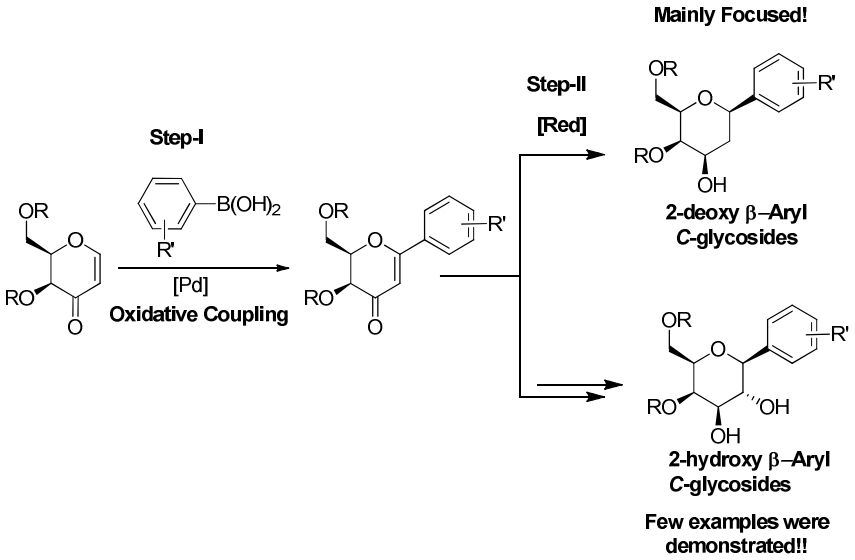
5.1 Introduction

As described in the Chapters 1-4, aryl-*C*-glycosides are important class of organic compounds found in nature with different biological activities [1, 2]. It is worth mentioning that recently many synthetic aryl-*C*-glycosides have been approved for the treatment of type-2 diabetes (i.e. SGLT1/SGLT2 inhibitors) [3]. As classified in the introdcution section of the thesis, the majority of aryl-*C*-glycosides exist in two different structures, namely 2-hydroxy-β-aryl-*C*-glycosides and 2-deoxy-β-aryl-*C*-glycosides. Between these, 2-deoxy-β-aryl *C*-glycoside units are present in many natural products including aquayminin, medermycin, galtamycinone, angucyclines, kidamycin, pluramycin A, saptomycin B, vineomycinone B_2 methyl ester, etc., [1, 4]. Considering their biological significance, numerous synthetic routes have been developed for their preparation. However, a formation of highly stereo-selective aryl-glycosidic bond remains one of the important challenges in synthetic carbohydrate chemistry.

Among the different routes [1, 5-6] as described in the introduction chapter, synthesis of 2-deoxy aryl *C*-glycosides from glycals via cross-coupling reactions received significant attention [1]. Numerous aryl donors including arylboronic acids [7], aryl halides [8], aryl hydrazines [9], aryl carboxylic acids [10], aryl sulfinates [11], aryl amines [12] and aryl sulfonyl chlorides [13] have been successfully employed in the coupling reaction. However, the major limitation of these methods is that the formation of α-selective aryl *C*-glycosides, while naturally occurring aryl-*C*-glycosides are β-anomers.

In this context, the chapters 2&3 described a palladium catalyzed aryldiazonium salts mediated stereospecific synthesis of α- and β-anomers of 2-deoxy aryl-*C*-glycosides from glycals and anti-glycals (i.e. *C*-3 configuration inverted glycals), respectively [14]. Later, in chapter 4, considering the explosive nature of aryldiazonium salts, we have explored green and stable arylboronic acids mediated synthesis of 2-deoxy aryl-*C*-glycosides via palladium catalyzed 1,4-conjucated addition reaction with glycal-enones (i.e. enones derived from glycals). However, this method provides α-selective 2-deoxy aryl-*C*-glycosides. During this study, we have observed the formation of C-1 arylated glycal-enones as a by-product (under most of the reaction conditions) which could serve as the potential precursors in β-selective aryl-*C*-glycosides synthesis.



Scheme 5.1 Palladium catalyzed oxidative-Heck coupling followed by reduction: Formation of β-Selective aryl *C*-glycosides

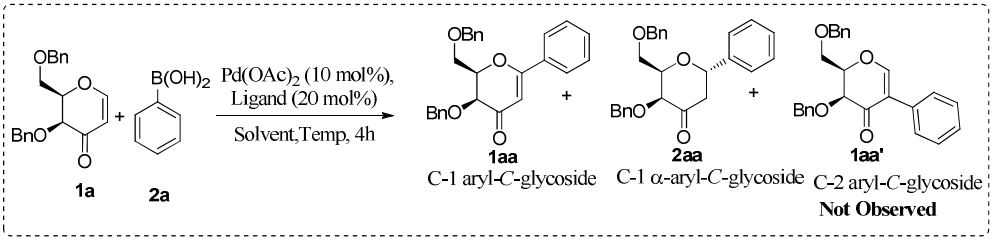
In this context, this chapter describes i) arylboronic acids mediated synthesis of C-1 arylated glycal-enones from corresponding glycal-enones via palladium catalyzed oxidative Heck-coupling reaction and ii) applications of C-1 arylated glycal-enones in the preparation of 2-deoxy β-aryl-*C*-glycosides (mainly focused) as well as 2-hydoxy β-aryl-*C*-glycosides (few examples were demonstrated) as shown in **Scheme 5.1** (**step I** and **II**)**.**

5.2 Results and Discussion

The first step of the reaction, i.e. regioselective oxidative Heck coupling reaction, is crucial, because there are possibilities for 1,4-conjugate addition reaction as well as *C*-2 arylation. Hence, at the outset, we have focused on the optimization of oxidative Heck coupling reaction using benzyl protected galactal enone **1a** and phenylboronic acid **2a** as model substrates in the presence of palladium acetate. The reaction was initially attempted in different solvents including THF, DMF and acetonitrile at 80°C for 4h with 10 mol% of palladium acetate (**Table 5.1**, **entries 1-3**). Among these solvents, only DMF gave the oxidative coupling product **1aa** in a trace amount (<10%). Considering the impact of ligands in cross-coupling reactions, the reaction was attempted with 2,2-bipyridyl ligand in DMF (**Table 5.1**,**entry4**). To our delight, the reaction provided the desired oxidative coupling product **1aa** in 55% yield with negligible amount of 1,4-addition product **2aa**. Moreover, we have not observed C_2-arylation product (**1aa'**) in the reaction. Encouraged, we further attempted the coupling reaction by varying the solvents. In this context, DMSO, DMA and NMP gave only oxidative coupling product **1aa** in 10-46% yields while acetonitrile, DCE, THF and

Dioxane gave a mixture of both **1aa** and **2aa** (**Table 5.1**, **entries 5-11**) in different ratio. On the other hand, the reaction provides only the conjugate addition product **2aa** in 39% yield in acetic acid (**Table 5.1**, **entry 12**).

Table 5.1 Optimization of the reaction conditions: Oxidative heck coupling between galactal derived enone **(1a)** and phenylboronic acid (**2a**).[a]



SN.	Solvents	Ligands (20 mol%)	Additive (2 equiv.)	Temp °C	Yield (%)[b]	
					(1aa)	(2aa)
1	THF	---	---	80	nd	nd
2	DMF	---	---	80	<10	nd
3	Acetonitrile	---	---	80	nd	nd
4	DMF	2,2'-bpy	---	80	55	nd
5	DMSO	2,2'-bpy	---	80	38	nd
6	DMA	2,2'-bpy	---	80	40	nd
7	NMP	2,2'-bpy	---	80	46	nd
8	Acetonitrile	2,2'-bpy	---	80	15	10
9	DCE	2,2'-bpy	---	80	10	12
10	THF	2,2'-bpy	---	80	15	20
11	Dioxane	2,2'-bpy	---	80	25	10
12	AcOH	2,2'-bpy	---	80	nd	39
13	DMF	1,10-Phen	---	80	68	nd
14	DMF	DABCO	---	80	nd	nd
15	DMF	Et_3N	---	80	nd	nd
16	DMF	Pyridine	---	80	nd	nd
17	DMF	DMAP	---	80	nd	nd
18	DMF	TMEDA	---	80	<10	nd
19	DMF	PPh_3	---	80	<10	nd
20	DMF	Dppe	---	80	<10	nd
21	DMF	1,10-Phen	Na_2CO_3	80	12	nd

22	DMF	1,10-Phen	Cs_2CO_3	80	15	nd
23	DMF	1,10-Phen	NaOAc	80	<10	nd
24[c]	DMF	1,10-Phen	---	100	20	nd
25[d]	DMF	1,10-Phen	---	100	45	nd
26[e]	DMF	1,10-Phen	---	100	39	nd
27[f]	DMF	1,10-Phen	---	100	30	nd
28	**DMF**	**1,10-Phen**	**---**	**100**	**86**	**<5**
29	DMF	1,10-Phen	---	120	87	<5
30	DMF	1,10-Phen	---	150	81	<5

[a]**Reaction condition:** Galactcal enone **1a** (81 mg, 0.25 mmol) and phenylboronic acid **2a** (61 mg, 0.5 mmol, 2 equiv.), $Pd(OAc)_2$ (10 mol%) and ligand (0.2 equiv.), additive (2 equiv.) were stirred in appropriate solvent (3 mL), under O_2 atmosphere. [b]Isolated yield. [c]$Pd(OAc)_2$ was replaced with $Pd(dba)_2$,[d]$Pd(OAc)_2$ was replaced with $Pd_2(dba)_3$, [e] $Pd(OAc)_2$ was replaced with $Pd(PPh_3)_4$. [f]$Pd(OAc)_2$ was replaced with $PdCl_2$.

Hence, we further screened the reaction condition with different nitrogen and phosphine ligands including 1,10-phenanthroline, DABCO (1,4-diazabicyclo[2.2.2]octane), triethyl amine, pyridine, DMAP (4-dimethylaminopyridine), TMEDA (tetramethylethylenediamine), triphenylphosphine, dppe (1,2-bis(diphenylphosphino)ethane) in DMF solvent (**Table 5.1**, **entries 13-20**). Among these ligands, 1,10-phenanthroline was found to be efficient by providing **1aa** in 68% yield**.** However, other ligands were found to be not suitable for this transformation. The impact of different bases were also investigated and observed very poor yields of the desired product (**Table 5.1**, **entries 21-23**).

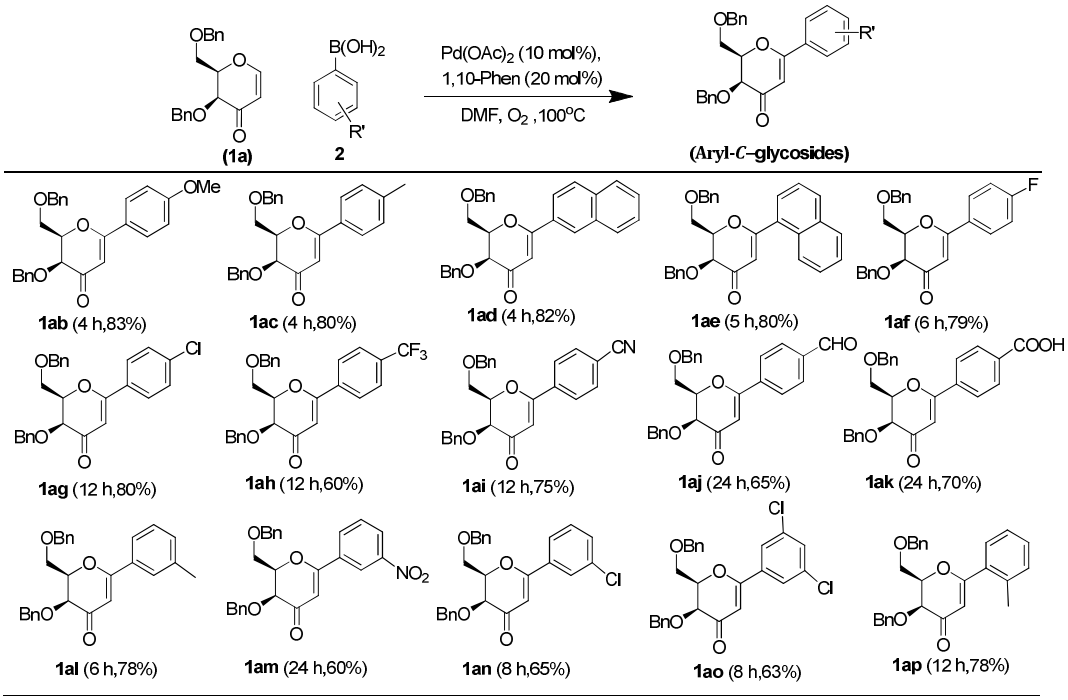
Further, we have screened different palladium catalysts including $Pd(dba)_2$, $Pd_2(dba)_3$, $Pd(PPh_3)_4$ and $PdCl_2$. These catalysts were found to be inferior to palladium acetate where the desired product **1aa** was obtained in low yields (**Table 5.1**, **entries 24-27**). Hence, we have attempted the reaction in elevated temperatures including 100 °C, 120

°C and 150 °C. To our delight, the desired product **1aa** was obtained in **86%** yield at 100 °C (**Table 5.1**, **entry 28**). Moreover, no improvement was achieved in terms of yield when the reaction was performed at 120 ^{0}C and 150 ^{0}C (**Table 5.1**, **entries 29 and 30**).

5.3 Substrates Scope

With optimised condition in our hand, we investigated scope of arylboronic acids in the coupling reaction with galactal enone **1a** (**Table 5.2**). Initially, the reactions were attempted with different arylboronic acids bearing electron donating and withdrawing substituent at the *para*-position. It was observed that the electron donating groups functionalized arylboronic acids (EDG) participated in the coupling reaction very efficiently and provided the desired products in 80-83% yields within 4-5 h (**Table 5.2**, **1ab-1ae**). On the other hand, electron withdrawing groups (EWG) functionalized arylboronic acids took little longer time (6-24 h) and provided the desired products in 60-80% yield (**Table 5.2**, **1af-1ak**). Further, we have investigated the reaction of *meta*-substituted as well as sterically hindered *ortho*-substituted arylboronic acids under optimized conditions. All these substrates participated in the coupling reaction smoothly and gave the desired products in good to excellent yields (**Table 5.2**, **1al-1ap**).

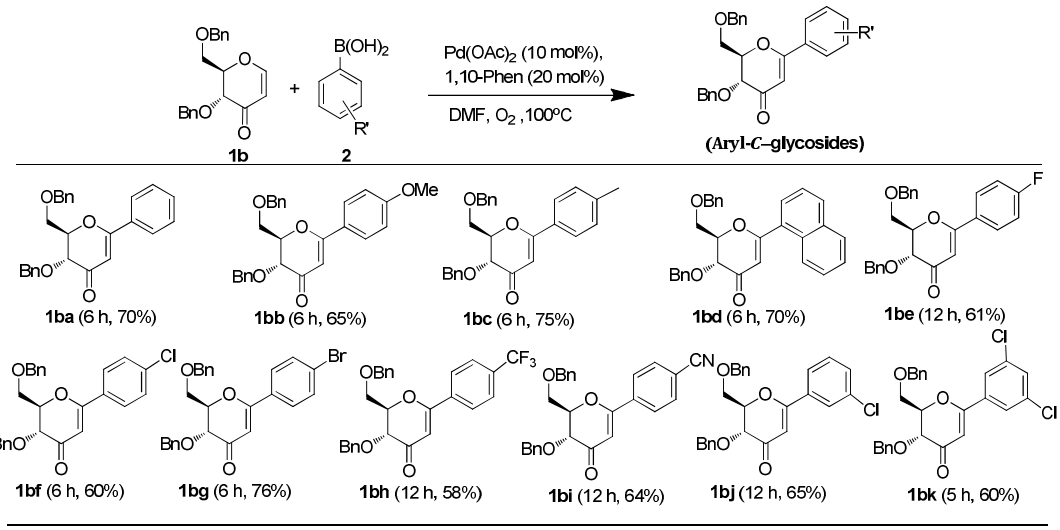
Table 5.2 Reaction of benzyl protected galactal enone **(1a)** with different arylboronic acids.[a,b]



[a]**Reaction condition**: Enone **1a** (0.25 mmol) and arylboronic acid **2** (0.5 mmol, 2.0 equiv.), $Pd(OAc)_2$(10 mol%) and 1,10-Phen (20 mol%) were stirred in DMF (3 mL) under O_2 baloon. [b]Isolated yield.

To elaborate the scope, we investigated the coupling reaction of benzyl protected glucal enone **(1b)** with different EDG and EWG substituted arylboronic acids. All these reactions proceeds smoothly with arylboronic acids under optimized conditions and afforded the desired products in 58-75% yields (**Table 5.3**, **1ba-1bk**).

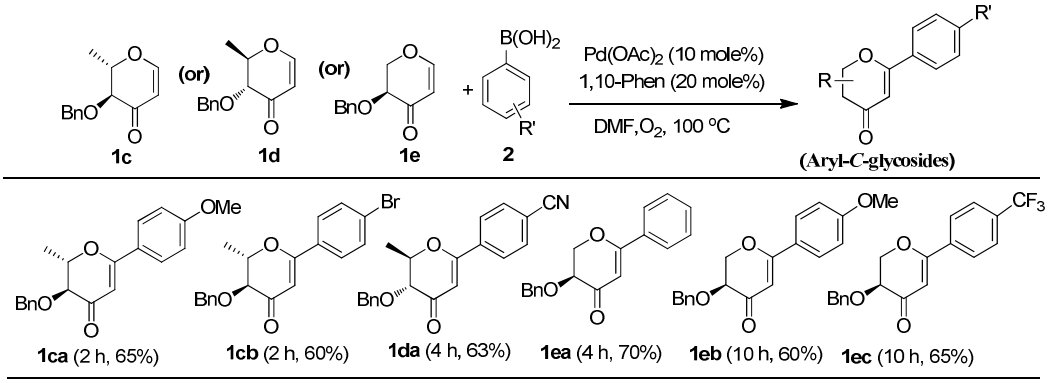
Table 5.3 Reaction of benzyl protected glucal enone **(1b)** with different arylboronic acids.[a,b]



[a]**Reaction condition**: Enone **1b** (0.25 mmol) and arylboronic acid **2** (0.5 mmol, 2.0 equiv.), $Pd(OAc)_2$(10 mol%) and 1,10-Phen (20 mol%) were stirred in DMF (3 mL) under O_2baloon. [b]Isolated yield.

Further in search of substrate scope, a different benzyl protected glycal-enones that are prepared from di-*O*-benzyl-L-rhamnal, di-*O*-benzyl-D-rhamnal and di-*O*-benzyl-L-arabinal (**1c, 1d, 1e)** were subjected to the oxidative coupling reactions (**Table 5.4**). To our delight, the reactions of L-rhamnal-enone (**1c)** and D-rhamnal-enone (**1d)** with different aryl boronic acids delivered the desired products in 60-65% yields within 2-4 h (**Table 5.4**, **1ca, 1cb and 1da**). Similarly, L-arabinal-enone **1e** also participated in the coupling reaction with different EDG and EWG substituted arylboronic acids and provided the corresponding arylated enones in good yields (**Table 5.4**, **1ea-1ec**)**.**

Table 5.4 Reaction of benzyl protected L-rhamnal enone (**1c**), D-rhamnal enone (**1d**), and L-arabinal enone (**1e**) with different arylboronic acids.[a,b]

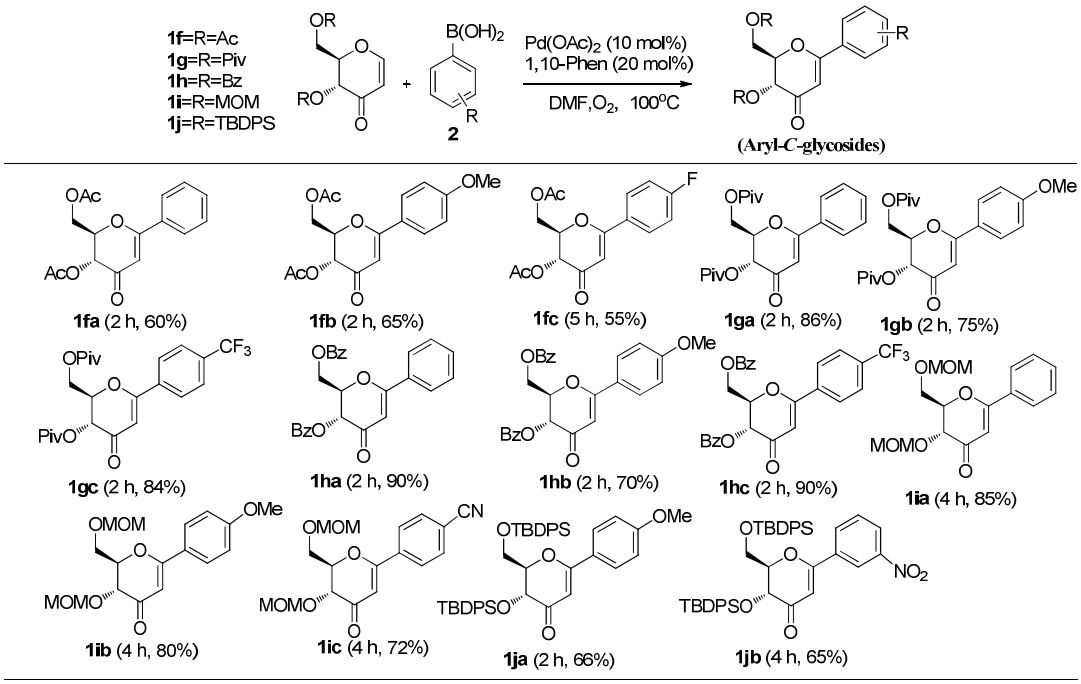


[a]**Reaction condition**: Enone **1c or 1d or 1e** (0.25 mmol) and arylboronic acid **2** (0.5 mmol, 2.0 equiv.), $Pd(OAc)_2$ (10 mol%) and 1,10-Phen (20 mol%) were stirred in a DMF (3 mL) under O_2 baloon. [b]Isolated yield.

5.4 Study of Protecting Group Compatibility

Having explored the scope of different arylboronic acids and glycal-enones, we investigated the compatibility of different traditional protecting groups in the coupling reaction. Acetyl, pivaloyl, benzoyl, MOM and TBDMS protected enones (**1f-1j**) were prepared and subjected to the oxidative coupling reaction with different EDG and EWG substituted arylboronic acids under optimized condition (**Table 5.5**). Pivaloyl and benzoyl protected enones participated in the coupling reaction in a short span of time and provided *C*-1 arylated enones in 70-90% yields (**Table 5.5**, **1ga-1hc**). On the other hand, acetyl protected enones gave the desired products relatively in low yields (**Table 5.5**, **1fa-1fc**)**.** However, to our delight, acid-sensitive MOM and TBDPS protected glycal-enones were also gave the oxidative coupling products with different arylboronic acids in 65-85 % of yields (**Table 5.5**, **1ia-1jb**).

