Supporting information

β-cyclodextrin-silica hybrid: a spatially controllable anchoring strategy for Cu(II)/Cu(I) complex immobilization.

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1. Materials and Methods

1.1. Materials

All commercially available reagents and solvents were purchased from Sigma-Aldrich (Milan, Italy) and used without further purification. SIPERNAT 320 amorphous silica was supplied by Evonik Degussa. β-CD was provided by Wacker Chemie (München, Germany). TLC Merck 60 F254 (0.25 mm) plates (Milan, Italy) were used to monitor CuAAC reactions. For GC-MS analyses a 30 m capillary column, i.d. of 0.25 mm and film thickness 0.25 μm was used. GC conditions were: injection split 1:10, injector temperature 250 °C, detector temperature 280 °C. Gas carrier: helium (1.2 mL/min), temperature program: from 50 °C (5 min) to 100 °C (1 min) at 10 °C/min, to 230 °C (1 min) at 20 °C/min, to 300 °C (5 min) at 20 °C/min. Chemical shifts of NMR spectra were calibrated to the residual proton and carbon resonances of the solvent; $CDCl_3$ (δH = 7.26, δC = 77.16). Chemical shifts (δ) are given in ppm and coupling constants (J) in Hz.

1.2. Synthesis of 6^I-O-p-Toluenesulfonyl-β-CD

The synthesis of 6^I-O-*p*-Toluenesulfonyl-β-CD was performed following published synthetic procedure.[1] Briefly, βCD (1.3 g, 1.14 mmol) was dissolved in water (30 mL) and the solution was transferred to the cavitating-tube reactor. 1-(p-toluenesulfonyl)imidazole (1.01 g, 4.58 mmol) was added and the mixture was sonicated for 10 min (19.2 kHz, 20W). 2 mL of aqueous NaOH (560 mg, 14 mmol) were added dropwise and after 30 min the suspension was transferred to a flask and NH_4Cl (1.67 g, 31.5 mmol) was added. After one night the mixture was filtered and washed with ice-cold water (5 mL) and acetone (5 mL). Finally the solid was dried under vacuum.

1.3. Catalyst preparation

1.3.1. Preparation of Si-Gly

(3-Glycidyloxypropyl)trimethoxysilane (0.040 mL) was dissolved in toluene (1 mL) and silica (0.100 g) was added. The mixture was sonicated 2 h in US bath (Power 200 W, Frequency 80 kHz). The product was filtered and washed with toluene and chloroform. Finally, it was dried under vacuum at room temperature for 12 h.

1.3.2. Preparation of Si-MonoAm

3-(Trimethoxysilyl)-propylamine (0.040 mL) was dissolved in toluene (1 mL) and silica (0.100 g) was added. The mixture was sonicated 2 h in US bath (Power 200 W, Frequency 80 kHz). The product was filtered and washed with toluene and chloroform. Finally, it was dried under vacuum at room temperature for 12 h.

1.3.3. Preparation of Si-TriAm

N^1-(3-Trimethoxysilylpropyl)diethylenetriamine (0.040 mL) was dissolved in toluene (1 mL) and silica (0.100 g) was added. The mixture was sonicated 2 h in US bath (Power 200 W, Frequency 80 kHz). The product was filtered and washed with toluene and chloroform. Finally, it was dried under vacuum at room temperature for 12 h.

1.3.4. Preparation of Si-Gly-CD

6^I amino-6^I-deoxy-β-CD (1 g, 0.88 mmol) was dissolved in DMF (15 mL). Si-Gly (1 g) was added. The suspension was irradiated under MW and US combined irradiation at 100 °C for 4 h (MW power 20 W, US power 35 W). The product was filtered and washed with water, methanol and chloroform. Finally, it was dried under vacuum at room temperature for 12 h.

1.3.5. Preparation of Si-MonoAm-CD

6I-O-*p*-Toluenesulfonyl-β-CD (1 g, 0.77 mmol) was dissolved in DMF (15 mL). Si-MonoAm (1 g) was added. The suspension was irradiated under MW and US combined irradiation at 100 °C for 4 h (MW power 20 W, US power 35 W). The product was filtered and washed with water, methanol and chloroform. Finally, it was dried under vacuum at room temperature for 12 h.

1.3.6. Preparation of Si-TriAm-CD

6I-O-*p*-Toluenesulfonyl-β-CD (1 g, 0.77 mmol) was dissolved in DMF (15 mL). Si-TriAm (1 g) was added. The suspension was irradiated under MW and US combined irradiation at 100 °C for 4 h (MW power 20 W, US power 35 W). The product was filtered and washed with water, methanol and chloroform. Finally, it was dried under vacuum at room temperature for 12 h.

