Electronic Supplementary Information (ESI)

Fast, ligand- and solvent free copper-catalyzed *Click* reactions in a ball mill

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General information:

Chemicals were purchased from Sigma Aldrich or Alfa Aesar and were used as received. Decyl azide (**2a**),[1] 1-ethynylcyclophan (**1m**),[2] 1,4-*bis*-ethynyl-2,5-*bis*-octyloxybenzene (**4c**),[3] 1,3,5-*tris*-ethynylbenzene (**6**),[4] mesityl azide (**2b**),[1] benzyl azide (**2c**)[1] and 2-azidoethyl-2,3,4,6-tetra-O-acetyl-*β*-D-glucopyranoside (**2e**)[5] were prepared according to literature procedures. Reactions were accomplished in a Fritsch *Pulverisette 7 classic line* planetary ball mill using 45 mL grinding beakers (zirconia, MgO-stabilised) and milling balls (6 × 15 mm; zirconia, MgO-stabilised). All used reaction vessels were purified with *aqua regia* prior to use to avoid any contamination or memory effects.

GC-FID and GC-MSD measurements were performed on a 7890GC and 6890N from Agilent Technologies, respectively. Measurement conditions GC-FID: HP 5, 30 m × 0.32 mm × 0.25 µm, H_2 – 10 psi, program: 70 °C (hold for 3 min), 15 K min^{-1} up to 280 °C (hold for 10 min), injector temperature: 280 °C, detector temperature: 300 °C. Measurement conditions GC.MSD: HP 5, 30 m × 0.32 mm × 0.25 µm, He – 10 psi, program: 70 °C (hold for 3 min), 15 K min^{-1} up to 280 °C (hold for 10 min), injector temperature: 280 °C, detector: EI (70 eV).

NMR spectra were recorded with a Bruker Avance 200 MHz system at room temperature in Chloroform-$[^2H]_3$ ($CDCl_3$) as solvent.

MALDI-TOF MS measurements were performed with an Ultraflex III TOF/TOF (Bruker Daltonics, Bremen, Germany) mass spectrometer equipped with a Nd-YAG laser and a collision cell. All spectra were measured in the positive ion reflectron mode using anthracene-1,8,9-triol as matrix. The instrument was calibrated prior to each measurement with an external PMMA standard $H(CH_2CCH_3COOCH_3)_nH$ þ Naþ (m/z 425 or 2526, measured with sodium iodide) from PSS in the required measurement range. MS and MS/MS data were processed using the software FlexAnalysis, PolyTools 1.0 and an isotope pattern calculator from Bruker Daltonics. NMR spectra were recorded with a Bruker Avance 200 MHz system at room temperature in Chloroform-$[^2H]_3$ ($CDCl_3$) as solvent using tetramethylsilane as internal standard.

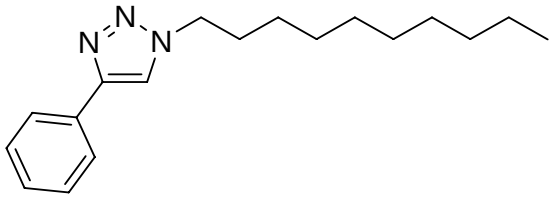
Size-exclusion chromatography (SEC) was carried out on a system equipped with a SCL-10A system controller, a LC-10AD pump and a RID-10A refractive index detector (all from Shimadzu, Duisburg, Germany) using a solvent mixture containing chloroform, triethylamine and *iso*-propanol (94:4:2) at a flow rate of 1 mL min^{-1} on a PSS-SDV linear M5mm column (PSS, Mainz, Germany) at room temperature. The system was calibrated with commercial polystyrene (370–67,500 Da) standards from PSS.

All product yields reported herein are GC-determined yields and are comparable with the isolated ones. Nevertheless, the reported yields were corrected by means of different FID-sensitivity for substrate and product. The reported yields are mean values from at least two independent experimental runs.

General reaction protocol:

The milling beakers (45 mL; zirconia) were equipped with 6 milling balls (d = 15 mm, zirconia). Afterwards SiO_2 (5 g), the alkyne (1.1 mmol), the azide (1 mmol) and $Cu(OAc)_2$ (5 mol%, 8 mg) were added in the given order. Milling was accomplished at 800 min^{-1} for 10 min. After cooling of the milling beakers to room temperature, the crude products were extracted on a frit with a thin silica layer using *tert*-butyl methyl ether (3 × 10 mL). The solvent was evaporated in vacuum, the crude products were dried and analyzed by GC-FID, ^{1}H, ^{13}C NMR spectroscopy and MALDI-TOF mass spectrometry after dissolution in an appropriate solvent.

Analytical data of products.



1-Decyl-4-phenyl-1*H*-1,2,3-triazol (3a): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.78 (2 H, d, J = 8.3 Hz), 7.71 (1 H, s), 7.41-7.20 (3 H, m), 4.29 (2 H, t, J = 7.3 Hz), 1.86 (2 H, quin, J = 6.9 Hz), 1.36-1.08 (14 H, m), 0.83 ppm (3 H, t, J = 6.5 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 147.45, 130.63, 128.59, 127.81, 125.46, 119.37, 50.18, 31.65, 30.13, 29.27, 29.19, 29.05, 28.81, 26.39, 22.46, 13.90 ppm; MALDI-TOF-MS (Dithranol): m / z= 286.18 ($[M+H]^+$).

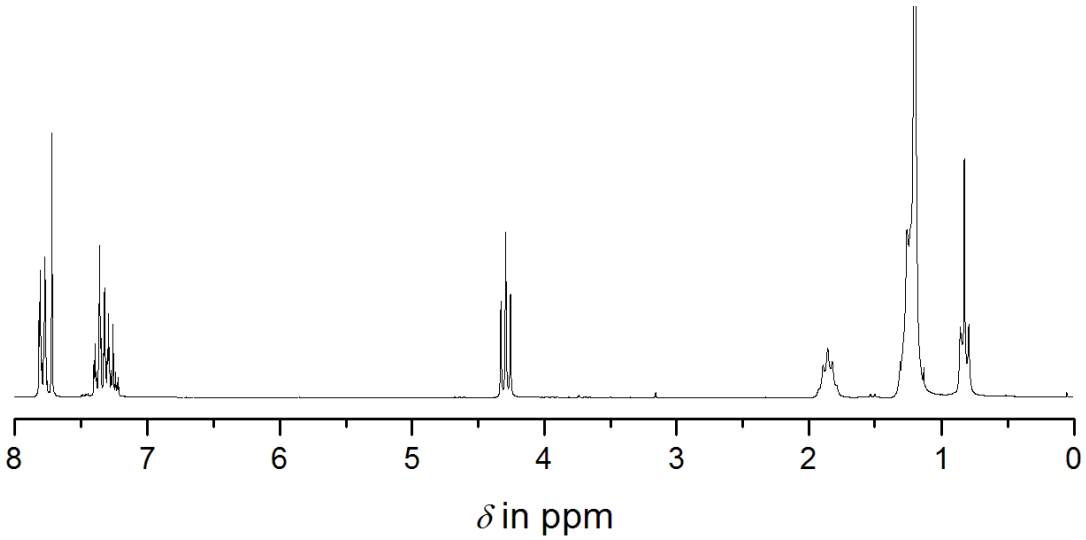


Figure 1a: ^{1}H NMR spectrum of **3a** ($CDCl_3$, 200 MHz).

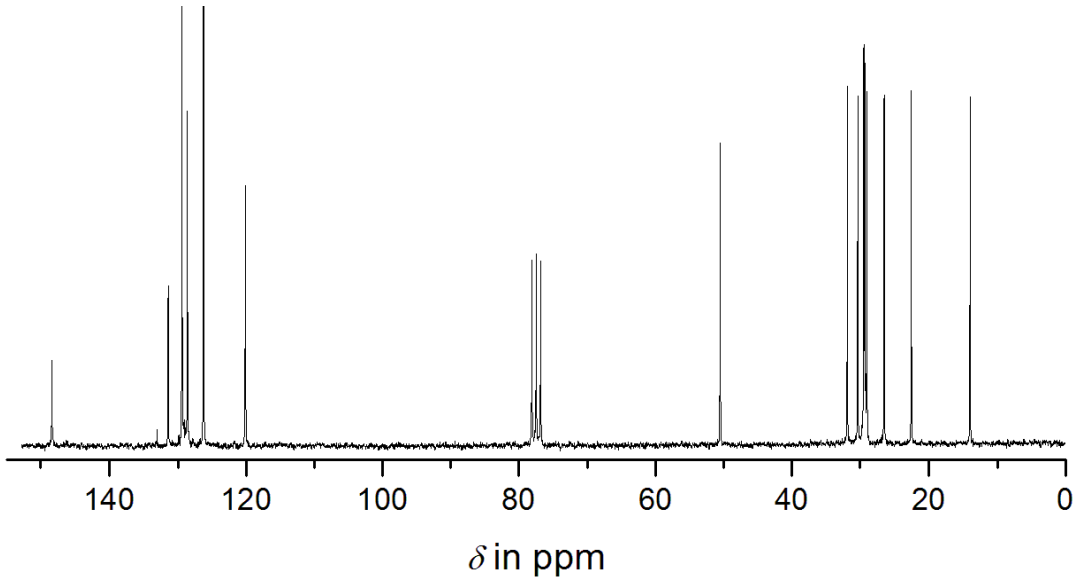
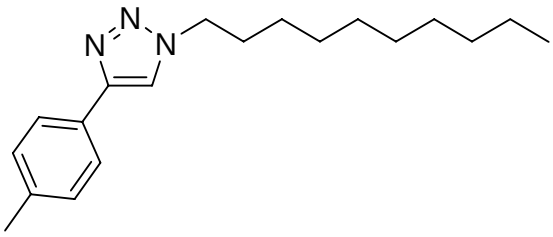


Figure 1b: ^{13}C NMR spectrum of **3a** ($CDCl_3$, 50 MHz).



1-Decyl-4-*p*-tolyl-1*H*-1,2,3-triazol (3b): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.68 (1 H, s), 7.67 (2 H, d, *J* = 8.2 Hz), 7.16 (2 H, d, *J* = 8.1 Hz), 4.28 (2 H, t, *J* = 7.3 Hz), 2.31 (3 H, s), 1.85 (2 H, quin, *J* = 6.8 Hz), 1.38-1.07 (14 H, m), 0.84 ppm (3 H, t, *J* = 6.5 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 147.47, 137.54, 129.24, 127.80, 125.34, 119.00, 50.11, 31.64, 30.11, 29.25, 29.17, 29.03, 28.80, 26.27, 22.43, 21.01, 13.87 ppm; MALDI-TOF-MS (Dithranol): m / z= 300.20 ($[M+H]^+$).

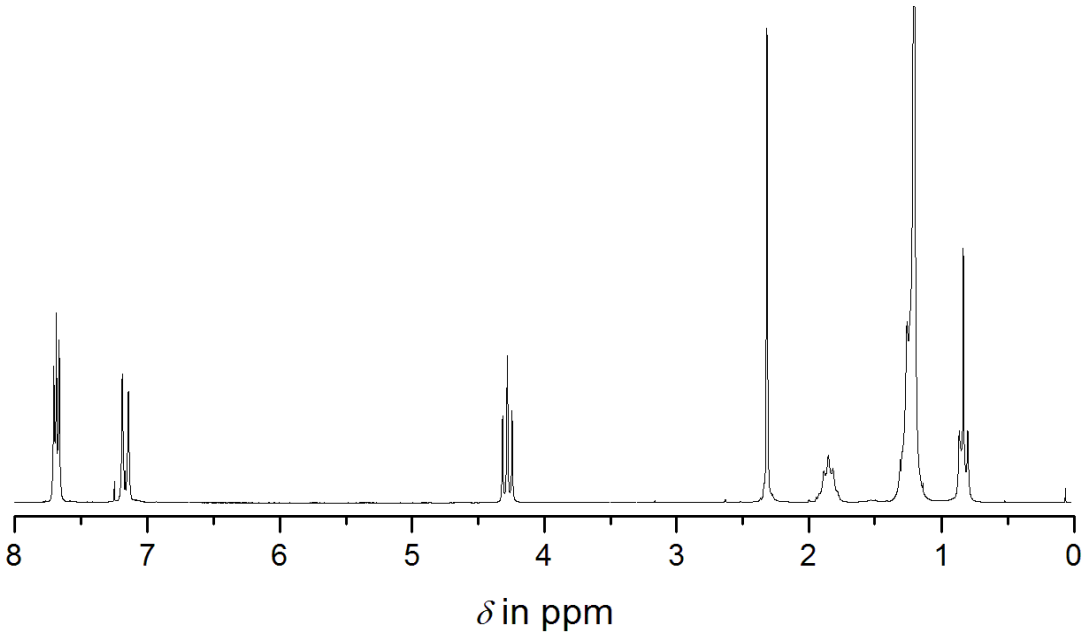


Figure 2a: ^{1}H NMR spectrum of **3b** ($CDCl_3$, 200 MHz).

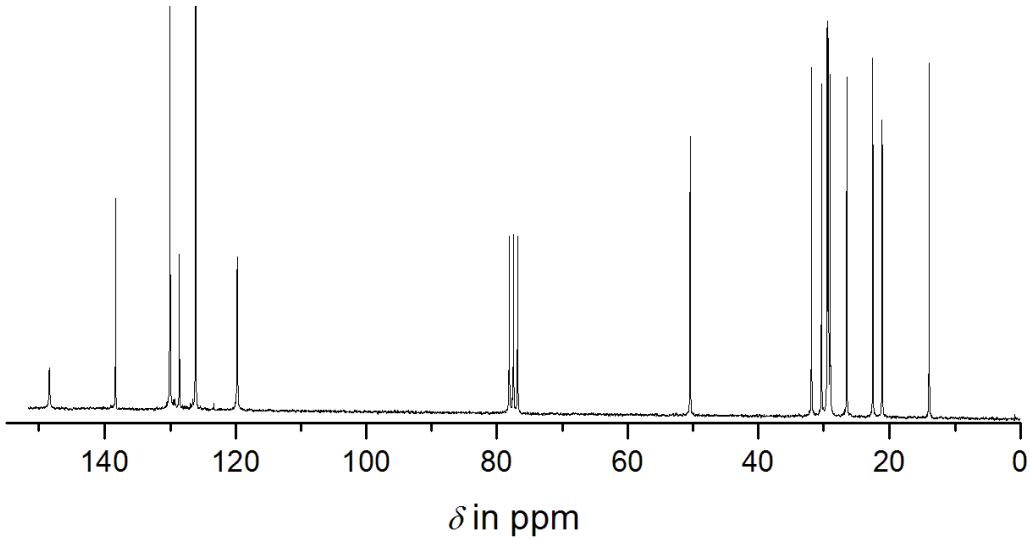
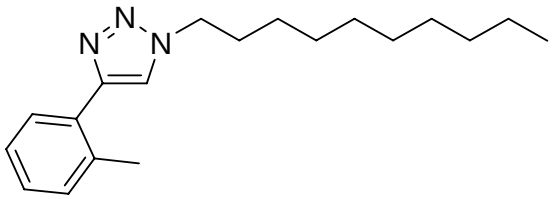


Figure 2b: ^{13}C NMR spectrum of **3b** ($CDCl_3$, 50 MHz).



1-Decyl-4-*o*-tolyl-1*H*-1,2,3-triazol (3c): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.78-7.67 (1 H, m), 7.62 (1 H, s), 7.25-7.15 (3 H, m), 4.32 (2 H, t, *J* = 7.2 Hz), 2.41 (3 H, s), 1.88 (2 H, quin, *J* = 6.9 Hz), 1.39-1.10 (14 H, m), 0.84 ppm (3 H, t, *J* = 6.4 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 146.67, 135.20, 130.62, 129.95, 128.60, 127.75, 125.80, 121.50, 50.05, 31.63, 30.11, 29.24, 29.14, 29.02, 28.77, 26.28, 22.43, 21.15, 13.87 ppm; MALDI-TOF-MS (Dithranol): m / z= 300.19 ($[M+H]^+$).

