Supplementary Information for

Facially Amphipathic Glycopolymers Inhibit Ice Recrystallization

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Materials

6,6-dimethylfulvene, furan, 5-norbornene-2-exo,3-exo-dimethanol, hexaethylene glycol, tosyl chloride, maleimide, toluene, diethyl ether, galactose, acetic anhydride, pyridine, *p*-toluene sulfonyl chloride, hexaethylene glycol, methyl iodide, sodium hydride (as a 60% dispersion in mineral oil), dichloromethane (DCM), hydrobromic acid in acetic acid (33%), triethylsilane, palladium hydroxide/carbon, methanol, ethanol, tetrahydrofuran (THF), triethylamine, potassium carbonate, silver carbonate, dimethylformamide (DMF), 4 Angstrom molecular sieves, ethanol, ethyl vinyl ether, Grubbs' 3rd generation metathesis catalyst, sucrose, sodium sulphate and deuterium oxide (D_2O) were purchased from Sigma Aldrich Co Ltd (Gillingham, UK) and used without further purification. Phosphate-buffered saline (PBS) solution was prepared using preformulated tablets in 200 mL of Milli-Q water (>18.2 Ω mean resistivity) to give [NaCl] = 0.138 M, [KCl] = 0.0027 M, and pH 7.4.

Physical and analytical methods

^{1}H and ^{13}C NMR Spectra (300 – 400 MHz and 75 MHz, respectively) were recorded using a Bruker DPX-300/400 Spectrometer under standard NMR conditions. Chemical shifts were recorded in ppm and referenced to solvent residual peaks, using MestReNova NMR Spectroscopy software.

ESI MS experiments were performed on an Agilent 6130B Single QUAD ESI-LC MS spectrometer in either positive or negative mode with an H_2O/MeOH (80:20) eluent feed, with samples dissolved in water, methanol or ethanol, unless otherwise stated.

IR experiments were carried out on a Bruker Vector 22 (ATR) FTIR Spectrometer in either the solid or thin film (volatile organic solvent) phase.

SEC/GPC data was acquired on either a THF or DMF (as applicable) Agilent 390-LC MDS instrument equipped with differential refractive index (DRI), viscometry (VS), dual angle light

scatter (LS) and dual wavelength UV detectors. System equipped with a PL-AS RT/MT2 autosampler, Shimadzu SPD-M20A microarray detector, a PL-gel 3 μm (50 × 7.5 mm) guard column and 2 × PL-gel 5 μm mixed-D columns (300 x 7.5 mm). Samples were filtered and suspended in the relevant HPLC grade solvent (THF containing 2% TEA; DMF with 5 mmol NH_4BF_4 additive), with a flow rate of 1 mL/min^{-1} at 50ºC. Refractive index recorded. Analyte samples were filtered through a nylon membrane with 0.22 μm pore size before injection. Respectively, experimental molar mass (Mn,SEC) and dispersity (Đ) values of synthesized polymers were determined by conventional calibration (relative to poly(methyl methacrylate) standards – Agilent EasyVials, 690 – 271400 Da) using Agilent GPC/SEC software. Refractive index recorded.

Absorption UV/Vis (Ultra-violet/visible spectroscopy) spectra were acquired on an Agilent Technologies Cary 60 Variable Temperature UV-Vis spectrophotometer at room temperature fitted with Holographic Grating (27.5 × 35 mm, 1200 lines/mm, blaze angle 8.6° at 240 nm), a double beam, Czerny-Turner monochromator, 1.5 nm fixed spectral bandwidth, full spectrum Xenon pulse lamp single source, dual silicon diode detectors, quartz overcoated optics, non-measurement phase stepping wavelength drive, room light immunity. Analysis undertaken using Agilent CaryWin UV Scan software. All sample spectra were acquired in Hellma Analytics High Precision Quartz UV Cuvettes.

Small-angle neutron scattering (SANS) experiments were performed on the KWS-2 instrument at FRM-2 research reactor in Garching (Gemany).[1] A q-range of 3.6 × 10^{-3} to 0.48 Å^{-1} was achieved utilizing an incident neutron wavelength of 5 Å with a spread of $\Delta\lambda/\lambda$ = 20% and sample-to-detector distances of 1.5, 8 and 20 m, as $q = (4\pi/\lambda)\sin(\theta/2)$, where λ is the wavelength and θ is the scattering angle. The samples were prepared in D_2O to provide good scattering contrast and placed in rectangular quartz cuvettes (Hellma, pathlength = 1 mm) and maintained at 25.0 ± 0.5 °C. The two-dimensional raw scattering data were corrected for detector

sensitivity, electronic and background noise, empty cuvette contribution, and then azimuthally integrated to give the one-dimensional intensity $I(q)$ using the instrument software QtiKWS. The data was converted to the absolute scale (cm^{-1}) through reference to the scattering from a secondary standard sample (Plexiglas). Finally, the data was corrected for the solvent contribution, which was measured separately.

Experimental Methods

Solubilization of insoluble samples for analysis

Insoluble samples for splat and UV-Vis analyses (see below) were added to a PBS solution and centrifuged (10K, 10 minutes) and the supernatant removed – to give a saturated solution of unknown concentration in PBS.

UV-Vis concentration determination of insoluble samples for analysis

Calibration: The spectrometer was calibrated with a DMSO 'blank' (machine zeroed and a background scan conducted). A stock solution of the species of interest was prepared (in DMSO) at a known concentration and serially diluted, and a spectrum acquired for each concentration in the 200 – 800 nm range (600 nm/min scan rate, 1.00 nm data interval, 0.1 s average time), to give a Beer-Lambert calibration plot.

Sample Concentration Analysis: 200 – 400 μL (typically) of the sample of interest was taken as a saturated solution in PBS, and condensed *in vacuo*. The dry residue was subsequently re-dissolved in the same volume of DMSO, mixed, and drawn up to separate the liquor from the insoluble PBS salts. The UV-Vis spectrum was then acquired, as above, with dilution employed (and corrected for) where necessary. The λ_{max} of the primary peak was identified and the absorbance recorded and intersected against the line of best fit of the Beer-Lambert plot of the stock calibrants to give the saturated samples concentration in PBS solution.

Ice recrystallization inhibition (splat) assay

Ice recrystallization inhibition was measured using a modified splat assay.[3] A 10 μL sample of the species of interest, dissolved in PBS buffer (pH 7.4), was dropped 1.40 m onto a chilled glass coverslip, resting on a thin aluminium block placed on dry ice. Upon hitting the coverslip, a wafer with diameter of approximately 10 mm and thickness 10 μm was formed instantaneously. The glass coverslip was transferred onto the Linkam cryostage and held at -8 ^{o}C under N_2 for 30 minutes. Photographs were obtained using an Olympus CX 41 microscope with a UIS-2 20x/0.45/∞/0-2/FN22 lens and crossed polarizers (Olympus Ltd, Southend-on-Sea, UK), equipped with a Canon DSLR 500D digital camera. Images were taken of the initial wafer (to ensure that a polycrystalline sample had been obtained) and again after 30 minutes. Image processing was conducted using Image J, which is freely available (National Institutes of Health, Bethesda, MD). In brief, the number of ice crystals in the field of view was measured, and the measurement repeated for three independent wafers. The average (mean) of these three measurements was then calculated to find the mean grain area (MGA). The average value and error was compared to that of a PBS buffer negative control.

Surface hydrophobicity mapping of polymers

Polymeric structures (containing 9 homo- or 9 regularly alternating hetero- ring opened monomer units) were assembled in ChemDraw Professional 16.0 (PerkinElmer Informatics Inc., Waltham, MA), assuming a 'classic' Grubbs' polymer architecture of 3:1 Trans/Cis along the unsaturated backbone. Chain end groups were not featured. The structures were then energy minimised in Chem3D and the resulting structures rendered in PyMOL (Schrödinger LLC, Cambridge, MA), which is freely available for educational use, and the surfaces on the structures were displayed. Hydrogens were then removed from the structure. The "color" command was then used to colour the polymer surface, with carbon (and so aliphatic hydrogen)

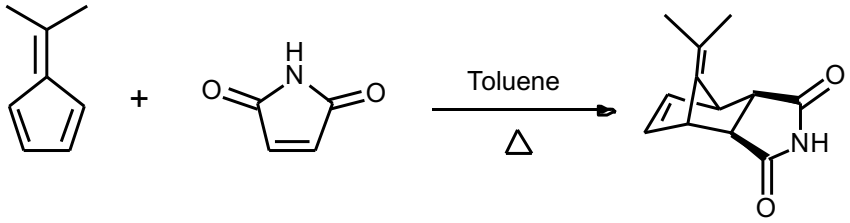
defined as hydrophobic (red), whilst oxygen and nitrogen (and so imide/alcoholic hydrogens) were defined as hydrophilic (blue).

Sucrose Sandwich Ice Shaping Assay

Samples dissolved in PBS buffer containing 45% sucrose were sandwiched between two glass coverslips and sealed with immersion oil. Samples were cooled to −50 °C on a Linkam Biological Cryostage BCS196 with T95-Linkpad system controller equipped with a LNP95-Liquid nitrogen cooling pump, using liquid nitrogen as the coolant (Linkam Scientific Instruments UK, Surrey, U.K.). The temperature was then increased to −8 °C and held for 1 hour to anneal. The samples were then heated at 0.05 °C.min^{-1} until few ice crystals remained and then cooled at 0.05 °C.min^{-1} and the shape of ice crystals observed. Micrographs were obtained every 0.1 °C using an Olympus CX41 microscope equipped with a UIS-2 20x/0.45/∞/0−2/FN22 lens (Olympus Ltd., Southend on sea, U.K.) and a Canon EOS 500D SLR digital. Image processing was conducted using ImageJ.

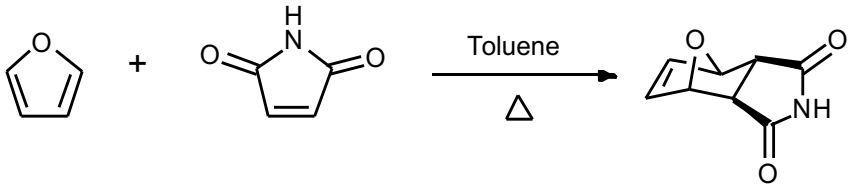
Synthetic Procedures

General Procedure for the Synthesis of (3aR,4R,7R,7aS)-8-(propan-2-ylidene)-3a,4,7,7a-tetrahydro-1H-4,7-methanoisoindole-1,3(2H)-dione – (*exo,exo*-fulvonorborneneimide)



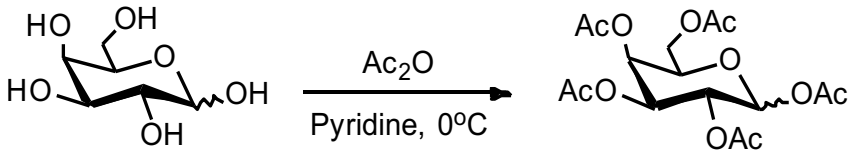
6,6-dimethylfulvene (2.4 mL, 2.12 g, 20 mmol) and maleimide (1.94 g, 20 mmol, 2 eqv) were dissolved in toluene (100 mL), and the reaction mixture stirred under reflux (135°C) for 24 hours, transitioning from a translucent orange solution to opaque after 60 minutes. The reaction mixture was then cooled to RT and condensed *in vacuo* to remove excess toluene and fulvene, and the solids washed with hot diethyl ether (3 x 20 mL) to yield the pure *exo,exo* product as a pale orange solid. 2.82 g (69%). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.61 (1H, s, N**H**), 6.42 (2H, t, *J* = 1.96 Hz, **H**C=C**H**), 3.74 (2H, t, *J* = 1.88 Hz, Bridge Base 2 x C**H**), 2.78 (2H, s, Fused Ring 2 x C**H**), 1.57 (7H, s, 2 x **Me**). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 206.96 (2 x HNR**C**=O), 137.67 (H**C**=**C**H / R_2-**C**=**C**-$(Me)_2$), 49.20 (**C**-C=O), 45.61 (**C**-HC=CH-**C**), 30.93 (2 x **Me**). IR (ATR): 3229 (NH), 3000 (C=C / C-H), 1759, 1705 (2 x C=O), 1369, 1345, 1182 (C-H), 689 cm^{-1} (C=C). m/z (ESI, -ve) Expected 202.1, Observed 202.1 [95%, $R2N^-$].

General Procedure for the Synthesis of (3aR,4R,7R,7aS)-3a,4,7,7a-tetrahydro-1H-4,7-epoxyisoindole-1,3(2H)-dione – (*exo,exo*-oxonorborneneimide)



Furan (15 mL, 14.04 g, 206.26 mmol, 10 equiv) and maleimide (2.00 g, 20.60 mmol) were dissolved in toluene (20 mL), and refluxed at 95 ºC for 48 hours, with the colourless mixture becoming white/opaque within 10 minutes. The reaction mixture was then cooled to RT, and then solids filtered and washed with cold toluene (100 mL) to give a white solid, and dried *in vacuo*. 2.19 g (64%). Characterization as previously reported.[2] ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.00 (1H, s, N**H**), 6.52 (2H, t, *J* = 0.91 Hz, **H**C=C**H**), 5.32 (2H, t, *J* = 0.92 Hz, Bridge Base 2 x C**H**), 2.89 (2H, s, Fused Ring 2 x C**H**). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 162.34 (2 x **C**=O), 136.59 (H**C**=**C**H), 80.99 (**C**-O-**C**), 48.71 (2 x **C**-C=O). IR (ATR): 3194 (NH); 3101, 3065, 2866, 2724 (CH); 1834, 1801; 1773, 1702 (2 x C=O); 1626, 1579 (C=C); 1345, 1301 (CH); 1148; 1065, 938, 842 cm^{-1} (C=C). m/z (ESI, +ve) Expected 164.0, Observed 164.1 [100%, M-H^+].

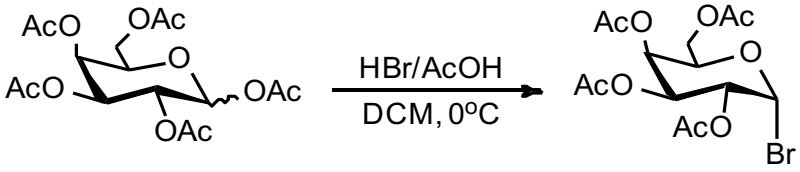
General Procedure for the Synthesis of D-galactose pentaacetate



To a solution of D-galactose (1.00 g, 5.55 mmol) in pyridine (20 mL) on ice, acetic anhydride (20 mL) was added slowly with stirring, and allowed to warm to RT overnight. To the resulting reaction mix, $CHCl_3$ (30 mL) was added and the mixture extracted from a chilled solution of HCl (3 x 30 mL, 1M). The combined organic phases were then extracted with saturated $NaHCO_3$ solution (3 x 30 mL), washed with brine (30 mL), dried over Na_2SO_4, and condensed *in vacuo* to give a thick colourless oil. 2.26 g (Quant%). Characterization as previously reported. [3] ^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.38 (1H, s, Anomeric **H-1**), 5.50 (1H, s, **H-4**), 5.34 (2H, s, **H-2,3**), 4.43 – 4.01 (3H, m, **H-5,6**',"), 2.27 – 1.92 (15H, m, 5 x **OAc**). 9:1 α:β. ^{13}C NMR (75 MHz, $CDCl_3$) δ = 170.14 – 168.92 (**C**=O-CH_3), 89.72 (**C-1**), 68.96 – 65.99 (**C-**

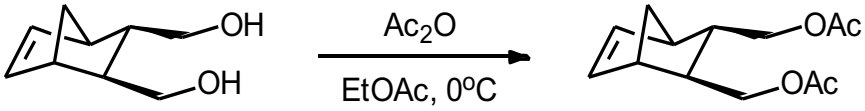
5,4,3,2), 61.25 (**C-6**), 21.26 – 19.87 (5 x C-O**C**H_3). m/z (ESI, +ve) Expected 413.11, Observed 412.9 [100%, M+Na^+].

