SUPPLEMENTARY INFORMATION 1

Synthesis of Phalluside-1 and Sch II Using 1,2-Metallate Rearrangements

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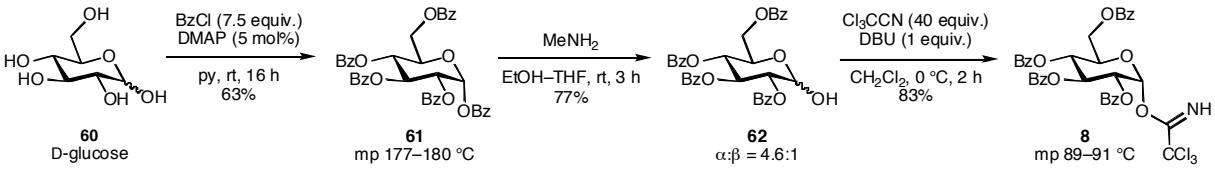
General Information and Materials

Reactions requiring anhydrous conditions were conducted under a nitrogen atmosphere in flame-dried glassware. Where appropriate, solvents and reagents were dried by distillation from the usual drying agent under a nitrogen atmosphere prior to use: THF and Et_2O from sodium benzophenone ketyl; CH_2Cl_2, MeCN, PhH and PhMe from CaH_2. All reactions were magnetically stirred and monitored by TLC using 0.25 mm E. Merck pre-coated silica gel plates visualised with UV light followed by phosphomolybdic acid. All organic extracts were dried over anhydrous sodium sulfate and concentrated using a Büchi rotary evaporator and a diaphragm pump (ca 10 mmHg). All NMR spectra were recorded on Bruker DPX-300 and DRX-500 spectrometers in the solvents specified. Chemical shifts (δ) are reported in ppm relative to the residual signals of chloroform (δ_H = 7.27, δ_C = 77.2), benzene (δ_H = 7.16, δ_C = 128.4), acetone (δ_H = 2.05, δ_C = 29.8), methanol (δ_H = 3.31, δ_C = 49.0), DMSO (δ_H = 2.50, δ_C = 39.5) or pyridine (δ_H = 7.19, δ_C = 123.5) unless stated otherwise. Coupling constants (J) are reported in Hertz (Hz) with multiplicities described using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, m = multiplet. Signal assignments are based on COSY and HMQC correlation experiments. In ^{13}C NMR spectra, multiplicities and signal assignments were determined using DEPT 135 and HMBC correlation experiments. Infrared spectra were recorded neat on NaCl plates or as a solid on a diamond transmission accessory using a Perkin Elmer FT-IR spectrometer; details are reported as ν_{max} in cm^{-1}, followed by a description using the following abbreviations: s = strong, m = medium, w = weak, br = broad. Mass spectrometric analyses were performed using a Microsmass LCT (ES mode), Bruker Daltonic (ES mode) or Waters GCT Premier (EI and CI mode) apparatus and are reported as values in atomic mass units followed by the peak intensity relative to the base peak (100%). Elemental analyses were performed using a Carlo Erba 1108 apparatus. Specific optical rotations were recorded at ambient temperature in the solvents specified on an AA-1000 polarimeter

and reported in 10^{-1}degcm^{2}g^{-1}. Melting points were measured using a Griffin melting point apparatus and are uncorrected.

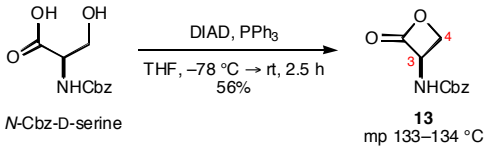
Synthesis of Phalluside-1

2,3,4,6-Tetra-*O*-benzoyl-α-D-glucopyranosyl trichloroacetimidate (8)



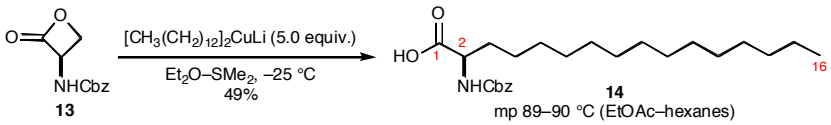
The title compound (mp 89–91 °C from Et_2O–hexane) was prepared in 3 steps (40% overall) from D-glucose as shown in the Scheme. The conversion of D-glucose to 2,3,4,6-tetra-*O*-benzoyl-D-glucopyranose (**62**) was described by Egusa et al.[1] and the conversion of **62** to the trichloroacetimidate **2** was described by Ziegler and Juisch.[2] The trichloroacetimidate **8** gave $[\alpha]_D^{21}$ = +82.8 (*c* 1.0, $CHCl_3$); lit.[2] $[\alpha]_D$ = +82.2 (*c* 1.0, $CHCl_3$).

N-(Benzyloxycarbonyl)-D-serine β-lactone (13)



The title compound, prepared in 56% yield from *N*-Cbz-D-serine by the procedure of Vederas and co-workers,[3] gave mp 133–134 °C, lit. mp 133–134 °C; $[\alpha]_D^{28}$ = +25.5 (*c* 1, MeCN), lit. $[\alpha]_D$ = –26.5 (*c* 1, MeCN) for the enantiomer.[3] IR (solid) ν_{max} = 3362 m, 1827 m, 1684 s, 1530 s cm^{-1}. ^{1}H NMR data recorded at 300 MHz were consistent with literature data recorded at 300 MHz.[4] ^{13}C NMR (75 MHz, $CDCl_3$): δ_C = 168.9 (C=O), 155.4 (Cbz C=O), 135.6 (C_{Ar}), 128.8 (2C_{Ar}H), 128.7 (C_{Ar}H), 128.6 (2C_{Ar}H), 68.0 (OCH_2), 66.5 (C4H_2), 59.8 (C3H).

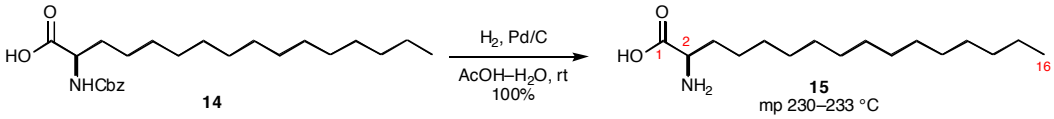
(*R*)-2-[(Benzyloxycarbonyl)amino]hexadecanoic acid (14)



1-Iodotridecane (2.83 g, 9.1 mmol, 10.0 equiv) was added dropwise to a solution of *tert*-butyllithium (1.69 M in pentane, 10.8 mL, 18.2 mmol, 20.0 equiv) in Et_2O (8 mL) at –78 °C using Et_2O (2 mL) for washing. The white suspension was stirred at –78 °C for 30 mins, 0 °C for 1 h and room temperature for 1 h. The reaction was cooled to 0 °C and a solution of freshly recrystallised CuBr•SMe_2 (recrystallised from SMe_2–pentane 2:1, 935 mg, 4.6 mmol, 5.0 equiv) in SMe_2 (10 mL) was added by cannula using SMe_2 (3 mL) for washing. The resulting brown/orange solution was

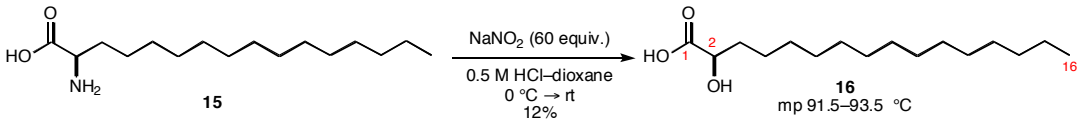
stirred at 0 °C for 1 h. The reaction mixture was cooled to –25 °C and a solution of oxetanone **13** (199 mg, 0.9 mmol) in THF (5 mL) added dropwise using THF (1 mL) for washing. After stirring at –25 °C for 2 h the brown mixture was poured into 0.5 M HCl (25 mL) and extracted with Et_2O (3×30 mL). The combined organic extracts were washed with brine (30 mL), dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography (SiO_2, hexane–EtOAc–AcOH 90:10:1) to give the title compound (180 mg, 0.44 mmol, 49%) as a colourless solid. A sample recrystallised from ethyl acetate–hexanes gave white crystals: mp 89–90 °C; lit.[5] mp 79–81 °C. $[\alpha]_D$ (26 °C) = –3.6 (*c* 0.4, $CHCl_3$). IR (solid): ν_{max} = 3316 m, 1747 m, 1687 s, 1535 m cm^{-1}. ^1H NMR spectroscopic data recorded at 300 MHz were consistent with literature data recorded at 200 MHz.[5] ^{13}C NMR (75MHz, $CDCl_3$): δ_C = 177.1 (C1), 156.2 (Cbz C=O), 136.3 (C_{Ar}), 128.7 ($2C_{Ar}H$), 128.4 ($C_{Ar}H$), 128.3 ($2C_{Ar}H$), 67.3 (OCH_2), 53.9 (C2H), 32.5 (CH_2), 32.1 (CH_2), 29.9, 29.8, 29.8, 29.7, 29.6, 29.3 (number of overlapping CH_2), 25.4 (CH_2), 22.9 (CH_2), 14.3 ($C16H_3$). LRMS (ES^+ mode): *m/z* (%) = 406.3 [$(M+H)^+$, 95], 423.2 [$(M+NH_4)^+$, 100].

(*R*)-2-Aminohexadecanoic acid (15)



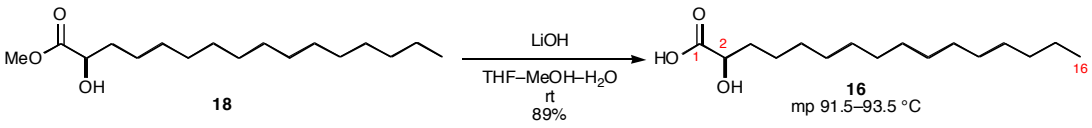
A solution of **14** (0.150 g, 0.37 mmol) in acetic acid (15 mL) and H_2O (7.5 mL) was stirred with 10% Pd on charcoal (60 mg) under an atmosphere of hydrogen for 16 h. THF (10 ml) was added and the mixture filtered through filter paper. The residue was washed with 1:1 THF–0.5 M HCl (5×20 mL) and the filtrate concentrated *in vacuo*. The residue was suspended in H_2O and lyophilised to give the title compound (0.100 g, 0.37 mmol, 100%) as a colourless solid: mp 230–233 °C; lit.[5] mp 233–236 °C. IR (solid): ν_{max} = 3420 m, 2918 s, 2849 m, 1719 m cm^{-1}. ^1H NMR (300 MHz, DMSO): δ_H = 8.36 (3H, br s, NH_3), 3.84 (1H, br s, C2H), 1.77 (2H, br s, $C3H_2$), 1.39 (2H, br s, $C4H_2$), 1.24 (22H, m, $C5H_2$–$C15H_2$), 0.85 (3H, distorted t, *J* = 6.4, $C16H_3$). ^{13}C NMR (75 MHz, DMSO): δ_C = 171.0 (C1), 51.9 (C2H), 31.3, 29.9, 29.0, 29.0, 28.8, 28.7, 28.5, 24.1, 22.1 ($C3H_2$–$C15H_2$), 13.9 ($C16H_3$). LRMS (ES^+ mode): *m/z* (%) = 272.1 [$(M+H)^+$, 59], 313.2 [$(M+H+K)^+$, 100]. HRMS (ES^+ mode): Found, 272.2583 $(M+H)^+$. $C_{16}H_{34}NO_2$ requires M, 272.2584.

(*R*)-2-Hydroxyhexadecanoic acid (16)



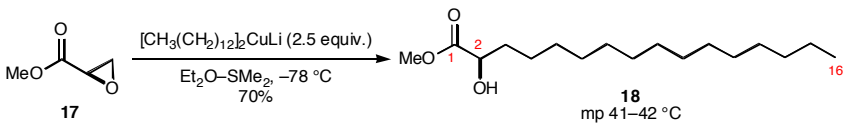
Sodium nitrite (127 mg, 1.84 mmol, 20.0 equiv) was added to a solution of amino acid **15** (25 mg, 0.092 mmol) in dioxane–0.5 M HCl (2:1, 7.5 mL) at 0 °C and the mixture stirred at 0 °C. After 30 min and 1 h further portions of sodium nitrite (2×127 mg, 3.68 mmol, 40.0 equiv) were added and the suspension stirred at 0 °C for 1 h then at room temperature for 16 h. Et_2O (15 mL) was added and the layers separated. The aqueous layer was extracted with Et_2O (2×15 mL). The combined organic extracts were washed with H_2O (10 mL) then brine (10 mL), dried over Na_2SO_4 and

concentrated *in vacuo*. The residue was purified by column chromatography (SiO_2, hexanes–Et_2O–AcOH 80:20:1) to give the title compound (3 mg, 0.011 mmol, 12%) as a colourless solid.



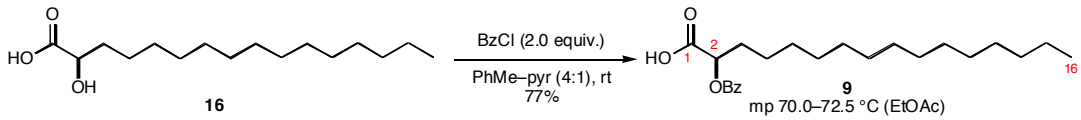
$LiOH•H_2O$ (715 mg, 14.5 mmol, 25 equiv) was added to a solution of **18** (195 mg, 0.68 mmol, 1.0 equiv) in THF–MeOH–H_2O (2:2:1, 25 mL) and the suspension stirred at room temperature for 5 h. The mixture was acidified to pH 1 by addition of 0.25 M HCl and extracted with ethyl acetate (3×20 mL). The combined organic extracts were washed with 0.25 M HCl (20 mL) and brine (20 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The resulting solid was recrystallised from 5:1 hexane/acetone to give the title compound (164 mg, 0.60 mmol, 89%) as white crystals: mp 91.5–93.5 °C; lit.[6] mp 92.5–93.5 °C. $[\alpha]_D^{28} = -3.7$ (*c* 0.5, $CHCl_3$); lit. $[\alpha]_D = -3.2$ (*c* 0.5, $CHCl_3$). IR (solid): ν_{max} = 3444 w, 2917 s, 2849 s, 1750 m cm^{-1}. The ^1H NMR spectroscopic data recorded at 300 MHz were consistent with the literature data recorded at 400 MHz.[7]

Methyl (*R*)-2-hydroxyhexadecanoate (18)



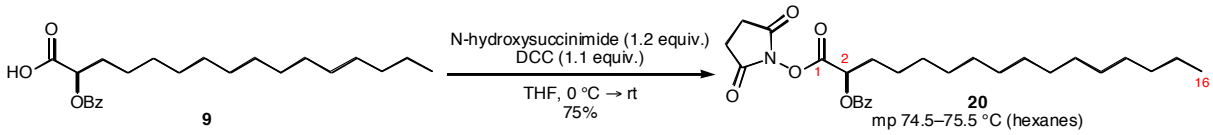
1-Iodotridecane (1.57 g, 5.1 mmol, 5.0 equiv) was added dropwise to a solution of *tert*-butyllithium (1.67 M in pentane, 5.1 mL, 8.6 mmol, 8.5 equiv) in Et_2O (5 mL) at –78 °C using pentane (1 mL) for washing. The colourless suspension was stirred at –78 °C for 30 min, 0 °C for 1 h and room temperature for 1 h. The reaction was cooled to 0 °C and a solution of freshly recrystallised $CuBr•SMe_2$ (recrystallised from SMe_2–pentane 2:1, 519 mg, 2.5 mmol, 2.5 equiv) in SMe_2 (4 mL) using SMe_2 (3 mL) for washing was added by cannula. The resulting orange solution was stirred at 0 °C for 1 h then cooled to –78 °C. A solution of methyl (*R*)-glycidate (**17**, 102 mg, 1.0 mmol, 1.0 equiv) in Et_2O (1 mL) was added dropwise using Et_2O (0.5 mL) for washing. The orange suspension was stirred at –78 to –60 °C for 2 h whereupon saturated aqueous NH_4Cl (10 mL) was added and the mixture allowed to warm to room temperature. The layers were separated and the aqueous phase extracted with Et_2O (3×20 mL). The combined organic extracts were washed with brine (20 mL), dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography (SiO_2, hexanes–Et_2O 20:1) to give the title compound (201 mg, 0.70 mmol, 70%) as a white solid: mp 41–42 °C; lit.[8] mp 45–46 °C. $[\alpha]_D^{28} = -1.0$ (*c* 1.8, EtOH); lit. $[\alpha]_D = -1.5$ (*c* 10, EtOH). IR (solid): ν_{max} = 3292 m, 2916 s, 2849 s, 1737 s cm^{-1}. The ^1H NMR spectroscopic data was consistent with the literature data recorded at 400 MHz.[7,9] ^{13}C NMR (75 MHz, $CDCl_3$): δ_C = 176.1 (C1), 70.6 (C2H), 52.7 (OCH_3), 34.6 ($C3H_2$), 32.1 (CH_2), 29.9 (CH_2), 29.8 ($3CH_2$), 29.7 (CH_2), 29.6 ($3CH_2$), 29.5 (CH_2), 24.9 (CH_2), 22.9 (CH_2), 14.3 ($C16H_3$). LRMS (ES^+ mode): *m/z* (%) = $[(M+H)^+, 100]$, $[(M+NH_4)^+, 55]$.