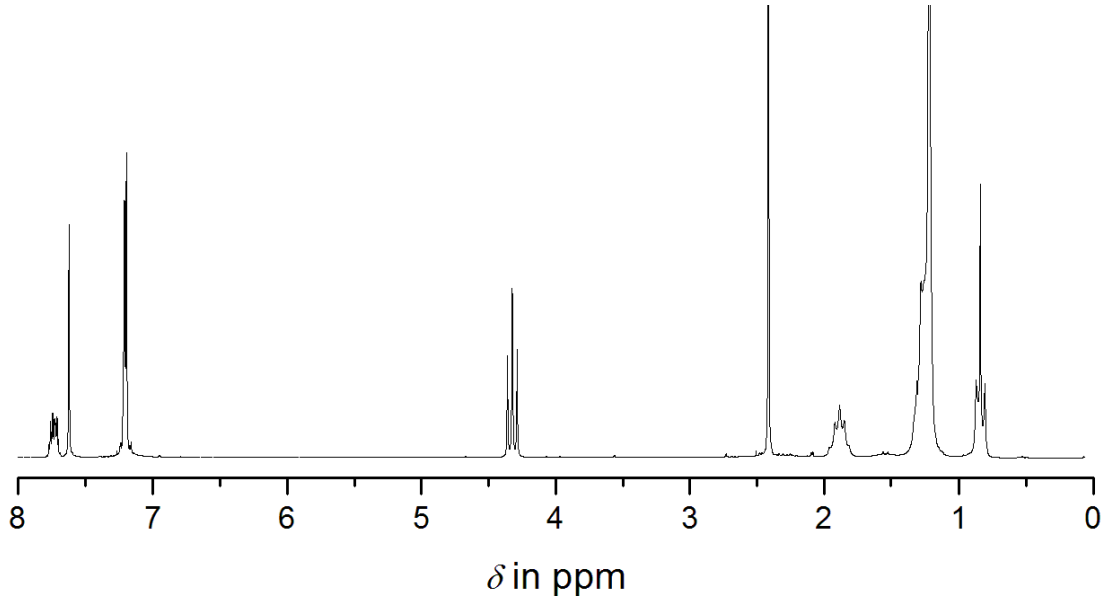


Figure 3a: ^{1}H NMR spectrum of **3c** ($CDCl_3$, 200 MHz).

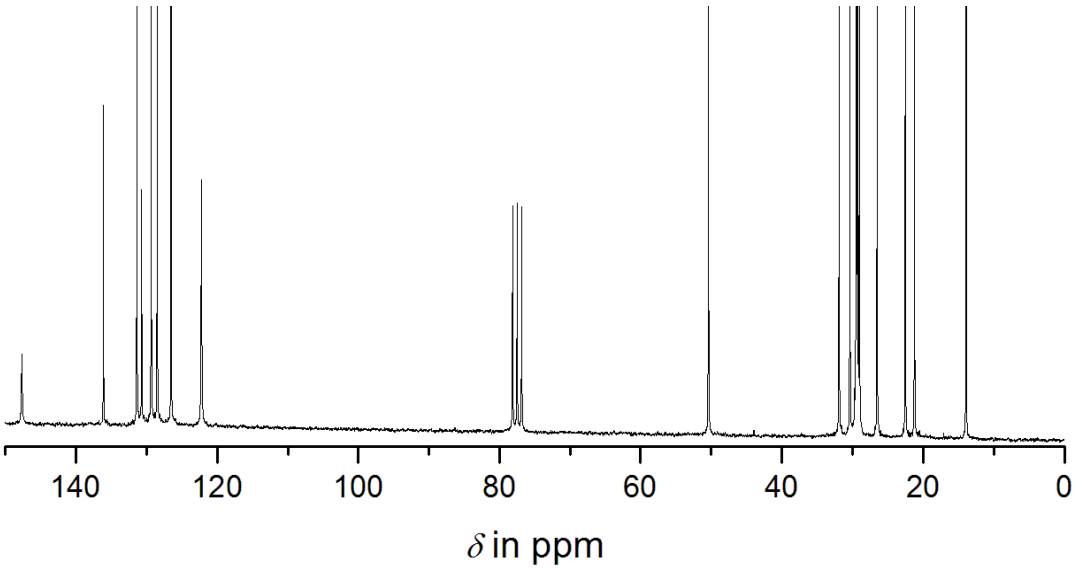
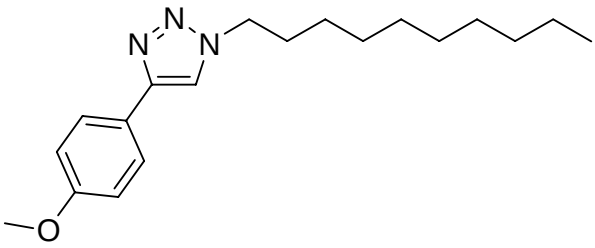


Figure 3b: ^{13}C NMR spectrum of **3c** ($CDCl_3$, 50 MHz).



1-Decyl-4-*p*-methoxyphenyl-1*H*-1,2,3-triazol (3d): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.72 (2 H, d, *J* = 8.9 Hz), 7.62 (1 H, s), 6.92 (2 H, d, *J* = 8.9 Hz), 4.32 (2 H, t, *J* = 7.2 Hz), 3.79 (3 H, s), 1.89 (2 H, quin, *J* = 6.9 Hz), 1.42-1.07 (14 H, m), 0.85 ppm (3 H, t, *J* = 6.6 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 159.92, 147.47, 126.88, 123.47, 118.54, 114.15, 55.21. 50.27, 31.79, 30.25, 29.31, 29.07, 28.93, 28.76, 26.43, 22.58, 13.99 ppm; MALDI-TOF-MS (Dithranol): m / z= 316.20 ($[M+H]^+$).

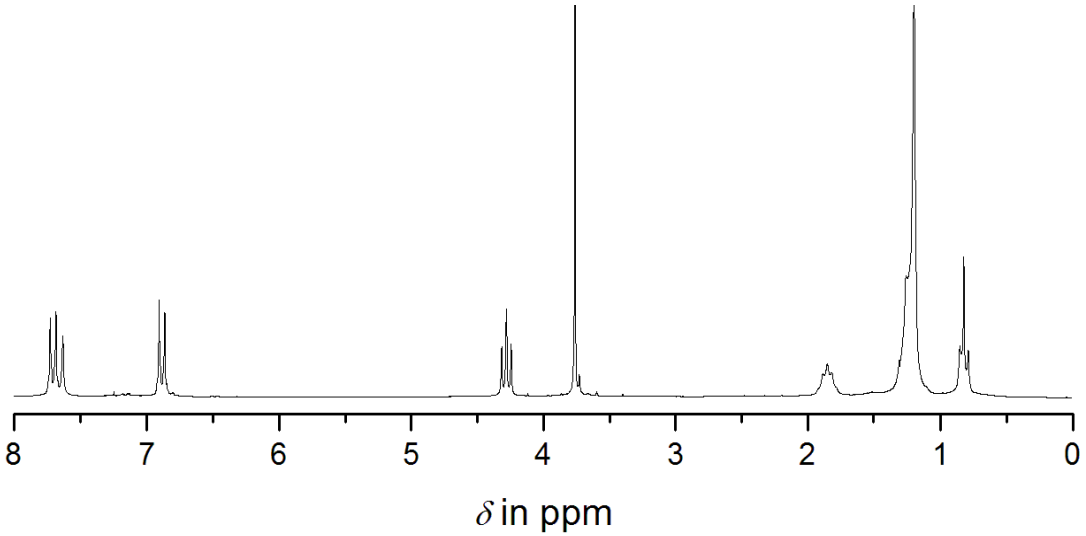


Figure 4a: ^{1}H NMR spectrum of **3d** ($CDCl_3$, 200 MHz).

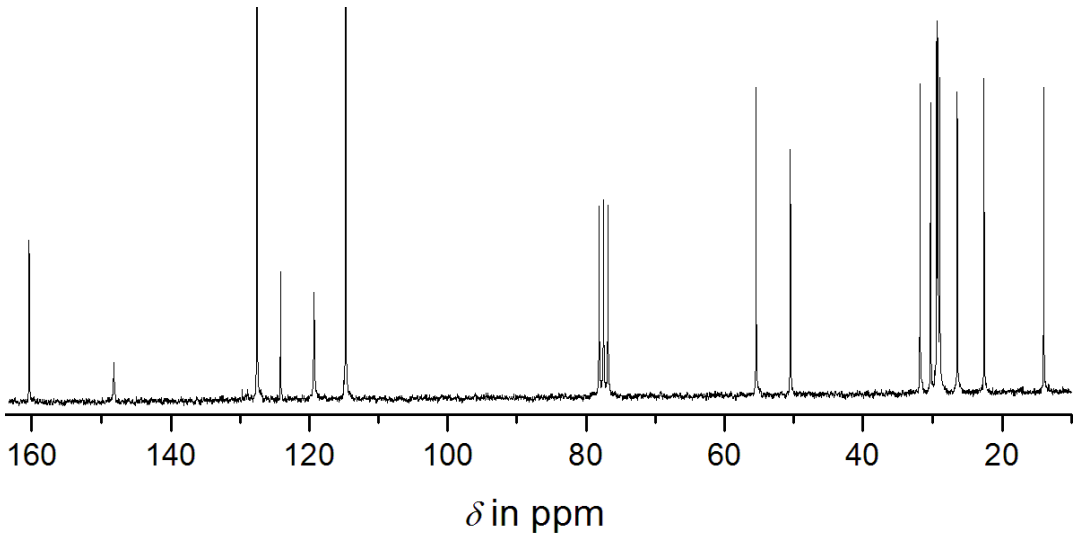
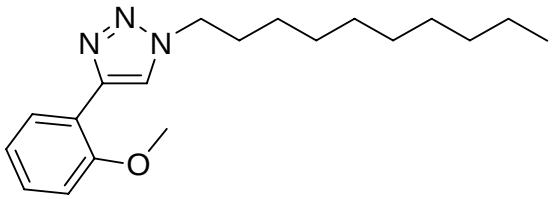


Figure 4b: ^{13}C NMR spectrum of **3d** ($CDCl_3$, 50 MHz).



1-Decyl-4-*o*-methoxyphenyl-1*H*-1,2,3-triazol (3e): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.31 (1 H, d, *J* = 8.3 Hz), 7.96 (1 H, s), 7.21 (1 H, t, *J* = 7.9 Hz), 6.99 (1 H, t, *J* = 7.5 Hz), 6.88 (1 H, d, *J* = 8.3 Hz), 4.28 (2 H, t, *J* = 7.2 Hz), 3.83 (3 H, s), 1.85 (2 H, quin, *J* = 6.9 Hz), 1.42-1.04 (14 H, m), 0.82 ppm (3 H, t, *J* = 6.5 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 155.38, 142.70, 128.47, 127.23, 122.72, 120.63, 119.36, 110.54, 55.05, 49.09, 31.59, 30.10, 29.20, 29.14, 28.99, 28.74, 26.23, 22.38, 13.82 ppm; MALDI-TOF-MS (Dithranol): m / z= 316.18 ($[M+H]^+$).

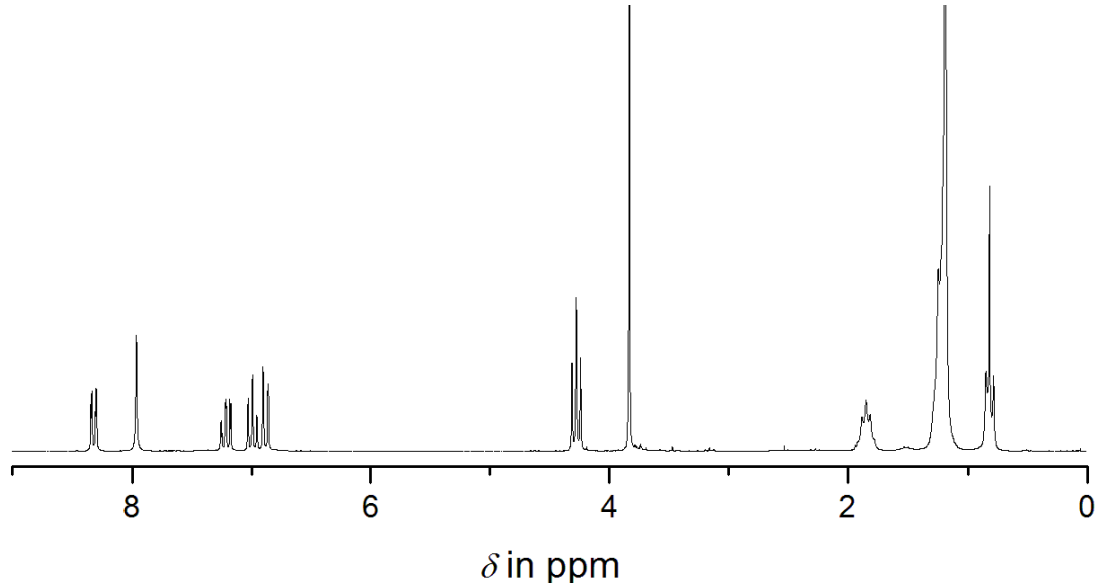


Figure 5a: ^{1}H NMR spectrum of **3e** ($CDCl_3$, 200 MHz).

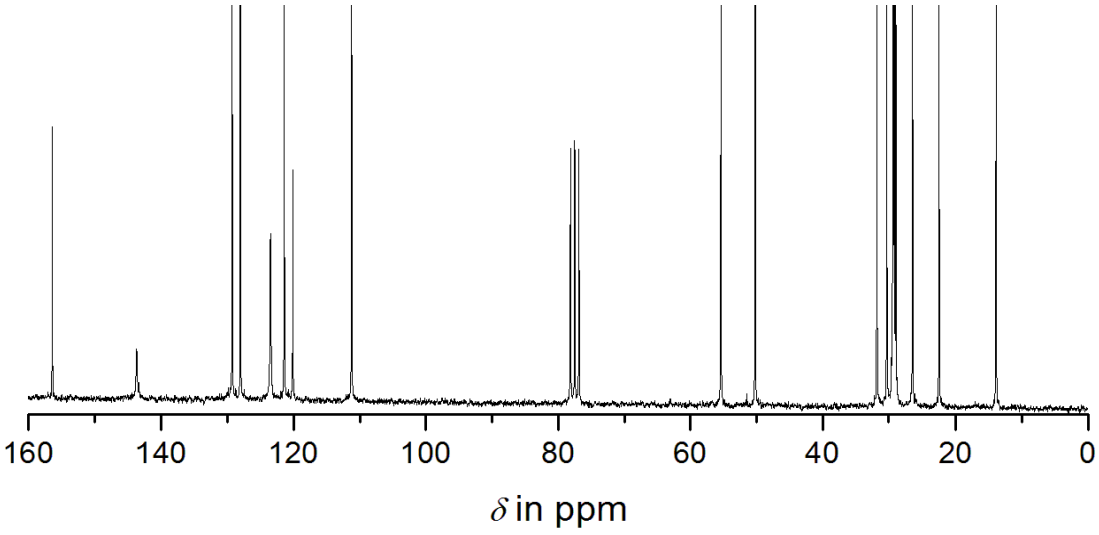
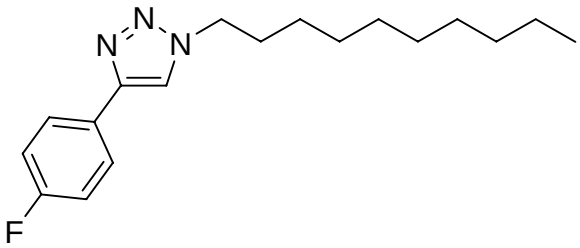


Figure 5b: ^{13}C NMR spectrum of **3e** ($CDCl_3$, 50 MHz).



1-Decyl-4-*p*-fluorphenyl-1*H*-1,2,3-triazol (3f): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.79-7.64 (4 H, m), 7.69 (1 H, s), 6.99 (4 H, t, *J* = 8.8 Hz), 4.27 (2 H, t, *J* = 7.3 Hz), 1.83 (2 H, quin, *J* = 7.0 Hz), 1.37-1.02 (14 H, m), 0.79 ppm (3 H, t, *J* = 6.5 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 164.66, 159.73, 146.37, 127.04, 126.87, 126.72, 126.65, 118.99, 115.50, 115.06, 49.98, 31.41, 29.89, 29.04, 28.96, 28.82, 28.57, 26.06, 22.58, 13.64 ppm; MALDI-TOF-MS (Dithranol): m / z= 304.19 ($[M+H]^+$).

