Synthesis of mycobacterial phenolic glycolipids

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Chapter 7

Aglycone analogues of Phenolic Glycolipids

Introduction

When a pathogen enters the host, exogenous glycolipids can be recognized by pattern recognition receptors (PRRs) of the innate immune system which can respond to a multitude of pathogen-associated molecular patterns (PAMPs).[1] The PRRs most associated with glycolipids include, but are not limited to, C-type lectin receptors (CLRs) and Toll-like receptors (TLRs). Recognition of PAMPs leads to the production of cytokines which recruit more immune cells to mount an effective inflammatory response. At a later stage antigens can be presented to the adaptive immune system through major histocompatibility complex (MHC) proteins on the surface of antigen presenting cells (APCs) such as dendritic cells, macrophages and B cells. This presentation may induce an immunological memory which is highly specific towards a single pathogen. The cluster of differentiation 1 (CD1) family of transmembrane glycoproteins, related to the class I MHC molecules, is expressed on the surface of various APCs and is capable of presenting lipids, and thereby also glycolipids, to the adaptive immune system. CD1b is thought to have the biggest hydrophobic grooves of the CD1 family and is therefore the most relevant for the presentation of long mycobacterial lipids (C_{25}-C_{80}).[2–4] It is thought that glycolipids expressed on the surface of pathogenic mycobacteria, such as *Mycobacterium tuberculosis*

and *M. leprae,* play a large role in their ability to dampen or evade the host immune response.[5–8] These pathogens are known to be able to remain dormant, hiding in cells of the host immune system for years before developing active disease.[9–12] Therefore much research has been performed to elucidate the exact structures of the relevant molecules and their interaction with (receptors of) the host immune system to unravel their exact mode of action, with the ultimate goal of finding a therapeutic target or vaccine candidate.[13]

To fully understand the structural determinants for binding to immune receptors, not only natural products but also analogues of natural products have been synthesized. The human immune system is able to differentiate between many endogenous and countless exogenous carbohydrates and with structural analogues it has been established that even small changes to the glycan may lead to a complete loss of recognition of glycolipids. Replacing the glucose of glucose monomycolate (GMM) with a mannose, galactose, arabinose or trehalose for instance, results in a complete loss of recognition by CD1b restricted T-cells, as does changing the position of the lipid tail on the carbohydrate.[3,14,15] The role of structural elements of the aglycone of glycolipids, such as chain length, *C*-methyl branches and distal cyclopropanes, methoxides and ketones, has been less established, however. Investigations using synthetic GMM, mycolic acids and sulfoglycolipids indicate that chain length is an important structural determinant for antigen presentation by CD1b.[15–19] The degree of *C*-methyl branching and the orientation thereof have been shown to have an influence on the activation of T-cells by sulfoglycolipids,[18,20] while the effect of distal decorations on mycolic acids depends on the T-cell line.[16] While it is not confirmed yet if phenolic glycolipids (PGLs) are presented by CD1b, PGLs are known to bind to TLR2[21–24] and TLR4,[25] both of which are known to have major hydrophobic pockets[26,27] and some PGLs are able to bind to human macrophage-inducible C-type lectin (Mincle).[28,29,30] PGLs contain a distal methyl and methoxide and multiple *C*-methyl branches in their lipid aglycone, but their role in shaping immune responses is not known. To further explore the role of the PGL aglycone in immune receptor interactions this Chapter describes the synthesis of multiple aglycone structural variants, with different degrees of aglycone complexity, of PGLs originating from *M. tuberculosis* and *M. leprae*.

The first aglycone analogues described in this chapter, are based on PGL-tb1 of *M. tuberculosis* and PGL-I of *M. leprae*, as depicted in Figure 1. Three different lipid analogues will be synthesized, changing the complexity on the phthiocerol and/or mycocerosic acids. With respect to the natural PGLs (**A**) analogues lacking either the distal *C*-methyl and methoxide of phthiocerol (**B**), the *C*-methyl branches of the mycocerosic acids (**C**) or both (**D**) will be generated. In addition, even simpler analogues bearing a C_{18} (**E**) or phenolic (**F**) aglycone will also be synthesized.

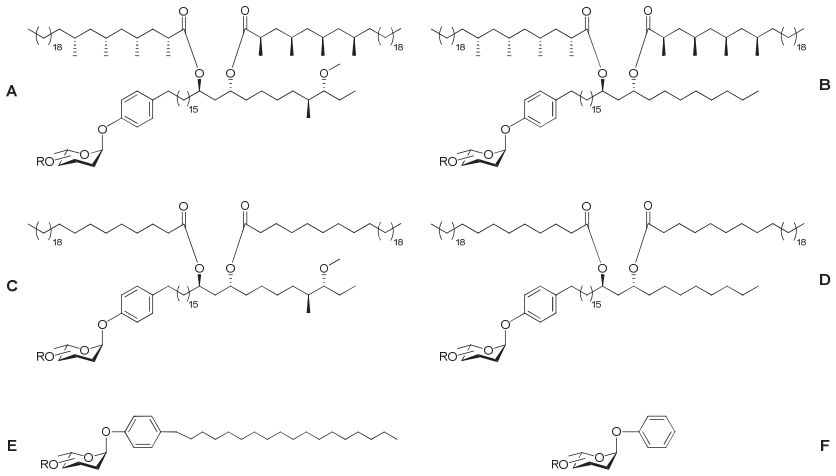


Figure 1. First group of proposed phenolic glycolipids with varying degrees of aglycone complexity.

Analogues **B**-**D** can be synthesized using the same strategy that was applied in the previous Chapters (4-6) of this thesis[31] and the building blocks for analogues **B**-**D** are depicted in Figure 2, alongside a retrosynthetic analysis to access these. Glycans protected with hydrogenation labile groups bearing an iodophenol on the reducing end can be coupled to either phthiocerol alkyne **1** or alkyne **3** using a Sonogashira cross coupling. The resulting diol can then be esterified with either mycocerosic acid (**2**) or commercially available octacosanoic acid (**4**). Thereafter hydrogenation leads to the global deprotection and concurrently reduces the conjugated internal alkyne which was formed in the Sonogashira reaction. The syntheses of phthiocerol alkyne **1** and iodoaryl bearing PGL-tb1 and PGL-I glycans are outlined in chapters 3, 4 and 5, respectively. Alkyne diol **3** is to be synthesized from iodide **5** (Chapter 3) and Weinreb amide **6** can be derived from ethyl 3-oxoundecanoate (**7**). Analogue **E** can be synthesized from the same glycans as **B**-**D** by

coupling the iodoaryl glycans with octadec-1-yne followed by hydrogenation and analogue **F** can be accessed by hydrogenation of the iodoaryl group.

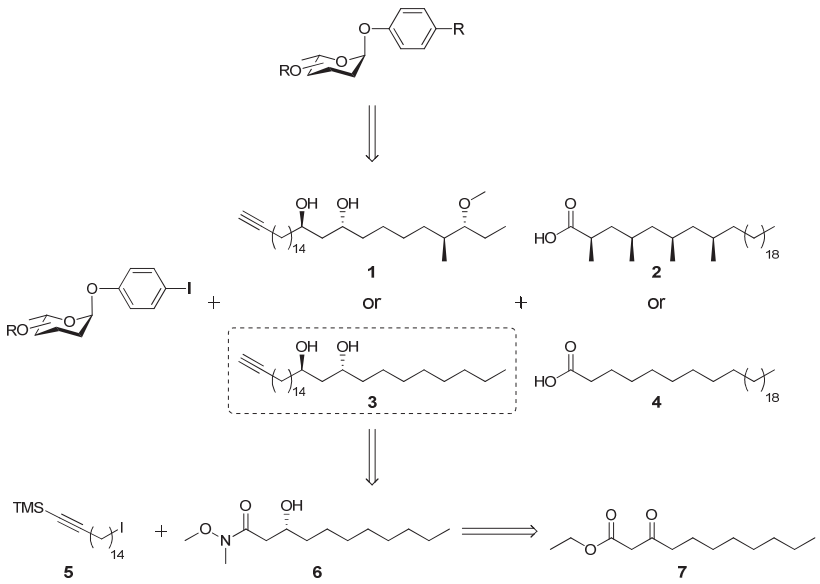


Figure 2. Retrosynthetic analysis of the analogues **B-D** outlined in Figure 1.

The second group of aglycone analogues targeted in this chapter, are based on PGL-III of *M. leprae*, a known Mincle ligand, which lacks the C-3 methyl of the terminal glucose of PGL-I (Figure 3).[32,33] This PGL-III glycan fits the criteria for binding to Mincle as it features a terminal C3,C4-*trans*-diequatorial diol,[34] which may enable bind to the Ca^{2+} ion coordinated by the receptor[30] and the C-6 methyl ether and relatively hydrophobic sugar attached to the C-1 position may bind to the shallow hydrophobic patches.[30,35,36] In order to confirm these hypothetical interactions and gain further understanding of the interaction between Mincle and PGL-III it would be worthwhile to obtain a crystal structure of Mincle bound to a ligand. PGL-III itself is not well suited for this purpose as crystallization studies often require a large excess of ligand and PGL-III is poorly soluble in water. An analogue with a more water soluble aglycone could possibly circumvent this problem, but binding to Mincle requires at least some hydrophobic interactions. Therefore, several PGL-III aglycones, of varying hydrophobicity, will be generated. All structures can be synthesized from iodoaryl glycan **8**, either by conjugation of

commercially available alkynes or phthiocerol alkyne **1** via a Sonogashira coupling followed by hydrogenation.

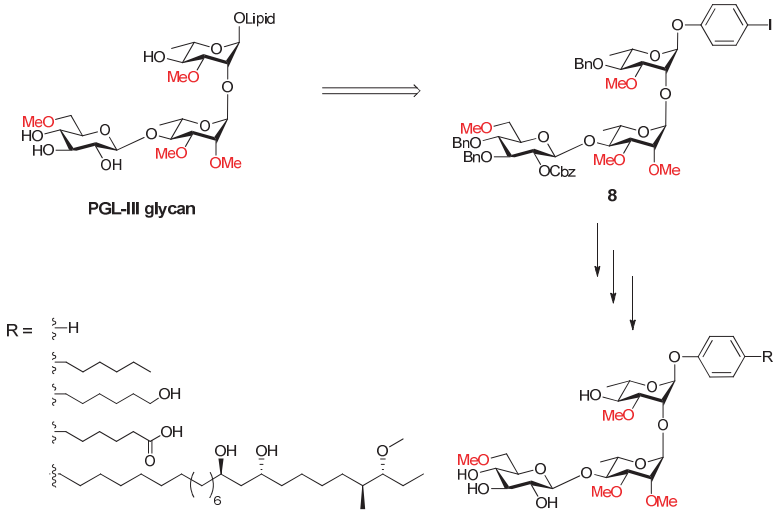
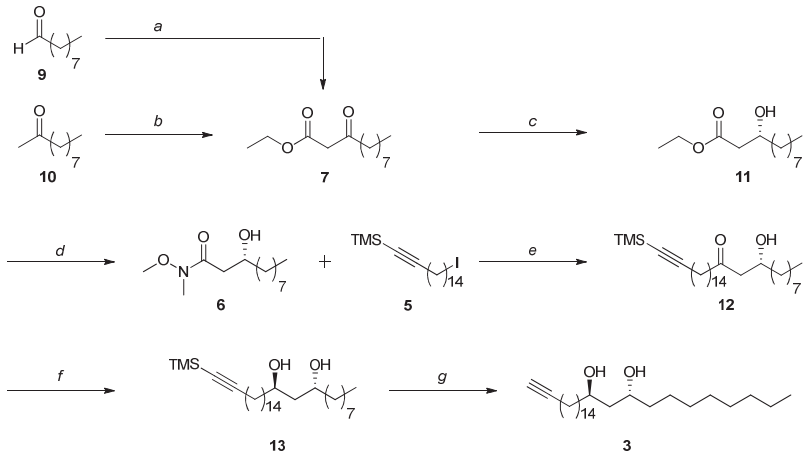


Figure 3. Analogues of PGL-III, carrying a more hydrophilic aglycone.

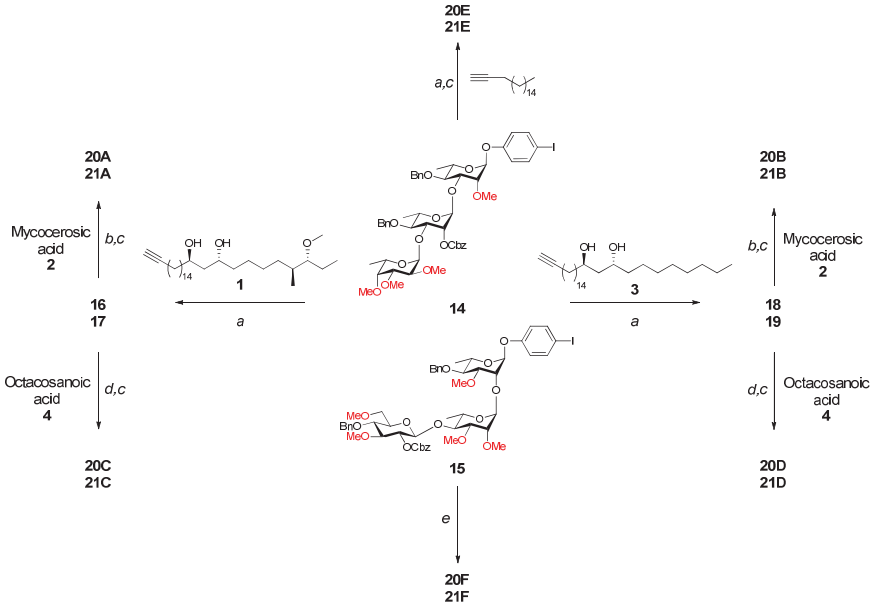
Results and discussion

The synthesis of alkyne diol **3** is depicted in Scheme 1. Ethyl 3-oxoundecanoate (**7**) was synthesized by elongating nonanal (**9**) with ethyl diazoacetate under the agency of $NbCl_5$,[37] a reaction that was also performed for the synthesis of phthiocerol, shown in Chapter 3. Alternatively, it could synthesized via a Claisen condensation of diethyl carbonate with 2-decanone by treatment with NaH in refluxing Et_2O,[38] a method that uses cheaper reagents and that can be more easily scaled up. The resulting keto-ester was then stereoselectively hydrogenated with a chiral Ruthenium catalyst developed by Noyori and co-workers[39,40] to give ß-hydroxyester **11** in 74% yield. The ethyl ester was then transformed into Weinreb amide **6** with *N,O*-dimethylhydroxylamine hydrochloride and $AlMe_3$ in DCM in 84% yield. Coupling of this amide to iodide **5** (chapter 3) under the agency of *t*-BuLi gave ß-hydroxyketone **12** in moderate yield. Finally, selective reduction of **12** to the 1,3-*anti* diol[41] followed by deprotection of the terminal alkyne gave diol **3** in 68% yield over 2 steps.



Scheme 1. Synthesis of diol **3**. Reagents and conditions: (a) Ethyl diazoacetate, $NbCl_5$, DCM, 58%, (b) diethyl carbonate, NaH, Et_2O, reflux, 66%, (c) (*R*)-[(RuCl(tol-BINAP))$_2$(μ-Cl)$_3$][NH_2Me_2], 20 bar H_2, EtOH, 74%, (d) N,O-dimethylhydroxylamine hydrochloride, $AlMe_3$, DCM, 84%, (e) *t*-BuLi, Et_2O, -70 °C, 52%, (f) $NMe_4BH(OAc)_3$, AcOH/MeCN/THF, 0 °C, 96%, (g) K_2CO_3, MeOH, 71%.

The synthesis of analogues **20A-F** and **21A-F** is depicted in Scheme 2 and the yields for the transformations have been summarized in Table 1. Trisaccharides **14** and **15** were coupled to phthiocerol to give diols **16** (Chapter 4) and **17** (Chapter 5) in 90% and 83% yield, respectively. From there on, PGL-tb1 (**20A**) has been synthesized in 77%, and PGL-I (**21A**) in 62% yield over 2 steps, being esterification and hydrogenation. Coupling of **14** and **15** to alkyne **3** gave diols **18** and **19** in 96% and 75% yield, respectively.



Scheme 2. Synthesis of aglycone analogues **20A**-**21F**. Reagents and conditions: (a) $Pd(PPh_3)_2Cl_2$, PPh_3, CuI, Et_3N, 40 °C, (b) DIC, DMAP, DCM, 0 °C → RT → 40 °C, (c) Pd/C, H_2, THF/EtOH, (d) DIC, DMAP, DCM, 40 °C, (e) 1. Pd/C, H_2, NH_4OAc, EtOH, 2. Pd/C, H_2, EtOH.

Esterification of these diols with mycocerosic acid followed by hydrogenation produced **20B** and **21B** in 63% and 61% yield over 2 steps, respectively. Diols **16**, **17**, **18** and **19** were also esterified with octacosanoic acid which, in contrast to mycocerosic acid, is not soluble in DCM at room temperature. Fortunately, octacosanoic acid is less prone to form unwanted byproducts than mycocerosic acid and the desired diesters were formed in good yields when the reaction was performed at 40 °C. Finally, hydrogenation gave **20C**, **21C**, **20D**, and **21D** in 63%, 67%, 59% and 54% yield over 2 steps, respectively. The C_{18}

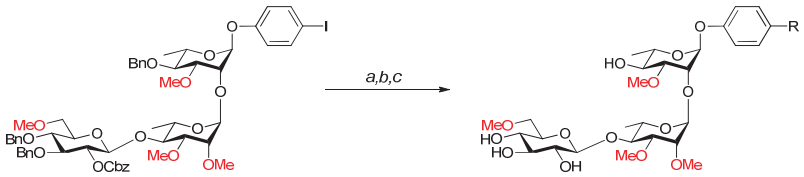
analogues **20E** and **21E** were synthesized from **14** and **15** in 59% and 56% yield over 2 steps, respectively. Attempts to form phenolic aglycone analogues **20F** and **21F** with standard hydrogenation conditions did not proceed well. Therefore, **20F** and **21F** were generated by means of a "double hydrogenation" procedure. At first, the starting material was dissolved in EtOH together with NH_4OAc and hydrogenated to selectively remove the Cbz moiety and reduce the aryl iodide.[42] After a quick work up to remove the catalyst and salts, the remaining benzyls were removed using standard hydrogenation conditions to give **20F** and **21F** in 92% and 94% yield over 2 steps, respectively.

Table 1. Yields of the assembly of aglycone analogues of PGL-tb1 and PGL-I.

Starting material	Sonogashira	Esterification	Hydrogenation	Overall yield	Product
14	90%	94%	82%	69%	**20A**
15	83%	79%	79%	52%	**21a**
14	96%	73%	86%	60%	**20B**
15	75%	77%	79%	46%	**21B**
14	90%	88%	72%	57%	**20C**
15	83%	86%	78%	56%	**21C**
14	96%	100%	59%	57%	**20D**
15	75%	91%	59%	40%	**21D**
14	89%	n.a.	66%	59%	**20E**
15	86%	n.a.	65%	56%	**21E**
14	n.a.	n.a.	92%	92%	**20F**
15	n.a.	n.a.	94%	94%	**21F**

The synthesis and yields of the series of PGL-III analogues is depicted in Table 2. Interestingly, trisaccharide **8** could, in contrast to **14** and **15**, be directly reduced under standard hydrogenation conditions to provide phenolic trisaccharide **22** in 77% yield. Sonogashira coupling of trisaccharide **8** to hex-1-yne, 5-hexyn-1-ol and phthiocerol alkyne **1**, followed by hydrogenation gave products **23**, **24** and **26** in 69%, 73% and 60% yield over 2 steps, respectively. Hexanoic acid derivative **25** was synthesized by coupling **8** to methyl 5-hexynoate, followed by hydrogenation and saponification. This provided **25** in 84% yield over 3 steps.

