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Regioselective Sulfonylation/Acylation of Carbohydrates Catalyzed by $FeCl_3$ Combined with Benzoyltrifluoroacetone and Its Mechanism Study

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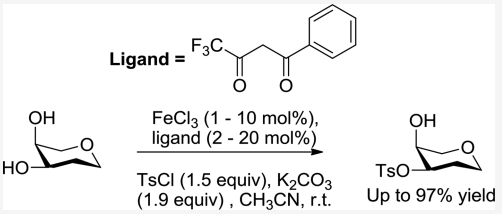
ABSTRACT: A catalytic amount of $FeCl_3$ combined with benzoyl trifluoroacetone (Hbtfa) ($FeCl_3$/Hbtfa = 1/2) was used to catalyze sulfonylation/acylation of diols and polyols using diisopropylethylamine (DIPEA) or potassium carbonate (K_2CO_3) as a base. The catalytic system exhibited high catalytic activity, leading to excellent isolated yields of sulfonylation/acylation products with high regioselectivities. Mechanism studies indicated that $FeCl_3$ initially formed [Fe(btfa)$_3$] (btfa = benzoyl trifluoroacetonate) with twice the amount of Hbtfa under basic conditions in the solvent acetonitrile at room temperature. Then, Fe(btfa)$_3$ and two hydroxyl groups of the substrates formed a five- or six-membered ring intermediate in the presence of the base. The subsequent reaction between the cyclic intermediate and a sulfonylation reagent led to the selective sulfonylation of the substrate. All key intermediates were captured in the high-resolution mass spectrometry assay, therefore demonstrating this mechanism for the first time.



INTRODUCTION

Regioselective protection strategies are as important as glycosylation strategies in carbohydrate chemistry due to the requirements of both the preparation of glycosyl donors and acceptors[1] and the modification of carbohydrates[2] to obtain valuable intermediates. One-pot selective protection strategies are particularly beneficial for the highly efficient synthesis of glycosyl donors and acceptors.[3] Many chiral or achiral catalysts with complex structures were developed to control site-selectivity, where researchers are less concerned about whether the catalysts are readily available and inexpensive.[4] Few catalysts with a simple structure[5] were developed to substitute toxic organotin reagents,[6] where researchers, such as our group,[7] are more concerned about the commercial availability, the low price, and the environmental friendliness of the used reagents. Our group has therefore recently developed green Fe(III) catalysts, [Fe(dibm)$_3$] (dibm = diisobutyrylmethane) for regioselective alkylation[7] and [Fe(acac)$_3$] (acac = acetylacetonate) for regioselective acylation.[8] [Fe(dipm)$_3$] (dipm = dipivaloylmethane) can play the same role as [Fe(dibm)$_3$], and it is less expesenve.[9] These methods have the advantages of green, convenient manipulation, high efficiency, high selectivity, good yield, and broad substrate scope. However, the mechanism has never been demonstrated.

Regioselective sulfonylation strategies are also important because selective sulfonated products are widely used as precursors for the synthesis of various biologically significant compounds and novel functional materials.[10] Organotin reagents were used in the earliest reports,[11] and organoboron catalysts[12] were later developed to avoid the use of toxic organotin reagents (Figure 1a). We have attempted to use [Fe(dibm)$_3$], [Fe(dipm)$_3$], or [Fe(acac)$_3$] to catalyze selective

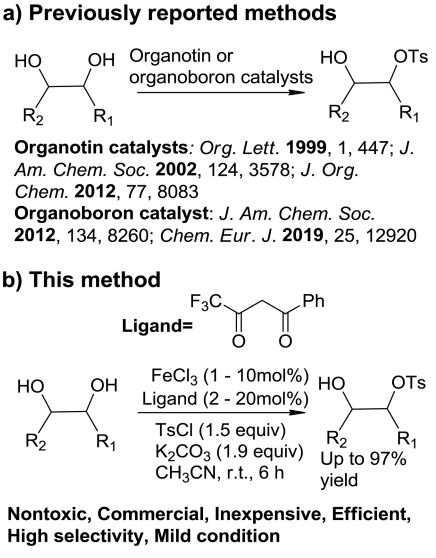


Figure 1. Regioselective sulfonylation of carbohydrate *cis*-diols. (a) Previously reported methods. (b) This method.

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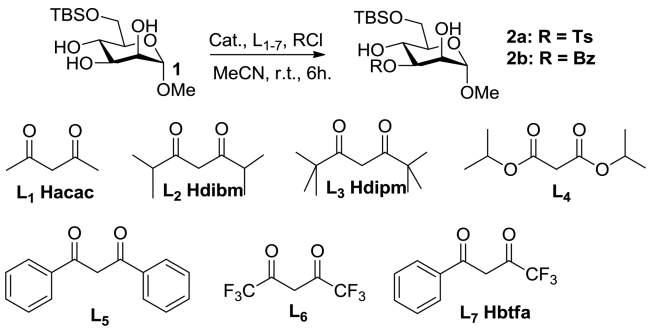
sulfonylation but failed. It is difficult to investigate such catalysts in which various metals coordinate acylacetone ligands due to availability, although we assumed that certain catalysts should be good catalysts for selective sulfonylation. Recently, we found that $FeCl_3$ combined with acetylacetone could be directly used as a catalyst to catalyze selective benzoylation with diisopropylethylamine (DIPEA) as a base.[13] Based on this, we investigated the effects of acylacetone ligands and various metal salts on the regioselective sulfonylation to find an optimal catalytic system. The challenge is addressed in this study (Figure 1b). We found that the combination of $FeCl_3$ and benzoyl trifluoroacetone (Hbtfa) ($FeCl_3$/Hbtfa = 1/2) was a good catalytic system for regioselective sulfonylation of substrates containing a *cis*-vicinal diol, a 1,2-diol, or a 1,3-diol. The method is superior to the reported methods, which uses only inorganic bases (K_2CO_3) instead of organic bases. The isolated yields and selectivities were similar or better than previous methods in most cases (Table S1 in the Supporting Information). This system also exhibited a higher catalytic activity for selective acylation than the use of $FeCl_3$ and acetylacetone. $FeCl_3$ is readily available in the laboratory. Benzoyl trifluoroacetone is also an inexpensive ($1−2/g) and nontoxic reagent (Table S2 in the Supporting Information). Furthermore, the catalytic mechanism was studied using high-resolution mass spectrometry (HRMS) to capture all key intermediates in the HRMS assay, therefore demonstrating the mechanism for the first time.

RESULTS AND DISCUSSION

Based on our studies on $FeCl_3$-catalyzed selective benzoylation with acetylacetone as a ligand, we started to explore the optimal catalytic system for selective sulfonylation of methyl-6-*O*-(*tert*-butyldimethylsilyl)-α-D-mannopyranoside **1** (Table 1). Therefore, 0.1 equiv of $FeCl_3$ was first tested with 0.3 equiv of various acylacetone-type ligands ($\mathbf{L_1}$−$\mathbf{L_7}$) in the presence of 1.5 equiv of *para*-toluenesulfonyl chloride (TsCl) and 1.9 equiv of diisopropylethylamine (DIPEA) in acetonitrile (entries 1and 2 in Table 1). After 6 h at room temperature, the sulfonylation products and the recovered **1** were isolated. The experimental results showed that $FeCl_3$ with the assistance of $\mathbf{L_1}$−$\mathbf{L_6}$ could not exhibit any catalytic activity on the sulfonylation since 80−86% yields of recovered **1** were isolated (entry 1). To our delight, $FeCl_3$ with the assistance of $\mathbf{L_7}$, benzoyl trifluoroacetone (Hbtfa), exhibited high catalytic activity for the selective sulfonylation (entry 2). Most of the starting material **1** was consumed, and 86% yield of 3-sulfonylated product **2a** was isolated. No or trace byproducts were observed, indicating a high site-selectivity. The absence of $\mathbf{L_7}$ (entries 3 and 4) or the absence of $FeCl_3$ resulted in low or no reaction conversion. We assumed that 0.1 equiv of $FeCl_3$ and 0.3 equiv of $\mathbf{L_7}$ initially form approximately 0.1 equiv of $Fe(btfa)_3$ in the presence of a base, which subsequently catalyzes the sulfonylation. As expected, $Fe(btfa)_3$ showed high catalytic activity in the sulfonylation, and only 1.5 equiv of DIPEA was used, thus leading to 92% isolated yield of **2a** (entry 5). $FeBr_3$, $Fe(OTf)_3$, and $FeCl_2$ exhibited lower catalytic activity than $FeCl_3$ (entries 6−8). Next, various metal salts in lieu of iron salts were tested in the sulfonylation. It was observed that $AlCl_3$, $NiCl_2$, $CrCl_3$, $SnCl_4$, $Ce(SO_4)_2$, or $Ce(NO_3)_4$ did not exhibit any catalytic activity; $CuCl_2$ and $BiCl_3$ also exhibited high catalytic activity (entries 9 and 10); and $MnCl_2$, $ZnCl_2$, and $CoCl_2$ exhibited moderate catalytic activity for this reaction (entries 11−13). We also used other bases (TEA, K_2CO_3, and Ag_2O) instead of DIPEA (entries 14−16). Good results were observed, especially when K_2CO_3 was used as the base (entry 15). An unexpected result is that $FeCl_3$ combined with 2 equiv of $\mathbf{L_7}$ exhibited the same catalytic activity as with 3 equiv of $\mathbf{L_7}$ (entry 17). However, $FeCl_3$ combined with 1 equiv of $\mathbf{L_7}$ exhibited lower catalytic activity (entry 18). We initially assumed that $Fe(btfa)_2Cl$ is formed from $FeCl_3$ and 2 equiv of $\mathbf{L_7}$ and $Fe(btfa)Cl_2$ is formed from $FeCl_3$ and 1 equiv of $\mathbf{L_7}$. $Fe(btfa)_2Cl$ exhibits the same catalytic activity as $Fe(btfa)_3$, but $Fe(btfa)Cl_2$ does not. Therefore, the optimum ratio of $FeCl_3$ to $\mathbf{L_7}$ is 1/2 for this catalytic system. The amount of the catalyst could be decreased to 0.05 equiv (entry 19). In this case, the 3-sulfonylated product **2a** was isolated in 85% yield when the reaction time was prolonged to 12 h. For a large scale (gram scale), **2a** was isolated in 93% yield within 8 h. All the reactions exhibited high site-selectivity since no or trace byproducts were observed. Selective acylation could also be catalyzed by this catalytic system, leading to 3-benzoylated product **2b** in 90% yield (entry 17). Similar results were obtained when K_2CO_3 was used as the base where **2a** and **2b** were isolated in 91 and 92% yield, respectively (entry 20).

Table 1. Comparison of Sulfonylation/Acylation of 1 under Various Conditions[a]



entry	catalytic system (0.1 equiv)	base (1.9 equiv)	isolated yield (%)	recovered **1** (%)
1	$FeCl_3$/$\mathbf{L_{1-6}}$ (1/3)	DIPEA	-[b]	80−86
2	$FeCl_3$/$\mathbf{L_7}$ (1/3)	DIPEA	**2a**: 86	-[b]
3	$FeCl_3$ (0.1)	DIPEA	-[b]	84
4	$\mathbf{L_7}$ (0.3)	DIPEA	-[b]	85
5	$Fe(btfa)_3$ (0.1)	DIPEA[c]	**2a**: 92	-[b]
6	$FeBr_3$/$\mathbf{L_7}$ (1/3)	DIPEA	**2a**: 27	62
7	$Fe(OTf)_3$/$\mathbf{L_7}$ (1/3)	DIPEA	**2a**: 35	56
8	$FeCl_2$/$\mathbf{L_7}$ (1/2)	DIPEA	**2a**: 34	56
9	$CuCl_2$/$\mathbf{L_7}$ (1/2)	DIPEA	**2a**: 90	-[b]
10	$BiCl_3$/$\mathbf{L_7}$ (1/3)	DIPEA	**2a**: 85	-[b]
11	$MnCl_2$/$\mathbf{L_7}$ (1/2)	DIPEA	**2a**: 63	30
12	$ZnCl_2$/$\mathbf{L_7}$ (1/2)	DIPEA	**2a**: 51	40
13	$CoCl_2$/$\mathbf{L_7}$ (1/2)	DIPEA	**2a**: 60	32
14	$FeCl_3$/$\mathbf{L_7}$ (1/3)	TEA	**2a**: 83	-[b]
15	$FeCl_3$/$\mathbf{L_7}$ (1/3)	K_2CO_3	**2a**: 91	-[b]
16	$FeCl_3$/$\mathbf{L_7}$ (1/3)	Ag_2O	**2a**: 80	-[b]
17	$FeCl_3$/$\mathbf{L_7}$ (1/2)	DIPEA	**2a**: 89; **2b**: 90	-[b]
18	$FeCl_3$/$\mathbf{L_7}$ (1/1)	DIPEA	**2a**: 67	27
19	$FeCl_3$/$\mathbf{L_7}$ (1/2)[d]	DIPEA	**2a**: 85[e], 93[f]	-[b]
20	$FeCl_3$/$\mathbf{L_7}$ (1/2)	K_2CO_3	**2a**: 91; **2b**: 92	-[b]

[a]Substrate **1** (0.1 mmol), RCl (1.5 equiv), MeCN (0.5 mL), room temperature (rt), 6 h. [b]Observation of no or trace compound. [c]1.5 equiv. [d]0.05 equiv. [e]12 h. [f]Large scale: substrate **1** (4 mmol, 1.232 g), TsCl (1.5 equiv), MeCN (20 mL), rt, 8 h.

