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Palladium(II)-catalyzed stereoselective synthesis of *C*-glycosides from glycals with diaryliodonium salts†

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An efficient palladium(II) mediated *C*-glycosylation of glycals with diaryliodonium salts is described, providing a new strategy for the synthesis of 2,3-dideoxy *C*-aryl glycosides with excellent stereoselectivity. The *C*-glycosylation of a diverse range of glycals, including D-glucal, D-galactal, D-allal, L-rhamnal, L-fucal, L-arabinal, D-maltal, and D-lactal, occurred effectively and the corresponding *C*-glycosides were obtained in moderate to good yields. This protocol is commended as a significant addition to the field of carbohydrate chemistry due to the rich functional group compatibility, broad range of substrate scope and exceptional α-stereoselectivity.

1. Introduction

C-Glycosides are an important part of carbohydrate chemistry since a variety of natural products with significant biological importance can be found in which *C*-glycosides are embedded.[1] Besides their potential bioactivity, *C*-glycosides are more stable than native *N*- or *O*-glycosylated residues, as *N*- or *O*-glycosidic bonds can be cleaved enzymatically under physiological conditions.[2–4] *C*-Glycosides can have comparable conformations to those of *O*-glycosides and, as a consequence, they can be beneficial as substantial mimics of biologically active natural *O*-glycosides and thus can be employed as potential therapeutic agents.[5–8] Chemical *C*-glycosylation has been well developed in recent years due to the extremely diverse structures of naturally existing *C*-glycosides. By activating the anomeric center with the exploitation of Lewis acid catalysts, *C*-nucleophiles have been utilized predominantly for the formulation of *C*-glycosidic linkages.[9–11] Often, this type of *C*-glycosylation involves nucleophilic reactions of organometallic reagents with glycosyl donors, which can be challenging due to the moisture and air sensitivity of the reagents. Therefore, much effort has been focused on developing milder, more efficient and highly stereoselective alternatives such as transition metal-catalyzed *C*-glycosylation.[10,12] Transition metal-catalyzed cross-coupling reactions are being developed as a diverse approach for the synthesis of naturally abundant *C*-glycosides and have emerged as a powerful method for the construction of *C*-glycosides.[9,13–17]

Diaryl-λ^3-iodanes, known as diaryliodonium salts, have been extensively utilized for the installation of functional groups as versatile aryl-transfer reagents that allow the arylation of a variety of arenes and heteroatom nucleophiles.[18–34] The loosely bound functional groups attached to the iodine centers give iodanes their metal-like properties, offering mild catalytic conditions for the enantioselective functionalization of natural products. So far, palladium mediated glycosylation strategies have been employed for the Heck-type cross-coupling between glycals and common aryl sources, *e.g.* arylboronic acids,[35–37] aromatic carboxylic acids,[38] phenyl hydrazines,[39] aryl sulfonyl chlorides,[40] sodium arylsulfinates,[41] aryl halides,[42] aryl diazonium salts,[43] arylzinc reagents,[44] *etc.* From this standpoint, we proposed that hypervalent iodinanes could be efficiently utilized as an alternative aryl source for the formation of aryl-*C*-glycosides, especially taking into account that these iodanes are typically bench-stable solids and can easily be obtained by the oxidation of aryl iodides or arenes. Even though the use of iodonium salts in carbohydrate chemistry is not new, the majority of the existing synthetic methodologies are centered upon *O*-arylation of carbohydrate derivatives.[45–47] So far, only Walczak and co-workers have applied diaryliodonium salts for the synthesis of *C*-glycosides by palladium mediated cross-coupling reactions with anomeric stannanes, in which they successfully achieved β-stereospecificity.[48] However, carbohydrate stannanes are toxic, potentially leading to environmental issues, and we envisioned that the use of

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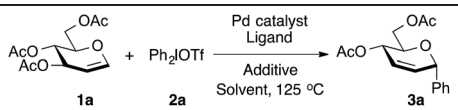
glycals would solve this problem if we were able to stereoselectively glycosylate them with diaryliodonium salts.

2. Results & discussion

Herein, we report the *C*-glycosylation of glycal derivatives with iodonium salts under palladium catalysis, leading to the highly α-stereoselective synthesis of aryl glycosides advancing in a Ferrier sequence. The present studies commenced by treating diphenyliodonium triflate (**2a**) and peracetyl glucal **1a** with a catalytic amount of palladium catalyst, which resulted in the stereoselective formation of **3a**. Earlier, we screened the efficacy of different types of palladium catalysts for their capacity to facilitate the stereoselective cross-coupling reaction of peracetylated D-glucal (**1a**). As summarized in Table 1, Pd$(PPh_3)_2Cl_2$ proved to be the best choice of catalyst under the present reaction conditions, even though $Pd(OAc)_2$, $Pd(TFA)_2$ and $Pd(MeCN)_2Cl_2$ were able to generate the desired product, but in all instances achieved lower yield. It is noteworthy that when we used Pd(0) (Table 1, entries 4 and 5) under the same reaction conditions no trace of the desired product was observed. Next, we assessed the solvent effects, and we found that the reaction didn't proceed in CH_2Cl_2, THF or toluene. However, the use of MeCN, CH_3NO_2 and 1,4-dioxane as the solvent provided 39%, 27% and 35% yield of the desired Ferrier product, respectively. Gratifyingly, choosing DMF gave the desired Ferrier product in 45% yield with complete α-selectivity after 48 h (Table 1, entry 7). It was noted that catalyst loading is also important under the present reaction conditions, since the yield dropped to 29% when we conducted the reaction with 5 mol% Pd$(PPh_3)_2Cl_2$.

Subsequently, we explored a range of different tetrabutylammonium salts that could substantially improve the yield. Screening of the tetrabutylammonium salts with different anions suggested that the *C*-glycosylation proceeded most efficiently in the presence of tetrabutylammonium chloride (1.5 equiv.) as the additive (Table 1, entry 16). The tertiary amine played a critical role as a ligand to achieve a high yield (Table 1, entry 16) under the present reaction conditions. Bulkier phosphine ligands, *e.g.* DPPP and DPPE, were inefficient. Among all the tertiary amines mentioned in Table 1, TEA proved to be highly effective in promoting the palladium-catalyzed glycosylation. After exploring the optimized reaction conditions, we then turned our attention to investigate the reactivities of a variety of leaving groups under the present reaction conditions (Table 2). We were taken by surprise after observing that the *tert*-butyloxycarbonyloxy group is not a wise choice as a leaving group since the yield went down to 23%. We observed a similar consequence with the ethoxy carbonyloxy group; although we got the desired product (16%), the ethoxy carbonyloxy group proved to be less efficient compared to the acetyl group. On both occasions, we ended up with an inseparable complex mixture, perhaps due to the poor stability of the compound at high temperatures. Other leaving groups such as benzoyl and pivaloyl turned out to be inactive under the standard conditions. These results suggest that the acetyl

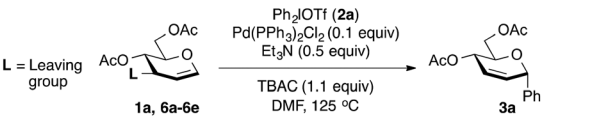
Table 1 Optimization of palladium-catalyzed Ferrier-type *C*-glycosylation with glycal **1a** and diphenyliodonium triflate (**2a**)[a]



Entry	Catalyst (%)	Solvent	Additive[b]	Ligand[c]	Yield[d] (%)
1	$Pd(OAc)_2$ (10)	DMF	None	TEA	19
2	$PdCl_2$ (10)	DMF	None	TEA	—
3	$Pd(TFA)_2$ (10)	DMF	None	TEA	23
4	$Pd(PPh_3)_4$ (10)	DMF	None	TEA	—
5	$Pd_2(dba)_3$ (10)	DMF	None	TEA	—
6	$Pd(MeCN)_2Cl_2$ (10)	DMF	None	TEA	36
7	$Pd(PPh_3)_2Cl_2$ (10)	DMF	None	TEA	45
8	$Pd(PPh_3)_2Cl_2$ (10)	DMF	None	None	12
9	$Pd(PPh_3)_2Cl_2$ (10)	THF	None	TEA	—
10	$Pd(PPh_3)_2Cl_2$ (10)	MeCN	None	TEA	39
11	$Pd(PPh_3)_2Cl_2$ (10)	CH_2Cl_2	None	TEA	—
12	$Pd(PPh_3)_2Cl_2$ (10)	Toluene	None	TEA	—
13	$Pd(PPh_3)_2Cl_2$ (10)	CH_3NO_2	None	TEA	27
14	$Pd(PPh_3)_2Cl_2$ (10)	1,4-Dioxane	None	TEA	35
15	$Pd(PPh_3)_2Cl_2$ (10)	DMF	TBAC	None	20
16	$Pd(PPh_3)_2Cl_2$ (10)	DMF	TBAC	TEA	76
17	$Pd(PPh_3)_2Cl_2$ (10)	DMF	TBAB	TEA	69
18	$Pd(PPh_3)_2Cl_2$ (10)	DMF	TBAI	TEA	52
19	$Pd(PPh_3)_2Cl_2$ (10)	DMF	TBAC	DIPEA	61
20	$Pd(PPh_3)_2Cl_2$ (10)	DMF	TBAC	TMEDA	45
21	$Pd(PPh_3)_2Cl_2$ (10)	DMF	TBAC	DPPE	—
22	$Pd(PPh_3)_2Cl_2$ (10)	DMF	TBAC	DPPP	—

[a] Reaction conditions: Unless otherwise noted, the reactions were carried out with **1a** (0.2 mmol), **2a** (0.4 mmol), cat. (10 mol%) in 2.0 mL of solvent for 48 h at 125 °C in a sealed tube. [b] 1.5 equiv. of additive were added. [c] Ligand added in 50 mol%. [d] Isolated yield based on **1a**. TEA: triethylamine; DIPEA: diisopropylethylamine; TBAC: tetrabutylammonium chloride; TBAB: tetrabutylammonium bromide; TBAI: tetrabutylammonium iodide; TMEDA: tetramethylethylenediamine; DPPE: 1,2-diphenylphosphinoethane; DPPP: 1,3-diphenylphosphinopropane.

