Synthesis of mycobacterial phenolic glycolipids

Dijk, J.H.M. van

Chapter 6

Synthesis of PGLs originating from *M. kansasii* and *M. gastri*

Koen Rijpkema, Rutger Groeneveld, Stavroula Karageorgi, Bas van den Berg and many LO1/LO3 students contributed to this chapter.

Introduction

Mycobacterium kansasii is a pathogenic nontuberculous mycobacterium that was first isolated in 1953.[1] *M. kansasii* is known to cause pulmonary disease resembling tuberculosis[2,3] and is often considered to be the most pathogenic nontuberculous mycobacterium.[4–7] Unlike other pathogenic mycobacteria, *M. kansasii* can be isolated from (tap) water and soil,[8–11] and human-to-human transmission is not thought to occur.[12] It has been postulated that this may be due to the relatively hydrophilic nature of its (glyco)lipids,[13] as it has been demonstrated that hydrophobicity increases aerosol transmission, which increases virulence and pathogenicity.[14] The first isolated phenolic glycolipid ever, discovered in 1957, originated from *M. kansasii* and it was called "Mycoside A".[15–20] It is also referred to as PGL-K7, and its structure was determined to be a triglycosyl phenolic glycolipid, carrying a 2-*O*-methyl-α-L-fucopyranosyl-(1→3)-2-*O*-methyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-methyl-α-L-rhamnopyranosyl glycan. Thereafter several more PGLs of *M. kansasii* have been discovered, isolated and almost all of their structures have been elucidated (Figure 1).[18–24] *M. gastri*, the "mycobacterium of the stomach", was found to produce the same PGLs as *M. kansasii*.[22,28,29]

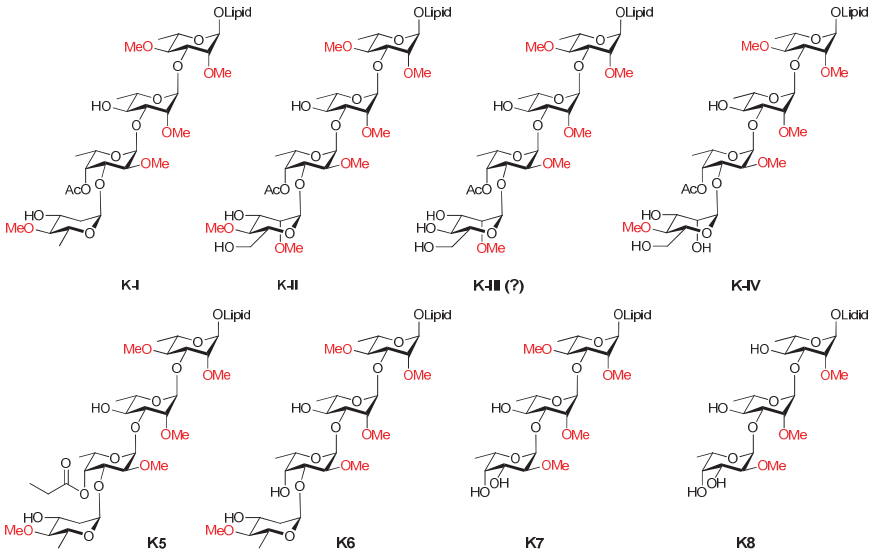


Figure 1. Glycoforms of *M. kansasii* and *M. gastri* PGLs, with the corresponding serovars below the structures.

Several syntheses of PGL glycans of *M. kansasii* have been published to date. Gurjar and Reddy were the first to synthesize a trisaccharide of *M. kansasii*.[30] Zegelaar-Jaarsveld *et al.* have reported the synthesis of three different tetrasaccharides (serovars I, II and IV), all bearing a tyramine moiety for conjugation purposes.[31–33] Lowary and coworkers have synthesized some of the natural glycans as well as many analogues of *M. kansasii* PGLs[34] and they have generated squaramide based glycoconjugates of these compounds as well.[35] However, in order to fully understand the interactions between PGLs and the host immune system, pure synthetic complete PGLs are required. Therefore, this chapter describes the synthesis of all known PGLs originating from *M. kansasii* and *M. gastri* as well as a hypothesized biosynthetic intermediate (K-III).[22,25]

The general strategy for the synthesis of these phenolic glycolipids follows the strategy described in Chapters 4 and 5 for the synthesis of complete PGLs (Figure 2).[36,37] Glycans bearing an iodophenol and protected with hydrogenation labile groups are to be synthesized from the 'reducing end', after which they can be attached to a phthiocerol

alkyne derivative using a Sonogashira cross coupling. The resulting diol can then be esterified with mycocerosic acids using Steglich conditions and a final hydrogenation will then lead to the global deprotection and concurrent reduction of the conjugated internal alkyne which is formed in the Sonogashira reaction.

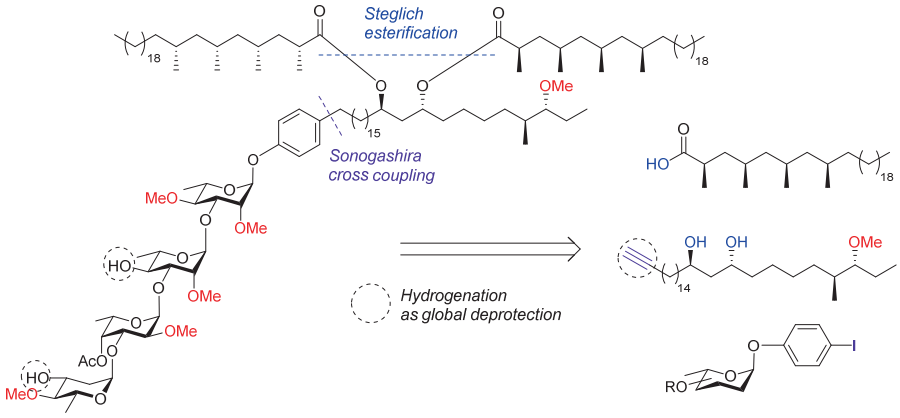


Figure 2. General synthetic strategy of *M. kansasii* PGLs with PGL K-I as an example.

This synthetic strategy requires the oligosaccharides to be protected with protecting groups that are susceptible to hydrogenation conditions. In Chapters 4 and 5 it was described that a carboxybenzyl (Cbz) protecting group can be used as a hydrogenation labile group which - in most cases - was capable of steering the stereoselective formation of 1,2-*trans* linkages by means of neighboring group participation. A common structural feature in the glycans of *M. kansasii* and *M. gastri* PGLs is the presence of a methyl ether on the C-2 position of the constituting monosaccharides, as well as the presence of a C-2 deoxy sugar. The C-2 methyl bearing rhamnosides are all 1,2-*trans* linked. It has previously been established that mannose configured donors acylated at the C-3 position are capable of selectively forming 1,2-*trans* linkages via remote participation.[38–40] It will therefore be investigated here, whether a C-3 Cbz moiety can provide a similar long range stereodirecting effect in the assembly of the PGLs outlined in this chapter as this could drastically improve the efficiency of the syntheses. The building blocks required for the synthesis of the various serotypes are depicted in Figure 3.

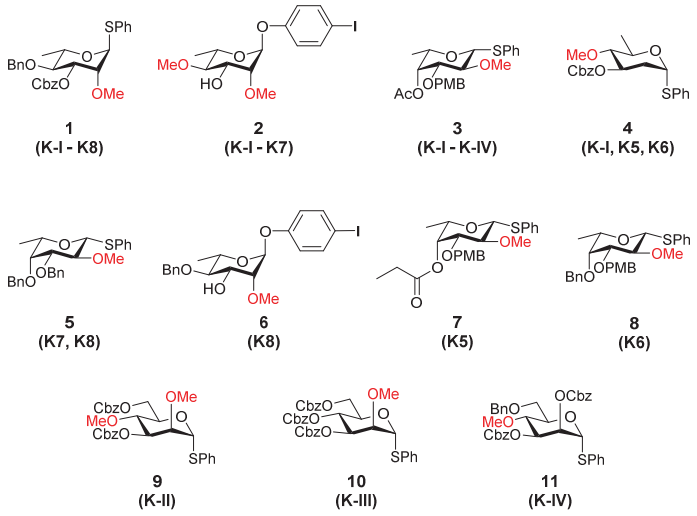
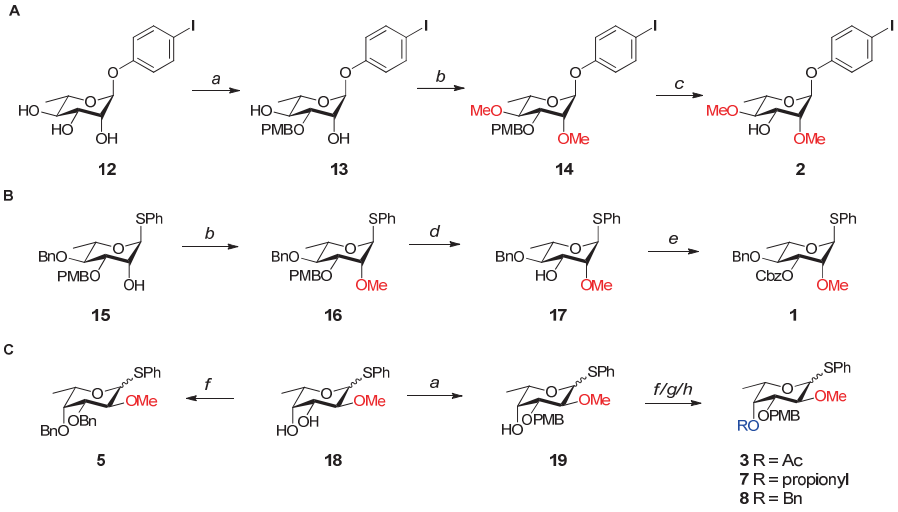


Figure 3. Required building blocks. Serovars which can be made with the corresponding building block are between brackets.

Four of the six tetrasaccharides outlined in Figure 1 (K-I – K-IV) contain the same trisaccharide core (phenyl (1→3)-2-*O*-methyl-4-*O*-acetyl-α-L-fucopyranosyl-(1→3)-2-*O*-methyl-α-L-rhamnopyranosyl-(1→3)-2,4-di-*O*-methyl-α-L-rhamnopyranose) which can be synthesized with acceptor **2** and donors **1** and **3**. Donor **1** bears a C-3 Cbz moiety for remote participation, which can then be removed under mild basic conditions. Previously, Zegelaar-Jaarsveld *et al.* performed a fucosylation reaction in the assembly of *M. kansasii* PGL glycans, with a donor that is very similar to donor **3** using IDCP as a mild promotor.[31] Based on the high stereoselectivity reported by Zegelaar-Jaarsveld, donor **3** was selected for the assembly of the K-I - K-IV glycans. In line with this approach, fucose donors **7**, **8** and **5** will be probed for the assembly of the PGLs of serovars K5, K6 and K7/K8, respectively. Instead of a post-glycosylation deoxygenation approach, as described by Zegelaar-Jaarsveld,[33] 2,6-dideoxy donor **4** was designed to minimize the number of steps in the tetrasaccharide stadium for the synthesis of serovars K-I, K5 and K6. Acceptor **6** has been described in Chapter 4 and can be used for the assembly of the serovar K8 PGL. Finally, thiomannosides **9**, **10** and **11**, all bearing a Cbz moiety for (remote) participation were projected to be used as the terminal building blocks for the PGLs of serovars K-II, K-III, and K-IV, respectively.

Results and Discussion

The synthesis of the required rhamnose and fucose building blocks is depicted in Scheme 1. Rhamnose acceptor **2** was synthesized from triol **12** in 40% yield over 3 steps. First the C-3 position was selectively protected with a PMB ether, [41] after which the methyl ethers were introduced on the C-2 and C-4 positions and the PMB was removed with a catalytic amount of HCl in HFIP.[42]

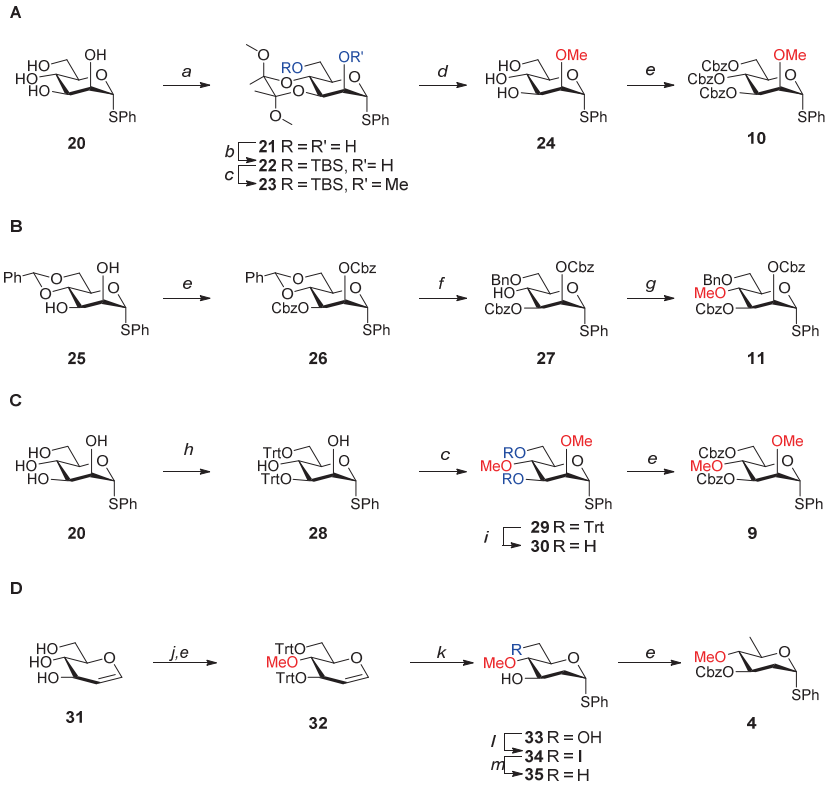


Scheme 1. Rhamnose and fucose building block synthesis. Reagents and conditions: (a) 1. Bu_2SnO, toluene reflux, 2. PMBCl, TBABr, toluene, reflux, 53% (**13**), 86% (**19**), (b) NaH, MeI, DMF, 0 °C → RT, 94%, (**14**), 97% (**16**), (c) HCl/HFIP, HFIP/DCM, 81%, (d) HCl/HFIP, TES, HFIP/DCM, 80%, (e) CbzCl, DMAP, DCM, 0 °C → RT, 100%. (f) NaH, BnBr, DMF, 0 °C → RT, 96%, (**5**), 96% (**8**), (g) Ac_2O, pyridine, DMAP, DCM 97%, (h) propionic anhydride, pyridine, DMAP, DCM 71%.

An alternative route towards this this acceptor from triol **12** involved the installation of an isopropylidene group on the 3,4-diol, methylation of the remaining alcohol, removal of the isopropylidene, regioselective installation of the PMB ether on the equatorial C-3 position, methylation of the C-4 alcohol and unmasking of the C-3 PMB ether. This latter route provided building block **2** in 66% yield over 6 steps. Rhamnose donor **1** was synthesized by methylating intermediate **15** (described in Chapter 4), removing the C-3 PMB ether and replacing it with a Cbz, giving **1** in 78% yield over 3 steps.

Fucose donor **5** was synthesized by benzylating diol **18** (described in Chapter 4), in 96% yield. Fucose donors **3, 7** and **8** could be formed from intermediate **19**, in turn regioselectively generated from **18**, in 97%, 71% and 96% yield, respectively.

The synthesis of the required terminal building blocks is depicted in Scheme 2. The installation of the C-2 methyl ether, present in thiomannoside **10** (Scheme **2A**) was accomplished by first protecting the 3,4-bis-equatorial diol of mannoside **20** with a butane 2,3-bisacetal (BDA),[43] after which the primary alcohol was silylated with TBSCl and imidazole in DMF. Subsequent methylation of the remaining C-2 alcohol and acidic hydrolysis of the BDA and silyl ether protecting groups was accomplished using 95% aqueous TFA, giving triol **24**, which was then reacted with CbzCl and DMAP in DCM[44] to provide donor **10** in 49% yield over 5 steps from **20**. Mannoside **11** was formed in three steps from benzylidene mannose **25** (Scheme **2B**). First the C-2 and C-3 positions were protected with a Cbz carbonate in 98% yield. Thereafter the benzylidene was reductively opened with TES and TFA to liberate the C-4 alcohol which was to be methylated. This turned out to be a challenging step as the adjacent Cbz groups can migrate or form a cyclic carbonate when conditions are used that are too basic or acidic. Initial conditions that were screened to accomplish this transformation included the use of MeI, Me_2S and Ag_2O in THF,[45] HBF_4 and $TMSCH_2N_2$ in DCM,[46] MeOTf and TTBP in DCM,[47] but all these conditions did not deliver a significant amount of the desired product, possibly due to the methylation of the anomeric thiophenol as a side reaction. Finally, it was found that the use of a large excess of trimethyloxonium tetrafluoroborate (BF_4OMe_3) and TTBP in DCM in combination with a short reaction time (<1 hour) delivered the desired product in 70% yield (63% over 3 steps from **25**). Using Proton Sponge® as an alternative sterically hindered base[48] also delivered the desired product but it proved to be much more difficult to remove traces of this compound, complicating product purification. For the 2,4-di-*O*-methyl mannosyl donor **9** (Scheme **2C**) a route was envisaged in which the C-3 and C-6 hydroxy groups are protected first, whereafter methylation can take place and removal of the temporary protecting groups then set the stage for introduction of a Cbz on the C-3 and C-6 positions.



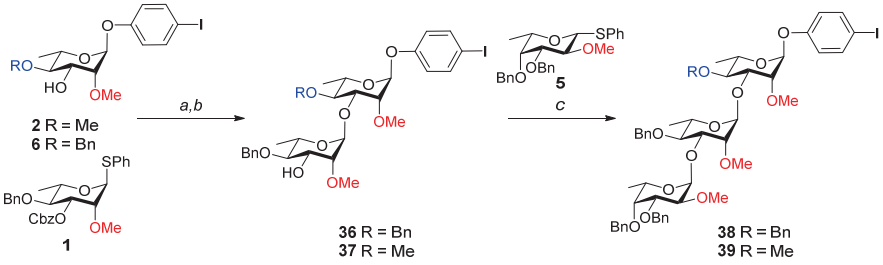
Scheme 2. Terminal sugar building block synthesis. Reagents and conditions: (a) 2,3-butadione, trimethyl orthoformate, CSA, MeOH reflux, 92%, (b) TBSCl, imidazole, DMF, 100%, (c) NaH, MeI, DMF, 0 °C → RT, 92%, (**23**), 90% (**29**), 62% (**32**), (d) 95% TFA, 74%, (e) CbzCl, DMAP, DCM, 0 °C → RT, 79% (**10**), 98% (**26**) 100% (**9**), 94% (**4**), (f) TES, TFA, DCM, 92%, (g) BF_4OMe_3, TTBP, DCM, 70%, (h) TrtCl, pyridine, 50 °C, 67%, (i) AcOH/H_2O, 4:1, 80 °C, 78%, (j) TrtCl, pyridine, 69 °C, 56%, (k) PhSH, [$Re^{V}OCl_3(Me_2S)(Ph_3PO)$], toluene, 75%, (l) I_2, PPh_3, imidazole, toluene, 69 °C, 61%, (m) Pd/C, H_2, $NaHCO_3$, DMF, 82%.

It has previously been reported that 3,6-di-*O* alkylated (Bn/PMB/All) mannosides can be prepared using tin ketal chemistry, but these results were difficult to reproduce.[32,49–51] It was also attempted to selectively protect the C-3 and C-6 positions using bulky pivaloyl esters,[52] which also have a low migratory aptitude under basic conditions.[53] Although the regioselective installation of the C-3- and C-6-pivaloyl esters proceeded smoothly, the subsequent methylation reaction using NaH and MeI produced an inseparable mixture of regioisomers. The methylation conditions used for the

transformation of **27** into **11** did not give any product, likely due to sterically encumbered environment of free alcohols and the relatively low reactivity of the axial C-2 hydroxyl of mannose. Finally, the trityl group was explored as a bulky, but base stable protecting group.[54] Although the yield for the installation of the trityl ethers at C-3 and C-6 positions was rather moderate (67%), the regioselectivity of the reaction was excellent and the product could be easily separated from its regioisomers. During the methylation that followed no migration occurred and the trityls could subsequently be easily removed using mild acidic conditions to replace them with a Cbz, giving donor **9** in 47% yield over 4 steps from **20**.

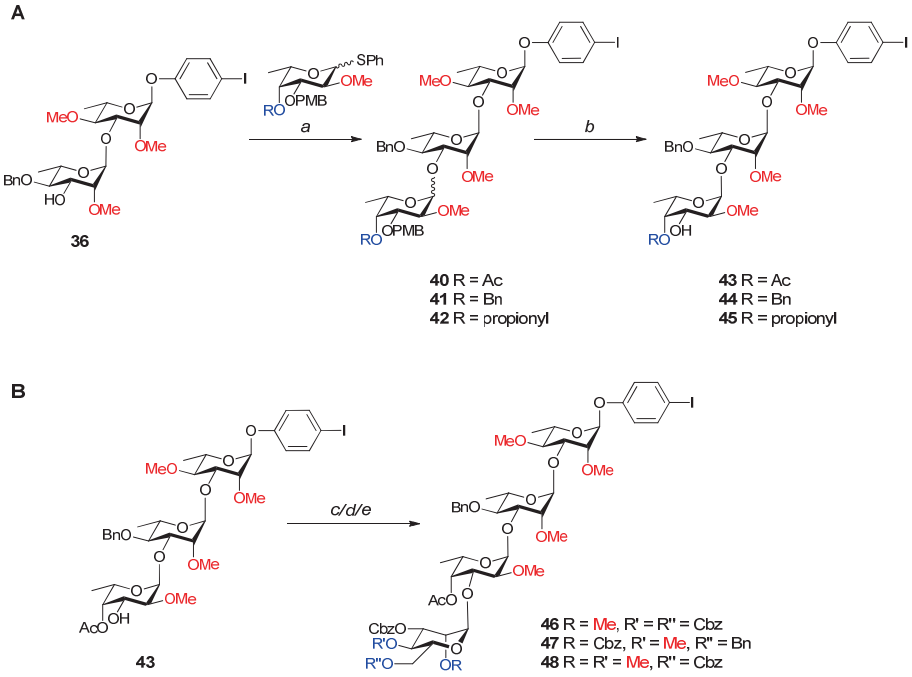
The synthesis of 2,6-dideoxydonor **4** started from D-glucal (Scheme **2D**). It was decided to methylate the C-4 position before deoxygenating the C-6 position as this would leave more options for regioselective manipulations. This way the same approach could be applied as in the assembly of mannose donor **9**. Thus, the C-3 and C-6 hydroxyls were selectively tritylated, after which the remaining free C-4 alcohol could be methylated under basic conditions to give peralkylated glucal **32** in 35% yield over 2 steps. From there on it was decided to first install the anomeric thiophenol before removing the trityls, as the presence of free alcohols during this reaction could possibly lead 1,6-anhydro sugars or polymerization products. In lieu of ordinary acidic conditions such as HCl in dioxane[55] or $PPh_3{\cdot}HBr$,[56] mild conditions using the rhenium complex ($[Re^{V}OCl_3(Me_2S)(Ph_3PO)]$) and PhSH were probed.[57] The first attempt with these conditions yielded a disheartening amount of product but close inspection of the reaction mixture revealed that mono and di-detritylated products were formed as major byproducts. This indicated that the rhenium complex could also cleave the trityl ethers, with PhSH possibly acting as a scavenger for the trityl cations. Therefore, the reaction was performed using a larger excess (4 equivalents) of PhSH and this delivered the desired thiophenol diol **33** in 75% yield. An Appel reaction with I_2, PPh_3 and imidazole next delivered the primary iodide **34** in 61% yield.[58] Reduction of the iodide with Bu_3SnH resulted in partial removal of the anomeric thiophenol, and therefore iodide **34** was hydrogenated with Pd/C and $NaHCO_3$ in DMF[59] to give **35** in 82% yield. Finally, the remaining free alcohol was protected with a Cbz carbonate to give 2,6-dideoxy donor **4** in 94% yield.

With all building blocks in hand, the synthesis of oligosaccharides could be undertaken, the start of which is depicted in Scheme 3. Rhamnose acceptors **2** and **6** were coupled to rhamnose donor **1** using the Ph_2SO/Tf_2O mediated pre-activation conditions to give the target disaccharides with excellent stereoselectivity. To aid in purification the C-3' Cbz was removed under mild basic conditions, to give disaccharide acceptors **36** and **37** in 83% and 85% yield over 2 steps, respectively. These could then be coupled to fucose donor **5** under the agency of IDCP to give the trisaccharides of the serovars K7 (**39**) and K8 (**38**) in good yields (99% and 74%, respectively) and selectivities (6:1).



Scheme 3. Synthesis of trisaccharides **38** and **39**. Reagents and conditions: (a) Ph_2SO, Tf_2O, TTBP, DCM -60 °C, (b) K_2CO_3, MeOH, 83% over 2 steps (**36**), 85% over 2 steps (**37**), (c) IDCP, Et_2O/DCE (4:1), 0 °C → 4 °C, 74% (6:1) (**38**), 99% (6:1) (**39**).

Alternatively, disaccharide acceptor **37** was coupled to fucose donors **3**, **7** and **8** (Scheme 4A). This produced trisaccharides **40, 41** and **42** in good yields and with good stereoselectivity. The resulting α/β-mixtures were difficult to separate. When the C-3'' PMB ether was removed this proved to be much easier and pure trisaccharide acceptors **43, 44** and **45** were synthesized in 53%, 65% and 67% yield over 2 steps, respectively.

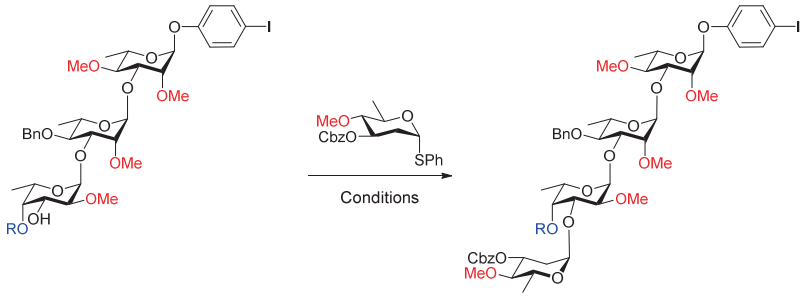


Scheme 4. A. Synthesis of trisaccharide acceptors **43**, **44** and **45**. Reagents and conditions: (a) IDCP, Et_2O/DCE (4:1), 0 °C → 4 °C, 67%, 6:1, (**40**), 84%, 6:1, (**42**), 96%, 6:1, (**41**), (b) DDQ, DCM/H_2O (19:1), 79% (**43**), 77% (**45**), 70% (**44**). **B**. Synthesis of tetrasaccharides **46**, **47** and **48**. Reagents and conditions: (c) Donor **10**, Ph_2SO, Tf_2O, TTBP, DCM -70 → 60 °C, 85% (**46**) (d) conditions c with donor **11**, 64% (**47**) (e) conditions c with donor **9,** 100% (**48**).

Trisaccharide acceptor **43** was then coupled to mannose donors **9, 10** and **11** under pre-activation conditions which stereoselectively delivered the α-linked tetrasaccharides **48**, **46** and **47** corresponding to the serovars K-II, K-III and K-IV, respectively, in good to excellent yields (Scheme 4B).

The coupling of dideoxydonor **4** to trisaccharide acceptors **43** and **44** was attempted with the same pre-activation conditions and this led to varying results which are described in Table 1. The glycosylation of acceptor **43**, carrying an acetyl on the C-4" position proceeded with a good yield (73%) but low selectivity (2:1). Coupling of **4** to benzylated acceptor **44** gave the tetrasaccharide in moderate yield (48%) but excellent stereoselectivity (1:0).

Table 1. Synthesis of tetrasaccharides **49**, **50** and **51**.



43 R = Ac
44 R = Bn
45 R = propionyl

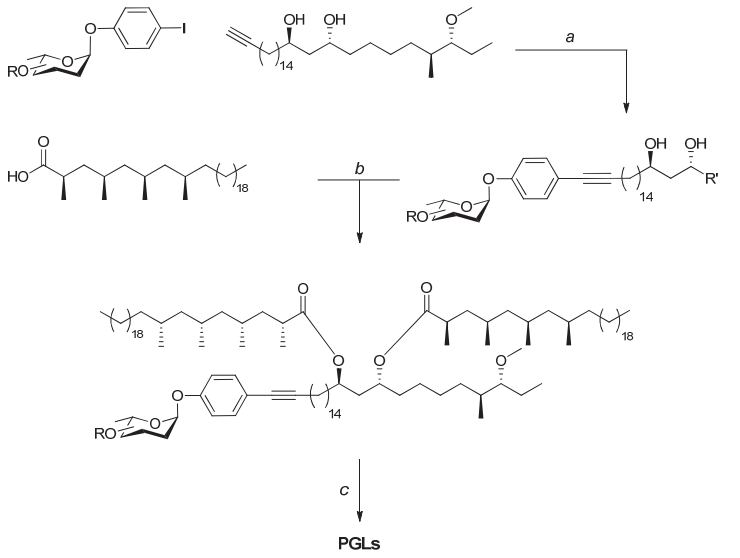
49 R = Ac
50 R = Bn
51 R = propionyl

Acceptor	Activator (eq)	Temperature	Solvent	Time	Yield	α/β
43	Ph_2SO (1.1) / Tf_2O (1.1)	-70 → -60 °C	DCM (0.05 M)	2 h	48%	1:0
42	Ph_2SO (1.1) / Tf_2O (1.1)	-70 → -60 °C	DCM (0.05 M)	2 h	73%	2:1
42	IDCP (1.5)	0 → 4 °C	DCM (0.05 M)	16 h	90%	4:1
44	IDCP (1.5)	0 → 4 °C	DCM (0.05 M)	16 h	89%	4:1
43	IDCP (1.5)	0 → 4 °C	DCM (0.05 M)	16 h	52%	1:0

This is in line with the results of the previous chapter, where it was found that a reactive acceptor was required in the glycosylations using the stereodirecting effect of the Cbz carbonate to give the α-product with good selectivity. While in Chapter 5 the reactivity of the acceptors originating from *M. leprae* and *M. haemophilum* were diminished because of steric factors, the relatively low reactivity of acceptor **43** is caused by the proximal electron-withdrawing substituent, which has been shown to strongly influence the nucleophilicity of the adjacent alcohol.[60] In an attempt to improve the results, the coupling of acetylated acceptor **43** was performed next using IDCP as activating agent. This produced the desired tetrasaccharide **49** in 90% yield with a 4:1 α/β ratio, a clear improvement over the pre-activation conditions. Encouraged by these results the propionyl bearing acceptor **45** was subjected to the same conditions and this provided tetrasaccharide **51** in 89% yield and with a 4:1 α/β-selectivity. When acceptor **44** was coupled to **4** using IDCP the yield only marginally improved in comparison to the reaction using pre-activation conditions. The excellent stereoselectivity was maintained

in this condensation. With all iodoaryl bearing glycans now prepared, the stage was set for the final steps of the PGL assembly, the yields of which are depicted in Table 2.

Table 2. Yields of final stages of PGL assembly.



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.

Starting glycan	Sonogashira	Esterification	Hydrogenation	Overall yield
38	79%	66%	84%	44%
39	78%	68%	61%	32%
46	85%	54%	89%	41%
47	65%	65%	78%	33%
48	73%	52%	88%	33%
49	100%	63%	100%	63%
50	81%	52%	86%	36%
51	82%	60%	83%	41%

The glycans were attached to the phthiocerol alkyne derivative using a Sonogashira cross-coupling in good yields. The resulting diols were then esterified with two equivalents of mycocerosic acid under Steglich conditions. The hydrogenation that followed uneventfully produced all known PGL*s* originating from *M. kansasii* and *M. gastrii* in good yields.

Conclusion

This chapter has described the synthesis of all known phenolic glycolipids originating from *Mycobacterium kansasii* and *M. gastri*. A common structural feature in the glycans is the presence of a methyl ether on the C-2 position of 1,2-*trans* linked monosaccharides. It was therefore investigated whether a C-3 Cbz protecting group could be used to steer the stereoselectivity via remote participation. The C-3 Cbz indeed proved to be an adequate protecting group enabling the stereoselective formation of the target tetrasaccharides. The iodoaryl-bearing glycans were then coupled to the phthiocerol alkyne derivative using a Sonogashira coupling, which was followed by a Steglich esterification of the resulting diol with mycocerosic acid. Finally, global deprotection with H_2 and Pd/C resulted in the complete assembly of all the phenolic glycolipids originating from *Mycobacterium kansasii* and *Mycobacterium gastri* and these are at present being investigated for their immunomodulatory capabilities.

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. Tf_2O used in glycosylations was dried by distillation over P_2O_5 and stored under N_2 atmosphere in a Schlenk flask at -20 °C. 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, 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 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: Pre-activation glycosylation:

Donor (2 eq), Ph_2SO (2.2 eq) and TTBP (5 eq) were dried by co-evaporation with toluene (3x) followed by 3 vacuum/nitrogen purges. The mixture was then dissolved in DCM (0.05 M) and flame-dried 3Å molecular sieves were added. The solution was then cooled to -70 °C after which Tf_2O (2.2 eq) was added to the solution. After stirring for 30 minutes, acceptor (1.0 eq), which was also dried by co-evaporation with toluene (3x) followed by 3 vacuum/nitrogen purges, was dissolved in DCM (0.2 M) and slowly added to the solution. After TLC analysis indicated the consumption of the acceptor (1-4 hours) the reaction was quenched by addition of NEt_3. The reaction mixture was then diluted with DCM, filtered over celite, washed with brine, dried with $MgSO_4$ and concentrated *in vacuo*. Purification by means of column chromatography.

General procedure B: IDCP mediated glycosylation:

Starting material (1.0 eq) and donor (2.0 eq) were co-evaporated together with toluene and subsequently dissolved in Et_2O/DCE (0.05 M, 4:1). Flame-dried 3Å molecular sieves were added and the resulting solution was stirred for 15 minutes while it was cooled to 0 °C, after which IDCP (3.0 eq) was added. The reaction was allowed to stir for 16 hours at 4 °C after which it was filtered over celite, diluted with Et_2O and transferred to a separation funnel. The organic layer was then washed with sat. aq. $Na_2S_2O_3$, sat. aq. $NaHCO_3$, sat. aq. $CuSO_4$ and brine, after which it was dried with $MgSO_4$ and concentrated *in vacuo*. Purification by means of column chromatography.

General procedure C: Sonogashira cross coupling

Iodoaryl glycoside (1.0 eq) was dissolved in freshly distilled NEt_3 (0.05 M) together with phthiocerol (1.2 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 D: Esterification with mycocerosic acid

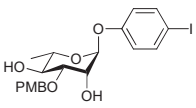
Starting material (1.0 eq) was dissolved in dry DCM (0.05 M) together with mycocerosic acid (3.0 eq) and DMAP (9 eq). The resulting mixture was cooled to 0 °C after which DIC (6 eq) was added. The reaction was allowed to stir for 16 hours while warming to rT, after which it was warmed to 40 °C and stirred for a further 5 hours. The reaction mixture was then diluted with Et_2O and the organic layers 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 E: Hydrogenation

A 1:1 mixture of EtOH and THF was purged with N_2, Pd/C (10 wt%, undetermined amount) was added and the resulting solution was again purged with N_2. The flask containing starting material (1.0 eq) was flushed

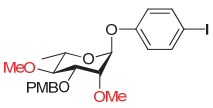
with N_2 and 5 mL of the Pd solution was added. The resulting mixture was again purged with N_2 and then with H_2 and allowed to stir under H_2 atmosphere (balloon) until TLC indicated complete conversion of the starting material and reaction intermediates to a single low running spot (DCM-MeOH 19:1). The reaction mixture was then purged with N_2 and filtered over a small amount of celite. Purification by means of column chromatography (DCM-MeOH 19:1).

4-iodophenyl 3-*O*-(4-methoxybenzyl)-α-L-rhamnopyranoside (13)



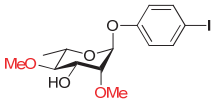
Compound **12** (11.0 g, 30 mmol, 1.0 eq) was dissolved in toluene (600 mL, 0.05 M) and Bu_2SnO (8.22 g, 33 mmol, 1.1 eq) was added to the solution. The mixture was refluxed for 1.5 hours and then cooled to 80 °C. PMBCl (5.3 mL, 39 mmol, 1.3 eq) and TBAB (11.6 g, 36 mmol, 1.2 eq) were added to the mixture and it was refluxed for 2 hours. The reaction mixture was then concentrated *in vacuo* and purified by means of column chromatography (*n*-pentane-Et_2O 1:1) to give the crude product (7.71 g, 15.9 mmol, 53%, mixture of regioisomers) as a slightly yellow oil. The product was used in the next step without further purification or analysis.

4-iodophenyl 2,4-di-*O*-methyl-3-*O*-(4-methoxybenzyl)-α-L-rhamnopyranoside (14)



Compound **13** (7.71 g, 15.9 mmol, 1.0 eq) was dissolved in dry DMF (125 mL, 0.13 M) and MeI (4 mL, 63.4 mmol, 4.0 eq) was added to the solution. The mixture was cooled to 0 °C, and NaH (60%, 1.58 g, 39.6 mmol, 2.5 eq) was then added. The reaction mixture was warmed to rt while stirring for 3 hours. The reaction was then quenched by addition of H_2O, and the aqueous layer was extracted with Et_2O (3x). The organic layers were combined, washed with brine, dried with $MgSO_4$ and concentrated *in vacuo*. Purification by means of column chromatography (*n*-pentane-Et_2O 4:1) gave the title compound (7.65 g, 14.9 mmol, 94%) as a pale oil. $[\alpha]_D^{25}$ = -89.0 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.55-7.53 (m, 2H, C*H*$_{arom}$); 7.35 (dd, 2H, *J* = 2.0, 6.8 Hz, C*H*$_{arom}$); 6.91-6.88 (m, 2H, C*H*$_{arom}$); 6.81 (dd, 2H, *J* = 2.0, 6.8 Hz, C*H*$_{arom}$); 5.44 (d, 1H, *J* = 2.0 Hz, H-1); 4.69 (dd, 2H, *J* = 11.4, 19.4 Hz, PhC*H*$_2$); 3.88 (dd, 1H, *J* = 3.2, 9.6 Hz, H-3); 3.79 (s, 3H, C*H*$_{3,PMB}$); 3.62-3.57 (m, 5H, H-2, H-5, OC*H*$_3$); 3.52 (s, 3H, OC*H*$_3$); 3.25 (t, 1H, *J* = 9.4 Hz, H-4); 1.25 (d, 3H, *J* = 6.4 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 159.2, 156.1 (C$_{q,arom}$); 138.3 (*C*H$_{arom}$); 130.5 (C$_{q,arom}$); 129.4, 118.6, 13.8 (*C*H$_{arom}$); 95.5 (C-1); 84.7 (*C*I$_{arom}$); 81.9 (C-4); 78.9 (C-3); 77.9 (C-2); 72.2 (Ph*C*H$_2$); 68.9 (C-5); 61.1, 59.6 (O*C*H$_3$); 55.2 (*C*H$_{3,PMB}$); 17.9 (C-6). IR (thin film, cm^{-1}): 1102, 1139, 1251, 1484, 1514, 1613. HRMS calculated for $C_{22}H_{27}IO_6Na$ 537.07500 $[M+Na]^+$; found 537.07459.

