Synthesis of mycobacterial phenolic glycolipids

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Chapter 4

Synthesis of PGLs originating from the *Mycobacterium tuberculosis* complex

Introduction

The *Mycobacterium tuberculosis* complex (MTBC) is a group of slow-growing species of mycobacteria which are genetically very similar to *Mycobacterium tuberculosis*.[1] Most of these species can cause tuberculosis in humans, which still is one of the most deadly infectious diseases worldwide, especially in countries which are heavily impacted by HIV/AIDS.[2] Approximately one third of the world population is thought to harbor a latent tuberculosis infection,[3] and these individuals are at risk to develop the active disease. Phenolic glycolipids are thought to play a major role in the virulence of many mycobacteria belonging to the MTBC.[4–8] While most strains of *M. tuberculosis* do not produce phenolic glycolipids, some isolates belonging to the W-Beijing family do and these show "hyperlethality" in murine disease models.[9–11] These strains produce a triglycosyl phenolic glycolipid, PGL-tb1, carrying a 2,3,4,-tri-*O*-methyl-α-L-fucopyranosyl-(1→3)-α-L-rhamnopyranosyl-(1→3)-2-*O*-methyl-α-L-rhamnopyranosyl trisaccharide on the phthiocerol lipid (Figure 1).[12] This PGL is also produced by some isolates of *M. africanum*[13] and the *M. canetti* strain.* The strains of *M. tuberculosis* that do not produce PGLs do produce *p*-hydroxybenzoic acid derivative II (*p*-HBAD-II), a biosynthetically closely related glycosylated phenol, bearing the same trisaccharide, as well as phthiocerol

* There is an ongoing discussion regarding whether or not *M. canetti* belongs to the MTBC as it is genetically closely related and can cause tuberculosis but there are contrasting specific phenotypic and genomic characteristics.[38]

dimycocerosate (PDIM), which resembles the lipid part of PGLs.[14–17] Other species of the MTBC, such as *M. bovis*, *M. microti*, *M. africanum* and *M. pinnipedii* almost exclusively produce a monoglycosylated PGL, also referred to as mycoside B, carrying a 2-*O*-methyl-α-L-rhamnopyranose. Some strains of *M. bovis* also produce a PGL having an α-L-rhamnopyranosyl-(1→3)-2-*O*-methyl-α-L-rhamnopyranose disaccharide,[18] and PGLs with variations in the methylation pattern, that arise from mutations in genes related to methyltransferases, have also been isolated.[19–21] Several syntheses of truncated and simplified versions of PGLs and related molecules have been reported (see Chapter 1).[8,15,22–26] 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 the MTBC.

The general strategy for the synthesis of these phenolic glycolipids is based on the total synthesis of PGL-tb1 as published by Barroso et al. (Figure 1).[26,27] Fully protected iodoaryl glycans are to be synthesized starting from the 'reducing end', after which they can be attached to a phthiocerol alkyne derivative in a Sonogashira cross coupling. The resulting diol can then be esterified with two mycocerosic acids under Steglich conditions and hydrogenation finally leads to the global deprotection and concomitant reduction of the conjugated internal alkyne which is formed in the Sonogashira reaction.

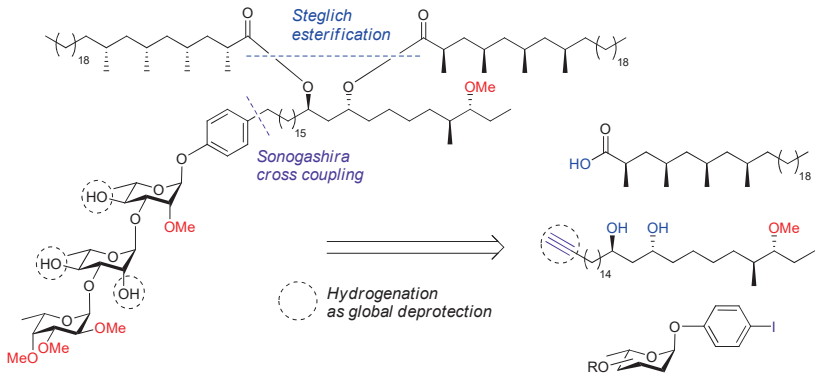


Figure 1. General synthetic strategy for phenolic glycolipids with PGL-tb1 as an example.

This synthetic strategy requires the oligosaccharides to be protected with protecting groups that can be removed under hydrogenation conditions. If 1,2-*trans* linkages were to be formed with ester based participating protecting groups these would

have to be removed and replaced with for example benzyl ethers before the Sonogashira cross coupling. To circumvent these extra protecting group manipulations, the carboxybenzyl (Cbz) protecting group will be probed, as this carbonate may provide anchimeric assistance, directing the formation the desired 1,2-*trans* linkages, while it is susceptible to hydrogenation.[28] Of note, the Cbz-group has found only very little application in the assembly of oligosaccharides. The retrosynthetic analysis of the MTBC glycans and the required building blocks are depicted in Figure 2.

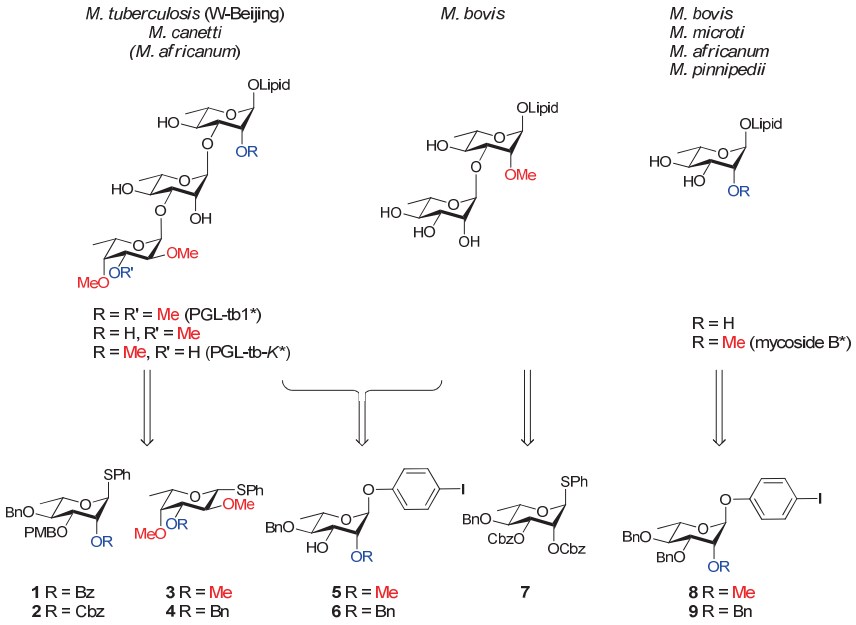
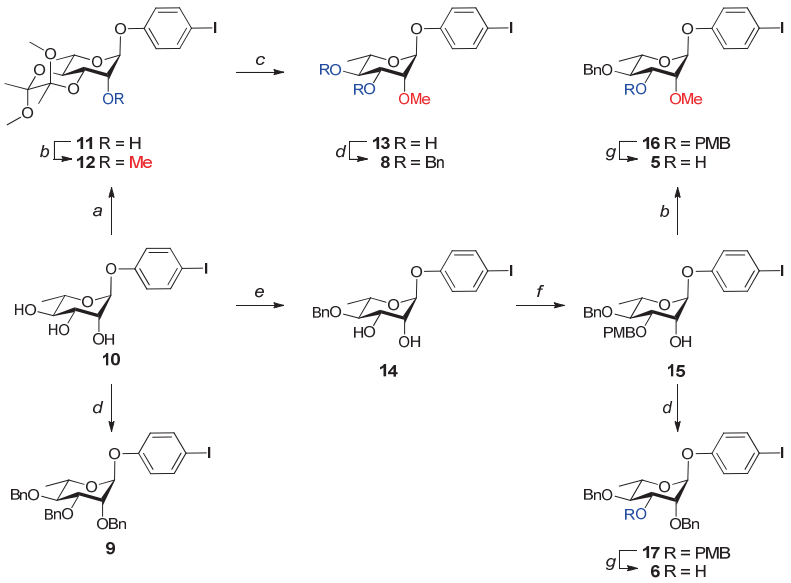


Figure 2. Retrosynthetic analysis of the glycans of MTBC PGLs. (* = trivial name)

The triglycosyl PGLs are to be synthesized from acceptors **5** and **6** and rhamnose donor **2**. In order to establish the efficacy of the Cbz group in PGL assembly, a route using the C-2 benzoyl bearing rhamnose donor **1** will be followed for comparison. The terminal fucose has to be fused to the disaccharide through a 1,2-*cis* linkage, and building blocks **3** and **4** will be probed for this purpose. This will require the conception of effective glycosylation chemistry that does not build on neighboring group participation. Acceptor **5** can also be used for the synthesis of the *M. bovis* disaccharide in combination with 2,3-di-*O*-Cbz donor **7**. The monoglycosylated PGLs are to be synthesized from **8** and **9**.

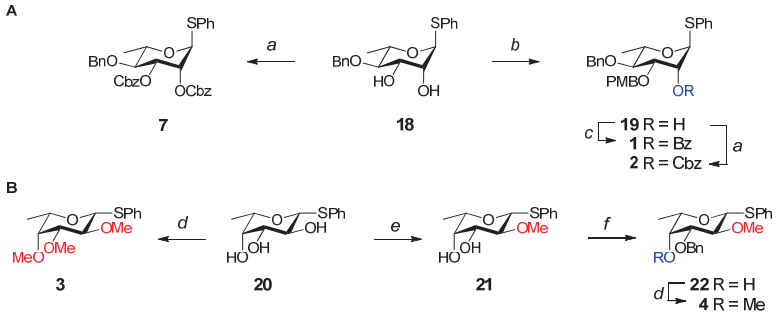
Results and discussion

All requisite iodoaryl bearing rhamnoses were synthesized from intermediate **10** as depicted in Scheme 1.[26] To generate mycoside B, the 3,4-diol in **10** was selectively protected with a butane 2,3-bisacetal (BDA) under mild conditions[29] to avoid hydrolysis of the anomeric phenol. After methylation of the C-2 alcohol in **11**, the BDA was hydrolyzed using acetic acid, after which the resulting diol **13** was benzylated to give iodophenyl rhamnose **8** in 37% yield over 4 steps. Perbenzylation of **10** gave **9** in 98% yield. Acceptors **5** and **6** were synthesized by selectively protecting the C-3 position of **14**, obtained from **10** by acetonide formation, benzylation and acetonide removal, with a *para*-methoxybenzyl ether by treatment of the diol with Bu_2SnO, followed by TBABr and PMBCl.[30] After methylation (to give **16**) or benzylation (providing **17**), the PMB ether was removed using a catalytic amount of HCl in HFIP[31] to give monosaccharide acceptors **5** and **6** in 79% and 63% over 3 steps, respectively.



Scheme 1. Reagents and conditions: (a) 2,3-butanedione, trimethyl orthoformate, $BF_3{\cdot}OEt_2$, MeOH, 0 °C → RT, 77%, (b) Na, MeI, DMF, 0 °C → RT, 87% (**8**), 80% (**16**), (c) $AcOH/H_2O$, 4:1, 80 °C, 65%, (d) NaH, BnBr, DMF, 0 °C → RT, 84% (**8**), 98% (**9**), 77% (**17**), (e) 1. DMP, CSA, acetone, 2. NaH, BnBr, DMF, 3. $AcOH/H_2O$, 4:1, 80 °C, 86% over 3 steps, (f) 1. Bu_2SnO, toluene reflux, 2. PMBCl, TBABr, toluene reflux, 99% (8:1), (g) HCl/HFIP, HFIP/DCM, 100% (**5**), 82% (**6**).

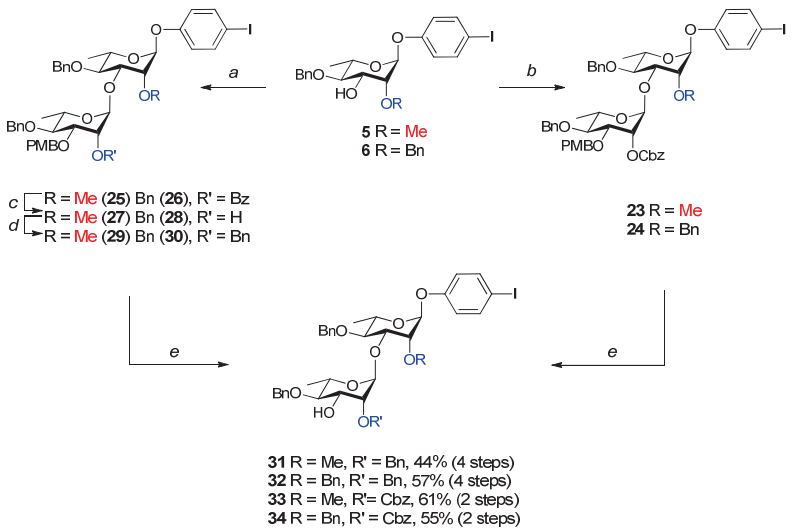
The synthesis of the required donors is depicted in Scheme 2. Donor **7** was synthesized from **18** in near quantitative yield by reacting the diol with CbzCl and DMAP in DCM.[32] Selective protection of the C-3 alcohol of **18** with a PMB ether provided **19** in 77% yield, from which benzoyl donor **1** and Cbz donor **2** were synthesized in 100% and 76% yield, respectively. Permethylation of triol **20** gave **3** in 87% yield. The synthesis of fucose donor **4** was accomplished by masking the 3,4-diol in **20** with an isopropylidene ketal, installation of the C-2 methyl ether and removal of the isopropylidene to provide intermediate **21** in 88% yield over 3 steps. A benzyl ether was then selectively installed on the C-3 position by using a catalytic amount of Bu_2SnCl_2 in acetonitrile,[33] after which the remaining free alcohol was methylated in 83% yield. Alternatively, this building block could be synthesized from triol **20** in 2 steps by directly benzylating the C-3 alcohol using organotin chemistry. However, this resulted in a lower overall yield because of the decreased selectivity of the benzylation reaction.



Scheme 2. Reagents and conditions: (a) CbzCl, DMAP, DCM, 0 °C → RT, 99% (**7**), 76% (**2**), (b) 1. Bu_2SnO, toluene, reflux, 2. PMBCl, TBABr, toluene, reflux, 77% (c) BzCl, pyridine, DCM, 0 °C → RT, 100%, (d) NaH, MeI, DMF, 0 °C → RT, 87% (**3**), 83% (**4**), (e) 1. DMP, CSA, acetone, 2. NaH, MeI, DMF, 0 °C → RT, 3. $AcOH/H_2O$, 4:1, 80 °C, 88% over 3 steps, (f) BnBr, TBABr, Bu_2SnCl_2, K_2CO_3, MeCN, 80 °C, 97%.

Scheme 3 depicts the synthesis of the disaccharide acceptors needed for the MTBC trisaccharide PGLs using either a benzoyl donor (left) or a Cbz donor (right). Benzoyl donor **1** was combined with C-2 methyl acceptor **5** or C-2 benzyl acceptor **6** to provide disaccharides **25** and **26** in 64% and 75% yield, respectively. Thereafter the benzoyl esters were removed and replaced with benzyl ethers to offer **29** and **30** in 81% and 77% yield over 2 steps, respectively. Then the C-3' PMB ethers were removed to give disaccharide acceptors **31** and **32** in 84% and 98% yield, respectively. In the alternative

route, Cbz donor **2** was used in combination with **5** and **6** to produce disaccharides **23** and **24** in 68% and 64% yield, respectively, whereafter only the PMB ether had to be removed. Although it was anticipated that the Cbz could migrate to the C-3' position or form a 2,3-carbonate under the acidic conditions needed for the removal of the PMB ether, neither of these byproducts were detected in significant amounts, possibly due to the very short reaction time (<2 minutes). The removal of the PMB ether gave disaccharide acceptors **33** and **34** in 89% and 86% yield, respectively. It was observed that prolonged reaction times led to the hydrolysis of the iodophenol on the reducing end. When DDQ was used instead of HCl in HFIP the disaccharide acceptors were produced in a slightly lower yield and removal of the C-4 benzyl ether was detected as a side reaction.



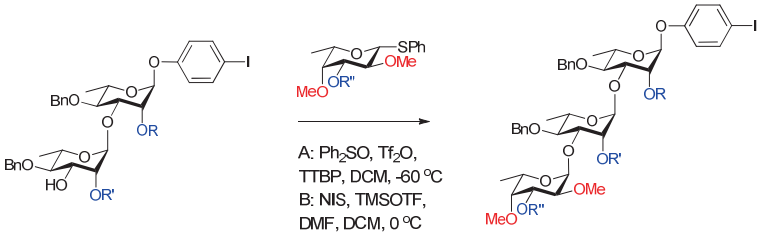
Scheme 3. Reagents and conditions: (a) Donor **1**, Ph_2SO, Tf_2O, TTBP, DCM -60 °C, 64% (**25**), 75% (**26**), (b) Donor **2**, Ph_2SO, Tf_2O, TTBP, DCM -60 °C, 68% (**23**), 64% (**24**), (c) Na, MeOH/THF, 81% (**27**), 86% (**28**), (d) NaH, BnBr, TBAI, DMF, 0 °C → RT, 100% (**29**), 90% (**30**), (e) HCl/HFIP, HFIP/DCM, 84% (**31**), 98% (**32**), 89% (**33**), 86% (**34**).

Overall, it can be concluded that the implementation of the Cbz group in the synthetic routes increases the efficiency. The disaccharides **31** and **33**, carrying a C-2 methyl ether were generated in 44% over four steps and 61% yield over two steps, respectively. Although the overall yield for disaccharide acceptors **32** and **34** did not differ much

between the Cbz and Bz routes, the Cbz route required only two steps, where the route with the Bz ester needed four steps.

The disaccharide acceptors could then be fucosylated to generate the PGL trisaccharides. For the fucosylation several reaction conditions were screened as summarized in Table 1 below. First the 1,2-*cis* glycosylation was attempted using Ph_2SO pre-activation conditions (method A). When acceptors **31** and **33** were combined with donor **3** trisaccharides **35** and **36** were produced in good yield with moderate stereoselectivity (5:1 and 4:1, respectively). Coupling of acceptors **32** and **34** to the same donor under the same conditions provided trisaccharides **37** and **38** in a 2:1 α/β ratio. Coupling of donor **4** to acceptor **33** produced trisaccharide **39** as a 3:2 α/β mixture. An alternative method was then applied using DMF as a stereodirecting additive.[34] First the donor was activated using stoichiometric amounts of both NIS and TMSOTf after which DMF was added (method B). This method improved the selectivity of the coupling of donor **3** to acceptor **33** from 4:1 to 10:1. In addition, coupling of donor **3** to acceptors **32** and **34** improved the selectivity of these couplings to 4:1 and 7:1, respectively. The use of method B improved the selectivity of the coupling of donor **4** to acceptor **33** from 3:2 to 5:1. From these results it appears that the stereoselectivity of the condensation reactions improves most when an acceptor is used that carries electron withdrawing protecting groups (*i.e.* the Cbz carbonate). It is hypothesized that upon activation of the glycosyl donor, the DMF additive generates a mixture of α- and β-glycosyl imidinium ion intermediates that are in rapid equilibrium. The β-imidinium ion is less stable and therefore more reactive than its α-counterpart.

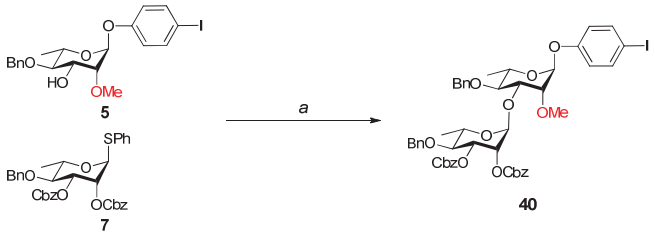
Table 1. Yields and selectivities of glycosylations using either Ph_2SO/Tf_2O (A) or NIS/TMSOTf (B).



Acceptor	Donor	Product	R	R'	R''	Method	Yield	Selectivity (α:β)
31	**3**	**35**	Me	Bn	Me	A	70%	5:1
33	**3**	**36**	Me	Cbz	Me	A	79%	4:1
33	**3**	**36**				B	73%	10:1
32	**3**	**37**	Bn	Bn	Me	A	85%	2:1
32	**3**	**37**				B	89%	4:1
34	**3**	**38**	Bn	Cbz	Me	A	78%	2:1
34	**3**	**38**				B	73%	7:1
33	**4**	**39**	Me	Cbz	Bn	A	88%	3:2
33	**4**	**39**				B	82%	5:1

Even though it is the minor component in the anomeric mixture, it represents the most important product forming intermediate as weak nucleophiles do not readily displace the more stable α-imidinium ion and weaker nucleophiles will react with better stereoselectivity.[35] It was noted that application of method B did lead to the formation of a minor side product resulting from silylation of the C-3' alcohol of the acceptor. Switching from TMSOTf to TfOH could circumvent this problem but this led to partial hydrolysis of the iodophenol on the reducing end.

The last glycan to be prepared was the *M. bovis* disaccharide, which was synthesized by coupling **5** and **7**. Donor **7**, carrying two Cbz carbonates was activated using the Ph_2SO/Tf_2O couple after which addition of acceptor **5** led to the formation of disaccharide **40** in 65% yield (Scheme 3).

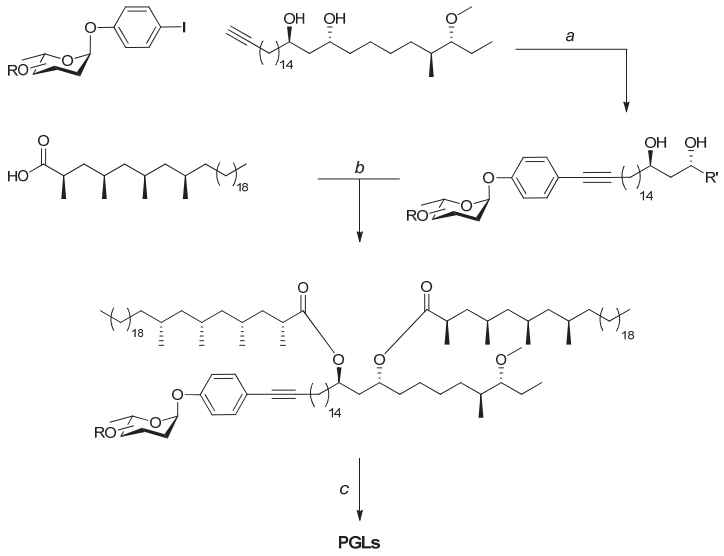


Scheme 4. Reagents and conditions: (a) Ph_2SO, Tf_2O, TTBP, DCM -60 °C, 65%

With all glycans in hand the stage was set for the connection of the lipids and complete the syntheses of the PGLs. The yields of the final steps of the assembly of PGLs is summarized in Table 2. First the glycans were coupled to the phthiocerol alkyne derivative using a Sonogashira cross coupling in excellent yields. For these reactions it

proved crucial to use triethylamine that was freshly was distilled from KOH (less than 24 hours before the reaction). A slight excess (1.2 equivalents) of alkyne was used. It was observed that a minor amount of the diyne byproduct, generated by coupling of two alkynes, was formed, the amount of which increased if more alkyne was used. The diols that resulted from the Sonogashira reaction could then be coupled to mycocerosic acid[36] under Steglich esterification conditions using di-*iso*-propylcarbodiimide. The best results were obtained if these reactions were started at 0 °C to minimize the amount of *N*-acyl di-*iso*-propylurea rearrangement product formed. While the low reaction temperature was required at the start of the reaction, it was observed that warming the reaction to 40 °C was required to achieve full conversion and the use of ambient temperature led to the generation of the mono- mycocerosic acid ester compounds. With these conditions the diols were esterified in good yields with the exception of the *M. bovis* disaccharide. In this case the retention time of the *N*-acyl urea rearrangement products during column chromatography was very similar to the retention time of the product and multiple rounds of purification were needed. After the esterification reaction the products were hydrogenated and this uneventfully completed the syntheses of all PGLs originating from the MTBC.

