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Reagent-Controlled Divergent Synthesis of *C*-Glycosides

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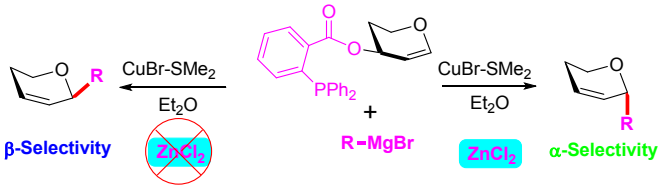
Graphic abstract:



Abstract: Leveraging on the exquisitely turning on or switching off the directing effect of the C3-OH located *o*-diphenylphosphanylbenzoyl (*o*-DPPB) group in glycals, a reagent-controlled protocol for divergent and regio- and stereo-selective synthesis of *C*-glycosides has been established. In particularly, the silence of the directing effect of *o*-DPPB was achieved by the introduction of $ZnCl_2$ additive, which is operationally simple and efficient. The flexibility of the novel protocol was exhibited not only by the easy access of both α- and β-*C*-glycosides but also by the versatility of the obtained formal Ferrier rearrangement products, which can be easily derivatized to various *C*-glycoside analogues owing to the embedded multi-functionalities.

Introduction

C-Glycosides are featured by attaching of the carbohydrate units to acceptors via carbon atoms instead of oxygen atoms, which exhibit dramatically enhanced stability toward both acidic and enzymatic hydrolysis in comparison to their *O*-congeners. Consequently, they have been widely applied as surrogates/mimetics of native *O*-glycosides during the development of novel biochemical probes and pharmaceuticals.[1] Also, as structural subunits *C*-glycosides occur in a wide variety of natural products with significant biological activities.[2] The biological relevance in combination with the synthetic challenges associated with *C*-glycosidic linkage constructions have been spurring the studies of seeking for highly efficient protocols of *C*-glycosylation, resulting in the establishment of diversities of approaches.[3] Among all methods, those commencing with glycals are drawing considerable attention from synthetic chemists owing to the formal Ferrier

rearrangement[4] products with multi-functionalities provide valuable handles for after-glycosylation derivatization.[5] With glycals as starting materials, four types of reactions have been devised to secure the formal Ferrier rearrangement products: acid-promoted Ferrier rearrangements,[6] allylic 1,3-substitutions,[7] Heck reactions,[8] and Tsuji-Trost reactions (Figure 1).[9] Nevertheless, some reactions suffer from limited stereo-diversity during the *C*-glycosydic linkage construction furnishing α-*C*-glycosides as the predominating or sole products. Moreover, the unsatisfactory coupling regioselectivity seriously impairs the synthetic efficiency frequently. Thus, to facilitate the diversity-oriented synthesis of *C*-glycosides with high efficiency, a reagent-controlled protocol to divergently furnish α/β-stereoisomers with full regioselectivity control is highly desired. In line with our continuous interest in *C*-glycosides synthesis,[10] a program was launched to pursue such an approach to realize the flexible and efficient synthesis of α/β *C*-glycosides.

The glycal allylic 1,3-substitution protocol is appealing as the non-catalyst version has been devised for the preparation of *C*-glycosides. However, to make the *C*-glycosylations proceed smoothly in the absence of catalyst either glycals with improved reactivity[7a,b] or organo-metallic nucleophiles with appropriate Lewis acidity[7c] have to be applied. Meanwhile, the obtained moderate regio- as well as stereo-selectivity leaves room for further optimization. Inspired by the seminal work of Breit and co-workers regarding *ortho*-diphenylphosphanylbenzoyl (*o*-DPPB) group-directed, copper-mediated allylic substitution with Grignard reagents (*o*-DDCMAS protocol),[11] we assumed that the *o*-DDCMAS method, after being modified according to the special glycal substrates, may find applications in stereoselective synthesis of *C*-glycosides. Moreover, theoretically, the divergency of the novel protocol can be achieved by switching on or turning off the directing effect of *o*-DPPB group to afford either syn-S_N2' or anti-S_N2' products, respectively, potentially overcoming the drawbacks associate with existing glycal allylic 1,3-substitution protocols for the preparation of *C*-glycosides (Figure 1).

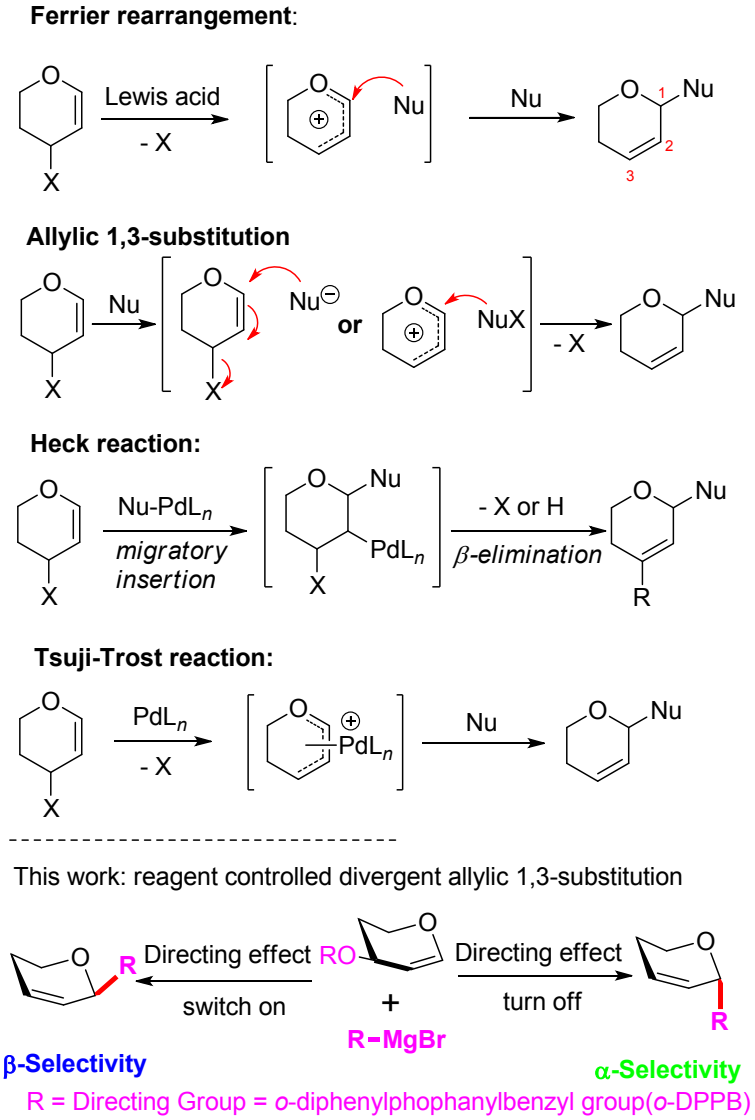


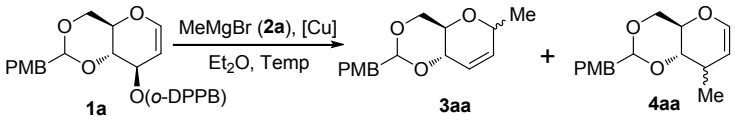
Figure 1. Various protocols for the synthesis of *C*-glycosides.

Results and discussion

The investigation started with the model coupling between **1a**[12] and methylmagnesium bromide **2a** (Table 1). Pleasantly, when treated with the identical conditions as those devised by Breit et al.,[11] the desired methyl-*C*-glycoside **3aa** were obtained β-stereoselectively in a moderate 40% yield accompanied by 15% yield of C-3 methylation isomer **4aa** as a mixture of α/β-isomers (α/β = 1 : 1). The exclusive formation of β-**3aa** verifying that the expected directing effect of *o*-DPPB group can indeed be exploited to forge β-*C*-glycoside, while the formation of **4aa** as a mixture of α/β-isomers indicates that the regio-byproduct was generated via a carbon-cationic intermediate. The reaction was proved to be highly temperature sensitive, and the synthetic efficiency of **3aa** as well as the regioselectivity of the coupling reaction dropped dramatically

when the reaction temperature varied (entries 2-5). Low temperature (-20 ^{o}C) largely halted the reaction leading to the detection of only trace amounts of **3aa** and **4aa** by TLC (entry 4); on the contrary high temperature (40 ^{o}C) compromised the regioselectivity seriously (almost 1 : 1 of **3aa** and **4aa** were isolated, entry 5). Besides ethyl ether, other ether-type solvents including THF, 1,4-dioxane, and MTBE were also checked under otherwise identical conditions, but inferior results were recorded in terms of yields and regioselectivity (entries 6-8). Although THF and dioxane provided extremely scrambled mixtures, the MTBE indeed afforded **3aa** but as the minor product in comparison to its C3-isomer, indicating that the MTBE solvent could reverse the regioselectivity of glycal allylic 1,3-substitution reaction from C1 to C3 to provide **4aa** as the major product (34% and 45% yield for **3aa** and **4aa**, respectively, entry 8). In order to further improve the synthetic efficiency of **3aa** while suppressing the formation of **4aa**, the applied amounts of Cu(I) and Grignard reagent were adjusted systematically (entries 9-16). Upon varying only one parameter, either the amount of copper catalyst (from 0.5 to 1.0 equivalents) or the amount of Grignard reagent (from 1.5 to 1.0 equivalents), deleterious effects on the coupling reaction were observed since diminished stereoselectivity (for **3aa**) and regioselectivity were obtained (entries 9 and 10). Thus, changing the two parameters simultaneously was then investigated (entries 11-16), and finally found that under the combined effect of 1.0 equivalent of copper catalyst and 2.0 equivalents of Grignard reagent the optimal results were obtained (β-**3aa** was isolated in 59% yield and no C-3 isomer **4aa** was isolated, entry 12). Efforts to further optimize the coupling reaction entailed increasing copper catalyst from 1.0 to 2.0 equivalents and Griganard reagent form 2.0 to 4.5 equivalents. However, unfortunately, only deteriorated results, as compared to the results of entry 12, were obtained (entries 13-16). Although the result that no reaction was detected in the absence of Cu(I) catalyst obtained in a control reaction fully demonstrates that copper salt is indispensable in the coupling reaction (entry 17), other copper salts, such as CuCl, CuBr, CuI, $Cu(OAc)_2$, as well as $Cu(acac)_2$, only presented inferior results with respect to the chemical yields and regioselectivity of the couplings (entries 18-22). Interestingly, similar to the solvent effect of MTBE, $Cu(OAc)_2$ and $Cu(acac)_2$ also biased the formation of the C3-regioisomer **4aa** (entries 21 and 22).

Table 1. Optimization of the conditions for the synthesis of β-*C*-glycosides.



Entry	[Cu] (eq)	MeMgBr (eq)	Temp (°C)	3aa[a] (α/β)[b]	4aa[c]
1	CuBr•SMe_2 (0.5)	1.5	30	40% (only β)	15%
2	CuBr•SMe_2 (0.5)	1.5	23	25% (only β)	11%
3	CuBr•SMe_2 (0.5)	1.5	0	10% (only β)	11%
4	CuBr•SMe_2 (0.5)	1.5	-20	trace	trace
5	CuBr•SMe_2 (0.5)	1.5	40	32% (only β)	28%
6[d]	CuBr•SMe_2 (0.5)	1.5	30	ND[e]	ND[e]
7[f]	CuBr•SMe_2 (0.5)	1.5	30	ND[e]	ND[e]
8[g]	CuBr•SMe_2 (0.5)	1.5	30	34% (only β)	45%
9	CuBr•SMe_2 (0.5)	1.0	30	25% (1 : 5)	15%
10	CuBr•SMe_2 (1.0)	1.5	30	38% (1 : 4.3)	8%
11	CuBr•SMe_2 (1.0)	1.0	30	30% (1 : 3.2)	25%
12	CuBr•SMe_2 (1.0)	2.0	30	59% (only β)	ND[e]
13	CuBr•SMe_2 (1.0)	3.0	30	39% (only β)	15%
14	CuBr•SMe_2 (1.5)	3.0	30	23% (only β)	15%
15	CuBr•SMe_2 (1.5)	4.5	30	30% (only β)	5%
16	CuBr•SMe_2 (2.0)	4.0	30	34% (1 : 3.2)	23%
17	--	2.0	30	ND[e]	ND[e]
18	CuCl (1.0)	2.0	30	28% (only β)	6%
19	CuBr (1.0)	2.0	30	40% (only β)	23%
20	CuI (1.0)	2.0	30	42% (only β)	5%
21	$Cu(OAc)_2$ (1.0)	2.0	30	31% (only β)	40%
22	$Cu(acac)_2$ (1.0)	2.0	30	23% (1 : 2.5)	40%

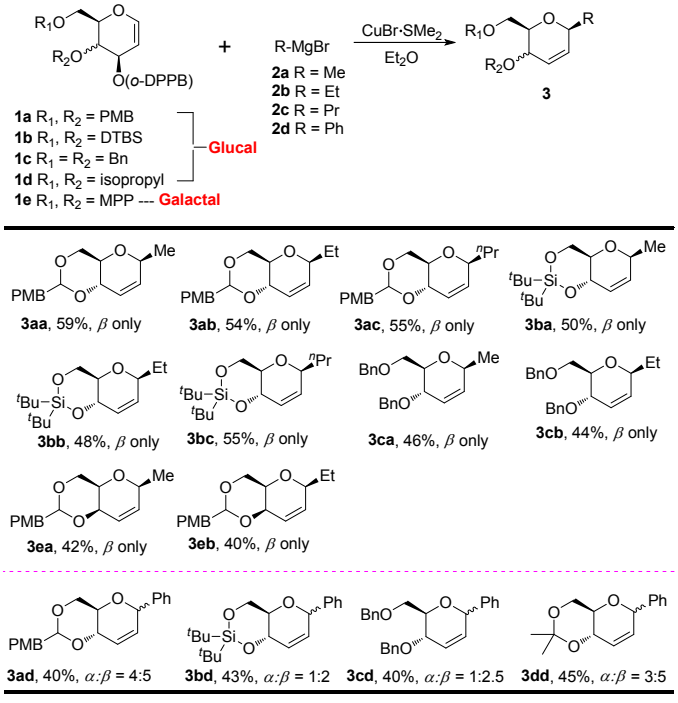
[a]Isolated yield. [b]a/β ratios were determined by ^{1}H NMR. [c]Isolated yield. [d]THF was used as solvent.[e]ND = Not Detected. [f]1.4-Dioxane was used as solvent. [g]MTBE was used as solvent.

With the optimal conditions in hand, the substrate scope was then checked with different glycals and various Grignard reagents (Table 2). As with the methylmagnesium bromide **2a**, ethyl and propyl Grignard reagents **2b** and **2c** also react with **1a** to furnish **3ab** and **3ac** β-selectively (54% and 55% yield, respectively). The di-*tert*-butylsilylene (DTBS) group was tolerated as a protecting group in the glucal substrate, and the condensation between **1b** and **2a-c** provided **3ba-bc** with excellent stereoselectivity (50%, 48%, and 55% yield). The desired β-stereoselectivity was maintained even with glucal **1c** in an opened 4,6-*O*-protecting pattern. Thus, upon treatment of **1c** with **2a-b**, the β-**3ca** and β-**3cb** were formed exclusively (46% for **3ca**

and 44% for **3cb**). In addition, the galactal derivative **1e** was also a competent substrate to participate in *C*-glycosylation reactions with **2a-b**, affording **3ea** and **3eb** β-selectively (**3ea**: 42% and **3eb**: 40%). The excellent β-stereoselectivity of the tested couplings demonstrates the robustness of the directing effect of *o*-DPPB group, relying on which the reactions proceed through a syn-S_N2' mechanism. The moderate synthetic efficiency results from the deacylation of the glycal substrates, which has been observed previously but to less extent in simply functionalized substrates.[13]

Phenyl Grignard reagent **2d** could also be used as a nucleophile to react with **1a-d** to give phenyl *C*-glycosides **3ad-dd**; however, only marginal β-stereoselectivity was secured. Similar problem has been encountered previously, and can be explained by the less nucleophilicity of aryl-Grignard reagents, which retards the directing group-involved syn-S_N2' process while accordingly favors the anti-S_N2' substitution to deliver α-*C*-glycosides.[13,14] All configuration of newly formed *C*-glycosydic linkages were unequivocally determined by NOE experiments, wherein evident correlations between H-1 and H-5 were observed.[12,15]

Table 2. The substrate scope investigation for the β-*C*-glycosylation protocol.[a]

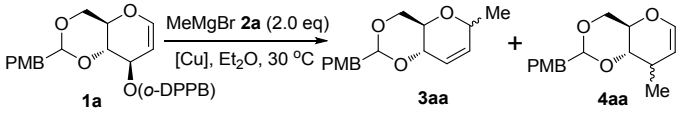


[a]Reaction conditions unless otherwise noted: **1** (0.2 mmol), CuBr•SMe_2 (0.2 mmol), RMgBr (0.4 mmol), Et_2O (4 mL), N_2 atmosphere, 30 °C, 7-8 h. Isolated yield and the a/β ratios were determined by ^{1}H NMR.