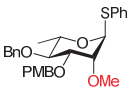
4-iodophenyl 2,4-di-*O*-methyl-α-L-rhamnopyranoside (2)



Compound **14** (7.65 g, 14.9 mmol, 1.0 eq) was dissolved in a mixture of DCM and HFIP (1:1, 150 mL, 0.1 M) after which a solution of HCl in HFIP (7.5 mL, 0.2 M, 0.1 eq) was added. After complete conversion of the starting material (5 min), indicated by a dark purple colour, the reaction was quenched by addition of sat. aq. $NaHCO_3$. The mixture was diluted with DCM, washed with 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 (4.74 g, 12.0 mmol, 81%) as a white amorphous solid. $[\alpha]_D^{25}$ = -77.7 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR

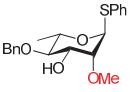
(400 MHz) δ: 7.59-7.56 (m, 2H, C*H*$_{arom}$); 6.86-6.83 (m, 2H, C*H*$_{arom}$); 5.50 (s, 1H, H-1); 4.01 (dd, 1H, *J* = 3.6, 9.2 Hz, H-3); 3.66-3.58 (m, 5H, H-2, H-5, OC*H*$_3$); 3.55 (s, 3H, OC*H*$_3$); 3.05 (t, 1H, *J* = 9.4 Hz, H-4; 1.26 (d, 3H, *J* = 6.4 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 156.3, (C$_{q,arom}$); 138.5, 118.7 (*C*H$_{arom}$); 94.6 (C-1); 84.9 (*C*I$_{arom}$); 83.6 (C-4); 80.4 (C-2); 71.2 (C-3); 68.3 (C-5); 61.1, 59.3 (O*C*H$_3$); 18.0 (C-6). IR (thin film, cm^{-1}): 1002, 1098, 1232, 1484, 3449. HRMS calculated for $C_{14}H_{19}IO_5Na$ 417.01749 [M+Na]$^+$; found 417.01694.

Phenyl 2-*O*-methyl-3-*O*-(4-methoxybenzyl)-4-*O*-benzyl-1-thio-α-L-rhamnopyranoside (16)



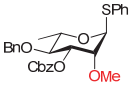
Compound **15** (30.2 g, 64.7 mmol, 1.0 eq) was dissolved in dry DMF (600 mL, 0.11 M) and MeI (8.0 mL, 129 mmol, 2.0 eq) was added to the solution. The mixture was cooled to 0 °C, and NaH (60%, 3.9 g, 97 mmol, 1.5 eq) was then added. The reaction mixture was warmed to rt while stirring for 1.5 hours. The reaction was then quenched by addition of H_2O, and the aqueous layer was extracted with Et_2O (3x). The organic layers were combined, washed with brine, dried with $MgSO_4$ and concentrated *in vacuo*. Purification by means of column chromatography (*n*-pentane-Et_2O 4:1) gave the title compound (26.7 g, 55.5 mmol, 96%) as a clear oil. $[\alpha]_D^{25}$ = -152.1 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.45-7.43 (m, 2H, C*H*$_{arom}$); 7.35-7.24 (m, 10H, C*H*$_{arom}$); 6.88 (dd, 2H, *J* = 8.8 Hz, C*H*$_{arom}$); 5.53 (d, 1H, *J* = 1.2 Hz, H-1); 4.95 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.67-4.61 (m, 3H, PhCH*H*, PhC*H*$_2$); 4.18-4.10 (m, 1H, H-5); 3.82-3.79 (m, 4H, H-3, C*H*$_{3,PMB}$); 3.68 (dd, 1H, *J* = 2.0, 3.2 Hz, H-2); 3.56 (t, 1H, *J* = 9.4 Hz, H-4); 3.45 (s, 3H, OC*H*$_3$); 1.32 (d, 3H, *J* = 6.4 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 159.5, 138.7, 134.9 (C$_{q,arom}$); 131.1, 130.3, 129.8, 129.1, 128.5, 128.1, 127.8, 127.3, 114.0 (*C*H$_{arom}$); 85.0 (C-1); 80.5 (C-4); 79.9 (C-2); 79.6 (C-3); 75.7, 72.2 (Ph*C*H$_2$); 69.3 (C-5); 58.6 (O*C*H$_3$); 55.4 (*C*H$_{3,PMB}$); 18.0 (C-6). IR (thin film, cm^{-1}): 1033, 1084, 1097, 1173, 1249, 1453, 1513, 1612. HRMS calculated for $C_{28}H_{32}O_5SNa$ 503.18681 [M+Na]$^+$; found 503.18596.

Phenyl 2-*O*-methyl-4-*O*-benzyl-1-thio-α-L-rhamnopyranoside (17)



Compound **16** (711 mg, 1.50 mmol, 1.0 eq) was dissolved in a mixture of DCM and HFIP (1:1, 1 mL, 0.1 M) and TES (0.7 mL, 4.6 mmol, 3.0 eq) was added to the solution. The resulting mixture was cooled to 0 °C and a solution of HCl in HFIP (3.8 mL, 0.2 M, 0.5 eq) was added. After stirring for 30 minutes the reaction was quenched by addition of sat. aq. $NaHCO_3$. The mixture was diluted with DCM, washed with brine, dried with $MgSO_4$ and concentrated *in vacuo*. Purification by means of column chromatography (*n*-pentane-Et_2O 7:3) gave the title compound (425 mg, 1.2 mmol, 80%) as a pale oil. Spectroscopic data were in accordance with those previously reported in the literature.[31]

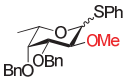
Phenyl 2-*O*-methyl-3-*O*-benzyloxycarbonyl-4-*O*-benzyl-1-thio-α-L-rhamnopyranoside (1)



Compound **17** (355 mg, 0.93 mmol, 1.0 eq) was dissolved in DCM (7.5 mL, 0.14 M) and DMAP (0.23 g, 1.9 mmol, 2.0 eq) was added to the solution. The mixture was cooled to 0 °C and CbzCl (0.3 mL, 1.9 mmol, 2.0 eq) was slowly added. The reaction was allowed to stir for 3 hours after while slowly warming to rt. The reaction was quenched by addition of 1 M HCl, and the organic layer was washed with sat. aq. $NaHCO_3$ and brine, dried with $MgSO_4$ and concentrated *in vacuo*. Purification by means of column chromatography (*n*-pentane Et_2O 4:1) gave the title compound (462 mg, 0.93 mmol, 100%) as a clear oil. $[\alpha]_D^{25}$ = -196.6 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.48-7.45 (m, 2H,

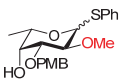
C*H*$_{arom}$); 7.40-7.23 (m, 13H, C*H*$_{arom}$); 5.53 (d, 1H, *J* = 1.2 Hz, H-1); 5.23-5.16 (m, 2H, PhC*H*$_2$); 5.06 (dd, 1H, *J* = 3.2, 9.6 Hz, H-3); 4.67 (dd, 2H, *J* = 10.8, 58.4 Hz, PhC*H*$_2$); 4.23 (dq, 1H, *J* = 3.2, 6.0 Hz, H-5); 3.96 (dd, 1H, *J* = 2.0, 3.2 Hz, H-2); 3.65 (t, 1H, *J* = 9.4 Hz, H-4); 3.42 (s, 3H, OC*H*$_3$); 1.33 (d, 3H, *J* = 6.0 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 154.7, 138.1, 135.3, 134.6 (C$_{q,arom}$); 131.4, 129.2, 128.7, 128.7, 128.5, 128.5, 128.1, 127.9, 127.5 (*C*H$_{arom}$); 84.8 (C-1); 80.1 (C-2); 79.1 (C-4); 78.1 (C-3); 75.5, 70.0 (Ph*C*H$_2$); 69.1 (C-5); 17.9 (C-6). IR (thin film, cm^{-1}): 1027, 1086, 1217, 1247, 1266, 1357, 1383, 1440, 1455, 1748. HRMS calculated for $C_{28}H_{30}O_6SNa$ 517.16608 [M+Na]$^+$; found 517.16551.

Phenyl 2-*O*-methyl-3,4-di-*O*-benzyl-1-thio-α-L-fucopyranoside (5)



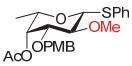
Compound **18** (1.73 g, 6.4 mmol, 1.0 eq) was dissolved in dry DMF (64 mL, 0.1 M) and BnBr (2.18 mL, 19.2 mmol, 3 eq) was added to the solution. The mixture was cooled to 0 °C, and NaH (60%, 0.62 g, 15.4 mmol, 2.4 eq) and TBAI (0.47 g, 1.28 mmol, 0.2 eq) were then added. The reaction mixture was warmed to rt while stirring for 3 hours. The reaction was quenched by addition of H_2O, and extracted with Et_2O (3x). The organic layers were combined, washed with brine, dried with $MgSO_4$ and concentrated *in vacuo*. Purification by means of column chromatography (*n*-pentane-Et_2O 4:1) gave the title compound (4.77 g, 6.15 mmol, 96 %) as an amorphous white solid. $[\alpha]_D^{25}$ = -21.9 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.58-7.56 (m, 2H, C*H*$_{arom}$); 7.43-7.18 (m, 13H, C*H*$_{arom}$); 5.00 (d, 1H, *J* = 11.6 Hz, PhC*H*H); 4.75 (dd, 2H, *J* = 11.6, 18.8 Hz, PhC*H*$_2$); 4.65 (d, 1H, *J* = 11.6 Hz, PhCH*H*); 4.48 (d, 1H, *J* = 9.6 Hz, H-1); 3.64-3.59 (m, 5H, H-2, H-3, OC*H*$_3$); 3.51-3.47 (m, 2H, H-4, H-5); 1.24 (d, 3H, *J* = 6.4 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 138.9, 138.8, 135.2 (C$_{q,arom}$); 128.8, 128.6, 128.3, 128.1, 127.8, 127.6, 127.6, 127.1 (*C*H$_{arom}$); 87.5 (C-1); 84.6 (C-4); 79.0 (C-3); 76.7 (C-2); 74.7 (Ph*C*H$_2$); 74.6 (C-5); 72.9 (Ph*C*H$_2$); 61.3 (O*C*H$_3$); 17.4 (C-6). IR (thin film, cm^{-1}): 1027, 1046, 1069, 1089, 1129, 1163, 1209, 1355, 1379, 1440, 1454, 1480, 1497. HRMS calculated for $C_{27}H_{30}O_4SNa$ 473.17625 [M+Na]$^+$; found 473.17568.

Phenyl 2-*O*-methyl-3-*O*-(4-methoxybenzyl)-1-thio-α/ß-L-fucopyranoside (19)



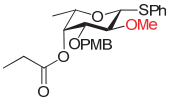
Compound **18** (9.48 g, 35 mmol, 1.0 eq) was dissolved in toluene (500 mL, 0.07 M) and Bu_2SnO (9.58 g, 38.5 mmol, 1.1 eq) was added to the solution. The mixture was refluxed for 2 hours and then cooled to 80 °C. PMBCl (6.2 mL, 45.5 mmol, 1.3 eq) and TBAB (13.54 g, 42 mmol, 1.2 eq) were added to the mixture and it was refluxed for 2 hours. The reaction mixture was then concentrated *in vacuo* and purification by means of column chromatography (*n*-pentane-Et_2O 1:1) gave the title compound (11.8 g, 30.2 mmol, 86%) as a slightly yellow oil. $[\alpha]_D^{25}$ = 16.0 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.60-7.57 (m, 2H, C*H*$_{arom}$); 7.33-7.25 (m, 5H, C*H*$_{arom}$); 6.93-6.90 (m, 2H, C*H*$_{arom}$); 4.64 (s, 2H, PhC*H*$_2$); 4.48 (d, *J* = 9.6 Hz, H-1); 3.80 (s, 3H, C*H*$_{3,PMB}$); 3.75 (d, 1H, *J* = 2.4 Hz, H-4); 3.54 (s, 3H, OC*H*$_3$); 3.52 (q, 1H, *J* = 6.4 Hz, H-5); 3.46 (dd, 1H, *J* = 3.4, 9.0 Hz, H-3); 3.36 (t, 1H, *J* = 9.4 Hz, H-2); 2.35 (bs, 1H, 4-O*H*); 1.34 (d, 3H, *J* = 6.4 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 159.5, 133.9 (C$_{q,arom}$); 132.0 (*C*H$_{arom}$); 129.9 (C$_{q,arom}$); 129.6, 128.9, 127.4, 114.0 (*C*H$_{arom}$); 87.3 (C-1); 82.5 (C-3); 78.5 (C-2); 74.2 (C-5); 71.9 (Ph*C*H$_2$); 69.5 (C-4); 61.3 (O*C*H$_3$); 55.4 (*C*H$_{3,PMB}$); 16.8 (C-6). IR (thin film, cm^{-1}): 1047, 1063, 1069, 1085, 1128, 1173, 1248, 1302, 1367, 1441, 1455, 1464, 1480, 1514, 1585, 1613, 2835, 2870, 2875, 2994, 3493. HRMS calculated for $C_{21}H_{26}O_5SNa$ 413.13986 [M+Na]$^+$; found 413.13908.

Phenyl 2-*O*-methyl-3-*O*-(4-methoxybenzyl)-4-*O*-acetyl-1-thio-α/ß-L-fucopyranoside (3)



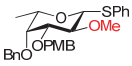
Compound **19** (3.80 g, 9.7 mmol, 1.0 eq) was dissolved in DCM (100 mL, 0.1 M) and Ac_2O (1.84 mL, 19.4 mmol, 2.0 eq) was added to the solution. The mixture was then cooled to 0 °C after which pyridine (1.6 mL, 19.4 mmol, 2.0 eq) and DMAP (0.119 g, 0.97 mmol, 0.1 eq) were added. After stirring for 3 hours the reaction was quenched by addition of MeOH and the resulting mixture was concentrated *in vacuo*. Thereafter the mixture was diluted with Et_2O and the organic layer was subsequently washed with H_2O, 1 M HCl, sat. aq. $NaHCO_3$ and brine. The organic layer was dried with $MgSO_4$, concentrated *in vacuo* and purification by means of column chromatography (*n*-pentane-Et_2O 4:1) gave the title compound (4.08 g, 9.4 mmol, 97%) as an amorphous white solid. $[\alpha]_D^{25}$ = -66.1 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.58-7.55 (m, 2H, C*H*$_{arom}$); 7.31-7.22 (m, 5H, C*H*$_{arom}$); 6.89-6.85 (m, 2H, C*H*$_{arom}$); 5.32 (d, 1H, *J* = 3.2 Hz, H-4); 4.67-4.63 (m, 1H, PhC*H*H); 4.52 (d, 1H, *J* = 10.0 Hz, H-1); 4.44 (d, 1H, *J* = 10.8 Hz, PhCH*H*); 3.78 (s, 3H, C*H*$_{3,PMB}$); 3.65 (q, 1H, *J* = 6.4 Hz, H-5); 3.57 (s, 3H, OC*H*$_3$); 3.52 (dd, 1H, *J* = 3.4, 9.4 Hz, H-3); 3.33 (dd, 1H, *J* = 9.2, 9.6 Hz, H-2); 2.15 (s, 3H, C*H*$_3$,Ac); 1.22 (d, 3H, *J* = 6.4 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 170.8 (*C*O$_{Ac}$); 159.4, 133.8 (C$_{q,arom}$); 132.1 (*C*H$_{arom}$); 129.9 (C$_{q,arom}$); 129.7, 128.8, 127.5, 113.9 (*C*H$_{arom}$); 87.4 (C-1); 80.9 (C-3); 78.1 (C-2); 73.0 (C-5); 71.5 (Ph*C*H$_2$); 69.8 (C-4); 61.3 (O*C*H$_3$); 55.3 (*C*H$_{3,PMB}$); 21.0 (*C*H$_{3,Ac}$); 16.9 (C-6). IR (thin film, cm^{-1}): 1065, 1128, 1175, 1248, 1371, 1441, 1514, 1613, 1739. HRMS calculated for $C_{23}H_{28}O_6SNa$ 455.1504 $[M+Na]^+$; found 455.14969.

Phenyl 2-*O*-methyl-3-*O*-(4-methoxybenzyl)-4-*O*-propionyl-1-thio-α/ß-L-fucopyranoside (7)



Compound **19** (3.74 g, 9.6 mmol, 1.0 eq) was dissolved in DCM (100 mL, 0.1 M) and propionic anhydride (2.45 mL, 19.2 mmol, 2.0 eq) was added to the solution. The mixture was then cooled to 0 °C after which pyridine (1.5 mL, 19.2 mmol, 2.0 eq) and DMAP (0.117 g, 0.96 mmol, 0.1 eq) were added. After stirring for 3 hours the reaction was quenched by addition of MeOH and the resulting mixture was concentrated *in vacuo*. Thereafter the mixture was diluted with Et_2O and the organic layer was subsequently washed with H_2O, 1 M HCl, sat. aq. $NaHCO_3$ and brine. The organic layer was dried with $MgSO_4$, concentrated *in vacuo* and purification by means of column chromatography (*n*-pentane-Et_2O 4:1) gave the title compound (3.03 g, 6.8 mmol, 71%) as an amorphous white solid. $[\alpha]_D^{25}$ = -54.0 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.58-7.55 (m, 2H, C*H*$_{arom}$); 7.31-7.22 (m, 5H, C*H*$_{arom}$); 6.89-6.84 (m, 2H, C*H*$_{arom}$); 5.35 (dd, 1H, *J* = 1.2, 3.4 Hz, H-4); 4.51 (d, 1H, *J* = 11.2 Hz, PhC*H*H); 4.48 (d, 1H, *J* = 8.8 Hz, H-1); 4.43 (d, 1H, *J* = 10.8 Hz, PhCH*H*); 3.79 (s, 3H, C*H*$_{3,PMB}$); 3.67 (q, 1H, *J* = 6.2 Hz, H-5); 3.56-3.51 (m, 4H, H-3, OC*H*$_3$); 3.31 (t, 1H, *J* = 9.2 Hz, H-2); 2.43 (q, 2H, *J* = 7.5 Hz, C*H*$_2$CH$_3$); 1.23 (d, 3H, *J* = 6.4 Hz, H-6); 1.16 (t, 3H, *J* = 7.4 Hz, CH$_2$C*H*$_3$). ^{13}C-APT NMR (101 MHz) δ: 174.5 (*C*O$_{Propionyl}$); 159.4, 133.7 (C$_{q,arom}$); 132.2 (*C*H$_{arom}$); 130.0 (C$_{q,arom}$); 129.8, 128.9, 127.5, 113.9 (*C*H$_{arom}$); 87.3 (C-1); 81.0 (C-3); 78.1 (C-2); 73.2 (C-5); 71.5 (Ph*C*H$_2$); 69.6 (C-4); 61.4 (OC*H*$_3$); 55.4 (*C*H$_{3,PMB}$); 27.7 (*C*H$_2$CH$_3$); 17.0 (C-6); 9.5 (CH$_2$*C*H$_3$). IR (thin film, cm^{-1}): 1065, 1085, 1102, 1128, 1182, 1249, 1302, 1441, 1514, 1613, 1736. HRMS calculated for $C_{24}H_{30}O_6SNa$ 469.1661 $[M+Na]^+$; found 469.16566.

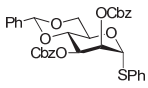
Phenyl 2-*O*-methyl-3-*O*-(4-methoxybenzyl)-4-*O*-benzyl-1-thio-α/ß-L-fucopyranoside (8)



Compound **19** (1.73 g, 6.4 mmol, 1.0 eq) was dissolved in dry DMF (64 mL, 0.1 M) and BnBr (2.18 mL, 19.2 mmol, 3.0 eq) was added to the solution. The mixture was cooled to

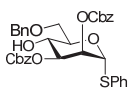
0 °C, and NaH (60%, 0.62 g, 15.4 mmol, 2.4 eq) and TBAI (0.47 g, 1.28 mmol, 0.2 eq) were then added. The reaction mixture was warmed to rt while stirring for 3 hours. The reaction was quenched by addition of H_2O, and extracted with Et_2O (3x). The organic layers were combined, washed with brine, dried with $MgSO_4$ and concentrated *in vacuo*. Purification by means of column chromatography (*n*-pentane-Et_2O 4:1) gave the title compound (4.77 g, 6.15 mmol, 96%) as an amorphous white solid. $[\alpha]_D^{25}$ = 6.5 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.58-7.55 (m, 2H, C*H*$_{arom}$); 7.35-7.19 (m, 10H, C*H*$_{arom}$); 6.91-6.86 (m, 2H, C*H*$_{arom}$); 4.98 (d, 1H, *J* = 11.6 Hz, PhC*H*H); 4.68-4.63 (m, 3H, PhCH*H*, PhC*H*$_2$); 4.48 (d, 1H, *J* = 8.8 Hz, H-1); 3.80 (s, 3H, C*H*$_{3,PMB}$); 3.60-3.56 (m, 5H, H-2, H-3, OC*H*$_3$); 3.49-3.47 (m, 2H, H-4, H-5); 1.23 (d, 3H, *J* = 6.0 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 159.3, 138.9, 134.4 (C$_{q,arom}$); 131.6 (*C*H$_{arom}$); 130.7 (C$_{q,arom}$); 129.3, 128.9, 128.8, 128.3, 128.1, 127.6, 127.1, 113.9 (*C*H$_{arom}$); 87.5 (C-1); 84.2 (C-4); 79.0 (C-3); 76.7 (C-2); 74.7 (C-5); 74.6, 72.6 (Ph*C*H$_2$); 61.3 (O*C*H$_3$); 55.4 (*C*H$_{3,PMB}$); 17.4 (C-6). IR (thin film, cm^{-1}): 1069, 1129, 1172, 1248, 1302, 1355, 1440, 1480, 1513. HRMS calculated for $C_{28}H_{32}O_5SNa$ 503.1868 [M+Na]$^+$; found 503.18618.

Phenyl 2,3-di-*O*-benzyloxycarbonyl-4,6-*O*-benzylidene-1-thio-α-D-mannopyranoside (26)



Compound **25** (2.59 g, 7.19 mmol, 1.0 eq) was dissolved in DCM (125 mL, 0.06 M) and DMAP (5.06 g, 41.5 mmol, 6.0 eq) was added to the solution. The mixture was cooled to 0 °C and CbzCl (2.92 mL, 20.7 mmol, 3.0 eq) was slowly added. The reaction was allowed to stir for 2 hours after while slowly warming to rt. The reaction was quenched by addition of 1 M HCl, and the organic layer was washed with sat. aq. $NaHCO_3$ and brine, dried with $MgSO_4$ and concentrated *in vacuo*. Purification by means of column chromatography (*n*-pentane Et_2O 7:3) gave the title compound (4.43 g, 7.04 mmol, 98%) as a clear oil. $[\alpha]_D^{25}$ = 33.1 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.47 (d, 2H, *J* = 3.2 Hz, C*H*$_{arom}$); 7.36-7.20 (m, 18H, C*H*$_{arom}$); 5.57 (s, 1H, H-1); 5.46 (s, 1H, H-2); 5.17 (s, 2H, PhC*H*$_2$); 5.09 (s, 2H, PhC*H*$_2$); 5.04 (d, 1H, *J* = 9.6 Hz, H-3); 4.52 (dd, 2H, *J* = 11.8, 82.2 Hz, PhC*H*$_2$); 4.37 (d, 1H, *J* = 5.2 Hz, H-5); 4.11 (dd, 1H, *J* = 9.6, 10.0 Hz, H-4); 3.80-3.73 (m, 2H, H-6); 2.95 (bs, 1H, 4-O*H*). ^{13}C-APT NMR (101 MHz) δ: 154.5, 154.4 (*C*O$_{Cbz}$); 137.8, 134.9, 134.7, 133.0 (C$_{q,arom}$); 132.2, 129.2, 128.7, 128.7, 128.6, 128.5, 128.5, 128.4, 128.0, 127.8, 127.6 (*C*H$_{arom}$); 85.6 (C-1); 76.1 (C-3); 74.6 (C-2); 73.6 (Ph*C*H$_2$); 72.3 (C-5); 70.3, 70.2 (Ph*C*H$_2$); 69.7 (C-6); 66.7 (C-4). IR (thin film, cm^{-1}): 1002, 1026, 1082, 1098, 1239, 1275, 1441, 1457, 1747, 1751, 3497. HRMS calculated for $C_{35}H_{34}O_9SNa$ 653.18212 [M+Na]$^+$; found 653.18133.

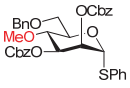
Phenyl 2,3-di-*O*-benzyloxycarbonyl-6-*O*-benzyl-1-thio-α-D-mannopyranoside (27)



Compound **26** (4.36 g, 6.94 mmol, 1.0 eq) was dissolved in DCM (70 mL, 0.1 M) and TES-H (11.1 mL, 69.4 mmol, 10.0 eq) was added to the solution. The mixture was cooled to 0 °C and TFA (5.3 mL, 69.4 mmol, 10.0 eq) was slowly added. The reaction was allowed to stir for 30 minutes while warming to rt. The reaction was quenched by addition of sat. aq. $NaHCO_3$ 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_2O 7:3) gave the title compound (4.03 g, 6.39 mmol, 92%) as a clear oil. $[\alpha]_D^{25}$ = 33.1 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.47 (d, 2H, *J* = 3.2 Hz, C*H*$_{arom}$); 7.36-7.20 (m, 18H, C*H*$_{arom}$); 5.57 (s, 1H, H-1); 5.46 (s, 1H, H-2); 5.17 (s, 2H, PhC*H*$_2$); 5.09 (s, 2H, PhC*H*$_2$); 5.04 (d, 1H, *J* = 9.6 Hz, H-3); 4.52 (dd, 2H, *J* = 11.8, 82.2 Hz, PhC*H*$_2$); 4.37 (d, 1H, *J* = 5.2 Hz, H-5); 4.11 (dd, 1H, *J* = 9.6, 10.0 Hz, H-4); 3.80-3.73 (m, 2H, H-6); 2.95 (bs, 1H, 4-O*H*). ^{13}C-APT NMR (101 MHz) δ: 154.5, 154.4 (*C*O$_{Cbz}$); 137.8,

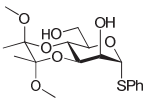
134.9, 134.7, 133.0 ($C_{q,arom}$); 132.2, 129.2, 128.7, 128.7, 128.6, 128.5, 128.5, 128.4, 128.0, 127.8, 127.6 (*C*H$_{arom}$); 85.6 (C-1); 76.1 (C-3); 74.6 (C-2); 73.6 (PhCH$_2$); 72.3 (C-5); 70.3, 70.2 (PhCH$_2$); 69.7 (C-6); 66.7 (C-4). IR (thin film, cm^{-1}): 1002, 1026, 1082, 1098, 1239, 1275, 1441, 1457, 1747, 1751, 3497. HRMS calculated for $C_{35}H_{34}O_9SNa$ 653.18212 [M+Na]$^+$; found 653.18133.

Phenyl 2,3-di-*O*-benzyloxycarbonyl-4-*O*-methyl-6-*O*-benzyl-1-thio-α-D-mannopyranoside (11)



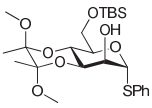
Compound **27** (0.53 g, 0.84 mmol, 1.0 eq) and TTBP (2.09 g, 8.4 mmol, 10.0 eq) were co-evaporated with toluene under inert atmosphere and flame dried (3Å) molecular sieves were added. The mixture was dissolved in DCM (28 ml, 0.03 M) and BF_4OMe_3 (1.24 g, 8.4 mmol, 10.0 eq) was added under a N_2 flow. The solution was stirred at rt for 45 minutes and quenched by addition of NEt_3. The reaction mixture was filtered over celite and concentrated *in vacuo*. Purification by means of column chromatography (*n*-pentane Et_2O 7:3) gave the title compound (0.38 g, 0.59 mmol, 70%) as a clear oil. $[\alpha]_D^{25}$ = 28.7 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.50-7.47 (m, 2H, C*H*$_{arom}$); 7.41-7.22 (m, 18H, C*H*$_{arom}$); 5.59 (d, 1H, *J* = 1.6 Hz, H-1); 5.42 (dd, 1H, *J* = 1.6, 3.2 Hz, H-2); 5.24-5.17 (m, 2H, PhC*H*$_2$); 5.11-5.07 (m, 3H, PhC*H*$_2$, H-3); 4.51 (dd, 2H, *J* = 12.0, 30.8 Hz, PHC*H*$_2$); 3.82-3.69 (m, 3H, H-4, H-6); 3.38 (s, 3H, OC*H*$_3$). ^{13}C-APT NMR (101 MHz) δ: 154.5, 154.3 (*C*O$_{Cbz}$); 138.2, 135.1, 134.8, 133.3 ($C_{q,arom}$); 132.1, 129.2, 128.7, 128.7, 128.5, 128.5, 128.4, 127.9, 127.9, 127.7 (*C*H$_{arom}$); 85.5 (C-1); 76.3 (C-3); 75.1 (C-2); 74.7 (C-4); 73.5 (PhCH$_2$); 72.7 (C-5); 70.3, 70.2 (PhCH$_2$); 68.7 (C-6); 60.9 (OCH$_3$). IR (thin film, cm^{-1}): 1000, 1026, 1053, 1065, 1085, 1089, 1100, 1158, 1275, 1441, 1457, 1498, 1751. HRMS calculated for $C_{36}H_{36}O_9SNa$ 667.19777 [M+Na]$^+$; found 667.19710.

Phenyl 3,4-*O*-(2,3-dimethoxybutane-2,3-diyl)-*O*-1-thio-α-D-mannopyranoside (21)



Compound **20** (14.0 g, 51.3 mmol, 1.0 eq) was dissolved in MeOH (366 mL, 0.14 M) and trimethyl orthoformate (22.4 mL, 205 mmol, 4.0 eq), 2,3-butanedione (6.75 mL, 76.9 mmol, 1.5 eq) and CSA (595 mg, 2.56 mmol, 0.05 eq) were added to the solution. The mixture was refluxed overnight after which the reaction was quenched by addition of NEt_3 (2.5 mL). The resulting mixture was concentrated *in vacuo* and purification by means of column chromatography (*n*-pentane-EtOAc 1:1) gave the title compound (16.8 g, 43.4 mmol, 85%) as an amorphous white solid. Spectroscopic data were in accordance with those previously reported in the literature.[61]

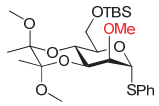
Phenyl 3,4-*O*-(2,3-dimethoxybutane-2,3-diyl)-6-O-*tert*-butyldimethylsilyl-1-thio-α-D-mannopyranoside (22)



Compound **21** (3.00 g, 7.76 mmol, 1.0 eq) was dissolved in dry DMF (78 mL, 0.1 M) and TBSCl (1.76 g, 11.6 mmol, 1.5 eq) was added to the solution. The mixture was cooled to 0 °C, and imidazole (1.06 g, 15.5 mmol, 2.0 eq) was then added. The reaction mixture was warmed to rt while stirring for 16 hours. The reaction was quenched by addition of H_2O, and after adding 20 mL of 1 M HCl was extracted with Et_2O (3x). The organic layers were combined, washed with brine, dried with $MgSO_4$ and concentrated *in vacuo*. Purification by means of column chromatography (*n*-pentane-Et_2O 4:1) gave the title compound (3.89 g, 7.76 mmol, 100%) as a clear oil. $[\alpha]_D^{25}$ = 246.0 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.40-7.37 (m, 2H, C*H*$_{arom}$); 7.21-7.11 (m, 3H, C*H*$_{arom}$); 5.43 (d, 1H, *J* = 0.4 Hz, H-1); 4.12-4.00 (m, 3H, H-2, H-4, H-5); 3.91 (dd, 1H, *J* = 3.2, 9.6 Hz, H-3); 3.78 (dd, 1H,

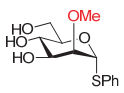
J = 4.4, 11.6 Hz, H-6); 3.70 (dd, 1H, *J* = 2.0, 11.6 Hz, H-6); 3.22 (s, 3H, OC$H_{3,BDA}$); 3.17 (s, 3H, OC$H_{3,BDA}$); 2.76 (bs, 1H, 2-O*H*); 1.25 (s, 3H, C$H_{3,BDA}$); 1.22 (s, 3H, C$H_{3,BDA}$); 0.78 (t, 9H, *J* = 2.8 Hz, C$H_{3,TBDMS}$); -0.05 (t, 3H, *J* = 2.8 Hz, C$H_{3,TBDMS}$) -0.08 (t, 3H, *J* = 2.8 Hz, C$H_{3,TBDMS}$). ^{13}C-APT NMR (101 MHz) δ: 134.5 ($C_{q,arom}$); 131.4, 129.0, 127.3 (CH_{arom}); 100.5, 99.9 ($C_{q,BDA}$); 88.0 (C-1); 72.5 (C-5); 71.2 (C-2); 69.0 (C-3); 63.0 (C-4); 61.6 (C-6); 48.2, 48.0 (OC$H_{3,BDA}$); 26.0 (C$H_{3,TBDMS}$); 18.5 ($C_{q,TBDMS}$); 17.9, 17.7 (C$H_{3,BDA}$); -5.0, -5.4 (C$H_{3,TBDMS}$). IR (thin film, cm^{-1}): 1026, 1050, 1073, 1096, 1115, 1163, 1189, 1252, 1281, 1362, 1378, 1441, 1462, 1472, 1482, 1751, 2858, 2886, 2928, 2951, 3454. HRMS calculated for $C_{24}H_{40}O_7SSiNa$ 523.21562 [M+Na]$^+$; found 523.21539.

Phenyl 2-*O*-methyl-3,4-*O*-(2,3-dimethoxybutane-2,3-diyl)-6-O-*tert*-butyldimethylsilyl-1-thio-α-D-mannopyranoside (23)



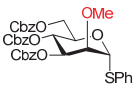
Compound **22** (4.00 g, 8.0 mmol, 1.0 eq) was dissolved in dry DMF (80 mL, 0.1 M) and MeI (0.75 mL, 12 mmol, 1.5 eq) was added to the solution. The mixture was cooled to 0 °C, and NaH (60%, 0.64 g, 16 mmol, 2.0 eq) was then added. The reaction mixture was warmed to rt while stirring for 3 hours. The reaction was then quenched by addition of H_2O, and the aqueous layer was extracted with Et_2O (3x). The organic layers were combined, 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 (3.78 g, 7.35 mmol, 92%) as a pale oil. $[\alpha]_D^{25}$ = 208.6 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.53-7.50 (m, 2H, CH_{arom}); 7.31-7.22 (m, 3H, CH_{arom}); 5.61 (d, 1H, *J* = 0.4 Hz, H-1); 4.18-4.16 (m, 1H, H-5); 4.10 (t, 1H, *J* = 10.0 Hz, H-4); 4.00 (dd, 1H, *J* = 2.8, 10.0 Hz, H-3); 3.86-3.84 (m, 2H, H-6); 3.73 (dd, 1H, *J* = 1.4, 2.6 Hz, H-2); 3.43 (s, 3H, OCH_3); 3.31 (s, 3H, OC$H_{3,BDA}$); 3.26 (s, 3H, OC$H_{3,BDA}$); 1.35 (s, 3H, C$H_{3,BDA}$); 1.30 (s, 3H, C$H_{3,BDA}$); 0.87 (s, 9H, C$H_{3,TBDMS}$); 0.05 (s, 3H, C$H_{3,TBDMS}$); 0.03 (s, 3H, C$H_{3,TBDMS}$). ^{13}C-APT NMR (101 MHz) δ: 135.1 ($C_{q,arom}$); 131.3, 130.4, 129.0, 127.3, 126.9 (CH_{arom}); 100.2, 99.6 ($C_{q,BDA}$); 85.2 (C-1); 80.2 (C-2); 72.9 (C-5); 68.9 (C-3); 63.4 (C-4); 61.8 (C-6); 57.8 (OCH_3); 48.1, 48.0 (OC$H_{3,BDA}$); 25.9 (C$H_{3,TBDMS}$); 18.4 ($C_{q,TBDMS}$); 17.9, 17.9 (C$H_{3,BDA}$); -5.1, -5.3 (C$H_{3,TBDMS}$). IR (thin film, cm^{-1}): 1052, 1076, 1115, 1123, 1128, 1132, 1192, 1252, 1375, 1457, 1464, 1472, 2833, 2856, 2929, 2951, 2992. HRMS calculated for 537.23182 $C_{25}H_{34}O_7SSiNa$ [M+Na]$^+$; found 537.23125.

Phenyl 2-*O*-methyl-1-thio-α-D-mannopyranoside (24)



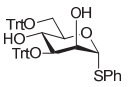
Compound **23** (0.90 g, 1.74 mmol, 1.0 eq) was dissolved in 95% TFA (17 mL, 0.1 M) and stirred for 2 minutes. The solution was then diluted with toluene and concentrated *in vacuo*. Purification by means of column chromatography (DCM-MeOH 19:1) gave the title compound (0.369 g, 1.29 mmol, 74%) as a clear oil. $[\alpha]_D^{25}$ = 145.1 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.52-7.47 (m, 2H, CH_{arom}); 7.30-7.21 (m, 3H, CH_{arom}); 5.57 (d, 1H, *J* = 0.8 Hz, H-1); 3.97 (t, 1H, *J* = 6.8 Hz, H-4); 3.77 (dd, 1H, *J* = 2.4, 12.0 Hz, H-6); 3.71-3.61 (m, 4H, H-2, H-3, H-5, H-6); 3.38 (OCH_3). ^{13}C-APT NMR (101 MHz) δ: 135.8 ($C_{q,arom}$); 132.9, 130.1, 128.6 (CH_{arom}); 86.4 (C-); 83.5 (C-2); 75.6 (C-4); 73.0 (C-3); 69.0 (C-5); 62.6 (C-6); 58.5 (OCH_3). IR (thin film, cm^{-1}): 1026, 1046, 1085, 1100, 1188, 1203, 1440, 1457, 1481, 1671, 1676, 1680, 1684, 2883, 2887, 2905, 2933, 3394. HRMS calculated for $C_{13}H_{18}O_5SNa$ 309.07726 [M+Na]$^+$; found 309.07665.

Phenyl 2-*O*-methyl-3,4,6-tri-*O*-benzyloxycarbonyl-1-thio-α-D-mannopyranoside (10)



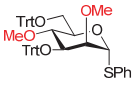
Compound **24** (0.349 g, 1.22 mmol, 1.0 eq) was dissolved in DCM (25 mL, 0.05 M) and DMAP (1.34 g, 11.0 mmol, 9.0 eq) was added to the solution. The mixture was cooled to 0 °C and CbzCl (1.03 mL, 7.31 mmol, 6.0 eq) was slowly added. The reaction was allowed to stir for 4 hours after while slowly warming to rt. The reaction was quenched by addition of 1 M HCl, and the organic layer was washed with sat. aq. $NaHCO_3$ and brine, dried with $MgSO_4$ and concentrated *in vacuo*. Purification by means of column chromatography (*n*-pentane-Et_2O 7:3) gave the title compound (0.66 g, 0.96 mmol, 79%) as a clear oil. $[\alpha]_D^{25}$ = 85.2 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.48-7.46 (m, 2H, C*H*$_{arom}$); 7.36-7.22 (m, 18H, C*H*$_{arom}$); 5.56 (s, 1H, H-1); 5.26 (t, 1H, *J* = 10.0 Hz, H-4); 5.16-5.04 (m, 7H, H-3, PhC*H*$_2$); 4.56-4.53 (m, 1H, H-5); 4.39 (dd, 1H, *J* = 6.0, 12.0 Hz, H-6); 4.25 (dd, 1H, *J* = 2.2, 11.8 Hz, H-6). 4.01 (d, 1H, *J* = 1.6 Hz, H-2); 3.36 (s, 3H, OC*H*$_3$). ^{13}C-APT NMR (101 MHz) δ: 154.9, 154.3, 154.2 (*C*O$_{Cbz}$); 135.2, 135.0, 134.9, 133.2 (C$_{q,arom}$); 131.9, 129.2, 129.1, 128.7, 128.6, 128.6, 128.5, 128.3, 128.3, 128.2, 128.0 (*C*H$_{arom}$); 84.8 (C-1); 78.9 (C-2); 75.2 (C-3); 70.9 (C-4); 70.3, 70.1, 69.8 (Ph*C*H$_2$); 69.2 (C-5); 66.2 (C-6); 58.7 (O*C*H$_3$). IR (thin film, cm^{-1}): 1025, 1066, 1189, 1243, 1266, 1278, 1382, 1441, 1457, 1751. HRMS calculated for $C_{37}H_{40}NO_{11}S$ 706.23166 $[M+Na]^+$; found 706.23158.

