Supplementary Material (ESI) for Chemical Communications

Supporting information

Carbohydrate-Functionalized Oligothiophenes for Concanavalin A Recognition

Sylvia Schmid,* Amaresh Mishra and Peter Bäuerle*

Institute of Organic Chemistry II and Advanced Materials, University of Ulm, Albert-Einstein-Allee 11, 89081 Ulm, Germany. Fax: +49 (0)731 50-22840 Tel: ++49 (0)731 50-22851; E-mail: sylvia..schmid@uni-ulm.de, peter.baeuerle@uni-ulm.de

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General information

Materials:

Dichloromethane (Merck) was distilled from CaH_2; *N*,*N*-diisopropylethylamine (DIPEA, Sigma Aldrich), copper(I)iodide (Merck), bis(triphenylphosphine) palladium(II)chloride and solvents were purchased from Merck which were distilled prior to use. For purification by column chromatography silica gel 60 (0.040-0.063 mm) from Merck was used. β-D-galactopyranose pentaacetate was purchased from *Alfa Aesar*. 5,5"α,α-Diiodo[2,2',3',5"]terthiophene **3** and 5,5'''-diiodo-3',5'''-bis(5-iodo-2-thienyl)-2,2':5',2'':4'',2'''-quaterthiophene **4** were prepared according to a literature protocol,[1,2] reference compounds 5,5''-bis(trimethylsilyl ethynyl)-2,2':3',2''-terthiophene **8** and 5,5'''-bis(trimethylsilyl ethynyl)-[3',5''-bis(5-trimethylsilyl ethynyl thien-2-yl)]-2,2':5',2'':4'',2'''-quaterthiophene **9** were also prepared as described.[2]

Instrumentation:

Nuclear magnetic resonance spectra were recorded on a *Bruker* AMX 500 (^{1}H NMR: 500 MHz), a *Bruker* Avance 400 (^{1}H NMR: 400 MHz, ^{13}C NMR: 100 MHz) or a *Bruker* DPX-400 spectrometer (^{1}H NMR: 400 MHz) at room temperature unless otherwise noted. Chemical shift values (δ) are given in parts per million using residual solvent protons (^{1}H NMR: δH = 7.26 for $CDCl_3$, δH = 2.49 for DMSO-d_6; δH = 3.33 for MeOD-d_4, ^{13}C NMR: δC = 77.0 for $CDCl_3$, δC = 49.05 for MeOD-d_4 and 39.43 for DMSO) as internal standard. Matrix-assisted laser desorption ionisation 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 a *Elementar Vario* EL (University of Ulm) and a *Carlo Erba* 1104 (University of Stuttgart). Melting points are uncorrected and were determined using a *Büchi* B-545 apparatus. 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. All reactions were monitored by TLC (aluminium plates, pre-coated with silica gel, *Merck* Si60 F254).

Cyclic voltammetry experiments were performed using a computer controlled *Metrohm* Autolab PGSTAT 10 Potentiostat in a three-electrode single-compartment cell (5 mL). The platinum working electrode consisted of a platinum wire sealed in a soft glass tube with a surface of A =

0.785 mm^2, which was polished down to 0.5 μm with Buehler polishing paste prior to use in order to obtain reproducible surfaces. The counter electrode consisted of a platinum wire and the reference electrode was a Ag/AgCl secondary electrode. A 0.1 M solution of tetrabutylammonium hexafluorophosphate (TBAHFP, Fluka) was used as electrolyte in dichloromethane, distilled over sulfuric acid in an argon atmosphere. In electrochemical characterization concentrations of 10^{-3} mol L^{-1} of the electroactive species were applied. CV-measurements were performed at 295 K using a scan rate of 100 mV s^{-1}. All potentials were internally referenced to the ferrocene /ferricenium couple (Fc/Fc^+).

Experimental Section

2-Propynyl-2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranoside, **1.**

α,β-D-mannopyranose pentaacetate (3.22 g, 8.24 mmol) and propargyl alcohol (0.77 ml, 13 mmol) were dissolved in 40 mL dry dichloromethane (DCM). The mixture was cooled to 0°C and boron trifluoride etherate (15 mmol, 2.13 g) was added in two portions. After removal of the cooling bath the reaction was stirred for 24 h. Subsequently, the mixture was quenched with saturated $NaHCO_3$ solution and the organic phase was dried over Na_2SO_4. Small amounts (ca. 7%) of the β-anomere were removed by column chromatography using *n*-hexane:ethylacetate as eluent. 2.7 g (84 %) of **1** were obtained as colorless solid.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.98 (s, 3H); 2.03 (s, 3H); 2.09 (s, 3H); 2.15 (s, 3H), 2.47 (t, 1H, J = 2.53 Hz); 4.01 (m,1H); 4.11 (dd, 1H, J = 12.1Hz, 2.5Hz); 4.25-4.30 (m, 3H); 5.02 (d, 1H, 1.96 Hz); 5.25 – 5.36 (3H, m) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 20.6, 20.7, 20.7, 20.8, 54.9, 62.4, 66.1, 68.9, 69.0, 69.4, 75.6, 77.9, 96.3, 169.7, 169.8, 169.9, 170.6 ppm; gated decoupled ^{13}C NMR spectroscopy indicated a $J_{C1\text{-}H1}$ value of 174.1 Hz. MS (CI) *m/z* = 387; Elemental analysis (%): found: C: 52.82, H: 5.72, calc. for $C_{17}H_{22}O_{10}$ C: 52.85, H: 5.74, $[\alpha]_D^{23}$ = +57.8 deg, c=0.27 g/dl in DCM.

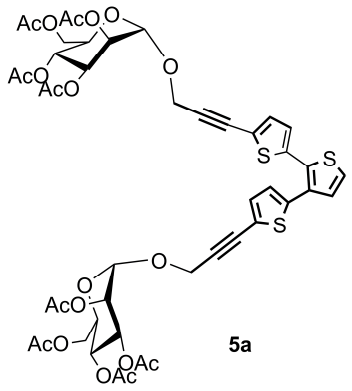
2-Propynyl-2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranoside, **2.**[3]

1.5 g (3.8 mmol) β-D-galactopyranose pentaacetate and propargyl alcohol (0.27 ml, 4.61 mmol) were dissolved in 30 mL dry dichloromethane. The mixture was cooled to 0°C and boron trifluoride etherate (5.76 mmol, 0.72 ml) was added in two portions. After removal of the cooling bath the reaction was stirred for 2 h. Subsequently, the mixture was quenched with anhydrous K_2CO_3 (480 mg) and after filtration the organic phase was dried over Na_2SO_4. After removal of the solvent small amounts of starting material was separated by column chromatography and 1.0 g (67 %) of **2** was yielded as a colorless solid.

^{1}H-NMR ($CDCl_3$, 400 MHz.) δ = 5.76 (d, 1H, 3.3 Hz, H4), 5.20 (dd, 1H, 7.9 Hz, 10.4 Hz, H2) 5.03 (dd, 1 H,10.5 Hz, 2.4 Hz, H-3), 4.72 (d, 1 H, 7.9 Hz,H-1), 4.25 (d, 2 H, J1,3 2.4 Hz, H-1), 4.12(m, 2 H, H-6), 3.91 (m, 1 H, H-5), 2.44 (t, 1 H, 2.4 Hz, H-3), 2.12, 2.05, 2.03, 1.96 (4 s, 12H,$OCOCH_3$ ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ = 20.5, 2x20.6, 20.7, 55.8, 61.1, 66.9, 68.4, 70.7, 70.8, 75.4, 78.1, 98.6, 169.5, 170.1, 170.2, 170.3 ppm.

Elemental analysis (%): found: C: H: 52.91, 5.73, calc. for $C_{17}H_{22}O_{10}$ C: 52.85, H: 5.74.

5,5”α,α-Di(-O-propargyl-2,3,4,6-tetraacetylmannoside)[2,2’,3’,5”]terthiophene, **5a.**



5a

In a two neck round bottom flask, first **3** (112 mg, 0.224 mmol) in 5 mL THF was degassed completely by bubbling with Ar-flow. Then catalyst $PdCl_2(PPh_3)_2$ (7.86 mg, 11.2 μmol, 4 mol %) and CuI (1.6 mg, 8.8 μmol, 2 mol%) were added and after 5 min 2-propynyl- α-D-mannopyranoside, **1** (190 mg, 0.492 mmol) and finally degassed diisopropylamine (10 mL) were added. The reaction mixture was stirred for 4-5 hrs. Then the catalytic residues were filtered and the filtrate evaporated in rotary evaporator. The solid obtained was purified by column chromatography (SiO_2, gradient elution using DCM → 10% EtOAc/DCM → 30% EtOAc/DCM) to obtain **5a** as colorless solid 188 mg (83 %), mp 69-74°C.

