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Synthesis of Flavonoid/Chromonoid–β-D-Ribofuranose Derivatives by Palladium-Catalyzed Cross-Coupling Reactions

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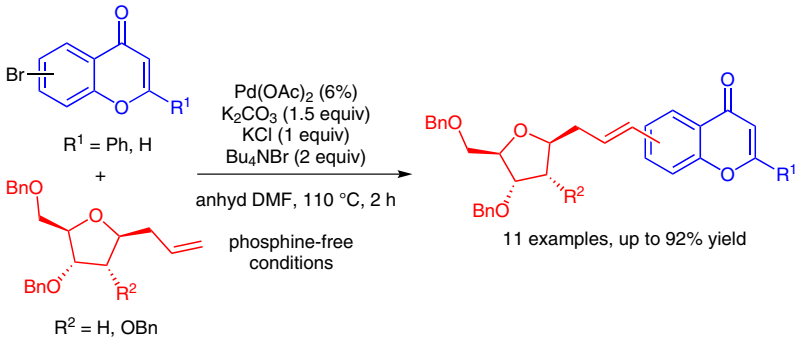
Dedicated to the memory of Professor Tamás Patonay.



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Abstract Structurally novel carbohydrate–flavone and –chromone derivatives with an unsaturated carbon bridge were synthesized by a phosphine-free palladium-catalyzed cross-coupling reaction.

Key words cross-coupling, catalysis, palladium, Mizoroki–Heck reaction, isomerism

The class of natural occurring *C*-glycosyl flavonoids that contain a *C*-glucopyranosyl moiety, for example, vitexin, orientin, isovitexin, and isoorientin (Figure 1), has recently attracted considerable attention from organic chemists, because these compounds possess a wide variety of biological activities, including anti-inflammatory activities[1] and antiviral activities.[2] The *C*-glycosyl flavonoid antioxidants kurilensin A and B were isolated from hot-water extracts of the leaves of the bamboo *Sasa kurilensis*.[3] What these compounds have common is that they all contain one or two activating groups, such as hydroxy or methoxy groups, in the 5- and 7-positions of the flavone skeleton.

C-Glycosyl compounds have an advantage over *O*-glycosides in that the C–C bond is not enzymatically degradable,[4] a feature that could be attractive in terms of the pharmacology of these compounds. In nature, the only *C*-glycosyl flavones known are those in which the aglycone is directly bonded to the carbohydrate unit at a one-bond distance. Science has no knowledge regarding changes in the biological activity resulting from modification of the distance between the aglycone moiety and the sugar moiety, because no such compounds have previously been synthesized.

Reported syntheses of the *C*-glycosyl flavones often start from acetophenone derivatives that already contain a sugar moiety, and they usually require additional steps

