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# Synthesis of an Exhaustive Library of Naturally Occurring Gal*f*-Man*p* and Gal*p*-Man*p* Disaccharides. Toward Fingerprinting According to Ring Size by Advanced Mass Spectrometry-Based IM-MS and IRMPD

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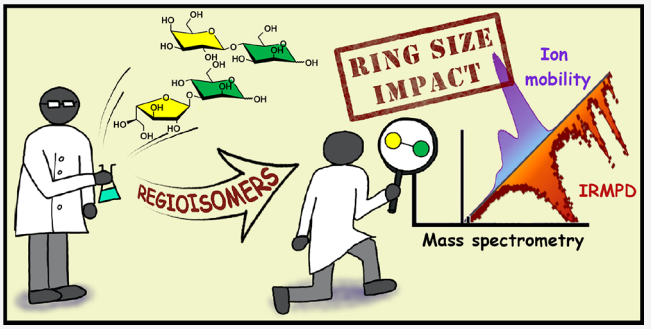
**ABSTRACT:** Nature offers a huge diversity of glycosidic derivatives. Among numerous structural modulations, the nature of the ring size of hexosides may induce significant differences on both biological and physicochemical properties of the glycoconjugate of interest. On this assumption, we expect that small disaccharides bearing either a furanosyl entity or a pyranosyl residue would give a specific signature, even in the gas phase. On the basis of the scope of mass spectrometry, two analytical techniques to register those signatures were considered, i.e., the ion mobility (IM) and the infrared multiple photon dissociation (IRMPD), in order to build up cross-linked databases. D-Galactose occurs in natural products in both tautomeric forms and presents all possible regioisomers when linked to D-mannose. Consequently, the four reducing Gal*f*-Man*p* disaccharides as well as the four Gal*p*-Man*p* counterparts were first synthesized according to a highly convergent approach, and IM-MS and IRMPD-MS data were second collected. Both techniques used afforded signatures, specific to the nature of the connectivity between the two glycosyl entities.




## INTRODUCTION

A huge diversity of glycans is observed in Nature. This results from the variety of sequencing, branching, connectivity between monosaccharides, minor but very important functional group modulations, the traditional OH group being opportunistically replaced by uronic acid, deoxy, or NHAc functions, and conjugation to lipids, nucleosides or proteins through *O*- or *N*-, *α*- or *β*-glycosidic bonds, to name only the most widespread modulations. This biodiversity is also widened by considering the possible tautomerism between pyranosides and furanosides. As a consequence, glycoconjugates are involved in many biological processes such as photosynthesis, intercellular and host−pathogen recognition phenomena, and maturation of proteins.[1] They can be also overexpressed by cancer cells[2] or used as markers of some infection diseases.[3] To decipher the complex biological and physicochemical properties of this family of biomolecules, analytical strategies are still being developed.[4] Very recently, low-temperature scanning tunneling microscopy allowed direct imaging of different conformers of some oligosaccharides with a subnanometer resolution.[5] On the contrary, neutron crystallography is able to study H-bond networks in protein binding sites.[6,7] Nevertheless, structural studies are mostly based on NMR[8] and mass spectrometry (MS) techniques[9] brilliantly complemented by modeling[10,11] and machine learning approaches.[12−14] Despite these advances, no single analytical technique is able to solve all of the structural elements in carbohydrates, and techniques still have to be improved in order to collect and cross-check data, to increase reliability of the analysis. They must also consider minor variations proposed by the living kingdom.

Mammals biosynthesize hexosyl-containing glycoconjugates exclusively in the pyranose form. However, some microorganisms are able to produce hexofuranosyl-containing polysaccharides and conjugates. For instance, galactose,[15−17] *N*-acetylgalactosamine,[18,19] and fucose[15] in their furanose form were identified in natural biomolecules with still unclear roles. Moreover, understanding why Nature sometimes prefers to biosynthesize hexofuranosides instead of the thermodynami-

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cally more stable pyranosidic counterparts, while the energy cost is higher, is not evident.

An analysis of the natural occurrence of galactofuranosides led us to focus on the galactofuranose (Gal*f*)-mannopyranose (Man*p*) sequence and thus the four possible regioisomers (Figure 1). The disaccharides with a (1→2)-, (1→3)-, or (1→6)-linkage, but not a (1→4)-bond, were identified in microorganisms,[15] some of them being pathogenic, for instance, *Trypanosoma*, *Leishmania*, and *Aspergillus* species. Surprisingly, the *β*-D-Gal*f*-(1→4)-D-Man*p* sequence was exclusively found in lichens.[20−24] On another side, the corresponding pyranosidic Gal*p*-Man*p* isomers were identified in different microorganisms: *Klebsiella* for the (1→2)-disaccharide,[25] *Rahnella* for the (1→3)-derivative,[26] *Leishmania*, *Escherichia coli* for the nondigestable epilactose with the (1→4)-linkage,[27,28] and *Burkholderia*,[29] KLH protein,[30] *Salmonella*[31] for the *β*-D-Gal*p*-(1→6)-D-Man*p*. This resulting orthogonality in Nature strengthens the need for consolidating analytical data to differentiate Gal*f* and Gal*p* residues.[32]

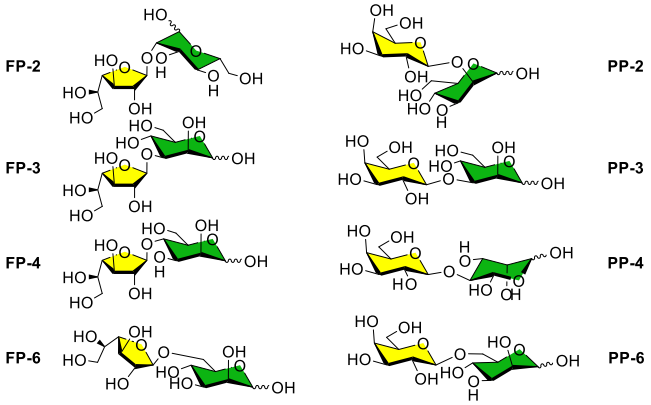


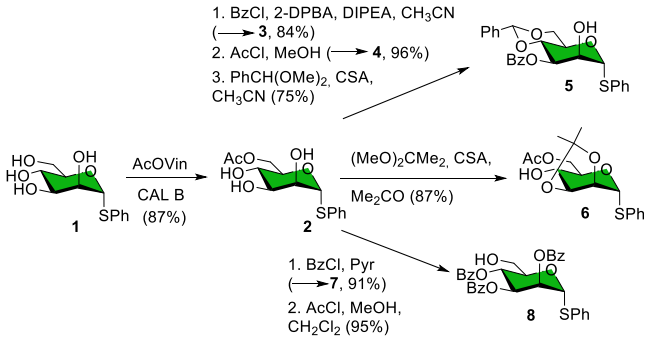

**Figure 1.** Defined disaccharides for IM-MS and IRMPD fingerprinting

In this context, we have initiated a program dealing with new analytical approaches of hexofuranosides based on mass spectrometry since this technique can be augmented to provide further structural and conformational information. We thus anticipated that ion-mobility mass spectrometry (IM-MS)[33,34] and infrared multiple photon dissociation (IRMPD)[35] spectroscopy are indeed suitable tools to assess the impact of the ring size and the branching pattern of small disaccharides on physicochemical properties. We thus expect that these techniques provide specific signatures for distinguishing furanosides from pyranosides. IM-MS separates ions, based on their gas-phase mobility in an electric field,[36] and can be used to determine specific structures.[37,38] IRMPD spectroscopy has been widely used, in combination with quantum chemistry, to elucidate the conformation of biomolecular ions in the gas phase.[39] Previous results demonstrate that IRMPD spectroscopy has sufficient structural resolution to yield distinctive signatures and to unambiguously distinguish Gal*p*NAc residues from Gal*f*NAc ones in the case of monosaccharides.[40] Here, we describe the synthesis of the eight isomers of naturally occurring reducing disaccharides Gal-Man, and we demonstrate that individual signatures can be obtained using adequate MS-based strategies, namely IM-MS and IRMPD spectroscopy. We expect that these signatures will be useful for the identification of the corresponding Gal-Man patterns in larger polysaccharides. Upon fragmentation, galactomannans will release specific disaccharidic fragments, whose fingerprints will match that of the synthetic library. The MS/MS strategy has been applied to the identification of the monosaccharide content (analyses were done on the monosaccharide fragments released upon fragmentation),[41−43] and IRMPD signatures of methyl furanoside and pyranoside derived from *N*-acetylgalactosamine have been previously reported.[40] We anticipate, however, that monosaccharidic fragments may isomerize upon fragmentation, especially the thermodynamically less stable hexofuranosyl residues, and this would adversely affect the analysis of monosaccharide entities in larger oligosaccharides. Therefore, we present the fingerprints of Gal*f*-Man*p* and Gal*p*-Man*p* disaccharides, for future analysis of oligosaccharides. The strategy offers the advantage that no additional efforts will be further required in terms of synthesis, as the eight disaccharides synthesized in this work will provide the library necessary for the structural study of larger polymers.

## RESULTS AND DISCUSSION

**Synthesis of Gal*f*-Containing Disaccharides and of Their Gal*p* Isomers.** To access the panel of the targeted unprotected and reducing disaccharides, four mannopyranosidic acceptors were first synthesized for further coupling with galactofuranosyl or galactopyranosyl donors. Considering the ease of preparation and structural modulation of thioglycosides, and the orthogonal properties toward other families of glycosyl donors, the phenyl thiomannopyranoside **1** was selected as the precursor for all acceptors (Scheme 1). The primary position was first selectively acetylated with vinyl acetate thanks to the action of the *Candida antartica* lipase B (CAL B) to afford **2** isolated in 87% yield.[44] This biocatalyzed acylation was interestingly performed on a large 20 g scale, and this consolidates our choice toward this compound as a key intermediate in our synthesis strategy. Moreover, intermediate **2** can act as acceptor for direct O-3 glycosylation without further protections. The pioneering works of Taylor,[45] dealing with the activation of the equatorial hydroxyl of 1,2-diols in carbohydrates with organoborinic catalysts, offers the opportunity to significantly increase the nucleophilicity of OH-3 in the *manno*-series. Consequently, this compound was indeed the key intermediate in our approach since it was either directly engaged in glycosylation reaction [(1→3)-disaccharides] or converted into the other required acceptors for (1→2)-, (1→4)-, and (1→6)-linkages, thus limiting the number of intermediates and synthetic steps. The synthesis of acceptor **5**

**Scheme 1. Synthesis of the Required Mannopyranosidic Acceptors**



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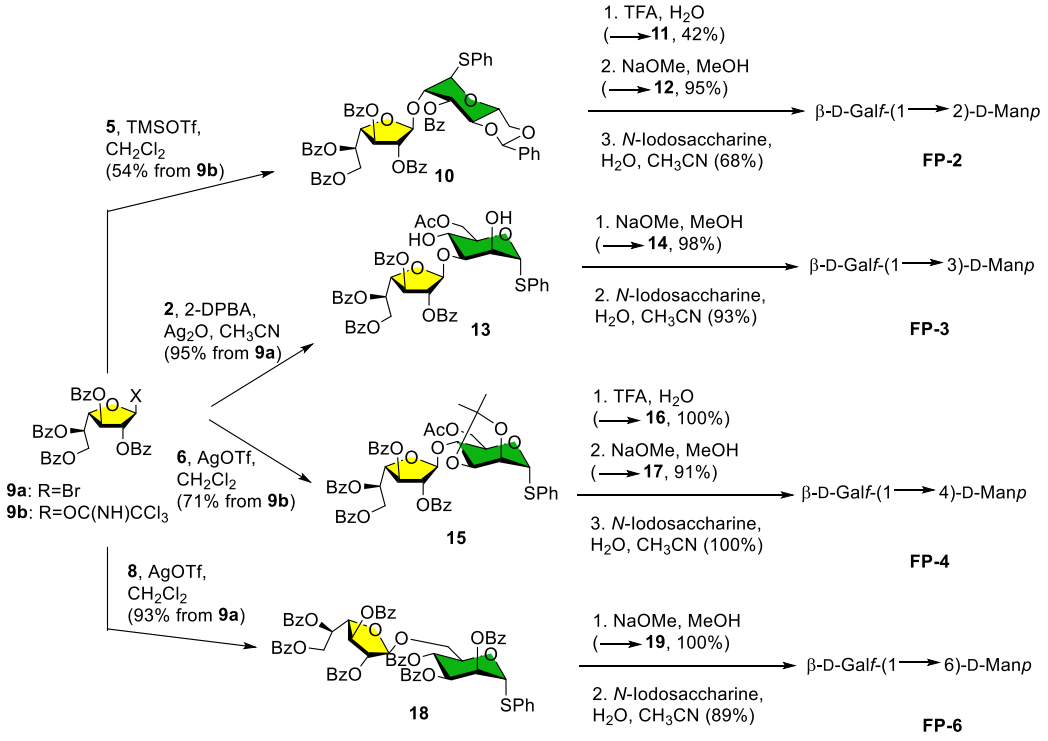
**Scheme 2. Synthesis of the Gal*f*-Containing Disaccharides FP**




with free OH-2 started with the specific benzoylation of **2** at position 3 in the presence of the borinate ester 2-aminoethyldiphenyl borinate (2-ADPB). The building block **3** thus obtained was then converted into the mannopyranoside **5** after selective deacetylation under acidic conditions and benzylidenation. This synthetic way was preferred to the sequence benzylidenation followed by 3-*O*-benzoylation since it was anticipated the possible formation of the O-2/O-3 acetalization concomitantly with the desired O-4/O-6 protection. Nevertheless, it took advantage of the *cis* arrangement of the hydroxyl groups in compound **2** for obtaining the derivative **6** bearing free OH-4 by acid-catalyzed acetalization with dimethoxypropane. Finally, a two-step benzoylation−deacetylation of **2** afforded **8** with a free primary position.

With the acceptors in hand, it was anticipated that glycosylation at positions 6 and 3 is easier than that at O-2 and O-4.[46] Moreover, it is recognized that conditions should be tuned according to the nature of the leaving group on the glycosyl donors but also on the basis of its furanose or the pyranose form. Our results did not depart from these general observations. The synthesis of disaccharides **FP-2**−**FP-6** was first considered starting with the known galactofuranosyl bromide **9a** (Scheme 2). As expected, the coupling reactions at O-2 and, in a lesser extent at O-4, were less efficient than the ones at O-3 under the Taylor's conditions and at the primary hydroxyl group. The preferred promoter was the soluble silver triflate in all cases except the O-3 linkage, for which it was shown that silver oxide was more efficient.[47] For these steps, the yields ranged from 24% for the less reactive O-2 on the mannoside **5** to 93% and 95% for acceptors **2** and **8**, respectively. It was, however, observed that limitations to afford **10** and **15** resulted from low reactivity of the donor **9a** for **10** and formation of the corresponding orthoester for **15**. Nevertheless, glycosylation of **5** and **6** with the trichloroacetimidate **9b** in the presence of TMSOTf as the catalyst gave the desired disaccharides **10** and **15** in improved 54% and 71% yields, respectively.

The disaccharides **10**, **13**, **15**, and **18** are characterized by two small $J_{H1-H2}$ coupling constants close or less to 1 Hz for both residues near 5.7 and 5.4 ppm (see the Supporting Information). Moreover, 2D-NMR analysis revealed that the former signal is correlated with a peak around 85 ppm, while the latter is correlated with the signal at 104 ppm. These data corroborate both the $\alpha$-mannopyranosidic and the expected $\beta$-galactofuranosidic linkages, respectively. Concerning the regioselectivity of the glycosylation of acceptor **2** catalyzed by 2-ADPB, it was also established on the $^{13}$C NMR data since the signal corresponding to C-3 was significantly up-shifted from 72.2 ppm for the monosaccharide **2** to 78.2 ppm for the disaccharide **13**. Finally, removal of protecting groups was performed under standard conditions: acidic hydrolysis for the acetals, Zemplen transesterification for the esters, and hydrolysis promoted by *N*-iodosaccharine[48] for the thioglycosides. It is noteworthy that the resulting reducing disaccharides were obtained in aqueous solution generally as mixtures of anomers as revealed by $^1$H NMR and corroborates previous data for **FP-2**[49] and **FP-3**.[50] The targeted structures thus tightly approach those ensuing hydrolysis of polysaccharides extracted from biomass. The developed synthetic strategy therefore allowed the synthesis of all possible regioisomers Gal*f*-Man*p* and complements well the one recently described for three Gal*f*-Man*p* derivatives but bearing an amino spacer arm at the reducing end.[51] Both anomers were unambiguously characterized thanks to the NMR spectra, with the help of TOCSY 1D-data, which allows isolation of the signals corresponding to the irradiated proton. Under these conditions, the spectrum of the minor $\beta$-anomer in water was fully assigned (see the Supporting Information).