2. Thermogravimetric analyses

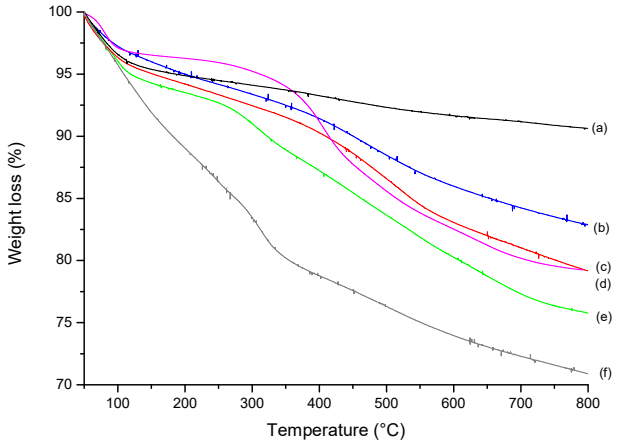

Figure S1. TGA profiles of organic inorganic silica derivatives, measured from 50 to 800 °C. On the left:(a) silica, (b) Si-Gly, (c) Si-MonoAm, (d) Si-TriAm, (e) Si-DiAm, (f) Si-DETA.

3. NMR characterization

1,5-bis(1-benzyl-1H-1,2,3-triazol-4-yl)pentane (1)

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.39 – 7.31 (m, 6H), 7.24 (d, *J* = 6.4 Hz, 4H), 7.19 (s, 2H), 5.47 (s, 4H), 2.66 (s, 4H), 1.66 (s, 4H), 1.38 (s, 2H).
^{13}C NMR (151 MHz, $CDCl_3$): δ 135.26, 129.38, 128.95, 128.31, 54.40, 29.29, 28.96, 25.85.

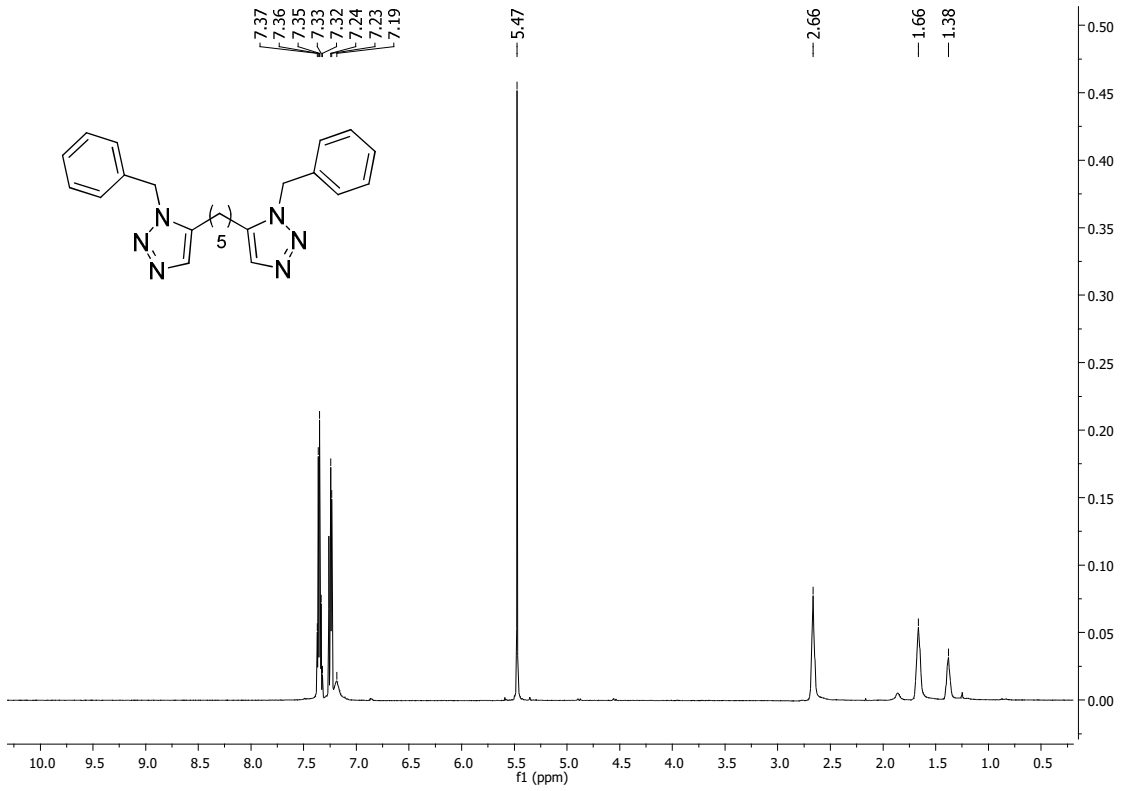

Figure S2. ^{1}H NMR of **1**.