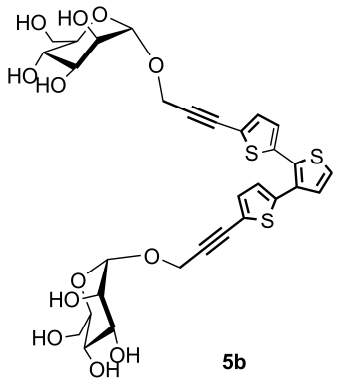
^{1}H NMR ($CDCl_3$) δ = 1.98, 2.03, 2.09, 2.15 (24H, $COCH_3$), 4.03 (m, 2H), 4.06 (m, 2H), 4.28 (d, J = 5.04 Hz, 1H), 4.31 (d, J = 4.8 Hz, 1H), 4.49 (s, 4H), 5.06 (m, 2H), 5.2-5.3 (m, 6H), 6.90 (d, J =3.8 Hz, 1H), 6.97 (d, J =3.8 Hz, 1H), 7.10-7.15 (m, 3H), 7.29 (d, J = 5.32 Hz, 1H) ppm.

^{13}C NMR ($CDCl_3$) δ = 20.61, 20.65, 20.70, 20.85 ($COCH_3$), 55.66, 55.72, 60.33, 62.23, 65.88, 68.92, 69.25, 80.11, 80.36, 88.0, 88.44, 96.22, 99.92, 121.86, 123.04, 125.48, 126.58, 127.75, 129.76, 131.23, 131.61, 133.23, 133.28, 136.62, 139.19, 169.65, 169.80, 169.88, 170.60 ppm.

MALDI-TOF mass m/z 1039.3 (M^+ + Na), 1055.2 (M^+ + K) (cald. for $C_{46}H_{48}O_{20}S_3$: 1016.08).

Elemental Analysis (%): cald. C: 54.32, H 4.76, S 9.46, for $C_{46}H_{48}O_{20}S_3$, found: C: 54.74, H 4.89, S 9.20

5,5”α,α-Di(-O-propargyl-mannoside)[2,2’,3’,5”]terthiophene, **5b**



5b

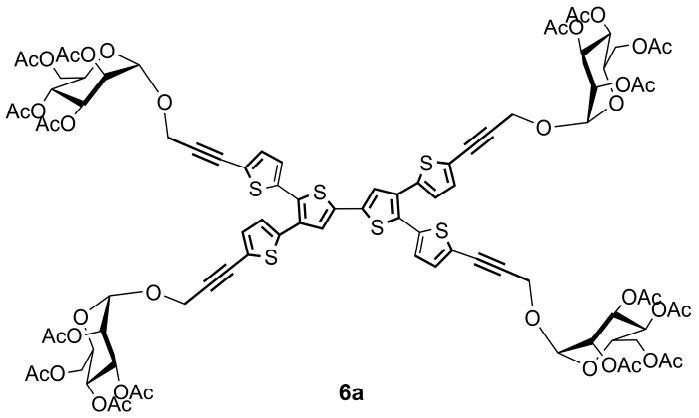
5a (80 mg, 0.086 mmol) was dissolved in a mixture of 30 ml methanol (abs.). After adding a catalytic amount sodium methanolate (0.02 ml, 0.3M) the reaction mixture was allowed stirring for 1hour. Neutralization with ion exchange resin Dowex Marathon C and subsequent filtration provided a clear solution. After removal of the solvent the deprotected **5b** was yielded as colorless solid in a 96 % yield (56 mg, 0.08 mmol).

^{1}H-NMR MeOD d_4, (400 MHz), δ = 7.49 (d, 5.31 Hz, 1H) 7.20 (d, 5.31 Hz, 1H), 7.18 (d, 3.79 Hz, 1H), 7.15 (d, 3.79 Hz, 1H), 7.02, d, 3.78 Hz, 1H (H1’), 7.00, d, 3.78 Hz, 1H (H1’), 5.01 (d, 1.52Hz , 2H), 4.52, d, 3.28 Hz, 4H, (CH_2), 3.88 – 3.82 (m, 4H) 3.60 – 3.76, 6H, (H2’’, H3’’, H4’’), 3.54 – 3.58 (m, 2H H5’’) ppm.

^{13}C -NMR MeOD d_4 (100 MHz), δ =140.16, 137.5, 134.1, 134.0, 133.4, 132.1, 130.6, 129.5, 128.1, 127.2, 125.2, 123.9, 100.2, 100.1, 91.2, 90.6, 80.1, 79.8, 75.2, 75.2, 72.5, 72.0, 68.4, 62.8, 55.7 ppm.

$C_{30}H_{32}O_{12}S_3 \cdot 3H_2O$ Elemental analysis calc . C 49.04, H 5.21, S 13.09, fd. C 49.19, H 5.05, S: 13.53. MS (ESI) calc. for $C_{30}H_{32}O_{12}S_3$ $[M + H]^+$ = 680.8, found 703.2 $(M + Na)^+$.

5,5’’’-bis(α,α-Di(-O-propargyl-2,3,4,6-tetraacetylmannoside)-[3’,5’’-bis(5-α,α-Di(-O-propargyl-2,3,4,6-tetraacetylmannoside thien-2-yl)]-2,2’:5’,2’’:4’’,2’’’-quaterthiophene, **6a.**



6a

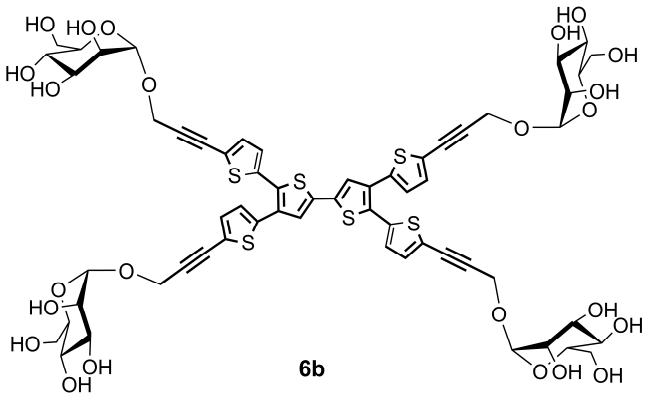
In a two neck round bottom flask, first 5,5'''-diiodo-3',5'''-bis(5-iodo-2-thienyl)-2,2':5',2'':4'',2''' , **4,** (122 mg, 122 μmol) was dissolved in Ar degassed THF (10 mL). Then catalyst $PdCl_2(PPh_3)_2$ (8.6 mg, 12.2 μmol, 10 mol %) and CuI (1.2 mg, 6.1 μmol, 5 mol%) were added and after 5 min propargyl mannose (190 mg, 0.492 mmol). Finally Ar degassed diisopropylamine (10 mL) was added. The reaction mixture was stirred for 4-5 hrs at r.t. Then the catalytic residues were filtered and the filtrate evaporated in rotary evaporator. The solid obtained was purified by column chromatography (SiO_2, gradient elution using DCM → 20% EtOAc/DCM → 40% EtOAc/DCM) to obtain **6a** as yellowish solid 85 mg (103 mg, 63 %), mp 69-85° C.

^{1}H NMR ($CDCl_3$, δ) 1.982, 2.033, 2.095, 2.155, 4.03-4.08 (br, 4H), 4.09, (t, 2H), 4.13, (t, 2H), 4.29 (dd, J = 1.86, 5.02, 2H), 4.31 (dd, J = 1.91, 5.05, 2H), 4.50, 4.51, (s, 8H), 5.05, 5.06, 5.07, 5.07, (s, 4H), 5.25-5.40 (m, 12H), 6.96 (d, *J* = 3.76 Hz, 2H), 7.00 (d, *J* = 3.82 Hz, 2H), 7.14 (d, *J* = 3.83 Hz, 2H), 7.16 (d, *J* = 3.77 Hz, 2H) 7.18 (s, 2H).^{13}C NMR ($CDCl_3$, δ) 20.60, 20.64, 20.691, 20.83, 55.72, 55.75, 62.31, 66.02, 68.95, 68.96, 69.02, 69.33, 69.35, 80.05, 80.23, 88.31, 88.90, 96.33, 122.53, 123.33, 126.83, 127.18, 127.66, 131.15, 132.06, 133.30, 135.18, 136.07, 138.37, 169.63, 169.76, 169.85, 170.56 ppm.

MALDI-TOF mass: calcd. 2032.1 found 2053.3 $(M + Na)^+$, 2069.2 $(M + K)^+$

Elemental analysis: cald. for $C_{92}H_{94}O_{40}S_6$ C: 54.38, H 4.66, S 9.47, fd. C: 54.13, H 4.78, S 9.45.

