Supporting Information

Key Role of the Linker in Pyrene-Linker-Carboxylate Surfactants for the Efficient Aqueous Dispersion of Multiwalled Carbon Nanotubes

Daniel J. Welsh,[1] Luke J. O'Driscoll,[1] Steven Bailey,[2] David Visontai,[2,3] Kara Howes,[1] Harry Frampton,[4] Martin R. Bryce,*[,1] and Colin J. Lambert*[,2]

[1] Department of Chemistry, Durham University, Durham, DH1 3LE, U.K.

[2] Department of Physics, Lancaster University, Lancaster, LA1 4YB, U.K.

[3] Present address: Department of Physics and Complex Systems, Eötvös University, H-1117 Budapest, Pázmány Péter Sétány 1/A, Hungary

[4] BP Exploration Operating Company Limited, Chertsey Road, Sunbury-on-Thames, Middlesex TW16 7BP, U.K.

Contents **Pages**

1. Synthetic Methods and Characterization Data

1.1. General. Unless otherwise stated reactions were conducted under an argon atmosphere which was dried by passage through a column of phosphorus pentoxide. All commercial chemicals were used without further purification. Anhydrous solvents were dried through an HPLC column on an Innovative Technology Inc. solvent purification system. Column chromatography was carried out using 40-60 μm mesh silica. Analytical thin layer chromatography was performed on pre-coated plates of silica gel (Merck, silica gel 60F254), visualization was made using ultraviolet light (254 nm or 365 nm), potassium permanganate TLC stain, or cerium molybdate TLC stain (stains were prepared following standard procedures).

NMR spectra were recorded on a Bruker Avance-400 spectrometer. Chemical shifts are reported in ppm relative to $CHCl_3$ as internal reference which was set to 7.27 ppm for ^{1}H NMR spectra and 77.23 ppm for ^{13}C NMR spectra. Melting points were determined in open-ended capillaries using a Stuart SMP40 automatic melting point apparatus at a ramping rate of 2 °C/min. ESI mass spectra were obtained using a TQD mass spectrometer equipped with an Acquity UPLC (Waters Ltd, UK). ASAP mass spectra were measured using a Xevo QToF mass spectrometer (Waters Ltd, UK) equipped with an Agilent 7890 GC (Agilent Technologies UK Ltd, UK). High resolution mass spectra (HRMS) were measured using a LCT Premier XE mass spectrometer equipped with an Acquity UPLC (Waters Ltd, UK) (4 d.p. data) or a LTQ FT mass spectrometer equipped with a Surveyor HPLC (Thermo-Finnigan Corporation) (5 d.p. data). For the TQD, Xevo QToF and LCT Premier XE mass spectrometers MS data was processed using MassLynx 4.1. Exact mass measurements utilised a lock-mass correction to provide < 3 mDa precision. Exact mass measurement used Elemental Composition version 4.0 embedded within MassLynx 4.1 (Waters Ltd, UK). For the LTQ FT mass spectrometer MS data was processed using QualBrowser version 2.0. UV-visible spectroscopic measurements used a Thermo Evolution 220 UV-visible spectrometer with an integrating sphere (ISA220) accessory, using the supplied Thermo INSIGHT software. TEM data were obtained using a JEOL 2100F FEG TEM operating at 80 kV. Samples were prepared by dropping *ca.* 20 μL of MWNT dispersion onto a holey-carbon TEM grid which was dried in air overnight.

1.2 Compound Nomenclature. The names assigned to the surfactants and intermediates, in addition to the associated compound numbers, are intended as a guide to their structures. The surfactant names use the following format: anchor-linker-head. The anchor group is denoted as either PBA (if derived from 1-pyrenebutyric acid via amide coupling) or PyrB (if derived from 1-

pyrenebutanol via ether synthesis). The linker group (if present) is denoted as either $(C6)_n$ (for C6 linkers derived from one or more 6-aminohexanoic acid moieties) or PEGn (for linkers derived from OEGs). The head group is denoted as either COONa (for 'G0' monocarboxylates) or $GX(ONa)_m$ (for higher generation dendrons, where X = generation number and m = 3X); for species with a PEGn linker this is preceded by CH_2CO to denote the additional moiety (derived from bromoacetic acid) present in these cases (used to allow the head group to be attached via amide coupling).

The names of intermediate species are based on the above convention, with the anchor or head groups omitted or replaced by e.g. protecting groups as appropriate to the structure of the molecules. Terminal groups of unsubstituted linkers are omitted for brevity: if not otherwise stated a C6 linker is assumed to be terminated by an amine (anchor end) or carboxylic acid (head end) moiety, and a PEG linker by alcohol groups.

1.3 General Synthetic Procedures

1.3a. Deprotection of tert-Butyl Esters:

The ester was dissolved in formic acid and stirred overnight at room temperature. The formic acid was removed under vacuum to afford the product with no further purification.

1.3b. Amide Coupling:

The carboxylic acid (1 eq.) was dissolved in anhydrous DCM. *N,N*-diisopropylethylamine (DIPEA) (2 eq.) and *N,N,N',N'*-tetramethyl-*O*-(benzotriazol-1-yl)uronium tetrafluoroborate (TBTU) (1 eq.) were added and the solution was stirred at either 0 °C (using an ice/water bath) or room temperature for 15 min. The amine (1 eq.) in anhydrous DCM was added dropwise to the stirred solution and the solution was then typically stirred for at least 17 h (longer reaction times did not appear to affect the yields) at room temperature (some variations are described in specific syntheses below). The mixture was then extracted three times with saturated $NaHCO_3$, three times with 1 M $NaHSO_4$ and twice with water. The organic layer was dried over $MgSO_4$ which was removed by filtration. After removal of the solvent the residue was purified by column chromatography (in some cases the residual tetramethylurea by-product was removed by distillation under vacuum prior to chromatography).

1.3c. Z-deprotection

Based on a literature procedure,[1] the Z-protected amine was dissolved in EtOH and Pd/C was added. The flask was subjected to several vacuum/H_2 purges and then stirred for 19 – 23 h under an atmosphere of H_2 at room temperature. Insoluble species were removed by filtration

through Celite, which was washed with EtOH. Evaporation of the filtrate afforded pure product with no further purification.

1.3d. Formation of Sodium Carboxylates:

These reactions were not conducted under argon. The mono- or tricarboxylic acid (1 eq.) was dissolved in methanol and stirred at room temperature. The solution was treated with 1.0000 M $NaOH_{(aq)}$ (exactly 1 eq. per carboxylic acid moiety) then stirred at room temperature for 30 min. The solvent was removed *in vacuo* and the residue was dissolved in distilled water which was lyophilised to give the product with no further purification. The highly hygroscopic products were stored under vacuum.

1.3e. Monotosylation of OEGs:

Based on a literature procedure,[2] Ag_2O (1.5 eq.), KI (0.2 eq.) and tosyl chloride (1.1 eq.) were dispersed in anhydrous DCM and stirred vigorously at 0 °C. The OEG (1 eq.) was added to the cooled mixture. After stirring at 0 °C for 15 – 60 min (dependant on the OEG) the reaction mixture was filtered through celite to remove inorganic species. The solvent was removed *in vacuo* to afford a crude oil which was purified using column chromatography.

1.3f. THP-protection of monotosylated OEGs:

Based on a literature procedure,[3] Ts-PEGn (1 eq.) was dissolved in anhydrous DCM and stirred at room temperature. Pyridinium *p*-toluenesulphonate (0.2 eq.) was added to the stirred mixture followed by 3,4-dihydro-2*H*-pyran (1.5 eq.) and the reaction was stirred at 40 °C for 20 h. After cooling to room temperature the reaction mixture was concentrated under vacuum then poured into ice-water and extracted twice with DCM. The organic layers were combined and washed with water and brine before drying over $MgSO_4$, which was removed by filtration. Removal of the solvent *in vacuo* afforded the crude material which was purified by column chromatography.

1.3g. Synthesis of OEGs monosubstituted with PyrB groups:

Based on a literature procedure,[4] NaH (5 eq.) was dispersed in anhydrous THF and stirred vigorously at room temperature. A solution of **PyrBOH** (1 eq.) in THF was carefully added drop-wise to the stirred solution which was then heated to 67 °C for 1–2 h. The reaction was then allowed to cool slightly such that reflux was no longer occurring (*ca* 50-60 °C for ease of addition of the next reagent). A solution of **Ts-PEGn-THP** (1.2 eq.) in THF was then added drop-wise and the reaction then stirred at 67 °C for 18 h. The reaction was then allowed to cool to room temperature before the solvent was removed under vacuum. The residue was dissolved in

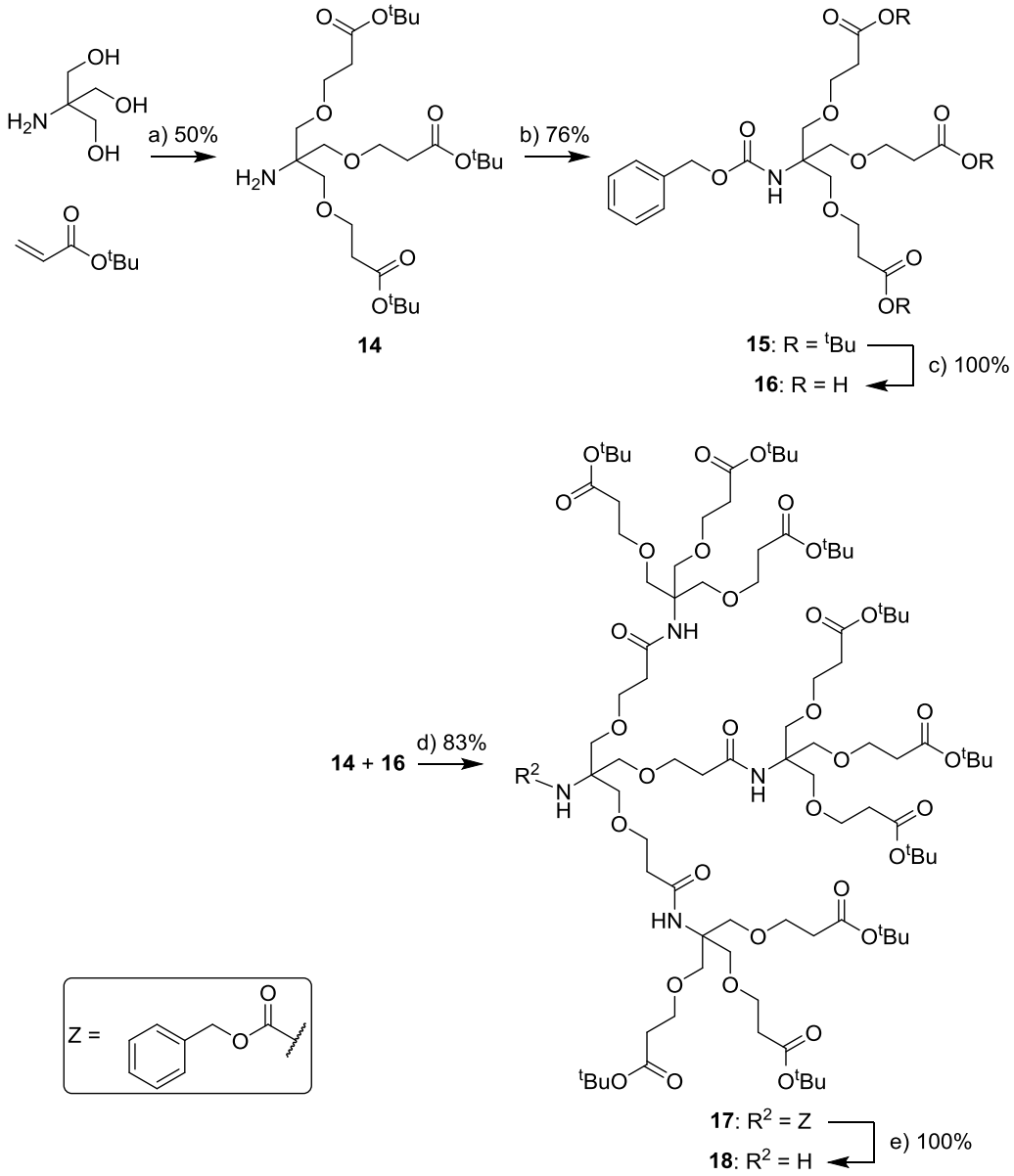
$CHCl_3$ and any insoluble materials were removed by filtration and washed thoroughly with $CHCl_3$. The combined filtrate was dried *in vacuo* then redissolved in a 10% solution of conc. HCl in THF which was stirred at room temperature for 18 h. The solution was concentrated *in vacuo* and treated with brine before extracting four times with DCM. The combined organic layers were dried over $MgSO_4$ which was then removed by filtration. Removal of the solvent *in vacuo* afforded the crude material which was purified by column chromatography.

1.3h. Addition of terminal acid:

A solution of **PyrB-PEGn** (1 eq.) in anhydrous THF was added dropwise to a vigorously stirred dispersion of NaH (13 eq.) in anhydrous THF and stirred at 40 °C for 1–2 h. Bromoacetic acid (1.2 or 1.5 eq.) was then added and the reaction was stirred at 40 °C for a further 16–20 h. The reaction was cooled to room temperature and then quenched with water. The THF was removed under vacuum. Brine was added to the aqueous solution which was extracted three times with ethyl acetate (*N.B*. the two layers separated very slowly, duration ca. 2–3 h). The aqueous layer was then acidified to pH 1 using 1 M HCl and extracted three times with ethyl acetate. These organic layers were combined and dried over Na_2SO_4 which was then removed by filtration. The solvent was removed *in vacuo* and excess bromoacetic acid removed by distillation under vacuum using a Kugelrohr (typically 120 °C, *ca.* 1 mbar for 30–45 min) to afford pure product.

1.4. Synthetic Details and Characterisation

*1.4.1: Surfactants **1-6***



Scheme S1. Reagents and Conditions: a) $NaOH_{(aq)}$, DMSO, 13 °C – RT, 96 h; b) $Na_2CO_{3(aq)}$, benzyl chloroformate, DCM, RT, 24 h; c) formic acid, RT, 18 h; d) DIPEA, TBTU, DCM, 0 °C – RT, 48 h; e) H_2, Pd/C, EtOH, RT, 21 h.

Tris(3-*tert*-butoxy-3-oxopropoxymethyl)aminomethane (14)

This compound was synthesised according to a literature procedure.[1] A solution of tris(hydroxymethyl)aminomethane (1.21 g, 10 mmol, 1 eq.) in DMSO which had been stored over molecular sieves (2.0 mL) was stirred at 13 °C using a xylene/liquid nitrogen bath. 5 M sodium hydroxide (0.2 mL, 1.0 mmol, 0.1 eq.) was added to this stirred solution. *tert*-Butyl acrylate (5.0 ml, 34 mmol, 3.4 eq.) was then added drop-wise over 10 min. The reaction was left

to stir and warm to room temperature over 96 h* before removing the solvents *in vacuo*. The crude material was purified by column chromatography (SiO_2, 2:1 EtOAc/hexane + 0.05% NH_4OH) to give **14** as a pale yellow oil (2.51 g, 50%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.63 (t, *J* = 6.5 Hz, 6H), 3.30 (s, 6H), 2.45 (t, *J* = 6.5 Hz, 6H), 1.67 (br s, 2H), 1.44 (s, 27H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 80.4, 72.9, 67.1, 55.9, 36.3, 28.1; HRMS-ES$^+$ *m/z*: [M+H]$^+$ calculated for $C_{25}H_{48}NO_9$ 506.3324; found: 506.3327.

Z-Protected Tris(3-*tert*-butoxy-3-oxopropoxymethyl)aminomethane (15)

This compound was synthesised according to a literature procedure.[1] A stirred solution of **14** (1.37 g, 2.72 mmol) in DCM (20 mL) was treated with 25% aqueous Na_2CO_3 (10 mL) at room temperature. Benzyl chloroformate (1.2 mL, 8.4 mmol) was then added drop-wise and the reaction stirred for a further 24 h, before the reaction mixture was extracted with DCM. The combined organic layers were dried over $MgSO_4$ which was then removed by filtration. Removal of the solvent *in vacuo* afforded the crude material which was purified by column chromatography (SiO_2, 2:1 hexane/EtOAc) to afford **15** as a colourless oil (1.33 g, 76%), with characterisation data in agreement with that previously reported.[1]

Z-Protected Tris(2-carboxyethoxymethyl)aminomethane (16)

This reaction was conducted based on general procedure 1.3a for deprotection of *tert*-butyl esters. The following reagents were used in the stated quantities: **15** (0.64 g, 1.0 mmol) and formic acid (10 mL). Triacid **16** was obtained as a colourless oil (0.47 g, 100 %), with characterisation data in agreement with that previously reported.[1]

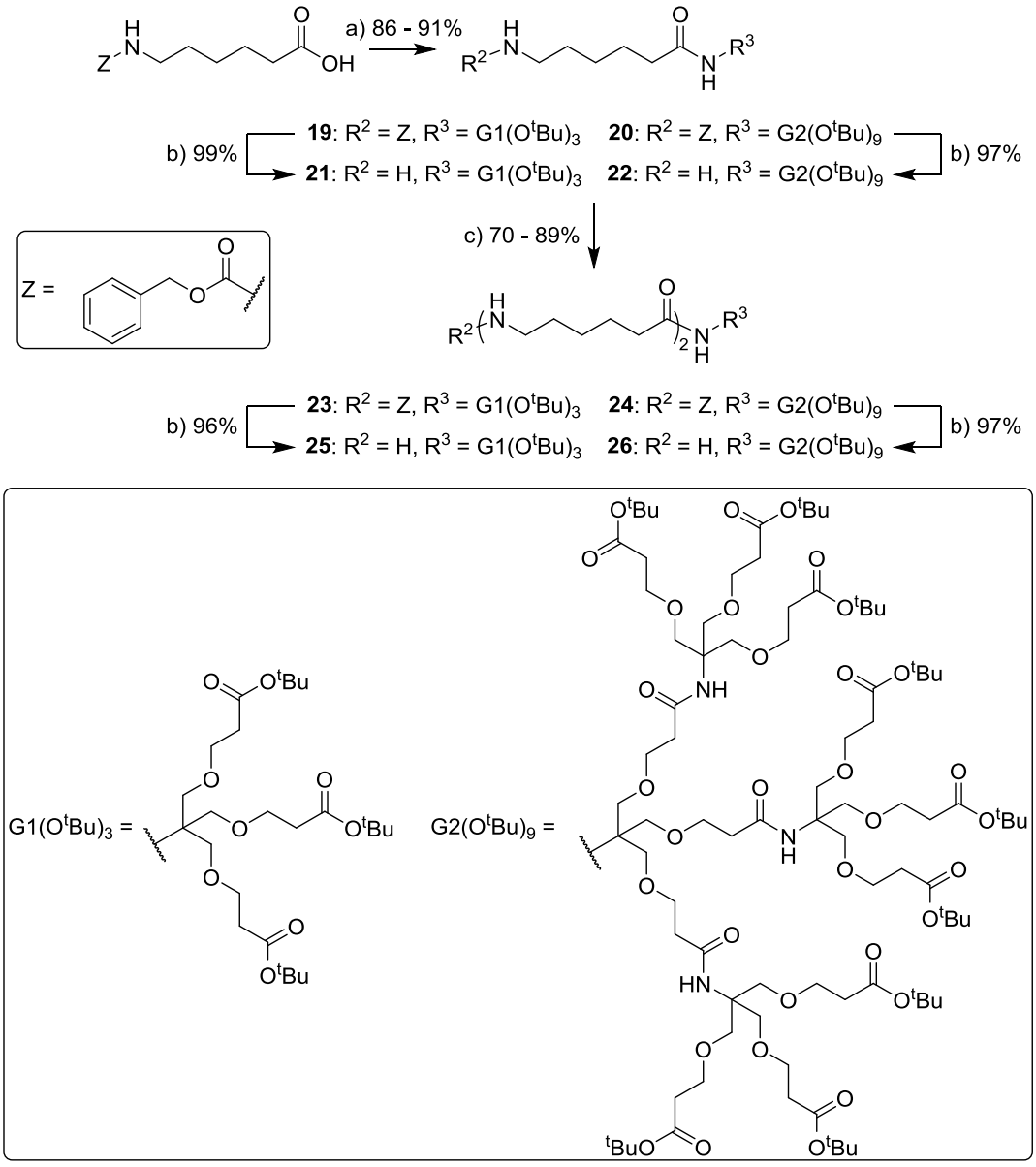
Z-Protected G2 Dendron (17)

This reaction was conducted based on general procedure 1.3b for amide coupling reactions. The following reagents were used in the stated quantities: **16** (0.43 g, 0.91 mmol, 1 eq.), DIPEA (0.57 mL, 3.29 mmol, 3.6 eq.), TBTU (1.05 g, 3.29 mmol, 3.6 eq.), **14** (1.66 g, 3.29 mmol, 3.6 eq.) and DCM (20 mL). This reaction was initially ice cooled and stirred for 48 h. Instead of washing with $NaHSO_4$ and water, in this case 1 M HCl (50 mL) and brine (50 mL) were used. The crude product was purified by column chromatography (silica, 2:1 EtOAc/hexane) to yield **17** as a clear, colourless oil (1.46 g, 83%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.36 (m, 5H), 6.28 (br s, 3H), 5.58 (br s, 1H), 5.03 (s, 2H), 3.60-3.66 (m, 48H), 2.43 (t, 18H), 2.43 (t, *J* = 6.5 Hz, 6H), 1.43 (s, 81H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 170.9, 155.2, 128.5, 128.1, 128.0, 136.9, 80.5, 69.4, 69.2, 67.6, 67.1, 66.1, 59.8, 58.9, 37.4, 36.2, 28.2; HRMS-ES$^+$ *m/z*: [M+H]$^+$ calculated for $C_{96}H_{165}N_4O_{35}$, 1934.1249; found, 1934.1289.

* A shorter reaction time of 48 h afforded a comparable yield of 48%.

G2 Dendron (18)

This reaction was conducted based on general procedure 1.3c for Z-deprotection. The following reagents were used in the stated quantities: **17** (1.4 g, 0.72 mmol), Pd/C (0.28 g, 20%) and EtOH (50 mL). The reaction was stirred for 21 h. **18** was isolated as a colourless oil (1.31 g, 100%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.21 (s, 3H), 3.64 (s, 24H), 3.59 (t, *J* = 6.3 Hz, 24H), 2.40 (t, *J* = 6.4 Hz, 24H), 1.40 (s, 81H)*; ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 170.9, 80.5, 73.0, 69.2, 67.6, 67.1, 59.9, 56.0, 37.6, 36.2, 28.2; HRMS-ES^{+} *m/z*: $[M+2H]^{2+}$ calculated for $C_{88}H_{160}N_4O_{33}$, 900.5482; found, 900.5493.



* The two protons associated with the terminal amino group are not visible.

Scheme S2. Reagents and Conditions: a) DIPEA, TBTU, DCM, 0 °C, 15 min, ii. **14** *or* **18**, 0 °C – RT, 60 h; b) H_2, Pd/C, EtOH, RT, 19 – 23 h; c) Z-6-aminohexanoic acid, DIPEA, TBTU, DCM, 0 °C – RT, 96 – 144 h.

Z-C6-G1(O^tBu)$_3$ (19)

This reaction was conducted based on general procedure 1.3b for amide coupling reactions. The following reagents were used in the stated quantities: Z-6-aminohexanoic acid (265 mg, 1 mmol, 1 eq.), DIPEA (0.35 mL, 2 mmol, 2 eq.), TBTU (321 mg, 1.00 mmol, 1 eq.), **14** (505 mg, 1.00 mmol, 1 eq.) and DCM (10 mL). This reaction was initially ice cooled, then stirred for 17 h. The crude product was purified using column chromatography (silica, DCM – 98:2 DCM/MeOH – 95:5 DCM/MeOH) to yield **19** as a pale yellow oil (680 mg, 91%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.28 (m, 5H); 6.04 (bs, 1H), 5.07 (s, 2H), 5.00 (bs, 1H), 3.68 (s, 6H), 3.61 (t, *J* = 6.4 Hz, 6H), 3.17 (q, *J* = 6.4 Hz, 2H), 2.41 (t, *J* = 6.4 Hz, 6H), 2.13 (t, *J* = 7.2 Hz, 2H), 1.63-1.24 (m*, 33H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 171.0, 156.5, 136.9, 128.5, 128.11, 128.06, 80.5, 69.3, 67.1, 66.6, 59.8, 41.0, 37.0, 36.3, 29.7, 28.2, 26.3, 25.2; HRMS-ES$^+$ *m/z*: $[M+Na]^+$ calculated for $C_{39}H_{64}N_2O_{12}Na$ 775.4357; found: 775.4359.

Z-C6-G2(O^tBu)$_9$ (20)

This reaction was conducted based on general procedure 1.3b for amide coupling reactions. The following reagents were used in the stated quantities: Z-6-aminohexanoic acid (59 mg, 0.22 mmol, 1 eq.), DIPEA (0.08 mL, 0.44 mmol, 2 eq.), TBTU (71 mg, 0.22 mmol, 1 eq.), **18** (0.40 g, 0.22 mmol, 1 eq.) and DCM (5 mL). In this case, the reagents were mixed at room temperature before immediately refluxing the reaction for 21 h then stirring at room temperature for a further 24 h. The crude product was purified using column chromatography (silica, DCM – 98:2 DCM/MeOH – 95:5 DCM/MeOH) to yield **20** as a clear colourless oil (0.39 g, 86%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.26 (m, 5H), 6.48 (s, 1H), 6.16 (s, 3H), 5.37 (t, *J* = 5.5 Hz, 1H), 5.05 (s, 2H), 3.66 (s, 24H), 3.64 – 3.54 (m, 24H), 3.16 (q, *J* = 6.7 Hz, 2H), 2.48 – 2.31 (m, 24H), 2.18 (t, *J* = 7.3 Hz, 2H), 1.64 – 1.29 (m†, 87H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3, 171.1, 171.0, 156.6, 136.9, 128.5, 128.2, 128.0, 80.6, 69.2, 67.6, 67.1, 66.5, 59.9, 59.8, 41.0, 37.3, 36.8, 36.2, 29.7, 28.2, 26.4, 25.4; HRMS-ES$^+$ *m/z*: $[M+2H]^{2+}$ calculated for $C_{102}H_{177}N_5O_{36}$, 1024.10811; found, 1024.11086.

C6-G1(O^tBu)$_3$ (21)

This reaction was conducted based on general procedure 1.3c for Z-deprotection. The following reagents were used in the stated quantities: **19** (0.64 g, 0.85 mmol), Pd/C (0.13 g, 20%) and EtOH (20 mL). The reaction was stirred for 19 h. **21** was isolated as a colourless oil (0.52 g,

* Including a distinguishable singlet at δ = 1.43 ppm
† Including a distinguishable singlet at δ = 1.42 ppm

99%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.00 (br s, 1H), 3.64 (s, 6H), 3.58 (t, *J* = 6.4 Hz, 6H), 2.62 (t, *J* = 6.8 Hz, 2H), 2.38 (t, *J* = 6.4 Hz, 6H), 2.09 (t, *J* = 7.6 Hz, 2H), 1.59-1.49 (m, 4H), 1.38 (s, 27H), 1.30-1.25 (m, 2H) [*]; ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 170.9, 80.4, 69.3, 67.1, 59.7, 42.1, 37.2, 36.2, 33.5, 28.2, 26.4, 25.5; HRMS-ES$^+$ *m/z*: $[M+H]^+$ calculated for $C_{31}H_{59}N_2O_{10}$, 619.4170; found, 619.4189.

C6-G2(O^{t}Bu)$_9$ (22)

This reaction was conducted based on general procedure 1.3c for Z-deprotection. The following reagents were used in the stated quantities: **20** (374 mg, 0.18 mmol), Pd/C (75 mg, 20%) and EtOH (20 mL). The reaction was stirred for 23 h. **22** was isolated as a clear, colourless oil (335 mg, 97%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.52 (s, 1H), 6.22 (s, 3H), 3.64 (s, 24H), 3.63 – 3.55 (m, 24H), 2.81 (t, *J* = 6.8 Hz, 2H), 2.48 – 2.33 (m, 24H), 2.19 (t, *J* = 7.0 Hz, 2H), 1.65 – 1.33 (m[†], 87H)[‡]; ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.4, 171.1, 170.9, 80.5, 69.3, 67.6, 67.1, 59.93, 59.87, 41.1, 37.3, 36.4, 36.2, 30.6, 28.2, 25.7, 24.7; MS-ES$^+$ *m/z*: 957 $[M+2H]^{2+}$.

