

SUPPLEMENTARY INFORMATION

A mesoporous metal-organic framework used to sustainably release copper(II) into reducing aqueous media to promote the CuAAC click reaction

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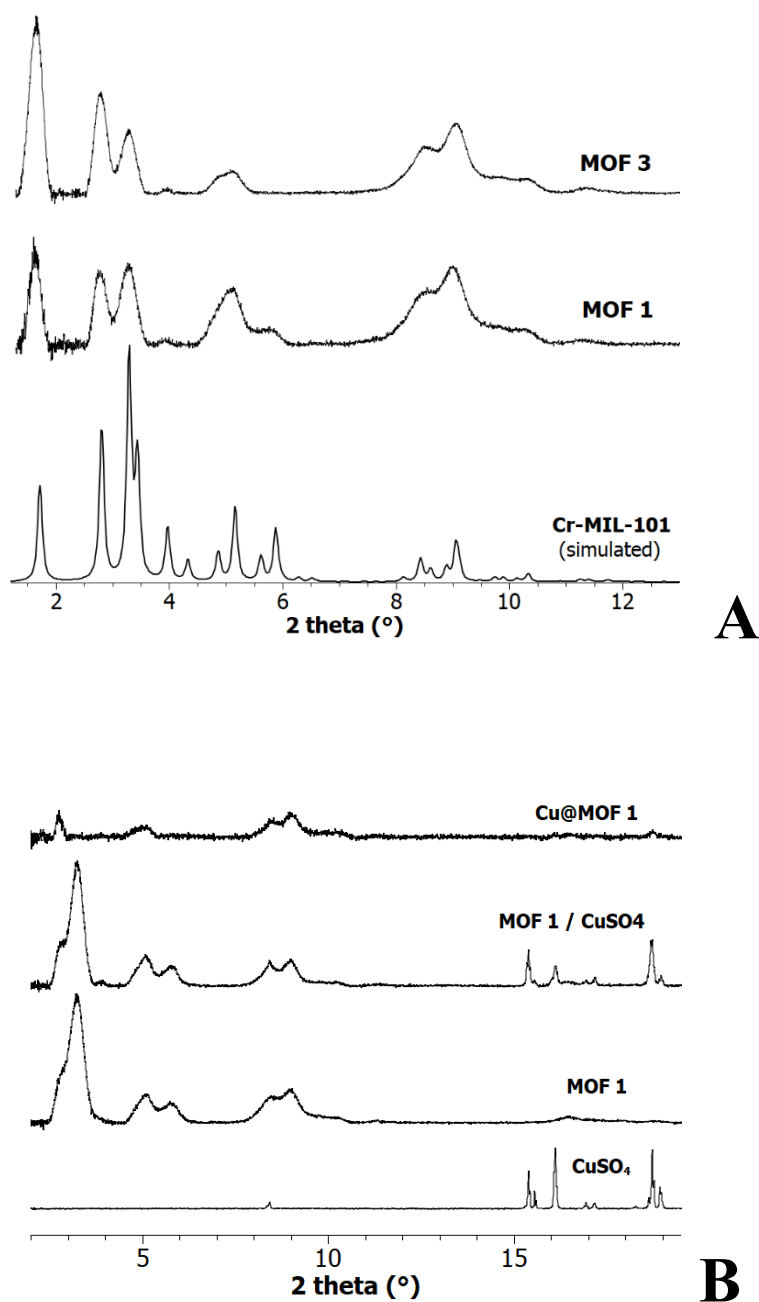


Figure S1. **A.** PXRD patterns simulated (1.54056 Å) from the crystal data of **Cr-MIL-101**, and recorded for a sample of **MOF 1** (Cr-MIL-101-NH₂) and **MOF 3** (Cr-MIL-101-TBTA). **B.** PXRD patterns recorded for a sample of CuSO₄·5H₂O, **MOF1**, **MOF1/CuSO₄** and **Cu@MOF1**.

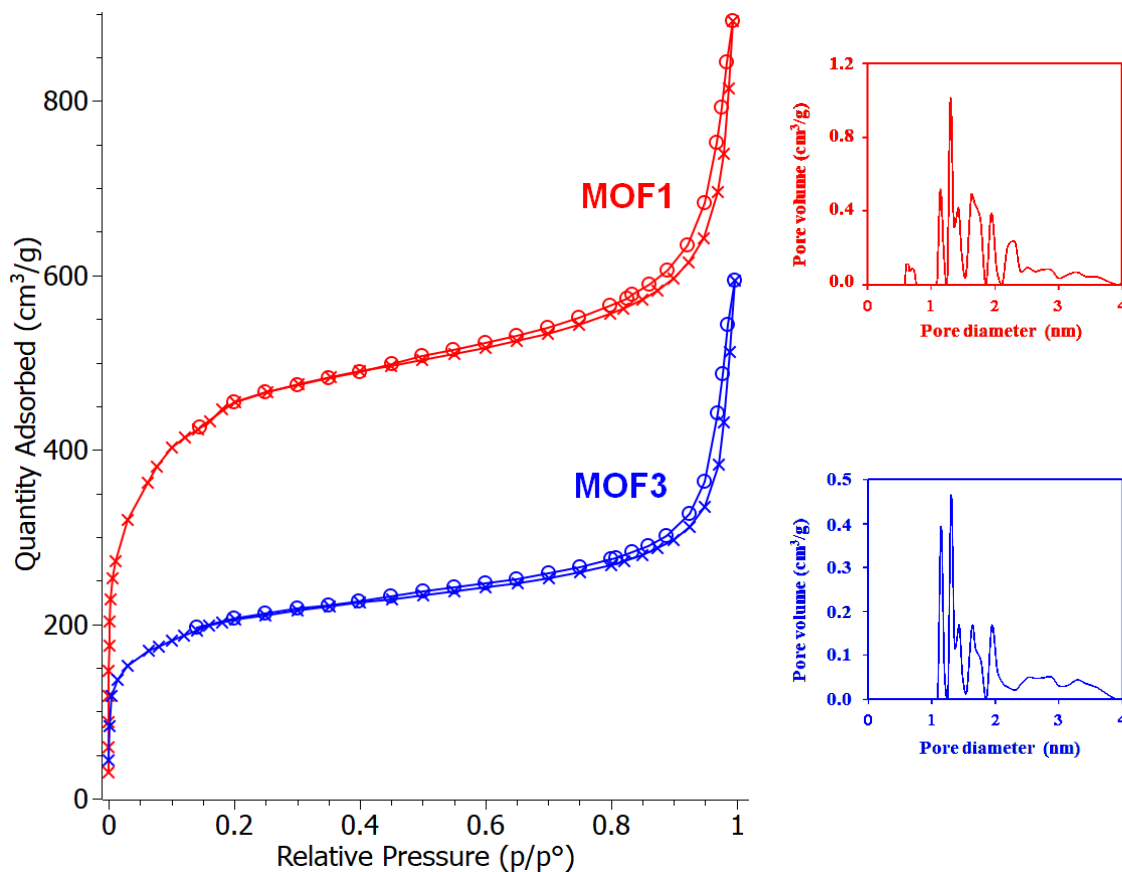


Figure S2. N₂ adsorption-desorption experiments and calculated pore size distribution of Cr-MIL-101-NH₂ (**MOF1**, red) and **MOF3** (blue). N₂ adsorption-desorption isotherms were performed on a Micromeritics ASAP 2020 apparatus and measured at liquid N₂ temperature (77 K).

A known amount of sample (about 50 mg) was loaded into the sample cell and degassed under vacuum (10⁻⁵ Torr) at 150 °C for 11 h. The BET specific surface areas (1620 m²/g for **MOF1** calculated in the P/P^o range 0.0617-0.2016 and 730 m²/g for **MOF3** calculated in the P/P^o range 0.0641-0.2015) and pore size distribution were calculated from the desorption isotherms.

- Calculated total pore volume (**MOF1** : 1.22 cm³/g, **MOF3** : 0.79 cm³/g).

- Calculated micropore volume and micropore surface area (**MOF1**: 0.560 cm³/g and 737 m²/g, respectively, **MOF3**: 0.252 cm³/g and 262 m²/g, respectively).