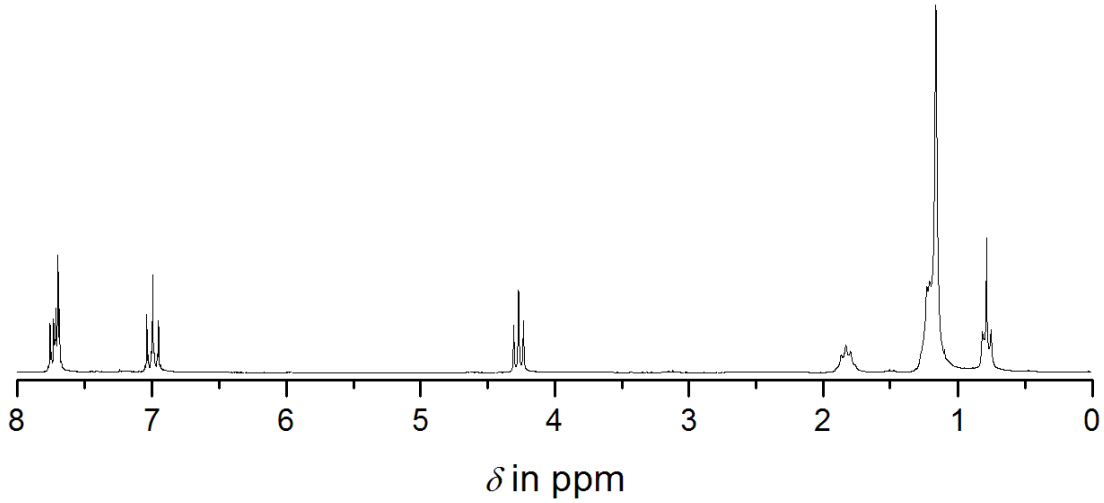


Figure 6a: ^{1}H NMR spectrum of **3f** ($CDCl_3$, 200 MHz).

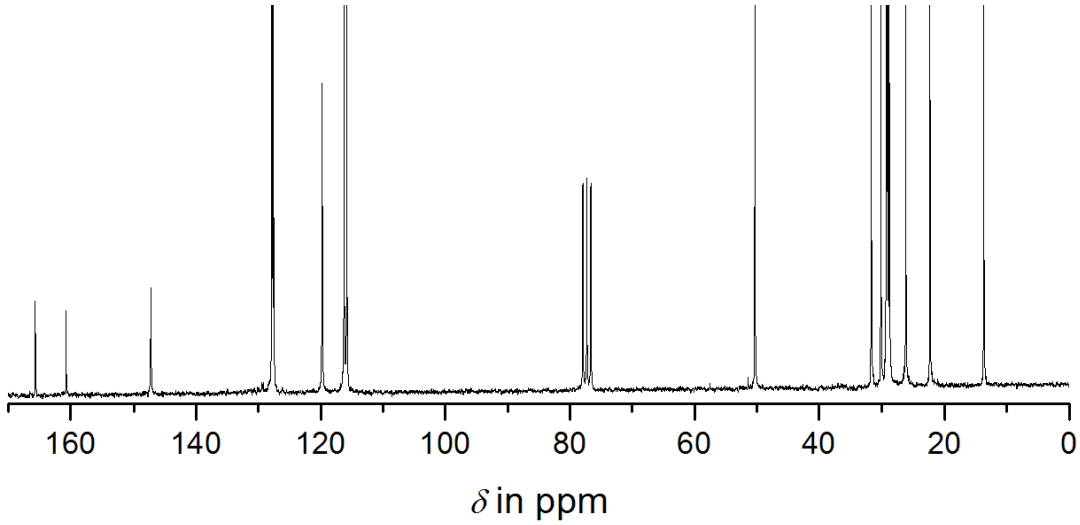
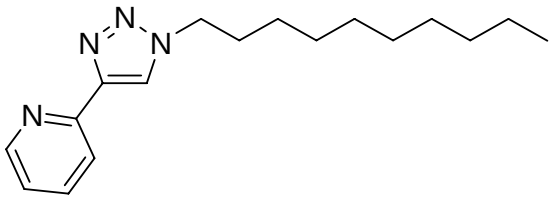


Figure 6b: ^{13}C NMR spectrum of **3f** ($CDCl_3$, 50 MHz).



2-(1-Decyl-1*H*-1,2,3-triazol-4-yl)pyridine (3g): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.47 (1 H, d, *J* = 2.3 Hz), 8.08 (1 H, d, *J* = 8.3 Hz), 8.05 (1 H, s), 7.65 (1 H, t, *J* = 7.8 Hz), 7.10 (1 H, t, *J* = 6.3 Hz), 4.30 (2 H, t, *J* = 7.1 Hz), 1.84 (2 H, quin, *J* = 6.8 Hz), 1.38-1.00 (14 H, m), 0.76 ppm (3 H, t, *J* = 6.4 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 150.30, 149.17, 148.12, 136.68, 122.56, 121.66, 119.99, 50.32, 31.64, 30.03, 29.25, 29.16, 29.04, 28.77, 26.25, 22.44, 13.89 ppm; MALDI-TOF-MS (Dithranol): m / z= 287.18 ($[M+H]^+$).

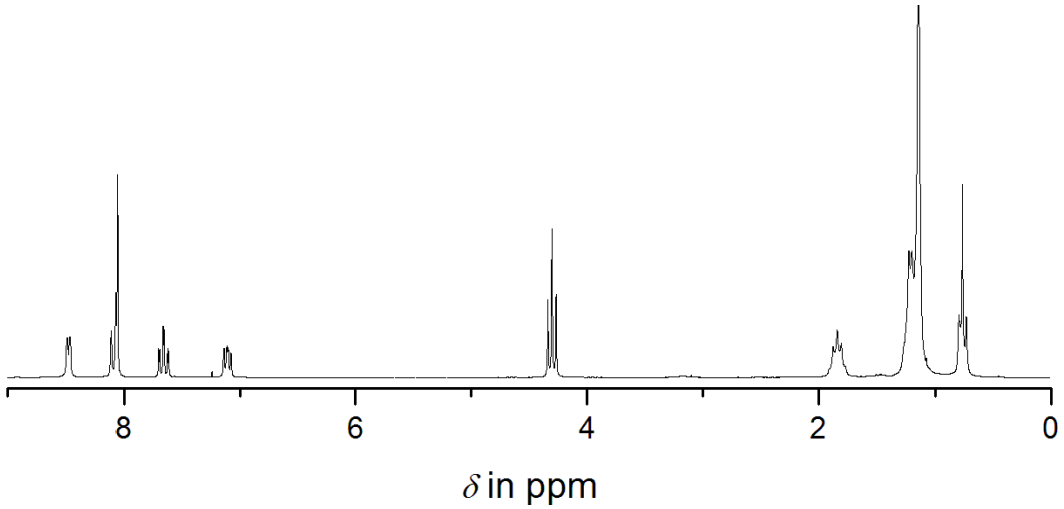


Figure 7a: ^{1}H NMR spectrum of **3g** ($CDCl_3$, 200 MHz).

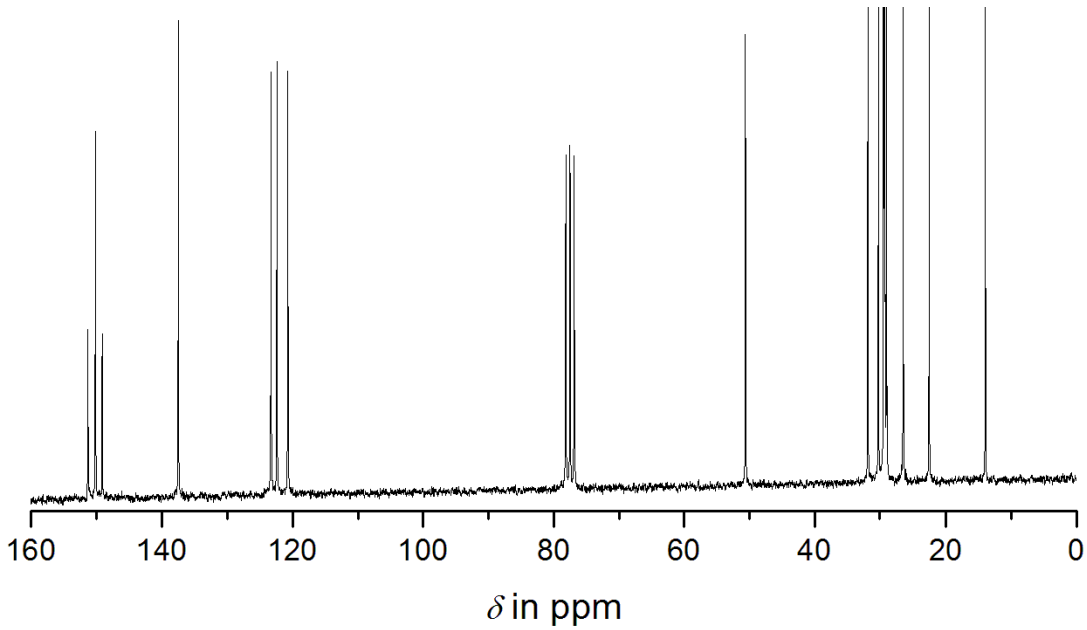
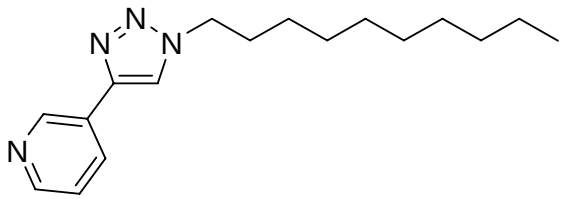


Figure 7b: ^{13}C NMR spectrum of **3g** ($CDCl_3$, 50 MHz).



3-(1-Decyl-1*H*-1,2,3-triazol-4-yl)pyridine (3h): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 9.18-8.33 (2 H, m), 8.10 (1 H, d, *J* = 8.0 Hz), 7.82 (1 H, s), 7.42-7.13 (1 H, m), 7.10 (1 H, t, *J* = 6.3 Hz), 4.32 (2 H, t, *J* = 7.2 Hz), 1.86 (2 H, quin, *J* = 6.9 Hz), 1.37-0.98 (14 H, m), 0.77 ppm (3 H, t, *J* = 6.3 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 148.88, 146.81, 144.42, 132.74, 126.82, 123.63, 119.76, 50.40, 31.63, 30.12, 29.26, 29.17, 29.04, 28.79, 26.29, 22.45, 13.89 ppm; MALDI-TOF-MS (Dithranol): m / z= 287.17 ($[M+H]^+$).

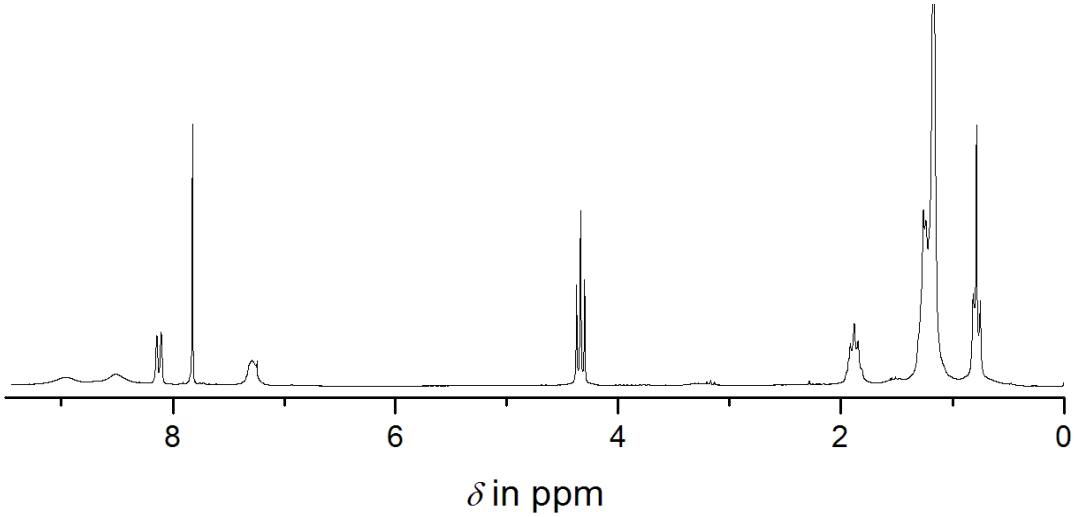


Figure 8a: ^{1}H NMR spectrum of **3h** ($CDCl_3$, 200 MHz).

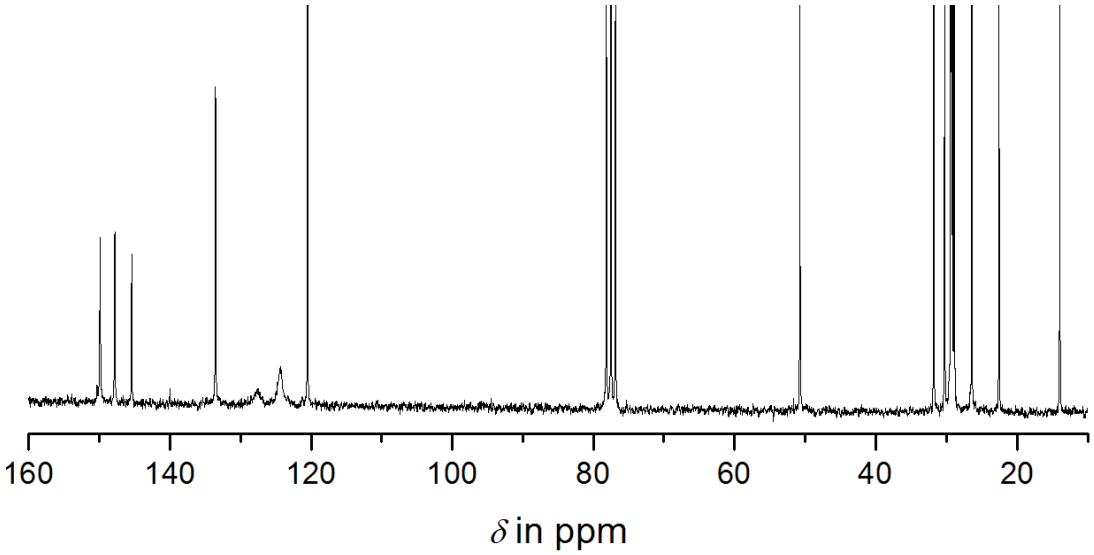
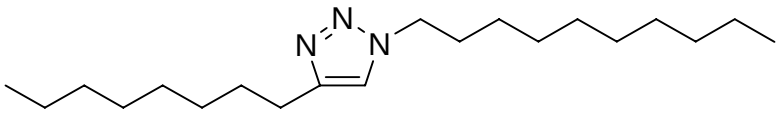


Figure 8b: ^{13}C NMR spectrum of **3h** ($CDCl_3$, 50 MHz).



1-Decyl-4-octyl-1*H*-1,2,3-triazole (3i): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.19 (1 H, s), 4.17 (2 H, t, *J* = 7.2 Hz), 2.57 (2 H, t, *J* = 7.2 Hz), 1.74 (2 H, quin, *J* = 6.7 Hz), 1.54 (2 H, t, *J* = 6.9 Hz), 1.33-1.02 (24 H, m), 0.74 ppm (3 H, t, *J* = 6.4 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 148.05, 120.23, 49.84, 31.56, 30.05, 29.17, 29.09, 28.96, 28.71, 26.22, 25.44, 22.35, 13.76 ppm; MALDI-TOF-MS (Dithranol): m / z= 322.29 ($[M+H]^+$).