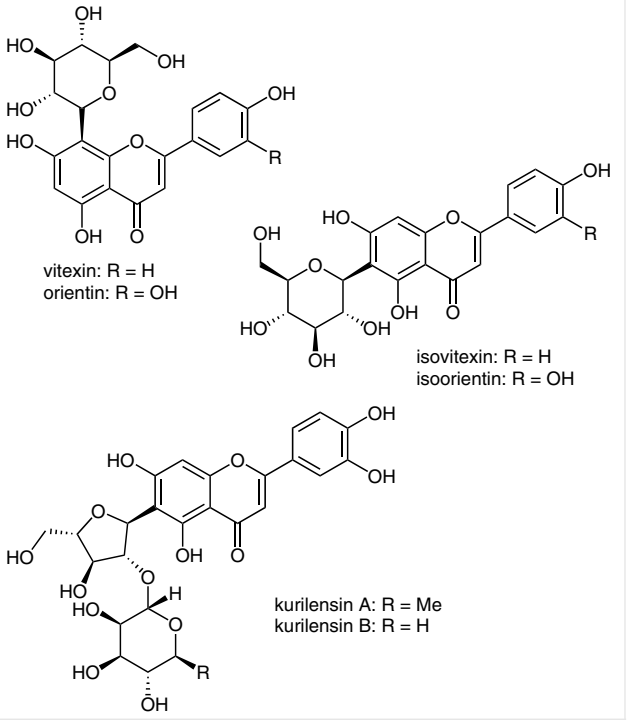


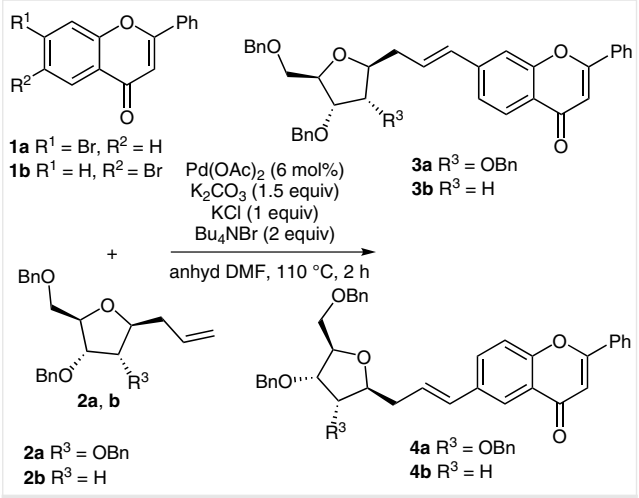
Figure 1 Natural occurring flavone *C*-glycosyl flavonoids

such as a Fries rearrangement, Friedel–Crafts reaction, Claisen–Schmidt condensation, or Baker–Venkataraman-type rearrangement followed by oxidative ring closure[5–8] to obtain the target molecule. At every step there is a chance of degrading the carbohydrate moiety. Although there are a few examples of direct C-glycosylation of the aglycone moiety,[9,10] the position of the carbohydrate unit in these transformations is usually controlled by a directing group (e.g., a hydroxy group). On the basis of these limitations, we want-

ed to perform a synthetic transformation in which the sugar part was introduced in the last step, and its position was controlled according to our aim.

Our goal was to synthesize *C*-glycosyl chromones and flavones by utilizing our previously acquired experience in palladium-catalyzed cross-coupling of oxygen-containing heterocycles, such as flavones or chromones. Our group has successfully developed several useful methods for the synthesis and transformation of chromones and flavones by using the Mizoroki–Heck reaction[11,12,13a] and its phosphine-free version under Jeffery's conditions.[13b] As a logical continuation of these studies, we wished to examine the reaction of bromoflavones or bromochromones with allyl ribofuranose compounds to give flavone or chromene β-D-ribofuranose derivatives containing various unsaturated linking groups. Moreover, syntheses of these new types of conjugate have not been previously investigated.

First, we used 6- and 7-bromoflavones (**1a** and **1b**, respectively) as our starting materials, and their reactions were carried out under our optimized cross-coupling reaction conditions (Scheme 1).[11,13a] As terminal alkenes, the protected 1-allyl-β-D-ribofuranose derivatives **2a** and **2b** were used as the carbohydrate units.



Scheme 1 Reaction of 7- and 6-bromoflavones (**1a**,**b**) with 1-allyl-β-D-ribofuranose derivatives **2a** and **2b** under Jeffery's conditions

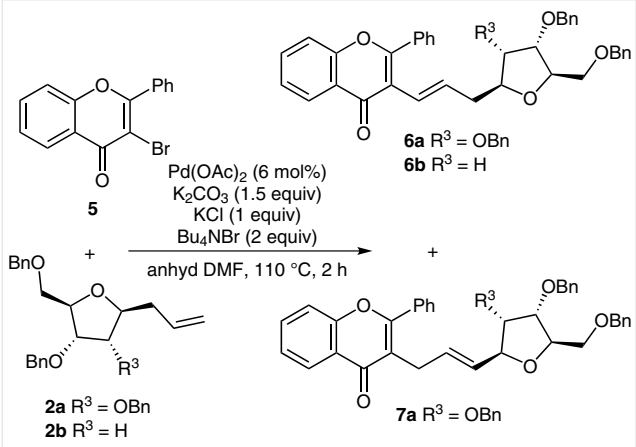
Initially, we performed the Mizoroki–Heck-type reaction of 7-bromoflavone (**1a**) with the 1-allyl-β-D-ribofuranose derivative **2a** in the presence of palladium(II) acetate and triphenylphosphine to give the corresponding flavone–ribose compound **3a** in 63% yield (Table 1, entry 1). Under phosphine-free Jeffery's conditions, product **3a** was isolated in a higher yield (89%; entry 2). We therefore used the phosphine-free conditions in all our subsequent reactions. A comparison of the yields of the cross-coupling reactions of the 1-allyl-β-D-ribofuranose **2a** and the 1-allyl-2-deoxy-β-D-ribofuranose **2b** revealed that furanose **2a** gave higher yields of the corresponding product in all cases (entries 2–5). This result can be explained by the easier coordination of palladium as a result of the presence, in the 2-position, of an *O*-benzyl group that acts as an oxygen-donor group.

