Supplementary Information

On-nanoparticle monolayers as a solute-specific, solvent-like phase

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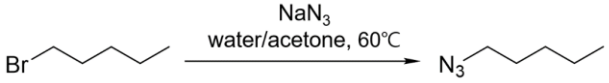
1 General considerations.

Unless otherwise stated, all chemicals, including solvents and reagents, were used from commercial sources without further purification. Copper (I) acetate was obtained from Alfa Aesar. C_{22} **(1a)**, C_{18}, **(1b)**, substrates **4(a-c)**, and **5(b,c)** were obtained from Tokyo Chemical Industries (TCI). C_6-bipy **(2a)** and C_4-bipy **(2b)** ligands, and substrates **(3)**, **5(a,d)** were synthesized following a procedure reported elsewhere[1]. The spectral data obtained agreed with literature reported values. For analytical thin-layer chromatography, silica gel on TLC Al foils 60/F_{254} was used (Sigma-Aldrich No. 60778) and visualized with UV irradiation (254 nm). Flash column chromatography was performed on silica gel 60 Å 220-440 mesh (Sigma-Aldrich No. 60738). Nuclear magnetic resonance (NMR) spectra were recorded on Bruker Advance III HD 400 MHz FT-NMR spectrometer, with working frequencies of 400.22 MHz and 600.22 for ^{1}H, and 100.65 MHz for ^{13}C nuclei. Chemical shifts are reported in ppm and referenced to the residual non-deuterated solvent frequencies – DMSO-*d*$_6$, δ 2.50 for ^{1}H and δ 39.5 for ^{13}C; $CDCl_3$, δ 7.26 for ^{1}H. The ^{1}H signals are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. High-resolution mass spectra were obtained on a JEOL JMS-700 mass spectrometer. Gold nanoparticles were imaged by high-resolution transmission electron microscopy (HR-TEM, JEOL JEM-2100F) at an accelerating voltage of 200 kV. Gold nanoparticles were synthesized according to a procedure reported in the literature[1,5] with slight modifications described in section S3.

2 Substrates preparation.

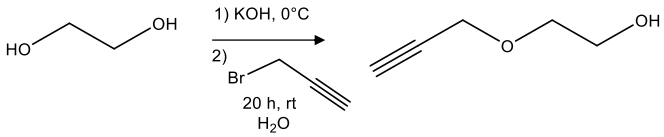
2.1 Synthesis of 1-azidopentane (3).



1-azidopentane was synthesized following a procedure reported elsewhere.[2] 1-bromopentane (2.97 g, 19.6 mmol) was added in 24 mL water/acetone (1:2; v/v), then NaN_3 (3.8 g, 58.9 mmol) was added, and the mixture was stirred at 60 ºC for 24 hours. The reaction mixture was cooled down to room temperature, and the organic solvent was removed under reduced pressure. The aqueous layer was extracted with 3 x 10 mL aliquots of CH_2Cl_2, and the combined organic layers were dried over anhydrous $MgSO_4$. Volatiles were removed under reduced pressure, and the azide was sufficiently pure to use without further purifications (2.02 g, 17.9 mmol, 91%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.22 (t, *J* = 7.0 Hz, 2H), 1.58 (s, 2H), 1.33 (s, 4H), 0.89 (t, *J* = 7.2 Hz, 3H).

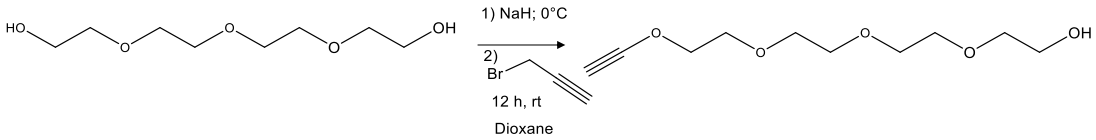
2.2 Synthesis of 2-(prop-2-yn-1-yloxy) ethan-1-ol (5a).



2-(prop-2-yn-1-yloxy) ethan-1-ol or **5a**, was synthesized following a procedure reported elsewhere.[3] Ethylene glycol (6.98 mL, 7.76 g, 125 mmol) was suspended in water (4.40 mL) and cooled to 0 °C. KOH (2.81 g, 50.0 mmol) was added, and propargyl bromide (80 w% in toluene, 2.79 mL, 25.0 mmol) was added dropwise. The reaction mixture was brought to room temperature and stirred for 20 hours. Then, it was hydrolyzed by the addition of water, the phases were separated and the aqueous layer was extracted with CH_2Cl_2 (3 x 15 mL). The combined organic layers were dried over Na_2SO_4, and the solvent was removed under reduced pressure. Purification by flash column chromatography (SiO_2, PE/EA 2:1) to give 5a (1.52 g, 15.2 mmol, 61 % yield) as a colorless liquid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.03 (s, 2H), 3.56 (t, *J* = 4.5 Hz, 2H), 3.49 – 3.41 (m, 2H), 3.35 (s, 1H), 2.38 (s, 1H).

2.3 Synthesis of 3,6,9,12-tetraoxapentadec-14-yn-1-ol (5d).



3,6,9,12-tetraoxapentadec-14-yn-1-ol was synthesized following a procedure reported elsewhere.[4] To a stirred suspension of sodium hydride (2.2 g, 40 mmol, 60% oil dispersion) in dioxane (20 mL) at 0 ºC, a solution of tetraethylene glycol (20.0 g, 100 mmol) was added in small portions. Then, propargyl bromide (3.8 mL, 25 mmol, 80 %w/w in toluene), diluted using dioxane (30 mL) was added dropwise to the mixture for 1 hour. The reaction mixture was stirred at room temperature for additional 12 hours. Then H_2O (20 mL) was added and stirred vigorously for 10 minutes. The solvents were evaporated under vacuum. The residue was dissolved in CH_2Cl_2 (200 mL) and washed with brine (3 x 50 mL). The organic layer was dried (Na_2SO_4), filtrated, and concentrated. The oil obtained was purified by flash column chromatography (CH_2Cl_2 / acetone, 9:1) to give 3,6,9,12-tetraoxapentadec-14-yn-1-ol (4.59 g, 19.75 mmol, 79% yield) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.07 (d, *J* = 2.4 Hz, 2H), 3.53 (s, 16H), 2.38 (s, 1H).

3 Synthesis, preparation and characterization of gold nanoparticles.

Gold nanoparticles were synthesized following a procedure reported[1,5] with slight changes described herein. Hydrogen tetrachloroaurate (III) hydrate ($HAuCl_4 \bullet H_2O$) (0.1 g) was first dissolved in toluene (10 mL) and oleylamine (10 mL) to prepare an orange-colored precursor solution. It was stirred at 29 °C under a N_2 flow for 10 minutes. Then, a reducing solution of borane tert-butylamine complex (TBAB, 0.5 mmol), toluene (1 mL), and oleylamine (1 mL) were prepared, sonicated, and quickly injected into the solution containing gold. The reaction mixture was allowed to react at a constant temperature (29 °C) for 1 hour. To precipitate the Au NPs, ethanol (70 mL) was added, and the Au NPs were collected by centrifugation (5000 rpm, 5 min), washed with ethanol, and re-dispersed in toluene (10 mL).

Two critical aspects of the procedure affect dispersion on diameter size: i) the magnetic stirrer rotation should not exceed 300 rpm (as higher the rpm, higher the dispersion), and ii) the addition of the reductant should be as fast as possible (burst nucleation). Adding the reductant dropwise increased dramatically the dispersion of nanoparticles' diameters.

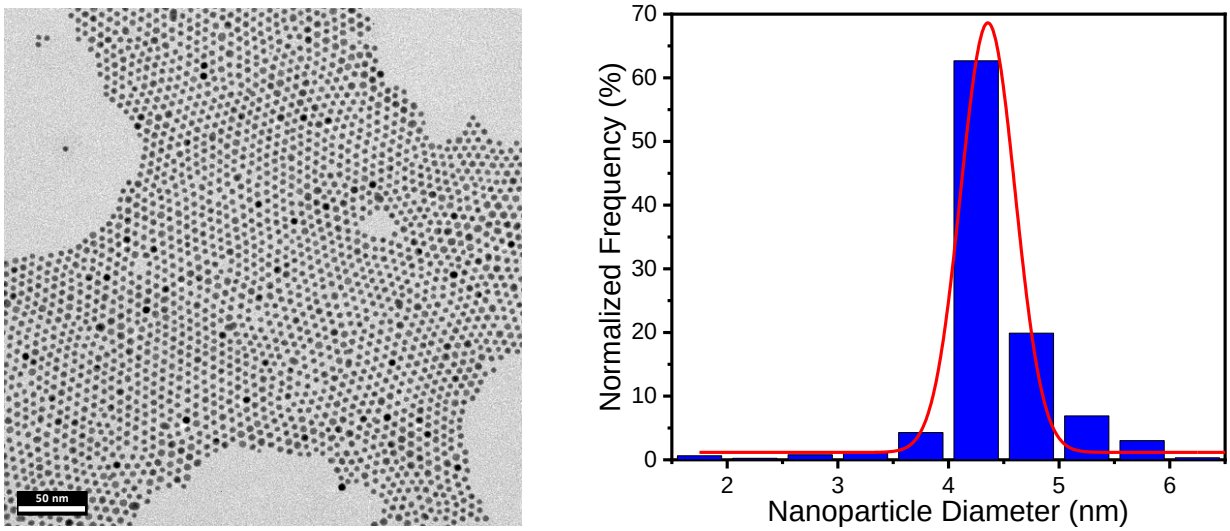


Figure S1. (left) Representative TEM images of as-synthesized Au nanoparticles, and (right) size distribution plot.

3.1 Nanoparticle functionalization and purification.

Thiol solution was first prepared by mixing C_6-bipy or C_4-bipy, 0.0287 mmol) with C_{22} or C_{18} as appropriate (0.0287 mmol) in chloroform (1 mL). In a typical procedure, the thiol solution was added into a 4 mL toluene solution of as-synthesized oleylamine-coated nanoparticles to perform ligand exchange (stirring, r.t, 2h). Then, Au NPs solution was separated into two 15 mL PTFE conical centrifuge tubes and filled up with methanol (inducing NPs aggregation). After centrifugation (5000 rpm, 5 min), a precipitate wass formed, the supernatant removed, and the tubes were refilled with fresh methanol. This process was repeated 5 times to ensure the complete removal of ligands' excess. Finally, all methanol was removed and the Au NPs (precipitate) were re-dispersed in 4 mL of chloroform and transferred to a vial.

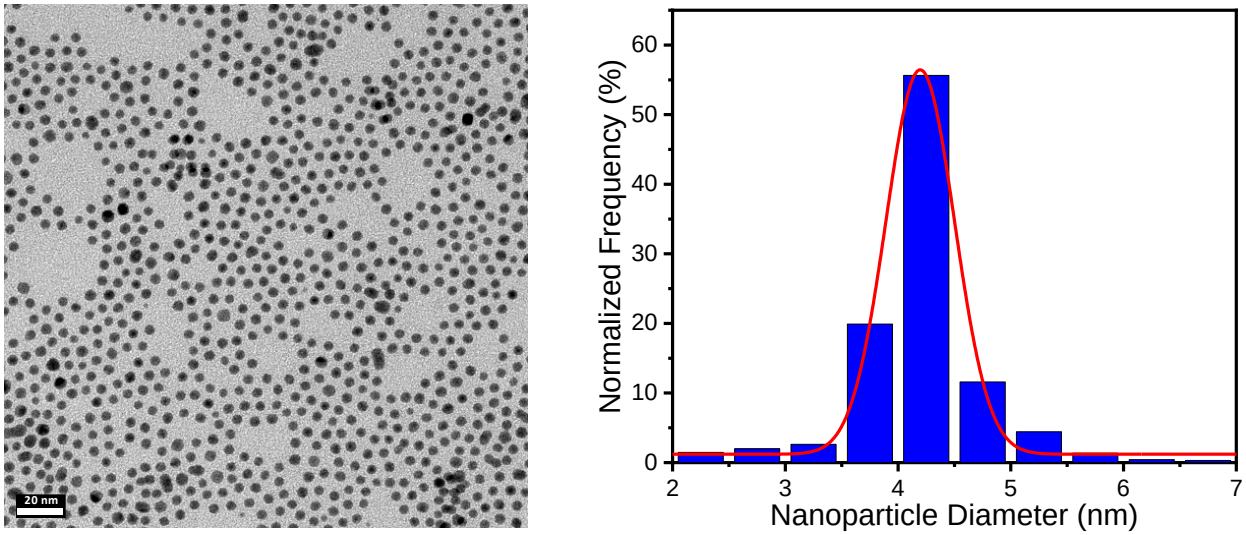


Figure S2. (left) Representative TEM image of as-synthesized Au nanoparticles after ligand exchange, and (right) size distribution plot when C_{22} and C_6-bipy were used as ligands.

3.2 Copper (I) acetate addition.

The purified nanoparticles in chloroform (4 mL) were added to a vial containing solid copper (I) acetate (CuAc), and this heterogeneous mixture was stirred for 2 hours under Ar. The amount of CuAc (0.1936 mg, 1.573 x 10^{-3} mmol) was 1.1 equivalents with respect to the number of bipy moieties attached to the surface of the nanoparticles. Next, the solution was transferred to a 50 mL PTFE conical centrifuge tube and centrifuged at 5000 rpm for 5 minutes to collect the excess solid (CuAc) at the tube's bottom (centrifugation did not aggregate the NPs from the chloroform solution). This centrifugation was repeated five times at least (each time transferring the supernatant containing the NPs to a fresh vial) to ensure complete removal of CuAc. Next, the solution was transferred into two clean 50 mL PTFE conical centrifuge tubes, filled with hexane, and centrifuged at 5000 rpm for 5 minutes, in order to precipitate the NPs. The supernatant was removed, the NPs were dried and then washed with water (5 times, 5000 rpm for 5 minutes). Then, NPs were collected in a 4 mL vial using a 1:1, MeOH:CH_3Cl mixture, the volatiles then were removed under high vacuum. Finally, the NPs were re-dispersed in 4 mL of chloroform.

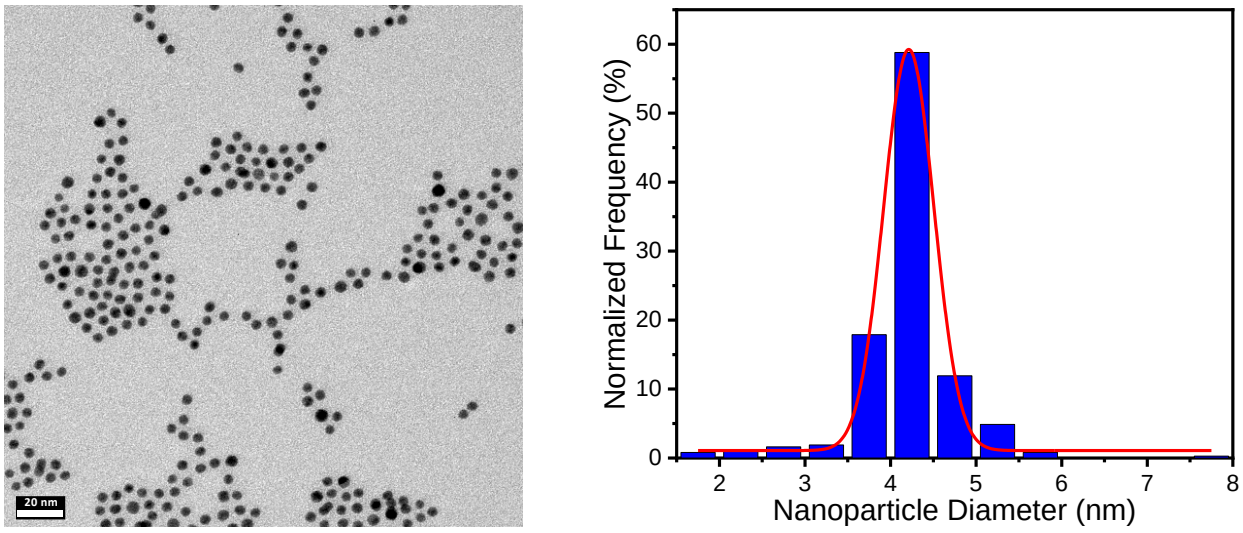


Figure S3. (left) Representative TEM image of as-synthesized Au nanoparticles copper addition (left), and (right) size distribution plot. C_{22} and C_6-bipy were used as ligands.

3.3 ICP-AES analysis.

The composition of the NPs loaded with copper was studied by ICP-AES, using average nanoparticle diameter of 4.4 nm and assuming that a thiol ligand on the surface of the AuNPs occupies 21.4 $Å^2$, and the %Cu was estimated according to literature[1].

% BiPy on AuNPs	Measured Au (mg)	Expected Cu (mg)	Measured Cu (mg)	% Cu
50	2.0367	0.0912999	0.1016570	55.7
50	2.6849	0.091300006	0.098244	53.8

3.4 Elemental Analysis.

Samples were submitted for elemental analysis as powder through precipitation of the nanocatalyst with MeOH and the ratio between nitrogen and sulfur was calculated.

% BiPy on AuNPs	Measured Nitrogen (mg)	Measured Sulfur (mg)	mmol Nitrogen	mmol Sulfur	Ratio N:S
50	0.005023658	0.010693763	0.000358661	0.000333503	1.075436842
50	0.008146408	0.019715682	0.000581608	0.000614866	0.945909888

4 Catalytic reactions.

4.1 General procedure triazoles' synthesis and competition reactions.

4.1.1 Synthesis of triazoles using the $CuSO_4$/NaAs catalyst.

In a vial was added 0.5 mmol of 1-azidopentane followed by 0.5 mmol of a hydrophilic and 0.5 mmol of a hydrophobic alkyne in 2 mL of THF. In another vial, $CuSO_4$ (4.99 mg, 0.03 mmol) and sodium ascorbate (10.15 mg, 0.05 mmol) were added and dissolved in 1 mL of H_2O, then the aqueous solution was added to the organic solution, and the mixture was stirred for 12 hours at 55 °C. Once the reaction was over, H_2O was added (10 mL) and extraction using CH_2Cl_2 (3 X 5 mL) was performed. The organic solution was dried using Na_2SO_4, filtered, and the volatiles were removed under reduced pressure.

The NMR characterizations were performed on the crude reaction mixture. This was possible because characteristic signals of the products (triazoles) do not overlap with precursors' signals (azide and alkyne).

4.1.2 Synthesis of triazoles in competition reactions using $CuSO_4$/NaAs catalyst.

In a vial was added 0.5 mmol of 1-azidopentane followed by 0.5 mmol of a hydrophilic and 0.5 mmol of a hydrophobic alkyne in 2 mL of THF. In another vial was added $CuSO_4$ (4.99 mg, 0.03 mmol) and NaAs (10.15 mg, 0.05 mmol) and dissolved in 1 mL of H_2O, then the aqueous solution was added to the organic solution and the mixture was stirred for 12 hours at 55 °C. Once the reaction was over, H_2O was added (10 mL) and washed with CH_2Cl_2 (3 x 5 mL). The organic solution was dried with Na_2SO_4, filtered and then the volatiles were removed under reduced pressure.

4.1.3 Synthesis of triazoles in competition reactions using nanoparticles catalyst.

In a vial that containing 1 mL of NPs catalyst solution ($CHCl_3$) (5.0 mg in term of gold atoms, 91.506 μg = 1.44 μmol in terms of Cu atoms in the mSAMs) was added 1-azidopentane (0.812 mg, 7.2 μmol) follow by 7.2 μmol of the corresponding both alkynes (hydrophilic and hydrophobic). The mixture was stirred for 12 hours at 55 °C under an Ar atmosphere. Once the reaction was over, volatiles were removed under high vacuum and the reaction crude dissolved in 0.6 mL of DMSO-d_6 and conversion was analyzed by ^{1}H-NMR.

4.2 1,2,3-triazoles synthesis.

4.2.1 Synthesis of 1-(1-pentyl-1H-1,2,3-triazol-4-yl)butan-1-ol (6a).

Compound (6a) was prepared following the general procedure described in section 4.1.1. The alkyne used was hex-1-yn-3-ol (4a).

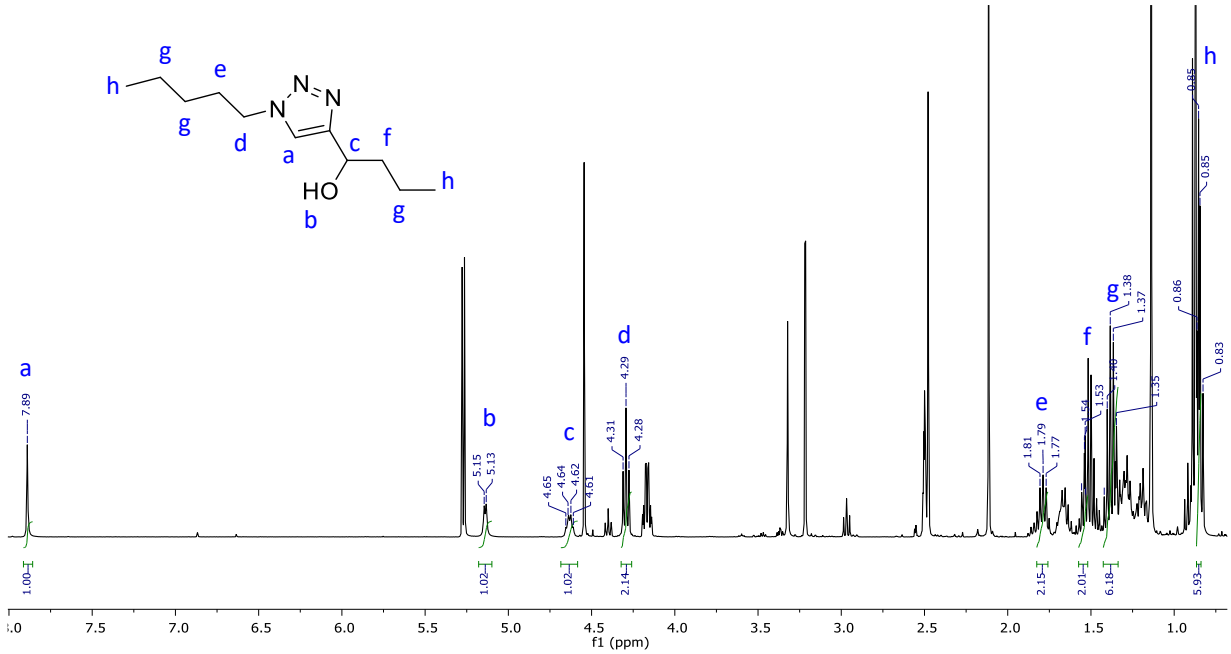


Figure S4. ^{1}H NMR spectrum of 1-(1-pentyl-1H-1,2,3-triazol-4-yl)butan-1-ol (6a).

4.2.2 Synthesis of 1-(1-pentyl-1H-1,2,3-triazol-4-yl)pentan-1-ol (6b).

Compound (6b) was prepared following the general procedure described in 4.1.1. The alkyne used was hept-1-yn-3-ol (4b).

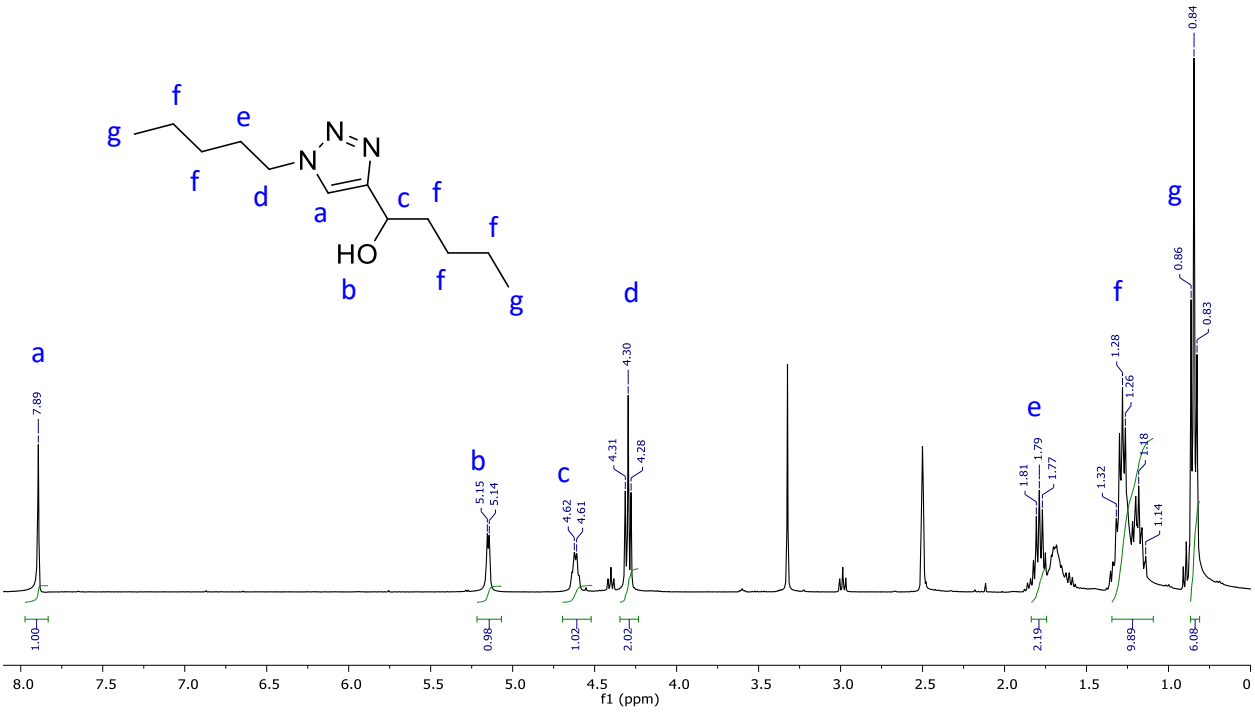


Figure S5. ^{1}H NMR spectrum of 1-(1-pentyl-1H-1,2,3-triazol-4-yl)pentan-1-ol (6b).

4.2.3 Synthesis of 1-(1-pentyl-1H-1,2,3-triazol-4-yl)hexan-1-ol (6c).

Compound (6c) was prepared following the general procedure described in 4.1.1. The alkyne used was oct-1-yn-3-ol (4c).

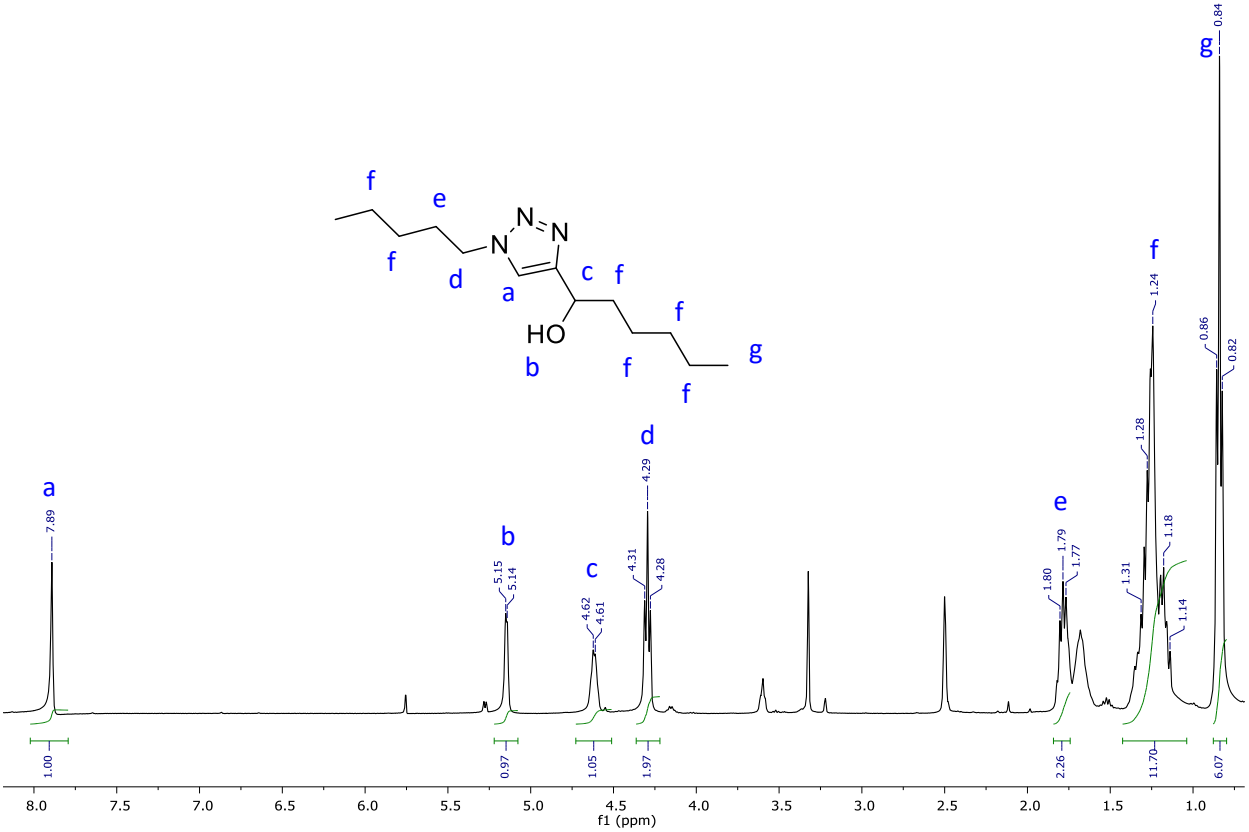


Figure S6. ^{1}H NMR spectrum of 1-(1-pentyl-1H-1,2,3-triazol-4-yl)hexan-1-ol (6c).

4.2.4 Synthesis of 2-((1-pentyl-1H-1,2,3-triazol-4-yl)methoxy)ethan-1-ol (7a).

Compound (7a) was prepared following the general procedure described in 4.1.1. The alkyne used was 2-(prop-2-yn-1-yloxy)ethan-1-ol (5a).

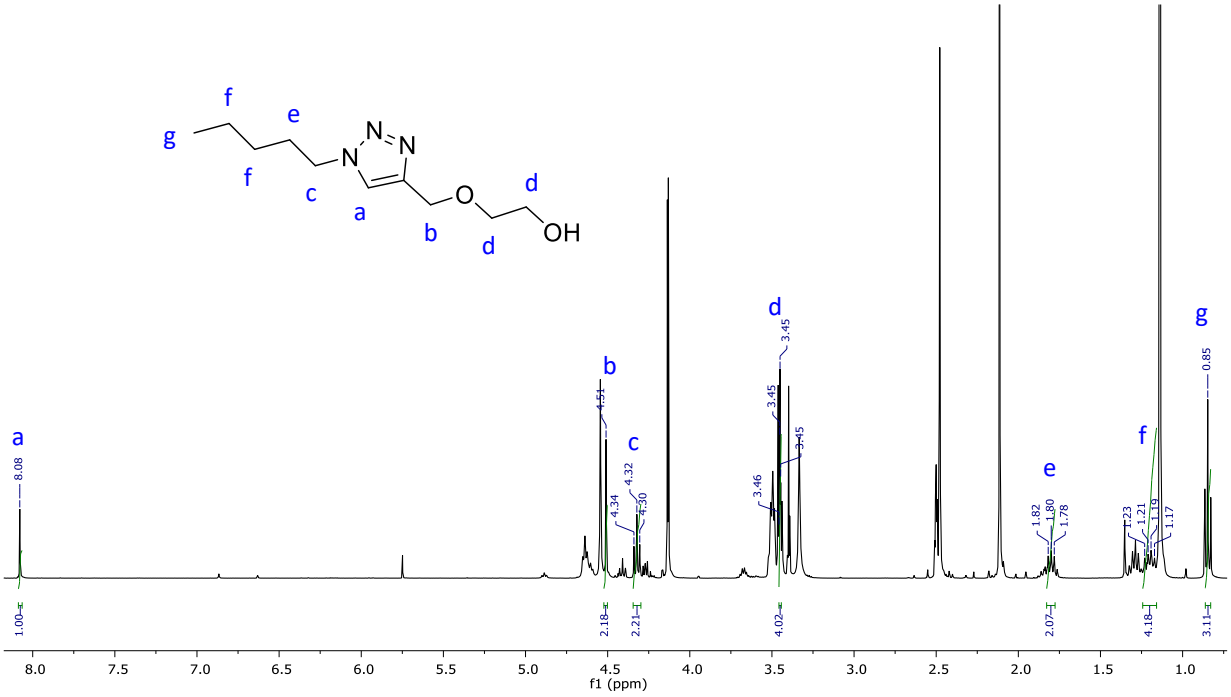


Figure S7. ^{1}H NMR spectrum of 2-((1-pentyl-1H-1,2,3-triazol-4-yl)methoxy)ethan-1-ol (7a).