5,5'''-bis(α,α-Di(-O-propargyl-mannoside)-[3',5''-bis(5-α,α-Di(-O-propargylmannoside thien-2-yl)]-2,2':5',2'':4'',2'''-quaterthiophene, **6b.**



6b

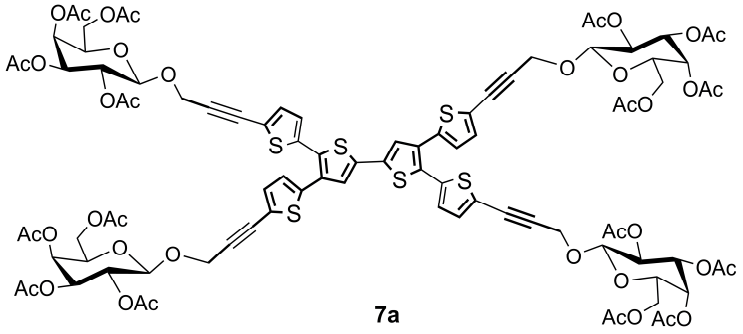
6a (50 mg, 24.6 μmol) was dissolved in a mixture of 30 ml (v/v) methanol (abs.)/THF mixture. After adding a catalytic amount sodium methanolate (0.02 ml, 0.3M) the reaction mixture was allowed stirring for 1 hour. Neutralization with ion exchange resin Dowex Marathon C and subsequent filtration provided a clear solution. After removal of the solvent the deprotected **6b** was yielded as colorless solid in a 89 % yield (30 mg, 22 μmol).

^{1}H-NMR DMSO d_6 (400 MHz) δ = 7.70, s, 2H , 7.37, d, 3.79 Hz, 2H, 7.36, d, 3.79 Hz, 2H , 7.30, d, 3.79 Hz, 2H, 7.26, d, 3.79 Hz, 2H, 4.81, d,1.26 Hz, 4H, 4.48, m (AB-System $CH_{2\ propargyl}$), 8H, (CH_2), 3.35 – 3.69, m, 24H ($CH_{2\text{-}6\ mannoside}$) ppm.

^{13}C-NMR DMSO d_6 (100 MHz) δ: 52.7, 54.3, 61.4, 67.2, 70.4, 71.2, 71.3, 74.9, 78.6, 78.9, 91.6, 92.3, 98.9, 99.0, 100.0, 122.67, 123.8, 126.4, 128.9, 129.4, 129.8, 130.3, 132.9, 133.9, 134.2, 135.2, 137.6.

MS (ESI) calc. for $C_{60}H_{62}O_{24}S_6$ $[M + H]^+$ = 1359.2, found 1381.6 $(M + Na)^+$.

5,5'''-Bis(α,α-Di(-O-propargyl-2,3,4,6-tetraacetylgalactoside)-[3',5''-bis(5-β,β-Di(-O-propargyl-2,3,4,6-tetraacetylgalactoside thien-2-yl)]-2,2':5',2'':4'',2'''-quaterthiophene, 7a



7a

In a two neck round bottom flask, first **4** (49.9 mg, 50 μmol) in 5 mL THF was degassed completely by bubbling with Ar-flow. Then catalyst $PdCl_2(PPh_3)_2$ (32 mg, 14 μmol, 7 mol %) and CuI (1.6 mg, 5 μmol, 2 mol%) were added and after 5 min 2-propynyl- β-D-galactopyranoside, **2** (85 mg, 0.22 mmol) and finally degassed diisopropylamine (10 mL) were added. The reaction mixture was stirred for 4-5 hrs. Then the catalytic residues were filtered and the filtrate evaporated in rotary evaporator. The solid obtained was purified by column chromatography (SiO_2, gradient elution using DCM → 10% EtOAc/DCM → 30% EtOAc/DCM) to obtain **7a** as colorless solid 80 mg (79 %).

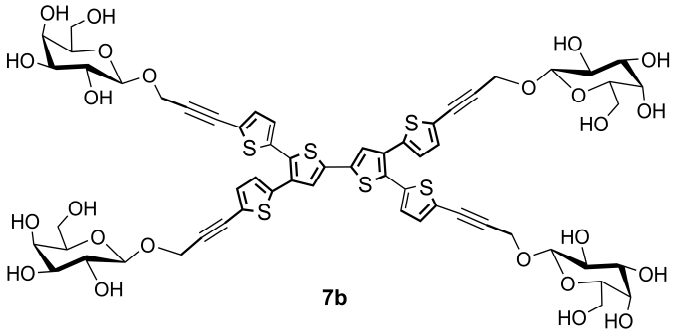
^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 1.98 (s, 12H, Ac,), 2.04 (s, 12H, Ac), 2.05 (s, 6H, Ac,), 2.06 (s, 6H, Ac), 2.15 (s, 12H, CH_3,), 3.96 (m, 4H, H5), 4.11-4. 23 (m, 8H, ($CH_{2galactose}$)), 4.62 (2s, $CH_{2\ propargyl}$, 8H), 4.72 (2d, 7.9 Hz, 4H, H1), 5.07 (m, 4H, 3.1 Hz,), 5.23 (m, 4H,), 5.40 (d, 3.3 Hz, 4H), 6.98 (d, 2H, 3.76 Hz,), 7.02 (d, 2H, 3.81 Hz,), 7.13 (d, 2H, 3.81 Hz), 7.16 (d, 2H, 3.76 Hz,), 7.20 (s, 2H) ppm, **^{13}C-NMR** ($CDCl_3$, 100.13 MHz) δ: 170.3, 170.2, 170.1, 169.5, 138.3, 136.0, 135.2, 133.0, 132.1, 67.0, 61.2, 57.0, 56.9, 20.8, 20.64, 20.61, 20.5 ppm.

MALDI-TOF mass: calcd. 2032.13 found 2032.0 $(M)^+$

Elemental analysis: cald. for $C_{92}H_{94}O_{40}S_6$. $8H_2O$ C: 50.78, H 5.09 fd. C: 50.55, H 5.02

HRMS: calcd. 2030.3646, fd. 2031.4051

5,5'''-Bis(α,α-Di(-O-propargyl-galactoside)-[3',5''-bis(5-β,β-Di(-O-propargylgalactoside thien-2-yl)]-2,2':5',2'':4'',2'''-quaterthiophene, **7b**



7b

7a (50 mg, 24.6 μmol) was dissolved in a mixture of 30 ml (v/v) methanol (abs.)/THF mixture. After adding a catalytic amount sodium methanolate the reaction mixture was allowed stirring for 1 hour. Neutralization with ion exchange resin *Dowex Marathon C* and subsequent filtration provided a clear solution. After removal of the solvent the **7b** was yielded as yellowish solid in a 80.1 % yield (27 mg, 19.9 μmol).

^{1}H-NMR DMSO d_6 (400 MHz) δ = 7.70, s, 2H , 7.36, d, 3.79 Hz, 2H, 7.35, d, 3.79 Hz, 2H , 7.29, d, 3.79 Hz, 2H, 7.26, d, 3.79 Hz, 2H, 4.58, m (AB-System $CH_{2\ propargyl}$), 8H, 4.24, d, 6.91 Hz, 4H, 3.35 – 3.69, m, 24H ($CH_{2\text{-}6\ galactose}$) ppm. **^{13}C-NMR** (DMSO d_6 100.13 MHz)

δ = 49.5, 50.2, 56.5, 60.6, 61.3, 67.3.1, 67.9, 68.9, 70.3, 71.2, 71.5, 72.7, 74.1, 74.8, 75. 7, 76.1, 7 7.7, 98.2, 102.2, 123.5, 133.3, 134.1, 134.3, 135.2 (2), 142.8 ppm.