Z-(C6)$_2$-G1(O^{t}Bu)$_3$ (23)

This reaction was conducted based on general procedure 1.3b for amide coupling reactions. The following reagents were used in the stated quantities: Z-6-aminohexanoic acid (1.11 g, 4.2 mmol, 1 eq.), DIPEA (1.46 mL, 8.4 mmol, 2 eq.), TBTU (1.35 g, 4.2 mmol, 1 eq.), **21** (2.6 g, 4.2 mmol, 1 eq.) and DCM (28 mL). This reaction was initially ice cooled then stirred for 96 h. The crude product was purified using column chromatography (silica, DCM – 98:2 DCM/MeOH – 95:5 DCM/MeOH) to yield **23** as clear, colourless oil (3.24 g, 89%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.21 (m, 5H), 6.12 (t, *J* = 4.6 Hz, 1H), 6.03 (s, 1H), 5.22 (t, *J* = 4.1 Hz, 1H), 5.02 (s, 2H), 3.64 (s, 6H), 3.58 (t, *J* = 6.3 Hz, 6H), 3.18 – 3.09 (m, 4H), 2.38 (t, *J* = 6.2 Hz, 6H), 2.09 (t, *J* = 7.3 Hz, 4H), 1.62 – 1.50 (m, 4H), 1.49 – 1.42 (m, 4H), 1.39 (s, 27H), 1.31 – 1.23 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 172.7, 170.9, 156.4, 136.8, 128.4, 127.90, 127.89, 80.4, 69.2, 67.0, 66.3, 59.6, 40.8, 39.1, 36.7, 36.4, 36.1, 29.6, 29.1, 28.1, 26.28, 26.27, 25.2, 25.0; HRMS-ES$^+$ *m/z*: $[M+H]^+$ calculated for $C_{45}H_{76}N_3O_{13}$, 866.5378; found, 866.5375.

Z-(C6)$_2$-G2(O^{t}Bu)$_9$ (24)

This reaction was conducted based on general procedure 1.3b for amide coupling reactions. The following reagents were used in the stated quantities: Z-6-aminohexanoic acid (22 mg, 84 μmol, 1 eq.), DIPEA (30 μl, 167 μmol, 2 eq.), TBTU (32 mg, 100 μmol, 1.2 eq.), **22** (0.16 g, 84 μmol, 1

[*] The two protons associated with the terminal amino group are not visible.
[†] Including a distinguishable singlet at δ = 1.40 ppm.
[‡] The two protons associated with the terminal amino group are not visible.

eq.) and DCM (5 mL). This reaction was initially ice cooled then stirred for 144 h. The crude product was purified using column chromatography (silica, DCM – 98:2 DCM/MeOH – 95:5 DCM/MeOH) to yield **24** as a clear colourless oil (0.126 g, 70%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.22 (m, 5H), 6.42 (s, 1H), 6.27 (dd, *J* = 5.9, 5.1 Hz, 1H), 6.14 (s, 3H), 5.10 (dd, *J* = 5.6, 5.0 Hz, 1H), 5.04 (s, 2H), 3.64 (s, 24H), 3.63 – 3.52 (m, 24H), 3.23 – 3.09 (m, 4H), 2.40 (t, *J* = 6.4 Hz, 24H), 2.20 – 2.06 (m, 4H), 1.65 – 1.25 (m*, 97H†); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3, 172.8, 171.0, 170.9, 156.5, 136.9, 128.5, 128.1, 128.0, 80.5, 69.3, 67.6, 67.2, 66.5, 59.91, 59.86, 41.0, 39.3, 37.3, 36.7, 36.5, 36.3, 29.8, 29.3, 28.2, 26.51, 26.47, 25.4, 25.2; HRMS-ES$^+$ *m/z*: $[M+2Na]^{2+}$ calculated for $C_{108}H_{186}N_6Na_2O_{37}$, 1102.63209; found, 1102.63224.

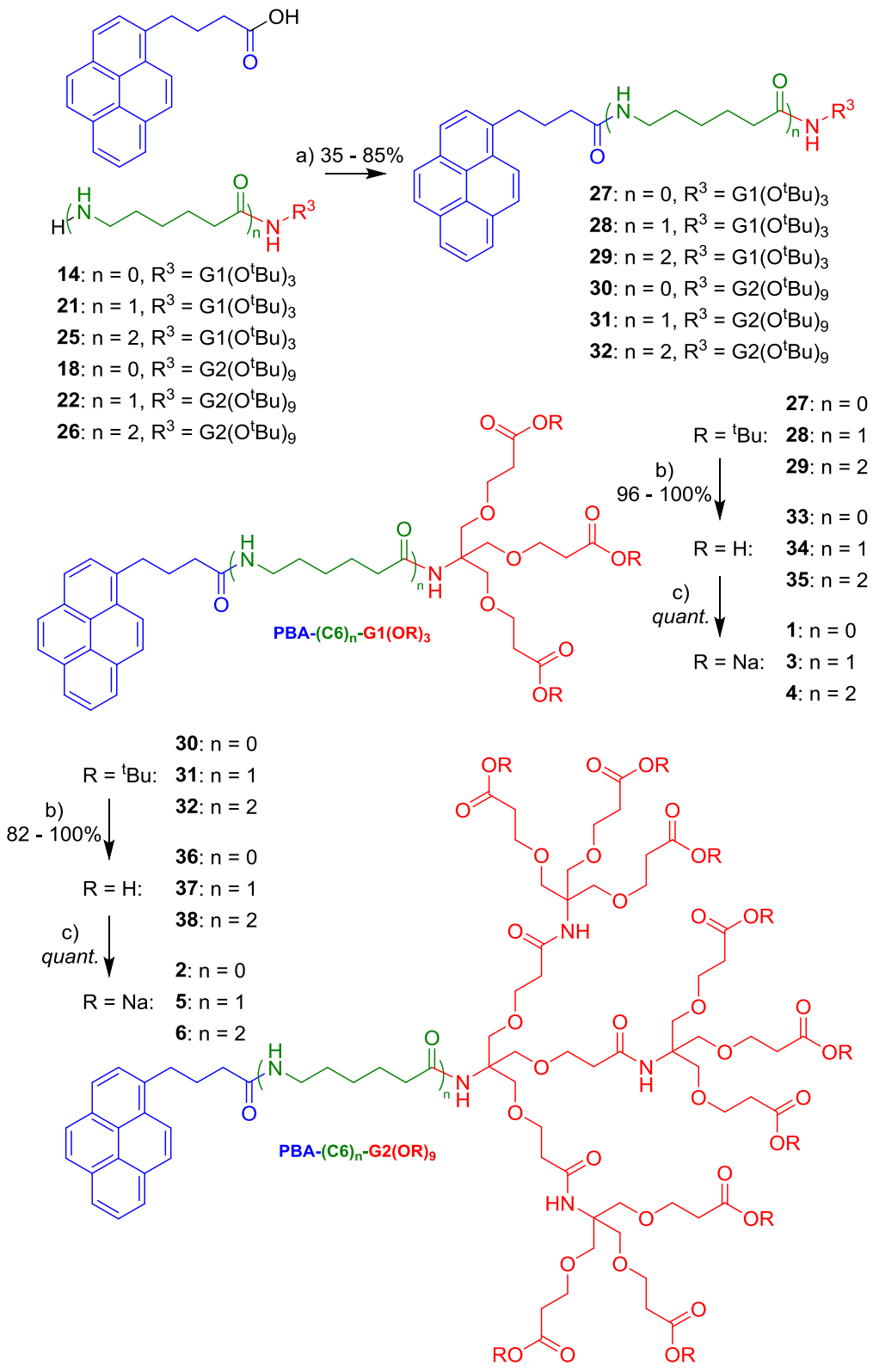
$(C6)_2$-G1$(O^tBu)_3$ (25)

This reaction was conducted based on general procedure 1.3c for Z-deprotection. The following reagents were used in the stated quantities: **23** (0.186 g, 0.21 mmol), Pd/C (37 mg, 20%) and EtOH (10 mL). The reaction was stirred for 21 h. **25** was isolated as a colourless oil (0.15 g, 96%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.14 (t, *J* = 5.5 Hz, 1H), 6.08 (s, 1H), 3.65 (s, 6H), 3.60 (t, *J* = 6.3 Hz, 6H), 3.37 (s, 2H), 3.19 (q, *J* = 6.8 Hz, 2H), 2.71 (t, *J* = 7.1 Hz, 2H), 2.40 (t, *J* = 6.2 Hz, 6H), 2.13 (q, *J* = 7.6 Hz, 4H), 1.66 – 1.53 (m, 4H), 1.53 – 1.44 (m, 4H), 1.41 (s, 27H), 1.35 – 1.26 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 172.9, 171.0, 80.5, 69.2, 67.0, 59.6, 41.8, 39.1, 36.8, 36.6, 36.2, 29.8, 29.2, 28.1, 26.6, 26.3, 25.6, 25.1; HRMS-ES$^+$ *m/z*: $[M+H]^+$ calculated for $C_{37}H_{70}N_3O_{11}$ 732.50049; found, 732.50073.

$(C6)_2$-G2$(O^tBu)_9$ (26)

This reaction was conducted based on general procedure 1.3c for Z-deprotection. The following reagents were used in the stated quantities: **24** (114 mg, 53 μmol), Pd/C (23 mg, 20%) and EtOH (5 mL). The reaction was stirred for 21 h. **26** was isolated as a clear, colourless oil (104 mg, 97%), ^{1}H NMR (400 MHz, CD_3OD) δ 3.74 – 3.68 (m, 24H), 3.68 – 3.60 (m, 24H), 3.17 (t, *J* = 7.2 Hz, 2H), 2.89 – 2.75 (m, 2H), 2.518 – 2.39 (m, 24H), 2.28 – 2.15 (m, 4H), 1.66 – 1.59 (m, 8H), 1.47 (s, 81H), 1.42 – 1.35 (m, 4H)‡; ^{13}C NMR (100 MHz, CD_3OD) δ 176.0, 175.7, 173.6, 172.7, 81.7, 70.23, 70.19, 68.9, 68.4, 61.49, 61.48, 41.5, 40.4, 38.2, 37.7, 37.3, 36.9, 30.7, 30.3, 28.6, 27.8, 27.3, 26.8, 26.6; HRMS-ES$^+$ *m/z*: $[M+H+Na]^{2+}$ calculated for $C_{100}H_{181}N_6NaO_{35}$ 1024.62273; found, 1024.62776.

* Including a distinguishable singlet at δ = 1.40 ppm.
† The expected integral for this peak is 93H, we attribute this discrepancy to the large size of the peak.
‡ Two protons associated with the terminal amino group and five protons associated with amide NH groups are not visible.



Scheme S3. Reagents and Conditions: a) DIPEA, TBTU, DCM, 0 °C – RT, or 0 °C – reflux, 1 – 7 days; b) formic acid, RT, 18 h; c) $NaOH_{(aq)}$, MeOH, RT, 30 min.

PBA-G1(O^tBu)$_3$ (27)

This reaction was conducted based on general procedure 1.3b for amide coupling reactions. The following reagents were used in the stated quantities: 1-pyrene butyric acid (0.57 g, 1.98 mmol 1 eq.), DIPEA (0.69 mL, 3.96 mmol, 2 eq.), TBTU (0.64 g, 1.98 mmol, 1 eq.), **14** (1.00 g, 1.98 mmol, 1 eq.) and DCM (45 mL). This reaction was initially ice cooled then stirred for 25 h. he crude product was purified using column chromatography (silica, 98:2 DCM/MeOH – 95:5 DCM/MeOH) to afford a beige oil, which consisted of **27** and residual tetramethyl urea (a by-product of the coupling reaction). The oil was dissolved in DCM (50 mL) and washed with water (3 × 150 mL). The organic phase was dried over $MgSO_4$, filtered and the solvent removed to afford **27** as a beige oil (1.28 g, 84%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 9.3 Hz, 1H), 8.18 – 8.04 (m, 4H), 8.03 – 7.91 (m, 3H), 7.87 (d, *J* = 7.8 Hz, 1H), 6.15 (s, 1H), 3.77 (s, 6H), 3.67 (t, *J* = 6.3 Hz, 6H), 3.43 – 3.32 (m, 2H), 2.45 (t, *J* = 6.3 Hz, 6H), 2.31 (t, *J* = 7.1 Hz, 2H), 2.25 – 2.13 (m, 2H), 1.40 (s, 27H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 170.9, 136.2, 131.4, 130.9, 129.8, 128.7, 127.5, 127.4, 127.2, 126.5, 125.7, 125.04, 124.97, 124.77, 124.75, 124.7, 123.5, 80.4, 69.2, 67.1, 59.7, 36.6, 36.2, 32.7, 28.1, 27.5; HRMS-ES$^+$ *m/z*: $[M+Na]^+$ calculated for $C_{45}H_{61}NO_{10}Na$, 798.4193; found, 798.4202.

PBA-C6-G1(O^tBu)$_3$ (28)

This reaction was conducted based on general procedure 1.3b for amide coupling reactions. The following reagents were used in the stated quantities: 1-pyrene butyric acid (0.47 g, 1.62 mmol, 1 eq.), DIPEA (0.56 mL, 3.23 mmol, 2 eq.), TBTU (0.52 g, 1.62 mmol, 1 eq.), **21** (1.00 g, 1.62 mmol, 1 eq.) and DCM (30 mL). This reaction was initially ice cooled then stirred for 96 h. The crude product was purified using column chromatography (silica, DCM – 98:2 DCM/MeOH – 95:5 DCM/MeOH – 9:1 DCM/MeOH) to afford **28** as a beige oil (1.21 g, 84%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 9.2 Hz, 1H), 8.18 – 8.12 (m, 2H), 8.12 – 8.06 (m, 2H), 8.04 – 7.94 (m, 3H), 7.85 (d, *J* = 7.8 Hz, 1H), 6.03 (s, 1H), 5.75 (t, *J* = 5.7 Hz, 1H), 3.68 (s, 6H), 3.61 (t, *J* = 6.3 Hz, 6H), 3.38 (t, *J* = 7.3 Hz, 2H), 3.29 – 3.18 (m, 2H), 2.41 (t, *J* = 6.3 Hz, 6H), 2.30 – 2.16 (m, 4H), 2.13 (t, *J* = 7.3 Hz, 2H), 1.63 – 1.24 (m*, 33H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 172.6, 171.0, 136.1, 131.5, 131.1, 130.0, 128.9, 127.6, 127.5, 126.8, 125.9, 125.2, 125.1, 125.0, 124.89, 124.86, 123.6, 80.6, 69.4, 67.2, 59.8, 39.4, 36.9, 36.3, 36.2, 33.0, 29.3, 28.2, 27.6, 26.5, 25.2; HRMS-ES$^+$ *m/z*: $[M+H]^+$ calculated for $C_{51}H_{73}N_2O_{11}$, 889.5214; found, 889.5248.

PBA-$(C6)_2$-G1(O^tBu)$_3$ (29)

This reaction was conducted based on general procedure 1.3b for amide coupling reactions. The following reagents were used in the stated quantities: 1-pyrene butyric acid (0.95 g, 3.28 mmol,

* Including a distinguishable singlet at δ = 1.42 ppm

1 eq.), DIPEA (1.14 mL, 6.56 mmol, 2 eq.), TBTU (1.05 g, 3.28 mmol, 1 eq.), **25** (2.4 g, 3.28 mmol, 1 eq.) and DCM (50 mL). This reaction was initially ice cooled then stirred for 23 h. 1 M NaOH was used in place of $NaHCO_3$ in the work up. The crude product was purified using column chromatography (silica, DCM – 98:2 DCM/MeOH – 95:5 DCM/MeOH) to afford **29** as a beige oil (2.8 g, 85%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 9.3 Hz, 1H), 8.18 – 8.10 (m, 2H), 8.10 – 8.04 (m, 2H), 8.02 – 7.91 (m, 3H), 7.83 (d, *J* = 7.8 Hz, 1H), 6.03 (s, 1H), 5.88 – 5.82 (m, 1.5H*), 3.68 (s, 6H), 3.62 (t, *J* = 6.3 Hz, 6H), 3.35 (t, *J* = 6.8 Hz, 2H), 3.25 – 3.10 (m, 4H), 2.42 (t, *J* = 6.3 Hz, 6H), 2.27 – 2.05 (m, 8H), 1.64 – 1.52 (m, 6H), 1.42 (s, 27H), 1.33 – 1.22 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 172.8, 172.7, 171.0, 136.1, 131.5, 131.0, 130.0, 128.9, 127.6, 127.41, 127.40, 126.7, 125.9, 125.2, 125.1, 124.94, 124.86, 124.8, 123.5, 80.6, 69.3, 67.2, 59.8, 39.28, 39.26, 36.9, 36.4, 36.3, 36.2, 32.9, 29.3, 29.2, 28.2, 27.6, 26.5, 26.4, 25.2, 25.1; HRMS-ES$^+$ *m/z*: $[M+H]^+$ calculated for $C_{57}H_{84}N_3O_{12}$, 1002.60495; found, 1002.60500.

PBA-G2(O^{t}Bu)$_9$ (30)

This reaction was conducted based on general procedure 1.3b for amide coupling reactions. The following reagents were used in the stated quantities: 1-pyrene butyric acid (32 mg, 0.11 mmol, 1 eq.), DIPEA (0.04 mL, 0.22 mmol, 2 eq.), TBTU (36 mg, 0.11 mmol, 1 eq.), **18** (0.2 g, 0.11 mmol, 1 eq.) and DCM (5 mL). This reaction was initially ice cooled and then refluxed for 16 h. The crude product was purified using column chromatography (silica, DCM – 98:2 DCM/MeOH – 95:5 DCM/MeOH) to afford **30** as a beige oil (0.18 g, 78%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 9.3 Hz, 1H), 8.15 – 8.05 (m, 4H), 8.01 – 7.91 (m, 3H), 7.88 (d, *J* = 7.8 Hz, 1H), 6.56 (s, 1H), 6.14 (s, 3H), 3.73 (s, 6H), 3.70 – 3.61 (m, 24H), 3.57 (t, *J* = 6.4 Hz, 18H), 3.36 (t, *J* = 7.6 Hz, 2H), 2.45 – 2.31 (m, 26H), 2.22 – 2.09 (m, 2H), 1.39 (s, 81H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 171.0, 170.9, 136.5, 131.4, 131.0, 129.8, 128.8, 127.54, 127.49, 127.3, 126.6, 125.8, 125.1, 125.0, 124.9, 124.8, 124.7, 123.7, 80.4, 69.21, 69.16, 67.6, 67.1, 59.9, 59.8, 37.2, 36.6, 36.2, 32.9, 28.1, 27.7; HRMS-ES$^+$ *m/z*: $[M+2H]^{2+}$ calculated for $C_{108}H_{174}N_4O_{34}$, 1035.59993; found, 1035.60010.

PBA-C6-G2(O^{t}Bu)$_9$ (31)

This reaction was conducted based on general procedure 1.3b for amide coupling reactions. The following reagents were used in the stated quantities: 1-pyrene butyric acid (24 mg, 84 μmol, 1 eq.), DIPEA (30 μl, 167 μmol, 2 eq.), TBTU (32 mg, 100 μmol, 1.2 eq.), **22** (0.16 g, 84 μmol, 1 eq.) and DCM (5 mL). This reaction was initially ice cooled then stirred for 6 days. The crude product was purified using column chromatography (silica, DCM – 98:2 DCM/MeOH – 95:5 DCM/MeOH) to afford **31** as a beige oil (0.139 g, 76%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 9.3 Hz, 1H), 8.19 – 8.13 (m, 2H), 8.12 – 8.07 (m, 2H), 8.04 – 7.95 (m, 3H), 7.87 (d, *J* = 7.8 Hz, 1H), 6.44 (s, 1H),

* The expected integral for this peak is 2H.

6.25 – 6.11 (m, 3H*), 3.67 (s, 24H), 3.66 – 3.51 (m, 24H), 3.39 (t, *J* = 7.4 Hz, 2H), 3.29 – 3.22 (m, 2H), 2.59 – 2.34 (m, 24H), 2.31 (t, *J* = 6.7 Hz, 2H), 2.25 – 2.15 (m, 4H), 1.66 – 1.35 (m†, 87H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.3, 172.7, 171.0, 170.9, 136.3, 131.5, 131.0, 130.0, 128.9, 127.6, 127.44, 127.40, 126.7, 125.9, 125.2, 125.1, 124.88, 124.86, 124.8, 123.6, 80.5, 69.29, 69.27, 67.6, 67.2, 59.92, 59.86, 39.5, 37.3, 36.8, 36.3, 36.1, 33.0, 29.4, 28.2, 27.7, 26.6, 25.3; HRMS-ES$^+$ *m/z*: $[M+2H]^{2+}$ calculated for $C_{114}H_{185}N_5O_{35}$, 1092.14196; found, 1092.14197.

PBA-(C6)$_2$-G2(O^{t}Bu)$_9$ (32)

This reaction was conducted based on general procedure 1.3b for amide coupling reactions. The following reagents were used in the stated quantities: 1-pyrene butyric acid (15 mg, 52 μmol, 1 eq.), DIPEA (17 μl, 99 μmol, 2 eq.), TBTU (20 mg, 62 μmol, 1.2 eq.), **26** (100 mg, 49 μmol, 1 eq.) and DCM (2.5 mL). This reaction was stirred for 7 days at room temperature. The crude product was purified using column chromatography (silica, 2:1 EtOAc/hexane – EtOAc – 99:1 EtOAc/MeOH – 90:10 EtOAc/MeOH (gradient increase)) to afford **32** as a beige oil (40 mg, 35%), ^{1}H NMR (600 MHz, CD_3OD) δ 8.32 (d, *J* = 9.2 Hz, 1H), 8.16 (t, *J* = 7.3 Hz, 2H), 8.14 – 8.08 (m, 2H), 8.06 – 8.00 (m, 2H), 7.98 (t, *J* = 7.6 Hz, 1H), 7.88 (d, *J* = 7.7 Hz, 1H), 7.20 (bs, 1H), 7.05 (bs, 2H‡), 3.88 – 3.66 (m, 24H), 3.66 – 3.47 (m, 24H), 3.36 (t, *J* = 7.5 Hz, 2H), 3.18 (t, *J* = 7.2 Hz, 2H), 3.11 (t, *J* = 7.0 Hz, 2H), 2.44 (t, *J* = 6.0 Hz, 24H), 2.34 (t, *J* = 7.2 Hz, 2H), 2.19 (t, *J* = 7.5 Hz, 2H), 2.17 – 2.10 (m, 4H), 1.64 – 1.39 (m§, 87H), 1.37 – 1.28 (m, 6H); ^{13}C NMR (151 MHz, CD_3OD) δ 174.0, 173.6, 171.6, 170.7, 135.3, 130.8, 130.3, 129.3, 127.9, 126.54, 126.47, 126.4, 125.7, 125.0, 124.2, 124.1, 124.0, 123.9, 123.8, 122.4, 79.7, 68.12, 66.8, 66.3, 59.44, 59.35, 38.29, 38.25, 36.13, 36.08, 35.2, 35.0, 34.9, 31.9, 28.2, 28.1, 27.1, 26.6, 25.7, 25.6, 24.67; HRMS-ES$^+$ *m/z*: $[M+2Na]^{2+}$ calculated for $C_{120}H_{194}N_6Na_2O_{36}$, 1171.16759; found, 1171.16808.

PBA-G1(OH)$_3$ (33)

This reaction was conducted based on general procedure 1.3a for deprotection of *tert*-butyl esters. The following reagents were used in the stated quantities: **27** (0.243 g, 0.31 mmol) and formic acid (5 mL). Triacid **33** was obtained as a tacky beige solid (0.182 g, 96%), ^{1}H NMR (400 MHz, Acetone-d_6) δ 8.34 (d, *J* = 9.3 Hz, 1H), 8.17 – 8.07 (m, 4H), 8.05 – 7.91 (m, 3H), 7.88 (d, *J* = 7.8 Hz, 1H), 6.57 (s, 1H), 3.76 (s, 6H), 3.68 (t, *J* = 6.3 Hz, 6H), 3.38 – 3.29 (m, 3H**), 2.52 (t, *J* = 6.2

* The expected integral for this peak is 4H.
† Including a distinguishable singlet at δ = 1.43 ppm
‡ The expected integral for this peak is 5H.
§ Including a distinguishable singlet at δ = 1.45 ppm
** The expected integral of this peak is 2. A triplet (*J* = 7.6 Hz) is overlapped by a singlet associated with residual CD_3OH, hence the discrepancy in the integral.

Hz, 6H), 2.31 (t, *J* = 7.0 Hz, 2H), 2.16 – 2.06 (m, 2H) *;^{13}C NMR (100 MHz, Acetone-d_6) δ 172.3, 171.9, 135.8, 130.5, 130.1, 128.9, 127.8, 126.72, 126.65, 126.3, 125.6, 125.0, 124.1, 124.03, 123.99, 123.9, 123.8, 122.8, 68.2, 66.0, 59.1, 35.3, 33.6, 31.6, 26.9; HRMS-ES$^+$ *m/z*: $[M+H]^+$ calculated for $C_{33}H_{38}NO_{10}$, 608.2496; found, 608.2493.

PBA-C6-G1(OH)$_3$ (34)

This reaction was conducted based on general procedure 1.3a for deprotection of *tert*-butyl esters. The following reagents were used in the stated quantities: **28** (0.28 g, 0.32 mmol) and formic acid (5 mL). Triacid **34** was obtained as a tacky beige solid (0.227 g, 100%), ^{1}H NMR (400 MHz, CD_3OD) δ 8.21 (d, *J* = 9.3 Hz, 1H), 8.13 – 8.06 (m, 2H), 8.02 (d, *J* = 8.3 Hz, 2H), 7.97 – 7.88 (m, 3H), 7.78 (d, *J* = 7.8 Hz, 1H), 3.63 (s, 6H), 3.61 (t, *J* = 6.1 Hz, 6H), 3.27 (t, *J* = 8.0 Hz, 2H), 3.14 (t, *J* = 7.0 Hz, 2H), 2.47 (t, *J* = 6.1 Hz, 6H), 2.29 (t, *J* = 7.4 Hz, 2H), 2.17 – 2.03 (m, 4H), 1.60 – 1.50 (m, 2H), 1.50 – 1.42 (m, 2H), 1.35 – 1.24 (m, 2H) †; ^{13}C NMR (100 MHz, CD_3OD) δ 176.1, 175.7, 175.4, 137.2, 132.7, 132.2, 131.2, 129.8, 128.44, 128.35, 128.3, 127.6, 126.9, 126.1, 126.0, 125.8, 125.7, 124.3, 70.0, 68.0, 61.3, 40.3, 37.5, 36.8, 35.7, 33.7, 30.0, 27.3, 26.5, 29.0; HRMS-ES$^+$ *m/z*: $[M+H]^+$ calculated for $C_{39}H_{49}N_2O_{11}$, 721.33309; found, 721.33383.

PBA-(C6)$_2$-G1(OH)$_3$ (35)

This reaction was conducted based on general procedure 1.3a for deprotection of *tert*-butyl esters. The following reagents were used in the stated quantities: **29** (60 mg, 60 μmol) and formic acid (2 mL). Triacid **35** was obtained as a tacky beige solid (50 mg, 100%), ^{1}H NMR (400 MHz, CD_3OD) δ 8.25 (d, *J* = 9.3 Hz, 1H), 8.15 – 8.09 (m, 2H), 8.06 (d, *J* = 8.2 Hz, 2H), 8.00 – 7.91 (m, 3H), 7.82 (d, *J* = 7.8 Hz, 1H), 3.66 (s, 6H), 3.63 (t, *J* = 6.1 Hz, 6H), 3.30 – 3.26 (m, 1H‡), 3.15 (t, = 7.0 Hz, 2H), 3.07 (t, *J* = 7.1 Hz, 2H), 2.49 (t, *J* = 6.1 Hz, 6H), 2.31 (t, *J* = 7.3 Hz, 2H), 2.20 – 2.03 (m, 6H), 1.62 – 1.19 (m, 15H§)**; ^{13}C NMR (100 MHz, CD_3OD + Acetone-d_6) δ 175.8, 175.6, 175.3, 174.9, 137.5, 132.7, 132.2, 131.2, 129.8, 128.6, 128.5, 128.4, 127.7, 127.1, 126.1, 126.0, 125.9, 124.5, 69.9, 68.0, 61.2, 40.13, 40.09, 37.5, 36.9, 36.8, 35.7, 33.8, 30.1, 30.0, 29.1, 27.5, 27.3, 26.6, 26.5; HRMS-ES$^+$ *m/z*: $[M+H]^+$ calculated for $C_{45}H_{60}N_3O_{12}$, 834.4177; found, 834.4180.

---

* Three protons associated with the carboxylic acid groups are not visible.

† Two protons associated with the amide NH groups and three protons associated with carboxylic acid groups are not visible.

‡ The expected integral of this peak is 2; however, the peak is partially overlapped by the solvent signal and cannot be fully resolved.

§ If this peak corresponds to only aliphatic protons, its expected integral is 12. However, the larger integral may relate to some of the labile protons not visible elsewhere, or to slight contamination by grease.

** Three protons associated with the amide NH groups and three protons associated with carboxylic acid groups are not visible – the former may lie within the multiplet at 1.62 – 1.19 ppm, but this is a significant difference to the visible NH proton signal at 6.57 ppm in compound **33**.