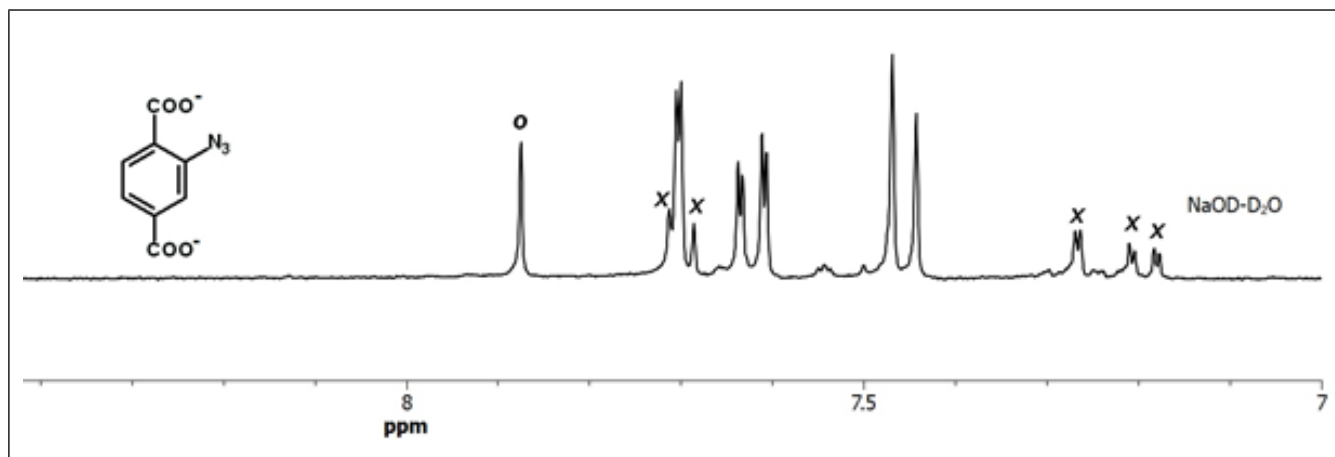


Figure S3. 7.0-8.4 ppm-range $^1\text{H-NMR}$ spectrum (300 MHz, NaOD/D₂O or d⁶-DMSO) of the digested **MOF 2**. For $^1\text{H-NMR}$ measurements, a MOF sample (≈ 10 mg) was suspended in D₂O (1 mL), and a solution of 40 wt% NaOD in D₂O (2 μL) was added. The solution was allowed to stand for 16 hours at room temperature, filtered on alumina (aluminum oxide 90 active neutral from Merck) to remove chromium salts, and then analyzed by NMR. It should be noted the presence of ≈ 20 % of remaining BDC-NH₂ (signals denoted “x”), and of BDC (signal denoted “o”) probably due to a deamination reaction.

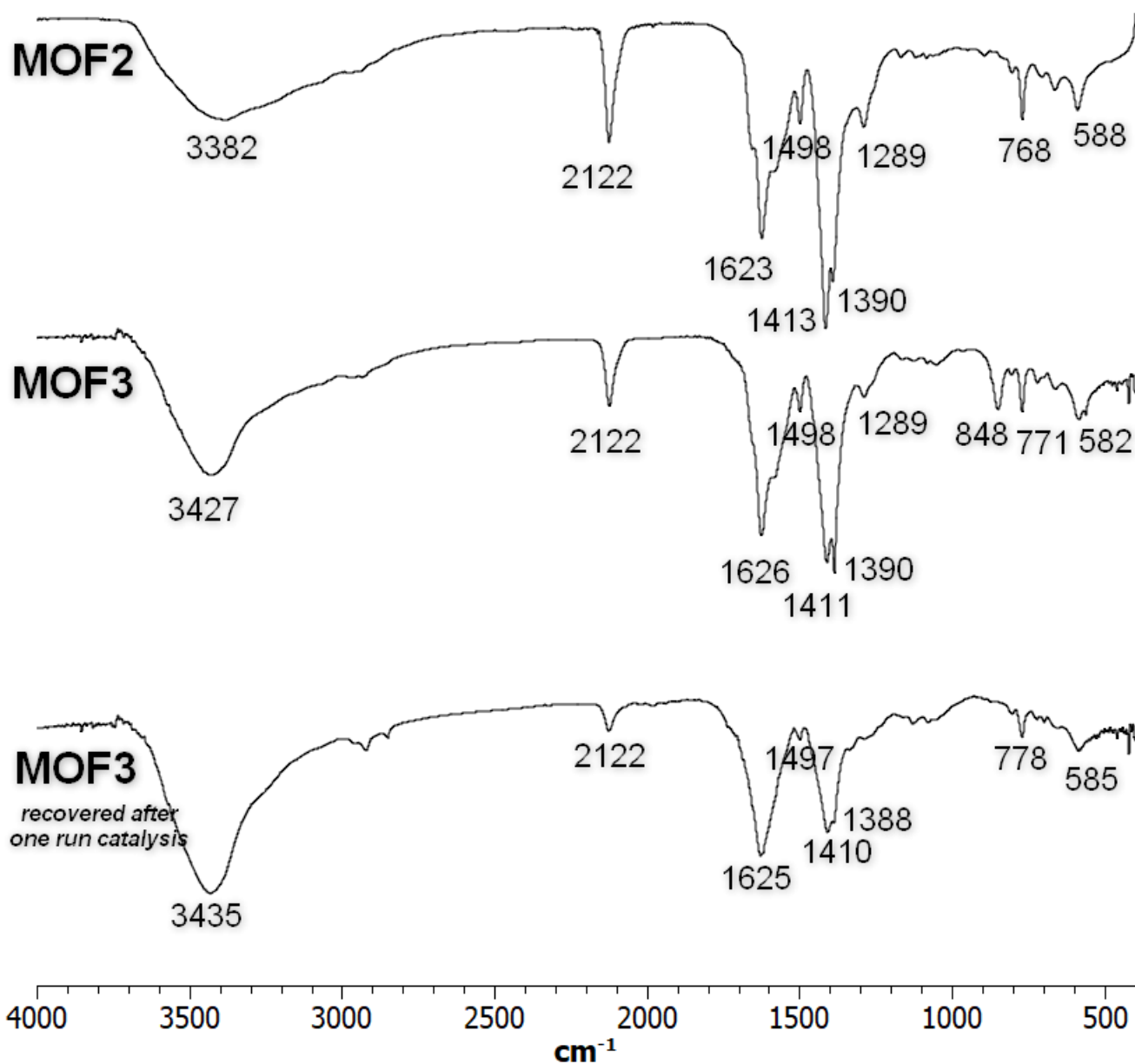


Figure S4. FT-IR spectra of **MOF 2** and **MOF 3** (as synthesized and after one reaction run) displaying azido bands at 2122 cm^{-1} .

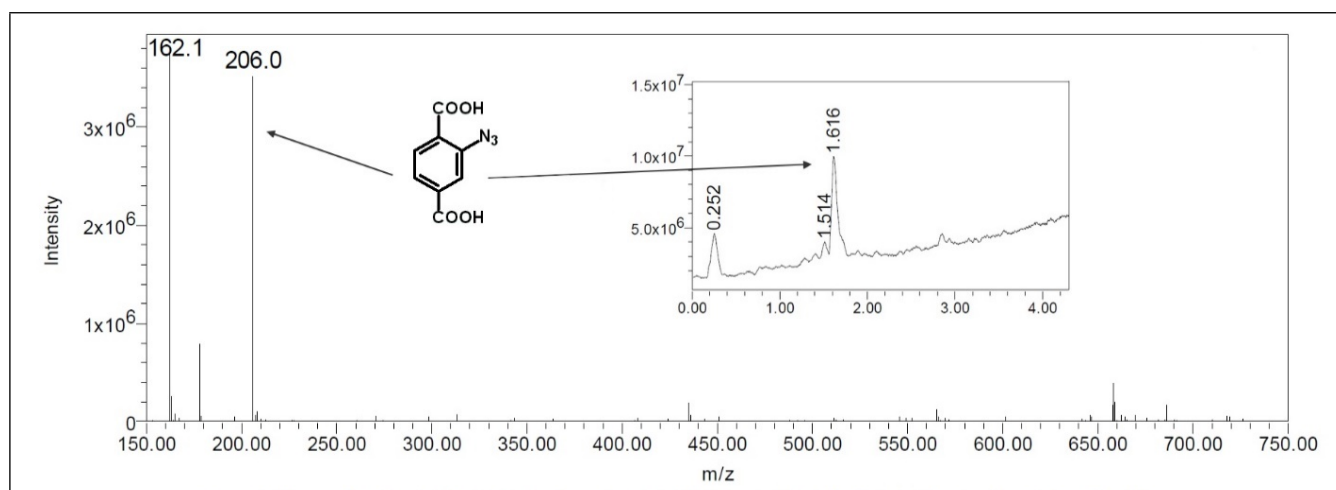


Figure S5. UPLC chromatogram (inset plot) of the digested products in approx. 0.02 M NaOH of **MOF 2** (retention time: 1.616 min) with the mass spectrum acquired in ESI negative mode corresponding to 2-azidoterephthalic acid ($C_8H_5N_3O_4$, MW=207.143).

