Synthesis of mycobacterial phenolic glycolipids

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Chapter 5

Synthesis of PGLs originating from *M. leprae* and *M. haemophilum*

L. Melanie Groot contributed to this chapter.

Introduction

Mycobacterium leprae is the etiological agent of leprosy, a chronic disease which often leads to irreversible deformities and lifelong handicaps.[1] The most prevalent PGL of this bacterium (3,6-di-*O*-methyl-ß-D-glucopyranosyl-(1→4)-2,3-di-*O*-methyl-α-L-rhamnopyranosyl-(1→2)-3-*O*-methyl-α-L-rhamnopyranosyl-(1→), PGL-I) constitutes up to 2% of its mass and is thought to play a major role in its pathogenicity (see Chapter 2).[2–11] Two other *M. leprae* triglycosyl PGLs (PGL-II and PGL-III) and a disaccharide PGL have also been detected, all of which are thought to be biosynthetic intermediates of PGL-I.[8,12] Of all known mycobacteria, *Mycobacterium haemophilum* is genetically the most closely associated to *M. leprae*. This "blood-loving" bacterium is a unique species that requires iron supplementation when grown in culture and, like *M. leprae*, prefers lower growth temperatures.[13] *M. haemophilum* also produces a distinct PGL (2,3-di-*O*-methyl-α-L-rhamnopyranosyl-(1→2)-3-*O*-methyl-α-L-rhamnopyranosyl-(1→4)-2,3-di-*O*-methyl-α-L-rhamnopyranosyl-(1→)), which is very similar to PGL-I.[14] A biosynthetic intermediate of this PGL has been found which lacks the C-2'' methyl ether.[15] Many syntheses of truncated *M. leprae* PGLs or variations thereof have been reported (see Chapters 1 & 2). However, in order to fully understand the interactions between PGLs and the host immune system, pure synthetic complete PGLs are required. Therefore, this Chapter describes the synthesis of all known PGLs originating from *M. leprae* and *M. haemophilum*.

The general strategy for the synthesis of these phenolic glycolipids is as described in Chapter 4 (Figure 1).[16,17] Glycans protected with hydrogenation labile groups bearing an iodophenol are to be synthesized from the 'reducing end', after which they can be attached to a phthiocerol alkyne derivative using a Sonogashira cross coupling. The resulting diol can then be esterified with mycocerosic acids using Steglich conditions and finally hydrogenation will lead to the global deprotection and concurrent reduction of the conjugated internal alkyne which is formed in the Sonogashira reaction.

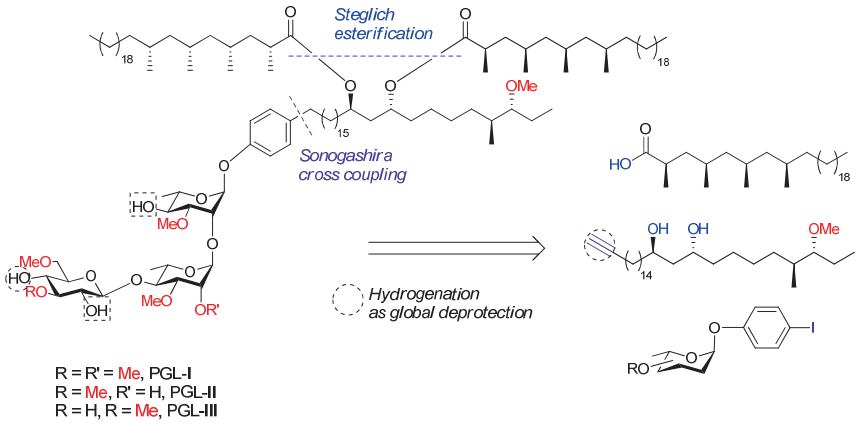


Figure 1. General synthetic strategy of *M. leprae* triglycosyl PGLs.

This synthetic strategy requires the oligosaccharides to be protected only with protecting groups which are susceptible to hydrogenation conditions. In Chapter 4 it was found that a carboxybenzyl (Cbz) protecting group could decrease the amount of synthetic steps required for the synthesis of MTBC PGLs, as it could be used as a hydrogenation labile group capable of selectively forming 1,2-*trans* linkages by means of neighboring group participation.[18] Four out of the six target compounds outlined in this Chapter contain a 1,2-*trans* linked terminal sugar which is not methylated on the C-2 position. Using a C-2 Cbz could therefore benefit the synthesis of these *M. leprae* and *M. haemophilum* PGLs. The retrosynthetic analysis of the target compounds and the resulting building blocks are depicted in Figure 2.

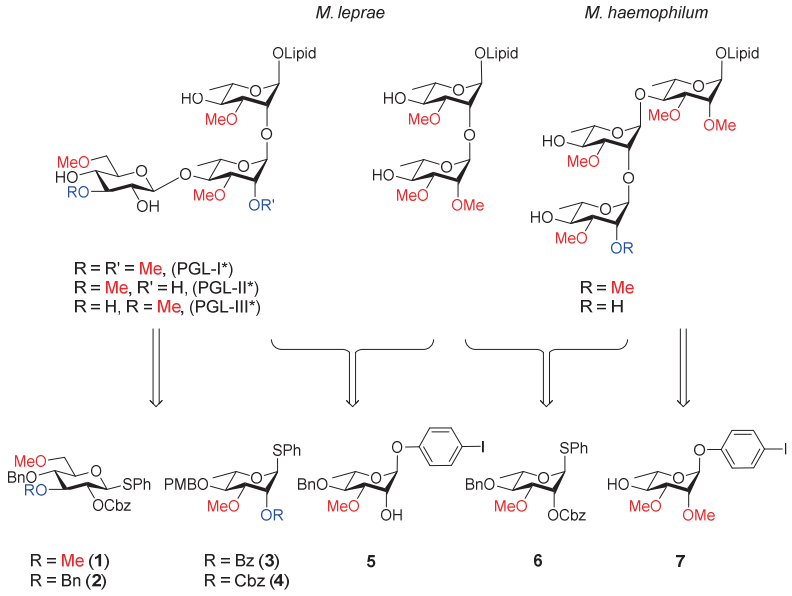
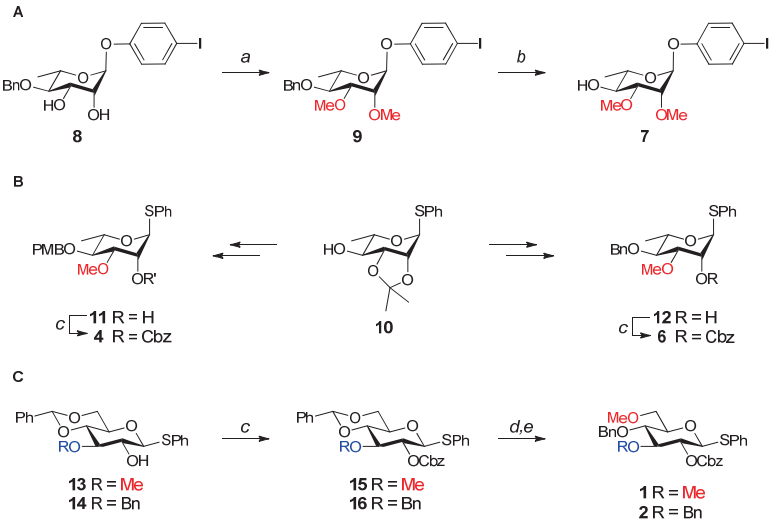


Figure 2. Retrosynthetic analysis of *M. leprae* and *M. haemophilum* glycans. (* = trivial name)

The triglycosyl PGLs of *M. leprae* are to be synthesized starting from acceptor **5** (Chapter 2), which will be coupled to either benzoyl rhamnose donor **3** or Cbz donor **4**. After the necessary protecting group manipulations, the resulting disaccharide acceptors are to be coupled to Cbz glucose donors **1** and **2**. For good measure the results obtained here with the novel Cbz-protected donors, will be compared to those of the corresponding Bz glucose donors used in Chapter 2. The PGLs of *M. haemophilum* are to be synthesized from acceptor **7** and two copies of donor **6**, after which the Cbz of the terminal rhamnose can be either left in place or replaced with a methyl ether. The *M. leprae* disaccharide can be synthesized with acceptor **5** and donor **6**.

Results and Discussion

The synthesis of the previously unreported building blocks is depicted in Scheme 1. The acceptor for the *M. haemophilum* PGLs (**7**) was synthesized by first methylating diol **8** (Scheme 1A) and then removing the C-4 benzyl ether using DDQ.[19]



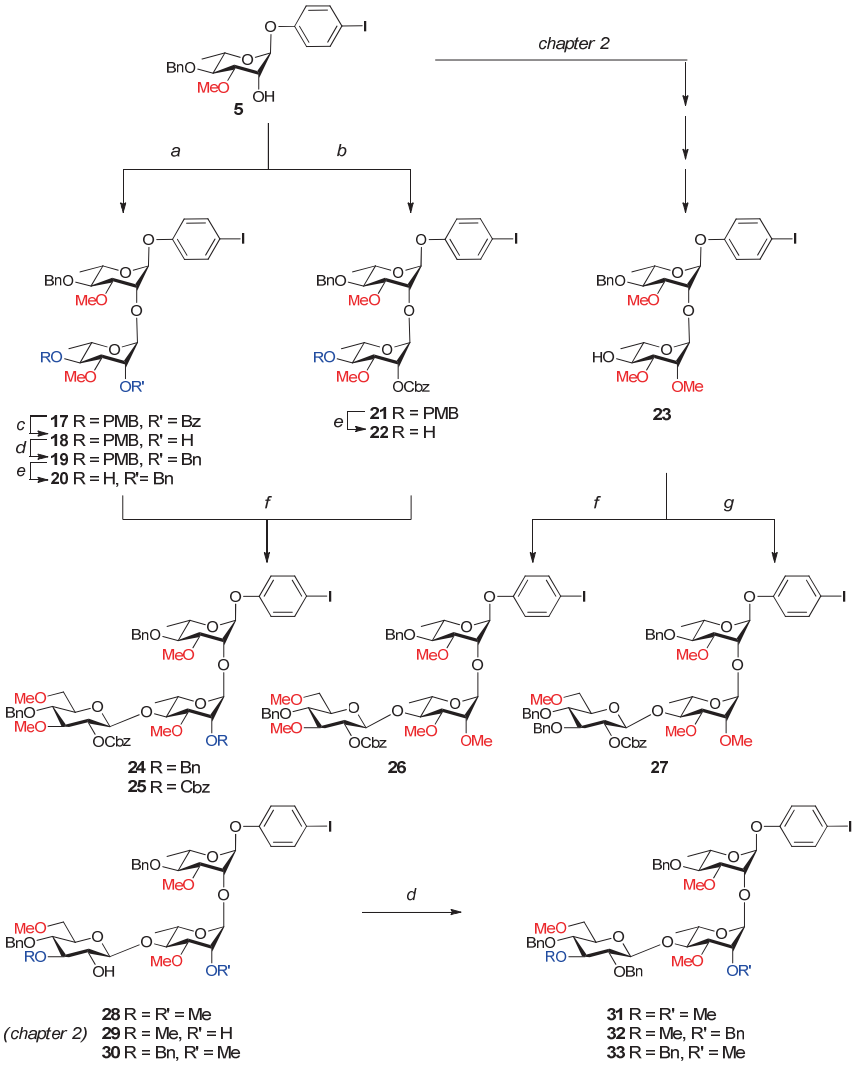
Scheme 1. Building block synthesis. Reagents and conditions: (a) NaH, MeI, DMF, 0 °C → RT, 97%, (b) DDQ, DCM/H_2O (19:1), 97%, (c) CbzCl, DMAP, DCM, 0 °C → RT, 94% (**11**), 68% (**12**), 89% (**13**), 81% (**14**), (d) $BH_3 \cdot THF$, TMSOTf, DCM, 99% (**15**), 91% (**16**), (e) BF_4OMe_3, TTBP, DCM, 78% (**1**), 72% (**2**).

This produced acceptor **7** in 94% yield over 2 steps. Rhamnose donors **4** and **6** (Scheme 1B) were synthesized by protecting the C-2 position of intermediate **11** (Chapter 2) and **12**[20] with a Cbz in 94% and 68% yield, respectively. Glucose donors **1** and **2** could be synthesized from C-3 alkylated benzylidenes **13** and **14** (Scheme 1C). After protection of the C-2 position with a Cbz, a reductive opening of the benzylidene ring with $BH_3 \cdot THF$ and TMSOTf liberated the primary alcohol. This alcohol could be methylated with trimethyloxonium tetrafluoroborate (BF_4OMe_3) and TTBP as a hindered base to prevent migration of the Cbz.† This gave the required glucose donors **1** and **2** in 69% and 53%

† A more detailed investigation of migration-free methylation conditions can be found in Chapter 6

yield over 3 steps, respectively. With the required building blocks in hand the assembly of the oligosaccharides could commence.

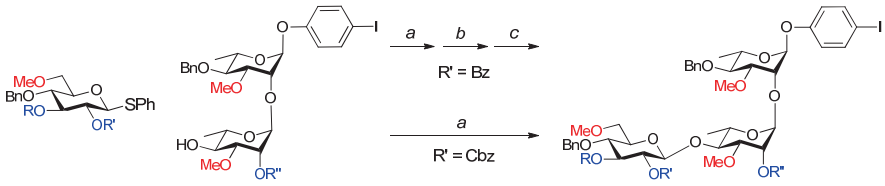
The synthesis of the *M. leprae* trisaccharides is depicted in Scheme 2. In order to fully investigate the potential benefit of using a Cbz group the trisaccharides were made both with benzoyl donors and Cbz donors where applicable. In the route of PGL-I and PGL-III only the glucose donor which is coupled to acceptor **23** (Chapter 2) could benefit from using a Cbz, while PGL-II has two positions which could potentially benefit from a Cbz (C-2' and C-2''). This leaves 3 different options: replacing two benzoyls with benzyls after the final glycosylation (**29** → **32**), replacing the C-2' benzoyl before the final glycosylation (to rule out any effect of the C-2'-*O*-Cbz on the final glycosylation) and coupling of the resulting acceptor to Cbz donor **1** (**20** → **24**) and using a Cbz on both C-2'and C-2'' (**22** → **25**). Coupling of donor **3** to acceptor **5** gave disaccharide **17** in 66% yield. Debenzoylation, subsequent benzylation and removal of the C-4' PMB ether with HCl in HFIP gave disaccharide acceptor **20** in 58% yield over 4 steps. When acceptor **5** was coupled to Cbz donor **4** this produced disaccharide **21** in a modest 47% yield. Multiple attempts were made to improve this yield but to no avail. The C-4' PMB ether was then removed to give disaccharide acceptor **22** in 46% yield over 2 steps. Coupling of disaccharide acceptors **20** and **22** to donor **1** produced trisaccharides **24** and **25** in a similar yield, 66% and 68%, respectively. When disaccharide acceptor **23** was coupled to donor **1**, trisaccharide **26** was produced in 80% yield. Coupling of **23** to donor **2** produced trisaccharide **27** in 96% yield. Benzylation of debenzoylated trisaccharides **28**, **29**, and **30**, which were synthesized as described in Chapter 2 gave protected trisaccharides **31**, **32** and **33** in 64%, 95% and 58% yield, respectively. The results of the synthesis of *M. leprae* of Chapter 2 and this Chapter are summarized in Table 1.



Scheme 2. Multiple synthetic routes towards protected *M. leprae* trisaccharides. Reagents and conditions: (a) Donor **3**, Ph_2SO, Tf_2O, TTBP, DCM -60 °C, 66%, (b) Donor **4**, Ph_2SO, Tf_2O, TTBP, DCM -60 °C, 47%, (c) Na, MeOH/THF, 97%, (d) NaH, BnBr, DMF, 0 °C → RT, 100% (**19**), 64% (**31**), 95% (**32**), 58% (**33**), (e) HCl/HFIP, HFIP/DCM, 90% (**20**), 98% (**22**), (f) Donor **1**, Ph_2SO, Tf_2O, TTBP, DCM -60 °C, 66% (**24**), 68% (**25**), 80% (**26**), (g) Donor **2**, Ph_2SO, Tf_2O, TTBP, DCM -60 °C, 96%.

In the route of PGL-I the glycosylation with donor **1** (Entry 2) gave a lower yield when compared to the benzoyl donor (Entry 1), but circumventing the subsequent debenzoylation and benzylation steps not only saved time but increased the overall yield from 36% over seven steps to 46% over five steps.

Table 1. Summarized yield comparisons of Bz and Cbz donors and acceptors for the assembly of *M. leprae* trisaccharides (* = result from Chapter 2).



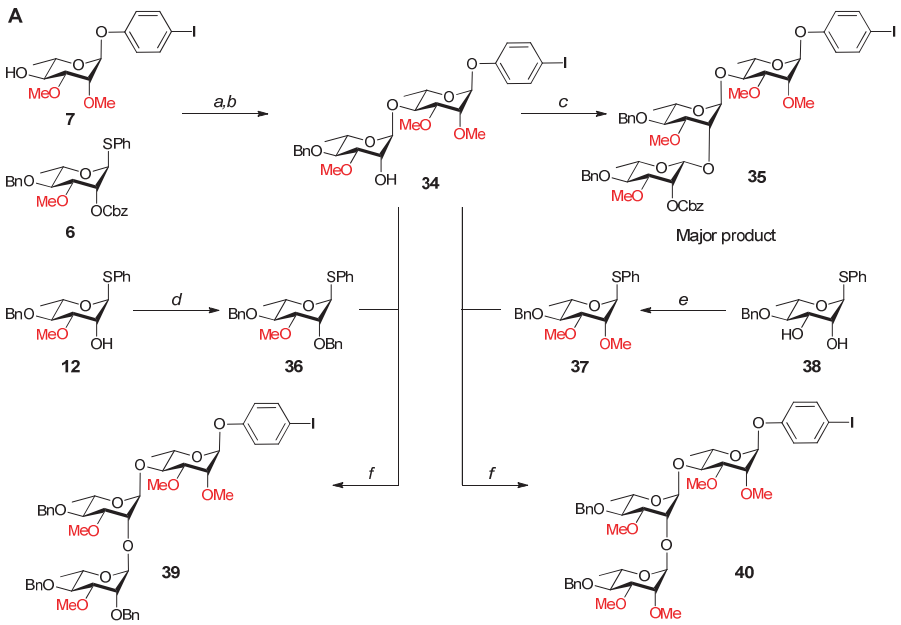
Reagents and conditions: (a) Ph_2SO, Tf_2O, TTBP, DCM -60 °C, (b) Na, MeOH/THF, (c) NaH, BnBr, DMF, 0 °C → RT.

Entry	Acceptor (Yield, steps)	R	R'	R''	PGL	a	b	c	Product	Yield (steps)
1	**23** (57%, 4)*	Me	Bz/ Bn	Me	**I**	100%*	99%*	64%	**31**	36% (7)
2	**23** (57%, 4)*	Me	Cbz	Me	**I**	80%	n.a.	n.a.	**26**	46% (5)
3	**34** (66%, 2)*	Me	Bz/ Bn	Bz/ Bn	**II**	88%*	84%*	95%	**32**	46% (5)
4	**20** (58%, 4)	Me	Cbz	Bz/ Bn	**II**	66%	n.a.	n.a.	**24**	38% (5)
5	**22** (46%, 2)	Me	Cbz	Cbz	**II**	68%	n.a.	n.a.	**25**	31% (3)
6	**23** (57%, 4)*	Bn	Bz/ Bn	Me	**III**	93%*	97%*	58%	**33**	30% (7)
7	**23** (57%, 4)*	Bn	Cbz	Me	**III**	96%	n.a.	n.a.	**27**	55% (5)

In a similar fashion the yield of the PGL-III trisaccharide was improved by Cbz glucose donor **2** from 30% over seven steps (Entry 6) to 55% over five steps (Entry 7). In the case of PGL-II, debenzoylation and subsequent benzylation in the trisaccharide stadium (Entry 3) gave protected trisaccharide **32** in 46% over a total of five steps. Entry 4 shows a slightly lower yield (38%) over the same number of steps and Entry 5 presents the PGL-II trisaccharide in 31% yield over three steps. Reducing the number of steps from five to three is an improvement in terms of time but leads to the lowest overall yield of all.

This was mostly due to the coupling of the Cbz bearing rhamnose donor **4** to acceptor **5**. Perhaps the intrinsically low reactivity of axial acceptor **5** could explain the difference in outcome between the Cbz glucose and rhamnose donors. This hypothesis can be tested during the assembly of *M. haemophilum* trisaccharides which is described below.

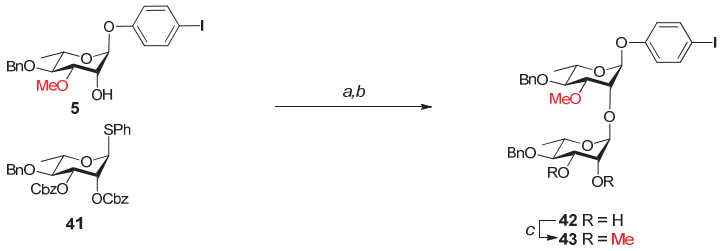
The synthesis of *M. haemophilum* trisaccharides started with the coupling of acceptor **7** to donor **6** (Scheme 3), which selectively produced the α-linked disaccharide. To aid in the purification the yield was determined after methanolysis of the C-2' Cbz under mild basic conditions, which gave disaccharide acceptor **34** in 65% yield over 2



Scheme 3. Synthesis of *M. haemophilum* trisaccharides **39** and **40** (**A**) *Reagents and conditions:* (a) Ph_2SO, Tf_2O, TTBP, DCM -60 °C, (b) K_2CO_3, MeOH, 65% over 2 steps (**34**), (c) Donor **6**, Ph_2SO, Tf_2O, TTBP, DCM -60 °C, (d) NaH, BnBr, DMF, 0 °C → RT, 86%, (e) NaH, MeI, DMF, 0 °C → RT, 92%, (f) IDCP, Et_2O/DCE (4:1), 0 °C → 4 °C, 95% (6:1) (**39**), 84% (4:1) (**40**).

steps. Encouraged by these results, disaccharide acceptor **34** was then coupled to donor **6**. However, this produced a 1:3 α/β mixture in moderate yield. This result is in line with the results that were obtained during the synthesis of *M. leprae* trisaccharides, whereby the Cbz protecting group is able to selectively and efficiently form 1,2-*trans* linkages when coupled to the reactive equatorial C-4 alcohol of rhamnose but to a much lesser extent

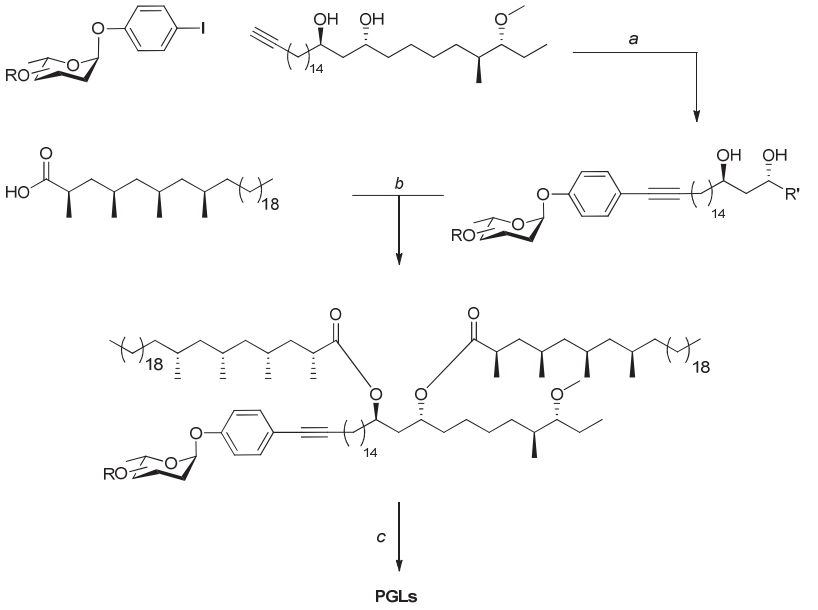
when coupled to the more unreactive axial C-2 alcohol. While these are interesting results that warrant further investigations, a new approach had to be taken to effectively synthesize the *M. haemophilum* trisaccharides. Therefore, as an alternative to rhamnose donor **6**, disaccharide acceptor **34** was coupled to peralkylated donors **36** and **37**, which were derived from **12** and **38**, respectively. These donors were chosen because of their high reactivity and these would limit the number of reactions required in the trisaccharide stadium. IDCP was used as a mild coupling reagent and trisaccharides **39** and **40** were obtained in 95% (α/β 6:1) and 84% (α/β 4:1) yield, respectively. The anomers could be separated by careful column chromatography. This leaves the *M. leprae* disaccharide as the final glycan to be synthesized (Scheme 4).