Table 2 Screening of leaving groups under the optimized reaction conditions[a]

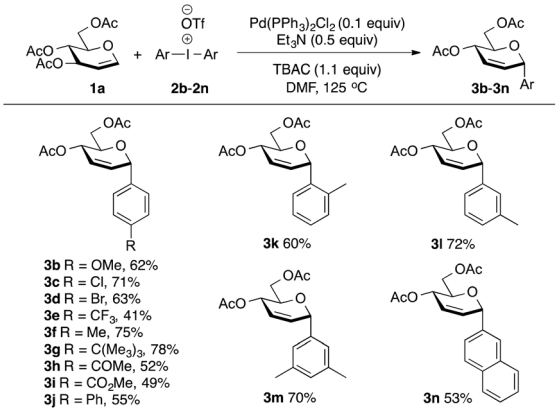


Entry	Leaving group	Time (h)	Temp (°C)	Yield of **4a**[b] (%)
1	*tert*-Butyloxycarbonyloxy (**6a**)	48	125	23
2	Carboxybenzyl (**6b**)	48	125	—
3	Benzoyl (**6c**)	48	125	—
4	Pivaloyl (**6d**)	48	125	—
5	Ethoxy carbonyloxy (**6e**)	48	125	16
6	Acetyl (**1a**)	48	125	76

[a] Reaction conditions: **1a**, **6a–6e** (0.2 mmol), **2a** (0.4 mmol), Pd$(PPh_3)_2Cl_2$ (10 mol%), TBAC (0.3 mmol), TEA (0.1 mmol) in a sealed tube. [b] Isolated yield based on **1a**.

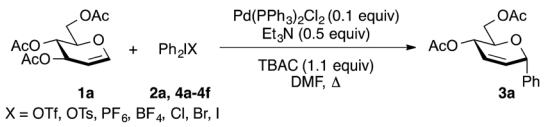
group at the C3 position is the ideal choice of leaving group under the optimized reaction conditions.

Next, 3,4,6-tri-*O*-acetyl-D-glucal was treated with various substituted symmetrical diaryliodonium triflates (Scheme 1). Notably, if the anionic counterion part of diphenyliodonium triflate was replaced with the corresponding chloride, bromide, *p*-toluenesulfonate, or hexafluorophosphate, no desired product was detected after 48 h (Table 3). Even though diphenyliodonium tetrafluoroborate and iodide provided the desired product, we obtained relatively low yields (37% and 29%, respectively). Among all the diaryliodonium salts assayed (Scheme 1), *meta*- and *para*-substituted diaryliodonium salts turned out to have better reactivities than *ortho*-diaryliodonium salts. Glycosylations of variable methyl-substituted diphenyliodonium triflates with peracetyl-D-glucal (**1a**) proceeded smoothly and provided the desired products (**3f**, **3k**, **3l**, and **3m**) in good to excellent yields (Scheme 1). The reaction of *tert*-butyl-, phenyl- and naphthyl-substituted diaryliodonium triflates with **1a** afforded the corresponding *C*-glycosides (**3g**, **3j** and **3n**, respectively) in moderate to good yields (Scheme 1). No trace of glycosylated product was detected with the substrate bearing a strongly electron-withdrawing NO_2 group (**2p**, see ESI†), possibly due to the decomposition of the iodonium salt at high temperature. However, the other electron-withdrawing groups, methoxy, chloro, bromo, CF_3, COMe, and CO_2Me were well tolerated and furnished the corresponding glycosylated products (**3b**, **3c**, **3d**, **3e**, **3h**, and **3i**, respectively) in moderate to excellent yields (Scheme 1). Attempts to selectively glycosylate 3,4,6-tri-*O*-acetyl-D-glucal with bis(2,4,6-trimethylphenyl)iodonium triflate (**2o**, see ESI†) failed. This is presumably due to the sterically congested mesityl group obstructing the approach of the aryl-palladium complex to the glycal, and thus the migratory insertion is restrained. All the aryl-*C*-glycosides were obtained with pure α-selectivity.



Scheme 1 Stereoselective *C*-glycosylation of glucal **1a** with symmetrical diaryliodonium triflates (**2b–2n**). Reaction conditions: All the reactions were carried out with 1 equiv. **1a**, 2 equiv. **2b–2n**, 10 mol% Pd $(PPh_3)_2Cl_2$, 50 mol% Et_3N and 1.5 equiv. TBAC for 48 h at 125 °C in a sealed tube. Yields of isolated products are given.

Table 3 Screening of a variety of iodanes under the optimized reaction conditions[a]



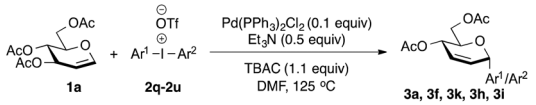
Entry	Iodanes	Temp (°C)	Time (h)	Yield[b] (%)
1	$Ph_2I^+OTs^-$ (**4a**)	125	48	—
2	$Ph_2I^+(BF_4)^-$ (**4b**)	125	48	37
3	$Ph_2I^+(PF_6)^-$ (**4c**)	125	48	—
4	$Ph_2I^+Cl^-$ (**4d**)	125	48	—
5	$Ph_2I^+Br^-$ (**4e**)	125	48	—
6	$Ph_2I^+I^-$ (**4f**)	125	48	29
7	$Ph_2I^+OTf^-$ (**2a**)	75	48	36
8	$Ph_2I^+OTf^-$ (**2a**)	100	48	49
9	$Ph_2I^+OTf^-$ (**2a**)	125	24	45
10	$Ph_2I^+OTf^-$ (**2a**)	125	48	76

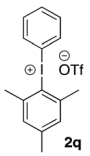
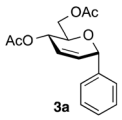
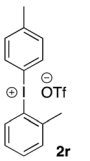
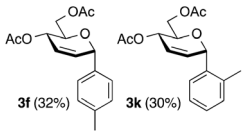
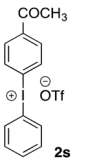
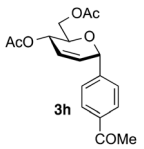
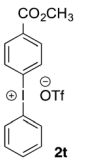
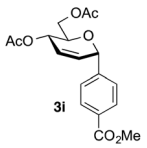
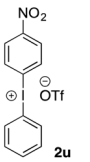
[a] Unless otherwise specified, the reactions were carried out with 0.2 mmol of **1a**, 0.4 mmol of iodonium salts, 0.02 mmol $Pd(PPh_3)_2Cl_2$, 0.1 mmol Et_3N in a sealed tube. [b] Isolated yield based on **1a**.

We next focused our attention on the scope of this methodology with unsymmetrical diaryliodonium triflates (Table 4). First, the reaction of (phenyl)(2,4,6-trimethylphenyl)iodonium triflate (**2q**) with peracetyl glucal (**1a**) was examined. The treatment of **2q** with **1a** gave the desired glycosylated product **3a** in 41% yield (Table 4, entry 1). Although the treatment of (2-tolyl)(4-tolyl)iodonium triflate (**2r**) provided both *para*- and *ortho*-methylphenyl glycoside (**3f** and **3k**) in a 1 : 1 ratio with α-stereoselectivity in 62% yield, other unsymmetrical diaryliodonium triflates with variable electron-withdrawing substituents like $COCH_3$, CO_2CH_3 and NO_2 proved to be less effective or unproductive under the present reaction conditions (Table 4, entries 3, 4 and 5).

Next, we investigated the glycal scope with various types of sugars like peracetylated D-galactal (**12a**), L-rhamnal (**13a**), L-fucal (**14**), L-arabinal (**15**), and D-allal (**16**). Gratifyingly, the glycosylation proceeded smoothly to give the anticipated Ferrier products (**19a**, **20a**, **21**, **22**, and **3a**/**3aβ**, respectively) in 51–79% yield with absolute α-selectivity, except for 3,4,6-tri-*O*-acetyl-D-allal, where we acquired both α- and β-glycosides in a 1 : 1 ratio. This was possibly attributed to the steric hindrance induced by the axial C3 acetate of D-allal, resulting in distortion of the π-Pd(IV) species to yield poor α-selectivity.[38,41,49,50] Beyond that, the applicability of the reported method to more complex structures, *i.e.* disaccharide glycals like peracetylated D-lactal (**17**) and peracetylated D-maltal (**18**), was subsequently investigated (Table 5). To our delight, in both instances, the reaction gave the desired phenyl glycoside in 61% and 55% yield, respectively, with the expected α-selectivity, which demonstrated that the method worked equally well for these higher analog glycals. Then, we subsequently assessed the reaction conditions with glycals equipped with various types of protecting groups (Table 6). The reaction conditions tolerated many widely used carbohydrate protecting groups, *e.g.* benzyl (**1b**, **12b**), *p*-methoxybenzyl (**1g**), diphenyl-*tert*-butylsilyl (**1d**, **12c**), pivalate (**1e**), benzoate (**1c**), and *p*-methoxybenzoate (**1f**), demonstrating the effectiveness of the reported method.

