Supporting information

Supramolecular gels derived from nucleoside based bolaamphiphiles as a light-sensitive soft material

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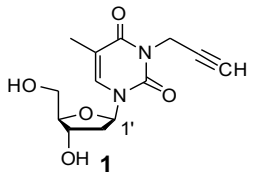
Synthesis

Reactions requiring anhydrous conditions were conducted with dry solvents under an inert atmosphere (argon). All other solvents or commercially available chemicals (Fluka, Sigma-Aldrich, Alfa-Aesar) were used as received. Reactions under microwaves conditions were conducted using a Discover® SP (CEM Corporation, France). Analytical thin layer chromatography (TLC) was carried out on aluminum-baked silica gel 60 F_{254} pre-coated plates (Merck) visualized using UV light (254 nm) and/or revealed with 10% conc. H_2SO_4 solution in ethanol or 1% aqueous $KMnO_4$ followed by heating. Column chromatography was performed on silica gel (0.043-0.063 mm). Compounds were characterized by ^1H, ^{13}C, COSY, HSQC experiments on Bruker Avance 300 (^1H: 300 MHz, ^{13}C: 75 MHz), Bruker Avance DPX 500 (^1H: 500 MHz, ^{13}C: 125 MHz) and Bruker Avance III 600 (^1H: 600 MHz) spectrometers. Chemical shifts (δ) are given in parts per million (ppm) and coupling constants J in Hertz (Hz); peak multiplicity is reported as follow: s = singlet, bs = broad singlet, d = doublet, t = triplet, m = multiplet. High Resolution Mass Spectrometry was performed on a Waters Q-TOF 2 (IECB, Bordeaux, France) and a Thermo Fisher Q-Exactive (CRMPO, Rennes, France) spectrometers in the positive electrospray ionization (ESI) mode.

***N*3-propargylthymidine (1)**



1

Chemical Formula: $C_{13}H_{16}N_2O_5$
Molecular Weight: 280,28

In a dry vial under an argon atmosphere, thymidine (500 mg, 2.06 mmol) was dissolved in anhydrous DMF (5 mL). After complete dissolution, NaH (60 % dispersion in oil, 95 mg, 2.37 mmol, 1.15 equiv) was added by portions. The mixture was firstly submitted to a microwave activation step (2 min, 40 °C, 200 W), then propargyl bromide (80 wt. % in toluene, 275 µl, 2.47 mmol, 1.2 equiv) was added, followed by a second activation step (45 min, 40 °C, 200 W). The reaction medium was quenched with MeOH (5 mL) and the solvents were evaporated under reduced pressure. The crude product was purified by flash chromatography on silica gel eluting with CH_2Cl_2/MeOH (90:10) to provide the title compound as a white solid (487 mg, 84 %).

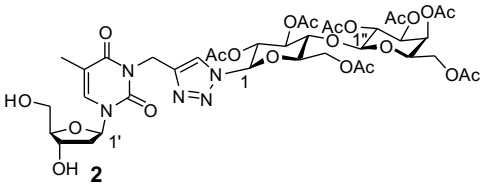
Rf: 0.50 (CH_2Cl_2/MeOH 90:10)

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 1.95 (d, *J*= 1.1 Hz, 3H, CH_3 thymine), 2.17 (t, *J*= 2.4 Hz, 1H, CH propargyl), 2.30-2.42 (m, 2H, H-2'), 2.42-2.51 (m, 2H, OH), 3.89 (ddd, *J*= 3.0, 11.8, 26.9 Hz, 2H, H-5'), 4.02 (AB system, *J*= 5.6 Hz, 1H, H-4'), 4.56-4.63 (m, 1H, H-3'), 4.70 (d, *J*= 2.3 Hz, 2H, CH_2 propargyl), 6.24 (apparent t, *J*= 6.7, 6.9 Hz, 1H, H-1'), 7.44 (d, *J*= 1.2 Hz, 1H, H-6 thymine).

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 13.4 (CH_3 thymine), 30.6 (CH_2 propargyl), 40.4 (C-2'), 62.5 (C-5'), 70.9 (CH propargyl), 71.6 (C-3'), 78.2 (C propargyl), 87.0 (C-4'), 87.3 (C-1'), 110.6 (C-5 thymine), 135.3 (C-6 thymine), 150.4, 162.6 (C=O thymine).

HRMS (ESI): (M+Na) Calcd. 303.0951, Found 303.0957.

***N*3-[(1-(2,3,6,2',3',4',6'-hepta-*O*-acetyl-*β*-D-lactcopyranosyl)-1*H*-1,2,3-triazol-4-yl)methyl]thymidine (2)**



Chemical Formula: $C_{39}H_{51}N_5O_{22}$
Molecular Weight: 941,85

Compound **1** (900 mg, 3.21 mmol) and 1-deoxy-1-azido-2,3,6,2',3',4',6'-hepta-*O*-acetyl-*β*-D-lactopyranose[1] (2.33 g, 3.53 mmol, 1.1 equiv) were first dissolved in 20 mL of ^{t}BuOH/H_2O (1:1). Copper sulfate pentahydrate (80 mg, 0.32 mmol, 0.1 equiv) and sodium ascorbate (127 mg, 0.64 mmol, 0.2 equiv) were successively added and the mixture was stirred at 65 °C for 15 hours. Solvents were removed under reduced pressure and the resulting solid was washed with water until washings were colorless. The crude product was purified by flash chromatography on silica gel eluting with EtOAc /MeOH (90:10) to provide the title compound as a white solid (1.94 g, 64 %).

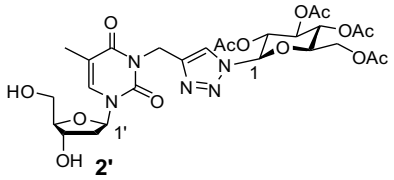
Rf: 0.40 (EtOAc/MeOH 90:10)

^{1}H NMR (300 MHz, acetone-*d6*) δ (ppm): 1.77 (s, 3H, OAc), 1.85 (d, *J*= 1.1 Hz, 3H, CH_3 thymine), 1.91 (s, 3H, OAc), 2.01-2.09 (m, 12H, OAc), 2.13 (s, 3H, OAc), 2.22-2.30 (m, 2H, H-2'), 3.75-3.83 (m, 2H, H-5'), 3.95 (AB system, *J*= 5.3 Hz, 1H, H-4'), 4.10-4.24 (m, 5H, H-4, H-5", H-6a, H-6"), 4.24-4.33 (m, 2H, H-5, OH), 4.39-4.59 (m, 3H, H-3', H-6b, OH), 4.90 (d, *J*= 7.4 Hz, 1H, H-1"), 5.03-5.13 (m, 2H, H-2", H-3"), 5.13-5.26 (m, 2H, NCH_2 triazole), 5.35-5.39 (m, 1H, H-4"), 5.41-5.50 (m, 1H, H-3), 5.55 (dd, *J*= 9.2, 9.5 Hz, 1H, H-2), 6.16 (d, *J*= 9.1 Hz, 1H, H-1), 6.36 (apparent t, *J*= 6.6, 6.9 Hz, 1H, H-1'), 7.85-7.90 (m, 1H, H-6 thymine), 8.00-8.05 (m, 1H, CH triazole).

^{13}C NMR (75 MHz, acetone-*d6*) δ (ppm): 13.3 (CH_3 thymine), 20.3, 20.6-20.8, 20.9 (OAc), 36.7 (NCH_2 triazole), 41.3 (C-2'), 61.9 (C-6"), 62.8 (C-5'), 63.1 (C-6), 68.1 (C-4"), 70.0 (C-2" or C-3"), 71.5 (C-2 or C-3, C-5), 71.8 (C-2" or C-3"), 72.1 (C-3'), 73.6 (C-2 or C-3), 76.4, 76.9 (C-4, C-5"), 85.7 (C-1), 86.5 (C-1'), 88.7 (C-4'), 101.8 (C-1"), 109.9 (C-5 thymine), 123.5 (CH triazole), 135.9 (C-6 thymine), 144.9 (C-4 triazole), 151.6, 163.5 (C=O thymine), 169.4, 169.8, 170.2, 170.3, 170.7, 170.8, 170.9 (C=O acetyl).

HRMS (ESI): (M+Na) Calcd. 964.2918, Found 964.2923.

_N_3-[(1-(2,3,4,6-tetra-_O_-acetyl-_β_-D-glucopyranosyl)-1_H_-1,2,3-triazol-4-yl)methyl]thymidine (2')



2'

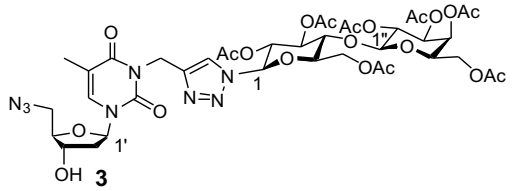
Chemical Formula: $C_{27}H_{35}N_5O_{14}$
Molecular Weight: 653,60

Compound **1** (1.94 g, 6.92 mmol) and 1-deoxy-1-azido-2,3,4,6-tetra-_O_-acetyl-_β_-D-glucopyranose[1] (2.58 g, 6.92 mmol, 1 equiv) were first dissolved in 60 mL of ^{t}BuOH/H_2O (1:1). Copper sulfate pentahydrate (172 mg, 0.69 mmol, 0.1 equiv) and sodium ascorbate (273 mg, 1.38 mmol, 0.2 equiv) were successively added and the mixture was heated at 65 °C for 15 hours. Solvents were removed under reduced pressure and the resulting solid was washed with water until washings were colorless. The crude product was purified by flash chromatography on silica gel eluting with EtOAc /MeOH (95:5) to provide the title compound as a white solid (2.90 g, 64 %). NMR spectroscopic data were in agreement with those previously described.[2]

Rf: 0.40 (EtOAc/MeOH 95/5)

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 1.84 (s, 3H, OAc), 1.91 (s, 3H, CH_3 thymine), 2.02 (s, 3H, OAc), 2.06 (s, 3H, OAc), 2.08 (s, 3H, OAc), 2.30-2.39 (m, 2H, H-2'), 3.79-3.91 (m, 2H, H-5'), 3.94-4.04 (m, 2H, H-5, OH), 4.07-4.34 (m, 3H, H-6, H-4'), 4.52-4.63 (m, 1H, H-3'), 5.10-5.33 (m, 3H, H-4, NCH_2 triazole), 5.34-5.50 (m, 2H, H-2, H-3), 5.83 (d, J= 8.9 Hz, 1H, H-1), 6.23 (t, J= 6.5 Hz, 1H, H-1'), 7.47-7.56 (m, 1H, H-6 thymine), 7.87 (s, 1H, CH triazole).

5'-azido-*N*3-[(1-(2,3,6,2',3',4',6'-hepta-*O*-acetyl-*β*-D-lactopyranosyl)-1*H*-1,2,3-triazol-4-yl)methyl]-5'-deoxythymidine (3)



Chemical Formula: $C_{39}H_{50}N_8O_{21}$
Molecular Weight: 966,86

Compound **2** (1.88 g, 2.00 mmol) was first dissolved in anhydrous DMF (20 mL). Then, triphenylphosphine (630 mg, 2.40 mmol, 1.2 equiv), sodium azide (650 mg, 10.00 mmol, 5 equiv) and carbon tetrabromide (796 mg, 2.40 mmol, 1.2 equiv) were successively added. The reaction mixture was stirred at room temperature for 24 hours and then treated with 50 mL of a 5 % w/v $NaHCO_3$ aqueous solution. After stirring for a further 30 min, the mixture was extracted with CH_2Cl_2 and the organic phase washed with water. After drying over Na_2SO_4 the solvents were removed under reduced pressure. The resulting solid was purified by flash chromatography on silica gel eluting with a step gradient of MeOH starting from 1 % to 5 % v/v in CH_2Cl_2 to provide the title compound as a white solid (1.17 g, 61 %).

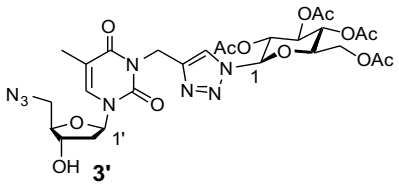
Rf: 0.20 (CH_2Cl_2/MeOH 95:5)

^{1}H NMR (300 MHz, acetone-*d6*) δ (ppm): 1.77 (s, 3H, OAc), 1.89 (d, *J*= 1.2 Hz, 3H, CH_3 thymine), 1.91 (s, 3H, OAc), 2.03 (s, 3H, OAc), 2.04 (s, 6H, OAc), 2.05 (s, 3H, OAc), 2.13 (s, 3H, OAc), 2.26-2.41 (m, 2H, H-2'), 3.59-3.78 (m, 2H, H-5'), 3.98-4.06 (m, 1H, H-4'), 4.11-4.25 (m, 5H, H-4, H-6a, H-5'', H-6''), 4.25-4.32 (m, 1H, H-5), 4.40-4.48 (m, 1H, H-3'), 4.51-4.58 (m, 1H, H-6b), 4.63 (d, *J*= 4.3 Hz, 1H, OH-3'), 4.90 (d, *J*= 7.6 Hz, 1H, H-1''), 5.04-5.15 (m, 2H, H-2'', H-3''), 5.15-5.27 (m, 2H, NCH_2 triazole), 5.38 (dd, *J*= 1.2, 3.2 Hz, 1H, H-4''), 5.46 (dd, *J*= 8.2, 9.6 Hz, 1H, H-3), 5.55 (apparent t, *J*= 9.1, 9.6 Hz, 1H, H-2), 6.16 (d, *J*= 9.1 Hz, 1H, H-1), 6.38 (t, *J*= 6.8 Hz, 1H, H-1'), 7.58 (d, *J*= 1.2 Hz, 1H, H-6 thymine), 8.01-8.05 (m, 1H, CH triazole).

^{13}C NMR (75 MHz, acetone-*d6*) δ (ppm): 13.3 (CH_3 thymine), 20.3, 20.6-20.8, 21.0 (OAc), 36.8 (NCH_2 triazole), 40.2 (C-2'), 53.1 (C-5'), 61.9 (C-6''), 63.1 (C-6), 68.1 (C-4''), 70.0 (C-3''), 71.5 (C-2), 71.8 (C-5), 72.3 (C-3', C-2''), 73.6 (C-3), 76.4, 76.9 (C-5'', C-4), 85.7 (C-1), 86.0 (C-4'), 86.4 (C-1'), 101.8 (C-1''), 109.9 (C-5 thymine), 123.6 (CH triazole), 135.4 (C-6 thymine), 144.9 (C-4 triazole), 151.6, 163.5 (C=O thymine), 169.4, 169.8, 170.2, 170.3, 170.7, 170.8, 170.9 (C=O acetyl).

HRMS (ESI): (M+Na) Calcd. 989.2983, Found 989.2988.

5'-azido-*N*3-[(1-(2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranosyl)-1*H*-1,2,3-triazol-4-yl)methyl]-5'-deoxythymidine (3')



3'

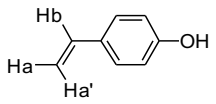
Chemical Formula: $C_{27}H_{34}N_8O_{13}$
Molecular Weight: 678,61

Compound **2'** (2.02 g, 3.09 mmol) was dissolved in anhydrous DMF (30 mL). Then, triphenylphosphine (973 mg, 3.71 mmol, 1.2 equiv), sodium azide (1.00 g, 15.45 mmol, 5 equiv) and carbon tetrabromide (1.23 g, 3.71 mmol, 1.2 equiv) were successively added. The reaction mixture was stirred at room temperature for 24 hours and then treated with 50 mL of a 5 % w/v $NaHCO_3$ aqueous solution. After stirring for a further 30 min, the mixture was extracted with CH_2Cl_2 and the organic layer washed with water. After drying over Na_2SO_4 the solvents were removed under reduced pressure. The resulting solid was purified by flash chromatography on silica gel eluting with a step gradient of MeOH starting from 1 % to 3 % v/v in CH_2Cl_2 to provide the title compound as a white solid (1.50 g, 71 %). NMR spectroscopic data were in agreement with those previously described.[1]

Rf: 0.30 (CH_2Cl_2/MeOH 95:5)

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 1.83 (s, 3H, OAc), 1.95 (s, 3H, CH_3 thymine), 2.01 (s, 3H, OAc), 2.05 (s, 3H, OAc), 2.08 (s, 3H, OAc), 2.15-2.27 (m, 1H, H-2'a), 2.34-2.46 (m, 1H, H-2'b), 3.67 (ddd, *J*= 3.4, 13.2, 39.3 Hz, 2H, H-5'), 3.94-4.02 (m, 1H, H-5), 4.02-4.09 (m, 1H, H-4'), 4.09-4.33 (m, 2H, H-6), 4.40-4.51 (m, 1H, H-3'), 5.13-5.33 (m, 3H, NCH_2 triazole, H-4), 5.33-5.50 (m, 2H, H-2, H-3), 5.84 (d, *J*= 9.0 Hz, 1H, H-1), 6.33 (t, *J*= 6.7 Hz, 1H, H-1'), 7.36 (s, 1H, H-6 thymine), 7.86 (s, 1H, CH triazole).