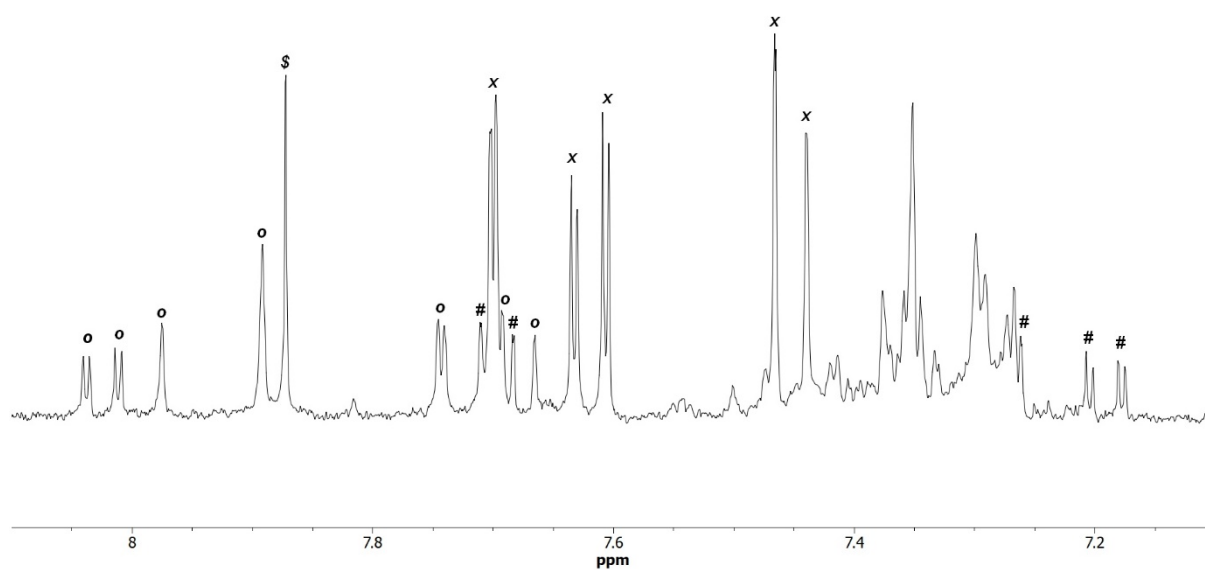


Figure S6. 7.1-8.1 ppm-range $^1\text{H-NMR}$ spectrum (300 MHz, NaOD/D₂O) of the digested **MOF 3**. For $^1\text{H-NMR}$ measurements, a MOF sample (≈ 10 mg) was suspended in D₂O (1 mL), and a solution of 40 wt% NaOD in D₂O (2 μL) was added. The solution was allowed to stand for 16 hours at room temperature, filtered on alumina and analyzed by NMR. Signals denoted “#” in the spectrum refer to BDC²⁻-NH₂, “x” to BDC²⁻-N₃, “o” to BDC²⁻-TBTA, and signal denoted “\$” refers to BDC²⁻.

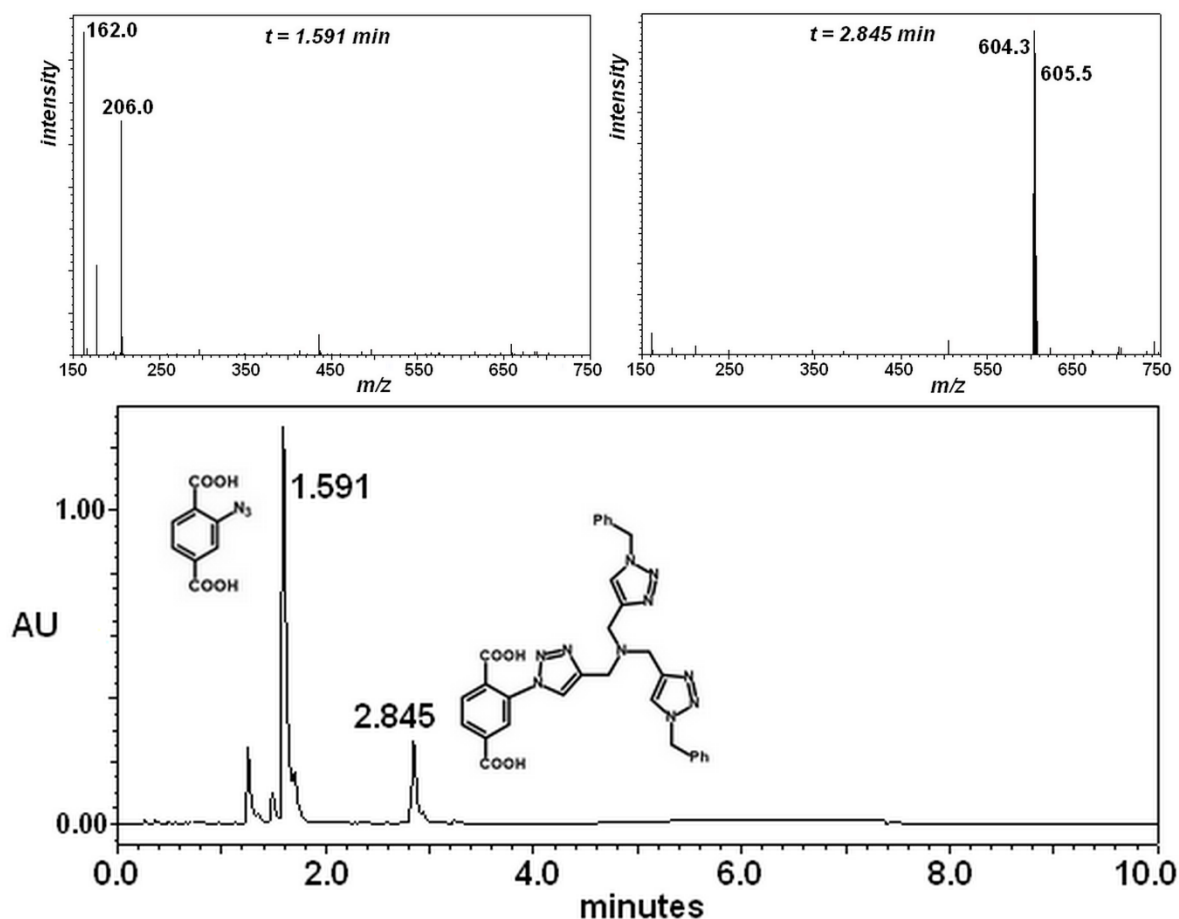


Figure S7. Mass spectra acquired in ESI negative mode of 2-azidoterephthalic acid (BDC-N₃, C₈H₅N₃O₄, MW 207.143) and of 2-[4-[[bis[(1-benzyltriazol-4-yl)methyl]amino]methyl] triazol-1-yl]terephthalic acid (BDC-TBTA, C₃₁H₂₈N₁₀O₄, MW 604.62) with the UPLC chromatogram (254 nm detection) of the digested products in ≈ 0.02 M NaOH of **MOF 3**; Retention times: 1.591 min for BDC-N₃ and 2.845 min for BDC-TBTA; Ratio: BDC-N₃ / BDC-TBTA 82/18.

