

Self-organizing Carbohydrate-Oligothiophene-Hybrids for Eukaryotic Membrane-labelling

Supporting information (SI)

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Physical measurements and instrumentation:

Nuclear magnetic resonance spectra were recorded on a *Bruker* AMX 500 spectrometer (¹H NMR: 500 MHz, ¹³C-NMR 125 MHz), a *Bruker* Avance 400 (¹H NMR: 400 MHz, ¹³C NMR: 100 MHz) at room temperature unless otherwise noted. Chemical shift values (δ) are given in parts per million using residual solvent protons (¹H NMR: $\delta_{\text{H}} = 7.26$ for CDCl₃, $\delta_{\text{H}} = 2.49$ for DMSO-d₆; $\delta_{\text{H}} = 3.33$ for MeOD-d₄, ¹³C NMR: $\delta_{\text{C}} = 77.0$ for CDCl₃, $\delta_{\text{C}} = 49.05$ for MeOD-d₄ and 39.43 for DMSO-d₆) as internal standard. The splitting patterns are described as follows: (s) singlet, (d) doublet, (t) triplet, qr (quartet), q (quintet), m (multiplet). Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) measurements were carried out on a *Bruker* Daltonik Reflex III mass spectrometer with the following matrices: 1,2,3-trihydroxyanthracene (dithranol), 2,5-dihydroxybenzoic acid (DHB) and T-2-(3-(4-t- Butyl-phenyl)- 2-methyl- 2-propenylidene) malononitrile (DCTB). Elemental analyses were performed on an *Elementar Vario* EL (Ulm University). Melting points are uncorrected and were determined using a *Büchi* B-545 apparatus or a Mettler Toledo Differential Scanning Calorimetry (DSC) 823^e measuring cell. Absorption spectra were recorded on a *Perkin Elmer* Lambda 19 spectrometer and fluorescence emission spectra on a *Perkin Elmer* LS 55 spectrometer in 1 cm cuvettes. Confocal laser scanning microscopy was accomplished with a Leica TCS-NT, equipped with an Argon-Krypton Laser, λ excitation at 490 nm. All reactions were monitored by TLC (aluminium plates, pre-coated with silica gel, *Merck* Si60 F254). Standard fluorescence microscopy was performed using a FITC filter (Chroma Technology exc. 480/30; em.535/40) of a Leica TCS NT inverted microscope, equipped with a

63x oil objective or with a Leica DM5000B fluorescence microscope with GFP filter cube (excitation BP 470/40 nm, emission 525/50 nm).

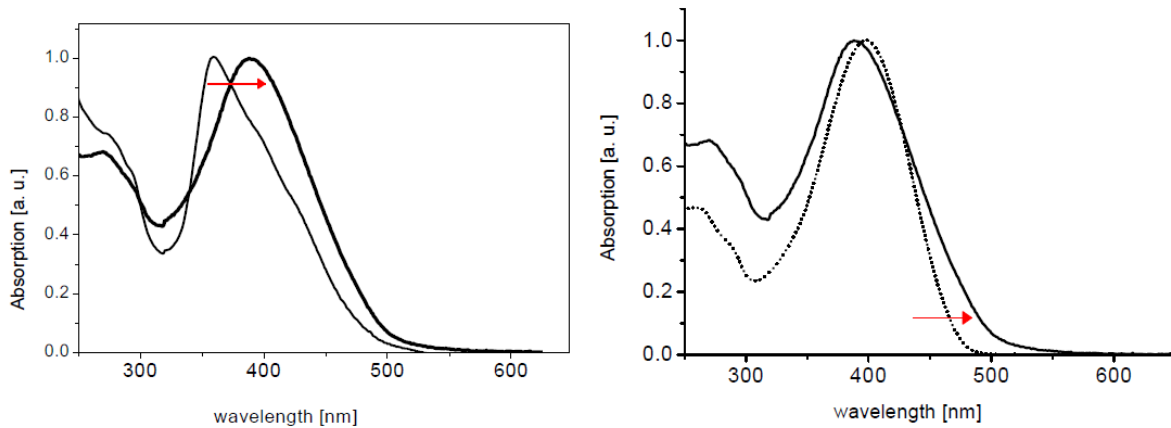


Fig. S1. Left: Normalized UV-spectra [$1 \cdot 10^{-6}$ M] of **D7** in MeOH/H₂O 2:1 (black) and MeOH/H₂O 1:99 (black, bold). After addition of water a red-shift (arrow) of $\lambda_{\text{max abs}}$ was induced related to **D7** in MeOH/H₂O 2:1. Right: comparison of the UV spectra of **D7** in pure MeOH (dotted) and MeOH/H₂O 1:99 (bold). Low energy absorption bands (arrow) indicated a slipped arrangement of the chromophores.

Preparation of egg yolk unilamellar vesicles (EY LUV): A solution of EYPC (25 mg, 0.03 mM) in MeOH/CHCl₃ 1:1 (2.0 ml) was evaporated on a rotary evaporator (40 °C). Removal of solvent residues was subsequently accomplished overnight *in vacuo*. The resulting film was hydrated with 1 ml buffer (100 mM KCl, 10 mM Tris, pH 7.0) for 30 min at 37 °C, subjected to freeze-thaw cycles (7×, liquid N₂, 37 °C water bath) and extrusions (15×) through a polycarbonate membrane (pore size, 100 nm). Extravesicular components were removed by size exclusion chromatography (Sephadex G-50, Sigma-Aldrich) with 100 mM NaCl, 10 mM Tris, pH 7.0. The collected fractions were diluted with buffer to 6 ml. Final conditions: ~2.5 mM EYPC; Vesicles were used within the week of preparation.

D7 or **L7** modified multi-lamellar DMPC vesicles were prepared according modified literature procedures: [41] A lipid stock solution containing 1-5 mole % of the respective hybrid was prepared in MeOH. The solution was heated and held about the transition temperature of DMPC (23 °C) and the solvent was removed by Argon flushing followed by vacuum drying to a constant weight. The resulting lipid/hybrid mixture was then suspended in HEPES buffer (pH = 7.3) to a concentration of 2.0-5.0 mg/ ml. Multilamellar vesicles were formed by self-assembly upon sonication of the resulting solution.

Methods for cell lysis: 1×10^7 cells were lysed with 200ml Pharmingen Lysis Buffer (10 mM Tris-HCL (pH 7.5), 10 mM $\text{NaH}_2\text{PO}_4/\text{NaHPO}_4$, 130 mM NaCl, 1% Triton X-100, 10 mM PPI), for 10 min on ice, centrifuged a $13,000 \times g$ for 30 min. Supernatant containing the plasma membrane vesicles was frozen at -20°C .

Cellular cytotoxicity of the OT-hybrids **D7** and **L7** was tested using established chromium-51 (^{51}Cr) release assay, essentially as described earlier by E. M. Schneider, G. P. Pawelec, S. Liangru and P. J. Wernet, *J. Immunol.*, 1984, 133, 173-9.