(*R*)-2-(Benzoyloxy)hexadecanoic acid (9)



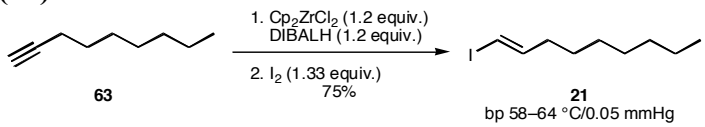
Benzoyl chloride (0.15 mL, 1.3 mmol, 2.0 equiv) was added dropwise to a solution of (*R*)-**16** (178 mg, 0.65 mmol, 1.0 equiv) in toluene (4 mL) and pyridine (1.0 mL) and the solution stirred at room temperature for 16 h. The mixture was concentrated *in vacuo* then saturated aqueous $NaHCO_3$ (20 mL) was added. The aqueous mixture was extracted with Et_2O (3×10 mL) and the combined organic extracts dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography (SiO_2, hexanes–Et_2O–AcOH 95:10:1) to give the title compound (187 mg, 0.50 mmol, 77%) as a colourless solid. A sample recrystallised from ethyl acetate gave a fluffy white solid: mp 70.0–72.5 °C. $[\alpha]_D^{28}$ = –7.5 (*c* 0.8, $CHCl_3$). IR (film): ν_{max} = 3400 w, 2925 s, 2854 s, 1726 s cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ_H = 8.10 (2H, d, *J* = 7.2 Hz, ArH), 7.60 (1H, t, *J* = 7.4 Hz, ArH), 7.47 (2H, t, *J* = 7.4 Hz, ArH), 5.27 (1H, br s, C2H), 2.04 (2H, br s, $C3H_2$), 1.54 (2H, br s, $C4H_2$), 1.40–1.25 (22H, m), 0.89 (3H, distorted t, *J* = 6.5 Hz, $C16H_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C = 166.3 (C1), 165.3 (Ar*C*=O), 133.6 ($C_{Ar}H$), 130.0 ($2C_{Ar}H$), 129.5 (C_{Ar}), 128.6 ($2C_{Ar}H$), 77.4 (C2H), 32.1 ($C3H_2$), 29.9 (CH_2), 29.8 (CH_2), 29.8 (CH_2), 29.7 (CH_2), 29.5 (CH_2), 29.3 (CH_2), 25.5 ($C4H_2$), 22.9 (CH_2), 14.3 ($C16H_3$). LRMS (ES^+ mode): *m/z* (%) = 377.1 $[(M+H)^+$, 52], 391.4 $[(M+15)^+$, 100], 394.4 $[(M+NH_4)^+$, 45). HRMS (ES^+ mode): Found, 399.2513 $(M+Na)^+$. $C_{23}H_{36}O_4Na$ requires M, 399.2511.

(*R*)-2,5-Dioxopyrrolidin-1-yl 2-(benzoyloxy)hexadecanoate (20)



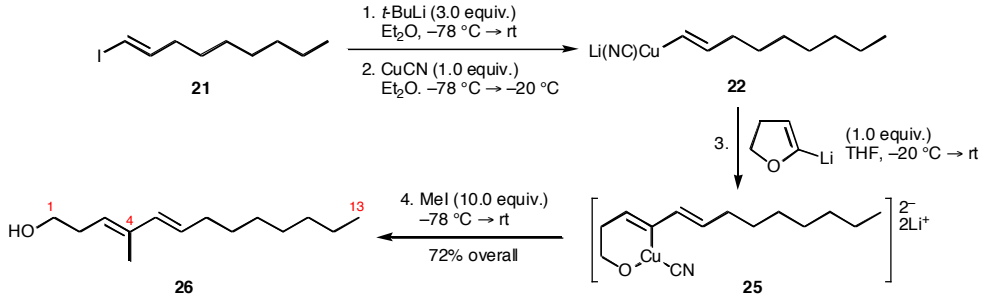
Dicyclohexylcarbodiimide (73 mg, 0.35 mmol, 1.1 equiv) was added to a suspension of **9** (121 mg, 0.32 mmol, 1.0 equiv) and *N*-hydroxysuccinimide (45 mg, 0.38 mmol, 1.2 equiv) in THF (5 mL) at 0 °C and the mixture stirred at 0 °C for 1 h then at room temperature for 1 h. Water (0.1 mL) was added to the white suspension and the mixture stirred at room temperature for 1 h. Hexane (5 mL) was added and the dicyclohexylurea precipitate filtered. The solid was washed with hexane/EtOAc (10:1, 2×10 mL) and the filtrate dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography (SiO_2, hexanes–EtOAc 3:1) to give a white solid which was recrystallised from hexane to give the title compound as a fluffy solid (113 mg, 0.24 mmol, 75%): mp 74.5–75.5 °C. $[\alpha]_D^{26}$ = +13.6 (*c* 0.7, $CHCl_3$). IR (film): ν_{max} = 2919 s, 2848 s, 1747 s, 1729 s cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ_H = 8.11 (2H, d, *J* = 7.7 Hz, ArH), 7.60 (1H, t, *J* = 7.7 Hz, ArH), 7.47 (2H, t, *J* = 7.7 Hz, ArH), 5.58 (1H, t, *J* = 6.8 Hz, C2H), 2.85 (4H, s, $2CH_2C$=O), 2.18–2.14 (2H, m, $C3H_2$), 1.62 (2H, apparent quintet, *J* = 7.7 Hz, $C4H_2$), 1.41–1.39 (2H, m, $C5H_2$), 1.35–1.26 (20H, m, $C6H_2$–$C15H_2$), 0.89 (3H, t, *J* = 6.8 Hz, $C16H_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C = 168.6 (2C=O), 166.3 (C1), 165.7 (ArC=O), 133.8 ($C_{Ar}H$), 130.2 ($2C_{Ar}H$), 129.0 (C_{Ar}), 128.7 ($2C_{Ar}H$), 70.9 (C2H), 32.1 ($C3H_2$), 31.6 (CH_2), 29.8 (CH_2), 29.8 (CH_2), 29.7 (CH_2), 29.5 ($2CH_2$), 29.3 (CH_2), 25.8 (CH_2), 25.0 (CH_2), 22.9 (CH_2), 14.3 ($C16H_3$). HRMS (ES^+ mode): Found, 496.2682, $(M+Na)^+$. $C_{27}H_{39}NO_6Na$ requires M, 496.2670. Anal. Calcd. for $C_{27}H_{39}NO_6$: C, 68.47; H, 8.30; N, 2.96. Found: C, 68.5; H, 8.40; N, 2.85%.

(*E*)-1-Iodonon-1-ene (21)



The title compound was prepared by the method of Huang and Negishi.[10] DIBALH (1 M in THF, 89 mL, 89 mmol, 1.5 equiv) was added dropwise to a solution of zirconocene dichloride (26.0 g, 89 mmol, 1.5 equiv) in THF (150 mL) at 0 °C and the colourless suspension stirred at 0 °C for 30 min. 1-Nonyne (**63**, 7.4 g, 59 mmol, 1.0 equiv) was added and the suspension stirred at room temperature for 2 h. The yellow solution was cooled to 0 °C and a solution of iodine (16.6 g, 65 mmol, 1.1 equiv) in THF (50 mL) was added. The red/brown mixture was stirred at 0 °C for 30 min then poured slowly into 1 M HCl (200 mL). The mixture was extracted with Et_2O (3×100 mL) and the combined organic extracts were washed with sodium thiosulfate (100 mL), $NaHCO_3$ (100 mL) and brine (100 mL), dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography (SiO_2, hexanes) followed by Kugelrhor distillation to give the title compound (11.13 g, 44 mmol, 75%) as a colourless oil: bp 58–64 °C (bath)/0.05 mmHg. IR (film): ν_{max} = 2925 s, 2854 s, 1605 w cm^{-1}. ^1H and ^{13}C NMR data recorded at 300 MHz and 75 MHz respectively were consistent with literature data recorded at 300 MHz and 75 MHz respectively.[11]

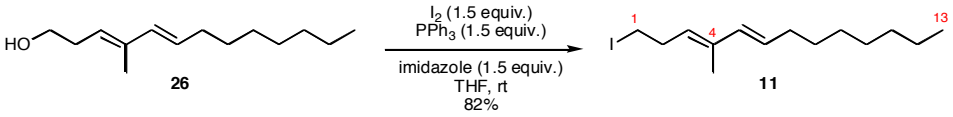
(3*E*,5*E*)-4-Methyltrideca-3,5-diene-1-ol (26)



(*E*)-1-Iodonon-1-ene (**21**, 11.1 g, 44.2 mmol, 1.5 equiv) was added to a solution of *tert*-butyllithium (1.71 M in pentane, 52 mL, 88.9 mmol, 3.0 equiv) in Et_2O (60 mL) at –78 °C. The resultant suspension was stirred at –78 °C for 30 min, 0 °C for 1 h and room temperature for 1 h. The reaction was cooled to –78 °C and added by cannula to a suspension of CuCN (2.6 g, 29.0 mmol, 1.0 equiv) in Et_2O at –78 °C. The mixture was stirred at –20 °C for 30 min. In a separate flask *tert*-butyllithium (1.71 M in pentane, 17.0 mL, 29.1 mmol, 1.0 equiv) was added to a solution of 2,3-dihydrofuran (2.2 mL, 2.0 g, 29.0 mmol, 1.0 equiv) in THF (30 mL) at –40 °C and the mixture allowed to warm to –5 °C over 1 h. The solution was cooled to –20 °C and the lithiated dihydrofuran added to the cuprate by cannula. The orange solution was stirred at –20 °C for 30 min, 0 °C for 1 h and room temperature for 1 h. The orange/red solution was cooled to –78 °C and MeI (18.0 mL, 289 mmol, 10.0 equiv) added. The mixture was stirred at –40 °C for 1 h and room temperature for 1 h. The black mixture was poured into saturated aqueous NH_4Cl (200 mL) and extracted with Et_2O (3×100 mL). The combined organic layers were washed with brine (150 mL), dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography (SiO_2, hexanes–Et_2O, 8:1) to give the title compound (4.45 g, 21.2 mmol, 72%) as a colourless oil.

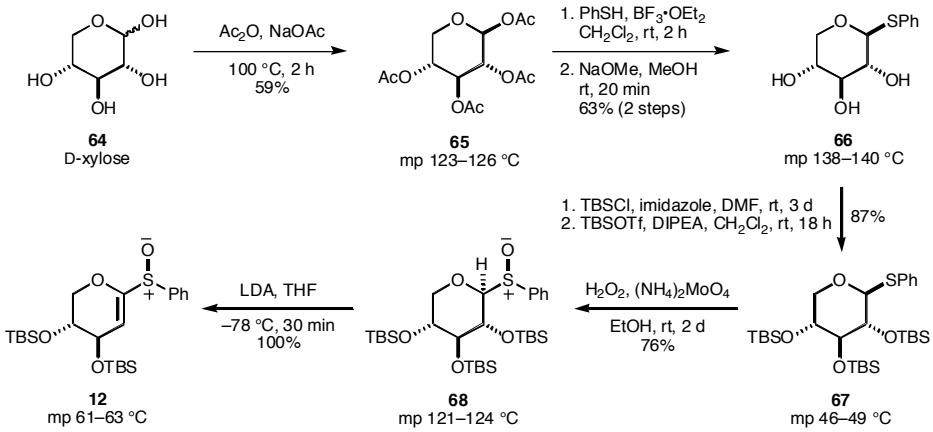
IR (film): ν_{max} = 3368 s, 2925 s, 1626 m cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 6.09 (1H, d, J = 15.4 Hz, C5H), 5.62 (1H, td, J = 6.8, 15.4 Hz, C6H), 5.37 (1H, t, J = 7.3 Hz, C3H), 3.68–3.66 (2H, m, C1H$_2$), 2.42 (2H, q, J = 6.8 Hz, C2H$_2$), 2.09 (2H, q, J = 7.3 Hz, C7H$_2$), 1.78 (3H, s, C4Me), 1.41–1.28 (10H, m, C8H$_2$–C12H$_2$), 0.89 (3H, t, J = 7.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C = 136.8 (C4), 134.4 (C5H), 129.3 (C6H), 125.4 (C3H), 62.6 (C2H), 33.0 (C7H$_2$), 32.0 (CH$_2$), 31.9 (CH$_2$), 29.8 (CH$_2$), 29.4 (2CH$_2$), 22.9 (CH$_2$), 14.3 (C4*Me*), 12.8 (C13H$_3$). LRMS (ES$^+$ mode): *m/z* (%) 233.2 [(M+Na)$^+$, 100]. HRMS (ES$^+$ mode): Found, 233.1887 (M+Na)$^+$. $C_{14}H_{26}ONa$ requires M, 233.1876. Anal. Calcd. for $C_{14}H_{26}O$: C, 79.94; H, 12.46. Found: C, 79.95; H, 12.40%.

(3*E*,5*E*)-1-Iodo-4-methyltrideca-3,5-diene (11)



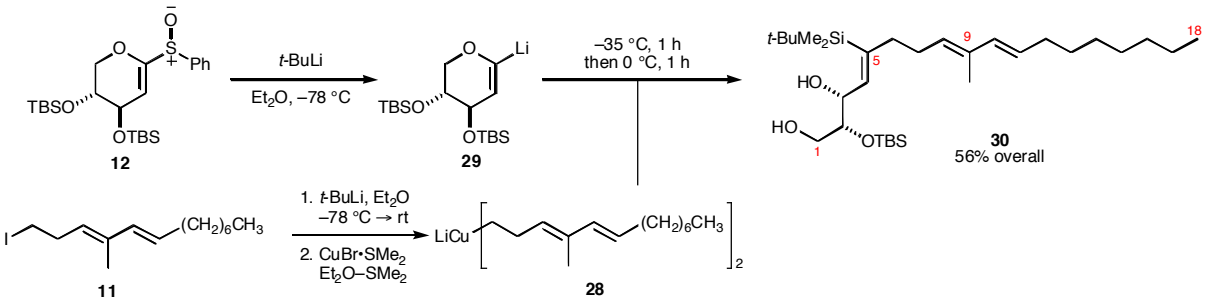
Iodine (6.6 g, 26.0 mmol, 1.5 equiv) was added to a solution of 4-methyltrideca-3,5-dien-1-ol (**26**, 3.67 g, 17.5 mmol, 1.0 equiv), imidazole (1.78 g, 26.1 mmol, 1.5 equiv) and triphenylphosphine (6.9 g, 26.3 mmol, 1.5 equiv) in THF (90 mL) at –10 °C. The reaction mixture was stirred at –10 °C for 1 h then at room temperature for 3 h. The mixture was poured into sodium thiosulfate (150 mL) and the organic phase separated. The aqueous phase was extracted with Et_2O (3×50 mL) and the combined organic layers were washed with brine (150 mL) and dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography (SiO_2, hexanes–Et_3N 99:1) to give the title compound (4.60 g, 14.4 mmol, 82%) as a colourless oil which was unstable to distillation. IR (film): ν_{max} = 2924 s, 2853 s, 1623 w cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 6.06 (1H, d, J = 15.8 Hz, C5H), 5.66 (1H, td, J = 6.8, 15.8 Hz, C6H), 5.31 (1H, t, J = 7.3 Hz, C3H), 3.14 (2H, t, J = 7.3 Hz C1H$_2$), 2.73 (2H, q, J = 7.3 Hz, C2H$_2$), 2.09 (2H, q, J = 7.3 Hz, C7H$_2$), 1.74 (3H, s, C4Me), 1.42–1.37 (2H, m, C8H$_2$), 1.32–1.28 (8H, m, C9H$_2$–C12H$_2$), 0.89 (3H, t, J = 7.3 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C = 136.0 (C4), 134.2 (C5H), 129.7 (C6H), 128.0 (C3H), 33.1 (C7H$_2$), 32.7 (C2H$_2$), 32.0 (CH$_2$), 29.7 (CH$_2$), 29.4 (2CH$_2$), 22.9 (C12H$_2$), 14.3 (C13H$_3$), 12.9 (C4*Me*), 5.4 (C1H$_2$). LRMS (EI$^+$ mode): *m/z* (%) 193.1 [(M–I)$^+$, 100], 320.1 [M$^+$, 68]. HRMS (EI$^+$ mode): Found, 320.1000, M$^+$. $C_{14}H_{25}I$ requires M, 320.1001.

1,2-Dideoxy-3,4-bis(*tert*-butyldimethylsilyl)-2-[(*S*$_S$)-phenylsulfinyl]-D-*threo*-pent-1-enopyranose (12)



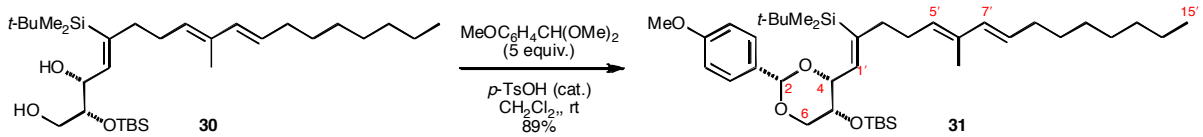
The title compound was prepared in 7 steps (see Scheme) from D-xylose (**64**) by the method of Jarowicki et al.[12] It gave mp 61–63 °C, lit.[12] mp 60–63 °C; $[\alpha]_D^{28}$ = –4.9 (*c* 1.0, $CHCl_3$), lit.[12] $[\alpha]_D$ = –2.5 (*c* 1.05, $CHCl_3$).

