Supporting Information
for
The search for new amphiphiles: synthesis of a modular, high-throughput library

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Experimental procedures, chemical characterisation data (including \(^{13}\)C NMR spectra) and preliminary SAXS analysis

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**General experimental**

All solvents used were HPLC grade and all chemicals were purchased from Sigma-Aldrich.

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AV400 spectrometer. \(^1\)H NMR and \(^{13}\)C NMR were recorded at 400 MHz and 100 MHz, respectively. \(^1\)H NMR chemical shifts are reported in ppm with the internal chloroform signal at 7.26 ppm. The data are reported as integration, s = singlet, d = doublet, t = triplet, q = quartet, non = nonet, m = multiplet, br = broad, app. = apparent, \(J\) = coupling constant(s) in Hz. \(^{13}\)C NMR chemical shifts are reported in ppm with the internal chloroform signal at 77.0 ppm.

Amphiphile \(^{13}\)C NMR spectra were recorded using a Bruker Avance III HD 600 MHz spectrometer with a TCI cryoprobe. The experimental parameters were: 32894.738 Hz sweep width, 1.00 s acquisition time, 1 s recycle delay and using a 90 degree excitation pulse of approximately 11.5 μs at 100 W. Samples were analysed in MeOD-\(d_4\) and chemical shifts reported in ppm (δ) relative to the solvent residual for methanol at 49.00 ppm.

Infrared spectra were recorded on a Nicolet 6700 FT-IR spectrometer using a diamond Smart iTR ATR attachment. Absorption maxima (\(\lambda_{\text{max}}\)) are described as s (strong), m (medium), w (weak), or br (broad) and are quoted in wavenumbers (cm\(^{-1}\)).

Accurate mass spectra for amphiphilic compounds were recorded on a Bruker AUtoflex III MALDI–TOF/TOF mass spectrometer. Experiment employed: positive ion, reflectron mode. The matrix employed was HCCA (\(\alpha\)-cyano-4-hydroxycinnamic acid).

Copper analysis was carried out on an Agilent 770 ICP-MS. Nitric acid at ca. 100 °C was used to digest the samples before being made up to 25 mL with Milli Q water. The solutions were then measured directly by ICP-MS.
Synthesis of double-chain tails

Prop-2-yn-1-yl 3-hydroxy-2-(hydroxymethyl)-2-methylpropanoate (2)[1]

To a stirred solution of 2,2-bis(hydroxymethyl)propionic acid (1.0 equiv) in DMF (5 mL/mmol) was added KOH (1.1 equiv). After stirring for 2 h at 100 °C, propargyl bromide (1.0 equiv) was added dropwise over 30 min. The solution was heated at 80 °C for 18 h, before the reaction mixture was cooled, filtered and concentrated in vacuo. The crude product was diluted with ether and subsequently washed with brine and sat. aq. NaHCO$_3$ solution. The organic fragment was dried over MgSO$_4$ and concentrated in vacuo to give the title compound (4.06 g, 69%) without the need for further purification. Spectroscopic data matched with the literature data.

General procedure A

To a stirred solution of carboxylic acid (2.5 equiv) and DMAP (0.2 equiv) in DCM at r.t. (5 mL/mmol) was added diisopropylcarbodiimide (2.2 equiv). Once dissolved, diol 2 (1.0 equiv) was added and stirring continued for 18 h. The reaction mixture was then diluted with DCM and washed with 1.0 M aq. HCl, sat. aq. NaHCO$_3$ solution and brine, dried over MgSO$_4$ and concentrated in vacuo to give the crude material.

2-Methyl-2-((prop-2-yn-1-yloxy)carbonyl)propane-1,3-diyi dioctanoate (3)
Synthesised in accordance with General Procedure A. Purification by column chromatography (4:1, petrol:ethyl acetate) afforded the compound (446 mg, 72%) as a yellow, viscous liquid; $\nu_{\text{max}}/\text{cm}^{-1}$ (thin film) 2927m, 2856m, 1738s, 1467m, 1378s, 1225m; $\delta_H$ (400 MHz, CDCl$_3$) 0.86 (6H, t, $J$ 7.1, 2× CH$_2$-CH$_3$), 1.20-1.32 (19H, m, CH$_3$ and 8×CH$_2$) 1.52-1.63 (4H, m, 2×O=C-CH$_2$-CH$_2$), 2.28 (4H, t, $J$ 7.8, 2×O=C-CH$_2$), 2.43 (1H, t, $J$ 2.2, =CH) 4.21 (2H, s, C-CH$_2$-O-), 4.22 (2H, s, C-CH$_2$-O-), 4.69 (2H, d, $J$ 3.0, =C-CH$_2$-O-); $\delta_C$ (100 MHz, CDCl$_3$) 14.2 (2×CH$_2$-CH$_3$), 17.8 (C-CH$_3$), 22.7 (2×CH$_2$-CH$_3$), 25.0 (2×CH$_2$), 29.0 (2×CH$_2$), 29.2 (2×CH$_3$), 31.8 (2×CH$_3$), 34.3 (2×CH$_2$), 46.5 (CR$_4$), 52.7 (=C-CH$_2$-O-), 65.3 (2×C-CH$_2$-O-), 75.3 (=CH), 77.4 (HC=CH), 172.3 (O=O), 173.4 (2×O=O); Accurate mass (ESI): Found: 425.2897 C$_{24}$H$_{41}$O$_6$ (MH$^+$) requires 425.2903.

2-Methyl-2-((prop-2-yn-1-yl)oxy)carbonyl)propane-1,3-diyi bis(decanoate) (4)

Synthesised in accordance with General Procedure A. Purification by column chromatography (5:1, petrol/ethyl acetate) afforded the compound (494 mg, 71%) as a colourless, viscous liquid; $\nu_{\text{max}}/\text{cm}^{-1}$ (thin film) 2924m, 2854m, 1740s, 1466m, 1377s, 1235m; $\delta_H$ (400 MHz, CDCl$_3$) 0.86 (6H, t, $J$ 6.1, 2× CH$_2$-CH$_3$), 1.25 (27H, br s, CH$_3$ and 12×CH$_2$), 1.53-1.63 (4H, m, 2× O=C-CH$_2$-CH$_2$), 2.28 (4H, t, $J$ 7.8, 2× O=C-CH$_2$), 2.41-2.45 (1H, m, =CH) 4.21 (2H, s, C-CH$_2$-O-), 4.22 (2H, s, C-CH$_2$-O-), 4.69 (2H, d, $J$ 3.0, =C-CH$_2$-O-); $\delta_C$ (100 MHz, CDCl$_3$) 14.3 (2×CH$_2$-CH$_3$), 17.8 (C-CH$_3$), 22.8 (2×CH$_2$-CH$_3$), 25.0 (2×CH$_2$), 29.3 (2×CH$_2$), 29.4 (2×CH$_2$), 29.6 (2×CH$_2$), 32.0 (2×CH$_2$), 34.3 (2×CH$_2$), 46.5 (CR$_4$), 52.7 (=C-CH$_2$-O-), 65.3 (2×C-CH$_2$-O-), 75.3 (=CH), 77.4 (HC=CH), 172.3 (O=O), 173.4 (2×O=O); Accurate mass (ESI): Found: 481.3524 C$_{28}$H$_{49}$O$_6$ (MH$^+$) requires 481.3524.
2-Methyl-2-((prop-2-yn-1-yloxy)carbonyl)propane-1,3-diyl bis(dodecanoate) (5)

Synthesised in accordance with General Procedure A. Purification by column chromatography (5:1, petrol:ether) afforded the compound (373 mg, 70%) as a colourless, viscous liquid; \( \nu_{\text{max}}/\text{cm}^{-1} \) (thin film) 2922m, 2853m, 1740s, 1466m, 1376s, 1232m; \( \delta_\text{H} \) (400 MHz, CDCl$_3$) 0.85 (6H, t, J 6.7, 2\times CH$_2$-CH$_3$), 1.19-1.33 (35H, m, CH$_3$ & 16\times CH$_2$) 1.52-1.62 (4H, m, 2\timesO=C-C$_3$H$_2$), 2.27 (4H, t, J 7.5, 2\timesO=C-C$_3$H$_2$), 2.41-2.45 (1H, m, \equivC H) 4.21 (2H, s, C-C$_3$H$_2$-O-), 4.22 (2H, s, C-C$_3$H$_2$-O-), 4.68 (2H, d, J 2.5, \equivC-C$_3$H$_2$-O-); \( \delta_\text{C} \) (100 MHz, CDCl$_3$) 14.3 (2\timesCH$_2$-C$_3$H$_3$), 17.8 (C-C$_3$H$_3$), 22.8 (2\timesCH$_2$-CH$_3$), 25.0 (2\timesCH$_3$), 29.3 (2\timesCH$_3$), 29.4 (2\timesCH$_3$), 29.5 (2\timesCH$_3$), 29.6 (2\timesCH$_3$), 29.8 (2\timesCH$_3$), 32.1 (CR$_4$), 52.7 (\equivC-C$_3$H$_2$-O-), 65.3 (2\timesC-C$_3$H$_2$-O-), 75.3 (\equivC-H), 77.3 (HC=C-), 172.3 (O=C), 173.4 (2\timesO=C); Accurate mass (ESI): Found: 537.4153 C$_{32}$H$_{57}$O$_6$ (MH$^+$) requires 537.4150.