Table S1^a. “Recyclability” of **Cu@MOF1** and **Cu@MOF3** materials in the CuAAC reaction between benzyl azide and 3-phenyl-1-propyne at room temperature in methanol/water 95/5. Reaction conditions: 3-phenyl-1-propyne (0.86 mmol, 1 equiv), benzyl azide (1.03 mmol, 1.2 equiv), sodium ascorbate (10 mg, 6 mol%), MOF (10 mg), methanol/water 95/5 (1 mL). After each run of 24 h, the solid material was centrifuged, washed with ethyl acetate, dried under vacuum, and then used directly in the next run.

run number	Cu@MOF1		Cu@MOF3	
	conversion %	yield %	conversion %	yield %
#1	100	94	100	95
#2	100	96	100	93
#3	96	95	100	95
#4	97	93	95	91
#5	70	75	86	74
#6	34	31	52	46

^aHistograms of these data are represented in **Fig.4**.

¹H- and ¹³C-NMR data and spectra of compounds 4 – 7, 8 – 10

¹H-NMR spectra were recorded on a Bruker Avance 300 spectrometer at 300 MHz using CDCl₃ as solvent. The residual proton signal of the deuterated solvent was used as an internal reference (CDCl₃ δ = 7.26 ppm).

J-MOD ¹³C- NMR spectra were recorded on a spectrometer on a Bruker Avance 300 spectrometer at 75 MHz. The carbon signal of the deuterated solvent was used as an internal reference (CDCl₃ δ = 77.0 ppm).

NMR data for **1,4-dibenzyl-1H-1,2,3-triazole (1)**, **4-benzyl-1-dodecyl-1H-1,2,3-triazole (2)**, **1-benzyl-4-phenyl-1H-1,2,3-triazole (3)** and **1-benzyl-4-hexyl-1H-1,2,3-triazole (9)** are consistent with data already published [ref. S1-S2]

1-Dodecyl-4-phenyl-1H-1,2,3-triazole (4) [ref. S3]

Purified by flash chromatography: gradient petroleum ether/ethyl acetate 95/5 to 20/80 in 15 min.

Yield: 94%

¹H NMR (300 MHz, CDCl₃) δ 7.83 (d, *J* = 7.3 Hz, 2H); 7.74 (s, 1H); 7.42 (t, *J* = 7.3 Hz, 2H); 7.32 (t, *J* = 7.3 Hz, 1H); 4.38 (t, *J* = 7.2 Hz, 2H); 1.93 (m, 2H); 1.29 (m, 18H); 0.87 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 147.7; 130.7; 128.8; 128.0; 125.6; 119.3; 50.4; 31.9; 30.3; 29.6; 29.5; 29.34; 29.28; 29.0; 26.5; 22.6; 14.1; LRMS (DCI-NH₃, M+H) Found: 314.2.

1-Benzyl-4-(3-methylphenyl)-1H-1,2,3-triazole (5)

Purified by flash chromatography: gradient petroleum ether/ethyl acetate 95/5 to 20/80 in 15 min.

Yield: 98%

¹H NMR (300 MHz, CDCl₃) δ 7.66 (br s, 2H); 7.56 (d, *J* = 7.5 Hz, 1H); 7.25-7.38 (m, 6H); 7.12 (d, *J* = 7.5 Hz, 1H); 5.54 (s, 2H); 2.37 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 148.2; 138.4; 134.6; 130.3; 129.0; 128.8; 128.6; 128.6; 127.9; 126.3; 122.7; 119.5; 54.1; 21.3; HRMS (DCI-CH₄, M+H) Calculated for C₁₆H₁₆N₃: 250.1344. Found: 340.1341.

9-(1-Benzyl-1H-1,2,3-triazol-4-yl)-9H-fluoren-9-ol (6)

Purified by flash chromatography: gradient petroleum ether/ethyl acetate 80/20 to 20/80 in 15 min.

Yield: 93%

¹H NMR (300 MHz, CDCl₃) δ 7.62 (m, 2H); 7.58 (m, 2H); 7.36 (td, *J* = 7.5 Hz, 1.3 Hz, 2H); 7.24-7.33 (m, 5H); 7.17-7.20 (m, 2H); 7.14 (s, 1H); 5.39 (s, 2H); 3.83 (s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 150.7; 147.8; 139.5; 134.3; 129.3; 128.9; 128.6; 128.2; 127.9; 124.8; 120.4; 120.1; 78.5; 54.0; HRMS (DCI-CH₄, M+H) Calculated for C₂₂H₁₈N₃O: 340.1450. Found: 340.1445.

9-(1-Dodecyl-1H-1,2,3-triazol-4-yl)-9H-fluoren-9-ol (7)

Purified by flash chromatography: gradient petroleum ether/ethyl acetate 80/20 to 20/80 in 15 min.

Yield: 97%

^1H NMR (300 MHz, CDCl_3) δ 7.62 (t, $J = 8.3$ Hz, 4H); 7.37 (td, $J = 7.3$ Hz, 1.2 Hz, 2H); 7.28 (td, $J = 7.4$ Hz, 1.1 Hz, 2H); 7.13 (s, 1H); 4.20 (t, $J = 7.3$ Hz, 2H); 3.88 (s, 1H); 1.79 (m, 2H); 1.25 (m, 18 H); 0.88 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 150.3; 148.0; 139.5; 129.3; 128.2; 124.8; 120.1; 78.5; 50.3; 31.8; 30.1; 29.5; 29.4; 29.3; 28.9; 26.4; 22.6; 14.1; HRMS (DCI- CH_4 , M+H) Calculated for $\text{C}_{27}\text{H}_{36}\text{N}_3\text{O}$: 418.2858. Found: 418.2668.

1-Benzyl-4-butyl-1H-1,2,3-triazole (8) [ref. 3]

Purified by flash chromatography: gradient petroleum ether/ethyl acetate 95/5 to 20/80 in 15 min.

Yield: 98%

^1H NMR (300 MHz, CDCl_3) δ 7.22-7.38 (m, 5H); 7.18 (s, 1H); 5.47 (s, 2H); 2.67 (t, $J = 7.5$ Hz, 2H); 1.61 (m, 2H); 1.34 (m, 2H); 0.89 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 134.9; 128.9; 128.5; 127.8; 53.9; 31.4; 25.3; 22.2; 13.7; LRMS (DCI- NH_3 , M+H) Found: 216.1.

1-Dodecyl-4-hexyl-1H-1,2,3-triazole (10)

Purified by flash chromatography: gradient petroleum ether/ethyl acetate 95/5 to 20/80 in 15 min.