Table 1 Yields of Cross-Coupling Reactions of 6- and 7-Bromoflavones (**1a**,**b**) with β-D-Ribose Derivatives **2a** and **2b**

Entry	Substrate	Ribose (R)	Method[a]	Product	Yield (%)
1	**1a**	OBn	Mizoroki–Heck	**3a**	63
2	**1a**	OBn	Jeffery	**3a**	89
3	**1a**	H	Jeffery	**3b**	68
4	**1b**	H	Jeffery	**4b**	75
5	**1b**	OBn	Jeffery	**4a**	92

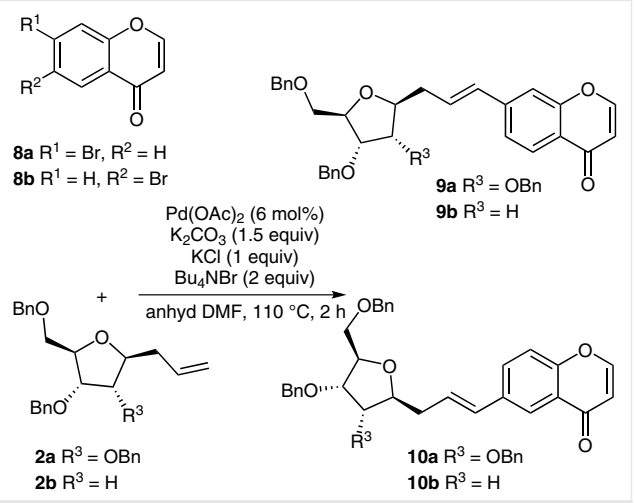
[a] Mizoroki–Heck reaction conditions: Et_3N, PPh_3, $Pd(OAc)_2$, NMP, 100–110 °C, 1–2 h. Jeffery reaction conditions: KCl, TBAB, K_2CO_3, $Pd(OAc)_2$, anhyd DMF, 100–110 °C, 1–2 h.

The transformation of 3-bromoflavone (**5**) into the flavone–ribofuranose compounds **6a** and **6b** was also successful; however, unlike the previous reactions, the palladium-catalyzed cross-coupling reaction of 3-bromoflavone (**5**) with allylribofuranoses **2a** or **2b** each gave two products **6** and **7** that were successfully separated and then characterized by means of two-dimensional NMR spectroscopy. This showed that migration of the double bond had occurred during the reaction, resulting in the formation of the two isomers **6** and **7** in approximately a 1:1 ratio (Scheme 2, Table 2). This isomerism occurred only in the case of 3-bromoflavone (**5**), and this type of phenomenon has precedents in the literature,[14] as other allyl derivatives are known to undergo similar isomerizations in the presence of palladium.

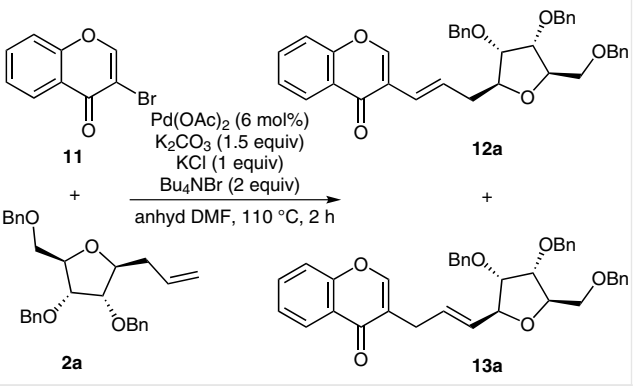


Scheme 2 Reactions of 3-bromoflavone (**5**) with 1-allyl-β-D-ribofuranose derivatives **2a**,**b**