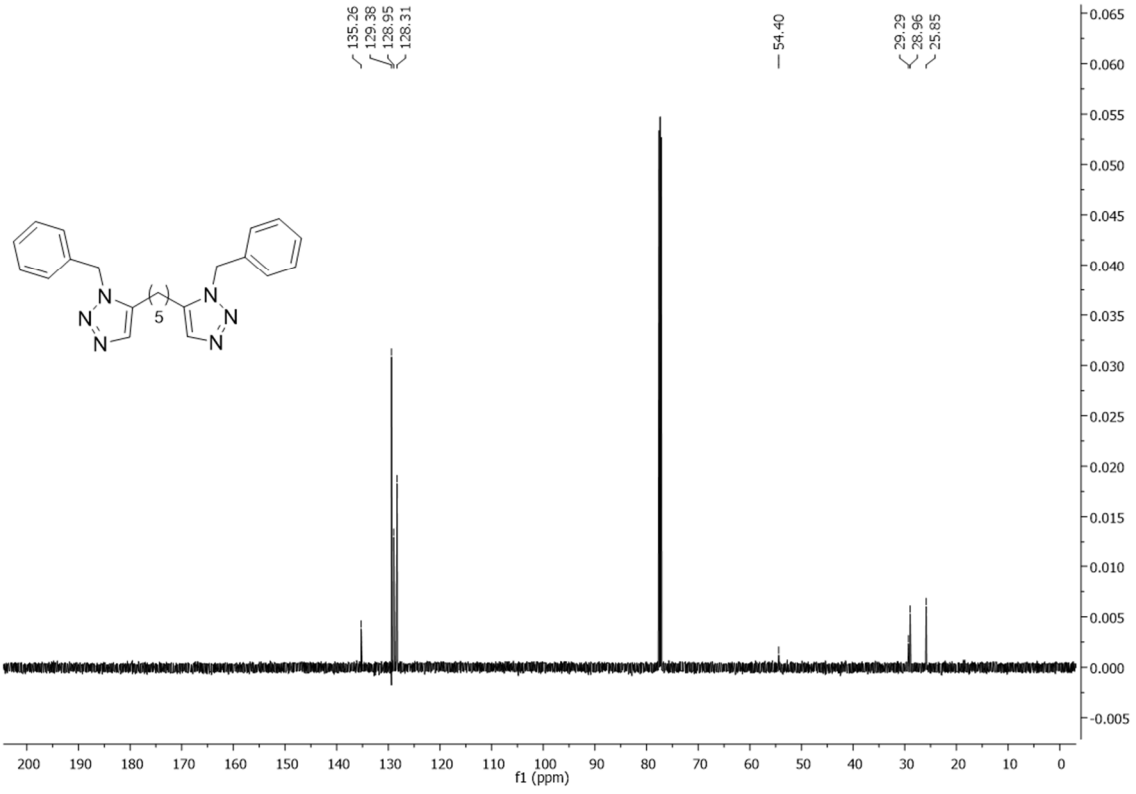

Figure S3. ^{13}C NMR of **1**.

1,6-bis(5-phenyl-1H-1,2,3-triazol-1-yl)hexane (2)

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.84 (d, *J* = 7.1 Hz, 2H), 7.76 (s, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 8.0 Hz, 1H), 4.40 (t, *J* = 7.0 Hz, 2H), 2.02 – 1.93 (m, 2H), 1.45 – 1.35 (m, 2H).
^{13}C NMR (151 MHz, $CDCl_3$): δ 130.51, 128.95, 128.27, 125.74, 120.23, 49.82, 29.84, 26.09.

