2.1 Introduction

As discussed in the Chapter 1, carbohydrates play an important role in biological system, which are used not only as source of energy, but also drugs, diagnostic tools, vaccines, drug targets, etc. [1]. Aryl *C*-glycoside is one of the distinct motifs found in various bio-active molecules and natural products, thus attracted tremendous interest in synthetic organic chemistry [2]. Aryl glycosides are typically achieved by Friedel-Crafts alkylation of electron-rich arenes with glycosyl donors [3] or by the reaction of protected aldonolactones with organometallic reagents such as aryllithium or Grignard reagents [4]. Alternatively, coupling reaction between glycosyl bromides and arylzinc reagent has been reported to provide β-arylated glycosides [5]. On the other hand, palladium catalysed coupling reaction of glycals with various aryl donors such as arylboronic acids [6], arylhydrazines [7], arylzinc reagents [8], aryl halides [9], etc. [2, 10] have been recently demonstrated for the preparation of various aryl *C*-glycosides (*Refer the section 1.6 in Chapter 1*).

2.2 Aryl Diazonium Salts

Arenediazonium salts are highly useful aryl donors which can be easily obtained from corresponding anilines [11]. Aryldiazonium salts have been identified as an efficient alternative to arylhalides and arylboronic acids in Pd-catalyzed cross-coupling reactions **(Figure 2.1)** [11a]. Recently, palladium mediated Heck-type cross coupling between glycal and arylboronic acid was explored by Ye *et al.* [6a,6c] and Mukherjee *et al.* [6b]. In this context, we have envisioned that arenediazonium salts can be used as an efficient alternative to arylboronic acids to prepare aryl-*C*-glycosides [12], because, the inherent

electrophilicity of diazonium salts might allow the coupling reaction under mild reaction conditions in the absence of ligand or base [11a, 11b].

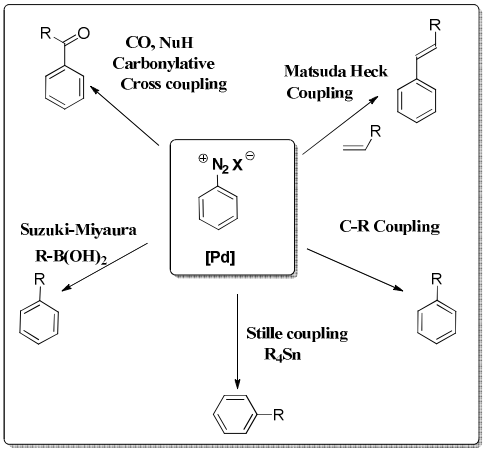


Figure 2.1 Palladium-Catalyzed *C-C* Coupling Reactions.

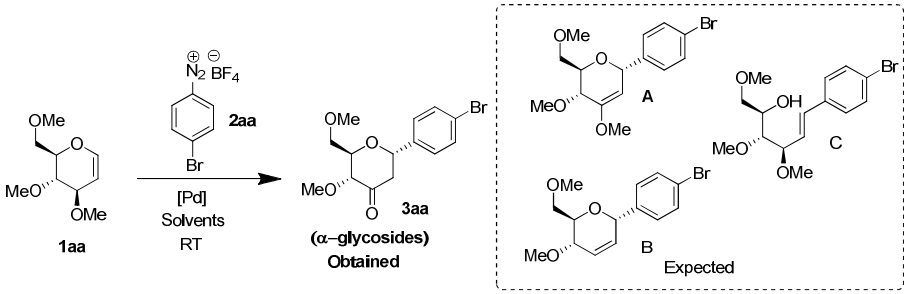
As part of our ongoing research on glycosylation reactions [13], here we demonstrated an efficient preparation of synthetically useful 2,3-deoxy 3-keto α-aryl-C-glycosides from the corresponding glycals and aryldiazonium salts in the presence of palladium catalyst.

2.3 Results and Discussion

At the outset, the glycosylation of *O*-per-methylated glucal (**1aa**) was investigated with 4-bromobenzenediazonium tetrafluoroborate (**2aa**) in various solvents in the presence of different palladium salts (**Table 2.1**). Initially, the reaction was performed with 5 mol% of palladium acetate in methanol at room temperature without any base or ligand. The reaction underwent smoothly resulting in a new product within 60 mins (Table 2.1, entry 1). Going by the previously reported literature pertaining to boronic acid and the glycal [6a, 6c, 6e], one of the Ferrier rearrangement products (**A**-**C**) was only expected as shown in Table 2.1. Surprisingly, unlike boronic acid, the reaction provided 2,3-

deoxy 3-keto α-aryl-*C*-glycoside (**3aa**) exclusively with 91% yield. In fact, formation of similar ketone product was previously reported with arylboronic acids, however, in the presence of external oxidants such as benzoquinone (BQ) or 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) [6c].

Table 2.1 Optimization of the reaction condition with 4-bromobenzenediazonium tetrafluoroborate.[a]



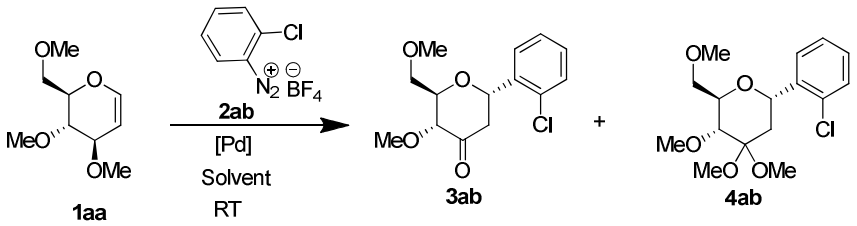
Entry	Catalyst (5 mol%)	Solvent	Time (h)	Yield (%)[b] **(3aa)**
1	$Pd(OAc)_2$	Methanol	1	91
2	$Pd(OAc)_2$	DCM	1	nd
3	$Pd(OAc)_2$	Dioxane	1	nd
4	$Pd(OAc)_2$	THF	1	~10
5	$Pd(OAc)_2$	CH_3CN	1	nd
6	$Pd(OAc)_2$	Toluene	1	nd
7	$Pd(OAc)_2$	CH_3COOH	1	nd
8	$Pd(OAc)_2$	DCM:H_2O (3:1)	2.5	70
9	$Pd(OAc)_2$	MeOH:H_2O (3:1)	1.5	87
10	$Pd(OAc)_2$	CH_3CN:H_2O (3:1)	1.5	90
11	$Pd(dba)_2$	Methanol	1	89
12	$Pd(PPh_3)_4$	Methanol	1	30
13	$Pd(TFA)_2$	Methanol	1	86
14	$PdCl_2$	Methanol	1	10
15	$Pd(CH_3CN)_2Cl_2$	Methanol	1	10

[a]**Reaction condition:** Glucal **1aa** (95 mg, 0.5 mmol) and diazonium salt **2aa** (152 mg, 0.56 mmol, 1.1 equiv.) were stirred in a solvent (4 mL) following which the catalyst (0.025 mmol) was added. [b]Isolated yield.

Encouraged, we further tested the reaction in other solvents including DCM, dioxane, THF, acetonitrile, toluene and acetic acid (Table 2.1, entries 2-7). Among them, THF provides **3aa** in ~ 10% yield (**Table 2.1, entry 4**), while other solvents failed to provide the desired product. Further, the reaction was tested with water mixed DCM, methanol and acetonitrile in the presence of 5 mol% of $Pd(OAc)_2$ at room temperature (**Table 2.1, entries 8-10**). Interestingly, acetonitrile-water (3:1) was found to be equally good as of methanol and gave the desired product **3aa** in 90% yield within 1.5 h (**Table 2.1, entry 10**). Further, the optimal conditions were investigated with other typically used Pd(0) and Pd(II) catalysts such as $Pd(dba)_2$, $Pd(PPh_3)_4$, $Pd(TFA)_2$, $PdCl_2$ and $PdCl_2(CH_3CN)_2$ (**Table 2.1, entry 11-15**). Among them, $Pd(dba)_2$ and $Pd(TFA)_2$ showed equal efficiency to that of palladium acetate (**Table 2.1, entry 11 & 13**), while other catalysts gave the desired product **3aa** in a low yield (i.e. <30%).

Although, methanol was seen to be an efficient medium, it provides dimethyl acetal **4ab** as the product during the reaction of glucal **1aa** with 2-chlorobenzenediazonium tetrafluoroborate (**2ab**) (**Table 2.2, entry 1**). In fact, other active catalysts such as $Pd(dba)_2$ and $P(TFA)_2$ also gave **4ab** as the only product in similar yields (**Table 2.2, entries 2&3**). Nevertheless, the desired product **3ab** was successfully obtained in 89% yield when the reaction was performed in acetonitrile-water medium (Table 2.2, entry 4). Under this condition, palladium acetate was found to be slightly better than $Pd(dba)_2$ and $P(TFA)_2$ (**Table 2.2, entries 5 & 6**).

Table 2.2 Optimization of reaction condition with 2-chlorobenzenediazonium tetrafluoroborate.[a]



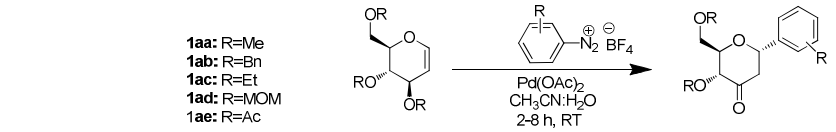
Entry	Metal salt	Solvent	Time (h)	Yield (%)[b]	
				3ab	**4ab**
1	$Pd(OAc)_2$	Methanol	1 h	nd	94
2	$Pd(dpa)_2$	Methanol	1 h	nd	90
3	$Pd(TFA)_2$	Methanol	1 h	nd	89
4	$Pd(OAc)_2$	$CH_3CN:H_2O$ (3:1)	1.5 h	89	nd
5	$Pd(dba)_2$	$CH_3CN:H_2O$ (3:1)	1.5 h	84	nd
6	$Pd(TFA)_2$	$CH_3CN:H_2O$ (3:1)	1.5 h	82	nd

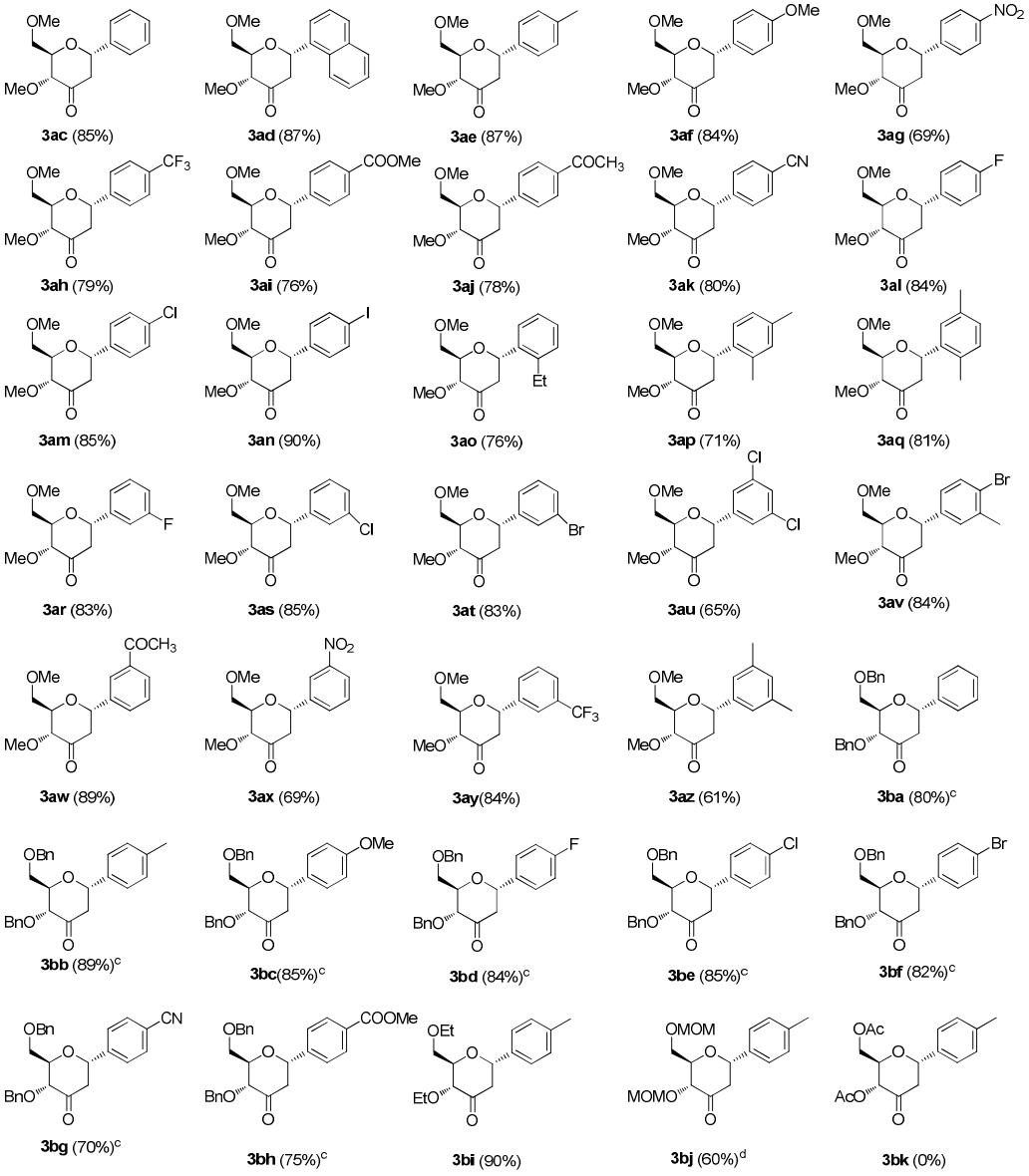
[a]**Reaction condition**: Glucal **1aa** (95 mg, 0.5 mmol) and diazonium salt **2ab** (125 mg, 0.55 mmol, 1.1 equiv.) were stirred in a solvent (4 mL) following which the catalyst (0.025 mmol) was added. [b]Isolated yield.

2.4 Substrates Scope

Having established the optimized condition, the reaction of permethylated glucal (**1aa**) with different aryldiazonium tetrafluoroborates was investigated and the results are summarized in (**Table 2.3**). The un-substituted phenyl and naphthyldizaonium salts as well as aryldizaonium salts bearing electron donating and withdrawing groups at the *para*- position underwent coupling reaction with glucal and gave the desired products **3ac-3an** in 69-90% yields. It was observed that strongly electron withdrawing groups (e.g. NO_2, CF_3, CO_2Me, $COCH_3$ and CN) functionalized phenyldiazonium salts gave the desired products (*i.e.***3ag-3ak**) in slightly lower yields (i.e. 69-80%).