To extend the scope of the oxygen-containing heteroaromatic derivatives, we treated the bromochromones **8a**,**b** with the 1-allyl-D-ribofuranoses **2a** and **2b** under Jeffery's



Scheme 3 Reactions of 7- and 6-bromochromones (**8a**,**b**) with 1-allyl-β-D-ribofuranose derivatives **2a** and **2b**



Scheme 4 Reaction of 3-bromochromone (**11**) with the 1-allyl-β-D-ribofuranose derivative **2a**

conditions (Scheme 3 and Table 3). The reaction of 6-bromochromone (**8b**) with ribofuranose derivatives **2a** and **2b** provided compounds **10a** and **10b**, respectively, in moderate yields (Table 3, entries 3 and 4), whereas 7-bromochromone (**8a**) gave the corresponding products **9a** and **9b**, respectively, in good yields (entries 1 and 2).

Table 2 Yields of Cross-Coupling Reactions of 3-Bromoflavone (**5**) with β-D-Riboses **2a** and **2b**

Substrate	R	Yield (%) of **6**	Yield (%) of **7**
2a	OBn	21	20
2b	H	19	18

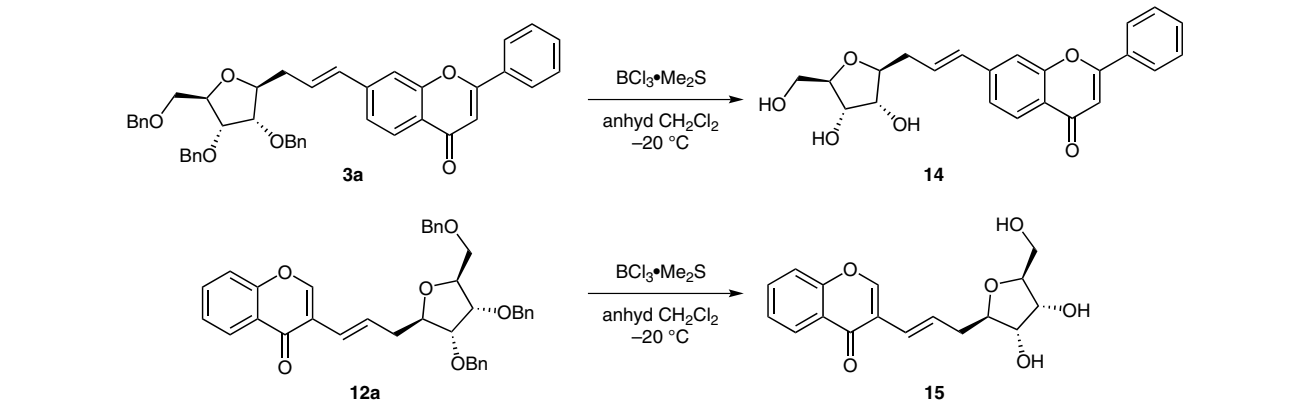
Table 3 Yields of the Cross-Coupling Reaction of 6- and 7-Bromochromones (**8a**,**b**) with β-D-Riboses **2a** and **2b**

Entry	Substrate	Ribose (R)	Product	Yield (%)
1	**8a**	OBn	**9a**	79
2	**8a**	H	**9b**	49
3	**8b**	OBn	**10a**	44
4	**8b**	H	**10b**	28

Next, the cross-coupling reaction of 3-bromochromone (**11**) was carried out with terminal alkene **2a** (Scheme 4). As in the case of 3-bromoflavone (**5**), two isomers **12a** and **13a** were isolated in a ~3:1 ratio (**12a**: 50%; **13a**: 18%).

Finally, the flavone derivative **3a** and chromone derivative **12a** were deprotected by treatment with boron trichloride–dimethyl sulfide complex[15] in dichloromethane at a low temperature to preserve the unsaturated linkage (Scheme 5). This protocol gave the corresponding products **14** and **15** in up to 77% yield.