Table 2. Yields of the 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
36	90%	94%	82%	69%
38	87%	75%	80%	52%
39	100%	74%	82%	61%
8	100%	84%	62%	52%
9	99%	75%	31%	23%
40	96%	51%	60%	29%

Conclusion

This chapter has described the synthesis of all phenolic glycolipids originating from the *Mycobacterium tuberculosis* complex. The presence of the two mycocerosic esters in the final products necessitated a strategy using a hydrogenation step for global deprotection. Therefore, in order to reduce the amount of steps required to assemble the oligosaccharides, the carboxybenzyl (Cbz) group has been probed as a participating

protecting group. Although there is relatively little precedent for the use of the Cbz-carbonate in oligosaccharide synthesis the group performed well and the Cbz protected donors selectively produced the desired α products in good yield. In the synthesis of the Mtb PGL trisaccharides, the stereoselective introduction of the 1,2-*cis* fucosyl linkages was achieved using an additive (DMF) based glycosylation method to provide the desired trisaccharides in good yields and selectivities. 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 all the phenolic glycolipids originating from the *Mycobacterium tuberculosis* complex 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 or $KMnO_4$ (7.5 g/L) and K_2CO_3 (50 g/L) in H_2O, followed by charring. Additional analysis with TLC-MS was used when needed.

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

NMR spectra were recorded at ambient temperature on a Bruker AV-400LIQ 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 (1.5 eq), Ph_2SO (2.0 eq) and TTBP (3.8 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 -60 °C after which Tf_2O (2.0 eq) was added to the solution. After stirring for 30 minutes, the acceptor (1.0 eq), which was also dried by co-evaporation with toluene (3x) followed by 3 vacuum/nitrogen purges, was dissolved in DCM (0.4 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: NIS mediated glycosylation:

Donor (1.5 eq) was dried by co-evaporation with toluene (3x) followed by 3 vacuum/nitrogen purges, and then dissolved in dry DCM (0.05 M) and flame-dried 3Å molecular sieves were added. DMF (24 eq) was added and the solution was cooled to 0 °C. NIS (1.5 eq) and TMSOTf (1.5 eq) were then added to the solution and the mixture was left to stir for 45 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 (0.4 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 NaS_2O_3 and brine, 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 (2-16 h). The solvent was then removed under a stream of N_2. The crude was transferred to a silica column in toluene and the column was flushed with toluene. Thereafter the product was purified by means of column chromatography.

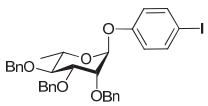
General procedure D: Esterification with mycocerosic acid

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 (6.0 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 layer was washed 1 M HCl, sat. aq. $NaHCO_3$ and brine, dried with $MgSO_4$ and concentrated *in vacuo*. Purification by means of column chromatography. Note: In order to detect the most prevalent byproducts, staining with $KMnO_4$ is required.

General procedure E: Hydrogenation

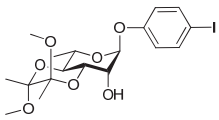
Starting material (1.0 eq) was dissolved in a mixture of THF and EtOH (1:1, 0.007 M) ans the solution was purged with N_2. Pd/C (10%, 1.0 eq) was then added to the solution and the resulting mixture was purged with H_2. The reaction was left to stir under H_2 atmosphere until TLC complete conversion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

4-iodophenyl 2,3,4-tri-*O*-benzyl-α-L-rhamnopyranoside (9)



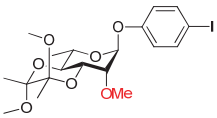
Compound **10** (0.73 g, 2.0 mmol, 1.0 eq) was dissolved in dry DMF (20 mL, 0.1 M) and BnBr (1.42 mL, 12 mmol, 6.0 eq) was added to the solution. The mixture was cooled to 0 °C, and NaH (60%, 0.29 g, 7.2 mmol, 3.6 eq) was then added. The reaction mixture was warmed to rt while stirring for 16 hours. The reaction was quenched by addition of H_2O, and 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 19:1) gave the title compound (1.24 g, 1.96 mmol, 98 %) as a pale oil. $[\alpha]_D^{25}$ = -62.8 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.54-7.50 (m, 2H, C*H*$_{arom}$); 7.39-7.24 (m, 15H, C*H*$_{arom}$); 6.75-6.72 (m, 2H, C*H*$_{arom}$); 5.41 (d, 1H, *J* = 2.0 Hz, H-1); 4.95 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.78 (dd, 2H, *J* = 12.4, 28.8 Hz, PhC*H*$_2$); 4.73-4.64 (m, 3H, PhCH*H*, PhC*H*$_2$); 4.02 (dd, 1H, *J* = 2.8, 8.8 Hz, H-3); 3.93 (d, 1H, *J* = 2.0, 2.8 Hz, H-2); 3.77-3.66 (m, 2H, H-4, H-5); 1.29 (d, 3H, *J* = 5.2 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 156.1, 138.5 (C$_{q,arom}$); 138.4 (*C*H$_{arom}$); 138.1 (C$_{q,arom}$); 128.6, 128.5, 128.5, 128.1, 128.1, 128.0, 127.8, 127.8, 118.7 (*C*H$_{arom}$); 96.3 (C-1); 84.8 (*C*I$_{arom}$); 80.4 (C-4); 79.8 (C-3); 75.6 (Ph*C*H$_2$); 74.6 (C-2); 73.2, 72.5 (Ph*C*H$_2$); 69.0 (C-5); 18.1 (C-6). IR (thin film, cm^{-1}): 1028, 1050, 1098, 1115, 1137, 1232, 1454, 1484. HRMS calculated for $C_{33}H_{33}IO_5Na$ 659.1270 [M+Na]$^+$; found 659.1274.

4-iodophenyl 3,4-*O*-(2,3-dimethoxybutane-2,3-diyl)-α-L-rhamnopyranoside (11)



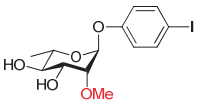
Compound **10** (0.366 g, 1.0 mmol, 1.0 eq) was dissolved in MeOH (10 mL, 0.1 M) and trimethyl orthoformate (0.44 mL, 4.0 mmol, 4.0 eq) and 2,3-butanedione (0.1 mL, 1.1 mmol, 1.1 eq) were added to the solution. The mixture was cooled to 0 °C and $BF_3{\cdot}OEt_2$ (12 µL, 0.1 mmol, 0.1 eq) was added to the solution. The mixture was stirred for 72 hours 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-Et_2O 3:2) gave the title compound (0.37 g, 0.77 mmol, 77%) as a pale oil. $[\alpha]_D^{25}$ = -136.4 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.58-7.54 (m, 2H, C*H*$_{arom}$); 6.84-6.80 (m, 2H, C*H*$_{arom}$); 5.49 (d, 1H, *J* = 1.2 Hz, H-1); 4.15-4.10 (m, 2H, H-2, H-3); 3.88-3.76 (m, 2H, H-4, H-5); 3.34 (s, 3H, OC*H*$_{3,BDA}$); 3.25 (s, 3H, OC*H*$_{3,BDA}$); 2.95 (bs, 1H, 2-O*H*); 1.36 (s, 3H, CC*H*$_{3,BDA}$); 1.31 (s, 3H, CC*H*$_{3,BDA}$); 1.22 (d, 3H, *J* = 6.0 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 156.0 (C$_{q,arom}$); 138.4, 118.7 (*C*H$_{arom}$); 100.4, 100.0 (*C*CH$_{3,BDA}$); 97.7 (C-1); 84.8 (*C*I$_{arom}$); 69.7 (C-2); 68.2 (C-4); 68.1 (C-3); 67.7 (C-5); 48.3, 47.8 (O*C*H$_{3,BDA}$); 17.9, 17.8 (C*C*H$_{3,BDA}$); 16.6 (C-6). IR (thin film, cm^{-1}): 1002, 1017, 1037, 1053, 1076, 1115, 1143, 1233, 1378, 1485, 2932, 3470. HRMS calculated for $C_{18}H_{25}IO_7Na$ 503.0543 [M+Na]$^+$; found 503.05388.

4-iodophenyl 2-*O*-methyl-3,4-*O*-(2,3-dimethoxybutane-2,3-diyl)-α-L-rhamnopyranoside (12)



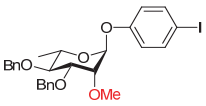
Compound **11** (2.95 g, 6.15 mmol, 1.0 eq) was dissolved in dry DMF (50 mL, 0.12 M) and MeI (0.57 mL, 9.23 mmol, 1.5 eq) was added to the solution. The mixture was cooled to 0 °C, and NaH (60%, 0.49 g, 12.3 mmol, 2.0 eq) was then added. The reaction mixture was warmed to rt while stirring for 4 hours. 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 (2.64 g, 5.34 mmol, 87%) as a pale oil. $[\alpha]_D^{25}$ = -181.2 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.57-7.55 (m, 2H, C*H*$_{arom}$); 6.84-6.80 (m, 2H, C*H*$_{arom}$); 5.49 (d, 1H, *J* = 1.6 Hz, H-1); 4.17 (dd, 1H, *J* = 3.0, 9.8 Hz, H-3); 3.83-3.74 (m, 2H, H-4, H-5); 3.63 (dd, 1H, *J* = 2.0, 2.8 Hz, H-2); 3.56 (s, 3H, OC*H*$_3$); 3.34 (s, 3H, OC*H*$_3$); 3.25 (s, 3H, OC*H*$_3$); 1.36 (s, 3H, OC*H*$_3$); 1.30 (s, 3H, OC*H*$_3$); 1.22 (d, 3H, *J* = 6.0 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 156.2 (C$_{q,arom}$); 138.5, 118.7 (*C*H$_{arom}$); 100.2, 99.8 (*C*CH$_{3,BDA}$); 96.1 (C-1); 84.9 (*C*I$_{arom}$); 78.5 (C-2); 68.6 (C-4); 68.3 (C-3); 68.0 (C-5); 59.6 (O*C*H$_3$); 48.2, 47.8 (O*C*H$_{3,BDA}$); 18.0 (*C*H$_{3,BDA}$); 16.8 (C-6). IR (thin film, cm^{-1}): 1037, 1055, 1080, 1115, 1142, 1232, 1484. HRMS calculated for $C_{19}H_{27}IO_7Na$ 517.0699 $[M+Na]^+$; found 517.0695.

4-iodophenyl 2-*O*-methyl-α-L-rhamnopyranoside (13)



Compound **12** (0.216 g, 0.44 mmol, 1.0 eq) was dissolved in a mixture of AcOH and H_2O (4:1, 50 mL, 0.01 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*. Purification by means of column chromatography (*n*-pentane-EtOAc 3:7) gave the title compound (0.108 g, 0.28 mmol, 65%) as a clear oil. $[\alpha]_D^{25}$ = -68.7 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.59-7.56 (m, 2H, C*H*$_{arom}$); 6.89-6.83 (m, 2H, C*H*$_{arom}$); 5.53 (d, 1H, *J* = 1.6 Hz, H-1); 3.93 (dd, 1H, *J* = 2.8, 8.8 Hz, H-3); 3.70-3.63 (m, 2H, H-2, H-5); 3.53 (s, 3H, OC*H*$_3$); 3.46 (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); 85.0 (*C*I$_{arom}$); 80.1 (C-2); 73.7 (C-4); 71.4 (C-3); 68.8 (C-5); 59.2 (O*C*H$_3$); 17.7 (C-6). IR (thin film, cm^{-1}): 1022, 1067, 1112, 1232, 1484, 3410. HRMS calculated for $C_{13}H_{17}IO_5Na$ 403.0018 $[M+Na]^+$; found 403.0013.

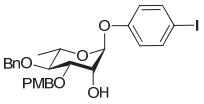
4-iodophenyl 2-*O*-methyl-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (8)



Compound **13** (74 mg, 0.2 mmol, 1.0 eq) was dissolved in dry DMF (2 mL, 0.1 M) after which BnBr (71 μL, 0.6 mmol, 3.0 eq) was added to the solution. The mixture was cooled to 0 °C, and NaH (60%, 32 mg, 0.8 mmol, 4.0 eq) was added. The 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 (94 mg, 0.17 mmol, 84%) as a pale oil. $[\alpha]_D^{25}$ = -92.5 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.57-7.53 (m, 2H, C*H*$_{arom}$); 7.44-7.40 (m, 2H, C*H*$_{arom}$); 7.37-7.26 (m, 8H, C*H*$_{arom}$); 6.82-6.78 (m, 2H, C*H*$_{arom}$); 5.47 (d, 1H, *J* = 2.0 Hz, H-1); 4.95 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.81-4.75 (m, 2H, PhC*H*$_2$); 4.63 (d, 1H, *J* = 10.8 Hz, PhCH*H*); 4.02 (dd, 1H, *J* = 3.2, 9.6 Hz, H-3); 3.73-3.68 (m, 2H, H-2, H-5); 3.60-3.56 (m, 4H, H-4, OC*H*$_3$); 1.26 (d, 3H, *J* = 6.0 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 156.2,

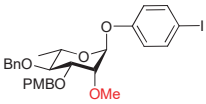
138.5 ($C_{q,arom}$); 138.5 (CH_{arom}); 138.4 ($C_{q,arom}$); 138.4, 128.6, 128.5, 128.1, 128.0, 127.9, 127.9, 118.7 (CH_{arom}); 95.6 (C-1); 84.3 (CI_{arom}); 80.3 (C-4); 79.6 (C-3); 78.0 (C-2); 75.7, 72.7 (PhCH_2); 69.0 (C-5); 59.8 (OCH_3); 18.1 (C-6). IR (thin film, cm^{-1}): 1047, 1138, 1178, 1232, 1454, 1484. HRMS calculated for $C_{27}H_{29}IO_5Na$ 583.0957 $[M+Na]^+$; found 583.0950.

4-iodophenyl 3-*O*-(4-methoxybenzyl)-4-*O*-benzyl-α-L-rhamnopyranoside (15)



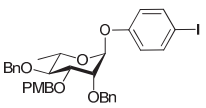
Compound **14**[26] (6.05 g, 13.3 mmol, 1.0 eq) was dissolved in toluene (500 mL, 0.03 M) and Bu_2SnO (3.63 g, 14.6 mmol, 1.1 eq) was added to the solution. The mixture was refluxed for 2 hours and then cooled to 80 °C. PMBCl (2.35 mL, 17.2 mmol, 1.3 eq) and TBAB (5.13 g, 15.9 mmol, 1.2 eq) were added 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) to give the tite compound (7.62 g, 13.2 mmol, 100%, 8:1 mixture of regioisomers) as a slightly yellow oil. $[\alpha]_D^{25}$ = -54.2 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.53-7.49 (m, 2H, CH_{arom}); 7.34-7.18 (m, 7H, CH_{arom}); 6.87-6.76 (m, 4H, CH_{arom}); 5.44 (d, 1H, *J* = 1.6 Hz, H-1); 4.87 (d, 1H, *J* = 11.2 Hz, PhC*H*H); 4.65-4.60 (m, 3H, PhC*H*H, PhCH_2); 4.09 (s, 1H, H-2); 3.97 (dd, 1H, *J* = 3.2, 8.8 Hz, H-3); 3.77-3.71 (m, 4H, $CH_{3,PMB}$, H-5); 3.51 (t, 1H, *J* = 9.2 Hz, H-4); 3.16 (bs, 1H, 2-O*H*); 1.24 (d, 3H, *J* = 6.4 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 159.4, 155.9 ($C_{q,arom}$); 138.3, 138.2 (CH_{arom}); 138.2, 129.8 ($C_{q,arom}$); 128.4, 127.9, 127.8, 118.6, 113.9 (CH_{arom}); 97.0 (C-1); 84.7 (CI_{arom}); 81.7 (C-4); 79.7 (C-3); 75.4 (PhCH_2); 72.0 (PhCH_2); 68.3 (C-5); 64.7 (C-2); 55.2 ($CH_{3,PMB}$); 17.9 (C-6). IR (thin film, cm^{-1}): 1028, 1072, 1234, 1249, 1484, 1513, 2925, 3483. HRMS calculated for $C_{27}H_{29}IO_6Na$ 599.0907 $[M+Na]^+$; found 599.0909.

4-iodophenyl 2-*O*-methyl-3-*O*-(4-methoxybenzyl)-4-*O*-benzyl-α-L-rhamnopyranoside (16)



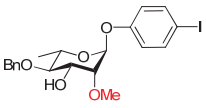
Compound **15** (6.22 g, 11.8 mmol, 1.0 eq) was dissolved in dry DMF (60 mL, 0.2 M) and MeI (1.47 mL, 23.7 mmol, 2.0 eq) was added to the solution. The mixture was cooled to 0 °C, and NaH (60%, 0.71 g, 17.8 mmol, 1.5 eq) was then added. The reaction mixture was warmed to rt while stirring for 3 hours. 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 4:1) gave the title compound (5.56 g, 9.4 mmol, 80%) as a pale oil. $[\alpha]_D^{25}$ = -103.1 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.61-7.57 (m, 2H, CH_{arom}); 7.38-7.26 (m, 7H, CH_{arom}); 6.90-6.86 (m, 2H, CH_{arom}); 6.82-6.78 (m, 2H, CH_{arom}); 5.46 (d, 1H, *J* = 1.6 Hz, H-1); 4.94 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.71-4.70 (m, 2H, PhCH_2); 4.62 (d, 1H, *J* = 10.8 Hz, PhCH*H*); 4.00 (dd, 1H, *J* = 3.2, 9.2 Hz, H-3); 3.81 (s, 3H, $CH_{3,PMB}$); 3.72-3.67 (m, 1H, H-5); 3.64-3.63 (m, 1H, H-2); 3.58-3.53 (m, 4H, H-4, OCH_3); 1.26 (d, 3H, *J* = 6.4 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 156.2, 138.6 ($C_{q,arom}$); 138.5 (CH_{arom}); 130.6 ($C_{q,arom}$); 129.7, 128.5, 128.1, 127.9, 118.7, 114.0 (CH_{arom}); 95.6 (C-1); 84.8 (CI_{arom}); 80.3 (C-4); 79.3 (C-3); 78.0 (C-2); 75.7, 72.4 (PhCH_2); 69.0 (C-5); 59.8 (OCH_3); 55.4 ($CH_{3,PMB}$); 18.1 (C-6). IR (thin film, cm^{-1}): 1098, 1139, 1233, 1249, 1484, 1513, 2924, 3462. HRMS calculated for $C_{28}H_{31}IO_6Na$ 613.1063 $[M+Na]^+$; found 613.1068.

4-iodophenyl 2,4-di-*O*-benzyl-3-*O*-(4-methoxybenzyl)-α-L-rhamnopyranoside (17)



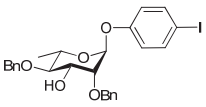
Compound **15** (7.37 g, 12.8 mmol, 1.0 eq) was dissolved in dry DMF (64 mL, 0.2 M) after which BnBr (3.0 mL, 25.6 mmol, 2 eq) and TBAI (0.47 g, 1.28 mmol, 0.1 eq) were added to the solution. The mixture was cooled to 0 °C, and NaH (60%, 0.77 g, 19.2 mmol, 1.2 eq) was added. The mixture was warmed to 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 (6.58 g, 9.82 mmol, 77%) as a pale oil. $[\alpha]_D^{25}$ = -50.1 ° (c = 0.8, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.56-7.51 (m, 2H, C*H*$_{arom}$); 7.41-7.26 (m, 12H, C*H*$_{arom}$); 6.90-6.85 (m, 2H, C*H*$_{arom}$); 6.75-6.71 (m, 2H, C*H*$_{arom}$); 5.39 (d, 1H, *J* = 2.0 Hz, H-1); 4.95 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.78 (dd, 2H, *J* = 12.4, 34.4 Hz, PhCH_2); 4.66 (m, 3H, PhCH*H*, PhCH_2); 4.00 (dd, 1H, *J* = 3.0, 9.0 Hz, H-3); 3.90-3.88 (m, 1H, H-2); 3.82 (s, 3H, C$H_{3,PMB}$); 3.70-3.63 (m, 2H, H-4, H-5); 1.27 (d, 3H, *J* = 6.0 Hz). ^{13}C-APT NMR (101 MHz) δ: 156.2, 138.6 (C$_{q,arom}$); 138.4 (*C*H$_{arom}$); 138.2, 130.6 (C$_{q,arom}$); 129.5, 128.6, 128.5, 128.1, 128.0, 127.9, 118.7, 113.9 (*C*H$_{arom}$); 96.4 (C-1); 84.7 (*C*I$_{arom}$); 80.4 (C-4); 79.6 (C-3); 75.6 (Ph*C*H$_2$); 74.7 (C-2); 73.2, 72.3 (Ph*C*H$_2$); 69.1 (C-5); 55.4 (*C*H$_{3,PMB}$); 18.2 (C-6). IR (thin film, cm^{-1}): 1029, 1137, 1233, 1248, 1484, 1513, 2921. HRMS calculated for $C_{34}H_{35}IO_6Na$ 689.1376 [M+Na]$^+$; found 689.1387.