Phenyl 3,6-di-*O*-trityl-1-thio-α-D-mannopyranoside (28)



Compound **20** (4.13 g, 15.2 mmol, 1.0 eq) was dissolved in pyridine (300 mL, 0.05 M) and TrtCl (33.8 g, 121 mmol, 8 eq) was added to the solution. The mixture was warmed to 50 °C and the reaction was allowed to stir for 60 hours. The reaction was then quenched by addition of sat. aq. $NaHCO_3$ and the resulting mixture was extracted with $CHCl_3$ (3×). The combined organic layers were dried with $MgSO_4$, concentrated *in vacuo* and co-evaporated with toluene to remove traces of pyridine. Purification by means of column chromatography (*n*-pentane-Et_2O 4:1) gave the title compound (7.65 g, 10.1 mmol, 67%) as a white fluffy solid. $[\alpha]_D^{25}$ = 98.1 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.58-7.55 (m, 6H, C*H*$_{arom}$); 7.46-7.40 (m, 8H, C*H*$_{arom}$); 7.34-7.15 (m, 21H, C*H*$_{arom}$); 5.30 (d, 1H, *J* = 1.6 Hz, H-1); 4.18-4.13 (m, 1H, H-5); 3.99 (dt, 1H, *J* = 3.2, 9.6 Hz, H-4); 3.78 (dd, 1H, *J* = 3.0, 9.0 Hz, H-3); 3.38 (dd, 1H, *J* = 3.2, 10.0 Hz, H-6); 3.33 (dd, 1H, *J* = 5.6, 10.0 H-6); 2.96 (dd, 1H, *J* = 3.4, 4.6 Hz, H-2); 2.43 (d, 1H, *J* = 4.0 Hz, 2-O*H*); 2.06 (d, 1H, *J* = 3.2 Hz, 4-O*H*). ^{13}C-APT NMR (101 MHz) δ: 144.4, 143.9, 134.2 (C$_{q,arom}$); 131.6, 130.5, 129.0, 129.0, 128.9, 128.3, 127.9, 127.7, 127.3, 127.1 (*C*H$_{arom}$); 87.7 (*C*Ph$_3$); 87.2 (C-1); 87.1 (*C*Ph$_3$); 75.3 (C-3); 72.6 (C-5); 70.6 (C-2); 68.3 (C-4); 64.7 (C-6). IR (thin film, cm^{-1}): 1002, 1032, 1219, 1441, 1448, 1491, 3566. HRMS calculated for $C_{50}H_{44}O_5SNa$ 779.28071 $[M+Na]^+$; found 779.28018.

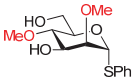
Phenyl 2,4-di-*O*-methyl-3,6-di-*O*-trityl-1-thio-α-D-mannopyranoside (29)



Compound **28** (1.45 g, 1.92 mmol, 1.0 eq) was dissolved in dry DMF (20 mL, 0.1 M) and MeI (0.48 mL, 7.68 mmol, 4.0 eq) was added to the solution. The mixture was cooled to 0 °C, and NaH (60%, 0.31 g, 7.68 mmol, 4.0 eq) was then added. The reaction mixture was warmed to rt while stirring for 3 hours. The reaction was then quenched by addition of H_2O, and the aqueous layer was extracted with Et_2O (3x). The organic layers were combined, washed with brine, dried with $MgSO_4$ and concentrated *in vacuo*. Purification by means of column chromatography (*n*-pentane-Et_2O 17:3) gave the title compound (1.36 g, 1.73 mmol, 90%) as a white fluffy solid. $[\alpha]_D^{25}$ = 77.2 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR

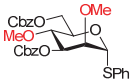
(300 MHz, T = 332K) δ: 7.60-7.55 (m, 6H, C*H*$_{arom}$); 7.49-7.41 (m, 8H, C*H*$_{arom}$); 7.30-7.13 (m, 21H, C*H*$_{arom}$); 5.41 (d, 1H, *J* = 2.4 Hz, H-1); 4.02-3.97 (m, 1H, H-5); 3.84 (dd, 1H, *J* = 2.7, 8.7 Hz, H-3); 3.58 (t, 1H, *J* = 8.9 Hz, H-4); 3.33-3.23 (m, 2H, H-6); 3.18 (s, 6H, OC*H*$_3$); 2.75 (d, 1H, *J* = 2.4 Hz, H-2). ^{13}C-APT NMR (75 MHz) δ: 145.2, 144.5, 135.6 (C$_{q,arom}$); 131.5, 129.7, 129.2, 128.9, 127.9, 127.8, 127.3, 127.1, 127.0 (*C*H$_{arom}$); 87.9, 86.8 (*C*Ph$_3$); 84.3 (C-1); 80.2 (C-2); 77.4 (C-4); 74.1 (C-3); 73.6 (C-5); 63.9 (C-6); 60.2, 56.9 (O*C*H$_3$). IR (thin film, cm^{-1}): 1099, 1232, 1448, 1484. HRMS calculated for $C_{52}H_{48}O_5SNa$ 807.31202 [M+Na]$^+$; found 807.31134.

Phenyl 2,4-di-*O*-methyl-1-thio-α-D-mannopyranoside (30)



Compound **29** (204 mg, 0.26 mmol, 1.0 eq) was dissolved in a mixture of AcOH and H_2O (4:1, 50 mL, 0.005 M) and the solution was warmed to 80 °C. The reaction was allowed to stir for 4 hours after which it was concentrated *in vacuo* and then co-evaporated with toluene. Purification by means of column chromatography (*n*-pentane-acetone 7:3) gave the title compound (68 mg, 0.20 mmol, 78%) as a clear oil. Spectroscopic data were in accordance with those previously reported in the literature.[62]

Phenyl 2,4-di-*O*-methyl-3,6-di-*O*-benzyloxycarbonyl-1-thio-α-D-mannopyranoside (9)



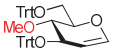
Compound **30** (0.392 g, 1.31 mmol, 1.0 eq) was dissolved in DCM (13 mL, 0.1 M) and DMAP (0.638 g, 5.22 mmol, 4.0 eq) was added to the solution. The mixture was cooled to 0 °C and CbzCl (0.55 mL, 3.92 mmol, 3.0 eq) was slowly added. The reaction was allowed to stir for 4 hours after while slowly warming to rt. The reaction was quenched by addition of 1 M HCl, and the organic layer was washed with sat. aq. $NaHCO_3$ and brine, dried with $MgSO_4$ and concentrated *in vacuo*. Purification by means of column chromatography (*n*-pentane-Et_2O 4:1) gave the title compound (0.742 g, 1.31 mmol, 100%) as a clear oil. $[\alpha]_D^{25}$ = 91.3 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.49-7.45 (m, 2H, C*H*$_{arom}$); 7.42-7.31 (m, 10H, C*H*$_{arom}$); 7.28-7.22 (m, 3H, C*H*$_{arom}$); 5.55 (d, 1H, *J* = 1.6 Hz, H-1); 5.25-5.18 (m, 2H, PhC*H*$_2$); 5.14 (s, 2H, PhC*H*$_2$); 4.97 (dd, 1H, *J* = 3.6, 9.6 Hz, H-3); 4.47-4.37 (m, 2H, H-6); 4.34-4.30 (m, 1H, H-5); 3.93 (dd, 1H, *J* = 2.0, 3.2 Hz, H-2); 3.67 (t, 1H, *J* = 9.6 Hz, H-4); 3.41 (s, 3H, OC*H*$_3$); 3.37 (s, 3H, OC*H*$_3$). ^{13}C-APT NMR (101 MHz) δ: 155.1, 154.5 (*C*O$_{Cbz}$); 135.2, 135.2, 133.8 (C$_{q,arom}$); 129.2, 128.7, 128.6, 128.6, 128.4, 128.4, 127.7 (*C*H$_{arom}$); 84.7 (C-1); 79.4 (C-2); 77.9 (C-3); 74.9 (C-4); 70.6 (C-5); 70.0, 69.8 (Ph*C*H$_2$); 66.6 (C-6); 60.8, 58.6 (O*C*H$_3$). IR (thin film, cm^{-1}): 1092, 1178, 1251, 1262, 1361, 1457, 1747. HRMS calculated for $C_{30}H_{36}O_9NS$ 586.21053 [M+Na]$^+$; found 586.21002.

3,6-di-*O*-trityl-D-glucal (52)

D-glucal (2.72 g, 18.6 mmol, 1.0 eq) was dissolved in pyridine (300 mL, 0.05 M) and TrtCl (20.7 g, 75 mmol, 4.0 eq) was added to the solution. The mixture was warmed to 69 °C and the reaction was allowed to stir at this temperature for 40 hours. The reaction was then quenched by addition of sat. aq. $NaHCO_3$ and the resulting mixture was extracted with $CHCl_3$ (3×). The combined organic layers were washed with sat. aq. $CuSO_4$ (2x), H_2O (2x), dried with $MgSO_4$, concentrated *in vacuo* and co-evaporated with toluene to remove traces of pyridine. The product was then purified with column chromatography to give the title compound (6.61 g, 10.48 mmol, 56%) as a white fluffy solid. $[\alpha]_D^{25}$ = 40.2 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.45-7.36 (m, 6H, C*H*$_{arom}$); 7.32-7.27 (m, 6H, C*H*$_{arom}$); 7.22-7.13 (m, 18H, C*H*$_{arom}$); 6.42-6.40 (m, 1H, H-1); 4.59-4.58 (m, 1H, H-2); 3.98-3.90 (m, 2H, H-5, H-6); 3.74 (s, 1H, H-3);

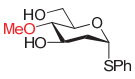
2.76 (d, 1H, *J* = 10.4 Hz, H-6); 2.44 (*s*, 1H, H-4); 1.54 (d, 1H, *J* = 3.2 Hz, 4-O*H*). ^{13}C-APT NMR (101 MHz) δ: 144.7, 144.0 ($C_{q,arom}$); 143.9 (C-1); 129.1, 128.9, 128.7, 128.0, 127.9, 127.3, 127.0 (CH_{arom}); 99.7 (C-2); 87.4, 86.6 (CPh_3); 78.4 (C-5); 67.4 (C-4); 66.9 (C-3); 62.7 (C-6). IR (thin film, cm^{-1}): 1003, 1027, 1039, 1095, 1219, 1450, 1490, 1647, 3439. HRMS calculated for $C_{44}H_{38}O_4Na$ 653.26623 [M+Na]$^+$; found 653.26640.

3,6-di-*O*-trityl-4-*O*-methyl-D-glucal (32)



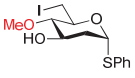
Compound **52** (6.50 g, 10.3 mmol, 1.0 eq) was dissolved in dry DMF (200 mL, 0.05 M) and MeI (1.28 mL, 20.6 mmol, 2.0 eq) was added to the solution. The mixture was cooled to 0 °C, and NaH (60%, 0.62 g, 15.5 mmol, 1.5 eq) was then added. The reaction mixture was warmed to rt while stirring for 3 hours. The reaction was then quenched by addition of H_2O, and the aqueous layer was extracted with Et_2O (3x). The organic layers were combined, washed with brine, dried with $MgSO_4$ and concentrated *in vacuo*. Purification by means of column chromatography (*n*-pentane-Et_2O 84:16) gave the title compound (4.11 g, 6.39 mmol, 62%) as a white fluffy solid. $[\alpha]_D^{25}$ = 76.8 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.47-7.43 (m, 6H, C*H*$_{arom}$); 7.31-7.28 (m, 6H, C*H*$_{arom}$); 7.26-7.13 (m, 18H, C*H*$_{arom}$); 6.51 (d, 1H, *J* = 6.4 Hz, H-1); 4.82 (dt, 1H, *J* = 1.6, 6.4 Hz, H-2); 4.17 (dd, 1H, *J* = 1.6, 9.2 Hz, H-5); 4.08 (dd, 1H, *J* = 9.2, 10.8 Hz, H-6); 3.77-3.75 (m, 1H, H-3); 2.83 (*s*, 3H, OC*H*$_3$); 2.60 (dd, 1H, *J* = 1.6, 10.8 Hz, H-6); 1.69 (d, 1H, *J* = 2.0 Hz, H-4). ^{13}C-APT NMR (101 MHz) δ: 144.8 ($C_{q,arom}$); 144.1 (C-1); 144.0 ($C_{q,arom}$); 129.2, 128.9, 128.7, 128.0, 127.9, 127.1, 127.0 (CH_{arom}); 99.4 (C-2); 87.6, 86.6 (CPh_3); 75.8 (C-4); 74.41 (C-5); 64.0 (C-3); 63.0 (C-6), 57.2 (O*C*H$_3$). IR (thin film, cm^{-1}): 1002, 1026, 1073, 1099, 1155, 1218, 1255, 1411, 1450, 1490, 1597, 1648. HRMS calculated for $C_{45}H_{40}O_4Na$ 667.28188 [M+Na]$^+$; found 667.28178.

Phenyl 2-deoxy-4-*O*-methyl-1-thio-α-D-glucopyranoside (33)



Compound **32** (2.46 g, 3.82 mmol, 1.0 eq) was dissolved in toluene (38 mL, 0.1 M). Thiophenol (1.56 mL, 15.3 mmol, 4.0 eq) and [$Re^VOCl_3(Me_2S)(Ph_3PO)$] (198 mg, 0.306 mmol, 0.08 eq) were added to the solution and the resulting mixture was stirred under N_2 atmosphere for 16 hours. Thereafter the reaction mixture was purified by means of column chromatography (*n*-pentane-acetone 6:4) to give the title compound (0.77 g, 2.87 mmol, 75%, α/ß >20:1) as an amorphous brown solid. ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.49-7.43 (m, 2H, C*H*$_{arom}$); 7.33-7.24 (m, 3H, C*H*$_{arom}$); 5.61 (d, 1H, *J* = 5.6 Hz, H-1); 4.10-4.03 (m, 2H, H-5, H-3); 3.82-3.75 (m, 2H, H-6); 3.60 (s, 3H, OC*H*$_3$); 3.15 (t, 1H, *J* = 9.2 Hz, H-4); 2.46 (bs, 1H, 3-O*H*); 2.36 (ddd, 1H, *J* = 0.8, 5.2, 13.6 Hz, H-2); 2.18-2.06 (m, 1H, H-2) 1.79 (bs, 1H, 6-O*H*). ^{13}C-APT NMR (100 MHz, $CDCl_3$) δ: 131.8, 129.2, 127.6 (CH_{arom}); 84.1 (C-1); 82.1 (C-4); 72.1 (C-5); 69.6 C-3); 62.1 (C-6); 61.0 (O*C*H$_3$); 38.1 (C-2). IR (thin film, cm^{-1}): 1026, 1043, 1181, 1440, 1448, 1481, 3401. HRMS calculated for $C_{13}H_{18}O_4SNa$ 293.08180 [M+Na]$^+$; found 293.08159. (due to the dark colour of the solution of this compound no optical rotation could be measured)

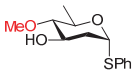
Phenyl 2,6-dideoxy-4-*O*-methyl-6-iodo-1-thio-α-D-glucopyranoside (34)



Compound **33** (0.76 g, 2.82 mmol, 1.0 eq) was dissolved in toluene (28 mL, 0.1 M) and PPh_3 (1.10 g, 4.23 mmol, 1.5 eq), imidazole (0.58 g, 8.46 mmol, 3.0 eq) and I_2 (1.43 g, 5.64 mmol, 2.0 eq) were added to the solution. The resulting mixture was warmed to 69 °C and stirred at this temperature for 1 hour after which it was cooled to rt and quenched with sat. aq. $Na_2S_2O_3$. The aqueous layer was extracted with Et_2O (3x) and the combined organic layers were washed with brine,

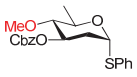
dried with $MgSO_4$ and concentrated *in vacuo*. Purification by means of column chromatography (*n*-pentane-Et_2O 4:1) gave the title compound (0.66 g, 1.73 mmol, 61%) as an amorphous white solid. $[\alpha]_D^{25}$ = 172.2 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.50-7.46 (m, 2H, C*H*$_{arom}$); 7.31-7.22 (m, 3H, C*H*$_{arom}$); 5.65 (d, 1H, *J* = 5.6 Hz, H-1); 4.11-4.05 (m, 1H, H-3); 3.83-3.79 (m, 1H, H-5); 3.68 (s, 3H, OC*H*$_3$); 3.50-3.43 (m, 2H, H-6); 3.00 (t, 1H, *J* = 9.0 Hz, H-4); 2.46 (bs, 1H, 3-O*H*); 2.36 (ddd, 1H, *J* = 1.0, 5.0, 13.6 Hz, H-2); 2.18-2.10 (m, 1H, H-2). ^{13}C-APT NMR (100 MHz, $CDCl_3$) δ: 134.7 ($C_{q,arom}$); 131.3, 129.1, 127.3 (*C*H$_{arom}$); 85.8 (C-4); 84.0 (C-1); 70.5 (C-3); 69.5 (C-5); 61.4 (O*C*H$_3$); 38.5 (C-2); 8.0 (C-6). IR (thin film, cm^{-1}): 1026, 1035, 1085, 1112, 1183, 1440, 1481, 3411. HRMS calculated for $C_{13}H_{18}IO_3S$ 381.00158 $[M+H]^+$; found 381.00103.

Phenyl 2,6-dideoxy-4-*O*-methyl-1-thio-α-D-glucopyranoside (35)



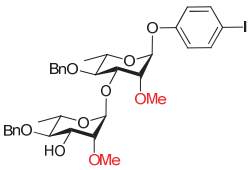
Compound **34** (0.623 g, 1.64 mmol, 1.0 eq) was dissolved in dry DMF (25 mL, 0.06 M) and $NaHCO_3$ (0.44 g, 5.24 mmol, 3.2 eq) was added to the solution. The mixture was purged with N_2 after which Pd/C (5 wt%, 0.70 g, 0.33 mmol, 0.2 eq) was added to the solution. The resulting mixture was purged with H_2 and allowed to stir under H_2 atmosphere for 20 hours. The reaction mixture was then purged with N_2, diluted with Et_2O and filtered over celite. Water was added and the aqueous layer was extracted with Et_2O (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 4:6) gave the title compound (0.34 g, 1.34 mmol, 82%) as an amorphous white solid. $[\alpha]_D^{25}$ = 284.3 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 7.48-7.40 (m, 2H, C*H*$_{arom}$); 7.29-7.22 (m, 3H, C*H*$_{arom}$); 5.56 (d, 1H, *J* = 5.6 Hz, H-1); 4.16-4.12 (m, 1H, H-5); 4.01-3.95 (m, 1H, H-3); 3.60 (s, 3H, OC*H*$_3$); 2.76 (t, 1H, *J* = 9.0 Hz, H-4); 2.35 (ddd, 1H, *J* = 1.2, 5.2, 9.2 Hz, H-2) 2.15-2.07 (m, 1H, H-2); 1.31 (d, 3H, *J* = 6.4 Hz, H-6). ^{13}C-APT NMR (100 MHz, $CDCl_3$). δ: 135.3 ($C_{q,arom}$); 131.3, 129.0, 127.2 (*C*H$_{arom}$); 88.4 (C-4); 83.9 (C-1); 69.4 (C-3); 68.1 (C-5); 61.0 (O*C*H$_3$); 38.4 (C-2); 18.2 (C-6). IR (thin film, cm^{-1}): 1026, 1036, 1105, 1183, 1440, 1481, 2926, 3440.

Phenyl 2,6-dideoxy-3-*O*-benzyloxycarbonyl-4-*O*-methyl-1-thio-α-D-glucopyranoside (4)



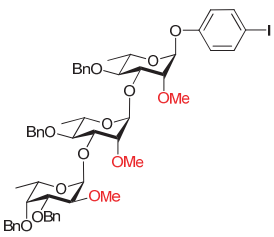
Compound **35** (0.34 g, 1.34 mmol, 1.0 eq) was dissolved in DCM (25 mL, 0.05 M) and DMAP (1.31 g, 10.7 mmol, 8.0 eq) was added to the solution. The mixture was cooled to 0 °C and CbzCl (0.95 mL, 6.70 mmol, 5.0 eq) was slowly added. The reaction was allowed to stir for 20 hours while slowly warming to rt. The reaction was then quenched by addition of 1 M HCl, and the organic layer was washed with sat. aq. $NaHCO_3$ and brine, dried with $MgSO_4$ and concentrated *in vacuo*. Purification by means of column chromatography (*n*-pentane-Et_2O 4:1) gave the title compound (0.49 g, 1.26 mmol, 94%) as an amorphous white solid. $[\alpha]_D^{25}$ = 52.3 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.46-7.34 (m, 7H, C*H*$_{arom}$); 7.31-7.22 (m, 3H, C*H*$_{arom}$); 5.55 (d, 1H, *J* = 5.6 Hz, H-1); 5.23-5.16 (m, 2H, PhC*H*$_2$); 5.09-5.03 (m, 1H, H-3); 4.20 (dq, 1H, *J* = 6.0, 9.2 Hz, H-5); 3.48 (s, 3H, OC*H*$_3$); 2.93 (t, 1H, *J* = 9.0 Hz, H-4); 2.48 (ddd, 1H, *J* = 1.6, 5.2, 13.2 Hz, H-2); 2.19-2.11 (m, 1H, H-2); 1.29 (d, 3H, *J* = 6.4 Hz, H-6). ^{13}C-APT NMR (100 MHz) δ: 154.5 (*C*O$_{Cbz}$); 135.3, 134.9 ($C_{q,arom}$); 131.4, 129.1, 128.8, 128.6, 127.3 (*C*H$_{arom}$); 84.5 (C-4); 83.1 (C-1); 76.0 (C-3); 69.9 (O*C*H$_2$); 68.2 (C-5); 60.7 (O*C*H$_3$); 36.1 (C-2); 17.9 (C-6). IR (thin film, cm^{-1}): 1061, 1081, 1093, 1113, 1217, 1256, 1292, 1747. HRMS calculated for $C_{21}H_{24}O_5SNa$ 411.12421 $[M+Na]^+$; found 411.12348.

4-iodophenyl 2-*O*-methyl-3-*O*-(2-*O*-methyl-4-*O*-benzyl-α-L-rhamnopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranoside (36)



Donor **1** (407 mg, 0.82 mmol, 1.5 eq), Ph_2SO (183 mg, 0.91 mmol, 1.7 eq) and TTBP (511 mg, 2.1 mmol, 3.8 eq) were dried by co-evaporation with toluene (3x) followed by 3 vacuum/nitrogen purges. The mixture was then dissolved in DCM (16 mL, 0.05 M) and flame-dried 3Å molecular sieves were added. The solution was then cooled to -70 °C after which Tf_2O (0.15 mL, 0.91 mmol, 1.7 eq) was added to the solution. After stirring for 30 minutes, acceptor **6** (258 mg, 0.55 mmol, 1.0 eq), which was also dried by co-evaporation with toluene (3x) followed by 3 vacuum/nitrogen purges, was dissolved in DCM (1.4 mL, 0.4 M) and slowly added to the solution. After TLC analysis indicated the consumption of the acceptor (3 hours) the reaction was quenched by addition of NEt_3. The reaction mixture was then diluted with DCM, filtered over celite, washed with brine, dried with $MgSO_4$ and concentrated *in vacuo*. The crude mixture was purified by means of column chromatography (*n*-pentane-Et_2O 3:1) and all fractions containing product were concentrated *in vacuo*. The resulting residue (416 mg, 0.49 mmol, 89% crude yield) was then dissolved in MeOH (10 mL, 0.05 M) and a catalytic amount of K_2CO_3 was added. The reaction was allowed to stir for 16 hours after which it was diluted with DCM, filtered over celite and concentrated *in vacuo*. Purification by means of column chromatography (*n*-pentane-Et_2O 1:1) gave the title compound (328 mg, 0.46 mmol, 83% over 2 steps) as a pale oil. $[\alpha]_D^{25}$ = -84.5 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.63-7.48 (m, 2H, C*H*$_{arom}$); 7.43-7.18 (m, 10H, C*H*$_{arom}$); 6.94-6.68 (m, 2H, C*H*$_{arom}$); 5.47 (d, 1H, *J* = 2.0 Hz, H-1); 5.15 (d, *J* = 1.6 Hz, H-1'); 4.90 (d, 1H, *J* = 11.2 Hz, PhC*H*H); 4.79 (d, 1H *J* = 11.2 Hz, PhCH*H*); 4.72-4.66 (m, 2H, PhC*H*H, PhCH*H*); 4.21 (dd, 1H, *J* = 3.2, 9.6 Hz, H-3); 4.00 (dt, 1H, *J* = 3.6, 9.2 Hz, H-3'); 3.87 (dq, 1H, *J* = 6.4, 9.4 Hz, H-5'); 3.81–3.65 (m, 2H, H-2, H-5); 3.61–3.53 (m, 4H, H-4, OC*H*$_3$); 3.47 (dd, 1H, *J* = 1.6, 3.6 Hz, H-2'); 3.29 (t, 1H, *J* = 9.4 Hz, H-4'); 3.20 (s, 3H, OC*H*$_3$); 2.38 (dd, 1H, *J* = 1.6, 9.2 Hz, 3'-O*H*); 1.35 (d, 3H, *J* = 6.4 Hz, 3H); 1.26 (d, 3H, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz) δ: 156.2, 138.6 (C$_{q,arom}$); 138.5 (C*H*$_{arom}$); 138.3 (C$_{q,arom}$); 128.6, 128.5, 128.1, 127.9, 127.8, 127.2, 118.7 (C*H*$_{arom}$); 98.7 (C-1'); 95.1 (C-1); 84.9 (C*I*$_{arom}$); 82.1 (C-4'); 81.0 (C-2'); 80.4 (C-4); 80.2 (C-2); 78.7 (C-3); 75.2, (Ph*C*H$_2$); 71.6 (C-3'); 69.2 (C-5); 68.0 (C-5'); 59.3, 58.7 (O*C*H$_3$); 18.2 (C-6'); 18.1 (C-6). IR (thin film, cm^{-1}): 1029, 1043, 1059, 1098, 1138, 1232, 1454, 1484, 2896, 2933, 3519. HRMS calculated for $C_{34}H_{41}IO_9Na$ 743.16875 $[M+Na]^+$; found 743.16895.

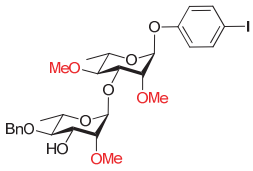
4-iodophenyl 2-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(2-*O*-methyl-3,4-di-*O*-benzyl-α-L-fucopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranoside (38)



The title compound was synthesized according to general procedure B using acceptor **36** (70 mg, 97 µmol, 1.0 eq), donor **5** (88 mg, 0.19 mmol, 2.0 eq) and IDCP (137 mg, 0.29 mmol, 3.0 eq). Column chromatography (*n*-pentane-Et_2O 1:1) gave the title compound (76 mg, 71 µmol, 74%, α-β 6:1) as a pale oil. $[\alpha]_D^{25}$ = -88.6 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.57-7.55 (m, 2H, C*H*$_{arom}$); 7.40-7.22 (m, 20H, C*H*$_{arom}$); 6.85-6.82 (m, 2H, C*H*$_{arom}$); 5.48 (d, 1H, *J* = 1.6 Hz, H-1); 5.23-5.19 (m, 2H, H-1", PhC*H*H); 5.15 (d, 1H, *J* = 1.2 Hz, H-1'); 5.00 (d, 1H, *J* = 11.6 Hz, PhC*H*H); 4.85-4.80

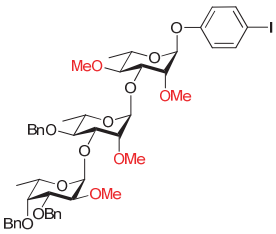
(m, 2H, PhC*H*H, PhC*H*H); 4.73 (d, 1H, *J* = 12.4 Hz, PhCH*H*); 4.67-4.63 (m, 2H, PhCH*H*, PhCH*H*); 4.54 (d, 1H, *J* = 11.2 Hz, PhCH*H*); 4.17 (dd, 1H, *J* = 3.2, 9.6 Hz, H-3); 4.09-4.02 (m, 2H, H-3', H-5"); 3.98-3.89 (m, 2H, H-3", H-5'); 3.82 (dd, 1H, *J* = 3.6, 10.0 Hz, H-2"); 3.75-3.66 (m, 4H, H-2, H-2', H-4", H-5); 3.55-3.44 (m, 5H, H-4, H-4', OCH_3); 3.39 (s, 3H, OCH_3); 3.21 (s, 3H, OCH_3); 1.33 (d, 3H, *J* = 6.4 Hz, H-6'); 1.24 (d, 3H, *J* = 6.0 Hz, H-6); 1.08 (d, 3H, *J* = 6.4 Hz, H-6"). ^{13}C-APT NMR (101 MHz) δ: 156.3, 139.2, 139.1, 138.8 ($C_{q,arom}$); 138.5 (*C*H$_{arom}$); 138.3 ($C_{q,arom}$); 128.5, 128.5, 128.4, 128.3, 127.9, 127.8, 127.7, 127.5, 127.5, 127.4, 118.7 (*C*H$_{arom}$); 100.1 (C-1"); 98.9 (C-1'); 94.8 (C-1); 84.9 (*C*I$_{arom}$); 80.7 (C-3'); 80.2 (C-2'); 79.9 (C-2); 79.8 (C-4); 79.6 (C-3); 78.9 (C-3"); 78.6 (C-2"); 77.8 (C-4"); 75.4, 75.2, 75.0, 72.9 (Ph*C*H$_2$); 69.1 (C-5); 68.7 (C-5'); 67.0 (C-5); 59.1, 59.1, 57.8 (OCH_3); 18.4 (C-6); 18.1 (C-6'); 17.1 (C-6"). IR (thin film, cm^{-1}): 1042, 1098, 1129, 1178, 1195, 1232, 1355, 1454, 1484, 2929, 2976, 3030. HRMS calculated for $C_{55}H_{65}IO_{13}Na$ 1083.33621 [M+Na]$^+$; found 1083.33613.

4-iodophenyl 2,4-di-*O*-methyl-3-*O*-(2-*O*-methyl-4-*O*-benzyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (37)



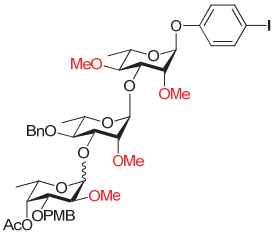
Donor **1** (0.742 g, 1.5 mmol, 1.5 eq), Ph_2SO (0.394 g, 1.95 mmol, 2.0 eq) and TTBP (0.932 g, 3.75 mmol, 3.8 eq) were dried by co-evaporation with toluene (3x) followed by 3 vacuum/nitrogen purges. The mixture was then dissolved in DCM (20 mL, 0.08 M) and flame-dried 3Å molecular sieves were added. The solution was then cooled to -65 °C after which Tf_2O (0.33 mL, 1.95 mmol, 2.0 eq) was added to the solution. After stirring for 30 minutes, acceptor **2** (0.394 g, 1.0 mmol, 1.0 eq), which was also dried by co-evaporation with toluene (3x) followed by 3 vacuum/nitrogen purges, was dissolved in DCM (2.5 mL, 0.4 M) and slowly added to the solution. After TLC analysis indicated the consumption of the acceptor (3 hours) the reaction was quenched by addition of NEt_3. The reaction mixture was then diluted with DCM, filtered over celite, washed with brine, dried with $MgSO_4$ and concentrated *in vacuo*. The crude mixture was purified by means of column chromatography (*n*-pentane-Et_2O 3:1) and all fractions containing product were concentrated *in vacuo*. The resulting residue (0.756 g, 0.97 mmol, 97% crude yield) was then dissolved in MeOH (20 mL, 0.05 M) and a catalytic amount of K_2CO_3 was added. The reaction was allowed to stir for 16 hours after which it was quenched with sat. aq. NH_4Cl and extracted with Et_2O (3x). The organic layers were combined, washed with 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 (0.549 g, 0.85 mmol, 85% over 2 steps) as a pale oil. $[\alpha]_D^{25}$ = -103.5 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.58-7.55 (m, 2H, C*H*$_{arom}$); 7.40-7.26 (m, 5H, C*H*$_{arom}$); 6.85-6.82 (m, 2H, C*H*$_{arom}$); 5.44 (d, 1H, *J* = 1.6 Hz, H-1); 5.22 (d, 1H, *J* = 1.2 Hz, H-1'); 4.79 (dd, 2H, *J* = 11.2, 89.6 Hz, Ph*C*H$_2$); 4.10 (dd, 1H, *J* = 3.2, 9.6 Hz, H-3); 4.00 (dt, 1H, *J* = 4.0, 9.2 Hz, H-3'); 3.89-3.82 (m, 1H, H-5'); 3.65 (dd, 1H, *J* = 2.0, 3.2 Hz, H-2); 3.63-3.56 (m, 2H, H-2', H-5); 3.54 (s, 3H, OCH_3); 3.52 (s, 3H, OCH_3); 3.51 (s, 3H, OCH_3); 3.31 (t, 1H, *J* = 9.4 Hz, H-4'); 3.24 (t, 1H, *J* = 9.6 Hz, H-4); 2.46 (dd, 1H, *J* = 5.2, 9.2 Hz, 3'-O*H*); 1.36 (d, 3H, *J* = 6.4 Hz, H-6'); 1.25 (d, 3H, *J* = 6.4 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 156.2, 138.5 ($C_{q,arom}$); 138.5, 128.5, 128.1, 127.9, 118.7 (*C*H$_{arom}$); 98.4 (C-1'); 95.2 (C-1); 84.9 (*C*I$_{arom}$); 82.4 (C-4); 82.1 (C-4'); 81.2 (C-2'); 80.1 (C-2); 78.2 (C-3); 75.3 (Ph*C*H$_2$); 69.1 (C-3'); 67.9 (C-5); 61.2, 59.4, 58.8 (OCH_3); 18.2 (C-6'); 17.9 (C-6). IR (thin film, cm^{-1}): 1001, 1008, 1028, 1041, 1098, 1139, 1233, 1264, 1483. HRMS calculated for $C_{28}H_{37}IO_9Na$ 667.13800 [M+Na]$^+$; found 667.13744.

4-iodophenyl 2,4-di-*O*-methyl-3-*O*-(2-*O*-methyl-3-O-(2-*O*-methyl-3,4-di-*O*-benzyl-α-L-fucopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (39)



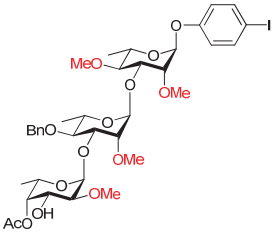
The title compound was synthesized according to general procedure B using acceptor **37** (59 mg, 92 µmol, 1.0 eq), donor **5** (82 mg, 0.18 mmol, 2.0 eq) and IDCP (129 mg, 0.27 mmol, 3.0 eq). Column chromatography (*n*-pentane-Et_2O 1:1) gave the title compound (89 mg, 90 µmol, 99%, α/β 6:1) as a pale oil. $[\alpha]_D^{25}$ = -95.0 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.58-7.54 (m, 2H, C*H*$_{arom}$); 7.40-7.25 (m, 15H, C*H*$_{arom}$); 6.84-6.81 (m, 2H, C*H*$_{arom}$); 5.45 (d, 1H, *J* = 1.6 Hz, H-1); 5.22-5.20 (m, 2H, H-1", PhC*H*H); 5.14 (d, 1H, *J* = 1.6 Hz, H-1'); 5.00 (d, 1H, *J* = 11.6 Hz, PhC*H*H); 4.85 (d, 1H, *J* = 12.0 Hz, PhC*H*H); 4.74 (d, 1H, *J* = 12.4 Hz, PhCH*H*); 4.67 (d, 1H, *J* = 11.6 Hz, PhCH*H*); 4.55 (d, 1H, *J* = 11.2 Hz, PhCH*H*); 4.11 (q, 1H, *J* = 6.4 Hz, H-5"); 4.05-3.91 (m, 4H, H-3, H-3', H-3", H-5'); 3.82 (dd, 1H, *J* = 3.8, 10.2 Hz, H-2"); 3.72-3.69 (m, 3H, H-2, H-2', H-4"); 3.60-3.45 (m, 11H, H-4', H-5, OC*H*$_3$); 3.39 (s, 3H, OC*H*$_3$); 3.20 (t, 1H, *J* = 9.6 Hz, H-4); 1.32 (d, 3H, *J* = 6.0 Hz, H-6'); 1.24 (d, 3H, *J* = 6.4 Hz, H-6); 1.14 (d, 3H, *J* = 6.4 Hz, H-6"). ^{13}C-APT NMR (101 MHz) δ: 156.3, 139.2, 139.1 138.7 (C$_{q,arom}$); 138.5, 128.6, 128.5, 128.4, 128.4, 127.9, 127.8, 127.6, 127.5, 127.5, 118.7 (*C*H$_{arom}$); 100.1 (C-1"); 98.8 (C-1'); 94.9 (C-1); 84.9 (*C*I$_{arom}$); 81.9 (C-4); 80.9 (C-2'); 80.7 (C-3'); 80.0 (C-2); 80.0 (C-3); 79.7 (C-4'); 79.0 (C-3"); 78.6 (C-2"); 77.7 (C-4"); 75.2, 75.0, 73.0 (Ph*C*H$_2$); 69.1 (C-5); 68.8 (C-5'); 66.9 (C-5"); 61.4, 59.2, 59.1, 58.0 (O*C*H$_3$); 18.4 (C-6'); 17.9 (C-6); 17.1 (C-6"). IR (thin film, cm^{-1}): 1042, 1072, 1099, 1175, 1193, 1232, 1357, 1379, 1454, 1484, 2830, 2932, 2974. HRMS calculated for $C_{49}H_{61}IO_{13}Na$ 1007.30545 $[M+Na]^+$; found 1007.30503.

4-iodophenyl 2,4-di-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(4-methoxybenzyl)-4-*O*-acetyl-L-fucopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (40)



The title compound was synthesized according to general procedure B using acceptor **37** (161 mg, 0.25 mmol, 1.0 eq), donor **3** (216 mg, 0.50 mmol, 2.0 eq) and IDCP (352 mg, 0.75 mmol, 3.0 eq). Column chromatography (*n*-pentane-Et_2O 4:6) gave the title compound (163 mg, 0.17 mmol, 74%, α/β 6:1) as a pale oil. The mixture was used in the next step without further purification or analysis.