Table 2.3 Reaction of protected glucal with different aryldiazonium salts.[a,b]





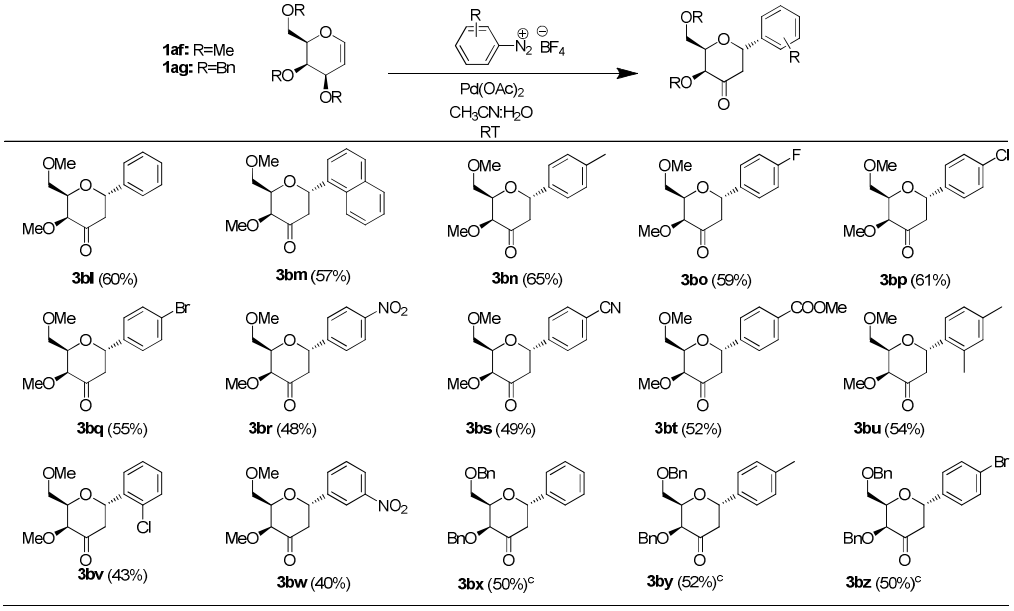
[a]**Reaction condition:** Glucal (0.5 mmol) and diazonium salt (1.1 equiv.) were stirred in CH_3CN:H_2O (4 mL, 3:1) following which the catalyst $Pd(OAc)_2$ (5.5 mg, 0.025 mmol) was added. [b]Isolated yield.[c] Glucal (0.24 mmol) and $Pd(OAc)_2$ (11 mg, 0.025 mmol) was used. [d] Glucal (0.35 mmol) and $Pd(OAc)_2$ (8 mg, 0.035 mmol) was used

Further, the *C*-arylation of glucal **1aa** was investigated with sterically hindered, *i.e. ortho*-functionalized phenyldiazonium salts. To our delight, the reactions were preceded with efficiency similar to that of *para*-substituted diazonium salts and gave the desired products **3ao-3aq** in 71-81% yields. Likewise, *C*-arylation of glucal (**1aa**) with *meta*-substituted diazonium salts was successfully accomplished to obtain the desired products **3ar-3az** in 61-89% yields.

Having studied the reaction with permethylated glycal (**1aa)** with different diazonium tetrafluoroborate salts, we further investigated the coupling of benzyl, ethyl and MOM-protected glucals (**1ab**-**1ad**) with different diazonium salts. All these reactions were preceded smoothly and gave the 3-keto *C*-aryl glucals **3ba-3bj** in 60-90% yields, which demonstrates the broad scope of the methodology. However, glycosylation was unsuccessful with tri-*O*-acetyl-D-glucal (**1ae**) in the presence of 4-methylbenzenediazonium tetrafluoroborate under optimized conditions (Table 2.3, **3bk**).

Encouraged by the results obtained with differently protected glucals and diazonium salts, the reaction of protected galactal was studied under optimized conditions (**Table 2.4**). Initially, *C*-arylation of permethylated galactal (**1af**) was investigated with aryldiazonium tetrafluoroborates bearing electron donating and withdrawing groups. To our delight, *C*-aryl glycosylation proceeded smoothly at room temperature and resulted in the desired products **3bl-3bt** in 52-65% yields.

Table 2.4 Reaction of protected galactal with different aryl diazonium salts.[a,b]

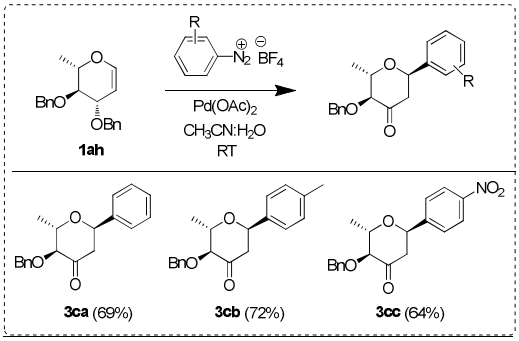


[a]**Reaction condition**: Galactal (0.5 mmol) and diazonium salt (1.1 equiv.) were stirred in CH_3CN:H_2O (4 mL, 3:1) following which the catalyst $Pd(OAc)_2$ (11 mg, 0.05 mmol) was added. [b]Isolated yield. [c] Glucal (0.24 mmol) and $Pd(OAc)_2$ (5.5 mg, 0.024mmol) was used.

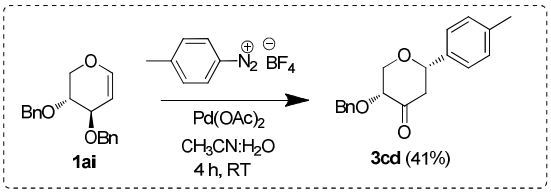
Similarly, sterically hindered *ortho*-substituted diazonium salts as well as *meta*-substituted diazonium salts also underwent glycosylation with galactal (**1ae**) and provided **3bu-3bw** in 40-55% yields. To increase scope of the methodology, perbenzylated galactal (**1ag**) was subjected for glycosylation with different diazonium salts, which provided the desired ketones **3bx**-**3bz** in >50% yields. Over all, it was observed that the reaction of galactals (**1af** and **1ag**) with aryldiazonium salts provided lower yields to that of glucals (**1aa**-**1ad**).

In order to study the versatility of this protocol, *C*-glycosylation of other hexose such as perbenzylated L-rhamnal and D-xylal (**1ah** and **1ai,** respectively) was investigated with different diazonim salts (**Table 2.5 and Scheme 2.1**).

Table 2.5 Reaction of benzyl protected L-rhamnal **1ah** with diazonium salts.[a,b]



[a]**Reaction condition**: Rhamnal (0.4 mmol) and diazonium salt (1.1 equiv.) were stirred in $CH_3CN:H_2O$ (4 mL, 3:1) following which the catalyst $Pd(OAc)_2$ (8 mg, 0.035 mmol) was added. [b]Isolated yield.

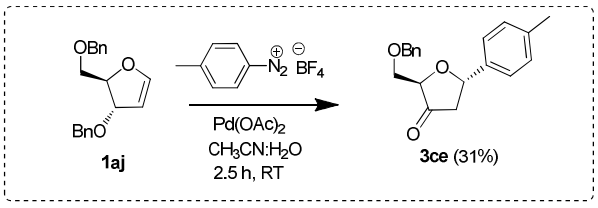


Scheme 2.1 Reaction of benzyl protected D-xylal **1ai** with 4-methylbenzenediazonium tetrafluoroborate

Similar to glucal, the reaction of L-rhamnal (**1ah**) with different diazonim salts proceeded smoothly under optimized conditions and gave the α-*C*-arylated products **3ca**-**3cc** in good to excellent yields (64-72%) (**Table 2.5**). Likewise, benzyl protected D-xylal (**1ai**) underwent *C*-arylation with 4-methylphenyldiazonium tetrafluoroborate successfully and gave the desired product **3cd** in 41% yield (**Scheme 2.1**).

Considering the biological significance of 2-deoxypentose sugars, 4-methylphenyldiazonium tetrafluoroborate was subjected for glycosylation with benzyl protected D-ribal (**1aj**). To our delight, similar to pyranose glycals, the desired 2,3-deoxy 3-keto α-*C*-glycosylated product **3ce** was obtained in 31% yield under optimized

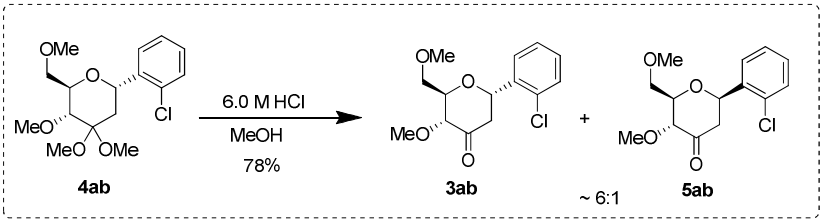
condition (**Scheme 2.2**). Overall, this protocol shows excellent substrate scope in *C*-aryl glycosylation reactions.



Scheme 2.2 Reaction of benzyl protected D-ribal **1aj** with 4-methylbenzenediazonium tetrafluoroborate

2.5 Acetal Deprotection and Epimerization of α-Aryl-*C*-Glycosides.

Of the two anomers of aryl-*C*-glycosides (i.e. α/β), β-isomerswere most commonly found in natural products [2].While attempting hydrolysis of dimethyl acetal **4ab**, we observed a mixture of anomeric products **3ab** (α-isomer) and **5ab** (β-isomer) in 6:1 ratio (**Scheme 2.3**).



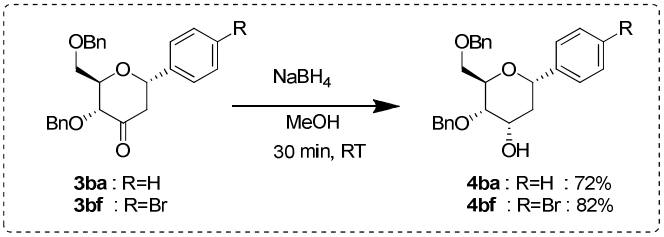
Scheme 2.3 Acid catalyzed hydrolysis of dimethyl acetal **4ab**

We propose that this acid catalyzed anomerization might be useful for the preparation of β-aryl-*C*-glycosides from corresponding α-glycosides.

2.6 Synthetic Application of the 2,3-Deoxy-3-Keto-α-Aryl-*C*-Glycosides

The resulted ketone compounds (*i.e.***3aa-3ce**) are expected to have wide applications in carbohydrate synthesis. For instance, these compounds can serve as the starting materials for the preparation of 2-deoxy *C*-aryl glycosides. Thus, we have attempted the

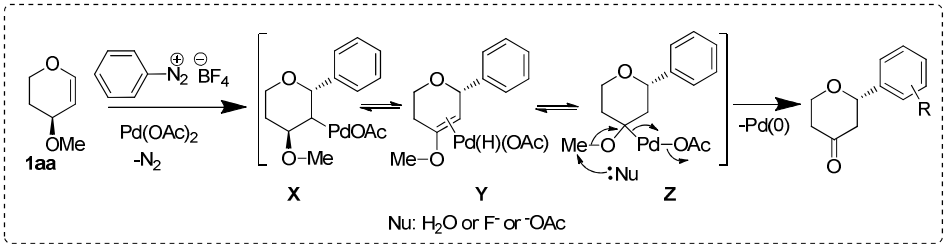
reduction of the ketones **3ba** and **3bf** using sodium borohydride in methanol. To our delight, the reaction proceeded smoothly at room temperature and gave 2-deoxy-α-aryl D-allose derivatives **4ba** and **4bf** in >70%, as a single isomer (**Scheme 2.4**) [14].



Scheme 2.4 Reduction of **3ba** and **3bf** using sodium borohydride.

2.7 Plausible Reaction Mechanism

A plausible mechanism of the palladium catalyzed *C*-arylation of glycal is shown in (**Scheme 2.5**) [11]. At first, the oxidative addition of the palladium to the aryldiazonium salt in the presence of glycal provides the intermediate **X** which undergoes β-elimination to form palladium enol ether **Y** [11c]. Palladium-hydride reinsertion provides the intermediate **Z** which undergoes reductive elimination to provide the desired ketone and palladium (0).



Scheme 2.5 Plausible mechanism for palladium catalyzed *C*-arylation of glycals

2.8 Summary and Conclusion

In summary, we have demonstrated a new reaction of diazonium salts with glycals in the presence of palladium catalysts. A wide range of glycals including protected D-

glucals, D-galactals, L-rhamanal, D-xylal and D-ribal underwent stereocontrolled *C*-glycosylation with different aryldiazonium tetrafluoroborates in the presence of 5-10 mol% of palladium acetate at room temperature. All the reactions provide 2,3-deoxy-3-keto α-aryl *C*-glycosides in good to excellent yields in a stereo-controlled manner under optimized condition. This simple method does not require base or ligand or additives, and thus providing scope for wide applications in organic synthesis

2.9 Experimental Section

2.9.1. Preparation of 3,4,6-tri-*O*-methyl-D-glucal (1aa): [15]

The commercially available 3,4,6-tri-*O*-acetyl-D-glucal (**1ae**) (5 g, 18.3 mmol) was stirred in MeOH (150 mL) at 0^{o}C to which NaOMe (108 mg, 2.0 mmol) was added. The mixture was stirred for 3 h and the solvent was evaporated to dryness. To the same flask, dry DMF (100 mL) was added and cooled to 0 ^{o}C after which NaH (3.6 g, 60% in mineral oil, 91 mmol) was added portion wise. The resulting mixture was stirred for 30 min at the same temperature to which methyl iodide (5.2mL, 80 mmol) was added slowly dropwise. The resulting mixture was stirred for overnight and quenched by saturated aqueous NH_4Cl (15 mL) and diluted with ethyl acetate (500 mL). The organic phase was washed with H_2O, brine, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by column chromatography (SiO_2, hexane: ethyl acetate =4:1) to afford **1aa** as a colorless oil in 80% yield (2.45 g). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.34 (d, *J* = 5.5 Hz, 1H), 4.78-4.77 (m, 1H), 3.91 (m, 1H), 3.83 (m, 1H), 3.64-3.57 (m, 2H), 3.49 (s, 3H), 3.41 (t, *J* = 7.0 Hz, 1H), 3.36-3.35 (m, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 144.4, 99.4, 76.5, 76.1, 75.7, 70.6, 59.1, 59.0, 55.6.

2.9.2. Preparation of tri-*O*-benzyl- D-glucal (1ab): [15]

The commercially available 3,4,6-tri-*O*-acetyl-D-glucal (1 g, 3.6 mmol) was stirred in MeOH (30 mL)at 0^{o}C to which NaOMe (22 mg, 0.2 mmol) was added. The mixture was stirred for 3 h and the solvent was evaporated to dryness. To the same flask, dry DMF (15 mL) was added and cooled to 0 ^{o}C followed by NaH (720 mg, 60% in mineral oil, 18 mmol) was added portion wise. The mixture was stirred for 20 min at the same temperature to which benzyl bromide (1.8mL, 16 mmol) was added slowly drop wise. The resulting mixture was stirred for overnight and quenched by saturated aqueous NH_4Cl (6 mL) and diluted with ethyl acetate (250 mL). The organic phase was washed with H_2O, brine, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by column chromatography (SiO_2, hexane: ethyl acetate = 20:1) to afford **1ab** as a white solid in 87% yield (1.3 g). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.38-7.26 (m, 15H), 6.43 (d, *J* = 5.5 Hz, 1H), 4.89-4.88 (m, 1H), 4.84 (d, *J* = 11.5 Hz, 1H), 4.65 (d, *J* = 12.0 Hz, 2H), 4.59-4.55 (m, 3H), 4.22 (m, 1H), 4.07 (m, 1H), 3.87 (t, *J* = 7.0 Hz, 1H), 3.83-3.76 (m, 2H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 144.6, 138.3, 138.1, 137.9, 128.3, 128.3, 128.3, 127.8, 127.7, 127.7, 127.6, 99.9, 76.7, 75.7, 74.3, 73.7, 73.4, 70.4, 68.4.

2.9.3. Preparation of 3,4,6-tri-*O*-ethyl-D-glucal (1ac): [16]

The compound **1ac** is prepared using the literature procedure employed for the preparation of **1aa**. To a solution of commercially available 3,4,6-tri-*O*-acetyl-D-glucal **1ag** (500 mg, 1.8 mmol) in MeOH (15 mL), NaOMe (10.8 mg, 0.2 mmol) was added at 0^{o}C. The mixture was stirred for 3 h and evaporated to dryness. To the same flask, dry

DMF (10 mL) was added and cooled to 0 ^{o}C followed by NaH (360 mg, 60% in mineral oil, 9 mmol) was added portion wise. The mixture was stirred for 20 min at the same temperature to which ethyl bromide (0.6 mL, 9 mmol) was added slowly drop wise. The resulting mixture was stirred for overnight and quenched by saturated aqueous NH_4Cl (3 mL) and diluted with ethyl acetate (180 mL). The organic phase was washed with H_2O, brine, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by column chromatography (SiO_2, hexane: ethyl acetate = 4:1) to afford **1ac** as a colorless oil in 75% yield (310 mg). NMR spectra were identical with literature data.[17] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.34 (d, *J* = 5.5 Hz, 1H), 4.76-4.75 (m, 1H), 3.95-3.90 (m, 2H), 3.81 (t, *J* = 7.5, 1H), 3.68 (s, 2H), 3.65-3.61 (m, 2H), 3.57-3.48 (m, 4H), 1.20-1.17 (m, 9H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 144.3, 100.4, 76.8,76.0, 74.7, 68.9, 67.1, 66.8, 63.9, 15.6, 15.5, 15.0.