General Procedure for the Synthesis of Acetobromo-α-D-galactose



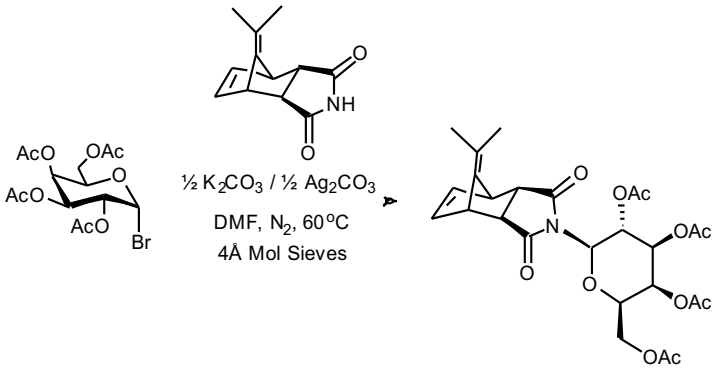
To a solution of D-galactose pentaacetate (1.62 g, 4.15 mmol) in anhydrous dichloromethane (20 mL) on ice, a large excess of hydrobromic acid in acetic acid (33% w/w, 5 mL, 27.81 mmol, 6.7 eqv) was added dropwise with stirring, and the reaction mix allowed to equilibrate for 1 hour with protection from ambient light. The resulting translucent orange solution was then extracted from a saturated solution of ice-cold $NaHCO_3$ (3 x 30 mL), leading to effervescence and a discolouration of the organic phase. The organic phase was then washed with ice-cold brine (30 mL), dried over Na_2SO_4, and condensed *in vacuo*, yielding a thick colourless oil, which slowly crystallised. 1.37 g (80%). Characterisation as previously reported.[4] ^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.70 (1H, d, *J* = 3.20 Hz, Anomeric **H-1**), 5.52 (1H, d, *J* = 2.9 Hz, **H-3**), 5.40 (1H, dd, J_1 = 10.70 Hz, J_2 = 3.40 Hz, **H-4**), 5.10 – 4.99 (1H, m, **H-2**) 4.54 – 4.04 (3H, m, **H-5,6**',''), 2.19 – 1.96 (12H, m, 4 x **OAc**). 1:0 α:β. ^{13}C NMR (75 MHz, $CDCl_3$) δ = 163.12 (**C**=O-CH_3), 88.11 (**C-1**), 71.06 – 66.97 (**C-5,4,3,2**), 60.83 (**C-6**), 20.75 – 20.55 (C-O**C**H_3). m/z (ESI, -ve) Expected 427.02, 428.02, Observed 427.1, 428.1 [100%, M+H_2O–H^+].

General Procedure for the Synthesis of ((1R,2S,3S,4R)-bicyclo[2.2.1]hept-5-ene-2,3-diyl)bis(methylene) diacetate – (5-Norbornene-2-*exo*,3-*exo*-dimethylacetate) – 'M1'



5-Norbornene-2-*exo*,3-*exo*-dimethanol (215.3 mg, 1.40 mmol) was dissolved in ethyl acetate (20 mL) on ice, and a large excess of acetic anhydride (10 mL) was added slowly with stirring, and allowed to equilibrate for one hour. The reaction mixture was subsequently condensed *in vacuo*, re-dissolved in DCM (30 mL), and extracted from a saturated solution of $NaHCO_3$ (3 x 30 mL). The combined organic phases were then dried over Na_2SO_4, and condensed *in vacuo*, to give a thick colourless oil. Subsequent chilling at –20°C yielded a white crystalline solid. 140 mg (42%). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.05 (2H, d, *J* = 2.3 Hz, **H-1**), 4.20 – 3.83 (4H, m, **H-4**), 2.61 (2H, s, **H-2**), 1.98 – 1.89 (6H, m, **H-6**), 1.73 (2H, d, J = 11.4 Hz, **H-3**), 1.44 – 1.17 (2H, m, **H-5**). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 169.84 (2 x **C**=O), 136.27 (H**C**=**C**H), 64.39 (2 x **C**-OC=O), 43.79 (**C**-C=C), 41.55 (R_2**C**H2), 38.68 (**C**-C-OC=O), 29.83, 19.98 (O**Ac**).

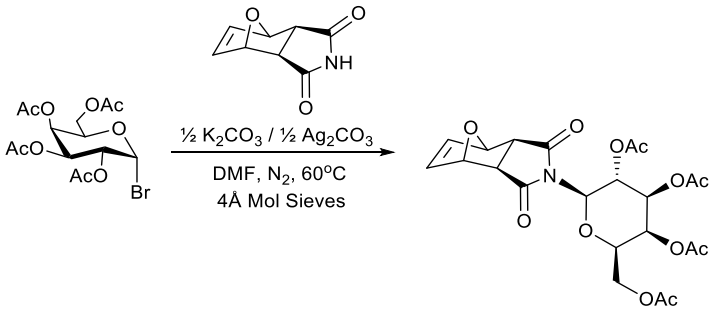
General Procedure for the Synthesis of (2R,3S,4S,5R,6R)-2-(acetoxymethyl)-6-((3aR,4R,7R,7aS)-1,3-dioxo-8-(propan-2-ylidene)-1,3,3a,4,7,7a-hexahydro-2H-4,7-methanoisoindol-2-yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate – (*exo,exo-fulvonorborneneimide galactopyranoside peracetate)* – 'M2'



exo,exo-fulvonorborneneimide (326 mg, 1.61 mmol), K_2CO_3 (111 mg, 0.80 mmol, 0.5 eqv), and acetobromo-α-D-galactose (600 mg, 1.46 mmol, 0.91 eqv) were dissolved in dry, deoxygenated DMF (20 mL) with 4 Å molecular sieves. Ag_2CO_3 (201 mg, 0.73 mmol, 0.46 eqv) was subsequently added with stirring, the reaction protected from light, and allowed to equilibrate at 60°C overnight. The dark green/brown reaction crude was then filtered, and

condensed *in vacuo* until a thick suspension remained, and re-dissolved in ethanol to precipitate the insoluble black solids of the silver oxide/bromide by-products, and again filtered. The filtrate was dissolved in $CHCl_3$ (30 mL) and extracted with saturated $NaHCO_3$ solution (3 x 30 mL), and the organic phase washed again with saturated NaCl solution (30 mL), water (30 mL), dried over Na_2SO_4 and condensed *in vacuo.* Solids were then taken up into hot diethyl ether (30 mL), filtered, and the filtrate condensed again to give an off-white/beige solid. 250 mg (32%). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.37 (2H, d, *J* = 10.5 Hz, **H**C=C**H**), 5.73 – 5.36 (2H, m, **H-1,4**), 5.36 – 4.97 (2H, m, **H-3,2**), 4.76 – 3.90 (4H, m, **H-5,6**',"), 3.71 (2H, s, Bridge Base 2 x C**H**), 2.74 (2H, s, Fused Ring 2 x C**H**), 2.09 – 1.94 (12H, m, 4 x **OAc**), 1.54 (4H, s, 2 x **Me**). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 207.03 (2 x HNR**C**=O), 177.47 (R_2-**C**=C-$(Me)_2$), 170.36 – 168.92 (4 x **C**=OAc + R_2-C=**C**-$(Me)_2$), 89.69 (**C-1**), 70.87 (2 x **C**-OC=O), 68.74 – 66.43 (**C-2,3,4,5**; 4 x **C**-C=OAc), 61.24 (**C-6**), 49.21 (**C**-C=O), 45.58 (**C**-HC=CH-**C**), 30.90 (2 x **Me**), 20.87 – 19.61 (4 x O**Ac**).

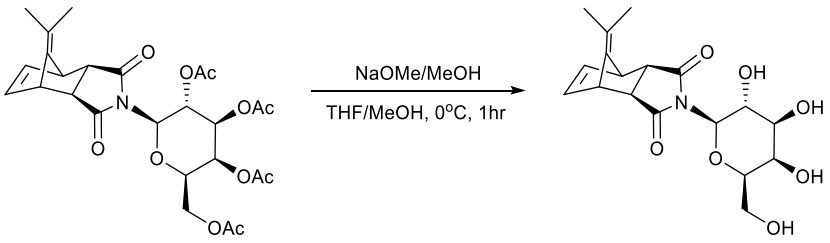
General Procedure for the Synthesis of (2R,3S,4S,5R,6R)-2-(acetoxymethyl)-6-((3aR,4R,7R,7aS)-1,3-dioxo-1,3,3a,4,7,7a-hexahydro-2H-4,7-epoxyisoindol-2-yl)tetrahydro-2H-pyran-3,4,5-triyl triacetate – (*exo,exo-oxonorborneneimide galactopyranoside peracetate*) – 'M3'



Synthetic procedure as described in the General Procedure for the Synthesis of exo,exo-fulvonorborneneimide galactopyranoside peracetate.

exo,exo-oxonorborneneimide (498 mg, 3.02 mmol), K_2CO_3 (210 mg, 1.51 mmol, 0.5 eqv), and acetobromo-α-D-galactose (1.13 g, 2.75 mmol, 0.91 eqv) were dissolved in dry, deoxygenated DMF (20 mL) with 4 Å molecular sieves. Ag_2CO_3 (380 mg, 0.73 mmol, 0.46 eqv) addition followed as previously prescribed. Workup as per previous, with the exception that toluene was used for the final wash in place of hot diethyl ether. Brown oil obtained, 340 mg (25%). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.37 (1H, s, **H**C=C**H**), 5.73 – 4.99 (5H, m, **H-1,4,** 2 x **H**C-O), 4.53 – 3.90 (5H, m, **H-2,3,5,6',"**), 2.12 – 1.95 (14H, m, 4 x OAc). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 171.18 – 167.26 (4 x **C**=OAc / 2 x HNR**C**=O), 132.05 (H**C**=**C**H), 128.62, 95.92 – 90.15 (**C**-O**C**, **C-1**), 71.67 – 66.11 (**C-2,3,4,5**), 61.76 - 61.24 (**C-6**, 2 x **C**-C=O), 23.49 – 18.11 (4 x O**Ac**).

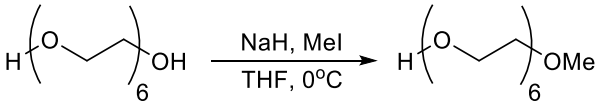
General Procedure for the Synthesis of (3aR,4R,7R,7aS)-8-(propan-2-ylidene)-2-((2R,3R,4S,5R,6R)-3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yl)-3a,4,7,7a-tetrahydro-1H-4,7-methanoisoindole-1,3(2H)-dione – (*exo,exo*-fulvonorborneneimide galactopyranoside)



exo,exo-fulvonorborneneimide galactopyranoside peracetate (200 mg, 0.375 mmol) was dissolved in THF/Methanol (2:1, 15 mL) and a large excess of methanolic sodium methoxide (30%, 5 mL) added with stirring at 0 °C. After 1 hour, the mixture (pH ~ 10) was neutralised on an Amberlite Ion Exchange column, and flushed sequentially with THF (20 mL) and methanol (20 mL). The collected fraction (pH ~ 6–7) was subsequently condensed *in vacuo* to yield an off-white solid. 50 mg (36%). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.71 (1H, s, **H**C=C**H**), 4.22 – 3.62 (4H, m, Carbohydrates), 3.09 – 2.95 (1H, m, Bridge Base 2 x C**H**), 2.50 (3H, m,

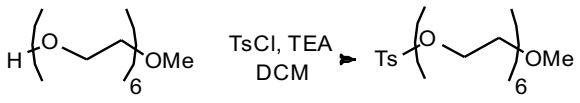
Fused Ring 2 x C**H**), 1.54 (6H, s, 2 x **Me**). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 140.31 (2 x H**C**=**C**H), 52.16 – 50.45 (**C-1,2,3,4,5,6**), 48.26 (**C**-C=O), 21.95 (2 x **Me)** .

General Procedure for the Synthesis of 2,5,8,11,14,17-hexaoxanonadecan-19-ol – (*Monomethoxyhexaethylene glycol*)



Hexaethylene glycol (1 g, 0.89 mL, 3.54 mmol) was dissolved in THF (10 mL) and cooled on ice, and sodium hydride (60% dispersion in mineral oil, 142 mg, 1 eqv, 3.54 mmol) added. Methyl iodide (503 mg, 0.22 mL, 1 eqv, 3.54 mmol) was then added slowly, dropwise, and stirred for 1 hour. The reaction mixture was quenched with NH_4Cl, warmed to RT, and diethyl ether added (30 mL). The aqueous phase was separated, and extracted with diethyl ether (3 x 30 mL), the organic phases combined, dried over Na_2SO_4, and condensed *in vacuo* to give a clear, off-yellow oil. 940 mg (89.5%). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.75 – 3.46 (27H, m, (($C\mathbf{H_2}C\mathbf{H_2}O)_5(C\mathbf{H_2})_2O\mathbf{H}$), 3.32 (3H, s, O**Me**). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 72.48 – 69.89 (**C**OR), 61.46 – 61.31 (**Me**), 58.64 – 31.38 (**C**H). m/z (ESI, -ve) Expected 296.2, Observed 313.9 [100%, $M+H_2O–H^-$].

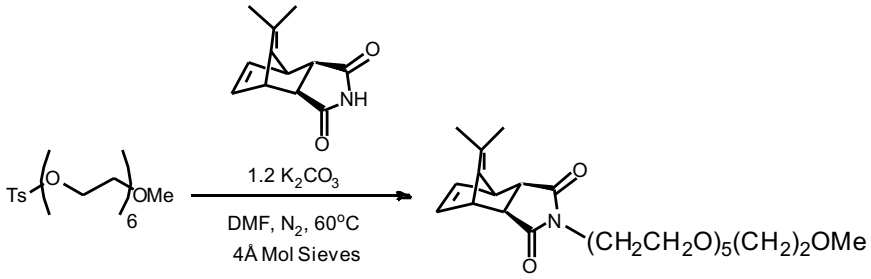
General Procedure for the Synthesis of 2,5,8,11,14,17-hexaoxanonadecan-19-yl 4-methylbenzenesulfonate – (*Monomethoxyhexaethylene glycol monotosylate*)



Monomethoxyhexaethylene glycol (920 mg, 3.10 mmol), triethylamine (0.52 mL, 1.2 eqv, 3.73 mmol), and tosyl chloride (710 mg, 1.2 eqv, 3.73 mmol) were dissolved in DCM (30 mL) and stirred for 16 hours. Water (30 mL) was subsequently added, and the aqueous phase separated

and extracted with DCM (3 x 30 mL). Organic phases were combined, condensed *in vacuo*, and solids precipitated from a minimal volume of cold THF (2 x 5 mL) and filtered. The organic liquor was then re-condensed, dissolved in DCM (30 mL), and washed with saturated $NaHCO_3$ solution (3 x 30 mL), dried over Na_2SO_4, and condensed again to yield a brown oil. 1 g (72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.83 – 7.30 (4H, m, Aromatic), 4.16 (2H, td, J_1 = 4.9, J_2 = 1.7 Hz, PEG C**H$_2$**), 3.80 – 3.50 (26H, m, (C**H$_2$**C**H$_2$**O)$_5$), 3.37 (3H, t, J = 1.5 Hz, O**Me**), 2.72 (2H, s, Ar-**Me**). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 144.80 (Aromatic), 132.96 – 126.32 (Aromatic), 72.38 – 68.64 (**C**OR), 61.64 (**Me**), 58.99 – 30.31 (**C**H), 21.63 (Ar-**Me**). m/z (ESI, +ve) Expected 450.2, Observed 473.1 [100%, M+Na$^+$].