(4*E*,8*E*,10*E*,2*R*,3*R*)-5-(*tert*-Butyldimethylsilyl)-2-*O*-(*tert*-butyldimethylsilyl)-9-methyl-octadec-4,8,10-triene-1,2,3-triol (30)



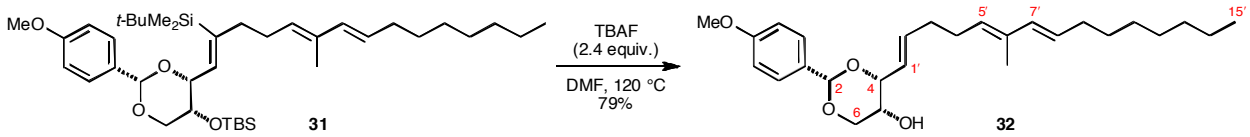
1-Iodo-4-methyltrideca-3,5-diene (**11**, 4.5 g, 14.1 mmol, 4.4 equiv) was added to a solution of *tert*-butyllithium (1.71 M in pentane, 16.5 mL, 28.2 mmol, 8.8 equiv) in Et_2O (15 mL) at –78 °C using pentane (2 mL) for washing. The resultant suspension was stirred at –78 °C for 30 min, 0 °C for 1 h and room temperature for 1 h. The reaction was cooled to 0 °C and a solution of *freshly prepared*[13] $CuBr{\bullet}SMe_2$ (724 mg, 3.5 mmol, 1.1 equiv) in SMe_2 (15 mL) was added by cannula using SMe_2 (10 mL) for washing. The resulting pale yellow solution of cuprate **28** was stirred at 0 °C for 1 h. In a separate flask *tert*-butyllithium (1.71 M in pentane, 1.9 mL, 3.2 mmol, 1.0 equiv) was added to a solution of sulfoxide **12** (1.50 g, 3.2 mmol, 1.0 equiv) in THF (0.52 mL, 6.4 mmol, 2.0 equiv) and Et_2O (7 mL), at –78 °C and the mixture stirred for 30 min to give the lithiated glycal **29**. The cuprate **28** was cooled to –35 °C and the lithiated glycal **29** added by cannula using Et_2O (2 mL) for washing. The reaction was stirred at –35 °C for 30 min then at 0 °C for 3 h. The mixture was added by cannula to degassed saturated aqueous NH_4Cl (100 mL) at 0 °C and the mixture stirred at room temperature for 15 min. The blue aqueous layer was separated and extracted with Et_2O (3×50 mL). The combined organic layers were washed with brine (150 mL), dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography (SiO_2, hexanes–Et_2O, 6:1) to give the title compound (963 mg, 1.8 mmol, 56%) as a colourless oil. $[\alpha]_D^{26}$ = –6.5 (*c* 1.1, $CHCl_3$). IR (film): ν_{max} = 3401 m, 2928 s, 2856 s, 1463 m cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ_H = 6.11 (1H, d, *J* = 9.8 Hz, C4H), 6.05 (1H, d, *J* = 15.4 Hz, C10H), 5.58 (1H, td, *J* = 6.8, 15.4 Hz, C11H), 5.36 (1H, t, *J* = 6.8 Hz, C8H), 4.29–4.25 (1H, m, C3H), 3.70–3.59 (3H, m, $C1H_2$, C2H), 2.34 (1H, d, *J* = 6.4 Hz, C3OH), 2.23–2.06 (6H, m, $C7H_2$, $C6H_2$, $C12H_2$), 1.90–1.87 (1H, m, C1OH), 1.73 (3H, s, C9Me), 1.40–1.37 (2H, m, $C13H_2$), 1.31–1.25 (8H, m), 0.95 (9H, s, $C(CH_3)_3$), 0.92 (9H, s, $C(CH_3)_3$), 0.89 (3H, t, *J* = 7.7 Hz, $C18H_3$), 0.20 (3H, s, SiMe), 0.17 (3H, s, SiMe), 0.15 (3H, s, SiMe), 0.14 (3H, s, SiMe). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C = 142.5 (C5), 141.8 (C4H), 134.7 (C10H), 134.0 (C9), 129.8 (C8H), 128.4 (C11H) 76.0 (C2H), 71.2 (C3H), 64.5 ($C1H_2$), 37.9 ($C6H_2$), 33.1 (CH_2), 32.0 (CH_2), 29.9 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.0 (CH_2), 27.2 (Me_3C), 26.1 (Me_3C), 22.9 (CH_2), 18.4 (Me_3C), 17.7 (Me_3C), 14.3 (C9*Me*), 12.7 ($C18H_3$), –2.8 ($SiCH_3$), –3.5 ($SiCH_3$), –4.0 ($SiCH_3$), –4.5 ($SiCH_3$). LRMS (ES^+ mode): *m/z* (%) 389.5 (100), 561.6 [$(M+Na)^+$, 78]. HRMS (EI^+ mode): Found, 561.4130, $(M+Na)^+$. $C_{31}H_{62}NaO_3Si_2$ requires M, 561.4130.

(2*S*,5*R*,4*R*)-4-[(1′*E*,5′*E*,7′*E*)-2-(*tert*-Butyldimethylsilyl)-6-methyl-pentadeca-1,5,7-trienyl]-5-(*tert*-butyldimethylsilyloxy)-2-(4-methoxyphenyl)-1,3-dioxane (31)



4-Methoxybenzaldehyde dimethyl acetal (0.78 mL, 4.3 mmol, 5.0 equiv), was added to a solution of diol **30** (464 mg, 0.65 mmol, 1.0 equiv) in CH_2Cl_2 (15 mL). *p*-TsOH (14 mg), was added and the mixture stirred at room temperature for 1 h. The reaction was then poured into saturated aqueous $NaHCO_3$ (30 mL) and extracted into Et_2O (3×20 mL). The combined organic extracts were washed with brine (30 mL), dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography (SiO_2, hexanes–Et_2O, 90:1) to give the title compound (504 mg, 0.77 mmol, 89%) as a colourless oil. $[\alpha]_D^{29}$ = 1.49 (*c* 1.5, $CHCl_3$). IR (film): ν_{max} = 2954 s, 2927 s, 2855 m, 1616 w cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ_H = 7.43 (2H, d, *J* = 8.9 Hz, ArH), 6.89 (2H, d, *J* = 8.9 Hz, ArH), 6.40 (1H, d, *J* = 9.4 Hz, C1′H), 6.05 (1H, d, *J* = 15.6 Hz, C7′H), 5.58 (1H, td, *J* = 7.1, 15.4 Hz, C8′H), 5.47 (1H, s, ArC*H*), 5.37 (1H, t, *J* = 7.3 Hz, C5′H), 4.46 (1H, d, *J* = 9.4 Hz, C4H), 4.15 (1H, d, *J* = 11.5 Hz, C6H_AH$_B$), 3.97 (1H, d, *J* = 11.5 Hz, C6H$_A$$H_B$), 3.80 (3H, s, OCH_3), 3.53 (1H, s, C5H), 2.28–2.19 (2H, m, C4′H), 2.14–2.06 (4H, m, C3′H, C9′H), 1.72 (3H, s, C6′Me), 1.40–1.24 (10H, m), 0.99 (9H, s, $C(CH_3)_3$), 0.94 (9H, s, $C(CH_3)_3$), 0.89 (3H, distorted t, *J* = 6.0 Hz, C15′H_3), 0.22 (3H, s, SiMe), 0.17 (3H, s, SiMe), 0.13 (3H, s, SiMe), 0.10 (3H, s, SiMe). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C = 160.2 (C_{Ar}OMe), 143.0 (C2′), 139.3 (C1′H), 134.7 (C7′H), 133.9 (C6′), 131.4 (C_{Ar}), 130.0 (C5′H), 128.2 (C8′H), 127.8 (2C_{Ar}H), 113.8 (2C_{Ar}H), 101.4 (Ph*C*H), 79.7 (C4H), 72.8 (C6H_2), 67.2 (C5H), 55.3 (OCH_3), 37.8 (C3′H_2), 33.1 (C9′H_2), 32.0 (CH_2), 29.9 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 28.7 (CH_2), 27.1 (*Me*$_3$C), 26.1 (*Me*$_3$C), 22.9 (CH_2), 18.5 (Me$_3$*C*), 18.0 (Me$_3$*C*), 14.3 (C15′H_3), 12.6 (C6′Me), –2.6 (SiMe), –3.6 (SiMe), –4.1 (SiMe), –4.5 (SiMe). LRMS (ES$^+$ mode): *m/z* (%) 679.5 [(M+Na)$^+$, 100]. HRMS (EI$^+$ mode): Found, 679.4550, (M+Na)$^+$. $C_{39}H_{68}NaO_4Si_2$ requires M, 679.4548. Anal. Calcd. for $C_{39}H_{68}O_4Si_2$: C, 71.28; H, 10.43. Found: C, 71.20; H, 10.55%.

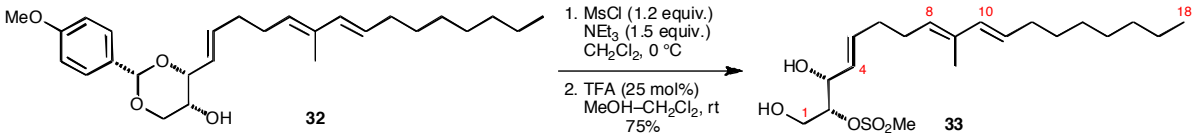
(2*S*,5*R*,4*R*)-4-[(1′*E*,5′*E*,7′*E*)-6-Methylpentadec-1,5,7-trienyl]-2-(4-methoxyphenyl)-1,3-dioxan-5-ol (32)



TBAF (463 mg, 1.8 mmol, 2.4 equiv) was added to a solution of **31** (484 mg, 0.74 mmol, 1.0 equiv) in DMF (10 mL) and the mixture heated at 120 °C for 10 min. The cooled mixture was poured into brine (50 mL) and extracted with Et_2O (3×25 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography (SiO_2, hexanes–Et_2O, 4:1) to give the title compound (249 mg, 0.58 mmol, 79%) as a colourless oil. $[\alpha]_D^{29}$ = 2.1 (*c* 2.0, $CHCl_3$). IR (film): ν_{max} = 3435 m, 2925 s, 2853 s, 1615 m, 1518 m cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ_H = 7.45 (2H, d, *J* = 8.5 Hz, ArH), 6.91 (2H, d, *J* = 9.0 Hz, ArH), 6.05 (1H, d, *J* = 15.6 Hz, C7′H), 5.88 (1H, td, *J* = 6.4, 15.6 Hz, C2′H), 5.70 (1H, dd, *J* = 6.0, 15.6 Hz, C1′H),

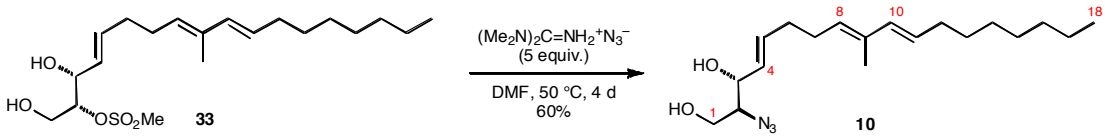
5.60 (1H, td, J = 7.0, 15.4 Hz, C8′H), 5.60 (1H, s, ArC*H*), 5.37 (1H, t, *J* = 7.1 Hz, C5′H), 4.40 (1H, d, *J* = 6.2 Hz, C4H), 4.23 (1H, dd, *J* = 1.9, 12.0 Hz, C6$H_A$$H_B$), 4.07 (1H, dd, *J* = 1.1, 11.8 Hz, C6$H_A$$H_B$), 3.82 (3H, s, OCH_3), 3.53 (1H, dt, *J* = 1.5, 10.5 Hz, C5H), 2.63 (1H, d, *J* = 10.5 Hz, OH), 2.26–2.15 (4H, m, C3′H, C4′H), 2.14–2.06 (2H, m, C9′H), 1.73 (3H, s, C6′Me), 1.41–1.29 (10H, m), 0.89 (3H, distorted t, *J* = 6.8 Hz, C15′H_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C = 160.2 (C_{Ar}OMe), 134.6 (C7′H), 134.5 (C2′H), 134.3 (C6′), 130.5 (C_{Ar}), 129.3 (C5′H), 128.3 (C8′H), 127.5 (2C_{Ar}H), 126.7 (C1′H), 113.8 (2C_{Ar}H), 101.5 (Ar*C*H), 80.7 (C4H), 72.5 (C6H_2), 66.4 (C5H), 55.4 (OCH_3), 33.0 (C9′H_2), 32.6 (C3′H_2), 32.0 (CH_2), 29.9 (CH_2), 29.4 (2CH_2), 27.8 (CH_2), 22.8 (CH_2), 14.3 (C15′H_3), 12.7 (C6′Me). LRMS (ES+ mode): *m/z* (%) 451.3 [(M+Na)$^+$, 41], 429.3 [(M+H)$^+$, 26], 338.2 [(M–90)$^+$, 100]. HRMS (ES+ mode): Found, 451.2829 (M+Na)$^+$. $C_{27}H_{40}O_4Na$ requires M, 451.2819.

(4*E*,8*E*,10*E*,2*S*,3*R*)-2-*O*-Methanesulfonyl-9-methyloctadeca-4,8,10-triene-1,2,3-triol (33)



MsCl (39 µl, 0.50 mmol, 1.5 equiv) was added to a solution of acetal **32** in CH_2Cl_2 (3 mL) and triethylamine (89 µl, 0.63 mmol, 1.9 equiv) at 0 °C and the solution stirred at 0 °C for 30 min. The mixture was diluted with CH_2Cl_2 (4 mL) poured into ice water (5 mL) and the layers separated. The organic layer was washed with 10% HCl (2×5 mL), $NaHCO_3$ (2×5 mL) and brine (5 mL), dried over Na_2SO_4 and concentrated *in vacuo*. The residue was dissolved in MeOH–CH_2Cl_2 (8.5 mL, 2.4:1) and TFA added (6 µL, 0.085 mmol, 25 mol%). The colourless solution was stirred at room temperature for 5 h. $NaHCO_3$ (500 mg), was added and the suspension stirred at room temperature for 30 min then concentrated *in vacuo*. The residue was purified by column chromatography (SiO_2, hexanes–Et_2O, 1:2) to give the title compound (99 mg, 0.26 mmol, 75%) as an unstable colourless oil which was used immediately in the next step. IR (film): ν_{max} = 3400 m, 2924 s, 2854 s, 1335 s, 1171 s cm^{-1}. LRMS (ES$^+$ mode): *m/z* (%) 411.2 [(M+Na)$^+$, 100]. HRMS (EI$^+$ mode): Found, 411.2179, (M+Na)$^+$. $C_{20}H_{36}NaO_5S$ requires M, 411.2176.

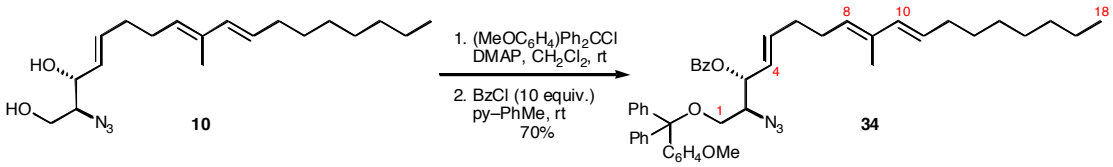
(4*E*,8*E*,10*E*,2*S*,3*R*)-2-Azido-9-methyloctadeca-4,8,10-triene-1,3-diol (10)



Tetramethylguanidinium azide (200 mg, 1.26 mmol, 5.0 equiv), was added to a solution of methanesulfonate **33** in DMF (2.5 mL) and the solution heated at 50 °C for 4 d. The orange/brown solution was concentrated *in vacuo* and the residue purified by column chromatography (SiO_2, hexanes–Et_2O, 1:1) to give the title compound (51 mg, 0.15 mmol, 60%) as a colourless oil. $[\alpha]_D^{25}$ = –26.5 (*c* 0.5, $CHCl_3$). IR (film): ν_{max} = 3400 m, 2925 s, 2854 m, 2101 s, 1681 w cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 6.05 (1H, d, *J* = 15.4 Hz, C10H), 5.83 (1H, td, *J* = 6.8, 15.0 Hz, C5H), 5.60–5.55 (2H, m, C11H, C4H), 5.34 (1H, t, *J* = Hz, C8), 4.26 (1H, br s, C3H), 3.84–3.75 (2H, m, C1H_2), 3.52–3.50 (1H, m, C2H), 2.26–2.22 (2H, m, C7H_2), 2.20–2.14 (2H, m, C6H_2), 2.11–2.04

(4H, m, C12H_2, 2 OH), 1.73 (3H, s, C9Me), 1.41–1.36 (2H, m, C13H_2), 1.34–1.28 (8H, m), 0.90–0.88 (3H, m, C18H_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C = 135.28 (C5H), 134.6 (C10H), 134.5 (C9), 129.0 (C8H), 128.8 (C4H), 128.5 (C11H) 73.9 (C3H), 66.9 (C2H), 62.8 (C1H_2), 33.0 (C12H_2), 32.5 (C6H_2), 32.0 (CH_2), 29.9 (CH_2), 29.4 (CH_2), 29.4 (CH_2), 27.7 (C7H_2), 22.9 (CH_2), 14.3 (C9*Me*), 12.7 (C18H_3). LRMS (ES$^+$ mode): *m/z* (%) 358.2 [(M+Na)$^+$, 100], 353.3 [(M+NH_4)$^+$, 58)]. HRMS (EI$^+$ mode): Found, 358.2461, (M+Na)$^+$. $C_{19}H_{33}N_3NaO_2$ requires M, 358.2465.