This strategy was next extended to the preparation of the Gal*p*-Man*p* isomers (Scheme 3), except for the disaccharide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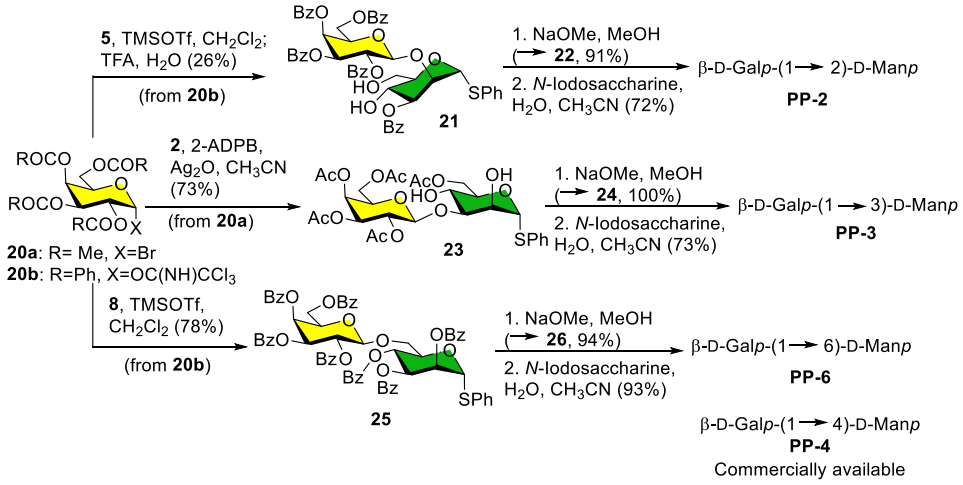
**Scheme 3. Synthesis of the Gal*p*-Containing Disaccharides PP**



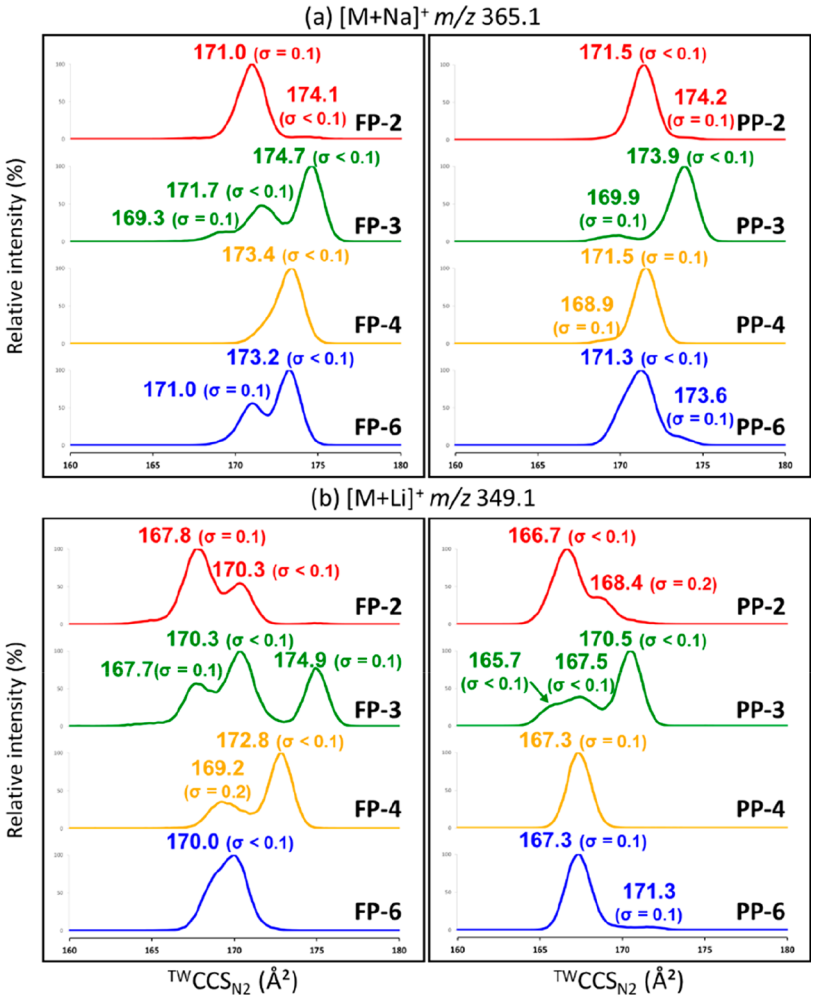




**Figure 2.** Extracted monoisotopic ion mobility spectra for the eight synthesized products as (a) $[M + Na]^+$ ($m/z$ 365.1) and (b) as $[M + Li]^+$ ($m/z$ 349.1). Standard deviations are given for three replicates. For both parts, the left panel corresponds to the galactofuranosyl-containing disaccharides and right panel to the pyranosyl-containaing ones. Color for the regiochemistry of the glycosidic bond: Gal-(1→2)-Man (red), Gal-(1→3)-Man (green), Gal-(1→4)-Man (orange), and Gal-(1→6)-Man (blue).

**PP-4**, which is commercially available. Considering the synthesis of **PP-3**, very efficient glycosidic coupling was obtained starting from the triol **2** and the bromide **20a** in the presence of the organoboron catalyst 2-ADPB and silver oxide. The standard deprotection steps afforded **PP-3** in 53% yield over the three steps. Unfortunately, a poor glycosylation yield was obtained using the same donor **20a** and the acceptor **5**. The targeted intermediate **21** was nevertheless prepared from the perbenzoylated galactopyranosyl trichloroacetimidate **20b**[52] and the same acceptor and isolated after removal of the



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benzylidene ring in 26% yield. Further deprotection steps gave the desired product **PP-2**[53] in satisfactory yield. Finally, and surprisingly, the formation of the (1→6)-linkage raised some difficulties. First attempts with the bromide **20a** activated by silver triflate transferred an acetyl group to the acceptor **8**. Unfortunately, adding diisopropylethyl amine as a base (DIPEA) to avoid the acid-catalyzed transesterification also resulted in the formation of an orthoester in 73% yield (results not shown). This was circumvented by using the trichloroacetimidate **20b** and trimethylsilyl triflate (TMSOTf), so that the disaccharide **25** was isolated in a 78% yield. Action of sodium methoxide followed by hydrolysis of the thiomannoside gave the wanted disaccharide **PP-6**.[54]

**Mass Spectrometry Analysis.** As a preliminary mass spectrometry analysis, the spectra of all disaccharides were recorded using traditional MS/MS approaches. It was evidenced that the Gal*f* moiety cannot be differentiated from its Gal*p* isomer, as the products do not generate specific fragments for a defined Gal*f*-Man*p*/Gal*p*-Man*p* pair (see Figure S1). We thus turned to gas phase analysis techniques that are sensitive to both the spatial arrangement and the regiochemistry of the ions: ion mobility (IM-MS) and IRMPD spectroscopy.

*Ion Mobility–Mass Spectrometry.* We first analyzed the synthesized disaccharides using positive electrospray ionization (ESI) time-of-flight mass spectrometry, hyphenated with a high-resolution cyclic ion mobility cell (Waters Select Series Cyclic IMS, Wilmslow, UK).[55] Arrival time distributions (ATDs) were then calibrated to give collision cross sections (CCSs), which represent the effective surface of the ions that interacts with the buffer gas during ion mobility experiments. We recorded the ion mobility of the $[M + Na]^+$ cations or $[M + Li]^+$ cations after four passes around the cyclic mobility cell, i.e., approximately a path of four meters. The resolving power of ion mobility is proportional to the path length of the ions, which, for four passes, yields a theoretical CCS/$\delta$CCS resolution of about 200, meaning that cyclic IM-MS can resolve conformers that differ by less than about 1 Å$^2$ in the case of the disaccharides studied here (i.e., having CCSs of around 170 Å$^2$). As shown in the literature, this level of IM resolution allows the gas-phase separation of isomers and conformers prior to their mass measurement.[56−58] After mass selection of each disaccharide using a quadrupole filter, we recorded the set of gas-phase conformations for each ion, translated into CCS distributions (CCSDs). As shown in Figure 2 for the eight **FP** and **PP** disaccharides, a single disaccharide can give a single conformer or multiple ones with different CCSs, intensities, and peak shapes. These features of the CCSD act as a fingerprint of each disaccharide. Notably, fitting gaussians under the curve can be used in order to estimate the number of conformers in CCSDs (full, deconvolved CCSDs are given in Figure S2).

Second, we measured the CCSDs of the eight synthesized products as $[M + Na]^+$ ions at $m/z$ 365.1 (Figure 2a). The $[M + Na]^+$ cations are most commonly used for MS and IM-MS analyses of neutral oligosaccharides as they offer a good compromise between ionization and ion transmission through IM drift cells, more than ammonium adducts. Alkali metal cations also favor the separation of conformers compared to protonated adducts. Figure 2.a can first be read "horizontally" to differentiate isomers differing by the Gal*f* or Gal*p* residue. Here, considering the maximum standard deviations of CCSs observed during replicates (differences are significant if above 0.5 Å$^2$), two kinds of signatures could be observed: (i) the isomers each display a single peak of different CCS or (ii) the isomers have shared CCSs but differ through the global distribution of the peaks. For instance, in (i), the case of **FP-4** and **PP-4**, their pattern is rather similar with one major peak (note, however, a slight broadening of the peak for **FP-4**, which suggests the presence of two conformers) but these single peaks have different CCSs (173.4 Å$^2$ for **FP-4** and 171.5 Å$^2$ for **PP-4**). In (ii), the case of **FP-3** and **PP-3**, a difference of less than 1 Å$^2$ is measured on the most extended conformation (174.7 Å$^2$ versus 173.9 Å$^2$). However, the overall pattern is different, with three conformations separated for **FP-3** compared to two conformations for **PP-3**. Notably, the **FP**-type samples appeared to produce more complex ATD patterns than **PP**-type ones. This behavior might be related to the greater flexibility of the furanose moiety,[59,60] resulting in different conformations.

The same reasoning can be made "vertically" to differentiate isomers differing in their regiochemistry. As an example, the **FP-2** sample had an intense signal at 171.0 Å$^2$ with another peak of lower intensity at 174.1 Å$^2$. In contrast, the **FP-3** sample exhibited a triplet of CCSDs, respectively, at 169.3, 171.7, and 174.7 Å$^2$. Although less pronounced differences in CCSD patterns were observed for the **PP**-type samples, most signatures remained distinctive. For example, the **PP-3** showed a doublet of CCSDs at 169.9 (minor species) and 173.9 Å$^2$, while the **PP-4** displayed a doublet at 168.9 (minor species) and 171.5 Å$^2$.

However, although the $[M + Na]^+$ adducts already provided distinctive signatures in most cases, some ambiguities remained regarding the samples **FP-2** and **PP-2**. They had similar profiles with a CCS difference below 1 Å$^2$. Moreover, regarding the regiochemistry, samples **PP-2** and **PP-4** have the same CCS and only differed through minor conformations. The samples were thus also analyzed as lithium adducts. As shown in Figure 2b, we achieved a better distinction in the IM-MS profiles for **FP-2** and **PP-2**, both in terms of the CCS values of the peaks and in terms of the number and intensities of the conformers (both harbor two peaks at, respectively, 167.8 and 170.3 Å$^2$ and 166.7 and 168.4 Å$^2$). The measurement of the IM-MS of the $[M + Li]^+$ adduct also yielded a completely different pattern for **PP-2** compared to **PP-6**. Although samples **PP-4** and **PP-6** have strikingly similar CCSDs when analyzed as $[M + Li]^+$ adducts (a main peak at 167.3 Å$^2$, with similar peak shapes), the combination of the $[M + Na]^+$ and $[M+Li]^+$ fingerprints is unambiguous and allows identification of both the galactosyl configuration and the regiochemistry of the glycosidic bond.

*Exploration of the IRMPD Sensitivity for the Identification of the Ring-Size and Regiochemistry.* IRMPD (InfraRed Multiple Photon Dissociation) spectroscopy is an advanced MS-based scheme that adds a dimension of laser spectroscopy to mass spectrometry analysis. Its main advantage is to allow simultaneous measurements of the mass and the infrared fingerprint of an ion. Two ions of the same mass will generally feature distinctive IR fingerprints if they have different spatial arrangements (3D conformation or isomeric form).[43] Here, we explore the sensitivity of this technique to resolve the two types of isomerism present in the synthesized model disaccharides, namely the regiochemistry of the Gal-Man bond and the form of the galactosyl entity as a five- or a six-membered ring.



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As mentioned in the previous section, $Li^+$ and $Na^+$ adducts are often used to increase ion signal and fragmentation in mass spectrometry of carbohydrates.[61] In the context of IRMPD spectroscopy, different ion adducts will lead to different spectroscopic fingerprints.[39,62] As previously reported, ion adducts can also be chosen to enhance the spectroscopic differentiation of carbohydrate isomers.[62] Generally, protonated ions feature more distinguishing IR fingerprints than other charge states (i.e., deprotonated ions or alkali adducts). In the present study, the disaccharides of interest are neutral and do not easily protonate; therefore, we use ammonium adducts for ionization and enhanced spectroscopic diagnostic.

The eight IRMPD spectra presented in Figure 3 were obtained using the setup previously described.[63] In short, the

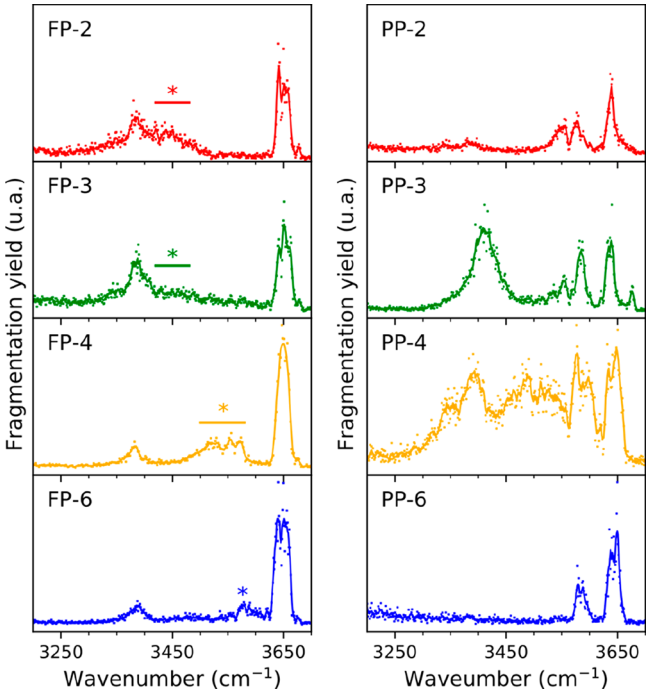


**Figure 3.** Left pannel: IRMPD spectra of galactofuranosyl-containing disaccharides. Right panel: galactopyranosyl-containing disaccharides. Color code for the regiochemistry of the glycosidic bond: Gal-(1→2)-Man (red), Gal-(1→3)-Man (green), Gal-(1→4)-Man (orange), Gal-(1→6)-Man (blue).

standards were prepared in water/methanol (50/50), and 0.1% of ammonium sulfate was added to promote the formation of ionic complexes $M{\cdot}NH_4^+$, which are easily detected by mass spectrometry. The ions of interest are detected at 360 $m/z$ and isolated in the ion trap where they are irradiated by the laser to record their IR fingerprints. The IRMPD spectra are presented between 3200 and 3700 cm$^{-1}$, which corresponds to the active range of NH and OH vibrations (elongation modes).