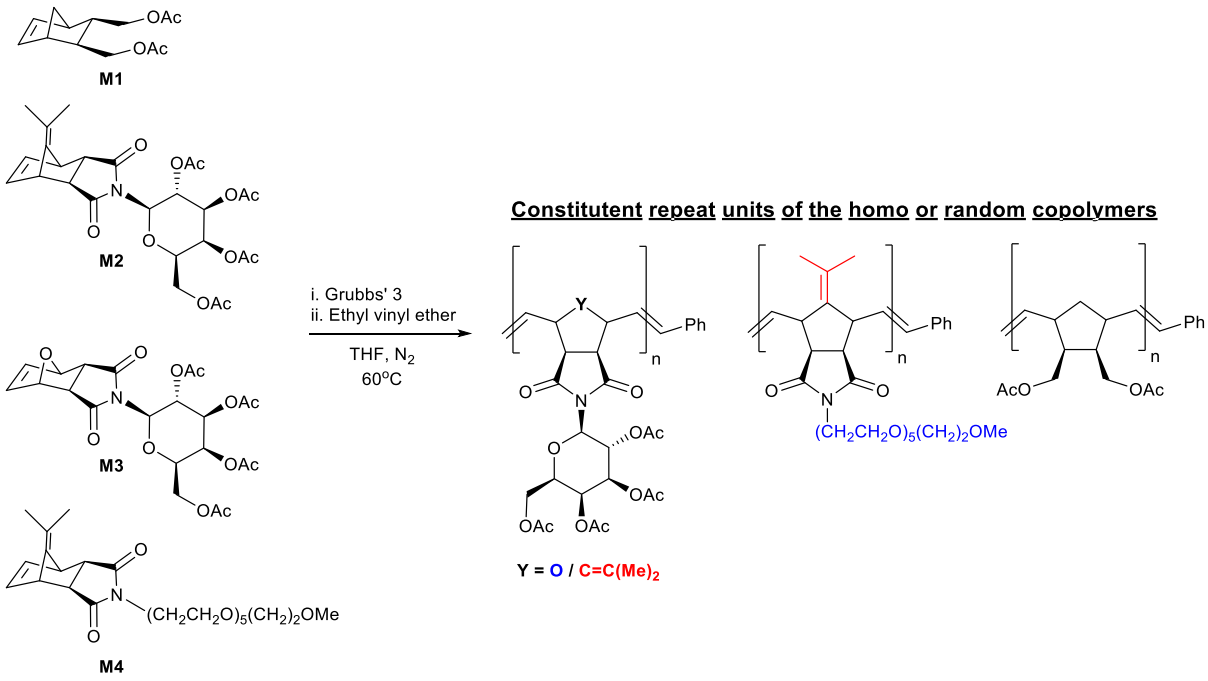
General Procedure for the Synthesis of (3aR,4R,7R,7aS)-2-(2,5,8,11,14,17-hexaoxanonadecan-19-yl)-8-(propan-2-ylidene)-3a,4,7,7a-tetrahydro-1H-4,7-methanoisoindole-1,3(2H)-dione – (*exo,exo-fulvonorborneneimide-PEG$_6$)* – 'M4'



Monomethoxyhexaethylene glycol monotosylate (1 g, 3.33 mmol) was dissolved in DMF (50 mL) with 4Å molecular sieves, K_2CO_3 (470 mg, 1.5 eqv, 5.00 mmol), and *exo,exo*-fulvonorborneneimide (677 mg, 1.5 eqv, 5.00 mmol) at 60°C with stirring for 24 hours. The crude was filtered, condensed *in vacuo*, and re-dissolved in ethyl acetate (30 mL). Saturated $NaHCO_3$ solution (30 mL) was added, the organic phase separated, and washed a further three times (3 x 30 mL) with saturated $NaHCO_3$ solution, and brine (1 x 30 mL). The organic phase was then dried over Na_2SO_4 and reduced to a small volume (~ 5 mL), before being precipitated from diethyl ether to yield an off-white solid. 530 mg (33%). The crude material was used in

the next stage without further purification. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.34 (2H, q, *J* = 1.9 Hz, H**C**=**C**H), 3.74 – 3.36 (27H, m, (C**H**$_2$C**H**$_2$O)$_5$, Bridge Base 2 x C**H**), 3.30 (1H, 2, O**Me**), 2.68 (2H, d, *J* = 10.4 Hz, Fused Ring 2 x C**H**), 1.46 (7H, d, *J* = 16.0 Hz, C=C(**Me**)$_2$),. ^{13}C NMR (75 MHz, $CDCl_3$) δ = 177.88 – 177.39 (2 x HNR**C**=O), 162.31 (Me_2-C=**C**), 140.9 (Me_2-**C**=C), 137.6 (H**C**=**C**H), 115.88, 71.87 – 67.09 (**C**OR), 61.57 (**Me**), 58.95 – 14.11 (**C**H, **C**NR). m/z (ESI, +ve) Expected 481.3, Observed 504.1 [100%, M+Na$^+$], 473.0 [75%, SM+Na$^+$].

General Procedure for the (co)polymerisation of the M1–M4 monomer libraries



The monomer(s) and Grubbs' 3 Metathesis Catalyst (See Table S1, below) were weighed into separate Schlenk flasks (or for some monomers, as a solution of known concentration in dry THF) and each made up to 10 mL and 5 mL with anhydrous THF, respectively, and purged/degassed with N_2 for 20 minutes. Mesitylene (3 drops) was added to the monomer solution prior to degassing. The catalyst and monomer solutions were then combined and heated at 50°C for 1 hour under nitrogen, with stirring. The Schlenk flask was subsequently cooled under liquid nitrogen (–196°C), a drop removed (for ^{1}H NMR conversion), and a large excess of ethyl vinyl ether (5 mL) introduced, with stirring for a further 30 minutes. The

polymer was then precipitated with a large excess (~ 45 mL) of an appropriate solvent (Table S1), and isolated by centrifugation (10K RPM, 10 minutes), to yield a solid mass (polymers generally brown through grey/beige). Polymers not containing acetate groups were then reprecipitated under the same conditions at least twice, and finally dried under compressed air. (Table 1 and Figures S1–2, below, for further polymer characterisation data).

poly(Fulvo): ^{1}H NMR (300 MHz, $CDCl_3$) δ = 5.35 (s, Carbohydrates + Backbone), 4.34 (br s, Carbohydrates + Backbone), 3.65 (br s, Carbohydrates), 3.27 (br s, Carbohydrates), 2.92 – 2.22 (m, Carbohydrates + Norbornene Ring), 2.06 – 1.78 (m, Carbohydrates + Norbornene Ring), 1.75 – 1.53 (m, Norbornene Ring), 1.50 – 1.16 (m, Norbornene Ring + Methylene's), 1.07 – 0.75 (m, Norbornene Ring + Methylene's). Cis/Trans n/d.

poly(Oxo): ^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.98 (m), 6.60 – 6.47 (m), 5.59 – 5.06 (m, Carbohydrates + Backbone), 4.77 – 4.31 (m, Carbohydrates), 4.26 – 3.90 (m, Carbohydrates + Norbornene Ring), 3.85 – 3.38 (m, Carbohydrates), 3.25 – 2.98 (m, Carbohydrates), 2.92 – 2.39 (m, Carbohydrates + Norbornene Ring), 2.24 – 1.94 (m, Ac), 1.01 – 0.77 (m, Norbornene Rings + Methylene's). Cis/Trans n/d.

poly(Fulvo-*co*-Oxo): ^{1}H NMR (400 MHz, *d*-DMSO) δ = 11.13 (s), 8.28 (s), 7.57 – 6.06 (m, Ph Chain End), 5.82 – 4.49 (m, Carbohydrates + Backbone), 4.26 – 3.86 (m, Carbohydrates + Norbornene Rings), 2.33 – 0.52 (m, Norbornene Rings + Methylene's). Cis/Trans n/d.

poly(Fulvo-*co*-Diol): ^{1}H NMR (400 MHz, *d*-DMSO) δ = 11.14 (br s), 7.36 (m, Ph Chain End), 5.54 – 4.62 (m, Carbohydrates + Backbone), 4.28 – 2.58 (m, Fulvo Norbornene Ring + Carbohydrates), 2.38 – 0.76 (m, Diol Norbornene Ring + Fulvo Methylene's). Cis/Trans n/d.

poly(Fulvo-*co*-FPEG): ^{1}H NMR (400 MHz, *d*-DMSO) δ = 11.13 (br s), 7.09 (s, Ph Chain End), 5.65 – 5.17 (m, Carbohydrates + Backbone), 4.43 (m), 4.20 – 3.95 (m, Carbohydrates + Norbornene Rings), 3.63 – 3.37 (m, PEG Pedant), 3.27 – 2.90 (m, PEG Pedant), 2.74 – 2.53

(m), 2.41 – 2.12 (m), 2.01 – 1.42 (m, Norbornene Ring + Methylene's), 1.34 – 0.82 (m). Cis/Trans n/d.

poly(Diol): ^{1}H NMR (400 MHz, *d*-DMSO) δ = 7.68 (s, Ph Chain End), 5.32 – 5.09 (m, Backbone), 4.98 – 4.86 (m, Backbone), 4.16 – 3.89 (m), 2.32 – 1.52 (m, Norbornene Ring), 1.39 – 0.76 (m, Methylene's). Cis/Trans 1:1.

poly(FPEG): ^{1}H NMR (400 MHz, *d*-DMSO) δ = 11.13 (br s), 7.09 (s, Ph Chain End), 5.60 – 5.20 (m, Backbone), 4.59 – 4.40 (m), 4.21 – 3.93 (m), 3.67 – 3.36 (m, PEG Pedant), 3.31 – 2.93 (m, PEG Pedant), 2.66 (s), 2.34 – 2.29 (m, Norbornene Ring) 1.83 – 1.41 (br s, Norbornene Ring + Methylene's). Cis/Trans 1:4.

poly(Fulvo-*co*-Diol) + H_2: ^{1}H NMR (400 MHz, *d*-DMSO) δ = 11.08 (s), 7.25 (br. s, Ph Chain End), 5.67 – 4.62 (m, Carbohydrates), 4.15 – 2.64 (m, Fulvo Norbornene Ring + Carbohydrates), 2.37 – 0.97 (m, Diol Norbornene Ring + Fulvo Methylene's), 0.96 – 0.76 (q, J = 7.7 Hz, Hydrogenated Fulvene), 0.66 – 0.32 (dq, J1 = 43.6, J1 = 7.9 Hz, Hydrogenated Fulvene). Cis/Trans n/d.

* n/d – Not possible to determine the cis/trans ratio in these instances due to unsaturated backbone signals overlapping with the carbohydrate signals.

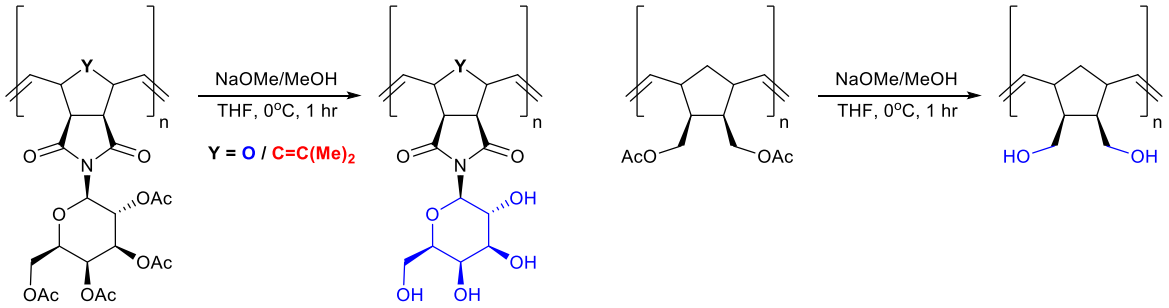
Acetylated Polymer Species	Monomer (mg, mmol)		Grubbs' 3 mg, µmol	Mn_{THEO} ($g.mol^{-1}$) †	Ratio A:B:G3	Precipitation Solvent (from THF)	Yield (mg)
	Monomer A	Monomer B					
poly(Fulvo)	**M2** (191.1, 0.358)	-	7.1, 8.03	25,000	46.9:0:1	Diethyl ether	54.1
poly(Oxo)	**M3** (184.3, 0.372)	-	16.3, 18.43	10,000	20.2:0:1	Pentane	8.1
poly(Fulvo-*co*-Oxo)	**M2** (100, 0.187)	**M3** (97.1, 0.196)	17.7, 20.01	10,000	19.4:19.4:1	Hexane	39.3
poly(Fulvo-*co*-Diol)-17 *	**M2** (100, 0.187)	**M1** (45, 0.187)	16.6, 18.74	10,000	10:10:1	Diethyl ether	8.5
poly(Fulvo-*co*-FPEG)	**M2** (52.6, 0.0986)	**M4** (47.4, 0.0984)	8.9, 10.06	10,000	19.7:19.7:1	Diethyl ether	63.4
poly(Diol)	**M1** (50, 0.210)	-	9, 10.18	10,000	20.6:0:1	Ethanol	33.1
Non-Acetylated							
poly(FPEG)	**M4** (100, 0.208)	-	8.9, 10.06	10,000	20.7:0:1	Hexane	66.5

Table S1. † Derived from Mn_{THEO} = [M]/[C]•(Mw)•Y, where [M] is the initial monomer(s) concentration, [C] is initial catalyst concentration, Mw is the monomer molecular weight(s), and Y is = 1 (assuming 100% conversion). *Representative example.

Deacetylated Polymer Species	Deprotected Yield (mg)	Post-Deprotection Dissolution Solvent *	Post-Deprotection Precipitation Solvent
poly(Fulvo)	50.8	THF	Diethyl ether
poly(Oxo)	3.3	THF	Pentane
poly(Fulvo-*co*-Oxo)	9.1	THF	Diethyl ether
poly(Fulvo-*co*-Diol)-17	3.6	THF	Hexane
poly(Fulvo-*co*-FPEG)	12.8	THF	Hexane
poly(Diol)	8.2	MeOH/THF (1:1)	Diethyl ether

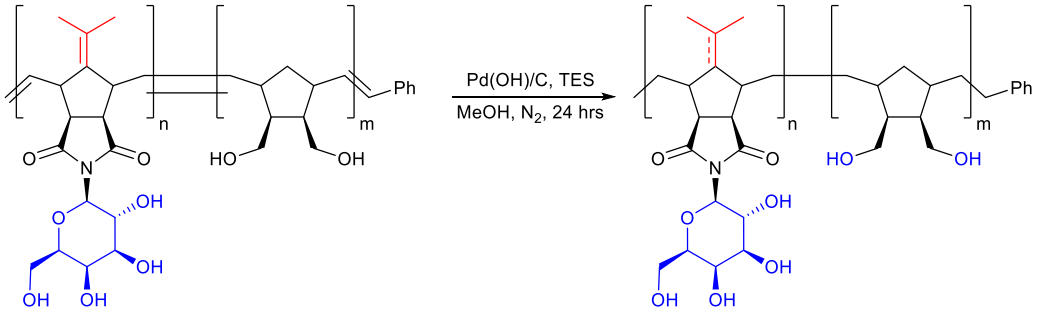
Table S2 * Addition of methanol maybe required (in addition to THF) to fully dissolve the deacetylated derivative.

General Procedure for the postpolymerisation modification (deacetylation) of acetylated polymer derivatives



The acetylated polymeric materials (See Table S2, above) were dissolved in THF/Methanol (2:1, 15 mL) and a large excess of methanolic sodium methoxide (30%, 5 mL) added with stirring at 0 °C. After 1 hour, the mixture (pH ~ 10) was neutralised on an Amberlite Ion Exchange column, and flushed sequentially with THF (20 mL) and methanol (20 mL). The collected fraction (pH ~ 6–7) was subsequently condensed *in vacuo*, and the deprotected polymer re-dissolved in an appropriate solvent (Table S2), and precipitated with a large excess (~ 45 mL) of an appropriate solvent (Table S2), and isolated by centrifugation (10K RPM, 10 minutes) to yield a solid mass (polymers generally brown through grey/beige). Polymers were then reprecipitated under the same conditions at least twice, and finally dried under compressed air. (Table S1–2, above, for polymer characterisation data).

General Procedure for the postpolymerisation modification (hydrogenation) of the polymer derivatives



Deacetylated *poly*(Fulvo-*co*-Diol) 17k (13 mg) was dissolved in methanol (5 mL) in a sealed system, under a nitrogen atmosphere. A solution of $Pd(OH)_2/C$ (10 mg) in methanol (5 mL) was introduced with stirring, and nitrogen bubbled through the mix for 5 minutes. Triethylsilane (0.5 mL) was then added in whole, leading to instantaneous effervescence and the *in-situ* generation of molecular H_2. The reaction mix was allowed to stir for 16 hours, with balloons attached for back pressure. The reaction was then subsequently filtered through a Celite plug, flushed with methanol (20 mL) and THF (20 mL), and condensed *in vacuo* to give the hydrogenated copolymeric derivative as a red mass. 14.7 mg.