2.9.4. Preparation of 3,4,6-tri-*O*-methoxymethyl-D-glucal (1ad): [18]

To a solution of commercially available 3,4,6-tri-*O*-acetyl-D-glucal **1ag** (500 mg, 1.8 mmol) in MeOH (15 mL), NaOMe (10.8 mg, 0.2 mmol) was added at 0^{o}C. The mixture was stirred for 3 h and evaporated to dryness to obtain crude D-glucal. It was purified by a short silica chromatography using DCM-methanol. The pure D-glucal was dissolved in anhydrous DCM (20 mL) and cooled to 0^{o}C after which diisopropylethyl amine (2.0 mL, 11 mmol) was added followed by the dropwise addition of chloromethyl methyl ether (0.8 mL). The reaction mixture was allowed to stir for 12 h at room temperature and again diisopropylethyl amine (2.0 mL, 11 mmol) was added followed by the dropwise addition of chloromethyl methyl ether (0.8 mL). Further the

reaction was allowed to stir for 12 h and diluted with DCM (100 ml).The organic layer was washed with solution of 1M HCl (50 mL), $NaHCO_3$ (50 mL), dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The crude product was purified by column chromatography (SiO_2, hexane:ethyl acetate = 20:1) to afford **1ad** as a colorless oil in 60% yield (300 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.37(d, *J* = 5.5 Hz, 1H), 4.84 (m, 1H), 4.78 (d, *J* = 6.0 Hz, 1H), 4.71 (d, *J* = 6.5 Hz, 1H), 4.67 (s, 2H), 4.63 (s, 2H), 4.13-4.08 (m, 2H), 3.83-3.77 (m, 3H), 3.37 (s, 3H), 3.34 (s, 6H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 144.1, 99.9, 96.6, 96.5, 95.3, 76.1, 72.5, 71.6, 65.7, 55.9, 55.4, 55.2.

2.9.5. Preparation of 3,4,6-tri-*O*-methyl- D-galactal (1af): [15]

The commercially available 3,4,6-tri-*O*-acetyl-D-galactal (**1ae**) (2g, 7.2 mmol) was stirred in MeOH (40 mL) at 0^{o}C to which NaOMe (44 mg, 0.8 mmol) was added. The mixture was stirred for 3 h and the solvent was evaporated to dryness. To the same flask, dry DMF (25 mL) was added and cooled to 0 ^{o}C to which NaH (1.5 g, 60% in mineral oil, 36 mmol) was added portion wise. The mixture was stirred for 30 min at the same temperature to which methyl iodide (2.6 mL, 40 mmol) was added slowly drop wise. The resulting mixture was stirred for overnight and quenched by saturated aqueous NH_4Cl (7 mL) and diluted with ethyl acetate (250 mL). The organic phase was washed with H_2O, brine, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by column chromatography (SiO_2, hexane:ethyl acetate = 4:1) to afford **1af** as a colorless oil in 74% yield (1.05 g). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.28 (d, *J* = 6.0 Hz, 1H), 4.77-4.75 (m, 1H), 4.11 (m, 1H),

3.92 (s, 1H), 3.65-3.63 (m, 2H), 3.55-3.52 (m, 1H), 3.50 (s, 3H), 3.36 (s, 3H), 3.34 (s, 3H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 143.8, 99.1, 74.9, 73.4, 72.1, 70.3, 59.6, 58.9, 56.4.

2.9.6. Preparation of 3,4,6-tri-*O*-benzyl-D-galactal (1ag): [15]

The commercially available 3,4,6-tri-*O*-acetyl-D-galactal (1g, 3.6 mmol) was stirred in MeOH (25 mL) at 0^{o}C to which NaOMe (22 mg, 0.4 mmol) was added. The mixture was stirred for 3 h and the solvent was evaporated to dryness. To the same flask, dry DMF (10 mL) was added and cooled to 0 ^{o}C followed by NaH (720 mg, 60% in mineral oil, 18 mmol) was added portion wise. The mixture was stirred for 20 min at the same temperature to which benzyl bromide (1.8 mL, 16 mmol) was added slowly dropwise. The resulting mixture was stirred for overnight and quenched by saturated aqueous NH_4Cl (3 mL) and diluted with ethyl acetate (250 mL). The organic phase was washed with H_2O, brine, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by column chromatography (SiO_2, hexane:ethyl acetate = 9:1) to afford **1ag** as a white solid in 73% yield (1.1 g). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.40-7.32 (m, 15H), 6.43 (d, *J* = 6.0 Hz, 1H), 4.95-4.92 (m, 2H), 4.71-4.65 (m, 3H), 4.56 (d, *J* = 12.0Hz, 1H), 4.48 (d, *J* = 12.0 Hz, 1H), 4.24 (m, 2H), 4.00 (s, 1H), 3.85 (t, *J* = 9.0 Hz, 1H), 3.72 (dd, *J* = 9.5, 4.5 Hz, 1H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 144.0, 138.3, 138.2, 137.8, 128.2, 128.2, 128.0, 127.7, 127.5, 127.4, 127.3, 99.8, 75.5, 73.2, 73.1, 71.1, 70.7, 70.6, 68.3.

2.9.7. Preparation of 3,4-di-*O*-benzyl-L-rhamnal (1ah): [19]

L-Rhamnose (5.0 g, 30.5 mmol) was suspended in acetic anhydride (22 mL) and cooled to 0 ^{o}C after which perchloric acid (0.25 mL) was added dropwise. The mixture was

allowed to stir for 3 h at room temperature and cooled to 0 ^{o}C to which hydrobromic acid (44 mL, 33% in AcOH) was added dropwise. The resulting mixture was stirred for overnight at room temperature and concentrated. The crude glycopyranosyl bromide was dissolved in CH_3CN and then Zinc dust (15 g, 228 mmol) and ammoniumchloride (12 g, 228 mmol) were added and stirred at 60^{o}C for 2.5 h. Upon completion of the reaction, the reaction mixture is filtrated and the filtrate was concentrated and purified by column chromatography (SiO_2, hexane:ethyl acetate = 2:1) to afford3,4-di-*O*-acetyl-L-rhamnose as colorless oil in 75% yield (4.9 g). To a solution of 3,4-di-O-acetyl-L-rhamnal (1 g, 4.6 mmol) in THF (30 mL), NaOH (736 mg, 18.4 mmol,), TBAI (50 mg, 0.13 mmol) and benzyl bromide (2.2 mL, 18.4 mmol) were added successively and the reaction mixture was allowed to stir for 5 h at room temperature. After completion, the reaction mixture was diluted with water and extracted with DCM. The organic layer was washed with water, dried over anhydrous Na_2SO_4, and evaporated. The crude residue was purified by column chromatography (SiO_2, hexane:ethyl acetate = 2:1) to afford 3,4-di-*O*-benzyl-L-rhamnose **1ah** as colourless oil in 50% yield (720 g). [19b] **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39-7.31 (m, 10H), 6.39 (d, *J* = 5.5 Hz, 1H), 4.92-4.88 (m, 2H), 4.73 (d, *J* = 11.5 Hz, 1H), 4.69 (d, *J* = 11.5 Hz, 1H), 4.60 (d, *J* = 11.5 Hz, 1H), 4.24 (d, *J* = 6.0 Hz, 1H), 3.99-3.97 (m, 1H), 3.51 (t, *J* = 7.5 Hz, 1H), 1.41 (d, *J* = 6.5 Hz, 3H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 144.7, 138.3, 138.2, 128.3, 127.9, 127.7, 127.7, 127.5, 100.0, 79.4, 76.3, 74.0, 73.9, 70.4, 17.4.

2.9.8. Preparation of 3,4-di-*O*-benzyl-D-xylal (1ai): [19]

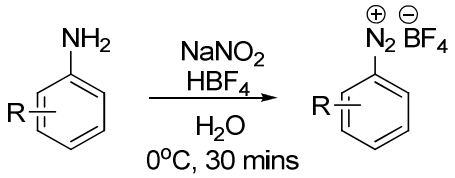
D-xylose (5.0 g, 33.5 mmol) was suspended in acetic anhydride (25 mL), perchloric acid (0.3 mL) was added dropwise at 0 ^{o}C. The mixture was allowed to stir for 3 h at room temperature and cooled to 0 ^{o}C to which hydrobromic acid (48 mL, 33% in AcOH) was added dropwise. The resulting mixture was stirred for overnight at room temperature and concentrated. The crude glycopyranosyl bromide was dissolved in CH_3CN and then Zinc dust (15 g, 228 mmol) and ammoniumchloride (12 g, 228 mmol) were added and stirred at 60^{o}C for 2.5 h. Upon completion of the reaction, the reaction mixture is filtrated and the filtrate was concentrated and purified by column chromatography (SiO_2, hexane:ethyl acetate = 2:1) to afford 3,4-di-*O*-acetyl-D-xylal as colorless oil in 50% yield (3.3 g). To a solution of 3,4-di-*O*-acetyl-D-xylal (1 g, 5 mmol) in THF (30 mL), NaOH (736 mg, 18.4 mmol,), TBAI (50 mg, 0.13 mmol) and benzyl bromide (2.2 mL, 18.4 mmol) were added successively and the reaction mixture was allowed to stir for 3 h at room temperature. After completion, the reaction mixture was diluted with water and extracted with DCM. The organic layer was washed with water, dried over anhydrous Na_2SO_4, and evaporated. The crude residue was purified by column chromatography (SiO_2, hexane:ethyl acetate = 9:1) to afford 3,4-di-*O*-benzyl-D-xylal **1ai** as colourless oil in 51% yield (743mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36-7.30 (m, 10H), 6.57 (d, *J* = 5.5 Hz, 1H), 4.96 (m, 1H), 4.68-4.65 (m, 2H), 4.62 (d, *J* = 11.5 Hz, 1H), 4.54 (d, *J* = 11.5 Hz, 1H), 4.13 (d, *J* = 11.5 Hz, 1H), 3.98 (d, *J* = 12.0 Hz, 1H), 3.86 (s, 1H), 3.69 (s, 1H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 146.6, 138.3, 137.8, 128.4, 128.3, 127.8, 127.7, 127.6, 127.6, 98.9, 72.6, 71.2, 69.9, 69.0, 63.9.

2.9.9. Preparation of 3,5-di-*O*-benzyl-D-ribal (1aj): [20]

D-Ribose (3.0 g., 20 mmol) was suspended in DCM (20 mL) to which acetic anhydride (11.23 g., 110 mmol) followed by pyridine (9.49 g., 120 mmol) was added at 0 ^{o}C. The resulting mixture was stirred for 12 hours at room temperature and quenched with water (20 mL). The aqueous layer was extracted with DCM (2X30 mL), washed with water, dried over saturated Na_2SO_4 and concentrated. The crude product was purified by short silica chromatography using 20% ethyl acetate in hexane to obtain D-ribofuranose 1,2,3,5-tetraacetate. Further, the ribose tetra-acetate was dissolved in HBr solution (33 wt % in acetic acid, 10.36 mL, 60 mmol) and stirred for 5 hours at room temperature. The reaction mixture was diluted with acetonitrile (25 mL) to which sodium acetate (3.28 g., 40 mmol), ammonium chloride (3.21 g., 60 mmol), and zinc dust (3.93 g., 40 mmol) were added successively. The reaction is allowed to stir for 2 hours at room temperature, then quenched with water, extracted with ethyl acetate (3X25 mL). The organic layer was washed with water, dried over anhydrous Na_2SO_4 and concentrated. The crude residue was purified by column chromatography (SiO_2, hexane:ethyl acetate= 9:1) to obtain 3,5-di-*O*-acetyl-D-ribal in 27.5 % yield. (1.1 g). To a solution of 3,5-di-*O*-acetyl-D-ribal (1 g, 5 mmol) in THF (25 mL), NaOH (736 mg, 18.4 mmol,), TBAI (50 mg, 0.13 mmol) and benzyl bromide (2.2 mL, 18.4 mmol) were added successively and the reaction mixture was allowed to stir for 3 h at room temperature. After completion, the reaction mixture was diluted with water and extracted with DCM. The organic layer was washed with water, dried over anhydrous Na_2SO_4, and evaporated. The crude residue was purified by column chromatography (SiO_2, hexane:ethyl acetate = 9:1) to afford 3,5-di-*O*-benzyl-D-ribal **1aj** as colourless oil in

55% yield (801 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.40-7.29 (m, 10H), 6.41 (d, *J* = 5.0 Hz, 1H), 4.88-4.87 (m, 1H), 4.72 (s, 2H), 4.69 (d, *J* = 12.0 Hz, 1H), 4.61 (d, *J* = 12.0 Hz, 1H), 4.09-4.39 (m, 3H), 3.76-3.74 (m, 1H).^{13}C NMR (125 MHz, $CDCl_3$) δ 146.5, 138.7, 137.9, 128.4, 128.3, 127.8, 127.7, 127.6, 127.5, 98.7, 73.1, 71.0, 70.7, 66.6, 63.2.

2.9.10. Preparation of aryldiazonium tetrafluoroborates:



Aryldiazonium tetrafluoroborates were prepared using literature procedure. [21] To a stirred solution of aniline (10 mmol) in 48% aq. HBF_4 (4 ml), a solution of $NaNO_2$ (0.69 g in 5 ml of deionized water, 10 mmol) was added at 0°C. The reaction mixture was stirred at 700 RPM for 30 min at 0°C. The resulting solid was filtered off, dissolved in 5 ml of acetone and precipitated by addition of 5 ml of diethyl ether. The resulting crystals were dried in high vacuum to obtain pure aryldiazonium tetrafluoroborates. All the compounds gave identical NMR spectra to those reported previously. 4-bromobenzenediazonium tetrafluoroborate **2aa** [21] (pink solid, 72%); 2-chlorobenzenediazonium tetrafluoroborate **2ab** [21] (white solid, 64%); benzenediazonium tetrafluoroborate **2ac** [21] (white solid, 70%); 1-napthyldiazonium tetrafluoroborate **2ad** [22] (Purple solid, 55%); 4-methylbenzenediazonium tetrafluoroborate **2ae** [21] (white solid, 80%); 4-methoxybenzenediazonium tetrafluoroborate **2af** [22] (white solid, 75%); 4-nitrobenzenediazonium

tetrafluoroborate **2ag** [21] (yellow solid, 69%); 4-(trifluoromethyl)benzenediazonium tetrafluoroborate **2ah** [23] (white solid, 70%); 4-(methoxycarbonyl)benzenediazonium tetrafluoroborate **2ai** [21] (white solid, 30%); 4-acetylbenzenediazonium tetrafluoroborate **2aj** [22] (white solid, 75%); 4-cyanobenzenediazonium tetrafluoroborate **2ak** [21] (light yellow solid, 70%); 4-fluorobenzenediazonium tetrafluoroborate **2al** [21] (white solid, 69%); 4-chlorobenzenediazonium tetrafluoroborate **2am** [24] (white solid, 80%); 4-iodobenzenediazonium tetrafluoroborate **2an** [25] (brown solid, 80%); 2-ethylbenzenediazonium tetrafluoroborate **2ao** [26] (white solid, 64%); 2,4-dimethylbenzenediazonium tetrafluoroborate **2ap** [27] (white solid, 60%); 2,5-dimethylbenzenediazonium tetrafluoroborate **2aq** [16] (white solid, 70%); 3-fluorobenzenediazonium tetrafluoroborate **2ar** [28] (white solid, 40%); 3-chlorobenzenediazonium tetrafluoroborate **2as** [21] (pink solid,59%); 3-bromobenzenediazonium tetrafluoroborate **2at** [25] (orange solid, 65%); 3,5-dichlorobenzenediazonium tetrafluoroborate **2au** [28] (white solid, %); 4-bromo-3-methylbenzenediazonium tetrafluoroborate **2av** [27] (white solid, 30%); 3-acetylbenzenediazonium tetrafluoroborate **2aw** [27] (white solid, 54%); 3-nitrobenzenediazonium tetrafluoroborate **2ax** [28] (white solid, 50%); 3-(trifluoromethyl)benzenediazonium tetrafluoroborate**2ay** [29] (Pink solid, 65%); 3,5-dimethylbenzenediazonium tetrafluoroborate **2az** [28] (white solid, 20%); 2,4-dimethoxybenzenediazonium tetrafluoroborate **2ba** [30] (purple solid, 60%).