PBA-G2(OH)$_9$ (36)

This reaction was conducted based on general procedure 1.3a for deprotection of *tert*-butyl esters. The following reagents were used in the stated quantities: **30** (0.17 g, 82 μmol) and formic acid (5 mL). Nonaacid **36** was obtained as a tacky beige solid (0.105 g, 82%), ^{1}H NMR (400 MHz, CD_3OD) δ 8.35 (d, *J* = 9.3 Hz, 1H), 8.22 – 8.09 (m, 4H), 8.06 – 7.94 (m, 3H), 7.91 (d, *J* = 7.7 Hz, 1H), 3.83 – 3.49 (m, 48H), 3.39 (t, *J* = 7.2 Hz, 2H), 2.66 – 2.34 (m, 26H), 2.24 – 2.09 (m, 2H)*; ^{13}C NMR (100 MHz, Acetone-d_6) δ 175.2, 173.7, 173.0, 137.6, 132.3, 131.9, 130.8, 129.6, 128.5, 128.4, 128.2, 127.4, 126.8, 125.9, 125.8, 125.72, 125.68, 125.67, 124.6, 69.8, 68.4, 67.8, 61.2, 61.1, 37.8, 37.1, 35.3, 33.5, 28.8; HRMS-ES$^+$ *m/z*: [M−H]$^-$ calculated for $C_{72}H_{99}N_4O_{34}$, 1563.61462; found, 1563.61237.

PBA-C6-G2(OH)$_9$ (37)

This reaction was conducted based on general procedure 1.3a for deprotection of *tert*-butyl esters. The following reagents were used in the stated quantities: **31** (0.125 g, 57 μmol) and formic acid (5 mL). Nonaacid **37** was obtained as a tacky beige solid (0.10 g, 100%), ^{1}H NMR (400 MHz, CD_3OD) δ 8.31 (d, *J* = 9.3 Hz, 1H), 8.16 (t, *J* = 6.6 Hz, 2H), 8.13 – 8.08 (m, 2H), 8.05 – 7.94 (m, 3H), 7.87 (d, *J* = 7.8 Hz, 1H), 3.78 – 3.45 (m, 48H), 3.35 (t, *J* = 7.7 Hz, 2H), 3.19 (t, *J* = 6.9 Hz, 2H), 2.50 (t, *J* = 6.0 Hz, 18H), 2.42 (t, *J* = 6.1 Hz, 6H), 2.34 (t, *J* = 7.3 Hz, 2H), 2.23 (t, *J* = 7.5 Hz, 2H), 2.19 – 2.08 (m, 2H), 1.67 – 1.56 (m, 2H), 1.56 – 1.46 (m, 2H), 1.41 – 1.31 (m, 2H)†; ^{13}C NMR (100 MHz, CD_3OD) δ 176.3, 175.8, 175.4, 174.0, 137.4, 132.8, 132.3, 131.4, 130.0, 128.6, 128.5, 128.4, 127.7, 127.0, 126.3, 126.1, 126.0, 125.9, 124.5, 70.1, 68.8, 68.2, 61.53, 61.49, 40.4, 38.1, 37.7, 36.9, 35.8, 33.8, 30.2, 29.2, 27.7, 26.7; HRMS-ES$^+$ *m/z*: [M−H]$^-$ calculated for $C_{78}H_{110}N_5O_{35}$, 1676.69868; found, 1676.69645.

PBA-(C6)$_2$-G2(OH)$_9$ (38)

This reaction was conducted based on general procedure 1.3a for deprotection of *tert*-butyl esters. The following reagents were used in the stated quantities: **32** (37 mg, 16 μmol) and formic acid (5 mL). Nonaacid **38** was obtained as a tacky beige solid (29 mg, 100%), ^{1}H NMR (400 MHz, CD_3OD) δ 8.33 (d, *J* = 9.3 Hz, 1H), 8.21 – 8.15 (m, 2H), 8.13 (d, *J* = 8.4 Hz, 2H), 8.04 (s, 2H), 7.99 (t, *J* = 7.7 Hz, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 3.77 – 3.60 (m, 48H), 3.36 (t, *J* = 7.8 Hz, 2H), 3.18 (t, *J* = 7.0 Hz, 2H), 3.10 (t, *J* = 7.0 Hz, 2H), 2.52 (t, *J* = 6.1 Hz, 18H), 2.44 (t, *J* = 6.2 Hz, 6H),

* Four protons associated with the amide NH groups and nine protons associated with carboxylic acid groups are not visible.

† Five protons associated with the amide NH groups and nine protons associated with carboxylic acid groups are not visible.

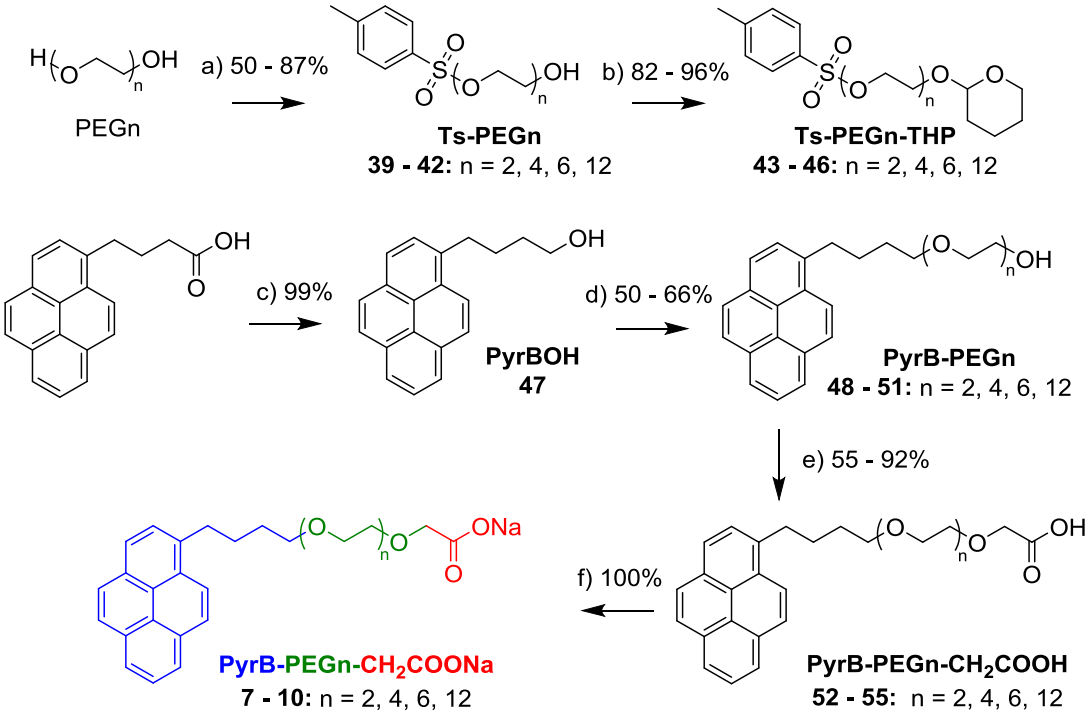
2.35 (t, *J* = 7.3 Hz, 2H), 2.24 – 2.09 (m, 6H), 1.65 – 1.30 (m, 13H*)†; HRMS-ES+ *m/z*: [M+Na]+ calculated for $C_{84}H_{122}N_6NaO_{36}$, 1814.78260; found, 1813.7921.

PBA-G1(ONa)$_3$ (1)

This reaction was conducted using general procedure 1.3d for formation of sodium carboxylates. The following reagents were used in the stated quantities: **33** (0.93 g, 1.53 mmol, 1 eq.), methanol (20 mL) and 1.00 M $NaOH_{(aq)}$ (4.59 mL, 3 eq.). **PBA-G1(ONa)$_3$** was obtained as a beige solid (1.03 g, 100%), ^{1}H NMR (400 MHz, D_2O) δ 8.08 (d, *J* = 7.6 Hz, 2H), 8.03 (d, *J* = 9.3 Hz, 1H), 7.99 – 7.85 (m, 5H), 7.72 (d, *J* = 7.9 Hz, 1H), 3.45 (t, *J* = 6.8 Hz, 6H), 3.28 (s, 6H), 3.15 (t, *J* = 7.0 Hz, 2H), 2.37 – 2.24 (m, 8H), 2.12 – 2.01 (m, 2H)‡.

Sodium salts **PBA-G2(ONa)$_9$ (2), PBA-C6-G1(ONa)$_3$ (3), PBA-(C6)$_2$-G1(ONa)$_3$ (4), PBA-C6-G2(ONa)$_9$ (5)** and **PBA-(C6)$_2$-G2(ONa)$_9$ (6)** were similarly obtained in near quantitative yields. Further characterisation of these salts, e.g. by IR spectroscopy, was not attempted due to their hygroscopic nature.

*1.4.2: Surfactants **7-10***



* The expected integral of this peak is 12; however, there is some overlap with a peak assigned to grease.
† Six protons associated with the amide NH groups and nine protons associated with carboxylic acid groups are not visible.
‡ The signal associated with the amide NH proton is not visible.

Scheme S4. Reagents and conditions: a) TsCl, Ag_2O, KI, DCM, 0 °C, 15 – 60 min; b) pyridinium *p*-toluenesulphonate, dihydropyran, DCM, 40 °C, 20 h; c) BH_3·THF, THF, RT, 72 h; d) i. NaH, THF, 67 °C, 1 – 2 h, ii. **Ts-PEG*n*-THP**, 67 °C, 18 h, iii. HCl/THF, RT, 18 h; e) i. NaH, THF, 40 °C, 1 h, ii. bromoacetic acid, 40 °C, 16 h; f) $NaOH_{(aq)}$, MeOH, RT, 30 min.

Ts-PEG2 (39)

This reaction was conducted using general procedure 1.3e for monotosylation of OEGs. The following reagents were used in the stated quantities: Ag_2O (1.100 g, 47.5 mmol, 1.5 eq.), KI (1.050 g, 6.3 mmol, 0.2 eq.), TsCl (6.630 g, 34.8 mmol, 1.1 eq.), PEG2 (3.0 mL, 31.6 mmol, 1 eq.) and DCM (300 mL). The reaction was stirred for 30 min following the addition of PEG2. **Ts-PEG2** was isolated using column chromatography (silica, EtOAc) as a pale yellow oil (4400 mg, 53%),^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 4.19 – 4.15 (m, 2H), 3.69 – 3.62 (m, 4H), 3.53 – 3.49 (m, 2H), 2.43 (s, 3H), 2.41 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1, 133.0, 130.0, 128.0, 72.6, 69.4, 68.6, 61.7, 21.7; MS-ES$^+$ *m/z*: 283.4 $[M+Na]^+$, 261.5 $[M+H]^+$; HRMS-ES$^+$ *m/z*: $[M+Na]^+$ calculated for $C_{11}H_{16}O_5SNa$, 283.0616; found, 283.0624.

Ts-PEG4 (40)

This reaction was conducted using general procedure 1.3e for monotosylation of OEGs. The following reagents were used in the stated quantities: Ag_2O (6.04 g, 26.1 mmol, 1.5 eq.), KI (577 mg, 3.5 mmol, 0.2 eq.), TsCl (3.64 g, 19.1 mmol, 1.1 eq.), PEG4 (3.0 mL, 17.4 mmol, 1 eq.) and DCM (170 mL). The reaction was stirred for 15 min following the addition of PEG4. **Ts-PEG4** was isolated using column chromatography (silica, EtOAc – 3:1 EtOAc/acetone) as a pale yellow oil (3.76 g, 62%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.3 Hz, 2H), 4.16 – 4.12 (m, 2H), 3.71 – 3.65 (m, 4H), 3.65 – 3.60 (m, 4H), 3.60 – 3.55 (m, 6H), 2.57 (bs, 1H), 2.43 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 133.2, 130.0, 128.1, 72.6, 70.9, 70.8, 70.6, 70.5, 69.4, 68.8, 61.9, 21.8; MS-ASAP$^+$ *m/z*: 349.1 $[M+H]^+$, 199.0 $[TsOCH_2CH_2]^+$; HRMS-ES$^+$ *m/z*: $[M+Na]^+$ calculated for $C_{15}H_{24}O_7SNa$, 371.11349; found, 371.11358.

Ts-PEG6 (41)

This reaction was conducted using general procedure 1.3e for monotosylation of OEGs. The following reagents were used in the stated quantities: Ag_2O (2.77 g, 11.93 mmol, 1.5 eq.), KI (264 mg, 1.59 mmol, 0.2 eq.), TsCl (1.67 g, 8.75 mmol, 1.1 eq.), PEG6 (2.0 mL, 7.96 mmol, 1 eq.) and DCM (80 mL). The reaction was stirred for 15 min following the addition of PEG6. **Ts-PEG6** was isolated using column chromatography (silica, 4:1 EtOAc/acetone) as a pale yellow oil (3.03 g, 87%),^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 2H), 4.18 – 4.13 (m, 2H), 3.70 – 3.56 (m, 22H), 2.58 (bs, 1H), 2.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0,

133.2, 130.0, 128.2, 72.7, 70.9, 70.80, 70.76, 70.75, 70.73, 70.70, 70.5, 69.4, 68.9, 61.9, 21.8; MS-ES$^+$ *m/z*: 459.8 [M+Na]$^+$; HRMS-ES$^+$ *m/z*: [M+Na]$^+$ calculated for $C_{19}H_{32}O_9SNa$, 459.1665; found, 459.1659.

Ts-PEG12 (42)

This reaction was conducted using general procedure 1.3e for monotosylation of OEGs. The following reagents were used in the stated quantities: Ag_2O (700 mg, 3.02 mmol, 1.5 eq.), KI (70 mg, 0.42 mmol, 0.2 eq.), TsCl (422 mg, 2.21 mmol, 1.1 eq.), PEG12 (1.10 g, 2.01 mmol, 1 eq.) and DCM (20 mL). The reaction was stirred for 1 h following the addition of PEG12. **Ts-PEG12** was isolated using column chromatography (silica, acetone) as a yellow oil (710 mg, 50%),^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 4.16 – 4.12 (m, 2H), 3.80 – 3.43 (m, 46H), 2.67 (bs, 1H), 2.43 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 133.3, 130.0, 128.2, 72.8, 71.0, 70.81, 70.76, 70.74, 70.73, 70.71, 70.5, 69.4, 68.9, 61.9, 21.8; MS-ES$^+$ *m/z*: 723.5 [M+Na]$^+$, 701.5 [M+H]$^+$; HRMS-ES$^+$ *m/z*: [M+Na]$^+$ calculated for $C_{31}H_{56}O_{15}SNa$, 723.3238; found, 723.3239.

Ts-PEG2-THP (43)

This reaction was conducted using general procedure 1.3f for THP protection of monotosylated OEGs. The following reagents were used in the stated quantities: **Ts-PEG2** (980 mg, 3.76 mmol, 1 eq.), pyridinium *p*-toluenesulphonate (190 mg, 0.76 mmol, 0.2 eq.), dihydropyran (0.51 mL, 5.59 mmol, 1.5 eq.) and DCM (25 mL). **Ts-PEG2-THP** was isolated using column chromatography (silica, 1:1 hexane/EtOAc – EtOAc) as a pale yellow oil (1.15 g, 89%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 4.63 – 4.56 (m, 1H), 4.20 – 4.15 (m, 2H), 3.89 – 3.78 (m, 2H), 3.74 – 3.69 (m, 2H), 3.64 – 3.59 (m, 2H), 3.57 – 3.46 (m, 2H), 2.45 (s, 3H), 1.87 – 1.77 (m, 1H), 1.77 – 1.65 (m, 1H), 1.63 – 1.47 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 133.3, 130.0, 128.2, 99.2, 70.9, 69.5, 68.9, 66.8, 62.5, 30.8, 25.6, 21.9, 19.7; MS-ES$^+$ *m/z*: 367.4 [M+Na]$^+$; HRMS-ES$^+$ *m/z*: [M+Na]$^+$ calculated for $C_{16}H_{24}O_6SNa$, 367.1191; found, 367.1222.

Ts-PEG4-THP (44)

This reaction was conducted using general procedure 1.3f for THP protection of monotosylated OEGs. The following reagents were used in the stated quantities: **Ts-PEG4** (3.74 g, 10.7 mmol, 1 eq.), pyridinium *p*-toluenesulphonate (0.54 g, 2.15 mmol, 0.2 eq.), dihydropyran (1.47 mL, 16.1 mmol, 1.5 eq.) and DCM (100 mL). **Ts-PEG4-THP** was isolated using column chromatography (silica, EtOAc) as a yellow oil (4.46 g, 96%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 4.62 (dd, *J* = 4.3, 3.0 Hz, 1H), 4.18 - 4.14 (m, 2H), 3.90 – 3.82 (m, 2H), 3.71

– 3.56 (m, 13H), 3.54 – 3.46 (m, 1H), 2.45 (s, 3H), 1.89 – 1.77 (m, 1H), 1.76 – 1.67 (m, 1H), 1.64 – 1.46 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 133.3, 130.0, 128.2, 99.2, 71.0, 70.9, 70.80, 70.75, 70.75, 69.4, 68.9, 66.9, 62.4, 30.8, 25.6, 21.8, 19.7; MS-ES$^+$ *m/z*: 455.2 $[M+Na]^+$, 349.1 [Ts-PEG4+H]$^+$; HRMS-ES$^+$ *m/z*: $[M+Na]^+$ calculated for $C_{20}H_{32}O_8SNa$, 455.1716; found, 455.1728.

Ts-PEG6-THP (45)

This reaction was conducted using general procedure 1.3f for THP protection of monotosylated OEGs. The following reagents were used in the stated quantities: **Ts-PEG6** (1.80 g, 4.12 mmol, 1 eq.), pyridinium *p*-toluenesulphonate (0.21 g, 0.84 mmol, 0.2 eq.), dihydropyran (0.56 mL, 6.14 mmol, 1.5 eq.) and DCM (50 mL). **Ts-PEG6-THP** was isolated using column chromatography (silica, EtOAc) as a yellow oil (1.95 g, 91%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 4.63 – 4.55 (m, 1H), 4.17 – 4.11 (m, 2H), 3.89 – 3.77 (m, 2H), 3.69 – 3.52 (m, 21H), 3.52 – 3.43 (m, 1H), 2.43 (s, 3H), 1.87 - 1.74 (m, 1H), 1.74 – 1.63 (m, 1H), 1.62 – 1.43 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 133.2, 130.0, 128.2, 99.1, 70.9, 70.8, 70.74, 70.70, 70.69, 69.4, 68.9, 66.8, 62.4, 30.8, 25.6, 21.8, 19.7; MS-ES$^+$ *m/z*: 543.6 $[M+Na]^+$; HRMS-ES$^+$ *m/z*: $[M+Na]^+$ calculated for $C_{24}H_{40}O_{10}SNa$, 543.2240; found, 543.2244.

Ts-PEG12-THP (46)

This reaction was conducted using general procedure 1.3f for THP protection of monotosylated OEGs. The following reagents were used in the stated quantities: **Ts-PEG12** (705 mg, 1.01 mmol, 1 eq.), pyridinium *p*-toluenesulphonate (51 mg, 0.20 mmol, 0.2 eq.), dihydropyran (0.14 mL, 1.53 mmol, 1.5 eq.) and DCM (20 mL). **Ts-PEG12-THP** was isolated using column chromatography (silica, EtOAc – 5:1 acetone/EtOAc) as a yellow oil (650 mg, 82%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 2H), 4.65 – 4.61 (m, 1H), 4.18 – 4.14 (m, 2H), 3.90 – 3.83 (m, 2H), 3.74 – 3.57 (m, 45H), 3.55 – 3.44 (m, 1H), 2.45 (s, 3H), 1.89 – 1.78 (m, 1H), 1.76 – 1.67 (m, 1H), 1.65 – 1.46 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 133.2, 130.0, 128.2, 99.1, 70.9, 70.80, 70.79, 70.77, 70.73, 70.72, 69.4, 68.9, 66.8, 62.4, 30.8, 25.6, 21.8, 19.7; MS-ES$^+$ *m/z*: 807.5 $[M+Na]^+$; HRMS-ES$^+$ *m/z*: $[M+Na]^+$ calculated for $C_{36}H_{64}O_{16}SNa$, 807.3813; found, 807.3829.

1-Pyrenebutanol, PyrBOH (47)

Our synthesis of **47**, which is commercially available, has been reported previously.[5]

PyrB-PEG2 (48)

This reaction was conducted using general procedure 1.3g for the synthesis of OEGs monosubstituted with PyrB groups. The following reagents were used in the stated quantities:

NaH (311 mg, 12.96 mmol, 5 eq.), **PyrBOH** (711 mg, 2.59 mmol, 1 eq.), **Ts-PEG2-THP** (1.07 g, 3.11 mmol, 1.2 eq.), THF (20 mL) and conc. HCl (7 mL) in THF (63 mL). **PyrB-PEG2** was isolated following column chromatography (silica, EtOAc) as a yellow oil (505 mg, 54%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 9.3 Hz, 1H), 8.20 – 8.14 (m, 2H), 8.14 – 8.09 (m, 2H), 8.06 – 7.96 (m, 3H), 7.88 (d, *J* = 7.8 Hz, 1H), 3.75 – 3.70 (m, 2H), 3.69 – 3.64 (m, 2H), 3.63 – 3.57 (m, 4H), 3.54 (t, *J* = 6.6 Hz, 2H), 3.38 (t, *J* = 7.7 Hz, 2H), 2.49 (bs, 1H), 1.99 – 1.89 (m, 2H), 1.84 – 1.75 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.0, 131.7, 131.1, 130.0, 128.8, 127.7, 127.5, 127.4, 126.8, 126.0, 125.31, 125.26, 125.02, 124.99, 124.9, 123.6, 72.7, 71.5, 70.7, 70.5, 62.1, 33.5, 29.9, 28.6; MS-ASAP^{+} *m/z*: 363.2 $[M+H]^{+}$, 362.2 $[M]^{+\cdot}$, 258.1 $[PyrB+H]^{+}$, 257.1 $[PyrB]^{+\cdot}$; HRMS-ASAP^{+} *m/z*: $[M]^{+\cdot}$ calculated for $C_{24}H_{26}O_3$, 362.1882; found, 362.1872.

PyrB-PEG4 (49)

This reaction was conducted using general procedure 1.3g for the synthesis of OEGs monosubstituted with PyrB groups. The following reagents were used in the stated quantities: NaH (289 mg, 12.04 mmol, 5 eq.), **PyrBOH** (661 mg, 2.41 mmol, 1 eq.), **Ts-PEG4-THP** (1.25 g, 2.89 mmol, 1.2 eq.), THF (16 mL) and conc. HCl (6 mL) in THF (54 mL). **PyrB-PEG4** was isolated following column chromatography (silica, EtOAc – 4:1 EtOAc/acetone) as a yellow oil (632 mg, 58%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 9.2 Hz, 1H), 8.20 – 8.14 (m, 2H), 8.14 – 8.08 (m, 2H), 8.06 – 7.96 (m, 3H), 7.88 (d, *J* = 7.8 Hz, 1H), 3.74 – 3.50 (m, 18H), 3.38 (t, *J* = 7.7 Hz, 2H), 2.56 (bs, 1H), 1.98 – 1.89 (m, 2H), 1.85 – 1.72 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.0, 131.6, 131.0, 129.9, 128.7, 127.6, 127.4, 127.3, 126.6, 125.9, 125.20, 125.16, 124.92, 124.90, 124.8, 123.6, 72.7, 71.4, 70.70, 70.68, 70.65, 70.4, 70.3, 61.8, 33.4, 29.8, 28.5; MS-ASAP^{+} *m/z*: 451.2 $[M+H]^{+}$, 450.2 $[M]^{+\cdot}$; HRMS-ASAP^{+} *m/z*: $[M]^{+\cdot}$ calculated for $C_{28}H_{34}O_5$, 450.2406; found, 450.2408.

PyrB-PEG6 (50)

This reaction was conducted using general procedure 1.3g for the synthesis of OEGs monosubstituted with PyrB groups. The following reagents were used in the stated quantities: NaH (600 mg, 25.00 mmol, 5 eq.), **PyrBOH** (1.36 g, 4.96 mmol, 1 eq.), **Ts-PEG6-THP** (3.10 g, 5.95 mmol, 1.2 eq.), THF (48 mL) and conc. HCl (20 mL) in THF (180 mL). **PyrB-PEG6** was isolated following column chromatography (silica, EtOAc – 1:1 EtOAc/acetone) as a yellow-brown oil (1.76 g, 66%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 9.2 Hz, 1H), 8.20 - 8.13 (m, 2H), 8.13 – 8.07 (m, 2H), 8.06 – 7.96 (m, 3H), 7.87 (d, *J* = 7.8 Hz, 1H), 3.75 - 3.69 (m, 2H), 3.69 – 3.56 (m, 22H), 3.53 (t, *J* = 6.5 Hz, 2H), 3.37 (t, *J* = 7.7 Hz, 2H), 2.58 (bs, 1H), 1.98 – 1.88 (m, 2H), 1.84 – 1.72 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.1, 131.6, 131.1, 130.0, 128.8, 127.7, 127.5, 127.4, 126.7, 126.0, 125.29, 125.25, 125.00, 124.98, 124.8, 123.7, 72.7, 71.4, 70.83, 70.80, 70.78, 70.76,

70.7, 70.6, 70.4, 62.0, 33.5, 29.9, 28.6; MS-ASAP$^+$ *m/z*: 539.3 $[M+H]^+$, 538.3 $[M]^{+\cdot}$; HRMS-ASAP$^+$ *m/z*: $[M]^{+\cdot}$ calculated for $C_{32}H_{42}O_7$, 538.2931; found 538.2927.

PyrB-PEG12 (51)

This reaction was conducted using general procedure 1.3g for the synthesis of OEGs monosubstituted with PyrB groups. The following reagents were used in the stated quantities: NaH (82 mg, 3.42 mmol, 5 eq.), **PyrBOH** (188 mg, 0.69 mmol, 1 eq.), **Ts-PEG12-THP** (644 mg, 0.82 mmol, 1.2 eq.), THF (8 mL) and conc. HCl (3 mL) in THF (27 mL). **PyrB-PEG12** was isolated following column chromatography (silica, EtOAc – 1:1 EtOAc/acetone) as a yellow oil (275 mg, 50%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 9.3 Hz, 1H), 8.19 – 8.13 (m, 2H), 8.12 – 8.07 (m, 2H), 8.05 – 7.94 (m, 3H), 7.86 (d, *J* = 7.8 Hz, 1H), 3.74 – 3.70 (m, 2H), 3.69 – 3.56 (m, 46H), 3.53 (t, *J* = 6.5 Hz, 2H), 3.36 (t, *J* = 7.7 Hz, 2H), 2.70 (bs, 1H), 1.97 – 1.87 (m, 2H), 1.82 – 1.73 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.0, 131.6, 131.1, 129.9, 128.8, 127.7, 127.4, 127.3, 126.7, 125.9, 125.22, 125.18, 125.0, 124.9, 124.8, 123.6, 72.6, 71.4, 70.8, 70.73, 70.70, 70.5, 70.3, 61.9, 33.5, 29.9, 28.6; MS-ES$^+$ *m/z*: 825.6 $[M+Na]^+$, 803.6 $[M+H]^+$; HRMS-ES$^+$ *m/z*: $[M+Na]^+$ calculated for $C_{44}H_{66}O_{13}Na$, 825.4401; found 825.4438.

PyrB-PEG2-CH_2COOH (52)

This reaction was conducted using general procedure 1.3h for addition of a terminal acid group. The following reagents were used in the stated quantities: **PyrB-PEG2** (475 mg, 1.31 mmol, 1 eq.), NaH (409 mg, 17.04 mmol, 13 eq.), bromoacetic acid (219 mg, 1.58 mmol, 1.2 eq.) and THF (25 mL). **PyrB-PEG2-CH_2COOH** was obtained as a brown oil (509 mg, 92%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.40 (bs, 1H), 8.29 (d, *J* = 9.3 Hz, 1H), 8.19 – 8.14 (m, 2H), 8.13 – 8.09 (m, 2H), 8.06 – 7.96 (m, 3H), 7.88 (d, *J* = 7.8 Hz, 1H), 4.12 (s, 2H), 3.71 – 3.63 (m, 6H), 3.61 – 3.57 (m, 2H), 3.54 (t, *J* = 6.6 Hz, 2H), 3.37 (t, *J* = 7.7 Hz, 2H), 1.98 – 1.89 (m, 2H), 1.83 – 1.74 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 137.0, 131.7, 131.1, 130.0, 128.8, 127.7, 127.5, 127.4, 126.7, 126.0, 125.30, 125.25, 125.02, 125.00, 124.9, 123.7, 71.7, 71.5, 71.0, 70.2, 70.1, 69.0, 33.5, 29.8, 28.6; MS-ASAP$^+$ *m/z*: 421.2 $[M+H]^+$, 420.2 $[M]^{+\cdot}$, 376.2 $[M\text{-}CO_2]^{+\cdot}$, 258.1 $[PyrB+H]^+$, 257.1 $[PyrB]^{+\cdot}$; HRMS-ASAP$^+$ (*m/z*): $[M]^{+\cdot}$ calculated for $C_{26}H_{28}O_5$, 420.1937; found, 420.1921.

