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Authors: Naoki Kise, Hiroaki Nagamine, and Toshihiko Sakurai

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Reductive Coupling

Electroreductive Intermolecular Coupling of Chromones with Benzophenones: Synthesis of 2-Diarylmethylchromones and Tetrasubstituted Furans

Naoki Kise,^{*,[a],[b]} Hiroaki Nagamine,^[a] and Toshihiko Sakurai^{[a],[b]}

Abstract: The electroreductive coupling of chromones with benzophenones in the presence of TMSCl gave adducts reacted at the 2-position of chromones as trimethylsilyl ethers. From 3-methyl- and 3-phenylchromones, 2,3-*cis*-adducts were formed predominantly. The *cis*-adducts were isomerized to *trans*-ones by treatment with DBU. The detrimethylsilylation of the adducts with 1 M HCl aq/dioxane produced the corresponding alcohols. The dehydrosilylation of the adducts or dehydration of the desilylated alcohols brought about 2-diarylmethylchromones. The detrimethylsilylation of the adducts with TBAF and subsequent treatment with NaH afforded ring-opening products. The dehydration of the ring-opening products obtained from 3-methyl- and 3-phenylchromones brought about tetrasubstituted furans or dihydrobenzofuran-3-ones. The dehydrogenation of the adducts with DDQ and subsequent desilylation with 1 M HCl aq/dioxane gave 2-(diarylhydroxymethyl)chromones.

Introduction

Chromone ring is the core skeleton of plant-derived flavonoids such as flavones and isoflavones (Figure 1). Recently, chromones are attracting much attention as a valid scaffold in medicinal chemistry.^[1] Therefore, the conjugate additions to chromones have extensively been studied for the synthesis of 2-substituted chromone derivatives.^[2] On the other hand, we have reported the electroreductive cross-coupling of heterocycles, such as phthalimides,^[3] indoles,^[4] uracils,^[5] and coumarins^[6] with carbonyl compounds. In this regard, we attempted the electroreductive cross-coupling of chromones with carbonyl compounds, since this reaction is expected to provide a new

synthetic route to 2-substituted chromones. Although the titanium(III)-mediated double-reductive coupling of chromones with acrylonitrile has been reported,^[7] the reductive coupling of chromones with carbonyl compounds is hitherto unknown (Scheme 1). We report in this paper that the cross-coupled products reacted at the 2-position of chromones were obtained as trimethylsilyl ethers by the electroreduction of chromones with benzophenones in the presence of TMSCl. From 2-substituted chromones ($R^1 = \text{Me, Ph; } R^2 = \text{H}$), 2,3-*cis*-adducts were produced with complete stereoselectivity (Scheme 1). In addition, we investigated several transformations of the adducts (Scheme 2). Direct dehydrosilylation of the adducts ($R^2 = \text{H}$) with cat. *p*-TsOH in refluxing xylene gave 2-diarylmethylchromones. The same compounds were obtained by desilylation of the trimethylsilyl ethers with 1 M HCl aq and subsequent dehydration of the resultant alcohols by reflux in cat. *p*-TsOH/toluene. In contrast, desilylation of the adducts with TBAF and subsequent treatment with NaH brought about ring-opening products. The ring-opening products ($R^1 = \text{Me, Ph; } R^2 = \text{H}$) were transformed to tetrasubstituted furans, which were attracting as pharmaceuticals and functional materials,^[8] by reflux in cat. TsOH/toluene. The *cis*-adducts ($R^1 = \text{Me, Ph; } R^2 = \text{H}$) could be isomerized to *trans*-alcohols by treatment with DBU and subsequent desilylation with 1 M HCl aq. The dehydrogenation of the adducts with DDQ in dioxane and following desilylation with 1 M HCl aq gave 2-(diarylhydroxymethyl)chromones. Reaction mechanisms of the electroreductive coupling and the transformations of the adducts were also discussed.

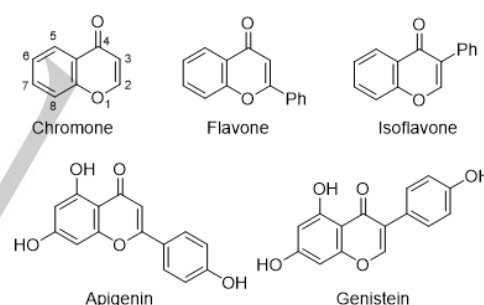
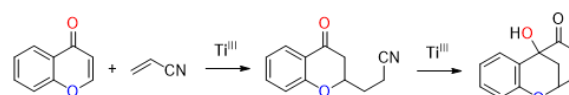
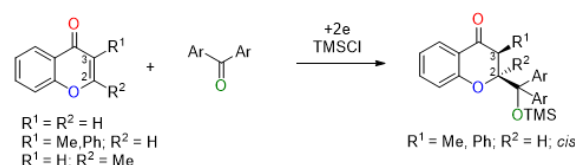


Figure 1. Chromone and Flavonoids (Flavones and Isoflavones).

Double-reductive coupling with acrylonitrile (Ref. 7)



Electroreductive coupling with benzophenones (This work)

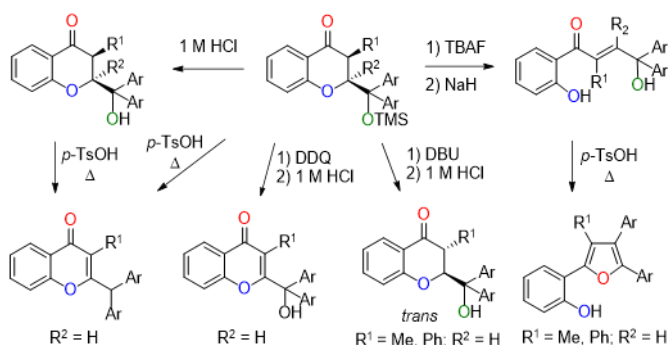


Scheme 1. Titanium-mediated double-coupling and electroreductive coupling of chromones.

[a] Prof. N. Kise, H. Nagamine, Dr. T. Sakurai
 Department of Chemistry and Biotechnology,
 Graduate School of Engineering, Tottori University
 4-101, Koyama-cho Minami, Tottori 680-8552, (Japan)
 E-mail: kise@tottori-u.ac.jp

[b] Prof. N. Kise, Dr. T. Sakurai
 Center for Research on Green Sustainable Chemistry
 Graduate School of Engineering, Tottori University
 4-101, Koyama-cho Minami, Tottori 680-8552, (Japan)

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Scheme 2. Transformation of adducts.

Results and Discussion

Electroreductive coupling of chromones with benzophenones

The electroreduction of chromones **1a–d** with benzophenones **2a–f** (2 equiv) was carried out in THF containing TMSCl (5 equiv) according to our already reported method^[3–6] and the results are summarized in Table 1. In all cases, the adducts coupled at the 2-position of **1a–d** with **2a–f** were obtained as trimethylsilyl ethers **3a–m** in moderate to high yields. It is noted that the electroreductive coupling of 3-methylchromone (**1b**) and isoflavone (**1c**) with **2a,b,d** gave the adducts **3g–k** as single diastereomers (>99% selectivity by ¹H NMR analysis) (runs 7–11). In addition, the electroreduction of substituted isoflavones **1e–h** with benzophenone (**2a**) also gave the corresponding adducts **3n–q** in moderate yields with complete stereoselectivity (Table 2). Of these adducts, the stereochemistry of **3i** was confirmed to be *cis* by X-ray crystallographic analysis. Therefore, the other adducts **3g,h,j,k,n–q** could be assumed to be *cis*-isomers. We have already observed similar *cis*-stereoselectivity in the electroreductive coupling of 1-alkoxycarbonyl-3-methoxycarbonylindoles,^[4] 5-substituted 1,3-dimethyluracils,^[5] and 3-methylcoumarin^[6] with aromatic ketones.

When the electroreductive coupling of **1a** with 4,4'-dimethoxybenzophenone (**2g**) was carried out under the same conditions as above, the desired cross-coupled product was not obtained at all; hydrodimer of chromone (**i**) and 4-(trimethylsilyl)chroman-2-one (**ii**) were formed in 35% (60:40 dr) and 8% yields, respectively. Incidentally, the electroreduction of chromone alone in the presence of TMSCl gave **i** (41%, 60:40 dr) and **ii** (10%) as shown in Scheme 3. Since we already reported CV data of benzophenones **2a–g**,^[6] we measured the CV of chromones **1a–g** under the same conditions to compare their first reduction peaks (Table 3). These results revealed that **1a** (–2.05 V vs SCE) is less reducible than **2a** (–1.85 V) but slightly more reducible than **2g** (–2.08 V). Hence, the reaction mechanism of the electroreductive coupling of chromones with benzophenones can be presumed as illustrated in Scheme 4. Initially, carbanion **A** is generated by the consecutive two-electron transfer to **2a** and O-silylation with TMSCl. The nucleophilic 1,4-addition of **A** to the 2-position in **1** and following O-silylation of resulting enolate anion **B** give silyl enol ether **C**. The labile **C** is readily desilylated to **3**

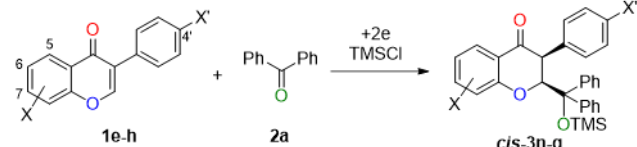
during workup. When R¹ is methyl or phenyl group, protonation at the 3-position in **C** occurs completely from the less hindered side (β side) to produce 2,3-*cis*-isomer of **3**.

Table 1. Electroreductive coupling of chromones **1a–d** with benzophenones **2a–f**.^[a]

Run	1	R ¹	R ²	2	Ar ₂ C=O	3	% Yield ^[b]
1	1a	H	H	2a	Ar = Ph	3a	87
2	1a	H	H	2b	Ar = 4-FC ₆ H ₄	3b	75
3	1a	H	H	2c		3c	52
4	1a	H	H	2d		3d	64
5	1a	H	H	2e		3e	94
6	1a	H	H	2f		3f	55
7	1b	Me	H	2a	Ar = Ph	<i>cis</i> - 3g	75
8	1b	Me	H	2b	Ar = 4-FC ₆ H ₄	<i>cis</i> - 3h	61
9	1b	Me	H	2d		<i>cis</i> - 3i	76
10	1c	Ph	H	2a	Ar = Ph	<i>cis</i> - 3j	64
11	1c	Ph	H	2b	Ar = 4-FC ₆ H ₄	<i>cis</i> - 3k	54
12	1d	H	Me	2a	Ar = Ph	3l	69
13	1d	H	Me	2b	Ar = 4-FC ₆ H ₄	3m	64

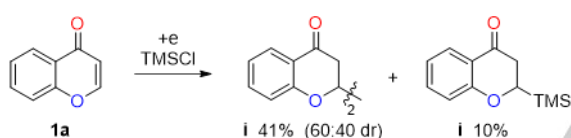
[a] Electroreduction was carried out in 0.3 M Bu₄ClO₄/THF using a Pt cathode at a constant current of 0.2 A (400 C; 4 F/mol). [b] Isolated yields.

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Table 2. Electroreductive coupling of isoflavones **1e-h** with **2a**.


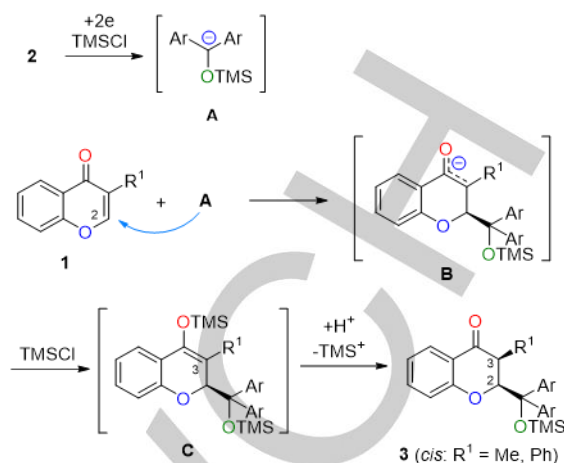
Run	1	X	X'	3	% Yield ^[a]
1	1e	6-MeO	H	cis-3n	71
2	1f	7-MeO	H	cis-3o	61
3	1g	7-MeO	MeO	cis-3p	55
4	1h	5,7-(MeO) ₂	MeO	cis-3q	56

[a] Electroreduction was carried out in 0.3 M Bu₄ClO₄/THF using a Pt cathode at a constant current of 0.2 A (400 C; 4 F/mol). [b] Isolated yields.

**Scheme 3.** Electroreduction of **1a** in the presence of TMSCl.**Table 3.** E_p Values of **1a-h** and **2a-f** derived from CV at 25 °C.

1	E _p (V vs. SCE) ^[a]	2	E _p (V vs. SCE) ^[a,b]
1a	-2.05	2a	-1.85
1b	-2.16	2b	-1.85
1c	-2.13	2c	-1.78
1d	-1.97	2d	-1.79
1e	-1.95	2e	-1.76
1f	-2.08	2f	-1.38
1g	-2.14	2g	-2.08

[a] 1st reduction peak in CV of 3 mM solution in 0.03 M Bu₄NClO₄/DMF at a Pt cathode at 0.1 V/s. In THF, clear reduction peaks could not be observed. [b] Reported data in ref. 6.

**Scheme 4.** Presumed reaction mechanism of electroreductive coupling of chromones **1** with benzophenones **2**.**Dehydrosilylation of 3**

Dehydrosilylation of the adducts ($R^2 = H$), **3a-e** and **cis-3g-k,n-q**, was carried out by reflux in xylene containing a catalytic amount of *p*-TsOH for 1-6 h (Table 4). In all cases, 4-diarylmethylchromones **4** were obtained as the sole products in good to excellent yields. These results show that initially formed *exo*-alkenes by dehydrosilylation of **3** rapidly isomerized to *endo*-alkenes **4** under the reflux conditions.

Desilylation of 3 with 1 M HCl/dioxane and subsequent dehydration

The trimethylsilyl ethers **3a-q** were stirred in 1 M HCl aq and dioxane (1:1) until almost all of **3a-q** were consumed (Table 5). From **3a-f**, desilylated alcohols **5a-f** were obtained after stirring at 25 °C for 2-6 h in high yields (runs 1-6). From 3- and 4-substituted adducts **3g-q**, the corresponding alcohols **5g-q** were obtained after stirring at 50 °C for 2-12 h in good to high yields (runs 7-17). In particular, **cis-5g-k** and **cis-5n-q** were formed as the sole products with retaining the stereochemistry (runs 7-11 and 14-17). The stereostructures of **cis-5g,i,o** were confirmed by X-ray crystallography. Dehydration of the resultant alcohols ($R^2 = H$), **5a-e** and **cis-5g-k,n-q**, with reflux in toluene containing a catalytic amount of *p*-TsOH for 1-3 h afforded 4-diarylmethylchromones **4** in good to excellent yields (runs 1-5, 7-11, and 14-17). Strangely enough, the hydration of **5f** under the same conditions resulted in a complex mixture (run 6).

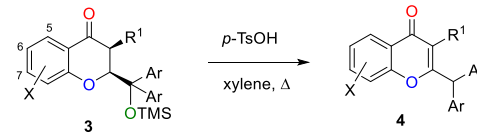
Ring-opening of adducts 3 to 6 by successive treatment with TBAF/THF and NaH, and subsequent recyclisation of 6 to 7 or 8

The treatment of **3a** with TBAF in THF at 25 °C for 10 min gave a mixture of the desilylated alcohol **5a** and its ring-opening product **6a** in 98% combined yield (**5a:6a** = 2:1~1:1). Therefore, the reaction mixture was successively treated *in situ* with one molar equivalent of NaH at 25 °C for 30 min to obtain **6a** as a sole product. The other adducts **3b-d,f-i,l** were treated under the same conditions to give **6b-d,f-i,l** as sole geometric isomers in

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good to excellent yields (Table 6). Of these products, **6a,c,f** were confirmed to be *E*-form by X-ray diffraction. The other **6** could also be estimated to be *E*-form. Next, we attempted the recyclisation of **6**. The dehydration of **6g,h** ($R^1 = \text{Me}$, $R^2 = \text{H}$) in refluxing toluene containing a catalytic amount of *p*-TsOH for 1 h gave tetrasubstituted furans **7g,h**, while that of **6a-f,i,l** ($R^1 = \text{H}$) under the same conditions resulted in formation of complex mixtures (Scheme 5). The adducts **cis-3j,k,n-q** derived from isoflavones **1c,e-h** were also transformed to the corresponding ring-opening products **6**. However, these compounds were unstable and could not be isolated. Therefore, the crude ring-opening products **6j,k,n-q** were immediately subjected to dehydration without isolation and the results are shown in Table 7. Tetraaryl-substituted furans **7j,k,n** were obtained from **cis-3j,k,n** (runs 1-3), whereas dihydrobenzofuran-3-ones **8o-q** were formed from **cis-3o-q** (runs 4-6). In later cases (runs 4-6), PPTS gave better results than *p*-TsOH as an acid-catalyst for dehydration.

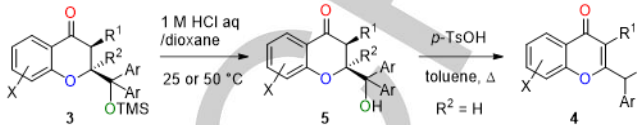
Table 4. Detrimethylsilyloxylation of **3** ($R^2 = \text{H}$).



Run	3	R^1	X	Time	4	% Yield ^[a]
1	3a	H	H	1 h	4a	89
2	3b	H	H	6 h	4b	98
3	3c	H	H	6 h	4c	77
4	3d	H	H	4 h	4d	92
5	3e	H	H	3 h	4e	75
6	cis-3g	Me	H	3 h	4g	81
7	cis-3h	Me	H	1 h	4h	96
8	cis-3i	Me	H	3 h	4i	98
9	cis-3j	Ph	H	1 h	4j	89
10	cis-3k	Ph	H	1 h	4k	90
11	cis-3n	Ph	6-MeO	1 h	4n	91
12	cis-3o	Ph	7-MeO	1 h	4o	93
13	cis-3p	4-MeOC ₆ H ₄	7-MeO	2 h	4p	92
14	cis-3q	4-MeOC ₆ H ₄	5,7-(MeO) ₂	1 h	4q	85

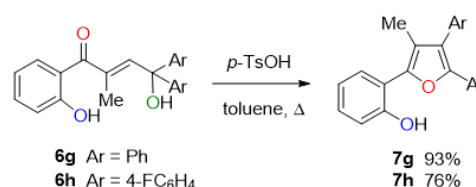
[a] Isolated yields.

Table 5. Desilylation of **3** with 1 M HCl aq/dioxane and subsequent dehydration.



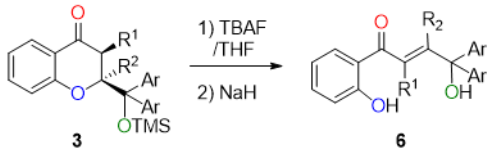
Run	3	R^1	R^2	5	% Yield ^[a]	4	% Yield ^[a]
1	3a	H	H	5a	90	4a	92
2	3b	H	H	5b	89	4b	87
3	3c	H	H	5c	94	4c	97
4	3d	H	H	5d	89	4d	80
5	3e	H	H	5e	88	4e	77
6	3f	H	H	5f	86	4f	No ^[b]
7	cis-3g	Me	H	cis-5g	79	4g	70
8	cis-3h	Me	H	cis-5h	77	4h	98
9	cis-3i	Me	H	cis-5i	95	4i	87
10	cis-3j	Ph	H	cis-5j	95	4j	71
11	cis-3k	Ph	H	cis-5k	88	4k	82
12	3l	H	Me	5l	76	–	–
13	3m	H	Me	5m	82	–	–
14	cis-3n	Ph	H	cis-5n	92	4n	93
15	cis-3o	Ph	H	cis-5o	94	4o	82
16	cis-3p	An ^[b]	H	cis-5p	82	4p	82
17	cis-3q	An ^[b]	H	cis-5q	93	4q	84

[a] Isolated yields. [b] Not obtained. [c] An = 4-MeOC₆H₄.