With the optimal conditions for preparation of β-*C*-glycosides settled, our attention was then turned to the generation of α-*C*-glycosides. Theoretically, upon silencing the directing effect of the *o*-DPPB group, then the formation of α-*C*-glycosides could be achieved through an anti-S_N2' mechanism. Keeping the aim of seeking reagent-controlled protocols for *C*-glycosides synthesis in mind, we decided to devise a novel approach different from the Breit's method,[11] which inevitably requires an extra step of *o*-DPPB group oxidation, to turn off the directing effect of *o*-DPPB group. In fact, the oxidative method of Breit's group was also checked; however, no desired *C*-glycosylation product were obtained, and the only detectable compounds from the reaction system were unchanged and deacylated **1a** (Table 3, entry 1). Besides *o*-DPPB, another frequently investigated directing group in allylic 1,3-substitution is picoloyl (Pico) group.[16] The directing effect of Pico group is achieved by coordinating with $MgBr_2$ *in situ* generated during the formation of organocopper reagents rather than directly steering the attacking approach of nucleophiles by complexing with organocopper species. Similarly, in our case an anti-S_N2' substitution mechanism can be exploited to prepare α-*C*-glycosides. As for *o*-DPPB group, the complexing affinity between $MgBr_2$ and phosphorus atom is rather low, laying a foundation for the establishment of the above discussed β-selective *C*-glycosylation method. To blocking the chelating phosphorus atom, $ZnCl_2$ was tried as an additive since ZnI_2 has been used to improve the regioselctivity of Pico group-involved allylic 1,3-substitution.[17] Under otherwise the identical conditions to the optical ones for β-*C*-glycosidic linkage construction, 0.5 equivalents of $ZnCl_2$ successfully reversed the glycosylation stereoselectivity of **1a** and **2a** from β only to α-predominantly (α/β = 3.5 : 1) albeit with moderate yield and unsatisfactory regioselectivity (24% yield of **3aa**, entry 2). The synthetic efficiency was shown to be highly additive dependent with 1.5 equivalents of $ZnCl_2$ affording the highest yield and satisfactory regioselectivity (88% yield of **3aa** and no **4aa** was detected, entry 4). Either reducing or raising the applied amounts of $ZnCl_2$ adversely affected the transformations both in yield and in regioselectivity (entries 3 and 5). Interestingly, the stereoselectivity was maintained (above 3 : 1 of α/β ratios) no matter how many equivalents of $ZnCl_2$ were added (entries 3-5). Although $ZnBr_2$ also provided good yield of **3aa**, however, the stereoselectivity and the regioselectivity of the reaction eroded (84%, α/β = 2.5 : 1, entry 6). On the contrary, the choice of ZnI_2 as an additive brought about evident decrease in chemical yield of **3aa** while keeping the stereo- and regio-selectivity unchanged (59% yield, α/β =

3.5 : 1, entry 7). Replacing $ZnCl_2$ with $AlCl_3$ completely destroyed the regioselctivity of the coupling reaction, leading to the formation of **3aa** and **4aa** with a ratio of 1 : 1 (entry 8). Attempts to further optimize the reaction by screening different Cu(I) salts, including CuCl, CuBr, and CuI, in the presence of $ZnCl_2$ uniformly met with failure, and no better results than those listed in entry **4** were recorded (entries 9-11). Cu(II) salts, such as $Cu(OAc)_2$ and $Cu(acac)_2$, did ameliorate the stereoseletivity to above 4.5 : 1, but the low conversion efficiency combined with the diminished regioselectivity nullified the improvement in chiral selectivity (entries 12, 13). Finally, the coupling between **1a** and **2a** was also conducted in the absence of copper catalyst under the otherwise identical conditions, but non-regioselectivity as well as compromised yield was observed (entry 14). However, the obtained α/β ratio (4 : 1) comparable to that of the optimal conditions reveals that the chelation of Zn(II) with *o*-DPPB directing group does not bias the formation of β-*C*-glycosides via a similar mechanism as that used for copper catalyst in the absence of $ZnCl_2$ additive.

Table 3. Optimization of conditions for the synthesis of *a*-*C*-glycosides.

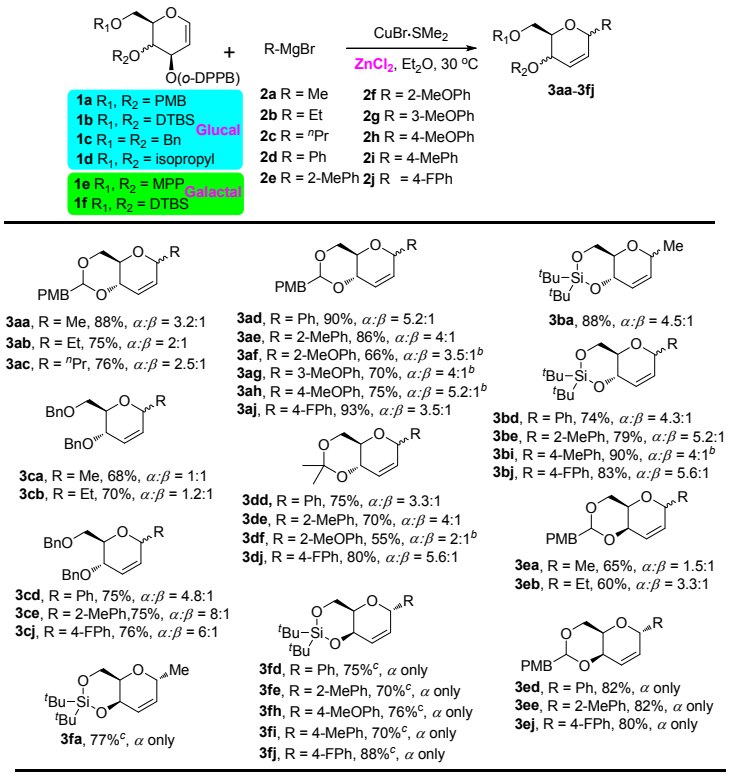


Entry	[Cu] (1.0 eq)	Additive (eq)	3aa[a] (α/β)[b]	4aa[c]
1[d]	$CuBr•SMe_2$	--	ND[e]	trace
2	$CuBr•SMe_2$	$ZnCl_2$ (0.5)	24% (3.5 : 1)	11%
3	$CuBr•SMe_2$	$ZnCl_2$ (1.0)	52% (3 : 1)	23%
4	$CuBr•SMe_2$	$ZnCl_2$ (1.5)	88% (3.2 : 1)	ND[e]
5	$CuBr•SMe_2$	$ZnCl_2$ (2.0)	50% (3.5 : 1)	8%
6	$CuBr•SMe_2$	$ZnBr_2$ (1.5)	84% (2.5 : 1)	10%
7	$CuBr•SMe_2$	ZnI_2 (1.5)	59% (3.5 : 1)	ND[e]
8	$CuBr•SMe_2$	$AlCl_3$ (1.5)	19% (1 : 2)	20%
9	CuCl	$ZnCl_2$ (1.5)	53% (3.5 : 1)	8%
10	CuBr	$ZnCl_2$ (1.5)	55% (3.4 : 1)	23%
11	CuI	$ZnCl_2$ (1.5)	23% (3.6 : 1)	10%
12	$Cu(OAc)_2$	$ZnCl_2$ (1.5)	24% (4.6 : 1)	6%
13	$Cu(acac)_2$	$ZnCl_2$ (1.5)	31% (4.7 : 1)	19%
14	--	$ZnCl_2$ (1.5)	30% (4 : 1)	30%

[a]Isolated yield. [b]α/β ratios were determined by ^{1}NMR. [c]Isolated yield. [d]With *o*-DPPB oxide ester of **1a** as glucal substrate. [e]ND = Not Detected.

The substrate scope in terms of both glycals and Grignard reagents were evaluated subsequently (Table 4). In glucal series substrates, those bearing either cyclic or open protecting groups on C4,6 hydroxy groups were well accommodated by the devised α-*C*-glycosylation protocol (**1a-d**). Moreover, apart from alkyl Grignard reagents (**2a-c**), ArMgBrs could also be used to condense with glucal-type substrates to forge phenyl *C*-glycosidic linkages (**2d-j**). Furthermore, galactals with different protecting groups were also proved to be viable substrates to react with both alkyl and aryl Grignard reagents (**1e-f**), affording α-*C*-glycosides as the major or predominant products. In comparison with the alkyl Grignard reagents, the aryl Grignard reagents tend to provide better α-stereoselectivity, as exemplified by glycal substrates **1c** and **1e**. In the case of **1c**, almost no stereoselectivity was obtained when alkyl Grignard reagents **2a-b** were selected as nucleophiles (around 1 : 1 of α/β ratios for **3ca** and **3cb**), while good α-stereoselectivity was recorded for aryl nucleophiles **2d-e** and **2j** (above 4.8 : 1 of α/β ratios for **3cd**, **3ce**, and **3cj**). For galactal substrate **1e**, alkyl Grignard reagents **2a-b** only presented moderate α-stereoselectivity (1.5 : 1 and 3.3 : 1, respectively, for **3ea** and **3eb**); however, aryl Grignard reagents **2d-e** and **2j** provided excellent α-stereoselectivity when coupled with **1e** (only α isomers were formed for **3ed-ee** and **3ej**). Resembling the low stereoselectivity of ArMgBr nucleophiles in β-*C*-glycosylation, the stereoselectivity discrepancy between alkyl and aryl Grignard reagents can also be ascribed to the low nucleophility of aryl Grignard reagents. Influenced by the bulky di-*tert*-butyl-silylene protecting group, galactal **1f** gave the desired α-*C*-glycosides exclusively with good yields, no matter either alkyl or aryl Grignard reagents were applied (above 70% yield for **3fd-fe** and **3fh-fj**). Although the low nucleophilicity of aryl Grignard reagents benefit to the α-stereoselectivity of *C*-glycosylation, prolonged reaction time and slight heating were frequently required to make the coupling reactions to proceed with reasonable rates and high yields. The α-configuration of all α-*C*-glycosides was established by NOE experiments, and the corresponding correlations between H-1 and H-5, which have been used to determine the β-stereoisomers, were not detected in the α-C-glycosides series.

Table 4. The substrate scope checking for the α-*C*-glycosylation protocol.[a]



[a]Reaction conditions unless otherwise noted: **1** (0.2 mmol), CuBr•SMe_2 (0.2 mmol), RMgBr (0.4 mmol), $ZnCl_2$ (0.3 mmol), Et_2O (4 mL), N_2 atmosphere, 30 °C, 7-8 h. Isolated yield and the a/β ratios were determined by ^1H NMR. [b]55 °C, 10 h. [c]55 °C, 24 h.

According to the experimental results as well as the precedent literature,[17] a plausible reaction mechanism was proposed as shown in Figure 2. Firstly, organocopper reagent was generated *in situ* through transmetallation with Grignard reagents. In the absence of any additive, coordination of the organocopper reagent with the phosphorus atom of *o*-DPPB, the double bond and the ring oxygen atom of glycal results in the formation of intermediate **A** with the copper reagent disposed on the β-face of glycal. Subsequently, intramolecular syn-S_N2' substitution would take place to produce β-*C*-glycosides (a). On the other hand, in the presence of $ZnCl_2$ additive, Zn(II) competes with organic Cu(I) species to coordinate with the phosphorus atom of *o*-DPPB and the ring oxygen atom of glycal, therefore forcing the approach of the *in situ* generated organocopper reagent from the α-face. As a result, the anti-S_N2' substitution products were obtained (b). As with the Pico group, the complexing of metal species to *o*-DPPB group will also facilitate its departure. Thus, the carbocation species-involved substitution could not be completely excluded.

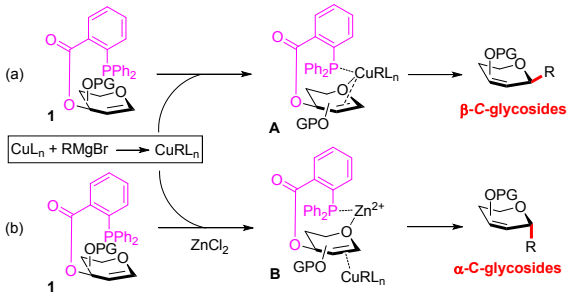
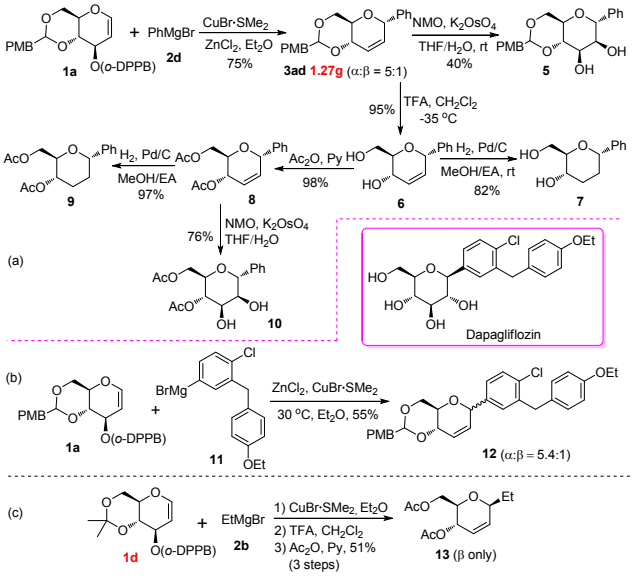


Figure 2. Plausible mechanism for the divergent synthesis of *C*-glycosides.

With the reagent-controlled protocol for the divergent preparation of *C*-glycosides established, the practicality as well as the flexibility of the protocol was then examined (Scheme 1). First of all, the coupling between **1a** and **2d** was scaled up to gram scale under the combined effect of Cu(I)/$ZnCl_2$, and, pleasantly, only a slight decrease in stereoselectivity and yield was observed for **3ad** (75% yield, α/β = 5 : 1, Scheme 1, a). Subsequently, the derivatization of α-**3ad** was then investigated (a). Dihydroxylation of α-**3ad** with K_2OsO_4/NMO[18] afforded diol intermediate **5** as a single diastereomer (40%). Upon treatment with TFA at low temperature, **3ad** was converted to **6** smoothly (95%), which was then transformed either to **7** by hydrogenolysis (82%) or to **9** via intermediate **8** through a sequence of acetylation and hydrogenolysis (95%, for 2 steps). In addition, dihydroxylation of **8** afforded **10** in a good yield of 76%. With the approval of dapagliflozin as a drug for the treatment of type-II diabetes by FDA in 2014, the synthesis of analogues thereof is drawing more and more interest from the synthetic chemists.[19] Applying our protocol, the *C*-glycosylation of **11**[20] with **1a** proceeded without any event, furnishing **12** with a α/β ratio of 5.4 : 1, from which the analogues of dapagliflozin could be easily accessed (b). Finally, the synthesis of ethyl *C*-glycoside **13** was also studied (c). Thus, when the coupling between **1b** and **2b** was carried out in the absence of additive, the desired β-ethyl-*C*-glycoside was formed exclusively, which was then advanced to **13** via successive deisopropylidenation and acetylation (51%, for 3 steps).



Scheme 1. Investigation of the scalability and flexibility of the divergent synthetic protocol of *C*-glycosylation.

Conclusions

In summary, a reagent-controlled protocol for the divergent synthesis of *C*-glycosides has been devised. With *o*-DPPB as a directing group, the β-*C*-glycosidic linkages were constructed through a syn-S_N2' substitution mechanism, while the α-*C*-glycosidic linkages were selectively forged by silencing the directing effect of *o*-DPPB group so as to favor the anti-S_N2' substitution mechanism. The turning off the directing effect of *o*-DPPB group was exquisitely achieved by the introduction of $ZnCl_2$ additive, thus being operationally easy and efficient. The protocol has been proven to be scalable and flexible in the synthesis of *C*-glycosides, thus may find broad applications in the future.

Experimental Section:

General Remarks

Commercial reagents were purchased and used without further purification, unless otherwise stated. ^1H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded using $CDCl_3$ or DMSO-d_6 as solvents. Chemical shifts are reported in ppm downfield to tetramethylsilane. Coupling constants are reported and expressed in Hz; splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (double doublet), dt (double triplet), dq (double quartet), br (broad). All reactions were carried out using freshly distilled and dried solvents. High resolution mass spectra were performed on Thermo Fusion LUMOS mass spectrometer. Column

chromatography was performed over silica gel (200-300 Mesh) using petroleum ether and ethyl acetate as the eluent. The chemical structures of the new *C*-glycosides were determined by 1-dimmentional (^{1}H and ^{13}C) and 2-dimmentional (gCOSY, gHMQS, and NOE) NMR spectra.

4,6-O-4-Methoxybenzylidene-D-glucal (S2)

To a solution of D-(+)-glucal **S1**[21] (14.6 g, 0.10 mol) and 4-methoxybenzaldehyde dimethyl acetal (29.5 mL, 0.15 mol) in dry DMF (150 mL), pyridinium *p*-toluenesulfonates (PPTS, 2.5 g, 0.01 mol) was added at 25 °C. The mixture was rotated on a Rotavapor for 4 h under reduced pressure to remove the *in situ* generated methanol at the same temperature. The resulting mixture was diluted with H_2O (70 mL) and extracted with CH_2Cl_2 (3 × 250 mL). The combined organic layers were washed successively with saturated aqueous NH_4Cl, H_2O, and brine, and were then dried over anhydrous Na_2SO_4. Filtration was followed by concentration *in vacuo* to give the crude product, which was further purified by flash chromatography on silica gel (EtOAc/PE = 1 : 2) to afford **S2**[22] (17.2 g, 65%) as a white solid: $[\alpha]_D^{23}$ = +45.8 (*c* 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.38 (d, *J* = 8.7 Hz, 2H), 6.92 (d, *J* = 8.7 Hz, 2H), 6.37 (dd, *J* = 1.7, 6.1 Hz, 1H), 5.63 (s, 1H), 5.27 (d, *J* = 5.7 Hz, 1H), 4.68 (dd, *J* = 6.1, 1.9 Hz, 1H), 4.25 – 4.20 (m, 2H), 3.83 – 3.77 (m, 2H), 3.75 (s, 3H), 3.73 – 3.68 (m, 1H); ^{13}C {^{1}H} NMR (100 MHz, DMSO-d_6) δ 159.6, 142.8, 130.0, 127.6, 113.3, 105.9, 100.6, 80.0, 68.5, 67.3, 65.0, 55.1; HRMS (ESI) m/z calcd for $C_{14}H_{16}O_5Na$ $[M + Na]^+$: 287.0890; found: 287.0887.

4,6-O-4-Methoxybenzylidene-D-galactal (S4)

To an ice-bath cooled solution of D-(+)-galactal **S3**[21] (1.46 g, 0.01 mol) and 4-methoxybenzaldehyde dimethyl acetal (2.95 mL, 0.015 mol) in freshly distilled CH_3CN (8 mL), PPTS (251 mg, 0.001 mol) was added at 0 °C. The reaction mixture was stirred at the same temperature for 30 min, then was warmed up to room temperature and the stirring was continued for another 24 h. The resulting mixture was diluted with H_2O (10 mL) and extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were washed successively with saturated aqueous NH_4Cl, H_2O, and brine, and were then dried over anhydrous Na_2SO_4. Filtration was followed by concentration *in vacuo* to give the crude product, which was further purified by flash chromatography on silica gel (EtOAc/PE = 1 : 2) to afford **S4** (1.05 g, 40%) as a white solid: $[\alpha]_D^{23}$ = -5.4 (*c* 2.28, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.37 (d, *J* = 8.7 Hz, 2H), 6.93 (d, *J* = 8.7 Hz, 2H), 6.75 (d, *J* = 6.2 Hz, 1H), 5.81 (s, 1H), 5.04 (dd, *J* = 6.2, 3.0 Hz, 1H), 4.95 (t, *J* =

5.6 Hz, 1H), 4.79 – 4.76 (m, 1H), 4.41 (d, J = 6.2 Hz, 1H), 3.86 (t, J = 6.6 Hz, 1H), 3.76 (s, 3H), 3.62 (t, J = 5.8 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 160.0, 148.2, 130.0, 128.4, 113.5, 101.3, 99.6, 76.3, 72.2, 69.1, 60.9, 55.2; HRMS (ESI) m/z calcd for $C_{14}H_{17}O_5$ $[M + H]^+$: 265.1070; found: 265.1071.

General procedure for the preparation of 1

4-Dimethylaminopyridine (DMAP, 0.5 equiv) and dicyclohexylcarbodiimide (DCC, 1.3 equiv) were added to a solution of *ortho*-diphenylphosphanylbenzoic acid (*o*-DPPBA, 1.1 equiv) in dry DCM (2.0 mL) at 0 °C. After being stirred for 30 min at the same temperature, a solution of glycal 3-OH intermediate (10 mmol) in DCM (2.0 mL) was added. The resulting reaction mixture was stirred for 10-12 h at 0 °C before EtOAc was added to dilute the reaction mixture. Filtration through a pad of *Celite* and concentration under reduced pressure gave a residue, which was further purified by silica gel column chromatography (petroleum ether/ethyl acetate) to afford product **1**.