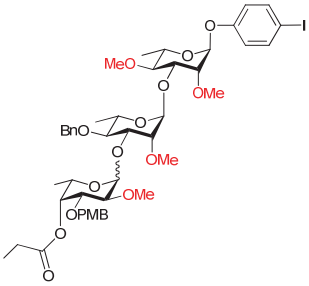
4-iodophenyl 2,4-di-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(2-*O*-methyl-4-*O*-acetyl-α-L-fucopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (43)



Compound **40** (163 mg, 0.17 mmol, 1.0 eq) was dissolved in DCM/H_2O (16:1, 1.7 mL, 0.1 M). After stirring for a few minutes DDQ (46 mg, 0.20 mmol, 1.2 eq) was added to the solution. The reaction was stirred vigorously for 4 hours after which it was quenched by addition of sat. aq. $NaHCO_3$. The organic layer was then washed sat. aq. $NaHCO_3$, dried with $MgSO_4$ and concentrated *in vacuo*. Purification by means of column chromatography (*n*-pentane-Et_2O 1:4) gave the title compound (113

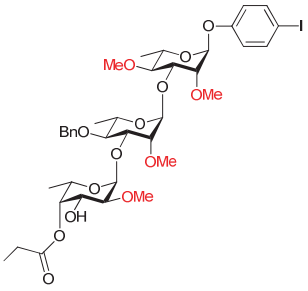
mg, 0.13 mmol, 79%) as a pale oil. $[\alpha]_D^{25}$ = -124.2 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.57 (dd, 2H, *J* = 2.0, 6.8 Hz, C*H*$_{arom}$); 7.38-7.27 (m, 5H, C*H*$_{arom}$); 6.84 (dd, 2H, *J* = 2.0, 6.8 Hz, C*H*$_{arom}$); 5.47 (d, 1H, *J* = 1.6 Hz, H-1); 5.29 (d, 1H, *J* = 2.4 Hz, H-4''); 5.24 (d, 1H, *J* = 3.6 Hz, H-1''); 5.19 (d, 1H, *J* = 1.2 Hz, H-1'); 5.13 (d, 1H, *J* = 11.2 Hz, PhC*H*H); 4.59 (d, 1H, *J* = 11.6 hz, PhCH*H*); 4.35 (q, 1H, *J* = 6.8 Hz, H-5''); 4.25 (dd, 1H, *J* = 3.4, 10.2 Hz, H-3''); 4.07-4.00 (m, 2H, H-3, H-3'); 3.96-3.92 (m, 1H, H-5'); 3.74-3.72 (m, 2H, H-2, H-2'); 3.62-3.57 (m, 1H, H-5); 3.54-3.45 (m, 11H, H-2'', H-4', OC*H*$_3$); 3.31 (s, 3H, OC*H*$_3$); 3.22 (t, 1H, *J* = 9.6 Hz, H-4); 2.35 (bs, 1H, 3''-O*H*); 2.19 (s, 3H, C*H*$_{3,Ac}$); 1.32 (d, 3H, *J* = 6.4 Hz, H-6'); 1.25 (d, 3H, *J* = 6.0 Hz, H-6); 1.15 (d, 3H, *J* = 6.8 Hz, H-6''). ^{13}C-APT NMR (101 MHz) δ: 171.3 (*C*O$_{Ac}$); 156.3, 139.1 (C$_{q,arom}$); 138.5, 128.4, 127.6, 127.5, 118.7 (*C*H$_{arom}$); 99.2 (C-1''); 98.5 (C-1'); 94.8 (C-1); 84.9 (*C*I$_{arom}$); 82.0 (C-3' and C-4); 80.7 (C-2); 80.1 (C-2'); 79.8 (C-3); 79.4 (C-4'); 78.5 (C-2''); 75.1 (Ph*C*H$_2$); 73.0 (C-4''); 69.1 (C-5); 68.8 (C-5'); 68.1 (C-3''); 65.3 (C-5''); 61.3, 59.1, 58.2, 57.8 (O*C*H$_3$); 21.0 (*C*H$_{3,Ac}$); 18.4 (C-6'); 17.9 (C-6); 16.6 (C-6''). IR (thin film, cm^{-1}): 1042, 1098, 1128, 1232, 1448, 1484, 1740, 3490. HRMS calculated for $C_{37}H_{51}IO_{14}Na$ 869.22212 $[M+Na]^+$; found 869.22114.

4-iodophenyl 2,4-di-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(4-methoxybenzyl)-4-*O*-propionyl-α-L-fucopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (42)



The title compound was synthesized according to general procedure B using acceptor **37** (66 mg, 102 µmol, 1.0 eq), donor **7** (91 mg, 0.20 mmol, 2.0 eq) and IDCP (144 mg, 0.31 mmol, 3.0 eq). Column chromatography (*n*-pentane-Et_2O 6:4) gave the title compound (84 mg, 86 µmol, 84%, α/β 6:1) as a pale oil. The mixture was used in the next step without further purification or analysis.

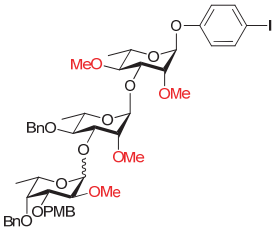
4-iodophenyl 2,4-di-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(2-*O*-methyl-4-*O*-propionyl-α-L-fucopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (45)



Compound **42** (180 mg, 0.18 mmol, 1.0 eq) was dissolved in DCM/H_2O (19:1, 2.0 mL, 0.1 M). After stirring for a few minutes DDQ (50 mg, 0.22 mmol, 1.2 eq) was added to the solution. The reaction was stirred vigorously for 1 hour after which it was quenched by addition of sat. aq. $NaHCO_3$. The organic layer was then washed sat. aq. $NaHCO_3$, dried with $MgSO_4$ and concentrated *in vacuo*. Purification by means of column chromatography (*n*-pentane-Et_2O 1:4) gave the title compound (121 mg, 0.14 mmol, 77%) as a pale oil. $[\alpha]_D^{25}$ = -119.6 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.57 (dd, 2H, *J* = 2.0, 6.8 Hz, C*H*$_{arom}$); 7.38-7.26 (m, 5H, C*H*$_{arom}$); 6.84 (dd, 2H, *J* = 2.2, 7.0 Hz, C*H*$_{arom}$); 5.46 (d, 1H, *J* = 1.6 Hz, H-1); 5.30 (d, 1H, *J* = 2.4 Hz, H-4''); 5.24 (d, 1H, *J* = 3.6 Hz, H-1''); 5.19 (d, 1H, *J* = 1.6 Hz, H-1'); 5.13 (d, 1H, *J* = 11.6 Hz, PhC*H*H); 4.59 (d, 1H, *J* = 11.6 hz, PhCH*H*); 4.35 (q, 1H, *J* = 6.8 Hz, H-5''); 4.25 (dd, 1H, *J* = 3.6, 10.0 Hz, H-3''); 4.07-4.00 (m, 2H, H-3, H-3'); 3.96-3.92 (m, 1H, H-5'); 3.74-3.71 (m, 2H, H-2, H-2'); 3.62-3.45 (m,

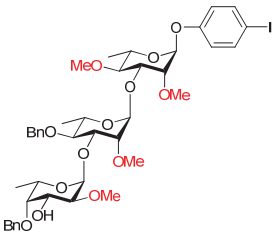
12H, H-2", H-4', H-5, OCH_3); 3.31 (s, 3H, OCH_3); 3.22 (t, 1H, *J* = 9.6 Hz, H-4); 2.47 (dq, 2H, *J* = 1.4, 7.5 Hz, CH_2CH$_3$); 2.35 (bs, 1H, 3"-O*H*); 1.32 (d, 3H, *J* = 6.0 Hz, H-6'); 1.25 (d, 3H, *J* = 6.4 Hz, H-6); 1.20 (t, 3H, *J* = 7.6 Hz, CH$_2$CH_3); 1.14 (d, 3H, *J* = 6.8 Hz, H-6"). ^{13}C-APT NMR (101 MHz) δ: 174.8 (*C*O$_{propionyl}$); 156.3, 139.0 (C$_{q,arom}$); 138.5, 128.3, 127.6, 127.5, 118.7 (*C*H$_{arom}$); 99.2 (C-1"); 98.5 (C-1'); 94.9 (C-1); 84.9 (*C*I$_{arom}$); 82.0 (C-4); 81.4 (C-3'); 80.7 (C-2); 80.1 (C-2'); 79.7 (C-3); 79.4 (C-4'); 78.5 (C-2"); 75.1 (Ph*C*H$_2$); 72.8 (C-4"); 69.1 (C-5); 68.8 (C-5'); 68.1 (C-3"); 65.3 (C-5"); 61.3, 59.1, 58.3, 57.8 (O*C*H$_3$); 27.7 (*C*H$_2$CH$_3$); 18.3 (C-6'); 17.9 (C-6); 16.5 (C-6") 9.4 (CH$_2$*C*H$_3$). IR (thin film, cm^{-1}): 1042, 1098, 1128, 1232, 1484, 1739, 3494. HRMS calculated for $C_{38}H_{53}IO_{14}Na$ 883.23777 [M+Na]$^+$; found 883.23735.

4-iodophenyl 2,4-di-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(4-methoxybenzyl)-4-*O*-benzyl-L-fucopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (41)



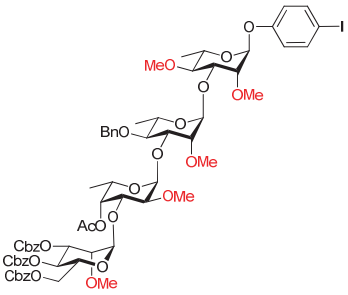
The title compound was synthesized according to general procedure B using acceptor **37** (129 mg, 0.20 mmol, 1.0 eq), donor **8** (192 mg, 0.40 mmol, 2.0 eq) and IDCP (281 mg, 0.60 mmol, 3.0 eq). Column chromatography (*n*-pentane-Et$_2$O 1:1) gave the title compound (190 mg, 0.19 mmol, 96%, α-β 6:1) as a pale oil. The mixture was used in the next step without further purification or analysis.

4-iodophenyl 2,4-di-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(2-*O*-methyl-4-*O*-benzyl-α-L-fucopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (44)



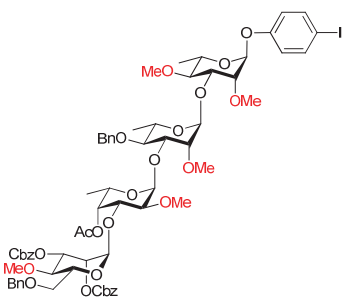
Compound **41** (190 mg, 0.19 mmol, 1.0 eq) was dissolved in DCM/H$_2$O (19:1, 1.9 mL, 0.1 M). After stirring for a few minutes DDQ (53 mg, 0.23 mmol, 1.2 eq) was added to the solution. The reaction was stirred vigorously for 4 hours after which it was quenched by addition of sat. aq. NaHCO$_3$. The organic layer was then washed sat. aq. NaHCO$_3$, dried with MgSO$_4$ and concentrated *in vacuo*. Purification by means of column chromatography (*n*-pentane-Et$_2$O 3:7) gave the title compound (121 mg, 0.14 mmol, 70%) as a pale oil. [α]$_D^{25}$ = -133.8 ° (c = 1.0, CHCl$_3$). ^{1}H-NMR (400 MHz) δ: 7.59-7.55 (m, 2H, C*H*$_{arom}$); 7.42-7.23 (m, 10H, C*H*$_{arom}$); 6.85-6.81 (m, 2H, C*H*$_{arom}$); 5.46 (d, 1H, *J* = 1.6 H-1); 5.22 (d, 1H, *J* = 3.6 Hz, H-1"); 5.16-5.12 (m, 2H, H-1', PhC*H*H); 4.81 (dd, 2H, *J* = 11.6, 60.8 Hz, PhC*H*$_2$); 4.59 (d, 1H, *J* = 11.6 Hz, PhCH*H*); 4.22-4.12 (m, 2H, H-3", H-5"); 4.05-3.99 (m, 2H, H-3, H-3'); 3.96-3.92 (m, 1H, H-5'); 3.74-3.67 (m, 3H, H-2, H-2', H-4"); 3.62-3.46 (m, 12H, H-2", H-4', H-5, OCH_3); 3.29 (s, 3H, OCH_3); 3.21 (t, 1H, *J* = 9.6 Hz, H-4); 2.35 (d, 1H, *J* = 4.8 Hz, 3"-O*H*); 1.31 (d, 3H, *J* = 6.4 Hz, H-6'); 1.25 (d, 3H, *J* = 6.4 Hz, H-6); 1.19 (d, 3H, *J* = 6.4 Hz, H-6"). ^{13}C-APT NMR (101 MHz) δ: 156.3, 139.2 (C$_{q,arom}$); 138.5, 128.5, 128.5, 128.3, 128.0, 127.5, 127.5, 118.7 *C*H$_{arom}$); 99.2 (C-1"); 98.7 (C-1'); 94.9 (C-1); 84.9 (*C*I$_{arom}$); 81.9 (C-4); 80.8 (C-3'); 80.1 (C-2' and C-2); 79.5, 79.4 (C-4' and C-4"); 78.9 (C-2"); 75.7, 75.0 (Ph*C*H$_2$); 70.6 (C-3"); 69.1 (C-5); 68.8 (C-5'); 66.7 (C-5"); 61.4, 59.1, 58.2, 57.9 (O*C*H$_3$); 18.4 (C-6'); 17.9 (C-6); 17.1 (C-6"). IR (thin film, cm^{-1}): 1040, 1073, 1098, 1128, 1232, 1484, 3479. HRMS calculated for $C_{42}H_{55}IO_{13}Na$ 917.25850 [M+Na]$^+$; found 917.25767.

4-iodophenyl 2,4-di-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(2-*O*-methyl-3,4,6-tri-*O*-benzyloxycarbonyl-α-D-mannopyranosyl)-4-*O*-acetyl-α-L-fucopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (46)



The title compound was synthesized according to general procedure A using acceptor **43** (72 mg, 85 µmol, 1.0 eq) and donor **10** (117 mg, 0.17 mmol, 2.0 eq). Column chromatography (*n*-pentane-Et_2O 3:7) gave the title compound (103 mg, 72 µmol, 96%) as a pale oil. $[\alpha]_D^{25}$ = -62.2 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.59-7.55 (m, 2H, C*H*$_{arom}$); 7.45-7.21 (m, 20H, C*H*$_{arom}$); 6.86-6.82 (m, 2H, C*H*$_{arom}$); 5.47 (d, 1H, *J* = 1.6 Hz, H-1); 5.28 (d, 1H, *J* = 2.8 Hz, H-4''); 5.23-5.05 (m, 11H, H-1', H-1'', H-1''', H-4''', PhC*H*$_2$, PhC*H*H); 4.93 (dd, 1H, *J* = 3.2, 10.0 Hz, H-3'''); 4.58 (d, 1H, *J* = 11.2 Hz, PhCH*H*); 4.35-4.29 (m, 3H, H-5'', H-6'''); 4.25 (dd, 1H, *J* = 3.6, 10.0 Hz, H-3''); 4.21-4.16 (m, 1H, H-5'''); 4.05 (dd, 1H, *J* = 3.2, 9.6 Hz, H-3); 4.01 (dd, 1H, *J* = 3.2, 9.6 Hz, H-3'); 3.98-3.89 (m, 1H, H-5'); 3.73-3.71 (m, 2H, H-2, H-2'''); 3.69 (dd, 1H, *J* = 1.6, 3.2 Hz, H-2'); 3.64-3.58 (m, 1H, H-5); 3.55-3.47 (m, 8H, H-2'', H-4', OC*H*$_3$); 3.40 (s, 3H, OC*H*$_3$); 3.33 (s, 3H, OC*H*$_3$); 3.25-3.19 (m, 4H, H-4, OC*H*$_3$); 2.18 (s, 3H, C*H*$_{3,Ac}$); 1.33 (d, 3H, *J* = 6.4 Hz, H-6'); 1.25 (d, 3H, *J* = 6.0 Hz, H-6); 1.09 (d, 3H, *J* = 6.4 Hz, H-6''). ^{13}C-APT NMR (101 MHz) δ: 170.9 (*C*O$_{Ac}$); 156.3 (C$_{q,arom}$); 155.0, 154.4, 154.3 (*C*O$_{Cbz}$); 139.1 (C$_{q,arom}$); 138.5 (*C*H$_{arom}$); 135.4, 135.2, 135.1 (C$_{q,arom}$); 128.7, 128.6, 128.6, 128.6, 128.5, 128.4, 128.3, 128.3, 128.2, 127.4, 127.4, 118.7 (*C*H$_{arom}$); 99.4 (C-1''); 98.8 (C-1'''); 98.4 (C-1'); 94.8 (C-1); 84.9 (*C*I$_{arom}$); 81.9 (C-4); 81.6 (C-3'); 80.6 (C-2'); 80.1 (C-2); 79.8 (C-3); 79.3 (C-4'); 78.6 (C-2''); 77.8 (C-2'''); 75.1 (Ph*C*H$_2$); 75.0 (C-3''); 73.8 (C-3'''); 72.9 (C-4''); 70.4 (C-4'''); 70.2, 69.8, 69.8 (Ph*C*H$_2$); 69.1 (C-5); 68.9 (C-5'''); 68.8 (C-5'); 66.4 (C-6'''); 65.3 (C-5''); 61.3, 59.1, 59.0, 58.5, 57.7 (O*C*H$_3$); 20.9 (*C*H$_{3,Ac}$); 18.3 (C-6'); 17.9 (C-6); 16.3 (C-6''). IR (thin film, cm^{-1}): 1020, 1043, 1098, 1129, 1176, 1236, 1385, 1455, 1484, 1747, 2833, 2929. HRMS calculated for $C_{68}H_{81}IO_{25}Na$ 1447.40038 $[M+Na]^+$; found 1447.40038.

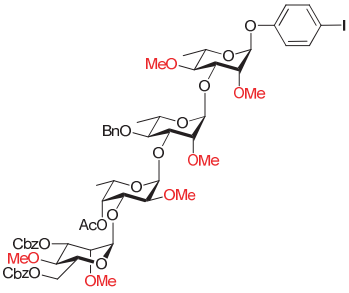
4-iodophenyl 2,4-di-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(2,3-di-*O*-benzyloxycarbonyl-4-*O*-methyl-6-*O*-benzyl-α-D-mannopyranosyl)-4-*O*-acetyl-α-L-fucopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (47)



The title compound was synthesized according to general procedure A using acceptor **43** (81 mg, 63 µmol, 1.0 eq) and donor **11** (53 mg, 0.12 mmol, 2.0 eq). Column chromatography (*n*-pentane-Et_2O 4:6) gave the title compound (55 mg, 40 µmol, 64%) as a pale oil. $[\alpha]_D^{25}$ = -72.3 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.57 (dd, 2H, *J* = 2.0, 6.8 Hz, C*H*$_{arom}$); 7.38-7.22 (m, 20H, C*H*$_{arom}$); 6.83 (dd, 2H, *J* = 2.0, 6.8 Hz, C*H*$_{arom}$); 5.46 (d, 1H, *J* = 2.0 Hz, H-1); 5.28 (d, 1H, *J* = 1.2 Hz, H-1'''); 5.26 (d, 1H, *J* = 3.6 Hz, H-4''); 5.20-5.15 (m, 5H, H-1', H-1'', H-2''', PhC*H*$_2$); 5.13-5.08 (m, 3H, PhC*H*$_2$, PhC*H*H); 4.99 (dd, 1H, *J* = 3.2, 10.0 Hz, H-3'''); 4.72 (d, 1H, *J* = 12.0 Hz, PhC*H*H); 4.56-4.50 (m, 2H, PhCH*H*, PhCH*H*); 4.33-4.26 (m, 2H, H-3'', H-5''); 4.07-3.98

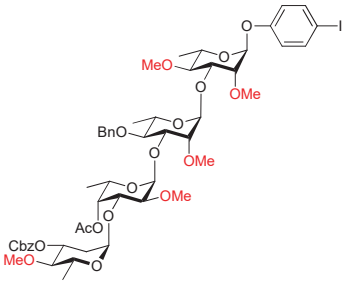
(m, 3H, H-3, H-3', H-5'''); 3.96-3.89 (m, 1H, H-5'); 3.80 (dd, 1H, *J* = 4.4, 11.2 Hz, H-6'''); 3.73-3.67 (m, 4H, H-2, H-2', H-4''', H-6'''); 3.63-3.47 (m, 9H, H-2'', H-4', H-5, OC*H*$_3$); 3.42 (s, 3H, OC*H*$_3$); 3.37 (s, 3H, OC*H*$_3$); 3.31 (s, 3H, OC*H*$_3$); 3.21 (t, 1H, *J* = 9.6 Hz, H-4); 1.33 (d, 3H, *J* = 6.4 Hz, H-6'); 1.25 (d, 3H, *J* = 6.0 Hz, H-6); 1.10 (d, 3H, *J* = 6.8 Hz, H-6''). ^{13}C-APT NMR (101 MHz) δ: 171.1 (*C*O$_{Ac}$); 156.3 (C$_{q,arom}$); 154.6, 154.5 (*C*O$_{Cbz}$); 139.1 (C$_{q,arom}$); 138.5 (*C*H$_{arom}$); 138.5, 135.3 (C$_{q,arom}$); 128.7, 128.7, 128.6, 128.5, 128.4, 128.4, 128.3, 127.9, 127.9, 127.6, 127.5, 118.7 (*C*H$_{arom}$); 99.7 (C-1''); 98.6 (C-1'''); 98.5 (C-1'); 94.9 (C-1); 84.9 (*C*I$_{arom}$); 82.0 (C-4); 81.6 (C-3'); 80.7 (C-2'); 80.1 (C-2); 79.7 (C-3); 79.4 (C-4;); 78.8 (C-2''); 75.8 (C-3'''); 75.4 (Ph*C*H$_2$); 74.2 (C-4'''); 73.6 (C-2'''); 73.6 (Ph*C*H$_2$); 73.0 (C-4''); 72.9 (C-3''); 72.1 (C-5'''); 70.1, 69.9 (Ph*C*H$_2$); 69.1 (C-5); 68.8 (C-5'); 65.3 (C-5''); 61.3, 60.8, 59.1, 58.9, 57.8 (O*C*H$_3$); 20.9 (*C*H$_{3,Ac}$); 18.3 (C-6'); 17.9 (C-6); 16.3 (C-6''). IR (thin film, cm^{-1}): 1044, 1097, 1127, 1216, 1234, 1273 1483, 1751. HRMS calculated for $C_{67}H_{81}IO_{23}Na$ 1403.41110 [M+Na]$^+$; found 1403.41046.

4-iodophenyl 2,4-di-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(2,4-di-*O*-methyl-3,6-di-*O*-benzyloxycarbonyl-α-D-mannopyranosyl)-4-*O*-acetyl-α-L-fucopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (48)



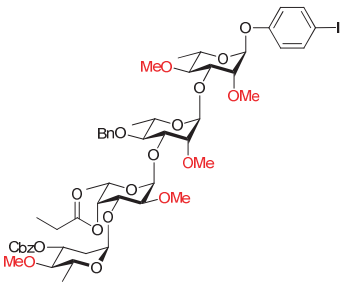
The title compound was synthesized according to general procedure A using acceptor **43** (63 mg, 74 µmol, 1.0 eq) and donor **9** (85 mg, 0.15 mmol, 2.0 eq). Column chromatography (*n*-pentane-Et$_2$O 3:7) gave the title compound (97 mg, 74 µmol, 100%) as a pale oil. [α]$_D^{25}$ = -79.4 ° (c = 1.0, CHCl$_3$). ^{1}H-NMR (400 MHz) δ: 7.59-7.55 (m, 2H, C*H*$_{arom}$); 7.39-7.21 (m, 15H, C*H*$_{arom}$); 6.86-6.82 (m, 2H, C*H*$_{arom}$); 5.46 (d, 1H, *J* = 1.6 Hz, H-1); 5.27 (dd, 1H, *J* = 0.8, 3.6 Hz, H-4''); 5.22-5.11 (m, 8H, H-1', H-1'', H-1''', PhC*H*$_2$, PhC*H*H); 4.87 (dd, 1H, *J* = 3.4, 9.8 Hz, H-3'''); 4.57 (d, 1H, *J* = 11.2 Hz, PhCH*H*); 4.47 (dd, 1H, *J* = 2.0, 11.6 Hz, H-6'''); 4.37-4.30 (m, 2H, H-5'', H-6'''); 4.24 (dd, 1H, *J* = 3.4, 10.2 Hz, H-3''); 4.05 (dd, 1H, *J* = 3.2, 9.6 Hz, H-3); 4.02-3.98 (m, 2H, H-3', H-5'''); 3.94-3.91 (m, 1H, H-5'); 3.72 (dd, 1H, *J* = 2.0, 3.2 Hz, H-2); 3.69 (dd, 1H, *J* = 2.0, 3.2 Hz, H-2'); 3.65 (dd, 1H, *J* = 2.0, 3.2 Hz, H-2'''); 3.63-3.56 (m, 2H, H-4''', H-5); 3.54-3.49 (m, 8H, H-2'', H-4', OC*H*$_3$); 3.44 (s, 3H, OC*H*$_3$); 3.39 (s, 3H, OC*H*$_3$); 3.24-3.21 (m, 4H, H-4, OC*H*$_3$); 2.19 (s, 3H, C*H*$_{3,Ac}$); 1.33 (d, 3H, *J* = 6.0 Hz, H-6'); 1.25 (d, 3H, *J* = 6.0 Hz, H-6); 1.10 (d, 3H, *J* = 6.8 Hz, H-6''). ^{13}C-APT NMR (101 MHz) δ: 170.9 (*C*O$_{Ac}$); 156.3 (C$_{q,arom}$); 155.3, 154.7 (*C*O$_{Cbz}$); 139.2 (C$_{q,arom}$); 138.5 (*C*H$_{arom}$); 135.4 (C$_{q,arom}$); 128.7, 128.6, 128.6, 128.6, 128.4, 128.3, 128.2, 127.4, 127.4, 118.7 (*C*H$_{arom}$); 99.5 (C-1''); 98.6 (C-1'''); 98.5 (C-1'); 94.8 (C-1); 84.9 (*C*I$_{arom}$); 82.0 (C-4); 81.6 (C-3'); 80.7 (C-2'); 80.1 (C-2); 79.8 (C-3); 79.4 (C-4'); 78.7 (C-2''); 78.3 (C-2'''); 77.5 (C-3'''); 75.2 (Ph*C*H$_2$); 74.4 (C-4'''); 73.5 (C-3''); 73.0 (C-4''); 70.2 (C-5'''); 69.7, 69.7 (Ph*C*H$_2$); 69.1 (C-5); 68.8 (C-5'); 66.9 (C-6'''); 65.3 (C-5''); 61.3, 60.6, 59.1, 59.0, 58.5, 57.8 (O*C*H$_3$); 20.9 (*C*H$_{3,Ac}$); 18.3 (C-6'); 17.9 (C-6); 16.3 (C-6''). IR (thin film, cm^{-1}): 1019, 1043, 1098, 1128, 1176, 1236, 1249, 1455, 1484, 1746, 2932. HRMS calculated for $C_{61}H_{77}IO_{23}Na$ 1327.37962 [M+Na]$^+$; found 1327.37925.

4-iodophenyl 2,4-di-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(3-*O*-benzyloxycarbonyl-4-*O*-methyl-2,6-dideoxy-α-D-glucopyranosyl)-4-*O*-acetyl-α-L-fucopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (49)



The title compound was synthesized according to general procedure B, but with DCM as solvent instead of Et_2O/DCE (1.2 mL, 0.05 M), using acceptor **43** (51 mg, 60 µmol, 1.0 eq), donor X (47 mg, 0.12 mmol, 2.0 eq) and IDCP (84 mg, 0.18 mmol, 3.0 eq). Column chromatography (*n*-pentane-Et_2O 4:6) gave the title compound (190 mg, 0.19 mmol, 90%, α/β 4:1) as a pale oil. $[\alpha]_D^{25}$ = -68.7 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.57 (dd, 2H, *J* = 2.0, 6.8 Hz, C*H*$_{arom}$); 7.38-7.25 (m, 10H, C*H*$_{arom}$); 6.83 (dd, 2H, *J* = 2.0, 6.8 Hz, C*H*$_{arom}$); 5.46 (d, 1H, *J* = 1.6 Hz, H-1); 5.23 (d, 1H, *J* = 2.8 Hz, H-4''); 5.20-5.11 (m, 6H, H-1', H-1'', H-1''', PhC*H*$_2$, PhC*H*H); 4.98-4.92 (m, 1H, H-3'''); 4.56 (d, 1H, *J* = 11.2 Hz, PhCH*H*); 4.33 (q, 1H, *J* = 6.4 Hz, H-5''); 4.18 (dd, 1H, *J* = 3.6, 10.4 Hz, H-3''); 4.07-4.00 (m, 2H, H-3, H-3'); 3.95-3.85 (m, 2H, H-5', H-5'''); 3.72-3.69 (m, 2H, H-2, H-2'); 3.61-3.44 (m, 15H, H-2'', H-4', H-5, OC*H*$_3$); 3.27 (s, 3H, OC*H*$_3$); 3.21 (t, 1H, *J* = 9.4 Hz, H-4); 2.87 (t, 1H, *J* = 9.4 Hz, H-4'''); 2.30 (dd, 1H, *J* = 4.8, 12.6 Hz, H-2'''); 2.20 (s, 3H, C*H*$_{3,Ac}$); 1.71 (dt, 1H, *J* = 3.0, 12.4 Hz, H-2'''); 1.36-1.21 (m, 9H, H-6, H-6', H-6'''); 1.12 (d, 3H, *J* = 6.8 Hz, H-6''). ^{13}C-APT NMR (101 MHz) δ: 171.0 (*C*O$_{Ac}$); 156.3 (C$_{q,arom}$); 154.6 (*C*O$_{Cbz}$); 139.2 (C$_{q,arom}$); 138.5 (*C*H$_{arom}$); 135.4 (C$_{q,arom}$); 128.7, 128.6, 128.4, 128.3, 127.6, 127.5, 118.7 (*C*H$_{arom}$); 99.8 (C-1''); 98.7 (C-1'''); 98.4 (C-1'); 94.9 (C-1); 84.9 (*C*I$_{arom}$); 84.2 (C-4'''); 82.0 (C-4); 81.4 (C-3'); 80.8 (C-2'); 80.1 (C-2); 79.8 (C-3); 79.5 (C-4'); 78.7 (C-2''); 75.4 (C-3'''); 75.2 (Ph*C*H$_2$); 73.3 (C-4''); 73.2 (C-3''); 69.7 (Ph*C*H$_2$); 69.1 (C-5); 68.8 (C-5'); 67.4 (C-5'''); 65.5 (C-5''); 61.3, 60.3, 59.1, 58.9, 57.8 (O*C*H$_3$); 35.7 (C-2'''); 21.0 (*C*H$_{3,Ac}$); 18.3 (C-6'); 18.1 (C-6'''); 17.9 (C-6); 16.5 (C-6''). IR (thin film,cm^{-1}): 1040, 1099, 1125, 1139, 1255, 1484, 1749, 2911, 2929. HRMS calculated for $C_{52}H_{69}IO_{19}Na$ 1147.33682 [M+Na]$^+$; found 1147.33699.

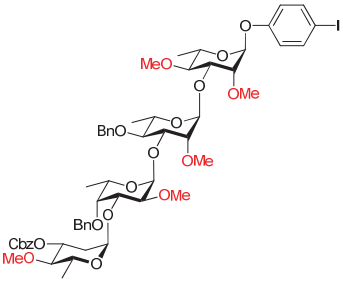
4-iodophenyl 2,4-di-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(3-*O*-benzyloxycarbonyl-4-*O*-methyl-2,6-dideoxy-α-D-glucopyranosyl)-4-*O*-propionyl-α-L-fucopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (51)



The title compound was synthesized according to general procedure B, but with DCM as solvent instead of Et_2O/DCE (2.4 mL, 0.05 M), using acceptor **45** (104 mg, 0.12 mmol, 1.0 eq), donor **4** (94 mg, 0.24 mmol, 2.0 eq) and IDCP (170 mg, 0.36 mmol, 3.0 eq). Column chromatography (*n*-pentane-Et_2O 4:6) gave the title compound (123 mg, 0.11 mmol, 89%, α/β 4:1) as a pale oil. $[\alpha]_D^{25}$ = -63.2 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.57 (dd, 2H, *J* = 2.0, 6.8 Hz, C*H*$_{arom}$); 7.38-7.25 (m, 10H, C*H*$_{arom}$); 6.83 (dd, 2H, *J* = 2.0, 6.8 Hz, C*H*$_{arom}$); 5.47 (d, 1H, *J* = 1.6 Hz, H-1); 5.28 (d, 1H, *J* = 2.8 Hz, H-4''); 5.24 (dd, 1H, *J* = 1.2, 3.6 Hz, H-4''); 5.22-5.13 (m, 6H, H-1', H-1'', H-1''', PhC*H*$_2$, PhC*H*H); 4.96-4.90 (m, 1H, H-3'''); 4.56 (d, 1H, *J* = 11.2 Hz, PhCH*H*); 4.33 (q, 1H, *J* = 6.4 Hz, H-5''); 4.18 (dd, 1H, *J* = 3.6, 10.4 Hz, H-3''); 4.07-4.00 (m, 2H, H-3, H-3'); 3.95-3.85 (m, 2H, H-5', H-5'''); 3.72-3.69 (m, 2H, H-

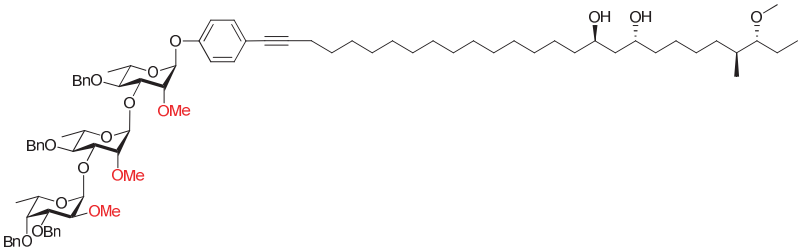
2, H-2'); 3.61-3.57 (m, 1H, H-5); 3.56-3.44 (m, 14H, H-2'', H-4', OC*H*$_3$); 3.27 (s, 3H, OC*H*$_3$); 3.21 (t, 1H, *J* = 9.6 Hz, H-4); 2.87 (t, 1H, *J* = 9.2 Hz, H-4'''); 2.54-2.42 (m, 2H, C*H*$_2$CH$_3$); 2.29 (ddd, 1H, *J* = 1.4, 5.2, 12.6 Hz, H-2'''); 1.74-1.67 (m, 1H, H-2'''); 1.34-1.29 (m, 6H, H-6', H-6'''); 1.26-1.21 (m, 6H, CH$_2$C*H*$_3$, H-6); 1.11 (d, 3H, *J* = 6.8 Hz, H-6''). ^{13}C-APT NMR (101 MHz) δ: 174.4 (*C*O$_{propionyl}$); 156.3 (C$_{q,arom}$); 154.6 (*C*O$_{Cbz}$); 139.2 (C$_{q,arom}$); 138.5 (*C*H$_{arom}$); 135.4 (C$_{q,arom}$); 128.7, 128.6, 128.4, 128.3, 127.7, 127.5, 118.7 (*C*H$_{arom}$); 99.9 (C-1''); 98.7 (C-1'''); 98.5 (C-1'); 94.9 (C-1); 84.9 (*C*I$_{arom}$); 84.1 (C-4'''); 82.0 (C-4); 81.4 (C-3'); 80.8 (C-2'); 80.1 (C-2); 79.7 (C-3); 78.7 (C-2''); 75.3 (C-3'''); 75.2 (Ph*C*H$_2$); 73.5 (C-3''); 73.1 (C-4''); 69.7 (Ph*C*H$_2$); 69.1 (C-5); 68.8 (C-5'); 67.8 (C-5'''); 65.6 (C-5''); 61.4, 60.1, 59.1, 59.0, 57.9 (O*C*H$_3$); 35.7 (C-2'''); 27.8 (*C*H$_2$CH$_3$); 18.3 (C-6'); 18.1 (C-6'''); 17.9 (C-6); 16.5 (C-6''); 9.7 (CH$_2$*C*H$_3$). IR (thin film, cm^{-1}): 1016, 1043, 1099, 1128, 1256, 1485, 1744, 2928. HRMS calculated for $C_{53}H_{71}IO_{19}Na$ 1161.35264 [M+Na]$^+$; found 1161.35290.

4-iodophenyl 2,4-di-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(3-*O*-benzyloxycarbonyl-4-*O*-methyl-2,6-dideoxy-α-D-glucopyranosyl)-4-*O*-benzyl-α-L-fucopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (50)



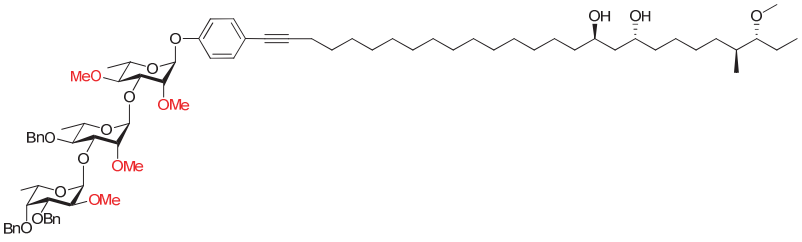
The title compound was synthesized according to general procedure B, but with DCM as solvent instead of Et$_2$O/DCE (2.6 mL, 0.05 M), using acceptor **44** (113 mg, 0.13 mmol, 1.0 eq), donor **4** (98 mg, 0.26 mmol, 2.0 eq) and IDCP (178 mg, 0.38 mmol, 3.0 eq). Column chromatography (*n*-pentane-Et$_2$O 1:1) gave the title compound (77 mg, 66 μmol, 52%) as a pale oil. $[\alpha]_D^{25}$ = -55.4 ° (c = 1.0, CHCl$_3$). ^{1}H-NMR (400 MHz) δ: 7.57 (dd, 2H, *J* = 2.0, 6.8 Hz, C*H*$_{arom}$); 7.45-7.24 (m, 15H, C*H*$_{arom}$); 6.83 (dd, 2H, *J* = 2.2, 7.0 Hz, C*H*$_{arom}$); 5.45 (d, 1H, *J* = 1.6 Hz, H-1); 5.24 (d, 1H, *J* = 2.8 Hz, H-1'''); 5.20-5.11 (m, 5H, H-1', H-1'', PhC*H*$_2$, PhC*H*H); 5.06 (d, 1H, *J* = 11.2 Hz, PhC*H*H); 4.57 (d, 1H, *J* = 11.2 Hz, PhC*H*H); 4.23-4.15 (m, 2H, H-3'', H-5''); 4.05-3.98 (m, 2H, H-3, H-3'); 3.95-3.86 (m, H-5', H-5'''); 3.75-3.71 (m, 3H, H-2, H-2', H-2''); 3.62-3.55 (m, 2H, H-4'', H-5); 3.53-3.46 (m, 13H, H-4', OC*H*$_3$); 3.25 (s, 3H, OC*H*$_3$); 3.20 (t, 1H, *J* = 9.6 Hz, H-4); 2.93 (t, 1H, *J* = 9.2 Hz, H-4'''); 2.42 (dd, 1H, *J* = 5.2, 12.0 Hz, H-2'''); 1.78 (dt, 1H, *J* = 3.6, 12.0 Hz, H-2'''); 1.34-1.31 (m, 6H, H-6', H-6'''); 1.24 (d, 3H, *J* = 6.4 Hz, H-6); 1.17 (d, 3H, *J* = 6.4 Hz, H-6''). ^{13}C-APT NMR (101 MHz) δ: 156.3 (C$_{q,arom}$); 154.5 (*C*O$_{Cbz}$); 139.3, 138.6 (C$_{q,arom}$); 138.5 (*C*H$_{arom}$); 135.4 (C$_{qarom}$); 128.7, 128.7, 128.5, 128.4, 128.3, 127.7, 127.6, 127.5, 127.4, 118.7 (*C*H$_{arom}$); 99.9 (C-1''); 98.6 (C-1'); 98.4 (C-1'''); 94.9 (C-1); 84.9 (*C*I$_{arom}$); 84.5 (C-4'''); 81.8 (C-4); 81.4 (C-3'); 80.8 (C-2'); 80.1 (C-3); 80.0 (C-2); 79.9 (C-4''); 79.4 (C-4'); 79.1 (C-2''); 76.0 (C-3'''); 75.6 (C-3''); 75.4, 75.1, 69.8 (Ph*C*H$_2$); 69.1 (C-5); 68.8 (C-5'); 68.0 (C-5'''); 67.1 (C-5''); 61.4, 60.8, 59.1, 58.6, 57.9 (O*C*H$_3$); 35.6 (C-2'''); 18.4 (C-6'); 18.3 (C-6'''); 17.9 (C-6); 17.1 (C-6''). IR (thin film, cm^{-1}): 1040, 1098, 1126, 1173, 1192, 1255, 1382, 1455, 1484, 1747, 2933. HRMS calculated for $C_{57}H_{73}IO_{18}Na$ 1195.37338 [M+Na]$^+$; found 1195.37337.