K562 cells were labelled with 50 μCi of $\text{Na}_2^{51}\text{CrO}_4$ and incubated with 10^{-6} M to 10^{-8} M solutions of **D7** or **L7**, respectively. Negative controls (referred as spontaneous release) were performed in the absence of **D7** and **L7** and with and without DMSO [dilution 10^{-4}]. Maximum cell lysis and toxicity was determined by adding 1 % Triton X100. Supernatants were removed after 4h and 16h of incubation and radioactivity was determined by a β -plate counter (Perkin Elmer/LKB, Freiburg, Germany).

Representative results are depicted in Table 1. The numbers represent cpm (counts per minute) of released chromium⁵¹ (^{51}Cr). The last column shows maximum release of $^{51}\text{Cr}^*$ from K562 in the presence of 1 % Triton X100.

spontaneous release DMSO [10^{-4}], 4h	release with L7 [0.5×10^{-6} M], 4h	release with D7 [0.5×10^{-6} M], 4h	maximum release with 1 % Triton X100, 4h
945.0	901.2	990.6	15440.3
820.8	897.9	916.8	14384.3
880.8	901.5	890.8	15212.8
			14090.6
			14733.7
			15027.5
spontaneous	release with L7 [0.5×10^{-6} M]	release with D7	maximum release with

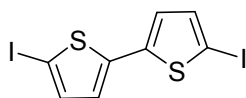
release [10^{-4} M DMSO], 16 h	M], 16h	[0.5×10^{-6} M], 16h	1 % Triton X100, 16h
1900.3	1694.3	1888.0	8409.0
1233.3	1694.0	1714.9	8613.3
1600.2	1650.1	1695.4	8499.5
			8898.6
			9487.5

Table 1 Chrom release of K562 cells incubated with L-(-) mannosidic OT-hybrid **L7** or D-(+) mannosidic OT-hybrid **D7**, respectively. Numbers represent cpm (counts per minute) of released chromate. Maximum release of radioactivity occurs in the presence of detergent 1 % Triton X100.

Chemicals: Dichloromethane, toluene, diethylether (Merck) were dried over CaH_2 and distilled; Tris(dibenzylideneacetone)dipalladium(0)-chloroform adduct, Tris-tert-butylphosphonium tetraflouoroborate, *N,N*-diisopropylamine (Sigma Aldrich), copper(I)iodide (Merck), bis(triphenylphosphine) palladium(II)chloride were purchased from Merck. For purification by column chromatography silica gel 60 (0.040-0.063 mm) from Sigma Aldrich was used. Solvents were distilled prior to use. **Materials:** 2-Propynyl-2,3,4,6-tetra-*O*-acetyl- α -D-(+)-mannopyranoside^[30] **5**, the enantiomeric 2-Propynyl-2,3,4,6-tetra-*O*-acetyl- α -L-(-)-mannopyranoside^[12b] and 3,4-diethylthiophene^[29] were prepared as previously described.

Abbreviations Calcd: Calculated; DCM: Dichloromethane; DIPA: Diisopropylamine; DMSO: Dimethylsulfoxide;; DMPC: 1,2-dimyristoyl-*sn*-glycero-3-phosphocholine; EYPC: Egg yolk phosphatidylcholine; HEPES: 2-(4-(2-Hydroxyethyl)-1-piperazinyl)-ethansulfonsäure buffer; LUVs: Large unilamellar vesicles; MeOH: Methanol; rt: room temperature; $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$: Bis(triphenylphosphine)palladium(II) dichloride; $[\text{Pd}_2(\text{dba})_3] \cdot \text{CHCl}_3$: Tris(dibenzylideneacetone)dipalladium (0)-chloroform adduct; $(\text{tBu})_3\text{PHBF}_4$: Tris-tert-butylphosphonium tetraflouoroborate. THF: Tetrahydrofuran; Tris: Tris(hydroxymethyl)-aminomethane.

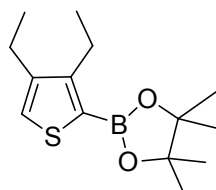
5,5'- diiodo-2,2'-bithiophene **1**



1

2 g (12.03 mM) of 5,5'-diiodo-2,2'-bithiophene **1** in 140 mL dry chloroform was cooled to 0°C and 7.86 g (24.66 mM, 2.05 eq.) of mercury (II) acetate were added (argon atmosphere). After addition, the reaction mixture was allowed to warm up to room temperature and stirring overnight. The thick solution was cooled to 0° C again and 6.26 g (24.66 mM, 2.05 eq.) of iodine were added under argon atmosphere. After 6 hours stirring at rt the solid mercury salts were removed by filtration. The filtrate was washed with saturated NaHCO₃-solution and the layers were separated. The organic phase was dried over MgSO₄ and the solvent was removed in *vacuo*. Further purification of the crude product by recrystallization from ethanol/chloroform (95:5 v/v) yielded 4.04 g (9.66 mM, 80.3 %) of the colorless product **4**, mp 165°-166° C. The NMR-data was in accord with literature. ^[31] ¹H-NMR (400 MHz, CDCl₃) δ = 6.78 (d, J= 3.9 Hz, 2H) 7.14 (d, J=3.9 Hz, 2H). ¹³C-NMR (100 MHz, CDCl₃) δ = 142.1, 137.7, 125.5, 72.5 [ppm]. C₈H₄I₂S₂ calc. MW 418.06, GC-MS (100/16/300°C): m/e = 418 (100%, M⁺), 291 (14 %, M⁺-I). Elemental analyses requires (%) C: 22.98, H: 0.96, found C: 22.17, H: 0.97.

2-(3,4-Diethyl-thiophene-2-yl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane **2**



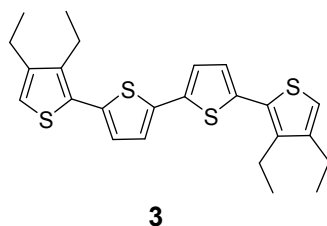
2

178.25 ml nBuLi (1.6 M in hexane, 285.2 mM) was drop wise added to a cooled solution of 40 g of 3,4-diethylthiophene (285 mM) in 400 ml absolute THF (-10°C, argon atmosphere). After addition, the temperature was kept for 30 minutes and then the mixture was allowed to warm up to room temperature and to stir for additional 1.5 hours. Subsequently, the reaction was cooled down again (-10°C) and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-

dioxaborolane (53.06 g, 285.6 mM) was added drop wise. Again, the reaction was allowed stirring for 30 minutes at -10° C and then to warm to 0°C. - For working up the reaction was quenched with saturated, aqueous NaHCO₃ solutions. After extraction of the aqueous phase with diethyl ether (3x150 mL), the layers were separated and the combined organic phases were dried over MgSO₄. The solvent was removed at the rotary evaporator and the desired product **2** was isolated by distillation (17 mbar, 155-158 °C). ¹H NMR indicated a purity of 95%, which corresponds to a yield of 80.0 %.

¹H NMR (400 MHz, CDCl₃): δ=7.24 (s, 1 H), 2.90 (qr, 2H), 2.64 (m, 2H), 1.38 (s, 12H, pinacol), 1.30(t, 3H), 1.17 (t, 3H) [ppm]; ¹³C NMR (CDCl₃, 100 MHz): δ = 154.45, 14.25, 16.13, 145.05, 126.54, 24.67, 83.15, 21.57 [ppm]. C₁₄H₂₃BO₂S calc. MW 266.20 GC-MS: m/e = 266 (M⁺). Elemental analysis calc. C 63.17, H 8.71; found: C 63.14, 8.79.