4-hydroxystyrene (4)



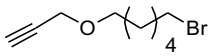
4

Chemical Formula: C_8H_8O
Molecular Weight: 120,15

An aqueous solution of 1.5 M KOH (28 mL, 4.63 mmol, 2.5 equiv) was added dropwise to 4-acetoxystyrene (283 µL, 1.85 mmol) at 0 °C and stirring continued at this temperature for 4 hours. Aqueous acetic acid (0.5 M solution, 8 mL) was added to bring the pH to 7. The mixture was then extracted with EtOAc, dried (Na_2SO_4) and concentrated under reduced pressure to give a white solid used in the next step without further purification (0.20 g, 90 %). NMR spectroscopic data were in agreement with those previously described.[3]

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 4.74-4.80 (m, 1H, OH), 5.13 (d, *J*= 10.8 Hz, 1H, Ha), 5.60 (d, *J*= 17.5 Hz, 1H, Ha'), 6.65 (dd, *J*= 10.9 Hz, 17.6 Hz, 1H, Hb), 6.76-6.83 (m, 2H, H ar), 7.27-7.35 (m, 2H, H ar).

1-bromo-6-propargyloxyhexane (5)



5

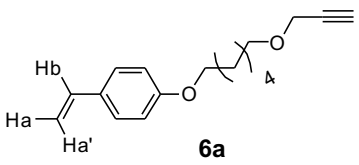
Chemical Formula: $C_9H_{15}BrO$
Molecular Weight: 219,12

To a solution of propargyl alcohol (1.16 mL, 20.00 mmol) in anhydrous DMF (40 mL) cooled at 0 °C, NaH (60 % dispersion in oil, 880 mg, 22.00 mmol, 1.1 equiv) was added by portions. After stirring for 30 min at room temperature, 1,6-dibromohexane (9.23 mL, 60.00 mmol, 3 equiv) was added at 0 °C. The mixture was stirred at room temperature for a further 15 hours and then quenched by the addition of a saturated NaCl aqueous solution (150 mL). The mixture was then extracted with petroleum ether and the organic layer washed with a saturated NaCl aqueous solution. The organic extracts were dried (Na_2SO_4) and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel eluting with a step gradient of EtOAc starting from 0 % to 10 % in petroleum ether to provide the title compound as a slightly yellow oil (2.23 g, 51 %). NMR spectroscopic data were in agreement with those previously described.[4]

Rf: 0.40 (petroleum ether/EtOAc 95:5)

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 1.27-1.47 (m, 4H, CH_2), 1.49-1.62 (m, 2H, C**H**$_2$CH$_2$O propargyl), 1.75-1.87 (m, 2H, C**H**$_2$CH$_2$Br), 2.39 (t, *J*= 2.3 Hz, 1H, CH propargyl), 3.35 (t, *J*= 6.8 Hz, 2H, CH_2O propargyl), 3.46 (t, *J*= 6.5 Hz, 2H, CH_2OBr), 4.05-4.09 (m, 2H, CH_2 propargyl).

4-[(6-(propargyloxy)hexyl)oxy]styrene (6a)



6a

Chemical Formula: $C_{17}H_{22}O_2$
Molecular Weight: 258,36

To a solution of 4-hydroxystyrene **4** (100 mg, 0.83 mmol) in anhydrous DMF (2 mL) was added potassium carbonate (138 mg, 1.00 mmol, 1.2 equiv) and the mixture was stirred for 5 min at room temperature, followed by the addition of compound **5** (219 mg, 1.00 mmol, 1.2 equiv). The reaction mixture was stirred at room temperature for a further 48 hours before evaporating under reduced pressure. The crude product was purified by flash chromatography on silica gel eluting with 100 % toluene to provide the title compound as a colorless oil (180 mg, 84 %).

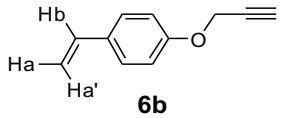
Rf: 0.20 (Toluene 100 %)

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 1.37-1.57 (m, 4H, CH_2), 1.58-1.71 (m, 2H, C**H**$_2$CH$_2$O propargyl), 1.73-1.87 (m, 2H, C**H**$_2$CH$_2$OPh), 2.44 (t, *J*= 2.4 Hz, 1H, CH propargyl), 3.53 (t, *J*= 6.5 Hz, 2H, CH_2O propargyl), 3.96 (t, *J*= 6.5 Hz, 2H, CH_2OPh), 4.14 (d, *J*= 2.4 Hz, 2H, CH_2 propargyl), 5.13 (dd, *J*= 0.9, 10.9 Hz, 1H, Ha), 5.62 (dd, *J*= 0.9, 17.6 Hz, 1H, Ha'), 6.67 (dd, *J*= 10.9 Hz, 17.6 Hz, 1H, Hb), 6.82-6.89 (m, 2H, H ar), 7.30-7.38 (m, 2H, H ar).

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 26.0 (CH_2), 29.3, 29.5 (**C**H_2CH$_2$OPh, **C**H_2CH$_2$O propargyl), 58.1 (CH_2 propargyl), 68.0 (CH_2OPh), 70.1 (CH_2O propargyl), 74.1 (CH propargyl), 80.2 (C propargyl), 111.5 (CHa, Ha'), 114.6, 127.4 (CH ar) 130.4 (Cq ar), 136.4 (CHb), 159.0 (Cq ar).

HRMS (ESI): (M+H) Calcd. 259.1693, Found 259.1696.

4-propargyloxystyrene (6b)



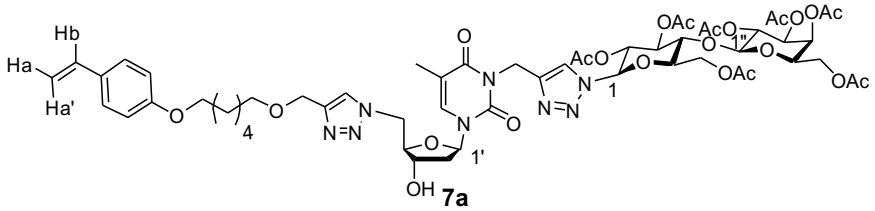
6b

Chemical Formula: $C_{11}H_{10}O$
Molecular Weight: 158,20

4-hydroxystyrene **4** (80 mg, 0.67 mmol) was first dissolved in anhydrous DMF (2 mL). Potassium carbonate (111 mg, 0.80 mmol, 1.2 equiv) was added and the solution was stirred 5 min at room temperature. Propargyl bromide (80 % wt. in toluene, 89 µL, 0.80 mmol, 1.2 equiv) was added and the reaction stirred at room temperature for a further 48 hours. The mixture was concentrated under reduced pressure and the crude product purified by flash chromatography on silica gel eluting with petroleum ether/EtOAc (93:7) to provide the title compound as a colorless oil (88 mg, 83 %).

Rf: 0.50 (petroleum ether/EtOAc 93:7)
^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.50-2.61 (m, 1H, CH propargyl), 4.71 (d, *J*= 2.1 Hz, 2H, CH_2 propargyl), 5.19 (d, *J*= 10.9 Hz, 1H, Ha), 5.67 (d, *J*= 17.6 Hz, 1H, Ha'), 6.70 (dd, *J*= 10.9 Hz, 17.6 Hz, 1H, Hb), 6.89-7.04 (m, 2H, H ar), 7.32-7.48 (m, 2H, H ar).
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 55.8 (CH_2 propargyl), 75.7 (CH propargyl), 78.6 (C propargyl), 112.2 (CHa, Ha'), 115.0, 127.5 (CH ar) 131.3 (Cq ar), 136.2 (CHb), 157.3 (Cq ar).
HRMS (ESI): (M+H) Calcd. 159.0803, Found 159.0810.

5'-[4-({[6-(4-ethenylphenoxy)hexyl]oxy}methyl)-1*H*-1,2,3-triazol-1-yl]-*N*3-[(1-(2,3,6,2',3',4',6'-hepta-*O*-acetyl-*β*-D-lactopyranosyl)-1*H*-1,2,3-triazol-4-yl)methyl]-5'-deoxythymidine (7a)



7a

Chemical Formula: $C_{56}H_{72}N_8O_{23}$
Molecular Weight: 1225,23

Compounds **3** (442 mg, 0.46 mmol) and **6a** (132 mg, 0.51 mmol, 1.1 equiv) were dissolved with stirring in 30 mL ^{t}BuOH/H_2O (1:1). Copper sulfate pentahydrate (11 mg, 0.046 mmol, 0.1 equiv) and sodium ascorbate (18 mg, 0.092 mmol, 0.2 equiv) were successively added and the

mixture was heated at 65 °C for 15 hours. Solvents were removed under reduced pressure and the resulting green solid was washed with water until washings were colorless. The crude product was purified by flash chromatography on silica gel eluting with CH_2Cl_2 /MeOH (93:7) to provide the title compound as a white solid (464 mg, 83 %).

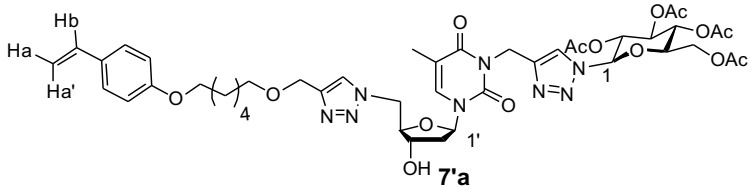
Rf: 0.40 (CH_2Cl_2/MeOH 93:7)

^{1}H NMR (300 MHz, acetone-*d6*) δ (ppm): 1.34-1.50 (m, 4H, CH_2), 1.50-1.64 (m, 2H, C**H**$_2$$CH_2OCH_2$ triazole), 1.67-1.78 (m, 5H, C**H**$_2$$CH_2OPh$, OAc), 1.86 (s, 3H, CH_3 thymine), 1.91 (s, 3H, OAc), 2.01 (s, 3H, OAc), 2.03 (s, 3H, OAc), 2.04 (s, 3H, OAc), 2.12 (s, 3H, OAc), 2.18-2.39 (m, 2H, H-2'), 3.42-3.55 (m, 2H, C**H**$_2$$OCH_2$ triazole), 3.96 (t, *J*= 6.5 Hz, 2H, CH_2OPh) , 4.07-4.35 (m, 7H, H-4, H-5, H-6a, H-4', H-5", H-6"), 4.47-4.61 (m, 4H, H-3', OCH_2 triazole, H-6b), 4.68-4.86 (m, 2H, H-5'), 4.90 (d, *J*= 7.5 Hz, 1H, H-1"), 5.03-5.26 (m, 5H, NCH_2 triazole, H-2", H-3", Ha), 5.37 (dd, *J*= 0.8, 3.2 Hz, 1H, H-4'), 5.41-5.59 (m, 2H, H-2, H-3), 5.62 (dd, *J*= 1.1, 17.6 Hz, 1H, Ha'), 6.16 (d, *J*= 9.1 Hz, 1H, H-1), 6.31 (t, *J*= 6.8 Hz, 1H, H-1'), 6.67 (dd, *J*= 11.0, 17.7 Hz, 1H, Hb), 6.82-6.93 (m, 2H, H ar), 7.28 (s, 1H, H-6 thymine), 7.33-7.43 (m, 2H, H ar), 7.96 (s, 1H, CH triazole), 8.06 (s, 1H, CH triazole).

^{13}C NMR (75 MHz, acetone-*d6*) δ (ppm): 13.2 (CH_3 thymine), 20.2-20.9 (OAc), 26.5, 26.6 (CH_2), 29.9, 30.3 (**C**H_2CH_2OPh, **C**$H_2CH_2OCH_2$ triazole), 36.7 (NCH_2 triazole), 39.6 (C-2'), 52.0 (C-5'), 61.8 (C-6"), 63.0 (C-6), 64.6 (OCH_2 triazole), 68.1 (C-4"), 68.5 (CH_2OPh), 70.0 (C-3"), 70.9 (**C**H_2OCH_2 triazole), 71.4 (C-2, C-5), 71.7 (C-2"), 72.2 (C-3'), 73.6 (C-3), 76.4, 76.8 (C-5", C-4), 85.4 (C-4'), 85.6 (C-1), 86.9 (C-1'), 101.7 (C-1"), 110.5 (C-5 thymine), 111.6 (CHa, Ha'), 115.3 (CH ar), 123.6, 125.1 (CH triazole), 128.2 (CH ar), 131.0 (Cq ar), 135.6 (C-6 thymine), 137.3 (CHb), 144.6, 145.9 (C-4 triazole), 151.4 (C=O thymine), 160.0 (Cq ar), 163.4 (C=O thymine), 169.4, 169.7, 170.1, 170.2, 170.6, 170.7, 170.9 (C=O acetyl).

HRMS (ESI): (M+H) Calcd. 1225.4789, Found 1225.4792.

5'-[4-({[6-(4-ethenylphenoxy)hexyl]oxy}methyl)-1*H*-1,2,3-triazol-1-yl]-*N*3-[(1-(2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranosyl)-1*H*-1,2,3-triazol-4-yl)methyl]-5'-deoxythymidine (7'a)



7'a

Chemical Formula: $C_{44}H_{56}N_8O_{15}$
Molecular Weight: 936,97

Compounds **3'** (100 mg, 0.15 mmol) and **6a** (44 mg, 0.17 mmol, 1.1 equiv) were dissolved with stirring in 12 mL ^{t}BuOH/H_2O (1:1). Copper sulfate pentahydrate (4 mg, 0.015 mmol, 0.1 equiv) and sodium ascorbate (6 mg, 0.030 mmol, 0.2 equiv) were successively added and the mixture was heated at 65 °C for 15 hours. Solvents were removed under reduced pressure and the resulting green solid was washed with water until washings were colorless. The crude product was purified by flash chromatography on silica gel eluting with CH_2Cl_2 /MeOH (95:5) to provide the title compound as a white solid (120 mg, 85 %).

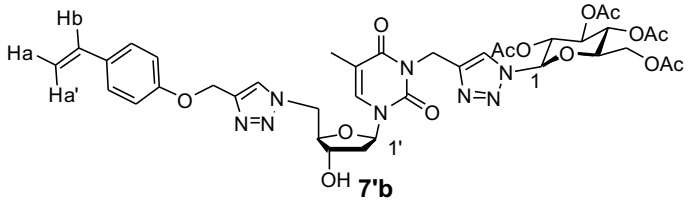
Rf: 0.50 (CH_2Cl_2/MeOH 95:5)

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 1.31-1.49 (m, 4H, CH_2), 1.53-1.64 (m, 2H, C**H**$_2$CH$_2$OCH$_2$ triazole), 1.68-1.77 (m, 2H, C**H**$_2$CH$_2$OPh), 1.80 (s, 3H, OAc), 1.87 (s, 3H, CH_3 thymine), 1.99 (s, 3H, OAc), 2.03 (s, 3H, OAc), 2.05 (s, 3H, OAc), 2.08-2.24 (m, 1H, H-2'a), 2.28-2.44 (m, 1H, H-2'b), 3.50 (t, *J*= 6.6 Hz, 2H, C**H**$_2$OCH$_2$ triazole), 3.91 (t, *J*= 6.5 Hz, 2H, CH$_2$OPh), 4.00 (ddd, *J*= 1.9, 4.5, 10.0 Hz, 2H, H-5), 4.05-4.17 (m, 1H, H-6a), 4.17-4.31 (m, 2H, H-4', H-6b), 4.43-4.60 (m, 3H, H-3', OCH$_2$ triazole), 4.63-4.73 (m, 2H, H-5'), 5.08 (dd, *J*= 0.9, 10.9 Hz, 1H, Ha), 5.13-5.30 (m, 3H, NCH$_2$ triazole, H-4), 5.42 (dt, *J*= 9.4, 18.7 Hz, 2H, H-2, H-3), 5.57 (dd, *J*= 0.9, 17.6 Hz, 1H, Ha'), 5.85 (d, *J*= 8.9 Hz, 1H, H-1), 6.23 (apparent t, *J*= 6.5, 6.7 Hz, 1H, H-1'), 6.62 (dd, *J*= 10.9, 17.6 Hz, 1H, Hb), 6.75-6.86 (m, 3H, H ar, H-6 thymine), 7.24-7.34 (m, 2H, H ar), 7.68 (s, 1H, CH triazole), 7.88 (s, 1H, CH triazole).

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 13.1 (CH_3 thymine), 20.2, 20.5, 20.7 (OAc), 25.8 (CH_2), 29.1, 29.5 (**C**H$_2$CH$_2$OPh, **C**H$_2$CH$_2$OCH$_2$ triazole), 35.9 (NCH$_2$ triazole), 39.0 (C-2'), 51.2 (C-5'), 61.5 (C-6), 64.0 (OCH$_2$ triazole), 67.6 (C-4), 67.8 (CH$_2$OPh), 70.2 (C-2), 70.9 (**C**H$_2$OCH$_2$ triazole), 71.2 (C-3'), 72.7 (C-3), 75.0 (C-5), 83.8 (C-4'), 85.5 (C-1), 86.4 (C-1'), 110.5 (C-5 thymine), 111.4 (CHa, Ha'), 114.5 (CH ar), 122.6, 124.4 (CH triazole), 127.3 (CH ar), 130.2

(C-6 thymine), 134.5 (Cq ar), 136.2 (CHb), 143.6, 145.4 (C-4 triazole), 150.5 (C=O thymine), 158.9 (Cq ar), 162.8 (C=O thymine), 168.8, 169.3, 169.9, 170.5 (C=O acetyl).
HRMS (ESI): (M+H) Calcd. 937.3938, Found 937.3954.

