Supporting Information for

Supramolecular Diversity through Click Chemistry: Switching from Nanomicelles to 1D Nanotubes and Tridimensional hydrogels

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General methods.

Chemicals employed all over this work were purchased from Aldrich Chemical Co. Dry solvents were purchased from SDS in *anhydrous grade* and in addition dried in a solvent purification system (Pure Solv MD5, Innovative Technology)**.** The monitoring of the reactions was carried out by TLC, employing aluminum sheets coated with silica gel 60 F_{254} (normal phase) purchased from Merk,. with detection by charring with phosphomolybdic acid/EtOH and sulphuric acid/EtOH. For flash chromatography, silica Gel (Merck 230-400 mesh) was used. The organic extracts were dried over anhydrous sodium sulfate and concentrated under vacuum. Columns were eluted with positive air pressure. Chromatographic eluents are given as volume to volume ratios (v/v). NMR spectra were recorded with a BRUKER AC-500 apparatus. Deuterated solvents are indicated in brackets. Chemical shift values (δ) are referred to tetramethylsilane (TMS), utilized as internal reference; then, the spectral signals were calibrated according to the non-deuterated residual peak of the solvent. Optical rotations $[\alpha]^{20}_{D}$ were determined with a Perkin-Elmer 341 polarimeter using a sodium lamp (λ = 589 nm) with a 10 cm cell length. UV/Vis spectra were recorded on a UV/vis Perkin Elmer Lambda 12, using quartz cuvettes. HR-MS were recorded on a Kratos MS-80RFA 241-MC apparatus. Transmission Electron Microscopy (TEM) images were taken by Philips CM 10 or CM 200 apparatuses with an accelerating voltage of 80 kV or 200 kV, respectively. Typically, a very small volume of the aqueous solutions (20 µL) was deposited over carbon-coated copper grids and uranyl acetate 2% as the negative stain. High resolution transmission electron microscopy (HRTEM) images were taken by a JEOL JEM-2200FS microscope, equipped with a field emission gun working at an accelerating voltage of 200 kV, a CEOS spherical aberration corrector and an Omega filter. Scanning electron microscopy (SEM) images were obtained on a JEOL JSM-5400 aparatus. Samples were prepared by depositing 15 µl of the suspension onto grids, allowing the grids to absorb for 2 minutes. Atomic force microscopy (AFM) images were taken by working on a tapping mode by a Pico Plus Molecular Imaging followed by a treatment with the WSxM 5.0 Develop 2.0 software. First, AFM samples were prepared by evaporation of the aqueous solutions previously deposited on a just exfoliated mica substrate (5 × 5 mm^2). Small angle X-ray scattering (SAXS) was performed on a *PANalytical X'Pert PRO*

NMR spectra were recorded with a Bruker AC-500 (^{1}H, 500 MHz) spectrometer. Chemical shifts are reported in ppm, and coupling constants are reported in Hz. Routine spectra were referenced to the residual proton or carbon signals of the solvent.

High-resolution mass spectra were recorded on a Kratos MS-80RFA 241-MC apparatus.

Optical rotations were determined with a Perkin-Elmer 341 polarimeter.

TEM analyses were performed on a Philips CM 10 or CM 200 apparatuses with an accelerating voltage of 80 kV or 200 kV, respectively. CM-120 operating at electron energy of 100 keV. Samples were prepared by depositing 15 µl of the suspension onto grids, allowing the grids to absorb for 2 minutes. Typically, a very small volume of the aqueous solutions (20 µL) was deposited over carbon-coated copper grids and uranyl acetate 2% as the negative stain. High resolution transmission electron microscopy (HRTEM) images were taken by a JEOL JEM-2200FS microscope, equipped with a field emission gun working at an accelerating voltage of 200 kV, a CEOS spherical aberration corrector and an Omega filter.

SEM images were obtained on a JEOL JSM-5400. Samples were prepared by depositing 15 µl of the suspension onto grids, allowing the grids to absorb for 2 minutes.

AFM images were taken by working on a tapping mode by Pico Plus Molecular Imaging followed by a treatment with the WSxM 5.0 Develop 2.0 software. AFM samples were prepared by evaporation of the aqueous solutions previously deposited on a just exfoliated mica substrate (5×5 mm^2).

UV-Vis spectra were obtained by Perkin-Elmer Lambda 12 Spectrometer.

Small angle X-ray scattering (SAXS) was performed on a *PANalytical X'Pert PRO* diffractometer .

Synthetic procedures and chemical characterizations

Compound 2. R_f = 0.20 (CH_2Cl_2/MeOH 5:1). $[\alpha]_D^{20}$ = -4.4 (*c* 0.6 in methanol). δ_H (500 MHz, MeOD, Me_4Si) 7.93 (1H, s, triazole), 4.60 (2H, t, *J* = 5.0 Hz, CH_2-triazole), 4.48-4.46 (3H, m, H-1, triazole-CH_2), 4.40 (1H, d, $J_{1',2'}$ 7.6 Hz, 1´-H), 4.02 (2H, s, $COCH_2O$), 3.95-3.91 (3H, m, $C\underline{H_2}CH_2$ triazole, 6a-H), 3.86-3.79 (3H, m, 6b-H, 4´-H-, 6´a-H), 3.75-3.46 (21H, m, 6b´-H, 6 CH_2O, 5´-H, 4-H, 2´-H, 3´-H, 3-H, 5-H, $C\underline{H_2}NH$), 3.32-3.28 (1H, d, $J_{2,3}$ = $J_{2,1}$ 9.5 Hz, 2-H), 2.95-2.77 (2H, m, SCH_2), 2.28-2.23 (6H, m, $C\underline{H_2}C{\equiv}C$, $COC\underline{H_2}CH_2$), 1.64 (2H, t, *J* 7.1 Hz, $COCH_2C\underline{H_2}$), 1.55-1.50 (4H, m, 2 $C\underline{H_2}CH_2C{\equiv}C$), 1.41-1.32 (26H, m, 13 CH_2) and 0.92 (3H, t, *J* 6.7 Hz, $C\underline{H_3}CH_2$). δ_C (125.7 MHz, MeOD, Me_4Si): δ 174.7 (NHCO), 171.4 (NHCO), 144.7 (C triazole), 123.7 (CH triazole), 103.7 (C-1´), 85.6 (C-1), 79.2 (C-5´), 79.1 (C-5), 76.6 ($CH_2\underline{C}{\equiv}C$) 76.5 ($CH_2C{\equiv}\underline{C}$, C-3´), 75.7 (C-4), 73.4 (C-3), 72.7 (C-2), 71.1 (C-2´), 70.6, 70.1, 70.0, 69.8, 69.1, 68.9 (C-4´), 65.1 (2 $CH_2C{\equiv}\underline{C}$), 61.1 (C-6´), 60.8 (C-6), 50.1 (CH_2-triazole), 39.1 (CH_2NH), 35.6 ($NHCO\underline{C}H_2CH_2$), 34.2 (triazole-CH_2), 31.7 ($\underline{C}H_2CH_2CH_3$), 29.4 (SCH_2), 29.3, 29.2, 29.1, 28.9, 28.8, 28.7, 28.5, 28.2, 25.5 ($COCH_2\underline{C}H_2$), 22.4 ($\underline{C}H_2CH_3$), 18.4 ($\underline{C}H_2C{\equiv}C$) and 13.2 ($CH_2\underline{C}H_3$). HRMS (ESI, m/z): $[M + Na]^+$ calcd for $C_{52}H_{89}N_5O_{16}SNa$: 1094.5923, found: 1094.5914.

Compound 6. R_f = 0.24 (CH_2Cl_2/MeOH 9:1). $[\alpha]_D^{20}$ = +66.0 (*c* 1.0 in chloroform). δ_H (500 MHz, MeOD, Me_4Si) 8.44 (1H, br s, NHCO), 7.97 (1H, s, triazole), 5.22 (1H, s, 1-H), 4.75-4.60 (2H, m, CH_2-triazole), 4.45 (2H, s, triazole-CH_2), 3.92-3.85 (3H, m, 3-H, 4-H, 6a-H), 3.76-3.72 (1H, m, 6b-H), 3.66-3.59 (2H, m, 2-H, 5-H), 3.27-3.09 (2H, m, SCH_2), 2.28-2.22 (6H, m, 2x$C\underline{H_2}C{\equiv}C$, $COC\underline{H_2}CH_2$), 1.63 (2H, t, *J* 6.8 Hz, $COCH_2C\underline{H_2}$), 1.56-1.49 (4H, m, 2x$C\underline{H_2}CH_2C{\equiv}C$), 1.41-1.32 (26H, m, 13xCH_2), 0.92 (3H, t, *J* 6.3 Hz, CH_3). δ_C (125.7 MHz, MeOD, Me_4Si) 174.9 (CO), 144.9 (C triazole), 123.5 (CH triazole), 85.6 (C-1), 76.5 ($\underline{C}{\equiv}C\text{-}C{\equiv}\underline{C}$), 74.0 (C-4), 72.0 (C-3), 71.6 (C-5), 67.5 (C-2), 65.1 ($C{\equiv}\underline{C\text{-}C}{\equiv}C$), 61.5 (C-6), 49.7 ($CH_2$-triazole), 35.6 ($NHCO\underline{C}H_2CH_2$), 34.2 (triazole-$CH_2$), 31.7 ($\underline{C}H_2CH_2CH_3$), 30.9 ($SCH_2$), 29.4, 29.3, 29.1, 28.9, 28.8, 28.7, 28.5, 28.2, 25.5 ($COCH_2\underline{C}H_2$), 22.4 ($\underline{C}H_2CH_3$), 18.4 (2 $\underline{C}H_2C{\equiv}C$), 13.1($CH_3$). HRMS (ESI, m/z): $[M + Na]^+$ calcd for $C_{36}H_{60}N_4O_6SNa$: 699.4131, found: 699.4108.

