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Electroreductive Intermolecular Coupling of Coumarins with Benzophenones: Synthesis of 4-(2-Hydroxyphenyl)-5,5-diaryl-γ-butyrolactones, 2-(2,2-Diaryl-2,3-dihydrobenzofuran-3-yl)acetic acids, and 4-Diarylmethylcoumarins

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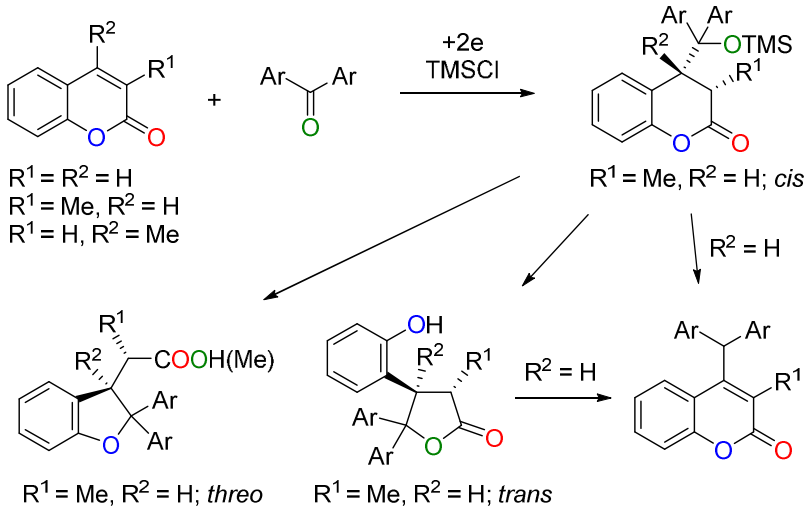
ABSTRACT

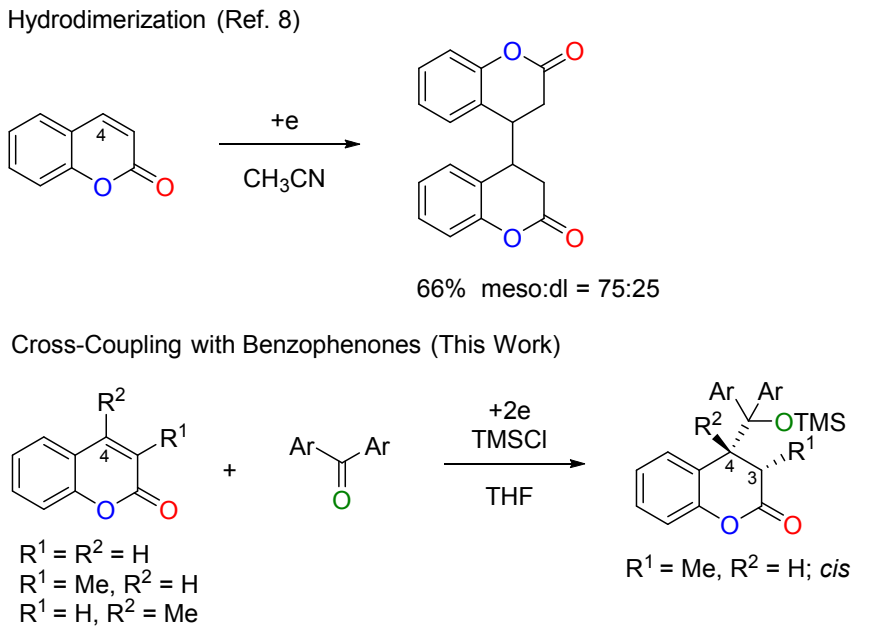
The electroreductive coupling of coumarins with benzophenones in the presence of TMSCl gave adducts reacted at the 4-position of coumarins as trimethylsilyl ethers. From 3-methylcoumarin, 3,4-*cis*-adducts were formed stereoselectively. The detrimethylsilylation of the adducts with 1 M HCl aq or TBAF in THF at 25 ºC produced 4-(2-hydroxyphenyl)-5,5-diaryl-γ-butyrolactones. The γ-butyrolactones were further transformed to 2-(2,2-diaryl-2,3-dihydrobenzofuran-3-yl)acetic acids by treatment with 1 M HCl aq at reflux temperature. The detrimethylsilylation of the adducts with 1 M HCl in MeOH afforded 2-(2,2-diaryl-2,3-dihydrobenzofuran-3-yl)acetic acid methyl esters. The detrimethylsiloxylation of the adducts or dehydration of the γ-butyrolactones brought about 4-diarylmethylcoumarins.



