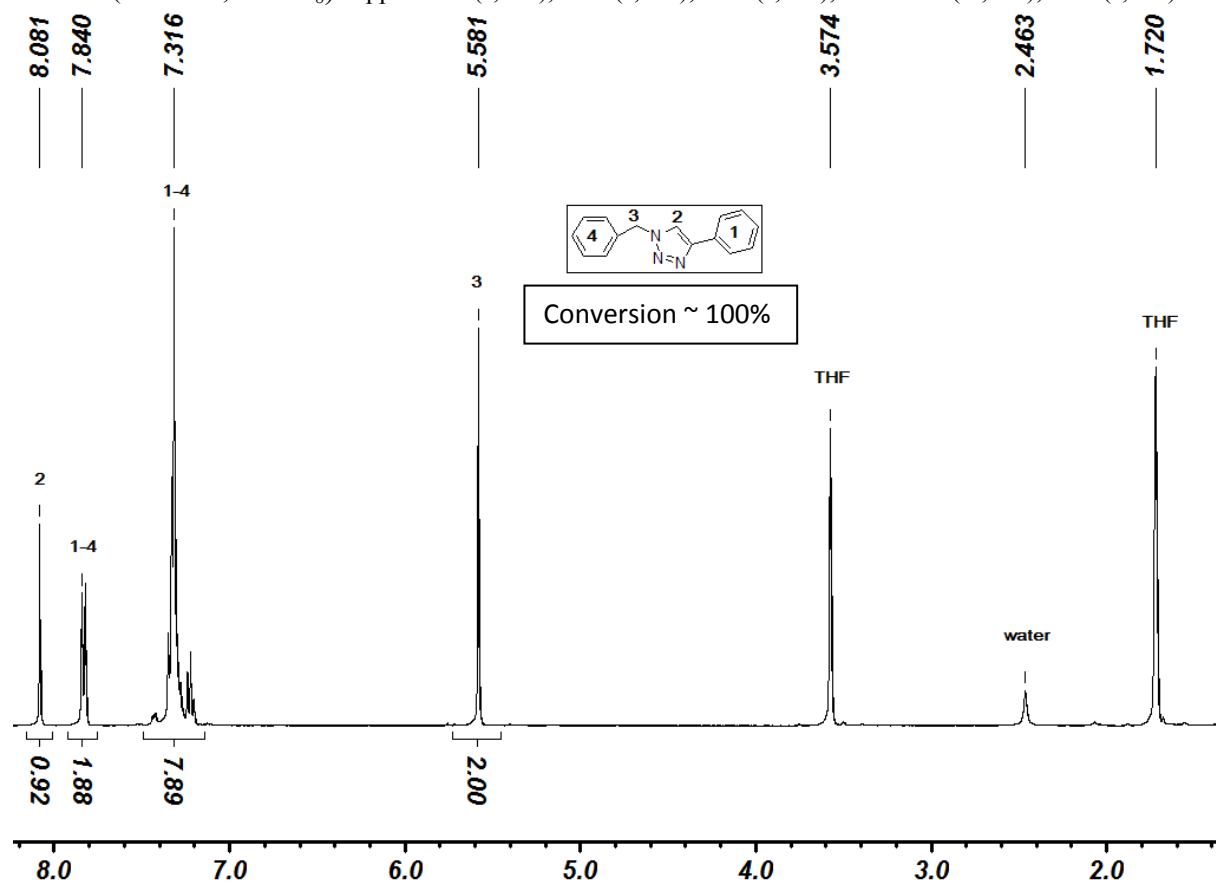^{1}H NMR (400 MHz, *THF-d$_8$*) δ ppm 1.48 (s, 6H), 2.07 (s, 1H), 5.49 (s, 2H), 7.45-7.11 (m, 5H), 7.56 (s, 1H)