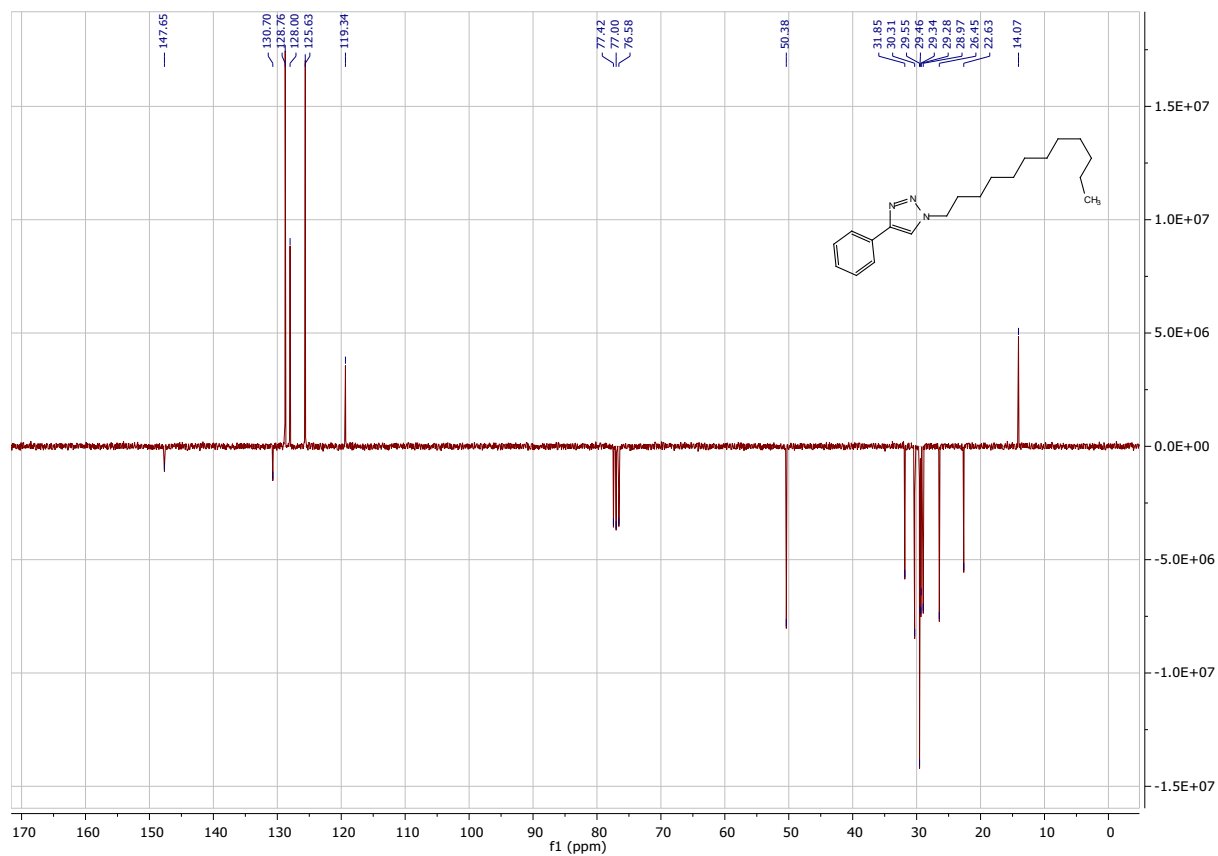
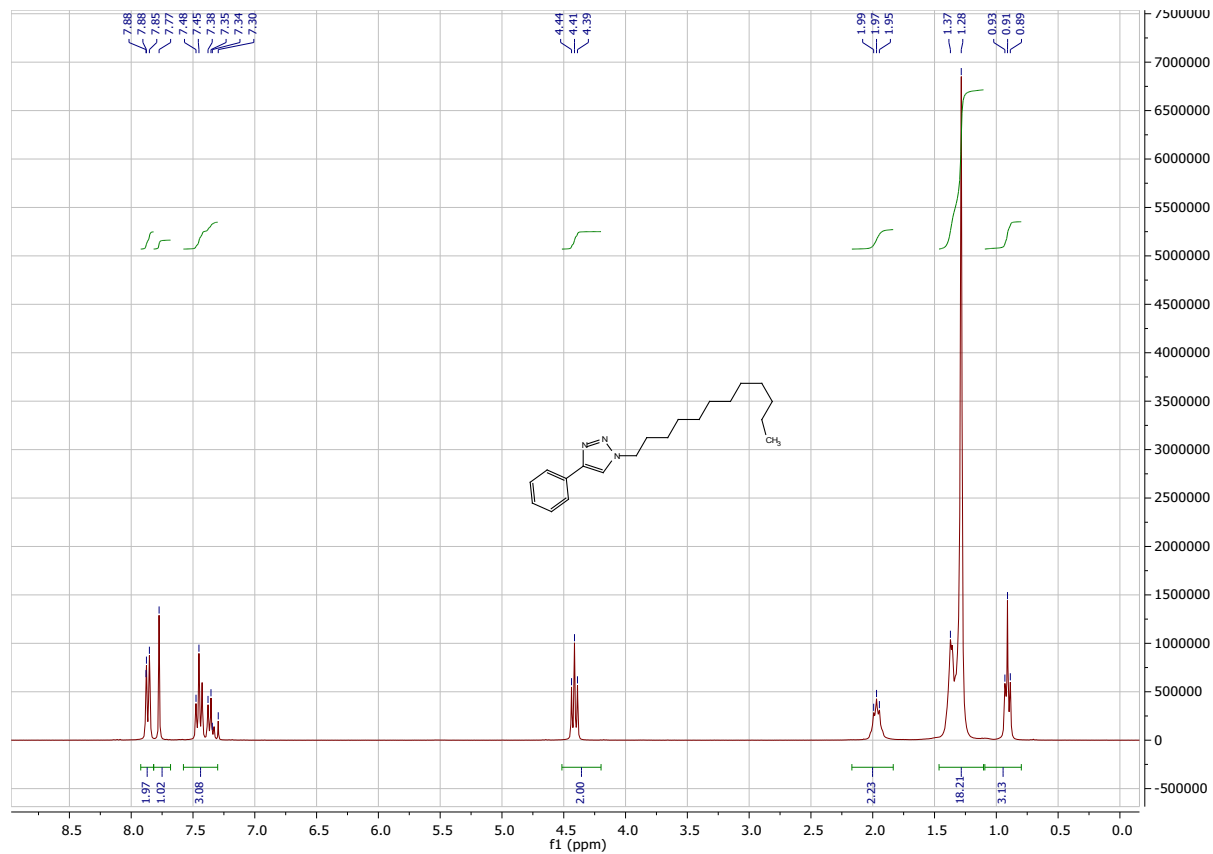
Yield: 96%

^1H NMR (300 MHz, CDCl_3) δ 4.26 (t, $J = 7.2$ Hz, 2H); 2.66 (t, $J = 7.5$ Hz, 2H); 1.84 (m, 2H); 1.62 (m, 2H); 1.21 (m, 27H); 0.84 (t, $J = 6.8$ Hz, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 148.3; 120.3; 50.1; 31.8; 31.5; 30.3; 29.5; 29.4; 29.3; 29.2; 28.9; 28.8; 26.4; 25.6; 22.6; 22.5; 14.0; 13.9; HRMS (DCI- CH_4 , M+H) Calculated for $\text{C}_{20}\text{H}_{40}\text{N}_3$: 322.3222. Found: 322.3225.