3-O-(ortho-Diphenylphosphanyl)benzoyl-4,6-O-4-methoxybenzylidene-D-glucal (1a)

Following the general procedure described above, 4,6-*O*-4-methoxybenzylidene-glucal **S2** (2.64 g, 10 mmol) was converted to **1a** (5.08 g, 92%) as a white solid: $[\alpha]_D^{23}$ = -143.1 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, DMSO-d_6) δ 7.97 (dt, J = 6.6, 3.8 Hz, 1H), 7.53 – 7.49 (m, 2H), 7.40 – 7.30 (m, 8H), 7.20 – 7.13 (m, 4H), 6.91 – 6.89 (m, 2H), 6.86 – 6.83 (m, 1H), 6.51 (dd, J = 6.0, 1.5 Hz, 1H), 5.54 (s, 1H), 5.50 (dt, J = 7.7, 1.8 Hz, 1H), 4.58 (dd, J = 6.1, 2.0 Hz, 1H), 4.28 (dd, J = 10.3, 5.0 Hz, 1H), 4.01 – 3.95 (m, 1H), 3.91 (dd, J = 10.3, 7.6 Hz, 1H), 3.78 (t, J = 10.1 Hz, 1H), 3.73 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 166.1 (d, J_{C-P} = 1.7 Hz), 159.6, 145.6, 139.2 (d, J_{C-P} = 27.3 Hz), 137.5 (d, J_{C-P} = 10.4 Hz), 137.3 (d, J_{C-P} = 12.1 Hz), 134.1 (d, J_{C-P} = 20.7 Hz), 133.9, 133.4 (d, J_{C-P} = 20.7 Hz), 132.4, 130.3 (d, J_{C-P} = 2.8 Hz), 129.5, 128.8, 128.6 (d, J_{C-P} = 7.0 Hz), 127.5, 113.4, 100.4, 99.9, 75.6, 69.5, 68.4, 67.1, 55.1; HRMS (ESI) m/z calcd for $C_{33}H_{30}O_6P$ $[M + H]^+$: 553.1775; found: 553.1774.

3-O-(ortho-Diphenylphosphanyl)benzoyl-4,6-O-(di-tert-butyl)silylene-D-glucal (1b)

Following the general procedure described above, 4,6-*O*-(di-*tert*-butyl)silylene-glucal **S5**[23] (2.86 g, 10 mmol) was converted to **1b** (4.88 g, 85%) as a colorless oil: $[\alpha]_D^{23}$ = -65.5 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, DMSO-d_6) δ 7.99 – 7.95 (m, 1H), 7.49 – 7.46 (m, 2H), 7.36 – 7.31 (m, 6H), 7.20 – 7.12 (m, 4H), 6.87 – 6.84 (m, 1H), 6.41 (dd, J = 6.0, 1.7 Hz, 1H), 5.43 (dt, J = 7.6, 1.9 Hz, 1H),

4.50 (dd, J = 6.1, 2.0 Hz, 1H), 4.16 – 4.09 (m, 2H), 3.96 – 3.87 (m, 2H), 0.97 (s, 9H), 0.89 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 166.0 (d, J_{C-P} = 1.9 Hz), 145.1, 139.4 (d, J_{C-P} = 27.5 Hz), 137.6 (d, J_{C-P} = 12.7 Hz), 137.4 (d, J_{C-P} = 12.1 Hz), 134.3 (d, J_{C-P} = 20.3 Hz), 133.8, 133.5 (d, J_{C-P} = 20.9 Hz), 133.2 (d, J_{C-P} = 20.7 Hz), 132.2, 130.0 (d, J_{C-P} = 2.9 Hz), 128.7 (d, J_{C-P} = 10.4 Hz), 128.6 (d, J_{C-P} = 7.2 Hz), 128.5, 99.8, 73.2, 72.5, 72.2, 65.0, 27.1, 26.6, 22.2, 19.4; HRMS (ESI) m/z calcd for $C_{33}H_{40}O_5PSi$ $[M + H]^+$: 575.2377; found: 575.2371.

3-O-(ortho-Diphenylphosphanyl)benzoyl-4,6-di-O-benzyl-D-glucal (1c)

Following the general procedure described above, 4,6-di-*O*-benzyl-glucal **S6**[24] (3.26 g, 10 mmol) was successfully converted to **1c** (5.77 g, 94%) as a colorless oil: $[\alpha]_D^{23}$ = -39.9 (*c* 3.15, $CHCl_3$); ^1H NMR (400 MHz, DMSO-d_6) δ 7.92 – 7.89 (m, 1H), 7.51 – 7.44 (m, 2H), 7.35 – 7.30 (m, 11H), 7.25 – 7.22 (m, 3H), 7.21 – 7.14 (m, 6H), 6.88 – 6.85 (m, 1H), 6.50 (dd, J = 6.1, 1.3 Hz, 1H), 5.39 – 5.37 (m, 1H), 4.58 (dd, J = 6.1, 3.1 Hz, 1H), 4.51 (t, J = 12.4 Hz, 4H), 4.18 – 4.14 (m, 1H), 3.82 (dd, J = 7.9, 5.9 Hz, 1H), 3.76 (dd, J = 10.9, 5.0 Hz, 1H), 3.67 (dd, J = 10.9, 3.0 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 165.7 (d, J_{C-P} = 2.1 Hz), 145.8, 139.6 (d, J_{C-P} = 27.4 Hz), 138.0 (d, J_{C-P} = 10.1 Hz), 137.5 (d, J_{C-P} = 6.4 Hz), 137.4 (d, J_{C-P} = 6.3 Hz), 133.9, 133.7 (d, J_{C-P} = 2.5 Hz), 133.6, 133.5 (d, J_{C-P} = 2.9 Hz), 133.3, 132.4, 130.3, 128.8 (3C), 128.7 (2C), 128.6 (2C), 128.2 (d, J_{C-P} = 9.2 Hz), 127.7, 127.6, 127.5 (d, J_{C-P} = 3.9 Hz), 98.2, 75.9, 72.9, 72.5, 72.4, 70.4, 67.7; HRMS (ESI) m/z calcd for $C_{39}H_{39}O_5PN$ $[M + NH_4]^+$: 632.2560; found: 632.2558.

3-O-(ortho-Diphenylphosphanyl)benzoyl-4,6-O-isopropylidene-D-glucal (1d)

Following the general procedure described above, 4,6-*O*-isopropylidene-glucal **S7**[25] (1.86 g, 10 mmol) was converted to **1d** (4.03 g, 85%) as a colorless oil: $[\alpha]_D^{23}$ = -104.8 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.97 (m, 1H), 7.38 – 7.32 (m, 2H), 7.31 – 7.19 (m, 10H), 6.90 – 6.87 (m, 1H), 6.22 (dd, J = 6.1, 1.5 Hz, 1H), 5.43 (dt, J = 7.7, 1.8 Hz, 1H), 4.56 (dd, J = 6.1, 2.0 Hz, 1H), 3.98 – 3.89 (m, 2H), 3.80 – 3.69 (m, 2H), 1.42 (s, 3H), 1.34 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.8 (d, J_{C-P} = 2.2 Hz), 145.3, 140.6 (d, J_{C-P} = 27.2 Hz), 138.2 (d, J_{C-P} = 11.4 Hz), 138.0 (d, J_{C-P} = 11.5 Hz), 134.6 (d, J_{C-P} = 19.4 Hz), 134.5, 134.3, 134.1 (d, J_{C-P} = 2.9 Hz), 133.9, 132.1, 130.8 (d, J_{C-P} = 2.9 Hz), 128.7, 128.6 (d, J_{C-P} = 7.3 Hz), 128.3, 101.0, 99.9, 70.5, 69.9, 69.8, 61.8, 29.0, 19.2; HRMS (ESI) m/z calcd for $C_{28}H_{27}O_5PNa$ $[M + Na]^+$: 497.1488; found: 497.1491.

3-O-(ortho-Diphenylphosphanyl)benzoyl-4,6-O-4-methoxybenzylidene-D-galactal (1e)

Following the general procedure described above, **S4** (2.64 g, 10 mmol) was converted to **1e** (2.21 g, 40%) as a white solid: $[\alpha]_D^{23}$ = +141.4 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, DMSO-d_6) δ 7.96 – 7.93 (m, 1H), 7.50 – 7.47 (m, 2H), 7.38 – 7.29 (m, 8H), 7.20 – 7.15 (m, 4H), 6.91 – 6.86 (m, 3H), 6.53 (dd, *J* = 6.4, 2.1 Hz, 1H), 5.58 (s, 1H), 5.53 (dt, *J* = 4.7, 2.1 Hz, 1H), 4.58 (dt, *J* = 6.4, 1.8 Hz, 1H), 4.48 – 4.47 (m, 1H), 4.15 (dd, *J* = 12.3, 1.8 Hz, 1H), 4.08 – 4.03 (m, 2H), 3.73 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 165.6 (d, J_{C-P} = 1.6 Hz), 159.4, 145.2, 139.6 (d, J_{C-P} = 27.3 Hz), 137.5 (d, J_{C-P} = 6.1 Hz), 137.4 (d, J_{C-P} = 6.4 Hz), 134.0 (d, J_{C-P} = 19.8 Hz), 133.7, 133.5 (d, J_{C-P} = 3.0 Hz), 133.3 (d, J_{C-P} = 2.8 Hz), 132.3, 130.5, 130.3 (d, J_{C-P} = 2.9 Hz), 128.8 (d, J_{C-P} = 2.3 Hz), 128.7, 128.6 (2C), 127.3, 113.3, 99.5, 97.3, 68.9, 68.4, 67.6, 66.4, 55.1; HRMS (ESI) m/z calcd for $C_{33}H_{30}O_6P$ $[M + H]^+$: 553.1774; found: 553.1770.

3-O-(ortho-Diphenylphosphanyl)benzoyl-4,6-O-(di-tert-butyl)silylene-D-galactal (1f)

Following the general procedure described above, 4,6-*O*-(di-*tert*-butyl)silylene-galactal **S8**[23] (2.86 g, 10 mmol) was converted to **1f** (4.94 g, 86%) as a white solid: $[\alpha]_D^{23}$ = +147.0 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, DMSO-d_6) δ 8.04 – 8.00 (m, 1H), 7.51 – 7.48 (m, 2H), 7.38 – 7.34 (m, 6H), 7.19 – 7.12 (m, 4H), 6.87 – 6.84 (m, 1H), 6.52 (dd, *J* = 6.4, 1.9 Hz, 1H), 5.30 (dt, *J* = 4.4, 2.0 Hz, 1H), 4.74 (dd, *J* = 5.4, 1.8 Hz, 1H), 4.64 (dt, *J* = 6.4, 1.8 Hz, 1H), 4.19 (dd, *J* = 12.7, 1.9 Hz, 1H), 4.12 (dd, *J* = 12.7, 1.8 Hz, 1H), 4.05 (s, 1H), 0.97 (s, 9H), 0.86 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 165.6, 145.7, 139.6 (d, J_{C-P} = 27.4 Hz), 137.7 (d, J_{C-P} = 12.9 Hz), 137.5 (d, J_{C-P} = 11.1 Hz), 134.3 (d, J_{C-P} = 20.2 Hz), 133.8, 133.6 (d, J_{C-P} = 20.8 Hz), 133.1 (d, J_{C-P} = 20.4 Hz), 132.3, 130.3 (d, J_{C-P} = 3.0 Hz), 128.7 (d, J_{C-P} = 12.4 Hz), 128.6 (2C), 128.5, 98.2, 72.5, 68.0, 66.8, 64.5, 27.3, 26.9, 22.7, 20.5; HRMS (ESI) m/z calcd for $C_{33}H_{40}O_5PSi$ $[M + H]^+$: 575.2377; found: 575.2370.

***3-O-(ortho-Diphenylphosphinyl)benzoyl-4,6-O-4-methoxybenzylidene-D-glucal* (S9)**

Aqueous H_2O_2 (30%, 171.3 mg, 5 mmol) was added to a magnetically stirred solution of **1a** (552.5 mg, 1 mmol) in THF (10 mL) at room temperature, the mixture was stirred at the same temperature for another 2 h before water (10 mL) was added to dilute the reaction mixture. The resulting solution was extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with H_2O and brine, and then dried over anhydrous Na_2SO_4. Filtration and concentration *in vacuo* gave a residue, which was purified by flash chromatography on silica gel (EtOAc/PE = 1 : 1) to afford product **S9** (500 mg, 88%) as a white solid: $[\alpha]_D^{23}$ = -165.7 (*c* 1.00, $CHCl_3$); ^1H NMR

(400 MHz, DMSO-d_6) δ 7.80 – 7.77 (m, 1H), 7.73 – 7.69 (m, 1H), 7.67 – 7.62 (m, 2H), 7.61 – 7.48 (m, 9H), 7.39 – 7.34 (m, 1H), 7.32 – 7.30 (m, 2H), 6.93 – 6.89 (m, 2H), 6.46 (dd, J = 6.1, 1.6 Hz, 1H), 5.45 (s, 1H), 5.36 (dt, J = 8.0, 1.8 Hz, 1H), 4.73 (dd, J = 6.2, 2.0 Hz, 1H), 4.25 (dd, J = 10.3, 5.2 Hz, 1H), 3.95 – 3.89 (m, 1H), 3.74 – 3.69 (m, 4H), 3.53 (dd, J = 10.3, 8.0 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 166.9 (d, J_{C-P} = 3.1 Hz), 159.6, 145.0, 135.8 (d, J_{C-P} = 6.0 Hz), 133.9 (d, J_{C-P} = 28.1 Hz), 133.9, 132.8 (d, J_{C-P} = 18.1 Hz), 132.2, 131.8, 131.4 (d, J_{C-P} = 9.6 Hz), 131.4 (d, J_{C-P} = 9.8 Hz), 131.2, 131.1 (d, J_{C-P} = 11.5 Hz), 130.0 (d, J_{C-P} = 8.4 Hz), 129.5, 128.6 (d, J_{C-P} = 12.0 Hz), 128.5 (d, J_{C-P} = 12.1 Hz), 127.6, 113.4, 100.5, 99.8, 75.3, 69.7, 68.2, 67.2, 55.1; HRMS (ESI) m/z calcd for $C_{33}H_{30}O_7P$ $[M + H]^+$: 569.1724; found: 569.1721.

General procedure for the synthesis of *C*-glycosides 3β

CuBr•SMe_2 (0.2 mmol) was added to a solution of **1** (0.2 mmol) in dry Et_2O (4 mL), and the mixture was stirred for 30 min at room temperature before RMgBr **2** (0.4 mmol) was added at 0 °C. The mixture was allowed to warm to 30 °C and was stirred for another 7-8 h at the same temperature, at which time TLC showed that all starting material **1** was consumed. Then the reaction was quenched by adding aqueous saturated NH_4Cl (2.5 mL), which was followed by the addition of EtOAc (10 mL) and NH_3•H_2O (12.5%, 2 mL). The resulting mixture was extracted with EtOAc (3 × 10 mL). The combined organic phases were washed with water then brine, and were then dried over anhydrous Na_2SO_4. Filtration and concentration *in vacuo* gave a residue, which was purified by chromatography on silica gel (EtOAc/PE) to afford **3β**.

General procedure for the preparation of *C*-glycosides 3α

To an ice-bath cooled suspension of CuBr•SMe_2 (0.2 mmol) and $ZnCl_2$ (1 M in Et_2O, 0.3 mmol) in dry Et_2O (2 mL) was added a solution of RMgBr **2** (0.4 mmol) slowly. The mixture was stirred at the same temperature for 60 min before the addition of a solution of ester **1** (0.2 mmol) in Et_2O (2 mL). The resulting mixture was allowed to warm to 30 °C or 55 °C and the stirring was continued for another 7-24 h, at which time TLC showed that all starting material **1** was consumed. Saturated aqueous solution of NH_4Cl (2.5 mL) and NH_3•H_2O (12.5%, 2 mL) were added successively after the reaction mixture was diluted with EtOAc (10 mL). The resulting mixture was extracted with EtOAc (3 × 10 mL). The combined organic extracts were washed with saturated aqueous NH_4Cl, H_2O, and brine successively, and were then dried over anhydrous Na_2SO_4. Filtration was followed by concentration *in vacuo* afforded the crude product, which was further purified by flash

chromatography on silica gel (using EtOAc/PE) to afford **3α** as predominant products.

Methyl 4,6-O-4-methoxybenzylidene-2,3-dideoxy-β-D-C-erythro-hex-2-enopyranoside (3aa)

Following the general procedure for the synthesis of β-*C*-glycosides, the coupling between **1a** and **2a** afforded **3aa** (30.6 mg, 59%) as a white solid after silica gel column chromatography (petroleum ether/ethyl acetate = 15 : 1): $[\alpha]_D^{23}$ = +26.3 (*c* 2.43, $CHCl_3$); ^1H NMR (400 MHz, DMSO-d_6) δ 7.34 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 5.84 (d, *J* = 9.7 Hz, 1H), 5.75 (dt, *J* = 10.2, 2.0 Hz, 1H), 5.61 (s, 1H), 4.40 – 4.37 (m, 1H), 4.19 – 4.14 (m, 2H), 3.74 – 3.70 (m, 4H), 3.48 – 3.42 (m, 1H), 1.17 (d, *J* = 6.8 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 159.5, 132.9, 130.2, 127.6, 125.3, 113.3, 100.9, 74.4, 71.6, 70.8, 68.5, 55.1, 20.7; HRMS (ESI) m/z calcd for $C_{15}H_{19}O_4$ $[M + H]^+$: 263.1278; found: 263.1275.

Ethyl 4,6-O-4-methoxybenzylidene-2,3-dideoxy-β-D-C-erythro-hex-2-enopyranoside (3ab)

Following the general procedure for the synthesis of β-*C*-glycosides, the coupling between **1a** and **2b** provided **3ab** (29.8 mg, 54%) as a white solid after silica gel column chromatography (petroleum ether/ethyl acetate = 15 : 1): $[\alpha]_D^{23}$ = +4.5 (*c* 0.55, $CHCl_3$); ^1H NMR (400 MHz, DMSO-d_6) δ 7.34 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 5.89 (d, *J* = 10.3 Hz, 1H), 5.76 (dt, *J* = 10.3, 2.1 Hz, 1H), 5.62 (s, 1H), 4.27 – 4.22 (m, 1H), 4.18 – 4.14 (m, 2H), 3.75 (s, 3H), 3.72 (d, *J* = 10.2 Hz, 1H), 3.46 – 3.40 (m, 1H), 1.63 – 1.42 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 159.5, 131.4, 130.2, 127.6, 126.2, 113.3, 100.8, 76.2, 74.5, 70.6, 68.5, 55.1, 27.4, 9.0; HRMS (ESI) m/z calcd for $C_{16}H_{21}O_4$ $[M + H]^+$: 277.1434; found: 277.1432.