Compound 7. R_f = 0.30 (CH_2Cl_2/MeOH 9:1). $[\alpha]_D^{20}$ = +38.0 (*c* 0.50 in methanol). δ_H (500 MHz, $CDCl_3$, Me_4Si) 7.82 (1H, s, triazole), 7.66 (1H, t, *J* 5.8 Hz, NHCO), 6.71 (1H, t, *J* 5.8 Hz, NHCO), 5.38 (1H, s, 1-H), 4.56 (2H, t, *J* 5.0 Hz, CH_2-triazole), 4.51 (2H, d, *J* 5.4 Hz, triazole-CH_2), 4.01 (2H, s, $COCH_2O$), 3.91-3.86 (5H, m, 4-H,2-H, 3-H, 5-H, 6a-H), 3.78 (1H, d, *J* 9.0 Hz, 6b-H), 3.70-3.64 (14H, m, 7xCH_2O), 3.59-3.49 (2H, m, CH_2NH), 2.92-2.71 (2H, m, SCH_2), 2.26 (4H, t, *J* 6.8 Hz, 2x$\underline{C}H_2C\equiv C$), 2.21 (2H, t, *J* 7.6 Hz, $COC\underline{H}_2CH_2$), 1.66-1.58 (2H, m, $COCH_2C\underline{H}_2$), 1.56-1.49 (4H, m, 2x$C\underline{H}_2CH_2C\equiv C$), 1.45-1.25 (26H, m, 13xCH_2), 0.91 (3H, t, *J* 6.6 Hz, CH_3). δ_C (125.7 MHz, $CDCl_3$, Me_4Si)173.7 (CO), 170.7 (CO), 144.7 (C triazole), 123.6 (CH triazole), 85.1 (C-1), 77.6 ($\underline{C}\equiv C-C\equiv C$), 77.4 ($C\equiv C-C\equiv\underline{C}$), 73.4 (C-4), 72.3 (C-3), 72.1 (C-5), 70.9, 70.5, 70.4, 70.2, 69.3, 67.1 (C-2), 65.3 ($C\equiv\underline{C}-C\equiv C$), 65.2 ($C\equiv C-\underline{C}\equiv C$), 61.3 (C-6), 50.3 ($CH_2$-triazole), 38.6 ($CH_2NH$), 36.4 ($NHCO\underline{C}H_2CH_2$), 34.8 (triazole-$CH_2$), 31.9 ($\underline{C}H_2CH_2CH_3$), 30.7 ($SCH_2$), 29.6, 29.5, 29.3, 29.2, 29.1, 29.0, 28.9, 28.8, 28.4, 28.3, 25.6 ($COCH_2\underline{C}H_2$), 22.7($\underline{C}H_2CH_3$), 19.2 (2x$\underline{C}H_2C\equiv C$), 14.1 ($CH_3$). HRMS (ESI, m/z): $[M + Na]^+$ calcd for $C_{46}H_{79}N_5O_{11}SNa$ 932.5395, found: 932.5377.

Compound 8. R_f = 0.50 (CH_2Cl_2/MeOH 5:1). $[\alpha]_D^{20}$ = +37.5 (*c* 0.75 in methanol). δ_H (500 MHz, MeOD, Me_4Si) 7.88 (1H, s, triazole), 5.29 (1H, s, 1-H), 4.56 (2H, t, *J* 5.1 Hz, CH_2-triazole), 4.41 (2H, s, triazole-CH_2), 3.99 (4H, s, 2x$COCH_2O$), 3.91-3.84 (5H, m, 4-H, 2-H, 3-H, 5-H, 6a-H), 3.73-3.41 (29H, m, 6b-H, 14xCH_2O), 3.34 (4H, s, 2x$C\underline{H}_2NH$), 2.89-2.70 (2H, m, SCH_2), 2.25-2.19 (6H, m,2x$\underline{C}H_2C\equiv C$, $COC\underline{H}_2CH_2$), 1.61 (2H, t, *J* 7.0 Hz, $COCH_2C\underline{H}_2$), 1.52-1.46 (4H, m, 2x$C\underline{H}_2CH_2C\equiv C$), 1.38-1.29 (26H, m, 13xCH_2), 0.89 (3H, t, *J* 6.8 Hz, CH_3). δ_C (125.7 MHz, MeOD, Me_4Si) 176.1 (CO), 172.9 (CO), 172.8 (CO), 146.2 (C triazole), 124.9 (CH triazole), 86.6 (C-1), 77.9 ($\underline{C}\equiv C-C\equiv\underline{C}$), 75.3 (C-4), 73.7 (C-3), 73.2 (C-5), 72.0, 71.9, 71.5, 71.3, 71.2, 70.5, 70.4, 68.9 (C-2), 66.4 ($C\equiv\underline{C}-\underline{C}\equiv C$), 62.9 (C-6), 51.4 ($CH_2$-triazole), 39.8 ($CH_2NH$), 39.7 ($CH_2NH$), 36.9 ($NHCO\underline{C}H_2CH_2$), 35.6 (triazole-$CH_2$), 33.1 ($\underline{C}H_2CH_2CH_3$), 31.4 ($SCH_2$), 30.7, 30.6, 30.5, 30.3, 30.2, 30.1, 30.0, 29.9, 29.8, 29.5, 26.9 ($COCH_2\underline{C}H_2$), 23.7 ($\underline{C}H_2CH_3$), 19.7 (2x$\underline{C}H_2C\equiv C$), 14.4 ($CH_3$). HRMS (ESI, m/z): $[M + Na]^+$ calcd for $C_{56}H_{98}N_6O_{16}SNa$: 1165.6658, found: 1165.6672.

- *Synthesis of compound **9***

To a solution of *N*-Boc-glycine **11** (63.5 mg, 0.21 mmol) in anhydrous methylene chloride (5 mL) were added sequentially diisopropylcarbodiimide (32.5 µL, 0.21

mmol), and DMAP (2.3 mg, 0.02 mmol). The resulting mixture was stirred for 5 min. under the same conditions and then, a solution of amine **10** (110 mg, 0.19 mmol) was added and the reaction further stirred for 16 h. Afterwards, the mixture was diluted with methylene chloride (50 mL) and washed sequentially with a 1M HCl solution (10 mL), neutralized with a saturated aqueous $NaHCO_3$ solution (20 mL) and finally with brine (20 mL). After drying over Na_2SO_4 and removal of solvent, the crude product was purified by silica gel chromatography, eluting with a mixture of CH_2Cl_2/MeOH (20:1) affording the corresponding product **12** (95 mg 63%) as a colorless oil. **12**. R_f = 0.30 (CH_2Cl_2/MeOH 20:1). $[\alpha]_D^{20}$ = +30.9 (*c* 1.0 in chloroform). δ_H (500 MHz, $CDCl_3$, Me_4Si) 7.35 (1H, br s, NHCO), 6.82 (1H, s, NHCO), 5.43 (1H, s, NHCO), 5.30-5.25 (3H, m, 1-H, 4-H, 2-H), 5.20 (1H, dd, $J_{3,4}$ 9.8 Hz, $J_{3,2}$ 3.3 Hz, 3-H), 4.37-4.33 (1H, m, 5-H), 4.28 (1H, dd, $J_{6a,6b}$ 12.1 Hz, $J_{6a,5}$ 5.1 Hz, 6a-H), 4.08 (1H, d, $J_{6b,6a}$ $J_{6b,5}$ 12.1 Hz, 6b-H), 3.98 (2H, s, $COCH_2O$), 3.76 (2H, br s, $NHCOC\underline{H_2}NH$), 3.67-3.43 (18H, m, 7xCH_2O, $SCH_2C\underline{H_2}$, $C\underline{H_2}NHCO$), 2.82-2.74 (2H, m, SCH_2), 2.14 (3H, s, CH_3COO), 2.06 (3H, s, CH_3COO), 2.03 (3H, s, CH_3COO), 1.96 (3H, s, CH_3COO), 1.42 (9H, s, $3CH_3$ Boc). δ_H (125.7 MHz, $CDCl_3$, Me_4Si) 170.6 (CO), 170.2 (CO), 169.9 (CO), 169.8 (CO), 169.7 (CO), 169.5 (CO), 82.4 (C-1), 70.9 (C-4), 70.5, 70.4, 70.2, 69.7, 69.4 (C-3), 69.1 (C-5), 66.2 (C-2), 62.4 (C-6), 41.9 ($CO\underline{C}H_2NHCO$), 39.2 (CH_2NH), 38.1 ($SCH_2\underline{C}H_2$), 31.0 (SCH_2), 28.3 ($3CH_3$ Boc), 20.9 (CH_3), 20.7 (CH_3), 20.6 (CH_3). HRMS (ESI, m/z): $[M + Na]^+$ calcd for $C_{33}H_{55}N_3O_{17}SNa$: 820.3150, found: 820.3156.

A 1:1 solution of TFA/CH_2Cl_2 (4 mL) was added over the protected amine **12** (90 mg, 0.11 mmol) and stirred for 5 h. After removal of the solvent under vacuum, the crude product was purified by silica gel chromatography, eluting with a mixture of CH_2Cl_2/MeOH (9:1), affording the free amine **13** (76 mg, 99%) as yellow syrup. R_f = 0.24 (CH_2Cl_2/MeOH 9:1). $[\alpha]_D^{20}$ = +23.1 (*c* 1.0 in methanol). δ_H (500 MHz, $CDCl_3$, Me_4Si) 5.44 (1H, s, 1-H), 5.34 (1H, d, $J_{4,3}$ $J_{4,5}$ 2.2 Hz, 4-H), 5.28 (1H, t, $J_{6b,6a}$ $J_{6b,6a}$ 10.0 Hz, 2-H), 5.18 (1H, dd, $J_{3,4}$ 10.4 Hz, $J_{3,2}$ 3.5 Hz, 3-H), 4.87 (2H, s, NH_2), 4.41-4.38 (1H, m, 5-H), 4.28 (1H, dd, $J_{6a,6b}$ 12.5 Hz, $J_{6a,5}$ 5.2 Hz, 6a-H), 4.08 (1H, dd, $J_{6b,6a}$ 12.1 Hz, $J_{6b,5}$ 2.2 Hz, 6b-H), 4.05 (2H, s, $COCH_2O$), 3.72-3.48 (20H, m, 7xCH_2O, $SCH_2C\underline{H_2}$, $C\underline{H_2}NHCO$, $COC\underline{H_2}NH_2$), 2.90-2.79 (2H, m, SCH_2), 2.16 (3H, s, CH_3COO), 2.07 (3H, s, CH_3COO), 2.06 (3H, s, CH_3COO), 1.97 (3H, s, CH_3COO). δ_C (125.7 MHz, MeOD, Me_4Si) 171.0 (CO), 170.2 (CO), 170.1 (CO), 166.2 (CO), 82.2 (C-1), 70.7 (C-4), 70.2,

69.8, 69.6, 69.5, 69.3 (C-3), 69.1 (C-5), 66.0 (C-2), 62.2 (C-6), 40.2 (CO<u>C</u>H_2NHCO), 39.1 (CH_2NH), 38.2 (SCH_2<u>C</u>H_2), 30.3 (SCH_2), 19.3 (CH_3), 19.2 (CH_3), 19.1 (CH_3). HRMS (ESI, m/z): $[M + Na]^+$ calcd for $C_{28}H_{47}N_3O_{15}SNa$: 720.2626, found: 720.2645.