Additional spectra

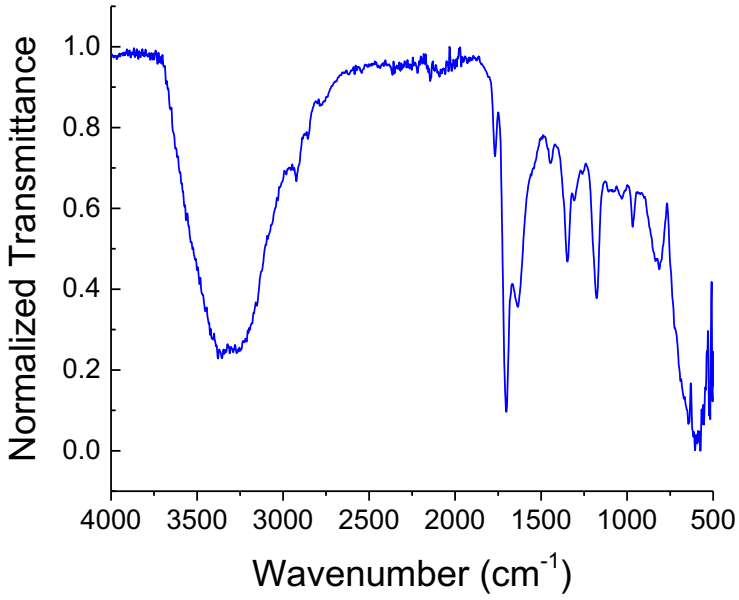


Figure S1 – IR spectrum of (incompletely deacetylated) *poly*(Fulvo-*co*-Oxo) residue

UV-VIS/Beer-Lambert plots of (insoluble) polymers and calibration curves

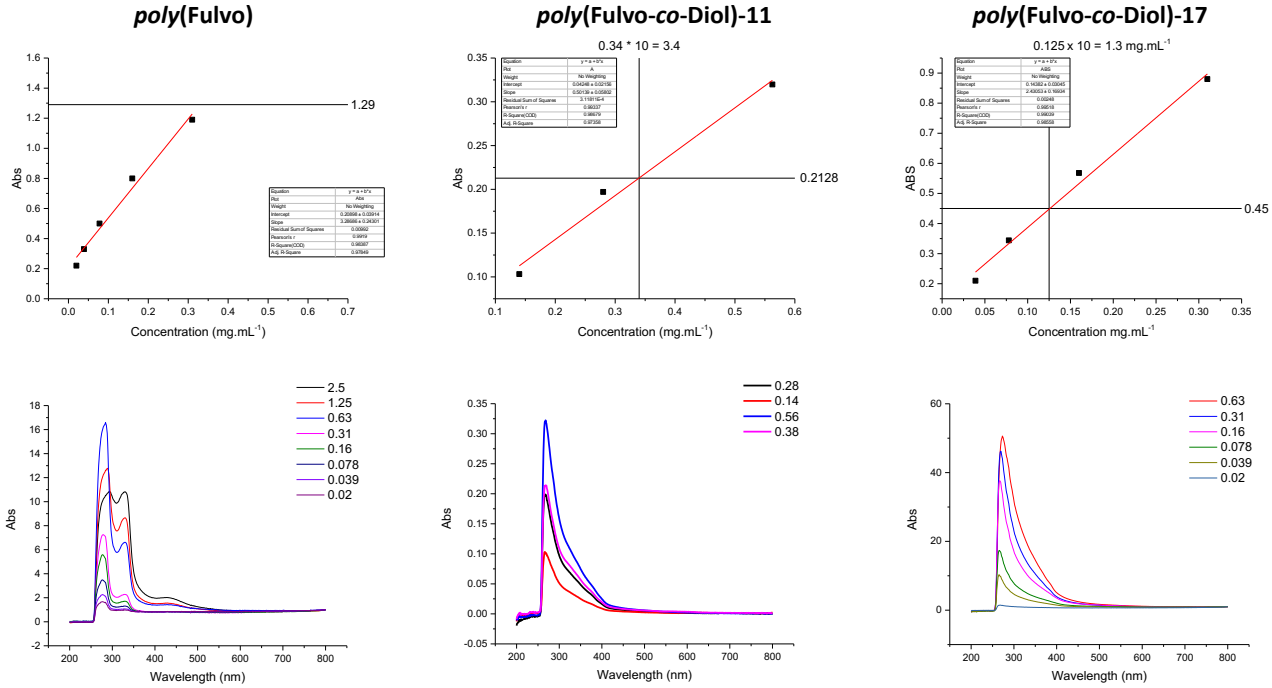


Figure S2 – Beer Lambert Plots (TOP) and UV-Vis spectra (BOTTOM) of the *poly*(Fulvo), *poly*(Fulvo-*co*-Diol)-11 and -17 polymer series, respectively

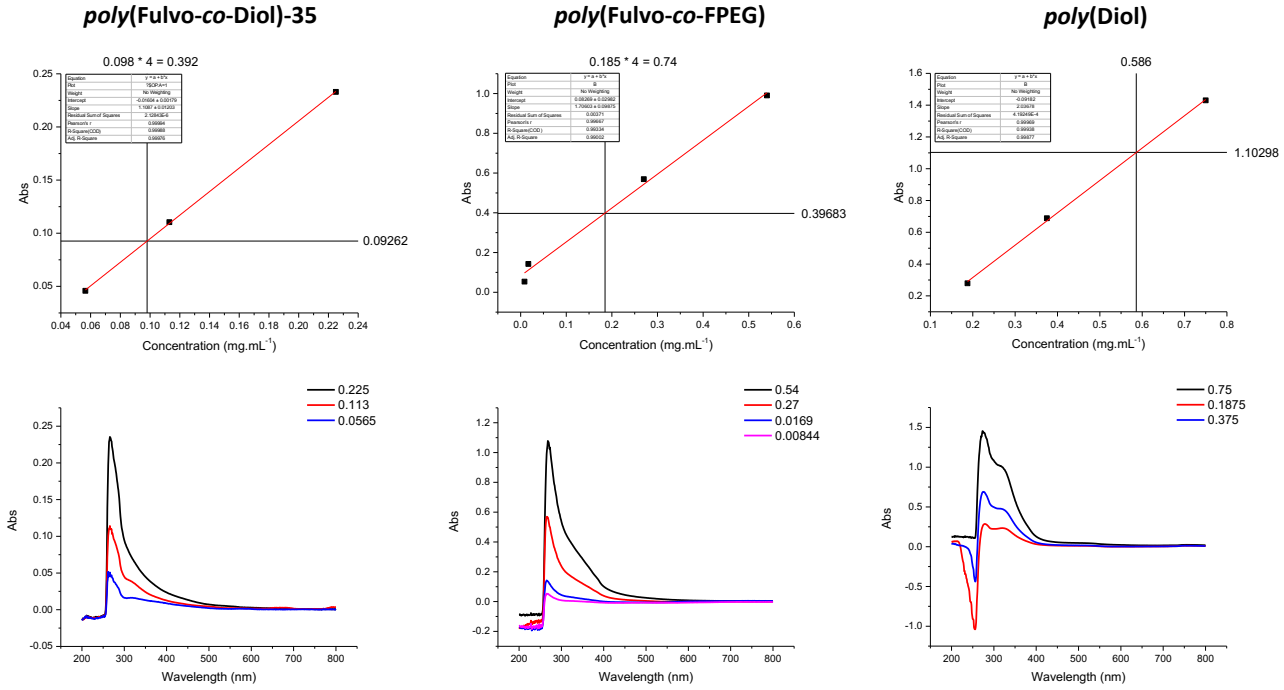


Figure S3 - Beer Lambert Plots (TOP) and UV-Vis spectra (BOTTOM) of *poly*(Fulvo-*co*-Diol)-35, *poly*(Fulvo-*co*-FPEG), and *poly*(Diol) polymer series, respectively.

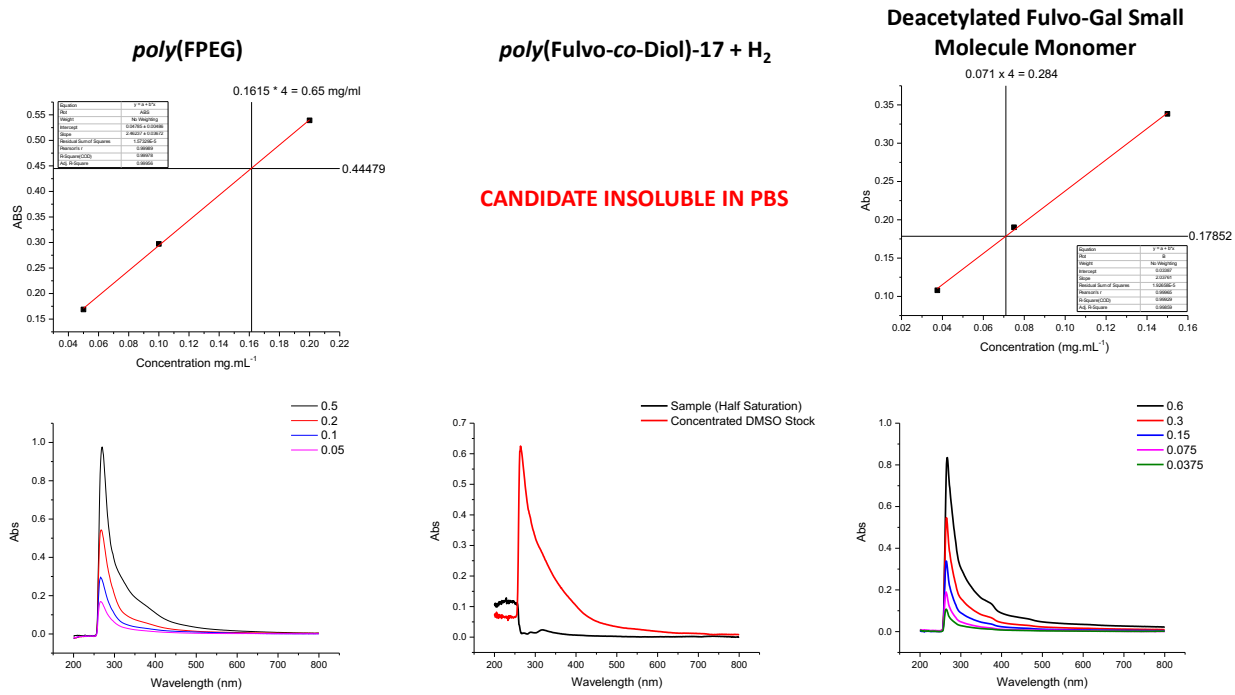


Figure S4– Beer Lambert Plots (TOP) and UV-Vis spectra (BOTTOM) of the *poly*(FPEG) and *poly*(Fulvo-*co*-Diol)-17 + H_2 polymer series, and deacetylated Fulvo-Gal monomer series, respectively.

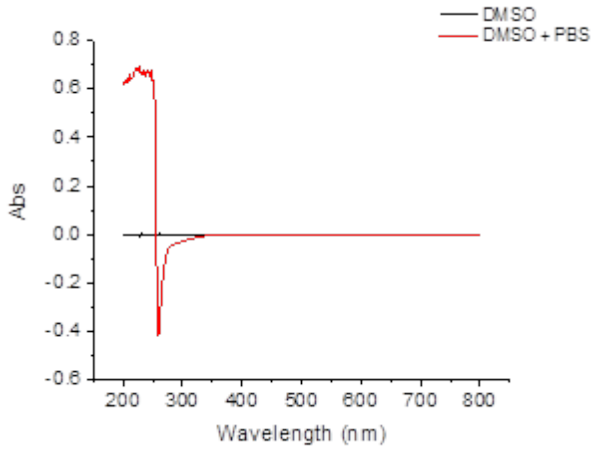


Figure S5 – UV/Vis spectrum of DMSO (background zeroed) and DMSO containing PBS salt

Additional 'splat' data

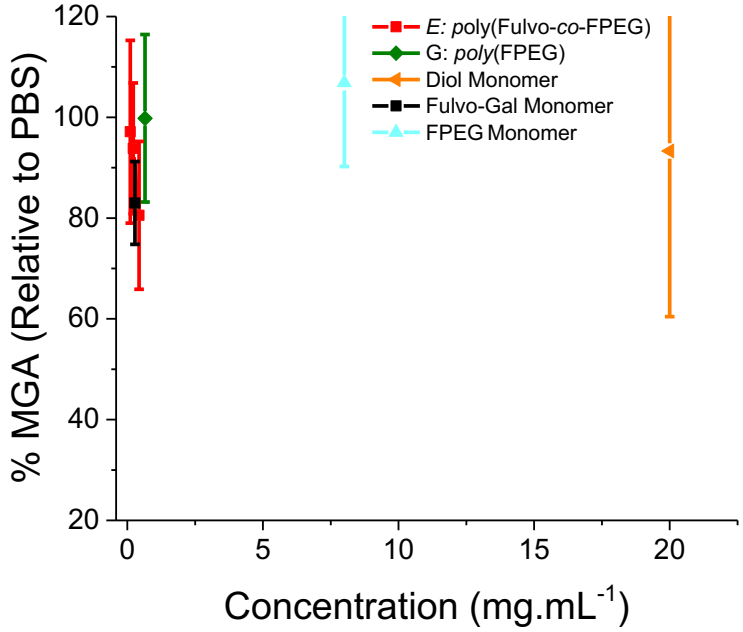
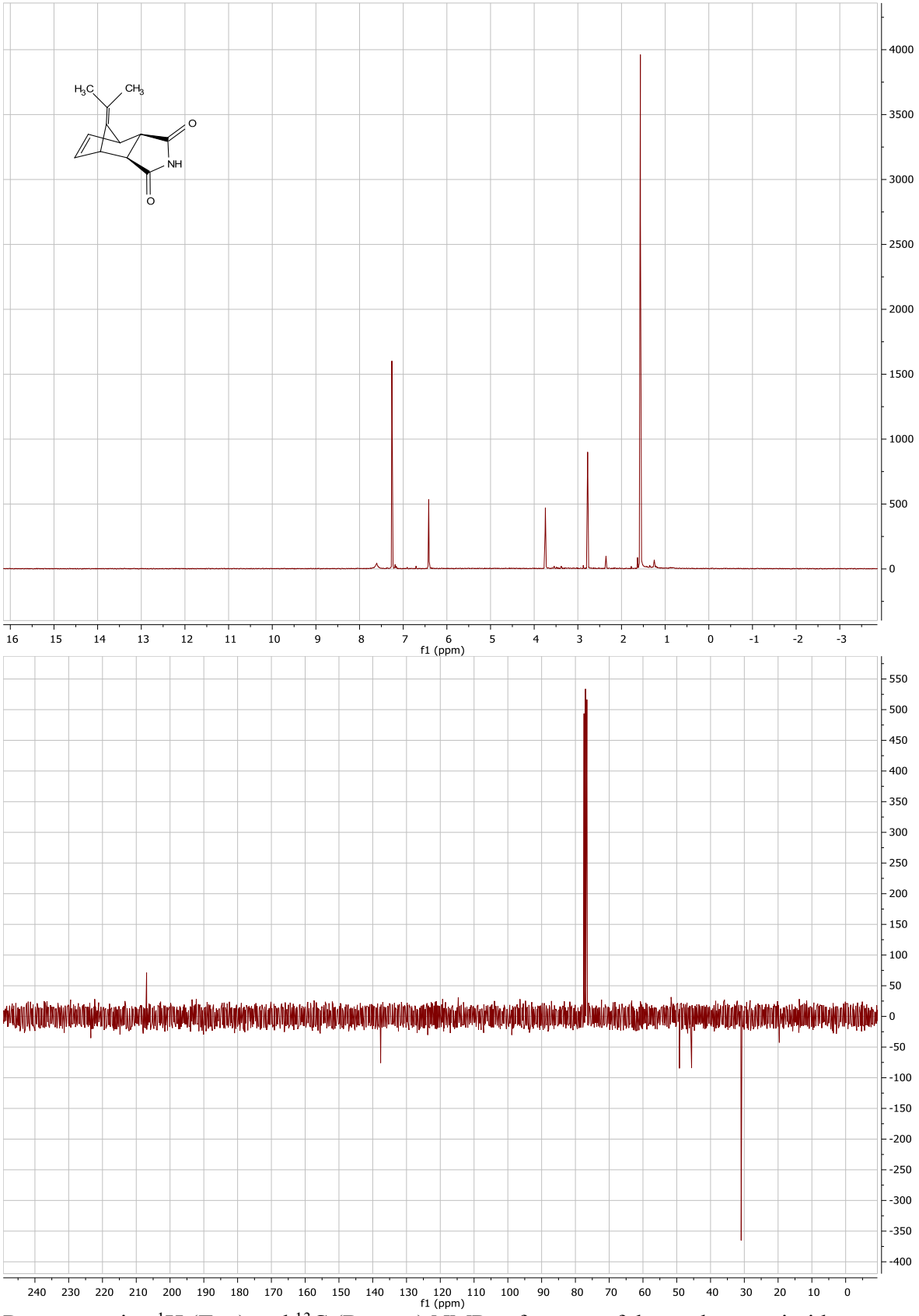
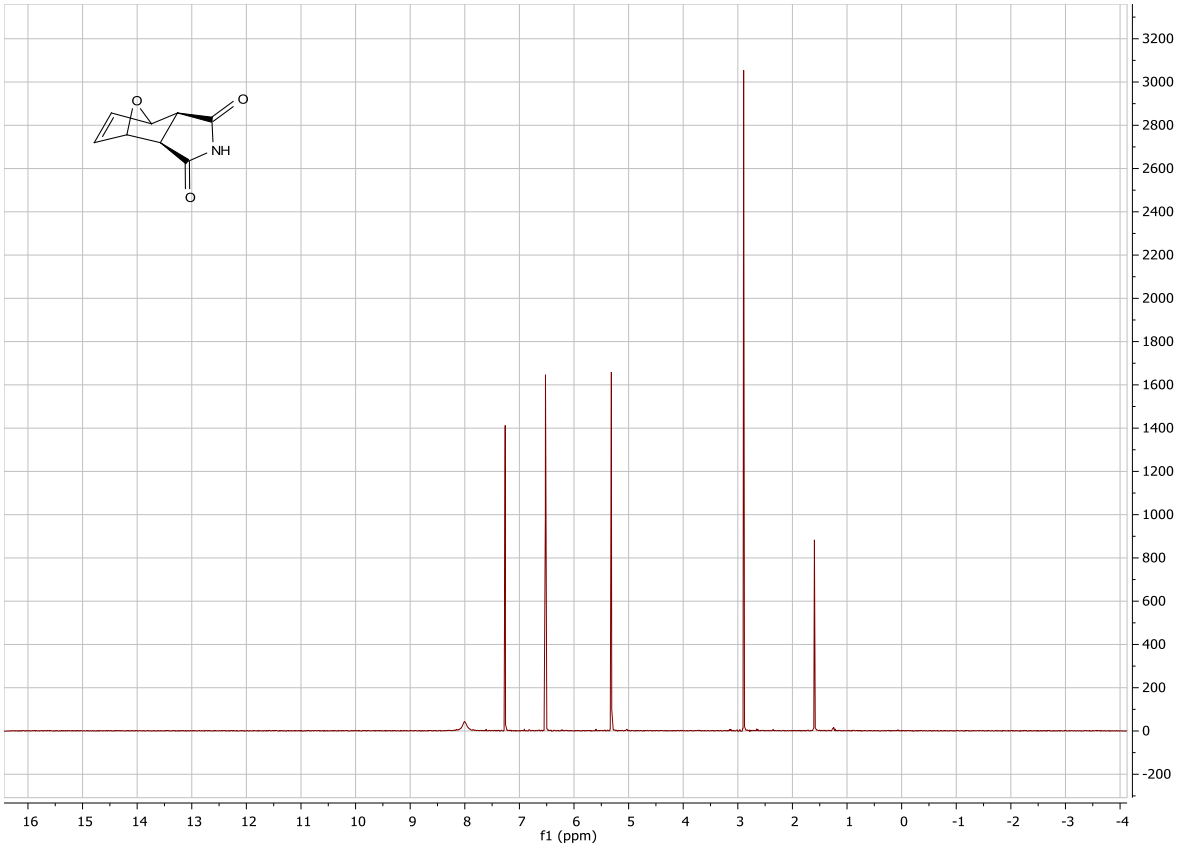