4-iodophenyl 2-*O*-methyl-4-*O*-benzyl-α-L-rhamnopyranoside (5)



Compound **16** (2.48 g, 2.5 mmol, 1.0 eq) was dissolved in a mixture of DCM and HFIP (1:1, 25 mL, 0.1 M) after which a solution of HCl in HFIP (1.25 mL, 0.2 M, 0.1 eq) was added. After complete conversion of the starting material, 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 (1.17 g, 2.48 mmol, 100%) as a pale oil. Spectroscopic data were in accordance with those previously reported in the literature.[26]

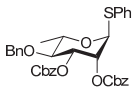
4-iodophenyl 2,4-di-*O*-benzyl-α-L-rhamnopyranoside (6)



Compound **17** (6.58 g, 9.8 mmol, 1.0 eq) was dissolved in a mixture of DCM and HFIP (1:1, 98 mL, 0.1 M) after which a solution of HCl in HFIP (4.9 mL, 0.2 M, 0.1 eq) was added. After complete conversion of the starting material, 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 4:1) gave the title compound (4.38 g, 8.0 mmol, 82%) as a pale oil. $[\alpha]_D^{25}$ = -51.5 ° (c =1.1, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.57-7.53 (m, 2H, C*H*$_{arom}$); 7.41-7.26 (m, 10H, C*H*$_{arom}$); 6.79-6.74 (m, 2H, C*H*$_{arom}$); 5.47 (d, 1H, *J* = 1.6 Hz, H-1); 4.90 (d, 1H, *J* = 11.2 Hz, PhC*H*H); 4.79 (d,1H, *J* = 11.6 Hz, PhC*H*H); 4.49-4.65 (m, 2H, PhCH*H*, PhCH*H*); 4.14-4.09 (m, 1H, H-3); 3.91-3.90 (m, 1H, H-2); 3.81-3.68 (m, 1H, H-5); 3.39 (t, 1H, *J* = 9.4 Hz, H-4); 2.33 (bs, 1H, 3-O*H*); 1.28 (d, 3H, *J* = 6.0 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 156.2, 138.5 (C$_{q,arom}$); 138.5 (*C*H$_{arom}$); 128.8, 128.6, 128.4, 128.2,

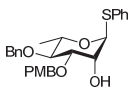
128.1, 128.0, 118.7 (*C*H$_{arom}$); 95.3 (C-1); 84.7 (*C*I$_{arom}$); 82.1 (C-4); 78.3 (C-2); 75.3, 73.5 (PhCH$_2$); 71.6 (C-3); 68.3 (C-5); 18.2 (C-6). IR (thin film, cm^{-1}): 1020, 1027, 1040, 1075, 1130, 1232, 1455, 1484, 2931, 3534. HRMS calculated for $C_{26}H_{27}IO_5Na$ 569.0801 [M+Na]$^+$; found 569.0806.

Phenyl 2,3-di-*O*-benzyloxycarbonyl-4-*O*-benzyl-1-thio-α-L-rhamnopyranoside (7)



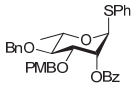
Compound **18** (376 mg, 1.09 mmol, 1.0 eq) was dissolved in DCM (11 mL, 0.1 M) and DMAP (0.66 g, 5.43 mmol, 5.0 eq) was added to the solution. The mixture was cooled to 0 °C and CbzCl (0.61 mL, 4.34 mmol, 4.0 eq) was slowly added. The reaction was allowed to stir for 4 hours after while slowly warming to rt. The reaction was quenched by addition of 1 M HCl, and the organic layer was washed with 1M HCl, 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 (0.66 g, 1.07 mmol, 99%) as a clear oil. $[\alpha]_D^{25}$ = -48.3 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.47-7.44 (m, 2H, C*H*$_{arom}$); 7.40-7.24 (m, 18H, C*H*$_{arom}$); 5.50 (d, 1H, *J* = 1.2 Hz, H-1); 5.46 (dd, 1H, *J* = 2.0, 3.2 Hz, H-2); 5.22-5.14 (m, 5H, H-3, PhC*H*$_2$, PhC*H*$_2$); 4.65 (dd, 2H, *J* = 11.0, 56.2 Hz, PhC*H*$_2$); 4.28 (dq, 1H, *J* = 3.2, 6.4 Hz, H-5); 3.63 (t, 1H, *J* = 9.6 Hz, H-4); 1.33 (d, 3H, *J* = 6.4 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 154.5, 154.3 (*C*O$_{Cbz}$); 137.9, 135.1, 134.8, 133.5 (C$_{q,arom}$); 132.1, 129.3, 128.8, 128.7, 128.6, 128.5, 128.0, 128.0, 128.0 (*C*H$_{arom}$); 85.5 (C-1); 78.7 (C-4); 76.3 (C-3); 75.6 (Ph*C*H$_2$); 75.5 (C-2); 70.4, 70.2 (Ph*C*H$_2$); 69.3 (C-5); 17.8 (C-6). IR (thin film, cm^{-1}): 1029, 1036, 1100, 1241, 1275, 1384, 1455, 1751. HRMS calculated for $C_{35}H_{34}O_8SNa$ 637.18666 [M+Na]$^+$; found 637.18633.

Phenyl 3-*O*-(4-methoxybenzyl)-4-*O*-benzyl-1-thio-α-L-rhamnopyranoside (19)



Compound **18** (16.3 g, 47 mmol, 1.0 eq) was dissolved in toluene (500 mL, 0.09 M) and Bu_2SnO (12.9 g, 51.7 mmol, 1.1 eq) was added to the solution. The mixture was refluxed for 2 hours and then cooled to 80 °C. PMBCl (8.31 mL, 61.1 mmol, 1.3 eq) and TBAB (18.2 g, 56.4 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 (16.8 g, 36.1 mmol, 77%) as a slightly yellow oil. The product was used in the next step without further analysis.

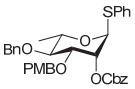
Phenyl 2-*O*-benzoyl-3-*O*-(4-methoxybenzyl)-4-*O*-benzyl-1-thio-α-L-rhamnopyranoside (1)



Compound **19** (8.52 g, 18.3 mmol, 1.0 eq) was dissolved in DCM (50 mL, 0.4 M) and pyridine (2.95 mL, 36.5 mmol, 2.0 eq) was added to the solution. The mixture was cooled to 0 °C and BzCl (4.24 mL, 36.5 mmol, 2.0 eq) was added. The reaction was allowed to stir for 4 hours while slowly warming to RT. The reaction was quenched by addition of H_2O, and the product was extracted with Et_2O (3x). The combined organic layers were washed with 1 M HCl, 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 (10.4 g, 18.3 mmol, 100%) as a clear oil. $[\alpha]_D^{25}$ = -39.4 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 8.08-8.06 (m, 2H, C*H*$_{arom}$); 7.50-7.11 (m, 16H, C*H*$_{arom}$); 6.81 (d, 2H, *J* = 8.8 Hz, C*H*$_{arom}$); 5.83 (d, 1H, *J* = 1.6 Hz, H-2); 5.54 (s, 1H, H-1); 4.93 (d, 1H, *J* = 11.2 Hz, PhC*H*H); 4.73 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.65 (d, 1H, *J* = 11.2 Hz, PhCH*H*); 4.52 (d, 1H, *J* = 10.8 Hz, PhCH*H*); 4.30-4.27 (m, 1H, H-5); 4.00 (dd, 1H, *J* = 3.2, 9.2 Hz, H-3); 3.76 (s, 3H, C*H*$_{3,PMB}$); 3.60 (t, 1H, *J* = 9.4 Hz, H-4); 1.38 (d, 3H, *J* = 6.0 Hz, H-6).

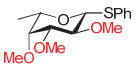
^{13}C-APT NMR (101 MHz) δ: 165.8 (CO_{Bz}); 159.4, 138.4, 134.0 ($C_{q,arom}$); 133.3, 131.8, 130.0, 129.9 (CH_{arom}); 129.8 ($C_{q,arom}$); 129.1, 128.5, 128.4, 128.2, 127.8, 127.7, 113.8 (CH_{arom}); 86.3 (C-1); 80.2 (C-4); 78.1 (C-3); 75.6, 71.4 (PhCH_2); 71.2 (C-2); 69.2 (C-5); 18.2 (C-6). IR (thin film, cm^{-1}): 1035, 1070, 1096, 1251, 1268, 1515, 1722. HRMS calculated for $C_{34}H_{34}O_6SNa$ 593.1974 [M+Na]$^+$; found 593.1976.

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



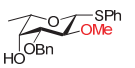
Compound **19** (8.16 g, 17.5 mmol, 1.0 eq) was dissolved in DCM (125 mL, 0.14 M) and DMAP (4.28 g, 35 mmol, 2.0 eq) was added to the solution. The mixture was cooled to 0 °C and CbzCl (5.0 mL, 35 mmol, 2.0 eq) was slowly added. The reaction was allowed to stir for 4 hours after while slowly warming to rt. The reaction was quenched by addition of 1 M HCl, and the organic layer was washed with 1M HCl, 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 (7.96 g, 13.3 mmol, 76%) as a clear oil. $[\alpha]_D^{25}$ = -61.5 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.46-7.42 (m, 2H, C*H*$_{arom}$); 7.39-7.24 (m, 15H, C*H*$_{arom}$); 6.85-6.82 (m, 2H, C*H*$_{arom}$); 5.50 (d, 1H, *J* = 1.6 Hz, H-1); 5.40 (dd, 1H, *J* = 1.6, 3.2 Hz, H-2); 5.17 (s, 2H, C$H_{2,Cbz}$); 4.91 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.68 (d, 1H, *J* = 11.0 Hz, PhC*H*H); 4.60 (d, 1H, *J* = 10.8 Hz, PhCH*H*); 4.52 (d, 1H, *J* = 11.0 Hz, PhCH*H*); 4.21-4.17 (m, 1H, H-5); 3.88 (dd, 1H, *J* = 3.2, 9.6 Hz, H-3); 3.80 (s, 3H, C$H_{3,PMB}$); 3.52 (t, 1H, *J* = 9.6 Hz, H-4); 1.32 (d, 3H, *J* = 6.4 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 159.4 ($C_{q,arom}$); 154.8 (CO_{Cbz}); 138.5, 135.1, 133.9 ($C_{q,arom}$); 131.9 (CH_{arom}); 129.9 ($C_{q,arom}$); 129.9, 129.2, 128.7, 128.7, 128.5, 128.5, 128.1, 127.9, 127.8 (CH_{arom}); 86.0 (C-1); 80.0 (C-4); 78.0 (C-3); 75.7 (PhCH_2); 74.8 (C-2); 71.7, 70.1 (PhCH_2); 69.3 (C-5); 55.4 ($CH_{3,PMB}$); 17.9 (C-6). IR (thin film, cm^{-1}): 1027, 1086, 1103, 1251, 1382, 1514, 1747. HRMS calculated for $C_{35}H_{36}O_7SNa$ 623.2079 [M+Na]$^+$; found 623.2074.

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



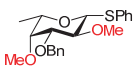
Compound **20** (0.55 g, 2.15 mmol, 1.0 eq) was dissolved in dry DMF (21.5 mL, 0.1 M) and MeI (0.8 mL, 12.9 mmol, 6.0 eq) was added to the solution. The mixture was cooled to 0 °C, and NaH (60%, 0.31 g, 7.74 mmol, 3.6 eq) was then added. The reaction mixture was warmed to rt while stirring for 2 hours after which it was quenched by addition of H_2O. The aqueous layer was extracted with Et_2O (3x) and 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 (0.56 g, 1.88 mmol, 87%) as a white amorphous solid. Spectroscopic data were in accordance with those previously reported in the literature.[37]

Phenyl 2-*O*-methyl-3-*O*-benzyl-1-thio-α-L-fucopyranoside (22)



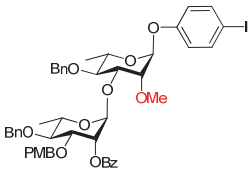
Compound **21** (1.18 g, 4.36 mmol, 1.0 eq) was dissolved in MeCN (44 mL, 0.1 M). To this solution Bu_2SnCl_2 (0.134 g, 0.44 mmol, 0.1 eq), TBABr (0.142 g, 0.44 mmol, 0.1 eq), BnBr (1.03 mL, 8.72 mmol, 2 eq) and K_2CO_3 (0.90 g, 6.54 mmol, 1.5 eq) were added and the resulting mixture was stirred for 16 hours at 80 °C. The mixture was then filtered over celite and concentrated *in vacuo*. Purification by means of column chromatography (*n*-pentane-Et_2O 6:4) gave the title compound (1.54 g, 4.22 mmol, 97%) as a pale oil. The product was used in the next step without further analysis.

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



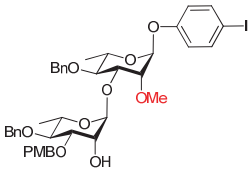
Compound **22** (1.54 g, 4.22 mmol, 1.0 eq) was dissolved in dry DMF (30 mL, 0.14 M) and MeI (0.54 mL, 8.72 mmol, 2.0 eq) was added to the solution. The mixture was cooled to 0 °C, and NaH (60%, 0.26 g, 6.54 mmol, 1.5 eq) was then added. The reaction mixture was warmed to rt while stirring for 3 hours after which it was quenched by addition of H_2O. The aqueous layer was extracted with Et_2O (3x) and 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 (1.36 g, 3.63 mmol, 86%) as a white amorphous solid. $[\alpha]_D^{25}$ = -17.7 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.55-7.53 (m, 2H, C*H*$_{arom}$); 7.41-7.18 (m, 6H, C*H*$_{arom}$); 4.78-4.69 (m, 2H, PhC*H*$_2$); 4.47 (d, 1H, *J* = 9.2 Hz, H-1); 3.62-3.60 (m, 6H, OC*H*$_3$); 3.53-3.42 (m, 3H, H-2, H-3, H-5); 3.31 (d, 1H, *J* = 2.8 Hz, H-4); 1.29 (d, 3H, *J* = 6.4 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 138.4, 134.5 (C$_{q,arom}$); 131.6, 128.8, 128.5, 127.8, 127.7, 127.1 (*C*H$_{arom}$); 87.7 (C-1); 83.9 (C-3); 79.6 (C-4); 79.3 (C-2); 74.5 (C-5); 72.7 (PhCH$_2$); 61.8, 61.2 (OCH$_3$); 16.9 (C-6). IR (thin film, cm^{-1}): 1027, 1045, 1085, 1102, 1128, 1164, 1194, 1440, 1455, 1480. HRMS calculated for $C_{21}H_{26}O_4SNa$ 397.1495 $[M+Na]^+$; found 397.1445.

4-iodophenyl 2-*O*-methyl-3-*O*-(2-*O*-benzoyl-3-*O*-(4-methoxybenzyl)-4-*O*-benzyl-α-L-rhamnopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranoside (25)



Prepared according to general procedure A using donor **1** (856 mg, 1.5 mmol, 1.5 eq) and acceptor **5** (470 mg, 1.0 mmol, 1.0 eq). The title compound was obtained after column chromatography (*n*-pentane-Et_2O 4:1) as a slightly yellow oil (894 mg, 0.64 mmol, 64%). $[\alpha]_D^{25}$ = -38.8 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 8.08-8.06 (m, 2H, C*H*$_{arom}$); 7.61-7.53 (m, 3H, C*H*$_{arom}$); 7.47 (t, 2H, *J* = 7.6 Hz, C*H*$_{arom}$); 7.37-7.17 (m, 13H, C*H*$_{arom}$); 6.83-6.79 (m, 2H, C*H*$_{arom}$); 6.75-6.72 (m, 2H, C*H*$_{arom}$); 5.75 (dd, 1H, *J* = 1.8, 3.0 Hz, H-2'); 5.48 (d, 1H, *J* = 1.6 Hz, H-1); 5.24 (d, 1H, *J* = 1.6 Hz, H-1'); 4.93 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.85 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.69-4.58 (m, 3H, PhC*H*H, PhCH*H*, PhCH*H*); 4.45 (d, 1H, *J* = 10.8 Hz, PhCH*H*); 4.23 (dd, 1H, *J* = 3.2, 9.2 Hz, H-3); 4.10-4.03 (m, 2H, H-3', H-5'); 3.74-3.66 (m, 5H, H-2, H-5, C*H*$_{3,PMB}$); 3.58-3.52 (m, 5H, H-4, H-4', OC*H*$_3$); 1.30 (d, 3H, *J* = 6.0 Hz, H-6'); 1.23 (d, 3H, *J* = 6.4 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 165.7 (*C*O$_{Bz}$); 159.2, 156.2, 138.6 (C$_{q,arom}$); 138.5 (*C*H$_{arom}$); 138.0 (C$_{q,arom}$); 133.3 (*C*H$_{arom}$); 130.2, 130.1 (C$_{q,arom}$); 130.0, 129.7, 128.6, 128.5, 128.5, 128.3, 128.2, 128.0, 127.8, 118.7, 113.8 (*C*H$_{arom}$); 100.0 (C-1'); 94.9 (C-1); 84.9 (*C*I$_{arom}$); 80.1 (C-4); 80.1 (C-4'); 80.0 (C-3); 78.9 (C-3'); 75.7, 75.5, 71.3 (PhCH$_2$); 69.7 (C-2); 69.1 (C-5); 68.6 (C-5'); 59.1, 55.3 (OCH$_3$); 18.5 (C-6'); 18.1 (C-6). IR (thin film, cm^{-1}): 1027, 1044, 1098, 1139, 1178, 1234, 1249, 1269, 1484, 1513, 1722. HRMS calculated for $C_{48}H_{51}IO_{11}Na$ 953.2374 $[M+Na]^+$; found 953.2390.

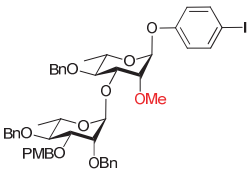
4-iodophenyl 2-*O*-methyl-3-*O*-(3-*O*-(4-methoxybenzyl)-4-*O*-benzyl-α-L-rhamnopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranoside (27)



Compound **25** (0.55 g, 0.59 mmol, 1.0 eq) was dissolved in THF (3 mL, 0.2 M). A small piece of sodium was dissolved in MeOH and 3 mL of this solution was added. The reaction was stirred for 2 hours after which it was quenched with sat. aq. NH_4Cl and extracted with Et_2O (3x). The organic

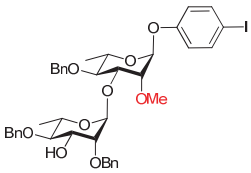
layers were combined, washed with brine, dried with $MgSO_4$ and concentrated *in vacuo*. Purification by means of column chromatography (*n*-pentane-Et_2O 4:6) gave the title compound (394 mg, 0.48 mmol, 81%) as a pale oil. $[\alpha]_D^{25}$ = -87.1 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.58-7.53 (m 2H, C*H*$_{arom}$); 7.37-7.22 (m, 12H, C*H*$_{arom}$); 6.85-6.80 (m, 4H, C*H*$_{arom}$); 5.47 (s, 1H, H-1); 5.15 (s, 1H, H-1'); 4.89 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.74 (d, 1H, *J* = 11.2 Hz, PhC*H*H); 4.65 (d, 1H, *J* = 10.8 Hz, PhCH*H*); 4.58-4.53 (m, 3H, PhCH*H*, PhC*H*$_2$); 4.17 (dd, 1H, *J* = 3.2, 9.6 Hz, H-3); 4.03 (s, 1H, H-2'); 3.98-3.94 (m, 1H, H-5'); 3.88 (dd, 1H, *J* = 3.0, 9.0 Hz, H-3'); 3.71-3.68 (m, 5H, H-2, H-5, C*H*$_{3,PMB}$); 3.55-3.45 (m, 5H, H-4, H-4', OC*H*$_3$); 2.47 (bs, 1H, 2-O*H*); 1.34 (d, 3H, *J* = 6.4 Hz, H-6'); 1.22 (d, 3H, *J* = 6.4 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 159.5, 156.2, 138.5 (C$_{q,arom}$); 138.4 (*C*H$_{arom}$); 138.1, 130.1 (C$_{q,arom}$); 129.6, 128.6, 128.5, 128.1, 128.0, 128.0, 127.9, 118.7, 114.0 (*C*H$_{arom}$); 101.5 (C-1'); 99.4 (C-1); 84.9 (*C*I$_{arom}$); 80.2 (C-4); 80.0 (C-2); 80.0 (C-4'); 79.6 (C-3'); 79.0 (C-3); 75.5, 75.5 (Ph*C*H$_2$); 71.9 (Ph*C*H$_2$); 69.1 (C-2'); 69.0 (C-5); 68.2 (C-5'); 59.0 (O*C*H$_3$); 55.3 (*C*H$_{3,PMB}$); 18.2 (C-6'); 18.0 (C-6). IR (thin film, cm^{-1}): 1029, 1042, 1080, 1099, 1138, 1234, 1249, 1269, 1484, 1515, 3503. HRMS calculated for $C_{41}H_{47}IO_{10}Na$ 849.2112 $[M+Na]^+$; found 849.2128.

4-iodophenyl 2-*O*-methyl-3-*O*-(2,4-di-*O*-benzyl-3-*O*-(4-methoxybenzyl)-α-L-rhamnopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranoside (29)



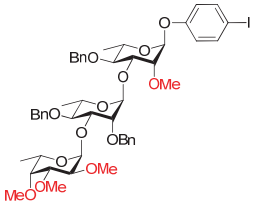
Compound **27** (0.34 g, 0.41 mmol, 1.0 eq) was dissolved in DMF (2 mL, 0.2 M) after which BnBr (0.1 mL, 0.82 mmol, 2.0 eq) and TBAI (15 mg, 0.04 mmol, 0.1 eq) were added to the solution. The mixture was cooled to 0 °C and NaH (60%, 33 mg, 0.82 mmol, 2.0 eq) was added. After stirring for 90 minutes the reaction was quenched by addition of H_2O. The aqueous layer was extracted with Et_2O (3x) and 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 (0.39 g, 0.41 mmol, 100%) as a pale oil. $[\alpha]_D^{25}$ = -63.5 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.59-7.53 (m, 2H, C*H*$_{arom}$); 7.45-7.16 (m, 17H, C*H*$_{arom}$); 6.84-6.79 (m, 4H, C*H*$_{arom}$); 5.46 (s, 1H, H-1); 5.14 (s, 1H, H-1'); 4.96 (d, 1H, *J* = 11.2 Hz, PhC*H*H); 4.67-4.64 (m, 2H, PhCH*H*, PhC*H*H); 4.57-4.48 (m, 5H, PhCH*H*, PhC*H*$_2$); 4.18-4.15 (m, 1H, H-3); 3.95-3.90 (m, 2H, H-3', H-5'); 3.79 (s, 1H, H-2'); 3.75-3.62 (m, 6H, C*H*$_{3,PMB}$, H-2, H-5, H-4'); 3.50-3.46 (m, 4H, H-4, OC*H*$_3$); 1.37 (d, 3H, *J* = 6.0 Hz, H-6'); 1.20 (d, 3H, *J* = 6.0 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 159.2, 156.3, 138.8 (C$_{q,arom}$); 138.4 (*C*H$_{arom}$) 138.4, 138.3, 130.7 (C$_{q,arom}$); 129.3, 128.6, 128.4, 128.4, 128.4, 128.1, 127.8, 127.7, 127.6, 127.6, 127.3, 118.7, 113.8 (*C*H$_{arom}$); 100.5 (C-1'); 94.9 (C-1); 84.9 (*C*I$_{arom}$); 80.5 (C-4'); 80.1 (C-2, C-4); 79.6 (C-3'); 78.8 (C-3); 75.9 (C-2'); 75.4, 75.1, 72.7, 71.9 (Ph*C*H$_2$); 69.0 (C-5); 68.9 (C-5'); 59.1 (O*C*H$_3$); 55.3 (*C*H$_{3,PMB}$); 18.3 (C-6'); 18.0 (C-6). IR (thin film, cm^{-1}): 1030, 1058, 1099, 1233, 1248, 1454, 1484, 1513. HRMS calculated for $C_{48}H_{53}IO_{10}Na$ 939.2581 $[M+Na]^+$; found 939.2593.