Table 2. Yields of the assembly of aglycone analogues of PGL-III.



Reagents and conditions: (a) $Pd(PPh_3)_2Cl_2$, PPh_3, CuI, Et_3N, 40 °C, (b) Pd/C, H_2, THF/EtOH, (c) 1 M NaOH, EtOH (1:4).

Sonogashira	Hydrogenation	Saponification	Overall yield	Product	R
n.a.	77%	n.a.	77%	**22**	**H**
91%	76%	n.a.	69%	**23**	**hexyl**
81%	90%	n.a.	73%	**24**	**6-hydrohexyl**
84%	100%	100%	84%	**25**	**6-carboxyhexyl**
81%	74%	n.a.	60%	**26**	**phthiocerol**

Conclusion

In order to gain understanding of the role of structural details in the lipid part of phenolic glycolipids in the detection and/or presentation of the compounds by the host immune system, the synthesis of several aglycone analogues with varying degrees of structural simplification has been achieved. This accomplishment highlights the flexibility of the highly convergent strategy to access PGL molecules, based on a late stage Sonogashira coupling of iodoaryl glycans and alkyne lipids, combined with a protecting group strategy which allows for hydrogenation as a single global deprotection step. The compounds synthesized in this chapter are at present being investigated for their immunomodulatory capabilities and used in crystallisation trials.

EXPERIMENTAL:

General procedures

All reactions were carried out in oven-dried glassware (80 °C). Prior to reactions, traces of water and solvent were removed by co-evaporation with toluene where appropriate. Reactions sensitive to air or moisture were carried out under N_2 atmosphere (balloon). Commercially available reagents and solvents (Aldrich Chemistry, Honeywell, Merck, Fischer Scientific, Biosolve, Fluka, VWR Chemicals, Acros Organics, Fluorochem, Brunschwig, Carbosynth) were used as received unless stated otherwise.

Solvents for reactions were reagent grade and dried by storage over flame dried 4 Å molecular sieves when needed. Et_2O used for column chromatography was distilled before use and stored over iron filings. EtOAc used for column chromatography was distilled before use. NEt_3 used for Sonogashira couplings was distilled from KOH, degassed with N_2, and stored over KOH for a maximum of 24 hours. DMAP used for Steglich esterifications was recrystallized from toluene before use.

Reaction progress was monitored using aluminium-supported silica gel TLC plates (Merck, Kieselgel 60, F254); visualization was carried out by irradiation with UV light (254 nm), and spraying with 20% H_2SO_4 in EtOH (w/v) or $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (25 g/L) and $(NH_4)_4Ce(SO_4)_4{\cdot}2H_2O$ (10 g/L) in 10% H_2SO_4 or $KMnO_4$ (7.5 g/L) and K_2CO_3 (50 g/L) in H_2O, followed by charring. Additional analysis with TLC-MS was used when needed.

Column chromatography was carried out using silica gel (Fluka, 40-63 μm mesh). The column was prepared using the apolar component mentioned in the corresponding experimental. If the apolar component was pentane the product was brought up in toluene. If the apolar component was DCM the product was brought up in DCM, possibly with a few drops of methanol if needed. Colum chromatography was performed using a gradient ranging from 0% polar component up to the ratio mentioned in the corresponding experimental in 2 to 5 steps depending on the ease of separation.

NMR spectra were recorded at ambient temperature on a Bruker AV-400LIQ or AV-850 spectrometer. Samples were prepared in $CDCl_3$ unless stated otherwise. Chemical shifts (δ) in $CDCl_3$ are reported in ppm relative to Me_4Si (δ: 0.00 ppm) for ^{1}H-NMR and $CDCl_3$ (δ: 77.16 ppm) for ^{13}C-NMR. Chemical shifts in CD_3OD are reported in ppm relative to H_2O (δ: 4.87 ppm) for ^{1}H-NMR and CD_3OD (δ: 49.00 ppm) for ^{13}C-NMR. ^{13}C-APT spectra are ^{1}H decoupled and structural assignment was achieved using HH-COSY and HSQC 2D experiments. Coupling constants (J) are given in Hz. Coupling constants of anomeric carbon atoms ($J_{H1,C1}$) were determined using HMBC-GATED experiments. Optical rotations were measured on an Anton Paar Modular Circular Polarimeter MCP 100/150. High resolution mass spectra were recorded on a Synapt G2-Si or a Q Exactive HF Orbitrap equipped with an electron spray ion source positive mode. Infrared spectra were recorded on a Perkin Elmer Spectrum 2 FT-IR.

General procedure A: Sonogashira cross coupling

Iodoaryl glycoside (1.0 eq) was dissolved in freshly distilled NEt_3 (0.05 M) together with alkyne (1.2-5 eq). A mixture of $Pd(PPh_3)_2Cl_2$, PPh_3 and CuI (ratio 1:1:2) was dissolved in freshly distilled NEt_3 and was stirred for 15 minutes at 40 °C. Of this cocktail, enough was added to the sugar/alkyne mixture to amount to 0.05 eq $Pd(PPh_3)_2Cl_2$, 0.05 eq PPh_3 and 0.1 eq CuI. The reaction was allowed to stir at 40 °C until the complete consumption of the starting material as indicated by TLC. The solvent was then removed under a stream of N_2. The crude was then transferred to a silica column in toluene and the column was flushed with toluene. Thereafter the product was purified by means of column chromatography.

General procedure B: Esterification – mycocerosic acid

Starting material (1.0 eq) was dissolved in dry DCM (0.05 M) together with mycocerosic acid (3.0 eq) and DMAP (9 eq). The resulting mixture was cooled to 0 °C after which DIC (6 eq) was added. The reaction was allowed to stir for 16 hours while warming to rT, after which it was warmed to 40 °C and stirred until all intermediates moved to single high running spot on TLC. The reaction mixture was then cooled to rT, diluted with Et_2O and the organic layer was washed 1 M HCl, sat. aq. $NaHCO_3$ and brine, dried with $MgSO_4$ and concentrated *in vacuo*. Purification by means of column chromatography. Note: In order to detect the most prevalent byproducts, staining with $KMnO_4$ is required.

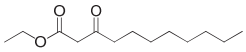
General procedure C: Esterification – octacosanoic acid

Starting material (1.0 eq) was dissolved in dry DCM (0.05 M) together with octacosanoic acid (3.0 eq) and DMAP (9 eq). DIC (6 eq) was added to the mixture and the solution was warmed to 40 °C. The reaction was allowed to stir for 24 hours or until all intermediates moved to single high running spot on TLC. The reaction mixture was then cooled to rT, diluted with Et_2O and the organic layer was washed 1 M HCl, sat. aq. $NaHCO_3$ and brine, dried with $MgSO_4$ and concentrated *in vacuo*. Purification by means of column chromatography. Note: In order to detect the most prevalent byproducts, staining with $KMnO_4$ is required.

General procedure D: Hydrogenation

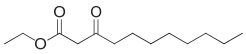
Starting material (1.0 eq) was dissolved in a mixture of THF and EtOH (1:1, 0.007 M) and the solution was purged with N_2. Pd/C (10%, 1.0 eq) was then added to the solution and the resulting mixture was purged with H_2. The reaction was left to stir under H_2 atmosphere until TLC complete conversion of the starting material and reaction intermediates to a single low running spot (DCM-MeOH 19:1). The reaction mixture was then purged with N_2, filtered over celite and concentrated *in vacuo*. Purification by means of column chromatography (DCM-MeOH 19:1).

Ethyl 3-oxoundecanoate (7)



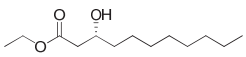
Nonanal (**9**) (1.52 mL, 8.49 mmol, 1.0 eq) was dissolved in DCM (85 mL, 0.1 M) and a catalytic amount [the amount was not weighed due to tendency for hydrolysis] of $NbCl_5$ was added to the solution and it was cooled to 0 °C. EDAA (87%, 1.53 mL, 12.7 mmol, 1.5 eq) was slowly added and the reaction was allowed to stir for 4 hours after which it was diluted with H_2O and extracted with DCM (3x). The combined organic layers were washed with brine, dried with $MgSO_4$ and concentrated *in vacuo*. Purification by means of column chromatography (*n*-pentane-Et_2O 9:1) gave the title compound (1.12 g, 4.9 mmol, 58%) as a clear oil. Spectroscopic data were in accordance with those previously reported in the literature.[43]

Ethyl 3-oxoundecanoate (7)



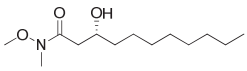
Diethyl carbonate (1.28 mL, 10.6 mmol, 4.0 eq) was dissolved in dry Et_2O (20 mL, 0.52 M) and NaH (60%, 0.211 g, 5.27 mmol, 2.0 eq) was added to the solution. The mixture was warmed to reflux and 2-decanone (0.5 mL, 2.64 mmol, 1.0 eq) was slowly added. The reaction was refluxed for 20 hours after which it was cooled to rt and quenched by addition of EtOH. The resulting sludge was filtered and concentrated *in vacuo* and purification by means of column chromatography (*n*-pentane-Et_2O 19:1) gave the title compound (0.397 g, 1.74 mmol, 66%) as a slightly yellow oil. Spectroscopic data were in accordance with those previously reported in the literature.[43]

Ethyl (3*R*)-3-hydroxyundecanoate (11)



Compound **7** (1.12 g, 4.9 mmol, 1.0 eq) was dissolved in EtOH (25 mL, 0.2 M) and (*R*)-[(RuCl(tol-BINAP))$_2$(μ-Cl)$_3$[NH_2Me_2] (87 mg, 49 μmol, 0.01 eq) was added to the solution. The mixture was purged with N_2 after which it was stirred under 22 bar of H_2 atmosphere for 24 hours. The mixture was then diluted with toluene, concentrated *in vacuo* and purification by means of column chromatography (*n*-pentane-Et_2O 7:3) gave **11** (0.84 g, 3.65 mmol, 74%) as a slightly green oil. $[\alpha]_D^{25}$ = -14.3° (c = 4.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 4.18 (q, 2H, *J* = 7.2 Hz, OC*H*$_2$); 4.02-3.97 (m, 1H, C*H*OH); 2.95 (d, 1H, *J* = 4.0 Hz, O*H*); 2.51 (dd, 1H, *J* = 2.8, 16.4 Hz, C*H*H); 2.40 (dd, 1H, *J* = 9.0, 16.4 Hz, CH*H*); 1.54-1.26 (m, 17H, C*H*$_2$, C*H*$_3$); 0.88 (t, 3H, *J* = 7.0 Hz, C*H*$_3$). ^{13}C-APT NMR (101 MHz) δ: 173.3 (*C*O); 68.2 (*C*H); 60.8, 41.4, 36.7, 32.0, 29.7, 29.4, 25.6, 22.8 (*C*H$_2$); 14.3, 14.3 (*C*H$_3$).

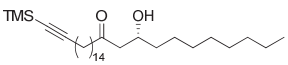
***N*-methoxy-*N*-methyl (3*R*)-hydroxyundecanamide (6)**



N,O-dimethylhydroxylamine hydrochloride (1.77 g, 18.2 mmol, 5.0 eq) was dissolved in dry DCM (25 mL) and the solution was cooled to 0 °C. A solution of $AlMe_3$ in toluene (2 M, 9.1 mL, 18.2 mmol, 5.0 eq) was added. This mixture was allowed to stir for 1 hour after which compound **11** (0.99 g, 3.61 mmol, 1.0 eq) was added and the reaction was allowed to stir for 3 hours while slowly warming to rt. The reaction was then quenched by addition of methanol and the resulting mixture was diluted with Et_2O. The organic layer was washed with 1 M HCl and the resulting aqueous layer was extracted with Et_2O. The organic layers were combined, washed with brine, dried with $MgSO_4$ and concentrated *in vacuo*. Purification by means of column chromatography (Et_2O) gave the title compound (751 mg, 3.06 mmol, 84%) as a clear oil. $[\alpha]_D^{25}$ = -36.3 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 4.06-3.98 (m, 1H, C*H*OH); 3.79 (d, 1H, *J* = 2.8 Hz, O*H*), 3.69 (s, 3H, OC*H*$_3$);

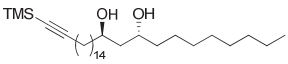
3.20 (s, 3H, NCH_3); 2.67 (d, 1H, J = 16.8 Hz, CHH); 2.44 (dd, 1H, J = 9.6, 16.8 Hz, CHH); 1.62–1.49 (m, 1H); 1.49– 1.23 (m, 14H, CH_2); 0.88 (t, 3H, J = 7.0 Hz, CH_3). ^{13}C-APT NMR (101 MHz) δ: 174.2 (CO); 68.0 (OCH$_3$); 61.4 (COH); 38.3, 36.7, 32.0 (CH$_2$); 32.0 (NCH$_3$); 29.8, 29.7, 29.4, 25.7, 22.8 (CH$_2$); 14.3 (CH$_3$). IR (thin film, cm^{-1}): 1076, 1388, 1465, 1648, 1653, 2855, 2926, 3443. HRMS calculated for $C_{13}H_{27}NO_3Na$ 268.18886 [M+Na]$^+$; found 268.18810.

(9*R*)-9-hydroxy-27-(trimethylsilyl)heptacos-26-yn-11-one (12)



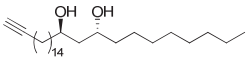
Compound **5** (0.595 g, 1.42 mmol, 2.2 eq) was dissolved in Et$_2$O (16 mL, 0.09 M) and the solution was cooled to -78 °C. A 1.7 M solution of *t*-BuLi in hexane (2.1 mL, 3.57 mmol, 5.4 eq) was added to the solution and the mixture was allowed to stir for 1 hour. After this time a solution of compound **6** (0.161 g, 0.66 mmol, 1.0 eq) in Et$_2$O (1.7 mL, 0.4 M) was slowly added and the reaction was allowed to stir for 1 hour. The reaction was then quenched by the addition of sat. aq. NH_4Cl and allowed to warm to rt. The layers were then separated and the organic layer was washed with H_2O and brine, dried with $MgSO_4$ and concentrated *in vacuo*. Purification by means of column chromatography (*n*-pentane-Et$_2$O 7:3) gave the title compound (162 mg, 0.34 mmol, 52%) as a white waxy solid. $[\alpha]_D^{25}$ = -21.3 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 4.05-4.01 (m, 1H, CHOH); 3.12 (bs, 1H, OH); 2.60 (dd, 1H, J = 2.8, 17.2 Hz, CHH); 2.50 (dd, 1H, J = 9.2, 17.6 Hz, CHH); 2.42 (t, 2H, J = 7.4 Hz, CH_2); 2.21 (t, 2H, J = 7.2 Hz, CH_2); 1.59-1.20 (m, 40H, CH_2); 0.89 (t, 3H, J = 7.0 Hz, CH_3) 0.15 (s, 9H, C$H_{3,TMS}$). ^{13}C-APT NMR (101 MHz) δ: 212.7 (CO); 107.9, 84.3 ($C_{q,alkyne}$); 67.7 (CHOH); 49.1, 43.8, 36.6, 32.0, 29.8, 29.7, 29.7, 29.6, 29.6, 29.5, 29.4, 29.3, 29.2, 28.9, 28.7, 25.6, 23.7, 22.8, 20.0 (CH$_2$); 14.2 (CH$_3$); 0.3 (CH$_{3,TMS}$). IR (thin film, cm^{-1}): 1006, 1066, 1079, 1249, 1468, 1701, 2850, 2918, 2958, 3410. HRMS calculated for $C_{30}H_{58}O_2SiNa$ 501.41038 [M+Na]$^+$; found 501.41007.

(9*R*,11*R*)-27-(trimethylsilyl)heptacos-26-yne-9,11-diol (13)



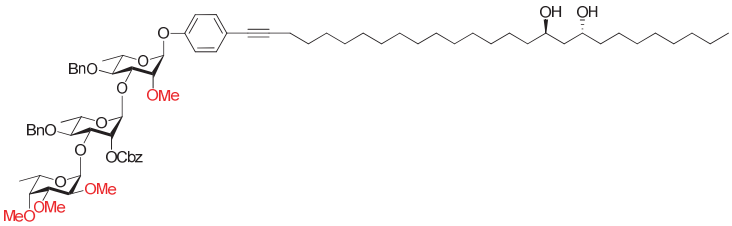
Compound **12** (92 mg, 0.192 mmol, 1.0 eq) was dissolved in a 12:12:1 mixture of MeCN AcOH and THF (50 mL, 0.004 M) and this solution was cooled to 0 °C. $Me_4NBH(OAc)_3$ (132 mg, 0.5 mmol, 6.0 eq) was added in 4 portions over 90 minutes and the reaction was allowed to stir for 1 more hour. The reaction was quenched by the addition of H_2O and the layers were separated. The aqueous layer was extracted with Et$_2$O (3×) and the combined organic layers were washed with sat. aq. $NaHCO_3$ (3×) and brine, dried with $MgSO_4$ and concentrated *in vacuo*. Purification of the product by means of column chromatography (*n*-pentane-Et$_2$O 1:1) gave the title compound (89 mg, 0.185 mmol, 96%) as a white waxy solid. $[\alpha]_D^{25}$ = -3.6 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 3.97-3.91 (m, 2H, CHOH); 2.21 (t, 2H, J = 7.2 Hz, CH_2); 1.76 (bs, 2H, OH); 1.62-1.26 (m, 44H, CH_2); 0.88 (t, 3H, J = 6.8 Hz, CH_3); 0.15 (s, 9H, C$H_{3,TMS}$). ^{13}C-APT NMR (101 MHz) δ: 108.0, 84.4 ($C_{q,alkyne}$); 69.7 (CHOH); 42.4, 37.7, 32.0, 29.8, 29.8, 29.7, 29.7, 29.4, 29.2, 29.0, 28.8, 25.9, 22.8, 20.0 (CH$_2$); 14.3 (CH$_3$); 0.3 (CH$_{3,TMS}$). IR (thin film, cm^{-1}): 1470, 2849, 2918, 3278. HRMS calculated for $C_{30}H_{60}O_2SiNa$ 503.42603 [M+Na]$^+$; found 503.42551.