Propyl 4,6-O-4-methoxybenzylidene-2,3-dideoxy-β-D-C-erythro-hex-2-enopyranoside (3ac)

Following the general procedure for the synthesis of β-*C*-glycosides, the coupling between **1a** and **2c** furnished **3ac** (32.0 mg, 55%) as a white solid after silica gel column chromatography (petroleum ether/ethyl acetate = 15 : 1): $[\alpha]_D^{23}$ = +15.6 (*c* 0.50, $CHCl_3$); ^1H NMR (400 MHz, DMSO-d_6) δ 7.34 (d, *J* = 8.7 Hz, 2H), 6.91 (d, *J* = 8.7 Hz, 2H), 5.87 (d, *J* = 10.4 Hz, 1H), 5.76 (dt, *J* = 10.3, 2.0 Hz, 1H), 5.61 (s, 1H), 4.29 – 4.25 (m, 1H), 4.16 (dd, *J* = 10.1, 4.3 Hz, 2H), 3.75 (s, 3H), 3.71 (d, *J* = 10.3 Hz, 1H), 3.46 – 3.40 (m, 1H), 1.55 – 1.43 (m, 2H), 1.41 – 1.33 (m, 2H), 0.88 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 159.5, 131.7, 130.2, 127.6, 125.9, 113.3, 100.8, 75.0, 74.5, 70.7, 68.5, 55.1, 36.6, 17.6, 13.9; HRMS (ESI) m/z calcd for $C_{17}H_{23}O_4$ $[M + H]^+$: 291.1591; found: 291.1588.

Phenyl 4,6-O-4-methoxybenzylidene-2,3-dideoxy-α/β-D-C-erythro-hex-2-enopyranoside (3ad)

Following the general procedure for the synthesis of β-*C*-glycosides, the coupling between **1a** and **2d** provided **3ad** (26.0 mg, 40%) as a mixture of α/β isomers with the β-**3ad** being the major product (α : β = 4:5). An aliquot of pure β-isomer was obtained for detailed characterization: $[\alpha]_D^{23}$ = +19.7 (*c* 1.70, $CHCl_3$); ^1H NMR (400 MHz, DMSO-d_6) δ 7.40 – 7.30 (m, 7H), 6.93 (d, *J* = 8.7 Hz, 2H), 6.00 (d, *J* = 9.6 Hz, 1H), 5.83 (dt, *J* = 10.4, 2.1 Hz, 1H), 5.69 (s, 1H), 5.37 (q, *J* = 2.5 Hz, 1H), 4.40 – 4.36 (m, 1H), 4.21 (dd, *J* = 10.0, 4.6 Hz, 1H), 3.81 (t, *J* = 10.2 Hz, 1H), 3.76 (s, 3H), 3.70 – 3.64 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 159.5, 140.1, 131.2, 130.1, 128.4, 128.0, 127.6, 127.2, 125.9, 113.4, 100.9, 77.5, 74.1, 71.2, 68.4, 55.2; HRMS (ESI) m/z calcd for $C_{20}H_{21}O_4$ $[M + H]^+$: 325.1434; found: 325.1437.

Methyl 4,6-O-(di-tert-butyl)silylene-2,3-dideoxy-β-D-C-erythro-hex-2-enopyranoside (3ba)

Following the general procedure for the synthesis of β-*C*-glycosides, the coupling between **1b** and **2a** provided **3ba** (28.4 mg, 50%) as a colorless oil after silica gel column chromatography (petroleum ether/ethyl acetate = 100 : 1): $[\alpha]_D^{23}$ = +6.1 (*c* 0.50, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 5.81 (dt, *J* = 10.3, 1.9 Hz, 1H), 5.60 (dt, *J* = 10.4, 1.8 Hz, 1H), 4.43 – 4.39 (m, 1H), 4.34 – 4.28 (m, 1H), 4.18 (dd, *J* = 10.2, 5.3 Hz, 1H), 3.88 (t, *J* = 10.2 Hz, 1H), 3.54 – 3.48 (m, 1H), 1.20 (d, *J* = 6.7 Hz, 3H), 1.05 (s, 9H), 0.99 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 131.1, 129.2, 74.9, 71.8, 70.4, 67.4, 27.7, 27.3, 22.8, 21.2, 20.2; HRMS (ESI) m/z calcd for $C_{15}H_{29}O_3Si$ $[M + H]^+$: 285.1881; found: 285.1885.

Ethyl 4,6-O-(di-tert-butyl)silylene-2,3-dideoxy-β-D-C-erythro-hex-2-enopyranoside (3bb)

Following the general procedure for the synthesis of β-*C*-glycosides, the coupling between **1b** and **2b** provided **3bb** (28.6 mg, 48.0%) as a colorless oil after silica gel column chromatography (petroleum ether/ethyl acetate =100 :1): $[\alpha]_D^{23}$ = +24.7 (*c* 0.20, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 5.84 (dt, *J* = 10.4, 1.9 Hz, 1H), 5.62 (dt, *J* = 10.4, 1.9 Hz, 1H), 4.40 – 4.36 (m, 1H), 4.19 – 4.12 (m, 2H), 3.87 (t, *J* = 10.2 Hz, 1H), 3.52 – 3.46 (m, 1H), 1.57 – 1.47 (m, 2H), 1.05 (s, 9H), 0.99 (s, 9H), 0.91 (t, *J* = 7.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 130.0, 129.6, 76.6, 74.8, 70.6, 67.5, 28.3, 27.7, 27.3, 22.8, 20.2, 9.2; HRMS (ESI) m/z calcd for $C_{16}H_{30}O_3SiNa$ $[M + Na]^+$: 321.1856; found: 321.1859.

Propyl 4,6-O-(di-tert-butyl)silylene-2,3-dideoxy-β-D-C-erythro-hex-2-enopyranoside (3bc)

Following the general procedure for the synthesis of β-*C*-glycosides, the coupling between **1b** and **2c** provided **3bc** (34.3 mg, 55%) as a white solid after silica gel column chromatography

(petroleum ether/ethyl acetate = 100 : 1): $[\alpha]_D^{23}$ = +27.6 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 5.82 (dt, *J* = 10.5, 2.0 Hz, 1H), 5.61 (dt, *J* = 10.4, 1.9 Hz, 1H), 4.40 – 4.36 (m, 1H), 4.21 – 4.15 (m, 2H), 3.86 (t, *J* = 10.2 Hz, 1H), 3.51 – 3.45 (m, 1H), 1.50 – 1.44 (m, 2H), 1.42 – 1.31 (m, 2H), 1.05 (s, 9H), 0.98 (s, 9H), 0.90 (t, *J* = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 130.1, 129.7, 75.4, 74.8, 70.6, 67.5, 37.6, 27.7, 27.3, 22.8, 20.2, 18.2, 14.2; HRMS (ESI) m/z calcd for $C_{17}H_{32}O_3SiNa$ $[M + Na]^+$: 335.2013; found: 335.2012.

Phenyl 4,6-O-(di-tert-butyl)silylene-2,3-dideoxy-α/β-D-C-erythro-hex-2-enopyranoside (3bd)

Following the general procedure for the synthesis of β-*C*-glycosides, the coupling between **1b** and **2d** provided **3bd** (29.8 mg, 43%) as a mixture of α/β epimers with the β-isomer as the major product (α:β = 1 : 2). An aliquot of pure β-**3bd** was obtained for detailed characterization: $[\alpha]_D^{23}$ = +2.4 (*c* 2.03, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.29 (m, 5H), 5.97 (dt, *J* = 10.3, 2.0 Hz, 1H), 5.74 (dt, *J* = 10.3, 1.9 Hz, 1H), 5.23 (d, *J* = 2.3 Hz, 1H), 4.59 – 4.56 (m, 1H), 4.22 (dd, *J* = 10.0, 5.0 Hz, 1H), 3.95 (t, *J* = 10.2 Hz, 1H), 3.76 – 3.70 (m, 1H), 1.08 (s, 9H), 1.02 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 140.3, 130.0, 129.5, 128.8, 128.4, 127.5, 78.4, 75.5, 70.3, 67.4, 27.7, 27.3, 22.9, 20.3; HRMS (ESI) m/z calcd for $C_{20}H_{31}O_3Si$ $[M + H]^+$: 347.2037; found: 347.2038.

Methyl 4,6-di-O-benzyl-2,3-dideoxy-β-D-C-erythro-hex-2-enopyranoside (3ca)

Following the general procedure for the synthesis of β-*C*-glycosides, the coupling between **1c** and **2a** provided **3ca** (29.7 mg, 46%) as a colorless oil after silica gel column chromatography (petroleum ether/ethyl acetate = 20 : 1): $[\alpha]_D^{23}$ = +28.4 (*c* 0.40, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.20 (m, 10H), 5.86 (dt, *J* = 10.2, 2.1 Hz, 1H), 5.73 (dt, *J* = 10.3, 1.5 Hz, 1H), 4.63 – 4.54 (m, 3H), 4.42 (d, *J* = 11.4 Hz, 1H), 4.30 – 4.23 (m, 1H), 4.01 – 3.98 (m, 1H), 3.75 – 3.70 (m, 1H), 3.64 – 3.60 (m, 2H), 1.23 (d, *J* = 6.8 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 138.5, 138.3, 133.4, 128.5 (2C), 128.1, 127.9, 127.7, 125.5, 77.3, 73.6, 71.2, 70.9, 67.0, 21.4; HRMS (ESI) m/z calcd for $C_{21}H_{25}O_3$ $[M + H]^+$: 325.1798; found: 325.1796.

Ethyl 4,6-di-O-benzyl-2,3-dideoxy-β-D-C-erythro-hex-2-enopyranoside (3cb)

Following the general procedure for the synthesis of β-*C*-glycosides, the coupling between **1c** and **2b** furnished **3cb** (29.8 mg, 44%) as a colorless oil after silica gel column chromatography (petroleum ether/ethyl acetate = 20 : 1): $[\alpha]_D^{23}$ = +33.7 (*c* 0.55, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.24 (m, 10H), 5.91 (dt, *J* = 10.3, 2.1 Hz, 1H), 5.77 (dt, *J* = 10.4, 1.5 Hz, 1H),

4.66 – 4.58 (m, 3H), 4.46 (d, J = 11.5 Hz, 1H), 4.10 – 4.06 (m, 1H), 4.01 – 3.98 (m, 1H), 3.78 – 3.73 (m, 1H), 3.67 – 3.60 (m, 2H), 1.62 – 1.58 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 138.6, 138.3, 131.9, 128.5, 128.4, 128.0 (2C), 127.8, 127.6, 126.2, 77.4, 76.0, 73.5, 71.2, 71.1, 70.0, 28.4, 9.4; HRMS (ESI) m/z calcd for $C_{22}H_{26}O_3Na$ $[M + Na]^+$: 361.1774; found: 361.1772.

Phenyl 4,6-di-O-benzyl-2,3-dideoxy-α/β-D-C-erythro-hex-2-enopyranoside (3cd)

Following the general procedure for the synthesis of β-*C*-glycosides, the coupling between **1c** and **2d** provided **3cd** (30.9 mg, 40.0%) as a mixture of α/β diastereomers with the β-isomer being the major product (α/β = 1 : 2.5). The pure β-**3cd** was obtained as a colorless oil after silica gel column chromatography (petroleum ether/ethyl acetate = 20 : 1) for detailed characterization: $[\alpha]_D^{23}$ = +86.0 (*c* 0.50, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.25 (m, 15H), 5.99 (dt, J = 10.3, 2.1 Hz, 1H), 5.85 (dt, J = 10.3, 1.7 Hz, 1H), 5.18 (q, J = 2.3 Hz, 1H), 4.67 – 4.50 (m, 4H), 4.17 – 4.14 (m, 1H), 3.85 – 3.79 (m, 2H), 3.73 (dd, J = 11.0, 5.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 140.9, 138.6, 138.2, 131.8, 128.6 (2C), 128.4, 128.1 (2C), 128.0, 127.9, 127.6, 127.3, 126.2, 78.0, 77.6, 73.6, 71.4, 70.7, 70.1; HRMS (ESI) m/z calcd for $C_{26}H_{27}O_3$ $[M + H]^+$: 387.1955; found: 387.1955.

Phenyl 4,6-O-isopropylidene-2,3-dideoxy-α/β-D-C-erythro-hex-2-enopyranoside (3dd)

Following the general procedure for the synthesis of β-*C*-glycosides, the coupling between **1d** and **2d** afforded **3dd** (22.2 mg, 45%) as a mixture of α/β diastereomers with the β-**3dd** as the predominating product (α/β = 3 : 5, determined by ^1H NMR).

Methyl 4,6-O-4-methoxybenzylidene-2,3-dideoxy-β-D-C-threo-hex-2-enopyranoside (3ea)

Following the general procedure for the synthesis of β-*C*-glycosides, the coupling between **1e** and **2a** afforded **3ea** (22.0 mg, 42%) as a colorless oil after silica gel column chromatography (petroleum ether/ethyl acetate = 12 : 1): $[\alpha]_D^{23}$ = -7.5 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, DMSO-d_6) δ 7.32 (d, J = 8.6 Hz, 2H), 6.90 (d, J = 8.8 Hz, 2H), 5.96 (d, J = 10.8 Hz, 1H), 5.87 – 5.83 (m, 1H), 5.55 (s, 1H), 4.24 – 4.20 (m, 2H), 4.15 (dd, J = 12.7, 2.5 Hz, 1H), 4.09 (dd, J = 12.8, 1.3 Hz, 1H), 3.74 (s, 3H), 3.38 (s, 1H), 1.21 (d, J = 6.8 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 159.3, 136.5, 131.0, 127.4, 122.9, 113.2, 99.4, 70.5, 69.6, 68.4, 67.8, 55.1, 20.6; HRMS (ESI) m/z calcd for $C_{15}H_{19}O_4$ $[M + H]^+$: 263.1278; found: 263.1277.

Ethyl 4,6-O-4-methoxybenzylidene-2,3-dideoxy-β-D-C-threo-hex-2-enopyranoside (3eb)

Following the general procedure for the synthesis of β-*C*-glycosides, the coupling between **1e** and **2b** gave **3eb** (22.1 mg, 40%) as a colorless oil after silica gel column chromatography (petroleum ether/ethyl acetate = 12 : 1): $[\alpha]_D^{23}$ = -2.7 (*c* 1.57, $CHCl_3$); ^1H NMR (400 MHz, DMSO-d_6) δ 7.32 (d, *J* = 8.6 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 5.97 (d, *J* = 10.7 Hz, 1H), 5.91 – 5.87 (m, 1H), 5.55 (s, 1H), 4.24 – 4.22 (m, 1H), 4.15 (dd, *J* = 12.7, 2.4 Hz, 1H), 4.11 – 4.02 (m, 2H), 3.74 (s, 3H), 3.45 (s, 1H), 1.61 – 1.50 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 159.4, 135.2, 131.1, 127.4, 123.6, 113.2, 99.4, 75.1, 69.6, 68.1, 68.0, 55.1, 27.2, 9.2; HRMS (ESI) m/z calcd for $C_{16}H_{21}O_4$ $[M + H]^+$: 277.1434; found: 277.1435.

Methyl 4,6-O-4-methoxybenzylidene-2,3-dideoxy-α/β-D-C-erythro-hex-2-enopyranoside (3aa)

Following the general procedure for the preparation of α-*C*-glycosides, the coupling between **1a** and **2a** under the effect of CuBr•SMe_2/$ZnCl_2$ provided **3aa** (46.1 mg, 88%) as a mixture of α/β diastereomers with α-**3aa** as the predominant product (α/β = 3.2:1). The pure α-**3aa** was obtained as a white solid for detailed characterization: $[\alpha]_D^{23}$ = +19.0 (*c* 1.63, $CHCl_3$); ^1H NMR (400 MHz, DMSO-d_6) δ 7.35 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 5.87 (d, *J* = 10.2 Hz, 1H), 5.77 (dt, *J* = 10.4, 2.5 Hz, 1H), 5.61 (s, 1H), 4.44 – 4.38 (m, 1H), 4.14 – 4.09 (m, 2H), 3.75 (s, 3H), 3.70 (t, *J* = 10.2 Hz, 1H), 3.48 – 3.42 (m, 1H), 1.25 (d, *J* = 6.8 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 159.5, 132.4, 130.2, 127.6, 125.7, 113.4, 100.9, 74.4, 69.7, 68.8, 64.8, 55.1, 19.0; HRMS (ESI) m/z calcd for $C_{15}H_{19}O_4$ $[M + H]^+$: 263.1278; found: 263.1275.

Ethyl 4,6-O-4-methoxybenzylidene-2,3-dideoxy-α/β-D-C-erythro-hex-2-enopyranoside (3ab)

Following the general procedure for the preparation of α-*C*-glycosides, the coupling between **1a** and **2b** under the effect of CuBr•SMe_2/$ZnCl_2$ provided **3ab** (41.4 mg, 75%) as a mixture of α/β diastereomers (α/β = 2 : 1) with the α-isomer being the predominant product. The pure α-**3ab** was obtained as a white solid for detailed characterization: $[\alpha]_D^{23}$ = +4.0 (*c* 1.83, $CHCl_3$); ^1H NMR (400 MHz, DMSO-d_6) δ 7.34 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 5.90 (d, *J* = 10.5 Hz, 1H), 5.82 (dt, *J* = 10.4, 2.3 Hz, 1H), 5.61 (s, 1H), 4.15 – 4.07 (m, 3H), 3.74 (s, 3H), 3.70 (d, *J* = 10.2 Hz, 1H), 3.42 – 3.38 (m, 1H), 1.68 – 1.50 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 159.5, 131.1, 130.2, 127.6, 126.1, 113.4, 100.9, 74.9, 74.6, 68.8, 65.2, 55.1, 25.9, 10.8; HRMS (ESI) m/z calcd for $C_{16}H_{21}O_4$ $[M + H]^+$: 277.1434; found: 277.1429.

Propyl 4,6-O-4-methoxybenzylidene-2,3-dideoxy-α/β-D-C-erythro-hex-2-enopyranoside (3ac)

Following the general procedure for the synthesis of α-*C*-glycosides, the coupling between **1a** and

2c under the effect of CuBr•SMe_2/$ZnCl_2$ provided **3ac** (44.1 mg, 76.0%) as a mixture of α/β diastereomers with the α-isomer being the predominant product (α/β = 2.5 : 1). The pure α-**3ac** was obtained as a white solid for detailed characterization: $[\alpha]_D^{23}$ = +3.3 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.34 (d, *J* = 8.7 Hz, 2H), 6.91 (d, *J* = 8.7 Hz, 2H), 5.88 (d, *J* = 10.0 Hz, 1H), 5.80 (dt, *J* = 10.5, 2.4 Hz, 1H), 5.61 (s, 1H), 4.20 (d, *J* = 7.9 Hz, 1H), 4.14 – 4.10 (m, 2H), 3.75 (s, 3H), 3.70 (t, *J* = 10.2 Hz, 1H), 3.43 – 3.37 (m, 1H), 1.65 (q, *J* = 9.2 Hz, 1H), 1.48 – 1.41 (m, 2H), 1.39 – 1.32 (m, 1H), 0.91 (t, *J* = 7.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 159.5, 131.3, 130.2, 127.6, 125.9, 113.3, 100.8, 74.6, 73.2, 68.8, 65.1, 55.1, 34.7, 19.0, 13.8; HRMS (ESI) m/z calcd for $C_{17}H_{23}O_4$ $[M + H]^+$: 291.1591; found: 291.1590.