4-iodophenyl 2-*O*-methyl-3-*O*-(2,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranoside (31)



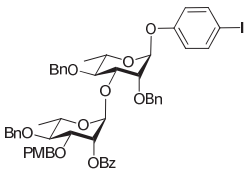
Compound **29** (0.39 g, 0.42 mmol, 1.0 eq) was dissolved in a mixture of DCM and HFIP (1:1, 4.2 mL, 0.1 M) after which a solution of HCl in HFIP (0.21 mL, 0.2 M, 0.1 eq) was added. After complete conversion of the starting material, indicated by a dark purple colour, the reaction was quenched by addition 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 (0.28 g, 0.35 mmol, 84%) as a pale oil. Spectroscopic data were in accordance with those previously reported in the literature.[26]

4-iodophenyl 2-*O*-methyl-3-*O*-(2,4-di-*O*-benzyl-3-*O*-(2,3,4-tri-*O*-methyl-α-L-fucopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranoside (35)



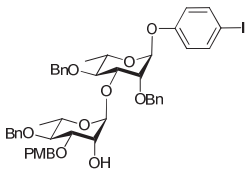
Prepared according to glycosylation procedure A using donor **3** (78 mg, 0.263 mmol, 1.5 eq) and acceptor **31** (139 mg, 0.175 mmol, 1.0 eq). The title compound was obtained after column chromatography (*n*-pentane-Et_2O 1:1) as a pale oil (120 mg, 0.122 mmol, 70%, α/ß 5:1). Spectroscopic data were in accordance with those previously reported in the literature.[26]

4-iodophenyl 2,4-di-*O*-benzyl-3-*O*-(2-*O*-benzoyl-3-*O*-(4-methoxybenzyl)-4-*O*-benzyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (26)



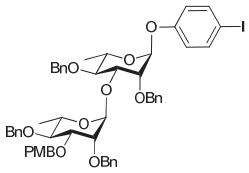
Prepared according to glycosylation procedure A using donor **1** (0.67 g, 1.17 mmol) and acceptor **6** (0.43 g, 0.78 mmol) the title compound was obtained after column chromatography (*n*-pentane-Et_2O 4:1) as a slightly yellow oil (0.60 g, 0.60 mmol, 77%). $[\alpha]_D^{25}$ = -26.7 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 8.06 (d, 2H, *J* = 7.2 Hz, C*H*$_{arom}$); 7.61-7.45 (m, 6H, C*H*$_{arom}$); 7.39-7.17 (m, 16H, C*H*$_{arom}$); 6.76-6.70 (m, 4H, C*H*$_{arom}$); 5.75 (d, 1H, *J* = 2.0 Hz, H-2'); 5.40 (d, 1H, *J* = 1.6 Hz, H-1); 5.28 (s, 1H, H-1'); 4.93 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.86 (d, 1H, *J* = 10.4 Hz, PhC*H*H); 4.79-4.61 (m, 5H, PhCH*H*, PhCH*H*, PhC*H*H, PhC*H*$_2$); 4.45 (d, 1H, *J* = 11.2 Hz, PhCH*H*); 4.28 (dd, 1H, *J* = 2.8, 8.8 Hz, H-3); 4.06 (dd, 1H, *J* = 3.2, 9.2 Hz, H-3'); 3.95-3.89 (m, 2H, H-2, H-5'); 3.74-3.66 (m, 5H, H-4, H-5, C*H*$_{3,PMB}$); 3.53 (t, 1H, *J* = 9.4 Hz, H-4'); 1.33 (d, 3H, *J* = 6.4 Hz, H-6'); 1.26 (d, 3H, *J* = 5.2 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 165.7 (*C*O$_{Bz}$); 159.3, 156.1, 138.8 (C$_{q,arom}$); 138.4 (*C*H$_{arom}$); 137.9 (C$_{q,arom}$); 133.3 (*C*H$_{arom}$); 130.1 (C$_{q,arom}$); 130.1, 130.0, 129.8, 128.7, 128.6, 128.5, 128.4, 128.2, 128.0, 128.0, 127.9, 127.9, 127.7, 118.7, 113.8 (*C*H$_{arom}$); 99.6 (C-1'); 95.9 (C-1); 84.8 (*C*I$_{arom}$); 80.7 (C-4); 80.1 (C-4'); 77.6 (C-3'); 77.4 (C-2); 77.3 (C-3); 75.6, 75.3, 73.2, 71.3 (Ph*C*H$_2$); 69.5 (C-2'); 69.3 (C-5); 68.7 (C-5'); 55.3 (*C*H$_{3,PMB}$); 18.4 (C-6'); 18.1 (C-6). IR (thin film, cm^{-1}): 1028, 1097, 1139, 1233, 1249, 1269, 1484, 1722. HRMS calculated for $C_{54}H_{55}IO_{11}Na$ 1029.2687 $[M+Na]^+$; found 1029.2698.

4-iodophenyl 2,4-di-*O*-benzyl-3-*O*-(3-*O*-(4-methoxybenzyl)-4-*O*-benzyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (28)



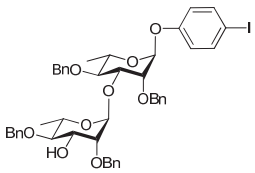
Compound **26** (0.60 g, 0.60 mmol, 1.0 eq) was dissolved in THF (3 mL, 0.2 M). A small piece of sodium was dissolved in MeOH and 3 mL of this solution was added. The reaction was stirred for 2 hours after which it was quenched with sat. aq. NH_4Cl and extracted with Et_2O (3x). The organic layers were 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 (465 mg, 0.52 mmol, 86%) as a pale oil. $[\alpha]_D^{25}$ = -76.7 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.55-7.51 (m, 2H, C*H*$_{arom}$); 7.39-7.22 (m, 17H, C*H*$_{arom}$); 6.82-6.75 (m, 4H, C*H*$_{arom}$); 5.40 (d, 1H, *J* = 1.6 Hz, H-1); 5.20 (s, 1H, H-1'); 4.90 (d, 1H, *J* = 11.2 Hz, PhC*H*H); 4.78-4.70 (m, 3H, PhC*H*H, PhC*H*$_2$); 4.65-4.55 (m, 4H, PhCH*H*, PhCH*H*, PhC*H*$_2$); 4.23 (dd, 1H, *J* = 3.2, 9.2 Hz, H-3); 4.00 (dd, 1H, *J* = 1.6, 2.8 Hz, H-2'); 3.90-3.83 (m, 3H, H-2, H-3', H-5'); 3.74-3.71 (m, 4H, H-5, C*H*$_{3,PMB}$); 3.64 (t, 1H, *J* = 9.4 Hz, H-4); 3.46 (t, 1H, *J* = 9.2 Hz, H-4'); 2.65 (bs, 1H, 2-O*H*); 1.28-1.25 (m, 6H, H-6, H-6'). ^{13}C-APT NMR (101 MHz) δ: 159.5, 156.1, 138.7 (C$_{q,arom}$); 138.4 (*C*H$_{arom}$); 138.0, 137.9, 130.0 (C$_{q,arom}$); 129.7, 128.7, 128.6, 128.4, 128.0, 128.0, 127.8, 127.7, 127.5, 118.8, 114.0 (*C*H$_{arom}$); 101.0 (C-1'); 95.9 (C-1); 84.9 (*C*I$_{arom}$); 80.8 (C-4); 79.9 (C-4'); 79.5 (C-3'); 77.5 (C-2, C-3); 75.5, 75.3, 73.2, 71.8 (Ph*C*H$_2$); 69.2 (C-5); 69.0 (C-2'); 68.2 (C-5'); 55.3 (*C*H$_{3,PMB}$); 18.1 (C-6); 18.1 (C-6'). IR (thin film, cm^{-1}): 1028, 1098, 1139, 1233, 1249, 1268, 1454, 1484, 1513, 3482. HRMS calculated for $C_{47}H_{51}IO_{10}Na$ 925.2425 $[M+Na]^+$; found 925.2437.

4-iodophenyl 2,4-di-*O*-benzyl-3-*O*-(2,4-di-*O*-benzyl-3-*O*-(4-methoxybenzyl)-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (30)



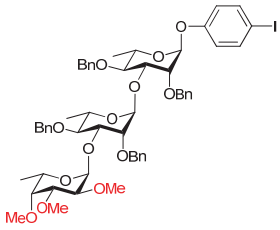
Compound **28** (0.50 g, 0.55 mmol, 1.0 eq) was dissolved in dry DMF (5.5 mL, 0.1 M) and BnBr (0.13 mL, 1.1 mmol, 2.0 eq) and TBAI (22 mg, 0.06 mmol, 0.1 eq) were added to the solution. The mixture was cooled to 0 °C, and NaH (60%, 44 mg, 1.1 mmol, 2.0 eq) was then added. The reaction mixture was warmed to rt while stirring for 2 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 7:3) gave the title compound (0.407 g, 0.50 mmol, 90%) as a pale oil. $[\alpha]_D^{25}$ = -54.2 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.55-7.52 (m, 2H, C*H*$_{arom}$); 7.39-7.20 (m, 22H, C*H*$_{arom}$); 6.78-6.75 (m, 4H, C*H*$_{arom}$); 5.38 (d, 1H, *J* = 2.0 Hz, H-1); 5.19 (s, 1H, H-1'); 4.97 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.77-4.46 (m, 9H, PhCH*H*, PhC*H*$_2$); 4.23 (dd, 1H, *J* = 3.0, 9.4 Hz, H-3); 3.92-3.83 (m, 3H, H-2', H-3', H-5'); 3.75-3.70 (5H, H-2, H-5, C*H*$_{3,PMB}$); 3.64-3.61 (m, 2H, H-4, H-4'); 1.31 (d, 3H, *J* = 6.4 Hz, H-6'); 1.21 (d, 3H, *J* = 6.0 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 159.2, 156.1, 139.0 (C$_{q,arom}$); 138.5 (*C*H$_{arom}$); 138.4, 138.3, 137.9, 130.7 (C$_{q,arom}$); 129.4, 128.6, 128.6, 128.4, 128.3, 128.0, 127.9, 127.8, 127.7, 127.6, 127.2, 118.7, 113.8 (*C*H$_{arom}$); 100.0 (C-1'); 96.0 (C-1); 84.8 (*C*I$_{arom}$); 80.6 (C-4'); 80.5 (C-4); 79.5 (C-3'); 77.6 (C-2', C-3); 75.8 (C-2); 75.2, 74.9, 73.2, 72.7, 72.0 (Ph*C*H$_2$); 69.2 (C-5); 68.9 (C-5'); 55.3 (*C*H$_{3,PMB}$); 18.3 (C-6'); 18.1 (C-6). IR (thin film, cm^{-1}): 1029, 1041, 1097, 1174, 1233, 1247, 1454, 1484, 1513. HRMS calculated for $C_{54}H_{57}IO_{10}Na$ 1015.2894 $[M+Na]^+$; found 1015.2900.

4-iodophenyl 2,4-di-*O*-benzyl-3-*O*-(2,4-di-*O*-benzyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (32)



Compound **30** (0.50 g, 0.50 mmol, 1.0 eq) was dissolved in a mixture of DCM and HFIP (1:1, 5 mL, 0.1 M) after which a solution of HCl in HFIP (0.25 mL, 0.2 M, 0.1 eq) was added. After complete conversion of the starting material, 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 (0.40 g, 0.46 mmol, 91%) as a pale oil. $[\alpha]_D^{25}$ = -51.7 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.55-7.53 (m, 2H, CH_{arom}); 7.40-7.22 (m, 18H, CH_{arom}); 7.16-7.14 (m, 2H, CH_{arom}); 6.79-6.77 (m, 2H, CH_{arom}); 5.41 (d, 1H, *J* = 2.0 Hz, H-1); 5.24 (s, 1H, H-1'); 4.91 (d, 1H, *J* = 11.4 Hz, PhC*H*H); 4.81-4.71 (m, 4H, PhCH_2); 4.64 (d, 1H, *J* = 11.4 Hz, PhCH*H*); 4.33 (d, 1H, *J* = 11.6 Hz, PhC*H*H); 4.28 (dd, 1H, *J* = 3.0, 9.4 Hz, H-3); 4.12 (d, 1H, *J* = 11.6 Hz, PhCH*H*); 4.00-3.88 (m 1H, H-3'); 3.83-3.68 (m, 5H, H-2, H-2', H-5, H-5', H-4); 3.33 (t, 1H, *J* = 9.2 Hz, H-4'); 2.31 (bs, 1H, 3-O*H*); 1.30 (d, 3H, *J* = 6.0 Hz, H-6'); 1.26 (d, 3H, *J* = 6.0 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 156.1, 138.8, 138.4 ($C_{q,arom}$); 138.4 (*C*H$_{arom}$); 137.8 ($C_{q,arom}$); 128.6, 128.6, 128.5, 128.4, 128.0, 127.9, 127.9, 127.8, 127.7, 127.7, 126.9, 118.7 (*C*H$_{arom}$); 99.0 (C-1'); 96.0 (C-1); 84.9 (*C*I$_{arom}$); 82.2 (C-4'); 80.8 (C-4); 79.1 (C-2'); 77.5 (C-2, C-3); 75.0, 74.9, 73.2, 72.6 (Ph*C*H$_2$); 71.7 (C-3'); 69.3 (C-5); 68.0 (C-5'); 18.2 (C-6'); 18.1 (C-6). IR (thin film, cm^{-1}): 1028, 1043, 1097, 1136, 1231, 1454, 1484, 3564. HRMS calculated for $C_{46}H_{49}IO_9Na$ 895.2319 $[M+Na]^+$; found 895.2335.

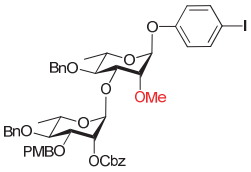
4-iodophenyl 2,4-di-*O*-benzyl-3-*O*-(2,4-di-*O*-benzyl-3-*O*-(2,3,4-tri-*O*-methyl-α-L-fucopyranosyl)-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (37)



Prepared according to glycosylation procedure B using donor **3** (52 mg, 0.17 mmol, 1.5 eq) and acceptor **32** (0.10 g, 0.12 mmol, 1.0 eq). The title compound was obtained after column chromatography (DCM-EtOAc 19:1) as a slightly yellow oil (0.11 g, 0.10 mmol, 89%, α:ß 4:1). $[\alpha]_D^{25}$ = -86.2 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.56-7.53 (m, 2H, CH_{arom}); 7.41 (d, 2H, *J* = 7.2 Hz, CH_{arom}); 7.34-7.20 (m, 18H, CH_{arom}); 6.80-6.78 (m, 2H, CH_{arom}); 5.44 (d, 1H, *J* = 1.6 Hz, H-1); 5.29 (H-1'); 5.20 (s, 1H, H-1''); 5.19 (d, 1H, *J* = 11.6 Hz, PhC*H*H); 4.85 (d, 1H, *J* = 11.8 Hz, PhC*H*H); 4.78 (s, 2H, PhCH_2); 4.72 (d, 1H, *J* = 11.8 Hz, PhCH*H*); 4.58 (d, 1H, *J* = 11.6 Hz, PhCH*H*); 4.47 (d, 1H, *J* = 12.2 Hz, PhC*H*H); 4.30 (dd, 1H, *J* = 2.8, 9.2 Hz, H-3); 4.15 (d, 1H, *J* = 12.2 Hz, PhCH*H*); 4.10 (dd, 1H, *J* = 3.0, 9.4 Hz, H-3'); 3.93 (dd, 1H, *J* = 2.0, 2.8 Hz, H-2); 3.88-3.84 (m, 1H, H-5'); 3.80-3.67 (m, 4H, H-2', H-5, H-4, H-5''); 3.61 (t, 1H, *J* = 9.2 Hz, H-4'); 3.55-3.50 (m, 8H, H-2'', H-4'', OCH_3); 3.28 (s, 3H, OCH_3); 3.21 (s, 1H, H-3''); 1.29 (d, 3H, *J* = 6.0 Hz, H-6'); 1.24 (d, 3H, *J* = 6.0 Hz, H-6); 1.02 (d, 3H, *J* = 6.4 Hz, H-6''). ^{13}C-APT NMR (101 MHz) δ: 156.1, 139.3, 138.5, 138.5 ($C_{q,arom}$); 138.4 (*C*H$_{arom}$); 137.8 ($C_{q,arom}$); 128.7, 128.5, 128.3, 128.2, 128.0, 127.9, 127.7, 127.5, 127.3, 127.3, 126.9, 118.7 (*C*H$_{arom}$); 99.6 (C-1''); 99.0 (C-1'); 95.9 (C-1); 84.8 (*C*I$_{arom}$); 80.5 (C-4''); 80.4 (C-4); 80.0 (C-4'); 79.2 (C-3'); 78.8 (C-2'); 78.0 (C-3, C-3''); 77.9 (C-2''); 77.8 (C-2); 74.8, 74.6, 73.2, 71.4 (Ph*C*H$_2$); 69.3 (C-5); 68.9 (C-5'); 66.4 (C-5''); 61.8, 59.1, 58.1 (O*C*H$_3$); 18.2 (C-6'); 18.0 (C-6); 16.7 (C-6''). IR (thin film, cm^{-1}): 1030, 1043,

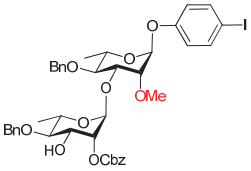
1095, 1129, 1233, 1455, 1484, 1497. HRMS calculated for $C_{55}H_{65}IO_{13}Na$ 1083.3368 $[M+Na]^+$; found 1083.3385.

4-iodophenyl 2-*O*-methyl-3-*O*-(2-*O*-benzyloxycarbonyl-3-*O*-(4-methoxybenzyl)-4-*O*-benzyl-α-L-rhamnopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranoside (23)



Prepared according to glycosylation procedure A using donor **2** (0.41 g, 0.68 mmol, 1.5 eq) and acceptor **5** (214 mg, 0.46 mmol, 1.0 eq). The title compound was obtained after column chromatography (*n*-pentane-Et_2O 4:1) as a slightly yellow oil (299 mg, 0.311 mmol, 68%). $[\alpha]_D^{25}$ = -21.7 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.55 (dd, 2H, *J* = 2.0, 6.8 Hz, C*H*$_{arom}$); 7.38-7.19 (m, 17H, C*H*$_{arom}$); 6.81 (dd, 2H, *J* = 2.0, 6.8 Hz, C*H*$_{arom}$); 6.77 (dd, 2H, *J* = 2.0, 6.4 Hz, C*H*$_{arom}$); 5.46 (d, 1H, *J* = 2.0 Hz, H-1); 5.31 (dd, 1H, *J* = 1.8, 3.0 Hz, H-2'); 5.19 (d, 1H, *J* = 1.6 Hz, H-1'); 5.15 (d, 2H, *J* = 2.0 Hz, PhC*H*$_2$); 4.91 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.80 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.64-4.55 (m, 3H, PhCH*H*, PhC*H*H, PhC*H*$_2$); 4.45 (d, 1H, *J* = 11.2 Hz, PhCH*H*); 4.20 (dd, 1H, *J* = 3.2, 9.6 Hz, H-3); 3.99-3.94 (m, 2H, H-3', H-5'); 3.72-3.65 (m, 5H, H-2, H-5, C*H*$_{3,PMB}$); 3.55-3.46 (m, 5H, H-4, H-4', OC*H*$_3$); 1.34 (d, 3H, *J* = 6.0 Hz, H-6'); 1.22 (d, 3H, *J* = 6.0 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 159.3, 156.2 (C$_{q,arom}$); 154.8 (*C*O$_{Cbz}$); 138.6 (C$_{q,arom}$); 138.5 (*C*H$_{arom}$); 138.0, 135.2, 130.2, 129.7 (C$_{q,arom}$); 128.7, 128.7, 128.6, 128.5, 128.5, 128.1, 128.1, 127.9, 127.8, 127.6, 118.7, 113.8 (*C*H$_{arom}$); 99.6 (C-1'); 94.8 (C-1); 84.9 (*C*I$_{arom}$); 80.1 (C-4); 79.9 (C-4'); 79.9 (C-2); 78.8 (C-3); 77.5 (C-3'); 75.6 (Ph*C*H$_2$); 73.3 (C-2'); 71.6, 70.0 (Ph*C*H$_2$); 69.0 (C-5); 68.7 (C-5'); 59.1 (O*C*H$_3$); 55.3 (*C*H$_{3,PMB}$); 18.2 (C-6'); 18.1 (C-6). IR (thin film, cm^{-1}): 1029, 1099, 1175, 1251, 1384, 1444, 1455, 1482, 1514, 1747. HRMS calculated for $C_{49}H_{53}IO_{12}Na$ 983.2479 $[M+Na]^+$; found 983.2474.

4-iodophenyl 2-*O*-methyl-3-*O*-(2-*O*-benzyloxycarbonyl-4-*O*-benzyl-α-L-rhamnopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranoside (33)

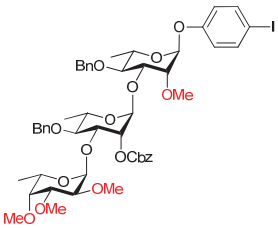


Compound **23** (0.25 g, 0.26 mmol, 1.0 eq) was dissolved in a mixture of DCM and HFIP (1:1, 2.6 mL, 0.1 M) after which a solution of HCl in HFIP (0.13 mL, 0.2 M, 0.1 eq) was added. After complete conversion of the starting material, indicated by a dark purple colour, the reaction was quenched by addition 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 (194 mg, 0.23 mmol, 89%) as a pale oil. $[\alpha]_D^{25}$ = -97.5 ° (c =1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.58-7.54 (m, 2H, C*H*$_{arom}$); 7.39-7.24 (m, 15H, C*H*$_{arom}$); 6.83-6.80 (m, 2H, C*H*$_{arom}$); 5.47 (d, 1H, *J* = 1.6 Hz, H-1); 5.22 (d, 1H, *J* = 1.2 Hz, H-1'); 5.14 (s, 2H, PhC*H*$_2$); 5.08 (dd, *J* = 1.6, 3.2 Hz, H-2'); 4.87-4.84 (m, 2H, PhC*H*H, PhC*H*H); 4.70 (d, 1H, *J* = 11.2 Hz, PhCH*H*); 4.58 (d, 1H, *J* = 10.8 Hz, PhCH*H*); 4.22-4.16 (m, 2H, H-3, H-3'); 3.97-3.93 (m, 1H, H-5'); 3.71-3.68 (m, 2H, H-2, H-5); 3.57-3.52 (m, 4H, H-4, OC*H*$_3$); 3.41 (t, 1H, *J* = 9.4 Hz, H-4'); 2.18 (bs, 1H, 3'-O*H*); 1.38 (d, 3H, *J* = 6.4 Hz, H-6'); 1.22 (d, 3H, *J* = 6.0 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 156.2 (C$_{q,arom}$); 154.8 (*C*O$_{Cbz}$); 138.5 (*C*H$_{arom}$); 138.3, 138.1, 134.9 (C$_{q,arom}$); 128.8, 128.8, 128.7, 128.6, 128.5, 128.2, 128.1, 128.0, 127.9, 118.7 (*C*H$_{arom}$); 99.2 (C-1'); 94.9 (C-1); 84.9 (*C*I$_{arom}$); 81.7 (C-4'); 80.3 (C-4); 80.0 (C-2); 78.6 (C-3); 76.6 (C-2'); 75.6, 75.5, 70.3 (Ph*C*H$_2$); 70.3 (C-3'); 69.1 (C-5); 68.3 (C-5'); 59.1 (O*C*H$_3$); 18.2 (C-6'); 18.1 (C-6).