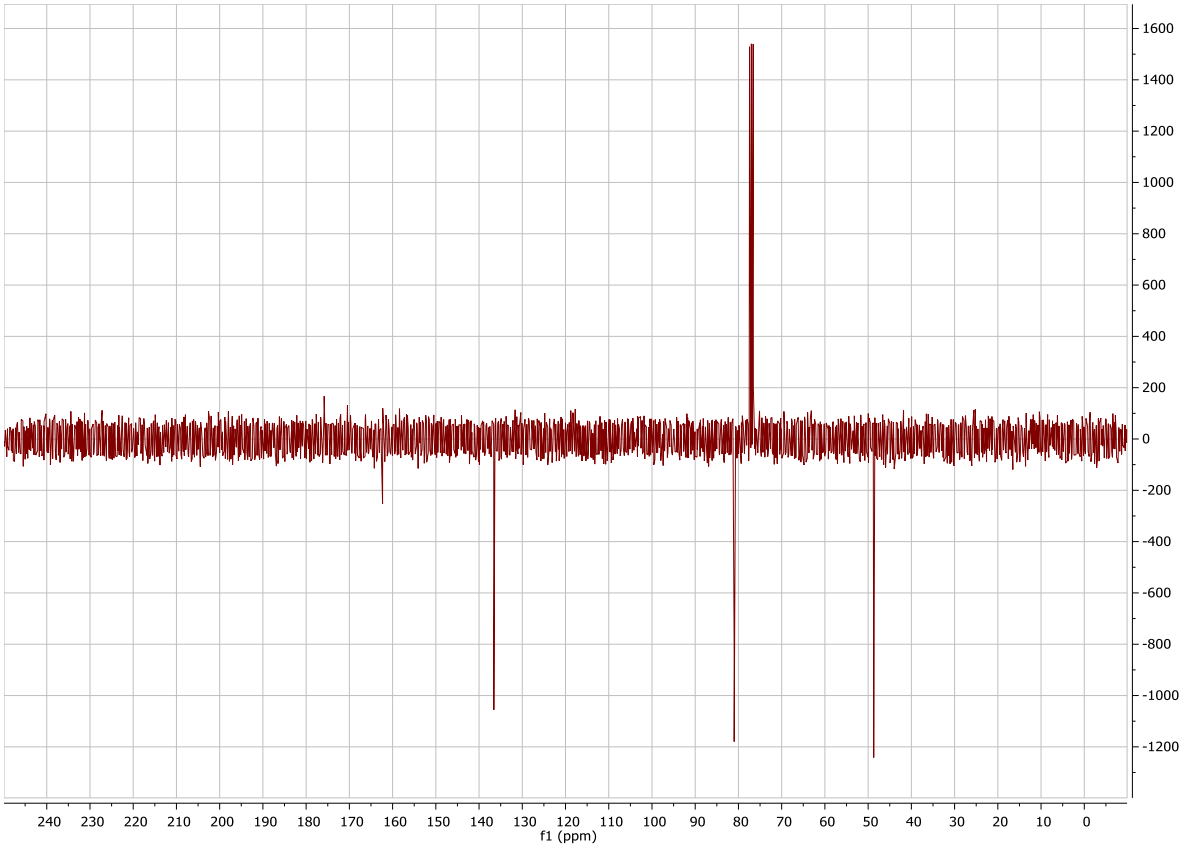
Figure S6 – Inactive Species

NMR Spectra of Synthesized Small Molecules

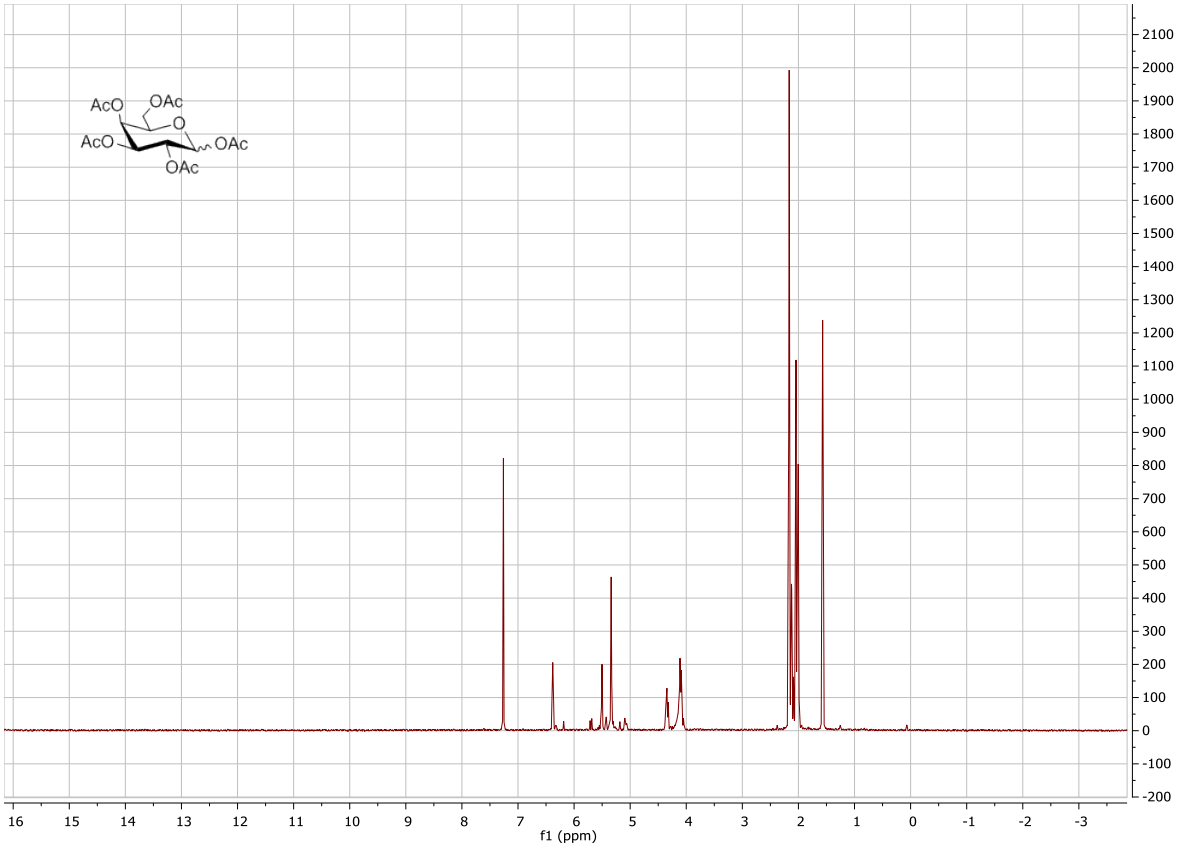


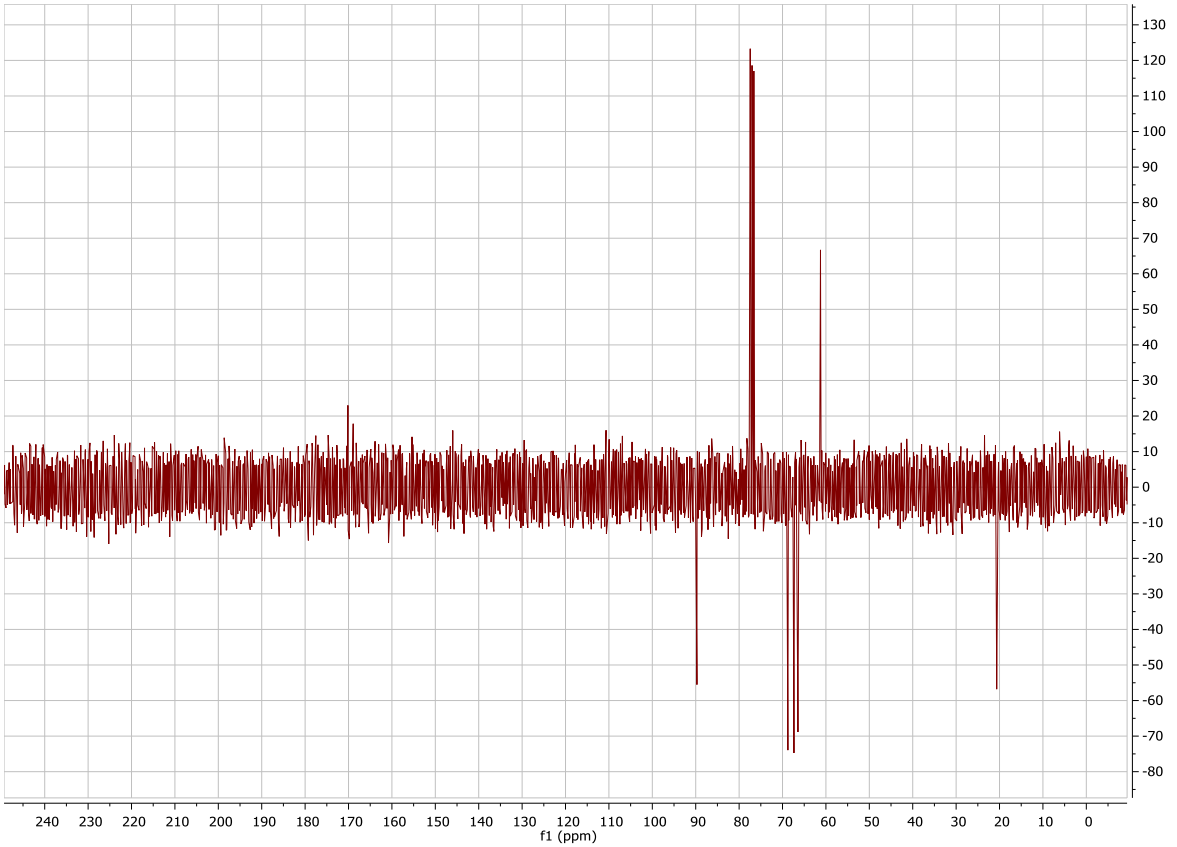
Representative ^{1}H (Top) and ^{13}C (Bottom) NMRs of *exo,exo*-fulvonorborneneimide



