Synthesis and Structural Characterization of 1-(E-1-Arylpropenon-3-yl)-3,4,6-tri-O-benzyl-D-glucals and Their Transformation into Pentasubstituted (2R,3S,4R)-Chromanes via Pd-Catalyzed Cross Dehydrogenative Coupling Reaction

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ABSTRACT: We have developed an efficient methodology for the synthesis of (2R,3S,4R)-2-hydroxymethyl-3,4-dihydroxy-6-aryl-7-aroylchromanes in which the chirality at the C-2, C-3, and C-4 positions is being drawn from D-glucopyranosyl aldehyde, which in turn can be efficiently synthesized from D-glucose. Thus, the synthesis starts with the transformation of sugar aldehyde into 1-(E-1-arylpropenon-3-yl)-3,4,6-tri-O-benzyl-D-glucals using Claisen−Schmidt type condensation reaction with different acetophenones and then to 1,2-disubstituted glucals via Pd(II)-catalyzed cross dehydrogenative coupling reaction, which in turn has been efficiently converted into (2R,3S,4R)-chromanes via 6π-electrocyclization and in situ dehydrogenative aromatization.

INTRODUCTION

Chromane scaffolds are important structural units often found in many natural products and bioactive compounds that exhibit anticancer,1 anti-HIV,2 antiplasmodial,3 antibacterial,4 and antifungal activities.5 The chromane core makes the structural framework of complex compounds, including constituents of vitamin E, catechin, micro Quinn, equol, hematoxalin, brazill, and other pharmaceutical drugs, such as symakalin, ormeloxifene, cromakalim, sideroxylonal A, procyandin B3, etc. (Figure 1).6

The biological importance of chiral chromanes accelerated the development of efficient methods for their synthesis. Among many reported strategies, the reaction of salicylaldehyde and enolates or their equivalents from acetophenones has gained prominent attention.7 In most of the reported methods, the oxygenated heterocyclic ring of chromane has been constructed on the prefunctionalized aromatic ring systems to get such structural motifs, which generated different levels of complexity in bringing defined chirality at the C-2, C-3, or C-4 position of chromanes.8 Due to these prefunctionalization issues, utility of Pd-catalyzed direct C–C bond formation via cross dehydrogenative coupling (CDC) reaction at the C-1 or C-2 position of glucals has emerged as an excellent tool with an advantage of higher atom economy and fewer steps than conventional synthesis.9

The arduous task of constructing an aromatic system onto the glycopyranose ring to synthesize chiral chromanes was first addressed by Werz and co-workers10 using functionalized 2-bromoglycals. Recently, we have reported the synthesis of tetrasubstituted 2R,3S-chromane from C-1-substituted glucal diene using Pd(II)-catalyzed oxidative cross coupling reaction of different alkenes followed by thermal oxidative electrocyclization.11 Herein, we report a better divergent route for the synthesis of 1-(E-1-arylpropenon-3-yl)-3,4,6-tri-O-benzyl-D-glucals and their transformation into pentasubstituted (2R,3S,4R)-chromanes via Pd(II)-catalyzed cross dehydrogenative coupling reaction with various alkenes followed by 6π-electrocyclization and in situ dehydrogenative aromatization.

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RESULTS AND DISCUSSION

The precursor C-glucopyranosyl aldehyde 1 for the synthesis of stereochemically defined chromanes was synthesized from D-glucose following a literature procedure.\(^1\) It was envisioned that Claisen−Schmidt condensation of C-glucosyl aldehyde with acetophenones in the presence of base should led to the formation of chalcone-type of compounds, i.e., 1-(E-1-arylpropen-3-yl)-3,4,6-tri-O-benzyl-D-glucals. With this aim, condensation of sugar aldehyde 1 with 4-methyl acetophenone (2a) was carried out in the presence of DBU and NaOMe as a base in EtOH and MeOH, respectively, which led to the formation of a mixture of glucal propenone 3a and glucal aldehyde 4 in different ratios with later as the dominant product (Scheme 1, Table 1, entries 1 and 2).

Further, the use of organic bases such as pyrrolidine, piperidine, or NEt\(_3\)-proline (1:1) in DCM, EtOH, or MeOH, respectively, for condensation of compounds 1 and 2a led to the exclusive formation of glucal aldehyde 4 in 75 to 78% yields (Table 1, entries 3−5).\(^13\) However, the use of Ba(OH)\(_2\), KOH, LiOH, and NaOH in EtOH led to the exclusive formation of glucal propenone 3a in 65, 75, 70, and 85% yields, respectively (Table 1, entries 6−9). The use of NaOAc in EtOH/H\(_2\)O (1:1) for the condensation reaction did not yield any product (Table 1, entries 10). The reaction carried out under the conditions of entry 9, but in the absence of acetophenone, (2a) led to the formation of glucal aldehyde 4 only in 92% yield (Table 1, entry 11). The analysis of results of these experiments showed that 5% aq. NaOH in EtOH is the most suitable and highest yielding base for synthesizing compounds 3a and also glucal aldehyde 4 in the absence of 4-methyl acetophenone (2a) (Table 1, entries 9 and 11). The optimized conditions were used for the synthesis of C-1-functionalized unsaturated sugar derivatives 3a−j by condensation of sugar aldehyde 1 with aryl methyl ketones 2a−j in 68−88% yields (Scheme 1).