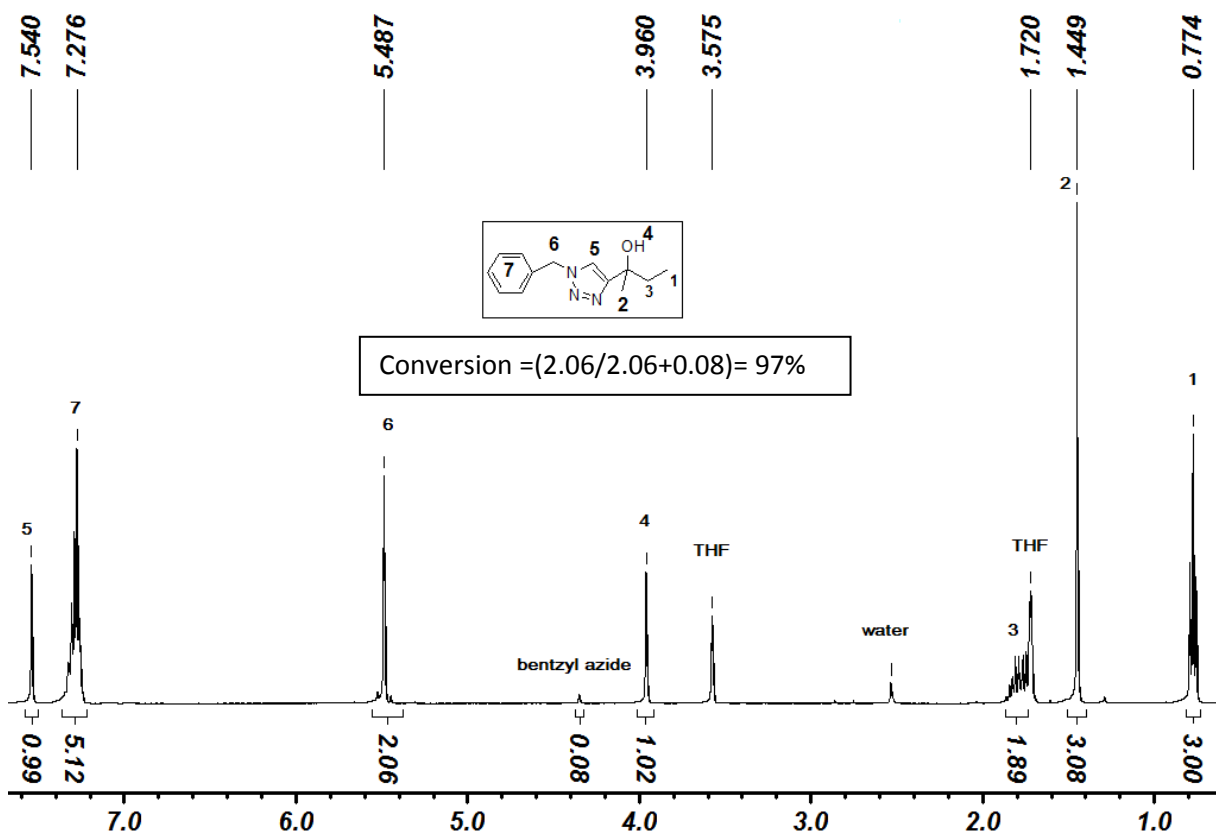**Fig. S5** ^{1}H NMR of 1-benzyl-4-phenyl-1H-1,2,3-triazole
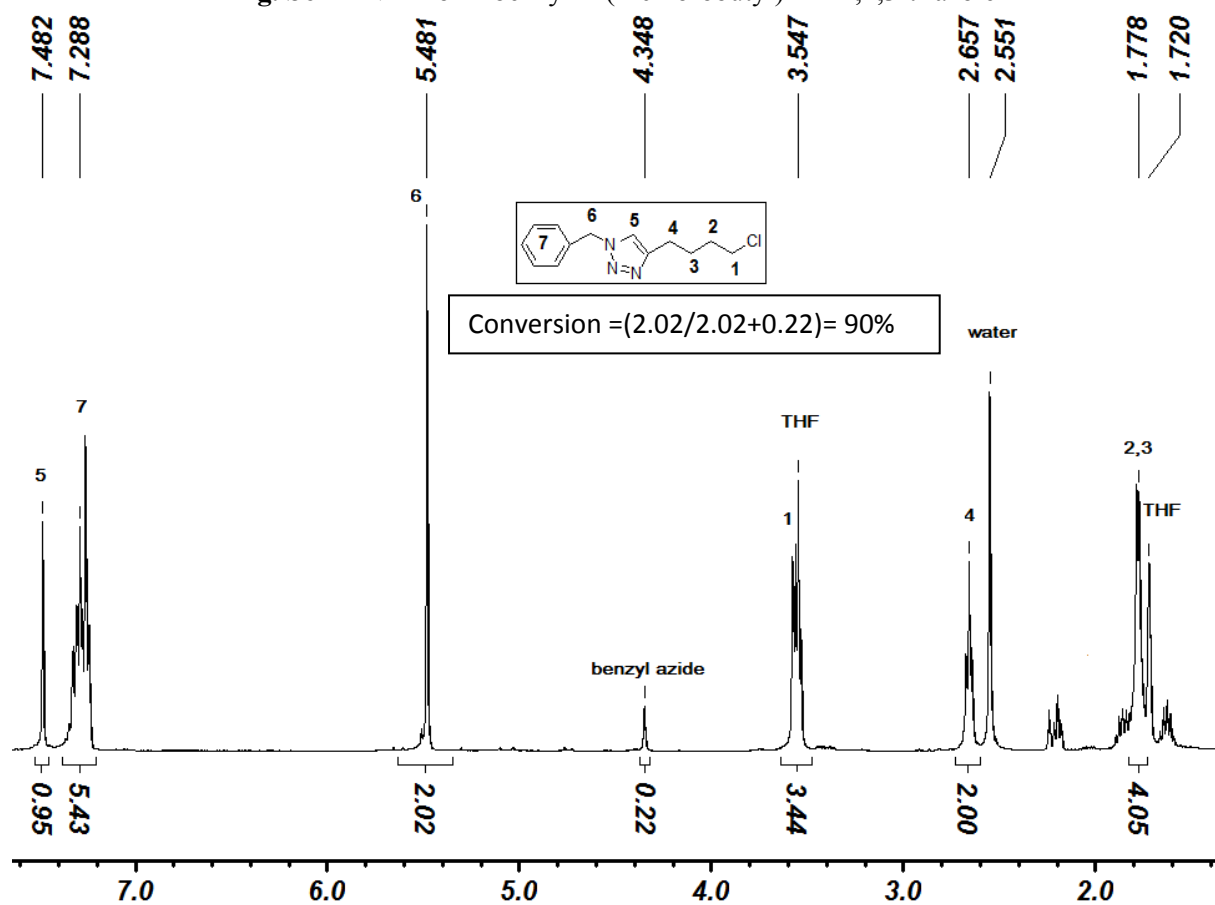
Fig. S6 ^{1}H NMR of 1-benzyl-4-(4-chlorobutyl)-1H-1,2,3-triazole