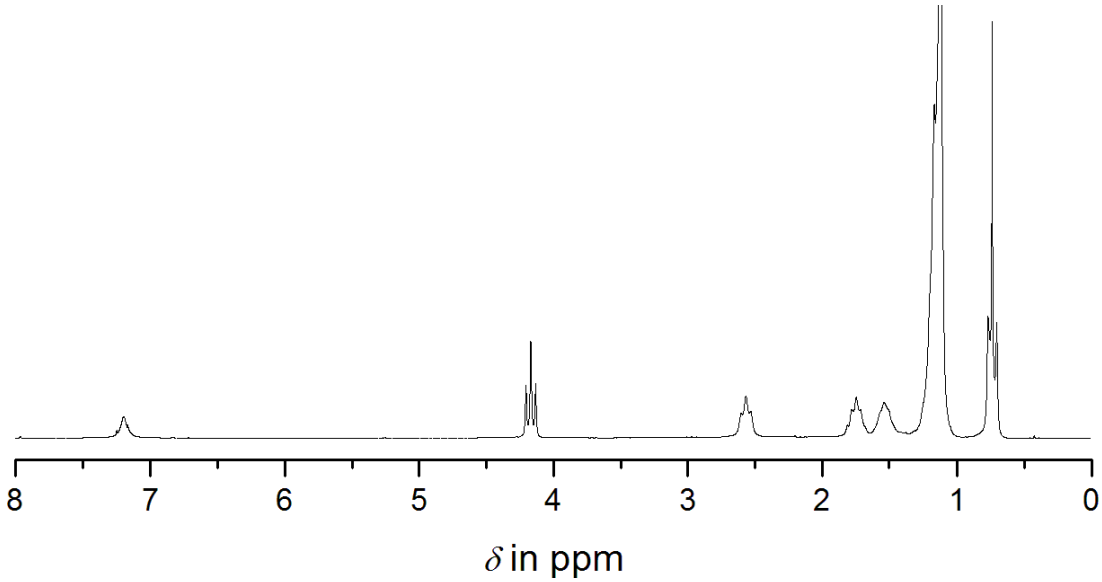


Figure 9a: ^{1}H NMR spectrum of **3i** ($CDCl_3$, 200 MHz).

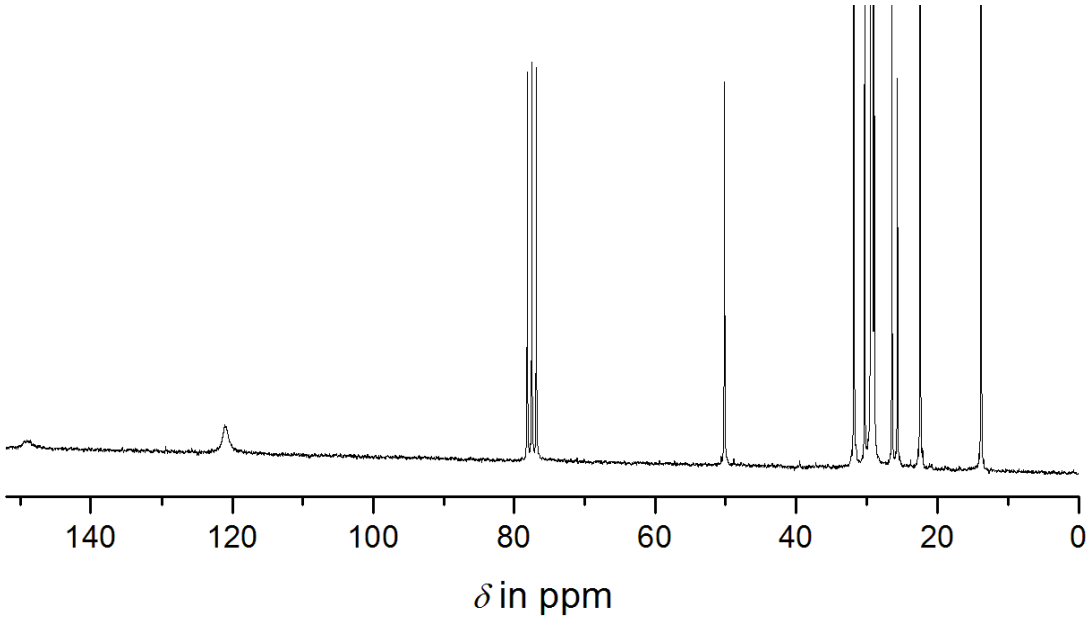
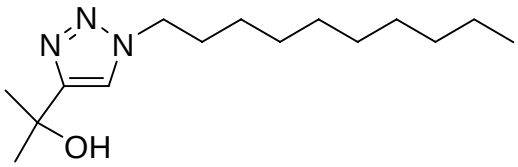


Figure 9b: ^{13}C NMR spectrum of **3i** ($CDCl_3$, 50 MHz).



2-(1-Decyl--1*H*-1,2,3-triazol-4-yl)propan-2-ol (3j): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.41 (1 H, s), 4.18 (2 H, t, *J* = 7.2 Hz), 3.55 (1 H, bs), 1.77 (2 H, quin, *J* = 6.8 Hz), 1.51 (6 H, s), 1.31-0.97 (14 H, m), 0.76 ppm (3 H, t, *J* = 6.5 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 155.58, 119.08, 68.12, 50.04, 31.58, 30.26, 30.04, 29.20, 29.12, 28.98, 28.75, 26.27, 22.38, 13.82 ppm; MALDI-TOF-MS (Dithranol): m / z= 268.18 ($[M+H]^+$).

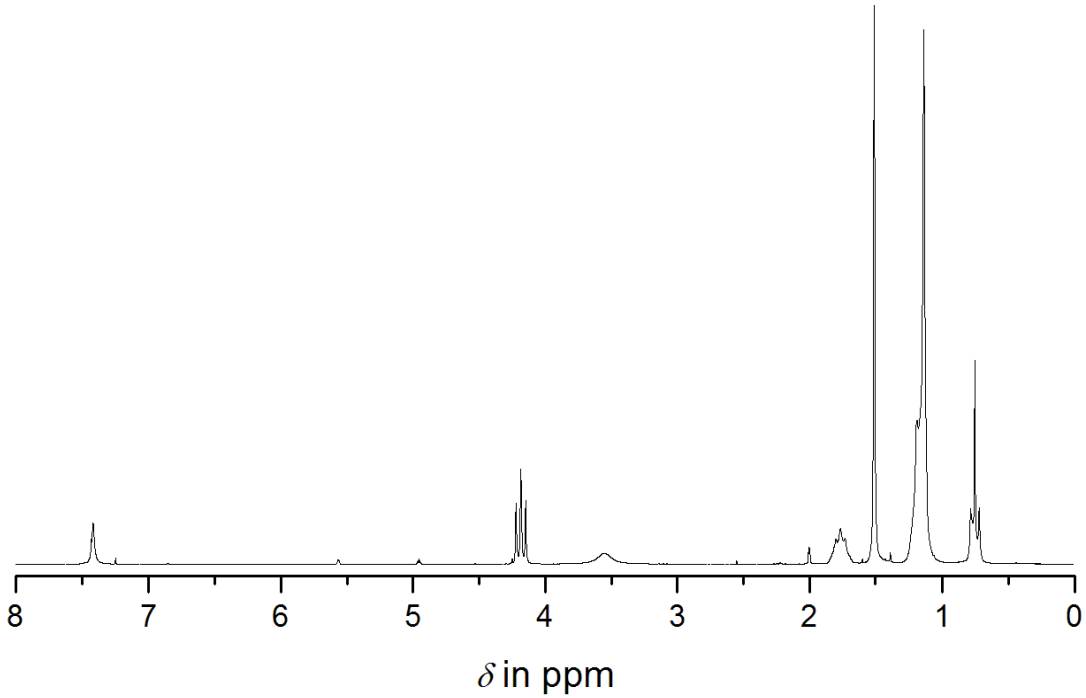


Figure 10a: ^{1}H NMR spectrum of **3j** ($CDCl_3$, 200 MHz).

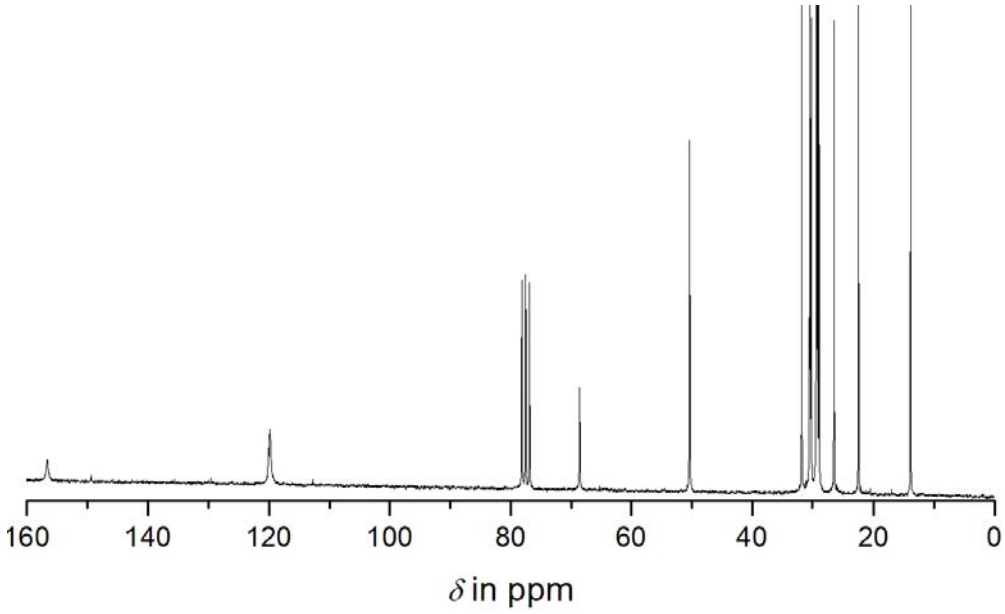
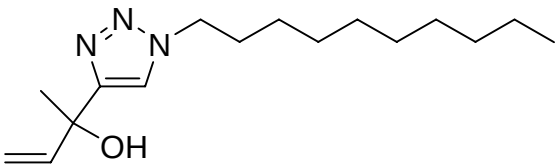


Figure 10b: ^{13}C NMR spectrum of **3j** ($CDCl_3$, 50 MHz).



2-(1-Decyl--1*H*-1,2,3-triazol-4-yl)but-3-en-2-ol (3k): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.40 (1 H, s), 6.12 (1 H, dd, *J* = 10.6 Hz, *J* = 17.5 Hz), 5.17 (1 H, dd, *J* = 1.1 Hz, *J* = 17.3 Hz), 4.97 (1 H, dd, *J* = 1.1 Hz, *J* = 10.6 Hz), 4.18 (2 H, t, *J* = 7.3 Hz), 3.83 (1 H, bs), 1.76 (2 H, quin, *J* = 6.8 Hz), 1.58 (3 H, s), 1.30-0.98 (14 H, m), 0.76 ppm (3 H, t, *J* = 6.3 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 153.43, 143.45, 119.86, 112.15, 70.48, 50.04, 31.56, 29.99, 29.17, 29.08, 28.95, 28.70, 28.30, 26.21, 22.35, 13.79 ppm; MALDI-TOF-MS (Dithranol): m / z= 280.18 ($[M+H]^+$).

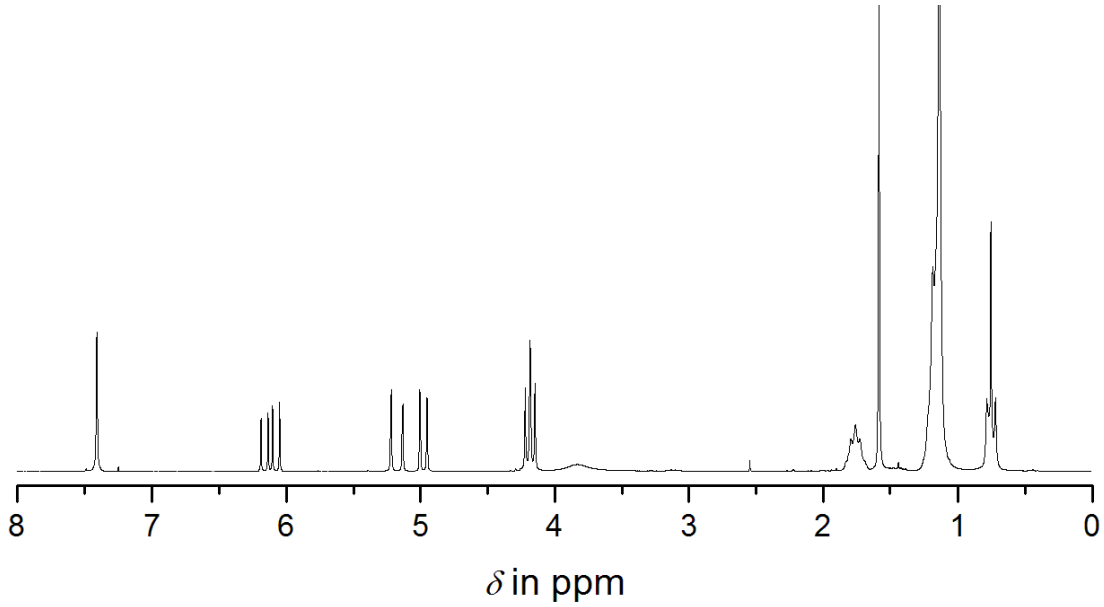


Figure 11a: ^{1}H NMR spectrum of **3k** ($CDCl_3$, 200 MHz).

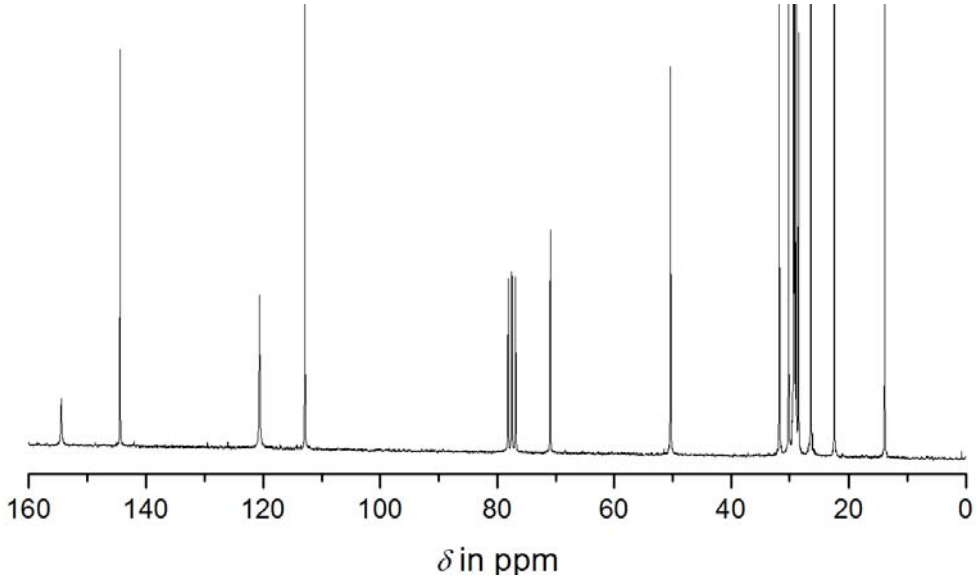
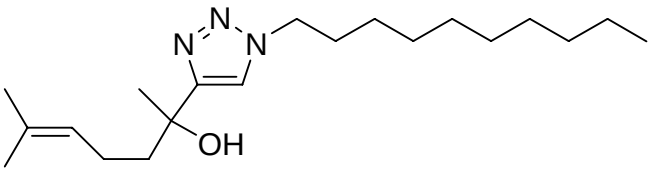


Figure 11b: ^{13}C NMR spectrum of **3k** ($CDCl_3$, 50 MHz).



2-(1-Decyl-1*H*-1,2,3-triazol-4-yl)-6-methylhept-5-en-2-ol (3l): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.39 (1 H, s), 4.95 (1 H, t, J = 6.2 Hz), 4.18 (2 H, t, J = 7.3 Hz), 3.51 (1 H, bs), 1.96 (6 H, m), 1.50 (3 H, s), 1.46 (3 H, s), 1.38 (3 H, s), 1.27-0.99 (14 H, m), 0.74 ppm (3 H, t, J = 6.3 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 154.64, 131.26, 123.95, 119.64, 70.81, 49.95, 42.83, 31.53, 29.99, 29.16, 29.08, 28.94, 28.70, 28.39, 26.20, 25.32, 22.54, 22.33, 17.27, 13.76 ppm; MALDI-TOF-MS (Dithranol): m / z= 336.23 ($[M+H]^+$).