![Figure 1. Examples of natural products and bioactive compounds with the chiral chromane-core.](https://doi.org/10.1021/acsomega.1c00103)

**Table 1. Condensation of 4-Methyl Acetophenone (2a) with Sugar Aldehyde 1 in Various Solvents at 25 °C in the Presence of Different Bases and Reaction Times Ranging from 2 to 24 h**

| entry | solvent | base | reaction time (h) | glucalpropenone 3a (% yield) | glucal aldehyde 4 (% yield) |
|-------|---------|------|-------------------|-----------------------------|-----------------------------|
| 1     | EtOH    | DBU  | 6                 | 25                          | 50                          |
| 2     | MeOH    | NaOMe| 3                 | 30                          | 50                          |
| 3     | DCM     | Pyrrolidine | 3 | 0                 | 75                          |
| 4     | EtOH    | Piperidine | 24   | 0                 | 75                          |
| 5     | MeOH    | NEt\(_3\)-proline (1:1) | 24   | 0                 | 78                          |
| 6     | EtOH    | Ba(OH)\(_2\) | 8 | 65                | 0                           |
| 7     | EtOH    | KOH  | 2                 | 75                          | 0                           |
| 8     | EtOH    | LiOH | 3                 | 70                          | 0                           |
| 9     | EtOH    | NaOH | 2                 | 85                          | 0                           |
| 10    | EtOH/ H\(_2\)O (1:1) | NaOAc | 24 | NR                | NR                          |
| 11    | EtOH    | NaOH | 2                 | 92                          | 0                           |

\(^{a}\)Reaction conditions: Compound 1 (0.181 mmol), 2a (0.181 mmol); \(^{b}\)base (1 equiv.); \(^{c}\)5% aq. base (1 mL); NR = No reaction. \(^{d}\)Solvent used (1 mL). \(^{e}\)Isolated yield. \(^{f}\)Reaction performed without 2a.

A representative mechanism for the synthesis of glucalpropenone 3a from the condensation of C-glucosyl aldehyde 1 and acetophenone (2a) is shown in Scheme 2. The formation of product 3a\(^1\) without a double bond in the sugar ring as shown in the bracket in Scheme 2 was not observed in any of the reaction conditions mentioned in Table 1.

The formation of a mixture of glucalpropenone 3a and glucal aldehyde 4 in condensation reaction in the presence of DBU in EtOH and NaOMe in MeOH (Table 1, entries 1 and 2), the exclusive formation of glucal aldehyde 4 in reactions at entries 3−5 in Table 1, and exclusive formation of compound...
3a in reactions at entries 6–9 in Table 1 have been observed. These results indicate that C-glucosyl aldehyde 1 first gets converted into glucal aldehyde 4, which then condenses with the enolate formed from acetophenone to yield compound 3a (Scheme 2). This is also supported by the HRMS (ESI) data analysis of the reaction mixture after time intervals of 10, 30, and 45 min of the addition of aq. NaOH to the mixture of compounds 1 and 2a, which showed peaks at \( m/z \) [M + Na]+ for aldehyde 1 (calcd 575.2404; found 575.2402), glucal propenone 3a (calcd 583.2455; found 583.2461), and glucal aldehyde 4 (calcd 467.1829; found 467.1820), but the corresponding peak for saturated sugar propenone 3a′, which should appear at \( m/z \) 691.3030, was not observed. It was also demonstrated that glucalpropenone 3a can also be prepared from condensation of glucal aldehyde 4 and 4-methyl acetophenone (2a) in EtOH in the presence of 5% aq. NaOH in 90% yield.

Three C-1-substituted glucalpropenones 3a–c out of the 10 compounds 3a–j synthesized by Claisen–Schmidt type condensation of sugar aldehyde 1 and aryl methyl ketones 2a–c were converted into 1,2-disubstituted glucals 6a–i by their Pd(II)-catalyzed cross dehydrogenative coupling (CDC) reaction with different terminal alkenes 5a–g. Initially, the Pd(II)-catalyzed CDC reaction for the synthesis of 1,2-disubstituted glucals was optimized by carrying out the reaction in the presence of different alkenes in a solvent or in a mixture of solvents. Thus, the reaction of glucalpropenone 3a and 4-methylstyrene (5a) in the presence of Pd(OAc)2 (10 mol %) and Cu(OAc)2, AgOAc, or AgOTf (2 equiv.) as an oxidant in a mixture of DMF/DMSO (9:1, v/v) at 80 °C led to the formation of the desired 1,2-disubstituted glucal 6a in 20, 50, and 40% yields, respectively (Table 2, entries 1–3). Usage of a mixture, rather than lone oxidants, i.e., Cu(OAc)2 (1 equiv.)/AgOAc (2 equiv.) or CuI (1 equiv.)/AgOTf (2 equiv.), in a mixture of DMF/DMSO (9:1, v/v) increased the yields of formation of 6a to 80 and 85%, respectively (Table 2, entries 4–5). However, a change of the solvent system from DMF/DMSO to pure THF, DMF, acetonitrile, acetone, and dichloroethane resulted in lower yields, while the use of dioxane and toluene did not yield the desired product 6a at all (Table 2, entries 6–12). The change of Pd-salt from Pd(OAc)2 to PdCl2 or Pd(PPh3)2Cl2 also resulted in the lowering of yields to 40 and 50% (Table 2, entries 13–14).