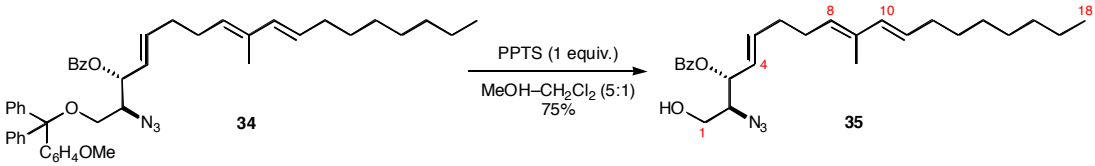
(2*S*,3*R*,4*E*,8*E*,10*E*)-2-Azido-3-*O*-benzoyl-1-*O*-[(4-methoxyphenyl)-diphenylmethoxy]-9-methyl-octadeca-4,8,10-triene-1,3-diol (34)



(4-Methoxyphenyl)diphenylmethyl chloride (18 mg, 0.057 mmol, 2.2 equiv) was added to a solution of diol **10** (9 mg, 0.026 mmol, 1.0 equiv), DMAP (0.2 mg, 1.6 μmol, 5 mol%) and Et_3N (11 μL, 0.079 mmol, 3.0 equiv) in CH_2Cl_2 (0.2 mL). The resulting orange solution was stirred at room temperature for 3 d. An additional portion of (4-methoxyphenyl)diphenylmethyl chloride (18 mg, 0.057 mmol, 2.2 equiv) and Et_3N (11 μL, 0.079 mmol, 3.0 equiv) was added and stirring continued for 2 d. The solution was concentrated *in vacuo* then saturated aqueous $NaHCO_3$ (5 mL) was added. The aqueous mixture was extracted with Et_2O (3×5 mL) and the combined organic extracts were washed with brine (10 mL), dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography (SiO_2, hexanes–Et_2O–Et_3N 25:1:1) to give the title compound, contaminated with (4-methoxyphenyl)diphenylmethyl chloride, as a colourless oil. Benzoyl chloride (30 μL, 0.26 mmol, 10 equiv) was added dropwise to a solution of the residue in toluene (0.4 mL) and pyridine (0.1 mL) and the resulting suspension stirred at room temperature for 16 h. The mixture was concentrated *in vacuo* then saturated aqueous $NaHCO_3$ (5 mL) was added. The aqueous mixture was extracted with Et_2O (3×5 mL) and the combined organic extracts were washed with brine (10 mL), dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography (SiO_2, hexanes–Et_3N 50:1) to give the title compound (13 mg, 0.018 mmol, 70%) as a colourless oil. $[\alpha]_D^{26}$ = 11.0 (*c* 0.4, $CHCl_3$). IR (film): ν_{max} = 2925 s, 2853 m, 2099 s, 1723 m, 1606 w, 1510 m cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 8.13 (2H, d, *J* = 6.9 Hz, ArH), 7.66 (4H, m, ArH), 7.44 (2H, d, *J* = 8.5 Hz, ArH), 7.17–7.10 (4H, m, ArH), 7.07–7.02 (5H, m, ArH), 6.70 (2H, d, *J* = 9.0 Hz, ArH), 6.18 (1H, d, *J* = 15.4 Hz, C10H), 5.97 (1H, dd, *J* = 5.1, 7.7 Hz, C3H), 5.83 (1H, td, *J* = 6.8, 15.4 Hz, C5H), 5.63–5.57 (1H, m, C11H), 5.55 (1H, dd, *J* = 7.7, 15.4 Hz, C4H), 5.33 (1H, t, *J* = 7.3 Hz, C8), 3.72 (1H, apparent q, *J* = 5.6 Hz, C2H), 3.47 (1H, dd, *J* = 6.4, 9.4 Hz, C1$H_A$$H_B$), 3.37 (1H, dd, *J* = 5.1, 9.8 Hz, C1$H_A$$H_B$), 3.27 (3H, s, OMe), 2.16–2.10 (2H, m, C12H_2), 2.03–1.99 (2H, m, C7H_2), 1.93–1.88 (2H, m, C6H_2), 1.64 (3H, s, C9Me), 1.43–1.37 (2H, m, C13H_2), 1.33–1.23 (8H, m), 0.91 (3H, t, *J* = 7.3 Hz, C18H_3). ^{13}C NMR (75 MHz, C_6D_6): δ_C = 165.4 (C=O), 159.7 (MeOC_{Ar}), 145.1 (C_{Ar}), 145.1 (C_{Ar}), 138.0 (C5H), 135.9 (C_{Ar}), 135.8 (C10H), 134.8 (C9), 133.4 (C_{Ar}H), 131.2 (2C_{Ar}H), 130.5 (2C_{Ar}H), 129.7 (C_{Ar}H), 129.3, 129.2, 129.0, 128.7, 128.6, 128.2, 127.7 (overlapping CH signals), 124.9 (C4H), 114.0 (C_{Ar}H), 87.9 (Ar_3C), 75.2 (C3H), 65.3 (C2H), 63.5 (C1H_2), 55.1 (OCH_3), 33.7 (C12H_2), 33.0 (C6H_2), 32.6 (CH_2), 30.5 (CH_2), 30.0 (CH_2), 28.1 (C7H_2), 23.4 (CH_2), 14.7 (C9*Me*), 13.1 (C18H_3). LRMS (ES$^+$

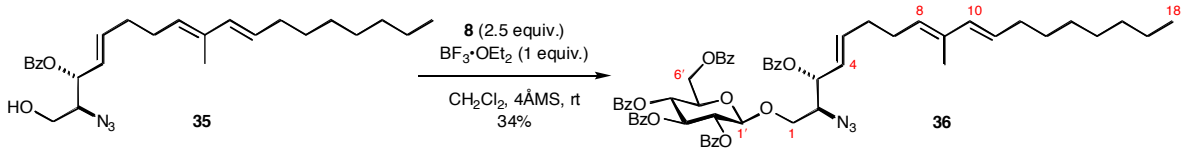
mode): *m/z* (%) 273.1 [(MMT)$^+$, 100], 734.5 [(M+Na)$^+$, 19]. HRMS (ES$^+$ mode): Found, 734.3924, (M+Na)$^+$. $C_{46}H_{53}N_3NaO_4$ requires M, 734.3928.

(2*S*,3*R*,4*E*,8*E*,10*E*)-2-Azido-3-*O*-benzoyl-9-methyl-octadeca-4,8,10-triene-1,3-diol (35)



PPTS (5 mg, 0.018 mmol, 1.0 equiv) was added to a solution of **34** (13 mg, 0.018 mmol, 1.0 equiv) in MeOH–DCM (0.6 mL, 5:1) and the colourless solution stirred at room temperature for 24 h. Saturated aqueous $NaHCO_3$ (5 mL) was added. The aqueous mixture was extracted with Et_2O (3×5 mL) and the combined organic extracts were washed with brine (10 mL), dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography (SiO_2, hexanes–Et_2O 8:1) to give the title compound (6 mg, 0.014 mmol, 75%) as a colourless oil. $[\alpha]_D^{26}$ = –53.9 (*c* 0.2, $CHCl_3$). IR (film): ν_{max} = 3401 m, 2924 s, 2102 m, 1720 m, 1599 w cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 8.07 (2H, dd, *J* = 1.3, 7.9 Hz, ArH), 7.59 (1H, tt, *J* = 1.3, 7.3 Hz, ArH), 7.47 (2H, t, *J* = 7.5 Hz, ArH), 6.02 (1H, d, *J* = 15.6 Hz, C10H), 5.96 (1H, td, *J* = 6.6, 14.5 Hz, C5H), 5.67–5.62 (2H, m, C3H, C4H), 5.56 (1H, td, *J* = 7.1, 15.6 Hz, C11H), 5.33 (1H, t, *J* = 7.1 Hz, C8H), 3.82 (1H, td, *J* = 4.3, 7.5 Hz, C2H), 3.75 (1H, dd, *J* = 4.1, 11.8 Hz, C1H_AH_B), 3.63 (1H, dd, *J* = 7.3, 11.8 Hz, C1H$_A$$H_B$), 2.26–2.20 (2H, m, C7H$_2$), 2.19–2.15 (2H, m, C6H$_2$), 2.07 (2H, apparent q, *J* = 7.1 Hz, C12H$_2$), 1.71 (3H, s, C9Me), 1.39–1.34 (2H, m, C13H$_2$), 1.32–1.23 (8H, m), 0.89 (3H, t, *J* = 7.3 Hz, C18H$_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C = 165.7 (C=O), 138.0 (C5H), 134.6 (C10H), 134.5 (C9), 133.5 (C$_{Ar}$H), 130.0 (2C$_{Ar}$H), 129.9 (C$_{Ar}$), 128.9 (C8H), 128.7 (2C$_{Ar}$H), 128.5 (C4H), 124.0 (C11H), 74.7 (C3H), 66.4 (C2H), 62.2 (C1H$_2$), 33.0 (C12H$_2$), 32.6 (C6H$_2$), 32.0 (CH$_2$), 29.9 (CH$_2$), 29.4 (CH$_2$), 29.4 (CH$_2$), 27.5 (C7H$_2$), 22.9 (CH$_2$), 14.3 (C9*Me*), 12.7 (C18H$_3$). LRMS (ES+ mode): *m/z* (%) = 462.3 [(M+Na)$^+$, 100]. HRMS (EI+ mode): Found, 462.2714, (M+Na)$^+$. $C_{26}H_{37}N_3NaO_3$ requires M, 462.2727.

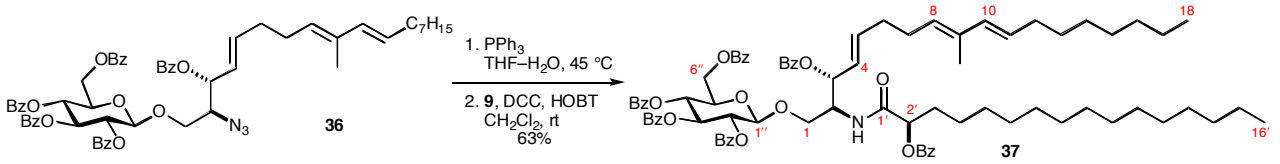
2′,3′,4′,6′-Tetra-*O*-benzoyl-*β*-D-glucopyranosyl-(2*S*,3*R*,4*E*,8*E*,10*E*)-2-azido-3-*O*-benzoyl-9-methyl-octadeca-4,8,10-triene-1,3-diol (36)



BF_3•OEt_2 (0.1 M in CH_2Cl_2, 0.75 mL, 0.075 mmol, 1.1 equiv) was added dropwise to a solution of azide **35** (30 mg, 0.068 mmol, 1.0 equiv) and trichloroacetimidate **8** (126 mg, 0.17 mmol, 2.5 equiv) in CH_2Cl_2 (3.5 mL) over 4 Å molecular sieves at 0 °C. The mixture was stirred at 0 °C for 10 min and room temperature for 2 h. Saturated aqueous $NaHCO_3$ (5 mL) was added and the mixture extracted with CH_2Cl_2 (3×5 mL). The combined extracts were washed with brine (5 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by column chromatography (SiO_2, hexanes–Et_2O, 4:1) to give a white solid which was dissolved in $CHCl_3$. Hexane was added and the white precipitate filtered. The filtrate was concentrated *in vacuo* to give the title compound (23 mg,

0.023 mmol, 34%) as a colourless oil. $[\alpha]_D^{25}$ = –3.8 (*c* 0.6, $CHCl_3$). IR (film): ν_{max} = 2920 m, 2851 w, 2098 m, 1727 s, 1601 m, 1451 m cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ_H = 8.04–7.97 (6H, m, ArH), 7.91 (2H, d, *J* = 7.3 Hz, ArH), 7.84 (2H, d, *J* = 7.3 Hz, ArH), 7.56–7.50 (4H, m, ArH), 7.45–7.28 (11H, m, ArH), 6.01 (1H, d, *J* = 15.8 Hz, C10H), 5.92 (1H, t, *J* = 9.4 Hz, C3′H), 5.75–5.67 (2H, m, C5H, C4′H), 5.59–5.48 (4H, m, C2′H, C3H, C4H, C11H), 5.25 (1H, t, *J* = 6.8 Hz, C8H), 4.89 (1H, d, *J* = 7.7 Hz, C1′H), 4.63 (1H, dd, *J* = 3.0, 12.0 Hz, C6′H_AH_B), 4.49 (1H, dd, *J* = 5.1, 12.0 Hz, C6′H_AH_B), 4.19–4.15 (1H, m, C5′H), 3.99–3.95 (2H, m, C1H_AH_B, C2H), 3.68–3.62 (1H, m, C1H_AH_B), 2.15–1.99 (6H, m, $C6H_2$, $C7H_2$, $C12H_2$), 1.68 (3H, s, C9Me), 1.41–1.35 (2H, m, $C13H_2$), 1.32–1.24 (8H, m, $C14H_2$–$C17H_2$), 0.89 (3H, distorted t, *J* = 7.3 Hz, $C18H_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C = 166.3 (C=O), 166.0 (C=O), 165.3 (C=O), 165.1 (2C=O), 138.3 (C5H), 134.7 (C10H), 134.4 (C9), 133.6 ($C_{Ar}H$), 133.4 ($C_{Ar}H$), 133.3 ($C_{Ar}H$), 133.3($C_{Ar}H$), 130.1 (C_{Ar}), 130.1 ($C_{Ar}H$), 130.0 ($C_{Ar}H$), 130.0 ($C_{Ar}H$), 129.9 ($C_{Ar}H$), 129.7 (C_{Ar}), 129.4 (C_{Ar}), 129.1 (C8H), 129.0 (C_{Ar}), 128.6 ($C_{Ar}H$), 128.5 ($C_{Ar}H$), 128.3 (C11H), 123.3 (C4H), 105.5 (C1′H), 74.9 (C3H), 73.0 (C3′H), 72.6 (C5′H), 71.9 (C2′H), 69.8 (C4′H), 68.4 ($C1H_2$), 63.6 (C2H), 63.2 (C6′H_2), 33.1 (CH_2), 32.5 (CH_2), 32.0 (CH_2), 29.9 (CH_2), 29.4 (CH_2), 29.4 (CH_2), 27.5 (CH_2), 22.9 (CH_2), 14.3 ($C18H_3$), 12.7 (C9*Me*). LRMS (ES^+ mode): *m/z* (%) = 1040.4 [$(M+Na)^+$, 100]. HRMS (EI^+ mode): Found, 1040.4349, $(M+Na)^+$. $C_{60}H_{63}N_3NaO_{12}$ requires M, 1040.4304.

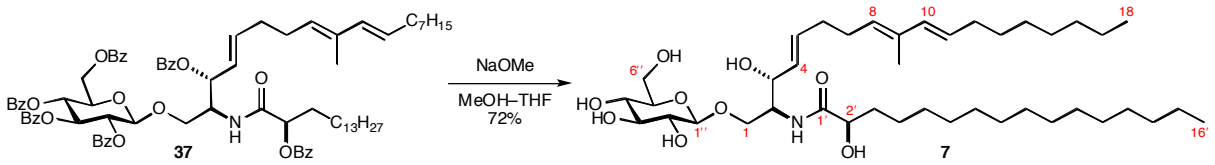
1-*O*-(2″,3″,4″,6″-Tetra-*O*-benzoyl-*β*-D-glucopyranosyl)-(2*S*,3*R*,4*E*,8*E*,10*E*)-2-[(2′*R*)-2′-((benzoyloxy)hexadecanoyl)amino]-3-*O*-benzoyl-9-methyl-4,8,10-octadecatriene-1,3-diol (37)



PPh_3 (9.5 mg, 0.047 mmol, 3.0 equiv) was added to a solution of azide **36** (16 mg, 0.016 mmol, 1.0 equiv) in THF (0.3 mL) and H_2O (10 μL) and the solution heated at 45 °C for 5 h. The reaction mixture was allowed to cool to room temperature then concentrated *in vacuo* and the residue dissolved in CH_2Cl_2 (0.5 mL). (*R*)-2-(benzoyloxy)hexadecanoic acid (**9**, 9 mg, 0.024 mmol, 1.5 equiv), DCC (5 mg, 0.024 mmol, 1.5 equiv) and HOBT (3 mg, 0.022 mmol, 1.4 equiv) were added and the mixture stirred at room temperature for 3 d. The colourless suspension was concentrated *in vacuo* and the residue purified by column chromatography (SiO_2, hexanes–Et_2O, 2:1) to give the title compound (13.5 mg, 0.010 mmol, 63%) as a colourless oil. $[\alpha]_D^{27}$ = +14.8 (*c* 0.3, $CHCl_3$). IR (film): ν_{max} = 2924 m, 2851 w, 1728 s, 1602 w, 1451 w cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ_H = 8.02 (2H, d, *J* = 7.9 Hz, ArH), 7.97 (2H, d, *J* = 7.9 Hz, ArH), 7.94 (2H, d, *J* = 7.7 Hz, ArH), 7.89 (2H, d, *J* = 7.9 Hz, ArH), 7.85 (2H, d, *J* = 7.3 Hz, ArH), 7.80 (2H, d, *J* = 7.9 Hz, ArH), 7.60 (1H, t, *J* = 7.7 Hz, ArH), 7.52–7.42 (7H, m, ArH), 7.38–7.27 (10H, m, ArH), 6.58 (1H, d, *J* =8.6 Hz, NH), 5.98 (1H, d, *J* = 15.7 Hz, C10H), 5.84 (1H, t, *J* = 9.4 Hz, C3″H), 5.79 (1H, td, *J* = 6.4, 15.8 Hz, C5H), 5.67 (1H, t, *J* = 6.4 Hz, C3H), 5.60 (1H, t, *J* = 9.4 Hz, C4″H), 5.55–5.49 (2H, m, C4H, C11H), 5.39 (1H, dd, *J* = 7.7, 9.4, C2″H), 5.26–5.22 (2H, m, C8H, C2′H), 4.82 (1H, d, *J* = 8.1 Hz, C1″H), 4.54–4.50 (2H, m, C1H_AH_B, C2H), 4.36 (1H, dd, *J* = 4.7, 12.0 Hz, C1H_AH_B), 4.09–4.07 (2H, m, C5″H, C6″H_AH_B), 3.74 (1H, dd, *J* = 5.1, 10.3 Hz, C6″H_AH_B), 2.09–1.97 (6H, m, $C6H_2$, $C7H_2$, $C12H_2$), 1.89–1.85 (2H, m, C3′H_2), 1.65 (3H, s, C9Me), 1.38–1.23 (34H, m, $C13H_2$–$C17H_2$, C4′H_2–C15′H_2), 0.88 (6H, distorted t, *J* = 6.8 Hz, $C18H_3$, C16′H_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C = 169.7 (amide C=O), 166.2 (C=O), 165.9 (C=O), 165.4 (C=O), 165.4 (C=O), 165.3 (C=O), 165.1

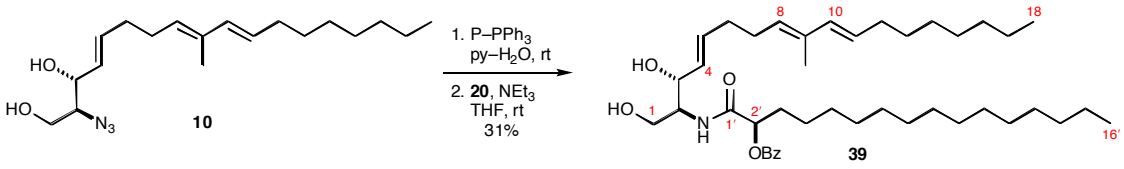
(C=O), 136.6 (C5H), 134.7 (C10H), 134.3 (C9), 133.7 ($C_{Ar}H$), 133.6 ($C_{Ar}H$), 133.5 ($C_{Ar}H$), 133.4 ($C_{Ar}H$), 133.4 ($C_{Ar}H$), 133.2 ($C_{Ar}H$), 133.1 ($C_{Ar}H$), 130.2 (C_{Ar}), 130.1 ($C_{Ar}H$), 130.0 ($C_{Ar}H$), 130.0 ($C_{Ar}H$), 129.9 ($C_{Ar}H$), 129.9 ($C_{Ar}H$), 129.7 (C_{Ar}), 129.6 (C_{Ar}), 129.3 (C_{Ar}), 129.2 (C8H), 129.0 (C_{Ar}), 129.0 (C_{Ar}), 128.8 ($C_{Ar}H$), 128.6 ($C_{Ar}H$), 128.6 ($C_{Ar}H$), 128.5 ($C_{Ar}H$), 128.5 ($C_{Ar}H$), 128.2 (C11H), 124.9 (C4H), 101.1 (C1′′H), 74.7 (C2′H), 74.2 (C3H), 73.0 (C3′′H), 72.6 (C5′′H), 72.1 (C2′′H), 69.6 (C4′′H), 67.5 (C6′′H_2), 63.1 (C1H_2), 51.1 (C2H), 33.1 (CH_2), 32.4 (CH_2), 32.1 (CH_2), 32.0 (CH_2), 31.8 (CH_2), 29.9 (CH_2), 29.9 (CH_2), 29.9 (CH_2), 29.8 (CH_2), 29.8 (CH_2), 29.8 (CH_2), 29.6 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 27.6 (CH_2), 22.9 (CH_2), 25.0 (CH_2), 22.9 (CH_2), 22.9 (CH_2), 14.3 (C18H_3), 12.7 (C9*Me*). LRMS (ES$^+$ mode): *m/z* (%) = 1372.8 [(M+Na)$^+$, 85], 1228.7 [(M–OBz)$^+$, 100]. HRMS (EI$^+$ mode): Found, 1372.6872, (M+Na)$^+$. $C_{83}H_{99}NNaO_{15}$ requires M, 1372.6907.