5'-[4-([4-ethenylphenoxy]methyl)-1*H*-1,2,3-triazol-1-yl]-*N*3-[(1-(2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranosyl)-1*H*-1,2,3-triazol-4-yl)methyl]-5'-deoxythymidine (7'b)



Chemical Formula: $C_{38}H_{44}N_8O_{14}$
Molecular Weight: 836,81

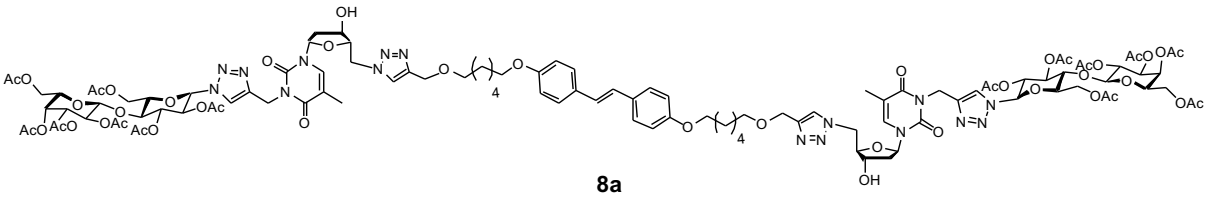
Compounds **3'** (650 mg, 0.96 mmol) and **6b** (152 mg, 0.96 mmol, 1.0 equiv) were dissolved with stirring in 60 mL ^{t}BuOH/H_2O (1:1). Copper sulfate pentahydrate (24 mg, 0.096 mmol, 0.1 equiv) and sodium ascorbate (38 mg, 0.19 mmol, 0.2 equiv) were successively added and the mixture was heated at 65 °C for 15 hours. Solvents were then removed under reduced pressure and the resulting green solid was washed with water until washings were colorless. The crude product was purified by flash chromatography on silica gel eluted with CH_2Cl_2 /MeOH (95:5) to provide the title compound as a white solid (720 mg, 90 %).

Rf: 0.30 (CH_2Cl_2/MeOH 95:5)
^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 1.78 (s, 3H, OAc), 1.84 (s, 3H, CH_3 thymine), 1.97 (s, 3H, OAc), 2.02 (s, 6H, OAc), 2.22-2.48 (m, 2H, H-2'), 3.77-3.88 (m, 1H, H-5), 3.98-4.09 (m, 1H, H-6a), 4.15-4.34 (m, 2H, H-4', H-6b), 4.44-4.58 (m, 1H, H-3'), 4.65-4.90 (m, 3H, H-5', OH), 5.03-5.25 (m, 6H, H-4, Ha, OCH_2 triazole, NCH_2 triazole), 5.25-5.46 (m, 2H, H-2, H-3), 5.52-5.67 (m, 2H, H-1, Ha'), 6.11 (apparent t, *J*= 6.7, 6.9 Hz, 1H, H-1'), 6.61 (dd, *J*= 10.9, 17.5 Hz, 1H, Hb), 6.80-6.94 (m, 3H, H ar, H-6 thymine), 7.27-7.37 (m, 2H, H ar), 7.86 (s, 1H, CH triazole), 7.91 (s, 1H, CH triazole).
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 13.1 (CH_3 thymine), 20.2, 20.6, 20.7 (OAc), 35.8 (NCH_2 triazole), 38.2 (C-2'), 51.4 (C-5'), 61.5, 61.6 (C-6, OCH_2 triazole), 67.6 (C-4), 70.2 (C-2), 71.6 (C-3'), 72.7 (C-3), 75.0 (C-5), 84.5 (C-4'), 85.6 (C-1), 88.3 (C-1'), 110.4 (C-5 thymine), 112.1 (CHa, Ha'), 114.8 (CH ar), 122.4, 125.4 (CH triazole), 127.5 (CH ar) 131.0 (Cq ar), 135.6 (C-

6 thymine), 136.0 (CHb), 143.6, 143.7 (C-4 triazole), 150.4 (C=O thymine), 158.1 (Cq ar), 162.9 (C=O thymine), 168.9, 169.4, 170.0, 170.6 (C=O acetyl).

HRMS (ESI): (M+H) Calcd. 837.3055, Found 837.3049.

(*E*)-1,2-bis{4-(((6-[1-(*N*3-[(1-(2,3,6,2',3',4',6'-hepta-*O*-acetyl-*β*-D-lactopyranosyl)-1*H*-1,2,3-triazol-4-yl)methyl]thymidin-5'-yl)-1*H*-1,2,3-triazol-4-yl]methoxy)hexyl)oxy)phenyl}ethene (8a)



8a

Chemical Formula: $C_{110}H_{140}N_{16}O_{46}$
Molecular Weight: 2422,40

Compound **7a** (150 mg, 0.12 mmol) was dissolved in anhydrous CH_2Cl_2 (4 mL). The mixture was submitted to a cycle of three "freeze pump thaw" to remove air before the addition of Hoveyda Grubbs II catalyst (4 mg, 0.0060 mmol, 0.05 equiv). Three "freeze pump thaw" were repeated on the solution and the reaction was stirred at 40 °C for 15 hours. Solvents were removed under reduced pressure and the resulting green solid was purified by flash chromatography on silica gel eluting with 2 to 5 % v/v MeOH in CH_2Cl_2 to provide the title compound as a slightly green solid (60 mg, 41 %).

Rf: 0.30 (CH_2Cl_2/MeOH 95:5)

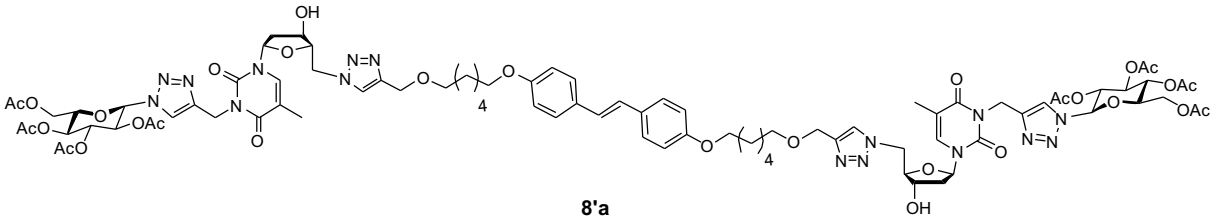
^{1}H NMR (300 MHz, acetone-*d6*) δ (ppm): 1.34-1.51 (m, 8H, CH_2), 1.51-1.64 (m, 4H, C**H**$_2$CH$_2$OCH$_2$ triazole), 1.68-1.81 (m, 10H, C**H**$_2$CH$_2$OPh, OAc), 1.86 (s, 6H, CH_3 thymine), 1.90 (s, 6H, OAc), 2.01 (s, 6H, OAc), 2.03 (s, 6H, OAc), 2.12 (s, 6H, OAc), 2.19-2.38 (m, 4H, H-2'), 3.49 (t, *J*= 6.4 Hz, 4H, C**H**$_2$OCH$_2$ triazole), 3.98 (t, *J*= 6.4 Hz, 4H, CH$_2$OPh), 4.06-4.34 (m, 14H, H-4, H-5, H-6a, H-4', H-5", H-6"), 4.45-4.62 (m, 8H, H-3', OCH$_2$ triazole, H-6b), 4.67-4.83 (m, 4H, H-5'), 4.89 (d, *J*= 7.3 Hz, 2H, H-1"), 5.00-5.24 (m, 8H, NCH$_2$ triazole, H-2", H-3"), 5.33-5.39 (m, 2H, H-4'), 5.39-5.58 (m, 4H, H-2, H-3), 6.15 (d, *J*= 9.1 Hz, 2H, H-1), 6.30 (t, *J*= 6.8 Hz, 2H, H-1'), 6.87-6.97 (m, 4H, H ar), 7.02 (s, 2H, H trans), 7.28 (s, 2H, H-6 thymine), 7.43-7.52 (m, 4H, H ar), 7.95 (s, 2H, CH triazole), 8.04 (s, 2H, CH triazole).

^{13}C NMR (75 MHz, acetone-*d6*) δ (ppm): 13.2 (CH_3 thymine), 20.3-21.0 (OAc), 26.6, 26.7 (CH_2), 29.9, 30.4 (**C**H$_2$CH$_2$OPh, **C**H$_2$CH$_2$OCH$_2$ triazole), 36.7 (NCH$_2$ triazole), 39.6 (C-2'), 52.1 (C-5'), 61.8 (C-6"), 63.1 (C-6), 64.7 (OCH$_2$ triazole), 68.1 (C-4"), 68.5 (CH$_2$OPh), 70.0

(C-3”), 70.9 (**C**H_2OCH_2 triazole), 71.4, 71.5 (C-2, C-5), 71.8 (C-2”), 72.3 (C-3’), 73.6 (C-3), 76.4, 76.8 (C-5”, C-4), 85.4 (C-4’), 85.7 (C-1), 87.0 (C-1’), 101.8 (C-1”), 110.5 (C-5 thymine), 115.5 (CH ar), 123.6, 125.1 (CH triazole), 126.8 (CH trans), 128.3 (CH ar), 131.3 (Cq ar), 135.7 (C-6 thymine), 144.7, 146.0 (C-4 triazole), 151.4 (C=O thymine), 159.6 (Cq ar), 163.3 (C=O thymine), 169.4, 169.7, 170.1, 170.2, 170.6, 170.7,170.9 (C=O acetyl).

HRMS (ESI): (M+H) Calcd. 2421.9186, Found 2421.9186.

(*E*)-1,2-bis{4-(((6-[1-(*N*3-[(1-(2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranosyl)-1*H*-1,2,3-triazol-4-yl)methyl]thymidin-5’-yl)-1*H*-1,2,3-triazol-4- yl]methoxy)hexyl)oxy)phenyl}ethene (8’a)



8'a

Chemical Formula: $C_{86}H_{108}N_{16}O_{30}$
Molecular Weight: 1845,89

Compound **7’a** (120 mg, 0.13 mmol) was dissolved in anhydrous CH_2Cl_2 (3 mL). The mixture was submitted to a cycle of three “freeze pump thaw” to remove air before addition of Hoveyda Grubbs II catalyst (4 mg, 0.0065 mmol, 0.05 equiv). Three “freeze pump thaw” were repeated on the solution and the reaction was stirred at 40 °C for 15 hours. After cooling to room temperature, the solvents were removed under reduced pressure and the resulting green solid was purified by flash chromatography on silica gel eluting with 5 to 10 % v/v of MeOH in CH_2Cl_2 to provide the title compound as a slightly yellow solid (56 mg, 47 %).

Rf: 0.30 (CH_2Cl_2/MeOH 95:5)

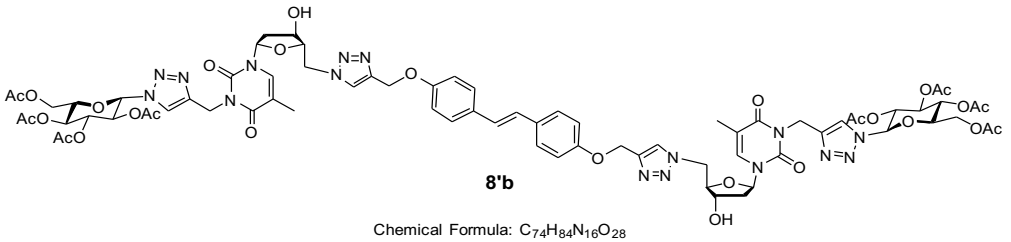
^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 1.34-1.53 (m, 8H, CH_2), 1.55-1.71 (m, 4H, C**H**$_2$$CH_2OCH_2$ triazole), 1.71-1.80 (m, 4H, C**H**$_2$$CH_2$OPh), 1.83 (s, 6H, OAc), 1.90 (s, 6H, CH_3 thymine), 2.01 (s, 6H, OAc), 2.05 (s, 6H, OAc), 2.08 (s, 6H, OAc), 2.10-2.25 (m, 2H, H-2’a), 2.30-2.43 (m, 2H, H-2’b), 3.52 (t, *J*= 6.5 Hz, 4H, C**H**$_2$$OCH_2$ triazole), 3.89-4.02 (m, 6H, C**H**$_2$OPh, H-5), 4.12 (dd, *J*= 1.8, 12.6 Hz, 2H, H-6a), 4.19 (AB system, *J*= 7.9 Hz, 2H, H-4’), 4.28 (dd, *J*= 4.9, 12.7 Hz, 2H, H-6b), 4.46-4.56 (m, 2H, H-3’), 4.56-4.62 (m, 4H, OCH_2 triazole), 4.62-4.71 (m, 4H, H-5’), 5.10-5.28 (m, 6H, NCH_2 triazole, H-4), 5.33-5.49 (m, 4H, H-2, H-3), 5.83 (d, *J*= 8.9 Hz, 2H, H-1), 6.23 (apparent t, *J*= 6.4, 6.6 Hz, 2H, H-1’), 6.73 (s,

2H, H-6 thymine), 6.81-6.89 (m, 4H, H ar), 6.91 (s, 2H, H trans), 7.35-7.43 (m, 4H, H ar), 7.62 (s, 2H, CH triazole), 7.85 (s, 2H, CH triazole).

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 13.1 (CH_3 thymine), 20.2, 20.5, 20.7 (OAc), 25.9 (CH_2), 29.2, 29.5 (**C**H_2CH_2OPh, **C**$H_2CH_2OCH_2$ triazole), 35.9 (NCH_2 triazole), 39.1 (C-2'), 51.3 (C-5'), 61.5 (C-6), 64.1 (OCH_2 triazole), 67.7 (C-4), 67.9 (CH_2OPh), 70.2 (C-2), 70.9 (**C**H_2OCH_2 triazole), 71.2 (C-3'), 72.8 (C-3), 75.0 (C-5), 83.9 (C-4'), 85.6 (C-1), 86.3 (C-1'), 110.6 (C-5 thymine), 114.7 (CH ar), 122.6, 124.4 (CH triazole), 126.1 (CH trans), 127.4 (CH ar), 130.3 (Cq ar), 134.5 (C-6 thymine), 143.6, 145.4 (C-4 triazole), 150.5 (C=O thymine), 158.5 (Cq ar), 162.8 (C=O thymine), 168.8, 169.3, 170.0, 170.6 (C=O acetyl).

HRMS (ESI): (M+H) Calcd. 1845.7496, Found 1845.7546.

(*E*)-1,2-bis{4-[1-(*N*3-[(1-(2,3,4,6-tetra-*O*-acetyl-*β*-D-glucopyranosyl)-1*H*-1,2,3-triazol-4-yl)methyl]thymidin-5'-yl)-1*H*-1,2,3-triazol-4-yl]methoxy)phenyl}ethene (8'b)



Compound **7'b** (300 mg, 0.36 mmol) was dissolved in anhydrous CH_2Cl_2 (9 mL). The mixture was submitted to a cycle of three "freeze pump thaw" to remove air before the addition of Hoveyda Grubbs II catalyst (11 mg, 0.018 mmol, 0.05 equiv). Three "freeze pump thaw" were repeated on the solution and the reaction was stirred at 40 °C for 15 hours. Solvents were removed under reduced pressure and the resulting green solid was purified by flash chromatography on silica gel eluting with 2 to 8 % v/v of MeOH in CH_2Cl_2 to provide the title compound as a slightly green solid (74 mg, 25 %).

Rf: 0.20 (CH_2Cl_2/MeOH 93:7)

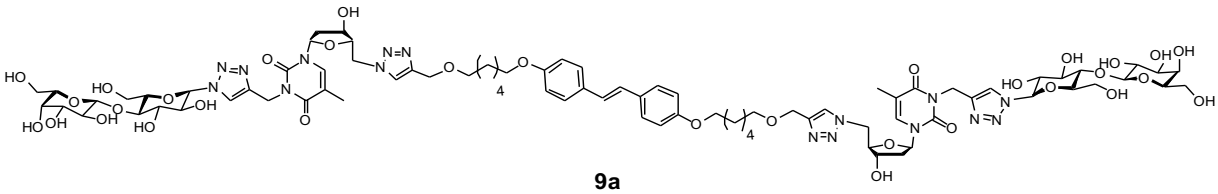
^{1}H NMR (300 MHz, $CDCl_3$/MeOD) δ (ppm): 1.75 (s, 6H, OAc), 1.81 (s, 6H, CH_3 thymine), 1.88 (s, 6H, OAc), 1.93 (s, 6H, OAc), 1.99 (s, 6H, OAc), 2.17-2.37 (m, 4H, H-2'), 3.75-3.87 (m, 2H, H-5), 3.94-4.07 (m, 2H, H-6a), 4.08-4.25 (m, 4H, H-4', H-6b), 4.28-4.41 (m, 2H, H-3'), 4.57-4.76 (m, 4H, H-5'), 5.00-5.23 (m, 10H, H-4, OCH_2 triazole, NCH_2 triazole), 5.23-5.39 (m, 4H, H-2, H-3), 5.57 (d, *J*= 8.6 Hz, 2H, H-1), 6.04 (t, *J*= 6.6 Hz, 2H, H-1'), 6.81 (s, 2H, H-

6 thymine), 6.83-6.94 (m, 6H, H ar, H trans), 7.30-7.41 (m, 4H, H ar), 7.81 (s, 2H, CH triazole), 7.89 (s, 2H, CH triazole).

