Palladium catalyzed stereocontrolled synthesis of C-aryl glycosides using arenediazonium salts at room temperature
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1. EXPERIMENTAL SECTION

General methods
All the reactions were carried out using oven dried glasswares. Solvents were evaporated with the help of rotary evaporator keeping the bath temperature below 50 °C. Thin layer chromatography was performed using pre-coated plates contained from E. Merck (TLC silica gel 60 F254). TLC plates were visualized by exposure to ultraviolet light (UV), then further analyzed by charring in stain solution (5% H2SO4 in MeOH). The column chromatography was performed on silica gel (100-200 mesh) using a mixture of ethyl acetate and hexane as an eluent. The NMR spectra were recorded on Bruker Avence 500 MHz NMR spectrometer. HRMS spectra were recorded on UHD Q-TOF using water’s Quattro Micro V 4.1. The TMS signals were taken as the reference 0.00 ppm for 1H NMR spectra and 77.0 ppm for 13C NMR spectra in CDCl3. Sometimes the residual solvent CDCl3 signal at 7.26 ppm was used an internal standard for 1H NMR spectra. Starting materials were purchased or prepared
using literature procedures as stated below. Solvents and chemicals were purchased from commercial sources and used without further purification. The palladium catalysts were purchased from Sigma Aldrich.

**Preparation of 3,4,6-tri-O-methyl-D-glucal (1aa)\(^1\):**

The commercially available 3,4,6-tri-O-acetyl-D-glucal \((1ae)\) (5 g, 18.3 mmol) was stirred in MeOH (150 mL) at 0°C to which NaOMe (108 mg, 2.0 mmol) was added. The mixture was stirred for 3 h and the solvent was evaporated to dryness. To the same flask, dry DMF (100 mL) was added and cooled to 0°C after which NaH (3.6 g, 60% in mineral oil, 91 mmol) was added portion wise. The resulting mixture was stirred for 30 min at the same temperature to which methyl iodide (5.2 mL, 80 mmol) was added slowly dropwise. The resulting mixture was stirred for overnight and quenched by saturated aqueous NH\(_4\)Cl (15 mL) and diluted with ethyl acetate (500 mL). The organic phase was washed with H\(_2\)O, brine, dried over anhydrous Na\(_2\)SO\(_4\) and evaporated under reduced pressure. The crude product was purified by column chromatography (SiO\(_2\), hexane:ethyl acetate = 4:1) to afford 1aa as a colorless oil in 80% yield (2.45 g). NMR spectra were identical with literature data.\(^1\) \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 6.34 (d, \(J = 5.5\) Hz, 1H), 4.78-4.77 (m, 1H), 3.91 (m, 1H), 3.83 (m, 1H), 3.64-3.57 (m, 2H), 3.49 (s, 3H), 3.41 (t, \(J = 7.0\) Hz, 1H), 3.36-3.35 (m, 6H). \(^1^3\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 144.4, 99.4, 76.5, 76.1, 75.7, 70.6, 59.1, 59.0, 55.6.

**Preparation of tri-O-benzyl-D-glucal (1ab)\(^1\):**

The commercially available 3,4,6-tri-O-acetyl-D-glucal (1 g, 3.6 mmol) was stirred in MeOH (30 mL) at 0°C to which NaOMe (22 mg, 0.2 mmol) was added. The mixture was stirred for 3 h and the solvent was evaporated to dryness. To the same flask, dry DMF (15 mL) was added and cooled to 0°C followed by NaH (720 mg, 60% in mineral oil, 18 mmol) was added portion wise. The mixture was stirred for 20 min at the same temperature to which benzyl bromide (1.8 mL, 16 mmol) was added slowly drop wise. The resulting mixture was stirred for overnight and quenched by saturated aqueous NH\(_4\)Cl (6 mL, 16 mmol) and diluted with ethyl acetate (250 mL). The organic phase was washed with H\(_2\)O, brine, dried over anhydrous Na\(_2\)SO\(_4\) and evaporated under reduced pressure. The crude product was purified by column chromatography (SiO\(_2\), hexane:ethyl acetate = 20:1) to afford 1ab as a white solid in 87% yield (1.3 g). NMR spectra were identical with literature data.\(^1\) \(^1\)H NMR (500 MHz, CDCl\(_3\))
$\delta$ 7.38-7.26 (m, 15H), 6.43 (d, $J = 5.5$ Hz, 1H), 4.89-4.88 (m, 1H), 4.84 (d, $J = 11.5$ Hz, 1H), 4.65 (d, $J = 12.0$ Hz, 2H), 4.59-4.55 (m, 3H), 4.22 (m, 1H), 4.07 (m, 1H), 3.87 (t, $J = 7.0$ Hz, 1H), 3.83-3.76 (m, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 144.6, 138.3, 138.1, 137.9, 128.3, 128.3, 127.8, 127.7, 127.7, 127.6, 99.9, 76.7, 75.7, 74.3, 73.7, 73.4, 70.4, 68.4.

**Preparation of 3,4,6-tri-O-ethyl-D-glucal (1ac):**

The compound 1ac is prepared using the literature procedure employed for the preparation of 1aa. To a solution of commercially available 3,4,6-tri-O-acetyl-D-glucal 1ag (500 mg, 1.8 mmol) in MeOH (15 mL), NaOMe (10.8 mg, 0.2 mmol) was added at 0°C. The mixture was stirred for 3 h and evaporated to dryness. To the same flask, dry DMF (10 mL) was added and cooled to 0°C followed by NaH (360 mg, 60% in mineral oil, 9 mmol) was added portion wise. The mixture was stirred for 20 min at the same temperature to which ethyl bromide (0.6 mL, 9 mmol) was added slowly drop wise. The resulting mixture was stirred for overnight and quenched by saturated aqueous NH$_4$Cl (3 mL) and diluted with ethyl acetate (180 mL). The organic phase was washed with H$_2$O, brine, dried over anhydrous Na$_2$SO$_4$ and evaporated under reduced pressure. The crude product was purified by column chromatography (SiO$_2$, hexane:ethyl acetate = 4:1) to afford 1ac as a colorless oil in 75% yield (310 mg). NMR spectra were identical with literature data. $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 6.34 (d, $J = 5.5$ Hz, 1H), 4.76-4.75 (m, 1H), 3.95-3.90 (m, 2H), 3.81 (t, $J = 7.5$, 1H), 3.68 (s, 2H), 3.65-3.61 (m, 2H), 3.57-3.48 (m, 4H), 1.20-1.17 (m, 9H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 144.3, 100.4, 76.8, 76.0, 74.7, 68.9, 67.1, 66.8, 63.9, 15.6, 15.5, 15.0.

**Preparation of 3,4,6-tri-O-methoxymethyl-D-glucal (1ad):**

To a solution of commercially available 3,4,6-tri-O-acetyl-D-glucal 1ag (500 mg, 1.8 mmol) in MeOH (15 mL), NaOMe (10.8 mg, 0.2 mmol) was added at 0°C. The mixture was stirred for 3 h and evaporated to dryness to obtain crude D-glucal. It was purified by a short silica chromatography using DCM-methanol. The pure D-glucal was dissolved in anhydrous DCM (20 mL) and cooled to 0°C after which diisopropylethyl amine (2.0 mL, 11 mmol) was added followed by the dropwise addition of chloromethyl methyl ether (0.8 mL). The reaction mixture was allowed to stir for 12 h at room temperature and again diisopropylethyl amine (2.0 mL, 11 mmol) was added followed by the
dropwise addition of chloromethyl methyl ether (0.8 mL). Further the reaction was allowed to stir for 12 h and diluted with DCM (100 ml). The organic layer was washed with solution of 1M HCl (50 mL), NaHCO$_3$ (50 mL), dried over anhydrous Na$_2$SO$_4$, and evaporated under reduced pressure. The crude product was purified by column chromatography (SiO$_2$, hexane:ethyl acetate = 20:1) to afford 1ad as a colorless oil in 60% yield (300 mg). NMR spectra were identical with literature data.$^3$ $^1$H NMR (500 MHz, CDCl$_3$) δ 6.37(d, $J = 5.5$ Hz, 1H), 4.84 (m, 1H), 4.78 (d, $J = 6.0$ Hz, 1H), 4.71 (d, $J = 6.5$ Hz, 1H), 4.67 (s, 2H), 4.63 (s, 2H), 4.13-4.08 (m, 2H), 3.83-3.77 (m, 3H), 3.37 (s, 3H), 3.34 (s, 6H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 144.1, 99.9, 96.6, 96.5, 95.3, 76.1, 72.5, 71.6, 65.7, 55.9, 55.4, 55.2.

Preparation of 3,4,6-tri-O-methyl-D-galactal (1af):$^1$

The commercially available 3,4,6-tri-O-acetyl-D-galactal (1ae) (2 g, 7.2 mmol) was stirred in MeOH (40 mL) at 0°C to which NaOMe (44 mg, 0.8 mmol) was added. The mixture was stirred for 3 h and the solvent was evaporated to dryness. To the same flask, dry DMF (25 mL) was added and cooled to 0°C to which NaH (1.5 g, 60% in mineral oil, 36 mmol) was added portion wise. The mixture was stirred for 30 min at the same temperature to which methyl iodide (2.6 mL, 40 mmol) was added slowly drop wise. The resulting mixture was stirred for overnight and quenched by saturated aqueous NH$_4$Cl (7 mL) and diluted with ethyl acetate (250 mL). The organic phase was washed with H$_2$O, brine, dried over anhydrous Na$_2$SO$_4$ and evaporated under reduced pressure. The crude product was purified by column chromatography (SiO$_2$, hexane:ethyl acetate = 4:1) to afford 1af as a colorless oil in 74% yield (1.05 g). NMR spectra were identical with literature data.$^1$ $^1$H NMR (500 MHz, CDCl$_3$) δ 6.28 (d, $J = 6.0$ Hz, 1H), 4.77-4.75 (m, 1H), 4.11 (m, 1H), 3.92 (s, 1H), 3.65-3.63 (m, 2H), 3.55-3.52 (m, 1H), 3.50 (s, 3H), 3.36 (s, 3H), 3.34 (s, 3H).

$^{13}$C NMR (125 MHz, CDCl$_3$) δ 143.8, 99.1, 74.9, 73.4, 72.1, 70.3, 59.6, 58.9, 56.4.

Preparation of 3,4,6-tri-O-benzyl-D-galactal (1ag):$^1$

The commercially available 3,4,6-tri-O-acetyl-D-galactal (1 g, 3.6 mmol) was stirred in MeOH (25 mL) at 0°C to which NaOMe (22 mg, 0.4 mmol) was added. The mixture was stirred for 3 h and the solvent was evaporated to dryness. To the same flask, dry DMF (10 mL) was added and cooled to 0°C followed by NaH (720 mg, 60% in mineral oil, 18 mmol) was added portion wise. The mixture was stirred for 20 min at the
same temperature to which benzyl bromide (1.8 mL, 16 mmol) was added slowly dropwise. The resulting mixture was stirred for overnight and quenched by saturated aqueous NH$_4$Cl (3 mL) and diluted with ethyl acetate (250 mL). The organic phase was washed with H$_2$O, brine, dried over anhydrous Na$_2$SO$_4$ and evaporated under reduced pressure. The crude product was purified by column chromatography (SiO$_2$, hexane:ethyl acetate = 9:1) to afford 1ag as a white solid in 73% yield (1.1 g). NMR spectra were identical with literature data.$^{1}$ $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.40-7.32 (m, 15H), 6.43 (d, $J = 6.0$ Hz, 1H), 4.95-4.92 (m, 2H), 4.71-4.65 (m, 3H), 4.56 (d, $J = 12.0$ Hz, 1H), 4.48 (d, $J = 12.0$ Hz, 1H), 4.24 (m, 2H), 4.00 (s, 1H), 3.85 (t, $J = 9.5$ Hz, 1H), 3.72 (dd, $J = 9.5$, 4.5 Hz, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 144.0, 138.3, 138.2, 137.8, 128.2, 128.0, 127.7, 127.5, 127.4, 127.3, 99.8, 75.5, 73.2, 73.1, 71.1, 70.7, 70.6, 68.3.

**Preparation of 3,4-di-O-benzyl-L-rhamnal (1ah):**$^4$

L-Rhamnose (5.0 g, 30.5 mmol) was suspended in acetic anhydride (22 mL) and cooled to 0 °C after which perchloric acid (0.25 mL) was added dropwise. The mixture was allowed to stir for 3 h at room temperature and cooled to 0 °C to which hydrobromic acid (44 mL, 33% in AcOH) was added dropwise. The resulting mixture was stirred for overnight at room temperature and concentrated. The crude glycopyranosyl bromide was dissolved in CH$_3$CN and then Zinc dust (15 g, 228 mmol) and ammonium chloride (12 g, 228 mmol) were added and stirred at 60°C for 2.5 h. Upon completion of the reaction, the reaction mixture is filtrated and the filtrate was concentrated and purified by column chromatography (SiO$_2$, hexane:ethyl acetate = 2:1) to afford 3,4-di-O-acetyl-L-rhamnose as colorless oil in 75% yield (4.9 g). NMR spectra were identical with literature.$^{18a}$ To a solution of 3,4-di-O-acetyl-L-rhamnal (1 g, 4.6 mmol) in THF (30 mL), NaOH (736 mg, 18.4 mmol.), TBAI (50 mg, 0.13 mmol) and benzyl bromide (2.2 mL, 18.4 mmol) were added successively and the reaction mixture was allowed to stir for 5 h at room temperature. After completion, the reaction mixture was diluted with water and extracted with DCM. The organic layer was washed with water, dried over anhydrous Na$_2$SO$_4$, and evaporated. The crude residue was purified by column chromatography (SiO$_2$, hexane:ethyl acetate = 2:1) to afford 3,4-di-O-benzyl-L-rhamnose 1ah as colourless oil in 50% yield (720 g).$^{4b}$ NMR spectra were identical with literature data.$^{15}$ $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.39-7.31 (m, 10H), 6.39 (d, $J = 5.5$ Hz, 1H), 4.92-4.88 (m, 2H), 4.73 (d, $J = 11.5$ Hz, 1H), 4.69 (d, $J = 11.5$ Hz, 1H), 4.60
(d, $J = 11.5$ Hz, 1H), 4.24 (d, $J = 6.0$ Hz, 1H), 3.99-3.97 (m, 1H), 3.51 (t, $J = 7.5$ Hz, 1H), 1.41 (d, $J = 6.5$ Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 144.7, 138.3, 138.2, 128.3, 127.9, 127.7, 127.5, 100.0, 79.4, 76.3, 74.0, 73.9, 70.4, 17.4.