4.2.5 Synthesis of 2-(2-((1-pentyl-1H-1,2,3-triazol-4-yl)methoxy)ethoxy)ethan-1-ol (7b).

Compound (7b) was prepared following the general procedure described in 4.1.1. The alkyne used was 2-(2-(prop-2-yn-1-yloxy)ethoxy)ethan-1-ol (5b).

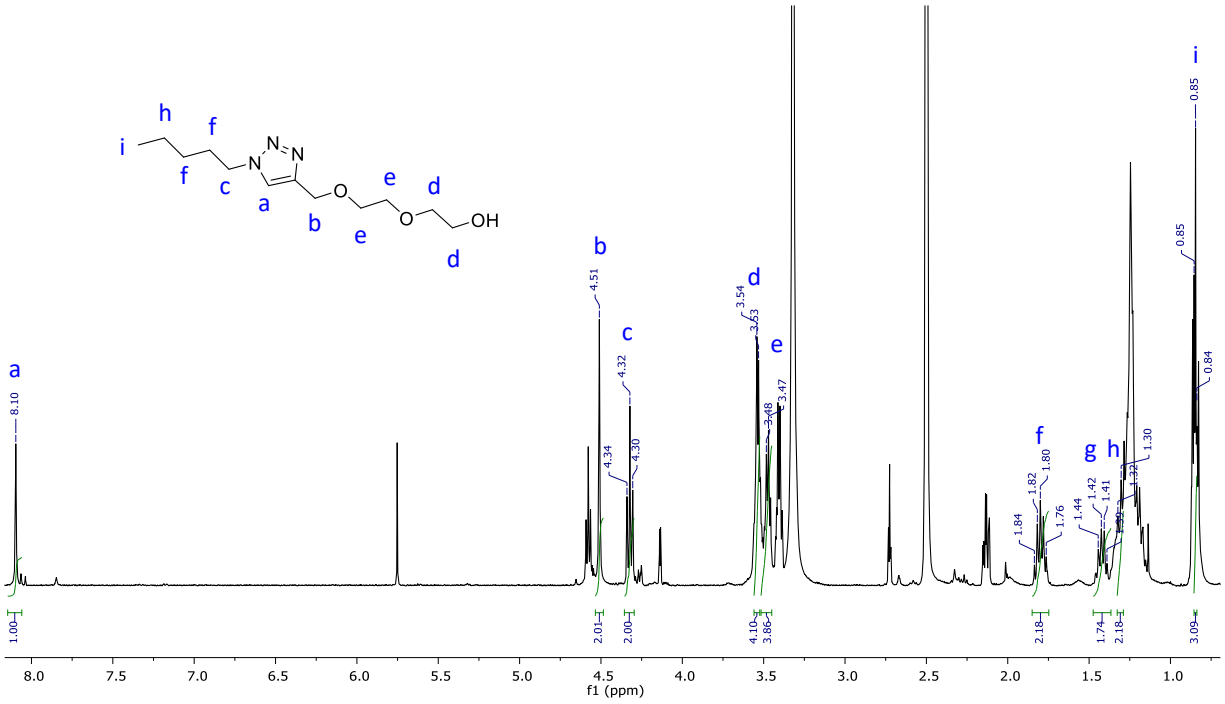


Figure S8. ^{1}H NMR spectrum of 2-(2-((1-pentyl-1H-1,2,3-triazol-4-yl)methoxy)ethoxy)ethan-1-ol (7b).

4.2.6 Synthesis of 2-(2-(2-((1-pentyl-1H-1,2,3-triazol-4-yl)methoxy)ethoxy)ethoxy)ethan-1-ol (7c).

Compound (7c) was prepared following the general procedure described in 4.1.1. The alkyne used was 2-(2-(2-(prop-2-yn-1-yloxy)ethoxy)ethoxy)ethan-1-ol (5c).

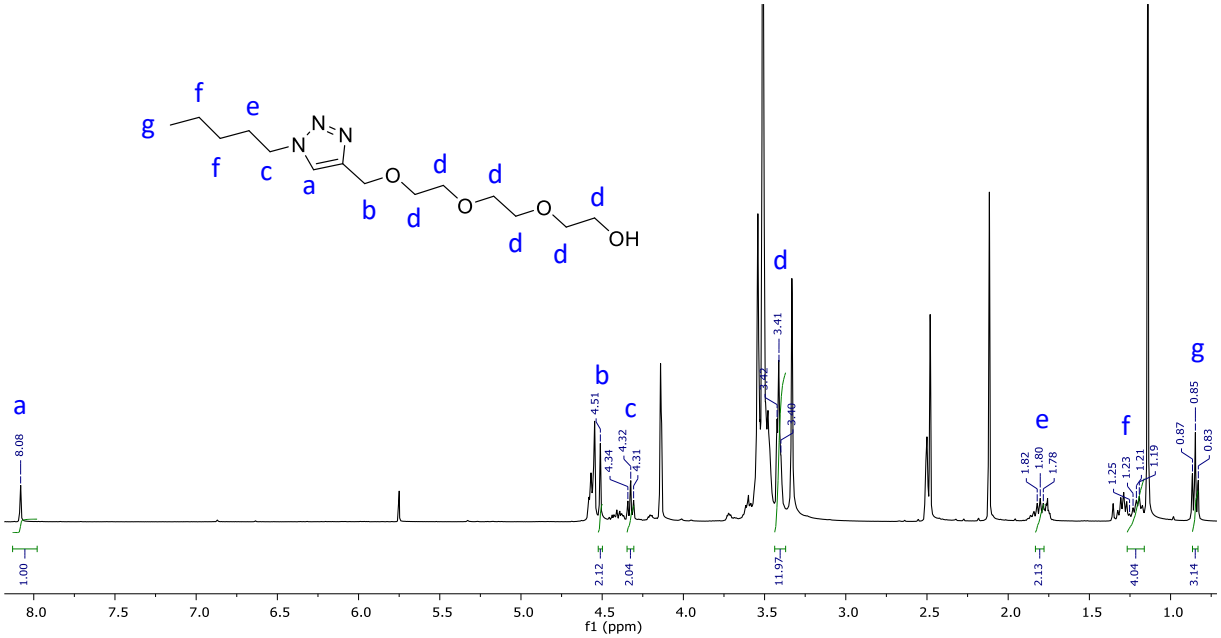


Figure S9. ^{1}H NMR spectrum of 2-(2-(2-((1-pentyl-1H-1,2,3-triazol-4-yl)methoxy)ethoxy)ethoxy)ethan-1-ol (7c).

4.2.7 Synthesis of 1-(1-pentyl-1H-1,2,3-triazol-4-yl)-2,5,8,11-tetraoxatridecan-13-ol (7d).

Compound (7d) was prepared following the general procedure described in 4.1.1. The alkyne used was 3,6,9,12-tetraoxapentadec-14-yn-1-ol (5d).

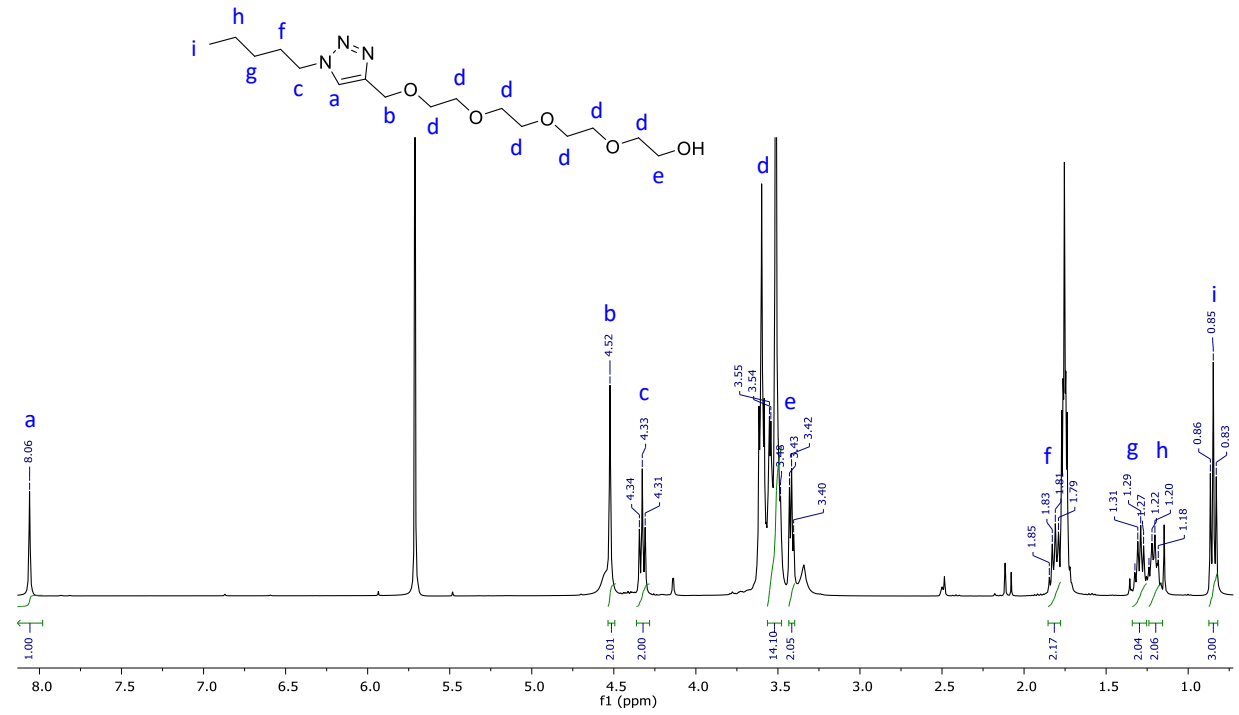
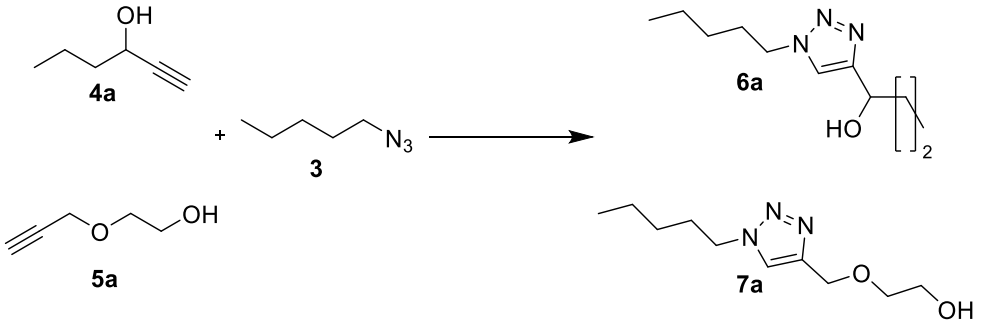


Figure S10. ^{1}H NMR spectrum of 1-(1-pentyl-1H-1,2,3-triazol-4-yl)-2,5,8,11-tetraoxatridecan-13-ol (7d).

4.3 Competition reactions.

4.3.1 Competition reaction between 4a and 5a (entries 1, 5 and I).



4.3.1.1 Competition reactions using $CuSO_4$/NaAs catalyst.

The competition reaction was performed following the general procedure described in 4.1.2, whereby the alkynes were the hydrophobic hex-1-yn-3-ol (4a) and the hydrophilic 2-(prop-2-yn-1-yloxy)ethan-1-ol (5a).

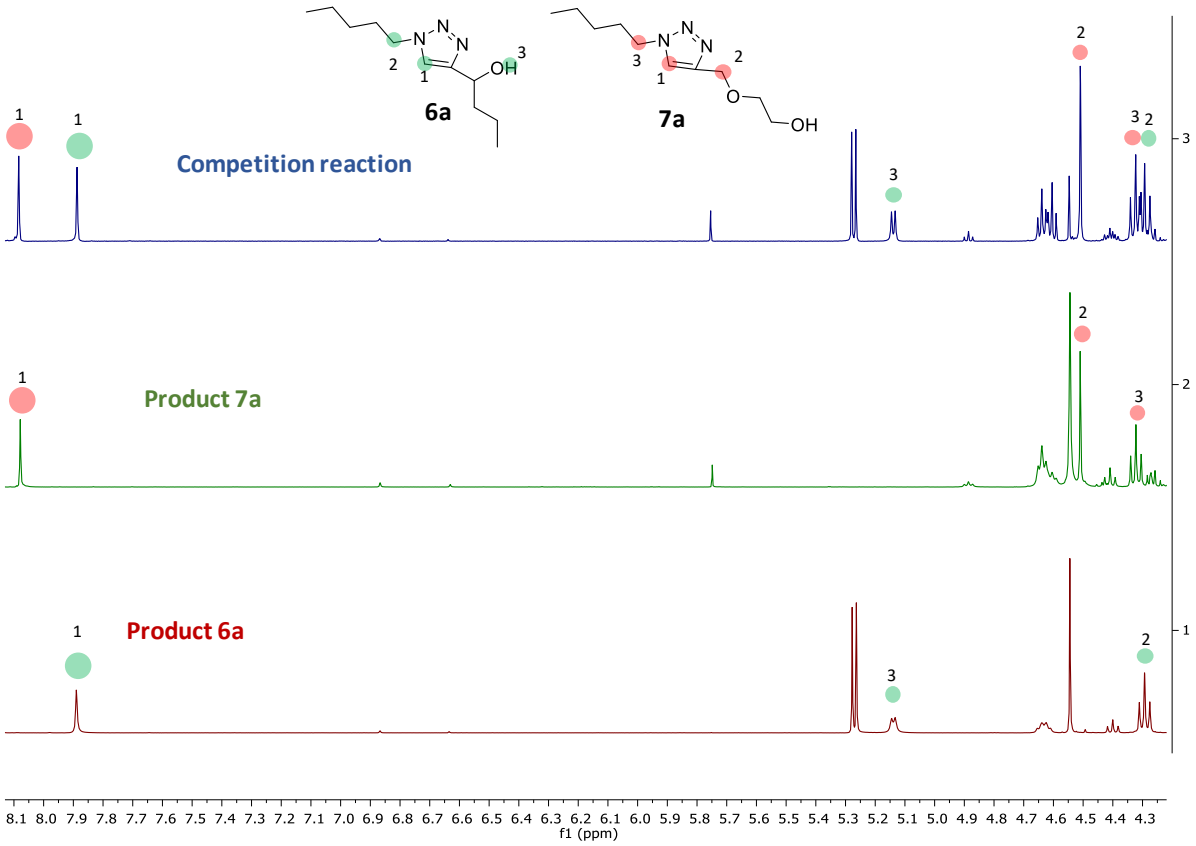


Figure S11. Entry I: stacked ^{1}H MNR spectra of the competitive reaction (blue), and triazole product(6a)(red) and 7a (green) when $CuSO_4$/NaAs was used as the catalyst. Hydrophobic to hydrophilic ratio = 1:1.9.

4.3.1.2 Competition reactions using Nanoparticles as the catalyst.

The competition reaction was performed following the general procedure described in section 4.1.3 using C_{22}-(C_6-bipy) or C_{18}-(C_6-bipy) as the catalyst. The alkynes used were the hydrophobic hex-1-yn-3-ol (4a) and the hydrophilic 2-(prop-2-yn-1-yloxy)ethan-1-ol (5a).

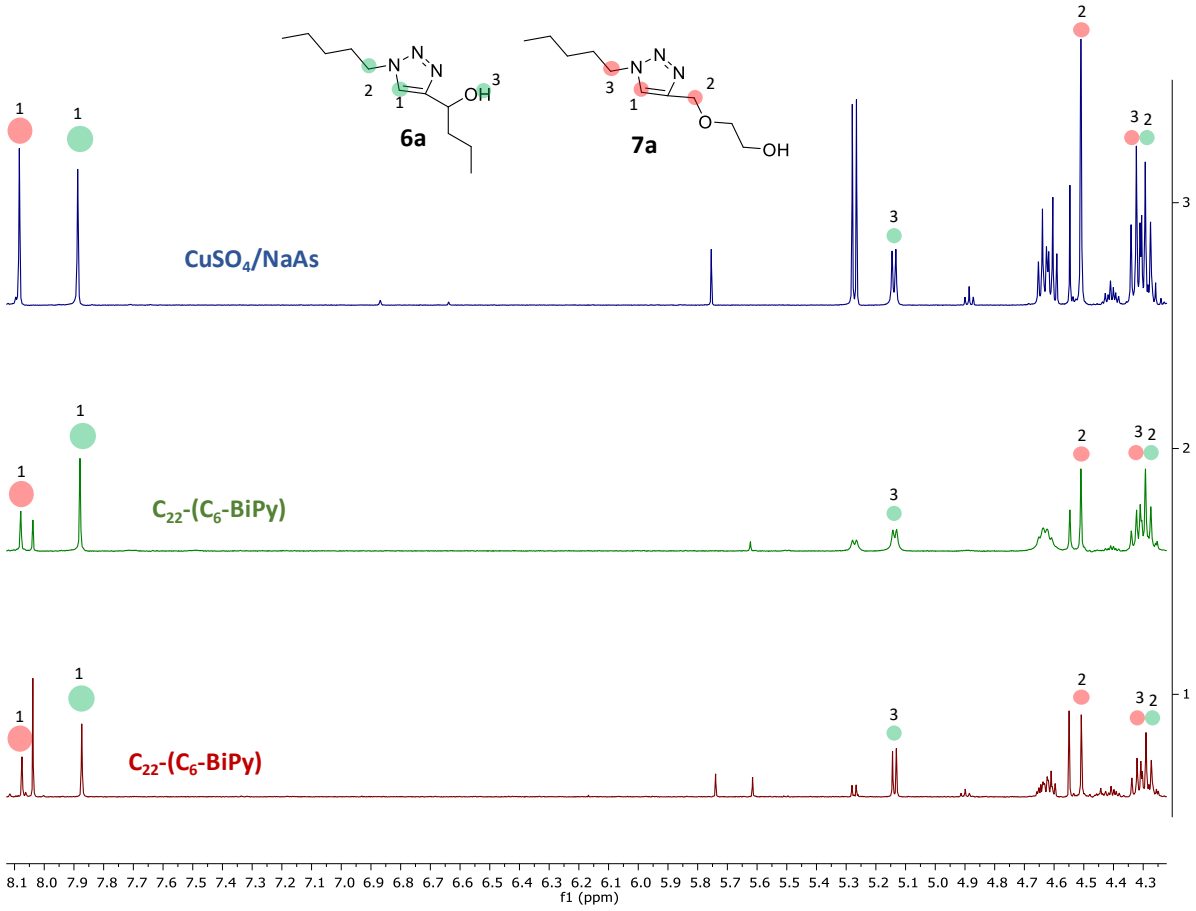


Figure S12. Entry 1: stacked ^{1}H MNR spectra of the competitive reaction when $CuSO_4$/NaAs (blue) and C_{22}-(C_6-bipy) (in duplicate, green and red) were used as catalyst. Average hydrophobic to hydrophilic ratio = 3.1:1.

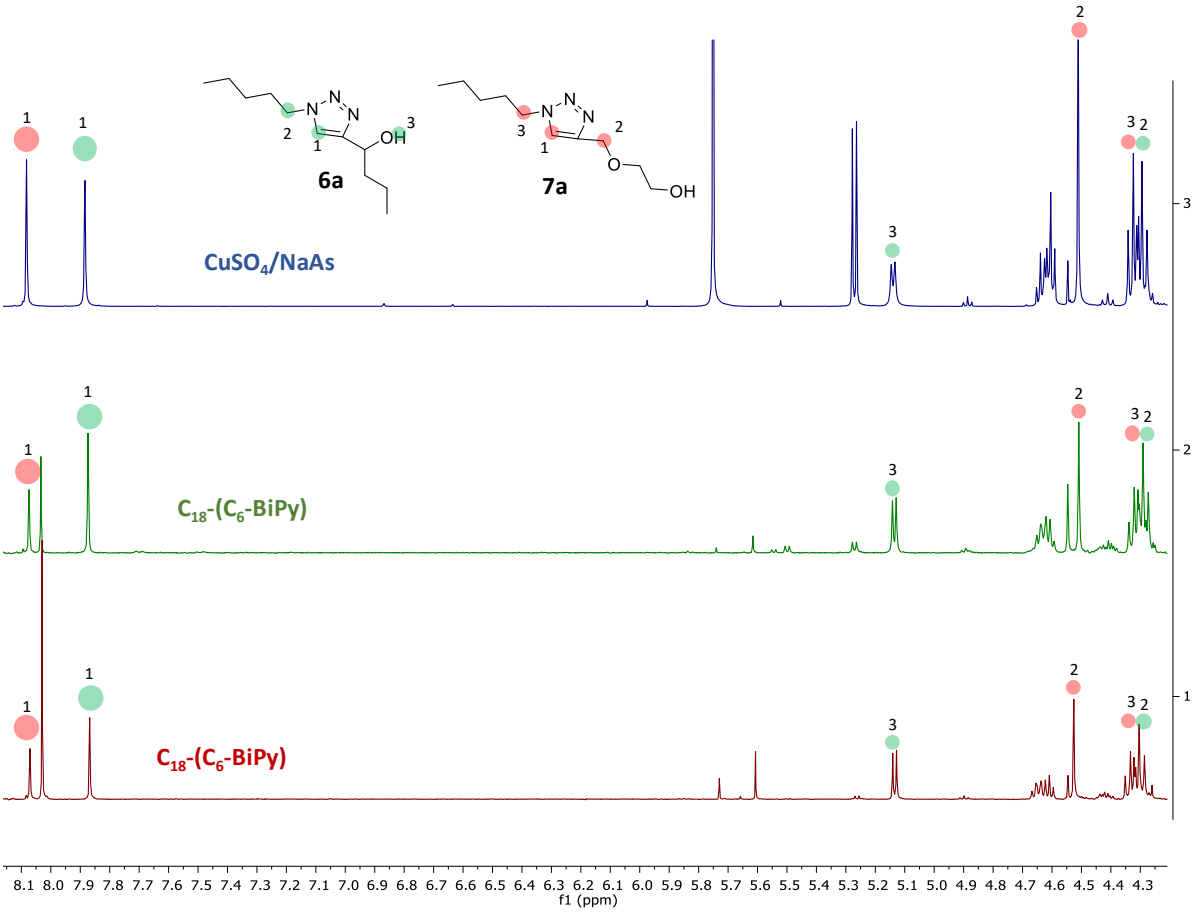
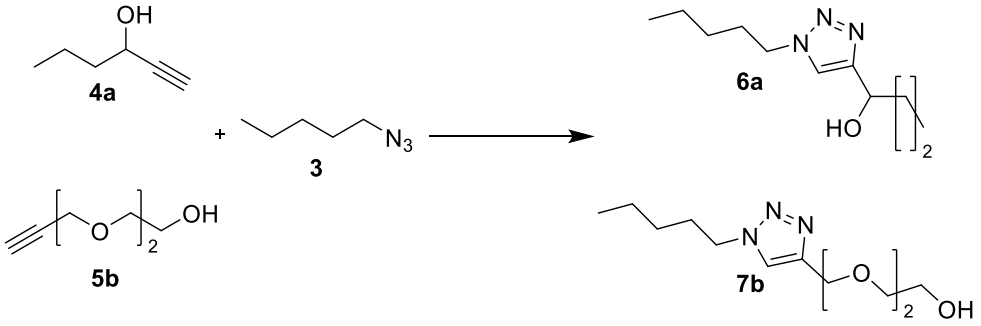


Figure S13. Entry 5: stacked ^{1}H MNR spectra of the competitive reaction when $CuSO_4$/NaAs (blue) and C_{18}-(C_6-bipy) (in duplicate, green and red) were used as catalyst. Average hydrophobic to hydrophilic ratio = 2.7:1.

4.3.2 Competition reaction between 4a and 5b (entries 2, 6 and II).



4.3.2.1 Competition reactions using $CuSO_4$/NaAs catalyst.

The competition reaction was performed following the general procedure described in 4.1.2, whereby the alkynes were the hydrophobic hex-1-yn-3-ol (4a) and the hydrophilic 2-(2-(prop-2-yn-1-yloxy)ethoxy)ethan-1-ol (5b).

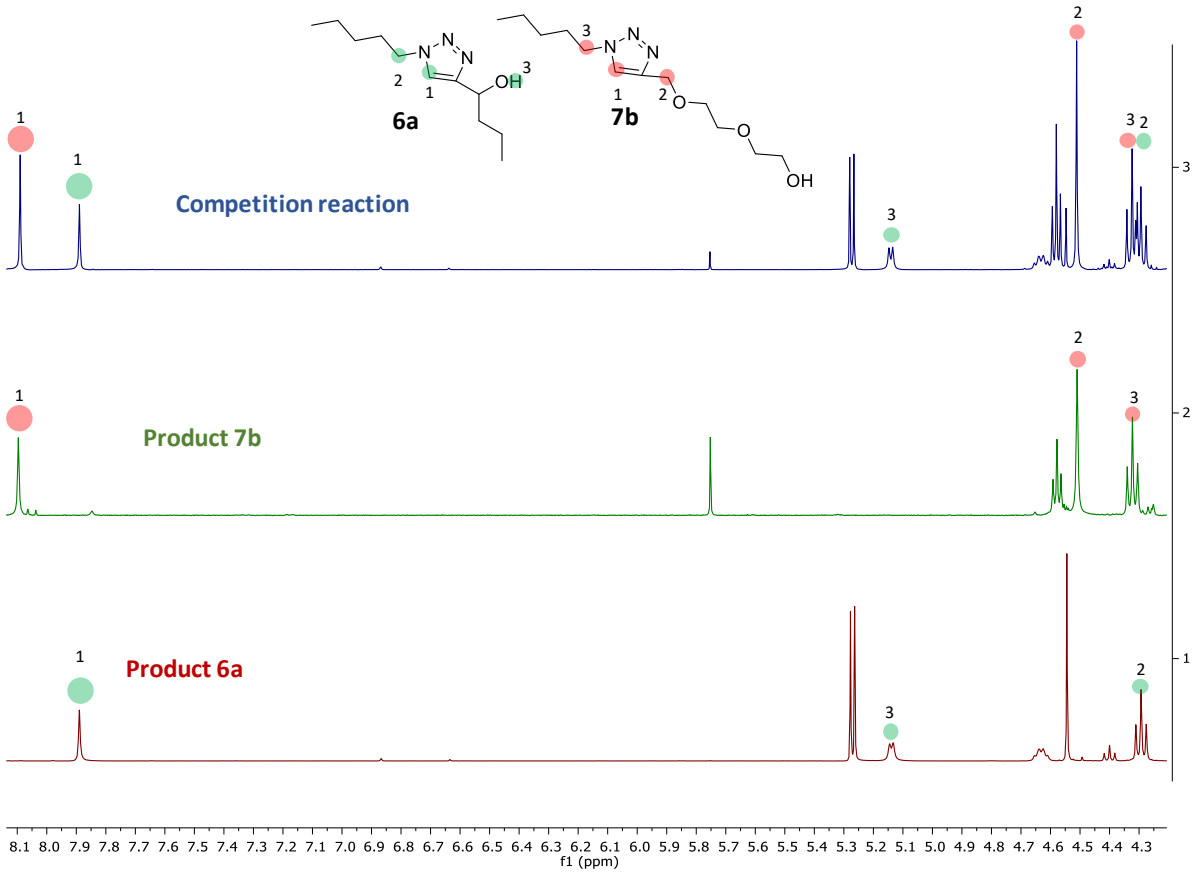


Figure S14. Entry II: stacked ^{1}H MNR spectra of the competitive reaction when $CuSO_4$/NaAs (blue), and triazole product (6a) (red) and (7b) (green) was used as the catalyst. $CuSO_4$/NaAs Hydrophobic to hydrophilic ratio = 1:1.7.

4.3.2.2 Competition reaction using Nanoparticles as catalyst.

The competition reaction was performed following the general procedure described in 4.1.3 and using C_{22}-(C_6-bipy) or C_{18}-(C_6-bipy) as catalyst. The alkynes hex-1-yn-3-ol (4a) and 2-(2-(prop-2-yn-1-yloxy)ethoxy)ethan-1-ol (5b) were used as the hydrophobic and hydrophilic precursors, respectively.

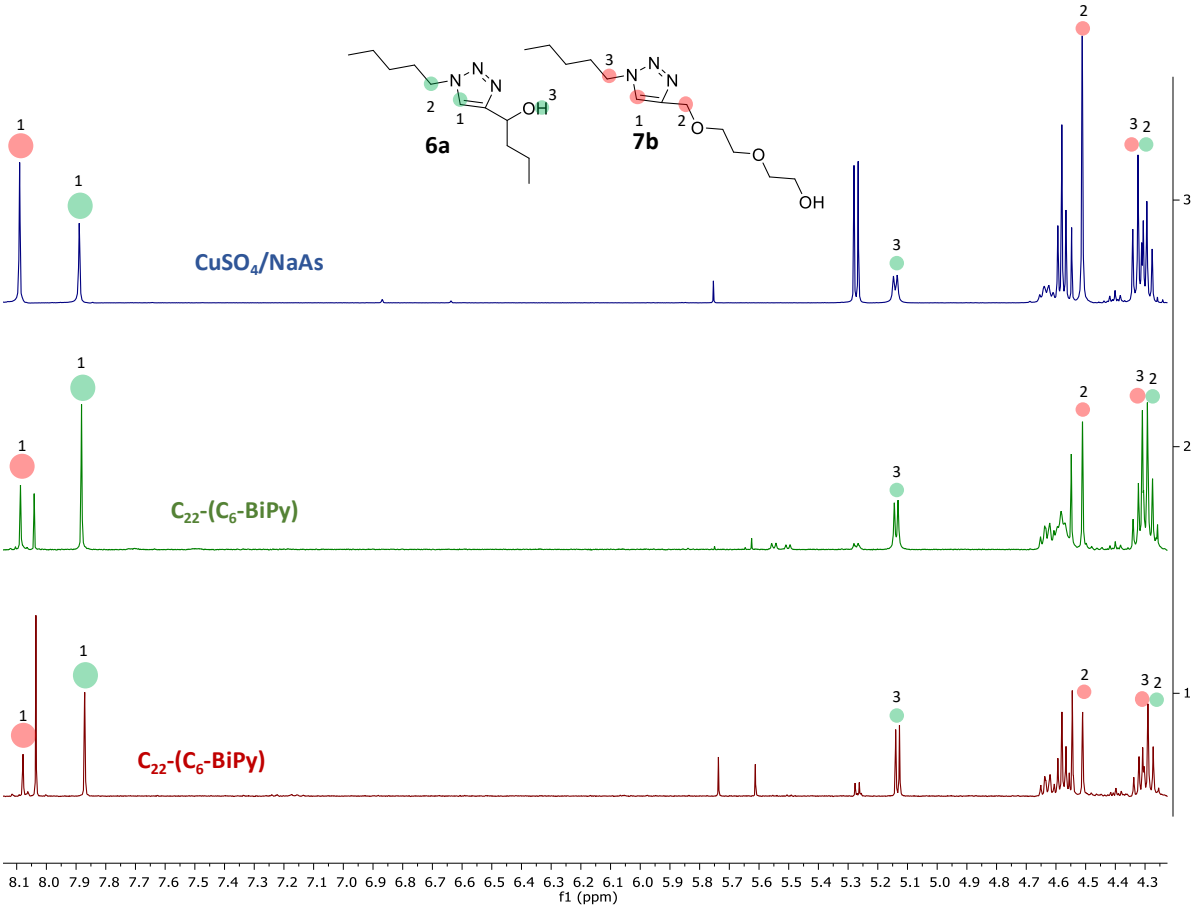


Figure S15. Entry 2: stacked ^{1}H MNR spectra of the competitive reaction when $CuSO_4$/NaAs (blue) and C_{22}-(C_6-bipy) (in duplicate, green and red) were used as catalyst. Average Hydrophobic to hydrophilic ratio = 3.4:1.