PyrB-PEG4-CH_2COOH (53)

This reaction was conducted using general procedure 1.3h for addition of a terminal acid group. The following reagents were used in the stated quantities: **PyrB-PEG4** (518 mg, 1.15 mmol, 1 eq.), NaH (359 mg, 14.96 mmol, 13 eq.), bromoacetic acid (240 mg, 1.73 mmol, 1.5 eq.) and THF (20 mL). **PyrB-PEG4-CH_2COOH** was obtained as a yellow-brown oil (535 mg, 91%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.19 (bs, 1H), 8.28 (d, *J* = 9.3 Hz, 1H), 8.19 – 8.13 (m, 2H), 8.13 – 8.08

(m, 2H), 8.06 – 7.95 (m, 3H), 7.87 (d, *J* = 7.8 Hz, 1H), 4.12 (s, 2H), 3.69 – 3.56 (m, 16H), 3.54 (t, *J* = 6.5 Hz, 2H), 3.36 (t, *J* = 7.7 Hz, 2H), 1.98 – 1.87 (m, 2H), 1.83 – 1.73 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 137.1, 131.6, 131.1, 129.9, 128.8, 127.7, 127.5, 127.3, 126.7, 126.0, 125.3, 125.2, 124.97, 124.96, 124.8, 123.7, 71.5, 71.4, 70.81, 70.75, 70.7, 70.6, 70.5, 70.2, 69.1, 33.5, 29.8, 28.6; MS-ASAP$^+$ *m/z*: 509.2 $[M+H]^+$, 508.2 $[M]^{+\cdot}$, 464.2 $[M-CO_2]^{+\cdot}$, 257.1 $[PyrB]^{+\cdot}$; HRMS-ASAP$^+$ (*m/z*): $[M]^{+\cdot}$ calculated for $C_{30}H_{36}O_7$, 508.2461; found, 508.2475.

PyrB-PEG6-CH_2COOH (54)

This reaction was conducted using general procedure 1.3h for addition of a terminal acid group. The following reagents were used in the stated quantities: **PyrB-PEG6** (1.60 g, 2.97 mmol, 1 eq.), NaH (0.93 g, 38.75 mmol, 13 eq.), bromoacetic acid (0.50 g, 3.60 mmol, 1.2 eq.) and THF (65 mL). **PyrB-PEG6-CH_2COOH** was obtained as a yellow-brown oil (1.24 g, 70%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.43 (bs, 1H), 8.27 (d, *J* = 9.3 Hz, 1H), 8.18 – 8.12 (m, 2H), 8.12 – 8.07 (m, 2H), 8.05 – 7.95 (m, 3H), 7.86 (d, *J* = 7.8 Hz, 1H), 4.14 (s, 2H), 3.72 – 3.67 (m, 2H), 3.67 – 3.55 (m, 22H), 3.53 (t, *J* = 6.5 Hz, 2H), 3.36 (t, *J* = 7.7 Hz, 2H), 1.97 – 1.87 (m, 2H), 1.82 – 1.73 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.9, 137.1, 131.7, 131.1, 130.0, 128.8, 127.7, 127.5, 127.4, 126.7, 126.0, 125.29, 125.25, 125.00, 124.99, 124.9, 123.7, 71.5, 71.4, 70.82, 70.79, 70.77, 70.75, 70.71, 70.68, 70.66, 70.61, 70.58, 70.5, 70.3, 69.3, 33.5, 29.9, 28.6; MS-ASAP$^+$ *m/z*: 597.3 $[M+H]^+$, 596.3 $[M]^{+\cdot}$, 257.1 $[PyrB]^{+\cdot}$; HRMS-ASAP$^+$ *m/z*: $[M+Na]^+$ calculated for $C_{34}H_{44}O_9$, 596.2985; found, 596.2987.

PyrB-PEG12-CH_2COOH (55)

This reaction was conducted using general procedure 1.3h for addition of a terminal acid group. The following reagents were used in the stated quantities: **PyrB-PEG12** (275 mg, 0.34 mmol, 1 eq.), NaH (107 mg, 4.46 mmol, 13 eq.), bromoacetic acid (57 mg, 0.41 mmol, 1.2 eq.) and THF (15 mL). **PyrB-PEG12-CH_2COOH** was obtained as a brown oil (161 mg, 55%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 9.3 Hz, 1H), 8.19 – 8.14 (m, 2H), 8.13 – 8.08 (m, 2H), 8.06 – 7.96 (m, 3H), 7.87 (d, *J* = 7.8 Hz, 1H), 4.17 (s, 2H), 3.78 – 3.72 (m, 2H), 3.72 - 3.51 (m, 48H), 3.37 (t, *J* = 7.8 Hz, 2H), 1.98 – 1.88 (m, 2H), 1.83 – 1.74 (m, 2H)*; ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.0, 137.1, 131.7, 131.1, 130.0, 128.8, 127.7, 127.5, 127.4, 126.7, 126.0, 125.29, 125.25, 125.01, 124.99, 124.9, 123.7, 71.6, 71.5, 70.89, 70.86, 70.82, 70.80, 70.76, 70.75, 70.73, 70.71, 70.66, 70.6, 70.4, 69.2, 33.5, 29.9, 28.6; MS-ES$^+$ *m/z*: 883.6 $[M+Na]^+$, 453.5 $[M+2Na]^{2+}$; HRMS-ASAP$^+$ *m/z*: $[M+Na]^+$ calculated for $C_{46}H_{68}O_{15}Na$, 883.4456; found, 883.4493.

PyrB-PEG2-CH_2COONa (7)

* The proton associated with carboxylic acid group is not visible.

This reaction was conducted using general procedure 1.3d for the formation of sodium carboxylates. The following reagents were used in the stated quantities: **PyrB-PEG2-CH_2COOH** (91 mg, 0.216 mmol, 1 eq.), methanol (5 mL) and 1.0000 M $NaOH_{(aq)}$ (0.216 mL, 1 eq.). **PyrB-PEG2-CH_2COONa** was obtained as a pale yellow hygroscopic solid (96 mg, 100%), ^{1}H NMR (400 MHz, D_2O) δ 7.39 (d, *J* = 6.2 Hz, 1H), 7.29 – 7.16 (m, 4H), 7.13 (t, *J* = 8.8 Hz, 2H), 7.01 (d, *J* = 8.8 Hz, 1H), 6.87 (d, *J* = 7.5 Hz, 1H), 3.73 (s, 2H), 3.24 – 3.18 (m, 2H), 3.08 – 3.03 (m, 2H), 2.83 (bs, 2H), 2.61 (bs, 2H), 2.40 (bs, 2H), 2.26 (bs, 2H), 0.80 (bs, 4H).

PyrB-PEG4-CH_2COONa (8)

This reaction was conducted using general procedure 1.3d for the formation of sodium carboxylates. The following reagents were used in the stated quantities: **PyrB-PEG4-CH_2COOH** (510 mg, 1.003 mmol, 1 eq.), methanol (15 mL) and 1.0000 M $NaOH_{(aq)}$ (1.003 mL, 1 eq.). **PyrB-PEG4-CH_2COONa** was obtained as a sticky brown hygroscopic solid (532 mg, 100%), ^{1}H NMR (400 MHz, D_2O) δ 7.42 (d, *J* = 4.9 Hz, 1H), 7.34 (d, *J* = 9.2 Hz, 1H), 7.31 – 7.22 (m, 3H), 7.19 (d, *J* = 9.1 Hz, 2H), 7.10 (d, *J* = 8.5 Hz, 1H), 6.96 (d, *J* = 7.5 Hz, 1H), 3.83 (s, 2H), 3.46 – 3.39 (m, 2H), 3.36 – 3.29 (m, 2H), 3.23 – 3.18 (m, 2H), 3.18 – 3.07 (m, 6H), 3.07 – 3.01 (m, 2H), 2.93 – 2.85 (m, 2H), 2.64 (bs, 2H), 2.39 (bs, 2H), 0.98 (bs, 4H).

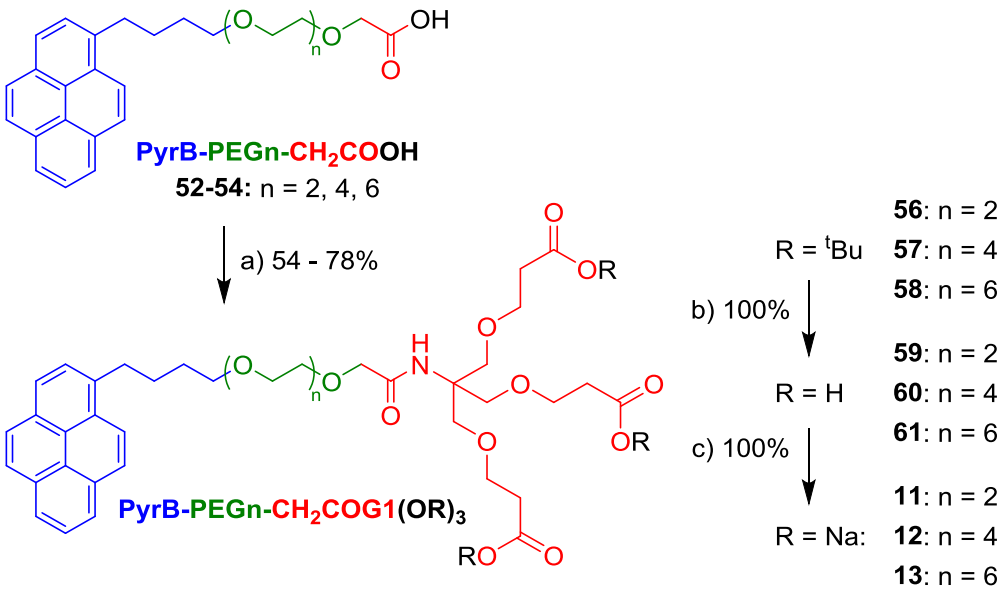
PyrB-PEG6-CH_2COONa (9)

This reaction was conducted using general procedure 1.3d for the formation of sodium carboxylates. The following reagents were used in the stated quantities: **PyrB-PEG6-CH_2COOH** (513 mg, 0.860 mmol, 1 eq.), methanol (10 mL) and 1.0000 M $NaOH_{(aq)}$ (0.860 mL, 1 eq.). **PyrB-PEG6-CH_2COONa** was obtained as a sticky brown hygroscopic solid (532 mg, 100%), ^{1}H NMR (400 MHz, D_2O) δ 7.46 (d, *J* = 7.1 Hz, 1H), 7.40 – 7.26 (m, 4H), 7.25 - 7.13 (m, 3H), 7.00 (d, *J* = 7.8 Hz, 1H), 3.88 (s, 2H), 3.56 – 3.51 (m, 2H), 3.51 – 3.46 (m, 2H), 3.42 – 3.36 (m, 2H), 3.36 – 3.31 (m, 2H), 3.31 – 3.24 (m, 4H), 3.24 – 3.17 (m, 8H), 3.17 – 3.11 (m, 2H), 3.02 – 2.95 (m, 2H), 2.73 (bs, 2H), 2.44 (bs, 2H), 1.04 (bs, 4H).

PyrB-PEG12-CH_2COONa (10)

This reaction was conducted using general procedure 1.3d for the formation of sodium carboxylates. The following reagents were used in the stated quantities: **PyrB-PEG12-CH_2COOH** (158 mg, 0.184 mmol, 1 eq.), methanol (5 mL) and 1.0000 M $NaOH_{(aq)}$ (0.184 mL, 1 eq.). **PyrB-PEG12-CH_2COONa** was obtained as a sticky brown hygroscopic solid (162 mg, 100%), ^{1}H NMR (400 MHz, D_2O) δ 7.55 – 7.15 (m, 8H), 7.05 (d, *J* = 7.5 Hz, 1H), 3.92 (s, 2H), 3.72 – 3.66 (m, 2H), 3.66 – 3.26 (m, 42H), 3.23 (bs, 2H), 3.08 (bs, 2H), 2.82 (bs, 2H), 2.50 (bs, 2H), 1.11 (bs, 4H).

*1.4.3: Surfactants **11-13***



Scheme S5. a) i. DIPEA, TBTU, DCM, 0 °C, 15 min, ii. **14**, 0 °C – RT, 22-72 h; b) formic acid, RT, 18 h; c) $NaOH_{(aq)}$, MeOH, RT, 30 min.

PyrB-PEG2-CH_2COG1(O^{t}Bu)$_3$ (56)

This reaction was conducted based on general procedure 1.3b for amide coupling reactions. The following reagents were used in the stated quantities: **PyrB-PEG2-CH_2COOH** (402 mg, 0.96 mmol, 1 eq.), DIPEA (0.33 mL, 1.89 mmol, 2 eq.), TBTU (307 mg, 0.96 mmol, 1 eq.), **G1(O^{t}Bu)$_3$**/(023) (483 mg, 0.96 mmol, 1 eq.) and DCM (10 mL). This reaction was initially ice cooled then stirred for 22 h. The crude product was purified by column chromatography (silica, EtOAc) to yield **PyrB-PEG2-CH_2COG1(O^{t}Bu)** as a yellow oil (468 mg, 54%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 9.3 Hz, 1H), 8.19 – 8.14 (m, 2H), 8.13 – 8.08 (m, 2H), 8.07 – 7.96 (m, 3H), 7.88 (d, *J* = 7.8 Hz, 1H), 6.75 (s, 1H), 3.88 (s, 2H), 3.71 (s, 6H), 3.68 – 3.61 (m, 12H), 3.61 – 3.57 (m, 2H), 3.54 (t, *J* = 6.6 Hz, 2H), 3.38 (t, *J* = 7.7 Hz, 2H), 2.44 (t, *J* = 6.5 Hz, 6H), 1.98 – 1.88 (m, 2H), 1.83 – 1.74 (m, 2H), 1.44 (s, 27H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 169.7, 137.0, 131.6, 131.1, 130.0, 128.8, 127.7, 127.5, 127.4, 126.8, 126.0, 125.29, 125.24, 125.03, 124.99, 124.9, 123.7, 80.6, 71.5, 71.2, 71.0, 70.9, 70.6, 70.4, 69.2, 67.3, 59.7, 36.5, 33.5, 29.9, 28.6, 28.3; MS-ES$^+$ *m/z*: 930.6 $[M+Na]^+$, 908.6 $[M+H]^+$; HRMS-ES$^+$ *m/z*: $[M+Na]^+$ calculated for $C_{51}H_{73}NO_{13}Na$, 930.4980; found, 930.5010.

PyrB-PEG4-CH_2COG1(O^{t}Bu)$_3$ (57)

This reaction was conducted based on general procedure 1.3b for amide coupling reactions. The following reagents were used in the stated quantities: **PyrB-PEG4-CH_2COOH** (640 mg,

1.27 mmol, 1 eq.), DIPEA (0.44 mL, 2.53 mmol, 2 eq.), TBTU (407 mg, 1.27 mmol, 1 eq.), **G1(O^{t}Bu)$_3$**/(023) (640 mg, 1.27 mmol, 1 eq.) and DCM (20 mL). This reaction was initially ice cooled then stirred for 72 h. The crude product was purified by column chromatography (silica, EtOAc) to yield **PyrB-PEG4-CH$_2$COG1(O^{t}Bu)** as a yellow oil (679 mg, 54%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 9.2 Hz, 1H), 8.20 – 8.14 (m, 2H), 8.14 – 8.07 (m, 2H), 8.06 – 7.96 (m, 3H), 7.87 (d, *J* = 7.7 Hz, 1H), 6.75 (s, 1H), 3.88 (s, 2H), 3.72 (s, 6H), 3.69 – 3.56 (m, 22H), 3.54 (t, *J* = 6.5 Hz, 2H), 3.37 (t, *J* = 7.8 Hz, 2H), 2.45 (t, *J* = 6.5 Hz, 6H), 2.00 – 1.87 (m, 2H), 1.83 – 1.74 (m, 2H), 1.45 (s, 27H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 169.7, 137.1, 131.6, 131.1, 130.0, 128.8, 127.7, 127.5, 127.4, 126.7, 126.0, 125.28, 125.24, 125.01, 124.98, 124.8, 123.7, 80.6, 71.5, 71.2, 71.0, 70.83, 70.82, 70.81, 70.79, 70.77, 70.6, 70.4, 69.2, 67.3, 59.7, 36.5, 33.5, 29.9, 28.6, 28.3; MS-ASAP$^+$ *m/z*: 996.5 $[M+H]^+$, 995.5 $[M]^{+\cdot}$, 508.2 $[PyrB\text{-}PEG4\text{-}CH_2CONH_3]^+$, 507.2 $[PyrB\text{-}PEG4\text{-}CH_2CONH_2]^{+\cdot}$, 450.2 $[PyrB\text{-}PEG4]^{+\cdot}$; HRMS-ASAP$^+$ *m/z*: $[M+H]^+$ calculated for $C_{55}H_{82}NO_{15}$, 996.5684; found, 996.5644.

PyrB-PEG6-CH$_2$COG1(O^{t}Bu)$_3$ (58)

This reaction was conducted based on general procedure 1.3b for amide coupling reactions. The following reagents were used in the stated quantities: **PyrB-PEG6-CH$_2$COOH** (670 mg, 1.12 mmol, 1 eq.), DIPEA (0.39 mL, 2.24 mmol, 2 eq.), TBTU (361 mg, 1.12 mmol, 1 eq.), **G1(O^{t}Bu)$_3$**/(023) (568 mg, 1.12 mmol, 1 eq.) and DCM (20 mL). This reaction was initially ice cooled and stirred for 72 h. The crude product was purified by column chromatography (silica, 3:1 EtOAc/acetone) to yield **PyrB-PEG6-CH$_2$COG1(O^{t}Bu)** as a yellow oil (946 mg, 78%), ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 9.2 Hz, 1H), 8.18 – 8.13 (m, 2H), 8.13 – 8.08 (m, 2H), 8.05 – 7.96 (m, 3H), 7.87 (d, *J* = 7.7 Hz, 1H), 6.75 (s, 1H), 3.89 (s, 2H), 3.72 (s, 6H), 3.69 – 3.55 (m, 30H), 3.53 (t, *J* = 6.5 Hz, 2H), 3.37 (t, *J* = 7.8 Hz, 2H), 2.45 (t, *J* = 6.5 Hz, 6H), 1.97 – 1.88 (m, 2H), 1.82 – 1.73 (m, 2H), 1.45 (s, 27H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 169.7, 137.0, 131.6, 131.1, 130.0, 128.8, 127.7, 127.5, 127.3, 126.7, 126.0, 125.3, 125.2, 124.98, 124.95, 124.8, 123.7, 80.6, 71.4, 71.2, 71.0, 70.82, 70.81, 70.78, 70.76, 70.73, 70.72, 70.6, 70.4, 69.2, 67.3, 59.7, 36.5, 33.5, 29.9, 28.6, 28.3; MS-ES$^+$ *m/z*: 1106.5 $[M+Na]^+$, 1084.3 $[M+H]^+$; HRMS-ES$^+$ *m/z*: $[M+H]^+$ calculated for $C_{59}H_{90}NO_{17}$, 1084.6209; found, 1084.6212.

PyrB-PEG2-CH$_2$COG1(OH)$_3$ (59)

This reaction was conducted using general procedure 1.3a for deprotection of *tert*-butyl esters. The following reagents were used in the stated quantities: **PyrB-PEG2-CH$_2$COG1(O^{t}Bu)$_3$** (266 mg, 0.29 mmol) and formic acid (5 mL). **PyrB-PEG2-CH$_2$COG1(OH)$_3$** was obtained as a yellow oil (217 mg, 100%), ^{1}H NMR (400 MHz, CD_3OD) δ 8.33 (d, *J* = 9.3 Hz, 1H), 8.22 – 8.15 (m, 2H),

8.13 (d, *J* = 8.8 Hz, 2H), 8.07 – 7.96 (m, 3H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.04 (s, 0.3H*), 3.83 (s, 2H), 3.66 (s, 6H), 3.64 – 3.60 (m, 10H), 3.60 – 3.52 (m, 6H), 3.38 (t, *J* = 7.7 Hz, 2H), 2.47 (t, *J* = 6.1 Hz, 6H), 1.99 – 1.87 (m, 2H), 1.82 - 1.70 (m, 2H)†; ^{13}C NMR (101 MHz, CD_3OD) δ 175.3, 172.2, 138.3, 132.9, 132.4, 131.2, 129.9, 128.6, 128.5, 128.3, 127.6, 127.0, 126.3, 126.2, 125.92, 125.89, 125.8, 124.6, 72.1, 71.9, 71.6, 71.5, 71.4, 71.1, 70.0, 68.1, 61.1, 35.8, 34.1, 30.7, 29.7; MS-ES$^-$ *m/z*: 738.4 [M-H]$^-$; HRMS-ES$^-$ *m/z*: [M-H]$^-$ calculated for $C_{39}H_{48}NO_{13}$, 738.3126; found, 738.3134.

PyrB-PEG4-CH_2COG1(OH)$_3$ (60)

This reaction was conducted using general procedure 1.3a for deprotection of *tert*-butyl esters. The following reagents were used in the stated quantities: **PyrB-PEG4-CH_2COG1(O^{t}Bu)$_3$** (228 mg, 0.23 mmol) and formic acid (5 mL). **PyrB-PEG4-CH_2COG1(OH)$_3$** was obtained as a yellow oil (190 mg, 100%), ^{1}H NMR (400 MHz, CD_3OD) δ 8.33 (d, *J* = 9.3 Hz, 1H), 8.22 – 8.15 (m, 2H), 8.12 (d, *J* = 8.4 Hz, 2H), 8.08 – 7.96 (m, 3H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.04 (s, 1H), 3.83 (s, 2H), 3.68 (s, 6H), 3.65 (t, *J* = 6.1 Hz, 6H), 3.62 – 3.45 (m, 18H), 3.37 (t, *J* = 7.8 Hz, 2H), 2.49 (t, *J* = 6.1 Hz, 6H), 1.98 – 1.87 (m, 2H), 1.80 - 1.70 (m, 2H)‡; ^{13}C NMR (101 MHz, CD_3OD) δ 175.3, 172.2, 138.3, 132.9, 132.3, 131.2, 129.9, 128.6, 128.5, 128.2, 127.6, 127.0, 126.24, 126.17, 125.93, 125.90, 125.8, 124.6, 72.1, 71.8, 71.53, 71.47, 71.42, 71.40, 71.3, 71.2, 70.0, 68.1, 61.1, 35.8, 34.2, 30.7, 29.7; MS-ES$^+$ *m/z*: 850.5 [M+Na]$^+$; HRMS-ES$^+$ *m/z*: [M+Na]$^+$ calculated for $C_{43}H_{57}NO_{15}Na$, 850.3626; found, 850.3618.

PyrB-PEG6-CH_2COG1(OH)$_3$ (61)

This reaction was conducted using general procedure 1.3a for deprotection of *tert*-butyl esters. The following reagents were used in the stated quantities: **PyrB-PEG6-CH_2COG1(O^{t}Bu)$_3$** (946 mg, 0.87 mmol) and formic acid (15 mL). **PyrB-PEG6-CH_2COG1(OH)$_3$** was obtained as a yellow oil (800 mg, 100%), ^{1}H NMR (400 MHz, CD_3OD) δ 8.34 (d, *J* = 9.3 Hz, 1H), 8.22 – 8.16 (m, 2H), 8.13 (d, *J* = 8.7 Hz, 2H), 8.08 – 7.97 (m, 3H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.06 (s, 1H), 3.86 (s, 2H), 3.69 (s, 6H), 3.66 (t, *J* = 6.1 Hz, 6H), 3.62 –3.43 (m, 26H), 3.38 (t, *J* = 7.8 Hz, 2H), 2.50 (t, *J* = 6.1 Hz, 6H), 1.98 - 1.88 (m, 2H), 1.80 – 1.71 (m, 2H)§; ^{13}C NMR (101 MHz, CD_3OD) δ 175.2, 172.2, 138.3, 132.9, 132.3, 131.2, 129.9, 128.6, 128.5, 128.2, 127.6, 127.0, 126.24, 126.18, 125.92, 125.89, 125.8, 124.6, 72.1, 71.9, 71.56, 71.55, 71.48, 71.47, 71.46, 71.45, 71.44, 71.42, 71.37, 71.2, 70.0, 68.1, 61.1, 35.8, 34.1, 30.7, 29.7; MS-ES$^-$ *m/z*: 914.5 [M-H]$^-$; HRMS-ES$^-$ *m/z*: [M-H]$^-$ calculated for $C_{47}H_{64}NO_{17}$, 914.4174; found, 914.4193.

* The expected integral of this peak is 1H.
† The three protons associated with carboxylic acid groups are not visible.
‡ The three protons associated with carboxylic acid groups are not visible.
§ The three protons associated with carboxylic acid groups are not visible.

PyrB-PEG2-CH_2COG1(ONa)$_3$ (11)

This reaction was conducted using general procedure 1.3d for formation of sodium carboxylates. The following reagents were used in the stated quantities: **PyrB-PEG2-CH_2COG1(OH)$_3$** (202 mg, 0.273 mmol, 1 eq.), methanol (5 mL) and 1.0000 M $NaOH_{(aq)}$ (0.819 mL, 3 eq.). **PyrB-PEG2-CH_2COG1(ONa)$_3$** was obtained as a hygroscopic yellow solid (220 mg, 100%), ^{1}H NMR (400 MHz, D_2O) δ 8.06 (d, *J* = 7.5 Hz, 1H), 8.01 (d, *J* = 7.6 Hz, 1H), 7.92 (d, *J* = 7.6 Hz, 1H), 7.90 – 7.82 (m, 4H), 7.78 (d, *J* = 9.3 Hz, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 3.68 (s, 2H), 3.49 (t, *J* = 6.9 Hz, 6H), 3.39 (s, 6H), 3.37 – 3.22 (m, 10H), 2.95 (t, *J* = 7.1 Hz, 2H), 2.31 (t, *J* = 6.9 Hz, 6H), 1.60 – 1.41 (m, 4H)*.

PyrB-PEG4-CH_2COG1(ONa)$_3$ (12)

This reaction was conducted using general procedure 1.3d for formation of sodium carboxylates. The following reagents were used in the stated quantities: **PyrB-PEG4-CH_2COG1(OH)$_3$** (180 mg, 0.217 mmol, 1 eq.), methanol (5 mL) and 1.0000 M $NaOH_{(aq)}$ (0.651 mL, 3 eq.). **PyrB-PEG4-CH_2COG1(ONa)$_3$** was obtained as a hygroscopic yellow solid (194 mg, 100%), ^{1}H NMR (400 MHz, D_2O) δ 7.67 – 7.60 (m, 2H), 7.55 (d, *J* = 7.4 Hz, 1H), 7.53 – 7.40 (m, 4H), 7.37 (d, *J* = 9.3 Hz, 1H), 7.15 (d, *J* = 7.9 Hz, 1H), 3.80 (s, 2H), 3.70 – 3.55 (m, 12H), 3.36 – 3.28 (m, 2H), 3.26 – 3.21 (m, 2H), 3.19 – 3.03 (m, 10H), 3.02 – 2.96 (m, 2H), 2.82 (bs, 2H), 2.56 (bs, 2H), 2.39 (t, *J* = 6.7 Hz, 6H), 1.14 (bs, 4H)†.

PyrB-PEG6-CH_2COG1(ONa)$_3$ (13)

This reaction was conducted using general procedure 1.3d for formation of sodium carboxylates. The following reagents were used in the stated quantities: **PyrB-PEG6-CH_2COG1(OH)$_3$** (753 mg, 0.822 mmol, 1 eq.), methanol (10 mL) and 1.0000 M $NaOH_{(aq)}$ (2.466 mL, 3 eq.). **PyrB-PEG6-CH_2COG1(ONa)$_3$** was obtained as a hygroscopic yellow solid (807 mg, 100%), ^{1}H NMR (400 MHz, D_2O) δ 7.63 – 7.53 (m, 2H), 7.53 – 7.44 (m, 2H), 7.44 – 7.30 (m, 4H), 7.12 (d, *J* = 7.8 Hz, 1H), 3.91 (s, 2H), 3.75 – 3.61 (m, 12H), 3.54 - 3.49 (m, 2H), 3.49 – 3.43 (m, 2H), 3.42 – 3.36 (m, 2H), 3.36 – 3.29 (m, 2H), 3.29 – 3.24 (m, 2H), 3.24 – 3.05 (m, 12H), 3.04 – 2.96 (m, 2H), 2.81 (bs, 2H), 2.54 (bs, 2H), 2.42 (t, *J* = 6.7 Hz, 6H), 1.12 (bs, 4H)‡.