First, all spectra display a common feature: an intense band around 3650 cm$^{-1}$. In addition, another intense feature is observed at 3575 cm$^{-1}$ only for the pyranose form, which makes a straightforward distinction between pyranose and furanose fingerprints. The 3200−3550 cm$^{-1}$ range is unique for each pyranose: **PP-6** hardly presents any vibrational activity besides the pyranose diagnostic doublet. **PP-2** presents a distinctive feature at 3547 cm$^{-1}$ and a weak NH band at 3380 cm$^{-1}$. **PP-3** and **PP-4** show an intense and broad NH feature in the same area. Additionally, **PP-4** shows a broad and intense feature around 3500 cm$^{-1}$.

Spectra are less distinctive of the regiochemistry of furanosyl-containing disaccharides, but some differences can be noticed. Besides the main band at 3650 cm$^{-1}$ (furanose diagnostic), all four spectra show a NH band in a close range (from 3380 to 3390 cm$^{-1}$). In addition, **FP-6** shows a weak band at 3580 cm$^{-1}$ (marked with a blue star); **FP-4** features a group of partly resolved bands in the 3500−3570 cm$^{-1}$ region (marked with an orange star); both **FP-2** and **FP-3** show a broadening of their NH band toward the high wavenumber, ranging to 3490 cm$^{-1}$ (marked with red and green stars). **FP-2** and **FP-3** only differ by the relative intensity of this shoulder (**FP-2**: high, **FP-3**: low).

Overall, the IRMPD spectra bear a strong diagnostic of the ring size: either one dominant band at 3650 cm$^{-1}$ for furanose or a doublet of bands at 3650/3575 cm$^{-1}$ for pyranose. In the case of Gal*p*-containing disaccharides, the IR fingerprint is also diagnostic of the regiochemistry because all **PP** spectra are distinguishable. For Gal*f*-containing disaccharides, the IRMPD approach proves less distinguising of the regiochemistry: **FP-2** and **FP-3** have close fingerprints.

## CONCLUSION

The results presented in this work, combining different fields in glycosciences, allowed us to highlight the impact of the ring size of the nonreducing galactosyl residue for each possible connectivity in the Gal*f*-Man*p* disaccharides. On one hand, this study showed that the metal adducts of the synthesized compounds have different gas-phase conformations, resulting in specific signatures in IM-MS for all Gal-Man disaccharides, according to the ring size for the galactosyl residue and to the connectivity between both entities. The same structural differences were strengthened on another hand, registering IR signals of the disaccharides in the gas phase.

As a result, we expect that the IM-MS and IRMPD data can be used as libraries of reference fingerprints for further analysis of unknown disaccharides and that they constitute the fundamentals of bringing out Gal*f* for pattern recognition in longer oligosaccharides. Therefore, we expect that this study paves the way to the screening of galactofuranose in natural polysaccharides.

## EXPERIMENTAL SECTION

**Synthesis.** *General Experimental Details.* All reagents were purchased from commercial sources and were used without further purification unless noted. 2,3,5,6-Benzoylgalactofuranosyl bromide **9a**[64] and trichloroacetimidate **9b**[65] as well as 2,3,4,6-benzoylgalactopyranosyl trichloroacetimidate **20b**[52] were synthesized according to literature procedures. Unless otherwise stated, all reactions were monitored by TLC on silica gel 60 $F_{254}$. TLC spots were detected under 254 nm UV light or by staining with cerium ammonium molybdate solution. For reactions that proceeded by heating, a metallic heating mantle was used. Column chromatography was performed on silica gel (50 μm). High-resolution masses were recorded in positive mode using direct electrospray ionization on a Waters Q-Tof 2 spectrometer.

NMR spectra were recorded on a Bruker Avance III 400 spectrometer operating at 400.13 MHz for $^1$H, equipped with a BBFO probe with a Z-gradient coil and a GREAT 1/10 gradient unit or on a Bruker Avance III operating at 500.13 MHz for $^1$H equipped with $^1$H and $^{13}$C cryo-probe. All experiments were carried out at 25 °C, and references for chemical shifts are external. Coupling constants $J$ were calculated in hertz (Hz). Proton and carbon NMR peaks were unambiguously assigned by COSY (double quantum filtered with


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gradient pulse for selection), HSQC (gradient echo-anti echo selection and shape pulse), and HMBC (echo-anti echo gradient selection, magnitude mode) correlation experiments as well as TOCSY. Mutiplicity are annotated as s (singlet), d (doublet), t (triplet), m (multiplet), or o (overlapping signals).

The zg30 Bruker pulse program was used for 1D $^{1}$H NMR, with a TD of 64k, a relaxation delay d1 = 2s and 32 scans or more. The spectrum width was set to 18 ppm. 2D COSY experiments were acquired using the cosygpdqf pulse program. Matrices consisting of 256−512 (t1) × 2048 (t2) complex data points were recorded. An AQ time of 0.25−0.5 s was used. Processing was performed with a QSINE function in both dimensions (SSB = 0). 2D TOCSY experiments were acquired using the dipsi2sisp pulse program with a mixing time of 150 ms in major cases. Matrices consisting of 256−400 (t1) × 4k−8k (t2) complex data points were recorded; 8−16 scans are carried out per t1 increment with 1.5 s recovery delay (d1) and AQ time of 0.3 to 0.7 s. Processing was performed with a QSINE function in both dimensions (SSB = 2). $^{13}$C NMR spectra were recorded at 100.61 MHz or at 125.13 MHz on cryo-probe. Several sequences as jmod, dept135, or zgpg30 were used with n*1024 scans depending on the concentration of the sample. TD was set to 64k and a relaxation delay of 2 s for a spectral width of 220 ppm was used.

2D HSQC ($^{1}$H−$^{13}$C) experiments were acquired using the hsqcetgpsisp2.2 pulse program for high sensitivity with an AQ = 0.25 to 0.5 s, d1 = 1.5 s, ns = 2 to 24 depending on the concentration. Generally, 256 experiences were acquired (t1). Fourier transform was performed in both dimensions with a SINE function (SSB = 3). 2D HMBC ($^{1}$H−$^{13}$C) experiments were performed with either the hmbcplrndqf or the impact-hmbc pulse program. D1 was set to 0.3 to 1.5 s, delay d6 for the evolution of long-range coupling was set to 65 ms, NS was depending on the concentration and the number of series was set at 256 to 512(t1). All of the data were processed with a SINE function in both dimensions (SSB = 3). To identify the $^{1}$H frequency of the mixture of anomers, the 1D-Tocsy experiment (selcssfdizs.2) from the Bruker library was used with 150 ms for mixing time and 16 for TD0 when the highest selectivity was required.

Further details, including NMR data, are described in the Supporting Information.

*Synthesis of Glycosyl Acceptors. Phenyl 6-O-Acetyl-1-thio-α-D-mannopyranoside (**2**).* To a solution of phenyl 1-thio-α-D-mannopyranoside **1** (20 g, 73.5 mmol) in dry THF (600 mL) were added vinyl acetate (17.6 mL, 0.19 mol) and Novozym 435 (3 g). The reaction mixture was allowed to stire at 45 °C for 65 h. The reaction mixture was filtered and concentrated under reduced pressure. The resulting residue was purified by column chromatography on silica gel (DCM/MeOH gradient from 100:0 up to 90:10) to afford **2** (19.97 g, 87%) as a beige solid. $^{1}$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.50−7.44 (m, 2H, $H_{arom}$), 7.31−7.22 (m, 3H, $H_{arom}$), 5.58 (d, 1H, $J$ = 1.3 Hz, H-1), 4.49 (dd, 1H, $J$ = 12.6, 6.9 Hz, H-6), 4.37−4.31 (m, 2H, H-5, H6′), 4.27 (dd, 1H, $J$ = 3.3, 1.3 Hz, H-2), 3.91 (dd, 1H, $J$ = 9.4, 3.3 Hz, H-2), 3.78 (t, 1H, $J$ = 9.4 Hz, H-3), 2.03 (s, 3H, $CH_3$). $^{13}$C{1H} NMR ($CDCl_3$, 100 MHz): $\delta$ 172.2 (CO), 133.7, 131.8, 129.1, 127.7 ($C_6H_5$), 87.9 (C-1), 72.2, 72.2 (C-2, C-3), 71.4 (C-5), 68.2(C-4), 63.9 (C-6), 21.0 ($CH_3$). HRMS (ESI) $m/z$: [M + Na]$^+$ Calcd for $C_{14}H_{18}O_6SNa$ 337.0716; Found 337.0718.

*Phenyl 6-O-Acetyl-3-O-benzoyl-1-thio-α-D-mannopyranoside (**3**).* To a solution of **2** (1.0 g, 3.2 mmol) in dry acetonitrile (20 mL) were added 2-aminoethyldiphenyl borinate (788 mg, 3.5 mmol), benzoyl chloride (1.2 mL, 10.0 mmol), and *N*,*N*-diisopropylethylamine (1.7 mL, 9.8 mmol) under anhydrous conditions. The reaction mixture was stirred at 40 °C for 17 h. The reaction mixture was then concentrated under reduced pressure, and the resulting residue was partitioned between DCM and aqueous saturated $NaHCO_3$ solution. The organic layer was washed with aqueous saturated $NaHCO_3$ solution (2×) and brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting residue was purified by column chromatography on silica gel (DCM/MeOH gradient from 100:0 to 90:10) to afford **3** (1.17 g, 84%) as a white solid. $^{1}$H NMR ($CDCl_3$, 400 MHz): $\delta$ 8.12−8.08 (m, 2H, $H_{arom}$), 7.62−7.28 (m, 8H, $H_{arom}$), 5.58 (d, 1H, $J$ = 1.6 Hz, H-1), 5.34 (dd, 1H, $J$ = 9.8, 3.1 Hz, H-3), 4.56 (dd, 1H, $J$ = 12.1, 5.1 Hz, H-6), 4.46 (dd, 1H, $J$ = 3.1, 1.6 Hz, H-2), 4.44 (ddd, 1H, $J$ = 9.8, 5.1, 2.2 Hz, H-5), 4.31 (dd, 1H, $J$ = 12.1, 2.2 Hz, H-6′), 4.11 (t, 1H, $J$ = 9.8 Hz, H-4), 2.09 (s, 3H, $CH_3$). $^{13}$C{1H} NMR ($CDCl_3$, 100 MHz): $\delta$ 171.7, 166.6 (CO), 133.8, 131.8, 130.0, 129.3, 128.7, 127.9 ($C_6H_5$), 88.0 (C-1), 75.1 (C-3), 72.1, 70.9 (C-2, C-5), 66.2 (C-4), 63.4 (C-6), 21.0 ($CH_3$). HRMS (ESI) $m/z$: [M + Na]$^+$ Calcd for $C_{21}H_{22}O_7SNa$ 441.0978; Found 441.0982.

*Phenyl 3-O-Benzoyl-1-thio-α-D-mannopyranoside (**4**).* To a solution of **3** (1.42 g, 2.41 mmol) in dry MeOH (30 mL) was added acetyl chloride (360 μL, 5.09 mmol) under anhydrous conditions. The reaction mixture was stirred at room temperature for 17 h. The reaction was then stopped by the addition of saturated aqueous $NaHCO_3$. The aqueous layer was extracted with DCM. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure to afford **4** (1.22 g, 96%) as a white solid. $^{1}$H NMR ($CDCl_3$, 400 MHz): $\delta$ 8.13−8.00 (m, 2H, $H_{arom}$), 7.63−7.27 (m, 8H, $H_{arom}$), 5.55 (d, 1H, $J$ = 1.6 Hz, H-1), 5.35 (dd, 1H, $J$ = 9.7, 3.1 Hz, H-3), 4.44 (dd, 1H, $J$ = 3.1, 1.6 Hz, H-2), 4.35 (t, 1H, $J$ = 9.7 Hz, H-4), 4.26 (dt, 1H, $J$ = 9.7, 3.3 Hz, H-5), 3.96 (dd, 1H, $J$ = 12.1, 3.7 Hz, H-6), 3.86 (dd, 1H, $J$ = 12.1, 2.8, H-6′). $^{13}$C{1H} NMR ($CDCl_3$, 100 MHz): $\delta$ 167.9, 167.0 (CO), 134.3, 133.7, 132.0, 130.0, 129.8, 129.3, 128.8, 127.9 ($C_6H_5$), 88.2 (C-1), 75.5 (C-3), 73.7 (C-5), 71.0 (C-2), 65.9 (C-4), 62.0 (C-6). HRMS (ESI) $m/z$: [M + Na]$^+$ Calcd for $C_{19}H_{20}O_6SNa$ 399.0873; Found 399.0875.

*Phenyl 3-O-Benzoyl-4,6-O-benzylidene-1-thio-α-D-mannopyranoside (**5**).* To a solution of **1** (620 mg, 1.65 mmol) in dry acetonitrile (10 mL) were added benzaldehyde dimethyl acetal (372 μL, 2.48 mmol) and camphorsulfonic acid (77 mg, 0.33 mmol) under anhydrous conditions. The reaction mixture was allowed to stir at 55 °C for 8 h. Then the medium was concentrated under reduced pressure and partitioned between DCM and aqueous saturated $NaHCO_3$ solution. The organic layer was washed with aqueous saturated $NaHCO_3$ solution (2×) and water. The combined organic phases were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The resulting residue was purified by column chromatography on silica gel (cyclohexane/EtOAc gradient from 100:0 to 70:30) to afford **5** (573 mg, 75%) as a white solid. $^{1}$H NMR ($CDCl_3$, 400 MHz): $\delta$ 8.08 (dd, 2H, $J$ = 8.4, 1.4 Hz, $H_{arom}$), 7.61−7.43 (m, 7H, $H_{arom}$), 7.37−7.29 (m, 6H, $H_{arom}$), 5.63 (s, 1H, H-7), 5.61 (d, 1H, $J$ = 1.4 Hz, H-1), 5.60 (dd, 1H, $J$ = 10.2, 3.2 Hz, H-3), 4.59 (dd, 1H, $J$ = 3.2, 1.4 Hz, H-2), 4.54 (td, 1H, $J$ = 10.2, 4.9 Hz, H-5), 4.37 (t, 1H, $J$ = 10.2 Hz, H-4), 4.28 (dd, 1H, $J$ = 10.2, 4.9 Hz, H-6), 3.92 (t, 1H, $J$ = 10.2 Hz, H-6′). $^{13}$C{1H} NMR ($CDCl_3$, 100 MHz): $\delta$ 165.6 (CO), 137.2, 133.6, 133.4, 132.0, 130.0, 129.7, 129.3, 129.2, 128.6, 128.4, 128.0, 126.3 ($C_6H_5$), 102.0 (C-7), 88.6 (C-1), 76.4 (C-4), 71.6, 71.4 (C-3, C-2), 68.7 (C-6), 65.3 (C-5). HRMS (ESI) $m/z$: [M + Na]$^+$ Calcd for $C_{26}H_{24}O_6SNa$ 487.1186; Found 487.1187.

*Phenyl 6-O-Acetyl-2,3-O-isopropylydene-1-thio-α-D-mannopyranoside (**6**).* To a solution of **2** (2.0 g, 3.37 mmol) in anhydrous acetone (30 mL) were added 2,2-dimethoxypropane (1.6 mL, 12.74 mmol) and camphorsulfonic acid (147 mg, 0.637 mmol) under anhydrous conditions. The mixture was stirred at room temperature for 17 h. Then the reaction was stopped by the addition of triethylamine and concentrated under reduced pressure. The resulting residue was dissolved in DCM, and the organic layer was washed with saturated aqueous $NaHCO_3$ (3×) followed by water. The organic layers were dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The resulting residue was purified by column chromatography on silica gel (cyclohexane/EtOAc gradient from 100:0 up to 80:20) to afford **6** (1.95 g, 87%) as a colorless oil. $^{1}$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.51−7.47 (m, 2H, $H_{arom}$), 7.34−7.27 (m, 3H, $H_{arom}$), 5.82 (s, 1H, H-1), 4.47−4.41 (m, 1H, H-6), 4.35 (dd, 1H, $J$ = 5.6, 1.0 Hz, H-2), 4.22−4.15 (m, 3H, H-3, H-5, H-6′), 3.60 (dd, 1H, $J$ = 10.2, 7.5 Hz, H-4), 2.02 (s, 3H, $CH_3$), 1.52 (s, 3H, $CH_3$), 1.37 (s, 3H, $CH_3$). $^{13}$C{1H} NMR ($CDCl_3$, 100 MHz): $\delta$ 171.7 (CO), 133.0, 132.0, 129.2, 127.9 ($C_6H_5$), 110.0 ($C(CH_3)_2$), 84.0 (C-1), 78.1 (C-3), 76.3 (C-2), 69.9 (C-4), 69.4 (C-5), 63.4 (C-6), 28.3, 26.4, 20.9


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($CH_3$). HRMS (ESI) $m/z$: $[M + Na]^+$ Calcd for $C_{17}H_{22}O_6SNa$ 377.1029; Found 377.1031.