^{13}C NMR (75 MHz, $CDCl_3$/MeOD) δ (ppm): 12.7 (CH_3 thymine), 19.8, 20.0, 20.1, 20.3 (OAc), 35.5 (NCH_2 triazole), 37.8 (C-2'), 50.9 (C-5'), 61.2 (C-6, OCH_2 triazole), 67.3 (C-4), 70.0 (C-2), 70.8 (C-3'), 72.3 (C-3), 74.6 (C-5), 83.9 (C-4'), 85.2 (C-1), 87.8 (C-1'), 110.1 (C-5 thymine), 114.7 (CH ar), 122.0, 125.1 (CH triazole), 126.0 (CH trans), 127.2 (CH ar), 130.6 (Cq ar), 135.2 (C-6 thymine), 143.2, 143.4 (C-4 triazole), 150.1 (C=O thymine), 157.4 (Cq ar), 162.7 (C=O thymine), 168.7, 169.2, 169.7, 170.5 (C=O acetyl).

HRMS (ESI): (M+H) Calcd. 1645.5719, Found 1645.5690.

(*E*)-1,2-bis{4-(((6-[1-(*N*3-[(1-(*β*-D-lactopyranosyl)-1*H*-1,2,3-triazol-4-yl)methyl]thymidin-5'-yl)-1*H*-1,2,3-triazol-4-yl]methoxy)hexyl)oxy)phenyl}ethene (9a)



9a

Chemical Formula: $C_{82}H_{112}N_{16}O_{32}$
Molecular Weight: 1833,88

Compound **8a** (110 mg, 0.045 mmol) was stirred in 8 mL of anhydrous MeOH/CH_2Cl_2 (3:1) until complete dissolution. Freshly prepared 1M sodium methoxide solution in methanol (14 drops) was added and the solution was stirred at room temperature until TLC (CH_2Cl_2/MeOH/H_2O 70:40:6) showed complete conversion (approx. 2 hours). Solvents were evaporated under reduced pressure and the resulting solid was submitted to a flash chromatography on silica gel eluting with CH_2Cl_2/MeOH/H_2O (70:40:6) to provide the title compound as a white solid (55 mg, 67 %).

Rf: 0.30 (CH_2Cl_2/MeOH/H_2O 70:40:6)

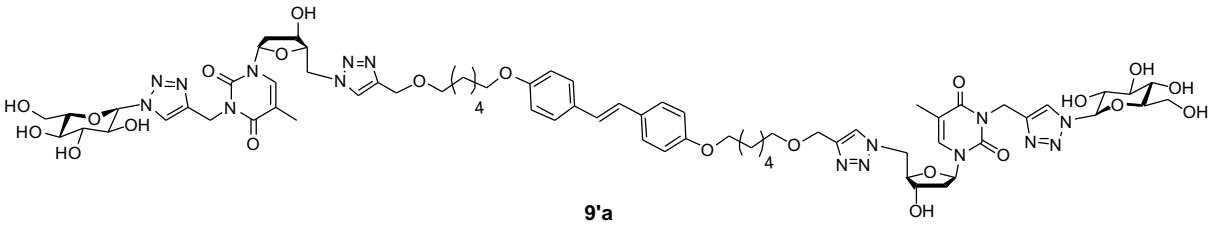
^{1}H NMR (500 MHz, DMSO-*d6*) δ (ppm): 1.28-1.44 (m, 8H, CH_2), 1.46-1.56 (m, 4H, C**H**$_2$$CH_2OCH_2$ triazole), 1.64-1.73 (m, 4H, C**H**$_2$$CH_2$OPh), 1.87 (s, 6H, CH_3 thymine), 2.10-2.27 (m, 4H, H-2'), 3.28-3.65 (m, 24H, C**H**$_2$$OCH_2$ triazole, H-3, H-4, H-5, H-6a, H-2", H-3", H-4", H-5"), 3.75 (dd, *J*= 6.0, 10.7 Hz, 2H, H-6b), 3.80-3.88 (m, 2H, H-2), 3.95 (t, *J*= 6.1 Hz, 4H, CH_2OPh), 4.08-4.15 (m, 2H, H-4'), 4.24 (d, *J*= 7.0 Hz, 2H, H-1"), 4.27-4.33 (m, 2H, H-3'), 4.43-4.52 (m, 4H, OCH_2 triazole), 4.57 (d, *J*= 4.2 Hz, OH), 4.60-4.67 (m, 2H, H-5'a), 4.67-4.76 (m, 6H, H-5'b, OH), 4.81-4.91 (m, 6H, OH), 5.05 (AB system, *J*= 14.5 Hz, 4H, NCH_2 triazole), 5.12-5.18 (m, 2H, OH), 5.51-5.57 (m, 4H, OH), 5.59 (d, *J*= 9.2 Hz, 2H, H-1), 6.22

(apparent t, *J*= 6.7, 6.9 Hz, 2H, H-1'), 6.86-6.95 (m, 4H, H ar), 7.01 (s, 2H, H trans), 7.40-7.52 (m, 6H, H ar, H-6 thymine), 8.08 (s, 2H, CH triazole), 8.13 (s, 2H, CH triazole).

^{13}C NMR (125 MHz, DMSO-*d6*) δ (ppm): 12.8 (CH_3 thymine), 25.4 (CH_2), 28.7 (**C**H_2CH_2OPh), 29.1 (**C**$H_2CH_2OCH_2$ triazole), 36.2 (NCH_2 triazole), 38.1 (C-2'), 51.1 (C-5'), 60.0, 60.4 (C-6", C-6), 63.3 (OCH_2 triazole), 67.4 (CH_2OPh), 68.2 (C-3 or C-4 or C-5 or C-2" or C-3" or C-4" or C-5"), 69.6 (**C**H_2OCH_2 triazole), 70.6 (C-3 or C-4 or C-5 or C-2" or C-3" or C-4" or C-5"), 70.7 (C-3'), 71.6 (C-2), 73.3, 75.2, 75.6, 77.8, 79.8 (C-3 or C-4 or C-5 or C-2" or C-3" or C-4" or C-5"), 84.2 (C-4'), 85.2 (C-1), 86.9 (C-1'), 103.8 (C-1"), 109.1 (C-5 thymine), 114.7 (CH ar), 122.5, 124.6 (CH triazole), 125.8 (CH trans), 127.5 (CH ar), 129.9 (Cq ar), 135.1 (C-6 thymine), 142.7, 144.3 (C-4 triazole), 150.3 (C=O thymine), 158.1 (Cq ar), 162.3 (C=O thymine).

HRMS (ESI): (M+H) Calcd. 1833.7707, Found 1833.7758.

(*E*)-1,2-bis{4-(((6-[1-(*N*3-[(1-(*β*-D-glucopyranosyl)-1*H*-1,2,3-triazol-4-yl)methyl]thymidin-5'-yl)-1*H*-1,2,3-triazol-4-yl]methoxy)hexyl)oxy)phenyl}ethene (9'a)



9'a

Chemical Formula: $C_{70}H_{92}N_{16}O_{22}$
Molecular Weight: 1509,60

Compound **8'a** (140 mg, 0.076 mmol) was stirred in 14 mL of anhydrous MeOH/CH_2Cl_2 (2:1) until complete dissolution. Freshly prepared 1M sodium methoxide solution in methanol (14 drops) was added and the solution was stirred at room temperature until TLC (CH_2Cl_2/MeOH 70/30) showed complete conversion (approx. 1 hour). Solvents were evaporated under reduced pressure and the resulting solid was submitted to a flash chromatography on silica gel eluting with CH_2Cl_2/MeOH (80:20 to 70:30) to provide the title compound as a white solid (58 mg, 51 %).

Rf: 0.20 (CH_2Cl_2/MeOH 70:30)

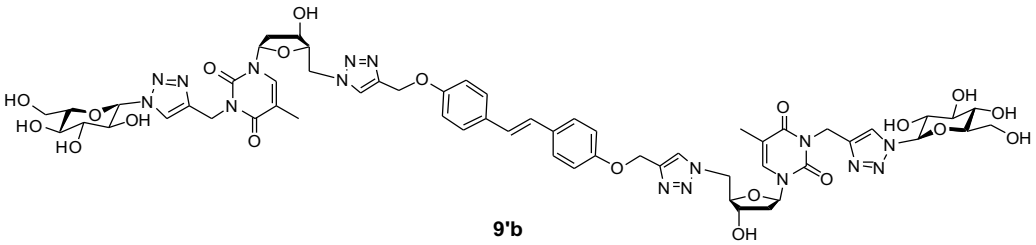
^{1}H NMR (300 MHz, $CDCl_3$/MeOD 50 °C) δ (ppm): 1.32-1.53 (m, 8H, CH_2), 1.53-1.67 (m, 4H, C**H**$_2$CH$_2$OCH$_2$ triazole), 1.67-1.81 (m, 4H, C**H**$_2$CH$_2$OPh), 1.89 (s, 6H, CH_3 thymine), 2.10-2.36 (m, 4H, H-2'), 3.43-3.61 (m, 10H, H-3, H-4, H-5, C**H**$_2$OCH$_2$ triazole), 3.65-3.77 (m, 2H,

H-6a), 3.77-3.90 (m, 4H, H-2, H-6b), 3.94 (t, *J*= 6.3 Hz, 4H, CH_2OPh), 4.08-4.17 (m, 2H, H-4'), 4.31-4.41 (m, 2H, H-3'), 4.50-4.59 (m, 4H, OCH_2 triazole), 4.59-4.76 (m, 4H, H-5'), 5.18 (s, 4H, NCH_2 triazole), 5.50 (d, *J*= 9.1 Hz, 2H, H-1), 6.16 (t, *J*= 6.5 Hz, 2H, H-1'), 6.77-6.93 (m, 6H, H ar, H trans), 7.04 (s, 2H, H-6 thymine), 7.30-7.43 (m, 4H, H ar), 7.77 (s, 2H, CH triazole), 7.93 (s, 2H, CH triazole).

^{13}C NMR (75 MHz, $CDCl_3$/MeOD 50 °C) δ (ppm): 13.0 (CH_3 thymine), 26.5 (CH_2), 29.9, 30.1 (**C**H_2CH_2OPh, **C**$H_2CH_2OCH_2$ triazole), 36.8 (NCH_2 triazole), 39.6 (C-2'), 52.1 (C-5'), 62.1 (C-6), 64.5 (OCH_2 triazole), 68.8 (CH_2OPh), 70.5 (C-3 or C-4 or C-5), 71.5 (**C**H_2OCH_2 triazole), 71.9 (C-3'), 73.5 (C-2), 78.0 (C-3 or C-4 or C-5), 80.5 (C-3 or C-4 or C-5), 85.0 (C-4'), 87.6 (C-1'), 89.1 (C-1), 111.1 (C-5 thymine), 115.6 (CH ar), 123.9, 125.4 (CH triazole), 127.0 (CH trans), 128.1 (CH ar), 131.4 (Cq ar), 136.1 (C-6 thymine), 143.9, 146.0 (C-4 triazole), 151.5 (C=O thymine), 159.5 (Cq ar), 164.3 (C=O thymine).

HRMS (ESI): (M+H) Calcd. 1509.6650, Found 1509.6697.

(*E*)-1,2-bis{4-[1-(*N*3-[(1-(*β*-D-glucopyranosyl)-1*H*-1,2,3-triazol-4-yl)methyl]thymidin-5'-yl)-1*H*-1,2,3-triazol-4-yl]methoxy)phenyl}ethene (9'b)



9'b

Chemical Formula: $C_{58}H_{68}N_{16}O_{20}$
Molecular Weight: 1309,27

Compound **8'b** (74 mg, 0.045 mmol) was stirred in 9 mL of anhydrous MeOH/CH_2Cl_2 (2:1) until complete dissolution. A freshly prepared 1M sodium methoxide solution in methanol (10 drops) was added and the solution was stirred at room temperature until TLC (CH_2Cl_2/MeOH/H_2O 70:30:4) showed complete conversion (approx. 1 hour). Solvents were removed under reduced pressure and the resulting solid was purified by flash chromatography on silica gel eluting with CH_2Cl_2/MeOH/H_2O (70:30:4) to provide the title compound as a white solid (41 mg, 70 %).

Rf: 0.20 (CH_2Cl_2/MeOH/H_2O 70:30:4)

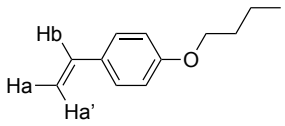
^{1}H NMR (500 MHz, DMSO-*d6*) δ (ppm): 1.88 (s, 6H, CH_3 thymine), 2.09-2.19 (m, 2H, H-2'a), 2.19-2.28 (m, 2H, H-2'b), 3.13-3.24 (m, 2H, H-3 or H-4 or H-5), 3.28-3.47 (m, 2H, H-3

or H-4 or H-5, H-6a), 3.60-3.70 (m, 2H, H-6b), 3.70-3.78 (m, 2H, H-2), 4.08-4.16 (m, 2H, H-4'), 4.25-4.35 (m, 2H, H-3'), 4.60-4.80 (m, 6H, H-5', OH), 5.02 (d, *J*= 14.9 Hz, 2H, NCH_{2A} triazole), 5.07 (d, *J*= 14.9 Hz, 2H, NCH_{2B} triazole) 5.11-5.20 (m, 6H, OCH_2 triazole, OH), 5.28 (d, *J*= 4.9 Hz, 2H, OH), 5.36 (d, *J*= 6.0 Hz, 2H, OH), 5.48 (d, *J*= 9.3 Hz, 2H, H-1), 5.57 (d, *J*= 4.2 Hz, 2H, OH), 6.23 (apparent t, *J*= 6.8, 7.0 Hz, 2H, H-1'), 6.94-7.10 (m, 6H, H ar, H trans), 7.41-7.54 (m, 6H, H ar, H-6 thymine), 8.12 (s,2H, CH triazole), 8.25 (s, 2H, CH triazole).

^{13}C NMR (125 MHz, DMSO-*d6*) δ (ppm): 12.8 (CH_3 thymine), 36.2 (NCH_2 triazole), 38.1 (C-2'), 51.3 (C-5'), 60.7 (C-6), 61.0 (OCH_2 triazole), 69.5 (C-3, C-4, C-5), 70.8 (C-3'), 71.9 (C-2), 77.0, 80.0 (C-3, C-4, C-5), 84.2 (C-4'), 85.3 (C-1'), 87.4 (C-1), 109.2 (C-5 thymine), 114.9 (CH ar), 122.5, 125.4 (CH triazole), 126.0 (CH trans), 127.5 (CH ar), 130.4 (Cq ar), 135.2 (C-6 thymine), 142.6, 142.7 (C-4 triazole), 149.9 (C=O thymine), 157.5 (Cq ar), 162.4 (C=O thymine).

HRMS (ESI): (M+H) Calcd. 1309.4874, Found 1309. 4926.

4-butoxystyrene (10)



10

Chemical Formula: $C_{12}H_{16}O$
Molecular Weight: 176,26

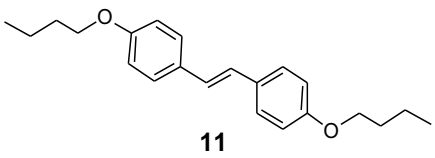
4-hydroxystyrene **4** (113 mg, 0.94 mmol) was dissolved in anhydrous DMF (2.5 mL). Potassium carbonate (156 mg, 1.13 mmol, 1.2 equiv) was added and the solution was stirred 5 min at room temperature. Bromobutane (121 µL, 1.13 mmol, 1.2 equiv) was added and the reaction stirred at room temperature for a further 48 hours. The mixture was concentrated under reduced pressure and the crude product purified by flash chromatography on silica gel eluting with petroleum ether/EtOAc (95:5) to provide the title compound as a colorless oil (100 mg, 60 %).

Rf: 0.50 (petroleum ether/EtOAc 95:5)

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 1.01 (t, *J*= 7.4 Hz, 3H, CH_3), 1.45-1.60 (m, 2H, CH_2), 1.74-1.86 (m, 2H, $OCH_2C\mathbf{H}_2$), 3.99 (t, *J*= 6.5 Hz, 2H, OCH_2), 5.15 (dd, *J*= 1.0, 10.9 Hz, 1H, Ha), 5.64 (dd, *J*= 1.0, 17.6 Hz, 1H, Ha'), 6.69 (dd, *J*= 10.9 Hz, 17.6 Hz, 1H, Hb), 6.83-6.92 (m, 2H, H ar), 7.31-7.40 (m, 2H, H ar).

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 14.0 (CH_3), 19.4 (CH_2), 31.4 ($OCH_2\mathbf{C}H_2$), 67.8 (OCH_2), 111.5 (CHa, Ha'), 114.6, 127.5 (CH ar) 130.3 (Cq ar), 136.4 (CHb), 159.1 (Cq ar).
HRMS (ESI): (M+H) Calcd. 177.1279, Found 177.1275.

(*E*)-4,4'-dibutoxystilbene (11)



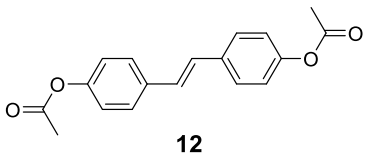
11

Chemical Formula: $C_{22}H_{28}O_2$
Molecular Weight: 324,46

Compound **10** (90 mg, 0.51 mmol) was dissolved in anhydrous CH_2Cl_2 (8 mL). The mixture was submitted to a cycle of three "freeze pump thaw" to remove air before the addition of Hoveyda Grubbs II catalyst (16 mg, 0.026 mmol, 0.05 equiv). Three "freeze pump thaw" were repeated on the solution and the reaction was stirred at 40 °C for 15 hours. Solvents were removed under reduced pressure and the resulting green solid was purified by flash chromatography on silica gel eluting with petroleum ether/EtOAc (97:3) to provide the title compound as a slightly green solid (49 mg, 59 %).