IR (thin film, cm^{-1}): 1020, 1043, 1098, 1138, 1233, 1262, 1484, 1747, 3444. HRMS calculated for $C_{41}H_{45}IO_{11}Na$ 863.1904 $[M+Na]^+$; found 863.1889.

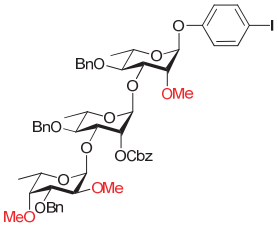
4-iodophenyl 2-*O*-methyl-3-*O*-(2-*O*-benzyloxycarbonyl-3-*O*-(2,3,4-tri-*O*-methyl-α-L-fucopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranoside (36)

Prepared according to glycosylation procedure B using donor **3** (48 mg, 0.16 mmol) and acceptor **33** (89 mg, 0.11 mmol) the title compound was obtained after column chromatography (DCM-EtOAc 9:1) as a pale oil (80 mg, 78µmol, 73%, α/ß 10:1). $[\alpha]_D^{25}$ = -99.0 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.57-7.54 (m, 2H, C*H*$_{arom}$); 7.42-7.26 (m, 15H, C*H*$_{arom}$); 6.82-6.80 (m, 2H, C*H*$_{arom}$); 5.48 (d, 1H, *J* = 1.6 Hz, H-1); 5.22-5.10 (m, 6H, H-1', H-1'', H-2', PhC*H*$_2$, PhC*H*H); 4.93 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.60-4.53 (m, 2H, PhCH*H*, PhCH*H*); 4.19 (dd, 2H, *J* = 2.8, 9.6 Hz, H-3, H-3'); 4.04-3.97 (m, 1H, H-5); 3.81 (q, 1H, *J* = 6.8 Hz, H-5''); 3.73 (dd, 1H, *J* = 2.0, 6.4 Hz, H-2); 3.71-3.61 (m, 1H, H-5'); 3.57-3.48 (m, 13H, H-2'', H-3'', H-4, H-4', OC*H*$_3$); 3.31 (s, 3H, OC*H*$_3$); 3.27 (d, 1H, *J* = 2.0 Hz, H-4''); 1.34 (d, 3H, *J* = 6.0 Hz, H-6); 1.19 (d, 3H, *J* = 6.4 Hz, H-6'); 0.97 (d, 3H, *J* = 6.8 Hz, H-6''). ^{13}C-APT NMR (101 MHz) δ: 156.2 (C$_{q,arom}$); 154.8 (*C*O$_{Cbz}$); 139.0 (C$_{q,arom}$); 138.5 (*C*H$_{arom}$); 138.1, 135.2 (*C*H$_{arom}$); 128.9, 128.9, 128.8, 128.5, 12.4, 127.9, 127.6, 127.5, 118.7 (*C*H$_{arom}$); 100.0 (C-1''); 99.5 (C-1'); 94.5 (C-1); 84.9 (*C*I$_{arom}$); 80.3 (C-4'); 80.1 (C-4); 80.0 (C-2); 79.8 (C-3''); 79.6 (C-3'); 79.3 (C-4'); 78.3 (C-3); 77.7 (C-2''); 76.8 (C-2'); 75.7, 75.1, 70.1 (Ph*C*H$_2$); 69.0 (C-5'); 68.7 (C-5); 67.1 (C-5''); 61.9, 59.1, 58.8, 58.2 (O*C*H$_3$); 18.2 (C-6); 18.1 (C-6'); 16.3 (C-6''). IR (thin film, cm^{-1}): 1045, 1099, 1138, 1178, 1196, 1233, 1262, 1358, 1384, 1454, 1484, 1747. HRMS calculated for $C_{50}H_{61}IO_{15}Na$ 1051.2953 $[M+Na]^+$; found 1051.2947.



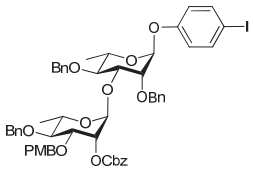
4-iodophenyl 2-*O*-methyl-3-*O*-(2-*O*-benzyloxycarbonyl-3-*O*-(2,4-di-*O*-methyl-3-*O*-benzyl-α-L-fucopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (39)

Prepared according to glycosylation procedure B using donor **4** (72 mg, 0.19 mmol, 1.5 eq) and acceptor **33** (107 mg, 0.127 mmol, 1.0 eq). The title compound was obtained after column chromatography (DCM-EtOAc 19:1) as a slightly yellow oil (115 mg, 0.104 mmol, 82%, α/ß 5:1). $[\alpha]_D^{25}$ = -80.3 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.57-7.54 (m, 2H, C*H*$_{arom}$); 7.39-7.24 (m, 20H, C*H*$_{arom}$); 6.81 (d, 2H, *J* = 8.8 Hz, C*H*$_{arom}$); 5.48 (s, 1H, H-1); 5.22-5.08 (m, 6H, H-1', H-1'', H-2', PhC*H*$_2$, PhC*H*H); 4.92 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.72 (dd, 2H, *J* = 12.4, 28.8 Hz, PhC*H*$_2$); 4.58-4.53 (m, 2H, PhCH*H*, PhCH*H*); 4.21-4.17 (m, 2H, H-3, H-3'); 4.03-3.96 (m, 1H, H-5); 3.83 (q, 1H, *J* = 6.4 Hz, H-5''); 3.79-3.63 (m, 4H, H-2, H-2'', H-3'', H-5'); 3.55-3.51 (m, 8H, H-4, H-4', OC*H*$_3$); 3.36 (s, 3H, OC*H*$_3$); 3.24 (d, 1H, *J* = 1.6 Hz, H-4''); 1.35 (d, 3H, *J* = 6.0 Hz, H-6); 1.21 (d, 3H, *J* = 6.4 Hz, H-6'); 0.95 (d, 3H, *J* = 6.4 Hz, H-6''). ^{13}C-APT NMR (101 MHz) δ: 156.2 (C$_{q,arom}$); 154.8 (*C*O$_{Cbz}$); 139.0, 139.0 (C$_{q,arom}$); 138.5 (*C*H$_{arom}$); 138.1, 135.2 (C$_{q,arom}$); 128.8, 128.8, 128.7, 128.7, 128.5, 128.5, 128.5, 128.4, 127.9, 127.8, 127.6, 127.4, 118.7 (*C*H$_{arom}$); 100.1 (C-1''); 99.5 (C-1'); 94.5 (C-1); 84.9 (*C*I$_{arom}$); 80.5 (C-4''); 80.0 (C-3'); 79.8 (C-2); 79.6 (C-4 and C-4'); 78.6 (C-3); 78.4 (C-3''); 78.2 (C-2''); 76.7 (C-2'); 75.7, 75.2, 72.7, 70.1 (Ph*C*H$_2$); 69.0 (C-5'); 68.7 (C-5); 67.2 (C-5''); 61.9, 59.4,



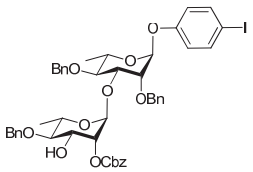
58.8 (O*C*H$_3$); 18.2 (C-6); 18.1 (C-6'); 16.2 (C-6''). IR (thin film, cm^{-1}): 1046, 1099, 1178, 1232, 1264, 1455, 1484, 1747. HRMS calculated for $C_{56}H_{65}IO_{15}Na$ 1127.3266 [M+Na]$^+$; found 1127.3263.

4-iodophenyl 2,4-di-*O*-benzyl-3-*O*-(2-*O*-benzyloxycarbonyl-3-*O*-(4-methoxybenzyl)-4-*O*-benzyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (24)



Prepared according to glycosylation procedure A using donor **2** (0.46 g, 0.75 mmol, 1.5 eq) and acceptor **6** (273 mg, 0.5 mmol, 1.0 eq). The title compound was obtained after column chromatography (*n*-pentane-Et$_2$O 4:1) as a slightly yellow oil (333mg, 0.32 mmol, 64%). $[\alpha]_D^{25}$ = -40.9 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.55-7.51 (m, 2H, C*H*$_{arom}$); 7.39-7.19 (m, 22H, C*H*$_{arom}$); 6.77-6.72 (m, 4H, C*H*$_{arom}$); 5.38 (d, 1H, *J* = 1.6 Hz, H-1); 5.30 (dd, 1H, *J* = 1.8, 3.0 Hz, H-2'); 5.24 (d, 1H, *J* = 1.6 Hz, H-1'); 5.17-5.10 (m, 2H, PhC*H*$_2$); 4.92 (d, 1H, *J* = 11.2 Hz, PhC*H*H); 4.82 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.71 (dd, 2H, *J* = 12.0, 22.0 Hz, PhC*H*$_2$); 4.64-4.58 (m, 3H, PhCH*H*, PhCH*H*, PhC*H*H); 4.44 (d, 1H, *J* = 11.2 Hz, PhCH*H*); 4.25 (dd, 1H, *J* = 3.0, 9.0 Hz, H-3); 3.95 (dd, 1H, *J* = 3.2, 9.2 Hz, H-3'); 3.87-3.83 (m, 2H, H-2, H-5'); 3.73-3.64 (m, 5H, H-4, H-5, C*H*$_{3,PMB}$); 3.46 (t, 1H, *J* = 9.4 Hz, H-4'); 1.28-1.24 (m, 6H, H-6, H-6'). ^{13}C-APT NMR (101 MHz) δ: 159.3, 156.1 (C$_{q,arom}$); 154.8 (*C*O$_{Cbz}$); 138.4 (C$_{q,arom}$); 138.4 (*C*H$_{arom}$); 138.0, 137.8, 135.2, 130.1 (C$_{q,arom}$); 129.8, 128.7, 128.7, 128.6, 128.5, 128.5, 128.4, 128.2, 128.0, 127.9, 127.9, 127.9, 127.7, 118.7, 113.8 (*C*H$_{arom}$); 99.2 (C-1'); 95.9 (C-1); 84.9 (*C*I$_{arom}$); 80.7 (C-4); 79.8 (C-4'); 77.4, 77.3 (C-2, C-3, and C-3'); 75.5, 75.4, 73.2 (Ph*C*H$_2$); 73.1 (C-2'); 71.6, 70.0 (Ph*C*H$_2$); 69.2 (C-5); 68.7 (C-5'); 55.3 (*C*H$_{3,PMB}$); 18.1 (C-6 and C-6'). IR (thin film, cm^{-1}): 1029, 1050, 1073, 1093, 1140, 1233, 1262, 1455, 1484, 1749, 2932. HRMS calculated for $C_{55}H_{57}IO_{12}Na$ 1059.2792 [M+Na]$^+$; found 1059.2778.

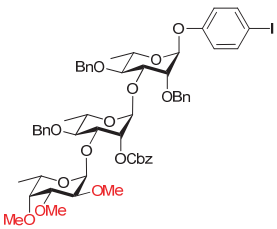
4-iodophenyl 2,4-di-*O*-benzyl-3-*O*-(2-*O*-benzyloxycarbonyl-4-*O*-benzyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (34)



Compound **24** (113 mg, 0.109 mmol, 1.0 eq) was dissolved in a mixture of DCM and HFIP (1:1, 1.08 mL, 0.1 M) after which a solution of HCl in HFIP (54 µL, 0.2 M, 0.1 eq) was added. After complete conversion of the starting material, 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$_2$O 7:3) gave the title compound (86 mg, 94 µmol, 86%) as a pale oil. $[\alpha]_D^{25}$ = -57.6 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.56-7.52 (m, 2H, C*H*$_{arom}$); 7.39-7.23 (m, 20H, C*H*$_{arom}$); 6.78-6.74 (m, 2H, C*H*$_{arom}$); 5.41 (d, 1H, *J* = 2.0 Hz, H-1); 5.25 (s, 1H, H-1'); 5.13 (s, 2H, PhC*H*$_2$); 5.10 (dd, 1H, *J* = 2.0, 3.6 Hz, H-2'); 4.87 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.81 (d, 1H, *J* = 11.2 Hz, PhC*H*H); 4.74 (s, 2H, PhC*H*$_2$); 4.68 (d, 1H, *J* = 11.6 Hz, PhCH*H*); 4.61 (d, 1H, *J* = 11.2 Hz, PhCH*H*); 4.25 (dd, 1H, *J* = 2.8, 8.8 Hz, H-3); 4.13 (dd, 1H, *J* = 2.8, 9.2 Hz, H-3'); 3.88-3.83 (m, 2H, H-2, H-5'); 3.74-3.66 (m, 2H, H-4, H-5); 3.39 (t, 1H, *J* = 9.0 Hz, H-4'); 2.15 (bs, 1H, O*H*); 1.30 (d, 3H, *J* = 6.4 Hz, H-6'); 1.26 (d, 3H, *J* = 6.0 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 156.1 (C$_{q,arom}$); 154.8 (*C*O$_{Cbz}$); 138.5 (*C*H$_{arom}$); 138.1, 137.8, 134.9 (C$_{q,arom}$); 128.8, 128.8, 128.7, 128.7, 128.6, 128.5, 128.1, 128.0, 128.0, 127.9, 127.8, 118.7 (*C*H$_{arom}$); 98.9 (C-1'); 95.8 (C-1); 84.9 (*C*I$_{arom}$); 81.7 (C-4'); 80.8 (C-4); 77.5 (C-2 and C-3); 76.4 (C-2'); 75.5, 75.3, 73.1 (Ph*C*H$_2$); 70.4 (C-3); 70.3 (Ph*C*H$_2$); 69.2 (C-5);

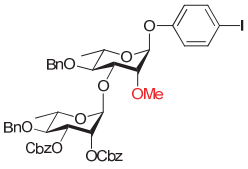
68.3 (C-5'); 18.1 (C-6 and C-6'). IR (thin film, cm^{-1}): 1000, 1029, 1043, 1096, 1136, 1232, 1264, 1454, 1484, 1749, 2931, 3504. HRMS calculated for $C_{47}H_{49}IO_{11}Na$ 939.2217 $[M+Na]^+$; found 939.2212.

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



Prepared according to glycosylation procedure B using donor **3** (40 mg, 0.14 mmol) and acceptor **34** (81 mg, 0.09 mmol) the title compound was obtained after column chromatography (DCM-EtOAc 15:1) as a pale oil (73 mg, 66 µmol, 73%, α/ß 7:1). $[\alpha]_D^{25}$ = -78.3 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.55-7.52 (m, 2H, CH_{arom}); 7.40-7.22 (m, 20H, CH_{arom}); 6.76 (d, 2H, *J* = 8.8 Hz, CH_{arom}); 5.43 (s, 1H, H-1); 5.27 (s, 1H, H-1'); 5.20-5.09 (m, 5H, H-1'', H-2', PhC*H*H, PhCH_2); 4.94 (d, 1H, *J* = 11.2 Hz, PhC*H*H); 4.74 (dd, 2H, *J* = 12.0, 16.4 Hz, PhCH_2); 4.59-4.55 (m, 2H, PhCH*H*, PhCH*H*); 4.25 (dd, 1H, *J* = 2.8, 8.4 Hz, H-3); 4.18 (dd, 1H, *J* = 3.2, 9.2 Hz, H-3'); 3.92-3.85 (m, 3H, H-2, H-5', H-5''); 3.72-3.62 (m, 2H, H-4, H-5); 3.57-3.44 (m, 9H, H-2'', H-4', H-4'', OCH_3); 3.29 (s, 1H, H-3''); 3.28 (s, 3H, OCH_3); 1.28 (d, 3H, *J* = 6.4 Hz, H-6); 1.21 (d, 3H, *J* = 5.2 Hz, H-6'); 1.03 (d, 3H, *J* = 6.8 Hz, H-6''). ^{13}C-APT NMR (101 MHz) δ: 156.1 ($C_{q,arom}$); 154.8 (CO_{Cbz}); 139.1 ($C_{q,arom}$); 138.4 (CH_{arom}); 138.2, 137.8, 135.2 ($C_{q,arom}$); 128.8, 128.8, 128.7, 128.4, 128.4, 128.4, 128.3, 128.0, 127.8, 127.4, 127.4, 118.7 (CH_{arom}); 99.8 (C-1''); 99.0 (C-1'); 95.6 (C-1); 84.8 (CI_{arom}); 80.4 (C-4); 80.3 (C-4'); 79.7 (C-4''); 79.3 (C-3''); 78.3 (C-3); 77.8 (C-2 and C-3'); 77.7 (C-2''); 76.6 (C-2'); 75.5, 74.9, 73.1, 70.0 (PhCH_2); 69.2 (C-5); 68.7 (C-5'); 67.1 (C-5''); 61.9, 59.1, 58.1 (OCH_3); 18.1 (C-6 and C-6'); 16.4 (C-6''). IR (thin film, cm^{-1}): 1042, 1098, 1130, 1233, 1262, 1455, 1484, 1747. HRMS calculated for $C_{56}H_{65}IO_{15}Na$ 1127.3266 $[M+Na]^+$; found 1127.3255.

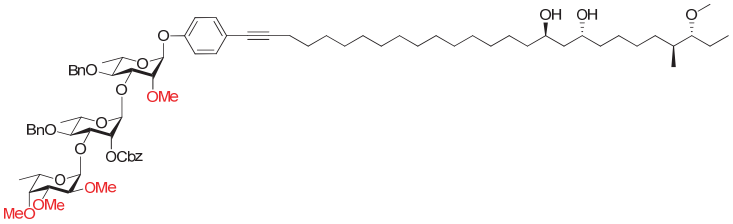
4-iodophenyl 2,4-di-*O*-benzyl-3-*O*-(2,3-di-*O*-benzyloxycarbonyl-4-*O*-benzyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (40)



Prepared according to glycosylation procedure A using donor **7** (90 mg, 0.146 mmol, 1.5 eq) and acceptor **5** (46 mg, 98 µmol, 1.0 eq). The title compound was obtained after column chromatography (*n*-pentane-Et_2O 3:1) as a pale oil (62 mg, 64 µmol, 65%). $[\alpha]_D^{25}$ = -46.4 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.59-7.53 (m, 2H, CH_{arom}); 7.38-7.22 (m, 20H, CH_{arom}); 6.84-6.79 (m, 2H, CH_{arom}); 5.46 (d, 1H, *J* = 1.6 Hz, H-1); 5.34-5.29 (m, 2H, H-2', H-3'); 5.19 (d, 1H, *J* = 1.6 Hz, H-1'); 5.16 (d, 2H, *J* = 1.2 Hz, PhCH_2); 5.12 (s, 2H, PhCH_2); 4.90 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.73 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.62-4.57 (m, 2H, PhCH*H*, PhCH*H*); 4.19 (dd, 1H, *J* = 3.0, 9.4 Hz, H-3); 4.06 (dq, 1H, *J* = 3.6, 6.4 Hz, H-5'); 3.72-3.66 (m, 2H, H-2, H-5); 3.62-3.55 (m, 2H, H-4, H-4'); 3.52 (s, 3H, OCH_3); 1.35 (d, 3H, *J* = 6.4 Hz, H-6'); 1.24 (d, 3H, *J* = 6.4 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 156.2 ($C_{q,arom}$); 154.5, 154.4 (CO_{Cbz}); 138.5 (CH_{arom}); 138.2, 138.0, 135.2, 134.9 ($C_{q,arom}$); 128.8, 128.8, 128.7, 128.7, 128.6, 128.5, 128.5, 128.3, 128.1, 128.0, 127.8, 118.7 (CH_{arom}); 99.3 (C-1'); 94.8 (C-1); 84.9 (CI_{arom}); 79.9 (C-2 and C-4); 79.6 (C-3); 78.5 (C-4'); 76.0 (C-3'); 75.7, 75.5 (PhCH_2); 74.1 (C-2'); 70.3, 70.1 (PhCH_2); 69.1 (C-5); 68.6 (C-5'); 59.1 (OCH_3); 18.1 (C-6); 18.1 (C-6'). IR (thin film, cm^{-1}): 1029, 1043, 1059, 1063, 1079, 1099,

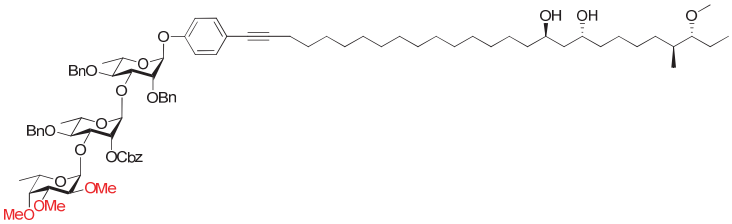
1126, 1236, 1273, 1455, 1484, 1751. HRMS calculated for $C_{49}H_{51}IO_{13}Na$ 997.22666 $[M+Na]^+$; found 997.22558.