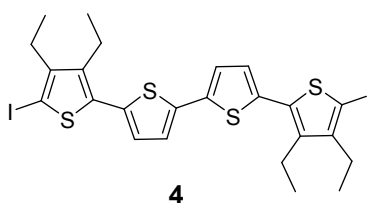
3,3''',4,4'''-Tetraethyl-[2,2';5',2'';5'',2''']quaterthiophene **3**



14.0 g (30 mM) 5,5'-diiodo-2,2'-bithiophene **1** and 22.3 g (83.7 mM) of 2-(3,4-diethylthiophene-2-yl)-4,4,5,5-tetramethyl-[1,3,2]dioxaborolane **2** were dissolved in 400 ml distilled THF. 100 ml 2M K₃PO₄ were added and the reaction mixture was carefully degassed by three cycles of vacuum and argon. After addition of 870 mg [Pd₂(dba)₃]·CHCl₃ (0.84 mM) and 480 mg (tBu)₃PHBF₄ (1.67 mM) the mixture was degassed again and loaded with argon. Subsequently, the reaction was allowed to stir at RT for 10 hours. For working up THF was removed by distillation and the aqueous solution was extracted with DCM. After drying the organic phase over Na₂SO₄ the solvent was removed by distillation and the obtained crude residue was purified by filtration from Silicagel 60 using petrol ether as eluent. Recrystallization from hexane yielded 12.5 grams (84.3 %) of the tetraethylated

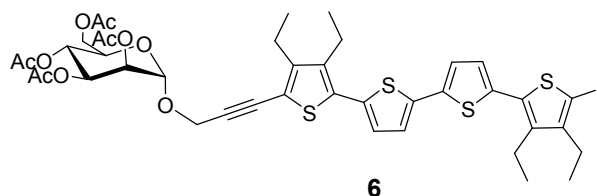
quaterthiophene **3** as a yellow solid, mp 134-135°C (DSC). ¹H-NMR (400 MHz, CDCl₃) δ: 7.12 (d, ³J = 3.8 Hz, 2H); 7.02 (d, ³J = 3.7 Hz, 2H); 6.89 (s, 2H); 2.77 (q, ³J = 7.5 Hz, 4H, CH₂); 2.60 (q, ³J = 7.5 Hz, 4H, CH₂); 1.30 (t, ³J = 7.5 Hz, 6H, CH₃); 1.21 (t, ³J = 7.5 Hz, 6H, CH₃) [ppm]. ¹³C-NMR (100 MHz, CDCl₃) δ: 144.88, 140.13, 136.74, 135.81, 130.66, 126.34, 123.79, 118.74, 22.22, 20.79, 14.90, 13.76 [ppm]. MS (CI) calculated monoisotopic mass for C₂₄H₂₆S₄ 442.72, found 442 [M⁺, 49%], 443 [M+H⁺, 100%] Elemental analysis requires (%) C: 65.11, H: 5.92, S: 28.97 found: C: 65.22, H 5.92, S 28.84.

5,5''Diiodo-3,3''',4,4'''-tetraethyl-[2,2';5',2'';5'',2''']quaterthiophene **4**



To an ice-cooled solution of 0.9 g (2 mM) of 3,3''',4,4'''-tetraethyl-[2,2';5',2'';5'',2'''] quaterthiophene **3** in 80 mL dry chloroform 1.59 g (5 mM) of mercury(II) acetate was added (argon atmosphere). The reaction mixture was allowed to warm to room temperature and allowed to stir overnight. The thick solution was cooled to 0° C again and 1.27 g (5 mM) of iodine was added under argon atmosphere. After 6h, the reaction was quenched by addition of saturated NaHCO₃-solution. The layers were separated and after extraction of the aqueous layer with dichloromethane the combined organic layers were washed with a saturated sodium bisulfate solution and water, and dried over Na₂SO₄. The solvent was removed in *vacuo* and further purification of the crude product via column chromatography (silicagel, eluent: *n*-hexane) yield 1.0 g (1.44 mM, 72 %) of the di-iodinated quaterthiophene **4** as an orange solid, mp 150° -151° C. ¹H-NMR (400 MHz, CDCl₃) δ [ppm]: 1.14, t, 6H, 7.55 Hz, 1.19, t, 6H, 7.56 Hz, 2.58, qr, 4H, 7.57 Hz, 2.79, qr, 4H, 7.55 Hz., 6.98, d, 2H, 3.78 Hz, 7.11, 2H, 3.78 Hz. ¹³C-NMR (100 MHz, CDCl₃): 148.54, 139.95, 137.01, 135.75, 134.73, 126.77, 123.96, 24.52, 21.62, 15.41, 14.34 [ppm] MS (MALDI-TOF) calculated monoisotopic mass for C₂₄H₂₄I₂S₄ 694.52, found 694.5 [M⁺] Elemental analyses requires (%) C: 41.50, H: 3.48, S: 18.47 found C: 41.31, H: 3.40, S: 18.29.

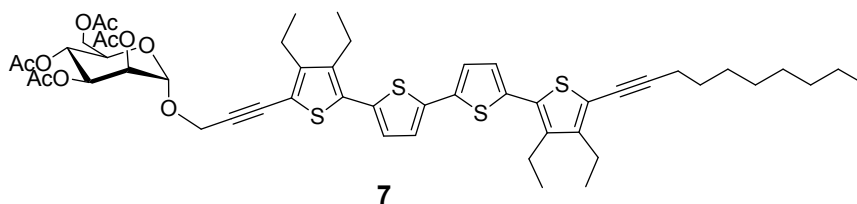
**3-(3,3',4,4'-tetraethyl-5'-iodo-2,2':5',2'':5'',2'''-quaterthiophen-5-yl)prop-2-yn-1-yl
2,3,4,6-tetra-O-acetyl- α -D-(+) mannopyranoside, **6****



150 mg (0.22 mM) Tetraethyl-diiodo-quaterthiophene **4** and 100 mg (0.26 mM) of the ester-protected propargyl- α -D-(+)mannoside **5** were dissolved in 24 ml carefully degassed diisopropylamine (DIPA) / THF mixture (1/ 2). Subsequently, 20 μ M Pd (PPh₃)₄Cl₂ and 10 μ mol CuI were added. After stirring overnight, the solvent was removed via rotary evaporator. The crude product was dissolved in dichloromethane and the organic layer was washed with water. Subsequently, the organic phase was dried over Na₂SO₄ and concentrated. Further purification via column chromatography afforded the anomerically pure mannose conjugate **6** as a yellow solid in a 50.1 % yield (104 mg, 0.11 mM).