Rf: 0.40 (petroleum ether/EtOAc 97:3)
^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 0.99 (t, *J*= 7.3 Hz, 6H, CH_3), 1.43-1.58 (m, 4H, CH_2), 1.71-1.85 (m, 4H, $OCH_2C\mathbf{H}_2$), 3.98 (t, *J*= 6.5 Hz, 4H, OCH_2), 6.85-6.91 (m, 4H, H ar), 6.92 (s, 2H, H trans), 7.38-7.45 (m, 4H, H ar).
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 14.0 (CH_3), 19.4 (CH_2), 31.5 ($OCH_2\mathbf{C}H_2$), 67.9 (OCH_2), 114.8 (CH ar), 126.2 (CH trans), 127.5 (CH ar) 130.4 (Cq ar), 158.7 (Cq ar).
HRMS (ESI): (M+H) Calcd. 325.2168, Found 325.2155.

***(E)*-4,4'-diacetoxystilbene (12)**



12

Chemical Formula: $C_{18}H_{16}O_4$
Molecular Weight: 296,32

4-acetoxystyrene (66 µL, 0.43 mmol) was dissolved in anhydrous CH_2Cl_2 (5 mL). The mixture was then submitted to a cycle of three "freeze pump thaw" to remove air before the addition of Hoveyda Grubbs II catalyst (13.8 mg, 0.022 mmol, 0.05 equiv). Three "freeze pump thaw" were repeated on the solution and the reaction was stirred at 40 °C for 15 hours. After cooling to room temperature, the solvents were removed under reduced pressure and the resulting green solid was purified by flash chromatography on silica gel eluting from 5 to 10 % v/v MeOH in EtOAc to provide the title compound as a slightly green solid (59 mg, 93 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.31 (s, 6H, OAc), 5.13 (d, J= 10.8 Hz, 1H, Ha), 7.03 (s, 2H, H trans), 7.06-7.12 (m, 4H, H ar), 7.48-7.54 (m, 4H, H ar).

^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 21.3 (OAc), 122.0 (CH ar), 127.6 (CH trans), 128.0 (CH ar), 135.1 (Cq ar), 150.2 (Cq ar), 169.6 (C=O acetyl).

Selected NMR Spectra

Compound **9a**, **9'a**, **9'b** and **11**

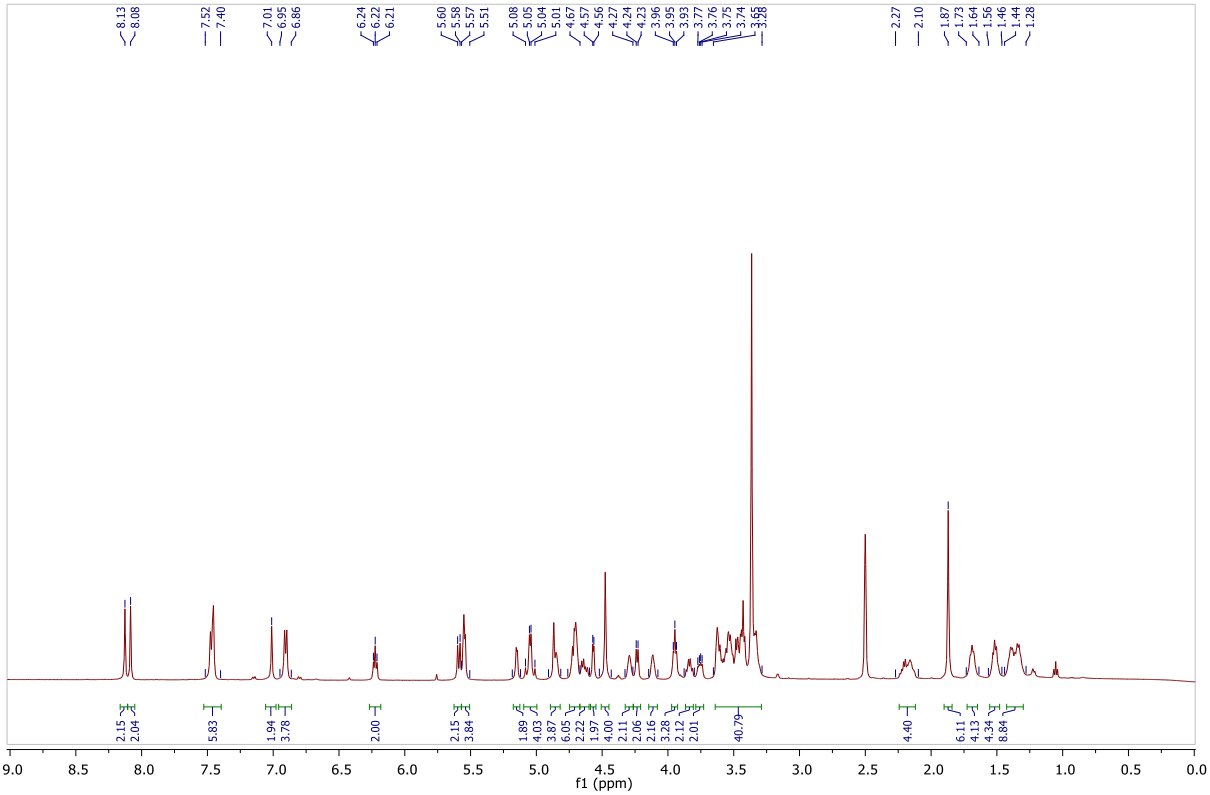


Figure SI1: ^{1}H NMR spectrum of bolaamphiphile **9a** in DMSO-*d6* (500 MHz).

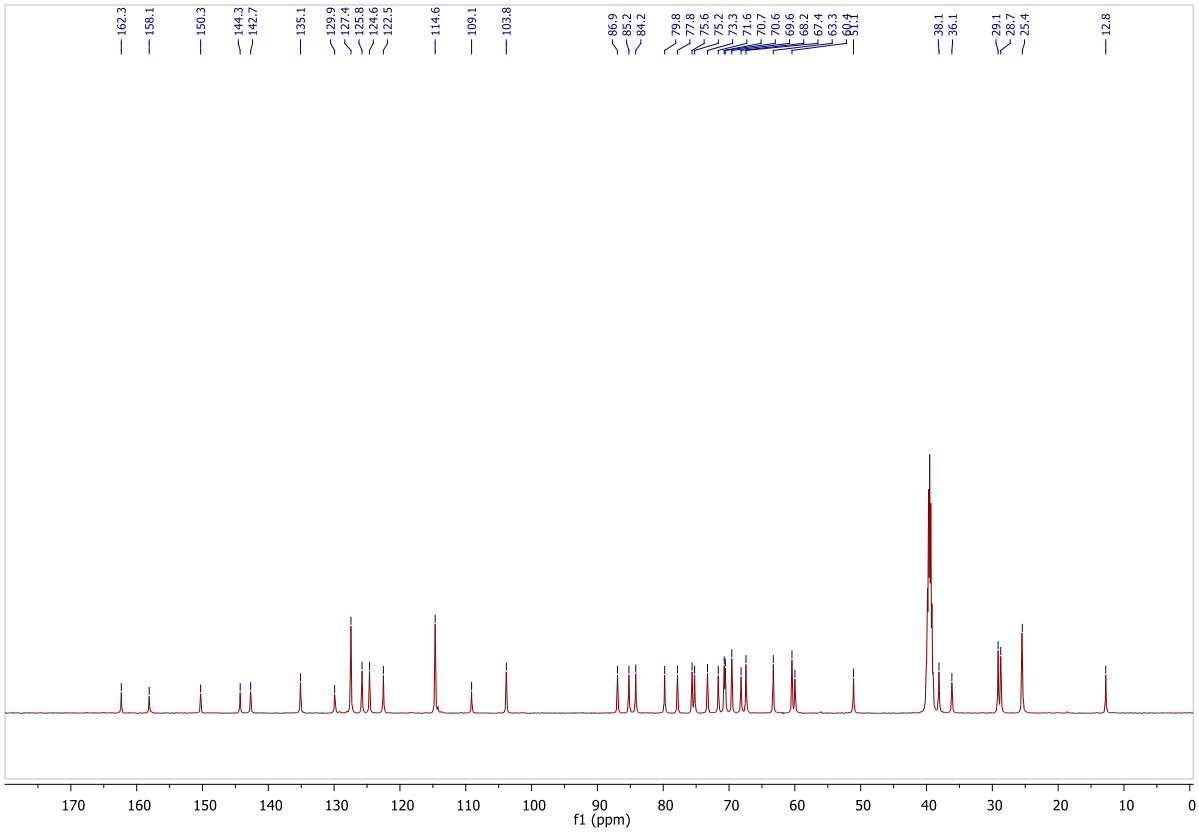


Figure SI2: ^{13}C NMR spectrum of bolaamphiphile **9a** in DMSO-*d6* (125 MHz).

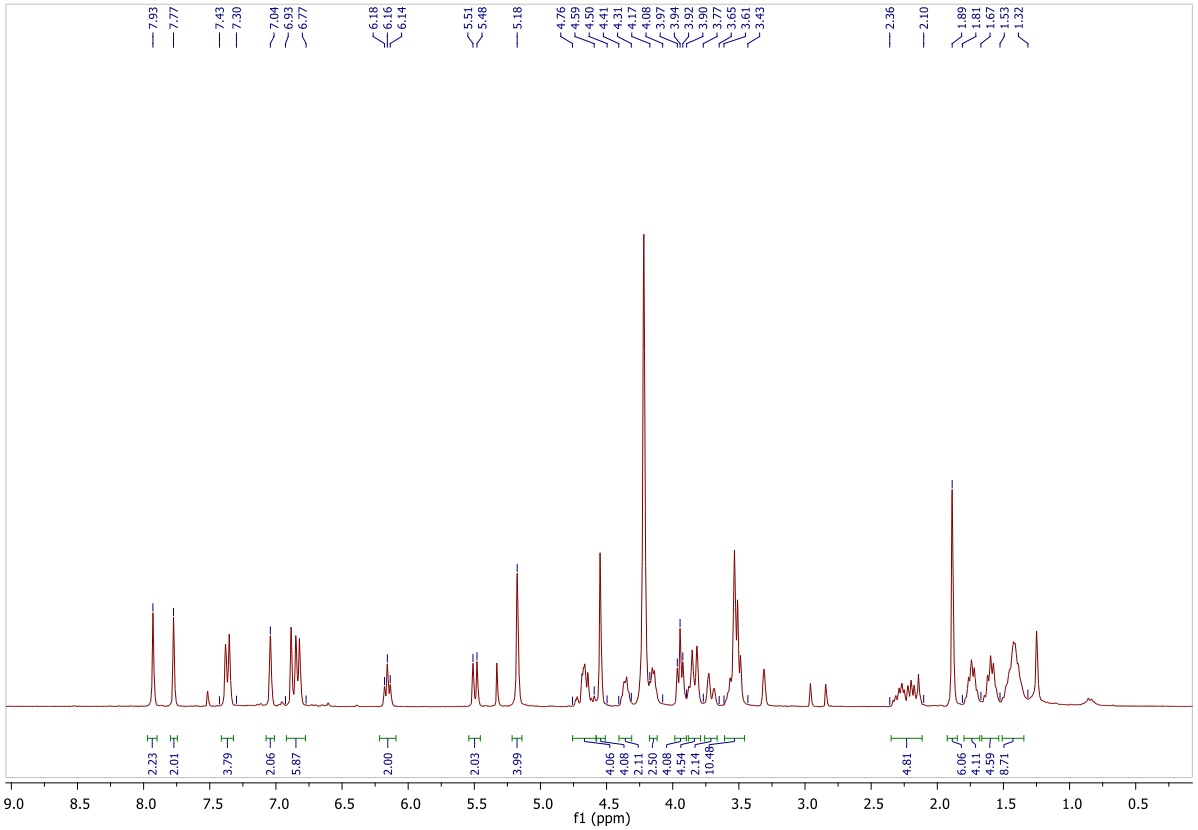


Figure SI3: ^{1}H NMR spectrum of bolaamphiphile **9'a** in DMSO-*d6* (300 MHz).

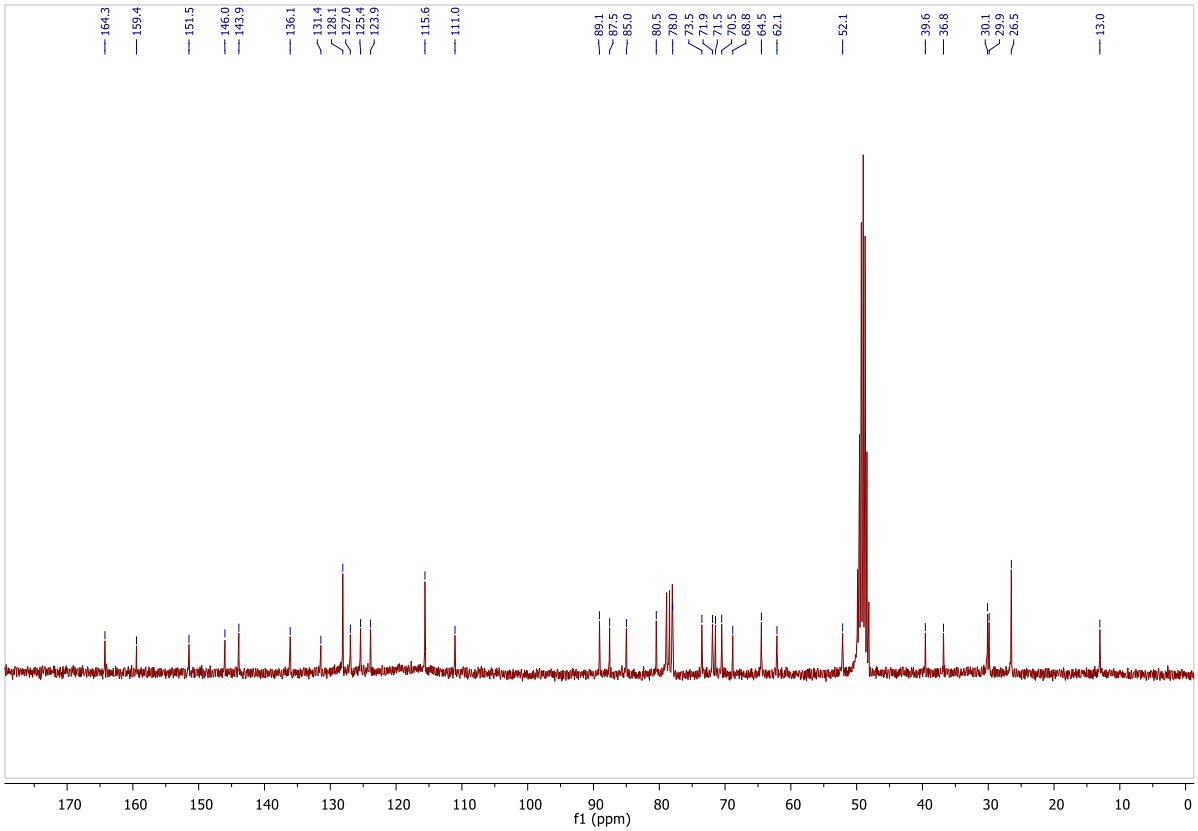


Figure SI4: ^{13}C NMR spectrum of bolaamphiphile **9'a** in DMSO-*d6* (75 MHz).

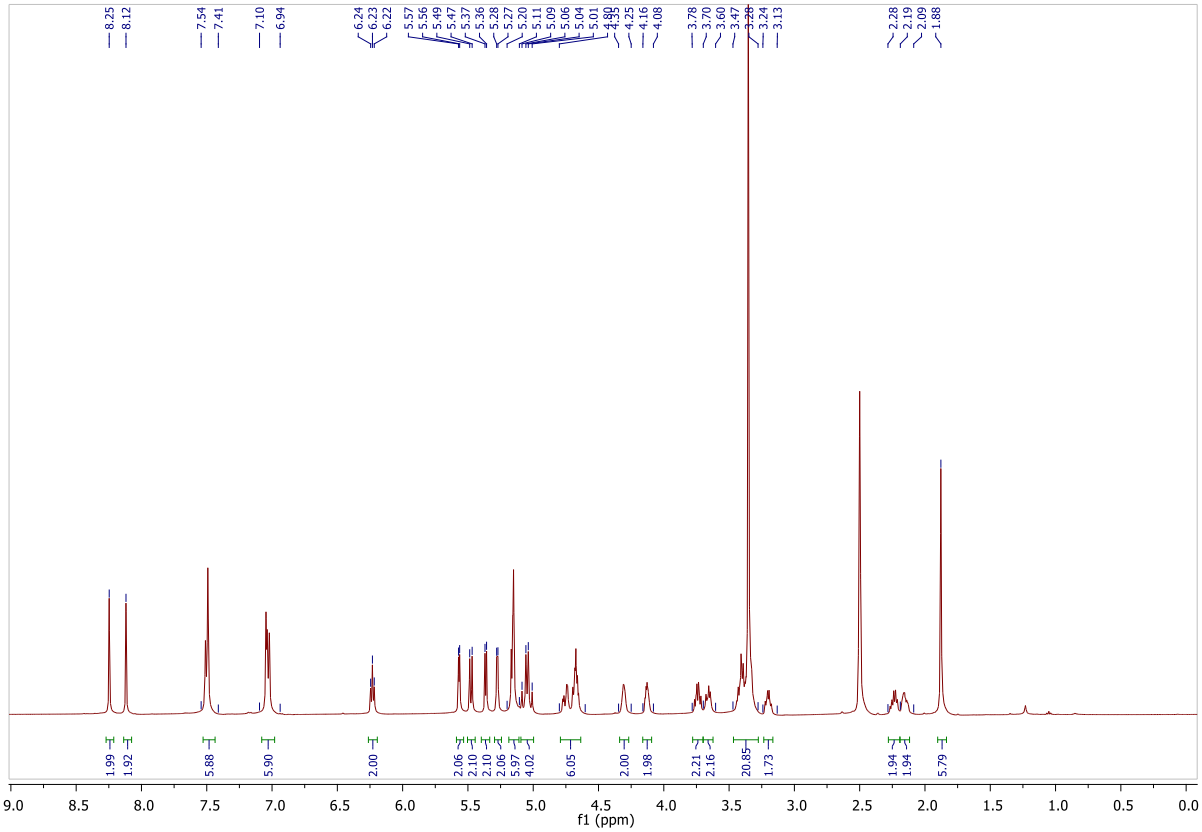


Figure SI5: ^{1}H NMR spectrum of bolaamphiphile **9'b** in DMSO-*d6* (500 MHz).