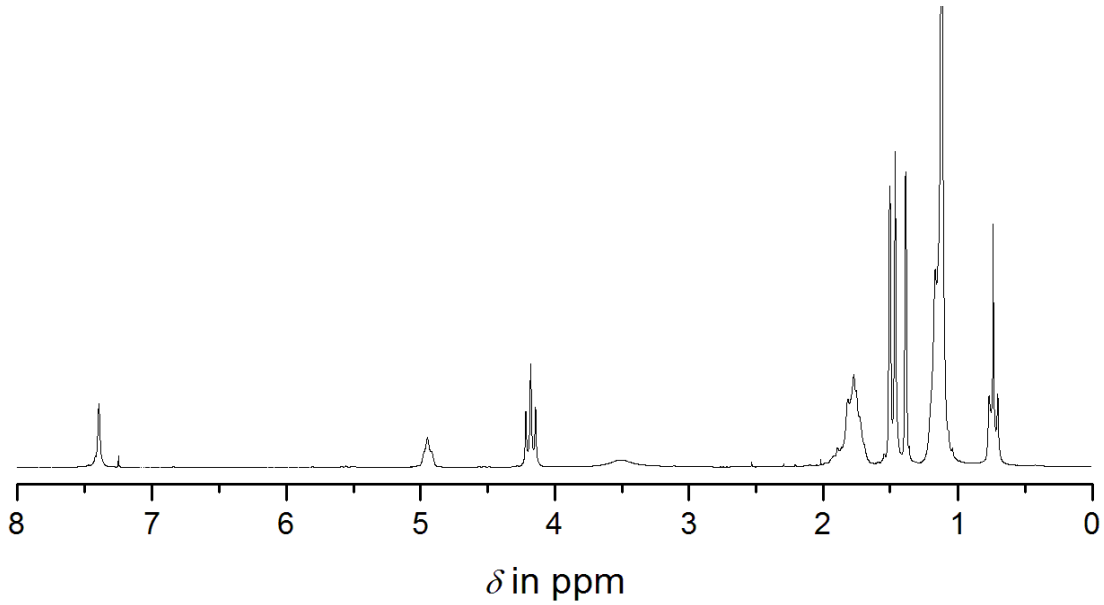


Figure 12a: ^{1}H NMR spectrum of **3l** ($CDCl_3$, 200 MHz).

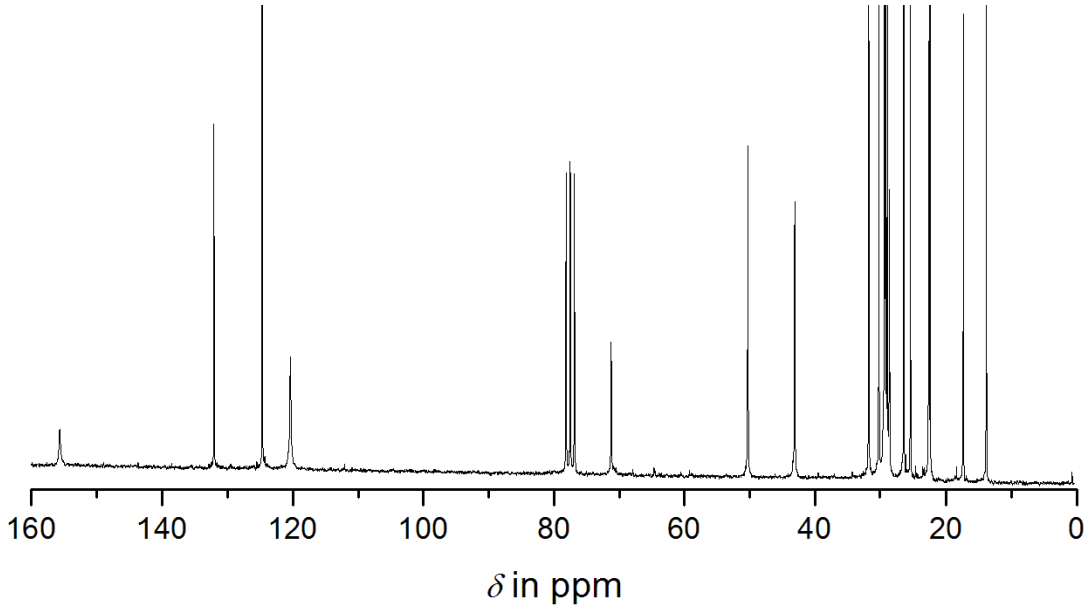
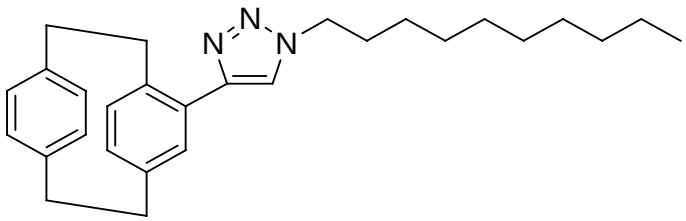


Figure 12b: ^{13}C NMR spectrum of **3l** ($CDCl_3$, 50 MHz).



1-Decyl-4-([2.2]paracyclophan-4-yl)-1*H*-1,2,3-triazol (3m): ^{1}H NMR (200 MHz, $CDCl_3$): δ =, 7.58 (1 H, s), 7.58 (1 H, s), 6.58-6.48 (6 H, m), 4.37 (2 H, t, J = 7.3 Hz), 3.93-3.73 (1 H, m), 3.70-3.20 (6 H, m), 1.94 (2 H, quin, J = 7.0 Hz), 1.48-1.15 (14 H, m), 0.88 ppm (3 H, t, J = 6.5 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 147.71, 139.73, 139.41, 139.17, 137.31, 135.62, 132.78, 132.66, 132.39, 132.28, 132.13, 130.96, 130.06, 121.09, 50.14, 31.41, 35.27, 35.03, 34.68, 34.37, 31.67, 30.19, 29.29, 29.26, 29.09, 28.83, 26.34, 22.50, 13.96 ppm; MALDI-TOF-MS (Dithranol): m / z= 416.29 ([M+H]$^+$).

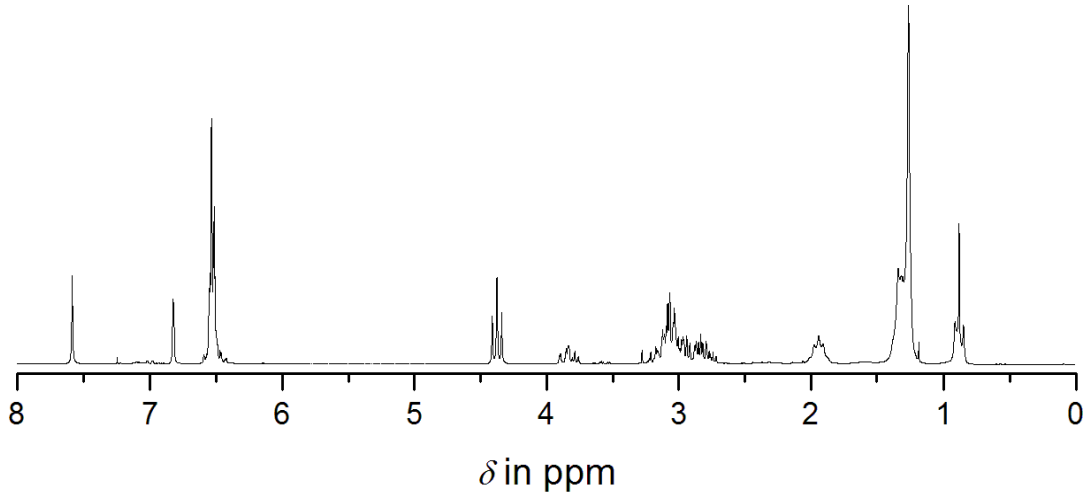


Figure 13a: ^{1}H NMR spectrum of **3m** ($CDCl_3$, 200 MHz).

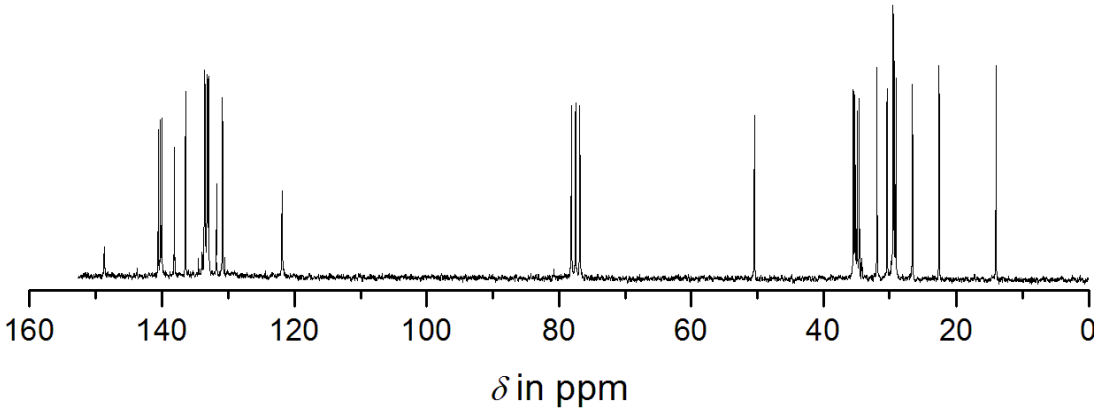
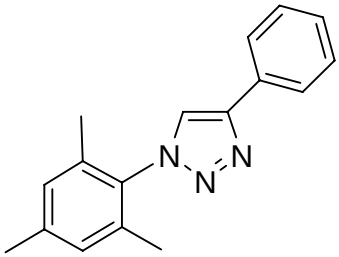


Figure 13b: ^{13}C NMR spectrum of **3m** ($CDCl_3$, 50 MHz).



1-Mesityl-4-phenyl-1*H*-1,2,3-triazole (3n): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.90 (2 H, d, *J* = 7.9 Hz), 7.82 (2 H, s), 7.48-7.25 (3 H, m), 6.96 (2 H, s), 2.33 (3 H, s), 1.97 ppm (6 H, s); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 147.40, 139.88, 134.91, 133.38, 130.41, 128.96, 128.73, 128.08, 125.59, 121.41, 20.97, 17.14 ppm; MALDI-TOF-MS (Dithranol): m / z= 749.63 ($[M+H]^+$).

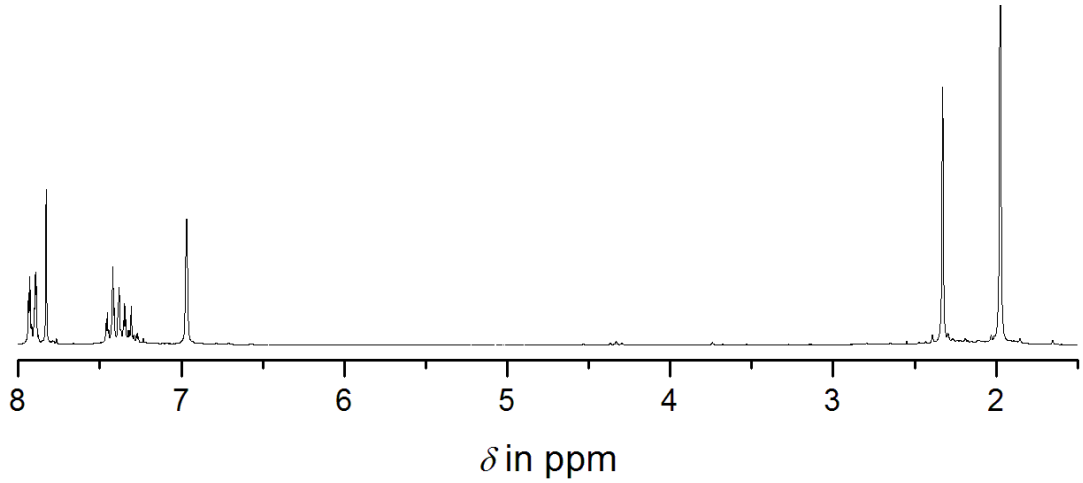


Figure 14a: ^{1}H NMR spectrum of **3n** ($CDCl_3$, 200 MHz).

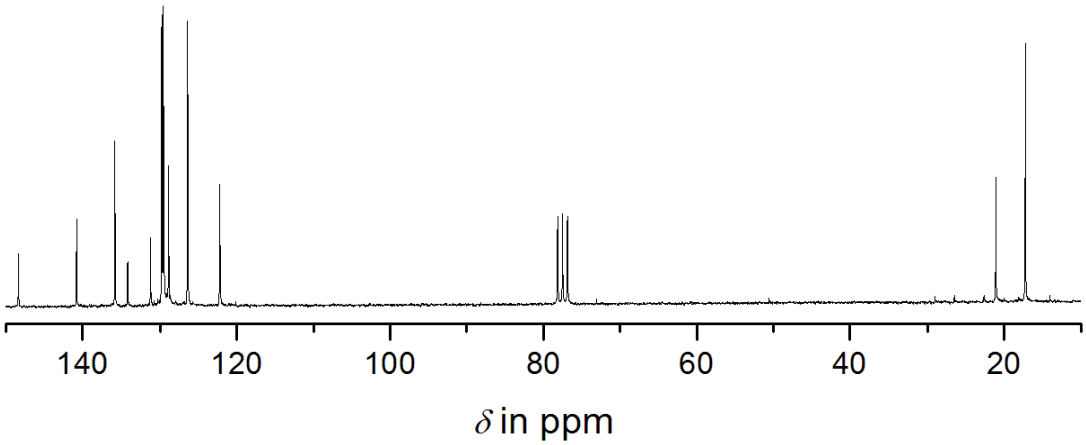
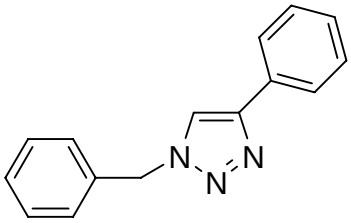


Figure 14b: ^{13}C NMR spectrum of **3n** ($CDCl_3$, 50 MHz).



1-Benzyl-4-phenyl-1*H*-1,2,3-triazole (3o): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.78 (2 H, d, = 8.2 Hz), 7.65 (1 H, s), 7.43-7.21 (8 H, m), 5.51 ppm (2 H, s); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 148.08, 134.63, 130.48, 133.38, 129.01, 128.62, 128.03, 127.91, 125.58, 119.49, 54.05 ppm; MALDI-TOF-MS (Dithranol): m / z= 236.08 ([M+H]$^{+}$).

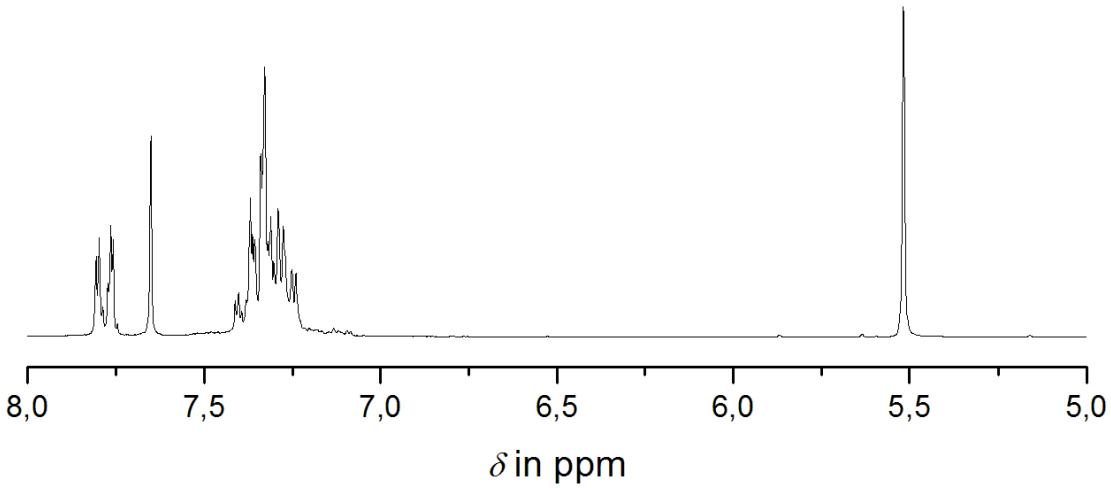


Figure 15a: ^{1}H NMR spectrum of **3o** ($CDCl_3$, 200 MHz).