(9*R*,11*R*)-heptacos-26-yne-9,11-diol (3)



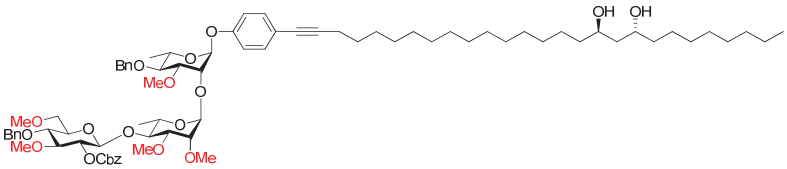
Compound **13** (105 mg, 0.218 mmol, 1.0 eq) was dissolved in MeOH (22 mL, 0.01 M) and K_2CO_3 (0.15 g, 1.09 mmol, 5.0 eq) was added solution and the reaction was allowed to stir overnight. The mixture was then diluted with Et_2O and H_2O, the layers were separated, and the aqueous layer was extracted with Et_2O (2×). The combined organic layers were washed with H_2O and brine, dried with $MgSO_4$ and concentrated *in vacuo*. Purification by means of column chromatography (*n*-pentane-Et_2O 1:1) gave the title compound (63 mg, 0.15 mmol, 71%) as a white waxy solid. $[\alpha]_D^{25}$ = -6.0 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 3.97-3.91 (m, 2H, C*H*OH); 2.18 (dt, 2H, *J* = 2.8, 7.2 Hz, CH_2); 2.12 (bs, 2H, O*H*); 1.94 (t, 1H, *J* = 2.6 Hz, CC*H*); 1.59 (t, 2H, *J* = 9.4 Hz, CH_2); 1.56-1.26 (m, 46H, CH_2); 0.88 (t, 3H, *J* = 6.8 Hz, CH_3). ^{13}C-APT NMR (101 MHz) δ: 85.0, 74.3 (C_{alkyne}); 69.7 (*C*OH); 68.2, 42.4, 37.6, 32.0, 29.9, 29.8, 29.8, 29.7, 29.7, 29.3, 28.9, 28.6, 25.9, 18.5 (*C*H_2); 14.3 (*C*H_3). IR (thin film, cm^{-1}): 1464, 1472, 2849, 2915, 3294, 3510. HRMS calculated for $C_{27}H_{52}O_2Na$ 431.38650 [M+Na]$^+$; found 431.38594.

4-((9*R*,11*R*)-heptacos-26-yne-9,11-diol)phenyl 2-*O*-methyl-3-*O*-(2-*O*-benzyloxycarbonyl-3-*O*-(2,3,4-tri-*O*-methyl-α-L-fucopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranoside (18)



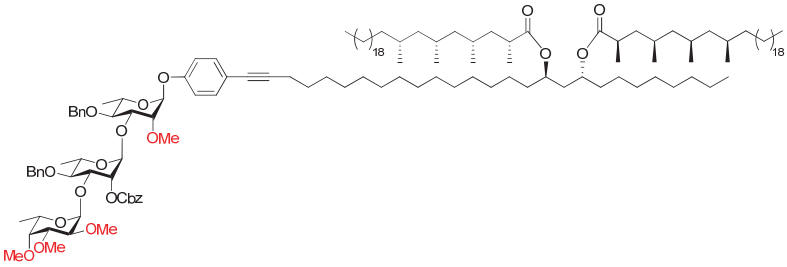
The title compound was synthesized according to general procedure A using glycan **14** (53 mg, 52 µmol, 1.0 eq) and alkyne **3** (25 mg, 62 µmol, 1.2 eq). Column chromatography (*n*-pentane-Et_2O 1:19) yielded the product (65 mg, 50 µmol, 96%) as a yellow oil. $[\alpha]_D^{25}$ = -83.2 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.42-7.26 (m, 17H, CH_{arom}); 6.94 (d, 2H, *J* = 8.8 Hz, CH_{arom}); 5.52 (d, 1H, *J* = 1.6 Hz, H-1); 5.22-5.10 (m, 6H, H-1', H-1'', H-2', PhCH_2, PhC*H*H); 4.93 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.60-4.53 (m, 2H, PhCH*H*, PhCH*H*); 4.22-4.18 (m, 2H, H-3, H-3'); 4.03-3.99 (m, 1H, H-5'); 3.93-3.90 (m, 2H, CH_{diol}); 3.81 (q, 1H, *J* = 6.4 Hz, H-5''); 3.74-3.66 (m, 2H, H-2, H-5); 3.57-3.48 (m, 13H, H-2'', H-3'', H-4, H-4', OCH_3); 3.33 (s, 3H, OCH_3); 3.31 (s, 3H, OCH_3); 3.27 (d, 1H, *J* = 1.6 Hz, H-4''); 2.37 (t, 2H, *J* = 7.2 Hz, C$H_{2,diol}$); 1.70-1.05 (m, 61H, H-6, H-6', C$H_{2,diol}$); 0.97 (d, 3H, *J* = 6.8 Hz, H-6''); 0.88 (t, 3H, *J* = 6.8 Hz, C$H_{3,diol}$). ^{13}C-APT NMR (101 MHz) δ: 155.6 ($C_{q,arom}$); 154.8 (CO_{Cbz}); 139.0, 138.1, 135.2 ($C_{q,arom}$); 133.0, 128.9, 128.9, 128.8, 128.6, 128.5, 128.5, 128.4, 127.8, 127.6, 127.5 (*C*H$_{arom}$); 118.0 ($C_{q,arom}$); 116.2 (*C*H$_{arom}$); 99.9 (C-1''); 99.5 (C-1'); 94.4 (C-1); 89.5 ($C_{q,alkyne}$); 80.3 (C-3); 80.1 ($C_{q,alkyne}$); 80.1 (C-2 and C-3''); 79.9, 79.7 (C-4 and C-4'); 79.3 (C-4''); 78.3 (C-3'); 77.7 (C-2''); 76.8 (C-2'); 75.7, 75.1, 70.1 (Ph*C*H$_2$); 69.6 (*C*OH$_{diol}$); 68.9 (C-5'); 68.7 (C-5); 67.1 (C-5''); 61.9, 59.1, 58.8, 58.2 (O*C*H$_3$); 42.4, 37.6, 32.0, 29.8, 29.7, 29.7, 29.7 29.4, 29.3, 29.1, 29.0, 25.9, 22.8, 19.5 (*C*H$_{2,diol}$); 18.2 (C-6); 18.0 (C-6'); 16.3 (C-6''); 14.3, (*C*H$_{3,diol}$). IR (thin film, cm^{-1}): 1003, 1040, 1142, 1235, 1261, 1457, 1485, 1507, 1747, 2360, 2850, 3387. HRMS calculated for $C_{77}H_{112}O_{17}Na$ 1331.77917 [M+]$^+$; found 1331.77936.

4-((9*R*,11*R*)-heptacos-26-yne-9,11-diol)phenyl 2-*O*-(2,3-di-*O*-methyl-4-*O*-(2-*O*-benzyloxycarbonyl-3,6-di-*O*-methyl-4-*O*-benzyl-ß-D-glucopyranosyl)-α-L-rhamnopyranosyl)-3-*O*-methyl-4-*O*-benzyl-α-L-rhamnopyranoside (19)



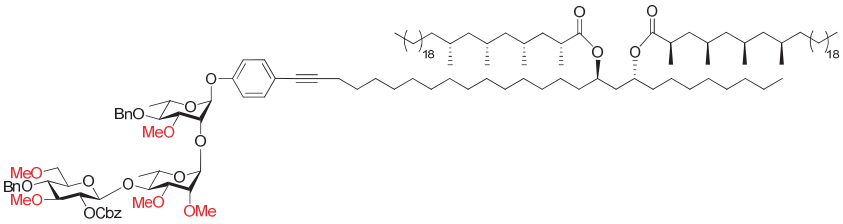
The title compound was synthesized according to general procedure A using glycan **15** (56 mg, 53 µmol, 1.0 eq) and alkyne **3** (26 mg, 63 µmol, 1.2 eq). Column chromatography (*n*-pentane-Et_2O 1:19) yielded the product (53 mg, 40 µmol, 75%) as a yellow oil. $[\alpha]_D^{25}$ = -61.9 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.40-7.26 (m, 17, C*H*$_{arom}$); 6.95 (dd, 2H, *J* = 2.0, 7.2 Hz, C*H*$_{arom}$); 5.47 (d, 1H, *J* = 2.0 Hz, H-1); 5.29-5.22 (m, 2H, PhC*H*$_2$); 5.18 (d, 1H, *J* = 1.2 Hz, H-1'); 4.89 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.79 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.74 (d, 1H, *J* = 8.0 Hz, H-1''); 4.67-4.62 (m, 3H, H-2'', PhCH*H*, PhCH*H*); 4.24 (dd, 1H, *J* = 1.8, 3.0 Hz, H-2); 3.96-3.90 (m, 2H, C*H*$_{diol}$); 3.79 (dd, 1H, *J* = 3.0, 9.4 Hz, H-3); 3.76-3.47 (m, 16H, H-2', H-4'', H-5, H-5', H-5'', H-6'', OC*H*$_3$); 3.45-3.39 (m, 2H, H-4, H-4'); 3.36-3.33 (m, 8H, H-3', H-3'', OC*H*$_3$); 2.38 (t, 2H, *J* = 7.0 Hz, C*H*$_{2,diol}$); 2.05 (bs, 2H, O*H*$_{diol}$); 1.61-1.05 (m, 64H, H-6, H-6', C*H*$_{2,diol}$); 0.88 (t, 3H, *J* = 6.8 Hz, C*H*$_{3,diol}$). ^{13}C-APT NMR (101 MHz) δ: 155.3 (C$_{q,arom}$); 154.8 (*C*O$_{Cbz}$); 138.5, 138.2, 135.6 (C$_{q,arom}$); 133.0, 128.8, 128.6, 128.6, 128.5, 128.4, 128.2, 128.1, 128.0, 127.9 (*C*H$_{arom}$); 118.0 (C$_{q,arom}$); 116.2 (*C*H$_{arom}$); 100.9 (C-1''); 98.5 (C-1'); 96.9 (C-1); 89.5 (C$_{q,alkyne}$); 84.9 (C-3''); 82.0 (C-3); 80.8 (C-4'); 80.1 (C-4); 80.1 (C$_{q,alkyne}$); 78.1 (C-2''); 77.7, 77.6 (C-4'' and C-5''); 77.0 (C-2'); 75.2, 75.0 (PhC*H*$_2$); 74.8 (C-3'); 73.0 (C-2); 71.0 (C-6''); 69.9 (PhC*H*$_2$); 69.6 (*C*H$_{diol}$); 68.7 (C-5); 67.9 (C-5'); 61.0, 59.8, 59.1, 58.3, 57.6 (O*C*H$_3$); 42.4, 37.6, 32.0, 29.8, 29.8, 29.7, 29.7, 29.5, 29.4, 29.3, 29.1, 29.0, 25.9, 25.5, 22.8, 19.5 (*C*H$_{2,diol}$); 18.2, 18.0 (C-6 and C-6'); 14.3 (*C*H$_{3,diol}$). IR (thin film, cm^{-1}): 1055, 1075, 1120, 1238, 1259, 1457, 1507, 1560, 1751, 2852, 2922, 3380. HRMS calculated for $C_{78}H_{114}O_{18}Na$ 1361.78974 [M+Na]$^+$; found 1361.79001.

4-((9*R*,11*R*)-heptacos-26-yne-9,11-diyl bismycocerosate)phenyl 2-*O*-methyl-3-*O*-(2-*O*-benzyloxycarbonyl-3-*O*-(2,3,4-tri-*O*-methyl-α-L-fucopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranoside (27)



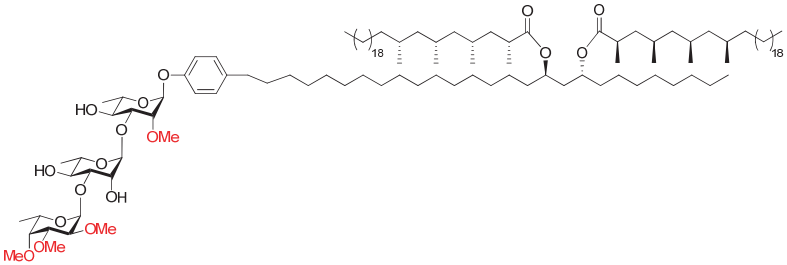
The title compound was synthesized according to general procedure D using diol **18** (24 mg, 18 µmol, 1.0 eq), mycocerosic acid (**2**) (26 mg, 55 µmol, 3.0 eq), DIC (17 µL, 110 µmol, 6.0 eq) and DMAP (20 mg, 165 µmol, 9.0 eq). Column chromatography (*n*-pentane-Et_2O 1:1) yielded the product (30 mg, 13 µmol, 73%) as a waxy solid. $[\alpha]_D^{25}$ = -68.5 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.41-7.26 (m, 17H, C*H*$_{arom}$); 6.93 (dd, 2H, *J* = 2.0, 6.8 Hz, C*H*$_{arom}$); 5.51 (d, 1H, *J* = 1.6 Hz, H-1); 5.22-5.10 (m, 6H, H-1', H-1'', H-2', PhC*H*$_2$, PhC*H*H); 4.93 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.84 (quint, 2H, *J* = 6.4 Hz, C*H*$_{diol}$); 4.60-4.53 (m, 2H, PhCH*H*, PhCH*H*); 4.22-4.18 (m, 2H, H-3, H-3'); 4.04-3.97 (m, 1H, H-5'); 3.81 (q, 1H, *J* = 6.4 Hz, H-5''); 3.74-3.68 (m, 2H, H-2, H-5); 3.57-3.48 (m, 13H, H-2'', H-3'', H-4, H-4', OC*H*$_3$); 3.31 (s, 3H, OC*H*$_3$); 3.27 (d, 1H, *J* = 1.6 Hz, H-4''); 2.57-2.47 (m, 2H, C*H*$_{Myc}$); 2.37 (t, 2H, *J* = 7.0 Hz, C*H*$_{2,diol}$); 1.77-1.70 (m, 4H, C*H*$_{2,Myc}$); 1.59-1.05 (m, 161H, H-6, H-6', C*H*$_{2,diol}$, C*H*$_{2,Myc}$); 1.02-0.93 (m, 5H, H-6'', C*H*$_{2,Myc}$); 0.91-0.83 (m, 36H, C*H*$_{3,diol}$, C*H*$_{3,Myc}$). ^{13}C-APT NMR (101 MHz) δ: 176.1 (*C*O$_{Myc}$); 155.7 (C$_{q,arom}$); 154.8 (*C*O$_{Cbz}$); 139.0, 138.2, 135.2 (C$_{q,arom}$); 133.0, 128.9, 128.9, 128.8, 128.5, 128.5, 128.4, 127.9, 127.6, 127.5 (*C*H$_{arom}$); 118.0 (C$_{q,arom}$); 116.2 (*C*H$_{arom}$); 100.0 (C-1''); 99.5 (C-1'); 94.4 (C-1); 89.5 (C$_{q,alkyne}$); 80.4 (C-3); 80.1 (C$_{q,alkyne}$); 80.1 (C-2 and C-3''); 79.9, 79.7 (C-4 and C-4'); 79.3 (C-4''); 78.3 (C-3'); 77.8 (C-2''); 76.8 (C-2'); 75.7, 75.1, 70.4 (Ph*C*H$_2$); 68.9 (C-5'); 68.7 (C-5); 67.1 (C-5''); 61.9, 59.1, 58.8, 58.2 (O*C*H$_3$); 45.7, 45.4 (*C*H$_{2,Myc}$); 41.1 (*C*H$_{2,diol}$); 37.9 (*C*H$_{Myc}$); 36.7 (*C*H$_{2,Myc}$); 34.8 (*C*H$_{2,diol}$); 32.1 (*C*H$_{2,Myc}$); 32.0, 30.2 (*C*H$_{2,diol}$) 30.1 (*C*H$_{Myc}$); 29.9, 29.9, 29.8, 29.8, 29.7, 29.5, 29.4, 29.2, 29.0, (*C*H$_2$); 28.2 (*C*H$_{Myc}$); 27.3 (*C*H$_{Myc}$); 27.1 (*C*H$_{2,Myc}$); 25.3 (*C*H$_{2,diol}$); 22.8, 22.8 (*C*H$_{2,Myc}$); 20.9, 20.6, 20.5 (*C*H$_{3,Myc}$); 19.6 (*C*H$_{2,diol}$); 18.6 (*C*H$_{3,Myc}$); 18.2 (C-6); 18.1 (C-6'); 16.4 (C-6''); 14.3 (*C*H$_{3,Myc}$). IR (thin film, cm^{-1}): 1030, 1102, 1120, 1179, 1261, 1379, 1438, 1457, 1454, 1507, 1734, 2853, 2923. HRMS calculated for $C_{141}H_{237}O_{19}$ 2235.76077 $[M+H]^+$; found 2235.76608.

4-((9*R*,11*R*)-heptacos-26-yne-9,11-diyl bismycocerosate)phenyl 2-*O*-(2,3-di-*O*-methyl-4-*O*-(2-*O*-benzyloxycarbonyl-3,6-di-*O*-methyl-4-*O*-benzyl-ß-D-glucopyranosyl)-α-L-rhamnopyranosyl)-3-*O*-methyl-4-*O*-benzyl-α-L-rhamnopyranoside (28)



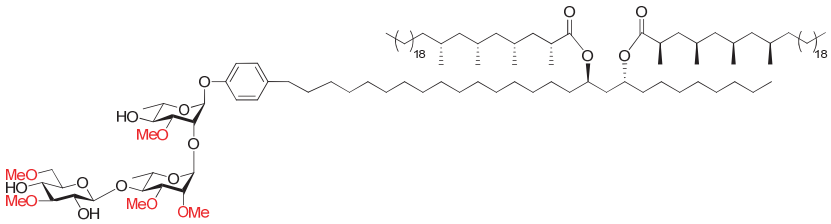
The title compound was synthesized according to general procedure D using diol **19** (23 mg, 17 µmol, 1.0 eq), mycocerosic acid (**2**) (25 mg, 52 µmol, 3.0 eq), DIC (16 µL, 103 µmol, 6.0 eq) and DMAP (19 mg, 155 µmol, 9.0 eq). Column chromatography (*n*-pentane-Et_2O 2:3) yielded the product (30 mg, 13 µmol, 77%) as a waxy solid. $[\alpha]_D^{25}$ = -36.5 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.42-7.26 (m, 17, C*H*$_{arom}$); 6.97-6.93 (m, 2H, C*H*$_{arom}$); 5.47 (d, 1H, *J* = 2.0 Hz, H-1); 5.29-5.22 (m, 2H, PhC*H*$_2$); 5.19 (d, 1H, *J* = 1.2 Hz, H-1'); 4.91-4.78 (m, 4H, PhC*H*H, C*H*$_{diol}$); 4.79 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.74 (d, 1H, *J* = 8.0 Hz, H-1''); 4.67-4.62 (m, 3H, H-2'', PhCH*H*, PhCH*H*); 4.24 (dd, 1H, *J* = 2.0, 2.8 Hz, H-2); 3.79 (dd, 1H, *J* = 3.0, 9.4 Hz, H-3); 3.74-3.47 (m, 16H, H-2', H-4'', H-5, H-5', H-5'', H-6'', OC*H*$_3$); 3.45-3.39 (m, 2H, H-4, H-4'); 3.36-3.33 (m, 8H, H-3', H-3'', OC*H*$_3$); 2.57-2.47 (m, 2H, C*H*$_{Myc}$); 2.37 (t, 2H, *J* = 7.0 Hz, C*H*$_{2,diol}$); 1.77-1.05 (m, 167H, H-6, H-6', C*H*$_{2,diol}$, C*H*$_{2,Myc}$,); 1.02-0.93 (m, 4H, C*H*$_{2,Myc}$); 0.91-0.83 (m, 36H, C*H*$_{3,diol}$, C*H*$_{3,Myc}$). ^{13}C-APT NMR (101 MHz) δ: 176.1 (*C*O$_{Myc}$); 155.3 (C$_{q,arom}$); 154.8 (*C*O$_{Cbz}$); 138.5, 138.3, 135.6 (C$_{q,arom}$); 133.0, 128.8, 128.6, 128.6, 128.5, 128.5, 128.3, 128.1, 128.0, 127.9 (*C*H$_{arom}$); 118.0 (C$_{q,arom}$); 116.2 (*C*H$_{arom}$); 100.9 (C-1''); 98.5 (C-1'); 96.9 (C-1); 89.5 (C$_{q,alkyne}$); 85.0 (C-3''); 82.0 (C-3); 80.8 (C-4'); 80.1 (C-4); 80.1 (C$_{q,alkyne}$); 78.1 (C-2''); 77.7, 77.6 (C-4'' and C-5''); 77.0 (C-2'); 75.3, 75.1 (Ph*C*H$_2$); 74.8 (C-3'); 73.0 (C-2); 71.1 (C-6''); 70.4 (*C*H$_{diol}$); 69.9 (Ph*C*H$_2$); 68.7 (C-5); 67.9 (C-5'); 61.0, 59.8, 59.1, 58.3, 57.6 (O*C*H$_3$); 45.7, 45.4 (*C*H$_{2,Myc}$); 41.1, 38.6 (*C*H$_{2,diol}$); 37.9 (*C*H$_{Myc}$); 36.7 (*C*H$_{2,Myc}$); 34.8 (*C*H$_{2,diol}$); 32.1 (*C*H$_{2,Myc}$); 32.0, 30.2 (*C*H$_{2,diol}$) 30.1 (*C*H$_{Myc}$); 29.9, 29.9, 29.8, 29.7, 29.5, 29.4, 29.2, 29.1, (*C*H$_2$); 28.2 (*C*H$_{Myc}$); 27.3 (*C*H$_{Myc}$); 27.1 (*C*H$_{2,Myc}$); 25.3 (*C*H$_{2,diol}$); 22.8, 22.8 (*C*H$_{2,Myc}$); 20.9, 20.6, 20.5 (*C*H$_{3,Myc}$); 19.6 (*C*H$_{2,diol}$); 18.6 (*C*H$_{3,Myc}$); 18.2 (C-6'); 18.0 (C-6); 14.3 (*C*H$_{3,Myc}$). IR (thin film, cm^{-1}): 1055, 1073, 1095, 1120, 1259, 1378, 1457, 1464, 1507, 1734, 2853, 2923. HRMS calculated for $C_{142}H_{239}O_{20}$ 2265.77825 $[M+H]^+$; found 2265.77134.