Scheme 4. Synthesis of *M. leprae* disaccharide **43**. *Reagents and conditions:* (a) Ph_2SO, Tf_2O, TTBP, DCM -60 °C, (b) K_2CO_3, MeOH, 69% over 2 steps, (c) NaH, MeI, DMF, 0 °C → RT, 77%.

Initially disaccharide **43** was to be synthesized from donor **6** like the *M. haemophilum* disaccharide acceptor. However, the results obtained during the glycosylation of donor **6** with hindered acceptor **34** were discouraging. Alternatively, disaccharide **43** could have been synthesized from 2,3-di-*O*-methyl rhamnose donor **37** but the stereoselectivity of this donor was relatively poor when it was coupled to **34**. Moreover, the resulting α/β mixture was particularly difficult to separate. It was therefore chosen to synthesize the disaccharide with 2,3-di-*O*-Cbz donor **41** which was used in Chapter 4 for the synthesis of the *M. bovis* disaccharide. Interestingly the combination of this donor with acceptor **5**, featuring an axial C-2 alcohol, selectively produced the α-product in good yield and after methanolysis and subsequent methylation the target disaccharide **43** was produced in 53% yield over 3 steps. With the final iodoaryl bearing glycan now prepared, the final steps of the PGL assembly could be undertaken, the yields of which are depicted in Table 2.

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 material	Sonogashira	Esterification	Hydrogenation	Overall yield
26	83%	79%	79%	52%
25	93%	80%	76%	57%
27	83%	76%	40%	25%
43	86%	81%	86%	60%
39	94%	79%	81%	60%
40	100%	80%	73%	58%

The glycans were attached to the phthiocerol alkyne derivative through a Sonogashira cross-coupling in excellent yields. The resulting diols were then esterified with two equivalents of mycocerosic acid under Steglich conditions in good yields. The hydrogenation that served as global deprotection proceeded smoothly in most cases. However, in the case of PGL-III only a moderate yield (40%) was obtained, even though

TLC analysis showed the formation of a single product. Perhaps part of the material was lost because of interactions with the catalyst or the Celite used during work-up.[21]

Conclusion

This Chapter describes the synthesis of all known phenolic glycolipids from *Mycobacterium leprae* and *M. haemophilum*. The carboxybenzyl (Cbz) protecting group, which was probed in Chapter 4, was applied in the synthesis of these complex glycolipids. For the *M. leprae* PGLs, glucose Cbz donors **1** and **2** were synthesized and these were successfully used in the assembly of the desired trisaccharides **25**, **26** and **27**. Although the yields for the glycosylation reactions were in most cases lower when compared to the corresponding benzoyl donors, the overall yield turned out higher as the debenzoylation and benzylation steps could be omitted. When rhamnose Cbz donor **4** was coupled to hindered acceptor **5** the yield was lower when compared to the benzoyl donor, and this low yield could not be compensated by circumventing the debenzoylation and benzylation steps. It seems that a relatively reactive acceptor is required in glycosylation reactions that use a donor with a C-2 Cbz group to outcompete the reactions featuring a donor with a C-2 benzoyl ester. This trend also holds true for the synthesis of *M. haemophilum* trisaccharides, where rhamnose donor **6** gave was coupled in good yield and selectivity to reactive acceptor **7**, but when the same donor was used for hindered disaccharide acceptor **34** the β product was isolated as the major product. The final rhamnosylations were therefore achieved with peralkylated donors **36** and **37** using IDCP as a mild activating agent. Finally, the *M. leprae* disaccharide **43** was synthesized using donor **41**, carrying a Cbz-group at both the C-2 and C-3 positions and which was used for the synthesis of the *M. bovis* disaccharide (Chapter 4). The iodoaryl-bearing glycans were then coupled to the phthiocerol alkyne derivative using a Sonogashra coupling, which was followed by a Steglich esterification of the resulting diol with mycocerosic acid. Finally, global deprotection with H_2 and Pd/C resulted in the complete assembly of all the phenolic glycolipids originating from *Mycobacterium leprae* and *haemophilum* 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 or AV-850 spectrometer. Samples were prepared in $CDCl_3$ unless stated otherwise. Chemical shifts (δ) in $CDCl_3$ are reported in ppm relative to Me_4Si (δ: 0.00 ppm) for ^{1}H-NMR and $CDCl_3$ (δ: 77.16 ppm) for ^{13}C-NMR. Chemical shifts in CD_3OD are reported in ppm relative to H_2O (δ: 4.87 ppm) for ^{1}H-NMR and CD_3OD (δ: 49.00 ppm) for ^{13}C-NMR. ^{13}C-APT spectra are ^{1}H decoupled and structural assignment was achieved using HH-COSY and HSQC 2D experiments. Coupling constants (J) are given in Hz. Coupling constants of anomeric carbon atoms ($J_{H1,C1}$) were determined using HMBC-GATED experiments. Optical rotations were measured on an Anton Paar Modular Circular Polarimeter MCP 100/150. High resolution mass spectra were recorded on a Synapt G2-Si or a Q Exactive HF Orbitrap equipped with an electron spray ion source positive mode. Infrared spectra were recorded on a Perkin Elmer Spectrum 2 FT-IR.

General procedure A: 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, 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: IDCP mediated glycosylation

Starting material (1.0 eq) and donor (1.5 eq) were coevaporated together with toluene and subsequently dissolved in Et_2O/DCE (0.05 M, 4:1). Flame-dried 3Å molecular sieves were added and the resulting solution was stirred for 15 minutes while it was cooled to 0 °C, after which IDCP (3.0 eq) was added. The reaction was allowed to stir while warming to rT. When TLC indicated complete consumption of the starting material the reaction mixture was filtered over celite, diluted with Et_2O and transferred to a separation funnel. The organic layer was then washed with sat. aq. $Na_2S_2O_3$, sat. aq. $NaHCO_3$, sat. aq. $CuSO_4$ and brine, after which it was dried with $MgSO_4$ and concentrated *in vacuo*. Purification by means of column chromatography.

General procedure C: Sonogashira cross coupling

Iodoaryl glycoside (1.0 eq) was dissolved in freshly distilled NEt_3 (0.05 M) together with phthiocerol (1.2 eq). A mixture of $Pd(PPh_3)_2Cl_2$, PPh_3 and CuI (ratio 1:1:2) was dissolved in freshly distilled NEt_3 and was stirred for 15 minutes at 40 °C. Of this cocktail, enough was added to the sugar/alkyne mixture to amount to 0.05 eq $Pd(PPh_3)_2Cl_2$, 0.05 eq PPh_3 and 0.1 eq CuI. The reaction was allowed to stir at 40 °C until the complete consumption of the starting material as indicated by TLC (2-16 h). The solvent was then removed under a stream of N_2. The crude was then transferred to a silica column in toluene and the column was flushed with toluene. Thereafter the product was purified by means of column chromatography.

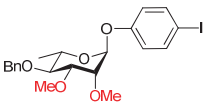
General procedure D: Esterification with mycocerosic acid

Starting material (1.0 eq) was dissolved in dry DCM (0.05 M) together with mycocerosic acid (3.0 eq) and DMAP (9 eq). The resulting mixture was cooled to 0 °C after which DIC (6 eq) was added. The reaction was allowed to stir for 16 hours while warming to rT, after which it was warmed to 40 °C and stirred for a further 5 hours. The reaction mixture was then diluted with Et_2O and the organic 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 on TLC, staining with $KMnO_4$ is required.

General procedure E: Hydrogenation

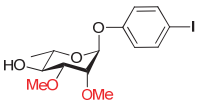
Starting material (1.0 eq) was dissolved in a mixture of THF and EtOH (1:1, 0.007 M) and the solution was purged with N_2. Pd/C (10%, 1.0 eq) was then added to the solution and the resulting mixture was purged with H_2. The reaction was left to stir under H_2 atmosphere until TLC complete conversion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

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



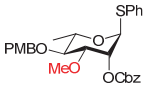
Compound **8** (2.74 g, 6.0 mmol, 1.0 eq) was dissolved in dry DMF (50 mL, 0.12 M) and MeI (1.12 mL, 18 mmol, 3.0 eq) was added to the solution. The mixture was cooled to 0 °C, and NaH (60%, 0.72 g, 18 mmol, 3.0 eq) was added. The reaction mixture was warmed to rt while stirring for 3 hours. The reaction was quenched by addition of H_2O, and extracted with Et_2O (3x). The organic layers were combined, washed with brine, dried with $MgSO_4$ and concentrated *in vacuo*. Purification by means of column chromatography (*n*-pentane-Et_2O 7:3) gave the title compound (2.81 g, 5.80 mmol, 97%) as a clear oil. $[\alpha]_D^{25}$ = -96.4 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.59-7.55 (m, 2H, C*H*$_{arom}$); 7.36-7.26 (m, 5H, C*H*$_{arom}$); 6.85-6.82 (m, 2H, C*H*$_{arom}$); 5.52 (s, 1H, H-1); 4.77 (dd, 2H, *J* = 10.8, 120.4 Hz, PhC*H*$_2$); 3.79-3.75 (m, 2H, H-2, H-3); 3.72-3.66 (m, 1H, H-5); 3.59 (s, 3H, OC*H*$_3$); 3.58 (s, 3H, OC*H*$_3$); 3.49 (t, 1H, *J* = 9.0 Hz, H-4); 1.25 (d, 3H, *J* = 6.0 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 156.2, 138.6 (C$_{q,arom}$); 138.5, 128.5, 128.1, 127.8, 118.7 (*C*H$_{arom}$); 95.3 (C-1); 84.9 (*C*I$_{arom}$); 81.3 (C-3); 80.3 (C-4); 77.3 (C-2); 68.8 (C-5); 59.5, 58.1 (O*C*H$_3$); 18.1 (C-6). IR (thin film, cm^{-1}): 1046, 1093, 1119, 1138, 1178, 1232, 1275, 1454, 1484. HRMS calculated for $C_{21}H_{25}IO_5Na$ 507.06389 $[M+Na]^+$; found 507.06400.

4-iodophenyl 2,3-di-*O*-methyl-α-L-rhamnopyranoside (7)



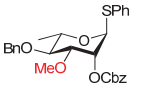
Compound **9** (0.58 g, 1.19 mmol, 1.0 eq) was dissolved in DCM/H_2O (20:1, 12 mL, 0.1 M) and the solution was cooled to 0 °C. After stirring for a few minutes DDQ (0.54 g, 2.38 mmol, 2.0 eq) was added to the solution. The reaction was stirred vigorously overnight after which it was quenched by addition of sat. aq. $NaHCO_3$. The organic layer was then washed sat. aq. $NaHCO_3$, dried with $MgSO_4$ and concentrated *in vacuo*. Purification by means of column chromatography (*n*-pentane-Et_2O 3:7) gave the title compound (455 mg, 1.15 mmol, 97%) as a pale oil. $[\alpha]_D^{25}$ = -66.8 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.60-7.57 (m, 2H, C*H*$_{arom}$); 6.88-6.84 (m, 2H, C*H*$_{arom}$); 5.54 (d, 1H, *J* = 2.0 Hz, H-1); 3.81 (dd, 1H, *J* = 2.0, 2.4 Hz, H-2); 3.70-3.58 (m, 3H, H-3, H-4, H-5); 3.55 (s, 3H, OC*H*$_3$); 3.54 (s, 3H, OC*H*$_3$); 2.60 (bs, 1H, 4-O*H*); 1.27 (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$_{arom}$); 95.6 (C-1); 85.0 (*C*I$_{arom}$); 80.9 (C-3); 75.8 (C-2); 71.5 (C-4); 69.2 (C-5); 59.4, 57.3 (O*C*H$_3$); 17.8 (C-6). IR (thin film, cm^{-1}): 1046, 1086, 1120, 1135, 1201, 1232, 1484, 3470. HRMS calculated for $C_{14}H_{20}IO_5$ 395.03499 $[M+H]^+$; found 395.03463.

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



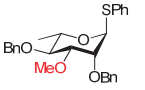
Compound **11** (14 mg, 0.37 mmol, 1.0 eq) was dissolved in DCM (2 mL, 0.2 M) and DMAP (124 mg, 0.94 mmol, 2.5 eq) was added to the solution. The mixture was cooled to 0 °C and CbzCl (0.11 mL, 0.75 mmol, 2.0 eq) was slowly added. The reaction was allowed to stir for 4 hours after while slowly warming to rt. The reaction was quenched by addition of 1 M HCl, and the organic layer was washed with 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 (184 mg, 0.35 mmol, 94%) as a clear oil. $[\alpha]_D^{25}$ = -105 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.47-7.43 (m, 2H, C*H*$_{arom}$); 7.42-7.23 (m, 12H, C*H*$_{arom}$); 6.90-6.86 (m, 2H, C*H*$_{arom}$); 5.51 (d, 1H, *J* = 1.6 Hz, H-1); 5.38 (dd, 1H, *J* = 1.6, 2.8 Hz, H-2); 5.18 (dd, 2H, *J* = 12.4, 18.0 Hz, PhC*H*$_2$); 4.68 (dd, 2H, *J* = 10.4, 28.4 Hz, PhC*H*$_2$); 4.19-4.15 (m, 1H, H-5); 3.79 (s, 3H, C*H*$_{3,PMB}$); 3.62 (dd, 1H, *J* = 3.2, 9.2 Hz, H-3); 3.49-3.43 (m, 4H, H-4, OC*H*$_3$); 1.31 (d, 3H, *J* = 6.0 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 159.4 (C$_{q,arom}$); 154.8 (*C*O$_{Cbz}$); 135.0, 134.0 (C$_{q,arom}$); 131.8 (*C*H$_{arom}$); 130.7 (C$_{q,arom}$); 129.8, 129.2, 128.7, 128.7, 128.6, 127.8, 113.9 (*C*H$_{arom}$); 85.9 (C-1); 80.6 (C-3); 79.8 (C-4); 75.3 (Ph*C*H$_2$); 74.4 (C-2); 70.1 (Ph*C*H$_2$); 69.2 (C-5); 58.0 (O*C*H$_3$); 55.4 (*C*H$_{3,PMB}$); 17.8 (C-6). IR (thin film, cm^{-1}): 1027, 1086, 1172, 1248, 1302, 1382, 1457, 1514, 1747. HRMS calculated for $C_{29}H_{36}NO_7S$ 542.2212 $[M+NH_4]^+$; found 542.2208.

Phenyl 2-*O*-benzyloxycarbonyl-3-*O*-methyl-4-*O*-benzyl)-1-thio-α-L-rhamnopyranoside (6)



Compound **12**[20] (3.30 g, 9.16 mmol, 1.0 eq) was dissolved in DCM (92 mL, 0.1 M) and DMAP (2.24 g, 18.3 mmol, 2.0 eq) was added to the solution. The mixture was cooled to 0 °C and CbzCl (2.58 mL, 18.3 mmol, 2.0 eq) was slowly added. The reaction was allowed to stir for 3 hours after while slowly warming to rt. The reaction was quenched by addition of 1 M HCl, and the organic layer was washed with sat. aq. $NaHCO_3$ and brine, dried with $MgSO_4$ and concentrated *in vacuo*. Purification by means of column chromatography (*n*-pentane Et_2O 4:1) gave the title compound (3.07 g, 6.2 mmol, 68%) as a clear oil. $[\alpha]_D^{25}$ = -116.2 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.46-7.43 (m, 2H, C*H*$_{arom}$); 7.41-7.24 (m, 13H, C*H*$_{arom}$); 5.52 (d, 1H, *J* = 1.6 Hz, H-1); 5.39 (dd, 1H, *J* = 2.0, 3.2 Hz, H-2); 5.18 (dd, 2H, *J* = 12.0, 18.0 Hz, PhC*H*$_2$); 4.76 (dd, 2H, *J* = 11.0, 113.0 Hz, PhC*H*$_2$); 4.22-4.18 (m, 1H, H-5); 3.63 (dd, 1H, *J* = 3.2, 9.2 Hz, H-3); 3.50-3.45 (m, 4H, H-4, OC*H*$_3$); 1.32 (d, 3H, *J* = 6.0 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 154.8 (*C*O$_{Cbz}$); 138.6, 135.0, 133.9 (C$_{q,arom}$); 131.9, 129.2, 128.7, 128.7, 128.6, 128.5, 128.1, 127.9, 127.8 (*C*H$_{arom}$); 85.9 (C-1); 80.6 (C-3); 80.2 (C-4); 75.6 (Ph*C*H$_2$); 74.4 (C-2); 70.2 (Ph*C*H$_2$); 69.2 (C-5); 58.0 (O*C*H$_3$); 17.8 (C-6). IR (thin film, cm^{-1}): 1027, 1086, 1100, 1262, 1382, 1454, 1482, 1747. HRMS calculated for $C_{28}H_{30}O_6SNa$ 517.16653 $[M+Na]^+$; found 517.16525.

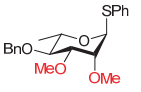
Phenyl 2,4-di-*O*-benzyl-3-*O*-methyl-1-thio-α-L-rhamnopyranoside (36)



Compound **12**[20] (1.26 g, 3.40 mmol, 1.0 eq) was dissolved in dry DMF (34 mL, 0.1 M) and BnBr (0.49 mL, 4.09 mmol, 1.2 eq) was added to the solution. The mixture was cooled to 0 °C, and NaH (60%, 0.20 g, 5.11 mmol, 1.5 eq) was added. The reaction mixture was warmed to rt while stirring for 6 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*

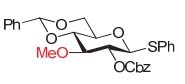
vacuo. Purification by means of column chromatography (*n*-pentane-Et_2O 7:3) gave the title compound (1.33 g, 2.94 mmol, 86%) as a clear oil. $[\alpha]_D^{25}$ = -21.4 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.40-7.22 (m, 15H, C*H*$_{arom}$); 5.52 (s, 1H, H-1); 4.94 (dd, 1H, *J* = 11.2 Hz, PhC*H*H); 4.76-4.62 (m, 3H, PhC*H*H, PhCH_2); 4.14 (dq, 1H, *J* = 2.0, 6.4 Hz, H-5); 4.05 (dd, 1H, *J* = 1.6, 2.0 Hz, H-2); 3.62-3.54 (m, 2H, H-3, H-4); 3.41 (s, 3H, OCH_3); 1.35 (d, 3H, *J* = 6.0 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 138.8, 138.0, 134.9 ($C_{q,arom}$); 131.4, 129.1, 128.5, 128.5, 128.1, 128.1, 127.9, 127.8, 127.4 (*C*H$_{arom}$); 85.8 (C-1); 82.2 (C-3); 80.6 (C-4); 75.9 (C-2); 75.5, 72.2 (Ph*C*H$_2$); 69.2 (C-5); 57.7 (O*C*H$_3$); 18.0 (C-6). IR (thin film, cm^{-1}): 1046, 1202, 1232, 1275, 1452, 1484, 1584, 3486. HRMS calculated for $C_{27}H_{30}O_4SNa$ 473.17570 [M+Na]$^+$; found 473.17562.

Phenyl 2,3-di-*O*-methyl-4-*O*-benzyl-1-thio-α-L-rhamnopyranoside (37)



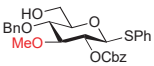
Compound **38** (2.39 g, 6.90 mmol, 1.0 eq) was dissolved in dry DMF (50 mL, 0.12 M) and MeI (1.3 mL, 20.7 mmol, 3.0 eq) was added to the solution. The mixture was cooled to 0 °C, and NaH (60%, 0.83 g, 15.7 mmol, 3.0 eq) was added. The reaction mixture was warmed to rt while stirring for 2 hours. The 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 (2.37 g, 6.33 mmol, 92%) as a clear oil. $[\alpha]_D^{25}$ = -108.2 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.48-7.45 (m, 2H, C*H*$_{arom}$); 7.39-7.23 (m, 8H, C*H*$_{arom}$); 5.60 (d, 1H, *J* = 1.6 Hz, H-1); 4.76 (dd, 2H, *J* = 10.8, 120.4 Hz, PhCH_2); 4.18-4.14 (m, H-5); 3.88 (dd, 1H, *J* = 1.8, 3.0 Hz, H-2); 3.58-3.47 (m, 8H, H-3, H-4, OCH_3); 1.33 (d, 3H, *J* = 6.0 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 138.7, 134.9 ($C_{q,arom}$); 131.1, 129.1, 128.5, 128.1, 127.8, 127.4 (*C*H$_{arom}$); 84.7 (C-1); 81.9 (C-3); 80.6 (C-4); 79.1 (C-2); 75.5 (Ph*C*H$_2$); 69.0 (C-5); 58.3, 57.9 (O*C*H$_3$); 17.9 (C-6). IR (thin film, cm^{-1}): 1027, 1086, 1116, 1454, 1482. HRMS calculated for $C_{21}H_{26}O_4SNa$ 397.14440 [M+Na]$^+$; found 397.14431.

Phenyl 2-*O*-benzyloxycarbonyl-3-*O*-methyl-4,6-*O*-benzylidene-1-thio-ß-D-glucopyranoside (15)



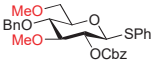
Compound **13** (0.57 g, 1.41 mmol, 1.0 eq) was dissolved in DCM (14 mL, 0.1 M) and DMAP (0.38 g, 3.10 mmol, 2.2 eq) was added to the solution. The mixture was cooled to 0 °C and CbzCl (0.4 mL, 2.82 mmol, 2.0 eq) was slowly added. The reaction was allowed to stir for 6 hours after while slowly warming to rt. The reaction was quenched by addition of 1 M HCl, and the organic layer was washed with sat. aq. $NaHCO_3$ and brine, dried with $MgSO_4$ and concentrated *in vacuo*. Purification by means of column chromatography (*n*-pentane Et_2O 4:1) gave the title compound (0.637 g, 1.25 mmol, 89%) as a white solid. $[\alpha]_D^{25}$ = 2.5 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.52-7.18 (m, 15H, C*H*$_{arom}$); 5.49 (s, 1H, PhC*H*); 5.23 (dd, 2H, *J* = 12.0, 22.8 Hz, PhC$H_{2,Cbz}$); 4.78-4.69 (m, 2H, H-1, H-2); 4.32 (dd, 1H, *J* = 5.0, 10.6 Hz, H-6); 3.74-3.68 (m, 1H, H-6); 3.62-3.49 (m, 5H, H-3, H-4, OCH_3); 3.46-3.39 (m, 1H, H-5). ^{13}C-APT NMR (101 MHz) δ: 154.3 (CO_{Cbz}); 137.0, 135.1 ($C_{q,arom}$); 132.9 (*C*H$_{arom}$); 132.0 ($C_{q,arom}$); 129.0, 128.9, 128.6, 128.5, 128.2, 128.0, 126.0 (*C*H$_{arom}$); 101.1 (Ph*C*H); 86.6 (C-1); 81.8 (C-4); 80.8 (C-3); 75.7 (C-2); 70.3 (C-5); 70.0 (Ph*C*H$_{2,Cbz}$); 68.4 (C-6); 60.7 (O*C*H$_3$). IR (thin film, cm^{-1}): 1026, 1070, 1093, 1248, 1382, 1457, 1753. HRMS calculated for $C_{28}H_{28}O_7SNa$ 531.1453 [M+Na]$^+$; found 531.1444.

Phenyl 2-*O*-benzyloxycarbonyl-3-*O*-methyl-4-*O*-benzyl-1-thio-ß-D-glucopyranoside (44)



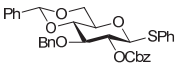
Compound **15** (0.63 g, 1.24 mmol, 1.0 eq.) was co-evaporated with toluene (3x) under N_2 atmosphere before it was dissolved in dry DCM (12.4 mL, 0.1 M). BH_3·THF (1 M in THF, 6.2 mL, 6.2 mmol, 5.0 eq.) was added dropwise to the solution after which TMSOTf (22 µL, 0.12 mmol, 0.1 eq.) was added to the mixture. The reaction mixture was stirred for 5 h and slowly quenched with NEt_3 (1.2 mL) followed by MeOH, which was added until the formation of H_2 ceased. The mixture was concentrated and co-evaporated with MeOH (2x). Purification by means of column chromatography (*n*-pentane-Et_2O 7:3) gave the title compound (0.628 g, 1.23 mmol, 99%) as a white solid. $[\alpha]_D^{25}$ = 16.9 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.45-7.25 (m, 15H, C*H*$_{arom}$); 5.27 (s, 2H, PhC*H*$_2$); 4.82 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.72-4.61 (m, 3H, H-1, H-2, PhCH*H*); 3.86 (dd, 1H, *J* = 2.4, 12.0 Hz, H-6); 3.67 (dd, 1H, *J* = 4.6, 12.0 Hz, H-6); 3.52-3.50 (m, 4H, H-3, OC*H*$_3$); 3.47-3.42 (m, 1H, H-4); 3.39-3.35 (m, 1H, H-5); 1.87 (bs, 1H, 6-O*H*). ^{13}C-APT NMR (101 MHz) δ: 154.4 (*C*O$_{Cbz}$); 137.8, 135.3 (C$_{q,arom}$); 132.7 (*C*H$_{arom}$); 132.5 (C$_{q,arom}$); 129.2, 129.1, 128.7, 128.7, 128.6, 128.5, 128.3, 128.2, 128.2, 128.1 (*C*H$_{arom}$); 86.2 (C-1); 86.0 (C-4); 79.5 (C-5); 77.0 (C-3); 76.4 (C-2); 75.2, 70.3 (Ph*C*H$_2$); 32.0 (C-6); 61.1 (O*C*H$_3$). IR (thin film, cm^{-1}): 1029, 1040, 1055, 1078, 1089, 1119, 1142, 1259, 1757, 2930. HRMS calculated for $C_{35}H_{36}O_7SNa$ 533.1610 [M+Na]$^+$; found 533.1605.