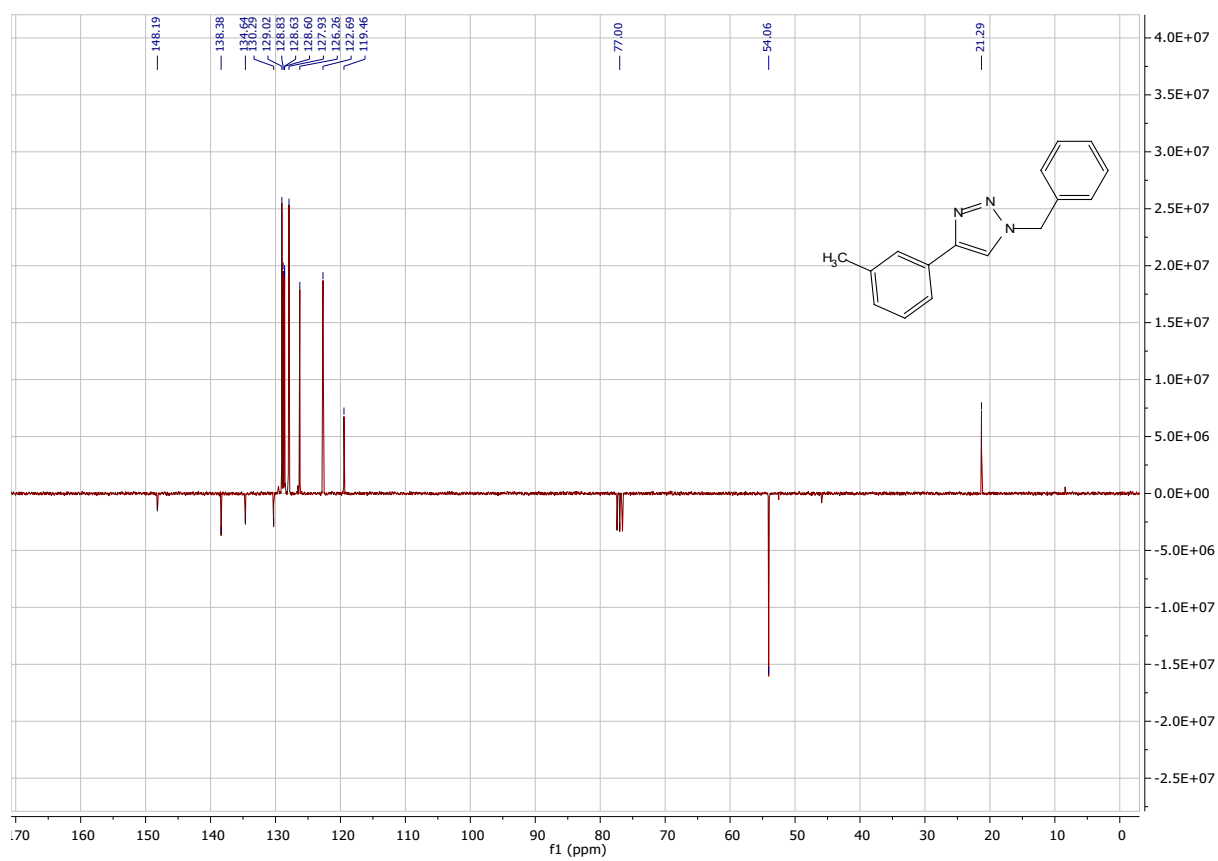
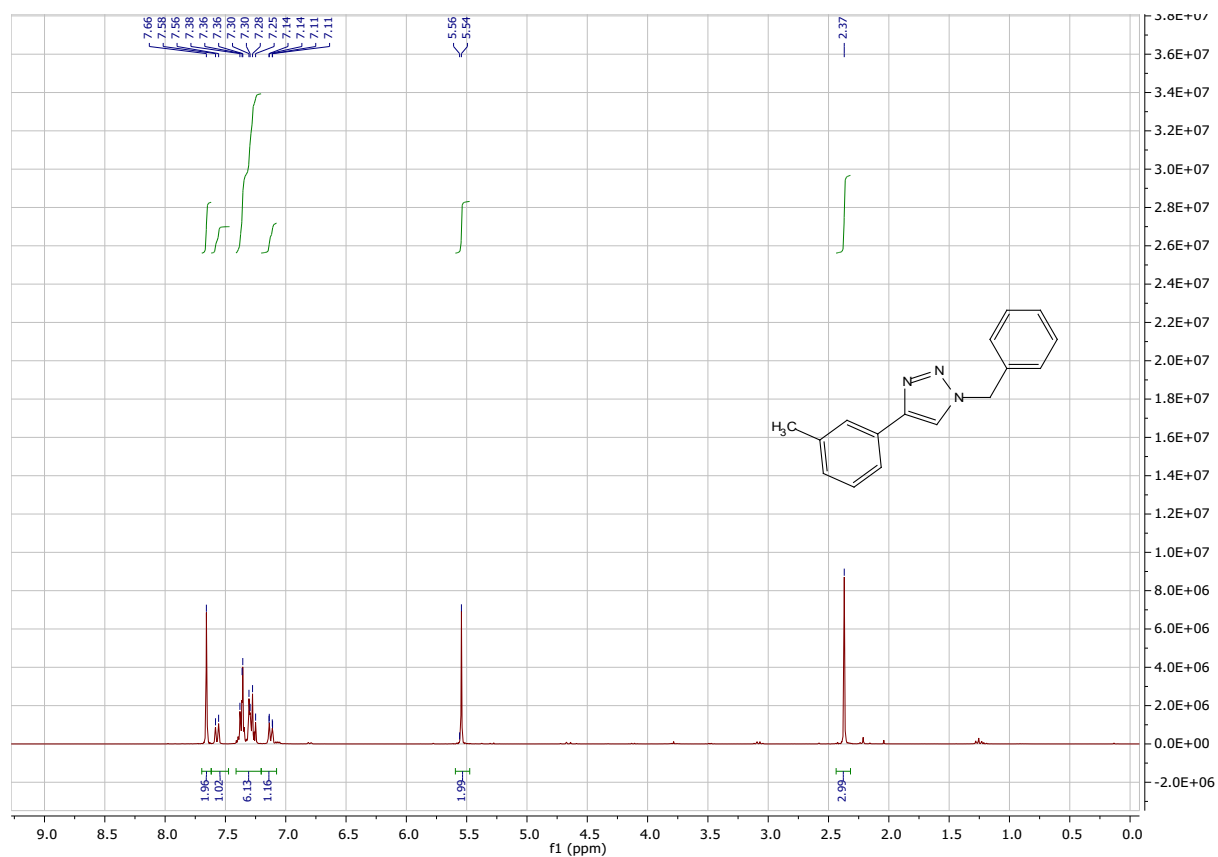
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- S3. Alonso, F.; Moglie, Y.; Radivoy, G.; Yus, M. Unsupported copper