The optimized conditions, i.e., the Pd(OAc)2-catalyst in the presence of a mixture of CuI (1 equiv.)/AgOTf (2 equiv.) as the oxidant in DMF/DMSO (9:1, v/v), were used for CDC reaction of glucalpropenone 3a with various styrenes and acrylates 5a–f, such as 4-methyl styrene (5a), styrene (5b), 4-

Table 2. Optimization of Condition for CDC Reaction of C-1-glucalpropenone 3a with 4-Methylstyrene (5a) to Synthesize 1,2-Disubstituted Glucal 6a at 80 °C for 12 h

| entry | catalyst (10 mol %) | oxidant (equiv.) | co-oxidant (equiv.) | solvent | yield of 6a (%)b |
|-------|--------------------|-----------------|-------------------|--------|-----------------|
| 1     | Pd(OAc)2           | Cu(OAc)2 (2)    | -                 | DMF/DMSO (9:1) | 20              |
| 2     | Pd(OAc)2           | AgOAc (2)       | -                 | DMF/DMSO (9:1) | 50              |
| 3     | Pd(OAc)2           | AgOTf(2)        | -                 | DMF/DMSO (9:1) | 40              |
| 4     | Pd(OAc)2           | Cu(OAc)2(1)     | AgOAc (2)         | DMF/DMSO (9:1) | 80              |
| 5     | Pd(OAc)2           | CuI (1)         | AgOTf (2)         | DMF/DMSO (9:1) | 85              |
| 6     | Pd(OAc)2           | Cu(OAc)2(1)     | AgOAc (2)         | THF     | 50              |
| 7     | Pd(OAc)2           | Cu(OAc)2(1)     | AgOAc (2)         | DMF     | 65              |
| 8     | Pd(OAc)2           | Cu(OAc)2(1)     | AgOAc (2)         | AcCN    | 55              |
| 9     | Pd(OAc)2           | Cu(OAc)2(1)     | AgOAc (2)         | acetone | 60              |
| 10    | Pd(OAc)2           | Cu(OAc)2(1)     | AgOAc (2)         | DCE     | 70              |
| 11    | Pd(OAc)2           | Cu(OAc)2(1)     | AgOAc (2)         | dioxane | NR              |
| 12    | Pd(OAc)2           | Cu(OAc)2(1)     | AgOAc (2)         | toluene | NR              |
| 13    | PdCl2              | CuI (1)         | AgOTf (2)         | DMF/DMSO (9:1) | 40              |
| 14    | Pd(PPh3)2Cl2       | CuI (1)         | AgOTf (2)         | DMF/DMSO (9:1) | 50              |

aReaction conditions: Compound 3a (0.18 mmol), 5a (0.2 mmol); solvent used (2 mL); NR = No reaction. bIsolated yield.
nitrostyrene (5c), 2-chlorostyrene (5d), 2,2,2-trifluoroethylacrylate (5e), and benzyl acrylate (5f), to afford the corresponding 1,2-disubstituted glucals 6a–f with (E)-stereoselectivity in 78–88% yields. The broader substrate scope of the optimized reaction was further demonstrated by the successful CDC reaction of glucalpropenone 3b with styrene 5b and glucalpropenone 3c with 4-methyl styrene (5a) and 4-methoxy styrene (5g) to afford 1,2-disubstituted glucals 6g–i in 80 to 90% yields (Scheme 3).

The CDC products 1,2-disubstituted glucals 6a–i containing an E,Z,E-triene system on 6π-electrocyclization in xylene in a sealed vessel at 160 °C followed by in situ dehydrogenative aromatization afforded (2R,3S,4R)-2-benzyloxymethyl-3,4-dihydroxy-6-aryl-7-aroyloxychromanes 7a–d and 7g–i in 66–73% yields. The electrocyclization of disubstituted glucals 6e and 6f bearing C-6 carbo(2,2,2-trifluoro)-ethoxy and carbobenzoxyl substituents led to the decomposition of the starting material (Scheme 4). The electrocyclization reaction carried out in hexamethylphosphoramide (HMPA), ethylene glycol, or nitrobenzene at different temperatures either led to no reaction or decomposition of the starting material or formation of the product albeit in much lower yield. Further, an attempt to isolate the cyclohexadiene intermediate on electrocyclization of 1,2-disubstituted glucals by carrying out the reaction at a different temperature under a N2 atmosphere or by cooling the incomplete reaction mixture to −10 °C was unsuccessful.

The debenzylation of compound 7a was initially tried by hydrogenation with 10% Pd/C-H2 in methanol at 25 °C. Although Pd/C-H2 in methanol efficiently afforded complete debenzylation in compound 7a, it also led to the reduction of benzoyl to the benzyl group at the C-7 position of chromane to afford compound 9a. Finally, debenzylation of chromane 7a–d and 7g–i were effected with 1 M BCl3 in DCM at −78 °C to afford (2R,3S,4R)-2-hydroxymethyl-3,4-dihydroxy-6-aryl-7-aroyloxychromanes 8a–d and 8g–i in 82–92% yields (Scheme 4).

A plausible mechanism for the formation of chromane 7 via Pd-catalyzed CDC reaction of glucalpropenone 3 with styrene/acrylate 5 followed by 6π-electrocyclization reaction of the resulting 1,2-disubstituted glucal 6 starts with the heteroatom-directed electrophilic reaction of Pd(II) species at the electron-rich C2-carbon of glucalpropenone 3. This follows
hydrogen abstraction resulting in the formation of C2-palladized intermediate I, which on olefin coordination and carbopalladation afforded C2-alkyl-palladium intermediate II. Finally, β-hydride elimination from the second intermediate led to the formation of 1,2-disubstituted glucal 6. The Pd(0) generated after the reductive elimination step is regenerated to active Pd(II) species by CuI and AgOTf to maintain the continuity of the catalytic cycle. Further, 1,2-disubstituted glucal 6 on heating in xylene at 160 °C undergoes 6π-electrocyclization to an unstable cyclic diene intermediate III that spontaneously undergoes in situ dehydrogenative aromatization to afford chiral chromane 7 (Scheme 5). The structures of all synthesized compounds, i.e., 3a−j, 4, 6a−i, 7a−d, 7g−i, 8a−d, 8g−i, and 9a, were unambiguously established based on their IR, 1H-, 13C-, 19F NMR spectra and HRMS data analysis. The structure of known compound 4 was further confirmed by comparison of its spectral data with those reported in the literature. Further, the structure of compound 8a was unambiguously confirmed based on their X-ray data analysis (Figure 2, details in the Supporting Information).