Table 5.5 Reaction of different protected glucal enones with different arylboronic acids.[a,b]

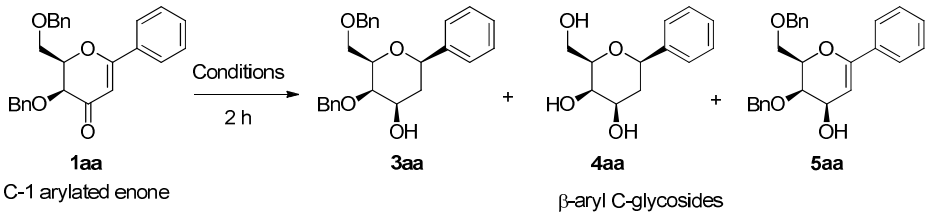


[a]**Reaction condition**: Enones (0.25 mmol) and arylboronic acid (0.5 mmol, 2.0 equiv.), $Pd(OAc)_2$ (10 mol%) and 1,10-Phen (20 mol%) were stirred in a DMF (3 mL) under O_2 baloon. [b]Isolated yield.

5.5 Stereo-selective Synthesis of 2-Deoxy-β-Aryl-*C*-Glycosides

Having explored the first step of the reaction, we investigated the second step i.e. stereoselective reduction of *C*-1 arylated enones. Benzyl protected galactal enone (**1aa**) was chosen as the model substrate and subjected to the reduction with different reducing agents including $NaBHAc_3$, $NaBH_4$, $LiAlH_4$ and Pd-C/H_2 (**Table 5.6**).

Table 5.6 Optimization of reaction condition for reduction from arylated enone **(1aa)** with different reducing agents.[a,b]



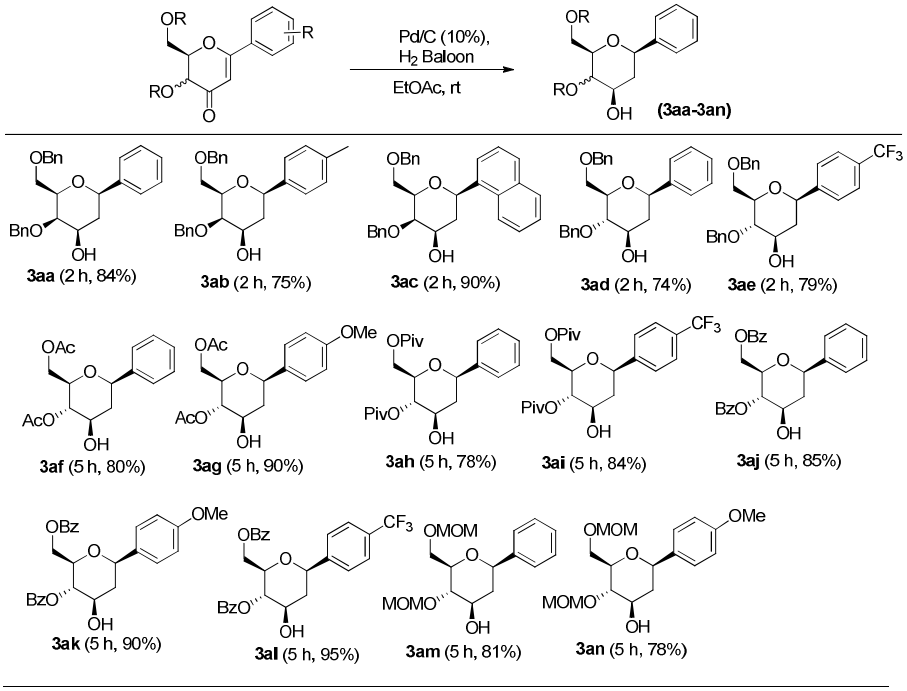
1aa C-1 arylated enone | **3aa** | **4aa** | **5aa** β-aryl C-glycosides

S No.	Conditions	(Yield %)		
		3aa	**4aa**	**5aa**
1	$NaBHAc_3$, MeOH, 0 °C - rt	nd	nd	nd
2	$NaBH_4$, MeOH, 0 °C -rt	<5	nd	75
3	$LiAlH_4$, THF, 0 °C -rt	<10	nd	70
4	Pd/C (10%), H_2 (1 atm.), MeOH, rt	45	40	nd
5	Pd/C (10%), H_2 (1 atm.), EtOAc, rt	84	<5	nd

[a]**Reaction condition**: Arylated enone **1aa** (0.15 mmol) and $NaBHAc_3$ or $NaBH_4$ or $LiAlH_4$ (1.2 equiv.) or 10% Pd/C (20 mg)/H_2-balloon were stirred in appropriate solvent (3 mL). [b]Isolated yield.

Among these reducing agents, Pd-C/H_2 in MeOH and EtOAc gave the desired β-anomer **3aa** stereoselectivity in 45% and 84% yields, respectively. In fact, we observed fully deprotected aryl β-glycoside **4aa** in 40% with Pd-C/H_2 in methanol due to its high reactivity. It is also interesting to note that the reduction of **1aa** with sodium borohydride and lithium aluminium hydride results in the formation of **5aa** as the major product (>70%) via chemo- and stereo- selective reduction of ketone group while no reaction was observed with $NaBHAc_3$.

Table 5.7 Stereo-selective hydrogenation of arylated enones with palladium on carbon[a,b]



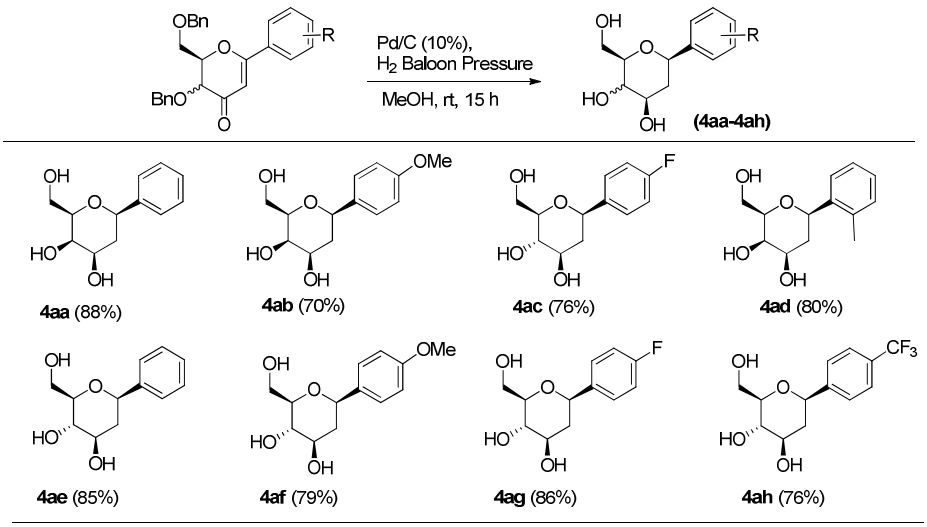
[a]**Reaction condition**: Arylated enone (0.15 mmol) and 10% Pd/C (20 mg) were stirred in a ethylacetate (3 mL) under H_2 baloon. [b]Isolated yield.

After successful identification of optimized condition for the second step, stereoselective hydrogenation of various *C*-1 arylated enones was investigated using Pd-C/H_2 in EtOAc. To our delight, benzyl, acetyl, pivaloyl, benzoyl and MOM protected *C*-1 arylated enones were successfully transformed into partially protected 2-deoxy β-aryl-*C*-Glycosides in good to excellent yields, i.e. 60-95% (**Table 5.7**, **3aa-3an**). In particular, benzyl protecting groups remained intact under the standard reaction condition.

Further, we have attempted preparation of fully deprotected 2-deoxy β-aryl-*C*-Glycosides from benzyl protected *C*-1 arylated enones **(Table 5.8)**. To our delight, this

transformation was achieved efficiently by using 10% Pd-C/H_2 in methanol. Under this condition, different benzyl protected *C*-1 arylated enones were directly transformed into corresponding unprotected *C*-aryl glycosides in 70-88% yields **(Table 5.8, 4aa-4ah)**.

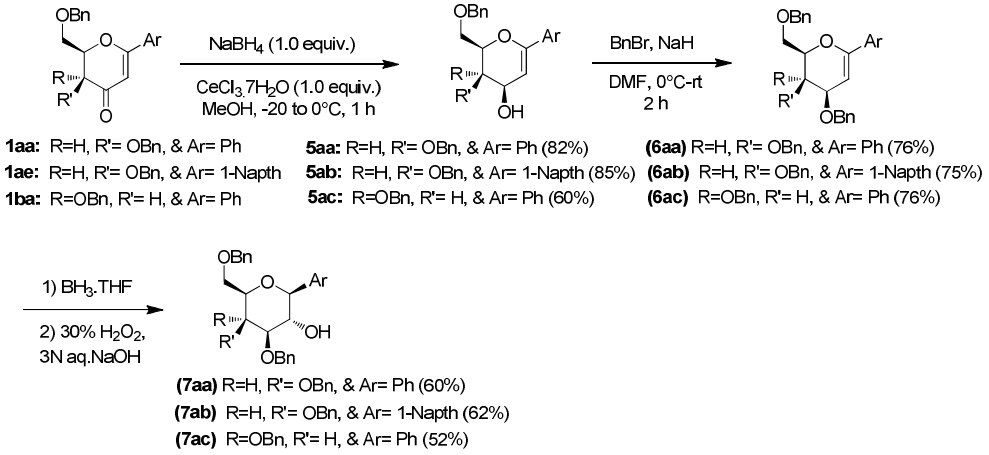
Table 5.8 Hydrogenation of arylated enones with palladium on carbon[a,b]



[a]**Reaction condition**: Arylated enone (0.15 mmol) and and 10% Pd/C (20 mg) were stirred in a CH_3OH (3 mL) under H_2 baloon. [b]Isolated yield.

5.6 Stereoselective Synthesis of 2-Hydroxy-β-Aryl-*C*-Glycosides

The *C*-1 arylated enones could serve as an important precursor for the preparation of 2-hydroxy-*β*-aryl-*C*-glycosides **(Scheme 5.2)**. For instance, chemo and stereoselective reduction of arylated enones **1aa, 1ae** and **1ba** with $NaBH_4$-$CeCl_3$ leads to the formation of allyl alcohols **5aa, 5ab** and **5ac** respectively. The resulted alcohols were protected with benzyl bromide and subjected to the hydroboration reaction to obtain 2-hydroxy-*β*-aryl-*C*-glycosides **7aa, 7ab** and **7ac** in good yields.

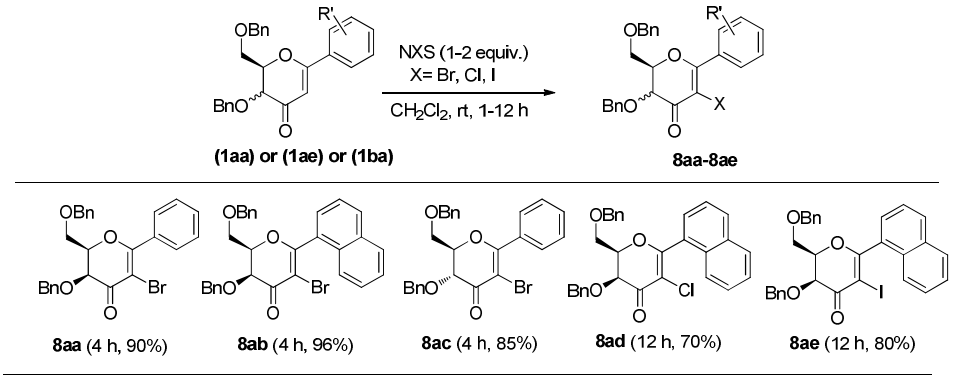


Scheme 5.2 Synthesis of 2-hydroxy-*β*-aryl-*C*-glycosides from *C*-1 arylated enones

5.7 *C*-2 Functionalization of Arylated Enones

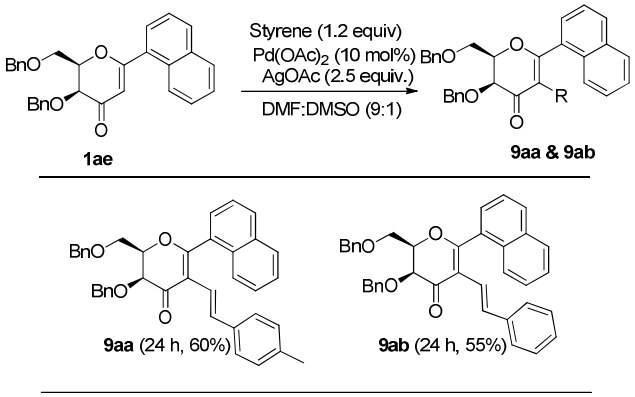
To demonstrate further usefulness of arylated enones, we have investigated the *C*-2 functionalization reactions such as halogenation and vinylation. Initially, we have attempted C-2 halogenation of the arylated enones **1aa, 1ae and 1ba** using N-halo succinimides **(Table 5.9)**.

Table 5.9 *C*-2 Halogenation of arylated enones.[a,b]



[a]**Reaction condition**: Arylated none (0.15 mmol) and NBS (1.0 equiv.), NCS, NIS (2.0 equiv.) in DCM. **(2)** Arylated none (0.1 mmol), styrene (1.5 equiv.), AgOAc (2.5 equiv) $Pd(OAc)_2$ (10 mol%) in DMF:DMSO (9:1, 3ml). [b]Isolated yield.

To our delight, *C*-2 selective bromination, chlorination and iodination were achieved in excellent yields at room temperature in dichloromethane (**Table 5.9**, **8aa-8ae**). Similarly, vinylation of arylated enone **1ae** was achieved by using 4-methylstyrene and styrene in the presence of $Pd(OAc)_2$ and silver acetate at 100 °C **(Scheme 5.3)** . This reaction provided the C-2 vinylated enones **9aa** and **9ab** in good yields 60% and 55% respectively in 24 h.

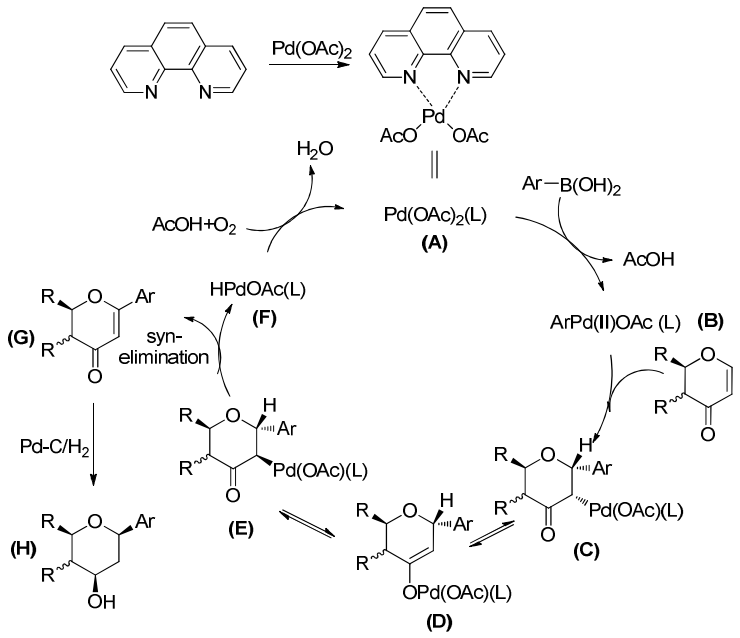


Scheme 5.3 *C*-2 Vinylation of arylated enones.

5.8 Plausible Reaction Mechanism

A plausible mechanism for the palladium catalyzed oxidative coupling reaction is shown in the **Scheme 5.5** [15]. Palladium acetate coordinates with 1,10-phenanthroline to form an electron rich palladium (II) complex **A** which undergoes transmetalation with arylboronic acid to form the complex **B**. Subsequently, the intermediate **B** is added to the enone from α-face to form intermediate **C**. This intermediate undergoes for palladotropic shift to form enolate **D** and rearranges to **E** which is suitable for syn-β-H elimination process. Finally reductive elimination leads to the formation of Pd(0)

intermediate **F** and C1-arylated enone **G**. The Pd(0) undergoes oxidation to Pd(II) while arylated enone **(G)** transformed into 2-deoxy β-*C*-aryl glycosides by hydrogenation reaction.



Scheme 5.4 Plausible mechanism of the reaction.

5.9 Summary and Conclusion

In conclusion, we have successfully developed an efficient method for regio- and stereoselective synthesis of 2-deoxy aryl-C-glycosides from enones derived glycals and arylboronic acids. A different glycal enones derived for D-glucal, D-galactal, L-rhamnal, D-rhamnal and L-arabinal underwent coupling reaction with electron donating and withdrawing functionalized arylboronic acids efficiently and provided regio-selective oxidized Heck coupled arylated enone products in good to excellent yields. Several sensitive functional groups in arylboronic acids including, halo, nitro, cyano, aldehyde, carboxylic acids, etc. were found to be stable under standard reaction

condition. Moreover, many protecting groups were found compatible during the coupling reaction. A controlled stereoselective reduction (hydrogenation) of C1-arylated enones provided 2-deoxy β-aryl-C-glycosides in excellent yields. The C-1 arylated enones were found to be efficient precursors for the preparation of 2-hydroxy-β-aryl-*C*-glycosides. Moreover, a regioselective C-2 halogenations and vinylation was achieved in excellent yields. We hope our studies gives new approach for the preparation of β-aryl-*C*-glycosides.

5.10 Experimental Section

The benzyl protected glycal-enones **1a-1d, 1f** and **1i** has been prepared as described in chapter 4. Preparation of other enones are described below,

5.10.1. Synthesis of (*S*)-3-(benzyloxy)-2H-pyran-4(3H)-one (1e)

Compound **1e** was prepared from 3,4-di-*O*-benzyl-L-arabinal using the general procedure **4.6.1** and purified by column chromatography on silica gel (EtOAc/petroleum ether (15:85)) to afford as a colourless oil (568 mg, 55% yield); Rf = 0.4 (EtOAc/petroleum ether (20:80)); $[\alpha]_D^{24}$ = - 86.5 (c = 0.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37–7.28 (m, 6H), 5.41 (dd, *J* = 6.0, 1.0 Hz, 1H), 4.85 (d, *J* = 11.9 Hz, 1H), 4.62 (d, *J* = 11.9 Hz, 1H), 4.47 (dd, *J* = 12.4, 6.4 Hz, 1H), 4.37 (dd, *J* = 12.4, 4.0 Hz, 1H), 3.84–3.81 (m, 1H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 190.3, 162.9, 137.1, 128.4, 128.1, 128.0, 105.3, 73.5, 72.5, 71.2. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{18}H_{17}O_3$: 281.1178; found: 281.1181.

5.10.2 Synthesis of 4,6-di-*O*-(2,2-dimethylpropanoate)-1,5-anhydro-2-deoxy-D-erythro-hex-1-en-3-ulose (1g)

To a stirred solution of **X** (prepared as in Chapter-4) (432 mg, 3 mmol) in CH_2Cl_2 (10 mL) were added trimethylacetyl chloride (1.1 mL, 9 mmol) followed by pyridine (1 mL) at room temperature. The solution was stirred for the 12 hours, and upon completion of the reaction (TLC monitoring), it was quenched with saturated aqueous $NaHCO_3$ and extracted with ethyl acetate. The organic layer was washed with brine, dried over Na_2SO_4. The combined organic layer evaporated and residue was purified by column chromatography SiO_2, EtOAc/petroleum ether (15:85) to gave the pure **1g** as white solid 730 mg (78% yield). R*f* =0.5 (EtOAc/petroleum ether (20:80)); $[\alpha]_D^{24}$ = +190 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 5.9 Hz, 1H), 5.53 (d, *J* = 13.1 Hz, 1H), 5.47 (d, *J* = 5.9 Hz, 1H), 4.66–4.63 (m, 1H), 4.40 (dd, *J* = 12.8, 1.9 Hz, 1H), 4.35 (dd, *J* = 12.8, 3.8 Hz, 1H), 1.26 (s, 9H), 1.22 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 187.9, 177.6, 176.3, 162.2, 105.3, 78.4, 67.6, 61.2, 38.9, 38.7, 27.0, 27.0. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{16}H_{25}O_6$: 313.1651; found: 313.1676.

5.10.3 Synthesis of 4,6-di-*O*-benzoyl-1,5-anhydro-2-deoxy-D-erythro-hex-1-en-3-ulose (1h)

To a stirred solution of **X** (prepared as in Chapter-4) (432 mg, 3 mmol) in CH_2Cl_2 (10 mL) were added benzoyl chloride (1.04 mL, 9 mmol) followed by pyridine (1 mL) at room temperature. The solution was stirred for the 12 hours, and after completion of the reaction (TLC monitoring), it was quenched with saturated aqueous $NaHCO_3$ and extracted with ethyl acetate. The organic layer was washed with brine, dried over Na_2SO_4. The combined organic layer evaporated and residue was purified by column

chromatography SiO_2, EtOAc/petroleum ether (20:80) to gave the pure **1h** as colorless viscous oil 950 mg (90% yield). R*f* =0.3 (EtOAc/petroleum ether (20:80)); $[\alpha]_D^{24}$ = +295 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.07–8.03 (m, 4H), 7.56–7.52 (m, 2H), 7.42–7.38 (m, 5H), 5.93 (d, *J* = 13.0 Hz, 1H), 5.51 (d, *J* = 5.9 Hz, 1H), 4.91–4.87 (m, 1H), 4.82 (dd, *J* = 12.7, 2.4 Hz, 1H), 4.57 (dd, *J* = 12.7, 4.4 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 187.3, 165.5, 164.6, 162.4, 133.4, 133.1, 129.7, 129.4, 128.9, 128.4, 128.2, 105.1, 78.1, 68.6, 61.9. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{20}H_{17}O_6$: 353.1025; found: 353.1043.