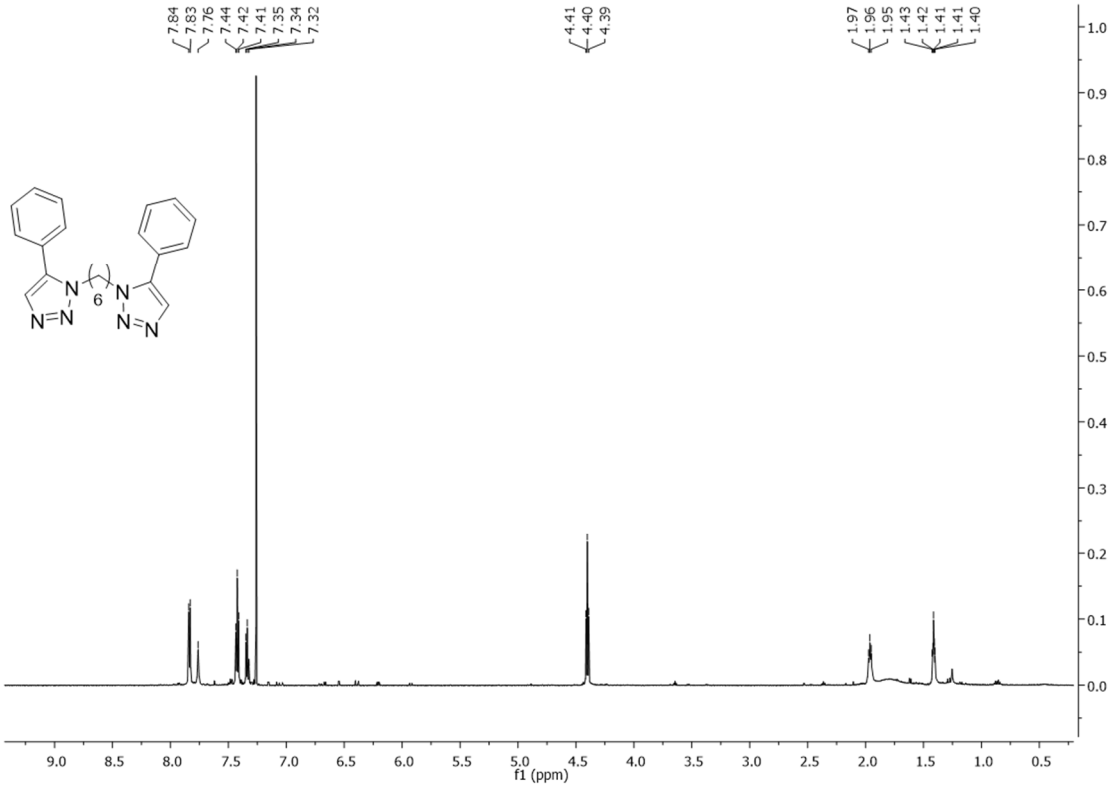

Figure S4. ^{1}H NMR of **2**.

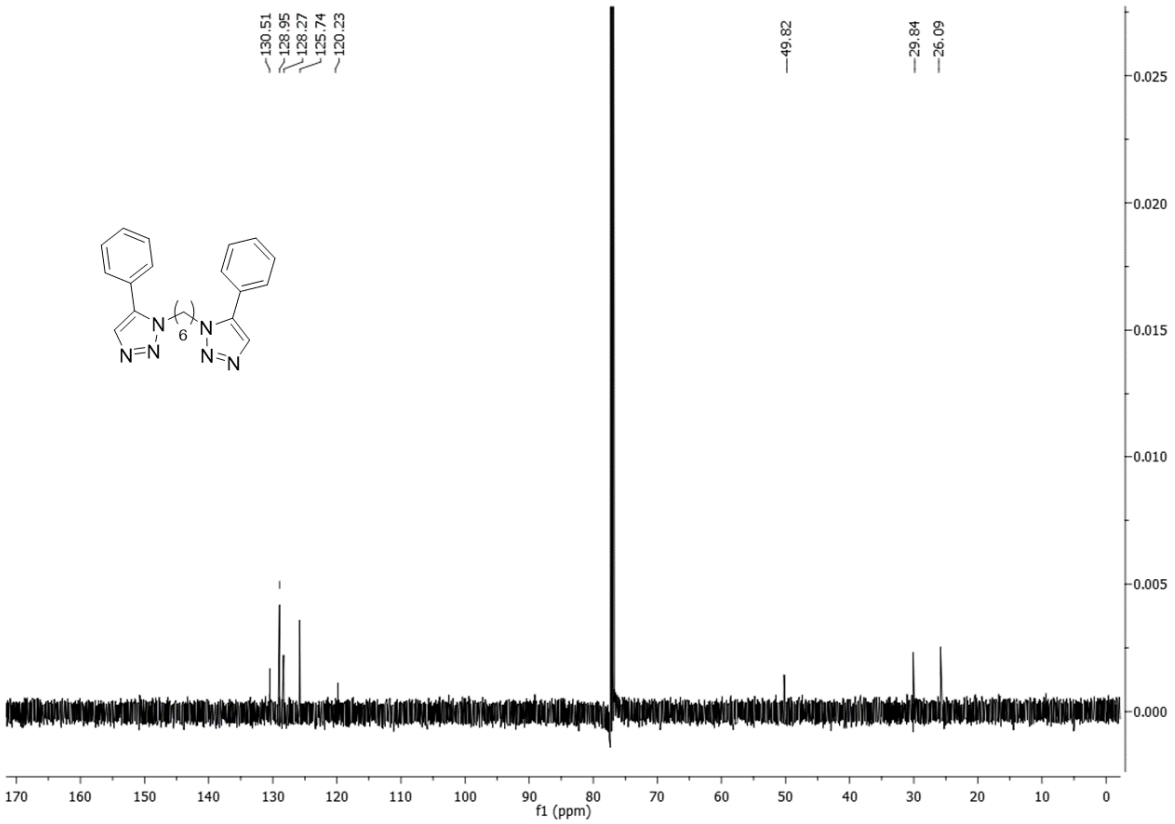

Figure S5. ^{13}C NMR of **2**.

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

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.39 – 7.32 (m, 4H), 7.26 (d, *J* = 1.6 Hz, 1H), 7.24 (d, *J* = 1.0 Hz, 1H), 5.48 (s, 2H), 4.10 (brs, 1H), 2.85 (s, 2H), 2.19 (s, 2H).
^{13}C NMR (151 MHz, $CDCl_3$): δ 145.73, 134.91, 129.45, 129.13, 128.47, 121.48, 61.72, 54.07, 29.62.