Phenyl 4,6-O-4-methoxybenzylidene-2,3-dideoxy-α/β-D-C-erythro-hex-2-enopyranoside (3ad)

Following the general procedure for the synthesis of α-*C*-glycosides, the coupling between **1a** and **2d** under the effect of CuBr•SMe_2/$ZnCl_2$ provided **3ad** (58.3 mg, 90%) as a mixture of α/β diastereomers with the α-isomer being the predominant product (α/β = 5.2:1). The pure α-**3ad** was obtained as a white solid for detailed characterization: $[\alpha]_D^{23}$ = +72.5 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.41 (d, *J* = 4.3 Hz, 4H), 7.36 – 7.32 (m, 3H), 6.90 (d, *J* = 8.7 Hz, 2H), 6.13 (t, *J* = 12.1, 2H), 5.65 (s, 1H), 5.38 (s, 1H), 4.28 (dt, *J* = 8.4, 1.9 Hz, 1H), 4.10 (dd, *J* = 10.2, 4.6 Hz, 1H), 3.77 (d, *J* = 10.3 Hz, 1H), 3.74 (s, 3H), 3.42 – 3.38 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 159.5, 139.7, 130.1, 129.6, 128.5, 127.8, 127.6, 127.2 (2C), 113.4, 101.0, 74.3, 74.1, 68.4, 65.3, 55.1; HRMS (ESI) m/z calcd for $C_{20}H_{21}O_4$ $[M + H]^+$: 325.1434; found: 325.1437.

Phenyl 4,6-O-4-methoxybenzylidene-2,3-dideoxy-α/β-D-erythro-hex-2-eno-C-pyranoside (3ad)---*in gram scale synthesis*

Following the general procedure for the synthesis of α-*C*-glycosides, the coupling between **1a** (2.76 g, 5.0 mmol) and **2d** (3M in ether, 3.34 mL, 10.0 mmol) under the effect of CuBr•SMe_2 (1.0 g, 5.0 mmol)/$ZnCl_2$ (1M in ether, 7.5 mL, 7.5 mmol) provided **3ad** (1.27 g, 75%) as a mixture of α/β diastereomers with the α-isomer being the predominant product (α/β = 5:1).

ortho-Methylphenyl

4,6-O-4-methoxybenzylidene-2,3-dideoxy-α/β-D-erythro-hex-2-eno-C-pyranoside (3ae)

Following the general procedure for the preparation of α-*C*-glycosides, the coupling between **1a** and **2e** under the effect of CuBr•SMe_2/$ZnCl_2$ provided **3ae** (58.2 mg, 86%) as a mixture of α/β diastereomers with the α-isomer being the predominant product (α/β = 4:1 and the value was

determined by ^{1}H NMR). The α/β isomers of **3ae** were inseparable by silica gel column chromatography (petroleum ether/ethyl acetate = 15 : 1), thus were determined as a mixture: $[\alpha]_D^{23}$ = +35.3 (*c* 1.68, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.37 (dd, *J* = 13.8, 8.4 Hz, 2H), 7.29 – 7.19 (m, 4H), 6.92 (t, *J* = 9.1 Hz, 2H), 6.21 (d, *J* = 10.4 Hz, 0.8H), 6.03 (dt, *J* = 10.7, 2.9 Hz, 1H), 5.83 (d, *J* = 10.4 Hz, 0.2H), 5.69 (s, 0.2H), 5.64 (s, 0.8H), 5.57 (d, *J* = 2.7 Hz, 0.2H), 5.55 (d, *J* = 2.7 Hz, 0.8H), 4.40 (d, *J* = 8.2 Hz, 0.2H), 4.28 (d, *J* = 8.2 Hz, 0.8H), 4.21 (dd, *J* = 10.2, 4.7 Hz, 0.2H), 3.95 (dd, *J* = 10.2, 4.7 Hz, 0.8H), 3.81 (d, *J* = 10.2 Hz, 0.2H), 3.76 (s, 0.6H), 3.74 (s, 2.4H), 3.71 (d, *J* = 10.2 Hz, 0.8H), 3.35 (s, 0.8H), 3.32 (d, *J* = 5.2 Hz, 0.2H), 2.40 (s, 2.4H), 2.35 (s, 0.6H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 159.5, 137.8, 137.4, 136.9, 135.8, 130.7, 130.4, 130.1 (2C), 129.5, 128.3, 127.9 (2C), 127.7, 127.6, 127.4, 126.0, 125.9, 125.3, 113.4, 113.3, 100.9, 75.3, 74.6, 74.2, 71.6, 71.3, 68.6, 68.4, 64.7, 55.1, 18.7; HRMS (ESI) m/z calcd for $C_{21}H_{22}O_4Na$ $[M + Na]^+$: 361.1410; found: 361.1408.

ortho-Methoxyphenyl

4,6-O-4-methoxybenzylidene-2,3-dideoxy-α/β-D-erythro-hex-2-eno-C-pyranoside (3af)

Following the general procedure for the preparation of α-*C*-glycosides, the coupling between **1a** and **2f** under the effect of CuBr•SMe_2/$ZnCl_2$ at 55 °C in a prolonged reaction time (10 h) provided **3af** as a mixture α/β diastereomers with the α-isomer being the predominant product, which were separated by silica gel column chromatography (petroleum ether/ethyl acetate = 20 : 1) for detailed characterization. The pure β-**3af** was obtained as a colorless oil (10.6 mg, 15%): $[\alpha]_D^{23}$ = +4.2 (*c* 2.13, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.37 (d, *J* = 8.7 Hz, 2H), 7.33 – 7.27 (m, 2H), 7.03 (d, *J* = 8.1 Hz, 1H), 6.97 – 6.91 (m, 3H), 5.95 (d, *J* = 10.3 Hz, 1H), 5.79 (dt, *J* = 10.3, 2.1 Hz, 1H), 5.69 (s, 1H), 5.67 (t, *J* = 2.7 Hz, 1H), 4.37 – 4.35 (m, 1H), 4.21 (dd, *J* = 10.0, 4.6 Hz, 1H), 3.82 (t, *J* = 9.8Hz, 4H), 3.76 (s, 3H), 3.70 – 3.64 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 159.5, 156.0, 130.6, 130.1, 129.0, 127.8, 127.6, 127.2, 125.8, 120.4, 113.4, 111.0, 100.9, 74.2, 71.7, 71.2, 68.4, 55.5, 55.1; HRMS (ESI) m/z calcd for $C_{21}H_{23}O_5$ $[M + H]^+$: 355.1540; found: 355.1537. Pure α-**3af** was obtained as a colorless oil (36.1 mg, 51%): $[\alpha]_D^{23}$ = +12.9 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.37 – 7.34 (m, 3H), 7.33 – 7.30 (m, 1H), 7.05 (d, *J* = 8.3 Hz, 1H), 6.98 (td, *J* = 7.4, 1.1 Hz, 1H), 6.92 – 6.90 (m, 2H), 6.12 (d, *J* = 9.5 Hz, 1H), 5.98 (dt, *J* = 10.4, 2.6 Hz, 1H), 5.65 (s, 1H), 5.60 (d, *J* = 2.6 Hz, 1H), 4.24 (d, *J* = 8.3 Hz, 1H), 4.10 (dd, *J* = 10.2, 4.7 Hz, 1H), 3.82 (s, 3H), 3.75 (s, 3H), 3.71 – 3.68 (m, 1H), 3.48 – 3.42 (m, 1H); ^{13}C

{^{1}H}NMR (100 MHz, DMSO-d_6) δ 159.5, 156.7, 130.1, 129.5, 129.2, 127.6 (2C), 127.4, 126.9, 120.0, 113.3, 111.4, 100.9, 74.4, 69.3, 68.5, 65.4, 55.5, 55.1; HRMS (ESI) m/z calcd for $C_{21}H_{23}O_5$ $[M + H]^+$: 355.1540; found: 355.1543.

meta-Methoxyphenyl

4,6-O-4-methoxybenzylidene-2,3-dideoxy-α/β-D-erythro-hex-2-eno-C-pyranoside (3ag)

Following the general procedure for the preparation of α-*C*-glycosides, the coupling between **1a** and **2g** under the effect of CuBr•SMe_2/$ZnCl_2$ at 55 °C in a prolonged reaction time (10 h) provided **3ag** (49.58 mg, 70%) as a colorless syrup in an inseparable mixture of α/β diastereomers with the desired α-isomer being the predominant product (α/β = 4:1, determined by ^{1}H NMR): $[\alpha]_D^{23}$ = +3.4 (*c* 2.90, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.40 – 7.28 (m, 3H), 6.98 (d, *J* = 7.8 Hz, 1H), 6.95 – 6.89 (m, 4H), 6.16 – 6.09 (m, 1.6H), 5.99 (d, *J* = 10.1 Hz, 0.2H), 5.84 – 5.81(m, 0.2H), 5.69 (s, 0.2H), 5.65 (s, 0.8H), 5.34 (d, *J* = 2.6 Hz, 1H), 4.38 (d, *J* = 8.4 Hz, 0.2H), 4.27 (d, *J* = 8.2 Hz, 0.8H), 4.21 (dd, *J* = 10.0, 4.5 Hz, 0.2H), 4.12 (dd, *J* = 10.2, 4.7 Hz, 0.8H), 3.84 – 3.74 (m, 7H), 3.42 – 3.36 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 159.5, 159.4, 141.3, 131.2, 130.0, 129.6, 129.5, 127.6, 127.1, 125.9, 119.2, 113.4, 113.3, 113.1, 112.9, 100.9, 77.3, 74.2, 74.1, 73.9, 71.1, 68.4, 65.5, 55.1 (2C); HRMS (ESI) m/z calcd for $C_{21}H_{22}O_5Na$ $[M + Na]^+$: 377.1359; found: 377.1357.

para-Methoxyphenyl

4,6-O-4-methoxybenzylidene-2,3-dideoxy-α/β-D-erythro-hex-2-eno-C-pyranoside (3ah)

Following the general procedure for the preparation of α-*C*-glycosides, the coupling between **1a** and **2h** under the effect of CuBr•SMe_2/$ZnCl_2$ at 55 °C in a prolonged reaction time (10 h) provided **3ah** (53.12 mg, 75%) as a colorless oil in an inseparable mixture of α/β diastereomers (α/β = 5.2 : 1, determined by ^{1}H NMR): $[\alpha]_D^{23}$ = +8.5 (*c* 2.13, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.36 – 7.30 (m, 4H), 7.00 – 6.95 (m, 2H), 6.91 – 6.89 (m, 2H), 6.13 – 6.05 (m, 1.68H), 5.99 (d, *J* = 10.4 Hz, 0.16H), 5.81 – 5.75 (m, 0.16H), 5.68 (s, 0.16H), 5.64 (s, 0.84H), 5.31 (d, *J* = 2.4 Hz, 1H), 4.36 (d, *J* = 8.4 Hz, 0.16H), 4.26 (d, *J* = 8.4 Hz, 0.84H), 4.19 (dd, *J* = 10.2, 4.6 Hz, 0.16H), 4.03 (dd, *J* = 10.2, 4.6 Hz, 0.84H), 3.76 (s, 3H), 3.74 (s, 3H), 3.72 (d, *J* = 10.4 Hz, 0.84H), 3.67 – 3.64 (m, 0.16H), 3.42 – 3.35 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 159.5, 158.9, 131.6, 130.1, 129.6, 129.0, 128.6, 127.6, 127.1, 113.8, 113.3, 100.9, 74.4, 73.8, 68.5, 64.8, 55.1; HRMS (ESI) m/z calcd for $C_{21}H_{22}O_5Na$ $[M + Na]^+$: 377.1359; found: 377.1356.

para-Fluorophenyl

4,6-O-4-methoxybenzylidene-2,3-dideoxy-α/β-D-erythro-hex-2-eno-C-pyranoside (3aj)

Following the general procedure for the preparation of α-*C*-glycosides, the coupling between **1a** and **2j** under the effect of CuBr•SMe_2/$ZnCl_2$ provided **3aj** as a mixture of α/β diastereomers (α/β = 3.5 : 1), which were separated by silica gel column chromatography (petroleum ether/ethyl acetate = 15 : 1). The pure β-**3aj** was obtained as a white solid (14.4 mg, 21%): $[\alpha]_D^{23}$ = +4.3 (*c* 1.93, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.41 – 7.36 (m, 4H), 7.20 (t, *J* = 8.9 Hz, 2H), 6.94 – 6.84 (m, 2H), 6.01 (d, *J* = 10.3 Hz, 1H), 5.82 (dt, *J* = 10.4, 2.1 Hz, 1H), 5.68 (s, 1H), 5.39 (s, 1H), 4.38 (dd, *J* = 7.5, 3.4 Hz, 1H), 4.20 (dd, *J* = 10.0, 4.6 Hz, 1H), 3.80 (t, *J* = 10.3 Hz, 1H), 3.76 (s, 3H), 3.68 – 3.63 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 161.7 (d, J_{C-F} = 244.8 Hz), 159.5, 136.4 (d, J_{C-F} = 3.0 Hz), 131.0, 130.1, 129.2 (d, J_{C-F} = 8.4 Hz), 127.6, 126.1, 115.2 (d, J_{C-F} = 21.5 Hz), 113.4, 100.9, 76.7, 74.1, 71.2, 68.4, 55.1; HRMS (ESI) m/z calcd for $C_{20}H_{20}FO_4$ [M + H]$^+$: 343.1340; found: 343.1343. The pure α-**3aj** was obtained as a white solid (49.3 mg, 72%): $[\alpha]_D^{23}$ = +10.3 (*c* 3.25, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.47 – 7.44 (m, 2H), 7.33 (d, *J* = 8.7 Hz, 2H), 7.23 (t, *J* = 8.9 Hz, 2H), 6.91 – 6.89 (m, 2H), 6.13 (t, *J* = 11.1 Hz, 2H), 5.65 (s, 1H), 5.38 (s, 1H), 4.29 – 4.26 (m, 1H), 4.09 (dd, *J* = 10.2, 4.6 Hz, 1H), 3.77 – 3.72 (m, 4H), 3.39 – 3.34 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 161.7 (d, J_{C-F} = 244.9 Hz), 159.5, 136.0 (d, J_{C-F} = 3.0 Hz), 130.0, 129.5 (d, J_{C-F} = 8.3Hz), 129.4, 127.6, 127.4, 115.3 (d, J_{C-F} = 21.3 Hz), 113.4, 101.0, 74.2, 73.4, 68.4, 65.1, 55.1; HRMS (ESI) m/z calcd for $C_{20}H_{20}FO_4$ [M + H]$^+$: 343.1340; found: 343.1344.

Methyl 4,6-O-(di-tert-butyl)silylene-2,3-dideoxy-α/β-D-C-erythro-hex-2-enopyranoside (3ba)

Following the general procedure for the synthesis of α-*C*-glycosides, the coupling between **1b** and **2a** under the effect of CuBr•SMe_2/$ZnCl_2$ provided **3ba** (49.96 mg, 88%) as a colorless oil in a mixture of α/β isomers (α/β = 4.5:1). An aliquot of pure α-**3ba** was obtained for detailed characterization: $[\alpha]_D^{23}$ = +3.6 (*c* 0.25, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.83 (dt, *J* = 10.3, 1.8 Hz, 1H), 5.63 (dt, *J* = 10.5, 2.4 Hz, 1H), 4.40 – 4.32 (m, 2H), 4.13 (dd, *J* = 9.9, 5.0 Hz, 1H), 3.84 (t, *J* = 10.1 Hz, 1H), 3.55 – 3.49 (m, 1H), 1.28 (d, *J* = 6.8 Hz, 3H), 1.05 (s, 9H), 0.99 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 130.5, 129.6, 70.5, 70.2, 68.4, 67.7, 27.6, 27.2, 22.8, 20.2, 19.4; HRMS (ESI) m/z calcd for $C_{15}H_{29}O_3Si$ [M + H]$^+$: 285.1881; found: 285.1883.

Phenyl 4,6-O-(di-tert-butyl)silylene-2,3-dideoxy-α/β-D-C-erythro-hex-2-enopyranoside (3bd)

Following the general procedure for the synthesis of α-*C*-glycosides, the coupling between **1b** and **2d** under the effect of CuBr•SMe_2/$ZnCl_2$ provided **3bd** (51.2 mg, 74%) as a white solid in a mixture of α/β isomers (α/β = 4.3:1). As the major product, an aliquot of pure α-**3bd** was obtained for detailed characterization: $[\alpha]_D^{23}$ = +4.1 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, 5H), 6.11 (dt, *J* = 10.4, 1.9 Hz, 1H), 5.94 (dt, *J* = 10.4, 2.6 Hz, 1H), 5.24 (q, *J* = 2.6 Hz, 1H), 4.50 – 4.46 (m, 1H), 4.02 (dd, *J* = 9.9, 5.0 Hz, 1H), 3.85 (t, *J* = 10.2 Hz, 1H), 3.57 – 3.51 (m, 1H), 1.06 (s, 9H), 0.95 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 139.6, 131.5, 128.6, 128.2, 128.1, 127.2, 75.1, 70.6, 68.4, 67.5, 27.6, 27.2, 22.9, 20.2; HRMS (ESI) m/z calcd for $C_{20}H_{31}O_3Si$ $[M + H]^+$: 347.2037; found: 347.2039.

2-Methylphenyl 4,6-O-(di-tert-butyl)silylene-2,3-dideoxy-α/β-D-C-erythro-hex-2-enopyranoside (3be)

Following the general procedure for the synthesis of α-*C*-glycosides, the coupling between **1b** and **2e** under the effect of CuBr•SMe_2/$ZnCl_2$ provided **3be** (56.9 mg, 79%) as a white solid in a mixture of α/β isomers (α/β = 5.2 : 1, determined by ^{1}H NMR). The α/β isomers of **3be** were inseparable by silica gel column chromatography, thus were characterized as a mixture: $[\alpha]_D^{23}$ = +22.5 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.26 (m, 2.5H), 7.25 – 7.18 (m, 1.5H), 6.18 (d, *J* = 10.4 Hz, 0.84H), 6.02 (d, *J* = 10.4 Hz, 0.16H), 5.93 – 5.89 (m, 0.84H), 5.79 – 5.75 (m, 0.16H), 5.48 (q, *J* = 3.0 Hz, 0.16H), 5.46 (q, *J* = 2.6 Hz, 0.84H), 4.63 – 4.60 (m, 0.16H), 4.52 – 4.48 (m, 0.84H), 4.24 (dd, J = 9.8, 5.0 Hz, 0.16H), 3.97 (t, *J* = 10.3 Hz, 0.16H), 3.95 – 3.92 (m, 0.84H), 3.84 (t, *J* = 10.1 Hz, 0.84H), 3.82 – 3.75 (m, 0.16H), 3.54 – 3.48 (m, 0.84H), 2.46 (s, 2.55H), 2.42 (s, 0.45H), 1.11 (s, 1.45H), 1.09 (s, 7.55H), 1.06 (s, 1.45H), 0.97 (s, 7.55H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 138.3, 138.0, 136.9, 136.2, 131.7, 131.0, 130.9, 130.1, 128.9, 128.5, 128.3, 127.6, 126.4, 125.4, 75.7, 75.6, 72.2, 70.9, 70.4, 68.1, 67.5, 67.4, 27.7, 27.6, 27.3, 27.2, 22.9 (2C), 20.3, 20.2, 19.2 (2C); HRMS (ESI) m/z calcd for $C_{21}H_{33}O_3Si$ $[M + H]^+$: 361.2194; found: 361.2199.