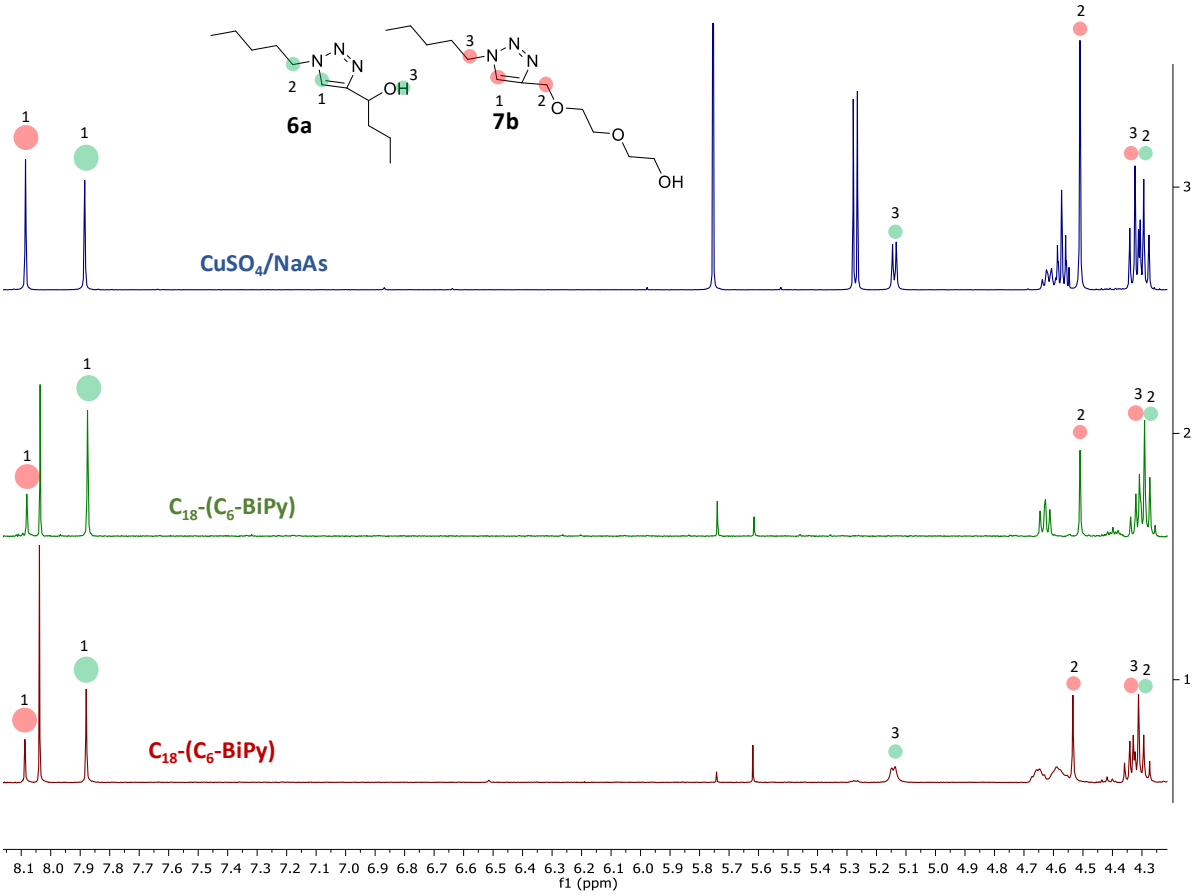
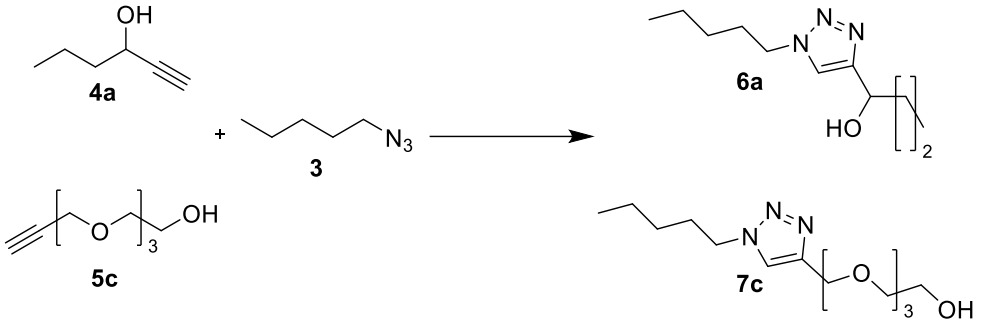


Figure S16. Entry 6: stacked ^{1}H MNR spectra of the competitive reaction when $CuSO_4$/NaAs (blue) and C_{18}-(C_6-bipy) (in duplicate, green and red) were used as catalyst. Average Hydrophobic to hydrophilic ratio = 3.5:1.

4.3.3 Competition reaction between 4a and 5c (entries 3, 7 and III).



4.3.3.1 Competition reaction using $CuSO_4$/NaAs catalysis.

The competition reaction was performed following the general procedure described in 4.1.2, whereby the alkynes hex-1-yn-3-ol (4a) and 2-(2-(2-(prop-2-yn-1-yloxy)ethoxy)ethoxy)ethan-1-ol (5c) where used as the hydrophobic and hydrophilic precursors, respectively.

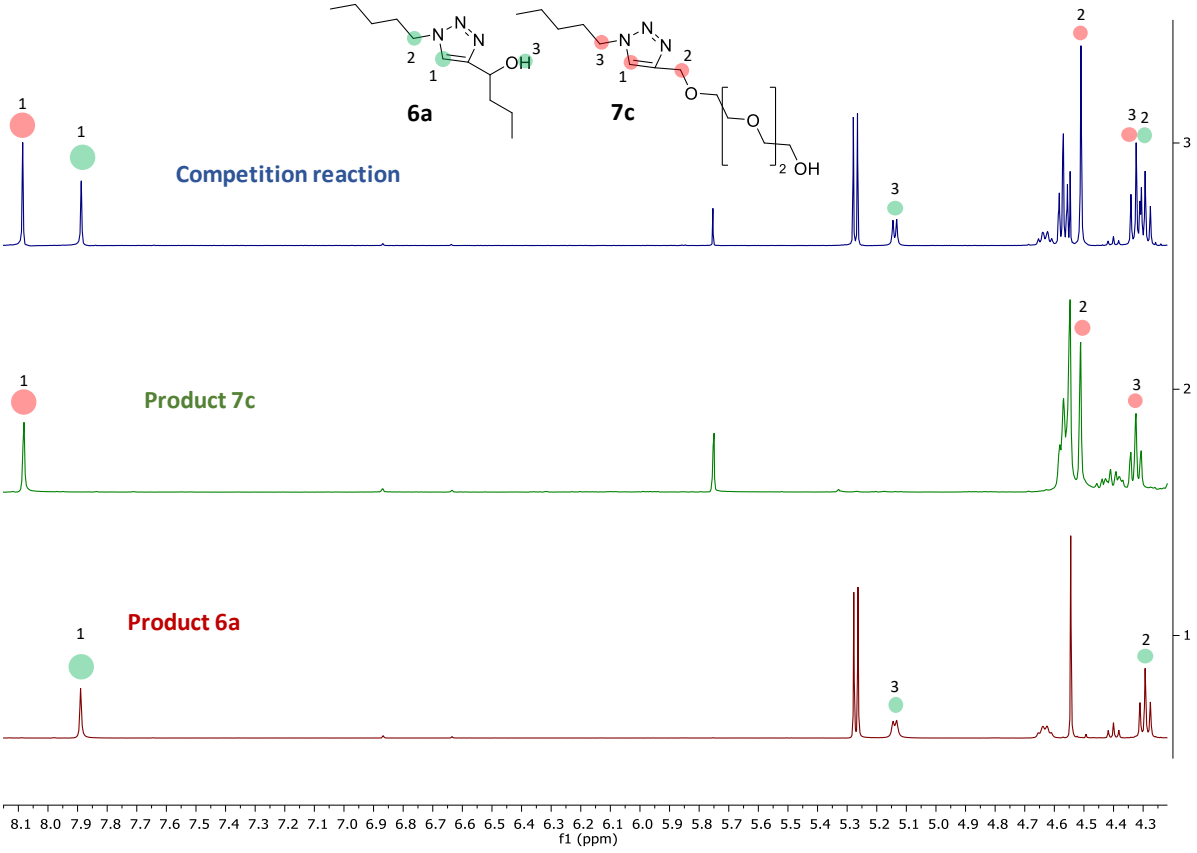


Figure S17. Entry III: stacked ^{1}H MNR spectra of the competitive reaction (blue), and triazole product (6a) (red) and 7c (green) when $CuSO_4$/NaAs was used as the catalyst. $CuSO_4$/NaAs Hydrophobic to hydrophilic ratio = 1:1.7.

4.3.3.2 Competition reaction using Nanoparticle catalyst.

The competition reaction was performed following the general procedure described in section 4.1.3 using C_{22}-(C_6-bipy) or C_{18}-(C_6-bipy) as catalyst, whereby the alkynes hex-1-yn-3-ol (4a) and 2-(2-(2-(prop-2-yn-1-yloxy)ethoxy)ethoxy)ethan-1-ol (5c) where used as the hydrophobic and hydrophilic precursors, respectively.

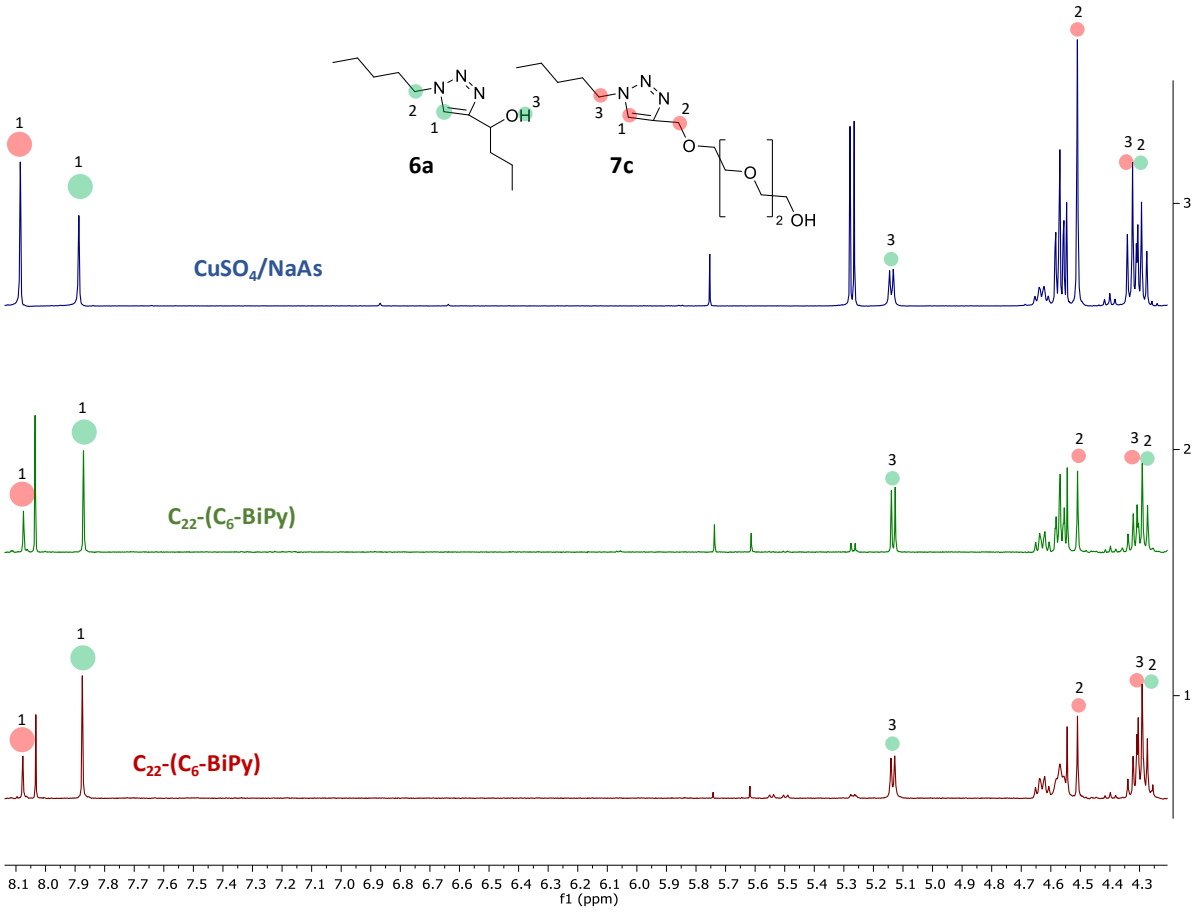


Figure S18. Entry 3: stacked ^{1}H MNR spectra of the competitive reaction when $CuSO_4$/NaAs (blue) and C_{22}-(C_6-bipy) (in duplicate, green and red) were used as catalyst. Hydrophobic to hydrophilic ratio = 3.9:1.

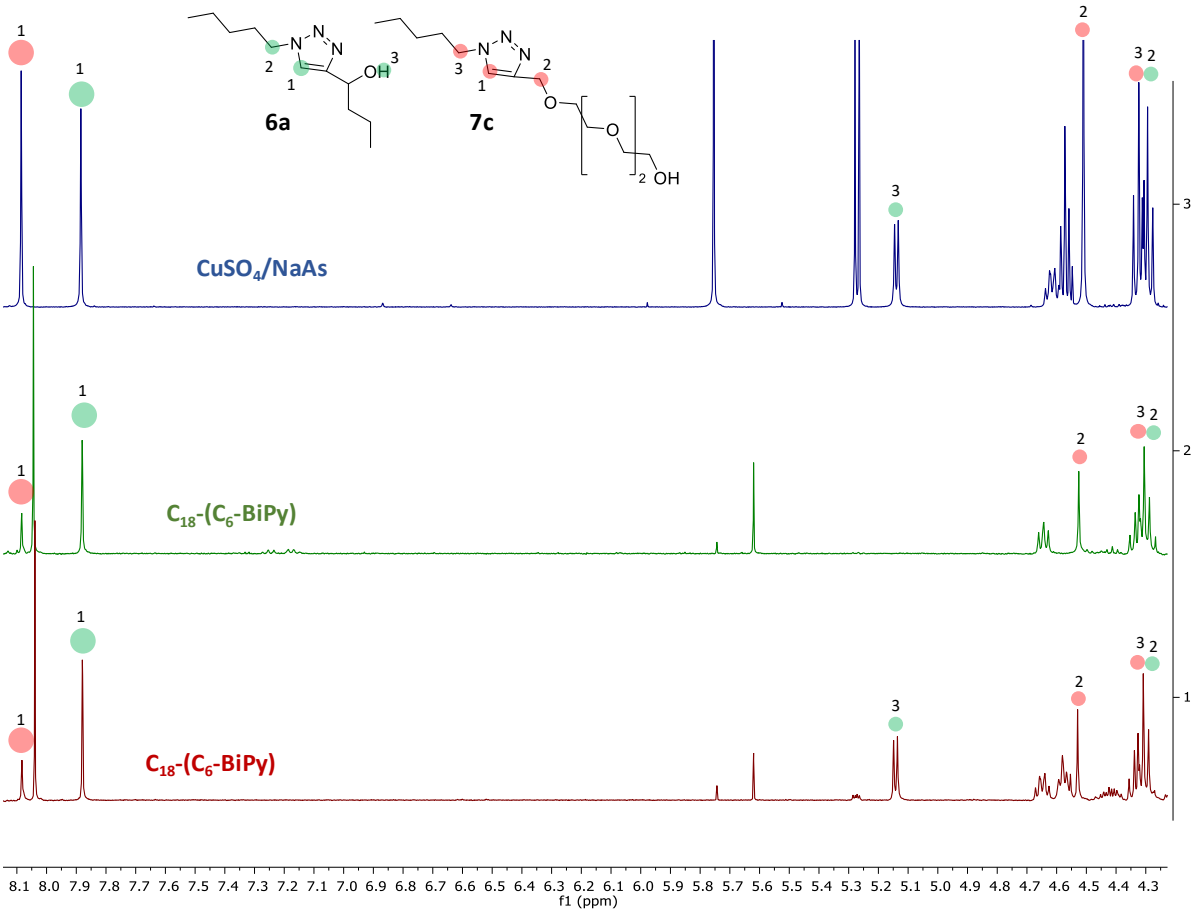
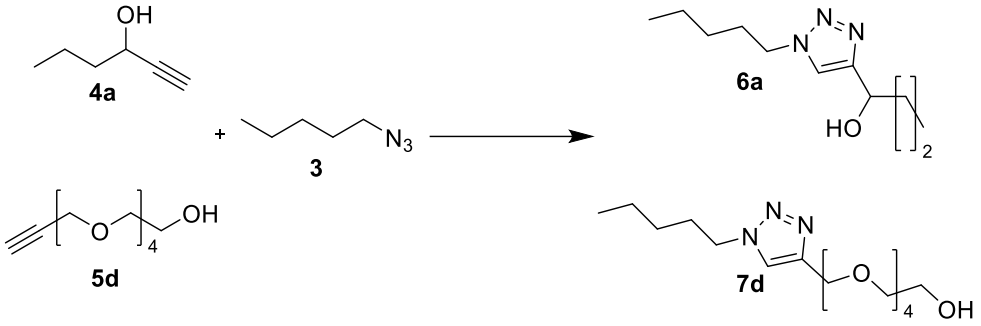


Figure S19. Entry 7: stacked ^{1}H MNR spectra of the competitive reaction when $CuSO_4$/NaAs (blue) and C_{18}-(C_6-bipy) (in duplicate, green and red) were used as catalyst. Hydrophobic to hydrophilic ratio = 4.0:1.

4.3.4 Competition reaction between 4a and 5d (entries 4, 8 and IV).



4.3.4.1 Competition reaction using $CuSO_4$/NaAs catalyst.

The competition reaction was performed following the general procedure described in section 4.1.2, whereby the alkynes hex-1-yn-3-ol (4a) and 3,6,9,12-tetraoxapentadec-14-yn-1-ol (5d) where used as the hydrophobic and hydrophilic precursors, respectively.

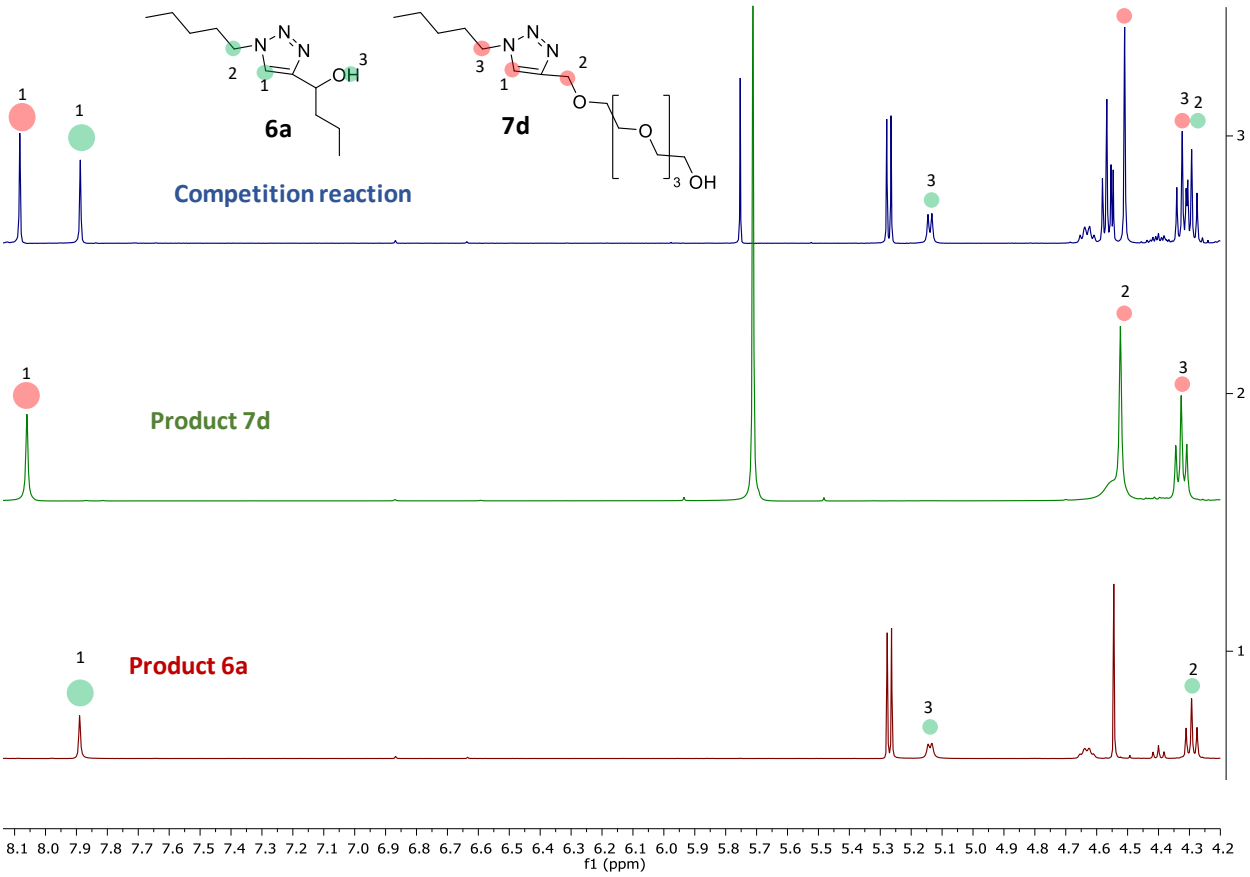


Figure S20. Entry IV: stacked ^{1}H MNR spectra of the competitive reaction (blue), and triazole product (6a) (red) and (7d) (green) when $CuSO_4$/NaAs was used as the catalyst. $CuSO_4$/NaAs hydrophobic to hydrophilic ratio = 1:1.7.

4.3.4.2 Competition reaction using Nanoparticle catalyst.

The competition reaction was performed following the general procedure described in section 4.1.3 using C_{22}-(C_6-bipy) or C_{18}-(C_6-bipy) as the catalyst. The alkynes hex-1-yn-3-ol (4a) and 3,6,9,12-tetraoxapentadec-14-yn-1-ol (5d) where used as the hydrophobic and hydrophilic precursors, respectively.

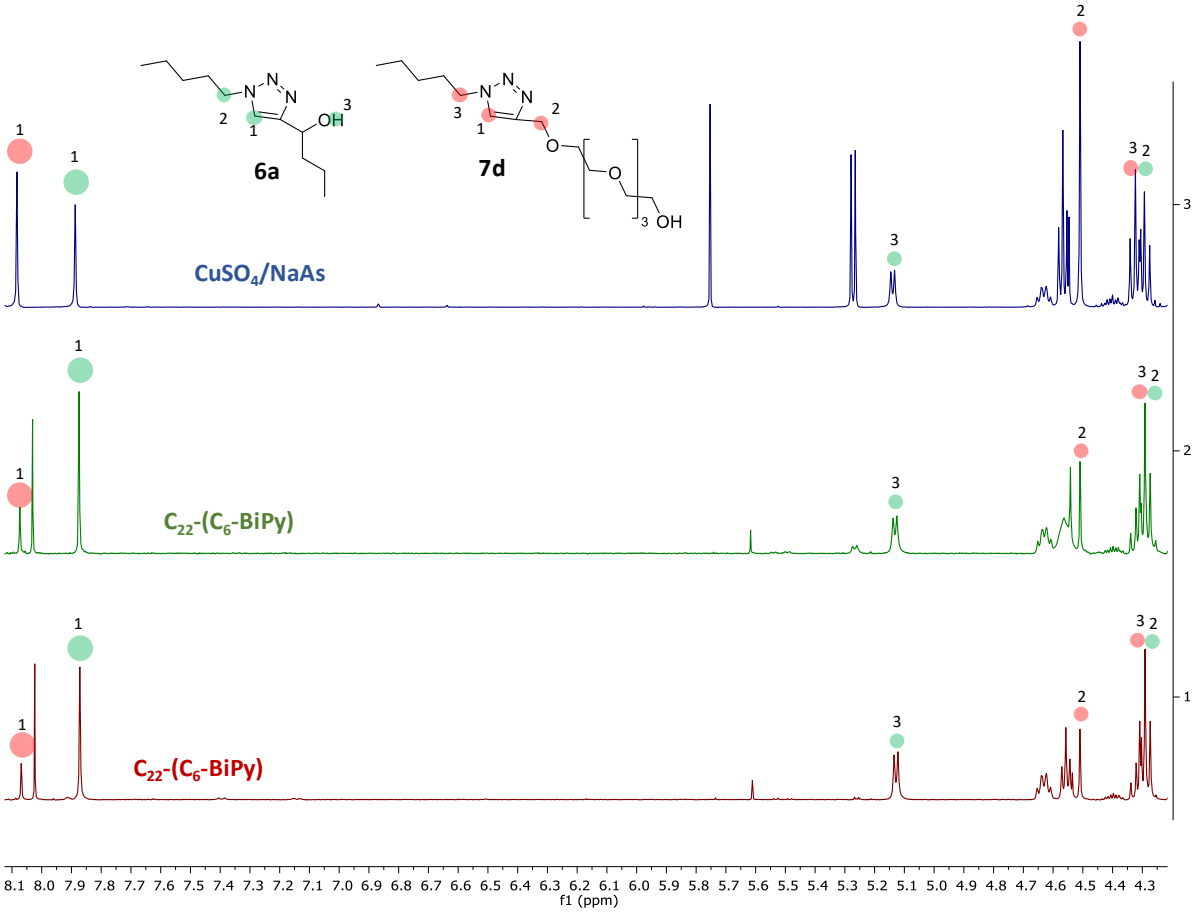


Figure S21. Entry 4: stacked ^{1}H MNR spectra of the competitive reaction when $CuSO_4$/NaAs (blue) and C_{22}-(C_6-bipy) (in duplicate, green and red) were used as catalyst. Average Au NPs hydrophobic to hydrophilic ratio = 4.9:1.

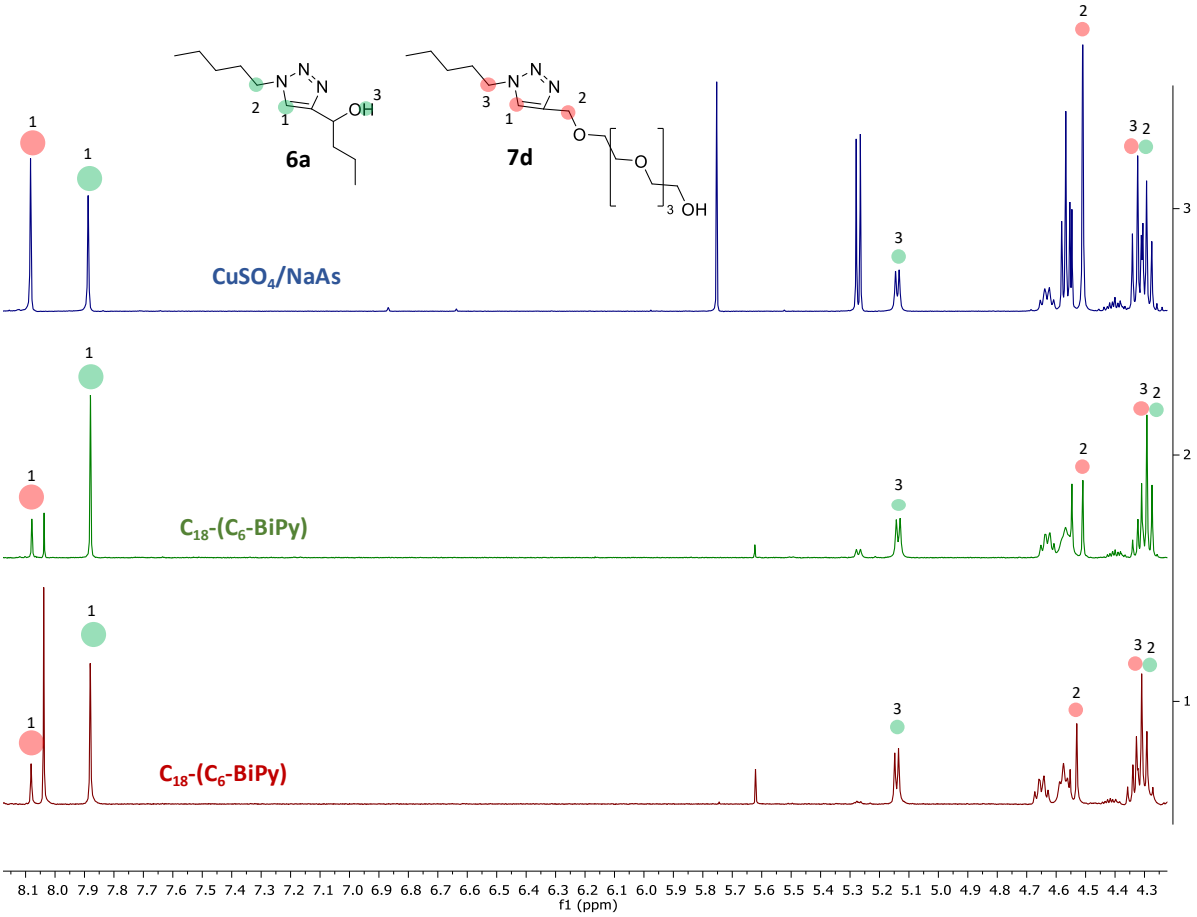
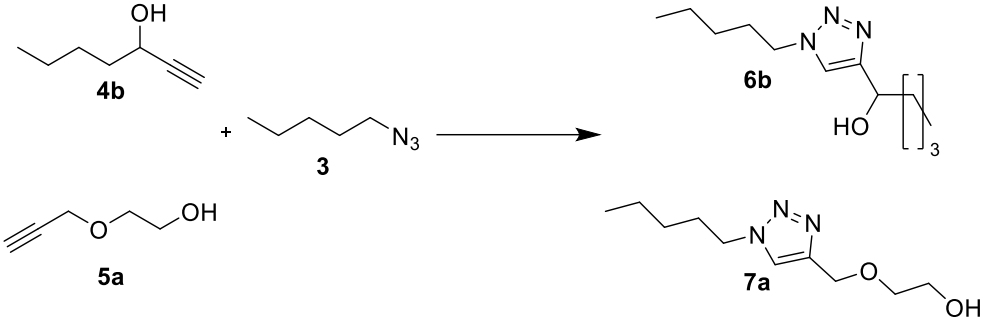


Figure S22. Entry 8: stacked ^{1}H MNR spectra of the competitive reaction when $CuSO_4$/NaAs (blue) and C_{18}-(C_6-bipy) (in duplicate, green and red) were used as catalyst. Average hydrophobic to hydrophilic ratio = 4.8:1.