4-((9*R*,11*R*)-heptacos-26-yne-9,11-diyl bismycocerosate)phenyl 2-*O*-methyl-3-*O*-(3-*O*-(2,3,4-tri-*O*-methyl-α-L-fucopyranosyl-α-L-rhamnopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranoside (20B)



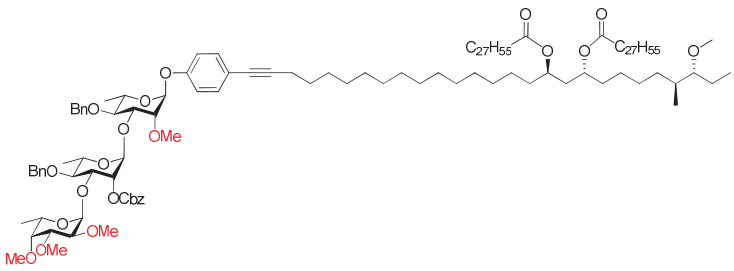
Compound **27** (27 mg, 12 µmol, 1.0 eq) was hydrogenated using general procedure C to give the title compound (20 mg, 10 µmol, 86%) as a pale oil. $[\alpha]_D^{25}$ = -44.6 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.10 (d, 2H, *J* = 8.4 Hz, C*H*$_{arom}$); 6.99 (dd, 2H, *J* = 2.0, 6.8 Hz, C*H*$_{arom}$); 5.51 (d, 1H, *J* = 1.6 Hz, H-1); 5.15-5.14 (m, 2H, H-1', H-1''); 4.84 (quint, 2H, *J* = 6.3 Hz, C*H*$_{diol}$); 4.11 (s, 1H, H-2'); 4.08-4.03 (m, 2H, H-3, H-5''); 3.97-3.90 (m, 1H, H-5'); 3.82-3.74 (m, 3H, H-2, H-3', H-5); 3.70-3.58 (m, 11H, H-2'', H-3'', H-4, H-4', O*H*, OC*H*$_3$); 3.52 (s, 3H, OC*H*$_3$); 3.49 (s, 3H, OC*H*$_3$); 3.48 (d, 1H, *J* = 1.2 Hz, H-4''); 2.57-2.50 (m, 4H, C*H*$_{2,Diol}$, C*H*$_{Myc}$); 2.28 (bs, 1H, O*H*); 2.16 (bs, 1H, O*H*); 1.77-0.81 (m, 270H, H-6, H-6', H-6'', C*H*$_{2,Diol}$, C*H*$_{Myc,}$ C*H*$_{2,Myc}$, C*H*$_{3,Myc}$). ^{13}C-APT NMR (101 MHz) δ: 176.2 (*C*O$_{Myc}$); 154.7, 137.0 (C$_{q,arom}$); 129.5, 116.3 (*C*H$_{arom}$); 102.3 (C-1''); 101.0 (C-1'); 95.0 (C-1); 83.3 (C-3'); 81.1 (C-3''); 80.2 (C-2); 80.1 (C-3); 79.1 (C-4''); 78.9 (C-2''); 71.9 (C-4'); 71.8 (C-4); 71.3 (C-2'); 70.5 (*C*H$_{diol}$); 69.2 (C-5); 68.8 (C-5'); 67.7 (C-5''); 62.1, 60.4, 58.7, 57.9 (O*C*H$_3$); 45.7, 45.4 (*C*H$_{2,Myc}$); 41.1, 38.6 (*C*H$_{2,diol}$); 37.9 (*C*H$_{Myc}$); 36.7 (*C*H$_{2,Myc}$); 34.8 (*C*H$_{2,diol}$); 32.1 (*C*H$_{2,Myc}$); 32.0 31.9, 30.2 (*C*H$_{2,diol}$); 30.1 (*C*H$_{Myc}$); 29.9, 29.9, 29.8, 29.8, 29.7, 29.7, 29.5, 29.4 (*C*H$_2$); 28.2 (*C*H$_{Myc}$); 27.3 (*C*H$_{Myc}$); 27.1 (*C*H$_{2,Myc}$); 25.7, 25.3 (*C*H$_{2,diol}$); 22.8, 22.8 (*C*H$_{2,Myc}$); 20.9, 20.6, 20.5, 18.6 (*C*H$_{3,Myc}$); 18.0, 17.9 (C-6 and C-6'); 16.8 (C-6''); 14.3 (*C*H$_{3,Myc}$). IR (thin film, cm^{-1}): 1043, 1100, 1129, 1173, 1229, 1378, 1460, 1484, 1508, 1734, 2853, 2923, 3436. HRMS calculated for $C_{119}H_{223}O_{17}$ 1925.66471 $[M+H]^+$; found 1925.66457.

4-((9*R*,11*R*)-heptacos-26-yne-9,11-diyl bismycocerosate)phenyl 2-*O*-(2,3-di-*O*-methyl-4-*O*-(3,6-di-*O*-methyl-ß-D-glucopyranosyl)-α-L-rhamnopyranosyl)-3-*O*-methyl-α-L-rhamnopyranoside (21B)



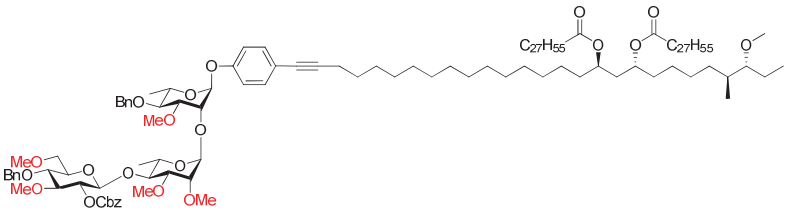
Compound **28** (22 mg, 9.7 µmol, 1.0 eq) was hydrogenated using general procedure C to give the title compound (15 mg, 7.7 µmol, 79%) as a pale oil. $[\alpha]_D^{25}$ = -23.9 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: ^{1}H-NMR (400 MHz) δ: 7.10 (d, 2H, *J* = 8.4 Hz, C*H*$_{arom}$); 6.94 (dd, 2H, *J* = 2.0, 6.8 Hz, C*H*$_{arom}$); 5.43 (d, 1H, *J* = 2.0 Hz, H-1); 5.10 (d, 1H, *J* = 1.2 Hz, H-1'); 4.91 (quint, 2H, *J* = 6.4 Hz, C*H*$_{diol}$); 4.41 (d, 1H, *J* = 7.6 Hz, H-1''); 4.23 (dd, 1H, *J* = 1.6, 2.8 Hz, H-2); 3.89 (d, 1H, *J* = 0.8 Hz, 2''-O*H*); 3.79-3.71 (m, 3H, H-2', H-5, H-5'); 3.68-3.60 (m, 8H, H-3, H-3', H-4', H-6'', OC*H*$_3$); 3.58-3.47 (m, 11H, H-4, H-4'', OC*H*$_3$); 3.45-3.38 (m, 5H, H-2'', H-5'', OC*H*$_3$); 3.17 (t, 1H, *J* = 9.0 Hz, H-3''); 2.81 (bs, 1H, O*H*); 2.56-2.48 (m, 4H, C*H*$_{2,diol}$, C*H*$_{Myc}$); 2.29 (bs, 1H, O*H*); 2.16 (bs, 1H, O*H*); 1.77-0.81 (m, 249H, H-6, H-6', C*H*$_{2,Diol}$, C*H*$_{Myc,}$ C*H*$_{2,Myc}$, C*H*$_{3,Myc}$). ^{13}C-APT NMR (101 MHz) δ: 176.2 (*C*O$_{Myc}$); 154.3, 137.0 (C$_{q,arom}$); 129.5, 116.1 (*C*H$_{arom}$); 105.8 (C-1''); 98.5 (C-1'); 97.5 (C-1); 85.6 (C-3''); 81.8 (C-4'); 81.5 (C-3); 80.3 (C-3'); 75.9 (C-2'); 75.1 (C-2''); 74.1 (C-5''); 73.0 (C-6''); 72.2 (C-2); 72.0 (C-4); 71.4 (C-4''); 70.5 (*C*H$_{diol}$); 69.1 (C-5); 68.4 (C-5'); 60.7, 59.7, 59.2, 57.8, 57.5, 56.7 (O*C*H$_3$); 38.6, 35.3 (*C*H$_2$); 34.9 (*C*H$_{Phth}$); 45.7, 45.4 (*C*H$_{2,Myc}$); 41.1, 38.6 (*C*H$_{2,diol}$); 37.9 (*C*H$_{Myc}$); 36.7 (*C*H$_{2,Myc}$); 35.3, 34.8 (*C*H$_{2,diol}$); 32.1 (*C*H$_{2,Myc}$); 32.0 31.9, 30.2 (*C*H$_{2,diol}$); 30.1 (*C*H$_{Myc}$); 29.9, 29.9, 29.8, 29.7, 29.7, 29.6, 29.5, 29.4 (*C*H$_2$); 28.2 (*C*H$_{Myc}$); 27.3 (*C*H$_{Myc}$); 27.1 (*C*H$_{2,Myc}$); 25.3 (*C*H$_{2,diol}$); 22.9, 22.8 (*C*H$_{2,Myc}$); 20.9, 20.6, 20.5, 18.6 (*C*H$_{3,Myc}$); 17.9 (C-6) 17.7 (C-6'); 14.3 (*C*H$_{3,Myc}$). IR (thin film, cm^{-1}): 1010, 1016, 1072, 1085, 1089, 1132, 1175, 1233, 1378, 1457, 1509, 1734, 2853, 2923, 3457. HRMS calculated for $C_{120}H_{225}O_{18}$ 1955.67196 $[M+H]^+$; found 1955.67024.

4-((3*R*,4*S*,9*R*,11*R*)-3-methoxy-4-methylheptacos-26-yne-9,11-diyl bisoctacosanoate)phenyl 2-*O*-methyl-3-*O*-(2-*O*-benzyloxycarbonyl-3-*O*-(2,3,4-tri-*O*-methyl-α-L-fucopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranoside (29)



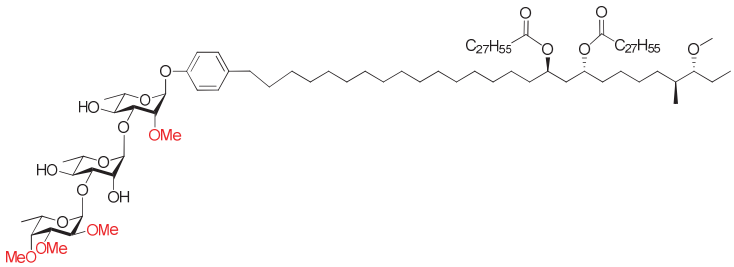
The title compound was synthesized according to general procedure D using diol **16** (22 mg, 16 µmol, 1.0 eq) and octacosanoic acid (**4**) (21 mg, 49 µmol, 3.0 eq), DIC (15 µL, 98 µmol, 6.0 eq) and DMAP (18 mg, 146 µmol, 9.0 eq). Column chromatography (*n*-pentane-Et_2O 1:1) yielded the product (31 mg, 14 µmol, 88%) as a waxy solid. $[\alpha]_D^{25}$ = -51.2 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.42-7.26 (m, 17H, C*H*$_{arom}$); 6.94 (d, 2H, *J* = 8.8 Hz, C*H*$_{arom}$); 5.51 (d, 1H, *J* = 1.6 Hz, H-1); 5.22-5.13 (m, 6H, H-1', H-1'', H-2', PhC*H*$_2$, PhC*H*H); 4.94-4.88 (m, 3H, PhC*H*H, C*H*$_{Phth}$); 4.60-4.53 (m, 2H, PhCH*H*, PhCH*H*); 4.22-4.18 (m, 2H, H-3, H-3'); 4.04-3.97 (m, 1H, H-5'); 3.81 (q, 1H, *J* = 6.4 Hz, H-5''); 3.74-3.66 (m, 2H, H-2, H-5); 3.57-3.48 (m, 13H, H-2'', H-3'', H-4, H-4', OC*H*$_3$); 3.33 (s, 3H, OC*H*$_3$); 3.31 (s, 3H, OC*H*$_3$); 3.27 (d, 1H, *J* = 1.6 Hz, H-4''); 2.88-2.83 (m, 1H, C*H*$_{Phth}$); 2.37 (t, 2H, *J* = 7.0 Hz, C*H*$_{2,Phth}$); 2.26 (t, 4H, *J* = 7.4 Hz, C*H*$_{2,oct}$); 1.75-1.05 (m, 188H, H-6, H-6', C*H*$_{2,Phth}$, C*H*$_{2,oct}$); 0.97 (d, 3H, *J* = 6.4 Hz, H-6''); 0.93-0.80 (m, 12H, C*H*$_{3,Phth}$, C*H*$_{3,oct}$). ^{13}C-APT NMR (101 MHz) δ: 173.5 (*C*O$_{Oct}$); 155.7 (C$_{q,arom}$); 154.8 (*C*O$_{Cbz}$); 139.0, 138.2, 135.2 (C$_{q,arom}$); 133.0, 128.9, 128.9, 128.8, 128.5, 128.5, 128.4, 127.9, 127.6, 127.6 (*C*H$_{arom}$); 118.0 (C$_{q,arom}$); 116.2 (*C*H$_{arom}$); 100.0 (C-1''); 99.5 (C-1'); 94.4 (C-1); 89.5 (C$_{q,alkyne}$); 86.8 (*C*H$_{Phth}$); 80.4 (C-3); 80.1 (C$_{q,alkyne}$); 80.1 (C-2 and C-3''); 79.9, 79.7 (C-4 and C-4'); 79.3 (C-4''); 78.3 (C-3'); 77.8 (C-2''); 76.8 (C-2'); 75.7, 75.1 (Ph*C*H$_2$); 70.2 (*C*H$_{Phth}$); 70.1 (Ph*C*H$_2$); 68.9 (C-5'); 68.7 (C-5); 67.1 (C-5''); 61.9, 59.1, 58.8, 58.2, 57.5 (O*C*H$_3$); 38.6 (*C*H$_{2,Phth}$); 34.9 (*C*H$_{Phth}$); 34.9, 32.7, 32.1, 29.9, 29.8, 29.7, 29.5, 29.4, 29.2, 29.0, 27.6, 25.7, 25.3, 25.1, 22.8, 22.5, 19.5 (*C*H$_2$); 18.2 (C-6); 18.1 (C-6'); 16.4 (C-6''); 14.9 (*C*H$_{3,Phth}$). 14.3 (*C*H$_{3,Oct}$); 10.2 (*C*H$_{3,Phth}$). IR (thin film, cm^{-1}): 1043, 1100, 1262, 1457, 1462, 1472, 1507, 1734, 2849, 2916. Despite multiple attempts, HRMS data for this molecule could not be obtained.

4-((3*R*,4*S*,9*R*,11*R*)-3-methoxy-4-methylheptacos-26-yne-9,11-diyl bisoctacosanoate)phenyl 2-*O*-(2,3-di-*O*-methyl-4-*O*-(2-*O*-benzyloxycarbonyl-3,6-di-*O*-methyl-4-*O*-benzyl-ß-D-glucopyranosyl)-α-L-rhamnopyranosyl)-3-*O*-methyl-4-*O*-benzyl-α-L-rhamnopyranoside (30)



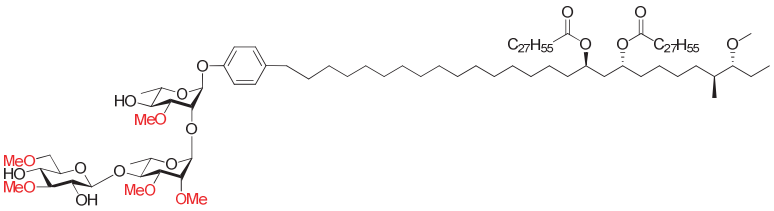
The title compound was synthesized according to general procedure D using diol **17** (25 mg, 18 µmol, 1.0 eq) and octacosanoic acid (**4**) (23 mg, 54 µmol, 3.0 eq), DIC (20 µL, 126 µmol, 7.0 eq) and DMAP (20 mg, 163 µmol, 9.0 eq). Column chromatography (*n*-pentane-Et_2O 1:1) yielded the product (34 mg, 15 µmol, 86%) as a waxy solid. $[\alpha]_D^{25}$ = -35.6 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.40-7.26 (m, 17, C*H*$_{arom}$); 6.95 (d, 2H, *J* = 8.8 Hz, C*H*$_{arom}$); 5.47 (s, 1H, H-1); 5.29-5.22 (m, 2H, PhC*H*$_2$); 5.19 (s, 1H, H-1'); 4.94-4.88 (m, 3H,PhC*H*H, C*H*$_{Phth}$); 4.79 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.74 (d, 1H, *J* = 8.0 Hz, H-1''); 4.67-4.62 (m, 3H, H-2'', PhCH*H*, PhCH*H*); 4.24 (s, 1H, H-2); 3.79 (dd, 1H, *J* = 3.2, 9.2 Hz, H-3); 3.76-3.47 (m, 16H, H-2', H-4'', H-5, H-5', H-5'', H-6'', OC*H*$_3$); 3.45-3.39 (m, 2H, H-4, H-4'); 3.36-3.33 (m, 8H, H-3', H-3'', OC*H*$_3$); 2.90-2.84 (m, 1H, C*H*$_{Phth}$); 2.38 (t, 2H, *J* = 7.2 Hz, C*H*$_{2,Phth}$); 2.26 (t, 4H, *J* = 7.4 Hz, C*H*$_{2,oct}$); 1.73 (t, 2H, *J* = 6.6 Hz, C*H*$_{2,oct}$); 1.68-1.03 (m, 168H, H-6, H-6', C*H*$_{2,Phth}$, C*H*$_{2,oct}$); 0.93-0.81 (m, 12H, C*H*$_{3,Phth,}$ C*H*$_{3,oct}$). ^{13}C-APT NMR (101 MHz) δ: 173.5 (*C*O$_{oct}$); 155.3 (C$_{q,arom}$); 154.9 (*C*O$_{Cbz}$); 138.5, 138.3, 135.6 (C$_{q,arom}$); 133.0, 128.8, 128.6, 128.6, 128.5, 128.5, 128.3, 128.1, 128.0, 127.9 (*C*H$_{arom}$); 118.0 (C$_{q,arom}$); 116.2 (*C*H$_{arom}$); 100.9 (C-1''); 98.5 (C-1'); 96.9 (C-1); 89.5 (C$_{q,alkyne}$); 86.8 (*C*H$_{Phth}$); 85.0 (C-3''); 82.0 (C-3); 80.8 (C-4'); 80.1 (C-4); 80.1 (C$_{q,alkyne}$); 78.1 (C-2''); 77.7, 77.6 (C-4'' and C-5''); 77.0 (C-2'); 75.3, 75.1 (Ph*C*H$_2$); 74.8 (C-3'); 73.0 (C-2); 71.1 (C-6''); 70.2 (*C*H$_{Phth}$), 69.9 (Ph*C*H$_2$); 68.7 (C-5); 67.9 (C-5'); 61.0, 59.8, 59.1, 58.3, 57.6, 57.5 (O*C*H$_3$); 34.9, 34.9, 34.7, 32.7, 32.1, 29.9, 29.7, 29.5, 29.4, 29.2, 29.0, 27.6, 25.7, 25.3, 25.1, 22.8, 22.5, 19.6 (*C*H$_2$); 18.2, 18.0 (C-6 and C-6'); 14.9 (*C*H$_{3,Phth}$); 14.3 (*C*H$_{3,Oct}$); 10.2 (*C*H$_{3,Phth}$). IR (thin film, cm^{-1}): 1073, 1079, 1120, 1176, 1198, 1261, 1454, 1464, 1472, 1508, 1736, 2849, 2916. Despite multiple attempts, HRMS data for this molecule could not be obtained.