1-*O*-(*β*-D-Glucopyranosyl)-(2*S*,3*R*,4*E*,8*E*,10*E*)-2-[(2′R)-2′-(hydroxyhexadecanoyl)amino]-9-methyl-4,8,10-octadecatriene-1,3-diol (phalluside 1) (7)



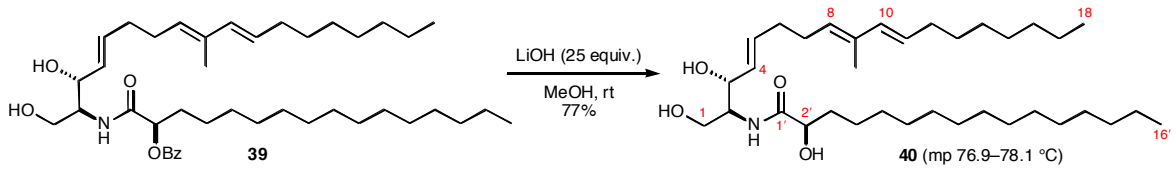
NaOMe (0.1 M in MeOH, 0.13 mL, 13 μmol, 1.9 equiv) was added to a solution of hexabenzoate **37** (9 mg, 6.7 μmol, 1.0 equiv) in THF (0.2 mL) at 0 °C and the colourless solution allowed to warm to room temperature over 2.5 h. The solution was cooled to 0 °C and AcOH (4 μL) was added. The solution was concentrated *in vacuo* and the residue was purified by column chromatography (SiO_2, CH_2Cl_2–MeOH, 8:1) to give the title compound (3.5 mg, 4.8 μmol, 72%) as a colourless solid. $[\alpha]_D^{29}$ = –22.5 (*c* 0.1, $CHCl_3$); lit. $[\alpha]_D$ = –21.4 (*c* 0.3, $CHCl_3$).[14] IR (film): ν_{max} = 3369 m, 2923 s, 2851 m, 1656 m, 1536 w, 1456 m cm^{-1}. ^{1}H and ^{13}C NMR spectroscopic data recorded at 500 MHz and 125 MHz respectively were consistent with literature data recorded at 500 MHz and 125 MHz respectively.[14] ^{1}H NMR (500 MHz, MeOH): δ_H = 6.03 (1H, d, *J* = 15.4 Hz, C10H), 5.74 (1H, td, *J* = 6.4, 15.4 Hz, C5H), 5.57 (1H, td, *J* = 7.3, 15.8 Hz, C11H), 5.50 (1H, dd, *J* = 7.3, 15.4 Hz, C4H), 5.36 (1H, t, *J* = 6.8 Hz, C8H), 4.27 (1H, d, *J* = 7.7 Hz, C1′′H), 4.15 (1H, t, *J* = 7.3 Hz, C3H), 4.12 (1H, dd, *J* = 5.1, 10.3 Hz, C1H_AH_B), 4.01–3.98 (2H, m, C2′H, C2H), 3.87 (1H, bd, *J* = 11.5 Hz, C6′′H_AH_B), 3.71 (1H, dd, *J* = 3.4, 10.3 Hz, C1H_AH_B), 3.67 (1H, dd, *J* = 5.1, 12.0 Hz, C6′′H_AH_B), 3.38–3.34 (1H, m, C3′′H), 3.29–3.27 (2H, m, C4′′H, C5′′H), 3.19 (1H, apparent t, *J* = 8.1, 8.6, C2′′H), 2.24–2.19 (2H, m, C7H_2), 2.13–2.06 (4H, m, C6H_2, C12H_2), 1.71 (3H, s, C9Me), 1.61–1.52 (2H, m, C3′H), 1.43–1.29 (34H, m, C13H_2–C17H_2, C4′H_2–C15′H_2), 0.90 (6H, t, *J* = 6.8 Hz, C18H_3, C16′H_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 177.2 (C=O), 136.1 (C10H), 135.2 (C9), 134.3 (C5H), 131.4 (C4H), 130.3 (C8H), 128.6 (C11H), 104.7 (C1′′H), 78.0 (C5′′H), 77.9 (C3′′H), 75.0 (C2′′H), 73.1 (C2′H), 72.8 (C3H), 71.6 (C4′′H), 69.7 (C1H_2), 62.7 (C6′′H_2), 54.6 (C2H), 35.9 (C3′H_2), 34.0 (C12H_2), 33.5 (C6H_2), 33.1 (CH_2), 33.0 (CH_2), 30.9 (CH_2), 30.8 (CH_2), 30.8 (CH_2), 30.8 (CH_2), 30.8 (CH_2), 30.7 (CH_2), 30.7 (CH_2), 30.5 (CH_2), 30.3 (CH_2), 28.8 (C7H_2), 26.2 (CH_2), 23.7 (CH_2), 14.4 (C18H_3, C16′H_3), 12.8 (C9*Me*). LRMS (ES$^+$ mode): *m/z* (%) 748.6 [(M+Na)$^+$, 100], 708.6 [(M–OH)$^+$, 36], 546.6 [(M–glucose)$^+$, 14]. HRMS (EI$^+$ mode): Found, 748.5313, (M+Na)$^+$. $C_{41}H_{75}NNaO_9$ requires M, 748.5334.

(4*E*,8*E*,10*E*,2*S*,3*R*)-*N*-[(2′*R*)-2′-((Benzoyloxy)hexadecanoyl)amino]-9-methyloctadeca-4,8,10-triene-1,3-diol (39)



Polymer-bound PPh_3 (Aldrich, 140 mg, 3 mmol/g, 0.42 mmol, 3.0 equiv) was added to a solution of azide **10** (46 mg, 0.14 mmol, 1.0 equiv) in pyridine (3.5 mL) and the suspension stirred at room temperature for 3 h. Water (3 mL) was added and the mixture stirred under nitrogen at room temperature for 2 d. The mixture was filtered and the filtrate concentrated *in vacuo* to give D-*erythro*-4,8,10-sphingatrienine (**38**) as a colourless solid (40 mg, 0.13 mmol) which was dissolved in THF (2 mL). *N*-Succinimidyl ester **20** (64 mg, 0.14 mmol, 1.05 equiv) was added followed by NEt_3 (0.04 mL, 0.26 mmol, 2.0 equiv) and the resultant solution stirred at room temperature for 20 h. The mixture was then poured into H_2O (20 mL) and extracted with EtOAc (3×10 mL). The combined organic extracts were washed with brine (20 mL), dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography (SiO_2, hexanes–Et_2O 1:2) to give the title compound (27 mg, 0.040 mmol, 31%) as a white waxy solid. $[\alpha]_D^{26} = -8.14$ (*c* 1.0, $CHCl_3$). IR (film): ν_{max} = 3275 m, 2923 s, 2853 m, 1728 s, 1661 s cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ_H = 8.08 (2H, d, *J* = 7.3 Hz, ArH), 7.61 (1H, t, *J* = 7.7 Hz, ArH), 7.48 (2H, t, *J* = 7.7 ArH), 6.92 (1H, d, *J* = 7.7 Hz, NH), 6.03 (1H, d, *J* = 15.8 Hz, C10H), 5.79 (1H, td, *J* = 6.4, 15.4 Hz, C5H), 5.60–5.52 (2H, m, C11H, C4H), 5.36 (1H, t, *J* = 6.4 Hz, C2′H), 5.31 (1H, t, *J* = 7.3, C8H), 4.36 (1H, apparent t, *J* = 4.7 Hz C3H), 3.95 (1H, dd, *J* = 3.4, 11.1 Hz, C1H_AH_B), 3.89 (1H, apparent sextet, *J* = 3.8 Hz, C2H), 3.69 (1H, dd, *J* = 3.4, 11.1 Hz, C1H_AH_B), 2.93–2.70 (2H, br s, 2 OH), 2.21–2.17 (2H, C7H_2), 2.13–2.06 (4H, m, C6H_2, C12H_2), 2.00–1.97 (2H, m, C3′H_2), 1.71 (3H, s, C9Me), 1.45–1.21 (38H, m), 0.89 (6H, t, *J* = 6.8 Hz, C18H_3, C16′H_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C = 170.7 (C1′=O), 166.0 (ArC=O), 134.5 (C10H), 134.4 (C9), 133.8 ($C_{Ar}H$), 133.5 (C5H), 129.9 (2$C_{Ar}H$), 129.4 (C_{Ar}), 129.2 (C4H), 129.1 (C8H), 128.8 (2$C_{Ar}H$), 128.4 (C11H), 75.1 (C2′H), 74.1 (C3H), 62.1 (C1H_2), 54.4 (C2H), 33.1 (C6H_2), 32.4 (CH_2), 32.1 (2CH_2), 32.0 (CH_2), 29.9 (2+ × CH_2), 29.8 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.4 (CH_2), 27.8 (CH_2), 25.1 (CH_2), 22.9 (2CH_2), 14.3 (C18H_3, C16′H_3), 12.7 (C9*Me*). LRMS (ES^+ mode): *m/z* (%) 690.5 [$(M+Na)^+$, 100], 668.5 [$(M+H)^+$, 13]. HRMS (ES^+ mode): Found, 690.5073, $(M+Na)^+$. $C_{42}H_{69}NO_5Na$ requires M, 690.5068.

(4*E*,8*E*,10*E*,2*S*,3*R*,)-*N*-[(2′*R*)-2′-(Hydroxyhexadecanoyl)amino]-9-methyloctadeca-4,8,10-triene-1,3-diol (40)

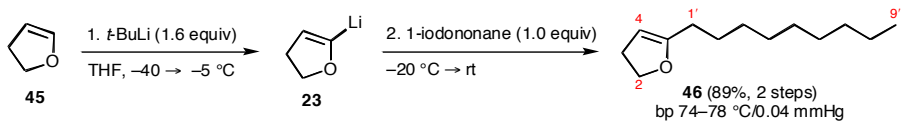


1M LiOH in H_2O (0.75 mL, 0.75 mmol, 25 equiv) was added to a solution of benzoate ester **39** (20 mg, 0.030 mmol, 1.0 equiv) in methanol–THF (5:1, 3.6 mL) and the mixture stirred at room temperature for 30 mins. The mixture was poured into EtOAc (10 mL) and washed with water (3×5

mL) and brine (10 mL). The organic layer was dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography (SiO_2, ethyl acetate) to give the title compound (13 mg, 0.023 mmol, 77%) as a white solid: mp 76.9–78.1 °C. $[\alpha]_D^{27}$ = +6.5 (*c* 0.4, $CHCl_3$). IR (film): ν_{max} = 3368 m, 2919 s, 2850 s, 1645 s, 1536 m cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ_H = 7.24 (1H, d, *J* = 8.1 Hz, NH), 6.04 (1H, d, *J* = 15.4 Hz, C10H), 5.80 (1H, td, *J* = 6.4, 15.4 Hz, C5H), 5.58 (1H, td, *J* = 6.8, 15.4, C11H), 5.53 (1H, dd, *J* = 6.4, 15.4 Hz, C4H), 5.33 (1H, t, *J* = 6.8 Hz, C8H), 4.27 (1H, m, C3H), 4.11 (1H, d, *J* = 4.7 Hz, C2′H), 3.94–3.85 (2H, m, C1H_AH_B, C2H), 3.75 (1H, dd, *J* = 2.6, 11.1 Hz, C1H_AH_B), 3.68–3.20 (3H, br m, 3 OH), 2.21 (2H, app q, *J* = 7.3 Hz, C7H_2), 2.14 (2H, app q, *J* = 7.3 Hz, C6H_2), 2.08 (2H, app q, *J* = 7.3 Hz, C12H_2), 1.83–1.80 (2H, m, C3′H_2), 1.72 (3H, s, C9Me), 1.65–1.58 (2H, m, C4′H_2), 1.45–1.21 (32H, m), 0.89, (6H, distorted t, *J* = 6.8 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C = 175.5 (C1′), 134.6 (C10H), 134.4 (C9), 133.8 (C5H), 129.1 (C4H, C8H), 128.5 (C11H), 74.3 (C3H), 72.7 (C2′H), 62.3 (C1H_2), 54.6 (C2H), 34.9 (C12H_2), 33.1 (CH_2), 32.5 (CH_2), 32.1 (CH_2), 32.0 (CH_2), 29.9 (2+CH_2), 29.9 (2+CH_2), 29.8 (CH_2), 29.8 (CH_2), 29.6 (CH_2), 29.6 (2+CH_2), 29.5 (CH_2), 29.4 (CH_2), 27.9 (CH_2), 25.3 (CH_2), 22.9 (CH_2), 22.9 (CH_2), 14.3 (C18H_3, C16′H_3), 12.7 (C9*Me*). LRMS (ES^+ mode): *m/z* (%) 546.6 [(M–17)$^+$, 100], 564.6 [(M+H)$^+$, 27], 586.6 [(M+Na)$^+$, 43]. HRMS (ES^+ mode): Found, 586.4799, (M+Na)$^+$. $C_{35}H_{65}NNaO_4$ requires M, 568.4806.

Synthesis of Sch II

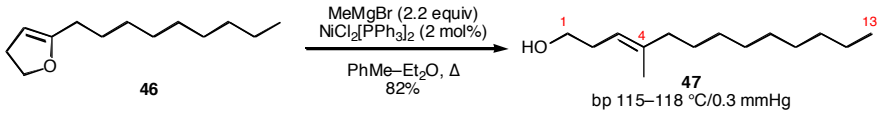
5-Nonyl-2,3-dihydrofuran (46)



tert-Butyllithium (1.66 M in pentane, 72 mL, 120 mmol, 1.6 equiv) was added to a solution of 2,3-dihydrofuran (10.7 mL, 143 mmol, 1.9 equiv) in THF (60 mL, 0.75 mol, 10 equiv) at –40 °C. The pale yellow solution was allowed to warm to –5 °C over 1 h before cooling to –20 °C whereupon 1-iodononane (15 mL, 75 mmol, 1.0 equiv) was added. The reaction mixture was allowed to warm slowly to room temperature (16 h) before cooling to 0 °C and pouring into saturated aqueous ammonium chloride (150 mL). The organic phase was diluted with Et_2O (150 mL), washed with brine (150 mL) and dried ($MgSO_4$) and concentrated *in vacuo*. The residue was purified by rapid short path distillation using glassware which had been washed with KOH in methanol then water and dried at 150 °C overnight. The title compound (13.0 g, 66 mmol, 89%) was obtained as a colourless oil: bp 74–78 °C/0.04 mmHg. IR (film): ν_{max} = 2926 s, 2855 m, 1667 m cm^{-1}. ^1H NMR (300 MHz, C_6D_6): δ_H = 4.75 (1H, br s with fine splitting, C4H), 4.33 (2H, t, *J* = 9.2 Hz, C2H_2), 2.56 (2H, dt, *J* = 2.0, 9.2 Hz, C3H_2), 2.38 (2H, t, *J* = 7.7 Hz, C1′H_2), 1.78 (2H, apparent quintet, *J* = 7.2 Hz, C2′H_2), 1.44 (12H, m, C3′H_2–C8′H_2), 1.10 (3H, distorted t, *J* = 6.7 Hz, C9′H_3). ^{13}C NMR (75 MHz, C_6D_6): δ_C = 160.1 (C5), 93.8 (C4H), 70.1 (C2H_2), 32.6 (CH_2), 30.7 (C3H_2), 30.3 (CH_2), 30.2 (CH_2), 30.1 (CH_2), 30.1 (CH_2), 28.8 (CH_2), 27.6 (C1′H_2), 23.5 (C2′H_2), 14.7 (C9′H_3). LRMS (ES^+ mode): *m/z* (%) = 196.9 [(M+H)$^+$, 100], 214.9 [(M+NH_4)$^+$, 22]. HRMS (ES^+ mode): Found, 197.1898, (M+H)$^+$. $C_{13}H_{25}O$ requires M, 197.1905.