Table 4 Screening of different unsymmetrical iodanes under the optimized reaction conditions[a]

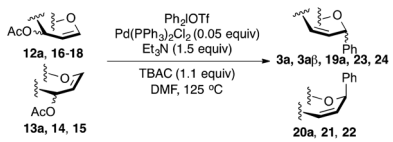


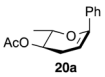
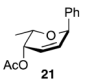
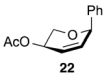
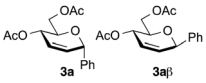
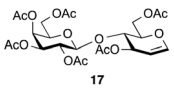
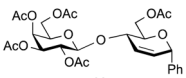
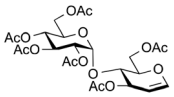
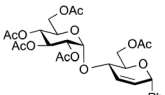
Entry	Unsymmetrical iodanes	Product	Yield[b] (%)
1	 **2q**	 **3a**	41%
2	 **2r**	 **3f** (32%) **3k** (30%)	62%
3	 **2s**	 **3h** COMe	21%
4	 **2t**	 **3i** CO_2Me	15%
5	 **2u**	N.R.	—

[a] Reaction conditions: Same as mentioned in Scheme 1. All the reactions were carried out with 1 mmol of **1a**, purified *via* plate TLC. [b] Isolated yield based on **1a**. N.R.: no reaction.

Based on the above experiments, a tentative mechanism for this transformation is proposed in Scheme 2. Considering that the reaction didn't occur in the presence of Pd(0), we ruled out the possibility of a Pd(II)/Pd(0) palladacycle. The reaction likely began by ligand exchange with $Pd(PPh_3)_2Cl_2$, followed by oxidative addition of the aryl triflate to form the Ar–Pd(IV)-OTf complex (**A**). It can be reasonably assumed that complex **A**, generated from diaryliodonium triflate, coordinates to the double bond on glycal, which gives rise to a Pd(IV)-glycal π-complex (**B**). Next, the insertion of glycal with Pd and formation of the aryl-*C*-glycosidic bond occur simultaneously from the α-face by *syn*-addition, leading to the generation of the Pd(IV)-glycal intermediate (**C**). This intermediate then undergoes anti-β-elimination of the acetyl group along with

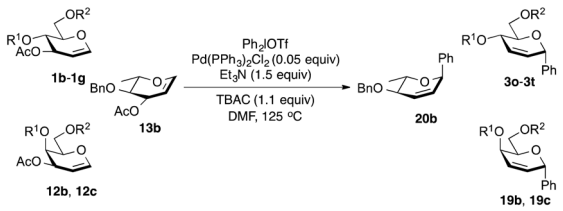
Table 5 Stereoselective *C*-glycosylation of variable glycals with diphenyliodonium triflate (**2a**)[a]



Entry	Glycal	Product	Yield (%)	α : β
1	 **12a**	 **19a**	79	1 : 0
2	 **13a**	 **20a**	65	1 : 0
3	 **14**	 **21**	51	1 : 0
4	 **15**	 **22**	69	1 : 0
5	 **16**	 **3a** **3aβ**	72	1 : 1
6	 **17**	 **23**	61	1 : 0
7	 **18**	 **24**	55	1 : 0

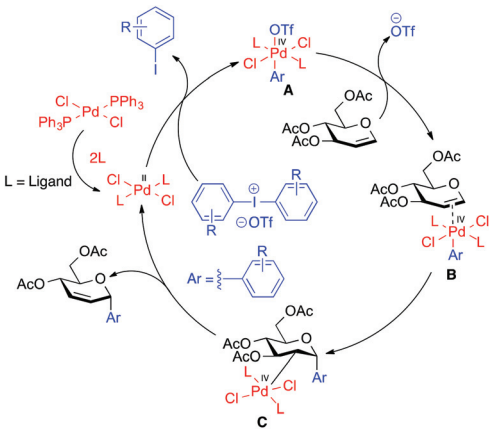
[a] Reaction conditions: Same as mentioned in Scheme 1. Isolated yield based on **1a**.

Table 6 Stereoselective *C*-glycosylation of different substituted glycals with diphenyliodonium triflate (**2a**)[a]



Entry	Glycal	R^1	R^2	Product	Yield[b] (%)
1	**1b**	Bn	Bn	**3o**	69%
2	**1c**	Bz	Ac	**3p**	70%
3	**1d**	TBDPS	Ac	**3q**	66%
4	**1e**	Piv	Ac	**3r**	73%
5	**1f**	PMBz	Ac	**3s**	72%
5	**1g**	PMB	PMB	**3t**	52%
6	**12b**	Bn	Bn	**19b**	78%
7	**12c**	TBDPS	Ac	**19c**	53%

[a] Reaction conditions: Same as mentioned in Scheme 1. [b] Isolated yield based on **1a**. PMBz: *p*-methoxybenzoyl.



Scheme 2 A proposed mechanism for the Pd-catalyzed *C*-glycosylation reaction.

reductive elimination of Pd(IV) to form the final α-*C*-aryl glycosides.

3. Conclusion

In summary, we have showcased the efficient palladium mediated *C*-glycosylation of iodonium salts with glycals. A broad variety of glycals, including protected D-glucal, D-galactal, D-allal, L-rhamnal, L-fucal, and L-arabinal, underwent stereoselective *C*-glycosylation with different diaryliodonium triflates in the presence of 10 mol% bis(triphenylphosphine)palladium(II) dichloride. All the reactions furnished α-aryl-*C*-glycosides in moderate to excellent yields under optimized conditions and the methodology could be expanded to the α-selective *C*-arylation of disaccharide-based glycal derivatives. Since a wide range of diaryliodonium salts are commercially available and could also be obtained in few steps from their corresponding aryl iodides, the protocol reported here opens up efficient access for broad implementation in aryl-*C*-glycoside-containing natural products.

4. Experimental section

4.1. General procedure for *C*-glycosylation of glycals

Glycal (1 equiv., 0.1–0.2 mmol), diaryliodonium salt (2 equiv., 0.2–0.4 mmol), $Pd(PPh_3)_2Cl_2$ (10 mol%, 0.1 equiv., 0.01–0.02 mmol) and tetrabutylammonium chloride (1.5 equiv., 0.15–0.3 mmol) were added to a dry 10 mL sealed tube. The tube was then placed under vacuum for 30 minutes. Et_3N (50 mol%, 0.5 equiv., 0.05–0.1 mmol) and dry DMF (2 mL per 0.1 mmol of glycal) were added to the reaction tube. The tube was tightly sealed and put in an oil bath at 125 °C. After 48 hours, the reaction mixture was concentrated under vacuum. The crude material was dissolved in EtOAc (7.5 mL per 0.1 mmol glycal) and washed twice with brine solution (10 mL per 0.1 mmol glycal). The organic layer was collected and dried over anhydrous Na_2SO_4. After this, the solvent was removed under vacuum and the crude material was purified by flash column chromatography to obtain the product of interest. Details of the experimental procedure and product characterization for each example can be found in the ESI.† The spectroscopic data for **3a–3i**, **3k–3o**, **19a**, **19b**, **20a**, **20b**, **21** and **3aβ** are consistent with the literature.[35,39–41,51]

4.1.1. Phenyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (3a).[39] Compound **3f** was prepared according to the general procedure in **4.1** from 3,4,6-tri-*O*-acetyl-D-glucal, **1a** (54 mg, 0.2 mmol), and biphenyliodonium triflate, **2a** (172 mg, 0.4 mmol), and obtained as a light-yellow oil in 76% yield (44.1 mg, 0.152 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.47–7.34 (m, 4H), 6.23 (dq, *J* 1.2 Hz, 10.4 Hz, 1H), 6.03 (dt, *J* 2.0 Hz, 10.4 Hz, 1H), 5.49 (q, *J* 2.4 Hz, 1H), 5.38–5.34 (m, 2H), 4.31 (dd, *J* 6.0 Hz, 12.0 Hz, 1H), 4.15 (dd, *J* 3.2 Hz, 12.0 Hz, 1H), 3.92–3.88 (m, 1H), 2.13 (s, 3H), 2.11 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.8, 170.5, 139.0, 131.6, 128.6, 128.3, 127.9, 125.1, 73.8, 69.5, 65.2, 63.0, 21.1, 20.8 ppm.

4.1.2. *p*-Methoxyphenyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (3b).[35] Compound **3b** was prepared according to the general procedure in **4.1** from 3,4,6-tri-*O*-acetyl-D-glucal, **1a** (54 mg, 0.2 mmol), and bis(4-methoxyphenyl)iodonium triflate, **2b** (196 mg, 0.4 mmol), and obtained as a colourless oil in 62% yield (39.8 mg, 0.124 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.35–7.32 (m, 2H), 6.92–6.89 (m, 2H), 6.15 (dq, *J* 1.6 Hz, 10.4 Hz, 1H), 5.98 (dt, *J* 2.4 Hz, 10.0 Hz, 1H), 5.32–5.28 (m, 2H), 4.25 (dd, *J* 5.6 Hz, 12.0 Hz, 1H), 4.07 (dd, *J* 3.2 Hz, 12.0 Hz, 1H), 3.84–3.80 (m, 4H), 2.09 (s, 3H), 2.07 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.9, 170.6, 159.8, 131.9, 131.1, 129.6, 125.2, 114.1, 73.6, 69.2, 65.4, 63.1, 55.5, 21.2, 20.9 ppm.