Preparation of 3,4-di-O-benzyl-D-xylal (1ai):$^4$

D-xylose (5.0 g, 33.5 mmol) was suspended in acetic anhydride (25 mL), perchloric acid (0.3 mL) was added dropwise at 0 °C. The mixture was allowed to stir for 3 h at room temperature and cooled to 0 °C to which hydrobromic acid (48 mL, 33% in AcOH) was added dropwise. The resulting mixture was stirred for overnight at room temperature and concentrated. The crude glycopyranosyl bromide was dissolved in CH$_3$CN and then Zinc dust (15 g, 228 mmol) and ammonium chloride (12 g, 228 mmol) were added and stirred at 60°C for 2.5 h. Upon completion of the reaction, the reaction mixture is filtrated and the filtrate was concentrated and purified by column chromatography (SiO$_2$, hexane:ethyl acetate = 2:1) to afford 3,4-di-O-acetyl-D-xylal as colorless oil in 50% yield (3.3 g).$^{4a}$ To a solution of 3,4-di-O-acetyl- D-xylal (1 g, 5 mmol) in THF (30 mL), NaOH (736 mg, 18.4 mmol,), TBAI (50 mg, 0.13 mmol) and benzyl bromide (2.2 mL, 18.4 mmol) were added successively and the reaction mixture was allowed to stir for 3 h at room temperature. After completion, the reaction mixture was diluted with water and extracted with DCM. The organic layer was washed with water, dried over anhydrous Na$_2$SO$_4$, and evaporated. The crude residue was purified by column chromatography (SiO$_2$, hexane:ethyl acetate = 9:1) to afford 3,4-di-O-benzyl-D- xylal 1ai as colourless oil in 51% yield (743 mg).$^{18b}$ NMR spectra were identical with literature data.$^5$ $^1$H NMR (500 MHz, CDCl$_3$) δ 7.36-7.30 (m, 10H), 6.57 (d, $J = 5.5$ Hz, 1H), 4.96 (m, 1H), 4.68-4.65 (m, 2H), 4.62 (d, $J = 11.5$ Hz, 1H), 4.54 (d, $J = 11.5$ Hz, 1H), 4.13 (d, $J = 11.5$ Hz, 1H), 3.98 (d, $J = 12.0$ Hz, 1H), 3.86 (s, 1H), 3.69 (s, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 146.6, 138.3, 137.8, 128.4, 128.3, 127.8, 127.7, 127.6, 127.6, 98.9, 72.6, 71.2, 69.9, 69.0, 63.9.

Preparation of 3,5-di-O-benzyl-D-ribal (1aj):$^6$

D-Ribose (3.0 g, 20 mmol) was suspended in DCM (20 mL) to which acetic anhydride (11.23 g., 110 mmol) followed by pyridine (9.49 g., 120 mmol) was added at 0 °C. The resulting mixture was stirred for 12 hours at room temperature and quenched with water (20 mL). The aqueous layer was extracted with DCM (2X30 mL), washed with water, dried over saturated Na$_2$SO$_4$ and concentrated. The crude product was purified
by short silica chromatography using 20% ethyl acetate in hexane to obtain D-ribofuranose 1,2,3,5-tetraacetate. Further, the ribose tetra-acetate was dissolved in HBr solution (33 wt% in acetic acid, 10.36 mL, 60 mmol) and stirred for 5 hours at room temperature. The reaction mixture was diluted with acetonitrile (25 mL) to which sodium acetate (3.28 g, 40 mmol), ammonium chloride (3.21 g, 60 mmol), and zinc dust (3.93 g, 40 mmol) were added successively. The reaction is allowed to stir for 2 hours at room temperature, then quenched with water, extracted with ethyl acetate (3X25 mL). The organic layer was washed with water, dried over anhydrous Na$_2$SO$_4$ and concentrated. The crude residue was purified by column chromatography (SiO$_2$, hexane:ethyl acetate = 9:1) to obtain 3,5-di-O-acetyl-D-ribal in 27.5% yield (1.1 g). To a solution of 3,5-di-O-acetyl-D-ribal (1 g, 5 mmol) in THF (25 mL), NaOH (736 mg, 18.4 mmol), TBAI (50 mg, 0.13 mmol) and benzyl bromide (2.2 mL, 18.4 mmol) were added successively and the reaction mixture was allowed to stir for 3 h at room temperature. After completion, the reaction mixture was diluted with water and extracted with DCM. The organic layer was washed with water, dried over anhydrous Na$_2$SO$_4$, and evaporated. The crude residue was purified by column chromatography (SiO$_2$, hexane:ethyl acetate = 9:1) to afford 3,5-di-O-benzyl-D-ribal 1aj as colourless oil in 55% yield (801 mg). NMR spectra were identical with literature data.\textsuperscript{7} $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.40-7.29 (m, 10H), 6.41 (d, $J=5.0$ Hz, 1H), 4.88-4.87 (m, 1H), 4.72 (s, 2H), 4.69 (d, $J=12.0$ Hz, 1H), 4.61 (d, $J=12.0$ Hz, 1H), 4.09-4.39 (m, 3H), 3.76-3.74 (m, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 146.5, 138.7, 137.9, 128.4, 128.3, 128.1, 127.8, 127.7, 127.6, 127.5, 98.7, 73.1, 71.0, 70.7, 66.6, 63.2.

Preparation of aryldiazonium tetrafluoroborates:

Aryldiazonium tetrafluoroborates were prepared using literature procedure.\textsuperscript{8} To a stirred solution of aniline (10 mmol) in 48% aq. HBF$_4$ (4 ml), a solution of NaNO$_2$ (0.69 g in 5 ml of deionized water, 10 mmol) was added at 0 °C. The reaction mixture was stirred at 700 RPM for 30 min at 0°C. The resulting solid was filtered off, dissolved in 5 ml of acetone and precipitated by addition of 5 ml of diethyl ether. The resulting crystals

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were dried in high vacuum to obtain pure aryldiazonium tetrafluoroborates. All the compounds gave identical NMR spectra to those reported previously. 4-bromobenzenediazonium tetrafluoroborate \(2\text{aa}^8\) (pink solid, 72%); 2-chlorobenzenediazonium tetrafluoroborate \(2\text{ab}^8\) (white solid, 64%); benzenediazonium tetrafluoroborate \(2\text{ae}^8\) (white solid, 70%); 1-naphthyl diazonium tetrafluoroborate \(2\text{ad}^9\) (Purple solid, 55%); 4-methylbenzenediazonium tetrafluoroborate \(2\text{ae}^8\) (white solid, 80%); 4-methoxybenzenediazonium tetrafluoroborate \(2\text{af}^9\) (white solid, 75%); 4-nitrobenzenediazonium tetrafluoroborate \(2\text{ag}^8\) (yellow solid, 69%); 4-(trifluoromethyl)benzenediazonium tetrafluoroborate \(2\text{ah}^{10}\) (white solid, 70%); 4-(methoxycarbonyl)benzenediazonium tetrafluoroborate \(2\text{ai}^8\) (white solid, 30%); 4-acetylbenzenediazonium tetrafluoroborate \(2\text{aj}^9\) (white solid, 75%); 4-cyanobenzenediazonium tetrafluoroborate \(2\text{ak}^8\) (light yellow solid, 70%); 4-fluorobenzenediazonium tetrafluoroborate \(2\text{al}^8\) (white solid, 69%); 4-chlorobenzenediazonium tetrafluoroborate \(2\text{am}^{11}\) (white solid, 80%); 4-iodobenzenediazonium tetrafluoroborate \(2\text{an}^{12}\) (brown solid, 80%); 2-ethylbenzenediazonium tetrafluoroborate \(2\text{ao}^{13}\) (white solid, 64%); 2,4-dimethylbenzenediazonium tetrafluoroborate \(2\text{ap}^{14}\) (white solid, 60%); 2,5-dimethylbenzenediazonium tetrafluoroborate \(2\text{aq}^{15}\) (white solid, 70%); 3-fluorobenzenediazonium tetrafluoroborate \(2\text{ar}^{16}\) (white solid, 40%); 3-chlorobenzenediazonium tetrafluoroborate \(2\text{as}^8\) (pink solid, 59%); 3-bromobenzenediazonium tetrafluoroborate \(2\text{at}^{12}\) (orange solid, 65%); 3,5-dichlorobenzenediazonium tetrafluoroborate \(2\text{au}^{16}\) (white solid, %); 4-bromo-3-methylbenzenediazonium tetrafluoroborate \(2\text{av}^{14}\) (white solid, 30%); 3-acetylbenzenediazonium tetrafluoroborate \(2\text{aw}^{14}\) (white solid, 54%); 3-nitrobenzenediazonium tetrafluoroborate \(2\text{ax}^{16}\) (white solid, 50%); 3-(trifluoromethyl)benzenediazonium tetrafluoroborate \(2\text{ay}^7\) (Pink solid, 65%); 3,5-dimethylbenzenediazonium tetrafluoroborate \(2\text{az}^{16}\) (white solid, 20%); 2,4-dimethoxybenzenediazonium tetrafluoroborate \(2\text{ba}^{17}\) (purple solid, 60%).

**General procedure used in the optimization table:**

The glycal, 3,4,6-tri-O-methyl-D-glucal (95 mg, 0.5 mmol) was stirred in an appropriate solvent (4 mL) in a oven dried 25 ml round bottom flask. 4-Bromobenzenediazonium tetrafluoroborate (152 mg, 0.56 mmol) and palladium acetate (5.5 mg, 0.05 mmol) was successively added at room temperature under open air atmosphere. The mixture was stirred and monitored by TLC. After completion (or appropriate time mentioned in the table), the reaction mixture was diluted with ethyl acetate (150 mL) and washed with water (100 mL) and filtered, dried over anhydrous...
Na$_2$SO$_4$. The organic layer was concentrated and purified by silica column chromatography (100-200 mesh) on silica gel using 20 % ethyl acetate in hexane which furnished 3aa as white foam.

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

Glycal (0.25-0.5 mmol) was dissolved in acetonitrile (3 mL) to which water (1 mL) was added. To the above solution, aryldiazonium tetrafluoroborate (1.1 equiv.) and palladium acetate (5-10 mol%) was successively added at room temperature under open air atmosphere. of the above mixture were added simultaneously aryldiazoniumtetrafluoroborate and palladium acetate at room temperature in an open air atmosphere. The reaction mixture was stirred for appropriate time (2-8 h), diluted with ethyl acetate (150 mL) and washed with water (100 mL). The organic layer was filtered, dried over anhydrous Na$_2$SO$_4$, concentrated and purified by silica column chromatography (100-200 mesh) on silica gel using ethyl acetate in hexane.

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

The compound 3aa was prepared using the general procedure. The reaction was carried out between tri-O-methyl-D-glucal 1aa (95 mg, 0.5 mmol) and 4-bromobenzenediazonium tetrafluoroborate 2aa (152 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of Pd(OAc)$_2$ (5.5 mg, 0.025 mmol) at room temperature for 1.5 h. Column chromatography purification was performed using 20 % ethyl acetate in hexane which furnished 3aa as white foam (147 mg, 90%); TLC $R_f=0.35$ (35 % ethyl acetate in hexane); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.40 (d, $J=8.5$ Hz, 2H), 7.18 (d, $J=8.0$ Hz, 2H), 5.34-5.32 (m, 1H), 3.88 (d, $J=8.0$ Hz, 1H), 3.54-3.49 (m, 3H), 3.42 (s, 3H), 3.35 (s, 3H), 2.99-2.92 (m, 2H). $^1$C NMR (125 MHz, CDCl$_3$) $\delta$ 206.1, 137.4, 131.8, 129.1, 122.3, 81.6, 74.6, 74.6, 71.5, 59.4, 59.4, 43.6. HRMS (ESI-TOF) (m/z): [M + H]$^+$ calcd for C$_{14}$H$_{18}$BrO$_4$ 329.0388; found, 329.0359.
(2R,3R,6S)-6-(2-Chlorophenyl)-3-methoxy-2-(methoxymethyl)dihydro-2H-pyran-4(3H)-one [3ab]

The compound 3ab was prepared using the general procedure. The reaction was carried out between tri-O-methyl-D-glucal 1aa (95 mg, 0.5 mmol) and 2-chlorobenzenediazonium tetrafluoroborate 2ab (127 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of Pd(OAc)$_2$ (5.6 mg, 0.025 mmol) at room temperature for 1.5 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished 3ab as colourless semi solid (126 mg, 89%); TLC R$_f$ = 0.40 (35 % ethyl acetate in hexane); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.41-7.39 (m, 1H), 7.31-7.29 (m, 1H), 7.20-7.16 (m, 2H), 5.64 (t, $J$ = 5.5 Hz, 1H), 3.87 (d, $J$ = 7.0 Hz, 1H), 3.77-3.74 (m, 1H), 3.57-3.51 (m, 2H), 3.43 (s, 3H), 3.32 (s, 3H), 2.91 (dd, $J$ = 15.0, 5.5 Hz, 1H), 2.78 (dd, $J$ = 15.0, 6.0 Hz, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 206.4, 136.9, 133.3, 129.9, 129.4, 128.2, 126.8, 81.4, 75.5, 71.9, 71.9, 59.3, 59.0, 44.3. HRMS (ESI-TOF) (m/z): [M + H]$^+$ calcd for C$_{14}$H$_{18}$ClO$_4$ 285.0894; found, 285.0868.

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

The compound 3ac was prepared using the general procedure. The reaction was carried out between tri-O-methyl-D-glucal 1aa (97 mg, 0.5 mmol) and benzenediazonium tetrafluoroborate 2ac (108 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of Pd(OAc)$_2$ (5.8 mg, 0.025 mmol) at room temperature for 2 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished 3ac as white foam (107 mg, 85%); TLC R$_f$ = 0.5 (35 % ethyl acetate in hexane); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.31-7.25 (m, 4H), 7.22-7.19 (m, 1H), 5.39-5.38 (m, 1H), 3.89 (d, $J$ = 8.0 Hz, 1H), 3.54-3.49 (m, 3H), 3.43 (d, $J$ = 2.0 Hz, 3H), 3.35 (d, $J$ = 2.0 Hz, 3H), 3.05-2.93 (m, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 206.4, 138.3, 128.6, 128.0, 127.3, 81.6, 75.1, 74.2, 71.4, 59.4, 59.3, 43.6. HRMS (ESI-TOF) (m/z): [M + H]$^+$ calcd for C$_{14}$H$_{19}$O$_4$ 251.1283; found, 251.1265.
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(2R,3R,6S)-3-Methoxy-2-(methoxymethyl)-6-(naphthalen-1-yl)dihydro-2H-pyran-4(3H)-one [3ad]

The compound 3ad was prepared using the general procedure. The reaction was carried out between tri-O-methyl-D-glucal 1aa (95 mg, 0.5 mmol) and 1-naphthylidiazonium tetrafluoroborate 2ad (135 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of Pd(OAc)$_2$ (5.7 mg, 0.025 mmol) at room temperature for 2 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished 3ad as white foam (131 mg, 87%); TLC $R_f$ = 0.48 (35 % ethyl acetate in hexane); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.31 (d, $J$ = 8.0 Hz, 1H), 7.77-7.71 (m, 2H), 7.49 – 7.27 (m, 4H), 6.03-6.02 (m, 1H), 4.01 (d, $J$ = 9.0 Hz, 1H), 3.46 (s, 3H), 3.40-3.38 (m, 1H), 3.32-3.30 (m, 5H), 3.18-3.11 (m, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 207.6, 133.9, 131.5, 129.5, 128.5, 126.3, 126.2, 125.9, 124.8, 124.7, 81.5, 73.8, 72.8, 71.1, 59.7, 59.3, 44.1. HRMS (ESI-TOF) (m/z): [M + H]$^+$ calcd for C$_{18}$H$_{21}$O$_4$ 301.1440; found, 301.1437.