Scheme 5. Plausible Reaction Mechanism for Formation of 1,2-Disubstituted Glucal 6 and Its Conversion into (2R,3S,4R)-Pentasubstituted Chromane 7

Figure 2. ORTEP diagram of compound 8a drawn in 50% thermal probability ellipsoids showing the atomic numbering scheme. Solvent molecules in the lattice are omitted for the sake of clarity. Only one molecule of the asymmetric unit has been shown.
defined chromanes for drug discovery application and therefore is more useful.

**EXPERIMENTAL SECTION**

**General.** All commercially available reagents and absorbents were used without further purification. All solvents were distilled before use. The IR spectra were recorded on a PerkinElmer model 2000 FTIR spectrometer by making a KBr disk for solid samples. $^{1}H$, $^{13}C$, and $^{19}F$-NMR spectra were recorded on JEOL Delta 400, 100.6, and 376 MHz spectrometers, respectively, using tetramethylsilane (TMS) as an internal standard. The chemical shift values are on the δ scale, and the coupling constant (J) are in hertz. HRMS recording was carried out using a Q-TOF mass spectrometer in ESI mode. The specific rotations of synthesized compounds were measured on a Rudolph autopol II automatic polarimeter using light of 589 nm wavelength. Analytical TLCs were performed on precoated fluorescent plates; visualization of the developed plates was performed under UV light or by charring with 5% alcoholic H$_2$SO$_4$ solution. Silica gel (100–200 mesh) was used for column chromatography.

**General Procedure for Synthesis of 1-[E-(1-Arylpropen-3-yl)-3,4,6-tri-O-benzyl-d-glucal (3a)].** To a solution of β-C-glucopyranosyl aldehyde 1 (600 mg, 1.09 mmol) and aryl methyl ketones 2a-j (1.09 mmol) in ethanol (12 mL), an aqueous solution of 5% NaOH (12 mL) was added dropwise with continuous stirring at 0 °C and further stirred for 2–6 h at 25 °C. After completion of the reaction as indicated by TLC examination, the reaction mixture was concentrated at reduced pressure keeping bath temperature below 40 °C and the thick liquid thus obtained was extracted with ethyl acetate (2 × 50 mL). The combined organic layer was dried over Na$_2$SO$_4$ filtered, and concentrated at reduced pressure to give the crude product, which was purified over a silica gel column with 5–10% ethyl acetate in petroleum ether as the eluent to afford pure products 3a–j in 68 to 88% yields.

$^{1}$H NMR (400 MHz, CDCl$_3$): δ 2.42 (s, 3H), 3.83–3.96 (m, 3H), 4.19–4.23 (m, 1H), 4.31 (dd, 1H, J = 3.2 and 5.8 Hz), 4.58–4.71 (m, 5H), 4.84 (d, 1H, J = 11.3 Hz), 5.35 (d, 1H, J = 3.1 Hz), 7.07 (d, 1H, J = 15.1 Hz), 7.25–7.37 (m, 18H), 7.89 (d, 2H, J = 8.0 Hz); $^{13}$C NMR (100.6 MHz, CDCl$_3$): δ 21.8, 68.4, 71.0, 73.5, 73.8, 74.1, 76.2, 77.3, 109.1, 123.0, 127.8, 127.9, 128.1, 128.6, 129.4, 130.2, 132.0, 136.7, 138.0, 138.1, 143.9, 150.7, 189.9; HRMS (ESI) m/z: [M + Na]$^+$ calcd for C$_{5}H$_{58}Na$_{3}$O$_{5}$ 832.2455; found 832.2461.

$^{1}$H NMR (400 MHz, CDCl$_3$): δ 2.42–2.43 (m, 1H), 4.31 (dd, 1H, J = 3.1 and 5.6 Hz), 4.58–4.71 (m, 5H), 4.84 (d, 1H, J = 11.4 Hz), 5.35 (d, 1H, J = 3.0 Hz), 6.95 (d, 2H, J = 8.6 Hz), 7.07 (d, 1H, J = 15.2 Hz), 7.25–7.37 (m, 16H), 7.99 (d, 2H, J = 8.8 Hz); $^{13}$C NMR (100.6 MHz, CDCl$_3$): δ 35.5, 66.8, 74.0, 73.4, 73.8, 74.1, 76.2, 77.3, 108.9, 113.9, 122.9, 127.7, 127.9, 128.0, 128.5, 128.6, 130.9, 131.0, 137.3, 138.1, 138.2, 150.8, 163.6, 188.6; HRMS (ESI) m/z: [M + Na]$^+$ calcd for C$_{57}H$_{48}Na$_{3}$O$_{5}$ 599.2404; found 599.2411.
3.95 (m, 3H), 4.20–4.22 (m, 1H), 4.30 (dd, 1H, J = 3.2 and 5.4 Hz), 4.58–4.70 (m, 5H), 4.84 (d, 1H, J = 11.3 Hz), 5.38 (d, 1H, J = 2.9 Hz), 7.08 (d, 1H, J = 15.0 Hz), 7.25–7.36 (m, 16H), 7.44 (d, 2H, J = 8.4 Hz), 7.91 (d, 2H, J = 8.4 Hz); \[^{13}C\](1H) NMR (100.6 MHz, CDCl₃): δ 68.3, 71.1, 73.5, 73.8, 74.0, 76.0, 77.3, 109.7, 122.4, 127.7, 127.8, 127.9, 128.0, 128.5, 128.6, 129.0, 131.6, 132.0, 138.1, 138.4, 139.0, 150.5, 189.0; HRMS (ESI) m/z: [M + Na]^+ calcd for C₃₆H₃₄NaO₆ 585.2279; found 585.2279.