MS (Maldi tof) calc. for $C_{60}H_{62}O_{24}S_6$ $[M + H]^+$ = 1358.2, found 1356.0

Elemental analysis: cald. for $C_{60}H_{62}O_{24}S_6 \cdot 7\ H_2O$ C: 48.51, H 5.16, S 12.95, fd. C: 48.38, H 5.12, S 12.90

Electrochemical characterization

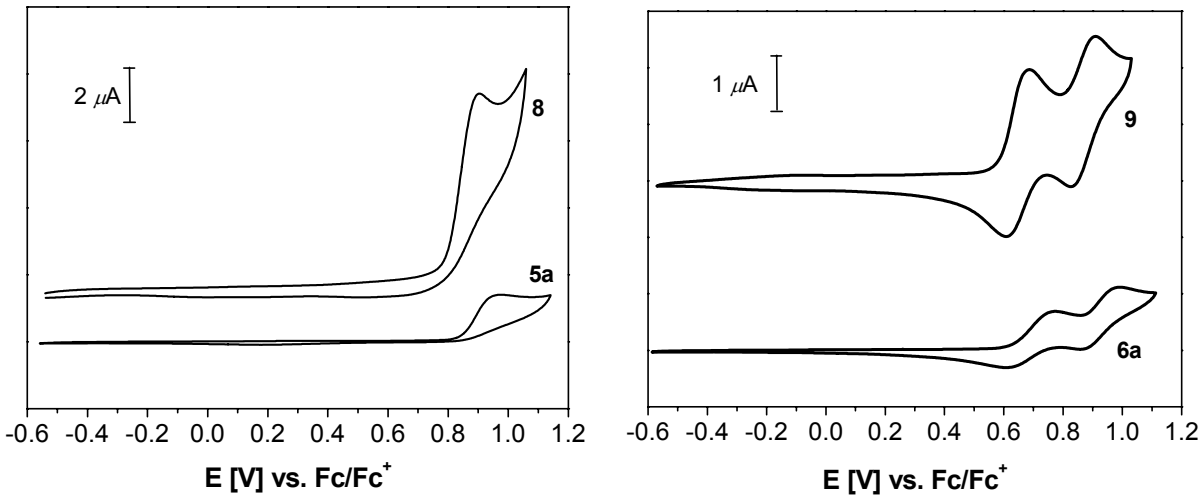


Fig. S1 right: CV of **5a** and **8** measured in dichloromethane/TBAHFP (0.1M), c = 10^{-3} mol L^{-1} vs. Fc/Fc^{+}, 295 K, scan rate = 100 mV s^{-1}.

Fig. S2 left: CV of **6a** and **9** measured in dichloromethane/TBAHFP (0.1M), c = 10^{-3} mol L^{-1} vs. Fc/Fc^{+}, 295 K, scan rate = 100 mV s^{-1}.

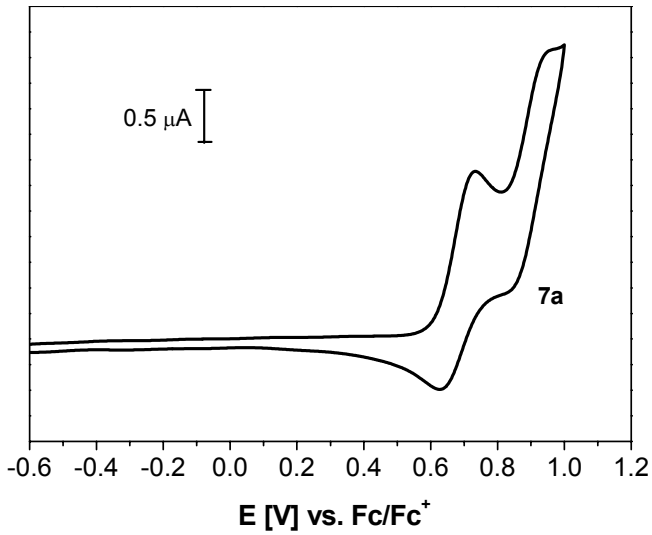


Fig. S3: CV of **7a** measured in dichloromethane/TBAHFP (0.1M), c = 10^{-3} mol L^{-1} vs. Fc/Fc^{+}, 295 K, scan rate = 100 mV s^{-1}.

Turbidiy analysis

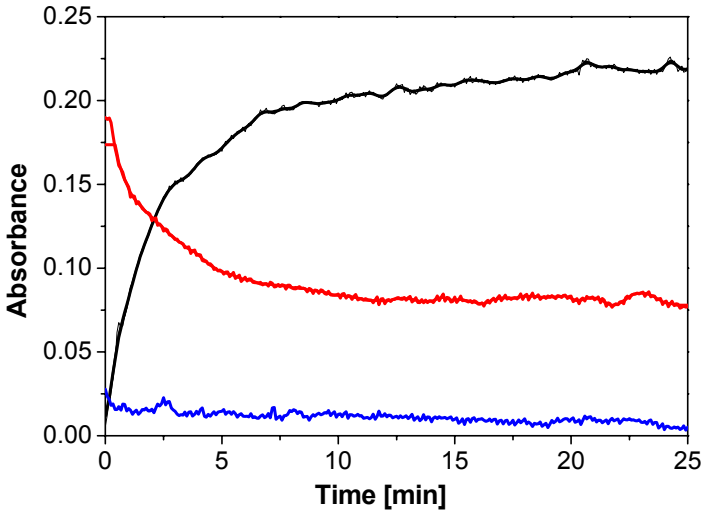


Fig. S4: Turbidity analysis in 0.1 M Hepes Buffer, 0.1 M $CaCl_2$, $MnCl_2$, blue curve: change of optical densitiy of **5b** upon addition of BSA, black curve: change of optical density of **5b** upon addition of Con A, red curve after 25 minutes 1 mg α-methylmannoside was added (measured at 500 nm).

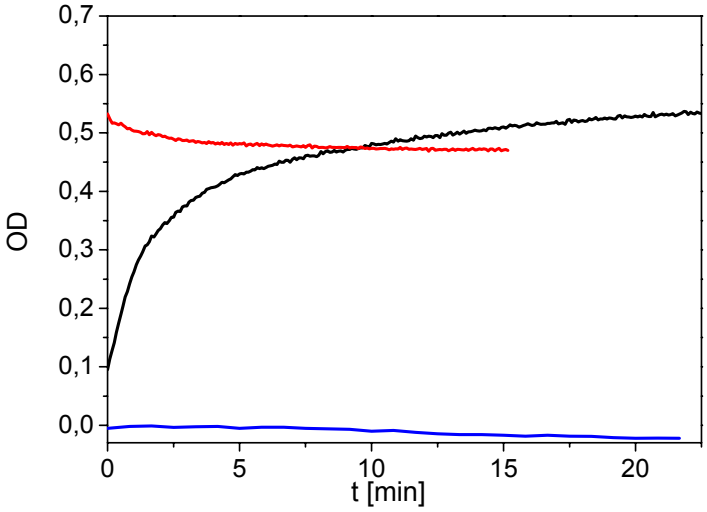


Fig. S5: Turbidity analysis in 0.1 M Hepes Buffer, 0.1 M $CaCl_2$, $MnCl_2$, blue curve: change of optical densitiy of **6b** upon addition of BSA black curve: change of optical densitiy of **6b** upon addition of ConA, red curve after 25 minutes 1 mg α-methylmannoside was added (measured at 500 nm).

Control experiment

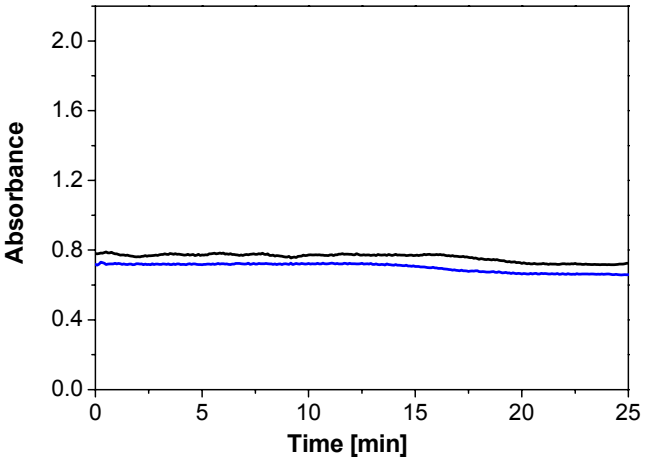


Fig. S6: Turbidity analysis in 0.1 M Hepes Buffer, 0.1 M $CaCl_2$, $MnCl_2$, black curve: optical densitiy of **7b** blue curve: change of optical densitiy of **7b** upon addition of Con A, measured at 500 nm