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

The compound 3ae was prepared using the general procedure. The reaction was carried out between tri-O-methyl-D-glucal 1aa (95 mg, 0.5 mmol) and 4-methylbenzenediazonium tetrafluoroborate 2ae (115 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of Pd(OAc)$_2$ (5.5 mg, 0.025 mmol) at room temperature for 2 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished 3ae as white foam (116 mg, 87%); TLC $R_f$ = 0.4 (15 % ethyl acetate in chloroform); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.18 (d, $J$ = 7.8 Hz, 2H), 7.06 (d, $J$ = 8.0 Hz, 2H), 5.36 (d, $J$ = 6.0 Hz, 1H), 3.88 (d, $J$ = 9.5 Hz, 1H), 3.52-3.46 (m, 3H), 3.42 (s, 3H), 3.34 (s, 3H), 3.02-2.93 (m, 2H), 2.24 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 206.7, 137.9, 135.2, 129.2, 127.4, 81.6, 75.0, 73.9, 71.4, 59.5, 59.3, 43.7, 20.9. HRMS (ESI-TOF) (m/z): [M + H]$^+$ calcd for C$_{15}$H$_{21}$O$_4$ 265.1440; found, 265.1417.

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

The compound 3af was prepared using the general procedure. The reaction was carried out between tri-O-methyl-D-glucal 1aa (95 mg, 0.5 mmol) and 4-methoxybenzenediazonium tetrafluoroborate 2af (124 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of Pd(OAc)$_2$ (5.5 mg, 0.025 mmol) at room temperature for 2 h. Column chromatography purification was performed using 20 % ethyl acetate in
hexane which furnished 3af as white foam (118 mg, 84%); TLC Rf = 0.28 (35 % ethyl acetate in hexane); ^1^H NMR (500 MHz, CDCl3) δ 7.21 (d, J = 8.0 Hz, 2H), 6.79-6.77 (m, 2H), 5.35 (dd, J = 6.5, 2.5 Hz, 1H), 3.89-3.87 (m, 1H), 3.70 (s, 3H), 3.53-3.47 (m, 3H), 3.43 (s, 3H), 3.34 (s, 3H), 3.01-2.93 (m, 2H). ^1^C NMR (125 MHz, CDCl3) δ 206.8, 159.3, 130.3, 128.8, 113.9, 81.7, 74.8, 73.8, 71.4, 59.5, 59.3, 55.1, 43.7. HRMS (ESI-TOF) (m/z): [M + H]^+ calcld for C_{15}H_{21}O_5 281.1389; found, 281.1370

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

The compound 3ag was prepared using the general procedure. The reaction was carried out between tri-O-methyl-D-glucal 1aa (95 mg, 0.5 mmol) and 4-nitrobenzenediazonium tetrafluoroborate 2ag (132 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of Pd(OAc)$_2$ (5.5 mg, 0.025 mmol) at room temperature for 4h. Column chromatography purification was performed using 25 % ethyl acetate in hexane which furnished 3ag as white foam (98 mg, 69%); TLC Rf = 0.25 (35 % ethyl acetate in hexane); ^1^H NMR (500 MHz, CDCl3) δ 8.13 (d, J = 8.0 Hz, 2H), 7.51 (d, J = 8.0 Hz, 2H), 5.44 (t, J = 4.5 Hz, 1H), 3.88 (d, J = 7.5 Hz, 1H), 3.61-3.57 (m, 3H), 3.41 (s, 3H), 3.35 (s, 3H), 3.02-2.94 (m, 2H). ^1^C NMR (125 MHz, CDCl3) δ 205.0, 147.5, 145.9, 127.9, 123.8, 81.4, 75.7, 74.4, 71.7, 59.3, 59.2, 43.7. HRMS (ESI-TOF) (m/z): [M + H]^+ calcld for C_{14}H_{18}NO_6 296.1134; found, 296.1108.

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

The compound 3ah was prepared using the general procedure. The reaction was carried out between tri-O-methyl-D-glucal 1aa (95 mg, 0.5 mmol) and 4-(trifluoromethyl)benzenediazonium tetrafluoroborate 2ah (145 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of Pd(OAc)$_2$ (5.5 mg, 0.025 mmol) at room temperature for 2 h. Column chromatography purification was performed using 20 % ethyl acetate in hexane which furnished 3ah as viscous oil (127 mg, 79%); TLC Rf = 0.30 (35 % ethyl acetate in hexane); ^1^H NMR (500 MHz, CDCl3) δ 7.53 (d, J = 7.5 Hz, 2H), 7.44 (d, J = 7.5 Hz, 2H), 5.41 (m, 1H), 3.88 (d, J = 7.0 Hz, 1H), 3.54 (m, 3H), 3.41 (s, 3H), 3.35 (s, 3H), 3.03-2.94 (m, 2H). ^1^C NMR (125 MHz, CDCl3) δ 205.6, 142.5, 130.4 (q, J$_C$-$F$ = 32.5 Hz), 127.5, 126.7 (q, J$_C$-$F$ = 3.8 Hz), 123.8 (q, J$_C$-$F$ = 272 Hz), 81.5, 75.2, 74.6, 71.6, 59.3, 59.3, 43.7. HRMS (ESI-TOF) (m/z): [M + H]^+ calcld for C_{19}H_{18}F_3O_4 319.1157; found, 319.1139.

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

The compound 3ai was prepared using the general procedure. The reaction was carried out between tri-O-methyl-D-glucal 1aa (95 mg, 0.5 mmol) and 4-(methoxycarbonyl)benzenediazonium tetrafluoroborate 2ai (140 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of Pd(OAc)₂ (5.5 mg, 0.025 mmol) at room temperature for 2 h. Column chromatography purification was performed using 20 % ethyl acetate in hexane which furnished 3ai as white foam (118 mg, 76%); TLC Rf = 0.24 (35 % ethyl acetate in hexane); ¹H NMR (500 MHz, CDCl₃) δ 7.94 (d, J = 8.0 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 5.41 (dd, J = 6.0, 3.5 Hz, 1H), 3.88 (d, J = 7.5 Hz, 1H), 3.84 (s, 3H), 3.53 (m, 3H), 3.41 (s, 3H), 3.35 (s, 3H), 3.04-2.94 (m, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 205.9, 166.6, 143.5, 130.0, 129.9, 127.2, 81.6, 75.0, 74.9, 71.6, 59.4, 52.2, 43.7. HRMS (ESI-TOF) (m/z): [M + H]⁺ calcd for C₁₆H₂₁O₆ 309.1338; found, 309.1339.

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

The compound 3aj was prepared using the general procedure. The reaction was carried out between tri-O-methyl-D-glucal 1aa (95 mg, 0.5 mmol) and 4-acetylbenzenediazonium tetrafluoroborate 2aj (130 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of Pd(OAc)₂ (5.5 mg, 0.025 mmol) at room temperature for 3 h. Column chromatography purification was performed using 20 % ethyl acetate in hexane which furnished 3aj as yellowish foam (115 mg, 78%); TLC Rf = 0.40 (15 % ethyl acetate in chloroform); ¹H NMR (500 MHz, CDCl₃) δ 7.86 (d, J = 8.0 Hz, 2H), 7.41 (d, J = 8.0 Hz, 2H), 5.41 (m, 1H), 3.88 (d, J = 8.0 Hz, 1H), 3.84 (s, 3H), 3.41 (s, 3H), 3.35 (s, 3H), 2.51 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ 205.7, 197.4, 143.6, 136.6, 128.6, 127.3, 81.5, 75.0, 74.7, 71.5, 59.3, 59.3, 43.6, 26.5. HRMS (ESI-TOF) (m/z): [M + H]⁺ calcd for C₁₆H₂₁O₅ 293.1389; found, 293.1393.

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

The compound 3ak was prepared using the general procedure. The reaction was carried out between tri-O-methyl-D-glucal 1aa (95 mg, 0.5 mmol) and 4-cyanobenzenediazonium tetrafluoroborate 2ak (121 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of Pd(OAc)₂
(5.5 mg, 0.025 mmol) at room temperature for 2.5 h. Column chromatography purification was performed using 20 % ethyl acetate in hexane which furnished 3ak as white foam (111 mg, 80%); TLC R_f = 0.26 (35 % ethyl acetate in hexane); ^1H NMR (500 MHz, CDCl_3) δ 7.58 (d, J = 8.0 Hz, 2H), 7.44 (d, J = 8.0 Hz, 2H), 5.40 (t, J = 5.0 Hz, 1H), 3.87 (d, J = 7.0 Hz, 1H), 3.59-3.55 (m, 3H), 3.41 (s, 3H), 3.35 (s, 3H), 3.00-2.93 (m, 2H).^13C NMR (125 MHz, CDCl_3) δ 205.3, 143.9, 132.5, 127.8, 118.3, 112.0, 81.4, 75.5, 74.6, 71.7, 59.4, 59.3, 43.6. HRMS (ESI-TOF) (m/z): [M + H]^+ calcd for C_{15}H_{18}NO_4 276.1236; found, 276.1229.

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

The compound 3al was prepared using the general procedure. The reaction was carried out between tri-O-methyl-D-glucal 1aa (95 mg, 0.5 mmol) and 4-fluorobenzenediazonium tetrafluoroborate 2al (116 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of Pd(OAc)_2 (5.5 mg, 0.025 mmol) at room temperature for 2 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished 3al as white foam (114 mg, 84%); TLC R_f = 0.42 (35 % ethyl acetate in hexane); ^1H NMR (500 MHz, CDCl_3) δ 7.32 (t, J=7.0 Hz, 2H), 6.99 (t, J = 8.0 Hz, 2H), 5.40 (m, 1H), 3.93 (d, J = 8.5 Hz, 1H), 3.58-3.50 (m, 3H), 3.47 (s, 3H), 3.39 (s, 3H), 3.07-2.98 (m, 2H). ^13C NMR (125 MHz, CDCl_3) δ 206.3, 162.4 (d, J_{C-F} = 247.5 Hz), 134.2(d, J_{C-F} = 3.3 Hz), 129.3 (d, J_{C-F} = 8.2 Hz), 116.0 (d, J_{C-F} = 21.5 Hz), 81.6, 74.6, 74.4, 71.5, 59.5, 59.4, 43.8. HRMS (ESI-TOF) (m/z): [M + Na]^+ calcd for C_{14}H_{17}FO_4Na 291.1009; found, 291.0985.

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

The compound 3am was prepared using the general procedure. The reaction was carried out between tri-O-methyl-D-glucal 1aa (95 mg, 0.5 mmol) and 4-chlorobenzenediazonium tetrafluoroborate 2am (126 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of Pd(OAc)_2 (5.5 mg, 0.025 mmol) at room temperature for 2 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished 3am as white foam (123 mg, 85%); TLC R_f = 0.42 (35 % ethyl acetate in hexane); ^1H NMR (500 MHz, CDCl_3) δ 7.33 (s, 4H), 5.44-5.43 (m, 1H), 3.96 (d, J = 8.0 Hz, 1H), 3.62-3.55 (m, 3H), 3.51 (s, 3H), 3.43 (s, 3H), 3.08-3.01 (m, 2H). ^13C NMR (125 MHz, CDCl_3) δ
(2R,3R,6S)-6-(4-Iodophenyl)-3-methoxy-2-(methoxymethyl)dihydro-2H-pyran-4(3H)-one [3an]

The compound 3an was prepared using the general procedure. The reaction was carried out between tri-O-methyl-D-glucal 1aa (95 mg, 0.5 mmol) and 4-iodobenzenediazonium tetrafluoroborate 2an (177 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of Pd(OAc)$_2$ (5.5 mg, 0.025 mmol) at room temperature for 2h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished 3an as brownish foam (170 mg, 90%); TLC R$_f$ = 0.63 (15 % ethyl acetate in chloroform); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.60 (d, $J$ = 7.5 Hz, 2H), 7.04 (d, $J$ = 8.0 Hz, 2H), 5.31 (m, 1H), 3.86 (d, $J$ = 8.5 Hz, 1H), 3.56-3.51 (m, 3H), 3.41 (s, 3H), 3.34 (s, 3H), 2.97-2.90 (m, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 205.9, 138.1, 137.7, 129.2, 94.0, 81.5, 74.7, 74.6, 71.5, 59.4, 59.3, 43.5. HRMS (ESI-TOF) (m/z): [M + H]$^+$ calcd for C$_{14}$H$_{18}$ClO$_4$ 285.0894; found, 285.0870.

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

The compound 3ao was prepared using the general procedure. The reaction was carried out between tri-O-methyl-D-glucal 1aa (95 mg, 0.5 mmol) and 2-ethylbenzenediazonium tetrafluoroborate 2ao (123 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of Pd(OAc)$_2$ (5.5 mg, 0.025 mmol) at room temperature for 2 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished 3ao as semi solid (106 mg, 76%); TLC R$_f$ = 0.47 (35 % ethyl acetate in hexane); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.20-7.17 (m, 3H), 7.07-7.04 (m, 1H), 5.59 (t, $J$ = 4.5 Hz, 1H), 3.93 (d, $J$ = 9.0 Hz, 1H), 3.50-3.41 (m, 6H), 3.32 (s, 3H), 2.94 (d, $J$ = 4.5 Hz, 2H), 2.80-2.67 (m, 2H), 1.16 (t, $J$ = 7.5 Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 207.7, 143.6, 135.8, 129.2, 128.7, 127.6, 125.7, 81.6, 73.9, 72.3, 71.6, 59.6, 59.4, 44.4, 25.1, 15.41. HRMS (ESI-TOF) (m/z): [M + H]$^+$ calcd for C$_{16}$H$_{23}$O$_4$ 279.1596; found, 279.1575.
(2R,3R,6S)-6-(2,4-Dimethylphenyl)-3-methoxy-2-(methoxymethyl)dihydro-2H-pyran-4(3H)-one [3ap]

The compound 3ap was prepared using the general procedure. The reaction was carried out between tri-O-methyl-D-glucal 1aa (95 mg, 0.5 mmol) and 2,4-dimethylbenzenediazonium tetrafluoroborate 2ap (123 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of Pd(OAc)$_2$ (5.5 mg, 0.025 mmol) at room temperature for 2 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished 3ap as white foam (100 mg, 71%); TLC $R_f = 0.48$ (35 % ethyl acetate in hexane); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.04 (d, $J = 8.0$ Hz, 1H), 6.94 (s, 1H), 6.85 (d, $J = 7.5$ Hz, 1H), 5.48 (t, $J = 4.5$ Hz, 1H), 3.91 (d, $J = 9.0$ Hz, 1H), 3.49-3.37 (m, 6H), 3.33 (s, 3H), 2.99-2.93 (m, 2H), 2.32 (s, 3H), 2.20 (s, 3H).$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 207.7, 138.2, 137.7, 133.3, 131.9, 127.6, 126.2, 81.6, 73.4, 72.8, 71.4, 59.6, 59.3, 44.0, 20.9, 19.4. HRMS (ESI-TOF) (m/z): [M + H]$^+$ calcd for C$_{16}$H$_{23}$O$_4$ 279.1596; found, 279.1575.