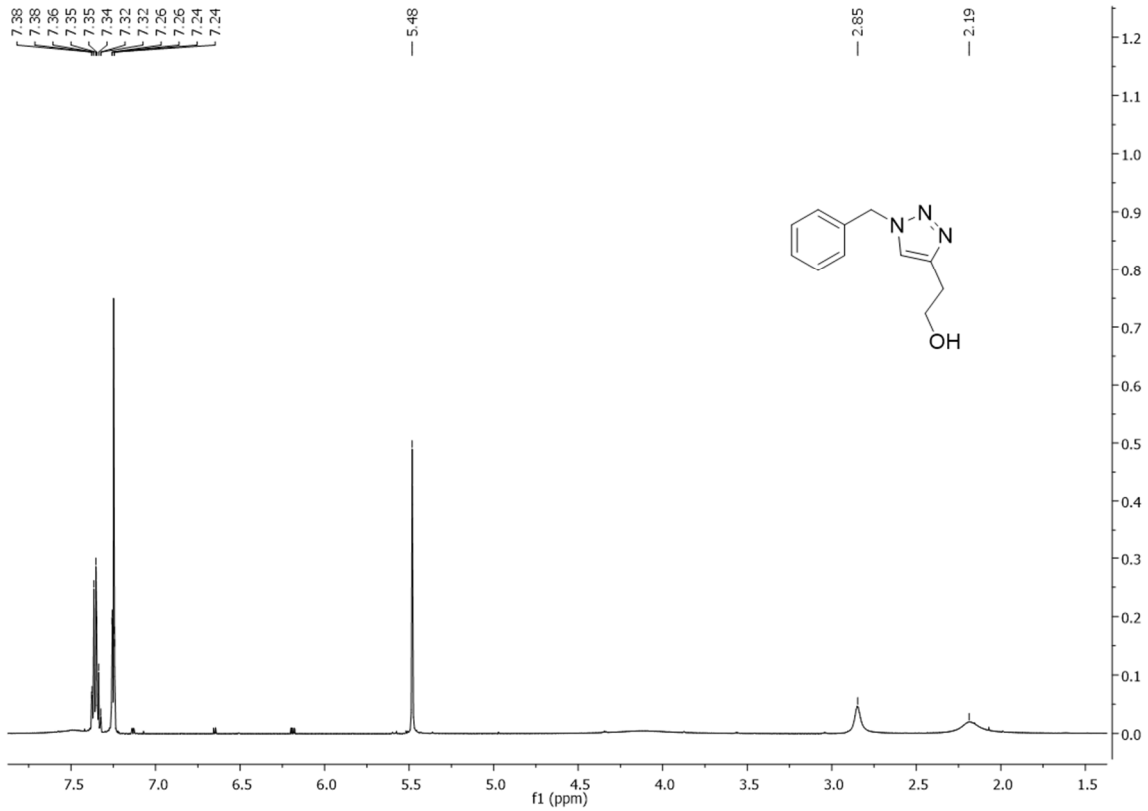

Figure S6. ^{1}H NMR of **3**.

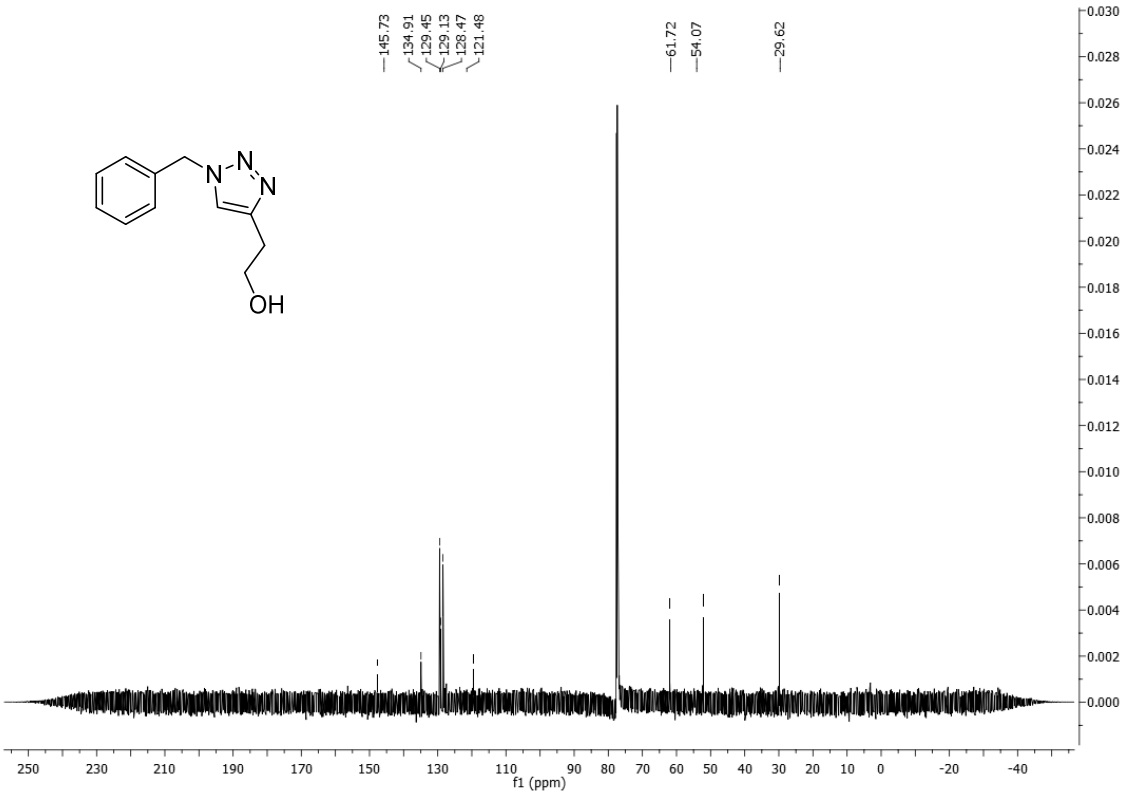

Figure S7. ^{13}C NMR of **3**.