4.3.5 Competition reaction between 4b and 5a (entries 9, 13 and V).



4.3.5.1 Competition reaction using $CuSO_4$/NaAs as the catalyst.

The competition reaction was done following the general procedure described in section 4.1.2. The alkynes used were the hydrophobic hept-1-yn-3-ol (4b) and the hydrophilic 2-(prop-2-yn-1-yloxy)ethan-1-ol (5a).

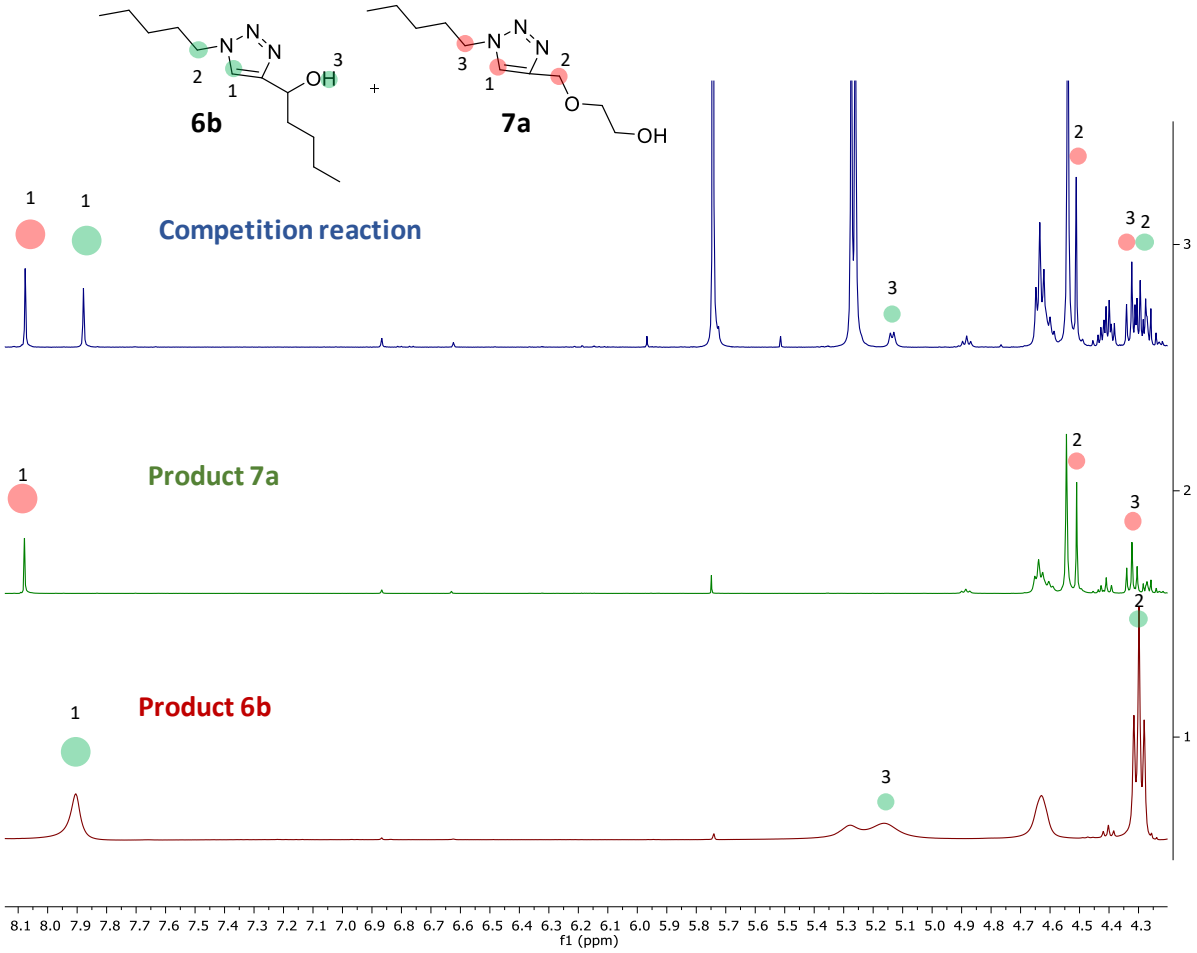


Figure S23. Entry V: stacked ^{1}H MNR spectra of the competitive reaction (blue), and triazole product (6b) (red) and (7a) (green) when $CuSO_4$/NaAs was used as the catalyst. $CuSO_4$/NaAs hydrophobic to hydrophilic ratio = 1:1.9.

4.3.5.2 Competition reaction using Nanoparticle catalyst.

The competition reaction was performed following the general procedure described in 4.1.3, wereby the alkynes were the hydrophobic hept-1-yn-3-ol (4b) and the hydrophilic 2-(prop-2-yn-1-yloxy)ethan-1-ol (5a).

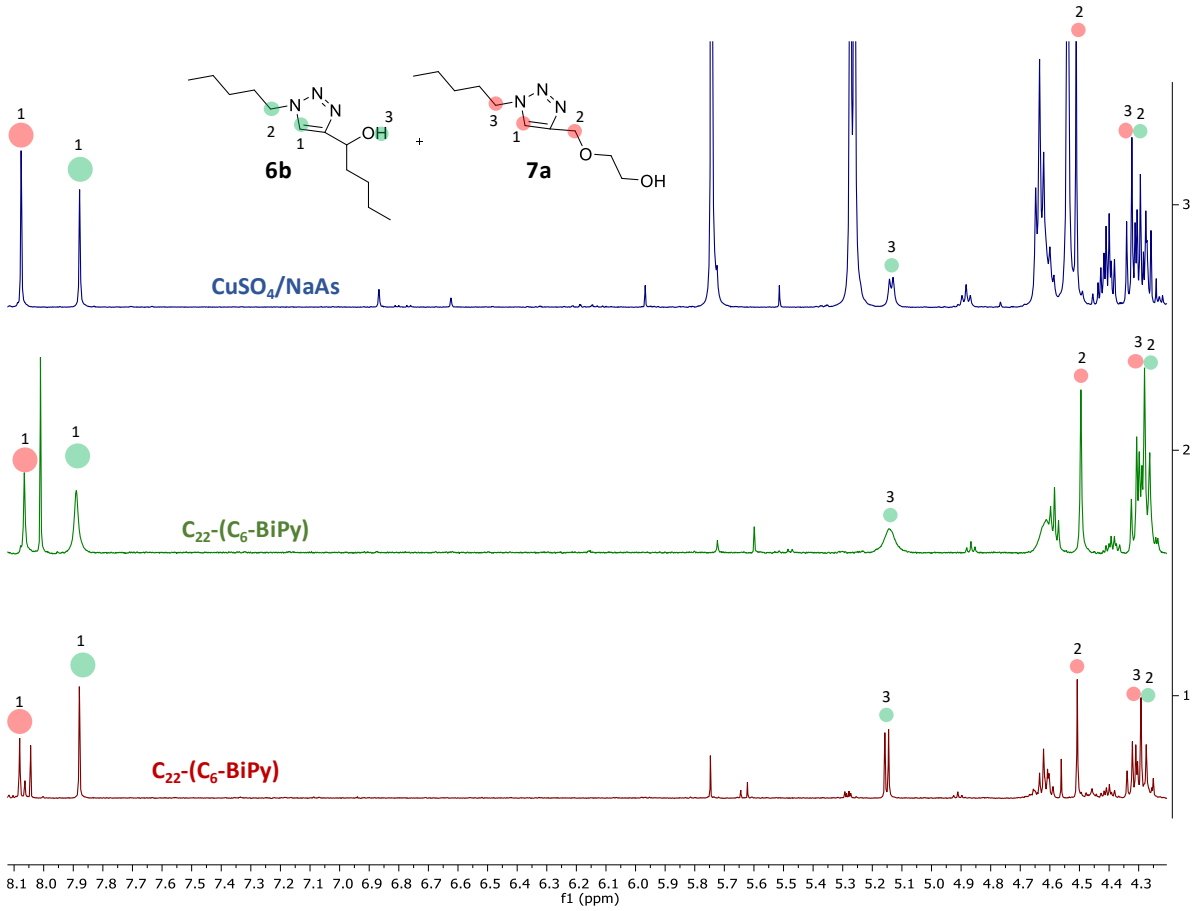


Figure S24. Entry 9: stacked ^{1}H MNR spectra of the competitive reaction when $CuSO_4$/NaAs (blue) and C_{22}-(C_6-bipy) (in duplicate, green and red) were used as catalyst. Average hydrophobic to hydrophilic ratio = 3.0:1.

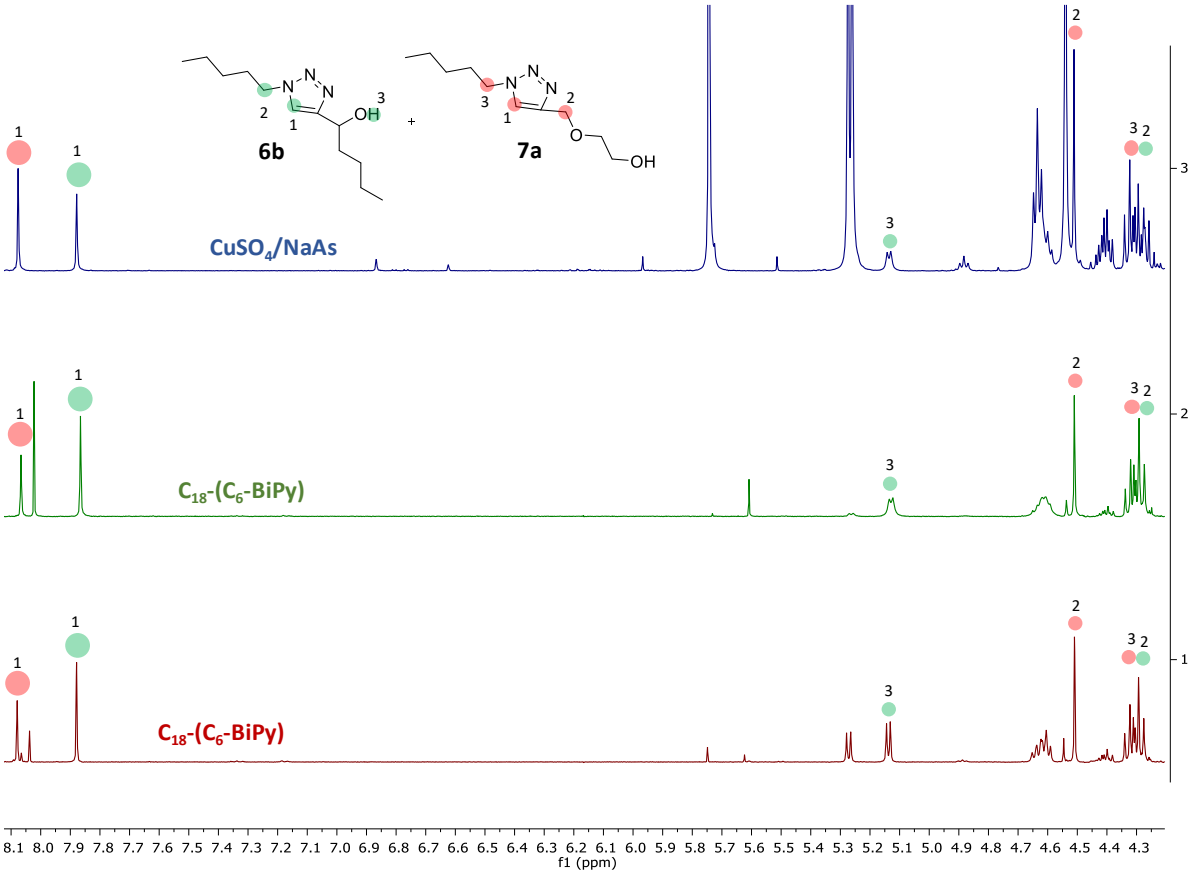
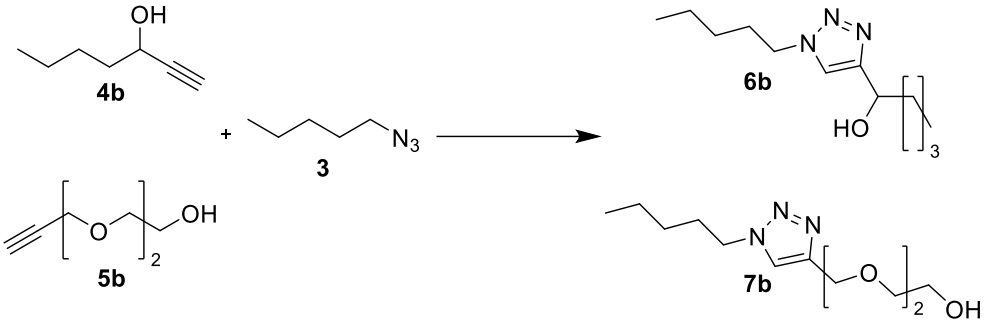


Figure S25. Entry 13: stacked ^{1}H MNR spectra of the competitive reaction when $CuSO_4$/NaAs (blue) and C_{18}-(C_6-bipy) (in duplicate, green and red) were used as catalyst. Average hydrophobic to hydrophilic ratio = 2.6:1.

4.3.6 Competition reaction between 4b and 5b (entries 10, 14 and VI).



4.3.6.1 Competition reaction using $CuSO_4$/NaAs catalyst.

The competition reaction was performed following the general procedure described in 4.1.2, whereby the alkynes were the hydrophobic hept-1-yn-3-ol (4b) and the hydrophilic 2-(2-(prop-2-yn-1-yloxy)ethoxy)ethan-1-ol (5b).

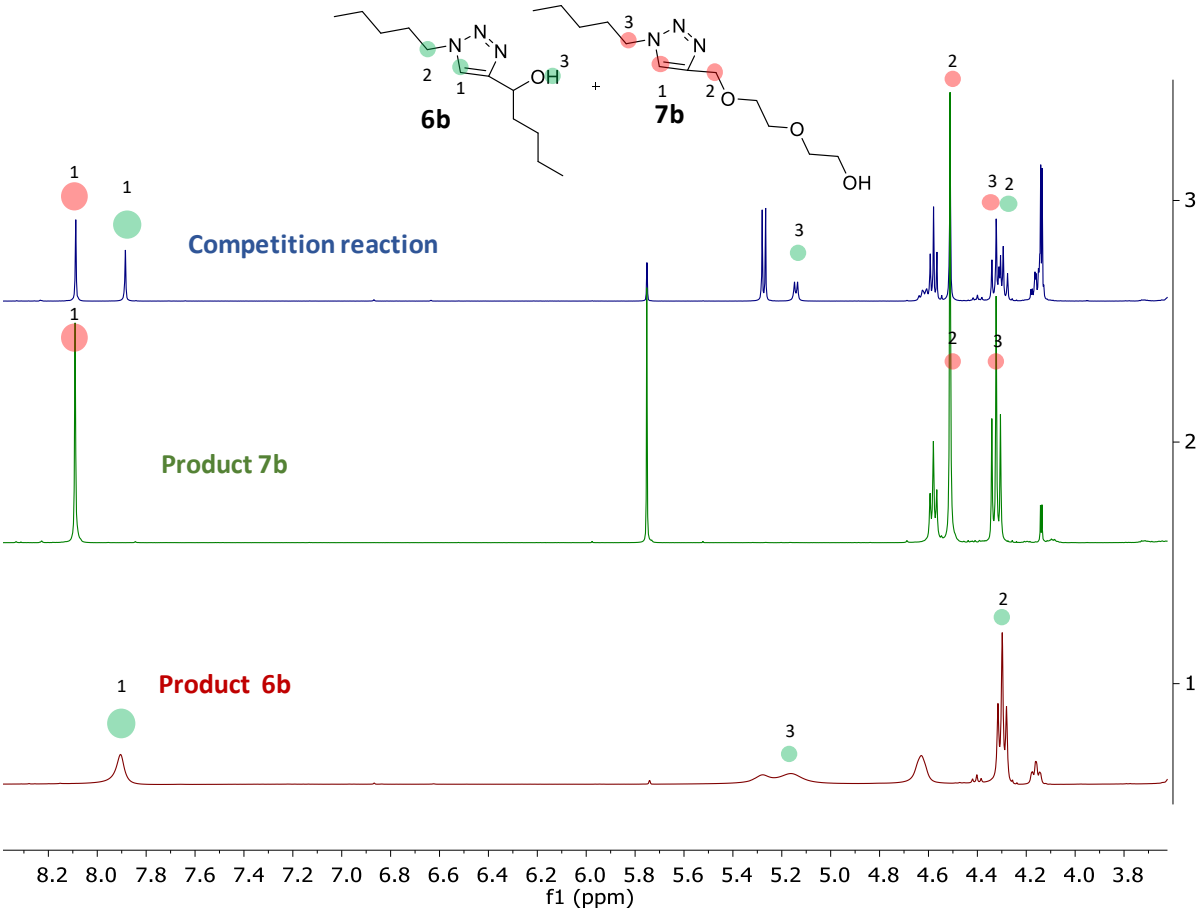


Figure S26. Entry VI: stacked ^{1}H MNR spectra of the competitive reaction when $CuSO_4$/NaAs (blue), and triazole product (6b) (red) and (7b) (green) was used as catalyst. $CuSO_4$/NaAs hydrophobic to hydrophilic ratio = 1:1.7.

4.3.6.2 Competition reaction using Nanoparticle catalyst.

The competition reaction was performed following the general procedure described in 4.1.3, whereby the alkynes were the hydrophobic hept-1-yn-3-ol (4b) and the hydrophilic 2-(2-(prop-2-yn-1-yloxy)ethoxy)ethan-1-ol (5b).

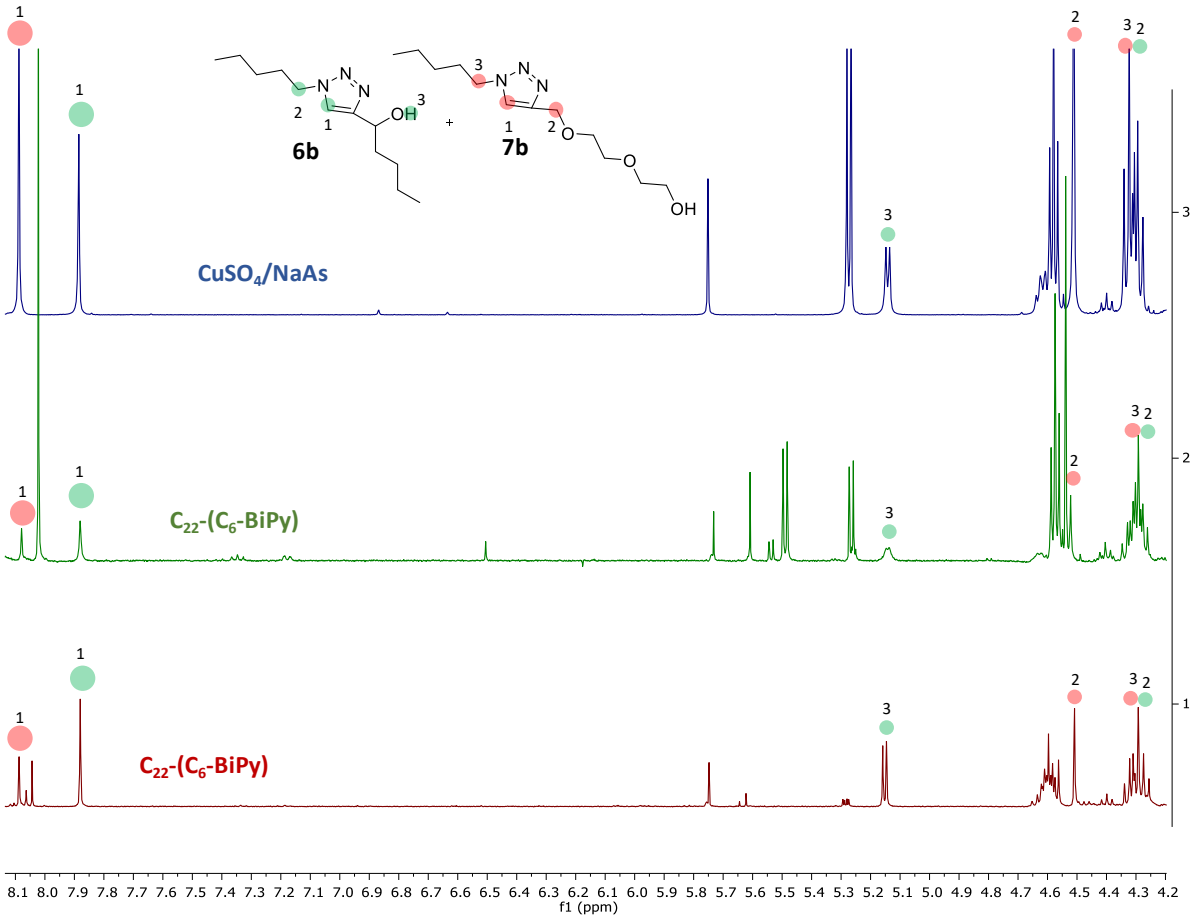


Figure S27. Entry 10: stacked ^{1}H MNR spectra of the competitive reaction when $CuSO_4$/NaAs (blue) and C_{22}-(C_6-bipy) (in duplicate, green and red) were used as catalyst. Average hydrophobic to hydrophilic ratio = 3.4:1.

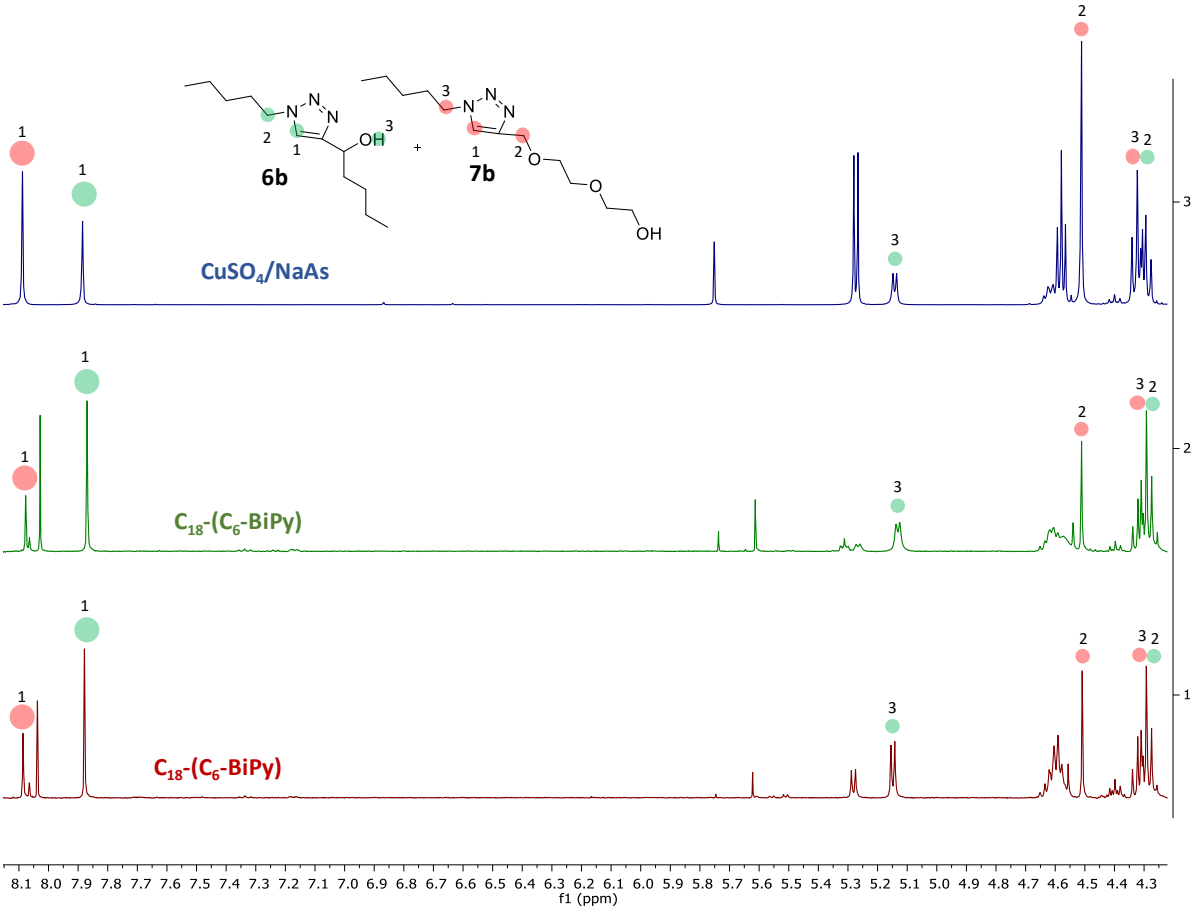
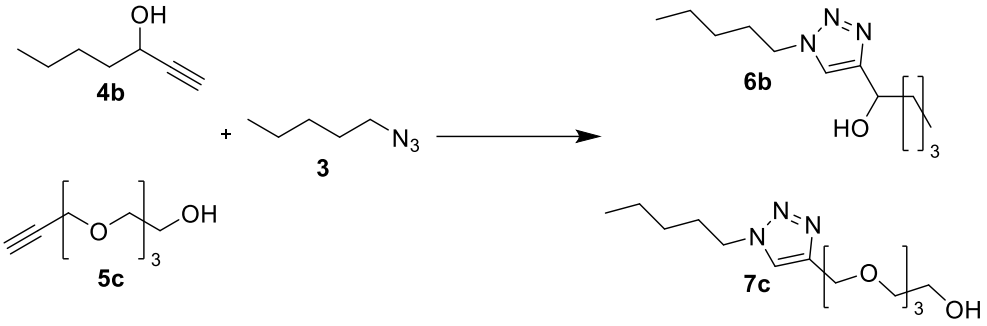


Figure S28. Entry 14: stacked ^{1}H MNR spectra of the competitive reaction when $CuSO_4$/NaAs (blue) and C_{18}-(C_6-bipy) (in duplicate, green and red) were used as catalyst. Average hydrophobic to hydrophilic ratio = 3.3:1.

4.3.7 Competition reaction between 4b and 5c (entries 11, 15 and VII).



4.3.7.1 Competition reaction using $CuSO_4$/NaAs catalyst.

The competition reaction was performed following the general procedure described in 4.1.2, whereby the alkynes were the hydrophobic hept-1-yn-3-ol (4b) and the hydrophilic 2-(2-(2-(prop-2-yn-1-yloxy)ethoxy)ethoxy)ethan-1-ol (5c).

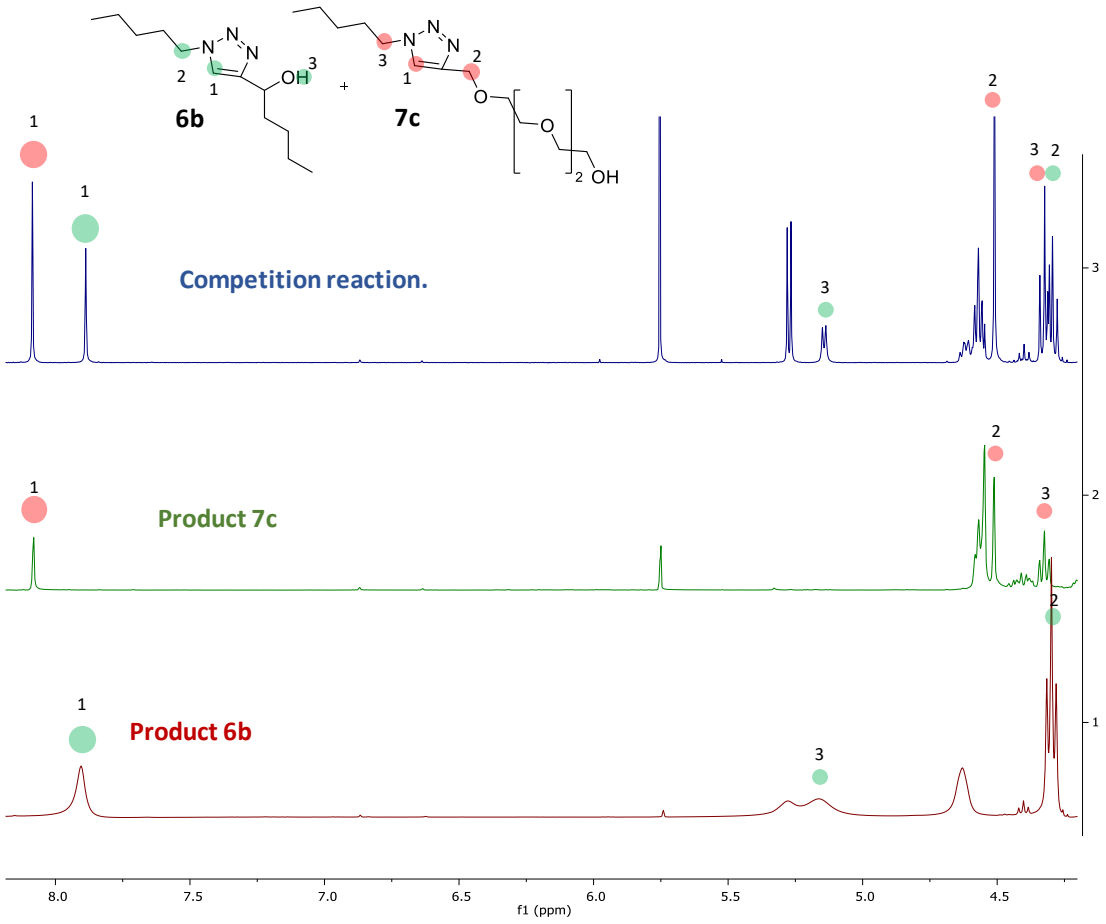


Figure S29. Entry VII, stacked ^{1}H MNR spectra of the competitive reaction when $CuSO_4$/NaAs (blue), and triazole product (6b) (red) and (7c) (green) was used as the catalyst. $CuSO_4$/NaAs hydrophobic to hydrophilic ratio = 1:1.7.

4.3.7.2 Competition reaction using Nanoparticle catalyst.

The competition reaction was performed following the general procedure described in 4.1.3, whereby the alkynes were the hydrophobic hept-1-yn-3-ol (4b) and the hydrophilic 2-(2-(2-(prop-2-yn-1-yloxy)ethoxy)ethoxy)ethan-1-ol (5c).