5.10.4 Synthesis of 4,6-di-*O*-tert-butyldiphenylsilyl-l,5-anhydro-2-deoxy-D-erythro-hex-l-en-3-ulose (1j)

To a stirred solution of **X** (prepared as in Chapter-4) (432 mg 3 mmol) in DMF (10 mL) were added tert-butyl(chloro)diphenylsilane (1.94 mL, 7.5 mmol) followed by imidazole (612.1 mg, 9 mmol) at room temperature. The resulting solution was stirred for the 12 hours, and after completion of the reaction (TLC monitoring), it was quenched with water and extracted with ethyl acetate. The organic layer was washed with brine, dried over Na_2SO_4. The combined organic layer evaporated and residue was purified by column chromatography (SiO_2, EtOAc/petroleum ether (10:90)) to gave the pure **1j** as colourless oil 1.12 g (60% yield). R*f* =0.6 (EtOAc/petroleum ether (10:90)).; $[\alpha]_D^{23}$ = +97.5 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.68–7.66 (m, 2H), 7.62–7.55 (m, 4H), 7.42–7.29 (m, 14H), 7.17 (d, *J* = 5.9 Hz, 1H), 5.21 (d, *J* = 5.9 Hz, 1H), 4.44 (d, *J* = 10.3 Hz, 1H), 4.38–4.34 (m, 1H), 3.95 (dd, *J* = 11.6, 2.9 Hz, 1H), 3.87 (dd, *J* = 11.6, 4.8 Hz, 1H), 1.01 (d, *J* = 4.1 Hz, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 191.3, 161.7, 135.8, 135.8, 135.7, 135.6, 134.8, 133.4, 133.4, 133.1, 133.0, 129.7,

129.7, 129.6, 129.4, 127.8, 127.7, 127.7, 127.6, 127.5, 127.3, 104.4, 83.6, 77.3,70.5, 62.5, 27.0, 26.8, 19.8, 19.2. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{38}H_{45}O_4Si_2$: 621.2856; found: 621.2861.

5.10.5. General procedure for synthesis of *C*-1 arylated enones via oxidative Heck reactions

To a stirred solution of glycals derived enone **1a-1j** (0.25 mmol) in dry DMF (3 mL) at room temperature under O_2 balloon pressure were added $Pd(OAc)_2$ (10 mol%) and 1,10-Phenanthroline (20 mol%) respectively. After stirring for 10 minutes the reaction mixture was heated at 90°C to which arylboronic acid **2** (0.50 mmol) was added and further stirred for appropriate time. After completion of reaction (TLC monitoring), it was cool to room temperature, diluted with ethyl acetate (30 mL) and filtered through pad of celite. The filtrate was evaporated in vacuo and the residue was purified by column chromatography (SiO_2, EtOAc/petroleum ether as eluent), to furnished respective oxidative coupled product.

5.10.6. General procedure for hydrogenation of *C*-1 arylated enones with 10% Pd-C/H_2 in ethyl acetate

C-1 arylated enones (0.15 mmol) were dissolved in EtOAc (3 mL) at room temperature, to the resulting solution was added 10% Pd/C (20 mg) and the RB flask was flushed with H_2 two times. This obtained solution was stirred under H_2 with balloon pressure for required time. The organic solution was filtered and the filtrate was concentrated in vacuo to dryness, the resultant residue was purified by column chromatography (SiO_2, EtOAc/petroleum ether as eluent) to afford the reduced product.

5.10.7 General procedure for hydrogenation of *C*-1 arylated enones with 20% Pd-C/H_2 in MeOH

C-1 arylated enones (0.15 mmol) was dissolved in MeOH (3 mL) at room temperature, to the resulting solution was added 10% Pd/C (20 mg) and the RB flask was flushed with H_2 two times. This obtained solution was stirred under H_2 with balloon pressure for required time. The organic solution was filtered and the filtrate was concentrated in vacuo to dryness, the resultant residue was purified by column chromatography (SiO_2, EtOAc/petroleum ether as eluent) to afford the reduced product.

5.10.8. General procedure for reduction of *C*-1 arylated enones with $NaBH_4$

The *C*-1 arylated enone (0.25 mmol) was dissolved in MeOH (10 mL), cool the reaction mixture and stirred it at −78 °C. To this solution $CeCl_3 \cdot 7H_2O$ (0.275 mmol) was added followed by $NaBH_4$ (0.275 mmol) in two portions. The resulting solution was stirred for 2 h at −78 °C and the reaction was quenched by addition of saturated aqueous NH_4Cl solution (1 mL). The reaction mixture was extracted with ethyl acetate (50 mL), the organic layer was washed with water (25 mL) and brine solution (25 mL) and dried over anhydrous Na_2SO_4. The organic solvent was removed under reduced pressure and residue was purified by column chromatography (SiO_2, EtOAc/petroleum ether as eluent) to afford the pure product.

5.10.9. General procedure for benzylation of 3-hydroxy *C*-1-arylated glycals

3-Hydroxy *C*-1-arylated glycals (0.2 mmol) was dissolved in dry DMF (10 mL), cool the reaction mixture and stirred it at 0 °C. To this solution benzyl bromide (0.6 mmol) was added followed by NaH (60% suspension in para□n oil, 0.2 mmol) at same temperature. The reaction mixture was stirred for the appropriate time at room

temperature. After completion, reaction was quenched with ice water and extracted with ethyl acetate (2 × 20 mL). The organic layer was washed with water (20 mL), brine solution (25 mL) and then dried over anhydrous Na_2SO_4. The organic solvent was removed under vacuo to furnished crude compound, which was further purified by column chromatography (SiO_2, EtOAc/petroleum ether as eluent) to afford corresponding pure product.

5.10.10. General procedure for hydroboration of tribenzyl-*C*-1-arylated glycals

Tri-*O*-benzyl-*C*-1-arylated glycal (0.15 mmol, 1 equiv) was dissolved in anhydrous THF (8 mL), cool the reaction mixture and stirred it at 0 °C. To this solution $BH_3 \cdot$ THF (1.5 mL, 1 M in THF, 10 equiv) was added drop wise at 0 °C under nitrogen atmosphere and stirred for 2.5 h. Then after 30% NaOH (2 mL) and 30% H_2O_2 (2 mL) solution were added slowly, and stirred it for 1 h at 0 °C and then allow it to stir for another 3 h at RT. Ethyl acetate (30 mL) was added for dilution and washed with water (15 mL), brine solution (15 mL). The resulting organic layer was dried over Na_2SO_4 and evaporated under reduced pressure to furnished crude residue. The residue was purified by column chromatography (SiO_2, EtOAc/petroleum ether as eluent)to afford corresponding pure product.

5.10.11. General procedure for halogenations of *C*-1 arylated enones with NXS

To a stirred solution of *C*-1 arylated enones (0.15 mmol, 1.0 equiv) in CH_2Cl_2 (3 mL) was added NBS (1.0 equiv), NIS, or NCS (2.0 equiv) at room temperature. The reaction mixture was stirred at same temperature for appropriate time until the TLC showed complete consumption of staring material. The organic solvent was concentrated to

dryness at reduced pressure and the residue was purified by column chromatography (SiO_2, EtOAc/petroleum ether as eluent) to furnished respective vinyl halide.

5.10.12. General procedure for vinylation of *C*-1 arylated Enones

To a stirred solution of *C*-1 arylated enone (0.1 mmol, 45 mg) in mixed solvents DMF and DMSO (3 mL, 10:1) was added styrene (0.15 mmol), palladium(II)acetate (0.01 mmol, 2.24 mg) and silver acetate (0.25 mmol, 42 mg). The reaction mixture was stirred at 100 °C for 24 h under open air conditions. After completion (TLC monitoring), ethyl acetate (20 mL) was added to dilute and filtered, washed with water (25 mL) then with brine solution(25 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and evaporated under vacuo. The residue was purified by column chromatography (SiO_2, EtOAc/petroleum ether as eluent) to afford the corresponding product.

5.11 Analytical Data for the Products

5.11.1. (*2R,3S*)-3-(benzyloxy)-2-((benzyloxy)methyl)-6-phenyl-2H-pyran-4(3H)-one (1aa)

The compound **1aa** was prepared using the general procedure **5.10.5.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (15:85) as eluent to afford as colourless waxy solid (86 mg, 86%); R*f* = 0.4 (EtOAc/petroleum ether (20:80)); $[\alpha]_D^{25}$= +28.6 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.76–7.74 (m, 2H), 7.49–7.46 (m, 1H), 7.42–7.39 (m, 2H), 7.36–7.26 (m, 10H), 6.03 (d, *J* = 1.3 Hz, 1H), 4.77 (d, *J* = 11.9 Hz, 1H), 4.67–4.64 (m, 1H), 4.61 (d, *J* = 11.9 Hz, 1H),

4.57–4.54 (m, 2H), 4.04 (dd, *J* = 10.2, 6.8 Hz, 1H), 3.91 (dd, *J* = 10.2, 5.6 Hz, 1H), 3.79 (dd, *J* = 2.4, 1.3 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 190.2, 169.7, 137.6, 137.1, 132.2, 131.7, 128.5, 128.4, 128.3, 128.2, 127.9, 127.8, 127.6, 126.6, 100.2, 80.4, 73.5, 71.9, 67.6. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{26}H_{25}O_4$: 401.1753; found: 401.1744.

5.11.2. (*2R,3S*)-3-(benzyloxy)-2-((benzyloxy)methyl)-6-(4-methoxyphenyl)-2H-pyran-4(3H)-one (1ab)

The compound **1ab** was prepared using the general procedure **5.10.5.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (20:80) as eluent to afford as white waxy solid (89 mg, 83%); R*f* = 0.3 (EtOAc/petroleum ether (20:80)); $[\alpha]_D^{26}$ = +82.9 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.8 Hz, 2H), 7.29–7.19 (m, 10H), 6.84 (d, *J* = 8.8 Hz, 2H), 5.88 (s, 1H), 4.70 (d, *J* = 11.9 Hz, 1H), 4.59–4.55 (m, 1H), 4.54 (d, *J* = 11.9 Hz, 1H), 4.51–4.47 (m, 2H), 3.97 (dd, *J* = 10.1, 6.9 Hz, 1H), 3.82 (dd, *J* = 10.2, 5.5 Hz, 1H), 3.77 (s, 3H), 3.70 (d, *J* = 1.1 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 190.1, 169.7, 162.6, 137.7, 137.2, 128.5, 128.4, 128.3, 128.2, 127.8, 127.8, 127.6, 124.5, 113.9, 98.9, 80.3, 73.6, 73.5, 71.9, 67.8, 55.4. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{27}H_{27}O_5$: 431.1858; found: 431.1845.

5.11.3. (*2R,3S*)-3-(benzyloxy)-2-((benzyloxy)methyl)-6-(p-tolyl)-2H-pyran-4(3H)-one (1ac)

The compound **1ac** was prepared using the general procedure **5.10.5.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (15:85) as eluent to afford as white waxy solid (83 mg, 80%); R*f* = 0.4 (EtOAc/petroleum ether (20:80)); $[\alpha]_D^{25}$ = +62.6 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.57 (d, *J* =

8.3 Hz, 2H), 7.29–7.19 (m, 10H), 7.13 (d, *J* = 8.1 Hz, 2H), 5.92 (d, *J* = 1.2 Hz, 1H), 4.79 (d, *J*= 11.9 Hz, 1H), 4.59–4.55 (m, 1H), 4.54–4.46 (m, 3H), 3.96 (dd, *J* = 10.2, 6.9 Hz, 1H), 3.82 (dd, *J* = 10.2, 5.6 Hz, 1H), 3.70 (dd, *J* = 2.4, 1.3 Hz, 1H), 2.31 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 190.2, 169.9, 142.4, 137.6, 137.2, 129.4, 129.3, 128.5, 128.4, 128.3, 128.2, 127.8, 127.8, 127.6, 126.9, 126.6, 99.6, 80.3, 73.6, 73.5, 71.9, 67.7, 21.5. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{27}H_{27}O_4$: 415.1909; found: 415.1900.

5.11.4. (*2R,3S*)-3-(benzyloxy)-2-((benzyloxy)methyl)-6-(naphthalen-2-yl)-2H-pyran-4(3H)-one (1ad)

The compound **1ad** was prepared using the general procedure **5.10.5.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (10:90) as eluent to afford as yellowish viscous oil (92 mg, 82%); R*f* = 0.6 (EtOAc/petroleum ether (20:80)); $[\alpha]_D^{25}$ = +56.3 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.31 (s, 1H), 7.88–7.82 (m, 3H), 7.75 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.56–7.50 (m, 2H), 7.36–7.27 (m, 10H), 6.16 (d, *J* = 1.2 Hz, 1H), 4.80 (d, *J* = 11.9 Hz, 1H), 4.74–4.71 (m, 1H), 4.65–4.57 (m, 3H), 4.11 (dd, *J* = 10.1, 6.9 Hz, 1H), 3.95 (dd, *J* = 10.1, 5.6 Hz, 1H), 3.84 (dd, *J* = 2.4, 1.3 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 190.2, 169.5, 137.6, 137.1, 134.8, 132.6, 129.4, 129.0, 128.4, 128.3, 128.3, 128.2, 127.9, 127.8, 127.8, 127.6, 127.5, 126.7, 122.8, 100.6, 80.5, 73.6, 73.5, 71.9, 67.6. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{30}H_{27}O_4$: 451.1909; found: 451.1903

5.11.5. (*2R,3S*)-3-(benzyloxy)-2-((benzyloxy)methyl)-6-(naphthalen-1-yl)-2H-pyran-4(3H)-one (1ae)

The compound **1ae** was prepared using the general procedure **5.10.5.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (10:90) as

eluent to afford as viscous oil (90 mg, 80%); R*f* = 0.6 (EtOAc/petroleum ether (20:80)); $[a]_D^{25}$ = +66.2 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.57–7.56 (m, 1H), 7.42–7.35 (m, 3H), 7.29–7.19 (m, 10H), 5.75 (d, *J* = 1.1 Hz, 1H), 4.78–4.72 (m, 2H), 4.54–4.48 (m, 2H), 4.44 (d, *J* = 11.8 Hz, 1H), 3.96 (dd, *J* = 10.3, 7.0 Hz, 1H), 3.84 (dd, *J* = 10.3, 5.4 Hz, 1H), 3.79 (dd, *J* = 2.1, 1.4 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 190.1, 172.5, 137.6, 137.2, 133.5, 131.4, 131.4, 130.4, 128.4, 128.3, 128.3, 128.1, 127.8, 127.7, 127.6, 127.4, 127.0, 126.2, 125.2, 124.8, 105.3, 80.9, 73.6, 73.5, 71.8, 67.7. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{30}H_{27}O_4$: 451.1909; found: 451.1912.

5.11.6. (*2R,3S*)-3-(benzyloxy)-2-((benzyloxy)methyl)-6-(4-fluorophenyl)-2H-pyran-4(3H)-one (1af)

The compound **1af** was prepared using the general procedure **5.10.5.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (15:85) as eluent to afford as white foam (83 mg, 79%); R*f* = 0.5 (EtOAc/petroleum ether (20:80)); $[a]_D^{25}$ = +58.6 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.68–7.65 (m, 2H), 7.28–7.18 (m, 10H), 7.03–6.99 (m, 2H), 5.88 (d, *J* = 1.2 Hz, 1H), 4.68 (d, *J* = 11.9 Hz, 1H), 4.58–4.55 (m, 1H), 4.52 (d, *J* = 11.9 Hz, 1H), 4.49–4.45 (m, 2H), 3.95 (dd, *J* = 10.2, 6.9 Hz, 1H), 3.81 (dd, *J* = 10.2, 5.5 Hz, 1H), 3.70 (dd, *J* = 2.3, 1.3 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 190.0, 168.6, 165.8, 163.8, 137.6, 137.0, 128.9, 128.9, 128.4, 128.4, 128.3, 128.2, 127.9, 127.8, 127.6, 115.8, 115.6, 100.0, 80.5, 73.5, 73.5, 71.9, 67.6. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{26}H_{24}FO_4$: 419.1659; found: 419.1646.

5.11.7. (*2R,3S*)-3-(benzyloxy)-2-((benzyloxy)methyl)-6-(4-chlorophenyl)-2H-pyran-4(3H)-one (1ag)

The compound **1ag** was prepared using the general procedure **5.10.5.** and column chromatography was performed on silica gel using petroleum ether/EtOAc (85:15) as eluent to afford as white foam (87 mg, 80%); R*f* = 0.5 (EtOAc/hexane (20:80)); $[a]_D^{25}$ = +63.1 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.60–7.58 (m, 2H), 7.31–7.19 (m, 12H), 5.90 (d, *J* = 1.1 Hz, 1H), 4.68 (d, *J* = 11.9 Hz, 1H), 4.58–4.55 (m, 1H), 4.53–4.45 (m, 3H), 3.95 (dd, *J* = 10.2, 6.9 Hz, 1H), 3.81 (dd, *J* = 10.2, 5.5 Hz, 1H), 3.70 (dd, *J* = 2.0, 1.3 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 190.0, 168.4, 137.9, 137.5, 137.0, 130.7, 128.9, 128.4, 128.3, 128.2, 127.9, 127.9, 127.8, 127.6, 100.3, 80.5, 73.5, 73.4, 71.9, 67.6. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{26}H_{24}ClO_4$: 435.1363; found: 435.1351.

5.11.8. (*2R,3S*)-3-(benzyloxy)-2-((benzyloxy)methyl)-6-(4-(trifluoromethyl)phenyl)-2H-pyran-4(3H)-one (1ah)

The compound **1ah** was prepared using the general procedure **5.10.5.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (15:85) as eluent to afford as yellowish viscous oil (70 mg, 60%); R*f* = 0.5 (EtOAc/petroleum ether (20:80)); $[a]_D^{25}$ = +29.5 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.2 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.29–7.20 (m, 10H), 5.97 (d, *J* = 1.2 Hz, 1H), 4.69 (d, *J* = 11.9 Hz, 1H), 4.61–4.58 (m, 1H), 4.53–4.45 (m, 3H), 3.97 (dd, *J* = 10.2, 6.9 Hz, 1H), 3.81 (dd, *J* = 10.2, 5.5 Hz, 1H), 3.73 (dd, *J* = 2.3, 1.3 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 190.1, 167.7, 137.5, 136.9, 135.7, 133.2, 133.0, 128.4, 128.3, 128.3, 128.0, 127.9, 127.7, 126.9, 125.5, 125.5, 124.6, 122.5, 101.3, 80.7, 73.6, 73.3, 72.0,

67.5. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{27}H_{24}F_3O_4$: 469.1627; found: 469.1614.

5.11.9. 4-((*2R,3S*)-3-(benzyloxy)-2-((benzyloxy)methyl)-4-oxo-3,4-dihydro-2H-pyran-6-yl)benzonitrile (1ai)

The compound **1ai** was prepared using the general procedure **5.10.5.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (25:75) as eluent to afford as yellowish oil (80 mg, 75%); R*f* = 0.3 (EtOAc/petroleum ether (20:80)); $[a]_D^{25}$ = +51.0 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.3 Hz, 2H), 7.62 (d, *J* = 8.5 Hz, 2H), 7.29–7.19 (m, 10H), 5.97 (d, *J* = 1.1 Hz, 1H), 4.68 (d, *J* = 11.9 Hz, 1H), 4.61–4.58 (m, 1H), 4.53–4.44 (m, 3H), 3.96 (dd, *J* = 10.2, 6.9 Hz, 1H), 3.81 (dd, *J* = 10.2, 5.5 Hz, 1H), 3.73–3.72 (m, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 189.9, 166.9, 137.4, 136.8, 136.5, 132.3, 128.4, 128.4, 128.3, 128.0, 127.9, 127.7, 127.0, 118.0, 114.8, 101.8, 80.8,73.6, 73.2, 72.0, 67.5. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{27}H_{24}NO_4$: 426.1705; found: 426.1697.

5.11.10. 4-((*2R,3S*)-3-(benzyloxy)-2-((benzyloxy)methyl)-4-oxo-3,4-dihydro-2H-pyran-6-yl)benzaldehyde (1aj)

The compound **1aj** was prepared using the general procedure **5.10.5.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (25:75) as eluent to afford as white waxy solid (70 mg, 65%); R*f* = 0.3 (EtOAc/petroleum ether (20:80)); $[a]_D^{25}$ = +51.5 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.99 (s, 1H), 7.86–7.82 (m, 4H), 7.30–7.21 (m, 10H), 6.02 (d, *J* = 1.3 Hz, 1H), 4.69 (d, *J* = 11.9 Hz, 1H), 4.62–4.59 (m, 1H), 4.55–4.46 (m, 3H), 3.98 (dd, *J* = 10.2, 6.9 Hz, 1H), 3.83 (dd, *J* = 10.2, 5.6 Hz, 1H), 3.74 (dd, *J* = 2.3, 1.3 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 191.4, 190.1, 167.8, 138.1, 137.7, 137.5, 136.9, 129.7, 128.5, 128.4, 128.3, 128.0,

127.9, 127.7, 127.2, 101.8, 80.8, 73.6, 73.4, 72.0, 67.5. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{27}H_{25}O_5$: 429.1702; found: 429.1688.

5.11.11. 4-((*2R,3S*)-3-(benzyloxy)-2-((benzyloxy)methyl)-4-oxo-3,4-dihydro-2H-pyran-6-yl)benzoic acid (1ak)

The compound **1ak** was prepared using the general procedure **5.10.5.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (50:50) as eluent to afford as white foam (78 mg, 70%); R*f* = 0.1 (EtOAc/petroleum ether (30:70)); $[a]_D^{26}$ = +37.5 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.5 Hz, 2H), 7.84 (d, *J* = 8.5 Hz, 2H), 7.37–7.28 (m, 10H), 6.11 (d, *J* = 0.8 Hz, 1H), 4.77 (d, *J* = 11.9 Hz, 1H), 4.71–4.68 (m, 1H), 4.63–4.54 (m, 3H), 4.06 (dd, *J* = 10.2, 6.9 Hz, 1H), 3.91 (dd, *J* = 10.2, 5.5 Hz, 1H), 3.82 (d, *J* = 0.7 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 190.4, 170.5, 168.3, 137.4, 137.0, 136.9, 132.6, 131.9, 130.3, 128.5, 128.4, 128.3, 128.0, 127.9, 127.7, 126.6, 115.3, 101.5, 80.7, 73.6, 73.3, 72.0, 67.5. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{27}H_{25}O_6$: 445.1651; found: 445.1644.

5.11.12. (*2R,3S*)-3-(benzyloxy)-2-((benzyloxy)methyl)-6-(m-tolyl)-2H-pyran-4(3H)-one (1al)

The compound **1al** was prepared using the general procedure **5.10.5.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (15:85) as eluent to afford as yellowish viscous oil (81 mg, 78%); R*f* = 0.5 (EtOAc/petroleum ether (20:80)); $[a]_D^{26}$ = +46.2 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.57–7.54 (m, 2H), 7.36–7.26 (m, 12H), 6.01 (d, *J* = 1.3 Hz, 1H), 4.77 (d, *J* = 11.9 Hz, 1H), 4.67–4.64 (m, 1H), 4.62–4.54 (m, 3H), 4.05 (dd, *J* = 10.2, 6.8 Hz, 1H), 3.91 (dd, *J* = 10.2, 5.7 Hz, 1H), 3.79 (dd, *J* = 2.5, 1.3 Hz, 1H), 2.38 (s, 3H). **^{13}C NMR** (125 MHz,

$CDCl_3$) δ 190.3, 170.0, 138.3, 137.7, 137.2, 132.6, 132.3, 128.5, 128.4, 128.3, 128.2, 127.8, 127.8, 127.6, 127.3, 123.9, 100.2, 80.5, 73.6, 73.6, 71.9, 67.7, 21.3. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{27}H_{27}O_4$: 415.1909; found: 415.1901.