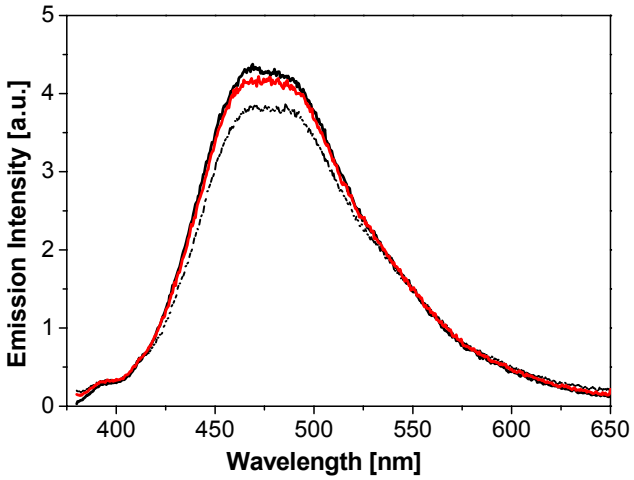
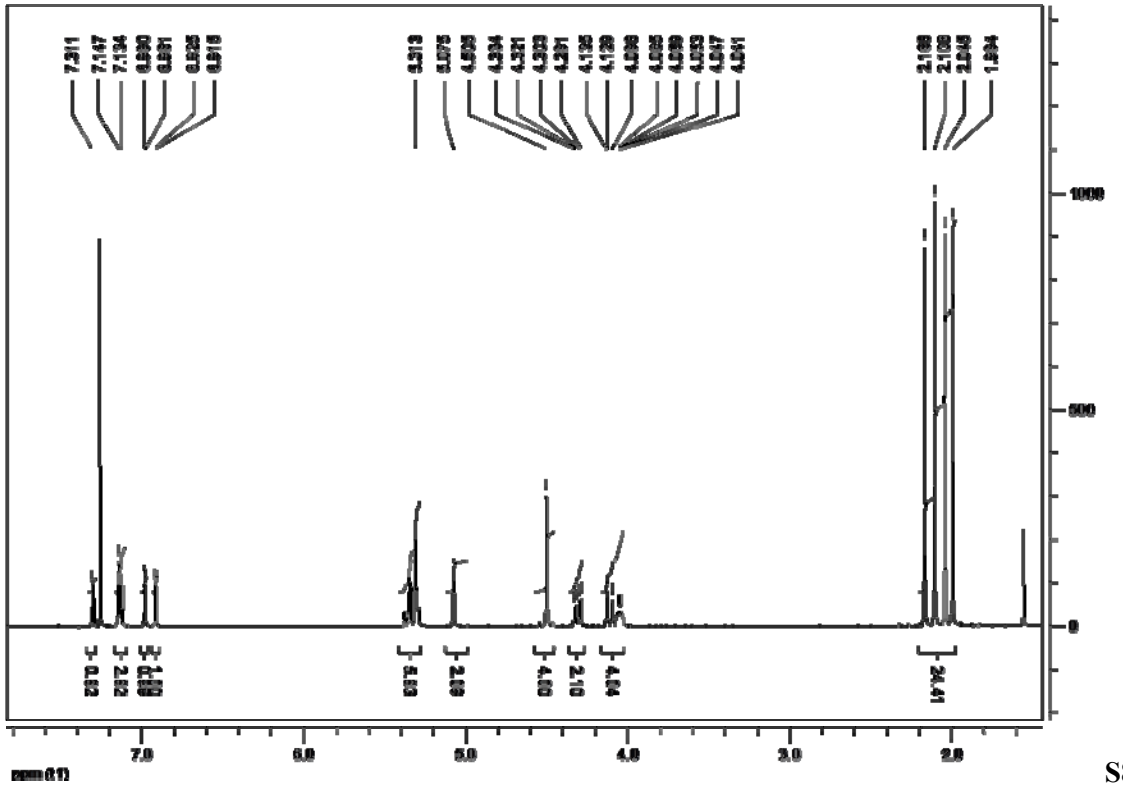
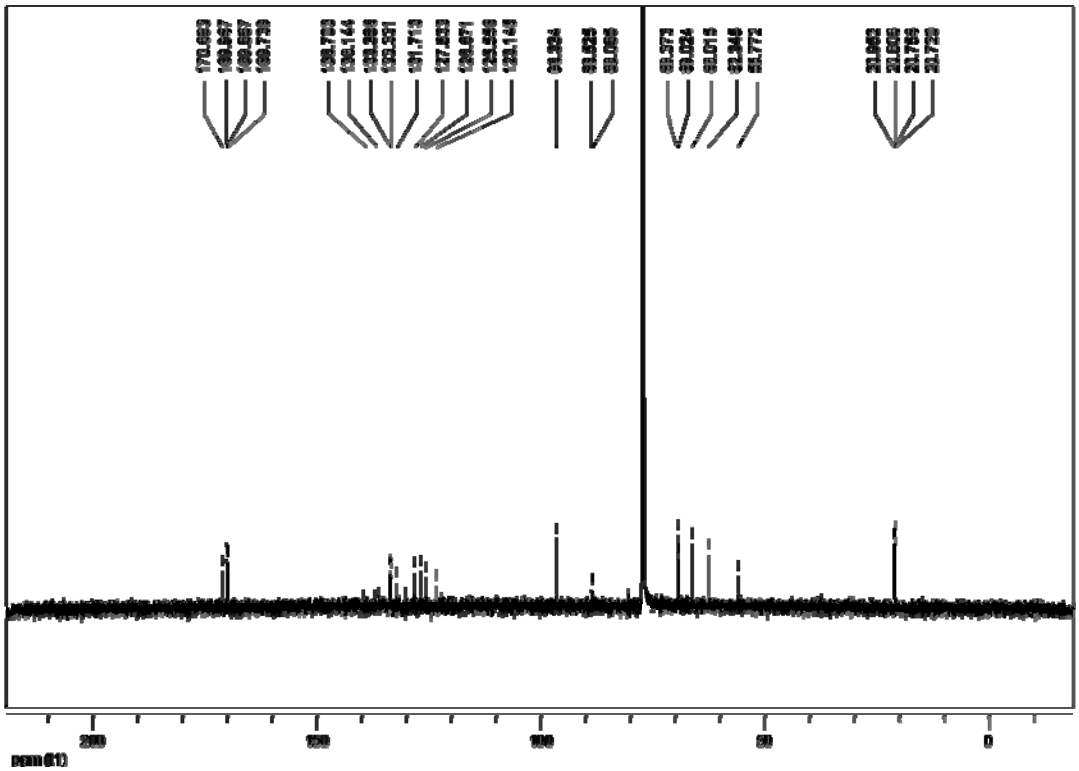


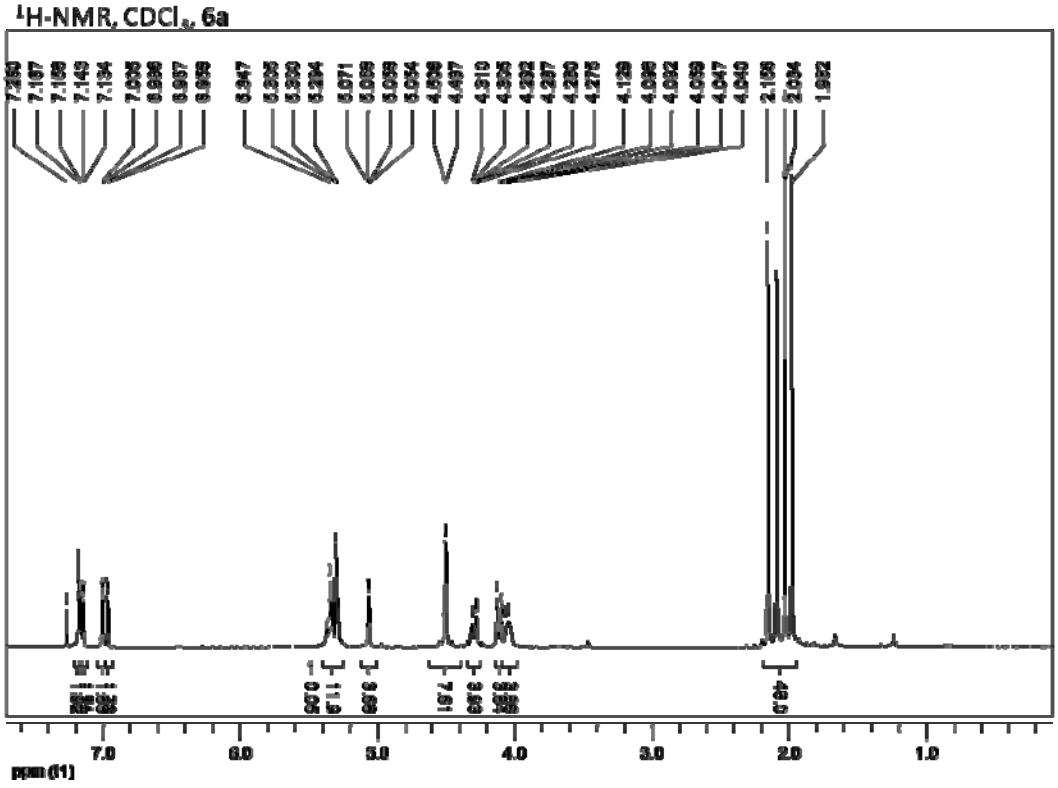
Fig. S7: Fluorescence spectra of **5b**, in 0.1 M Hepes Buffer, 0.1 M $CaCl_2$, $MnCl_2$, and $CaCl_2$ [1 mM] (dark line), quenched emission upon addition of Con A (dotted) and 20 min stirring, restored emission after addition of 1 mg α-methylmannoside (red), $\lambda_{excitation}$ = 360 nm.