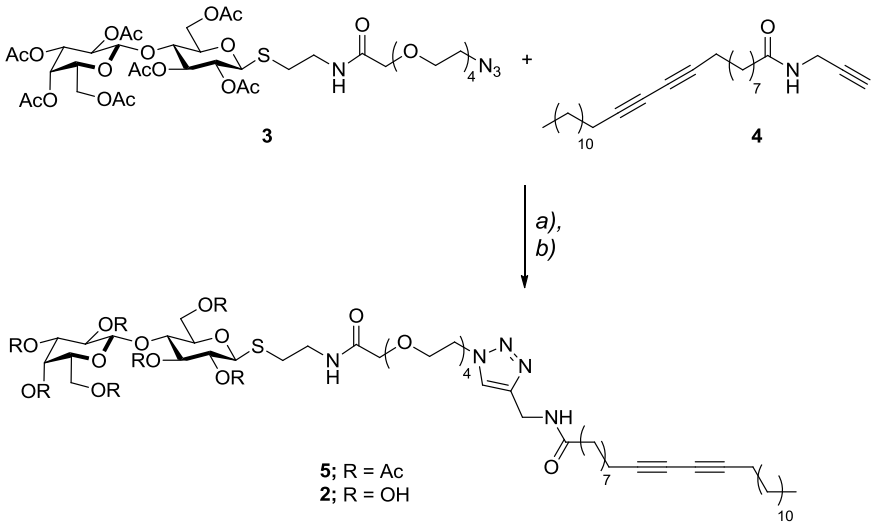
TBTU (42 mg, 0.20 mmol) and DIPEA (22 μL, 0.13 mmol) were added sequentially at room temperature and under an argon atmosphere to a solution of 10,12-pentacosadiyonic acid **14** (55 mg, 0.15 mmol) in dry DMF (1 mL). The resulting solution was stirred for 5 min. and then, a solution of compound **13** (82 mg, 0.12 mmol) and DIPEA (43 μL, 0.25 mmol) in dry DMF (1 mL) was added slowly. The afforded mixture was stirred for 14 h. under an argon atmosphere before the solvent was removed under vacuum. The obtained residue was dissolved in CH_2Cl_2 (100 mL), washed with a 1 M HCl solution (20 mL) and neutralized with a saturated aqueous $NaHCO_3$ (30 mL), and finally with brine (20 mL). After drying over Na_2SO_4 and removal of solvent, the crude product was subjected to a chromatographic column with CH_2Cl_2/MeOH (20:1). Following this procedure **15** (65 mg, 52%) was obtained as a yellowish oil compound with R_f = 0.40 (CH_2Cl_2/MeOH 20:1). $[\alpha]_D^{20}$ = +34.2 (*c* 1.0, $CHCl_3$). δ_H (500 MHz, $CDCl_3$, Me_4Si) 7.38 (1H, s, NHCO), 6.87 (1H, s, NHCO), 6.47 (1H, s, NHCO), 5.33-5.28 (3H, m, 1-H, 2-H, 4-H), 5.23 (1H, dd, $J_{3,4}$ 10.0 Hz, $J_{3,2}$ 3.3 Hz, 3-H), 4.39-4.35 (1H, m, 5-H), 4.30 (1H, dd, $J_{6a,6b}$ 12.4 Hz, $J_{6a,5}$ 5.5 Hz, 6a-H), 4.11 (1H, dd, $J_{6b,6a}$ 12.2 Hz, $J_{6b,5}$ 2.2 Hz, 6b-H), 4.01 (2H, s, $COCH_2O$), 3.91 (2H, d, *J* 4.7 Hz, CO<u>C</u>H_2NHCO), 3.71-3.52 (16H, m, 7xCH_2O, SCH_2<u>C</u>H_2), 3.47-3.45 (2H, m, OCH_2<u>C</u>H_2NH), 2.87-2.75 (2H, m, SCH_2), 2.24-2.20 (6H, m, 2x<u>C</u>H_2C≡C, CO<u>C</u>H_2CH_2), 2.16 (3H, s, CH_3COO), 2.09 (3H, s, CH_3COO), 2.05 (3H, s, CH_3COO), 1.98 (3H, s, CH_3COO), 1.64 (2H, m, $COCH_2$<u>C</u>H_2), 1.52-1.47 (4H, m, 2x<u>C</u>H_2CH_2C≡C), 1.38-1.25 (26H, m, 13 CH_2), 0.87 (3H, t, *J* 6.7 Hz, <u>C</u>H_3CH_2). δ_C (500 MHz, $CDCl_3$, Me_4Si) 173.4 (CO), 170.6 (CO), 170.2 (CO), 169.9 (CO), 169.8 (CO), 169.7 (CO), 168.9 (CO), 82.4 (C1), 77.6 (CH_2C≡<u>C</u>), 77.4 (CH_2<u>C</u>≡C), 70.9 (C-4), 70.5, 70.4, 70.3, 70.2, 69.6, 69.4 (C-3), 69.2 (C-5), 66.2 (C-2), 65.3 (CH_2<u>C</u>≡C), 65.2 (CH_2<u>C</u>≡C), 62.4 (C-6), 42.8 (CO<u>C</u>H_2NHCO), 39.3 (CH_2NH), 38.2 (SCH_2<u>C</u>H_2), 36.4 (NHCO<u>C</u>H_2CH_2), 31.9 (<u>C</u>$H_2CH_2CH_3$), 31.1 (SCH_2), 29.6, 29.5, 29.3, 29.2, 29.1, 28.9, 28.8, 28.3, 25.6 ($COCH_2$<u>C</u>H_2CH_2), 22.7 (<u>C</u>H_2CH_3), 20.9 (CH_3), 20.7 (CH_3), 20.6 (CH_3), 19.2 (2 <u>C</u>H_2C≡C), 14.1 (<u>C</u>H_3CH_2). HRMS (ESI, m/z): $[M + Na]^+$ calcd for $C_{53}H_{87}N_3O_{16}SNa$: 1076.5705, found: 1076.5729.

Starting from ompound **14** (58 mg, 0.06 mmol) and following the general procedure for the Zemplen deacetylation, free neoglycolipid **9** (40 mg, 82%) was obtained as white solid.

Compound 9. R_f = 0.28 (CH_2Cl_2/MeOH 9:1). $[\alpha]_D^{20}$ = +42.7 (*c* 1.0 in methanol). δ_H (500 MHz, MeOD, Me_4Si) 5.32 (1H, s, 1-H), 4.03 (2H, s, $COCH_2O$), 3.95-3.92 (2H, m, 4-H, 2-H), 3.90-3.86 (3H, m, $COCH_2NHCO$, 6a-H), 3.77-3.47 (19H, m, 7xCH_2O, 3-H, 5-H, 6b-H, SCH_2CH_2), 3.42 (2H, t, *J* 5.7 Hz, OCH_2CH_2NH), 2.92-2.74 (2H, m, SCH_2), 2.31-2.25 (6H, m, $2CH_2C{\equiv}C$, $COCH_2CH_2$), 1.65 (2H, t, *J* 6.8 Hz, $COCH_2CH_2$), 1.56-1.50 (4H, m, 2x$CH_2CH_2C{\equiv}C$), 1.42-1.32 (26H, m, 13 CH_2), 0.93 (3H, t, *J* 6.8 Hz, CH_3). δ_C (125.7 MHz, MeOD, Me_4Si) 176.7 (CO), 172.9 (CO), 171.8 (CO), 86.5 (C-1), 77.9 ($CH_2C{\equiv}C$), 77.8 ($CH_2C{\equiv}C$), 75.2 (C-4), 73.6 (C-3), 73.1 (C-5), 71.9, 71.5, 71.4, 71.3, 71.2, 70.5, 68.9 (C-2), 66.4 ($2CH_2C{\equiv}C$), 62.8 (C-6), 43.5 ($COCH_2NHCO$), 40.3 (CH_2NH), 39.7 (SCH_2CH_2), 36.9 ($NHCOCH_2CH_2$), 33.1 ($CH_2CH_2CH_3$), 31.4 (SCH_2), 30.7, 30.6, 30.5, 30.3, 30.1, 30.0, 29.8, 29.5, 26.7 ($COCH_2CH_2$), 23.7 (CH_2CH_3), 19.7 (2 $CH_2C{\equiv}C$), 14.5 (CH_3CH_2). HRMS (ESI, m/z): $[M + Na]^+$ calcd for $C_{45}H_{79}N_3O_{12}SNa$: 908.5282, found: 908.5270.

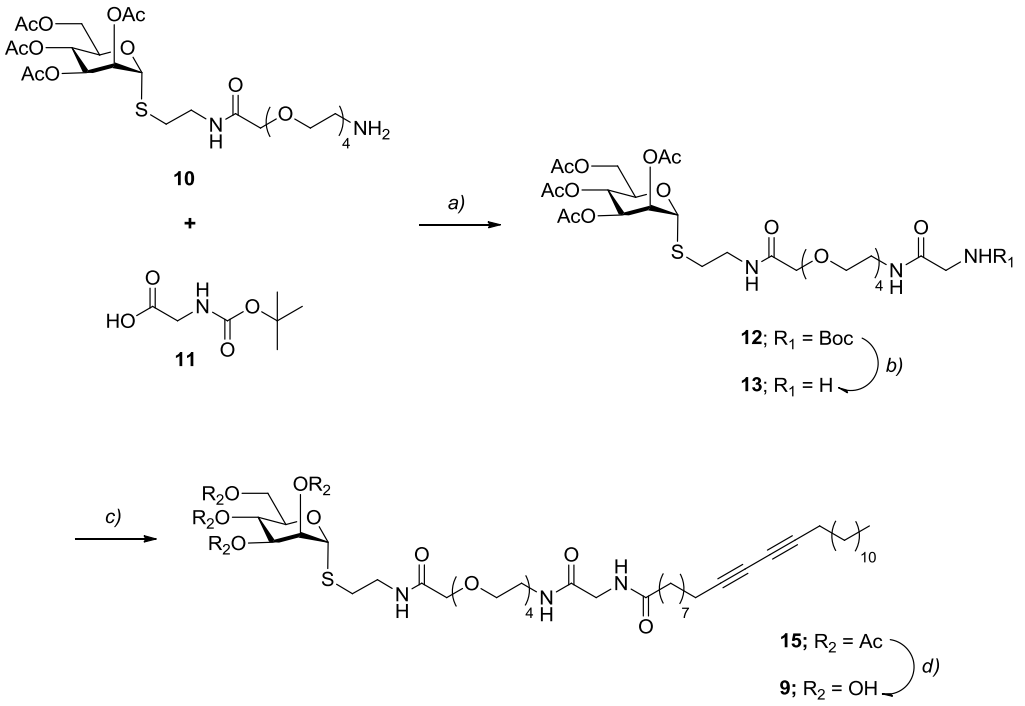
Synthetic schemes

Scheme 1. Convergent synthesis of neoglycolipid **2** by CuCAAC:



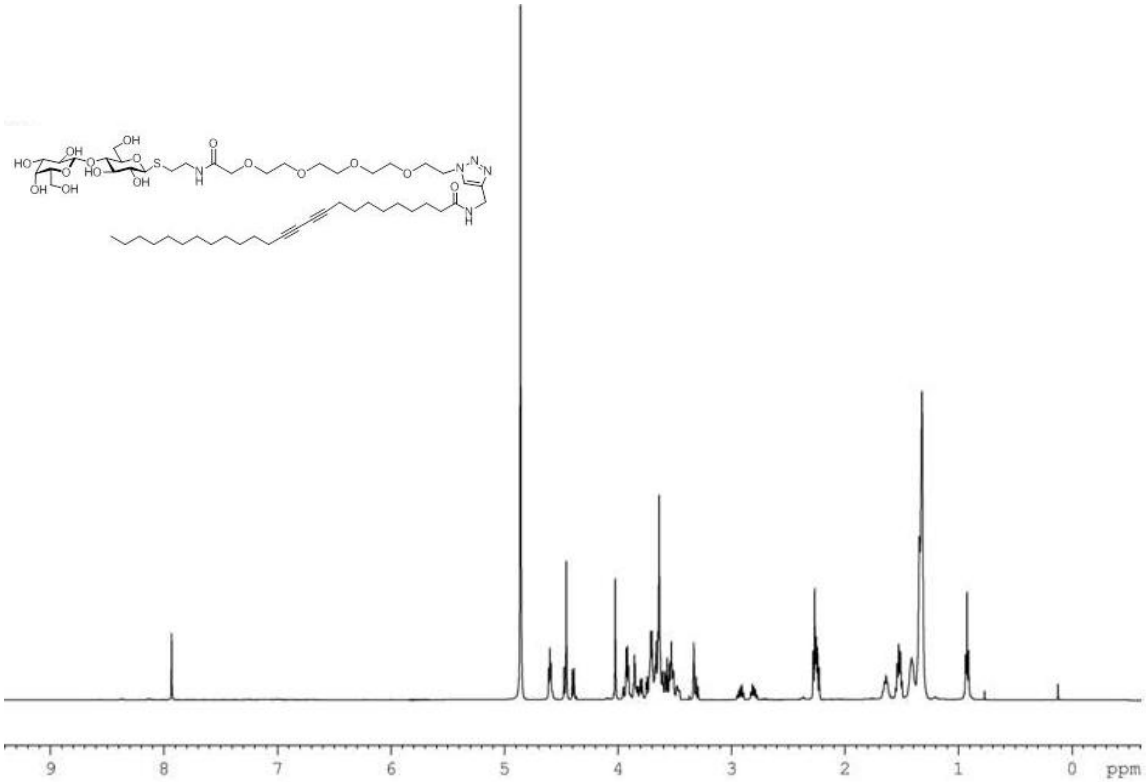
a) CuI, DIPEA, CH_2Cl_2, rt, overnight; (88%). *b*) *i*) NaOMe, MeOH, rt; 1h. *ii*) Amberlyst Ir-120; (67%).

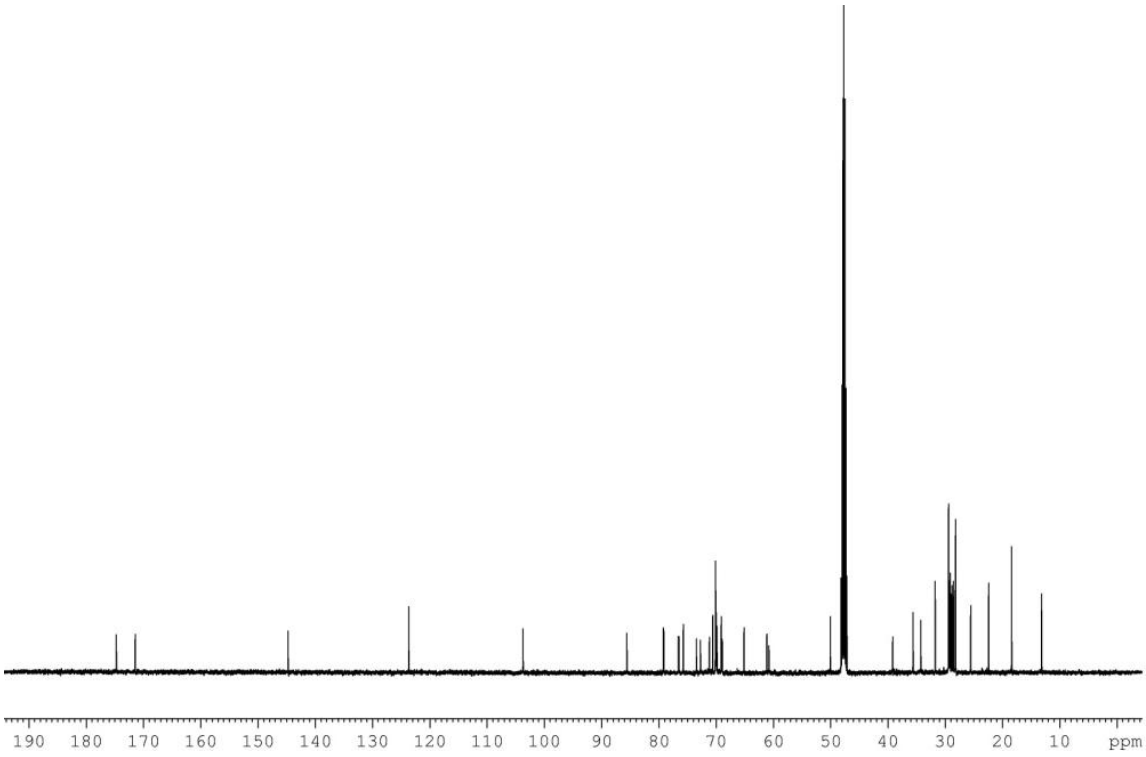
Scheme 2. Synthesis of neoglycolipid **9** by an amidation reaction:

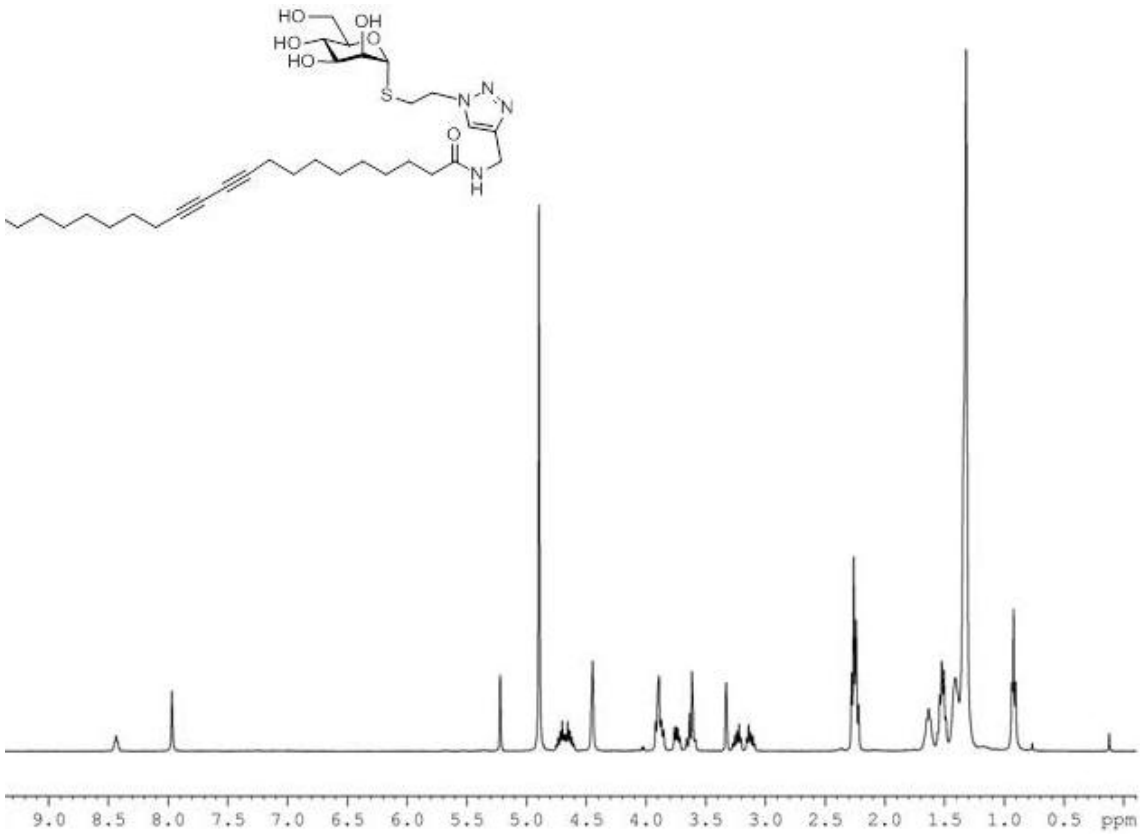


a) *i)* DIPC, DMAP, CH_2Cl_2, rt, 16h.; (63%), *b*) TFA, CH_2Cl_2, rt, 5h.; (99%.), *c*) *i*) PCDA (**14**), TBTU, DIPEA, DMF, rt, 5min., *ii*) **13**, DIPEA, DMF, rt, 14h; (52%), *d*) *i*) NaOMe, MeOH, rt; 1h. *ii*) Amberlyst Ir-120; (82%).