5.11.13. (*2R,3S*)-3-(benzyloxy)-2-((benzyloxy)methyl)-6-(3-nitrophenyl)-2H-pyran-4(3H)-one(1am)

The compound **1am** was prepared using the general procedure **5.10.5.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (30:70) as eluent to afford as yellowish viscous oil (67 mg, 60%); R*f* = 0.2 (EtOAc/petroleum ether (20:80)); $[\alpha]_D^{25}$ = +12.1 (c = 0.05, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.55 (t, *J* = 1.9 Hz, 1H), 8.26 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.97 (d, *J* = 7.9 Hz, 1H), 7.55 (t, *J* = 8.0 Hz, 1H), 7.31–7.20 (m, 10H), 6.02 (d, *J* = 1.1 Hz, 1H), 4.69 (d, *J* = 11.9 Hz, 1H), 4.64–4.61 (m, 1H), 4.55–4.50 (m, 2H), 4.47 (d, *J* = 11.9 Hz, 1H), 4.00 (dd, *J* = 10.1, 6.9 Hz, 1H), 3.83 (dd, *J* = 10.1, 5.5 Hz, 1H), 3.75–3.74 (m, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 189.9, 166.6, 148.4, 137.4, 136.8, 134.2, 132.0, 129.7, 128.5, 128.4, 128.3, 128.0, 127.9, 127.7, 126.0, 121.6, 101.4, 80.9, 73.7, 73.3, 72.1, 67.5. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{26}H_{24}NO_6$: 446.1604; found: 446.1607.

5.11.14. (*2R,3S*)-3-(benzyloxy)-2-((benzyloxy)methyl)-6-(3-chlorophenyl)-2H-pyran-4(3H)-one (1an)

The compound **1an** was prepared using the general procedure **5.10.5.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (15:85) as eluent to afford as yellowish viscous oil (71 mg, 65%); R*f* = 0.5 (EtOAc/petroleum ether (20:80)); $[\alpha]_D^{25}$ = +31.1 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.67 (t,

J = 1.7 Hz, 1H), 7.54 (d, *J* = 7.9 Hz, 1H), 7.38–7.36 (m, 1H), 7.30–7.20 (m, 11H), 5.92 (s, 1H), 4.69 (d, *J* = 11.9 Hz, 1H), 4.59–4.56 (m, 1H), 4.53–4.45 (m, 3H), 3.96 (dd, *J* = 10.1, 6.8 Hz, 1H), 3.82 (dd, *J* = 10.1, 5.6 Hz, 1H), 3.72 (dd, *J* = 2.2, 1.3 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 190.1, 168.0, 137.5, 137.0, 134.8, 134.1, 131.6, 129.8, 128.5, 128.4, 128.3, 128.3, 127.9, 127.9, 127.7, 126.7, 124.7, 100.8, 80.6, 73.6, 73.4, 72.0, 67.5. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{26}H_{24}ClO_4$: 435.1363; found: 435.1357.

5.11.15. (*2R,3S*)-3-(benzyloxy)-2-((benzyloxy)methyl)-6-(3,5-dichlorophenyl)-2H-pyran-4(3H)-one (1ao)

The compound **1ao** was prepared using the general procedure **5.10.5.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (15:85) as eluent to afford as white foam (74 mg, 63%); R*f* = 0.4 (EtOAc/petroleum ether (20:80)); $[\alpha]_D^{25}$ = +42.3 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 1.9 Hz, 2H), 7.38 (t, *J* = 1.9 Hz, 1H), 7.30–7.21 (m, 10H), 5.88 (d, *J* = 1.3 Hz, 1H), 4.67 (d, *J* = 11.9 Hz, 1H), 4.58–4.55 (m, 1H), 4.53–4.49 (m, 2H), 4.45 (d, *J* = 11.9 Hz, 1H), 3.94 (dd, *J* = 10.1, 6.9 Hz, 1H), 3.80 (dd, *J* = 10.1, 5.6 Hz, 1H), 3.71 (dd, *J* = 2.4, 1.3 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 189.9, 166.5, 137.4, 136.8, 135.4, 135.3, 131.3, 128.5, 128.4, 128.3, 128.0, 127.9, 127.7, 125.0, 101.3, 80.8, 73.6, 73.2, 72.0, 67.4. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{26}H_{23}Cl_2O_4$: 469.0973; found: 469.0958.

5.11.16. (*2R,3S*)-3-(benzyloxy)-2-((benzyloxy)methyl)-6-(o-tolyl)-2H-pyran-4(3H)-one (1ap)

The compound **1ap** was prepared using the general procedure **5.10.5.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (15:85) as

eluent to afford as viscous oil (81 mg, 78%); R*f* = 0.5 (EtOAc/petroleum ether (20:80)); $[a]_D^{25}$ = +47.4 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33–7.32 (m, 1H), 7.26–7.18 (m, 11H), 7.14–7.11 (m, 2H), 5.55 (d, *J* = 1.3 Hz, 1H), 4.70 (d, *J* = 11.9 Hz, 1H), 4.59–4.56 (m, 1H), 4.48 (dd, *J* = 11.9, 8.0 Hz, 2H), 4.43 (d, *J* = 11.9 Hz, 1H), 3.89 (dd, *J* = 10.2, 6.9 Hz, 1H), 3.78 (dd, *J* = 10.2, 5.6 Hz, 1H), 3.69 (dd, *J* = 2.2, 1.4 Hz, 1H), 2.32 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 190.1, 173.2, 137.5, 137.2, 136.9, 133.3, 131.0, 130.5, 128.8, 128.4, 128.3, 128.3, 128.0, 127.8, 127.7, 127.6, 126.8, 125.7, 104.3, 80.4, 73.5, 73.5, 71.7, 67.7, 20.5. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{27}H_{27}O_4$: 415.1909; found: 415.1915.

5.11.17. (*2R,3R*)-3-(benzyloxy)-2-((benzyloxy)methyl)-6-phenyl-2H-pyran-4(3H)-one (1ba)

The compound **1ba** was prepared using the general procedure **5.10.5.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (15:85) as eluent to afford as yellowish viscous oil (70 mg, 70%); R*f* = 0.5 (EtOAc/petroleum ether (20:80)); $[a]_D^{26}$ = +252 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.77–7.75 (m, 2H), 7.53–7.49 (m, 1H), 7.47–7.44 (m, 2H), 7.40–7.31 (m, 10H), 6.00 (s, 1H), 5.16 (d, *J* = 11.1 Hz, 1H), 4.72–4.69 (m, 1H), 4.64–4.60 (m, 3H), 4.33 (d, *J* = 11.4 Hz, 1H), 3.97–3.92 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 194.0, 169.4, 137.6, 137.5, 132.1, 131.7, 128.6, 128.5, 128.4, 128.3, 127.9, 127.8, 127.6, 126.9, 126.6, 100.3, 80.8, 74.5, 73.7, 73.4, 67.9. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{26}H_{25}O_4$: 401.1753; found: 401.1746.

5.11.18. (*2R,3R*)-3-(benzyloxy)-2-((benzyloxy)methyl)-6-(4-methoxyphenyl)-2H-pyran-4(3H)-one (1bb)

The compound **1bb** was prepared using the general procedure **5.10.5.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (20:80) as eluent to afford as white waxy solid (70 mg, 65%); R*f* = 0.3 (EtOAc/petroleum ether (20:80)); $[a]_D^{25}$ = +254 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.70–7.67 (m, 2H), 7.37–7.28 (m, 10H), 6.94–6.91 (m, 2H), 5.90 (s, 1H), 5.14 (d, *J* = 11.2 Hz, 1H), 4.68 (d, *J* = 11.2 Hz, 1H), 4.63–4.55 (m, 3H), 4.26 (d, *J* = 11.2 Hz, 1H), 3.93–3.87 (m, 2H), 3.85 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 193.7, 169.3, 162.5, 137.7, 137.6, 128.5, 128.4, 128.3, 128.3, 127.8, 127.7, 127.6, 124.4, 114.0, 98.9, 80.7, 74.4, 73.7, 73.4, 68.0, 55.4. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{27}H_{27}O_5$: 431.1858; found: 431.1850.

5.11.19. (*2R,3R*)-3-(benzyloxy)-2-((benzyloxy)methyl)-6-(p-tolyl)-2H-pyran-4(3H)-one (1bc)

The compound **1bc** was prepared using the general procedure **5.10.5.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (15:85) as eluent to afford as white foam (78 mg, 75%); R*f* = 0.5 (EtOAc/petroleum ether (20:80)); $[a]_D^{24}$ = +288 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.2 Hz, 2H), 7.37–7.26 (m, 10H), 7.22 (d, *J* = 8.4 Hz, 2H), 5.94 (s, 1H), 5.13 (d, *J* = 11.2 Hz, 1H), 4.68 (d, *J* = 11.2 Hz, 1H), 4.63–4.55 (m, 3H), 4.27 (d, *J* = 11.2 Hz, 1H), 3.94–3.88 (m, 2H), 2.39 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 193.8, 169.5, 142.3, 137.7, 137.6, 129.4, 129.3, 128.4, 128.3, 127.8, 127.7, 127.6, 126.6, 99.7, 80.8, 74.4, 73.7, 73.4, 68.0, 21.5. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{27}H_{27}O_4$: 415.1909; found: 415.1901.

5.11.20. (*2R,3R*)-3-(benzyloxy)-2-((benzyloxy)methyl)-6-(naphthalen-1-yl)-2H-pyran-4(3H)-one (1bd)

The compound **1bd** was prepared using the general procedure **5.10.5.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (18:82) as eluent to afford as yellowish viscous oil (79 mg, 70%); R*f* = 0.4 (EtOAc/petroleum ether (20:80)); $[a]_D^{26}$ = +278 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 8.3 Hz, 1H), 7.88–7.86 (m, 1H), 7.64 (dd, *J* = 7.1, 1.1 Hz, 1H), 7.53–7.45 (m, 3H), 7.41–7.27 (m, 10H), 5.80 (s, 1H), 5.17 (d, *J* = 11.2 Hz, 1H), 4.77–4.72 (m, 2H), 4.60 (d, *J* = 12.0 Hz, 1H), 4.55 (d, *J* = 12.0 Hz, 1H), 4.42 (d, *J* = 11.3 Hz, 1H), 3.94 (d, *J* = 3.3 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 193.6, 172.1, 137.7, 137.6, 133.6, 131.4, 131.3, 130.3, 128.5, 128.4, 128.4, 128.4, 128.3, 127.9, 127.7, 127.6, 127.3, 127.0, 126.3, 125.3, 124.8, 105.6, 81.4, 74.4, 73.9, 73.5, 68.1. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{30}H_{27}O_4$: 451.1909; found: 451.1914.

5.11.21. (*2R,3R*)-3-(benzyloxy)-2-((benzyloxy)methyl)-6-(4-fluorophenyl)-2H-pyran-4(3H)-one (1be)

The compound **1be** was prepared using the general procedure **5.10.5.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (15:85) as eluent to afford as white foam (64 mg, 61%); R*f* = 0.5 (EtOAc/petroleum ether (20:80)); $[a]_D^{26}$ = +264 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.74–7.71 (m, 2H), 7.37–7.28 (m, 10H), 7.10 (t, *J* = 8.7 Hz, 2H), 5.91 (s, 1H), 5.12 (d, *J* = 11.2 Hz, 1H), 4.67 (d, *J* = 11.2 Hz, 1H), 4.62–4.56 (m, 3H), 4.27 (d, *J* = 11.2 Hz, 1H), 3.93–3.87 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 193.7, 168.3, 165.8, 163.8, 137.6, 137.5, 128.9, 128.8, 128.4, 128.3, 127.9, 127.8, 127.7, 115.9, 115.7, 100.1, 80.9, 74.5, 73.7, 73.5,

67.9. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{26}H_{24}FO_4$: 419.1659; found: 419.1640.

5.11.22. (*2R,3R*)-3-(benzyloxy)-2-((benzyloxy)methyl)-6-(4-chlorophenyl)-2H-pyran-4(3H)-one (1bf)

The compound **1bf** was prepared using the general procedure **5.10.5.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (10:90) as eluent to afford as white foam (65 mg, 60%); R*f* = 0.6 (EtOAc/petroleum ether (20:80)); $[a]_D^{25}$ = +271 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.66–7.64 (m, 2H), 7.40–7.28 (m, 12H), 5.93 (s, 1H), 5.12 (d, *J* = 11.2 Hz, 1H), 4.67 (d, *J* = 11.2 Hz, 1H), 4.62–4.56 (m, 3H), 4.28 (d, *J* = 11.2 Hz, 1H), 3.93–3.87 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 193.7, 168.1, 137.9, 137.6, 137.4, 130.6, 128.9, 128.4, 128.3, 127.9, 127.9, 127.8, 127.7, 100.4, 80.9, 74.5, 73.6, 73.4, 67.8. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{26}H_{24}ClO_4$: 435.1363; found: 435.1355.

5.11.23. (*2R,3R*)-3-(benzyloxy)-2-((benzyloxy)methyl)-6-(4-bromophenyl)-2H-pyran-4(3H)-one (1bg)

The compound **1bg** was prepared using the general procedure **5.10.5.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (10:90) as eluent to afford as white foam (91 mg, 76%); R*f* = 0.6 (EtOAc/petroleum ether (20:80)); $[a]_D^{27}$ = +244 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.58–7.53 (m, 4H), 7.36–7.27 (m, 10H), 5.93 (s, 1H), 5.12 (d, *J* = 11.2 Hz, 1H), 4.67 (d, *J* = 11.2 Hz, 1H), 4.61–4.55 (m, 3H), 4.28 (d, *J* = 11.3 Hz, 1H), 3.92–3.87 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 193.7, 168.2, 137.6, 137.4, 131.8, 131.1, 128.4, 128.3, 128.0, 127.9, 127.8, 127.6, 126.3, 100.4, 80.9, 74.4, 73.6, 73.4, 67.8. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{26}H_{24}BrO_4$: 479.0858; found: 479.0851.

5.11.24. (*2R,3R*)-3-(benzyloxy)-2-((benzyloxy)methyl)-6-(4-(trifluoromethyl) phenyl)-2H-pyran-4(3H)-one (1bh)

The compound **1bh** was prepared using the general procedure **5.10.5.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (10:90) as eluent to afford as white foam (68 mg, 58%); R*f* = 0.6 (EtOAc/petroleum ether (20:80)); $[a]_D^{25}$ = +228 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.2 Hz, 2H), 7.68 (d, *J* = 8.3 Hz, 2H), 7.37–7.28 (m, 10H), 6.00 (s, 1H), 5.12 (d, *J* = 11.1 Hz, 1H), 4.68 (d, *J* = 11.1 Hz, 1H), 4.63–4.56 (m, 3H), 4.30 (d, *J* = 11.2 Hz, 1H), 3.95–3.89 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 193.7, 167.5, 137.6, 137.3, 135.7, 133.2, 133.0, 128.4, 128.4, 128.3, 128.0, 127.9, 127.7, 126.9, 125.6, 125.6, 124.7, 122.5, 101.5, 81.2, 74.5, 73.7, 73.5, 67.9. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{27}H_{24}F_3O_4$: 469.1627; found: 469.1621.

5.11.25. 4-((*2R,3R*)-3-(benzyloxy)-2-((benzyloxy)methyl)-4-oxo-3,4-dihydro-2H-pyran-6-yl)benzonitrile (1bi)

The compound **1bi** was prepared using the general procedure **5.10.5.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (25:75) as eluent to afford as white foam (68 mg, 64%); R*f* = 0.3 (EtOAc/petroleum ether (20:80)); $[a]_D^{25}$ = +290 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.82–7.78 (m, 2H), 7.72–7.69 (m, 2H), 7.36–7.29 (m, 10H), 6.00 (s, 1H), 5.10 (d, *J* = 11.1 Hz, 1H), 4.67 (d, *J* = 11.1 Hz, 1H), 4.62–4.55 (m, 3H), 4.30 (d, *J* = 11.1 Hz, 1H), 3.94–3.88 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 193.5, 166.7, 137.5, 137.2, 136.4, 132.3, 128.4, 128.4, 128.3, 128.0, 127.9, 127.7, 127.0, 118.0, 114.8, 101.9, 81.2, 74.5, 73.6, 73.5, 67.8. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{27}H_{24}NO_4$: 426.1705; found: 426.1701.

5.11.26. (*2R,3R*)-3-(benzyloxy)-2-((benzyloxy)methyl)-6-(3-chlorophenyl)-2H-pyran-4(3H)-one (1bj)

The compound **1bj** was prepared using the general procedure **5.10.5.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (15:85) as eluent to afford as viscous oil (71 mg, 65%); R*f* = 0.5 (EtOAc/petroleum ether (20:80)); $[a]_D^{26}$ = +331 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.73–7.71 (m, 1H), 7.59–7.57 (m, 1H), 7.46–7.42 (m, 1H), 7.37– 7.30 (m, 11H), 5.95 (s, 1H), 5.12 (d, *J* = 11.1 Hz, 1H), 4.69–4.66 (m, 1H), 4.62–4.56 (m, 3H), 4.29 (d, *J* = 11.2 Hz, 1H), 3.94–3.88 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 193.6, 167.7, 137.6, 137.4, 134.8, 134.0, 131.5, 129.8, 128.4, 128.3, 127.9, 127.8, 127.6, 126.6, 124.6, 100.8, 81.0, 74.4, 73.7, 73.4, 67.7. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{26}H_{24}ClO_4$: 435.1363; found: 435.1359.

5.11.27. (*2R,3R*)-3-(benzyloxy)-2-((benzyloxy)methyl)-6-(3,5-dichlorophenyl)-2H-pyran-4(3H)-one (1bk)

The compound **1bk** was prepared using the general procedure **5.10.5.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (10:90) as eluent to afford as viscous oil (70 mg, 60%); R*f* = 0.6 (EtOAc/petroleum ether (20:80)); $[a]_D^{26}$ = +287 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 1.7 Hz, 2H), 7.46 (s, 1H), 7.36–7.28 (m, 10H), 5.91 (s, 1H), 5.10 (d, *J* = 11.1 Hz, 1H), 4.66 (d, *J* = 11.1 Hz, 1H), 4.62–4.55 (m, 3H), 4.28 (d, *J* = 11.2 Hz, 1H), 3.93–3.86 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 193.5, 166.3, 137.5, 137.3, 135.5, 135.3, 131.2, 128.5, 128.4, 128.3, 128.0, 127.9, 127.7, 124.9, 101.4, 81.2, 74.5, 73.6, 73.4, 67.6. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{26}H_{23}Cl_2O_4$: 469.0973; found: 469.0979.

5.11.28. (*2S,3S*)-3-(benzyloxy)-6-(4-methoxyphenyl)-2-methyl-2H-pyran-4(3H)-one (1ca)

The compound **1ca** was prepared using the general procedure **5.10.5.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (10:90) as eluent to afford as white foam (53 mg, 65%); R*f* = 0.5 (EtOAc/petroleum ether (20:80)); $[a]_D^{26}$ = -396 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 7.9 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 1H), 6.92–6.90 (m, 2H), 5.99 (d, *J* = 1.1 Hz, 1H), 5.10 (d, *J* = 11.6 Hz, 1H), 4.72 (d, *J* = 11.6 Hz, 1H), 4.62–4.57 (m, 1H), 3.84 (s, 3H), 3.78 (d, *J* = 9.9 Hz, 1H), 1.52 (d, *J* = 6.4 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 193.4, 169.1, 162.4, 137.5, 128.4, 128.3, 127.9, 124.6, 113.9, 98.8, 78.2, 78.1, 73.8, 55.3, 17.3. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{20}H_{21}O_4$: 325.1440; found: 325.1431.

5.11.29. (*2S,3S*)-3-(benzyloxy)-6-(4-bromophenyl)-2-methyl-2H-pyran-4(3H)-one (1cb)

The compound **1cb** was prepared using the general procedure **5.10.5.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (10:90) as eluent to afford as white foam (56 mg, 60%); R*f* = 0.6 (EtOAc/petroleum ether (20:80)); $[a]_D^{26}$ = -296 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.58–7.53 (m, 4H), 7.41–7.40 (m, 2H), 7.37–7.33 (m, 2H), 7.32–7.28 (m, 1H), 5.94 (s, 1H), 5.08 (d, *J* = 11.5 Hz, 1H), 4.71 (d, *J* = 11.5 Hz, 1H), 4.65–4.59 (m, 1H), 3.78 (d, *J* = 9.9 Hz, 1H), 1.53 (d, *J* = 6.4 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 193.4, 168.0, 137.3, 131.8, 131.3, 128.4, 128.4, 128.0, 127.9, 126.3, 100.3, 78.5, 78.0, 73.8, 17.2. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{19}H_{18}BrO_3$: 373.0439; found: 373.0435.

5.11.30. 4-((*2R,3R*)-3-(benzyloxy)-2-methyl-4-oxo-3,4-dihydro-2H-pyran-6-yl)benzonitrile (1da)

The compound **1da** was prepared using the general procedure **5.10.5.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (15:85) as eluent to afford as white foam (50 mg, 63%); R*f* = 0.4 (EtOAc/petroleum ether (20:80)); $[a]_D^{25}$ = +281 (c = 0.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83–7.80 (m, 2H), 7.72–7.70 (m, 2H), 7.41–7.30 (m, 5H), 6.01 (s, 1H), 5.07 (d, *J* = 11.5 Hz, 1H), 4.72–4.63 (m, 2H), 3.81 (d, *J* = 9.8 Hz, 1H), 1.54 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 193.3, 166.5, 137.1, 136.6, 134.1, 132.3, 128.4, 128.4, 128.1, 126.9, 118.0, 116.3, 114.8, 101.8, 78.8, 76.7, 73.9, 17.2.**HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{20}H_{18}NO_3$: 320.1287; found: 320.1292.