4-Methylphenyl 4,6-O-(di-tert-butyl)silylene-2,3-dideoxy-α/β-D-C-erythro-hex-2-enopyranoside (3bi)

Following the general procedure for the synthesis of α-*C*-glycosides, the coupling between **1b** and **2i** under the effect of CuBr•SMe_2/$ZnCl_2$ at 55 °C in an extended reaction time (10 h) provided **3bi** as a mixture of α/β diastereomers, which was separated by silica gel column chromatography

(petroleum ether/ethyl acetate = 100 : 1). The pure β-**3bi** was obtained as a white solid for detailed characterization (12.9 mg, 18%): $[\alpha]_D^{23}$ = +40.0 (*c* 0.43, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 7.9 Hz, 2H), 7.15 (d, *J* = 7.9 Hz, 2H), 5.96 (dt, *J* = 10.3, 1.9 Hz, 1H), 5.72 (dt, *J* = 10.3, 1.9 Hz, 1H), 5.19 (d, *J* = 2.4 Hz, 1H), 4.58 – 4.54 (m, 1H), 4.21 (dd, *J* = 10.0, 5.0 Hz, 1H), 3.93 (t, *J* = 10.3 Hz, 1H), 3.74 – 3.68 (m, 1H), 2.33 (s, 3H), 1.07 (s, 9H), 1.02 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 138.2, 137.3, 129.9, 129.6, 129.4, 127.5, 78.1, 75.5, 70.4, 67.4, 27.7, 27.3, 22.9, 21.3, 20.2; HRMS (ESI) m/z calcd for $C_{21}H_{32}O_3SiNa$ $[M + Na]^+$: 383.2013; found: 383.2015. The pure α-**3bi** was also obtained (51.9 mg, 72%) as a white solid for full characterization: $[\alpha]_D^{23}$ = -6.0 (*c* 0.85, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 7.8 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 6.07 (dt, *J* = 10.4, 1.8 Hz, 1H), 5.89 (dt, *J* = 10.5, 2.5 Hz, 1H), 5.18 (d, *J* = 2.6 Hz, 1H), 4.46 – 4.43 (m, 1H), 3.98 (dd, *J* = 9.9, 5.0 Hz, 1H), 3.81 (t, *J* = 10.1 Hz, 1H), 3.55 – 3.49 (m, 1H), 2.35 (s, 3H), 1.04 (s, 9H), 0.93 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 138.1, 136.5, 131.3, 129.3, 128.2, 127.4, 75.0, 70.6, 68.2, 67.5, 27.6, 27.2, 22.9, 21.3, 20.2; HRMS (ESI) m/z calcd for $C_{21}H_{32}O_3SiNa$ $[M + Na]^+$: 383.2013; found: 383.2014.

4-Fluorophenyl 4,6-O-(di-tert-butyl)silylene-2,3-dideoxy-α/β-D-C-erythro-hex-2-enopyranoside (3bj)

Following the general procedure for the synthesis of α-*C*-glycosides, the coupling between **1b** and **2j** under the effect of $CuBr{\bullet}SMe_2/ZnCl_2$ provided **3bj** (60.5 mg, 83%) as a white solid in a mixture of α/β isomers (α/β = 5.6 : 1, determined by ^1H NMR). The α/β isomers of **3bj** were inseparable by the silica gel column chromatography, thus were characterized as a mixture: $[\alpha]_D^{23}$ = +7.2 (*c* 1.93, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.28 (m, 2H), 7.09 – 7.00 (m, 2H), 6.12 (d, *J* = 10.4 Hz, 0.85H), 5.98 (d, *J* = 10.2 Hz, 0.15H), 5.91 (dt, *J* = 10.4, 2.5 Hz, 0.85H), 5.70 (dt, *J* = 10.3, 2.0 Hz, 0.15H), 5.21 (s, 1H), 4.56 (d, *J* = 8.7 Hz, 0.15H), 4.47 (d, *J* = 8.6 Hz, 0.85H), 4.22 (dd, *J* = 10.0, 5.1 Hz, 0.15H), 3.99 (dd, *J* = 9.9, 5.1 Hz, 0.85H), 3.93 (t, *J* = 10.3 Hz, 0.15H), 3.83 (t, *J* = 10.2 Hz, 0.85H), 3.75 – 3.69 (m, 0.15H), 3.50 – 3.44 (m, 0.85H), 1.08 (s, 1.35H), 1.06 (s, 7.65H), 1.02 (s, 1.35H), 0.95 (s, 7.65H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.7 (d, J_{C-F} = 247.8 Hz), 135.4 (d, J_{C-F} = 3.2 Hz), 131.8, 130.3, 130.0 (d, J_{C-F} = 8.2 Hz), 129.3, 129.2, 127.0, 115.5 (d, J_{C-F} = 21.5 Hz), 74.4, 70.5, 70.3, 68.2, 67.4, 27.6 (2C), 27.2 (2C), 22.9, 22.8, 20.2 (2C); HRMS (ESI) m/z calcd for $C_{20}H_{33}FNO_3Si$ $[M + NH_4]^+$: 382.2208; found: 382.2207.

Methyl 4,6-di-O-benzyl-2,3-dideoxy-α/β-D-C-erythro-hex-2-enopyranoside (3ca)

Following the general procedure for the synthesis of α-*C*-glycosides, the coupling between **1c** and **2a** under the effect of CuBr•SMe_2/$ZnCl_2$ provided **3ca** (44.1 mg, 68%) as a colorless oil in a mixture of α/β diastereomers (α/β = 1 : 1). An aliquot of pure α-**3ca** was obtained for detailed characterization: $[\alpha]_D^{23}$ = +19.5 (*c* 0.65, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.22 (m, 10H), 5.84 (dt, *J* = 10.4, 2.0 Hz, 1H), 5.76 (dt, *J* = 10.4, 2.0 Hz, 1H), 4.57 (dd, *J* = 11.9, 5.2 Hz, 2H), 4.50 (d, *J* = 12.3 Hz, 1H), 4.45 (d, *J* = 11.6 Hz, 1H), 4.38 – 4.33 (m, 1H), 3.94 (dd, *J* = 7.0, 2.2 Hz, 1H), 3.79 (dt, *J* = 7.4, 4.0 Hz, 1H), 3.67 – 3.60 (m, 2H), 1.26 (d, *J* = 6.8 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 138.4 (2C), 133.2, 128.5 (2C), 128.1, 128.0, 127.8, 127.7, 124.9, 73.5, 71.1, 71.0, 70.1, 69.4, 68.7, 19.2; HRMS (ESI) m/z calcd for $C_{21}H_{25}O_3$ $[M + H]^+$: 325.1798; found: 325.1800.

Ethyl 4,6-di-O-benzyl-2,3-dideoxy-α/β-D-C-erythro-hex-2-enopyranoside (3cb)

Following the general procedure for the synthesis of α-*C*-glycosides, the coupling between **1c** and **2b** under the effect of CuBr•SMe_2/$ZnCl_2$ provided **3cb** (47.3 mg, 70%) as a colorless syrup in a mixture of α/β diastereomers (α/β = 1.2 : 1). An aliquot of pure α-**3cb** was obtained for detailed characterization: $[\alpha]_D^{23}$ = +18.0 (*c* 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.23 (m, 10H), 5.88 (dt, *J* = 10.4, 2.0 Hz, 1H), 5.82 (dt, *J* = 10.4, 1.9 Hz, 1H), 4.62 – 4.44 (m, 4H), 4.09 – 4.04 (m, 1H), 3.99 – 3.96 (m, 1H), 3.77 (dt, *J* = 7.3, 4.0 Hz, 1H), 3.69 – 3.62 (m, 2H), 1.72 – 1.65 (m, 1H), 1.54 – 1.48 (m, 1H), 0.98 (t, *J* = 7.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 138.4 (2C), 132.0, 128.5 (2C), 128.1, 128.0, 127.8, 127.7, 125.2, 74.0, 73.5, 71.2, 71.1, 70.3, 69.5, 26.5, 10.7; HRMS (ESI) m/z calcd for $C_{22}H_{27}O_3$ $[M + H]^+$: 339.1955; found: 339.1958.

Phenyl 4,6-di-O-benzyl-2,3-dideoxy-α/β-D-C-erythro-hex-2-enopyranoside (3cd)

Following the general procedure for the preparation of α-*C*-glycosides, the coupling between **1c** and **2d** under the effect of CuBr•SMe_2/$ZnCl_2$ provided **3cd** (58.0 mg, 75%) as a colorless oil in a mixture of α/β isomers with the α-**3cd** as the predominant product (α/β = 4.8:1). An aliquot of pure α-**3cd** was obtained for detailed characterization: $[\alpha]_D^{23}$ = +25.0 (*c* 0.75, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.39 (m, 2H), 7.32 – 7.28 (m, 5H), 7.26 – 7.20 (m, 8H), 6.12 – 6.04 (m, 2H), 5.27 (t, *J* = 2.3 Hz, 1H), 4.56 (dd, *J* = 14.2, 11.8 Hz, 2H), 4.43 (dd, *J* = 14.6, 11.8 Hz, 2H), 4.15 (dq, *J* = 7.7, 1.8 Hz, 1H), 3.68 – 3.63 (m, 2H), 3.60 – 3.55 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 139.7, 138.4, 138.3, 129.7, 128.5 (2C), 128.4, 128.2, 128.1, 128.0, 127.9, 127.7, 127.3, 74.3, 73.4, 71.3, 70.8, 70.3, 69.3; HRMS (ESI) m/z calcd for $C_{26}H_{27}O_3$ $[M + H]^+$: 387.1955;

found: 387.1957.

2-Methylphenyl 4,6-di-O-benzyl-2,3-dideoxy-α/β-D-C-erythro-hex-2-enopyranoside (3ce)

Following the general procedure for the preparation of α-*C*-glycosides, the coupling between **1c** and **2e** under the effect of CuBr•SMe_2/$ZnCl_2$ provided **3ce** as a mixture of α/β diastereomers with the α-**3ce** as the predominant product. The α- and β-**3ce** were separated by silica gel column chromatography (petroleum ether/ethyl acetate = 15 : 1) for detailed characterization. The pure β-**3ce** was obtained as a colorless oil (6.4 mg, 8%): $[\alpha]_D^{23}$ = +2.3 (*c* 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 11H), 7.20 – 7.14 (m, 3H), 6.04 – 6.01 (m, 1H), 5.88 (dt, *J* = 10.2, 1.5 Hz, 1H), 5.39 (q, *J* = 2.2 Hz, 1H), 4.68 – 4.52 (m, 4H), 4.18 (d, *J* = 7.9 Hz, 1H), 3.88 – 3.81 (m, 2H), 3.74 (dd, *J* = 10.8, 5.4 Hz, 1H), 2.39 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 138.6, 138.3, 136.1, 131.1, 130.7, 128.6, 128.4, 128.1, 128.0, 127.9 (2C), 127.6, 127.5, 126.4, 126.3, 78.2, 75.1, 73.6, 71.4, 70.8, 70.2, 19.3; HRMS (ESI) m/z calcd for $C_{27}H_{28}O_3K$ $[M + K]^+$: 439.1670; found: 439.1677. The pure α-**3ce** was obtained as a colorless syrup for detailed characterization (53.6 mg, 67%): $[\alpha]_D^{23}$ = +3.2 (*c* 0.45, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.25 (m, 11H), 7.21 – 7.18 (m, 2H), 7.14 – 7.10 (m, 1H), 6.19 (dt, *J* = 10.4, 2.1 Hz, 1H), 6.02 (ddd, *J* = 10.4, 3.2, 1.7 Hz, 1H), 5.47 (q, *J* = 2.4 Hz, 1H), 4.64 (d, *J* = 11.5 Hz, 1H), 4.53 (q, *J* = 5.8 Hz, 2H), 4.43 (d, *J* = 12.2 Hz, 1H), 4.23 – 4.19 (m, 1H), 3.66 – 3.59 (m, 2H), 3.54 – 3.49 (m, 1H), 2.47 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 138.4 (2C), 136.9, 130.9, 130.0, 128.9, 128.5, 128.4, 128.1, 128.0, 127.9, 127.7, 125.4, 73.3, 71.8, 71.4, 70.6 (2C), 69.2, 19.4; HRMS (ESI) m/z calcd for $C_{27}H_{29}O_3$ $[M + H]^+$: 401.2111; found: 401.2107.

4-Fluorophenyl 4,6-di-O-benzyl-2,3-dideoxy-α/β-D-C-erythro-hex-2-enopyranoside (3cj)

Following the general procedure for the preparation of α-*C*-glycosides, the coupling between **1c** and **2j** under the effect of CuBr•SMe_2/$ZnCl_2$ provided **3cj** (61.5 mg, 76%) as a colorless oil in a mixture of α/β isomers with the α-**3cj** as the major product (α/β = 6 : 1, determined by ^{1}H NMR). The α and β isomers were inseparable by silica gel column chromatography, thus were characterized as a mixture: $[\alpha]_D^{23}$ = +37.0 (*c* 2.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.34 (m, 2H), 7.33 – 7.24 (m, 10H), 7.03 – 6.98 (m, 2H), 6.13 (dt, *J* = 10.4, 2.1 Hz, 0.86H), 6.04 (ddd, *J* = 10.4, 3.1, 1.6 Hz, 0.86H), 6.00 (dt, *J* = 10.5, 2.2 Hz, 0.14H), 5.81 (dt, *J* = 10.4, 1.8 Hz, 0.14H), 5.26 (q, *J* = 2.4 Hz, 0.86H), 5.15 (q, *J* = 2.5 Hz, 0.14H), 4.66 – 4.56 (m, 2H), 4.53 – 4.43 (m, 2H), 4.19 – 4.12 (m, 1H), 3.84 – 3.78 (m, 0.28H), 3.74 – 3.70 (m, 0.14H), 3.69 – 3.62 (m,

1.72H), 3.60 – 3.55 (m, 0.86H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 162.5 (d, J_{C-F} = 247.2 Hz), 138.4, 138.2 (2C), 138.1, 136.7 (d, J_{C-F} = 3.3 Hz), 135.4 (d, J_{C-F} = 3.3 Hz), 131.5, 129.9 (d, J_{C-F} = 8.1Hz), 129.4, 129.0 (d, J_{C-F} = 8.2 Hz), 128.5 (2C), 128.4, 128.0, 127.9 (2C), 127.8, 127.7, 127.6, 127.4, 126.4, 115.5 (d, J_{C-F} = 21.6 Hz), 115.3 (d, J_{C-F} = 21.4 Hz), 77.9, 73.5 (2C), 73.4, 71.4, 71.3, 70.7, 70.5, 70.2, 69.9, 69.2; HRMS (ESI) m/z calcd for $C_{26}H_{25}FO_3Na$ $[M + Na]^+$: 427.1680; found: 427.1677.

Phenyl 4,6-O-isopropylidene-2,3-dideoxy-α/β-D-C-erythro-hex-2-enopyranoside (3dd)

Following the general procedure for the preparation of α-*C*-glycosides, the coupling between **1d** and **2d** under the effect of CuBr•SMe_2/$ZnCl_2$ provided **3dd** (36.9 mg, 75%) as a white solid in a mixture of α/β diastereomers with the α-**3dd** as the predominating product (α/β = 3.3 : 1, determind by ^1H NMR). The α and β isomers were inseparable by the silica gel column chromatography (petroleum ether/ethyl acetate = 15 : 1), thus were characterized as a mixture: $[\alpha]_D^{23}$ = +0.4 (*c* 1.90, $CHCl_3$); ^1H NMR (400 MHz, DMSO-d_6) δ 7.42 – 7.36 (m, 3H), 7.35 – 7.28 (m, 2H), 6.08 (dt, *J* = 10.4, 2.6 Hz, 0.77H), 5.99 (dt, *J* = 10.4, 1.7 Hz, 0.77H), 5.87 (dd, *J* = 10.0, 2.2 Hz, 0.23H), 5.76 (dt, *J* = 10.6, 2.1Hz, 0.23H), 5.34 – 5.30 (m, 1H), 4.39 (dd, *J* = 12.0, 3.4 Hz, 0.23H), 4.29 (dd, *J* = 8.5, 1.9 Hz, 0.77H), 3.85 – 3.77 (m, 0.46H), 3.76 – 3.70 (m, 1.54H), 3.51 – 3.45 (m, 0.23H), 3.26 – 3.20 (m, 0.77H), 1.51 (s, 0.7H), 1.48 (s, 2.3H), 1.34 (s, 0.7H), 1.29 (s, 2.3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 140.3, 139.9, 130.8, 129.1, 128.4, 128.3, 127.9 (2C), 127.7, 127.2, 127.1, 126.6, 99.2, 77.5, 74.0, 72.2, 67.1, 67.0, 66.4, 62.3, 29.1 (2C), 19.2, 19.1; HRMS (ESI) m/z calcd for $C_{15}H_{19}O_3$ $[M + H]^+$: 247.1329; found: 247.1330.