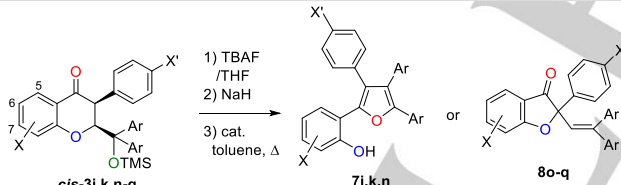
Scheme 5. Recyclisation of **6g,h**.

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Table 6. Desilylation of **3a-l** with TBAF and subsequent ring-opening.


Run	3	R ¹	R ²	6	% Yield ^[a]
1	3a	H	H	6a	98
2	3b	H	H	6b	91
3	3c	H	H	6c	68
4	3d	H	H	6d	89
5	3f	H	H	6f	98
6	<i>cis</i> - 3g	Me	H	6g	90
7	<i>cis</i> - 3h	Me	H	6h	64
8	<i>cis</i> - 3i	Me	H	6i	97
9	3l	H	Me	6l	91

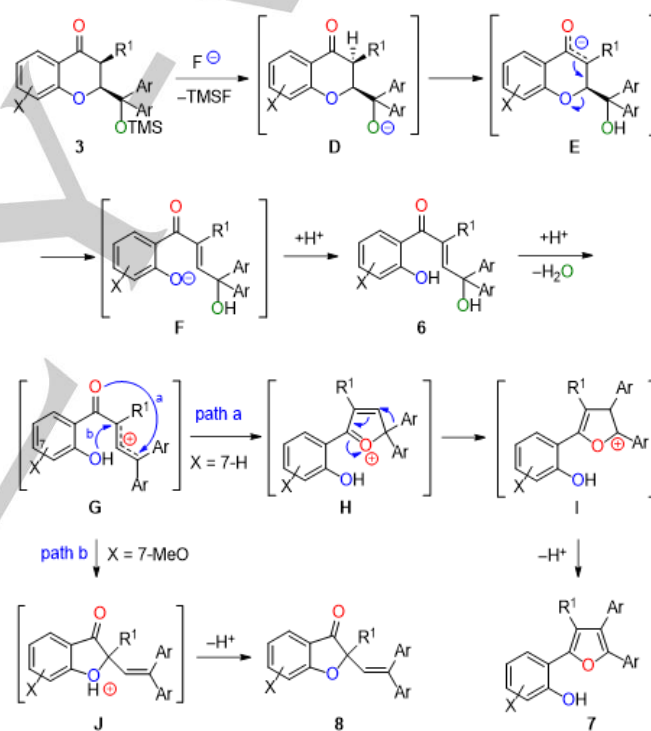
[a] Isolated yields.

Table 7. Desilylation, ring-opening, and recyclisation of *cis*-**3j,k,n-q**.


Run	3	X	Cat.	Product	% Yield ^[a]
1	<i>cis</i> - 3j	H	<i>p</i> -TsOH	7j	75
2	<i>cis</i> - 3k	H	<i>p</i> -TsOH	7k	50
3	<i>cis</i> - 3n	6-MeO	<i>p</i> -TsOH	7n	61
4	<i>cis</i> - 3o	7-MeO	PPTS	8o	74
5	<i>cis</i> - 3p	7-MeO	PPTS	8p	95
6	<i>cis</i> - 3q	5,7-(MeO) ₂	PPTS	8q	87

[a] Isolated yields.

The presumed reaction mechanism of the transformation of **3** to **6** and subsequent dehydration of **6** to **7** and **8** is exhibited in Scheme 6. Desilylation of **3** with TBAF generates alkoxide anion **D**, and then enolate anion **E** is formed by proton migration of **D**. Ring-opening of **E** to **F** by retro 1,4-addition of phenoxide anion and subsequent protonation give ring opening product **6**. In the recyclisation of **6**, allyl cation **G** is formed by dehydration after protonation to the *tert*-hydroxy group of **6**. Intramolecular nucleophilic addition of the carbonyl oxygen atom to the allyl cation in **G** (path a), aryl migration in cyclized cation **H**, and subsequent deprotonation of resultant carbocation **I** produce tetrasubstituted furan **7**. On the other hand, nucleophilic addition of the phenolic hydroxyl oxygen atom to the allyl cation in **G** (path b) and following deprotonation of cyclized cation **J** afford dihydrobenzofuran-3-one **8**. From the results shown in Scheme 5 and Table 6, it seems that 7-methoxy substitution in **3** (X = 7-MeO) makes path b more favourable than path a, although the reason is unclear at present.

**Scheme 6.** Presumed reaction mechanism of transformation of **3** to **6** and dehydration of **6** to **7** and **8**.**Isomerization of *cis*-**3** and subsequent desilylation to **5****

The isomerization of *cis*-**3g** was carried out by treatment with cat. DBU in THF at 50 °C for 24 h to give an equilibrium diastereomeric mixture of **3g** (65:35 dr). Since the diastereomers of **3g** could not be separated, the mixture was subsequently desilylated with 1 M HCl aq/dioxane (1:1) at 50 °C for 2 h to give **5g** (*trans*:*cis* = 65:35). The other *cis*-isomers of **3h-k,n-q** were isomerized and desilylated to *trans*-alcohols **5h-k,n-q** under the same conditions

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(Table 8). Of these, the stereoconfigurations of **trans-5g,h,j** were unambiguously confirmed to be *trans* by X-ray crystallography.

The ^1H NMR chemical shifts of 2-H and 3-H, and coupling constants between 2-H and 3-H ($J_{2,3}$) of *cis*- and *trans*-**5g-k,n-q** are exhibited in Table 9. In 3-methyl substituted chromones **5g-i**, the $J_{2,3}$ values for *trans*-isomers were larger (4.6–6.6 Hz) than those for *cis*-ones (1.7–2.4 Hz). However, the $J_{2,3}$ values for both isomers were similar (2.3–3.4 Hz) in 3-aryl substituted chromones **5j,k,n-q**. The chemical shifts of 3-H for *cis*-isomers were more upfield (0.39–0.60 ppm) than those for *trans*-ones in all cases, whereas the chemical shifts of 2-H for both isomers were very close with differences within 0.10 ppm.

Table 8. Isomerization of **cis-3** and subsequent desilylation with 1 M HCl.

Run	<i>cis</i> -3	R ¹	5	% Yield ^[a]	<i>trans</i> : <i>cis</i> ^[b]
1	cis-3g	Me	5g	86	65:35
2	cis-3h	Me	5h	89	66:34
3	cis-3i	Me	5i	88	70:30
4	cis-3j	Ph	5j	69	95:5
5	cis-3k	Ph	5k	64	95:5
6	cis-3n	Ph	5n	65	94:6
7	cis-3o	Ph	5o	80	90:10
8	cis-3p	4-MeOC ₆ H ₄	5p	87	92:8
9	cis-3q	4-MeOC ₆ H ₄	5q	74	76:24

[a] Isolated yields. [b] Determined by ^1H NMR analysis.

Dehydrogenation of 5

Dehydrogenation of **5** (R¹ = H, Me; R² = H) with DDQ in refluxing dioxane in the presence of TMSCl gave 2-(diarylhydroxymethyl)chromones **9** (Table 10). The corresponding **9a-e** were obtained in good to excellent yields from **5a-e** (R¹ = H) (runs 1–5), although further dehydrogenated product **9d** was formed as a by-product in the case of the oxidation of **5c** (run 3). The oxidation of **3a** under the same conditions also gave **9a** (84%) with a small amount of silyl ether of **9a** (>5%). From **cis-5g** and **cis-5h** (R¹ = Me), the yields of **9g** and **9h** were decreased, since benzophenones **2a** (34%) and **2b** (12%) were also formed together with **1b** by oxidative cleavage of **cis-5g** and **cis-5h**, respectively (runs 6 and 7). The oxidation of **trans-5g** gave the result (**9g** in 45% yield) substantially same as the

reaction of **cis-5g** (run 6). Unfortunately, the treatment of **cis-5j** (R¹ = Ph) with DDQ brought about **1d** and **2a** (70% each yields) and the desired dehydrogenated product **9j** could not be obtained at all (run 8).

Table 9. ^1H NMR chemical shifts of 2-H and 3-H, and coupling constants ($J_{2,3}$) of 2,3-*cis*- and *trans*-substituted chromones **5g-k,n-q**.

	<i>cis</i>			<i>trans</i>		
5	2-H (δ)	3-H (δ)	$J_{2,3}$ (Hz)	2-H (δ)	3-H (δ)	$J_{2,3}$ (Hz)
5g	5.33	2.33	1.7	5.23	2.85	4.6
5h	5.23	2.31	1.9	5.13	2.83	5.0
5i	5.24	2.05	2.4	5.15	2.65	6.6
5j	5.64	3.59	2.7	5.70	4.03	2.3
5k	5.54	3.56	2.7	5.61	4.03	3.4
5n	5.59	3.56	2.7	5.65	4.01	2.4
5o	5.66	3.54	2.7	5.68	3.97	2.4
5p	5.64	3.50	2.8	5.64	3.92	2.6
5q	5.60	3.44	2.7	5.58	3.83	2.6

Table 10. Dehydrogenation of **5** (R² = H).

Run	5	R ¹	9	% Yield ^[a]
1	5a	H	9a	90
2	5b	H	9b	92
3	5c	H	9c	50 ^[b]
4	5d	H	9d	75
5	5e	H	9e	91
6	cis-5g^[c]	Me	9g	46
7	cis-5h	Me	9h	60
8	cis-5j	Ph	9j	No ^[d]

[a] Isolated yields. [b] **9d** (24%) was formed as a by-product.

[c] **trans-5g** gave the same result. [d] Not obtained.

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Conclusions

The electroreductive intermolecular coupling of chromones **1a-h** with benzophenones **2a-f** in the presence of TMSCl in THF gave the adducts reacted at the 2-position of **1a-h** as TMS ethers **3a-q**. From 2-methylchromone (**1b**) and 2-arylchromones (isoflavones) **1c,e-h**, only 2,3-*cis*-adducts **cis-3g-k,n-q** were selectively obtained. The detrimethylsiloxylation of **3a-e** and **cis-3g-k,n-q** with refluxing in cat. *p*-TsOH/xylene afforded 2-diarylmethylchromones **4a-e,g,k,n-q**. The treatment of **3a-q** with 1 M HCl/dioxane gave the corresponding desilylated alcohols **5a-q**. The dehydration of **5a-e** and **cis-5g-k,n-q** with refluxing in cat. *p*-TsOH/toluene also afforded **4a-e,g,k,n-q**. The successive treatment of **3a-d,f,l** and **cis-3g-i** with TBAF and NaH gave ring-opening products **6a-d,f,i,l**. The dehydration of **6g,h** produced tetrasubstituted furans **7g,h**. The successive treatment of **cis-3j,k,n-q** with TBAF and NaH, and the dehydration of the crude resultant ring-opening products afforded tetraaryl-substituted furans **7j,k,n** and dihydrobenzofuran-3-ones **8o-q**. The treatment of **cis-3g-k,n-q** with DBU and following desilylation with 1 M HCl/dioxane gave isomerized alcohols **trans-5g-k,n-q**. The dehydrogenation of **5a-e** and **cis-5g,h** with DDQ in dioxane formed 2-(diarylhydroxymethyl)chromones **9a-e,g,h**.

Experimental Section

General methods. Column chromatography was performed on silica gel 60. THF was freshly distilled from sodium benzophenone ketyl radical. DMF, TMSCl, and TEA were distilled from CaH₂. ¹H NMR (500 MHz) and ¹³C NMR (125 MHz) spectra were measured on a JEOL JNM-ECP500 spectrometer in the solvents indicated; chemical shifts (δ) are given in ppm relative to tetramethylsilane (TMS) as an internal standard. IR spectra were recorded on a Shimadzu IRAffinity-1 infrared spectrometer; wavenumbers (ν̄) are given in cm⁻¹. HRMS were measured on a Thermo Scientific Exactive FTMS spectrometer. Melting points were uncorrected.

Starting materials. Chromones **1a**,^[2f] **1b**,^[7] **1c**,^[2f] and isoflavones **1d**,^[7] **1e**,^[9] **1f**,^[9] **1g**,^[10] **1h**,^[11] were prepared by reported methods.

Typical procedure of electroreductive coupling. A 0.3 M solution of Bu₄NClO₄ in THF (15 mL) was placed in the cathodic chamber of a divided cell (40 mL beaker, 3 cm diameter, 6 cm height) equipped with a platinum cathode (5 × 5 cm²), a platinum anode (2 × 1 cm²), and a ceramic cylindrical diaphragm (1.5 cm diameter). A 0.3 M solution of Et₄NOTs in DMF (4 mL) was placed in the anodic chamber (inside the diaphragm). Chromone (**1a**) (146 mg, 1.0 mmol), benzophenone (**2a**) (368 mg, 2.0 mmol), TMSCl (0.64 mL, 5.0 mmol), and TEA (0.70 mL, 5.0 mmol) were added to the cathodic chamber. After 400 C (4.0 F/mol) of electricity was passed at a constant current of 200 mA at 25 °C under nitrogen atmosphere, the catholyte was evaporated in vacuo. The residue was dissolved in diethyl ether (20 mL) and insoluble solid was filtered off. After removal of the solvent in vacuo, the residue was purified by column chromatography on silica gel (hexanes-EtOAc) to give **3a** (350 mg, 0.869 mmol) in 87% yield.

2-(Diphenyl(trimethylsilyl)oxy)methyl)chroman-4-one (3a): White solid (350 mg, 87%). *R*_f: 0.5 (hexanes/ethyl acetate, 10:1). Mp 205–207 °C. ¹H NMR (500 MHz, CDCl₃): δ = −0.06 (s, 9H), 2.29 (dd, 1H, *J* = 2.4, 17.2 Hz), 2.76 (dd, 1H, *J* = 13.9, 17.2 Hz), 5.36 (dd, 1H, *J* = 2.4, 13.9 Hz), 6.99–

7.08 (m, 2H), 7.21–7.34 (m, 8H), 7.44–7.53 (m, 3H), 7.87–7.91 (m, 1H). ¹³C NMR (125 MHz, CDCl₃): δ = 2.0 (q), 37.7 (t), 80.2 (d), 82.0 (s), 117.8 (d), 121.2 (s), 121.7 (d), 126.7 (d), 127.1 (d), 127.2 (d), 127.3 (d), 127.8 (d), 128.1 (d), 128.2 (d), 136.1 (d), 136.1 (s), 144.1 (s), 144.2 (s), 160.8 (s), 192.9 (s). IR (ATR): ν̄ = 1684, 1607 cm⁻¹. HRMS (ESI⁺) calcd for C₂₅H₂₇O₃Si [M + H⁺] 403.1729, found 403.1722.

2-(Bis(4-fluorophenyl)((trimethylsilyl)oxy)methyl)chroman-4-one

(3b): White solid (329 mg, 75%). *R*_f: 0.5 (hexanes/ethyl acetate, 10:1). Mp 148–149 °C. ¹H NMR (500 MHz, CDCl₃): δ = −0.06 (s, 9H), 2.33 (dd, 1H, *J* = 1.9, 17.0 Hz), 2.69 (dd, 1H, *J* = 13.8, 17.0 Hz), 5.28 (dd, 1H, *J* = 1.9, 13.8 Hz), 6.95–7.09 (m, 6H), 7.25–7.29 (m, 2H), 7.39–7.44 (m, 2H), 7.50–7.54 (m, 1H), 7.88–7.91 (m, 1H). ¹³C NMR (125 MHz, CDCl₃): δ = 1.9 (s), 37.6 (t), 80.0 (d), 81.2 (s), 114.7 (d, *J*_{CCF} = 21.6 Hz), 115.0 (d, *J*_{CCF} = 21.9 Hz), 117.6 (d), 121.1 (s), 121.9 (d), 127.1 (d), 128.6 (d, *J*_{CCF} = 7.2 Hz), 129.8 (d, *J*_{CCF} = 7.8 Hz), 136.1 (s), 139.7 (s, *J*_{CCCCF} = 2.7 Hz), 139.8 (s, *J*_{CCCCF} = 2.7 Hz), 160.5 (s), 161.9 (s, *J*_{CF} = 247.1 Hz), 162.0 (s, *J*_{CF} = 247.1 Hz), 192.3 (s). IR (ATR): ν̄ = 1694, 1605 cm⁻¹. HRMS (ESI⁺) calcd for C₂₅H₂₅F₂O₃Si [M + H⁺] 439.1541, found 439.1531.

2-(5-((Trimethylsilyl)oxy)-10,11-dihydro-5H-dibenzo[a,d][7]annulen-5-yl)chroman-4-one (3c):

Colorless paste (223 mg, 52%). *R*_f: 0.35 (hexanes/ethyl acetate, 20:1). ¹H NMR (500 MHz, CDCl₃): δ = −0.14 (s, 9H), 2.17 (dd, 1H, *J* = 13.5, 16.6 Hz), 2.85–2.92 (m, 2H), 3.02 (dd, 1H, *J* = 11.3, 15.5 Hz), 3.15 (dd, 1H, *J* = 7.5, 15.5 Hz), 3.71 (dd, 1H, *J* = 11.3, 14.0 Hz), 5.02 (dd, 1H, *J* = 2.4, 13.2 Hz), 6.71–6.75 (m, 1H), 6.87–6.91 (m, 1H), 7.09–7.16 (m, 2H), 7.19–7.28 (m, 4H), 7.30–7.34 (m, 1H), 7.73–7.76 (m, 1H), 7.77–7.80 (m, 1H), 7.85–7.89 (m, 1H). ¹³C NMR (125 MHz, CDCl₃): δ = 1.8 (q), 36.4 (t), 36.8 (t), 38.9 (t), 84.4 (s), 87.5 (d), 117.6 (d), 120.8 (s), 120.9 (d), 124.9 (d), 126.0 (d), 126.4 (d), 127.6 (d), 128.0 (d), 129.4 (d), 130.1 (d), 131.4 (d), 131.7 (d), 135.4 (d), 138.6 (s), 141.8 (s), 143.0 (s), 160.9 (s), 193.0 (s). IR (ATR): ν̄ = 1690, 1605 cm⁻¹. HRMS (ESI⁺) calcd for C₂₇H₂₉O₃Si [M + H⁺] 429.1886, found 429.1875.