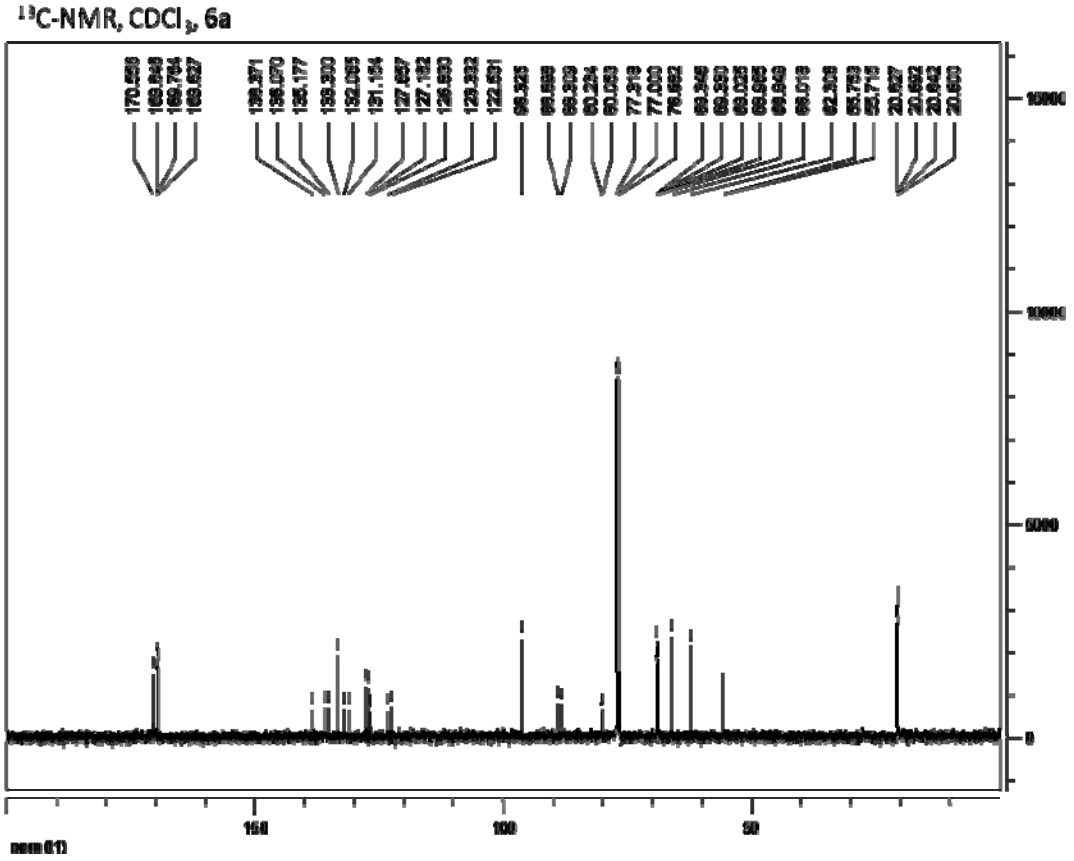
^{1}H-NMR, $CDCl_3$, 5a



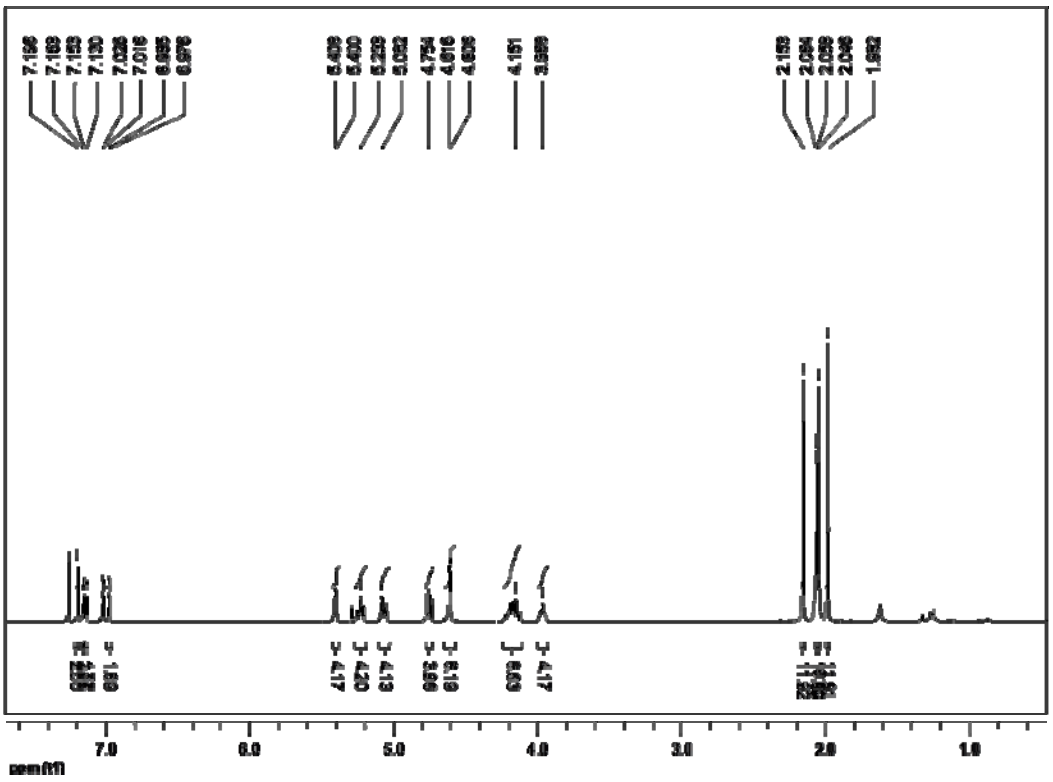
^{13}C-NMR, $CDCl_3$, 5a



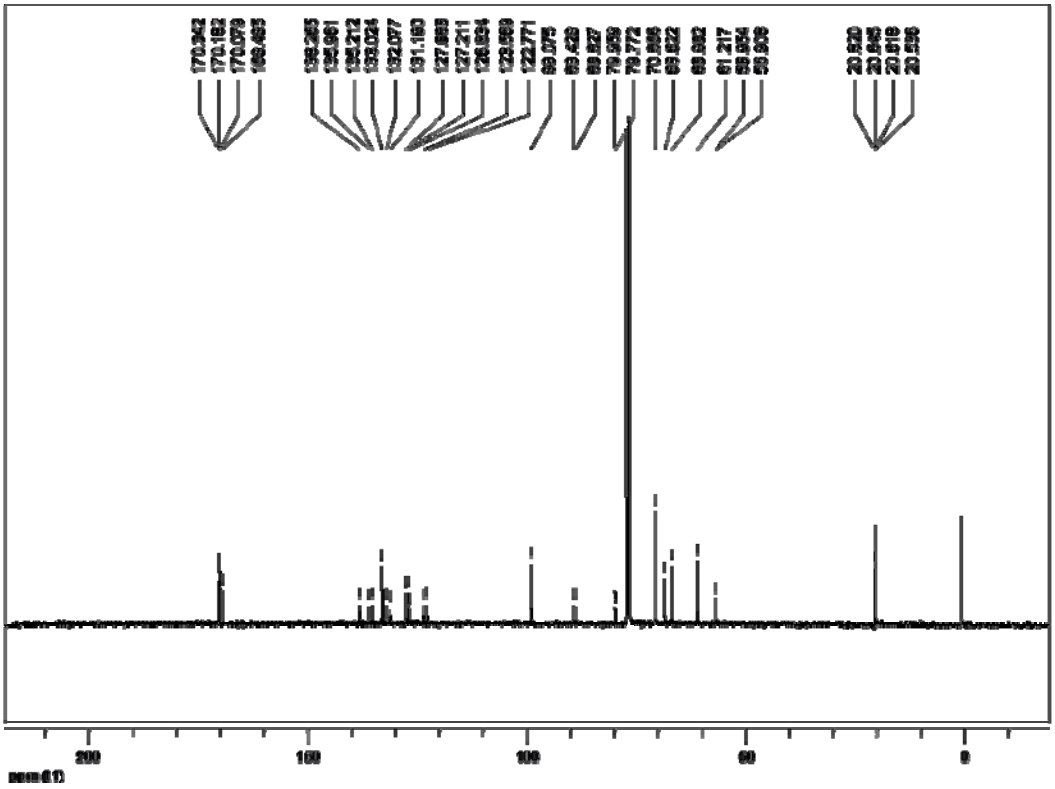

^{1}H-NMR, CDCl$_3$, 6a
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)