*1.5: ^{1}H NMR Spectra of Surfactant **1** and precursors **33 – 38***

We were unable to record satisfactory spectra of surfactants **2** – **6** following the conversion of **34** – **38** to their carboxylate salts. We therefore present the ^{1}H NMR spectra of **1** together with

* The proton associated with amide NH group is not visible.
† The proton associated with amide NH group is not visible.
‡ The proton associated with amide NH group is not visible.

those of the 6 precursor carboxylic acids **33** – **38**. In previous comparable studies the acid form of structurally related surfactants was isolated and characterised and the carboxylate formed *in situ* without characterisation.[6-9] The purity of the precursor acids should be representative of the resulting salts as only stoichiometric base and solvent are used in the conversion. All spectra were recorded at 400 MHz.

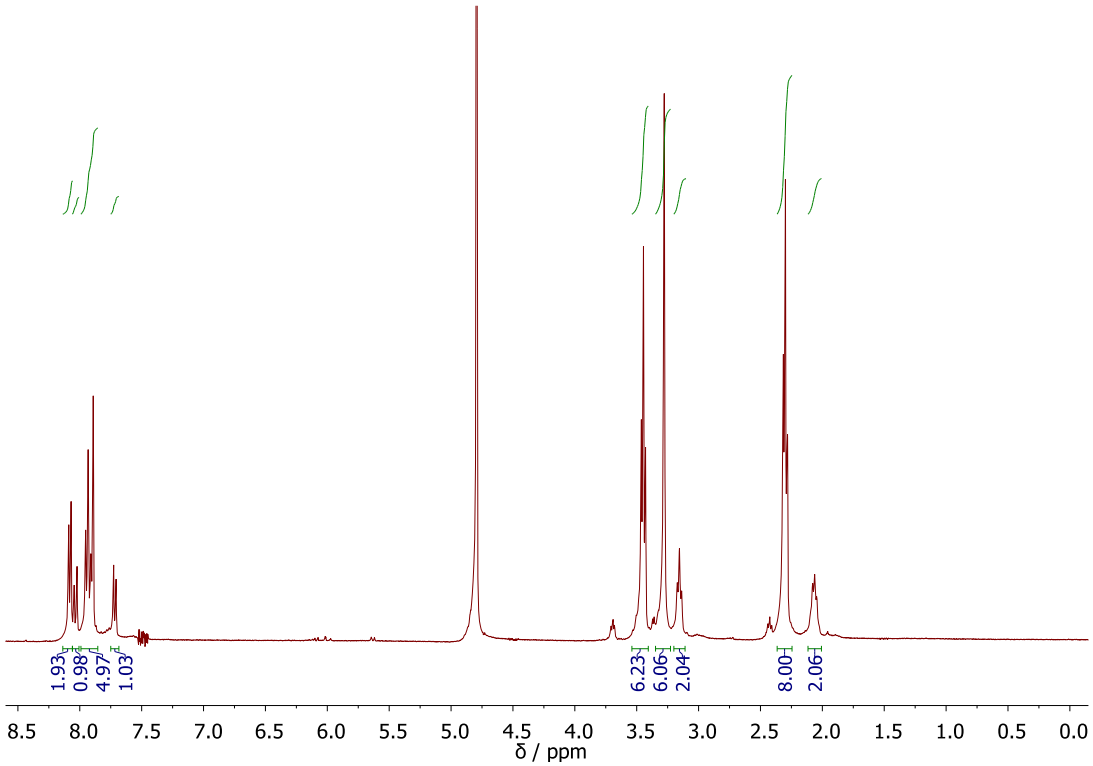


Figure S1. PBA-G1(ONa)$_3$ (1) in D_2O

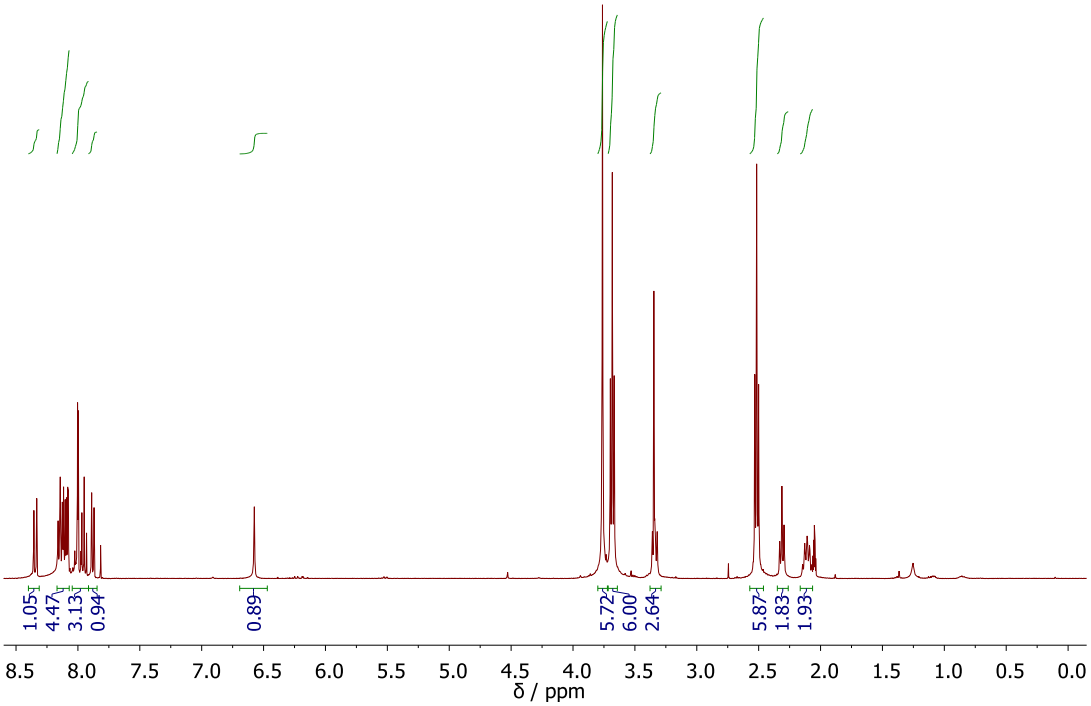


Figure S2. PBA-G1(OH)$_3$ (33) in Acetone-d$_6$

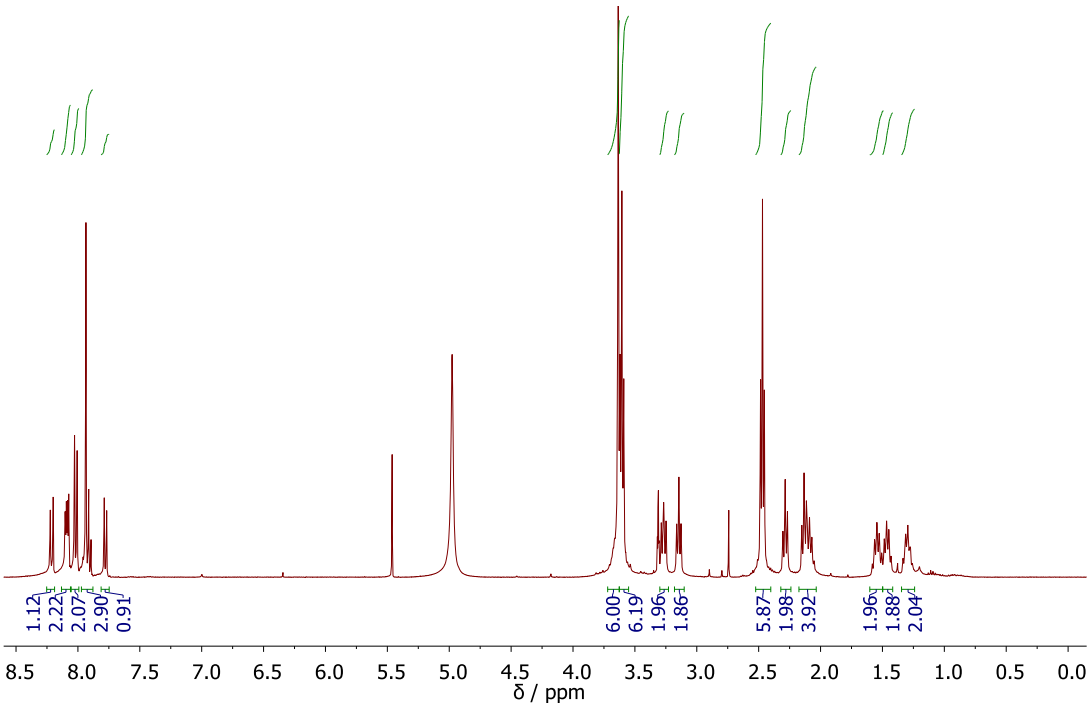


Figure S3. PBA-C6-G1(OH)$_3$ (34) in CD$_3$OD

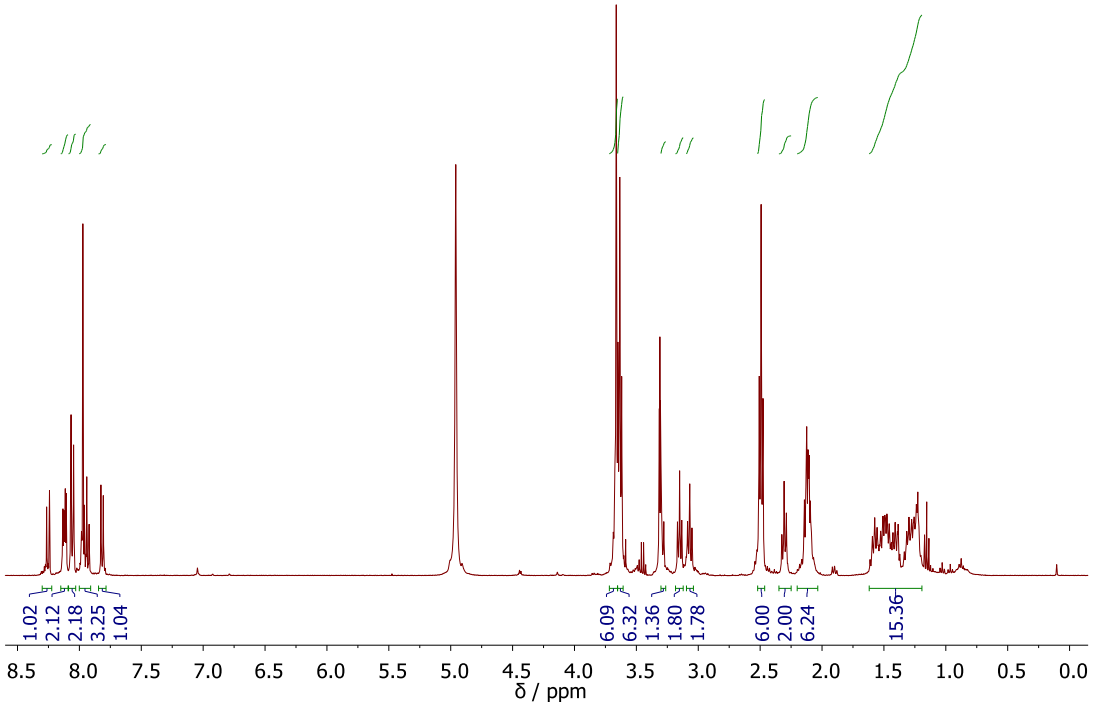


Figure S4. PBA-$(C6)_2$-$G1(OH)_3$ (35) in CD_3OD

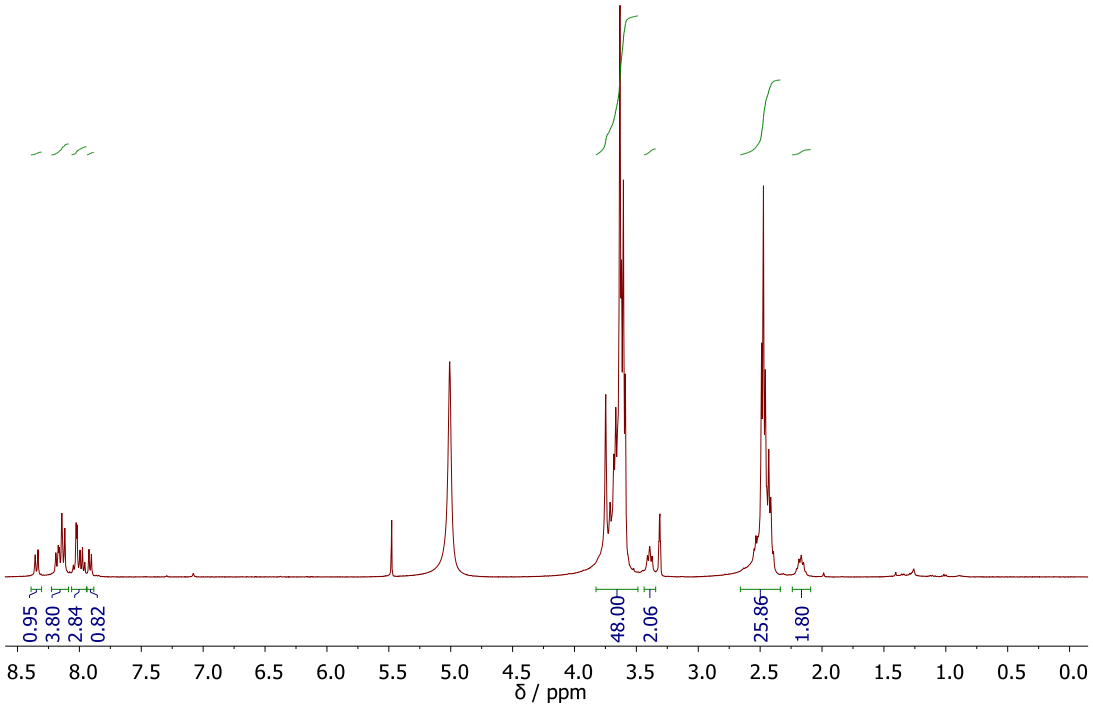


Figure S5. PBA-$G2(OH)_9$ (36) in CD_3OD

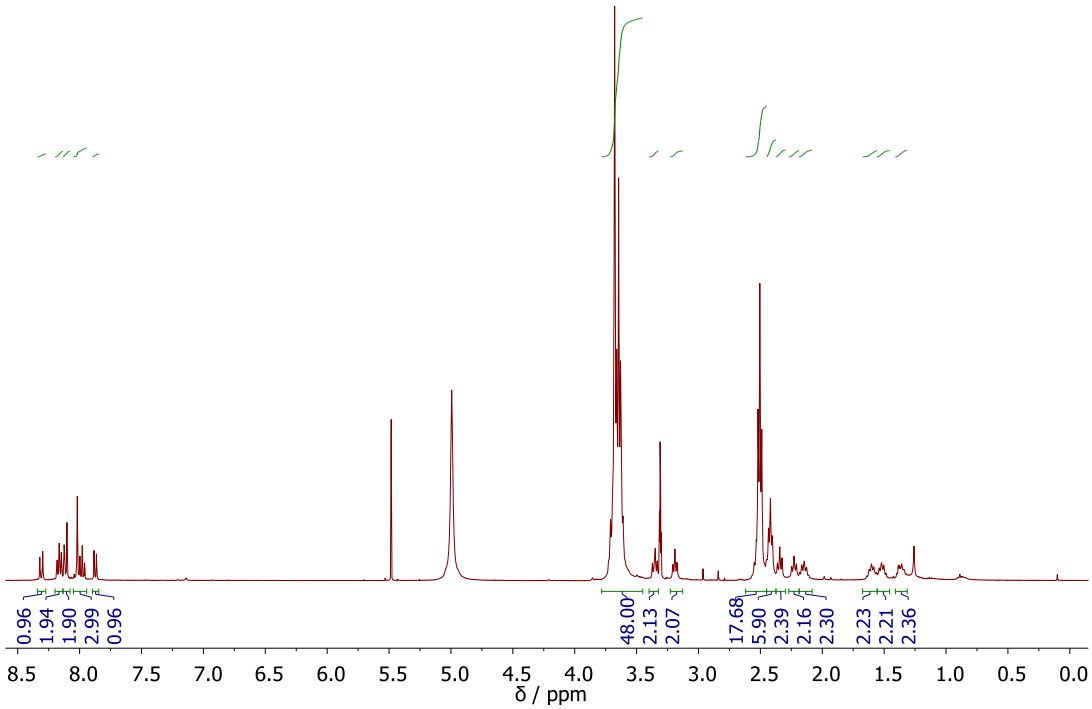


Figure S6. PBA-C6-G2(OH)$_9$ (37) in CD$_3$OD

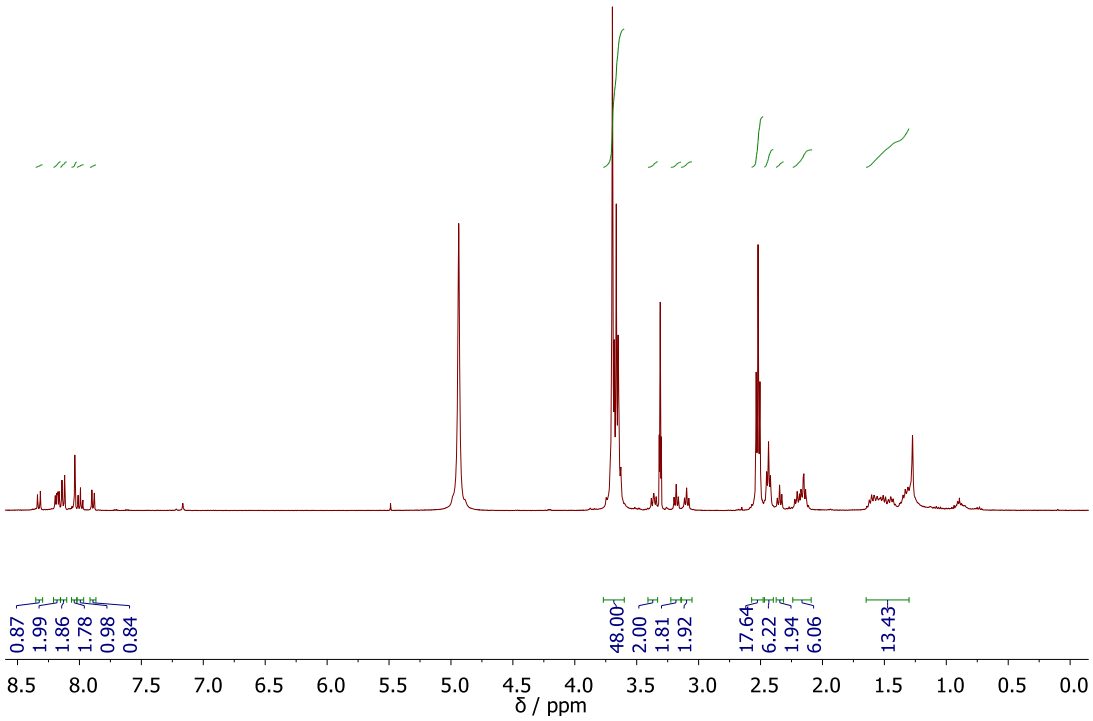


Figure S7. PBA-(C6)$_2$-G2(OH)$_9$ (38) in CD$_3$OD

*1.6: ^{1}H NMR Spectra of Surfactants **7 – 13***

Unlike surfactants **2** – **6**, the PEG linker surfactants **7** – **13** afforded suitable ^{1}H NMR spectra, presented below. All spectra were recorded at 400 MHz.

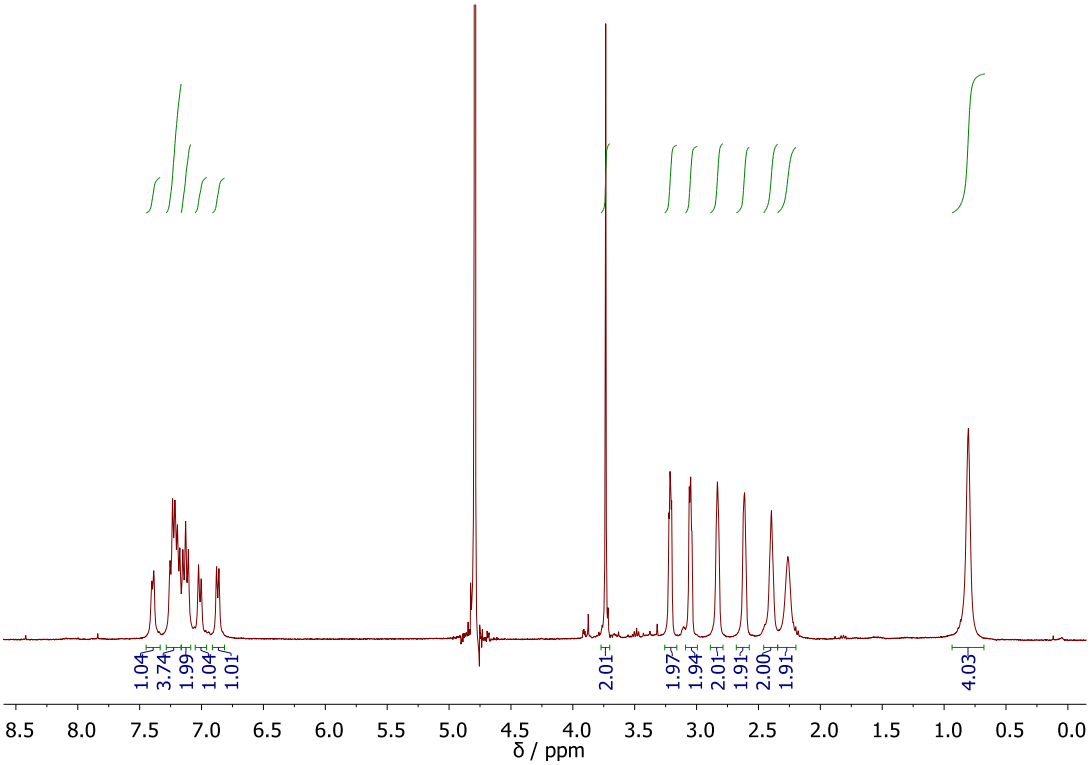


Figure S8. PyrB-PEG2-CH_2COONa (7) in D_2O

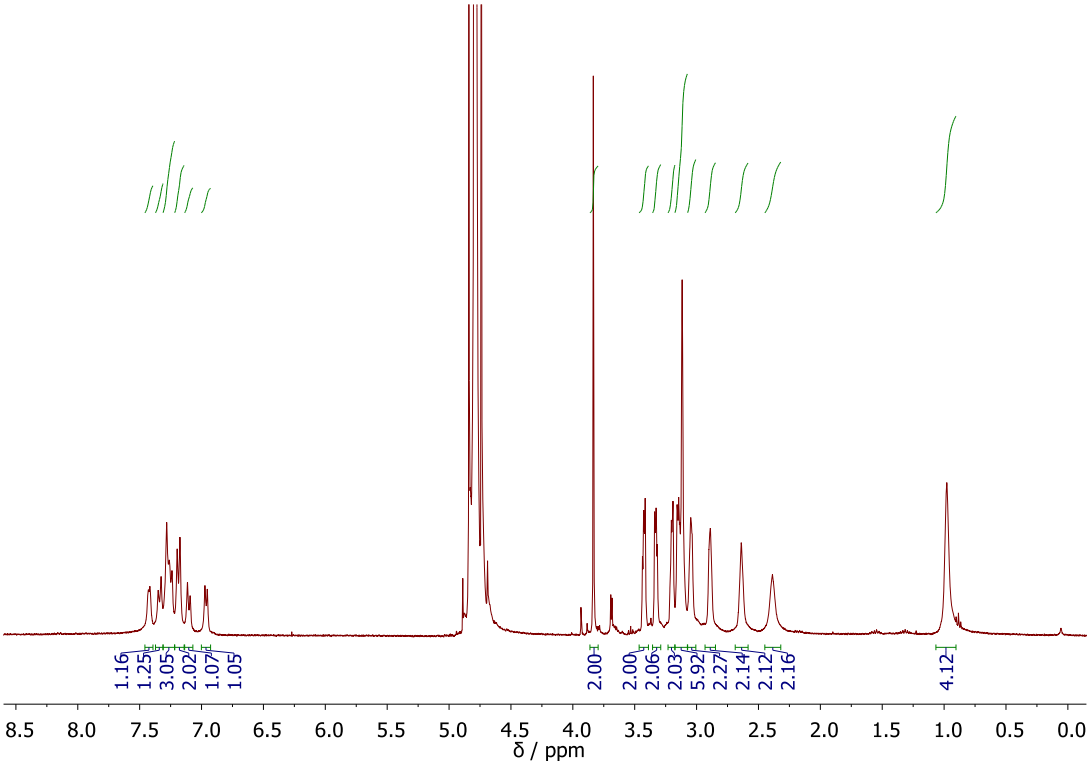


Figure S9. PyrB-PEG4-CH_2COONa (8) in D_2O

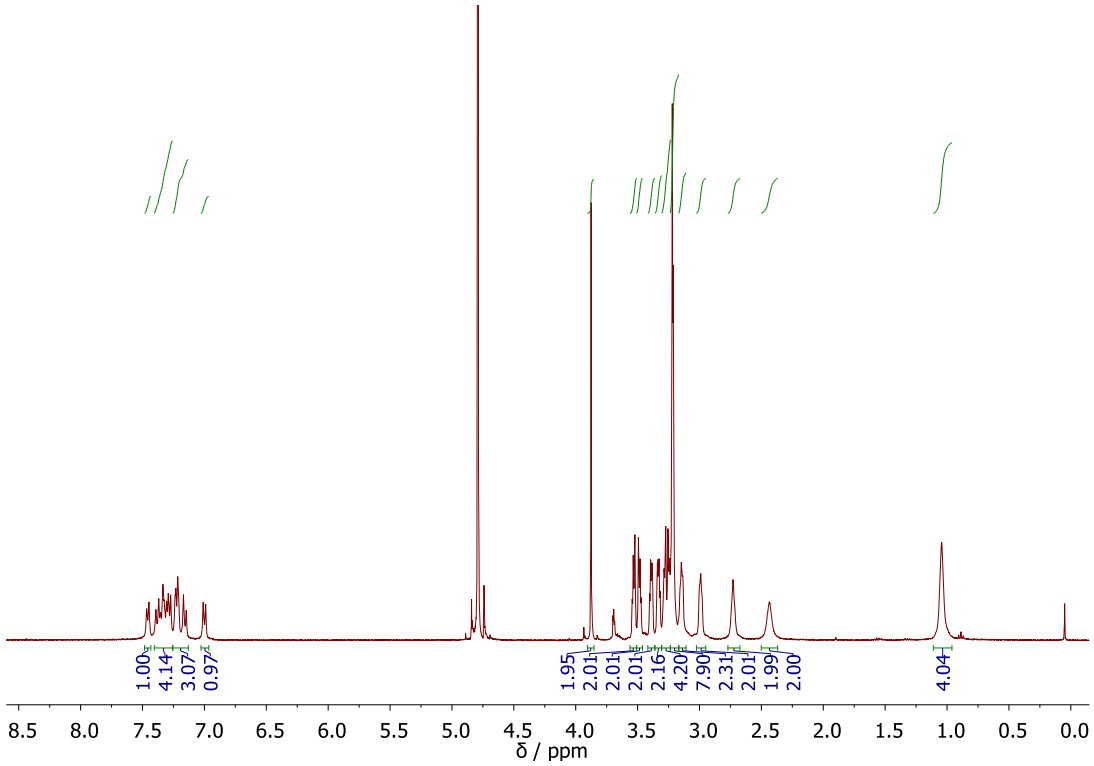


Figure S10. PyrB-PEG6-CH_2COONa (9) in D_2O.