4.1.3. *p*-Chlorophenyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (3c).[51] Compound **3c** was prepared according to the general procedure in **4.1** from 3,4,6-tri-*O*-acetyl-D-glucal, **1a** (54 mg, 0.2 mmol), and bis(4-chlorophenyl)iodonium triflate, **2c** (200 mg, 0.4 mmol), and obtained as a colourless oil in 71% yield (45.6 mg, 0.14 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.34 (s, 4H), 6.14 (dd, *J* 1.6 Hz, 6.4 Hz, 1H), 5.99 (dt, *J* 2.4 Hz, 10.4 Hz, 1H), 5.30–5.27 (m, 2H), 4.25 (dd, *J* 6.4 Hz, 12.0 Hz, 1H), 4.09 (dd, *J* 2.8 Hz, 12.0 Hz, 1H), 3.80 (sext, *J* 3.2 Hz, 1H), 2.08 (s, 3H), 2.07 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.8, 170.5, 137.6, 134.3, 131.2, 129.4, 128.9, 125.6, 73.1, 69.7, 65.1, 63.0, 21.1, 20.9 ppm.

4.1.4. *p*-Bromophenyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (3d).[41] Compound **3d** was prepared according to the general procedure in **4.1** from 3,4,6-tri-*O*-acetyl-D-glucal, **1a** (54 mg, 0.2 mmol), and bis(4-bromophenyl)iodonium triflate, **2d** (235 mg, 0.4 mmol), and obtained as a colourless oil in 63% yield (46 mg, 0.125 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.51 (dd, *J* 2.0 Hz, 6.4 Hz, 2H), 7.29 (dd, *J* 2.0 Hz, 6.4 Hz, 2H), 6.14 (dq, *J* 1.6 Hz, 2.8 Hz, 1H), 6.00 (dt, *J* 2.4 Hz, 10.0 Hz, 1H), 5.26–5.31 (m, 2H), 4.26 (dd, *J* 6.4 Hz, 12.0 Hz, 1H), 4.09 (dd, *J* 3.2 Hz, 12.0 Hz, 1H), 3.82–3.78 (m, 1H), 2.09 (s, 3H), 2.08 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$)

δ = 170.9, 170.5, 138.2, 131.9, 131.1, 129.7, 125.6, 122.5, 73.2, 69.8, 65.1, 63.0, 21.2, 20.9 ppm.

4.1.5. *p*-Trifluoromethylphenyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (3e).[35] Compound **3e** was prepared according to the general procedure in **4.1** from 3,4,6-tri-*O*-acetyl-D-glucal, **1a** (54 mg, 0.2 mmol), and bis(4-trifluoromethylphenyl)iodonium triflate, **2e** (227 mg, 0.4 mmol), and obtained as a colourless oil in 41% yield (29.2 mg, 0.082 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.64 (d, *J* 8.0 Hz, 2H), 7.54 (d, *J* 8.0 Hz, 2H), 6.19 (dq, *J* 1.6 Hz, 10.4 Hz, 1H), 6.02 (dt, *J* 2.4 Hz, 10.4 Hz, 1H), 5.36 (dt, *J* 1.2 Hz, 1H), 5.31–5.28 (m, 1H), 4.28 (dd, *J* 6.0 Hz, 12.0 Hz, 1H), 4.12 (dd, *J* 3.2 Hz, 12.0 Hz, 1H), 3.83 (sext, 3.2 Hz, 1H), 2.09 (s, 3H), 2.08 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.8, 170.5, 143.3, 130.9, 130.6 (q, 32.3 Hz), 128.1, 125.71, 125.66, 125.6, 124.2 (q, 270.4 Hz), 73.0, 70.2, 65.0, 62.9, 21.1, 20.9 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ = −62.6 ppm.

4.1.6. *p*-Methylphenyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (3f).[41] Compound **3f** was prepared according to the general procedure in **4.1** from 3,4,6-tri-*O*-acetyl-D-glucal, **1a** (54 mg, 0.2 mmol), and bis(4-tolyl)iodonium triflate, **2f** (184 mg, 0.4 mmol), and obtained as a colourless oil in 75% yield (45.2 mg, 0.15 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.30 (d, *J* 8.0 Hz, 2H), 7.18 (d, *J* 8.0 Hz, 2H), 6.19–6.15 (m, 1H), 5.97 (dt, *J* 2.0 Hz, 10.4 Hz, 1H), 5.33–5.30 (m, 2H), 4.26 (dd, *J* 5.6 Hz, 12.0 Hz, 1H), 4.08 (dd, *J* 2.8 Hz, 12.0 Hz, 1H), 3.85–3.81 (m, 1H), 2.36 (s, 3H), 2.08 (s, 3H), 2.07 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.9, 170.6, 138.2, 136.0, 131.8, 129.3, 128.1, 125.1, 73.8, 69.3, 65.3, 63.1, 21.3, 21.1, 20.9 ppm.

4.1.7. *p-tert*-Butylphenyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (3g).[40] Compound **3g** was prepared according to the general procedure in **4.1** from 3,4,6-tri-*O*-acetyl-D-glucal, **1a** (54 mg, 0.2 mmol), and bis(4-*tert*-butylphenyl)iodonium triflate, **2g** (217 mg, 0.4 mmol), and obtained as a colourless oil in 78% yield (54 mg, 0.156 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.40 (dd, *J* 2.0 Hz, 6.4 Hz, 2H), 7.34 (dd, *J* 2.0 Hz, 6.0 Hz, 2H), 6.20–6.17 (m, 1H), 5.98 (dt, *J* 2.4 Hz, 10.4 Hz, 1H), 5.33–5.30 (m, 2H), 4.28 (dd, *J* 6.0 Hz, 12.0 Hz, 1H), 4.10 (dd, *J* 3.2 Hz, 12.0 Hz, 1H), 3.88–3.84 (m, 1H), 2.09 (s, 3H), 2.08 (s, 3H), 1.33 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.9, 170.6, 151.4, 136.0, 131.9, 127.8, 125.6, 124.9, 73.7, 69.5, 65.3, 63.1, 34.7, 31.5, 21.2, 20.9 ppm.

4.1.8. *p*-Acetylphenyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (3h).[51] Compound **3h** was prepared according to the general procedure in **4.1** from 3,4,6-tri-*O*-acetyl-D-glucal, **1a** (54 mg, 0.2 mmol), and bis(4-acetylphenyl)iodonium triflate, **2h** (206 mg, 0.4 mmol), and obtained as a colourless oil in 52% yield (34.3 mg, 0.103 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.05 (d, *J* 8.4 Hz, 2H), 7.49 (d, *J* 8.0 Hz, 2H), 6.20 (dq, *J* 1.6 Hz, 10.4 Hz, 1H), 6.01 (dt, *J* 2.8 Hz, 10.4 Hz, 1H), 5.36 (q, *J* 2.0 Hz, 1H), 5.31–5.28 (m, 1H), 4.27 (dd, *J* 6.4 Hz, 12.0 Hz, 1H), 4.12 (dd, *J* 3.2 Hz, 12.0 Hz, 1H), 3.92 (s, 3H), 3.83 (sext, *J* 3.2 Hz, 1H), 2.09 (s, 3H), 2.08 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 197.7, 170.8, 170.4, 144.3, 137.0, 130.9, 128.7, 127.9, 125.5, 73.2, 70.0, 65.0, 62.9, 52.2, 26.7, 21.1, 20.9 ppm. HRMS calcd for $C_{18}H_{20}O_6$ + H^+ $(M + H)^+$: 333.1338, found: 333.1337.

4.1.9. *p*-Carbomethoxyphenyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (3i).[39] Compound **3i** was prepared according to the general procedure in **4.1** from 3,4,6-tri-*O*-acetyl-D-glucal, **1a** (54 mg, 0.2 mmol), and bis(4-carbomethoxyphenyl)iodonium triflate, **2i** (219 mg, 0.4 mmol), and obtained as a colourless oil in 49% yield (34 mg, 0.098 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.02 (dd, *J* 1.6 Hz, 6.8 Hz, 2H), 7.47 (d, *J* 8.4 Hz, 2H), 6.14 (dq, *J* 1.2 Hz, 10.4 Hz, 1H), 5.99 (dt, *J* 2.4 Hz, 10.4 Hz, 1H), 5.34 (q, *J* 2.4 Hz, 1H), 5.29–5.25 (m, 1H), 4.25 (dd, *J* 6.4 Hz, 12.0 Hz, 1H), 4.10 (dd, *J* 2.8 Hz, 12.0 Hz, 1H), 3.90 (s, 3H), 3.81 (sext, *J* 3.2 Hz, 1H), 2.07 (s, 3H), 2.06 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.8, 170.4, 166.8, 144.2, 131.0, 130.1, 129.9, 127.6, 125.5, 73.2, 70.0, 65.0, 62.9, 52.2, 21.1, 20.8 ppm.