4-((3*R*,4*S*,9*R*,11*R*)-3-methoxy-4-methylheptacos-26-yne-9,11-diol)phenyl 2-*O*-methyl-3-*O*-(2-*O*-methyl-3-O-(2-*O*-methyl-3,4-di-*O*-benzyl-α-L-fucopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranosyl))-4-*O*-benzyl-α-L-rhamnopyranoside (53)



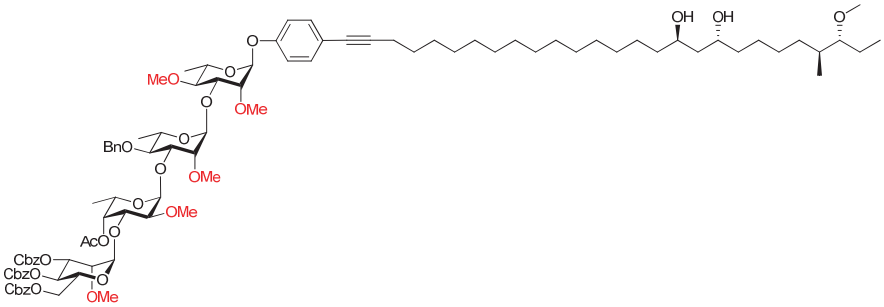
The title compound was synthesized according to general procedure C using **38** (30 mg, 28.3 µmol, 1.0 eq) and phthiocerol (15 mg, 34.0 µmol, 1.2 eq). Column chromatography (*n*-pentane-Et_2O 3:7) yielded the title compound (31 mg, 22.4 µmol, 79%) as a yellow oil. $[\alpha]_D^{25}$ = -86.6 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.40-7.22 (m, 22H, C*H*$_{arom}$); 6.97-6.94 (m, 2H, C*H*$_{arom}$); 5.51 (d, 1H, *J* = 2.0 Hz, H-1); 5.23-5.19 (m, 2H, H-1'', PhC*H*H); 5.15 (d, 1H, *J* = 1.6 Hz, H-1'); 5.00 (d, 1H, *J* = 11.6 Hz, PhC*H*H); 4.85-4.80 (m, 2H, PhC*H*H, PhC*H*H); 4.73 (d, 1H, *J* = 12.4 Hz, PhCH*H*); 4.67-4.63 (m, 2H, PhCH*H*); 4.54 (d, 1H, *J* = 10.8 Hz, PhCH*H*); 4.17 (dd, 1H, *J* = 2.8, 9.6 Hz, H-3); 4.08-4.03 (m, 2H, H-3', H-5''); 3.98-3.91 (m, 4H, H-3'', H-5', C*H*$_{Phth}$); 3.82 (dd, 1H, *J* = 3.6, 10.0 Hz, H-2''); 3.74-3.66 (m, 4H, H-2, H-2', H-4'', H-5); 3.55-3.44 (m, 5H, H-4, H-4', OC*H*$_3$); 3.39 (s, 3H, OC*H*$_3$); 3.34 (s, 3H, OC*H*$_3$); 3.21 (s, 3H, OC*H*$_3$); 2.90-2.84 (m, 1H, C*H*$_{Phth}$); 2.37 (t, 2H, *J* = 7.0 Hz, C*H*$_{2,Phth}$); 2.32 (bs, 2H O*H*); 1.56-1.23 (m, 47H, H-6, H-6', C*H*$_{Phth}$, C*H*$_{2,Phth}$); 1.11-1.07 (m, 5H, H-6'', C*H*$_{2,Phth}$); 0.93-0.89 (m, 3H, C*H*$_{3,Phth}$); 0.83 (d, 3H, *J* = 6.8 Hz, C*H*$_{3,Phth}$). ^{13}C-APT NMR (101 MHz) δ: 155.7, 139.3, 139.1, 138.8, 138.3 (C$_{q,arom}$); 133.0 128.5, 128.5, 128.5, 128.4, 128.3, 127.9, 127.8, 127.7, 127.5, 127.5, 127.4 (C*H*$_{arom}$); 118.0 (C$_{q,arom}$); 116.2 (*C*H$_{arom}$); 100.1 (C-1''); 98.9 (C-1'); 94.7 (C-1); 89.5 (C$_{q,alkyne}$); 86.8 (*C*H$_{Phth}$); 80.7 (C-3'); 80.3 (C-2'); 80.1 (C$_{q,alkyne}$); 80.0 (C-2); 79.9 (C-4); 79.7 (C-3); 78.9 (C-3''); 78.6 (C-2''); 77.8 (C-4''); 75.3, 75.2, 75.0, 72.9 (Ph*C*H$_2$); 69.6, 69.6 (*C*H$_{Phth}$); 69.0 (C-5); 68.7 (C-5'); 67.0 (C-5); 59.1, 59.0 57.9, 57.5 (O*C*H$_3$); 42.4, 37.7 (*C*H$_{2,Phth}$); 34.9 (*C*H$_{Phth}$); 32.8, 29.8, 29.8, 29.7, 29.3, 29.1, 29.0, 27.7, 26.3, 25.9, 22.5, 19.5 (*C*H$_{2,Phth}$); 18.3 (C-6); 18.1 (C-6'); 17.1 (C-6''); 14.9, 10.2 (*C*H$_{3,Phth}$). IR (thin film, cm^{-1}): 1043, 1098, 1233, 1454, 1507, 2853, 2926, 3411. HRMS calculated for $C_{84}H_{120}O_{16}Na$ 1407.84686 $[M+Na]^+$; found 1408.84643.

4-((3*R*,4*S*,9*R*,11*R*)-3-methoxy-4-methylheptacos-26-yne-9,11-diol)phenyl 2,4-di-*O*-methyl-3-*O*-(2-*O*-methyl-3-O-(2-*O*-methyl-3,4-di-*O*-benzyl-α-L-fucopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (54)



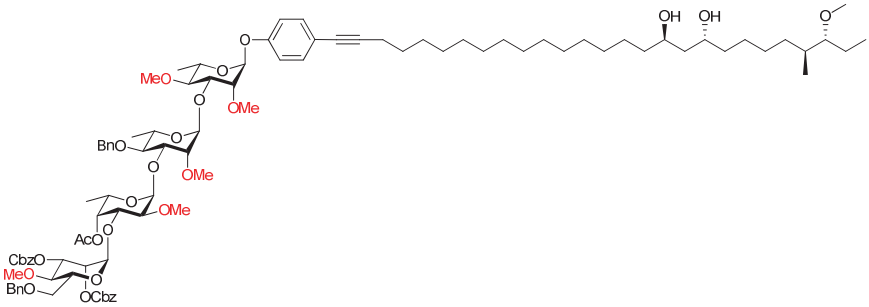
The title compound was synthesized according to general procedure C using **39** (27 mg, 27.3 µmol, 1.0 eq) and phthiocerol (15 mg, 32.8 µmol, 1.2 eq). Column chromatography (*n*-pentane-Et_2O 1:4) yielded the title compound (28 mg, 21.4 µmol, 78%) as a yellow oil. $[\alpha]_D^{25}$ = -83.8 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.40-7.25 (m, 17H, C*H*$_{arom}$); 6.96-6.93 (m, 2H, C*H*$_{arom}$); 5.48 (d, 1H, *J* = 1.6 Hz, H-1); 5.22-5.19 (m, 2H, H-1", PhC*H*H); 5.15 (d, 1H, *J* = 1.6 Hz, H-1'); 5.00 (d, 1H, *J* = 11.6 Hz, PhC*H*H); 4.85 (d, 1H, *J* = 12.4 Hz, PhC*H*H); 4.74 (d, 1H, *J* = 12.4 Hz, PhCH*H*); 4.67 (d, 1H, *J* = 11.6 Hz, PhCH*H*); 4.55 (d, 1H, *J* = 11.2 Hz, PhCH*H*); 4.11 (q, 1H, *J* = 6.8 Hz, H-5"); 4.06-3.91 (m, 6H, H-3, H-3', H-3", H-5', C*H*$_{Phth}$); 3.82 (dd, 1H, *J* = 3.6, 10.0 Hz, H-2"); 3.72-3.69 (m, 3H, H-2, H-2', H-4"); 3.60-3.45 (m, 11H, H-4', H-5, OC*H*$_3$); 3.39 (s, 3H, OC*H*$_3$); 3.34 (s, 3H, OC*H*$_3$); 3.20 (t, 1H, *J* = 9.6 Hz, H-4); 2.90-2.84 (m, 1H, C*H*$_{Phth}$); 2.37 (t, 2H, *J* = 7.0 Hz, C*H*$_{2,Phth}$); 2.32 (bs, 2H, O*H*$_{Phth}$); 1.62-1.23 (m, 47H, H-6, H-6', C*H*$_{Phth}$, C*H*$_{2,Phth}$); 1.11-1.07 (m, 5H, H-6'', C*H*$_{2,Phth}$); 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: 155.7, 139.2, 139.1 138.7 (C$_{q,arom}$); 133.0, 128.6, 128.5, 128.4, 128.4, 128.0, 127.9, 127.8, 127.6, 127.5, 127.5 (*C*H$_{arom}$); 118.0 (C$_{q,arom}$); 116.2 (*C*H$_{arom}$); 100.1 (C-1"); 98.7 (C-1'); 94.8 (C-1); 89.5 (C$_{q,alkyne}$); 86.8 (*C*H$_{Phth}$); 81.9 (C-4); 80.9 (C-2'); 80.6 (C-3'); 80.1 (C$_{q,alkyne}$); 80.1 (C-2); 80.0 (C-3); 79.7 (C-4'); 79.0 (C-3"); 78.6 (C-2"); 77.7 (C-4"); 75.2, 75.0, 73.0 (Ph*C*H$_2$); 69.6, 69.6 (*C*H$_{Phth}$); 69.0 (C-5); 68.8 (C-5'); 66.9 (C-5"); 61.4, 59.2, 59.1, 58.0, 57.5 (O*C*H$_3$); 42.4, 37.6 (*C*H$_{2,Phth}$); 34.9 (*C*H$_{Phth}$); 32.8, 29.8, 29.8, 29.7, 29.3, 29.1, 29.0, 27.7, 26.3, 25.9, 22.5, 19.5 (*C*H$_{2,Phth}$); 18.4 (C-6); 17.9 (C-6'); 17.1 (C-6"); 14.9, 10.2 (*C*H$_{3,Phth}$). IR (thin film, cm^{-1}): 1043, 1099, 1233, 1357, 1454, 1507, 2853, 2926, 3453. HRMS calculated for $C_{78}H_{117}O_{16}$ 1309.83361 $[M+H]^+$; found 1309.83422.

4-((3*R*,4*S*,9*R*,11*R*)-3-methoxy-4-methylheptacos-26-yne-9,11-diol)phenyl 2,4-di-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(2-*O*-methyl-3,4,6-tri-*O*-benzyloxycarbonyl-α-D-mannopyranosyl)-4-*O*-acetyl-α-L-fucopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (55)



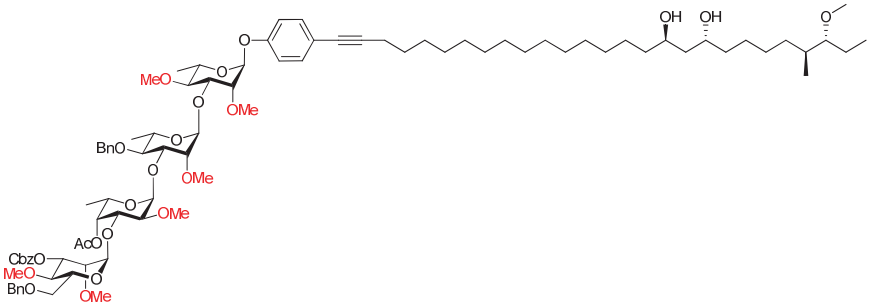
The title compound was synthesized according to general procedure C using **46** (40 mg, 27.7 µmol, 1.0 eq) and phthiocerol (15 mg, 33.2 µmol, 1.2 eq). Column chromatography (*n*-pentane-Et_2O 1:9) yielded the title compound (41 mg, 23.4 µmol, 85%) as a yellow oil. $[\alpha]_D^{25}$ = -53.5 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.37-7.21 (m, 22H, C*H*$_{arom}$); 6.98-6.95 (m, 2H, C*H*$_{arom}$); 5.50 (d, 1H, *J* = 1.6 Hz, H-1); 5.27 (d, 1H, *J* = 2.8 Hz, H-4''); 5.23-5.05 (m, 11H, H-1', H-1'', H-1''', H-4''', PhC*H*$_2$, PhC*H*H); 4.93 (dd, 1H, *J* = 3.2, 10.0 Hz, H-3'''); 4.58 (d, 1H, *J* = 11.2 Hz, PhCH*H*); 4.35-4.29 (m, 3H, H-5'', H-6'''); 4.25 (dd, 1H, *J* = 3.6, 10.4 Hz, H-3''); 4.21-4.16 (m, 1H, H-5'''); 4.07 (dd, 1H, *J* = 3.2, 9.6 Hz, H-3); 4.00 (dd, 1H, *J* = 3.2, 9.6 Hz, H-3'); 3.95-3.91 (m, 3H, H-5', C*H*$_{Phth}$); 3.73-3.71 (m, 2H, H-2, H-2'''); 3.69 (dd, 1H, *J* = 1.8, 3.0 Hz, H-2'); 3.64-3.60 (m, 1H, H-5); 3.54-3.48 (m, 8H, H-2'', H-4', OC*H*$_3$); 3.40 (s, 3H, OC*H*$_3$); 3.34 (s, 3H, OC*H*$_3$); 3.33 (s, 3H, OC*H*$_3$); 3.23-3.18 (m, 4H, H-4, OC*H*$_3$); 2.90-2.84 (m, 1H, C*H*$_{Phth}$); 2.38 (t, 2H, *J* = 7.0 Hz, C*H*$_{2,Phth}$); 2.32 (bs, 2H, O*H*$_{Phth}$); 2.18 (s, 3H, C*H*$_{3,Ac}$); 1.62-1.23 (m, 47H, H-6, H-6', C*H*$_{Phth}$, C*H*$_{2,Phth}$); 1.11-1.07 (m, 5H, H-6'', C*H*$_{2,Phth}$); 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: 170.9 (*C*O$_{Ac}$); 155.7 (C$_{q,arom}$); 155.1, 154.5, 154.4 (*C*O$_{Cbz}$); 139.2, 135.4, 135.2, 135.1 (C$_{q,arom}$); 133.0, 128.7, 128.6, 128.6, 128.5, 128.4, 128.3, 128.2, 127.4, 127.4 (*C*H$_{arom}$); 118.1 (C$_{q,arom}$); 116.2 (*C*H$_{arom}$); 99.5 (C-1''); 98.8 (C-1'''); 98.5 (C-1'); 94.7 (C-1); 89.6 (C$_{q,alkyne}$); 86.8 (*C*H$_{Phth}$); 82.0 (C-4); 81.7 (C-3'); 80.7 (C-2'); 80.2 (C-2); 80.1 (C$_{q,alkyne}$); 79.9 (C-3); 79.4 (C-4'); 78.7 (C-2''); 77.8 (C-2'''); 75.2 (Ph*C*H$_2$); 75.0 (C-3''); 73.8 (C-3''); 72.9 (C-4''); 70.5 (C-4'''); 70.2, 69.8, 69.8 (Ph*C*H$_2$); 69.6, 69.6 (*C*H$_{Phth}$); 69.1 (C-5); 68.9 (C-5'''); 68.8 (C-5'); 66.4 (C-6'''); 65.4 (C-5''); 61.3, 59.1, 59.0, 58.5, 57.7, 57.5 (O*C*H$_3$); 42.4, 37.7 (*C*H$_{2,Phth}$); 34.9 (*C*H$_{Phth}$); 32.8, 29.8, 29.8, 29.7, 29.3, 29.1, 29.0, 27.7, 26.3, 25.9, 22.5 (*C*H$_{2,Phth}$); 20.9 (*C*H$_{3,Ac}$); 19.5 (*C*H$_{2,Phth}$); 18.3 (C-6); 18.0 (C-6'); 16.3 (C-6''); 14.9, 10.2 (*C*H$_{3,Phth}$). IR (thin film, cm^{-1}): 1045, 1098, 1128, 1235, 1457, 1507, 1747, 2853, 2927, 3440. HRMS calculated for $C_{97}H_{136}O_{28}Na$ 1771.91103 $[M+Na]^+$; found 1171.91207.

4-((3*R*,4*S*,9*R*,11*R*)-3-methoxy-4-methylheptacos-26-yne-9,11-diol)phenyl 2,4-di-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(2,3-di-*O*-benzyloxycarbonyl-4-*O*-methyl-6-*O*-benzyl-α-D-mannopyranosyl)-4-*O*-acetyl-α-L-fucopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (56)



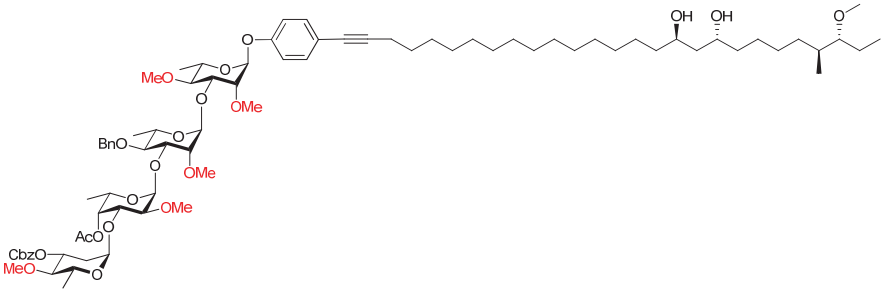
The title compound was synthesized according to general procedure C using **47** (32 mg, 23.3 µmol, 1.0 eq) and phthiocerol (13 mg, 28.0 µmol, 1.2 eq). Column chromatography (*n*-pentane-Et_2O 1:4) yielded the title compound (26 mg, 15.2 µmol, 65%) as a yellow oil. $[\alpha]_D^{25}$ = -82.3 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.39-7.22 (m, 22H, C*H*$_{arom}$); 6.98-6.94 (m, 2H, C*H*$_{arom}$); 5.49 (d, 1H, *J* = 1.2 Hz, H-1); 5.28 (d, 1H, *J* = 1.6 Hz, H-1'''); 5.26 (d, 1H, *J* = 2.8 Hz, H-4''); 5.20-5.15 (m, 5H, H-1', H-1'', H-2''', PhC*H*$_2$); 5.13-5.08 (m, 3H, PhC*H*$_2$, PhC*H*H); 4.99 (dd, 1H, *J* = 3.2, 9.6 Hz, H-3'''); 4.72 (d, 1H, *J* = 12.0 Hz, PhC*H*H); 4.56-4.50 (m, 2H, PhCH*H*, PhCH*H*); 4.32-4.26 (m, 2H, H-3'', H-5''); 4.07 (dd, 1H, *J* = 3.2, 9.6 Hz, H-3); 4.01-3.91 (m, 5H, H-3', H-5', H-5''', C*H*$_{Phth}$); 3.80 (dd, 1H, *J* = 4.4, 11.2 Hz, H-6'''); 3.73-3.68 (m, 4H, H-2, H-2', H-4''', H-6'''); 3.64-3.47 (m, 9H, H-2'', H-4', H-5, OC*H*$_3$); 3.42 (s, 3H, OC*H*$_3$); 3.37 (s, 3H, OC*H*$_3$); 3.34 (s, 3H, OC*H*$_3$); 3.31 (s, 3H, OC*H*$_3$); 3.21 (t, 1H, *J* = 9.6 Hz, H-4); 2.90-2.84 (m, 1H, C*H*$_{Phth}$); 2.38 (t, 2H, *J* = 7.0 Hz, C*H*$_{2,Phth}$); 2.32 (bs, 2H, O*H*$_{Phth}$); 2.18 (s, 3H, C*H*$_{3,Ac}$); 1.62-1.23 (m, 47H, H-6, H-6', C*H*$_{Phth}$, C*H*$_{2,Phth}$); 1.11-1.07 (m, 5H, H-6'', C*H*$_{2,Phth}$); 0.91 (t, 3H, *J* = 7.2 Hz, C*H*$_{3,Phth}$); 0.83 (d, 3H, *J* = 6.8 Hz, C*H*$_{3,Phth}$). ^{13}C-APT NMR (101 MHz) δ: 171.1 (*C*O$_{Ac}$); 155.7 (C$_{q,arom}$); 154.6, 154.5 (*C*O$_{Cbz}$); 139.1, 138.5, 135.3, 135.0 (C$_{q,arom}$); 133.0, 128.7, 128.7, 128.6, 128.5, 128.4, 128.3, 128.3, 127.9, 127.9, 127.6, 127.5 (*C*H$_{arom}$); 118.1 (C$_{q,arom}$); 116.2 (*C*H$_{arom}$); 99.7 (C-1''); 98.6 (C-1'''); 98.4 (C-1'); 94.8 (C-1); 89.6 (C$_{q,alkyne}$); 86.8 (*C*H$_{Phth}$); 82.1 (C-4); 81.8 (C-3'); 80.7 (C-2'); 80.2 (C$_{q,alkyne}$); 80.1 (C-2); 79.8 (C-3); 79.4 (C-4;); 78.8 (C-2''); 75.8 (C-3'''); 75.4 (PhCH$_2$); 74.2 (C-4'''); 73.6 (C-2'''); 73.5 (Ph*C*H$_2$); 73.0 (C-4''); 72.9 (C-3''); 72.1 (C-5'''); 70.1, 69.9 (Ph*C*H$_2$); 69.6, 69.6 (*C*H$_{Phth}$); 69.0 (C-5); 68.8 (C-5'); 65.3 (C-5''); 61.3, 60.7, 59.1, 58.9, 57.8, 57.5 (OCH$_3$); 42.4, 37.7 (*C*H$_{2,Phth}$); 34.9 (*C*H$_{Phth}$); 32.8, 29.8, 29.8, 29.7, 29.3, 29.1, 29.0, 27.7, 26.3, 25.9, 22.5 (*C*H$_{2,Phth}$); 20.9 (*C*H$_{3,Ac}$); 19.5 (*C*H$_{2,Phth}$); 18.3 (C-6); 17.9 (C-6'); 16.3 (C-6''); 15.0, 10.2 (*C*H$_{3,Phth}$). IR (thin film, cm^{-1}): 1045, 1098, 1235, 1274, 1382, 1455, 1507, 1750, 2853, 2926, 3411. HRMS calculated for $C_{96}H_{136}O_{26}Na$ 1727.92120 $[M+Na]^+$; found 1727.92198.

4-((3*R*,4*S*,9*R*,11*R*)-3-methoxy-4-methylheptacos-26-yne-9,11-diol)phenyl 2,4-di-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(2,4-di-*O*-methyl-3,6-di-*O*-benzyloxycarbonyl-α-D-mannopyranosyl)-4-*O*-acetyl-α-L-fucopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (57)



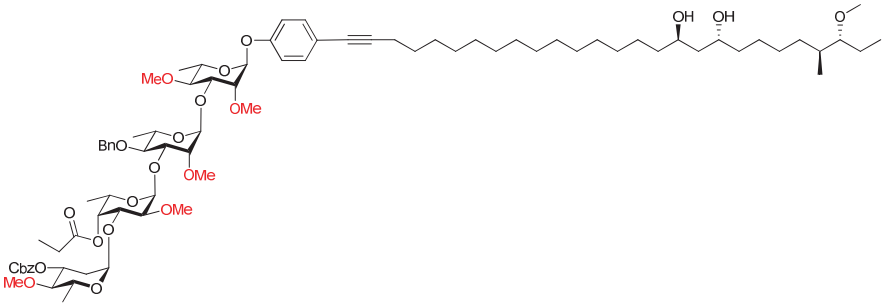
The title compound was synthesized according to general procedure C using **48** (23 mg, 17.6 µmol, 1.0 eq) and phthiocerol (10 mg, 21.1 µmol, 1.2 eq). Column chromatography (*n*-pentane-Et_2O 1:9) yielded the title compound (21 mg, 12.9 µmol, 73%) as a yellow oil. $[\alpha]_D^{25}$ = -64.3 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.39-7.21 (m, 17H, C*H*$_{arom}$); 6.98-6.95 (m, 2H, C*H*$_{arom}$); 5.49 (d, 1H, *J* = 1.6 Hz, H-1); 5.26 (d, 1H, *J* = 2.8 Hz, H-4''); 5.21-5.11 (m, 8H, H-1', H-1'', H-1''', PhC*H*$_2$, PhC*H*H); 4.87 (dd, 1H, *J* = 3.2, 10.0 Hz, H-3'''); 4.57 (d, 1H, *J* = 11.2 Hz, PhCH*H*); 4.47 (dd, 1H, *J* = 1.8, 11.6 Hz, H-6'''); 4.37-4.31 (m, 2H, H-5'', H-6'''); 4.24 (dd, 1H, *J* = 3.6, 10.0 Hz, H-3''); 4.05 (dd, 1H, *J* = 3.2, 9.6 Hz, H-3); 4.02-3.94 (m, 4H, H-3', H-5''', C*H*$_{Phth}$); 3.94-3.91 (m, 1H, H-5'); 3.72 (dd, 1H, *J* = 2.0, 3.2 Hz, H-2); 3.69 (dd, 1H, *J* = 1.6, 2.8 Hz, H-2'); 3.65 (dd, 1H, *J* = 1.8, 3.0 Hz, H-2'''); 3.63-3.58 (m, 2H, H-4''', H-5); 3.53-3.50 (m, 8H, H-2'', H-4', OC*H*$_3$); 3.41 (s, 3H, OC*H*$_3$); 3.39 (s, 3H, OC*H*$_3$); 3.34 (s, 3H, OC*H*$_3$); 3.24-3.21 (m, 4H, H-4, OC*H*$_3$); 2.90-2.84 (m, 1H, C*H*$_{Phth}$); 2.39-2.26 (4H, C*H*$_{2,Phth}$, O*H*$_{Phth}$); 2.19 (s, 3H, C*H*$_{3,Ac}$); 1.62-1.23 (m, 47H, H-6, H-6', C*H*$_{Phth}$, C*H*$_{2,Phth}$); 1.11-1.07 (m, 5H, H-6'', C*H*$_{2,Phth}$); 0.91 (t, 3H, *J* = 7.2 Hz, C*H*$_{3,Phth}$); 0.83 (d, 3H, *J* = 6.8 Hz, C*H*$_{3,Phth}$). ^{13}C-APT NMR (101 MHz) δ: 170.9 (*C*O$_{Ac}$); 155.7 (C$_{q,arom}$); 155.3, 154.7 (*C*O$_{Cbz}$); 139.2, 135.4 (C$_{q,arom}$); 138.5, 128.7, 128.7, 128.6, 128.6, 128.4, 128.3, 128.2, 127.4 (*C*H$_{arom}$); 118.1 (C$_{q,arom}$); 116.2 (*C*H$_{arom}$); 99.6 (C-1''); 98.6 (C-1'''); 98.5 (C-1'); 94.7 (C-1); 89.6 (*C*H$_{Phth}$); 82.0 (C-4); 81.7 (C-3'); 80.7 (C-2'); 80.2 (C$_{q,alkyne}$); 80.1 (C-2); 79.8 (C-3); 79.4 (C-4'); 78.7 (C-2''); 78.3 (C-2'''); 77.5 (C-3'''); 75.2 (Ph*C*H$_2$); 74.4 (C-4'''); 73.5 (C-3''); 73.0 (C-4''); 70.2 (C-5'''); 69.8, 69.7 (Ph*C*H$_2$); 69.6, 69.6 (*C*H$_{Phth}$); 69.0 (C-5); 68.8 (C-5'); 66.9 (C-6'''); 65.3 (C-5''); 61.3, 60.7, 59.1, 59.0, 58.6, 57.8, 57.5 (O*C*H$_3$); 42.4, 37.7 (*C*H$_{2,Phth}$); 34.9 (*C*H$_{Phth}$); 32.8, 29.8, 29.8, 29.7, 29.3, 29.1, 29.0, 27.7, 26.3, 25.9, 22.5 (*C*H$_{2,Phth}$); 20.9 (*C*H$_{3,Ac}$); 19.5 (*C*H$_{2,Phth}$); 18.3 (C-6); 17.9 (C-6'); 16.3 (C-6''); 14.9, 10.2 (*C*H$_{3,Phth}$). IR (thin film, cm^{-1}): 1043, 1096, 1128, 1251, 1457, 1507, 1747, 2853, 2926, 3433. HRMS calculated for $C_{90}H_{132}O_{26}Na$ 1651.88990 $[M+Na]^+$; found 1651.89174.

4-((3*R*,4*S*,9*R*,11*R*)-3-methoxy-4-methylheptacos-26-yne-9,11-diol)phenyl 2,4-di-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(3-*O*-benzyloxycarbonyl-4-*O*-methyl-2,6-dideoxy-α-D-glucopyranosyl)-4-*O*-acetyl-α-L-fucopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (58)



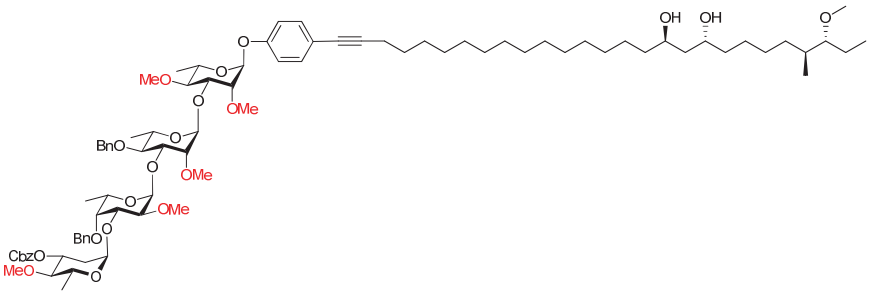
The title compound was synthesized according to general procedure C using **49** (35 mg, 30.8 µmol, 1.0 eq) and phthiocerol (17 mg, 37.0 µmol, 1.2 eq). Column chromatography (*n*-pentane-Et_2O 1:9) yielded the title compound (36 mg, 24.8 µmol, 81%) as a yellow oil. $[\alpha]_D^{25}$ = -71.6 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.39-7.23 (m, 12H, C*H*$_{arom}$); 6.97-6.94 (m, 2H, C*H*$_{arom}$); 5.49 (d, 1H, *J* = 1.6 Hz, H-1); 5.23 (d, 1H, *J* = 2.8 Hz, H-4''); 5.20-5.11 (m, 6H, H-1', H-1'', H-1''', PhC*H*$_2$, PhC*H*H); 4.98-4.92 (m, 1H, H-3'''); 4.56 (d, 1H, *J* = 11.2 Hz, PhCH*H*); 4.33 (q, 1H, *J* = 6.8 Hz, H-5''); 4.18 (dd, 1H, *J* = 3.8, 10.2 Hz, H-3''); 4.08-4.00 (m, 2H, H-3, H-3'); 3.95-3.85 (m, 4H, H-5', H-5''', C*H*$_{Phth}$); 3.72-3.69 (m, 2H, H-2, H-2'); 3.61-3.46 (m, 15H, H-2'', H-4', H-5, OC*H*$_3$); 3.34 (s, 3H, OC*H*$_3$); 3.27 (s, 3H, OC*H*$_3$); 3.21 (t, 1H, *J* = 9.6 Hz, H-4); 2.89-2.85 (m, 2H, H-4''', C*H*$_{Phth}$); 2.45-2.25 (m, 5H, H-2''', C*H*$_{2,Phth}$, O*H*$_{Phth}$); 2.20 (s, 3H, C*H*$_{3,Ac}$); 1.71-1.24 (m, 53H, H-2''', H-6, H-6', H-6''', C*H*$_{2,Phth}$); 1.11-1.07 (m, 5H, C*H*$_{2,Phth}$, H-6''); 0.91 (t, 3H, *J* = 7.2 Hz, C*H*$_{3,Phth}$); 0.83 (d, 3H, *J* = 6.8 Hz, C*H*$_{3,Phth}$). ^{13}C-APT NMR (101 MHz) δ: 171.0 (*C*O$_{Ac}$); 155.7 (C$_{q,arom}$); 154.6 (*C*O$_{Cbz}$); 139.2, 135.4 (C$_{q,arom}$); 133.0, 128.7, 128.6, 128.4, 128.3, 127.6, 127.5 (*C*H$_{arom}$); 118.1 (C$_{q,arom}$); 116.2 (*C*H$_{arom}$); 99.9 (C-1''); 98.7 (C-1'''); 98.4 (C-1'); 94.8 (C-1); 89.5 (C$_{q,alkyne}$); 86.8 (*C*H$_{Phth}$); 84.2 (C-4'''); 82.0 (C-4); 81.5 (C-3'); 80.8 (C-2'); 80.1 (C$_{q,alkyne}$); 80.1 (C-2); 79.8 (C-3); 79.5 (C-4'); 78.7 (C-2''); 75.4 (C-3'''); 75.2 (Ph*C*H$_2$); 73.4 (C-4''); 73.2 (C-3''); 69.7 (Ph*C*H$_2$); 69.6, 69.6 (*C*H$_{Phth}$); 69.0 (C-5); 68.8 (C-5'); 67.6 (C-5'''); 65.5 (C-5''); 61.3, 60.3, 59.1, 58.9, 57.8, 57.5 (O*C*H$_3$); 42.4, 37.6 (*C*H$_{2,Phth}$); 35.7 (C-2'''); 34.9 (*C*H$_{Phth}$); 32.7, 29.8, 29.8, 29.7, 29.3, 29.1, 28.9, 27.7, 26.3, 25.9, 22.5 (*C*H$_{2,Phth}$); 21.0 (*C*H$_{3,Ac}$); 19.5 (*C*H$_{2,Phth}$); 18.3 (C-6'); 18.1 (C-6'''); 17.9 (C-6); 16.5 (C-6''); 14.9, 10.2 (*C*H$_{3,Phth}$). IR (thin film, cm^{-1}): 1043, 1098, 1235, 1256, 1507, 1744, 2853, 2928, 3449. HRMS calculated for $C_{81}H_{124}O_{22}Na$ 1471.84765 $[M+Na]^+$; found 1471.84802.

4-((3*R*,4*S*,9*R*,11*R*)-3-methoxy-4-methylheptacos-26-yne-9,11-diol)phenyl 2,4-di-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(3-*O*-benzyloxycarbonyl-4-*O*-methyl-2,6-dideoxy-α-D-glucopyranosyl)-4-*O*-propionyl-α-L-fucopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (59)



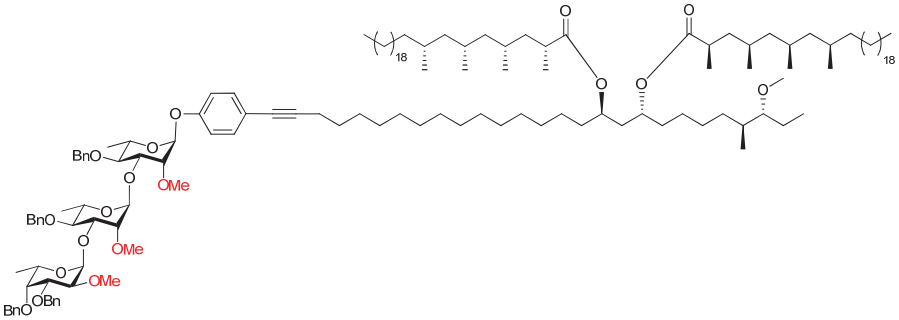
The title compound was synthesized according to general procedure C using **51** (35 mg, 30.9 µmol, 1.0 eq) and phthiocerol (17 mg, 37.1 µmol, 1.2 eq). Column chromatography (*n*-pentane-Et_2O 1:4) yielded the title compound (37 mg, 25.3 µmol, 82%) as a yellow oil. $[\alpha]_D^{25}$ = -60.7 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.39-7.23 (m, 12H, C*H*$_{arom}$); 6.98-6.94 (m, 2H, C*H*$_{arom}$); 5.49 (d, 1H, *J* = 1.6 Hz, H-1); 5.24 (dd, 1H, *J* = 2.8, 3.6 Hz, H-4''); 5.20-5.13 (m, 5H, H-1', H-1'', PhC*H*$_2$, PhC*H*H); 5.11 (d, 1H, *J* = 2.8 Hz, H-1'''); 4.96-4.90 (m, 1H, H-3'''); 4.56 (d, 1H, *J* = 11.6 Hz, PhCH*H*); 4.33 (q, 1H, *J* = 7.2 Hz, H-5''); 4.18 (dd, 1H, *J* = 3.6, 9.6 Hz, H-3''); 4.07-4.00 (m, 2H, H-3, H-3'); 3.95-3.85 (m, 4H, H-5', H-5''', C*H*$_{Phth}$); 3.72-3.69 (m, 2H, H-2, H-2'); 3.61-3.57 (m, 1H, H-5); 3.54-3.45 (m, 14H, H-2'', H-4', OC*H*$_3$); 3.34 (s, 3H, OC*H*$_3$); 3.27 (s, 3H, OC*H*$_3$); 3.21 (t, 1H, *J* = 9.6 Hz, H-4); 2.90-2.85 (m, 2H, H-4''', C*H*$_{Phth}$); 2.54-2.38 (m, 7H, H-2''', COC*H*$_2$CH$_3$, C*H*$_{2,Phth}$, O*H*$_{Phth}$); 1.77-1.07 (m, 53H, H-2''', H-6, H-6', H-6'', H-6''', COCH$_2$C*H*$_3$, C*H*$_{2,Phth}$); 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: 174.4 (*C*O$_{propionyl}$); 155.7 (C$_{q,arom}$); 154.6 (*C*O$_{Cbz}$); 139.2, 135.4 (C$_{q,arom}$); 133.0, 128.7, 128.6, 128.4, 128.3, 128.3, 127.6, 127.5 (*C*H$_{arom}$); 118.1 (C$_{q,arom}$); 116.2 (*C*H$_{arom}$); 99.9 (C-1''); 98.7 (C-1'''); 98.4 (C-1'); 94.8 (C-1); 89.5 (C$_{q,alkyne}$); 86.8 (*C*H$_{Phth}$); 84.1 (C-4'''); 82.0 (C-4); 81.4 (C-3'); 80.8 (C-2'); 80.2 (C$_{q,alkyne}$); 80.1 (C-2); 79.8 (C-3); 79.5 (C-4'); 78.7 (C-2''); 75.3 (C-3'''); 75.2 (Ph*C*H$_2$); 73.5 (C-3''); 73.1 (C-4''); 69.6 (Ph*C*H$_2$); 69.6, 69.6 (*C*H$_{Phth}$); 69.0 (C-5); 68.8 (C-5'); 67.5 (C-5'''); 65.6 (C-5''); 61.3, 60.1, 59.1, 59.0, 57.9, 57.5 (O*C*H$_3$); 42.4, 37.6 (*C*H$_{2,Phth}$); 35.7 (C-2'''); 34.9 (*C*H$_{Phth}$); 32.7, 29.8, 29.8, 29.7, 29.3, 29.1, 28.9 (*C*H$_{2,Phth}$); 27.8 (*C*H$_{2,Propionyl}$); 27.7, 26.3, 25.9, 22.5, 19.5 (*C*H$_{2,Phth}$); 18.3 (C-6'); 18.1 (C-6'''); 17.9 (C-6); 16.5 (C-6''); 14.9, 10.2 (*C*H$_{3,Phth}$), 9.7 (*C*H$_{3,Propionyl}$). IR (thin film, cm^{-1}): 1043, 1099, 1256, 1382, 1457, 1507, 1744, 2855, 2928, 3454. HRMS calculated for $C_{82}H_{126}O_{22}Na$ 1485.86330 [M+Na]$^+$; found 1485.86337.