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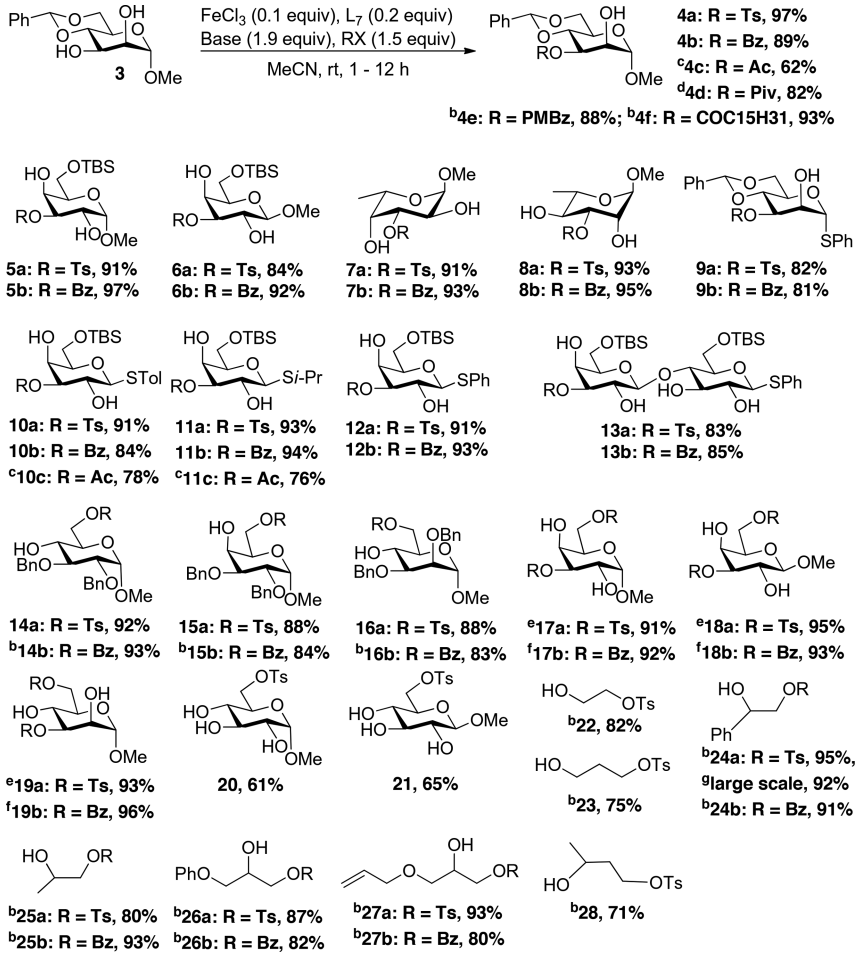

Figure 2. Regioselective sulfonylation and acylation of substrates containing *cis*-,1,2-, or 1,3-diol.[a] Reaction conditions: [a]K_2CO_3 (1.9 equiv), $\mathbf{L}_7$ (0.2 equiv), $FeCl_3$ (0.1 equiv), RCl (1.5 equiv), MeCN (0.5 mL), rt, 1−12 h. [b]DIPEA (1.9 equiv). [c]DIPEA (1.6 equiv), AcCl (1.2 equiv), 2−4 h. [d]DIPEA (1.9 equiv), 50 °C, 5 h. [e]K_2CO_3 (4.0 equiv), RCl (3.0 equiv), 4−12 h. [f]DIPEA (4.0 equiv), RCl (3.0 equiv), 3 h. [g]Substrate (8 mmol, 1.104 g), DIPEA (1.9 equiv), $\mathbf{L}_7$ (0.02 equiv), $FeCl_3$ (0.01 equiv), TsCl (1.5 equiv), MeCN (20 mL), 3 h.

Acetylation showed much poorer selectivity than benzoylation likely due to relative ease of acetyl migration.[8,14]

We further evaluated the substrate scope of this method (Figure 2). Thus, $\mathbf{L}_7$ (0.2 equiv), $FeCl_3$ (0.1 equiv), K_2CO_3/DIPEA (1.9 equiv), and the substrates containing a *cis*-diol moiety, a 1,2-diol moiety, or a 1,3-diol moiety were mixed in the solvent. Subsequently, a sulfonylation or acylation reagent (1.2−1.5 equiv) was added, and these reactions were proceeding at room temperature for 1−12 h. Methyl 4,6-benzylidine α-mannoside **3** was first chosen to be tested with TsCl and various acylation reagents, such as BzCl, AcCl, PivCl, PMBzCl, and $C_{15}H_{31}COCl$. The 3-protected products **4a−f** were isolated in 62−97% yields, indicating the generality of the method.

All glycosides containing a *cis*-diol were selectively sulfonylated, benzoylated, or acetylated at the equatorial hydroxyl groups, leading to 76−97% yields of products **5−13**. However, the catalytic system could not exhibit any catalytic activity to glycoside *trans*-diols. The catalytic system also exhibited high catalytic activity to substrates containing 1,2-diol or 1,3-diol. Thus, the 6-protected products **14−16** were isolated in 83−93% yields starting from glycoside substrates where 4- and 6-positions are free, and the products **22−28** were isolated in 71−95% yields starting from noncarbohydrate substrates. For glycoside substrates containing both *cis*-diol and 1,3-diol, such as free methyl galactosides and mannosides, there is no or poor selectivity between the equatorial hydroxyl group and the primary hydroxyl group in the reaction. Therefore, with 4 equiv of base and 3 equiv of TsCl/BzCl for these substrates, leading to isolated 91−96% yields of products **17−19** where both 3- and 6-positions reacted. For free methyl glucosides, 2 equiv of base and 1.9 equiv of TsCl were used, leading to isolated 61−65% yields of 6-position protected products **20** and **21** since no *cis*-diol competed with 1,3-diol in the sulfonylation. The relative low yields of **20** and **21** are likely due to the poor solubility of the substrates in acetonitrile. The sulfonylation of phenylene glycol was also tested in a large scale. The catalytic system exhibited very high catalytic activity to this substrate. Thus, $FeCl_3$ (0.01 equiv) and $\mathbf{L}_7$ (0.02 equiv) were used in this reaction, and the primary group sulfonylated product **24a** was isolated in 92% yield within only 3 h of reaction.

The catalytic system does not catalyze or accelerate the sulfonylation of glycoside *trans*-diols, monohydroxy substrates, and diols as shown with glycoside *trans*-diols **29** and **30**, alcohol **31**, and 1,4-butanediol **32** with this method (Figure 3). The competitive sulfonylation of a mixture of diol **33** and its corresponding monohydric alcohol **31** only led to **24a**, the sulfonylation product of **33**. The sulfonylation of a mixture of ethylene glycol **35** and1,4-butanediol **32** in a competitive

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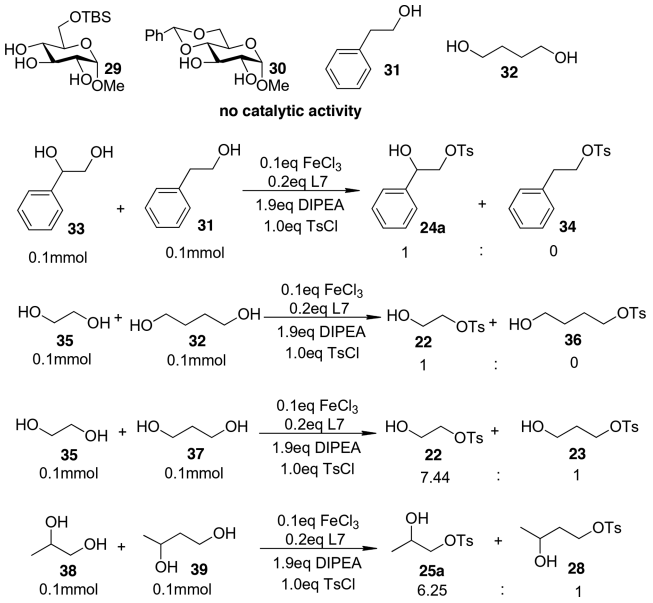

Figure 3. Competitive experiments.

reaction only led to **22**, the sulfonylation product of **35**. These experiments may support the formation of cyclic intermediates with five- and six-membered rings by the iron catalyst and diols. The sulfonylation of a mixture of a 1,2-diol (**35**/**38**) and a 1,3-diol (**37**/**39**) in a competitive reaction led mainly to sulfonylation of the 1,2-diol. The ratios of the sulfonylated products of 1,2-diol and 1,3-diol are 7.44/1 (**22**/**23**) and 6.25/1 (**25a**/**28**). These results support the formation of five-membered ring intermediates more easily than the formation of six-membered ring chelates between diols and the iron catalyst.

By comparing the structures of $\mathbf{L}_5$, $\mathbf{L}_6$, and $\mathbf{L}_7$, it seems that a ligand having an electron-withdrawing group at one end and an electron-donating group at the other side plays a key role for the good sulfonylation activity of the catalytic system. Therefore, $\mathbf{L}_8$ (the trifluoromethyl group of $\mathbf{L}_7$ being substituted by the methyl group), $\mathbf{L}_9$ (the trifluoromethyl group of $\mathbf{L}_7$ being substituted by the ethoxide group), $\mathbf{L}_{10}$ (the phenyl group of $\mathbf{L}_7$ being substituted by the methyl group), $\mathbf{L}_{11}$ (the phenyl group of $\mathbf{L}_7$ being substituted by the *p*-chloride phenyl group), and $\mathbf{L}_{12}$ (the phenyl group of $\mathbf{L}_7$ being substituted by the thienyl group) were further tested in the sulfonylation of **1** (Figure 4). It was observed that $FeCl_3$ combined with $\mathbf{L}_8$ or $\mathbf{L}_{10}$ exhibited no or low catalytic activity, $FeCl_3$ combined with $\mathbf{L}_9$ or $\mathbf{L}_{11}$ exhibited moderate catalytic activity, and $FeCl_3$ combined with $\mathbf{L}_{12}$ exhibited as high catalytic activity as $FeCl_3$ combined with $\mathbf{L}_7$. $FeCl_3$ combined with $\mathbf{L}_{11}$ exhibited lower catalytic activity than $FeCl_3$ combined with $\mathbf{L}_7$, which is likely due to the weaker electron-donating ability of the *p*-chloride phenyl group than the phenyl group.

In order to confirm whether $Fe(btfa)_2Cl$ is formed by the reaction of $FeCl_3$ and 2 equiv of $\mathbf{L}_7$, we crystallized a product from the reaction of $FeCl_3$ with 2.0 equiv of $\mathbf{L}_7$ and crystallized the other product of $FeCl_3$ with 3.0 equiv of $\mathbf{L}_7$, respectively. However, these two products are identical by comparison with their X-ray diffraction (XRD) spectrum (Figure S1 in the Supporting Information). The mixture of $FeCl_3$ with 2.0 equiv of $\mathbf{L}_7$ in the presence of DIPEA in acetonitrile was tested by HRMS. The strong signals of 740.0030 and 724.0272 were observed, indicating a $Fe(btfa)_3$ molecule with a K^+ and a Na^+ (calculated values: 739.9941 and 724.0201), respectively. A weak signal of 486.0015 was found, which likely represents $^+Fe(btfa)_2$ (the calculated value: 485.9984). These results indicated that $Fe(btfa)_3$ instead of $Fe(btfa)_2Cl$ is formed from the reaction of $FeCl_3$ and 2 equiv of $\mathbf{L}_7$. Supposed that $\mathbf{L}_7$ is completely consumed during the reaction, 0.067 and 0.1 equiv of $Fe(btfa)_3$ would be formed from the reaction of 0.1 equiv of $FeCl_3$ with 0.2 and 0.3 equiv of $\mathbf{L}_7$, respectively. One question is why the identical catalytic activity was observed under these two conditions. Based on these facts, a catalytic mechanism was proposed in Figure 5. In the first step, the key iron catalyst FeX_3 is formed by $FeCl_3$ and ligand X in the presence of a base. FeX_3 then forms a cyclic intermediate (**a** or **b**) with a diol substrate in the presence of the base while releasing an X molecule. The cyclic intermediate will further react with the sulfonylation/acylation reagent to produce a regioselective sulfonylated/acylated product going through the intermediate **c**. This explains why the catalytic system ($FeCl_3/\mathbf{L}_7$ = 1/2) exhibits the same catalytic activity as the catalytic system ($FeCl_3/\mathbf{L}_7$ = 1/3) since the ratio of Fe to X is 1/2 in the cyclic intermediate. We could not crystallize intermediate **a** nor study the mechanism by NMR due to the existence of the iron(III).