2-(1-undecyl-1H-1,2,3-triazol-4-yl)ethan-1-ol (4)

^{1}H NMR (600 MHz, $CDCl_3$): δ 4.32 (t, *J* = 6.8 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.95 – 2.79 (m, 2H), 1.91 – 1.85 (m, 2H), 1.29 (d, *J* = 11.7 Hz, 4H), 1.27 – 1.26 (m, 2H), 1.25 – 1.23 (m, 10H), 0.87 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$): δ 142.20, 132.09, 60.73, 32.20, 30.55, 29.85, 29.65, 29.32, 26.88, 22.99, 21.37, 14.47.

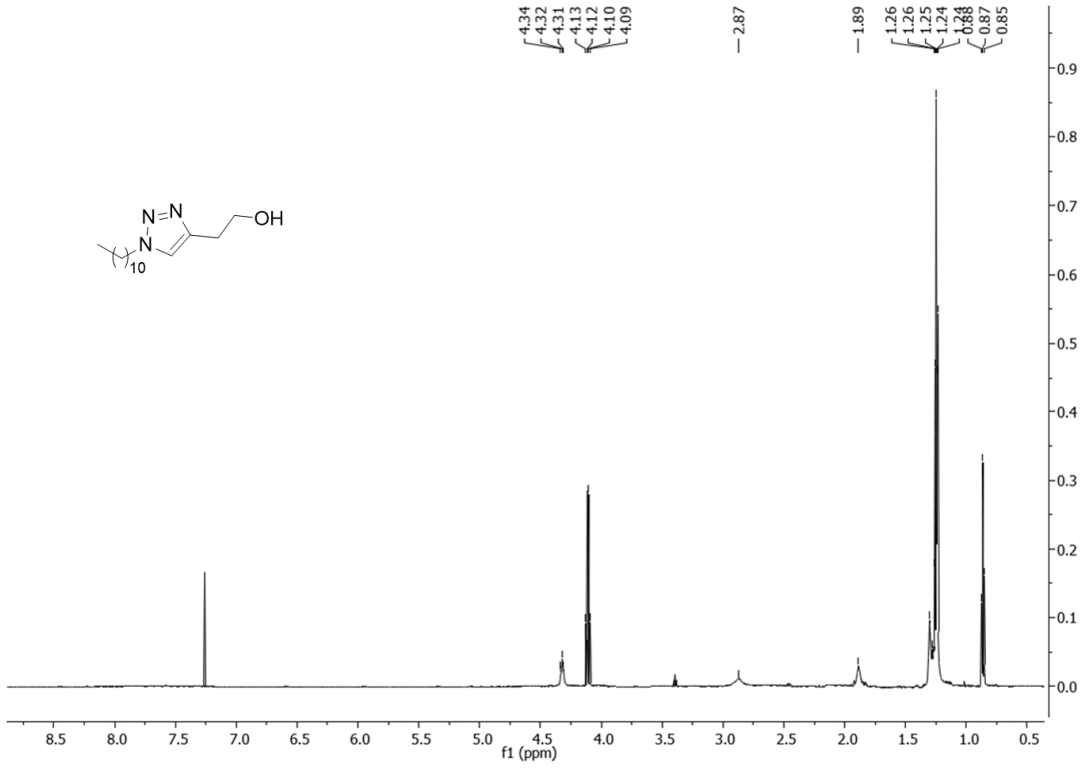

Figure S8. ^{1}H NMR of **4**.