5.11.31. (*S*)-3-(benzyloxy)-6-phenyl-2H-pyran-4(3H)-one (1ea)

The compound **1ea** was prepared using the general procedure **5.10.5.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (10:90) as eluent to afford as white foam (49 mg, 70%); R*f* = 0.6 (EtOAc/petroleum ether (20:80)); $[a]_D^{26}$ = -82.8 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.75–7.72 (m, 2H), 7.50–7.28 (m, 8H), 6.01 (d, *J* = 0.7 Hz, 1H), 4.91 (d, *J* = 12.0 Hz, 1H), 4.69–4.63 (m, 2H), 4.54 (dd, *J* = 12.1, 3.9 Hz, 1H), 3.92–3.90 (m, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 191.0, 170.0, 137.3, 132.2, 131.7, 128.6, 128.4, 128.1, 127.9, 126.5, 100.4, 73.1, 72.5, 71.2. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{18}H_{17}O_3$: 281.1178; found: 281.1187.

5.11.32. (*S*)-3-(benzyloxy)-6-(4-methoxyphenyl)-2H-pyran-4(3H)-one (1eb)

The compound **1eb** was prepared using the general procedure **5.10.5.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (20:80) as

eluent to afford as white foam (47 mg, 60%); R*f* = 0.4 (EtOAc/petroleum ether (20:80)); $[a]_D^{26}$ = -59.0 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.70–7.67 (m, 2H), 7.40–7.25 (m, 5H), 6.93–6.90 (m, 2H), 5.94 (d, *J* = 0.7 Hz, 1H), 4.91 (d, *J* = 12.0 Hz, 1H), 4.69 (d, *J* = 12.0 Hz, 1H), 4.62 (dd, *J* = 12.0, 6.2 Hz, 1H), 4.51 (dd, *J* = 12.1, 3.8 Hz, 1H), 3.89–3.87 (m, 1H), 3.84 (s, 3H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 190.8, 170.0, 162.6, 137.4, 128.4, 128.1, 127.9, 124.5, 114.0, 99.0, 73.1, 72.4, 71.1, 55.4. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{19}H_{19}O_4$: 311.1283; found: 311.1285.

5.11.33. (*S*)-3-(benzyloxy)-6-(4-(trifluoromethyl)phenyl)-2H-pyran-4(3H)-one (1ec)

The compound **1ec** was prepared using the general procedure **5.10.5.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (15:85) as eluent to afford as white foam (57 mg, 65%); R*f* = 0.5 (EtOAc/petroleum ether (20:80)); $[a]_D^{26}$ = -46.1 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.2 Hz, 2H), 7.68 (d, *J* = 8.3 Hz, 2H), 7.40–7.29 (m, 5H), 6.04 (d, *J* = 0.7 Hz, 1H), 4.90 (d, *J* = 11.9 Hz, 1H), 4.71–4.66 (m, 2H), 4.56 (dd, *J* = 12.2, 3.8 Hz, 1H), 3.93–3.91 (m, 1H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 190.8, 168.1, 137.1, 135.7, 133.3, 128.5, 128.2, 128.1, 126.8, 125.6, 125.6, 101.6, 72.9, 72.5, 71.5. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{19}H_{16}F_3O_3$: 349.1052; found: 349.1066.

5.11.34. ((*2R,3R*)-3-acetoxy-4-oxo-6-phenyl-3,4-dihydro-2H-pyran-2-yl)methyl acetate (1fa)

The compound **1fa** was prepared using the general procedure **5.10.5.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (20:80) as eluent to afford as colorless viscous oil (46 mg, 60%); R*f* = 0.6 (EtOAc/petroleum ether (30:70)); $[a]_D^{25}$ = +112 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.75–7.73 (m,

2H), 7.54–7.51 (m, 1H), 7.47–7.44 (m, 2H), 6.06 (s, 1H), 5.62 (d, *J* = 12.9 Hz, 1H), 4.77–4.73 (m, 1H), 4.54 (d, *J* = 3.2 Hz, 2H), 2.22 (s, 3H), 2.13 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 188.1, 170.4, 169.7, 169.3, 132.1, 131.4, 128.7, 126.6, 100.2, 78.0, 67.8, 61.5, 20.6, 20.4. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{16}H_{17}O_6$: 305.1025; found: 305.1017.

5.11.35. ((*2R,3R*)-3-acetoxy-6-(4-methoxyphenyl)-4-oxo-3,4-dihydro-2H-pyran-2-yl)methyl acetate (1fb)

The compound **1fb** was prepared using the general procedure **5.10.5.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (30:70) as eluent to afford as white waxy solid (54 mg, 65%); R*f* = 0.4 (EtOAc/petroleum ether (30:70)); $[a]_D^{25}$ = +306 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.71–7.68 (m, 2H), 7.96–6.94 (m, 2H), 5.98 (s, 1H), 5.60 (d, *J* = 12.8 Hz, 1H), 4.74–4.70 (m, 1H), 4.52 (d, *J* = 3.3 Hz, 2H), 3.86 (s, 3H), 2.22 (s, 3H), 2.13 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 187.9, 170.4, 169.7, 169.3, 162.8, 128.5, 123.6, 114.2, 98.8, 77.8, 67.8, 61.5, 55.4, 20.6, 20.5. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{17}H_{19}O_7$: 335.1131; found: 335.1139.

5.11.36. ((*2R,3R*)-3-acetoxy-6-(4-fluorophenyl)-4-oxo-3,4-dihydro-2H-pyran-2-yl)methyl acetate (1fc)

The compound **1fc** was prepared using the general procedure **5.10.5.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (15:85) as eluent to afford as colorless viscous oil (44 mg, 55%); R*f* = 0.5 (EtOAc/petroleum ether (30:70)); $[a]_D^{27}$ = +288 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.77–7.74 (m, 2H), 7.17–7.13 (m, 2H), 6.01 (d, *J* = 2.2 Hz, 1H), 5.63–5.59 (m, 1H), 4.78–4.74 (m,

1H), 4.54–4.54 (m, 2H), 2.22 (d, *J* = 2.5 Hz, 3H), 2.14 (d, *J* = 2.2 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 187.9, 170.3, 169.2, 168.6, 166.0, 163.9, 128.9, 128.8, 127.6, 127.6, 116.0, 115.8, 99.9, 78.0, 67.7, 61.4, 20.5, 20.4. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{16}H_{16}FO_6$: 323.0931; found: 323.0932.

5.11.37. (*2R,3R*)-4-oxo-6-phenyl-2-((pivaloyloxy)methyl)-3,4-dihydro-2H-pyran-3-yl pivalate (1ga)

The compound **1ga** was prepared using the general procedure **5.10.5.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (10:90) as eluent to afford as white foam (83 mg, 86%); R*f* = 0.6 (EtOAc/petroleum ether (10:90)); $[a]_D^{25}$ = +229 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.3 Hz, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 6.05 (s, 1H), 5.59 (d, *J* = 12.9 Hz, 1H), 4.81–4.77 (m, 1H), 4.56 (dd, *J* = 12.7, 1.7 Hz, 1H), 4.43 (dd, *J* = 12.7, 4.6 Hz, 1H), 1.29 (s, 9H), 1.24 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 188.3, 177.8, 176.6, 169.6, 132.0, 131.6, 128.7, 126.5, 100.3, 78.3, 67.6, 61.6, 38.9, 38.8, 27.1, 27.1. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{22}H_{29}O_6$: 389.1964; found: 389.1965.

5.11.38. (*2R,3R*)-6-(4-methoxyphenyl)-4-oxo-2-((pivaloyloxy)methyl)-3,4-dihydro-2H-pyran-3-yl pivalate (1gb)

The compound **1gb** was prepared using the general procedure **5.10.5.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (15:85) as eluent to afford as white foam (78 mg, 75%); R*f* = 0.4 (EtOAc/petroleum ether (10:90)); $[a]_D^{25}$ = +269 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.71–7.68 (m, 2H), 7.96–6.93 (m, 2H), 5.96 (s, 1H), 5.57 (d, *J* = 12.8 Hz, 1H), 4.77–4.74 (m, 1H), 4.55 (dd, *J* = 12.7, 1.8 Hz, 1H), 4.41 (dd, *J* = 12.7, 4.6 Hz, 1H), 3.86 (s, 3H), 1.29 (s, 9H), 1.24 (s,

9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 188.1, 177.8, 176.6, 169.5, 162.7, 128.4, 123.7, 114.1, 98.8, 78.1, 67.5, 61.6, 55.4, 38.9, 38.8, 27.0, 27.0. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{23}H_{31}O_7$: 419.2070; found: 419.2076.

5.11.39. (*2R,3R*)-4-oxo-2-((pivaloyloxy)methyl)-6-(4-(trifluoromethyl)phenyl)-3,4-dihydro-2H-pyran-3-yl pivalate (1gc)

The compound **1gc** was prepared using the general procedure **5.10.5.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (10:90) as eluent to afford as colorless viscous oil (96 mg, 84%); R*f* = 0.6 (EtOAc/petroleum ether (10:90)); $[\alpha]_D^{25}$ = +193 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 7.8 Hz, 1H), 7.60 (t, *J* = 7.9 Hz, 1H), 6.09 (s, 1H), 5.58 (d, *J* = 12.9 Hz, 1H), 4.86–4.82 (m, 1H), 4.55 (dd, *J* = 12.7, 2.0 Hz, 1H), 4.47 (dd, *J* = 12.7, 5.1 Hz, 1H), 1.30 (s, 9H), 1.25 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 188.0, 177.8, 176.6, 167.7, 132.5, 131.8, 131.5, 131.3, 131.0, 129.6, 129.4, 128.4, 128.4, 126.7, 124.6, 123.4, 123.3, 123.3, 123.3, 122.4, 120.3, 101.1, 78.6, 67.6, 61.6, 38.9, 38.8, 27.0. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{23}H_{28}F_3O_6$: 457.1838; found: 457.1837.

5.11.40. ((*2R,3R*)-3-(benzoyloxy)-4-oxo-6-phenyl-3,4-dihydro-2H-pyran-2-yl)methyl benzoate (1ha)

The compound **1ha** was prepared using the general procedure **5.10.5.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (20:80) as eluent to afford as white foam (96 mg, 90%); R*f* = 0.4 (EtOAc/petroleum ether (20:80)); $[\alpha]_D^{27}$ = +349 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.11–8.06 (m, 4H), 7.75–7.79 (m, 2H), 7.60–7.55 (m, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.46–7.42 (m, 6H), 6.14

(s, 1H), 6.01 (d, *J* = 12.8 Hz, 1H), 5.09–5.05 (m, 1H), 4.99 (dd, *J* = 12.6, 2.4 Hz, 1H), 4.69 (dd, *J* = 12.6, 4.7 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 188.0, 169.8, 165.9, 165.0, 133.5, 133.3, 132.1, 131.4, 130.0, 129.7, 129.2, 128.8, 128.7, 128.4, 128.4, 126.6, 100.3, 78.2, 68.7, 62.4. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{26}H_{21}O_6$: 429.1338; found: 429.1342.

5.11.41. ((*2R,3R*)-3-(benzoyloxy)-6-(4-methoxyphenyl)-4-oxo-3,4-dihydro-2H-pyran-2-yl)methyl benzoate (1hb)

The compound **1hb** was prepared using the general procedure **5.10.5.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (25:75) as eluent to afford as white foam (80 mg, 70%); R*f* = 0.3 (EtOAc/petroleum ether (20:80)); $[\alpha]_D^{27}$ = +356 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.11–8.06 (m, 4H), 7.73–7.70 (m, 2H), 7.59–7.54 (m, 2H), 7.46–7.41 (m, 4H), 6.95–6.92 (m, 2H), 6.06 (s, 1H), 5.98 (d, *J* = 12.7 Hz, 1H), 5.06–5.02 (m, 1H), 4.97 (dd, *J* = 12.6, 2.5 Hz, 1H), 4.68 (dd, *J* = 12.6, 4.7 Hz, 1H), 3.84 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 187.7, 169.7, 165.9, 165.0, 162.8, 133.5, 133.3, 130.0, 129.7, 129.3, 128.8, 128.5, 128.4, 128.4, 123.6, 114.1, 98.8, 78.0, 68.7, 62.4, 55.4. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{27}H_{23}O_7$: 459.1444; found: 459.1450.

5.11.42. ((*2R,3R*)-3-(benzoyloxy)-4-oxo-6-(4-(trifluoromethyl)phenyl)-3,4-dihydro-2H-pyran-2-yl)methyl benzoate (1hc)

The compound **1hc** was prepared using the general procedure **5.10.5.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (25:75) as eluent to afford as white foam (112 mg, 90%); R*f* = 0.3 (EtOAc/petroleum ether (20:80)); $[\alpha]_D^{26}$ = +296 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.11–8.06 (m,

4H), 8.03 (s, 1H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 7.8 Hz, 1H), 7.61–7.56 (m, 3H), 7.47–7.43 (m, 4H), 6.18 (s, 1H), 5.99 (d, *J* = 12.7 Hz, 1H), 5.13–5.09 (m, 1H), 5.00 (dd, *J* = 12.7, 2.4 Hz, 1H), 4.71 (dd, *J* = 12.7, 5.2 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 187.7, 167.9, 165.9, 165.0, 133.6, 133.4, 132.4, 131.8, 131.6, 131.3, 131.0, 130.1, 129.7, 129.4, 129.2, 128.6, 128.5, 128.5, 128.5, 124.6, 123.5, 123.4, 122.4, 101.2, 78.5, 68.8, 62.3. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{27}H_{20}F_3O_6$: 497.1212; found: 497.1215.

5.11.43. (*2R,3R*)-3-(methoxymethoxy)-2-((methoxymethoxy)methyl)-6-phenyl-2H-pyran-4(3H)-one (1ia)

The compound **1ia** was prepared using the general procedure **5.10.5.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (10:90) as eluent to afford as white foam (65 mg, 85%); R*f* = 0.6 (EtOAc/petroleum ether (20:80)); $[a]_D^{25}$ = +333 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.75–7.73 (m, 2H), 7.51–7.48 (m, 1H), 7.45–7.41 (m, 2H), 5.98 (s, 1H), 5.05 (d, *J* = 6.6 Hz, 1H), 4.86 (d, *J* = 6.6 Hz, 1H), 4.77–4.74 (m, 2H), 4.61–4.58 (m, 1H), 4.47 (d, *J* = 11.7 Hz, 1H), 4.10 (dd, *J* = 11.6, 2.4 Hz, 1H), 3.99 (dd, *J* = 11.6, 4.4 Hz, 1H), 3.49 (s, 3H), 3.42 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 193.0, 169.4, 132.0, 131.8, 128.6, 126.5, 100.2, 97.3, 96.7, 80.7, 71.2, 65.5, 56.4, 55.4. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{16}H_{21}O_6$: 309.1338; found: 309.1332.

5.11.44. (*2R,3R*)-3-(methoxymethoxy)-2-((methoxymethoxy)methyl)-6-(4-methoxyphenyl)-2H-pyran-4(3H)-one (1ib)

The compound **1ib** was prepared using the general procedure **5.10.5.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (20:80) as

eluent to afford as colorless viscous oil (68 mg, 80%); R*f* = 0.4 (EtOAc/petroleum ether (20:80)); $[a]_D^{26}$ = +340 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.9 Hz, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 5.90 (s, 1H), 5.06 (d, *J* = 6.6 Hz, 1H), 4.86 (d, *J* = 6.6 Hz, 1H), 4.77–4.74 (m, 2H), 4.59–4.55 (m, 1H), 4.43 (d, *J* = 11.6 Hz, 1H), 4.09 (dd, *J* = 11.5, 2.4 Hz, 1H), 3.98 (dd, *J* = 11.5, 4.5 Hz, 1H), 3.85 (s, 3H), 3.49 (s, 3H), 3.42 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 192.7, 169.3, 162.5, 128.4, 124.2, 114.0, 98.8, 97.3, 96.7, 80.47, 71.2, 65.5, 56.3, 55.4, 55.3. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{17}H_{23}O_7$: 339.1444; found: 339.1444. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{17}H_{23}O_7$: 339.1444; found: 339.1447.

5.11.45. 4-((*2R,3R*)-3-(methoxymethoxy)-2-((methoxymethoxy)methyl)-4-oxo-3,4-dihydro-2H-pyran-6-yl)benzonitrile (1ic)

The compound **1ic** was prepared using the general procedure **5.10.5.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (30:70) as eluent to afford as white foam (60 mg, 72%); R*f* = 0.3 (EtOAc/petroleum ether (20:80)); $[a]_D^{25}$ = +280 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.85–7.83 (m, 2H), 7.74–7.72 (m, 2H), 6.02 (s, 1H), 5.03 (d, *J* = 6.7 Hz, 1H), 4.85 (d, *J* = 6.7 Hz, 1H), 4.76–4.73 (m, 2H), 4.65–4.61 (m, 1H), 4.48 (d, *J* = 11.6 Hz, 1H), 4.10 (dd, *J* = 11.6, 2.4 Hz, 1H), 4.00 (dd, *J* = 11.6, 4.4 Hz, 1H), 3.49 (s, 3H), 3.41 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 192.7, 166.7, 136.2, 132.4, 126.9, 117.9, 114.9, 101.9, 97.3, 96.7, 81.0, 71.1, 65.4, 56.4, 55.5. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{17}H_{20}NO_6$: 334.1291; found: 334.1286.

5.11.46. (*2R,3R*)-3-((tert-butyldiphenylsilyl)oxy)-2-(((tert-butyldiphenylsilyl)oxy) methyl)-6-(4-methoxyphenyl)-2H-pyran-4(3H)-one (1ja)

The compound **1ja** was prepared using the general procedure **5.10.5.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (10:90) as eluent to afford as colourless viscous oil (120 mg, 66%); R*f* = 0.4 (EtOAc/petroleum ether (10:90)); $[a]_D^{25}$ = +236 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.74–7.29 (m, 2H), 7.68–7.64 (m, 6H), 7.63–7.59 (m, 2H), 7.48– 7.43 (m, 2H), 7.40–7.29 (m, 10H), 6.92–6.90 (m, 2H), 5.76 (s, 1H), 4.56–4.50 (m, 2H), 4.12 (dd, *J* = 11.6, 1.7 Hz, 1H), 4.04–4.01 (m, 1H), 3.88 (s, 3H), 1.05 (d, *J* = 7.8 Hz, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 191.8, 168.9, 162.3, 135.8, 135.8, 135.7, 135.6, 133.7, 133.6, 133.2, 133.0, 129.7, 129.5, 129.2, 128.4, 127.6, 127.6, 127.4, 127.1, 124.6, 113.9, 98.3, 83.3, 70.0, 62.9, 55.4, 27.1, 26.7, 19.9, 19.2. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{45}H_{51}O_5Si_2$: 727.3275; found: 727.3265.

5.11.47. (*2R,3R*)-3-((tert-butyldiphenylsilyl)oxy)-2-(((tert-butyldiphenylsilyl) oxy)methyl)-6-(3-nitrophenyl)-2H-pyran-4(3H)-one (1jb)

The compound **1jb** was prepared using the general procedure **5.10.5.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (20:80) as eluent to afford as colourless viscous oil (120 mg, 65%); R*f* = 0.4 (EtOAc/petroleum ether (20:80)); $[a]_D^{25}$ = +242 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.48 (t, *J* = 1.8 Hz, 1H), 8.31–8.29 (m, 1H), 7.86 (d, *J* = 7.9 Hz, 1H), 7.70 (d, *J* = 6.8 Hz, 2H), 7.65–7.60 (m, 4H), 7.59–7.55 (m, 3H), 7.43–7.27 (m, 12H), 5.86 (s, 1H), 4.59–4.53 (m, 2H), 4.11 (dd, *J* = 11.7, 2.1 Hz, 1H), 3.99 (dd, *J* = 11.7, 4.6 Hz, 1H), 1.03 (d, *J* = 5.6 Hz, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 191.7, 165.9, 148.4, 135.8, 135.8, 135.6,

135.6, 134.2, 133.3, 133.2, 132.9, 132.8, 132.0, 129.7, 129.7, 129.7, 129.6, 129.4, 127.7, 127.6, 127.5, 127.2, 125.7, 121.4, 101.0, 84.0, 70.1, 62.7, 27.0, 26.7, 19.8, 19.1. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{44}H_{48}NO_6Si_2$: 742.3020; found: 742.3026.

5.11.48. (*2R,3R,4R,6R*)-3-(benzyloxy)-2-((benzyloxy)methyl)-6-phenyltetrahydro-2H-pyran-4-ol (3aa)

The compound **3aa** was prepared using the general procedure **5.10.6.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (25:75) as eluent to afford as yellowish viscous oil (51 mg, 84%) ; R*f* = 0.2 (EtOAc/petroleum ether (20:80)); $[\alpha]_D^{23}$ = +28.6 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36–7.24 (m, 15H), 4.79 (d, *J* = 11.8 Hz, 1H), 4.65 (d, *J* = 11.8 Hz, 1H), 4.56 (d, *J* = 11.8 Hz, 1H), 4.52 (d, *J* = 11.8 Hz, 1H), 4.38 (dd, *J* = 11.4, 2.1 Hz, 1H), 3.84–3.81 (m, 2H), 3.78–3.68 (m, 3H), 2.00–1.96 (m, 1H), 1.92–1.85 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 141.4, 138.6, 137.8, 128.5, 128.4, 128.2, 127.8, 127.8, 127.7, 127.7, 127.5, 126.0, 77.9, 77.4, 75.6, 75.1, 73.4, 70.0, 68.8, 38.0. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{26}H_{29}O_4$: 405.2066; found: 405.2059.

5.11.49. (*2R,3R,4R,6R*)-3-(benzyloxy)-2-((benzyloxy)methyl)-6-(p-tolyl)tetrahydro-2H-pyran-4-ol (3ab)

The compound **3ab** was prepared using the general procedure **5.10.6.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (30:70) as eluent to afford as yellowish viscous oil (47 mg, 75%); R*f* = 0.1 (EtOAc/petroleum ether (20:80)); $[\alpha]_D^{24}$ = +33.4 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.35–7.23 (m, 12H), 7.12 (d, *J* = 7.8 Hz, 2H), 4.79 (d, *J* = 11.8 Hz, 1H), 4.64 (d, *J* = 11.8 Hz, 1H), 4.53 (q, *J* = 11.8 Hz, 2H), 4.35 (dd, *J* = 11.2, 2.2 Hz, 1H), 3.84–3.80 (m, 2H),

3.77–3.66 (m, 3H), 2.31 (s, 3H), 1.98–1.94 (m, 1H), 1.92–1.82 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 138.6, 138.4, 137.9, 137.2, 128.9, 128.5, 128.4, 127.8, 127.8, 127.7, 127.7, 126.0, 77.8, 77.4, 75.6, 75.1, 73.4, 70.1, 68.8, 37.9, 21.1. **HRMS** (ESI): m/z [M + Na]$^+$ calcd for $C_{27}H_{30}NaO_4$: 441.2042; found: 441.2031.