nanoparticles in the 1,3-dipolar cycloaddition of terminal alkynes and azides. *Eur. J. Org. Chem.* **2010**, 1875-1884.

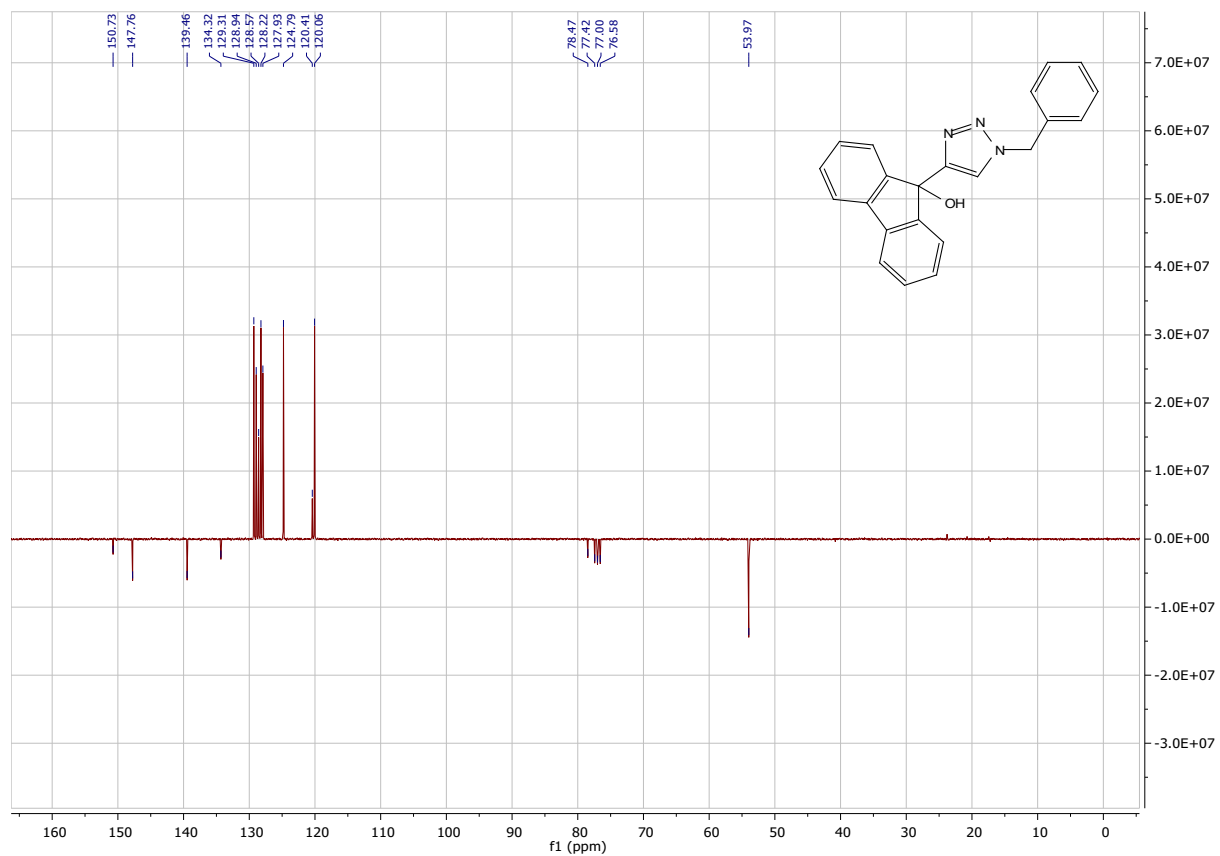
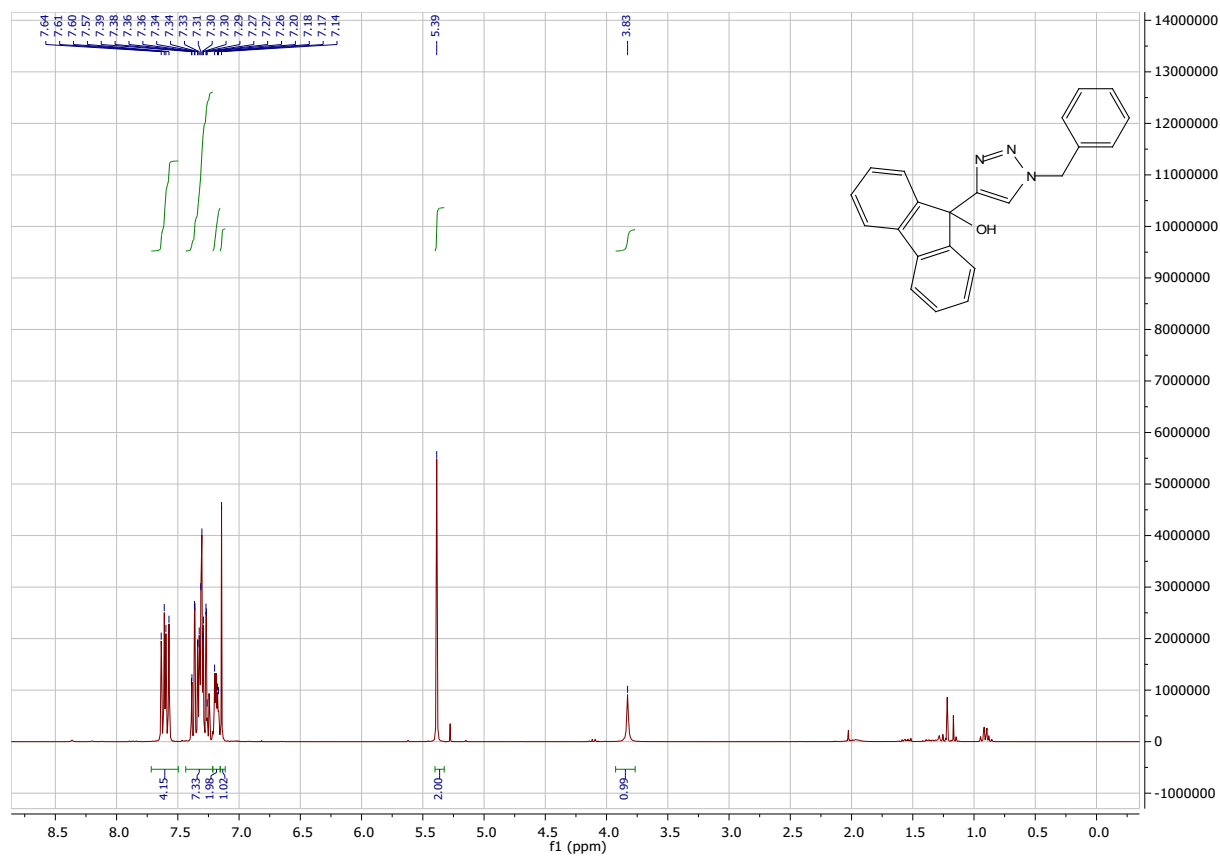
Compound 4