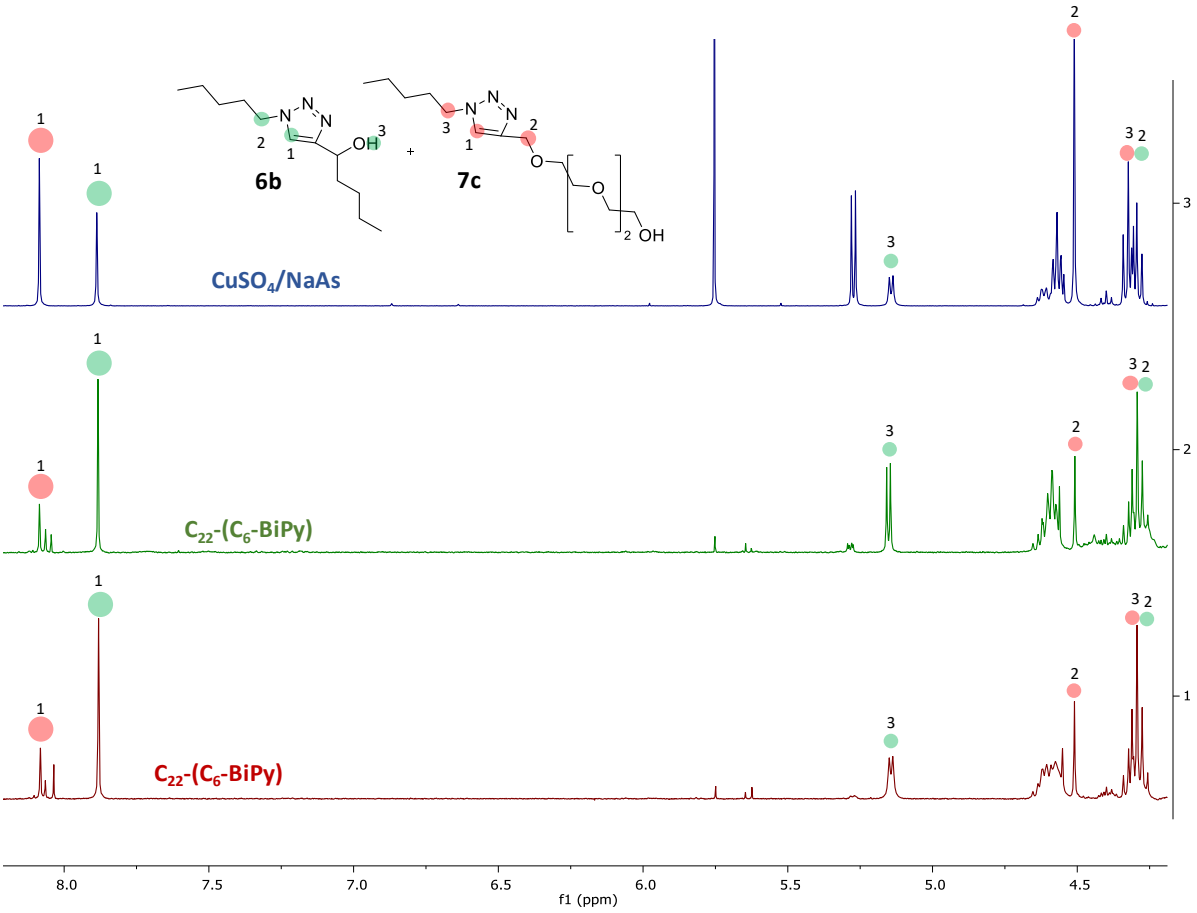


Figure S30. Entry 11, stacked ^{1}H MNR spectra of the competitive reaction when $CuSO_4$/NaAs (blue) and C_{22}-(C_6-biyy) (in duplicate, green and red) were used as catalyst. Average hydrophobic to hydrophilic ratio = 4.9:1.

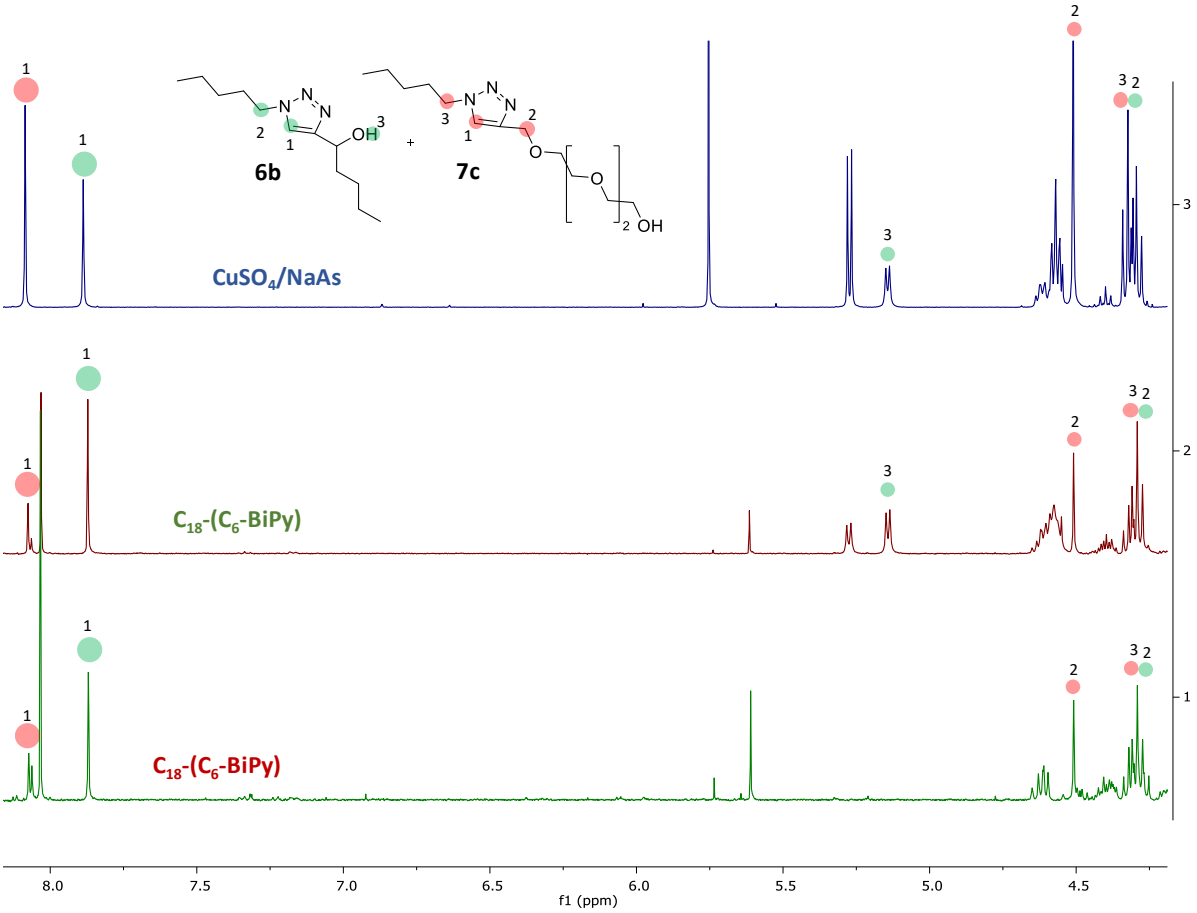
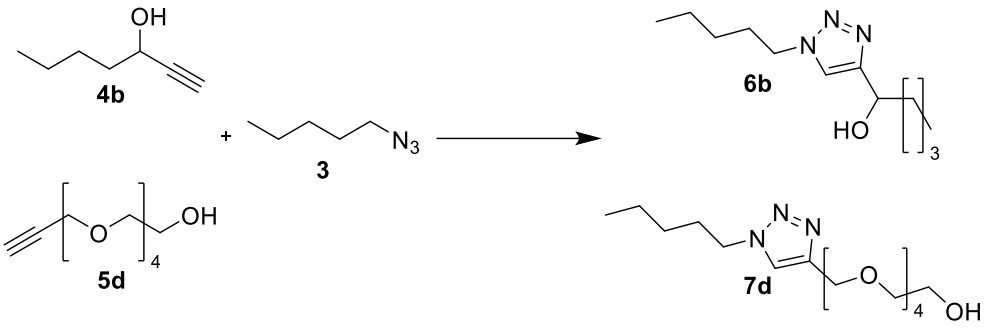


Figure S31. Entry 15, stacked ^{1}H MNR spectra of the competitive reaction when $CuSO_4$/NaAs (blue) and C_{18}-(C_6-bipy) (in duplicate; green and red) were used as catalyst. Average hydrophobic to hydrophilic ratio = 3.7:1.

4.3.8 Competition reaction between 4b and 5d (entries 12, 16 and VIII).



4.3.8.1 Competition reaction using $CuSO_4$/NaAs catalyst.

The competition reaction was performed following the general procedure described in 4.1.2, whereby the alkynes were the hydrophobic hept-1-yn-3-ol (4b) and the hydrophilic 3,6,9,12-tetraoxapentadec-14-yn-1-ol (5d).

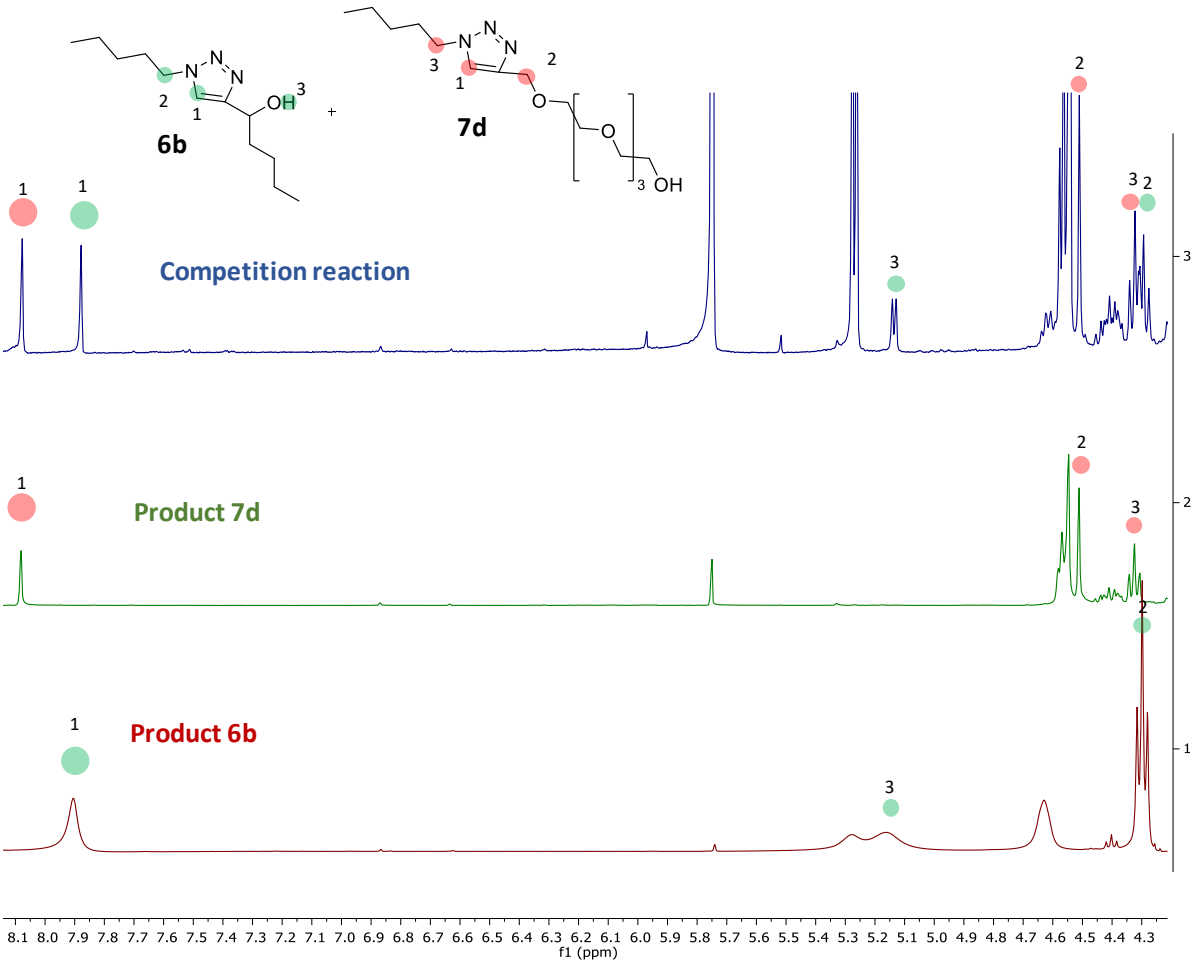


Figure S32. Entry VIII: stacked ^{1}H MNR spectra of the competitive reaction when $CuSO_4$/NaAs (blue), and triazole product 6b (red) and(7d) (green) were used as catalyst. $CuSO_4$/NaAs hydrophobic to hydrophilic ratio = 1:1.9.

4.3.8.2 Competition reaction using Nanoparticle catalyst.

The competition reaction was performed following the general procedure described in 4.1.3, whereby the alkynes were the hydrophobic hept-1-yn-3-ol (4b) and the hydrophilic 3,6,9,12-tetraoxapentadec-14-yn-1-ol (5d).

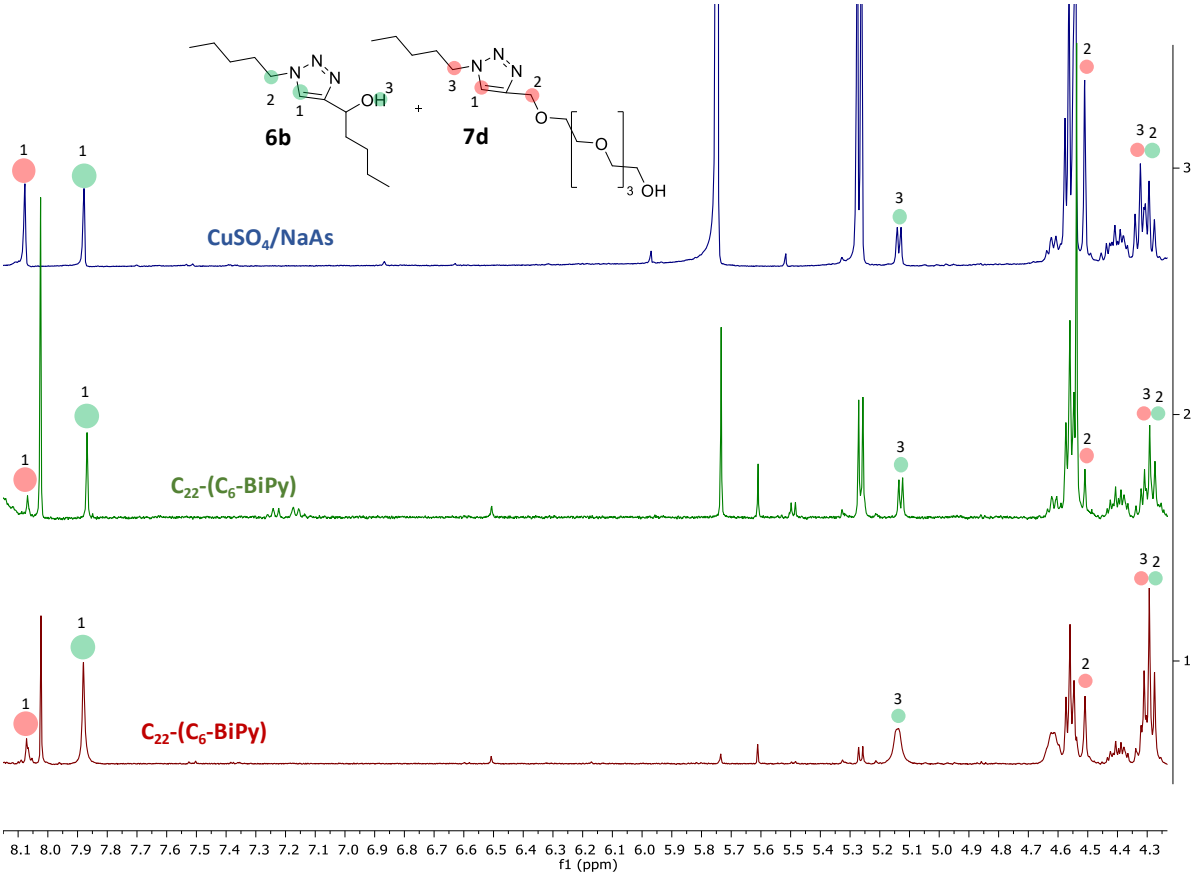


Figure S33. Entry 12: stacked ^{1}H MNR spectra of the competitive reaction when $CuSO_4$/NaAs (blue) and C_{22}-(C_6-bipy) (in duplicate, green and red) were used as catalyst. Average hydrophobic to hydrophilic ratio = 6.2:1.

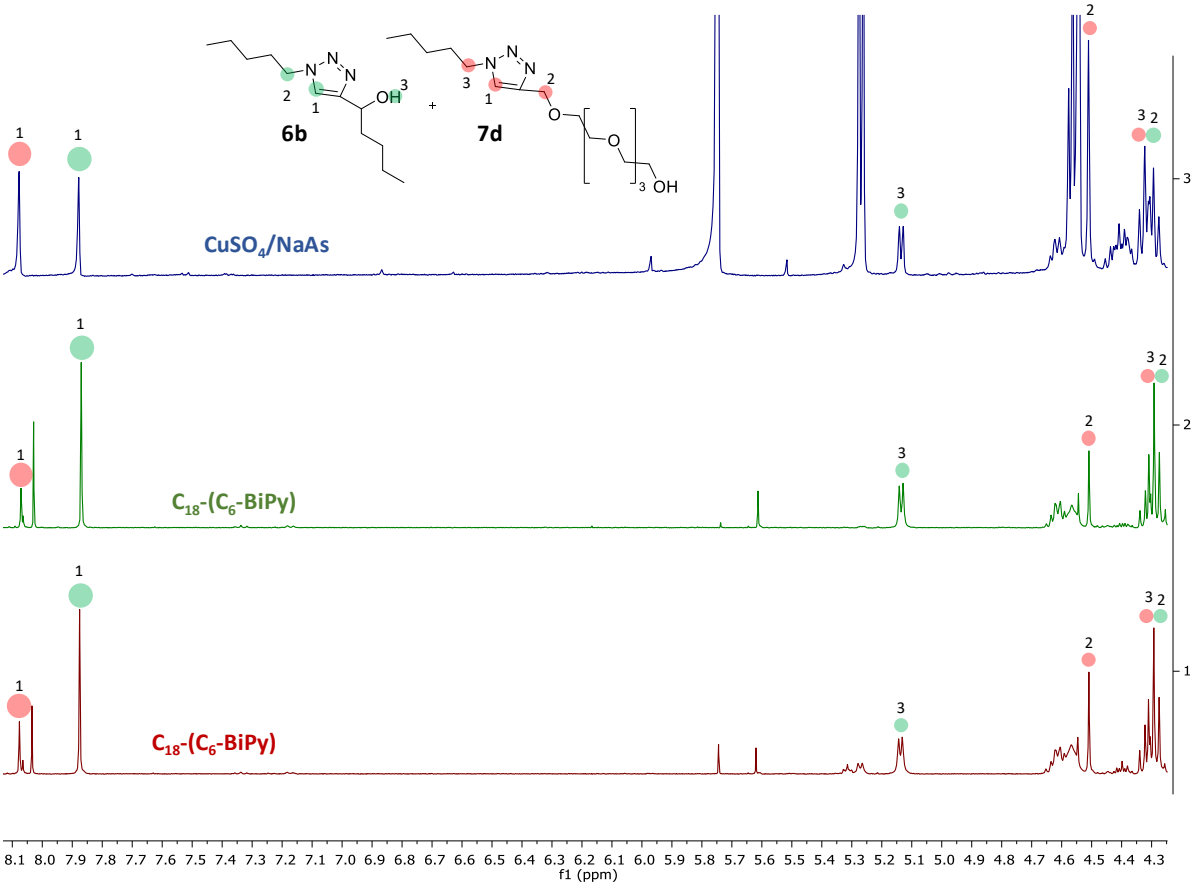
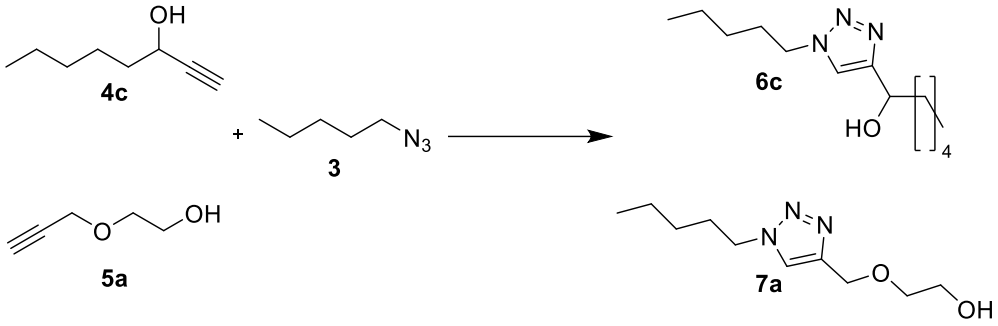


Figure S34: Entry 16: stacked ^{1}H MNR spectra of the competitive reaction when $CuSO_4$/NaAs (blue) and C_{18}-(C_6-bipy) (in duplicate, green and red) were used as catalyst. Average hydrophobic to hydrophilic ratio = 4.1:1.

4.3.9 Competition reaction between 4c and 5a (entries 17, 21, 25, 29 and IX).



4.3.9.1 Competition reaction using $CuSO_4$/NaAs catalyst.

The competition reaction was performed following the general procedure described in 4.1.2, whereby the alkynes were the hydrophobic oct-1-yn-3-ol (4c) and the hydrophilic 2-(prop-2-yn-1-yloxy)ethan-1-ol (5a).

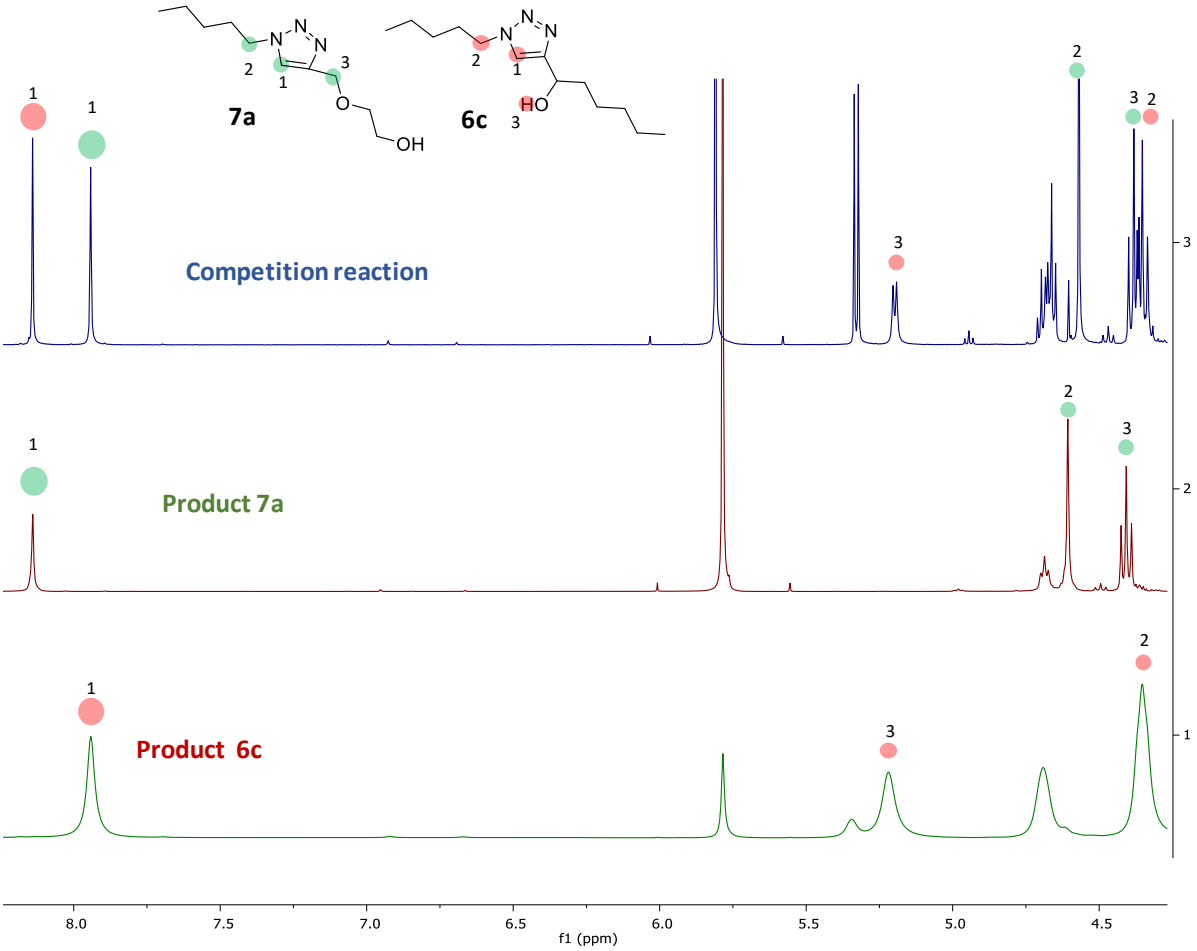


Figure S35. Entry IX: stacked ^{1}H MNR spectra of the competitive reaction when $CuSO_4$/NaAs (blue), and triazole product(6c) (red) and 7a (green) were used as catalyst. $CuSO_4$/NaAs hydrophobic to hydrophilic ratio = 1:1.8.

4.3.9.2 Competition reaction using Nanoparticle catalyst.

The competition reaction was performed following the general procedure described in 4.1.3 using C_{22}-(C_6-bipy) or C_{18}-(C_6-bipy) as catalyst. The alkynes were the hydrophobic oct-1-yn-3-ol (4c) and the hydrophilic 2-(prop-2-yn-1-yloxy)ethan-1-ol (5a).

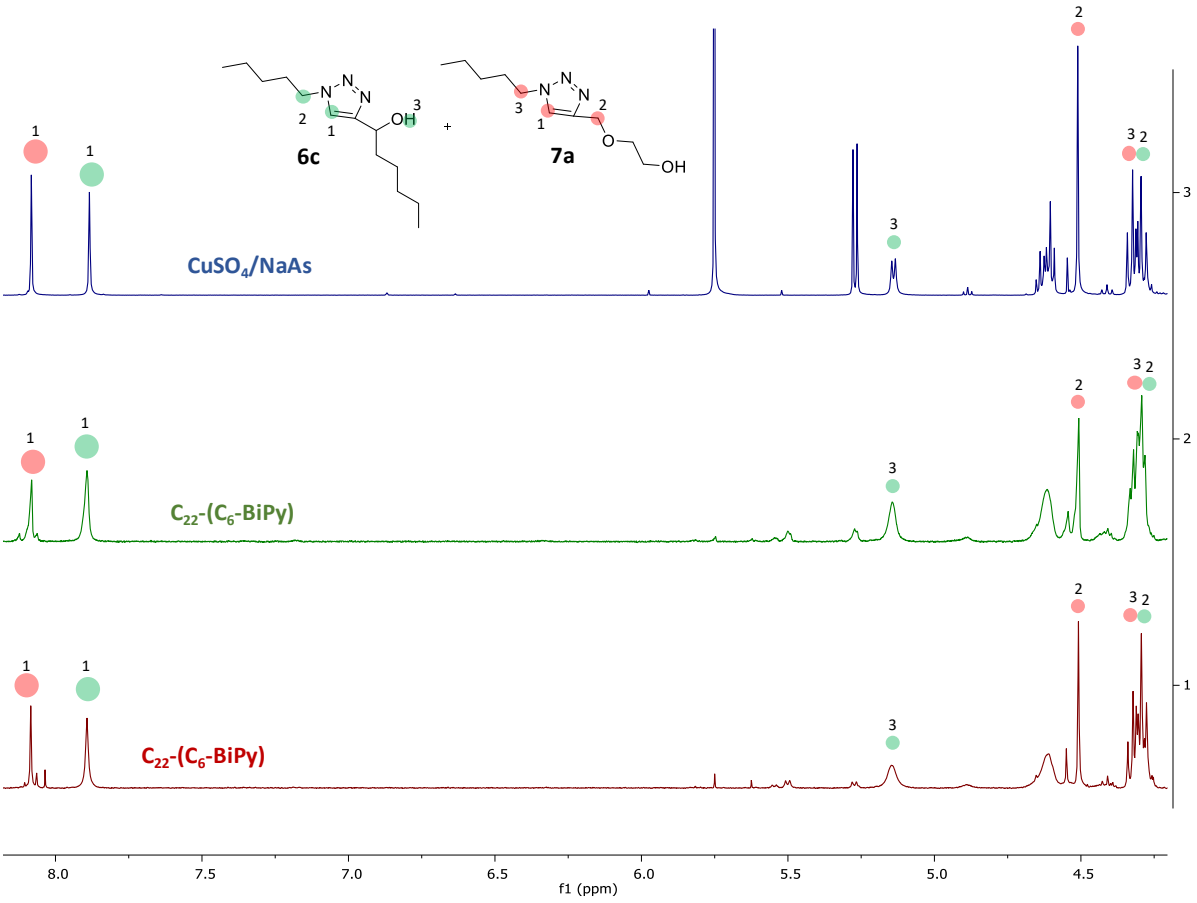


Figure S36. Entry 17: stacked ^{1}H MNR spectra of the competitive reaction when $CuSO_4$/NaAs (blue) and C_{22}-(C_6-bipy) (in duplicate, green and red) were used as catalyst. Average hydrophobic to hydrophilic ratio = 3.0:1.

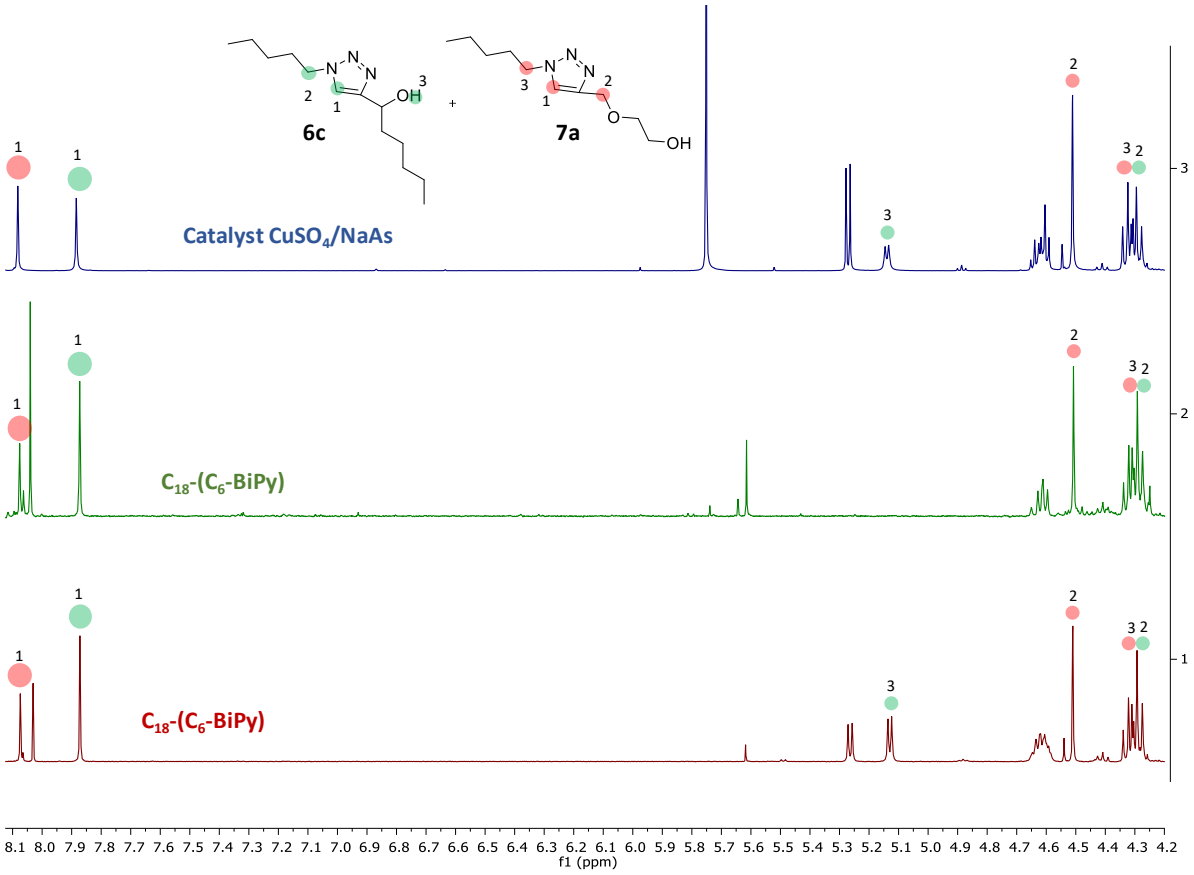


Figure S37. Entry 21: stacked ^{1}H MNR spectra of the competitive reaction when $CuSO_4$/NaAs (blue) and C_{18}-(C_6-BiPy) (in duplicate, green and red) were used as catalyst. Average hydrophobic to hydrophilic ratio = 2.9:1.