¹H-NMR (CDCl₃, 400 MHz): δ = 7.13 (d, J = 3.8 Hz, H-3'; 1 H), 7.12 (d, J = 3.8 Hz, H-4'; 1 H) 7.05 (d, J = 3.8 Hz, H-3''; 1 H), 6.99 (d, J = 3.8 Hz, H-4''; 1 H), 5.40-5.29 (m, 3 H; H-2, H-3, H-4), 5.12 (d, 1 H), 4.56 (m, 2 H), 4.35-4.31 (dd, 1 H, J = 5.0 Hz, 12.3 Hz), 4.12 (dd, 1 H, J = 2.4 Hz, 12.2 Hz), 4.08 (m, 1 H) 2.83-2.56 (m, 8H; CH₂), 2.17 (s, 3H; OAc), 2.12 (s, 3 H; OAc), 2.05 (s, 3 H; OAc), 2.00 (s, 3 H; OAc), 1.22-1.12 (m, 12 H; CH₃) ppm. **¹³C-NMR** (CDCl₃, 100 MHz): δ = 170.59, 169.81, 169.81, 169.63, 150.65, 148.37, 139.89, 139.63, 137.00, 134.55, 132.11, 126.88, 126.67, 123.96, 115.76, 96.06, 90.16, 80.16, 73.91, 68.95, 68.83, 65.92, 62.26, 55.79, 24.44, 20.63, 15.37, 15.13, 14.84, 14.31 ppm. **MS** (MALDI-TOF), *m/z*: calc.: 952.95, found: 952.5 [M]. - The L-(-) mannosidic counterpart revealed identical NMR data.

3-[5'''-(dec-1-yn-1-yl)-3,3''',4,4'''-tetraethyl-2,2':5',2'':5'',2'''-quaterthiophene-5-yl]prop-2-yn-1-yl 2,3,4,6-tetra-O-acetyl- α -D-(+)mannopyranoside, **7**



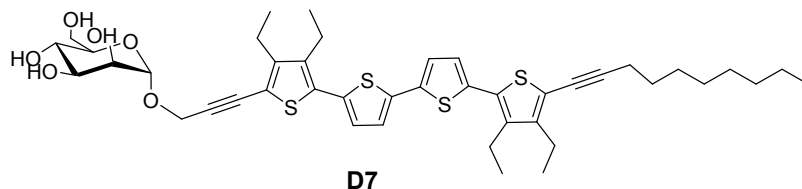
70 mg (74 μ M) of the D-(+)-mannosidic quaterthiophene **6** and 12 mg (90 μ M) 1-decyne were dissolved in 8 ml carefully degassed Di-isopropylamine/THF (1/2) solvent mixture. 5.1 mg (7.2 μ M) of Pd (PPh₃)₂Cl₂ and, after 5 min, 1.8 mg (4.5 μ M) CuI were added. The mixture was allowed to stir overnight. Subsequently, the solvent was removed under reduced pressure and the crude product was purified via column chromatography using n-hexane/ethylacetate (2/5) as eluent. The ester-protected **7** was isolated in 82 % yield (55 mg (57 μ M) as orange solid.

¹H-NMR (CDCl₃, 400 MHz): δ = 7.11 (d, J = 3.8 Hz, 2 H), 7.05 (d, J = 3.8 Hz, 1 H), 7.02 (d, J = 3.8 Hz, 1 H), 5.40-5.29 (m, 3 H; H-2, H-3, H-4), 5.12 (d, J = 1.5 Hz, 1 H; H-1), 4.56 (m, 2 H; H-7, H-7'), 4.35 (dd, J = 5.0 Hz, 12.3 Hz, 1 H; H-6), 4.12 (dd, 2 H, J = 2.4 Hz, 12.2 Hz), 4.08 (m, 1 H), 2.77-2.63 (m, 8 H; CH₂), 2.46 (t, 2 H; α -CH₂), 2.17 (s, 3 H; OAc), 2.11 (s, 3 H; OAc), 2.05 (s, 3 H; OAc), 2.00 (s, 3 H; OAc), 1.64-1.57 (m, 2 H; β -CH₂), 1.49-1.42 (m, 2 H; γ -CH₂), 1.31-1.24 (m, 8 H; CH₂), 1.24-1.20 (m, 12 H; CH₃), 0.89 (t, 3 H; alkyl-CH₃) ppm.

¹³C-NMR (CDCl₃, 101 MHz): δ = 170.72, 169.93, 169.70, 150.70, 148.38, 139.65, 139.52, 137.24, 136.47, 135.33, 132.22, 126.93, 126.43, 124.04, 123.88, 118.35, 115.75, 113.64, 97.84, 96.10, 90.18, 69.35, 69.00, 65.94, 62.31, 55.84, 31.82, 29.21, 29.08, 28.84, 28.68, 22.65, 21.87, 21.73, 21.08, 21.01, 20.88, 20.75, 19.85, 15.21, 15.18, 14.88, 14.77, 14.11 ppm. **MS** (MALDI-TOF), *m/z* calc.: 962.32, found: 962.7 [M]⁺. Elemental analysis calc.: C: 64.3 %, H: 6.67 %, S: 20.19 % found: C: 64.34 %, H: 6.67 %, S: 20.14 %.

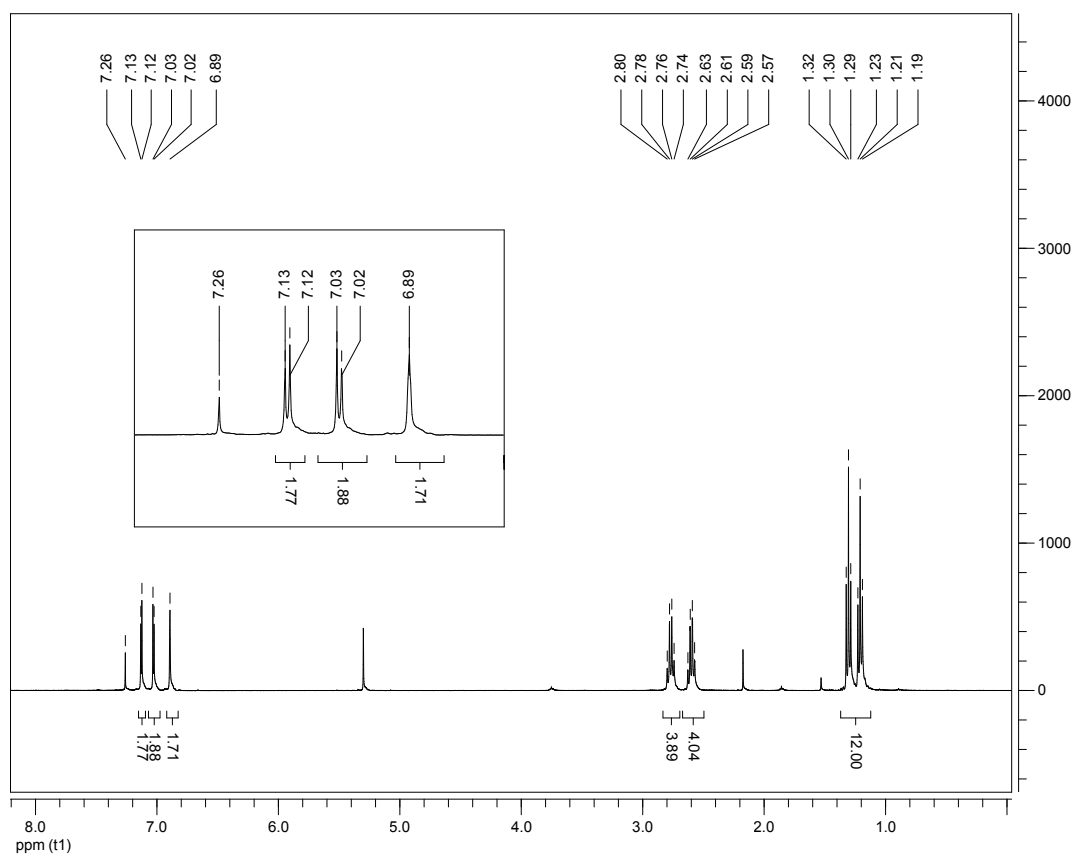
The opposite enantiomer (3-[5'''-(dec-1-yn-1-yl)-3,3''',4,4'''-tetraethyl-2,2':5',2'':5'',2'''-quaterthiophen-5-yl]prop-2-yn-1-yl 2,3,4,6-tetra-O-acetyl- α -L-(-)mannopyranoside) displayed identical NMR data.