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*-benzyloxycarbonyl-3-*O*-(2,3,4-tri-*O*-methyl-α-L-fucopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranoside (41)



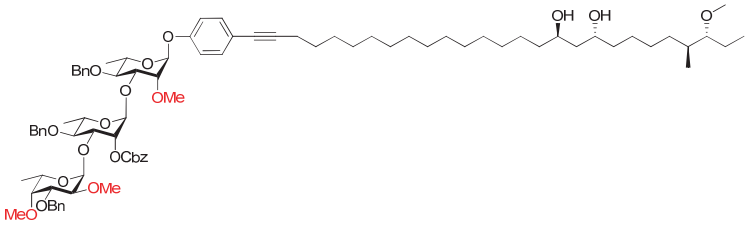
The title compound was synthesized according to general procedure C using **36** (65 mg, 63 µmol, 1.0 eq) and phthiocerol (34 mg, 74 µmol, 1.2 eq). Column chromatography (*n*-pentane-Et_2O 1:4) yielded the title compound (77 mg, 57 µmol, 90%) as a pale oil. $[\alpha]_D^{25}$ = -78.7 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.41-7.26 (m, 17H, C*H*$_{arom}$); 6.94 (d, 2H, *J* = 8.4 Hz, C*H*$_{arom}$); 5.52 (d, 1H, *J* = 1.6 Hz, H-1); 5.23-5.13 (m, 6H, H-1', H-1'', H-2', PhCH_2, PhC*H*H); 4.93 (d, 1H, *J* = 11.2 Hz, PhC*H*H); 4.60-4.53 (m, 2H, PhCH*H*, PhCH*H*); 4.21-4.18 (m, 2H, H-3, H-3'); 4.05-3.90 (m, 3H, H-5', C*H*$_{,Phth}$); 3.81 (q, 1H, *J* = 6.4 Hz, H-5''); 3.74-3.65 (m, 2H, H-2, H-5); 3.57-3.48 (m, 13H, H-2'', H-3'', H-4, H-4', OCH_3); 3.33 (s, 3H, OCH_3); 3.31 (s, 3H, OCH_3); 3.27 (d, 1H, *J* = 1.6 Hz, H-4''); 2.90-2.84 (m, 1H, C*H*$_{Phth}$); 2.50 (bs, 2H, O*H*); 2.37 (t, 2H, *J* = 7.2 Hz, C$H_{2,Phth}$); 1.70-1.18 (m, 53H, C$H_{2,Phth}$, H-6, H-6'); 1.15-1.05 (m, 2H, C*H*$_{Phth}$); 0.97 (d, 3H, *J* = 6.4 Hz, H-6''); 0.91 (t, 3H, *J* = 7.6 Hz, C$H_{3,Phth}$); 0.83 (d, 3H, *J* = 6.8 Hz, C$H_{3,Phth}$). ^{13}C-APT NMR (101 MHz) δ: 155.6 ($C_{q,arom}$); 154.8 (*C*O$_{Cbz}$); 139.0, 138.1, 135.2 ($C_{q,arom}$); 132.9, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 127.8, 127.6, 127.5 (*C*H$_{arom}$); 118.0 ($C_{q,arom}$); 116.2 (*C*H$_{arom}$); 99.9 (C-1''); 99.5 (C-1'); 94.4 (C-1); 89.5 ($C_{q,alkyne}$); 86.8 (*C*H$_{Phth}$); 80.3 (C-3); 80.1 ($C_{q,alkyne}$); 80.1 (C-2 and C-3''); 79.8, 79.6 (C-4 and C-4'); 79.3 (C-4''); 78.3 (C-3'); 77.7 (C-2''); 76.8 (C-2'); 75.7, 75.1, 70.1 (Ph*C*H$_2$); 69.6, 69.5 (*C*H$_{Phth}$); 68.9 (C-5'); 68.6 (C-5); 67.1 (C-5''); 61.8, 59.0, 58.8, 58.1, 57.5 (O*C*H$_3$); 42.4, 37.6 (*C*H$_{2,Phth}$); 34.9 (*C*H$_{Phth}$); 32.7, 29.8, 29.7, 29.7, 29.3, 29.0, 28.9, 27.7, 26.2, 25.9, 22.5, 19.5 (*C*H$_{2,Phth}$); 18.2 (C-6); 18.0 (C-6'); 16.3 (C-6''); 14.9, 10.2 (*C*H$_{3,Phth}$). IR (thin film, cm^{-1}): 1043, 1099, 1130, 1138, 1235, 1262, 1384, 1457, 1507, 1747, 2855, 2926, 3430. HRMS calculated for $C_{79}H_{116}O_{18}Na$ 1375.8059 $[M+Na]^+$; found 1375.8055.

4-((3*R*,4*S*,9*R*,11*R*)-3-methoxy-4-methylheptacos-26-yne-9,11-diol)phenyl 2,4-di-*O*-benzyl-3-*O*-(2-*O*-benzyloxycarbonyl-3-*O*-(2,3,4-tri-*O*-methyl-α-L-fucopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (42)



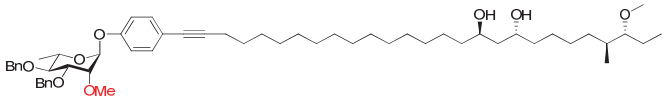
The title compound was synthesized according to general procedure C using **38** (33 mg, 30 µmol, 1.0 eq) and phthiocerol (16 mg, 36 µmol, 1.2 eq). Column chromatography (*n*-pentane-Et_2O 1:4) yielded the title compound (37 mg, 26 µmol, 87%) as a yellow oil. $[\alpha]_D^{25}$ = -71.8 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.41-7.23 (m, 22H, C*H*$_{arom}$); 6.89 (d, 2H, *J* = 8.8 Hz, C*H*$_{arom}$); 5.47 (d, 1H, *J* = 1.6 Hz, H-1); 5.27 (d, 1H, *J* = 1.2 Hz, H-1'); 5.19-5.11 (m, 5H, H-1'', H-2', PhC*H*$_2$, PhC*H*H); 4.93 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.74 (dd, 2H, *J* = 11.8, 21.0 Hz, PhC*H*$_2$); 4.59-4.55 (m, 2H, PhCH*H*, PhCH*H*); 4.27 (dd, 1H, *J* = 3.2, 8.8 Hz, H-3); 4.18 (dd, 1H, *J* = 3.4, 9.4 Hz, H-3'); 3.95-3.84 (m, 5H, H-2, H-5', H-5'', C*H*$_{Phth}$); 3.74-3.65 (m, 2H, H-4, H-5); 3.57-3.44 (m, 9H, H-2'', H-3'', H-4', OC*H*$_3$); 3.34 (s, 3H, OC*H*$_3$); 3.29 (d, 1H, *J* = 1.6 Hz, H-4''); 3.28 (s, 3H, OC*H*$_3$); 2.89-2.85 (m, 1H, C*H*$_{Phth}$); 2.37 (t, 2H, *J* = 7.2 Hz, C*H*$_{2,Phth}$); 1.75-1.17 (m, 54H, H-6, H-6', C*H*$_{2,Phth}$); 1.03 (d, 3H, *J* = 6.4 Hz, H-6''); 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: 155.6 (C$_{q,arom}$); 154.8 (*C*O$_{Cbz}$); 139.1, 138.2, 137.8, 135.2 (C$_{q,arom}$); 132.9, 128.8, 128.8, 128.7, 128.4, 128.4, 128.3, 128.0, 127.9, 127.8, 127.4, 127.4 (*C*H$_{arom}$); 118.0 (C$_{q,arom}$); 116.3 (*C*H$_{arom}$); 99.8 (C-1''); 99.0 (C-1'); 95.5 (C-1); 89.5 (C$_{q,alkyne}$); 86.8 (*C*H$_{Phth}$); 80.5 (C-4); 80.4 (C-4'); 80.1 (C$_{q,alkyne}$); 79.8 (C-3''); 79.3 (C-4''); 78.3 (C-3); 77.9 (C-2); 77.8 (C-3'); 77.7 (C-2''); 76.6 (C-2'); 75.6, 74.9, 73.0, 70.1 (PhC*H*$_2$); 69.7, 69.6 (*C*H$_{Phth}$); 69.1 (C-5'); 68.7 (C-5); 67.1 (C-5''); 61.9, 59.1, 58.2, 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$_{2,Phth}$); 18.1 (C-6 and C-6'); 16.4 (C-6''); 14.9, 10.2 (*C*H$_{3,Phth}$). IR (thin film, cm^{-1}): 1045, 1099, 1132, 1175, 1235, 1264, 1384, 1455, 1507, 1747, 2926, 3396. HRMS calculated for $C_{85}H_{120}O_{18}Na$ 1451.8372 $[M+Na]^+$; found 1451.8371.

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



The title compound was synthesized according to general procedure C using **39** (57 mg, 52 µmol, 1.0 eq) and phthiocerol (28 mg, 62 µmol, 1.2 eq). Column chromatography (*n*-pentane-Et_2O 4:1) yielded the title compound (74 mg, 52 µmol, 100%) as a yellow oil. $[\alpha]_D^{25}$ = -75.5 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.38-7.26 (m, 22H, C*H*$_{arom}$); 6.93 (d, 2H *J* = 8.8 Hz, C*H*$_{arom}$); 5.51 (d, 1H, *J* = 1.6 Hz, H-1); 5.21-5.10 (m, 6H, H-1', H-1'', H-2', PhC*H*$_2$, PhC*H*H); 4.92 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.71 (dd, 2H, *J* = 10.8. 27.6 Hz, PhC*H*$_2$); 4.58-4.52 (m, 2H, PhCH*H*, PhCH*H*); 4.20 (dd, 2H, *J* = 3.2, 9.6 Hz, H-3, H-3'); 4.02-3.90 (m, 3H, H-5', C*H*$_{Phth}$); 3.83 (q, 1H, *J* = 6.4 Hz, H-5''); 3.79-3.62 (m, 4H, H-2, H-2'', H-3'', H-5); 3.55-3.51 (m, 8H, H-4, H-4', OC*H*$_3$); 3.35 (s, 3H, OC*H*$_3$); 3.34 (s, 3H, OC*H*$_3$); 3.24 (d, 1H, *J* = 2.0 Hz, H-4''); 2.90-2.84 (m, 1H, C*H*$_{Phth}$); 2.37 (t, 2H, *J* = 7.0 Hz, C*H*$_{2,Phth}$); 1.62-1.26 (m, 51H, H-6', C*H*$_{2,Phth}$); 1.19 (d, 3H, *J* = 6.0 Hz, H-6); 1.15-1.05 (m, 2H, C*H*$_{2,Phth}$); 0.95-0.89 (m, 6H, H-6'', C*H*$_{3,Phth}$); 0.83 (d, 3H, *J* = 6.8 Hz, C*H*$_{3,Phth}$). ^{13}C-APT NMR (101 MHz) δ: 155.6 (C$_{q,arom}$); 154.7 (*C*O$_{Cbz}$); 139.0, 139.0, 138.1, 135.2 (C$_{q,arom}$); 133.0, 128.8, 128.8, 128.5, 128.5, 128.5, 128.4, 128.3, 127.8, 127.8, 127.6, 127.4 (*C*H$_{arom}$); 118.0 (C$_{q,arom}$); 116.2 (*C*H$_{arom}$); 100.1 (C-1''); 99.4 (C-1'); 94.4 (C-1); 89.5 (C$_{q,alkyne}$); 86.8 (*C*H$_{Phth}$); 80.5 (C-4''); 80.1 (C$_{q,alkyne}$); 80.1 (C-2); 80.0 (C-3); 79.9 (C-4'), 79.6 (C-4); 78.6 (C-3''); 78.3 (C-3'); 78.2 (C-2''); 76.7 (C-2'); 75.7, 75.2, 72.7, 70.0 (PhC*H*$_2$); 69.6, 69.5 (*C*H$_{Phth}$); 68.9 (C-5); 68.6 (C-5'); 67.2 (C-5''); 61.9, 59.4, 58.8, 57.5 (O*C*H$_3$); 42.4, 37.6 (*C*H$_{2,Phth}$); 34.9 (*C*H$_{Phth}$); 32.7, 29.8, 29.8, 29.7, 29.3, 29.1, 28.9, 27.7, 26.2, 25.9, 22.5, 19.5 (*C*H$_{2,Phth}$); 18.2 (C-6'); 18.0 (C-6); 16.2 (C-6''); 14.9, 10.2 (*C*H$_{3,Phth}$). IR (thin film, cm^{-1}): 1045, 1100, 1137, 1263, 1455, 1507, 1748, 2926, 3408. HRMS calculated for $C_{85}H_{120}O_{18}Na$ 1451.8372 $[M+Na]^+$; found 1451.8367.

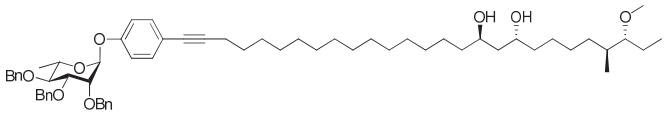
4-((3*R*,4*S*,9*R*,11*R*)-3-methoxy-4-methylheptacos-26-yne-9,11-diol)phenyl 2-*O*-methyl-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (44)



The title compound was synthesized according to general procedure C using **8** (29 mg, 52 µmol, 1.0 eq) and phthiocerol (28 mg, 62 µmol, 1.2 eq). Column chromatography (*n*-pentane-Et_2O 4:1) yielded the title compound (46 mg, 52 µmol, 100%) as a yellow oil. $[\alpha]_D^{25}$ = -74.4 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.42 (d, 2H, *J* = 6.8 Hz, C*H*$_{arom}$); 7.38-7.28 (m, 10H, C*H*$_{arom}$); 6.93 (d, 2H, *J* = 8.8 Hz, C*H*$_{arom}$); 5.51 (d, 1H, *J* = 2.0 Hz, H-1); 4.95 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.83-4.74 (m, 2H, PhC*H*$_2$); 4.63 (d, 1H, *J* = 10.8 Hz, PhCH*H*); 4.04 (dd, 1H, *J* = 3.2, 9.6 Hz, H-3); 3.99-3.89 (m, 2H, C*H*$_{Phth}$); 3.75-3.68 (m, 2H, H-2, H-5); 3.60-3.55 (m, 4H, H-4,

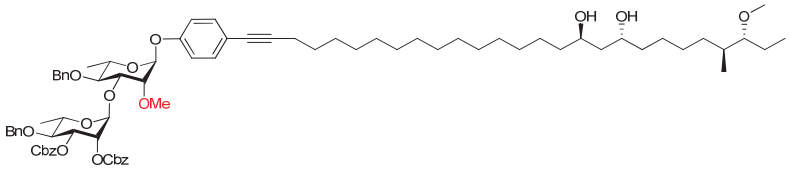
OCH_3); 3.34 (s, 3H, OCH_3); 2.90-2.83 (m, 1H, CH_{Phth}); 2.37 (t, 2H, *J* = 7.0 Hz, C$H_{2,Phth}$); 1.75-1.17 (m, 45H, H-6, C$H_{2,Phth}$); 1.16-1.03 (m, 2H, C$H_{2,Phth}$); 0.91 (t, 3H, *J* = 7.4 Hz, C$H_{3,Phth}$); 0.83 (d, 3H, *J* = 6.8 Hz, C$H_{3,Phth}$). ^{13}C-APT NMR (101 MHz) δ: 155.6, 138.6, 138.5 ($C_{q,arom}$); 133.0, 128.6, 128.5, 128.1, 128.0, 127.9, 127.8 (*C*H$_{arom}$); 118.0 ($C_{q,arom}$); 116.2 (*C*H$_{arom}$); 95.4 (C-1); 89.5 ($C_{q,alkyne}$); 86.8 (*C*H$_{Phth}$); 80.4 (C-4); 80.1 ($C_{q,alkyne}$); 79.7 (C-3); 78.1 (C-2); 75.7, 72.7 (Ph*C*H$_2$); 69.6, 69.6 (*C*H$_{Phth}$); 68.9 (C-5); 59.7, 57.5 (O*C*H$_3$); 42.4, 37.6 (*C*H$_{2,Phth}$); 34.9 (*C*H$_{Phth}$); 32.7, 29.8, 29.8, 29.7, 29.3, 29.1, 29.0, 27.7, 26.3, 25.9, 22.5, 19.5 (*C*H$_{2,Phth}$); 18.1 (C-6); 14.9, 10.2 (*C*H$_{3,Phth}$). IR (thin film, cm^{-1}): 1047, 1098, 1139, 1233, 1454, 1507, 2853, 3400. HRMS calculated for $C_{56}H_{84}O_8Na$ 907.6064 [M+Na]$^+$; found 907.6058.

4-((3*R*,4*S*,9*R*,11*R*)-3-methoxy-4-methylheptacos-26-yne-9,11-diol)phenyl 2,3,4-tri-*O*-benzyl-α-L-rhamnopyranoside (45)



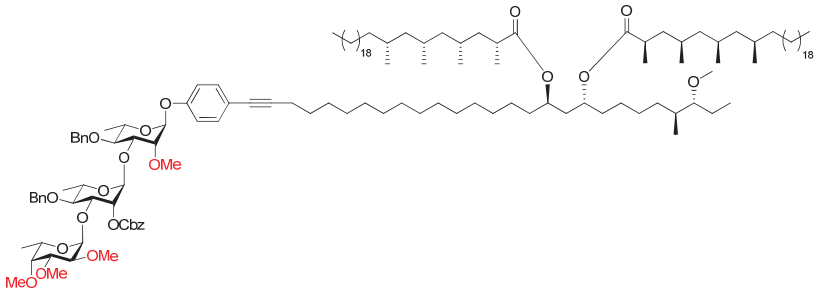
The title compound was synthesized according to general procedure C using **9** (32 mg, 50 µmol, 1.0 eq) and phthiocerol (27 mg, 60 µmol, 1.2 eq). Column chromatography (*n*-pentane-Et_2O 4:1) yielded the title compound (48 mg, 50 µmol, 99%) as a yellow oil. $[\alpha]_D^{25}$ = -38.1 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.39-7.26 (m, 17H, C*H*$_{arom}$); 6.86 (dd, 2H, *J* = 2.0, 7.2 Hz, C*H*$_{arom}$); 5.45 (d, 1H, *J* = 2.0 Hz, H-1); 4.94 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.68 (dd, 2H, *J* = 12.4, 25.2 Hz, PhC*H*$_2$); 4.70-4.64 (m, 3H, PhC*H*$_2$, PhCH*H*); 4.04 (dd, 1H, *J* = 3.0, 9.0 Hz, H-3); 3.96-3.90 (m, 3H, H-2, C*H*$_{Phth}$); 3.74-3.68 (m, 2H, H-4, H-5); 3.34 (s, 3H, OC*H*$_3$); 2.90-2.84 (m, 1H, C*H*$_{Phth}$); 2.37 (t, 1H, *J* = 7.0 Hz, C*H*$_{2,Phth}$); 2.00 (bs, 2H, O*H*$_{Phth}$); 1.62-1.09 (m, 63H, C*H*$_{Phth}$, C*H*$_{2,Phth}$); 0.91 (t, 3H, *J* = 7.6 Hz, C*H*$_{3,Phth}$); 0.83 (d, 3H, *J* = 6.8 Hz, C*H*$_{3,Phth}$). ^{13}C-APT NMR (101 MHz) δ: 155.6, 138.6, 138.2 ($C_{q,arom}$); 133.0, 128.6, 128.6, 128.5, 128.2, 128.1, 128.0, 127.8, 127.8 (*C*H$_{arom}$); 117.9 ($C_{q,arom}$); 116.2 (*C*H$_{arom}$); 96.2 (C-1); 89.5 ($C_{q,alkyne}$); 80.5 (C-4); 80.1 ($C_{q,alkyne}$); 80.0 (C-3); 75.6 (Ph*C*H$_2$); 74.7 (C-2); 73.2, 72.6 (Ph*C*H$_2$); 69.7, 69.6 (*C*H$_{Phth}$) 69.0 (C-5); 57.6 (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$_{2,Phth}$); 18.1 (C-6); 15.0, 10.2 (*C*H$_{3,Phth}$). IR (thin film, cm^{-1}): 1029, 1046, 1098, 1126, 1233, 1455, 1507, 2855, 2926, 3418. HRMS calculated for $C_{62}H_{89}O_8$ 961.6557 [M+H]$^+$; found 961.6546.

4-((3*R*,4*S*,9*R*,11*R*)-3-methoxy-4-methylheptacos-26-yne-9,11-diol)phenyl 2,4-di-*O*-benzyl-3-*O*-(2,3-di-*O*-benzyloxycarbonyl-4-*O*-benzyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (46)



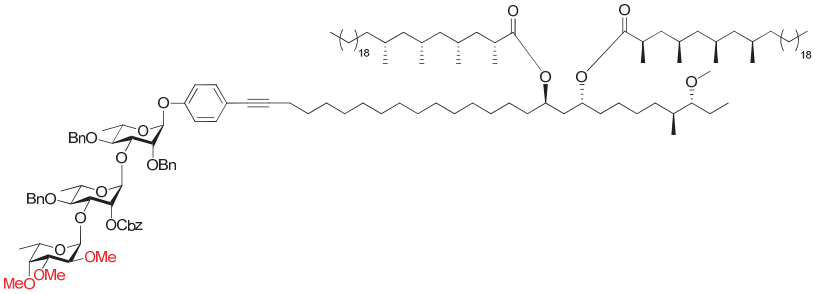
The title compound was synthesized according to general procedure C using **40** (34 mg, 34 µmol, 1.0 eq) and phthiocerol (19 mg, 41 µmol, 1.2 eq). Column chromatography (*n*-pentane-Et_2O 4:1) yielded the title compound (43 mg, 33 µmol, 96%) as a yellow oil. $[\alpha]_D^{25}$ = -40.7 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.38-7.22 (m, 22H, C*H*$_{arom}$); 6.95-6.92 (m, 2H, C*H*$_{arom}$); 5.50 (d, 1H, *J* = 1.6 Hz, H-1); 5.34-5.29 (m, 2H, H-2', H-3'); 5.19 (d, 1H, *J* = 2.0 Hz, H-1'); 5.16 (s, 2H, PhC*H*$_2$); 5.12 (s, 2H, PhC*H*$_2$); 4.90 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.73 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.62-4.57 (m, 2H, PhCH*H*, PhCH*H*); 4.20 (dd, 1H, *J* = 3.2, 9.6 Hz, H-3); 4.10-4.03 (m, 1H, H-5'); 3.98-3.90 (m, 2H, C*H*$_{Phth}$); 3.73-3.69 (m, 2H, H-2, H-5); 3.62-3.52 (m, 5H, H-4, H-4', OC*H*$_3$); 3.34 (s, 3H, OC*H*$_3$); 2.88-2.85 (m, 1H, C*H*$_{Phth}$); 2.37 (t, 2H, *J* = 7.0 Hz, C*H*$_{2,Phth}$); 1.70-1.02 (m, 64H, H-6, H-6', C*H*$_{Phth}$, C*H*$_{2,Phth}$); 0.91 (t, 3H, *J* = 7.4 Hz, C*H*$_{3,Phth}$); 0.83 (d, 3H, *J* = 7.2 Hz, C*H*$_{3,Phth}$). ^{13}C-APT NMR (101 MHz) δ: 155.6 (C$_{q,arom}$); 154.5, 154.4 (*C*O$_{Cbz}$); 138.2, 138.0, 135.2, 135.0 (C$_{q,arom}$); 133.0, 128.8, 128.8, 128.7, 128.7, 128.6, 128.5, 128.5, 128.3, 128.1, 128.0, 127.8 (*C*H$_{arom}$); 118.0 (C$_{q,arom}$); 116.2 (*C*H$_{arom}$); 99.3 (C-1'); 94.7 (C-1); 89.5 (C$_{q,alkyne}$); 86.8 (*C*H$_{Phth}$); 80.1 (C$_{q,alkyne}$); 80.0 (C-2 and C-4); 79.6 (C-3); 78.6 (C-4'); 76.1 (C-3'); 75.7, 75.5 (Ph*C*H$_2$); 74.1 (C-2'); 70.2, 70.1 (Ph*C*H$_2$); 69.6, 69.6 (*C*H$_{Phth}$); 69.0 (C-5); 68.6 (C-5'); 59.1, 57.5 (O*C*H$_3$); 42.4, 37.6 (*C*H$_{2,Phth}$); 34.9 (*C*H$_{Phth}$); 32.8, 29.8, 29.7, 29.3, 29.1, 29.0, 27.7, 26.3, 25.9, 22.5, 19.5 (*C*H$_{2,Phth}$); 18.1 (C-6); 18.1 (C-6'); 14.9, 10.2 (*C*H$_{3,Phth}$). IR (thin film, cm^{-1}): 1047, 1052, 1056, 1078, 1096, 1100, 1120, 1125, 1139, 1236, 1275, 1382, 1484, 1507, 1753, 1753, 2855, 2926, 3411. HRMS calculated for $C_{78}H_{107}O_{16}$ 1299.75536 $[M+H]^+$; found 1299.75560.