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

The compound 3aq was prepared using the general procedure. The reaction was carried out between tri-O-methyl-D-glucal 1aa (95 mg, 0.5 mmol) and 2,5-dimethylbenzenediazonium tetrafluoroborate 2aq (122 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of Pd(OAc)$_2$ (5.5 mg, 0.025 mmol) at room temperature for 4 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished 3aq as semi solid (113 mg, 81%); TLC $R_f = 0.65$ (15 % ethyl acetate in chloroform); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.00-6.99 (m, 2H), 6.94-6.93 (m, 1H), 5.48-5.47 (m, 1H), 3.91 (d, $J = 9.0$ Hz, 1H), 3.51-3.42 (m, 6H), 3.33 (s, 3H), 2.99-2.90 (m, 2H), 2.30 (s, 3H), 2.20 (s, 3H).$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 207.4, 136.3, 135.2, 134.4, 130.9, 129.0, 128.1, 81.8, 73.8, 72.9, 71.6, 59.6, 59.3, 44.0, 21.0, 19.1. HRMS (ESI-TOF) (m/z): [M + H]$^+$ calcd for C$_{16}$H$_{23}$O$_4$ 279.1596; found, 279.1596.

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

The compound 3ar was prepared using the general procedure. The reaction was carried out between tri-O-methyl-D-glucal 1aa (95 mg, 0.5 mmol) and 3-fluorobenzenediazonium tetrafluoroborate 2ar (117 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of Pd(OAc)$_2$
(5.5 mg, 0.025 mmol) at room temperature for 3 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished 3ar as brownish semi solid (112 mg, 83%); TLC R_f = 0.6 (15 % ethyl acetate in chloroform); ^1H NMR (500 MHz, CDCl_3)  δ 7.25-7.21 (m, 1H), 7.06 (t, J = 8.5 Hz, 2H), 6.90 (t, J = 8.5 Hz, 1H), 5.35 (m, 1H), 3.88 (d, J = 7.5 Hz, 1H), 3.55-3.54 (m, 3H), 3.42 (s, 3H), 3.35 (s, 3H), 3.00-2.92 (m, 2H). ^13C NMR (125 MHz, CDCl_3) δ 205.8, 162.9 (d, J_C-F = 247.0 Hz), 141.11 (d, J_C-F = 6.7 Hz), 130.2 (d, J_C-F = 8.2 Hz), 122.7 (d, J_C-F = 2.8 Hz), 115.1 (d, J_C-F = 22.1 Hz), 114.4 (d, J_C-F = 22.1 Hz) 81.5, 74.8, 74.6, 71.5, 59.3, 59.3, 43.6. HRMS (ESI-TOF) (m/z): [M + H]^+ calcd for C_{14}H_{18}O_4 269.1189; found, 269.1199.

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

The compound 3as was prepared using the general procedure. The reaction was carried out between tri-O-methyl-D-glucal 1aa (95 mg, 0.5 mmol) and 3-chlorobenzenediazonium tetrafluoroborate 2as (125 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of Pd(OAc)_2 (5.5 mg, 0.025 mmol) at room temperature for 3 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished 3as as viscous oil (122 mg, 85%); TLC R_f = 0.46 (35 % ethyl acetate in hexane); ^1H NMR (500 MHz, CDCl_3)  δ 7.20-7.16 (m, 3H), 5.33 (dd, J = 6.0, 3.5 Hz, 1H), 3.88 (d, J = 8.0 Hz, 1H), 3.58-3.54 (m, 3H), 3.42 (s, 3H), 3.35 (s, 3H), 2.99-2.90 (m, 2H). ^13C NMR (125 MHz, CDCl_3) δ 205.7, 140.7, 134.8, 129.9, 128.3, 127.5, 125.2, 81.5, 74.9, 74.6, 71.6, 59.3, 43.7. HRMS (ESI-TOF) (m/z): [M + H]^+ calcd for C_{14}H_{18}ClO_4 285.0894; found, 285.0876.

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

The compound 3at was prepared using the general procedure. The reaction was carried out between tri-O-methyl-D-glucal 1aa (95 mg, 0.5 mmol) and 3-bromobenzenediazonium tetrafluoroborate 2at (152 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of Pd(OAc)_2 (5.5 mg, 0.025 mmol) at room temperature for 2.5 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished 3at as brownish oil (138 mg, 83%); TLC R_f = 0.64 (15 % ethyl acetate in chloroform); ^1H NMR (500 MHz, CDCl_3) δ 7.48 (s, 1H), 7.34 (d, J = 8.0 Hz, 1H), 7.21 (m, J = 7.5 Hz, 1H), 7.13 (t, J = 7.5 Hz, 1H), 5.32 (m, 1H), 3.87 (d, J = 8.0 Hz, 1H), 3.58-3.54 (m, 3H), 3.41
(s, 3H), 3.35 (s, 3H), 2.98-2.89 (m, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 205.6, 140.9, 131.2, 130.3, 130.1, 125.6, 122.9, 81.5, 74.9, 74.5, 71.5, 59.3, 43.6. HRMS (ESI-TOF) (m/z): [M + H]$^+$ calcd for C$_{14}$H$_{18}$BrO$_4$ 329.0388; found, 329.0393.

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

The compound 3au was prepared using the general procedure. The reaction was carried out between tri-O-methyl-D-glucal 1aa (95 mg, 0.5 mmol) and 3,5-dichlorobenzenediazonium tetrafluoroborate 2au (145 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of Pd(OAc)$_2$ (5.5 mg, 0.025 mmol) at room temperature for 4 h. Column chromatography purification was performed using 15% ethyl acetate in hexane which furnished 3au as colourless oil (105 mg, 65%); TLC $R_f$ = 0.64 (15% ethyl acetate in chloroform); $^1$H NMR (500 MHz, CDCl$_3$) δ 7.20 (m, 3H), 5.28 (m, 1H), 3.86 (d, $J = 7.5$ Hz, 1H), 3.64-3.63 (m, 1H), 3.56 (s, 2H), 3.41 (s, 3H), 3.35 (s, 3H), 2.93-2.86 (m, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 205.0, 142.3, 135.4, 128.3, 125.5, 81.4, 75.5, 74.1, 71.7, 59.4, 59.2, 43.7. HRMS (ESI-TOF) (m/z): [M + H]$^+$ calcd for C$_{14}$H$_{17}$ClO$_2$ 319.0504; found, 319.0506.

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

The compound 3av was prepared using the general procedure. The reaction was carried out between tri-O-methyl-D-glucal 1aa (95 mg, 0.5 mmol) and 4-bromo-3-methylbenzenediazonium tetrafluoroborate 2av (160 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of Pd(OAc)$_2$ (5.5 mg, 0.025 mmol) at room temperature for 2 h. Column chromatography purification was performed using 15% ethyl acetate in hexane which furnished 3av as brownish oil (145 mg, 84%); TLC $R_f$ = 0.3 (15% ethyl acetate in chloroform); $^1$H NMR (500 MHz, CDCl$_3$) δ 7.40 (d, $J = 8.0$ Hz, 1H), 7.16 (s, 1H), 6.97 (d, $J = 8.0$ Hz, 1H), 5.29 (m, 1H), 3.86 (d, $J = 7.5$ Hz, 1H), 3.54-3.49 (m, 3H), 3.41 (s, 3H), 3.34 (s, 3H), 2.97-2.89 (m, 2H), 2.29 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 206.0, 138.1, 137.7, 132.4, 129.6, 126.2, 124.6, 81.5, 74.5, 74.5, 71.5, 59.3, 59.2, 43.6, 22.8. HRMS (ESI-TOF) (m/z): [M + H]$^+$ calcd for C$_{15}$H$_{20}$BrO$_4$ 343.0545; found, 343.0547.
(2R,3R,6S)-6-(3-Acetylphenyl)-3-methoxy-2-(methoxymethyl)dihydro-2H-pyran-4(3H)-one [3aw]

The compound 3aw was prepared using the general procedure. The reaction was carried out between tri-O-methyl-D-glucal 1aa (95 mg, 0.5 mmol) and 3-acetylbenzenediazonium tetrafluoroborate 2aw (130 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of Pd(OAc)$_2$ (5.5 mg, 0.025 mmol) at room temperature for 2 h. Column chromatography purification was performed using 20 % ethyl acetate in hexane which furnished 3aw as colourless oil (131 mg, 89%); TLC $R_f$ = 0.3 (15 % ethyl acetate in chloroform); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.91 (s, 1H), 7.81 (d, $J$ = 7.0 Hz, 1H), 7.51 (d, $J$ = 7.5 Hz, 1H), 7.38 (t, $J$ = 7.5 Hz, 1H), 5.42 (m, 1H), 3.88 (d, $J$ = 8.0 Hz, 1H), 3.57-3.54 (m, 3H), 3.41 (s, 3H), 3.35 (s, 3H), 3.06-2.95 (m, 2H), 2.53 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 205.7, 197.7, 139.2, 137.5, 131.5, 129.0, 127.9, 127.2, 81.6, 75.0, 74.8, 71.6, 59.3, 59.3, 43.8, 26.6. HRMS (ESI-TOF) (m/z): [M + H]$^+$ calcld for C$_{16}$H$_{21}$O$_5$ 293.1389; found, 293.1391.

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

The compound 3ax was prepared using the general procedure. The reaction was carried out between tri-O-methyl-D-glucal 1aa (95 mg, 0.5 mmol) and 3-nitrobenzenediazonium tetrafluoroborate 2ax (132 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of Pd(OAc)$_2$ (5.5 mg, 0.025 mmol) at room temperature for 4 h. Column chromatography purification was performed using 25 % ethyl acetate in hexane which furnished 3ax as yellowish oil (103 mg, 69%); TLC $R_f$ = 0.30 (35 % ethyl acetate in hexane); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.22 (s, 1H), 8.09 (d, $J$ = 8.5 Hz, 1H), 7.65 (d, $J$ = 7.5 Hz, 1H), 7.48 (t, $J$ = 8.0 Hz, 1H), 5.45 (t, $J$ = 5.0 Hz, 1H), 3.89 (d, $J$ = 7.5 Hz, 1H), 3.65-3.55 (m, 3H), 3.41 (s, 3H), 3.36 (s, 3H), 3.04-2.95 (m, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 205.7, 197.7, 139.2, 137.5, 131.5, 129.0, 127.9, 127.2, 81.6, 75.0, 74.8, 71.6, 59.3, 59.3, 43.8, 26.6. HRMS (ESI-TOF) (m/z): [M + H]$^+$ calcld for C$_{14}$H$_{18}$NO$_6$ 296.1134; found, 296.1068.

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

The compound 3ay was prepared using the general procedure. The reaction was carried out between tri-O-methyl-D-glucal 1aa (95 mg, 0.5 mmol) and 3-(trifluoromethyl)benzenediazonium tetrafluoroborate 2ay (144 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of
Pd(OAc)$_2$ (5.5 mg, 0.025 mmol) at room temperature for 2 h. Column chromatography purification was performed using 15% ethyl acetate in hexane which furnished 3ay as colourless oil (135 mg, 84%); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.60 (s, 1H), 7.49-7.47 (m, 2H), 7.40 (t, $J_{CF}$ = 7.5 Hz, 1H), 5.41-5.39 (m, 1H), 3.87 (d, $J_{CF}$ = 8.0 Hz, 1H), 3.62-3.59 (m, 1H), 3.56-3.55 (m, 2H), 3.41 (s, 3H), 3.35 (s, 3H), 3.03-2.92 (m, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 205.4, 139.8, 131.3 ($J_{CF}$ = 32.4 Hz), 129.1, 124.9 ($J_{CF}$ = 3.7 Hz), 124.0 ($J_{CF}$ = 3.7 Hz), 123.8 ($J_{CF}$ = 272 Hz), 81.5, 75.3, 74.7, 71.7, 59.3, 59.2, 43.8. HRMS (ESI-TOF) (m/z): [M + H]$^+$ calcd for C$_{15}$H$_{18}$F$_3$O$_4$ 319.1157; found, 319.1160.

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

The compound 3az was prepared using the general procedure. The reaction was carried out between tri-O-methyl-D-glucal 1aa (95 mg, 0.5 mmol) and 3,5-dimethylbenzenediazonium tetrafluoroborate 2az (122 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of Pd(OAc)$_2$ (5.5 mg, 0.025 mmol) at room temperature for 3.5 h. Column chromatography purification was performed using 15% ethyl acetate in hexane which furnished 3az as colourless solid (86 mg, 61%); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 6.90-6.83 (m, 3H), 5.30-5.29 (m, 1H), 3.87 (d, $J_{CF}$ = 8.5 Hz, 1H), 3.57-3.49 (m, 3H), 3.43 (s, 3H), 3.34 (s, 3H), 3.01-2.98 (m, 1H), 2.90-2.88 (m, 1H), 2.21 (s, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 206.5, 138.4, 138.1, 129.7, 125.1, 81.7, 75.1, 74.2, 71.5, 59.4, 59.2, 43.7, 21.2. HRMS (ESI-TOF) (m/z): [M + H]$^+$ calcd for C$_{16}$H$_{23}$O$_4$ 279.1596; found, 279.1595.

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

The compound 3ba was prepared using the general procedure. The reaction was carried out between tri-O-benzyl-D-glucal 1ab (100 mg, 0.24 mmol) and benzenediazonium tetrafluoroborate 2ac (52 mg, 0.27 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of Pd(OAc)$_2$ (5.5 mg, 0.025 mmol) at room temperature for 5 h. Column chromatography purification was performed using 10% ethyl acetate in hexane which furnished 3ba as white foam (77 mg, 80%); TLC $R_f = 0.28$ (20% ethyl acetate in hexane); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.30 (d, $J_{CF}$ = 7.5 Hz, 2H), 7.26-7.19 (m, 13H), 5.40-5.39 (m, 1H), 4.76 (d, $J = 11.5$ Hz, 1H), 4.60 (d, $J = 12.0$ Hz, 1H), 4.39 (d, $J = 12.0$ Hz, 1H), 4.34 (d, $J = 11.0$ Hz,
1H), 4.17 (d, J = 8.5 Hz, 1H), 3.65-3.56 (m, 3H), 3.05-2.93 (m, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 206.4, 138.5, 137.7, 137.3, 128.6, 128.3, 128.1, 128.1, 127.8, 127.7, 127.3, 79.5, 75.1, 74.5, 73.5, 73.3, 69.0, 43.8. HRMS (ESI-TOF) (m/z): [M + H]$^+$ calcd for C$_{28}$H$_{30}$O$_4$ 403.1909; found, 403.1916.

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

The compound 3bb was prepared using the general procedure. The reaction was carried out between tri-O-benzyl-D-glucal 1ab (100 mg, 0.24 mmol) and 4-methylbenzenediazonium tetrafluoroborate 2ae (55 mg, 0.27 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of Pd(OAc)$_2$ (5.5 mg, 0.025 mmol) at room temperature for 4 h. Column chromatography purification was performed using 10 % ethyl acetate in hexane which furnished 3bb as white foam (89 mg, 89%); TLC $R_f$ = 0.65 (30 % ethyl acetate in hexane); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.25-7.18 (m, 12H), 7.06 (d, J = 7.5 Hz, 2H), 5.39-5.37 (m, 1H), 4.77 (d, J = 11.0 Hz, 1H), 4.52 (d, J = 12.0 Hz, 1H), 4.40 (d, J = 12.0 Hz, 1H), 4.34 (d, J = 11.0 Hz, 1H), 4.16 (d, J = 8.5 Hz, 1H), 3.63-3.57 (m, 3H), 3.04-2.94 (m, 2H), 2.23 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 206.6, 137.9, 137.8, 137.3, 135.4, 129.3, 128.3, 128.33, 128.1, 127.8, 127.7, 127.4, 79.6, 75.0, 74.3, 73.5, 73.4, 69.0, 43.9, 21.0. HRMS (ESI-TOF) (m/z): [M + H]$^+$ calcd for C$_{27}$H$_{29}$O$_4$ 417.2066; found, 417.2070.