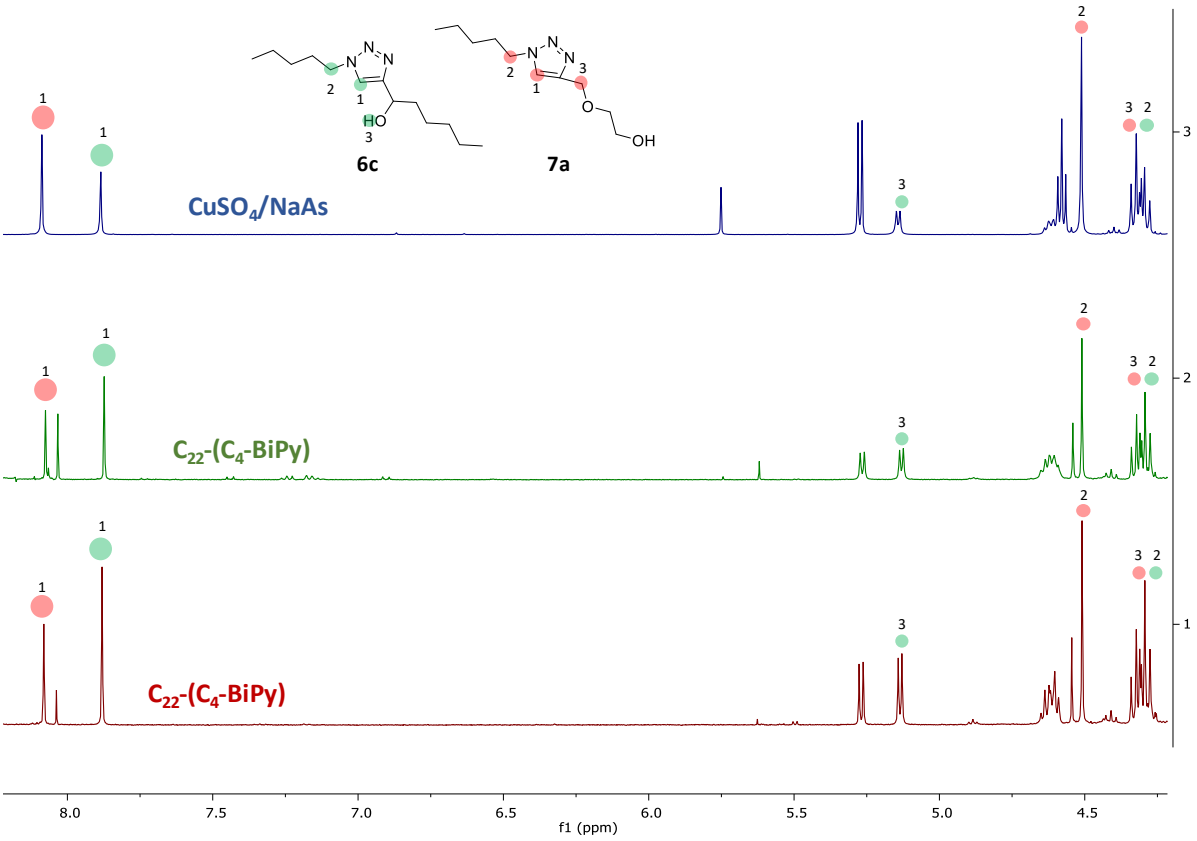


Figure S38. Entry 25: stacked ^{1}H MNR spectra of the competitive reaction when $CuSO_4$/NaAs (blue) and C_{22}-(C_4-bipy) (in duplicate, green and red) were used as catalyst. Average hydrophobic to hydrophilic ratio = 2.9:1.

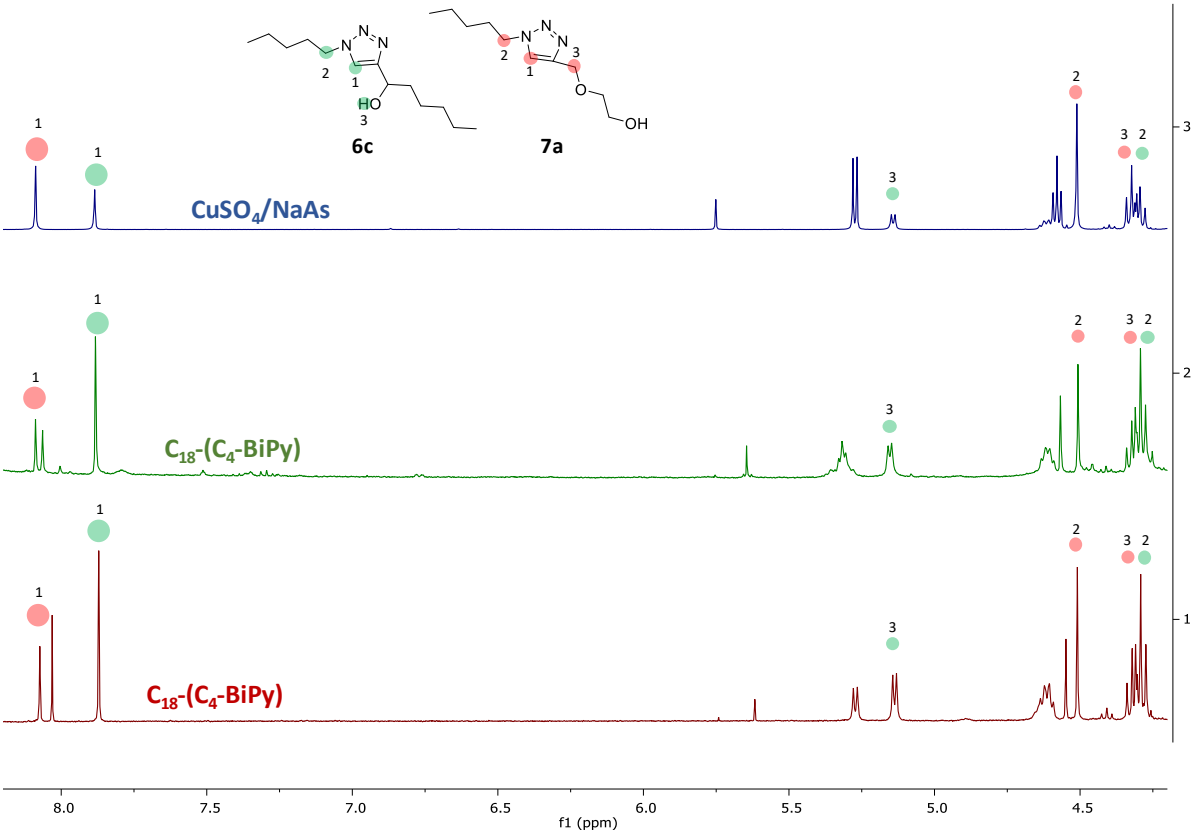
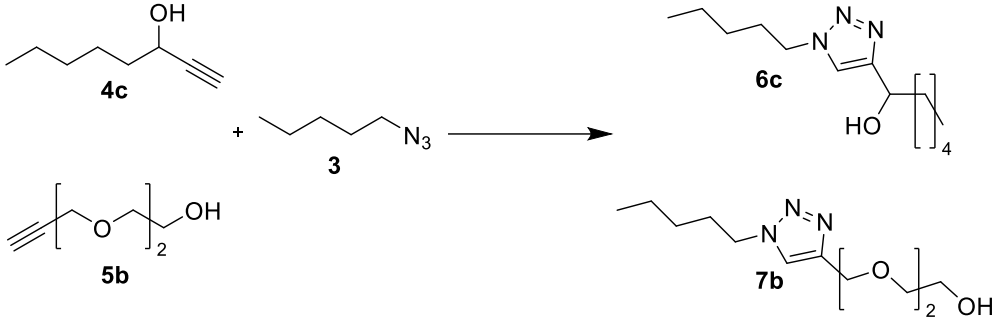


Figure S39. Entry 29: stacked ^{1}H MNR spectra of the competitive reaction when $CuSO_4$/NaAs (blue) and C_{18}-(C_4-bipy) (in duplicate, green and red) were used as catalyst. Average hydrophobic to hydrophilic ratio = 2.9:1.

4.3.10 Competition reaction between 4c and 5b (entries 18, 22, 26, 30 and X).



4.3.10.1 Competition reaction using $CuSO_4$/NaAs as catalyst.

The competition reaction was performed following the general procedure described in 4.1.2, whereby the hydrophobic oct-1-yn-3-ol (4c) and the hydrophilic 2-(2-(prop-2-yn-1-yloxy)ethoxy)ethan-1-ol (5b) alkynes were used.

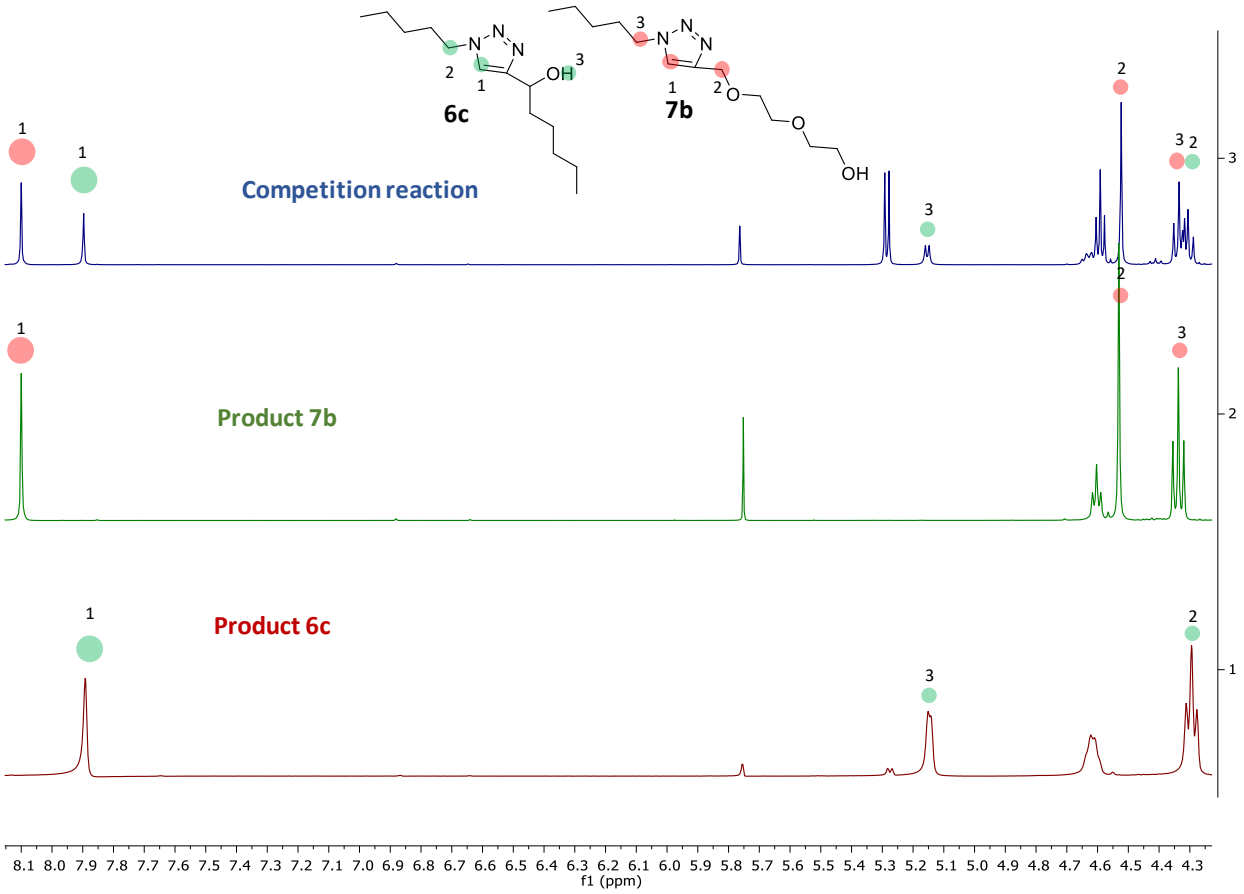


Figure S40. Entry X: stacked ^{1}H MNR spectra of the competitive reaction (blue), and triazole product (6c) (red) and 7b (green) when $CuSO_4$/NaAs was used as the catalyst. $CuSO_4$/NaAs hydrophobic to hydrophilic ratio = 1:1.6.

4.3.10.2 Competition reaction using Nanoparticle catalyst.

The competition reaction was performed following the general procedure described in 4.1.3 using C_{22}-(C_6-bipy), C_{18}-(C_6-bipy), C_{22}-(C_4-bipy) or C_{18}-(C_4-bipy) as the catalyst, and the hydrophobic oct-1-yn-3-ol (4c) and hydrophilic 2-(2-(prop-2-yn-1-yloxy)ethoxy)ethan-1-ol (5b) alkynes.

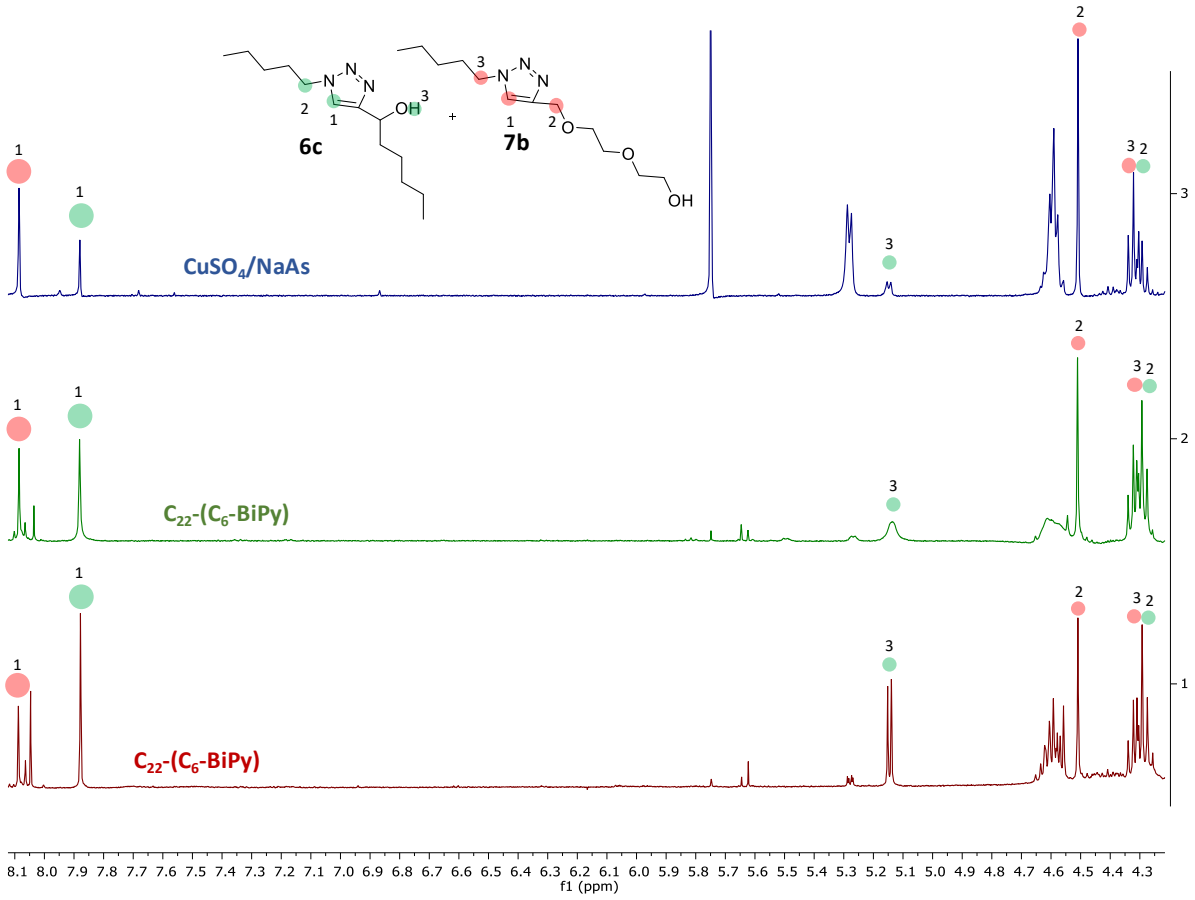


Figure S41. Entry 18: stacked ^{1}H MNR spectra of the competitive reaction when $CuSO_4$/NaAs (blue) and C_{22}-(C_6-bipy) (in duplicate, green and red) were used as catalyst. Average hydrophobic to hydrophilic ratio = 3.0:1.

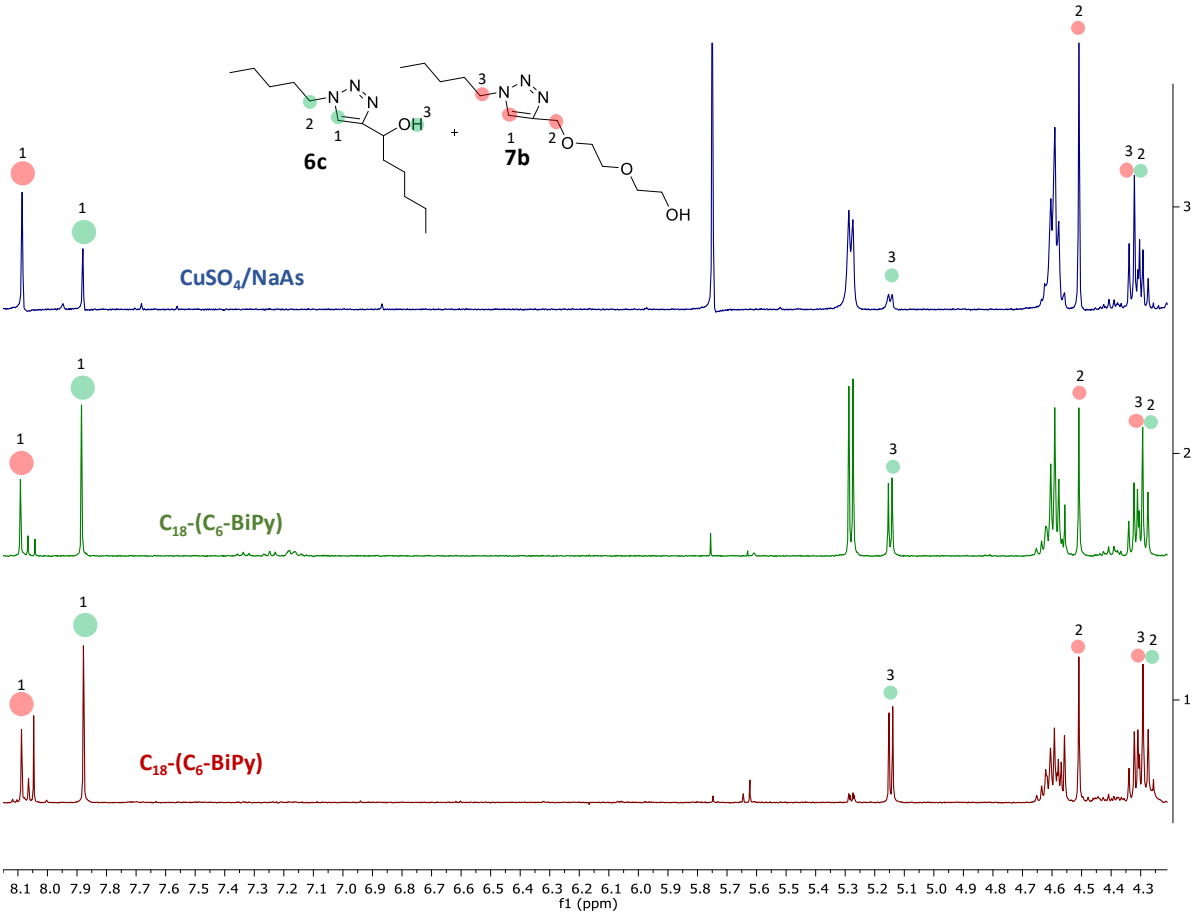


Figure S42. Entry 22: stacked ^{1}H MNR spectra of the competitive reaction when $CuSO_4$/NaAs (blue) and C_{18}-(C_6-BiPy) (in duplicate, green and red) were used as catalyst. Average hydrophobic to hydrophilic ratio = 3.0:1.

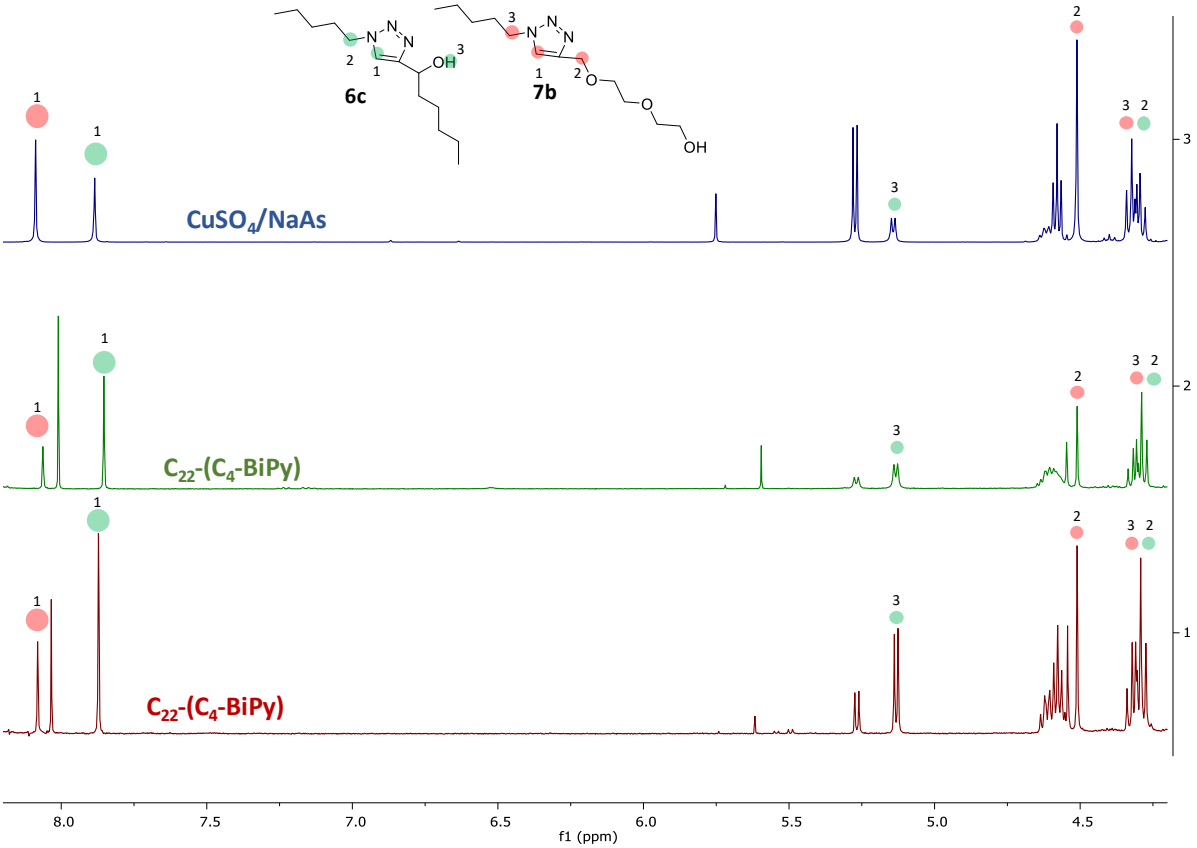


Figure S43. Entry 26: stacked ^{1}H MNR spectra of the competitive reaction when $CuSO_4$/NaAs (blue) and C_{22}-(C_4-bipy) (in duplicate, green and red) were used as catalyst. Average hydrophobic to hydrophilic ratio = 3.0:1.

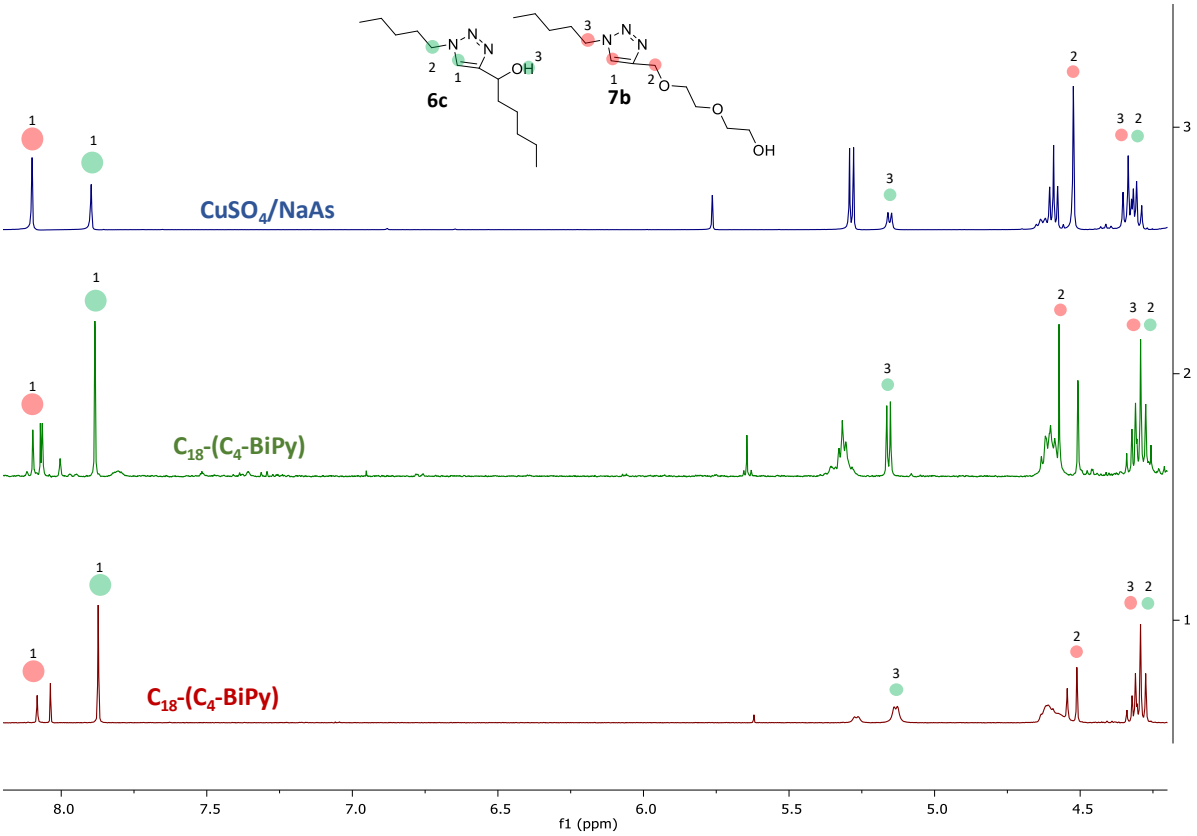
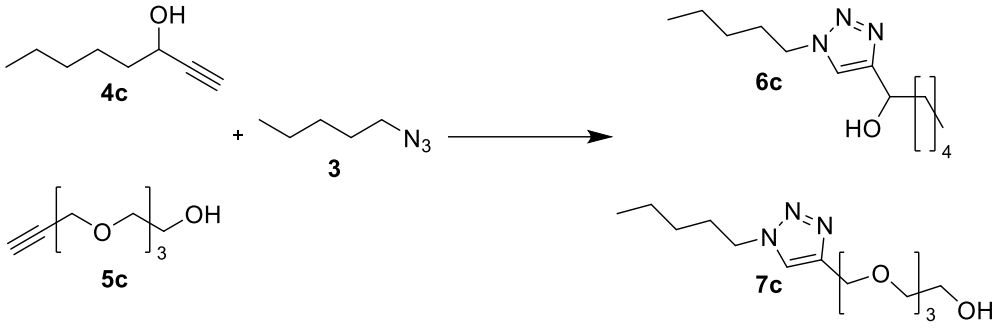


Figure S44. Entry 30: stacked ^{1}H MNR spectra of the competitive reaction when $CuSO_4$/NaAs (blue) and C_{18}-(C_4-bipy) (in duplicate, green and red) were used as catalyst. Average hydrophobic to hydrophilic ratio = 3.1:1.

4.3.11 Competition reaction between 4c and 5c (entries 19, 23, 27, 31 and XI).



4.3.11.1 Competition reaction using $CuSO_4$ as the catalysis.

The competition reaction was performed following the general procedure described in 4.1.2, whereby the alkynes were the hydrophobic oct-1-yn-3-ol (4c) and the hydrophilic 2-(2-(2-(prop-2-yn-1-yloxy)ethoxy)ethoxy)ethan-1-ol (5c).

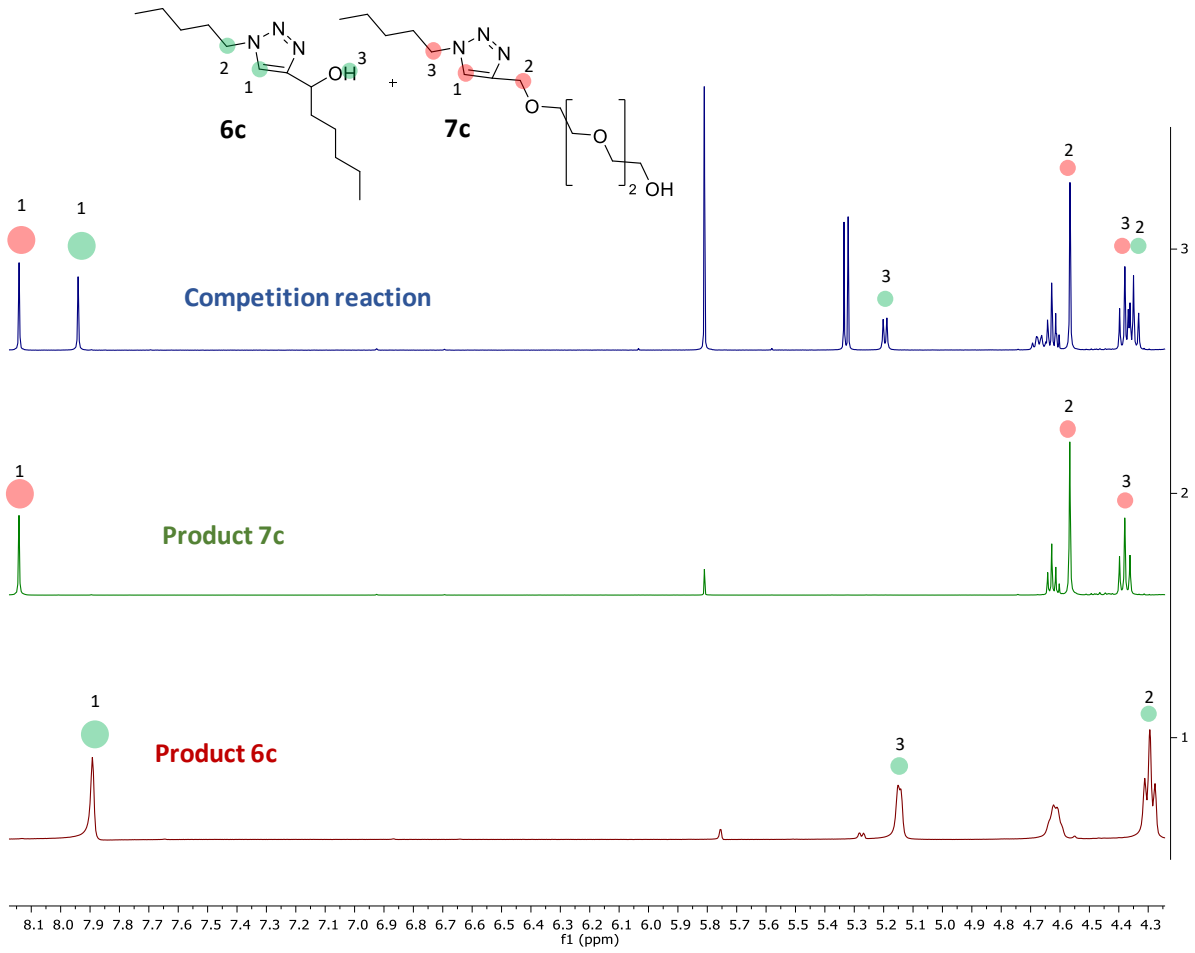


Figure S45. Entry XI: stacked ^{1}H MNR spectra of the competitive reaction (blue), and triazole product (6c) (red) and (7c) (green) when $CuSO_4$/NaAs was used as catalyst. $CuSO_4$/NaAs hydrophobic to hydrophilic ratio = 1:2.0.