Phenyl 2-*O*-benzyloxycarbonyl-3,6-di-*O*-methyl-4-*O*-benzyl-1-thio-ß-D-glucopyranoside (1)



Compound **44** (179 mg, 0.35 mmol, 1.0 eq.) and TTBP (362 mg, 1.46 mmol, 4.0 eq) were co-evaporated with toluene (3x) under N_2 atmosphere and dissolved in dry DCM (7.2 mL, 0.05 M) and flame-dried rod shaped 3Å molecular sieves were added. Trimethyloxonium tetrafluoroborate (160 mg, 1.08 mmol, 3.0 eq) was then added to the mixture and the reaction was left to stir for 1.5 hours. The reaction was quenched with NEt_3 (0.5 mL), filtered over celite, 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 (143 mg, 0.27 mmol, 78%) as a white solid. $[\alpha]_D^{25}$ = 13.9 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.43-7.22 (m, 15H, C*H*$_{arom}$); 5.27 (s, 2H, PhC*H*$_{2,Cbz}$); 4.81 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.73 (t, 1H, *J* = 9.4 Hz, H-2); 4.62-4.59 (m, 2H, H-1, PhCH*H*); 3.66-3.55 (m, 3H, H-3, H-6); 3.49 (s, 3H, OC*H*$_3$); 3.48-3.39 (m, 2H, H-4, H-5); 3.36 (s, 3H, OC*H*$_3$). 13C-APT NMR (101 MHz) δ: 154.4 (*C*O$_{Cbz}$); 138.1, 135.3, 133.1 (C$_{q,arom}$); 128.9, 128.7, 128.6, 128.6, 128.4, 128.2, 128.2, 128.1, 128.0 (*C*H$_{arom}$); 86.4 (C-1); 86.3 (C-4); 79.2 (C-5); 77.0 (C-3); 76.7 (C-2); 75.1 (Ph*C*H$_2$); 71.1 (C-6); 70.1 (Ph*C*H$_{2,Cbz}$); 60.9, 59.5 (O*C*H$_3$). IR (thin film, cm^{-1}): 1002, 1026, 1076, 1088, 1143, 1148, 1251, 1381, 1455, 1756, 2929. HRMS calculated for $C_{29}H_{32}O_7SNa$ 547.1766 [M+Na]$^+$; found 547.1761.

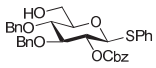
Phenyl 2-*O*-benzyloxycarbonyl-3-*O*-benzyl-4,6-*O*-benzylidene-1-thio-ß-D-glucopyranoside (16)



Compound **14** (2.03 g, 4.51 mmol, 1.0 eq) was dissolved in DCM (173 mL, 0.03 M) and DMAP (1.65 g, 13.5 mmol, 3.0 eq) was added to the solution. The mixture was cooled to 0 °C and CbzCl (1.9 mL, 13.5 mmol, 3.0 eq) was slowly added. The reaction was allowed to stir for 5 hours after while slowly warming to rt. The reaction was quenched by addition of 1 M HCl, and the organic layer was washed with sat. aq. $NaHCO_3$ and brine, dried with $MgSO_4$ and concentrated *in vacuo*. Purification by means of column chromatography (*n*-pentane Et_2O 4:1) gave the title compound (2.14 g, 3.66 mmol, 81%) as a white solid. $[\alpha]_D^{25}$ = 7.2 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.46-7.22 (m, 20H, C*H*$_{arom}$); 5.56

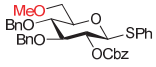
(s, 1H, PhC*H*); 5.23 (s, 2H, PhC$H_{2,Cbz}$); 4.85-4.82 (m, 2H, H-2, PhC*H*H); 4.73-4.64 (m, 2H, H-1, PhCH*H*); 4.37 (dd, 1H, *J* = 4.8, 10.4 Hz, H-6); 3.82-3.70 (m, 3H, H-3, H-4, H-6); 3.51-3.45 (m, 1H, H-5). ^{13}C-APT NMR (101 MHz) δ: 154.3 (CO_{Cbz}); 138.0, 137.1, 135.2 ($C_{q,arom}$); 133.2 (CH_{arom}); 131.9 ($C_{q,arom}$); 129.2, 129.1, 128.7, 128.5, 128.4, 127.9, 127.8, 126.1 (CH_{arom}); 101.3 (Ph*C*H); 86.7 (C-1); 81.2 (C-4); 79.9 (C-3); 75.8 (C-2); 74.7 (Ph*C*H$_2$); 70.6 (C-5); 70.2 (Ph*C*H$_{2,Cbz}$); 68.6 (C-6). IR (thin film, cm^{-1}): 1027, 1069, 1096, 1249, 1312, 1382, 1441, 1455, 1754. HRMS calculated for $C_{34}H_{32}O_7SNa$ 607.1766 [M+Na]$^+$; found 607.1761.

Phenyl 2-*O*-benzyloxycarbonyl-3,4-di-*O*-benzyl-1-thio-ß-D-glucopyranoside (45)



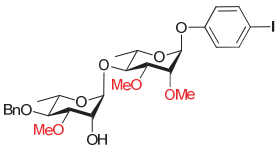
Compound **16** (257 mg, 0.44 mmol, 1.0 eq.) was co-evaporated with toluene (3x) under N_2 atmosphere before it was dissolved in dry DCM (4.4 mL, 0.1 M). A 1M solution of BH_3·THF (4.4 mL, 4.4 mmol, 10.0 eq) in THF was added dropwise to the solution after which TMSOTf (0.08 mL, 0.44 mmol, 1.0 eq) was added to the mixture. The reaction mixture was stirred for 4 h and slowly quenched with NEt_3 (1 mL) followed by MeOH, which was added until the formation of H_2 ceased. The mixture was concentrated and co-evaporated with MeOH (2x). Purification by means of column chromatography (*n*-pentane-Et_2O 7:3) gave the title compound (0.234 g, 0.40 mmol, 91%) as a white solid. $[\alpha]_D^{25}$ = 21.5 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.45-7.41 (m, 2H, CH_{arom}); 7.37-7.17 (m, 18H, CH_{arom}); 5.18 (dd, 2H, *J* = 12.2, 16.6 Hz, PhC$H_{2,Cbz}$); 4.83-4.74 (m, 3H, H-2, PhC*H*H, PhC*H*H); 4.68-4.60 (m, 3H, H-1, PhCH*H*, PhCH*H*); 3.86 (dd, 1H, *J* = 2.4, 12.0 Hz, H-6); 3.74-3.57 (m, 2H, H-4, H-6); 3.40 (t, 1H, *J* = 2.4 Hz, H-3); 3.39-3.36 (m, 1H, H-5); 2.11 (bs, 1H, 6-O*H*). ^{13}C-APT NMR (101 MHz) δ: 154.3 (CO_{Cbz}); 137.8, 137.7, 135.1 ($C_{q,arom}$); 129.1, 129.0, 128.6, 128.5, 128.4, 128.4, 128.1, 128.0, 127.8, 127.8 (CH_{arom}); 85.9 (C-1); 84.0 (C-4); 79.5 (C-5); 77.1 (C-3); 76.3 (C-2); 75.5, 75.1 (Ph*C*H$_2$); 70.1 (Ph*C*H$_{2,Cbz}$); 61.8 (C-6). IR (thin film, cm^{-1}): 1002, 1012, 1027, 1039, 1072, 1090, 1146, 1252, 1454, 1731, 1756, 2928. HRMS calculated for $C_{34}H_{34}O_7SNa$ 609.1923 [M+Na]$^+$; found 609.1918.

Phenyl 2-*O*-benzyloxycarbonyl-3,4-di-*O*-benzyl-6-*O*-methyl-1-thio-ß-D-glucopyranoside (2)



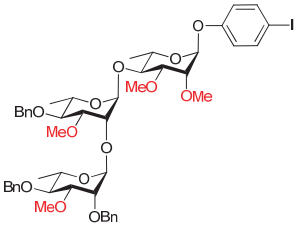
Compound **45** (135 mg, 0.23 mmol, 1.0 eq.) and TTBP (229 mg, 0.92 mmol, 4.0 eq) were co-evaporated with toluene (3x) under N_2 atmosphere and dissolved in dry DCM (4.6 mL, 0.05 M) and flame-dried rod shaped 3Å molecular sieves were added. Trimethyloxonium tetrafluoroborate (102 mg, 0.69 mmol, 3.0 eq) was then added to the mixture and the reaction was left to stir for 2 hours. The reaction was quenched with NEt_3 (0.5 mL), filtered over celite, 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 (99 mg, 0.165 mmol, 72%) as a white solid. $[\alpha]_D^{25}$ = 26.1 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.48-7.44 (m, 2H, CH_{arom}); 7.39-7.18 (m, 18H, CH_{arom}); 5.19 (dd, 2H, *J* = 12.2, 19.4 Hz, PhC$H_{2,Cbz}$); 4.85-4.74 (m, 3H, H-2, PhC*H*H, PhC*H*H); 4.68-4.60 (m, 3H, H-1, PhCH*H*, PhCH*H*); 3.73-3.59 (m, 4H, H-3, H-4, H-6); 3.47-3.43 (m, 1H, H-5); 3.37 (OCH_3). ^{13}C-APT NMR (101 MHz) δ: 154.3 (CO_{Cbz}); 138.0, 138.0, 135.2, 133.1 ($C_{q,arom}$); 132.6, 129.0, 128.7, 128.7, 128.6, 128.5, 128.1, 128.1, 128.0, 127.9, 127.8 (CH_{arom}); 86.5 (C-1); 84.4 (C-4); 79.3 (C-5); 77.5 (C-3); 76.4 (C-2); 75.6, 75.3 (Ph*C*H$_2$); 71.2 (C-6); 70.2 (Ph*C*H$_{2,Cbz}$); 59.6 (O*C*H$_3$). IR (thin film, cm^{-1}): 1000, 1026, 1076, 1142, 1246, 1362, 1381, 1440, 1454, 1753. HRMS calculated for $C_{35}H_{36}O_7SNa$ 623.2079 [M+Na]$^+$; found 623.2074.

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



Donor **6** (0.554 g, 1.12 mmol, 1.5 eq), Ph_2SO (0.295 g, 1.46 mmol, 2.0 eq) and TTBP (0.696 g, 2.80 mmol, 3.8 eq) were dried by co-evaporation with toluene (3x) followed by 3 vacuum/nitrogen purges. The mixture was then dissolved in DCM (20 mL, 0.08 M) and flame-dried 3Å molecular sieves were added. The solution was then cooled to -65 °C after which Tf_2O (0.244 mL, 1.46 mmol, 2.0 eq) was added to the solution. After stirring for 30 minutes, acceptor **7** (0.294 g, 0.747 mmol, 1.0 eq), which was also dried by co-evaporation with toluene (3x) followed by 3 vacuum/nitrogen purges, was dissolved in DCM (1.9 mL, 0.4 M) and slowly added to the solution. After TLC analysis indicated the consumption of the acceptor (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 (*n*-pentane-Et_2O 3:1) and all fractions containing product were concentrated *in vacuo*. The resulting residue (0.424 g, 0.55 mmol, 73% crude yield) was then dissolved in MeOH (11 mL, 0.05 M) and a catalytic amount of K_2CO_3 was added. The reaction was allowed to stir for 16 hours after which it was quenched with sat. aq. NH_4Cl and extracted with Et_2O (3x). The organic layers were combined, washed with brine, dried with $MgSO_4$ and concentrated *in vacuo*. Purification by means of column chromatography (*n*-pentane-Et_2O 1:1) gave the title compound (0.314 g, 0.49 mmol, 65% over 2 steps) as a pale oil. $[\alpha]_D^{25}$ = -109.8 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.60-7.56 (m, 2H, C*H*$_{arom}$); 7.36-7.26 (m, 5H, C*H*$_{arom}$); 6.87-6.83 (m, 2H, C*H*$_{arom}$); 5.49 (d, 1H, *J* = 1.6 Hz, H-1); 5.21 (d, 1H, *J* = 2.0 Hz, H-1'); 4.70 (dd, 2H, *J* = 11.0 87.6 Hz, PhC*H*$_2$); 4.09 (dd, 1H, *J* = 2.0, 4.8 Hz, H-2'); 3.78-3.73 (m, 2H, H-2, H-5'); 3.69-3.62 (m, 3H, H-3, H-4, H-5); 3.55 (s, 3H, OC*H*$_3$); 3.51-3.48 (m, 7H, H-3', OC*H*$_3$); 3.38 (t, 1H, *J* = 9.2 Hz, H-4'); 2.40 (d, 1H, *J* = 2.0 Hz, 2'-O*H*); 1.35-1.25 (m, 6H, H-6, H-6'). ^{13}C-APT NMR (101 MHz) δ: 156.3, 138.5 (C$_{q,arom}$); 138.5, 128.5, 128.1, 127.9, 118.7 (*C*H$_{arom}$); 101.1 (C-1'); 95.7 (C-1); 85.0 (*C*I$_{arom}$); 81.7 (C-3'); 81.5 (C-3); 79.9 (C-4'); 78.5 (C-4); 76.3 (C-2); 75.3 (Ph*C*H$_2$); 68.4 (C-2'); 68.3 (C-5); 68.1 (C-5'); 59.5, 57.5, 57.3 (O*C*H$_3$); 18.3 (C-6); 17.8 (C-6'). IR (thin film, cm^{-1}): 1089, 1116, 1203, 1232, 1452, 1484, 2931, 3476. HRMS calculated for $C_{28}H_{37}IO_9Na$ 667.13745 [M+Na]$^+$; found 667.13729.

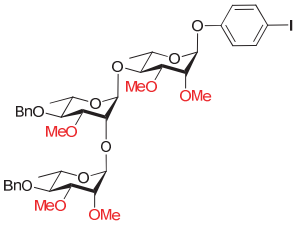
4-iodophenyl 2,3-di-*O*-methyl-4-*O*-(2-*O*-(2,4-di-*O*-benzyl-3-*O*-methyl-α-L-rhamnopyranoside)-3-*O*-methyl-4-*O*-benzyl-α-L-rhamnopyranoside)-α-L-rhamnopyranoside (39)



Prepared according to general procedure B using donor **36** (71 mg, 0.158 mmol, 1.5 eq), acceptor **34** (68 mg, 0.106 mmol, 1.0 eq) and IDCP (149 mg, 0.149 mmol, 3.0 eq) the title compound was obtained after column chromatography (DCM-EtOAc 9:1) as a slightly orange oil (99 mg, 0.100 mmol, 95%, α/ß 6:1). $[\alpha]_D^{25}$ = -71.4 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.59-7.55 (m, 2H, C*H*$_{arom}$); 7.47-7.43 (m, 2H, C*H*$_{arom}$); 7.40-7.26 (m, 13H, C*H*$_{arom}$); 6.99-6.95 (m, 2H, C*H*$_{arom}$); 5.46 (d, 1H, *J* = 2.0 Hz, H-1); 5.14 (d, 1H, *J* = 1.6 Hz, H-1'); 5.13 (d, 1H, *J* = 1.6 Hz, H-1''); 4.93 (d, 1H, *J* = 11.6 Hz, PhC*H*H); 4.80-4.78 (m, 3H, PhC*H*H, PhC*H*$_2$); 4.63 (d, 1H, *J* = 11.2 Hz, PhCH*H*); 4.55 (d, 1H, *J* = 11.2 Hz, PhCH*H*); 4.04 (dd, 1H, *J* = 2.0, 2.4 Hz, H-2'); 3.88 (dd, 1H, *J* = 2.0, 2.8 Hz, H-2''); 3.80-3.75 (m, 2H, H-2, H-

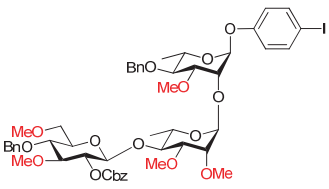
5''); 3.71-3.55 (m, 5H, H-3, H-3', H-4, H-5, H-5'); 3.53-3.42 (m, 11H, H-3'', H-4'', OC*H*$_3$); 3.34 (s, 3H, OC*H*$_3$); 3.28 (t, 1H, *J* = 9.4 Hz, H-4'); 1.33 (d, 3H, *J* = 6.0 Hz, H-6''); 1.22-1.19 (m, 6H, H-6, H-6'). ^{13}C-APT NMR (101 MHz) δ: 156.3, 139.1, 138.6, 138.5 (C$_{q,arom}$); 138.5, 128.8, 128.5, 128.4,, 128.3, 128.2, 127.9, 127.8, 127.8, 127.6, 118.7 (*C*H$_{arom}$); 100.7 (C-1'); 99.2 (C-1''); 96.0 (C-1); 85.0 (*C*I$_{arom}$); 82.2 (C-3'); 81.9 (C-3); 81.5 (C-3''); 80.8 (C-4''); 80.0 (C-4'); 77.8 (C-4); 76.2 (C-2); 75.2 (Ph*C*H$_2$); 74.0 (C-2''); 73.4 (C-2'); 72.6 (Ph*C*H$_2$); 68.6 (C-5''); 68.4 (C-5'); 68.3 (C-5''); 59.7, 57.9, 57.8, 57.4 (O*C*H$_3$); 18.4 (C-6''); 18.3 (C-6'); 17.9 (C-6). IR (thin film, cm^{-1}): 1055, 1092, 1118, 1203, 1232, 1454, 1484. HRMS calculated for $C_{49}H_{61}IO_{13}Na$ 1007.30491 [M+Na]$^+$; found 1007.30508.

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



Prepared according to general procedure B using donor **37** (67 mg, 0.179 mmol, 1.5 eq), acceptor **34** (77 mg, 0.120 mmol, 1.0 eq) and IDCP (168 mg, 0.359 mmol, 3.0 eq) the title compound was obtained after column chromatography (DCM-EtOAc 9:1) as a slightly orange oil (91 mg, 0.100 mmol, 84%, α/ß 4:1). $[\alpha]_D^{25}$ = -102.2 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.58-7.56 (m, 2H, C*H*$_{arom}$); 7.37-7.26 (m, 10H, C*H*$_{arom}$); 6.86-6.83 (m, 2H, C*H*$_{arom}$); 5.47 (d, 1H, *J* = 2.0 Hz, H-1); 5.17 (d, 1H, *J* = 1.6 Hz, H-1'); 5.15 (d, 1H, *J* = 1.6 Hz, H-1''); 4.92 (d, 1H, *J* = 11.2 Hz, PhC*H*H); 4.84 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.64-4.59 (m, 2H, PhCH*H*, PhCH*H*); 4.08 (dd, 1H, *J* = 2.0, 2.8 Hz, H-2'); 3.79-3.60 (m, 8H, H-2, H-2'', H-3, H-3'', H-4, H-5, H-5', H-5''); 3.54-3.48 (m, 13H, H-3', OC*H*$_3$); 3.45-3.32 (m, 5H, H-4', H-4'', OC*H*$_3$); 1.31 (d, 3H, *J* = 6.4 Hz, H-6'); 1.25-1.22 (m, 6H, H-6, H-6''). ^{13}C-APT NMR (101 MHz) δ: 156.3, 139.0, 138.7 (C$_{q,arom}$); 138.5, 128.5, 128.4, 128.2, 127.9, 127.8, 127.6 (*C*H$_{arom}$); 118.7 (*C*H$_{arom}$); 100.7 (C-1'); 98.5 (C-1''); 96.0 (C-1); 85.0 (*C*I$_{arom}$); 82.1 (C-3'); 81.9 (C-3); 81.2 (C-3''); 80.7 (C-4''); 80.1 (C-4'); 77.9 (C-4); 77.8 (C-2''); 76.2 (C-2); 75.3, 75.1 (Ph*C*H$_2$); 73.7 (C-2'); 68.7 (C-5'); 68.4 (C-5''); 68.3 (C-5); 59.7, 59.2, 58.1, 58.0, 57.3 (O*C*H$_3$); 18.4 (C-6'); 18.1, 18.0 (C-6, and C-6''). IR (thin film, cm^{-1}): 1029, 1075, 1093, 1119, 1176, 1232, 1484. HRMS calculated for $C_{43}H_{57}IO_{13}Na$ 931.27361 [M+Na]$^+$; found 931.27320.

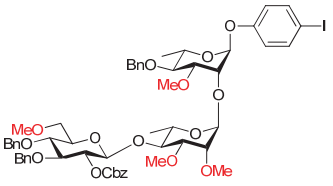
4-iodophenyl 2-*O*-(2,3-di-*O*-methyl-4-*O*-(2-*O*-benzyloxycarbonyl-3,6-di-*O*-methyl-4-*O*-benzyl-ß-D-glucopyranosyl)-α-L-rhamnopyranosyl)-3-*O*-methyl-4-*O*-benzyl-α-L-rhamnopyranoside (26)



Prepared according to general procedure A using donor **1** (2.57 g, 4.9 mmol, 1.4 eq) and acceptor **23** (2.23 g, 3.47 mmol, 1.0 eq). The title compound was obtained after column chromatography (*n*-pentane-Et$_2$O 2:3) as a pale oil (2.93 g, 2.77 mmol, 80%). $[\alpha]_D^{25}$ = -63.7 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.58 (dd, 2H, *J* = 2.0, 6.8 Hz, C*H*$_{arom}$); 7.40-7.26 (m, 15H, C*H*$_{arom}$); 6.82 (dd, 2H, *J* = 2.2, 7.0 Hz, C*H*$_{arom}$); 5.43 (d, 1H, *J* = 1.6 Hz, H-1); 5.29-5.22 (m, 2H, PhC*H*$_2$); 5.18 (d, 1H, *J* = 1.2 Hz, H-1'); 4.89 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.79 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.74 (d, 1H, *J* = 8.0 Hz, H-1''); 4.67-4.62 (m, 3H, H-2'', PhCH*H*, PhCH*H*); 4.24 (t, 1H, *J* = 2.4 Hz, H-2); 3.78 (dd, 1H, *J* = 3.2, 9.2 Hz, H-3); 3.75-3.33

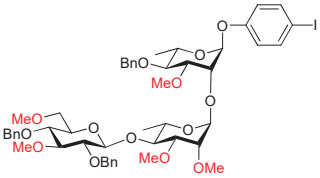
(m, 27H, H-2', H-3, H-3', H-3'', H-4, H-4', H-4'', H-5, H-5', H-5'', H-6'', OC*H*$_3$); 1.29-1.26 (m, 6H, H-6, H-6'). ^{13}C-APT NMR (101 MHz) δ: 155.9 (C$_{q,arom}$); 154.8 (*C*O$_{Cbz}$); 138.5 (*C*H$_{arom}$); 138.4, 138.2, 135.6 (C$_{q,arom}$); 128.8, 128.6, 128.6, 128.5, 128.4, 128.2, 128.1, 128.0, 127.9, 118.6 (*C*H$_{arom}$); 100.9 (C-1''); 98.5 (C-1'); 97.0 (C-1); 84.9 (*C*I$_{arom}$); 84.9 (C-3''); 80.8 (C-4'); 80.0 (C-4); 78.1 (C-3); 77.6 (C-4''); 77.6 (C-5''); 76.9 (C-2); 75.2, 75.0 (Ph*C*H$_2$); 74.8 (C-3'); 72.9 (C-2); 71.0 (Ph*C*H$_2$); 69.8 (C-6''); 68.8, 67.9 (C-5 and C-5'); 61.0, 59.8, 59.1, 58.3, 57.6 (O*C*H$_3$); 18.2, 18.0 (C-6 and C-6'). IR (thin film, cm^{-1}): 1029, 1055, 1072, 1092, 1120, 1139, 1235, 1259, 1454, 1484, 1757, 2932. HRMS calculated for $C_{51}H_{63}IO_{16}Na$ 1081.3058 [M+Na]$^+$; found 1081.3053.