2-Methylphenyl 4,6-O-isopropylidene-2,3-dideoxy-α/β-D-C-erythro-hex-2-enopyranoside (3de)

Following the general procedure for the preparation of α-*C*-glycosides, the coupling between **1d** and **2e** under the effect of CuBr•SMe_2/$ZnCl_2$ provided **3de** (36.4 mg, 70%) as a white solid in a mixture of α/β diastereomers with the α-**3de** as the predominant product (α/β = 4 : 1, determined by ^1H NMR); The α and β isomers of **3de** were inseparable by silica gel column chromatography, thus were characterized as a mixture: $[\alpha]_D^{23}$ = +7.8 (*c* 2.03, $CHCl_3$); ^1H NMR (400 MHz, DMSO-d_6) δ 7.31 – 7.14 (m, 4H), 6.08 (d, *J* = 10.6 Hz, 0.8H), 5.96 (dt, *J* = 10.4, 2.6 Hz, 0.8H), 5.88 (d, *J* = 9.8 Hz, 0.2H), 5.78 – 5.75 (m, 0.2H), 5.52 – 5.48 (m, 1H), 4.40 (d, *J* = 8.7 Hz, 0.2H), 4.29 (d, *J* = 6.8 Hz, 0.8H), 3.84 – 3.75 (m, 0.4H), 3.70 (t, *J* = 10.5 Hz, 0.8H), 3.55 (dd, *J* = 10.4, 5.0 Hz, 0.8H), 3.51 – 3.47 (m, 0.2H), 3.19 – 3.13 (m, 0.8H), 2.37 (s, 2.4H), 2.33 (s, 0.6H), 1.51 (s,

0.6H), 1.48 (s, 2.4H), 1.34 (s, 0.6H), 1.30 (s, 2.4H); $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6) δ 138.0, 137.3, 137.1, 135.7, 130.7, 130.4, 130.1, 129.0, 128.4, 128.2, 127.9, 127.8, 127.5, 126.7, 125.9, 125.3, 99.2 (2C), 75.1, 72.4, 71.5, 67.3, 67.0, 65.7, 62.3, 62.2, 29.1, 29.0, 19.2, 19.1, 18.7, 18.6; HRMS (ESI) m/z calcd for $C_{16}H_{21}O_3$ $[M + H]^+$: 261.1485; found: 261.1486.

2-Methoxyphenyl 4,6-O-isopropylidene-2,3-dideoxy-α/β-D-C-erythro-hex-2-enopyranoside (3df)

Following the general procedure for the preparation of α-*C*-glycosides, the coupling between **1d** and **2f** under the effect of CuBr•SMe_2/$ZnCl_2$ at 55 °C in an extended reaction time (10 h) provided **3df** as a mixture of α/β diastereomers. The α and β isomers of **3df** were separated by silica gel column chromatography (petroleum ether/ethyl acetate = 15 : 1), and the β-**3df** (10.1 mg, 18%) was obtained as a colorless syrup: $[\alpha]_D^{23}$ = +10.8 (*c* 1.13, $CHCl_3$); ^1H NMR (400 MHz, DMSO-d_6) δ 7.33 – 7.26 (m, 2H), 7.01 (dd, *J* = 8.3, 1.1 Hz, 1H), 6.93 (t, *J* = 8.6, 1H), 5.82 (dt, *J* = 10.3, 1.8 Hz, 1H), 5.72 (dt, *J* = 10.2, 2.1 Hz, 1H), 5.61 (q, *J* = 2.4 Hz, 1H), 4.33 – 4.35 (m, 1H), 3.85 – 3.82 (m, 1H), 3.80 (s, 3H), 3.78 – 3.75 (m, 1H), 3.51 – 3.45 (m, 1H), 1.51 (s, 3H), 1.33 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6) δ 155.9, 130.2, 129.0, 128.0, 127.3, 126.4, 120.4, 111.0, 99.2, 72.2, 71.6, 67.0, 62.3, 55.5, 29.1, 19.2; HRMS (ESI) m/z calcd for $C_{16}H_{21}O_4$ $[M + H]^+$: 277.1434; found: 277.1437. The pure α-**3df** (20.4 mg, 37%) was also obtained as a colorless syrup: $[\alpha]_D^{23}$ = +0.7 (*c* 1.85, $CHCl_3$); ^1H NMR (400 MHz, DMSO-d_6) δ 7.33 (t, *J* = 7.6 Hz, 1H), 7.26 (d, *J* = 7.5 Hz, 1H), 7.04 (dd, *J* = 8.3, 1.1 Hz, 1H), 6.97 (t, *J* = 8.0 Hz, 1H), 6.00 (dt, *J* = 10.4, 1.7 Hz, 1H), 5.92 (dt, *J* = 10.4, 2.5 Hz, 1H), 5.55 (q, *J* = 2.6 Hz, 1H), 4.28 – 4.24 (m, 1H), 3.80 (s, 3H), 3.74 – 3.69 (m, 2H), 3.30 – 3.25 (m, 1H), 1.48 (s, 3H), 1.30 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, DMSO-d_6) δ 156.6, 129.4, 128.8, 128.1, 127.5, 127.1, 120.0, 111.3, 99.1, 69.2, 67.1, 66.5, 62.3, 55.5, 29.1, 19.1; HRMS (ESI) m/z calcd for $C_{16}H_{21}O_4$ $[M + H]^+$: 277.1434; found: 277.1436.

4-Fluorophenyl 4,6-O-isopropylidene-2,3-dideoxy-α/β-D-C-erythro-hex-2-enopyranoside (3dj)

Following the general procedure for the preparation of α-*C*-glycosides, the coupling between **1d** and **2j** under the effect of CuBr•SMe_2/$ZnCl_2$ provided **3dj** (42.3 mg, 80%) as a white solid in a mixture of α/β diastereomers with the α-**3dj** as the major product (α/β = 5.6 : 1, determined by ^1H NMR). The α/β isomers of **3dj** were inseparable by the silica gel column chromatography, thus was characterized as a mixture: $[\alpha]_D^{23}$ = +1.4 (*c* 1.43, $CHCl_3$); ^1H NMR (400 MHz, DMSO-d_6) δ 7.44 – 7.37 (m, 2H), 7.24 – 7.15 (m, 2H), 6.06 (dt, *J* = 10.4, 2.5 Hz, 0.85H), 6.00 (d, *J* = 10.0 Hz, 0.85H), 5.85 (d, *J* = 10.2 Hz, 0.15H), 5.75 (dt, *J* = 10.6, 2.0 Hz, 0.15H), 5.33 (q, *J* = 2.5 Hz, 1H),

4.40 (d, J = 8.4 Hz, 0.15H), 4.29 (d, J = 8.7 Hz, 0.85H), 3.84 – 3.79 (m, 0.3H), 3.77 – 3.69 (m, 1.7H), 3.50 – 3.44 (m, 0.15H), 3.22 – 3.16 (m, 0.85H), 1.50 (s, 0.45H), 1.48 (s, 2.55H), 1.33 (s, 0.45H), 1.29 (s, 2.55H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 161.7 (d, J_{C-F} = 244.5 Hz), 161.6 (d, J_{C-F} = 244.7 Hz), 136.5 (d, J_{C-F} = 3.0 Hz), 136.1 (d, J_{C-F} = 3.0 Hz), 130.6, 129.3 (d, J_{C-F} = 8.4 Hz), 129.3 (d, J_{C-F} = 8.3 Hz), 128.9, 128.1, 126.8, 115.2 (d, J_{C-F} = 21.3 Hz), 115.1 (d, J_{C-F} = 21.5 Hz), 99.2, 76.6, 73.3, 72.2, 67.0, 66.8, 66.2, 62.2 (2C), 29.1, 29.0, 19.1 (2C); HRMS (ESI) m/z calcd for $C_{15}H_{18}FO_3$ $[M + H]^+$: 265.1234; found: 265.1235.

Methyl 4,6-O-4-methoxybenzylidene-2,3-dideoxy-α/β-D-C-threo-hex-2-enopyranoside (3ea)

Following the general procedure for the preparation of α-*C*-glycosides, the coupling between **1e** and **2a** under the effect of CuBr•SMe_2/$ZnCl_2$ provided **3ea** (34.1 mg, 65%) as a mixture of α/β diastereomers with the α-**3ea** as the major product (α/β = 1.5 : 1). The pure α-**3ea** was obtained as a colorless oil: $[\alpha]_D^{23}$ = -33.6 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, DMSO-d_6) δ 7.31 (d, J = 8.6 Hz, 2H), 6.90 (d, J = 8.7 Hz, 2H), 6.03 (dd, J = 10.1, 3.4 Hz, 1H), 5.88 – 5.83 (m, 1H), 5.54 (s, 1H), 4.45 – 4.42 (m, 1H), 4.19 – 4.15 (m, 2H), 4.03 (d, J = 12.6 Hz, 1H), 3.74 (s, 3H), 3.60 (s, 1H), 1.20 (d, J = 6.8 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 159.3, 136.3, 131.0, 127.5, 121.9, 113.2, 99.5, 69.7, 68.5, 67.4, 61.9, 55.1, 18.0; HRMS (ESI) m/z calcd for $C_{15}H_{19}O_4$ $[M + H]^+$: 263.1278; found: 263.1276.

Ethyl 4,6-O-4-methoxybenzylidene-2,3-dideoxy-α/β-D-C-threo-hex-2-enopyranoside (3eb)

Following the general procedure for the preparation of α-*C*-glycosides, the coupling between **1e** and **2b** under the effect of CuBr•SMe_2/$ZnCl_2$ provided **3eb** (33.1 mg, 60%) as a mixture of α/β diastereomers with the α-isomer as the predominant product (α/β = 3.3:1). The pure α-**3eb** was obtained after silica gel column chromatography (petroleum ether/ethyl acetate = 15 : 1) as a colorless oil: $[\alpha]_D^{23}$ = -11.7 (*c* 2.55, $CHCl_3$); ^1H NMR (400 MHz, DMSO-d_6) δ 7.32 (d, J = 8.7 Hz, 2H), 6.90 (d, J = 8.7 Hz, 2H), 6.07 (dd, J = 10.2, 3.4 Hz, 1H), 5.89 – 5.85 (m, 1H), 5.54 (s, 1H), 4.18 – 4.14 (m, 2H), 4.11 (q, J = 4.7 Hz, 1H), 4.05 (d, J = 12.5 Hz, 1H), 3.74 (s, 3H), 3.53 (d, J = 2.6 Hz, 1H), 1.63 – 1.45 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 159.3, 135.2, 131.0, 127.4, 122.2, 113.2, 99.5, 73.8, 69.7, 67.4, 62.0, 55.1, 24.6, 10.6; HRMS (ESI) m/z calcd for $C_{16}H_{21}O_4$ $[M + H]^+$: 277.1434; found: 277.1434.

Phenyl 4,6-O-4-methoxybenzylidene-2,3-dideoxy-α-D-C-threo-hex-2-enopyranoside (3ed)

Following the general procedure for the preparation of α-*C*-glycosides, the coupling between **1e**

and **2d** under the effect of CuBr•SMe_2/$ZnCl_2$ provided **3ed** (53.2 mg, 82%) exclusively as a white solid after silica gel column chromatography (petroleum ether/ethyl acetate = 12 : 1): $[\alpha]_D^{23}$ = -18.0 (*c* 2.13, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.41 – 7.38 (m, 4H), 7.36 – 7.30 (m, 3H), 6.92 (d, *J* = 8.7 Hz, 2H), 6.40 (dd, *J* = 10.2, 3.8 Hz, 1H), 6.15 – 6.10 (m, 1H), 5.56 (s, 1H), 5.43 (dd, *J* = 3.8, 2.1 Hz, 1H), 4.24 (dd, *J* = 5.5, 1.8 Hz, 1H), 4.11 (dd, *J* = 12.7, 2.5 Hz, 1H), 4.01 (d, *J* = 12.7 Hz, 1H), 3.75 (s, 3H), 3.36 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 159.4, 139.2, 132.7, 131.0, 128.4, 127.7, 127.5, 124.1, 113.3, 99.5, 73.3, 69.4, 67.2, 62.7, 55.1; HRMS (ESI) m/z calcd for $C_{20}H_{21}O_4$ $[M + H]^+$: 325.1434; found: 325.1434.

2-Methylphenyl 4,6-O-4-methoxybenzylidene-2,3-dideoxy-α-D-C-threo-hex-2-enopyranoside (3ee)

Following the general procedure for the preparation of α-*C*-glycosides, the coupling between **1e** and **2e** under the effect of CuBr•SMe_2/$ZnCl_2$ provided **3ee** (55.4 mg, 82%) exclusively as a white solid after silica gel column chromatography (petroleum ether/ethyl acetate = 12 : 1): $[\alpha]_D^{23}$ = -123.3 (*c* 0.65, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.35 (d, *J* = 8.7 Hz, 2H), 7.27 – 7.22 (m, 2H), 7.19 – 7.13 (m, 2H), 6.91 (d, *J* = 8.7 Hz, 2H), 6.25 (dd, *J* = 10.2, 3.4 Hz, 1H), 6.21 – 6.17 (m, 1H), 5.60 (dd, *J* = 3.5, 1.7 Hz, 1H), 5.54 (s, 1H), 4.28 (dd, *J* = 5.0, 1.8 Hz, 1H), 4.05 (dd, *J* = 12.7, 2.5 Hz, 1H), 3.87 (d, *J* = 12.7 Hz, 1H), 3.75 (s, 3H), 3.23 (s, 1H), 2.46 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 159.3, 138.0, 136.1, 132.9, 131.0, 130.8, 128.4, 128.2, 127.5, 125.0, 124.7, 113.2, 99.4, 71.2, 69.5, 67.6, 62.4, 55.1, 18.8; HRMS (ESI) m/z calcd for $C_{21}H_{22}O_4K$ $[M + K]^+$: 377.1150; found: 377.1149.

4-Fluorophenyl 4,6-O-4-methoxybenzylidene-2,3-dideoxy-α-D-C-threo-hex-2-enopyranoside (3ej)

Following the general procedure for the preparation of α-*C*-glycosides, the coupling between **1e** and **2j** under the effect of CuBr•SMe_2/$ZnCl_2$ provided **3ej** (54.7 mg, 80%) as a white solid after silica gel column chromatography (petroleum ether/ethyl acetate = 12 : 1): $[\alpha]_D^{23}$ = -26.0 (*c* 2.33, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.42 (dd, *J* = 8.5, 5.7 Hz, 2H), 7.34 (d, *J* = 8.8 Hz, 2H), 7.21 (t, *J* = 8.9 Hz, 2H), 6.91 (d, *J* = 8.7 Hz, 2H), 6.37 (dd, *J* = 10.2, 3.8 Hz, 1H), 6.15 − 6.11 (m, 1H), 5.55 (s, 1H), 5.43 (t, *J* = 2.9 Hz, 1H), 4.24 (dd, *J* = 5.5, 1.8 Hz, 1H), 4.10 (dd, *J* = 12.8, 2.5 Hz, 1H), 4.00 (d, *J* = 12.7 Hz, 1H), 3.75 (s, 3H), 3.32 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 161.7 (d, J_{C-F} = 244.9 Hz), 159.4, 135.5 (d, J_{C-F} = 3.0 Hz), 132.5, 131.0, 129.9 (d,

J_{C-F} = 8.3 Hz), 127.5, 124.2, 115.1 (d, J_{C-F} = 21.3 Hz), 113.2, 99.5, 72.6, 69.4, 67.1, 62.6, 55.1; HRMS (ESI) m/z calcd for $C_{20}H_{20}FO_4$ $[M + H]^+$: 343.1340; found: 343.1341.

Methyl 4,6-O-(di-tert-butyl)silylene-2,3-dideoxy-α-D-C-threo-hex-2-enopyranoside (3fa)

Following the general procedure for the preparation of α-*C*-glycosides, the coupling between **1f** and **2a** under the effect of CuBr•SMe_2/$ZnCl_2$ at 55 °C in an extended reaction time (24 h) provided **3fa** (43.8 mg, 77%) exclusively as a colorless syrup after silica gel column chromatography (petroleum ether/ethyl acetate = 100 : 1): $[\alpha]_D^{23}$ = -80.6 (*c* 0.80, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.93 – 5.88 (m, 1H), 5.80 – 5.77 (m, 1H), 4.45 (t, *J* = 4.0 Hz, 1H), 4.33 (dd, *J* = 9.1, 5.3 Hz, 1H), 4.23 – 4.15 (m, 2H), 3.84 (q, *J* = 3.7 Hz, 1H), 1.21 (d, *J* = 6.8 Hz, 3H), 1.03 (s, 9H), 1.00 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 132.4, 125.8, 68.5, 68.0, 66.1, 65.5, 27.5, 27.3, 22.5, 21.1, 19.4; HRMS (ESI) m/z calcd for $C_{15}H_{28}O_3SiNa$ $[M + Na]^+$: 307.1700; found: 307.1689.

Phenyl 4,6-O-(di-tert-butyl)silylene-2,3-dideoxy-α-D-C-threo-hex-2-enopyranoside (3fd)

Following the general procedure for the preparation of α-*C*-glycosides, the coupling between **1f** and **2d** under the effect of CuBr•SMe_2/$ZnCl_2$ at 55 °C in an extended reaction time (24 h) provided **3fd** (51.9 mg, 75%) exclusively as a white solid after silica gel column chromatography (petroleum ether/ethyl acetate = 100 : 1): $[\alpha]_D^{23}$ = -130.2 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.22 (m, 5H), 6.13 – 6.09 (m, 1H), 6.05 (dd, *J* = 10.3, 3.1 Hz, 1H), 5.22 (t, *J* = 2.3 Hz, 1H), 4.40 (t, *J* = 3.8 Hz, 1H), 4.14 (dd, *J* = 12.0, 2.5 Hz, 1H), 4.06 (dd, *J* = 12.0, 3.7 Hz, 1H), 3.60 (q, *J* = 3.2 Hz, 1H), 1.00 (s, 9H), 0.98 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 139.6, 129.5, 128.5, 128.1 (2C), 127.8, 73.7, 68.8, 66.0 (2C), 27.6, 27.4, 22.8, 21.0; HRMS (ESI) m/z calcd for $C_{20}H_{31}O_3Si$ $[M + H]^+$: 347.2037; found: 347.2038.

2-Methylphenyl 4,6-O-(di-tert-butyl)silylene-2,3-dideoxy-α-D-C-threo-hex-2-enopyranoside (3fe)

Following the general procedure for the preparation of α-*C*-glycosides, the coupling between **1f** and **2e** under the effect of CuBr•SMe_2/$ZnCl_2$ at 55 °C in an extended reaction time (24 h) provided **3fe** (50.4 mg, 70%) exclusively as a white solid after silica gel column chromatography (petroleum ether/ethyl acetate = 100 : 1): $[\alpha]_D^{23}$ = -77.0 (*c* 1.60, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.24 (m, 3H), 7.20 – 7.15 (m, 1H), 6.30 – 6.25 (m, 1H), 6.09 (dd, *J* = 10.3, 3.4 Hz, 1H), 5.49 (t, *J* = 2.7 Hz, 1H), 4.53 (t, *J* = 3.8 Hz, 1H), 4.20 (dd, *J* = 11.9, 2.5 Hz, 1H), 4.08 (dd, *J* = 11.9, 3.7 Hz, 1H), 3.63 (q, *J* = 3.1 Hz, 1H), 2.53 (s, 3H), 1.11 (s, 9H), 1.09 (s, 9H); ^{13}C{^{1}H}

NMR (100 MHz, $CDCl_3$) δ 138.4, 136.9, 131.1, 129.8, 128.4, 128.3 (2C), 125.3, 71.2, 68.6, 66.2, 66.1, 27.5, 27.4, 22.8, 21.1, 19.2; HRMS (ESI) m/z calcd for $C_{21}H_{33}O_3Si$ $[M + H]^+$: 361.2194; found: 361.2197.