4.1.10. 4-Biphenyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (3j). Compound **3j** was prepared according to the general procedure in **4.1** from 3,4,6-tri-*O*-acetyl-D-glucal, **1a** (54 mg, 0.2 mmol), and bis(4-biphenyl)iodonium triflate, **2j** (233 mg, 0.4 mmol), and obtained as a colourless oil in 55% yield (40 mg, 0.109 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.62–7.34 (m, 9H), 6.23 (dq, *J* 1.6 Hz, 10.4 Hz, 1H), 6.02 (dt, *J* 2.4 Hz, 10.4 Hz, 1H), 5.38 (q, *J* 2.4 Hz, 1H), 5.35–5.32 (m, 1H), 4.30 (dd, *J* 6.0 Hz, 12.0 Hz, 1H), 4.13 (dd, *J* 3.2 Hz, 12.0 Hz, 1H), 3.91–3.87 (m, 1H), 2.10 (s, 3H), 2.09 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.9, 170.6, 141.4, 140.8, 138.1, 131.7, 129.0, 128.5, 127.6, 127.4, 127.3, 125.3, 73.6, 69.7, 65.3, 63.1, 21.2, 20.9 ppm. HRMS calcd for $C_{22}H_{22}O_5$ + H^+ $(M + H)^+$: 367.1544, found: 367.1545.

4.1.11. *o*-Methylphenyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (3k).[35] Compound **3k** was prepared according to the general procedure in **4.1** from 3,4,6-tri-*O*-acetyl-D-glucal, **1a** (54 mg, 0.2 mmol), and bis(2-tolyl)iodonium triflate, **2k** (184 mg, 0.4 mmol), and obtained as a colourless oil in 60% yield (36.5 mg, 0.12 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.31 (d, *J* 7.6 Hz, 1H), 7.27–7.16 (m, 3H), 6.13 (dq, *J* 1.2 Hz, 10.4 Hz, 1H), 6.04 (dt, *J* 2.4 Hz, 10.4 Hz, 1H), 5.49 (q, *J* 2.4 Hz, 1H), 5.32–5.29 (m, 2H), 4.25 (dd, *J* 6.0 Hz, 12.0 Hz, 1H), 4.03 (dd, *J* 3.2 Hz, 12.0 Hz, 1H), 3.79 (sext, *J* 3.2 Hz, 1H), 2.46 (s, 3H), 2.09 (s, 3H), 2.03 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.9, 170.6, 138.3, 136.3, 132.1, 131.1, 128.7, 128.6, 125.6, 125.5, 71.4, 69.4, 65.4, 63.0, 21.2, 20.9, 19.2 ppm.

4.1.12. *m*-Methylphenyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (3l).[39] Compound **3l** was prepared according to the general procedure in **4.1** from 3,4,6-tri-*O*-acetyl-D-glucal, **1a** (54 mg, 0.2 mmol), and bis(3-tolyl)iodonium triflate, **2l** (184 mg, 0.4 mmol), and obtained as a colourless oil in 72% yield (43.8 mg, 0.12 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.30–7.15 (m, 4H), 6.19 (dq, *J* 1.6 Hz, 10.4 Hz, 1H), 5.99 (dt, *J* 2.4 Hz, 10.0 Hz, 1H), 5.33–5.31 (m, 2H), 4.28 (dd, *J* 6.0 Hz, 12.0 Hz, 1H), 4.12 (dd, *J* 3.2 Hz, 12.0 Hz, 1H), 3.89–3.86 (m, 1H), 2.39 (s, 3H), 2.10 (s, 3H), 2.09 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.9, 170.6, 139.0, 138.4, 131.8, 129.1,

128.7, 128.5, 125.02, 124.96, 73.8, 69.6, 65.3, 63.1, 21.6, 21.2, 20.9 ppm.

4.1.13. 3,5-Dimethylphenyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (3m).[51] Compound **3m** was prepared according to the general procedure in **4.1** from 3,4,6-tri-*O*-acetyl-D-glucal, **1a** (54 mg, 0.2 mmol), and bis(3,5-dimethylphenyl)iodonium triflate, **2m** (195 mg, 0.4 mmol), and obtained as a colourless oil in 70% yield (44.5 mg, 0.14 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.01 (s, 2H), 6.96 (s, 1H), 6.17 (dq, *J* 1.6 Hz, 10.4 Hz, 1H), 5.96 (dt, *J* 2.4 Hz, 10.4 Hz, 1H), 5.31–5.28 (m, 1H), 5.25 (d, *J* 2.0 Hz, 1H), 4.27 (dd, *J* 6.0 Hz, 12.0 Hz, 1H), 4.12 (dd, *J* 3.2 Hz, 12.0 Hz, 1H), 5.96 (sext, *J* 3.2 Hz, 1H), 2.33 (s, 6H), 2.09 (s, 3H), 2.08 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.9, 170.6, 139.0, 138.2, 132.0, 129.9, 125.7, 124.8, 73.8, 69.7, 65.3, 63.2, 21.5, 21.2, 20.9 ppm. HRMS calcd for $C_{18}H_{22}O_5$ + Na^+ $(M + Na)^+$: 341.1365, found: 341.1367.

4.1.14. 2-Naphthyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (3n).[40] Compound **3n** was prepared according to the general procedure in **4.1** from 3,4,6-tri-*O*-acetyl-D-glucal, **1a** (54 mg, 0.2 mmol), and bis(2-naphthyl)iodonium triflate, **2n** (212 mg, 0.4 mmol), and obtained as a colourless oil in 53% yield (36 mg, 0.106 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.88–7.82 (m, 4H), 7.56 (dd, *J* 1.6 Hz, 8.4 Hz, 1H), 7.52–7.49 (m, 2H), 6.31 (dq, *J* 1.6 Hz, 10.4 Hz, 1H), 6.06 (dt, *J* 2.4 Hz, 10.4 Hz, 1H), 5.49 (q, *J* 2.0 Hz, 1H), 5.36 (dq, *J* 2.0 Hz, 7.6 Hz, 1H), 4.28 (dd, *J* 6.0 Hz, 12.0 Hz, 1H), 4.10 (dd, *J* 3.2 Hz, 12.0 Hz, 1H), 3.89–3.85 (m, 1H), 2.10 (s, 3H), 2.08 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.9, 170.6, 136.5, 133.3, 133.2, 131.6, 128.6, 128.3, 127.8, 127.1, 126.50, 126.47, 126.0, 125.6, 74.0, 69.6, 65.4, 63.2, 21.2, 20.9 ppm. HRMS calcd for $C_{20}H_{20}O_5$ + H^+ $(M + H)^+$: 341.1389, found: 341.1392.

4.1.15. Phenyl 4,6-di-*O*-benzyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (3o).[39] Compound **3o** was prepared according to the general procedure in **4.1** from 3-*O*-acetyl-4,6-di-*O*-benzyl-D-glucal, **1b**[52] (74 mg, 0.2 mmol), and diphenyliodonium triflate, **2a** (172 mg, 0.4 mmol), and obtained as a colourless oil in 69% yield (53.3 mg, 0.138 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.45–7.27 (m, 15H), 6.15 (dt, *J* 1.5 Hz, *J* 10.0 Hz, 1H), 6.11 (dq, *J* 1.0 Hz, *J* 10.5 Hz, 1H), 5.32 (d, *J* 1.5 Hz, 1H), 4.63 (d, *J* 11.5 Hz, 1H), 4.60 (d, *J* 12.0 Hz, 1H), 4.51 (d, *J* 11.5 Hz, 1H), 4.41 (d, *J* 12.0 Hz, 1H), 4.21 (d, *J* 2.0 Hz, *J* 8.0 Hz, 1H), 3.73–3.69 (m, 2H), 3.64–3.61 (m, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ = 139.7, 138.4, 138.3, 129.7, 128.52, 128.48, 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 ppm.

4.1.16. Phenyl 4-*O*-acetyl-2,3-dideoxy-6-*O*-benzoyl-α-D-*erythro*-hex-2-enopyranoside (3p). Compound **3p** was prepared according to the general procedure in **4.1** from 3,4-di-*O*-acetyl-6-*O*-benzoyl-D-glucal, **1c**[53] (67 mg, 0.2 mmol), and diphenyliodonium triflate, **2a** (172 mg, 0.4 mmol), and obtained as a colourless oil in 70% yield (49.3 mg, 0.14 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.04 (d, *J* 1.2 Hz, 8.4 Hz, 2H), 7.60–7.33 (m, 5H), 6.25 (dq, *J* 1.2 Hz, 10.4 Hz, 1H), 6.12 (dt, *J* 2.4 Hz, 10.4 Hz, 1H), 5.59–5.55 (m, 1H), 5.39 (q, *J* 2.0 Hz, 1H), 4.31 (dd, *J* 6.0 Hz, *J* 12.0 Hz, 1H), 4.20 (dd, *J* 3.2 Hz, *J* 12.0 Hz, 1H), 4.06–4.02 (m, 1H), 2.05 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.9, 166.2, 139.2, 133.4, 131.9, 130.0, 129.9, 128.7, 128.6, 128.4, 128.0, 125.2, 73.9, 69.7, 66.0, 63.3, 20.9 ppm. HRMS calcd for $C_{21}H_{20}O_5$ + H^+ $(M + H)^+$: 353.1389, found: 353.1382.