*Phenyl 6-O-Acetyl-2,3,4-tri-O-benzoyl-1-thio-α-D-mannopyranoside (**7**).* To a solution of **2** (10 g, 31.8 mmol) in dry pyridine (300 mL) was added dropwise benzoyl chloride (14.8 mL, 0.13 mol) at 0 °C under anhydrous conditions. The reaction mixture was stirred at room temperature for 17 h. The reaction mixture was then concentrated under reduced pressure. The residue was dissolved in EtOAc, and the organic layer was washed with aqueous 1 M HCl, followed by water, saturated aqueous $NaHCO_3$, and brine. The resulting aqueous layers were extracted with EtOAc, and the combined organic layers were dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The resulting residue was purified by column chromatography on silica gel (cyclohexane/EtOAc gradient from 100:0 up to 80:20) to afford **7** (18.12 g, 91%) as a white solid. $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 8.13−8.08 (m, 2H, $H_{arom}$), 8.03−7.98 (m, 2H, $H_{arom}$), 7.90−7.83 (m, 2H, $H_{arom}$), 7.71−7.23 (m, 14H, $H_{arom}$), 6.02 (t, 1H, $J$ = 10.1 Hz, H-4), 5.97 (dd, 1H, $J$ = 3.2, 1.6 Hz, H-2), 5.86 (dd, 1H, $J$ = 10.1, 3.2 Hz, H-3), 5.79 (d, 1H, $J$ = 1.6 Hz, H-1), 4.88 (ddd, 1H, $J$ = 10.1, 5.5, 2.7 Hz, H-5), 4.43 (dd, 1H, $J$ = 12.2, 5.5 Hz, H-6), 4.30 (dd, 1H, $J$ = 12.2, 2.7 Hz, H-6′). $^{13}C\{1H\}$ NMR ($CDCl_3$, 100 MHz): $\delta$ 170.6, 165.7, 165.5, 165.4 (CO), 133.8, 133.7, 133.5, 132.8, 132.3, 130.0, 130.0, 129.9, 129.4, 129.4, 129.0, 128.9, 128.7, 128.6, 128.5, 128.3 ($C_6H_5$), 86.0 (C-1), 72.0 (C-2), 70.4 (C-3), 69.8 (C-5), 67.2 (C-4), 62.9 (C-6). HRMS (ESI) $m/z$: $[M + Na]^+$ Calcd for $C_{35}H_{30}O_9SNa$ 649.1503; Found 649.1501.

*Phenyl 2,3,4-Tri-O-benzoyl-1-thio-α-D-mannopyranoside (**8**).* To a solution of **7** (4.89 g, 7.82 mmol) in a mixture of dry DCM/dry MeOH 1:1 (80 mL) was added acetyl chloride (830 μL, 11.73 mmol) under anhydrous conditions. The mixture was stirred at room temperature for 17 h. The reaction was then stopped by the addition of saturated aqueous $NaHCO_3$. The resulting aqueous layer was extracted with DCM (2×). The combined organic layers were dried over $MgSO_4$, and solvent was removed under reduced pressure to afford **8** (4.34 g, 95%) as a white solid. The measured spectroscopic data are in concordance with the literature.[66] HRMS (ESI) $m/z$: $[M + Na]^+$ Calcd for $C_{33}H_{28}O_8SNa$ 607.1397; Found 607.1405.

*Synthesis of Galactofuranosyl-Containing Disaccharides **FP**. Phenyl 2,3,5,6-Tetra-O-benzoyl-β-D-galactofuranosyl-(1→2)-3-O-benzoyl-4,6-O-benzylidene-1-thio-α-D-mannopyranoside (**10**).* To a solution of trichloroacetimidate galactofuranosyl **9b** (72 mg, 0.1 mmol) and **5** (35 mg, 0.075 mmol) in anhydrous DCM (5 mL) were added activated 4 Å molecular sieves (100 mg). The mixture was cooled to 0 °C and stirred for 15 min before dropwise addition of TMSOTf (0.02 M in DCM, 1.1 mL, 0.022 mmol). The temperature was maintained at 0 °C, and the reaction was followed by TLC (cyclohexane/EtOAc 8/2). After 2 h, no starting material remained so triethylamine was added and the solution was filtered on a pad of Celite. The resulting filtrate was evaporated under vacuo, and the residue was purified by column chromatography on silica gel (cyclohexane/EtOAc gradient from 90:10 up to 70:30) to give **10** (42 mg, 54%) as an oil. $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 8.20 (ddd, 2H, $J$ = 7.1, 2, 1.5 Hz, $H_{arom}$), 8.00 (ddd, 2H, $J$ = 8.3, 2.8, 1.7 Hz, $H_{arom}$), 7.92 (ddd, 2H, $J$ = 8.1, 2.9, 1.6 Hz, $H_{arom}$), 7.87 (ddd, 2H, $J$ = 8.0, 2.9, 1.7 Hz, $H_{arom}$), 7.80 (ddd, 2H, $J$ = 8.1, 2.9, 1.7 Hz, $H_{arom}$), 7.60 (tt, 1H, $J$ = 7.5, 1.6 Hz, $H_{arom}$), 7.53 (ddd, 2H, $J$ = 6.5, 2.9, 1.7 Hz, $H_{arom}$), 7.50−8.44 (m, 7H, $H_{arom}$), 7.40−7.27 (m, 12H, $H_{arom}$), 7.24−7.16 (m, 3H, $H_{arom}$), 5.68 (ddd, 1H, $J$ = 7.5, 4.1, 3.0 Hz, H-5b), 5.67 (d, 1H, $J$ = 1.6 Hz, H-1a), 5.63 (s, 1H, H-1b), 5.63 (dd, 1H, $J$ = 4.1, 0.9 Hz, H-3b), 5.62 (dd, 1H, $J$ = 10.3, 3.4 Hz, H-3a), 5.56 (d, 1H, $J$ = 0.9 Hz, H-2b), 5.43 (s, 1H, H-7), 4.82 (dd, 1H, $J$ = 3.4, 1.5 Hz, H-2a), 4.45 (dd, 1H, $J$ = 10.3, 9.4 Hz, H-4a), 4.38 (t, 1H, $J$ = 4.1 Hz, H-4b), 4.30 (dd, 1H, $J$ = 10.3, 5.0 Hz, H-6a), 4.27 (dd, 1H, $J$ = 12.2, 7.5 Hz, H-6b), 4.55 (td, 1H, $J$ = 10.3, 5.0 Hz, H-5a), 4.12 (dd, 1H, $J$ = 12.2, 3.0 Hz, H-6′b), 3.96 (t, 1H, $J$ = 10.3 Hz, H-6′a). $^{13}C\{1H\}$ NMR ($CDCl_3$, 100 MHz): $\delta$ 165.96, 165.70, 165.68, 165.48, 165.44 (CO), 137.28, 133.91, 133.61, 133.57, 133.44, 133.30, 133.10, 132.11, 130.06, 129.93, 129.80, 129.66, 129.55, 129.54, 129.37, 129.36, 129.26, 128.75, 128.69, 128.64, 128.59, 128.52, 128.46, 128.45, 128.05, 126,28, 125,74 ($C_6H_5$), 103.97 (C-7), 102.00 (C-1b), 85.96 (C-1a), 83.05 (C-4b), 81.53 (C-2b), 77.68 (C-3b), 76.43 (C-4a), 74.81 (C-2a), 70.56 (C-3a), 70.35 (C-5b), 68.67 (C-6a), 65.45 (C-5a), 63.65 (C-6b). HRMS (ESI) $m/z$: $[M + Na]^+$ Calcd for $C_{60}H_{50}O_{15}SNa$ 1065.2763; Found 1065.2761.

*Phenyl 2,3,5,6-Tetra-O-benzoyl-β-D-galactofuranosyl-(1→2)-3-O-benzoyl-1-thio-α-D-mannopyranoside (**11**).* To a solution of disaccharide **10** (440 mg, 0.42 mmol) in DCM (5 mL) were added 1 drop of water and TFA (180 μL, 1.33 mmol). The mixture was stirred during 1 h 30 at room temperature. The reaction was then quenched by addition of triethylamine and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (DCM/MeOH gradient from 100:0 to 95:5) to afford **11** (171 mg, 42%) as a white solid. $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 8.16−8.10 (m, 2H, $H_{arom}$), 8.00−7.93 (m, 4H, $H_{arom}$), 7.90−7.86 (m, 2H, $H_{arom}$), 7.82−7.78 (m, 2H, $H_{arom}$), 7.64−7.27 (m, 16H, $H_{arom}$), 7.25−7.15 (m, 4H, $H_{arom}$), 5.79 (dt, 1H, $J$ = 7.5, 3.4 Hz, H-5b), 5.68 (d, 1H, $J$ = 1.7 Hz, H-1a), 5.62 (d, 1H, $J$ = 4.5 Hz, H-3b), 5.52 (d, 1H, $J$ = 0.8 Hz, H-2b), 5.44 (s, 1H, H-1b), 5.40 (dd, 1H, $J$ = 9.8, 3.2 Hz, H-3a), 4.69 (dd, 1H, $J$ = 3.2, 1.7 Hz, H-2a), 4.47 (t, 1H, $J$ = 9.8 Hz, H-4a), 4.43 (t, 1H, $J$ = 4.5 Hz, H-4b), 4.37 (dd, 1H, $J$ = 12.1, 7.5 Hz, H-6b), 4.31 (dt, 1H, $J$ = 9.8, 3.6 Hz, H-5a), 4.24 (dd, 1H, $J$ = 12.1, 3.4 Hz, H-6′b), 3.96 (d, 2H, $J$ = 3.6 Hz, H-6a). $^{13}C\{1H\}$ NMR ($CDCl_3$, 100 MHz): $\delta$ 166.3, 166.0, 165.7, 165.6, 165.6 (CO), 133.9, 133.8, 133.6, 133.5, 133.3, 133.1, 132.3, 130.1, 129.9, 129.8, 129.7, 129.6, 129.5, 129.4, 129.1, 128.8, 128.7, 128.6, 128.5, 128.5, 128.4, 128.1 ($C_6H_5$), 103.8 (C-1b), 85.1 (C-1a), 82.9 (C-4b), 82.1 (C-2b), 77.7 (C-3b), 74.2 (C-2a), 74.1 (C-3a), 73.7 (C-5a), 70.3 (C-5b), 66.4 (C-4a), 63.6 (C-6b), 62.3 (C-6a). HRMS (ESI) $m/z$: $[M + Na]^+$ Calcd for $C_{53}H_{46}O_{15}SNa$ 977.2450; Found 977.2452.

*Phenyl β-D-Galactofuranosyl-(1→2)-1-thio-α-D-mannopyranoside (**12**).* To a solution of disaccharide **11** (122 mg, 0.013 mmol) in anhydrous MeOH (2 mL) was added a solution of MeONa in MeOH (0.054M, 473 μL, 25 μmol). The mixture was then stirred overnight at room temperature. Then the solution was neutralized by the addition of IR 120-$H^+$ form resin. After filtration, the filtrate was evaporated under reduced pressure. The resulting residue was suspended in water and the biphasic solution was washed with DCM (3×). The aqueous phase was finally freeze-dried to afford **12** (53 mg, 95%) as a pulverulent white powder. $^1H$ NMR ($D_2O$, 400 MHz): $\delta$ 7.64−7.57 (m, 2H, $H_{arom}$), 7.47−7.40 (m, 3H, $H_{arom}$), 5.69 (s, 1H, H-1a), 5.15 (d, 1H, $J$ = 1.0 Hz, H-1b), 4.32 (dd, 1H, $J$ = 3.5, 1.3 Hz, H-2a), 4.21−4.16 (m, 1H, H-5a), 4.16−4.14 (m, 1H, H-2b), 4.11−4.05 (m, 2H, H-4b, H-3b), 3.93 (dd, 1H, $J$ = 9.8, 3.5 Hz, H-3a), 3.88−3.76 (m, 3H, H-5b, H-6a), 3.75 (t, 1H, $J$ = 9.8 Hz, H-4a), 3.70 (dd, 1H, $J$ = 11.8, 4.4 Hz, H-6b), 3.65 (dd, 1H, $J$ = 11.6, 7.3 Hz, H-6′b). $^{13}C\{1H\}$ NMR ($D_2O$, 100 MHz): $\delta$ 132.6, 132.3, 129.4, 128.4 ($C_6H_5$), 104.8 (C-1b), 84.8 (C-1a), 82.9 (C-4b), 81.1 (C-2b), 76.7 (C-3b), 75.5 (C-2a), 73.7 (C-5a), 70.6 (C-5b), 70.3 (C-3a), 67.2 (C-4a), 62.7 (C-6b), 60.6 (C-6a). HRMS (ESI) $m/z$: $[M + Na]^+$ Calcd for $C_{18}H_{26}O_{10}SNa$ 457.1139; Found 457.1142.

*β-D-Galactofuranosyl-(1→2)-D-mannopyranose (**FP-2**).* To a solution of the disaccharide **12** (35 mg, 0.08 mmol) in a mixture of acetonitrile/$H_2O$ 1:1 (1 mL) was added *N*-iodosaccharine (87 mg, 0.28 mmol). The resulting mixture was stirred for 2 h 30 at room temperature. Then the solvent was evaporated under reduced pressure. The resulting residue was partitioned between DCM and water. The resulting organic layer was further extracted with water (2×). The combined aqueous layers were finally freeze-dried. The resulting solid was purified by column chromatography on silica gel (EtOAc/AcOH/$H_2O$/MeOH gradient from 9:0.5:0.5:0 up to 5:2:2:1) to afford **FP-2** (19 mg, 68%) as a solid. HRMS (ESI) $m/z$: $[M + Na]^+$ Calcd for $C_{12}H_{22}O_{11}Na$ 365.1054; Found 365.1057.

**FP-2*α*** (major). $^1H$ NMR ($D_2O$, 400 MHz): $\delta$ 5.32 (d, 1H, $J$ = 1.6 Hz, H-1a), 5.12 (d, 1H, $J$ = 2 Hz, H-1b), 4.15 (t, 1H, $J$ = 2.2 Hz, H-2b), 4.01 (dd, 1H, $J$ = 3.4, 1.6 Hz, H-2a), 4.09−4.07 (m, 2H, H-3b, H-4b), 3.89 (dd, 1H, $J$ = 9.7, 3.4 Hz, H-3a), 3.87 (dd, 1H, $J$ = 11.7, 2.0 Hz, H-6a), 3.85−3.81 (m, 1H, H-5a, H-5b), 3.65 (t, 1H, $J$ = 9.7 Hz, H-4a), 3.76 (dd, 1H, $J$ = 11.7, 6.0 Hz, H-6′a), 3.72 (dd, 1H, $J$ = 11.8, 4.3 Hz, H-6b), 3.65 (dd, 1H, $J$ = 11.8, 7.3 Hz, H-6′b). $^{13}C\{1H\}$


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NMR ($D_2O$, 100 MHz): δ 105.7 (C-1b), 91.3 (C-1a), 82−7 (C-4b), 81.0 (C-2b), 76.5 (C-3b), 69.4 (C-3a),72.5 (C-5a), 70.6 (C-5b), 75.5 (C-2a), 67.1 (C-4a), 62.7 (C-6b), 60.8 (C-6a).