In summary, treatment of bromoflavones or bromochromones with 1-allyl-β-D-ribofuranose derivatives in the presence of a palladium catalyst under phosphine-free conditions gave the expected novel structures in good yields.[16] In some cases, migration of the double bond was observed, resulting in the formation of isomers that were successfully separated. These results clearly demonstrate the usefulness



Scheme 5 Debenzylation of 1-allyl-β-D-ribofuranose derivatives **3a** and **12a**

of this method for the synthesis of interesting target molecules with possible biological activities. Biological assays of the synthesized carbohydrate–flavone and –chromone derivatives have already started. Investigations are also in progress on syntheses of other structurally novel derivatives containing carbohydrate moieties bearing various unsaturated side chains.

Acknowledgment

Financial support by the Hungarian Scientific Research Fund OTKA (grant number PD 106244) is gratefully acknowledged. M.Sc. Olena Davydova (Department of Organic Chemistry, Univ. Rostock) is thanked for performing large-scale syntheses of the *C*-glycoside starting materials.

Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0035-1561273.

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(16) **Flavone–Ribose Derivatives: General Procedures**
Conditions A (*Jeffery's Conditions*): A stirred mixture of bromoflavone **1a** or **1b** (75 mg, 0.249 mmol), allyl derivative **2a** or **2b** (0.249 mmol, 1.0 equiv), K_2CO_3 (52 mg, 0.375 mmol, 1.5 equiv), KCl (19 mg, 0.250 mmol, 1.0 equiv), TBAB (162 mg, 0.500 mmol, 2.0 equiv), and $Pd(OAc)_2$ (4 mg, 0.015 mmol, 6 mol%) in anhyd DMF (5 mL) was heated at 110 °C for 2 h under N_2. The mixture was cooled, silica gel was added, and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography.
Condition B (*Classic Mizoroki–Heck Conditions*): A stirred mixture of bromoflavone **1a** or **1b** (75 mg, 0.249 mmol), allyl derivative **2a** (0.249 mmol, 1.0 equiv), Et_3N (39 µL, 0.274 mmol, 1.1 equiv), Ph_3P (7 mg, 0.025 mmol, 10 mol%), and $Pd(OAc)_2$ (4 mg, 0.015 mmol, 6 mol%) in anhyd DMF (5 mL) was heated at 110 °C for 2 h under N_2. The mixture was cooled, silica gel was added, and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography.
7-[(1*E*)-3-{(2*S*,3*S*,4*R*,5*R*)-3,4-Bis(benzyloxy)-5-[(benzyloxy)-methyl]tetrahydrofuran-2-yl}prop-1-en-1-yl]-2-phenyl-4*H*-chromen-4-one (3a)