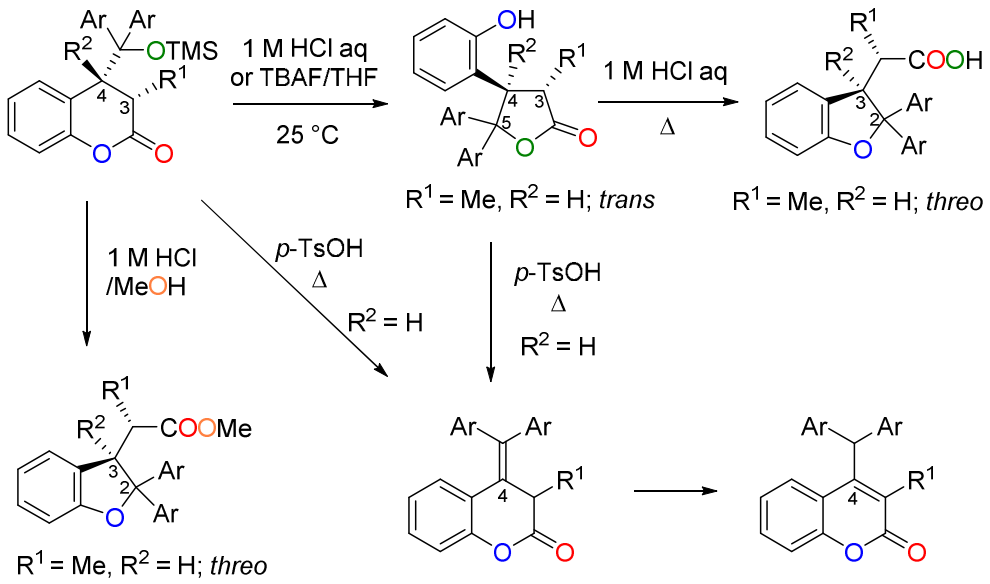
INTRODUCTION

Recently, 3- and 4-subsutituted coumarin derivatives are extensively investigated as pharmacologically active compounds, such as anticancer, antineurodegenerative, and antituberculous agents.[1] Therefore, the synthesis of 3- and 4-subsutituted coumarins attracts much attention from the synthetic chemists.[2,3] On the other hand, electroreduction is one of the useful method for the reductive coupling of carbonyl compounds[4] and we have reported the electroreductive cross-coupling of heterocycles, such as phthalimides,[5] indoles,[6] and uracils,[7] with carbonyl compounds. In this context, we attempted the electroreductive cross-coupling of coumarins with carbonyl compounds, since this type of reaction is previously unknown and expected to provide a new synthetic route to 4-subsutituted coumarin derivatives. We have already reported the electroreductive hydrodimerization of coumarin at its 4-position.[8] In contrast, we report in this paper that the cross-coupled products reacted at the 4-position of coumarins were obtained as trimethylsilyl ethers by the electroreduction of coumarins with benzophenones in the presence of TMSCl (Scheme 1). From 3-methylcoumarin (R^1 = Me, R^2 = H), 3,4-*cis*-adducts were formed with complete stereoselectivity. At first, we expected that 4-substituted coumarins can be prepared from the adducts by detrimethylsilylation of the trimethylsilyl ethers and subsequent dehydration of the resultant alcohols. Contrary to our expectation, the adducts were immediately transformed to 4-(2-hydroxyphenyl)-5,5-diaryl-γ-butyrolactones by desilylation under acidic (1 M HCl aq) or basic (TBAF in THF) conditions at 25 ºC (Scheme 2). Under acidic conditions with 1 M HCl aq at reflux temperature, the γ-butyrolactones further transformed to 2-(2,2-diaryl-2,3-dihydrobenzofuran-3-yl)acetic acids, while their methyl esters were formed by treatment of the adducts with 1 M HCl in MeOH. Eventually, 4-substituted coumarin derivatives could be obtained by direct dehydrosiloxylation of the adducts or dehydration of the γ-butyrolactones with cat. *p*-TsOH in refluxing toluene or xylene. Reaction mechanisms of the electroreductive coupling and the transformations of the adducts were also discussed.