4-iodophenyl 2-*O*-(2,3-di-*O*-methyl-4-*O*-(2-*O*-benzyloxycarbonyl-3,4-di-*O*-benzyl-6-*O*-methyl-ß-D-glucopyranosyl)-α-L-rhamnopyranosyl)-3-*O*-methyl-4-*O*-benzyl-α-L-rhamnopyranoside (27)



Prepared according to general procedure A using donor **2** (105 mg, 0.17 mmol, 1.5 eq) and acceptor **23** (91 mg, 0.12 mmol) the title compound was obtained after column chromatography (*n*-pentane-Et$_2$O 1:4) as a slightly yellow oil (127 mg, 0.11 mmol, 96%). [α]$_D^{25}$ = -66.3 ° (c = 1.0, CHCl$_3$). ^{1}H-NMR (400 MHz) δ: 7.58 (dd, 2H, *J* = 2.0, 6.8 Hz, C*H*$_{arom}$); 7.36-7.21 (m, 20H, C*H*$_{arom}$); 6.83 (dd, 2H, *J* = 2.2, 7.0 Hz, C*H*$_{arom}$); 5.44 (d, 1H, *J* = 1.6 Hz, H-1); 5.24-5.15 (m, 3H, H-1', PhC*H*$_2$); 4.89 (d, 1H, *J* = 7.2 Hz, PhC*H*H); 4.80-4.76 (m, 4H, H-1'', H-2'', PhC*H*H, PhC*H*H); 4.70-4.62 (m, 3H, PhCH*H*, PhCH*H*, PhCH*H*); 4.24 (dd, 1H, *J* = 2.0, 2.8 Hz, H-2); 3.80-3.63 (m, 9H, H-2', H-3, H-3'', H-4'', H-5, H-5', H-5'', H-6''); 3.56-3.42 (m, 10H, H-4, H-4', H-6'', OC*H*$_3$, OC*H*$_3$); 3.37-3.27 (m, 7H, H-3'', OC*H*$_3$); 1.30-1.26 (m, 6H, H-6, H-6'). ^{13}C-APT NMR (101 MHz) δ: 155.9 (C$_{q,arom}$); 154.7, (*C*O$_{Cbz}$); 138.5 (*C*H$_{arom}$); 138.4, 138.3, 138.2, 135.5 (C$_{q,arom}$); 128.7, 128.6, 128.5, 128.5, 128.4, 128.1, 128.1, 127.9, 127.9, 127.7, 127.7, 118.6 (*C*H$_{arom}$); 101.0 (C-1''); 98.5 (C-1'); 97.0 (C-1); 84.9 (*C*I$_{arom}$); 83.3 (C-4''); 81.9 (C-3); 80.8, 80.0 (C-4 and C-4'); 78.2 (C-2''); 77.8, 77.7, 76.9 (C-2', C-3'', and C-5''); 75.4, 75.2, 75.1 (Ph*C*H$_2$); 74.9 (C-3'); 72.9 (C-2); 71.1 (C-6''); 69.8 (Ph*C*H$_2$); 68.8, 67.9 (C-5 and C-5'); 59.8, 59.1, 58.3, 57.6 (O*C*H$_3$); 18.2, 18.0 (C-6 and C-6'). IR (thin film, cm^{-1}): 1005, 1016, 1030, 1053, 1072, 1093, 1120, 1140, 1236, 1259, 1484, 1757. HRMS calculated for $C_{57}H_{67}IO_{16}Na$ 1157.3371 [M+Na]$^+$; found 1157.3366.

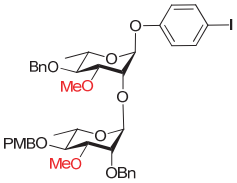
4-iodophenyl 2-*O*-(2,3-di-*O*-methyl-4-*O*-(2,4-di-*O*-benzyl-3,6-di-*O*-methyl-ß-D-glucopyranosyl)-α-L-rhamnopyranosyl)-3-*O*-methyl-4-*O*-benzyl-α-L-rhamnopyranoside (31)



Trisaccharide **28**[22] (20 mg, 22 µmol, 1.0 eq) was dissolved in DMF (1 mL, 0.02 M) and BnBr (13 µL, 011 mmol, 5.0 eq) was added to the solution. The solution was cooled to 0 °C and it was stirred for 5 minutes before NaH (4 mg, 0.11 mmol, 5.0 eq) was added. The reaction mixture was stirred for 4 hours while slowly warming to rT. The reaction was quenched by addition of H$_2$O, and extracted with Et$_2$O (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$_2$O, 1:4) gave the title compound (14 mg, 14 µmol, 64%) as a pale oil. [α]$_D^{25}$ = -77.0 ° (c = 1.0, CHCl$_3$). ^{1}H NMR (400 MHz) δ 7.60-7.53 (m, 2H, C*H*$_{arom}$); 7.44-7.34 (m, 2H, C*H*$_{arom}$); 7.39-7.28 (m, 9H, C*H*$_{arom}$); 7.32-7.24 (m, 4H, C*H*$_{arom}$); 6.85-6.78 (m, 2H, C*H*$_{arom}$); 5.47 (d, 1H, *J* = 2.0 Hz, H-1); 5.16

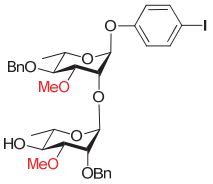
(d, 1H, *J* = 2.0 Hz, H-1'); 4.94-4.88 (m, 2H, PhC*H*H, PhC*H*H); 4.82 (d, 1H, *J* = 10.8 Hz, PhCH*H*); 4.78-4.70 (m, 2H, H-1'', PhC*H*H); 4.66-4.61 (m, 2H, PhCH*H*, PhCH*H*); 4.22 (dd, 1H, *J* = 2.0, 2.8 Hz, H-2); 3.82-3.61 (m, 5H, H-2', H-3, H-4'', H-5, H-5'); 3.67-3.62 (m, 4H, H-6'', OCH_3); 3.59-3.42 (m, 10H, H-3', H-4, H-4', H-6'', OCH_3); 3.36-3.29 (m, 8H, H-3'', H-5'', OCH_3); 3.25 (dd, 1H, *J* = 7.6, 9.2 Hz, H-2''); 1.30 (d, 3H, *J* = 6.0 Hz, H-6'); 1.26 (d, 3H, *J* = 6.4 Hz, H-6). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.1, 139.3, 138.6 ($C_{q,arom}$); 138.6, 128.6, 128.3, 128.2, 128.1, 127.9, 127.5, 118.7 (*C*H$_{arom}$); 103.1 (C-1''); 98.9 (C-1'); 97.2 (C-1); 86.8 (C-3''); 84.9 (*C*I$_{arom}$); 82.8 (C-2''); 81.6 (C-3); 81.1 (C-3'); 80.1 (C-4''); 80.0 (C-4); 77.9 (C-4'); 75.3, 75.0, 74.6 (Ph*C*H$_2$); 74.5 (C-5''); 73.7 (C-2); 71.3 (C-6''); 68.8 (C-5); 68.1 (C-5'); 61.4, 59.8, 59.1, 58.3, 57.4 (O*C*H$_3$); 18.2 (C-6 and C-6'). IR (thin film, cm^{-1}): 1005, 1030, 1053, 1073, 1089, 1122, 1140, 1232, 1454, 1484, 2932. HRMS calculated for $C_{50}H_{63}IO_{14}Na$ 1037.3160 [M+Na]$^+$; found 1037.3155.

4-iodophenyl 2-*O*-(2-*O*-benzyl-3-*O*-methyl-4-*O*-(4-methoxybenzyl)-α-L-rhamnopyranosyl)-3-*O*-methyl-4-*O*-benzyl-α-L-rhamnopyranoside (19)



Compound **18**[22] (125 mg, 0.17 mmol, 1.0 eq) was dissolved in dry DMF (1.7 mL, 0.1 M) and BnBr (0.04 mL, 0.33 mmol, 1.5 eq) was added to the solution. The mixture was cooled to 0 °C, and NaH (60%, 10 mg, 0.25 mmol, 1.2 eq) and TBAI (3 mg, 8 µmol, 0.05 eq) were 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 (146 mg, 0.17 mmol, 100%) as a clear oil. $[\alpha]_D^{25}$ = -79 ° (c =0.7, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.56-7.52 (m, 2H, C*H*$_{arom}$); 7.46-7.44 (m, 2H, C*H*$_{arom}$); 7.38-7.26 (m, 10H, C*H*$_{arom}$); 6.90-6.87 (m, 2H, C*H*$_{arom}$); 6.78-6.74 (m, 2H, C*H*$_{arom}$); 5.37 (d, 1H, *J* = 2.0 Hz, H-1); 5.09 (d, 1H, *J* = 1.6 Hz, H-1'); 4.86-4.70 (m, 4H, PhC*H*H, PhC*H*H, PhC*H*$_2$); 4.59-4.54 (m, 2H, PhCH*H*, PhCH*H*); 4.13-4.12 (m, 1H, H-2); 3.92-3.91 (m, 1H, H-2'); 3.80 (s, 3H, C*H*$_{3,PMB}$); 3.74-3.69 (m, 2H, H-3, H-5'); 3.64-3.58 (m, 2H, H-3', H-5); 3.52 (t, 1H, *J* = 9.2 Hz, H-4'); 3.48 (s, 3H, OCH_3); 3.45 (s, 3H, OCH_3); 3.32 (t, 1H, *J* = 9.6 Hz, H-4); 1.29 (d, 3H, *J* = 6.0 Hz, H-6'); 1.18 (d, 3H, *J* = 6.0 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 159.4, 156.1 ($C_{q,arom}$); 138.5 (*C*H$_{arom}$); 138.5, 138.4, 130.9 ($C_{q,arom}$); 129.9, 128.5, 128.5, 128.2, 128.2, 127.9, 127.9, 118.6, 114.0 (*C*H$_{arom}$); 99.8 (C-1'); 97.0 (C-1); 84.7 (*C*I$_{arom}$); 81.6 (C-3); 81.5 (C-3'); 80.3 (C-4'); 79.9 (C-4); 75.3, 75.1 (Ph*C*H$_2$); 74.1 (C-2'); 73.3 (C-2); 72.8 (Ph*C*H$_2$); 68.7 (C-5); 68.6 (C-5'); 58.0, 58.0 (O*C*H$_3$); 55.5 (*C*H$_{3,PMB}$); 18.2 (C-6'); 18.1 (C-6). IR (thin film, cm^{-1}): 1035, 1070, 1090, 1120, 1175, 1233, 1248, 1454, 1484, 1514. HRMS calculated for $C_{42}H_{49}IO_{10}Na$ 863.2268 [M+Na]$^+$; found 863.2263.

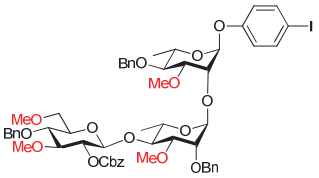
4-iodophenyl 2-*O*-(2-*O*-benzyl-3-*O*-methyl-α-L-rhamnopyranosyl)-3-*O*-methyl-4-*O*-benzyl-α-L-rhamnopyranoside (20)



Compound **19** (139 mg, 0.17 mmol, 1.0 eq) was dissolved in a mixture of DCM and HFIP (1:1, 1.7 mL, 0.1 M) after which a solution of HCl in HFIP (0.09 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

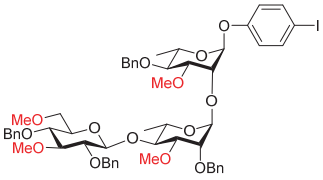
$MgSO_4$ and concentrated *in vacuo*. Purification by means of column chromatography (*n*-pentane-Et_2O 1:1) gave the title compound (107 mg, 0.15 mmol, 90%) as a pale oil. $[\alpha]_D^{25}$ = -65.8 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.58-7.54 (m, 2H, C*H*$_{arom}$); 7.44-7.42 (m, 2H, C*H*$_{arom}$); 7.33-7.25 (m, 8H, C*H*$_{arom}$); 6.81-6.78 (m, 2H, C*H*$_{arom}$); 5.42 (d, 1H, *J* = 2.0 Hz, H-1); 5.18 (d, 1H, *J* = 1.6 Hz, H-1'); 4.86 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.72 (dd, 2H, *J* = 12.6, 21.8 Hz, PhCH_2); 4.61 (d, 1H, *J* = 10.8 Hz, PhCH*H*); 4.18 (dd, 1H, *J* = 2.0, 2.8 Hz, H-2); 3.93 (dd, 1H, *J* = 1.8, 3.0 Hz, H-2'); 3.79-3.65 (m, 4H, H-3, H-4', H-5, H-5'); 3.50 (s, 3H, OCH_3); 3.43 (dd, 1H, *J* = 3.2, 9.2 Hz, H-3'); 3.38-3.34 (m, 4H, H-4, OCH_3); 1.32 (d, 3H, *J* = 6.0 Hz, H-6); 1.21 (d, 3H, *J* = 6.4 Hz, H-6'). ^{13}C-APT NMR (101 MHz) δ: 156.0 (C$_{q,arom}$); 138.5 (*C*H$_{arom}$); 138.4, 138.1 (C$_{q,arom}$); 128.5, 128.3, 128.1, 128.0, 127.9, 118.6 (*C*H$_{arom}$); 99.6 (C-1'); 97.0 (C-1); 84.8 (*C*I$_{arom}$); 81.7 (C-3); 80.9 (C-3'); 79.9 (C-4); 75.2 (Ph*C*H$_2$); 73.4 (C-2); 72.5 (Ph*C*H$_2$); 72.4 (C-2'); 71.7 (C-4'); 69.0 (C-5'); 68.7 (C-5); 58.1, 57.0 (O*C*H$_3$); 18.1 (C-6'); 18.0 (C-6). IR (thin film, cm^{-1}): 1031, 1049, 1072, 1120, 1137, 1233, 1455, 1484, 2931, 3470. HRMS calculated for $C_{34}H_{41}IO_9Na$ 743.1693 [M+Na]$^+$; found 743.1708.

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



Prepared according to general procedure A using donor **1** (73 mg, 0.14 mmol, 1.5 eq) and acceptor **20** (67 mg, 0.09 mmol, 1.0 eq). The title compound was obtained after column chromatography (*n*-pentane-Et_2O 7:3) as a pale oil (70 mg, 0.06 mmol, 66%). $[\alpha]_D^{25}$ = -46.8 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.59-7.55 (m, 2H, C*H*$_{arom}$); 7.44-7.26 (m, 20H, C*H*$_{arom}$); 6.83-6.79 (m, 2H, C*H*$_{arom}$); 5.40 (d, 1H, *J* = 2.0Hz, H-1); 5.24 (s, 2H, Ph*C*H$_2$); 5.16 (d, 1H, *J* = 1.6 Hz, H-1'); 4.85-4.73 (m, 5H, H-1'', Ph*C*H$_2$, PhC*H*H); 4.67-4.57 (m, 3H, H-2'', PhCH*H*); 4.18 (dd, 1H, *J* = 2.4, 2.8 Hz, H-2); 3.83 (dd, 1H, *J* = 1.6, 3.2 Hz, H-2'); 3.74-3.64 (m, 5H, H-3, H-5, H-5', H-5'', H-6''); 3.61-3.54 (m, 2H, H-4', H-6''); 3.50 (s, 3H, OCH_3); 3.48 (s, 3H, OCH_3); 3.41-3.32 (m, 7H, H-3', H-3'', H-4, H-4'', OCH_3); 3.21 (s, 3H, OCH_3); 1.30 (d, 3H, *J* = 5.6 Hz, H-6'); 1.21 (d, 3H, *J* = 6.0 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 156.0 (C$_{q,arom}$); 154.8 (*C*O$_{Cbz}$); 138.5 (*C*H$_{arom}$); 138.5, 138.3, 138.2, 135.6 (C$_{q,arom}$); 128.7, 128.6, 128.6, 128.5, 128.5, 128.4, 128.3, 128.2, 128.2, 128.0, 127.9, 118.7 (*C*H$_{arom}$); 101.1 (C-1''); 99.3 (C-1'); 97.0 (C-1); 85.0 (C-4''); 84.9 (*C*I$_{arom}$); 81.9 (C-3); 81.0 (C-3'); 79.9 (C-4); 78.1 (C-5''); 78.1 (C-2''); 77.7 (C-4'); 75.3, 75.0 (Ph*C*H$_2$); 74.8 (C-3''); 73.1 (C-2'); 72.7 (C-2); 72.6 (Ph*C*H$_2$); 71.1 (C-6''); 69.8 (Ph*C*H$_2$); 68.8, 68.0 (C-5 and C-5'); 61.0, 59.8, 58.2, 57.5 (O*C*H$_3$); 18.1 (C-6 and C-6'). IR (thin film, cm^{-1}): 1000, 1027, 1055, 1120, 1139, 1205, 1235, 1259, 1325, 1348, 1385, 1454, 1484, 1497, 1756, 2932, 2968. HRMS calculated for $C_{57}H_{67}IO_{16}Na$ 1157.33660 [M+Na]$^+$; found 1157.33649.

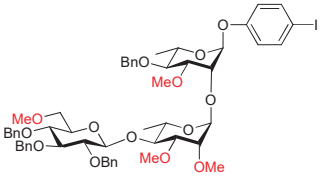
4-iodophenyl 2-*O*-(2,3-di-*O*-methyl-4-*O*-(2,4-di-*O*-benzyl-3,6-di-*O*-methyl-ß-D-glucopyranosyl)-α-L-rhamnopyranosyl)-3-*O*-methyl-4-*O*-benzyl-α-L-rhamnopyranoside (32)



Trisaccharide **29**[22] (14 mg, 15 µmol, 1.0 eq) was dissolved in DMF (1.5 mL, 0.01 M) and BnBr (9 µL, 77 µmol, 5.0 eq) was added to the solution. The solution was cooled to 0 °C and it was stirred for 5 minutes before NaH (3 mg, 77 µmol, 5.0 eq) was added. The reaction mixture was stirred for 16 hours while slowly warming

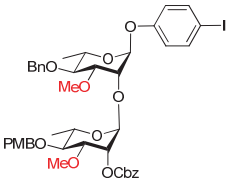
to rt. The reaction was quenched by addition of H_2O, and extracted with Et_2O (3x). The organic layers were combined, washed with brine, dried with $MgSO_4$ and concentrated *in vacuo*. Purification by means of column chromatography (*n*-pentane-Et_2O 3:2) gave the title compound (16 mg, 15 µmol, 95%) as a pale oil. $[\alpha]_D^{25}$ = -47.7 ° (c = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz) δ: 7.56 (dd, 2H, *J*= 2.0, 7.0 Hz, C*H*$_{arom}$); 7.43-7.25 (m, 20H, C*H*$_{arom}$); 6.80 (dd, 2H, *J* = 2.2, 7.0 Hz, C*H*$_{arom}$); 5.44 (d, 1H, *J* = 2.0 Hz, H-1); 5.12 (d, 1H, *J*= 1.6 Hz H-1'); 4.91 (d, 2H, *J* = 11.6 Hz PhC*H*$_2$); 4.84 (dd, 2H, *J* = 6.8, 10.0 Hz, PhC*H*$_2$); 4.74-4.71 (m, 4H, PhC*H*$_2$); 4.63 (d, 1H, *J* = 10.8 Hz, PhCH); 4.58 (d, 1H, *J* = 10.8 Hz, PhCH*H*); 4.16 (dd, 1H, *J* = 2.0, 3.2 Hz, H-2); 3.87 (dd, 1H, *J* = 2.0, 3.2 Hz, H-2); 3.80-3.63 (m, 8H, H-3, H-4'', H-5, H-5', H-6'', OC*H*$_3$); 3.57 (dd, 1H, *J* = 1.6, 11.2 Hz, H-6''); 3.53-3.47 (m, 5H, H-3', H-4', OC*H*$_3$); 3.39-3.32 (m, 6H, H-3'', H-4, H-5'', OC*H*$_3$); 3.25 (dd, 1H, *J* = 7.8, 9.0 Hz, H-2''); 3.21 (s, 3H, OC*H*$_3$); 1.33 (d, 3H, *J*= 6.0 Hz, H-6'); 1.22 (d, 3H, *J*= 6.4 Hz, H-6). ^{13}C-APT NMR (100 MHz) δ: 156.1, 139.2, 138.6, 138.5 (C$_{q,arom}$); 138.4 (*C*H$_{arom}$); 138.2 (C$_{q,arom}$); 128.5, 128.5, 128.3, 128.3,128.2, 128.1, 127.9, 127.8, 127.5, 118.7 (*C*H$_{arom}$); 103.2 (C-1''); 99.7 (C-1'); 97.2 (C-1); 86.8 (C-3''); 84.9 (*C*I$_{arom}$); 82.7 (C-2''); 81.5 (C-3); 81.3 (C-3'); 80.0 (C-4); 77.9 (C-4'); 77.4 (C-4''); 75.3, 74.9, 74.6, (Ph*C*H$_2$); 74.5 (C-5''); 73.4 (C-2); 73.1 (C-2'); 72.6,(Ph*C*H$_2$); 71.3 (C-6''); 68.8 (C-5); 68.1 (C-5'); 61.4, 59.7, 58.0, 57.4 (O*C*H$_3$); 18.3 (C-6'), 18.2 (C-6). IR (thin film, cm^{-1}): 1000, 1029, 1073, 1120, 1140, 1205, 1232, 1279, 1454, 1484, 2929, 2972. HRMS calculated for $C_{56}H_{67}IO_{14}Na$ 1113.3473 $[M+Na]^+$; found 1113.3468.

4-iodophenyl 2-*O*-(2,3-di-*O*-methyl-4-*O*-(2,3,4-tri-*O*-benzyl-6-*O*-methyl-ß-D-glucopyranosyl)-α-L-rhamnopyranosyl)-3-*O*-methyl-4-*O*-benzyl-α-L-rhamnopyranoside (33)



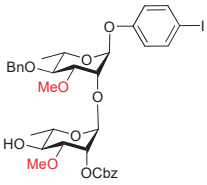
Trisaccharide **30**[22] (215 mg, 0.22 mmol, 1.0 eq) was dissolved in DMF (11 mL, 0.02 M) and cooled to 0 °C. To the solution were added BnBr (0.26 mL, 2.2 mmol, 10 eq) and TBAI (16 mg, 43 µmol, 0.2 eq) and it was stirred for 5 minutes before NaH (36 mg, 1.1 mmol, 5.0 eq) was added. The reaction mixture was stirred for 2 h while slowly warming to rT. 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 1:4) gave the title compound (135 mg, 0.12 mmol, 58%) as a pale oil. $[\alpha]_D^{25}$ = -21.6 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.58-7.54 (m, 2H, C*H*$_{arom}$); 7.38-7.12 (m, 20H, C*H*$_{arom}$); 6.82 (dd, 2H, *J*= 2.8, 11.6 Hz, C*H*$_{arom}$); 5.15 (s, 1H, H-1); 5.17 (s, 1H, H-1'); 4.98-4.74 (m, 8H, Ph*C*H$_2$); 4.66-4.63 (m, 2H, PhCH*H*, H-1''); 4.23 (d, 1H, *J* = 2.0 Hz, H-2); 3.81-3.50 (m, 18H, H-2', H-3, H-3', H-3'', H-4', H-4'', H-5, H-5', H-6''); 3.45 (t, 1H, *J* = 9.4 Hz, H-4); 3.40-3.35 (m, 8H, H-2'', H-5'', OC*H*$_3$); 1.29 (d, 3H, *J*= 7.2 Hz, H-6'); 1.26 (d, 3H, *J*= 6.4 Hz, H-6). ^{13}C-APT NMR (100 MHz) δ: 156.1, 139.0, 138.9 (C$_{q,arom}$); 138.5 (*C*H$_{arom}$); 138.5, 138.4 (C$_{q,arom}$); 128.5, 128.4, 128.3, 128.1, 128.1, 127.9, 127.9, 127.8, 127.8, 127.5, 127.5, 125.8, 118.6, 118.5 (*C*H$_{arom}$); 103.1 (C-1''); 98.8 (C-1'); 96.8 (C-1); 84.9 (*C*I$_{arom}$); 84.9 (C-4''); 82.9 (C-2''); 81.5 (C-3); 81.0 (C-4'); 80.0 (C-4); 77.9 (C-3''); 76.7 (C-2'); 76.7 (C-3''); 75.7, 75.2, 75.0 74.7; 74.6 (C-5''); 73.7 (C-2); 71.3 (C-6''); 68.8 (C-5), 68.1 (C-5'); 59.7, 59.1, 58.2, 57.3 (O*C*H$_3$); 18.2, 18.2 (HC6 and C-6'). IR (thin film, cm^{-1}): 1029, 1055, 1072, 1090, 1120, 1139, 1203, 1232, 1454, 1484. HRMS calculated for $C_{56}H_{67}IO_{14}Na$ 1113.3473 $[M+Na]^+$; found 1113.3468.