2.9.11 General procedure used in the optimization table

The glycal, 3,4,6-tri-*O*-methyl-D-glucal (95 mg, 0.5 mmol) was stirred in an appropriate solvent (4 mL) in oven dried 25 ml round bottom flask. 4-Bromobenzenediazoniumtetrafluoroborate (152 mg, 0.56 mmol) and palladium acetate (5.5 mg, 0.05 mmol) was successively added at room temperature under open air atmosphere. The mixture was stirred and monitored by TLC. After completion (or appropriate time mentioned in the table), the reaction mixture was diluted with ethyl acetate (150 mL) and washed with water (100 mL) and filtered, dried over anhydrous Na_2SO_4, The organic layer was concentrated and purified by silica column chromatography (100-200 mess) on silica gel using 20 % ethyl acetate in hexane which furnished **3aa** as white foam.

2.9.12. General procedure for the preparation of *C*-glycosides:

Glycal (0.25-0.5 mmol) was dissolved in acetonitrile (3 mL) to which water (1 mL) was added. To the above solution, aryldiazoniumtetrafluoroborate (1.1 equiv.) and palladium acetate (5-10 mol%) were successively added at room temperature under open air atmosphere. The reaction mixture was stirred for appropriate time (2-8 h), diluted with ethyl acetate (150 mL) and washed with water (100 mL). The organic layer was filtered, dried over anhydrous Na_2SO_4, concentrated and purified by silica column chromatography (100-200 mess) on silica gel using ethyl acetate in hexane.

2.10 Analytical Data of the Synthesized Aryl-*C*-Glycoside Products

2.10.1. (*2R,3R,6S*)-6-(4-Bromophenyl)-3-methoxy-2-(methoxymethyl)dihydro-2H-pyran-4(3H)-one [3aa]

The compound **3aa** was prepared using the general procedure and completed in 1.5 h. Column chromatography purification was performed using 20 % ethyl acetate in hexane which furnished **3aa** as white foam (147 mg, 90%); TLC R_f = 0.35 (35 % ethyl acetate in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.5 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 5.34-5.32 (m, 1H), 3.88 (d, *J* = 8.0 Hz, 1H), 3.54-3.49 (m, 3H), 3.42 (s, 3H), 3.35 (s, 3H), 2.99-2.92 (m, 2H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 206.1, 137.4, 131.8, 129.1, 122.3, 81.6, 74.6, 74.6, 71.5, 59.4, 59.4, 43.6. **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{14}H_{18}BrO_4$ 329.0388; found, 329.0359.

2.10.2. (*2R,3R,6S*)-6-(2-Chlorophenyl)-3-methoxy-2-(methoxymethyl)dihydro-2H-pyran-4(3H)-one [3ab]

The compound **3ab** was prepared using the general procedure and completed in 1.5 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished **3ab** as colourless semi solid (126 mg, 89%); TLC R_f = 0.40 (35 % ethyl acetate in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41-7.39 (m, 1H), 7.31-7.29 (m, 1H), 7.20-7.16 (m, 2H), 5.64 (t, *J* = 5.5 Hz, 1H), 3.87 (d, *J* = 7.0 Hz, 1H), 3.77-3.74 (m, 1H), 3.57-3.51 (m, 2H), 3.43 (s, 3H), 3.32 (s, 3H), 2.91 (dd, *J* = 15.0, 5.5 Hz, 1H), 2.78 (dd, *J* = 15.0, 6.0 Hz, 1H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 206.4, 136.9, 133.3, 129.9, 129.4, 128.2, 126.8, 81.4, 75.5, 71.9, 71.9, 59.3, 59.0, 44.3. **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{14}H_{18}ClO_4$ 285.0894; found, 285.0868.

2.10.3. (*2R,3R,6S*)-3-Methoxy-2-(methoxymethyl)-6-phenyldihydro-2H-pyran-4(3H)-one [3ac]

The compound **3ac** was prepared using the general procedure and completed in 2 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished **3ac** as white foam (107 mg, 85%); TLC R_f = 0.5 (35 % ethyl acetate in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31-7.25 (m, 4H), 7.22-7.19 (m, 1H), 5.39-5.38 (m, 1H), 3.89 (d, *J* = 8.0 Hz, 1H), 3.54-3.49 (m, 3H), 3.43 (d, *J* = 2.0 Hz, 3H), 3.35 (d, *J* = 2.0 Hz, 3H), 3.05-2.93 (m, 2H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 206.4, 138.3, 128.6, 128.0, 127.3, 81.6, 75.1, 74.2, 71.4, 59.4, 59.3, 43.6. **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{14}H_{19}O_4$ 251.1283; found, 251.1265.

2.10.4. (*2R,3R,6S*)-3-Methoxy-2-(methoxymethyl)-6-(naphthalen-1-yl)dihydro-2H-pyran-4(3H)-one [3ad]

The compound **3ad** was prepared using the general procedure and completed in 2 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished **3ad** as white foam (131 mg, 87%); TLC R_f = 0.48 (35 % ethyl acetate in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.0 Hz, 1H), 7.77-7.71 (m, 2H), 7.49 – 7.27 (m, 4H), 6.03-6.02 (m, 1H), 4.01 (d, *J* = 9.0 Hz, 1H), 3.46 (s, 3H), 3.40-3.38 (m, 1H), 3.32-3.30 (m, 5H), 3.18-3.11 (m, 2H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 207.6, 133.9, 133.5, 131.5, 129.5, 128.5, 126.3, 126.2, 125.9, 124.8, 124.7, 81.5, 73.8, 72.8, 71.1, 59.7, 59.3, 44.1. **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{18}H_{21}O_4$ 301.1440; found, 301.1437.

2.10.5 (*2R,3R,6S*)-3-Methoxy-2-(methoxymethyl)-6-p-tolyldihydro-2H-pyran-4(3H)-one [3ae]

The compound **3ae** was prepared using the general procedure and completed in 2 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished **3ae** as white foam (116 mg, 87%); TLC R_f = 0.4 (15 % ethyl acetate in chloroform); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.18 (d, *J* = 7.8 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 5.36 (d, *J* = 6.0 Hz, 1H), 3.88 (d, *J* = 9.5 Hz, 1H), 3.52-3.46 (m, 3H), 3.42 (s, 3H), 3.34 (s, 3H), 3.02-2.93 (m, 2H), 2.24 (s, 3H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 206.7, 137.9, 135.2, 129.2, 127.4, 81.6, 75.0, 73.9, 71.4, 59.5, 59.3, 43.7, 20.9. **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{15}H_{21}O_4$ 265.1440; found, 265.1417.

2.10.6. (*2R,3R,6S*)-3-Methoxy-2-(methoxymethyl)-6-(4-methoxyphenyl)dihydro-2H-pyran-4(3H)-one [3af]

The compound **3af** was prepared using the general procedure and completed in 2 h. Column chromatography purification was performed using 20 % ethyl acetate in hexane which furnished **3af** as white foam (118 mg, 84%); TLC R_f = 0.28 (35 % ethyl acetate in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.0 Hz, 2H), 6.79-6.77 (m, 2H), 5.35 (dd, *J* = 6.5, 2.5 Hz, 1H), 3.89-3.87 (m, 1H), 3.70 (s, 3H), 3.53-3.47 (m, 3H), 3.43 (s, 3H), 3.34 (s, 3H), 3.01-2.93 (m, 2H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 206.8, 159.3, 130.3, 128.8, 113.9, 81.7, 74.8, 73.8, 71.4, 59.5, 59.3, 55.1, 43.7. **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{15}H_{21}O_5$ 281.1389; found, 281.1370

2.10.7. (*2R,3R,6S*)-3-Methoxy-2-(methoxymethyl)-6-(4-nitrophenyl)dihydro-2H-pyran-4(3H)-one [3ag]

The compound **3ag** was prepared using the general procedure and completed in 4 h. Column chromatography purification was performed using 25 % ethyl acetate in hexane

which furnished **3ag** as white foam (98 mg, 69%); TLC R_f = 0.25 (35 % ethyl acetate in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 5.44 (t, *J* = 4.5 Hz, 1H), 3.88 (d, *J* = 7.5 Hz, 1H), 3.61-3.57 (m, 3H), 3.41 (s, 3H), 3.35 (s, 3H), 3.02-2.94 (m, 2H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 205.0, 147.5, 145.9, 127.9, 123.8, 81.4, 75.7, 74.4, 71.7, 59.3, 59.2, 43.7. **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{14}H_{18}NO_6$ 296.1134; found, 296.1108.

2.10.8. (*2R,3R,6S*)-3-Methoxy-2-(methoxymethyl)-6-(4-(trifluoromethyl)phenyl) dihydro-2H-pyran-4(3H)-one [3ah]

The compound **3ah** was prepared using the general procedure and completed in 2 h. Column chromatography purification was performed using 20 % ethyl acetate in hexane which furnished **3ah** as viscous oil (127 mg, 79%); TLC R_f = 0.30 (35 % ethyl acetate in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.5 Hz, 2H), 7.44 (d, *J* = 7.5 Hz, 2H), 5.41 (m, 1H), 3.88 (d, *J* = 7.0 Hz, 1H), 3.54 (m, 3H), 3.41 (s, 3H), 3.35 (s, 3H), 3.03-2.94 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 205.6, 142.5, 130.4 (q, $J_{C\text{-}F}$ = 32.5 Hz), 127.5, 126.7 (q, $J_{C\text{-}F}$ = 3.8 Hz), 123.8 (q, $J_{C\text{-}F}$ = 272 Hz), 81.5, 75.2, 74.6, 71.6, 59.3, 59.3, 43.7.**HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{15}H_{18}F_3O_4$ 319.1157; found, 319.1139.

2.10.9. Methyl 4-((*2S,5R,6R*)-5-methoxy-6-(methoxymethyl)-4-oxotetrahydro-2H-pyran-2-yl)benzoate [3ai]

The compound **3ai** was prepared using the general procedure and completed in 2 h. Column chromatography purification was performed using 20 % ethyl acetate in hexane which furnished **3ai** as white foam (118 mg, 76%); TLC R_f = 0.24 (35 % ethyl acetate in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.0 Hz,

2H), 5.41 (dd, *J* = 6.0, 3.5 Hz, 1H), 3.88 (d, *J* = 7.5 Hz, 1H), 3.84 (s, 3H), 3.53 (m, 3H), 3.41 (s, 3H), 3.35 (s, 3H), 3.04-2.94 (m, 2H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 205.9, 166.6, 143.5, 130.0, 129.9, 127.2, 81.6, 75.0, 74.9, 71.6, 59.4, 52.2, 43.7. **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{16}H_{21}O_6$ 309.1338; found, 309.1339.

2.10.10. (*2R,3R,6S*)-6-(4-Acetylphenyl)-3-methoxy-2-(methoxymethyl)dihydro-2H-pyran-4(3H)-one [3aj]

The compound **3aj** was prepared using the general procedure and completed in 3 h. Column chromatography purification was performed using 20 % ethyl acetate in hexane which furnished **3aj** as yellowish foam (115 mg, 78%); TLC R_f = 0.40 (15 % ethyl acetate in chloroform); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 5.41 (m, 1H), 3.88 (d, *J* = 8.0 Hz, 1H), 3.53 (s, 3H), 3.41 (s, 3H), 3.35 (s, 3H), 3.04-3.94 (m, 2H), 2.51 (s, 3H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 205.7, 197.4, 143.6, 136.6, 128.6, 127.3, 81.5, 75.0, 74.7, 71.5, 59.3, 59.3, 43.6, 26.5. **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{16}H_{21}O_5$ 293.1389; found, 293.1393.

2.10.11. 4-((*2S,5R,6R*)-5-Methoxy-6-(methoxymethyl)-4-oxotetrahydro-2H-pyran-2-yl)benzonitrile [3ak]

The compound **3ak** was prepared using the general procedure and completed in 2.5 h. Column chromatography purification was performed using 20 % ethyl acetate in hexane which furnished **3ak** as white foam (111 mg, 80%); TLC R_f = 0.26 (35 % ethyl acetate in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 5.40 (t, *J* = 5.0 Hz, 1H), 3.87 (d, *J* = 7.0 Hz, 1H), 3.59-3.55 (m, 3H), 3.41 (s, 3H), 3.35 (s, 3H), 3.00-2.93 (m, 2H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 205.3, 143.9, 132.5,

127.8, 118.3, 112.0, 81.4, 75.5, 74.6, 71.7, 59.4, 59.3, 43.6. **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{15}H_{18}NO_4$ 276.1236; found, 276.1229.

2.10.12. (*2R,3R,6S*)-6-(4-Fluorophenyl)-3-methoxy-2-(methoxymethyl)dihydro-2H-pyran-4(3H)-one [3al]

The compound **3al** was prepared using the general procedure and completed in 2 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished **3al** as white foam (114 mg, 84%); TLC R_f = 0.42 (35 % ethyl acetate in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32 (t, J=7.0 Hz, 2H), 6.99 (t, *J* = 8.0 Hz, 2H), 5.40 (m, 1H), 3.93 (d, *J* = 8.5 Hz, 1H), 3.58-3.50 (m, 3H), 3.47 (s, 3H), 3.39 (s, 3H), 3.07-2.98 (m, 2H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 206.3, 162.4 (d, J_{C-F} = 247.5 Hz), 134.2(d, J_{C-F} = 3.3 Hz), 129.3 (d, J_{C-F} = 8.2 Hz), 116.0 (d, J_{C-F} = 21.5 Hz), 81.6, 74.6, 74.4, 71.5, 59.5, 59.4, 43.8. **HRMS** (ESI-TOF) (m/z): $[M + Na]^+$ calcd for $C_{14}H_{17}FO_4Na$ 291.1009; found, 291.0985.

2.10.13. (*2R,3R,6S*)-6-(4-Chlorophenyl)-3-methoxy-2-(methoxymethyl)dihydro-2H-pyran-4(3H)-one [3am]

The compound **3am** was prepared using the general procedure and completed in 2 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished 3am as white foam (123 mg, 85%); TLC R_f = 0.42 (35 % ethyl acetate in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33 (s, 4H), 5.44-5.43 (m, 1H), 3.96 (d, *J* = 8.0 Hz, 1H), 3.62-3.55 (m, 3H), 3.51 (s, 3H), 3.43 (s, 3H), 3.08-3.01 (m, 2H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 206.1, 136.9, 134.1, 128.8, 128.8, 81.6, 74.6, 74.6, 71.5, 59.5, 59.4, 43.7. **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{14}H_{18}ClO_4$ 285.0894; found, 285.0870.

2.10.14. (*2R,3R,6S*)-6-(4-Iodophenyl)-3-methoxy-2-(methoxymethyl)dihydro-2H-pyran-4(3H)-one [3an]

The compound **3an** was prepared using the general procedure and completed in 2 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished **3an** as brownish foam (170 mg, 90%); TLC R_f = 0.63 (15 % ethyl acetate in chloroform); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.5 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 5.31 (m, 1H), 3.86 (d, *J* = 8.5 Hz, 1H), 3.56-3.51 (m, 3H), 3.41 (s, 3H), 3.34 (s, 3H), 2.97-2.90 (m, 2H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 205.9, 138.1, 137.7, 129.2, 94.0, 81.5, 74.7, 74.6, 71.5, 59.4, 59.3, 43.5. **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{14}H_{18}IO_4$ 377.0250; found, 377.0250.

2.10.15 (*2R,3R,6S*)-6-(2-Ethylphenyl)-3-methoxy-2-(methoxymethyl)dihydro-2H-pyran-4(3H)-one [3ao]

The compound **3ao** was prepared using the general procedure and completed in 2 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished **3ao** as semi solid (106 mg, 76%); TLC R_f = 0.47 (35 % ethyl acetate in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.20-7.17 (m, 3H), 7.07-7.04 (m, 1H), 5.59 (t, *J* = 4.5 Hz, 1H), 3.93 (d, *J* = 9.0 Hz, 1H), 3.50-3.41 (m, 6H), 3.32 (s, 3H), 2.94 (d, *J* = 4.5 Hz, 2H), 2.80-2.67 (m, 2H), 1.16 (t, *J* = 7.5 Hz, 3H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 207.7, 143.6, 135.8, 129.2, 128.7, 127.6, 125.7, 81.6, 73.9, 72.3, 71.6, 59.6, 59.4, 44.4, 25.1, 15.41. **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{16}H_{23}O_4$ 279.1596; found, 279.1575.