Scheme 1. Electroreductive Hydorodimerization and Cross-Coupling of Coumarins



Scheme 2. Transformation of Adducts



RESULTS AND DISCUSSION

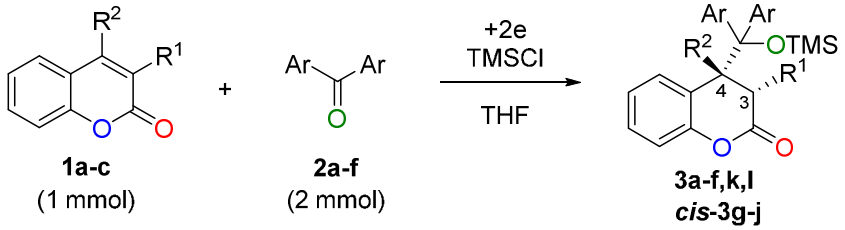
Electroreductive Coupling of Coumarins with Benzophenones.

The electroreduction of coumarins **1a-c** with benzophenones **2a-f** (2 equiv) was carried out in THF containing TMSCl (5 equiv) according to our already reported method[5-7] and the results are summarized in Table 1. As a cathode material, Pt, Au, Ag, Cu, Sn, and Pb brought about almost the same yields (70-75%) of 4-(diphenyl((trimethylsilyl)oxy)methyl)chroman-2-one (**3a**) in the reaction of **1a** with **2a** (run 1). In all cases, the adducts coupled at the 4-position of **1a-c** with **2a-f** were obtained as trimethylsilyl ethers **3a-l** in moderate to high yields. It is noted that the electroreductive coupling of 3-methylcoumarin (**1b**: R^1 = Me, R^2 = H) with **2a-d** gave the adducts **3g-j** as single diastereomers (>99% selectivity by ^{1}H NMR analysis) (runs 7-10). Of these adducts, **3j** was confirmed to be *cis*-isomer by X-ray crystallographic analysis. The other adducts **3g-i** could, therefore, be assumed to be *cis*-isomers. We have already observed similar *cis*-selective additions in the electroreduction of 1-alkoxycarbonyl-3-methyxycarbonylindoles[6] and 1,3-dimethyluracils[7] with aromatic ketones.

Unfortunately, the electroreductive coupling of **1a** with 4,4'-dimethoxybenzophenone (**2g**) under the same conditions as above afforded the hydrodimer of **1a** (**4**) as the major product (42%) and the desired cross-coupled product **3m** was obtained in a low yield (28%) with a trace amount (4%) of 4-(trimethylsilyl)chroman-2-one (**5**) as shown in Scheme 3. Since already reported CV data of coumarins[9] and benzophenones[10] were recorded under different conditions, we measured the CV of **1a-c** and **2a-g** under the same conditions to compare their first reduction peaks (Table 2). These results revealed that **1a** (−1.88 V vs SCE) is slightly less reducible than **2a** (−1.85 V) but more reducible than **2g** (−2.08 V). Therefore, the reaction mechanism of the electroreductive coupling of coumarins with benzophenones can be presumed as illustrated in Scheme 4. Initially, carbanion **A** is generated by the two-electron transfer to **2a** and *O*-silylation with TMSCl. The nucleophilic 1,4-addition of **A** to **1a** and following *O*-silylation of the resulting enolate anion **B** give silyl ketene acetal **C**. The labile **C** is readily desilylated to **3a** during workup. When R^1 is