3-[5'''-(dec-1-yn-1-yl)-3,3''',4,4'''-tetraethyl-2,2':5',2'':5'',2'''-quaterthiophene-5-yl]prop-2-yn-1-yl- α -D-(+)mannopyranoside (D7**)**

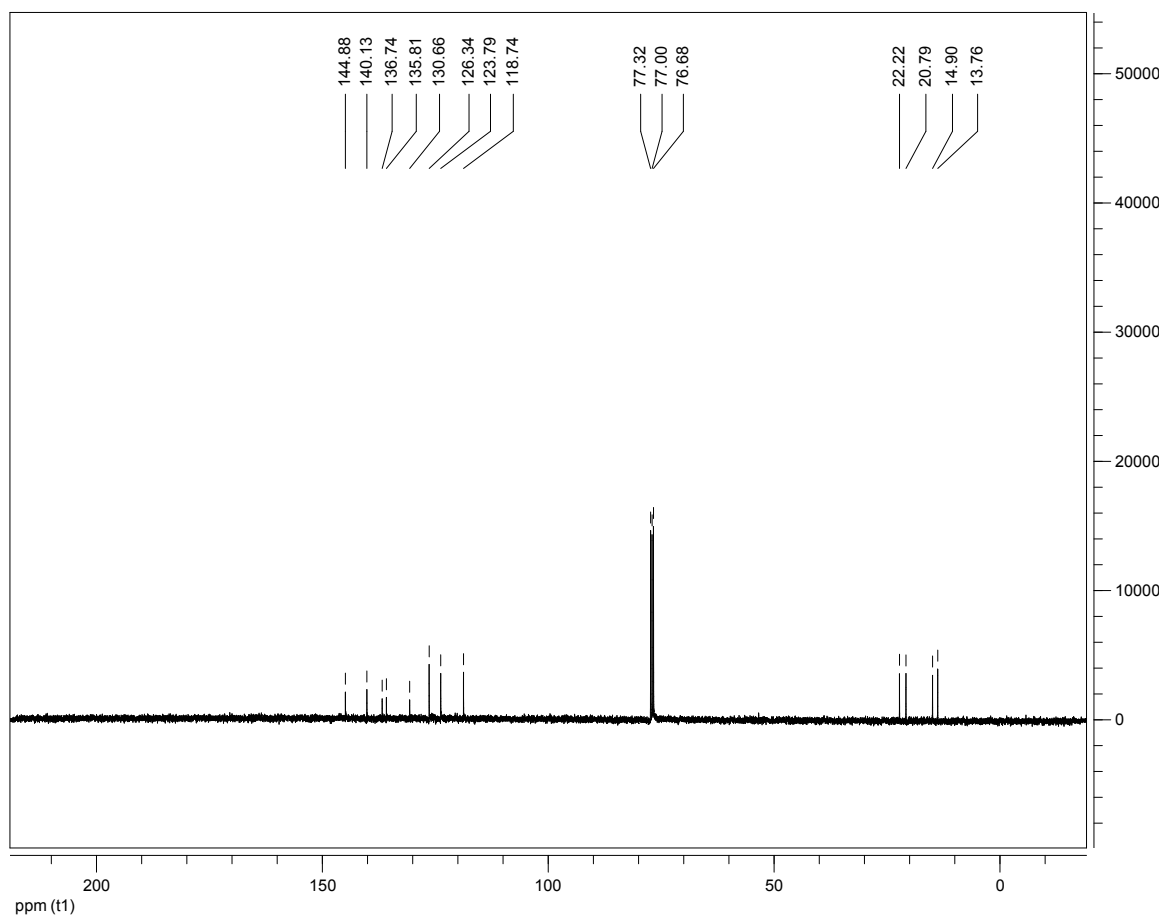


55 mg (0.057 mM) of the ester-protected D-(+) mannosidic quaterthiophene hybrid **7** were dissolved in 16 mL *abs.* THF / MeOH (1/1) and catalytic amount of sodium methanolate (0.3 M in MeOH) were added. After stirring for 1 hour the mixture was brought to pH 6 using ion exchanger Dowex marathon C. After removal of the solvent 41.0 mg (0.053 mM, 92.3%) of the deprotected hybrid **D7** were afforded. **¹H-NMR** (DMSO, 400 MHz): δ = 7.39 (d, J = 3.8 Hz, 2 H), 7.23 (d, J = 3.9 Hz, 1 H), 7.18 (d, J = 3.9 Hz, 1 H), 4.88 (d, J = 5.3 Hz, 1H; OH), 4.85 (s (br), 1H; H-1), 4.79 (d, J = 5.3 Hz, 1H; OH), 4.66 (d, J = 5.3 Hz, 1 H; OH), 4.58-4.46 (m, 3H; OH, H-5, H-6'), 3.70-3.62 (m, 2H), 3.48-3.43 (m, 2H), 2.74-2.61 (m, 8H; CH₂), 1.56-1.53 (m, 2H; β -CH₂), 1.43 (m, 2H; γ -CH₂), 1.27 (m, 8 H; CH₂), 1.16 (m, 12 H; CH₃), 0.87 (t, 3H; CH₃) ppm. **¹³C-NMR** (CDCl₃, 100 MHz): δ = 150.39, 148.61, 139.89, 139.77, 136.26, 135.75, 134.26, 133.72, 130.98, 129.19, 127.76, 127.31, 125.32, 125.22, 117.63, 115.72, 98.69, 98.44, 93.33, 78.47, 74.50, 70.86, 70.16, 66.75, 61.07, 53.98, 31.36, 28.80, 28.56, 28.28, 28.13, 22.26, 21.52, 21.38, 20.74, 19.15, 15.15, 14.94, 14.82, 14.10 ppm. **MS** (MALDI-TOF) *m/z*: calc.: 794.28, found: 794.5 [M]⁺. (C₄₃H₅₄O₆S₄ · 2MeOH): calc.: C: 62.90 %, H: 7.27 % found: C: 63.21, H: 7.12 %. The opposite enantiomer (3-[5'''-(dec-1-yn-1-yl)-3,3''',4,4'''-tetraethyl-2,2':5',2'':5'',2'''-quaterthiophene-5-yl]prop-2-yn-1-yl- α -L-(-)mannopyranoside (**L7**) display identical NMR data.