5.11.50. (*2R,3R,4R,6R*)-3-(benzyloxy)-2-((benzyloxy)methyl)-6-(naphthalen-1-yl)tetrahydro-2H-pyran-4-ol (3ac)

The compound **3ac** was prepared using the general procedure **5.10.6.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (30:70) as eluent to afford as yellowish viscous oil (62 mg, 90%); R*f* = 0.2 (EtOAc/petroleum ether (20:80)); $[\alpha]_D^{24}$ = +29.2 (c = 0.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20–8.18 (m, 1H), 7.84–7.81 (m, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.57 (d, *J* = 6.9 Hz, 1H), 7.46–7.42 (m, 3H), 7.40–7.35 (m, 4H), 7.34–7.26 (m, 6H), 5.02 (dd, *J* = 11.4, 2.2 Hz, 1H), 4.82 (d, *J* = 11.7 Hz, 1H), 4.71 (d, *J* = 11.8 Hz, 1H), 4.57 (d, *J* = 11.8 Hz, 1H), 4.51 (d, *J* = 11.8 Hz, 1H), 3.98–3.89 (m, 3H), 3.82–3.79 (m, 1H), 3.75–3.72 (dd, *J* = 9.2, 5.8 Hz, 1H), 2.24–2.17 (m, 1H), 2.14–2.10 (m, 1H), 1.83 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 138.6, 137.8, 136.7, 133.9, 130.6, 128.7, 128.5, 128.4, 127.8, 127.8, 127.7, 127.6, 125.9, 125.4, 125.2, 123.9, 123.8, 77.7, 76.2, 75.8, 75.1, 73.5, 70.2, 68.9, 36.7. **HRMS** (ESI): m/z [M + Na]$^+$ calcd for $C_{30}H_{30}NaO_4$: 477.2042; found: 477.2037.

5.11.51. (*2R,3S,4R,6R*)-3-(benzyloxy)-2-((benzyloxy)methyl)-6-phenyltetrahydro-2H-pyran-4-ol (3ad)

The compound **3ad** was prepared using the general procedure **5.10.6.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (25:75) as eluent to afford as yellowish viscous oil (45 mg, 74%); R*f* = 0.3 (EtOAc/petroleum

ether (20:80)); $[\alpha]_D^{24}$ = +19.4 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39–7.27 (m, 15H), 4.74–4.68 (m, 3H), 4.62–4.59 (m, 1H), 4.47 (dd, *J* = 11.6, 1.8 Hz, 1H), 3.90–3.81 (m, 3H), 3.56–3.49 (m, 2H), 2.25–2.21 (m, 1H), 1.91 (s, 1H), 1.76–1.69 (m, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 141.3, 138.4, 138.3, 128.8, 128.6, 128.3, 128.3, 128.0, 127.8, 127.6, 127.6, 127.5, 125.9, 80.2, 79.3, 77.6, 74.7, 73.6, 73.1, 69.4, 40.9. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{26}H_{29}O_4$: 405.2066; found: 405.2060.

5.11.52. (*2R,3S,4R,6R*)-3-(benzyloxy)-2-((benzyloxy)methyl)-6-(4-(trifluoromethyl) phenyl)tetrahydro-2H-pyran-4-ol (3ae)

The compound **3ae** was prepared using the general procedure **5.10.6.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (30:70) as eluent to afford as yellowish viscous oil (56 mg, 79%); R*f* = 0.2 (EtOAc/petroleum ether (20:80)); $[\alpha]_D^{24}$ = +28.5 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 8.1 Hz, 2H), 7.39–7.28 (m, 10H), 4.74–4.67 (m, 3H), 4.61 (d, *J* = 12.2 Hz, 1H), 4.52 (d, *J* = 11.1 Hz, 1H), 3.91–3.80 (m, 3H), 3.57–3.49 (m, 2H), 2.27–2.23 (m, 1H), 1.83 (s, 1H), 1.71–1.64 (m, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 145.2, 138.2, 138.1, 128.7, 128.4, 128.1, 128.0, 127.8, 127.6, 126.1, 125.3, 125.3, 80.0, 79.2, 76.86, 74.7, 73.6, 72.9, 40.8. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{27}H_{28}F_3O_4$: 473.1940; found: 473.1940.

5.11.53. ((*2R,3S,4R,6R*)-3-acetoxy-4-hydroxy-6-phenyltetrahydro-2H-pyran-2-yl)methyl acetate (3af)

The compound **3af** was prepared using the general procedure **5.10.6.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (40:60) as eluent to afford as yellowish viscous oil (37 mg, 80%); R*f* = 0.1 (EtOAc/petroleum

ether (30:70)); $[\alpha]_D^{25}$ = +45.2 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.37–7.27 (m, 5H), 4.81 (t, *J* = 9.4 Hz, 1H), 4.49 (dd, *J* = 11.6, 2.0 Hz, 1H), 4.31 (dd, *J* = 12.2, 5.1 Hz, 1H), 4.19 (dd, *J* = 12.2, 2.2 Hz, 1H), 3.95–3.90 (m, 1H), 3.71–3.68 (m, 1H), 2.37–2.33 (m, 2H), 2.14 (s, 3H), 2.07 (s, 3H), 1.80 (dt, *J* = 13.1, 11.6 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.6, 170.9, 140.3, 128.4, 127.8, 125.7, 77.5, 75.8, 73.5, 71.6, 63.1, 41.5, 20.9, 20.7. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{16}H_{21}O_6$: 309.1338; found: 309.1324.

5.11.54. ((*2R,3S,4R,6R*)-3-acetoxy-4-hydroxy-6-(4-methoxyphenyl)tetrahydro-2H-pyran-2-yl)methyl acetate (3ag)

The compound **3ag** was prepared using the general procedure **5.10.6.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (50:50) as eluent to afford as yellowish viscous oil (46 mg, 90%); R*f* = 0.1 (EtOAc/petroleum ether (40:60)); $[\alpha]_D^{24}$ = +31.1 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.6 Hz, 2H), 6.90–6.87 (m, 2H), 4.79 (t, *J* = 9.4 Hz, 1H), 4.44 (dd, *J* = 11.5, 1.4 Hz, 1H), 4.30 (dd, *J* = 12.1, 5.0 Hz, 1H), 4.18 (dd, *J* = 12.1, 2.1 Hz, 1H), 3.94–3.89 (m, 1H), 3.79 (s, 3H), 3.71–3.67 (m, 1H), 2.34–2.30 (m, 1H), 2.15 (s, 3H), 2.07 (s, 3H), 1.85–1.78 (m, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 171.7, 170.9, 159.3, 132.5, 127.2, 113.8, 75.8, 73.6, 71.7, 63.1, 55.2, 41.3, 20.9, 20.8. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{17}H_{23}O_7$: 339.1444; found: 339.1445.

5.11.55. (*2R,3S,4R,6R*)-4-hydroxy-6-phenyl-2-((pivaloyloxy)methyl)tetrahydro-2H-pyran-3-yl pivalate (3ah)

The compound **3ah** was prepared using the general procedure **5.10.6.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (30:70) as

eluent to afford as yellowish viscous oil (46 mg, 78%); R*f* = 0.6 (EtOAc/petroleum ether (30:70)); $[\alpha]_D^{22}$ = +91.3 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.35–7.32 (m, 4H), 7.30–7.27 (m, 1H), 4.80 (t, *J* = 9.4 Hz, 1H), 4.50 (dd, *J* = 11.6, 2.0 Hz, 1H), 4.29 (dd, *J* = 12.1, 2.0 Hz, 1H), 4.22 (dd, *J* = 12.1, 4.5 Hz, 1H), 3.96–3.91 (m, 1H), 3.77–3.74 (m, 1H), 2.40–2.36 (m, 1H), 2.30 (s, 1H), 1.81–1.74 (m, 1H), 1.25 (s, 9H), 1.22 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 179.4, 178.1, 140.5, 128.4, 127.8, 125.6, 77.3, 76.0, 73.4, 72.1, 62.6, 41.8, 39.0, 38.8, 27.1, 27.0. **HRMS** (ESI): m/z [M + H]$^+$ calcd for $C_{22}H_{33}O_6$: 393.2277; found: 393.2271.

5.11.56. (*2R,3S,4R,6R*)-4-hydroxy-2-((pivaloyloxy)methyl)-6-(4-(trifluoromethyl) phenyl)tetrahydro-2H-pyran-3-yl pivalate (3ai)

The compound **3ai** was prepared using the general procedure **5.10.6.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (25:75) as eluent to afford as yellowish viscous oil (58 mg, 84%); R*f* = 0.5 (EtOAc/petroleum ether (30:70)); $[\alpha]_D^{21}$ = +105 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.55–7.45 (m, 3H), 4.81 (t, *J* = 9.4 Hz, 1H), 4.56 (dd, *J* = 11.6, 1.7 Hz, 1H), 4.31 (dd, *J* = 12.1, 1.9 Hz, 1H), 4.21 (dd, *J* = 12.2, 4.7 Hz, 1H), 3.97–3.92 (m, 1H), 3.79–3.75 (m, 1H), 2.47 (s, 1H), 2.43–2.39 (m, 1H), 1.78–1.70 (m, 1H), 1.25 (s, 9H), 1.22 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 179.3, 178.1, 141.6, 131.2, 130.9, 130.6, 130.4, 129.1, 128.8, 128.8, 127.2, 125.1, 124.5, 124.5, 124.5, 122.9, 122.5, 122.5, 122.5, 122.4, 120.7, 76.4, 76.0, 73.2, 71.8, 62.4, 41.7, 39.0, 38.8, 27.0, 27.0. **HRMS** (ESI): m/z [M + H]$^+$ calcd for $C_{23}H_{32}F_3O_6$: 461.2151; found: 461.2147.

5.11.57. ((*2R,3S,4R,6R*)-3-(benzoyloxy)-4-hydroxy-6-phenyltetrahydro-2H-pyran-2-yl)methyl benzoate (3aj)

The compound **3aj** was prepared using the general procedure **5.10.6.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (35:65) as eluent to afford as yellowish viscous oil (55 mg, 85%); R*f* = 0.3 (EtOAc/petroleum ether (30:70)); $[\alpha]_D^{24}$ = +76.4 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.06–8.04 (m, 2H), 8.01–7.99 (m, 2H), 7.58–7.49 (m, 2H), 7.44–7.40 (m, 2H), 7.39–7.27 (m, 7H), 5.18 (t, *J* = 9.4 Hz, 1H), 4.66 (dd, *J* = 12.0, 2.8 Hz, 1H), 4.59 (dd, *J* = 11.6, 1.7 Hz, 1H), 4.47 (dd, *J*= 12.0, 5.1 Hz, 1H), 4.15–4.10 (m, 1H), 4.04–4.01 (m, 1H), 2.65 (s, 1H), 2.45–2.41 (m, 1H), 1.93–1.86 (m, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 167.1, 166.3, 140.4, 133.5, 132.9, 129.9, 129.8, 129.6, 129.2, 128.4, 128.4, 128.3, 128.2, 127.8, 125.7, 77.4, 75.9, 74.7, 71.9, 64.0, 41.5. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{26}H_{25}O_6$: 433.1651; found: 433.1641.

5.11.58. ((*2R,3S,4R,6R*)-3-(benzoyloxy)-4-hydroxy-6-(4-methoxyphenyl)tetrahydro-2H-pyran-2-yl)methyl benzoate (3ak)

The compound **3ak** was prepared using the general procedure **5.10.6.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (40:60) as eluent to afford as yellowish viscous oil (63 mg, 90%); R*f* = 0.3 (EtOAc/petroleum ether (30:70)); $[\alpha]_D^{22}$ = +86.8 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.06–8.04 (m, 2H), 8.00–7.98 (m, 2H), 7.58–7.49 (m, 2H), 7.44–7.36 (m, 4H), 7.31–7.29 (m, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 5.17 (t, *J* = 9.4 Hz, 1H), 4.64 (dd, *J* = 12.0, 2.8 Hz, 1H), 4.55 (dd, *J* = 11.5, 1.5 Hz, 1H), 4.46 (dd, *J* = 12.0, 5.1 Hz, 1H), 4.14–4.09 (m, 1H), 4.03–4.00 (m, 1H), 2.79 (s, 1H), 2.63 (s, 1H), 2.42–2.38 (m, 1H), 1.95–1.88 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 167.1, 166.3, 159.2, 133.5, 132.9, 132.6, 129.9, 129.8, 129.6, 129.2, 128.4, 128.2, 127.1, 113.8, 75.9, 74.8, 71.9, 64.1, 55.2, 41.3. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{27}H_{26}NaO_7$: 485.1576; found: 485.1599.

5.11.59. ((*2R,3S,4R,6R*)-3-(benzoyloxy)-4-hydroxy-6-(4-(trifluoromethyl) phenyl)tetrahydro-2H-pyran-2-yl)methyl benzoate (3al)

The compound **3al** was prepared using the general procedure **5.10.6.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (35:65) as eluent to afford as yellowish viscous oil (71 mg, 95%); R*f* = 0.4 (EtOAc/petroleum ether (30:70)); $[\alpha]_D^{23}$ = +67.2 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.08–8.06 (m, 2H), 8.02–8.00 (m, 2H), 7.64 (s, 1H), 7.60–7.51 (m, 4H), 7.48–7.37 (m, 5H), 5.16 (t, *J* = 9.4 Hz, 1H), 4.70–4.64 (m, 2H), 4.48 (dd, *J* = 12.1, 5.3 Hz, 1H), 4.17–4.12 (m, 1H), 4.07–4.03 (m, 1H), 2.48–2.44 (m, 1H), 2.35 (s, 1H), 1.90–1.82 (m, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 167.1, 166.3, 141.4, 133.6, 133.0, 130.9, 130.6, 129.9, 129.7, 129.6, 129.1, 128.9, 128.5, 128.3, 125.1, 124.6, 124.6, 122.9, 122.6, 122.6, 76.6, 76.0, 74.6, 71.7, 63.8, 41.4. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{27}H_{24}F_3O_6$: 501.1525; found: 501.1551.

5.11.60. (*2R,3S,4R,6R*)-3-(methoxymethoxy)-2-((methoxymethoxy)methyl)-6-phenyltetrahydro-2H-pyran-4-ol (3am)

The compound **3am** was prepared using the general procedure **5.10.6.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (40:60) as eluent to afford as yellowish viscous oil (38 mg, 81%); R*f* = 0.5 (EtOAc/petroleum ether (40:60)); $[\alpha]_D^{24}$ = -11.3 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36–7.24 (m, 6H), 4.79 (d, *J* = 6.8 Hz, 1H), 4.75 (d, *J* = 6.8 Hz, 1H), 4.71 (d, *J* = 6.4 Hz,

1H), 4.68 (d, *J* = 6.4 Hz, 1H), 4.48 (dd, *J* = 11.7, 1.9 Hz, 1H), 3.87–3.78 (m, 3H), 3.59–3.55 (m, 1H), 3.49 (s, 3H), 3.37–3.33 (m, 4H), 2.33–2.29 (m, 1H), 1.73–1.65 (m, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 141.2, 128.2, 127.5, 125.8, 98.1, 96.8, 83.1, 77.9, 77.3, 71.6, 66.9, 55.9, 55.2, 40.2. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{16}H_{25}O_6$: 313.1651; found: 313.1681.

5.11.61. (*2R,3S,4R,6R*)-3-(methoxymethoxy)-2-((methoxymethoxy)methyl)-6-(4-methoxyphenyl)tetrahydro-2H-pyran-4-ol (3an)

The compound **3an** was prepared using the general procedure **5.10.6.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (50:50) as eluent to afford as yellowish viscous oil (40 mg, 78%); R*f* = 0.4 (EtOAc/petroleum ether (40:60)); $[\alpha]_D^{24}$ = -25.3 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 4.76 (dd, *J* = 18.3, 6.8 Hz, 2H), 4.68 (q, *J* = 6.4 Hz, 2H), 4.43 (dd, *J* = 11.6, 1.6 Hz, 1H), 3.85–3.76 (m, 6H), 3.57–3.54 (m, 1H), 3.49 (s, 3H), 3.36–3.32 (m, 4H), 2.29–2.25 (m, 1H), 1.74–1.66 (m, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 159.0, 133.4, 127.1, 113.6, 98.1, 96.8, 83.2, 77.8, 71.6, 66.9, 55.9, 55.2, 55.2, 40.0. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{17}H_{27}O_7$: 343.1757; found: 343.1772.

5.11.62. (*2R,3R,4R,6R*)-2-(hydroxymethyl)-6-phenyltetrahydro-2H-pyran-3,4-diol (4aa)

The compound **4aa** was prepared using the general procedure **5.10.7.** and column chromatography was performed on silica gel using EtOAc/Methanol (95:05) as eluent to afford as waxy white solid (30 mg, 88%); R*f* = 0.3 (EtOAc); $[\alpha]_D^{24}$ = +11.6 (c = 0.1, MeOH); **^{1}H NMR** (500 MHz, MeOD) δ 7.33 (d, *J* = 7.3 Hz, 2H), 7.23–7.20 (m, 2H),

7.16–7.13 (m, 1H), 4.33 (dd, *J* = 11.1, 2.5 Hz, 1H), 3.77–3.69 (m, 3H), 3.64 (dd, *J* = 11.4, 5.2 Hz, 1H), 3.49–3.46 (m, 1H), 1.85–1.74 (m, 2H). **^{13}C NMR** (125 MHz, MeOD) δ 143.5, 129.3, 128.6, 127.4, 80.9, 79.6, 71.3, 69.2, 63.4, 37.7. **HRMS** (ESI): m/z [M + H]$^+$ calcd for $C_{12}H_{17}O_4$: 225.1127; found: 225.1130.

5.11.63. (*2R,3R,4R,6R*)-2-(hydroxymethyl)-6-(4-methoxyphenyl)tetrahydro-2H-pyran-3,4-diol (4ab)

The compound **4ab** was prepared using the general procedure **5.10.7.** and column chromatography was performed on silica gel using EtOAc/methanol (90:10) as eluent to afford as yellowish viscous oil (27 mg, 70%); R*f* = 0.2 (EtOAc); $[a]_D^{24}$ = +9.6 (c = 0.1, MeOH); **^{1}H NMR** (500 MHz, MeOD) δ 7.25 (d, *J* = 8.6 Hz, 2H), 6.77 (d, *J* = 8.7 Hz, 2H), 4.28 (dd, *J* = 11.5, 2.0 Hz, 1H), 3.75– 3.68 (m, 3H), 3.67 (s, 3H), 3.65–3.61 (m, 1H), 3.46 (t, *J* = 6.0 Hz, 1H), 1.84 (dd, *J* = 24.0, 11.6 Hz, 1H), 1.74–1.70 (m, 1H). **^{13}C NMR** (125 MHz, MeOD) δ 160.7, 135.6, 128.8, 114.6, 80.9, 79.3, 71.3, 69.2, 63.4, 55.8, 37.5. **HRMS** (ESI): m/z [M + H]$^+$ calcd for $C_{13}H_{19}O_5$: 255.1232; found: 255.1235.

5.11.64. (*2R,3R,4R,6R*)-6-(4-fluorophenyl)-2-(hydroxymethyl)tetrahydro-2H-pyran-3,4-diol(4ac)

The compound **4ac** was prepared using the general procedure **5.10.7.** and column chromatography was performed on silica gel using EtOAc/methanol (95:05) as eluent to afford as white foam (28 mg, 76%); R*f* = 0.3 (EtOAc); $[a]_D^{24}$ = +14.5 (c = 0.1, MeOH); **^{1}H NMR** (500 MHz, MeOD) δ 7.36–7.34 (m, 2H), 6.95–6.92 (m, 2H), 4.34 (dd, *J* = 10.3, 3.5 Hz, 1H), 3.76–3.70 (m, 3H), 3.63 (dd, *J* = 11.4, 5.1 Hz, 1H), 3.48–3.46 (m, 1H), 1.82–1.75 (m, 2H). **^{13}C NMR** (125 MHz, MeOD) δ 164.6, 162.7, 139.7, 139.7,

129.4, 129.3, 115.9, 115.8, 80.9, 78.8, 71.2, 69.2, 63.4, 37.7. **HRMS** (ESI): m/z [M + H]$^+$ calcd for $C_{12}H_{16}FO_4$: 243.1033; found: 243.1035.

5.11.65. (*2R,3R,4R,6R*)-2-(hydroxymethyl)-6-(o-tolyl)tetrahydro-2H-pyran-3,4-diol (4ad)

The compound **4ad** was prepared using the general procedure **5.10.7.** and column chromatography was performed on silica gel using EtOAc/methanol (95:05) as eluent to afford as white foam (29 mg, 80%); R*f* = 0.3 (EtOAc); $[\alpha]_D^{24}$ = +12.6 (c = 0.1, MeOH); **^{1}H NMR** (500 MHz, MeOD) δ 7.42 (d, *J* = 7.0 Hz, 1H), 7.08–7.01(m, 3H), 4.53 (d, *J* = 11.3 Hz, 1H), 3.78–3.68 (m, 3H), 3.64 (dd, *J* = 11.4, 5.1 Hz, 1H), 3.51–3.48 (m, 1H), 2.25 (s, 3H), 1.85 (dd, *J* = 24.0, 11.6 Hz, 1H), 1.74–1.74 (m, 1H). **^{13}C NMR** (125 MHz, MeOD) δ 141.2, 136.2, 131.2, 128.5, 127.2, 127.1, 81.1, 76.4, 71.4, 69.3, 63.5, 35.99, 19.28. **HRMS** (ESI): m/z [M + H]$^+$ calcd for $C_{13}H_{19}O_4$: 239.1283; found: 239.1286.

5.11.66. (*2R,3S,4R,6R*)-2-(hydroxymethyl)-6-phenyltetrahydro-2H-pyran-3,4-diol(4ae)

The compound **4ae** was prepared using the general procedure **5.10.7.** and column chromatography was performed on silica gel using EtOAc/methanol (95:05) as eluent to afford as white foam (29 mg, 85%); R*f* = 0.3 (EtOAc); $[\alpha]_D^{24}$ = +22.5 (c = 0.1, MeOH); **^{1}H NMR** (500 MHz, MeOD) δ 7.30–7.29 (m, 2H), 7.22–7.19 (m, 2H), 7.16–7.13 (m, 1H), 4.42–4.34 (m, 1H), 3.81 (dd, *J* = 11.9, 2.2 Hz, 1H), 3.66–3.59 (m, 2H), 3.29–3.25 (m, 1H), 3.19–3.17 (m, 1H), 2.06 (ddd, *J* = 12.9, 4.9, 1.9 Hz, 1H), 1.55–1.48 (m, 1H). **^{13}C NMR** (125 MHz, MeOD) δ 143.3, 129.3, 128.6, 127.2, 82.3, 78.9, 74.2, 73.4, 63.4, 42.9. **HRMS** (ESI): m/z [M + H]$^+$ calcd for $C_{12}H_{17}O_4$: 225.1127; found: 225.1131.