White crystals; mp 126–127 °C; yield (conditions A): 147 mg (89%); yield (conditions B): 104 mg (63%). IR (KBr): 2922, 2903, 2856, 1639, 1624, 1450, 1372, 1101, 697 cm^{-1}. ^1H NMR (360 MHz, $CDCl_3$): δ = 2.45–2.63 (m, 2 H), 3.52 (m, 2 H), 3.66 (t, *J* = 6.1 Hz, 1 H), 3.93 (t, *J* = 4.6 Hz, 1 H), 4.21 (m, 2 H), 4.42–4.64 (m, 6 H), 6.44 (s, 2 H), 6.80 (s, 1 H), 7.29 (m, 15 H), 7.39 (s, 1 H), 7.52 (m, 4 H), 7.90 (m, 2 H), 8.10 (d, *J* = 8.2 Hz, 1 H). ^{13}C NMR (90 MHz, $CDCl_3$): δ = 36.7, 70.3, 71.7, 72.0, 73.3, 79.8, 80.0, 81.6, 107.6, 114.9, 122.5, 123.1, 125.6, 126.2, 127.4, 127.6, 127.7, 128.0, 128.1, 128.3, 128.9, 130.5, 130.7, 131.4, 131.8, 137.7, 138.0, 143.2, 156.5, 163.2, 178.1. Anal. Calcd for $C_{44}H_{40}O_6$: C, 79.50; H, 6.06. Found: C, 79.54; H, 6.10.
6-[(1*E*)-3-{(2*S*,3*S*,4*R*,5*R*)-3,4-Bis(benzyloxy)-5-[(benzyloxy)-methyl]tetrahydrofuran-2-yl}prop-1-en-1-yl]-2-phenyl-4*H*-chromen-4-one (4a)
White crystals; mp 89–90 °C; yield (conditions A): 152 mg (92%). IR (KBr): 3029, 2875, 1639, 1614, 1451, 1360, 1097, 731, 697 cm^{-1}. ^1H NMR (360 MHz, $CDCl_3$): δ = 2.52–2.59 (m, 2 H), 3.52 (m, 2 H), 3.66 (t, *J* = 5.8 Hz, 1 H), 3.91 (t, *J* = 4.6 Hz, 1 H), 4.15–4.22 (m, 2 H), 4.43–4.62 (m, 6 H), 6.25–6.34 (m, 1 H), 6.37–6.48 (m, 1 H), 6.79 (s, 1 H), 7.28 (m, 14 H), 7.43 (t, *J* = 6.6 Hz, 1 H), 7.50 (m, 4 H), 7.59 (d, *J* = 6.6 Hz, 1 H), 7.90 (m, 2 H), 8.08 (s, 1 H). ^{13}C NMR (90 MHz, $CDCl_3$): δ = 36.7, 70.2, 71.7, 71.9, 73.3, 77.1, 79.8, 80.1, 81.3, 107.3, 118.1, 122.6, 123.7, 126.1, 127.4, 127.6, 127.6, 127.7, 127.9, 128.2, 128.7, 128.9, 130.5, 131.0, 131.4, 131.6, 134.7, 137.6, 137.7, 138.7, 155.2, 163.1, 178.2. Anal. Calcd for $C_{44}H_{40}O_6$: C, 79.50; H, 6.06. Found: C, 79.55; H, 6.08.
6-[(1*E*)-3-{(2*S*,4*S*,5*R*)-4-(Benzyloxy)-5-[(benzyloxy)methyl]-tetrahydrofuran-2-yl}prop-1-en-1-yl]-2-phenyl-4*H*-chromen-4-one (4b)
White crystals; mp 82–83 °C; yield (conditions A): 104 mg (75%). IR (KBr): 3059, 3030, 2902, 2876, 1650, 1615, 1453, 1360, 1097, 741, 698 cm^{-1}. ^1H NMR (360 MHz, $CDCl_3$): δ = 1.67–1.80 (m, 2 H), 2.43–2.61 (m, 2 H), 3.46–3.59 (m, 2 H), 4.00–4.04 (m, 1 H), 4.15–4.17 (m, 1 H), 4.23–4.29 (m, 1 H), 4.50 (s, 2 H), 4.56 (s, 2 H), 6.29–6.36 (m, 1 H), 6.49–6.53 (m, 1 H), 6.79 (s, 1 H), 7.31 (m, 8 H), 7.45 (m, 4 H), 7.67 (d, *J* = 8.7 Hz, 1 H), 7.89 (m, 2 H), 8.12 (d, *J* = 7.2 Hz, 1 H). ^{13}C NMR (90 MHz, $CDCl_3$): δ = 37.6, 38.6, 70.9, 73.3, 73.3, 78.1, 81.0, 83.5, 107.3, 118.1, 122.5, 123.7, 126.1, 127.5, 128.1, 128.2, 128.7, 128.9, 130.4, 131.2, 131.5, 131.6, 134.8, 138.0, 138.1, 155.2, 163.1, 178.3. Anal. Calcd for $C_{37}H_{34}O_5$: C, 79.55; H, 6.13; H, 6.06. Found: C, 79.57; H, 6.09.