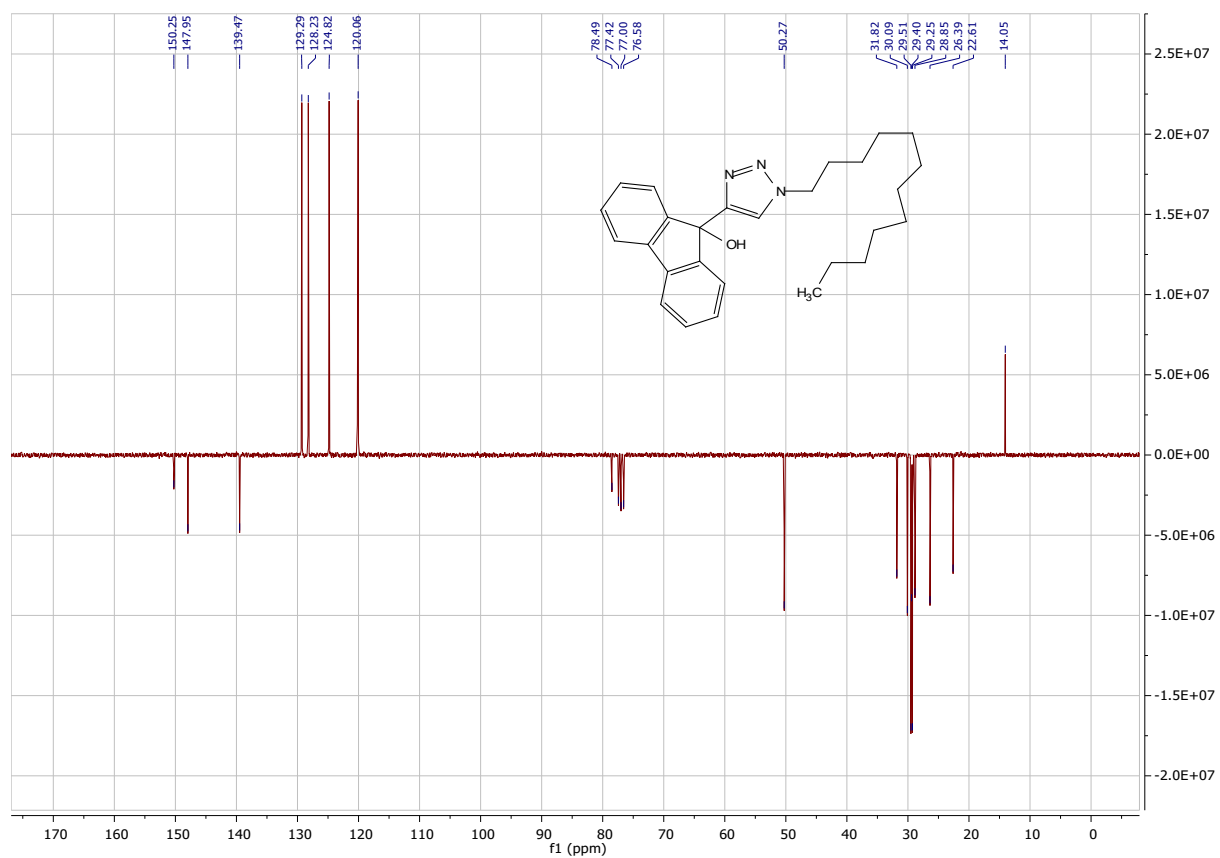
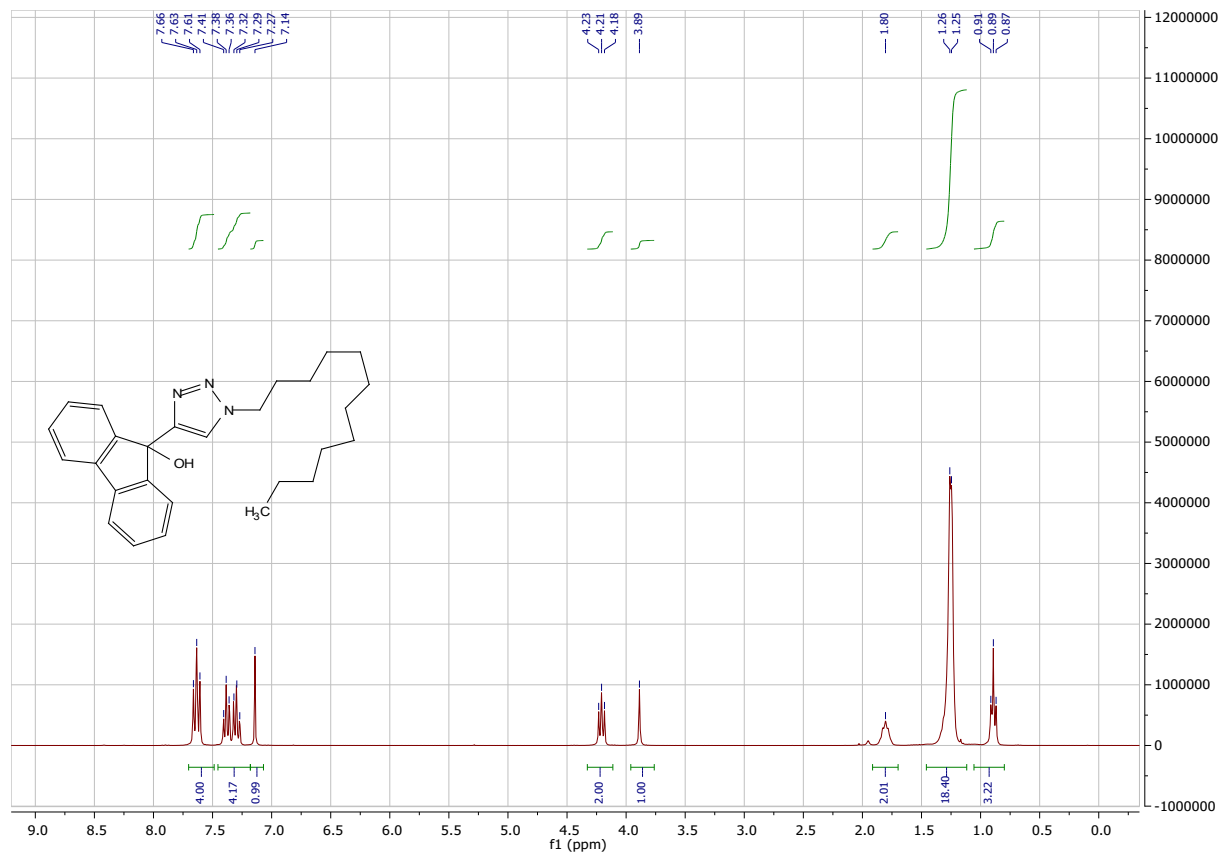
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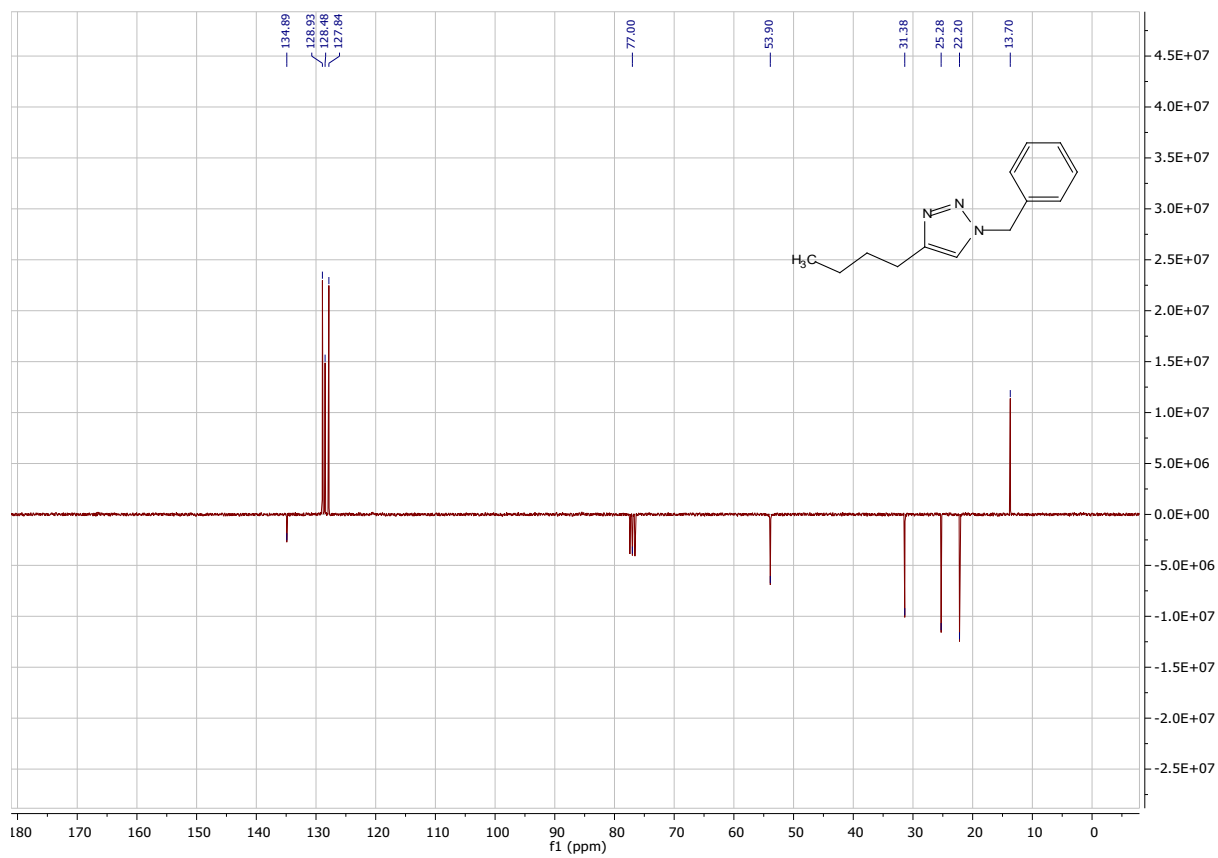
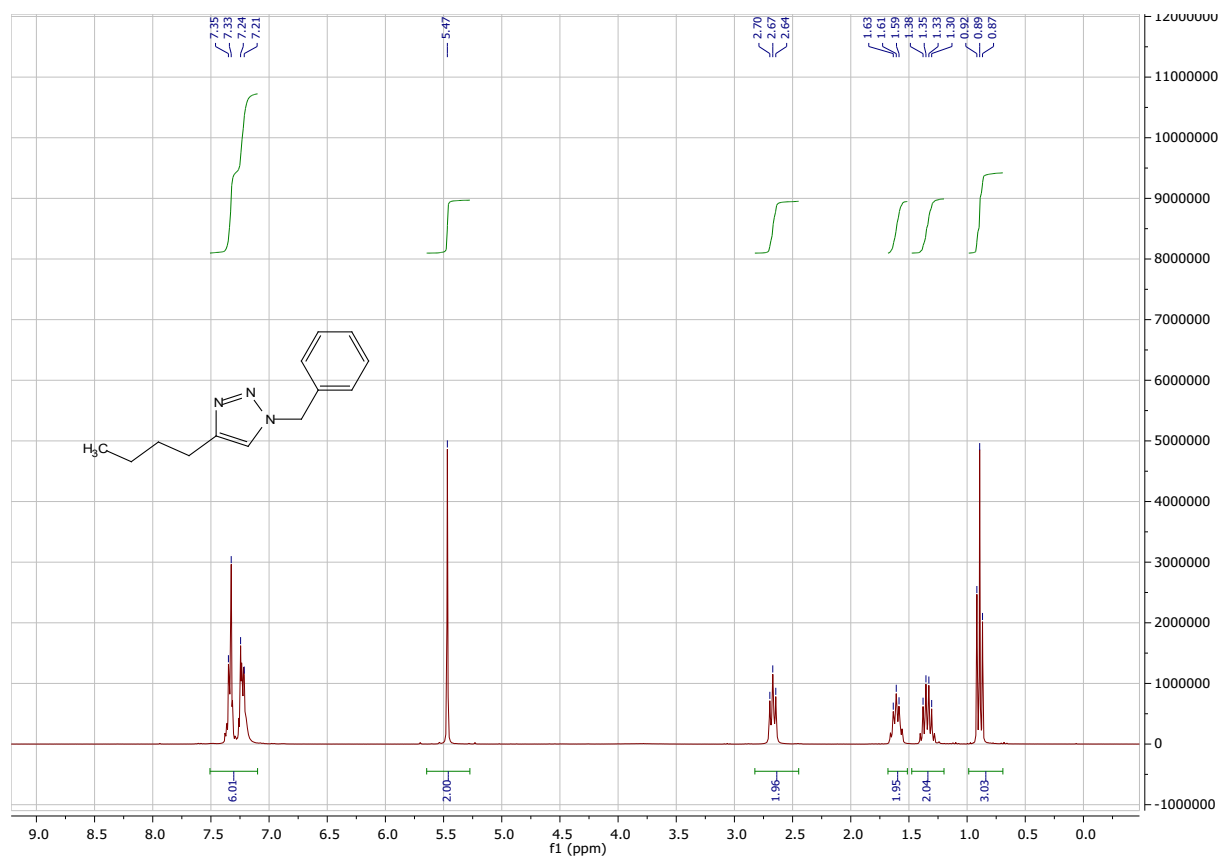
Compound 6



Compound 7



Compound 8



Compound 10