4-((3*R*,4*S*,9*R*,11*R*)-3-methoxy-4-methylheptacos-26-yne-9,11-diol)phenyl 2,4-di-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(3-*O*-benzyloxycarbonyl-4-*O*-methyl-2,6-dideoxy-α-D-glucopyranosyl)-4-*O*-benzyl-α-L-fucopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (60)



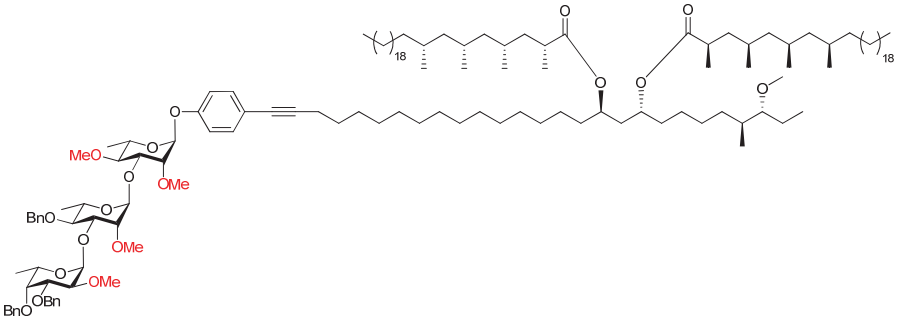
The title compound was synthesized according to general procedure C using **50** (39 mg, 34.1 µmol, 1.0 eq) and phthiocerol (19 mg, 40.9 µmol, 1.2 eq). Column chromatography (*n*-pentane-Et_2O 1:4) yielded the title compound (51 mg, 34.1 µmol, 100%) as a yellow oil. $[\alpha]_D^{25}$ = -53.2 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.45-7.26 (m, 17H, C*H*$_{arom}$); 6.83 (dd, 2H, *J* = 1.8, 7.0 Hz, C*H*$_{arom}$); 5.49 (d, 1H, *J* = 1.6 Hz, H-1); 5.24 (d, 1H, *J* = 2.8 Hz, H-1'''); 5.18-5.11 (m, 6H, H-1', H-1'', H-3''' PhCH_2, PhC*H*H); 5.06 (d, 1H, *J* = 11.6 Hz, PhC*H*H); 4.64 (d, 1H, *J* = 11.2 Hz, PhCH*H*); 4.57 (d, 1H, *J* = 11.2 Hz, PhCH*H*); 4.23-4.17 (m, 2H, H-3'', H-5''); 4.06-3.86 (m, 6H, H-3, H-3', H-5', H-5''', C*H*$_{Phth}$); 3.75-3.71 (m, 3H, H-2, H-2', H-2''); 3.62-3.55 (m, 2H, H-4'', H-5); 3.52-3.46 (m, 13H, H-4', OCH_3); 3.34 (s, 3H, OCH_3); 3.25 (s, 3H, OCH_3); 3.20 (t, 1H, *J* = 9.6 Hz, H-4); 2.93 (t, 1H, *J* = 9.2 Hz, H-4'''); 2.90-2.84 (m, 1H, C*H*$_{Phth}$); 2.42 (dd, 1H, *J* = 5.2, 12.0 Hz, H-2'''); 2.42-2.36 (m, 5H, H-2''', C$H_{2,Phth}$, O*H*$_{Phth}$); 1.79-1.62 (m, 3H, H-2''', C$H_{2,Phth}$); 1.59-1.10 (m, 53H, H-2''', H-6, H-6', H-6'', H-6''', C$H_{2,Phth}$); 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: 155.7 (C$_{q,arom}$); 154.5 (*C*O$_{Cbz}$); 139.3, 138.6, 135.4 (C$_{q,arom}$); 128.7, 128.7, 128.5, 128.4, 128.3, 127.7, 127.6, 127.4 (*C*H$_{arom}$); 118.0 (C$_{q,arom}$); 116.2 (*C*H$_{arom}$); 99.9 (C-1''); 98.6 (C-1'); 98.3 (C-1'''); 94.7 (C-1); 89.5 (C$_{q,alkyne}$); 86.8 (*C*H$_{Phth}$); 84.5 (C-4'''); 81.9 (C-4); 81.4 (C-3'); 80.8 (C-2'); 80.1 (C-3); 80.1 (C-2); 79.9 (C-4''); 79.4 (C-4'); 79.1 (C-2''); 76.0 (C-3'''); 75.6 (C-3''); 75.4, 75.1, 69.7 (Ph*C*H_2); 69.6, 69.6 (*C*H$_{Phth}$); 69.0 (C-5); 68.8 (C-5'); 68.0 (C-5'''); 67.1 (C-5''); 61.4, 60.8, 59.0, 58.6, 57.9; 57.5 (OCH_3); 42.4, 37.6 (*C*H$_{2,Phth}$); 35.6 (C-2'''); 34.9 (*C*H$_{Phth}$); 32.7, 29.8, 29.8, 29.7, 29.3, 29.1, 28.9, 27.7, 26.3, 25.9, 22.5, 19.5 (*C*H$_{2,Phth}$); 18.4 (C-6'); 18.2 (C-6'''); 17.9 (C-6); 17.0 (C-6''); 14.9, 10.2 (*C*H$_{3,Phth}$). IR (thin film, cm^{-1}): 1040, 1099, 1455, 1507, 1749, 2853, 2928, 3436. HRMS calculated for $C_{86}H_{128}O_{21}Na$ 1519.88403 $[M+Na]^+$; found 1519.88543.

4-((3*R*,4*S*,9*R*,11*R*)-3-methoxy-4-methylheptacos-26-yne-9,11-diyl bismycocerosate)phenyl 2-*O*-methyl-3-*O*-(2-*O*-methyl-3-O-(2-*O*-methyl-3,4-di-*O*-benzyl-α-L-fucopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranosyl))-4-*O*-benzyl-α-L-rhamnopyranoside (61)



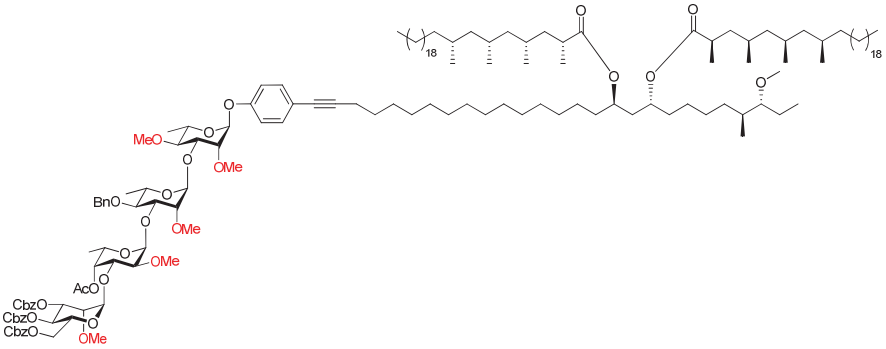
The title compound was synthesized according to general procedure D using **53** (30 mg, 21.7 µmol, 1.0 eq), mycocerosic acid (31 mg, 65.0 µmol, 3.0 eq), DIC (20 µL, 130 µmol, 6.0 eq) and DMAP (24 mg, 195 µmol, 9.0 eq). Column chromatography (*n*-pentane-Et_2O 7:3) yielded the title compound (30 mg, 14.3 µmol, 66%) as a waxy solid. $[\alpha]_D^{25}$ = -82.1 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.40-7.22 (m, 22H, C*H*$_{arom}$); 6.95 (d, 2H, *J* = 8.8 Hz, CH$_{arom}$); 5.51 (d, 1H, *J* = 1.6 Hz, H-1); 5.23-5.19 (m, 2H, H-1'', PhC*H*H); 5.15 (d, 1H, *J* = 1.6 Hz, H-1'); 5.00 (d, 1H, *J* = 11.6 Hz, PhC*H*H); 4.89-4.80 (m, 4H, PhC*H*H, PhC*H*H, C*H*$_{Phth}$); 4.73 (d, 1H, *J* = 12.0 Hz, PhCH*H*); 4.67-4.63 (m, 2H, PhCH*H,* PhCH*H*); 4.54 (d, 1H, *J* = 11.2 Hz, PhCH*H*); 4.19 (dd, 1H, *J* = 3.2, 9.6 Hz, H-3); 4.09-4.03 (m, 2H, H-3', H-5''); 3.98-3.89 (m, 2H, H-3'', H-5'); 3.82 (dd, 1H, *J* = 3.6, 10.4 Hz, H-2''); 3.77-3.66 (m, 4H, H-2, H-2', H-4'', H-5); 3.56-3.44 (m, 5H, H-4, H-4', OC*H*$_3$); 3.39 (s, 3H, OC*H*$_3$); 3.33 (s, 3H, OC*H*$_3$); 3.21 (s, 3H, OC*H*$_3$); 2.90-2.84 (m, 1H, C*H*$_{Phth}$); 2.57-2.48 (m, 2H, C*H*$_{Myc}$); 2.37 (t, 2H, *J* = 7.2 Hz, C*H*$_{2,Phth}$); 1.75-0.81 (m, 220H, H-6, H-6', H-6'', C*H*$_{Phth}$, C*H*$_{2,Phth}$, C*H*$_{3,Phth}$, C*H*$_{Myc,}$ C*H*$_{2,Myc}$, C*H*$_{3,Myc}$). ^{13}C-APT NMR (101 MHz) δ: 176.1, 176.1 (*C*O$_{Myc}$); 155.7, 139.3, 139.1, 138.8 (C$_{q,arom}$); 133.0 128.8, 128.5, 128.5, 128.4, 128.3, 127.9, 127.8, 127.7, 127.5, 127.5, 127.4 (C*H*$_{arom}$); 118.0 (C$_{q,arom}$); 116.2 (*C*H$_{arom}$); 100.1 (C-1''); 98.9 (C-1'); 94.7 (C-1); 89.5 (C$_{q,alkyne}$); 86.8 (*C*H$_{Phth}$); 80.7 (C-3'); 80.3 (C-2'); 80.1 (C$_{q,alkyne}$); 80.0 (C-2); 79.9 (C-4); 79.7 (C-3); 78.9 (C-3''); 78.6 (C-2''); 77.9 (C-4''); 75.4, 75.2, 75.0, 72.9 (PhC*H*$_2$); 70.4 (*C*H$_{Phth}$); 69.0 (C-5); 68.7 (C-5'); 67.0 (C-5); 59.1, 59.0 57.8, 57.5 (O*C*H$_3$); 45.6, 45.4 (*C*H$_{2,Myc}$); 41.1, 38.6 (*C*H$_{2,Phth}$); 37.9, 37.9 (*C*H$_{Myc}$); 36.8 (*C*H$_{2,Myc}$); 34.9 (*C*H$_{Phth}$); 34.8, 32.8 (*C*H$_{2,Phth}$); 32.1 (*C*H$_{2,Myc}$); 30.4 (*C*H$_{2,Phth}$); 30.2 (*C*H$_{Myc}$); 30.1, 29.9, 29.9, 29.8, 29.8, 29.8, 29.7, 29.5, 29.4, 29.2, 29.0 (*C*H$_2$); 28.2 (*C*H$_{Myc}$); 27.6 (*C*H$_{2,Phth}$); 27.3 (*C*H$_{Myc}$); 27.1 (*C*H$_{2,Myc}$); 25.7, 25.3 (*C*H$_{2,Phth}$); 22.8 (*C*H$_{2,Myc}$); 22.5 (*C*H$_{2,Phth}$); 20.9, 20.6, 20.6, 20.5 (*C*H$_{3,Myc}$); 19.6 (*C*H$_{2,Phth}$); 18.6 (*C*H$_{3,Myc}$); 18.3 (C-6'); 18.1 (C-6); 17.1 (C-6''); 14.8 (*C*H$_{3,Phth}$); 14.3 (*C*H$_{3,Myc}$); 10.2 (*C*H$_{3,Phth}$). IR (thin film, cm^{-1}): 1043, 1099, 1175, 1233, 1378, 1457, 1507, 1733, 2853, 2923. 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 bismycocerosate)phenyl 2,4-di-*O*-methyl-3-*O*-(2-*O*-methyl-3-O-(2-*O*-methyl-3,4-di-*O*-benzyl-α-L-fucopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (62)



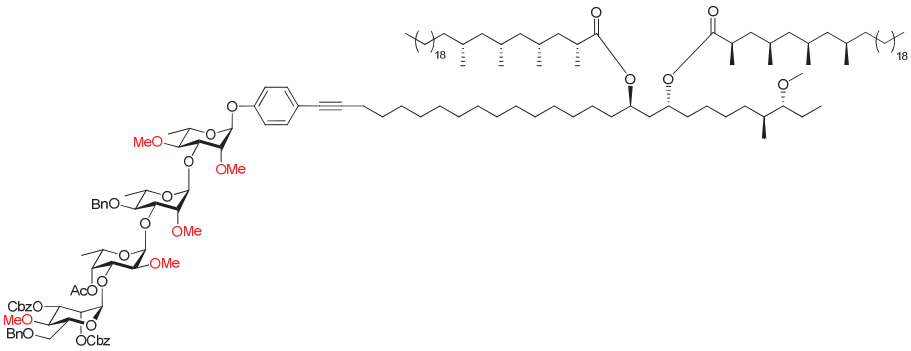
The title compound was synthesized according to general procedure D using **54** (26 mg, 19.9 µmol, 1.0 eq), mycocerosic acid (29 mg, 59.6 µmol, 3.0 eq), DIC (18 µL, 119 µmol, 6.0 eq) and DMAP (22 mg, 179 µmol, 9.0 eq). Column chromatography (*n*-pentane-Et_2O 7:3) yielded the title compound (30 mg, 13.4 µmol, 68%) as a waxy solid. $[\alpha]_D^{25}$ = -57.5 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.40-7.25 (m, 17H, C*H*$_{arom}$); 6.95 (d, 2H, *J* = 8.8 Hz, CH$_{arom}$); 5.48 (d, 1H, *J* = 1.6 Hz, H-1); 5.22-5.10 (m, 2H, H-1'', PhC*H*H); 5.15 (d, 1H, *J* = 1.6 Hz, H-1'); 5.00 (d, 1H, *J* = 11.6 Hz, PhC*H*H); 4.87-4.69 (m, 3H, PhC*H*H, C*H*$_{Phth}$); 4.67 (d, 1H, *J* = 11.6 Hz, PhCH*H*); 4.55 (d, 1H, *J* = 11.2 Hz, PhCH*H*); 4.11 (q, 1H, *J* = 6.8 Hz, H-5''); 4.06-3.91 (m, 4H, H-3, H-3', H-3'', H-5'); 3.82 (dd, 1H, *J* = 3.6, 10.4 Hz, H-2''); 3.72-3.69 (m, 3H, H-2, H-2', H-4''); 3.62-3.55 (m, 1H, H-5); 3.53-3.45 (m, 10H, H-4', OC*H*$_3$); 3.39 (s, 3H, OC*H*$_3$); 3.32 (s, 3H, OC*H*$_3$); 3.20 (t, 1H, *J* = 9.6 Hz, H-4); 2.88-2.84 (m, 1H, C*H*$_{Phth}$); 2.57-2.48 (m, 2H, C*H*$_{Myc}$); 2.37 (t, 2H, *J* = 7.0 Hz, C*H*$_{2,Phth}$); 1.75-0.81 (m, 218H, C*H*$_{Phth}$, C*H*$_{2,Phth}$, C*H*$_{3,Phth}$, C*H*$_{Myc,}$ C*H*$_{2,Myc}$, C*H*$_{3,Myc}$, H-6, H-6', H-6''). ^{13}C-APT NMR (101 MHz) δ: 176.1, 176.1 (*C*O$_{Myc}$); 155.7, 139.3, 139.1 138.7 (C$_{q,arom}$); 133.0, 128.6, 128.5, 128.4, 128.4, 128.0, 127.9, 127.8, 127.6, 127.5, 127.5 (*C*H$_{arom}$); 118.1 (C$_{q,arom}$); 116.2 (*C*H$_{arom}$); 100.1 (C-1''); 98.8 (C-1'); 94.8 (C-1); 89.5 (C$_{q,alkyne}$); 86.8 (*C*H$_{Phth}$); 81.9 (C-4); 80.9 (C-2'); 80.7 (C-3'); 80.1 (C-2); 80.1 (C-3); 79.7 (C-4'); 79.0 (C-3''); 78.6 (C-2''); 77.7 (C-4''); 75.2, 75.0, 73.0 (PhC*H*$_2$); 70.4 (*C*H$_{Phth}$); 69.0 (C-5); 68.8 (C-5'); 66.9 (C-5''); 61.4, 59.2, 59.1, 58.0, 57.5 (OC*H*$_3$); 45.6, 45.4 (C*H*$_{2,Myc}$); 41.1, 38.6 (*C*H$_{2,Phth}$); 37.9, 37.9 (*C*H$_{Myc}$); 36.8 (*C*H$_{2,Myc}$); 34.9 (*C*H$_{Phth}$); 34.8, 32.8 (*C*H$_{2,Phth}$); 32.1 (*C*H$_{2,Myc}$); 30.3 (*C*H$_{2,Phth}$); 30.2 (*C*H$_{Myc}$); 30.1, 29.9, 29.9, 29.8, 29.8, 29.8, 29.7, 29.5, 29.4, 29.2, 29.0 (*C*H$_2$); 28.2 (*C*H$_{Myc}$); 27.6 (*C*H$_{2,Phth}$); 27.3 (*C*H$_{Myc}$); 27.1 (*C*H$_{2,Myc}$); 25.7, 25.3 (*C*H$_{2,Phth}$); 22.8 (*C*H$_{2,Myc}$); 22.5 (*C*H$_{2,Phth}$); 20.9, 20.6, 20.6, 20.5 (*C*H$_{3,Myc}$); 19.6 (*C*H$_{2,Phth}$); 18.6 (*C*H$_{3,Myc}$); 18.4 (C-6'); 17.9 (C-6); 17.1 (C-6''); 14.8 (*C*H$_{3,Phth}$); 14.3 (*C*H$_{3,Myc}$); 10.2 (*C*H$_{3,Phth}$). IR (thin film, cm^{-1}): 1045, 1100, 1175, 1233, 1378, 1507, 1733, 2853, 2923. 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 bismycocerosate)phenyl 2,4-di-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(2-*O*-methyl-3,4,6-tri-*O*-benzyloxycarbonyl-α-D-mannopyranosyl)-4-*O*-acetyl-α-L-fucopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (62)



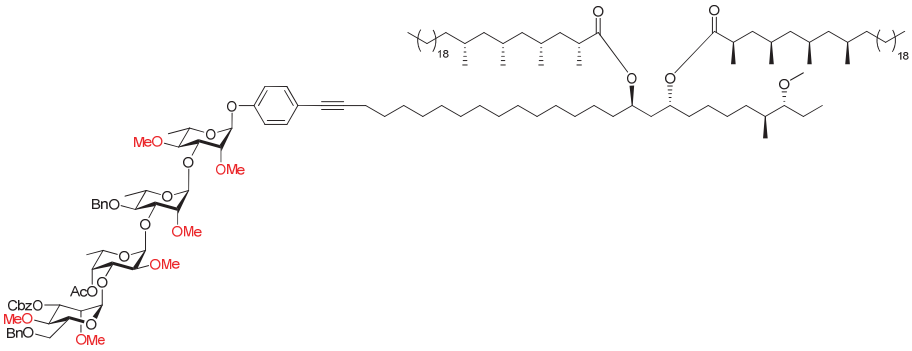
The title compound was synthesized according to general procedure D using **55** (34 mg, 19.4 µmol, 1.0 eq), mycocerosic acid (28 mg, 58.3 µmol, 3.0 eq), DIC (18 µL, 117 µmol, 6.0 eq) and DMAP (21 mg, 175 µmol, 9.0 eq). Column chromatography (*n*-pentane-Et_2O 6:4) yielded the title compound (28 mg, 10.5 µmol, 54%) as a waxy solid. $[\alpha]_D^{25}$ = -48.1 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.37-7.21 (m, 22H, C*H*$_{arom}$); 6.98-6.95 (m, 2H, C*H*$_{arom}$); 5.50 (d, 1H, *J* = 1.6 Hz, H-1); 5.27 (d, 1H, *J* = 2.8 Hz, H-4''); 5.23-5.05 (m, 11H, H-1', H-1'', H-1''', H-4''', PhC*H*$_2$, PhC*H*H); 4.93 (dd, 1H, *J* = 3.2, 10.0 Hz, H-3'''); 4.89-4.80 (m, 2H, C*H*$_{Phth}$); 4.58 (d, 1H, *J* = 11.2 Hz, PhCH*H*); 4.35-4.29 (m, 3H, H-5'', H-6'''); 4.25 (dd, 1H, *J* = 3.6, 10.0 Hz, H-3''); 4.20-4.16 (m, 1H, H-5'''); 4.07 (dd, 1H, *J* = 3.2, 9.6 Hz, H-3); 4.00 (dd, 1H, *J* = 3.0, 9.4 Hz, H-3'); 3.95-3.91 (m, 3H, H-5', C*H*$_{Phth}$); 3.73-3.71 (m, 2H, H-2, H-2'''); 3.69 (dd, 1H, *J* = 1.8, 3.0 Hz, H-2'); 3.64-3.60 (m, 1H, H-5); 3.54-3.48 (m, 8H, H-2'', H-4', OC*H*$_3$); 3.40 (s, 3H, OC*H*$_3$); 3.33 (s, 3H, OC*H*$_3$); 3.33 (s, 3H, OC*H*$_3$); 3.23-3.18 (m, 4H, H-4, OC*H*$_3$); 2.88-2.84 (m, 1H, C*H*$_{Phth}$); 2.55-2.50 (m, 2H C*H*$_{Myc}$); 2.38 (t, 2H, *J* = 7.2 Hz, C*H*$_{2,Phth}$); 2.18 (s, 3H, C*H*$_{3,Ac}$); 1.75-0.81 (m, 198H, H-6, H-6', H-6'', C*H*$_{Phth}$, C*H*$_{2,Phth}$, C*H*$_{3,Phth}$, C*H*$_{Myc,}$ C*H*$_{2,Myc}$, C*H*$_{3,Myc}$). ^{13}C-APT NMR (101 MHz) δ: 176.2, 176.1 (*C*O$_{Myc}$); 170.9 (*C*O$_{Ac}$); 155.7 (C$_{q,arom}$); 155.1, 154.5, 154.4 (*C*O$_{Cbz}$); 139.2, 135.4, 135.2, 135.1 (C$_{q,arom}$); 133.0, 128.7, 128.6, 128.6, 128.5, 128.4, 128.3, 128.2, 127.4 (*C*H$_{arom}$); 118.1 (C$_{q,arom}$); 116.2 (*C*H$_{arom}$); 99.5 (C-1''); 98.8 (C-1'''); 98.5 (C-1'); 94.7 (C-1); 89.6 (C$_{q,alkyne}$); 86.8 (*C*H$_{Phth}$); 82.0 (C-4); 81.7 (C-3'); 80.7 (C-2'); 80.2 (C-2); 80.1 (C$_{q,alkyne}$); 79.9 (C-3); 79.4 (C-4'); 78.7 (C-2''); 77.8 (C-2'''); 75.2 (Ph*C*H$_2$); 75.0 (C-3''); 73.8 (C-3''); 72.9 (C-4''); 70.5 (C-4'''); 70.4 (*C*H$_{Phth}$); 70.2, 69.8, 69.8 (Ph*C*H$_2$); 69.0 (C-5); 69.0 (C-5'''); 68.8 (C-5'); 66.4 (C-6'''); 65.4 (C-5''); 61.3, 59.2, 59.0, 58.5, 57.8, 57.5 (O*C*H$_3$); 45.6, 45.4 (*C*H$_{2,Myc}$); 41.1, 38.6 (*C*H$_{2,Phth}$); 37.9, 37.9 (*C*H$_{Myc}$); 36.8 (*C*H$_{2,Myc}$); 34.9 (*C*H$_{Phth}$); 34.8, 32.8 (*C*H$_{2,Phth}$); 32.1 (*C*H$_{2,Myc}$); 30.2 (*C*H$_{2,Phth}$); 30.1 (*C*H$_{Myc}$); 29.9, 29.9, 29.8, 29.5, 29.4, 29.2, 29.0 (*C*H$_2$); 28.2 (*C*H$_{Myc}$); 27.6 (*C*H$_{2,Phth}$); 27.3 (*C*H$_{Myc}$); 27.1 (*C*H$_{2,Myc}$); 25.7, 25.3 (*C*H$_{2,Phth}$); 22.8 (*C*H$_{2,Myc}$); 22.5 (*C*H$_{2,Phth}$); 20.9, 20.6, 20.6, 20.5 (*C*H$_{3,Myc}$); 19.6 (*C*H$_{2,Phth}$); 18.6 (*C*H$_{3,Myc}$); 18.3 (C-6'); 18.0 (C-6); 16.3 (C-6''); 14.8 (*C*H$_{3,Phth}$); 14.3 (*C*H$_{3,Myc}$); 10.2 (*C*H$_{3,Phth}$). IR (thin film, cm^{-1}): 1019, 1045, 1099, 1129, 1175, 1235, 1378, 1457, 1507, 1744, 2853, 2923. 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 bismycocerosate)phenyl 2,4-di-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(2,3-di-*O*-benzyloxycarbonyl-4-*O*-methyl-6-*O*-benzyl-α-D-mannopyranosyl)-4-*O*-acetyl-α-L-fucopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside



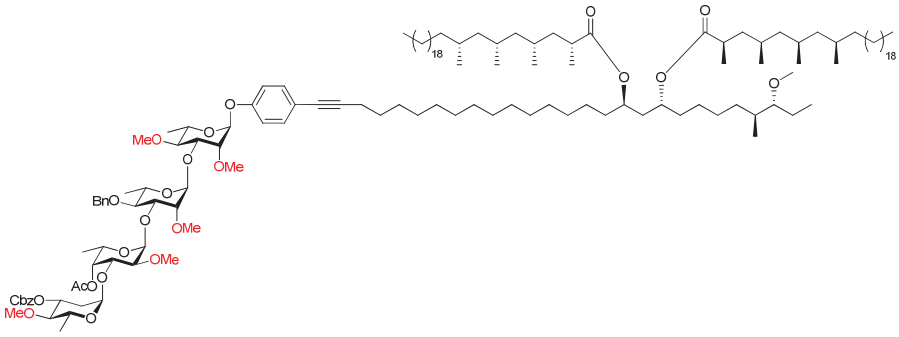
The title compound was synthesized according to general procedure D using **56** (26 mg, 15.2 µmol, 1.0 eq), mycocerosic acid (22 mg, 45.7 µmol, 3.0 eq), DIC (14 µL, 91.4 µmol, 6.0 eq) and DMAP (17 mg, 137 µmol, 9.0 eq). Column chromatography (*n*-pentane-Et_2O 6:4) yielded the title compound (26 mg, 9.88 µmol, 65%) as a waxy solid. $[\alpha]_D^{25}$ = -47.8 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.39-7.22 (m, 22H, C*H*$_{arom}$); 6.98-6.94 (m, 2H, C*H*$_{arom}$); 5.49 (d, 1H, *J* = 1.6 Hz, H-1); 5.28 (d, 1H, *J* = 2.0 Hz, H-1'''); 5.26 (d, 1H, *J* = 3.6 Hz, H-4''); 5.20-5.15 (m, 5H, H-1', H-1'', H-2''', PhC*H*$_2$); 5.13-5.08 (m, 3H, PhC*H*$_2$, PhC*H*H); 4.99 (dd, 1H, *J* = 3.0, 9.8 Hz, H-3'''); 4.88-4.80 (m, 2H, C*H*$_{Phth}$); 4.72 (d, 1H, *J* = 12.0 Hz, PhC*H*H); 4.56-4.50 (m, 2H, PhCH*H*, PhCH*H*); 4.32-4.26 (m, 2H, H-3'', H-5''); 4.07 (dd, 1H, *J* = 3.2, 9.6 Hz, H-3); 4.02-3.91 (m, 3H, H-3', H-5', H-5'''); 3.80 (dd, 1H, *J* = 4.0, 11.2 Hz, H-6'''); 3.73-3.68 (m, 4H, H-2, H-2', H-4''', H-6'''); 3.63-3.47 (m, 9H, H-2'', H-4', H-5, OC*H*$_3$); 3.42 (s, 3H, OC*H*$_3$); 3.37 (s, 3H, OC*H*$_3$); 3.33 (s, 3H, OC*H*$_3$); 3.31 (s, 3H, OC*H*$_3$); 3.21 (t, 1H, *J* = 9.4 Hz, H-4); 2.90-2.84 (m, 1H, C*H*$_{Phth}$); 2.55-2.50 (m, 2H, C*H*$_{Myc}$); 2.37 (t, 2H, *J* = 7.0 Hz, C*H*$_{2,Phth}$); 2.21 (s, 3H, C*H*$_{3,Ac}$); 1.75-0.81 (m, 198H, H-6, H-6', H-6'', C*H*$_{Phth}$, C*H*$_{2,Phth}$, C*H*$_{3,Phth}$, C*H*$_{Myc,}$ C*H*$_{2,Myc}$, C*H*$_{3,Myc}$). ^{13}C-APT NMR (101 MHz) δ: 176.2, 176.1 (*C*O$_{Myc}$); 171.1 (*C*O$_{Ac}$); 155.7 (C$_{q,arom}$); 154.6, 154.5 (*C*O$_{Cbz}$); 139.1, 138.5, 135.3, 135.0 (C$_{q,arom}$); 133.0, 128.7, 128.7, 128.6, 128.5, 128.4, 128.3, 128.3, 127.9, 127.9, 127.6, 127.5 (*C*H$_{arom}$); 118.1 (C$_{q,arom}$); 116.2 (*C*H$_{arom}$); 99.7 (C-1''); 98.6 (C-1'''); 98.4 (C-1'); 94.8 (C-1); 89.5 (C$_{q,alkyne}$); 86.8 (*C*H$_{Phth}$); 82.1 (C-4); 81.8 (C-3'); 80.7 (C-2'); 80.2 (C$_{q,alkyne}$); 80.1 (C-2); 79.8 (C-3); 79.4 (C-4;); 78.8 (C-2''); 75.8 (C-3'''); 75.4 (Ph*C*H$_2$); 74.2 (C-4'''); 73.7 (C-2'''); 73.6 (Ph*C*H$_2$); 73.0 (C-4''); 72.9 (C-3''); 72.1 (C-5'''); 70.4 (*C*H$_{Phth}$); 70.1, 69.9 (Ph*C*H$_2$); 69.0 (C-5); 68.8 (C-5'); 65.3 (C-5''); 61.3, 60.7, 59.1, 58.9, 57.8, 57.5 (O*C*H$_3$); 45.6, 45.4 (*C*H$_{2,Myc}$); 41.1, 38.6 (*C*H$_{2,Phth}$); 37.9 (*C*H$_{Myc}$); 36.8 (*C*H$_{2,Myc}$); 34.9 (*C*H$_{Phth}$); 34.8, 32.8 (*C*H$_{2,Phth}$); 32.1 (*C*H$_{2,Myc}$); 30.2 (*C*H$_{2,Phth}$); 30.1 (*C*H$_{Myc}$); 29.9, 29.9, 29.8, 29.8, 29.5, 29.4, 29.2, 29.0 (*C*H$_2$); 28.2 (*C*H$_{Myc}$); 27.6 (*C*H$_{2,Phth}$); 27.3 (*C*H$_{Myc}$); 27.1 (*C*H$_{2,Myc}$); 25.7, 25.3 (*C*H$_{2,Phth}$); 22.8 (*C*H$_{2,Myc}$); 22.5 (*C*H$_{2,Phth}$); 20.9 (*C*H$_{3,Ac}$); 20.6, 20.5 (*C*H$_{3,Myc}$); 19.6 (*C*H$_{2,Phth}$); 18.6 (*C*H$_{3,Myc}$); 18.3 (C-6'); 17.9 (C-6); 16.3 (C-6''); 14.8 (*C*H$_{3,Phth}$); 14.3 (*C*H$_{3,Myc}$); 10.2 (*C*H$_{3,Phth}$). IR (thin film, cm^{-1}): 1045, 1099, 1173, 1235, 1275, 1378, 1507, 1749, 2853, 2923. 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 bismycocerosate)phenyl 2,4-di-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(2,4-di-*O*-methyl-3,6-di-*O*-benzyloxycarbonyl-α-D-mannopyranosyl)-4-*O*-acetyl-α-L-fucopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (65)



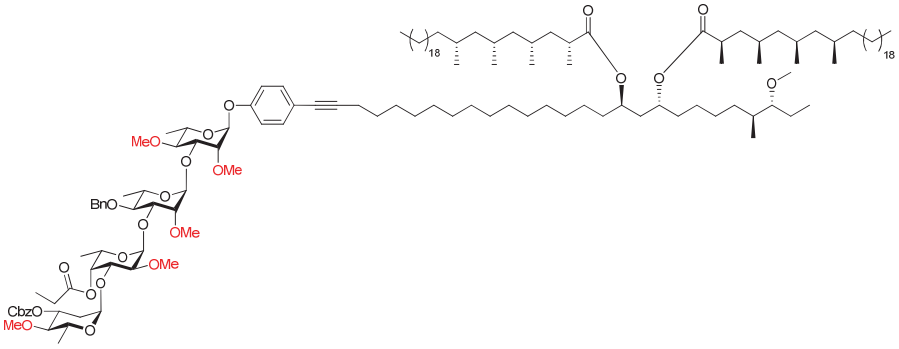
The title compound was synthesized according to general procedure D using **57** (20 mg, 12.3 µmol, 1.0 eq), mycocerosic acid (18 mg, 36.8 µmol, 3.0 eq), DIC (11 µL, 73.6 µmol, 6.0 eq) and DMAP (14 mg, 110 µmol, 9.0 eq). Column chromatography (*n*-pentane-Et_2O 1:1) yielded the title compound (16 mg, 6.37 µmol, 52%) as a waxy solid. $[\alpha]_D^{25}$ = -86.6 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.39-7.21 (m, 17H, C*H*$_{arom}$); 6.96 (d, 2H, *J* = 8.8 Hz, C*H*$_{arom}$); 5.49 (d, 1H, *J* = 1.6 Hz, H-1); 5.26 (d, 1H, *J* = 3.2 Hz, H-4''); 5.20-5.11 (m, 8H, H-1', H-1'', H-1''', PhC*H*$_2$, PhC*H*H); 4.88-4.83 (m, 3H, H-3''', C*H*$_{Phth}$); 4.57 (d, 1H, *J* = 11.6 Hz, PhCH*H*); 4.47 (dd, 1H, *J* = 1.8, 11.8 Hz, H-6'''); 4.37-4.31 (m, 2H, H-5'', H-6'''); 4.24 (dd, 1H, *J* = 3.4, 10.2 Hz, H-3''); 4.06 (dd, 1H, *J* = 3.0, 9.4 Hz, H-3); 4.02-3.94 (m, 2H, H-3', H-5'''); 3.94-3.91 (m, 1H, H-5'); 3.72 (dd, 1H, *J* = 2.0, 3.2 Hz, H-2); 3.69 (dd, 1H, *J* = 1.6, 2.8 Hz, H-2'); 3.65 (dd, 1H, *J* = 1.8, 3.0 Hz, H-2'''); 3.66-3.58 (m, 2H, H-4''', H-5); 3.53-3.50 (m, 8H, H-2'', H-4', OC*H*$_3$); 3.41 (s, 6H, OC*H*$_3$); 3.34 (s, 3H, OC*H*$_3$);); 3.33 (s, 3H, OC*H*$_3$); 3.24-3.18 (m, 4H, H-4, OC*H*$_3$); 2.86-2.82 (m, 1H, C*H*$_{Phth}$); 2.55-2.50 (m, 2H, C*H*$_{Myc}$); 2.37 (t, 2H, *J* = 7.0 Hz, C*H*$_{2,Phth}$); 2.19 (s, 3H, C*H*$_{3,Ac}$); 1.75-0.81 (m, 222H, H-6, H-6', H-6'', C*H*$_{Phth}$, C*H*$_{2,Phth}$, C*H*$_{3,Phth}$, C*H*$_{Myc,}$ C*H*$_{2,Myc}$, C*H*$_{3,Myc}$). ^{13}C-APT NMR (101 MHz) δ: 176.2, (*C*O$_{Myc}$); 171.0 (*C*O$_{Ac}$); 155.7 (C$_{q,arom}$); 155.3, 154.7 (*C*O$_{Cbz}$); 139.2, 135.4 (C$_{q,arom}$); 133.0, 128.7, 128.7, 128.6, 128.6, 128.4, 128.3, 128.2, 127.5, 127.4 (*C*H$_{arom}$); 118.1 (C$_{q,arom}$); 116.2 (*C*H$_{arom}$); 99.6 (C-1''); 98.6 (C-1'''); 98.5 (C-1'); 94.7 (C-1); 89.6 (*C*H$_{Phth}$); 82.1 (C-4); 81.7 (C-3'); 80.7 (C-2'); 80.2 (C$_{q,alkyne}$); 80.1 (C-2); 79.9 (C-3); 79.4 (C-4'); 78.7 (C-2''); 78.3 (C-2'''); 77.5 (C-3'''); 75.2 (Ph*C*H$_2$); 74.4 (C-4'''); 73.5 (C-3''); 73.0 (C-4''); 70.4 (*C*H$_{Phth}$); 70.2 (C-5'''); 69.8, 69.7 (Ph*C*H$_2$); 69.0 (C-5); 68.8 (C-5'); 66.9 (C-6'''); 65.3 (C-5''); 61.3, 60.7, 59.1, 59.0, 58.6, 57.8, 57.5 (O*C*H$_3$); 45.6, 45.4 (*C*H$_{2,Myc}$); 41.1, 38.6 (*C*H$_{2,Phth}$); 37.9 (*C*H$_{Myc}$); 36.8 (*C*H$_{2,Myc}$); 34.9 (*C*H$_{Phth}$); 34.8, 32.8 (*C*H$_{2,Phth}$); 32.1 (*C*H$_{2,Myc}$); 30.2 (*C*H$_{2,Phth}$); 30.1 (*C*H$_{Myc}$); 29.9, 29.9, 29.8, 29.5, 29.4, 29.2, 29.0 (*C*H$_2$); 28.2 (*C*H$_{Myc}$); 27.6 (*C*H$_{2,Phth}$); 27.3 (*C*H$_{Myc}$); 27.1 (*C*H$_{2,Myc}$); 25.7, 25.3 (*C*H$_{2,Phth}$); 22.8 (*C*H$_{2,Myc}$); 22.5 (*C*H$_{2,Phth}$); 20.9 (*C*H$_{3,Ac}$); 20.6, 20.5 (*C*H$_{3,Myc}$); 19.6 (*C*H$_{2,Phth}$); 18.6 (*C*H$_{3,Myc}$); 18.3 (C-6'); 18.0 (C-6); 16.3 (C-6''); 14.8 (*C*H$_{3,Phth}$); 14.3 (*C*H$_{3,Myc}$); 10.2 (*C*H$_{3,Phth}$). IR (thin film, cm^{-1}): 1043, 1098, 1129, 1175, 1252, 1378, 1457, 1507, 1740, 2853, 2923. 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 bismycocerosate)phenyl 2,4-di-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(3-*O*-benzyloxycarbonyl-4-*O*-methyl-2,6-dideoxy-α-D-glucopyranosyl)-4-*O*-acetyl-α-L-fucopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (66)