**General Procedure for the Synthesis of 1,2-Disubstituted Glucal (6a–i).** Glucalpropones 3a–c (400 mg, 1 equiv.), styrenes/acrylates 5a–g (1.1 equiv.), AgOTf (2 equiv.), CuI (1 equiv.), and Pd(OAc)₂ (10 mol %) in a solvent mixture of DMF/DMSO (8 mL, v/v 9/1) were stirred at 80 °C in a 15 mL sealed tube for 12 h. After completion of the reaction as indicated on TLC examination, the resulting mixture was cooled to room temperature and extracted with ethyl acetate (2 × 50 mL). The combined organic phase was washed with brine (1 × 20 mL), dried over Na₂SO₄ and filtered. The organic phase was concentrated at reduced pressure, and the resulting residue was purified by silic gel column chromatography using ethyl acetate/petroleum ether (5–10%) as the eluent to furnish the desired products 6a–i in 78 to 90% yields.

1-[1-(4-Methylphenyl)propen-3-yl]-2-(4-methyl)styryl-3,4,6-tri-0-benzyl-o-glucal (6b). It was obtained as a yellow solid (410 mg) in 85% yield; mp: 182–185 °C; IR (KBr, cm⁻¹): 3030, 2916 1724, 1654, 1604, 1573, 1502, 1452, 1367, 1288, 1209, 1180, 1093, 1022, 956, 846, 812, 738, 694; [\[^{13}C\]m] = −14.38 (c 0.1, dichloromethane); \[^{1}H\] NMR (400 MHz, CDCl₃): δ 2.35 (s, 3H), 2.43 (s, 3H), 3.82–3.89 (m, 2H), 4.18 (t, 1H, J = 4.0 Hz), 4.43–4.51 (dd, 3H, J = 10.7 and 20.4 Hz), 4.57 (s, 2H), 4.62 (d, 1H, J = 3.1 Hz), 4.74–4.81 (m, 2H), 6.60 (d, 1H, J = 15.9 Hz), 7.13 (d, 2H, J = 7.7 Hz), 7.24 (d, 3H, J = 7.0 Hz), 7.28–7.37 (m, 18H), 7.56 (d, 1H, J = 14.7 Hz), 7.93 (d, 2H, J = 7.1 Hz); \[^{13}C\](1H) NMR (100.6 MHz, CDCl₃): δ 21.4, 21.8, 68.5, 69.3, 71.1, 72.2, 73.3, 73.5, 76.0, 118.5, 121.8, 123.8, 126.5, 127.7, 127.8, 128.0, 128.1, 128.2, 128.4, 128.5, 128.6, 128.7, 128.9, 129.3, 129.4, 132.7, 134.9, 135.6, 136.7, 137.9, 138.1, 143.9, 148.9, 189.6; HRMS (ESI) m/z: [M + H]^+ calcd for C₄₆H₄₉O₇ 677.3262; found 677.3257.
1H, J = 14.7 Hz), 7.83–7.89 (m, 3H), 8.09 (d, 2H, J = 8.7 Hz); 13C[1H] NMR (100.6 MHz, CDCl3): δ 21.9, 68.8, 69.7, 70.3, 72.2, 73.5, 73.9, 75.9, 116.9, 124.2, 125.2, 126.2, 126.8, 127.3, 127.7, 127.9, 128.2, 128.3, 128.5, 128.6, 128.7, 128.9, 129.5, 130.2, 135.3, 137.2, 137.7, 138.0, 140.4, 144.3, 146.6, 150.8, 189.3; HRMS (ESI) m/z: [M + H]+ calc for C47H45O7 721.3160; found 721.3168.

1-[1-(4-Methylphenyl)propenon-3-yl]-2-(2-chloro)styryl-3,4,6-tri-O-benzyl-D-glucal (6d). It was obtained as a yellow solid (397 mg) in 80% yield; mp: 165–168 °C; IR (KBr, cm−1): 3034, 2928, 2875, 1651, 1606, 1575, 1496, 1369, 1323, 1290, 1211, 1182, 1095, 1031, 954, 910, 846, 815, 736, 694; [α]250 = +76.33 (c 0.1, dichloromethane); 1H NMR (400 MHz, CDCl3): δ 2.43 (s, 3H), 3.76–3.86 (m, 2H), 4.11 (t, 1H, J = 3.7 Hz), 4.51–4.61 (m, 6H), 4.75 (s, 2H), 7.11 (d, 1H, J = 16.0 Hz), 7.18 (d, 1H, J = 7.4 Hz), 7.25 (d, 6H, J = 6.6 Hz), 7.29–7.34 (m, 10H), 7.37 (d, 4H, J = 4.3 Hz), 7.59 (d, 1H, J = 14.7 Hz), 7.68 (d, 1H, J = 7.8 Hz), 7.92–7.96 (m, 3H); 13C[1H] NMR (100.6 MHz, CDCl3): δ 21.8, 68.4, 70.7, 71.0, 72.1, 72.9, 73.5, 75.9, 117.8, 124.5, 125.5, 126.4, 127.1, 127.7, 127.8, 128.0, 128.1, 128.2, 128.3, 128.5, 128.7, 129.8, 129.9, 132.5, 133.3, 135.5, 136.5, 137.7, 137.8, 141.4, 149.1, 189.5; HRMS (ESI) m/z: [M + H]+ calc for C46H44O5S 679.2715; found 679.2709.