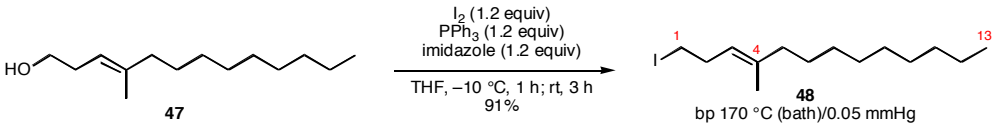
Use of base-washed glassware and low distillation temperatures is essential to minimise the isomerisation of the endocyclic enol ether to the more thermodynamically stable exocyclic enol ether.[15]

(E)-4-Methyltridec-3-en-1-ol (47)



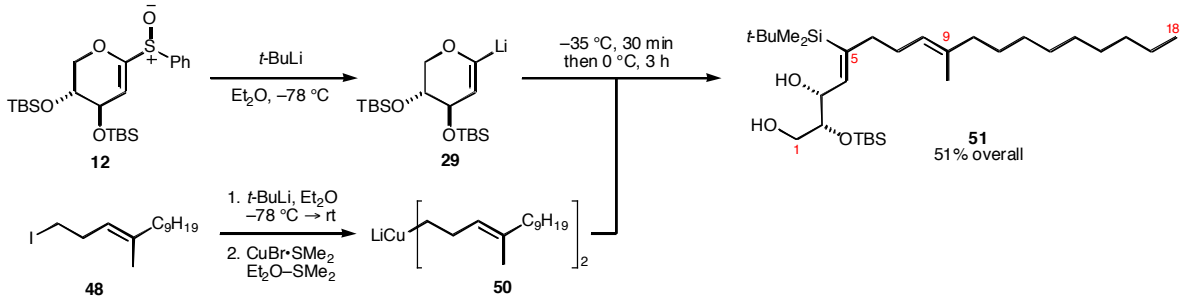
Methylmagnesium bromide (3.0 M in Et_2O, 0.88 mL, 2.6 mmol, 4 mol%) was added dropwise to a suspension of $Ni(PPh_3)_2Cl_2$ (861 mg, 1.3 mmol, 2 mol%) in dry toluene (5 mL) and the red/brown mixture stirred for 15 min. Methylmagnesium bromide (3.0 M in Et_2O, 48 mL, 144.8 mmol, 2.2 equiv) and 5-nonyl-2,3-dihydrofuran (**46**, 12.9 g, 65.8 mmol, 1.0 equiv) in toluene (5 mL) were then added and the mixture heated under reflux for 4 h. The reaction mixture was cooled to 0 °C and poured as a slow stream onto vigorously stirred aqueous ammonium chloride (200 mL). Stirring was continued for 10 mins until the solution was colourless. The organic layer was separated and the aqueous layer extracted with Et_2O (3×100 mL). The combined organic layers were washed with brine (100 mL), dried ($MgSO_4$) and concentrated *in vacuo*. The residue was purified by Kugelrohr distillation to give the title compound (11.4 g, 53.8 mmol, 82%) as a colourless oil: bp 115–118 °C (bath)/0.3 mmHg. IR (film): ν_{max} = 3337 m (OH), 2925 s, 2854 s, 1667 w, 1466 m, 1048 m cm^{-1}. ^1H and ^{13}C NMR spectroscopic data recorded at 300 MHz and 75 MHz respectively were consistent with literature data recorded at 400 and 25 MHz.[7] LRMS (ES^+ mode): *m/z* (%) = 254.3 (M^++H+K, 100).

(*E*)-1-Iodo-4-methyltridec-3-ene (48)



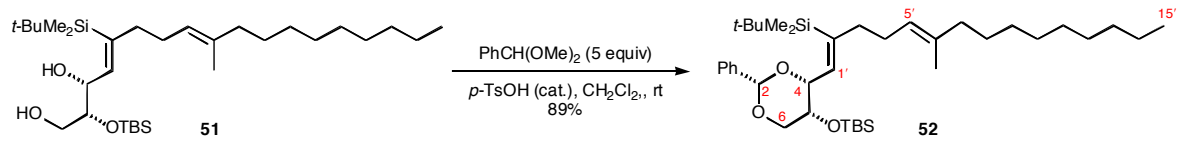
Iodine (7.2 g, 28.3 mmol, 1.2 equiv) was added to a solution of 4-methyltridec-3-en-1-ol (5.0 g, 23.6 mmol, 1.0 equiv), imidazole (1.9 g, 28.3 mmol, 1.2 equiv) and triphenylphosphine (7.4 g, 28.3 mmol, 1.2 equiv) in THF (75 mL) at –10 °C. The reaction mixture was stirred at –10 °C for 1 h then at room temperature for 3 h. The mixture was poured into $Na_2S_2O_3$ (100 mL) and the organic phase separated. The aqueous phase was extracted with Et_2O (3×50 mL) and the combined organic extracts were washed with sat. aq $Na_2S_2O_3$ (50 mL), then brine (50 mL), dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by column chromatography (SiO_2, hexanes) followed by Kugelrohr distillation to give the title compound (6.9 g, 21.6 mmol, 91%) as a colourless oil: bp 170 °C (bath)/0.05 mmHg. IR (film): ν_{max} = 2925 s, 2853 s, 1663 w, 1465 m cm^{-1}. ^1H NMR spectroscopic data recorded at 300 MHz were consistent with literature data recorded at 400 MHz.[7] ^{13}C NMR (75 MHz, $CDCl_3$): δ_C = 138.7 (C4), 122.8 (C3H), 39.8 ($C5H_2$), 32.6 ($C2H_2$), 30.1 (CH_2), 29.8 (CH_2), 29.7 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 27.9 (CH_2), 22.9 (CH_2), 16.4 (C4*Me*), 14.3 ($C13H_3$), 6.4 ($C1H_2$). LRMS (ES^+ mode): *m/z* (%) = 435.5 (M^++72+41, 35), 394.5 (M^++72, 100), 323.3 (M^++H, 10).

(4*Z*,8*E*,2*R*,3*R*)-5-(*tert*-Butyldimethylsilyl)-2-*O*-(*tert*-butyldimethylsilyl)-9-methyl-octadec-4,8-dien-1,3-diol (51)



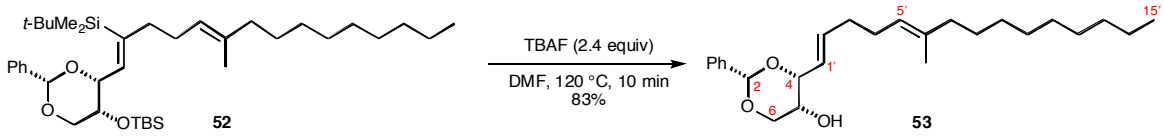
1-Iodo-4-methyl-tridec-3-ene (**48**, 5.5 g, 17.2 mmol, 4.4 equiv) was added to a solution of *tert*-butyllithium (1.72 M in pentane, 20 mL, 43.3 mmol, 8.8 equiv) in Et_2O (20 mL) at –78 °C using pentane (2 mL) for washing. The colourless suspension was stirred at –78 °C for 30 min, 0 °C for 1 h and room temperature for 1 h. The mixture was cooled to 0 °C and a solution of *freshly prepared*[13] $CuBr•SMe_2$ (882 mg, 4.3 mmol, 1.1 equiv) in SMe_2 (20 mL) was added by cannula using SMe_2 (15 mL) for washing. The resulting pale yellow solution of the cuprate **50** was stirred at 0 °C for 1 h. In a separate flask *tert*-butyllithium (1.72 M in pentane, 2.3 mL, 3.9 mmol, 1.0 equiv) was added to a solution of **12** (1.83 g, 3.9 mmol, 1.0 equiv) in THF (0.63 mL, 7.8 mmol, 2.0 equiv) and Et_2O (10 mL), at –78 °C and the mixture stirred for 30 min to give the lithiated glycal **29**. The cuprate **50** was cooled to –35 °C and the lithiated glycal **29** added by cannula using Et_2O (2 mL) for washing. The reaction was stirred at –35 °C for 30 min then at 0 °C for 3 h. The mixture was added by cannula to degassed saturated aqueous NH_4Cl (100 mL) at 0 °C and the mixture stirred at room temperature for 15 min. The blue aqueous layer was separated and extracted with Et_2O (3×50 mL). The combined organic layers were washed with brine (150 mL), dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography (SiO_2, hexanes–Et_2O, 8:1) to give the title compound (1.1 g, 2.0 mmol, 51%) as a colourless oil. $[\alpha]_D^{28}$ = –6.8 (*c* 1.6, $CHCl_3$). IR (film): ν_{max} = 3369 m (OH), 2927 s, 2855 s, 1609 m, 1463 m cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ_H = 6.11 (1H, d, *J* = 9.8 Hz, C4H), 5.11 (1H, br s, C8H), 4.27 (1H, m, C3H), 3.65–3.60 (3H, m, $C1H_2$, C2H), 2.34 (1H, d, *J* = 6.4 Hz, OH), 2.10–2.00 (5H, m, $C6H_2$, $C7H_2$, OH), 1.95 (2H, m, $C10H_2$), 1.58 (3H, s, C9Me), 1.39–1.22 (14H, m), 0.94 (9H, s, *t*-Bu), 0.92 (9H, s, *t*-Bu), 0.89 (3H, distorted t, $C18H_3$), 0.19 (3H, s, SiMe), 0.17 (3H, s, SiMe), 0.14 (3H, s, SiMe), 0.14 (3H, s, SiMe). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C = 142.8 (C5), 141.5 (C4H), 135.9 (C9), 123.7 (C8H), 76.0 (C2H), 71.2 (C3H), 64.4 ($C1H_2$), 39.9 ($C10H_2$), 38.2 ($C6H_2$), 32.1 (CH_2), 29.8 (CH_2), 29.8 (CH_2), 29.5 ($2CH_2$), 28.9 (CH_2), 28.1 (CH_2), 27.2 (CMe_3), 26.1 (CMe_3), 22.9 (CH_2), 18.4 (CMe_3), 17.7 (CMe_3), 16.1 (C9*Me*), 14.3 ($C18H_3$), –2.7 (SiMe), –3.5 (SiMe), –4.1 (SiMe), –4.5 (SiMe). LRMS (ES^+ mode): *m/z* = 563.5 $(M+Na)^+$. HRMS (ES^+ mode): Found, 563.4290 $(M+Na)^+$. $C_{31}H_{64}O_3NaSi_2$ requires M, 563.4292.

(2*S*,4*R*,5*R*)-4-[(1′*Z*,5′*E*)-2-(*tert*-Butyldimethylsilyl)-6′-methyl-pentadeca-1′,5′-dienyl]-5-(*tert*-butyldimethylsilyloxy)-2-phenyl-1,3-dioxane (52)



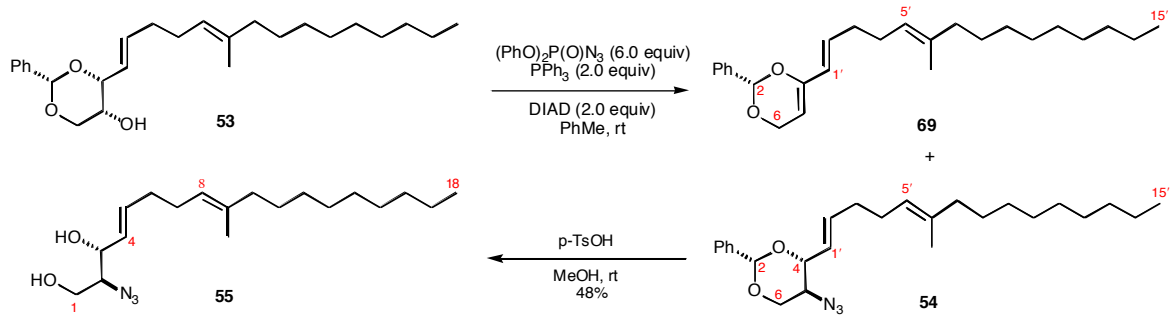
Benzaldehyde dimethyl acetal (1.75 mL, 11.7 mmol, 5.0 equiv), was added to a solution of **51** (1.26 g, 2.33 mmol, 1.0 equiv) in CH_2Cl_2 (75 mL). *p*-TsOH (75 mg), was added and the mixture stirred at room temperature for 1 h. The reaction was then poured into saturated aqueous $NaHCO_3$ (100 mL) and extracted into Et_2O (3×50 mL). The combined organic extracts were washed with brine (100 mL), dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography (SiO_2, hexanes–Et_2O, 75:1) to give the title compound (1.30 g, 2.07 mmol, 89%) as a colourless oil. $[\alpha]_D^{29}$ = +3.6 (*c* 1.2, $CHCl_3$). IR (film): ν_{max} = 3325 m, 2927 s, 2856 s, 1610 m, 1462 m cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ_H = 7.51–7.50 (2H, m, ArH), 7.36–7.32 (3H, m, ArH), 6.40 (1H, d, *J* = 9.8 Hz, C1′H), 5.51 (1H, s, C2CH), 5.11 (1H, br s, C5′H), 4.47 (1H, dd, *J* = 1.3, 9.5 Hz, C4H), 4.16 (1H, dd, *J* = 1.3, 12.0 Hz, C6$H_A$$H_B$), 3.99 (1H, dd, *J* = 1.3, 12.0 Hz, C6$H_A$$H_B$), 3.54 (1H, s, C5H), 2.09 (4H, m, C3′H, C4′H), 1.95 (2H, t, *J* = 6.9 Hz, C7′H), 1.57 (3H, s, C6′Me), 1.48–1.27 (14H, m), 0.99 (9H, s, *t*-Bu), 0.95 (9H, s, *t*-Bu), 0.89 (3H, distorted t, *J* = 7.0 Hz, C15′H_3), 0.12 (3H, s, SiMe), 0.18 (3H, s, SiMe), 0.13 (3H, s, SiMe), 0.11 (3H, s, SiMe). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C = 143.3 (C2′), 139.2 (C_{Ar}), 138.7 (C6′), 135.8 (C1′H), 129.0 (C_{Ar}H), 128.4 (2C_{Ar}H), 126.6 (2C_{Ar}H), 123.8 (C5′H), 101.6 (C2H), 79.8 (C4H), 72.9 (C6H_2), 67.3 (C5H), 39.9 (C7′H_2), 38.2 (C3′H_2), 32.1 (CH_2), 29.8 (C4′H_2), 29.7 (CH_2), 29.5 (2CH_2), 28.6 (CH_2), 28.1 (CH_2), 27.1 (C*Me*$_3$), 26.1 (C*Me*$_3$), 22.9 (CH_2), 18.5 (*C*Me$_3$), 18.0 (*C*Me$_3$), 16.1 (C6′*Me*), 14.3 (C15′H_3), –2.5 (SiMe), –3.6 (SiMe), –4.2 (SiMe), –4.5 (SiMe). LRMS (ES$^+$ mode): *m/z* (%) = 646.5 (M^++NH_4^+, 55), (M^++34, 100). Anal. Calcd. for $C_{38}H_{68}O_3Si_2$: C, 72.55; H, 10.89. Found: C, 72.85; H, 11.05%.

(2*S*,4*R*,5*R*)-4-[(1′*E*,5′*E*)-9-Methylpentadec-1′,5′-dienyl]-2-phenyl-1,3-dioxan-5-ol (53)



TBAF (1.0 M in THF, 5.0 mL, 5.0 mmol, 2.4 equiv) was added to a solution of **52** (1.30 g, 2.1 mmol, 1.0 equiv) in DMF (15 mL) and the mixture heated at 120 °C for 10 min. The cooled mixture was poured into brine (100 mL) and extracted with Et_2O (3×50 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography (SiO_2, hexanes–Et_2O, 10:1) to give the title compound (688 mg, 1.7 mmol, 83%) as a colourless oil. $[\alpha]_D^{28}$ = –5.7 (*c* 1.0, $CHCl_3$). IR (film): ν_{max} = 3392 m, 2925 s, 2854 s, 1607 m, 1453 m cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ_H = 7.54–7.50 (2H, m, ArH), 7.41–7.34 (3H, m, ArH), 5.86 (1H, td, *J* = 6.4, 15.8 Hz, C2′H), 5.68 (1H, dd, *J* = 6.4, 15.8 Hz, C1′H), 5.63 (1H, s, C2H), 5.12 (1H, br s, C5′H), 4.42 (1H, d, *J* = 6.4 Hz, C4H), 4.26 (1H, dd, *J* = 1.7, 12.0 Hz, C6$H_A$$H_B$), 4.09 (1H, dd, *J* = 1.3, 12.0 Hz, C6$H_A$$H_B$), 3.55 (1H, d, *J* = 9.0 Hz, C5H), 2.65 (1H, d, *J* = 10.3 Hz, OH), 2.12–2.08 (4H, m, C3′H_2, C4′H_2), 1.97 (2H, t, *J* = 7.3 Hz, C7′H_2), 1.59 (3H, s, C6′Me), 1.39–1.22 (14H, m), 0.88 (3H, distorted t, *J* = 6.8 Hz, C15′H_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C = 138.0 (C_{Ar}), 136.3 (C6′), 135.0 (C2′H), 129.2 (C_{Ar}H), 128.5 (2C_{Ar}H), 126.3 (2C_{Ar}H), 126.2 (C1′H), 123.4 (C5′H), 101.6 (C2H), 80.8 (C4H), 72.6 (C6H_2), 66.5 (C5H), 39.9 (C7′H_2), 32.9 (C3′H_2), 32.1 (CH_2), 29.8 (CH_2), 29.8 (CH_2), 29.5 (CH_2), 29.5 (CH_2), 28.2 (CH_2), 27.6 (C4′H_2), 22.9 (CH_2), 16.2 (C6′*Me*), 14.3 (C15′H_3). LRMS (ES$^+$ mode): *m/z* (%) = 295.1 (M^+–105, 91), 418.3 (M^++NH_4^+, 100). HRMS (ES$^+$ mode): Found, 423.2871 (M+Na)$^+$. $C_{26}H_{40}O_3Na$ requires M, 423.2875. Anal. Calcd. for $C_{26}H_{40}O_3$: C, 77.95; H, 10.06. Found: C, 77.95; H, 10.10%.