2-Methyl-2-((prop-2-yn-1-yloxy)carbonyl)propane-1,3-diyl bis(tetradecanoate) (6)

Synthesised in accordance with General Procedure A. Purification by column chromatography (5:1, petrol/ether) afforded the compound (337 mg, 56%) as a colourless, viscous liquid; \( \nu_{\text{max}}/\text{cm}^{-1} \) (thin film) 2921m, 2851m, 1740s, 1467m, 1377s, 1237m; \( \delta_\text{H} \) (400 MHz, CDCl$_3$) 0.85 (6H, t, J 6.7, 2\times CH$_2$-CH$_3$), 1.18-1.33 (43H, m, CH$_3$ and 20\times CH$_2$) 1.52-1.62 (4H, m, 2\timesO=C-C$_3$H$_2$-CH$_3$), 2.27 (4H, t, J 7.5, 2\timesO=C-C$_3$H$_2$), 2.43 (1H, t, J 2.8, \equivCH), 4.21 (2H, s, C-C$_3$H$_2$-O-), 4.22 (2H, s, C-C$_3$H$_2$-O-), 4.68 (2H, d, J 2.8, \equivC-C$_3$H$_2$-O-); \( \delta_\text{C} \) (100 MHz, CDCl$_3$) 14.3 (2\timesCH$_2$-CH$_3$), 17.8 (C-C$_3$H$_3$), 22.8 (2\timesCH$_2$-CH$_3$), 25.0 (2\timesCH$_3$), 29.3 (2\timesCH$_3$), 29.4 (2\timesCH$_3$), 29.5 (2\timesCH$_3$), 29.6 (2\timesCH$_3$), 29.8 (2\timesCH$_3$), 29.9 (2\timesCH$_3$), 32.1 (2\timesCH$_3$), 34.3 (2\timesCH$_3$), 46.5 (CR$_4$), 52.7 (\equivC-C$_3$H$_2$-O-), 65.3 (2\timesC-
CH₂-O-), 75.3 (≡CH), 77.3 (HC≡C-), 172.3 (O=C), 173.4 (2xO=C); Accurate mass (ESI): Found: 593.4774 C₃₆H₆₅O₆ (MH⁺) requires 593.4776.

2-Methyl-2-((prop-2-yn-1-yloxy)carbonyl)propane-1,3-diyl bis(hexadecanoate) (7)

Synthesised in accordance with General Procedure A. Purification by column chromatography (5:1, petrol/ether) afforded the compound (410 mg, 62%) as a white solid; νmax/cm⁻¹ (thin film) 2916m, 2849m, 1732s, 1463m, 1378s, 1245m; δH (400 MHz, CDCl₃) 0.86 (6H, t, J 6.8, 2x CH₂-C₃H₃), 1.18-1.34 (51H, m, CH₃ & 24xCH₂) 1.53-1.63 (4H, m, 2xO=C-CH₂-CH₂), 2.27 (4H, t, J 7.1, 2xO=C-CH₂), 2.43 (1H, t, J 2.4, ≡CH) 4.21 (2H, s, C-CH₂-O-), 4.22 (2H, s, C-CH₂-O-), 4.68 (2H, d, J 2.4, ≡C-CH₂-O-); δC (100 MHz, CDCl₃) 14.3 (2xCH₂-CH₃), 17.8 (C-CH₃), 22.9 (2xCH₂-CH₃), 25.0 (2xCH₂), 29.3 (2xCH₂), 29.4 (2xCH₂), 29.5 (2xCH₂), 29.6 (2xCH₂), 29.8 (2xCH₂), 29.8 (4xCH₂), 29.9 (4xCH₂), 32.1 (2xCH₂), 34.3 (2xCH₂), 46.5 (CR₄), 52.7 (≡C-CH₂-O-), 65.3 (2xC-CH₂-O-), 75.3 (≡CH), 77.3 (HC≡C-), 172.3 (O=C), 173.4 (2xO=C); Accurate mass (ESI): Found: 649.5399 C₄₀H₇₃O₆ (MH⁺) requires 649.5402.

2-Methyl-2-((prop-2-yn-1-yloxy)carbonyl)propane-1,3-diyl bis(octadecanoate) (8)

Synthesised in accordance with General Procedure A. Purification by column chromatography (5:1, petrol/ether) afforded the compound (410 mg, 62%) as a white solid; νmax/cm⁻¹ (thin film) 2915m, 2849m, 1732s, 1380m, 1235m; δH (400 MHz, CDCl₃) 0.86 (6H, t, J 6.8, 2x CH₂-CH₃), 1.18-1.33 (59H, m, CH₃ and 28xCH₂) 1.53-1.61 (4H, m, 2xO=C-CH₂-CH₂), 2.27 (4H, t, J 7.4, 2xO=C-
2-Methyl-2-((prop-2-yn-1-yloxy)carbonyl)propane-1,3-diyI bis(3,7,11,15-tetramethylhexadecanoate) (9)

Synthesised in accordance with General Procedure A. Purification by column chromatography (5:1, petrol/ether) afforded the compound (303 mg, 52%) as a colourless, viscous oil; \( \nu_{\text{max}} / \text{cm}^{-1} \) (thin film) 2953m, 2925m, 2868m, 1741s, 1462m, 1377m, 1236m; \( \delta_{\text{H}} \) (400 MHz, CDCl\(_3\)) 0.79-0.87 (24H, app. dd, J 6.8, 6.5, 8×CH-CH\(_3\)), 0.89 (6H, d, J 6.5, 2×O=C-CH\(_2\)-CH-CH\(_3\)), 0.99-1.40 (43H, m, CH\(_3\) and 18×CH\(_2\) and 4×CH), 1.50 (2H, m, J 6.8, 2×CH\(_2\)-CH-(CH\(_3\))\(_2\)), 1.83-1.96 (2H, m, 2×O=C-CH\(_2\)-CH), 2.08 (2H, dd, J 14.5, 8.3, 2×O=C-CHH\(^\prime\)-CH), 2.29 (2H, dd, J 15.1, 5.8, 2×O=C-CHH\(^\prime\)-CH), 2.43 (1H, t, J 2.5, \( \equiv \text{CH} \)), 4.19-4.24 (4H, s, 2×C-CH\(_2\)-O-), 4.68 (2H, d, J 2.5, \( \equiv \text{CH}_2\)-O-); \( \delta_{\text{C}} \) (100 MHz, CDCl\(_3\)) 17.8 (C-CH\(_3\)), 19.8 (CH-CH\(_3\)), 19.8 (CH-CH\(_3\)), 19.8 (2×CH-CH\(_3\)), 19.9 (CH-CH\(_3\)), 19.9 (CH-CH\(_3\)), 22.8 (2×CH-CH\(_3\)), 22.9 (2×CH-CH\(_3\)), 24.5 (2×CH\(_2\)-CH-CH\(_2\)), 24.6 (2×CH\(_2\)-CH-CH\(_2\)), 25.0 (2×CH\(_2\)-CH-CH\(_2\)), 28.1 (3×R\(_3\)CH), 30.5 (2×R\(_3\)CH), 32.9 (3×R\(_3\)CH), 37.2 (2×CH\(_2\)-CH), 37.3 (CH\(_2\)-CH), 37.4 (CH\(_2\)-CH), 37.4 (2×CH\(_2\)-CH), 37.6 (2×CH\(_2\)-CH), 37.6 (2×CH\(_2\)-CH), 39.5 (2×CH\(_2\)-CH-(CH\(_3\))\(_2\)), 41.8 (O=C-CH\(_2\)-CH), 41.8 (O=C-CH\(_2\)-CH), 46.4 (CR\(_4\)), 52.7 (\( \equiv \text{CH}_2\)-O-), 65.3 (2×C-CH\(_2\)-O-), 75.3 (\( \equiv \text{CH} \)), 77.3 (HC=CH), 172.2 (O=C), 172.9 (2×O=C); Accurate mass (ESI): Found: 761.6643 C\(_{48}\)H\(_{89}\)O\(_6\) (MH\(^+\)) requires 761.6661.
(7Z,7’Z)-2-Methyl-2-((prop-2-yn-1-yloxy)carbonyl)propane-1,3-diyl bis(hexadec-7-enoate) (10)