4-iodophenyl 2-*O*-(2-*O*-benzyloxycarbonyl-3-*O*-methyl-4-*O*-(4-methoxybenzyl)-α-L-rhamnopyranosyl)-3-*O*-methyl-4-*O*-benzyl-α-L-rhamnopyranoside (21)



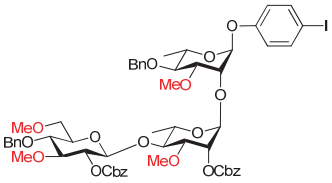
Prepared according to glycosylation procedure A using donor **4** (393 mg, 0.75 mmol, 1.5 eq) and acceptor **5** (235 mg, 0.5 mmol, 1.0 eq). The title compound was obtained after column chromatography (*n*-pentane-Et_2O 4:1) as a slightly yellow oil (206 mg, 0.23 mmol, 47%). $[\alpha]_D^{25}$ = -69.5 ° (c =0.8, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.56-7.53 (m, 2H, C*H*$_{arom}$); 7.42-7.24 (m, 10H, C*H*$_{arom}$); 6.89-6.87 (m, 2H, C*H*$_{arom}$); 6.79-6.76 (m, 2H, C*H*$_{arom}$); 5.41 (s, 1H, H-1); 5.28-5.27 (m, 1H, H-2'); 5.27-5.18 (m, 2H, PhC*H*$_2$); 5.14 (s, 1H, H-1'); 4.90 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.81 (d, 1H, *J* = 10.4 Hz, PhC*H*H); 4.63 (d, 1H, *J* = 10.8 Hz, PhCH*H*); 4.53 (d, 1H, *J* = 10.4 Hz, PhCH*H*); 4.17 (t, 1H, *J* = 2.2 Hz, H-2); 3.79-3.65 (m, 7H, H-3, H-3', H-5, H-5', C*H*$_{3,PMB}$); 3.53 (s, 3H, OC*H*$_3$); 3.52 (s, 3H, OC*H*$_3$); 3.44-3.37 (m, 2H, H-4, H-4'); 1.28 (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: 159.4, 156.0 (C$_{q,arom}$); 154.8 (*C*O$_{Cbz}$); 138.5 (C$_{q,arom}$); 138.5 (*C*H$_{arom}$); 135.2, 130.7 (C$_{q,arom}$); 128.7, 128.5, 128.5, 128.1, 127.8, 118.6, 114.0 (*C*H$_{arom}$); 99.0 (C-1'); 96.8 (C-1); 84.8 (*C*I$_{arom}$); 81.4 (C-3); 79.9 (C-3'); 79.9 (C-4); 79.6 (C-4'); 75.3, 75.3 (Ph*C*H$_2$); 73.5 (C-2); 72.6 (C-2'); 70.0 (Ph*C*H$_2$); 68.8 (C-5'); 68.5 (C-5); 58.1, 58.0 (O*C*H$_3$); 55.4 (*C*H$_{3,PMB}$); 18.1 (C-6'); 18.0 (C-6). IR (thin film, cm^{-1}): 1036, 1072, 1093, 1120, 1173, 1233, 1264, 1387, 1457, 1484, 1513, 1750. HRMS calculated for $C_{43}H_{49}IO_{12}Na$ 907.2166 [M+Na]$^+$; found 907.2143.

4-iodophenyl 2-*O*-(2-*O*-benzyloxycarbonyl-3-*O*-methyl-α-L-rhamnopyranosyl)-3-*O*-methyl-4-*O*-benzyl-α-L-rhamnopyranoside (22)



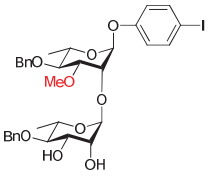
Compound **21** (192 mg, 0.22 mmol, 1.0 eq) was dissolved in a mixture of DCM and HFIP (1:1, 2.2 mL, 0.1 M) after which a solution of HCl in HFIP (0.11 mL, 0.2 M, 0.1 eq) was added. After complete conversion of the starting material, indicated by a dark purple colour, the reaction was quenched by addition 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 (163 mg, 0.21 mmol, 98%) as a pale oil. $[\alpha]_D^{25}$ = -49.9 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.58-7.55 (m, 2H, C*H*$_{arom}$); 7.46-7.29 (m, 10H, C*H*$_{arom}$); 6.82-6.79 (m, 2H, C*H*$_{arom}$); 5.45 (d, 1H, *J* = 2.0 Hz, H-1); 5.28 (dd, 1H, *J* = 1.8, 2.6 Hz, H-2'); 5.20-5.18 (m, 3H, H-1', PhC*H*$_2$); 4.91 (d, 1H, *J* = 11.2 Hz, PhC*H*H); 4.65 (d, 1H, *J* = 10.8 Hz, PhCH*H*); 4.21 (dd, 1H, *J* = 2.4, 2.8 Hz, H-2); 3.81-3.68 (m, 3H, H-3, H-5, H-5'); 3.58-3.52 (m, 5H, H-3', H-4', OC*H*$_3$); 3.47-3.42 (m, 4H, H-4, OC*H*$_3$); 2.45 (d, 1H, *J* = 2.0 Hz, 4'-O*H*); 1.30 (d, 3H, *J* = 6.4 Hz, H-6); 1.25 (d, 3H, *J* = 6.4 Hz, H-6'); ^{13}C-APT NMR (101 MHz) δ: 156.0 (C$_{q,arom}$); 154.8 (*C*O$_{Cbz}$); 138.5 (*C*H$_{arom}$); 138.5, 135.1 (C$_{q,arom}$); 128.7, 128.5, 128.5, 128.2, 127.9, 118.6 (*C*H$_{arom}$); 99.2 (C-1'); 96.9 (C-1); 84.9 (*C*I$_{arom}$); 81.4 (C-3); 79.9 (C-4); 79.4 (C-4'); 75.3 (Ph*C*H$_2$); 73.5 (C-2); 71.6 (C-3'); 71.3 (C-2'); 70.1 (Ph*C*H); 68.9 (C-5); 68.8 (C-5'); 58.2, 57.7 (O*C*H$_3$); 18.2 (C-6'); 17.8 (C-6). IR (thin film, cm^{-1}): 1033, 1049, 1073, 1092, 1138, 1232, 1264, 1385, 1445, 1454, 1484, 1747, 2932, 3450. HRMS calculated for $C_{35}H_{41}IO_{11}Na$ 787.1591 [M+Na]$^+$; found 787.1567.

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



Prepared according to glycosylation procedure A using donor **1** (67 mg, 0.12 mmol, 1.5 eq) and acceptor **22** (63 mg, 0.08 mmol, 1.0 eq). The title compound was obtained after column chromatography (*n*-pentane-Et_2O 3:2) as a slightly yellow oil (66 mg, 0.06 mmol, 68%). $[\alpha]_D^{25}$ = -54.7 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.57 (dd, 2H, *J* = 2.0, 7.2 Hz, C*H*$_{arom}$); 7.42-7.24 (m, 20H, C*H*$_{arom}$); 6.81 (d, 2H, *J* = 9.2 Hz, C*H*$_{arom}$); 5.44 (d, 1H, *J* = 1.2 Hz, H-1); 5.25-5.14 (m, 6H, H-1', H-2', PhC*H*$_2$); 4.93 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.80 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.69-4.62 (m, 4H, H-1'', H-2'', PhCH*H*, PhCH*H*); 4.22 (dd, 1H, *J* = 2.0, 2.8 Hz, H-2); 3.78-3.45 (m, 15H, H-3, H-3', H-4, H-4', H-4'', H-5, H-5', H-6'', OC*H*$_3$); 3.40-3.34 (m, 5H, H-3'', H-5'', OC*H*$_3$); 3.26 (s, 3H, OC*H*$_3$); 1.30-1.25 (m, 6H, H-6, H-6'). ^{13}C-APT NMR (101 MHz) δ: 155.9 (C$_{q,arom}$); 154.8, 154.8 (*C*O$_{Cbz}$); 138.5 (*C*H$_{arom}$); 138.5, 138.3, 135.5, 135.1 (C$_{q,arom}$); 128.8, 128.7, 128.7, 128.6, 128.5, 128.5, 128.2, 128.1, 128.0, 127.9, 118.7 (*C*H$_{arom}$); 101.2 (C-1''); 98.7 (C-1'); 96.9 (C-1); 84.9 (*C*I$_{arom}$); 84.9 (C-3''); 81.6 (C-3); 79.9 (C-3'); 79.3 (C-4); 78.0 (C-2''); 77.9 (C-4''); 77.5 (C-4'); 75.3, 75.0 (PhC*H*$_2$); 74.8 (C-5''); 72.8 (C-2); 72.1 (C-2'); 71.0 (C-6''); 70.1, 69.9 (PhC*H*$_2$); 68.8, 67.9 (C-5 and C-5'); 60.9, 59.8, 58.2, 57.8 (OC*H*$_3$); 18.1, 17.9 (C-6 and C-6'). IR (thin film, cm^{-1}): 1003, 1035, 1057, 1073, 1140, 1262, 1385, 1455, 1484, 1751. HRMS calculated for $C_{58}H_{67}IO_{18}Na$ 1201.3270 $[M+Na]^+$; found 1201.3257.

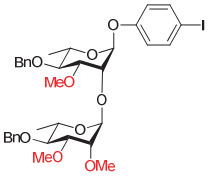
4-iodophenyl 2-*O*-(4-*O*-benzyl-α-L-rhamnopyranosyl)-3-*O*-methyl-4-*O*-benzyl-α-L-rhamnopyranoside (42)



Donor **41** (74 mg, 0.12 mmol, 1.0 eq), Ph_2SO (32 mg, 0.16 mmol, 1.3 eq) and TTBP (75 mg, 0.30 mmol, 2.5 eq) were dried by co-evaporation with toluene (3x) followed by 3 vacuum/nitrogen purges. The mixture was then dissolved in DCM (2.5 mL, 0.05 M) and flame-dried 3Å molecular sieves were added. The solution was then cooled to -65 °C after which Tf_2O (26 µL, 0.16 mmol, 1.3 eq) was added to the solution. After stirring for 30 minutes, acceptor **5** (113 mg, 0.24 mmol, 2.0 eq), which was also dried by co-evaporation with toluene (3x) followed by 3 vacuum/nitrogen purges, was dissolved in DCM (0.6 mL, 0.4 M) and slowly added to the solution. After TLC analysis indicated the consumption of the acceptor (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 (*n*-pentane-Et_2O 3:1) and all fractions containing product were concentrated *in vacuo*. The resulting residue (90 mg, 0.092 mmol, 77% crude yield) was then dissolved in MeOH (3 mL, 0.03 M) and a catalytic amount of K_2CO_3 was added. The reaction was allowed to stir for 16 hours after which it was quenched with sat. aq. NH_4Cl and extracted with Et_2O (3x). The organic layers were combined, washed with brine, dried with $MgSO_4$ and concentrated *in vacuo*. Purification by means of column chromatography (*n*-pentane-acetone 7:3) gave the title compound (59 mg, 0.084 mmol, 69% over 2 steps) as a pale oil. $[\alpha]_D^{25}$ = -82.3 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.58-7.54 (m, 2H, C*H*$_{arom}$); 7.40-7.25 (m, 10H, C*H*$_{arom}$); 6.81-6.78 (m, 2H, C*H*$_{arom}$); 5.44 (d, 1H, *J* = 1.6 Hz, H-1); 5.08 (d, 1H, *J* = 1.6 Hz, H-1'); 4.86 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.75 (s, 2H, PhC*H*$_2$); 4.59 (d, 1H,

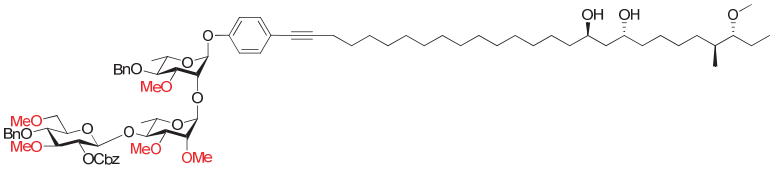
J = 10.8 Hz, PhCH*H*); 4.19 (dd, 1H, *J* = 2.4, 4.8 Hz, H-2); 4.12 (dd, 1H, *J* = 1.6, 3.2 Hz, H-2'); 4.00 (dd, 1H, *J* = 3.4, 9.0 Hz, H-3'); 3.84 (dq, 1H, *J* = 3.2, 6.0 Hz, H-5'); 3.75 (dd, 1H, *J* = 3.0, 9.4 Hz, H-3); 3.68 (dq, 1H, *J* = 3.6, 6.4 Hz, H-5); 3.52 (s, 3H, OC*H*$_3$); 3.43-3.37 (m, 2H, H-4, H-4'); 1.34 (d, 3H, *J* = 6.0 Hz, H-6'); 1.22 (d, 3H, *J* = 6.4 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 156.1 (C$_{q,arom}$); 138.5 (*C*H$_{arom}$); 138.2 (C$_{q,arom}$); 128.8, 128.5, 128.3, 128.2, 128.1, 127.9, 118.6 (*C*H$_{arom}$); 101.1 (C-1'); 96.9 (C-1); 84.8 (*C*I$_{arom}$); 81.6 (C-4'); 81.5 (C-3); 80.2 (C-4); 75.5, 75.3 (Ph*C*H$_2$); 73.7 (C-2); 71.3 (C-3'); 71.2 (C-2'); 68.8 (C-5); 68.2 (C-5'); 58.2 (O*C*H$_3$); 18.2 (C-6'); 18.1 (C-6). IR (thin film, cm^{-1}): 1029, 1049, 1073, 1099, 1105, 1139, 1178, 1232, 1278, 1454, 1484, 3431. HRMS calculated for $C_{33}H_{39}IO_9Na$ 729.15310 [M+Na]$^+$; found 729.15255.

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



Compound **42** (44 mg, 62 µmol, 1.0 eq) was dissolved in dry DMF (0.6 mL, 0.1 M) and MeI (16 µL, 0.249 mmol, 4.0 eq) was added to the solution. The mixture was cooled to 0 °C, and NaH (60%, 8 mg, 0.19 mmol, 3.0 eq) was 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 1:1) gave the title compound (33 mg, 45 µmol, 72%) as a clear oil. $[\alpha]_D^{25}$ = -87.6 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.55 (dd, 2H, *J* = 3.2, 12.0 Hz, C*H*$_{arom}$); 7.37-7.25 (m, 10H, C*H*$_{arom}$); 6.79 (d, 2H, *J* = 8.8 Hz, C*H*$_{arom}$); 5.41 (s, 1H, H-1); 5.15 (s, 1H, H-1'); 4.93-4.87 (m, 2H, PhC*H*H, PhC*H*H); 4.66-4.59 (m, 2H, PhCH*H*, PhCH*H*); 4.20 (s, 1H, H-2); 3.77-3.62 (m, 5H, H-2', H-3, H-3', H-5, H-5'); 3.57 (s, 3H, OC*H*$_3$); 3.56 (s, 3H, OC*H*$_3$); 3.55 (s, 3H, OC*H*$_3$); 3.48-3.39 (m, 2H, H-4, H-4'); 1.29 (d, 3H, *J* = 6.4 Hz, H-6'); 1.23 (d, 3H, *J* = 6.4 Hz, H-6). ^{13}C-APT NMR (101 MHz) δ: 156.1, 138.6 (C$_{q,arom}$); 138.5, 128.6, 128.5, 128.2, 128.1, 127.9, 127.9, 118.6 (*C*H$_{arom}$); 98.9 (C-1'); 97.0 (C-1); 84.8 (*C*I$_{arom}$); 81.7 (C-3'); 81.2 (C-3); 80.5 (C-4); 80.0 (C-4'); 77.6 (C-2'); 75.6, 75.3 (Ph*C*H$_2$); 73.5 (C-2); 68.8 (C-5); 68.5 (C-5'); 59.2, 58.2, 58.1 (O*C*H$_3$); 18.1 (C-6'); 18.1 (C-6). IR (thin film, cm^{-1}): 1029, 1052, 1072, 1096, 1120, 1232, 1484. HRMS calculated for $C_{35}H_{43}IO_9Na$ 757.18440 [M+Na]$^+$; found 757.18410.

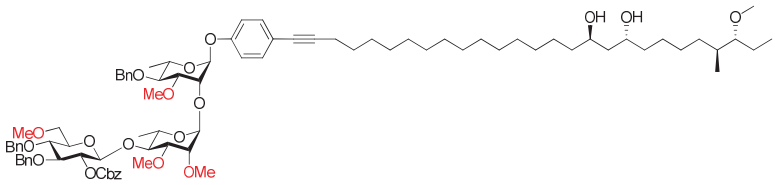
4-((3*R*,4*S*,9*R*,11*R*)-3-methoxy-4-methylheptacos-26-yne-9,11-diol)phenyl 2-*O*-(2,3-di-*O*-methyl-4-*O*-(2-*O*-benzyloxycarbonyl-3,6-di-*O*-methyl-4-*O*-benzyl-ß-D-glucopyranosyl)-α-L-rhamnopyranosyl)-3-*O*-methyl-4-*O*-benzyl-α-L-rhamnopyranoside (44)



The title compound was synthesized according to general procedure C using **26** (23 mg, 22 µmol, 1.0 eq) and phthiocerol (12 mg, 26 µmol, 1.2 eq). Column chromatography (DCM-acetone 4:1) yielded the product (25 mg, 18 µmol, 83%) as a yellow oil. $[\alpha]_D^{25}$ = -50.9 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.40-7.26 (m, 17, C*H*$_{arom}$); 6.96-6.94 (m, 2H, C*H*$_{arom}$); 5.47 (d, 1H, *J* = 1.6 Hz, H-1); 5.39-5.32 (m, 2H, PhC*H*$_2$); 5.18 (d, 1H, *J* =

1.2 Hz, H-1'); 4.89 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.79 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.74 (d, 1H, *J* = 8.0 Hz, H-1''); 4.67-4.62 (m, 3H, H-2'', PhCH*H*, PhCH*H*); 4.24 (s, 1H, H-2); 3.96-3.90 (m, 2H, C*H*$_{Phth}$); 3.67-3.33 (m, 30H, H-2', H-3, H-3', H-3'', H-4, H-4', H-4'', H-5, H-5', H-5'', H-6'', OC*H*$_3$); 2.90-2.84 (m, 1H, C*H*$_{Phth}$); 2.38 (t, 2H, *J* = 7.2 Hz, C*H*$_{2,Phth}$); 2.05 (bs, 2H, O*H*$_{Phth}$); 1.72-1.64 (m, 1H, C*H*$_{Phth}$); 1.62-1.05 (m, 60H, C*H*$_{2,Phth}$, H-6, 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: 155.3 (C$_{q,arom}$); 154.8 (*C*O$_{Cbz}$); 138.5, 138.3, 135.6 (C$_{q,arom}$); 133.0, 128.8, 128.6, 128.6, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9 (*C*H$_{arom}$); 118.0 (C$_{q,arom}$); 116.2 (*C*H$_{arom}$); 100.9 (C-1''); 98.5 (C-1'); 96.9 (C-1); 89.5 (C$_{q,alkyne}$); 86.8 (*C*H$_{Phth}$); 85.0 (C-3''); 82.0 (C-3); 80.8 (C-4'); 80.1 (C-4); 80.1 (C$_{q,alkyne}$); 78.1 (C-2''); 77.7, 77.6 (C-4'' and C-5''); 77.0 (C-2'); 75.3, 75.0 (Ph*C*H$_2$); 74.8 (C-3'); 73.0 (C-2); 71.1 (C-6''); 69.9 (Ph*C*H$_2$); 69.6, 69.6 (*C*H$_{Phth}$); 68.7 (C-5); 67.9 (C-5'); 61.0, 59.8, 59.1, 58.3, 57.6, 57.5 (O*C*H$_3$); 42.4, 37.7 (*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$_{2,Phth}$); 18.2, 18.0 (C-6 and C-6'); 14.9, 10.2 (*C*H$_{3,Phth}$). IR (thin film, cm^{-1}): 1000, 1030, 1055, 1075, 1093, 1122, 1139, 1175, 1205, 1235, 1259, 1383, 1455, 1507, 1749, 2854, 2928, 3470. HRMS calculated for $C_{80}H_{118}O_{19}Na$ 1405.8165 [M+Na]$^+$; found 1405.8160.

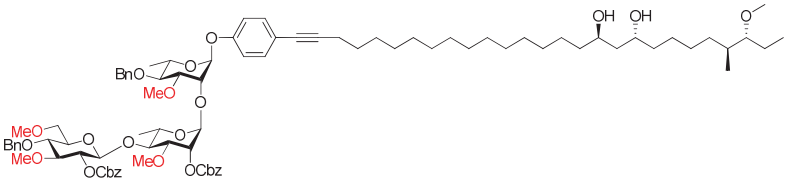
4-((3*R*,4*S*,9*R*,11*R*)-3-methoxy-4-methylheptacos-26-yne-9,11-diol)phenyl 2-*O*-(2,3-di-*O*-methyl-4-*O*-(2-*O*-benzyloxycarbonyl-3,4-di-*O*-benzyl-6-*O*-methyl-ß-D-glucopyranosyl)-α-L-rhamnopyranosyl)-3-*O*-methyl-4-*O*-benzyl-α-L-rhamnopyranoside (45)



The title compound was synthesized according to general procedure C using **27** (62 mg, 55 µmol, 1.0 eq) and phthiocerol (30 mg, 66 µmol, 1.2 eq). Column chromatography (DCM-EtOAc 1:1) yielded the product (66 mg, 45 µmol, 83%) as a yellow oil. [α]$_D^{25}$ = -51.3 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.36-7.21 (m, 22H, C*H*$_{arom}$); 6.96-6.94 (m, 2H, C*H*$_{arom}$); 5.48 (d, 1H, *J* = 1.6 Hz, H-1); 5.24-5.15 (m, 3H, H-1', PhC*H*$_2$); 4.89 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.80-4.76 (m, 4H, H-1'', H-2'', PhC*H*H, PhC*H*H); 4.69-4.62 (m, 3H, PhCH*H*, PhCH*H*, PhCH*H*); 4.24 (d, 1H, *J* = 2.0 Hz, H-2); 3.98-3.89 (m, 2H, C*H*$_{Phth}$); 3.79 (dd, 1H, *J* = 3.0, 9.4 Hz, H-3); 3.76-3.61 (m, 7H, H-2', H-3'', H-4'', H-5, H-5', H-5'', H-6''); 3.58-3.42 (m, 7H, H-6'', OC*H*$_3$); 3.38-3.33 (m, 7H, H-3', OC*H*$_3$); 2.90-2.82 (m, 1H, C*H*$_{Phth}$); 2.38 (t, 1H, *J* = 7.0 Hz, C*H*$_{2,Phth}$); 1.95 (bs, 2H, O*H*$_{Phth}$); 1.72-1.64 (m, 1H, C*H*$_{Phth}$); 1.62-1.25 (m, 47H, C*H*$_{2,Phth}$, H-6, H-6'); 1.15-1.05 (m, 1H, C*H*$_{2,Phth}$); 0.91 (t, 3H, *J* = 7.4 Hz, C*H*$_{3,Phth}$); 0.83 (d, 3H, *J* = 6.8 Hz, $CH_{3,Phth}$). ^{13}C-APT NMR (101 MHz) δ: 155.3 (C$_{q,arom}$); 154.7 (*C*O$_{Cbz}$); 138.5, 138.4, 138.2, 135.5 (C$_{q,arom}$); 133.0, 128.8, 128.6, 128.6, 128.5, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7 (*C*H$_{arom}$); 118.0 (C$_{q,arom}$); 116.2 (*C*H$_{arom}$); 101.1 (C-1''); 98.6 (C-1'); 96.9 (C-1); 89.5 (C$_{q,alkyne}$); 86.8 (*C*H$_{Phth}$); 83.3 (C-4''); 82.0 (C-3); 80.8, 80.1 (C-4 and C-4'); 80.1 (C$_{q,alkyne}$); 78.2 (C-2''); 77.9, 77.8 77.0 (C-2', C-3'', C-5''); 75.4, 75.3, 75.2 (Ph*C*H$_2$); 75.0 (C-3') 73.0 (C-2); 71.1 (C-6''); 69.9 (Ph*C*H$_2$); 69.7, 69.6 (*C*H$_{Phth}$); 68.7 (C-5); 68.0 (C-5'); 59.9, 59.1, 58.3, 57.6, 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$_{2,Phth}$); 18.2, 18.1 (C-6 and C-6'); 14.9, 10.2 (*C*H$_{3,Phth}$). IR (thin film, cm^{-1}): 1002, 1009,

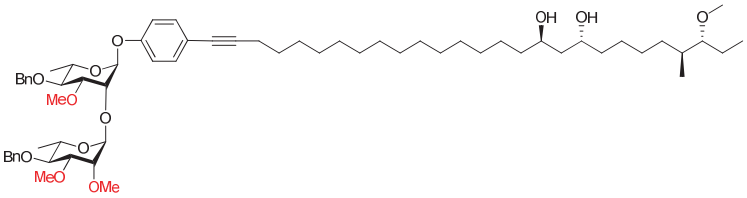
1020, 1027, 1053, 1073, 1093, 1110, 1120, 1136, 1143, 1236, 1263, 1457, 1507, 1734, 2855, 2869, 2927, 2965, 2969. HRMS calculated for $C_{86}H_{122}O_{19}Na$ 1481.8478 [M+Na]$^+$; found 1481.8473.