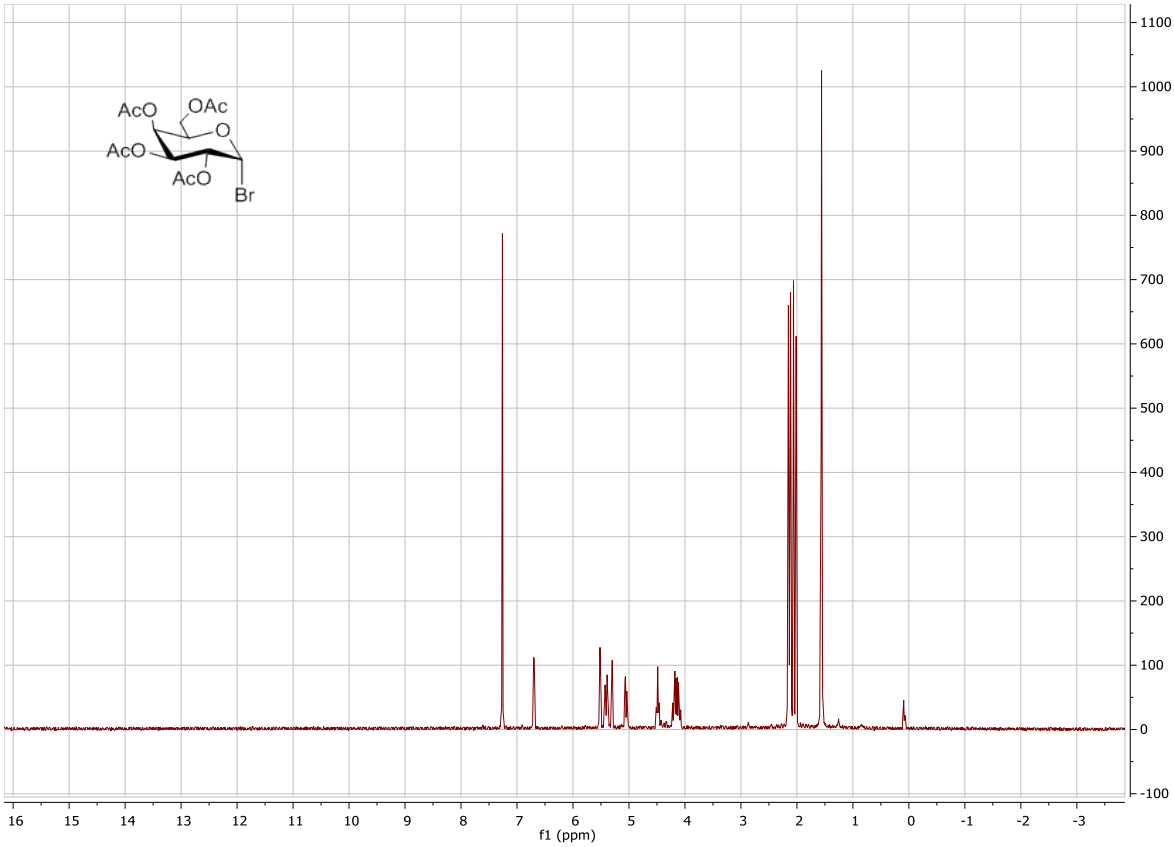


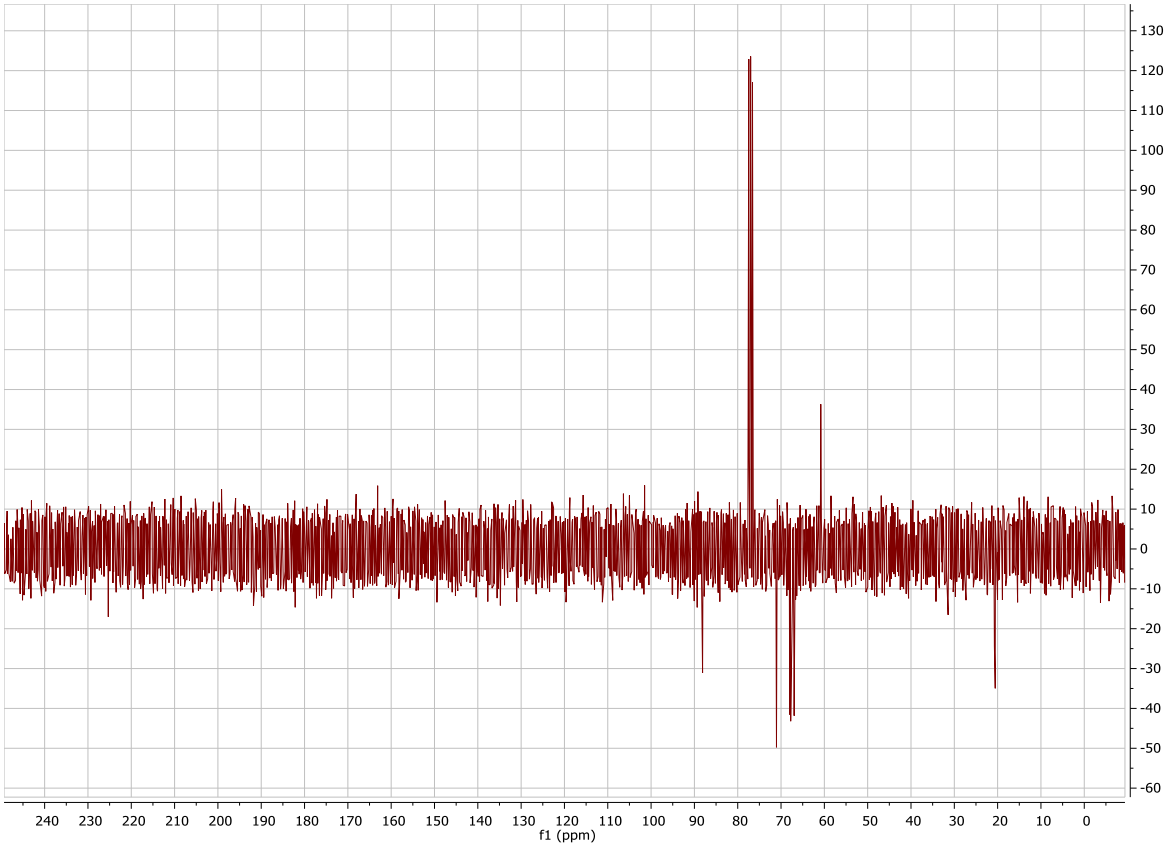
Representative ^{1}H (Top) and ^{13}C (Bottom) NMRs of *exo,exo*-oxonorborneneimide



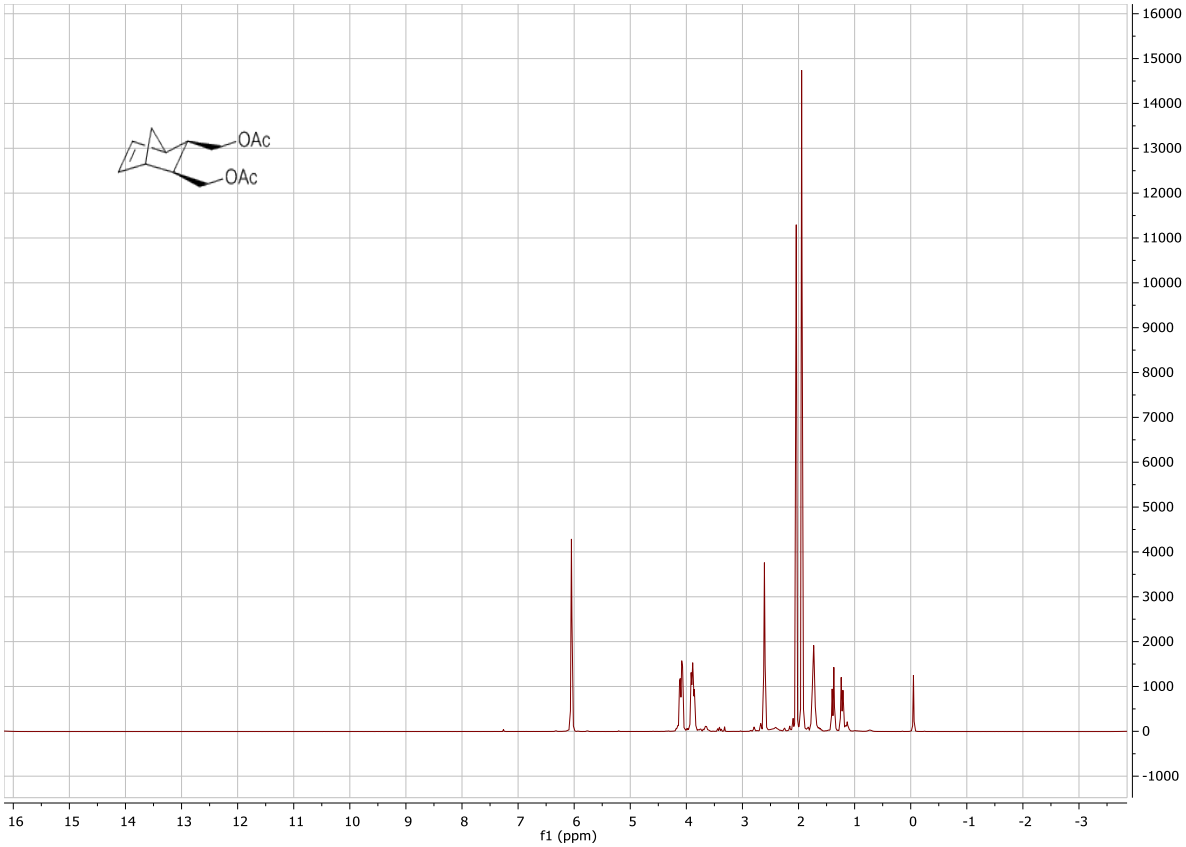


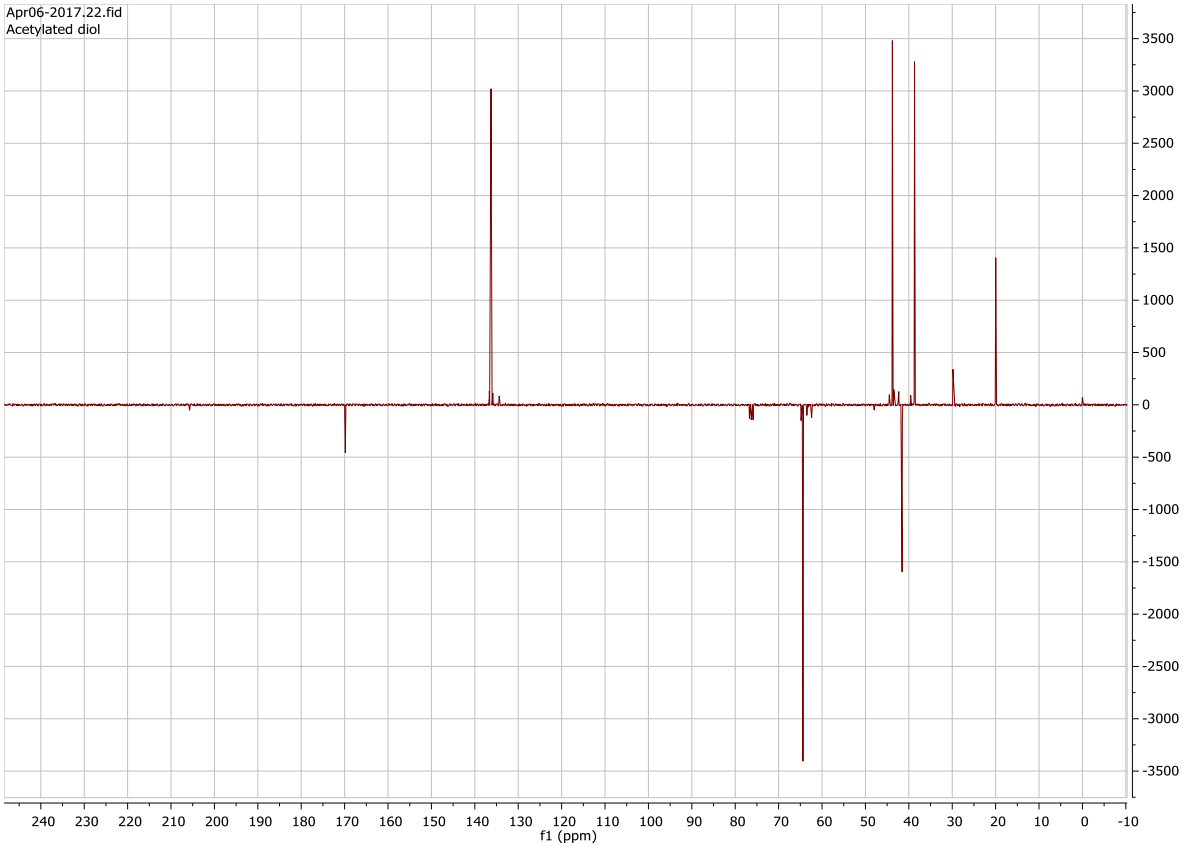
Representative ^{1}H (Top) and ^{13}C (Bottom) NMRs of D-Galactose pentaacetate



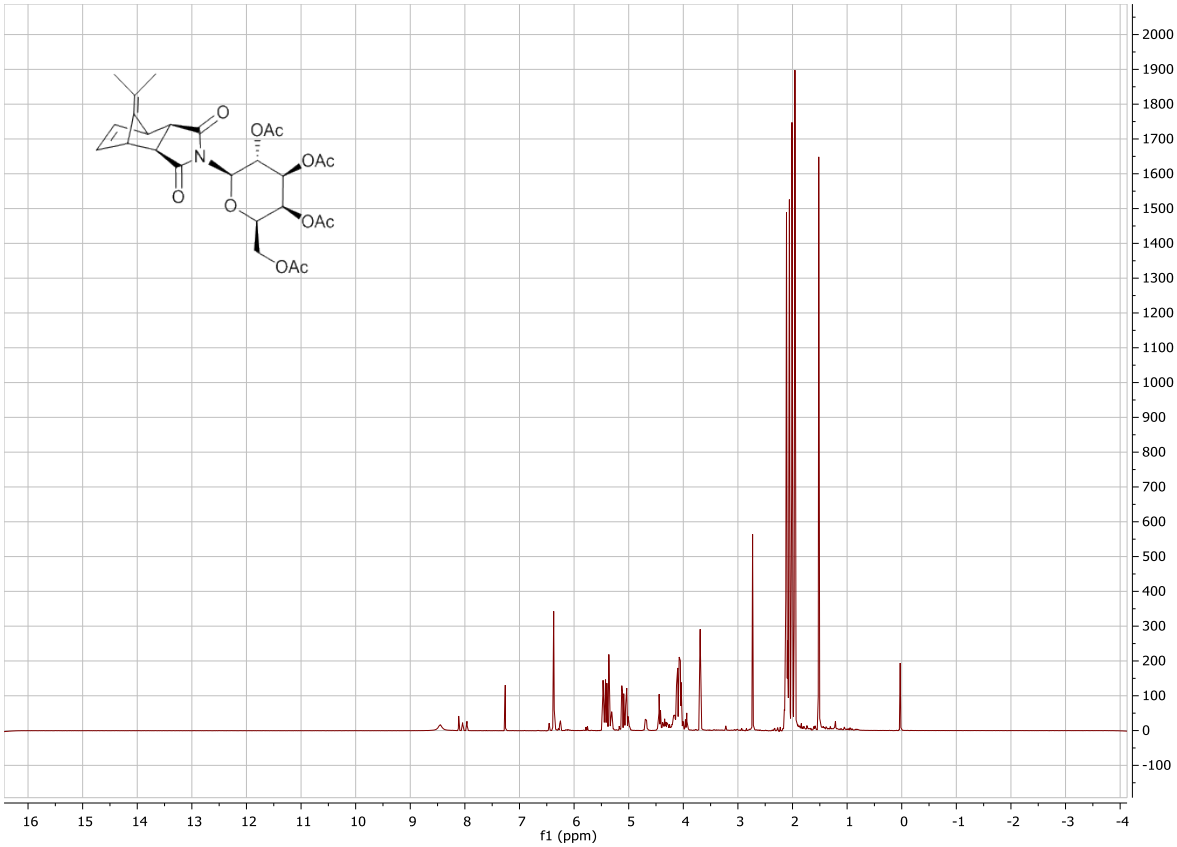


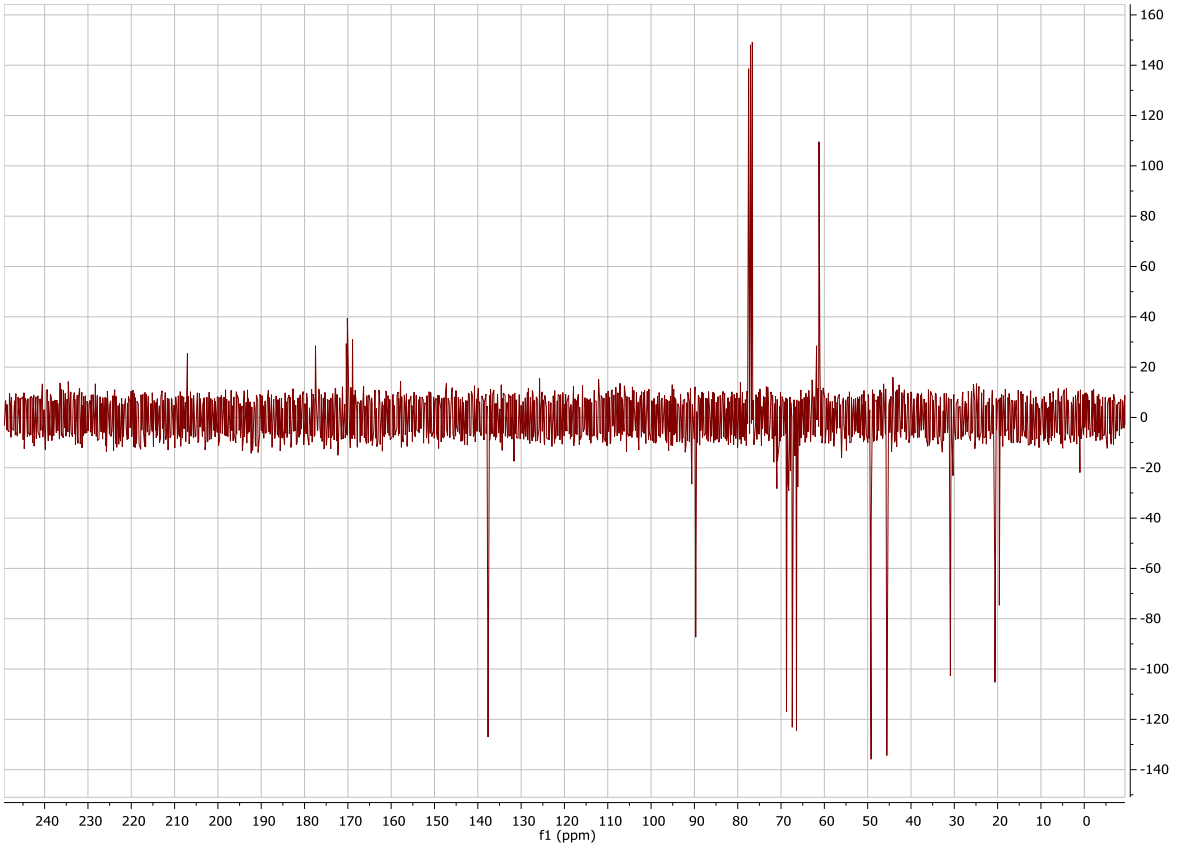
Representative ^{1}H (Top) and ^{13}C (Bottom) NMRs of Acetobromo-α-D-Galactose