2-(5-((Trimethylsilyl)oxy)-5H-dibenzo[a,d][7]annulen-5-yl)chroman-4-one (3d):

White solid (273 mg, 64%). *R*_f: 0.25 (hexanes/ethyl acetate, 20:1). Mp 230–231 °C. ¹H NMR (500 MHz, CDCl₃): δ = 0.38 (s, 9H), 1.72 (dd, 1H, *J* = 4.3, 17.8 Hz), 2.70 (dd, 1H, *J* = 14.8, 17.8 Hz), 5.62 (dd, 1H, *J* = 4.3, 14.8 Hz), 6.68–6.72 (m, 1H), 6.90–6.97 (m, 2H), 7.02 (d, 1H, *J* = 11.6 Hz), 7.27–7.39 (m, 5H), 7.43–7.51 (m, 2H), 7.77–7.81 (m, 1H), 7.81–7.85 (m, 1H), 7.93–7.97 (m, 1H). ¹³C NMR (125 MHz, CDCl₃): δ = 3.8 (q), 37.8 (t), 75.1 (d), 83.3 (s), 113.1 (d), 120.7 (s), 121.4 (d), 124.9 (d), 126.0 (d), 126.6 (d), 126.9 (d), 127.0 (d), 128.3 (d), 129.1 (d), 129.2 (d), 129.4 (d), 131.3 (d), 131.4 (s), 131.8 (d), 131.9 (s), 136.0 (d), 138.6 (s), 139.5 (s), 160.9 (s), 192.7 (s). IR (ATR): ν̄ = 1686, 1605 cm⁻¹. HRMS (ESI⁺) calcd for C₂₇H₂₇O₃Si [M + H⁺] 427.1729, found 427.1716.

2-(9-((Trimethylsilyl)oxy)-9H-xanthen-9-yl)chroman-4-one (3e):

White solid (392 mg, 94%). *R*_f: 0.3 (hexanes/ethyl acetate, 20:1). Mp 167–168 °C. ¹H NMR (500 MHz, CDCl₃): δ = −0.13 (s, 9H), 2.47 (dd, 1H, *J* = 13.2, 16.6 Hz), 2.58 (dd, 1H, *J* = 3.0, 16.6 Hz), 4.63 (dd, 1H, *J* = 3.0, 13.2 Hz), 6.85–6.93 (m, 2H), 7.13–7.19 (m, 4H), 7.33–7.41 (m, 3H), 7.55–7.59 (m, 1H), 7.71–7.75 (m, 1H), 7.77–7.80 (m, 1H). ¹³C NMR (125 MHz, CDCl₃): δ = 1.7 (q), 38.0 (t), 72.6 (s), 85.1 (d), 116.0 (d), 116.5 (d), 118.0 (d), 120.8 (s), 121.1 (d), 122.6 (s), 122.8 (d), 122.9 (d), 123.3 (s), 126.5 (d), 128.1 (d), 128.8 (d), 129.5 (d), 129.8 (d), 135.7 (d), 150.4 (s), 150.6 (s), 161.1 (s), 192.3 (s). IR (ATR): ν̄ = 1690, 1607, 1576 cm⁻¹. HRMS (ESI⁺) calcd for C₂₅H₂₅O₄Si [M + H⁺] 417.1522, found 417.1510.

2-(9-((Trimethylsilyl)oxy)-9H-fluoren-9-yl)chroman-4-one (3f):

Yellow paste (220 mg, 55%). *R*_f: 0.3 (hexanes/ethyl acetate, 20:1). ¹H NMR (500 MHz, CDCl₃): δ = −0.28 (s, 9H), 2.45 (dd, 1H, *J* = 3.3, 16.8 Hz), 2.54 (dd, 1H, *J* = 12.7, 16.8 Hz), 4.72 (dd, 1H, *J* = 3.3, 12.7 Hz), 6.93–6.97 (m, 1H), 7.03–7.06 (m, 1H), 7.27–7.33 (m, 2H), 7.38–7.47 (m, 3H), 7.54–7.57 (m, 1H),

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7.63-7.66 (m, 2H), 7.69-7.71 (m, 1H), 7.78-7.81 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ = 1.2 (q), 37.8 (t), 82.6 (d), 84.8 (s), 117.9 (d), 120.0 (d), 120.1 (d), 120.98 (d), 121.00 (d), 125.3 (d), 126.51 (d), 126.53 (d), 127.6 (d), 127.7 (d), 129.4 (d), 129.5 (d), 135.7 (d), 139.9 (s), 140.4 (s), 144.9 (s), 145.6 (s), 161.7 (s), 192.4 (s). IR (ATR): $\tilde{\nu}$ = 1690, 1605 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{25}\text{H}_{25}\text{O}_3\text{Si}$ [M + H $^+$] 401.1573, found 401.1562.

(2R*,3R*)-2-(Diphenyl((trimethylsilyl)oxy)methyl)-3-methylchroman-4-one (cis-3g): Colorless paste (312 mg, 75%). *R*_f: 0.35 (hexanes/ethyl acetate, 20:1). ^1H NMR (500 MHz, CDCl_3): δ = -0.04 (s, 9H), 1.11 (d, 3H, *J* = 7.5 Hz), 2.18-2.24 (m, 1H), 5.27 (d, 1H, *J* = 2.3 Hz), 7.08-7.14 (m, 2H), 7.22-7.31 (m, 8H), 7.34-7.39 (m, 2H), 7.54-7.58 (m, 1H), 7.91-7.94 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ = 2.0 (q), 11.5 (q), 42.4 (d), 81.3 (d), 82.1 (s), 117.3 (d), 119.8 (s), 121.8 (d), 125.9 (d), 127.1 (d), 127.4 (d), 127.9 (d), 128.0 (d), 128.2 (d), 128.4 (d), 135.9 (d), 144.9 (s), 145.8 (s), 160.8 (s), 197.0 (s). IR (ATR): $\tilde{\nu}$ = 1690, 1605 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{26}\text{H}_{29}\text{O}_3\text{Si}$ [M + H $^+$] 417.1886, found 417.1875.

(2R*,3R*)-2-(Bis(4-fluorophenyl)((trimethylsilyl)oxy)methyl)-3-methylchroman-4-one (cis-3h): Colorless paste (276 mg, 61%). *R*_f: 0.25 (hexanes/ethyl acetate, 20:1). ^1H NMR (500 MHz, CDCl_3): δ = -0.03 (s, 9H), 1.06 (d, 3H, *J* = 7.5 Hz), 2.24 (q, 1H, *J* = 7.5 Hz), 5.18 (s, 1H), 6.95-7.03 (m, 4H), 7.09-7.13 (m, 2H), 7.23-7.28 (m, 2H), 7.33-7.37 (m, 2H), 7.54-7.59 (m, 1H), 7.91-7.94 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ = 2.0 (q), 11.3 (q), 42.3 (d), 81.4 (s), 81.5 (d), 114.8 (d, *J*_{CCF} = 20.7 Hz), 115.1 (d, *J*_{CCF} = 21.3 Hz), 117.2 (d), 119.8 (s), 122.1 (d), 127.9 (d, *J*_{CCCF} = 7.5 Hz), 128.1 (d), 130.2 (d, *J*_{CCCF} = 7.5 Hz), 135.9 (d), 140.6 (s, *J*_{CCCF} = 3.6 Hz), 141.5 (s, *J*_{CCCF} = 3.3 Hz), 160.6 (s), 161.9 (s, *J*_{CF} = 247.1 Hz), 162.0 (s, *J*_{CF} = 247.1 Hz), 196.4 (s). IR (ATR): $\tilde{\nu}$ = 1690, 1603 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{26}\text{H}_{27}\text{F}_2\text{O}_3\text{Si}$ [M + H $^+$] 453.1698, found 453.1685.

(2R*,3R*)-3-Methyl-2-(5-((trimethylsilyl)oxy)-5H-dibenzo[a,d][7]annulen-5-yl)chroman-4-one (cis-3i): White solid (335 mg, 76%). *R*_f: 0.2 (hexanes/ethyl acetate, 20:1). Mp 198-199 °C. ^1H NMR (500 MHz, CDCl_3): δ = 0.47 (s, 9H), 0.85 (d, 3H, *J* = 7.5 Hz), 2.18-2.24 (m, 1H), 5.36 (d, 1H, *J* = 2.9 Hz), 6.76-6.80 (m, 1H), 6.93-7.06 (m, 3H), 7.23-7.38 (m, 5H), 7.40-7.46 (m, 2H), 7.73-7.77 (m, 1H), 7.78-7.82 (m, 1H), 7.98-8.01 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ = 4.4 (q), 10.9 (q), 43.1 (d), 79.3 (d), 83.7 (s), 117.5 (d), 119.6 (s), 121.3 (d), 124.8 (d), 125.6 (d), 126.5 (d), 126.8 (d), 127.6 (d), 127.9 (d), 128.8 (d), 129.0 (d), 129.1 (d), 131.6 (d), 131.9 (s), 132.1 (s), 132.3 (d), 135.4 (d), 140.3 (s), 140.7 (s), 160.9 (s), 196.4 (s). IR (ATR): $\tilde{\nu}$ = 1688, 1603 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{28}\text{H}_{29}\text{O}_3\text{Si}$ [M + H $^+$] 441.1886, found 441.1875.

(2R*,3R*)-2-(Diphenyl((trimethylsilyl)oxy)methyl)-3-phenylchroman-4-one (cis-3j): Colorless paste (306 mg, 64%). *R*_f: 0.3 (hexanes/ethyl acetate, 20:1). IR (ATR): $\tilde{\nu}$ = 1690, 1605 cm^{-1} . ^1H NMR (500 MHz, CDCl_3): δ = -0.21 (s, 9H), 3.76 (d, 1H, *J* = 2.9 Hz), 5.53 (d, 1H, *J* = 2.9 Hz), 6.75-6.81 (m, 2H), 6.91-6.96 (m, 2H), 6.98-7.06 (m, 4H), 7.10-7.14 (m, 1H), 7.19-7.33 (m, 8H), 7.59-7.64 (m, 1H), 7.93-7.97 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ = 1.9 (q), 53.7 (d), 81.3 (s), 82.9 (d), 117.7 (d), 120.7 (s), 122.3 (d), 126.6 (d), 126.9 (d), 127.6 (d), 127.88 (d), 127.93 (d), 128.0 (d), 128.7 (d), 128.9 (d), 129.7 (d), 134.1 (s), 136.2 (d), 143.9 (s), 144.8 (s), 161.1 (s), 192.0 (s). IR (ATR): $\tilde{\nu}$ = 1690, 1605 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{31}\text{H}_{31}\text{O}_3\text{Si}$ [M + H $^+$] 479.2042, found 479.2033.

(2R*,3R*)-2-(Bis(4-fluorophenyl)((trimethylsilyl)oxy)methyl)-3-phenylchroman-4-one (cis-3k): Colorless paste (278 mg, 54%). *R*_f: 0.3 (hexanes/ethyl acetate, 20:1). ^1H NMR (500 MHz, CDCl_3): δ = -0.14 (s, 9H), 3.92 (d, 1H, *J* = 2.9 Hz), 6.47 (d, 1H, *J* = 2.9 Hz), 6.58-6.63 (m, 2H), 6.73-6.76 (m, 2H), 6.88-6.93 (m, 2H), 6.97-7.02 (m, 3H), 7.11-7.16 (m, 3H), 7.17-7.22 (m, 3H), 7.59-7.63 (m, 1H), 7.93-7.95 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ = 1.9 (q), 53.6 (d), 80.3 (s), 82.3 (d), 113.4 (d, *J*_{CCF} = 20.4 Hz), 114.8 (d, *J*_{CCF} = 21.0 Hz), 117.6 (d), 120.4 (s), 122.5 (d), 126.7 (d),

128.1 (d), 128.7 (d), 129.5 (d), 130.0 (d, *J*_{CCCF} = 8.4 Hz), 130.4 (d, *J*_{CCCF} = 7.8 Hz), 133.8 (s), 136.2 (d), 138.9 (s, *J*_{CCCF} = 2.4 Hz), 140.5 (s, *J*_{CCCF} = 2.4 Hz), 160.7 (s), 161.6 (s, *J*_{CF} = 245.9 Hz), 162.2 (s, *J*_{CF} = 248.3 Hz), 191.4 (s). IR (ATR): $\tilde{\nu}$ = 1690, 1605, 1504 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{31}\text{H}_{29}\text{F}_2\text{O}_3\text{Si}$ [M + H $^+$] 515.1854, found 515.1837.

2-(Diphenyl((trimethylsilyl)oxy)methyl)-2-methylchroman-4-one (3l): White solid (287 mg, 69%). *R*_f: 0.35 (hexanes/ethyl acetate, 20:1). Mp 145-147 °C. ^1H NMR (500 MHz, CDCl_3): δ = -0.17 (brs, 9H), 1.56 (brs, 3H), 2.26 (brs, 1H), 3.39 (brs, 1H), 6.99-7.04 (m, 1H), 7.05-7.09 (m, 1H), 7.24-7.32 (m, 6H), 7.40-7.47 (m, 2H), 7.50-7.66 (m, 3H), 7.85-7.90 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ = 1.7 (q), 20.5 (q), 44.7 (t), 86.1 (brs), 87.0 (brs), 118.2 (d), 120.6 (s), 120.8 (d), 126.4 (d), 127.2 (d), 127.3 (d), 127.37 (d), 127.41 (d), 129.3 (brd), 130.6 (brd), 136.2 (d), 144.4 (s), 159.2 (s), 192.7 (s). IR (ATR): $\tilde{\nu}$ = 1680, 1603 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{26}\text{H}_{29}\text{O}_3\text{Si}$ [M + H $^+$] 417.1886, found 417.1872.

2-(Bis(4-fluorophenyl)((trimethylsilyl)oxy)methyl)-2-methylchroman-4-one (3m): White solid (290 mg, 64%). *R*_f: 0.3 (hexanes/ethyl acetate, 20:1). Mp 166-167 °C. ^1H NMR (500 MHz, CDCl_3): δ = -0.16 (s, 9H), 1.53 (brs, 3H), 2.24 (brs, 1H), 3.33 (brd, 1H, *J* = 16.0 Hz), 6.95-7.07 (m, 6H), 7.35-7.43 (m, 2H), 7.50-7.64 (m, 3H), 7.85-7.91 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ = 1.8 (q), 20.5 (q), 44.5 (t), 85.5 (s), 86.9 (s), 114.2 (d, *J*_{CCF} = 19.2 Hz), 114.3 (d, *J*_{CCF} = 20.4 Hz), 118.1 (d), 120.5 (s), 121.1 (d), 126.5 (d), 131.1 (brd), 132.3 (brd), 136.3 (d), 139.8 (brs), 140.0 (s, *J*_{CCCF} = 2.7 Hz), 159.0 (s), 161.98 (s, *J*_{CF} = 248.3 Hz), 162.01 (s, *J*_{CF} = 248.3 Hz), 192.3 (s). IR (ATR): $\tilde{\nu}$ = 1690, 1603 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{26}\text{H}_{27}\text{F}_2\text{O}_3\text{Si}$ [M + H $^+$] 453.1698, found 453.1686.

(2R*,3R*)-2-(Diphenyl((trimethylsilyl)oxy)methyl)-6-methoxy-3-phenylchroman-4-one (cis-3n): Colorless paste (361 mg, 71%). *R*_f: 0.5 (hexanes/ethyl acetate, 5:1). ^1H NMR (500 MHz, CDCl_3): δ = -0.21 (s, 9H), 3.74 (d, 1H, *J* = 2.9 Hz), 3.80 (s, 3H), 5.48 (d, 1H, *J* = 2.9 Hz), 6.77-6.80 (m, 2H), 6.91-6.96 (m, 2H), 6.98-7.04 (m, 4H), 7.15-7.18 (m, 1H), 7.19-7.25 (m, 5H), 7.28-7.32 (m, 3H), 7.35-7.37 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ = 1.8 (q), 53.4 (d), 55.6 (q), 81.2 (s), 82.9 (d), 108.7 (d), 118.9 (d), 120.4 (s), 125.3 (d), 126.5 (d), 126.76 (d), 126.79 (d), 127.5 (d), 127.7 (d), 127.8 (d), 127.9 (d), 128.8 (d), 129.6 (d), 134.1 (s), 143.8 (s), 144.8 (s), 154.6 (s), 155.6 (s), 191.8 (s). IR (ATR): $\tilde{\nu}$ = 1686, 1616 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{32}\text{H}_{33}\text{O}_4\text{Si}$ [M + H $^+$] 509.2148, found 509.2136.

(2R*,3R*)-2-(Diphenyl((trimethylsilyl)oxy)methyl)-7-methoxy-3-phenylchroman-4-one (cis-3o): White solid (310 mg, 61%). *R*_f: 0.25 (hexanes/ethyl acetate, 10:1). Mp 90-92 °C. ^1H NMR (500 MHz, CDCl_3): δ = -0.20 (s, 9H), 3.72 (d, 1H, *J* = 2.9 Hz), 3.93 (s, 3H), 5.54 (d, 1H, *J* = 2.9 Hz), 6.65 (d, 1H, *J* = 2.3 Hz), 6.69 (dd, 1H, *J* = 2.3, 8.7 Hz), 6.75-6.78 (m, 2H), 6.90-6.94 (m, 2H), 6.97-7.05 (m, 4H), 7.20-7.24 (m, 4H), 7.29-7.32 (m, 3H), 7.88 (d, 1H, *J* = 8.7 Hz). ^{13}C NMR (125 MHz, CDCl_3): δ = 1.9 (q), 53.5 (d), 55.7 (q), 81.2 (s), 83.0 (d), 100.9 (d), 110.4 (d), 114.2 (s), 126.5 (d), 126.76 (d), 126.81 (d), 127.6 (d), 127.86 (d), 127.88 (d), 128.8 (d), 129.6 (d), 130.3 (d), 134.4 (s), 143.8 (s), 144.8 (s), 162.9 (s), 166.1 (s), 190.8 (s). IR (ATR): $\tilde{\nu}$ = 1676, 1607, 1570 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{32}\text{H}_{33}\text{O}_4\text{Si}$ [M + H $^+$] 509.2148, found 509.2134.

(2R*,3R*)-2-(Diphenyl((trimethylsilyl)oxy)methyl)-7-methoxy-3-(4-methoxyphenyl)chroman-4-one (cis-3p): White solid (296 mg, 55%). *R*_f: 0.4 (hexanes/ethyl acetate, 5:1). Mp 208-210 °C. ^1H NMR (500 MHz, CDCl_3): δ = -0.19 (s, 9H), 3.68 (s, 3H), 3.70 (d, 1H, *J* = 2.9 Hz), 3.92 (s, 3H), 5.52 (d, 1H, *J* = 2.9 Hz), 6.44-6.49 (m, 2H), 6.63-6.64 (m, 1H), 6.66-6.70 (m, 3H), 6.99-7.06 (m, 3H), 7.20-7.23 (m, 4H), 7.28-7.32 (m, 3H), 7.87-7.89 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ = 1.9 (q), 52.6 (d), 55.1 (q), 55.7 (q), 81.1 (s), 82.8 (d), 100.8 (d), 110.4 (d), 113.5 (d), 114.2 (s), 126.6 (d), 126.8 (d), 127.6 (d), 127.9 (d), 128.0 (d), 128.8 (d), 130.3 (d), 130.6 (d), 143.9 (s), 144.9 (s), 158.2 (s), 162.9 (s), 166.1 (s), 191.1 (s). IR

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(ATR): $\tilde{\nu}$ = 1680, 1672, 1607, 1584, 1570, 1512 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{33}\text{H}_{35}\text{O}_5\text{Si}$ [$\text{M} + \text{H}^+$] 539.2254, found 539.2239.