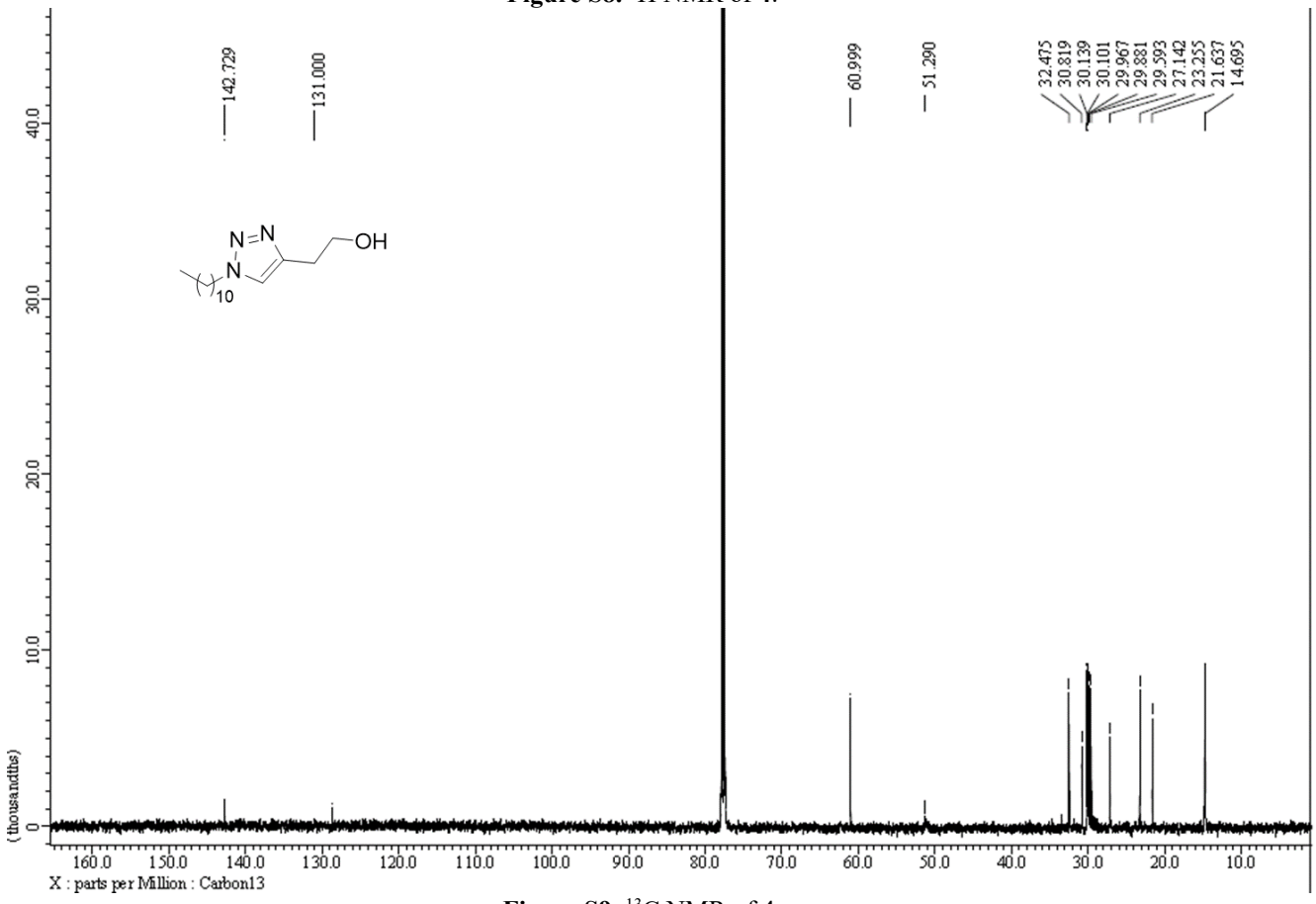

Figure S9. ^{13}C NMR of **4**.

4-phenyl-1-undecyl-1H-1,2,3-triazole (5)

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.82 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.73 (s, 1H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.33 (dt, *J* = 9.1, 4.3 Hz, 1H), 4.38 (t, *J* = 7.3 Hz, 2H), 1.96 – 1.90 (m, 2H), 1.38 – 1.30 (m, 4H), 1.29 – 1.15 (m, 12H), 0.86 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$): δ 130.92, 129.19, 128.51, 126.08, 119.79, 50.87, 32.22, 30.68, 29.77, 29.35, 26.84, 23.01, 14.44.