4-((3*R*,4*S*,9*R*,11*R*)-3-methoxy-4-methylheptacos-26-yne-9,11-diyl bisoctacosanoate)phenyl 2-*O*-methyl-3-*O*-(3-*O*-(2,3,4-tri-*O*-methyl-α-L-fucopyranosyl)-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (20C)



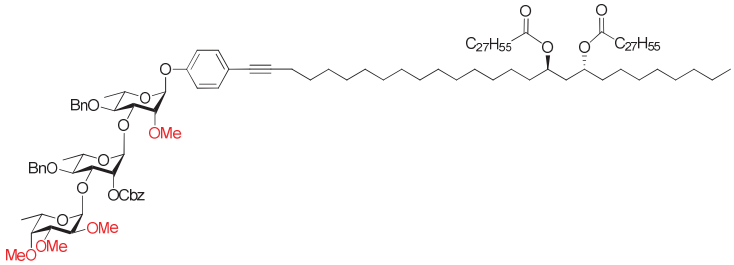
Compound **29** (31 mg, 14 µmol, 1.0 eq) was hydrogenated using general procedure C to give the title compound (19 mg, 10 µmol, 72%) as a pale oil. $[\alpha]_D^{25}$ = -40.4 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.10 (d, 2H, *J* = 8.4 Hz, C*H*$_{arom}$); 6.99 (dd, 2H, *J* = 2.0, 6.8 Hz, C*H*$_{arom}$); 5.51 (d, 1H, *J* = 1.6 Hz, H-1); 5.15-5.14 (m, 2H, H-1', H-1"); 4.91 (quint, 2H, *J* = 6.4 Hz, C*H*$_{Phth}$); 4.11 (s, 1H, H-2'); 4.08-4.03 (m, 2H, H-3, H-5"); 3.98-3.91 (m, 1H, H-5'); 3.84-3.74 (m, 3H, H-2, H-3', H-5); 3.70-3.58 (m, 11H, H-2", H-3", H-4, H-4', O*H*, OC*H*$_3$); 3.52 (s, 3H, OC*H*$_3$); 3.49 (s, 3H, OC*H*$_3$); 3.48 (d, 1H, *J* = 1.2 Hz, H-4"); 3.33 (s, 3H, OC*H*$_3$); 2.88-2.83 (m, 1H, C*H*$_{Phth}$); 2.55 (t, 2H, *J* = 7.8 Hz, C*H*$_{2,Phth}$); 2.29-2.20 (m, 5H, C*H*$_{2,Oct}$, O*H*); 2.15 (bs, 1H, O*H*); 1.77-0.98 (m, 168H, H-6, H-6', H-6", C*H*$_{2,Phth}$, C*H*$_{2,oct}$); 0.93-0.81 (m, 12H, C*H*$_{3,Phth}$, C*H*$_{3,Oct}$). ^{13}C-APT NMR (101 MHz) δ: 173.5 (*C*O$_{Oct}$); 154.7, 137.0 (C$_{q,arom}$); 129.5, 116.3 (*C*H$_{arom}$); 102.3 (C-1"); 101.0 (C-1'); 95.0 (C-1); 86.8 (*C*H$_{Phth}$); 83.3 (C-3'); 81.1 (C-3"); 80.2 (C-2); 80.1 (C-3); 79.1 (C-4"); 78.9 (C-2"); 71.9 (C-4'); 71.8 (C-4); 71.3 (C-2'); 70.2 (*C*H$_{Phth}$); 69.2 (C-5); 68.7 (C-5'); 67.7 (C-5"); 62.1, 60.4, 58.7, 57.9, 57.5 (OCH$_3$); 38.6, 35.3 (*C*H$_{2,Phth}$); 34.9 (*C*H$_{Phth}$); 34.9, 34.7, 32.7 (*C*H$_{2,Phth}$); 32.1 (*C*H$_{2,Oct}$); 31.9 (*C*H$_{2,Phth}$); 29.9, 29.9, 29.8, 29.7, 29.5, 29.4 (*C*H$_2$); 27.6 (*C*H$_{2,Phth}$); 25.7, 25.3, 25.2 (*C*H$_{2,Phth}$); 22.9 (*C*H$_{2,Oct}$); 22.5 (*C*H$_{2,Phth}$); 18.0, 17.9 (C-6 and C-6'); 16.8 (C-6"); 14.9 (*C*H$_{3,Phth}$); 14.3 (*C*H$_{3,Oct}$); 10.2 (*C*H$_{3,Phth}$). IR (thin film, cm^{-1}): 1060, 1118, 1464, 1472, 1734, 2849, 2916, 3394. Despite multiple attempts, HRMS data for this molecule could not be obtained.

4-((3*R*,4*S*,9*R*,11*R*)-3-methoxy-4-methylheptacos-26-yne-9,11-diyl bisoctacosanoate)phenyl 2-*O*-(2,3-di-*O*-methyl-4-*O*-(3,6-di-*O*-methyl-ß-D-glucopyranosyl)-α-L-rhamnopyranosyl)-3-*O*-methyl-α-L-rhamnopyranoside (21C)



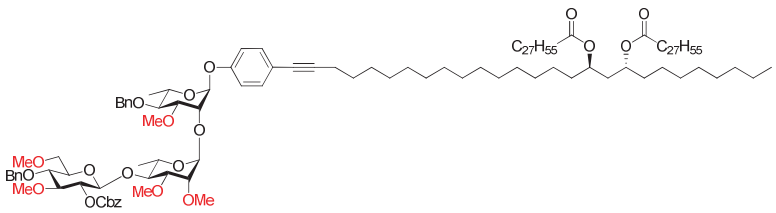
Compound **30** (33 mg, 15 µmol, 1.0 eq) was hydrogenated using general procedure C to give the title compound (22 mg, 12 µmol, 78%) as a pale oil. $[\alpha]_D^{25}$ = -27.6 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.10 (d, 2H, *J* = 8.8 Hz, C*H*$_{arom}$); 6.94 (d, 2H, *J* = 8.8 Hz, C*H*$_{arom}$); 5.43 (d, 1H, *J* = 1.6 Hz, H-1); 5.10 (d, 1H, *J* = 1.6 Hz, H-1'); 4.91 (quint, 2H, *J* = 6.3 Hz, C*H*$_{Phth}$); 4.41 (d, 1H, *J* = 8.0 Hz, H-1''); 4.23 (dd, 1H, *J* = 1.6, 2.8 Hz, H-2); 3.89 (bs, 1H, 2''-O*H*); 3.79-3.71 (m, 3H, H-2', H-5, H-5'); 3.68-3.60 (m, 8H, H-3, H-3', H-4', H-6'', OC*H*$_3$); 3.58-3.49 (m, 11H, H-4, H-4'', OC*H*$_3$); 3.46-3.39 (m, 5H, H-2'', H-5'', OC*H*$_3$); 3.17 (t, 1H, *J* = 9.0 Hz, H-3''); 2.88-2.82 (m, 1H, C*H*$_{Phth}$); 2.55 (t, 2H, *J* = 8.0 Hz, C*H*$_{2,Phth}$); 2.30-2.20 (m, 4H, C*H*$_{2,oct}$); 1.77-1.03 (m, 176H, H-6, H-6', C*H*$_{2,Phth}$, C*H*$_{2,oct}$); 0.93-0.86 (m, 12H, C*H*$_{3,Phth}$, C*H*$_{3,Oct}$). ^{13}C-APT NMR (101 MHz) δ: 173.5 (*C*O$_{oct}$); 154.3, 137.0 (C$_{q,arom}$); 129.5, 116.1 (*C*H$_{arom}$); 105.7 (C-1''); 98.5 (C-1'); 97.5 (C-1); 86.8 (*C*H$_{Phth}$); 85.6 (C-3''); 81.7 (C-4'); 81.5 (C-3); 80.3 (C-3'); 75.9 (C-2'); 75.1 (C-2''); 74.2 (C-5''); 73.0 (C-6''); 72.2 (C-2); 72.0 (C-4); 71.4 (C-4''); 70.2 (*C*H$_{Phth}$); 69.1 (C-5); 68.4 (C-5'); 60.7, 59.7, 59.2, 57.8, 57.5, 56.7 (O*C*H$_3$); 38.6, 35.3 (*C*H$_{2,Phth}$); 34.9 (*C*H$_{Phth}$); 34.9, 34.7, 32.7 (*C*H$_{2,Phth}$); 32.1 (*C*H$_{2,oct}$); 31.9 (*C*H$_{2,Phth}$); 29.9, 29.8, 29.7, 29.5, 29.4 (*C*H$_2$); 27.6 (*C*H$_{2,Phth}$); 25.7, 25.3, 25.2 (*C*H$_{2,Phth}$); 22.9 (*C*H$_{2,oct}$); 22.5 (*C*H$_{2,Phth}$); 17.9 (C-6); 17.7 (C-6'); 14.9 (*C*H$_{3,Phth}$); 14.3 (*C*H$_{3,oct}$); 10.2 (*C*H$_{3,Phth}$). IR (thin film, cm^{-1}): 1070, 1119, 1464, 1472, 1511, 1736, 2849, 2916, 3444. Despite multiple attempts, HRMS data for this molecule could not be obtained.

4-((9*R*,11*R*)-heptacos-26-yne-9,11-diyl bis octacosanoate)phenyl 2-*O*-methyl-3-*O*-(2-*O*-benzyloxycarbonyl-3-*O*-(2,3,4-tri-*O*-methyl-α-L-fucopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranoside (31)



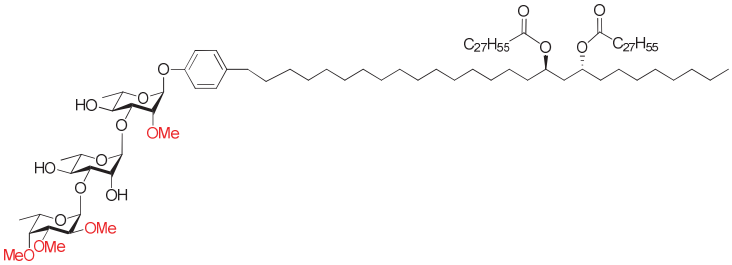
The title compound was synthesized according to general procedure D using diol **18** (33 mg, 25 µmol, 1.0 eq) and octacosanoic acid (**4**) (33 mg, 77 µmol, 3.0 eq), DIC (27 µL, 176 µmol, 7.0 eq) and DMAP (28 mg, 227 µmol, 9.0 eq). Column chromatography (*n*-pentane-Et_2O 1:1) yielded the product (53 mg, 25 µmol, 100%) as a waxy solid. $[\alpha]_D^{25}$ = -51.5 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.41-7.26 (m, 17H, C*H*$_{arom}$); 6.94 (d, 2H, *J* = 9.2 Hz, C*H*$_{arom}$); 5.51 (d, 1H, *J* = 1.6 Hz, H-1); 5.22-5.13 (m, 6H, H-1', H-1'', H-2', PhC*H*$_2$, PhC*H*H); 4.98-4.88 (m, 3H, PhC*H*H, C*H*$_{diol}$); 4.60-4.53 (m, 2H, PhCH*H*, PhCH*H*); 4.22-4.18 (m, 2H, H-3, H-3'); 4.04-3.97 (m, 1H, H-5'); 3.81 (q, 1H, *J* = 6.4 Hz, H-5''); 3.74-3.66 (m, 2H, H-2, H-5); 3.57-3.48 (m, 13H, H-2'', H-3'', H-4, H-4', OC*H*$_3$); 3.33 (s, 3H, OC*H*$_3$); 3.31 (s, 3H, OC*H*$_3$); 3.27 (d, 1H, *J* = 1.6 Hz, H-4''); 2.37 (t, 2H, *J* = 7.2 Hz, C*H*$_{2,Phth}$); 2.28 (t, 4H, *J* = 8.2 Hz, C*H*$_{2,oct}$); 1.77-1.04 (m, 172H, H-6, H-6'C*H*$_{2,diol}$, C*H*$_{2,Oct}$); 0.97 (d, 3H, *J* = 6.8 Hz, H-6''); 0.90-0.86 (m, 9H, C*H*$_{3,diol}$, C*H*$_{3,oct}$). ^{13}C-APT NMR (101 MHz) δ: 173.5 (*C*O$_{Oct}$); 155.7 (C$_{q,arom}$); 154.8 (*C*O$_{Cbz}$); 139.0, 138.2, 135.2 (C$_{q,arom}$); 133.0, 128.9, 128.9, 128.8, 128.5, 128.5, 128.4, 127.8, 127.6, 127.5 (*C*H$_{arom}$); 118.0 (C$_{q,arom}$); 116.2 (*C*H$_{arom}$); 99.9 (C-1''); 99.5 (C-1'); 94.4 (C-1); 89.5 (C$_{q,alkyne}$); 80.3 (C-3); 80.1 (C$_{q,alkyne}$); 80.1 (C-2 and C-3''); 79.9, 79.7 (C-4 and C-4'); 79.3 (C-4''); 78.3 (C-3'); 77.7 (C-2''); 76.8 (C-2'); 75.7, 75.1, 70.2 (Ph*C*H$_2$); 68.9 (C-5'); 68.7 (C-5); 67.1 (C-5''); 61.9, 59.1, 58.8, 58.2 (O*C*H$_3$); 38.6, 34.9, 34.7, 32.1, 32.0, 29.9, 29.8, 29.7, 29.7, 29.5, 29.4, 29.1, 29.0, 25.3, 25.1, 22.8, 19.5 (*C*H$_2$); 18.2 (C-6); 18.0 (C-6'); 16.4 (C-6''); 14.3 (*C*H$_{3,oct}$ and *C*H$_{3,diol}$). IR (thin film, cm^{-1}): 1235, 1258, 1457, 1464, 1472, 1507, 1736, 2849, 2916. Despite multiple attempts, HRMS data for this molecule could not be obtained.

4-((9*R*,11*R*)-heptacos-26-yne-9,11-diyl bis octacosanoate)phenyl 2-*O*-(2,3-di-*O*-methyl-4-*O*-(2-*O*-benzyloxycarbonyl-3,6-di-*O*-methyl-4-*O*-benzyl-ß-D-glucopyranosyl)-α-L-rhamnopyranosyl)-3-*O*-methyl-4-*O*-benzyl-α-L-rhamnopyranoside (32)



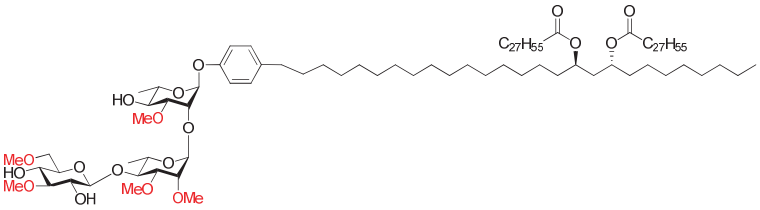
The title compound was synthesized according to general procedure D using diol **19** (30 mg, 22 µmol, 1.0 eq) and octacosanoic acid (**4**) (29 mg, 67 µmol, 3.0 eq), DIC (24 µL, 157 µmol, 7.0 eq) and DMAP (25 mg, 202 µmol, 9.0 eq). Column chromatography (*n*-pentane-Et_2O 1:1) yielded the product (44 mg, 20 µmol, 91%) as a waxy solid. $[\alpha]_D^{25}$ = -35.5 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.40-7.26 (m, 17, C*H*$_{arom}$); 6.95 (dd, 2H, *J* = 2.0, 6.8 Hz, C*H*$_{arom}$); 5.47 (d, 1H, *J* = 1.6 Hz, H-1); 5.29-5.22 (m, 2H, PhC*H*$_2$); 5.19 (d, 1H, *J* = 1.2 Hz, H-1'); 4.94-4.88 (m, 3H, PhC*H*H, C*H*$_{diol}$); 4.79 (d, 1H, *J* = 11.2 Hz, PhC*H*H); 4.74 (d, 1H, *J* = 8.0 Hz, H-1''); 4.67-4.62 (m, 3H, H-2'', PhCH*H*, PhCH*H*); 4.24 (dd, 1H, *J* = 1.6, 3.2 Hz, H-2); 3.79 (dd, 1H, *J* = 3.2, 9.2 Hz, H-3); 3.76-3.47 (m, 16H, H-2', H-4'', H-5, H-5', H-5'', H-6'', OC*H*$_3$); 3.45-3.39 (m, 2H, H-4, H-4'); 3.36-3.33 (m, 8H, H-3', H-3'', OC*H*$_3$); 2.38 (t, 2H, *J* = 7.2 Hz, C*H*$_{2,diol}$); 2.26 (t, 4H, *J* = 9.0 Hz, C*H*$_{2,oct}$); 1.73 (t, 2H, *J* = 6.6 Hz, C*H*$_{2,oct}$); 1.68-1.05 (m, 206H, H-6, H-6', C*H*$_{2,diol}$, C*H*$_{2,oct}$); 0.90-0.83 (m, 9H, C*H*$_{3,diol}$, C*H*$_{3,oct}$). ^{13}C-APT NMR (101 MHz) δ: 173.5 (*C*O$_{oct}$); 155.3 (C$_{q,arom}$); 154.8 (*C*O$_{Cbz}$); 138.5, 138.3, 135.6 (C$_{q,arom}$); 133.0, 128.8, 128.6, 128.6, 128.5, 128.5, 128.3, 128.1, 128.0, 127.9 (*C*H$_{arom}$); 118.0 (C$_{q,arom}$); 116.2 (*C*H$_{arom}$); 100.9 (C-1''); 98.5 (C-1'); 96.9 (C-1); 89.5 (C$_{q,alkyne}$); 85.0 (C-3''); 82.0 (C-3); 80.8 (C-4'); 80.1 (C-4); 80.1 (C$_{q,alkyne}$); 78.1 (C-2''); 77.7, 77.6 (C-4'' and C-5''); 77.0 (C-2'); 75.3, 75.0 (PhCH_2); 74.8 (C-3'); 73.0 (C-2); 71.1 (C-6''); 70.2 (*C*H$_{diol}$); 69.9 (PhCH_2); 68.7 (C-5); 67.9 (C-5'); 61.0, 59.8, 59.1, 58.3, 57.6 (O*C*H$_3$); 34.9, 34.7, 32.1, 32.0, 29.9, 29.8, 29.7, 29.5, 29.4, 29.2, 29.0, 25.3, 25.1, 22.8, 19.6 (*C*H$_{2,diol}$); 18.2, 18.0 (C-6 and C-6'); 14.3 (*C*H$_{3,oct}$ and *C*H$_{3,diol}$). IR (thin film, cm^{-1}): 1036, 1063, 1076, 1096, 1123, 1259, 1462, 1472, 1507, 1736, 2849, 2916. Despite multiple attempts, HRMS data for this molecule could not be obtained.