Conversion =(2.02/2.02+0.22)= 90%

Fig. S7 ^{1}H NMR of 2-(1-benzyl-1H-1,2,3-triazol-4-yl)butan-2-ol

Conversion ~ 100%
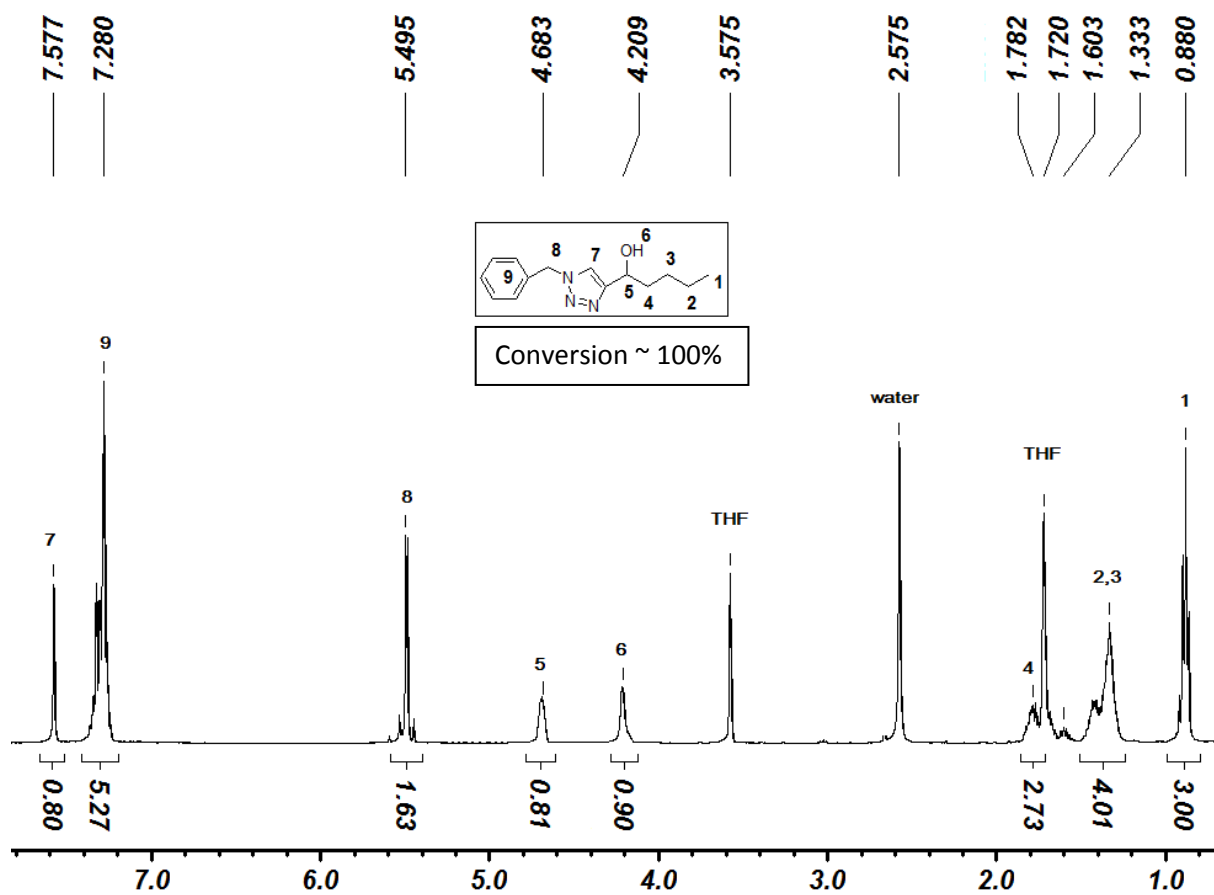
Fig. S8 ^{1}H NMR of 1-(1-benzyl-1H-1,2,3-triazol-4-yl)pentan-1-ol