**FP-2*β*** (minor). $^1$H NMR ($D_2O$, 400 MHz): δ 4.98 (s, 1H, H-1a), 5.27 (d, 1H, *J* = 1.7 Hz, H-1b), 4.23 (dd, 1H, *J* = 3.8, 1.7 Hz, H-2b), 4.11 (d, 1H, *J* = 3.6 Hz, H-2a), 4.16−4.12 (m, 1H, H-4b), 4.13 (dd, 1H, *J* = 6.2, 3.8 Hz, H-3b), 3.67 (dd, 1H, *J* = 9.8, 3.6 Hz, H-3a), 3.89−3.85 (o, 1H, H-6a), 3.85−3.81 (m, 1H, H-5b), 3.69−3.65 (o, 1H, H-5a), 3.90−3.87 (o, 1H, H-4a), 3.75−3.68 (o, 1H, H-6′a), 3.75−3.70 (o, 1H, H-6b), 3.67−3.63 (o, 1H, H-6′b). $^{13}$C{1H} NMR ($D_2O$, 100 MHz): δ 108.2 (C-1b), 94.0 (C-1a), 83.0 (C-4b), 80.7 (C-2b), 76.4 (C-3b), 69.4 (C-3a),72.2 (C-5a), 70.6 (C-5b), 76.7 (C-2a), 67.0 (C-4a), 62.7 (C-6b), 61.0 (C-6a).

*Phenyl 2,3,5,6-Tetra-O-benzoyl-β-D-galactofuranosyl-(1→3)-6-O-acetyl-1-thio-α-D-mannopyranoside (**13**).* Bromide donor **9a** (200 mg, 0.3 mmol), acceptor **2** (47 mg, 0.15 mmol), and 2-aminoethyl diphenylborinate (34 mg, 0.15 mmol) were suspended in dry acetonitrile (4 mL) in the presence of activated 4 Å molecular sieves under a nitrogen atmosphere. The mixture was stirred 30 min at room temperature before addition of $Ag_2O$ (35 mg, 0.15 mmol). The mixture was then allowed to stir at room temperature in the dark, and the reaction was followed by TLC (cylohexane/EtOAc 7:3 and DCM/MeOH 9:1). After 2 h of stirring, no acceptor remained. Then, the solution was filtered on a plug of Celite, and the filtrate was evaporated under vacuum. The resulting crude was purified by column chromatography on silica gel (cyclohexane/EtOAc gradient from 9:1 up to 7:3) to give **13** (127 mg, 95%) as a white solid. $^1$H NMR ($CDCl_3$, 400 MHz): δ 8.14−7.90 (m, 8H, $H_{arom}$), 7.61−7.27 (m, 12H, $H_{arom}$), 5.95 (td, 1H, *J* = 5.3, 3.5 Hz, H-5b), 5.73 (dd, 1H, *J* = 5.9, 2.1 Hz, H-3b), 5.62 (d, 1H, *J* = 1.3 Hz, H-1a), 5.49 (s, 1H, H-1b), 5.48 (dd, 1H, *J* = 2.2, 0.8 Hz, H-2b), 4.93 (dd, 1H, *J* = 5.9, 3.5 Hz, H-4b), 4.81 (d, 2H, *J* = 5.3 Hz, H-6b), 4.42 (dd, 1H, *J* = 12.1, 5.8 Hz, H-6a), 4.34 (dd, 2H, *J* = 12.2, 2.1 Hz, H-6′a), 4.34−4.32 (m, 1H,H-2a), 4.32−4.28 (m, 1H, H-5a), 3.98−3.90 (m, 2H, H-3a, H-4a), 2.06 (s, 3H, $CH_3$). $^{13}$C{1H} NMR ($CDCl_3$, 100 MHz): δ 171.4, 166.5, 166.3, 165.8, 165.7 (CO), 133.9, 133.6, 133.5, 133.4, 131.8, 130.1, 130.1, 130.0, 130.0, 129.6, 129.5, 129.2, 128.8, 128.7, 128.7, 128.6, 128.6, 127.8 ($C_6H_5$), 104.1 (C-1b), 87.4 (C-1a), 83.2 (C-2b), 81.4 (C-4b), 78.2 (C-3a), 77.0 (C-3b), 71.5 (C-5a), 70.2 (C-5b), 69.6 (C-2a), 66.3 (C-4a), 63.7 (C-6a), 63.2 (C-6b), 21.2 ($CH_3$). HRMS (ESI) *m*/*z*: $[M + Na]^+$ Calcd for $C_{48}H_{44}O_{15}SNa$ 915.2293; Found 915.2289.

*Phenyl β-D-Galactofuranosyl-(1→3)-1-thio-α-D-mannopyranoside (**14**).* To a solution of **13** (400 mg, 0.448 mmol) in anhydrous MeOH (5 mL) was added MeONa (0.54 M in MeOH, 170 μL, 0.090 mmol). The mixture was stirred for 17 h at room temperature. Then the solution was neutralized by the addition of IR 120-$H^+$ form resin. After filtration, the filtrate was evaporated under reduced pressure. The resulting residue was suspended in water, and the biphasic solution was washed with DCM (3×). The aqueous phase was finally freeze-dried to afford **14** (190 mg, 98%) as a white powder. $^1$H NMR ($D_2O$, 400 MHz): δ 7.63−7.58 (m, 2H, $H_{arom}$), 7.47−7.40 (m, 3H, $H_{arom}$), 5.57 (d, 1H, *J* = 1.7 Hz, H-1a), 5.19 (d, 1H, *J* = 1.6 Hz, H-1b), 4.44 (dd, 1H, *J* = 3.2, 1.7 Hz, H-2a), 4.24−4.20 (m, 1H, H-5a), 4.18 (dd, 1H, *J* = 3.2, 1.6 Hz, H-2b), 4.14−4.07 (m, 2H, H-3b, H-4b), 3.96 (dd, 1H, *J* = 9.7, 3.2 Hz, H-3a), 3.90−3.85 (m, 1H, H-5b), 3.82 (t, 1H, *J* = 9.7 Hz, H-4a), 3.85−3.76 (m, 2H, H-6a), 3.74 (dd, 1H, *J* = 11.8, 4.5 Hz, H-6b), 3.69 (dd, 1H, *J* = 11.8, 7.4 Hz, H-6′b). $^{13}$C{1H} NMR ($D_2O$, 100 MHz): δ 132.6, 132.2, 129.4, 128.4 ($C_6H_5$), 104.3 (C-1b), 87.8 (C-1a), 82.9 (C-4b), 81.3 (C-2b), 77.0 (C-3b), 75.6 (C-3a), 73.5 (C-5a), 70.7 (C-5b), 68.1 (C-2a), 65.3 (C-4a), 62.8 (C-6b), 60.7 (C-6a). HRMS (ESI) *m*/*z*: $[M + Na]^+$ Calcd for $C_{18}H_{26}O_{10}SNa$ 457.1139; Found 457.1138.

*β-D-Galactofuranosyl-(1→3)-D-mannopyranose (**FP-3**).* To a solution of **14** (14 mg, 0.032 mmol) in a mixture of acetonitrile/$H_2O$ 1:1 (4 mL) was added *N*-iodosaccharine (35 mg, 0.113 mmol). The mixture was stirred for 2 h at room temperature. Then $Et_3N$ was added, and the resulting reaction mixture was concentrated under reduced pressure. The residue was partitioned between DCM and water. The resulting organic layer was further extracted with water (2×). The combined aqueous layers were finally freeze-dried. The resulting solid was purified by column chromatography on silica gel (EtOAc/AcOH/$H_2O$/MeOH gradient from 9:0.5:0.5:0 up to 5:2:2:1) to afford **FP-3** (10 mg, 93%) as a solid. HRMS (ESI) *m*/*z*: $[M + Na]^+$ Calcd for $C_{12}H_{22}O_{11}Na$ 365.1054; Found 365.1058.

**FP-3*α*** (major). $^1$H NMR ($D_2O$, 400 MHz): δ 5.24 (d, 1H, *J* = 1.8 Hz, H-1a), 5.18 (d, 1H, *J* = 1.5 Hz, H-1b), 4.18 (dd, 1H, *J* = 3.0, 1.5 Hz, H-2b), 4.15 (dd, 1H, *J* = 3.2, 1.8 Hz, H-2a), 4.10 (dd, 1H, *J* = 6.6, 3.0 Hz, H-3b), 4.09 (dd, 1H, *J* = 6.6, 3.8 Hz, H-4b), 3.95 (dd, 1H, *J* = 9.5, 3.2 Hz, H-3a), 3.92 (dd, 1H, *J* = 12.3, 2.3 Hz, H-6a), 3.90−3.85 (m, 2H, H-5a, H-5b), 3.77 (t, 1H, *J* = 9.5 Hz, H-4a), 3.77 (dd, 1H, *J* = 12.3, 6.1 Hz, H-6′a), 3.74 (dd, 1H, *J* = 11.6, 4.4 Hz, H-6b), 3.69 (dd, 1H, *J* = 11.6, 7.0 Hz, H-6′b). $^{13}$C{1H} NMR ($D_2O$, 100 MHz): δ 104.4 (C-1b), 93.9 (C-1a), 83.0 (C-4b), 81.4 (C-2b), 77.0 (C-3b), 75.1 (C-3a), 72.6 (C-5a), 70.7 (C-5b), 67.4 (C-2a), 65.1 (C-4a), 62.7 (C-6b), 61.1 (C-6a).

**FP-3*β*** (minor). $^1$H NMR ($D_2O$, 400 MHz): δ 5.20 (d, 1H, *J* = 1.4 Hz, H-1b), 4.92 (s, 1H, H-1a), 4.18 (dd, 1H, *J* = 3.0, 1.5 Hz, H-2b), 4.10 (d, 1H, *J* = 3.1 Hz, H-2a), 4.11 (dd, 1H, *J* = 6.6, 3.0 Hz, H-3b), 4.09 (dd, 1H, *J* = 6.6, 3.8 Hz, H-4b), 3.83−3.79 (m, 1H, H-3a), 3.94 (dd, 1H, *J* = 11.9, 2.2 Hz, H-6a), 3.90−3.85 (m, 1H, H-5b), 3.83−3.74 (o, 1H, H-6′a), 3.74 (dd, 1H, *J* = 11.6, 4.4 Hz, H-6b), 3.69 (dd, 1H, *J* = 11.6, 7.0 Hz, H-6′b), 3.68 (dd, 1H, *J* = 9.9, 3.1 Hz, H-4a), 3.45 (ddd, 1H, *J* = 9.9, 6.3, 2.2 Hz, H-5a). $^{13}$C{1H} NMR ($D_2O$, 100 MHz): δ 104.1 (C-1b), 93.6 (C-1a), 82.9 (C-4b), 81.4 (C-2b), 77.4 (C-3a), 77.1 (C-3b), 76.0 (C-5a), 70.7 (C-5b), 67.7 (C-2a), 64.9 (C-4a), 62.7 (C-6b), 61.0 (C-6a).

*Phenyl 2,3,5,6-Tetra-O-benzoyl-β-D-galactofuranosyl-(1→4)-6-O-acetyl-3,4-O-isopropylidene-1-thio-α-D-mannopyranoside (**15**).* To a solution of galactofuranosyl trichloroacetimidate **9b** (50 mg, 70 μmol) and **6** (18 mg, 50 μmol) in anhydrous DCM (5 mL) were added activated 4 Å molecular sieves (100 mg). The mixture was cooled to 0 °C and stirred for 15 min before dropwise addition of TMSOTf (0.02 M in DCM, 750 μL, 15 μmol). The temperature was maintained at 0 °C, and the reaction was followed by TLC (cyclohexane/EtOAc 7:3). After 2 h, no starting material remained so triethylamine was added and the solution was filtered on a pad of Celite. The resulting filtrate was evaporated under vacuo and the residue was purified by column chromatography on silica gel (cyclohexane/EtOAc gradient from 9:1 up to 7:3) to give **15** (34 mg, 71%) as an oil. $^1$H NMR ($CDCl_3$, 400 MHz): δ 8.14−8.07 (m, 4H, $H_{arom}$), 8.00−7.96 (m, 2H, $H_{arom}$), 7.87−7.83 (m, 2H, $H_{arom}$), 7.63−7.27 (m, 17 H, $H_{arom}$), 6.18 (dt, 1H, *J* = 8.0, 3.5 Hz, H-5b), 5.84 (s, 1H, H-1a), 5.61 (dt, 1H, *J* = 5.4, 0.9 Hz, H-3b), 5.39−5.36 (m, 2H, H-2b, H-1b), 4.84 (dd, 1H, *J* = 5.4, 2.9 Hz, H-4b), 4.79 (dd, 1H, *J* = 12.1, 3.5 Hz, H-6b), 4.74 (dd, 1H, *J* = 12.1, 8.0 Hz, H-6′b), 4.42−4.31 (m, 3H, H-5a, H-6a), 4.35 (dd, 1H, *J* = 5.5, 0.9 Hz, H-2a), 4.27 (dd, 1H, *J* = 7.3, 5.5 Hz, H-3a), 3.92 (dd, 1H, *J* = 9.8, 7.3 Hz, H-4a), 1.96 (s, 3H, $COCH_3$), 1.65 (s, 3H, $CH_3$), 1.37 (s, 3H, $CH_3$). $^{13}$C{1H} NMR ($CDCl_3$, 100 MHz): δ 170.7, 166.4, 165.9, 165.9, 165.8 (CO), 133.7, 133.5, 133.4, 133.2, 133.0, 131.9, 130.2, 130.1, 130.0, 129.9, 129.7, 129.3, 129.2, 128.9, 128.7, 128.6, 128.5, 128.5, 127.9 ($C_6H_5$), 110.1 ($C(CH_3)_2$), 105.7 (C-1b), 84.1 (C-1a), 82.4 (C-2b), 81.6 (C-4b), 77.4, 77.3 (C-3a, C-3b), 76.5 (C-2a), 75.1 (C-4a), 70.3 (C-5b), 68.3 (C-5a), 64.8 (C-6b), 62.8 (C-6a), 28.0, 26.6 ($CH_3$), 21.0 ($COCH_3$). HRMS (ESI) *m*/*z*: $[M + Na]^+$ Calcd for $C_{51}H_{48}O_{15}SNa$ 955.2606; Found 955.2605.

*Phenyl 2,3,5,6-Tetra-O-benzoyl-β-D-galactofuranosyl-(1→4)-6-O-acetyl-1-thio-α-D-mannopyranoside (**16**).* To a solution of **15** (108 mg, 0.116 mmol) in DCM (5 mL) were added 1 drop of water and TFA (44 μL, 0.579 mmol). The mixture was stirred during 15 h at room temperature. Then the reaction was quenched by addition of triethylamine, and the solvent was removed under reduced pressure. The resulting residue was purified by column chromatography on silica gel (cyclohexane/EtOAc gradient from 1:0 to 6:4) to afford **16** (103 mg, 100%) as a white solid. $^1$H NMR ($CDCl_3$, 400 MHz): δ 8.12−7.89 (m, 7H, $H_{arom}$), 7.62−7.27 (m, 18H, $H_{arom}$), 6.00 (dt, 1H, *J* = 6.2, 4.7 Hz, H-5b), 5.73 (dd, 1H, *J* = 5.2, 1.8 Hz, H-3b), 5.60 (d, 1H, *J* = 1.4 Hz, H-1a), 5.47 (dd, 1H, *J* = 1.9, 0.8 Hz, H-2b), 5.39 (s, 1H, H-1b), 4.91 (dd, 1H, *J* = 5.1, 4.6 Hz, H-4b), 4.81 (dd, 1H, *J* =


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11.9, 4.7 Hz, H-6b), 4.72 (dd, 1H, $J$ = 11.9, 6.2 Hz, H-6′b), 4.49–4.38 (m, 3H, H-5a, H-6a), 4.21 (dd, 1H, $J$ = 2.6, 1.4 Hz, H-2a), 3.96–3.90 (m, 2H, H-3a, H-4a), 2.00 (s, 3H, $CH_3$). $^{13}C\{1H\}$ NMR ($CDCl_3$, 100 MHz): $\delta$ 170.9, 166.3, 165.8, 165.7, 165.7 (CO), 133.9, 133.8, 133.6, 133.6, 133.4, 131.7, 130.1, 130.1, 130.0, 129.9, 129.5, 129.4, 129.3, 128.8, 128.7, 128.7, 128.7, 128.6, 127.8 ($C_6H_5$), 108.0 (C1-b), 87.2 (C-1a), 82.6 (C-2b), 82.0 (C-4b), 78.7 (C-4a), 77.2 (C-3b), 71.9 (C-2a), 70.8 (C-3a), 70.4 (C-5b), 69.4 (C-5a), 63.1, 63.0 (C-6a, C-6b), 21.2 ($CH_3$). HRMS (ESI) $m/z$: $[M + Na]^+$ Calcd for $C_{48}H_{44}O_{15}SNa$ 915.2293; Found 915.2290.