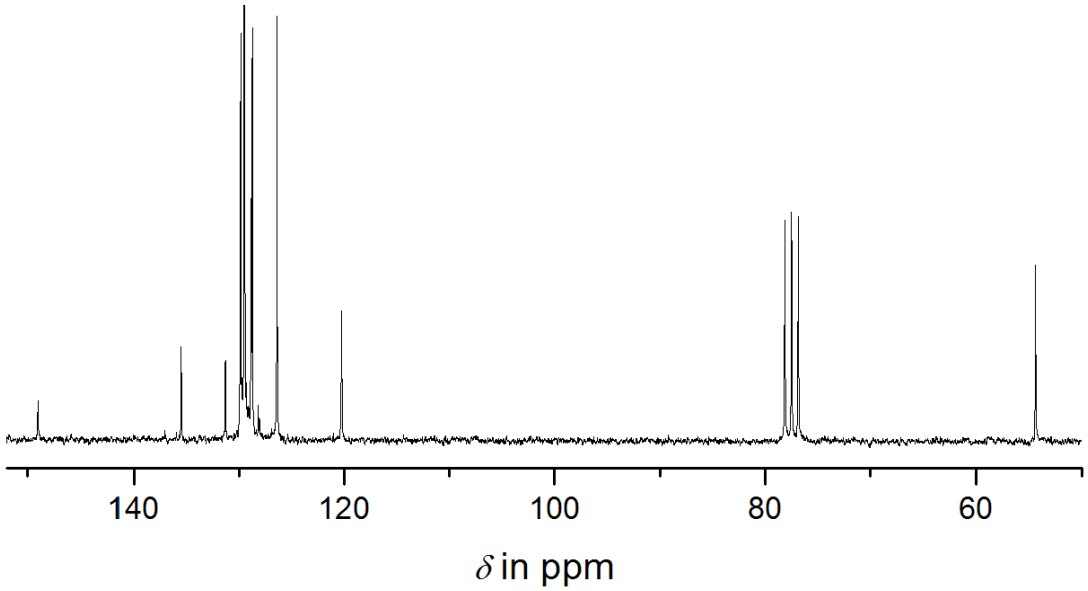
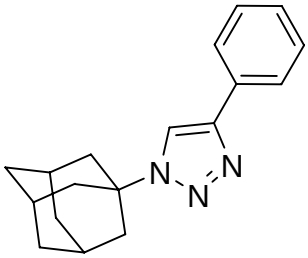


Figure 15b: ^{13}C NMR spectrum of **3o** ($CDCl_3$, 50 MHz).



1-Adamantyl-4-phenyl-1*H*-1,2,3-triazole (3p): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.81 (2 H, d, = 8.1 Hz), 7.79 (1 H, s), 7.43-7.20 (3 H, m), 2.26 (9 H, s), 1.78 ppm (6 H, s); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 146.71, 131.10, 128.76, 127.78, 125.60, 115.99, 59.55, 42.99, 35.91, 29.43 ppm; MALDI-TOF-MS (Dithranol): m / z= 280.21 ($[M+H]^+$).

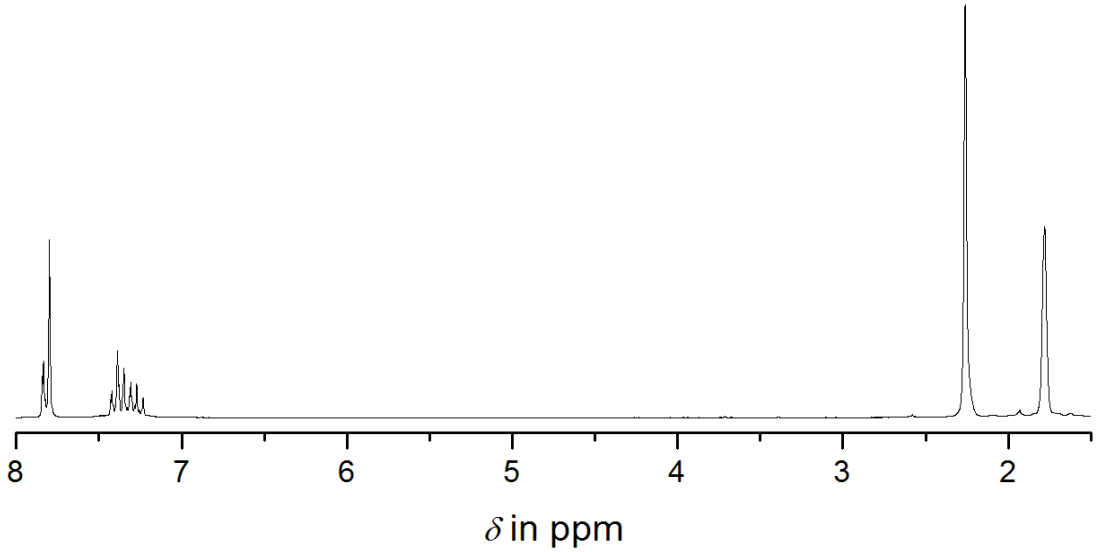


Figure 16a: ^{1}H NMR spectrum of **3p** ($CDCl_3$, 200 MHz).

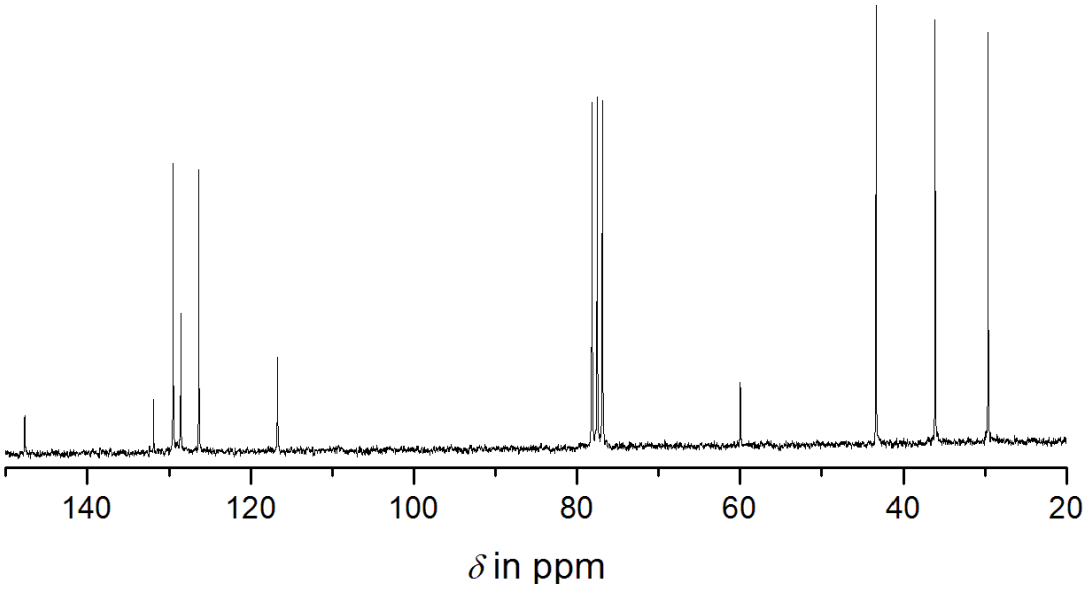
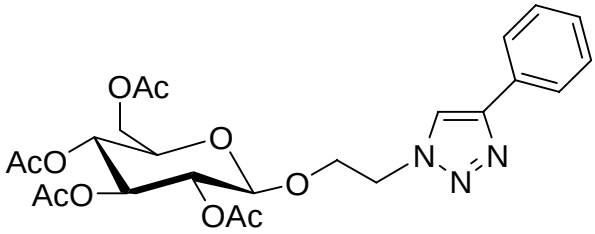


Figure 16b: ^{13}C NMR spectrum of **3p** ($CDCl_3$, 50 MHz).



1-(1-Ethoxy-2,3,4,6-tetra-*O*-acetyl-*β*-*D*-glucopyranosyl)-4-phenyl-1*H*-1,2,3-triazole (3q): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.77 (1 H, s), 7.75 (2 H, d, J = 6.9 Hz), 7.40-7.15 (3 H, m), 5.13-4.83 (3 H, m), 4.64-4.33 (3 H, m), 4.23-4.09 (2 H, m), 4.23-4.09 (2 H, m), 4.03 (1 H, d, J = 12.4 Hz), 3.89-3.72 (1 H, m), 3.67-3.53 (1 H, m), 1.95 (3 H, s), 1.90 (3 H, s), 1.86 (3 H, s), 1.62 ppm (3 H, s); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 170.26, 169.73, 169.16, 169.15, 147.27, 131.84, 130.31, 128.57, 127.86, 125.39, 121.21, 100.23, 72.23, 71.64, 70.73, 68.01, 67.59, 61.46, 49.77, 20.39, 20.25, 20.24, 20.06 ppm; MALDI-TOF-MS (Dithranol): m / z= 520.18 ($[M+H]^+$).

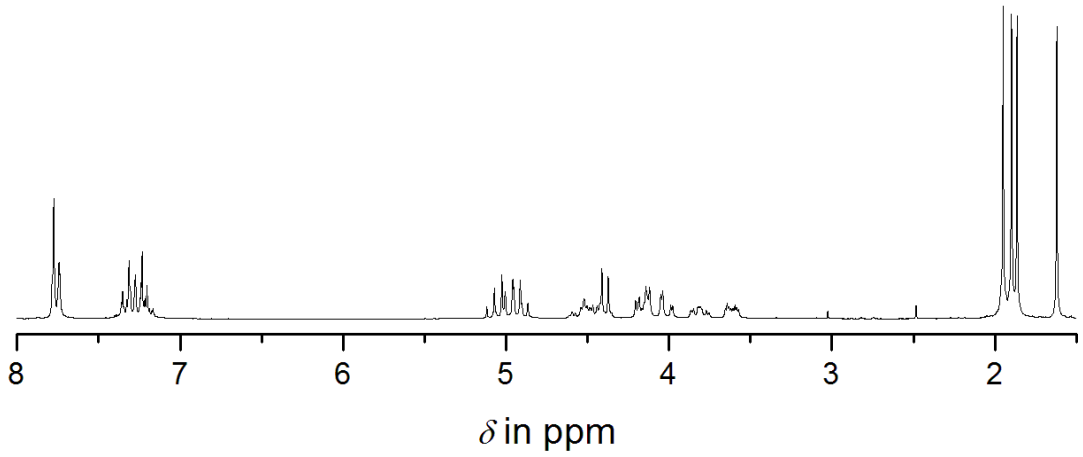


Figure 17a: ^{1}H NMR spectrum of **3q** ($CDCl_3$, 200 MHz).

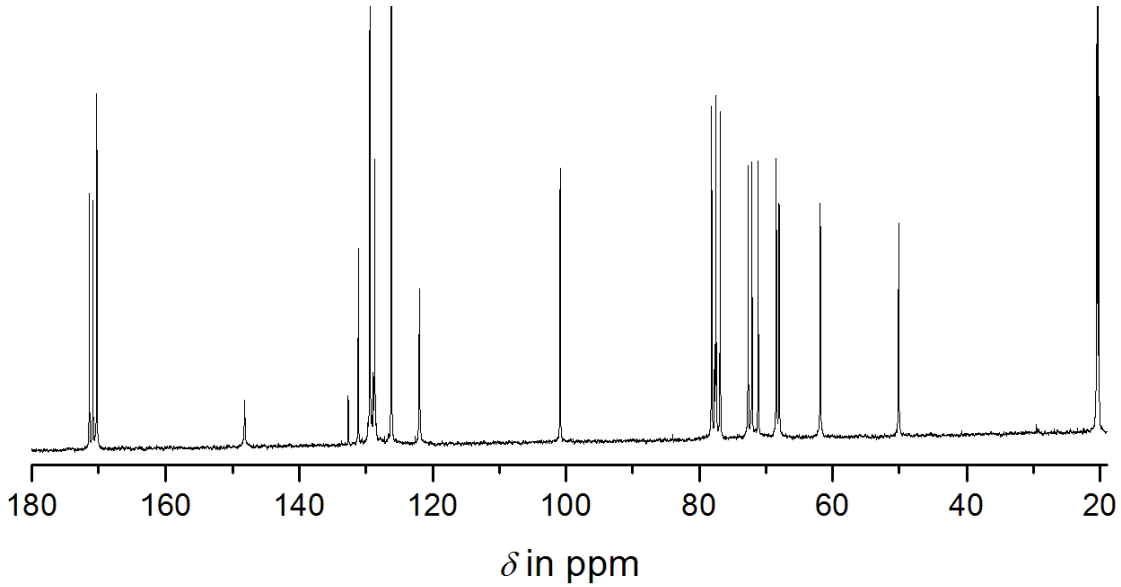
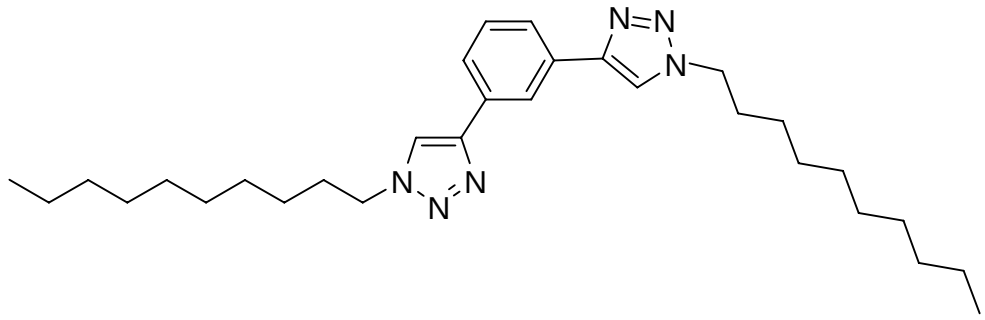


Figure 17b: ^{13}C NMR spectrum of **3q** ($CDCl_3$, 50 MHz).



1-Decyl-4-(3-(1-decyl-1*H*-1,2,3-triazol-4-yl)phenyl)-1*H*-1,2,3-triazole (5a): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.26 (2 H, s) 7.90-7.69 (3 H, m), 7.42 (1 H, t, *J* = 7.7 Hz), 4.35 (4 H, t, *J* = 7.2 Hz), 1.90 (4 H, quin, *J* = 6.9 Hz), 1.43-1.10 (28 H, m), 0.83 ppm (6 H, t, *J* = 6.5 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 147.30, 131.20, 129.26, 125.11, 122.69, 119.68, 50.37, 31.74, 30.21, 29.35, 29.26, 29.12, 28.89, 26.38, 22.53, 13.96 ppm; MALDI-TOF-MS (Dithranol): m / z= 493.39 ($[M+H]^+$).

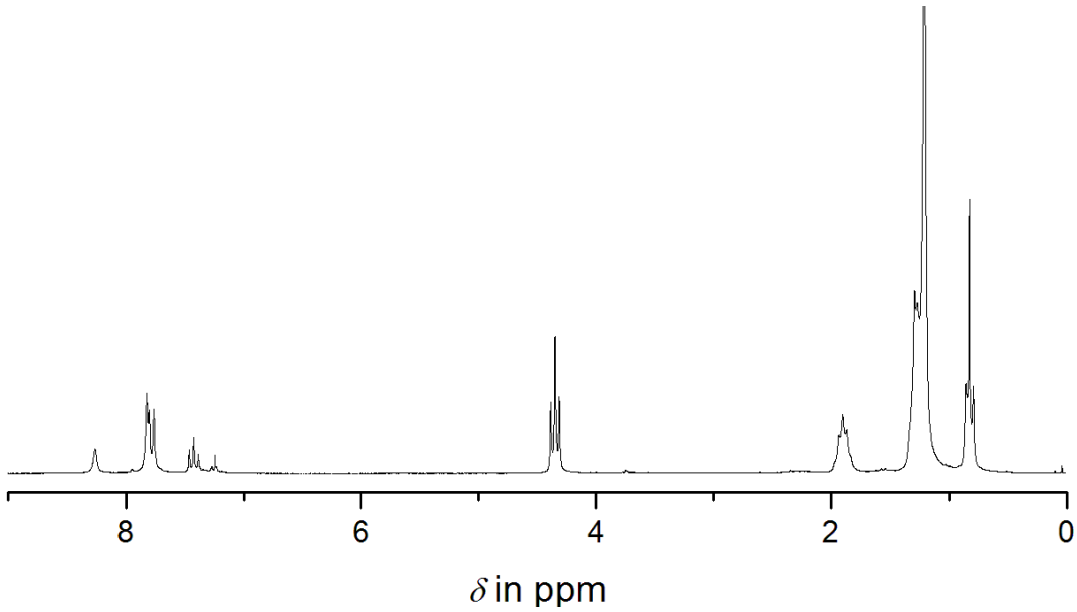


Figure 18a: ^{1}H NMR spectrum of **5a** ($CDCl_3$, 200 MHz).