2.10.16. (*2R,3R,6S*)-6-(2,4-Dimethylphenyl)-3-methoxy-2-(methoxymethyl)dihydro -2H-pyran-4(3H)-one [3ap]

The compound **3ap** was prepared using the general procedure and completed in 2 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished **3ap** as white foam (100 mg, 71%); TLC R_f = 0.48 (35 % ethyl acetate in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.04 (d, *J* = 8.0 Hz, 1H), 6.94 (s, 1H), 6.85 (d, *J* = 7.5 Hz, 1H), 5.48 (t, *J* = 4.5 Hz, 1H), 3.91 (d, *J* = 9.0 Hz, 1H), 349-3.37 (m, 6H), 3.33 (s, 3H), 2.99-2.93 (m, 2H), 2.32 (s, 3H), 2.20 (s, 3H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 207.7, 138.2, 137.7, 133.3, 131.9, 127.6, 126.2, 81.6, 73.4, 72.8, 71.4, 59.6, 59.3, 44.0, 20.9, 19.4. **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{16}H_{23}O_4$ 279.1596; found, 279.1575.

2.10.17. (*2R,3R,6S*)-6-(2,5-Dimethylphenyl)-3-methoxy-2-(methoxymethyl)dihydro -2H-pyran-4(3H)-one [3aq]

The compound **3aq** was prepared using the general procedure and completed in 4 h. Column chromatography purification was performed using15 % ethyl acetate in hexane which furnished **3aq** as semi solid (113 mg, 81%); TLC R_f = 0.65 (15 % ethyl acetate in chloroform); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.00-6.99 (m, 2H), 6.94-6.93 (m, 1H), 5.48-5.47 (m, 1H), 3.91 (d, *J* = 9.0 Hz, 1H), 3.51-3.42 (m, 6H), 3.33 (s, 3H), 2.99-2.90 (m, 2H), 2.30 (s, 3H), 2.20 (s, 3H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 207.4, 136.3, 135.2, 134.4, 130.9, 129.0, 128.1, 81.8, 73.8, 72.9, 71.6, 59.6, 59.3, 44.0, 21.0, 19.1. **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{16}H_{23}O_4$ 279.1596; found, 279.1596.

2.10.18. (*2R,3R,6S*)-6-(3-Fluorophenyl)-3-methoxy-2-(methoxymethyl)dihydro-2H-pyran-4(3H)-one [3ar]

The compound **3ar** was prepared using the general procedure and completed in 3 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished **3ar** as brownish semi solid (112 mg, 83%);TLC R_f = 0.6 (15 % ethyl acetate in chloroform); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.25-7.21 (m, 1H), 7.06 (t, *J* = 8.5 Hz, 2H), 6.90 (t, *J* = 8.5 Hz, 1H), 5.35 (m, 1H), 3.88 (d, *J* = 7.5 Hz, 1H), 3.55-3.54 (m, 3H), 3.42 (s, 3H), 3.35 (s, 3H), 3.00-2.92 (m, 2H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 205.8, 162.9 (d, J_{C-F} = 247.0 Hz), 141.11 (d, J_{C-F} = 6.7 Hz), 130.2 (d, J_{C-F} = 8.2 Hz), 122.7 (d, J_{C-F} = 2.8 Hz) , 115.1 (d, J_{C-F} = 22.1 Hz), 114.4 (d, J_{C-F} = 22.1 Hz) 81.5, 74.8, 74.6, 71.5, 59.3, 59.3, 43.6. **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{14}H_{18}FO_4$ 269.1189; found, 269.1199.

2.10.19. (*2R,3R,6S*)-6-(3-Chlorophenyl)-3-methoxy-2-(methoxymethyl)dihydro-2H-pyran-4(3H)-one [3as]

The compound **3as** was prepared using the general procedure and completed in 3 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished **3as** as viscous oil (122 mg, 85%); TLC R_f = 0.46 (35 % ethyl acetate in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.20-7.16 (m, 3H), 5.33 (dd, *J* = 6.0, 3.5 Hz, 1H), 3.88 (d, *J* = 8.0 Hz, 1H), 3.58-3.54 (m, 3H), 3.42 (s, 3H), 3.35 (s, 3H), 2.99-2.90 (m, 2H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 205.7, 140.7, 134.8, 129.9, 128.3, 127.5, 125.2, 81.5, 74.9, 74.6, 71.6, 59.3, 43.7. **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{14}H_{18}ClO_4$ 285.0894; found, 285.0876.

2.10.20. (*2R,3R,6S*)-6-(3-Bromophenyl)-3-methoxy-2-(methoxymethyl)dihydro-2H-pyran-4(3H)-one [3at]

The compound **3at** was prepared using the general procedure and completed in 2.5 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished **3at** as brownish oil (138 mg, 83%); TLC R_f = 0.64 (15 % ethyl acetate in chloroform); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.48 (s, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.21 (m, *J* = 7.5 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 5.32 (m, 1H), 3.87 (d, *J* = 8.0 Hz, 1H), 3.58-3.54 (m, 3H), 3.41 (s, 3H), 3.35 (s, 3H), 2.98-2.89 (m, 2H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 205.6, 140.9, 131.2, 130.3, 130.1, 125.6, 122.9, 81.5, 74.9, 74.5, 71.5, 59.3, 43.6. **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{14}H_{18}BrO_4$ 329.0388; found, 329.0393.

2.10.21. (*2R,3R,6S*)-6-(3,5-Dichlorophenyl)-3-methoxy-2-(methoxymethyl)dihydro-2H-pyran-4(3H)-one [3au]

The compound **3au** was prepared using the general procedure and completed in 4 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished **3au** as colourless oil (105 mg, 65%); TLC R_f = 0.64 (15 % ethyl acetate in chloroform); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.20 (m, 3H), 5.28 (m, 1H), 3.86 (d, *J* = 7.5 Hz, 1H), 3.64-3.63 (m, 1H), 3.56 (s, 2H), 3.41 (s, 3H), 3.35 (s, 3H), 2.93-2.86 (m, 2H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 205.0, 142.3, 135.4, 128.3, 125.5, 81.4, 75.5, 74.1, 71.7, 59.4, 59.2, 43.7. **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{14}H_{17}C_{l2}O_4$ 319.0504; found, 319.0506.

2.10.22. (*2R,3R,6S*)-6-(4-Bromo-3-methylphenyl)-3-methoxy-2-(methoxymethyl) dihydro-2H-pyran-4(3H)-one [3av]

The compound **3av** was prepared using the general procedure and completed in 2 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished **3av** as brownish oil (145 mg, 84%); TLC R_f = 0.3 (15 % ethyl acetate in chloroform); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.0 Hz, 1H), 7.16 (s, 1H), 6.97 (d, *J* = 8.0 Hz, 1H), 5.29 (m, 1H), 3.86 (d, *J* = 7.5 Hz, 1H), 3.54-3.49 (m, 3H), 3.41 (s, 3H), 3.34 (s, 3H), 2.97-2.89 (m, 2H), 2.29 (s, 3H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 206.0, 138.1, 137.7, 132.4, 129.6, 126.2, 124.6, 81.5, 74.5, 74.5, 71.5, 59.3, 59.2, 43.6, 22.8. **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{15}H_{20}BrO_4$ 343.0545; found, 343.0547.

2.10.23. (*2R,3R,6S*)-6-(3-Acetylphenyl)-3-methoxy-2-(methoxymethyl)dihydro-2H-pyran-4(3H)-one [3aw]

The compound **3aw** was prepared using the general procedure and completed in 2 h. Column chromatography purification was performed using 20 % ethyl acetate in hexane which furnished **3aw** as colourless oil (131 mg, 89%); TLC R_f = 0.3 (15 % ethyl acetate in chloroform); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.81 (d, *J* = 7.0 Hz, 1H), 7.51 (d, *J* = 7.5 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 5.42 (m, 1H), 3.88 (d, *J* = 8.0 Hz, 1H), 3.57-3.54 (m, 3H), 3.41 (s, 3H), 3.35 (s, 3H), 3.06-2.95 (m, 2H), 2.53 (s, 3H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 205.7, 197.7, 139.2, 137.5, 131.5, 129.0, 127.9, 127.2, 81.6, 75.0, 74.8, 71.6, 59.3, 59.3, 43.8, 26.6. **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{16}H_{21}O_5$ 293.1389; found, 293.1391.

2.10.24. (*2R,3R,6S*)-3-Methoxy-2-(methoxymethyl)-6-(3-nitrophenyl)dihydro-2H-pyran-4(3H)-one [3ax]

The compound **3ax** was prepared using the general procedure and completed in 4 h. Column chromatography purification was performed using 25 % ethyl acetate in hexane which furnished **3ax** as yellowish oil (103 mg, 69%); TLC R_f = 0.30 (35 % ethyl acetate in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.22 (s, 1H), 8.09 (d, *J* = 8.5 Hz, 1H), 7.65 (d, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 1H), 5.45 (t, *J* = 5.0 Hz, 1H), 3.89 (d, *J* = 7.5 Hz, 1H), 3.65-3.55 (m, 3H), 3.41 (s, 3H), 3.36 (s, 3H), 3.04-2.95 (m, 2H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 205.0, 148.5, 141.1, 132.8, 129.7, 123.0, 122.1, 81.4, 75.7, 74.3, 71.8, 59.4, 59.2, 43.9. **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{14}H_{18}NO_6$ 296.1134; found, 296.1068.

2.10.25. (*2R,3R,6S*)-3-Methoxy-2-(methoxymethyl)-6-(3-(trifluoromethyl)phenyl) dihydro-2H-pyran-4(3H)-one [3ay]

The compound **3ay** was prepared using the general procedure and completed in 2 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished **3ay** as colourless oil (135 mg, 84%); TLC R_f = 0.6 (15 % ethyl acetate in chloroform); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.49-7.47 (m, 2H), 7.40 (t, *J* = 7.5 Hz, 1H), 5.41-5.39 (m, 1H), 3.87 (d, *J* = 8.0 Hz, 1H), 3.62-3.59 (m, 1H), 3.56-3.55 (m, 2H), 3.41 (s, 3H), 3.35 (s, 3H), 3.03-2.92 (m, 2H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 205.4, 139.8, 131.3 (q, $J_{C\text{-}F}$ = 32.4 Hz), 129.1, 124.9 (q, $J_{C\text{-}F}$ = 3.7 Hz) , 124.0 (q, $J_{C\text{-}F}$ = 3.7 Hz), 123.8 (q, $J_{C\text{-}F}$ = 272 Hz), 81.5, 75.3, 74.7, 71.7, 59.3, 59.2, 43.8. **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{15}H_{18}F_3O_4$ 319.1157; found, 319.1160.

2.10.26. (*2R,3R,6S*)-6-(3,5-Dimethylphenyl)-3-methoxy-2-(methoxymethyl) dihydro-2H-pyran-4(3H)-one [3az]

The compound **3az** was prepared using the general procedure and completed in 3.5 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished **3az** as colourless solid (86 mg, 61%); TLC R_f = 0.42 (35 % ethyl acetate in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.90-6.83 (m, 3H), 5.30-5.29 (m, 1H), 3.87 (d, *J* = 8.5 Hz, 1H), 3.57-3.49 (m, 3H), 3.43 (s, 3H), 3.34 (s, 3H), 3.01-2.98 (m, 1H), 2.90-2.88 (m, 1H), 2.21 (s, 6H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 206.5, 138.4, 138.1, 129.7, 125.1, 81.7, 75.1, 74.2, 71.5, 59.4, 59.2, 43.7, 21.2. **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{16}H_{23}O_4$ 279.1596; found, 279.1595.

2.10.27. (*2R,3R,6S*)-3-(Benzyloxy)-2-(benzyloxymethyl)-6-phenyldihydro-2H-pyran-4(3H)-one [3ba]

The compound **3ba** was prepared using the general procedure and completed in 5 h. Column chromatography purification was performed using 10 % ethyl acetate in hexane which furnished **3ba** as white foam (77 mg, 80%); TLC R_f = 0.28 (20 % ethyl acetate in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.30 (d, *J* = 7.5 Hz, 2H), 7.26-7.19 (m, 13H), 5.40-5.39 (m, 1H), 4.76 (d, *J* = 11.5 Hz, 1H), 4.50 (d, *J* = 12.0 Hz, 1H), 4.39 (d, *J* = 12.0 Hz, 1H), 4.34 (d, *J* = 11.0 Hz, 1H), 4.17 (d, *J* = 8.5 Hz, 1H), 3.65-3.56 (m, 3H), 3.05-2.93 (m, 2H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 206.4, 138.5, 137.7, 137.3, 128.6, 128.3, 128.3, 128.1, 128.1, 127.8, 127.8, 127.7, 127.3, 79.5, 75.1, 74.5, 73.5, 73.3, 69.0, 43.8. **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{26}H_{27}O_4$ 403.1909; found, 403.1916.

2.10.28. (*2R,3R,6S*)-3-(Benzyloxy)-2-(benzyloxymethyl)-6-p-tolyldihydro-2H-pyran-4(3H)-one [3bb]

The compound **3bb** was prepared using the general procedure and completed in 4 h. Column chromatography purification was performed using 10 % ethyl acetate in hexane which furnished **3bb** as white foam (89 mg, 89%); TLC R_f = 0.65 (30 % ethyl acetate in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.25-7.18 (m, 12H), 7.06 (d, *J* = 7.5 Hz, 2H), 5.39-5.37 (m, 1H), 4.77 (d, *J* = 11.0 Hz, 1H), 4.52 (d, *J* = 12.0 Hz, 1H), 4.40 (d, *J* = 12.0 Hz, 1H), 4.34 (d, *J* = 11.0 Hz, 1H), 4.16 (d, *J* = 8.5 Hz, 1H), 3.63-3.57 (m, 3H), 3.04-2.94 (m, 2H), 2.23 (s, 3H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 206.6, 137.9, 137.8, 137.3, 135.4, 129.3, 128.3, 128.33, 128.1, 127.8, 127.8, 127.7, 127.4, 79.6, 75.0, 74.3, 73.5, 73.4, 69.0, 43.9, 21.0. **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{27}H_{29}O_4$ 417.2066; found, 417.2070.

2.10.29. (*2R,3R,6S*)-3-(Benzyloxy)-2-(benzyloxymethyl)-6-(4-methoxyphenyl) dihydro-2H-pyran-4(3H)-one [3bc]

The compound **3bc** was prepared using the general procedure and completed in 4 h. Column chromatography purification was performed using 12 % ethyl acetate in hexane which furnished **3bc** as white foam (88 mg, 85%); TLC R_f = 0.25 (15 % ethyl acetate in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.26-7.18 (m, 12H), 6.77 (d, *J* = 8.5 Hz, 2H), 5.37 (dd, *J* = 6.5, 2.5 Hz, 1H), 4.77 (d, *J* = 11 Hz, 1H), 4.51 (d, *J* = 12. Hz, 1H), 4.39 (d, *J* = 12. Hz, 1H), 4.34 (d, *J* = 11. Hz, 1H), 4.16 (d, *J* = 9 Hz, 1H), 3.69 (s, 3H), 3.62-3.54 (m, 3H), 3.03-2.94 (m Hz, 2H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 206.7, 159.3, 137.8, 137.3, 130.5, 128.8, 128.3, 128.3, 128.1, 127.8, 127.8, 127.7, 113.9, 79.6, 74.8, 74.0,

73.5, 73.4, 68.9, 55.2, 43.9. **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{14}H_{18}BrO_4$ 433.2015; found, 433.2000.