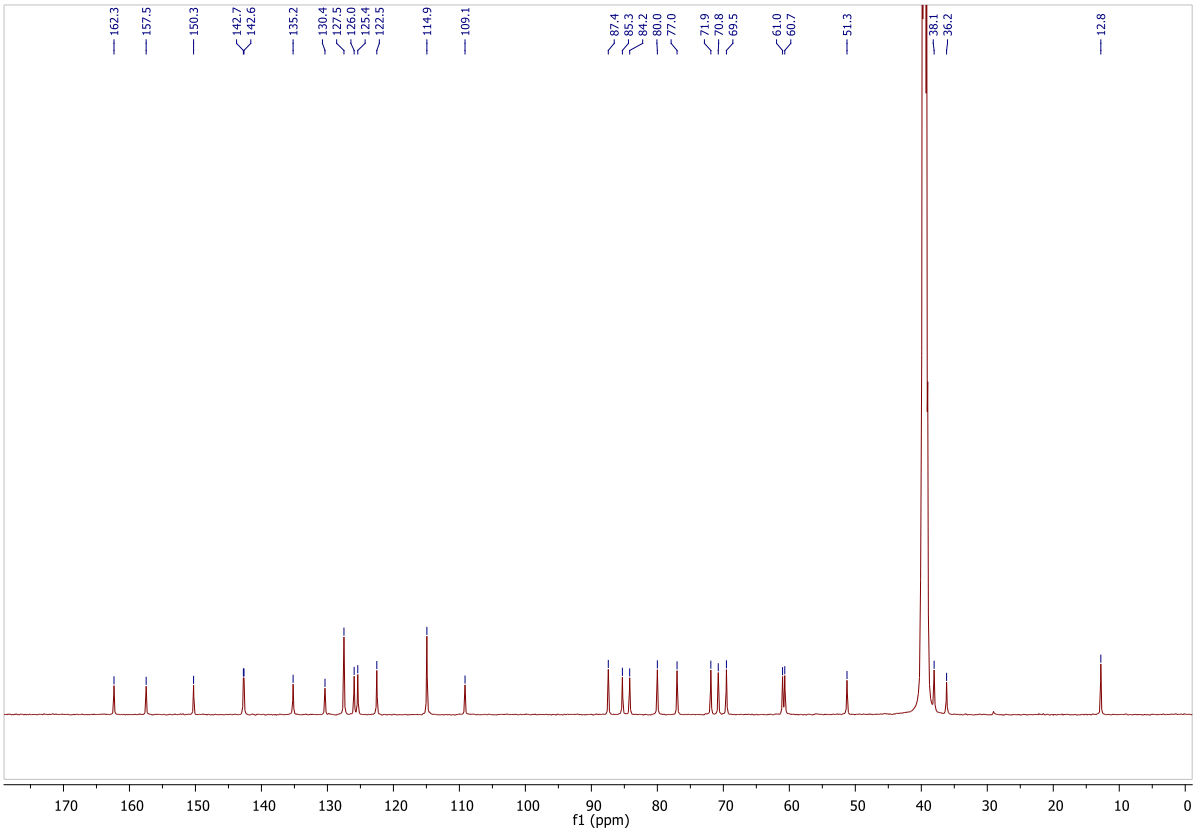


Figure SI6: ^{13}C NMR spectrum of bolaamphiphile **9'b** in DMSO-*d6* (125 MHz).

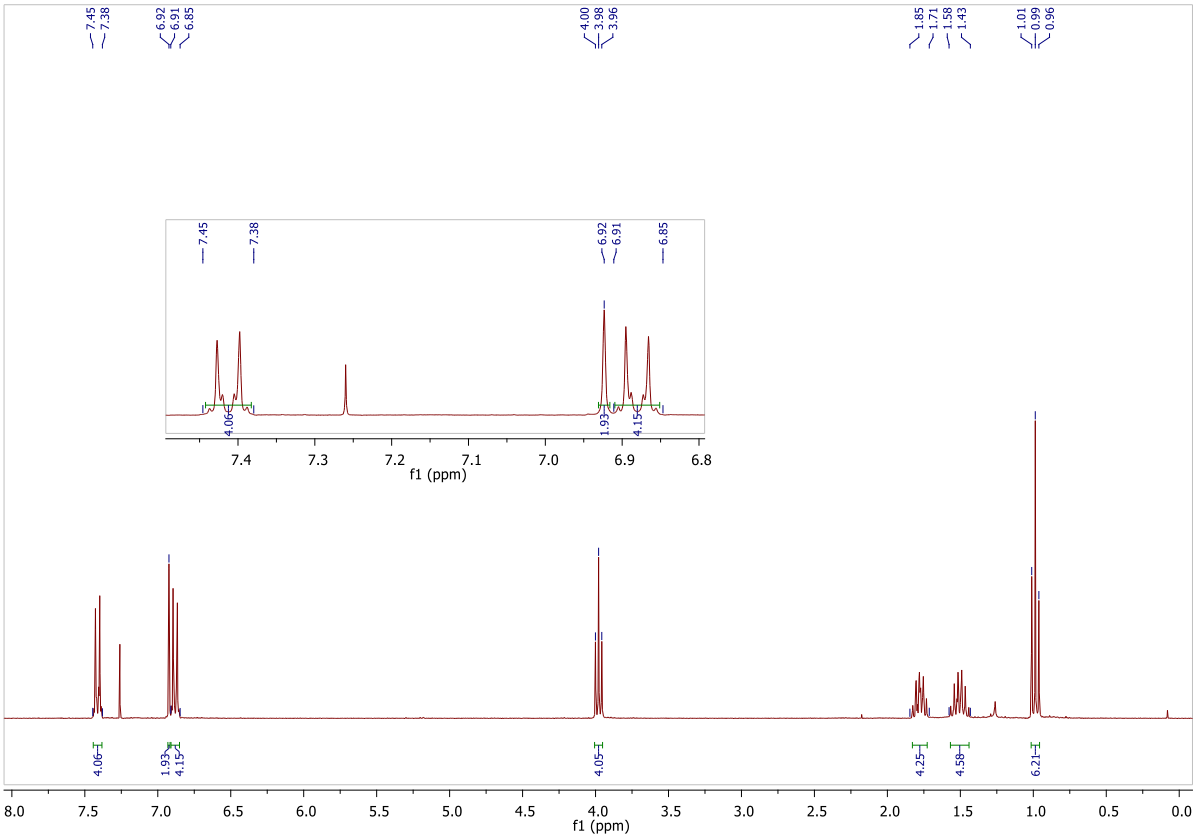


Figure SI7: ^{1}H NMR spectrum of **11** in DMSO-*d6* (300 MHz).

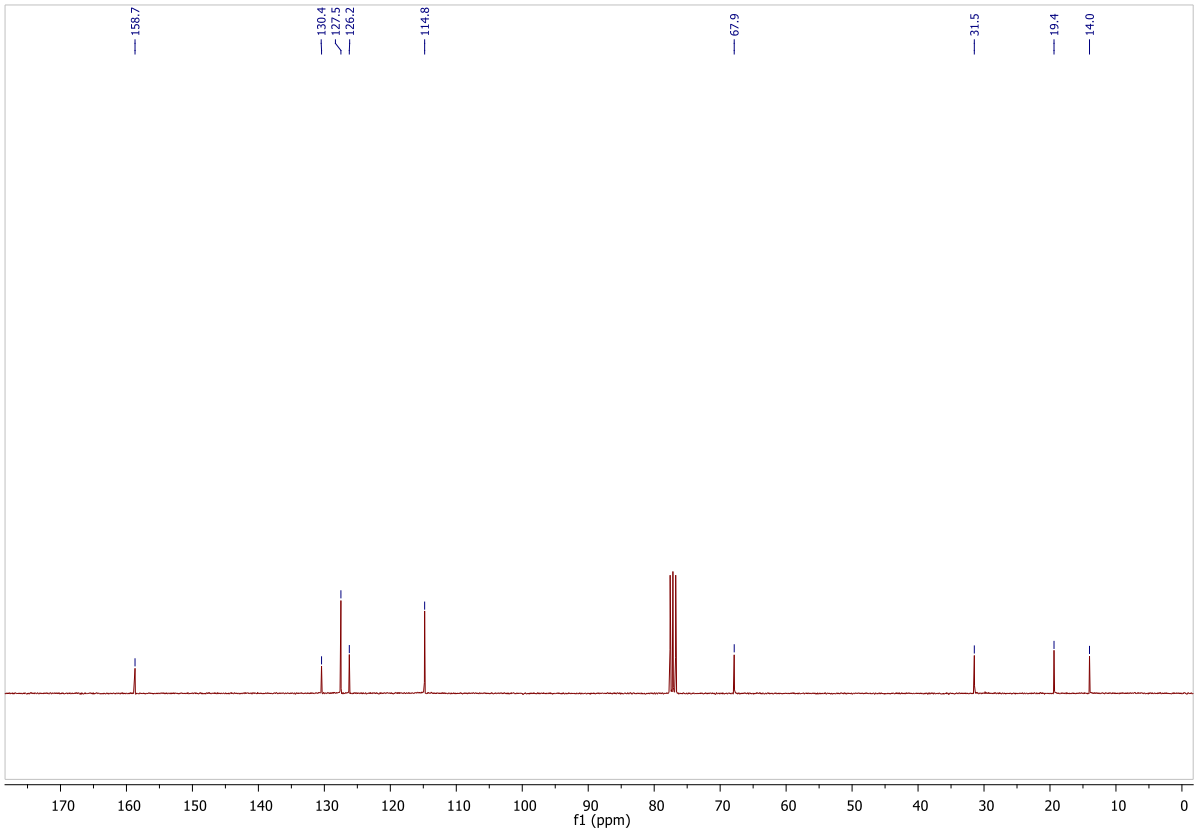


Figure SI8: ^{13}C NMR spectrum of **11** in DMSO-*d6* (75 MHz).

Physico-chemical studies

UV irradiation of GNBAs in solution

Photoisomerization experiments from *E*- to *Z*-stilbene under UV light were performed under irradiation at 336 nm using an optical bench equipped with a xenon-mercury lamp and a high-intensity monochromator using ferrioxalate actinometry (Φ = 1.23). Solutions in quartz cuvette with 1 cm optical path length were flushed with nitrogen for 10 min before irradiation. All irradiations were recorded at room temperature with a fixed distance of 5 cm between the sample cell and the monochromator. A temperature increase of ca. 4 °C resulting from the UV lamp in use was measured. Absorbance spectra were measured on a Varian Carry 5000 (Agilent, Palo Alto, California, US) spectrophotometer. The calculated molar extinction coefficients of the *E* and *Z* isomers are shown in Figure SI9. The composition of the solution in function of the irradiation time was calculated from the molar extinction coefficients and absorbances at the maximum of absorption of the *E*-isomer (λ_{max} = 326 nm in MeOH and 332 nm in DMSO; Figures SI10-SI13).

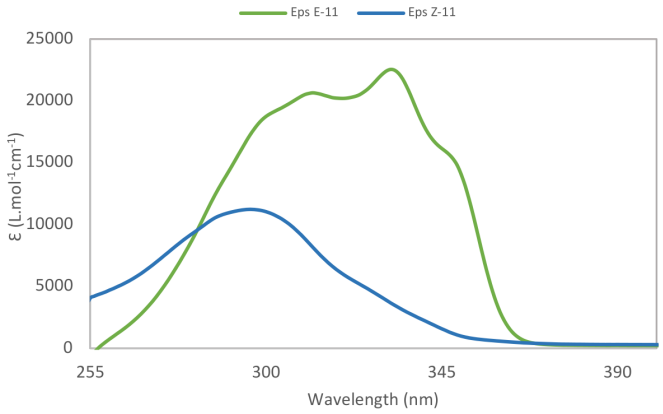


Figure SI9: Calculated absorption spectra of *Z*-**11** (blue line) and *E*-**11** (green line) in DMSO.

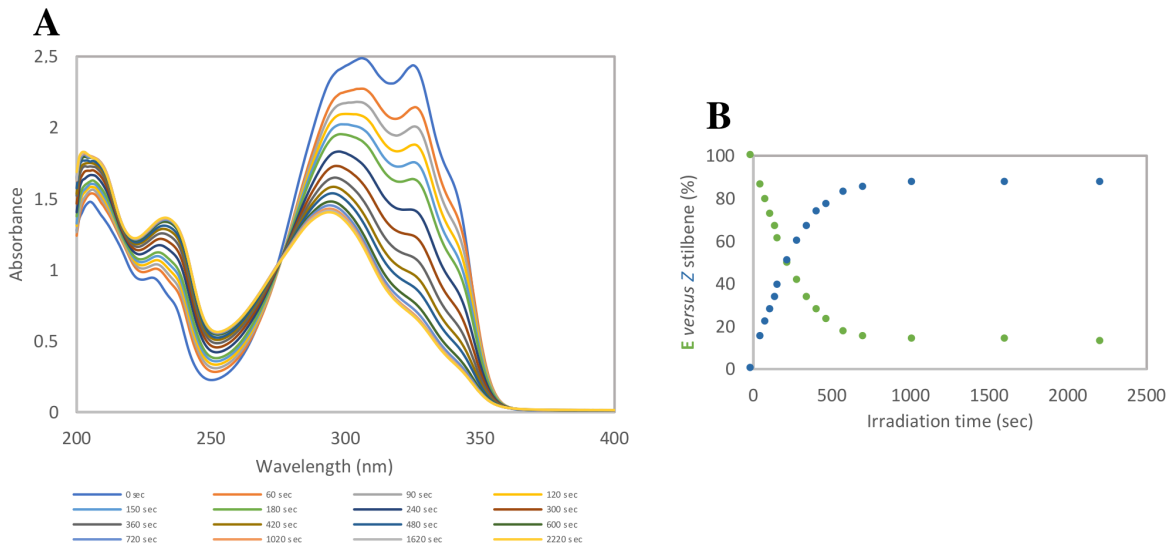


Figure SI10: Spectral changes in the electronic absorption spectrum of **11** (80.1 µM in MeOH) upon irradiation at 336 nm (A; UV spectra recorded between 255 and 395 nm) and variation of the composition of the solution *versus* irradiation time (B).

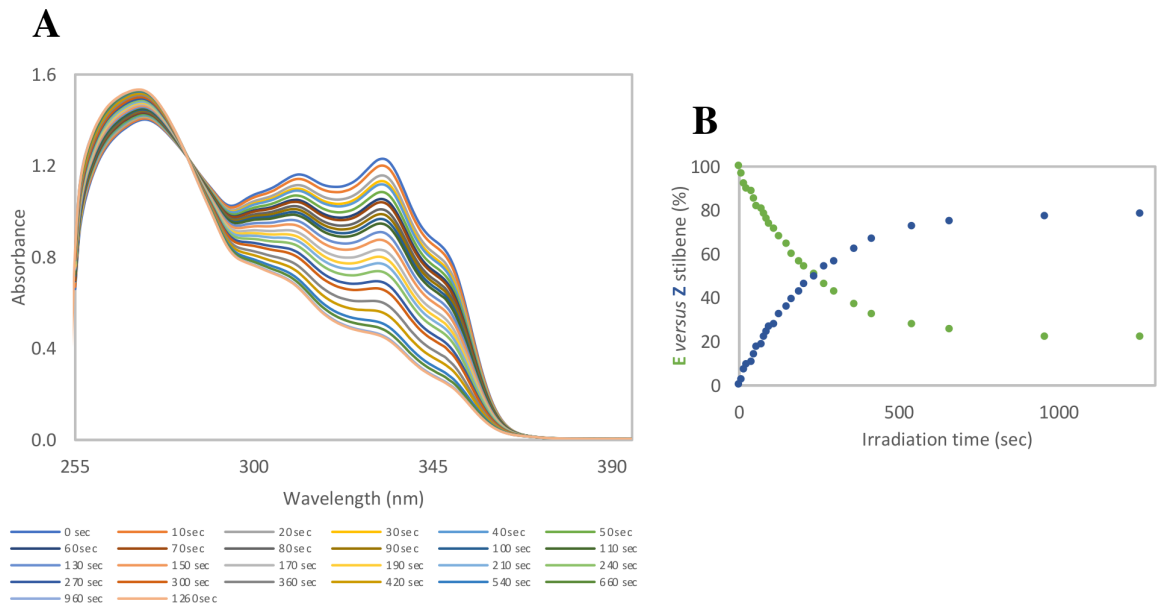


Figure SI11: Spectral changes in the electronic absorption spectrum of bolaamphiphile **9a** (81.8 µM in DMSO) upon irradiation at 336 nm (A; UV spectra recorded between 255 and 395 nm) and variation of the composition of the solution *versus* irradiation time (B).