(2R*,3R*)-2-(Diphenyl(trimethylsilyloxy)methyl)-5,7-dimethoxy-3-(4-methoxyphenyl)chroman-4-one (cis-3q): Colorless paste (318 mg, 56%). *R*_f: 0.35 (hexanes/ethyl acetate, 1:1). ^1H NMR (500 MHz, CDCl_3): δ = -0.19 (s, 9H), 3.62 (d, 1H, *J* = 2.9 Hz), 3.68 (s, 3H), 3.83 (s, 3H), 3.91 (s, 3H), 5.48 (d, 1H, *J* = 2.9 Hz), 6.14 (d, 1H, *J* = 2.3 Hz), 6.28 (d, 1H, *J* = 2.3 Hz), 6.42-6.46 (m, 2H), 6.67-6.71 (m, 2H), 6.96-7.06 (m, 3H), 7.16-7.24 (m, 4H), 7.25-7.32 (m, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ = 1.7 (q), 53.8 (d), 54.9 (q), 55.4 (q), 55.8 (q), 80.8 (s), 81.8 (d), 93.0 (d), 93.1 (d), 104.7 (s), 113.1 (d), 126.4 (d), 126.6 (d), 126.7 (s), 127.3 (d), 127.66 (d), 127.71 (d), 128.6 (d), 130.5 (d), 143.8 (s), 144.8 (s), 157.9 (s), 163.1 (s), 164.1 (s), 165.8 (s), 189.5 (s). IR (ATR): $\tilde{\nu}$ = 1676, 1605, 1570, 1510 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{34}\text{H}_{37}\text{O}_6\text{Si}$ [$\text{M} + \text{H}^+$] 569.2359, found 569.2345.

[2,2'-Bichromane]-4,4'-dione (i: 67:33 diastereomeric mixture): White solid (60 mg, 41%). *R*_f: 0.5, 0.55 (hexanes/ethyl acetate, 2:1). ^1H NMR (500 MHz, CDCl_3): δ = 2.79 (dd, 1.33H, *J* = 2.9, 17.0 Hz), 2.96-3.00 (m, 1.33H), 3.29 (dd, 1.33H, *J* = 13.2, 17.0 Hz), 4.64-4.69 (m, 1.33H), 4.70-4.76 (m, 0.67 H), 7.00-7.10 (m, 4H), 7.49-7.55 (m, 2H), 7.90-7.95 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3): δ = major: 38.9 (t), 77.5 (d), 117.92 (d), 120.8 (s), 121.9 (d), 127.97 (s), 136.3 (d), 160.7 (s), 191.4 (s), minor: 38.8 (t), 77.8 (d), 117.94 (d), 120.9 (s), 122.0 (d), 127.02 (s), 136.4 (d), 160.5 (s), 190.8 (s). IR (ATR): $\tilde{\nu}$ = 1678, 1601, 1576 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{18}\text{H}_{15}\text{O}_4$ [$\text{M} + \text{H}^+$] 295.0970, found 295.0963.

2-(Trimethylsilyl)chroman-4-one (ii): Colorless paste (22 mg, 10%). *R*_f: 0.55 (hexanes/ethyl acetate, 10:1). ^1H NMR (500 MHz, CDCl_3): δ = 0.17 (s, 9H), 2.53-2.58 (m, 1H), 2.78-2.85 (m, 1H), 4.22-4.27 (m, 1H), 6.93-6.99 (m, 2H), 7.41-7.46 (m, 1H), 7.86-7.89 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ = -4.3 (q), 38.3 (t), 72.5 (d), 117.8 (d), 120.7 (d), 121.2 (s), 124.1 (d), 135.5 (d), 163.7 (s), 192.7 (s). IR (ATR): $\tilde{\nu}$ = 1690, 1605, 1574 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{12}\text{H}_{17}\text{O}_2\text{Si}$ [$\text{M} + \text{H}^+$] 221.0998, found 221.0994.

Dehydrosiloxylation of 3. A solution of **3a** (201 mg, 0.50 mmol) and *p*-TsOH (10 mg) in xylene (10 mL) was refluxed using Dean-Stark apparatus under nitrogen atmosphere for 1 h. After the solvent was removed *in vacuo*, the residue was purified by column chromatography on silica gel (hexanes-EtOAc) to give **4a** (139 mg, 0.446 mmol) in 89% yield.

2-Benzhydryl-4H-chromen-4-one (4a): Yellow solid (139 mg, 89%). *R*_f: 0.35 (hexanes/ethyl acetate, 5:1). Mp 153-154 °C. ^1H NMR (500 MHz, CDCl_3): δ = 5.38 (s, 1H), 6.10 (s, 1H), 7.17-7.42 (m, 12H), 7.59-7.66 (m, 1H), 8.15-8.21 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ = 55.9 (d), 112.4 (d), 118.0 (d), 123.6 (s), 125.0 (d), 125.6 (d), 127.4 (d), 128.7 (d), 128.9 (d), 133.6 (d), 138.8 (d), 156.4 (s), 169.8 (s), 178.3 (s). IR (ATR): $\tilde{\nu}$ = 1651, 1603 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{22}\text{H}_{17}\text{O}_2$ [$\text{M} + \text{H}^+$] 313.1229, found 313.1222.

2-(Bis(4-fluorophenyl)methyl)-4H-chromen-4-one (4b): Colorless paste (171 mg, 98%). *R*_f: 0.25 (hexanes/ethyl acetate, 5:1). ^1H NMR (500 MHz, CDCl_3): δ = 5.33 (s, 1H), 6.06 (s, 1H), 7.02-7.08 (m, 4H), 7.15-7.21 (m, 4H), 7.34-7.42 (m, 2H), 7.61-7.66 (m, 1H), 8.17-8.20 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ = 54.4 (d), 112.3 (d), 115.8 (d, *J*_{CCF} = 21.6 Hz), 117.9 (d), 123.6 (s), 125.2 (d), 125.7 (d), 130.5 (d, *J*_{CCCF} = 7.8 Hz), 133.8 (d), 134.4 (s), 156.3 (s), 162.1 (s, *J*_{CF} = 247.1 Hz), 169.2 (s). IR (ATR): $\tilde{\nu}$ = 1647, 1601 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{22}\text{H}_{15}\text{F}_2\text{O}_2$ [$\text{M} + \text{H}^+$] 349.1040, found 349.1033.

2-(10,11-Dihydro-5H-dibenzo[a,d][7]annulen-5-yl)-4H-chromen-4-one (4c): Yellow solid (130 mg, 77%). *R*_f: 0.3 (hexanes/ethyl acetate, 5:1). Mp 165-167 °C. ^1H NMR (500 MHz, CDCl_3): δ = 2.81-2.89 (m, 2H), 3.30-3.39

(m, 2H), 5.16 (s, 1H), 5.94 (s, 1H), 7.14-7.19 (m, 2H), 7.19-7.28 (m, 5H), 7.31-7.36 (m, 3H), 7.54-7.59 (m, 1H), 8.12-8.15 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ = 32.1 (t), 57.8 (d), 111.2 (d), 118.0 (d), 123.3 (s), 124.9 (d), 125.4 (d), 126.4 (d), 128.1 (d), 130.6 (d), 131.7 (d), 133.4 (d), 135.4 (d), 139.8 (s), 156.1 (s), 170.5 (s), 178.2 (s). IR (ATR): $\tilde{\nu}$ = 1643, 1607 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{24}\text{H}_{19}\text{O}_2$ [$\text{M} + \text{H}^+$] 339.1385, found 339.1378.

2-(5H-Dibenzo[a,d][7]annulen-5-yl)-4H-chromen-4-one (4d): White solid (126 mg, 92%). *R*_f: 0.2 (hexanes/ethyl acetate, 5:1). Mp 207-209 °C. ^1H NMR (500 MHz, CDCl_3): δ = 5.36 (d, 1H, *J* = 1.5 Hz), 5.69 (d, 1H, *J* = 1.5 Hz), 6.85 (s, 2H), 7.08-7.10 (m, 1H), 7.28-7.32 (m, 1H), 7.34-7.39 (m, 4H), 7.41-7.45 (m, 2H), 7.46-7.53 (m, 3H), 8.07-8.09 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ = 57.1 (d), 110.2 (d), 117.8 (d), 123.3 (s), 124.8 (d), 125.3 (d), 127.6 (d), 128.9 (d), 129.6 (d), 130.3 (d), 130.7 (d), 133.2 (s), 134.5 (s), 135.5 (s), 156.0 (s), 167.5 (s), 178.1 (s). IR (ATR): $\tilde{\nu}$ = 1639 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{24}\text{H}_{17}\text{O}_2$ [$\text{M} + \text{H}^+$] 337.1229, found 337.1224.

2-(9H-Xanthen-9-yl)-4H-chromen-4-one (4e): Yellow solid (122 mg, 75%). *R*_f: 0.3 (hexanes/ethyl acetate, 5:1). Mp 168-170 °C. ^1H NMR (500 MHz, CDCl_3): δ = 5.23 (s, 1H), 6.07 (s, 1H), 7.08-7.12 (m, 2H), 7.18-7.21 (m, 2H), 7.30-7.38 (m, 6H), 7.57-7.61 (m, 1H), 8.10-8.13 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ = 43.7 (d), 109.8 (d), 117.0 (d), 117.9 (d), 118.8 (s), 123.5 (d), 125.0 (d), 125.5 (d), 129.1 (d), 129.2 (d), 133.5 (d), 151.6 (s), 156.3 (s), 169.2 (s), 178.3 (s). IR (ATR): $\tilde{\nu}$ = 1647, 1603 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{22}\text{H}_{15}\text{O}_3$ [$\text{M} + \text{H}^+$] 327.1021, found 327.1015.

2-Benzhydryl-3-methyl-4H-chromen-4-one (4g): White solid (132 mg, 81%). *R*_f: 0.35 (hexanes/ethyl acetate, 5:1). Mp 185-186 °C. ^1H NMR (500 MHz, CDCl_3): δ = 2.20 (s, 3H), 5.70 (s, 1H), 7.24-7.37 (m, 12H), 7.55-7.60 (m, 1H), 8.19-8.22 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ = 9.9 (q), 52.8 (d), 117.7 (d), 117.9 (s), 122.4 (s), 124.7 (d), 125.8 (d), 127.2 (d), 128.6 (d), 129.0 (d), 133.1 (d), 139.3 (s), 155.7 (s), 163.4 (s), 178.3 (s). IR (ATR): $\tilde{\nu}$ = 1624, 1609, 1599 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{23}\text{H}_{19}\text{O}_2$ [$\text{M} + \text{H}^+$] 327.1385, found 327.1379.

2-(Bis(4-fluorophenyl)methyl)-3-methyl-4H-chromen-4-one (4h): White solid (174 mg, 96%). *R*_f: 0.35 (hexanes/ethyl acetate, 5:1). Mp 154-156 °C. ^1H NMR (500 MHz, CDCl_3): δ = 2.18 (s, 3H), 5.65 (s, 1H), 7.00-7.06 (m, 4H), 7.18-7.23 (m, 4H), 7.25-7.28 (m, 1H), 7.34-7.38 (m, 1H), 7.57-7.61 (m, 1H), 8.18-8.22 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ = 9.8 (q), 51.3 (d), 115.6 (d, *J*_{CCF} = 21.6 Hz), 117.6 (d), 118.0 (s), 122.5 (s), 124.9 (d), 125.9 (d), 130.4 (d, *J*_{CCCF} = 8.4 Hz), 133.3 (d), 135.0 (s, *J*_{CCCF} = 3.6 Hz), 155.6 (s), 162.0 (s, *J*_{CF} = 246.5 Hz), 162.8 (s), 178.2 (s). IR (ATR): $\tilde{\nu}$ = 1632, 1605 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{23}\text{H}_{17}\text{F}_2\text{O}_2$ [$\text{M} + \text{H}^+$] 363.1197, found 363.1190.

2-(5H-Dibenzo[a,d][7]annulen-5-yl)-3-methyl-4H-chromen-4-one (4i): White solid (172 mg, 98%). *R*_f: 0.25 (hexanes/ethyl acetate, 5:1). Mp 188-189 °C. ^1H NMR (500 MHz, CDCl_3): δ = 1.82 (s, 3H), 5.53 (s, 1H), 6.91 (s, 2H), 7.04-7.08 (m, 1H), 7.26-7.33 (m, 3H), 7.34-7.40 (m, 4H), 7.47-7.53 (m, 3H), 8.09-8.13 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ = 9.9 (q), 55.4 (d), 117.6 (d), 117.7 (s), 122.2 (s), 124.5 (d), 125.7 (d), 127.1 (d), 128.7 (d), 129.2 (d), 129.5 (d), 130.9 (d), 132.8 (d), 135.3 (s), 136.2 (s), 154.9 (s), 162.7 (s), 178.4 (s). IR (ATR): $\tilde{\nu}$ = 1624, 1616, 1605 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{25}\text{H}_{19}\text{O}_2$ [$\text{M} + \text{H}^+$] 351.1385, found 351.1377.

2-Benzhydryl-3-phenyl-4H-chromen-4-one (4j): White solid (173 mg, 89%). *R*_f: 0.35 (hexanes/ethyl acetate, 5:1). Mp 182-184 °C. ^1H NMR (500 MHz, CDCl_3): δ = 5.40 (s, 1H), 7.17-7.22 (m, 4H), 7.23-7.34 (m, 8H), 7.35-7.47 (m, 5H), 7.59-7.65 (m, 1H), 8.21-8.26 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ = 53.0 (d), 117.9 (d), 123.5 (s), 124.8 (s), 125.0 (d), 126.2 (d), 127.2 (d), 128.2 (d), 128.6 (d), 128.9 (d), 130.3 (d), 132.8 (s), 133.5 (d), 139.8 (s), 155.9 (s), 164.5 (s), 177.2 (s). IR (ATR): $\tilde{\nu}$ = 1643, 1622, 1599,

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1574 cm⁻¹. HRMS (ESI+) calcd for C₂₈H₂₁O₂ [M + H]⁺ 389.1542, found 389.1531.

2-(Bis(4-fluorophenyl)methyl)-3-phenyl-4H-chromen-4-one (4k): White solid (191 mg, 90%). *R*_f: 0.40 (hexanes/ethyl acetate, 5:1). Mp 178–179 °C. ¹H NMR (500 MHz, CDCl₃): δ = 5.35 (s, 1H), 6.98–7.04 (m, 4H), 7.11–7.17 (m, 4H), 7.21–7.25 (m, 2H), 7.36–7.48 (m, 5H), 7.63–7.67 (m, 1H), 8.22–8.25 (m, 1H). ¹³C NMR (125 MHz, CDCl₃): δ = 51.5 (d), 115.6 (d, *J*_{CCF} = 21.6 Hz), 117.7 (d), 123.4 (s), 124.7 (s), 125.2 (d), 126.3 (d), 128.3 (d), 128.7 (d), 130.2 (d), 130.4 (d, *J*_{CCF} = 8.4 Hz), 132.5 (s), 133.7 (d), 135.4 (s, *J*_{CCCF} = 3.0 Hz), 155.8 (s), 162.0 (s, *J*_{CF} = 247.1 Hz), 162.9 (s), 177.1 (s). IR (ATR): $\tilde{\nu}$ = 1639, 1622, 1614, 1601, 1576, 1504 cm⁻¹. HRMS (ESI+) calcd for C₂₈H₁₉F₂O₂ [M + H]⁺ 425.1353, found 425.1343.

2-Benzhydryl-6-methoxy-3-phenyl-4H-chromen-4-one (4n): White solid (190 mg, 91%). *R*_f: 0.55 (hexanes/ethyl acetate, 2:1). Mp 201–202 °C. ¹H NMR (500 MHz, CDCl₃): δ = 3.88 (s, 3H), 5.38 (s, 1H), 7.16–7.20 (m, 3H), 7.22 (dd, 1H, *J* = 2.9, 9.2 Hz), 7.25–7.35 (m, 10H), 7.38–7.46 (m, 3H), 7.59 (d, 1H, *J* = 2.9 Hz). ¹³C NMR (125 MHz, CDCl₃): δ = 53.0 (d), 55.9 (q), 105.3 (d), 119.3 (d), 123.5 (d), 124.0 (s), 127.1 (d), 128.1 (d), 128.5 (d), 128.9 (d), 130.3 (d), 133.0 (s), 139.9 (s), 150.7 (s), 156.9 (s), 164.3 (s), 177.0 (s). IR (ATR): $\tilde{\nu}$ = 1639, 1616, 1578 cm⁻¹. HRMS (ESI+) calcd for C₂₉H₂₃O₃ [M + H]⁺ 419.1647, found 419.1639.

2-Benzhydryl-7-methoxy-3-phenyl-4H-chromen-4-one (4o): White solid (195 mg, 93%). *R*_f: 0.25 (hexanes/ethyl acetate, 5:1). Mp 228–229 °C. ¹H NMR (500 MHz, CDCl₃): δ = 3.88 (s, 3H), 5.38 (s, 1H), 6.76 (d, 1H, *J* = 2.3 Hz), 6.95 (dd, 1H, *J* = 2.3, 9.0 Hz), 7.17–7.21 (m, 4H), 7.24–7.35 (m, 8H), 7.38–7.46 (m, 3H), 8.13 (d, 1H, *J* = 9.0 Hz). ¹³C NMR (125 MHz, CDCl₃): δ = 52.9 (d), 55.8 (q), 99.9 (d), 114.5 (d), 117.3 (s), 124.6 (s), 127.1 (d), 127.6 (d), 128.1 (d), 128.5 (d), 128.6 (d), 128.9 (d), 130.3 (d), 132.9 (s), 139.9 (s), 157.6 (s), 163.95 (s), 164.02 (s), 176.6 (s). IR (ATR): $\tilde{\nu}$ = 1647, 1622, 1597, 1568 cm⁻¹. HRMS (ESI+) calcd for C₂₉H₂₃O₃ [M + H]⁺ 419.1647, found 419.1640.

2-Benzhydryl-7-methoxy-3-(4-methoxyphenyl)-4H-chromen-4-one (4p): White solid (206 mg, 92%). *R*_f: 0.4 (hexanes/ethyl acetate, 2:1). Mp 181–182 °C. ¹H NMR (500 MHz, CDCl₃): δ = 3.84 (s, 3H), 3.88 (s, 3H), 5.43 (s, 1H), 6.75 (d, 1H, *J* = 2.4 Hz), 6.92–6.98 (m, 3H), 7.17–7.23 (m, 6H), 7.25–7.34 (m, 6H), 8.13 (d, 1H, *J* = 9.2 Hz). ¹³C NMR (125 MHz, CDCl₃): δ = 52.9 (d), 55.3 (q), 55.8 (q), 99.9 (d), 114.1 (d), 114.4 (d), 117.3 (s), 124.2 (s), 125.0 (s), 127.1 (d), 127.6 (d), 128.6 (d), 128.9 (d), 131.5 (d), 140.1 (d), 157.6 (d), 159.4 (s), 164.0 (s), 176.8 (s). IR (ATR): $\tilde{\nu}$ = 1632, 1611, 1570, 1512 cm⁻¹. HRMS (ESI+) calcd for C₃₀H₂₅O₄ [M + H]⁺ 449.1753, found 449.1740.