4.1.17. Phenyl 4-*O*-acetyl-2,3-dideoxy-6-*O*-*tert*-butyldiphenylsilyl-α-D-*erythro*-hex-2-enopyranoside (3q). Compound **3q** was prepared according to the general procedure in **4.1** from 3,4-di-*O*-acetyl-6-*O*-(*tert*-butyl diphenylsilyl)-D-glucal, **1d**[54] (94 mg, 0.2 mmol), and diphenyliodonium triflate, **2a** (172 mg, 0.4 mmol), and obtained as a colourless oil in 66% yield (64.2 mg, 0.132 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.68–7.31 (s, 15H), 6.17 (dq, *J* 1.2 Hz, 10.4 Hz, 1H), 5.95 (ddd, *J* 2.0 Hz, 2.8 Hz, 10.4 Hz, 1H), 5.29–5.26 (m, 2H), 3.85–3.73 (m, 3H), 1.98 (s, 3H), 1.04 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.6, 139.8, 135.9, 135.8, 133.6, 132.2, 129.80, 129.77, 128.6, 128.0, 127.83, 127.78, 124.9, 73.5, 72.9, 65.6, 63.8, 27.0, 21.2, 19.4 ppm. HRMS calcd for $C_{30}H_{35}O_4Si$ + H^+ $(M + H)^+$: 487.2305, found: 487.2300.

4.1.18. Phenyl 4-*O*-acetyl-2,3-dideoxy-6-*O*-pivaloyl-α-D-*erythro*-hex-2-enopyranoside (3r). Compound **3r** was prepared according to the general procedure in **4.1** from 3,4-di-*O*-acetyl-6-*O*-pivaloyl-D-glucal, **1e** (63 mg, 0.2 mmol), and diphenyliodonium triflate, **2a** (172 mg, 0.4 mmol), and obtained as a colourless oil in 73% yield (48.6 mg, 0.146 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.43–7.30 (m, 5H), 6.20 (dq, *J* 1.6 Hz, 10.4 Hz, 1H), 5.98 (dt, *J* 2.4 Hz, 10.4 Hz, 1H), 5.30 (q, *J* 2.0 Hz, 1H), 6.25 (dq, *J* 2.4 Hz, 7.2 Hz, 1H), 4.22–4.15 (m, 2H), 3.89–3.85 (m, 1H), 2.09 (s, 3H), 1.16 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 178.4, 170.6, 139.2, 131.9, 128.6, 128.3, 128.0, 125.1, 73.7, 70.0, 65.4, 63.3, 38.9, 27.3, 21.2 ppm. HRMS calcd for $C_{19}H_{24}O_5$ + H^+ $(M + H)^+$: 333.1702, found: 333.1703.

4.1.19. Phenyl 4-*O*-acetyl-2,3-dideoxy-6-*O*-*p*-methoxybenzoyl-α-D-*erythro*-hex-2-enopyranoside (3s). Compound **3s** was prepared according to the general procedure in **4.1** from 3,4-di-*O*-acetyl-6-*O*-(4-methoxybenzoyl)-D-glucal, **1f** (70 mg, 0.2 mmol), and diphenyliodonium triflate, **2a** (172 mg, 0.4 mmol), and obtained as a colourless oil in 70% yield (49.3 mg, 0.14 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99–7.96 (m, 2H), 7.44–7.31 (m, 5H), 6.93–7.90 (m, 2H), 6.24 (dd, *J* 1.2 Hz, 10.4 Hz, 1H), 6.02 (dq, *J* 2.4 Hz, 10.4 Hz, 1H), 5.40–5.35 (m, 2H), 4.43 (d, *J* 6.4 Hz, *J* 12.0 Hz, 1H), 4.38 (dd, *J* 4.0 Hz, *J* 12.0 Hz, 1H), 4.02–3.98 (m, 1H), 3.86 (s, 3H), 2.08 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.6, 166.2, 163.6, 139.2, 131.9, 131.8, 128.6, 128.2, 127.9, 125.2, 122.5, 113.8, 73.7, 69.9, 65.6, 63.5, 55.5, 21.2 ppm. HRMS calcd for $C_{22}H_{22}O_6$ + H^+ $(M + H)^+$: 383.1495, found: 383.1499.

4.1.20. Phenyl 4,6-di-*O*-*p*-methoxybenzyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (3t). Compound **3t** was prepared according to the general procedure in **4.1** from 3-*O*-acetyl-4,6-di-*O*-(*p*-methoxybenzyl)-D-glucal, **1g** (86 mg, 0.2 mmol), and diphenyliodonium triflate, **2a** (172 mg, 0.4 mmol), and obtained as a colourless oil in 52% yield (46.4 mg, 0.104 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.44 (d, *J* 7.2 Hz, 2H), 7.36–7.27 (m, 5H), 7.23 (d, *J* 8.8 Hz, 2H), 7.18 (d, *J* 8.4 Hz, 1H), 6.87–6.84 (m, 4H), 6.14–6.06 (m, 2H), 5.31 (bs, 1H), 4.54

(d, *J* 11.2 Hz, 1H), 4.53 (d, *J* 11.6 Hz, 1H), 4.41 (d, *J* 10.4 Hz, 1H), 4.41 (d, *J* 11.6 Hz, 1H), 4.17–4.15 (m, 1H), 3.793 (s, 3H), 3.787 (s, 3H), 3.69–3.64 (m, 2H), 3.59–3.55 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.5, 159.4, 139.8, 130.6, 129.63, 129.60, 128.5, 128.2, 127.9, 127.4, 114.0, 113.9, 74.2, 73.0, 71.0, 70.1, 69.0, 55.40, 55.38 ppm. HRMS calcd for $C_{28}H_{30}O_5$ + Na^+ $(M + Na)^+$: 469.1991, found: 469.1992.

4.1.21. Phenyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*threo*-hex-2-enopyranoside (19a).[39] Compound **19a** was prepared according to the general procedure in **4.1** from 3,4,6-tri-*O*-acetyl-D-galactal, **12a** (54 mg, 0.2 mmol), and diphenyliodonium triflate, **2a** (172 mg, 0.4 mmol), and obtained as a light-yellow oil in 79% yield (45.8 mg, 0.158 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.39–7.30 (m, 5H), 6.40 (ddd, *J* 0.4 Hz, 3.6 Hz, 10.4 Hz, 1H), 6.19 (ddd, *J* 2.0 Hz, 5.2 Hz, 10.0 Hz, 1H), 5.40 (dd, *J* 2.4 Hz, 3.2 Hz, 1H), 5.11 (dd, *J* 2.4 Hz, 4.8 Hz, 1H), 4.21 (dd, *J* 5.6 Hz, 11.2 Hz, 1H), 4.16 (dd, *J* 7.2 Hz, 11.2 Hz, 1H), 3.96–3.92 (m, 1H), 2.11 (s, 3H), 1.99 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.63, 170.62, 138.5, 133.4, 128.6, 128.3, 127.9, 123.6, 73.9, 68.5, 63.9, 62.9, 21.0, 20.8 ppm.

4.1.22. Phenyl 4,6-di-*O*-benzyl-2,3-dideoxy-α-D-*threo*-hex-2-enopyranoside (19b).[39] Compound **19b** was prepared according to the general procedure in **4.1** from 3-*O*-acetyl-4,6-di-*O*-benzyl-D-galactal, **12b**[55] (74 mg, 0.2 mmol), and diphenyliodonium triflate, **2a** (172 mg, 0.4 mmol), and obtained as a colourless oil in 78% yield (60.3 mg, 0.156 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.43–7.27 (m, 15H), 6.30 (ddd, *J* 0.4 Hz, 3.6 Hz, 10.0 Hz, 1H), 6.19 (ddd, *J* 2.0 Hz, 4.8 Hz, 10.4 Hz, 1H), 5.39 (t, *J* 2.4 Hz, 1H), 4.72 (d, *J* 12.0 Hz, 1H), 4.65 (d, *J* 12.0 Hz, 1H), 4.55 (d, *J* 12.0 Hz, 1H), 4.51 (d, *J* 11.6 Hz, 1H), 4.02–3.98 (m, 1H), 3.91–3.89 (m, 1H), 3.83 (dd, *J* 5.6 Hz, 10.0 Hz, 1H), 3.76 (dd, *J* 6.8 Hz, 10.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 139.4, 138.8, 138.5, 132.3, 128.50, 128.46, 128.4, 128.0, 127.9, 127.8, 127.7, 127.6, 125.3, 73.8, 73.4, 71.4, 71.1, 69.3, 68.5 ppm.

4.1.23. Phenyl 4-*O*-acetyl-6-*O*-*tert*-butyldiphenylsilyl-2,3-dideoxy-α-D-*threo*-hex-2-enopyranoside (19c). Compound **19c** was prepared according to the general procedure in **4.1** from 3,4-di-*O*-acetyl-6-*O*-(*tert*-butyl diphenylsilyl)-D-galactal, **12c**[56] (94 mg, 0.2 mmol), and diphenyliodonium triflate, **2a** (172 mg, 0.4 mmol), and obtained as a colourless oil in 53% yield (51.5 mg, 0.106 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.68–7.62 (m, 4H), 7.46–7.29 (m, 11H), 6.17 (dq, *J* 1.2 Hz, 10.4 Hz, 1H), 5.94 (dt, *J* 2.0 Hz, 10.4 Hz, 1H), 5.30–5.26 (m, 2H), 3.85–3.72 (m, 3H), 1.97 (s, 3H), 1.03 (s, 9H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.6, 139.8, 135.9, 135.8, 133.6, 132.2, 129.80, 129.77, 128.6, 128.0, 127.84, 127.83, 127.79, 124.9, 73.5, 72.9, 65.6, 63.8, 29.9, 27.0, 21.2, 19.4 ppm. HRMS calcd for $C_{30}H_{35}O_4Si$ + H^+ $(M + H)^+$: 487.2305, found: 487.2306.