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*-benzyloxycarbonyl-3-*O*-(2,3,4-tri-*O*-methyl-α-L-fucopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranoside (47)



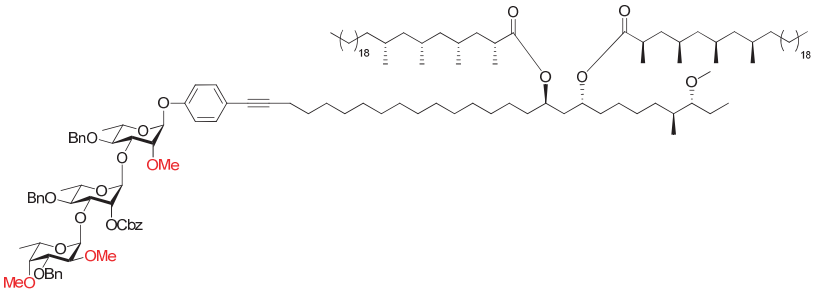
The title compound was synthesized according to general procedure D using **41** (30 mg, 22 µmol, 1.0 eq), mycocerosic acid (32 mg, 66 µmol, 3.0 eq), DIC (21 µL, 133 µmol, 6.0 eq) and DMAP (24 mg, 199 µmol, 9.0 eq). Column chromatography (*n*-pentane-Et_2O 3:1) yielded the title compound (48 mg, 21 µmol, 94%) as a waxy solid. $[\alpha]_D^{25}$ = -53.9 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.44-7.24 (m, 17H, C*H*$_{arom}$); 6.95-6.92 (m, 2H, C*H*$_{arom}$); 5.51 (d, 1H, *J* = 2.0 Hz, H-1); 5.22 (d, 1H, *J* = 1.6 Hz, H-1'); 5.20-5.10 (m, 5H, H-1'', H-2', PhC*H*$_2$, PhC*H*H); 4.93 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.84 (quint, 2H, *J* = 6.4 Hz, C*H*$_{Phth}$); 4.60-4.53 (m, 2H, PhCH*H*, PhCH*H*); 4.22-4.18 (m, 2H, H-3, H-3'); 4.04-3.97 (m, 1H, H-5'); 3.81 (q, 1H, *J* = 6.4 Hz, H-5''); 3.74-3.65 (m, 2H, H-2, H-5); 3.57-3.48 (m, 13H, H-2'', H-3'', H-4, H-4', OC*H*$_3$); 3.33 (s, 3H, OC*H*$_3$); 3.31 (s, 3H, OC*H*$_3$); 3.27 (d, 1H, *J* = 1.6 Hz, H-4''); 2.88-2.83 (m, 1H, C*H*$_{Phth}$); 2.55-2.50 (m, 2H, C*H*$_{Myc}$); 2.37 (t, 2H, *J* = 7.0 Hz, C*H*$_{2,Phth}$); 1.77-0.81 (m, 209H, 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 (C$_{q,arom}$); 154.8 (*C*O$_{Cbz}$); 139.0, 138.2, 135.2 (C$_{q,arom}$); 133.0, 128.9, 128.9, 128.8, 128.6, 128.5, 128.5, 128.4, 127.9, 127.6, 127.5 (*C*H$_{arom}$); 118.0 (C$_{q,arom}$); 116.2 (*C*H$_{arom}$); 100.0 (C-1''); 99.5 (C-1'); 94.4 (C-1); 89.5 (C$_{q,alkyne}$); 86.8 (*C*H$_{Phth}$); 80.4 (C-3); 80.1 (C-2 and C-3''); 79.9, 79.7 (C-4 and C-4'); 79.3 (C-4''); 78.3 (C-3'); 77.7 (C-2''); 75.7, 75.1 (Ph*C*H$_2$); 70.4 (*C*H$_{Phth}$); 70.1 (Ph*C*H$_2$); 68.9 (C-5); 68.6 (C-5'); 67.1 (C-5''); 61.9, 59.1, 58.8, 58.2, 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, 29.8, 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$_{3,Myc}$); 18.2 (C-6'); 18.1 (C-6); 16.4 (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}): 1047, 1098, 1130, 1139, 1176, 1261, 1457, 1464, 1472, 1507, 1736, 2849, 2916. HRMS calculated for $C_{143}H_{241}O_{20}$ 2280.79031 $[M+H]^+$; found 2280.80360

4-((3*R*,4*S*,9*R*,11*R*)-3-methoxy-4-methylheptacos-26-yne-9,11-diyl bismycocerosate)phenyl 2,4-di-*O*-benzyl-3-*O*-(2-*O*-benzyloxycarbonyl-3-*O*-(2,3,4-tri-*O*-methyl-α-L-fucopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (48)



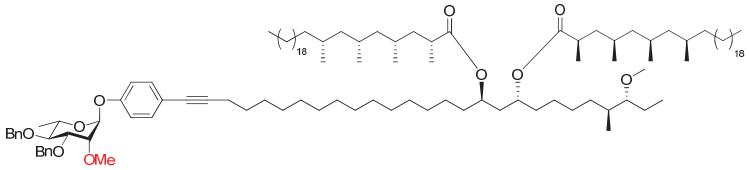
The title compound was synthesized according to general procedure D using **42** (33 mg, 23 µmol, 1.0 eq), mycocerosic acid (33 mg, 69 µmol, 3.0 eq), DIC (21 µL, 138 µmol, 6.0 eq) and DMAP (25 mg, 207 µmol, 9.0 eq). Column chromatography (*n*-pentane-Et_2O 7:3) yielded the title compound (41 mg, 17 µmol, 75%) as a waxy solid. $[\alpha]_D^{25}$ = -49.7 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.41-7.23 (m, 22H, C*H*$_{arom}$); 6.89 (dd, 2H, *J* = 2.0, 7.2 Hz, C*H*$_{arom}$); 5.47 (d, 1H, *J* = 2.0 Hz, H-1); 5.27 (d, 1H, *J* = 1.2 Hz, H-1'); 5.20-5.09 (m, 5H, H-1'', H-2', PhC*H*$_2$, PhC*H*H); 4.93 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.84 (quint, 2H, *J* = 6.2 Hz, C*H*$_{Phth}$); 4.74 (dd, 2H, *J* = 12.0, 21.2 Hz, PhC*H*$_2$); 4.59-4.55 (m, 2H, PhCH*H*, PhCH*H*); 4.27 (dd, 1H, *J* = 3.2, 8.8 Hz, H-3); 4.18 (dd, 1H, *J* = 3.4, 9.2 Hz, H-3'); 3.91-3.84 (m, 3H, H-2, H-5', H-5''); 3.74-3.65 (m, 2H, H-4, H-5); 3.57-3.47 (m, 9H, H-2'', H-3'', H-4', OC*H*$_3$); 3.33 (s, 3H, OC*H*$_3$); 3.29 (d, 1H, *J* = 1.6 Hz, H-4''); 3.28 (s, 3H, OC*H*$_3$); 2.89-2.85 (m, 1H, C*H*$_{Phth}$); 2.55-2.50 (m, 2H, C*H*$_{Myc}$); 2.37 (t, 2H, *J* = 7.2 Hz, C*H*$_{2,Phth}$); 1.77-0.81 (m, 243H, 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$_{Myc}$); 155.6 (C$_{q,arom}$); 154.8 (*C*O$_{Cbz}$); 139.1, 138.2, 137.8, 135.2 (C$_{q,arom}$); 132.9, 128.9, 128.8, 128.7, 128.4, 128.4, 128.3, 128.0, 127.9, 127.8, 127.4, 127.4 (*C*H$_{arom}$); 118.0 (C$_{q,arom}$); 116.2 (*C*H$_{arom}$); 99.8 (C-1''); 99.0 (C-1'); 95.5 (C-1); 89.5 (C$_{q,alkyne}$); 86.8 (*C*H$_{Phth}$); 80.5 (C-4); 80.4 (C-4'); 80.1 (C$_{q,alkyne}$); 79.8 (C-3''); 79.3 (C-4''); 78.4 (C-3); 77.9 (C-2); 77.8 (C-3'); 77.7 (C-2''); 76.6 (C-2'); 75.6, 74.9, 73.0 (Ph*C*H$_2$); 70.4 (*C*H$_{Phth}$); 70.1 (Ph*C*H$_2$); 69.1 (C-5); 68.7 (C-5'); 67.1 (C-5''); 61.9, 59.1, 58.2, 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$_{2,Myc}$); 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, 29.5, 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, 20.5, 20.5 (*C*H$_{3,Myc}$); 19.6 (*C*H$_{2,Phth}$); 18.6 (*C*H$_{3,Myc}$); 18.0 (C-6 and C-6'); 16.4 (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}): 1029, 1102, 1130, 1175, 1236, 1261, 1379, 1455, 1464, 1507, 1736, 2850, 2921. HRMS calculated for $C_{149}H_{245}O_{20}$ 2355.81828 $[M+H]^+$; found 2355.82501.

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*-benzyloxycarbonyl-3-*O*-(2,4-di-*O*-methyl-3-*O*-benzyl-α-L-fucopyranosyl)-4-*O*-benzyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (49)



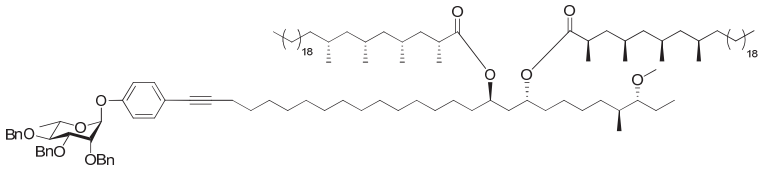
The title compound was synthesized according to general procedure D using **43** (33 mg, 33 µmol, 1.0 eq), mycocerosic acid (33 mg, 69 µmol, 3.0 eq), DIC (21 µL, 138 µmol, 6.0 eq) and DMAP (25 mg, 138 µmol, 9.0 eq). Column chromatography (*n*-pentane-Et_2O 2:3) yielded the title compound (40 mg, 17 µmol, 74%) as a waxy solid. $[\alpha]_D^{25}$ = -50.3 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.40-7.24 (m, 22H, C*H*$_{arom}$); 6.95-6.92 (m, 2H, C*H*$_{arom}$); 5.51 (d, 1H, *J* = 1.6 Hz, H-1); 5.22-5.07 (m, 6H, H-1', H-1'', H-2', PhC*H*$_2$, PhC*H*H); 4.92 (d, 1H, *J* = 10.4 Hz, PhC*H*H); 4.89-4.80 (m, 2H, C*H*$_{Phth}$); 4.71 (dd, 2H, *J* = 12.4, 29.2 Hz, PhC*H*$_2$); 4.58-4.53 (m, 2H, PhCH*H*, PhCH*H*); 4.20 (dd, 2H, *J* = 3.2, 9.6 Hz, H-3, H-3'); 4.04-3.95 (m, 1H, H-5'); 3.83 (q, 1H, *J* = 6.4 Hz, H-5''); 3.79-3.63 (m, 4H, H-2, H-2'', H-3'', H-5); 3.55-3.51 (m, 8H, H-4, H-4', OC*H*$_3$); 3.35 (s, 3H, OC*H*$_3$); 3.33 (s, 3H, OC*H*$_3$); 3.24 (d, 1H, *J* = 2.0 Hz, H-4''); 2.88-2.83 (m, 1H, C*H*$_{Phth}$); 2.55-2.50 (m, 2H, C*H*$_{Myc}$); 2.37 (t, 2H, *J* = 7.2 Hz, C*H*$_{2,Phth}$); 1.77-0.81 (m, 213H, 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 (C$_{q,arom}$); 154.8 (*C*O$_{Cbz}$); 139.1, 139.0, 138.2, 135.2 (C$_{q,arom}$); 128.9, 128.8, 128.5, 128.5, 128.4, 127.9, 127.8, 127.6, 127.5 (*C*H$_{arom}$); 118.0 (C$_{q,arom}$); 116.2 (*C*H$_{arom}$); 100.1 (C-1''); 99.5 (C-1'); 94.4 (C-1); 89.5 (C$_{q,alkyne}$); 86.8 (*C*H$_{Phth}$); 80.6 (C-4''); 80.1 (C-2); 80.0 (C-3); 79.9 (C-4'); 79.6 (C-4); 78.6 (C-3''); 78.4 (C-3'); 78.3 (C-2''); 76.7 (C-2'); 75.7, 75.2, 72.7 (Ph*C*H$_2$); 70.4 (*C*H$_{Phth}$); 70.1 (Ph*C*H$_2$); 68.9 (C-5); 68.4 (C-5'); 67.2 (C-5''); 61.9, 59.4, 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 (*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, 29.8, 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$_{3,Myc}$); 18.2 (C-6'); 18.1 (C-6); 16.2 (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}): 1046, 1102, 1139, 1176, 1262, 1379, 1457, 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-*O*-methyl-3,4-di-*O*-benzyl-α-L-rhamnopyranoside (50)



The title compound was synthesized according to general procedure D using **44** (22 mg, 25 µmol, 1.0 eq), mycocerosic acid (36 mg, 75 µmol, 3.0 eq), DIC (23 µL, 149 µmol, 6.0 eq) and DMAP (27 mg, 224 µmol, 9.0 eq). Column chromatography (*n*-pentane-Et_2O 4:1) yielded the title compound (38 mg, 21 µmol, 84%) as a waxy solid. $[\alpha]_D^{25}$ = -33.3 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.43-7.40 (m, 2H, C*H*$_{arom}$); 7.37-7.26 (m, 10H, C*H*$_{arom}$); 6.94-6.91 (m, 2H, C*H*$_{arom}$); 5.51 (d, 1H, *J* = 2.0 Hz, H-1); 4.95 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.89-4.80 (m, 2H, C*H*$_{Phth}$); 4.78 (s, 2H, PhC*H*$_2$); 4.64 (d, 1H, *J* = 10.8 Hz, PhCH*H*); 4.03 (dd, 1H, *J* = 3.2, 9.2 Hz, H-3); 3.76-3.70 (m, 1H, H-5); 3.68 (dd, 1H, *J* = 2.0, 3.2 Hz, H-2); 3.60-3.55 (m, 4H, H-4, OC*H*$_3$); 3.33 (s, 3H, OC*H*$_3$); 2.89-2.83 (m, 1H, C*H*$_{Phth}$); 2.57-2.48 (m, 2H, C*H*$_{Myc}$); 2.37 (t, 2H, *J* = 7.0 Hz, C*H*$_{2,Phth}$); 1.77-0.81 (m, 235H, 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$_{Myc}$); 155.7, 138.6, 138.5 (C$_{q,arom}$); 133.0, 128.6, 128.5, 128.1, 128.1, 127.9, 127.8 (*C*H$_{arom}$); 118.0 (C$_{q,arom}$); 116.2 (*C*H$_{arom}$); 95.4 (C-1); 89.5 (C$_{q,alkyne}$); 86.8 (*C*H$_{Phth}$); 80.4 (C-4); 80.1 (C$_{q,alkyne}$); 79.7 (C-3); 78.1 (C-2); 75.7, 72.7 (Ph*C*H$_2$); 70.4 (*C*H$_{Phth}$); 68.9 (C-5); 59.7, 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 (*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, 20.6, 20.6, 20.5 (*C*H$_{3,Myc}$); 19.6 (*C*H$_{2,Phth}$); 18.6 (*C*H$_{3,Myc}$); 18.1 (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}): 1099, 1176, 1378, 1457, 1464, 1507, 1734, 2853, 2923. HRMS calculated for $C_{120}H_{209}O_{10}$ 1810.58403 $[M+H]^+$; found 1810.58417.

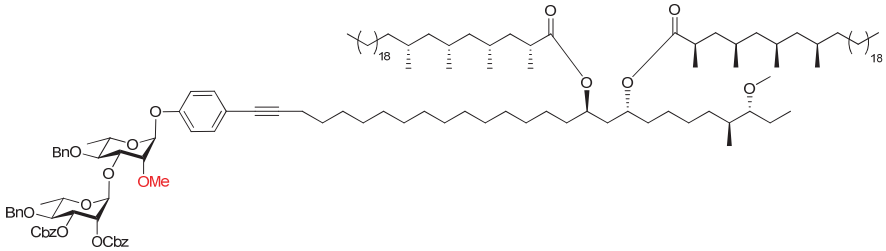
4-((3*R*,4*S*,9*R*,11*R*)-3-methoxy-4-methylheptacos-26-yne-9,11-diyl bismycocerosate)phenyl 2,3,4-tri-*O*-benzyl-α-L-rhamnopyranoside (51)



The title compound was synthesized according to general procedure D using **45** (23 mg, 24 µmol, 1.0 eq), mycocerosic acid (35 mg, 72 µmol, 3.0 eq), DIC (22 µL, 144 µmol, 6.0 eq) and DMAP (26 mg, 215 µmol, 9.0 eq). Column chromatography (*n*-pentane-Et_2O 19:1) yielded the title compound (33 mg, 17 µmol, 73%) as a waxy solid. $[\alpha]_D^{25}$ = -26.4 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.37-7.26 (m, 17H, C*H*$_{arom}$); 6.88-6.85 (m, 2H, C*H*$_{arom}$); 5.45 (d, 1H, *J* = 2.0 Hz, H-1); 4.96 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.87-4.74 (m, 4H, PhC*H*$_2$, C*H*$_{Phth}$); 4.73-4.64 (m, 3H, PhCH*H*, PhC*H*$_2$); 4.04 (dd, 1H, *J* = 3.0, 9.0 Hz, H-3); 3.93 (dd, 1H, *J* = 2.0, 2.8 Hz, H-2); 3.78-3.66 (m, 2H, H-4, H-5); 3.33 (s, 3H, OC*H*$_3$); 2.89-2.83 (m, 1H, C*H*$_{Phth}$); 2.57-2.48 (m, 2H, C*H*$_{Myc}$); 2.37 (t, 2H, *J*

= 7.0 Hz, C$H_{2,Phth}$); 1.77-0.81 (m, 212H, H-6, CH_{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$_{Myc}$); 155.6, 138.6, 138.2 (C$_{q,arom}$); 132.9, 128.6, 128.6, 128.5, 128.2, 128.1, 128.0, 127.8, 127.8 (*C*H$_{arom}$); 117.9 (C$_{q,arom}$); 116.2 (*C*H$_{arom}$); 96.2 (C-1); 89.5 (C$_{q,alkyne}$); 86.8 (*C*H$_{Phth}$); 80.5 (C-4); 80.1 (C$_{q,alkyne}$); 80.0 (C-3); 75.6 (PhCH$_2$); 74.7 (C-2); 73.2, 72.6 (PhCH$_2$); 70.4 (*C*H$_{Phth}$); 69.0 (C-5); 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, 29.8, 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$_{2,Phth}$); 22.9 (*C*H$_{2,Myc}$); 22.5 (*C*H$_{2,Phth}$); 20.9, 20.6, 20.6 (*C*H$_{3,Myc}$); 19.6 (*C*H$_{2,Phth}$); 18.6 (*C*H$_{3,Myc}$); 18.1 (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}): 1099, 1175, 1233, 1378, 1457, 1507, 1734, 2853, 2923. HRMS calculated for $C_{126}H_{213}O_{10}$ 1886.61533 [M+H]$^+$; found 1886.61566.

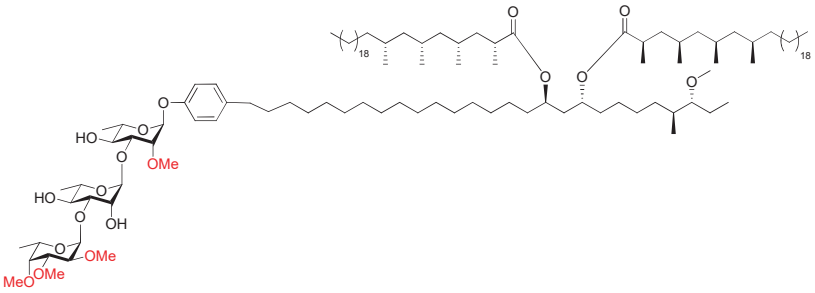
4-((3*R*,4*S*,9*R*,11*R*)-3-methoxy-4-methylheptacos-26-yne-9,11-diyl bismycocerosate)phenyl 2,4-di-*O*-benzyl-3-*O*-(2,3-di-*O*-benzyloxycarbonyl-4-*O*-benzyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (52)



The title compound was synthesized according to general procedure D using **46** (37 mg, 28 μmol, 1.0 eq), mycocerosic acid (41 mg, 85 μmol, 3.0 eq), DIC (26 μL, 171 μmol, 6.0 eq) and DMAP (31 mg, 256 μmol, 9.0 eq). Column chromatography (*n*-pentane-Et$_2$O 17:3) yielded the title compound (32 mg, 14 μmol, 51%) as a waxy solid. [α]$_D^{25}$ = -24.9 ° (c = 1.0, CHCl$_3$). ^{1}H-NMR (400 MHz) δ: 7.37-7.24 (m, 22H, *C*H$_{arom}$); 6.93 (d, 2H, *J* = 8.8 Hz, *C*H$_{arom}$); 5.50 (d, 1H, *J* = 1.6 Hz, H-1); 5.34-5.29 (m, 2H, H-2', H-3'); 5.19 (d, 1H, *J* = 1.6 Hz, H-1'); 5.16 (s, 2H, PhC*H*$_2$); 5.12 (s, 2H, PhC*H*$_2$); 4.91-4.83 (m, 3H, PhC*H*H, C*H*$_{Phth,}$ C*H*$_{Phth}$); 4.73 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.62-4.57 (m, 2H, PhCH*H*, PhCH*H*); 4.20 (dd, 1H, *J* = 3.2, 9.6 Hz, H-3); 4.10-4.03 (m, 1H, H-5'); 3.73-3.69 (m, 2H, H-2, H-5); 3.62-3.52 (m, 5H, H-4, H-4', OC*H*$_3$); 3.33 (s, 3H, OC*H*$_3$); 2.88-2.85 (m, 1H, C*H*$_{Phth}$); 2.55-2.50 (m, 2H, C*H*$_{Myc}$); 2.37 (t, 2H, *J* = 7.2 Hz, C*H*$_{2,Phth}$); 1.77-0.81 (m, 208H, 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$_{Myc}$); 155.7 (C$_{q,arom}$); 154.5, 154.4 (*C*O$_{Cbz}$); 138.3, 138.0, 135.3, 135.0 (C$_{q,arom}$); 133.0, 128.8, 128.7, 128.7, 128.6, 128.5, 128.5, 128.3, 128.1, 128.0, 127.8 (*C*H$_{arom}$); 118.0 (C$_{q,arom}$); 116.2 (*C*H$_{arom}$); 99.3 (C-1'); 94.7 (C-1); 89.5 (C$_{q,alkyne}$); 86.8 (*C*H$_{Phth}$); 80.1 (C$_{q,alkyne}$); 80.0 (C-2 and C-4); 79.6 (C-3); 78.6 (C-4'); 76.1 (C-3'); 75.7, 75.5 (PhCH$_2$); 74.1 (C-2'); 70.4 (*C*H$_{Phth}$); 70.2, 70.1 (PhCH$_2$); 69.0 (C-5); 68.6 (C-5'); 59.1, 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, 20.6, 20.6, 20.5 (*C*H$_{3,Myc}$); 19.6 (*C*H$_{2,Phth}$); 18.6 (*C*H$_{3,Myc}$);

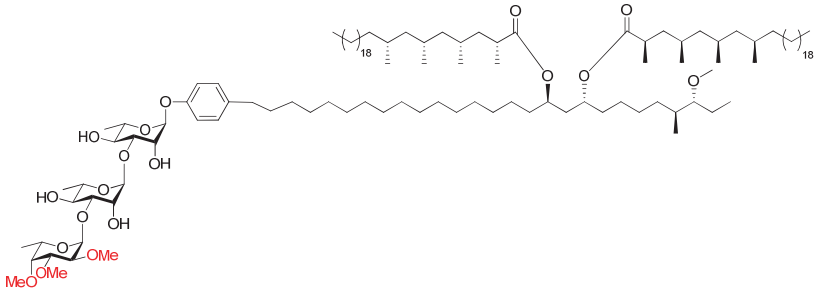
18.1 (C-6); 18.1 (C-6'); 14.8 ($CH_{3,Phth}$); 14.3 ($CH_{3,Myc}$); 10.3 ($CH_{3,Phth}$). IR (thin film, cm^{-1}): 1029, 1047, 1078, 1082, 1100, 1140, 1176, 1236, 1275, 1378, 1457, 1507, 1736, 1753, 2853, 2925. HRMS calculated for $C_{142}H_{231}O_{18}$ 2225.71890 $[M+H]^+$; found 2225.72535.