We envisioned whether the intermediate **a**, **b**, or **c** could be captured by HRMS detection. If this was the case, the mechanism shown in Figure 5 would be confirmed. We first

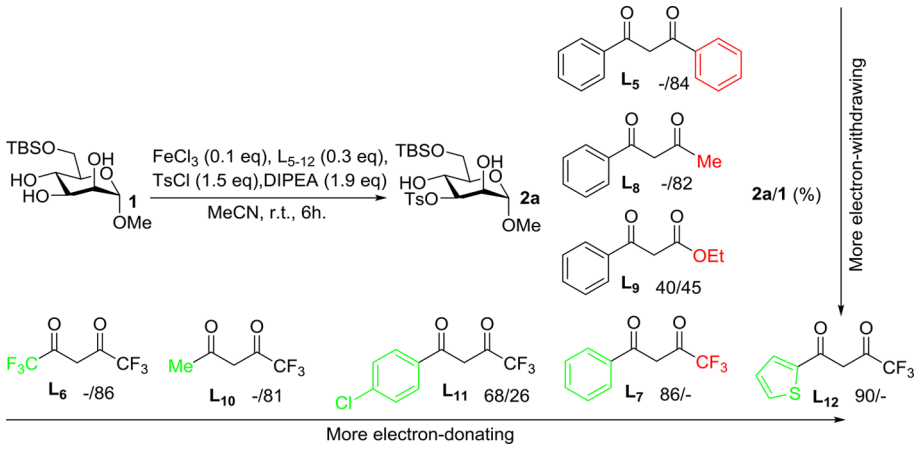

Figure 4. Comparing the catalytic activity of $FeCl_3$ combined with $\mathbf{L}_5$–$\mathbf{L}_{12}$.

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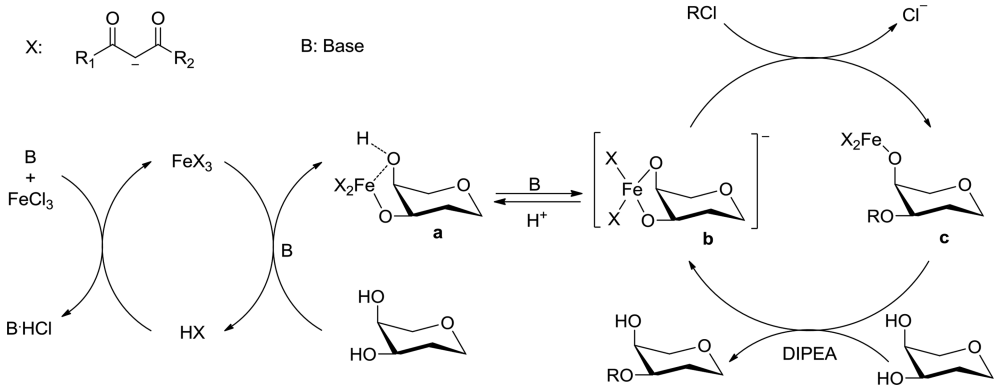

Figure 5. Proposed mechanism for $FeCl_3$-catalyzed sulfonylation and acylation in the presence of $\mathbf{L_7}$.

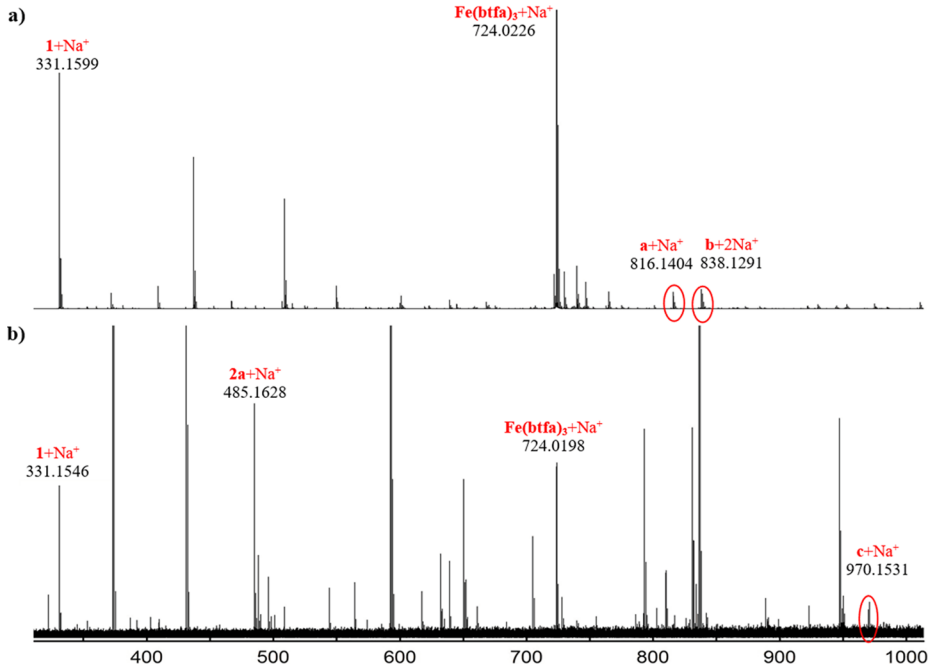

Figure 6. HRMS detection for (a) mannoside **1** with 1.0 equiv of $Fe(btfa)_3$ in the presence of 2.0 equiv of DIPEA in acetonitrile, and b) 0.5 equiv of TsCl was added in the abovementioned mixture.

mixed mannoside **1** with 1.0 equiv of $Fe(btfa)_3$ in the presence of 2.0 equiv of DIPEA in acetonitrile. The mixture was subjected to HRMS analysis after stirring at room temperature for 5 h. To our delight, two strong signals of 331.1599 (raw material **1**, the calculated value with Na^+: 331.1547) and 724.0226 ($Fe(btfa)_3$) and two weak signals of 816.1404 (intermediate **a**, the calculated value with Na^+: 816.1458) and 838.1291 (intermediate **b**, the calculated value with $2Na^+$: 838.1278) were observed (Figure 6a). After 0.5 equiv of TsCl was added at rt for 5 h, this mixture was subjected to HRMS detection. The strong signals of 331.1546 (raw material **1**), 485.1628 (sulfonylation product **2a**, the calculated value with Na^+: 485.1636), and 724.0198 ($Fe(btfa)_3$) and a weak signal of 970.1531 (intermediate **c**, the calculated value with Na^+: 970.1547) were observed (Figure 6b). However, the signal around 816.1458−838.1278 (intermediate **a** or **b**) could not be observed in this case, which might indicate that intermediate **a** or **b** is extremely active and difficult to survive in the presence of an acylation reagent. Consequently, the capture of the intermediates **a**, **b**, and **c** by HRMS demonstrated the proposed mechanism in Figure 5.

Based on this mechanism, the formation rate of products is approximately proportional to the amount of the cyclic intermediate in light of a kinetic analysis (Figure S4 in the Supporting Information). Furthermore, the formation rate of products is approximately proportional to the ligand when the ratio of ligand is less than twice the amount of $FeCl_3$, whereas the formation rate of products remained unchanged when the amount of the ligand is larger than or equal to twice the amount of $FeCl_3$. Under low conversion conditions, the ratio of product yields should be approximately equal to the ratio of the corresponding ligand amounts when two reactions proceed for the same reaction time. To further validate this conjecture, we explored the catalytic effects at various ratios of $FeCl_3/\mathbf{L_7}$ ($FeCl_3/\mathbf{L_7}$ = 1/3, 1/2, 1/1.5, 1/1.2, and 1/1) where the ^1H NMR yield for sulfonylation of **1** was detected after 1 h of reaction (Figure 7). As expected, the yields of **2a** were 86 and 84%, respectively, with the ratios of $FeCl_3/\mathbf{L_7}$ being 1/3 and 1/2. The yields of **2a** decreased to 77, 67, and 56%, respectively, with the ratios of $FeCl_3/\mathbf{L_7}$ being 1/1.5, 1/1.2, and 1/1. Comparing the two reactions in which the ratio of their ligand amounts equal to 1.2, we found that the ratio of their

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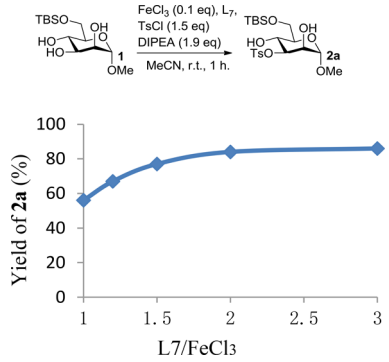

Figure 7. Yields of **2a** with various ratios of $FeCl_3/L_7$.

corresponding yields (67%/56%) just equal to 1.2, supporting our assumptions.

CONCLUSIONS

It was demonstrated that $FeCl_3$ could catalyze the regioselective sulfonylation/acylation with the help of acylacetone ligands having an electron-withdrawing group at one end and an electron-donating group on the other side. High isolated yields and selectivities for sulfonylation/acylation were achieved, where the scope of substrates and acylation reagents are wide. $FeCl_3$ initially forms $[FeL_3]$ with an acylacetone ligand in the presence of a base and then $[FeL_3]$ catalyzed the sulfonylation/acylation. The optimized ratio of $FeCl_3$ to the ligand is 1/2. Mechanism studies have demonstrated that $[Fe(btfa)_3]$ was formed from $FeCl_3$ with 2 equiv of benzoyl trifluoroacetone under basic conditions in the solvent acetonitrile at room temperature. $[Fe(btfa)_3]$ further reacted with two hydroxyl groups of a substrate in the presence of the base to form a five- or six-membered ring intermediate while releasing a benzoyl trifluoroacetonate molecule. The cyclic intermediate subsequently reacted with a sulfonylation/acylation reagent, leading to regioselective sulfonylation/acylation of the substrate. The released benzoyl trifluoroacetonate could react with excess $FeCl_3$ to form $[Fe(btfa)_3]$ again until $FeCl_3$ is completely consumed in this cycle. All key intermediates have been observed by HRMS detection, therefore confirming the mechanism for the first time. In comparison with the reaction using the catalyst, $Fe(acac)_3$, similar or higher isolated yields and selectivities were achieved for benzoylation in most cases. Either $FeCl_3$ or benzoyl trifluoroacetonate is a common, cheap, and nontoxic reagent in the laboratory. In particular, K_2CO_3 can be used instead of DIPEA as a base in this catalytic system, thereby making the process much greener.

EXPERIMENTAL SECTION

General Methods. All chemicals were purchased as reagent grade and used without further purification. The solvents were purified before use. CH_3CN was distilled over CaH_2. Chemical reactions were monitored by thin-layer chromatography using precoated silica gel 60 (0.25 mm in thickness) plates. Flash column chromatography was performed on silica gel 60 (SDS 0.040−0.063 mm). Spots were visualized by UV light (254 nm) and charred with a solution of H_2SO_4 in ethanol. ^1H NMR and ^{13}C NMR spectra were recorded at 298 K in $CDCl_3$ or CD_3OD using the residual signals from $CDCl_3$ (^1H: δ = 7.26 ppm) or CD_3OD (^1H: δ = 3.31 ppm) as an internal standard. Peak assignments of ^1H were determined by analysis of coupling constants and assisted by 2D ^1H COSY.

General Method for Regioselective Sulfonylation/Acylation of Diols and Polyols. Substrates were allowed to react with TsCl or acyl chloride (1.2−3.0 equiv) in the presence of $FeCl_3$ (0.01−0.1 equiv), benzoyl trifluoroacetone (0.02−0.2 equiv), and *N,N*-diisopropylethylamine or K_2CO_3 (1.6−4.0 equiv) in dry acetonitrile at room temperature for 1−12 h. The concentrated reaction mixture was directly purified by flash column chromatography, affording the pure sulfonylation/acylation products.

*Methyl-3-O-(4-toluenesulfonyl)-6-O-(tert-butyldimethylsilyl)-α-D-mannopyranoside (**2a**).*[12b] Methyl-6-*O*-(*tert*-butyldimethylsilyl)-α-D-mannopyranoside (0.1 mmol, 30.8 mg) was allowed to react with K_2CO_3 (26.3 mg, 1.9 equiv) and *p*-toluenesulfonyl chloride (28.6 mg, 1.5 equiv) in dry acetonitrile (0.5 mL) at room temperature for 6 h in the presence of $FeCl_3$ (1.6 mg, 0.1 equiv) and phenyltrifluoroacetone (4.4 mg, 0.2 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether = 1/3), affording compound **2a** as a viscous pale yellow oil (42.0 mg, 91%). ^1H NMR (400 MHz, CD_3OD): δ 7.84 (d, J = 8.0 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H), 4.56 (d, J = 1.2 Hz, 1H), 4.48 (dd, J = 9.2 and 3.2 Hz, 1H), 3.91−3.85 (m, 2H), 3.78−3.72 (m, 2H), 3.48−3.43 (m, 1H), 3.33 (s, 3H), 2.44 (s, 3H), 0.90 (s, 9H), 0.07 (s, 6H).