5.11.67. (*2R,3S,4R,6R*)-2-(hydroxymethyl)-6-(4-methoxyphenyl)tetrahydro-2H-pyran-3,4-diol(4af)

The compound **4af** was prepared using the general procedure **5.10.7.** and column chromatography was performed on silica gel using EtOAc/methanol (90:10) as eluent to afford as yellowish viscous oil (30 mg, 79%); R*f* = 0.3 (EtOAc); $[\alpha]_D^{24}$ = +26.2 (c = 0.1, MeOH); **^{1}H NMR** (500 MHz, MeOD) δ 7.21 (d, *J* = 8.7 Hz, 2H), 6.77 (d, *J* = 8.8 Hz, 2H), 4.35 (dd, *J* = 11.5, 1.8 Hz, 1H), 3.80 (dd, *J* = 11.9, 2.3 Hz, 1H), 3.67 (s, 3H), 3.64–3.60 (m, 2H), 3.27–3.24 (m, 1H), 3.19–3.15 (m, 1H), 2.04–2.00 (m, 1H), 1.57 – 1.50 (m, 1H). **^{13}C NMR** (125 MHz, MeOD) δ 160.7, 135.3, 128.6, 114.7, 82.3, 78.6, 74.3, 73.5, 63.4, 55.8, 42.7. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{13}H_{19}O_5$: 255.1232; found: 255.1237.

5.11.68. (*2R,3S,4R,6R*)-6-(4-fluorophenyl)-2-(hydroxymethyl)tetrahydro-2H-pyran-3,4-diol (4ag)

The compound **4ag** was prepared using the general procedure **5.10.7.** and column chromatography was performed on silica gel using EtOAc / methanol (95:05) as eluent to afford as colourless viscous oil (31 mg, 86%); R*f* = 0.3 (EtOAc); $[\alpha]_D^{24}$ = +28.4 (c = 0.1, MeOH); **^{1}H NMR** (500 MHz, MeOD) δ 7.33–7.31 (m, 2H), 6.96–6.92 (m, 2H), 4.41 (dd, *J* = 11.5, 1.5 Hz, 1H), 3.81 (dd, *J* = 11.9, 2.2 Hz, 1H), 3.66–3.58 (m, 2H), 3.28–3.25 (m, 1H), 3.20–3.16 (m, 1H), 2.07 (ddd, *J* = 12.9, 4.9, 2.0 Hz, 1H), 1.49 (dd, *J* = 24.3, 11.5 Hz, 1H). **^{13}C NMR** (125 MHz, MeOD) δ 164.6, 162.7, 139.4, 139.4, 129.1, 129.1, 116.0, 115.8, 82.3, 78.1, 74.1, 73.3, 63.4, 42.9. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{12}H_{16}FO_4$: 243.1033; found: 243.1030.

5.11.69. (*2R,3S,4R,6R*)-2-(hydroxymethyl)-6-(4-(trifluoromethyl)phenyl) tetrahydro-2H-pyran-3,4-diol(4ah)

The compound **4ah** was prepared using the general procedure **5.10.7.** and column chromatography was performed on silica gel using EtOAc/methanol (95:05) as eluent to afford as colourless viscous oil (33 mg, 76%); R*f* = 0.3 (EtOAc); $[\alpha]_D^{24}$ = +33.7 (c = 0.1, MeOH); **^{1}H NMR** (500 MHz, MeOD) δ 7.64 (s, 1H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.45 (d, *J* = 8.1 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 1H), 4.52 (dd, *J* = 11.5, 1.6 Hz, 1H), 3.83 (dd, *J* = 11.9, 2.2 Hz, 1H), 3.69–3.61 (m, 2H), 3.31–3.28 (m, 1H), 3.21–3.19 (m, 1H), 2.12 (ddd, *J* = 12.8, 4.9, 2.0 Hz, 1H), 1.46 (dd, *J* = 24.3, 11.5 Hz, 1H). **^{13}C NMR** (125 MHz, MeOD) δ 144.8, 131.8, 131.5, 130.9, 130.1, 126.9, 125.2, 125.2, 125.2, 124.8, 123.8, 123.8, 123.8, 123.8, 82.4, 77.9, 74.1, 73.2, 63.3, 43.0. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{13}H_{16}F_3O_4$: 293.1001; found: 293.1011.

5.11.70. (*2R,3R,4R*)-3-(benzyloxy)-2-((benzyloxy)methyl)-6-phenyl-3,4-dihydro-2H-pyran-4-ol (5aa)

The compound **5aa** was prepared using the general procedure **5.10.8.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (15:85) as eluent to afford as white foam (165 mg, 82%); R*f* = 0.5 (EtOAc/petroleum ether (20:80)); $[\alpha]_D^{24}$ = +13.6 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.31–7.25 (m, 13H), 5.31 (d, *J* = 3.2 Hz, 1H), 4.73 (d, *J* = 11.7 Hz, 1H), 4.68 (d, *J* = 11.7 Hz, 1H), 4.56 (d, *J* = 12.0 Hz, 1H), 4.51–4.46 (m, 2H), 4.36–4.33 (m, 1H), 3.96 (dd, *J* = 4.6, 2.4 Hz, 1H), 3.90 (dd, *J* = 10.0, 6.3 Hz, 1H), 3.76 (dd, *J* = 10.0, 6.0 Hz, 1H), 2.46 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 151.8, 137.7, 137.7, 134.4, 128.5, 128.4, 128.3, 128.0, 127.9, 127.9, 127.7, 125.0, 98.7, 75.4, 74.0, 73.4,

72.7, 68.0, 63.6. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{26}H_{27}O_4$: 403.1909; found: 403.1912.

5.11.71. (*2R,3R,4R*)-3,4-bis(benzyloxy)-2-((benzyloxy)methyl)-6-phenyl-3,4-dihydro-2H-pyran (6aa)

The compound **6aa** was prepared using the general procedure **5.10.9.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (10:90) as eluent to afford as colourless viscous oil (75 mg, 76%); R*f* = 0.6 (EtOAc/petroleum ether (10:90)); $[a]_D^{24}$ = - 8.5 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 7.9, 1.7 Hz, 2H), 7.37–7.29 (m, 18H), 5.41 (d, *J* = 2.7 Hz, 1H), 4.89 (d, *J* = 12.0 Hz, 1H), 4.70–4.68 (m, 3H), 4.52 (d, *J* = 11.9 Hz, 1H), 4.48 (d, *J* = 11.9 Hz, 1H), 4.40–4.37 (m, 1H), 4.34 (t, *J* = 3.5 Hz, 1H), 4.05–4.04 (m, 1H), 3.90 (dd, *J* = 10.2, 6.9 Hz, 1H), 3.82 (dd, *J* = 10.2, 5.4 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 151.8, 138.5, 138.4, 138.1, 134.6, 128.5, 128.3, 128.3, 128.2, 128.0, 127.8, 127.6, 127.6, 127.5, 127.4, 125.2, 96.1, 76.1, 73.4, 73.1, 71.6, 71.0, 68.3. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{33}H_{33}O_4$: 493.2379; found: 493.2384.

5.11.72. (*2S,3S,4R,5S,6R*)-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)-2-phenyltetrahydro-2H-pyran-3-ol (7aa)

The compound **7aa** was prepared using the general procedure **5.10.10.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (20:80) as eluent to afford as colourless viscous oil (46 mg, 60%); R*f* = 0.4 (EtOAc/petroleum ether (20:80)); $[a]_D^{24}$ = +25.4 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz,) δ 7.42 (d, *J* = 7.6 Hz, 2H), 7.36–7.27 (m, 18H), 4.93 (d, *J* = 11.5 Hz, 1H), 4.77 (d, *J* = 12.1 Hz, 1H), 4.65–4.60 (m, 2H), 4.48 (d, *J* = 12.1 Hz, 1H), 4.44 (d, *J* = 12.0 Hz, 1H), 4.15–4.09 (m,

3H), 3.78–3.75 (m, 1H), 3.68 (t, *J* = 8.2 Hz, 1H), 3.62 (dd, *J* = 8.7, 5.6 Hz, 1H), 3.57 (dd, *J* = 8.6, 2.8 Hz, 1H), 1.97 (s, 1H). **^{13}C NMR** (125 MHz,) δ 138.8, 138.7, 138.0, 137.8, 128.5, 128.3, 128.3, 128.2, 128.2, 127.9, 127.8, 127.7, 127.6, 127.6, 127.4, 83.8, 82.5, 77.3, 76.7, 74.4, 73.5, 73.3, 71.9, 71.7, 68.6. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{33}H_{35}O_5$: 511.2484; found: 511.2487.

5.11.73. (*2R,3R,4R*)-3-(benzyloxy)-2-((benzyloxy)methyl)-6-(naphthalen-1-yl)-3,4-dihydro-2H-pyran-4-ol (5ab)

The compound **5ab** was prepared using the general procedure **5.10.8.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (20:80) as eluent to afford as white foam (193 mg, 85%); R*f* = 0.4 (EtOAc/petroleum ether (20:80)); $[\alpha]_D^{24}$ = +33.2 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.2 Hz, 1H), 7.79 (d, *J* = 6.5 Hz, 2H), 7.48–7.41 (m, 2H), 7.40–7.27 (m, 12H), 5.04 (d, *J* = 2.3 Hz, 1H), 4.82 (d, *J* = 11.6 Hz, 1H), 4.76 (d, *J* = 11.6 Hz, 1H), 4.59– 4.51 (m, 3H), 4.47–4.44 (m, 1H), 4.09 (dd, *J* = 4.0, 2.3 Hz, 1H), 3.93 (dd, *J* = 9.9, 6.1 Hz, 1H), 3.83 (dd, *J* = 9.9, 6.4 Hz, 1H), 2.45 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 153.6, 138.0, 137.6, 133.7, 133.5, 131.2, 129.1, 128.5, 128.4, 128.4, 128.0, 127.8, 127.8, 127.7, 127.6, 126.5, 126.1, 126.0, 125.7, 124.9, 103.3, 75.6, 74.2, 73.5, 72.8, 68.0, 63.9. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{30}H_{29}O_4$: 453.2066; found: 453.2064.

5.11.74. (*2R,3R,4R*)-3,4-bis(benzyloxy)-2-((benzyloxy)methyl)-6-(naphthalen-1-yl)-3,4-dihydro-2H-pyran (6ab)

The compound **6ab** was prepared using the general procedure **5.10.9.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (10:90) as eluent to afford as colourless viscous oil (82 mg, 75%); R*f* = 0.6 (EtOAc/petroleum

ether (10:90)); $[a]_D^{23}$ = - 11.5 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.2 Hz, 1H), 7.77 (d, *J* = 8.1 Hz, 2H), 7.49 (dd, *J* = 7.0, 1.3 Hz, 1H), 7.41–7.39 (m, 3H), 7.37–7.23 (m, 15H), 5.16 (d, *J* = 0.9 Hz, 1H), 5.01 (d, *J* = 11.7 Hz, 1H), 4.72–4.69 (m, 3H), 4.53 (d, *J* = 11.9 Hz, 1H), 4.49–4.47 (m, 2H), 4.41 (s, 1H), 4.16 (d, *J* = 1.4 Hz, 1H), 3.96–3.93 (m, 1H), 3.89–3.86 (m, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 153.5, 138.7, 138.5, 138.0, 133.9, 133.4, 131.4, 129.0, 128.3, 128.3, 128.2, 128.2, 128.1, 127.9, 127.8, 127.8, 127.7, 127.7, 127.6, 127.5, 127.4, 127.4, 126.6, 126.2, 126.1, 125.7, 124.9, 100.6, 76.2, 73.3, 73.3, 70.8, 68.2. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{37}H_{35}O_4$: 543.2535; found: 543.2538.

5.11.75. (*2S,3S,4R,5S,6R*)-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)-2-(naphthalen-1-yl)tetrahydro-2H-pyran-3-ol (7ab)

The compound **7ab** was prepared using the general procedure **5.10.10.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (20:80) as eluent to afford as viscous oil (52 mg, 62%); R*f* = 0.4 (EtOAc/petroleum ether (20:80)); $[a]_D^{24}$ = +17.5 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.51 (d, *J* = 8.5 Hz, 1H), 7.80–7.76 (m, 2H), 7.53 (d, *J* = 6.9 Hz, 1H), 7.42–7.25 (m, 18H), 5.04 (d, *J* = 11.3 Hz, 1H), 4.80 (d, *J* = 11.8 Hz, 1H), 4.71–4.65 (m, 3H), 4.58 (t, *J* = 9.3 Hz, 1H), 4.48 (d, *J* = 11.8 Hz, 1H), 4.44 (d, *J* = 11.8 Hz, 1H), 4.18 (d, *J* = 2.3 Hz, 1H), 3.85 (dd, *J* = 7.5, 5.7 Hz, 1H), 3.74 (t, *J* = 8.4 Hz, 1H), 3.65–3.62 (m, 2H), 1.88 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 138.9, 138.1, 137.8, 134.2, 134.0, 131.5, 129.1, 128.4, 128.3, 128.2, 127.9, 127.7, 127.5, 127.5, 127.4, 126.7, 125.8, 125.4, 125.3, 124.9, 84.0, 77.3, 74.5, 73.5, 73.5, 72.1, 70.8, 68.6. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{37}H_{37}O_5$: 561.2641; found: 561.2649.

5.11.76. (*2R,3S,4R*)-3-(benzyloxy)-2-((benzyloxy)methyl)-6-phenyl-3,4-dihydro-2H-pyran-4-ol (5ac)

The compound **5ac** was prepared using the general procedure **5.10.8.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (20:80) as eluent to afford as white foam (121 mg, 60%); R*f* = 0.5 (EtOAc/petroleum ether (20:80)); $[\alpha]_D^{24}$ = +36.2 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 7.9, 1.7 Hz, 2H), 7.36–7.27 (m, 13H), 5.30 (d, *J* = 3.0 Hz, 1H), 4.83 (d, *J* = 11.6 Hz, 1H), 4.75 (d, *J* = 11.6 Hz, 1H), 4.67 (d, *J* = 11.9 Hz, 1H), 4.62 (d, *J* = 12.2 Hz, 1H), 4.49 (dd, *J* = 6.3, 3.0 Hz, 1H), 4.17–4.14 (m, 1H), 3.92 (d, *J* = 3.2 Hz, 2H), 3.78 (dd, *J* = 8.9, 6.4 Hz, 1H), 2.02 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 152.4, 138.3, 137.9, 134.2, 128.6, 128.5, 128.3, 128.2, 128.1, 127.9, 127.8, 127.7, 127.6, 127.5, 126.9, 125.1, 98.6, 77.3, 77.1, 73.5, 73.5, 69.8, 68.9. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{26}H_{27}O_4$: 403.1909; found: 403.1910.

5.11.77. (*2R,3S,4R*)-3,4-bis(benzyloxy)-2-((benzyloxy)methyl)-6-phenyl-3,4-dihydro-2H-pyran (6ac)

The compound **6ac** was prepared using the general procedure **5.10.9.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (10:90) as eluent to afford as yellowish viscous oil (76 mg, 76%); R*f* = 0.6 (EtOAc/petroleum ether (10:90)); $[\alpha]_D^{24}$ = - 54.3 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 7.9, 1.7 Hz, 2H), 7.35–7.26 (m, 18H), 5.43 (d, *J* = 3.1 Hz, 1H), 4.86 (d, *J* = 11.4 Hz, 1H), 4.70 (dd, *J* = 11.5, 8.5 Hz, 2H), 4.65–4.64 (m, 1H), 4.63 (d, *J* = 6.5 Hz, 2H), 4.38 (dd, *J* = 6.0, 3.1 Hz, 1H), 4.27–4.24 (m, 1H), 3.98 (dd, *J* = 8.4, 6.0 Hz, 1H), 3.94–3.87 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 152.7, 138.5, 138.2, 134.5, 128.6,

128.4, 128.3, 128.3, 128.3, 128.2, 128.1, 128.1, 127.9, 127.7, 127.7, 127.6, 127.6, 127.5, 125.2, 96.0, 77.3, 76.6, 74.4, 73.5, 73.4, 70.4, 68.6. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{33}H_{33}O_4$: 493.2379; found: 493.2382.

5.11.78. (*2S,3S,4R,5R,6R*)-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)-2-phenyltetrahydro-2H-pyran-3-ol (7ac)

The compound **7ac** was prepared using the general procedure **5.10.10.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (20:80) as eluent to afford as colourless viscous oil (40 mg, 52%); R*f* = 0.5 (EtOAc/petroleum ether (20:80)); $[\alpha]_D^{24}$ = +29.4 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz,) δ 7.41–7.22 (m, 20H), 4.94 (d, *J* = 11.4 Hz, 1H), 4.87 (dd, *J* = 11.0, 5.0 Hz, 2H), 4.65 (d, *J* = 11.8 Hz, 2H), 4.55 (s, 1H), 4.16 (d, *J* = 9.2 Hz, 1H), 3.81–3.76 (m, 3H), 3.71–3.67 (m, 1H), 3.64–3.60 (m, 2H), 1.86 (s, 1H). **^{13}C NMR** (125 MHz,) δ 138.6, 138.4, 138.2, 138.1, 128.5, 128.4, 128.4, 128.3, 128.0, 127.8, 127.7, 127.4, 86.4, 82.0, 79.5, 78.1, 75.7, 75.3, 75.0, 73.4, 69.0. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{33}H_{35}O_5$: 511.2484; found: 511.2479.

5.11.79. (*2R,3S*)-3-(benzyloxy)-2-((benzyloxy)methyl)-5-bromo-6-phenyl-2H-pyran-4(3H)-one (8aa)

The compound **8aa** was prepared using the general procedure **5.10.11.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (10:90) as eluent to afford as yellowish viscous oil (65 mg, 90%); R*f* = 0.6 (EtOAc/petroleum ether (20:80)); $[\alpha]_D^{24}$ = +119 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.8 Hz, 2H), 7.48–7.45 (m, 1H), 7.42–7.39 (m, 2H), 7.35–7.26 (m, 10H), 4.78 (d, *J* = 11.9 Hz, 1H), 4.71–4.68 (m, 1H), 4.56–4.49 (m, 3H), 4.01 (d, *J* = 2.3 Hz, 1H), 3.94

(dd, *J* = 10.1, 6.7 Hz, 1H), 3.84 (dd, *J* = 10.2, 5.9 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 184.0, 168.7, 137.4, 136.8, 133.1, 131.4, 129.6, 128.4, 128.4, 128.3, 128.0, 127.9, 127.8, 127.6, 99.1, 80.3, 73.9, 73.6, 72.1, 67.0. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{26}H_{24}BrO_4$: 479.0858; found: 479.0875.

5.11.80. (*2R,3S*)-3-(benzyloxy)-2-((benzyloxy)methyl)-5-bromo-6-(naphthalen-1-yl)-2H-pyran-4(3H)-one (8ab)

The compound **8ab** was prepared using the general procedure **5.10.11.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (10:90) as eluent to afford as yellowish viscous oil (77 mg, 96%); R*f* = 0.6 (EtOAc/petroleum ether (20:80)); $[\alpha]_D^{23}$ = +33.7 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.2 Hz, 1H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 6.8 Hz, 1H), 7.51–7.48 (m, 2H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.38–7.21 (m, 10H), 4.87–4.81 (m, 2H), 4.62 (d, *J* = 11.8 Hz, 1H), 4.52 (d, *J* = 11.9 Hz, 1H), 4.46 (d, *J* = 11.9 Hz, 1H), 4.13 (d, *J* = 2.3 Hz, 1H), 3.90 (d, *J* = 6.3 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 183.7, 169.8, 137.3, 136.8, 133.3, 131.3, 130.8, 129.7, 128.4, 128.4, 128.3, 128.2, 128.0, 127.8, 127.6, 127.1, 126.4, 124.8, 124.7, 101.6, 80.6, 73.9, 73.6, 72.1, 66.9. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{30}H_{26}BrO_4$: 529.1014; found: 529.1026.

5.11.81. (*2R,3R*)-3-(benzyloxy)-2-((benzyloxy)methyl)-5-bromo-6-phenyl-2H-pyran-4(3H)-one (8ac)

The compound **8ac** was prepared using the general procedure **5.10.11.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (15:85) as eluent to afford as yellowish viscous oil (61 mg, 85%); R*f* = 0.5 (EtOAc/petroleum ether (20:80)); $[\alpha]_D^{24}$ = +291 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.76–

7.74 (m, 2H), 7.50–7.47 (m, 1H), 7.45–7.42 (m, 2H), 7.38–7.28 (m, 10H), 5.14 (d, *J* = 11.0 Hz, 1H), 4.68 (d, *J* = 11.0 Hz, 1H), 4.63–4.60 (m, 1H), 4.59 (d, *J* = 12.1 Hz, 1H), 4.54 (d, *J* = 12.1 Hz, 1H), 4.44 (d, *J* = 11.5 Hz, 1H), 3.92–3.86 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 187.9, 168.5, 137.5, 137.2, 133.0, 131.4, 129.5, 128.5, 128.4, 128.4, 128.0, 127.9, 127.8, 127.6, 98.4, 80.9, 74.5, 74.3, 73.5, 67.7. **HRMS** (ESI): m/z [M + H]$^+$ calcd for $C_{26}H_{24}BrO_4$: 479.0858; found: 479.0857.

5.11.82. (*2R,3S*)-3-(benzyloxy)-2-((benzyloxy)methyl)-5-chloro-6-(naphthalen-1-yl)-2H-pyran-4(3H)-one (8ad)

The compound **8ad** was prepared using the general procedure **5.10.11.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (10:90) as eluent to afford as yellowish viscous oil (51 mg, 70%); R*f* = 0.6 (EtOAc/petroleum ether (20:80)); $[\alpha]_D^{23}$ = +186 (c = 0.1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.59 (d, *J* = 6.5 Hz, 1H), 7.53–7.49 (m, 2H), 7.47–7.43 (m, 1H), 7.37–7.22 (m, 10H), 4.87 (d, *J* = 11.8 Hz, 1H), 4.83–4.80 (m, 1H), 4.62 (d, *J* = 11.8 Hz, 1H), 4.53 (d, *J* = 11.8 Hz, 1H), 4.47 (d, *J* = 11.9 Hz, 1H), 4.10 (d, *J* = 2.2 Hz, 1H), 3.91 (d, *J* = 6.3 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 183.6, 168.5, 137.4, 136.9, 133.3, 131.0, 129.9, 129.8, 128.5, 128.4, 128.4, 128.3, 128.1, 127.8, 127.6, 127.4, 127.1, 126.4, 124.9, 124.7, 111.3, 80.6, 74.1, 73.6, 72.2, 67.0. **HRMS** (ESI): m/z [M + H]$^+$ calcd for $C_{30}H_{26}ClO_4$: 485.1520; found: 485.1542.