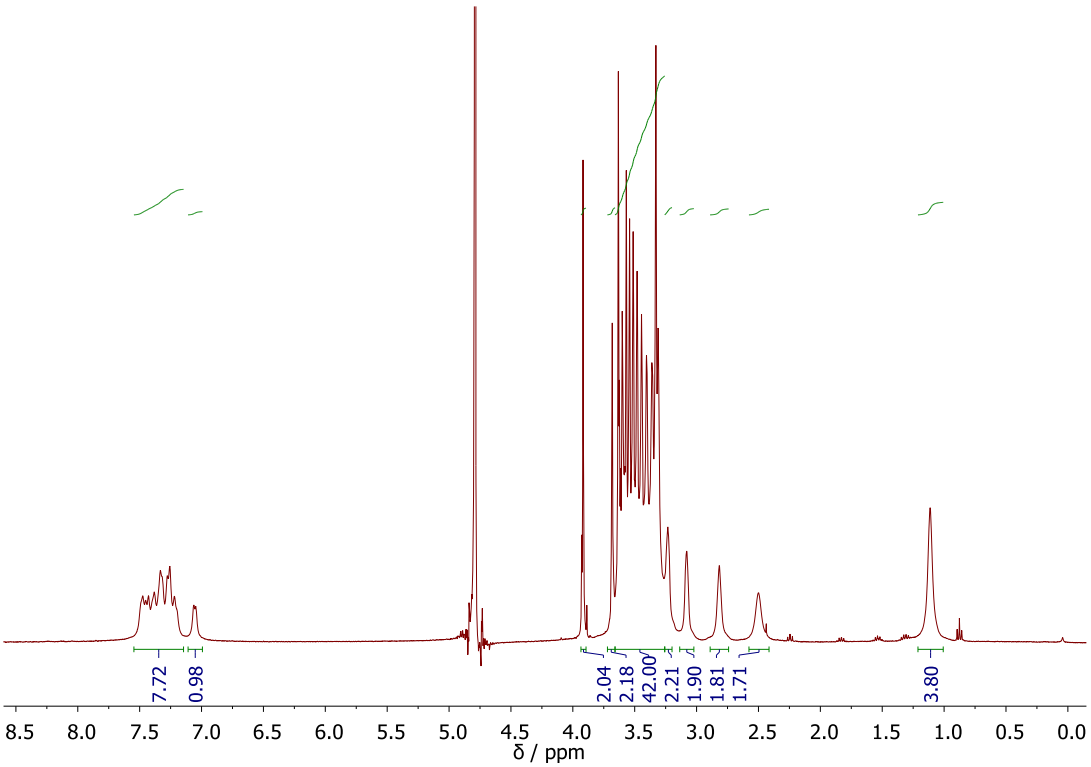


Figure S11. PyrB-PEG12-CH_2COONa (10) in D_2O

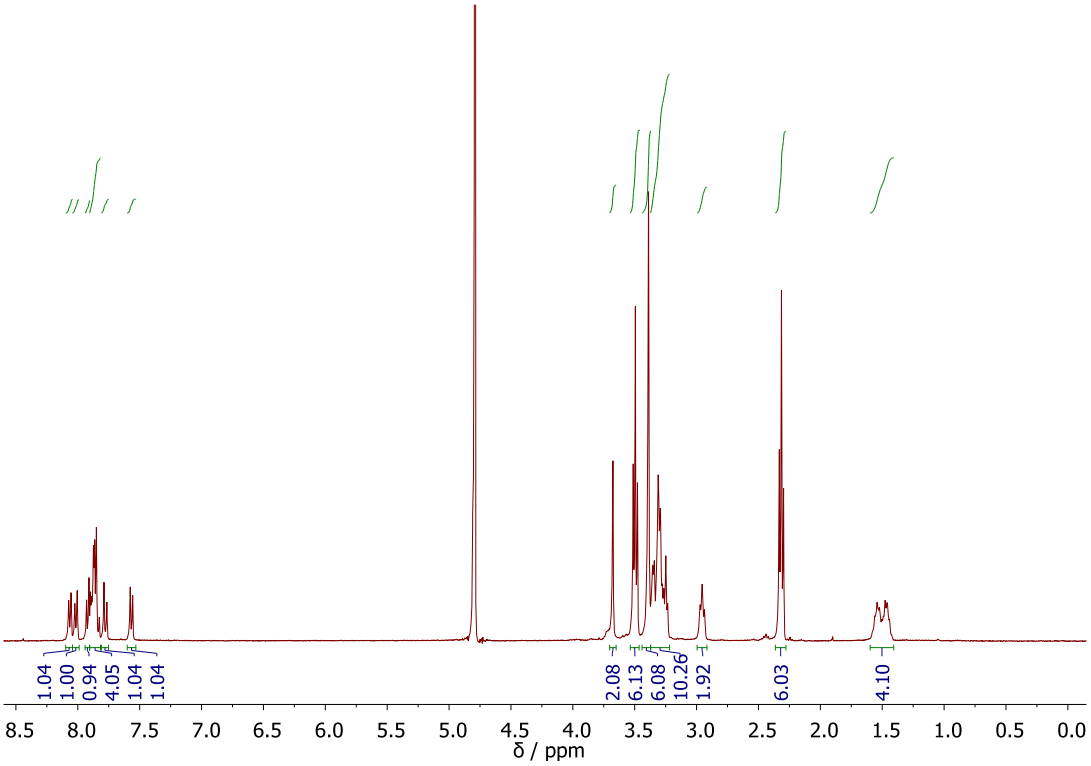


Figure S12. PyrB-PEG2-$CH_2COG1(ONa)_3$ (11) in D_2O

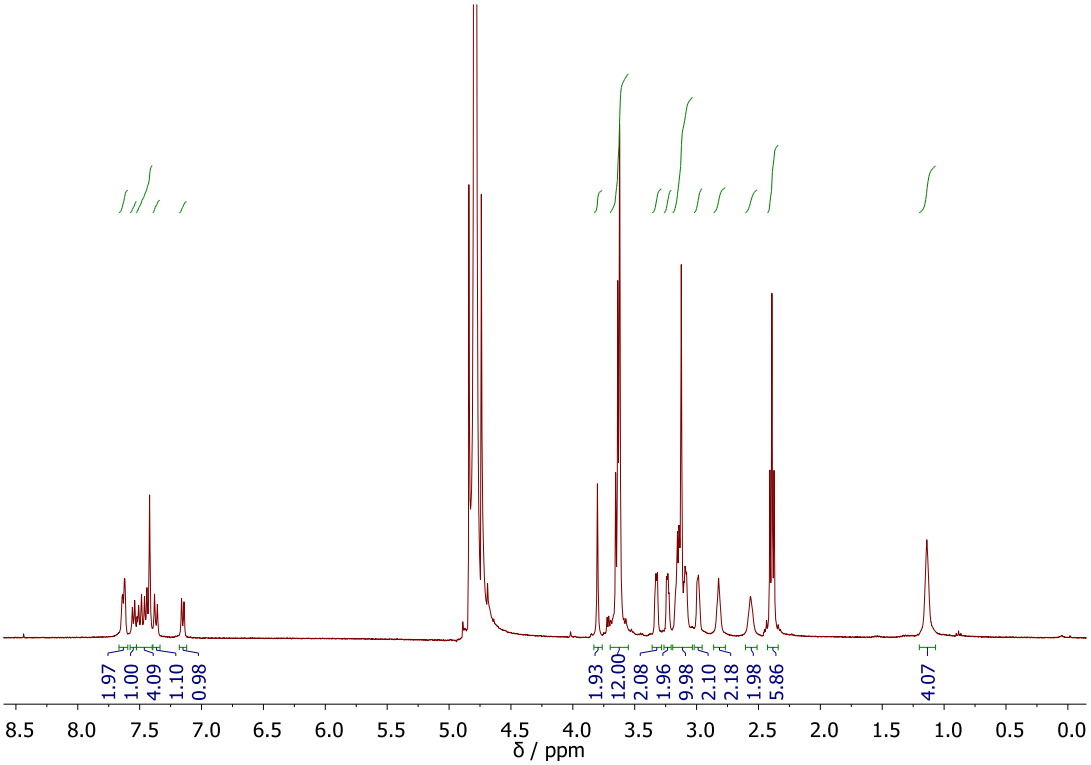


Figure S13. PyrB-PEG4-$CH_2COG1(ONa)_3$ (12) in D_2O

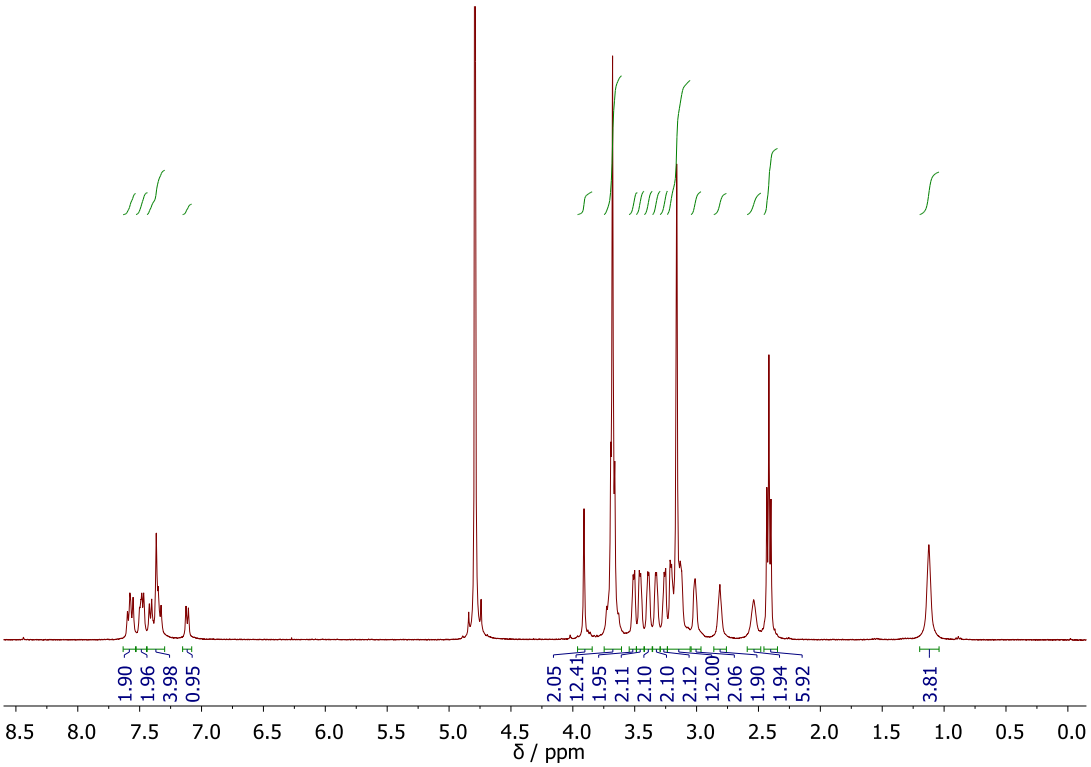


Figure S14. PyrB-PEG6-$CH_2COG1(ONa)_3$ (13) in D_2O

1.7: ^{1}H NMR Spectra of Key Intermediates

Below are ^{1}H NMR spectra of selected intermediates from the syntheses of surfactants **1** – **13**. All spectra were recorded at 400 MHz, unless otherwise stated.

1.7.1: *tert*-Butyl ester protected precursors of C6 linker surfactants

N.B. The top of the large peak relating to the *tert*-butyl moiety at around 1.4 ppm is cropped for clarity in all spectra.

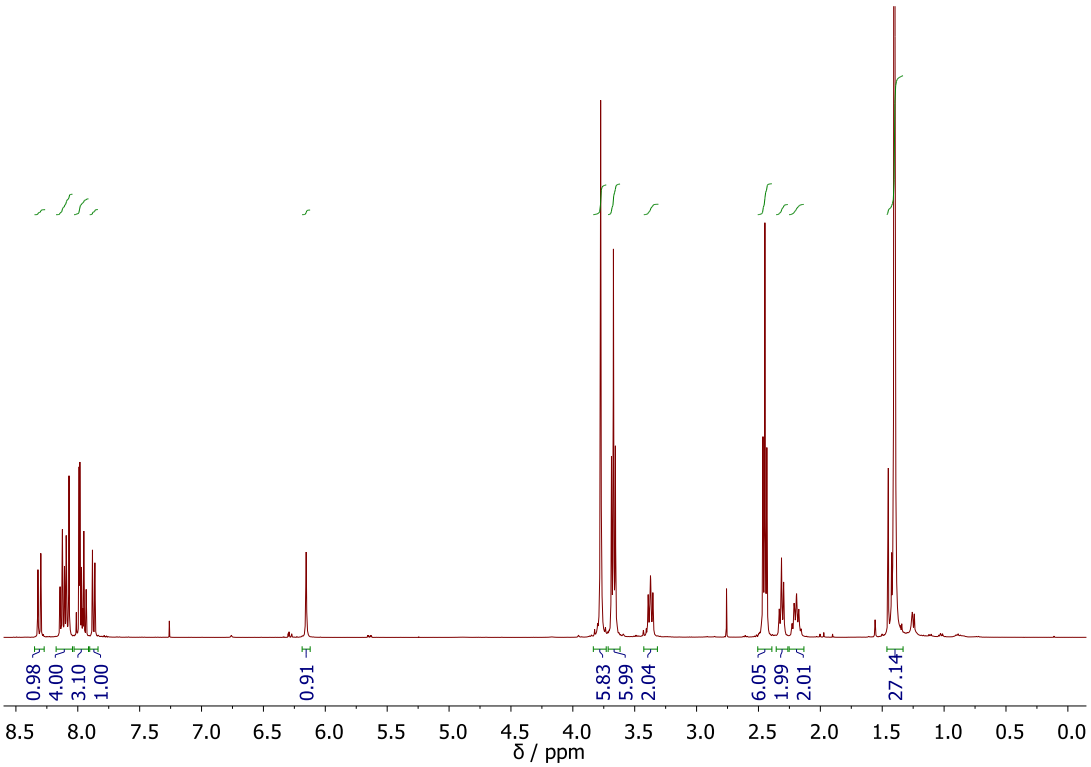


Figure S15. PBA-G1($O^{t}Bu$)$_3$ (27) in $CDCl_3$

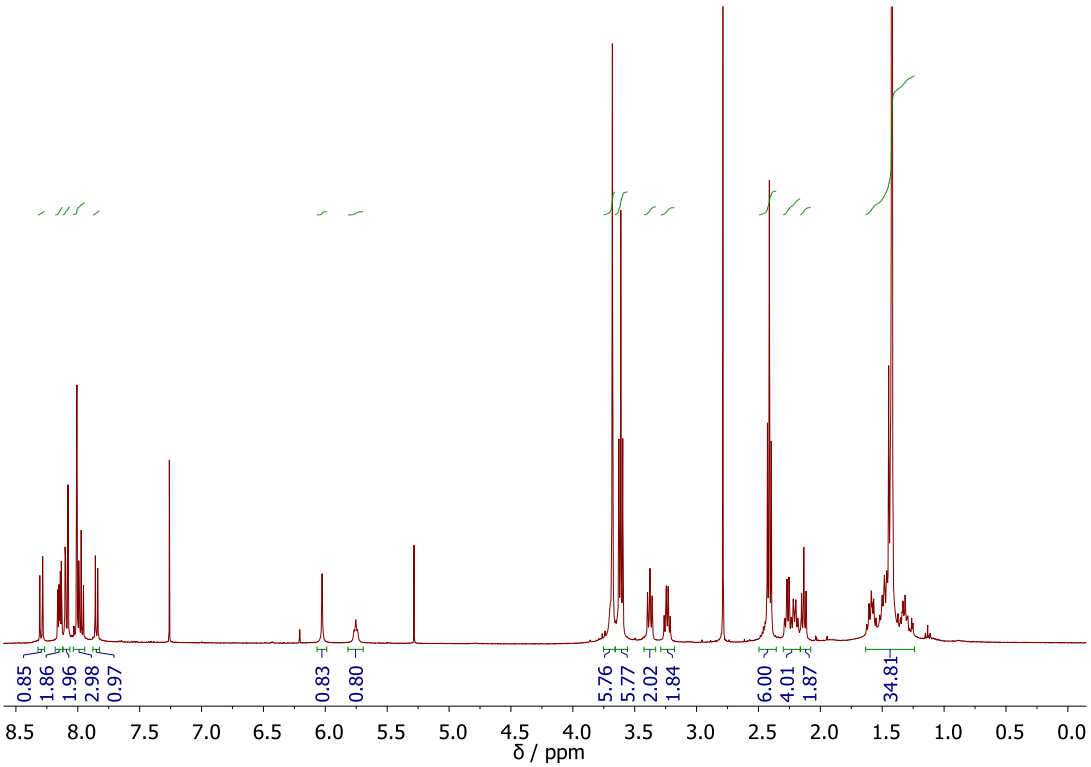


Figure S16. PBA-C6-G1(O^tBu)$_3$ (28) in $CDCl_3$

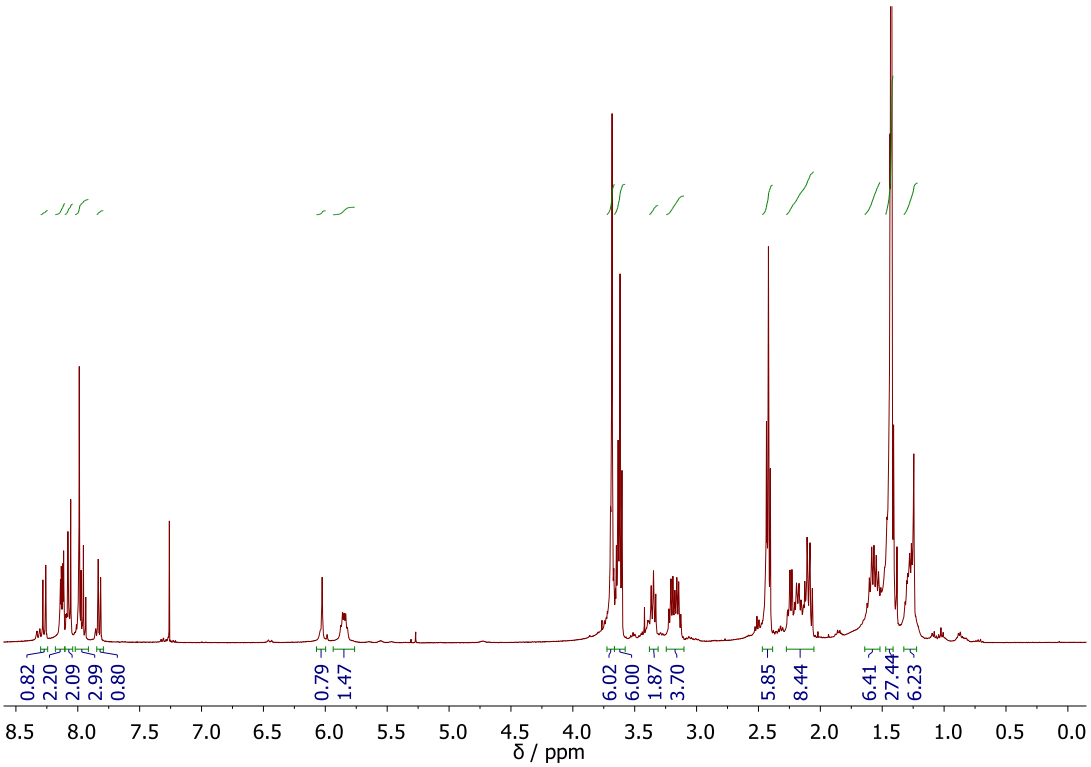


Figure S17. PBA-(C6)$_2$-G1(O^tBu)$_3$ (29) in $CDCl_3$

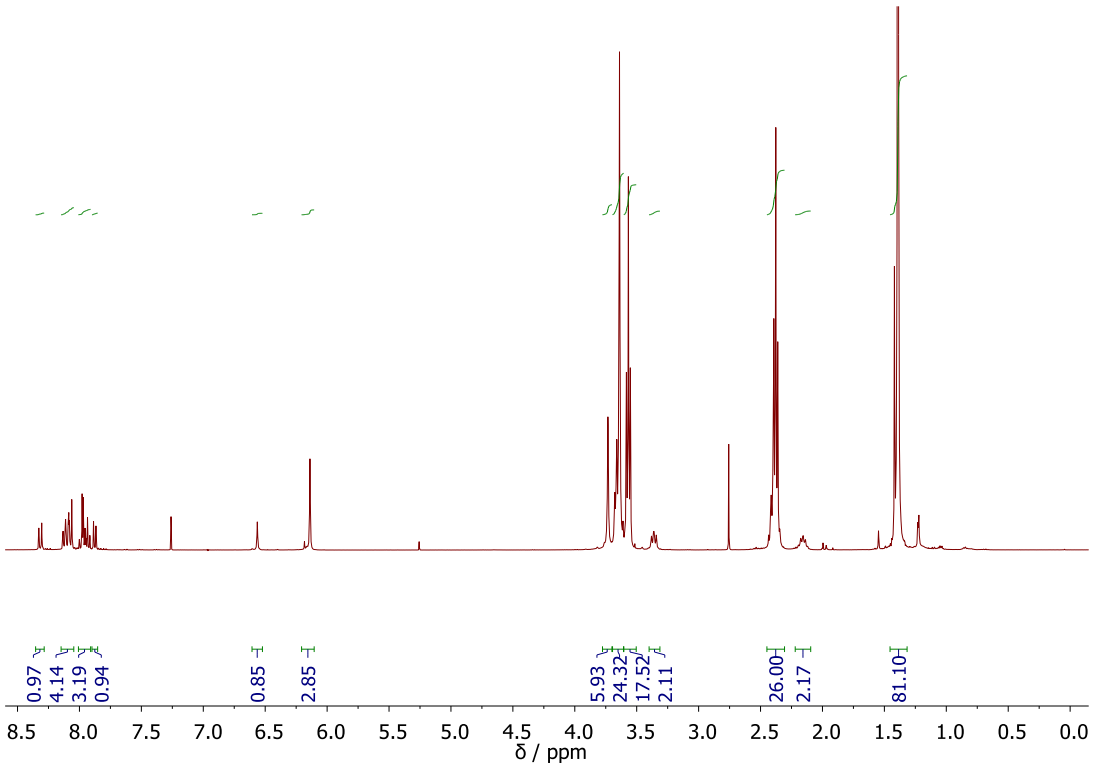


Figure S18. PBA-G2(O^{t}Bu)$_9$ (30) in CDCl$_3$

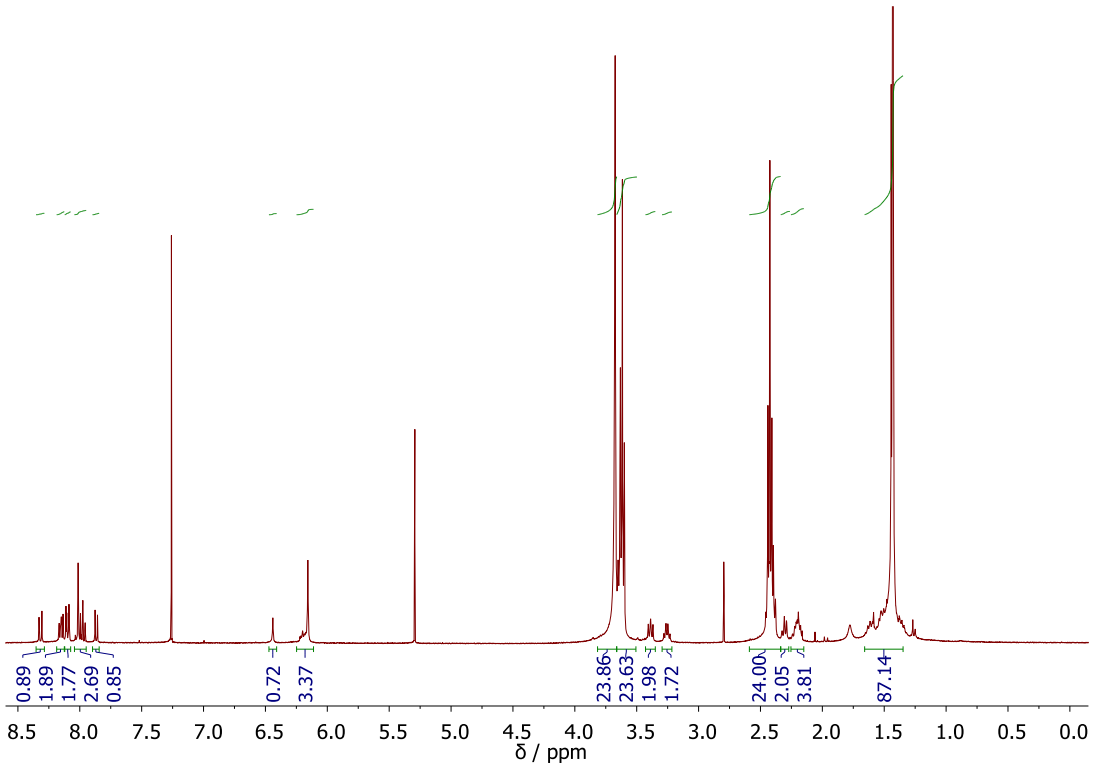


Figure S19. PBA-C6-G2(O^{t}Bu)$_9$ (31) in CDCl$_3$

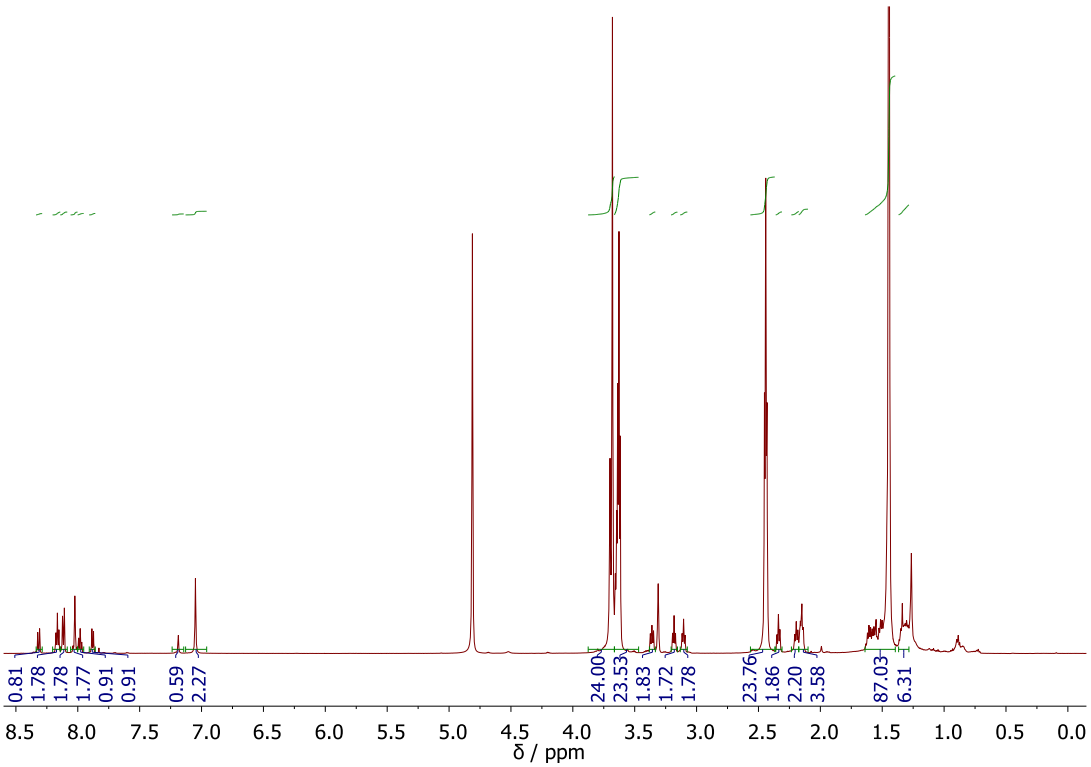


Figure S20. PBA-$(C6)_2$-G2$(O^tBu)_9$ (32) in CD_3OD (600 MHz)

1.7.2: Z-protected C6-functionalised head groups

N.B. The top of the large peak relating to the *tert*-butyl moiety at around 1.4 ppm is cropped for clarity in all spectra.