4-((3*R*,4*S*,9*R*,11*R*)-3-methoxy-4-methylheptacos-9,11-diyl bismycocerosate)phenyl 2-*O*-methyl-3-*O*-(3-*O*-(2,3,4-tri-*O*-methyl-α-L-fucopyranosyl)-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (53)



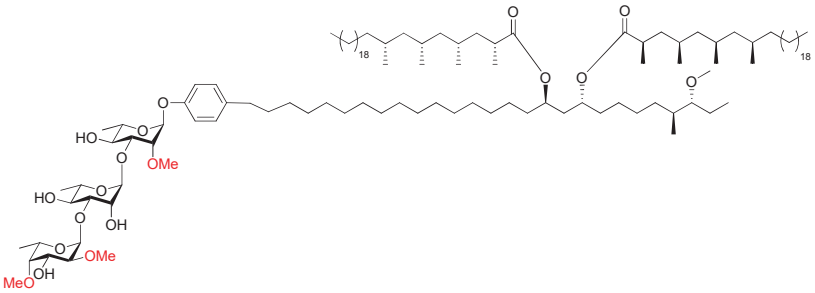
The title compound was synthesized according to general procedure E using **47** (33 mg, 14 µmol, 1.0 eq) and Pd/C (10%, 15 mg, 14 µmol, 1.0 eq). Column chromatography (DCM-MeOH 19:1) yielded the title compound (23 mg, 12 µmol, 82%) as a waxy solid. $[\alpha]_D^{25}$ = -48.4 ° (c = 0.5, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.10 (d, 2H, *J* = 8.4 Hz, CH_{arom}); 6.99 (d, 2H, *J* = 8.8 Hz, CH_{arom}); 5.51 (d, 1H, *J* = 1.6 Hz, H-1); 5.15-5.14 (m, 2H, H-1', H-1"); 4.84 (quint, 2H, *J* = 6.4 Hz, CH_{Phth}); 4.11 (s, 1H, H-2'); 4.07-4.03 (m, 2H, H-3, H-5"); 3.98-3.91 (m, 1H, H-5'); 3.82-3.74 (m, 3H, H-2, H-3', H-5); 3.70-3.64 (m, 4H, H-2", H-3", H-4, H-4'); 3.61 (s, 3H, OCH_3); 3.58 (s, 3H, OCH_3); 3.52 (s, 3H, OCH_3); 3.49 (s, 3H, OCH_3); 3.48 (d, 1H, *J* = 1.6 Hz, H-4"); 3.33 (s, 3H, OCH_3); 2.88-2.83 (m, 1H, CH_{Phth}); 2.58-2.48 (m, 4H, C$H_{2,Phth}$, CH_{Myc}); 2.27 (bs, 1H, O*H*); 2.16 (bs, 1H, O*H*); 1.77-0.81 (m, 203H, H-6, H-6', H-6", CH_{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 (CO_{Myc}); 154.7, 137.0 ($C_{q,arom}$); 129.5, 116.3 (CH_{arom}); 102.3 (C-1"); 100.9 (C-1'); 95.0 (C-1); 86.8 (CH_{Phth}); 83.3 (C-3'); 81.1 (C-3"); 80.2 (C-2); 80.1 (C-3); 79.1 (C-4"); 78.9 (C-2"); 71.9 (C-4'); 71.8 (C-4); 71.3 (C-2'); 70.4 (CH_{Phth}); 69.2 (C-5); 68.8 (C-5'); 67.6 (C-5"); 62.1, 60.4, 58.7, 57.9, 57.5 (OCH_3); 45.6, 45.4 (C$H_{2,Myc}$); 41.1, 38.6 (C$H_{2,Phth}$); 37.9, 37.9 (CH_{Myc}); 36.8 (C$H_{2,Myc}$); 34.9 (CH_{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 (CH_{Myc}); 29.9, 29.9, 29.8, 29.7, 29.5 (CH_2); 28.2 (CH_{Myc}); 27.6 (C$H_{2,Phth}$); 27.3 (CH_{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, 18.6 (C$H_{3,Myc}$); 18.0, 17.9 (C-6 and C-6'); 16.8 (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}): 1020, 1043, 1095, 1229, 1259, 1379, 1460, 1508, 1731, 1736, 2853, 2923, 3420. HRMS calculated for $C_{121}H_{227}O_{18}$ 1969.68761 $[M+H]^+$; found 1969.68884.

4-((3*R*,4*S*,9*R*,11*R*)-3-methoxy-4-methylheptacos-9,11-diyl bismycocerosate)phenyl 3-*O*-(3-*O*-(2,3,4-tri-*O*-methyl-α-L-fucopyranosyl)-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (54)



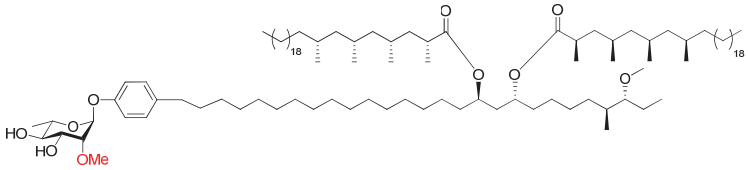
The title compound was synthesized according to general procedure E using **48** (35 mg, 15 µmol, 1.0 eq) and Pd/C (10%, 16 mg, 15 µmol, 1.0 eq). Column chromatography (DCM-acetone 7:3) yielded the title compound (23 mg, 12 µmol, 80%) as a waxy solid. $[\alpha]_D^{25}$ = -47.8 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.09 (d, 2H, *J* = 8.8 Hz, CH_{arom}); 6.97 (d, 2H, *J* = 8.4 Hz, CH_{arom}); 5.45 (d, 1H, *J* = 1.6 Hz, H-1); 5.20 (d, 1H, *J* = 1.2 Hz, H-1'); 5.16 (d, 1H, *J* = 3.2 Hz, H-1''); 4.84 (quint, 2H, *J* = 6.2 Hz, CH_{Phth}); 4.18 (dd, 1H, *J* = 2.0, 3.2 Hz, H-2); 4.12 (dd, 1H, *J* = 1.6, 3.2 Hz, H-2'); 4.10-4.02 (m, 2H, H-3, H-5''); 3.92-3.76 (m, 3H, H-3', H-5, H-5'); 3.71-3.64 (m, 4H, H-2'', H-3'', H-4, H-4'); 3.61 (s, 3H, OCH_3); 3.59 (s, 3H, OCH_3); 3.52 (s, 3H, OCH_3); 3.48 (d, 1H, *J* = 1.6 Hz, H-4''); 3.33 (s, 3H, OCH_3); 2.88-2.83 (m, 1H, CH_{Phth}); 2.58-2.48 (m, 4H, C$H_{2,Phth}$, CH_{Myc}); 1.77-0.81 (m, 192H, H-6, H-6', H-6'', CH_{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$_{Myc}$); 154.3, 137.0 (C$_{q,arom}$); 129.4, 116.3 (*C*H$_{arom}$); 101.8 (C-1''); 101.0 (C-1'); 97.9 (C-1); 86.8 (*C*H$_{Phth}$); 83.2 (C-3'); 81.1 (C-3''); 79.7 (C-3); 79.0 (C-4''); 78.8 (C-2''); 72.2 (C-4); 71.6 (C-4'); 71.2 (C-2'); 70.8 (C-2); 70.4 (*C*H$_{Myc}$); 69.1 (C-5'); 68.8 (C-5); 67.7 (C-5''); 62.1, 60.4, 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, 35.3 (*C*H$_{2,Myc}$); 34.9 (*C*H$_{Phth}$); 34.8, 32.8 (*C*H$_{2,Phth}$); 32.1 (*C*H$_{2,Myc}$); 31.8, 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, 20.6, 18.6 (*C*H$_{3,Myc}$); 17.8 (C-6) 17.8 (C-6'); 16.8 (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}): 1045, 1090, 1228, 1172, 1229, 1261, 1378, 1457, 1511, 1734, 2853, 2922, 3441. HRMS calculated for $C_{120}H_{225}O_{18}$ 1955.67196 $[M+H]^+$; found 1955.67222.

4-((3*R*,4*S*,9*R*,11*R*)-3-methoxy-4-methylheptacos-9,11-diyl bismycocerosate)phenyl 2-*O*-methyl-3-*O*-(3-*O*-(2,4-di-*O*-methyl-α-L-fucopyranosyl)-α-L-rhamnopyranosyl)-α-L-rhamnopyranoside (55)



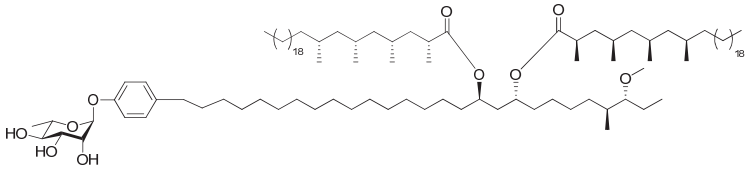
The title compound was synthesized according to general procedure E using **49** (41 mg, 17 µmol, 1.0 eq) and Pd/C (10%, 19 mg, 17.4 µmol, 1.0 eq). Column chromatography (DCM-MeOH 19:1) yielded the title compound (28 mg, 14 µmol, 82%) as a waxy solid. $[\alpha]_D^{25}$ = -44.7 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.10 (d, 2H, *J* = 8.4 Hz, C*H*$_{arom}$); 6.99 (d, 2H, *J* = 8.8 Hz, C*H*$_{arom}$); 5.51 (d, 1H, *J* = 1.6 Hz, H-1); 5.18 (d, 1H, *J* = 3.6 Hz, H-1''); 5.13 (d, 1H, *J* = 1.2 Hz, H-1'); 4.84 (quint, 2H, *J* = 6.4 Hz, C*H*$_{Phth}$); 4.16-4.11 (m, 2H, H-2', H-5''); 4.04 (dd, 2H, *J* = 3.0, 9.4 Hz, H-3, H-3''); 3.98-3.91 (m, 1H, H-5'); 3.81-3.74 (m, 3H, H-2, H-3', H-5); 3.70-3.61 (m, 5H, H-4, H-4', OC*H*$_3$); 3.58 (s, 3H, OC*H*$_3$); 3.50-3.47 (m, 4H, H-2'', OC*H*$_3$); 3.40 (d, 1H, *J* = 2.4 Hz, H-4''); 3.33 (s, 3H, OC*H*$_3$); 2.88-2.83 (m, 1H, C*H*$_{Phth}$); 2.58-2.48 (m, 4H, C*H*$_{2,Phth}$, C*H*$_{Myc}$); 1.77-0.81 (m, 191H, 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$_{Myc}$); 154.7, 137.0 (C$_{q,arom}$); 129.5, 116.3 (*C*H$_{arom}$); 102.3 (C-1''); 99.9 (C-1'); 95.0 (C-1); 86.8 (*C*H$_{Phth}$); 83.0 (C-3'); 82.5 (C-4''); 80.2 (C-3); 80.1 (C-2''); 80.1 (C-2); 71.9 (C-4); 71.6 (C-4'); 71.2 (C-2'); 70.6 (C-3''); 70.4 (*C*H$_{Phth}$); 69.2 (C-5); 68.8 (C-5'); 67.6 (C-5''); 62.6, 59.8, 58.7, 57.7 (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, 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); 17.9 (C-6'); 16.9 (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, 1129, 1150, 1173, 1261, 1378, 1461, 1510, 1734, 2853, 2923, 3414. HRMS calculated for $C_{120}H_{225}O_{18}$ 1955.67196 [M+H]$^+$; found 1955.67295.

4-((3*R*,4*S*,9*R*,11*R*)-3-methoxy-4-methylheptacos-9,11-diyl bismycocerosate)phenyl 2-*O*-methyl-α-L-rhamnopyranoside (56)



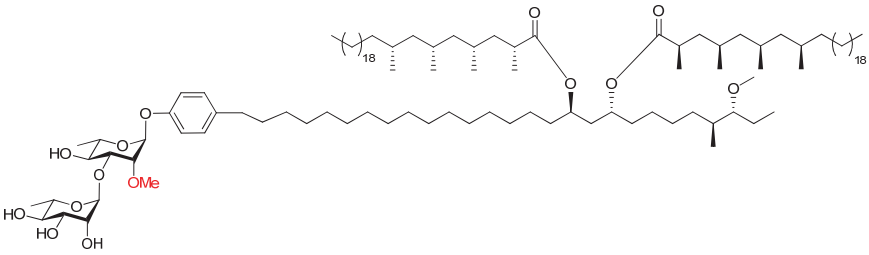
The title compound was synthesized according to general procedure E using **50** (27 mg, 15 µmol, 1.0 eq) and Pd/C (10%, 16 mg, 15 µmol, 1.0 eq). Column chromatography (DCM-acetone 19:1) yielded the title compound (15 mg, 9 µmol, 62%) as a waxy solid. $[\alpha]_D^{25}$ = -7.63 ° (c = 0.8, $CHCl_3$). ^{1}H-NMR (850 MHz) δ: 7.10 (d, 2H, *J* = 8.5 Hz, C*H*$_{arom}$); 6.99 (dd, 2H, *J* = 1.7, 6.8 Hz, C*H*$_{arom}$); 5.55 (d, 1H, *J* = 1.7 Hz, H-1); 4.84 (quint, 2H. *J* = 6.4 Hz, C*H*$_{Phth}$); 3.92 (dt, 1H, *J* = 4.0, 9.8 Hz, H-3); 3.76 (dq, 1H, *J* = 6.0, 9.4 Hz, H-5); 3.66 (dd, 1H, *J* = 1.7, 4.3 Hz, H-2); 3.53 (s, 3H, OC*H*$_3$); 3.44 (t, 1H, *J* = 9.4 Hz, H-4); 3.33 (s, 3H, OC*H*$_3$); 2.87-2.85 (m, 1H, C*H*$_{Phth}$); 2.56-2.51 (m, 4H, C*H*$_{Myc}$, C*H*$_{2,Phth}$); 2.37 (d, 1H, *J* = 9.4 Hz, 3-O*H*); 2.34 (bs, 1H, 4-O*H*); 1.77-0.81 (m, 199H, 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 (214 MHz) δ: 176.2, 176.1 (*C*O$_{Myc}$); 154.6, 137.0 (C$_{q,arom}$); 129.5, 116.2 (*C*H$_{arom}$); 94.8 (C-1); 86.8 (*C*H$_{Phth}$); 80.3 (C-2); 74.2 (C-4); 71.5 (C-3); 70.4, 70.4 (*C*H$_{Phth}$); 68.5 (C-5); 59.1, 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, 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$_{3,Myc}$); 17.7 (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}): 1007, 1050, 1096, 1129, 1176, 1231, 1261, 1378, 1511, 1736, 2853, 2923, 3394. HRMS calculated for $C_{106}H_{201}O_{10}$ 1634.52143 $[M+H]^+$; found 1634.52059.

4-((3*R*,4*S*,9*R*,11*R*)-3-methoxy-4-methylheptacos-9,11-diyl bismycocerosate)phenyl α-L-rhamnopyranoside (57)



The title compound was synthesized according to general procedure E using **51** (22 mg, 12 µmol, 1.0 eq) and Pd/C (10%, 12 mg, 10 µmol, 1.0 eq). Column chromatography (DCM-MeOH 19:1) yielded the title compound (6 mg, 4 µmol, 32%) as a waxy solid. $[\alpha]_D^{25}$ = -28 ° (c = 0.2, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: δ: 7.09 (d, 2H, *J* = 8.8 Hz, C*H*$_{arom}$); 6.97 (dd, 2H, *J* = 2.0, 6.8 Hz, C*H*$_{arom}$); 5.48 (d, 1H, *J* = 1.6 Hz, H-1); 4.84 (quint, 2H, *J* = 6.4 Hz, C*H*$_{Phth}$); 4.14 (s, 1H, H-2); 4.01-3.97 (m, 1H, H-3); 3.84-3.77 (m, 1H, H-5); 3.56-3.52 (m, 1H, H-4); 3.33 (s, 3H, OC*H*$_3$); 2.88-2.84 (m, 1H, C*H*$_{Phth}$); 2.56-2.50 (m, 4H, C*H*$_{2,Phth}$, C*H*$_{Myc}$); 1.77-0.81 (m, 176H, 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$_{Myc}$); 154.4, 137.0 (C$_{q,arom}$); 129.5, 116.3 (*C*H$_{arom}$); 98.0 (C-1); 86.8 (*C*H$_{Phth}$); 73.8 (C-4); 71.8 (C-3); 71.0 (C-2); 70.5 (*C*H$_{Phth}$); 68.5 (C-5); 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$_{2,Myc}$); 31.8, 30.2 (*C*H$_{2,Phth}$); 30.1 (*C*H$_{Myc}$);30.0, 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$_{2,Phth}$); 22.9 (*C*H$_{2,Myc}$); 22.5 (*C*H$_{2,Phth}$); 20.9, 20.6, 20.5, 18.6 (*C*H$_{3,Myc}$); 17.7 (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}): 1100, 1129, 1173, 1261, 1378, 1457, 1511, 1736, 2853, 2923, 3398. HRMS calculated for $C_{105}H_{199}O_{10}$ 1620.50578 $[M+H]^+$; found 1620.50542.



4-((3*R*,4*S*,9*R*,11*R*)-3-methoxy-4-methylheptacos-9,11-diyl bismycocerosate)phenyl 2-*O*-methyl-3-*O*-(α-L-rhamnopyranoside)-α-L-rhamnopyranoside (58)

The title compound was synthesized according to general procedure E using **52** (23 mg, 10 µmol, 1.0 eq) and Pd/C (10%, 11 mg, 10 µmol, 1.0 eq). Column chromatography (DCM-MeOH 9:1) yielded the title compound (11 mg, 6 µmol, 60%) as a waxy solid. $[\alpha]_D^{25}$ = -23.0 ° (c = 0.5, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.10 (d, 2H, *J* = 8.8 Hz, C*H*$_{arom}$); 6.98 (d, 2H, *J* = 8.4 Hz, C*H*$_{arom}$); 5.49 (s, 1H, H-1); 5.10 (s, 1H, H-1'); 4.84 (quint, 2H, *J* = 6.4 Hz, C*H*$_{Myc}$); 4.06-4.01 (m, 2H, H-2', H-3); 3.86-3.79 (m, 2H, H-3', H-5'); 3.76-3.72 (m, 2H, H-2, H-5); 3.59 (t, 1H, *J* = 9.6 Hz, H-4); 3.51-3.42 (m, 4H, H-4', OC*H*$_3$); 3.33 (s, 3H, OC*H*$_3$); 2.89-2.85 (m, 1H, C*H*$_{Phth}$); 2.56-2.50 (m, 4H, C*H*$_{2,Phth}$, C*H*$_{Myc}$); 2.27 (bs, 1H, O*H*); 1.77-0.81 (m, 195H, 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: 176.3 (*C*O$_{Myc}$); 154.6, 137.0 (C$_{q,arom}$); 129.4, 116.3 (*C*H$_{arom}$); 102.5 (C-1'); 95.2 (C-1); 86.8 (*C*H$_{Phth}$); 80.3 (C-2); 79.2 (C-3); 73.0 (C-4'); 71.9 (C-4); 71.4 (C-3'); 70.7 (C-2'); 70.5 (*C*H$_{Phth}$); 69.3 (C-5); 68.9 (C-5'); 58.9, 57.5 (O*C*H$_3$); 45.6, 45.4 (*C*H$_{2,Myc}$); 41.1, 38.5 (*C*H$_{2,Phth}$); 37.9 (*C*H$_{Myc}$); 36.7, 35.3 (*C*H$_{2,Myc}$); 34.9 (*C*H$_{Phth}$); 34.8, 32.7 (*C*H$_{2,Phth}$); 32.0 (*C*H$_{2,Myc}$); 31.8, 30.2 (*C*H$_{2,Phth}$); 30.0 (*C*H$_{Myc}$); 29.9, 29.8, 29.8, 29.7, 29.5 (*C*H$_2$); 28.1 (*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$_{2,Myc}$); 22.4 (*C*H$_{2,Phth}$); 20.8, 20.6, 20.5, 18.5 (*C*H$_{3,Myc}$); 17.8 (C-6 and C-6'); 14.7 (*C*H$_{3,Phth}$); 14.2 (*C*H$_{3,Myc}$); 10.2 (*C*H$_{3,Phth}$). IR (thin film, cm^{-1}): 1098, 1130, 1173, 1229, 1261, 1378, 1457, 1511, 1736, 2853, 2923, 3396. HRMS calculated for $C_{112}H_{211}O_{14}$ 1781.58275 $[M+H]^+$; found 1781.58272.

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