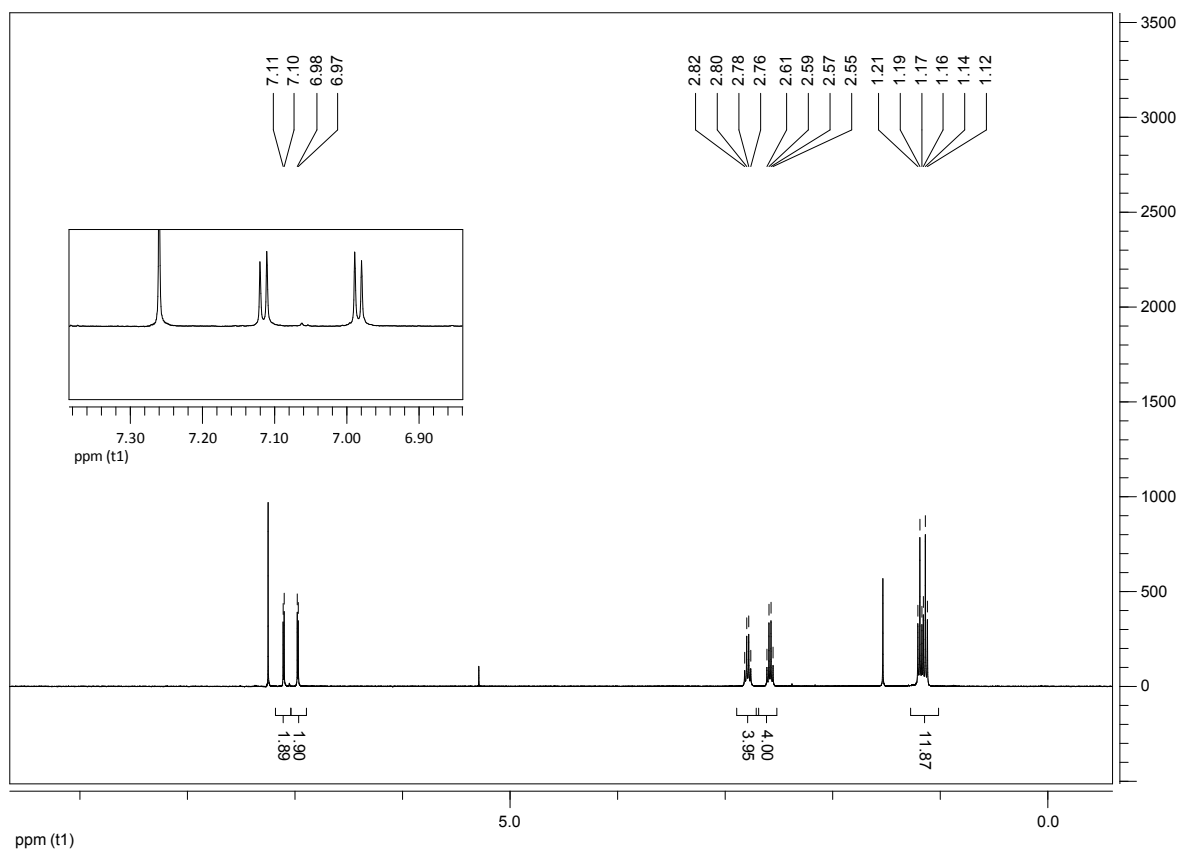
¹H NMR (CDCl₃) 3,3''',4,4'''-Tetraethyl-[2,2';5',2'';5'',2''']quaterthiophene **3**



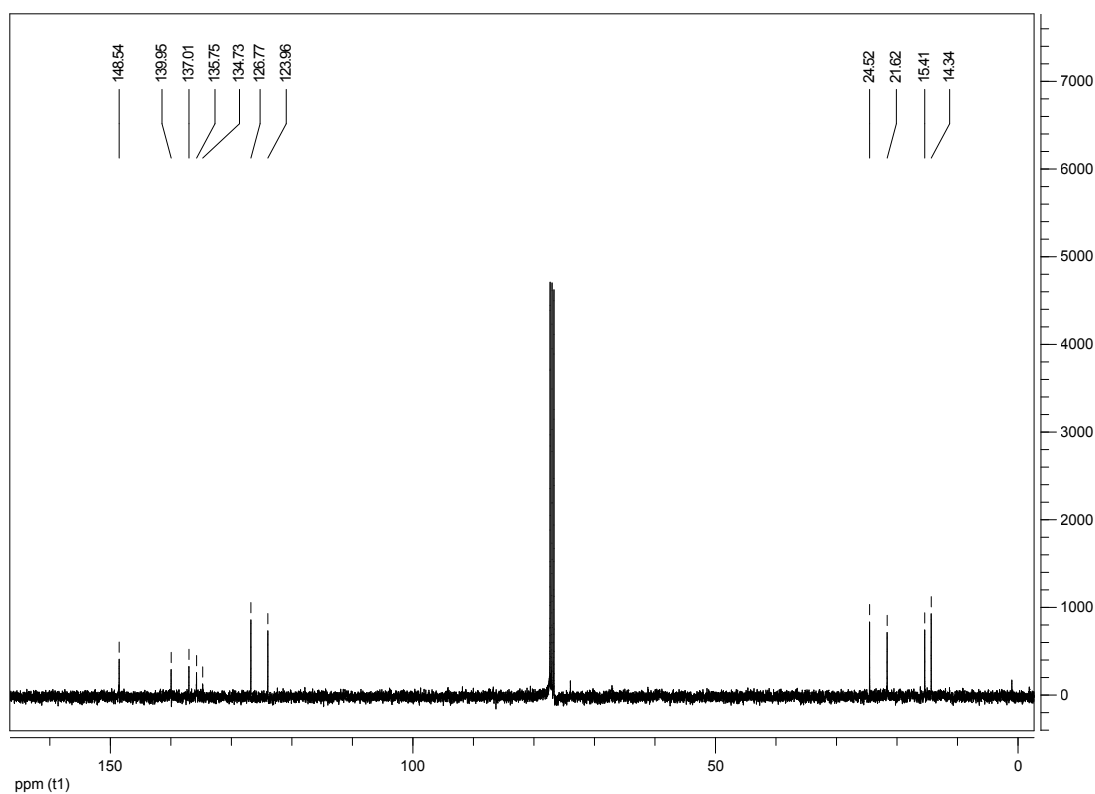
¹³C NMR (CDCl₃) 3,3''',4,4'''-Tetraethyl-[2,2';5',2'';5'',2''']quaterthiophene **3**