*Phenyl β-D-Galactofuranosyl-(1→4)-1-thio-α-D-mannopyranoside (**17**).* To a solution of **16** (275 mg, 0.31 mmol) in anhydrous MeOH (3 mL) was added MeONa (0.54 M in MeOH, 120 μL, 0.062 mmol). The mixture was stirred for 17 h at room temperature. Then the solution was neutralized by the addition of IR 120-$H^+$ form resin. After filtration, the filtrate was evaporated under reduced pressure. The resulting residue was suspended in water, and the biphasic solution was washed with DCM (3×). The aqueous phase was finally freeze-dried to afford **17** (122 mg, 91%) as a white powder. $^1H$ NMR ($D_2O$, 400 MHz): $\delta$ 7.58–7.54 (m, 2H, $H_{arom}$), 7.43–7.37 (m, 3H, $H_{arom}$), 5.50 (d, 1H, $J$ = 1.8 Hz, H-1a), 5.08 (d, 1H, $J$ = 2.2 Hz, H-1b), 4.24 (dd, 1H, $J$ = 3.3, 1.8 Hz, H-2a), 4.24–4.20 (m, 1H, H-5a), 4.13–4.05 (m, 3H, H-2b, H-3b, H-4b), 3.95 (dd, 1H, $J$ = 9.5, 3.3 Hz, H-3a), 3.85 (t, 1H, $J$ = 9.6 Hz, H-4a), 3.83–3.78 (m, 3H, H-6a, H-5b), 3.69 (dd, 1H, $J$ = 11.7, 4.6 Hz, H-6b), 3.64 (dd, 1H, $J$ = 11.7, 7.3 Hz, H-6′b). $^{13}C\{1H\}$ NMR ($D_2O$, 100 MHz): $\delta$ 132.6, 132.3, 129.4, 128.3 ($C_6H_5$), 107.9 (C-1b), 87.9 (C-1a), 82.6 (C-4b), 81.0 (C-2b), 75.9 (C-3b), 75.2 (C-4a), 72.4 (C-5a), 71.3 (C-2a), 70.5 (C-5b), 69.7 (C-3a), 62.7 (C-6b), 60.1 (C-6a). HRMS (ESI) $m/z$: $[M + Na]^+$ Calcd for $C_{18}H_{26}O_{10}SNa$ 457.1139; Found 457.1135.

*β-D-Galactofuranosyl-(1→4)-D-mannopyranose (**FP-4**).* To a solution of **17** (100 mg, 0.23 mmol) in a mixture of acetonitrile/$H_2O$ 1:1 (10 mL) was added *N*-iodosaccharine (249 mg, 0.81 mmol). The mixture was stirred for 1 h at room temperature. Then the reaction mixture was concentrated under reduced pressure, and the residue was partitioned between DCM and water. The resulting organic layer was further extracted with water (2×). The combined aqueous layers were finally freeze-dried. The resulting solid was purified by column chromatography on silica gel (EtOAc/AcOH/$H_2O$/MeOH gradient from 9:0.5:0.5:0 up to 5:2:2:1) to afford **FP-4** (87 mg, 100%) as a solid. HRMS (ESI) $m/z$: $[M + Na]^+$ Calcd for $C_{12}H_{22}O_{11}Na$ 365.1054; Found 365.1058.

**FP-4*α*** (major). $^1H$ NMR ($(CD_3)_2CO$, 500 MHz): $\delta$ 5.07 (d, 1H, $J$ = 1.7 Hz, H-1a), 5.01 (d, 1H, $J$ = 2.5 Hz, H-1b), 3.99 (dd, 1H, $J$ = 4.5, 2.5 Hz, H-2b), 4.091 (dd, 1H, $J$ = 6.6, 3.3 Hz, H-4b), 4.04 (dd, 1H, $J$ = 6.6, 4.5 Hz, H-3b), 3.86–3.81 (m, 1H, H-4a), 3.84–3.82 (m, 1H, H-2a), 3.83–3.79 (m, 1H, H-3a), 3.78–3.69 (m, 3H, H-6a, H-5a), 3.73 (dt, 1H, $J$ = 6.4, 3.3 Hz, H-5b), 3.57–3.61 (m, 2H, H-6b). $^{13}C\{1H\}$ NMR ($D_2O$, 125 MHz): $\delta$ 109.07 (C-1b), 94.81 (C-1a), 83.80 (C-4b), 81.92 (C-2b), 77.27 (C-3b), 75.62 (C-4a), 72.00 (C-5a), 71.74 (C-2a), 71.32 (C-5b), 70.22 (C-3a), 63.46 (C-6b), 61.27 (C-6a).

**FP-4*β*** (minor). $^1H$ NMR ($(CD_3)_2CO$, 500 MHz): $\delta$ 5.01 (d, 1H, $J$ = 2.5 Hz, H-1b), 4.75 (d, 1H, $J$ = 1.1 Hz, H-1a), 4.093 (dd, 1H, $J$ = 6.6, 3.3 Hz, H-4b), 4.04 (dd, 1H, $J$ = 6.6, 4.5 Hz, H-3b), 3.98 (dd, 1H, $J$ = 4.5, 2.5 Hz, H-2b), 3.86 (dd, 1H, $J$ = 3.3, 1.1 Hz, H-2a), 3.78 (dd, 1H, $J$ = 12.1, 2.2 Hz, H-6a), 3.75 (t, 1H, $J$ = 9.6 Hz, H-4a), 3.726 (dt, 1H, $J$ = 6.4, 3.3 Hz, H-5b), 3.70 (dd, 1H, $J$ = 12.1, 4.6 Hz, H-6′a), 3.60 (dd, 1H, $J$ = 9.6, 3.3 Hz, H-3a), 3.57–3.61 (m, 2H, H-6b), 3.31 (ddd, 1H, $J$ = 9.6, 4.6, 2.2 Hz, H-5a). $^{13}C\{1H\}$ NMR ($D_2O$, 125 MHz): $\delta$ 109.07 (C-1b), 94.70 (C-1a), 83.93 (C-4b), 81.88 (C-2b), 77.27 (C-3b), 76.09 (C-5a), 75.04 (C-4a), 73.08 (C-3a), 71.99 (C-2a), 71.32 (C-5b), 63.41 (C-6b), 61.23 (C-6a).

*Phenyl 2,3,5,6-Tetra-O-benzoyl-β-D-galactofuranosyl-(1→6)-2,3,4-tri-O-benzoyl-1-thio-α-D-mannopyranoside (**18**).* To a solution of donor **9a** (850 mg, 1.29 mmol) and acceptor **8** (502 mg, 0.86 mmol) in anhydrous dichloromethane (10 mL) were added activated 4 Å molecular sieves. The media was stirred during 15 min at room temperature under nitrogen atmosphere. Then AgOTf (244 mg, 0.95 mmol) was added, and the reaction was stirred in the dark for 6 h. Then the reaction was quenched by addition of triethylamine, and the resulting suspension was filtered on Celite. The filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel (cyclohexane/EtOAc gradient from 1:0 up to 7:3) to afford 18 (930 mg, 93%) as a white powder. $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 8.11–7.81 (m, 16H, $H_{arom}$), 7.65–7.40 (m, 13H, $H_{arom}$), 7.38–7.21 (m, 10H, $H_{arom}$), 7.17–7.11 (m, 1H, $H_{arom}$), 5.98 (t, 1H, $J$ = 10.0 Hz, H-4a), 5.98–5.95 (m, 1H, H-2a), 5.95–5.94 (m, 1H, H-5b), 5.86 (dd, 1H, $J$ = 10.0, 3.2 Hz, H-3a), 5.76 (d, 1H, $J$ = 1.5 Hz, H-1a), 5.61 (ddd, 1H, $J$ = 5.1, 1.4, 0.6 Hz, H-3b), 5.56 (d, 1H, $J$ = 1.4 Hz, H-2b), 5.39 (s, 1H, H-1b), 4.91 (ddd, 1H, $J$ = 8.9, 6.5, 2.1 Hz, H-5a), 4.67–4.63 (m, 2H, H-6b), 4.61 (dd, 1H, $J$ = 5.1, 3.7 Hz, H-4b), 4.05 (dd, 1H, $J$ = 11.5, 2.3 Hz, H-6a), 3.92 (dd, 1H, $J$ = 11.5, 6.5 Hz, H-6′a). $^{13}C\{1H\}$ NMR ($CDCl_3$, 100 MHz): $\delta$ 166.2, 165.8, 165.7, 165.7, 165.6, 165.6, 165.3 (CO),133.7, 133.6, 133.4, 133.4, 133.3, 133.1, 132.3, 132.2, 130.1, 130.1, 130.0, 130.0, 129.9, 129.9, 129.8, 129.7, 129.6, 129.4, 129.4, 129.3, 129.2, 129.0, 129.0, 128.8, 128.8, 128.7, 128.6, 128.5, 128.5, 128.4, 128.4, 128.3 ($C_6H_5$), 106.6 (C-1b), 86.2 (C-1a), 82.0 (C-4b), 81.9 (C-2b), 77.7 (C-3b), 72.2 (C-5b), 71.4 (C-5a), 70.5, 70.5 (C-2a, C-3a), 67.6 (C-4a), 66.9 (C-6a), 63.7 (C-6b). HRMS (ESI) $m/z$: $[M + Na]^+$ Calcd for $C_{67}H_{54}O_{17}SNa$ 1185.2974; Found 1185.2972.

*Phenyl β-D-Galactofuranosyl-(1→6)-1-thio-α-D-mannopyranoside (**19**).* To a solution of **18** (688 mg, 0.59 mmol) in anhydrous MeOH (10 mL) was added MeONa (5.4 M in MeOH, 27 μL, 0.14 mmol). The mixture was stirred for 17 h at room temperature. Then the solution was neutralized by the addition of IR 120-$H^+$ form resin. After filtration, the filtrate was evaporated under reduced pressure. The resulting residue was suspended in water and the biphasic solution was washed with DCM (3×). The aqueous phase was finally freeze-dried to afford **19** (257 mg, 100%) as a powder. $^1H$ NMR ($CD_3OD$, 400 MHz): $\delta$ 7.57–7.53 (m, 2H, $H_{arom}$), 7.37–7.26 (m, 3H, $H_{arom}$), 5.37 (d, 1H, $J$ = 1.2 Hz, H-1a), 4.93 (s, 1H, H-1b), 4.21 (ddd, 1H, $J$ = 8.7, 6.3, 2.3 Hz, H-5a), 4.08 (dd, 1H, $J$ = 2.9, 1.6 Hz, H-2a), 4.02 (dd, 1H, $J$ = 11.0, 2.3 Hz, H-6a), 4.00–3.95 (m, 3H, H-2b, H-3b, H-4b), 3.74–3.64 (m, 4H, H-3a, H-4a, H-6′a, H-5b), 3.61 (d, 2H, $J$ = 6.2 Hz, H-6b). $^{13}C\{1H\}$ NMR ($CD_3OD$, 100 MHz): $\delta$ 135.7, 133.2, 132.9, 130.1, 128.6 ($C_6H_5$), 109.9 (C-1b), 90.5 (C-1a), 84.8 (C-4b), 83.0 (C-2b), 79.1 (C-3b), 74.4 (C-5a), 73.6 (C-2a), 73.1 (C-3a), 72.5 (C-5b), 69.1 (C-4a), 68.2 (C-6a), 64.6 (C-6b). HRMS (ESI) $m/z$: $[M + Na]^+$ Calcd for $C_{18}H_{26}O_{10}SNa$ 457.1139; Found 457.1140.

*β-D-Galactofuranosyl-(1→6)-D-mannopyranose (**FP-6**).* To a solution of **19** (270 mg, 0.62 mmol) in a mixture of acetonitrile/$H_2O$ 1:1 (10 mL) was added *N*-iodosaccharine (731 mg, 2.36 mmol). The mixture was stirred for 1 h at room temperature. Then the reaction mixture was concentrated under reduced pressure, and the residue was partitioned between DCM and water. The resulting organic layer was further extracted with water (2×). The combined aqueous layers were finally freeze-dried. The resulting solid was purified by column chromatography on silica gel (EtOAc/AcOH/$H_2O$/MeOH gradient from 9:0.5:0.5:0 up to 5:2:2:1) to afford **FP-6** (193 mg, 89%) as a solid. HRMS (ESI) $m/z$: $[M + Na]^+$ Calcd for $C_{12}H_{22}O_{11}Na$ 365.1054; Found 365.1058.

**FP-6*α***. $^1H$ NMR ($CD_3OD$, 500 MHz): $\delta$ 5.06 (d, 1H, $J$ = 1.8 Hz, H-1a), 4.95 (s, 1H, H-1b), 4.02 (dd, 1H, $J$ = 4.7, 3.2 Hz, H-4b), 3.99–3.96 (m, 2H, H-2b, H-3b), 3.96 (dd, 1H, $J$ = 10.9, 2.5 Hz, H-6a), 3.89 (ddd, 1H, $J$ = 9.6, 5.6, 2.5 Hz, H-5a), 3.79 (dd, 1H, $J$ = 3.3, 1.8 Hz, H-2a), 3.75–3.71 (m, 1H, H-5b), 3.75 (dd, 1H, $J$ = 9.2, 3.3 Hz, H-3a), 3.65 (dd, 1H, $J$ = 10.9, 5.6 Hz, H-6′a), 3.64–3.59 (m, 2H, H-6b), 3.61 (t, 1H, $J$ = 9.6 Hz, H-4a). $^{13}C\{1H\}$ NMR ($CD_3OD$, 125 MHz): $\delta$ 109.45 (C-1b), 95.60 (C-1a), 84.97 (C-4b), 82.12 (C-2b), 78.82 (C-3b), 72.41 (C-2a), 72.31, 72.28 (C-5a, C-5b), 71.92 (C-3a), 68.96 (C-4a), 68.17 (C-6a), 64.18 (C-6b).

**FP-6*β***. $^1H$ NMR ($CD_3OD$, 500 MHz): $\delta$ 4.95 (s, 1H, H-1b), 4.73 (d, 1H, $J$ = 0.9 Hz, H-1a), 4.02–4.01 (o, 1H, H-3b), 4.02–3.96 (o, 1H, H-6a), 4.00–3.98 (o, 1H, H-4b), 3.98–3.96 (o, 1H, H-2b), 3.91–3.88 (o, 1H, H-5b), 3.81 (dd, 1H, $J$ = 3.3, 0.9 Hz, H-2a), 3.66–3.60 (m, 3H, H-6′a, H-6b), 3.56 (t, 1H, $J$ = 9.6 Hz, H-4a), 3.44 (dd, 1H, $J$ = 9.6, 3.3 Hz, H-3a), 3.35 (ddd, 1H, $J$ = 9.6, 5.9, 2.6 Hz, H-5a).


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$^{13}C\{1H\}$ NMR ($CD_3OD$, 100 MHz): $\delta$ 109.56 (C-1b), 95.35 (C-1a), 85.00 (C-4b), 82.16 (C-2b), 78.80 (C-3b), 76.37 (C-5a), 75.01 (C-3a), 72.72 (C-2a), 72.31 or 72.28 (C-5b), 68.48 (C-4a), 68.06 (C-6a), 64.18 (C-6b).