4-((9*R*,11*R*)-heptacos-26-yne-9,11-diyl bis octacosanoate)phenyl 2-*O*-methyl-3-*O*-(3-*O*-(2,3,4-tri-*O*-methyl-α-L-fucopyranosyl)-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (20D)



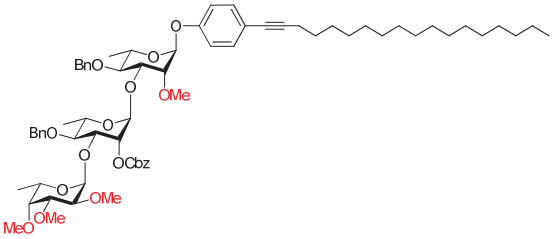
Compound **31** (56 mg, 25 µmol, 1.0 eq) was hydrogenated using general procedure C to give the title compound (27 mg, 15 µmol, 59%) as a pale oil. $[\alpha]_D^{25}$ = -48.0 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.10 (d, 2H, *J* = 8.4 Hz, C*H*$_{arom}$); 6.99 (dd, 2H, *J* = 2.0, 6.8 Hz, C*H*$_{arom}$); 5.51 (d, 1H, *J* = 1.6 Hz, H-1); 5.15-5.14 (m, 2H, H-1', H-1''); 4.91 (quint, 2H, *J* = 6.4 Hz, C*H*$_{diol}$); 4.11 (dd, 1H, *J* = 1.6, 3.2 Hz, H-2'); 4.09-4.03 (m, 2H, H-3, H-5''); 3.99-3.90 (m, 1H, H-5'); 3.83-3.74 (m, 3H, H-2, H-3', H-5); 3.70-3.57 (m, 11H, H-2'', H-3'', H-4, H-4', O*H*, OC*H*$_3$); 3.52 (s, 3H, OC*H*$_3$); 3.49 (s, 3H, OC*H*$_3$); 3.48 (d, 1H, *J* = 1.2 Hz, H-4''); 2.55 (t, 2H, *J* = 7.6 Hz, C*H*$_{2,diol}$); 2.32-2.18 (m, 5H, C*H*$_{2,oct}$, O*H*); 1.77-1.03 (m, 168H, H-6, H-6', H-6'', C*H*$_{diol}$, C*H*$_{2,oct}$); 0.92-0.86 (m, 12H, C*H*$_{3,diol}$, C*H*$_{3,oct}$). ^{13}C-APT NMR (101 MHz) δ: 173.5 (*C*O$_{Oct}$); 154.7, 137.0 (C$_{q,arom}$); 129.5, 116.3 (*C*H$_{arom}$); 102.3 (C-1''); 100.9 (C-1'); 95.0 (C-1); 83.3 (C-3'); 81.1 (C-3''); 80.2 (C-2); 80.2 (C-3); 79.1 (C-4''); 78.9 (C-2''); 71.9 (C-4'); 71.8 (C-4); 71.3 (C-2'); 70.2 (*C*H$_{diol}$); 69.2 (C-5); 68.8 (C-5'); 67.6 (C-5''); 62.1, 60.4, 58.7, 57.9 (O*C*H$_3$); 38.6, 35.3 (*C*H$_{2,Diol}$); 34.9, 34.7 (*C*H$_{2,Diol}$); 32.1 (*C*H$_{2,Oct}$); 32.0 (*C*H$_{2,Diol}$); 29.9, 29.9, 29.8, 29.8, 29.7, 29.6, 29.5, 29.5, 29.4, 29.4 (*C*H$_2$); 25.3, 25.2 (*C*H$_{2,Diol}$); 22.8 (*C*H$_{2,Oct}$); 22.8 (*C*H$_{2,Diol}$); 18.0, 17.9 (C-6 and C-6'); 16.8 (C-6''); 14.3 (*C*H$_{3,oct}$ and *C*H$_{3,diol}$). IR (thin film, cm^{-1}): 1041, 1132, 1262, 1464, 1472, 1736, 2849, 2916, 3420. Despite multiple attempts, HRMS data for this molecule could not be obtained.

4-((9*R*,11*R*)-heptacos-26-yne-9,11-diyl bis octacosanoate)phenyl 2-*O*-(2,3-di-*O*-methyl-4-*O*-(3,6-di-*O*-methyl-ß-D-glucopyranosyl)-α-L-rhamnopyranosyl)-3-*O*-methyl-α-L-rhamnopyranoside (21D)



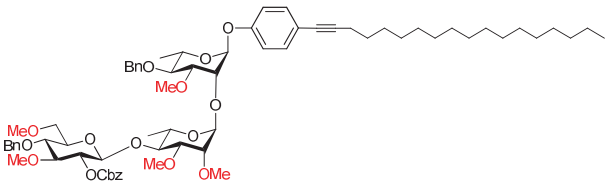
Compound **32** (44 mg, 20 µmol, 1.0 eq) was hydrogenated using general procedure C to give the title compound (22 mg, 12 µmol, 59%) as a pale oil. $[\alpha]_D^{25}$ = -47.6 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.10 (d, 2H, *J* = 8.8 Hz, C*H*$_{arom}$); 6.94 (dd, 2H, *J* = 2.0, 6.8 Hz, C*H*$_{arom}$); 5.43 (d, 1H, *J* = 2.0 Hz, H-1); 5.10 (d, 1H, *J* = 1.6 Hz, H-1'); 4.91 (quint, 2H, *J* = 6.4 Hz, C*H*$_{diol}$); 4.41 (d, 1H, *J* = 7.6 Hz, H-1"); 4.23 (dd, 1H, *J* = 2.0, 2.4 Hz, H-2); 3.89 (d, 1H, *J* = 0.8 Hz, 2"-O*H*); 3.79-3.72 (m, 3H, H-2', H-5, H-5'); 3.68-3.60 (m, 8H, H-3, H-3', H-4', H-6", OC*H*$_3$); 3.58-3.49 (m, 11H, H-4, H-4", OC*H*$_3$); 3.45-3.35 (m, 5H, H-2", H-5", OC*H*$_3$); 3.17 (t, 1H, *J* = 9.0 Hz, H-3"); 2.81 (s, 1H, O*H*); 2.55 (t, 2H, *J* = 7.8 Hz, C*H*$_{2,diol}$); 2.29-2.22 (m, 5H, C*H*$_{2,oct}$, O*H*); 1.73 (t, 2H, 6.6 Hz, C*H*$_2$); 1.63-1.38 (m, 17H, C*H*$_2$); 1.34-1.03 (m, 168H, C*H*$_2$, H-6, H-6'); 0.90-0.86 (m, 9H, C*H*$_3$). ^{13}C-APT NMR (101 MHz) δ: 173.5 (*C*O$_{oct}$); 154.3, 137.0 (C$_{q,arom}$); 129.5, 116.1 (*C*H$_{arom}$); 105.8 (C-1"); 98.5 (C-1'); 97.5 (C-1); 85.6 (C-3"); 81.8 (C-4'); 81.5 (C-3); 80.3 (C-3'); 75.9 (C-2'); 75.1 (C-2"); 74.1 (C-5"); 73.0 (C-6"); 72.2 (C-2); 72.0 (C-4); 71.4 (C-4"); 70.2 (*C*H$_{diol}$); 69.1 (C-5); 68.4 (C-5'); 60.7, 59.8, 59.2, 57.8, 56.7 (O*C*H$_3$); 38.6, 35.3 (*C*H$_{2,diol}$); 34.9, 34.7 (*C*H$_{2,diol}$); 32.1 (*C*H$_{2,oct}$); 32.0, 31.9 (*C*H$_{2,diol}$); 29.9, 29.8, 29.8, 29.7, 29.6, 29.5, 29.4, 29.4 (*C*H$_2$); 25.3, 25.2 (*C*H$_{2,diol}$); 22.8 (*C*H$_{2,oct}$); 22.8 (*C*H$_{2,diol}$); 17.9 (C-6); 17.7 (C-6'); 14.3 (*C*H$_{3,oct}$ and *C*H$_{3,diol}$). IR (thin film, cm^{-1}): 1012, 1129, 1198, 1235, 1458, 1464, 1472, 1508, 1736, 2849, 2916, 3444. Despite multiple attempts, HRMS data for this molecule could not be obtained.

4-(octadec-1-ynyl)phenyl 2-*O*-methyl-3-*O*-(2-*O*-benzyloxycarbonyl-3-*O*-(2,3,4-tri-*O*-methyl-α-L-fucopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranoside (33)



The title compound was synthesized according to general procedure A using **14** (30 mg, 29 µmol, 1.0 eq) and 1-octadecyn (37 mg, 146 µmol, 5.0 eq). Column chromatography (*n*-pentane-Et_2O 1:1) yielded the product (30 mg, 26 µmol, 89%) as a yellow oil. $[\alpha]_D^{25}$ = -100.1 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.44-7.24 (m, 17H, C*H*$_{arom}$); 6.95-6.91 (m, 2H, C*H*$_{arom}$); 5.51 (d, 1H, *J* = 1.6 Hz, H-1); 5.22-5.10 (m, 6H, H-1', H-1'', H-2', PhC*H*$_2$, PhC*H*H); 4.93 (d, 1H, *J* = 10.4 Hz, PhC*H*H); 4.60-4.53 (m, 2H, PhCH*H*, PhCH*H*); 4.22-4.18 (m, 2H, H-3, H-3'); 4.03-3.97 (m, 1H, H-5'); 3.81 (q, 1H, *J* = 6.4 Hz, H-5''); 3.76-3.68 (m, 2H, H-2, H-5); 3.59-3.48 (m, 13H, H-2'', H-3'', H-4, H-4', OC*H*$_3$); 3.31 (s, 3H, OC*H*$_3$); 3.27 (d, 1H, *J* = 2.0 Hz, H-4''); 2.37 (t, 2H, *J* = 7.0 Hz, C*H*$_2$); 1.58 (quint, 2H, *J* = 6.8 Hz, C*H*$_2$); 1.44-1.17 (m, 34H, H-6, H-6', C*H*$_2$) 0.97 (d, 3H, *J* = 6.4 Hz, H-6''); 0.88 (t, 3H, *J* = 6.8 Hz, C*H*$_3$). ^{13}C-APT NMR (101 MHz) δ: 155.7 (C$_{q,arom}$); 154.8 (*C*O$_{Cbz}$); 139.0, 138.2, 135.2 (C$_{q,arom}$); 133.0, 128.9, 128.9, 128.8, 128.6, 128.5, 128.5, 128.4, 127.8, 127.6, 127.5 (*C*H$_{arom}$); 118.0 (C$_{q,arom}$); 116.2 (*C*H$_{arom}$); 100.0 (C-1''); 99.5 (C-1'); 94.4 (C-1); 89.5 (C$_{q,alkyn}$); 80.4 (C-4'); 80.1 (C-4); 79.9 (C-2); 79.7 (C-3''); 79.6 (C-3'); 79.3 (C-4''); 78.3 (C-3); 77.8 (C-2''); 76.8 (C-2'); 75.7, 75.1, 70.1 (Ph*C*H$_2$); 68.9 (C-5'); 68.7 (C-5); 67.1 (C-5''); 61.9, 59.1, 58.8, 58.2 (O*C*H$_3$); 32.1, 29.8, 29.8, 29.7, 29.5, 29.3, 29.1, 29.0, 22.8, 19.5 (*C*H$_2$); 18.2 (C-6); 18.1 (C-6'); 16.4 (C-6''); 14.3 (*C*H$_3$). IR (thin film, cm^{-1}): 1009, 1045, 1098, 1176, 1235, 1357, 1382, 1457, 1484, 1507, 1747, 2853, 2926. HRMS calculated for $C_{68}H_{94}O_{15}Na$ 1173.64849 [M+Na]$^+$; found 1173.64598.

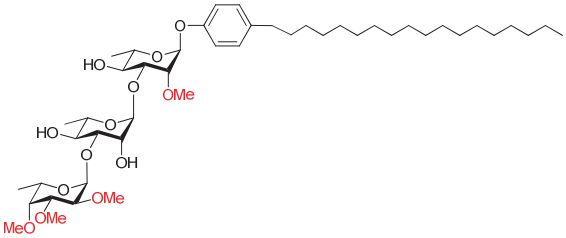
4-(octadec-1-ynyl)phenyl 2-*O*-(2,3-di-*O*-methyl-4-*O*-(2-*O*-benzyloxycarbonyl-3,6-di-*O*-methyl-4-*O*-benzyl-ß-D-glucopyranosyl)-α-L-rhamnopyranosyl)-3-*O*-methyl-4-*O*-benzyl-α-L-rhamnopyranoside (34)



The title compound was synthesized according to general procedure A using **15** (26 mg, 25 µmol, 1.0 eq) and 1-octadecyne (31 mg, 123 µmol, 5.0 eq). Column chromatography (*n*-pentane-Et_2O 1:1) yielded the product (25 mg, 21 µmol, 86%) as a yellow oil. $[\alpha]_D^{25}$ = -50.9 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.42-7.26 (m, 17, C*H*$_{arom}$); 6.97-6.92 (m, 2H, C*H*$_{arom}$); 5.47 (d, 1H, *J* = 1.6 Hz, H-1); 5.29-5.22 (m, 2H, Ph*C*H$_2$); 5.19

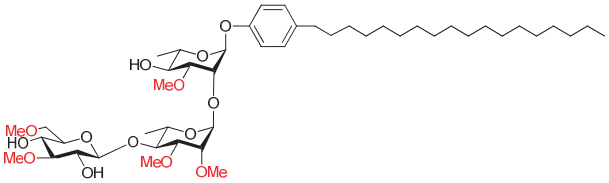
(d, 1H, *J* = 1.2 Hz, H-1'); 4.89 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.79 (d, 1H, *J* = 10.8 Hz, PhCHH); 4.74 (d, 1H, *J* = 8.0 Hz, H-1''); 4.67-4.62 (m, 3H, H-2'', PhCH*H*, PhCH*H*); 4.24 (dd, 1H, *J* = 1.6, 3.2 Hz, H-2); 3.81-3.31 (m, 27H, H-2', H-3, H-3', H-3'', H-4, H-4', H-4'', H-5, H-5', H-5'', H-6'', OCH_3); 2.38 (t, 2H, *J* = 7.0 Hz, CH_2); 1.62-1.55 (m, 2H, CH_2); 1.45-1.37 (m, 2H, CH_2); 1.36-1.24 (m, 34H, H-6, H-6', CH_2); 0.88 (t, 3H, *J* = 6.8 Hz, CH_3).^{13}C-APT NMR (101 MHz) δ: 155.3 ($C_{q,arom}$); 154.8 (CO_{Cbz}); 138.5, 138.3, 135.6 ($C_{q,arom}$); 133.0, 128.8, 128.6, 128.6, 128.5, 128.5, 128.3, 128.1, 128.0, 127.9 (CH_{arom}); 118.0 ($C_{q,arom}$); 116.2 (CH_{arom}); 100.9 (C-1''); 98.5 (C-1'); 96.9 (C-1); 89.5 ($C_{q,alkyne}$); 85.0 (C-4''); 82.0 (C-2); 80.8 (C-4'); 80.1 (C-4); 80.1 ($C_{q,alkyne}$); 78.1 (C-2''); 77.7, 77.6 (C-3 and C-5''); 77.0 (C-2'); 75.3, 75.0 (PhCH_2); 74.8 (C-3'); 73.0 (C-2); 71.1 (C-6''); 69.9 (PhCH_2); 68.7 (C-5); 67.9 (C-5'); 61.0, 59.8, 59.1, 58.3, 57.6, (OCH_3); 32.1, 29.8, 29.8, 29.7, 29.5, 29.3, 29.1, 29.0, 22.8, 19.5 (CH_2); 18.2, 18.0 (C-6 and C-6'); 14.9 (CH_3). IR (thin film, cm^{-1}): 1017, 1056, 1075, 1093, 1120, 1139, 1206, 1259, 1384, 1454, 1484, 1507, 1606, 1756, 2853, 2923. HRMS calculated for $C_{69}H_{96}O_{16}Na$ 1203.65906 [M+Na]$^+$; found 1203.65660.

4-octadecylphenyl 2-*O*-methyl-3-*O*-(3-*O*-(2,3,4-tri-*O*-methyl-α-L-fucopyranosyl-α-L-rhamnopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranoside (20E)



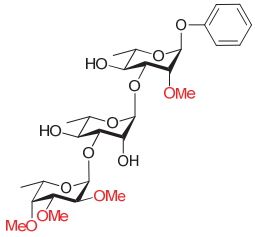
Compound **33** (25 mg, 22 µmol, 1.0 eq) was hydrogenated using general procedure C to give the title compound (12 mg, 14 µmol, 66%) as a pale oil. $[\alpha]_D^{25}$ = -91.8 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.10 (d, 2H, *J* = 8.4 Hz, CH_{arom}); 6.99 (dd, 2H, *J* = 2.2, 6.6 Hz, CH_{arom}); 5.51 (d, 1H, *J* = 1.6 Hz, H-1); 5.15-5.14 (m, 2H, H-1', H-1''); 4.11 (s, 1H, H-2'); 4.09-4.03 (m, 2H, H-3, H-5''); 3.97-3.90 (m, 1H, H-5'); 3.81-3.74 (m, 3H, H-2, H-3', H-5); 3.70-3.57 (m, 10H, H-2'', H-3'', H-4, H-4', OCH_3); 3.52 (s, 3H, OCH_3); 3.49 (s, 3H, OCH_3); 3.48 (d, 1H, *J* = 1.6 Hz, H-4''); 2.55 (t, 2H, *J* = 7.6 Hz, CH_2); 2.35 (bs, 1H, O*H*); 2.21 (bs, 1H, O*H*); 1.55 (quint, 2H, *J* = 7.6 Hz, CH_2); 1.36 (d, 3H, *J* = 6.4 Hz, H-6'); 1.34-1.25 (m, 38H, H-6, H-6'', CH_2); 0.88 (t, 3H, *J* = 7.4 Hz, CH_3). ^{13}C-APT NMR (101 MHz) δ: 154.7, 137.0 ($C_{q,arom}$); 129.5, 116.3 (CH_{arom}); 102.3 (C-1''); 100.9 (C-1'); 95.0 (C-1); 83.3 (C-3'); 81.1 (C-3''); 80.2 (C-2); 80.0 (C-3); 79.1 (C-4''); 78.9 (C-2''); 71.9 (C-4'); 71.7 (C-4); 71.3 (C-2'); 69.2 (C-5); 68.8 (C-5'); 67.6 (C-5''); 62.1, 60.4, 58.7, 57.9 (OCH_3); 35.3, 32.1, 29.8, 29.8, 29.7, 29.5, 29.5, 22.8 (CH_2); 18.0, 17.9 (C-6 and C-6'); 16.8 (C-6''); 14.3 (CH_3). IR (thin film, cm^{-1}): 1043, 1089, 1129, 1195, 1229, 1510, 2852, 2923, 3433. HRMS calculated for $C_{46}H_{84}O_{13}N$ 858.59372 [M+NH_4]$^+$; found 858.59328.