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

The compound 3bc was prepared using the general procedure. The reaction was carried out between tri-O-benzyl-D-glucal 1ab (100 mg, 0.24 mmol) and 4-methoxybenzenediazonium tetrafluoroborate 2af (60 mg, 0.27 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of Pd(OAc)$_2$ (5.5 mg, 0.025 mmol) at room temperature for 4 h. Column chromatography purification was performed using 12 % ethyl acetate in hexane which furnished 3bc as white foam (88 mg, 85%); TLC $R_f$ = 0.25 (15 % ethyl acetate in hexane); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.26-7.18 (m, 12H), 6.77 (d, J = 8.5 Hz, 2H), 5.37 (dd, J = 6.5, 2.5 Hz, 1H), 4.77 (d, J = 11 Hz, 1H), 4.51 (d, J = 12 Hz, 1H), 4.39 (d, J = 12 Hz, 1H), 4.34 (d, J = 11 Hz, 1H), 4.16 (d, J = 9 Hz, 1H), 3.69 (s, 3H), 3.62-3.54 (m, 3H), 3.03-2.94 (m Hz, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 206.7, 159.3,
137.8, 137.3, 130.5, 128.8, 128.3, 128.1, 127.8, 127.7, 113.9, 79.6, 74.8, 74.0, 73.5, 73.4, 68.9, 55.2, 43.9. HRMS (ESI-TOF) (m/z): [M + H]^+ calcd for C_{14}H_{15}BrO_4 433.2015; found, 433.2000.

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

The compound **3bd** was prepared using the general procedure. The reaction was carried out between tri-O-benzyl-D-glucal **1ab** (100 mg, 0.24 mmol) and 4-fluorobenzenediazonium tetrafluoroborate **2al** (56 mg, 0.27 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of Pd(OAc)$_2$ (5.5 mg, 0.025 mmol) at room temperature for 4 h. Column chromatography purification was performed using 8 % ethyl acetate in hexane which furnished **3bd** as white foam (85 mg, 84%); TLC $R_f = 0.62$ (30 % ethyl acetate in hexane); $^1$H NMR (500 MHz, CDCl$_3$) δ 7.29-7.17 (m, 12H), 6.93 (t, $J = 8.0$ Hz, 2H), 5.37 (m, 1H), 4.75 (d, $J = 11.5$ Hz, 1H), 4.50 (d, $J = 12.0$ Hz, 1H), 4.40 (d, $J = 12.0$ Hz, 1H), 4.34 (d, $J = 11.0$ Hz, 1H), 4.15 (d, $J = 8.0$ Hz, 1H), 3.62-3.55 (m, 3H), 3.01-2.93 (m, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 206.2, 162.4 (d, $J_{C-F} = 247.5$ Hz), 137.7, 137.2, 134.2 (d, $J_{C-F} = 3.3$ Hz), 129.3 (d, $J_{C-F} = 8.2$ Hz), 128.3, 128.3, 128.1, 127.9, 127.8, 127.7, 115.5 (d, $J_{C-F} = 21.5$ Hz), 79.4, 74.6, 74.6, 73.5, 73.3, 69.0, 44.0. HRMS (ESI-TOF) (m/z): [M + H]^+ calcd for C$_{26}$H$_{26}$FO$_4$ 421.1815; found, 421.1813.

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

The compound **3be** was prepared using the general procedure. The reaction was carried out between tri-O-benzyl-D-glucal **1ab** (100 mg, 0.24 mmol) and 4-chlorobenzenediazonium tetrafluoroborate **2am** (60 mg, 0.27 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of Pd(OAc)$_2$ (5.5 mg, 0.025 mmol) at room temperature for 4 h. Column chromatography purification was performed using 8 % ethyl acetate in hexane which furnished **3be** as white foam (89 mg, 85%); TLC $R_f = 0.4$ (15 % ethyl acetate in hexane); $^1$H NMR (500 MHz, CDCl$_3$) δ 7.25-7.17 (m, 14H), 6.93 (t, $J = 8.0$ Hz, 2H), 5.37 (m, 1H), 4.75 (d, $J = 11.0$ Hz, 1H), 4.50 (d, $J = 12.0$ Hz, 1H), 4.40 (d, $J = 12.0$ Hz, 1H), 4.33 (d, $J = 11.0$ Hz, 1H), 4.15 (d, $J = 8.5$ Hz, 1H), 3.62-3.56 (m, 3H), 3.00-2.92 (m, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 206.0, 137.7, 137.2, 137.1, 134.1, 128.8, 128.7, 128.3, 128.1, 127.9, 127.8, 127.7, 79.4, 74.8, 74.5, 73.5, 73.3, 69.0, 43.9. HRMS (ESI-TOF) (m/z): [M + H]^+ calcd for C$_{26}$H$_{26}$ClO$_4$ 437.1520; found, 437.1521.
(2R,3R,6S)-3-(Benzyloxy)-2-(benzyloxymethyl)-6-(4-bromophenyl)dihydro-2H-pyran-4(3H)-one [3bf]

The compound 3bf was prepared using the general procedure. The reaction was carried out between tri-O-benzyl-D-glucal 1ab (100 mg, 0.24 mmol) and 4-bromobenzenediazonium tetrafluoroborate 2aa (72 mg, 0.27 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of Pd(OAc)$_2$ (5.5 mg, 0.025 mmol) at room temperature for 4 h. Column chromatography purification was performed using 10 % ethyl acetate in hexane which furnished 3bf as white foam (94 mg, 82%); TLC $R_f = 0.29$ (15 % ethyl acetate in hexane); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.38 (d, $J = 7.5$ Hz, 2H), 7.31-7.13 (m, 12H), 5.34 (m, 1H), 4.74 (d, $J = 11.5$ Hz, 1H), 4.50 (d, $J = 12.5$ Hz, 1H), 4.39 (d, $J = 12.5$ Hz, 1H), 4.33 (d, $J = 11.0$ Hz, 1H), 4.14 (d, $J = 8.5$ Hz, 1H), 3.63-3.56 (m, 3H), 2.99-2.91 (m, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 205.9, 137.7, 137.6, 137.1, 131.8, 129.0, 128.3, 128.3, 128.1, 127.9, 127.8, 127.7, 122.2, 79.3, 74.9, 74.6, 73.5, 73.3, 69.0, 43.8. HRMS (ESI-TOF) (m/z): [M + H]$^+$ calcd for C$_{26}$H$_{26}$BrO$_4$ 481.1014; found, 481.1020.

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

The compound 3bg was prepared using the general procedure. The reaction was carried out between tri-O-benzyl-D-glucal 1ab (100 mg, 0.24 mmol) and 4-cyanobenzenediazonium tetrafluoroborate 2ak (58 mg, 0.27 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of Pd(OAc)$_2$ (5.5 mg, 0.025 mmol) at room temperature for 4 h. Column chromatography purification was performed using 10 % ethyl acetate in hexane which furnished 3bg as white foam (72 mg, 70%); TLC $R_f = 0.25$ (30 % ethyl acetate in hexane); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.55 (d, $J = 7.5$ Hz, 2H), 7.42 (d, $J = 7.5$ Hz, 2H), 7.25-7.18 (m, 10H), 5.40 (m, 1H), 4.72 (d, $J = 11.0$ Hz, 1H), 4.49 (d, $J = 12.5$ Hz, 1H), 4.40 (d, $J = 12.5$ Hz, 1H), 4.33 (d, $J = 11.0$ Hz, 1H), 4.13 (d, $J = 8.0$ Hz, 1H), 3.67-3.66 (m, 1H), 3.61 (s, 2H), 3.00-2.92 (m, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 205.2, 144.1, 137.5, 136.9, 132.4, 128.4, 128.3, 128.1, 128.0, 127.8, 127.7, 118.3, 112.0, 79.1, 75.7, 74.5, 73.5, 73.2, 69.1, 43.8. HRMS (ESI-TOF) (m/z): [M + H]$^+$ calcd for C$_{27}$H$_{26}$NO$_4$ 428.1862; found, 428.1858.
Methyl 4-((2S,5R,6R)-5-(benzyloxy)-6-(benzyloxymethyl)-4-oxotetrahydro-2H-pyran-2-yl)benzoate [3bh]

The compound 3bh was prepared using the general procedure. The reaction was carried out between tri-O-benzyl-D-glucal 1ab (100 mg, 0.24 mmol) and 4-(methoxycarbonyl)benzenediazonium tetrafluoroborate 2ai (67 mg, 0.27 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of Pd(OAc)₂ (5.5 mg, 0.025 mmol) at room temperature for 4 h. Column chromatography purification was performed using 10 % ethyl acetate in hexane which furnished 3bh as white foam (83 mg, 75%); TLC Rf = 0.24 (15 % ethyl acetate in hexane); ¹H NMR (500 MHz, CDCl₃) δ 7.92 (d, J = 7.5 Hz, 2H), 7.38 (d, J = 7.5 Hz, 2H), 7.26-7.17 (m, 10H), 5.41 (m, 1H), 4.74 (d, J = 11.5 Hz, 1H), 4.50 (d, J = 12.5 Hz, 1H), 4.40 (d, J = 12.0 Hz, 1H), 4.34 (d, J = 11.5 Hz, 1H), 4.15 (d, J = 8.0 Hz, 1H), 3.82 (s, 3H), 3.67-3.60 (m, 3H), 3.04-2.93 (m, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 205.7, 166.5, 143.7, 137.6, 137.1, 129.9, 129.8, 128.3, 128.3, 128.1, 127.9, 127.7, 127.7, 127.1, 79.3, 75.2, 74.8, 73.5, 73.2, 69.1, 52.1, 43.9. HRMS (ESI-TOF) (m/z): [M + Na]⁺ calcd for C₂₈H₂₈O₆Na 483.1784; found, 483.1778.

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

The compound 3bi was prepared using the general procedure. The reaction was carried out between tri-O-ethyl-D-glucal 1ac (115 mg, 0.5 mmol) and 4-methylbenzenediazonium tetrafluoroborate 2ae (113 mg, 0.55 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of Pd(OAc)₂ (5.5 mg, 0.025 mmol) at room temperature for 2 h. Column chromatography purification was performed using 10 % ethyl acetate in hexane which furnished 3bi as white foam (131 mg, 90%); TLC Rf = 0.64 (30 % ethyl acetate in hexane); ¹H NMR (500 MHz, CDCl₃) δ 7.18 (d, J = 8.0 Hz, 2H), 7.05 (d, J = 7.5 Hz, 2H), 5.36 (d, J = 6.0 Hz, 1H), 4.03 (d, J = 8.5 Hz, 1H), 3.78-3.75 (m, 1H), 3.56-3.50 (m, 4H), 3.44-3.38 (m, 2H), 3.01-2.99 (m, 2H), 2.23 (s, 3H), 1.17-1.11 (m, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 206.9, 137.7, 135.4, 129.2, 127.3, 80.2, 74.9, 74.2, 69.1, 67.2, 66.9, 43.6, 20.9, 15.0, 14.9. HRMS (ESI-TOF) (m/z): [M + H]⁺ calcd for C₁₇H₂₅O₄ 293.1753; found, 293.1748.
The compound 3bj was prepared using the general procedure. The reaction was carried out between tri-O-(methoxymethyl ether)-D-glucal 1ad (100 mg, 0.35 mmol) and 4-methylbenzenediazonium tetrafluoroborate 2ae (82 mg, 0.4 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of Pd(OAc)$_2$ (8 mg, 0.035 mmol) at room temperature for 7 h. Column chromatography purification was performed using 30 % ethyl acetate in hexane which furnished 3bj as colorless solid (75 mg, 60%); TLC $R_f = 0.45$ (15 % ethyl acetate in chloroform); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.20-7.18 (m, 2H), 7.08 (d, $J = 8.0$ Hz, 2H), 5.38 (d, $J = 6.0$ Hz, 1H), 4.71 (d, $J = 6.5$ Hz, 2H), 4.64-4.61 (m, 3H), 4.29 (d, $J = 8.0$ Hz, 1H), 3.70-3.65 (m, 2H), 3.61 (d, $J = 9.0$ Hz, 1H), 3.35 (s, 3H), 3.31 (s, 3H), 3.04 (d, $J = 9.5$ Hz, 21H), 2.98-2.94 (m, 2H), 2.25 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 205.8, 138.0, 135.3, 129.3, 127.3, 96.9, 96.7, 76.7, 75.0, 74.2, 66.7, 56.3, 55.5, 43.9, 21.0. HRMS (ESI-TOF) (m/z): [M + H]$^+$ calcd for C$_{17}$H$_{25}$O$_6$ 325.1651; found, 325.1661.

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

The compound 3bl was prepared using the general procedure. The reaction was carried out between tri-O-methyl-D-galactal 1ae (95 mg, 0.5 mmol) and benzenediazonium tetrafluoroborate 2ae (107 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of Pd(OAc)$_2$ (11 mg, 0.05 mmol) at room temperature for 4 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished 3bl as colourless semi solid (76 mg, 60%); TLC $R_f = 0.50$ (35 % ethyl acetate in hexane); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.32-7.19 (m, 5H), 5.25 (dd, $J = 9.5$, 3.5 Hz, 1H), 4.43-4.40 (m, 1H), 3.92 (dd, $J = 6.5$, 1.0 Hz, 1H), 3.69-3.62 (m, 2H), 3.47 (s, 3H), 3.25 (s, 3H), 2.76-2.72
(m, 1H), 2.61-2.56 (m, 1H).\(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 203.9, 140.4, 128.5, 127.9, 125.8, 82.1, 75.8, 74.8, 71.0, 59.3, 59.0, 47.9. HRMS (ESI-TOF) (m/z): [M + H]\(^+\) calcd for C\(_{14}\)H\(_{19}\)O\(_2\) 251.1283; found, 251.1265

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

The compound 3bm was prepared using the general procedure. The reaction was carried out between tri-O-methyl-D-galactal 1ae (95 mg, 0.5 mmol) and 1-naphthyldiazonium tetrafluoroborate 2ad (135 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of Pd(OAc)\(_2\) (11 mg, 0.05 mmol) at room temperature for 2.5 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished 3bm as light purple solid (88 mg, 58%); TLC \(R_f\) = 0.5 (35 % ethyl acetate in hexane); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.04 (d, \(J = 8.0\) Hz, 1H), 7.80.-7.73 (m, 2H), 7.56 (d, \(J = 6.5\) Hz, 1H), 7.48-7.38 (m, 3H), 6.02 (d, \(J = 9.0\) Hz, 1H), 4.42 (s, 1H), 3.97 (d, \(J = 5.5\) Hz, 1H), 3.77-3.66 (m, 2H), 3.50 (s, 3H), 3.28 (s, 3H), 2.98-2.95 (m, 1H), 2.78-2.74 (m, 1H).\(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 204.4, 135.8, 133.8, 130.4, 128.8, 128.7, 126.3, 125.7, 125.2, 123.4, 123.2, 82.2, 75.7, 71.9, 70.9, 59.3, 59.1, 46.7. HRMS (ESI-TOF) (m/z): [M + H]\(^+\) calcd for C\(_{18}\)H\(_{21}\)O\(_4\) 301.1440; found, 301.1390.