5.11.83. (*2R,3S*)-3-(benzyloxy)-2-((benzyloxy)methyl)-5-iodo-6-(naphthalen-1-yl)-2H-pyran-4(3H)-one (8ae)

The compound **8ae** was prepared using the general procedure **5.10.11.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (10:90) as eluent to afford as yellowish viscous oil (70 mg, 80%); R*f* = 0.6 (EtOAc/petroleum ether (20:80)); $[\alpha]_D^{23}$ = +232 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.94–7.92 (m, 1H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.52–7.49 (m, 3H), 7.37–7.21 (m, 12H), 4.84–4.82 (m, 2H), 4.60 (d, *J* = 11.8 Hz, 1H), 4.52 (d, *J* = 11.9 Hz, 1H), 4.46 (d, *J* = 11.9 Hz, 1H), 4.15 (d, *J* = 2.1 Hz, 1H), 3.91 (d, *J* = 6.2 Hz, 2H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ 185.4, 137.4, 136.9, 133.3, 130.6, 128.4, 128.4, 128.2, 128.0, 127.8, 127.6, 127.1, 126.4, 124.7, 73.6, 72.9, 72.2, 67.0. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{30}H_{26}IO_4$: 577.0876; found: 577.0892.

5.11.84. (*2R,3S*)-3-(benzyloxy)-2-((benzyloxy)methyl)-5-((E)-4-methylstyryl)-6-(naphthalen-1-yl)-2H-pyran-4(3H)-one (9aa)

The compound **9aa** was prepared using the general procedure **5.10.12.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (15:85) as eluent to afford as yellowish viscous oil (34 mg, 60%); R*f* = 0.7 (EtOAc/petroleum ether (30:70)); $[\alpha]_D^{24}$ = +54.6 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.96–7.88 (m, 3H), 7.55–7.48 (m, 3H), 7.43–7.25 (m, 15H), 6.20 (d, *J* = 16.1 Hz, 1H), 4.89 (d, *J* = 11.9 Hz, 1H), 4.84–4.82 (m, 1H), 4.68 (d, *J* = 11.9 Hz, 1H), 4.55 (d, *J* = 11.9 Hz, 1H), 4.49 (d, *J* = 11.9 Hz, 1H), 3.99 (d, *J* = 1.8 Hz, 1H), 3.93 (d, *J* = 6.2 Hz, 2H), 2.22 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 190.1, 137.6, 137.4, 136.7, 135.5, 130.5, 129.0, 128.4, 128.3, 128.1, 127.9, 127.7, 127.7, 127.0, 126.3, 125.9, 125.4, 124.8, 119.8, 79.9,

74.7, 73.6, 72.0, 67.4, 21.0. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{39}H_{35}O_4$: 567.2535; found: 567.2531.

5.11.85. (*2R,3S*)-3-(benzyloxy)-2-((benzyloxy)methyl)-6-(naphthalen-1-yl)-5-((E)-styryl)-2H-pyran-4(3H)-one (9ab)

The compound **9ab** was prepared using the general procedure **5.10.12.** and column chromatography was performed on silica gel using EtOAc/petroleum ether (15:85) as eluent to afford as yellowish viscous oil (30 mg, 55%); R*f* = 0.7 (EtOAc/petroleum ether (30:70)); $[\alpha]_D^{24}$ = +43.6 (c = 0.1, $CHCl_3$); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 8.1 Hz, 2H), 7.56–7.45 (m, 4H), 7.40–7.24 (m, 10H), 7.13 (t, *J* = 7.4 Hz, 2H), 7.06 (dd, *J* = 16.6, 7.0 Hz, 3H), 6.25 (d, *J* = 16.0 Hz, 1H), 4.90 (d, *J* = 11.9 Hz, 1H), 4.84 (s, 1H), 4.68 (d, *J* = 11.8 Hz, 1H), 4.55 (d, *J* = 11.9 Hz, 1H), 4.49 (d, *J* = 11.8 Hz, 1H), 4.01 (s, 1H), 3.94 (d, *J* = 6.1 Hz, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 190.1, 138.3, 137.6, 137.3, 131.1, 130.7, 130.6, 128.4, 128.3, 128.2, 128.1, 127.9, 127.7, 127.7, 127.13, 126.9, 126.4, 126.0, 125.4, 124.8, 120.8, 112.8, 79.7, 74.7, 73.6, 72.0, 67.4. **HRMS** (ESI): m/z $[M + H]^+$ calcd for $C_{38}H_{33}O_4$: 553.2379; found: 553.2376.

5.12 Spectra of Few Synthesized Compounds

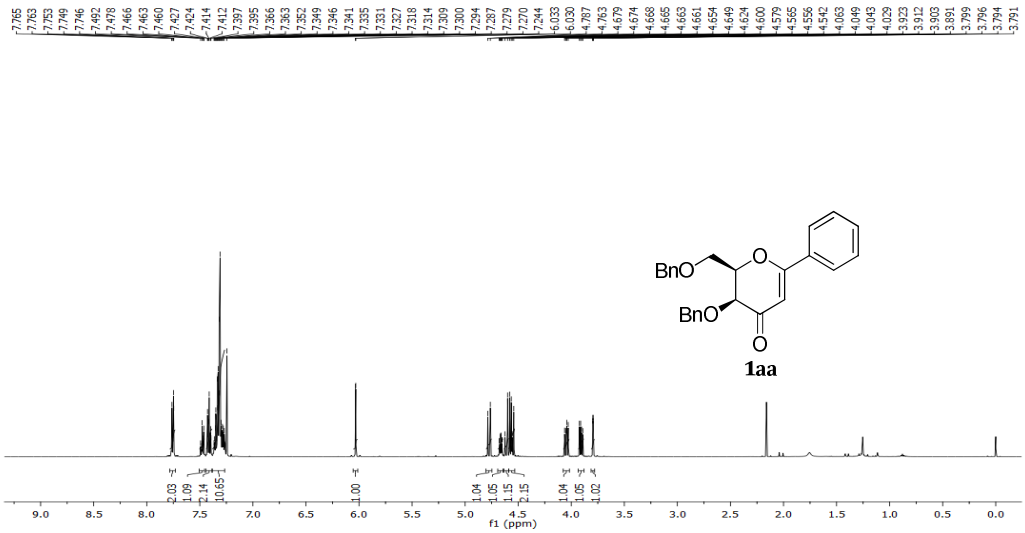


Figure- 5.1 ^{1}H NMR Spectra for **1aa** in **$CDCl_3$**

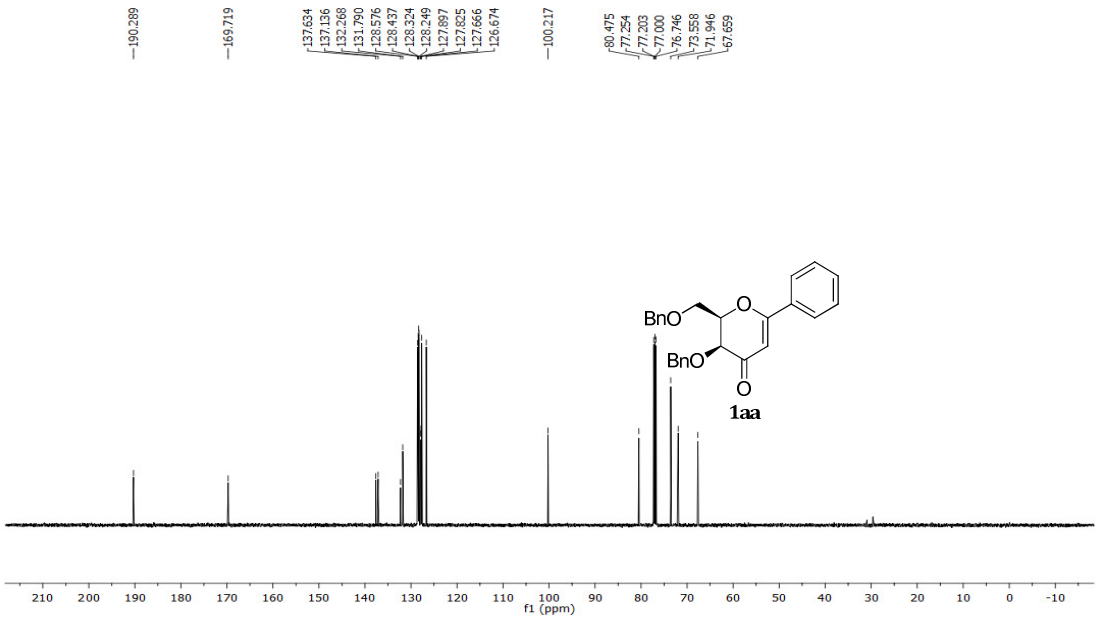


Figure- 5.2 ^{13}C NMR Spectra for **1aa** in **$CDCl_3$**

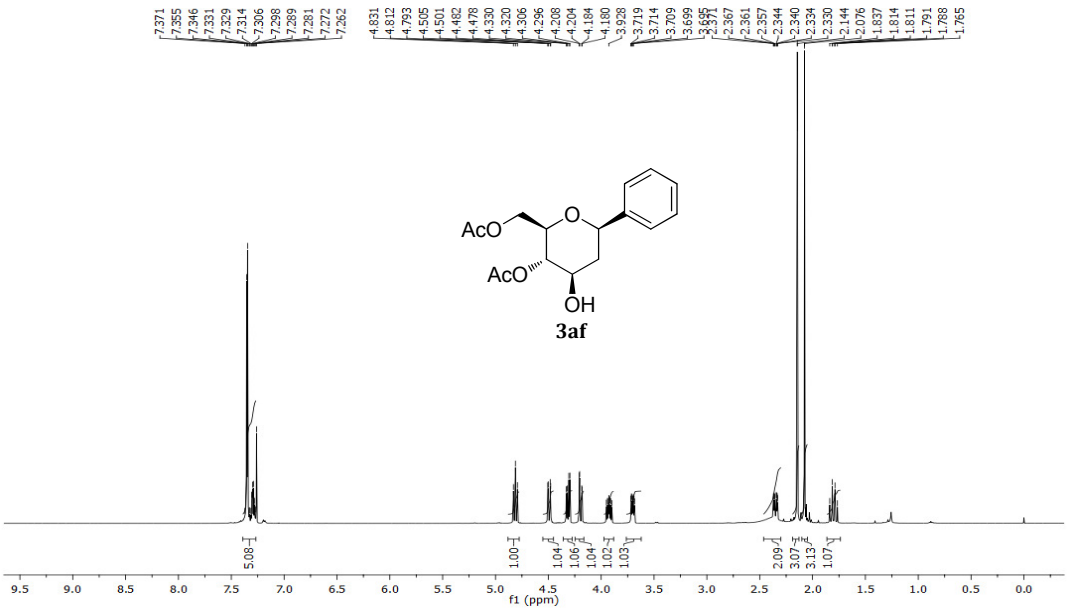


Figure- 5.3 ^{1}H NMR Spectra for **3af** in **$CDCl_3$**

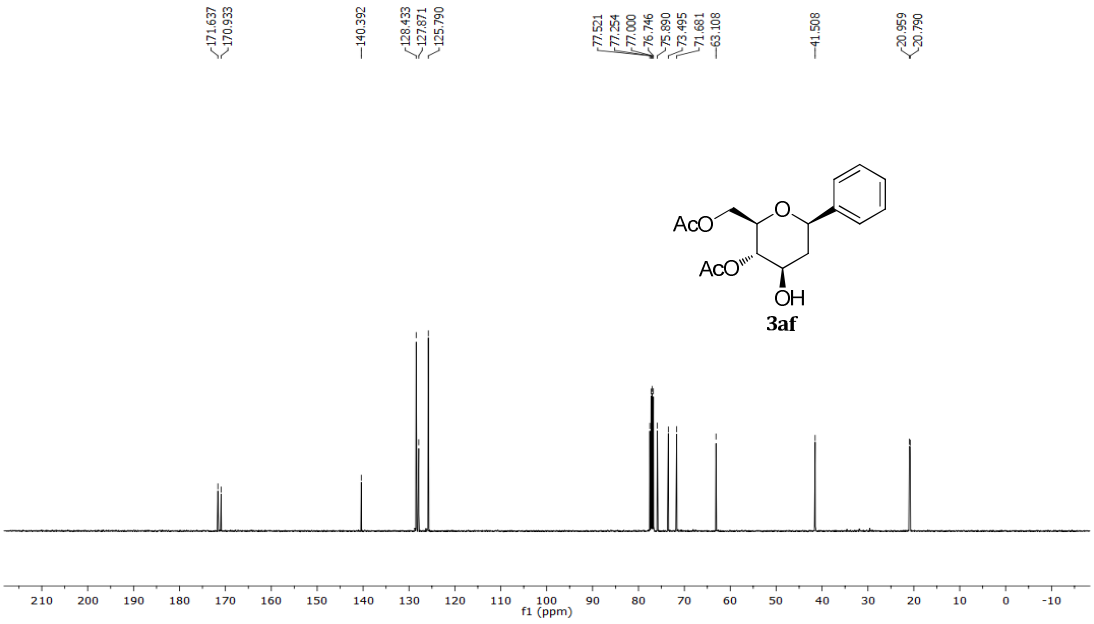


Figure- 5.4 ^{13}C NMR Spectra for **3af** in **$CDCl_3$**

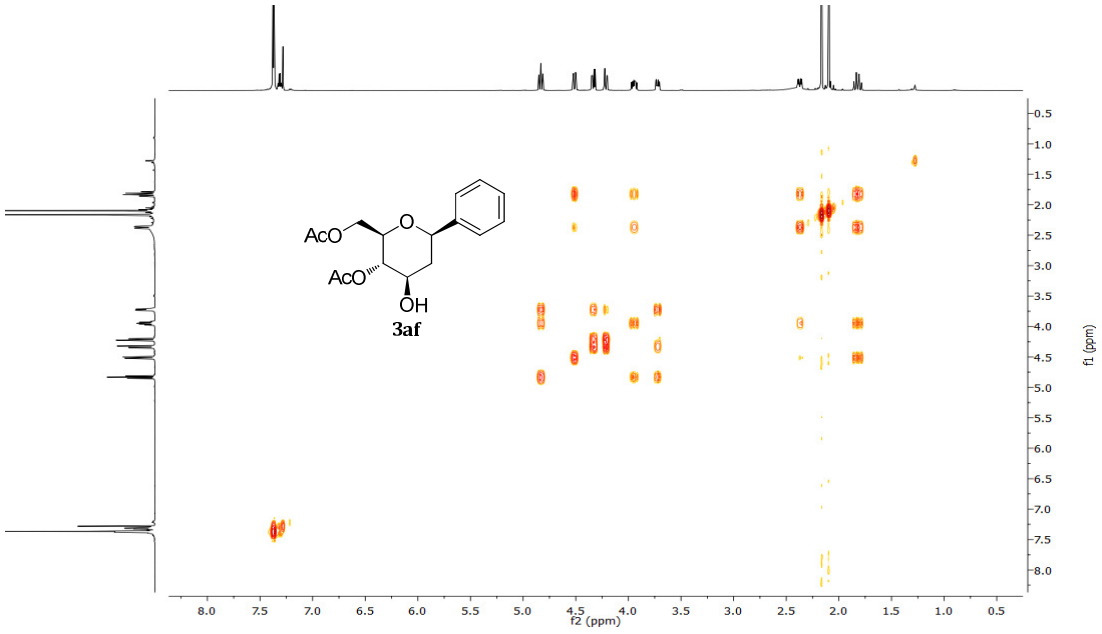


Figure- 5.5 COSY Spectra for **3af** in **$CDCl_3$**

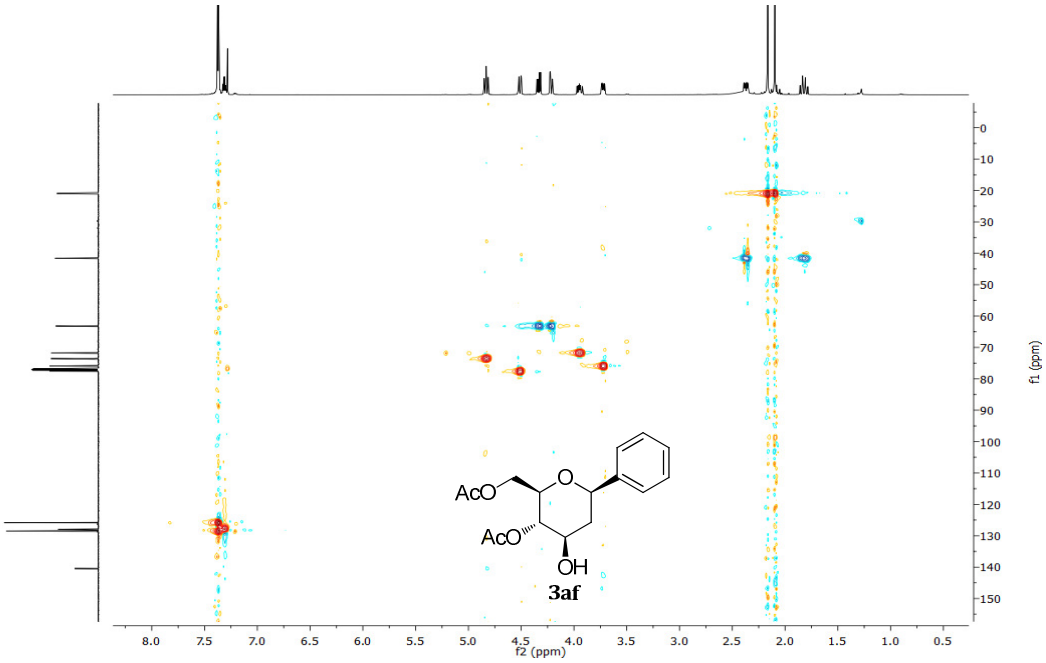


Figure- 5.6 HSQC Spectra for **3af** in **$CDCl_3$**

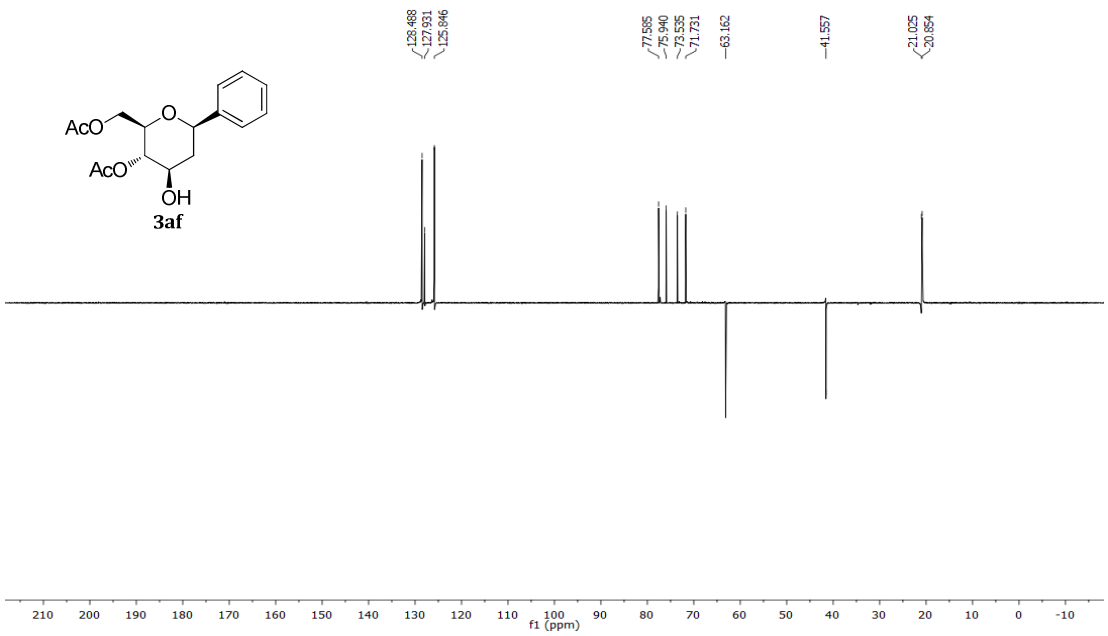


Figure- 5.7 DEPT-135 Spectra for **3af** in **$CDCl_3$**

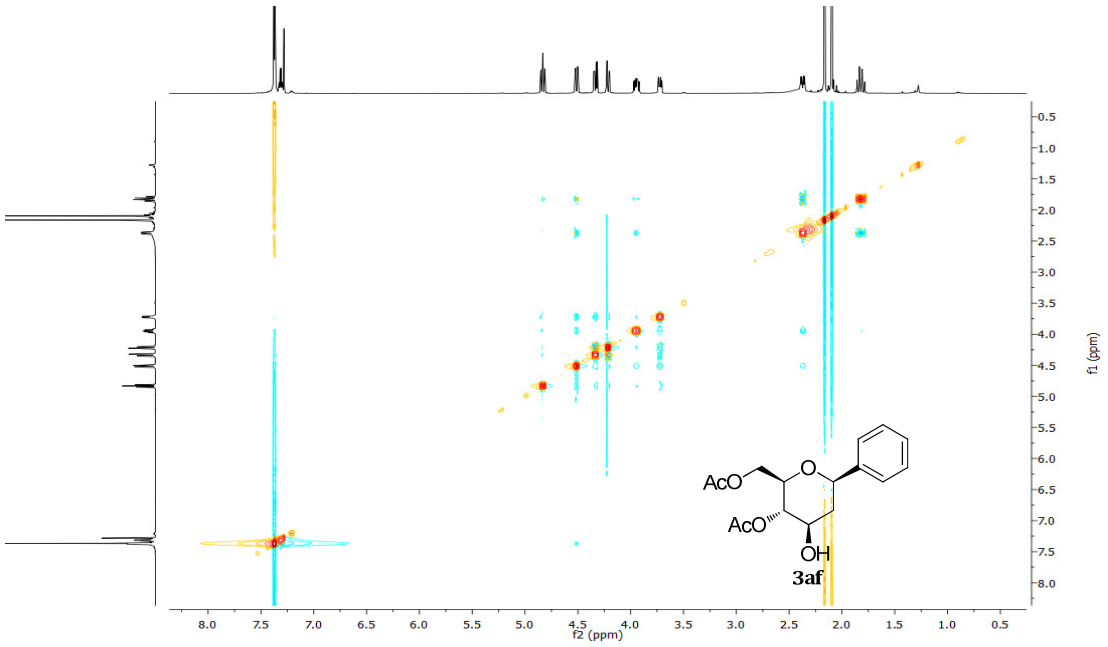


Figure- 5.8 NOESY Spectra for **3af** in **$CDCl_3$**

5.13 References

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