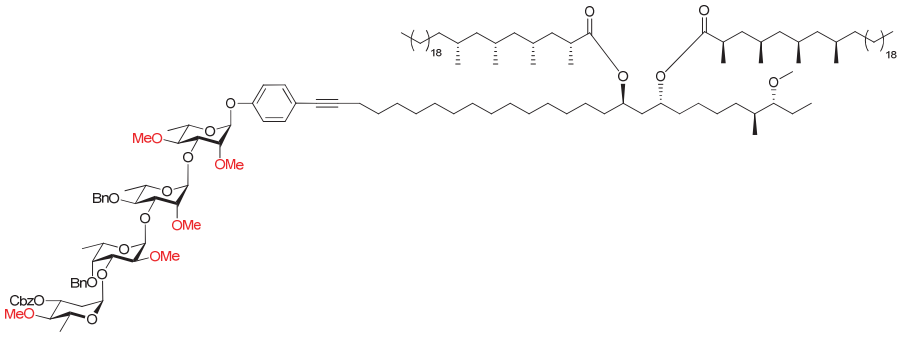
The title compound was synthesized according to general procedure D using **58** (29 mg, 20.3 µmol, 1.0 eq), mycocerosic acid (29 mg, 60.8 µmol, 3.0 eq), DIC (19 µL, 122 µmol, 6.0 eq) and DMAP (22 mg, 183 µmol, 9.0 eq). Column chromatography (*n*-pentane-Et_2O 6:4) yielded the title compound (25 mg, 10.5 µmol, 52%) as a waxy solid. $[\alpha]_D^{25}$ = -41.4 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.39-7.23 (m, 12H, C*H*$_{arom}$); 6.96 (d, 2H, *J* = 8.8 Hz, C*H*$_{arom}$); 5.49 (*s*, 1H, H-1); 5.23 (d, 1H, *J* = 3.2 Hz, H-4''); 5.20-5.11 (m, 6H, H-1', H-1'', H-1''', PhC*H*$_2$, PhC*H*H); 4.97-4.92 (m, 1H, H-3'''); 4.89-4.80 (m, 2H, C*H*$_{Phth}$); 4.56 (d, 1H, *J* = 11.2 Hz, PhCH*H*); 4.33 (q, 1H, *J* = 7.2 Hz, H-5''); 4.18 (dd, 1H, *J* = 3.4, 10.2 Hz, H-3''); 4.06 (dd, 1H, *J* = 2.8, 9.2 Hz, H-3''); 4.06 (dd, 1H, *J* = 2.8, 9.2 Hz, H-3); 4.02 (dd, 1H, *J* = 3.0, 9.2 Hz, H-3'); 3.95-3.85 (m, 2H, H-5', H-5'''); 3.72-3.70 (m, 2H, H-2, H-2'); 3.63-3.46 (m, 15H, H-2'', H-4', H-5, OC*H*$_3$); 3.33 (s, 3H, OC*H*$_3$); 3.27 (s, 3H, OC*H*$_3$); 3.21 (t, 1H, *J* = 9.6 Hz, H-4); 2.89-2.85 (m, 2H, H-4''', C*H*$_{Phth}$); 2.54-2.51 (m, 2H, C*H*$_{Myc}$); 2.37 (t, 2H, *J* = 7.0 Hz, C*H*$_{2,Phth}$); 2.30 (dd, 1H, *J* = 4.4, 12.2 Hz, H-2'''); 2.20 (s, 3H, C*H*$_{3,Ac}$); 1.75-0.81 (m, 206H, H-2''', H-6, H-6', H-6'', H-6''', C*H*$_{Phth}$, C*H*$_{2,Phth}$, C*H*$_{3,Phth}$, C*H*$_{Myc,}$ C*H*$_{2,Myc}$, C*H*$_{3,Myc}$). ^{13}C-APT NMR (101 MHz) δ: 176.2 (*C*O$_{Myc}$); 171.0 (*C*O$_{Ac}$); 155.7 (C$_{q,arom}$); 154.6 (*C*O$_{Cbz}$); 139.2, 135.4 (C$_{q,arom}$); 133.0, 128.7, 128.6, 128.4, 128.3, 127.6, 127.5 (*C*H$_{arom}$); 118.1 (C$_{q,arom}$); 116.2 (*C*H$_{arom}$); 99.9 (C-1''); 98.7 (C-1'''); 98.5 (C-1'); 94.7 (C-1); 89.5 (C$_{q,alkyne}$); 86.8 (*C*H$_{Phth}$); 84.2 (C-4'''); 82.1 (C-4); 81.5 (C-3'); 80.8 (C-2'); 80.1 (C$_{q,alkyne}$); 80.1 (C-2); 79.9 (C-3); 79.5 (C-4'); 78.7 (C-2''); 75.4 (C-3'''); 75.2 (Ph*C*H$_2$); 73.4 (C-4''); 73.2 (C-3''); 70.4 (*C*H$_{Phth}$); 69.7 (Ph*C*H$_2$); 69.0 (C-5); 68.8 (C-5'); 67.7 (C-5'''); 65.5 (C-5''); 61.3, 60.3, 59.1, 58.9, 57.8, 57.5 (O*C*H$_3$); 45.6, 45.4 (*C*H$_{2,Myc}$); 41.1, 38.6 (*C*H$_{2,Phth}$); 37.9 (*C*H$_{Myc}$); 36.7 (*C*H$_{2,Myc}$); 35.7 (C-2'''); 34.9 (*C*H$_{Phth}$); 34.8, 32.8 (*C*H$_{2,Phth}$); 32.1 (*C*H$_{2,Myc}$); 30.2 (*C*H$_{2,Phth}$); 30.1 (*C*H$_{Myc}$); 29.9, 29.9, 29.8, 29.5, 29.4, 29.2, 29.0 (*C*H$_2$); 28.2 (*C*H$_{Myc}$); 27.6 (*C*H$_{2,Phth}$); 27.3 (*C*H$_{Myc}$); 27.1 (*C*H$_{2,Myc}$); 25.7, 25.3 (*C*H$_{2,Phth}$); 22.8 (*C*H$_{2,Myc}$); 22.5 (*C*H$_{2,Phth}$); 21.0 (*C*H$_{3,Ac}$); 20.9, 20.6, 20.5 (*C*H$_{3,Myc}$); 19.6 (*C*H$_{2,Phth}$); 18.6 (*C*H$_{3,Myc}$); 18.3 (C-6'); 18.1 (C-6'''); 17.9 (C-6); 16.5 (C-6''); 14.8 (*C*H$_{3,Phth}$); 14.3 (*C*H$_{3,Myc}$); 10.2 (*C*H$_{3,Phth}$). IR (thin film, cm^{-1}): 1043, 1100, 1175, 1235, 1258, 1378, 1457, 1507, 1736, 2853, 2923. 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 bismycocerosate)phenyl 2,4-di-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(3-*O*-benzyloxycarbonyl-4-*O*-methyl-2,6-dideoxy-α-D-glucopyranosyl)-4-*O*-propionyl-α-L-fucopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (67)



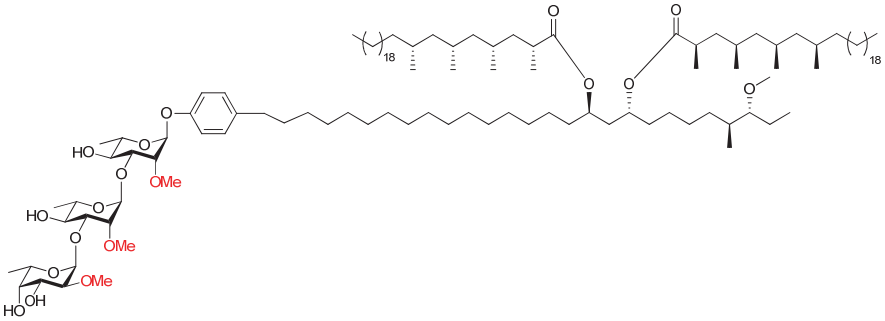
The title compound was synthesized according to general procedure D using **59** (29 mg, 19.6 µmol, 1.0 eq), mycocerosic acid (28 mg, 58.8 µmol, 3.0 eq), DIC (18 µL, 118 µmol, 6.0 eq) and DMAP (22 mg, 176 µmol, 9.0 eq). Column chromatography (*n*-pentane-Et_2O 6:4) yielded the title compound (28 mg, 11.7 µmol, 60%) as a waxy solid. $[\alpha]_D^{25}$ = -41.0 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.38-7.26 (m, 12H, C*H*$_{arom}$); 6.96 (d, 2H, *J* = 8.8 Hz, CH_{arom}); 5.49 (d, 1H, *J* = 1.6 Hz, H-1); 5.24 (d, 1H, *J* = 2.8 Hz, H-4''); 5.24 (dd, 1H, *J* = 2.8, 3.6 Hz, H-4''); 5.20-5.13 (m, 5H, H-1', H-1'', PhC*H*$_2$, PhC*H*H); 5.10 (d, 1H, *J* = 2.8 Hz, H-1'''); 4.96-4.83 (m, 3H, H-3''', C*H*$_{Phth}$); 4.56 (d, 1H, *J* = 11.2 Hz, PhCH*H*); 4.33 (q, 1H, *J* = 7.6 Hz, H-5''); 4.18 (dd, 1H, *J* = 3.4, 10.2 Hz, H-3''); 4.08-4.00 (m, 2H, H-3, H-3'); 3.95-3.85 (m, 2H, H-5', H-5'''); 3.72-3.69 (m, 2H, H-2, H-2'); 3.63-3.59 (m, 1H, H-5); 3.54-3.45 (m, 14H, H-2'', H-4', OC*H*$_3$); 3.33 (s, 3H, OC*H*$_3$); 3.27 (s, 3H, OC*H*$_3$); 3.21 (t, 1H, *J* = 9.6 Hz, H-4); 2.89-2.84 (m, 2H, H-4''', C*H*$_{Phth}$); 2.54-2.42 (m, 4H, C*H*$_{Myc}$, COC*H*$_2$CH$_3$); 2.35 (t, 2H, *J* = 7.2 Hz, C*H*$_{2,Phth}$); 2.29 (dd, 1H, *J* = 5.2, 11.6 Hz, H-2'''); 1.75-0.81 (m, 193H, H-2''', H-6, H-6', H-6'', H-6''', COCH$_2$C*H*$_3$, C*H*$_{Phth}$, C*H*$_{2,Phth}$, C*H*$_{3,Phth}$, C*H*$_{Myc}$, C*H*$_{2,Myc}$, C*H*$_{3,Myc}$). ^{13}C-APT NMR (101 MHz) δ: 176.1 (*C*O$_{Myc}$); 174.4 (*C*O$_{propionyl}$); 155.7 (C$_{q,arom}$); 154.6 (*C*O$_{Cbz}$); 139.2, 135.4 (C$_{q,arom}$); 133.0, 128.7, 128.6, 128.4, 128.3, 128.3, 127.6, 127.5 (*C*H$_{arom}$); 118.1 (C$_{q,arom}$); 116.2 (*C*H$_{arom}$); 99.9 (C-1''); 98.7 (C-1'''); 98.5 (C-1'); 94.8 (C-1); 89.5 (C$_{q,alkyne}$); 86.8 (*C*H$_{Phth}$); 84.1 (C-4'''); 82.1 (C-4); 81.5 (C-3'); 80.8 (C-2'); 80.2 (C$_{q,alkyne}$); 80.1 (C-2); 79.8 (C-3); 79.5 (C-4'); 78.7 (C-2''); 75.3 (C-3'''); 75.2 (Ph*C*H$_2$); 73.5 (C-3''); 73.1 (C-4''); 70.4 (*C*H$_{Phth}$); 69.7 (Ph*C*H$_2$); 69.0 (C-5); 68.8 (C-5'); 67.6 (C-5'''); 65.6 (C-5''); 61.3, 60.1, 59.1, 59.0, 57.9, 57.5 (O*C*H$_3$); 45.6, 45.4 (*C*H$_{2,Myc}$); 41.1, 38.6 (*C*H$_{2,Phth}$); 37.9 (*C*H$_{Myc}$); 36.8 (*C*H$_{2,Myc}$); 35.8 (C-2'''); 34.9 (*C*H$_{Phth}$); 34.8, 32.8 (*C*H$_{2,Phth}$); 32.1 (*C*H$_{2,Myc}$); 30.2 (*C*H$_{2,Phth}$); 30.1 (*C*H$_{Myc}$); 29.9, 29.9, 29.8, 29.8, 29.5, 29.4, 29.2, 29.0 (*C*H$_2$); 28.2 (*C*H$_{Myc}$); 27.9 (*C*H$_{2,Propionyl}$); 27.6 (*C*H$_{2,Phth}$); 27.3 (*C*H$_{Myc}$); 27.1 (*C*H$_{2,Myc}$); 25.7, 25.3 (*C*H$_{2,Phth}$); 22.8 (*C*H$_{2,Myc}$); 22.5 (*C*H$_{2,Phth}$); 20.9, 20.6, 20.6, 20.5 (*C*H$_{3,Myc}$); 19.6 (*C*H$_{2,Phth}$); 18.6 (*C*H$_{3,Myc}$);18.3 (C-6'); 18.1 (C-6'''); 17.9 (C-6); 16.5 (C-6''); 14.8 (*C*H$_{3,Phth}$); 14.3 (*C*H$_{3,Myc}$); 10.3 (*C*H$_{3,Phth}$); 9.7 (*C*H$_{3,Propionyl}$). IR (thin film, cm^{-1}): 1043, 1100, 1129, 1175, 1256, 1379, 1464, 1507, 1736, 2853, 2923. 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 bismycocerosate)phenyl 2,4-di-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(3-*O*-benzyloxycarbonyl-4-*O*-methyl-2,6-dideoxy-α-D-glucopyranosyl)-4-*O*-benzyl-α-L-fucopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (68)



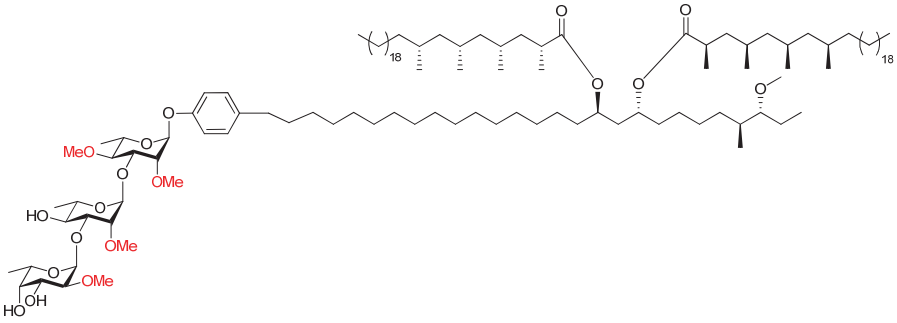
The title compound was synthesized according to general procedure D using **60** (37 mg, 24.3 µmol, 1.0 eq), mycocerosic acid (35 mg, 72.9 µmol, 3.0 eq), DIC (23 µL, 146 µmol, 6.0 eq) and DMAP (27 mg, 219 µmol, 9.0 eq). Column chromatography (*n*-pentane-Et_2O 6:4) yielded the title compound (38 mg, 15.3 µmol, 63%) as a waxy solid. $[\alpha]_D^{25}$ = -35.2 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.45-7.26 (m, 17H, C*H*$_{arom}$); 6.95 (d, 2H, *J* = 9.2 Hz, C*H*$_{arom}$); 5.48 (d, 1H, *J* = 1.6 Hz, H-1); 5.24 (d, 1H, *J* = 2.4 Hz, H-1'''); 5.18-5.11 (m, 6H, H-1', H-1'', H-3''', PhC*H*$_2$, PhC*H*H); 5.06 (d, 1H, *J* = 11.6 Hz, PhC*H*H); 4.89-4.80 (m, 2H, C*H*$_{Phth}$); 4.64 (d, 1H, *J* = 11.6 Hz, PhCH*H*); 4.57 (d, 1H, *J* = 11.6 Hz, PhCH*H*); 4.23-4.17 (m, 2H, H-3'', H-5''); 4.06-3.86 (m, 4H, H-3, H-3', H-5', H-5'''); 3.75-3.71 (m, 3H, H-2, H-2', H-2''); 3.62-3.57 (m, 2H, H-4'', H-5); 3.52-3.42 (m, 13H, H-4', OC*H*$_3$); 3.33 (s, 3H, OC*H*$_3$); 3.24 (s, 3H, OC*H*$_3$); 3.20 (t, 1H, *J* = 9.6 Hz, H-4); 2.93 (t, 1H, *J* = 9.2 Hz, H-4'''); 2.88-2.84 (m, 1H, C*H*$_{Phth}$); 2.54-2.51 (m, 2H, C*H*$_{Myc}$); 2.42-2.36 (m, 3H, H-2''', C*H*$_{2,Phth}$); 1.75-0.81 (m, 206H, H-2''', H-6, H-6', H-6'', H-6''', C*H*$_{Phth}$, C*H*$_{2,Phth}$, C*H*$_{3,Phth}$, C*H*$_{Myc,}$ C*H*$_{2,Myc}$, C*H*$_{3,Myc}$). ^{13}C-APT NMR (101 MHz) δ: 176.2, 176.1 (*C*O$_{Myc}$); 155.7 (C$_{q,arom}$); 154.5 (*C*O$_{Cbz}$); 139.4, 138.6, 135.4 (C$_{q,arom}$); 128.7, 128.7, 128.5, 128.4, 128.3, 127.7, 127.6, 127.4 (*C*H$_{arom}$); 118.1 (C$_{q,arom}$); 116.2 (*C*H$_{arom}$); 99.9 (C-1''); 98.6 (C-1'); 98.4 (C-1'''); 94.8 (C-1); 89.5 (C$_{q,alkyne}$); 86.8 (*C*H$_{Phth}$); 84.5 (C-4'''); 81.9 (C-4); 81.4 (C-3'); 80.9 (C-2'); 80.2 (C$_{q,alkyne}$); 80.1 (C-3); 80.1 (C-2); 79.9 (C-4''); 79.4 (C-4'); 79.2 (C-2''); 76.0 (C-3'''); 75.7 (C-3''); 75.4, 75.1 (Ph*C*H$_2$); 70.4 (*C*H$_{Phth}$); 69.8 (Ph*C*H$_2$); 69.0 (C-5); 68.8 (C-5'); 68.0 (C-5'''); 67.1 (C-5''); 61.4, 60.9, 59.0, 58.6, 57.9; 57.5 (O*C*H$_3$); 45.6, 45.4 (*C*H$_{2,Myc}$); 41.1, 38.6 (*C*H$_{2,Phth}$); 37.9 (*C*H$_{Myc}$); 36.8 (*C*H$_{2,Myc}$); 35.6 (C-2'''); 34.9 (*C*H$_{Phth}$); 34.8, 32.8 (*C*H$_{2,Phth}$); 32.1 (*C*H$_{2,Myc}$); 30.2 (*C*H$_{2,Phth}$); 30.1 (*C*H$_{Myc}$); 29.9, 29.9, 29.8, 29.8, 29.8, 29.7, 29.5, 29.4, 29.2, 29.0 (*C*H$_2$); 28.2 (*C*H$_{Myc}$); 27.6 (*C*H$_{2,Phth}$); 27.3 (*C*H$_{Myc}$); 27.1 (*C*H$_{2,Myc}$); 25.7, 25.3 (*C*H$_{2,Phth}$); 22.8 (*C*H$_{2,Myc}$); 22.5 (*C*H$_{2,Phth}$); 20.9, 20.6, 20.6, 20.5 (*C*H$_{3,Myc}$); 19.6 (*C*H$_{2,Phth}$); 18.6 (*C*H$_{3,Myc}$); 18.4 (C-6'); 18.3 (C-6'''); 17.9 (C-6); 17.1 (C-6''); 14.8 (*C*H$_{3,Phth}$); 14.3 (*C*H$_{3,Myc}$); 10.2 (*C*H$_{3,Phth}$). IR (thin film, cm^{-1}): 1040, 1100, 1128, 1175, 1256, 1507, 1734, 2853, 2923. 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-9,11-diyl bismycocerosate)phenyl 2-*O*-methyl-3-*O*-(2-*O*-methyl-3-O-(2-*O*-methyl-α-L-fucopyranosyl)-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (69)



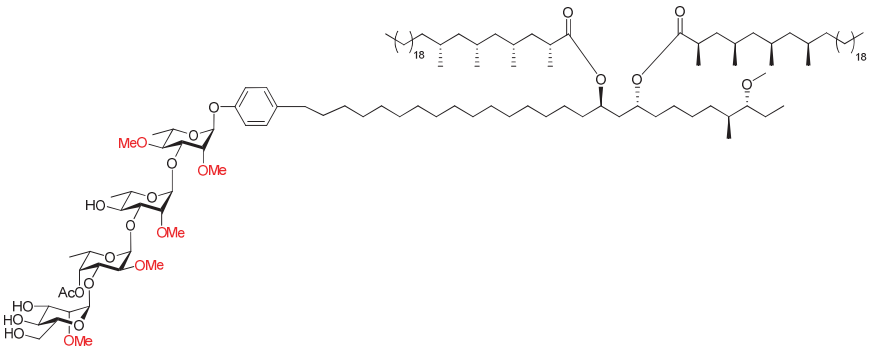
Compound **61** (28 mg, 12.1 µmol, 1.0 eq) was hydrogenated using general procedure E to give the title compound (20 mg, 10.2 µmol, 84%) as a pale oil. $[\alpha]_D^{25}$ = -42.4 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.10 (d, 2H, *J* = 8.8 Hz, C*H*$_{arom}$); 6.99 (d, 2H, *J* = 8.8 Hz, C*H*$_{arom}$); 5.51 (d, 1H, *J* = 1.2 Hz, H-1); 5.21 (d, 1H, *J* = 1.2 Hz, H-1'); 5.15 (d, 1H, *J* = 3.6 Hz, H-1''); 4.84 (quint, 2H, *J* = 6.4 Hz, C*H*$_{Phth}$); 4.22 (q, 1H, *J* = 6.4 Hz, H-5''); 4.08-4.03 (m, 2H, H-3, H-3''); 3.94-3.87 (m, 1H, H-5'); 3.83 (d, 1H, *J* = 2.4 Hz, H-4''); 3.81-3.75 (m, 4H, H-2, H-3', H-5', O*H*); 3.72-3.63 (m, 3H, H-2', H-4, H-4'); 3.55-3.44 (m, 10H, H-2'', OCH_3); 3.33 (s, 3H, OCH_3); 2.88-2.84 (m, 1H, C*H*$_{Phth}$); 2.57-2.50 (m, 5H, C*H*$_{2,Phth}$, C*H*$_{Myc}$, O*H*); 1.77-0.80 (m, 222H, H-6, H-6', H-6'', C*H*$_{Phth}$, C*H*$_{2,Phth}$, C*H*$_{3,Phth}$, C*H*$_{Myc,}$ C*H*$_{2,Myc}$, C*H*$_{3,Myc}$). ^{13}C-APT NMR (101 MHz) δ: 176.2, 176.2 (*C*O$_{Myc}$); 154.7, 137.1 (C$_{q,arom}$); 129.5, 116.2 (*C*H$_{arom}$); 99.9 (C-1''); 99.3 (C-1'); 95.0 (C-1); 86.8 (*C*H$_{Phth}$); 83.1 (C-3'); 80.3 (C-2 and C-2'); 80.3 (C-3); 79.5 (C-2''); 72.0 (C-4''); 71.7 (C-4'); 71.6 (C-4); 70.4 (*C*H$_{Phth}$); 69.9 (C-3''); 69.2 (C-5); 69.1 (C-5'); 66.7 (C-5''); 59.4, 58.7, 58.7, 57.5 (O*C*H$_3$); 45.6, 45.4 (*C*H$_{2,Myc}$); 41.1, 38.6 (*C*H$_{2,Phth}$); 37.9 (*C*H$_{Myc}$); 36.8, 35.3 (*C*H$_{2,Myc}$); 34.9 (*C*H$_{Phth}$); 34.8, 32.8 (*C*H$_{2,Phth}$); 32.1 (*C*H$_{2,Myc}$); 31.9, 30.2 (*C*H$_{2,Phth}$); 30.1 (*C*H$_{Myc}$); 29.9, 29.9, 29.8, 29.7, 29.5 (*C*H$_2$); 28.2 (*C*H$_{Myc}$); 27.6 (*C*H$_{2,Phth}$); 27.3 (*C*H$_{Myc}$); 27.1 (*C*H$_{2,Myc}$); 25.7, 25.3 (*C*H$_{2,Phth}$); 22.8 (*C*H$_{2,Myc}$); 22.5 (*C*H$_{2,Phth}$); 20.9, 20.6, 20.5, 20.5, 18.6 (*C*H$_{3,Myc}$); 18.2 (C-6) 17.9 (C-6'); 16.5 (C-6''); 14.8 (*C*H$_{3,Phth}$); 14.3 (*C*H$_{3,Myc}$); 10.3 (*C*H$_{3,Phth}$). IR (thin film, cm^{-1}): 1036, 1098, 1129, 1173, 1378, 1464, 1508, 1734, 2853, 2923, 3427. HRMS calculated for $C_{120}H_{225}O_{18}$ 1955.67196 $[M+H]^+$; found 1955.67197.

4-((3*R*,4*S*,9*R*,11*R*)-3-methoxy-4-methylheptacos-9,11-diyl bismycocerosate)phenyl 2,4-di-*O*-methyl-3-*O*-(2-*O*-methyl-3-O-(2-*O*-methyl-α-L-fucopyranosyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (70)



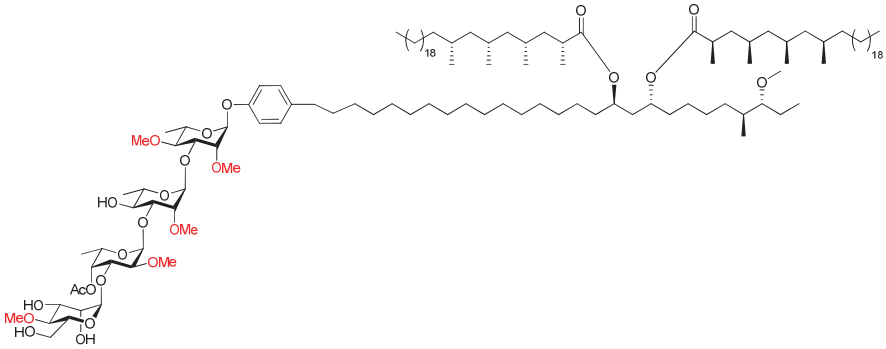
Compound **62** (28 mg, 12.5 µmol, 1.0 eq) was hydrogenated using general procedure E to give the title compound (15 mg, 7.6 µmol, 61%) as a pale oil. $[\alpha]_D^{25}$ = -55.6 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.09 (d, 2H, *J* = 8.4 Hz, C*H*$_{arom}$); 6.97 (d, 2H, *J* = 8.8 Hz, C*H*$_{arom}$); 5.48 (d, 1H, *J* = 1.2 Hz, H-1); 5.19 (d, 1H, *J* = 1.2 Hz, H-1'); 5.14 (d, 1H, *J* = 4.0 Hz, H-1''); 4.84 (quint, 2H, *J* = 6.4 Hz, C*H*$_{Phth}$); 4.25 (q, 1H, *J* = 6.4 Hz, H-5''); 4.12 (dd, 1H, *J*= 3.4, 9.8 Hz, H-3); 4.06 (dd, 1H, *J* = 3.2, 10.0 Hz, H-3''); 3.91-3.86 (m, 1H, H-5'); 3.83 (d, 1H, *J* = 2.8 Hz, H-4''); 3.78 (dd, 1H, *J* = 3.2, 9.6 Hz, H-3'); 3.73-3.61 (m, 3H, H-2, H-2', H-4', H-5); 3.56-3.45 (m, 13H, H-2'', OC*H*$_3$); 3.33 (s, 3H, OC*H*$_3$); 3.23 (t, 1H, *J* = 9.6 Hz, H-4); 2.88-2.84 (m, 1H, C*H*$_{Phth}$); 2.72 (bs, 1H, O*H*); 2.56-2.48 (m, 4H, C*H*$_{2,Phth}$, C*H*$_{Myc}$); 2.41 (bs, 1H, O*H*); 1.77-0.81 (m, 221H, H-6, H-6', H-6'', C*H*$_{Phth}$, C*H*$_{2,Phth}$, C*H*$_{3,Phth}$, C*H*$_{Myc,}$ C*H*$_{2,Myc}$, C*H*$_{3,Myc}$). ^{13}C-APT NMR (101 MHz) δ: 176.1 (*C*O$_{Myc}$); 154.6, 137.0 (C$_{q,arom}$); 129.4, 116.2 (*C*H$_{arom}$); 99.8 (C-1''); 99.4 (C-1'); 95.1 (C-1); 86.8 (*C*H$_{Phth}$); 83.0 (C-3'); 82.4 (C-4); 80.6, 80.5 (C-2 and C-2'); 79.5 (C-2''); 79.3 (C-3) 72.0 (C-4''); 71.7 (C-4'); 70.4 (*C*H$_{Phth}$); 69.9 (C-3''); 69.1 (C-5); 68.9 (C-5'); 66.5 (C-5''); 61.2, 59.4, 58.7, 58.7, 57.5 (O*C*H$_3$); 45.6, 45.4 (*C*H$_{2,Myc}$); 41.1, 38.6 (*C*H$_{2,Phth}$); 37.9 (*C*H$_{Myc}$); 36.8, 35.3 (*C*H$_{2,Myc}$); 34.9 (*C*H$_{Phth}$); 34.8, 32.8 (*C*H$_{2,Phth}$); 32.1 (*C*H$_{2,Myc}$); 31.9, 30.2 (*C*H$_{2,Phth}$); 30.1 (*C*H$_{Myc}$); 29.9, 29.9, 29.8, 29.7, 29.5 (*C*H$_2$); 28.2 (*C*H$_{Myc}$); 27.6 (*C*H$_{2,Phth}$); 27.3 (*C*H$_{Myc}$); 27.1 (*C*H$_{2,Myc}$); 25.7, 25.3 (*C*H$_{2,Phth}$); 22.8 (*C*H$_{2,Myc}$); 22.5 (*C*H$_{2,Phth}$); 20.9, 20.6, 20.5, 20.5, 18.6 (*C*H$_{3,Myc}$); 18.0 (C-6) 18.0 (C-6'); 16.5 (C-6''); 14.8 (*C*H$_{3,Phth}$); 14.3 (*C*H$_{3,Myc}$); 10.3 (*C*H$_{3,Phth}$). IR (thin film, cm^{-1}): 1100, 1132, 1173, 1229, 1378, 1461, 1510, 1734, 2853, 2923, 3421. HRMS calculated for $C_{121}H_{227}O_{18}Na$ 1969.68761 $[M+H]^+$; found 1969.68743.

4-((3*R*,4*S*,9*R*,11*R*)-3-methoxy-4-methylheptacos-9,11-diyl bismycocerosate)phenyl 2,4-di-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(2-*O*-methyl-α-D-mannopyranosyl)-4-*O*-acetyl-α-L-fucopyranosyl)-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (71)



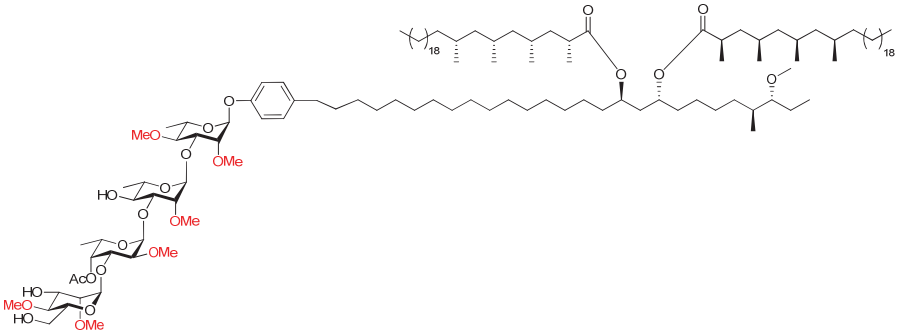
Compound **63** (22 mg, 8.2 µmol, 1.0 eq) was hydrogenated using general procedure E to give the title compound (16 mg, 7.3 µmol, 89%) as a pale oil. $[\alpha]_D^{25}$ = -37.8 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (500 MHz) δ: 7.09 (d, 2H, *J* = 8.5 Hz, C*H*$_{arom}$); 6.97 (d, 2H, *J* = 9.0 Hz, C*H*$_{arom}$); 5.47 (d, 1H, *J* = 1.5 Hz, H-1); 5.26 (d, 1H, *J* = 2.5 Hz, H-4''); 5.21-5.20 (m, 2H, H-1', H-1'''); 5.12 (d, 1H, *J* = 3.5 Hz, H-1''); 4.84 (quint, 2H, *J* = 6.3 Hz, C*H*$_{Phth}$); 4.31 (q, 1H, *J* = 6.5 Hz, H-5''); 4.22 (dd, 1H, *J* = 3.5, 10.0 Hz, H-3'''); 4.12 (dd, 1H, *J* = 3.3, 9.8 Hz, H-3); 3.92-3.85 (m, 2H, H-5', H-6'''); 3.83-3.77 (m, 2H, H-3', H-6'''); 3.73-3.44 (m, 24H, H-2, H-2', H-2'', H-2''', H-3''', H-4', H-4''', H-5, H-5''', OC*H*$_3$); 3.33 (s, 3H, OC*H*$_3$); 3.27 (t, 1H, *J* = 9.5 Hz, H-4); 2.87-2.84 (m, 1H, C*H*$_{Phth}$); 2.56-2.48 (m, 4H, C*H*$_{2,Phth}$, C*H*$_{Myc}$); 2.17 (s, 3H, C*H*$_{3,Ac}$); 1.76-0.81 (m, 185H, H-6, H-6', H-6'', C*H*$_{Phth}$, C*H*$_{2,Phth}$, C*H*$_{3,Phth}$, C*H*$_{Myc,}$ C*H*$_{2,Myc}$, C*H*$_{3,Myc}$). ^{13}C-APT NMR (125 MHz) δ: 176.2, 176.1 (*C*O$_{Myc}$); 170.9 (*C*O$_{Ac}$); 154.6, 137.0 (C$_{q,arom}$); 129.5, 116.3 (*C*H$_{arom}$); 100.5 (C-1''); 99.3 (C-1'); 98.3 (C-1'''); 95.1 (C-1); 86.8 (*C*H$_{Phth}$); 83.5 (C-3'); 82.4 (C-4); 80.7 (C-2'); 80.5 (C-2); 80.2 (C-2'''); 79.7 (C-2''); 79.2 (C-3); 74.3 (C-3''); 73.4 (C-4''); 72.5 (C-5'''); 71.7 (C-4'); 71.4 (C-3'''); 70.4 (*C*H$_{Phth}$); 69.4 (C-4'''); 69.0 (C-5'); 68.9 (C-5); 65.9 (C-5''); 62.8 (C-6'''); 61.2, 59.8, 59.1, 58.9, 58.7, 57.5 (O*C*H$_3$); 45.6, 45.4 (*C*H$_{2,Myc}$); 41.1, 38.6 (*C*H$_{2,Phth}$); 37.9, 37.9 (*C*H$_{Myc}$); 36.8, 35.3 (*C*H$_{2,Myc}$); 35.0 (*C*H$_{Phth}$); 34.8, 32.8 (*C*H$_{2,Phth}$); 32.1 (*C*H$_{2,Myc}$); 31.9, 30.2 (*C*H$_{2,Phth}$); 30.1 (*C*H$_{Myc}$); 29.9, 29.9, 29.8, 29.7, 29.5 (*C*H$_2$); 28.2 (*C*H$_{Myc}$); 27.6 (*C*H$_{2,Phth}$); 27.4 (*C*H$_{Myc}$); 27.1 (*C*H$_{2,Myc}$); 25.7, 25.3 (*C*H$_{2,Phth}$); 22.8 (*C*H$_{2,Myc}$); 22.5 (*C*H$_{2,Phth}$); 21.0 (*C*H$_{3,Ac}$); 20.9, 20.6, 20.6, 20.5, 18.6 (*C*H$_{3,Myc}$); 18.0 (C-6) 18.0 (C-6'); 16.4 (C-6''); 14.9 (*C*H$_{3,Phth}$); 14.3 (*C*H$_{3,Myc}$); 10.3 (*C*H$_{3,Phth}$). IR (thin film, cm^{-1}): 1040, 1073, 1100, 1135, 1173, 1233, 1378, 1464, 1510, 1734, 2853, 2923, 3429. HRMS calculated for $C_{130}H_{240}O_{24}$ 2187.76665 $[M+H]^+$; found 2187.76668.

4-((3*R*,4*S*,9*R*,11*R*)-3-methoxy-4-methylheptacos-9,11-diyl bismycocerosate)phenyl 2,4-di-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(4-*O*-methyl-α-D-mannopyranosyl)-4-*O*-acetyl-α-L-fucopyranosyl)-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (72)



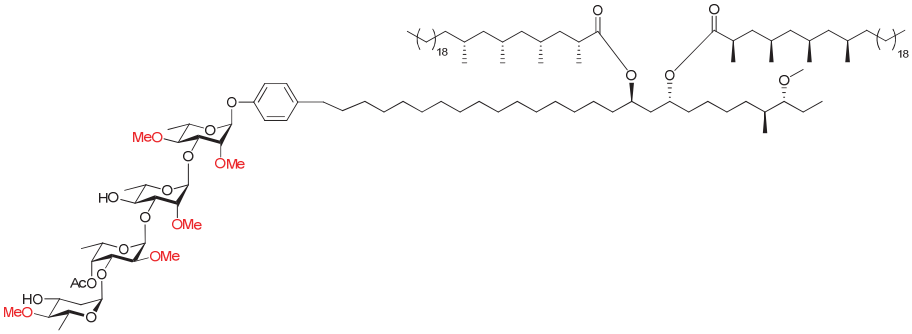
Compound **64** (23 mg, 8.7 µmol, 1.0 eq) was hydrogenated using general procedure E to give the title compound (15 mg, 6.9 µmol, 78%) as a pale oil. $[\alpha]_D^{25}$ = -37.2 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (500 MHz) δ: 7.09 (d, 2H, *J* = 9.0 Hz, C*H*$_{arom}$); 6.97 (d, 2H, *J* = 8.5 Hz, C*H*$_{arom}$); 5.47 (d, 1H, *J* = 1.5 Hz, H-1); 5.23 (d, 1H, *J* = 3.0 Hz, H-4''); 5.20 (s, 1H, H-1'); 5.13-5.12 (m, 2H, H-1'', H-1'''); 4.84 (quint, 2H, *J* = 6.5 Hz, C*H*$_{Phth}$); 4.29 (q, 1H, *J* = 6.6 Hz, H-5''); 4.21 (dd, 1H, *J* = 3.5, 10.0 Hz, H-3''); 4.11 (dd, 1H, *J* = 3.3, 9.8 Hz, H-3); 4.00-3.95 (m, 2H, H-2''', O*H*); 3.91-3.85 (m, 2H, H-5', H-6'''); 3.79-3.77 (m, 3H, H-3', H-3''', H-6'''); 3.71-3.62 (m, 5H, H-2, H-2', H-4, H-5, H-5'''); 3.59-3.46 (m, 14H, H-2'', H-4''', OC*H*$_3$); 3.33 (s, 3H, OC*H*$_3$); 3.22 (t, 1H, *J* = 9.8 Hz, H-4); 3.04 (bs 1H, O*H*); 2.87-2.84 (m, 1H, C*H*$_{Phth}$); 2.56-2.50 (4H, C*H*$_{2,Phth}$, C*H*$_{Myc}$); 2.15 (s, 3H, C*H*$_{3,Ac}$); 1.76-0.81 (m, 186H, H-6, H-6', H-6'', C*H*$_{Phth}$, C*H*$_{2,Phth}$, C*H*$_{3,Phth}$, C*H*$_{Myc,}$ C*H*$_{2,Myc}$, C*H*$_{3,Myc}$). ^{13}C-APT NMR (125 MHz) δ: 176.1 (*C*O$_{Myc}$); 170.8 (*C*O$_{Ac}$); 154.6, 137.0 (C$_{q,arom}$); 129.5, 116.3 (*C*H$_{arom}$); 101.5 (C-1''); 100.3 (C-1'''); 99.1 (C-1'); 95.1 (C-1); 86.8 (*C*H$_{Phth}$); 83.3 (C-3'); 82.4 (C-4); 80.6 (C-2); 80.5 (C-2'); 79.5 (C-2''); 79.3 (C-3); 77.0 (C-4'''); 74.0 (C-3''); 73.3 (C-4''); 72.4 (C-5'''); 71.5 (C-4'); 71.2 (C-3'''); 71.1 (C-2'''); 70.4 (*C*H$_{Phth}$); 69.4 (C-4'''); 69.1 (C-5'); 68.8 (C-5); 65.9 (C-5''); 62.0 (C-6'''); 61.2, 60.6, 59.6, 59.1, 58.4, 57.5 (O*C*H$_3$); 45.7, 45.4 (*C*H$_{2,Myc}$); 41.1, 38.6 (*C*H$_{2,Phth}$); 37.9, 37.9 (*C*H$_{Myc}$); 36.8, 35.3 (*C*H$_{2,Myc}$); 35.0 (*C*H$_{Phth}$); 34.8, 32.8 (*C*H$_{2,Phth}$); 32.1 (*C*H$_{2,Myc}$); 31.9, 30.2 (*C*H$_{2,Phth}$); 30.1 (*C*H$_{Myc}$); 29.9, 29.9, 29.8, 29.7, 29.5 (*C*H$_2$); 28.2 (*C*H$_{Myc}$); 27.6 (*C*H$_{2,Phth}$); 27.4 (*C*H$_{Myc}$); 27.1 (*C*H$_{2,Myc}$); 25.7, 25.3 (*C*H$_{2,Phth}$); 22.8 (*C*H$_{2,Myc}$); 22.5 (*C*H$_{2,Phth}$); 21.0 (*C*H$_{3,Ac}$); 20.9, 20.6, 20.6, 20.5, 18.6 (*C*H$_{3,Myc}$); 18.1 (C-6) 18.0 (C-6'); 16.4 (C-6''); 14.9 (*C*H$_{3,Phth}$); 14.3 (*C*H$_{3,Myc}$); 10.3 (*C*H$_{3,Phth}$). IR (thin film, cm^{-1}): 1099, 1129, 1175, 1235, 1378, 1461, 1510, 1736, 2853, 2923, 3410. HRMS calculated for $C_{130}H_{240}O_{24}$ 2187.76665 $[M+H]^+$; found 2187.76633.