2-Benzhydryl-5,7-dimethoxy-3-(4-methoxyphenyl)-4H-chromen-4-one (4q): White solid (203 mg, 85%). *R*_f: 0.35 (hexanes/ethyl acetate, 1:2). Mp 225–226 °C. ¹H NMR (500 MHz, CDCl₃): δ = 3.83 (s, 3H), 3.84 (s, 3H), 3.88 (s, 3H), 5.35 (s, 1H), 6.31–6.35 (m, 2H), 6.90–6.95 (m, 2H), 7.14–7.22 (m, 6H), 7.24–7.34 (m, 6H). ¹³C NMR (125 MHz, CDCl₃): δ = 52.5 (d), 55.2 (q), 55.7 (q), 56.2 (q), 92.4 (d), 96.0 (d), 108.8 (s), 113.8 (d), 125.0 (s), 125.2 (s), 127.1 (d), 128.5 (d), 128.9 (d), 131.7 (d), 140.2 (s), 159.2 (s), 159.4 (s), 161.2 (s), 161.6 (s), 163.9 (s), 176.3 (s). IR (ATR): $\tilde{\nu}$ = 1636, 1609, 1572, 1510 cm⁻¹. HRMS (ESI+) calcd for C₃₁H₂₇O₅ [M + H]⁺ 479.1858, found 479.1849.

Desilylation of 3 with 1 M HCl aq and dioxane. To a solution of **3a** (201 mg, 0.50 mmol) in dioxane (5 mL) was added 1 M HCl aq (5 mL) at 25 °C, and then the solution was stirred at this temperature for 2 h. The mixture was neutralized with sat. NaHCO₃ aq and extracted with ethyl acetate (10 mL × 3). After removal of the solvent *in vacuo*, the residue was purified by

column chromatography on silica gel (hexanes–EtOAc) to give **5a** (149 mg, 0.452 mmol) in 90% yield.

2-(Hydroxydiphenylmethyl)chroman-4-one (5a): White solid (149 mg, 90%). *R*_f: 0.4 (hexanes/ethyl acetate, 5:1). Mp 174–175 °C. ¹H NMR (500 MHz, CDCl₃): δ = 2.26 (dd, 1H, *J* = 2.0, 17.2 Hz), 2.97 (s, 1H), 3.07 (dd, 1H, *J* = 13.8, 17.2 Hz), 5.41 (dd, 1H, *J* = 2.0, 13.8 Hz), 6.92–6.96 (m, 1H), 7.03–7.08 (m, 1H), 7.20–7.25 (m, 1H), 7.27–7.33 (m, 3H), 7.35–7.41 (m, 4H), 7.45–7.51 (m, 1H), 7.56–7.61 (m, 2H), 7.87–7.91 (m, 1H). ¹³C NMR (125 MHz, CDCl₃): δ = 37.5 (t), 78.7 (s), 80.5 (d), 117.9 (d), 121.1 (s), 121.9 (d), 125.6 (d), 126.8 (d), 127.0 (d), 127.4 (d), 128.3 (d), 128.5 (d), 136.1 (d), 141.9 (s), 144.3 (s), 160.9 (s), 192.8 (s). IR (ATR): $\tilde{\nu}$ = 3526 (br), 1686, 1605 cm⁻¹. HRMS (ESI+) calcd for C₂₂H₁₉O₃ [M + H]⁺ 331.1334, found 331.1315.

2-(Bis(4-fluorophenyl)(hydroxy)methyl)chroman-4-one (5b): Yellow paste (163 mg, 89%). *R*_f: 0.35 (hexanes/ethyl acetate, 5:1). ¹H NMR (500 MHz, CDCl₃): δ = 2.24 (dd, 1H, *J* = 2.3, 17.2 Hz), 3.009 (dd, 1H, *J* = 13.8, 17.2 Hz), 3.012 (brs, 1H), 5.31 (dd, 1H, *J* = 13.8, 17.2 Hz), 6.89–6.94 (m, 1H), 6.97–7.10 (m, 5H), 7.30–7.37 (m, 2H), 7.45–7.56 (m, 3H), 7.86–7.90 (m, 1H). ¹³C NMR (125 MHz, CDCl₃): δ = 37.4 (t), 78.2 (s), 80.4 (d), 115.2 (d, *J*_{CCF} = 21.6 Hz), 115.4 (d, *J*_{CCF} = 21.3 Hz), 117.8 (d), 121.0 (s), 122.2 (d), 127.1 (d), 127.5 (d, *J*_{CCCF} = 8.4 Hz), 128.7 (d, *J*_{CCCF} = 8.4 Hz), 136.2 (d), 137.6 (s, *J*_{CCCF} = 3.3 Hz), 139.9 (s, *J*_{CCCF} = 2.7 Hz), 160.6 (s), 162.0 (s, *J*_{CF} = 247.1 Hz), 162.1 (s, *J*_{CF} = 247.1 Hz), 192.3 (s). IR (ATR): $\tilde{\nu}$ = 3447 (br), 1682, 1603 cm⁻¹. HRMS (ESI+) calcd for C₂₂H₁₇F₂O₃ [M + H]⁺ 367.1146, found 367.1138.

2-(5-Hydroxy-10,11-dihydro-5H-dibenzo[a,d][7]annulen-5-yl)chroman-4-one (5c): White solid (168 mg, 94%). *R*_f: 0.2 (hexanes/ethyl acetate, 10:1). Mp 153–155 °C. ¹H NMR (500 MHz, CDCl₃): δ = 2.35 (dd, 1H, *J* = 2.9, 17.3 Hz), 2.93 (dd, 1H, *J* = 13.2, 17.3 Hz), 2.96–3.07 (m, 2H), 3.30–3.39 (m, 1H), 3.34 (brs, 1H), 3.46–3.54 (m, 1H), 5.49 (dd, 1H, *J* = 2.9, 13.2 Hz), 6.74–6.80 (m, 1H), 6.95–7.01 (m, 1H), 7.09–7.15 (m, 2H), 7.19–7.31 (m, 4H), 7.36–7.42 (m, 1H), 7.79–7.84 (m, 1H), 7.86–7.91 (m, 1H), 7.95–8.00 (m, 1H). ¹³C NMR (125 MHz, CDCl₃): δ = 33.7 (t), 33.9 (t), 38.1 (t), 78.8 (s), 82.0 (d), 118.0 (d), 120.8 (s), 121.7 (d), 126.0 (d), 126.6 (d), 126.8 (d), 126.9 (d), 127.0 (d), 127.8 (d), 128.2 (d), 130.8 (d), 130.9 (d), 135.9 (d), 137.6 (s), 137.7 (s), 139.3 (s), 141.3 (s), 160.7 (s), 192.7 (s). IR (ATR): $\tilde{\nu}$ = 3545 (br), 1695, 1605 cm⁻¹. HRMS (ESI+) calcd for C₂₄H₂₁O₃ [M + H]⁺ 357.1491, found 357.1482.

2-(5-Hydroxy-5H-dibenzo[a,d][7]annulen-5-yl)chroman-4-one (5d): White solid (158 mg, 89%). *R*_f: 0.25 (hexanes/ethyl acetate, 10:1). Mp 222–224 °C. ¹H NMR (500 MHz, CDCl₃): δ = 1.83 (dd, 1H, *J* = 2.7, 17.5 Hz), 2.84 (dd, 1H, *J* = 14.3, 17.5 Hz), 3.53 (s, 1H), 5.41 (dd, 1H, *J* = 2.7, 14.3 Hz), 6.64–6.70 (m, 1H), 6.90–7.01 (m, 3H), 7.28–7.40 (m, 5H), 7.43–7.48 (m, 1H), 7.50–7.56 (m, 1H), 7.75–7.81 (m, 1H), 7.97–8.07 (m, 2H). ¹³C NMR (125 MHz, CDCl₃): δ = 37.9 (t), 76.0 (d), 77.2 (s), 117.9 (d), 120.6 (s), 121.6 (d), 124.8 (d), 125.0 (d), 126.7 (d), 127.0 (d), 127.3 (d), 128.9 (d), 129.2 (d), 129.39 (d), 129.41 (d), 131.3 (d), 131.5 (d), 131.98 (s), 132.04 (s), 135.8 (d), 136.6 (s), 139.8 (s), 160.7 (s), 192.7 (s). IR (ATR): $\tilde{\nu}$ = 3549 (br), 1690, 1599 cm⁻¹. HRMS (ESI+) calcd for C₂₄H₁₉O₃ [M + H]⁺ 355.1334, found 355.1326.

2-(9-Hydroxy-9H-xanthen-9-yl)chroman-4-one (5e): White solid (152 mg, 88%). *R*_f: 0.25 (hexanes/ethyl acetate, 5:1). Mp 172–174 °C. ¹H NMR (500 MHz, CDCl₃): δ = 2.30–2.41 (m, 2H), 3.42 (s, 1H), 4.60 (dd, 1H, *J* = 4.2, 12.2 Hz), 6.93–7.01 (m, 2H), 7.15–7.22 (m, 4H), 7.34–7.40 (m, 2H), 7.42–7.47 (m, 1H), 7.70–7.75 (m, 2H), 7.80–7.85 (m, 1H). ¹³C NMR (125 MHz, CDCl₃): δ = 37.8 (t), 70.3 (s), 83.9 (d), 116.2 (d), 116.4 (d), 117.8 (d), 120.6 (s), 121.5 (d), 122.6 (s), 122.8 (s), 123.36 (d), 123.40 (d), 126.7 (d), 126.8 (d), 127.7 (d), 129.6 (d), 129.8 (d), 135.9 (d), 150.8 (s), 150.9 (s),

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160.6 (s), 191.7 (s). IR (ATR): $\tilde{\nu}$ = 3435 (br), 1667, 1601 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{22}\text{H}_{17}\text{O}_4$ [$\text{M} + \text{H}^+$] 345.1127, found 345.1121.

2-(9-Hydroxy-9H-fluoren-9-yl)chroman-4-one (5f): Yellow paste (141 mg, 86%). *R_f*: 0.2 (hexanes/ethyl acetate, 5:1). ^1H NMR (500 MHz, CDCl_3): δ = 2.11 (dd, 1H, J = 2.9, 17.0 Hz), 2.20 (dd, 1H, J = 13.9, 17.0 Hz), 3.29 (brs, 1H), 4.98 (dd, 1H, J = 2.9, 13.9 Hz), 7.00-7.06 (m, 1H), 7.17-7.21 (m, 1H), 7.26-7.35 (m, 2H), 7.38-7.5 (m, 2H), 7.51-7.56 (m, 2H), 7.63-7.68 (m, 2H), 7.73-7.77 (m, 1H), 7.79-7.83 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ = 37.8 (t), 82.2 (d), 82.8 (s), 117.8 (d), 120.2 (d), 120.3 (d), 120.8 (s), 121.7 (d), 123.9 (d), 125.9 (d), 126.9 (d), 128.1 (d), 128.3 (d), 129.6 (d), 130.0 (d), 136.1 (d), 140.2 (s), 140.4 (s), 144.2 (s), 144.3 (s), 161.1 (s), 191.8 (s). IR (ATR): $\tilde{\nu}$ = 3428 (br), 1684, 1605 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{22}\text{H}_{17}\text{O}_3$ [$\text{M} + \text{H}^+$] 329.1178, found 329.1171.

(2R*,3R*)-2-(Hydroxydiphenylmethyl)-3-methylchroman-4-one (cis-5g): White solid (136 mg, 79%). *R_f*: 0.55 (hexanes/ethyl acetate, 5:1). Mp 153-155 °C. ^1H NMR (500 MHz, CDCl_3): δ = 1.30 (d, 3H, J = 6.9 Hz), 2.30-2.36 (m, 1H), 3.10 (brs, 1H), 5.32 (d, 1H, J = 1.7 Hz), 6.97-7.01 (m, 1H), 7.07-7.11 (m, 1H), 7.21-7.36 (m, 6H), 7.39-7.43 (m, 2H), 7.48-7.53 (m, 3H), 7.90-7.93 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ = 11.3 (q), 42.3 (d), 79.6 (s), 81.2 (d), 117.5 (d), 119.8 (s), 122.1 (d), 125.3 (d), 126.6 (d), 127.27 (d), 127.32 (d), 128.0 (d), 128.3 (d), 128.5 (d), 135.8 (d), 141.9 (s), 145.9 (s), 160.7 (s), 196.5 (s). IR (ATR): $\tilde{\nu}$ = 3385 (br), 1678, 1605 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{23}\text{H}_{21}\text{O}_3$ [$\text{M} + \text{H}^+$] 345.1491, found 345.1485.

(2R*,3R*)-2-(bis(4-fluorophenyl)(hydroxy)methyl)-3-methylchroman-4-one (cis-5h): White solid (146 mg, 77%). *R_f*: 0.45 (hexanes/ethyl acetate, 5:1). Mp 152-154 °C. ^1H NMR (500 MHz, CDCl_3): δ = 1.28 (d, 3H, J = 7.2 Hz), 2.28-2.34 (m, 1H), 3.11 (s, 1H), 5.23 (d, 1H, J = 1.9 Hz), 6.96-7.05 (m, 5H), 7.08-7.13 (m, 1H), 7.34-7.39 (m, 2H), 7.43-7.47 (m, 2H), 7.50-7.54 (m, 1H), 7.90-7.94 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ = 11.2 (q), 42.3 (d), 79.0 (s), 81.1 (d), 115.2 (d, J_{CCF} = 21.0 Hz), 115.5 (d, J_{CCF} = 21.6 Hz), 117.4 (d), 119.8 (s), 122.4 (d), 127.1 (d, J_{CCCF} = 8.4 Hz), 128.1 (d), 128.4 (d, J_{CCCF} = 8.4 Hz), 136.0 (d), 137.7 (s, J_{CCCF} = 3.0 Hz), 141.6 (s, J_{CCCF} = 3.6 Hz), 160.4 (s), 161.9 (s, J_{CF} = 247.1 Hz), 162.0 (s, J_{CF} = 247.1 Hz), 196.1 (s). IR (ATR): $\tilde{\nu}$ = 3547 (br), 3460 (br), 1695, 1686, 1603 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{23}\text{H}_{19}\text{F}_2\text{O}_3$ [$\text{M} + \text{H}^+$] 381.1302, found 381.1291.

(2R*,3R*)-2-(5-Hydroxy-5H-dibenzo[a,d][7]annulen-5-yl)-3-methylchroman-4-one (cis-5i): White solid (175 mg, 95%). *R_f*: 0.45 (hexanes/ethyl acetate, 5:1). Mp 248-250 °C. ^1H NMR (500 MHz, CDCl_3): δ = 1.09 (d, 3H, J = 7.4 Hz), 2.02-2.07 (m, 1H), 3.82 (s, 1H), 5.24 (d, 1H, J = 2.4 Hz), 6.72-6.77 (m, 1H), 6.93-7.00 (m, 3H), 7.28-7.38 (m, 5H), 7.43-7.53 (m, 2H), 7.76-7.80 (m, 1H), 8.01-8.06 (m, 1H), 8.10-8.14 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ = 10.8 (q), 42.8 (d), 77.6 (s), 77.9 (d), 117.5 (d), 119.2 (s), 121.8 (d), 124.7 (d), 124.9 (d), 126.9 (d), 127.2 (d), 127.7 (d), 128.9 (d), 129.0 (d), 129.3 (d), 129.5 (d), 131.5 (d), 131.7 (d), 131.8 (s), 132.3 (s), 135.5 (d), 136.7 (s), 141.1 (s), 160.4 (s), 196.2 (s). IR (ATR): $\tilde{\nu}$ = 3470 (br), 1682, 1607 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{25}\text{H}_{21}\text{O}_3$ [$\text{M} + \text{H}^+$] 369.1491, found 369.1482.

(2R*,3R*)-2-(Hydroxydiphenylmethyl)-3-phenylchroman-4-one (cis-5j): Colorless paste (193 mg, 95%). *R_f*: 0.45 (hexanes/ethyl acetate, 5:1). ^1H NMR (500 MHz, CDCl_3): δ = 2.41 (s, 1H), 3.59 (d, 1H, J = 2.7 Hz), 5.64 (d, 1H, J = 2.7 Hz), 6.91-6.96 (m, 2H), 7.09-7.17 (m, 2H), 7.18-7.37 (m, 11H), 7.46-7.51 (m, 2H), 7.56-7.61 (m, 1H), 7.94-7.98 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ = 53.1 (d), 79.8 (s), 82.7 (d), 118.1 (d), 120.7 (s), 122.6 (d), 125.6 (d), 126.1 (d), 127.1 (d), 127.5 (d), 127.9 (d), 128.3 (d), 128.48 (d), 128.54 (d), 128.8 (d), 129.6 (d), 134.1 (s), 136.5 (d), 142.3 (s), 145.0 (s), 161.2 (s), 191.3 (s). IR (ATR): $\tilde{\nu}$ = 3447 (br), 1684, 1645, 1605 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{28}\text{H}_{23}\text{O}_3$ [$\text{M} + \text{H}^+$] 407.1647, found 407.1636.

(2R*,3R*)-2-(Bis(4-fluorophenyl)(hydroxy)methyl)-3-phenylchroman-4-one (cis-5k): Colorless paste (195 mg, 88%). *R_f*: 0.4 (hexanes/ethyl acetate, 5:1). ^1H NMR (500 MHz, CDCl_3): δ = 2.43 (brs, 1H), 3.56 (d, 1H, J = 2.7 Hz), 5.54 (d, 1H, J = 2.7 Hz), 6.91-7.01 (m, 4H), 7.02-7.08 (m, 2H), 7.10-7.28 (m, 7H), 7.39-7.44 (m, 2H), 7.59-7.64 (m, 1H), 7.94-7.98 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ = 53.2 (d), 79.2 (s), 82.6 (d), 115.1 (d, J_{CCF} = 21.0 Hz), 115.4 (d, J_{CCF} = 21.0 Hz), 118.0 (d), 120.6 (s), 122.9 (d), 127.6 (d, J_{CCCF} = 7.8 Hz), 127.96 (d, J_{CCCF} = 7.8 Hz), 127.99 (d), 128.6 (d), 128.9 (d), 129.4 (d), 133.8 (s), 136.6 (d), 138.1 (s, J_{CCCF} = 2.4 Hz), 140.7 (s, J_{CCCF} = 2.4 Hz), 160.9 (s), 161.8 (s, J_{CF} = 247.1 Hz), 162.1 (s, J_{CF} = 247.1 Hz), 190.9 (s). IR (ATR): $\tilde{\nu}$ = 3433 (br), 1686, 1603, 1506 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{28}\text{H}_{21}\text{F}_2\text{O}_3$ [$\text{M} + \text{H}^+$] 443.1459, found 443.1447.

2-(Hydroxydiphenylmethyl)-2-methylchroman-4-one (5l): Colorless paste (131 mg, 76%). *R_f*: 0.35 (hexanes/ethyl acetate, 5:1). ^1H NMR (500 MHz, CDCl_3): δ = 1.54 (s, 3H), 2.53 (brd, 1H, J = 16.1 Hz), 3.12 (brs, 1H), 3.30 (brd, 1H, J = 16.1 Hz), 6.98-7.03 (m, 1H), 7.03-7.08 (m, 1H), 7.22-7.35 (m, 6H), 7.48-7.53 (m, 1H), 7.60-7.67 (m, 4H), 7.82-7.86 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ = 19.6 (q), 44.2 (t), 81.7 (s), 86.5 (s), 118.3 (d), 120.5 (s), 121.2 (d), 126.4 (d), 127.3 (d), 127.4 (d), 127.68 (d), 127.72 (d), 128.3 (d), 128.8 (d), 136.2 (d), 143.2 (s), 143.5 (s), 158.6 (s), 192.5 (s). IR (ATR): $\tilde{\nu}$ = 3466 (br), 1676, 1605 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{23}\text{H}_{21}\text{O}_3$ [$\text{M} + \text{H}^+$] 345.1491, found 345.1483.