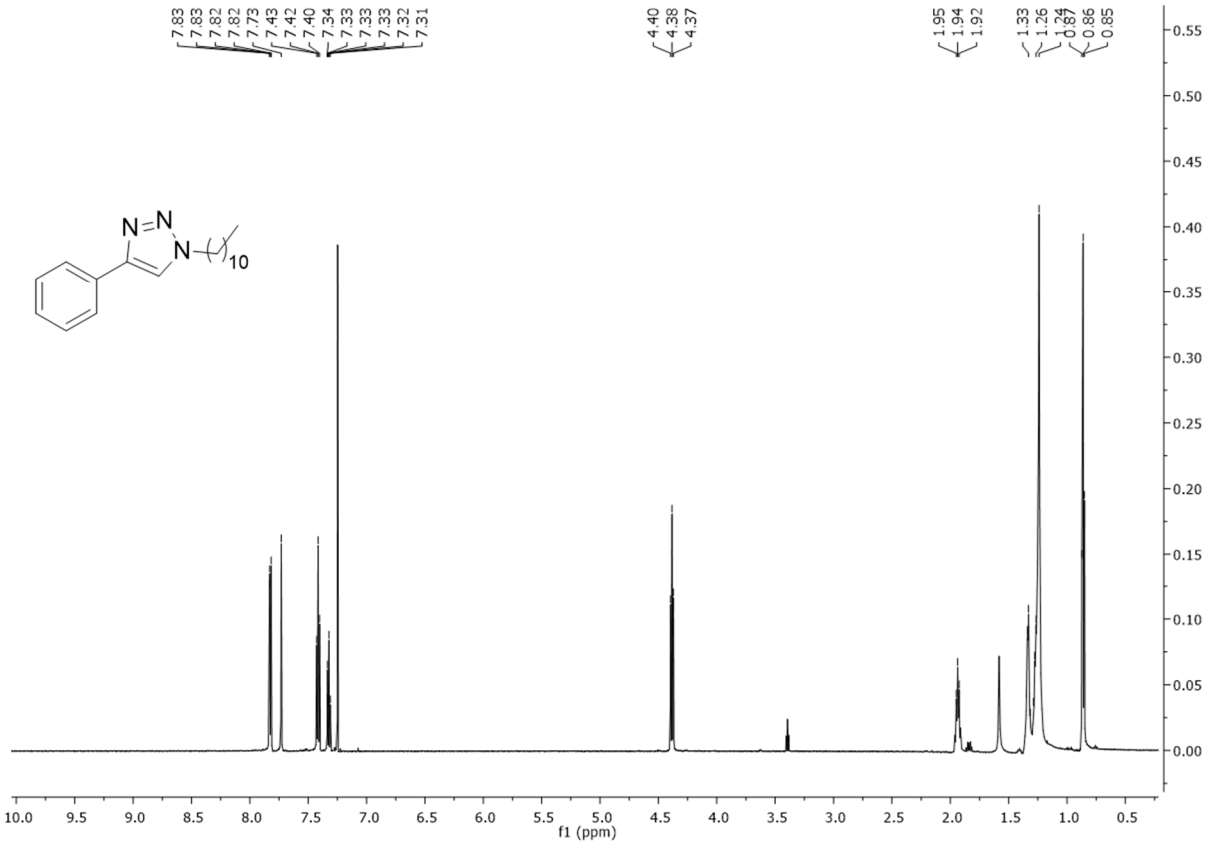

Figure S10. ^{1}H NMR of **5**.

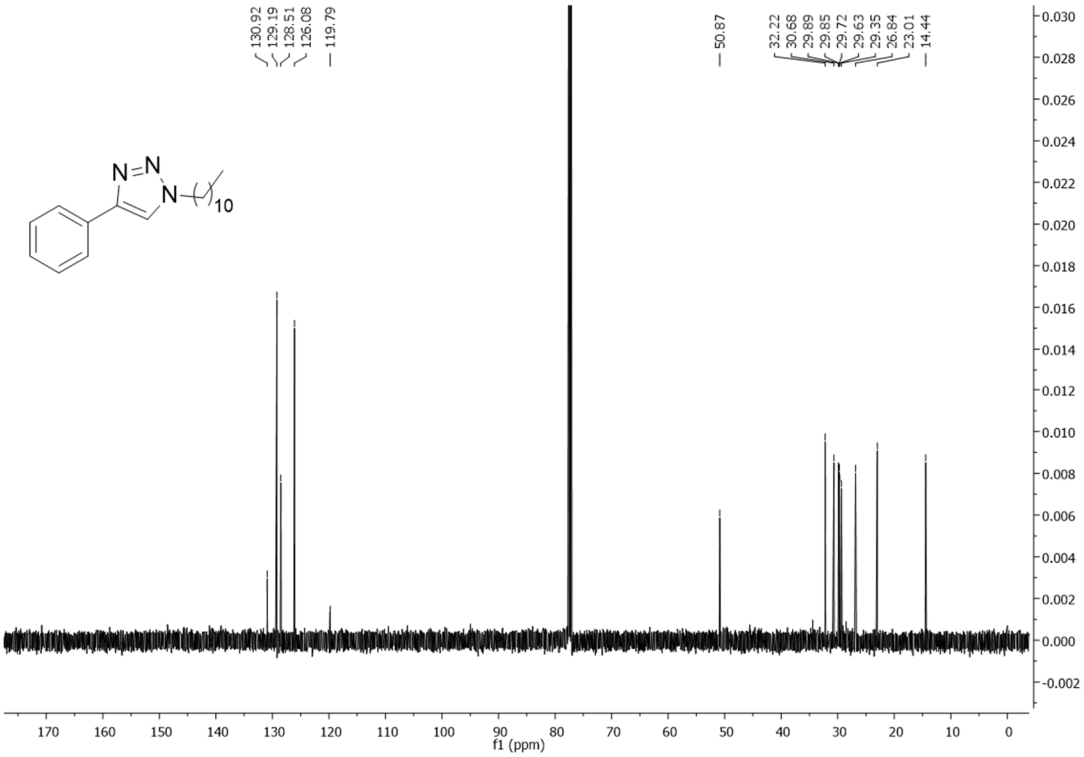

Figure S11. ^{13}C NMR of **5**.

4. References

1. Trotta, F.; Martina, K.; Robaldo, B.; Barge, A.; Cravotto, G. Recent advances in the synthesis of cyclodextrin derivatives under microwaves and power ultrasound. *Journal of Inclusion Phenomena and Macrocyclic Chemistry* **2007**, *57*, 3-7, doi:10.1007/s10847-006-9169-z.