4-((3*R*,4*S*,9*R*,11*R*)-3-methoxy-4-methylheptacos-26-yne-9,11-diol)phenyl 2-*O*-(2-*O*-benzyloxycarbonyl-3-*O*-methyl-4-*O*-(2-*O*-benzyloxycarbonyl-3,6-di-*O*-methyl-4-*O*-benzyl-ß-D-glucopyranosyl)-α-L-rhamnopyranosyl)-3-*O*-methyl-4-*O*-benzyl-α-L-rhamnopyranoside (46)



The title compound was synthesized according to general procedure C using **25** (59 mg, 50 µmol, 1.0 eq) and phthiocerol (27 mg, 60 µmol, 1.2 eq). Column chromatography (DCM-acetone 4:1) yielded the product (70 mg, 47 µmol, 93%) as a yellow oil. $[\alpha]_D^{25}$ = -174.8 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.41-7.26 (m, 22H, C*H*$_{arom}$); 6.94 (dd, 2H, *J* = 2.0, 8.8 Hz, C*H*$_{arom}$); 5.47 (d, 1H, *J* = 1.6 Hz, H-1); 5.25-5.17 (m, 6H, H-1', H-2', PhC*H*$_2$); 4.92 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.80 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.67-4.61 (m, 4H, H-1'', H-2'', PhCH*H*, PhCH*H*); 4.22 (s, 1H, H-2); 3.96-3.90 (m, 2H, C*H*$_{Phth}$); 3.64-3.47 (m, 15H, H-3, H-3', H-4, H-4', H-4'', H-5, H-5', H-6'', OC*H*$_3$); 3.37-3.33 (m, 8H, H-3'', H-5'', OC*H*$_3$); 3.26 (s, 3H, OC*H*$_3$); 2.90-2.84 (m, 1H, C*H*$_{Phth}$); 2.38 (t, 2H, *J* = 7.2 Hz, C*H*$_{2,Phth}$); 2.05 (bs, 2H, O*H*$_{Phth}$); 1.62-1.05 (m, 60H, H-6, H-6', C*H*$_{2,Phth}$); 0.91 (t, 3H, *J* = 7.4 Hz, C*H*$_{3,Phth}$); 0.83 (d, 3H, *J* = 6.8 Hz, C*H*$_{3,Phth}$). ^{13}C-APT NMR (101 MHz) δ: 155.3 (C$_{q,arom}$); 154.8, 154.8 (*C*O$_{Cbz}$); 138.5, 138.3, 135.5, 135.1 (C$_{q,arom}$); 133.0, 128.8, 128.7, 128.7, 128.6, 128.5, 128.5, 128.2, 128.2, 128.0, 127.8 (*C*H$_{arom}$); 118.0 (C$_{q,arom}$); 116.2 (*C*H$_{arom}$); 101.3 (C-1''); 98.8 (C-1'); 96.7 (C-1); 89.5 (C$_{q,alkyne}$); 86.8 (*C*H$_{Phth}$); 84.9 (C-3''); 81.7 (C-3); 80.1 (C$_{q,alkyne}$); 80.0 (C-3'); 79.3 (C-4); 78.0 (C-4''); 77.9 (C-2''); 77.6 (C-4'); 75.3, 75.0 (Ph*C*H$_2$); 74.8 (C-5''); 72.9 (C-2); 72.1 (C-2'); 71.1 (C-6''); 70.1, 69.9 (Ph*C*H$_2$); 69.6, 69.6 (*C*H$_{Phth}$); 68.8 (C-5'); 67.9 (C-5); 61.0, 59.8, 58.2, 57.8, 57.5 (O*C*H$_3$); 42.4, 37.7 (*C*H$_{2,Phth}$); 34.9 (*C*H$_{Phth}$); 32.8, 29.8, 29.8, 29.7, 29.3, 29.1, 29.0, 27.7, 26.3, 25.9, 22.5, 19.5 (*C*H$_{2,Phth}$); 18.1, 17.9 (C-6 and C-6'); 14.9, 10.2 (*C*H$_{3,Phth}$). IR (thin film, cm^{-1}): 1029, 1037, 1057, 1073, 1093, 1125, 1142, 1262, 1507, 1753, 2855, 2926. HRMS calculated for $C_{87}H_{122}O_{21}Na$ 1525.8376[M+Na]$^+$; found 1525.8374.

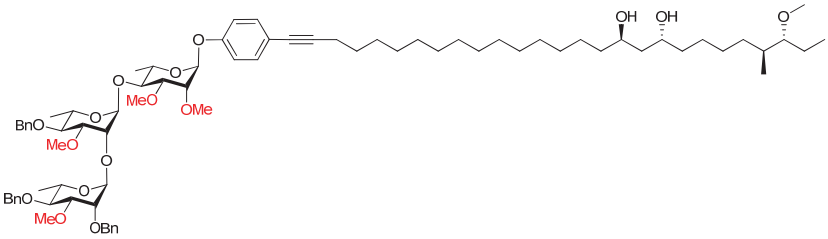
4-((3*R*,4*S*,9*R*,11*R*)-3-methoxy-4-methylheptacos-26-yne-9,11-diol)phenyl 2-*O*-(2,3-di-*O*-methyl-4-*O*-benzyl-α-L-rhamnopyranosyl)-3-*O*-methyl-4-*O*-benzyl-α-L-rhamnopyranoside (47)



The title compound was synthesized according to general procedure C using **43** (29 mg, 39 µmol, 1.0 eq) and phthiocerol (21 mg, 47 µmol, 1.2 eq). Column chromatography (*n*-pentane-Et_2O 1:9) yielded the

product (36 mg, 34 µmol, 86%) as a yellow oil. $[\alpha]_D^{25}$ = -80.1 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.38-7.26 (m, 12H, C*H*$_{arom}$); 6.93-6.90 (m, 2H, C*H*$_{arom}$); 5.44 (d, 1H, *J* = 2.0 Hz, H-1); 5.15 (d, 1H, *J* = 1.6 Hz, H-1'); 4.93-4.87 (m, 2H, PhC*H*H, PhC*H*H); 4.66-4.59 (m, 2H, PhCH*H*, PhCH*H*); 4.20 (dd, 1H, *J* = 2.0, 3.2 Hz, H-2); 3.98-3.89 (m, 2H, C*H*$_{Phth}$); 3.79-3.68 (m, 4H, H-2', H-3, H-5. H-5'); 3.64 (dd, 1H, *J* = 3.2, 9.2 Hz, H-3'); 3.57 (s, 3H, OC*H*$_3$); 3.56 (s, 3H, OC*H*$_3$); 3.55 (s, 3H, OC*H*$_3$); 3.47-3.41 (m, 2H, H-4, H-4'); 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*$_{Phth}$); 1.70-1.22 (m, 49H, H-6, H-6', C*H*$_{Phth}$, C*H*$_{2,Phth}$); 1.15-1.05 (m, 2H, 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: 155.5, 138.7, 138.5 ($C_{q,arom}$); 133.0, 128.5, 128.5, 128.2, 128.1, 127.9, 127.8 (*C*H$_{arom}$); 117.9 ($C_{q,arom}$); 116.1 (*C*H$_{arom}$); 98.9 (C-1'); 96.9 (C-1); 89.5 ($C_{q,alkyne}$); 86.8 (*C*H$_{Phth}$); 81.8 (C-3); 81.2 (C-3'); 80.6 (C-4'); 80.1 ($C_{q,alkyne}$); 80.1 (C-4); 77.6 (C-2'); 75.5, 75.3 (Ph*C*H$_2$); 73.6 (C-2); 69.6, 69.6 (*C*H$_{Phth}$); 68.7 (C-5); 68.5 (C-5'); 59.2, 58.2, 58.1, 57.5 (O*C*H$_3$); 42.4, 37.7 (*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}): 1032, 1036, 1055, 1073, 1095, 1123, 1233, 1454, 1507, 2853, 2927, 3451. HRMS calculated for $C_{64}H_{99}O_{12}$ 1059.71310 $[M+H]^+$; found 1059.71213.

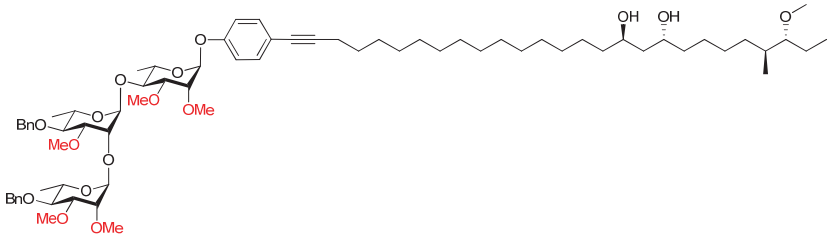
4-((3*R*,4*S*,9*R*,11*R*)-3-methoxy-4-methylheptacos-26-yne-9,11-diol)phenyl 2,3-di-*O*-methyl-4-*O*-(2-*O*-(2,4-di-*O*-benzyl-3-*O*-methyl-α-L-rhamnopyranoside)-3-*O*-methyl-4-*O*-benzyl-α-L-rhamnopyranoside)-α-L-rhamnopyranoside (48)



The title compound was synthesized according to general procedure C using **39** (32 mg, 33 µmol, 1.0 eq) and phthiocerol (18 mg, 39 µmol, 1.2 eq). Column chromatography (*n*-pentane-Et_2O 1:4) yielded the product (40 mg, 31 µmol, 94%) as a yellow oil. $[\alpha]_D^{25}$ = -63.5 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.47-7.44 (m, 2H, C*H*$_{arom}$); 7.38-7.26 (m, 15H, C*H*$_{arom}$); 6.99-6.95 (m, 2H, C*H*$_{arom}$); 5.50 (d, 1H, *J* = 2.0 Hz, H-1); 5.15 (d, 1H, *J* = 2.0 Hz, H-1'); 5.14 (d, 1H, *J* = 2.0 Hz, H-1''); 4.93 (d, 1H, *J* = 11.6 Hz, PhC*H*H); 4.80-4.78 (m, 3H, PhC*H*H, Ph*CH*$_2$); 4.63 (d, 1H, *J* = 11.2 Hz, PhCH*H*); 4.55 (d, 1H, *J* = 11.2 Hz, PhCH*H*); 4.05 (dd, 1H, *J* = 2.0, 2.4 Hz, H-2'); 3.97-3.89 (m, 2H, C*H*$_{Phth}$); 3.88 (dd, 1H, *J* = 2.0, 3.2 Hz, H-2''); 3.80-3.76 (m, 2H, H-2, H-5''); 3.70-3.58 (m, 5H, H-3, H-3', H-4, H-5, H-5'); 3.53-3.42 (m, 14H, H-3'', H-4'', OC*H*$_3$); 3.34 (s, 3H, OC*H*$_3$); 3.28 (t, 1H, *J* = 9.4 Hz, H-4'); 2.88-2.85 (m, 1H, C*H*$_{Phth}$); 2.37 (t, 2H, *J* = 7.0 Hz, C*H*$_{2,Phth}$); 1.73-1.63 (m, 2H, C*H*$_{2,Phth}$); 1.63-1.02 (m, 56H, H-6, H-6', H-6'', C*H*$_{Phth}$, C*H*$_{2,Phth}$); 0.91 (t, 1H, *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: 155.8, 139.1, 138.7, 138.5 ($C_{q,arom}$); 133.0, 128.5, 128.4,, 128.3, 128.2, 127.9, 127.8, 127.8, 127.6 (*C*H$_{arom}$); 118.1 ($C_{q,arom}$); 116.3 (*C*H$_{arom}$); 100.7 (C-1'); 99.2 (C-1''); 95.8 (C-1); 89.6 ($C_{q,alkyne}$); 86.8 (*C*H$_{Phth}$); 82.2 (C-3'); 81.9 (C-3); 81.5 (C-3''); 80.8 (C-4''); 80.1 ($C_{q,alkyne}$); 79.9 (C-4'); 77.8 (C-4); 76.2 (C-2); 75.2 (Ph*C*H$_2$); 74.0 (C-2''); 73.4 (C-2'); 72.6 (Ph*C*H$_2$); 69.6, 69.6 (*C*H$_{Phth}$); 68.6 (C-5''); 68.3 (C-

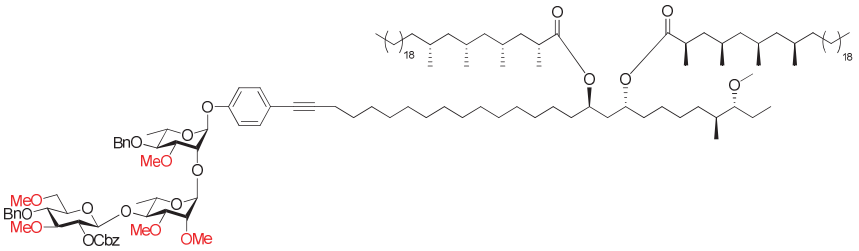
5 and C-5''); 59.7, 57.9, 57.8, 57.5, 57.3 (O*C*H$_3$); 42.4, 37.6 (*C*H$_{2,Phth}$); 34.9 (*C*H$_{Phth}$); 32.8, 29.8, 29.8, 29.7, 29.3, 29.1, 29.0, 27.7, 26.3, 25.9, 22.5, 19.5 (*C*H$_{2,Phth}$); 18.4, 18.3, 17.9 (C-6, C-6' and C-6''); 14.9, 10.2 (*C*H$_{3,Phth}$). IR (thin film, cm^{-1}): 1000, 1020, 1029, 1056, 1073, 1093, 1119, 1136, 1233, 1457, 1484, 1507, 2855, 2868, 2926, 2966, 3451. HRMS calculated for $C_{78}H_{120}O_{16}N$ 1326.86016 $[M+NH_4]^+$; found 1326.85909.

4-((3*R*,4*S*,9*R*,11*R*)-3-methoxy-4-methylheptacos-26-yne-9,11-diol)phenyl 2,3-di-*O*-methyl-4-*O*-(2-*O*-(2,3-di-*O*-methyl-4-*O*-benzyl-α-L-rhamnopyranoside)-3-*O*-methyl-4-*O*-benzyl-α-L-rhamnopyranoside)-α-L-rhamnopyranoside (49)



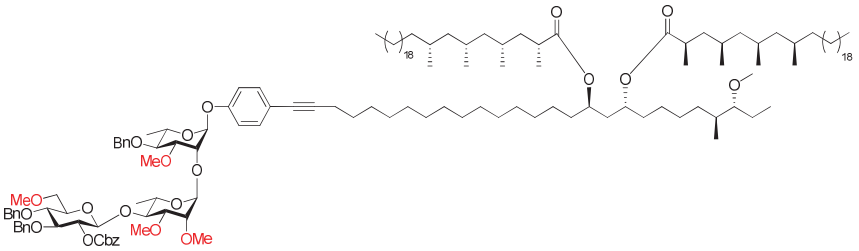
The title compound was synthesized according to general procedure C using **40** (30 mg, 33 µmol, 1.0 eq) and phthiocerol (18 mg, 39 µmol, 1.2 eq). Column chromatography (*n*-pentane-Et$_2$O 1:9) yielded the product (40 mg, 33 µmol, 100%) as a yellow oil. $[\alpha]_D^{25}$ = -72.2 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.37-7.26 (m, 12H, C*H*$_{arom}$); 6.99-6.96 (m, 2H, C*H*$_{arom}$); 5.50 (d, 1H, *J* = 2.0 Hz, H-1); 5.17 (d, 1H, *J* = 1.6 Hz, H-1'); 5.15 (d, 1H, *J* = 1.6 Hz, H-1''); 4.92 (d, 1H, *J* = 11.2 Hz, PhC*H*H); 4.84 (d, 1H, *J* = 10.8 Hz, PhC*H*H); 4.64-4.60 (m, 2H, PhCH*H*, PhCH*H*); 4.09 (dd, 1H, *J* = 2.0, 2.4 Hz, H-2'); 3.98-3.90 (m, 2H, C*H*$_{Phth}$); 3.79-3.61 (m, 8H, H-2, H-2'', H-3, H-3'', H-4, H-5, H-5', H-5''); 3.54-3.49 (m, 16H, H-3', O*CH*$_3$); 3.45-3.32 (m, 5H, H-4', H-4'', O*CH*$_3$); 2.88-2.85 (m, 1H, C*H*$_{Phth}$); 2.38 (t, 2H, *J* = 7.2 Hz, C*H*$_{2,Phth}$); 1.73-1.00 (m, 65H, H-6, H-6', H-6'', C*H*$_{Phth}$, C*H*$_{2,Phth}$); 0.91 (t, 3H, *J* = 7.2 Hz, C*H*$_{3,Phth}$); 0.83 (d, 3H, *J* = 6.8 Hz, C*H*$_{3,Phth}$). ^{13}C-APT NMR (101 MHz) δ: 155.8, 139.0, 138.7 (C$_{q,arom}$); 133.0, 128.5, 128.4, 128.2, 127.9, 127.8, 127.6 (*C*H$_{arom}$); 118.1 (C$_{q,arom}$); 116.3 (*C*H$_{arom}$); 100.7 (C-1'); 98.4 (C-1''); 95.9 (C-1); 89.6 (C$_{q,alkyne}$); 86.8 (*C*H$_{Phth}$); 82.2 (C-3'); 82.0 (C-3); 81.2 (C-3''); 80.7 (C-4''); 80.1 (C$_{q,alkyne}$); 80.0 (C-4'); 77.9 (C-4); 77.8 (C-2''); 76.2 (C-2); 75.3, 75.1 (Ph*C*H$_2$); 73.7 (C-2'); 69.6, 69.6 (*C*H$_{Phth}$); 68.6 (C-5'); 68.3 (C-5 and C-5''); 59.7, 59.2, 58.1, 58.0, 57.5, 57.3 (O*C*H$_3$); 42.4, 37.6 (*C*H$_{2,Phth}$); 34.9 (*C*H$_{Phth}$); 32.8, 29.8, 29.8, 29.7, 29.3, 29.1, 29.0, 27.7, 26.3, 25.9, 22.5, 19.5 (*C*H$_{2,Phth}$); 18.4, 18.1, 18.0 (C-6, C-6' and C-6''); 14.9, 10.2 (*C*H$_{3,Phth}$). IR (thin film, cm^{-1}): 1002, 1029, 1055, 1073, 1093, 1120, 1233, 1454, 1507, 2853, 2928, 3454. HRMS calculated for $C_{72}H_{113}O_{16}$ 1234.80572 $[M+H]^+$; found 1234.80391.

4-((3*R*,4*S*,9*R*,11*R*)-3-methoxy-4-methylheptacos-26-yne-9,11-diyl bismycocerosate)phenyl 2-*O*-(2,3-di-*O*-methyl-4-*O*-(2-*O*-benzyloxycarbonyl-3,6-di-*O*-methyl-4-*O*-benzyl-ß-D-glucopyranosyl)-α-L-rhamnopyranosyl)-3-*O*-methyl-4-*O*-benzyl-α-L-rhamnopyranoside (50)



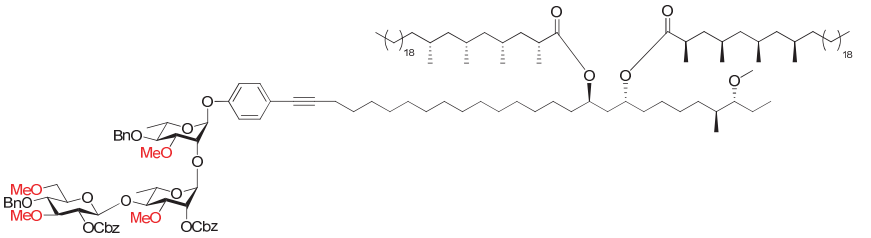
The title compound was synthesized according to general procedure D using **44** (34 mg, 25 µmol, 1.0 eq), mycocerosic acid (35 mg, 74 µmol, 3.0 eq), DIC (23 µL, 147 µmol, 6.0 eq) and DMAP (27 mg, 221 µmol, 9.0 eq). Column chromatography (*n*-pentane-Et_2O 1:1) yielded the product (45 mg, 19 µmol, 79%) as a waxy solid. $[\alpha]_D^{25}$ = -36.3 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.45-7.26 (m, 17H, C*H*$_{arom}$); 6.96-6.93 (m, 2H, C*H*$_{arom}$); 5.47 (d, 1H, *J* = 1.6 Hz, H-1); 5.26 (dd, 2H, *J* = 3.6, 12.2 Hz, PhC*H*$_2$); 5.19 (d, 1H, *J* = 1.2 Hz, H-1'); 4.91-4.78 (m, 4H, PhC*H*H, PhC*H*H, C*H*$_{Phth}$); 4.74 (d, 1H, *J* = 8.0 Hz, H-1''); 4.67-4.62 (m, 3H, PhCH*H*, PhCH*H*, H-2''); 4.24 (dd, 1H, *J* = 2.2, 2.6 Hz, H-2); 3.79 (dd, 1H, *J* = 3.2, 9.2 Hz, H-3); 3.76-3.49 (m, 17H, H-2, H-4', H-4'', H-5, H-5', H-6'', OC*H*$_3$); 3.47-3.39 (m, 2H, H-3', H-4); 3.37-3.31 (m, 11H, H-3'', H-5'', OC*H*$_3$); 2.88-2.84 (m, 1H, C*H*$_{Phth}$); 2.55-2.50 (m, 2H, C*H*$_{Myc}$); 2.37 (t, 2H, *J* = 7.0 Hz, C*H*$_{2,Phth}$); 1.77-0.81 (m, 204H, C*H*$_{Phth}$, C*H*$_{2,Phth}$, C*H*$_{3,Phth}$, C*H*$_{Myc,}$ C*H*$_{2,Myc}$, C*H*$_{3,Myc}$, H-6, H-6'). ^{13}C-APT NMR (101 MHz) δ: 176.1 (*C*O$_{Myc}$); 155.3 (C$_{q,arom}$); 154.8 (*C*O$_{Cbz}$); 138.5, 138.3, 133.0 (C$_{q,arom}$); 128.8, 128.6, 128.6, 128.5, 128.5, 128.3, 128.1, 128.0, 127.9 (*C*H$_{arom}$); 118.0 (C$_{q,arom}$); 116.2 (*C*H$_{arom}$); 100.9 (C-1''); 98.5 (C-1'); 96.9 (C-1); 89.5 (C$_{q,alkyne}$); 86.8 (*C*H$_{Phth}$); 85.0 (C-3''); 82.0 (C-3); 80.8 (C-3'); 80.1 (C$_{q,alkyne}$); 80.1 (C-4); 78.1 (C-2''); 77.7 (C-4'); 77.6 (C-4''); 77.0 (C-2'); 75.3, 75.1 (Ph*C*H$_2$); 74.8 (C-5''); 73.0 (C-2); 71.1 (C-6''); 70.4 (*C*H$_{Phth}$); 69.9 (Ph*C*H$_2$); 68.7 (C-5); 67.9 (C-5'); 61.0, 59.8, 59.1, 58.3, 57.6, 57.5 (O*C*H$_3$); 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, 29.1 (*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 (*C*H$_{3,Myc}$); 19.6 (*C*H$_{2,Phth}$); 18.6 (*C*H$_{3,Myc}$); 18.2 (C-6); 18.0 (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}): 1093, 1173, 1259, 1378, 1457, 1464, 1507, 1734, 1760, 2853, 2923. HRMS calculated for $C_{144}H_{243}O_{21}$ 2309.79755 $[M+H]^+$; found 2309.80566.