4.3.11.2 Competition reaction using Nanoparticle catalyst.

The competition reaction was performed following the general procedure described in 4.1.3 using C_{22}-(C_6-bipy), C_{18}-(C_6- bipy), C_{22}-(C_4- bipy) or C_{18}-(C_4- bipy) as the catalyst, and hydrophobic oct-1-yn-3-ol (4c) and hydrophilic 2-(2-(2-(prop-2-yn-1-yloxy)ethoxy)ethoxy)ethan-1-ol (5c) alkynes.

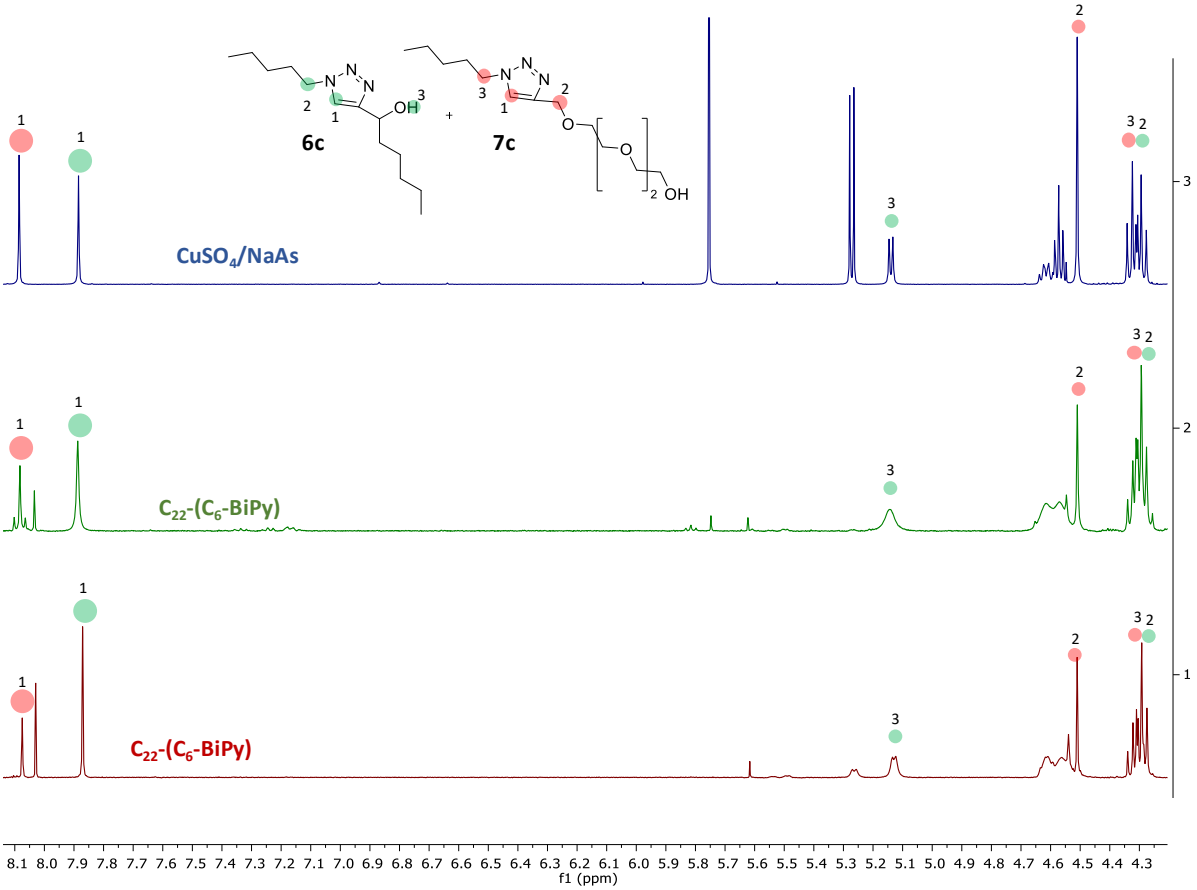


Figure S46. Entry 19: stacked ^{1}H MNR spectra of the competitive reaction when $CuSO_4$/NaAs (blue) and C_{22}-(C_6- bipy) (in duplicate, green and red) were used as catalyst. Average hydrophobic to hydrophilic ratio = 3.9:1.

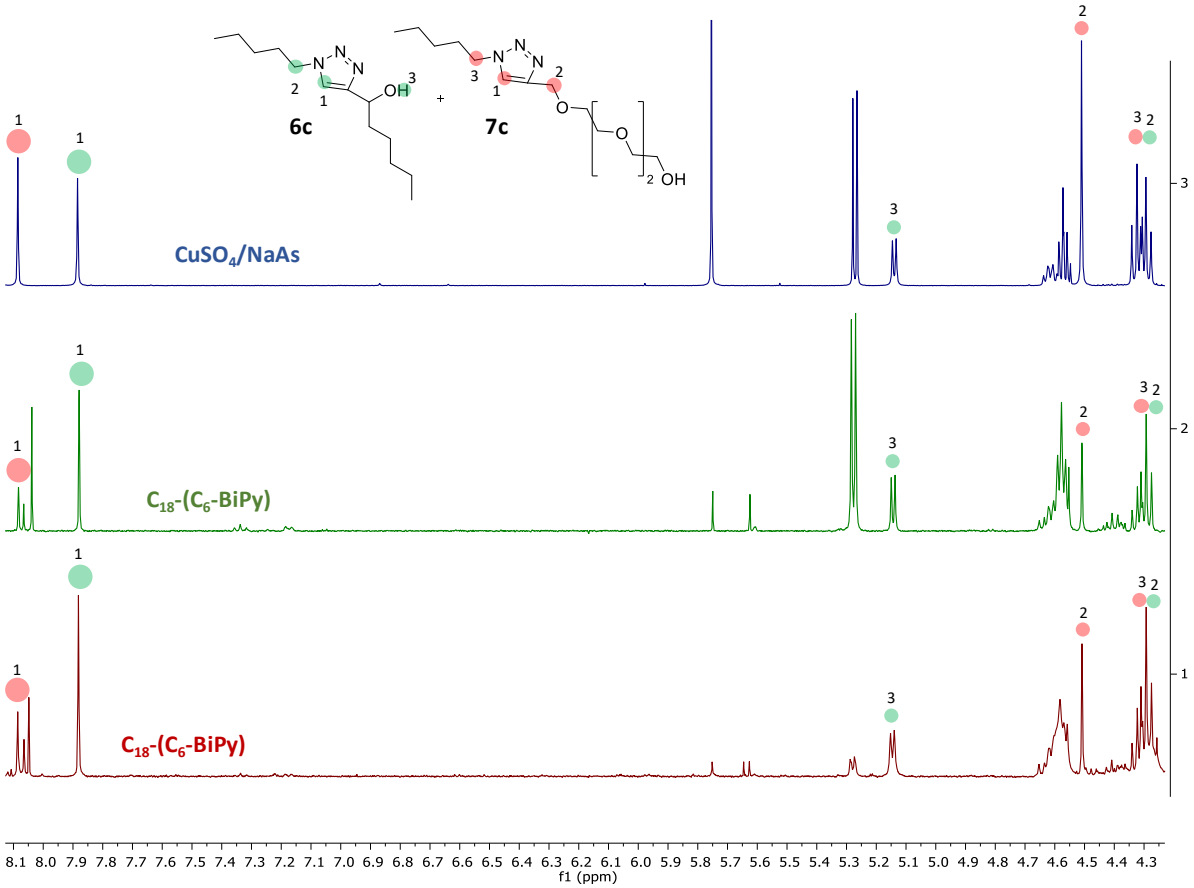


Figure S47. Entry 23: stacked ^{1}H MNR spectra of the competitive reaction when $CuSO_4$/NaAs (blue) and C_{18}-(C_6- bipy) (in duplicate, green and red) were used as catalyst. Average hydrophobic to hydrophilic ratio = 3.9:1.

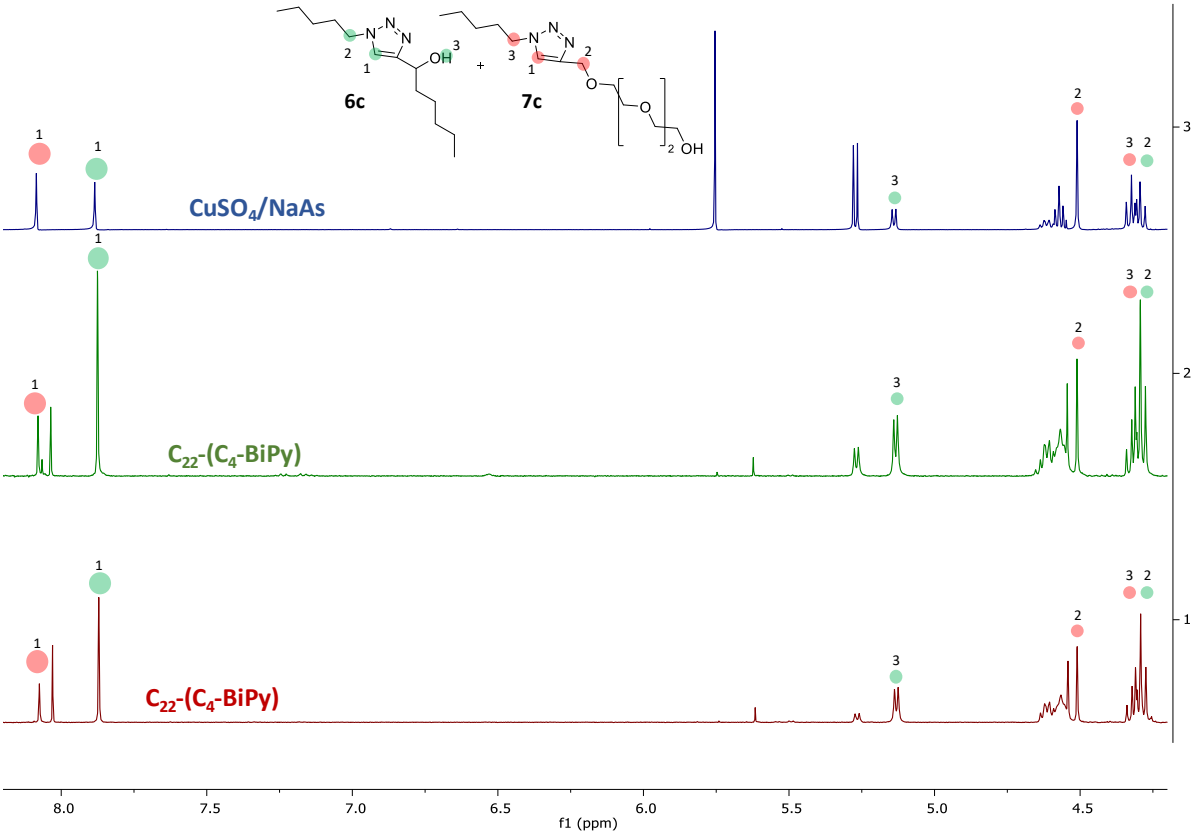


Figure S48. Entry 27: stacked ^{1}H MNR spectra of the competitive reaction when $CuSO_4$/NaAs (blue) and C_{22}-(C_4- bipy) (in duplicate; green and red) were used as catalyst. Average hydrophobic to hydrophilic ratio = 3.9:1.

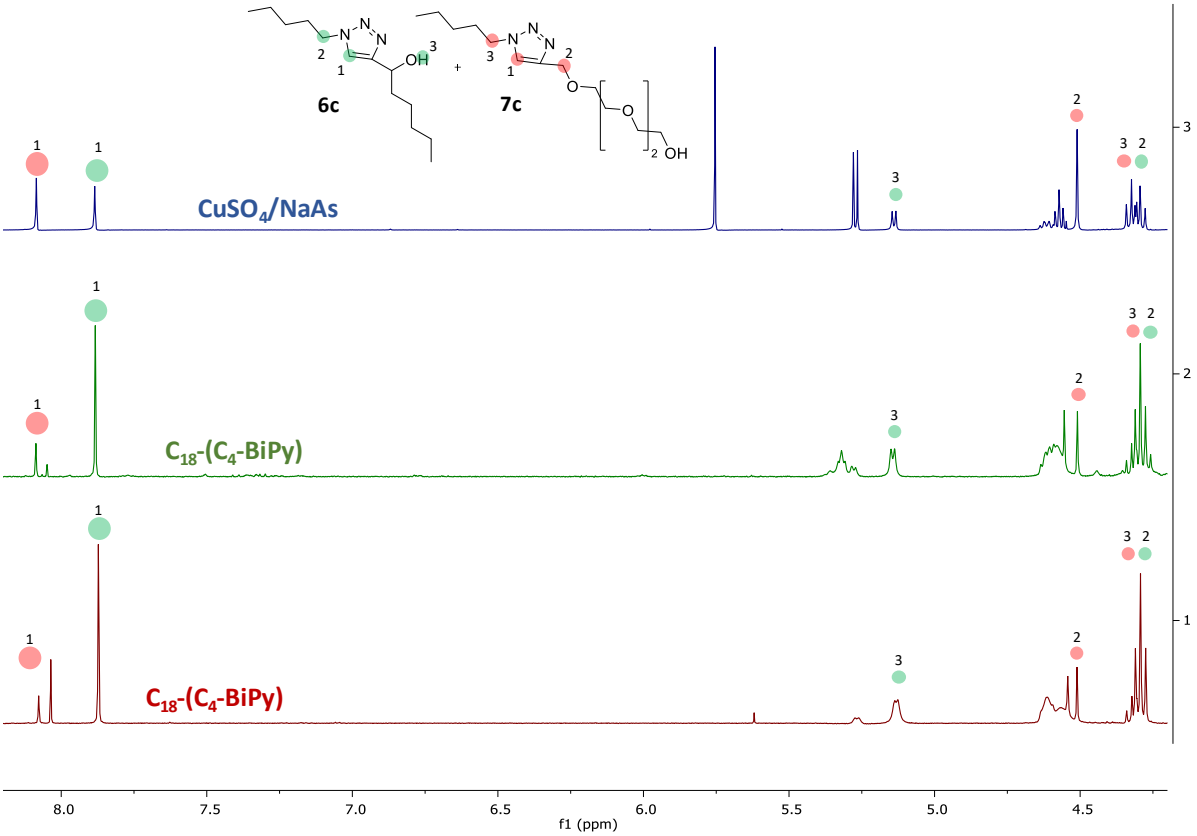
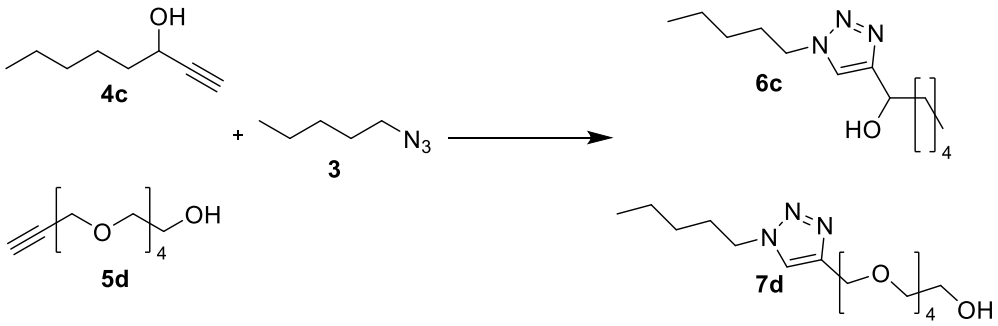


Figure S49. Entry 31: stacked ^{1}H MNR spectra of the competitive reaction when $CuSO_4$/NaAs (blue) and C_{18}-(C_4- bipy) (in duplicate, green and red) were used as catalyst. Average hydrophobic to hydrophilic ratio = 3.7:1.

4.3.12 Competition reaction between 4c and 5d (entries 20, 24, 28, 32 and XII).



4.3.12.1 Competition reaction using $CuSO_4$ as catalyst.

The competition reaction was performed following the general procedure described in 4.1.2, whereby the alkynes were the hydrophobic oct-1-yn-3-ol (4c) and the hydrophilic 3,6,9,12-tetraoxapentadec-14-yn-1-ol (5d).

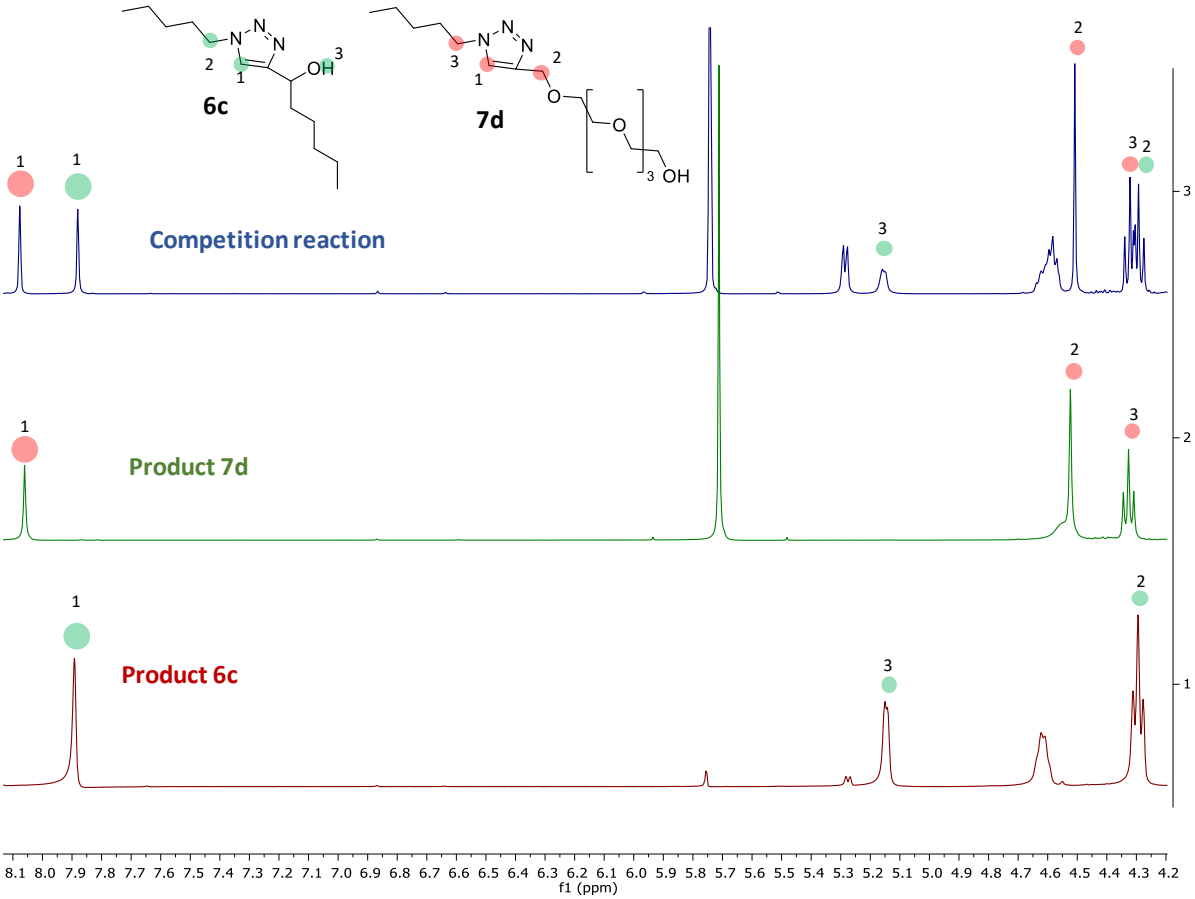


Figure S50. Entry XII: stacked ^{1}H MNR spectra of the competitive reaction (blue), and triazole product (6c) (red) and (7d) (green) when $CuSO_4$/NaAs was used as catalyst. $CuSO_4$/NaAs hydrophobic to hydrophilic ratio = 1:1.3.

4.3.12.2 Competition reaction using Nanoparticle catalyst.

The competition reaction was performed following the general procedure described in 4.1.3 using C_{22}-(C_6- bipy), C_{18}-(C_6- bipy), C_{22}-(C_4- bipy) or C_{18}-(C_4- bipy) as the catalyst, and the hydrophobic oct-1-yn-3-ol (4c) and hydrophilic 3,6,9,12-tetraoxapentadec-14-yn-1-ol (5d) alkyne substrates.

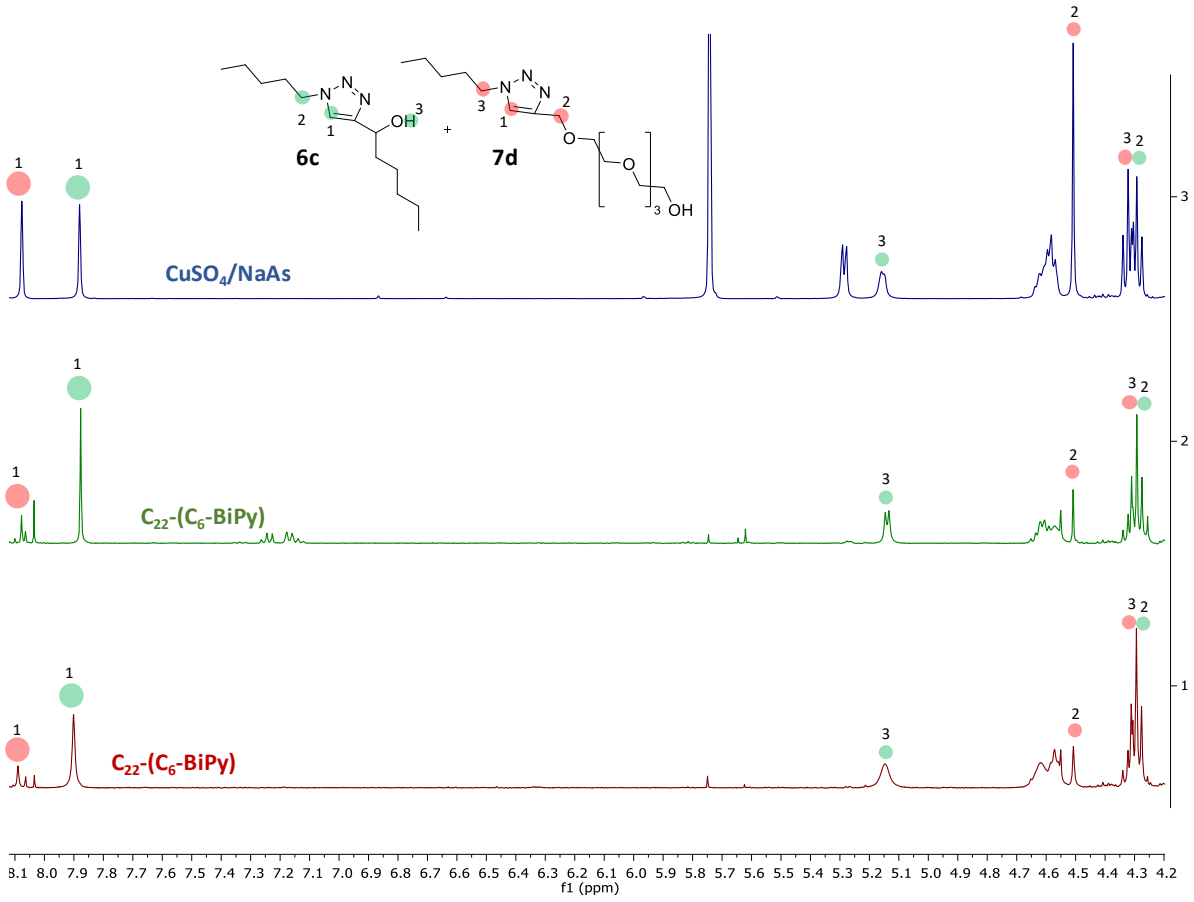


Figure S51. Entry 20: stacked ^{1}H MNR spectra of the competitive reaction when $CuSO_4$/NaAs (blue) and C_{22}-(C_6- bipy) (in duplicate, green and red) were used as catalyst. Average hydrophobic to hydrophilic ratio = 4.5:1.

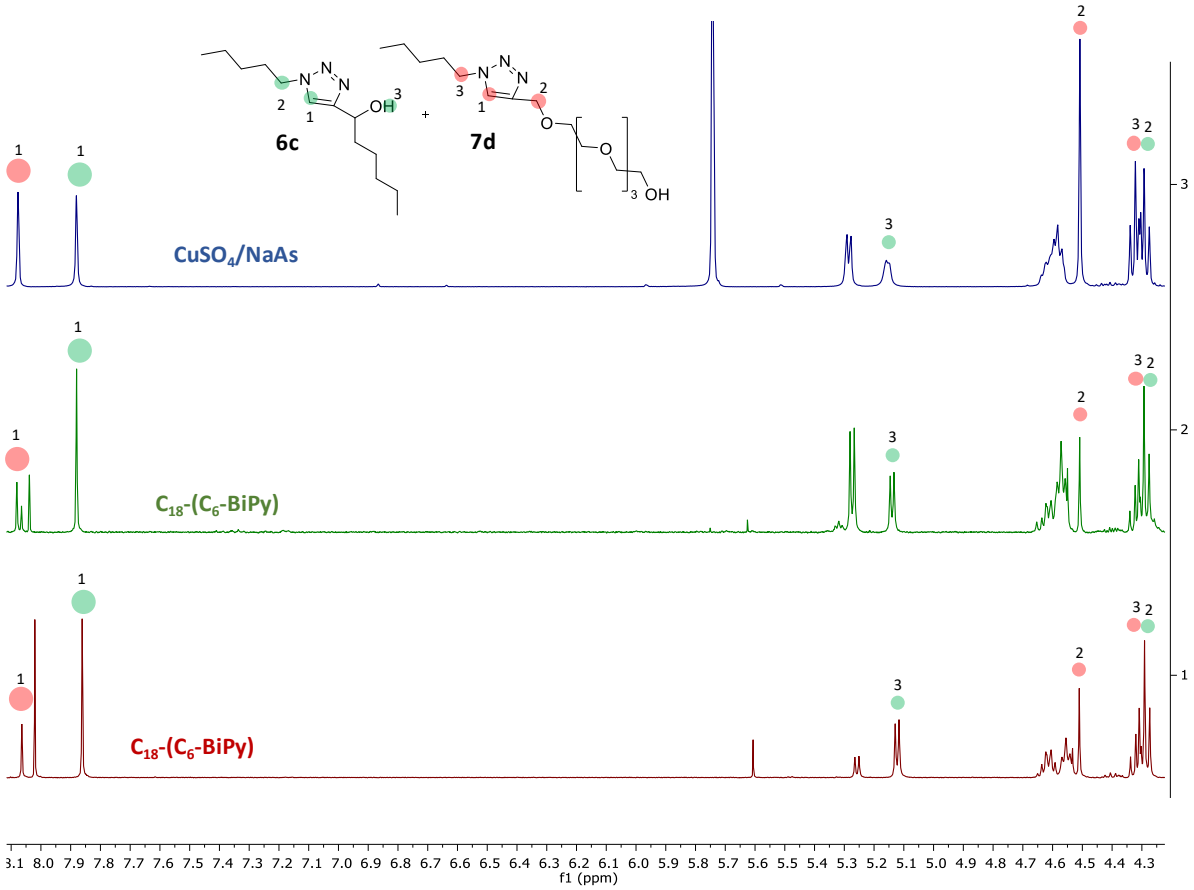


Figure S52. Entry 24: stacked ^{1}H MNR spectra of the competitive reaction when $CuSO_4$/NaAs (blue) and C_{18}-(C_6- bipy) (in duplicate, green and red) were used as catalyst. Average hydrophobic to hydrophilic ratio = 4.4:1.

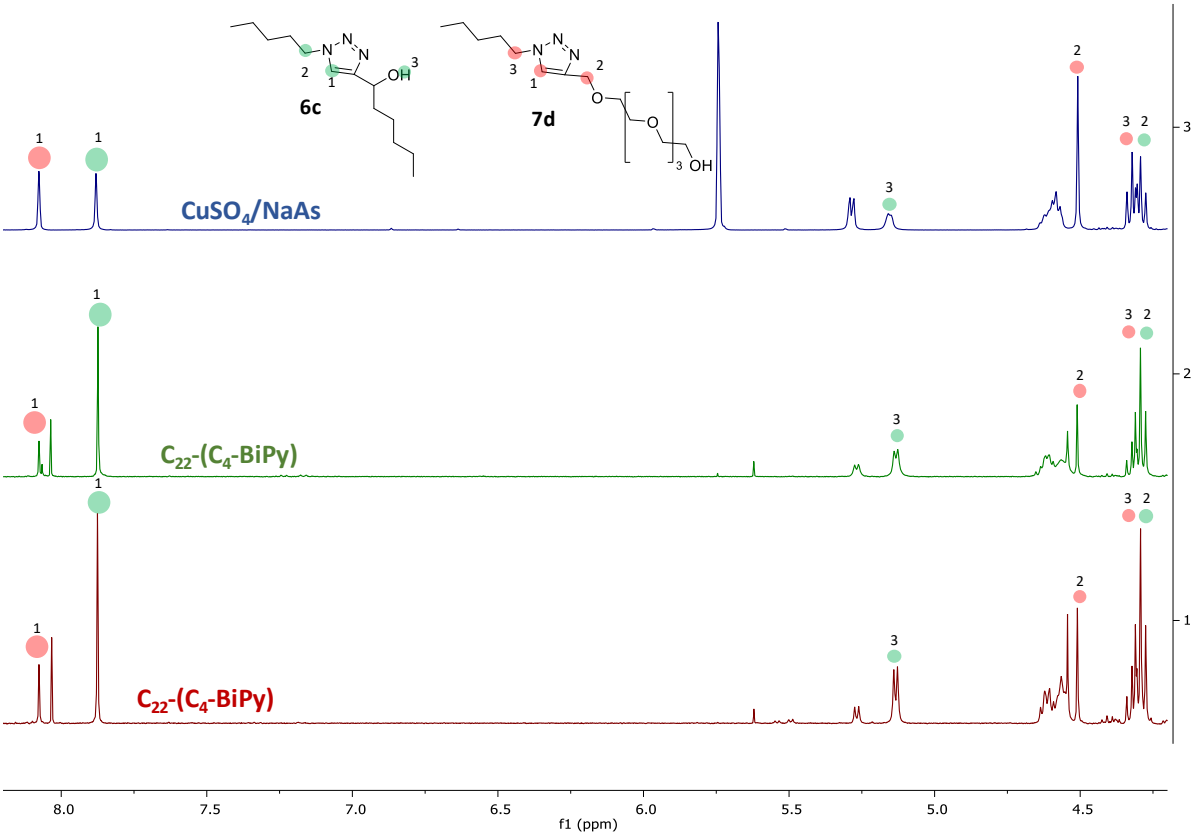


Figure S53. Entry 28: stacked ^{1}H MNR spectra of the competitive reaction when $CuSO_4$/NaAs (blue) and C_{22}-(C_4- bipy) (in duplicate, green and red) were used as catalyst. Average hydrophobic to hydrophilic ratio = 4.4:1.