*Synthesis of Galactopyranosyl-Containing Disaccharides* ***PP****. Phenyl 2,3,4,6-Tetra-O-benzoyl-β-D-galactopyranosyl-(1→2)-3-O-benzoyl-1-thio-α-D-mannopyranoside (**21**).* To a solution of trichloroacetimidate galactopyranosyl **20b** (207 mg, 0.28 mmol) and **5** (100 mg, 0.21 mmol) in anhydrous DCM (10 mL) were added activated 4 Å molecular sieves (100 mg). The mixture was cooled to 0 °C and stirred for 15 min before dropwise addition of TMSOTf (0.02 M in DCM, 3.2 mL, 0.06 mmol). The temperature was maintained at 0 °C and reaction was followed by TLC (cyclohexane/EtOAc 8/2). After 2 h, no starting material remained, so triethylamine was added and the solution was filtered on a pad of Celite. The filtrate was evaporated in vacuo. The resulting residue was dissolved in DCM (10 mL), and water (10 μL) and TFA (124 μL, 1.62 mmol) were added successively. The reaction mixture was stirred at room temperature for 24 h. Then triethylamine was added, and the reaction media was washed with water (3×), dried over $MgSO_4$, and evaporated. The residue was purified by column chromatography on silica gel (cyclohexane/EtOAc gradient from 90:10 up to 60:40) to give **21** (53 mg, 26% over two steps) as an oil. $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 8.12 (dd, 2H, $J$ = 8.5, 1.3 Hz, $H_{arom}$), 8.09 (dd, 2H, $J$ = 8.6, 1.3 Hz, $H_{arom}$), 7.94 (dd, 2H, $J$ = 8.5, 1.2 Hz, $H_{arom}$), 7.88 (dd, 2H, $J$ = 8.4, 1.3 Hz, $H_{arom}$), 7.76 (dd, 2H, $J$ = 8.4, 1.2 Hz, $H_{arom}$), 7.68 (tt, 1H, $J$ = 7.5, 1.3 Hz, $H_{arom}$), 7.59−7.51 (m, 3H, $H_{arom}$), 7.49−7.18 (m, 12H, $H_{arom}$), 7.14 (td, 2H, $J$ = 7.3, 1.3 Hz, $H_{arom}$), 7.07 (dd, 2H, $J$ = 7.3, 1.3 Hz, $H_{arom}$), 5.89 (dd, 1H, $J$ = 3.5, 0.9 Hz, H-4b), 5.81 (dd, 1H, $J$ = 10.5, 7.8 Hz, H-2b), 5.61 (dd, 1H, $J$ = 10.5, 3.5 Hz, H-3b), 5.24 (d, 1H, $J$ = 2.1 Hz, H-1a), 5.21 (dd, 1H, $J$ = 9.7, 3.1 Hz, H-3a), 4.75 (d, 1H, $J$ = 7.8 Hz, H-1b), 4.56 (dd, 1H, $J$ = 3.1, 2.1 Hz, H-2a), 4.53 (t, 1H, $J$ = 9.7 Hz, H-4a), 4.14 (dd, 1H, $J$ = 6.5, 0.9 Hz, H-5b), 4.04 (apparent td, 1H, $J$ = 9.7, 3.0 Hz, H-5a), 4.00 (dd, 1H, $J$ = 11.4, 6.5 Hz, H-6b), 3.93 (dd, 1H, $J$ = 11.4, 6.5 Hz, H-6′b), 3.79 (dd, 1H, $J$ = 12.1, 3.6 Hz, H-6a), 3.68 (dd, 1H, $J$ = 12.1, 2.4 Hz, H-6′a). $^{13}C\{1H\}$ NMR ($CDCl_3$, 100 MHz): $\delta$ 166.77, 165.89, 165.57, 165.48 (COPh), 134.03, 133.89, 133.56, 133.53, 133.38, 130.31, 130.13, 130.07, 129.95, 129.92, 129.90, 129.64, 129.45, 129.33, 129.22, 129.14, 128.88, 128.80, 128.72, 128.54, 128.46, 128.35, 127.25 ($C_6H_5$), 101.44 (C-1b), 85.28 (C-1a), 77.90 (C-2a), 73.80 (C-3a), 73.55 (C-5a), 71.60 (C-5b), 71.01 (C-3b), 70.24 (C-2b), 68.00 (C-4b), 65.11 (C-4a), 61.97 (C-6a), 61.70 (C-6b). HRMS (ESI) $m/z$: $[M + Na]^+$ Calcd for $C_{53}H_{46}O_{15}SNa$ 977,2455; Found 977,2536.

*Phenyl β-D-Galactopyranosyl-(1→2)-1-thio-α-D-mannopyranoside (**22**).* To a solution of **21** (36 mg, 0.05 mmol) in anhydrous MeOH (1 mL) was added MeONa (0.054 M in MeOH, 200 μL, 11 μmol). The mixture was stirred for 17 h at room temperature. Then the solution was neutralized by the addition of IR 120-$H^+$ form resin. After filtration, the filtrate was evaporated under reduced pressure. The resulting residue was suspended in water and the biphasic solution was washed with DCM (3×). The aqueous phase was finally freeze-dried to afford **22** (20 mg, 91%) as a powder. $^1H$ NMR ($D_2O$, 400 MHz): $\delta$ 7.64−7.57 (m, 2H, $H_{arom}$), 7.47−7.39 (m, 3H, $H_{arom}$), 5.67 (d, 1H, $J$ = 1.4 Hz, H-1a), 4.91 (dd, 1H, $J$ = 3.4, 1.1 Hz, H-4b), 4.46 (d, 1H, $J$ = 7.5 Hz, H-1b), 4.44 (dd, 1H, $J$ = 3.5, 1.4 Hz, H-2a), 4.17 (ddd, 1H, $J$ = 9.9, 4.5, 2.9 Hz, H-5a), 3.94 (dd, 1H, $J$ = 9.9, 3.5 Hz, H-3a), 3.85−3.81 (m, 2H, H-6a), 3.81 (dd, 1H, $J$ = 12.0, 7.9 Hz, H-6b), 3.80 (t, 1H, $J$ = 9.9 Hz, H-4a), 3.74 (dd, 1H, $J$ = 12.0, 3.9 Hz, H-6′b), 3.66 (ddd, 1H, $J$ = 7.9, 3.9, 1.1 Hz, H-5b), 3.64 (dd, 1H, $J$ = 11.1, 3.3 Hz, H-3b), 3.57 (dd, 1H, $J$ = 11.1, 7.5 Hz, H-2b). $^{13}C\{1H\}$ NMR ($D_2O$, 100 MHz): $\delta$ 132.71, 132.14, 129.45, 128.47 ($C_6H_5$), 101.45 (C-1b), 85.83 (C-1a), 78.17 (C-2a), 75.25 (C-5b), 73.56 (C-5a), 72.47 (C-3b), 70.40 (C-2b), 70.32 (C-3a), 68.60 (C-4b), 66.97 (C-4a), 61.11 (C-6b), 60.19 (C-6a). HRMS (ESI) $m/z$: $[M + Na]^+$ Calcd for $C_{18}H_{26}O_{10}SNa$ 457.1139; Found 457.1141.

*β-D-Galactopyranosyl-(1→2)-D-mannopyranoside (**PP-2**).* To a solution of **22** (18 mg, 4 μmol) in a mixture of acetonitrile/$H_2O$ 1:1 (5 mL) was added *N*-iodosaccharine (45 mg, 15 μmol). The mixture was stirred for 2 h at room temperature. Then the reaction mixture was concentrated under reduced pressure, and the residue was partitioned between DCM and water. The resulting organic layer was further extracted with water (2×). The combined aqueous layers were finally freeze-dried. The resulting solid was purified by column chromatography on silica gel (EtOAc/AcOH/$H_2O$/MeOH gradient from 9:0.5:0.5:0 up to 5:2:2:1) to afford **PP-2** (10 mg, 72%) as a solid. HRMS (ESI) $m/z$: $[M + Na]^+$ Calcd for $C_{12}H_{22}O_{11}Na$ 365.1054; Found 365.1056.

**PP-2*α*** (major). $^1H$ NMR ($(CD_3)_2CO$, 500 MHz): $\delta$ 5.22 (d, 1H, $J$ = 1.8 Hz, H-1a),4.38−4.33 (m, 1H, H-1b), 3.98 (dd, 1H, $J$ = 3.4, 1.8 Hz, H-2a), 3.85−3.84 (m, 1H, H-3b), 3.77 (dd, 1H, $J$ = 9.5, 3.4 Hz, H-3a), 3.75−3.72 (m, 2H, H-5a, H-6b), 3.74−3.72 (m, 2H, H-6a), 3.65 (dd, 1H, $J$ = 11.7, 4.0 Hz, H-6′b), 3.65 (t, 1H, $J$ = 9.5 Hz, H-4a), 3.60 (ddd, 1H, $J$ = 7.8, 4.2, 0.9 Hz, H-5b), 3.59−3.56 (m, 1H, H-4b), 3.57−3.55 (m, 1H, H-2b). $^{13}C\{1H\}$ NMR ($(CD_3)_2CO$, 125 MHz): $\delta$ 103.3 (C-1b), 92.92 (C-1a), 79.16 (C-2a), 75.99 (C-5b), 73.3 (C-4b), 73.09 (C-5a), 71.10 (C-2b), 70.32 (C-3a), 69.25 (C-3b), 67.87 (C-4a), 61.66 (C-6b), 60.86 (C-6a).

**PP-2*β*** (minor). $^1H$ NMR ($(CD_3)_2CO$, 500 MHz): $\delta$ 4.84 (d, 1H, $J$ = 0.9 Hz, H-1a), 4.44 (d, 1H, $J$ = 7.7 Hz, H-1b), 4.05 (dd, 1H, $J$ = 2.9, 0.9 Hz, H-2a), 3.85−3.84 (o, 1H, H-3b), 3.81 (o, 2H, H-6a), 3.73 (o, 1H, H-6b), 3.67 (o, 1H, H-6′b), 3.64 (o, 1H, H-2b), 3.62 (o, 1H, H-5b), 3.58−3.54 (o, 1H, H-3a), 3.56 (o, 1H, H-4b), 3.54 (o, 1H, H-4a), 3.25 (ddd, 1H, $J$ = 8.3, 5.9, 2.2 Hz, H-5a). $^{13}C\{1H\}$ NMR ($(CD_3)_2CO$, 125 MHz): $\delta$ 105.22 (C-1b), 94.37 (C-1a), 81.50 (C-2a), 77.14 (C-5a), 76.21 (C-5b), 73.44 (C-4b), 73.14 (C-3a), 71.81 (C-2b), 69.28 (C-3b), 67.70 (C-4a), 61.52 (C-6a), 61.61 (C-6b).

*Phenyl 2,3,4,6-Tetra-O-acetyl-β-D-galactopyranosyl-(1→3)-6-O-acetyl-1-thio-α-D-mannopyranoside (**23**).* Bromide donor **20a** (956 mg, 2.3 mmol), acceptor **2** (487 mg, 1.55 mmol), and 2-aminoethyl diphenylborinate (349 mg, 1.55 mmol) were suspended in anhydrous $CH_3CN$ (20 mL) in the presence of activated 4 Å molecular sieves under a nitrogen atmosphere. The mixture was stirred for 15 min at room temperature before addition of $Ag_2O$ (359 mg, 1.55 mmol). The mixture was then allowed to stir at room temperature in the dark for 3 h. Then the solution was filtered on a plug of Celite, and the filtrate was evaporated under vacuum. The resulting crude was purified by column chromatography on silica gel (cyclohexane/EtOAc gradient from 10:1 up to 6:4) to give **23** (1.46 g, 73%) as a white solid. $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 7.50−7.46 (m, 2H, $H_{arom}$), 7.34−7.27 (m, 3H, $H_{arom}$), 5.59 (d, 1H, $J$ = 1.3 Hz, H-1a), 5.43 (dd, 1H, $J$ = 3.4, 1.0 Hz, H-4b), 5.25 (dd, 1H, $J$ = 10.6, 7.9 Hz, H-2b), 5.07 (dd, 1H, $J$ = 10.6, 3.4 Hz, H-3b), 4.62 (d, 1H, $J$ = 7.9 Hz, H-1b), 4.40−4.30 (m, 2H, H-6a), 4.34−4.28 (m, 1H, H-5a), 4.19 (dd, 1H, $J$ = 11.4, 5.3 Hz, H-6b), 4.13 (dd, 1H, $J$ = 11.4, 7.6 Hz, H-6′b), 4.09 (dd, 1H, $J$ = 3.4, 1.3 Hz, H-2a), 4.05 (ddd, 1H, $J$ = 7.6, 5.3, 1.0 Hz, H-5b), 3.91 (t, 1H, $J$ = 9.0 Hz, H-4a), 3.74 (dd, 1H, $J$ = 9.0, 3.4 Hz, H-3a), 2.17 (s, 3H, $CH_3$), 2.11 (s, 3H, $CH_3$), 2.08 (s, 3H, $CH_3$), 2.02 (s, 3H, $CH_3$), 2.01 (s, 3H, $CH_3$). $^{13}C\{1H\}$ NMR ($CDCl_3$, 100 MHz): $\delta$ 171.0, 170.6, 170.2, 170.1, 170.1 (CO), 133.0, 131.9, 129.3, 128.0 ($C_6H_5$), 102.1 (C-1b), 87.1 (C-1a), 84.5 (C-3a), 71.6 (C-2a), 71.5 (C-5b), 70.9 (C-5a), 70.5 (C-3b), 69.2 (C-2b), 66.9 (C-4a), 66.3 (C-4b), 63.5 (C-6a), 61.8 (C-6b), 21.0, 20.8, 20.7, 20.7 ($CH_3$). HRMS (ESI) $m/z$: $[M + Na]^+$ Calcd for $C_{28}H_{36}O_{15}SNa$ 667.1667; Found 667.1665.

*Phenyl β-D-Galactopyranosyl-(1→3)-1-thio-α-D-mannopyranoside (**24**).* To a solution of **23** (350 mg, 0.54 mmol) in anhydrous MeOH (5 mL) was added MeONa (0.054 M in MeOH, 2 mL, 0.11 mmol). The mixture was stirred for 17 h at room temperature. Then the solution was neutralized by the addition of IR 120-$H^+$ form resin. After filtration, the filtrate was evaporated under reduced pressure. The resulting residue was suspended in water and the biphasic solution was washed with DCM (3×). The aqueous phase was finally freeze-dried to afford **24** (235 mg, 100%) as of a white powder. $^1H$ NMR ($D_2O$, 400 MHz): $\delta$ 7.62−7.57 (m, 2H, $H_{arom}$), 7.46−7.40 (m, 3H, $H_{arom}$), 5.58 (d, 1H, $J$ = 1.6 Hz, H-1a), 4.54 (d, 1H, $J$ = 7.6 Hz, H-1b), 4.42 (dd, 1H, $J$ = 3.3, 1.7 Hz, H-2a), 4.20 (ddd, 1H, $J$ = 9.7, 5.5, 2.5 Hz, H-5a), 4.07 (dd, 1H, $J$ = 9.7, 3.1 Hz, H-3a), 3.94 (d, 1H, $J$ = 3.3 Hz, H-4b), 3.86 (t, 1H, $J$ = 9.6 Hz, H-4a), 3.88−3.75 (m, 4H, H-6a, H-6b), 3.74−3.70 (m, 1H, H-5b), 3.68 (ddd, 1H, $J$ = 9.9, 3.3,


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0.5 Hz, H-3b), 3.62 (dd, 1H, $J$ = 9.9, 7.6 Hz, H-2b). $^{13}$C{1H} NMR ($D_2O$, 100 MHz): $\delta$ 132.7, 132.1, 129.4, 128.4 ($C_6H_5$), 101.0 (C-1b), 87.7 (C-1a), 78.6 (C-3a), 75.3 (C-5b), 73.6 (C-5a), 72.6 (C-3b), 70.7 (C-2b), 69.1 (C-2a), 68.6 (C-4b), 65.4 (C-4a), 61.0, 60.7 (C-6a, C-6b). HRMS (ESI) $m/z$: $[M + Na]^+$ Calcd for $C_{18}H_{26}O_{10}SNa$ 457.1139; Found 457.1143.

*β-D-Galactopyranosyl-(1→3)-D-mannopyranose (**PP-3**).* To a solution of **24** (231 mg, 0.53 mmol) in a mixture of acetonitrile/$H_2O$ 1:1 (5 mL) was added *N*-iodosaccharine (576 mg, 1.86 mmol). The mixture was stirred for 2 h at room temperature. Then the reaction mixture was concentrated under reduced pressure, and the residue was partitioned between DCM and water. The resulting organic layer was further extracted with water (2×). The combined aqueous layers were finally freeze-dried. The resulting solid was purified by column chromatography on silica gel (EtOAc/AcOH/$H_2O$/MeOH gradient from 9:0.5:0.5:0 up to 5:2:2:1) to afford **PP-3** (132 mg, 73%) as a solid. HRMS (ESI) $m/z$: $[M + Na]^+$ Calcd for $C_{12}H_{22}O_{11}Na$ 365.1054; Found 365.1055.