Synthesised in accordance with General Procedure A. Purification by column chromatography (5:1, petrol/ether) afforded the compound (410 mg, 62%) as a colourless, viscous oil; \( \nu_{\text{max}}/\text{cm}^{-1} \) (thin film) 2916m, 2849m, 1733s, 1473m, 1213m; \( \delta_{\text{H}} \) (400 MHz, CDCl\(_3\)) 0.86 (6H, t, \( J \) 6.5, 2\( \times \) CH\(_2\)-CH\(_3\)), 1.20-1.34 (35H, m, \( \text{CH}_3 \) & 16\( \times \)CH\(_2\)), 1.52-1.62 (4H, m, 2\( \times \)O=CH-CH\(_2\)-CH\(_2\)), 1.94-2.04 (8H, m, 4\( \times \)=CH-CH\(_2\)), 2.28 (4H, t, \( J \) 7.4, 2\( \times \)O=CH-CH\(_2\)-CH\(_2\)), 4.21 (2H, s, C-CH=CH\(_2\)), 4.22 (2H, s, C-CH=CH\(_2\)), 4.68 (2H, d, \( J \) 2.2, \( \equiv \text{CH} \)), 5.32 (4H, dt, \( J \) 5.6, 3.6, 2\( \times \)=CH-CH\(_2\)); \( \delta_{\text{C}} \) (100 MHz, CDCl\(_3\)) 14.3 (2\( \times \)CH\(_2\)-CH\(_3\)), 17.8 (C-CH=CH\(_2\)), 22.8 (2\( \times \)CH=CH\(_2\)), 25.0 (2\( \times \)CH\(_2\)), 27.3 (2\( \times \)=C-CH\(_2\)), 27.4 (2\( \times \)CH=CH\(_2\)), 29.1 (2\( \times \)CH\(_2\)), 29.3 (2\( \times \)CH\(_2\)), 29.9 (2\( \times \)CH\(_2\)), 31.9 (2\( \times \)CH\(_2\)), 34.3 (2\( \times \)CH\(_2\)), 46.8 (CR\(_d\)), 52.7 (\( \equiv \text{C-CH}_2\text{-O-} \)), 65.3 (2\( \times \)C-CH\(_2\)-O-), 75.3 (\( \equiv \text{CH} \)), 77.3 (HC=CH-), 129.9 (2\( \times \)C=CH), 130.1 (2\( \times \)C=CH), 172.2 (O=CH), 173.4 (2\( \times \)O=CH); Accurate mass (ESI): Found: 667.4906 C\(_{40}\)H\(_{68}\)O\(_6\)Na (M\( ^{Na+} \)) requires 667.4908.

(Z)-2-Methyl-2-((prop-2-yn-1-yloxy)carbonyl)propane-1,3-diyl dioleate (11)

Synthesised in accordance with General Procedure A. Purification by column chromatography (5:1, petrol/ether) afforded the compound (464 mg, 76%) as a colourless, viscous oil; \( \nu_{\text{max}}/\text{cm}^{-1} \) (thin film) 2922m, 2853m, 1742s, 1465m, 1463m, 1377m, 1237m; \( \delta_{\text{H}} \) (400 MHz, CDCl\(_3\)) 0.86 (6H, t, \( J \) 6.8, 2\( \times \) CH\(_2\)-CH\(_3\)), 1.19-1.34 (47H, m, \( \text{CH}_3 \) and 22\( \times \)CH\(_2\)) 1.53-1.62 (4H, m, 2\( \times \)O=CH-CH\(_2\)-CH\(_2\)), 1.95-2.02 (8H, m, 4\( \times \)=CH-CH\(_2\)), 2.28 (4H, t, \( J \) 6.2, 2\( \times \)O=CH-CH\(_2\)), 2.43 (1H, t, \( J \) 2.5, \( \equiv \text{CH} \)), 4.21 (2H, s, C-CH\(_2\)-CH\(_2\))
O-), 4.22 (2H, s, C-CH$_2$O-), 4.68 (2H, d, J 2.5, =C-CH$_2$O-), 5.32 (4H, dt, J 5.6, 3.4, 2x-CH=CH-);
δ$_c$ (100 MHz, CDCl$_3$) 14.3 (2xCH$_2$-CH$_3$), 17.8 (C-CH$_3$), 22.8 (2xCH$_2$-CH$_3$), 25.0 (2xCH$_2$), 27.3 (2x=C-CH$_2$), 27.4 (2xCH$_2$C=), 29.3 (2xCH$_2$), 29.3 (2xCH$_2$), 29.5 (2xCH$_2$), 29.7 (2xCH$_2$), 29.9 (2xCH$_2$), 29.9 (2xCH$_2$), 32.1 (2xCH$_2$), 34.3 (2xCH$_2$), 46.5 (CR$_4$), 52.7 (=C-CH$_2$O-), 65.3 (2x=C-CH$_2$O-), 75.3 (=CH), 77.3 (HC=C-), 129.9 (2xC=C) 130.2 (2xC=C), 172.3 (O=C), 173.4 (2xO=C); Accurate mass (ESI): Found: 701.5712 C$_{44}$H$_{77}$O$_6$ (MH$^+$) requires 701.5715.

(Z)-2-Methyl-2-((prop-2-yn-1-yroxy)carbonyl)propane-1,3-diyl bis(docos-13-enoate) (12)

Synthesised in accordance with General Procedure A. Purification by column chromatography (5:1, petrol/ether) afforded the compound (487 mg, 69%) as a colourless, viscous oil; $\nu_{\text{max}}$/cm$^{-1}$ (thin film) 2921m, 2852m, 1743s, 1465m, 1377m, 1236m; δ$_h$ (400 MHz, CDCl$_3$) 0.86 (6H, t, J 6.5, 2xCH$_2$-CH$_3$), 1.19-1.34 (63H, m, CH$_3$ and 30xCH$_2$) 1.52-1.61 (4H, m, 2xO=C-CH$_2$-CH$_2$), 1.99 (8H, q, J 6.4, 4x=CH-CH$_2$), 2.28 (4H, t, J 7.3, 2xO=C-CH$_2$), 2.43 (1H, t, J 2.5, =CH), 4.21 (2H, s, C-CH$_2$O-), 4.22 (2H, s, C-CH$_2$O-), 4.69 (2H, d, J 2.5, =C-CH$_2$O-), 5.32 (4H, J 8.9, 4.5, 2x-CH=CH-); δ$_c$ (100 MHz, CDCl$_3$) 14.3 (2xCH$_2$-CH$_3$), 17.8 (C-CH$_3$), 22.8 (2xCH$_2$-CH$_3$), 25.0 (2xCH$_2$), 27.4 (4x=C-CH$_2$), 29.3 (2xCH$_2$), 29.4 (2xCH$_2$), 29.5 (2xCH$_2$), 29.6 (2xCH$_2$), 29.7 (4xCH$_2$), 29.7 (2xCH$_2$), 29.8 (2xCH$_2$), 29.9 (2xCH$_2$), 32.1 (2xCH$_2$), 34.3 (2xCH$_2$), 46.5 (CR$_4$), 52.7 (=C-CH$_2$O-), 65.3 (2x=C-CH$_2$O-), 75.3 (=CH), 77.3 (HC=C-), 130.0 (2xC=C) 130.1 (2xC=C), 172.3 (O=C), 173.4 (2xO=C); Accurate mass (ESI): Found: 813.6971 C$_{52}$H$_{93}$O$_6$ (MH$^+$) requires 813.6974.
Synthesised in accordance with General Procedure A. Purification by column chromatography (5:1, petrol/ether) afforded the compound (192 mg, 40%) as a colourless, viscous oil; ν\textsubscript{max}/cm\textsuperscript{-1} (thin film) 2925m, 2852m, 1742s, 1465m, 1377m, 1236m; δ\textsubscript{H} (400 MHz, CDCl\textsubscript{3}) 0.86 (6H, t, J 6.7, 2\times CH\textsubscript{2}-CH\textsubscript{3}), 1.20-1.38 (35H, m, CH\textsubscript{3} and 16\times CH\textsubscript{2}) 1.53-1.62 (4H, m, 2\times O=CH-CH\textsubscript{2}), 2.02 (8H, q, J 6.7, 4\times =CH-CH\textsubscript{2}), 2.28 (4H, t, J 7.4, 2\times O=CH-CH\textsubscript{2}), 2.43 (1H, t, J 2.5, =CH), 2.75 (4H, t, J 6.5, C=CH\textsubscript{2}-C=C), 4.21 (2H, s, CH=CH\textsubscript{2}-O-), 4.22 (2H, s, CH=CH\textsubscript{2}-O-), 4.69 (2H, d, J 2.5, =CH=CH\textsubscript{2}-O-), 5.26-5.40 (8H, m, 4\times =CH=CH-); δ\textsubscript{C} (100 MHz, CDCl\textsubscript{3}) 14.2 (2\times CH\textsubscript{2}-CH\textsubscript{3}), 17.8 (C-CH\textsubscript{3}), 22.7 (2\times CH\textsubscript{2}-CH\textsubscript{3}), 25.0 (2\times CH\textsubscript{2}), 25.8 (2\times =C-CH\textsubscript{2}=C-), 27.4 (4\times =C-CH\textsubscript{2}), 29.2 (2\times CH\textsubscript{2}), 29.3 (2\times CH\textsubscript{2}), 29.3 (2\times CH\textsubscript{2}), 29.5 (2\times CH\textsubscript{2}), 29.8 (2\times CH\textsubscript{2}), 31.7 (2\times CH\textsubscript{3}), 34.2 (2\times CH\textsubscript{2}), 46.5 (CR\textsubscript{4}), 52.7 (=C-CH\textsubscript{2}=O-), 65.3 (2\times C-CH\textsubscript{2}=O-), 75.3 (=CH), 77.3 (HC=CH-), 128.1 (2\times C=C) 128.2 (2\times C=C), 130.2 (2\times C=C), 130.4 (2\times C=C), 172.2 (O=C), 173.4 (2\times O=C); Accurate mass (ESI): Found: 697.5385 C\textsubscript{44}H\textsubscript{73}O\textsubscript{6} (MH\textsuperscript{+}) requires 697.5405.
Synthesis of triple chain tails