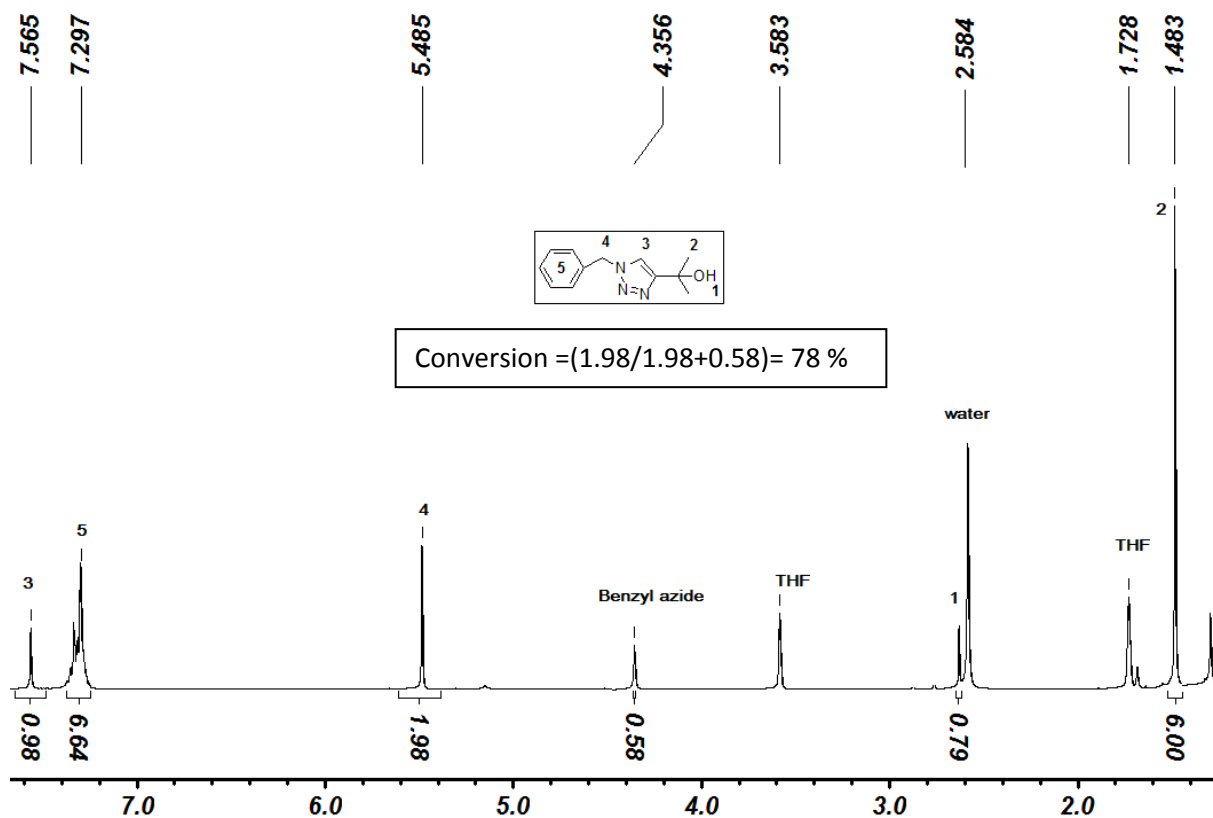

Conversion =(1.98/1.98+0.58)= 78 %

Fig. S9 ^{1}H NMR of 2-(1-benzyl-1H-1,2,3-triazol-4-yl)propan-2-ol

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