*Methyl-3-O-benzoyl-6-O-(tert-butyldimethylsilyl)-α-D-mannopyranoside (**2b**).*[5a] Methyl-6-*O*-(*tert*-butyldimethylsilyl)-α-D-mannopyranoside (0.1 mmol, 30.8 mg) was allowed to react with K_2CO_3 (26.3 mg, 1.9 equiv) and benzoyl chloride (18 μL, 1.5 equiv) in dry acetonitrile (0.5 mL) at room temperature for 4 h in the presence of $FeCl_3$ (1.6 mg, 0.1 equiv) and phenyltrifluoroacetone (4.4 mg, 0.2 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether = 1/3), affording compound **2b** as a yellow oil (37.9 mg, 92%). ^1H NMR (400 MHz, CD_3OD): δ 8.13−8.11 (m, 2H), 7.62−7.59 (m, 1H), 7.50−7.46 (m, 2H), 5.20 (dd, J = 9.6 and 3.2 Hz, 1H), 4.67 (d, J = 0.8 Hz, 1H), 4.09 (dd, J = 2.8 and 1.2 Hz, 1H), 4.02 (dd, J = 11.2 and 1.6 Hz, 1H), 3.96 (t, J = 10.0 Hz, 1H), 3.86 (dd, J = 10.8 and 6.4 Hz, 1H), 3.69−3.64 (m, 1H), 3.43 (s, 3H), 0.94 (s, 9H), 0.13 (s, 3H), 0.13 (s, 3H).

*Methyl-3-O-(4-toluenesulfonyl)-4,6-O-benzylidene-α-D-mannopyranoside (**4a**).*[15] Methyl-4,6-*O*-benzylidene-α-D-mannopyranoside (0.1 mmol, 28.2 mg) was allowed to react with K_2CO_3 (26.3 mg, 1.9 equiv) and *p*-toluenesulfonyl chloride (28.6 mg, 1.5 equiv) in dry acetonitrile (0.5 mL) at room temperature for 6 h in the presence of $FeCl_3$ (1.6 mg, 0.1 equiv) and phenyltrifluoroacetone (4.4 mg, 0.2 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether = 1/2), affording compound **4a** as a light yellow oil (42.3 mg, 97%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 8.0 Hz, 2H), 7.38−7.30 (m, 3H), 7.20 (d, J = 7.2 Hz, 2H), 7.04 (d, J = 7.6 Hz, 2H), 5.40 (s, 1H), 4.78−4.76 (m, 2H), 4.33 (s, 1H), 4.25−4.18 (m, 1H), 4.09 (t, J = 8.8 Hz, 1H), 3.83−3.74 (m, 2H), 3.38 (s, 3H), 2.31 (s, 3H).

*Methyl-3-O-benzoyl-4,6-O-benzylidene-α-D-mannopyranoside (**4b**).*[13] Methyl-4,6-*O*-benzylidene-α-D-mannopyranoside (0.1 mmol, 28.2 mg) was allowed to react with K_2CO_3 (26.3 mg, 1.9 equiv) and benzoyl chloride (18 μL, 1.5 equiv) in dry acetonitrile (0.5 mL) at room temperature for 2.5 h in the presence of $FeCl_3$ (1.6 mg, 0.1 equiv) and phenyltrifluoroacetone (4.4 mg, 0.2 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether = 1/2), affording compound **4b** as a white solid (34.4 mg, 89%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.07−8.05 (m, 2H), 7.58−7.53 (m, 1H), 7.45−7.41 (m, 4H), 7.33−7.30 (m, 3H), 5.60 (s, 1H), 5.55 (dd, J = 10.4 and 3.2 Hz, 1H), 4.78 (d, J = 1.6 Hz,1H), 4.34−4.25 (m, 3H), 4.03−3.97 (m, 1H), 3.93−3.88 (m, 1H), 3.43 (s, 3H).

*Methyl-3-O-acetyl-4,6-O-benzylidene-α-D-mannopyranoside (**4c**).*[16] Methyl-4,6-*O*-benzylidene-α-D-mannopyranoside (0.1 mmol, 28.2 mg) was allowed to react with *N,N*-diisopropylethylamine (28 μL, 1.6 equiv) and acetyl chloride (9 μL, 1.2 equiv) in dry acetonitrile (0.5 mL) at room temperature for 2 h in the presence of $FeCl_3$ (1.6 mg, 0.1 equiv) and phenyltrifluoroacetone (4.4 mg, 0.2 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether = 1/2), affording compound **4c** as a colorless syrup (20.0 mg, 62%). ^1H NMR (400 MHz, $CDCl_3$): δ

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7.46−7.44 (m, 2H), 7.39−7.35 (m, 3H), 5.55 (s, 1H), 5.33 (dd, J = 3.2 and 10.4 Hz, 1H), 4.75 (d, J = 0.8 Hz, 1H), 4.29 (dd, J = 4.0 and 9.6 Hz, 1H), 4.15 (s, 1H), 4.09 (t, J = 9.6 Hz, 1H), 3.96−3.90 (m, 1H), 3.88−3.83 (m, 1H), 3.41 (s, 3H), 2.13 (s, 3H).

*Methyl-3-O-pivaloyl-4,6-O-benzylidene-α-D-mannopyranoside (**4d**).*[17] Methyl-4,6-*O*-benzylidene-α-D-mannopyranoside (0.1 mmol, 28.2 mg) was allowed to react with *N*,*N*-diisopropylethylamine (34 μL, 1.9 equiv) and pivaloyl chloride (19 μL, 1.5 equiv) in dry acetonitrile (0.5 mL) at 50 °C for 5 h in the presence of $FeCl_3$ (1.6 mg, 0.1 equiv) and phenyltrifluoroacetone (4.4 mg, 0.2 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether = 1/2), affording compound **4d** as a white powder (30.0 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43−7.42 (m, 2H), 7.35−7.33 (m, 3H), 5.57 (s, 1H), 5.32 (dd, J = 10.0 and 2.4 Hz, 1H), 4.75 (s, 1H), 4.30 (dd, J = 9.2 and 3.2 Hz, 1H), 4.13−4.08 (m, 2H), 3.95−3.84 (m, 2H), 3.40 (s, 3H), 2.15 (br s, 1H), 1.23 (s, 9H).

*Methyl-3-O-(4-methoxybenzoyl)-4,6-O-benzylidene-α-D-mannopyranoside (**4e**).* Methyl-4,6-*O*-benzylidene-α-D-mannopyranoside (0.1 mmol, 28.2 mg) was allowed to react with *N*,*N*-diisopropylethylamine (34 μL, 1.9 equiv) and *p*-methoxybenzoyl chloride (25.6 mg, 1.5 equiv) in dry acetonitrile (0.5 mL) at room temperature for 5 h in the presence of $FeCl_3$ (1.6 mg, 0.1 equiv) and phenyltrifluoroacetone (4.4 mg, 0.2 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether = 1/1), affording compound **4e** as a colorless oil (36.6 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03−8.00 (m, 2H, Ar**H**), 7.44−7.42 (m, 2H, Ar**H**), 7.33−7.30 (m, 3H, Ar**H**), 6.92−6.88 (m, 2H, Ar**H**), 5.60 (s, 1H, PhC**H**), 5.52 (dd, J = 10.4 and 3.6 Hz, 1H, **H-3**), 4.79 (d, J = 1.6 Hz, 1H, **H-1**), 4.34−4.23 (m, 3H, **H-2**, **H-4**, **H-6a**), 4.03−3.88 (m, 2H, **H-5**, **H-6b**), 3.84 (s, 3H, PhO**CH$_3$**), 3.44 (s, 3H, O**CH$_3$**). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 165.4, 163.7, 137.4, 132.4, 132.0, 129.1, 128.3, 126.3, 122.2, 113.8, 102.0, 101.6, 77.3, 76.3, 71.3, 70.0, 69.0, 63.9, 55.6, 55.3 ppm. R_f: 0.75 (ethyl acetate/petroleum ether = 1/1). HRMS (ESI-TOF) m/z calcd. for $C_{22}H_{24}O_8Na$ [M + Na]$^+$: 439.1363; found: 439.1361.

*Methyl-3-O-palmitoyl-4,6-O-benzylidene-α-D-mannopyranoside (**4f**).* Methyl-4,6-*O*-benzylidene-α-D-mannopyranoside (0.1 mmol, 28.2 mg) was allowed to react with *N*,*N*-diisopropylethylamine (34 μL, 1.9 equiv) and palmitoyl chloride (41.2 mg, 1.5 equiv) in dry acetonitrile (0.5 mL) at room temperature for 2 h in the presence of $FeCl_3$ (1.6 mg, 0.1 equiv) and phenyltrifluoroacetone (4.4 mg, 0.2 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether = 1/2), affording compound **4f** as a colorless oil (48.4 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45−7.43 (m, 2H, Ar**H**), 7.36−7.33 (m, 3H, Ar**H**), 5.55 (s, 1H, PhC**H**), 5.35 (dd, J = 10 and 3.2 Hz, 1H, **H-3**), 4.74 (d, J = 1.2 Hz, 1H, **H-1**), 4.29 (dd, J = 9.6 and 4.4 Hz, 1H, **H-6a**), 4.14−4.13 (m, 1H, **H-2**), 4.09 (t, J = 9.6 Hz, 1H, **H-4**), 3.96−3.90 (m, 1H, **H-6b**), 3.88−3.83 (m, 1H, **H-5**), 3.41 (s, 3H, O**CH$_3$**), 2.39−2.35 (m, 2H, $CH_3(\mathbf{CH_2})_{14}CO$), 1.65−1.58 (m, 2H, $CH_3(\mathbf{CH_2})_{14}CO$), 1.32−1.21 (m, 24H, $CH_3(\mathbf{CH_2})_{14}CO$), 0.90−0.86 (m, 3H, $\mathbf{CH_3}(CH_2)_{14}CO$). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 172.8, 137.3, 129.1, 128.3, 126.2, 101.9, 101.5, 76.3, 70.5, 70.0, 69.0, 63.8, 55.2, 34.5, 32.0, 29.8, 29.8, 29.8, 29.8, 29.7, 29.5, 29.5, 29.4, 29.1, 25.2, 22.8, 14.2 ppm. R_f: 0.8 (ethyl acetate/petroleum ether = 1/2). HRMS (ESI-TOF) m/z calcd. for $C_{30}H_{48}O_7Na$ [M + Na]$^+$: 543.3292; found: 543.3296.

*Methyl-3-O-(4-toluenesulfonyl)-6-O-(tert-butyldimethylsilyl)-α-D-galactopyranoside (**5a**).*[12b] Methyl-6-*O*-(*tert*-butyldimethylsilyl)-α-D-galactopyranoside (0.1 mmol, 30.8 mg) was allowed to react with K_2CO_3 (26.3 mg, 1.9 equiv) and *p*-toluenesulfonyl chloride (28.6 mg, 1.5 equiv) in dry acetonitrile (0.5 mL) at room temperature for 5 h in the presence of $FeCl_3$ (1.6 mg, 0.1 equiv) and phenyltrifluoroacetone (4.4 mg, 0.2 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether = 1/3), affording compound **5a** as a white solid (42.0 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H), 4.79 (d, J = 4.0 Hz, 1H), 4.63 (dd, J = 10.0 and 2.8 Hz, 1H), 4.20 (d, J = 2.4 Hz, 1H), 4.05 (dd, J = 9.6 and 3.6 Hz, 1H), 3.87−3.77 (m, 2H), 3.72 (t, J = 5.2 Hz, 1H), 3.38 (s, 3H), 2.42 (s, 3H), 0.87 (s, 9H), 0.06 (s, 6H).

*Methyl-3-O-benzoyl-6-O-(tert-butyldimethylsilyl)-α-D-galactopyranoside (**5b**).*[5a] Methyl-6-*O*-(*tert*-butyldimethylsilyl)-α-D-galactopyranoside (0.1 mmol, 30.8 mg) was allowed to react with K_2CO_3 (26.3 mg, 1.9 equiv) and benzoyl chloride (18 μL, 1.5 equiv) in dry acetonitrile (0.5 mL) at room temperature for 2 h in the presence of $FeCl_3$ (1.6 mg, 0.1 equiv) and phenyltrifluoroacetone (4.4 mg, 0.2 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether = 1/2), affording compound **5b** as a pale yellow solid (40.0 mg, 97%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11−8.09 (m, 2H), 7.57−7.54 (m, 1H), 7.45−7.41 (m, 2H), 5.26 (dd, J = 10.0 and 2.0 Hz, 1H), 4.89 (d, J = 3.6 Hz, 1H), 4.31 (s, 1H), 4.24 (dd, J = 10 and 3.2 Hz, 1H), 3.95−3.84 (m, 3H), 3.45 (s, 3H), 0.89 (s, 9H), 0.09 (s, 6H).

*Methyl-3-O-(4-toluenesulfonyl)-6-O-(tert-butyldimethylsilyl)-β-D-galactopyranoside (**6a**).*[12b] Methyl-6-*O*-(*tert*-butyldimethylsilyl)-β-D-galactopyranoside (0.1 mmol, 30.8 mg) was allowed to react with K_2CO_3 (26.3 mg, 1.9 equiv) and *p*-toluenesulfonyl chloride (28.6 mg, 1.5 equiv) in dry acetonitrile (0.5 mL) at room temperature for 12 h in the presence of $FeCl_3$ (1.6 mg, 0.1 equiv) and phenyltrifluoroacetone (4.4 mg, 0.2 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether = 1/2), affording compound **6a** as a white solid (38.8 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 4.44 (dd, J = 9.6 and 3.2 Hz, 1H), 4.16 (d, J = 7.6 Hz, 1H), 4.14 (d, J = 3.2 Hz, 1H), 3.89−3.79 (m, 3H), 3.50 (s, 3H), 3.46−3.43 (m, 1H), 2.42 (s, 3H), 0.86 (s, 9H), 0.05 (s, 6H).