\[ N-(1,3\text{-Dihydroxy-2-(hydroxymethyl)propan-2-yl})\text{pent-4-namide (15)} \]

\[
\begin{align*}
\text{H}_2\text{N} & \quad \text{O} \\
\text{OH} & \quad \text{O} \\
\text{OH} & \quad \text{O} \\
\end{align*}
\]

\[
\begin{align*}
\text{EEDQ, EtOH} \rightarrow & \quad \text{O} \\
\text{OH} & \quad \text{O} \\
\text{OH} & \quad \text{O} \\
\end{align*}
\]

To a stirred solution of tri-(hydroxymethyl)-methylamine (TRIS) (1.1 equiv) and \( N \)-ethoxycarbonyl-2-ethoxy-1,2-dihydroquinoline (EEDQ) (1.2 equiv) in ethanol (5 mL/mmol) was added 4-pentyneonic acid (1.0 equiv). The reaction mixture was heated to 60 °C and stirred for 20 h. The reaction mixture was cooled, filtered and concentrated in vacuo to give the crude material. Purification by column chromatography (5:2 ethyl acetate/petrol) afforded the compound (951 mg, 84%) as a white solid; \( \nu_{\text{max}}/\text{cm}^{-1} \) (thin film) 3446br, 2935br, 1656s, 1389m, 1215m; \( \delta_{\text{H}} \) (400 MHz, MeOD) 2.25 (1H, s, \( \equiv\text{C}H\)), 2.44 (4H, m, \( \equiv\text{C}CH\_2\text{CH}_\text{2}-\text{C}=\text{O} \)), 3.70 (6H, s, 3×CH\_2-OH); \( \delta_{\text{C}} \) (100 MHz, CDCl\text{3}) 14.4 (\( \equiv\text{C}CH\_2 \)), 35.2 (CH\_2-C=O), 61.3 (3×CH\_2-OH), 62.5 (C-NH), 69.1 (\( \equiv\text{CH} \)), 82.4 (\( \equiv\text{C}CH\_2 \)), 173.8 (O=O); Accurate mass (ESI): Found: 202.1076 C\text{9}H\text{16}O\text{4}N (MH\text{+}) requires 202.1079.

General procedure B

\[
\begin{align*}
\text{OH} & \quad \text{O} \\
\text{OH} & \quad \text{O} \\
\text{OH} & \quad \text{O} \\
\end{align*}
\]

To a stirred solution of carboxylic acid (3.5 equiv) and DMAP (0.3 equiv) in DCM at rt (5 mL/mmol) was added diisopropylcarbodiimide (3.3 equiv). Once dissolved, propargyl amide 15 (1.0 equiv) was added and stirring continued for 18 h. The reaction was then diluted with DCM and washed with 1.0 M aq. HCl, sat. aq. NaHCO\text{3} solution and brine, dried over MgSO\text{4} and concentrated in vacuo to give the crude product.
2-((Octanoyloxy)methyl)-2-(pent-4-ynamido)propane-1,3-diyi dioctanoate (16)

Synthesised in accordance with General Procedure B. Purification by column chromatography (5:1, petrol/ethyl acetate) afforded the compound (556 mg, 77%) as a colourless, viscous liquid; ν\textsubscript{max}/cm\textsuperscript{-1} (thin film) 3313br, 2924m, 2855m, 1737s, 1661s, 1546m, 1464m, 1379m; δ\textsubscript{H} (400 MHz, CDCl\textsubscript{3}) 0.86 (9H, t, J 6.1, 3× CH\textsubscript{2}-CH\textsubscript{3}), 1.19-1.34 (24H, m, 12×C\textsubscript{H}\textsubscript{2}), 1.53-1.65 (6H, m, 3×O=C-CH\textsubscript{2}-CH\textsubscript{3}), 1.95 (1H, t, J 2.5, ≡CH), 2.26-2.37 (8H, m, ≡C-CH\textsubscript{2}-CH\textsubscript{2}, overlays t, J 7.8, 3×O=C-CH\textsubscript{3}), 2.41-2.47 (2H, m, ≡C-CH\textsubscript{2}), 4.40 (6H, s, 3×CH\textsubscript{2}-O·), 6.02 (1H, br s, NH); δ\textsubscript{C} (100 MHz, CDCl\textsubscript{3}) 14.2 (3×CH\textsubscript{2}-CH\textsubscript{3}), 14.9 (≡C-CH\textsubscript{2}-CH\textsubscript{2}), 22.7 (3×CH\textsubscript{2}-CH\textsubscript{3}), 25.0 (3×CH\textsubscript{2}), 29.1 (3×CH\textsubscript{2}), 29.2 (3×CH\textsubscript{2}), 31.8 (3×CH\textsubscript{2}), 34.2 (3×CH\textsubscript{2}), 36.0 (≡C-CH\textsubscript{2}-CH\textsubscript{2}), 58.6 (CR\textsubscript{2}N), 62.7 (3×C-CH\textsubscript{2}-O·), 69.5 (≡CH), 82.8 (HC≡C·), 171.2 (O=C), 173.6 (3×O=C); Accurate mass (ESI): Found: 580.4212 C\textsubscript{33}H\textsubscript{58}O\textsubscript{7}N (MH\textsuperscript{+}) requires 580.4213.

2-((Decanoyloxy)methyl)-2-(pent-4-ynamido)propane-1,3-diyi bis(decanoate) (17)

Synthesised in accordance with General Procedure B. Purification by column chromatography (6:1, petrol/ethyl acetate) afforded the compound (520 mg, 72%) as a white solid; ν\textsubscript{max}/cm\textsuperscript{-1} (thin film) 2923m, 2854m, 1740s, 2854m, 1737s, 1686s, 1544m, 1466m, 1379m; δ\textsubscript{H} (400 MHz, CDCl\textsubscript{3}) 0.85 (9H, t, J 6.8, 3× CH\textsubscript{2}-CH\textsubscript{3}), 1.19-1.33 (36H, m, 18×CH\textsubscript{2}) 1.53-1.63 (6H, m, 3×O=C-CH\textsubscript{2}-CH\textsubscript{3}), 1.96 (1H, t, J 2.8, ≡CH), 2.26-2.37 (8H, m, ≡C-CH\textsubscript{2}-CH\textsubscript{2}, overlays t, J 7.1, 3×O=C-CH\textsubscript{2}), 2.43-2.48 (2H, m, ≡C-
CH\textsubscript{2}), 4.41 (6H, s, 3×CH\textsubscript{2}-O-), 6.02 (1H, br s, NH); δ\textsubscript{C} (100 MHz, CDCl\textsubscript{3}) 14.3 (3×CH\textsubscript{2}-CH\textsubscript{3}), 14.9 (≡C-CH\textsubscript{2}-CH\textsubscript{2}), 22.8 (3×CH\textsubscript{2}-CH\textsubscript{3}), 25.0 (3×CH\textsubscript{2}), 29.3 (3×CH\textsubscript{2}), 29.4 (6×CH\textsubscript{2}), 29.6 (3×CH\textsubscript{2}), 32.0 (3×CH\textsubscript{2}), 34.3 (3×CH\textsubscript{2}), 36.0 (≡C-CH\textsubscript{2}-CH\textsubscript{2}), 58.7 (CR\textsubscript{3}N), 62.7 (3×C-CH\textsubscript{2}-O-), 69.5 (≡CH), 82.8 (HC≡C-), 171.2 (O=C), 173.6 (3×O=C); Accurate mass (ESI): Found: 664.5148 C\textsubscript{39}H\textsubscript{70}O\textsubscript{7}N (MH\textsuperscript{+}) requires 664.5147.