1-[1-(4-Methylphenyl)propenon-3-yl]-2-(2,2,2-trifluoro-ethyl acrylat-3-yl)-3,4,6-tri-O-benzyl-D-glucal (6e). It was obtained as a pale yellow gel (397 mg) in 80% yield; mp: 184–188 °C; IR (KBr, cm−1): 2922, 2858, 1739, 1655, 1581, 1458, 1370, 1294, 1213, 1180, 1105, 1036, 1011, 956, 824, 743, 697; [α]250 = +12.60 (c 0.1, dichloromethane); 1H NMR (400 MHz, CDCl3): δ 2.35 (s, 3H), 3.81–3.88 (m, 2H), 4.16–4.18 (m, 1H), 4.45–4.51 (m, 3H), 4.56–4.62 (m, 3H), 4.77 (s, 2H), 6.59 (d, 1H, J = 15.9 Hz), 7.13 (d, 2H, J = 6.5 Hz), 7.23–7.36 (m, 18H), 7.49 (d, 1H, J = 14.7 Hz), 7.60–7.62 (m, 2H), 7.87–7.89 (m, 2H), 7.97 (d, 1H, J = 14.7 Hz); 13C[1H] NMR (100.6 MHz, CDCl3): δ 21.4, 68.5, 69.5, 71.0, 72.2, 73.1, 73.5, 76.0, 119.2, 121.6, 123.0, 126.5, 127.7, 127.8, 128.1, 128.4, 128.6, 129.5, 129.7, 130.2, 132.0, 133.6, 134.7, 136.8, 137.5, 137.8, 138.1, 184.8, 188.9; HRMS (ESI) m/z: [M + H]+ calc for C45H44BrO4 741.2210; found 741.2208.

1-[1-(4-Methylphenyl)propenon-3-yl]-2-(4-methoxy)-styryl-3,4,6-tri-O-benzyl-D-glucal (6f). It was obtained as a white solid (388 mg) in 80% yield; mp: 182–187 °C; IR (KBr, cm−1): 2921, 2853, 1647, 1579, 1510, 1456, 1368, 1279, 1172, 1098, 1030, 1005, 951, 819, 736, 679; [α]250 = +81.09 (c 0.1, dichloromethane); 1H NMR (400 MHz, CDCl3): δ 3.80–3.89 (m, 5H), 4.16–4.18 (m, 1H), 4.42–4.45 (m, 2H), 4.50 (d, 1H, J = 11.2 Hz), 4.57 (s, 2H), 4.60 (d, 1H, J = 3.4 Hz), 4.77 (dd, 2H, J = 3.3 and 12.0 Hz), 6.57 (d, 1H, J = 16.0 Hz), 6.87 (d, 2H, J = 8.7 Hz), 7.14 (d, 1H, J = 16.0 Hz), 7.22–7.24 (m, 2H), 7.28–7.37 (m, 15H), 7.48 (d, 1H, J = 14.7 Hz), 7.61 (d, 2H, J = 8.5 Hz), 7.88 (d, 2H, J = 8.5 Hz), 7.97 (d, 1H, J = 14.7 Hz); 13C[1H] NMR (100.6 MHz, CDCl3): δ 55.4, 68.5, 69.4, 71.1, 72.2, 73.2, 73.5, 76.0, 114.2, 119.2, 120.6, 122.8, 127.7, 127.8, 127.9, 128.0, 128.1, 128.4, 128.6, 128.7, 129.0, 130.9, 131.0, 131.3, 133.1, 136.7, 137.6, 137.8, 138.1, 148.2, 159.5, 188.9; HRMS (ESI) m/z: [M + H]+ calc for C45H44O4Br 757.2159; found 757.2163.

**General Procedure for the Synthesis of Chiral Chromane Derivatives (7a–d and 7g–i).** In a 15 mL sealed tube, compound 6a–i (350 mg, 1 equiv.) was dissolved in xylene (5 mL) and the reaction mixture was stirred at 160 °C for 2 h (progress of reaction was monitored by thin layer chromatography). After completion, the solvent was removed over a rotary evaporator and the thick liquid thus obtained was extracted with ethyl acetate (2 × 15 mL). The organic phase was washed with saturated aqueous NaCl (1 × 10 mL), dried over Na2SO4 and filtered. Ethyl acetate was evaporated on a rotavapor, and the resulting residue was purified by silica gel column chromatography using 5–10% ethyl acetate in petroleum ether as an eluent to obtain the desired products.
It was obtained as a pale yellow oily compound (255 mg) in 73% yield; IR (cm⁻¹, thin film): 3060, 3027, 2922, 2888, 1657, 1598, 1505, 1452, 1412, 1362, 1295, 1254, 1212, 1168, 1085, 1023, 911, 842, 802, 741, 697; [α]D² = +53.56 (c 0.1, dichloromethane); ¹H NMR (400 MHz, CDCl₃): δ 3.78 (s, 3H), 3.86 (ddd, 2H, J = 4.6, 10.8, and 14.2 Hz), 4.17 (t, 1H, J = 6.9 Hz), 4.39 (dt, 1H, J = 4.1 and 7.8 Hz), 4.60 (d, 2H, J = 1.9 Hz), 4.72−4.83 (m, 2H, J = 4.0 and 15.6 Hz), 7.03−7.14 (m, 4H, J = 2.1 Hz), 7.29−7.39 (m, 2H, J = 4.1 Hz), 7.16 (d, 4H, J = 4.4 Hz), 7.28−7.35 (m, 17H), 7.65 (d, 2H, J = 8.9 Hz). ¹³C NMR (100 MHz, CDCl₃): δ 55.5, 68.8, 72.7, 73.6, 73.7, 74.0, 77.3, 113.5, 117.0, 123.7, 127.0, 127.9, 128.1, 128.3, 128.5, 128.6, 128.9, 130.1, 130.9, 132.5, 133.7, 137.8, 138.0, 139.9, 140.3, 152.6, 163.5, 196.6; HRMS (ESI) m/z: [M + H]⁺ calcd for C₄₅H₄₁O₅ 677.2898; found 677.2879.