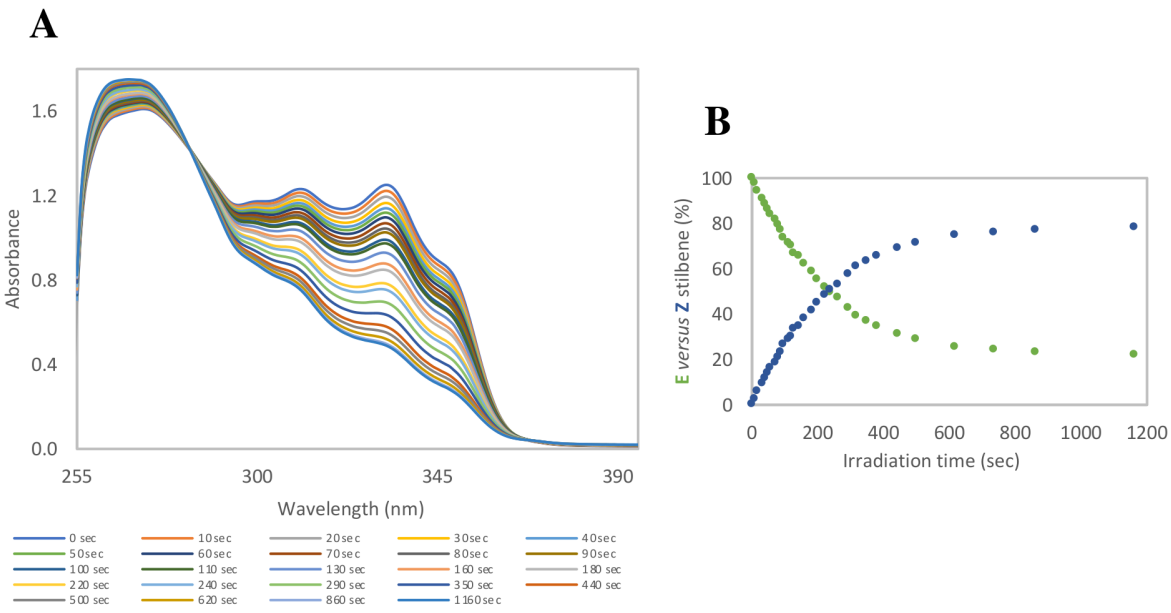


Figure SI12: Spectral changes in the electronic absorption spectrum of bolaamphiphile **9'a** (84.8 µM in DMSO) upon irradiation at 336 nm (A; UV spectra recorded between 255 and 395 nm) and variation of the composition of the solution *versus* irradiation time (B).

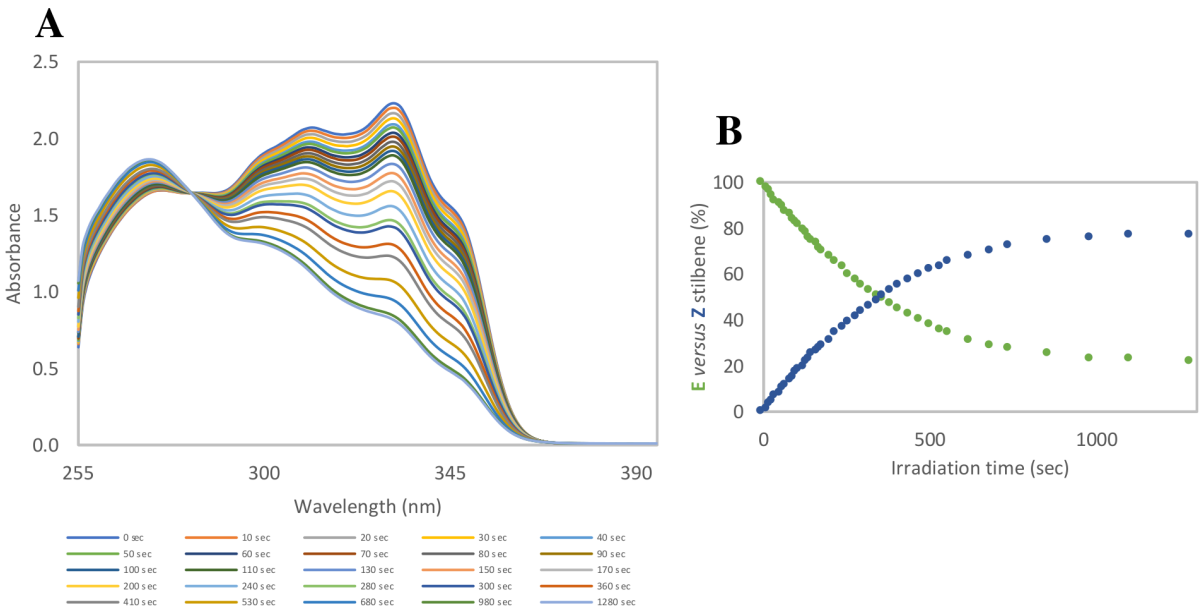
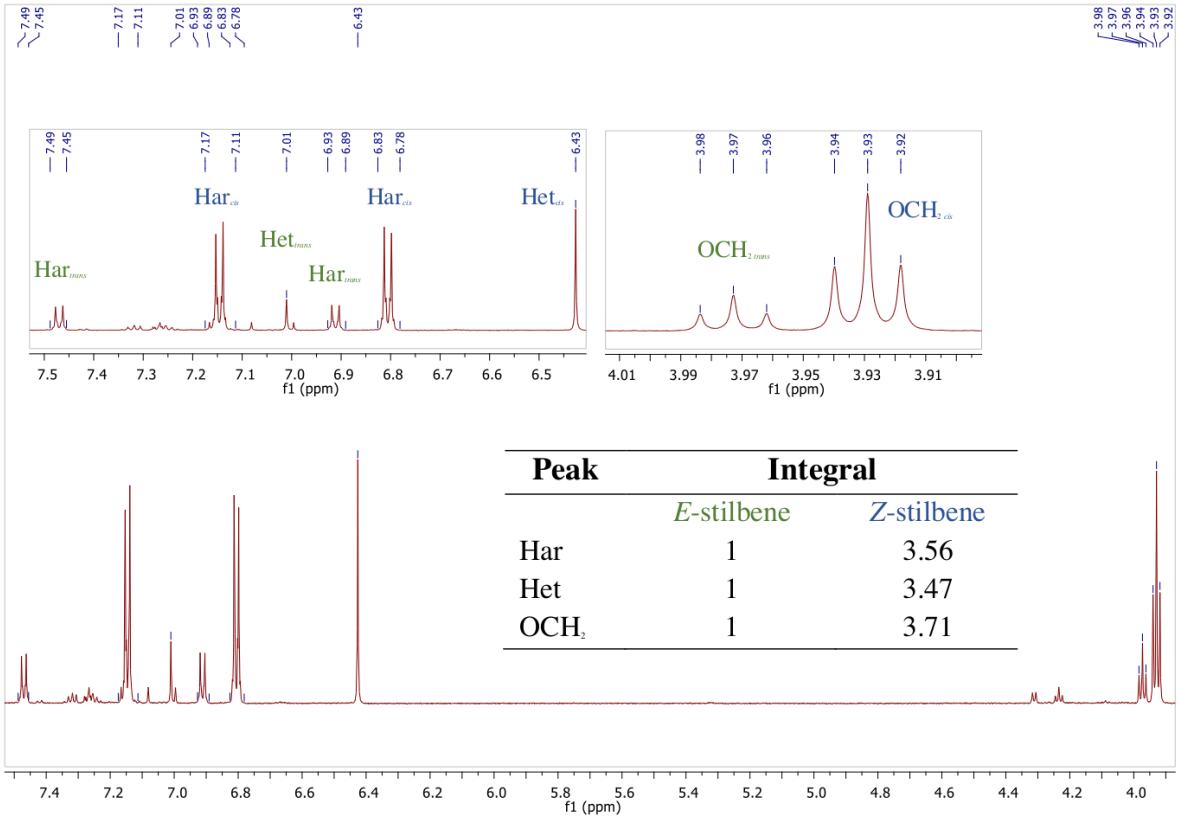


Figure SI13: Spectral changes in the electronic absorption spectrum of bolaamphiphile **9'b** (122.2 µM in DMSO) upon irradiation at 336 nm (A; UV spectra recorded between 255 and 395 nm) and variation of the composition of the solution *versus* irradiation time (B).



Peak	Integral	
	E-stilbene	*Z*-stilbene
Har	1	3.56
Het	1	3.47
OCH_2	1	3.71

Figure SI14: ^{1}H NMR spectrum of **11** in DMSO-*d6* after UV irradiation (600 MHz).

Quantum yields in solution

The $\Phi_{E\rightarrow Z}$ quantum yield was determined at low conversion from the changes in the absorption spectrum and the molar extinction coefficients of the *E* and *Z* isomers calculated from the composition and absorbance of the PSS. From this, the $\Phi_{Z\rightarrow E}$ can be determined from:[5]

$$\frac{[E]}{[Z]} = \frac{\Phi_{Z\rightarrow E}}{\Phi_{E\rightarrow Z}} \bullet \frac{\varepsilon_Z}{\varepsilon_E}$$

In MeOH, the calculated $\Phi_{E\rightarrow Z}$ and $\Phi_{Z\rightarrow E}$ are similar (Table SI15). Within experimental error, these values are identical to those determined by Lewis and Liu for an analogous 4,4'-bis(2-hydroxyethoxy)stilbene diether in MeOH.[6] In DMSO, the efficiency of the *Z* to *E* photoisomerization is considerably enhanced and compensates for the somewhat lower absorption of the *Z* isomer at the irradiation wavelength in DMSO *versus* MeOH. In the case of bolaamphiphiles **9a**, **9'a**, **9'b**, the composition of the irradiated samples was determined from their absorption spectrum using the molar extinction coefficients of model compound **11** in DMSO, thereby avoiding weighting errors due to the possible presence of residual moisture or solvent.

Table SI15: Isomerization quantum yields in solution (λ_{ex} = 336 nm).

Compound	ε_{336} (*E*) ($M^{-1}cm^{-1}$)	ε_{336} (*Z*) ($M^{-1}cm^{-1}$)	$\Phi_{E\rightarrow Z}$	$\Phi_{Z\rightarrow E}$	**PSS** ([*E*] / [*Z*])
11 (MeOH)	22890	3740	0.37	0.33	0.15[a]
11 (DMSO)	21180	2940	0.39	0.80	0.28[a]
9a[b]	-	-	0.31	0.72	0.33[c]
9'a[b]	-	-	0.30	0.81	0.38[c]
9'b[b]	-	-	0.36	0.84	0.32[c]

[a] From NMR; [b] In DMSO; [c] Calculated using ε_{336} of **11** in DMSO.

*Infrared experiments of intermediate **12** in solution*

Solutions of **12** in DCM irradiated or not at 312 nm were lyophilized for 1 day. Each sample was prepared by mixing 1.5 mg of lyophilized compound with 150 mg of KBr powder and then compressed with a mechanical die press to obtain translucent pellets. Spectra were acquired in transmission mode using a Fourier Transform Infrared spectrometer (FT-IR 4600, Jasco Inc., Tokyo, Japan) controlled by spectra manager software. All spectra were recorded by averaging 16 accumulations with 4.0 cm^{-1} resolution between 4000 and 400 cm^{-1}.

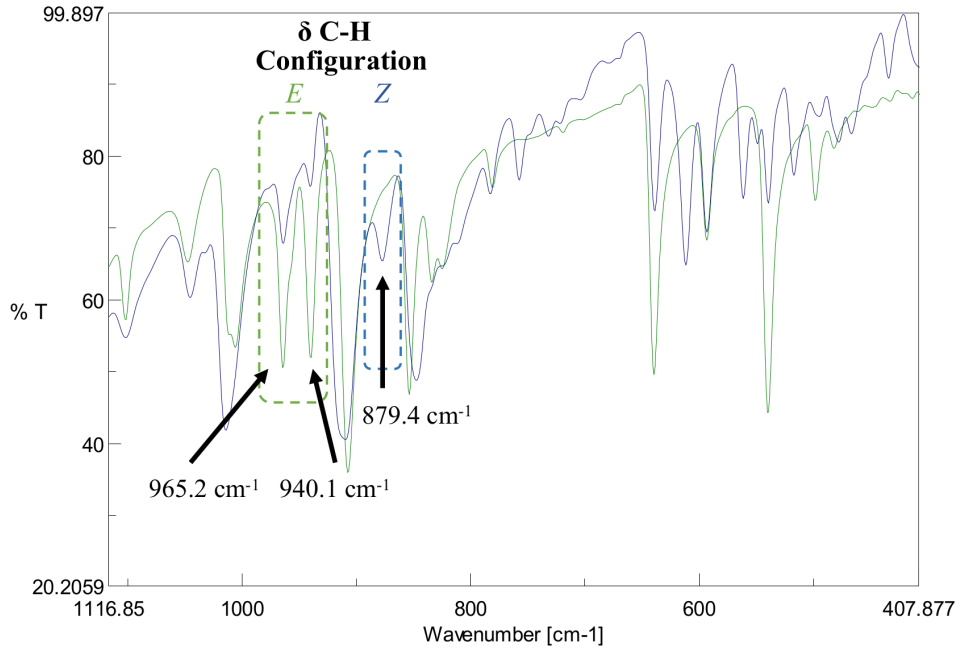


Figure SI16: KBr pellet spectra of **12** before irradiation (green) and after 3h of irradiation at 312 nm (blue). Spectra were acquired between 1200 and 400 cm^{-1}.

Gelation test / Critical Gelation Concentration (CGC)

Solutions of solvents containing bolaamphiphiles **9a**, **9'a** and **9'b** in plastic vials were heated at different temperatures for 15 min and stirred at 800 rpm using a Thermomixer compact (Eppendorf, Hauppauge, NY, USA). They were then sonicated at room temperature for 30 min using an ultrasound bath FB 11205 (37 kHz, Fischer Scientific, Strasbourg, France). Gel behavior was assessed when no flow could be observed once the test tube was turned upside-down. CGC experiments were performed by successively diluting the sample, heating and sonicating until no gel formation could be observed.

Table SI17: Gelation studies.

Solvent	Heating (°C)	9a	9'a	9'b
Dichloromethane	40	I	I	I
Chloroform	65	I	I	I
Acetone	60	I	I	I
Tetrahydrofuran	65	I	I	I
Acetonitrile	80	P	P	I
Methanol	65	I	I	I
Ethanol*	80	P	P	I
Water*	70	P	P	I
Water / Acetonitrile (1:1) *	80	P	gS	I
Water / Ethanol (1:1) *	80	**OG** (0.5 % w/v)	**OG** (1 % w/v)	I
Water / Ethanol (1:3) *	80	**OG**	gS	I
Water / Ethanol (3:1) *	80	gS	**OG**	I

*Milli-Q water and absolute ethanol were used for gelation tests.
I = insoluble, P = precipitate, OG = opaque gel, gS = gelatinous solution. Critical gelation concentrations are mentioned in brackets.

Rheology

Rheological experiments were performed on a Malvern Kinexus® Pro+ rheometer (Malvern Instruments Ltd., Orsay, France) equipped with a Peltier temperature control system on the lower plate. All experiments were conducted at 25 ± 0.01 °C with an upper steel cone geometry (diameter: 20 mm, angle: 1 °, gap: 0.3 mm), unless otherwise stated. A solvent trap was added to prevent solvent evaporation and to control temperature. Gel samples previously prepared in plastic vials were placed under gel state with a spatula on the lower geometry and submitted to sinusoidal oscillations after a rest of 45 min. Linear viscoelastic region (LVR), in which G' and G" displayed no dependence towards the applied strain, was measured by an amplitude strain sweep experiment (strain: 0.01 to 100 %, constant frequency: 5 Hz for **9a**, 1 Hz for **9'a**). Further experiments were conducted within the LVR as frequency sweep (frequency: 0.10 to 10 Hz, constant strain: 0.05 % for **9a**, 0.02 % for **9'a**) and gel-sol transition temperature assays (temperature: 20 to 90 °C, ramp: 2 °C/min, constant frequency: 1 Hz, constant strain: 0.05 % for **9a**, 0.02 % for **9'a**). Transition temperatures were recorded when G' became inferior to G". Thixotropic experiments were performed at a fixed frequency of 1 Hz and 3 steps: 1) low strain (0.05 % for **9a**, 0.02 % for **9'a**, within LVR) for 5 min; 2) high strain (50 %, outside LVR) for 2 min; 3) low strain (0.05 % for **9a**, 0.02 % for **9'a**, within LVR) for 60 min. All experiments

were at least repeated three times for each sample. Standard deviations were calculated from at least three experiments and used to determine the estimated error.