2-((Dodecanoyloxy)methyl)-2-(pent-4-ynamido)propane-1,3-diyl didodecanoate (18)

Synthesised in accordance with General Procedure B. Purification by column chromatography (6:1, petrol/ethyl acetate) afforded the compound (527 mg, 71%) as a white solid; ν\textsubscript{max}/cm\textsuperscript{-1} (thin film) 2917s, 2849s, 1735s, 1651s, 1557m, 1468m, 1373m, 1269m; δ\textsubscript{H} (400 MHz, CDCl\textsubscript{3}) 0.86 (9H, t, J 6.7, 3×CH\textsubscript{2}-C\textsubscript{H}\textsubscript{3}), 1.20-1.33 (48H, m, 24×CH\textsubscript{2}), 1.54-1.63 (6H, m, 3×O=C-CH\textsubscript{2}-CH\textsubscript{2}), 1.96 (1H, t, J 2.5, ≡CH), 2.27-2.37 (8H, m, ≡C-CH\textsubscript{2}-CH\textsubscript{2}, overlays t, J 7.4, 3×O=C-CH\textsubscript{2}), 2.43-2.49 (2H, m, ≡C-CH\textsubscript{2}), 4.41 (6H, s, 3×CH\textsubscript{2}-O-), 6.03 (1H, br s, NH); δ\textsubscript{C} (100 MHz, CDCl\textsubscript{3}) 14.3 (3×CH\textsubscript{2}-CH\textsubscript{3}), 14.9 (≡C-CH\textsubscript{2}-CH\textsubscript{2}), 22.8 (3×CH\textsubscript{2}-CH\textsubscript{3}), 25.0 (3×CH\textsubscript{2}), 29.3 (3×CH\textsubscript{2}), 29.4 (3×CH\textsubscript{2}), 29.5 (3×CH\textsubscript{2}), 29.6 (3×CH\textsubscript{2}), 32.1 (3×CH\textsubscript{2}), 34.3 (3×CH\textsubscript{2}), 36.0 (≡C-CH\textsubscript{2}-CH\textsubscript{2}), 58.7 (CR\textsubscript{3}N), 62.7 (3×C-CH\textsubscript{2}-O-), 69.5 (≡CH), 82.8 (HC≡C-), 171.2 (O=C), 173.6 (3×O=C); Accurate mass (ESI): Found: 748.6082 C\textsubscript{45}H\textsubscript{82}O\textsubscript{7}N (MH\textsuperscript{+}) requires 748.6086.

2-(Pent-4-ynamido)-2-((tetradecanoyloxy)methyl)propane-1,3-diyl ditetradecanoate (19)
Synthesised in accordance with General Procedure B. Purification by column chromatography (3:1, petrol/ether) afforded the compound (492 mg, 79%) as a white solid; ν\text{max}/cm\(^{-1}\) (thin film) 2916s, 2849s, 1736s, 1652s, 1555m, 1469m, 1373m, 1269m; δ\(_H\) (400 MHz, CDCl\(_3\)) 0.86 (9H, t, \(J=6.4, 3\times\text{CH}_2-\text{CH}_3\)), 1.17-1.33 (60H, m, 30×CH\(_2\)), 1.54-1.63 (6H, m, 3×O=CH-CH\(_2\)-CH\(_2\)), 1.96 (1H, t, \(J=2.7, \equiv\text{CH}\)), 2.26-2.37 (8H, m, \equiv\text{C-CH}_2-\text{CH}_2), overlays t, \(J=7.7, 3\times\text{O-CH}_2\), 2.43-2.49 (2H, m, \equiv\text{C-CH}_2), 4.41 (6H, s, 3×CH\(_2\)-O-), 6.03 (1H, br s, \text{NH}); δ\(_C\) (100 MHz, CDCl\(_3\)) 14.3 (3×CH\(_2\)-CH\(_3\)), 14.9 (≡C-CH\(_2\)-CH\(_2\)), 22.9 (3×CH\(_2\)-CH\(_3\)), 25.0 (3×CH\(_2\)), 29.3 (3×CH\(_2\)), 29.4 (3×CH\(_2\)), 29.5 (3×CH\(_2\)), 29.6 (3×CH\(_2\)), 29.8 (6×CH\(_2\)), 29.8 (3×CH\(_2\)), 29.8 (3×CH\(_2\)), 32.1 (3×CH\(_2\)), 34.3 (3×CH\(_2\)), 36.0 (≡C-CH\(_2\)-CH\(_2\)), 58.7 (CR\(_3\)N), 62.7 (3×C-CH\(_2\)-O-), 69.5 (≡C), 82.8 (HC≡C-), 171.2 (O=C), 173.6 (3×O=C); Accurate mass (ESI): Found: 832.7024 C\(_{51}\)H\(_{91}\)O\(_7\)N (MH\(^+\)) requires 832.7025.

2-((Palmitoyloxy)methyl)-2-(pent-4-ynamido)propane-1,3-diyl dipalmitate (20)

Synthesised in accordance with General Procedure B. Purification by column chromatography (5:1, petrol/ether) afforded the compound (442 mg, 61%) as a white solid; ν\text{max}/cm\(^{-1}\) (thin film) 2916s, 2849s, 1736s, 1652s, 1552m, 1469m, 1373m, 1266m; δ\(_H\) (400 MHz, CDCl\(_3\)) 0.86 (9H, t, \(J=6.2, 3\times\text{CH}_2-\text{CH}_3\)), 1.19-1.34 (72H, m, 36×CH\(_2\)), 1.54-1.63 (6H, m, 3×O=CH-CH\(_2\)-CH\(_2\)), 1.96 (1H, t, \(J=2.7, \equiv\text{CH}\)), 2.27-2.37 (8H, m, \equiv\text{C-CH}_2-\text{CH}_2), overlays t, \(J=7.4, 3\times\text{O-CH}_2\), 2.43-2.50 (2H, m, \equiv\text{C-CH}_2), 4.41 (6H, s, 3×CH\(_2\)-O-), 6.03 (1H, br s, \text{NH}); δ\(_C\) (100 MHz, CDCl\(_3\)) 14.3 (3×CH\(_2\)-CH\(_3\)), 14.9 (≡C-CH\(_2\)-CH\(_2\)), 22.9 (3×CH\(_2\)-CH\(_3\)), 25.0 (3×CH\(_2\)), 29.3 (3×CH\(_2\)), 29.4 (3×CH\(_2\)), 29.5 (3×CH\(_2\)), 29.7 (3×CH\(_2\)), 29.8 (6×CH\(_2\)), 29.8 (6×CH\(_2\)), 29.9 (6×CH\(_2\)), 32.1 (3×CH\(_2\)), 34.3 (3×CH\(_2\)), 36.0 (≡C-CH\(_2\)-CH\(_2\)), 58.7 (CR\(_3\)N), 62.7 (3×C-CH\(_2\)-O-), 69.5 (≡C), 82.8 (HC≡C-), 171.2 (O=C), 173.6 (3×O=C); Accurate mass (ESI): Found: 916.7965 C\(_{40}\)H\(_{73}\)O\(_6\) (MH\(^+\)) requires 916.7964.
2-(Pent-4-ynamido)-2-(((3,7,11,15-tetramethylhexadecanoyl)oxy)methyl)propane-1,3-diyl bis(3,7,11,15-tetramethylhexadecanoate) (21)

Synthesised in accordance with General Procedure B. Purification by column chromatography (5:1, petrol/ether) afforded the compound (293 mg, 61%) as a colourless, viscous oil; $\nu_{\text{max}}$/cm$^{-1}$ (thin film) 2953s, 2924s, 2868s, 1742s, 1658s, 1546m, 1462m, 1378m, 1244m; $\delta_{\text{H}}$ (400 MHz, CDCl$_3$) 0.81-0.87 (36H, app. dd, $J$ 6.8, 6.5, 12×CH-$\text{CH}_2$), 0.91 (6H, d, $J$ 6.5, 3×O=C-$\text{CH}_2$-$\text{CH}$-$\text{CH}_3$), 0.98-1.41 (60H, m, 27×$\text{CH}_2$ and 6×$\text{CH}$), 1.50 (3H, app. non, $J$ 6.5, 3×$\text{CH}_2$-$\text{CH}$-(CH$_3$)$_2$), 1.86-1.98 (3H, m, 3×O=C-$\text{CH}$-$\text{CH}$ overlays t, $J$ 2.7, ≡$\text{CH}$), 2.10 (3H, dd, $J$ 14.4, 8.5, 3×O=C-$\text{CHH}^-$-$\text{CH}$), 2.28-2.37 (9H, m, 3×O=C-$\text{CHH}^-$-$\text{CH}$ and 3×O=C-$\text{CH}_2$), 2.42-2.49 (2H, m, ≡$\text{C}$-$\text{CH}_2$), 4.42 (6H, s, 3×$\text{CH}_2$-O-), 6.06 (1H, br s, NH); $\delta_{\text{C}}$ (100 MHz, CDCl$_3$) 14.9 (≡$\text{C}$-$\text{CH}_2$-$\text{CH}_2$), 19.7 ($\text{CH}_3$), 19.8 ($\text{CH}_3$), 19.8 (2×$\text{CH}_3$), 19.8 (3×$\text{CH}_3$), 19.9 ($\text{CH}_3$), 19.9 ($\text{CH}_3$), 22.8 (3×$\text{CH}_3$) 22.9 (3×$\text{CH}_3$), 24.5 (3×$\text{CH}_2$), 24.6 (3×$\text{CH}_2$), 25.0 (3×$\text{CH}_2$), 28.1 (3×$\text{CH}$), 30.5 (3×$\text{CH}$), 32.9 (3×$\text{CH}$), 33.0 (3×$\text{CH}$), 36.0 (≡$\text{C}$-$\text{CH}_2$-$\text{CH}_2$), 37.2 (3×$\text{CH}_2$), 37.3 ($\text{CH}_2$), 37.4 ($\text{CH}_2$), 37.4 (2×$\text{CH}_2$), 37.5 ($\text{CH}_2$), 37.6 (2×$\text{CH}_2$), 37.6 (2×$\text{CH}_2$), 37.7 ($\text{CH}_2$), 39.5 (3×$\text{CH}_2$-$\text{CH}$-(CH$_3$)$_2$), 41.7 (O=C-$\text{CH}_2$-$\text{CH}$), 41.8 (O=C-$\text{CH}_2$-$\text{CH}$), 41.8 (O=C-$\text{CH}_2$-$\text{CH}$), 58.7 ($\text{CR}_3$N), 62.7 (3×$\text{CH}_2$-O-), 69.5 (≡$\text{CH}$), 82.8 (HC≡C-), 171.1 (O=C), 173.1 (3×O=C); Accurate mass (ESI): Found: 1084.9813 $\text{C}_{69}$H$_{130}$O$_7$N (MH$^+$) requires 1084.9849.