4-octadecylphenyl 2-*O*-(2,3-di-*O*-methyl-4-*O*-(3,6-di-*O*-methyl-ß-D-glucopyranosyl)-α-L-rhamnopyranosyl)-3-*O*-methyl-α-L-rhamnopyranoside (21E)



Compound **34** (21 mg, 18 µmol, 1.0 eq) was hydrogenated using general procedure C to give the title compound (10 mg, 11 µmol, 65%) as a pale oil. $[\alpha]_D^{25}$ = -19.1 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.10 (d, 2H, *J* = 8.8 Hz, C*H*$_{arom}$); 6.96-6.93 (m, 2H, C*H*$_{arom}$); 5.43 (d, 1H, *J* = 2.0 Hz, H-1); 5.10 (d, 1H, *J* = 1.6 Hz, H-1'); 4.41 (d, 1H, *J* = 7.6 Hz, H-1''); 4.23 (dd, 1H, *J* = 2.4, 4.8 Hz, H-2); 3.89 (d, 1H, *J* = 1.2 Hz, 2''-O*H*); 3.78-3.72 (m, 3H, H-2', H-5, H-5'); 3.68-3.49 (m, 19H, H-3, H-3', H-4, H-4', H-4'', H-6'', OC*H*$_3$); 3.45-3.39 (m, 5H, H-2'', H-5'', OC*H*$_3$); 3.17 (t, 1H, *J* = 9.2 Hz, H-3''); 2.81 (d, 1H, *J* = 1.6 Hz, O*H*); 2.55 (t, 2H, *J* = 7.8 Hz, C*H*$_2$); 2.30 (d, 1H, *J* = 1.6 Hz, O*H*); 2.29-2.22 (m, 4H, CH_2); 1.73 (t, 2H, *J* = 6.6 Hz, C*H*$_2$); 1.61-1.56 (m, 2H, C*H*$_2$); 1.34-1.25 (m, 38H, H-6, H-6', C*H*$_2$); 0.88 (t, 3H, *J* = 6.8 Hz, C*H*$_3$). ^{13}C-APT NMR (101 MHz) δ: 154.3, 137.0 (C$_{q,arom}$); 129.5, 116.1 (*C*H$_{arom}$); 105.8 (C-1''); 98.5 (C-1'); 97.5 (C-1); 85.6 (C-3''); 81.8 (C-4'); 81.5 (C-3); 80.3 (C-3'); 75.9 (C-2'); 75.1 (C-2''); 74.1 (C-5''); 73.0 (C-6''); 72.2 (C-2); 72.0 (C-4); 71.4 (C-4''); 69.1 (C-5); 68.4 (C-5'); 60.7, 59.8, 59.2, 57.8, 56.7 (O*C*H$_3$); 35.3, 32.1, 29.8, 29.8, 29.7, 29.5, 29.5, 22.8 (*C*H$_2$); 17.9 (C-6); 17.7 (C-6'); 14.3 (*C*H$_3$). IR (thin film, cm^{-1}): 1016, 1067, 1120, 1198, 1229, 1510, 2853, 2923, 3443. HRMS calculated for $C_{47}H_{82}O_{14}Na$ 893.55968 $[M+Na]^+$; found 893.55943.

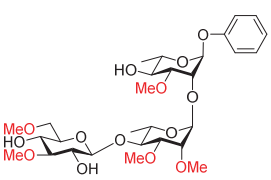
Phenyl 2-*O*-methyl-3-*O*-(3-*O*-(2,3,4-tri-*O*-methyl-α-L-fucopyranosyl-α-L-rhamnopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranoside (20F)



Compound **14** (40 mg, 39 µmol, 1.0 eq) was dissolved in EtOH (5 mL, 0.01 M) together with NH_4OAc (10 mg, 130 µmol, 3.3 eq)) and the solution was purged with N_2. A catalytic amount of Pd/C (10%) was then added and the resulting mixture was purged with H_2. The reaction was left to stir under H_2 atmosphere until all intermediates converged to a single spot on TLC (m/z = 791 ($M+Na^+$)) after which the solution was filtered over celite, diluted with H_2O and extracted with DCM (3x). The combined organic layers were washed with brine, dried with $MgSO_4$ and concentrated *in vacuo*. The resulting residue was then subjected to general hydrogenation procedure C to give the title compound (21 mg, 36 µmol, 92%) as a pale oil. $[\alpha]_D^{25}$ = -123.4 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.29 (t, 2H, *J* = 7.6 Hz, C*H*$_{arom}$); 7.08 (dd, 2H, *J* = 0.5, 8.6 Hz, C*H*$_{arom}$); 7.03 (t, 2H, *J* = 7.8 Hz, C*H*$_{arom}$); 5.56 (d, 1H, *J* = 1.2 Hz, H-1); 5.15-5.14 (m, 2H, H-1', H-1''); 4.11 (s, 1H, H-2'); 4.09-4.03 (m, 3H, H-3, H-5'', O*H*); 3.96-3.90 (m, 1H, H-5'); 3.82-3.71 (m, 3H, H-2, H-3', H-5); 3.69-3.58 (m, 10H, H-2'', H-3'', H-4, H-4', OC*H*$_3$); 3.55-3.45 (m, 7H, H-4'', OC*H*$_3$); 2.45 (d, 1H, *J* = 3.2 Hz, O*H*); 2.29 (d, 1H, *J* = 3.2 Hz, O*H*); 1.37 (d, 3H, *J* = 6.0 Hz, H-6'); 1.30-1.25 (m, 6H, H-6, H-6''). ^{13}C-APT NMR (101 MHz) δ: 156.6, (C$_{q,arom}$); 129.7, 122.4 116.4 (*C*H$_{arom}$); 102.3 (C-1''); 100.9 (C-1'); 94.8 (C-1); 83.2 (C-3'); 81.1 (C-3''); 80.1 (C-2); 79.9 (C-3); 79.1 (C-4''); 78.9 (C-2''); 71.9 (C-4'); 71.7 (C-4); 71.3 (C-2'); 69.3 (C-5);

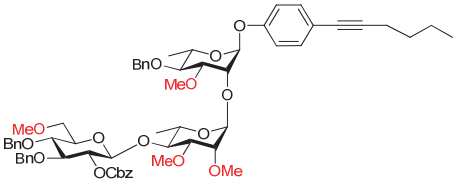
68.8 (C-5'); 67.6 (C-5''); 62.1, 60.4, 58.8, 57.9 (O*C*H$_3$); 18.0 (C-6') 17.9 (C-6); 16.8 (C-6''). IR (thin film, cm^{-1}): 1042, 1089, 1128, 1365, 1495, 2853, 2925, 3419. HRMS calculated for $C_{28}H_{44}O_{13}Na$ 611.26741 [M+Na]$^+$; found 611.26758.

Phenyl 2-*O*-(2,3-di-*O*-methyl-4-*O*-(3,6-di-*O*-methyl-ß-D-glucopyranosyl)-α-L-rhamnopyranosyl)-3-*O*-methyl-α-L-rhamnopyranoside (21F)



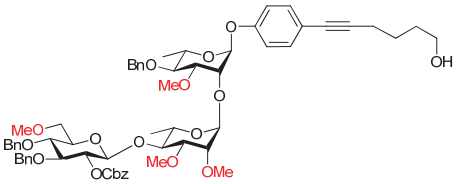
Compound **15** (51 mg, 48 µmol, 1.0 eq) was dissolved in EtOH (5 mL, 0.01 M) together with NH_4OAc (12 mg, 156 µmol, 3.2 eq)) and the solution was purged with N_2. A catalytic amount of Pd/C (10%) was then added and the resulting mixture was purged with H_2. The reaction was left to stir under H_2 atmosphere until all intermediates converged to a single spot on TLC (m/z = 821 (M+Na$^+$)) after which the solution was filtered over celite, diluted with H_2O and extracted with DCM (3x). The combined organic layers were washed with brine, dried with $MgSO_4$ and concentrated *in vacuo*. The resulting residue was then subjected to general hydrogenation procedure C to give the title compound (28 mg, 45 µmol, 94%) as a pale oil. $[\alpha]_D^{25}$ = -64.3 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.29-7.27 (m, 2H, C*H*$_{arom}$); 7.06-7.01 (m, 3H, C*H*$_{arom}$); 5.48 (d, 1H, *J* = 2.0 Hz, H-1); 5.11 (d, 1H, *J* = 1.6 Hz, H-1'); 4.41 (d, 1H, *J* = 8.0 Hz, H-1''); 4.24 (dd, 1H, *J* = 2.4, 4.8 Hz, H-2); 3.89 (d, 1H, *J* = 1.2 Hz, 2''-O*H*); 3.78-3.71 (m, 3H, H-2', H-5, H-5'); 3.69-3.49 (m, 19H, H-3, H-3', H-4, H-4', H-4'', H-6'', OC*H*$_3$); 3.45-3.38 (m, 5H, H-2'', H-5'', OC*H*$_3$); 3.17 (t, 1H, *J* = 9.0 Hz, H-3''); 2.94 (d, *J* = 1.6 Hz, 1H, O*H*); 2.45 (d, *J* = 1.6 Hz, 1H, O*H*); 1.34 (d, 3H, *J* = 6.0 Hz, H-6'); 1.27 (d, 3H, *J* = 6.0 Hz, H-6'). ^{13}C-APT NMR (101 MHz) δ: 156.2 (C$_{q,arom}$); 129.7, 122.4, 116.3 (*C*H$_{arom}$); 105.7 (C-1''); 98.6 (C-1'); 97.2 (C-1); 85.6 (C-3''); 81.7 (C-4'); 81.5 (C-3); 80.3 (C-3'); 75.8 (C-2'); 75.1 (C-2''); 74.2 (C-5''); 72.9 (C-6''); 72.2 (C-2); 71.9 (C-4); 71.2 (C-4''); 69.1 (C-5); 68.4 (C-5'); 60.7, 59.7, 59.2, 57.8, 56.7 (O*C*H$_3$); 17.9 (C-6); 17.7 (C-6'). IR (thin film, cm^{-1}): 1009, 1069, 1120, 1228, 1387, 1494, 2854, 2928, 3429. HRMS calculated for $C_{29}H_{46}O_{14}Na$ 641.27798 [M+H]$^+$; found 641.27776.

4-(hex-1-ynyl)phenyl 2-*O*-(2,3-di-*O*-methyl-4-*O*-(2-*O*-benzyloxycarbonyl-3,4-di-*O*-benzyl-6-*O*-methyl-ß-D-glucopyranosyl)-α-L-rhamnopyranosyl)-3-*O*-methyl-4-*O*-benzyl-α-L-rhamnopyranoside (35)



The title compound was synthesized according to general procedure A using glycan **8** (46 mg, 41 µmol, 1.0 eq) and 1-hexyne (14 µL, 122 µmol, 3.0 eq). Column chromatography (*n*-pentane-Et_2O 4:6) yielded the product (40 mg, 37 µmol, 91%) as a yellow oil. $[\alpha]_D^{25}$ = -60.9 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.37-7.21 (m, 22H, C*H*$_{arom}$); 6.96-6.94 (m, 2H, C*H*$_{arom}$); 5.48 (d, 1H, *J* = 1.6 Hz, H-1); 5.24-5.15 (m, 3H, H-1', PhC*H*$_{2,Cbz}$); 4.89 (d, 1H, *J* = 11.2 Hz, PhC*H*H); 4.80-4.76 (m, 4H, PhC*H*H, PhC*H*H, H-1'', H-2''); 4.70-4.62 (m, 3H, PhCH*H*, PhCH*H*, PhCH*H*); 4.25 (dd, 1H, *J* = 2.4, 2.8 Hz, H-2); 3.79 (dd, 1H, *J* = 3.0, 9.4 Hz, H-3); 3.76-3.61 (m, 7H, H-2', H-3'', H-4'', H-5, H-5', H-5'', H-6''); 3.57-3.43 (m, 9H, H-4, H-4', H-6'', OC*H*$_3$); 3.39-3.32 (m, 7H, H-3', OC*H*$_3$); 2.39 (t, 1H, *J* = 7.0 Hz, C*H*$_2$); 1.63-1.52 (m, 2H, C*H*$_2$); 1.51-1.42 (m, 2H, C*H*$_2$); 1.32-1.25 (m, 6H, H-6, H-6'); 0.94 (t, 3H, *J* = 7.4 Hz, C*H*$_3$). ^{13}C-APT NMR (101 MHz) δ: 155.3 (C$_{q,arom}$); 154.7 (*C*O$_{Cbz}$); 138.5, 138.4, 138.2, 135.5 (C$_{q,arom}$); 133.0, 128.8, 128.6, 128.6, 128.5, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7 (*C*H$_{arom}$); 118.0 (C$_{q,arom}$); 116.2 (*C*H$_{arom}$); 101.1 (C-1''); 98.5 (C-1'); 96.9 (C-1); 89.4 (C$_{q,alkyne}$); 83.3 (C-4''); 82.0 (C-3); 80.8, 80.1 (C-4 and C-4'); 80.1 (C$_{q,alkyne}$); 78.2 (C-2''); 77.9, 77.7 (C-3'', C-5''); 77.0 (C-2'); 75.4, 75.2, 75.1 (Ph*C*H$_2$); 75.0 (C-3') 73.0 (C-2); 71.1 (C-6''); 69.9 (Ph*C*H$_2$); 68.7 (C-5); 68.0 (C-5'); 59.9, 59.1, 58.3, 57.6, (O*C*H$_3$); 31.0, 22.1, 19.2 (*C*H$_2$); 18.2, 18.1 (C-6 and C-6'); 13.8 (*C*H$_3$). IR (thin film, cm^{-1}): 1030, 1055, 1072, 1093, 1120, 1140, 1258, 1387, 1454, 1507, 1757, 2929. HRMS calculated for $C_{63}H_{76}O_{16}Na$ 1111.50256 $[M+Na]^+$; found 1111.50185.

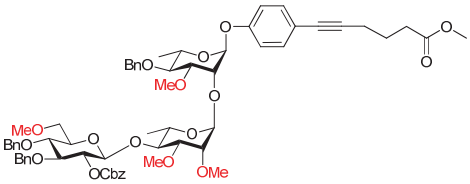
4-(1-hydroxyhex-6-ynyl)phenyl 2-*O*-(2,3-di-*O*-methyl-4-*O*-(2-*O*-benzyloxycarbonyl-3,4-di-*O*-benzyl-6-*O*-methyl-ß-D-glucopyranosyl)-α-L-rhamnopyranosyl)-3-*O*-methyl-4-*O*-benzyl-α-L-rhamnopyranoside (36)



The title compound was synthesized according to general procedure A using glycan **8** (53 mg, 47 µmol, 1.0 eq) and 5-hexyn-1-ol (15 µL, 140 µmol, 3.0 eq). Column chromatography (*n*-pentane-Et_2O 1:4) yielded the product (42 mg, 38 µmol, 81%) as a yellow oil. $[\alpha]_D^{25}$ = -105.3 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.36-7.21 (m, 22H, C*H*$_{arom}$); 6.96 (dd, 2H, *J* = 2.2, 7.0 Hz, C*H*$_{arom}$); 5.48 (d, 1H, *J* = 2.0 Hz, H-1); 5.24-5.15 (m, 3H, H-

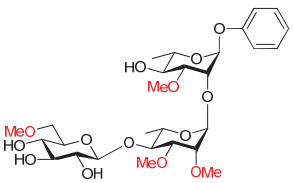
1', PhCH_2); 4.89 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.80-4.76 (m, 4H, PhC*H*H, PhC*H*H, H-1'', H-2''); 4.69-4.62 (m, 3H, PhCH*H*, PhCH*H*, PhCH*H*); 4.25 (dd, 1H, *J* = 2.0, 2.8 Hz, H-2); 3.79 (dd, 1H, *J* = 3.0, 9.4 Hz, H-3); 3.76-3.61 (m, 9H, H-2', H-3'', H-4'', H-5, H-5', H-5'', H-6", CH_2OH); 3.56-3.42 (m, 9H, H-4, H-4', H-6'', OCH_3); 3.39-3.34 (m, 7H, H-3', OCH_3); 2.44 (t, 1H, *J* = 7.0 Hz, C$H_{2,Phth}$); 1.77-1.59 (m, 4H, CH_2); 1.29 (d, 3H, *J* = 6.4 Hz, H-6'); 1.26 (d, 3H, *J* = 6.4 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 155.3 ($C_{q,arom}$); 154.7 (CO_{Cbz}); 138.5, 138.4, 138.2, 135.5 ($C_{q,arom}$); 133.0, 128.8, 128.6, 128.6, 128.5, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7 (CH_{arom}); 117.8 ($C_{q,arom}$); 116.2 (CH_{arom}); 101.1 (C-1''); 98.5 (C-1'); 96.9 (C-1); 88.9 ($C_{q,alkyne}$); 83.3 (C-4''); 82.0 (C-3); 80.8, 80.6 (C-4 and C-4'); 80.1 ($C_{q,alkyne}$); 78.2 (C-2''); 77.9, 77.7 (C-3" and C-5"); 77.0 (C-2'); 75.4, 75.2, 75.1 (PhCH_2); 75.0 (C-3') 73.0 (C-2); 71.1 (C-6''); 69.9 (PhCH_2); 68.7 (C-5); 68.0 (C-5'); 62.6 (CH_2OH); 59.8, 59.1, 58.3, 57.6, (OCH_3); 32.0, 25.2, 19.3 (CH_2); 18.2, 18.0 (C-6 and C-6'). IR (thin film, cm^{-1}): 1055, 1072, 1092, 1120, 1140, 1258, 1455, 1507, 1747, 2932. HRMS calculated for $C_{63}H_{80}O_{17}N$ 1122.54208 $[M+NH_4]^+$; found 1122.54262.