4-((3*R*,4*S*,9*R*,11*R*)-3-methoxy-4-methylheptacos-26-yne-9,11-diyl bismycocerosate)phenyl 2-*O*-(2,3-di-*O*-methyl-4-*O*-(2-*O*-benzyloxycarbonyl-3,4-di-*O*-benzyl-6-*O*-methyl-ß-D-glucopyranosyl)-α-L-rhamnopyranosyl)-3-*O*-methyl-4-*O*-benzyl-α-L-rhamnopyranoside (51)



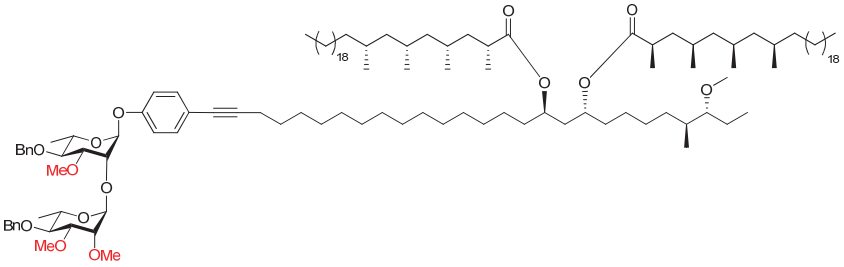
The title compound was synthesized according to general procedure D using **45** (26 mg, 18 µmol, 1.0 eq), mycocerosic acid (25 mg, 53 µmol, 3.0 eq), DIC (16 µL, 105 µmol, 6.0 eq) and DMAP (19 mg, 158 µmol, 9.0 eq). Column chromatography (*n*-pentane-Et_2O 1:1) yielded the product (32 mg, 13.4 µmol, 76%) as a waxy solid. $[\alpha]_D^{25}$ = -32.9 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.37-7.21 (m, 22H, C*H*$_{arom}$); 6.97-6.93 (m, 2H, C*H*$_{arom}$); 5.48 (d, 1H, *J* = 1.6 Hz, H-1); 5.24-5.15 (m, 3H, H-1', PhC*H*$_2$,); 4.91-4.73 (m, 7H, H-1", H-2", C*H*$_{Phth}$, PhC*H*H, PhC*H*H, PhC*H*H); 4.70-4.62 (m, 3H, PhCH*H*, PhCH*H*, PhCH*H*); 4.25 (dd, 1H, *J* = 2.4, 2.8 Hz, H-2); 3.79 (dd, 1H, *J* = 3.0, 9.4 Hz, H-3); 3.76-3.60 (m, 7H, H-2', H-3'', H-4', H-4'', H-5, H-5', H-6''); 3.59-3.51 (m, 7H, H-6", OC*H*$_3$); 3.48-3.41 (m, 2H, H-3', H-4); 3.38-3.31 (m, 10H, H-5", OC*H*$_3$); 2.88-2.83 (m, 1H, C*H*$_{Phth}$); 2.55-2.50 (m, 2H, C*H*$_{Myc}$); 1.77-0.81 (m, 181H, C*H*$_{Phth}$, C*H*$_{2,Phth}$, C*H*$_{3,Phth}$, C*H*$_{Myc,}$ C*H*$_{2,Myc}$, C*H*$_{3,Myc}$, H-6, H-6'). ^{13}C-APT NMR (101 MHz) δ: 176.1, 176.1 (*C*O$_{Myc}$); 155.3 (C$_{q,arom}$); 154.7 (*C*O$_{Cbz}$); 138.5, 138.4, 138.2, 135.5 (C$_{q,arom}$); 133.0, 128.8, 128.6, 128.6, 128.5, 128.5, 128.4, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7 (*C*H$_{arom}$); 118.0 (C$_{q,arom}$); 116.2 (*C*H$_{arom}$); 101.1 (C-1''); 98.5 (C-1'); 96.9 (C-1); 89.5 (C$_{q,alkyne}$); 86.8 (*C*H$_{Phth}$); 83.3 (C-3"); 82.0 (C-3); 80.8 (C-3'); 80.1 (C$_{q,alkyne}$); 80.1 (C-4); 78.2 (C-2"); 77.9 (C-4'); 77.7 (C-4''); 77.0 (C-2'); 75.4, 75.3, 75.2 (Ph*C*H$_2$); 75.0 (C-5''); 73.0 (C-2); 71.1 (C-6''); 70.4 (*C*H$_{Phth}$); 69.9 (Ph*C*H$_2$); 68.7 (C-5); 68.0 (C-5'); 59.9, 59.1, 58.3, 57.6, 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$_{Myc}$); 36.7 (*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, 29.7, 29.5, 29.4, 29.2, 29.1 (*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$_{3,Myc}$); 18.2 (C-6); 18.0 (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}): 1073, 1095, 1140, 1259, 1379, 1457, 1464, 1507, 1734, 1756, 1763, 2853, 2923. HRMS calculated for $C_{150}H_{247}O_{21}$ 2385.82885 [M+H]$^+$; found 2385.83921.

4-((3*R*,4*S*,9*R*,11*R*)-3-methoxy-4-methylheptacos-26-yne-9,11-diyl bismycocerosate)phenyl 2-*O*-(2-*O*-benzyloxycarbonyl-3-*O*-methyl-4-*O*-(2-*O*-benzyloxycarbonyl-3,6-di-*O*-methyl-4-*O*-benzyl-ß-D-glucopyranosyl)-α-L-rhamnopyranosyl)-3-*O*-methyl-4-*O*-benzyl-α-L-rhamnopyranoside (52)



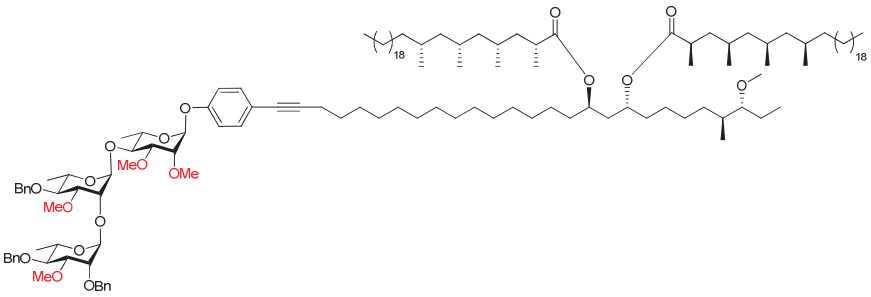
The title compound was synthesized according to general procedure D using **46** (37 mg, 25 µmol, 1.0 eq), mycocerosic acid (35 mg, 74 µmol, 3.0 eq), DIC (23 µL, 148 µmol, 6.0 eq) and DMAP (27 mg, 221 µmol, 9.0 eq). Column chromatography (*n*-pentane-Et_2O 4:1) yielded the product (48 mg, 20 µmol, 80%) as a waxy solid. $[\alpha]_D^{25}$ = -35.1 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.42-7.26 (m, 22H, C*H*$_{arom}$); 6.95-6.92 (m, 2H, C*H*$_{arom}$); 5.47 (d, 1H, *J* = 2.0 Hz, H-1); 5.28-5.14 (m, 6H, H-1', H-2', PhC*H*$_2$, PhC*H*$_2$); 4.93-4.78 (m, 4H, PhC*H*H, PhC*H*H, C*H*$_{Phth}$); 4.69-4.61 (m, 4H, H-1", H-2", PhCH*H*, PhCH*H*); 4.22 (dd, 1H, *J* = 2.0, 3.2 Hz, H-2); 3.78 (dd, 1H, *J* = 3.2, 9.2 Hz, H-3); 3.75-3.61 (m, 3H, H-5, H-5', H-6"); 3.59-3.45 (m, 11H, H-3', H-4, H-4', H-4'', H-6", OC*H*$_3$); 3.39-3.33 (m, 8H, H-3", H-5", OC*H*$_3$); 3.26 (s, 3H, OC*H*$_3$); 2.87-2.84 (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, 205H, H-6, H-6', C*H*$_{Phth}$, C*H*$_{2,Phth}$, C*H*$_{3,Phth}$, C*H*$_{Myc,}$ C*H*$_{2,Myc}$, C*H*$_{3,Myc}$). ^{13}C-APT NMR (101 MHz) δ: 176.2, 176.1 (*C*O$_{Myc}$); 155.3 (C$_{q,arom}$); 154.8 (*C*O$_{Cbz}$); 138.6, 138.3, 135.5, 135.1 (C$_{q,arom}$); 133.0, 128.8, 128.8, 128.7, 128.7, 128.6, 128.6, 128.5, 128.5, 128.2, 128.2, 128.0, 127.9 (*C*H$_{arom}$); 118.0 (C$_{q,arom}$); 116.2 (*C*H$_{arom}$); 101.3 (C-1"); 98.8 (C-1'); 96.7 (C-1); 89.5 (C$_{q,alkyne}$); 86.8 (*C*H$_{Phth}$); 84.9 (C-3"); 81.7 (C-3); 80.1 (C$_{q,alkyne}$); 80.0 (C-4); 79.3 (C-3'); 78.0 (C-4'); 78.0 (C-4"); 77.6 (C-2"); 75.4, 75.0 (Ph*C*H$_2$); 74.8 (C-5"); 72.9 (C-2); 72.1 (C-2'); 71.1 (C-6"); 70.4 (*C*H$_{Phth}$); 70.1, 69.9 (Ph*C*H$_2$); 68.8 (C-5); 67.9 (C-5'); 61.0, 59.8, 58.2, 57.8, 57.5 (O*C*H$_3$); 45.6, 45.4 (*C*H$_{2,Myc}$); 41.1, 38.6 (*C*H$_{2,Phth}$); 37.9 (*C*H$_{Myc}$); 36.8 (*C*H$_{2,Myc}$); 34.9 (*C*H$_{Phth}$); 34.8, 32.8 (*C*H$_{2,Phth}$); 32.1 (*C*H$_{2,Myc}$); 30.2 (*C*H$_{2,Phth}$); 30.1 (*C*H$_{Myc}$); 29.9, 29.9, 29.8, 29.5, 29.4, 29.2, 29.1 (*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 (*C*H$_{3,Myc}$); 19.6 (*C*H$_{2,Phth}$); 18.6 (*C*H$_{3,Myc}$); 18.1 (C-6); 17.9 (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}): 1095, 1176, 1259, 1379, 1457, 1507, 1736, 1756, 2853, 2923. HRMS calculated for $C_{151}H_{247}O_{23}$ 2429.81868 [M+H]$^+$; found 2429.82801.

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



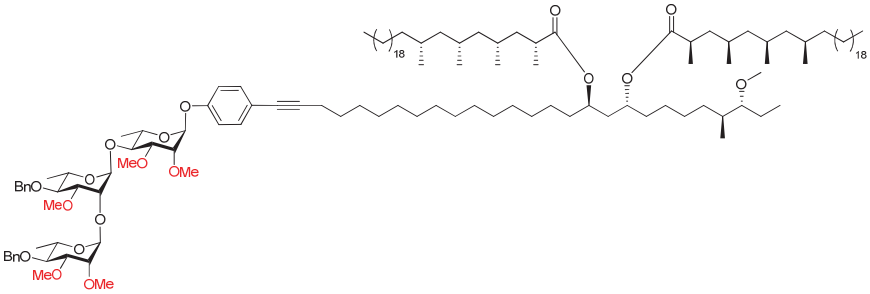
The title compound was synthesized according to general procedure D using **47** (29 mg, 27 µmol, 1.0 eq), mycocerosic acid (39 mg, 82 µmol, 3.0 eq), DIC (25 µL, 164 µmol, 6.0 eq) and DMAP (32 mg, 264 µmol, 9.0 eq). Column chromatography (*n*-pentane-Et_2O 3:2) yielded the product (44 mg, 22 µmol, 81%) as a waxy solid. $[\alpha]_D^{25}$ = -53.2 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.38-7.26 (m, 12H, C*H*$_{arom}$); 6.91 (d, 2H, *J* = 8.8 Hz, CH$_{arom}$); 5.44 (d, 1H, *J* = 1.6 Hz, H-1); 5.15 (d, 1H, *J* = 1.6 Hz, H-1'); 4.93-4.83 (m, 4H, PhC*H*H, PhC*H*H, C*H*$_{Phth}$); 4.66-4.59 (m, 2H, PhCH*H*, PhCH*H*); 4.20 (dd, 1H, *J* = 1.6, 3.2 Hz, H-2); 3.79-3.68 (m, 4H, H-2', H-3, H-5. H-5'); 3.64 (dd, 1H, *J* = 3.2, 9.2 Hz, H-3'); 3.57 (s, 3H, OC*H*$_3$); 3.56 (s, 3H, OC*H*$_3$); 3.55 (s, 3H, OC*H*$_3$); 3.47-3.39 (m, 2H, H-4, H-4'); 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, 229H, 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$_{Myc}$); 155.5, 138.7, 138.6 (C$_{q,arom}$); 133.0, 128.5, 128.5, 128.2, 128.1, 127.9, 127.8 (*C*H$_{arom}$); 117.9 (C$_{q,arom}$); 116.1 (*C*H$_{arom}$); 98.9 (C-1'); 96.9 (C-1); 89.5 (C$_{q,alkyne}$); 86.8 (*C*H$_{Phth}$); 81.8 (C-3); 81.2 (C-3'); 80.6 (C-4'); 80.1 (C$_{q,alkyne}$); 80.1 (C-4); 77.6 (C-2'); 75.5, 75.3 (Ph*C*H$_2$); 73.6 (C-2); 70.4 (*C*H$_{Phth}$); 68.7 (C-5); 68.5 (C-5'); 59.2, 58.2, 58.1, 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, 29.7, 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, 20.5, 20.5 (*C*H$_{3,Myc}$); 19.5 (*C*H$_{2,Phth}$); 18.6 (*C*H$_{3,Myc}$); 18.1 (C-6); 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}): 1053, 1096, 1123, 1132, 1176, 1233, 1379, 1457, 1465, 1507, 1734, 2853, 2923. HRMS calculated for $C_{128}H_{223}O_{14}$ 1985.68006 $[M+H]^+$; found 1985.68007.

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



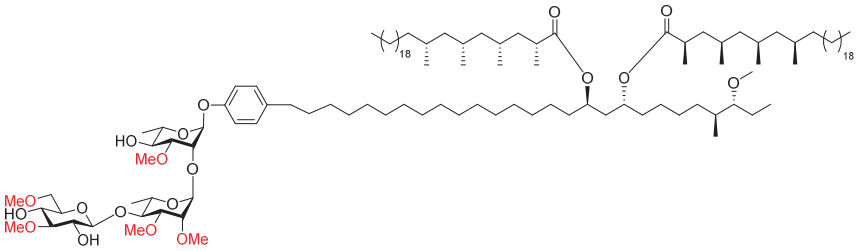
The title compound was synthesized according to general procedure D using **48** (32 mg, 24 µmol, 1.0 eq), mycocerosic acid (35 mg, 73 µmol, 3.0 eq), DIC (23 µL, 147 µmol, 6.0 eq) and DMAP (27 mg, 220 µmol, 9.0 eq). Column chromatography (*n*-pentane-Et_2O 7:3) yielded the product (43 mg, 19 µmol, 79%) as a waxy solid. $[\alpha]_D^{25}$ = -37.3 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.47-7.44 (m, 2H, C*H*$_{arom}$); 7.37-7.26 (m, 15H, C*H*$_{arom}$); 6.99-6.95 (m, 2H, C*H*$_{arom}$); 5.50 (d, 1H, *J* = 1.6 Hz, H-1); 5.15 (d, 1H, *J* = 2.0 Hz, H-1'); 5.14 (d, 1H, *J* = 1.6 Hz, H-1''); 4.93 (d, 1H, *J* = 11.2 Hz, PhC*H*H); 4.88-4.78 (m, 5H, PhC*H*H, PhC*H*$_2$, C*H*$_{Phth}$); 4.63 (d, 1H, *J* = 11.2 Hz, PhCH*H*); 4.55 (d, 1H, *J* = 11.2 Hz, PhCH*H*); 4.05 (dd, 1H, *J* = 2.0, 2.4 Hz, H-2'); 3.88 (dd, 1H, *J* = 1.8, 3.0 Hz, H-2''); 3.81-3.73 (m, 2H, H-2, H-5''); 3.71-3.57 (m, 5H, H-3, H-3', H-4, H-5, H-5'); 3.53-3.42 (m, 14H, H-3'', H-4'', OC*H*$_3$); 3.33 (s, 3H, OC*H*$_3$); 3.28 (t, 1H, *J* = 9.4 Hz, H-4'); 2.88-2.85 (m, 1H, C*H*$_{Phth}$); 2.57-2.48 (m, 2H, C*H*$_{Myc}$); 2.37 (t, 2H, *J* = 7.2 Hz, C*H*$_{2,Phth}$); 1.77-0.93 (m, 180H, 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*$_{3,Myc}$); 0.91-0.81 (m, 41H, C*H*$_{3,Phth}$, C*H*$_{Myc,}$ C*H*$_{3,Myc}$). ^{13}C-APT NMR (101 MHz) δ: 171.1, 171.1 (*C*O$_{Myc}$); 155.8, 139.1, 138.7, 138.5 (C$_{q,arom}$); 133.0, 128.5, 128.4, 128.3, 128.2, 127.9, 127.8, 127.8, 127.6 (*C*H$_{arom}$); 118.1 (C$_{q,arom}$); 116.3 (*C*H$_{arom}$); 100.7 (C-1'); 99.2 (C-1''); 95.9 (C-1); 89.6 (C$_{q,alkyne}$); 86.8 (*C*H$_{Phth}$); 82.2 (C-3'); 82.0 (C-3); 81.5 (C-3''); 80.8 (C-4''); 80.1 (C$_{q,alkyne}$); 80.0 (C-4'); 77.8 (C-4); 76.3 (C-2); 75.1 (Ph*C*H$_2$); 74.0 (C-2''); 73.4 (C-2'); 72.6 (Ph*C*H$_2$); 70.4 (*C*H$_{Phth}$); 68.6 (C-5''); 68.3 (C-5 and C-5''); 59.7, 57.9, 57.8, 57.5, 57.3 (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$_{3,Myc}$); 18.4, 18.3, 17.9 (C-6, C-6', and 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}): 1055, 1069, 1095, 1120, 1139, 1176, 1259, 1378, 1457, 1464, 1507, 1734, 2853, 2951. HRMS calculated for $C_{142}H_{241}O_{18}$ 2234.79375 $[M+H]^+$; found 2234.79804.

4-((3*R*,4*S*,9*R*,11*R*)-3-methoxy-4-methylheptacos-26-yne-9,11-diyl bismycocerosate)phenyl 2,3-di-*O*-methyl-4-*O*-(2-*O*-(2,3-di-*O*-methyl-4-*O*-benzyl-α-L-rhamnopyranoside)-3-*O*-methyl-4-*O*-benzyl-α-L-rhamnopyranoside)-α-L-rhamnopyranoside (55)



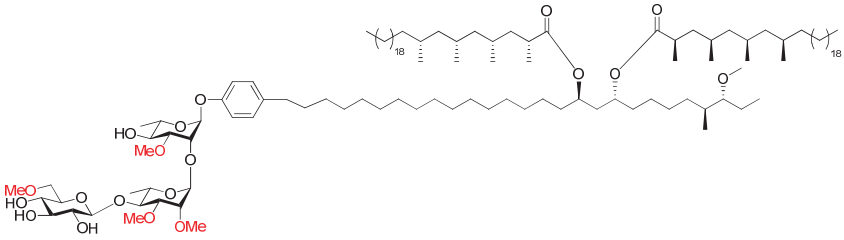
The title compound was synthesized according to general procedure D using **49** (27 mg, 22 µmol, 1.0 eq), mycocerosic acid (32 mg, 66 µmol, 3.0 eq), DIC (20 µL, 131 µmol, 6.0 eq) and DMAP (24 mg, 197 µmol, 9.0 eq). Column chromatography (*n*-pentane-Et_2O 1:1) yielded the product (38 mg, 18 µmol, 80%) as a waxy solid. $[\alpha]_D^{25}$ = -45.1 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.37-7.25 (m, 12H, C*H*$_{arom}$); 6.99-6.96 (m, 2H, C*H*$_{arom}$); 5.50 (d, 1H, *J* = 2.0 Hz, H-1); 5.18 (d, 1H, *J* = 1.6 Hz, H-1'); 5.15 (d, 1H, *J* = 1.6 Hz, H-1''); 4.92 (d, 1H, *J* = 11.2 Hz, PhC*H*H); 4.88-4.81 (m, 3H, PhC*H*H, C*H*$_{Phth}$); 4.64-4.60 (m, 2H, PhCH*H*, PhCH*H*); 4.09 (dd, 1H, *J* = 2.0 2.4 Hz, H-2'); 3.79-3.60 (m, 8H, H-2, H-2", H-3, H-3", H-4, H-5, H-5', H-5"); 3.54-3.49 (m, 16H, H-3', O*CH*$_3$); 3.45-3.33 (m, 5H, H-4', H-4", O*CH*$_3$); 2.88-2.85 (m, 1H, C*H*$_{Phth}$); 2.57-2.48 (m, 2H, C*H*$_{Myc}$); 2.37 (t, 2H, *J* = 7.0 Hz, C*H*$_{2,Phth}$); 1.77-0.93 (m, 184H, 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*$_{3,Myc}$); 0.91-0.81 (m, 43H, C*H*$_{3,Phth}$, C*H*$_{Myc,}$ C*H*$_{3,Myc}$). ^{13}C-APT NMR (101 MHz) δ: 176.1, 176.1 (*C*O$_{Myc}$); 155.8, 139.0, 138.7 (C$_{q,arom}$); 133.0, 128.5, 128.4, 128.3, 128.2, 127.9, 127.8, 127.6 (*C*H$_{arom}$); 118.1 (C$_{q,arom}$); 116.3 (*C*H$_{arom}$); 100.7 (C-1'); 98.5 (C-1"); 95.9 (C-1); 89.6 (C$_{q,alkyne}$); 86.8 (*C*H$_{Phth}$); 82.2 (C-3'); 82.0 (C-3); 81.2 (C-3"); 80.7 (C-4"); 80.1 (C$_{q,alkyne}$); 80.0 (C-4'); 77.9 (C-4); 77.8 (C-2"); 76.2 (C-2); 75.3, 75.1 (Ph*C*H$_2$); 73.8 (C-2'); 70.4 (*C*H$_{Phth}$); 68.7 (C-5"); 68.3 (C-5 and C-5"); 59.7, 59.2, 58.1, 58.0, 57.5, 57.3 (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, 29.7, 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, 20.5, 20.5 (*C*H$_{3,Myc}$); 19.6 (*C*H$_{2,Phth}$); 18.6 (*C*H$_{3,Myc}$); 18.4, 18.1, 18.0 (C-6, C-6', and 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}): 1006, 1030, 1056, 1096, 1120, 1175, 1235, 1258, 1378, 1457, 1462, 1507, 1734, 2853, 2923. HRMS calculated for $C_{136}H_{237}O_{18}$ 2159.76586 $[M+H]^+$; found 2159.76870.