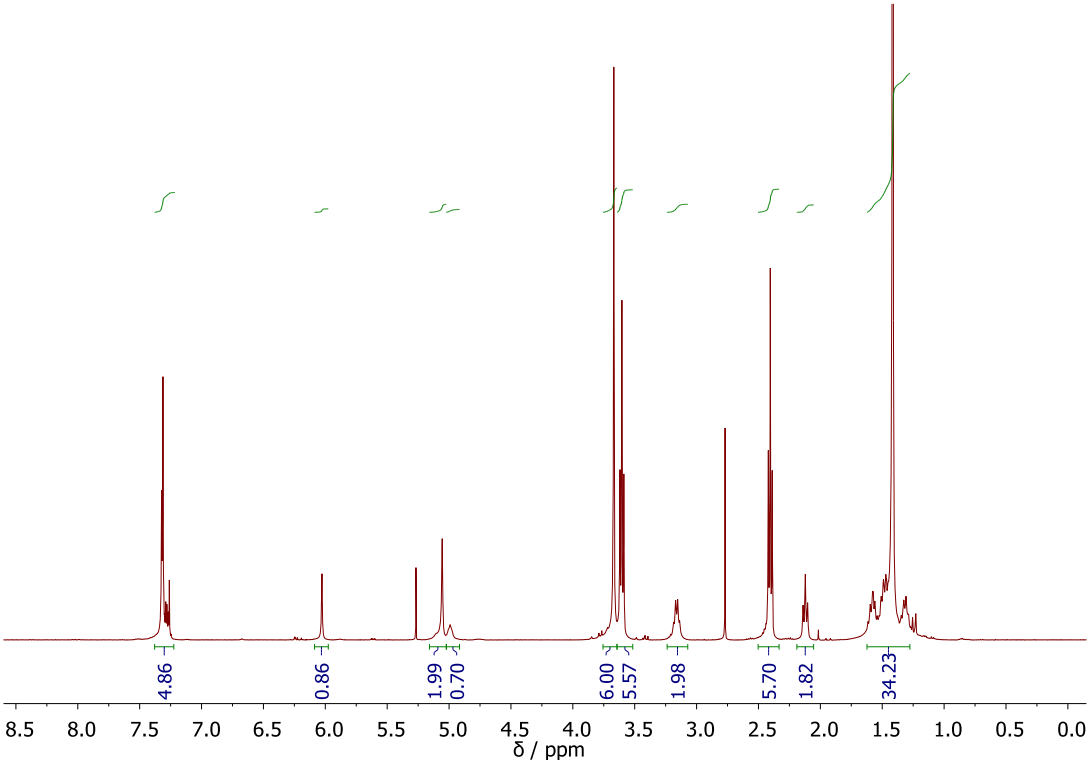


Figure S21. Z-C6-G1(O^tBu)$_3$ (19) in $CDCl_3$

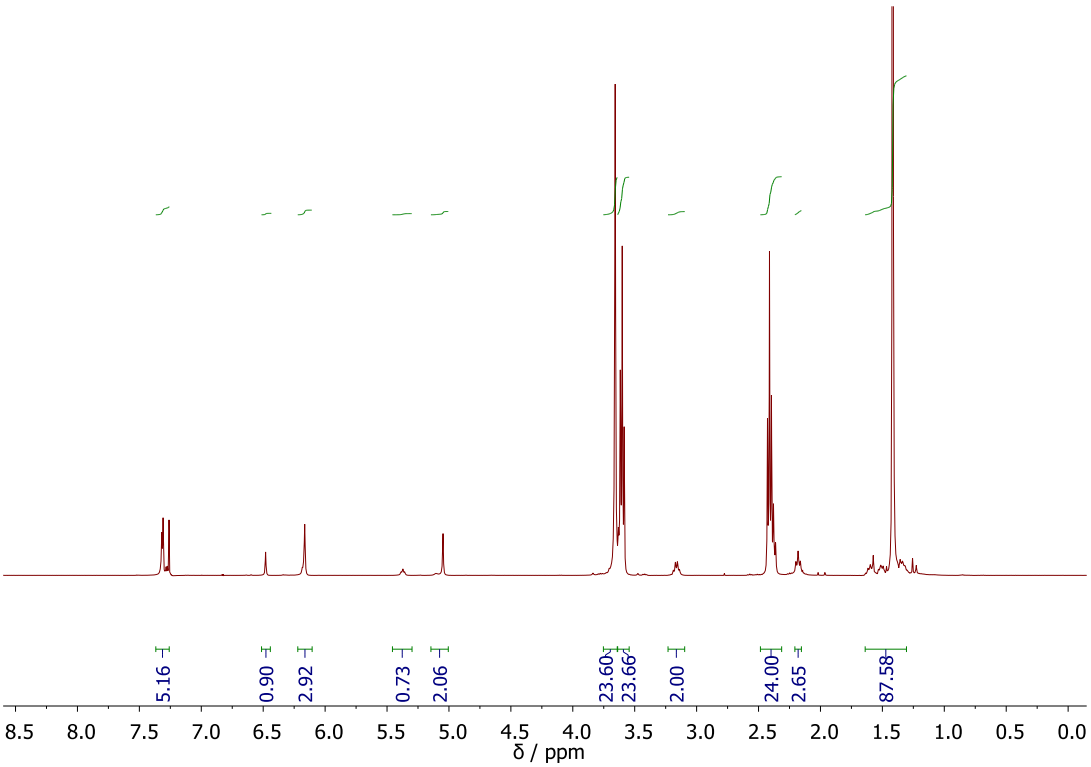


Figure S22. Z-C6-G2(O^{t}Bu)$_9$ (20) in CDCl$_3$

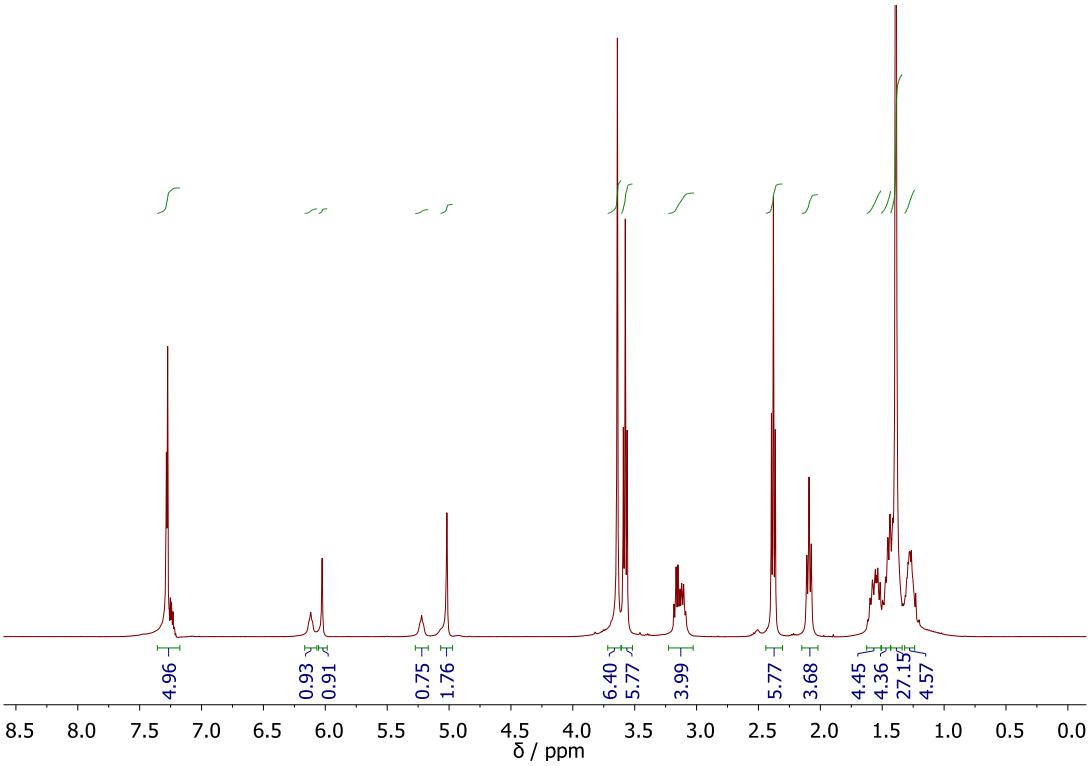


Figure S23. Z-(C6)$_2$-G1(O^{t}Bu)$_3$ (23) in CDCl$_3$

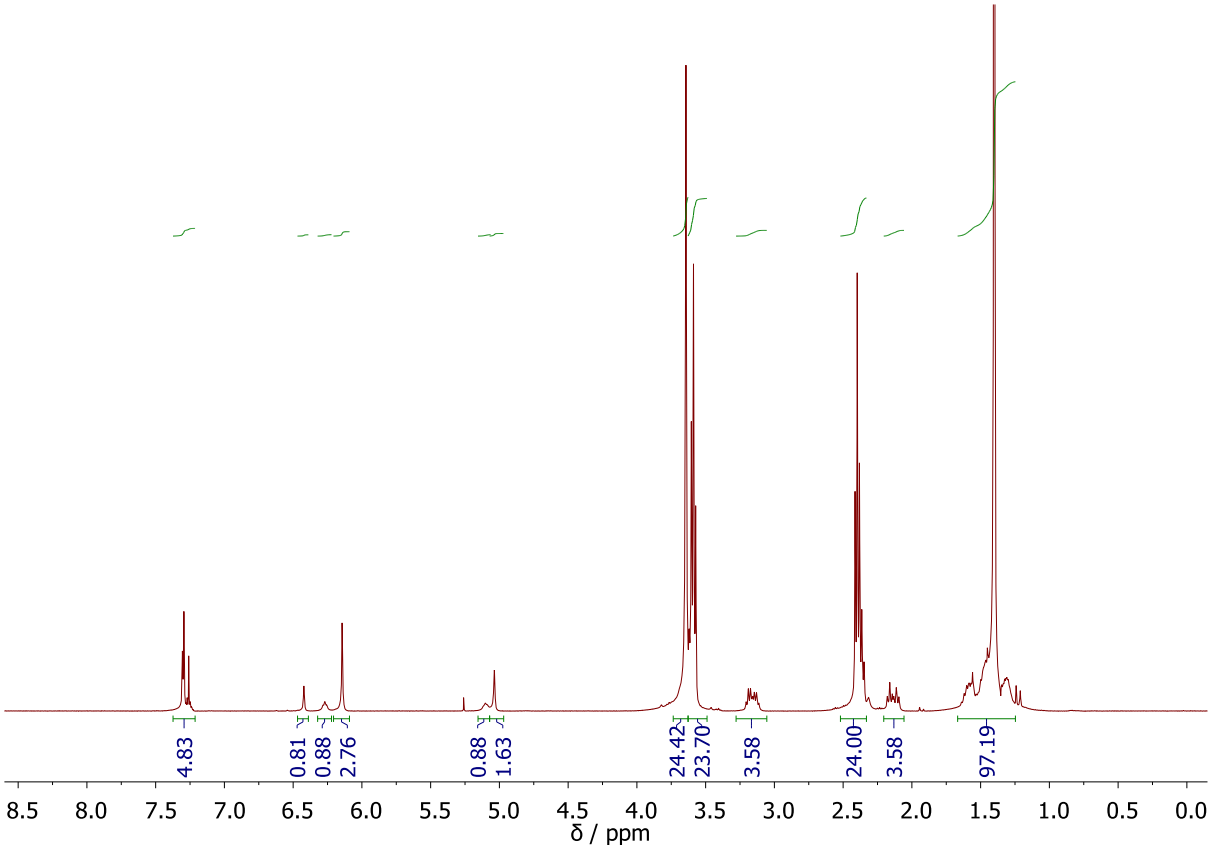


Figure S24. Z-$(C6)_2$-G2$(O^tBu)_9$ (24) in $CDCl_3$

1.7.3: Acid precursors of PEG linker surfactants

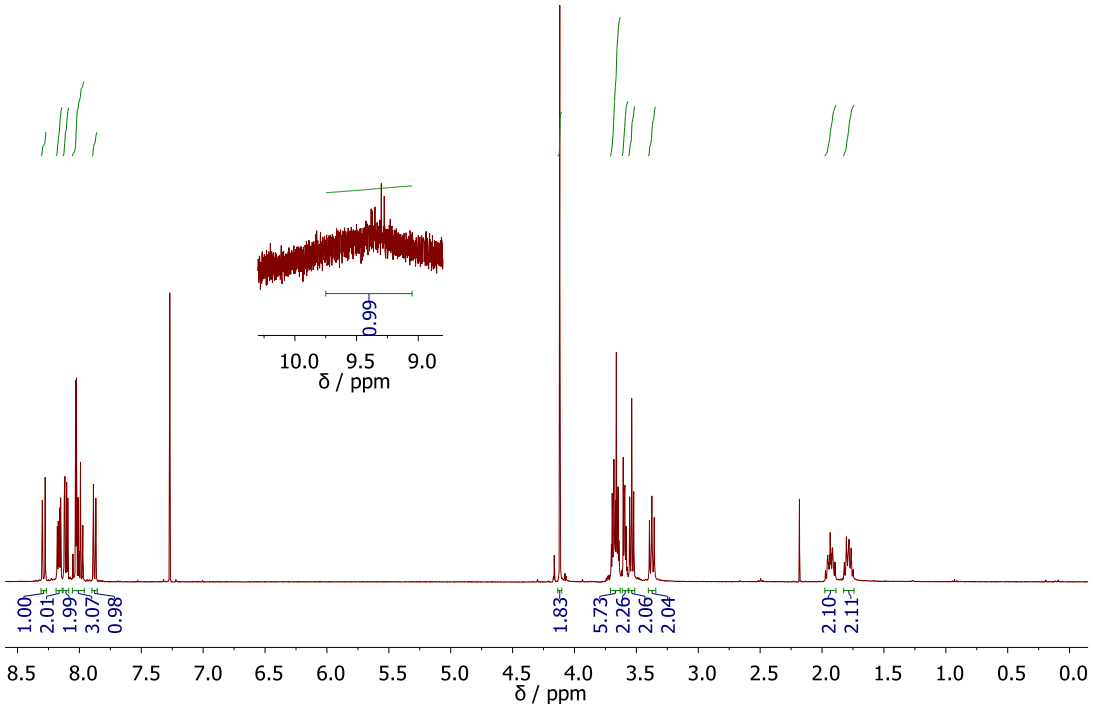


Figure S25. PyrB-PEG2-CH_2COOH (52) in $CDCl_3$. The inset peak is separated to allow use of the same *x*-axis as other spectra for ease of comparison.

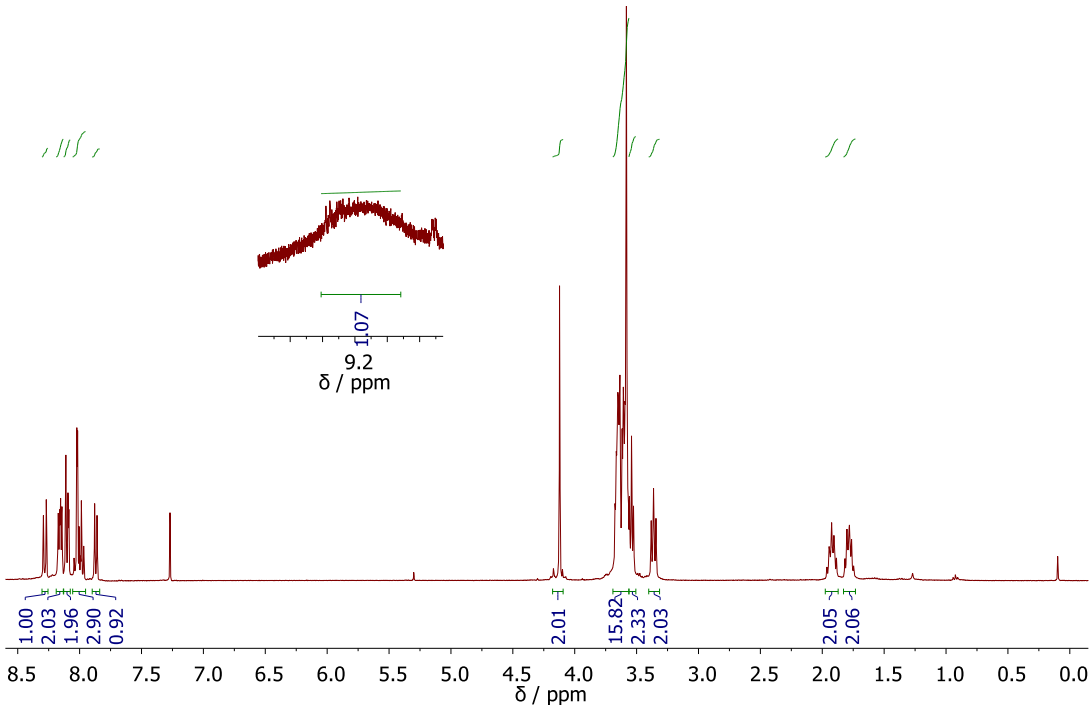


Figure S26. PyrB-PEG4-CH_2COOH (53) in $CDCl_3$. The inset peak is separated to allow use of the same *x*-axis as other spectra for ease of comparison.

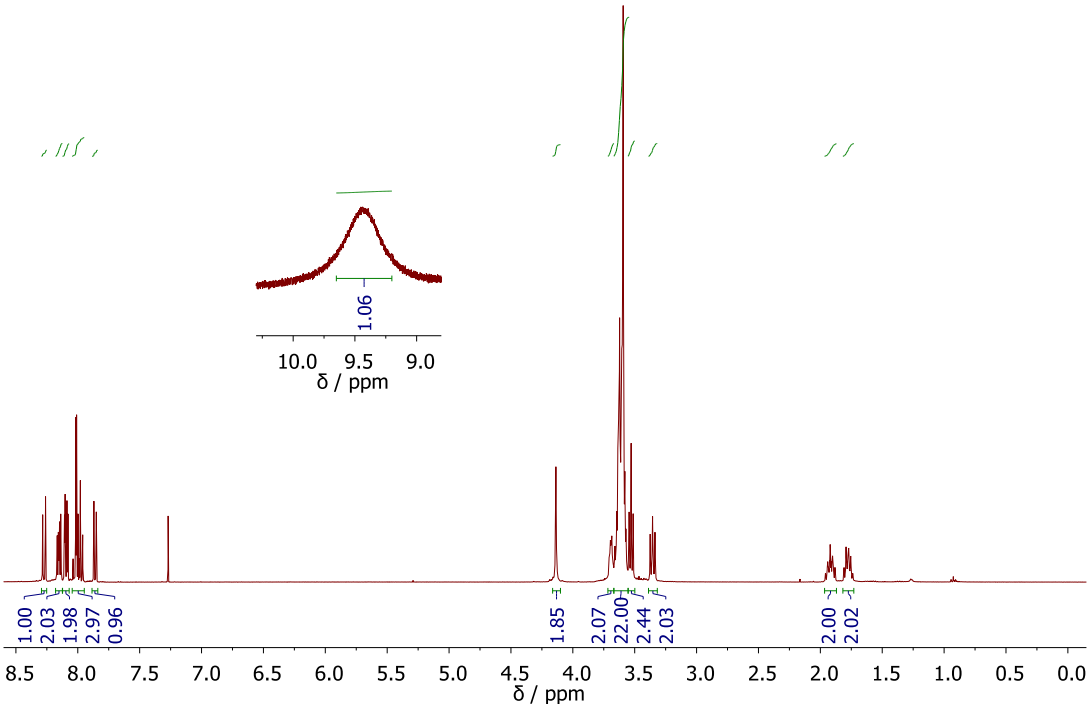


Figure S27. PyrB-PEG6-CH_2COOH (54) in $CDCl_3$. The inset peak is separated to allow use of the same *x*-axis as other spectra for ease of comparison.

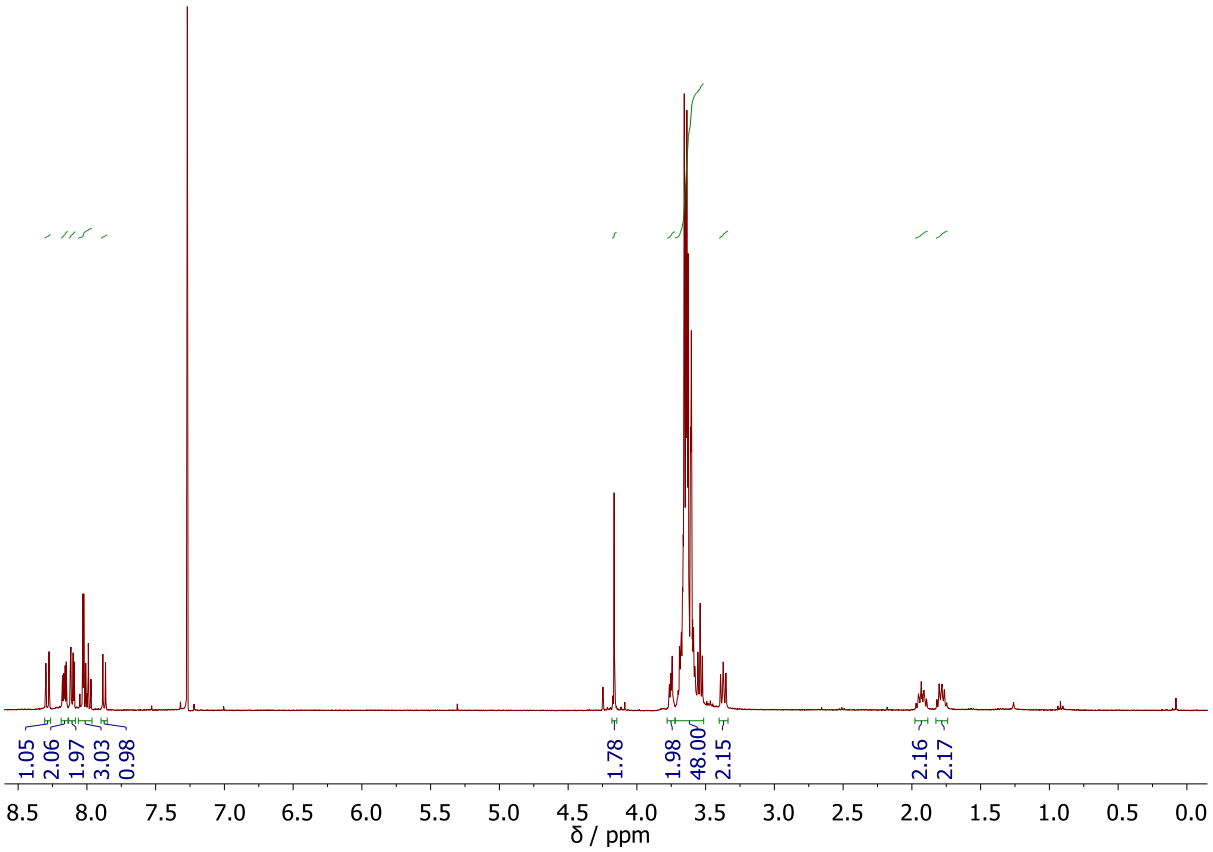


Figure S28. PyrB-PEG12-CH_2COOH (55) in $CDCl_3$

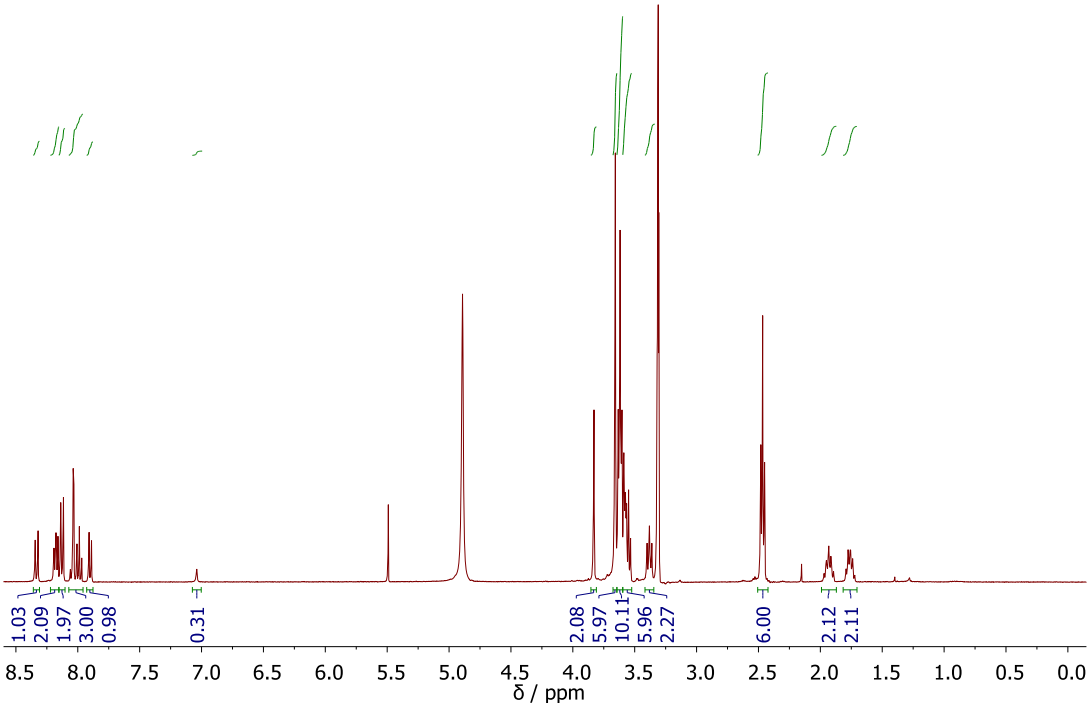


Figure S29. PyrB-PEG2-$CH_2COG1(OH)_3$ (59) in CD_3OD

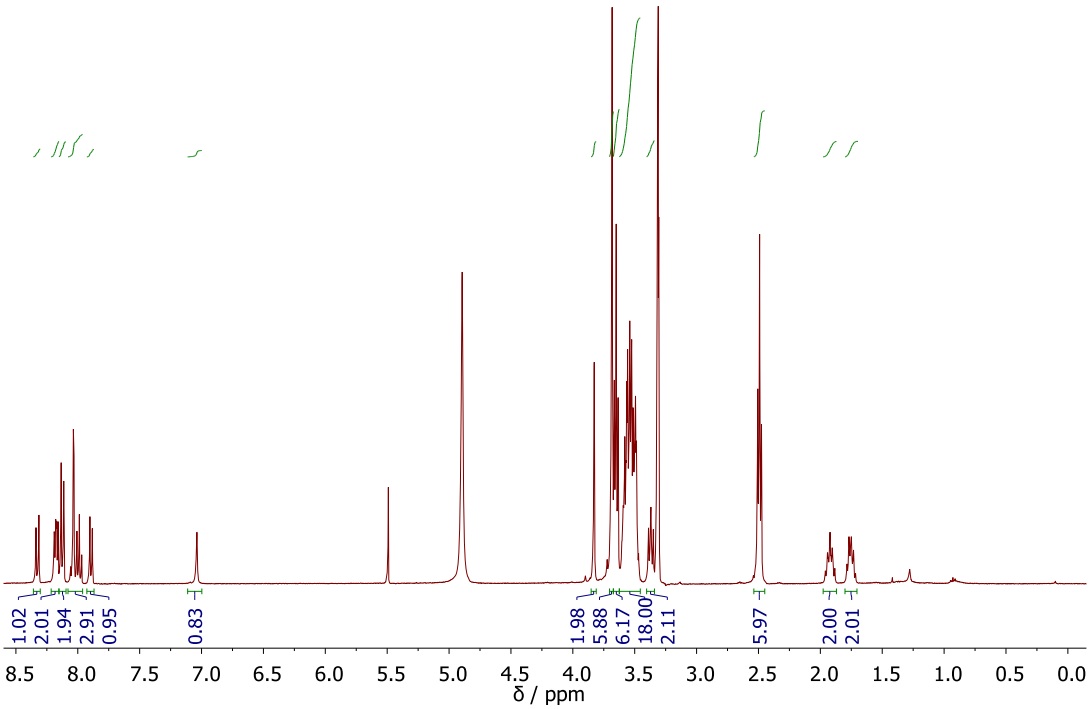


Figure S30. PyrB-PEG4-$CH_2COG1(OH)_3$ (60) in CD_3OD

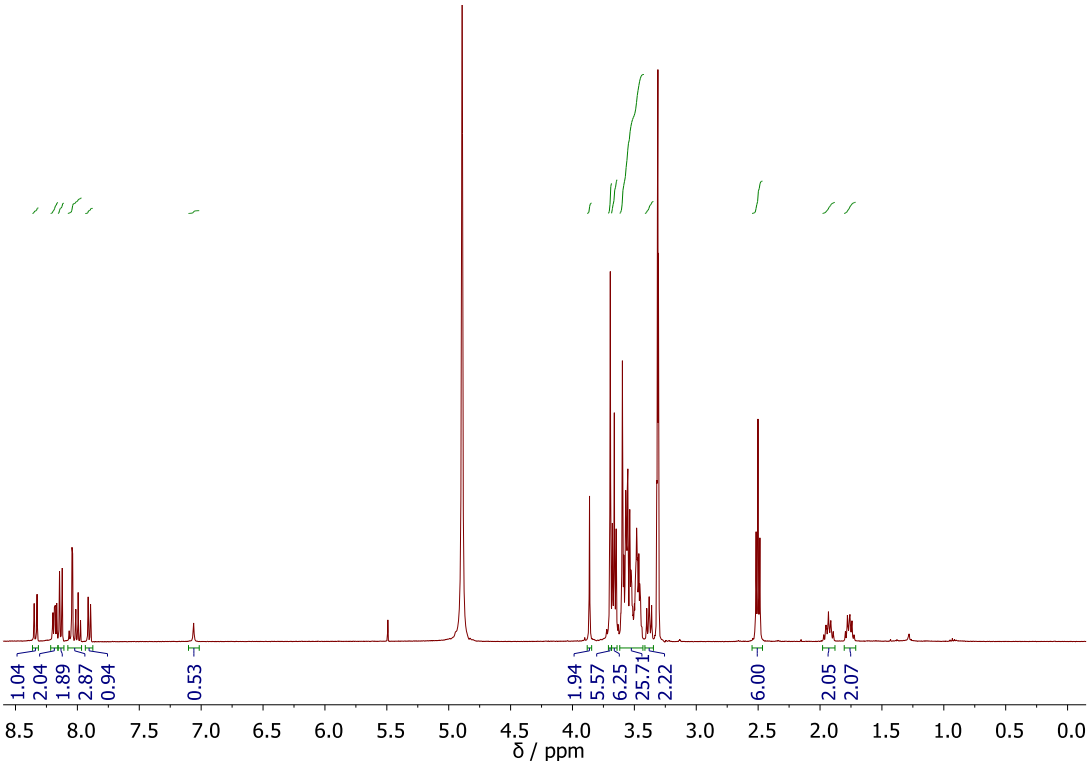


Figure S31. PyrB-PEG6-$CH_2COG1(OH)_3$ (61) in CD_3OD

1.7.4: *tert*-Butyl ester protected precursors of G1 PEG linker surfactants

N.B. The top of the large peak relating to the *tert*-butyl moiety at around 1.4 ppm is cropped for clarity in all spectra.