*Methyl-3-O-benzoyl-6-O-(tert-butyldimethylsilyl)-β-D-galactopyranoside (**6b**).*[13] Methyl-6-*O*-(*tert*-butyldimethylsilyl)-β-D-galactopyranoside (0.1 mmol, 30.8 mg) was allowed to react with K_2CO_3 (26.3 mg, 1.9 equiv) and benzoyl chloride (18 μL, 1.5 equiv) in dry acetonitrile (0.5 mL) at room temperature for 2.5 h in the presence of $FeCl_3$ (1.6 mg, 0.1 equiv) and phenyltrifluoroacetone (4.4 mg, 0.2 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether = 1/3), affording compound **6b** as a colorless oil (37.9 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11−8.09 (m, 2H), 7.58−7.54 (m, 1H), 7.45−7.41 (m, 2H), 5.07 (dd, J = 10.0 and 3.2 Hz, 1H), 4.32−4.28 (m, 2H), 4.04 (dd, J = 10.0 and 7.6 Hz, 1H), 3.96 (dd, J = 10.4 and 5.6 Hz, 1H), 3.90 (dd, J = 10.8 and 4.8 Hz, 1H), 3.61−3.57 (m, 4H), 0.89 (s, 9H), 0.08 (s, 6H).

*Methyl-3-O-(4-toluenesulfonyl)-α-L-fucopyranoside (**7a**).*[12b] Methyl-α-L-fucopyranoside (0.1 mmol, 17.8 mg) was allowed to react with K_2CO_3 (26.3 mg, 1.9 equiv) and *p*-toluenesulfonyl chloride (28.6 mg, 1.5 equiv) in dry acetonitrile (0.5 mL) at room temperature for 2.5 h in the presence of $FeCl_3$ (1.6 mg, 0.1 equiv) and phenyltrifluoroacetone (4.4 mg, 0.2 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether = 1/1), affording compound **7a** as a viscous pale yellow oil (30.2 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 7.6 Hz, 2H), 4.74 (d, J = 3.6 Hz, 1H), 4.63 (dd, J = 10.0 and 2.8 Hz, 1H), 4.00−3.90 (m, 3H), 3.38 (s, 3H), 2.43 (s, 3H), 1.27 (d, J = 6.4 Hz, 3H).

*Methyl-3-O-benzoyl-α-L-fucopyranoside (**7b**).*[5a] Methyl-α-L-fucopyranoside (0.1 mmol, 17.8 mg) was allowed to react with K_2CO_3 (26.3 mg, 1.9 equiv) and benzoyl chloride (17.5 μL, 1.5 equiv) in dry acetonitrile (0.5 mL) at room temperature for 2 h in the presence of $FeCl_3$ (1.6 mg, 0.1 equiv) and phenyltrifluoroacetone (4.4 mg, 0.2 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether = 1/2), affording compound **7b** as a pale yellow solid (26.2 mg, 93%). ^{1}H NMR (400 MHz, CD_3OD): δ 8.12 (d, J = 7.6 Hz, 2H), 7.62−7.59 (m, 1H), 7.50−7.46 (m, 2H), 5.23 (dd, J = 10.4 and 2.8 Hz, 1H), 4.75 (d, J = 3.6 Hz, 1H), 4.15 (dd, J = 10.4 and 3.6 Hz, 1H), 4.06 (dd, J = 12.8 and 6.4 Hz, 1H), 3.96 (d, J = 2.0 Hz, 1H), 3.44 (s, 3H), 1.25 (d, J = 6.4 Hz, 3H).

*Methyl-3-O-(4-toluenesulfonyl)-α-L-rhamnopyranoside (**8a**).*[12b] Methyl-α-L-rhamnopyranoside (0.1 mmol, 17.8 mg) was allowed to react with K_2CO_3 (26.3 mg, 1.9 equiv) and *p*-toluenesulfonyl chloride

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(28.6 mg, 1.5 equiv) in dry acetonitrile (0.5 mL) at room temperature for 2 h in the presence of $FeCl_3$ (1.6 mg, 0.1 equiv) and phenyltrifluoroacetone (4.4 mg, 0.2 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether = 1/1), affording compound **8a** as a viscous pale yellow oil (30.9 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 4.61−4.58 (m, 2H), 3.97 (br s, 1H), 3.71−3.58 (m, 2H), 3.32 (s, 3H), 2.82 (d, J = 2.8 Hz, 1H), 2.62 (d, J = 3.2 Hz, 1H), 2.43 (s, 3H), 1.30 (d, J = 6.0 Hz, 3H).

*Methyl-3-O-benzoyl-α-L-rhamnopyranoside (**8b**).*[5a] Methyl-α-L-rhamnopyranoside (0.1 mmol, 17.8 mg) was allowed to react with K_2CO_3 (26.3 mg, 1.9 equiv) and benzoyl chloride (18 μL, 1.5 equiv) in dry acetonitrile (0.5 mL) at room temperature for 2 h in the presence of $FeCl_3$ (1.6 mg, 0.1 equiv) and phenyltrifluoroacetone (4.4 mg, 0.2 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether = 1/2), affording compound **8b** as a yellow oil (26.8 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, J = 7.6 Hz, 2H), 7.57−7.53 (m, 1H), 7.43−7.39 (m, 2H), 5.23 (d, J = 6.0 Hz, 1H), 4.66 (s, 1H), 4.12 (s, 1H), 3.80−3.75 (m, 2H), 3.37 (s, 3H), 1.35 (d, J = 5.2 Hz, 3H).

*Phenyl-3-O-(4-toluenesulfonyl)-4,6-O-benzylidene-1-thio-α-D-mannopyranoside (**9a**).* Phenyl-4,6-*O*-benzylidene-1-thio-α-D-mannopyranoside (0.1 mmol, 36.0 mg) was allowed to react with K_2CO_3 (26.3 mg, 1.9 equiv) and *p*-toluenesulfonyl chloride (28.6 mg, 1.5 equiv) in dry acetonitrile (0.5 mL) at room temperature for 4 h in the presence of $FeCl_3$ (1.6 mg, 0.1 equiv) and phenyltrifluoroacetone (4.4 mg, 0.2 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether = 1/3), affording compound **9a** as a light yellow oil (42.1 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, J = 8.0 Hz, 2H, Ar**H**), 7.47−7.45 (m, 2H, Ar**H**), 7.39−7.29 (m, 6H, Ar**H**), 7.23−7.21 (m, 2H, Ar**H**), 7.09 (d, J = 8.0 Hz, 2H, Ar**H**), 5.57 (d, J = 0.8 Hz, 1H, **H-1**), 5.41 (s, 1H, PhC**H**), 4.82 (dd, J = 10.0 and 3.2 Hz, 1H, **H-3**), 4.58 (s, 1H, **H-2**), 4.33−4.27 (m, 1H, **H-5**), 4.18−4.13 (m, 2H, **H-4**, **H-6a**), 3.80 (t, J = 10.0 Hz, 1H, **H-6b**), 3.13 (br s, 1H, O**H**), 2.34 (s, 3H, Ar**CH**$_3$). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 145.0, 137.0, 132.9, 132.8, 132.1, 129.8, 129.4, 129.2, 128.3, 128.2, 126.3, 101.9, 88.3, 78.6, 75.7, 72.1, 68.4, 65.4, 21.9 ppm. R_f: 0.6 (ethyl acetate/petroleum ether = 1/3). HRMS (ESI-TOF) m/z calcd. for $C_{26}H_{26}O_7S_2Na$ [M + Na]$^+$: 537.1012; found: 537.1001.

*Phenyl-3-O-benzoyl-4,6-O-benzylidene-1-thio-α-D-mannopyranoside (**9b**).*[8] Phenyl-4,6-*O*-benzylidene-1-thio-α-D-mannopyranoside (0.1 mmol, 36.0 mg) was allowed to react with K_2CO_3 (26.3 mg, 1.9 equiv) and benzoyl chloride (18 μL, 1.5 equiv) in dry acetonitrile (0.5 mL) at room temperature for 2 h in the presence of $FeCl_3$ (1.6 mg, 0.1 equiv) and phenyltrifluoroacetone (4.4 mg, 0.2 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether = 1/3), affording compound **9b** as a white solid (37.6 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, J = 8.0 Hz, 2H), 7.60−7.57 (m, 1H), 7.52−7.44 (m, 6H), 7.34−7.30 (m, 6H), 5.62−5.58 (m, 3H), 4.59−4.51 (m, 2H), 4.37 (t, J = 9.6 Hz), 4.27 (dd, J = 10.4 and 4.8 Hz, 1H), 3.92 (t, J = 10.0 Hz, 1H).

*p-Tolyl-3-O-(4-toluenesulfonyl)-6-O-(tert-butyldimethylsilyl)-1-thio-β-D-galactopyranoside (**10a**).* *p*-Tolyl-6-*O*-(*tert*-butyldimethylsilyl)-1-thio-β-D-galactopyranoside (0.1 mmol, 40.1 mg) was allowed to react with K_2CO_3 (26.3 mg, 1.9 equiv) and *p*-toluenesulfonyl chloride (28.6 mg, 1.5 equiv) in dry acetonitrile (0.5 mL) at room temperature for 5 h in the presence of $FeCl_3$ (1.6 mg, 0.1 equiv) and phenyltrifluoroacetone (4.4 mg, 0.2 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether = 1/3), affording compound **10a** as a colorless oil (50.5 mg, 91%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.83 (d, J = 8.4 Hz, 2H, Ar**H**), 7.41 (d, J = 7.8 Hz, 2H, Ar**H**), 7.30 (d, J = 7.8 Hz, 2H, Ar**H**), 7.06 (d, J = 7.8 Hz, Ar**H**), 4.49 (dd, J = 9.6 and 3.0 Hz, 1H, **H-3**), 4.45 (d, J = 9.6 Hz, 1H, **H-1**), 4.20 (s, 1H, **H-4**), 3.90−3.83 (m, 3H, **H-2**, **H-6a**, **H-6b**), 3.48 (t, J = 4.8 Hz, 1H, **H-5**), 2.40 (s, 3H, Ar**CH**$_3$), 2.30 (s, 3H, Ar**CH**$_3$), 0.88 (s, 9H, Si(C(**CH**$_3$)$_3$)(CH$_3$)$_2$), 0.08 (s, 3H, Si(C(CH$_3$)$_3$)(**CH**$_3$)$_2$), 0.07 (s, 3H, Si(C(CH$_3$)$_3$)-(**CH**$_3$)$_2$). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 145.1, 138.3, 133.6, 133.3, 129.8, 129.8, 128.0, 127.9, 88.6, 84.3, 77.6, 68.8, 66.7, 62.9, 25.9, 21.7, 21.2, 18.2, −5.4 ppm. R_f: 0.4 (ethyl acetate/petroleum ether = 1/3). HRMS (ESI-TOF) m/z calcd. for $C_{26}H_{38}O_7S_2SiNa$ [M + Na]$^+$: 577.1720; found: 577.1712.

*p-Tolyl-3-O-benzoyl-6-O-(tert-butyldimethylsilyl)-1-thio-β-D-galactopyranoside (**10b**).*[13] *p*-Tolyl-6-*O*-(*tert*-butyldimethylsilyl)-1-thio-β-D-galactopyranoside (0.1 mmol, 40.1 mg) was allowed to react with K_2CO_3 (26.3 mg, 1.9 equiv) and benzoyl chloride (18 μL, 1.5 equiv) in dry acetonitrile (0.5 mL) at room temperature for 2 h in the presence of $FeCl_3$ (1.6 mg, 0.1 equiv) and phenyltrifluoroacetone (4.4 mg, 0.2 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether = 1/3), affording compound 10b as a viscous pale yellow oil (42.4 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, J = 8.0 Hz, 2H), 7.57−7.40 (m, 5H), 7.13 (d, J = 7.6 Hz, 2H), 5.10 (dd, J = 9.6 and 2.4 Hz, 1H), 4.58 (d, J = 9.6 Hz, 1H), 4.35 (s, 1H), 4.07−3.91 (m, 3H), 3.63−3.60 (m, 1H), 2.35 (s, 3H), 0.91 (s, 9H), 0.12 (s, 3H), 0.10 (s, 3H).