(2R,3S,4R)-2-Benzoyloxymethyl-3,4-dibenzyloxy-6-phenyl-7-(4-methyl)phenyl-7-(4-methyl)benzolchromene (7c). It was obtained as a brown oily compound (230 mg) in 72% yield; IR (cm⁻¹, thin film): 3075, 3024, 2862, 1605, 1522, 1477, 1345, 1217, 1106, 1069, 1020, 1005, 933, 851, 792, 749; [α]D² = −16.36 (c 0.1, dichloromethane); ¹H NMR (400 MHz, CDCl₃): δ 2.25 (s, 3H), 3.83−3.93 (m, 2H, J = 4.1 Hz, δ 7.03−7.14 (m, 4H, J = 2.1 Hz), 4.74−4.84 (m, 5H, J = 4.0 Hz), 7.28−7.32 (m, 2H, J = 7.8 Hz), 7.33−7.35 (m, 17H), 7.40 (d, 2H, J = 8.5 Hz), 7.51 (d, 2H, J = 8.6 Hz). ¹³C NMR (100 MHz, CDCl₃): δ 21.1, 68.8, 72.8, 73.6, 73.7, 74.0, 77.4, 112.1, 124.9, 127.9, 128.0, 128.1, 130.2, 130.8, 130.9, 132.8, 138.7, 138.9, 140.3, 143.9, 152.2, 179; HRMS (ESI) m/z: [M + H]⁺ calcd for C₄₅H₄₁O₅ 677.2898; found 677.2879.

(2R,3S,4R)-2-Benzoyloxymethyl-3,4-dibenzyloxy-6-(4-nitro)phenyl-7-(4-methyl)benzolchromene (7c). It was obtained as a brown oily compound (230 mg) in 66% yield; IR (cm⁻¹, thin film): 3062, 3030, 2921, 2858, 1710, 1602, 1601, 1564, 1516, 1454, 1344, 1291, 1254, 1212, 1177, 1094, 1028, 914, 854, 746, 699; [α]D² = −9.81 (c 0.1, dichloromethane); ¹H NMR (400 MHz, CDCl₃): δ 2.28 (s, 3H), 3.81 (ddd, 2H, J = 4.0, 10.9, and 14.0 Hz), 4.11 (t, 1H, J = 7.0 Hz), 4.33−4.37 (m, 1H), 4.54 (d, 2H, J = 1.7 Hz), 4.66−4.80 (m, 5H, J = 8.5 Hz), 6.96 (s, 1H), 7.05 (d, 2H, J = 8 Hz), 7.17−7.25 (m, 10H), 7.27 (s, 8H), 7.52 (d, 2H, J = 8.0 Hz), 7.97 (d, 2H, J = 8.5 Hz). ¹³C NMR (100 MHz, CDCl₃): δ 21.8, 68.6, 73.1, 73.7, 73.8, 73.9, 76.5, 77.7, 117.7, 123.6, 124.4, 127.9, 128.1, 128.2, 128.5, 128.7, 129.3, 129.6, 130.3, 131.0, 131.5, 134.3, 137.7, 139.7, 140.2, 144.6, 146.7, 153.6, 196.7; HRMS (ESI) m/z: [M + H]⁺ calcd for C₄₅H₄₆NO₂ 706.2799; found 706.2809.

(2R,3S,4R)-2-Benzoyloxymethyl-3,4-dibenzyloxy-6-(2-chlorophenyl)-7-(4-methyl)benzolchromene (7d). It was obtained as a pale yellow oily compound (241 mg) in 74% yield; IR (cm⁻¹, thin film): 3032, 2981, 2882, 1663, 1607, 1566, 1458, 1406, 1364, 1297, 1212, 1170, 1087, 916, 831, 749, 699; [α]D² = +37.53 (c 0.1, dichloromethane); ¹H NMR (400 MHz, CDCl₃): δ 2.25 (s, 3H), 3.78−3.85 (m, 2H, J = 4.12−4.15 (m, 1H), 4.33 (s, 1H), 4.47−4.62 (m, 3H), 4.64−4.76 (m, 4H), 6.98−7.07 (m, 5H), 7.14−7.27 (m, 18H), 7.53 (d, 2H, J = 8.1 Hz). ¹³C NMR (100.6 MHz, CDCl₃): δ 21.7, 68.8, 71.4, 72.1, 73.6, 76.5, 77.2, 77.6, 117.6, 122.3, 126.4, 127.7, 127.8, 127.9, 128.0, 128.4, 128.5, 128.7, 129.4, 130.2, 132.0, 132.8, 143.4, 137.8, 138.0, 143.6, 152.9, 196.3; HRMS (ESI) m/z: [M + H]⁺ calcd for C₄₆H₄₆ClO₂ 695.2559; found 695.2555.

General Procedure for the Synthesis of Chiral Trihydroxycromane Derivatives (8a−d and 7g−i). In a 15 mL glass reaction tube, compound 7a−d and 7g−i (200 mg) was dissolved in dichloromethane (2 mL) and stirred at −78 °C. After 10 min, 1 M BCl₃ in dichloromethane (1 mL) was added dropwise to the reaction mixture and stirring was continued for another 0.5 to 1 h (progress of the reaction was monitored by TLC). On completion, the temperature of the reaction mixture was raised to −40 °C, and methanol (1 mL) was added.
was added and stirred for another 15 min. Further, the reaction mixture was stirred at room temperature for half an hour, neutralized with AmberliteIRA-402(OH) exchange resin, and filtered. The filtrate was concentrated using a rotovap, and the crude product thus obtained was purified by silica gel column chromatography using 0.5–2% methanol in chloroform as an eluent to obtain the desired products 8a–d and 8g–i in 82–92% yields.