515
(7Z,7’Z)-2-((((Z)-hexadec-7-enoxy)methyl)-2-(pent-4-ynamido)propane-1,3-diyl bis(hexadec-7-enoate) (22)

![Chemical structure of compound 22](image)

Synthesised in accordance with General Procedure B. Purification by column chromatography (5:1, petrol/ether) afforded the compound (240 mg, 53%) as a colourless, viscous oil; \( \nu_{\max} / \text{cm}^{-1} \) (thin film) 2923s, 2853s, 1743s, 1658s, 1545m, 1465m, 1378m, 1239m; \( \delta_{\text{H}} \) (400 MHz, CDCl\(_3\)) 0.86 (9H, t, \( J \) 6.2, 3×CH\(_2\)-C\( \)H\(_3\)), 1.20-1.35 (48H, m, 24×C\( \)H\(_2\)), 1.54-1.64 (6H, m, 3×O=C-CH\(_2\)-C\( \)H\(_2\)), 1.94-2.04 (13H, m, 6×=CH-CH\(_2\) overlays \( \equiv \)CH), 2.26-2.38 (8H, m, \( \equiv \)C-CH\(_2\)-CH\(_3\), overlays t, \( J \) 7.6, 3×O=C-CH\(_3\)), 2.43-2.49 (2H, m, \( \equiv \)C-CH\(_2\)-CH\(_2\)-O-), 4.41 (6H, s, 3×CH\(_2\)-O-), 5.32 (6H, dt, \( J \) 5.6, 3.4, 3×-CH=CH-), 6.03 (1H, br s, NH); \( \delta_{\text{C}} \) (100 MHz, CDCl\(_3\)) 14.3 (3×CH\(_2\)-CH\(_3\)), 14.9 (\( \equiv \)C-CH\(_2\)-CH\(_3\)), 22.8 (3×CH\(_2\)-CH\(_3\)), 25.0 (3×CH\(_2\)), 27.3 (3×=C-CH\(_2\)), 27.4 (3×CH\(_2\)-C=), 29.1 (3×CH\(_2\)), 29.3 (3×CH\(_2\)), 29.3 (6×CH\(_2\)), 29.9 (3×CH\(_2\)), 31.9 (3×CH\(_2\)), 34.2 (3×CH\(_2\)), 36.0 (\( \equiv \)C-CH\(_2\)-CH\(_2\)), 58.7 (CR\(_3\)N), 62.7 (3×=C-CH\(_2\)-O-), 69.6 (\( \equiv \)CH), 82.8 (HC=\( \equiv \)C-), 129.9 (3×C=\( \equiv \)C) 130.2 (3×C=\( \equiv \)C), 171.2 (O=C), 173.6 (3×O=C);

Accurate mass (ESI): Found: 910.7496 C\(_{57}\)H\(_{100}\)O\(_7\)N (MH\(^+\)) requires 910.7494.

(Z)-2-((Oleoyloxy)methyl)-2-(pent-4-ynamido)propane-1,3-diyl dioleate (23)

![Chemical structure of compound 23](image)

(516)
Synthesised in accordance with General Procedure B. Purification by column chromatography (5:1, petrol/ether) afforded the compound (501 mg, 63%) as a colourless, viscous oil; \( \nu_{\text{max}} / \text{cm}^{-1} \) (thin film) 2922s, 2853s, 1742s, 1660s, 1545m, 1465m, 1378m, 1274m; \( \delta_{\text{H}} \) (400 MHz, CDCl\(_3\)) 0.86 (9H, t, \( J=6.8 \), 3x CH\(_2\)-CH\(_3\)), 1.19-1.35 (60H, m, 30xCH\(_2\)), 1.54-1.64 (6H, m, 3xO=C-CH\(_2\)-CH\(_3\)), 1.94-2.03 (13H, m, 6x=CH=CH\(_2\) overlays \( \equiv\text{CH} \), 2.26-2.37 (8H, m, =C-CH\(_2\)-CH\(_2\), overlays t, \( J=7.4 \), 3xO=C-CH\(_2\)), 2.43-2.49 (2H, m, =C-CH\(_3\)), 4.41 (6H, s, 3xCH\(_2\)-O-), 5.32 (6H, dt, \( J=5.7, 3.6 \), 3x-CH=CH-), 6.03 (1H, br s, NH); \( \delta_{\text{C}} \) (100 MHz, CDCl\(_3\)) 14.3 (3xCH\(_2\)-CH\(_3\)), 14.9 (≡C-CH\(_2\)-CH\(_2\)), 22.8 (3xCH\(_2\)-CH\(_3\)), 25.0 (3xCH\(_2\)), 27.3 (3x=CH=CH\(_2\)), 27.4 (3xC=C=), 29.3 (3xCH\(_2\)), 29.5 (3xCH\(_2\)), 29.7 (3xCH\(_2\)), 29.9 (3xCH\(_2\)), 32.1 (3xCH\(_3\)), 34.2 (3xCH\(_2\)), 36.0 (≡C-CH\(_2\)-CH\(_2\)), 58.7 (CR\(_3\)N), 62.7 (3x-C-CH\(_2\)-O-), 69.6 (≡CH), 82.8 (HC≡C-), 129.8 (3x=C=C) 130.2 (3x=C=C), 171.2 (O=C), 173.6 (3xO=C); Accurate mass (ESI): Found: 994.8415 C\(_{63}\)H\(_{112}\)O\(_7\)N (MH\(^+\)) requires 994.8441.

(13Z,13'Z)-2-(((Z)-Docos-13-enoyloxy)methyl)-2-(pent-4-ynamido)propane-1,3-diyl bis(docos-13-enoate) (24)

![Diagram of the compound](image-url)
(3×=C-CH₂), 29.3 (3×CH₂), 29.4 (3×CH₂), 29.5 (6×CH₂), 29.5 (3×CH₂), 29.7 (3×CH₂), 29.7 (3×CH₂), 29.8 (3×CH₂), 29.9 (3×CH₂), 30.0 (3×CH₂), 32.1 (3×CH₂), 34.3 (3×CH₂), 36.0 (≡C-CH₂-CH₂), 58.7 (CR₃N), 62.7 (3×C-CH₂-O-), 69.5 (≡CH), 82.8 (HC≡C-), 130.0 (3×C=C) 130.1 (3×C=C), 171.20 (O=C), 173.6 (3×O=C); Accurate mass (ESI): Found: 1163.0320 C₇₅H₁₃₆O₇N (MH⁺) requires 1163.0313.

Synthesis of sugar head groups

(2S,3R,4S,5R)-tetrahydro-2H-pyran-2,3,4,5-tetrayl tetraacetate (31)[2]

To a stirred suspension of anhydrous sodium acetate (4.36 g, 53.2 mmol) in acetic anhydride (25 mL) heated at reflux was added D(+)-xylose (2.0 g, 13.3 mmol). The reaction mixture was heated for 3 h before cooling to 100 °C and immediately transferred to an ice–water mixture and stirred vigorously until a gum formed. After decanting the aqueous portion, the gum was dissolved in DCM and washed successively with sat. aq. NaHCO₃ solution and brine. The organic layer was dried over MgSO₄ anhydrous and concentrated in vacuo. The title compound (4.05g, 97%) was obtained as a white solid and was used in subsequent reactions without further purification.