*p-Tolyl-3-O-acetyl-6-O-(tert-butyldimethylsilyl)-1-thio-β-D-galactopyranoside (**10c**).*[8] *p*-Tolyl-6-*O*-(*tert*-butyldimethylsilyl)-1-thio-β-D-galactopyranoside (0.1 mmol, 40.1 mg) was allowed to react with *N*,*N*-diisopropylethylamine (28 μL, 1.6 equiv) and acetyl chloride (9 μL, 1.2 equiv) in dry acetonitrile (0.5 mL) at room temperature for 3 h in the presence of $FeCl_3$ (1.6 mg, 0.1 equiv) and phenyltrifluoroacetone (4.4 mg, 0.2 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether = 1/2), affording compound **10c** as a viscous pale yellow oil (34.6 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 4.85 (dd, J = 9.2 Hz and 2.4 Hz, 1H), 4.50 (d, J = 9.6 Hz, 1H), 4.22 (d, J = 2.0 Hz, 1H), 3.98 (dd, J = 10.8 and 4.8 Hz, 1H), 3.92−3.83 (m, 2H), 3.53 (t, J = 3.6 Hz, 1H), 2.33 (s, 3H), 2.14 (s, 3H), 0.90 (s, 9H), 0.12 (s, 3H), 0.10 (s, 3H).

*Isopropylthio-3-O-(4-toluenesulfonyl)-6-O-(tert-butyldimethylsilyl)-β-D-galactopyranoside (**11a**).*[12b] Isopropylthio-6-*O*-(*tert*-butyldimethylsilyl)-β-D-galactopyranoside (0.1 mmol, 35.2 mg) was allowed to react with K_2CO_3 (26.3 mg, 1.9 equiv) and *p*-toluenesulfonyl chloride (28.6 mg, 1.5 equiv) in dry acetonitrile (0.5 mL) at room temperature for 5 h in the presence of $FeCl_3$ (1.6 mg, 0.1 equiv) and phenyltrifluoroacetone (4.4 mg, 0.2 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether = 1/3), affording compound **11a** as a viscous yellow oil (47.1 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 4.50 (dd, J = 9.2 and 2.8 Hz, 1H), 4.37 (d, J = 10.0 Hz, 1H), 4.21 (s, 1H), 3.89−3.78 (m, 3H), 3.48 (t, J = 5.2 Hz, 1H), 3.22−3.15 (m, 1H), 2.43 (s, 3H), 1.29 (d, J = 6.8 Hz, 6H), 0.86 (s, 9H), 0.05 (s, 6H).

*Isopropylthio-3-O-benzoyl-6-O-(tert-butyldimethylsilyl)-β-D-galactopyranoside (**11b**).*[13] Isopropylthio-6-*O*-(*tert*-butyldimethylsilyl)-β-D-galactopyranoside (0.1 mmol, 35.2 mg) was allowed to react with K_2CO_3 (26.3 mg, 1.9 equiv) and benzoyl chloride (18 μL, 1.5 equiv) in dry acetonitrile (0.5 mL) at room temperature for 1 h in the presence of $FeCl_3$ (1.6 mg, 0.1 equiv) and phenyltrifluoroacetone (4.4 mg, 0.2 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether = 1/3), affording compound **11b** as a viscous yellow oil (43.0 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, J = 7.6 Hz, 2H), 7.57 (t, J = 7.2 Hz, 1H), 7.46−7.42 (m, 2H), 5.11 (dd, J = 9.6 and 2.0 Hz, 1H), 4.51 (d, J = 9.6 Hz, 1H), 4.33 (s, 1H), 4.07 (t, J = 9.6 Hz, 1H), 3.96−3.86 (m, 2H), 3.62 (t, J = 4.4 Hz, 1H), 3.29−3.23 (m, 1H), 1.37 (s, 3H), 1.35 (s, 3H), 0.88 (s, 9H), 0.08 (s, 6H).

*Isopropylthio-3-O-acetyl-6-O-(tert-butyldimethylsilyl)-β-D-galactopyranoside (**11c**).*[8] Isopropylthio-6-*O*-(*tert*-butyldimethylsilyl)-β-D-galactopyranoside (0.1 mmol, 35.2 mg) was allowed to react with *N*,*N*-diisopropylethylamine (28 μL, 1.6 equiv) and acetyl chloride (9 μL, 1.2 equiv) in dry acetonitrile (0.5 mL) at room temperature for 3.5 h in the presence of $FeCl_3$ (1.62 mg, 0.1 equiv) and phenyltrifluoroacetone (4.4 mg, 0.2 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether = 1/2), affording compound **11c** as a viscous pale yellow oil (29.9 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.85 (dd, J = 9.2 and 2.0 Hz, 1H), 4.44 (d, J = 10.0 Hz, 1H), 4.21 (d, J = 1.6

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Hz, 1H), 3.92−3.83 (m, 3H), 3.53 (t, J = 4.4 Hz, 1H), 3.26−3.19 (m, 1H), 2.17 (s, 3H), 1.33 (d, J = 6.4 Hz, 6H), 0.87 (s, 9H), 0.07 (s, 3H), 0.07 (s, 3H).

*Phenyl-3-O-(4-toluenesulfonyl)-6-O-(tert-butyldimethylsilyl)-1-thio-β-D-galactopyranoside (**12a**).* Phenyl-6-*O*-(*tert*-butyldimethylsilyl)-1-thio-β-D-galactopyranoside (0.1 mmol, 36.8 mg) was allowed to react with K_2CO_3 (26.3 mg, 1.9 equiv) and *p*-toluenesulfonyl chloride (28.6 mg, 1.5 equiv) in dry acetonitrile (0.5 mL) at room temperature for 2 h in the presence of $FeCl_3$ (1.6 mg, 0.1 equiv) and phenyltrifluoroacetone (4.4 mg, 0.2 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether = 1/3), affording compound **12a** as a light yellow oil (49.1 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, J = 8.4 Hz, 2H, Ar**H**), 7.55−7.50 (m, 2H, Ar**H**), 7.33−7.26 (m, 5H, Ar**H**), 4.51−4.48 (m, 2H, **H-3**, **H-1**), 4.23 (t, J = 2.8 Hz, 1H, **H-4**), 3.93−3.84 (m, 3H, **H-2**, **H-6a**, **H-6b**), 3.50 (t, J = 5.2 Hz, 1H, **H-5**), 2.43 (s, 3H, Ar**CH$_3$**), 0.89 (s, 9H, Si(C(**CH$_3$**)$_3$)(CH$_3$)$_2$), 0.08 (s, 3H, Si(C-(CH$_3$)$_3$)(**CH$_3$**)$_2$), 0.07 (s, 3H, Si(C(CH$_3$)$_3$)(**CH$_3$**)$_2$). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 145.2, 133.7, 132.8, 131.8, 129.9, 129.1, 128.3, 128.1, 88.6, 84.2, 77.8, 68.9, 66.9, 63.0, 25.9, 21.8, 18.3, −5.3 ppm. R_f: 0.6 (ethyl acetate/petroleum ether = 1/3). HRMS (ESI-TOF) m/z calcd. for $C_{25}H_{36}O_7S_2SiNa$ [M + Na]$^+$: 563.1564; found: 563.1569.

*Phenyl-3-O-benzoyl-6-O-(tert-butyldimethylsilyl)-1-thio-β-D-galactopyranoside (**12b**).*[13] Phenyl-6-*O*-(*tert*-butyldimethylsilyl)-1-thio-β-D-galactopyranoside (0.1 mmol, 36.8 mg) was allowed to react with K_2CO_3 (26.3 mg, 1.9 equiv) and benzoyl chloride (18 μL, 1.5 equiv) in dry acetonitrile (0.5 mL) at room temperature for 2 h in the presence of $FeCl_3$ (1.6 mg, 0.1 equiv) and phenyltrifluoroacetone (4.4 mg, 0.2 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether = 1/3), affording compound **12b** as a viscous pale yellow oil (45.6 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10−8.08 (m, 2H), 7.62−7.54 (m, 3H), 7.45−7.41 (m, 2H), 7.33−7.30 (m, 3H), 5.11 (dd, J = 9.6 and 3.2 Hz, 1H), 4.65 (d, J = 9.6 Hz, 1H), 4.36 (d, J = 2.8 Hz, 1H), 4.09 (t, J = 9.6 Hz, 1H), 4.02−3.91 (m, 2H), 3.64 (t, J = 4.8 Hz, 1H), 0.91 (s, 9H), 0.12 (s, 3H), 0.10 (s, 3H).

*Phenyl-3′-O-(4-toluenesulfonyl)-6,6′-di-O-(tert-butyldimethylsilyl)-1-S-β-D-lactoside (**13a**).* Phenyl-6,6′-di-*O*-(*tert*-butyldimethylsilyl)-1-*S*-β-D-lactoside (0.1 mmol, 66.3 mg) was allowed to react with K_2CO_3 (26.3 mg, 1.9 equiv) and *p*-toluenesulfonyl chloride (28.6 mg, 1.5 equiv) in dry acetonitrile (0.5 mL) at room temperature for 6 h in the presence of $FeCl_3$ (1.6 mg, 0.1 equiv) and phenyltrifluoroacetone (4.4 mg, 0.2 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether = 1/1), affording compound **13a** as a light yellow oil (67.8 mg, 83%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.82 (d, J = 7.8 Hz, 2H, Ar**H**), 7.54−7.53 (m, 2H, Ar**H**), 7.30 (d, J = 8.4 Hz, 2H, Ar**H**), 7.28−7.24 (m, 3H, Ar**H**), 4.49 (d, J = 9.6 Hz, 1H, **H-1**), 4.34−4.32 (m, 2H, **H-1′**, **H-3′**), 4.15 (br s, 1H, **H-4′**), 3.89−3.80 (m, 5H, **H-2′**, **H-6a**, **H-6b**, **H-6a′**, **H-6b′**), 3.63 (t, J = 9.0 Hz, 1H, **H-3**), 3.54−3.48 (m, 2H, **H-4**, **H-5′**), 3.35 (d, J = 9.6 Hz, 1H, **H-5**), 3.31 (t, J = 9.0 Hz, 1H, **H-2**), 2.42 (s, 3H, Ar**CH$_3$**), 0.86 (s, 9H, Si(C(**CH$_3$**)$_3$)(CH$_3$)$_2$), 0.85 (s, 9H, Si(C(**CH$_3$**)$_3$)(CH$_3$)$_2$), 0.05 (s, 3H, Si(C(CH$_3$)$_3$)(**CH$_3$**)$_2$), 0.03 (s, 9H, Si(C(CH$_3$)$_3$)(**CH$_3$**)$_2$). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 145.1, 133.3, 133.3, 129.9, 129.8, 128.9, 128.2, 128.1, 103.8, 87.3, 83.3, 80.3, 78.9, 76.2, 74.5, 71.7, 67.7, 62.7, 61.7, 26.0, 26.0, 25.9, 25.8, 21.8, 18.4, 18.3, −3.5, −5.1, −5.2, −5.4, −5.4 ppm. R_f: 0.7 (ethyl acetate/petroleum ether = 1/1). HRMS (ESI-TOF) m/z calcd. for $C_{37}H_{60}O_{12}S_2Si_2Na$ [M + Na]$^+$: 839.2957; found: 839.2975.

*Phenyl-3′-O-benzoyl-6,6′-di-O-(tert-butyldimethylsilyl)-1-S-β-D-lactoside (**13b**).*[13] Phenyl-6,6′-di-*O*-(*tert*-butyldimethylsilyl)-1-*S*-β-D-lactoside (0.1 mmol, 66.3 mg) was allowed to react with K_2CO_3 (26.3 mg, 1.9 equiv) and benzoyl chloride (18 μL, 1.5 equiv) in dry acetonitrile (0.5 mL) at room temperature for 1 h in the presence of $FeCl_3$ (1.6 mg, 0.1 equiv) and phenyltrifluoroacetone (4.4 mg, 0.2 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether = 1/1), affording compound **13b** as a viscous colorless oil (65.2 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, J = 7.6 Hz, 2H), 7.59−7.55 (m, 3H), 7.46−7.42 (m, 2H), 7.29−7.26 (m, 3H), 5.02 (dd, J = 10.0 and 2.4 Hz, 1H), 4.52−4.48 (m, 2H), 4.29 (d, J = 2.0 Hz, 1H), 4.09−4.05 (m, 1H), 3.94−3.89 (m, 4H), 3.69−3.58 (m, 3H), 3.44−3.35 (m, 2H), 0.90 (s, 9H), 0.87 (s, 9H), 0.09 (s, 6H), 0.07 (s, 6H).

*Methyl-2,3-di-O-benzyl-6-O-(4-toluenesulfonyl)-α-D-glucopyranoside (**14a**).*[18] Methyl-2,3-di-*O*-benzyl-α-D-glucopyranoside (0.1 mmol, 37.4 mg) was allowed to react with K_2CO_3 (26.3 mg, 1.9 equiv) and *p*-toluenesulfonyl chloride (28.6 mg, 1.5 equiv) in dry acetonitrile (0.5 mL) at room temperature for 12 h in the presence of $FeCl_3$ (1.6 mg, 0.1 equiv) and phenyltrifluoroacetone (4.4 mg, 0.2 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether = 1/3), affording compound **14a** as a gummy liquid (48.6 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, J = 8.4 Hz, 2H), 7.38−7.29 (m, 12H), 4.99 (d, J = 11.2 Hz, 1H), 4.77−4.62 (m, 3H), 4.55 (d, J = 3.6 Hz, 1H), 4.23−4.22 (m, 2H), 3.76−3.69 (m, 2H), 3.48−3.41 (m, 2H), 3.33 (s, 3H), 2.43 (s, 3H).