^{1}H- and ^{13}C-NMR spectra



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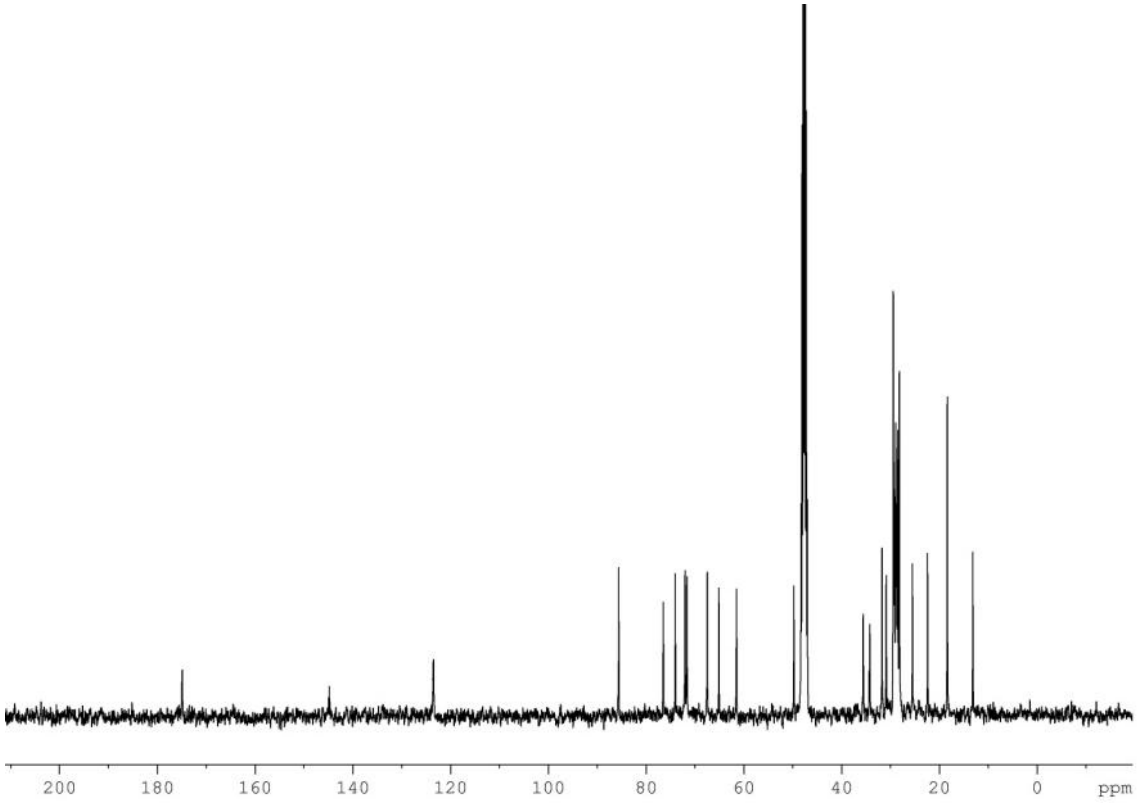
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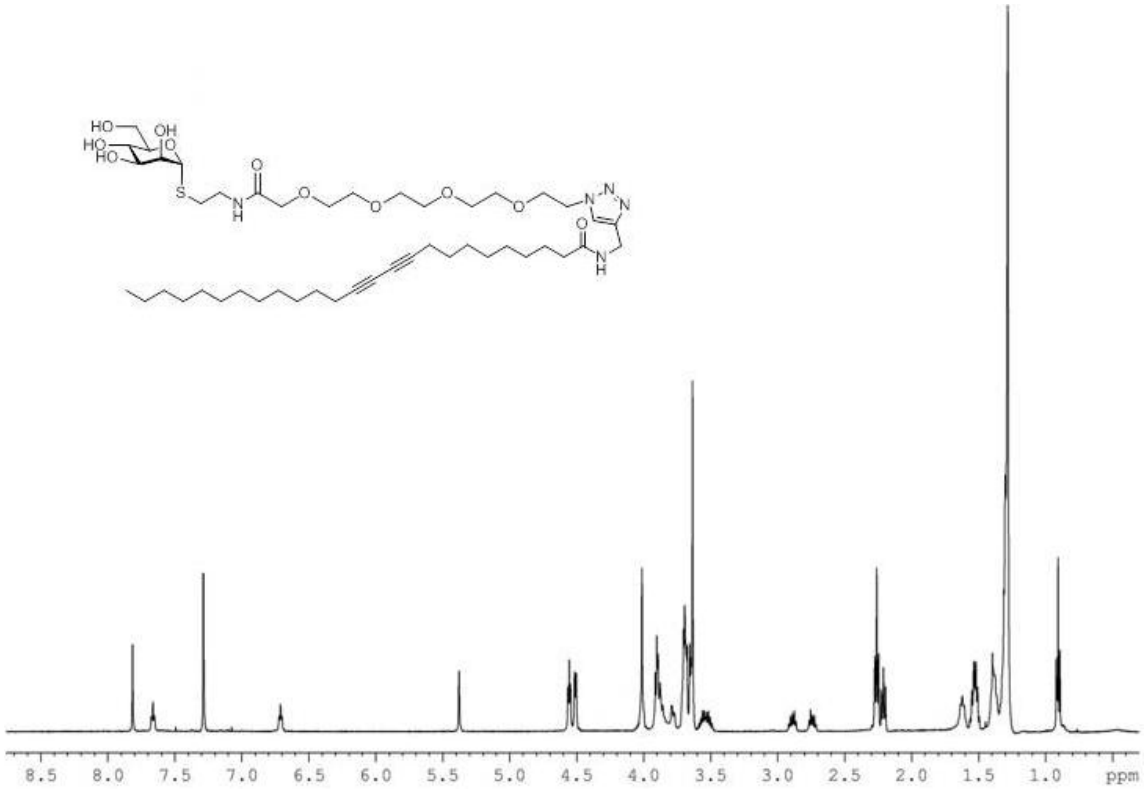
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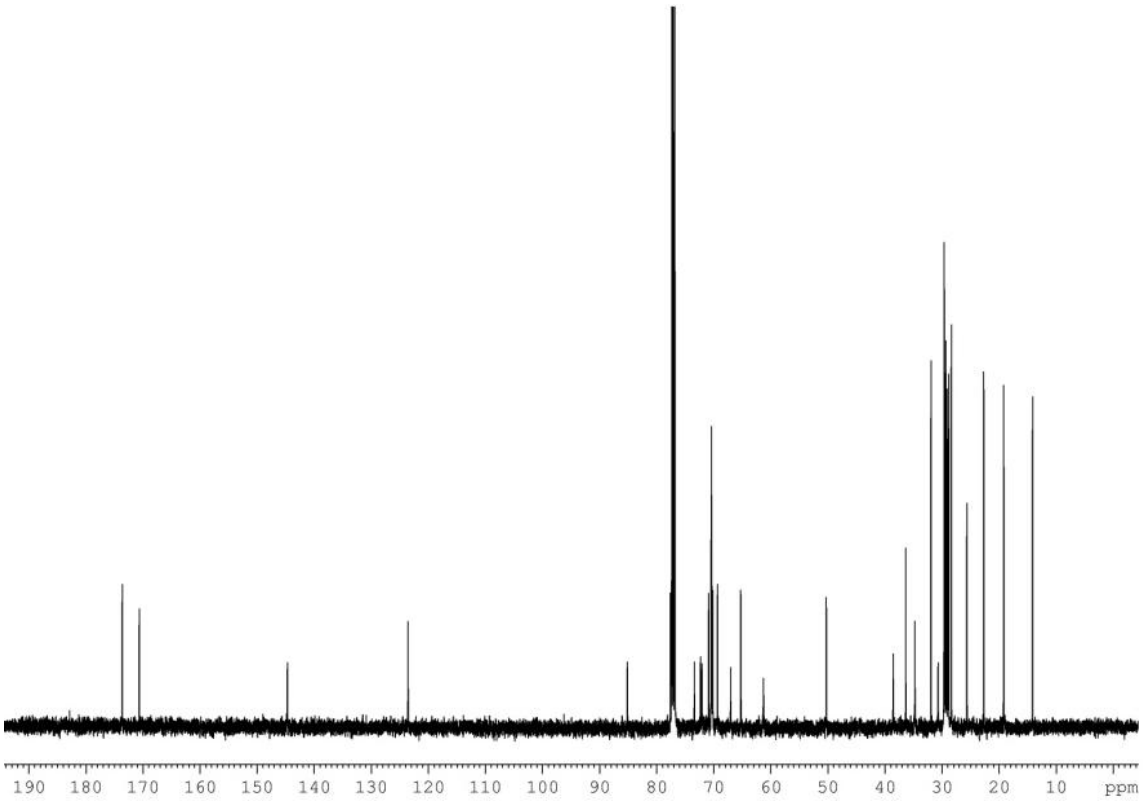
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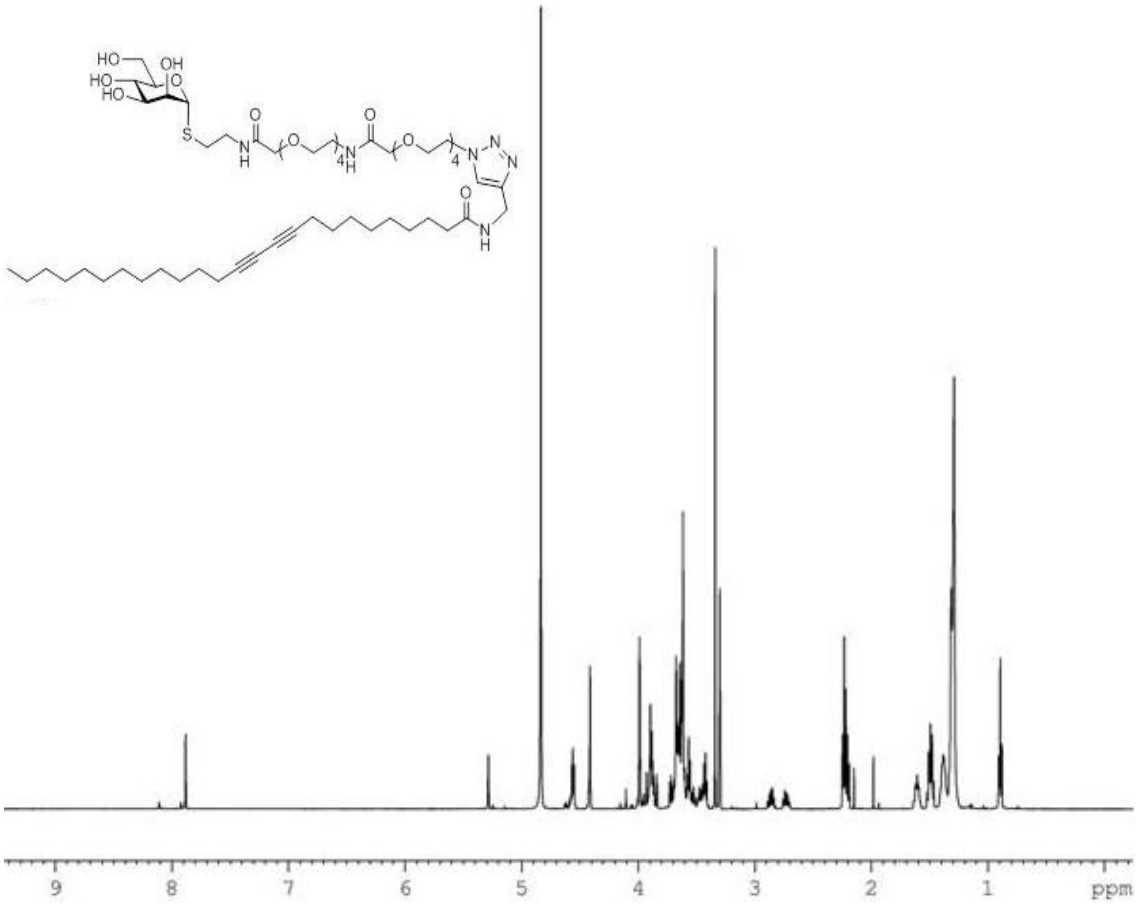