Methyl 6-(4-(2-*O*-(2,3-di-*O*-methyl-4-*O*-(2-*O*-benzyloxycarbonyl-3,4-di-*O*-benzyl-6-*O*-methyl-ß-D-glucopyranosyl)-α-L-rhamnopyranosyl)-3-*O*-methyl-4-*O*-benzyl-α-L-rhamnopyranosyl))phenylhex-5-ynoate (37)



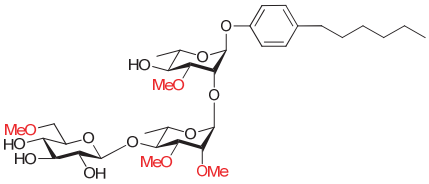
The title compound was synthesized according to general procedure A using glycan **8** (55 mg, 48 µmol, 1.0 eq) and methyl 5-hexynoate (19 µL, 145 µmol, 3.0 eq). Column chromatography (*n*-pentane-Et_2O 4:6) yielded the product (65 mg, 50 µmol, 96%) as a yellow oil. $[\alpha]_D^{25}$ = -64.4 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.37-7.21 (m, 22H, CH_{arom}); 6.97-6.95 (m, 2H, CH_{arom}); 5.48 (d, 1H, *J* = 1.6 Hz, H-1); 5.24-5.15 (m, 3H, H-1', PhCH_2); 4.89 (d, 1H, *J* = 11.2 Hz, PhC*H*H); 4.80-4.76 (m, 4H, PhC*H*H, PhC*H*H, H-1'', H-2''); 4.70-4.62 (m, 3H, PhCH*H*, PhCH*H*, PhCH*H*); 4.25 (dd, 1H, *J* = 1.6, 3.2 Hz, H-2); 3.79 (dd, 1H, *J* = 3.0, 9.4 Hz, H-3); 3.76-3.61 (m, 10H, H-2', H-3'', H-4'', H-5, H-5', H-5'', H-6", COOCH_3); 3.57-3.42 (m, 9H, H-4, H-4', H-6'', OCH_3); 3.39-3.32 (m, 7H, H-3', OCH_3); 2.53-2.45 (m, 4H, CH_2); 1.92 (quint, 2H, *J* = 7.2 Hz, CH_2); 1.29 (d, 3H, *J* = 6.0 Hz, H-6'); 1.26 (d, 3H, *J* = 6.0 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 173.8 (*C*OOCH$_3$); 155.5 ($C_{q,arom}$); 154.7 (CO_{Cbz}); 138.5, 138.4, 138.2, 135.5 ($C_{q,arom}$); 133.1, 128.8, 128.6, 128.6, 128.5, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7 (CH_{arom}); 117.6 ($C_{q,arom}$); 116.2 (CH_{arom}); 101.1 (C-1''); 98.5 (C-1'); 96.9 (C-1); 87.8 ($C_{q,alkyne}$); 83.3 (C-4''); 82.0 (C-3); 81.1 ($C_{q,alkyne}$); 80.8, 80.1 (C-4 and C-4'); 78.2 (C-2''); 77.9, 77.7 (C-3" and C-5"); 77.0 (C-2'); 75.4, 75.2, 75.1 (PhCH_2); 75.0 (C-3') 72.9 (C-2); 71.1 (C-6''); 69.9 (PhCH_2); 68.8 (C-5); 68.0 (C-5'); 59.8, 59.1, 58.3, 57.6, (OCH_3); 51.7 (COO*C*H$_3$); 33.0, 24.1, 19.0 (CH_2); 18.2, 18.0 (C-6 and C-6'). IR (thin film, cm^{-1}): 1029, 1055, 1072, 1092, 1120, 1140, 1205, 1256, 1314, 1384, 1454, 1507, 1740, 1754, 2932. HRMS calculated for $C_{64}H_{76}O_{18}Na$ 1155.49239 $[M+Na]^+$; found 1155.49253.

Phenyl 2-*O*-(2,3-di-*O*-methyl-4-*O*-(6-*O*-methyl-ß-D-glucopyranosyl)-α-L-rhamnopyranosyl)-3-*O*-methyl-α-L-rhamnopyranoside (22)



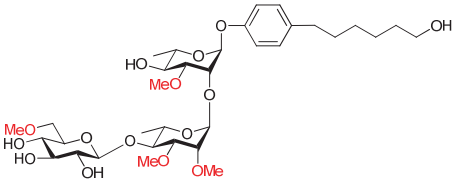
Compound **8** (34 mg, 30 µmol, 1.0 eq) was hydrogenated using general procedure C to give the title compound (14 mg, 23 µmol, 77%) as a pale oil. $[\alpha]_D^{25}$ = -53.7 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.33-7.28 (m, 2H, C*H*$_{arom}$); 7.05-7.02 (m, 3H, C*H*$_{arom}$); 5.49 (d, 1H, *J* = 1.6 Hz, H-1); 5.11 (d, 1H, *J* = 1.2 Hz, H-1'); 4.45 (d, 1H, *J* = 7.6 Hz, H-1''); 4.24 (dd, 1H, *J* = 1.6, 3.2 Hz, H-2); 4.12 (bs, 1H, O*H*); 3.79-3.59 (m, 8H, H-2', H-3, H-3', H-4', H-5, H-5', H-6''); 3.57-3.35 (m, 18H, H-2'', H-3'', H-4, H-4'', H-5'', OC*H*$_3$); 2.52 (bs, 1H, O*H*); 1.34 (d, 3H, *J* = 6.4 Hz, H-6'); 1.27 (d, 3H, *J* = 6.0 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 156.2 (C$_{q,arom}$); 129.7, 122.4, 116.3 (*C*H$_{arom}$); 105.2 (C-1''); 98.5 (C-1'); 97.2 (C-1); 81.5, (C-3); 81.3 (C-4'); 80.3 (C-3'); 76.6 (C-3''); 75.9 (C-2'); 74.8 (C-2''); 74.3 (C-4''); 72.9 (C-6''); 72.3 (C-2); 71.9 (C-4); 71.5 (C-5''); 69.2 (C-5); 68.3 (C-5'); 59.8, 59.1, 57.8, 56.7 (O*C*H$_3$); 17.9 (C-6); 17.7 (C-6'). IR (thin film, cm^{-1}): 1009, 1067, 1118, 1202, 1229, 1457, 2931, 3400. HRMS calculated for $C_{28}H_{44}O_{14}Na$ 627.26233 [M+Na]$^+$; found 627.26222.

4-hexylphenyl 2-*O*-(2,3-di-*O*-methyl-4-*O*-(6-*O*-methyl-ß-D-glucopyranosyl)-α-L-rhamnopyranosyl)-3-*O*-methyl-α-L-rhamnopyranoside (23)



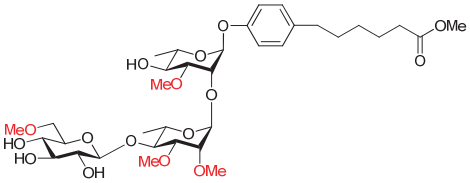
Compound **35** (32 mg, 29 µmol, 1.0 eq) was hydrogenated using general procedure C to give the title compound (15 mg, 22 µmol, 74%) as a pale oil. $[\alpha]_D^{25}$ = -50.3 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.10 (d, 2H, *J* = 8.4 Hz, C*H*$_{arom}$); 6.95 (dd, 2H, *J* = 2.0, 6.8 Hz, C*H*$_{arom}$); 5.44 (d, 1H, *J* = 2.0 Hz, H-1); 5.10 (d, 1H, *J* = 1.6 Hz, H-1'); 4.45 (d, 1H, *J* = 7.6 Hz, H-1''); 4.24 (dd, 1H, *J* = 2.0, 2.8 Hz, H-2); 4.09 (bs, 1H, O*H*); 3.78-3.59 (m, 8H, H-2', H-3, H-3', H-4', H-5, H-5', H-6''); 3.57-3.35 (m, 18H, H-2'', H-3'', H-4, H-4'', H-5'', OC*H*$_3$); 3.21 (bs, 2H, O*H*); 2.55 (t, 2H, *J* = 7.6 Hz, C*H*$_2$); 2.45 (bs, 1H, O*H*); 1.58 (quint, 2H, *J* = 7.2 Hz, C*H*$_2$); 1.33-1.25 (m, 12H, C*H*$_2$, H-6, H-6'); 0.88 (t, 3H, *J* = 6.8 Hz, C*H*$_3$). ^{13}C-APT NMR (101 MHz) δ: 154.3, 137.0 (C$_{q,arom}$); 129.5, 116.1 (*C*H$_{arom}$); 105.2 (C-1''); 98.4 (C-1'); 97.4 (C-1); 81.5, (C-3); 81.4 (C-4'); 80.3 (C-3'); 76.6 (C-3''); 75.9 (C-2'); 74.8 (C-2''); 74.2 (C-4''); 73.0 (C-6''); 72.3 (C-2); 71.9 (C-4); 71.6 (C-5''); 69.1 (C-5); 68.3 (C-5'); 59.8, 59.1, 57.8, 56.7 (O*C*H$_3$); 35.3, 31.9, 31.8, 29.1, 22.8 (*C*H$_2$); 17.9 (C-6); 17.7 (C-6'); 14.2 (*C*H$_3$). IR (thin film, cm^{-1}): 1013, 1066, 1116, 1457, 1510, 2856, 2929, 3427. HRMS calculated for $C_{34}H_{56}O_{14}Na$ 711.35623 [M+Na]$^+$; found 711.35585.

4-(6-hydroxyhexyl)phenyl 2-*O*-(2,3-di-*O*-methyl-4-*O*-(6-*O*-methyl-ß-D-glucopyranosyl)-α-L-rhamnopyranosyl)-3-*O*-methyl-α-L-rhamnopyranoside (24)



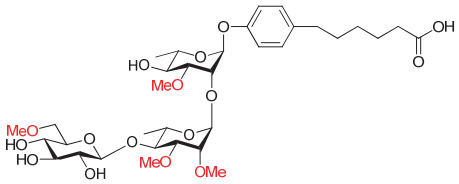
Compound **36** (28 mg, 25 µmol, 1.0 eq) was hydrogenated using general procedure C to give the title compound (16 mg, 23 µmol, 90%) as a pale oil. $[\alpha]_D^{25}$ = -39.6 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.10 (d, 2H, *J* = 8.8 Hz, C*H*$_{arom}$); 6.95 (dd, 2H, *J* = 2.0, 6.4 Hz, C*H*$_{arom}$); 5.43 (d, 1H, *J* = 2.0 Hz, H-1); 5.11 (d, 1H, *J* = 1.6 Hz, H-1'); 4.45 (d, 1H, *J* = 7.6 Hz, H-1''); 4.24 (dd, 1H, *J* = 1.6, 3.2 Hz, H-2); 4.03 (bs, 1H, O*H*); 3.78-3.72 (m, 3H, H-2', H-5, H-5'); 3.70-3.58 (m, 7H, H-3, H-3', H-4', H-6'', C*H*$_2$OH); 3.57-3.35 (m, 17H, H-2'', H-3'', H-4, H-4'', H-5'', OC*H*$_3$); 3.08 (bs, 1H, O*H*); 2.98 (bs, 1H, O*H*); 2.56 (t, 2H, *J* = 7.6 Hz, C*H*$_2$); 2.45 (bs, 1H, O*H*); 1.59 (quint, 4H, *J* = 7.2 Hz, C*H*$_2$); 1.40-1.33 (m, 4H, C*H*$_2$); 1.33 (d, 3H, *J* = 6.4 Hz, H-6'); 1.28 (d, 3H, *J* = 6.4 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 154.3, 136.8 (C$_{q,arom}$); 129.5, 116.2 (*C*H$_{arom}$); 105.3 (C-1''); 98.4 (C-1'); 97.5 (C-1); 81.5, (C-3); 81.4 (C-4'); 80.3 (C-3'); 76.6 (C-3''); 75.9 (C-2'); 74.8 (C-2''); 74.1 (C-4''); 73.0 (C-6''); 72.2 (C-2); 72.0 (C-4); 71.8 (C-5''); 69.1 (C-5); 68.3 (C-5'); 63.1 (*C*H$_2$OH); 59.8, 59.1, 57.8, 56.7 (O*C*H$_3$); 35.2, 32.8, 31.7, 29.2, 25.7 (*C*H$_2$); 17.9 (C-6); 17.7 (C-6'). IR (thin film, cm^{-1}): 1007, 1066, 1118, 1199, 1229, 1508, 2929, 3398. HRMS calculated for $C_{34}H_{60}O_{15}N$ 722.39575 $[M+NH_4]^+$; found 722.39540.

Methyl 6-(4-(2-*O*-(2,3-di-*O*-methyl-4-*O*-(6-*O*-methyl-ß-D-glucopyranosyl)-α-L-rhamnopyranosyl)-3-*O*-methyl-α-L-rhamnopyranosyl))phenyl hexanoate (38)



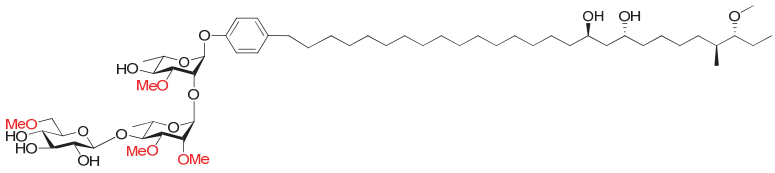
Compound **37** (31 mg, 27 µmol, 1.0 eq) was hydrogenated using general procedure C to give the title compound (11 mg, 15 µmol, 55%) as a pale oil. Spectroscopic data were accordance with those previously reported in the literature.[44]

4-(6-carboxyhexyl)phenyl 2-*O*-(2,3-di-*O*-methyl-4-*O*-(6-*O*-methyl-ß-D-glucopyranosyl)-α-L-rhamnopyranosyl)-3-*O*-methyl-α-L-rhamnopyranoside (25)



Compound **38** (11 mg, 15 µmol, 1.0 eq) was dissolved in EtOH/1N NaOH (3:1, 4 mL, 0.004 M) and the resulting mixture was allowed to stir for 16 hours. The mixture was then neutralized with amberlite H^+, filtered and concentrated *in vacuo*. Column chromatography (DCM-MeOH 4:1) gave the title compound (11 mg, 15 µmol, 100%) as a pale oil. $[\alpha]_D^{25}$ = -253.3 ° (c = 0.2, MeOH). ^{1}H-NMR (500 MHz, CD_3OD) δ: 7.13 (dd, 2H, *J* = 2.3, 6.8 Hz, CH_{arom}); 6.96 (dd, 2H, *J* = 2.0, 6.5 Hz, CH_{arom}); 5.52 (d, 1H, *J* = 1.5 Hz, H-1); 5.12 (d, 1H, *J* = 2.0 Hz, H-1'); 4.57 (d, 1H, *J* = 8.0 Hz, H-1''); 4.25 (dd, 1H, *J* = 2.0, 3.0 Hz, H-2); 3.79-3.76 (m, 2H, H-2', H-5'); 3.72-3.58 (m, 8H, H-3, H-3', H-4', H-5, H-6'', CH_2OH); 3.53-3.46 (m, 7H, H-4, OCH_3); 3.40-3.28 (m, 6H, H-3'', H-4, H-5'', OCH_3); 3.17 (t, 1H, *J* = 8.5 Hz, H-2''); 2.59 (t, 2H, *J* = 7.5 Hz, CH_2); 2.29 (t, 2H, *J* = 7.2 Hz, CH_2); 1.59 (quint, 4H, *J* = 7.5 Hz, CH_2); 1.40-1.33 (m, 2H, CH_2); 1.27 (d, 3H, *J* = 6.0 Hz, H-6'); 1.24 (d, 3H, *J* = 6.0 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 177.9 (*C*OOH); 155.9, 137.9 ($C_{q,arom}$); 130.5, 117.4 (*C*H$_{arom}$); 104.9 (C-1''); 100.4 (C-1'); 98.9 (C-1); 82.2 (C-3); 82.0 (C-4'); 79.1 (C-3'); 77.9 (C-3''); 77.8 (C-2'); 76.9 (C-4); 76.0 (C-2); 75.6 (C-2''); 73.3 (C-4''); 73.1 (C-6''); 71.7 (C-5''); 69.2 (C-5); 68.3 (C-5'); 59.8, 59.1, 58.5, 57.5 (O*C*H$_3$); 35.9, 35.1, 32.5, 29.8, 26.0 (*C*H$_2$); 18.3 (C-6); 18.2 (C-6'). IR (thin film, cm^{-1}): 1067, 1119, 1199, 1229, 1510, 1717, 2923, 3409. HRMS calculated for $C_{34}H_{54}O_{16}Na$ 741.33041 $[M+Na]^+$; found 741.33005.

4-((3*R*,4*S*,9*R*,11*R*)-3-methoxy-4-methylheptacos-26-yne-9,11-diol)phenyl 2-*O*-(2,3-di-*O*-methyl-4-*O*-(6-*O*-methyl-ß-D-glucopyranosyl)-α-L-rhamnopyranosyl)-3-*O*-methyl-α-L-rhamnopyranoside (26)



4-((3*R*,4*S*,9*R*,11*R*)-3-methoxy-4-methylheptacos-26-yne-9,11-diol)phenyl 2-*O*-(2,3-di-*O*-methyl-4-*O*-(2-*O*-benzyloxycarbonyl-3,4-di-*O*-benzyl-6-*O*-methyl-ß-D-glucopyranosyl)-α-L-rhamnopyranosyl)-3-*O*-methyl-4-*O*-benzyl-α-L-rhamnopyranoside (Chapter 5, 26 mg, 18 µmol, 1.0 eq) was hydrogenated using general procedure C to give the title compound (14 mg, 13 µmol, 74%) as a pale oil. $[\alpha]_D^{25}$ = -38.4 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.10 (d, 2H, *J* = 8.8 Hz, CH_{arom}); 6.95 (d, 2H, *J* = 8.4 Hz, CH_{arom}); 5.43 (d, 1H, *J* = 1.2 Hz, H-1); 5.10 (d, 1H, *J* = 1.2 Hz, H-1'); 4.45 (d, 1H, *J* = 7.6 Hz, H-1''); 4.23 (d, 1H, *J* = 2.4 Hz, H-2); 4.09 (bs, 1H, O*H*); 3.98-3.90 (m, 2H, CH_{Phth}); 3.78-3.71 (m, 3H, H-2', H-5, H-5'); 3.69-3.60 (m, 5H, H-3, H-3', H-4', H-6''); 3.58-3.47 (m, 12H, H-3'', H-4, H-5'', OCH_3); 3.46-3.34 (m, 8H, H-2'', H-4'', OCH_3); 2.88-2.79 (m, 1H, CH_{Phth}); 2.55 (t, 2H, *J* = 7.6 Hz, C$H_{2,Phth}$); 2.49 (bs, 2H, O*H*); 1.72-1.64 (m, 1H, CH_{Phth}); 1.62-1.25 (m, 51H, H-6, H-6',

C$H_{2,Phth}$); 1.15-1.05 (m, 1H, CH_{Phth}); 0.91 (t, 3H, J = 7.4 Hz, C$H_{3,Phth}$); 0.83 (d, 3H, J = 6.8 Hz, C$H_{3,Phth}$). ^{13}C-APT NMR (101 MHz) δ: 154.3, 137.0 ($C_{q,arom}$); 129.5, 116.2 (CH_{arom}); 105.2 (C-1''); 98.4 (C-1'); 97.5 (C-1); 86.8 (CH_{Phth}); 81.5, (C-3); 81.3 (C-4'); 80.3 (C-3'); 76.6 (C-3''); 75.9 (C-2'); 74.8 (C-2''); 74.3 (C-4''); 72.9 (C-6''); 72.2 (C-2); 71.9 (C-4); 71.5 (C-5''); 69.6, 69.5 (CH_{Phth}); 69.1 (C-5); 68.3 (C-5'); 59.8, 59.1, 57.8, 57.5, 56.7 (OCH_3); 42.4, 37.6, 35.2 ($CH_{2,Phth}$); 34.9 (CH_{Phth}); 32.8, 31.8, 29.8, 29.7, 29.6, 29.4, 27.7, 26.3, 25.9, 22.5 ($CH_{2,Phth}$); 17.9, 17.7 (C-6 and C-6'); 15.0, 10.2 ($CH_{3,Phth}$). IR (thin film, cm^{-1}): 1012, 1070, 1116, 1228, 1511, 2855, 2925, 3363. HRMS calculated for $C_{57}H_{102}O_{17}Na$ 1081.70092 $[M+Na]^+$; found 1081.70035.

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