2.10.30. (*2R,3R,6S*)-3-(Benzyloxy)-2-(benzyloxymethyl)-6-(4-fluorophenyl)dihydro-2H-pyran-4(3H)-one [3bd]

The compound **3bd** was prepared using the general procedure and completed in 4 h. Column chromatography purification was performed using8 % ethyl acetate in hexane which furnished **3bd** as white foam (85 mg, 84%); TLC R_f = 0.62 (30 % ethyl acetate in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.29-7.17 (m, 12H), 6.93 (t, *J* = 8.0 Hz, 2H), 5.37 (m, 1H), 4.75 (d, *J* = 11.5 Hz, 1H), 4.50 (d, *J* = 12.0 Hz, 1H), 4.40 (d, *J* = 12.0 Hz, 1H), 4.34 (d, *J* = 11.0 Hz, 1H), 4.15 (d, *J* = 8.0 Hz, 1H), 3.62-3.55 (m, 3H), 3.01-2.93 (m, 2H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 206.2, 162.4 (d, J_{C-F} = 247.5 Hz), 137.7, 137.2, 134.2 (d, J_{C-F} = 3.3 Hz), 129.3 (d, J_{C-F} = 8.2 Hz), 128.3, 128.3, 128.1, 127.9, 127.8, 127.7, 115.5 (d, J_{C-F} = 21.5 Hz), 79.4, 74.6, 74.6, 73.5, 73.3, 69.0, 44.0. **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{26}H_{26}FO_4$ 421.1815; found, 421.1813.

2.10.31. (*2R,3R,6S*)-3-(Benzyloxy)-2-(benzyloxymethyl)-6-(4-chlorophenyl) dihydro-2H-pyran-4(3H)-one [3be]

The compound **3be** was prepared using the general procedure and completed in 4 h. Column chromatography purification was performed using 8 % ethyl acetate in hexane which furnished **3be** as white foam (89 mg, 85%); TLC R_f = 0.4 (15 % ethyl acetate in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.25-7.17 (m, 14H), 5.36 (m, 1H), 4.75 (d, *J* = 11.0 Hz, 1H), 4.50 (d, *J* = 12.0 Hz, 1H), 4.40 (d, *J* = 12.0 Hz, 1H), 4.33 (d, *J* = 11.0 Hz, 1H), 4.15 (d, *J* = 8.5 Hz, 1H), 3.62-3.56 (m, 3H), 3.00-2.92 (m, 2H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 206.0, 137.7, 137.2, 137.1, 134.1, 128.8, 128.7, 128.3, 128.3, 128.1,

127.9, 127.8, 127.7, 79.4, 74.8, 74.5, 73.5, 73.3, 69.0, 43.9. **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{26}H_{26}ClO_4$ 437.1520; found, 437.1521.

2.10.32. (*2R,3R,6S*)-3-(Benzyloxy)-2-(benzyloxymethyl)-6-(4-bromophenyl) dihydro-2H-pyran-4(3H)-one [3bf]

The compound **3bf** was prepared using the general procedure and completed in 4 h. Column chromatography purification was performed using10 % ethyl acetate in hexane which furnished **3bf** as white foam (94 mg, 82%); TLC R_f = 0.29 (15 % ethyl acetate in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.5 Hz, 2H), 7.31-7.13 (m, 12H), 5.34 (m, 1H), 4.74 (d, *J* = 11.5 Hz, 1H), 4.50 (d, *J* = 12.5 Hz, 1H), 4.39 (d, *J* = 12.5 Hz, 1H), 4.33 (d, *J* = 11.0 Hz, 1H), 4.14 (d, *J* = 8.5 Hz, 1H), 3.63-3.56 (m, 3H), 2.99-2.91 (m, 2H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 205.9, 137.7, 137.6, 137.1, 131.8, 129.0, 128.3, 128.3, 128.1, 127.9, 127.8, 127.7, 122.2, 79.3, 74.9, 74.6, 73.5, 73.3, 69.0, 43.8. **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{26}H_{26}BrO_4$ 481.1014; found, 481.1020.

2.10.33. 4-((*2S,5R,6R*)-5-(Benzyloxy)-6-(benzyloxymethyl)-4-oxotetrahydro-2H-pyran-2-yl)benzonitrile [3bg]

The compound **3bg** was prepared using the general procedure and completed in 4 h. Column chromatography purification was performed using 10 % ethyl acetate in hexane which furnished **3bg** as white foam (72 mg, 70%); TLC R_f = 0.25 (20 % ethyl acetate in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.5 Hz, 2H), 7.42 (d, *J* = 7.5 Hz, 2H), 7.25-7.18 (m, 10H), 5.40 (m, 1H), 4.72 (d, *J* = 11.0 Hz, 1H), 4.49 (d, *J* = 12.5 Hz, 1H), 4.40 (d, *J* = 12.5 Hz, 1H), 4.33 (d, *J* = 11.0 Hz, 1H), 4.13 (d, *J* = 8.0 Hz, 1H), 3.67-3.66 (m, 1H), 3.61 (s, 2H), 3.00-2.92 (m, 2H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 205.2, 144.1, 137.5, 136.9, 132.4, 128.4, 128.3, 128.1, 128.0, 127.8, 127.7, 118.3, 112.0, 79.1,

75.7, 74.5, 73.5, 73.2, 69.1, 43.8. **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{27}H_{26}NO_4$ 428.1862; found, 428.1858.

2.10.34. Methyl-4-((*2S,5R,6R*)-5-(benzyloxy)-6-(benzyloxymethyl)-4-oxtetrahydro-2H-pyran-2-yl)benzoate [3bh]

The compound **3bh** was prepared using the general procedure and completed in 4 h. Column chromatography purification was performed using 10 % ethyl acetate in hexane which furnished **3bh** as white foam (83 mg, 75%); TLC R_f = 0.24 (15 % ethyl acetate in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.5 Hz, 2H), 7.38 (d, *J* = 7.5 Hz, 2H), 7.26-7.17 (m, 10H), 5.41 (m, 1H), 4.74 (d, *J* = 11.5 Hz, 1H), 4.50 (d, *J* = 12.5 Hz, 1H), 4.40 (d, *J* = 12.0 Hz, 1H), 4.34 (d, *J* = 11.5 Hz, 1H), 4.15 (d, *J* = 8.0 Hz, 1H), 3.82 (s, 3H), 3.67-3.60 (m, 3H), 3.04-2.93 (m, 2H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 205.7, 166.5, 143.7, 137.6, 137.1, 129.9, 129.8, 128.3, 128.3, 128.1, 127.9, 127.7, 127.7, 127.1, 79.3, 75.2, 74.8, 73.5, 73.2, 69.1, 52.1, 43.9. **HRMS** (ESI-TOF) (m/z): $[M + Na]^+$ calcd for $C_{28}H_{28}O_6Na$ 483.1784; found, 483.1778.

2.10.35. (*2R,3R,6S*)-3-Ethoxy-2-(ethoxymethyl)-6-p-tolyldihydro-2H-pyran-4(3H)-one [3bi]

The compound **3bi** was prepared using the general procedure and completed in 2 h. Column chromatography purification was performed using 10 % ethyl acetate in hexane which furnished **3bi** as white foam (131 mg, 90%); TLC R_f = 0.64 (30 % ethyl acetate in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.18 (d, *J*= 8.0 Hz, 2H), 7.05 (d, *J* = 7.5 Hz, 2H), 5.36 (d, *J* = 6.0 Hz, 1H), 4.03 (d, *J* = 8.5 Hz, 1H), 3.78-3.75 (m, 1H), 3.56-3.50 (m, 4H), 3.44-3.38 (m, 2H), 3.01-2.99 (m, 2H), 2.23 (s, 3H), 1.17-1.11 (m, 6H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 206.9, 137.7, 135.4, 129.2, 127.3, 80.2, 74.9, 74.2, 69.1,

67.2, 66.9, 43.6, 20.9, 15.0, 14.9. **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{17}H_{25}O_4$ 293.1753; found, 293.1748.

2.10.36. (*2R,3R,6S*)-3-(Methoxymethoxy)-2-((methoxymethoxy)methyl)-6-p-tolyl dihydro-2H-pyran-4(3H)-one [3bj]

The compound **3bj** was prepared using the general procedure and completed in 7 h. Column chromatography purification was performed using 30 % ethyl acetate in hexane which furnished **3bj** as colorless solid (75 mg, 60%); TLC R_f = 0.45 (15 % ethyl acetate in chloroform); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.20-7.18 (m, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 5.38 (d, *J* = 6.0 Hz, 1H), 4.71 (d, *J* = 6.5 Hz, 2H), 4.64-4.61 (m, 3H), 4.29 (d, *J* = 8.0 Hz, 1H), 3.70-3.65 (m, 2H), 3.61 (d, *J* = 9.0 Hz, 1H), 3.35 (s, 3H), 3.31 (s, 3H), 3.04 (d, *J* = 9.5 Hz, 21H), 2.98-2.94 (m, 2H), 2.25 (s, 3H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 205.8, 138.0, 135.3, 129.3, 127.3, 96.9, 96.7, 76.7, 75.0, 74.2, 66.7, 56.3, 55.5, 43.9, 21.0. **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{17}H_{25}O_6$ 325.1651; found, 325.1661.

2.10.37. ((*2R,3R,6S*)-3-Acetoxy-4-oxo-6-p-tolyltetrahydro-2H-pyran-2-yl)methyl acetate [3bk]

The reaction was carried out between3,4,6-tri-*O*-acetyl-D-glucal **1ag** (100 mg, 0.37 mmol) and 4-methylbenzenediazonium tetrafluoroborate **2ae** (83 mg, 0.4 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$ (5.6 mg, 0.025 mmol) at room temperature for 5 h. The desired product **3bk** was not obtained.

2.10.38. (*2R,3S,6S*)-3-Methoxy-2-(methoxymethyl)-6-phenyldihydro-2H-pyran-4(3H)-one [3bl]

The compound **3bl** was prepared using the general procedure and completed in 4 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane

which furnished **3bl** as colourless semi solid (76 mg, 60%); TLC R_f = 0.50 (35 % ethyl acetate in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32-7.19 (m, 5H), 5.25 (dd, *J* = 9.5, 3.5 Hz, 1H), 4.43-4.40 (m, 1H), 3.92 (dd, *J* = 6.5, 1.0 Hz, 1H), 3.69-3.62 (m, 2H), 3.47 (s, 3H), 3.25 (s, 3H), 2.76-2.72 (m, 1H), 2.61-2.56 (m, 1H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 203.9, 140.4, 128.5, 127.9, 125.8, 82.1, 75.8, 74.8, 71.0, 59.3, 59.0, 47.9. **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{14}H_{19}O_4$ 251.1283; found, 251.1265

2.10.39. (*2R,3S,6S*)-3-Methoxy-2-(methoxymethyl)-6-(naphthalen-1-yl)dihydro-2H-pyran-4(3H)-one [3bm]

The compound **3bm** was prepared using the general procedure and completed in 2.5 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished **3bm** as light purple solid (88 mg, 58%); TLC R_f = 0.5 (35 % ethyl acetate in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.0 Hz, 1H), 7.80.-7.73 (m, 2H), 7.56 (d, *J* = 6.5 Hz, 1H), 7.48-7.38 (m, 3H), 6.02 (d, *J* = 9.0 Hz, 1H), 4.42 (s, 1H), 3.97 (d, *J* = 5.5 Hz, 1H), 3.77-3.66 (m, 2H), 3.50 (s, 3H), 3.28 (s, 3H), 2.98-2.95 (m, 1H), 2.78-2.74 (m, 1H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 204.4, 135.8, 133.8, 130.4, 128.8, 128.7, 126.3, 125.7, 125.2, 123.4, 123.2, 82.2, 75.7, 71.9, 70.9, 59.3, 59.1, 46.7. **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{18}H_{21}O_4$ 301.1440; found, 301.1390.

2.10.40. (*2R,3S,6S*)-3-Methoxy-2-(methoxymethyl)-6-p-tolyldihydro-2H-pyran-4(3H)-one [3bn]

The compound **3bn** was prepared using the general procedure and completed in 3 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished **3bn** as colourless semi solid (86 mg, 65%); TLC R_f = 0.52 (35 % ethyl acetate in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.20-7.18 (m, 2H), 7.10 (d, *J* = 8.0

Hz, 2H), 5.21 (dd, *J* = 9.5, 3.5 Hz, 1H), 4.38 (m, 1H), 3.89 (d, *J* = 5.5 Hz, 3H), 3.67-3.63 (m, 2H), 3.47 (s, 3H), 3.26 (s, 3H), 2.73 (dd, *J* = 14.0, 3.5 Hz, 1H), 2.61-2.57 (m, 1H), 2.26 (s, 3H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 204.1, 137.7, 137.5, 129.2, 125.9, 82.2, 75.7, 74.8, 71.1, 59.3, 59.0, 47.75, 21.0. **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{15}H_{21}O_4$ 265.1440; found, 265.1436.

2.10.41. (*2R,3S,6S*)-6-(4-Fluorophenyl)-3-methoxy-2-(methoxymethyl)dihydro-2H-pyran-4(3H)-one [3bo]

The compound **3bo** was prepared using the general procedure and completed in 3 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished **3bo** as colourless semi solid (79 mg, 59%); TLC R_f = 0.65 (35 % ethyl acetate in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.29-7.27 (m, 2H), 6.97 (t, *J* = 8.5 Hz, 2H), 5.23 (dd, *J* = 10.0, 3.5 Hz, 1H), 4.41-4.38 (m, 1H), 3.91 (d, *J* = 5.5 Hz, 1H), 3.69-3.61 (m, 2H), 3.47 (s, 3H), 3.25 (s, 3H), 2.72 (dd, *J* = 14.0, 3.5 Hz, 1H), 2.57-2.52 (m, 1H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 203.6, 162.4 (d, J_{C-F} = 247.5 Hz), 136.4 (d, J_{C-F} = 3.3 Hz), 127.6 (d, J_{C-F} = 8.2 Hz), 115.4 (d, J_{C-F} = 21.5 Hz), 82.1, 75.9, 74.3, 71.0, 59.3, 59.1, 47.9. **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{14}H_{18}FO_4$ 269.1189; found, 269.1154.

2.10.42. (*2R,3S,6S*)-6-(4-Chlorophenyl)-3-methoxy-2-(methoxymethyl)dihydro-2H-pyran-4(3H)-one [3bp]

The compound **3bp** was prepared using the general procedure and completed in 3 h. Column chromatography purification was performed using15 % ethyl acetate in hexane which furnished **3bp** as colourless semi solid (87 mg, 61%); TLC R_f = 0.60 (35 % ethyl acetate in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.27-7.23 (m, 4H), 5.23 (dd, *J* =

10.0, 3.5 Hz, 1H), 4.40-4.39 (m, 1H), 3.90 (d, *J* = 5.5 Hz, 1H), 3.69-3.61 (m, 2H), 3.47 (s, 3H), 3.25 (s, 3H), 2.72 (dd, *J* = 14.5, 3.5 Hz, 1H), 2.54-2.49 (m, 1H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 203.4, 139.1, 133.6, 128.7, 127.2, 82.0, 75.9, 74.2, 71.1, 59.3, 59.1, 47.8. **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{14}H_{18}ClO_4$ 285.0894; found, 285.0874.

2.10.43. (*2R,3S,6S*)-6-(4-Bromophenyl)-3-methoxy-2-(methoxymethyl)dihydro-2H-pyran-4(3H)-one [3bq]

The compound **3bq** was prepared using the general procedure and completed in 3 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished **3bq** as brownish semi solid (91 mg, 55%); TLC R_f = 0.48 (35 % ethyl acetate in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.5 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 5.22 (dd, *J* = 10.0, 3.5 Hz, 1H), 4.41 (t, *J* = 5.5 Hz, 1H), 3.90 (d, *J* = 6.5 Hz, 1H), 3.69-3.61 (m, 2H), 3.48 (s, 3H), 3.25 (s, 3H), 2.72 (dd, *J* = 14.5, 3.0 Hz, 1H), 2.53-2.48 (m, 2H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 203.5, 139.6, 131.6, 127.5, 121.8, 82.0, 75.9, 74.3, 71.1, 59.3, 59.2, 47.8. **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{14}H_{18}BrO_4$ 329.0388; found, 329.0361.