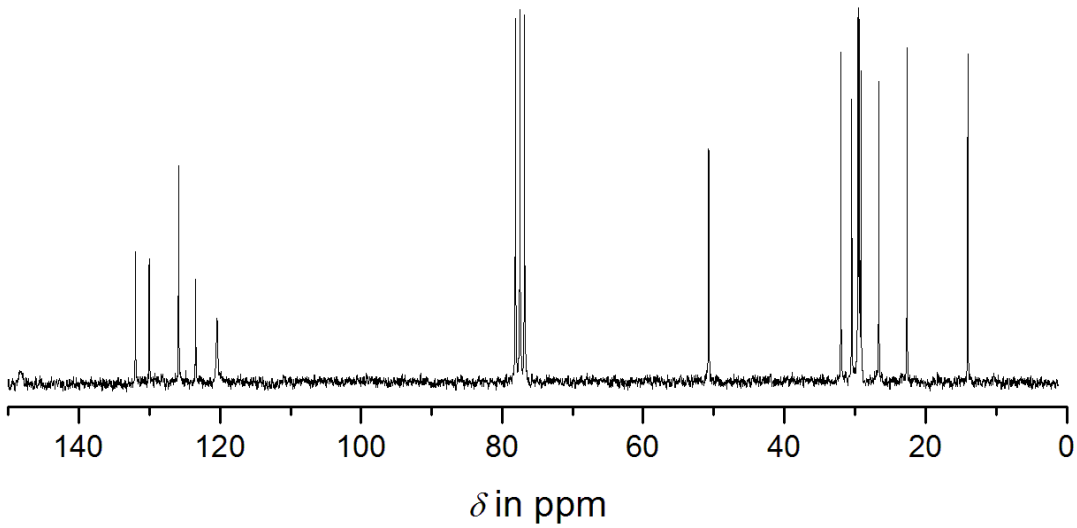
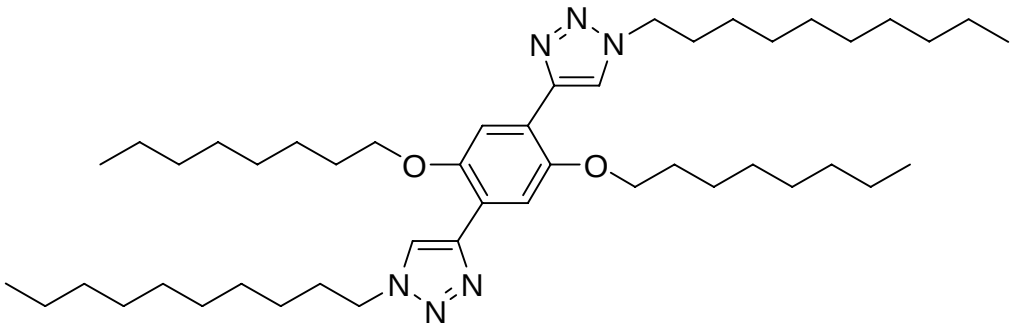


Figure 18b: ^{13}C NMR spectrum of **5a** ($CDCl_3$, 50 MHz).



1-Decyl-4-(4-(1-decyl-1*H*-1,2,3-triazol-4-yl)-2,5-bis(octyloxy)phenyl)-1*H*-1,2,3-triazole (5c): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.09 (1 H, s), 7.98 (1 H, s), 4.38 (4 H, t, *J* = 7.1 Hz), 4.38 (4 H, t, *J* = 7.1 Hz), 4.17 (4 H, t, *J* = 6.5 Hz) 1.90 (2 H, quin, *J* = 6.9 Hz), 1.45-1.10 (14 H, m), 0.84 ppm (3 H, t, *J* = 6.5 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 146.23, 132.95, 123.14, 121.09, 119.36, 110.73, 68.89, 50.25, 31.86, 30.36, 29.67, 29.28, 29.23, 29.05, 28.89, 26.53, 26.35, 22.65, 14.05, 13.96 ppm; MALDI-TOF-MS (Dithranol): m / z= 749.63 ($[M+H]^+$).

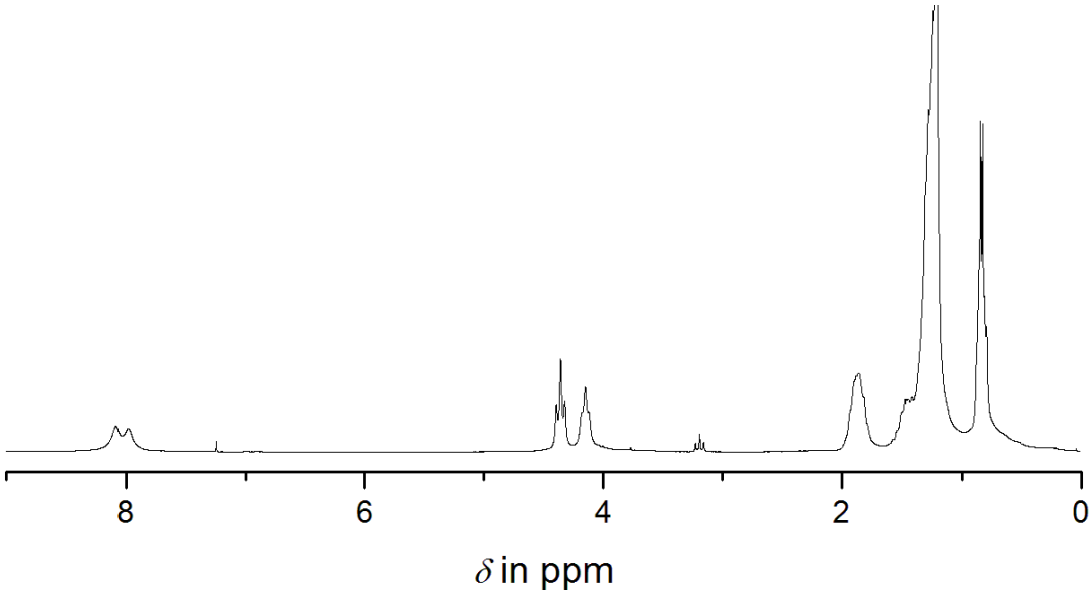


Figure 19a: ^{1}H NMR spectrum of **5c** ($CDCl_3$, 200 MHz).

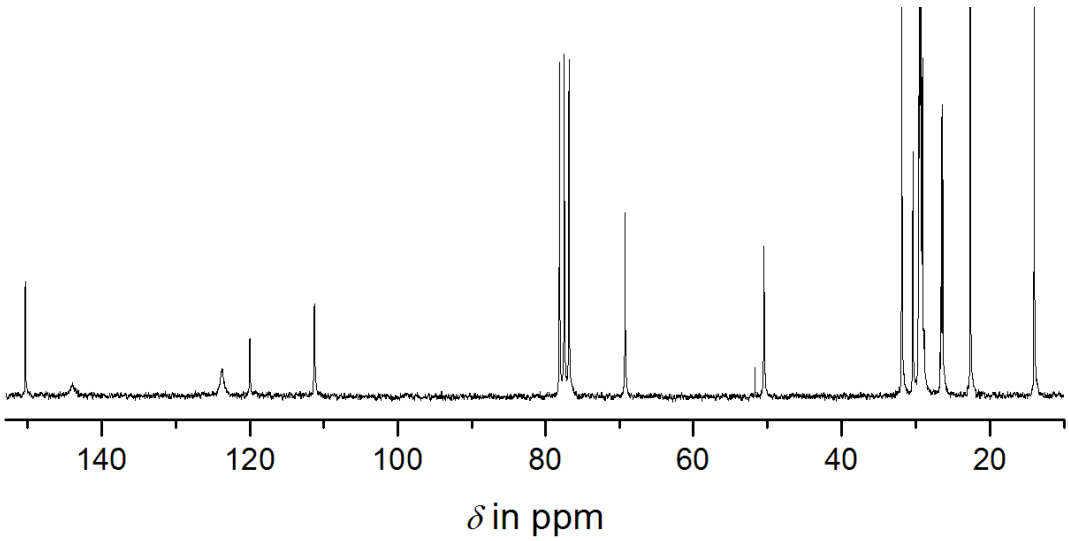
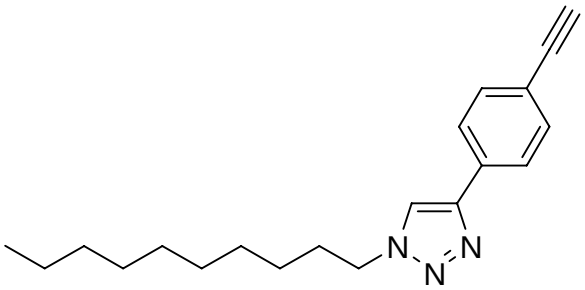


Figure 19b: ^{13}C NMR spectrum of **5c** ($CDCl_3$, 50 MHz).



1-Decyl-4-(4-ethynylphenyl)-1*H*-1,2,3-triazole (5d): ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.76 (2 H, d, *J* = 8.6 Hz), 7.72 (1 H, s), 7.50 (2 H, d, *J* = 8.4 Hz), 4.34 (2 H, t, *J* = 7.2 Hz), 3.09 (1 H, s), 1.90 (2 H, quin, *J* = 6.9 Hz), 1.45-1.10 (14 H, m), 0.84 ppm (3 H, t, *J* = 6.5 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 146.87, 132.54, 131.10, 125.40, 121.60, 119.71, 83.43, 77.78, 50.42, 31.28, 29.64, 29.31, 29.19, 28.94, 28.78, 26.43, 22.60, 14.01 ppm; MALDI-TOF-MS (Dithranol): m / z= 310.18 ($[M+H]^+$).

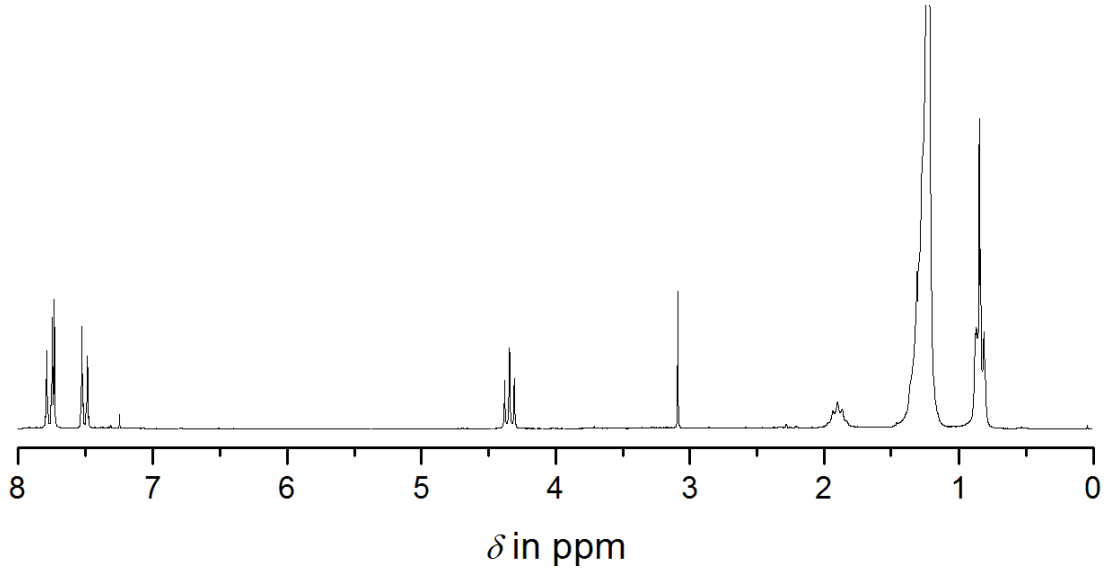


Figure 20a: ^{1}H NMR spectrum of **5d** ($CDCl_3$, 200 MHz).

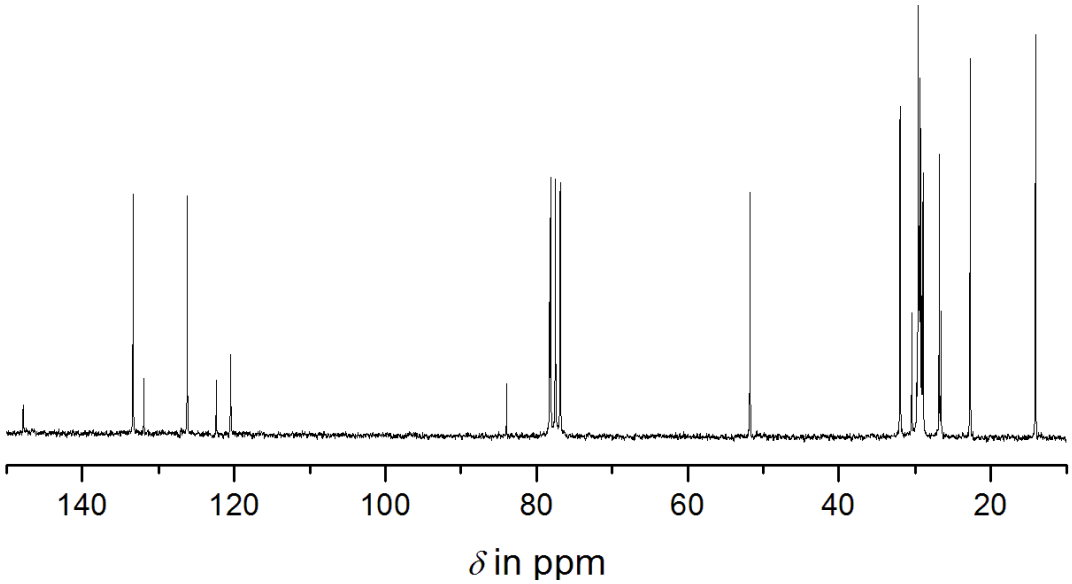


Figure 20b: ^{13}C NMR spectrum of **5d** ($CDCl_3$, 50 MHz).

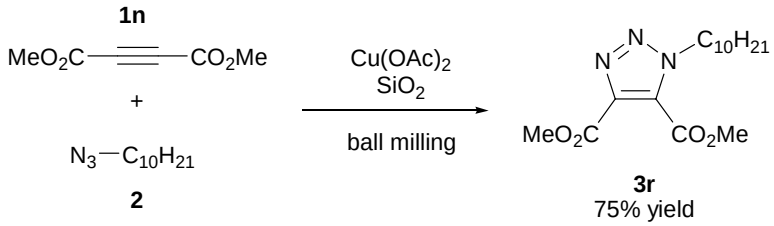
Catalyst screening (cf. manuscript)**:**

Table S1 Influence of different copper compounds on the reaction of phenylacetylene (**1a**) and decyl azide (**2a**; Scheme 1).[a]

Catalyst	Time [min]	*X*(**2a**)[b] [%]	*S*(**3a**)[b] [%]
$Cu(OAc)_2$	5	83 (> 99)	93 (97)
$CuSO_4$	5	64	90
CuI	5	77	94
$Cu(OAc)_2$	10	> 99	95
$CuSO_4$	10	98	96
CuI	10	99	94

[a] Reaction conditions: 1.1 mmol **1a**, 1 mmol **2a**, 5 mol% catalyst, 5 g SiO_2; ZrO_2 beaker (45 mL), 6 × ZrO_2 milling balls (15 mm), ν_{rot} = 800 min^{-1}. [b] GC-FID analysis. Values in parenthesis: 5 mol% of sodium ascorbate were added.

Synthesis and analytical data of compound 3r (cf. manuscript)**:**



Scheme S1. Synthesis of dimethylester **3r** from dimethylacetylendicarboxylate (**1n**) and decyl azide (**2a**) in a planetary ball mill.

Dimethyl-1-decyl-1*H*-1,2,3-triazole-4,5-dicarboxylate (**3r**): The milling beaker (45 mL; zirconia) was equipped with 6 milling balls (d = 15 mm, zirconia). Afterwards SiO_2 (5 g), dimethylacetylendicarboxylate (**1n**; 156 mg, 1.1 mmol), decyl azide (**2a**; 183 mg, 1 mmol) and $Cu(OAc)_2$ (5 mol%, 8 mg) were added in the given order. Milling was accomplished at 800 min^{-1} for 10 min. After cooling of the milling beakers to room temperature, the crude product was extracted on a frit with a thin silica layer using *tert*-butyl methyl ether (3 × 10 mL). The solvent was evaporated in vacuum, the crude products were dried and analyzed by GC-FID, ^{1}H, ^{13}C NMR spectroscopy and MALDI-TOF mass spectrometry after dissolution in an appropriate solvent. 75% yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 4.49 (2 H, t, J = 7.2 Hz), 3.91 (3 H, s), 3.87 (3 H, s), 1.80 (2 H, quin, J = 6.9 Hz), 1.36-0.98 (14 H, m), 0.78 ppm (3 H, t, J = 6.5 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 160.41, 158.89, 139.68, 129.68, 53.18, 52.40, 50.41, 31.64, 30.02, 29.22, 29.14, 29.04, 28.79, 26.11, 22.44, 13.86 ppm; MALDI-TOF-MS (Dithranol): m / z= 326.23 ($[M+H]^{+}$).