4.1.24. Phenyl 4-*O*-acetyl-2,3,6-trideoxy-α-L-*erythro*-hex-2-enopyranoside (20a).[39] Compound **20a** was prepared according to the general procedure in **4.1** from 3,4-di-*O*-acetyl-L-rhamnal, **13a** (43 mg, 0.2 mmol), and diphenyliodonium triflate, **2a** (172 mg, 0.4 mmol), and obtained as a colourless oil in 65% yield (30.2 mg, 0.13 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.39–7.29 (m, 5H), 6.12 (dq, *J* 1.2 Hz, 10.4 Hz, 1H), 5.95 (ddd, *J* 2.4 Hz, 3.2 Hz, 10.4 Hz, 1H), 5.23 (q, *J* 2.0 Hz, 1H), 5.06–5.02 (m, 1H), 3.86 (quint, *J* 6.4 Hz, 1H), 2.10 (s, 3H), 1.25 (d, *J* 6.4 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.8, 139.9, 132.3, 128.6, 128.2, 128.0, 124.5, 73.0, 70.1, 68.2, 21.3, 17.5 ppm.

4.1.25. Phenyl 4-*O*-benzyl-2,3,6-trideoxy-α-L-*erythro*-hex-2-enopyranoside (20b).[39] Compound **20b** was prepared according to the general procedure in **4.1** from 3-*O*-acetyl-4-*O*-benzyl-L-rhamnal, **13b**[57] (52 mg, 0.2 mmol), and diphenyliodonium triflate, **2a** (172 mg, 0.4 mmol), and obtained as a colourless oil in 49% yield (27.5 mg, 0.098 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.43–7.28 (m, 10H), 6.14–6.07 (m, 2H), 5.22 (bs, 1H), 4.69 (d, *J* 11.6 Hz, 1H), 4.61 (d, *J* 11.6 Hz, 1H), 3.77–3.72 (m, 2H), 1.26 (d, *J* 6.0 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 140.2, 138.6, 130.4, 128.6, 128.5, 128.1, 128.04, 127.96, 127.9, 126.7, 75.9, 73.7, 71.1, 68.0, 18.3 ppm.

4.1.26. Phenyl 4-*O*-acetyl-2,3,6-trideoxy-α-L-*threo*-hex-2-enopyranoside (21). Compound **21** was prepared according to the general procedure in **4.1** from 3,4-di-*O*-acetyl-L-fucal, **14**[58] (43 mg, 0.2 mmol), and diphenyliodonium triflate, **2a** (172 mg, 0.4 mmol), and obtained as a white solid in 51% yield (23.7 mg, 0.102 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.38–7.31 (m, 5H), 6.35 (dd, *J* 3.2 Hz, 10.0 Hz, 1H), 6.15 (ddd, *J* 2.0 Hz, 4.8 Hz, 10.0 Hz, 1H), 5.34 (t, *J* 2.4 Hz, 1H), 5.03 (q, *J* 2.4 Hz, 1H), 3.88–3.84 (m, 1H), 2.13 (s, 3H), 1.16 (d, *J* 6.4 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.9, 139.2, 133.2, 128.6, 128.1, 128.0, 124.2, 74.0, 66.30, 66.28, 21.1, 16.2 ppm. HRMS calcd for $C_{14}H_{16}O_3$ + H^+ $(M + H)^+$: 233.1178, found: 233.1174.

4.1.27. Phenyl 4-*O*-acetyl-2,3-dideoxy-α-L-*erythro*-pent-2-enopyranoside (22). Compound **22** was prepared according to the general procedure in **4.1** from 3,4-di-*O*-acetyl-L-arabinal, **15**[59] (40 mg, 0.2 mmol), and diphenyliodonium triflate, **2a** (172 mg, 0.4 mmol), and obtained as a colourless oil in 69% yield (30.1 mg, 0.138 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.36–7.30 (m, 5H), 6.15 (dq, *J* 1.2 Hz, 10.4 Hz, 1H), 6.05 (dq, *J* 2.4 Hz, 10.4 Hz, 1H), 5.30–5.26 (m, 1H), 4.43 (q, *J* 2.0 Hz, 1H), 4.05 (dd, *J* 4.4 Hz, *J* 12.0 Hz, 1H), 4.69 (dd, *J* 5.6 Hz, *J* 12.0 Hz, 1H), 2.11 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.6, 139.3, 133.3, 128.6, 128.3, 127.8, 124.6, 75.2, 64.8, 21.1 ppm. HRMS calcd for $C_{13}H_{14}O_3$ + Na^+ $(M + Na)^+$: 241.0841, found: 241.0836.

4.1.28. Phenyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside and phenyl 4,6-di-*O*-acetyl-2,3-dideoxy-β-D-*erythro*-hex-2-enopyranoside (3a and 3aβ).[39] Compounds **3a** and **3aβ** were prepared according to the general procedure in **4.1** from 3,4,6-tri-*O*-acetyl-D-allal, **16**[60] (54 mg, 0.2 mmol), and diphenyliodonium triflate (172 mg, 0.4 mmol), and obtained as colourless oils in 72% yield (41.8 mg, 0.144 mmol) as a 1 : 1 α : β mixture. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.43–7.29 (m, 10H), 6.18 (dq, *J* 1.2 Hz, 10.0 Hz, 1H), 5.99 (dt, *J* 2.0 Hz, 10.0 Hz, 1H), 5.92 (dt, *J* 1.6 Hz, 10.0 Hz, 1H), 5.83 (dt, *J* 2.0 Hz, 10.0 Hz, 1H), 5.44–5.40 (m, 1H), 5.34–5.29 (m, 2H), 5.21 (dd, *J* 2.4 Hz, 3.6 Hz, 1H), 4.30–4.19 (m, 3H), 4.10 (dd, *J* 3.2 Hz, 12.0 Hz, 1H), 3.96–3.92 (m, 1H), 3.87–3.83 (m, 1H), 2.11 (s, 3H), 2.09 (s, 3H), 2.08 (s, 3H), 2.07 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$)

δ = 171.0, 170.9, 170.5, 170.4, 140.0, 139.1, 132.9, 131.7, 128.8, 128.6, 128.4, 128.3, 128.0, 127.3, 125.11, 125.08, 77.7, 75.0, 73.8, 69.6, 65.7, 65.2, 63.9, 63.0, 21.1, 20.93, 20.86 ppm.

4.1.29. Phenyl 4-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-6-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (23). Compound **23** was prepared according to the general procedure in **4.1** from 3,6-di-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-D-glucal, **17** (56 mg, 0.1 mmol), and diphenyliodonium triflate, **2a** (86 mg, 0.2 mmol), and obtained as a colourless oil in 61% yield (35.3 mg, 0.061 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.41–7.30 (m, 5H), 6.19–6.11 (m, 2H), 5.39 (d, *J* 3.2 Hz, 1H), 5.30 (bs, 1H), 5.21 (dd, *J* 8.0 Hz, 10.4 Hz, 1H), 5.01 (dd, *J* 3.2 Hz, 10.4 Hz, 1H), 4.60 (q, *J* 7.6 Hz, 1H), 4.22–4.09 (m, 5H), 3.92 (t, *J* 6.4 Hz, 1H), 3.71–3.67 (m, 1H), 2.15 (s, 3H), 2.08 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 1.97 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.9, 170.5, 170.4, 170.2, 169.6, 139.0, 130.2, 128.6, 128.31, 128.28, 128.2, 102.3, 74.2, 73.3, 71.11, 71.06, 69.1, 69.0, 67.2, 63.4, 61.5, 21.0, 20.77, 20.75, 20.7 ppm. HRMS calcd for $C_{28}H_{34}O_{13}$ + NH_4^+ $(M + NH_4)^+$: 596.2342, found: 596.2343.