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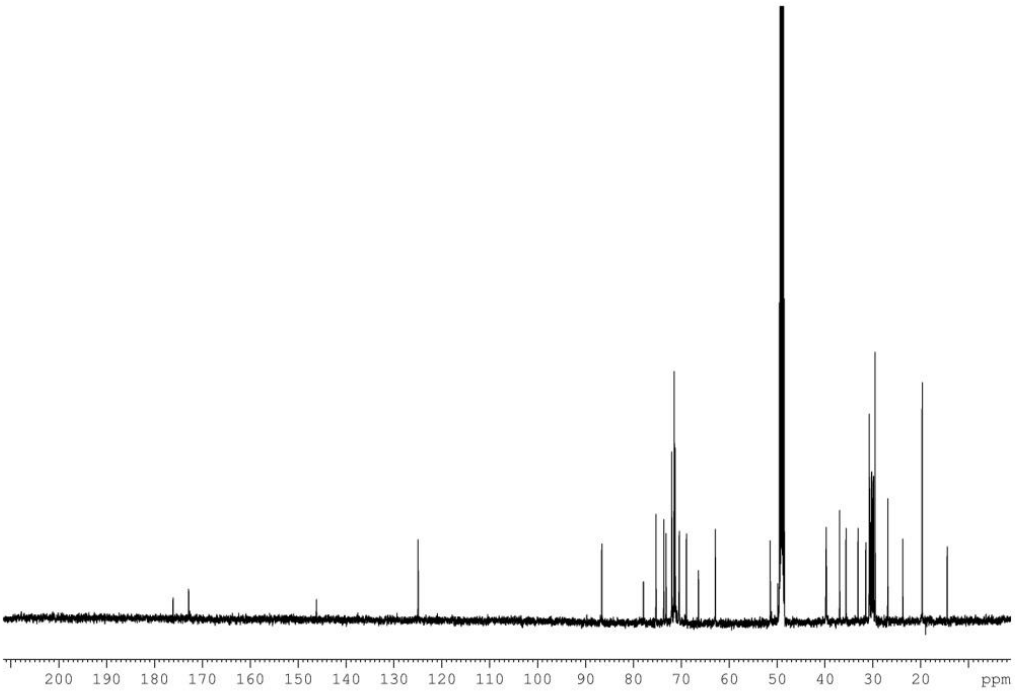
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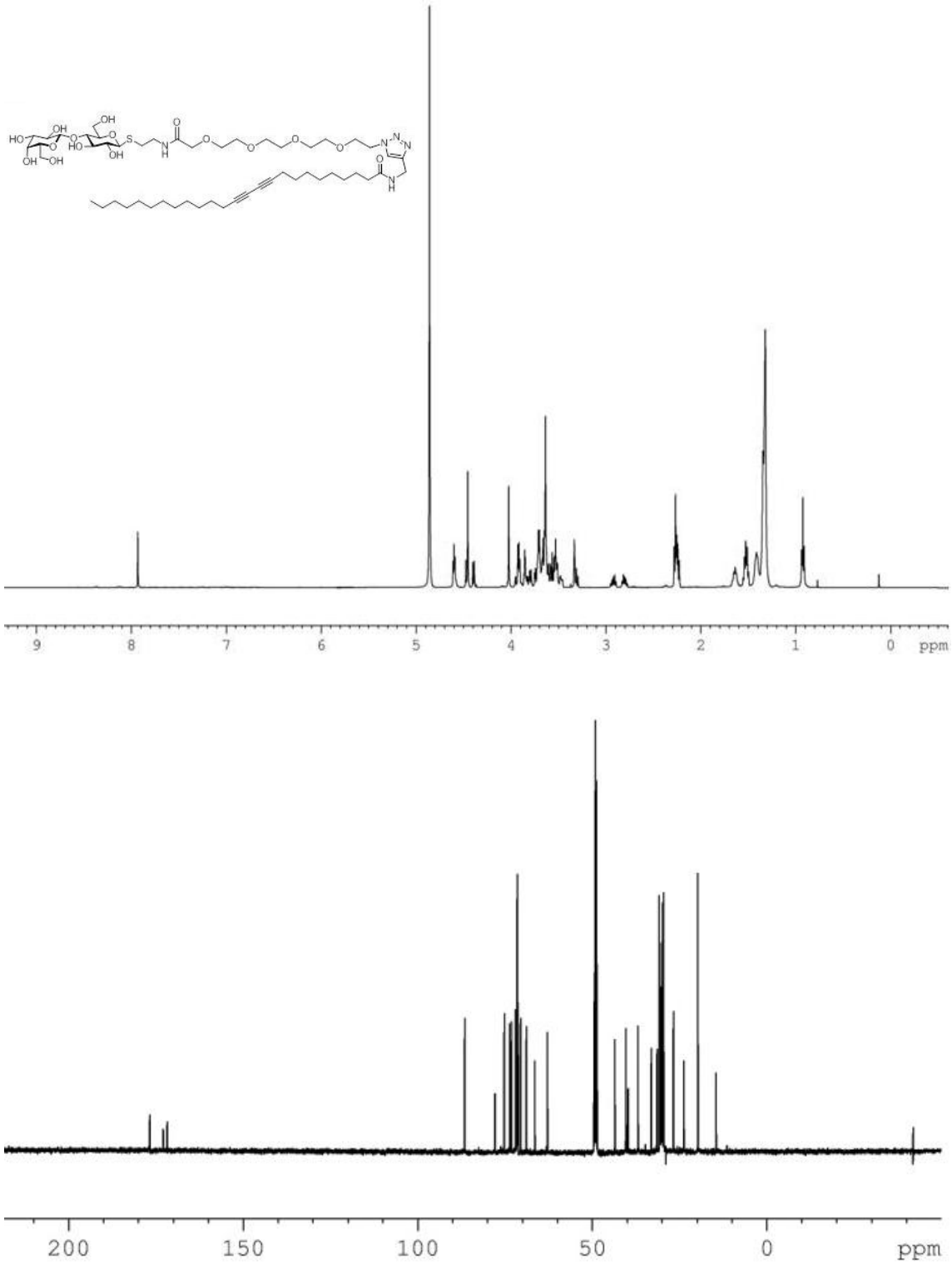
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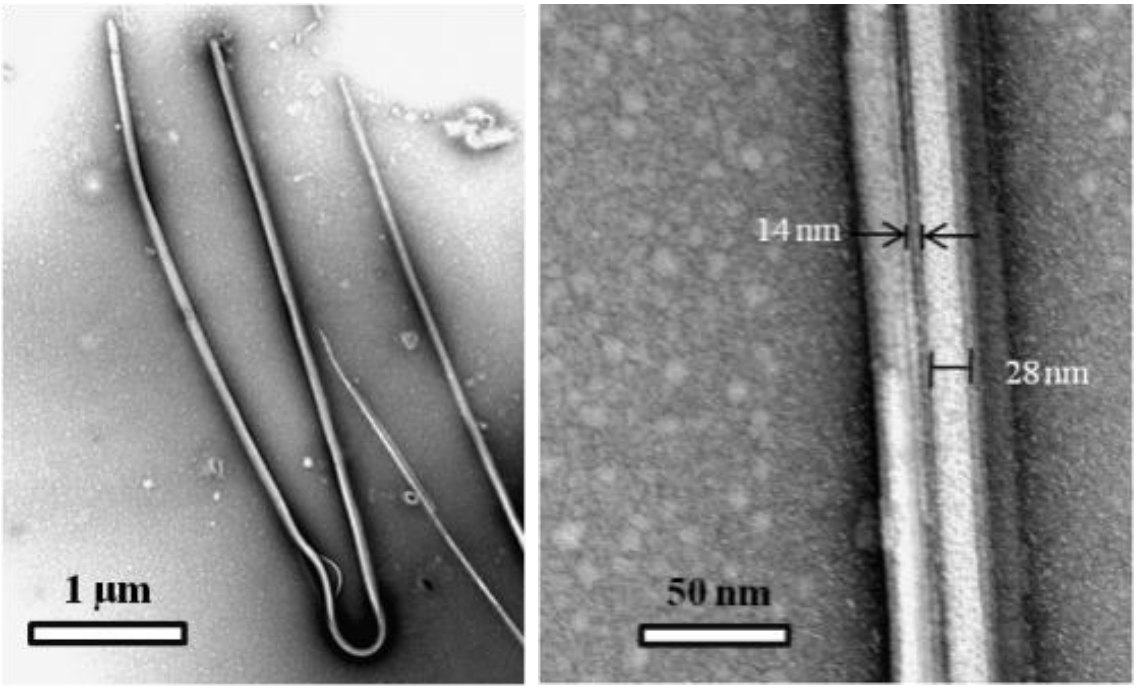
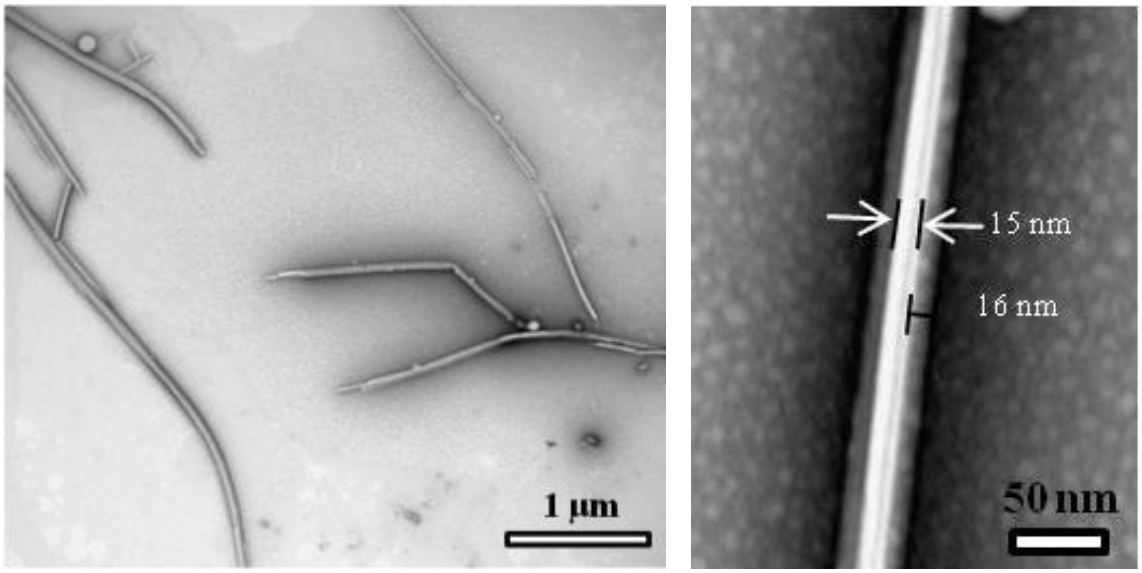
Supplementary SEM micrographs