2-(Bis(4-fluorophenyl)(hydroxy)methyl)-2-methylchroman-4-one (5m): Colorless paste (156 mg, 82%). *R_f*: 0.3 (hexanes/ethyl acetate, 5:1). ^1H NMR (500 MHz, CDCl_3): δ = 1.53 (s, 3H), 2.50 (d, 1H, J = 16.6 Hz), 3.03 (brs, 1H), 3.24 (d, 1H, J = 16.6 Hz), 6.97-7.07 (m, 6H), 7.51-7.56 (m, 1H), 7.57-7.64 (m, 4H), 7.84-7.87 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ = 19.6 (q), 44.1 (t), 81.2 (s), 86.4 (s), 114.7 (d, J_{CCF} = 21.6 Hz), 118.2 (d), 120.5 (s), 121.6 (d), 126.6 (d), 130.1 (d, J_{CCCF} = 7.5 Hz), 130.6 (d, J_{CCCF} = 7.5 Hz), 136.4 (d), 138.8 (s), 139.1 (s), 158.4 (s), 161.9 (s, J_{CF} = 247.1 Hz), 162.0 (s, J_{CF} = 247.7 Hz), 192.1 (s). IR (ATR): $\tilde{\nu}$ = 3450 (br), 1678, 1603 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{23}\text{H}_{19}\text{F}_2\text{O}_3$ [$\text{M} + \text{H}^+$] 381.1302, found 381.1290.

(2R*,3R*)-2-(Hydroxydiphenylmethyl)-6-methoxy-3-phenylchroman-4-one (cis-5n): Colorless paste (201 mg, 92%). *R_f*: 0.35 (hexanes/ethyl acetate, 5:1). ^1H NMR (500 MHz, CDCl_3): δ = 2.40 (brs, 1H), 3.56 (dd, 1H, J = 2.7 Hz), 3.80 (s, 3H), 5.59 (dd, 1H, J = 2.7 Hz), 6.93-6.97 (m, 2H), 7.05 (d, 1H, J = 8.9 Hz), 7.17-7.36 (m, 12H), 7.37 (d, 1H, J = 3.3 Hz), 7.45-7.49 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3): δ = 52.8 (d), 55.7 (q), 79.7 (s), 82.8 (d), 108.6 (d), 119.3 (d), 120.6 (s), 125.59 (d), 125.63 (d), 126.0 (d), 127.0 (d), 127.4 (d), 127.8 (d), 128.2 (d), 128.4 (d), 128.7 (d), 129.5 (d), 134.1 (s), 142.3 (s), 145.1 (s), 154.9 (s), 155.8 (s), 191.4 (s). IR (ATR): $\tilde{\nu}$ = 3551 (br), 1680, 1616 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{29}\text{H}_{25}\text{O}_4$ [$\text{M} + \text{H}^+$] 437.1753, found 437.1744.

(2R*,3R*)-2-(Hydroxydiphenylmethyl)-7-methoxy-3-phenylchroman-4-one (cis-5o): White solid (205 mg, 94%). *R_f*: 0.3 (hexanes/ethyl acetate, 5:1). Mp 101-102 °C. ^1H NMR (500 MHz, CDCl_3): δ = 2.36 (brs, 1H), 3.54 (d, 1H, J = 2.7 Hz), 3.87 (s, 3H), 5.66 (d, 1H, J = 2.7 Hz), 6.56 (d, 1H, J = 2.3 Hz), 6.70 (dd, 1H, J = 2.3, 8.7 Hz), 6.91-6.95 (m, 2H), 7.19-7.36 (m, 11H), 7.48-7.51 (m, 2H), 7.89 (d, 1H, J = 9.0 Hz). ^{13}C NMR (125 MHz, CDCl_3): δ = 52.8 (d), 55.7 (q), 79.7 (s), 82.8 (d), 101.0 (d), 111.2 (d), 114.2 (s), 125.5 (d), 125.9 (d), 127.0 (d), 127.5 (d), 127.8 (d), 128.3 (d), 128.4 (d), 128.8 (d), 129.5 (d), 130.1 (d), 134.3 (s), 142.4 (s), 145.0 (s), 163.2 (s), 166.4 (s), 190.1 (s). IR (ATR): $\tilde{\nu}$ = 3418 (br), 1728, 1670, 1599, 1578, 1560 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{29}\text{H}_{25}\text{O}_4$ [$\text{M} + \text{H}^+$] 437.1753, found 437.1743.

(2R*,3R*)-2-(Hydroxydiphenylmethyl)-7-methoxy-3-(4-methoxyphenyl)chroman-4-one (cis-5p): White solid (191 mg, 82%). *R_f*: 0.55 (hexanes/ethyl acetate, 2:1). Mp 226-228 °C. ^1H NMR (500 MHz, CDCl_3): δ = 2.42 (brs, 1H), 3.50 (d, 1H, J = 2.8 Hz), 3.76 (s, 3H), 3.86 (s,

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3H), 5.63 (d, 1H, $J = 2.8$ Hz), 6.56 (d, 1H, $J = 2.3$ Hz), 6.69 (dd, 1H, $J = 2.3, 8.7$ Hz), 6.74-6.78 (m, 2H), 6.84-6.88 (m, 2H), 7.20-7.36 (m, 8H), 7.48-7.52 (m, 2H), 7.88 (d, 1H, $J = 8.7$ Hz). ^{13}C NMR (125 MHz, CDCl_3): $\delta = 51.8$ (d), 55.1 (q), 55.7 (q), 79.7 (s), 82.6 (d), 100.9 (d), 111.1 (d), 114.1 (s), 114.3 (d), 125.5 (d), 125.9 (d), 127.0 (d), 127.4 (d), 128.2 (d), 128.4 (d), 130.0 (d), 130.6 (d), 142.6 (s), 144.8 (s), 159.2 (s), 163.2 (s), 166.3 (s), 190.3 (s). IR (ATR): $\tilde{\nu} = 3456$ (br), 1672, 1599, 1599, 1578. 1510 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{30}\text{H}_{27}\text{O}_5$ [$\text{M} + \text{H}^+$] 467.1858, found 467.1845.

(2R*,3R*)-2-(Hydroxydiphenylmethyl)-5,7-dimethoxy-3-(4-methoxyphenyl)chroman-4-one (cis-5q): White solid (231 mg, 93%). *R_f*: 0.35 (hexanes/ethyl acetate, 1:1). Mp 116-117 °C. ^1H NMR (500 MHz, CDCl_3): $\delta = 2.40$ (brs, 1H), 3.44 (d, 1H, $J = 2.7$ Hz), 3.75 (s, 3H), 3.84 (s, 3H), 3.85 (s, 3H), 5.60 (d, 1H, $J = 2.7$ Hz), 6.15 (d, 1H, $J = 2.2$ Hz), 6.20 (d, 1H, $J = 2.2$ Hz), 6.73-6.77 (m, 2H), 6.87-6.91 (m, 2H), 7.19-7.38 (m, 8H), 7.47-7.51 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3): $\delta = 53.1$ (d), 55.1 (q), 55.7 (q), 56.1 (q), 79.6 (s), 81.8 (d), 93.5 (d), 93.7 (d), 104.9 (s), 114.2 (d), 125.5 (d), 125.9 (d), 126.1 (s), 126.9 (d), 127.4 (d), 128.2 (d), 128.4 (d), 130.7 (d), 142.7 (s), 144.8 (s), 159.1 (s), 163.2 (s), 164.6 (s), 166.2 (s), 188.8 (s). IR (ATR): $\tilde{\nu} = 3534$ (br), 1740, 1674, 1601, 1754, 1508 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{31}\text{H}_{29}\text{O}_6$ [$\text{M} + \text{H}^+$] 497.1964, found 497.1952.

Dehydration of 5. A solution of **5a** (165 mg, 0.50 mmol) and *p*-TsOH (10 mg) in toluene (10 mL) was refluxed using Dean-Stark apparatus under nitrogen atmosphere for 1 h. After the solvent was removed *in vacuo*, the residue was purified by column chromatography on silica gel (hexanes-EtOAc) to give **4a** (144 mg, 0.462 mmol) in 92% yield.

Desilylation of 3 with TBAF and subsequent treatment with NaH. To a solution of **3a** (201 mg, 0.50 mmol) in THF (10 mL) was added 1 M TBAF in THF (0.50 mL, 0.50 mmol) at 25 °C. After being stirring for 10 min, to the mixture was added NaH (40% in oil, 30 mg, 0.50 mmol) and the mixture was stirred for 30 min at this temperature. After addition of AcOH (60 mg, 1.0 mmol), the solvent was removed *in vacuo*. The residue was purified by column chromatography on silica gel (hexanes-EtOAc) to give **6a** (162 mg, 0.491 mmol) in 98% yield.

(E)-4-Hydroxy-1-(2-hydroxyphenyl)-4,4-diphenylbut-2-en-1-one (6a): Yellow solid (162 mg, 98%). *R_f*: 0.4 (hexanes/ethyl acetate, 5:1). Mp 140-141 °C. ^1H NMR (500 MHz, CDCl_3): $\delta = 2.51$ (brs, 1H), 6.88-6.93 (m, 1H), 6.98-7.02 (m, 1H), 7.29-7.42 (m, 10H), 7.46-7.51 (m, 1H), 7.54 (d, 1H, $J = 15.0$ Hz), 7.73 (d, 1H, $J = 15.0$ Hz), 7.84-7.89 (m, 1H), 12.68 (s, 1H). ^{13}C NMR (125 MHz, CDCl_3): $\delta = 79.4$ (s), 118.4 (d), 118.9 (d), 119.7 (s), 121.0 (d), 126.8 (d), 127.9 (d), 128.5 (d), 130.1 (d), 136.6 (d), 144.2 (s), 152.5 (d), 163.4 (s), 194.2 (s). IR (ATR): $\tilde{\nu} = 3431$ (br), 1645, 1620, 1582 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{22}\text{H}_{19}\text{O}_3$ [$\text{M} + \text{H}^+$] 331.1334, found 331.1329.

(E)-4,4-Bis(4-fluorophenyl)-4-hydroxy-1-(2-hydroxyphenyl)but-2-en-1-one (6b): Yellow solid (153 mg, 91%). *R_f*: 0.35 (hexanes/ethyl acetate, 5:1). Mp 117-119 °C. ^1H NMR (500 MHz, CDCl_3): $\delta = 2.40$ (brs, 1H), 6.88-6.93 (m, 1H), 6.96-7.00 (m, 1H), 7.01-7.07 (m, 4H), 7.32-7.37 (m, 4H), 7.46-7.52 (m, 2H), 7.63 (d, 1H, $J = 15.0$ Hz), 7.81-7.85 (m, 1H), 12.58 (brs, 1H). ^{13}C NMR (125 MHz, CDCl_3): $\delta = 78.7$ (s), 115.5 (d, $J_{\text{CCF}} = 21.6$ Hz), 118.5 (d), 119.0 (d), 119.7 (s), 121.4 (d), 128.7 (d, $J_{\text{CCCF}} = 8.4$ Hz), 130.0 (d), 136.7 (d), 140.0 (s, $J_{\text{CCCF}} = 30$ Hz), 151.8 (d), 162.3 (s, $J_{\text{CF}} = 247.7$ Hz), 163.5 (s), 194.0 (s). IR (ATR): $\tilde{\nu} = 3447$ (br), 1647, 1616, 1597 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{22}\text{H}_{17}\text{F}_2\text{O}_3$ [$\text{M} + \text{H}^+$] 367.1146, found 367.1135.

(E)-3-(5-Hydroxy-10,11-dihydro-5H-dibenzo[a,d][7]annulen-5-yl)-1-(2-hydroxyphenyl)prop-2-en-1-one (6c): Yellow solid (121 mg, 68%). *R_f*: 0.3 (hexanes/ethyl acetate, 10:1). Mp 122-123 °C. ^1H NMR (500 MHz, CDCl_3): $\delta = 2.53$ (s, 1H), 2.98-3.06 (m, 2H), 3.29-3.38 (m, 2H), 6.83-6.88 (m, 1H), 6.95-6.98 (m, 1H), 7.01 (d, 1H, $J = 15.2$ Hz), 7.13-7.18 (m, 2H),

7.21-7.31 (m, 4H), 7.43-7.48 (m, 1H), 7.52 (d, 1H, $J = 15.2$ Hz), 7.57-7.60 (m, 1H), 7.87-7.93 (m, 2H), 12.53 (s, 1H). ^{13}C NMR (125 MHz, CDCl_3): $\delta = 33.6$ (t), 77.7 (s), 118.5 (d), 118.9 (d), 119.7 (s), 122.3 (d), 126.3 (d), 126.6 (d), 128.2 (d), 129.9 (d), 130.5 (d), 136.6 (d), 138.9 (s), 141.4 (s), 153.2 (s), 163.4 (s). IR (ATR): $\tilde{\nu} = 3242$ (br), 1636, 1582 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{24}\text{H}_{21}\text{O}_3$ [$\text{M} + \text{H}^+$] 357.1491, found 357.1477.

(E)-3-(5-Hydroxy-5H-dibenzo[a,d][7]annulen-5-yl)-1-(2-hydroxyphenyl)prop-2-en-1-one (6d): Yellow solid (158 mg, 89%). *R_f*: 0.25 (hexanes/ethyl acetate, 10:1). Mp 149-151 °C. ^1H NMR (500 MHz, CDCl_3): $\delta = 2.62$ (brs, 1H), 6.79-6.87 (m, 2H), 6.92-6.97 (m, 1H), 7.03 (s, 2H), 7.30-7.52 (m, 9H), 7.95-8.00 (m, 2H), 12.47 (s, 1H). ^{13}C NMR (125 MHz, CDCl_3): $\delta = 75.5$ (s), 118.4 (d), 118.8 (d), 119.5 (s), 123.26 (d), 123.29 (d), 127.1 (d), 128.8 (d), 129.2 (d), 129.9 (d), 131.7 (d), 132.7 (s), 136.5 (d), 140.7 (s), 151.4 (d), 163.2 (s), 194.5 (s). IR (ATR): $\tilde{\nu} = 3466$ (br), 3377, 1634, 1578 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{24}\text{H}_{19}\text{O}_3$ [$\text{M} + \text{H}^+$] 355.1334, found 355.1327.

(E)-3-(9-Hydroxy-9H-fluoren-9-yl)-1-(2-hydroxyphenyl)prop-2-en-1-one (6f): Yellow solid (161 mg, 98%). *R_f*: 0.3 (hexanes/ethyl acetate, 5:1). Mp 158-159 °C. ^1H NMR (500 MHz, CDCl_3): $\delta = 2.39$ (brs, 1H), 6.91-7.01 (m, 3H), 7.29-7.35 (m, 2H), 7.39-7.52 (m, 5H), 7.65-7.70 (m, 2H), 7.76 (d, 1H, $J = 15.0$ Hz), 7.94-7.99 (m, 1H), 12.62 (brs, 1H). ^{13}C NMR (125 MHz, CDCl_3): $\delta = 82.3$ (s), 118.4 (d), 118.8 (d), 119.7 (s), 120.4 (d), 121.2 (d), 124.7 (d), 128.4 (d), 129.8 (d), 130.1 (d), 136.5 (d), 139.6 (s), 146.4 (s), 149.3 (d), 163.5 (s), 194.0 (s). IR (ATR): $\tilde{\nu} = 3418$ (br), 1639, 1618, 1587 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{22}\text{H}_{17}\text{O}_3$ [$\text{M} + \text{H}^+$] 329.1178, found 329.1172.

(E)-4-Hydroxy-1-(2-hydroxyphenyl)-2-methyl-4,4-diphenylbut-2-en-1-one (6g): Yellow paste (155 mg, 90%). *R_f*: 0.45 (hexanes/ethyl acetate, 5:1). ^1H NMR (500 MHz, CDCl_3): $\delta = 1.57$ (d, 3H, $J = 1.7$ Hz), 2.57 (brs, 1H), 6.57-6.60 (m, 1H), 6.80-6.86 (m, 1H), 6.98-7.02 (m, 1H), 7.26-7.31 (m, 2H), 7.33-7.39 (m, 4H), 7.41-7.50 (m, 5H), 7.60-7.65 (m, 1H), 11.84 (s, 1H). ^{13}C NMR (125 MHz, CDCl_3): $\delta = 15.1$ (q), 79.2 (s), 118.4 (d), 118.6 (d), 126.3 (d), 127.5 (d), 128.4 (d), 132.7 (d), 136.3 (d), 137.9 (s), 142.8 (d), 146.0 (s), 163.1 (s), 204.2 (s). IR (ATR): $\tilde{\nu} = 3447$ (br), 1620, 1597 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{23}\text{H}_{21}\text{O}_3$ [$\text{M} + \text{H}^+$] 345.1491, found 345.1483.

(E)-4,4-Bis(4-fluorophenyl)-4-hydroxy-1-(2-hydroxyphenyl)-2-methylbut-2-en-1-one (6h): Yellow paste (122 mg, 64%). *R_f*: 0.4 (hexanes/ethyl acetate, 5:1). ^1H NMR (500 MHz, CDCl_3): $\delta = 1.97$ (d, 3H, $J = 1.3$ Hz), 2.55 (s, 1H), 6.51 (q, 1H, $J = 1.3$ Hz), 6.81-6.86 (m, 1H), 6.99-7.08 (m, 5H), 7.36-7.42 (m, 4H), 7.45-7.49 (m, 1H), 7.54-7.58 (m, 1H), 11.81 (s, 1H). ^{13}C NMR (125 MHz, CDCl_3): $\delta = 15.2$ (q), 78.6 (s), 115.4 (d, $J_{\text{CCF}} = 21.3$ Hz), 118.3 (s), 118.6 (d), 118.7 (d), 128.1 (d, $J_{\text{CCCF}} = 8.4$ Hz), 132.5 (d), 136.5 (d), 138.4 (s), 141.7 (d), 141.8 (s, $J_{\text{CCCF}} = 3.6$ Hz), 162.1 (s, $J_{\text{CF}} = 248.0$ Hz), 163.3 (s), 204.0 (s). IR (ATR): $\tilde{\nu} = 3449$ (br), 1620, 1599 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{23}\text{H}_{19}\text{F}_2\text{O}_3$ [$\text{M} + \text{H}^+$] 381.1302, found 381.1294.

(E)-3-(5-Hydroxy-5H-dibenzo[a,d][7]annulen-5-yl)-1-(2-hydroxyphenyl)-2-methylprop-2-en-1-one (6i): Yellow paste (179 mg, 97%). *R_f*: 0.45 (hexanes/ethyl acetate, 5:1). ^1H NMR (500 MHz, CDCl_3): $\delta = 1.60$ (d, 3H, $J = 1.6$ Hz), 2.70 (brs, 1H), 6.05 (s, 1H, $J = 1.6$ Hz), 6.84-6.90 (m, 1H), 6.91-6.95 (m, 1H), 7.15 (s, 2H), 7.25-7.30 (m, 2H), 7.33-7.38 (m, 2H), 7.41-7.47 (m, 3H), 7.62-7.67 (m, 1H), 8.01-8.06 (m, 2H), 11.67 (s, 1H). ^{13}C NMR (125 MHz, CDCl_3): $\delta = 13.6$ (q), 75.0 (s), 118.1 (s), 118.2 (d), 118.3 (d), 123.0 (d), 126.6 (d), 128.7 (d), 128.8 (d), 132.0 (d), 133.3 (d), 136.3 (d), 138.8 (s), 142.9 (s), 144.6 (s), 163.0 (s), 204.0 (s). IR (ATR): $\tilde{\nu} = 3460$ (br), 1620, 1595 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{25}\text{H}_{21}\text{O}_3$ [$\text{M} + \text{H}^+$] 369.1491, found 369.1480.