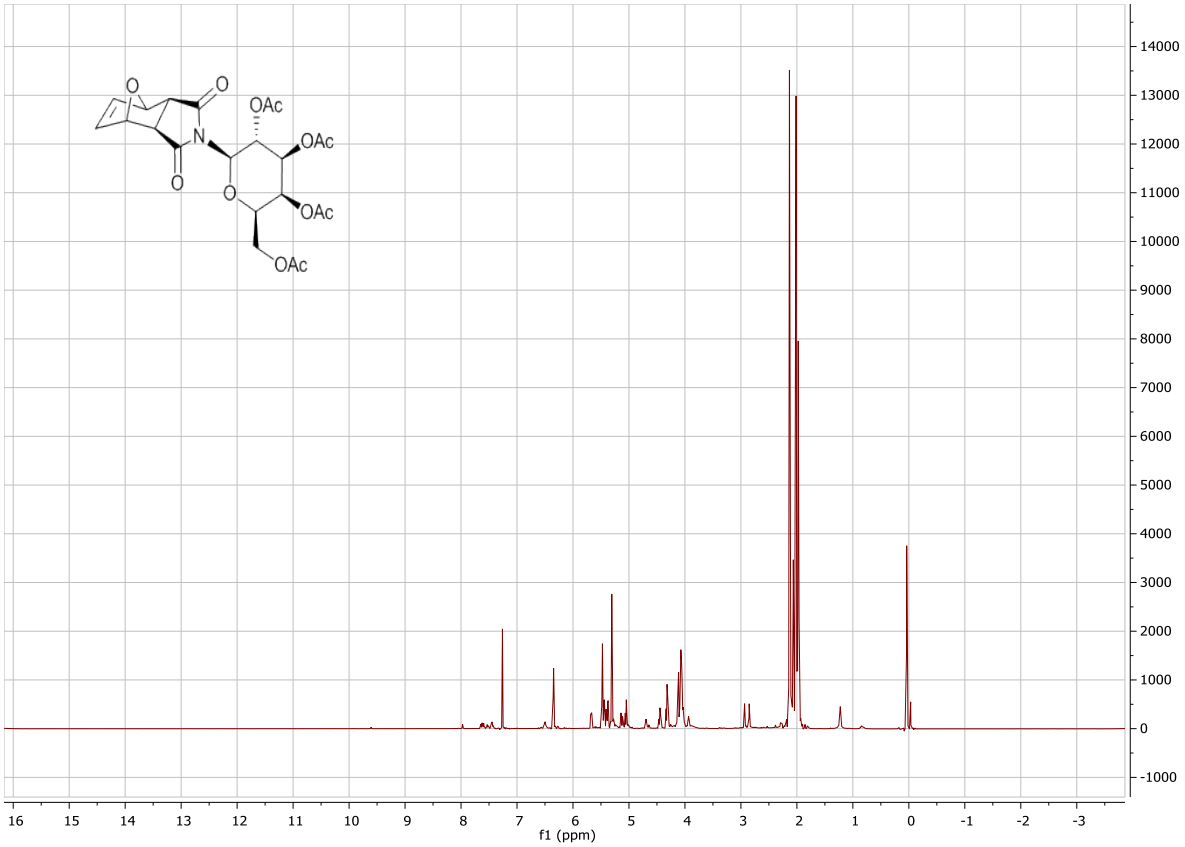


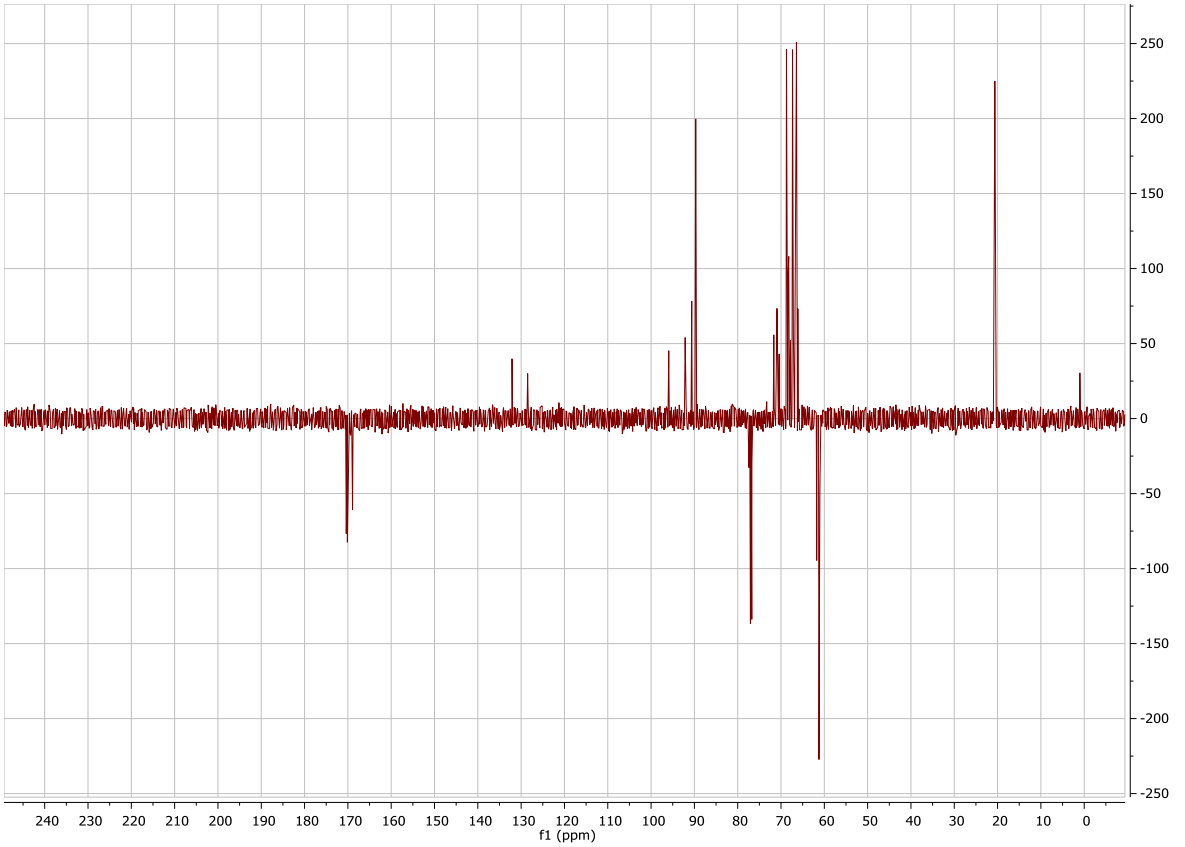
Representative ^{1}H (Top) and ^{13}C (Bottom) NMRs of M1