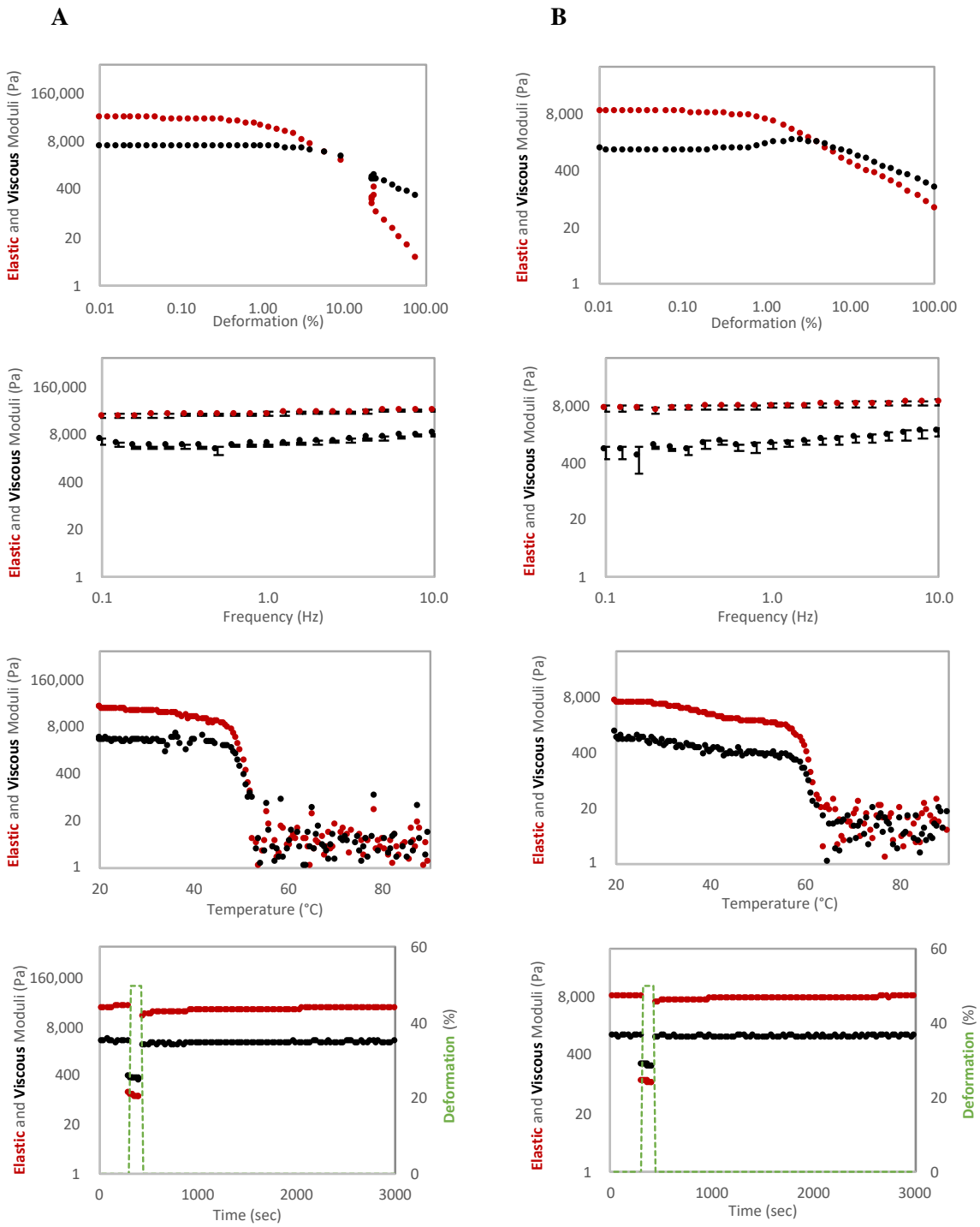


Figure SI18: Amplitude strain sweep, frequency sweep, gel-sol transition and thixotropic experiments of **9a** (A; 2.4 % (w/v)) and **9'a** (B; 2 % (w/v)) based-gels.

Table SI19: Rheological properties of bolaamphiphiles **9a** and **9'a**.

Gel	Yield point (%)	Flow point (%)	G' (kPa)	G" (kPa)	T $_{GelSol}$ (°C)
9a (2.4 % w/v)	0.20 ± 0.03	5.0 ± 0.9	30.0 ± 2.6	4.1 ± 0.3	54.3 ± 0.9
9'a (2 % w/v)	0.36 ± 0.07	4.8 ± 0.8	8.0 ± 0.9	1.0 ± 0.2	60.2 ± 1.5

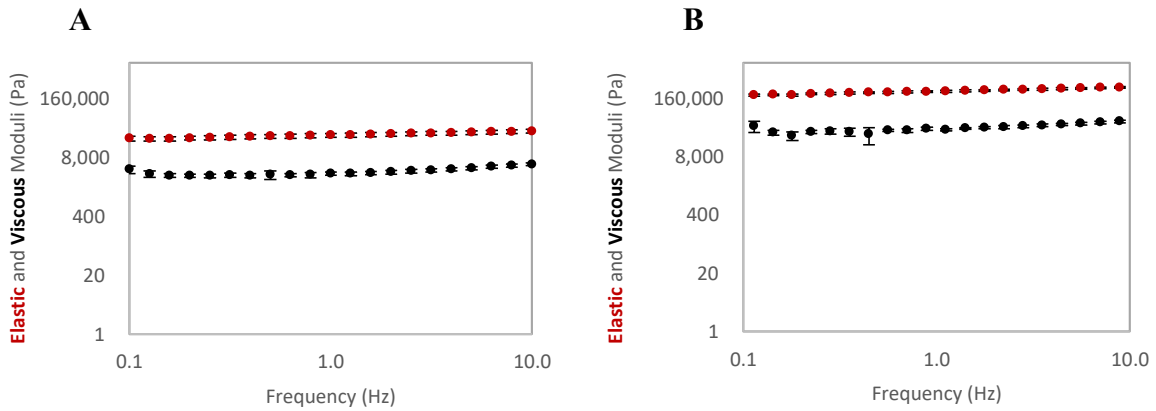


Figure SI20: Frequency sweep experiments of **9a** (A; 2.4 % (w/v)) and **9'a** (B; 2 % (w/v)) based-gels after extrusion through a syringe.

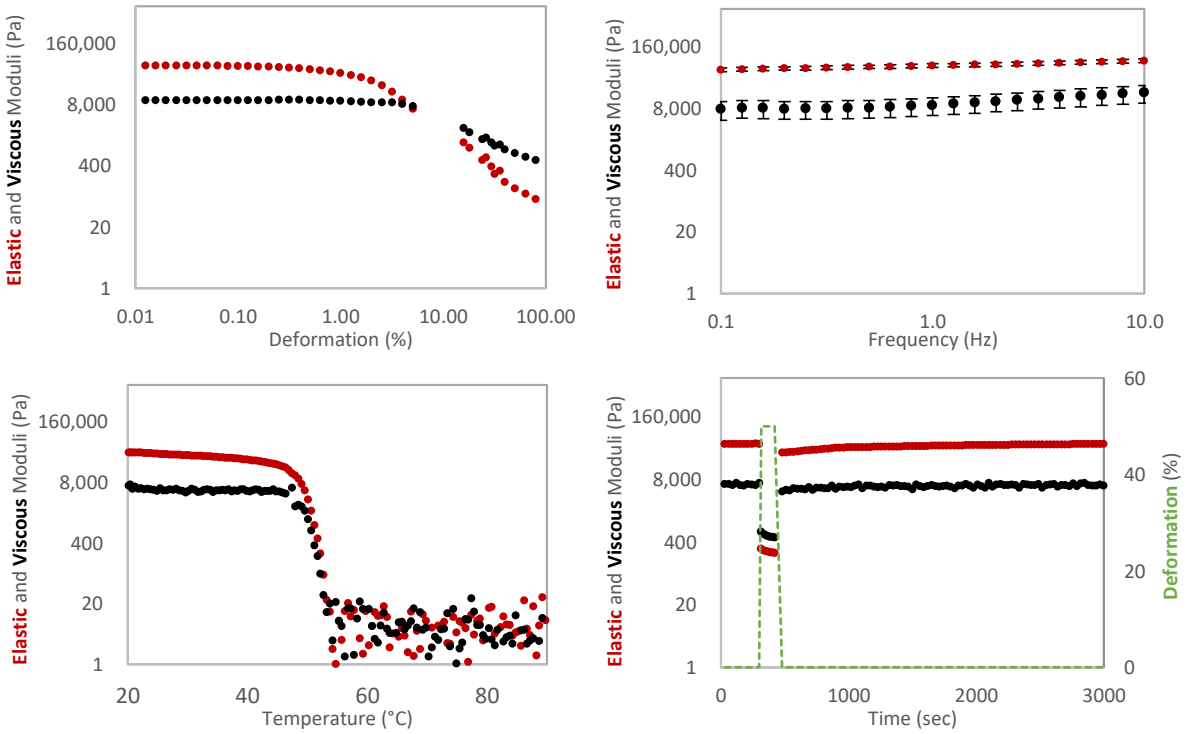
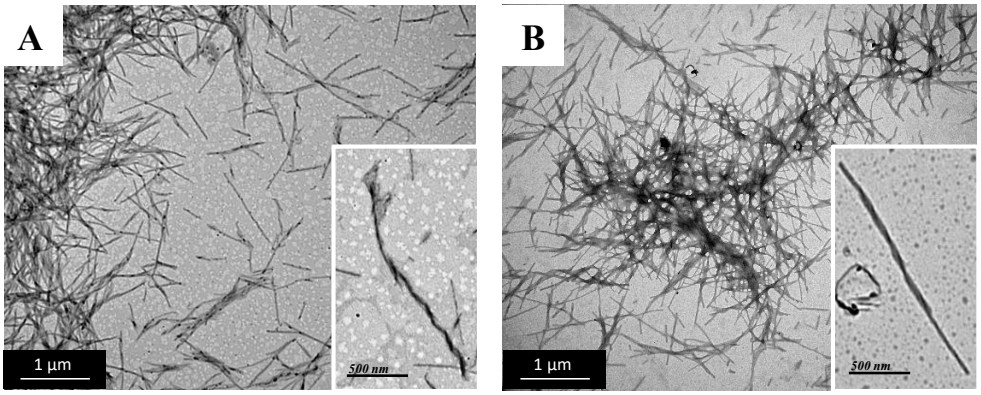


Figure SI21: Amplitude strain sweep, frequency sweep, gel-sol transition and thixotropic experiments of **9a** based-gel at 5 % (w/v).

Transmission Electron Microscopy (TEM)

TEM images were obtained using a Hitachi H7650 combined with an ORIUS SC1000 11 MPX (GATAN). Hydrogel samples of **9a** and **9'a** at 2.4 % (w/v) and 2 % (w/v) respectively, were placed on a carbon-coated grid (Delta Microscopies, France) for 3 min before drying at room temperature.



C

	9a	**9'a**
Diameter (nm)	27.5 ± 5.6	19.3 ± 4.8
Pitch (nm)	146.3 ± 17.8	137.9 ± 30.7

Figure SI22: Transmission electronic microscopy of **9a** (A; 2.4 % (w/v)) and **9'a** (B; 2 % (w/v)) based-gels. Insets show a zoom of helicoidal fibers. Scale bars: 1µm and 500 nm; C) Mean diameter and pitch of fibers.

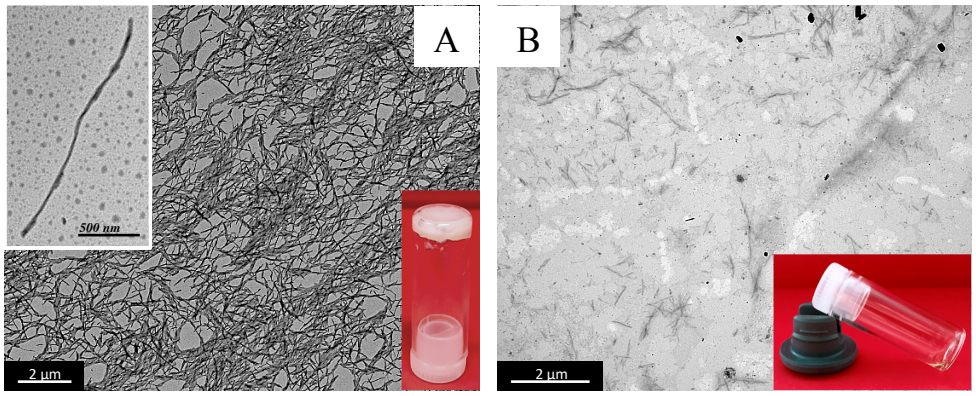


Figure SI23: Optical and transmission electronic microscopy of **9a** based-gel at 5 % (w/v) before (A) and after (B) irradiation at 312 nm. Insets show a zoom of helicoidal fibers. Scale bars: 2 µm and 500 nm.

UV irradiation and experiments of GNBAs based-gels and sols

Photoisomerization experiments from *E*- to *Z*-stilbene under UV light were performed under irradiation at 312 nm with a VL-6M UV lamp 6 W (estimated P = 16 $mW.cm^{-2}$) (Fischer Scientific, Illkirch-Graffenstaden, France) in glass vials. Gel (2.4 % (w/v) for **9a** and 2 % (w/v) for **9'a**) and sol states were lyophilized for 5 hours and solubilized in DMSO at 81.8 µM and 84.8 µM for **9a** and **9'a** respectively. A temperature increase of ca. 4 °C resulting from the UV lamp in use was measured. Absorbance spectra were measured on a V-630 UV-Visible spectrophotometer (Jasco Inc., Tokyo, Japan) between 255 nm and 395 nm.

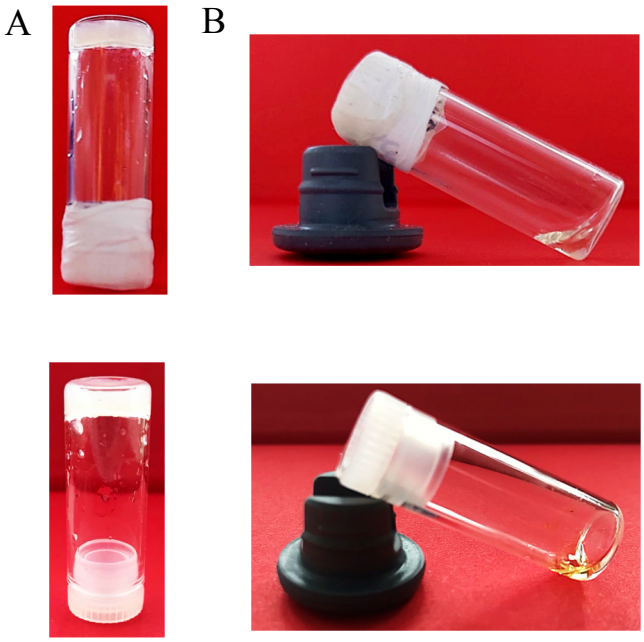


Figure SI24: Optical images of **9a** (up) and **9'a** (down) based-gels at 2.4 % (w/v) and 2 % (w/v) respectively A - before and B - after irradiation at 312 nm.

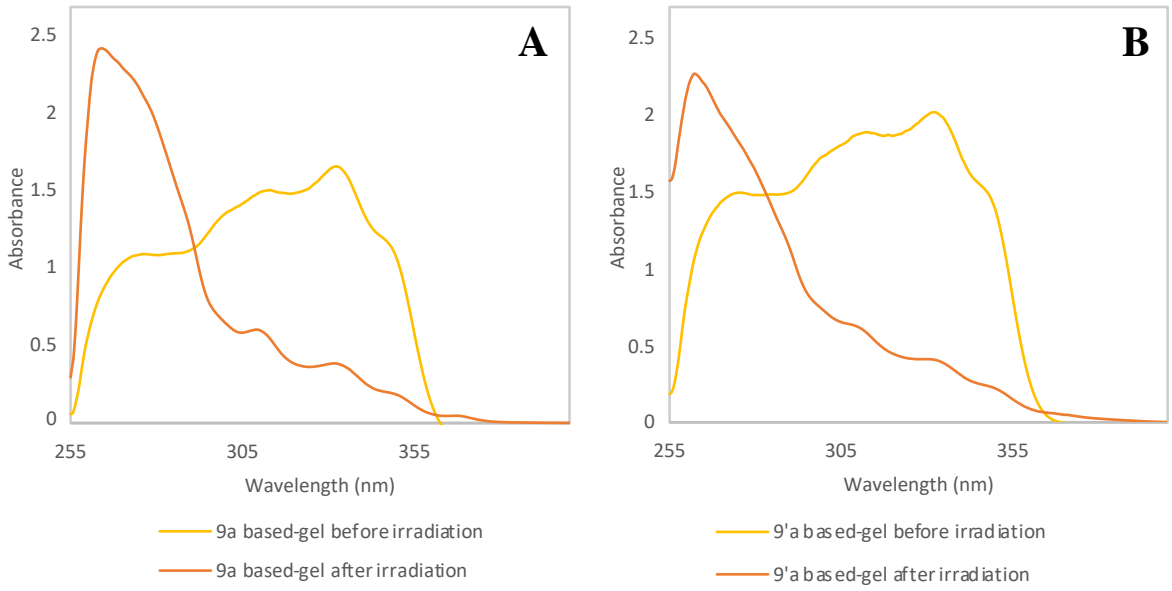


Figure SI25: **9a** (A; 2.4 % (w/v)) and **9'a** (B; 2 % (w/v)) based-gels dissolved in DMSO (81.8 µM and 84.8 µM respectively) after irradiation or not at 312 nm. UV spectra were recorded between 255 and 395 nm.

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