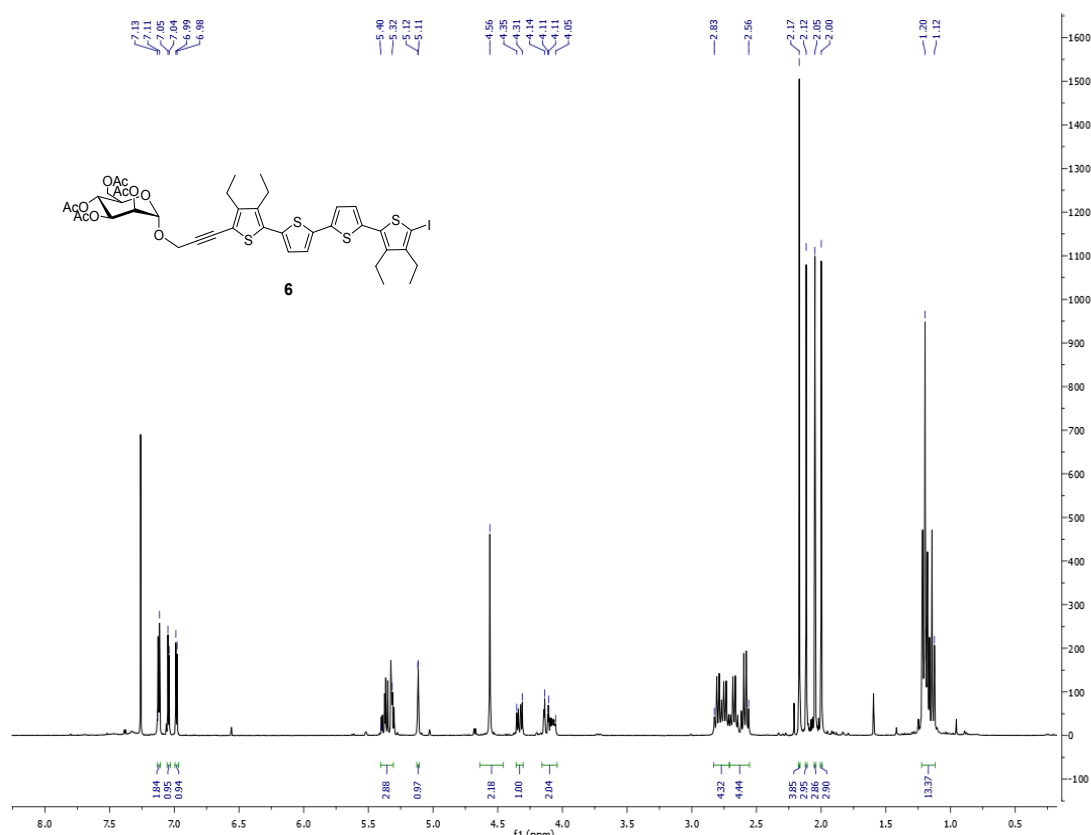
^1H NMR (CDCl₃) 5,5''Diiodo-3,3''',4,4'''-tetraethyl-[2,2';5',2'';5'',2''']quaterthiophene **4**



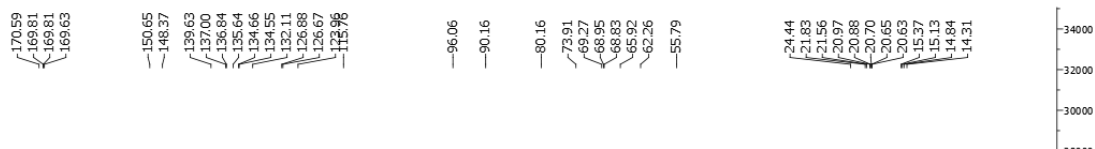
^{13}C NMR (CDCl₃) 5,5''Diiodo-3,3''',4,4'''-tetraethyl-[2,2';5',2'';5'',2''']quaterthiophene **4**



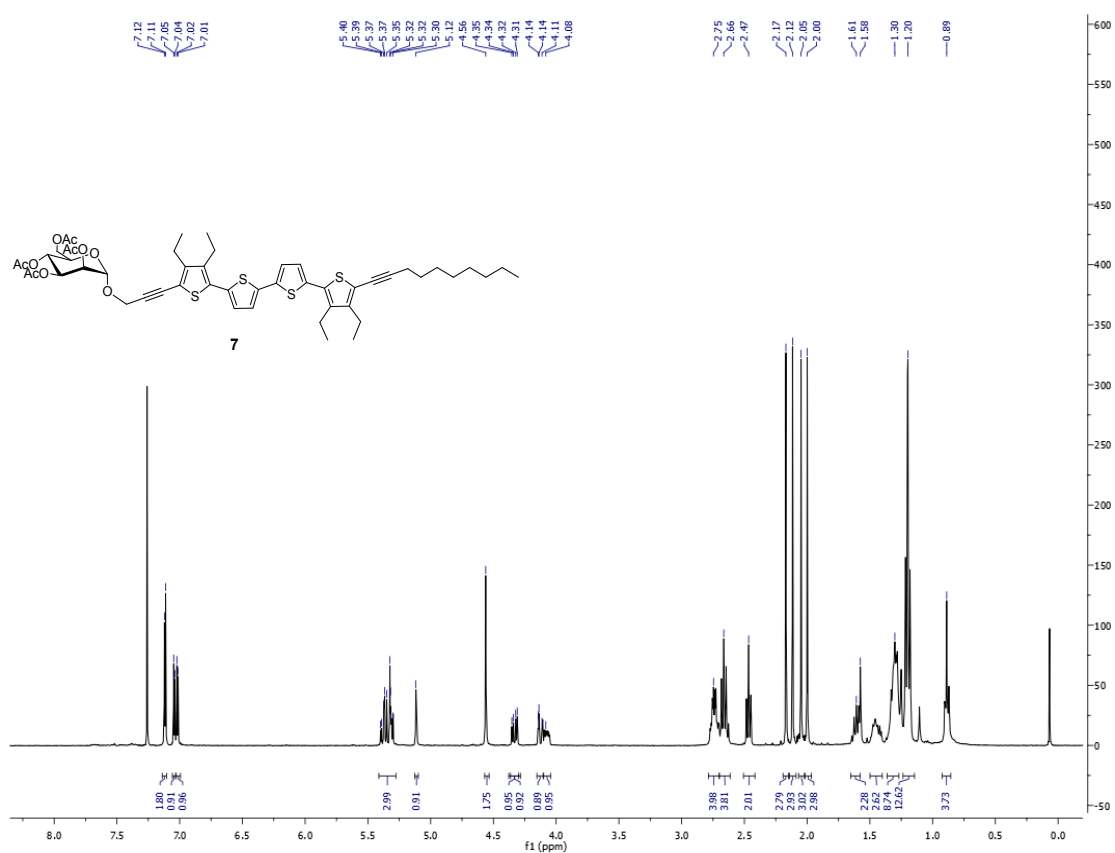
^1H NMR (CDCl_3) 3-(3,3''',4,4'''-tetraethyl-5'''-iodo-2,2':5',2'':5'',2'''-quaterthiophen-5-yl)prop-2-yn-1-yl 2,3,4,6-tetra-*O*-acetyl- α -D-(+) mannopyranoside, **6**