4-((3*R*,4*S*,9*R*,11*R*)-3-methoxy-4-methylheptacos-26-yne-9,11-diyl bismycocerosate)phenyl 2-*O*-(2,3-di-*O*-methyl-4-*O*-(3,6-di-*O*-methyl-ß-D-glucopyranosyl)-α-L-rhamnopyranosyl)-3-*O*-methyl-α-L-rhamnopyranoside (56)



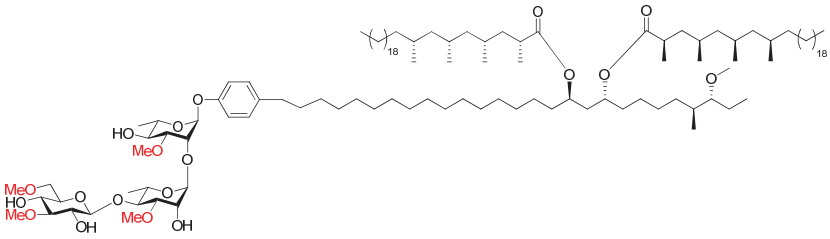
The title compound was synthesized according to general procedure E using **50** (32 mg, 14 µmol, 1.0 eq) and Pd/C (10%, 15 mg, 14 µmol, 1.0 eq). Column chromatography (DCM-acetone 3:2) yielded the product (22 mg, 11 µmol, 79%) as a waxy solid. $[\alpha]_D^{25}$ = -25.2 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (850 MHz) δ: 7.10 (d, 2H, *J* = 9.4 hz, C*H*$_{arom}$); 6.94 (d, 2H, *J* = 8.5 Hz, C*H*$_{arom}$); 5.43 (d, 1H, *J* = 1.7 Hz, H-1); 5.10 (d, 1H, *J* = 1.7 Hz, H-1'); 4.84 (quint, 2H, *J* = 6.4 Hz, C*H*$_{Phth}$); 4.41 (d, 1H, *J* = 7.7 Hz, H-1"); 4.22 (dd, 1H, *J* = 1.7, 3.4 Hz, H-2); 3.89 (s, 1H, 2"-O*H*); 3.77-3.74 (m, 3H, H-2', H-5, H-5'); 3.69-3.66 (m, 4H, H-3', OC*H*$_3$); 3.65-3.61 (m, 4H, H-3, H-4', H-6"); 3.58 (dt, 1H, *J* = 1.7, 9.4 Hz, H-4); 3.55-3.52 (m, 4H, H-4", OC*H*$_3$); 3.50 (s, 3H, OC*H*$_3$); 3.48 (s, 3H, OC*H*$_3$); 3.17 (t, 1H, *J* = 9.4 Hz, H-3");); 2.87-2.84 (m, 1H, C*H*$_{Phth}$); 2.80 (bs, 1H, 4"-O*H*); 2.56-2.51(m, 4H, C*H*$_{2,Phth}$, C*H*$_{Myc}$); 2.30 (bs, 1H, 4-O*H*); 1.77-0.81 (m, 190H, 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 (214 MHz) δ: 176.2, 176.1 (*C*O$_{Myc}$); 154.3, 137.0 (C$_{q,arom}$); 129.5, 116.1 (*C*H$_{arom}$); 105.6 (C-1"); 98.5 (C-1'); 97.4 (C-1); 86.8 (*C*H$_{Phth}$); 85.6 (C-3"); 81.8 (C-4'); 81.5 (C-3); 80.3 (C-3'); 75.6 (C-2'); 75.1 (C-2"); 74.1 (C-5"); 73.0 (C-6"); 72.2 (C-2); 71.9 (C-4); 71.4 (C-4"); 70.4, 70.4 (*C*H$_{Phth}$); 69.1 (C-5); 68.4 (C-5'); 60.7, 59.7, 59.2, 57.8, 57.5, 56.7 (O*C*H$_3$); 45.6, 45.6, 45.4 45.4 (*C*H$_{2,Myc}$); 41.1, 41.1, 38.5 (*C*H$_{2,Phth}$); 37.9, 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$_{2,Phth}$); 30.0 (*C*H$_{Myc}$); 29.9, 29.9, 29.9, 29.9, 29.8, 29.8, 29.7, 29.7, 29.6, 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$_{2,Phth}$); 20.9, 20.6, 20.5, 20.5, 18.6, 18.6 (*C*H$_{3,Myc}$); 17.9 (C-6); 17.7 (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}): 1010, 1070, 1123, 1175, 1229, 1261, 1378, 1457, 1464, 1511, 1734, 2853, 2922, 3434. HRMS calculated for $C_{122}H_{229}O_{19}$ 1998.69476 $[M+H]^+$; found 1998.69683.

4-((3*R*,4*S*,9*R*,11*R*)-3-methoxy-4-methylheptacos-26-yne-9,11-diyl bismycocerosate)phenyl 2-*O*-(2,3-di-*O*-methyl-4-*O*-(6-*O*-methyl-ß-D-glucopyranosyl)-α-L-rhamnopyranosyl)-3-*O*-methyl-α-L-rhamnopyranoside (57)



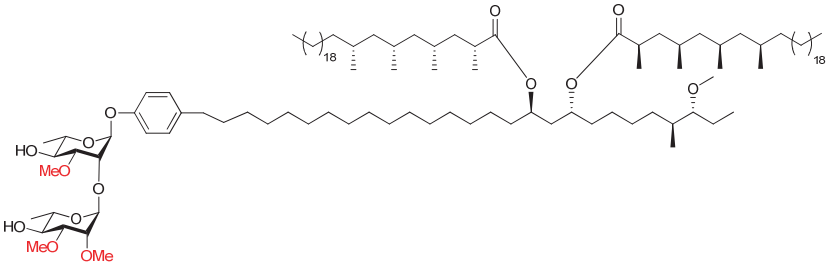
The title compound was synthesized according to general procedure E using **51** (24 mg, 10 µmol, 1.0 eq) and Pd/C (10%, 11 mg, 10 µmol, 1.0 eq). Column chromatography (DCM-MeOH 19:1) yielded the product (8 mg, 4 µmol, 40%) as a waxy solid. $[\alpha]_D^{25}$ = -28 ° (c = 0.2, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.10 (d, 2H, *J* = 8.8 Hz, C*H*$_{arom}$); 6.94 (d, 2H, *J* = 8.8 Hz, C*H*$_{arom}$); 5.43 (d, 1H, *J* = 2.0 Hz, H-1); 5.11 (d, 1H, *J* = 1.6 Hz, H-1'); 4.84 (quint, 2H, *J* = 6.4 Hz, C*H*$_{Phth}$); 4.45 (d, 1H, *J* = 7.6 Hz, H-1"); 4.23 (dd, 1H, *J* = 1.6, 2.8 Hz, H-2); 3.99 (bs, 1H, O*H*); 3.79-3.71 (m, 3H, H-2', H-5, H-5'); 3.69-3.60 (m, 5H, H-3, H-3', H-4', H-6"); 3.58-3.54 (m, 6H, H-3", H-4, H-5", OC*H*$_3$); 3.50 (s, 3H, OC*H*$_3$); 3.49 (s, 3H, OC*H*$_3$); 3.46-3.42 (m, 1H, H-4"); 3.39-3.36 (m, 4H, H-2", OC*H*$_3$); 3.35 (s, 3H, OC*H*$_3$); 2.98 (bs, 1H, O*H*); 2.88-2.79 (m, 2H, C*H*$_{Phth}$, O*H*); 2.57-2.50 (m, 4H, C*H*$_{2,Phth}$, C*H*$_{Myc}$); 2.32 (bs, 1H, O*H*); 1.77-0.81 (m, 207H, H-6, H-6', C*H*$_{Phth}$, C*H*$_{2,Phth}$, C*H*$_{3,Phth}$, C*H*$_{Myc,}$ C*H*$_{2,Myc}$, C*H*$_{3,Myc}$,). ^{13}C-APT NMR (101 MHz) δ: 176.2 (*C*O$_{Myc}$); 154.3, 137.0 (C$_{q,arom}$); 129.5, 116.1 (*C*H$_{arom}$); 105.3 (C-1"); 98.5 (C-1'); 97.5 (C-1); 86.8 (*C*H$_{Phth}$); 81.5 (C-3); 81.5 (C-4'); 80.3 (C-3'); 76.7 (C-3"); 75.9 (C-2'); 74.8 (C-2"); 74.0 (C-4"); 73.1 (C-6"); 72.3 (C-2); 72.0 (C-4); 71.9 (C-5"); 70.4 (*C*H$_{Phth}$); 69.1 (C-5); 68.3 (C-5'); 59.8, 59.1, 57.8, 57.5, 56.7 (O*C*H$_3$); 45.6, 45.4 (*C*H$_{2,Myc}$); 41.1, 38.6 (*C*H$_{2,Phth}$); 37.9 (*C*H$_{Myc}$); 36.8, 35.3 (*C*H$_{2,Myc}$); 34.9 (*C*H$_{Phth}$); 34.8, 32.8 (*C*H$_{2,Phth}$); 32.1 (*C*H$_{2,Myc}$); 31.9, 30.2 (*C*H$_{2,Phth}$); 30.1 (*C*H$_{Myc}$); 29.9, 29.9, 29.8, 29.7, 29.6, 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, 20.6 18.6, 18.5 (*C*H$_{3,Myc}$); 17.9 (C-6); 17.7 (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}): 1016, 1069, 1123, 1229, 1261, 1378, 1457, 1511, 1736, 2853, 2923, 3436. HRMS calculated for $C_{121}H_{227}O_{19}$ 1985.68253 $[M+H]^+$; found 1985.68265.

4-((3*R*,4*S*,9*R*,11*R*)-3-methoxy-4-methylheptacos-26-yne-9,11-diyl bismycocerosate)phenyl 2-*O*-(3-*O*-methyl-4-*O*-(3,6-di-*O*-methyl-4-*O*-benzyl-ß-D-glucopyranosyl)-α-L-rhamnopyranosyl)-3-*O*-methyl-α-L-rhamnopyranoside (58)



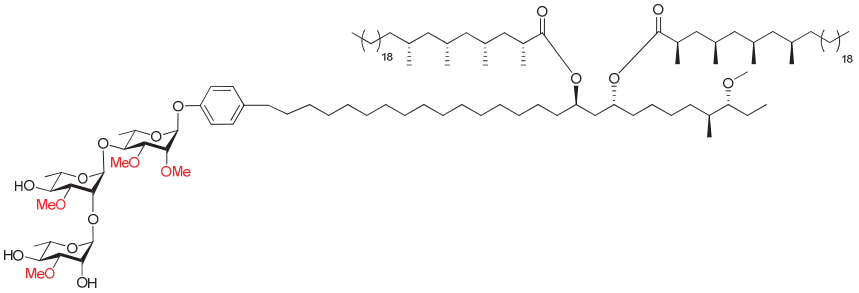
The title compound was synthesized according to general procedure E using **52** (37 mg, 15 µmol, 1.0 eq) and Pd/C (10%, 16 mg, 15 µmol, 1.0 eq). Column chromatography (DCM-MeOH 11:1) yielded the product (23 mg, 12 µmol, 76%) as a waxy solid. $[\alpha]_D^{25}$ = -24.4 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (850 MHz) δ: 7.10 (d, 2H, *J* = 8.5 Hz, C*H*$_{arom}$); 6.95-6.94 (m, 2H, C*H*$_{arom}$); 5.46 (d, 1H, *J* = 1.7 Hz, H-1); 5.08 (d, 1H, *J* = 1.7 Hz, H-1'); 4.84 (quint, 2H, *J* = 6.4 Hz, C*H*$_{Phth}$); 4.39 (d, 1H, *J* = 7.7 Hz, H-1"); 4.22 (dd, 1H, *J* = 2.4, 2.8 Hz, H-2); 4.20 (s, 1H, H-2'); 3.82 (dq, 1H, *J* = 3.4, 6.0 Hz, H-5'); 3.76 (dq, 1H, *J* = 3.4, 6.0 Hz, H-5); 3.71 (s, 1H, 2"-O*H*); 3.69 (s, 3H, OC*H*$_3$); 3.66-3.63 (m, 4H, H-3, H-3', H-6"); 3.61-3.57 (m, 2H, H-4, H-4'); 3.55 (dt, 1H, *J* = 2.0, 8.9 Hz, H-4"); 3.51 (s, 3H, OC*H*$_3$); 3.51 (s, 3H, OC*H*$_3$); 3.45-3.39 (m, 2H, H-2", H-5"); 3.18 (t, 1H, *J* = 8.9 Hz, H-3"); 2.87-2.85 (m, 2H, C*H*$_{Phth}$, 4"-O*H*); 2.55-2.53 (m, 4H, C*H*$_{2,Phth}$, C*H*$_{Myc}$); 2.34 (bs, 2H, 4-O*H*, 2'-O*H*); 1.77-0.81 (m, 189H, 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 (214 MHz) δ: 176.2, 176.1 (*C*O$_{Myc}$); 154.3, 137.0 (C$_{q,arom}$); 129.5, 116.1 (*C*H$_{arom}$); 105.7 (C-1"); 100.6 (C-1'); 97.4 (C-1); 86.8 (*C*H$_{Phth}$); 85.4 (C-3"); 81.2 (C-3); 81.1 (C-4'); 80.6 (C-3'); 75.2 (C-2"); 74.3 (C-5"); 73.0 (C-6"); 72.5 (C-2); 71.8 (C-4); 71.4 (C-4"); 70.4, 70.4 (*C*H$_{Phth}$); 69.0 (C-5); 67.9 (C-5'); 66.9 (C-2'); 60.8, 59.8, 57.7, 57.5, 56.9 (O*C*H$_3$); 45.6, 45.6, 45.4 45.4 (*C*H$_{2,Myc}$); 41.1, 41.1, 38.5 (*C*H$_{2,Phth}$); 37.9, 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$_{2,Phth}$); 30.0 (*C*H$_{Myc}$); 29.9, 29.9, 29.9, 29.9, 29.9, 29.9, 29.8, 29.8, 29.7, 29.7, 29.7, 29.6, 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$_{2,Phth}$); 20.9, 20.6, 20.5, 20.5, 18.6 (*C*H$_{3,Myc}$); 17.9 (C-6); 17.6 (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}): 1016, 1066, 1132, 1232, 1261, 1378, 1457, 1511, 1736, 2853, 2923, 3451. HRMS calculated for $C_{121}H_{227}O_{19}$ 1985.68253 $[M+H]^+$; found 1985.68284.

4-((3*R*,4*S*,9*R*,11*R*)-3-methoxy-4-methylheptacos-26-yne-9,11-diyl bismycocerosate)phenyl 2-*O*-(2,3-di-*O*-methyl-α-L-rhamnopyranosyl)-3-*O*-methyl-α-L-rhamnopyranoside (59)



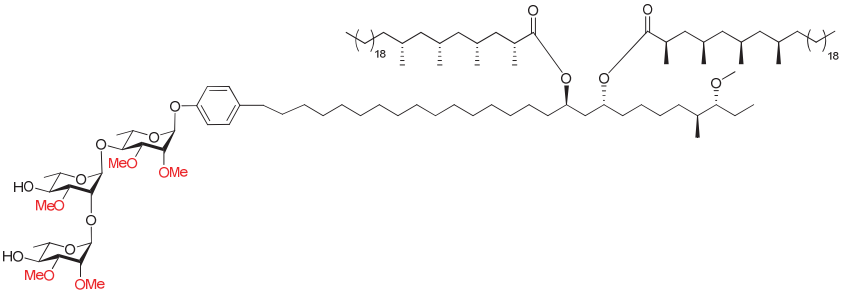
The title compound was synthesized according to general procedure E using **53** (28 mg, 14 µmol, 1.0 eq) and Pd/C (10%, 15 mg, 14 µmol, 1.0 eq). Column chromatography (DCM-MeOH 19:1) yielded the product (22 mg, 12 µmol, 86%) as a waxy solid. $[\alpha]_D^{25}$ = -21.7 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.10 (d, 2H, *J* = 8.4 Hz, C*H*$_{arom}$); 6.96 (dd, 2H, *J* = 2.0, 6.8 Hz, C*H*$_{arom}$); 5.48 (d, 1H, *J* = 1.6 Hz, H-1); 5.14 (d, 1H, *J* = 1.6 Hz, H-1'); 4.84 (quint, 2H, *J* = 6.4 Hz, C*H*$_{Phth}$); 4.26 (dd, 1H, *J* = 1.6, 2.8 Hz, H-2); 3.78-3.71 (m, 3H, H-2', H-5, H-5'); 3.67-3.54 (m, 6H, H-3, H-4, H-4', OC*H*$_3$); 3.51 (s, 3H, OC*H*$_3$); 3.49 (s, 3H, OC*H*$_3$); 3.46 (dd, 1H, *J* = 3.0, 9.4 Hz, H-3'); 3.33 (s, 3H, OC*H*$_3$); 2.87-2.85 (m, 1H, C*H*$_{Phth}$); 2.57-2.52 (m, 4H, C*H*$_{2,Phth}$, C*H*$_{Myc}$); 2.37 (d, 1H, *J* = 1.2 Hz, 4-O*H*); 2.32 (s, 1H, 4'-O*H*); 1.77-0.81 (m, 191H, H-6, H-6', C*H*$_{Phth}$, C*H*$_{2,Phth}$, C*H*$_{3,Phth}$, C*H*$_{Myc,}$ C*H*$_{2,Myc}$, C*H*$_{3,Myc}$). ^{13}C-APT NMR (101 MHz) δ: 176.1 (*C*O$_{Myc}$); 154.3, 137.0 (C$_{q,arom}$); 129.5, 116.2 (*C*H$_{arom}$); 98.8 (C-1'); 97.6 (C-1); 86.8 (*C*H$_{Phth}$); 81.6 (C-3); 80.8 (C-3'); 76.0 (C-2'); 72.0 (C-2); 71.9 (C-4'); 71.7 (C-4); 70.4 (*C*H$_{Phth}$); 69.1 (C-5); 69.0 (C-5'); 59.1, 57.7, 57.5, 57.2 (O*C*H$_3$); 45.6, 45.4 (*C*H$_{2,Myc}$); 41.1, 38.5 (*C*H$_{2,Phth}$); 37.9, 37.9 (*C*H$_{Myc}$); 36.8, 35.3 (*C*H$_{2,Myc}$); 34.9 (*C*H$_{Phth}$); 34.8, 32.8 (*C*H$_{2,Phth}$); 32.1 (*C*H$_{2,Myc}$); 31.9, 30.2 (*C*H$_{2,Phth}$); 30.1 (*C*H$_{Myc}$); 29.9, 29.9, 29.8, 29.7, 29.5 (*C*H$_2$); 28.2 (*C*H$_{Myc}$); 27.6 (*C*H$_{2,Phth}$); 27.3 (*C*H$_{Myc}$); 27.1 (*C*H$_{2,Myc}$); 25.7, 25.3 (*C*H$_{2,Phth}$); 22.9 (*C*H$_{2,Myc}$); 22.5 (*C*H$_{2,Phth}$); 20.9, 20.6, 20.6, 20.5, 18.6 (*C*H$_{3,Myc}$); 17.9 (C-6); 17.9 (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}): 1069, 1129, 1175, 1232, 1378, 1464, 1511, 1734, 2853, 2923, 3434. HRMS calculated for $C_{114}H_{215}O_{14}$ 1809.61405 $[M+H]^+$; found 1809.61455.

4-((3*R*,4*S*,9*R*,11*R*)-3-methoxy-4-methylheptacos-26-yne-9,11-diyl bismycocerosate)phenyl 2,3-di-*O*-methyl-4-*O*-(2-*O*-(3-*O*-methyl-α-L-rhamnopyranoside)-3-*O*-methyl-α-L-rhamnopyranoside)-α-L-rhamnopyranoside (60)



The title compound was synthesized according to general procedure E using **54** (28 mg, 13 µmol, 1.0 eq) and Pd/C (10%, 13 mg, 13 µmol, 1.0 eq). Column chromatography (DCM-MeOH 19:1) yielded the product (20 mg, 10 µmol, 81%) as a waxy solid. $[\alpha]_D^{25}$ = -29.0 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.10 (d, 2H, *J* = 8.4 Hz, C*H*$_{arom}$); 6.96 (dd, 2H, *J* = 2.0, 6.8 Hz, C*H*$_{arom}$); 5.50 (d, 1H, *J* = 2.0 Hz, H-1); 5.28 (d, 1H, *J* = 1.6 Hz, H-1'); 5.12 (d, 1H, *J* = 1.2 Hz, H-1''); 4.84 (quint, 2H, *J* = 6.4 Hz, C*H*$_{Phth}$); 4.15-4.13 (m, 2H, H-2', H-2''); 3.79-3.71 (m, 6H, H-2, H-3, H-4, H-5, H-5', H-5''); 3.55-3.52 (m, 8H, H-4', H-4'', OC*H*$_3$); 3.48 (s, 3H, OC*H*$_3$); 3.46 (s, 3H, OC*H*$_3$); 3.42 (dd, 1H, *J* = 3.2, 9.2 Hz, H-3''); 3.36 (dd, 1H, *J* = 2.8, 9.6 Hz, H-3'); 3.33 (s, 3H, OC*H*$_3$); 2.87-2.85 (m, 1H, C*H*$_{Phth}$); 2.57-2.52 (m, 4H, C*H*$_{2,Phth}$, C*H*$_{Myc}$); 2.32 (bs, 1H, 4'-O*H*); 2.30 (bs, 1H, 4''-O*H*); 2.18 (bs, 1H, 2''-O*H*); 1.77-0.81 (m, 211H, 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 (100 MHz) δ: 176.2, 176.1 (*C*O$_{Myc}$); 154.6, 137.0 (C$_{q,arom}$); 129.5, 116.3 (*C*H$_{arom}$); 100.9 (C-1'); 100.5 (C-1''); 96.1 (C-1); 86.8 (*C*H$_{Phth}$); 82.0 (C-3); 81.7 (C-3'); 81.0 (C-3''); 78.0 (C-4); 76.3 (C-2); 71.8 (C-2'); 71.6 (C-4'and C-4''); 70.4 (*C*H$_{Phth}$); 69.2 (C-5'); 68.2 (C-5''); 67.0 (C-5); 59.6, 57.5, 57.4, 57.2, 57.2 (O*C*H$_3$); 45.6, 45.4 (*C*H$_{2,Myc}$); 41.1, 38.6 (*C*H$_{2,Phth}$); 37.9, 37.9 (*C*H$_{Myc}$); 36.8, 35.3 (*C*H$_{2,Myc}$); 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$_{2,Phth}$); 22.9 (*C*H$_{2,Myc}$); 22.5 (*C*H$_{2,Phth}$); 20.9, 20.6, 20.6, 18.6 (*C*H$_{3,Myc}$); 18.5 (C-6''); 17.9 (C-6 and 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}): 1016, 1093, 1175, 1229, 1261, 1378, 1457, 1511, 1736, 2853, 2822, 3466. HRMS calculated for $C_{121}H_{227}O_{18}$ 1968.68420 $[M+H]^+$; found 1968.68577.

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



The title compound was synthesized according to general procedure E using **55** (24 mg, 11 µmol, 1.0 eq) and Pd/C (10%, 12 mg, 11 µmol, 1.0 eq). Column chromatography (DCM-MeOH 24:1) yielded the product (16 mg, 8 µmol, 73%) as a waxy solid. $[\alpha]_D^{25}$ = -36.1 ° (c = 1.0, $CHCl_3$). ^{1}H-NMR (400 MHz) δ: 7.10 (d, 2H, *J* = 8.4 Hz, C*H*$_{arom}$); 6.96 (dd, 2H, *J* = 2.0, 6.4 Hz, C*H*$_{arom}$); 5.50 (d, 1H, *J* = 1.6 Hz, H-1); 5.26 (d, 1H, *J* = 1.6 Hz, H-1'); 5.15 (d, 1H, *J* = 1.6 Hz, H-1''); 4.84 (quint, 2H, *J* = 6.4 Hz, C*H*$_{Phth}$); 4.16 (dd, 1H, *J* = 2.0, 2.4 Hz, H-2'); 3.79-3.70 (m, 6H, H-2, H-3, H-4, H-5, H-5', H-5''); 3.68 (dd, 1H, *J* = 1.8, 3.0 Hz, H-2''); 3.58-3.41 (m, 18H, H-3'', H-4', H-4'', OC*H*$_3$); 3.37 (dd, 1H, *J* = 2.6, 9.4 Hz, H-3'); 3.33 (s, 3H, OC*H*$_3$); 2.88-2.83 (m, 1H, C*H*$_{Phth}$); 2.57-2.52 (m, 4H, C*H*$_{2,Phth}$, C*H*$_{Myc}$); 2.29 (bs, 2H, 4'-O*H*, 4''-OH); 1.77-0.81 (m, 218H, C*H*$_{Phth}$, C*H*$_{2,Phth}$, C*H*$_{3,Phth}$, C*H*$_{Myc,}$ C*H*$_{2,Myc}$, C*H*$_{3,Myc}$, H-6, H-6', H-6''). ^{13}C-APT NMR (100 MHz) δ: 176.2, 176.1 (*C*O$_{Myc}$); 154.6, 137.0 (C$_{q,arom}$); 129.5, 116.3 (*C*H$_{arom}$); 101.0 (C-1'); 98.3 (C-1''); 96.1 (C-1); 86.8 (*C*H$_{Phth}$); 82.1 (C-3 and C-3'); 80.8 (C-3''); 77.9 (C-4); 76.3 (C-2); 76.1 (C-2''); 71.8, 71.7 (C-4'and C-4''); 71.2 (C-2') 70.4 (*C*H$_{Phth}$); 69.2 (C-5'); 68.8 (C-5''); 68.0 (C-5); 59.6, 59.2, 57.5, 57.5, 57.1, 57.1 (O*C*H$_3$); 45.6, 45.4 (*C*H$_{2,Myc}$); 41.1, 38.6 (*C*H$_{2,Phth}$); 37.9, 37.9 (*C*H$_{Myc}$); 36.8, 35.3 (*C*H$_{2,Myc}$); 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, 20.6, 20.5, 18.6 (*C*H$_{3,Myc}$); 18.5 (C-6'); 17.9, 17.7 (C-6 and 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}): 1009, 1075, 1082, 1093, 1106, 1122, 1262, 1378, 1457, 1464, 1510, 1736, 2853, 2923, 3430. HRMS calculated for $C_{122}H_{229}O_{18}$ 1983.70326 $[M+H]^+$; found 1983.70441.

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