3-[(1*E*)-3-{(2*S*,3*S*,4*R*,5*R*)-3,4-Bis(benzyloxy)-5-[(benzyloxy)-methyl]tetrahydrofuran-2-yl}prop-1-en-1-yl]-2-phenyl-4*H*-chromen-4-one (6a)

Colorless oil; yield (conditions A): 55 mg (40%). IR (KBr): 3059, 3027, 2919, 2896, 2880, 1648, 1631, 1612, 1467, 1396, 1104, 762, 696 cm^{-1}. ^1H NMR (360 MHz, $CDCl_3$): δ = 2.33–2.43 (m, 2 H), 3.52 (m, 2 H), 3.69 (t, *J* = 5.4 Hz, 1 H), 3.87 (t, *J* = 5.2 Hz, 1 H), 4.15 (m, 2 H), 4.48–4.57 (m, 6 H), 6.10 (d, *J* = 15.8 Hz, 1 H), 6.91 (m, 1 H), 7.24 (m, 15 H), 7.44 (m, 6 H), 7.64 (m, 2 H), 8.26 (d, *J* = 7.6 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 28.7, 70.5, 72.2, 73.4, 77.8, 77.9, 81.4, 81.5, 81.9, 118.0, 119.6, 123.0, 124.9, 125.8, 127.6, 127.7, 127.9, 128.1, 128.3, 128.4, 128.6, 129.9, 130.4, 131.4, 133.2, 133.6, 138.1, 138.3, 156.2, 162.4, 177.9. Anal. Calcd for $C_{44}H_{40}O_6$: C, 79.50; H, 6.06. Found: C, 79.55; H, 6.09.

3-[(1*E*)-3-{(2*S*,4*S*,5*R*)-4-(Benzyloxy)-5-[(benzyloxy)-methyl]tetrahydrofuran-2-yl}prop-1-en-1-yl]-2-phenyl-4*H*-chromen-4-one (6b)

Colorless oil; yield (conditions A): 29 mg (21%). IR (KBr): 2954, 2923, 2853, 1637, 1465, 1315, 1097, 758, 696 cm^{-1}. ^1H NMR (360 MHz, $CDCl_3$): δ = 1.61–1.68 (m, 1 H), 2.06 (dd, *J* = 13.1, 4.9 Hz, 1 H), 2.31–2.52 (m, 2 H), 3.41–3.55 (m, 2 H), 3.99–4.01 (m, 1 H), 4.08–4.10 (m, 1 H), 4.16–4.19 (m, 1 H), 4.49 (s, 2 H), 4.54 (s, 2 H), 6.16 (d, *J* = 15.8 Hz, 1 H), 6.79–6.84 (m, 1 H), 7.29 (m, 8 H), 7.38 (m, 5 H), 7.47 (m, 2 H), 7.56 (m, 3 H), 8.26 (d, *J* = 8.1 Hz, 1 H). ^{13}C NMR (90 MHz, $CDCl_3$): δ = 37.5, 39.9, 70.9, 71.0, 73.3, 78.2, 81.2, 83.4, 117.7, 117.9, 123.1, 123.5, 124.9, 126.2, 126.3, 127.6, 128.3, 129.0, 129.7, 130.4, 133.2, 133.3, 138.2, 155.5, 162.0, 177.5. Anal. Calcd for $C_{37}H_{34}O_5$: C, 79.55; H, 6.13; H, 6.06. Found: C, 79.58; H, 6.15.

Chromone–Ribose Derivatives; General Procedure

A stirred mixture of bromochromone **8a** or **8b** (56 mg, 0.249 mmol), allyl derivative **2a** or **2b** (0.249 mmol, 1.0 equiv), K_2CO_3 (52 mg, 0.375 mmol, 1.5 equiv), KCl (19 mg, 0.250 mmol, 1.0 equiv), TBAB (162 mg, 0.500 mmol, 2.0 equiv), and $Pd(OAc)_2$ (4 mg, 0.015 mmol, 6 mol%) in dry DMF (5 mL) was heated at 110 °C for 2 h under N_2. The mixture was cooled, silica gel was added, and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography.

7-[(1*E*)-3-{(2*S*,3*S*,4*R*,5*R*)-3,4-Bis(benzyloxy)-5-[(benzyloxy)methyl]tetrahydrofuran-2-yl}prop-1-en-1-yl]-4*H*-chromen-4-one (9a)