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(E)-4-Hydroxy-1-(2-hydroxyphenyl)-3-methyl-4,4-diphenylbut-2-en-1-one (6f): Yellow paste (157 mg, 91%). *R_f*: 0.45 (hexanes/ethyl acetate, 5:1). ¹H NMR (500 MHz, CDCl₃): δ = 2.11 (d, 3H, *J* = 1.2 Hz), 2.67 (brs, 1H), 6.82–6.86 (m, 1H), 6.96–6.99 (m, 1H), 7.02 (d, 1H, *J* = 1.2 Hz), 7.32–7.47 (m, 11H), 7.57–7.60 (m, 1H), 12.64 (s, 1H). ¹³C NMR (125 MHz, CDCl₃): δ = 17.8 (q), 83.9 (s), 118.4 (d), 118.8 (d), 120.8 (s), 122.3 (d), 127.9 (d), 128.0 (d), 128.3 (d), 130.1 (d), 136.2 (d), 143.6 (s), 159.9 (s), 163.0 (s), 197.7 (s). IR (ATR): $\tilde{\nu}$ = 3435 (br), 1636, 1582 cm⁻¹. HRMS (ESI⁺) calcd for C₂₃H₂₁O₃ [M + H⁺] 345.1491, found 345.1482.

Dehydration of 6. A solution of **6g** (86 mg, 0.25 mmol) and *p*-TsOH (10 mg) in toluene (10 mL) was refluxed using Dean-Stark apparatus under nitrogen atmosphere for 1 h. After the solvent was removed *in vacuo*, the residue was purified by column chromatography on silica gel (hexanes-EtOAc) to give **7g** (76 mg, 0.233 mmol) in 93% yield.

2-(3-Methyl-4,5-diphenylfuran-2-yl)phenol (7g): Colorless paste (76 mg, 93%). *R_f*: 0.55 (hexanes/ethyl acetate, 5:1). ¹H NMR (500 MHz, CDCl₃): δ = 2.07 (s, 3H), 6.95 (s, 1H), 6.99–7.03 (m, 1H), 7.06–7.09 (m, 1H), 7.18–7.31 (m, 4H), 7.35–7.38 (m, 2H), 7.39–7.50 (m, 6H). ¹³C NMR (125 MHz, CDCl₃): δ = 10.1 (q), 116.8 (d), 117.0 (s), 120.29 (d), 120.32 (s), 125.3 (d), 125.6 (s), 127.4 (d), 127.7 (d), 128.4 (d), 128.5 (d), 128.9 (d), 129.6 (d), 130.0 (d), 130.3 (s), 133.3 (s), 145.7 (s), 147.4 (s), 153.5 (s). IR (ATR): $\tilde{\nu}$ = 3524 (br), 1601 cm⁻¹. HRMS (ESI⁺) calcd for C₂₃H₁₉O₂ [M + H⁺] 327.1385, found 327.1379.

2-(4,5-Bis(4-fluorophenyl)-3-methylfuran-2-yl)phenol (7h): White solid (69 mg, 76%). *R_f*: 0.45 (hexanes/ethyl acetate, 5:1). Mp 126–127 °C. ¹H NMR (500 MHz, CDCl₃): δ = 2.04 (s, 3H), 6.68 (s, 1H), 6.92–6.98 (m, 2H), 6.99–7.03 (m, 1H), 7.04–7.07 (m, 1H), 7.13–7.19 (m, 2H), 7.27–7.37 (m, 5H), 7.41–7.44 (m, 1H). ¹³C NMR (125 MHz, CDCl₃): δ = 10.0 (q), 115.6 (d, *J*_{CCF} = 21.6 Hz), 116.1 (d, *J*_{CCF} = 21.6 Hz), 116.8 (d), 116.9 (s), 120.2 (s), 120.4 (d), 124.2 (s), 126.5 (s, *J*_{CCCF} = 3.6 Hz), 127.2 (d, *J*_{CCCF} = 8.4 Hz), 128.6 (d), 129.1 (s, *J*_{CCCF} = 3.0 Hz), 129.8 (d), 131.7 (d, *J*_{CCCF} = 8.4 Hz), 145.8 (s), 147.0 (s), 153.5 (s), 162.0 (s, *J*_{CF} = 248.3 Hz), 162.4 (s, *J*_{CCF} = 247.1 Hz). IR (ATR): $\tilde{\nu}$ = 3524 (br), 1601 cm⁻¹. HRMS (ESI⁺) calcd for C₂₃H₁₇F₂O₂ [M + H⁺] 363.1197, found 363.1191.

2-(3,4,5-Triphenylfuran-2-yl)phenol (7j): White solid (73 mg, 75%). *R_f*: 0.55 (hexanes/ethyl acetate, 5:1). Mp 140–141 °C. ¹H NMR (500 MHz, CDCl₃): δ = 6.65 (s, 1H), 6.75–6.80 (m, 1H), 6.96–7.00 (m, 1H), 7.05–7.09 (m, 2H), 7.12–7.31 (m, 13H), 7.43–7.47 (m, 2H). ¹³C NMR (125 MHz, CDCl₃): δ = 116.4 (s), 117.1 (d), 120.2 (d), 124.3 (s), 125.76 (s), 125.84 (d), 127.4 (d), 127.7 (d), 128.5 (d), 128.6 (d), 129.2 (d), 129.9 (d), 130.0 (d), 130.2 (s), 130.3 (d), 131.9 (s), 132.6 (s), 146.0 (s), 148.2 (s), 153.4 (s). IR (ATR): $\tilde{\nu}$ = 3510 (br), 1603, 1578 cm⁻¹. HRMS (ESI⁺) calcd for C₂₈H₂₁O₂ [M + H⁺] 389.1542, found 389.1534.

2-(4,5-Bis(4-fluorophenyl)-3-phenylfuran-2-yl)phenol (7k): Red solid (53 mg, 50%). *R_f*: 0.5 (hexanes/ethyl acetate, 5:1). Mp 168–169 °C. ¹H NMR (500 MHz, CDCl₃): δ = 6.44 (brs, 1H), 6.77–6.81 (m, 1H), 6.95–7.01 (m, 5H), 7.03–7.07 (m, 2H), 7.09–7.16 (m, 3H), 7.20–7.27 (m, 4H), 7.38–7.43 (m, 2H). ¹³C NMR (125 MHz, CDCl₃): δ = 115.7 (d, *J*_{CCF} = 21.6 Hz), 115.8 (d, *J*_{CCF} = 21.6 Hz), 116.3 (s), 117.2 (d), 120.3 (d), 122.9 (s), 125.6 (s), 126.4 (s, *J*_{CCCF} = 3.6 Hz), 127.6 (d), 127.8 (d, *J*_{CCCF} = 8.4 Hz), 128.4 (d, *J*_{CCCF} = 3.6 Hz), 128.6 (d), 129.3 (d), 129.9 (d), 130.1 (d), 131.6 (s), 132.0 (d, *J*_{CCF} = 7.8 Hz), 146.1 (s), 147.6 (s), 153.4 (s), 162.2 (s, *J*_{CF} = 247.1 Hz), 163.3 (s, *J*_{CF} = 248.3 Hz). IR (ATR): $\tilde{\nu}$ = 3530 (br), 1609, 1597, 1574, 1514 cm⁻¹. HRMS (ESI⁺) calcd for C₂₈H₁₉F₂O₂ [M + H⁺] 425.1353, found 425.1345.

4-Methoxy-2-(3,4,5-triphenylfuran-2-yl)phenol (7n): White solid (64 mg, 61%). *R_f*: 0.5 (hexanes/ethyl acetate, 5:1). Mp 146–147 °C. ¹H NMR (500

MHz, CDCl₃): δ = 3.44 (s, 3H), 6.45 (brs, 1H), 6.63 (d, 1H, *J* = 3.0 Hz), 6.78 (dd, 1H, *J* = 3.0, 9.0 Hz), 6.90 (d, 1H, *J* = 9.0 Hz), 7.10–7.14 (m, 2H), 7.15–7.20 (m, 2H), 7.21–7.30 (m, 9H), 7.44–7.46 (m, 2H). ¹³C NMR (125 MHz, CDCl₃): δ = 55.3 (q), 112.2 (d), 116.3 (s), 117.0 (d), 118.2 (d), 124.3 (s), 125.8 (d), 127.4 (d), 127.5 (d), 127.8 (d), 128.51 (d), 128.54 (d), 130.1 (d), 130.2 (s), 130.3 (d), 132.1 (s), 132.5 (s), 146.1 (s), 147.4 (s), 148.0 (s), 152.8 (s). IR (ATR): $\tilde{\nu}$ = 3545 (br), 3522 (br), 1618, 1603, 1595, 1558 cm⁻¹. HRMS (ESI⁺) calcd for C₂₉H₂₃O₃ [M + H⁺] 419.1647, found 419.1640.

2-(2,2-Diphenylvinyl)-6-methoxy-2-phenylbenzofuran-3(2H)-one (8o): Colorless paste (77 mg, 74%). *R_f*: 0.5 (hexanes/ethyl acetate, 5:1). ¹H NMR (500 MHz, CDCl₃): δ = 3.81 (s, 3H), 6.14 (d, 1H, *J* = 2.2 Hz), 6.52 (dd, 1H, *J* = 8.6, 2.2 Hz), 6.55 (s, 1H), 6.97–7.02 (m, 2H), 7.08–7.13 (m, 3H), 7.20–7.40 (m, 9H), 7.54–7.58 (m, 2H). ¹³C NMR (125 MHz, CDCl₃): δ = 55.8 (q), 91.5 (s), 95.8 (d), 111.6 (d), 112.5 (s), 125.2 (d), 125.9 (d), 126.2 (d), 126.9 (d), 127.3 (d), 127.4 (d), 127.9 (d), 128.0 (d), 128.1 (d), 128.5 (d), 129.6 (d), 138.9 (s), 139.0 (s), 141.7 (s), 146.7 (s), 168.0 (s), 173.6 (s), 197.7 (s). IR (ATR): $\tilde{\nu}$ = 1705, 1609, 1593 cm⁻¹. HRMS (ESI⁺) calcd for C₂₉H₂₃O₃ [M + H⁺] 419.1647, found 419.1639.

2-(2,2-Diphenylvinyl)-6-methoxy-2-(4-methoxyphenyl)benzofuran-3(2H)-one (8p): Colorless paste (107 mg, 95%). *R_f*: 0.3 (hexanes/ethyl acetate, 5:1). ¹H NMR (500 MHz, CDCl₃): δ = 3.77 (s, 3H), 3.80 (s, 3H), 6.09 (d, 1H, *J* = 2.1 Hz), 6.515 (s, 1H), 6.521 (dd, 1H, *J* = 2.1, 8.6 Hz), 6.83–6.87 (m, 2H), 6.98–7.02 (m, 2H), 7.09–7.14 (m, 3H), 7.20–7.26 (m, 5H), 7.37 (d, 1H, *J* = 8.6 Hz), 7.44–7.48 (m, 2H). ¹³C NMR (125 MHz, CDCl₃): δ = 55.3 (q), 55.8 (q), 91.5 (s), 95.8 (d), 111.5 (d), 112.6 (s), 113.9 (s), 125.9 (d), 126.1 (d), 126.7 (d), 126.8 (d), 127.3 (d), 127.4 (d), 127.9 (d), 128.1 (d), 129.5 (d), 131.8 (s), 139.0 (s), 141.8 (s), 146.4 (s), 159.4 (s), 168.0 (s), 173.5 (s), 198.0 (s). IR (ATR): $\tilde{\nu}$ = 1707, 1609, 1508 cm⁻¹. HRMS (ESI⁺) calcd for C₃₀H₂₅O₄ [M + H⁺] 449.1753, found 449.1742.

2-(2,2-Diphenylvinyl)-4,6-dimethoxy-2-(4-methoxyphenyl)benzofuran-3(2H)-one (8q): White solid (104 mg, 87%). *R_f*: 0.3 (hexanes/ethyl acetate, 2:1). Mp 90–91 °C. ¹H NMR (500 MHz, CDCl₃): δ = 3.768 (s, 3H), 3.774 (s, 3H), 3.84 (s, 3H), 5.67 (d, 1H, *J* = 1.7 Hz), 5.90 (d, 1H, *J* = 1.7 Hz), 6.52 (s, 1H), 6.80–6.84 (m, 2H), 7.01–7.05 (m, 2H), 7.13–7.17 (m, 3H), 7.21–7.25 (m, 5H), 7.42–7.46 (m, 2H). ¹³C NMR (125 MHz, CDCl₃): δ = 55.3 (q), 55.8 (q), 55.9 (q), 88.7 (d), 91.5 (s), 92.8 (d), 102.9 (s), 113.8 (d), 126.4 (d), 126.6 (d), 126.8 (d), 127.2 (d), 127.4 (d), 127.8 (d), 128.1 (d), 129.5 (d), 131.3 (s), 139.3 (s), 142.0 (s), 145.7 (s), 159.3 (s), 159.4 (s), 169.6 (s), 174.1 (s), 195.4 (s). IR (ATR): $\tilde{\nu}$ = 1699, 1614, 1591, 1508 cm⁻¹. HRMS (ESI⁺) calcd for C₃₁H₂₇O₅ [M + H⁺] 479.1858, found 479.1843.

Isomerization of *cis*-3 with DBU and subsequent desilylation. A solution of *cis*-**3g** (104 mg, 0.25 mmol) and DBU (10 mg) in THF (5 mL) was stirred at 50 °C for 24 h. To a solution was added 1 M HCl aq (5 mL) at 50 °C, and then the solution was stirred at this temperature for 2 h. The mixture was neutralized with sat. NaHCO₃ aq and extracted with ethyl acetate (10 mL × 3). After removal of the solvent *in vacuo*, the residue was purified by column chromatography on silica gel (hexanes-EtOAc) to give *trans*-**5g** (48 mg, 0.14 mmol) and *cis*-**5g** (26 mg, 0.075 mmol) in 86% combined yield (*trans*:*cis* = 65:35).

(2*R,3*S**)-2-(Hydroxydiphenylmethyl)-3-methylchroman-4-one (*trans*-**5g**):** White solid (48 mg, 56%). *R_f*: 0.4 (hexanes/ethyl acetate, 5:1). Mp 160–162 °C. ¹H NMR (500 MHz, CDCl₃): δ = 1.13 (d, 3H, *J* = 7.5 Hz), 2.43 (brs, 1H), 2.82–2.87 (m, 1H), 5.23 (d, 1H, *J* = 4.6 Hz), 6.76–6.80 (m, 1H), 6.95–6.99 (m, 1H), 7.21–7.28 (m, 3H), 7.29–7.36 (m, 4H), 7.37–7.42 (m, 2H), 7.52–7.56 (m, 2H), 7.80–7.84 (m, 1H). ¹³C NMR (125 MHz, CDCl₃): δ = 15.9 (q), 40.8 (d), 81.7 (s), 85.7 (d), 117.2 (d), 120.0 (s), 121.2 (d), 125.8 (d), 126.7 (d), 127.3 (d), 128.2 (d), 128.5 (d), 135.6 (d), 143.3 (s), 144.4 (s),

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159.5 (s), 194.9 (s). IR (ATR): $\tilde{\nu}$ = 3474, 1686, 1609 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{23}\text{H}_{21}\text{O}_3$ [$\text{M} + \text{H}^+$] 345.1491, found 345.1484.

(2R*,3S*)-2-(bis(4-fluorophenyl)(hydroxy)methyl)-3-methylchroman-4-one (trans-5h): White solid (56 mg, 59%). *R*_f: 0.45 (hexanes/ethyl acetate, 5:1). Mp 170–171 °C. ^1H NMR (500 MHz, CDCl_3): δ = 1.13 (d, 3H, *J* = 7.5 Hz), 2.42 (brs, 1H), 2.79–2.85 (m, 1H), 5.13 (d, 1H, *J* = 5.0 Hz), 6.78 (d, 1H, *J* = 8.5 Hz), 6.96–7.05 (m, 5H), 7.32–7.44 (m, 3H), 7.46–7.52 (m, 2H), 7.79–7.83 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ = 15.7 (q), 40.8 (d), 80.8 (s), 85.6 (d), 115.0 (d, *J*_{CCF} = 21.0 Hz), 115.4 (d, *J*_{CCF} = 21.6 Hz), 117.1 (d), 120.0 (s), 121.4 (d), 126.8 (d), 127.8 (d, *J*_{CCCF} = 8.4 Hz), 128.7 (d, *J*_{CCCF} = 8.4 Hz), 135.7 (d), 139.2 (s, *J*_{CCCF} = 3.6 Hz), 139.9 (s, *J*_{CCCF} = 3.0 Hz), 159.4 (s), 161.92 (s, *J*_{CF} = 247.1 Hz), 161.94 (s, *J*_{CF} = 247.1 Hz), 194.5 (s). IR (ATR): $\tilde{\nu}$ = 3420 (br), 1674, 1605 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{23}\text{H}_{19}\text{F}_2\text{O}_3$ [$\text{M} + \text{H}^+$] 381.1302, found 381.1293.

(2R*,3S*)-2-(5-Hydroxy-5H-dibenzo[a,d][7]annulen-5-yl)-3-methylchroman-4-one (trans-5i): Colorless paste (57 mg, 62%). *R*_f: 0.4 (hexanes/ethyl acetate, 5:1). ^1H NMR (500 MHz, CDCl_3): δ = 0.74 (d, 3H, *J* = 7.5 Hz), 2.62–2.69 (m, 1H), 3.06 (s, 1H), 5.16 (d, 1H, *J* = 6.6 Hz), 6.42 (d, 1H, *J* = 8.3 Hz), 6.92–6.96 (m, 1H), 6.98 (d, 1H, *J* = 11.6 Hz), 7.07 (d, 1H, *J* = 11.6 Hz), 7.28–7.36 (m, 4H), 7.38–7.41 (m, 1H), 7.42–7.48 (m, 2H), 7.71 (d, 1H, *J* = 8.0 Hz), 7.78–7.81 (m, 1H), 7.96 (d, 1H, *J* = 8.1 Hz). ^{13}C NMR (125 MHz, CDCl_3): δ = 13.8 (q), 41.4 (d), 80.0 (d), 80.4 (s), 117.2 (d), 119.9 (s), 121.2 (d), 123.8 (d), 124.8 (d), 126.8 (d), 126.9 (d), 127.4 (d), 128.9 (d), 129.3 (d), 129.4 (d), 129.5 (d), 131.2 (d), 132.0 (d), 132.2 (s), 132.5 (s), 135.4 (d), 137.7 (s), 140.3 (s), 160.0 (s), 194.9 (s). IR (ATR): $\tilde{\nu}$ = 3547 (br), 1686, 1599, 1582 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{25}\text{H}_{21}\text{O}_3$ [$\text{M} + \text{H}^+$] 369.1491, found 369.1484.