(2R,3R,4S,5R)-2-azidotetrahydro-2H-pyran-3,4,5-triyl triacetate (32)[3]

To a stirred solution of FeCl₃ (64 mg, 0.40 mmol) in dry DCM (10 mL) was added xylose tetraacetate 31 (4.18 g, 13.3 mmol) in DCM (20 mL). After stirring for 5 min, a solution of trimethylsilyl azide in DCM (10 mL) was added dropwise. The progress of reaction was monitored by thin layer chromatography (1:2 ethyl acetate/petrol). Once complete consumption of the starting material was observed, the reaction was quenched with sat. aq. NaHCO₃ solution. After separation, the aqueous layer was extracted with DCM and the combined organic extracts washed with brine, dried over
MgSO₄ and concentrated in vacuo to give the crude product. Purification by column chromatography (1:2 ethyl acetate/petrol benzene) afforded the title compound (2.29 g, 58%) as a colourless viscous oil. Data matched literature values.[³]

1-Azido-1-β-D-xylopyranoside (27)[⁴]

To a stirred solution of azide 32 (2.26 g, 7.60 mmol) in methanol (20 mL) was added a catalytic amount of sodium methoxide (10 mg, 0.18 mmol). After stirring for 1 h the reaction mixture was neutralised with Amberlite IR-120[H⁺] resin. The reaction mixture was filtered and concentrated in vacuo to afford the title compound (1.25 g, 96%) as a white solid without the need for further purification; δₓ (400 MHz, MeOD) 3.09 (1H, app. t, J 8.4, CHOH-CHN₃), 3.22-3.31 (2H, m, COH-CHOH-COH & COH-CHOH-CH₂), 3.42-3.50 (1H, m, O-CHH'), 3.90 (1H, dd, J 10.6, 5.0, O-CHH'), 4.39 (1H, d, J 8.4, CHN₃); δᵺ (100 MHz, CDCl₃) 67.8 (CH₂), 69.6 (C-OH), 73.5 (C-OH), 76.8 (C-OH), 91.4 (C-N₃).
Amphiphile synthesis and characterisation

General procedure

To each of 24 glass vials (18 mm × 45 mm) in a 4 × 6 array aluminium reaction block, was added a solution of azido sugar (1.0 equiv, ca. 15 mg) in 2:1 t-BuOH/water (1.5 mL). Alkyne (1.0 equiv) was added and the reaction block heated, with stirring, to 40 °C. After dissolution, copper powder (ca. 150 mg) was added and the reaction stirred for 24–48 h. The reaction mixture was cooled, diluted with ethanol (2 mL) and filtered through Celite® into 24 glass vials (25 mm × 75 mm). Concentration in vacuo on a Genevac EZ-2, followed by vacuum oven drying (50 °C, 3 h), afforded the amphiphile products.

MALDI–TOF results

Table S1: Double-chain amphiphiles.

| Sugar   | Double chain tail | Amphiphile | Predicted mass [MNa]+ | Experimental mass [MNa]+ |
|---------|------------------|------------|------------------------|--------------------------|
| Glucose | C7               | 33         | 652.3                  | 652.4                    |
| Glucose | C9               | 34         | 708.4                  | 708.5                    |
| Glucose | C11              | 35         | 764.5                  | 764.6                    |
| Glucose | C13              | 36         | 820.5                  | 820.6                    |
| Glucose | Phyt             | 37         | 988.8                  | 988.8                    |
| Glucose | Palm             | 38         | 872.6                  | 872.7                    |
| Glucose | Ole              | 39         | 928.6                  | 928.7                    |
| Glucose | Eruc             | 40         | 1040.7                 | 1040.8                   |
| Glucose | Lin              | 41         | 924.7                  | 924.7                    |
| Galactose | C7            | 42         | 652.3                  | 652.1                    |
| Galactose | C9            | 43         | 708.4                  | 708.3                    |
| Galactose | C11           | 44         | 764.5                  | 764.4                    |
| Galactose | C13           | 45         | 820.5                  | 820.6                    |
| Galactose | C15           | 46         | 876.6                  | 876.5                    |
| Galactose | C17           | 47         | 932.7                  | 932.6                    |
| Galactose | Phyt           | 48         | 988.7                  | 988.7                    |
| Galactose | Palm          | 49         | 872.6                  | 872.5                    |
| Galactose | Ole          | 50         | 928.6                  | 928.6                    |
| Galactose | Eruc          | 51         | 1040.7                 | 1040.7                   |
| Galactose | Lin          | 52         | 924.6                  | 924.6                    |
| Xylose  | C7               | 53         | 622.3                  | 622.3                    |
| Xylose  | C9               | 54         | 678.4                  | 678.5                    |
| Xylose  | C11              | 55         | 734.5                  | 734.6                    |
| Xylose  | C13              | 56         | 790.5                  | 790.7                    |
| Xylose  | C15              | 57         | 846.6                  | 846.7                    |
| Xylose  | C17              | 58         | 902.6                  | 902.8                    |
| Xylose  | Phyt             | 59         | 958.8                  | 958.8                    |
| Xylose  | Palm             | 60         | 842.5                  | 842.7                    |
| Xylose  | Ole              | 61         | 898.6                  | 898.7                    |
| Sugar     | Double chain tail | Amphiphile | Predicted mass [MNa]^+ | Experimental mass [MNa]^+ |
|-----------|------------------|------------|------------------------|--------------------------|
| Xylose    | Eruc             | 62         | 1010.7                 | 1010.9                   |
| Xylose    | Lin              | 63         | 894.7                  | 894.7                    |
| Mannose   | C7               | 64         | 652.3                  | 652.2                    |
| Mannose   | C9               | 65         | 708.4                  | 708.3                    |
| Mannose   | C11              | 66         | 764.5                  | 764.4                    |
| Mannose   | Phyt             | 67         | 988.7                  | 988.7                    |
| Mannose   | Palm             | 68         | 872.6                  | 872.5                    |
| Mannose   | Ole              | 69         | 928.6                  | 928.6                    |
| Lactose   | C7               | 70         | 814.1                  | 814.3                    |
| Lactose   | C9               | 71         | 870.5                  | 870.4                    |
| Lactose   | C11              | 72         | 926.6                  | 926.5                    |
| Lactose   | C13              | 73         | 982.6                  | 982.5                    |
| Lactose   | Phyt             | 74         | 1150.8                 | 1150.8                   |
| Lactose   | Palm             | 75         | 1034.6                 | 1034.6                   |
| Lactose   | Ole              | 76         | 1090.7                 | 1090.7                   |
| Lactose   | Eruc             | 77         | 1202.8                 | 1203.5                   |
| Lactose   | Lin              | 78         | 1086.1                 | Not found                |

Table S2: Triple chain amphiphiles.
13C NMR results

A selection of 15 amphiphiles (3 for each sugar) were randomly selected for 13C NMR spectroscopy and cover a range of different double and triple chain tails.

Glucose – 2 × Ole (39)

δC (100 MHz, CD3OD) 13.1 (×2), 16.7, 22.3 (×2), 24.6 (×2), 26.7 (×4), 28.7 (×2), 28.8 (×2), 28.9 (×2), 29.0 (×2), 29.1 (×2), 29.2 (×2), 29.4 (×2), 29.5 (×2), 31.7 (×2), 33.4 (×2), 46.2, 57.4, 61.0, 64.8 (×2), 69.5, 72.6, 77.1, 79.8, 88.2, 123.9, 129.4 (×2), 129.5 (×2), 142.2, 172.5, 173.3 (×2).

Galactose – 2 × C13 (45)

δC (100 MHz, CD3OD) 13.1 (×2), 16.7, 22.3 (×2), 24.6 (×2), 28.8 (×2), 29.0 (×2), 29.1 (×2), 29.2 (×2), 29.4 (×2), 29.4 (×2), 29.4 (×2), 29.4 (×2), 31.7 (×2), 33.4 (×2), 46.2, 57.5, 60.9, 64.8 (×2), 68.9, 70.1, 73.9, 78.6, 88.9, 123.4, 142.4, 172.5, 173.4 (×2).

Galactose – 2 × Palm (49)

δC (100 MHz, CD3OD) 13.1 (×2), 16.7, 22.3 (×2), 24.6 (×2), 26.7 (×2), 26.8 (×2), 28.7 (×2), 28.7 (×2), 28.8 (×2), 28.9 (×2), 29.4 (×2), 29.4 (×2), 29.4 (×2), 31.5 (×2), 33.4 (×2), 46.2, 57.5, 60.9, 64.8 (×2), 68.9, 70.1, 73.6, 78.6, 88.9, 123.4, 129.4 (×2), 129.5 (×2), 142.4, 172.5, 173.4 (×2).