(4*E*,8*E*,2*S*,3*R*)-2-Azido-9-methyloctadeca-4,8-diene-1,3-diol (55)



Triphenylphosphine (839 mg, 3.2 mmol, 2.0 equiv) was added to a solution of alcohol **53** (638 mg, 1.6 mmol, 1.0 equiv) in toluene (30 mL). Diphenylphosphoryl azide (2.1 mL, 9.6 mmol, 6.0 equiv) was then added followed immediately by diisopropyl azodicarboxylate (0.63 mL, 3.2 mmol, 2.0 equiv). The yellow mixture was stirred at room temperature for 18 h. The mixture was concentrated *in vacuo* and the residue purified by column chromatography (SiO_2, hexane–Et_2O, 110:1) to give a mixture of the azide **54** and and the elimination product **69**. Diagnostic signals for both components could be discerned by ^{1}H NMR spectroscopy:

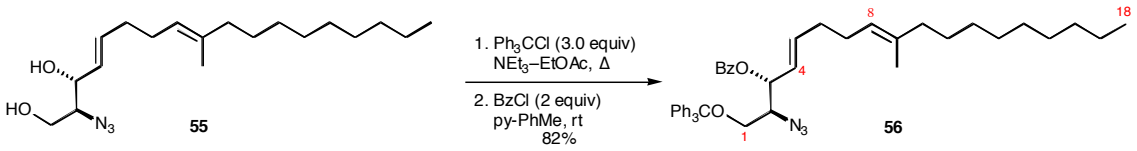
(2*S*,5*S*,4*R*)-5-Azido-4-[(1′*E*,5′*E*)-6-methylpentadec-1,5-dienyl]-2-phenyl-1,3-dioxane (**54**)
^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.59–7.56 (2H, m, ArH), 7.46–7.41 (3H, m, ArH), 6.11 (1H, td, *J* = 6.4, 15.4 Hz, C2′H), 5.85 (1H, s, C2H), 5.83 (1H, d, *J* = 15.9 Hz, C1′H), 5.15 (1H, br s, C5′H), 4.92 (1H, br s, C5H), 4.61 (1H, d, *J* = 16.4 Hz, C6H_AH$_B$), 4.45 (1H, dd, *J* = 3.6, 16.4 Hz, C6H$_A$$H_B$), 2.16–2.09 (4H, br s, C3′H_2, C4′H_2), 1.96 (2H, t, *J* = 7.2 Hz, C7′H_2), 1.58 (3H, s, C6′Me), 1.39–1.22 (14H, m, C8′H_2–C14′H_2), 0.89 (3H, distorted t, *J* = 6.9 Hz, C15′H_3).

6-[(1′*E*,5′*E*)-6-methylpentadec-1,5-dienyl]-2-phenyl-4*H*-1,3-dioxine (**69**)
^{1}H NMR (300 MHz, $CDCl_3$): δ_H 7.50–7.48 (2H, m, ArH), 7.41–7.36 (3H, m, ArH), 6.00 (1H, td, *J* = 6.0, 15.6 Hz, C2′H), 5.62 (1H, dd, *J* = 7.4, 15.4 Hz, C1′H), 5.51 (1H, s, C2H), 5.14 (1H, br s, C5′H), 4.35 (1H, dd, *J* = 5.4, 11.0 Hz, C6H_AH$_B$), 4.07 (1H, apparent t, *J* = 7.9 Hz, C4H), 3.63 (1H, apparent t, *J* = 11.0 Hz, C6H$_A$$H_B$), 3.53–3.46 (1H, m, C5H), 2.15 (4H, br s, C3′H_2, C4′H_2), 1.97 (2H, t, *J* = 7.2 Hz, C7′H_2), 1.60 (3H, s, C6′Me), 1.40–1.25 (14H, m, C8′H_2–C14′H_2), 0.89 (3H, distorted t, *J* = 6.9 Hz, C15′H_3).

p-TsOH (80 mg, 0.46 mmol) was added to the mixture of **54** and **69** (645 mg, 1.6 mmol, 1.0 equiv) in methanol (20 mL) and the solution stirred at room temperature for 18 h. Na_2CO_3 (2.0 g) was then added and the suspension stirred for 15 min before concentrating the mixture *in vacuo*. The residue was purified by column chromatography (eluting with hexanes–Et_2O 1:1) to give the title azide **55** (257 mg, 0.76 mmol, 48% over 2 steps) as a colourless oil. $[\alpha]_D^{22}$ = –38.5 (*c* 1.1, $CHCl_3$). IR (film): ν_{max} = 3350 m, 2925 s, 2854 m, 2103 m, 1610 m cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 5.83 (1H, td, *J* = 6.4, 15.4 Hz, C5H), 5.57 (1H, dd, *J* = 7.2, 15.4 Hz, C4H), 5.10 (1H br s, C8H), 4.26 (1H, t, *J* = 6.1 Hz, C3H), 3.78 (2H, m, C1H_2), 3.52 (1H, q, *J* = 5.4 Hz, C2H), 2.14–2.10 (4H, m, C6H_2, C7H_2), 2.05–2.01 (2H, m, 2 OH), 1.96 (2H, t, *J* = 7.7 Hz, C10H_2), 1.59 (3H, s, C9Me), 1.39–1.22 (14H, m), 0.89 (3H, distorted t, *J* = 6.5 Hz, C18H_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C = 136.5 (C9), 135.8 (C5H), 128.4 (C4H), 123.2 (C8H), 74.0 (C3H), 66.9 (C2H), 62.8 (C1H_2), 39.9 (C10H_2), 32.7

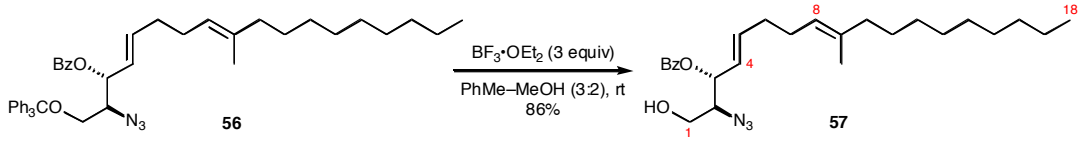
($C6H_2$), 32.1 (CH_2), 29.8 (CH_2), 29.8 (CH_2), 29.5 (CH_2), 29.5 (CH_2), 28.2 (CH_2), 27.5 ($C7H_2$), 22.9 (CH_2), 16.2 (C9*Me*), 14.3 ($C18H_3$). LRMS (ES^+ mode): *m/z* (%) = 355.1 (M^++NH_4^+, 100). HRMS (ES^+ mode): Found, 360.2627 $(M+Na)^+$. $C_{19}H_{35}O_2N_3Na$ requires M, 360.2627.

(2*S*,3*R*,4*E*,8*E*)-2-Azido-3-*O*-benzoyl-9-methyl-1-*O*-triphenylmethyl-octadeca-4,8-diene-1,3-diol (56)



TrCl (7 mg, 0.025 mmol, 1.0 equiv) was added to a solution of diol **55** (8.5 mg, 0.025 mmol, 1.0 equiv) in EtOAc (0.5 mL) and Et_3N (4 μL, 0.029 mmol, 1.2 equiv) and the solution heated under reflux for 5 h. Additional portions of TrCl (7 mg, 0.025 mmol, 1.0 equiv) and Et_3N (4 μL, 0.029 mmol, 1.2 equiv) were added after 2 h and 4 h. The mixture was concentrated *in vacuo* and the residue dissolved in toluene (0.2 mL) and pyridine (0.05 mL). BzCl (7.0 mg, 0.05 mmol, 2.0 equiv) was added and the resulting suspension stirred at room temperature for 10 h. The mixture was concentrated *in vacuo*, saturated $NaHCO_3$ (5 mL) was added and the mixture extracted with Et_2O (3×5 mL). The combined organic extracts were washed with brine (10 mL), dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography (SiO_2, hexanes–Et_2O, 50:1) to give the title compound (14 mg, 0.020 mmol, 82%, 2 steps) as a colourless oil. $[\alpha]_D^{25}$ = –18.2 (*c* 2, $CHCl_3$). IR (film): ν_{max} = 2926 s, 2099 m, 1724 m cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ_H = 7.78 (2H, d, *J* = 7.4 Hz, ArH), 7.58 (1H, t, *J* = 7.3 Hz, ArH), 7.48–7.43 (8H, m, ArH), 7.30–7.22 (9H, m, ArH), 5.86 (1H, td, *J* = 6.0, 15.4 Hz, C5H), 5.66 (1H, dd, *J* = 5.1, 7.7 Hz, C3H), 5.48 (1H, dd, *J* = 7.7, 15.4 Hz, C4H), 5.07–5.05 (1H, m, C8H), 3.87 (1H, td, *J* = 5.1, 6.4 Hz, C2H), 3.33 (1H, dd, *J* = 6.4, 9.8 Hz, C1H_AH_B), 3.24 (1H, dd, *J* = 5.1, 9.8 Hz, C1H_AH_B), 2.05–2.00 (4H, m, $C6H_2$, $C7H_2$), 1.92 (2H, t, *J* = 7.3 Hz, $C10H_2$), 1.56 (3H, s, C9Me), 1.37–1.23 (14H, m, $C11H_2$–$C17H_2$), 0.90 (3H, distorted t, *J* = 6.8 Hz, $C18H_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C = 165.3 (C=O), 143.6 ($3C_{Ar}$), 137.9 (C5H), 136.3 (TrC), 133.2 ($C_{Ar}H$), 130.1 (C_{Ar}), 129.9 ($2C_{Ar}H$), 128.5 ($6C_{Ar}H$), 128.3 ($2C_{Ar}H$), 128.1 ($6C_{Ar}H$), 127.3 ($3C_{Ar}H$), 123.5 (C4H), 123.1 (C8H), 87.4 (C9), 74.8 (C3H), 64.6 (C2H), 62.9 ($C1H_2$), 39.8 ($C10H_2$), 32.7 ($C6H_2$), 32.1 (CH_2), 29.8 (CH_2), 29.7 (CH_2), 29.5 (CH_2), 29.5 (CH_2), 28.1 (CH_2), 27.3 (CH_2), 22.9 ($C7H_2$), 16.1 (C9*Me*), 14.3 ($C18H_3$). LRMS (ES^+ mode): *m/z* (%) = 391.1 (100), 706.5 (M^++NH_4^+, 75). HRMS (ES^+ mode): Found, $(M+H)^+$, 706.4000. $C_{45}H_{53}N_3O_3Na$ requires M, 706.3985.

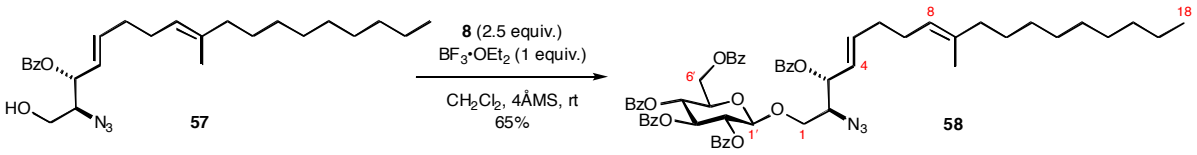
(2*S*,3*R*,4*E*,8*E*)-2-Azido-3-*O*-benzoyl-9-methyl-octadeca-4,8-diene-1,3-diol (57)



BF_3•OEt_2 (11 μL, 0.87 mmol, 3.0 equiv) was added dropwise to a solution of trityl ether **56** (20 mg, 0.29 mmol, 1.0 equiv) in toluene–MeOH (3:2, 1.0 mL) and the solution stirred at room temperature for 16 h. $NaHCO_3$ (10 mL) was added and the mixture extracted with Et_2O (3×10 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated *in vacuo*. The residue was

purified by column chromatography (SiO_2, hexanes–Et_2O, 5:1 to 3:1) to give the title compound (11 mg, 0.25 mmol, 86%) as a colourless oil. $[\alpha]_D^{24}$ = –55.8 (*c* 0.4, $CHCl_3$). IR (film): ν_{max} = 3400 m, OH, 2926 s, 2105 m, 1723 m cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ_H = 8.07 (2H, d, *J* = 7.3 Hz, ArH), 7.58 (1H, t, *J* = 7.7 Hz, ArH), 7.47 (2H, t, *J* = 7.7 Hz, ArH), 5.99–5.94 (1H, m, C5H), 5.66–5.61 (2H, m, C3H, C4H), 5.09 (1H, t, *J* = 6.8 Hz), 3.83–3.80 (1H, m, C2H), 3.79–3.74 (1H, m, C1H_AH_B), 3.66–3.62 (1H, m, C1H_AH_B), 2.15–2.10 (4H, m, $C6H_2$, $C7H_2$), 1.96–1.92 (3H, m, $C10H_2$, OH), 1.57 (3H, s, C9Me), 1.36–1.21 (14H, m, $C11H_2$–$C17H_2$), 0.89 (3H, distorted t, *J* = 7.1 Hz, $C18H_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C = 165.6 (C=O), 138.5 (C5H), 136.6 (C9), 133.5 ($C_{Ar}H$), 130.0 ($2C_{Ar}H$), 129.9 (C_{Ar}), 128.9 ($2C_{Ar}H$), 123.7 (C4H), 123.0 (C8H), 74.7 (C3H), 66.4 (C2H), 62.2 ($C1H_2$), 39.8 ($C10H_2$), 32.8 ($C6H_2$), 32.1 (CH_2), 29.8 (CH_2), 29.7 (CH_2), 29.5 ($2CH_2$), 28.1 (CH_2), 27.3 (CH_2), 22.9 ($C7H_2$), 16.2 (C9*Me*), 14.3 ($C18H_3$). LRMS (ES^+ mode): *m/z* (%) = 292.3 (M^+–OBz, $–N_2$, 100), 464.3 (M^++Na, 78). HRMS (ES^+ mode): Found, $(M+Na)^+$, 464.289419. $C_{26}H_{39}N_3O_3Na$ requires M, 464.288363.

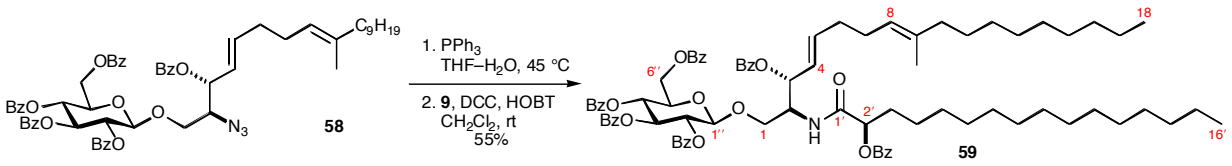
2′,3′,4′,6′-Tetra-*O*-benzoyl-*β*-D-glucopyranosyl-(2*S*,3*R*,4*E*,8*E*)-2-azido-3-*O*-benzoyl-9-methyl-octadeca-4,8-diene-1,3-diol (58)



BF_3•OEt_2 (0.1 M in CH_2Cl_2, 0.45 mL, 0.045 mmol, 1.0 equiv) was added dropwise to a solution of azide **57** (20 mg, 0.045 mmol, 1.0 equiv) and trichloroacetimidate **8** (84 mg, 0.11 mmol, 2.5 equiv) in CH_2Cl_2 over 4Å molecular sieves at 0 °C. The mixture was stirred at 0 °C for 10 min and room temperature for 1 h. Saturated aqueous $NaHCO_3$ (10 mL) was added and the mixture extracted with CH_2Cl_2 (3×10 mL). The combined extracts were dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by column chromatography (SiO_2, hexanes–Et_2O, 4:1 to 3:1) to give a colourless solid which was dissolved in $CHCl_3$. Petroleum ether was added and the white precipitate filtered. The filtrate was concentrated *in vacuo* to give the title compound (30 mg, 0.029 mmol, 65%) as a colourless oil. $[\alpha]_D^{26}$ = –10.9 (*c* 1.1, $CHCl_3$). IR (film): ν_{max} = 2926 m, 2106 m, 1728 s cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ_H = 8.03–7.97 (6H, m, ArH), 7.90 (2H, d, *J* = 7.3 Hz, ArH), 7.83 (2H, d, *J* = 7.3 Hz, ArH), 7.48–7.40 (4H, m, ArH), 7.36–7.19 (11H, m, ArH), 5.91 (1H, t, *J* = 9.6 Hz, C3′H), 5.77–5.68 (2H, m, C5H, C4′H), 5.58–5.56 (2H, m, C2′H, C3H), 5.49 (1H, dd, *J* = 8.1, 15.4 Hz, C4H), 5.01 (1H, m, C8H), 4.91 (1H, d, *J* = 8.1 Hz, C1′H), 4.63 (1H, dd, *J* = 3.0, 12.0 Hz, C6′H_AH_B), 4.49 (1H, dd, *J* = 5.1, 12.0 Hz, C6′H_AH_B), 4.19–4.17 (1H, m, C5′H), 3.97–3.94 (2H, m, C1H_AH_B, C2H), 3.70–3.64 (1H, m, C1H_AH_B), 1.97 (4H, br s, $C6H_2$, $C7H_2$), 1.90 (2H, t, *J* = 6.8 Hz, $C10H_2$), 1.52 (3H, s, C9Me), 1.32–1.22 (14H, m, $C11H_2$–$C17H_2$), 0.89 (3H, distorted t, *J* = 6.8 Hz, $C18H_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C = 166.7 (C=O), 166.4 (C=O), 165.4 (C=O), 165.6 (2C=O), 139.0 (C5H), 136.7 (C9), 134.0 ($C_{Ar}H$), 133.8 ($C_{Ar}H$), 133.7 ($C_{Ar}H$), 130.5 ($C_{Ar}H$), 130.4 ($C_{Ar}H$), 130.4 ($C_{Ar}H$), 130.3 ($C_{Ar}H$), 130.3 ($C_{Ar}H$), 130.1 (C_{Ar}), 129.8 (C_{Ar}), 129.3 (C_{Ar}), 129.0 ($C_{Ar}H$), 128.9 ($C_{Ar}H$), 123.5 (C8H), 123.4 (C4H), 105.5 (C1′H), 75.3 (C3H), 73.3 (C3′H), 73.0 (C5′H), 72.2 (C2′H), 70.1 (C4′H), 68.9 ($C1H_2$), 64.0 (C2H), 63.6 (C6′H_2), 40.2 ($C10H_2$), 33.1 ($C6H_2$), 32.5 (CH_2), 30.9 (CH_2), 30.3 (CH_2), 30.2 (CH_2), 30.2 (CH_2), 29.9 (CH_2), 28.5 (CH_2), 27.7 ($C7H_2$), 23.3 (CH_2), 16.6 (C9*Me*), 14.7 ($C18H_3$). LRMS (ES^+ mode): *m/z* (%) = 1043.0 (M^++Na,

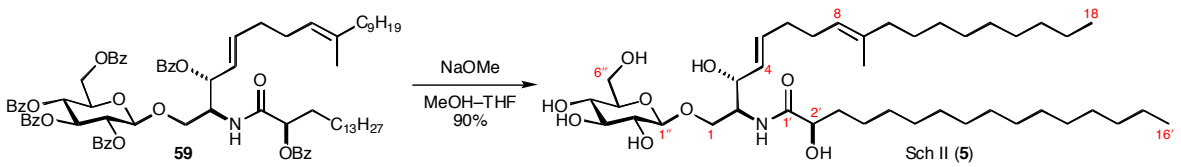
100), 1037.9 (M^++NH_4^+, 87). HRMS (ES^+ mode): Found, $(M+Na)^+$, 1042.4448. $C_{60}H_{65}N_3O_{12}Na$ requires M, 1042.4460.