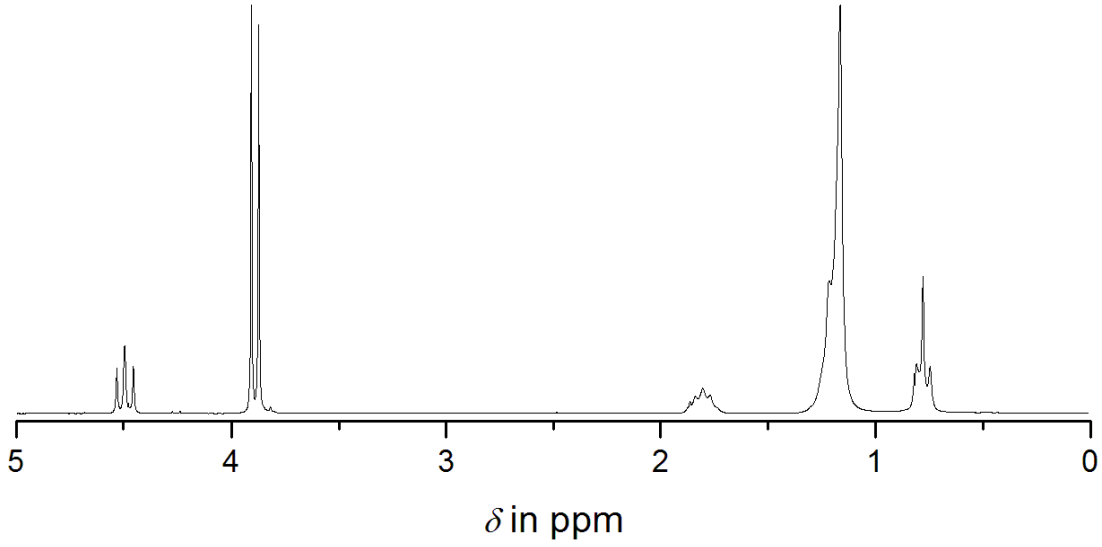


Figure 21a: ^{1}H NMR spectrum of **3r** ($CDCl_3$, 200 MHz).

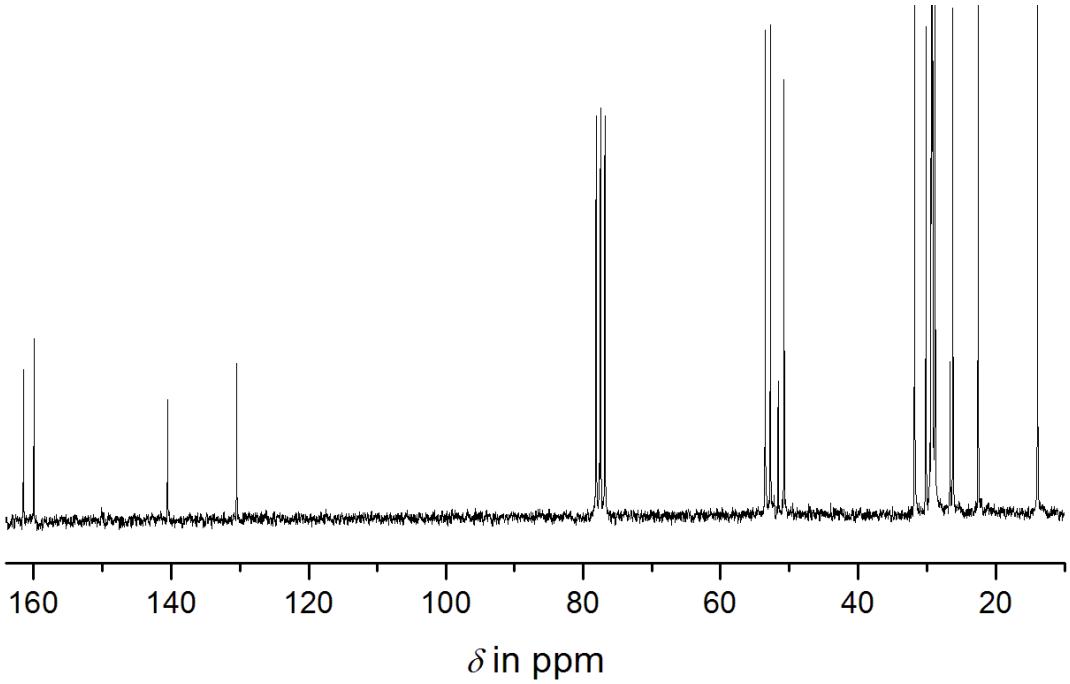
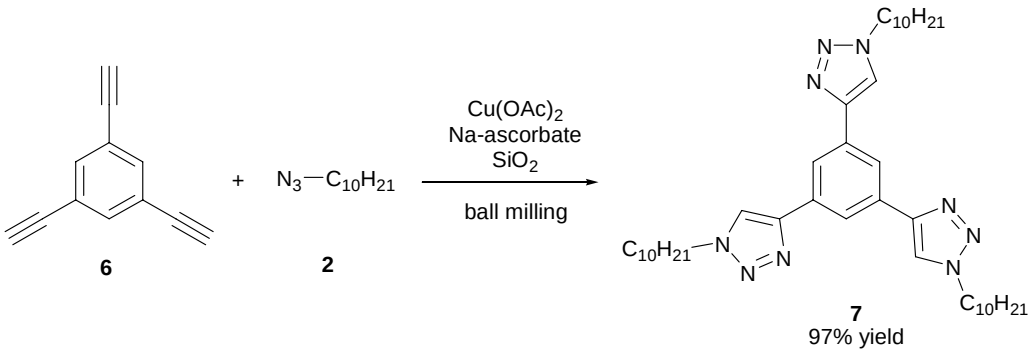


Figure 21b: ^{13}C NMR spectrum of **3r** ($CDCl_3$, 50 MHz).

Synthesis and analytical data of compound 7 (cf. manuscript)**:**



Scheme S2. Synthesis of compound **7** from 1,3,5-*tris*-ethynylbenzene (**6**) and decyl azide (**2a**) in a planetary ball mill.

4-(3,5-*bis*(1-Decyl-1*H*-1,2,3-triazol-4-yl)phenyl)-1-decyl-1*H*-1,2,3-triazole (**7**): The milling beaker (45 mL; zirconia) was equipped with 6 milling balls (*d* = 15 mm, zirconia). Afterwards SiO_2 (5 g), 1,3,5-*tris*-ethynylbenzene (**6**; 75 mg, 0.5 mmol), decyl azide (**2a**; 293 mg, 1.6 mmol), sodium ascorbate (5 mol%, 10 mg) and $Cu(OAc)_2$ (5 mol%, 8 mg) were added in the given order. Milling was accomplished at 800 min^{-1} for 10 min. After cooling of the milling beakers to room temperature, the crude product was extracted on a frit with a thin silica layer using *tert*-butyl methyl ether (3 × 10 mL). The solvent was evaporated in vacuum, the crude products were dried and analyzed by GC-FID, ^{1}H, ^{13}C NMR spectroscopy and MALDI-TOF mass spectrometry after dissolution in an appropriate solvent. 97% isolated yield. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.15 (3 H, s), 7.84 (3 H, s), 4.24 (6 H, t, *J* = 7.1 Hz), 1.78 (6 H, quin, *J* = 6.6 Hz), 1.33-0.96 (42 H, m), 0.72 ppm (9 H, t, *J* = 6.7 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 146.60, 131.62, 121.68, 119.99, 50.12, 31.53, 29.93, 29.15, 28.93, 28.70, 28.50, 26.17, 22.31, 13.71 ppm; MALDI-TOF-MS (Dithranol): m / z= 700.58 ($[M+H]^+$).

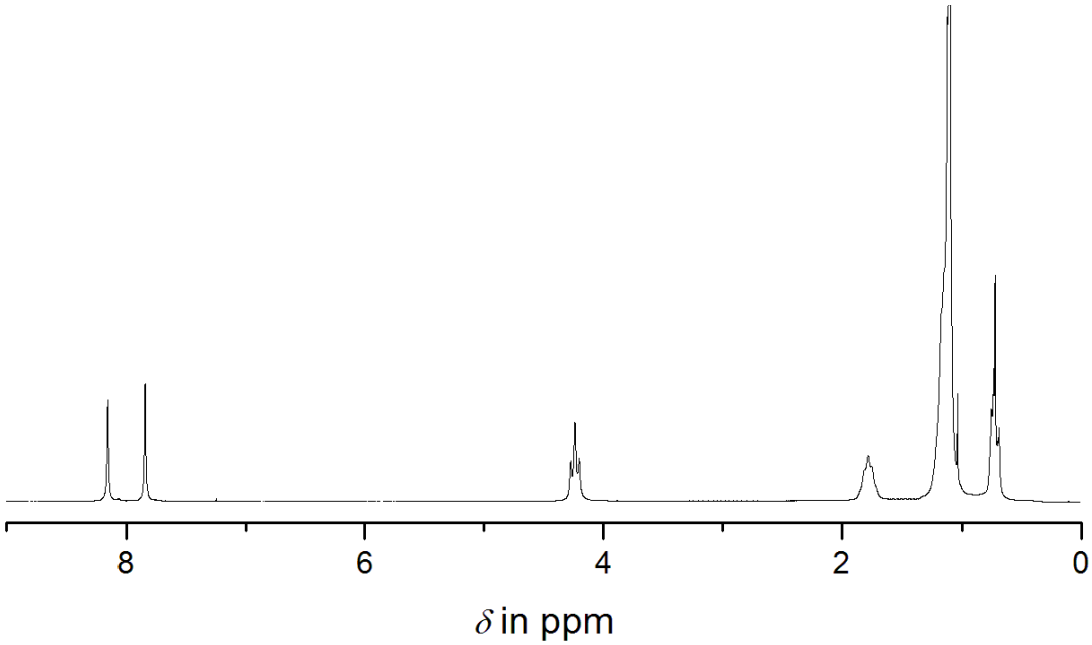


Figure 22a: ^{1}H NMR spectrum of **7** ($CDCl_3$, 200 MHz).

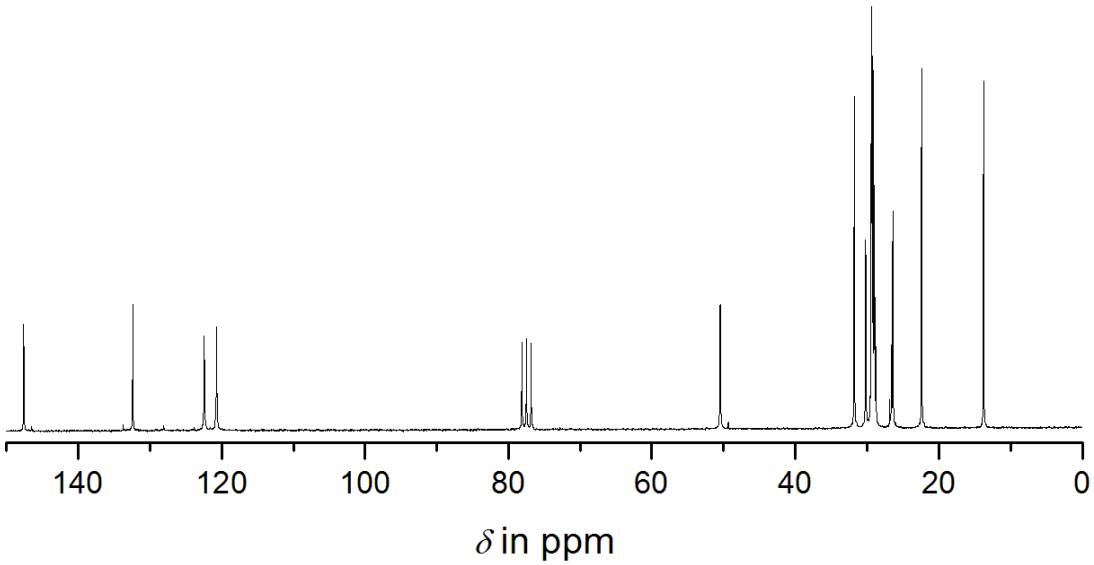


Figure 22b: ^{13}C NMR spectrum of **7** ($CDCl_3$, 50 MHz).

Synthesis of ethynyl functionalised polystyrene (8):

CuBr (0.179 g, 1.250 mmol) was added to a 25 mL two-neck round-bottom flask. The flask was sealed with a rubber septum, degassed and back-filled with Argon. A solution of styrene (11.57 mL, 0.1 mol) and PMDETA (0.261 mL, 1.250 mmol) in anisole (10 mL) was transferred to the flask via a syringe. After 10 min, prop-2-ynyl 2-bromo-2-methylpropanoate (0.256 g, 1.250 mmol) was added via syringe. The flask was placed in an oil bath at 110 °C and the polymerization was allowed to proceed for 2 h. After the reaction was finished the flask was taken from the oil bath and precipitated in ice-cold methanol. Copper was removed by dissolving the polymer in dichloromethane and passing through basic alumina. Second precipitation from dichloromethane in methanol yielded 3.5 g of **8** (M_n = 2.500 g / mol, PDI = 1.08).

Synthesis of 1,12-diazidododecane (10):

1,12-Dibromododecane (1.64 g, 5 mmol) was dissolved in 15 mL dry DMF and purged with argon. Subsequently, sodium azide (975 mg, 15 mmol) was added and the solution was stirred at room temperature overnight. After addition of water the mixture was extracted twice with diethyl ether. The combined organic phases were dried with magnesium sulfate and the solvent was evaporated. 1.1 g (4.3 mmol, 86%) 1,12-diazidododecane were obtained as a slightly orange oil. ^{1}H NMR (200 MHz, aceton-D_6) : δ = 3.31 (4 H, t, J = 6.9 Hz), 1.57 (4 H , q, J = 6.9 Hz), 1.40-1.31 ppm (16 H , m); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 51.1, 29.38, 29.36, 29.00, 28.68, 26.54 ppm.

Analytical data of polymers 12a and 12b (cf. manuscript)**:**

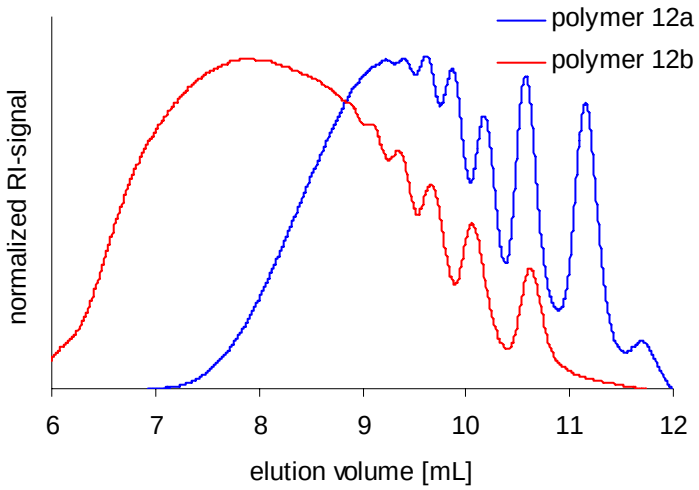


Figure S1. SEC analysis of polymer **12a** and **12b** prepared by $Cu(OAc)_2$-catalysed 1,3-dipolar cycloaddition of 1,12-diazidododecane (**10**) and *bis*-ethynyl compounds (**11a** and **11b**) in a ball mill (cf. Table 3 of the manuscript).

References:

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[2] L. Bondarenko, I. Dix, H. Hinrichs and H. Hopf, *Synthesis*, 2004, **16**, 2751.
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[5] M. Pocci, S. Alfei, F. Lucchesini, V. Bertini and B. Idini, *Tetrahedron*, 2009, **30**, 5684.