*Methyl-2,3-di-O-benzyl-6-O-benzoyl-α-D-glucopyranoside (**14b**).*[19] Methyl-2,3-di-*O*-benzyl-α-D-glucopyranoside (0.1 mmol, 37.4 mg) was allowed to react with *N*,*N*-diisopropylethylamine (34 μL, 1.9 equiv) and benzoyl chloride (18 μL, 1.5 equiv) in dry acetonitrile (0.5 mL) at room temperature for 2.5 h in the presence of $FeCl_3$ (1.6 mg, 0.1 equiv) and phenyltrifluoroacetone (4.4 mg, 0.2 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether = 1/3), affording compound **14b** as a colorless oil (44.5 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, J = 8.0 Hz, 2H), 7.58−7.54 (m, 1H), 7.45−7.32 (m, 12H), 5.02 (d, J = 11.2 Hz, 1H), 4.80−4.76 (m, 2H), 4.69−4.60 (m, 3H), 4.52 (d, J = 12 Hz, 1H), 3.89−3.82 (m, 2H), 3.56−3.52 (m, 2H), 3.45 (s, 3H).

*Methyl-2,3-di-O-benzyl-6-O-(4-toluenesulfonyl)-α-D-galactopyranoside (**15a**).*[20] Methyl-2,3-di-*O*-benzyl-α-D-galactopyranoside (0.1 mmol, 37.4 mg) was allowed to react with K_2CO_3 (26.3 mg, 1.9 equiv) and *p*-toluenesulfonyl chloride (28.6 mg, 1.5 equiv) in dry acetonitrile (0.5 mL) at room temperature for 12 h in the presence of $FeCl_3$ (1.6 mg, 0.1 equiv) and phenyltrifluoroacetone (4.4 mg, 0.2 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether = 1/3), affording compound **15a** as a colorless syrup (46.5 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, J = 8.4 Hz, 2H), 7.38−7.28 (m, 12H), 4.77 (d, J = 12.0 Hz, 2H), 4.68−4.61 (m, 2H), 4.59 (d, J = 3.6 Hz, 1H), 4.22−4.11 (m, 2H), 3.95−3.92 (m, 2H), 3.84 (dd, J = 9.6 and 3.2 Hz, 1H), 3.75 (dd, J = 9.6 and 3.6 Hz, 1H), 3.33 (s, 3H), 2.43 (s, 3H).

*Methyl-2,3-di-O-benzyl-6-O-benzoyl-α-D-galactopyranoside (**15b**).*[19] Methyl-2,3-di-*O*-benzyl-α-D-galactopyranoside (0.1 mmol, 37.4 mg) was allowed to react with *N*,*N*-diisopropylethylamine (34 μL, 1.9 equiv) and benzoyl chloride (18 μL, 1.5 equiv) in dry acetonitrile (0.5 mL) at room temperature for 6 h in the presence of $FeCl_3$ (1.6 mg, 0.1 equiv) and phenyltrifluoroacetone (4.4 mg, 0.2 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether = 1/3), affording compound **15b** as a white amorphous solid (40.1 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, J = 8.0 Hz, 2H), 7.57 (t, J = 7.2 Hz, 1H), 7.46−7.29 (m, 12H), 4.83 (d, J = 11.2 Hz, 2H), 4.73−4.66 (m, 3H), 4.58−4.48 (m, 2H), 4.07−4.04 (m, 2H), 3.93−3.85 (m, 2H), 3.37 (s, 3H).

*Methyl-2,3-di-O-benzyl-6-O-(4-toluenesulfonyl)-α-D-mannopyranoside (**16a**).* Methyl-2,3-di-*O*-benzyl-α-D-mannopyranoside (0.1 mmol, 37.4 mg) was allowed to react with K_2CO_3 (26.3 mg, 1.9 equiv) and *p*-toluenesulfonyl chloride (28.6 mg, 1.5 equiv) in dry acetonitrile (0.5 mL) at room temperature for 2 h in the presence of $FeCl_3$ (1.6 mg, 0.1 equiv) and phenyltrifluoroacetone (4.4 mg, 0.2 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether = 1/3), affording compound **16a** as a light yellow oil (46.5 mg, 88%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.80 (d, J = 7.8 Hz, 2H, Ar**H**), 7.36−7.27 (m, 12H, Ar**H**), 4.71 (s, 1H, **H-1**), 4.65 (d, J = 12.0 Hz, 1H, C**H$_2$**Ph), 4.61 (d, J = 12.0 Hz, 1H, C**H$_2$**Ph), 4.56 (d, J = 11.4 Hz, 1H, C**H$_2$**Ph), 4.43 (d, J = 12.0 Hz, 1H, C**H$_2$**Ph), 4.39 (d, J = 10.8 Hz, 1H, **H-6a**), 4.24 (dd, J = 10.8 and 6.6 Hz, 1H, **H-6b**), 3.87 (t, J = 9.6 Hz, 1H, **H-4**), 3.77−3.73 (m, 2H, **H-2**, **H-5**), 3.65 (dd, J = 9.6 and 3.0 Hz, 1H, **H-3**), 3.30

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(s, 3H, OCH_3), 2.42 (s, 3H, $ArCH_3$). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 144.7, 138.0, 137.9, 133.1, 129.8, 128.6, 128.5, 128.1, 128.0, 127.9, 127.9, 99.1, 79.5, 73.7, 72.7, 71.7, 70.5, 69.6, 66.4, 55.1, 21.7 ppm. R_f: 0.4 (ethyl acetate/petroleum ether = 1/3). HRMS (ESI-TOF) m/z calcd. for $C_{28}H_{32}O_8SNa$ $[M + Na]^+$: 551.1710; found:551.1701.

*Methyl-2,3-di-O-benzyl-6-O-benzoyl-α-D-mannopyranoside (**16b**).*[19] Methyl-2,3-di-*O*-benzyl-α-D-mannopyranoside (0.1 mmol, 37.4 mg) was allowed to react with *N*,*N*-diisopropylethylamine (34 μL, 1.9 equiv) and benzoyl chloride (18 μL, 1.5 equiv) in dry acetonitrile (0.5 mL) at room temperature for 2 h in the presence of $FeCl_3$ (1.6 mg, 0.1 equiv) and phenyltrifluoroacetone (4.4 mg, 0.2 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether = 1/3), affording compound **16b** as a colorless oil (39.7 mg, 83%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, J = 7.6 Hz, 2H), 7.54 (t, J = 7.2 Hz, 1H), 7.40−7.28 (m, 12H), 4.82 (s, 1H), 4.70−4.61 (m, 5H), 4.52 (d, J = 11.6 Hz, 1H), 4.12 (t, J = 9.6 Hz, 1H), 3.87−3.82 (m, 2H), 3.75 (dd, J = 9.2 and 2.0 Hz, 1H), 3.38 (s, 3H).

*Methyl-3,6-di-O-(4-toluenesulfonyl)-α-D-galactopyranoside (**17a**).*[11c] Methyl-α-D-galactopyranoside (0.1 mmol, 19.4 mg) was allowed to react with K_2CO_3 (55.3 mg, 4.0 equiv) and *p*-toluenesulfonyl chloride (57.2 mg, 3.0 equiv) in dry acetonitrile (0.5 mL) at room temperature for 4.5 h in the presence of $FeCl_3$ (1.6 mg, 0.1 equiv) and phenyltrifluoroacetone (4.4 mg, 0.2 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether = 2/1), affording compound **17a** as a light yellow oil (45.7 mg, 91%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, J = 7.6 Hz, 2H), 7.78 (d, J = 7.6 Hz, 2H), 7.34 (d, J = 7.6 Hz, 4H), 4.72 (d, J = 2.0 Hz, 1H), 4.55 (d, J = 8.8 Hz, 1H), 4.21−4.13 (m, 3H), 3.99−3.92 (m, 2H), 3.35 (s, 3H), 2.44 (s, 6H).

*Methyl-3,6-di-O-benzyl-α-D-galactopyranoside (**17b**).*[13] Methyl-α-D-galactopyranoside (0.1 mmol, 19.4 mg) was allowed to react with *N*,*N*-diisopropylethylamine (70 μL, 4.0 equiv) and benzoyl chloride (35.0 μL, 3.0 equiv) in dry acetonitrile (0.5 mL) at room temperature for 2.5 h in the presence of $FeCl_3$ (1.6 mg, 0.1 equiv) and phenyltrifluoroacetone (4.4 mg, 0.2 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether = 1/1), affording compound **17b** as a colorless oil (37.0 mg, 92%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.10−8.00 (m, 4H), 7.58−7.53 (m, 2H), 7.45−7.41 (m, 4H), 5.34 (dd, J = 10.0 and 1.6 Hz, 1H), 4.93 (d, J = 2.4 Hz, 1H), 4.62−4.58 (m, 1H), 4.53−4.49 (m, 1H), 4.25−4.20 (m, 3H), 3.47 (s, 3H).

*Methyl-3,6-di-O-(4-toluenesulfonyl)-β-D-galactopyranoside (**18a**).*[21] Methyl-β-D-galactopyranoside (0.1 mmol, 19.4 mg) was allowed to react with K_2CO_3 (55.3 mg, 4.0 equiv) and *p*-toluenesulfonyl chloride (57.2 mg, 3.0 equiv) in dry acetonitrile (0.5 mL) at room temperature for 4.5 h in the presence of $FeCl_3$ (1.6 mg, 0.1 equiv) and phenyltrifluoroacetone (4.4 mg, 0.2 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether = 2/1), affording compound **18a** as a light yellow oil (47.7 mg, 95%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, J = 8.0 Hz, 2H), 7.78 (d, J = 7.6 Hz, 2H), 7.34 (d, J = 7.2 Hz, 4H), 4.38 (dd, J = 9.6 and 1.6 Hz, 1H), 4.23−4.17 (m, 2H), 4.14−4.11 (m, 2H), 3.76−3.71 (m, 2H), 3.44 (s, 3H), 2.43 (s, 6H).

*Methyl-3,6-di-O-benzyl-β-D-galactopyranoside (**18b**).*[13] Methyl-β-D-galactopyranoside (0.1 mmol, 19.4 mg) was allowed to react with *N*,*N*-diisopropylethylamine (70 μL, 4.0 equiv) and benzoyl chloride (35.0 μL, 3.0 equiv) in dry acetonitrile (0.5 mL) at room temperature for 2.5 h in the presence of $FeCl_3$ (1.6 mg, 0.1 equiv) and phenyltrifluoroacetone (4.4 mg, 0.2 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether = 1/1), affording compound **18b** as a white solid (37.4 mg, 93%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, J = 7.6 Hz, 2H), 8.01 (d, J = 7.6 Hz, 2H), 7.58−7.51 (m, 2H), 7.44−7.37 (m, 4H), 5.13 (dd, J = 10.0 and 2.8 Hz, 1H), 4.65−4.54 (m, 2H), 4.35 (d, J = 7.6 Hz, 1H), 4.24 (d, J = 2.8 Hz, 1H), 4.09−4.05 (m, 1H), 3.97−3.94 (m, 1H), 3.57 (s, 3H).

*Methyl-3,6-di-O-(4-toluenesulfonyl)-α-D-mannopyranoside (**19a**).*[11c] Methyl-α-D-mannopyranoside (0.1 mmol, 19.4 mg) was allowed to react with K_2CO_3 (55.3 mg, 4.0 equiv) and *p*-toluenesulfonyl chloride (57.2 mg, 3.0 equiv) in dry acetonitrile (0.5 mL) at room temperature for 12 h in the presence of $FeCl_3$ (1.6 mg, 0.1 equiv) and phenyltrifluoroacetone (4.4 mg, 0.2 equiv). The reaction mixture was directly purified by flash column chromatography (methanol/dichloromethane = 1/20), affording compound **19a** as a pale yellow oil (46.7 mg, 93%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, J = 8.0 Hz, 2H), 7.79 (d, J = 8.0 Hz, 2H), 7.34 (t, J = 9.6 Hz, 4H), 4.63−4.59 (m, 2H), 4.33−4.25 (m, 2H), 4.03−3.97 (m, 2H), 3.71 (d, J = 6.4 Hz, 1H), 3.29 (s, 3H), 2.44 (s, 3H), 2.43 (s, 3H).

*Methyl-3,6-di-O-benzyl-α-D-mannopyranoside (**19b**).*[13] Methyl-α-D-mannopyranoside (0.1 mmol, 19.4 mg) was allowed to react with *N*,*N*-diisopropylethylamine (70 μL, 4.0 equiv) and benzoyl chloride (35.0 μL, 3.0 equiv) in dry acetonitrile (0.5 mL) at room temperature for 2.5 h in the presence of $FeCl_3$ (1.6 mg, 0.1 equiv) and phenyltrifluoroacetone (4.4 mg, 0.2 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether = 1/1), affording compound **19b** as a colorless oil (38.6 mg, 96%). ^1H NMR (400 MHz, $CDCl_3$): δ 8.07−8.04 (m, 4H), 7.57−7.52 (m, 2H), 7.44−7.38 (m, 4H), 5.35 (dd, J = 9.6 and 2.8 Hz, 1H), 4.77−4.70 (m, 2H, **H-1**), 4.60 (dd, J = 11.6 and 0.8 Hz, 1H), 4.17−4.10 (m, 2H), 4.01−3.97 (m, 1H), 3.41 (s, 3H).