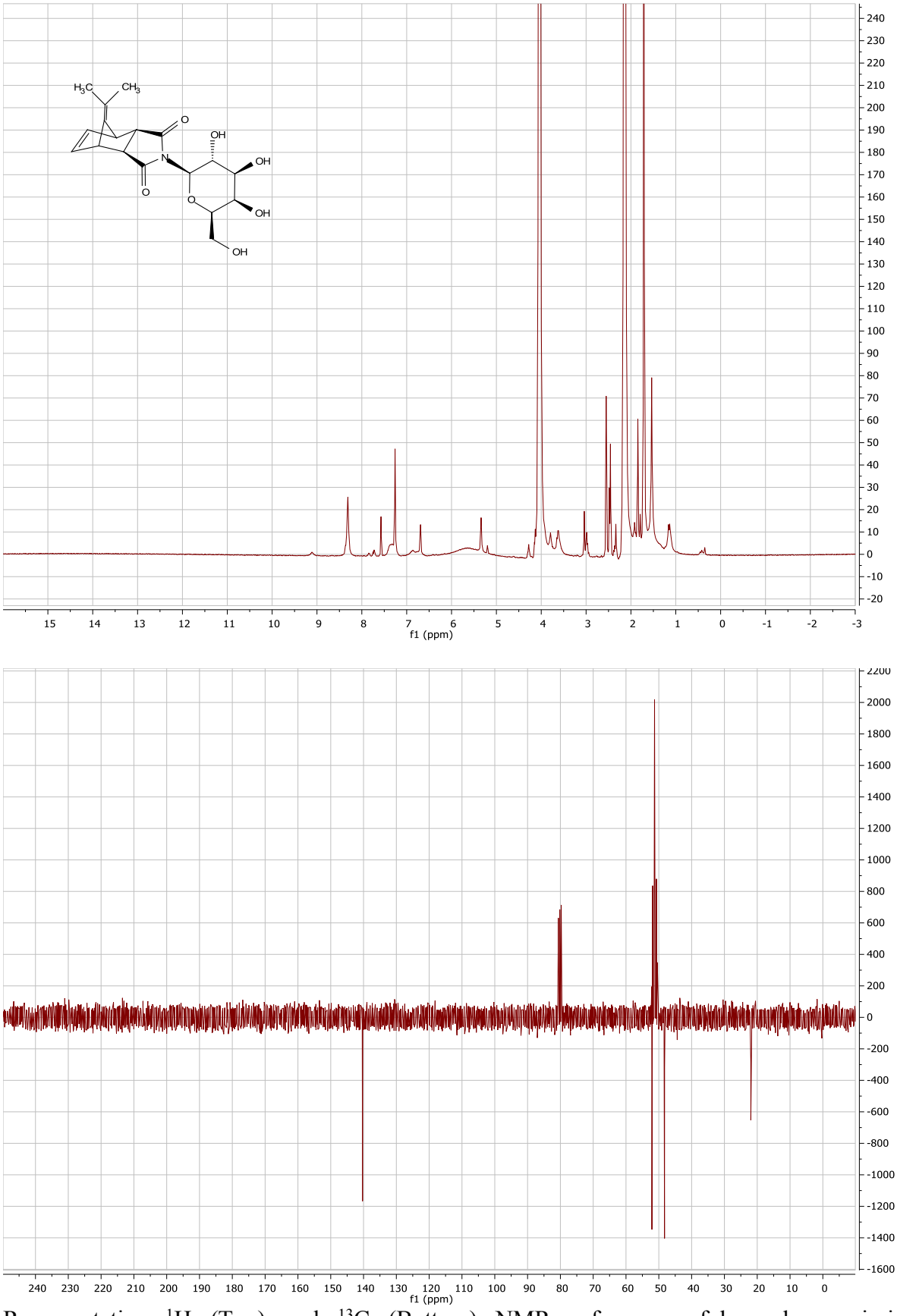


Representative ^{1}H (Top) and ^{13}C (Bottom) NMRs of M2

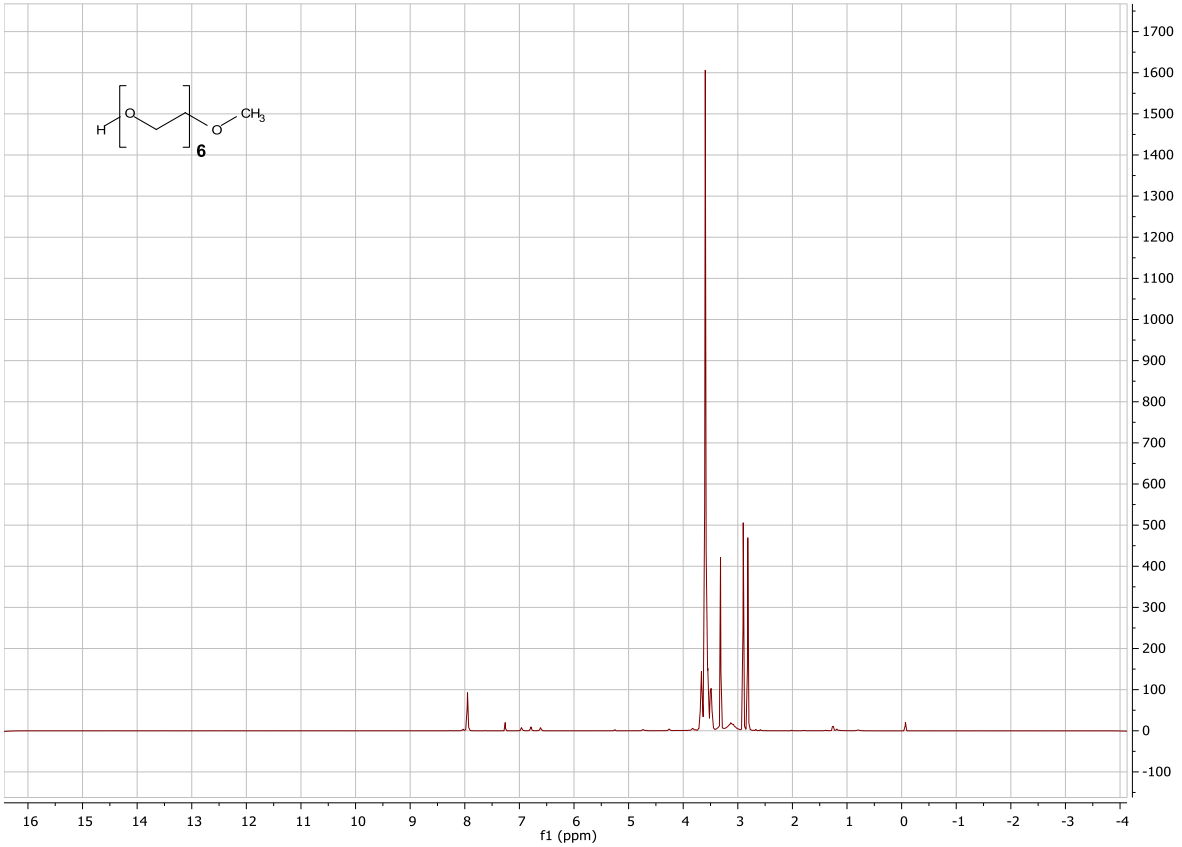


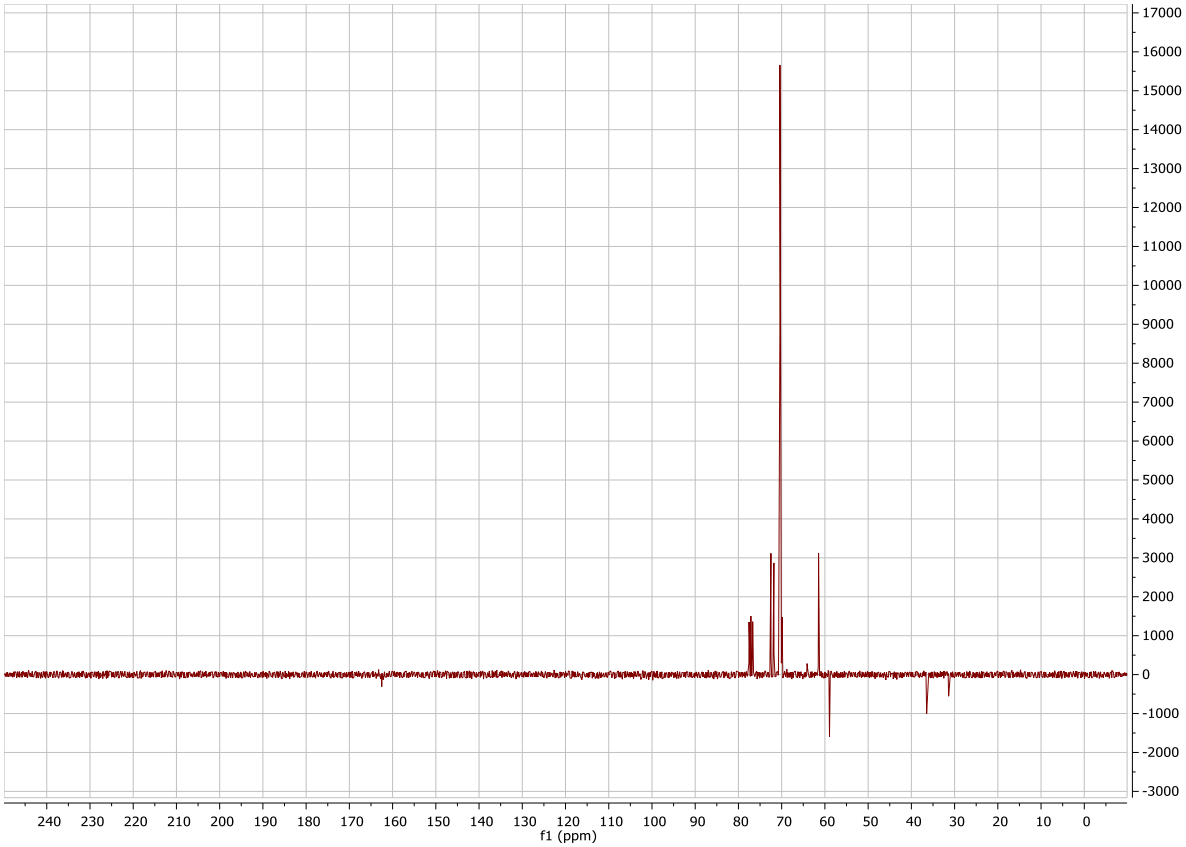


Representative ^{1}H (Top) and ^{13}C (Bottom) NMRs of M3

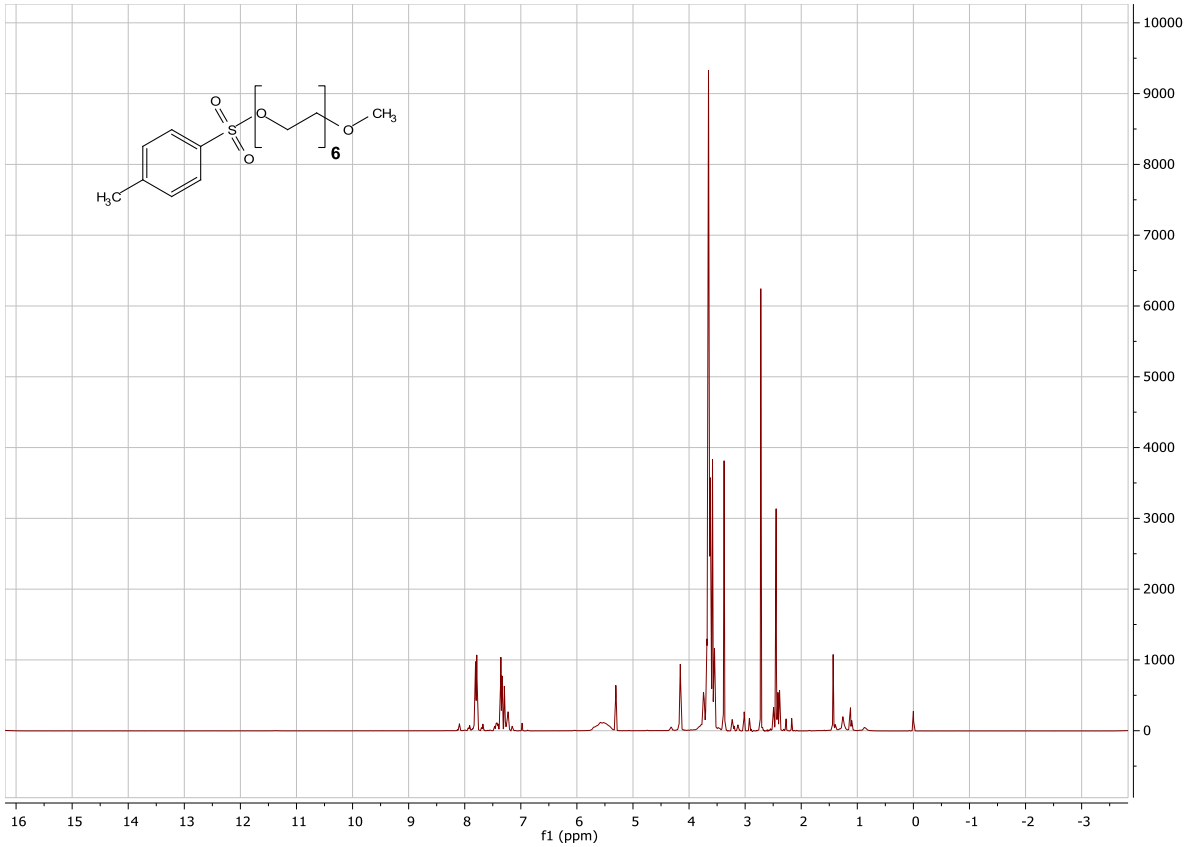


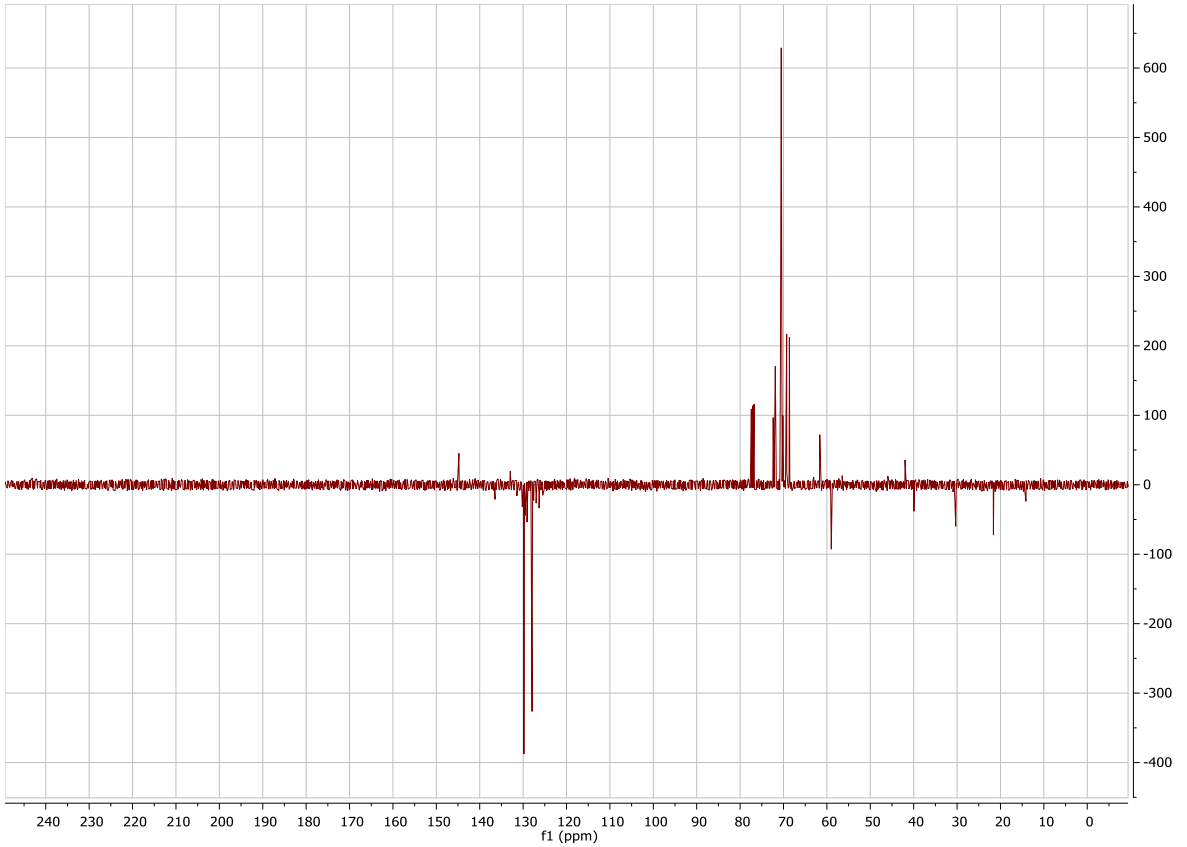
Representative ^{1}H (Top) and ^{13}C (Bottom) NMRs of *exo*,*exo*-fulvonorborneneimide galactopyranoside



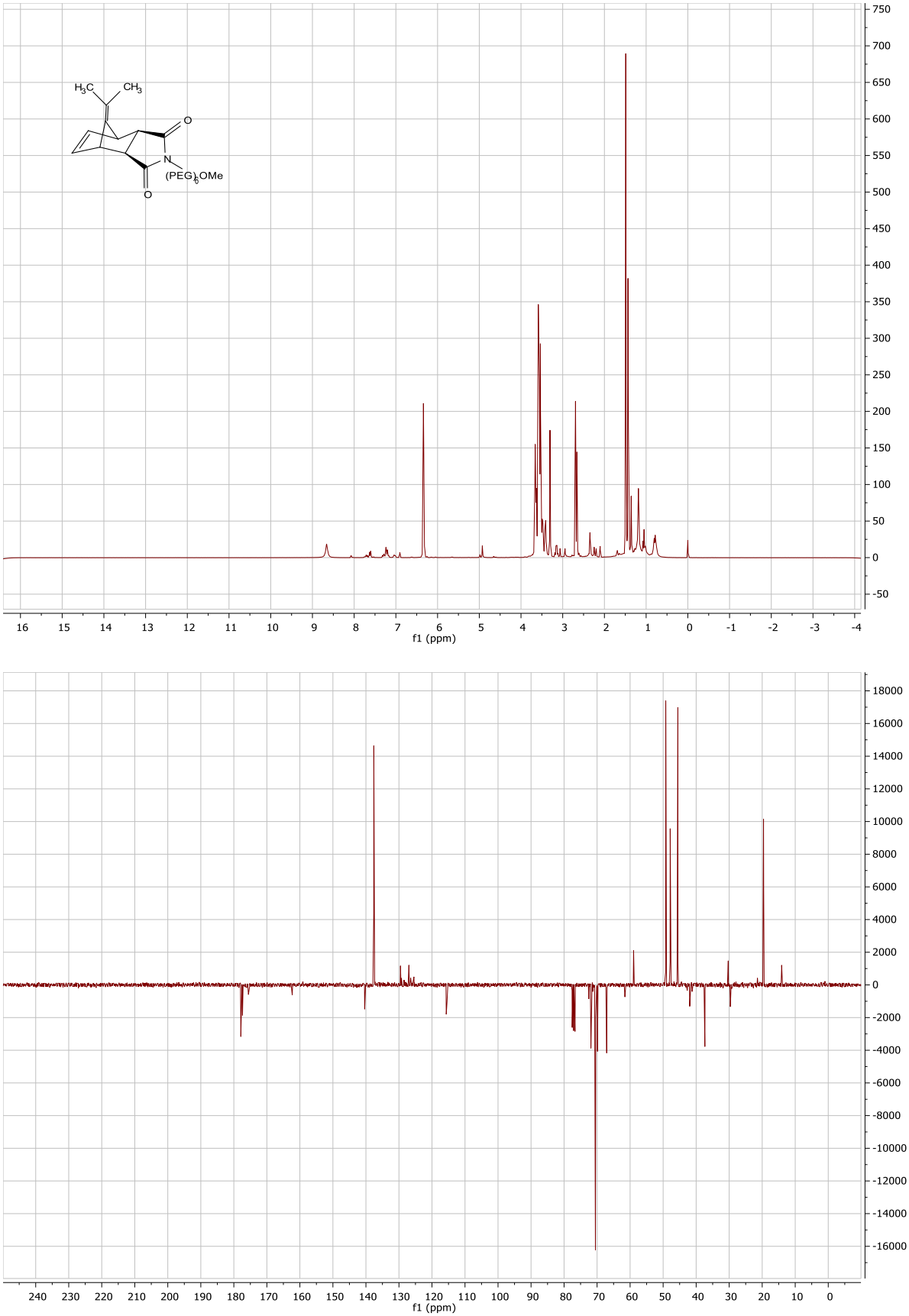


Representative ^{1}H (Top) and ^{13}C (Bottom) NMRs of Monomethoxyhexaethylene glycol





Representative ^{1}H (Top) and ^{13}C (Bottom) NMRs of Monomethoxyhexaethylene glycol monotosylate



Representative ^{1}H (Top) and ^{13}C (Bottom) NMRs of M4

Comprehensive small-angle neutron scattering (SANS) data analysis

SANS is a popular characterization technique employed to yield structural information at the nanometre length scale. The standard equation for absolute neutron scattering by macromolecules in solution combines form factor, $P(q)$, of the polymer with the interparticle scattering factor, $S(q)$, represented in the equation:

$$I(q) = \frac{1}{V}\frac{d\sigma}{d\Omega} = (\Delta\rho)^2(\Phi_{vol}V_{chain}P(q)\,S(q)) \qquad \textbf{Eq. S1}$$

where $(\Delta\rho)^2 = (\rho_{HA} - \rho_{H2O})^2$ is the contrast factor per unit volume between the polymer and the solvent. V_{chain} is the volume of the N monomers in a chain and Φ_{vol} is the volume fraction of monomer. In a dilute polymer solution, where intermolecular effects should be diminished, the scattering can be assumed to be arising from isolated chains without interactions and without excluded volume (*i.e.* $S(q) \approx 1$ and therefore, $I(q) \approx P(q)$).

A Porod plot ($I(q)$ *vs.* q) yields an exponent that suggests a sub-structural dimensionality from which the overall particle shape can be estimated. The SANS data of *poly*(Fulvo-*co*-Diol)-11 and *poly*(Fulvo-*co*-Diol)-17 (Figure 5, manuscript) display Porod exponents in the low q region ($q < 0.02$ Å^{-1}) of $\sim q^{-3.5}$, suggesting the formation of mass fractals.[5] Fractals are self-similar structures that appear analogous at different length scales. Furthermore, *poly*(Fulvo-*co*-Diol)-11 and *poly*(Fulvo-*co*-Diol)-17 exhibit characteristic crossovers in the q dependence of the scattering intensity from that of aggregates (q^{-3}) to that typical for rigid rods (q^{-1}),[6] which is characteristic of polymer associations.[7] For high molecular weight polymers, such as these, the only pertinent quantity, which can be determined, is the persistence length, b_t, which accounts for the effective rigidity of the uncharged chain. This was achieved using the method described below.

Rigid rods[8] and Gaussian chain molecules[9] show characteristic asymptotic behaviour with the particle scattering factors, $P(q)$, given by Equations S2 and S3, respectively:

$$P(q) \rightarrow \pi/(qL) \qquad \text{(rigid rod)} \qquad \textbf{Eq. S2}$$

$$P(q) \rightarrow \frac{2}{q^2 < S^2 >} = \frac{12}{q^2 L l C_\infty} = \frac{12}{q^2 L l_k} \qquad \text{(Gaussian coil)} \qquad \textbf{Eq. S3}$$

where

$$q = \left(\frac{4\pi}{\lambda}\right) sin\left(\frac{\theta}{2}\right) \quad \textbf{Eq. S4}$$

and θ is the scattering angle. $L = nl$ is the contour length of the chain or the rod, $C_\infty = \langle r^2 \rangle / (nl^2)$ is the characteristic ratio at large degree of polymerisation, l is the average bond length, n is the number of bonds in a molecule and $l_k = lC_\infty$ is the Kuhn segment length. Finally, $l_k = 2b_t$, where b_t is the persistence length.

Due to the correlation between neighbouring bonds, short chains do not behave like Gaussian coils but approach the properties of a rigid rod when the chain becomes shorter than one Kuhn segment in length.[10,11] Typically, the characteristic slope of a Gaussian chain (q^{-2}) appears at low q-values, where the overall structure of the molecule is observed. Upon increasing q, shorter chains are 'seen', and eventually at larger q the form factor of the rod particle becomes apparent (slope of q^{-1}).

The transition from coil-like to rod-like behaviour is expected to occur at the point which both the rod and Gaussian coil scattering functions (Equations S2 and S3) have the same value.[11]. This condition leads to the following:

$$q^* = \frac{12}{\pi l_k} = \frac{3.82}{l_k} = \frac{1.91}{b_t} \quad \textbf{Eq. S5}$$

Thus, the persistence length can be estimated from the approximate point where the characteristic slopes intersect each other (marked with q^* in Figure 5). The estimated persistence lengths for *poly*(Fulvo-*co*-Diol)-11 and *poly*(Fulvo-*co*-Diol)-17 are 38.9 and 44.4 Å, respectively. However, it has to be noted that Equation S5 was originally derived for a transition from the q^{-2} regime to the q^{-1} regime.[11,12] Due to the obvious presence of large aggregates in these samples, as indicated by the slope of $q^{-3.5}$, the overlap may actually occur at a lower q region, but is masked by aggregate scattering.[7] Thus, these values should be taken as the minimum persistence lengths for each polymer. Nevertheless, each b_t is much larger than the monomer length (~10 Å), which suggests that the chain backbones are locally stiff.[7] Furthermore, given the approximate contour length, L, of both polymer chains (490 Å and 760 Å for *poly*(Fulvo-*co*-Diol)-11 and *poly*(Fulvo-*co*-Diol)-17, respectively), the large b_t suggests rigid rather than highly flexible aggregates of potentially rod-like structures.

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