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

The compound 3bn was prepared using the general procedure. The reaction was carried out between tri-O-methyl-D-galactal 1ae (95 mg, 0.5 mmol) and 4-methylbenzenediazonium tetrafluoroborate 2ae (114 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of Pd(OAc)\(_2\) (11 mg, 0.05 mmol) at room temperature for 3 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished 3bn as colourless semi solid (86 mg, 65%); TLC \(R_f\) = 0.52 (35 % ethyl acetate in hexane); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.20-7.18 (m, 2H), 7.10 (d, \(J = 8.0\) Hz, 2H), 5.21 (dd, \(J = 9.5, 3.5\) Hz, 1H), 4.38 (m, 1H), 3.89 (d, \(J = 5.5\) Hz, 3H), 3.67-3.63 (m, 2H), 3.47 (s, 3H), 3.26 (s, 3H), 2.73 (dd, \(J = 14.0, 3.5\) Hz, 1H), 2.61-2.57 (m, 1H), 2.26 (s, 3H).\(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 204.1, 137.7, 137.5, 129.2, 125.9, 82.2, 75.7, 74.8, 71.1, 59.3, 59.0, 47.75, 21.0. HRMS (ESI-TOF) (m/z): [M + H]\(^+\) calcd for C\(_{15}\)H\(_{21}\)O\(_4\) 265.1440; found, 265.1436.
(2R,3S,6S)-6-(4-Fluorophenyl)-3-methoxy-2-(methoxymethyl)dihydro-2H-pyran-4(3H)-one [3bo]

The compound 3bo was prepared using the general procedure. The reaction was carried out between tri-O-methyl-D-galactal 1ae (95 mg, 0.5 mmol) and 4-fluorobenzenediazonium tetrafluoroborate 2al (117 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of Pd(OAc)$_2$ (11 mg, 0.05 mmol) at room temperature for 3h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished 3bo as colourless semi solid (79 mg, 59%); TLC $R_f$= 0.65 (35 % ethyl acetate in hexane); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.29-7.27 (m, 2H), 6.97 (t, $J$ = 8.5 Hz, 2H), 5.23 (dd, $J$ = 10.0, 3.5 Hz, 1H), 4.41-4.38 (m, 1H), 3.91 (d, $J$ = 5.5 Hz, 1H), 3.69-3.61 (m, 2H), 3.47 (s, 3H), 3.25 (s, 3H), 2.72 (dd, $J$ = 14.0, 3.5 Hz, 1H), 2.57-2.52 (m, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 203.6, 162.4 (d, $J_{C\text{-}F}$ = 247.5 Hz), 136.4 (d, $J_{C\text{-}F}$ = 3.3 Hz), 127.6 (d, $J_{C\text{-}F}$ = 8.2 Hz), 115.4 (d, $J_{C\text{-}F}$ = 21.5 Hz), 82.1, 75.9, 74.3, 71.0, 59.3, 59.1, 47.9. HRMS (ESI-TOF) (m/z): [M + H]$^+$ calcd for C$_{14}$H$_{18}$FO$_4$ 269.1189; found, 269.1154.

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

The compound 3bp was prepared using the general procedure. The reaction was carried out between tri-O-methyl-D-galactal 1ae (95 mg, 0.5 mmol) and 4-chlorobenzenediazonium tetrafluoroborate 2am (126 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of Pd(OAc)$_2$ (11 mg, 0.05 mmol) at room temperature for 3 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished 3bp as colourless semi solid (87 mg, 61%); TLC $R_f$= 0.60 (35 % ethyl acetate in hexane); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.27-7.23 (m, 4H), 5.23 (dd, $J$ = 10.0, 3.5 Hz, 1H), 4.40-4.39 (m, 1H), 3.90 (d, $J$ = 5.5 Hz, 1H), 3.69-3.61 (m, 2H), 3.47 (s, 3H), 3.25 (s, 3H), 2.72 (dd, $J$ = 14.5, 3.5 Hz, 1H), 2.54-2.49 (m, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 203.4, 139.1, 133.6, 128.7, 127.2, 82.0, 75.9, 74.2, 71.1, 59.3, 59.1, 47.8. HRMS (ESI-TOF) (m/z): [M + H]$^+$ calcd for C$_{14}$H$_{18}$ClO$_4$ 285.0894; found, 285.0874.
(2R,3S,6S)-6-(4-Bromophenyl)-3-methoxy-2-(methoxymethyl)dihydro-2H-pyran-4(3H)-one [3bq]

The compound 3bq was prepared using the general procedure. The reaction was carried out between tri-O-methyl-D-galactal 1ae (95 mg, 0.5 mmol) and 4-bromobenzenediazonium tetrafluoroborate 2aa (150 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of Pd(OAc)$_2$ (11 mg, 0.05 mmol) at room temperature for 3 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished 3bq as brownish semi solid (91 mg, 55%); TLC $R_f$ = 0.48 (35 % ethyl acetate in hexane); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.42 (d, $J$ = 7.5 Hz, 2H), 7.18 (d, $J$ = 8.0 Hz, 2H), 5.22 (dd, $J$ = 10.0, 3.5 Hz, 1H), 4.41 (t, $J$ = 5.5 Hz, 1H), 3.90 (d, $J$ = 6.5 Hz, 1H), 3.69-3.61 (m, 2H), 3.48 (s, 3H), 3.25 (s, 3H), 2.72 (dd, $J$ = 14.5, 3.0 Hz, 1H), 2.53-2.48 (m, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 203.5, 139.6, 131.6, 127.5, 121.8, 82.0, 75.9, 74.3, 71.1, 59.3, 59.2, 47.8. HRMS (ESI-TOF) (m/z): [M + H]$^+$ calcd for C$_{14}$H$_{18}$BrO$_4$ 329.0388; found, 329.0361.

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

The compound 3br was prepared using the general procedure. The reaction was carried out between tri-O-methyl-D-galactal 1ae (95 mg, 0.5 mmol) and 4-nitrobenzenediazonium tetrafluoroborate 2ag (131 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of Pd(OAc)$_2$ (11 mg, 0.05 mmol) at room temperature for 8 h. Column chromatography purification was performed using 20 % ethyl acetate in hexane which furnished 3br as semi solid (72 mg, 48%); TLC $R_f$ = 0.40 (35 % ethyl acetate in hexane); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.16 (d, $J$ = 8.5 Hz, 2H), 7.49 (d, $J$ = 8.0 Hz, 2H), 5.49 (dd, $J$ = 10.5, 2.5 Hz, 1H), 4.48-4.47 (m, 1H), 3.95 (d, $J$ = 6.5 Hz, 1H), 3.74-3.64 (m, 2H), 3.51 (s, 3H), 3.26 (s, 3H), 2.78-2.75 (m, 1H), 2.50-2.45 (m, 1H). $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 203.5, 139.6, 131.6, 127.5, 121.8, 82.0, 75.9, 74.3, 71.1, 59.3, 59.2, 47.8. HRMS (ESI-TOF) (m/z): [M + H]$^+$ calcd for C$_{14}$H$_{18}$NO$_6$ 296.1134; found, 296.1143.

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

The compound 3bs was prepared using the general procedure. The reaction was carried out between tri-O-methyl-D-galactal 1ae (95 mg, 0.5 mmol) and 4-cyanobenzenediazonium tetrafluoroborate 2ak (120 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of Pd(OAc)$_2$
(11 mg, 0.05 mmol) at room temperature for 6 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished 3bs as colourless semi solid (68 mg, 49%); TLC Rf = 0.42 (35 % ethyl acetate in hexane); 1H NMR (500 MHz, CDCl3) δ 7.59 (d, J = 8.0 Hz, 2H), 7.42 (d, J = 8.0 Hz, 2H), 5.33 (dd, J = 10.0, 3.0 Hz, 1H), 4.45 (m, 1H), 3.92 (d, J = 6.0 Hz, 1H), 3.72-3.70 (m, 1H), 3.66-3.63 (m, 1H), 3.49 (s, 3H), 3.25 (s, 3H), 2.74 (dd, J = 14.0, 3.5 Hz, 1H), 2.49-2.44 (m, 1H). 13C NMR (126 MHz, CDCl3) δ 202.8, 146.0, 132.4, 126.3, 118.5, 111.7, 81.8, 76.2, 74.1, 71.3, 59.4, 59.3, 47.8. HRMS (ESI-TOF) (m/z): [M + H]^+ calcd for C15H18NO4 276.1236; found, 276.1223.

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

The compound 3bt was prepared using the general procedure. The reaction was carried out between tri-O-methyl-D-galactal 1ae (95 mg, 0.5 mmol) and 4-(methoxycarbonyl)benzenediazonium tetrafluoroborate 2ai (139 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of Pd(OAc)2 (11 mg, 0.05 mmol) at room temperature for 4 h. Column chromatography purification was performed using 18 % ethyl acetate in hexane which furnished 3bt as yellowish solid (80 mg, 52%); TLC Rf = 0.45 (35 % ethyl acetate in hexane); 1H NMR (500 MHz, CDCl3) δ 7.96 (d, J = 8.5 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 5.32 (dd, J = 9.5, 2.5 Hz, 1H), 4.44 (m, 1H), 3.93 (d, J = 6.0 Hz, 1H), 3.84 (s, 3H), 3.71-3.63 (m, 2H), 3.49 (s, 3H), 3.26 (s, 3H), 2.75 (dd, J = 14.5, 3.0 Hz, 1H), 2.54-2.49 (m, 1H). 13C NMR (125 MHz, CDCl3) δ 203.3, 166.6, 145.7, 129.7, 125.6, 82.0, 76.1, 74.4, 71.2, 59.3, 59.2, 52.1, 47.9. HRMS (ESI-TOF) (m/z): [M + H]^+ calcd for C16H21O6 309.1338; found, 309.1375.

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

The compound 3bu was prepared using the general procedure. The reaction was carried out between tri-O-methyl-D-galactal 1ae (95 mg, 0.5 mmol) and 2,4-dimethylbenzenediazonium tetrafluoroborate 2ap (122 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of Pd(OAc)2 (11 mg, 0.05 mmol) at room temperature for 5 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished 3bu as colourless solid (76 mg, 54%); TLC Rf = 0.40 (35 % ethyl acetate in hexane); 1H NMR (500 MHz, CDCl3) δ 7.25 (d, J = 7.5 Hz, 1H), 6.96 (d, J=7.5Hz,1H), 6.91(s, 1H). 5.44 (dd, J = 9.0, 3.0 Hz, 1H), 4.36-4.35 (m, 1H), 3.92 (d, J=6.5 Hz, 1H), 3.68-3.64 (m, 2H), 3.47 (s, 3H), 3.25 (s, 3H), 2.67 (dd, J = 14.5, 3.5 Hz, 1H), 2.62-2.58 (m, 1H), 2.25 (s, 3H), 2.22 (s, 3H). 13C NMR (125 MHz, CDCl3) δ
204.4, 137.6, 135.3, 135.2, 131.3, 126.9, 125.5, 82.2, 75.66, 71.6, 71.1, 59.2, 59.0, 46.5, 20.9, 18.9. HRMS (ESI-TOF) (m/z): [M + H]^+ calcd for C_{16}H_{21}O_{4} 279.1596; found, 279.1610.

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

The compound 3av was prepared using the general procedure. The reaction was carried out between tri-O-methyl-D-galactal 1ae (95 mg, 0.5 mmol) and 2-chlorobenzenediazonium tetrafluoroborate 2ba (127 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of Pd(OAc)$_2$ (11 mg, 0.05 mmol) at room temperature for 4 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished 3av as yellowish semi solid (60 mg, 43%); TLC $R_f$ = 0.60 (15 % ethyl acetate in chloroform); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.55-7.54 (m, 1H), 7.28-7.14 (m, 3H), 5.62 (dd, $J$ = 10.5, 2.5 Hz, 1H), 4.52-4.50 (m, 1H), 3.99(d, $J$ = 6.0 Hz, 1H), 3.69-3.68 (m, 2H), 3.51 (s, 3H), 3.27 (s, 3H), 2.84 (dd, $J$ = 14.5, 3.0 Hz, 1H), 2.40-2.34 (m, 1H).$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 203.2, 138.5, 131.8, 129.4, 128.9, 127.2, 126.8, 82.0, 76.3, 71.4, 70.9, 59.3, 59.3, 46.8. HRMS (ESI-TOF) (m/z): [M + H]^+ calcd for C$_{14}$H$_{18}$ClO$_4$ 285.0894; found, 285.0890.

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

The compound 3bw was prepared using the general procedure. The reaction was carried out between tri-O-methyl-D-galactal 1ae (95 mg, 0.5 mmol) and 3-nitrobenzenediazonium tetrafluoroborate 2ax (140 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of Pd(OAc)$_2$ (11 mg, 0.05 mmol) at room temperature for 8 h. Column chromatography purification was performed using 20 % ethyl acetate in hexane which furnished 3bw as yellowish semi solid (60 mg, 40%); TLC $R_f$ = 0.3 (35 % ethyl acetate in hexane); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.24 (s, 1H), 8.19 (d, $J$ = 7.0 Hz, 1H), 7.60 (d, $J$ = 7.5 Hz, 1H), 7.47 (t, $J$ = 8.0 Hz, 1H), 5.39 (dd, $J$ = 10.0, 2.5 Hz, 1H), 4.49 (t, $J$ = 4.5 Hz, 1H), 3.97 (d, $J$ = 6.5 Hz, 1H), 3.74-3.64 (m, 2H), 3.51 (s, 3H), 3.27 (s, 3H), 2.77 (dd, $J$ = 14.5, 3.5 Hz, 1H), 2.53-2.48 (m, 1H).$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 202.6, 148.4, 143.1, 131.7, 129.5, 122.8, 120.8, 81.8, 76.3, 73.9, 71.3, 59.4, 59.3, 48.1. HRMS (ESI-TOF) (m/z): [M + H]^+ calcd for C$_{14}$H$_{18}$NO$_6$ 296.1134; found, 296.1115.

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

The compound 3bx was prepared using the general procedure. The reaction was carried out between tri-O-benzyl-D-galactal 1af (100 mg, 0.24 mmol) and benzenediazonium tetrafluoroborate 2ac (66 mg, 0.27 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of Pd(OAc)$_2$ (5.5 mg, 0.024 mmol) at room temperature for 4 h. Column chromatography purification was performed using 10% ethyl acetate in hexane which furnished 3bx as colourless semi solid (48 mg, 50%); TLC $R_f$ = 0.48 (15% ethyl acetate in hexane); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.28-7.17 (m, 15H), 5.25 (dd, $J = 9.5$, 2.5 Hz, 1H), 4.86 (d, $J = 12.0$ Hz, 1H), 4.51 (d, $J = 4.5$ Hz, 1H), 4.48 (d, $J = 4.5$ Hz, 1H), 4.42 (d, $J = 12.0$ Hz, 1H), 4.37 (s, 1H), 4.09 (d, $J = 6.5$ Hz, 1H), 3.78-3.71 (m, 2H), 2.73 (dd, $J = 14.5$, 3.0 Hz, 1H), 2.59-2.54 (m, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 204.1, 140.5, 137.9, 137.4, 128.5, 128.4, 128.3, 128.0, 12.9, 127.8, 127.6, 127.5, 125.9, 79.2, 76.4, 74.7, 73.5, 72.6, 68.4, 47.9 HRMS (ESI-TOF) (m/z): [M + H]$^+$ calcd for C$_{26}$H$_{27}$O$_4$ 403.1909; found, 403.1916.