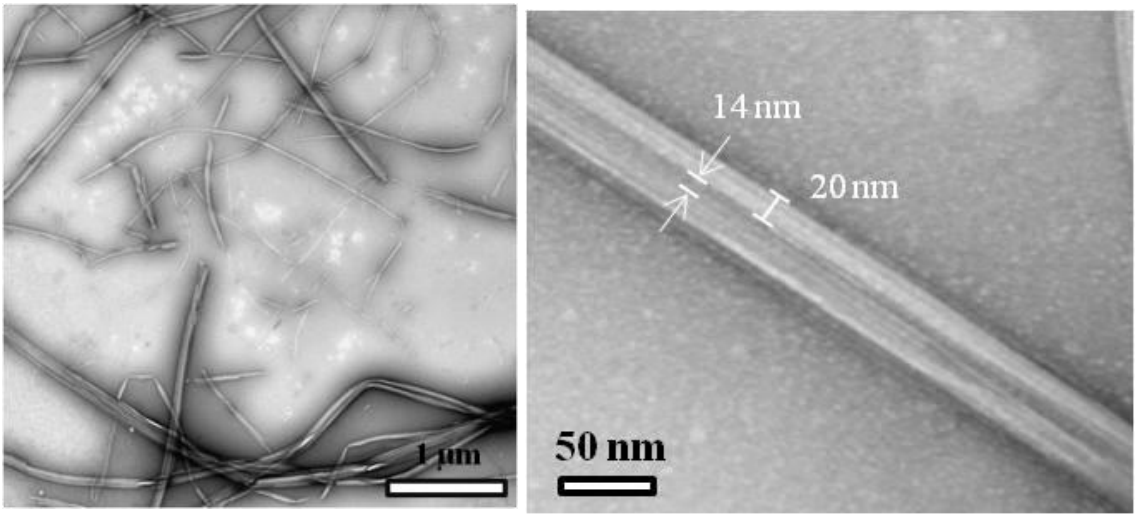
S1. TEM micrographs of derivative **9**



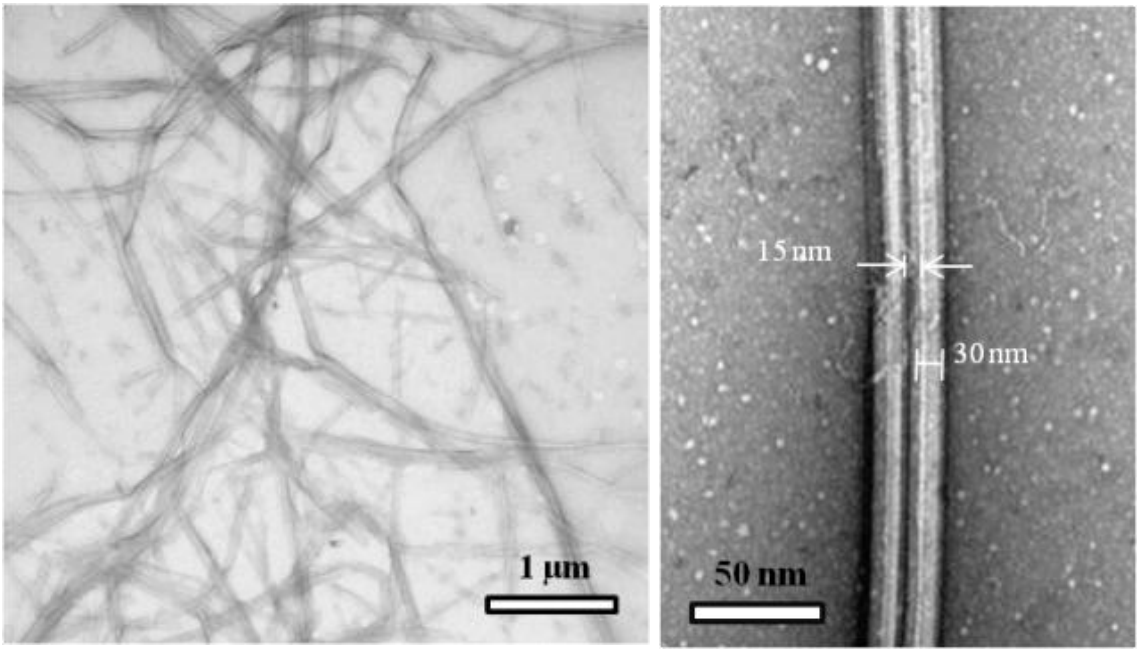
S2. TEM micrographs of derivative **6**



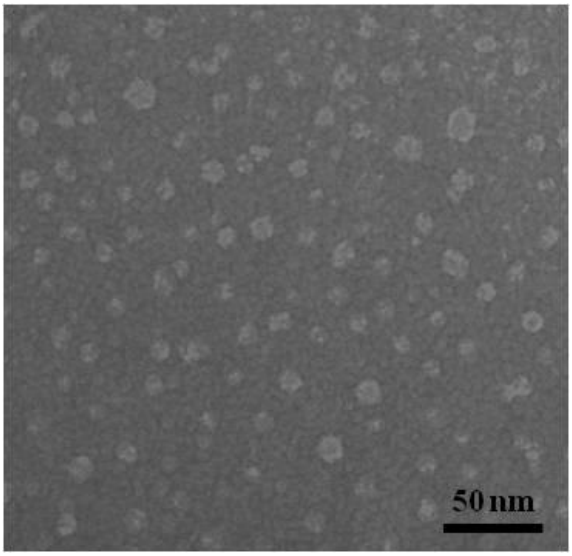
S3. TEM micrographs of derivative **7**



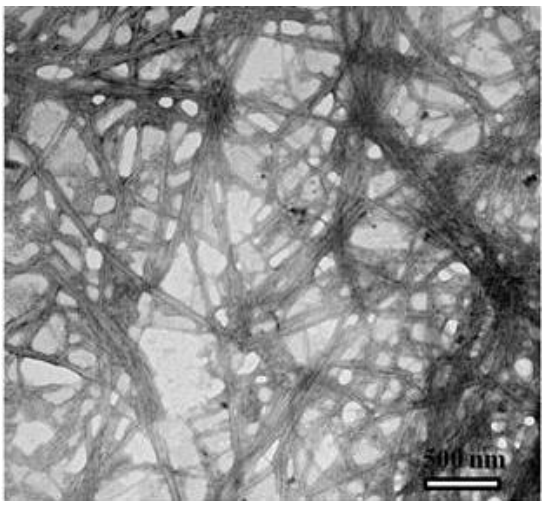
S4. TEM micrographs of derivative **8**

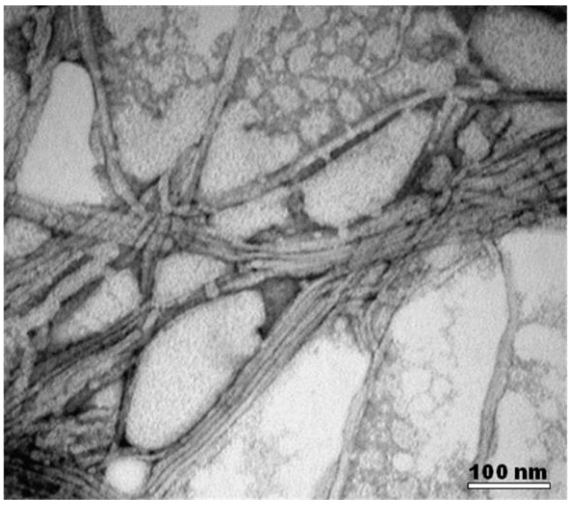


S5. TEM micrographs of derivative **9**



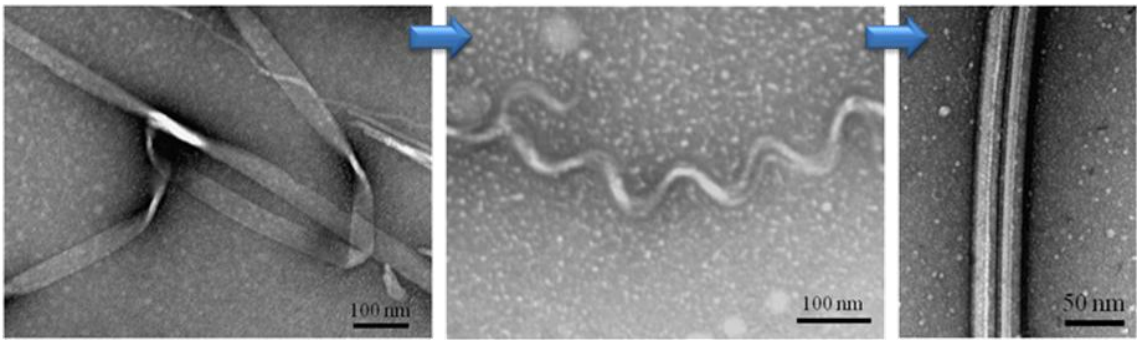
S6. Large-scale height TEM image of photopolymerized hydrogel derived from **7**