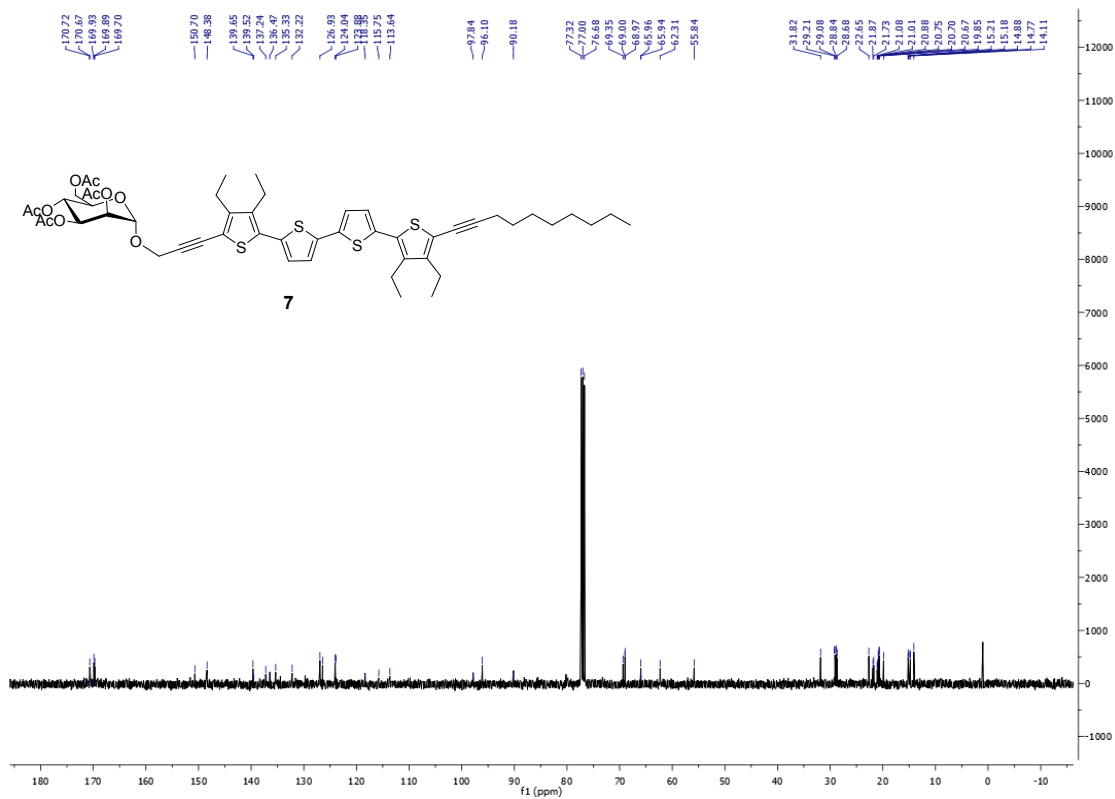
^{13}C NMR (CDCl_3) 3-(3,3''',4,4'''-tetraethyl-5'''-iodo-2,2':5',2'':5'',2'''-quaterthiophen-5-yl)prop-2-yn-1-yl 2,3,4,6-tetra-*O*-acetyl- α -D-(+) mannopyranoside, **6**



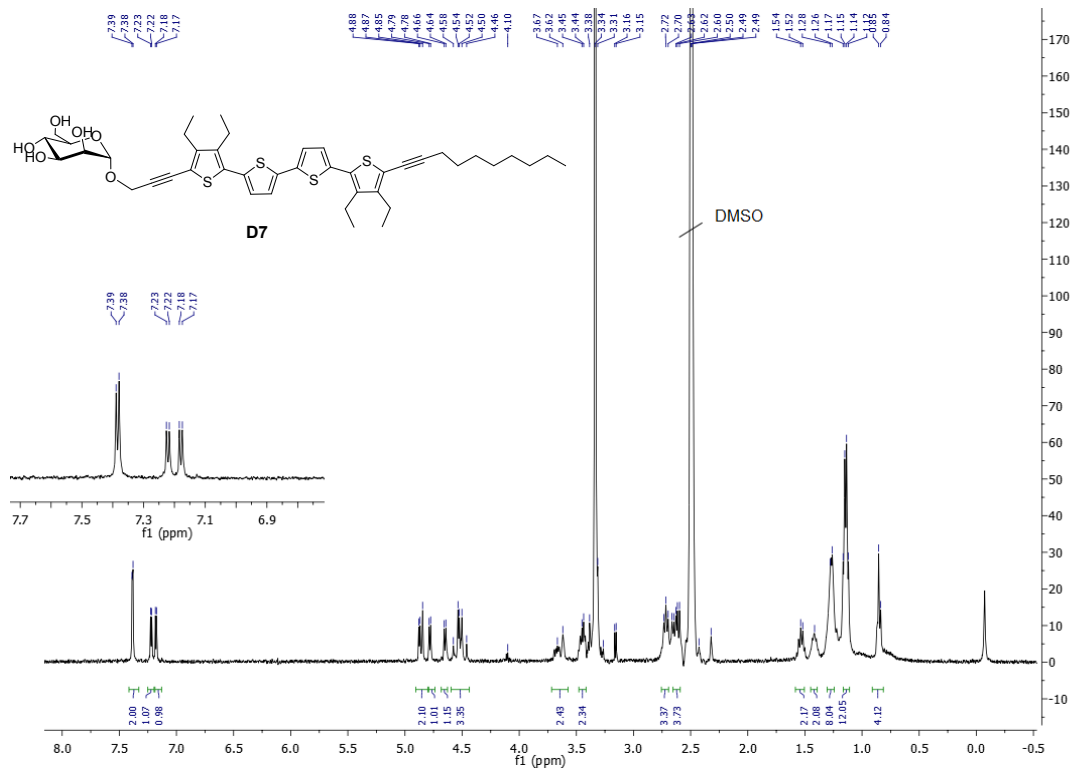
¹H NMR (CDCl₃) 3-[5'''-(dec-1-yn-1-yl)-3,3''',4,4'''-tetraethyl-2,2':5',2'':5'',2'''-quaterthiophen-5-yl]prop-2-yn-1-yl 2,3,4,6-tetra-O-acetyl-α-D-(+)mannopyranoside, **7**



¹³C NMR (CDCl₃) 3-[5'''-(dec-1-yn-1-yl)-3,3''',4,4'''-tetraethyl-2,2':5',2'':5'',2'''-quaterthiophen-5-yl]prop-2-yn-1-yl 2,3,4,6-tetra-O-acetyl-α-D-(+)mannopyranoside, **7**



^1H NMR (DMSO d_6) 3-[5'''-(dec-1-yn-1-yl)-3,3''',4,4'''-tetraethyl-2,2':5',2'':5'',2'''-quarterthiophene-5-yl]prop-2-yn-1-yl- α -D-(+)-mannopyranoside, **D7**



^{13}C NMR (CDCl_3) 3-[5'''-(dec-1-yn-1-yl)-3,3''',4,4'''-tetraethyl-2,2':5',2'':5'',2'''-quarterthiophene-5-yl]prop-2-yn-1-yl- α -D-(+)-mannopyranoside, **D7**