(2R,35,4R)-2-Hydroxymethyl-3,4-dihydroxy-6-(4-methyl)-phenyl-7-(4-methyl)benzoylchromane (8a). It was obtained as an off white solid compound (106 mg) in 92% yield; mp: 110 °C; IR (KBr, cm⁻¹): 3370, 3290, 2921, 1656, 1574, 1457, 1394, 1294, 1219, 1112, 1006, 918, 824, 779, 768; [α]₂⁰ = +86.59 (c 0.1, chloroform); ¹H NMR (400 MHz, DMSO-d₆): δ 2.17 (3H, s), 3.58–3.72 (2H, m), 3.79–3.81 (1H, m), 3.92–3.96 (1H, m), 4.15–4.54 (1H, m), 4.75 (t, 1H, J = 5.7 Hz), 5.46 (d, 1H, J = 5.2 Hz), 5.78 (d, 1H, J = 6.3 Hz), 6.77 (s, 1H), 6.89–7.02 (m, 4H), 7.45–7.47 (m, 3H), 7.56 (d, 1H, J = 8.6 Hz); ¹³C{¹H} NMR (100.6 MHz, DMSO-d₆): δ 21.1, 61.0, 68.1, 70.4, 80.7, 115.3, 127.3, 128.4, 128.8, 130.0, 130.3, 130.8, 132.4, 139.3, 140.4, 152.8, 157.3, 195.9; HRMS (ESI) m/z: [M + H⁺]⁺ calcd for C₂₄H₂₃BrO₅ 407.1489; found 407.1480.

(2R,35,4R)-2-Hydroxymethyl-3,4-dihydroxy-6-(4-bromo)benzoyl-chromane (8b). It was obtained as a white solid compound (105 mg) in 83% yield; mp: 140–144 °C; IR (KBr, cm⁻¹): 3390, 2921, 1664, 1576, 1457, 1394, 1294, 1219, 1112, 1006, 918, 824, 779, 768; [α]₂⁰ = +37.31 (c 0.1, chloroform); ¹H NMR (400 MHz, DMSO-d₆): δ 3.69–3.75 (1H, m), 3.80–3.85 (1H, m), 4.15–4.54 (1H, m), 4.75 (t, 1H, J = 5.7 Hz), 5.46 (d, 1H, J = 5.2 Hz), 5.78 (d, 1H, J = 6.3 Hz), 6.77 (s, 1H), 6.98–7.02 (m, 4H), 7.45–7.47 (m, 3H), 7.56 (d, 1H, J = 8.6 Hz); ¹³C{¹H} NMR (100.6 MHz, DMSO-d₆): δ 21.1, 61.0, 68.1, 70.4, 80.7, 115.3, 127.3, 128.8, 128.8, 130.0, 130.3, 131.8, 132.2, 137.1, 138.2, 139.6, 152.7, 195.7; HRMS (ESI) m/z: [M + H⁺]⁺ calcd for C₂₄H₂₃BrO₅ 469.0645; found 469.0641.

(2R,35,4R)-2-Hydroxymethyl-3,4-dihydroxy-6-(4-methoxy)phenyl-7-(4-bromo)benzoyl-chromane (8i). It was obtained as a white solid compound (106 mg) in 88% yield; IR (KBr, cm⁻¹): 3392, 2925, 2854, 1652, 1596, 1569, 1447, 1419, 1257, 1214, 1170, 1115, 1061, 1026, 908, 847, 759, 701, 667; [α]₂⁰ = +70.35 (c 0.1, chloroform); ¹H NMR (400 MHz, DMSO-d₆): δ 2.17, 61.0, 68.1, 70.4, 80.7, 115.3, 127.3, 128.4, 128.8, 130.0, 130.3, 130.8, 132.4, 139.3, 140.4, 152.8, 157.3, 195.9; HRMS (ESI) m/z: [M + H⁺]⁺ calcd for C₂₄H₂₃ClO₅ 425.1102; found 425.1121.
chromatography using 1% methanol in chloroform as an eluent to get the pure desired product as a white solid (104 mg) in 90% yield. mp: 140–143 °C. IR (KBr, cm⁻¹): 3304, 3024, 2928, 1616, 1568, 1485, 1413, 1366, 1324, 1286, 1222, 1121, 1014, 997, 912, 879, 815, 767, 700; [α]D 20 = +71.72 (c 0.1, dichloromethane). \(^{1}H NMR (400 MHz, DMSO-d_6): \delta 2.23 (s, 3H), 3.34 (s, 3H), 3.51 (m, 1H), 3.78 (s, 2H), 3.80–3.84 (m, 2H), 4.44 (t, 1H, J = 6.9 Hz), 7.14 (d, 2H, J = 7.9 Hz), 7.19–7.22 (m, 3H); \(^{13}C(NMR (100 MHz, DMSO-d_6): \delta 21.1, 21.3, 38.8, 61.2, 68.7, 70.6, 80.3, 116.9, 124.2, 129.1, 129.3, 129.4, 129.6, 129.9, 134.2, 135.3, 136.2, 138.5, 138.7, 139.0, 153.0; HRMS (ESI) m/z: [M + Na]⁺ calc for \(\text{C}_2\text{H}_2\text{O}_4\text{Na} \) 413.1723; found 413.1755.

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