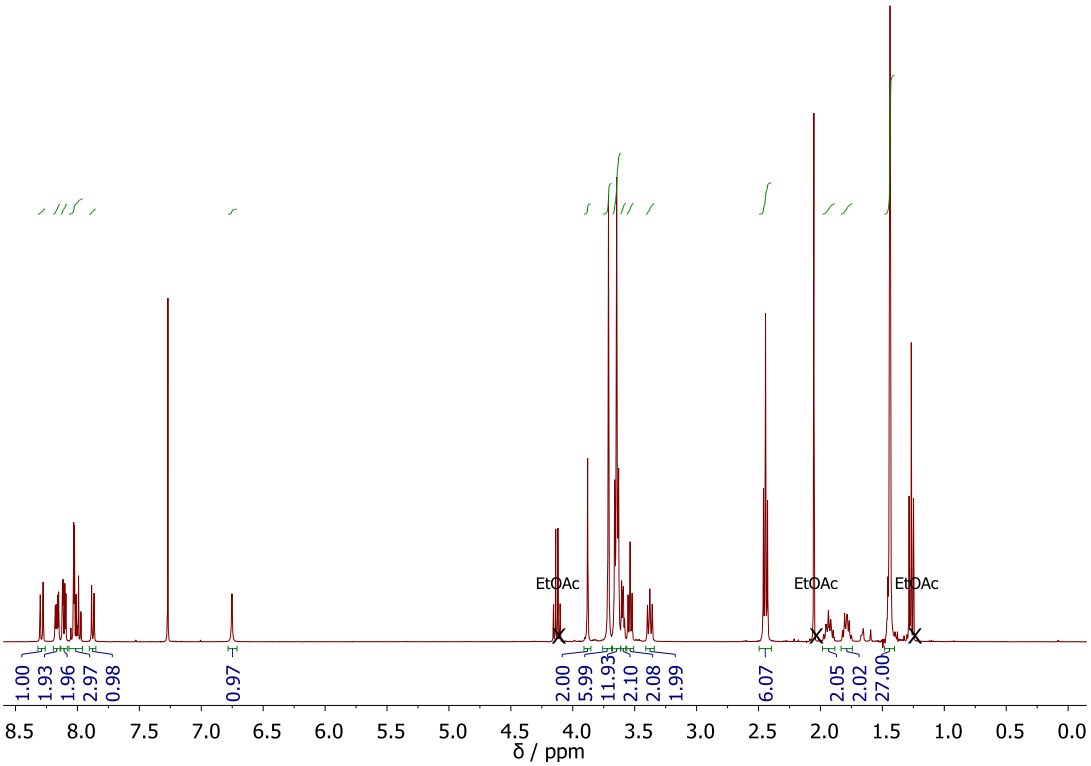


Figure S32. PyrB-PEG2-CH_2COG1(O^tBu)$_3$ (56) in $CDCl_3$

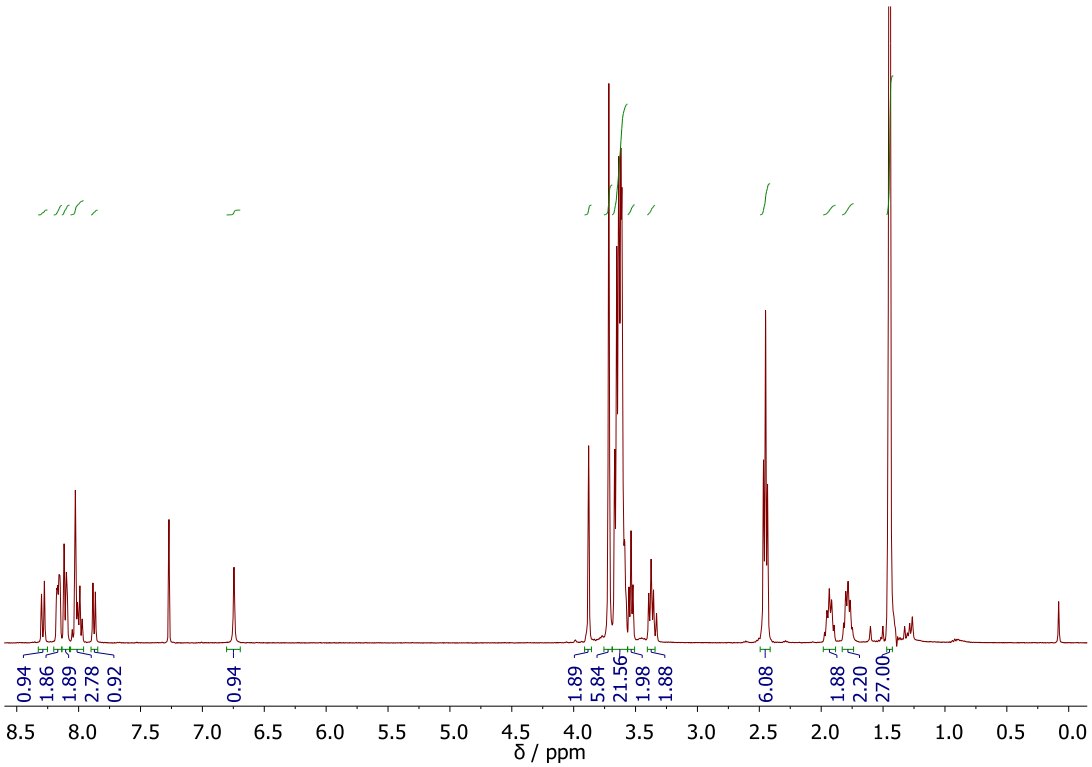


Figure S33. PyrB-PEG4-$CH_2COG1(O^tBu)_3$ (57) in $CDCl_3$

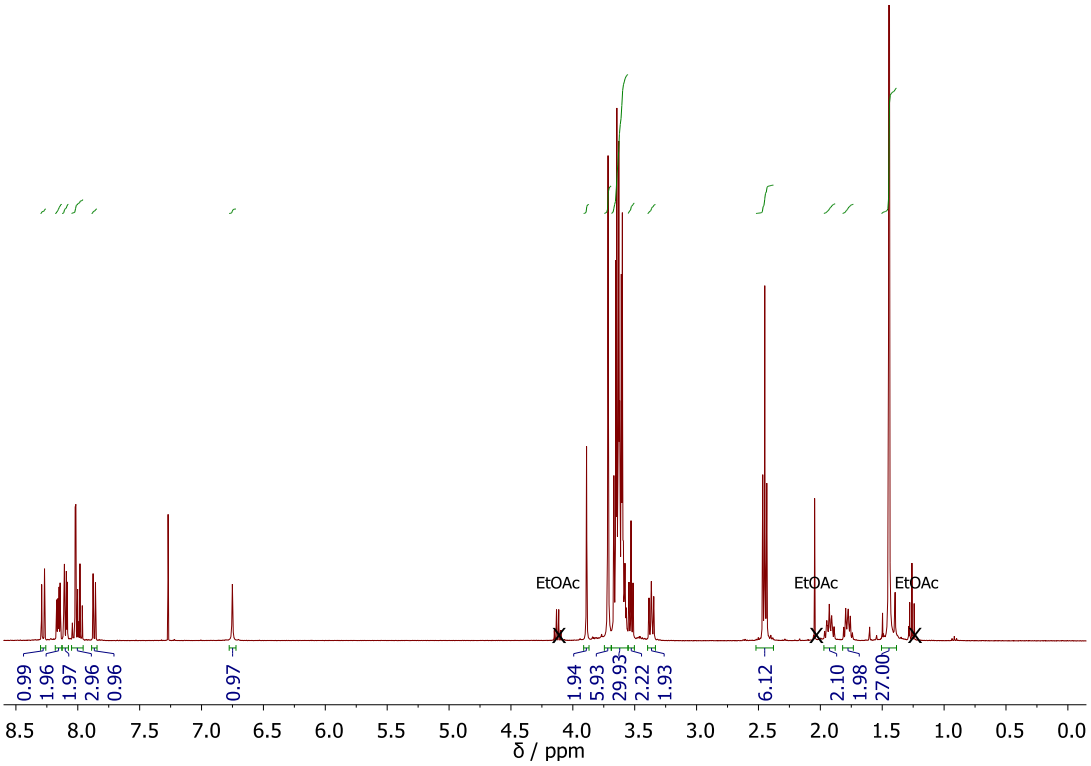


Figure S34. PyrB-PEG6-$CH_2COG1(O^tBu)_3$ (58) in $CDCl_3$

1.7.5: PEG-functionalised pyrenebutanol intermediates (PyrB-PEGn)

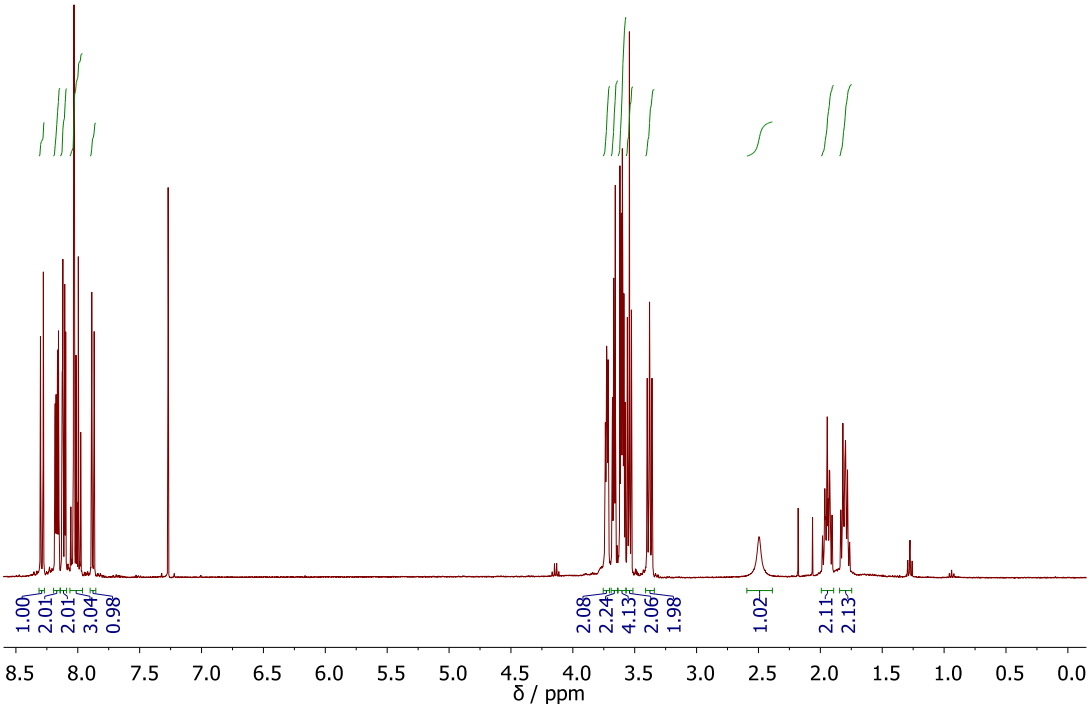


Figure S35. PyrB-PEG2 (48) in $CDCl_3$

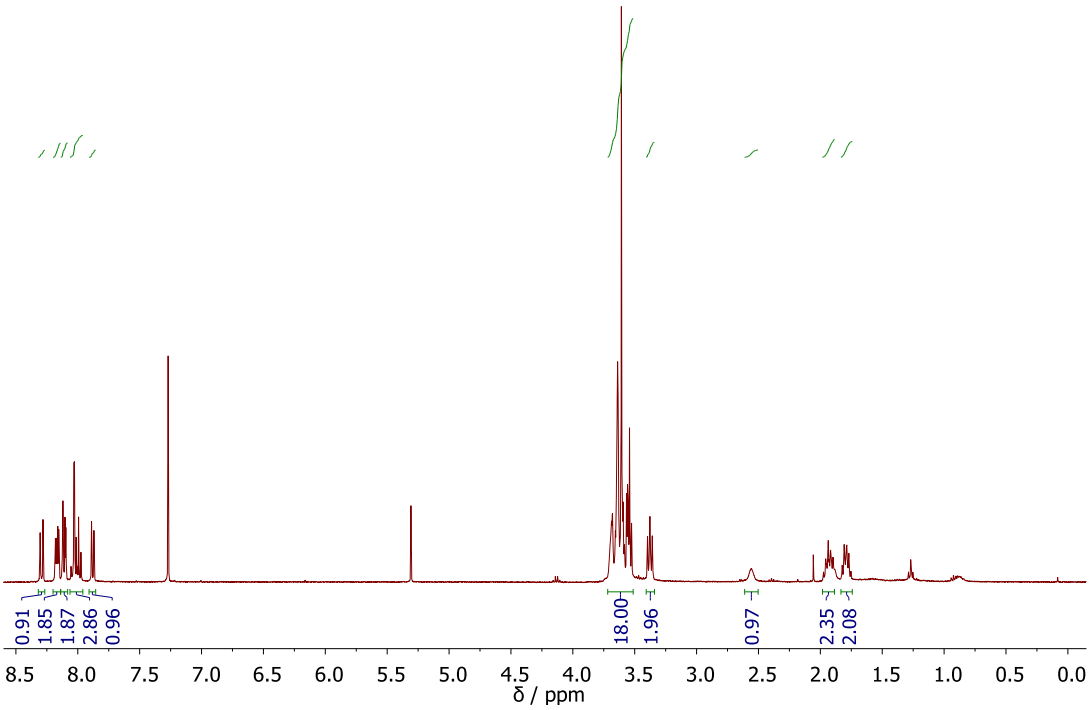


Figure S36. PyrB-PEG4 (49) in $CDCl_3$

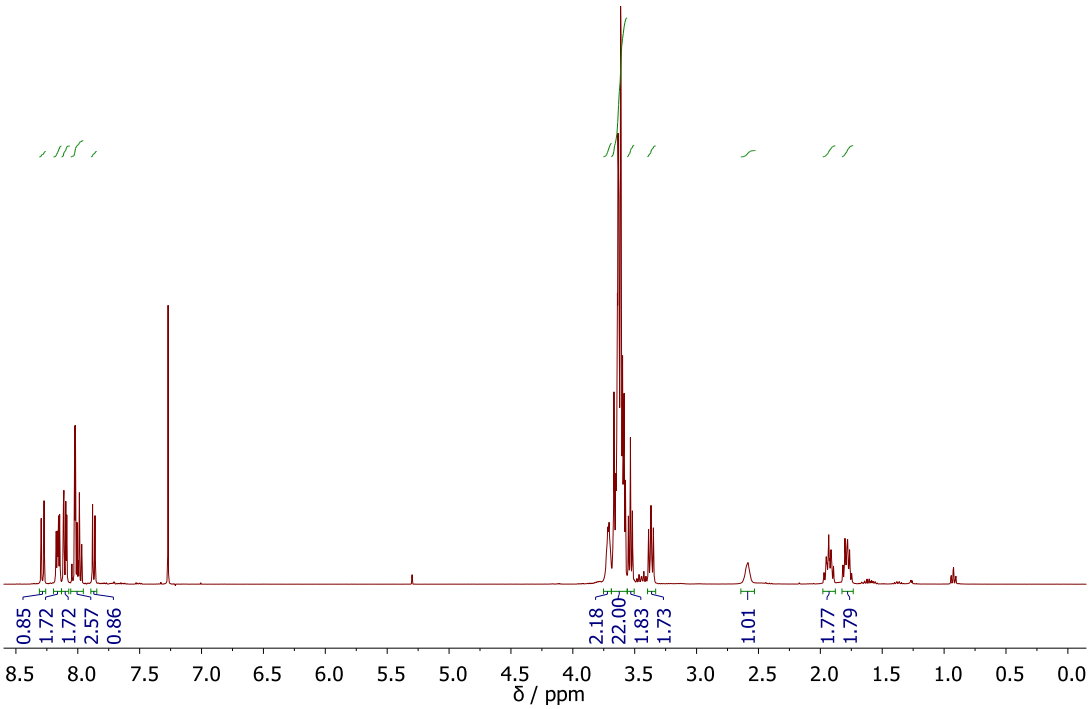


Figure S37. PyrB-PEG6 (50) in $CDCl_3$

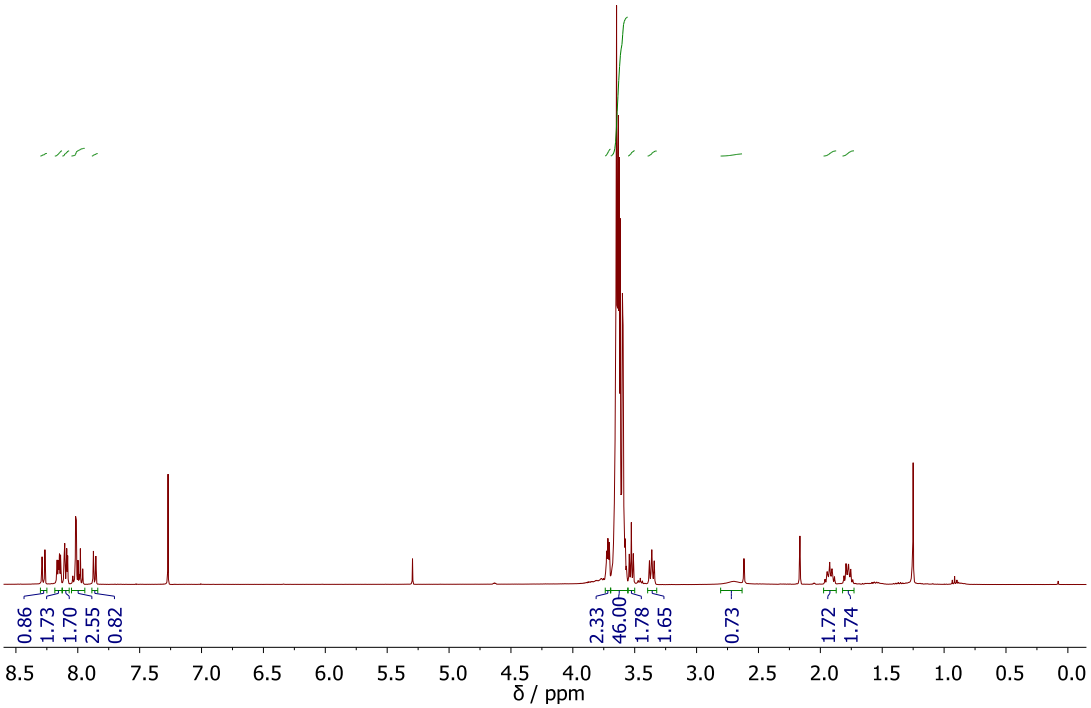


Figure S38. PyrB-PEG12 (51) in $CDCl_3$

2. Analytical Procedures

2.1 Preparation of MWNT Dispersions

The MWNTs were purchased from NanoAmor. The following values were quoted: purity: 95+%, outer diameter: 20-30 nm, internal diameter: 5-10 nm, length: 10-30 μm. A solution of surfactant (3 mL, 1 mM in Millipore water or 0.6 M NaCl) was added to a 7 mL glass vial containing MWNTs (1 mg). The mixture was cooled over an ice-water bath and ultrasonicated using a Cole-Parmer 750-Watt ultrasonic homogeniser (1/8" tapered tip, 20% amplitude, 2 min with a 20 sec on/off pulse cycle), followed by sonication in a 13 L Bandelin Sonorex Digital Ultrasonic Bath (100% power) at RT for a further 2 min. 2 mL of the resulting dispersion was transferred to a 2 mL Eppendorf tube and centrifuged at 2500 *g* for 30 min (Hermle Z323). The supernatant dispersion was decanted and analyzed.

2.2 Determination of MWNT Apparent Extinction Coefficient, ε

3 MWNT dispersions were prepared based on the above procedure, using 15 mg of MWNTs (15 mg) and 1 mM SDS (5 mL) in each case. Two 2 mL aliquots from each sample were subjected to our standard centrifugation conditions and the supernatants recombined to give *ca*. 3 mL of dispersion. Dilute dispersions for UV-visible spectroscopy were prepared by diluting aliquots with the parent SDS solution. Based on the method of Liu *et al.*[10] a further 1.7 mL was transferred to a 50 mL centrifuge tube and treated with acetone (25 mL) to induce precipitation. The suspension was then centrifuged at 7000 *g* for 30 min (Hermle Z323) and the supernatant decanted. Acetone treatment (25 mL), centrifugation (7000 *g*, 30 min) and decanting of the supernatant was repeated twice. The residue was then suspended in the minimum amount of acetone and transferred to a pre-weighed vial. The solvent was removed by gentle heating on a hot plate and the residue further dried by heating overnight in an oven at *ca.* 70 °C. The mass of the dried sample was then used to determine the concentration of the dispersion. This allowed the concentration of serially diluted dispersions which were analysed using UV-visible spectroscopy to be calculated and used to calculate the apparent extinction coefficient, ε. The effect of light scattering by MWNTs on ε was accounted for by using an integrating sphere during spectroscopic analysis; however, we acknowledge that the obtained value must account for any absorption phenomena associated with the MWNTs.

2.3 UV-visible Spectroscopic Analysis of MWNT Dispersions

A sample of dispersion was diluted 10-fold using the parent surfactant solution and its absorbance measured using a Thermo Evolution 220 UV-visible spectrometer fitted with an integrating sphere (ISA220), using the parent surfactant solution as a baseline. Typically, 3

samples were prepared and the mean absorbance at 500 nm was used to calculate C_{MWNT} using the Beer-Lambert law.

2.4 MWNT Dispersion: Calculation of apparent extinction coefficient, ε:

It has been widely reported that CNT dispersions obey the Beer-Lambert law, $A = \varepsilon c l$, where A is the absorbance of a dispersion at a given wavelength, ε is the extinction coefficient of the dispersed CNTs at that wavelength, c is the concentration of the dispersion and l is the path length of the sample.[11-13] Relatively few literature values of ε are available for MWNTs. These include values of 46.0 ± 1.4 mL mg^{-1} cm^{-1} at 500 nm reported for covalently functionalized MWNTs,[13] 42.2 ± 0.3 mL mg^{-1} cm^{-1} at 500 nm for polymer-functionalized MWNTs dispersed in chloroform,[14] 39.92 mL mg^{-1} cm^{-1} for acid treated MWNTs dispersed in water,[11] and 41.14 mL mg^{-1} cm^{-1} at 500 nm for MWNTs dispersed in xylene.[11] We considered it important to establish a value of ε that was based on dispersions of non-covalently functionalised MWNTs and was specific to the batch of MWNTs used throughout our study.

We therefore determined ε by adapting the method of Liu *et al.*,[10] who showed that MWNTs dispersed in SDS can be precipitated by adding excess acetone (see analytical procedures for details). Compared to our standard dispersion conditions this required an increased volume of dispersion so that sufficient was available for both UV-visible absorption and precipitation procedures. We also used an increased MWNT loading to afford more concentrated dispersions, which would increase the mass of precipitated MWNTs and reduce the impact of any weighing errors.

The data used to calculate ε is shown in Figure S39. Each data set shows a linear relationship between absorbance and C_{MWNT}. As 1 cm path length cuvettes were used, for each sample ε (in mL mg^{-1} cm^{-1}) is equal to the gradient of the trend line. The results of three experiments show excellent agreement, averaging to ε = 49.9 ± 1.2 mL mg^{-1} cm^{-1} at 500 nm (where the error is the standard deviation of the three results). This value was used to calculate C_{MWNT} for all other dispersions and agrees reasonably well with literature data.

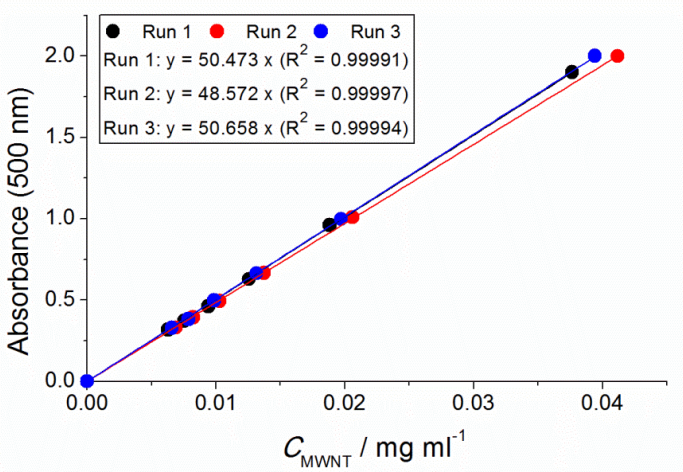


Figure S39: The apparent extinction coefficient, ε, (at 500 nm) of the MWNTs used in this work was obtained by plotting the absorbance of dilutions prepared from a sample of known concentration against their concentration.

2.5 MWNT Dispersion Concentrations:

Table S1: C_{MWNT} in a range of 1 mM surfactant solutions in Millipore (DI) water and 0.6 M NaCl. Errors are the standard deviation of 3 results except for **SDS**, **SDBS**, **SC**, **SDOC** and **SPB**, which are from 6 results, and **PBA-(C6)$_2$-G2(ONa)$_9$** which represents a single experiment only. % MWNTs dispersed is relative to the maximum value possible in the conditions used, 333.3 mg L^{-1}.

	DI			0.6 M NaCl		
Surfactant	C_{MWNT} / mg L^{-1}	Error (σ) / mg L^{-1}	% MWNTs Dispersed	C_{MWNT} / mg L^{-1}	Error (σ) / mg L^{-1}	% MWNTs Dispersed
SDS	108	7	32	-	-	-
SDBS	94	18	28	-	-	-
SC	95	6	29	-	-	-
SDOC	91	9	27	-	-	-
SPB	57	7	17	-	-	-
Triton X-100	134	5	40	73	4	22
1	86	2	26	4	0	1
3	73	10	22	54	4	16
4	74	3	22	76	6	23
2	76	1	23	18	0	5
5	69	11	21	66	6	20
6	88	-	26	78	-	23
7	107	5	32	48	3	15
8	137	9	41	88	7	27
9	148	1	44	131	18	39
10	129	9	39	165	22	49
11	110	3	33	74	6	22
12	104	4	31	114	11	34
13	105	8	32	154	7	46

N.B. **SDS**, **SDBS**, **SC**, **SDOC** and **SPB** were insufficiently soluble in 0.6 M NaCl to enable dispersions to be prepared under our standard conditions.

Table S2: C_{MWNT} in a range of 1 mM surfactant solutions in 0.6 M NaCl and 0.3 M $CaCl_2$. Errors are the standard deviation of 3 results. % MWNTs dispersed is relative to the maximum value possible in the conditions used, 333.3 mg L^{-1}.

	0.6 M KCl			**0.3 M $CaCl_2$**		
Surfactant	**C_{MWNT} / mg L^{-1}**	**Error (σ) / mg L^{-1}**	**% MWNTs Dispersed**	**C_{MWNT} / mg L^{-1}**	**Error (σ) / mg L^{-1}**	**% MWNTs Dispersed**
1	17	4	5	0	0	0
3	81	10	24	0	0	0
4	91	4	27	-	-	-
9	130	1	39	12	1	4
13	144	8	43	3	1	1

3. References

(1) C. M. Cardona and R. E. Gawley, *J. Org. Chem.,* 2002, **67**, 1411.

(2) A. Bouzide and G. Sauvé, *Org. Lett.,* 2002, **4**, 2329.

(3) F. A. Loiseau, K. K. Hii and A. M. Hill, *J. Org. Chem.,* 2004, **69**, 639.

(4) K. Fujimoto, Y. Muto and M. Inouye, *Bioconjugate Chem.,* 2008, **19**, 1132.

(5) L. J. O'Driscoll, D. J. Welsh, S. W. D. Bailey, D. Visontai, H. Frampton, M. R. Bryce and C. J. Lambert, *Chem. Eur. J.*, 2015, **21**, 3891.

(6) A. Ebel, W. Donaubauer, F. Hampel and A. Hirsch, *Eur. J. Org. Chem.,* 2007, **2007**, 3488.

(7) C. Backes, U. Mundloch, A. Ebel, F. Hauke and A. Hirsch, *Chem. Eur. J.*,2010, **16,** 3314.

(8) C. D. Schmidt, C. Böttcher and A. Hirsch, *Eur. J. Org. Chem.,* 2007, **2007**, 5497.

(9) C. Backes, F. Hauke and A. Hirsch, *Phys. Status Solidi B,* 2013, **250**, 2592.

(10)J. Liu, O. Bibari, P. Mailley, J. Dijon, E. Rouviere, F. Sauter-Starace, P. Caillat, F. Vinet and G. Marchand, *New J. Chem.,* 2009, **33**, 1017.

(11)Z. F. Li, G. H. Luo, W. P. Zhou, F. Wei, R. Xiang and Y. P. Liu, *Nanotechnology,* 2006, **17**, 3692.

(12)D. H. Marsh, G. A. Rance, M. H. Zaka, R. J. Whitby and A. N. Khlobystov, *Phys. Chem. Chem. Phys.,* 2007, **9**, 5490.

(13)M. D. Clark and R. Krishnamoorti, *J. Phys. Chem. C,* 2009, **113,** 20861.

(14)D. Baskaran, J. W. Mays and M. S. Bratcher, *Chem. Mater.,* **2005**, *17*, 3389.