4.1.30. Phenyl 4-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-6-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (24). Compound **24** was prepared according to the general procedure in **4.1** from 3,6-di-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-D-glucal, **18**[59] (56 mg, 0.1 mmol), and diphenyliodonium triflate, **2a** (86 mg, 0.2 mmol), and obtained as a colourless oil in 55% yield (31.8 mg, 0.055 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.40–7.32 (m, 5H), 6.18 (dq, *J* 1.2 Hz, 10.4 Hz, 1H), 5.96 (dt, *J* 2.4 Hz, 10.4 Hz, 1H), 5.44 (t, *J* 10.0 Hz, 1H), 5.35 (d, *J* 3.6 Hz, 1H), 5.29 (q, *J* 2.4 Hz, 1H), 5.06 (t, *J* 10.0 Hz, 1H), 4.85 (dd, *J* 4.0 Hz, 10.4 Hz, 1H), 4.32 (dd, *J* 5.6 Hz, 12.0 Hz, 1H), 4.28–4.20 (m, 3H), 4.11–4.05 (m, 2H), 3.84–3.80 (m, 1H), 2.08 (s, 6H), 2.05 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 169.8, 169.7, 169.3, 169.2, 168.7, 138.1, 131.0, 127.7, 127.4, 126.9, 123.6, 93.6, 72.9, 70.1, 69.3, 69.2, 69.0, 67.6, 67.3, 62.5, 61.0, 19.9, 19.80, 19.79, 19.75, 19.7 ppm. HRMS calcd for $C_{28}H_{34}O_{13}$ + H^+ $(M + H)^+$: 579.2080, found: 579.2078.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

1 P. G. Hultin, *Curr. Top. Med. Chem.*, 2005, **5**, 1299–1331.
2 A. C. Drohat and A. Maiti, *Org. Biomol. Chem.*, 2014, **12**, 8367–8378.
3 R. Wolfenden, X. Lu and G. Young, *J. Am. Chem. Soc.*, 1998, **120**, 6814–6815.
4 Y. Sakano, J. Fukushima and T. Kobayashi, *Agric. Biol. Chem.*, 1983, **47**, 2211–2216.
5 A. Dondoni and A. Marra, *Chem. Rev.*, 2000, **100**, 4395–4421.
6 E. Leclerc, X. Pannecoucke, M. Etheve-Quelquejeu and M. Sollogoub, *Chem. Soc. Rev.*, 2013, **42**, 4270–4283.
7 G. Yang, J. Schmieg, M. Tsuji and R. W. Franck, *Angew. Chem., Int. Ed.*, 2004, **43**, 3818–3822.
8 R. W. Franck and M. Tsuji, *Acc. Chem. Res.*, 2006, **39**, 692–701.
9 Y. Yang and B. Yu, *Chem. Rev.*, 2017, **117**, 12281–12356.
10 X. Li and J. Zhu, *Eur. J. Org. Chem.*, 2016, 4724–4767.
11 A. A. Ansari, Y. S. Reddy and Y. D. Vankar, *Beilstein J. Org. Chem.*, 2014, **10**, 300–306.
12 R. G. dos Santos, A. R. Jesus, J. M. Caio and A. P. Rauter, *Curr. Org. Chem.*, 2011, **15**, 128–148.
13 K. Kitamura, Y. Ando, T. Matsumoto and K. Suzuki, *Chem. Rev.*, 2018, **118**, 1495–1598.
14 H. Liao, J. Ma, H. Yao and X.-W. Liu, *Org. Biomol. Chem.*, 2018, **16**, 1791–1806.
15 L. Adak, S. Kawamura, G. Toma, T. Takenaka, K. Isozaki, H. Takaya, A. Orita, H. C. Li, T. K. M. Shing and M. Nakamura, *J. Am. Chem. Soc.*, 2017, **139**, 10693–10701.
16 K. Sakamoto, M. Nagai, Y. Ebe, H. Yorimitsu and T. Nishimura, *ACS Catal.*, 2019, **9**, 1347–1352.
17 F. Zhu, M. J. Rourke, T. Yang, J. Rodriguez and M. A. Walczak, *J. Am. Chem. Soc.*, 2016, **138**, 12049–12052.
18 S.-K. Kang, H.-W. Lee, S.-B. Jang, T.-H. Kim and S.-J. Pyun, *J. Org. Chem.*, 1996, **61**, 2604–2605.
19 V. K. Aggarwal and B. Olofsson, *Angew. Chem., Int. Ed.*, 2005, **44**, 5516–5519.
20 A. E. Allen and D. W. C. MacMillan, *J. Am. Chem. Soc.*, 2011, **133**, 4260–4263.
21 C. J. Teskey, S. M. A. Sohel, D. L. Bunting, S. G. Modha and M. F. Greaney, *Angew. Chem., Int. Ed.*, 2017, **56**, 5263–5266.
22 B. Vaddula, J. Leazer and R. S. Varma, *Adv. Synth. Catal.*, 2012, **354**, 986–990.
23 M. Ochiai, Y. Kitagawa, N. Takayama, Y. Takaoka and M. Shiro, *J. Am. Chem. Soc.*, 1999, **121**, 9233–9234.
24 Q. Y. Toh, A. McNally, S. Vera, N. Erdmann and M. J. Gaunt, *J. Am. Chem. Soc.*, 2013, **135**, 3772–3775.
25 M. E. Kieffer, K.V. Chuang and S. E. Reisman, *Chem. Sci.*, 2012, **3**, 3170–3174.
26 J. Malmgren, A. Nagendiran, C.-W. Tai, J.-E. Bäckvall and B. Olofsson, *Chem. – Eur. J.*, 2014, **20**, 13531–13535.
27 L. Ackermann, M. Dell'Acqua, S. Fenner, R. Vicente and R. Sandmann, *Org. Lett.*, 2011, **13**, 2358–2360.
28 B. R. Vaddula, A. Saha, J. Leazer and R. S. Varma, *Green Chem.*, 2012, **14**, 2133–2136.
29 R. J. Phipps, L. McMurray, S. Ritter, H. A. Duong and M. J. Gaunt, *J. Am. Chem. Soc.*, 2012, **134**, 10773–10776.

30 V. V. Zhdankin and P. J. Stang, *Chem. Rev.*, 2008, **108**, 5299–5358.
31 E. A. Merritt and B. Olofsson, *Angew. Chem., Int. Ed.*, 2009, **48**, 9052–9070.
32 A. Yoshimura and V. V. Zhdankin, *Chem. Rev.*, 2016, **116**, 3328–3435.
33 M. Wang, S. Chen and X. Jiang, *Chem. – Asian J.*, 2018, **13**, 2195–2207.
34 I. D. Hyatt, L. Dave, N. David, K. Kaur, M. Medard and C. Mowdawallla, *Org. Biomol. Chem.*, 2019, **17**, 7822–7848.
35 J. Ramnauth, O. Poulin, S. Rakhit and S. P. Maddaford, *Org. Lett.*, 2001, **3**, 2013–2015.
36 D.-C. Xiong, L.-H. Zhang and X.-S. Ye, *Org. Lett.*, 2009, **11**, 1709–1712.
37 C.-F. Liu, D.-C. Xiong and X.-S. Ye, *J. Org. Chem.*, 2014, **79**, 4676–4686.
38 S. Xiang, S. Cai, J. Zeng and X.-W. Liu, *Org. Lett.*, 2011, **13**, 4608–4611.
39 Y. Bai, L. M. H. Kim, H. Liao and X.-W. Liu, *J. Org. Chem.*, 2013, **78**, 8821–8825.
40 A. K. Kusunuru, S. K. Yousuf, M. Tatina and D. Mukherjee, *Eur. J. Org. Chem.*, 2015, 459–462.
41 J. Ma, S. Xiang, H. Jiang and X.-W. Liu, *Eur. J. Org. Chem.*, 2015, 949–952.
42 H.-H. Li and X.-S. Ye, *Org. Biomol. Chem.*, 2009, **7**, 3855–3861.
43 A. K. Singh and J. Kandasamy, *Org. Biomol. Chem.*, 2018, **16**, 5107–5112.
44 D. P. Steinhuebel, J. J. Fleming and J. Du Bois, *Org. Lett.*, 2002, **4**, 293–295.
45 G. L. Tolnai, U. J. Nilsson and B. Olofsson, *Angew. Chem., Int. Ed.*, 2016, **55**, 11226–11230.
46 W. Shang, Z.-D. Mou, H. Tang, X. Zhang, J. Liu, Z. Fu and D. Niu, *Angew. Chem., Int. Ed.*, 2018, **57**, 314–318.
47 N. Lucchetti and R. Gilmour, *Chem. – Eur. J.*, 2018, **24**, 16266–16270.
48 D. Yi, F. Zhu and M. A. Walczak, *Org. Lett.*, 2018, **20**, 1936–1940.
49 H.-H. Li and X.-S. Ye, *Org. Biomol. Chem.*, 2009, **7**, 3855–3861.
50 T. Mabit, A. Siard, F. Legros, S. Guillarme, A. Martel, J. Lebreton, F. Carreaux, G. Dujardin and S. Collet, *Chem. – Eur. J.*, 2018, **24**, 14069–14074.
51 A. R. Yeager, G. K. Min, J. A. Porco Jr. and S. E. Schaus, *Org. Lett.*, 2006, **8**, 5065–5068.
52 S. Fischer and C. H. Hamann, *J. Carbohydr. Chem.*, 1995, **14**, 327–339.
53 R. P. Spencer, C. L. Cavallaro and J. Schwartz, *J. Org. Chem.*, 1999, **64**, 3987–3995.
54 K. C. Nicolaou, H. J. Mitchell, N. F. Jain, N. Winssinger, R. Hughes and T. Bando, *Angew. Chem., Int. Ed.*, 1999, **38**, 240–244.
55 F. Bosse, L. A. Marcaurelle and P. H. Seeberger, *J. Org. Chem.*, 2002, **67**(19), 6659–6670.
56 A. Kirschning, *J. Org. Chem.*, 1995, **60**, 1228–1232.
57 R. Lihammar, J. Rönnols, G. Widmalm and J.-E. Bäckvall, *Chem. – Eur. J.*, 2014, **20**, 14756–14762.
58 I. A. Gagarinov, T. Fang, L. Liu, A. D. Srivastava and G.-J. Boons, *Org. Lett.*, 2015, **17**, 928–931.
59 B. K. Shull, Z. Wu and M. Koreeda, *J. Carbohydr. Chem.*, 1996, **15**, 955–964.
60 R. Xiao, E. L. Dane, J. Zeng, C. J. McKnight and M. W. Grinstaf, *J. Am. Chem. Soc.*, 2017, **139**, 14217–14223.