^{13}C-NMR, CDCl$_3$, 6a
170.556
169.848
169.764
169.627
139.371
138.070
135.177
130.300
132.005
131.154
127.857
127.182
126.930
123.332
122.571
96.523
69.668
68.309
60.254
60.053
77.318
77.000
76.682
69.348
69.350
69.025
68.882
68.849
68.518
62.303
55.753
55.715
20.927
20.892
20.843
20.800
150
100
50
ppm (t1)

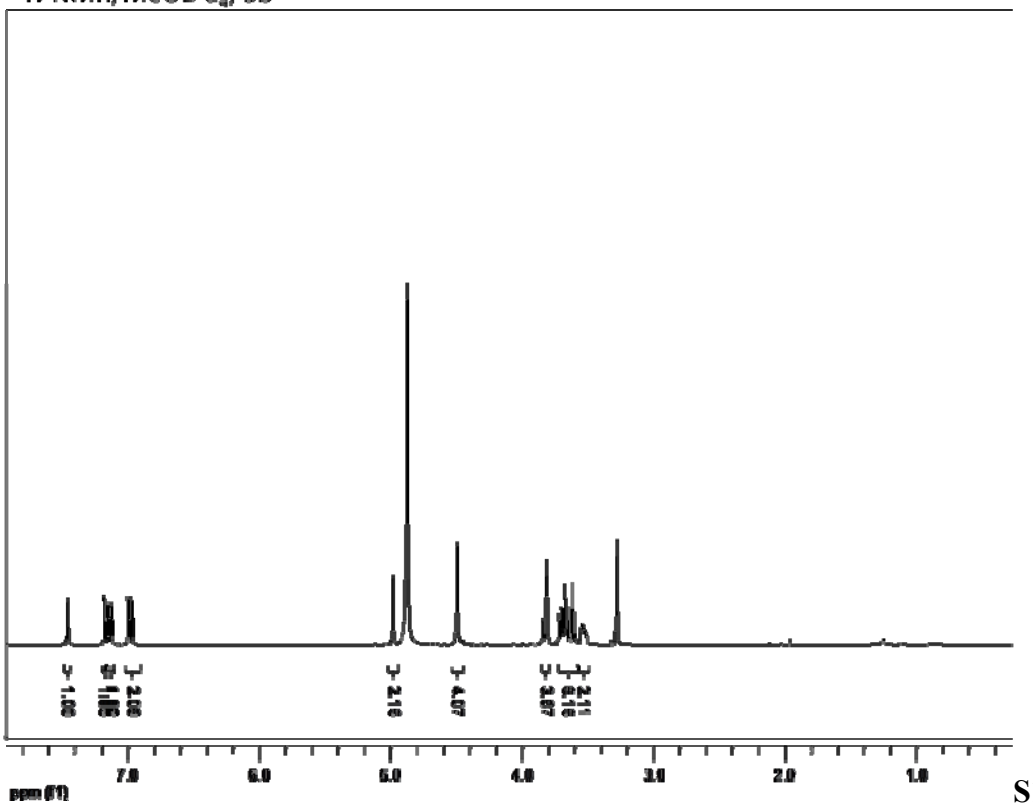
^{1}H-NMR, $CDCl_3$, 7a



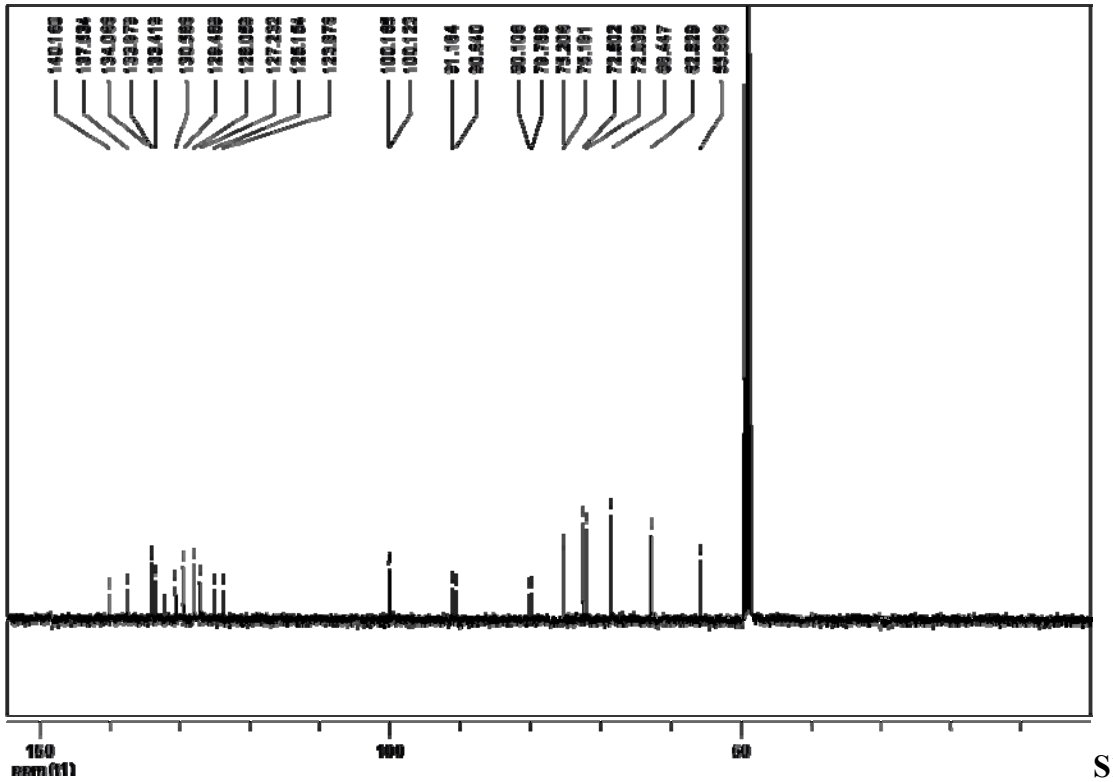
^{13}C-NMR, $CDCl_3$, 7a



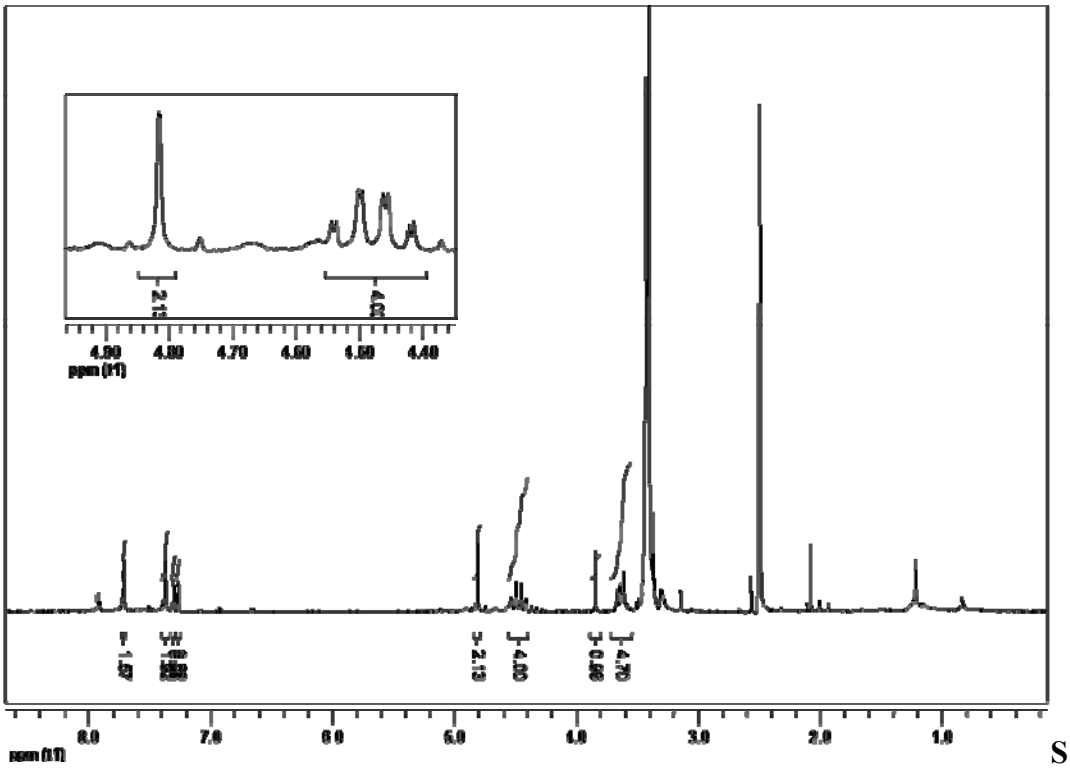
^{1}H-NMR, MeOD d_4, 5b