4-Methoxyphenyl 4,6-O-(di-tert-butyl)silylene-2,3-dideoxy-α-D-C-threo-hex-2-enopyranoside (3fh)

Following the general procedure for the preparation of α-*C*-glycosides, the coupling between **1f** and **2h** under the effect of CuBr•SMe_2/$ZnCl_2$ at 55 °C in an extended reaction time (24 h) provided **3fh** (57.2 mg, 76%) exclusively as a white solid after silica gel column chromatography (petroleum ether/ethyl acetate = 100 : 1): $[\alpha]_D^{23}$ = -56.2 (*c* 0.55, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.23 (m, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 6.15 – 6.11 (m, 1H), 6.05 (dd, *J* = 10.3, 3.3 Hz, 1H), 5.20 (t, *J* = 2.4 Hz, 1H), 4.42 (t, *J* = 3.8 Hz, 1H), 4.17 (dd, *J* = 12.0, 2.5 Hz, 1H), 4.06 (dd, *J* = 12.0, 3.6 Hz, 1H), 3.77 (s, 3H), 3.60 (q, *J* = 3.2 Hz, 1H), 1.02 (s, 9H), 1.01 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 159.6, 131.6, 129.8, 129.6, 127.7, 113.8, 73.4, 68.6, 66.1, 66.0, 55.4, 27.6, 27.4, 22.8, 21.0; HRMS (ESI) m/z calcd for $C_{21}H_{32}O_4SiNa$ $[M + Na]^+$: 399.1962; found: 399.1960.

4-Methylphenyl 4,6-O-(di-tert-butyl)silylene-2,3-dideoxy-α-D-C-threo-hex-2-enopyranoside (3fi)

Following the general procedure for the preparation of α-*C*-glycosides, the coupling between **1f** and **2i** under the effect of CuBr•SMe_2/$ZnCl_2$ at 55 °C in an extended reaction time (24 h) provided **3fi** (50.4 mg, 70%) exclusively as a white solid after silica gel column chromatography (petroleum ether/ethyl acetate = 100 : 1): $[\alpha]_D^{23}$ = -89.5 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 7.9 Hz, 2H), 6.18 – 6.14 (m, 1H), 6.09 (dd, *J* = 10.4, 3.2 Hz, 1H), 5.24 (t, *J* = 2.4 Hz, 1H), 4.44 (t, *J* = 3.9 Hz, 1H), 4.20 (dd, *J* = 12.0, 2.5 Hz, 1H), 4.10 (dd, *J* = 12.0, 3.6 Hz, 1H), 3.64 (q, *J* = 3.1 Hz, 1H), 2.34 (s, 3H), 1.05 (s, 9H), 1.04 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 137.9, 136.5, 129.7, 129.2, 128.1, 127.6, 73.6, 68.7, 66.0 (2C), 27.5, 27.4, 22.8, 21.3, 21.0; HRMS (ESI) m/z calcd for $C_{21}H_{32}O_3SiNa$ $[M + Na]^+$: 383.2013; found: 383.2015.

4-Fluorophenyl 4,6-O-(di-tert-butyl)silylene-2,3-dideoxy-α-D-C-threo-hex-2-enopyranoside (3fj)

Following the general procedure for the preparation of α-*C*-glycosides, the coupling between **1f**

and **2j** under the effect of CuBr•SMe_2/$ZnCl_2$ at 55 °C in an extended reaction time (24 h) provided **3fj** (64.1 mg, 88%) as a white solid after silica gel column chromatography (petroleum ether/ethyl acetate = 100 : 1): $[\alpha]_D^{23}$ = -111.6 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 8.5, 5.6 Hz, 2H), 7.05 – 7.00 (m, 2H), 6.20 – 6.16 (m, 1H), 6.08 (dd, *J* = 10.3, 3.3 Hz, 1H), 5.25 (t, *J* = 2.5 Hz, 1H), 4.45 (t, *J* = 3.9 Hz, 1H), 4.21 (dd, *J* = 12.0, 2.4 Hz, 1H), 4.10 (dd, *J* = 12.0, 3.6 Hz, 1H), 3.61 (q, *J* = 3.2 Hz, 1H), 1.05 (s, 9H), 1.05 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.6 (d, J_{C-F} = 247.5 Hz), 135.4 (d, J_{C-F} = 3.3 Hz), 129.9 (d, J_{C-F} = 8.2 Hz), 129.3, 128.1, 115.4 (d, J_{C-F} = 21.5 Hz), 73.1, 68.8, 65.9, 27.5, 27.4, 22.8, 21.0; HRMS (ESI) m/z calcd for $C_{20}H_{29}FO_3SiNa$ $[M + Na]^+$: 387.1762; found: 387.1764.

Phenyl 4,6-O-para-methoxybenzylidene-α-D-C-mannopyranoside (5)

Potassium osmate(VI) dihydrate (10.3 mg, 0.028 mmol) and 4-methyl-morpholin-4-oxide (65.6 mg, 0.56 mmol) were added to a stirred solution of **3adα** (90.8 mg, 0.28 mmol) in a mixed solvent of THF (2.8 mL) and water (0.11 mL, 6.2 mmol). The resulting mixture was stirred at room temperature for 24 h before water (10 mL) was added to dilute the reaction mixture. The resulting mixture was extracted with ethyl acetate (3 × 10 mL), and the combined organic layer was washed with brine (2 × 10 mL) and dried over anhydrous sodium sulfate. Filtration was followed by concentration under vacuum afforded the crude product, which was purified by flash chromatography on silica gel (EtOAc/PE = 1 : 1) to give **5** (40 mg, 40%) as a colorless syrup: $[\alpha]_D^{23}$ = +12.0 (*c* 2.13, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.43 (d, *J* = 4.3 Hz, 4H), 7.34 – 7.30 (m, 3H), 6.88 – 6.86 (m, 2H), 5.54 (s, 1H), 5.15 (d, *J* = 3.9 Hz, 1H), 5.08 (d, *J* = 6.0 Hz, 1H), 4.99 (s, 1H), 4.54 – 4.52 (m, 1H), 4.16 (dd, *J* = 10.2, 4.8 Hz, 1H), 3.97 (t, *J* = 9.5 Hz, 1H), 3.76 (d, *J* = 10.2 Hz, 1H), 3.72 (s, 3H), 3.54 – 3.49 (m, 1H), 3.30 – 3.24 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 159.5, 137.7, 130.3, 128.7, 127.7, 127.3, 126.0, 113.2, 101.1, 79.2, 79.0, 70.6, 67.9 (2C), 66.3, 55.1; HRMS (ESI) m/z calcd for $C_{20}H_{22}O_6K$ $[M + K]^+$: 397.1048; found: 397.1051.

Phenyl 2,3-dideoxy-α-D-C-erythro-hex-2-enopyranoside (6)

To a solution of compound **3adα** (162.2 mg, 0.5 mmol) in DCM (5 mL) was slowly added CF_3COOH (90%, 0.35 mL) at -35 °C, the mixture was stirred at the same temperature for 3 h. Then the reaction mixture was poured into a solution of saturated aqueous $NaHCO_3$, and the resulting mixture was extracted with DCM (3 × 10 mL). The combined organic layer was washed

with brine (2 × 10 mL), and dried over anhydrous sodium sulfate. Filtration was followed by concentration under vacuum, and the obtained residue was purified by flash column chromatography on silica gel (PE/EtOAc = 1 : 1) to give product **6** (98 mg, 95%) as a colorless syrup: $[\alpha]_D^{23}$ = -4.9 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, DMSO-d_6) δ 7.44 (d, *J* = 7.1 Hz, 2H), 7.38 – 7.34 (m, 2H), 7.30 – 7.26 (m, 1H), 6.10 – 6.06 (m, 1H), 5.89 (dt, *J* = 10.3, 2.1 Hz, 1H), 5.22 (q, *J* = 2.5 Hz, 1H), 4.96 (s, 1H), 4.62 (s, 1H), 3.89 – 3.87 (m, 1H), 3.63 (dd, *J* = 11.7, 2.5 Hz, 1H), 3.48 (dd, *J* = 11.7, 6.2 Hz, 1H), 3.28 – 3.23 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 140.6, 130.7, 128.8, 128.6, 127.7 (2C), 74.7, 72.8, 62.4, 61.5; HRMS (ESI) m/z calcd for $C_{12}H_{15}O_3$ $[M + H]^+$: 207.1016; found: 207.1014.

Phenyl 2,3-dideoxy-α-D-C-glucopyranoside (7)

To a solution of compound **6** (74 mg, 0.36 mmol) in MeOH /EtOAc (1:1, 10 mL) was added 10% Pd/C (12.6 mg), the resultant suspension was stirred at room temperature under H_2 (1 atm) atmosphere for 11 h. Then the suspension was filtered through a pad of *Celite* (eluent MeOH), and the filtrate was concentrated *in vacuo*. The obtained residue was purified by flash chromatography on silica gel (EtOAc/PE = 1 : 1) to give product **7** (61.4 mg, 82%) as a colorless syrup: $[\alpha]_D^{23}$ = +13.8 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, DMSO-d_6) δ 7.42 (d, *J* = 7.7 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.24 (t, *J* = 7.2 Hz, 1H), 4.80 (t, *J* = 4.8 Hz, 1H), 4.60 (s, 2H), 3.65 (dd, *J* = 11.5, 4.0 Hz, 1H), 3.52 (dd, *J* = 11.4, 6.4 Hz, 1H), 3.45 – 3.41 (m, 1H), 3.36 – 3.32 (m, 1H), 2.22 – 2.14 (m, 1H), 1.86 – 1.74 (m, 2H), 1.45 – 1.36 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 141.7, 128.4, 126.8, 126.4, 77.6, 71.6, 64.7, 61.1, 27.7, 26.6; HRMS (ESI) m/z calcd for $C_{12}H_{17}O_3$ $[M + H]^+$: 209.1172; found: 209.1171.

Phenyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-C-erythro-hex-2-enopyranoside (8)

To a solution of compound **6** (88.4 mg, 0.43 mmol) in pyridine (1 mL) was added acetic anhydride (0.4 mL, 4.3 mmol), the mixture was stirred at room temperature for 3 h before ethyl acetate was added to dilute the reaction. The resulting mixture was washed successively with water, 1M HCl, saturated aqueous $NaHCO_3$, and brine, and was then dried over anhydrous Na_2SO_4. Filtration was followed by concentration *in vacuo* afforded a residue, which was further purified by flash chromatography on silica gel (PE/EtOAc = 10 : 1) to give product **8** (122.3 mg, 98%) as a colorless syrup: $[\alpha]_D^{23}$ = +33.5 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.30 (m, 5H), 6.20 – 6.17 (m, 1H), 6.01 – 5.97 (m, 1H), 5.34 – 5.29 (m, 2H), 4.27 (dd, *J* = 12.0, 5.9 Hz,

1H), 4.10 (dd, *J* = 12.0, 3.1 Hz, 1H), 3.86 – 3.82 (m, 1H), 2.08 (s, 3H), 2.07 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 170.9, 170.6, 138.9, 131.6, 128.6, 128.3, 128.0, 125.1, 73.8, 69.4, 65.1, 63.0, 21.2, 20.9; HRMS (ESI) m/z calcd for $C_{16}H_{19}O_5$ $[M + H]^+$: 291.1227; found: 291.1229.

Phenyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-C-glucopyranoside (9)

Similar procedure as that used for the synthesis of **7** was adopted to convert **8** (104.5 mg, 0.36 mmol) to **9** (102 mg, 97%) as a colorless syrup after silica gel column chromatography (petroleum ether/ethyl acetate = 10 : 1): $[\alpha]_D^{23}$ = +17.8 (*c* 0.65, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 4H), 7.23 – 7.19 (m, 1H), 4.86 (t, *J* = 5.1 Hz, 1H), 4.79 – 4.74 (m, 1H), 4.32 (dd, *J* = 11.8, 6.5 Hz, 1H), 4.09 (dd, *J* = 11.8, 3.9 Hz, 1H), 3.83 – 3.79 (m, 1H), 2.21 – 2.12 (m, 1H), 2.04 (s, 3H), 2.01 – 1.99 (m, 1H), 1.97 (s, 3H), 1.95 – 1.87 (m, 1H), 1.74 – 1.66 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 171.0, 170.4, 140.4, 128.7, 127.6, 126.6, 72.9, 72.2, 67.9, 62.7, 26.2, 25.0, 21.3, 21.0; HRMS (ESI) m/z calcd for $C_{16}H_{21}O_5$ $[M + H]^+$: 293.1384; found: 293.1385.

Phenyl 4,6-di-O-acetyl-α-D-C-mannopyranoside (10)

Similar procedure as that used for the synthesis of **5** was adopted to convert **8** (81.2 mg, 0.28 mmol) to **10** (69.4 mg, 76%) as a colorless syrup after silica gel column chromatography (petroleum ether/ethyl acetate = 1 : 1): $[\alpha]_D^{23}$ = +2.2 (*c* 1.93, $CHCl_3$); ^1H NMR (400 MHz, DMSO-d_6) δ 7.39 – 7.33 (m, 4H), 7.30 – 7.26 (m, 1H), 5.45 (d, *J* = 4.6 Hz, 1H), 4.91 (dd, *J* = 5.6, 4.0 Hz, 1H), 4.86 (d, *J* = 6.7 Hz, 1H), 4.73 (d, *J* = 7.2 Hz, 1H), 4.63 (dd, *J* = 12.0, 8.4 Hz, 1H), 4.03 (dd, *J* = 12.1, 3.3 Hz, 1H), 3.93 – 3.89 (m, 1H), 3.81 (dt, *J* = 7.9, 3.6 Hz, 1H), 3.73 – 3.70 (m, 1H), 2.05 (s, 3H), 1.99 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 170.4, 170.0, 139.3, 128.3, 127.6, 127.3, 73.7, 72.7, 71.2, 69.0, 68.1, 61.8, 21.0, 20.8; HRMS (ESI) m/z calcd for $C_{16}H_{21}O_7$ $[M + H]^+$: 325.1282; found: 325.1284.

(3-para-Ethoxybenzyl-4-chloro)phenyl

4,6-O-para-methoxybenzylidene-2,3-dideoxy-α-D-C-erythro-hex-2-enopyranosid (12)

Following the general procedure for the preparation of α-*C*-glycosides, the coupling between **1a** and freshly prepared **11**[20] under the effect of $CuBr{\bullet}SMe_2$/ $ZnCl_2$ provided **12** as a mixture of α/β diastereomers. The **12α** and **12β** were separated by silica gel column chromatography (petroleum ether/ethyl acetate = 15 : 1), and were characterized separately. The pure **12β** (8.8 mg, 9%) was obtained as a colorless syrup: $[\alpha]_D^{23}$ = +4.3 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, DMSO-d_6) δ 7.43 (d, *J* = 8.2 Hz, 1H), 7.36 (d, *J* = 8.7 Hz, 2H), 7.32 (d, *J* = 2.1 Hz, 1H), 7.23 (dd, *J* = 8.2, 2.1

Hz, 1H), 7.09 (d, *J* = 8.5 Hz, 2H), 6.92 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 6.00 (d, *J* = 10.3 Hz, 1H), 5.81 (dt, *J* = 10.3, 2.1 Hz, 1H), 5.67 (s, 1H), 5.35 (q, *J* = 2.2 Hz, 1H), 4.35 (dd, *J* = 7.7, 3.6 Hz, 1H), 4.19 (dd, *J* = 10.1, 4.6 Hz, 1H), 3.99 (d, *J* = 2.6 Hz, 2H), 3.96 (t, *J* = 7.0 Hz, 2H), 3.79 (d, *J* = 10.2 Hz, 1H), 3.75 (s, 3H), 3.67 – 3.61 (m, 1H), 1.29 (t, *J* = 7.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 159.5, 156.9, 139.4, 138.8, 132.5, 131.0, 130.8, 130.0, 129.5, 129.4, 127.6, 126.7, 126.3, 114.4, 113.4, 100.9, 76.7, 74.0, 71.1, 68.3, 62.9, 55.1, 37.5, 14.6; HRMS (ESI) m/z calcd for $C_{29}H_{30}ClO_5$ $[M + H]^+$: 493.1776; found: 493.1776. The pure **12α** (45.3 mg, 46%) was also obtained as a colorless syrup: $[\alpha]_D^{23}$ = +14.1 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, DMSO-d_6) δ 7.45 (d, *J* = 8.2 Hz, 1H), 7.34 – 7.32 (m, 3H), 7.27 (dd, *J* = 8.3, 2.2 Hz, 1H), 7.11 (d, *J* = 8.5 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 6.10 (t, *J* = 12.4 Hz, 2H), 5.64 (s, 1H), 5.35 (d, *J* = 2.6 Hz, 1H), 4.25 (dd, *J* = 8.5, 2.6 Hz, 1H), 4.06 (dd, *J* = 10.1, 4.7 Hz, 1H), 4.02 (s, 2H), 3.95 (q, *J* = 7.0 Hz, 2H), 3.76 – 3.71 (m, 4H), 3.32 – 3.28 (m, 1H), 1.28 (t, *J* = 7.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 159.5, 157.0, 139.0 (2C), 132.3, 131.0, 130.0, 129.7, 129.6, 129.4, 129.2, 127.6, 127.4, 126.6, 114.4, 113.3, 100.9, 74.1, 73.4, 68.3, 65.5, 62.9, 55.1, 37.5, 14.6; HRMS (ESI) m/z calcd for $C_{29}H_{30}ClO_5$ $[M + H]^+$: 493.1776; found: 493.1780.

Ethyl 4,6-di-O-acetyl-2,3-dideoxy-β-D-C-erythro-hex-2-enopyranoside (13)

Following the general procedure for the synthesis of β-*C*-glycosides, the coupling between **1d** and **2b** proceeded smoothly to provide the corresponding ethyl *C*-glycoside, which was then subjected to deisopropylidenation and acetylation under the identical conditions as those applied for the synthesis of **8** from **3ad** via intermediate **6**. Compound **13** was obtained with a 51% overall yield as a colorless syrup after silica gel column chromatography (petroleum ether/ethyl acetate = 10 : 1): $[\alpha]_D^{23}$ = +44.0 (*c* 0.15, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 5.82 (dt, *J* = 10.3, 1.6 Hz, 1H), 5.73 (dt, *J* = 10.4, 2.1 Hz, 1H), 5.27 – 5.23 (m, 1H), 4.23 (dd, *J* = 12.0, 2.6 Hz, 1H), 4.16 (t, *J* = 5.9 Hz, 1H), 4.13 – 4.11 (m, 1H), 3.73 – 3.69 (m, 1H), 2.09 (s, 3H), 2.08 (s, 3H), 1.63 – 1.58 (m, 2H), 0.93 (t, *J* = 7.5 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 171.2, 170.6, 132.9, 125.2, 76.0, 74.4, 66.0, 64.0, 28.1, 21.2, 21.0, 9.0; HRMS (ESI) m/z calcd for $C_{12}H_{19}O_5$ $[M + H]^+$: 243.1227; found: 243.1228.

Associated content

The Supporting Information is available free of charge

Copies of 1D and 2D NMR spectra for all new compounds

Notes

The authors declare no competing financial interest.

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