methyl group, protonation at the 3-position in **C** occurs predominantly from the less hindered side (β side) to produce *cis*-isomer of **3g**. Incidentally, the electroreduction of **1a** in the presence of TMSCl gave **5** in 39% yield and the hydrodimer **4** in 24% yield (Scheme 5). The electroreductive trimethylsilylation of **1a** to **5** probably proceeds through the trimethylsilylation of carbanion **D** generated by the two-electron transfer to **1a** followed by *O*-silylation with TMSCl and subsequent desilylation of the resultant ketene silyl acetal **E** during workup.

Table 1. Electroreductive Coupling of Coumarins 1a-c with Benzophenones 2a-f[a]



run	**1**	R^1	R^2	**2**	$Ar_2C=O$	**3**	% yield[b]
1	**1a**	H	H	**2a**	Ar = Ph	**3a**	75
2	**1a**	H	H	**2b**	Ar = 4-FC_6H_4	**3b**	73
3	**1a**	H	H	**2c**	dibenzosuberone	**3c**	86
4	**1a**	H	H	**2d**	dibenzosuberenone	**3d**	89
5	**1a**	H	H	**2e**	9-fluorenone	**3e**	80
6	**1a**	H	H	**2f**	xanthone	**3f**	78
7	**1b**	Me	H	**2a**	Ar = Ph	***cis*-3g**	86[c]
8	**1b**	Me	H	**2b**	Ar = 4-FC_6H_4	***cis*-3h**	84[c]
9	**1b**	Me	H	**2c**	dibenzosuberone	***cis*-3i**	52[c]
10	**1b**	Me	H	**2d**	dibenzosuberenone	***cis*-3j**	86[c]
11	**1c**	H	Me	**2a**	Ar = Ph	**3k**	83
12	**1c**	H	Me	**2b**	Ar = 4-FC_6H_4	**3l**	62

[a]Electroreduction was carried out in 0.3 M Bu_4NClO_4/THF using a Pt cathode at a constant current of 0.2 A (2 *F*/mol for **2**). [b]Isolated yields. [c]Obtained as *cis* only.

Scheme 3. Electroreduction of 1a and 2g

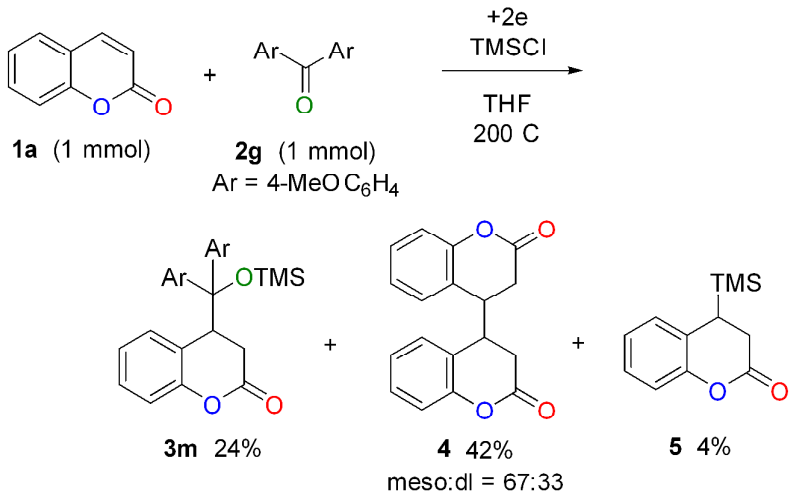
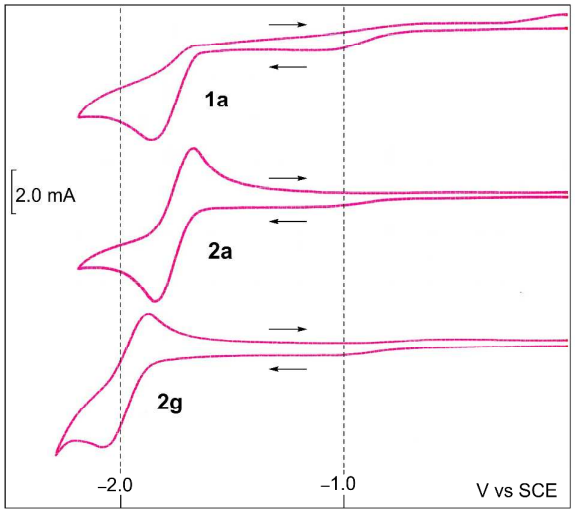