(2R*,3S*)-2-(Hydroxydiphenylmethyl)-3-phenylchroman-4-one (trans-5j): White solid (70 mg, 69%). *R*_f: 0.4 (hexanes/ethyl acetate, 5:1). Mp 178–179 °C. ^1H NMR (500 MHz, CDCl_3): δ = 2.35 (s, 1H), 4.03 (d, 1H, *J* = 2.3 Hz), 5.70 (d, 1H, *J* = 2.3 Hz), 6.81–6.85 (m, 1H), 6.93–6.98 (m, 1H), 7.14–7.35 (m, 11H), 7.37–7.44 (m, 3H), 7.50–7.55 (m, 2H), 7.76–7.81 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ = 51.0 (d), 82.5 (s), 85.1 (d), 117.3 (d), 120.4 (s), 121.2 (d), 126.0 (d), 126.8 (d), 127.45 (d), 127.48 (d), 127.9 (d), 128.2 (d), 128.6 (d), 128.9 (d), 135.9 (d), 137.9 (s), 143.0 (s), 143.9 (s), 159.7 (s), 190.8 (s). IR (ATR): $\tilde{\nu}$ = 3439 (br), 1672, 1605 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{28}\text{H}_{23}\text{O}_3$ [$\text{M} + \text{H}^+$] 407.1647, found 407.1634.

(2R*,3S*)-2-(Bis(4-fluorophenyl)(hydroxy)methyl)-3-phenylchroman-4-one (trans-5k): White solid (67 mg, 61%). *R*_f: 0.35 (hexanes/ethyl acetate, 5:1). Mp 120–122 °C. ^1H NMR (500 MHz, CDCl_3): δ = 2.35 (brs, 1H), 4.03 (d, 1H, *J* = 3.4 Hz), 5.61 (d, 1H, *J* = 3.4 Hz), 6.85 (d, 1H, *J* = 8.3 Hz), 6.94–7.03 (m, 5H), 7.10–7.14 (m, 2H), 7.20–7.25 (m, 3H), 7.31–7.36 (m, 2H), 7.42–7.51 (m, 3H), 7.78 (dd, 1H, *J* = 1.7, 7.7 Hz). ^{13}C NMR (125 MHz, CDCl_3): δ = 51.3 (d), 81.5 (s), 85.0 (d), 115.1 (d, *J*_{CCF} = 21.6 Hz), 115.4 (d, *J*_{CCF} = 21.0 Hz), 117.3 (d), 120.3 (s), 121.6 (d), 127.0 (d), 127.6 (d), 128.0 (d, *J*_{CCCF} = 7.2 Hz), 128.1 (d), 128.8 (d, *J*_{CCCF} = 8.1 Hz), 129.0 (d), 136.1 (d), 137.3 (s), 138.6 (s, *J*_{CCCF} = 2.7 Hz), 139.5 (s, *J*_{CCCF} = 3.0 Hz), 159.4 (s), 161.9 (s, *J*_{CF} = 247.1 Hz), 162.0 (s, *J*_{CF} = 247.1 Hz), 190.7 (s). IR (ATR): $\tilde{\nu}$ = 3235 (br), 1676, 1605, 1504 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{28}\text{H}_{21}\text{F}_2\text{O}_3$ [$\text{M} + \text{H}^+$] 443.1459, found 443.1447.

(2R*,3S*)-2-(Hydroxydiphenylmethyl)-6-methoxy-3-phenylchroman-4-one (trans-5n): White solid (67 mg, 61%). *R*_f: 0.3 (hexanes/ethyl acetate, 5:1). Mp 206–207 °C. ^1H NMR (500 MHz, CDCl_3): δ = 2.36 (brs, 1H), 3.75 (s, 3H), 4.01 (d, 1H, *J* = 2.4 Hz), 5.65 (d, 1H, *J* = 2.4 Hz), 6.77 (d, 1H, *J* = 9.2 Hz), 7.02 (dd, 1H, *J* = 3.2, 9.2 Hz), 7.13–7.18 (m, 2H), 7.19–7.35 (m, 10H), 7.37–7.41 (m, 2H), 7.50–7.55 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3): δ = 50.8 (d), 55.7 (q), 82.5 (s), 85.0 (d), 107.4 (d), 118.6 (d), 120.2 (s), 125.0 (d), 125.9 (d), 126.8 (d), 127.40 (d), 127.43 (d), 127.5 (d), 127.9 (d), 128.2 (d), 128.6 (d), 128.9 (d), 142.9 (s), 144.0 (s), 153.9 (s), 154.1 (s),

191.0 (s). IR (ATR): $\tilde{\nu}$ = 3311 (br), 1674, 1618 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{29}\text{H}_{25}\text{O}_4$ [$\text{M} + \text{H}^+$] 437.1753, found 437.1743.

(2R*,3S*)-2-(Hydroxydiphenylmethyl)-7-methoxy-3-phenylchroman-4-one (trans-5o): White solid. *R*_f: 0.15 (hexanes/ethyl acetate, 5:1). Mp 240–241 °C (recryst from ethyl acetate). ^1H NMR (500 MHz, CDCl_3): δ = 2.35 (brs, 1H), 3.79 (s, 3H), 3.97 (d, 1H, *J* = 2.4 Hz), 5.68 (d, 1H, *J* = 2.4 Hz), 6.27 (d, 1H, *J* = 2.3 Hz), 6.52 (dd, 1H, *J* = 2.3, 8.6 Hz), 7.11–7.17 (m, 2H), 7.19–7.36 (m, 9H), 7.37–7.42 (m, 2H), 7.51–7.56 (m, 2H), 7.74 (d, 1H, *J* = 8.6 Hz). ^{13}C NMR (125 MHz, CDCl_3): δ = 50.8 (d), 55.6 (q), 82.4 (s), 85.6 (d), 100.6 (d), 109.4 (d), 114.2 (s), 126.0 (d), 126.8 (d), 127.4 (d), 127.5 (d), 127.9 (d), 128.2 (d), 128.6 (d), 128.7 (d), 128.9 (d), 138.4 (s), 143.0 (s), 144.0 (s), 161.5 (s), 166.0 (s), 189.6 (s). IR (ATR): $\tilde{\nu}$ = 3246 (br), 1668, 1609, 1582 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{29}\text{H}_{25}\text{O}_4$ [$\text{M} + \text{H}^+$] 437.1753, found 437.1745.

(2R*,3S*)-2-(Hydroxydiphenylmethyl)-7-methoxy-3-(4-methoxyphenyl)chroman-4-one (trans-5p): White solid (93 mg, 80%). *R*_f: 0.55 (hexanes/ethyl acetate, 2:1). Mp 177–178 °C. ^1H NMR (500 MHz, CDCl_3): δ = 2.35 (brs, 1H), 3.73 (s, 3H), 3.78 (s, 3H), 3.92 (d, 1H, *J* = 2.6 Hz), 5.64 (d, 1H, *J* = 2.6 Hz), 6.26 (d, 1H, *J* = 2.4 Hz), 6.52 (dd, 1H, *J* = 2.4, 8.8 Hz), 6.73–6.78 (m, 2H), 7.03–7.08 (m, 2H), 7.20–7.36 (m, 6H), 7.36–7.41 (m, 2H), 7.51–7.56 (m, 2H), 7.73 (d, 1H, *J* = 8.8 Hz). ^{13}C NMR (125 MHz, CDCl_3): δ = 50.1 (d), 55.2 (q), 55.5 (q), 82.3 (s), 85.7 (d), 100.6 (d), 109.3 (d), 114.1 (s), 114.3 (d), 126.0 (d), 126.8 (d), 127.35 (d), 127.39 (d), 128.2 (d), 128.5 (d), 128.7 (d), 129.0 (d), 130.2 (s), 143.1 (s), 144.0 (s), 158.8 (s), 161.5 (s), 165.9 (s), 189.9 (s). IR (ATR): $\tilde{\nu}$ = 3258 (br), 1668, 1609, 1580, 1508 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{30}\text{H}_{27}\text{O}_4$ [$\text{M} + \text{H}^+$] 467.1858, found 467.1846.

(2R*,3S*)-2-(Hydroxydiphenylmethyl)-5,7-dimethoxy-3-(4-methoxyphenyl)chroman-4-one (trans-5q): White solid (70 mg, 56%). *R*_f: 0.35 (hexanes/ethyl acetate, 1:1). Mp 126–127 °C. ^1H NMR (500 MHz, CDCl_3): δ = 2.39 (brs, 1H), 3.73 (s, 3H), 3.77 (s, 3H), 3.79 (s, 3H), 3.83 (d, 1H, *J* = 2.6 Hz), 5.58 (d, 1H, *J* = 2.6 Hz), 5.91–5.93 (m, 1H), 6.00–6.01 (m, 1H), 6.71–6.76 (m, 2H), 7.05–7.09 (m, 2H), 7.18–7.39 (m, 9H), 7.52–7.57 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ = 51.4 (d), 55.2 (q), 55.5 (q), 56.0 (q), 82.2 (s), 85.0 (d), 92.6 (d), 93.1 (d), 114.1 (d), 125.9 (d), 126.7 (d), 127.3 (d), 127.8 (d), 128.2 (d), 128.5 (d), 129.0 (d), 130.4 (s), 142.9 (s), 144.3 (s), 158.7 (s), 162.0 (s), 163.0 (s), 165.7 (s), 188.5 (s). IR (ATR): $\tilde{\nu}$ = 3460 (br), 1732, 1665, 1607, 1576, 1510 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{31}\text{H}_{29}\text{O}_7$ [$\text{M} + \text{H}^+$] 497.1964, found 497.1955.

Dehydrogenation of 5 with DDQ. To a solution of **5a** (66 mg, 0.20 mmol) in dioxane (5 mL) was added DDQ (57 mg, 0.25 mmol) and TMSCl (0.035 mL, 0.25 mmol), and then the solution was refluxed for 6 h. After removal of the solvent *in vacuo*, the residue was purified by column chromatography on silica gel (hexanes–EtOAc) to give **9a** (59 mg, 0.180 mmol) in 90% yield.

2-(Hydroxydiphenylmethyl)-4H-chromen-4-one (9a): White solid (90%). *R*_f: 0.4 (hexanes/ethyl acetate, 2:1). Mp 216–217 °C. ^1H NMR (500 MHz, CDCl_3): δ = 3.34 (brs, 1H), 6.37 (s, 1H), 7.32–7.44 (m, 12H), 7.62–7.67 (m, 1H), 8.16–8.21 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ = 80.5 (s), 111.3 (d), 118.0 (d), 123.6 (s), 125.4 (d), 125.8 (d), 127.6 (d), 128.39 (d), 128.42 (d), 133.9 (d), 142.3 (s), 156.1 (s), 169.5 (s), 178.5 (s). IR (ATR): $\tilde{\nu}$ = 3177 (br), 1628, 1603 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{22}\text{H}_{17}\text{O}_3$ [$\text{M} + \text{H}^+$] 329.1178, found 329.1172.

2-(Bis(4-fluorophenyl)(hydroxy)methyl)-4H-chromen-4-one (9b): White solid (67 mg, 92%). *R*_f: 0.35 (hexanes/ethyl acetate, 2:1). Mp 173–174 °C. ^1H NMR (500 MHz, CDCl_3): δ = 3.79 (brs, 1H), 6.42 (s, 1H), 7.01–7.07 (m, 4H), 7.32–7.42 (m, 6H), 7.62–7.67 (m, 1H), 8.13 (dd, 1H, *J* = 1.4,

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7.9 Hz). ^{13}C NMR (125 MHz, CDCl_3): δ = 79.5 (s), 110.7 (d), 115.3 (d, J_{CCF} = 21.3 Hz), 117.9 (d), 123.4 (s), 125.5 (d), 125.8 (d), 129.5 (d, J_{CCCF} = 8.4 Hz), 134.1 (d), 138.3 (s, J_{CCCF} = 3.0 Hz), 156.0 (s) 162.5 (s, J_{CF} = 248.3 Hz), 169.6 (s), 178.5 (s). IR (ATR): $\tilde{\nu}$ = 3196 (br), 1628, 1601, 1508 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{22}\text{H}_{15}\text{F}_2\text{O}_3$ [$\text{M} + \text{H}^+$] 365.0989, found 365.0982.

2-(5-Hydroxy-10,11-dihydro-5H-dibenzo[a,d][7]annulen-5-yl)-4H-chromen-4-one (9c): Colorless paste (35 mg, 50%). *R*_f: 0.4 (hexanes/ethyl acetate, 2:1). ^1H NMR (500 MHz, CDCl_3): δ = 2.85-2.93 (m, 2H), 3.17-3.26 (m, 2H), 3.48 (brs, 1H), 6.15 (s, 1H), 7.11-7.14 (m, 2H), 7.20 (d, 1H, J = 8.4 Hz), 7.24-7.35 (m, 5H), 7.53-7.57 (m, 1H), 7.93-7.96 (m, 2H), 8.10 (dd, 1H, J = 1.6, 7.9 Hz). ^{13}C NMR (125 MHz, CDCl_3): δ = 32.7 (t), 78.7 (s), 110.4 (d), 118.3 (d), 123.5 (s), 125.4 (d), 125.6 (d), 126.5 (d), 128.5 (d), 130.6 (d), 133.9 (d), 137.8 (s) 139.5 (s), 156.1 (s), 170.8 (s), 178.9 (s). IR (ATR): $\tilde{\nu}$ = 3285 (br), 1622, 1591, 1570 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{24}\text{H}_{19}\text{O}_3$ [$\text{M} + \text{H}^+$] 355.1334, found 355.1328.

2-(5-Hydroxy-5H-dibenzo[a,d][7]annulen-5-yl)-4H-chromen-4-one (9d): White solid (53 mg, 75%). *R*_f: 0.35 (hexanes/ethyl acetate, 2:1). Mp 268-269 °C. ^1H NMR (500 MHz, CDCl_3): δ = 3.62 (brs, 1H), 5.72 (s, 1H), 6.86 (s, 2H), 7.02 (d, 1H, J = 8.2 Hz), 7.26-7.30 (m, 2H), 7.32-7.39 (m, 4H), 7.47-7.54 (m, 3H), 8.03 (dd, 1H, J = 1.6, 7.9 Hz), 8.07 (d, 1H, J = 8.2 Hz). ^{13}C NMR (125 MHz, CDCl_3): δ = 78.3 (s), 109.7 (d), 118.1 (d), 123.3 (s), 123.9 (d), 125.1 (d), 125.3 (d), 127.4 (d), 128.56 (d), 128.60 (d), 131.2 (d), 132.9 (s), 133.6 (d), 138.5 (s), 155.8 (s) 170.3 (s), 178.9 (s). IR (ATR): $\tilde{\nu}$ = 3348 (br), 1630, 1614, 1593, 1560 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{24}\text{H}_{17}\text{O}_3$ [$\text{M} + \text{H}^+$] 353.1178, found 353.1174.

2-(9-Hydroxy-9H-xanthen-9-yl)-4H-chromen-4-one (9e): White solid (62 mg, 91%). *R*_f: 0.4 (hexanes/ethyl acetate, 2:1). Mp 235-236 °C. ^1H NMR (500 MHz, CDCl_3): δ = 3.06 (brs, 1H), 7.01 (s, 1H), 7.10-7.17 (m, 3H), 7.21-7.33 (m, 3H), 7.36-7.41 (m, 2H), 7.46-7.52 (m, 1H), 7.59 (dd, 2H, J = 1.4, 7.9 Hz), 8.12 (dd, 1H, J = 1.5, 8.0 Hz). ^{13}C NMR (125 MHz, CDCl_3): δ = 69.1 (s), 107.4 (d), 116.7 (d), 118.1 (d), 118.3 (s), 122.4 (s), 123.4 (s), 123.7 (d), 125.0 (d), 125.5 (d), 127.8 (d), 130.2 (d), 133.5 (d), 150.2 (s), 156.1 (s) 170.0 (s), 178.9 (s). IR (ATR): $\tilde{\nu}$ = 3366 (br), 1643, 1601, 1570 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{22}\text{H}_{15}\text{O}_4$ [$\text{M} + \text{H}^+$] 343.0970, found 343.0965.

2-(Hydroxydiphenylmethyl)-3-methyl-4H-chromen-4-one (9g): White solid (31 mg, 46%). *R*_f: 0.15 (hexanes/ethyl acetate, 5:1). Mp 204-205 °C. ^1H NMR (500 MHz, CDCl_3): δ = 1.83 (s, 3H), 3.46 (brs, 1H), 7.19 (d, 1H, J = 8.6 Hz), 7.35-7.39 (m, 11H), 7.56-7.61 (m, 1H), 8.21 (dd, 1H, J = 1.6, 8.0 Hz). ^{13}C NMR (125 MHz, CDCl_3): δ = 10.6 (q), 82.3 (s), 117.7 (d), 119.6 (s), 122.0 (s), 124.9 (d), 125.8 (d), 127.5 (d), 128.2 (d), 128.3 (d), 133.4 (d), 143.2 (s) 155.0 (s), 164.3 (s), 179.3 (s). IR (ATR): $\tilde{\nu}$ = 3364 (br), 1611, 1603, 1566 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{23}\text{H}_{19}\text{O}_3$ [$\text{M} + \text{H}^+$] 343.1334, found 343.1331.

2-(Bis(4-fluorophenyl)(hydroxy)methyl)-3-methyl-4H-chromen-4-one (9h): White solid (45 mg, 60%). *R*_f: 0.45 (hexanes/ethyl acetate, 2:1). Mp 230-231 °C. ^1H NMR (500 MHz, CDCl_3): δ = 1.83 (s, 3H), 3.68 (brs, 1H), 7.03-7.09 (m, 4H), 7.14 (d, 1H, J = 8.2 Hz), 7.32-7.37 (m, 5H), 7.55-7.59 (m, 1H), 8.16 (dd, 1H, J = 1.7, 8.0 Hz). ^{13}C NMR (125 MHz, CDCl_3): δ = 10.5 (q), 81.6 (s), 115.3 (d, J_{CCF} = 21.3 Hz), 117.6 (d), 119.6 (s), 121.9 (s), 125.1 (d), 125.9 (d), 129.3 (d, J_{CCCF} = 8.4), 133.5 (d), 139.1 (s, J_{CCCF} =

3.3 Hz), 155.0 (s) 162.5 (s, J_{CF} = 248.3 Hz), 179.1 (s). IR (ATR): $\tilde{\nu}$ = 3292 (br), 1616, 1601, 1591, 1584, 1508 cm^{-1} . HRMS (ESI+) calcd for $\text{C}_{23}\text{H}_{17}\text{F}_2\text{O}_3$ [$\text{M} + \text{H}^+$] 379.1146, found 379.1141.

Conflict of interest

The authors declare no conflict of interest.

Keywords: Electroreductive Coupling • Chromones • Isoflavones • 2-Diarylmethylchromones • Tetrasubstituted Furans

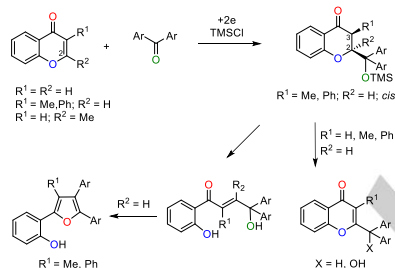
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The electroreductive coupling of chromones with benzophenones in the presence of TMSCl gave adducts reacted at the 2-position of chromones as trimethylsilyl ethers. From 3-methyl- and 3-phenylchromones, 2,3-*cis*-adducts were formed predominantly. 2-Diarylmethylchromones were obtained by dehydrosilylation of the adducts. Tetrasubstituted furans were also synthesized from the adducts through ring-opening products.



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Toshihiko Sakurai

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