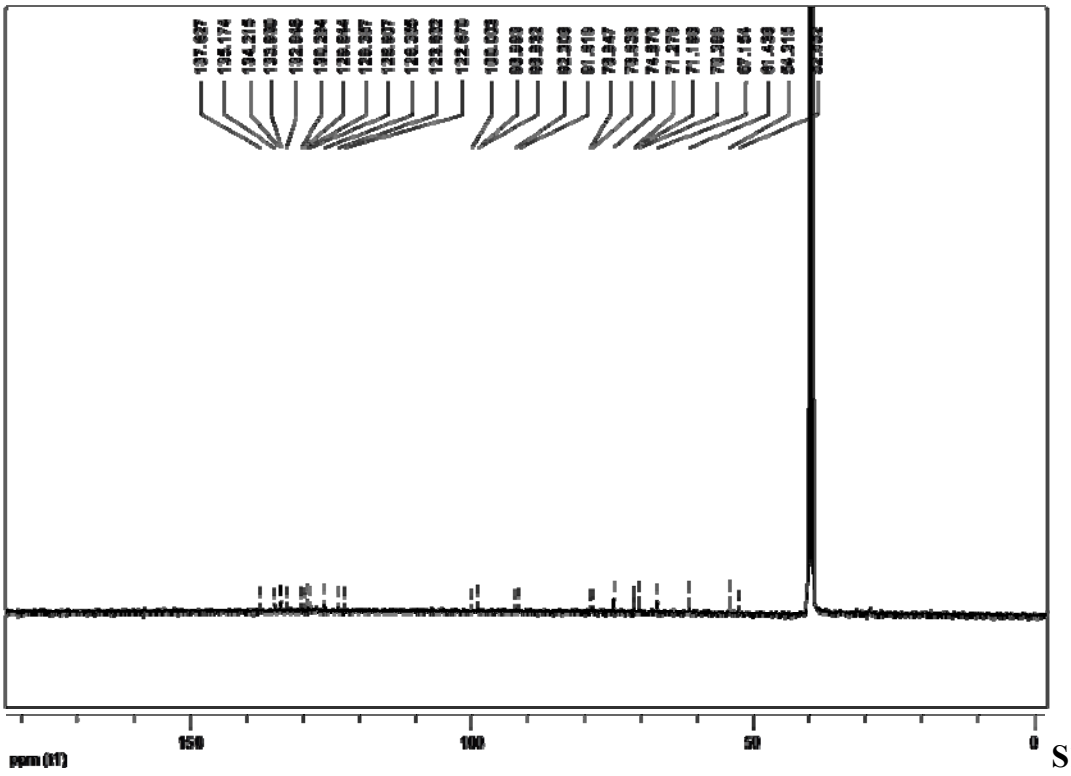
^{13}C-NMR, MeOD-d_4, 5b



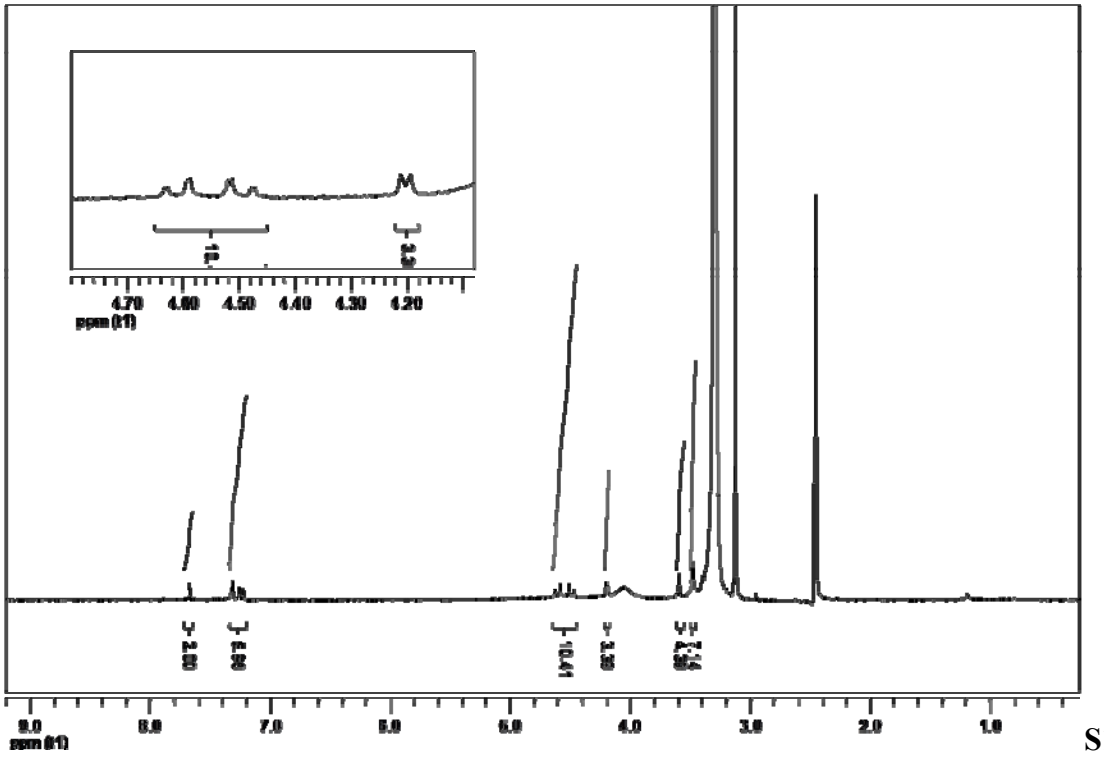
^{1}H-NMR, DMSO d_6, 6b



^{13}C-NMR, DMSO d_6, 6b



^{1}H-NMR, DMSO d_6, 7b



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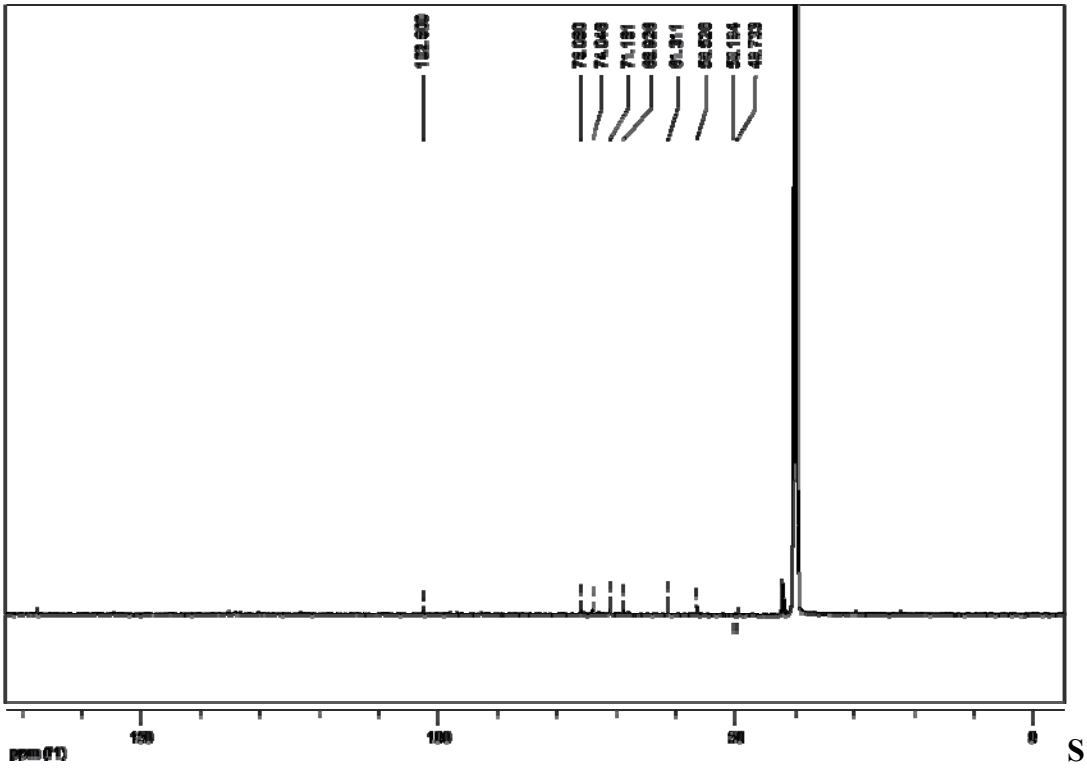
^{13}C-NMR, DMSO d_6, 7b



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3 a)H. B. Mereyala, S. R. Gurrala, *Carbohydrate Research*, 1998, **307**, 351-354; b) D. J. Wardrop, W. Zhang, J. Fritz, *Org. Lett*., 2002, **4**, 4, 489-492