2.10.44. (*2R,3S,6S*)-3-Methoxy-2-(methoxymethyl)-6-(4-nitrophenyl)dihydro-2H-pyran-4(3H)-one [3br]

The compound **3br** was prepared using the general procedure and completed in 8 h. Column chromatography purification was performed using 20 % ethyl acetate in hexane which furnished **3br** as semi solid (72 mg, 48%); TLC R_f = 0.40 (35 % ethyl acetate in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.5 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 5.49 (dd, *J* = 10.5, 2.5 Hz, 1H), 4.48-4.47 (m, 1H), 3.95 (d, *J* = 6.5 Hz, 1H), 3.74-

3.64 (m, 2H), 3.51 (s, 3H), 3.26 (s, 3H), 2.78-2.75 (m, 1H), 2.50-2.45 (m, 1H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 202.6, 148.0, 147.4, 126.4, 123.8, 81.8, 76.3, 74.0, 71.3, 59.4, 59.3, 48.0. **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{14}H_{18}NO_6$ 296.1134; found, 296.1143.

2.10.45. 4-((*2S,5S,6R*)-5-Methoxy-6-(methoxymethyl)-4-oxotetrahydro-2H-pyran-2-yl)benzonitrile [3bs]

The compound **3bs** was prepared using the general procedure and completed in 6 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished **3bs** as colourless semi solid (68 mg, 49%); TLC R_f = 0.42 (35 % ethyl acetate in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 5.33 (dd, *J* = 10.0, 3.0 Hz, 1H), 4.45 (m, 1H), 3.92 (d, *J* = 6.0 Hz, 1H), 3.72-3.70 (m, 1H), 3.66-3.63 (m, 1H), 3.49 (s, 3H), 3.25 (s, 3H), 2.74 (dd, *J* = 14.0, 3.5 Hz, 1H), 2.49-2.44 (m, 1H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 202.8, 146.0, 132.4, 126.3, 118.5, 111.7, 81.8, 76.2, 74.1, 71.3, 59.4, 59.3, 47.8. **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{15}H_{18}NO_4$ 276.1236; found, 276.1223.

2.10.46. Methyl-4-((*2S,5S,6R*)-5-methoxy-6-(methoxymethyl)-4-oxotetrahydro-2H-pyran-2-yl)benzoate [3bt]

The compound **3bt** was prepared using the general procedure and completed in 4 h. Column chromatography purification was performed using 18 % ethyl acetate in hexane which furnished **3bt** as yellowish solid (80 mg, 52%); TLC R_f = 0.45 (35 % ethyl acetate in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 5.32 (dd, *J* = 9.5, 2.5 Hz, 1H), 4.44 (m, 1H), 3.93 (d, *J* = 6.0 Hz, 1H), 3.84 (s, 3H), 3.71-3.63 (m, 2H), 3.49 (s, 3H), 3.26 (s, 3H), 2.75 (dd, *J* = 14.5, 3.0 Hz, 1H),

2.54-2.49 (m, 1H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 203.3, 166.6, 145.7, 129.9, 129.7, 125.6, 82.0, 76.1, 74.4, 71.2, 59.3, 59.2, 52.1, 47.9. **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{16}H_{21}O_6$ 309.1338; found, 309.1375.

2.10.47. (*2R,3S,6S*)-6-(2,4-Dimethylphenyl)-3-methoxy-2-(methoxymethyl)dihydro-2H-pyran-4(3H)-one [3bu]

The compound **3bu** was prepared using the general procedure and completed in 5 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished **3bu** as colourless solid (76 mg, 54%); TLC R_f = 0.40 (35 % ethyl acetate in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.25 (d, *J* = 7.5 Hz, 1H), 6.96 (d, *J*=7.5Hz,1H), 6.91(s, 1H). 5.44 (dd, *J* = 9.0, 3.0 Hz, 1H), 4.36-4.35 (m, 1H), 3.92 (d, *J*=6.5 Hz, 1H), 3.68-3.64 (m, 2H), 3.47 (s, 3H), 3.25 (s, 3H), 2.67 (dd, *J* = 14.5, 3.5 Hz, 1H), 2.62-2.58 (m, 1H), 2.25 (s, 3H), 2.22 (s, 3H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 204.4, 137.6, 135.3, 135.2, 131.3, 126.9, 125.5, 82.2, 75.66 71.6, 71.1, 59.2, 59.0, 46.5, 20.9, 18.9. **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{16}H_{23}O_4$ 279.1596; found, 279.1610.

2.10.48. (*2R,3S,6S*)-6-(2-Chlorophenyl)-3-methoxy-2-(methoxymethyl)dihydro-2H-pyran-4(3H)-one [3bv]

The compound **3av** was prepared using the general procedure and completed in 4 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished **3av** as yellowish semi solid (60 mg, 43%); TLC R_f = 0.60 (15 % ethyl acetate in chloroform);**^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.55-7.54 (m, 1H), 7.28-7.14 (m, 3H), 5.62 (dd, *J* = 10.5, 2.5 Hz, 1H), 4.52-4.50 (m, 1H), 3.99(d, *J* = 6.0 Hz, 1H), 3.69-3.68 (m, 2H), 3.51 (s, 3H), 3.27 (s, 3H), 2.84 (dd, *J* = 14.5, 3.0 Hz, 1H), 2.40-2.34 (m,

1H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 203.2, 138.5, 131.8, 129.4, 128.9, 127.2, 126.8, 82.0, 76.3, 71.4, 70.9, 59.3, 59.3, 46.8. **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{14}H_{18}ClO_4$ 285.0894; found, 285.0890.

2.10.49. (*2R,3S,6S*)-3-Methoxy-2-(methoxymethyl)-6-(3-nitrophenyl)dihydro-2H-pyran-4(3H)-one [3bw]

The compound **3bw** was prepared using the general procedure and completed in 8 h. Column chromatography purification was performed using 20 % ethyl acetate in hexane which furnished **3bw** as yellowish semi solid (60 mg, 40%); TLC R_f = 0.3 (35 % ethyl acetate in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.24 (s, 1H), 8.19 (d, *J* = 7.0 Hz, 1H), 7.60 (d, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 8.0 Hz, 1H), 5.39 (dd, *J* = 10.0, 2.5 Hz, 1H), 4.49 (t, *J* = 4.5 Hz, 1H), 3.97 (d, *J* = 6.5 Hz, 1H), 3.74-3.64 (m, 2H), 3.51 (s, 3H), 3.27 (s, 3H), 2.77 (dd, *J* = 14.5, 3.5 Hz, 1H), 2.53-2.48 (m, 1H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 202.6, 148.4, 143.1, 131.7, 129.5, 122.8, 120.8, 81.8, 76.3, 73.9, 71.3, 59.4, 59.3, 48.1. **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{14}H_{18}NO_6$ 296.1134; found, 296.1115.

2.10.50. (*2R,3S,6S*)-3-(Benzyloxy)-2-(benzyloxymethyl)-6-phenyldihydro-2H-pyran-4(3H)-one [3bx]

The compound **3bx** was prepared using the general procedure and completed in 4 h. Column chromatography purification was performed using 10 % ethyl acetate in hexane which furnished **3bx** as colourless semi solid (48 mg, 50%); TLC R_f = 0.48 (15 % ethyl acetate in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.28-7.17 (m, 15H), 5.25 (dd, *J* = 9.5, 2.5 Hz, 1H), 4.86 (d, *J* = 12.0 Hz, 1H), 4.51 (d, *J* = 4.5 Hz, 1H), 4.48 (d, *J* = 4.5 Hz, 1H), 4.42 (d, *J* = 12.0 Hz, 1H), 4.37 (s, 1H), 4.09 (d, *J* = 6.5 Hz, 1H), 3.78-3.71 (m,

2H), 2.73 (dd, *J* = 14.5, 3.0 Hz, 1H), 2.59-2.54 (m, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 204.1, 140.5, 137.9, 137.4, 128.5, 128.4, 128.3, 128.0, 12.9, 127.8, 127.6, 127.5, 125.9, 79.2, 76.4, 74.7, 73.5, 72.6, 68.4, 47.9 **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{26}H_{27}O_4$ 403.1909; found, 403.1916.

2.10.51. (*2R,3S,6S*)-3-(Benzyloxy)-2-(benzyloxymethyl)-6-p-tolyldihydro-2H-pyran-4(3H)-one [3by]

The compound **3by** was prepared using the general procedure and completed in 4 h. Column chromatography purification was performed using 10 % ethyl acetate in hexane which furnished **3by** as semi solid (52 mg, 52%); TLC R_f = 0.47 (15 % ethyl acetate in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.27-7.14 (m, 13H), 7.08 (d, *J* = 7.5 Hz, 2H), 5.22 (d, *J* = 9.0 Hz, 1H), 4.85 (d, *J* = 12.5 Hz, 1H), 4.49 (d, *J* = 13.0 Hz, 2H), 4.42 (d, *J* = 12.5 Hz, 1H), 4.34 (s, 1H), 4.08 (d, *J* = 6.0 Hz, 1H), 3.77-3.70 (m, 2H), 2.74-2.71 (m, 1H), 2.60-2.55 (m, 1H), 2.25 (s, 3H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 204.3, 137.9, 137.8, 137.4, 137.4, 129.2, 128.4, 128.3, 127.9, 127.8, 127.6, 127.5, 126.0, 79.2, 76.3, 74.7, 73.5, 72.6, 68.4, 47.8, 21.1 **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{27}H_{29}O_4$ 417.2066; found, 417.2061.

2.10.52. (*2R,3S,6S*)-3-(Benzyloxy)-2-(benzyloxymethyl)-6-(4-bromophenyl) dihydro-2H-pyran-4(3H)-one [3bz]

The compound **3bz** was prepared using the general procedure and completed in 4 h. Column chromatography purification was performed using 10 % ethyl acetate in hexane which furnished **3bz** as yellowish foam (58 mg, 50%); TLC R_f = 0.50 (15 % ethyl acetate in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.0 Hz, 2H), 7.39-7.28 (m, 11H), 7.23 (d, *J* = 8.0 Hz, 2H), 5.31 (dd, *J* = 10.0, 3.0 Hz, 1H), 4.97 (d, *J* = 12.0 Hz,

1H), 4.62-4.58 (m, 2H), 4.52 (d, *J* = 12.5 Hz, 1H), 4.46 (s, 1H), 4.18 (d, *J* = 6.5 Hz, 1H), 3.88-3.81 (m, 2H), 2.81 (dd, *J* = 14.5, 3.0 Hz, 1H), 2.62-2.57 (m, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 203.7, 139.6, 137.8, 137.3, 131.6, 128.5, 128.3, 128.0, 127.8, 127.6, 127.6, 121.8, 79.0, 76.5, 74.1, 73.6, 72.7, 68.5, 47.8. **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{26}H_{26}BrO_4$ 481.1014; found, 481.1019.

2.10.53. (*2S,3S,6R*)-3-(Benzyloxy)-2-methyl-6-phenyldihydro-2H-pyran-4(3H)-one [3ca]

The compound **3ca** was prepared using the general procedure and completed in 1.5 h. Column chromatography purification was performed using 8% ethyl acetate in hexane which furnished **3ca** as white foam (73 mg, 69%); TLC R_f = 0.25 (15 % ethyl acetate in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.42-7.28 (m, 10H), 5.33 (t, *J*= 4.0 Hz, 1H), 4.89 (d, *J* = 11.5 Hz, 1H), 4.52 (d, *J* = 11.5 Hz, 1H), 3.87-3.84 (m, 1H), 3.70 (d, *J* = 7.5 Hz, 1H), 3.18 (dd, *J* = 14.0, 3.5 Hz, 1H), 2.96 (dd, *J* = 14.5, 6.5 Hz, 1H), 1.33 (d, *J* = 6.3 Hz, 3H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 206.3, 139.0, 137.2, 128.6, 128.3, 128.1, 128.0, 127.9, 127.1, 84.7, 74.6, 73.0, 71.9, 44.4, 18.0. **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{19}H_{21}O_3$ 297.1491; found, 297.1499.

2.10.54. (*2S,3S,6R*)-3-(Benzyloxy)-2-methyl-6-p-tolyldihydro-2H-pyran-4(3H)-one [3cb]

The compound **3cb** was prepared using the general procedure and completed in 1.5 h. Column chromatography purification was performed using 8 % ethyl acetate in hexane which furnished **3cb** as white foam (79 mg, 72%); TLC R_f = 0.40 (15 % ethyl acetate in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.27-7.19 (m, 7H), 7.07 (d, *J* = 7.5 Hz, 2H), 5.20 (m, 1H), 4.78 (d, *J* = 11.5 Hz, 1H), 4.41 (d, *J* = 11.5 Hz, 1H), 3.73-3.70 (m, 1H),

3.58 (d, *J* = 8.0 Hz, 1H), 3.05 (d, *J* = 14.0 Hz, 1H), 2.85 (dd, *J* = 14.0, 6.5 Hz, 1H), 2.24 (s, 3H), 1.21 (m, *J* = 7.4 Hz, 3H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 206.6, 137.9, 137.3, 136.0, 129.3, 128.4, 128.2, 128.0, 127.2, 84.8, 74.6, 73.0, 71.6, 44.5, 21.0, 18.2. **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{20}H_{23}O_3$ 311.1647; found, 311.1639.

2.10.55. (*2S,3S,6R*)-3-(Benzyloxy)-2-methyl-6-(4-nitrophenyl)dihydro-2H-pyran-4(3H)-one [3cc]

The compound **3cc** was prepared using the general procedure and completed in 1.5 h. Column chromatography purification was performed using 12 % ethyl acetate in hexane which furnished **3cc** as white foam (78 mg, 64%); TLC R_f = 0.24 (15 % ethyl acetate in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.5 Hz, 2H), 7.55 (d, *J* = 8.5 Hz, 2H), 7.34-7.28 (m, 5H), 5.29 (t, *J* = 2.5 Hz, 1H), 4.79 (d, *J* = 11.5 Hz, 1H), 4.46 (d, *J* = 11.5 Hz, 1H), 3.88-3.84 (m, 1H), 3.66 (d, *J* = 6.5 Hz, 1H), 3.11 (dd, *J* = 14.0, 5.0 Hz, 1H), 2.91 (dd, *J* = 14.0, 6.0 Hz, 1H), 1.29 (d, *J* = 6.5 Hz, 3H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 205.4, 147.6, 146.4, 136.9, 128.4, 128.2, 128.1, 127.7, 123.8, 84.1, 73.6, 73.2, 72.9, 44.5, 17.5. **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{19}H_{20}NO_5$ 342.1341; found, 342.1341.

2.10.56. (*2S,5R*)-5-(Benzyloxy)-2-p-tolyldihydro-2H-pyran-4(3H)-one [3cd]

The compound **3cd** was prepared using the general procedure. The reaction was carried out between di-*O*-benzyl-D-xylal **1ah** (110 mg, 0.37 mmol) and 4-methylbenzenediazonium tetrafluoroborate **2ae** (85 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$ (8.5 mg, 0.037 mmol) at room temperature for 4 h. Column chromatography purification was performed using 8 %

ethyl acetate in hexane which furnished **3cd** as colourless semi solid (45 mg, 41%); TLC R_f = 0.24 (15 % ethyl acetate in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39-7.28 (m, 7H), 7.21 (d, *J* = 8.0 Hz, 2H), 4.73-4.69 (m, 2H), 4.53 (d, *J* = 12.0 Hz, 1H), 4.33 (dd, *J* = 12.5, 2.5 Hz, 1H), 3.86-3.83 (m, 1H), 3.75 (s, 1H), 3.20 (dd, *J* = 13.5, 10.0 Hz, 1H), 2.63 (d, *J* = 13.5 Hz, 1H), 2.37 (s, 3H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 206.4, 138.0, 137.0, 129.3, 128.5, 128.1, 128.1, 126.0, 80.1, 79.6, 71.7, 70.5, 47.2, 21.1. **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{19}H_{21}O_3$ 297.1491; found, 297.1501.