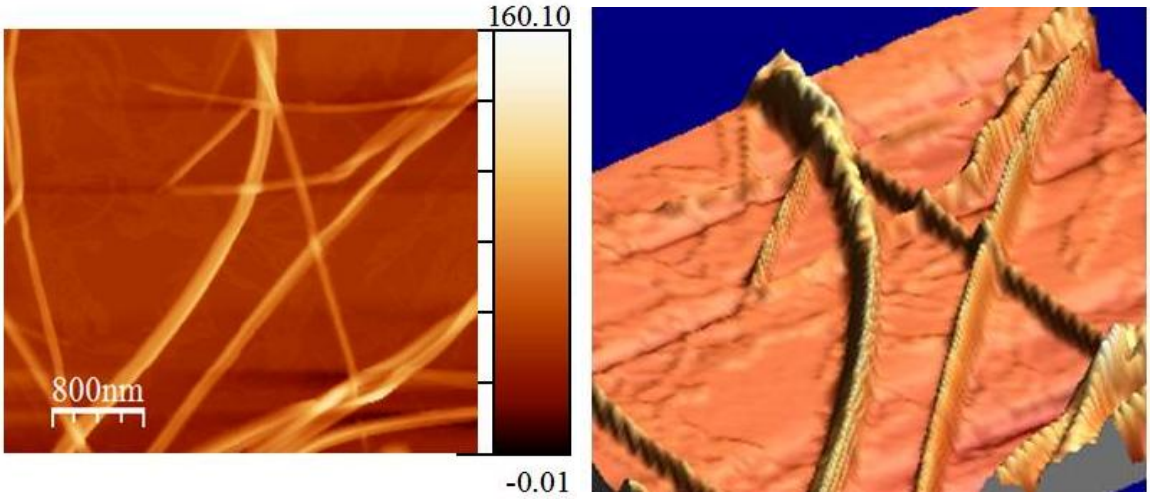


Supplementary AFM micrographs

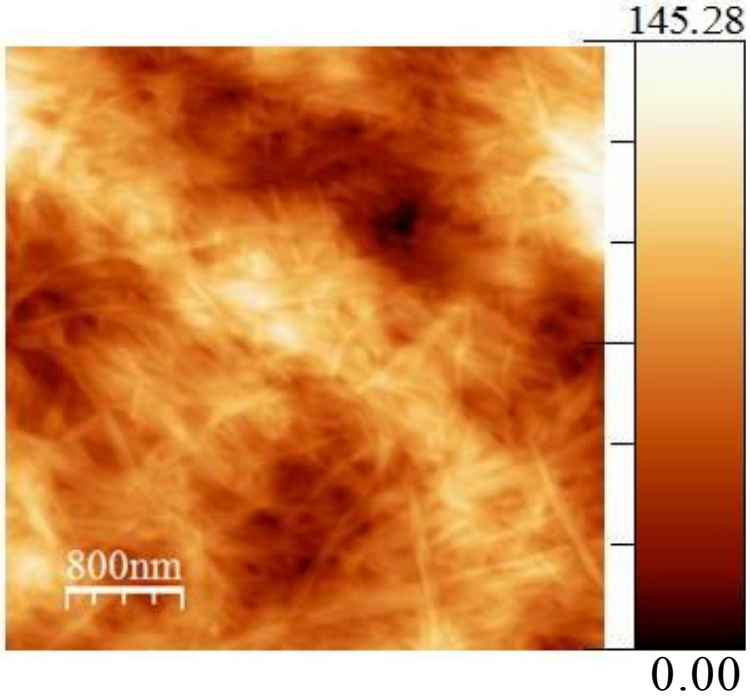
S7. Time-dependent set of TEM micrographs taken during the process of NLT formation from compound **8** in the curse of time.



S8. Bi-dimensional and tri-dimensional AFM images (tapping mode) of derivative **8**

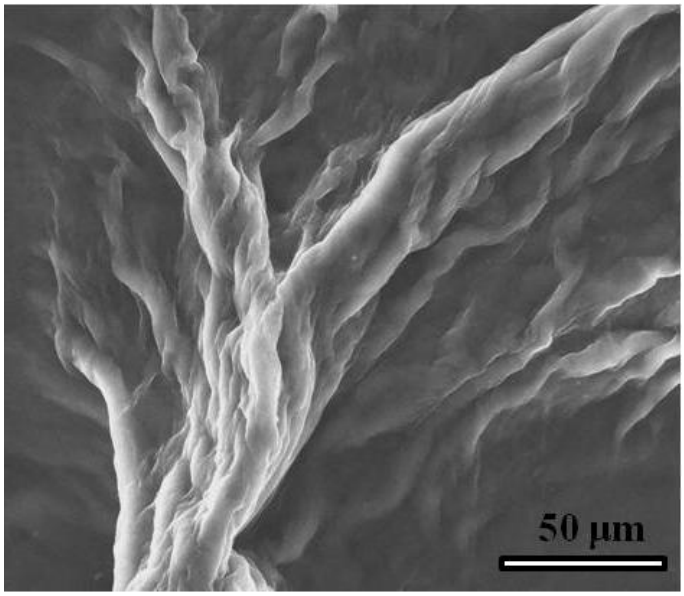


S9. AFM image of photo-polymerized hydrogel derived from **7**



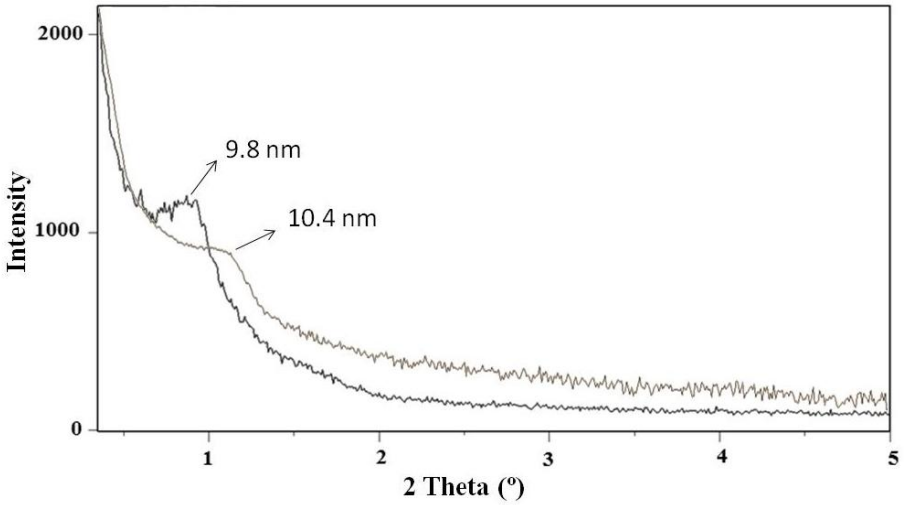
Supplementary SEM micrographs

S10. SEM image of photo-polymerized hydrogel derived from **7**

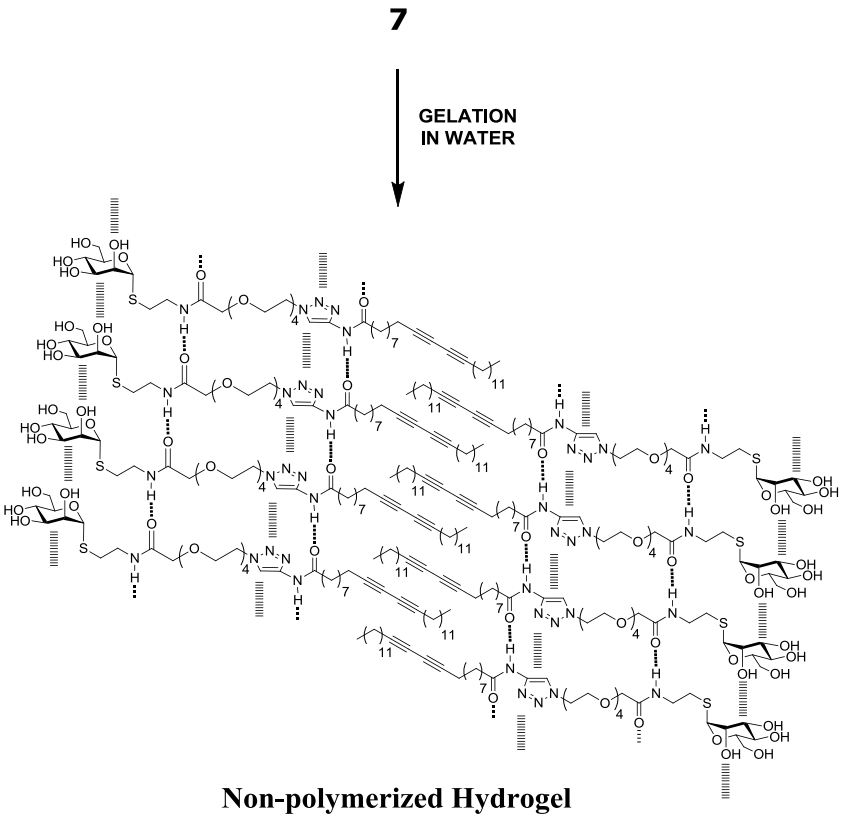


S11. Correlation functions obtained from the SAXS intensity profile of photo-polymerized hydrogel derived from **7** (dark grey) and LNTs derived from **9** (pale grey), together with their extrapolated at their intensity maxima of the characteristic distances of consecutive and repeat of assemblies partially ordered.

Supplementary SAXS correlation functions



S12. Synthesis and structural representations of the intimate structure of fibers composing the non-polymerized and photo-polymerized hydrogels derived from **7,** together with the H-bonding (sugars, amides), π-π (triazoles) and solvophobic interactions (lipophilic tails) participating in the assembly thereof.



Non-polymerized Hydrogel

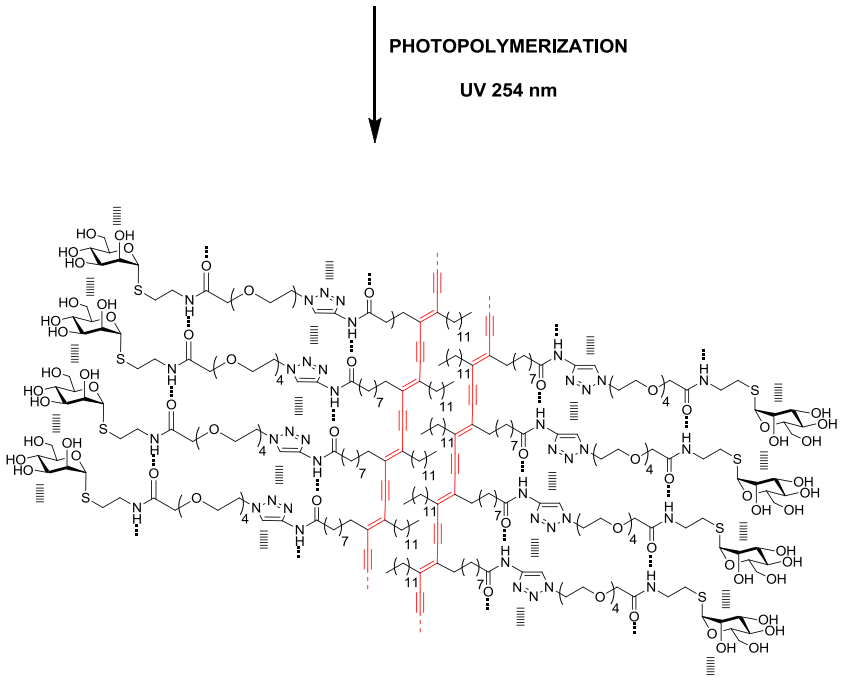


Photo-polymerized Hydrogel

S13. UV/Vis spectrum of topotecan (TPT) in water (above), and its spectrophotometrical calibration curve (below) used to study its release from the photo-polymerized hydrogel derived from **7**.