Colorless oil; yield: 115 mg (79%). IR (KBr): 3063, 3029, 2901, 2865, 1654, 1621, 1430, 1127, 1027, 736, 698 cm^{-1}. ^1H NMR (360 MHz, $CDCl_3$): δ = 2.43–2.57 (m, 2 H), 3.50 (m, 2 H), 3.61–3.66 (m, 1 H), 3.90 (m, 1 H), 4.19 (m, 2 H), 4.44–4.62 (m, 6 H), 6.24 (d, *J* = 5.9 Hz, 1 H), 6.38 (m, 2 H), 7.27 (m, 17 H), 7.72 (d, *J* = 5.9 Hz, 1 H), 8.05 (d, *J* = 8.2 Hz, 1 H). ^{13}C NMR (90 MHz, $CDCl_3$): δ = 36.5, 70.1, 71.5, 71.7, 73.2, 76.8, 79.7, 79.9, 81.4, 112.7, 114.8, 122.8, 123.2, 125.5, 127.3, 127.4, 127.5, 127.6, 127.8, 127.9, 128.1, 130.4, 137.5, 137.6, 137.8, 137.9, 143.0, 155.0, 156.6, 177.0. Anal. Calcd for $C_{38}H_{36}O_6$: C, 77.53; H, 6.16. Found: C, 77.58; H, 6.19.

3-[(1*E*)-3-{(2*S*,3*S*,4*R*,5*R*)-3,4-Bis(benzyloxy)-5-[(benzyloxy)methyl]tetrahydrofuran-2-yl}prop-1-en-1-yl]-4*H*-chromen-4-one (12a)

Colorless oil; yield: 73 mg (50%). IR (KBr): 3063, 3029, 2901, 2865, 1654, 1621, 1430, 1127, 1027, 736, 698 cm^{-1}. ^1H NMR (360 MHz, $CDCl_3$): δ = 2.16–2.56 (m, 2 H), 3.53 (m, 2 H), 3.68 (t, *J* = 5.6 Hz, 1 H), 3.89 (t, *J* = 4.9 Hz, 1 H), 4.16 (m, 2 H), 4.48–4.61 (m, 6 H), 6.32 (d, *J* = 15.8 Hz, 1 H), 6.47 (m, 1 H), 7.28 (m, 15 H), 7.40 (m, 2 H), 7.64 (t, *J* = 7.2 Hz, 1 H), 7.76 (s, 1 H), 8.24 (d, *J* = 7.9 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 37.4, 70.3, 71.7, 72.0, 73.3, 77.1, 79.3, 80.5, 81.2, 117.9, 121.9, 122.4, 124.0, 124.9, 126.1, 127.5, 127.6, 127.8, 128.0, 128.3, 128.4, 128.9, 133.3, 137.8, 138.1, 151.9, 155.8, 176.4. Anal. Calcd for $C_{38}H_{36}O_6$: C, 77.53; H, 6.16. Found: C, 77.58; H, 6.18.

3-[(2*E*)-3-{(2*S*,3*S*,4*R*,5*R*)-3,4-Bis(benzyloxy)-5-[(benzyloxy)methyl]tetrahydrofuran-2-yl}prop-2-en-1-yl]-4*H*-chromen-4-one (13a)

Colorless oil; yield: 26 mg (18%). IR (KBr): 2924, 2856, 1718, 1646, 1609, 1464, 1126, 1100, 751, 698 cm^{-1}. ^1H NMR (360 MHz, $CDCl_3$): δ = 3.22 (m, 2 H), 3.51–3.52 (m, 2 H), 3.66 (t, *J* = 6.1 Hz, 1 H), 3.91 (t, *J* = 4.9 Hz, 1 H), 4.00–4.21 (m, 2 H), 4.44–4.61 (m, 6 H), 5.56 (dd, *J* = 15.3, 7.3 Hz, 1 H), 5.94 (dt, *J* = 15.3, 6.8 Hz, 1 H), 7.28 (m, 15 H), 7.35 (m, 2 H), 7.65 (m, 2 H), 8.22 (d, *J* = 7.2 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 29.8, 70.4, 72.0, 72.2, 73.5, 77.5, 81.4, 81.5, 81.6, 118.1, 123.0, 123.8, 125.0, 126.0, 127.7, 127.8, 127.8, 128.0, 128.1, 128.3, 128.4, 130.2, 131.5, 133.5, 138.0, 138.9, 152.8, 156.5, 177.5. Anal. Calcd for $C_{38}H_{36}O_6$: C, 77.53; H, 6.16. Found: C, 77.55; H, 6.19.