**PP-3*α*** (major). $^1$H NMR ($D_2O$, 400 MHz): $\delta$ 5.24 (d, 1H, $J$ = 1.9 Hz, H-1a), 4.55 (d, 1H, $J$ = 7.6 Hz, H-1b), 4.14 (dd, 1H, $J$ = 3.2, 1.9 Hz, H-2a), 4.08 (dd, 1H, $J$ = 9.4, 3.2 Hz, H-3a), 3.96−3.94 (m, 1H, H-4b), 3.94−3.88 (m, 2H, H-6a), 3.90−3.85 (m, 1H, H-5a), 3.82−3.74 (m, 3H, H-4a, H-6b), 3.76−3.71 (m, 1H, H-5b), 3.71 (dd, 1H, $J$ = 9.8, 3.3 Hz, H-3b), 3.626 (dd, 1H, $J$ = 9.8, 7.6 Hz, H-2b). $^{13}$C{1H} NMR ($D_2O$, 100 MHz): $\delta$ 101.00 (C-1b), 93.74 (C-1a), 78.11 (C-3a), 75.30 (C-5b), 72.63 (C-3b), 72.32 (C-5a), 70.75 (C-2b), 68.39 (C-2a), 68.66 (C-4b), 65.27 (C-4a), 61.1 (C-6a), 60.96 (C-6b).

**PP-3*β*** (minor). $^1$H NMR ($D_2O$, 400 MHz): $\delta$ 4.92 (d, 1H, $J$ = 0.7 Hz, H-1a), 4.56 (d, 1H, $J$ = 7.7 Hz, H-1b), 4.17 (dd, 1H, $J$ = 3.1, 0.7 Hz, H-2a), 3.96−3.94 (o, 1H, H-4b), 3.92 (dd, 1H, $J$ = 9.7, 3.1 Hz, H-3a), 3.92 (dd, 1H, $J$ = 12.5, 2.5 Hz, H-6a), 3.82−3.77 (o, 2H, H-6b), 3.76−3.71 (o, 1H, H-5b), 3.75 (dd, 1H, $J$ = 12.5, 6.4 Hz, H-6′a), 3.72−3.69 (o, 1H, H-3b), 3.71 (t, 1H, $J$ = 9.7 Hz, H-4a), 3.631 (dd, 1H, $J$ = 10.0, 7.7 Hz, H-2b), 3.44 (ddd, 1H, $J$ = 9.7, 6.4, 2.5 Hz, H-5a). $^{13}$C{1H} NMR ($D_2O$, 100 MHz): $\delta$ 100.75 (C-1b), 93.53 (C-1a), 80.18 (C-3a), 72.62 (C-5b), 75.90 (C-5a), 75.32 (C-3b), 70.75 (C-2b), 68.79 (C-2a), 68.65 (C-4b), 65.07 (C-4a), 61.09 (C-6b), 60.99 (C-6a).

*Phenyl 2,3,4,6-Tetra-O-benzoyl-β-D-galactopyranosyl-(1→6)-2,3,4-O-benzoyl-1-thio-α-D-mannopyranoside (**25**).* To a solution of galactopyranosyl trichloroacetimidate **20b** (329 mg, 0.44 mmol) and **8** (200 mg, 0.34 mmol) in anhydrous DCM (15 mL) were added activated 4 Å molecular sieves (100 mg). The mixture was stirred for 30 min at room temperature before the dropwise addition of TMSOTf (0.02 M in DCM, 5.1 mL, 0.10 mmol). After 3 h, triethylamine was added, and the solution was filtered on a pad of Celite. The resulting filtrate was evaporated under vacuo, and the residue was purified by column chromatography on silica gel (cyclohexane/EtOAc gradient from 9:1 up to 8:2) to give **25** (309 mg, 78%) as an oil. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 8.07−7.98 (m, 6H, $H_{arom}$), 7.95−7.86 (m, 4H, $H_{arom}$), 7.81−7.76 (m, 4H, $H_{arom}$), 7.63−7.55 (m, 4H, $H_{arom}$), 7.55−7.33 (m, 16H, $H_{arom}$), 7.31−7.21 (m, 6H, $H_{arom}$), 5.95 (dd, 1H, $J$ = 3.4, 1.0 Hz, H-4b), 5.90 (dd, 1H, $J$ = 2.9, 1.6 Hz, H-2a), 5.86 (dd, 1H, $J$ = 10.4, 8.0 Hz, H-2b), 5.82 (dd, 1H, $J$ = 9.7, 2.7 Hz, H-4a), 5.79 (dd, 1H, $J$ = 9.7, 2.9 Hz, H-3a), 5.66 (d, 1H, $J$ = 1.6 Hz, H-1a), 5.54 (dd, 1H, $J$ = 10.4, 3.4 Hz, H-3b), 4.91 (d, 1H, $J$ = 8.0 Hz, H-1b), 4.94−4.88 (m, 1H, H-5a), 4.56 (dd, 1H, $J$ = 11.3, 6.7 Hz, H-6b), 4.34 (dd, 1H, $J$ = 11.3, 6.7 Hz, H-6′b), 4.22 (dd, 1H, $J$ = 6.7, 1.0 Hz, H-5b), 4.17 (dd, 1H, $J$ = 11.8, 1.9 Hz, H-6a), 4.04 (dd, 1H, $J$ = 11.8, 6.1 Hz, H-6′a). $^{13}$C{1H} NMR ($CDCl_3$, 100 MHz): $\delta$ 166.10, 165.72, 165.68, 165.57, 165.54, 165.49, 165.47 (COPh), 133.66, 133.63, 133.42, 133.38, 133.36, 133.25, 133.05, 132.15, 130.15, 130.10, 129.97, 129.93, 129.90, 129.88, 129.72, 129.49, 129.31, 129.27, 129.08, 129.01, 128.94, 128.77, 128.71, 128.63, 128.61, 128.42, 128.41, 128.27, 128.24 ($C_6H_5$), 101.95 (C-1b), 86.12 (C-1a), 71.85 (C-5a), 71.52 (C-5b), 72.00 (C-2a, C-3b), 70.45 (C-3a), 69.66 (C-2b), 69.02 (C-6a), 68.21 (C-4b), 67.45 (C-4a), 61.92 (C-6b). HRMS (ESI) $m/z$: $[M + Na]^+$ Calcd for $C_{67}H_{54}O_{17}SNa$ 1185.2979; Found 1185.2961.

*Phenyl β-D-Galactopyranosyl-(1→6)-1-thio-α-D-mannopyranoside (**26**).* To a solution of **25** (77 mg, 0.084 mmol) in anhydrous MeOH (1 mL) was added MeONa (0.054 M in MeOH, 312 μL, 0.017 mmol). The mixture was stirred for 17 h at room temperature. Then the solution was neutralized by the addition of IR 120-$H^+$ form resin. After filtration, the filtrate was evaporated under reduced pressure. The resulting residue was suspended in water and the biphasic solution was washed with DCM (3×). The aqueous phase was finally freeze-dried to afford **26** (34 mg, 94%) as a powder. $^1$H NMR ($CD_3OD$, 400 MHz): $\delta$ 7.58−7.50 (m, 2H, $H_{arom}$), 7.37−7.25 (m, 3H, $H_{arom}$), 5.39 (d, 1H, $J$ = 1.5 Hz, H-1a), 4.28 (d, 1H, $J$ = 7.7 Hz, H-1b), 4.22 (ddd, 1H, $J$ = 9.7, 5.3, 2.2 Hz, H-5a), 4.13 (dd, 1H, $J$ = 11.2, 2.3 Hz, H-6b), 4.09 (dd, 1H, $J$ = 3.3, 1.5 Hz, H-2a), 3.86 (dd, 1H, $J$ = 11.2, 5.4 Hz, H-6′b), 3.85−3.67 (m, 5H, H-3a, H-4a, H-6a, H-4b), 3.57 (dd, 1H, $J$ = 9.7, 7.6 Hz, H-2b), 3.51−3.47 (m, 1H, H-5b), 3.46 (dd, 1H, $J$ = 9.7, 3.4 Hz, H-3b). $^{13}$C{1H} NMR ($CD_3OD$, 100 MHz): $\delta$ 135.5, 133.4, 130.2, 128.7 ($C_6H_5$), 105.3 (C-1b), 90.7 (C-1a), 76.8 (C-5b), 74.8 (C-3b), 74.6 (C-5a), 73.6 (C-2a), 73.0 (C-3a), 72.6 (C-2b), 70.3 (C-4a or C-4b), 69.8 (C-6a), 68.7 (C-4a or C-4b), 62.5 (C-6b). HRMS (ESI) $m/z$: $[M + Na]^+$ Calcd for $C_{18}H_{26}O_{10}SNa$ 457.1139; Found 457.1143.

*β-D-Galactopyranosyl-(1→6)-α-D-mannopyranose (**PP-6**).* To a solution of **26** (53 mg, 0.122 mmol) in a mixture of ACN/$H_2O$ 1:1 (10 mL) was added *N*-iodosaccharine (130 mg, 0.427 mmol). The mixture was stirred for 1 h at room temperature. Then the reaction mixture was concentrated under reduced pressure, and the residue was partitioned between DCM and water. The resulting organic layer was further extracted with water (2×). The combined aqueous layers were finally freeze-dried. The resulting solid was purified by column chromatography on silica gel (EtOAc/AcOH/$H_2O$/MeOH gradient from 9:0.5:0.5:0 up to 5:2:2:1) to afford **PP-6** (39 mg, 93%) as a solid.

**PP-6*α*** (major). $^1$H NMR ($D_2O$, 400 MHz): $\delta$ 5.18 (d, 1H, $J$ = 1.6 Hz, H-1a), 4.45 (d, 1H, $J$ = 7.8 Hz, H-1b), 4.18 (dd, 1H, $J$ = 11.4, 1.8 Hz, H-6a), 4.07−3.96 (m, 1H, H-5a), 3.94 (dd, 1H, $J$ = 3.3, 1.6 Hz, H-2a), 3.93 (d, 1H, $J$ = 3.3 Hz, H-4b), 3.91 (dd, 1H, $J$ = 11.4, 5.9 Hz, H-6′a), 3.86 (dd, 1H, $J$ = 9.7, 2.2 Hz, H-3a), 3.81 (dd, 1H, $J$ = 11.6, 7.9 Hz, H-6b), 3.77 (o, 1H, H-6′b), 3.75 (t, 1H, $J$ = 9.7 Hz, H-4a), 3.75−3.70 (m, 1H, H-5b), 3.66 (dd, 1H, $J$ = 9.8, 3.3 Hz, H-3b), 3.57 (dd, 1H, $J$ = 9.8, 7.8 Hz, H-2b). $^{13}$C{1H} NMR ($D_2O$, 100 MHz): $\delta$ 103.3 (C-1b), 94.1 (C-1a), 75.1 (C-5b), 72.6 (C-3b), 71.3 (C-5a), 70.7 (C-2b), 70.6 (C-2a), 70.1 (C-3a), 68.8 (C-6a), 68.6 (C-4b), 66.5 (C-4a), 61.0 (C-6b). HRMS (ESI) $m/z$: $[M + Na]^+$ Calcd for $C_{12}H_{22}O_{11}Na$ 365.1054; Found 365.1058.

**PP-6*β*** (minor). $^1$H NMR ($D_2O$, 400 MHz): $\delta$ 4.91 (t, 1H, $J$ = 1.0 Hz, H-1a), 4.46 (d, 1H, $J$ = 7.8 Hz, H-1b), 4.23 (dd, 1H, $J$ = 11.2, 1.9 Hz, H-6a), 3.95 (dd, 1H, $J$ = 3.3, 1.6 Hz, H-2a), 3.94 (o, 1H, H-4b), 3.85 (o, 1H, H-6′a), 3.77 (o, 2H, H-6b), 3.71 (o, 1H, H-5b), 3.71−3.66 (m, 2H, H-3a, H-4a), 3.66 (dd, 1H, $J$ = 9.8, 3.3 Hz, H-3b), 3.57 (dd, 1H, $J$ = 9.8, 7.8 Hz, H-2b), 3.55 (o, 1H, H-5a). $^{13}$C{1H} NMR ($D_2O$, 100 MHz): $\delta$ 103.3 (C-1b), 93.7 (C-1a), 75.1 (C-5b), 75.0 (C-5a), 72.9 (C-3a), 72.6 (C-3b), 71.2 (C-2a), 70.7 (C-2b), 68.8 (C-6a), 68.6 (C-4b), 66.4 (C-4a), 61.0 (C-6b).

*Ion Mobility−Mass Spectrometry.* The synthesized disaccharides were analyzed on a Select Series Cyclic IMS (Waters, Wilmslow, UK), equipped with a cyclic Traveling Wave Ion Mobility Spectrometry (TWIMS) cell.[55] Arrival time distributions (ATDs) were recorded with the Quartz v. 6 software and processed with the MassLynx v. 4.2 software (both from Waters, Wilmslow, UK). ATDs are reported according to Gabelica et al.[67]

Samples were dissolved at 1 μg/mL in 50/50 methanol/water (v/v), doped with 0.5 mM NaCl, and then infused at 5 μL/min in the electrospray ion source. Samples were also analyzed at 1 μg/mL doped with 0.1 mM LiCl. All IM-MS analyses were performed in triplicates. The disaccharides were analyzed in positive-ion mode (in the $m/z$ 50−1200 range), with MS/MS selection of $m/z$ 365.1 in the quadrupole prior to ion mobility separation. The detailed instrumental parameters are given in the Supporting Information.

The following sequence of events was used to perform IMS analyses at a TW height of 22 V and TW velocity of 375 m/s: (i)


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injection in the IMS cell (10 ms); (ii) separation (see Table S1); and (iii) ejection to TOF analyzer (13.2 ms). As long as the ions remain in the fourth pass, their arrival times do not change: the slight differences in separation times serve the purpose of setting a window to observe the full ATD.

Data were processed using Driftscope 2.9 and MassLynx 4.2 (Waters, Wilmslow, UK) to extract the monoisotopic ion mobility spectra. ATDs were then calibrated to give CCSDs using MajorMix calibration solution (Waters, Wilmslow, UK)[68,69] ($R^2$ = 0.999).

*IRMPD.* IRMPD spectra are obtained using a commercial mass spectrometer equipped with an electrospray ion source and a Paul trap (LCQ classic ThermoFisher) with custom-made modifications. The trap was drilled to allow irradiation of the ion cloud by the beam of a YAG-pumped tunable infrared OPO/OPA system (laserVision), which delivers 8 ns, 10 Hz, 13 mJ pulses in the 2700−3700 $cm^{-1}$. A mechanical shutter ensures the synchronization of the laser injection with the desired stage of the MS sequence.

The samples were prepared at 30 $\mu$M in water/methanol (50/50), and 0.1% of ammonium sulfate was added to promote the formation of ionic complexes $[M + NH_4]^+$. The ions are produced by electrospray ionization and directed to the ion trap through a set of ion multipoles and isolated based on their mass-to-charge ratio at $m/z$ 360. The isolated ions are further held in the trap for a period of 800 ms, during which they are irradiated by the laser. If the IR wavelength is resonant with one of the vibrational frequencies of the ions, multiple photons can be absorbed and their energy redistributed through internal vibrational coupling (IVR). This increases the internal energy of the ion, which results in fragmentation, in a very similar way to traditional collisional activation. The trapped ion (remaining parent and photofragments) are then ejected from the trap and the resulting mass spectrum is recorded. This sequence is repeated thorough the spectral range of interest and the photofragmentation yield is plotted as a function of the wavenumber. The data shown are averaged three times.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.1c00250.

$^1H$ and $^{13}C$ NMR spectra of acceptors as well as galactofuranosyl- and galactopyranosyl-containing disaccharides, IM-MS and IRMPD technical descriptions, and MS/MS and IRMPD spectra of the eight disaccharides (PDF)

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### Notes

The authors declare no competing financial interest.

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