4-((3*R*,4*S*,9*R*,11*R*)-3-methoxy-4-methylheptacos-9,11-diyl bismycocerosate)phenyl 2,4-di-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(2,4-di-*O*-methyl-α-D-mannopyranosyl)-4-*O*-acetyl-α-L-fucopyranosyl)-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (73)



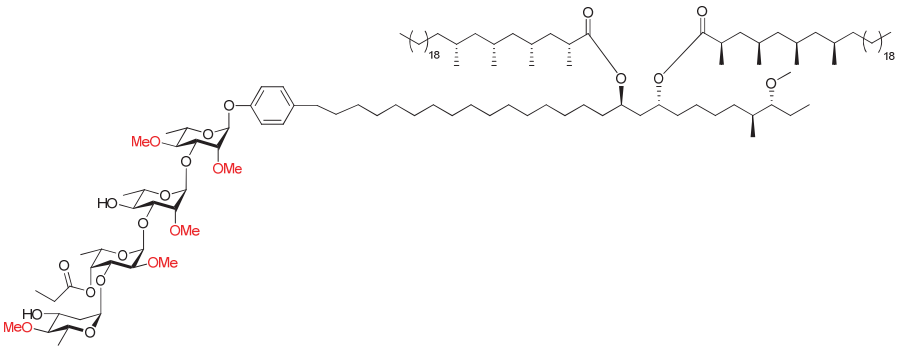
Compound **65** (13 mg, 5.2 µmol, 1.0 eq) was hydrogenated using general procedure E to give the title compound (10 mg, 4.5 µmol, 88%) as a pale oil. $[\alpha]_D^{25}$ = -41.0 ° (c = 0.5, $CHCl_3$). ^{1}H-NMR (500 MHz) δ: 7.09 (d, 2H, *J* = 9.0 Hz, C*H*$_{arom}$); 6.97 (d, 2H, *J* = 8.5 Hz, C*H*$_{arom}$); 5.47 (d, 1H, *J* = 1.5 Hz, H-1); 5.24 (d, 1H, *J* = 2.5 Hz, H-4''); 5.19 (d, 1H, *J* = 1.0 Hz, H-1'''); 5.16 (d, 1H, *J* = 1.5 Hz, H-1'); 5.12 (d, 1H, *J* = 4.0 Hz, H-1''); 4.84 (quint, 2H, *J* = 6.5 Hz, C*H*$_{Phth}$); 4.29 (q, 1H, *J* = 6.8 Hz, H-5''); 4.19 (dd, 1H, *J* = 3.5, 10.0 Hz, H-3''); 4.12 (dd, 1H, *J* = 3.0, 9.5 Hz, H-3); 3.99-3.86 (m, 2H, H-5', H-6''');; 3.91-3.85 (m, 2H, H-5', H-6'''); 3.79-3.61 (m, 8H, H-2, H-2', H-3', H-3''', H-4', H-5, H-5''', H-6'''); 3.59-3.52 (m, 16H, H-2'', OC*H*$_3$); 3.48-3.47 (m, 4H, H-2''', OC*H*$_3$); 3.23 (t, 1H, *J* = 9.5 Hz, H-4); 2.87-2.84 (m, 1H, C*H*$_{Phth}$); 2.56-2.50 (4H, C*H*$_{2,Phth}$, C*H*$_{Myc}$); 2.39 (bs, 1H, OH); 2.22 (t, 1H, *J* = 7.8 Hz, O*H*); 2.15 (s, 3H, C*H*$_{3,Ac}$); 1.75-0.81 (m, 224H, H-6, H-6', H-6'', C*H*$_{Phth}$, C*H*$_{2,Phth}$, C*H*$_{3,Phth}$, C*H*$_{Myc}$, C*H*$_{2,Myc}$, C*H*$_{3,Myc}$). ^{13}C-APT NMR (125 MHz) δ: 176.1 (*C*O$_{Myc}$); 170.7 (*C*O$_{Ac}$); 154.6, 137.0 (C$_{q,arom}$); 129.5, 116.3 (*C*H$_{arom}$); 100.6 (C-1''); 99.4 (C-1'); 98.4 (C-1'''); 95.1 (C-1); 86.8 (*C*H$_{Phth}$); 83.5 (C-3'); 82.4 (C-4); 80.7 (C-2'); 80.7 (C-2'''); 80.5 (C-2); 79.7 (C-2''); 79.2 (C-3); 78.0 (C-4'''); 74.6 (C-3''); 73.2 (C-4''); 72.2 (C-3'''); 71.8 (C-4'); 71.1 (C-5'''); 70.4 (*C*H$_{Phth}$); 69.4 (C-4'''); 69.0 (C-5'); 68.9 (C-5); 66.0 (C-5''); 62.4 (C-6'''); 61.2, 60.6, 59.8, 59.1, 58.9, 58.7, 57.5 (O*C*H$_3$); 45.7, 45.4 (*C*H$_{2,Myc}$); 41.1, 38.6 (*C*H$_{2,Phth}$); 37.9, 37.9 (*C*H$_{Myc}$); 36.8, 35.3 (*C*H$_{2,Myc}$); 35.0 (*C*H$_{Phth}$); 34.9, 32.8 (*C*H$_{2,Phth}$); 32.1 (*C*H$_{2,Myc}$); 31.9, 30.2 (*C*H$_{2,Phth}$); 30.1 (*C*H$_{Myc}$); 29.9, 29.9, 29.7, 29.5 (*C*H$_2$); 28.2 (*C*H$_{Myc}$); 27.6 (*C*H$_{2,Phth}$); 27.4 (*C*H$_{Myc}$); 27.1 (*C*H$_{2,Myc}$); 25.7, 25.3 (*C*H$_{2,Phth}$); 22.8 (*C*H$_{2,Myc}$); 22.5 (*C*H$_{2,Phth}$); 21.0 (*C*H$_{3,Ac}$); 20.9, 20.6, 20.5, 18.6 (*C*H$_{3,Myc}$); 18.0 (C-6) 18.0 (C-6'); 16.4 (C-6''); 14.9 (*C*H$_{3,Phth}$); 14.3 (*C*H$_{3,Myc}$); 10.3 (*C*H$_{3,Phth}$). IR (thin film, cm^{-1}): 1096, 1173, 1233, 1378, 1464, 1510, 1734, 2853, 2923, 3424. HRMS calculated for $C_{131}H_{243}O_{24}$ 2201.78230 $[M+H]^+$; found 2201.78198.

4-((3*R*,4*S*,9*R*,11*R*)-3-methoxy-4-methylheptacos-9,11-diyl bismycocerosate)phenyl 2,4-di-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(4-*O*-methyl-2,6-dideoxy-α-D-glucopyranosyl)-4-*O*-acetyl-α-L-fucopyranosyl)-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (74)



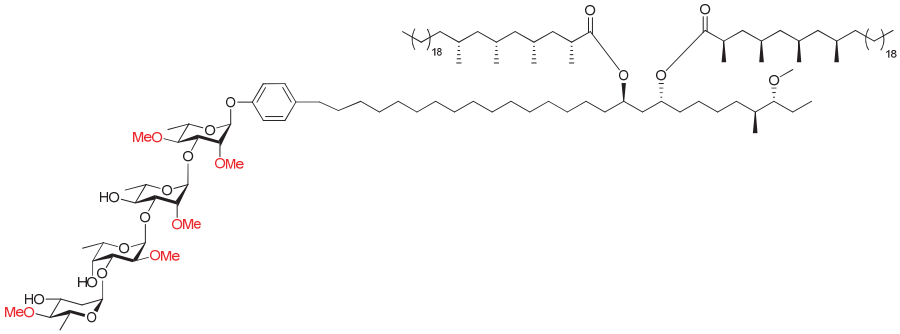
Compound **66** (18 mg, 7.6 μmol, 1.0 eq) was hydrogenated using general procedure E to give the title compound (14 mg, 6.5 μmol, 86%) as a pale oil. $[\alpha]_D^{25}$ = -38.8 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (500 MHz) δ: 7.09 (d, 2H, *J* = 8.5 Hz, C*H*$_{arom}$); 6.97 (d, 2H, *J* = 8.5 Hz, C*H*$_{arom}$); 5.47 (d, 1H, *J* = 2.0 Hz, H-1); 5.18-5.17 (m, 2H, H-1', H-4''); 5.09-5.08 (m, 2H, H-1'', H-1'''); 4.84 (quint, 2H, *J* = 6.5 Hz, C*H*$_{Phth}$); 4.29 (q, 1H, *J* = 6.8 Hz, H-5''); 4.16-4.11 (m, 2H, H-3, H-3''); 3.88-3.82 (m, 2H, H-3''', H-5'); 3.79-3.74 (m, 3H, H-3', H-5'''); 3.71-3.68 (m, 2H, H-2, H-5); 3.63-3.62 (m, 2H, H-2', H-4'); 3.57-3.47 (m, 16H, H-2'', OC*H*$_3$); 3.33 (s, 3H, OC*H*$_3$); 3.23 (t, 1H, *J* = 9.5 Hz, H-4); 2.87-2.84 (m, 1H, C*H*$_{Phth}$); 2.70 (t, 1H, *J* = 9.0 Hz, H-4'''); 2.55-2.50 (m, 4H, C*H*$_{Myc,}$ C*H*$_{2,Phth}$); 2.16-2.12 (m, 4H, H-2''', C*H*$_{3,Ac}$); 1.76-0.81 (m, 197H, H-2''', H-6, H-6', H-6'', H-6''', C*H*$_{Phth}$, C*H*$_{2,Phth}$, C*H*$_{3,Phth}$, C*H*$_{Myc,}$ C*H*$_{2,Myc}$, C*H*$_{3,Myc}$). ^{13}C-APT NMR (125 MHz) δ: 176.2, 176.1 (*C*O$_{Myc}$); 170.7 (*C*O$_{Ac}$); 154.6, 137.0 (C$_{q,arom}$); 129.5, 116.3 (*C*H$_{arom}$); 101.0 (C-1''); 99.5 (C-1'); 99.4 (C-1'''); 95.2 (C-1); 88.1 (C-4'''); 86.8 (*C*H$_{Phth}$); 83.6 (C-3'); 82.5 (C-4); 80.7 (C-2'); 80.5 (C-2); 79.7 (C-2''); 79.0 (C-3); 74.1 (C-3''); 73.7 (C-4''); 71.7 (C-4'); 70.4 (*C*H$_{Phth}$); 69.1 (C-5'); 68.9 (C-5); 68.0 (C-3'''); 67.7 (C-5'''); 66.1 (C-5''); 61.2, 60.4, 60.0, 59.1, 58.8, 57.5 (O*C*H$_3$); 45.6, 45.4 (*C*H$_{2,Myc}$); 41.1, 38.6 (*C*H$_{2,Phth}$); 37.9, 37.9 (*C*H$_{Myc}$); 37.7, 36.8, 35.3 (*C*H$_{2,Myc}$); 34.9 (*C*H$_{Phth}$); 34.8, 32.8 (*C*H$_{2,Phth}$); 32.1 (*C*H$_{2,Myc}$); 31.9, 30.5 (*C*H$_{2,Phth}$); 30.2 (*C*H$_{Myc}$); 30.1, 29.9, 29.9, 29.8, 29.7, 29.7, 29.5 (*C*H$_2$); 28.2 (*C*H$_{Myc}$); 27.6 (*C*H$_{2,Phth}$); 27.3 (*C*H$_{Myc}$); 27.1 (*C*H$_{2,Myc}$); 25.7, 25.3 (*C*H$_{2,Phth}$); 22.8 (*C*H$_{2,Myc}$); 22.5 (*C*H$_{2,Phth}$); 21.0 (*C*H$_{3,Ac}$); 20.9, 20.6, 20.6, 20.5, 18.6 (*C*H$_{3,Myc}$); 18.3 (C-6'''); 18.0 (C-6) 18.0 (C-6'); 16.5 (C-6''); 14.9 (*C*H$_{3,Phth}$); 14.3 (*C*H$_{3,Myc}$); 10.3 (*C*H$_{3,Phth}$). IR (thin film, cm^{-1}): 1132, 1173, 1233, 1378, 1464, 1510, 1734, 2853, 2923, 3440. HRMS calculated for $C_{130}H_{240}O_{22}Na$ 2177.75877 [M+Na]$^+$; found 2177.75981.

4-((3*R*,4*S*,9*R*,11*R*)-3-methoxy-4-methylheptacos-9,11-diyl bismycocerosate)phenyl 2,4-di-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(4-*O*-methyl-2,6-dideoxy-α-D-glucopyranosyl)-4-*O*-propionyl-α-L-fucopyranosyl)-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (75)



Compound **67** (20 mg, 8.4 µmol, 1.0 eq) was hydrogenated using general procedure E to give the title compound (15 mg, 6.9 µmol, 83%) as a pale oil. $[\alpha]_D^{25}$ = -37.3 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (500 MHz) δ: 7.09 (d, 2H, *J* = 9.0 Hz, C*H*$_{arom}$); 6.97 (d, 2H, *J* = 8.5 Hz, C*H*$_{arom}$); 5.47 (d, 1H, *J* = 1.5 Hz, H-1); 5.19-5.18 (m, 2H, H-1', H-4''); 5.09-5.08 (m, 2H, H-1'', H-1'''); 4.84 (quint, 2H, *J* = 6.5 Hz, C*H*$_{Phth}$); 4.29 (q, 1H, *J* = 6.8 Hz, H-5''); 4.16-4.11 (m, 2H, H-3, H-3''); 3.88-3.81 (m, 2H, H-3''', H-5'); 3.77-3.73 (m, 3H, H-3', H-5'''); 3.71-3.68 (m, 2H, H-2, H-5); 3.65-3.62 (m, 2H, H-2', H-4'); 3.57-3.47 (m, 16H, H-2'', OC*H*$_3$); 3.33 (s, 3H, OC*H*$_3$); 3.23 (t, 1H, *J* = 9.8 Hz, H-4); 2.87-2.84 (m, 1H, C*H*$_{Phth}$); 2.70 (t, 1H, *J* = 9.3 Hz, H-4'''); 2.55-2.50 (m, 4H, C*H*$_{Myc,}$ C*H*$_{2,Phth}$); 2.44 (dq, 2H, *J* = 2.2, 7.5 Hz, COC*H*$_2$CH$_3$); 2.34 (bs, 1H, O*H*); 2.13 (dd, 1H, *J* = 5.0, 12.0 Hz, H-2''); 1.76-0.81 (m, 197H, H-2''', H-6, H-6', H-6'', H-6''', COCH$_2$C*H*$_3$, C*H*$_{Phth}$, C*H*$_{2,Phth}$, C*H*$_{3,Phth}$, C*H*$_{Myc,}$ C*H*$_{2,Myc}$, C*H*$_{3,Myc}$). ^{13}C-APT NMR (125 MHz) δ: 176.2, 176.1 (*C*O$_{Myc}$); 174.2 (*C*O$_{Propionyl}$); 154.6, 137.0 (C$_{q,arom}$); 129.4, 116.3 (*C*H$_{arom}$); 101.0 (C-1''); 99.5 (C-1'); 99.4 (C-1'''); 95.2 (C-1); 88.0 (C-4'''); 86.8 (*C*H$_{Phth}$); 83.6 (C-3'); 82.5 (C-4); 80.7 (C-2'); 80.5 (C-2); 79.7 (C-2''); 79.0 (C-3); 74.4 (C-3''); 73.4 (C-4''); 71.8 (C-4'); 70.4 (*C*H$_{Phth}$); 69.1 (C-5'); 68.9 (C-5); 67.9 (C-3'''); 67.6 (C-5'''); 66.1 (C-5''); 61.2, 60.2, 60.0, 59.1, 58.8, 57.5 (O*C*H$_3$); 45.6, 45.4 (*C*H$_{2,Myc}$); 41.1, 38.6 (*C*H$_{2,Phth}$); 37.9, 37.9 (*C*H$_{Myc}$); 37.8, 36.8, 35.3 (*C*H$_{2,Myc}$); 34.9 (*C*H$_{Phth}$); 34.8, 32.8 (*C*H$_{2,Phth}$); 32.1 (*C*H$_{2,Myc}$); 31.9, 30.2 (*C*H$_{2,Phth}$); 30.1 (*C*H$_{Myc}$); 29.9, 29.9, 29.8, 29.7, 29.7, 29.5 (*C*H$_2$); 28.2 (*C*H$_{Myc}$); 27.8 (CO*C*H$_2$CH$_3$); 27.6 (*C*H$_{2,Phth}$); 27.3 (*C*H$_{Myc}$); 27.1 (*C*H$_{2,Myc}$); 25.7, 25.3 (*C*H$_{2,Phth}$); 22.8 (*C*H$_{2,Myc}$); 22.5 (*C*H$_{2,Phth}$); 20.9, 20.6, 20.6, 20.5, 18.6 (*C*H$_{3,Myc}$); 18.3 (C-6'''); 18.0 (C-6) 18.0 (C-6'); 16.5 (C-6''); 14.9 (*C*H$_{3,Phth}$); 14.3 (*C*H$_{3,Myc}$); 10.3 (*C*H$_{3,Phth}$); 9.7 (COCH$_2$*C*H$_3$). IR (thin film, cm^{-1}): 1042, 1100, 1132, 1175, 1231, 1378, 1462, 1510, 1736, 2853, 2923, 3464. HRMS calculated for $C_{130}H_{240}O_{24}Na$ 2191.77442 [M+Na]$^+$; found 2191.77772.

4-((3*R*,4*S*,9*R*,11*R*)-3-methoxy-4-methylheptacos-9,11-diyl bismycocerosate)phenyl 2,4-di-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(2-*O*-methyl-3-*O*-(4-*O*-methyl-2,6-dideoxy-α-D-glucopyranosyl)-α-L-fucopyranosyl) -α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (76)



Compound **68** (31 mg, 12.8 µmol, 1.0 eq) was hydrogenated using general procedure E to give the title compound (27 mg, 12.8 µmol, 100%) as a pale oil. $[\alpha]_D^{25}$ = -31.0 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (500 MHz) δ: 7.09 (d, 2H, *J* = 8.5 Hz, C*H*$_{arom}$); 6.97 (d, 2H, *J* = 8.5 Hz, C*H*$_{arom}$); 5.46 (d, 1H, *J* = 1.5 Hz, H-1); 5.17-5.16 (m, 2H, H-1', H-1'''); 5.06 (d, 1H, *J* = 4.0 Hz, H-1''); 4.84 (quint, 2H, *J* = 6.5 Hz, C*H*$_{Phth}$); 4.29 (q, 1H, *J* = 6.8 Hz, H-5''); 4.11 (dd, 1H, *J* = 3.3, 9.8 Hz, H-3''); 4.03 (dd, 1H, *J* = 3.0, 10.0 Hz, H-3); 4.00-3.95 (m, 1H, H-3'''); 3.88-3.83 (m, 1H, H-5'); 3.79-3.60 (m, 9H, H-2, H-2', H-3', H-4', H-4'', H-5, H-5''', O*H*); 3.60-3.45 (m, 16H, H-2'', OC*H*$_3$); 3.33 (s, 3H, OC*H*$_3$); 3.23 (t, 1H, *J* = 9.8 Hz, H-4); 2.87-2.84 (m, 1H, C*H*$_{Phth}$); 2.74 (t, 1H, *J* = 9.3 Hz, H-4'''); 2.55-2.50 (m, 4H, C*H*$_{Myc,}$ C*H*$_{2,Phth}$); 2.36 (bs, 1H, O*H*); 2.24-2.18 (m, 2H, H-2''', O*H*); 1.76-0.81 (m, 209H, H-2''', H-6, H-6', H-6'', H-6''', C*H*$_{Phth}$, C*H*$_{2,Phth}$, C*H*$_{3,Phth}$, C*H*$_{Myc,}$ C*H*$_{2,Myc}$, C*H*$_{3,Myc}$). ^{13}C-APT NMR (125 MHz) δ: 176.1 (*C*O$_{Myc}$); 154.6, 137.0 (C$_{q,arom}$); 129.4, 116.3 (*C*H$_{arom}$); 101.0 (C-1''); 99.6 (C-1'); 99.3 (C-1'''); 95.2 (C-1); 88.0 (C-4'''); 86.8 (*C*H$_{Phth}$); 83.5 (C-3'); 82.4 (C-4); 80.8 (C-2'); 80.5 (C-2); 79.0 (C-3); 78.9 (C-2''); 77.2 (C-3''); 72.4 (C-4''); 71.8 (C-4'); 70.4 (*C*H$_{Phth}$); 69.1 (C-5'); 68.9 (C-3'''); 68.7 (C-5); 68.1 (C-5'''); 66.4 (C-5''); 61.2, 61.2, 60.0, 59.2, 58.8, 57.5 (O*C*H$_3$); 45.6, 45.4 (*C*H$_{2,Myc}$); 41.1, 38.6 (*C*H$_{2,Phth}$); 37.9, 37.9 (*C*H$_{Myc}$); 36.8, 35.3 (*C*H$_{2,Myc}$); 35.0 (*C*H$_{Phth}$); 34.8, 32.8 (*C*H$_{2,Phth}$); 32.1 (*C*H$_{2,Myc}$); 31.9, 30.2 (*C*H$_{2,Phth}$); 30.1 (*C*H$_{Myc}$); 29.9, 29.9, 29.8, 29.7, 29.5 (*C*H$_2$); 28.2 (*C*H$_{Myc}$); 27.6 (*C*H$_{2,Phth}$); 27.4 (*C*H$_{Myc}$); 27.1 (*C*H$_{2,Myc}$); 25.7, 25.3 (*C*H$_{2,Phth}$); 22.8 (*C*H$_{2,Myc}$); 22.5 (*C*H$_{2,Phth}$); 20.9, 20.6, 20.6, 20.5, 18.6 (*C*H$_{3,Myc}$); 18.4 (C-6'''); 18.0 (C-6) 18.0 (C-6'); 16.4 (C-6''); 14.9 (*C*H$_{3,Phth}$); 14.3 (*C*H$_{3,Myc}$); 10.3 (*C*H$_{3,Phth}$). IR (thin film, cm^{-1}): 1036, 1100, 1132, 1175, 1232, 1378, 1464, 1510, 1734, 2853, 2923, 3446. HRMS calculated for $C_{128}H_{240}O_{24}Na$ 2135.74820 [M+Na]$^+$; found 2135.74993.

References:

1. Buhler, V. B. & Pollak, A. Human Infection with Atypical Acid-Fast Organisms: Report of Two Cases with Pathologic Findings. *Am. J. Clin. Pathol.* **23**, 363–374 (1953).
2. Shitrit, D. *et al.* Differentiation of Mycobacterium kansasii infection from Mycobacterium tuberculosis infection: comparison of clinical features, radiological appearance, and outcome. *Eur. J. Clin. Microbiol. Infect. Dis.* **26**, 679–684 (2007).
3. Matveychuk, A., Fuks, L., Priess, R., Hahim, I. & Shitrit, D. Clinical and radiological features of Mycobacterium kansasii and other NTM infections. *Respir. Med.* **106**, 1472–1477 (2012).
4. Gommans, E. P. A. T. *et al.* Risk factors for mortality in patients with pulmonary infections with non-tuberculous mycobacteria: A retrospective cohort study. *Respir. Med.* **109**, 137–145 (2015).
5. Hernández-Garduño, E., Rodrigues, M. & Elwood, R. K. The incidence of pulmonary non-tuberculous mycobacteria in British Columbia, Canada. *Int. J. Tuberc. Lung Dis.* **13**, 1086–93 (2009).
6. van Ingen, J. *et al.* Clinical relevance of non-tuberculous mycobacteria isolated in the Nijmegen-Arnhem region, The Netherlands. *Thorax* **64**, 502–506 (2009).
7. Prevots, D. R. & Marras, T. K. Epidemiology of Human Pulmonary Infection with Nontuberculous Mycobacteria. *Clin. Chest Med.* **36**, 13–34 (2015).
8. Falkinham, J. O. Nontuberculous mycobacteria in the environment. *Clin. Chest Med.* **23**, 529–51 (2002).
9. von Reyn, C. F. *et al.* Isolation of Mycobacterium avium complex from water in the United States, Finland, Zaire, and Kenya. *J. Clin. Microbiol.* **31**, 3227–3230 (1993).
10. Saleem, N., Saba, R., Maddika, S. & Weinstein, M. Mycobacterium kansasii Infection in a Patient Receiving Biologic Therapy—Not All Reactive Interferon Gamma Release Assays Are Tuberculosis. *Am. J. Med. Sci.* **353**, 394–397 (2017).
11. Steadham, J. E. High-catalase strains of Mycobacterium kansasii isolated from water in Texas. *J. Clin. Microbiol.* **11**, 496–498 (1980).
12. Prevots, D. R. & Marras, T. K. Epidemiology of Human Pulmonary Infection with Nontuberculous Mycobacteria. *Clin. Chest Med.* **36**, 13–34 (2015).
13. Jankute, M. *et al.* The role of hydrophobicity in tuberculosis evolution and pathogenicity. *Sci. Rep.* **7**, 1–10 (2017).
14. Falkinham, J. O. Mycobacterial Aerosols and Respiratory Disease. *Emerg. Infect. Dis.* **9**, 763–767 (2003).
15. Smith, D. W., Randall, H. M., Gastambide-Odier, M. M. & Koevoet, A. L. The Characterization of Mycobacterial Strains by the Composition of their Lipid Extracts. *Ann. N. Y. Acad. Sci.* **69**, 145–157 (1957).
16. Smith, D. W., Randall, H. M., MacLennan, A. P. & Lederer, E. Mycosides: A new class of type-specific glycolipids of mycobacteria. *Nature* **186**, 887–888 (1960).
17. Gastambide-Odier, M. & Villé, C. [Deoxysugars isolated from mycoside A: identification of acetyl derivatives of methyl 2,4-DI-O-methyl-rhamnopyranoside, 2-O-methyl-rhamofuranoside, 3-O-methyl-rhamnofuranoside, 2-O-methyl-fucopyranoside and 3-O-methyl-fucofuranoside]. *Bull. Soc. Chim. Biol. (Paris).* **52**, 679–93 (1970).
18. Gastambide-Odier, M., Sarda, P. & Lederer, E. Structure des aglycones des mycosides A et B. *Tetrahedron Lett.* **6**, 3135–3143 (1965).
19. Gastambide-Odier, M. & Sarda, P. Contribution à l'étude de la structure et de la biosynthèse de glycolipides spécifiques isolés de mycobactéries: les mycosides A et B. *Pneumonol. Pneumonol.* **142**, 241–255 (1970).

20. Smith, D. W. & Randall, H. M. Mycosides of mycobacteria. *Am. Rev. Respir. Dis.* **92**, 34–41 (1965).

21. GILLERON, M., VENISSE, A., RIVIÈRE, M., SERVIN, P. & PUZO, G. Carbohydrate epitope structural elucidation by 1H-NMR spectroscopy of a new Mycobacterium kansasii phenolic glycolipid antigen. *Eur. J. Biochem.* **193**, 449–457 (1990).

22. GILLERON, M. *et al.* Structural and immunological properties of the phenolic glycolids from Mycobacterium gastri and Mycobacterium kansasii. *Eur. J. Biochem.* **189**, 167–173 (1990).

23. Watanabe, M., Aoyagi, Y., Ohta, A. & Minnikin, D. E. Structures of phenolic glycolipids from Mycobacterium kansasii. *Eur. J. Biochem.* **248**, 93–98 (1997).

24. Fournief, J.-J., Rivieres, M., Papas, F. & Puzou, G. THE JOURNAL OF BIOLOGICAL CHEMISTRY Structural Elucidation of the Major Phenolic Glycolipid from Mycobacterium kansasii 11. PRESENCE OF A NOVEL DIDEOXYHEXOSE* X+(1-3)2-0-Me-4-O-Ac-Fucp(1-3) .2-0-Me-Rhap(l-3)2,4-di-O-Me-Rhapl-pbenolglycol. **262**, 3180–3184 (1987).

25. Rivière, M., Fournié, J. J. & Puzo, G. A novel mannose containing phenolic glycolipid from Mycobacterium kansasii. *J. Biol. Chem.* **262**, 14879–14884 (1987).

26. Fournie, J. J., Riviere, M., Papa, F. & Puzo, G. Structural elucidation of the major phenolic glycolipid from Mycobacterium kansasii. II. Presence of a novel dideoxyhexose. *J. Biol. Chem.* **262**, 3180–3184 (1987).

27. FOURNIE, J. -J, RIVIERE, M. & PUZO, G. Absolute configuration of the unique 2,6-dideoxy-4-O-methyl-arabino-hexopyranose of the major phenolic glycolipid antigen from Mycobacterium kansasii. *Eur. J. Biochem.* **168**, 181–183 (1987).

28. Vercellone, A., Rivière, M., Fournié, J. J. & Puzo, G. Structural analogy between the major phenolic glycolipid antigens from two Myobacteria species: kansasii and gastri. *Chem. Phys. Lipids* **48**, 129–134 (1988).

29. Papa, F., Vaquero, M. & David, H. L. Chromatographic and serologic identity of the specific phenolglycolipids PGL-K1 from Mycobacterium kansasii and PGL-G1 from M. Gastri. *Ann. Inst. Pasteur. Microbiol.* **139**, 149–157 (1988).

30. Gurjar, M. K. & Reddy, K. R. Synthesis of tri-saccharide segments of a phenolic glycolipid of Mycobacterium kansasii. *Carbohydr. Res.* **226**, 233–238 (1992).

31. Zegelaar-Jaarsveld, K., van der Marel, G. A. & van Boom, J. H. Iodonium ion assisted synthesis of a common inner core trisaccharide fragment corresponding to the cell-wall phenolic glycolipid of Mycobacterium kansasii. *Tetrahedron* **48**, 10133–10148 (1992).

32. Zegelaar-Jaarsveld, K., Duynstee, H. I., van der Marel, G. A. & van Boom, J. H. Iodonium ion-assisted synthesis of tetrameric fragments corresponding to the cell wall phenolic glycolipids of Mycobacterium kansasii serovars II and IV. *Tetrahedron* **52**, 3575–3592 (1996).

33. Zegelaar-Jaarsveld, K., Smits, S. A. W., van Straten, N. C. R., van der Marel, G. A. & van Boom, J. H. Iodonium ion-assisted synthesis of a tetrameric fragment corresponding to the cell wall phenolic glycolipids of Mycobacterium kansasii serovar I. *Tetrahedron* **52**, 3593–3608 (1996).

34. Elsaidi, H. R. H. & Lowary, T. L. Effect of phenolic glycolipids from Mycobacterium kansasii on proinflammatory cytokine release. A structure - activity relationship study. *Chem. Sci.* **6**, 3161–3172 (2015).

35. Zheng, R. B. *et al.* Insights into Interactions of Mycobacteria with the Host Innate Immune System from a Novel Array of Synthetic Mycobacterial Glycans. *ACS Chem. Biol.* **12**, 2990–3002 (2017).

36. Barroso, S. *et al.* Total Synthesis of the Triglycosyl Phenolic Glycolipid PGL-tb1 from Mycobacterium tuberculosis. *Angew. Chemie Int. Ed.* **51**, 11774–11777 (2012).

37. Barroso, S., Geerdink, D., Ter Horst, B., Casas-Arce, E. & Minnaard, A. J. Total synthesis of the phenolic glycolipid mycoside B and the glycosylated p-hydroxybenzoic acid methyl ester HBAD-I, virulence markers of mycobacterium tuberculosis. *European J. Org. Chem.* 4642–4654 (2013)

doi:10.1002/ejoc.201300437.

38. Kim, K. S. & Suk, D. H. Remote Participation of Protecting Groups at Remote Positions of Donors in Glycosylations. *Trends Glycosci. Glycotechnol.* **23**, 53–66 (2011).

39. Baek, J. Y., Lee, B.-Y., Jo, M. G. & Kim, K. S. β-Directing Effect of Electron-Withdrawing Groups at O -3, O -4, and O -6 Positions and α-Directing Effect by Remote Participation of 3- O -Acyl and 6- O -Acetyl Groups of Donors in Mannopyranosylations. *J. Am. Chem. Soc.* **132**, 7229–7229 (2010).

40. Komarova, B. S., Tsvetkov, Y. E. & Nifantiev, N. E. Design of α-Selective Glycopyranosyl Donors Relying on Remote Anchimeric Assistance. *Chem. Rec.* **16**, 488–506 (2016).

41. Cheshev, P. E., Khatuntseva, E. A., Tsvetkov, Y. E., Shashkov, A. S. & Nifantiev, N. E. Synthesis of Aminoethyl Glycosides of the Ganglioside GM 1 and Asialo-GM 1 Oligosaccharide Chains. *Russ. J. Bioorganic Chem.* **30**, 60–70 (2004).

42. Volbeda, A. G. *et al.* Chemoselective Cleavage of p-Methoxybenzyl and 2-Naphthylmethyl Ethers Using a Catalytic Amount of HCl in Hexafluoro-2-propanol. *J. Org. Chem.* **80**, 8796–8806 (2015).

43. Montchamp, J. L., Tian, F., Hart, M. E. & Frost, J. W. Butane 2,3-bisacetal protection of vicinal diequatorial diols. *J. Org. Chem.* **61**, 3897–3899 (1996).

44. Nakamura, H. *et al.* Total synthesis of (-)-caprazamycin a. *Angew. Chemie - Int. Ed.* **54**, 3136–3139 (2015).

45. Saksena, R., Adamo, R. & Kováč, P. Studies toward a conjugate vaccine for anthrax. Synthesis and characterization of anthrose [4,6-dideoxy-4-(3-hydroxy-3-methylbutanamido)-2-O-methyl-D-glucopyranose] and its methyl glycosides. *Carbohydr. Res.* **340**, 1591–1600 (2005).

46. Aoyama, T. & Shioiri, T. Trimethylsilyldiazomethane: a convenient reagent for the preparation of (E)-1-trimethylsilyl-1-alkenes. *Tetrahedron Lett.* **29**, 6295–6296 (1988).

47. Arnarp, J. & Lonngren, J. Alkylation of Carbohydrates with Alkyl Trifluoromethansesulfonates. *Acta Chem. Scand* **32**, 465–467 (1978).

48. Williams, D. R., Plummer, S. V. & Patnaik, S. Formal Synthesis of Leucascandrolide A. *Angew. Chemie Int. Ed.* **42**, 3934–3938 (2003).

49. Lichtenthaler, F. W., Oberthür, M. & Peters, S. Directed and efficient syntheses of β(1→4)-linked galacto-oligosaccharides. *European J. Org. Chem.* 3849–3869 (2001) doi:10.1002/1099-0690(200110)2001:20<3849::AID-EJOC3849>3.0.CO;2-Q.

50. Sato, K. I. *et al.* Novel synthetic approaches to manβ1-4GLCNAc and LeX units from N-acetyllactosamine. *J. Carbohydr. Chem.* **17**, 703–727 (1998).

51. David, S., Thieffry, A. & Veyrières, A. A mild procedure for the regiospecific benzylation and allylation of polyhydroxy-compounds via their stannylene derivatives in non-polar solvents. *J. Chem. Soc., Perkin Trans. 1* 1796–1801 (1981) doi:10.1039/P19810001796.

52. Jiang, L. & Chan, T.-H. Regioselective Acylation of Hexopyranosides with Pivaloyl Chloride. *J. Org. Chem.* **63**, 6035–6038 (1998).

53. Roslund, M. U. *et al.* Acyl Group Migration and Cleavage in Selectively Protected β- <scp>d</scp> -Galactopyranosides as Studied by NMR Spectroscopy and Kinetic Calculations. *J. Am. Chem. Soc.* **130**, 8769–8772 (2008).

54. Koto, S., Morishima, N., Yoshida, T., Uchino, M. & Zen, S. Ditritylation of Methyl and Benzyl α-D-Gluco-, -Manno-, and -Galactopyranosides and Preparation of Their Partially Benzylated Derivatives. *Bull. Chem. Soc. Jpn.* **56**, 1171–1175 (1983).

55. Tanaka, H., Yoshizawa, A. & Takahashi, T. Direct and stereoselective synthesis of β-linked 2,6-deoxyoligosaccharides. *Angew. Chemie - Int. Ed.* **46**, 2505–2507 (2007).

56. Bolitt, V., Mioskowski, C., Lee, S. G. & Falck, J. R. Direct preparation of 2-deoxy-D-glucopyranosides from glucals without Ferrier rearrangement. *J. Org. Chem.* **55**, 5812–5813 (1990).

57. Sherry, B. D., Loy, R. N. & Toste, F. D. Rhenium (V) -Catalyzed Synthesis of 2-Deoxy- r -glycosides. 4510–4511 (2004).

58. Karageorgi, S. Total synthesis of Mycobacterium kansasii oligosaccharides.

59. Jakas, A. *et al.* Synthesis of anthrose lipidic derivative as mimic of B. anthracis BclA glycoprotein for use in ELISA-like binding assays. *J. Carbohydr. Chem.* **35**, 69–85 (2016).

60. Hansen, T. *et al.* Defining the SN1 Side of Glycosylation Reactions: Stereoselectivity of Glycopyranosyl Cations. *ACS Cent. Sci.* **5**, 781–788 (2019).

61. Crich, D., Cai, W. & Dai, Z. Highly diastereoselective α-mannopyranosylation in the absence of participating protecting groups. *J. Org. Chem.* **65**, 1291–1297 (2000).

62. Elferink, H. *et al.* The Glycosylation Mechanisms of 6,3-Uronic Acid Lactones. *Angew. Chemie - Int. Ed.* **58**, 8746–8751 (2019).