1-*O*-(2″,3″,4″,6″-Tetra-*O*-benzoyl-*β*-D-glucopyranosyl)-(2*S*,3*R*,4*E*,8*E*)-2-[(2′*R*)-2′-((benzoyloxy)hexadecanoyl)amino]-3-*O*-benzoyl-9-methyl-4,8-octadecadiene-1,3-diol (59)



PPh_3 (19 mg, 0.093 mmol, 3.0 equiv) was added to a solution of azide **58** (32 mg, 0.031 mmol, 1.0 equiv) in THF (0.5 mL) and H_2O (3 μL) and the solution heated at 45 °C. The reaction mixture was allowed to cool to room temperature then concentrated *in vacuo* and the residue dissolved in CH_2Cl_2 (0.5 mL). (*R*)-2-(Benzoyloxy)hexadecanoic acid (**9**, 17 mg, 0.047 mmol, 1.5 equiv), DCC (10 mg, 0.047 mmol, 1.5 equiv) and HOBT (6 mg, 0.047 mmol, 1.5 equiv) were added and the mixture stirred at room temperature for 3 d. The colourless suspension was concentrated *in vacuo* and the residue purified by column chromatography (SiO_2, hexanes–Et_2O, 2:1) to give the title compound (23 mg, 0.017 mmol, 55%) as a colourless oil. $[\alpha]_D^{25}$ = +21.9 (*c* 0.35, $CHCl_3$). IR (film): ν_{max} = 2925 m, 2853 m, 1729 s, 1602 w, 1517 w, 1451 m cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ_H = 8.02 (2H, d, *J* = 7.3 Hz, ArH), 7.97 (2H, d, *J* = 7.3 Hz, ArH), 7.94 (2H, d, *J* = 7.3 Hz, ArH), 7.89 (2H, d, *J* = 7.3 Hz, ArH), 7.85 (2H, d, *J* = 7.3 Hz, ArH), 7.80 (2H, d, *J* = 7.3 Hz, ArH), 7.59 (1H, t, *J* = 7.3H, ArH), 7.52–7.42 (8H, m, ArH), 7.38–7.28 (9H, m, ArH), 6.59 (1H, d, *J* = 9.0 Hz, NH), 5.86 (2H, m, C3″H, C5H), 5.67 (1H, t, *J* = 6.8 Hz, C3H), 5.58 (1H, t, *J* = 9.8 Hz, C4″H), 5.51 (1H, dd, *J* = 7.3, 15.4 Hz, C4H), 5.39 (1H, dd, *J* = 7.7, 9.4 Hz, C2″H), 5.25 (1H, t, *J* = 6.0 Hz, C2′H), 4.99 (1H, s, C8H), 4.83 (1H, d, *J* = 7.7 Hz, C1″H), 4.55–4.50 (2H, m, C2H, C1H_AH_B), 4.36 (1H, dd, *J* = 4.7, 12.0 Hz, C1H$_A$$H_B$), 4.08 (2H, dd, *J* = 4.7, 10.7 Hz, C5″H, C6″H_AH_B), 3.76 (1H, dd, *J* = 5.6, 10.7 Hz, C6″H$_A$$H_B$), 1.95 (4H, br s, C6$H_2$, C7$H_2$), 1.90–1.85 (4H, m, C3′$H_2$, C10$H_2$), 1.51 (3H, s, C9Me), 1.35–1.18 (38H, m, C11H_2–C17H_2, C4′H_2–C15′H_2), 0.89 (6H, t, *J* = 7.3 Hz, C18H_3, C16′H_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C = 169.7 (C1′=O), 166.2 (C=O), 165.9 (C=O), 165.4 (C=O), 165.3 (2C=O), 165.1 (C=O), 137.0 (C5H), 136.2 (C9), 133.7 (C_{Ar}H), 133.6 (C_{Ar}H), 133.4 (C_{Ar}H), 133.2 (C_{Ar}H), 133.2 (2C_{Ar}H), 130.2 (C_{Ar}), 130.0 (2+ × C_{Ar}H), 129.9 (2+ × C_{Ar}H), 129.8 (2+ × C_{Ar}H), 129.6 (C_{Ar}), 129.5 (C_{Ar}), 129.2 (C_{Ar}), 129.0 (C_{Ar}), 128.8 (2C_{Ar}H), 128.6 (2C_{Ar}H), 128.5 (2C_{Ar}H), 128.5 (C_{Ar}), 124.5 (C4H), 123.2 (C8H), 101.1 (C1″H), 74.7 (C2′H), 74.1 (C3H), 72.9 (C3″H), 72.5 (C5″H), 72.90 (C2″H), 69.6 (C4″H), 67.4 (C6″H), 63.1 (C1H_2), 51.1 (C2H), 39.9 (C10H_2), 32.6 (CH_2), 32.1 (2CH_2), 31.8 (CH_2), 29.9 (2+ × CH_2), 29.8 (2CH_2), 29.8 (CH_2), 29.6 (CH_2), 29.6 (2+ × CH_2), 28.2 (CH_2), 27.4 (CH_2), 24.9 (CH_2), 22.9 (2CH_2), 16.1 (C9*Me*), 14.3 (C18H_3, C16′H_3). LRMS (ES^+ mode): *m/z* (%) = 1231.1 [(M–OBz)$^+$, 100], 1375.2 [(M+Na)$^+$, 30]. HRMS (ES^- mode): Found, 1350.7076, $(M-H)^+$. $C_{83}H_{100}NO_{15}$ requires M, 1350.7098.

1-*O*-(*β*-D-Glucopyranosyl)-(2*S*,3*R*,4*E*,8*E*)-2-[(2′*R*)-2′-(hydroxyhexadecanoyl)amino]-9-methyl-4,8-octadecadiene-1,3-diol (5)



NaOMe (0.1 M in MeOH, 0.32 mL, 0.032 mmol, 2.0 equiv) was added to a solution of hexabenzoate **59** (21 mg, 0.016 mmol, 1.0 equiv) in THF (0.3 mL) at 0 °C and the colourless solution allowed to warm to room temperature over 2.5 h. The solution was cooled to 0 °C and AcOH (10 μL) was added. The filtrate was concentrated *in vacuo* and the residue was purified by column chromatography (SiO_2, CH_2Cl_2–MeOH, 8:1) to give the title compound (10 mg, 0.014 mmol, 90%) as a white solid. $[\alpha]_D^{26}$ = –6.7 (*c* 0.4, $CHCl_3$); lit.[7] $[\alpha]_D$ = –7.4 (*c* 0.3, $CHCl_3$). $[\alpha]_D^{25}$ = +7.0 (*c* 0.4, MeOH); lit.[16] $[\alpha]_D$ = +5.1 (*c* 0.3, MeOH). IR (film): ν_{max} = 3368 m, 2922 s, 2852 m, 1728 w, 1637 m, 1536 w, 1465 m cm^{-1}. ^{1}H NMR (500 MHz, d_5-pyridine): δ_H = 8.35 (1H, d, *J* = 8.6 Hz), 6.00 (1H, dd, *J* = 5.6, 15.8 Hz, C4H), 5.93 (1H, br d, *J* = 15.8 Hz, C5H), 5.25 (1H, br s, C8H), 4.90 (1H, d, *J* = 7.7 Hz, C1′′H), 4.80–4.78 (1H, m, C2H), 4.75 (1H, m, C3H), 4.70 (1H, dd, *J* = 6.0, 10.7 Hz, C1H_AH$_B$), 4.56 (1H, br s, C2′H), 4.50 (1H, d, *J* = 11.1 Hz, C6′′H_AH$_B$), 4.34 (1H, dd, *J* = 4.7, 11.5 Hz, C6′′H$_A$$H_B$), 4.23–4.20 (3H, m, C1H$_A$$H_B$, C3′′H, C4′′H), 4.02 (1H, br s, C2′′H), 3.89 (1H, br s, C5′′H), 2.23–2.11 (4H, m, C6H$_2$, C7H$_2$), 2.00 (2H, t, *J* = 7.3 Hz, C10H$_2$), 1.79 (1H, m, C3′H_AH$_B$), 1.78 (1H, m, C3′H$_A$$H_B$), 1.60 (3H, s, C9Me), 1.35 (4H, m, C11H$_2$, C4′H$_2$), 1.32–1.17 (34H, m, C12H$_2$–C17H$_2$, C5′H$_2$–C15′H$_2$), 0.85 (6H, t, *J* = 6.8 Hz, C18H$_3$, C16′H$_3$). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C = 175.7 (C1′=O), 135.7 (C9), 132.4 (C5H), 131.9 (C4H), 124.1 (C8H), 105.6 (C1′′H), 78.5 (C5′′H), 78.4 (C3′′H), 75.1 (C2′′H), 72.5 (C3H), 72.3 (C2′H), 71.5 (C4′′H), 70.1 (C1H$_2$), 62.7 (C6′′H$_2$), 54.6 (C2H), 40.0 (C10H$_2$), 35.6 (C3′H$_2$), 33.0 (C6H$_2$), 32.1 (C16H$_2$, C14′H$_2$), 30.0, 29.9, 29.63, 29.60 (C12H$_2$–C15H$_2$, C5′H$_2$–C13′H$_2$), 28.3 (C11H$_2$), 28.2 (C7H$_2$), 25.9 (C4′H$_2$), 22.9 (C17H$_2$, C15′H$_2$), 16.1 (C9*Me*), 14.2 (C18H$_3$, C16′H$_3$). LRMS (ES$^+$ mode): *m/z* (%) = 750.6 [(M+Na)$^+$, 100], 728 [(M+1)$^+$, 26], 710.7 [(M–OH)$^+$, 43]. HRMS (ES$^-$ mode): Found, 726.5516, (M–H)$^-$. $C_{41}H_{76}NO_9$ requires M, 726.5526.

Table 1. Comparison of ^{1}H and ^{13}C NMR Spectroscopic Data for Synthetic and Natural Phalluside-1

	Synthetic Phalluside-1[a]				Phalluside-1 from *Allostichaster inaequalis*[a,b]			
Assignment	**δ_H**	**Multiplicity**	***J*(Hz)**	**δ_C**	**δ_H**	**Multiplicity**	***J*(Hz)**	**δ_C**
1	3.71	dd	10.3, 3.4	69.7	3.70	dd	10.3, 3.6	69.7
	4.12	dd	10.3, 5.1	—	4.10	dd	10.3, 5.4	
2	4.01–3.98	m	—	54.6	3.99	m	—	54.6
3	4.15	t	7.3	72.8	4.13	br t	7.5	72.8
4	5.50	dd	15.4, 7.3	131.4	5.48	dd	15.2, 7.0	131.3
5	5.74	dt	15.4, 6.4	134.3	5.74	dt	15.2, 6.3	134.4
6	2.13–2.06	m	—	33.5	2.20	m	—	33.9
7	2.24–2.19	m	—	28.8	2.07	m	—	35.5
8	5.36	t	6.8	130.3	5.35	t	6.8	128.5
9	—	—	—	135.2	—	—	—	135.0
10	6.03	d	15.4	136.1	6.02	d	15.4	136.1
11	5.57	dt	15.8, 7.3	128.6	5.56	dt	15.4, 7.1	130.3
12	2.13–2.06	m	—	34.0	—			—
13–17	1.43–1.29	m	—	33.5–30.3, 26.2, 23.7	1.30–1.24	br s	—	33.0–30.3
18	0.90	t	6.8	14.4	0.89	t	6.6	14.4
C9*Me*	1.71	s	—	12.8	1.70	s		12.8
1′	—	—	—	177.2	—	—	—	177.0
2′	4.01–3.98	m	—	73.1	3.98	m	—	73.1
3′	1.61–1.52	—	—	35.9	—	—	—	—
4′–15′	1.43–1.29	m	—	33.5–30.3	1.30–1.24	br s	—	33.0–30.3
16′	0.90	t	6.8	14.4	—	—	—	14.4
1″	4.27	d	7.7	104.7	4.26	d	7.7	104.7
2″	3.19	dd	8.6, 8.1	75.0	3.19	dd	9.1, 7.7	74.9
3″	3.39–3.34	m	—	77.9	3.38	m	—	77.9
4″	solvent	—	—	71.6	solvent	—	—	71.3
5″	3.28–3.27	m	—	78.0	3.26	m	—	77.9
6″	3.67	dd	12.0, 5.1	62.7	3.66	dd	11.9, 5.0	62.5
	3.87	br d	11.5		3.825	br d	12.0	

[a] Recorded in CD_3OD at 500 MHz (^{1}H) and 125 MHz (^{13}C).
[b] M. E. D. de Vivar, A. M. Seldes and M. S. Maier, *Lipids*, 2002, **37**, 597.

Table 2. Comparison of ^{1}H NMR Spectroscopic Data for Synthetic and Natural Sch II

	Our Synthetic Sch II[a]			Literature Synthetic Sch II[b]			Sch II from *Tuber indicum*[c]		
Assignment	**δ_H**	**Multiplicity**	***J*(Hz)**	**δ_H**	**Multiplicity**	***J*(Hz)**	**δ_H**	**Multiplicity**	***J*(Hz)**
1	4.70	dd	6.0, 10.7	4.69	dd	5.4, 10.7	4.69	dd	6.0. 10.7
	4.20–4.23	m	—	4.18	m	—	4.20	m	—
2	4.78–4.80	m	—	4.78	m	—	4.75	m	—
3	4.75	m	—	4.73	m	—	4.72	m	—
4	6.00	dd	15.8, 5.6	5.99	dd	15.4, 5.1	5.94	dd	15.3, 6.8
5	5.93	br d	15.8	5.90	br d	15.4	5.97	dt	15.3, 6.8
6	2.11–2.23	m	—	2.12	m	—	2.14	m	—
7	2.11–2.23	m	—	2.12	m	—	2.14	m	—
8	5.25	br s	—	5.22	m	—	5.25	m	—
10	2.00	t	7.3	1.99	t	7.3	2.00	br t	7.5
11	1.35	m	—	1.35	m	—	1.35	m	—
12 to17	1.17–1.32	m	—	1.23	s-like	—	1.20–1.35	m	—
18	0.85	t	6.8	0.84	t	6.6	0.86	t	6.9
C9*Me*	1.60	s	—	1.59	s	—	1.61	s	—
NH	8.35	d	8.6	8.34	d	8.5	8.36	d	8.7
2′	4.56	br s	—	4.55	dd	3.8, 7.9	4.57	m	—
3′	1.78, 1.79	m, m	—	1.73	br	—	1.74, 2.14	m, m	—
4′–15′	1.17–1.32	m	—	1.23	s-like	—	1.20–1.35	m	—
16′	0.86	t	6.9	0.86	t	6.9	0.86	t	6.9
1″	4.90	d	7.7	4.88	d	7.6	4.90	d	7.6
2″	4.02	br s	—	4.00	dd	7.6, 9.0	4.03	m	—
3″	4.20–4.23	m	—	4.18	m	—	4.20	m	—
4″	4.20–4.23	m	—	4.18	m	—	4.19	m	—
5″	3.89	br s	—	3.87	br d	11.8	3.89	m	—
6″	4.50	d	11.1	4.48	dd	2.3, 11.5	4.48	br d	11.8
	4.34	dd	4.7, 11.5	4.31	dd	5.2, 11.8	4.33	dd	5.0, 11.8

[a] Recorded in pyridine-d_5 at 500 MHz.
[b] Recorded in pyridine-d_5 at 270 MHz: T. Murakami, R. Hirono and K. Furusawa, *Tetrahedron*, 2005, **61**, 9233.
[c] Recorded in pyridine-d_5 at 400 MHz: J. M. Gao, W. M. Zhu, S. Q. Zhang, X. Zhang, A. L. Zhang, H. Chen, Y. Y. Sun and M. Tang, *Eur. J. Lipid Sci. Technol.*, 2004, **106**, 815.

Table 3. Comparison of ^{13}C NMR Spectroscopic Data for Synthetic and Natural Sch II

Assignment	δ_C for Our Synthetic Sch II[a]	δ_C for Literature Synthetic Sch II[b]	δ_C for Sch II from *Tuber indicum*[c]
1	70.1	70.0	70.1
2	54.6	54.5	54.7
3	72.5	72.4	72.5
4	131.9	131.8	131.8
5	132.4	132.3	132.3
6	33.0	33.0	33.0
7	28.2	28.1	32.1
8	124.1	124.1	124.2
9	135.7	135.8	135.5
10	40.0	39.9	39.9
11	28.3	28.3	28.4
12 to 15	30.0–29.6	30.0–29.6	30.0–29.6
16	32.1	32.1	32.1
17	22.9	22.9	22.9
18	14.2	14.2	14.2
C9Me	16.1	16.0	16.1
1′	175.7	175.7	175.6
2′	72.3	72.2	72.4
3′	35.6	35.6	35.7
4′	25.9	25.8	—
4′/5′–13′	30.0–29.6	30.0–29.6	30.0–29.6
14′	32.1	32.1	28.2
15′	22.9	22.9	22.9
16′	14.2	14.2	14.2
1″	105.6	105.5	105.5
2″	75.1	75.0	75.1
3″	78.4	78.3	78.4
4″	71.5	71.4	71.6
5″	78.5	78.4	78.4
6″	62.7	62.5	62.7

[a] Recorded in pyridine-d_5 at 125 MHz.
[b] Recorded in pyridine-d_5 at 67.8 MHz: T. Murakami, R. Hirono and K. Furusawa, *Tetrahedron*, 2005, **61**, 9233.
[c] Recorded in pyridine-d_5 at 100 MHz: J. M. Gao, W. M. Zhu, S. Q. Zhang, X. Zhang, A. L. Zhang, H. Chen, Y. Y. Sun and M. Tang, *Eur. J. Lipid Sci. Technol.*, 2004, **106**, 815.

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