Xylose – 2 × C15 (57)

δC (100 MHz, CD3OD) 13.1 (×2), 16.7, 22.3 (×2), 24.6 (×2), 28.8 (×2), 29.0 (×2), 29.1 (×2), 29.2 (×2), 29.4 (×2), 29.4 (×4), 29.4 (×4), 29.7 (×2), 31.7 (×2), 33.4 (×2), 46.2, 57.4, 64.9 (×2), 68.5, 69.2, 72.5, 77.2, 88.9, 123.8, 142.2, 172.6, 173.3 (×2).

Mannose – 2 × C7 (64)

δC (100 MHz, CD3OD) 13.0 (×2), 16.6, 22.3 (×2), 24.6 (×2), 28.7 (×2), 28.7 (×2), 31.5 (×2), 33.4 (×2), 46.2, 57.4, 61.1, 64.8 (×2), 67.2, 68.7, 71.2, 77.4, 87.0, 124.6, 142.5, 172.5, 173.3 (×2).
Mannose – $2 \times$ Phyt (67)

$\delta_C$ (100 MHz, CD$_3$OD) 16.8, 18.7, 18.7, 18.8 (×2), 18.8, 18.8, 21.6 (×2), 21.7 (×2), 24.0, 24.1, 24.1 (×2), 24.5, 24.5, 27.8 (×2), 30.1, 30.1, 32.5 (×2), 32.6 (×2), 36.5, 36.6, 36.8, 36.8, 36.9, 36.9, 37.0, 37.1, 37.1, 37.2, 39.2 (×2), 41.0, 41.1, 46.1, 57.4, 61.1, 64.8 (×2), 67.2, 68.7, 71.2, 77.3, 87.0, 124.5, 142.5, 172.5, 172.7 (×2).

Lactose – $2 \times$ C9 (71)

$\delta_C$ (100 MHz, CD$_3$OD) 13.0 (×2), 16.6, 22.3 (×2), 25.6 (×2), 28.8 (×2), 29.0 (×4), 29.2 (×2), 31.7 (×2), 33.4 (×2), 46.2, 57.4, 60.1, 61.1, 64.8 (×2), 68.9, 71.1, 72.2, 73.4, 75.5, 75.8, 78.2, 88.0, 103.7, 123.9, 142.2, 172.5, 173.4 (×2).

Lactose – $2 \times$ Eruc (77)

$\delta_C$ (100 MHz, CD$_3$OD) 13.1 (×2), 16.7, 22.4 (×2), 24.6 (×2), 26.8 (×4), 28.7 (×2), 28.8 (×4), 28.9 (×2), 29.0 (×2), 29.1 (×4), 29.2 (×4), 29.4 (×4), 29.5 (×2), 31.7 (×2), 33.4 (×2), 46.2, 57.4, 60.1, 61.1, 64.8 (×2), 68.9, 71.1, 72.2, 73.4, 75.5, 75.8, 78.2, 88.0, 103.7, 123.9, 129.4 (×2), 129.5 (×2), 142.2, 172.5, 173.3 (×2).

Glucose – $3 \times$ C9 (80)

$\delta_C$ (100 MHz, CD$_3$OD) 13.1 (×3), 21.0, 22.3 (×3), 24.6 (×3), 28.8 (×3), 29.0 (×3), 29.1 (×3), 29.2 (×3), 31.7 (×3), 33.5 (×3), 35.0, 57.7, 61.0, 61.6 (×3), 69.5, 72.6, 77.1, 79.7, 88.2, 121.3, 146.2, 173.3 (×3), 173.5.

Glucose – $3 \times$ Palm (83)

$\delta_C$ (100 MHz, CD$_3$OD) 13.0 (×3), 21.1, 22.3 (×3), 24.6 (×3), 28.7 (×3), 28.7 (×3), 28.8 (×3), 28.8 (×3), 29.4 (×3), 29.4 (×3), 31.5 (×3), 33.4 (×3), 35.4, 60.6, 61.0 (×3), 62.3, 69.5, 72.6, 77.1, 79.7, 88.2, 121.4, 129.4 (×3), 129.5 (×3), 146.2, 174.2, 174.6 (×3).
Galactose – 3 × Phyt (89)

\( \delta_C \) (100 MHz, CD\textsubscript{3}OD) 18.7, 18.8, 18.9, 21.0, 21.7 (×3), 21.8 (×3), 24.1, 24.1, 24.1 (×3), 24.2, 24.5 (×3), 27.8 (×3), 30.1 (×3), 32.5, 32.5 (×3), 32.6 (×2), 35.1, 36.6 (×3), 36.7 (×3), 36.8, 36.9, 36.9, 37.0, 37.0 (×3), 37.1 (×3), 37.1 (×3), 37.2, 37.2, 39.2 (×3), 41.1 (×2), 41.1, 57.6, 61.0, 61.6 (×3), 68.9, 70.0, 73.9, 78.5, 88.8, 120.8, 146.3, 172.6 (×3), 173.5.

Xylose – 3 × C11 (95)

\( \delta_C \) (100 MHz, CD\textsubscript{3}OD) 13.2 (×3), 21.3, 22.5 (×3), 24.8 (×3), 29.0 (×3), 29.1 (×3), 29.2 (×3), 29.3 (×3), 29.5 (×6), 31.8 (×3), 33.6 (×3), 35.5, 61.2 (×3), 62.4, 68.6, 69.4, 72.6, 77.3, 88.9, 121.3, 146.4, 174.4, 174.8 (×3).

Xylose – 3 × Eruc (99)

\( \delta_C \) (100 MHz, CD\textsubscript{3}OD) 13.0 (×3), 21.1, 22.3 (×3), 24.6 (×3), 26.7 (×3), 26.7 (×3), 28.8 (×3), 28.9 (×3), 29.0 (×3), 29.1 (×3), 29.2 (×3), 29.2 (×3), 29.3 (×3), 29.4 (×3), 29.4 (×3), 31.7 (×3), 33.4 (×3), 35.3, 61.0 (×3), 62.3, 68.4, 69.3, 72.5, 77.2, 88.8, 121.2, 129.4 (×3), 129.5 (×3), 146.3, 174.2, 176.6 (×3).

Mannose – 3 × Ole (105)

\( \delta_C \) (100 MHz, CD\textsubscript{3}OD) 13.0 (×3), 21.0, 22.3 (×3), 24.6 (×3), 26.7 (×3), 26.7 (×3), 28.7 (×3), 28.8 (×3), 28.8 (×3), 28.8 (×3), 29.0 (×3), 29.2 (×3), 29.4 (×3), 29.4 (×3), 31.7 (×3), 33.4 (×3), 35.3, 61.0 (×3), 61.2, 62.3, 67.2, 68.7, 71.1, 77.1, 86.9, 122.1, 129.4 (×3), 129.5 (×3), 146.5, 174.2, 174.6 (×3).

Lactose – 3 × C7 (106)

\( \delta_C \) (100 MHz, CD\textsubscript{3}OD) 13.0 (×3), 21.0, 22.2 (×3), 24.6 (×3), 28.7 (×3), 28.1 (×3), 31.4 (×3), 33.4 (×3), 35.2, 60.1, 60.6, 61.0, 61.1 (×3), 61.7, 71.1, 72.2, 73.4, 75.4, 75.8, 78.1, 78.3, 87.9, 103.7, 121.3, 146.3, 173.5 (×3), 174.7.
$^{13}$C NMR spectra

Glucose - 2 x Oleic
Amphiphile 39

Galactose - 2 x C13
Amphiphile 45
Galactose - 2 x Palmitoleic
Amphiphile 49

Xylose - 2 x C15
Amphiphile 57
**Mannose - 2 x C7**
**Amphiphile 64**

**Mannose - 2 x Phytanic**
**Amphiphile 67**
Lactose - 2 x C9
Amphiphile 71

Lactose - 2 x Erucic
Amphiphile 77
Glucose - 3 x C9
Amphiphile 80

Glucose - 3 x Palmitoleic
Amphiphile 83
Galactose - 3 x Phytanic Amiphile 89

Xylose - 3 x C11 Amiphile 95
Xylose - 3 x Erucic Amiphile 99

Mannose - 3 x Oleic Amiphile 105
Preliminary SAXS analysis

The internal liquid crystalline structure was determined using small-angle X-ray scattering. Each amphiphile was dispensed into a 96-well plate and an excess of water (70% w/v) was added to each well using a Mosquito® liquid dispensing robot. The samples were equilibrated under controlled conditions of temperature and humidity for 5 days before SAXS analysis was carried out. Samples were analysed within the 96-well plate using a bespoke sample holder at the SAXS beamline at the Australian Synchrotron. The resulting diffraction patterns were analysed using the IDL-based AXcess software package[5] and the number and distribution of reflections used to assign the mesophase.

Table S3: SAXS data for compounds 33, 53 and 70 at 70% w/v at 25 °C.

| Amphiphile       | Phase   | Lattice parameter (Å) |
|------------------|---------|-----------------------|
| Glucose − 2 × C7 | 33      | IA3D                  |
| Xylose − 2 × C7  | 53      | Micellar              |
| Lactose − 2 × C7 | 70      | Lamellar              |

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