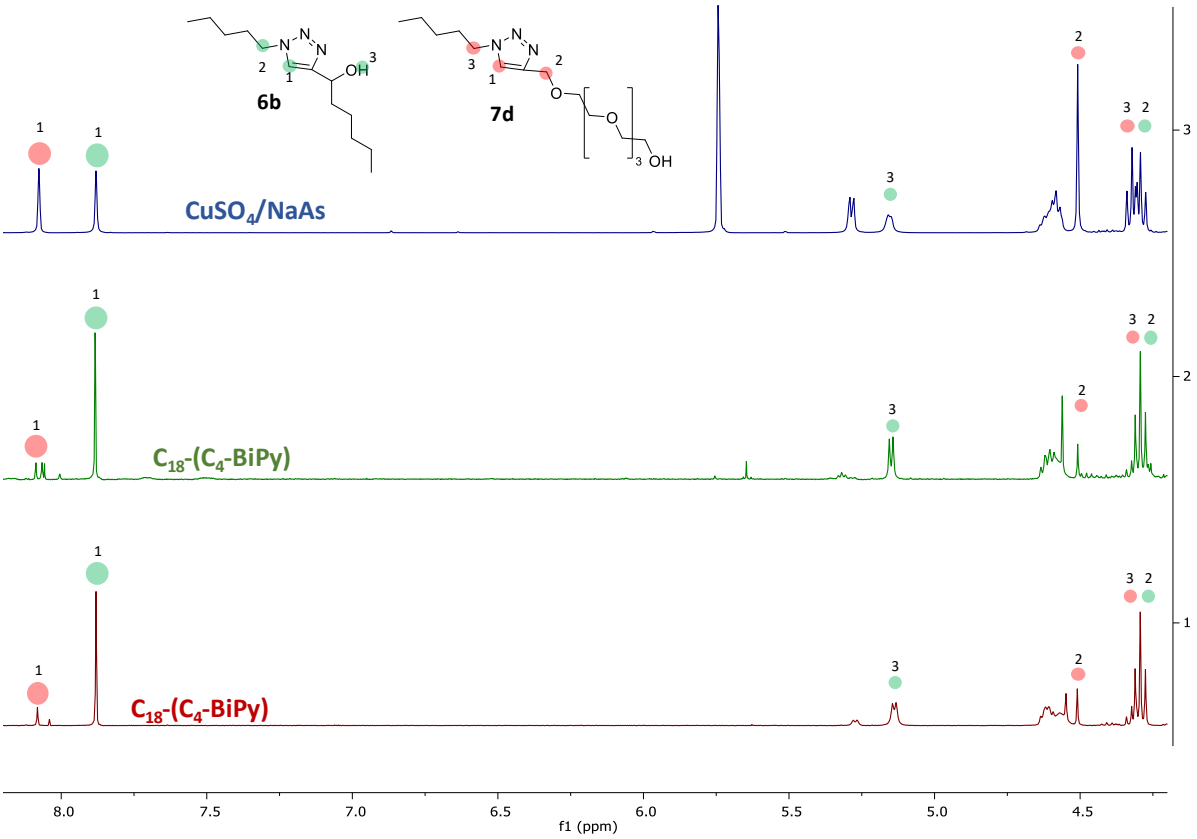


Figure S54. Entry 32: stacked ^{1}H MNR spectra of the competitive reaction when $CuSO_4$/NaAs (blue) and C_{18}-(C_4- bipy) (in duplicate, green and red) were used as catalyst. Average hydrophobic to hydrophilic ratio = 5.5:1.

5 Control experiments.

5.1 Control experiment using copper (I) acetate without Au NPs addition.

To study the influence of the copper (I) acetate on catalysis (without the use of nanoparticles, and otherwise under the same condition), we performed the competition reaction and compared this result with that of a reaction using $CuSO_4$/NaAs as the catalyst. As shown in Figure S55, no significant difference was found in the competitive reaction.

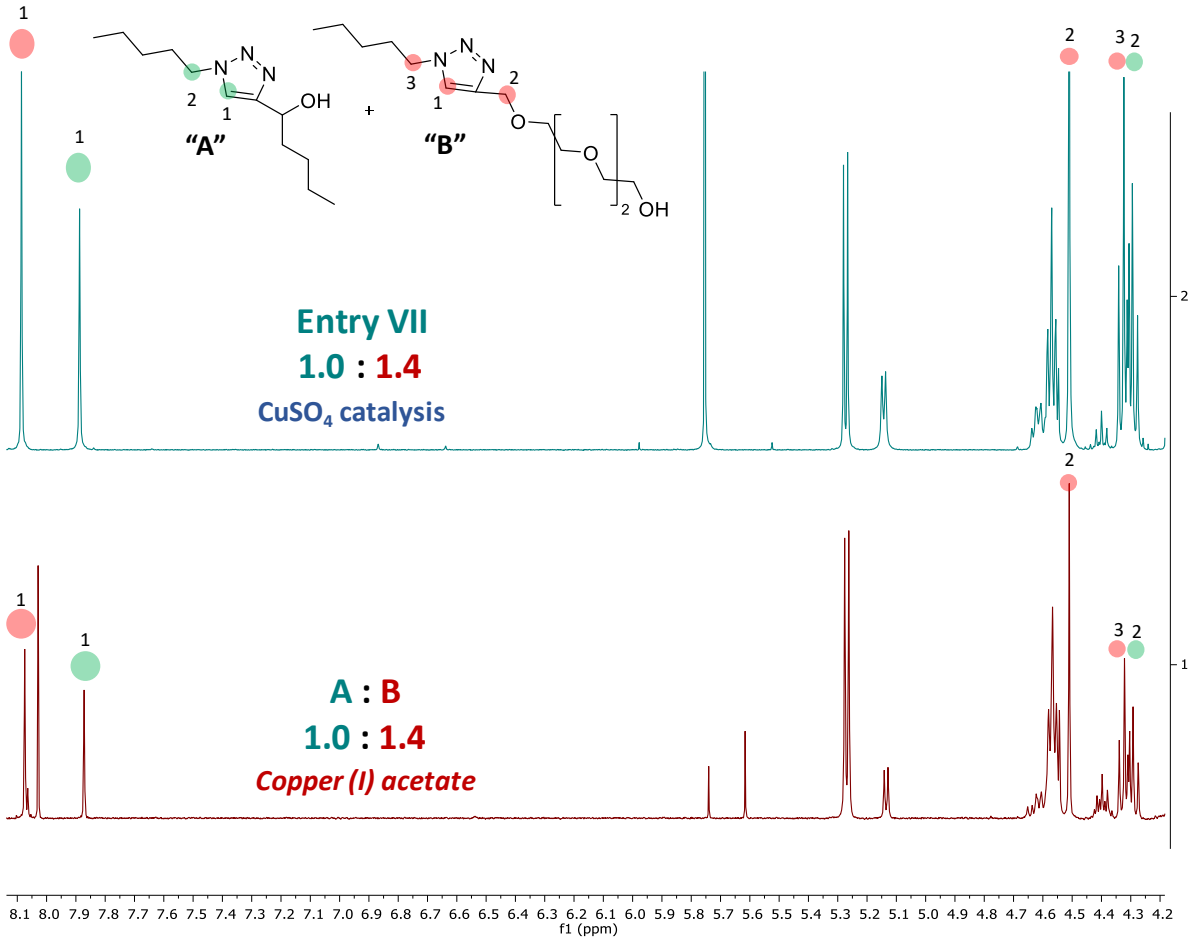


Figure S55. Stacked ^{1}H-NMR spectra of the competitive reaction using copper (I) acetate as the catalyst (red) and comparison with the competition reaction using $CuSO_4$/NaAs as the catalyst (green).

5.2 Control experiment without catalyst and nanoparticles.

A competition reaction in which neighter copper or nanoparticles were used was carried out and compared against the $CuSO_4$/NaAs catalyst. As expected, no product formation was found in the former case.

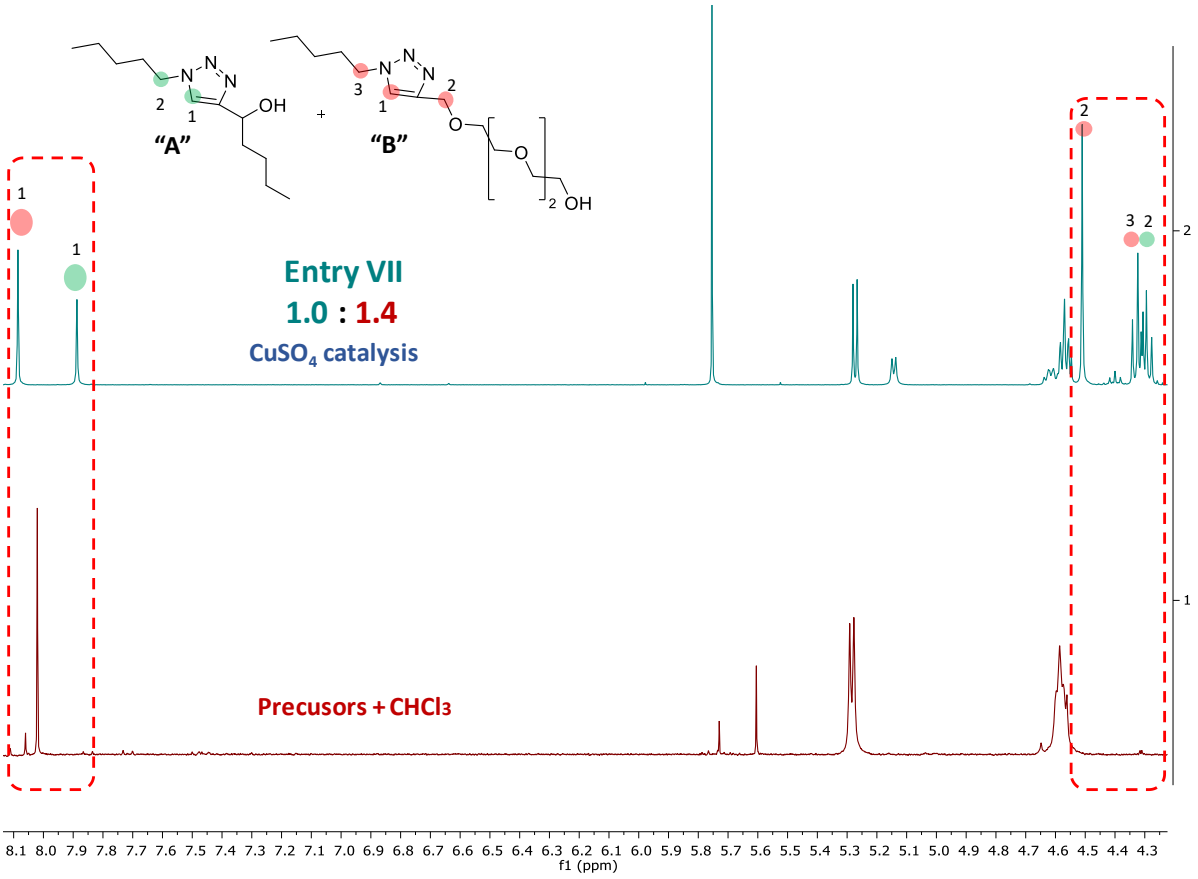


Figure S56. Stacked ^{1}H-NMR spectra of the competitive reaction control experiment without catalyst and nanoparticles load (red) and $CuSO_4$/NaAs (green).

5.3 Control experiment of the washing procedure.

This control experiment investigated the competition reaction with copper (I) acetate as the catalyst (without nanoparticles), following the washing procedure used on nanoparticles described in **section 3.2**. The results were compared against $CuSO_4$/NaAs. No product was found, indicating that the copper (I) acetate was removed after washing.

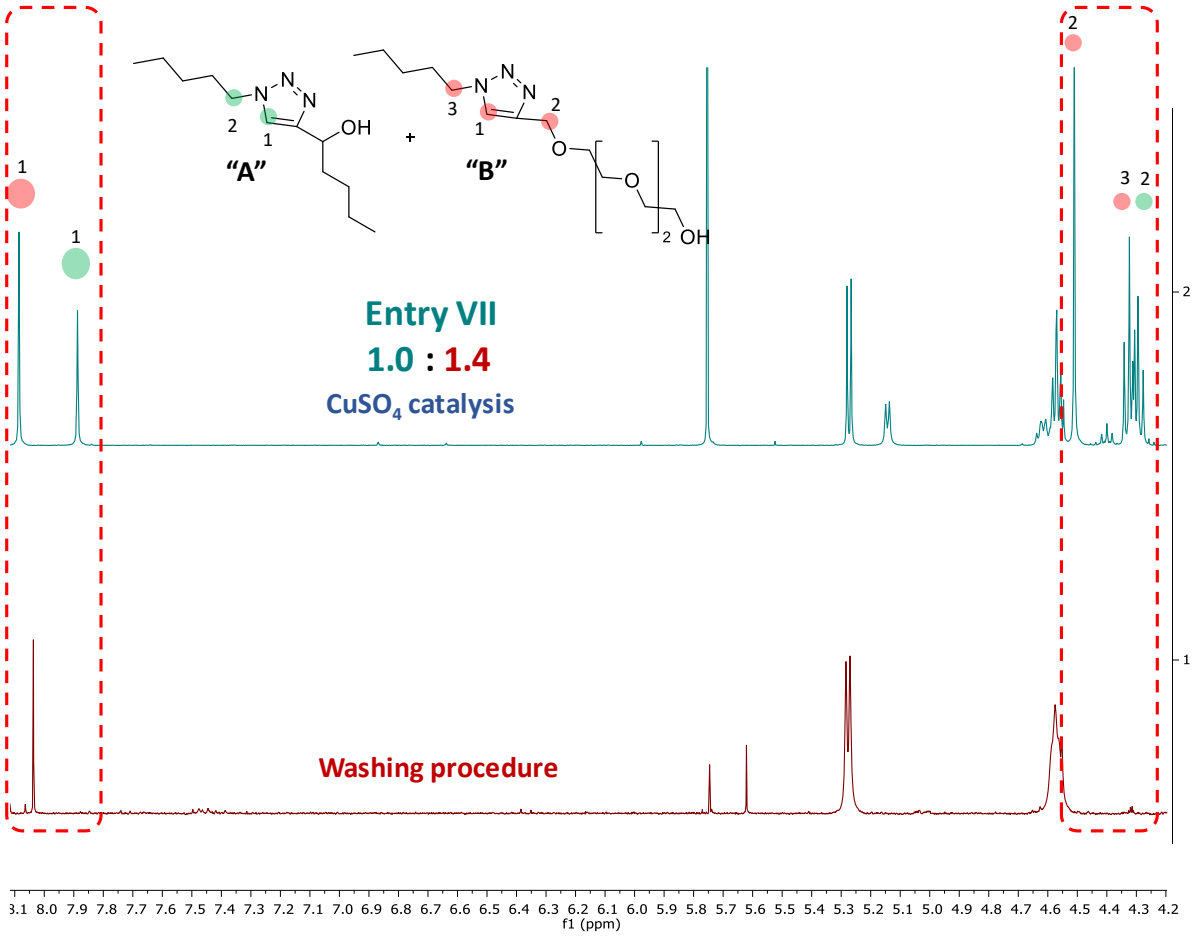


Figure S57. Stacked ^{1}H-NMR spectra control experiment of the washing procedure using copper (I) acetate as a catalyst (red) and comparison with competition reaction using CuSO4/NaAs as a catalyst (green).

5.4 Control experiment with nanoparticles without copper (I) load.

A competition reaction using C_{22}-(C_6-bipy) without copper load was used and compared against the $CuSO_4$/NaAs catalyst. As expected, no product formation was observed in the former case.

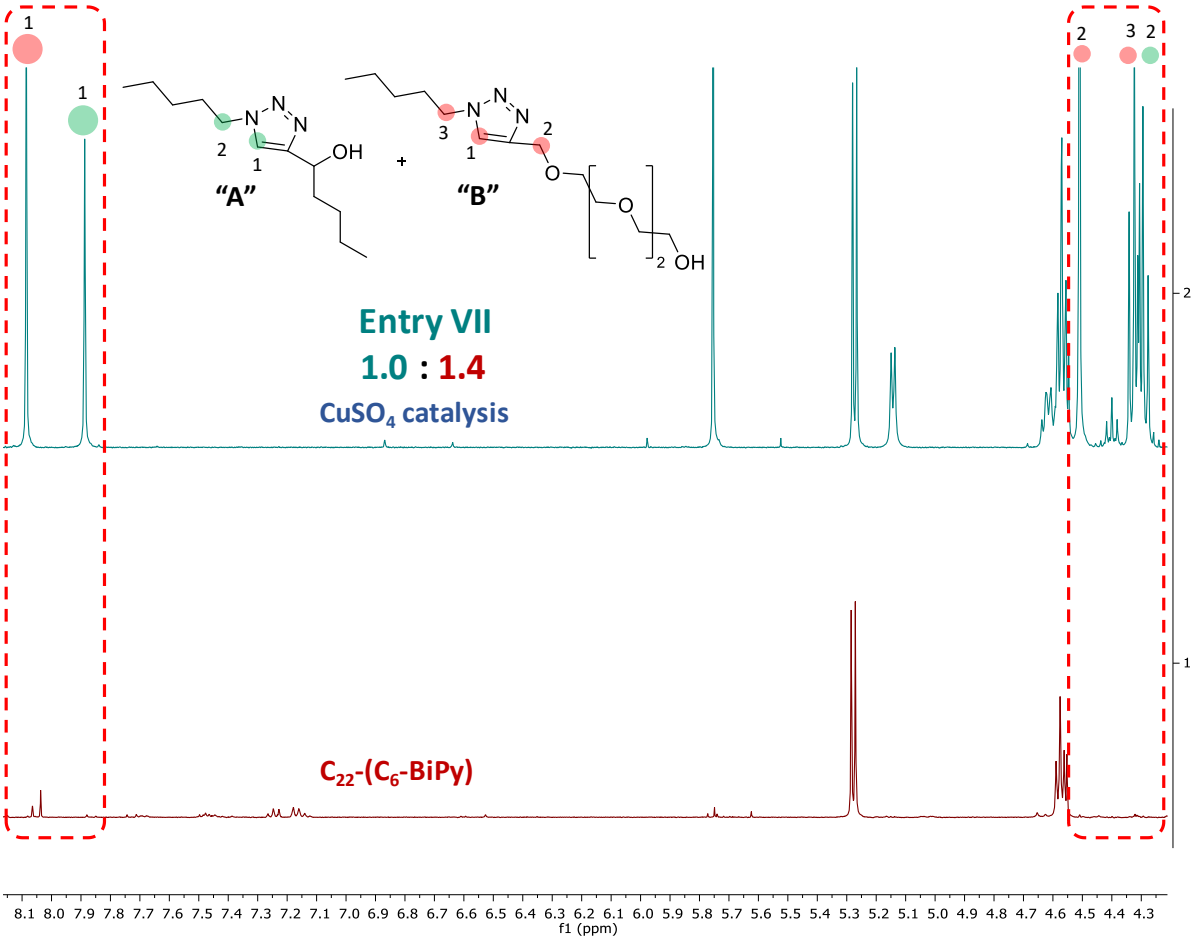


Figure S58. Stacked ^{1}H-NMR spectra of the control experiment using nanoparticles C_{22}-(C_6-bipy), without loading copper (I) acetate to the AuNPs (red) and comparison with competition reaction using $CuSO_4$/NaAs as a catalyst (green).

6 Experimental details of ^{1}H-NMR kinetics.

6.1 General Procedure.

A screw-cap NMR tube was loaded with C_{22}-(C_6- bipy) (1.44 μmol in terms of Cu atoms in the Au NPs) dissolved in $CDCl_3$, the alkyne (4c), and 2 μL of N,N-diisopropylethylamine. After 1-azidopentane was added, the tube was immediately loaded into a 600 Mhz Varian NMR (VNMRS 600). The temperature was increased from rt to 55 °C and after ~15 minutes, the reaction was monitored every 3 minutes by collecting ^{1}H-NMR spectra. The signal at 4.37 ppm, attributed to the -CH_2- next to the alkyne group in the starting material (4c), and the signal at 4.33 ppm attributed to the -CH_2- next to triazole ring in the product (6c) were analyzed. The conversion over time was calculated by the ratio between the integrals values the alkyne (4c) : triazole (6c).

6.1.1 Kinetic analysis using Azide:Alkyne at 1:1 ratio

Following the procedure described in Section S6.1, 41.6 μL of a $CDCl_3$ stock solution of the alkyne (4c) (0.17 mM), Au NPs (1.44 μmol in terms of Cu atoms in the Au NPs) dissolved in 542.4 μL of $CDCl_3$ and 65.9 μL of a stock solution of 1-azidopentane (3) [0.15 mM] were used.

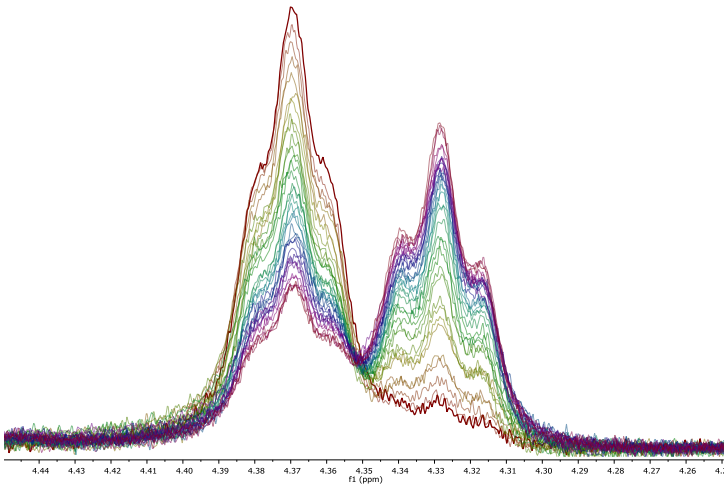


Figure S59. Superimposed ^{1}H NMR spectra over time when a 1:1 ratio azide:alkyne was used. The signal at 4.37 (decrease) and 4.33 (increase) ppm, are attributed to (4c) and (6c), respectively.

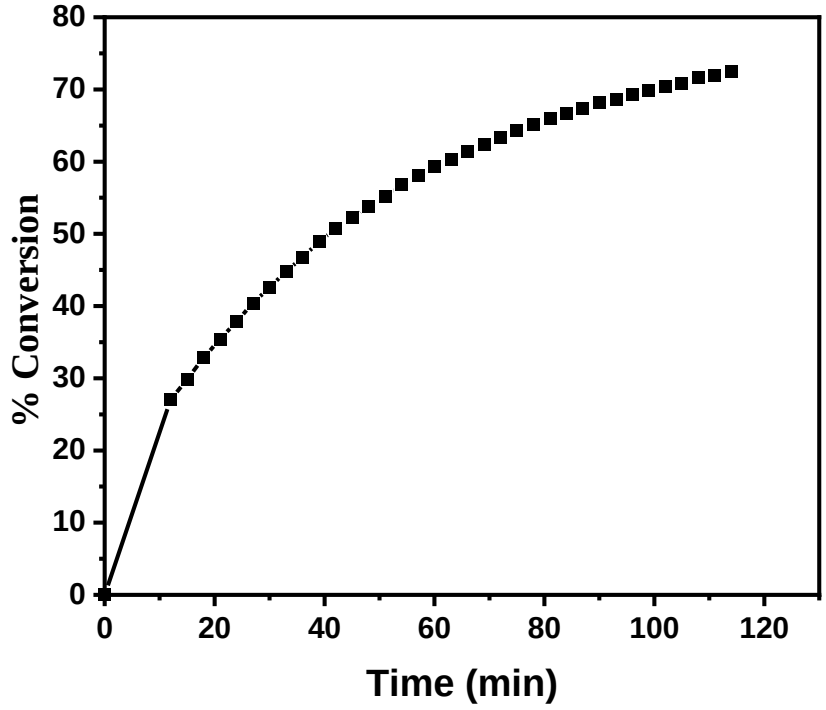


Figure 60. Plot of conversion overtime of the alkyne (4c) obtained by analyzing the integrals values extracted from Figure S59.

6.1.2 Kinetic analysis using Azide:Alkyne at 3:1 ratio.

Following the procedure described in Section S6.1, 41.6 μL of a $CDCl_3$ stock solution of the alkyne **4c** (0.17 mM), Au NPs (1.44 μmol in terms of Cu atoms in the Au NPs) dissolved in 410.7 μL of $CDCl_3$ and 197.7 μL of a stock solution of 1-azidopentane [0.15 mM] were used. [4c] = [3] = 0.011 M.

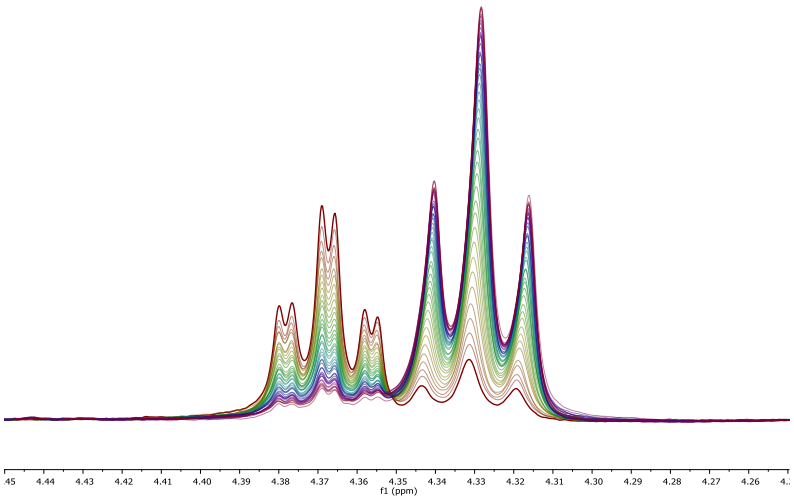


Figure S61. Superimposed ^{1}H NMR spectra overtime when a 3:1 ratio azide:alkyne was used. The signal at 4.37 (decrease) and 4.33 (increase) ppm, are attributed to (4c) and (6c), respectively.

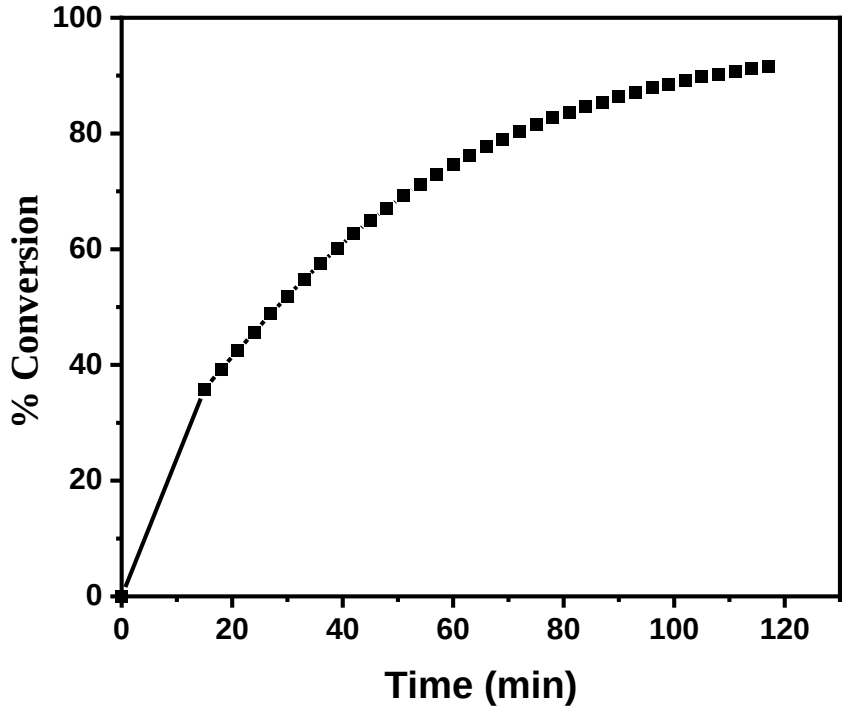


Figure S62. Plot of conversion over time of the alkyne (4c) obtained by analyzing the integrals values extracted from Figure S61.

6.1.3 Kinetic analysis using Azide:Alkyne at 1:3 ratio.

Following the procedure described in Section S6.1, 124.8 μL of a $CDCl_3$ stock solution of the alkyne **4c** (0.17 mM), 459.3 μL of a $CDCl_3$Au NPs (1.44 μmol in terms of Cu atoms in the Au NPs), and 65.9 μL of a stock solution of 1-azidopentane [0.15 mM] were used. [4c] = [3] = 0.011 M.

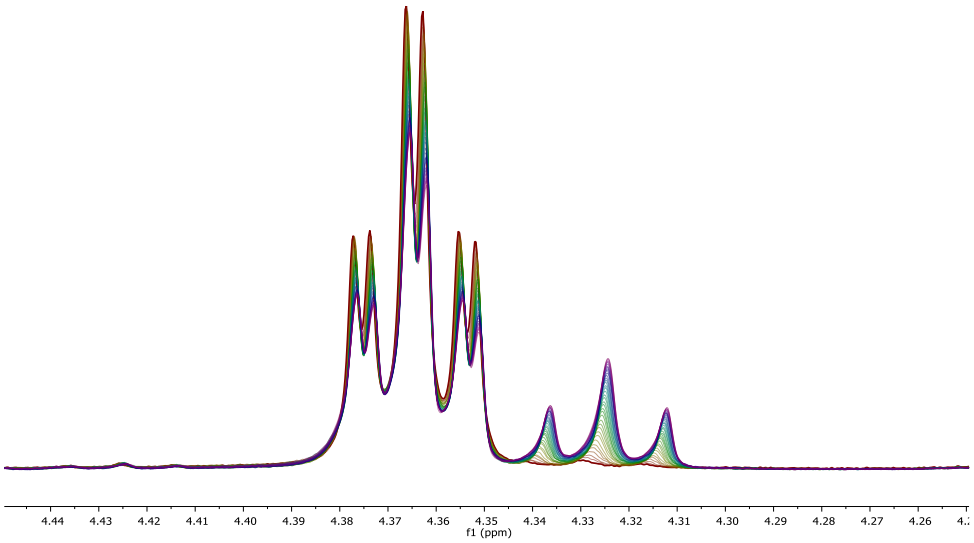


Figure S63. Superimposed ^{1}H NMR spectra over time when a 1:3 ratio azide:alkyne was used. The signal at 4.37 (decrease) and 4.33 (increase) ppm, are attributed to (4c) and (6c), respectively.

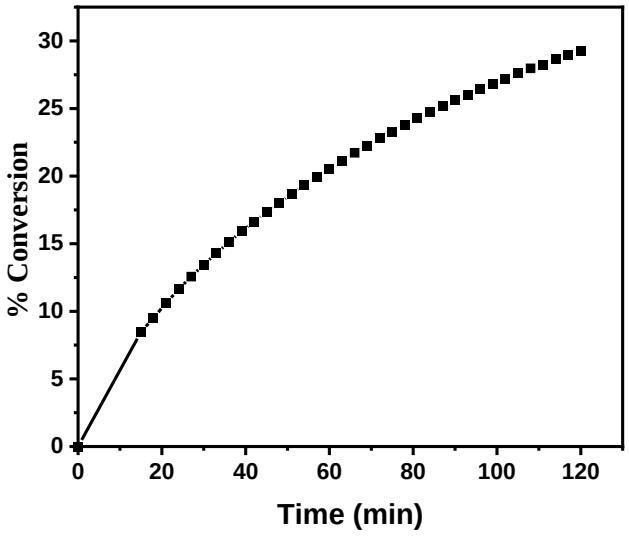


Figure S64. Plot of conversion over time of the alkyne (4c) obtained by analyzing the integrals values extracted from Figure S63.

7 Supplementary references.

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