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

The compound 3by was prepared using the general procedure. The reaction was carried out between tri-O-benzyl-D-galactal 1af (100 mg, 0.24 mmol) and 4-methylbenzenediazonium tetrafluoroborate 2ae (55 mg, 0.27 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of Pd(OAc)$_2$ (5.5 mg, 0.024 mmol) at room temperature for 4 h. Column chromatography purification was performed using 10% ethyl acetate in hexane which furnished 3by as semi solid (52 mg, 52%); TLC $R_f$ = 0.47 (15% ethyl acetate in hexane); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.27-7.14 (m, 13H), 7.08 (d, $J = 7.5$ Hz, 2H), 5.22 (d, $J = 9.0$ Hz, 1H), 4.85 (d, $J = 12.5$ Hz, 1H), 4.49 (d, $J = 13.0$ Hz, 2H), 4.42 (d, $J = 12.5$ Hz, 1H), 4.34 (s, 1H), 4.08 (d, $J = 6.0$ Hz, 1H), 3.77-3.70 (m, 2H), 2.74-2.71 (m, 1H), 2.60-2.55 (m, 1H), 2.25 (s, 3H).$^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 204.3, 137.9, 137.8, 137.4, 137.4, 129.2, 128.4, 128.3, 127.9, 127.8, 127.6, 127.5, 126.0, 79.2, 76.3, 74.7, 73.5, 72.6, 68.4, 47.8, 21.1 HRMS (ESI-TOF) (m/z): [M + H]$^+$ calcd for C$_{27}$H$_{29}$O$_4$ 417.2066; found, 417.2061.
(2R,3S,6S)-3-(Benzyloxy)-2-(benzyloxymethyl)-6-(4-bromophenyl)dihydro-2H-pyran-4(3H)-one [3bz]

The compound 3bz was prepared using the general procedure. The reaction was carried out between tri-O-benzyl-D-galactal 1af (100 mg, 0.24 mmol) and 4-bromobenzenediazonium tetrafluoroborate 2aa (72 mg, 0.27 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of Pd(OAc)$_2$ (5.5 mg, 0.024 mmol) at room temperature for 4 h. Column chromatography purification was performed using 10 % ethyl acetate in hexane which furnished 3bz as yellowish foam (58 mg, 50%); TLC R$_f$ = 0.50 (15 % ethyl acetate in hexane); $^1$H NMR (500 MHz, CDCl$_3$) δ 7.50 (d, J = 8.0 Hz, 2H), 7.39-7.28 (m, 11H), 7.23 (d, J = 8.0 Hz, 2H), 5.31 (dd, J = 10.0, 3.0 Hz, 1H), 4.97 (d, J = 12.0 Hz, 1H), 4.62-4.58 (m, 2H), 4.52 (d, J = 12.5 Hz, 1H), 4.46 (s, 1H), 4.18 (d, J = 6.5 Hz, 1H), 3.88-3.81 (m, 2H), 2.81 (dd, J = 14.5, 3.0 Hz, 1H), 2.62-2.57 (m, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 203.7, 139.6, 137.8, 137.3, 131.6, 128.5, 128.3, 128.0, 127.8, 127.6, 127.6, 121.8, 79.0, 76.5, 74.1, 73.6, 72.7, 68.5, 47.8. HRMS (ESI-TOF) (m/z): [M + H]$^+$ calcd for C$_{26}$H$_{26}$BrO$_4$ 481.1014; found, 481.1019.

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

The compound 3ca was prepared using the general procedure. The reaction was carried out between 3,4-di-O-benzyl-L-rhamnal 1ag (110 mg, 0.35 mmol) and benzenediazonium tetrafluoroborate 2ac (75 mg, 0.4 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of Pd(OAc)$_2$ (8 mg, 0.035 mmol) at room temperature for 1.5 h. Column chromatography purification was performed using 8 % ethyl acetate in hexane which furnished 3ca as white foam (73 mg, 69%); TLC R$_f$ = 0.25 (15 % ethyl acetate in hexane); $^1$H NMR (500 MHz, CDCl$_3$) δ 7.42-7.28 (m, 10H), 5.33 (t, J= 4.0 Hz, 1H), 4.89 (d, J = 11.5 Hz, 1H), 4.52 (d, J = 11.5 Hz, 1H), 3.87-3.84 (m, 1H), 3.70 (d, J = 7.5 Hz, 1H), 3.18 (dd, J = 14.0, 3.5 Hz, 1H), 2.96 (dd, J = 14.5, 6.5 Hz, 1H), 1.33 (d, J = 6.3 Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 206.3, 139.6, 137.8, 137.3, 131.6, 128.5, 128.3, 128.0, 127.8, 127.6, 127.6, 121.8, 79.0, 76.5, 74.1, 73.6, 72.7, 68.5, 47.8. HRMS (ESI-TOF) (m/z): [M + H]$^+$ calcd for C$_{19}$H$_{21}$O$_3$ 297.1491; found, 297.1499.
(2S,3S,6R)-3-(Benzyloxy)-2-methyl-6-p-tolyldihydro-2H-pyran-4(3H)-one [3cb]

The compound 3cb was prepared using the general procedure. The reaction was carried out between 3,4-di-O-benzyl-L-rhamnan 1ag (110 mg, 0.35 mmol) and 4-methylbenzenediazonium tetrafluoroborate 2ae (81 mg, 0.4 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of Pd(OAc)$_2$ (8 mg, 0.035 mmol) at room temperature for 1.5 h. Column chromatography purification was performed using 8 % ethyl acetate in hexane which furnished 3cb as white foam (79 mg, 72%); TLC $R_f= 0.40$ (15 % ethyl acetate in hexane); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.27-7.19 (m, 7H), 7.07 (d, $J = 7.5$ Hz, 2H), 5.20 (m, 1H), 4.78 (d, $J = 11.5$ Hz, 1H), 4.41 (d, $J = 11.5$ Hz, 1H), 3.73-3.70 (m, 1H), 3.58 (d, $J = 8.0$ Hz, 1H), 3.05 (d, $J = 14.0$ Hz, 1H), 2.85 (dd, $J = 14.0$, 6.5 Hz, 1H), 2.24 (s, 3H), 1.21 (m, $J = 7.4$ Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 206.6, 137.9, 137.3, 136.0, 129.3, 128.4, 128.2, 128.0, 127.2, 84.8, 74.6, 73.0, 71.6, 44.5, 21.0, 18.2. HRMS (ESI-TOF) (m/z): [M + H]$^+$ calcd for C$_{20}$H$_{23}$O$_3$ 311.1647; found, 311.1639.

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

The compound 3cc was prepared using the general procedure. The reaction was carried out between 3,4-di-O-benzyl-L-rhamnan 1ag (110 mg, 0.35 mmol) and 4-nitrobenzenediazonium tetrafluoroborate 2ag (93 mg, 0.4 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of Pd(OAc)$_2$ (8 mg, 0.035 mmol) at room temperature for 1.5 h. Column chromatography purification was performed using 12 % ethyl acetate in hexane which furnished 3cc as white foam (78 mg, 64%); TLC $R_f= 0.24$ (15 % ethyl acetate in hexane); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.19 (d, $J = 8.5$ Hz, 2H), 7.55 (d, $J = 8.5$ Hz, 2H), 7.34-7.28 (m, 5H), 5.29 (t, $J = 2.5$ Hz, 1H), 4.79 (d, $J = 11.5$ Hz, 1H), 4.46 (d, $J = 11.5$ Hz, 1H), 3.88-3.84 (m, 1H), 3.66 (d, $J = 6.5$ Hz, 1H), 3.11 (dd, $J = 14.0$, 5.0 Hz, 1H), 2.91 (dd, $J = 14.0$, 6.0 Hz, 1H), 1.29 (d, $J = 6.5$ Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 205.4, 147.6, 146.4, 136.9, 128.4, 128.2, 128.1, 127.7, 123.8, 84.1, 73.6, 73.2, 72.9, 44.5, 17.5. HRMS (ESI-TOF) (m/z): [M + H]$^+$ calcd for C$_{19}$H$_{20}$NO$_5$ 342.1341; found, 342.1341.
(2S,5R)-5-(Benzyloxy)-2-p-tolyldihydro-2H-pyran-4(3H)-one [3cd]

The compound 3cd was prepared using the general procedure. The reaction was carried out between di-O-benzyl-D-xylal 1ah (110 mg, 0.37 mmol) and 4-methylbenzenediazonium tetrafluoroborate 2ae (85 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of Pd(OAc)$_2$ (8.5 mg, 0.037 mmol) at room temperature for 4 h. Column chromatography purification was performed using 8 % ethyl acetate in hexane which furnished 3cd as colourless semi solid (45 mg, 41%); TLC $R_f$ = 0.24 (15 % ethyl acetate in hexane); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.39-7.28 (m, 7H), 7.21 (d, $J = 8.0$ Hz, 2H), 4.73-4.69 (m, 2H), 4.53 (d, $J = 12.0$ Hz, 1H), 4.33 (dd, $J = 12.5$, 2.5 Hz, 1H), 3.86-3.83 (m, 1H), 3.75 (s, 1H), 3.20 (dd, $J = 13.5$, 10.0 Hz, 1H), 2.63 (d, $J = 13.5$ Hz, 1H), 2.37 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 206.4, 138.0, 137.0, 129.3, 128.5, 128.1, 126.0, 80.1, 79.6, 71.7, 70.5, 47.2, 21.1. HRMS (ESI-TOF) (m/z): [M + H]$^+$ calcd for C$_{19}$H$_{21}$O$_3$ 297.1491; found, 297.1501.

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

The compound 3ce was prepared using the general procedure. The reaction was carried out between di-O-benzyl-D-ribal 1ai (100 mg, 0.34 mmol) and 4-methylbenzenediazonium tetrafluoroborate 2ae (77 mg, 0.37 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of Pd(OAc)$_2$ (8 mg, 0.034 mmol) at room temperature for 2.5 h. Column chromatography purification was performed using 8 % ethyl acetate in hexane which furnished 3ce as white foam (31 mg, 31%); TLC $R_f$ = 0.25 (15 % ethyl acetate in hexane); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.31-7.24 (t, 5H), 7.14 (d, $J = 7.5$ Hz, 2H), 7.09 (d, $J = 7.5$ Hz, 2H), 4.86 (d, $J = 12.0$ Hz, 1H), 4.54-4.51 (m, 2H), 4.35-4.32 (m, 1H), 4.13-4.09 (m, 1H), 3.54 (t, $J = 11.0$ Hz, 1H), 2.66-2.59 (m, 2H), 2.26 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 204.9, 138.0, 137.3, 136.8, 129.3, 128.5, 128.0, 127.9, 125.5, 80.6, 78.9, 72.7, 70.5, 49.7, 21.1. HRMS (ESI-TOF) (m/z): [M + H]$^+$ calcd for C$_{19}$H$_{21}$O$_3$ 297.1491; found, 297.1482.

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

The compound 4ab was prepared using the general procedure while methanol is used as the solvent. The reaction was carried out between tri-O-methyl-D-glucal 1aa (95 mg, 0.5 mmol) and 2-chlorobenzenediazonium tetrafluoroborate 2ab (127 mg, 0.56 mmol) in methanol (4 mL) in the
presence of Pd(OAc)$_2$ (5.6 mg, 0.025 mmol) at room temperature for 1 h. Column chromatography purification was performed using 15% ethyl acetate in hexane which furnished 3ab as viscous liquid (157 mg, 94%); TLC $R_f = 0.38$ (35% ethyl acetate in hexane); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.60 (d, $J = 7.5$ Hz, 1H), 7.23-7.18 (m, 2H), 7.10 (t, $J = 7.5$ Hz, 1H), 4.98 (d, $J = 11.5$ Hz, 1H), 4.40 (t, $J = 6.0$ Hz, 1H), 3.80-3.77 (m, 1H), 3.52 (dd, $J = 10.5, 5.0$ Hz, 1H), 3.43 (s, 3H), 3.32 (s, 3H), 3.27 (s, 3H), 3.18 (s, 4H), 2.06 (d, $J = 14.0$ Hz, 1H), 1.68 (t, $J = 13.0$ Hz, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 139.1, 131.2, 128.9, 128.4, 127.8, 127.2, 98.7, 75.7, 74.5, 70.6, 67.0, 59.0, 57.3, 47.7, 47.5, 34.1. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for C$_{16}$H$_{24}$ClO$_5$ 331.1312; found, 331.1331.

**Procedure for the deprotection of dimethyl acetal 4ab:**

To a solution of acetal 4ab (76 mg, 0.23 mmol) in methanol (2 mL), 6N HCl (5 mL) was added at room temperature and stirred for 1 h. The resulting solution was diluted with ethyl acetate (100 mL) and washed with saturated NaHCO$_3$ and brine solutions. The organic layer was dried over anhydrous Na$_2$SO$_4$, concentrated and purified by column chromatography using 15% ethyl acetate in hexane which furnished a mixture of inseparable 3ab and 5ab ($\alpha/\beta$=6:1) in 76% yield (51 mg).

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

To a stirred solution of ketone 3ba (150 mg, 0.37 mmol) in methanol (7 mL), sodium borohydride (15 mg, 0.4 mmol) was added at 0-4°C. The reaction mixture was stirred for 30 mins at the same temperature, diluted with ethyl acetate (50 mL) and washed with saturated ammonium chloride solution. The organic layer was dried over anhydrous Na$_2$SO$_4$, concentrated and purified in column chromatography using 15% ethyl acetate in hexane which furnished 4ba as a white foam in 72% yield (108 mg). TLC $R_f = 0.25$ (20% ethyl acetate in hexane); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.32-7.16 (m, 15H), 4.67-4.64 (m, 2H), 4.52-4.44 (m, 3H), 4.29 (s, 1H), 4.03-4.01 (m, 1H), 3.68-3.63 (m, 3H), 2.01-1.99 (m, 2H), 1.92 (d, $J = 13.0$ Hz, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 141.7, 137.8, 137.8, 128.4, 128.4, 128.2, 127.8, 127.8, 127.8, 127.7, 127.6, 127.4, 126.0, 75.4, 73.4, 73.0, 72.6, 71.5, 69.2, 66.0, 36.6. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for C$_{26}$H$_{26}$O$_4$ 405.2066; found, 405.2019.
(2R,3S,4S,6S)-3-(benzyloxy)-2-(benzyloxymethyl)-6-(4-bromophenyl)tetrahydro-2H-pyran-4-ol [4bf]

To a stirred solution of ketone 3bf (100 mg, 0.21 mmol) in methanol (7 mL), sodium borohydride (11 mg, 0.28 mmol) was added at 0-4 °C. The reaction mixture was stirred for 30 mins at the same temperature, diluted with ethyl acetate (50 mL) and washed with saturated ammonium chloride solution. The organic layer was dried over anhydrous Na₂SO₄, concentrated and purified in column chromatography using 20 % ethyl acetate in hexane which furnished 4bf as viscous oil in 82% yield (83 mg). TLC R_f = 0.26 (15 % ethyl acetate in hexane); ^1H NMR (500 MHz, CDCl₃) δ 7.35 (d, J = 7.5 Hz, 2H), 7.25-7.18 (m, 12H), 4.63 (d, J = 10.5 Hz, 2H), 4.50 (d, J = 12 Hz, 1H), 4.44 (d, J = 12.5 Hz, 1H), 4.22 (s, 1H), 4.02-4.01 (m, 1H), 3.65-3.61 (m, 3H), 2.14 (bs, 1H), 2.01-1.88 (m, 2H). ^13C NMR (125 MHz, CDCl₃) δ 140.8, 137.7, 137.7, 131.2, 128.4, 127.9, 127.8, 127.7, 127.6, 121.1, 75.3, 73.4, 72.4, 72.3, 71.5, 69.1, 65.8, 36.3. HRMS (ESI-TOF) (m/z): [M + H]^+ calcd for C₂₆H₂₈BrO₄ 483.1171; found, 483.1163.