2.10.57. (*2R,5S*)-2-(Benzyloxymethyl)-5-p-tolyldihydrofuran-3(2H)-one [3ce]

The compound **3ce** was prepared using the general procedure. The reaction was carried out between di-*O*-benzyl-D-ribal **1ai** (100 mg, 0.34 mmol) and 4-methylbenzenediazonium tetrafluoroborate **2ae** (77 mg, 0.37 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$ (8 mg, 0.034 mmol) at room temperature for 2.5 h. Column chromatography purification was performed using 8 % ethyl acetate in hexane which furnished **3ce** as white foam (31 mg, 31%); TLC R_f = 0.25 (15 % ethyl acetate in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31-7.24 (t, 5H), 7.14 (d, *J* = 7.5 Hz, 2H), 7.09 (d, *J* = 7.5 Hz, 2H), 4.86 (d, *J* = 12.0 Hz, 1H), 4.54-4.51 (m, 2H), 4.35-4.32 (m, 1H), 4.13-4.09 (m, 1H), 3.54 (t, *J* = 11.0 Hz, 1H), 2.66-2.59 (m, 2H), 2.26 (s, 3H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 204.9, 138.0, 137.3, 136.8, 129.3, 128.5, 128.4, 128.0, 127.9, 125.5, 80.6, 78.9, 72.7, 70.5, 49.7, 21.1. **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{19}H_{21}O_3$ 297.1491; found, 297.1482.

2.10.58. (*2R,3R,6S*)-6-(2-Chlorophenyl)-3,4,4-trimethoxy-2-(methoxymethyl) tetrahydro-2H-pyran [4ab]

The compound **4ab** was prepared using the general procedure while methanol is used as the solvent. The reaction was carried out between tri-*O*-methyl-D-glucal **1aa** (95 mg, 0.5 mmol) and 2-chlorobenzenediazonium tetrafluoroborate **2ab** (127 mg, 0.56 mmol) in methanol (4 mL) in the presence of $Pd(OAc)_2$ (5.6 mg, 0.025 mmol) at room temperature for 1 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished **3ab** as viscous liquid (157 mg, 94%); TLC R_f = 0.38 (35 % ethyl acetate in hexane);**^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.5 Hz, 1H), 7.23-7.18 (m, 2H), 7.10 (t, *J* = 7.5 Hz, 1H), 4.98 (d, *J* = 11.5 Hz, 1H), 4.40 (t, *J* = 6.0 Hz, 1H), 3.80-3.77 (m, 1H), 3.52 (dd, *J* = 10.5, 5.0 Hz, 1H), 3.43 (s, 3H), 3.32 (s, 3H), 3.27 (s, 3H), 3.18 (s, 4H), 2.06 (d, *J* = 14.0 Hz, 1H), 1.68 (t, *J* = 13.0 Hz, 1H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 139.1, 131.2, 128.9, 128.4, 127.8, 127.2, 98.7, 75.7, 74.5, 70.6, 67.0, 59.0, 57.3, 47.7, 47.5, 34.1. **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{16}H_{24}ClO_5$ 331.1312; found, 331.1331.

2.11 Experimental Part for the Synthetic application of 2,3-Deoxy-α-Aryl-*C*-glycosides

2.11.1 Procedure for the deprotection of dimethyl acetal 4ab

To a solution of acetal **4ab** (76 mg 0.23 mmol) in methanol (2 mL), 6N HCl (5 mL) was added at room temperature and stirred for 1h. The resulting solution was diluted with ethyl acetate (100 mL) and washed with saturated $NaHCO_3$ and brine solutions. The organic layer was dried over anhydrous Na_2SO_4, concentrated and purified by column chromatography using 15 % ethyl acetate in hexane which furnished a mixture of inseparable **3ab** and **5ab** (α/β=6:1) in 76% yield (51 mg).

2.11.2 (*2R,3S,4S,6S*)-3-(benzyloxy)-2-(benzyloxymethyl)-6-phenyltetrahydro-2H-pyran-4-ol [4ba]

To a stirred solution of ketone **3ba** (150 mg, 0.37 mmol) in methanol (7 mL), sodium borohydride (15 mg, 0.4 mmol) was added at 0-4 ^{o}C. The reaction mixture was stirred for 30 mins at the same temperature, diluted with ethyl acetate (50 mL) and washed with saturated ammonium chloride solution. The organic layer was dried over anhydrous Na_2SO_4, concentrated and purified in column chromatography using 15 % ethyl acetate in hexane which furnished **4ba** as a white foam in 72% yield (108 mg). TLC R_f = 0.25 (20 % ethyl acetate in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32-7.16 (m, 15H), 4.67-4.64 (m, 2H), 4.52-4.44 (m, 3H), 4.29 (s, 1H), 4.03-4.01 (m, 1H), 3.68-3.63 (m, 3H), 2.01-1.99 (m, 2H), 1.92 (d, *J* = 13.0 Hz, 1H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 141.7, 137.8, 137.8, 128.4, 128.4, 128.2, 127.8, 127.8, 127.7, 127.6, 127.4, 126.0, 75.4, 73.4, 73.0, 72.6, 71.5, 69.2, 66.0, 36.6. **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{26}H_{29}O_4$ 405.2066; found, 405.2019.

2.11.3 (*2R,3S,4S,6S*)-3-(benzyloxy)-2-(benzyloxymethyl)-6-(4-bromophenyl) tetrahydro-2H-pyran-4-ol [4bf]

To a stirred solution of ketone **3bf** (100 mg, 0.21 mmol) in methanol (7 mL), sodium borohydride (11 mg, 0.28 mmol) was added at 0-4 ^{o}C. The reaction mixture was stirred for 30 mins at the same temperature, diluted with ethyl acetate (50 mL) and washed with saturated ammonium chloride solution. The organic layer was dried over anhydrous Na_2SO_4, concentrated and purified in column chromatography using 20 % ethyl acetate in hexane which furnished **4bf** as viscous oil in 82% yield (83 mg). TLC R_f = 0.26 (15 % ethyl acetate in hexane);**^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.5 Hz, 2H), 7.25-7.18 (m, 12H), 4.63 (d, *J* = 10.5 Hz, 2H), 4.50 (d, *J* = 12 Hz, 1H), 4.44

(d, *J* = 12.5 Hz, 1H), 4.22 (s, 1H), 4.02-4.01 (m, 1H), 3.65-3.61 (m, 3H), 2.14 (bs, 1H), 2.01-1.88 (m, 2H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 140.8, 137.7, 137.7, 131.2, 128.5, 128.4, 127.9, 127.8, 127.7, 127.6, 121.1, 75.3, 73.4, 72.4, 72.3, 71.5, 69.1, 65.8, 36.3. **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{26}H_{28}BrO_4$ 483.1171; found, 483.1163.

2.11.4 (*2R,3S,4S,6S*)-3,4-bis(benzyloxy)-2-(benzyloxymethyl)-6-phenyltetra hydro-2H-pyran (5ba)

The alcohol **4ba** (100 mg, 0.25 mmol) was stirred in dry DMF (3 mL) was added and cooled to 0 ^oC after which NaH (12 mg, 60% in mineral oil) was added. The mixture was stirred for 5 min at the same temperature to which benzyl bromide (0.038 mL, 1.5 equiv.) was added. The resulting mixture was stirred for 60 mins and quenched by saturated aqueous NH_4Cl (1 mL) and diluted with ethyl acetate (50 mL). The organic phase was washed with H_2O, brine, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by column chromatography using 10% ethyl acetate in hexane to afford **5ba** as viscous oil in 81% yield (100 mg). TLC R_f = 0.34 (20 % ethyl acetate in hexane); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.45-7.28 (m, 20H), 4.78-4.75 (m, 3H), 4.55 (d, *J* = 17.5 Hz, 4H), 4.47 (s, 1H), 4.95 (d, *J* = 10 Hz, 1H), 3.91 (s, 1H), 3.75-3.68 (m, 2H), 2.45-2.38 (m, 1H), 2.04 (d, *J* = 12.5 Hz, 1H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 141.9, 138.6, 138.4, 137.9, 128.40, 128.2, 128.2, 127.8, 127.6, 127.5, 127.4, 127.3, 126.0, 74.5, 73.7, 73.5, 73.2, 72.6, 71.6, 70.0, 68.9, 33.7. **HRMS** (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{33}H_{35}O_4$ 495.2535; found, 495.2515.

2.12 Spectral Data for Few Products

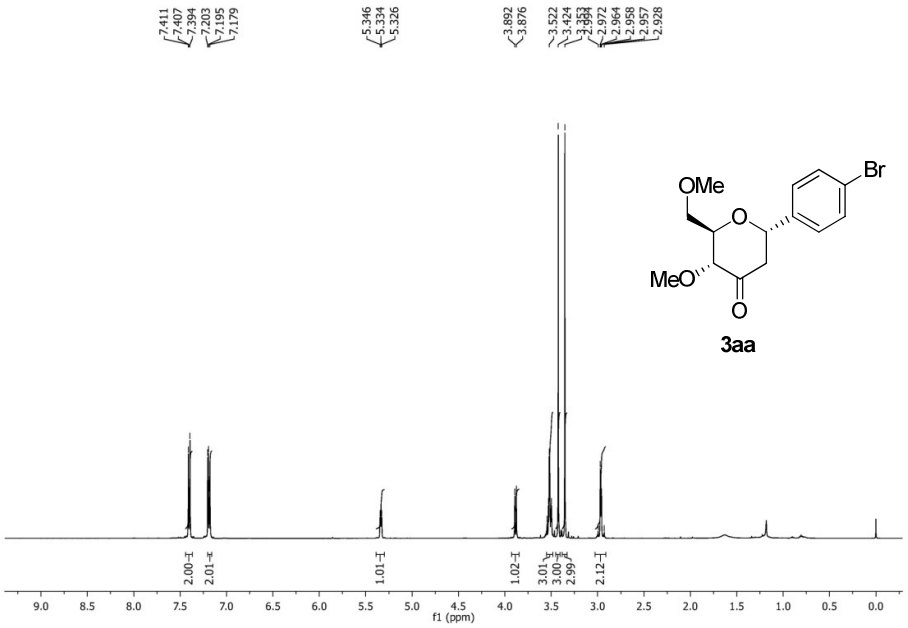


Figure 2.2 ^{1}H-NMR spectrum of compound 3aa in $CDCl_3$

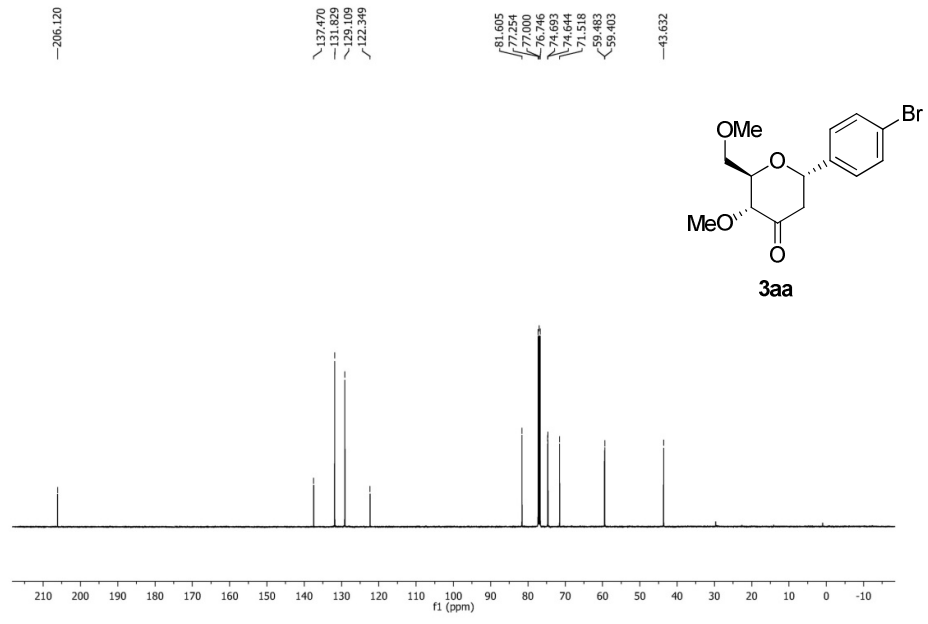


Figure 2.3 ^{13}C-NMR spectrum of compound 3aa in $CDCl_3$

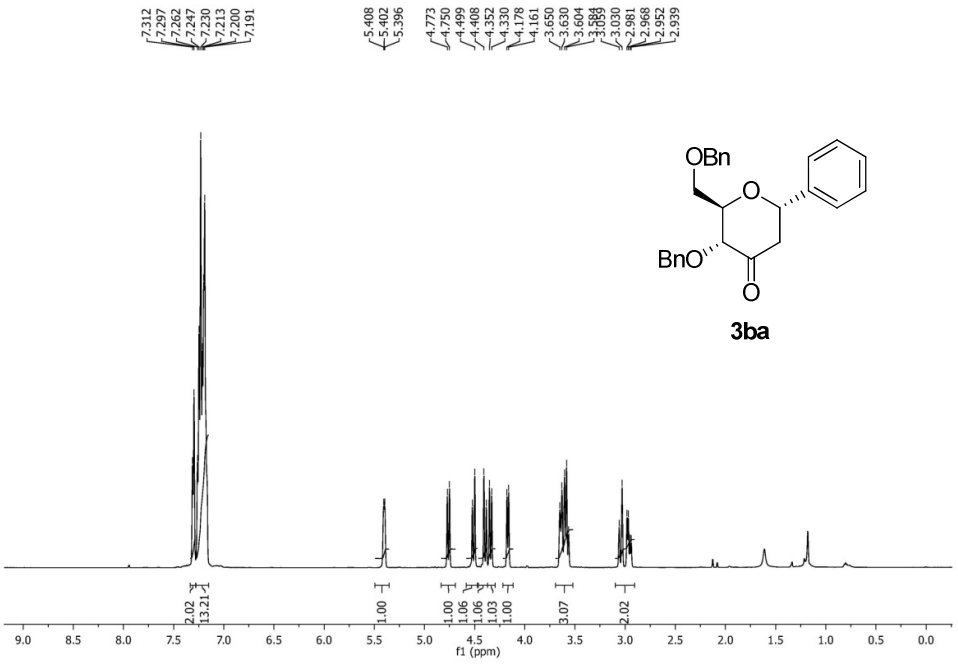


Figure 2.4 ^{1}H-NMR spectrum of compound **3ba** in **$CDCl_3$**

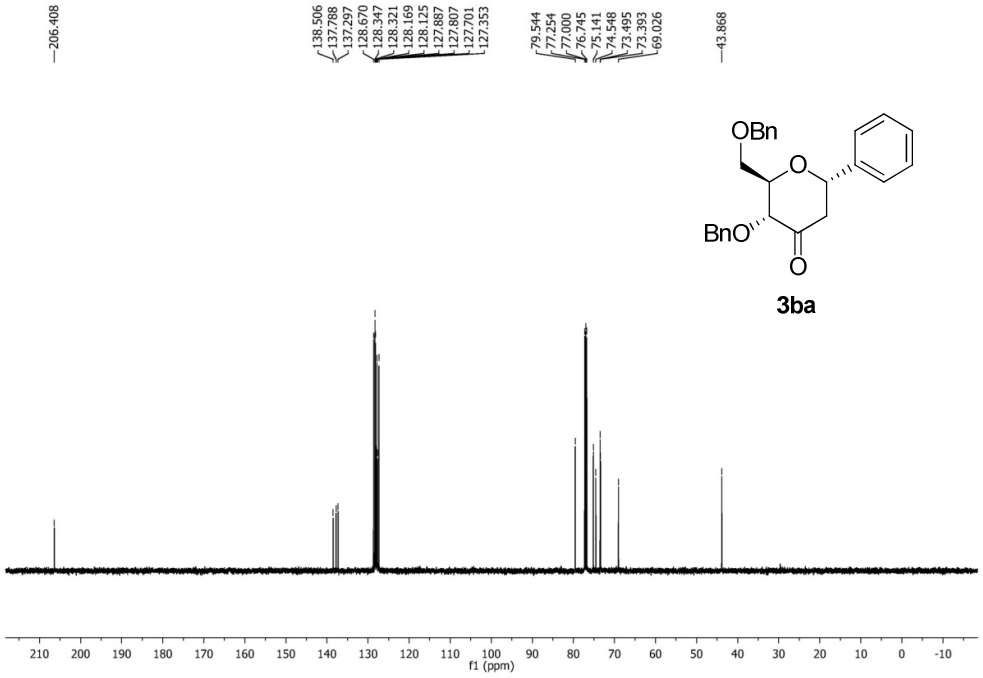


Figure 2.5 ^{13}C-NMR spectrum of compound **3ba** in **$CDCl_3$**

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