*Methyl-6-O-(4-toluenesulfonyl)-α-D-glucopyranoside (**20**).*[22] Methyl-α-D-glucopyranoside (0.2 mmol, 38.8 mg) was allowed to react with *N*,*N*-diisopropylethylamine (67 μL, 1.9 equiv) and *p*-toluenesulfonyl chloride (57.2 mg, 1.5 equiv) in dry acetonitrile (1 mL) at room temperature for 8 h in the presence of $FeCl_3$ (3.2 mg, 0.1 equiv) and phenyltrifluoroacetone (8.8 mg, 0.2 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate), affording compound **20** as a colorless oil (42.4 mg, 61%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.4 Hz, 2H), 4.66 (d, J = 3.6 Hz, 1H), 4.32−4.22 (m, 2H), 3.74−3.68 (m, 2H), 3.50−3.41 (m, 2H), 3.32 (s, 3H), 2.42 (s, 3H).

*Methyl-6-O-(4-toluenesulfonyl)-β-D-glucopyranoside (**21**).* Methyl-β-D-glucopyranoside (0.2 mmol, 38.8 mg) was allowed to react with *N*,*N*-diisopropylethylamine (67 μL, 1.9 equiv) and *p*-toluenesulfonyl chloride (57.2 mg, 1.5 equiv) in dry acetonitrile (1 mL) at room temperature for 4 h in the presence of $FeCl_3$ (3.2 mg, 0.1 equiv) and phenyltrifluoroacetone (8.8 mg, 0.2 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate), affording compound **21** as a colorless oil (45.2 mg, 65%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, J = 8.4 Hz, 2H, Ar**H**), 7.31 (d, J = 8.0 Hz, 2H, Ar**H**), 4.27 (d, J = 2.4 Hz, 2H, **H-6a**, **H-6b**), 4.18 (d, J = 7.6 Hz, 1H, **H-1**), 3.52−3.45 (m, 3H, **H-3**, **H-4**, **H-5**), 3.42 (s, 3H, OCH_3), 3.31 (t, J = 8.0 Hz, 1H, **H-2**), 2.41 (s, 3H, $ArCH_3$). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 145.1, 132.8, 130.0, 128.1, 103.4, 76.3, 73.4, 73.3, 69.7, 69.3, 57.1, 21.8 ppm. R_f: 0.45 (ethyl acetate). HRMS (ESI-TOF) m/z calcd. for $C_{14}H_{20}O_8SNa$ $[M + Na]^+$: 371.0771; found: 371.0772.

*2-Hydroxyethyl 4-toluenesulfonate (**22**).* 1,2-Ethanediol (0.2 mmol, 12.4 mg) was allowed to react with *N*,*N*-diisopropylethylamine (67.0 μL, 1.9 equiv) and *p*-toluenesulfonyl chloride (57.2 mg, 1.5 equiv) in dry acetonitrile (0.5 mL) at room temperature for 6 h in the presence of $FeCl_3$ (3.2 mg, 0.1 equiv) and phenyltrifluoroacetone (8.8 mg, 0.2 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether = 1/2), affording compound **22** as a pale yellow oil (35.4 mg, 82%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 4.09 (t, J = 4.4 Hz, 2H), 3.77 (t, J = 4.8 Hz, 2H), 2.42 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 145.2, 132.6, 130.0, 128.0, 71.8, 60.5, 21.7 ppm. R_f: 0.3 (ethyl acetate/petroleum ether = 1/2). HRMS (ESI-TOF) m/z calcd. for $C_9H_{12}O_4SNa$ $[M + Na]^+$: 239.0349; found: 239.0350.

*3-Hydroxypropyl 4-toluenesulfonate (**23**).*[23] 1,3-Propanediol (0.2 mmol, 15.2 mg) was allowed to react with *N*,*N*-diisopropylethylamine (67.0 μL, 1.9 equiv) and *p*-toluenesulfonyl chloride (57.2 mg, 1.5 equiv) in dry acetonitrile (0.5 mL) at room temperature for 6 h in the

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presence of $FeCl_3$ (3.2 mg, 0.1 equiv) and phenyltrifluoroacetone (8.8 mg, 0.2 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether = 1/2), affording compound **23** as a colorless oil (34.5 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 4.16 (t, J = 6.4 Hz, 2H), 3.68 (t, J = 6.0 Hz, 2H), 2.43 (s, 3H), 1.89−1.83 (m, 2H).

*2-Hydroxy-2-phenylethyl 4-toluenesulfonate (**24a**).*[12b] 1-Phenyl-1,2-ethanediol (0.2 mmol, 27.6 mg) was allowed to react with *N,N*-diisopropylethylamine (67.0 μL, 1.9 equiv) and *p*-toluenesulfonyl chloride (57.2 mg, 1.5 equiv) in dry acetonitrile (0.5 mL) at room temperature for 12 h in the presence of $FeCl_3$ (3.2 mg, 0.1 equiv) and phenyltrifluoroacetone (8.8 mg, 0.2 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether = 1/3), affording compound **24a** as a colorless oil (55.5 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, J = 8.0 Hz, 2H), 7.36−7.27 (m, 7H), 4.97 (dd, J = 8.0 and 2.4 Hz, 1H), 4.14 (dd, J = 10.4 and 2.8 Hz, 1H), 4.06−4.01 (m, 1H), 2.44 (s, 3H).

*2-Hydroxy-2-phenylethyl Benzoate (**24b**).*[12b] 1-Phenyl-1,2-ethanediol (0.2 mmol, 27.6 mg) was allowed to react with *N,N*-diisopropylethylamine (67.0 μL, 1.9 equiv) and benzoyl chloride (35.0 μL, 1.5 equiv) in dry acetonitrile (0.5 mL) at room temperature for 2 h in the presence of $FeCl_3$ (3.2 mg, 0.1 equiv) and phenyltrifluoroacetone (8.8 mg, 0.2 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether = 1/3), affording compound **24b** as a beige solid (44.0 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (dd, J = 7.6 Hz, 2H), 7.59−7.56 (m, 1H), 7.46−7.31 (m, 7H), 5.10 (dd, J = 8.0 and 2.8 Hz, 1H), 4.52 (dd, J = 11.2 and 3.2 Hz, 1H), 4.45−4.40 (m, 1H), 2.80 (br s, 1H).

*1-O-(4-Toluenesulfonyl)-2-propanol (**25a**).*[12b] 1,2-Propanediol (0.2 mmol, 15.2 mg) was allowed to react with *N,N*-diisopropylethylamine (67.0 μL, 1.9 equiv) and *p*-toluenesulfonyl chloride (57.2 mg, 1.5 equiv) in dry acetonitrile (0.5 mL) at room temperature for 12 h in the presence of $FeCl_3$ (3.2 mg, 0.1 equiv) and phenyltrifluoroacetone (8.8 mg, 0.2 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether = 1/2), affording compound **25a** as a colorless oil (36.8 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, J = 7.6 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 4.02−3.96 (m, 2H), 3.86−3.82 (m, 1H), 2.44 (s, 3H), 2.38 (br s, 1H), 1.14 (d, J = 6.0 Hz, 3H).

*1-O-Benzoyl-2-propanol (**25b**).*[13] 1,2-Propanediol (0.2 mmol, 15.2 mg) was allowed to react with *N,N*-diisopropylethylamine (67.0 μL, 1.9 equiv) and benzoyl chloride (35.0 μL, 1.5 equiv) in dry acetonitrile (0.5 mL) at room temperature for 2 h in the presence of $FeCl_3$ (3.2 mg, 0.1 equiv) and phenyltrifluoroacetone (8.8 mg, 0.2 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether = 1/3), affording compound **25b** as a colorless oil (33.5 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05−8.03 (m, 2H), 7.58−7.54 (m, 1H), 7.45−7.41 (m, 2H), 4.35−4.30 (m, 1H), 4.22−4.15 (m, 2H), 2.50 (br s, 1H), 1.29−1.27 (m, 3H).

*1-O-(4-Toluenesulfonyl)-3-phenoxy-2-propanol (**26a**).*[24] 3-Phenoxy-1,2-propanediol (0.2 mmol, 33.6 mg) was allowed to react with *N,N*-diisopropylethylamine (67.0 μL, 1.9 equiv) and *p*-toluenesulfonyl chloride (57.2 mg, 1.5 equiv) in dry acetonitrile (0.5 mL) at room temperature for 12 h in the presence of $FeCl_3$ (3.2 mg, 0.1 equiv) and phenyltrifluoroacetone (8.8 mg, 0.2 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether = 1/3), affording compound **26a** as a white crystal (56.0 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, J = 8.4 Hz, 2H), 7.31−7.25 (m, 4H), 6.97 (t, J = 7.2 Hz, 1H), 6.82 (d, J = 8.0 Hz, 2H), 4.25−4.17 (m, 3H), 3.97 (d, J = 3.6 Hz, 2H), 2.41 (s, 3H).

*1-O-Benzoyl-3-phenoxy-2-propanol (**26b**).*[13] 3-Phenoxy-1,2-propanediol (0.2 mmol, 33.6 mg) was allowed to react with *N,N*-diisopropylethylamine (67.0 μL, 1.9 equiv) and benzoyl chloride (35.0 μL, 1.5 equiv) in dry acetonitrile (0.5 mL) at room temperature for 3.5 h in the presence of $FeCl_3$ (3.2 mg, 0.1 equiv) and phenyltrifluoroacetone (8.8 mg, 0.2 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether = 1/3), affording compound **26b** as a colorless oil (44.6 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, J = 7.6 Hz, 2H), 7.60−7.56 (m, 1H), 7.47−7.43 (m, 2H), 7.32−7.28 (m, 2H), 7.01−6.93 (m, 3H), 4.59−4.51 (m, 2H), 4.42−4.36 (m, 1H), 4.16−4.08 (m, 2H), 2.73 (br s, 1H).

*2-Hydroxy-3-allyloxypropyl 4-Toluenesulfonate (**27a**).*[25] 3-Allyloxy-1,2-propanediol (0.2 mmol, 26.4 mg) was allowed to react with *N,N*-diisopropylethylamine (67.0 μL, 1.9 equiv) and *p*-toluenesulfonyl chloride (57.2 mg, 1.5 equiv) in dry acetonitrile (0.5 mL) at room temperature for 12 h in the presence of $FeCl_3$ (3.2 mg, 0.1 equiv) and phenyltrifluoroacetone (8.8 mg, 0.2 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether = 1/3), affording compound **27a** as a pale yellow oil (53.2 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H), 5.87−5.77 (m, 1H), 5.24−5.16 (m, 2H), 4.11−3.94 (m, 5H), 3.50−3.42 (m, 2H), 2.44 (s, 3H), 2.32 (br s, 1H).

*2-Hydroxy-3-allyloxypropyl Benzoate (**27b**).*[13] 3-Allyloxy-1,2-propanediol (0.2 mmol, 26.4 mg) was allowed to react with *N,N*-diisopropylethylamine (67.0 μL, 1.9 equiv) and benzoyl chloride (35.0 μL, 1.5 equiv) in dry acetonitrile (0.5 mL) at room temperature for 2 h in the presence of $FeCl_3$ (3.2 mg, 0.1 equiv) and phenyltrifluoroacetone (8.8 mg, 0.2 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether = 1/3), affording compound **27b** as a colorless oil (37.8 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06−8.04 (m, 2H), 7.58−7.55 (m, 1H), 7.46−7.42 (m, 2H), 5.95−5.85 (m, 1H), 5.31−5.19 (m, 2H), 4.45−4.37 (m, 2H), 4.19−4.14 (m, 1H), 4.06−4.04 (m, 2H), 3.63−3.53 (m, 2H), 2.54 (br s, 1H).

*3-Hydroxybutyl 4-toluenesulfonate (**28**).*[12b] 1,3-Butanediol (0.2 mmol, 18.0 mg) was allowed to react with *N,N*-diisopropylethylamine (67.0 μL, 1.9 equiv) and *p*-toluenesulfonyl chloride (57.2 mg, 1.5 equiv) in dry acetonitrile (0.5 mL) at room temperature for 12 h in the presence of $FeCl_3$ (3.2 mg, 0.1 equiv) and phenyltrifluoroacetone (8.8 mg, 0.2 equiv). The reaction mixture was directly purified by flash column chromatography (ethyl acetate/petroleum ether = 1/2), affording compound **28** as a colorless oil (34.6 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 7.6 Hz, 2H), 4.24−4.18 (m, 1H), 4.12−4.07 (m, 1H), 3.94−3.89 (m, 1H), 2.43 (s, 3H), 2.00 (br s, 1H), 1.83−1.77 (m, 1H), 1.72−1.64 (m, 1H), 1.16 (d, J = 6.4 Hz, 3H).

■ ASSOCIATED CONTENT

Supporting Information

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Copies of NMR spectra of products (PDF)

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Notes

The authors declare no competing financial interest.

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