(2R,3S,4S,6S)-3,4-bis(benzyloxy)-2-(benzyloxymethyl)-6-phenyltetrahydro-2H-pyran (5ba)

The alcohol 4ba (100 mg, 0.25 mmol) was stirred in dry DMF (3 mL) was added and cooled to 0 °C after which NaH (12 mg, 60% in mineral oil) was added. The mixture was stirred for 5 min at the same temperature to which benzyl bromide (0.038 mL, 1.5 equiv.) was added. The resulting mixture was stirred for 60 mins and quenched by saturated aqueous NH₄Cl (1 mL) and diluted with ethyl acetate (50 mL). The organic phase was washed with H₂O, brine, dried over anhydrous Na₂SO₄ and evaporated under reduced pressure. The crude product was purified by column chromatography using 10% ethyl acetate in hexane to afford 5ba as viscous oil in 81% yield (100 mg). TLC R_f = 0.34 (20 % ethyl acetate in hexane); ^1H NMR (500 MHz, CDCl₃) δ 7.45-7.28 (m, 20H), 4.78-4.75 (m, 3H), 4.55 (d, J = 17.5 Hz, 4H), 4.47 (s, 1H), 4.95 (d, J = 10 Hz, 1H), 3.91 (s, 1H), 3.75-3.68 (m, 2H), 2.45-2.38 (m, 1H), 2.04 (d, J = 12.5 Hz, 1H). ^13C NMR (125 MHz, CDCl₃) δ 141.9, 138.6, 138.4, 137.9, 128.40, 128.2, 128.2, 127.8, 127.6, 127.5, 127.4, 126.3, 74.5, 73.7, 73.5, 73.2, 72.6, 71.6, 70.0, 68.9, 33.7. HRMS (ESI-TOF) (m/z): [M + H]^+ calcd for C₃₃H₃₅O₄ 495.2535; found, 495.2515.

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References


Figure S1: $^1$H-NMR spectrum of compound 1aa in CDCl$_3$
Figure S2: $^{13}$C-NMR spectrum of compound 1aa in CDCl$_3$
Figure S3: $^1$H-NMR spectrum of compound 1ab in CDCl$_3$
Figure S4: $^{13}$C-NMR spectrum of compound 1ab in CDCl$_3$
Figure S5: $^1$H-NMR spectrum of compound 1ac in CDCl$_3$
Figure S6: $^{13}$C-NMR spectrum of compound 1ac in CDCl$_3$
Figure S7: $^1$H-NMR spectrum of compound 1ad in CDCl$_3$
Figure S8: $^{13}$C-NMR spectrum of compound 1ad in CDCl$_3$
Figure S9: $^1$H-NMR spectrum of compound 1af in CDCl$_3$. 
Figure S10. $^{13}$C-NMR spectrum of compound 1af in CDCl$_3$
Figure S11: $^1$H-NMR spectrum of compound 1ag in CDCl$_3$
Figure S12: $^{13}$C-NMR spectrum of compound 1ag in CDCl$_3$.
Figure S13: $^1$H-NMR spectrum of compound 1ah in CDCl$_3$
Figure S14: $^{13}$C-NMR spectrum of compound 1ah in CDCl$_3$
Figure S15: $^1$H-NMR spectrum of compound 1ai in CDCl$_3$
Figure S16: $^{13}$C-NMR spectrum of compound 1ai in CDCl$_3$
Figure S17: $^1\text{H}-\text{NMR}$ spectrum of compound 1aj in CDCl$_3$
Figure S18: $^{13}$C-NMR spectrum of compound 1aj in CDCl$_3$
Figure S19: $^1$H-NMR spectrum of compound 3aa in CDCl$_3$
Figure S20: $^{13}$C-NMR spectrum of compound 3aa in CDCl$_3$
Figure S21: $^1$H-NMR spectrum of compound 3ab in CDCl$_3$
Figure S22: $^{13}$C-NMR spectrum of compound 3ab in CDCl$_3$
Figure S23: $^1$H-NMR spectrum of compound 3ac in CDCl$_3$
Figure S24: $^{13}$C-NMR spectrum of compound 3ac in CDCl$_3$
Figure S25: $^1$H-NMR spectrum of compound 3ad in CDCl$_3$
Figure S26: $^{13}$C-NMR spectrum of compound 3ad in CDCl$_3$
Figure S27: $^1$H-NMR spectrum of compound 3ae in CDCl$_3$
Figure S28: $^{13}$C-NMR spectrum of compound 3ae in CDCl$_3$
Figure S29: $^1$H-NMR spectrum of compound 3af in CDCl$_3$
Figure S30: $^{13}$C-NMR spectrum of compound 3af in CDCl$_3$

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Figure S31: $^1$H-NMR spectrum of compound 3ag in CDCl$_3$
Figure S32. $^{13}$C-NMR spectrum of compound 3ag in CDCl$_3$
Figure S33: $^1$H-NMR spectrum of compound 3ah in CDCl$_3$
Figure S34: $^{13}$C-NMR spectrum of compound 3ah in CDCl$_3$
Figure S35: $^1$H-NMR spectrum of compound 3ai in CDCl$_3$
Figure S36: $^{13}$C-NMR spectrum of compound 3ai in CDCl$_3$
Figure S37: $^1$H-NMR spectrum of compound 3aj in CDCl$_3$
Figure S38: $^{13}$C-NMR spectrum of compound 3aj in CDCl$_3$
Figure S39: $^1$H-NMR spectrum of compound 3ak in CDCl$_3$
Figure S40: $^{13}$C-NMR spectrum of compound 3ak in CDCl$_3$
Figure S41: $^1$H-NMR spectrum of compound 3al in CDCl$_3$
Figure S42: $^{13}$C-NMR spectrum of compound 3al in CDCl$_3$
Figure S43: $^1$H-NMR spectrum of compound 3am in CDCl$_3$
Figure S44: $^{13}$C-NMR spectrum of compound 3am in CDCl$_3$
Figure S45: $^1$H-NMR spectrum of compound 3an in CDCl$_3$
Figure S46: $^{13}$C-NMR spectrum of compound 3an in CDCl$_3$
Figure S47: $^1$H-NMR spectrum of compound 3ao in CDCl$_3$
Figure S48: $^{13}$C-NMR spectrum of compound 3ao in CDCl$_3$
Figure S49: $^1$H-NMR spectrum of compound 3ap in CDCl$_3$
Figure S50: $^{13}$C-NMR spectrum of compound 3ap in CDCl$_3$
Figure S51: $^1$H-NMR spectrum of compound 3aq in CDCl$_3$
Figure S52: $^{13}$C-NMR spectrum of compound 3aq in CDCl$_3$
Figure S53: $^1$H-NMR spectrum of compound 3ar in CDCl$_3$
Figure S54: $^{13}$C-NMR spectrum of compound 3ar in CDCl$_3$
Figure S55: $^1$H-NMR spectrum of compound 3as in CDCl$_3$
Figure S56: $^{13}$C-NMR spectrum of compound 3as in CDCl$_3$
Figure S57: $^1$H-NMR spectrum of compound 3at in CDCl$_3$
Figure S58: $^{13}$C-NMR spectrum of compound 3at in CDCl$_3$
Figure S59: $^1$H-NMR spectrum of compound 3au in CDCl$_3$
Figure S60: $^{13}$C-NMR spectrum of compound 3au in CDCl$_3$
Figure S61: $^1$H-NMR spectrum of compound 3av in CDCl$_3$
Figure S62: $^{13}$C-NMR spectrum of compound 3av in CDCl$_3$. 
Figure S63: $^1$H-NMR spectrum of compound 3aw in CDCl$_3$
Figure S64: $^{13}$C-NMR spectrum of compound 3aw in CDCl$_3$
Figure S65: $^1$H-NMR spectrum of compound 3ax in CDCl$_3$
Figure S66: $^{13}$C-NMR spectrum of compound 3ax in CDCl$_3$
Figure S67: $^1$H-NMR spectrum of compound 3ay in CDCl$_3$
Figure S68: $^{13}$C-NMR spectrum of compound 3ay in CDCl$_3$
Figure S69: $^1$H-NMR spectrum of compound 3az in CDCl$_3$
Figure S70: $^{13}$C-NMR spectrum of compound 3az in CDCl$_3$
Figure S71: $^1$H-NMR spectrum of compound 3ba in CDCl$_3$
Figure S72: $^{13}$C-NMR spectrum of compound 3ba in CDCl$_3$
Figure S73: $^1$H-NMR spectrum of compound 3bb in CDCl$_3$
Figure S74: $^{13}$C-NMR spectrum of compound 3bb in CDCl$_3$
Figure S75: $^1$H-NMR spectrum of compound 3bc in CDCl$_3$
Figure S76: $^{13}$C-NMR spectrum of compound 3bc in CDCl$_3$
Figure S77: $^1$H-NMR spectrum of compound 3bd in CDCl$_3$
Figure S78: $^{13}$C-NMR spectrum of compound 3bd in CDCl$_3$
Figure S79: $^1$H-NMR spectrum of compound 3be in CDCl$_3$
Figure S80: $^{13}$C-NMR spectrum of compound 3be in CDCl$_3$
Figure S81: $^1$H-NMR spectrum of compound 3bf in CDCl$_3$
Figure S82: $^{13}$C-NMR spectrum of compound 3bf in CDCl$_3$

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Figure S83: $^1$H-NMR spectrum of compound 3bg in CDCl$_3$
Figure S84: $^{13}$C-NMR spectrum of compound 3bg in CDCl$_3$
Figure S85: $^1$H-NMR spectrum of compound 3bh in CDCl$_3$
Figure S86: $^{13}$C-NMR spectrum of compound 3bh in CDCl$_3$
Figure S87: $^1$H-NMR spectrum of compound 3bi in CDCl$_3$
Figure S88: $^{13}$C-NMR spectrum of compound 3bi in CDCl$_3$
Figure S89: $^1$H-NMR spectrum of compound 3bj in CDCl$_3$
Figure S90: $^{13}$C-NMR spectrum of compound 3bj in CDCl$_3$
Figure S91: $^1$H-NMR spectrum of compound 3bl in CDCl$_3$
Figure S92: $^{13}$C-NMR spectrum of compound 3bl in CDCl$_3$
Figure S93: $^1$H-NMR spectrum of compound 3bm in CDCl$_3$
Figure S94: $^{13}$C-NMR spectrum of compound 3bm in CDCl$_3$
Figure S95: $^1$H-NMR spectrum of compound 3bn in CDCl$_3$
Figure S96: $^{13}$C-NMR spectrum of compound 3bn in CDCl$_3$
Figure S97: $^1$H-NMR spectrum of compound 3bo in CDCl$_3$
Figure S98: $^{13}$C-NMR spectrum of compound 3bo in CDCl$_3$
Figure S99: $^1$H-NMR spectrum of compound 3bp in CDCl$_3$
Figure S100: $^{13}$C-NMR spectrum of compound 3bp in CDCl$_3$
Figure S101: $^1$H-NMR spectrum of compound 3bq in CDCl$_3$
Figure S102: $^{13}$C-NMR spectrum of compound 3bq in CDCl$_3$
Figure S103: $^1$H-NMR spectrum of compound 3br in CDCl$_3$
Figure S104: $^{13}$C-NMR spectrum of compound 3br in CDCl$_3$
Figure S105: $^1$H-NMR spectrum of compound 3bs in CDCl$_3$
Figure S106: $^{13}$C-NMR spectrum of compound 3bs in CDCl$_3$
Figure S107: $^1$H-NMR spectrum of compound 3bt in CDCl$_3$
Figure S108: $^{13}$C-NMR spectrum of compound 3bt in CDCl$_3$
Figure S109: $^1$H-NMR spectrum of compound 3bu in CDCl$_3$
Figure S110: $^{13}$C-NMR spectrum of compound 3bu in CDCl$_3$

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Figure S111: $^1$H-NMR spectrum of compound 3bv in CDCl$_3$
Figure S112: $^{13}$C-NMR spectrum of compound 3bv in CDCl$_3$
Figure S113: $^1$H-NMR spectrum of compound 3bw in CDCl$_3$
Figure S114: $^{13}$C-NMR spectrum of compound 3bw in CDCl$_3$
Figure S115: $^1$H-NMR spectrum of compound 3bx in CDCl$_3$
Figure S116: $^{13}$C-NMR spectrum of compound 3bx in CDCl$_3$
Figure S117: $^1$H-NMR spectrum of compound 3by in CDCl$_3$
Figure S118: $^{13}$C-NMR spectrum of compound 3by in CDCl$_3$
Figure S119: $^1$H-NMR spectrum of compound 3bz in CDCl$_3$
Figure S120: $^{13}$C-NMR spectrum of compound 3bz in CDCl$_3$
Figure S121: $^1$H-NMR spectrum of compound 3ca in CDCl$_3$
Figure S122: $^{13}$C-NMR spectrum of compound 3ca in CDCl$_3$
Figure S123: $^1$H-NMR spectrum of compound 3cb in CDCl$_3$
Figure S124: $^{13}$C-NMR spectrum of compound 3cb in CDCl$_3$
Figure S125: $^1$H-NMR spectrum of compound 3cc in CDCl$_3$
Figure S126: $^{13}$C-NMR spectrum of compound 3cc in CDCl$_3$
Figure S127: $^1$H-NMR spectrum of compound 3cd in CDCl$_3$
Figure S128: $^{13}$C-NMR spectrum of compound 3cd in CDCl$_3$
Figure S129: $^1$H-NMR spectrum of compound 3ce in CDCl$_3$
Figure S130: $^{13}$C-NMR spectrum of compound 3ce in CDCl$_3$
Figure S131: $^1$H-NMR spectrum of compound 4ab in CDCl$_3$
Figure S132: $^{13}$C-NMR spectrum of compound 4ab in CDCl$_3$
Figure S133: $^1$H-NMR spectrum of compound 4ba in CDCl$_3$
Figure S134: $^{13}$C-NMR spectrum of compound 4ba in CDCl$_3$
Figure S135: $^1$H-NMR spectrum of compound 4bf in CDCl$_3$
Figure S136: $^{13}$C-NMR spectrum of compound 4bf in CDCl$_3$
Figure S137: $^1$H-NMR spectrum of compound 5ab in CDCl$_3$
Figure S138: $^{13}$C-NMR spectrum of compound 5ab in CDCl$_3$. 

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Figure S139: $^1$H-NMR spectrum of compound 3ab+5ab in CDCl$_3$
Figure S140: $^{13}$C-NMR spectrum of compound 3ab+5ab in CDCl$_3$