Table 2. E_p values of 1a-c and 2a-g Derived from CV at 25 °C.

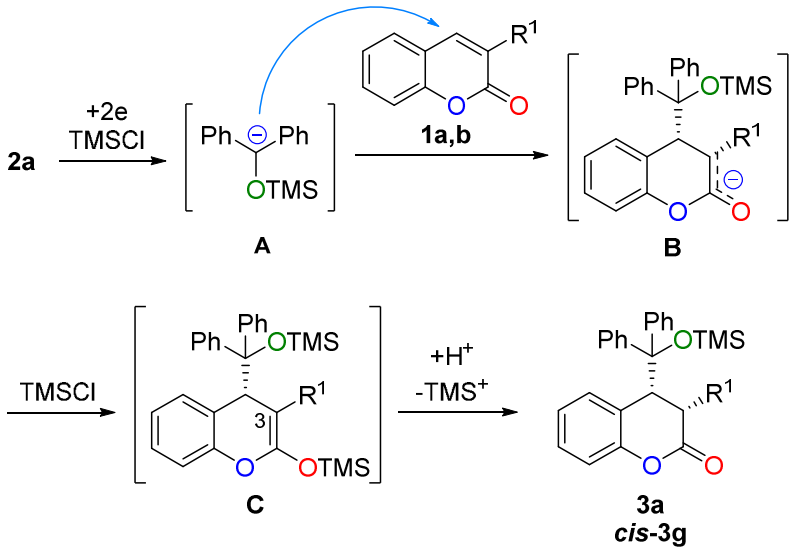
compound	E_p (V vs. SCE)[a]
1a	−1.88
1b	−1.96
1c	−1.94
2a	−1.85
2b	−1.85
2c	−1.78
2d	−1.79
2e	−1.38
2f	−1.76
2g	−2.08

CV data of 1a, 2a, and 2g.

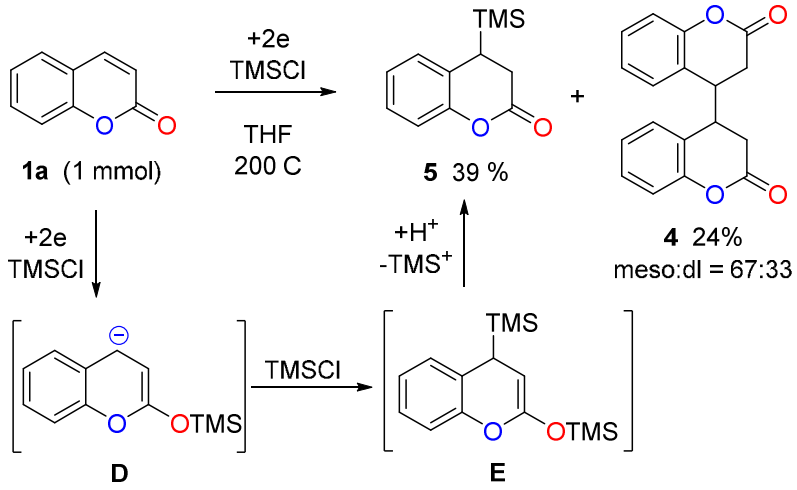


[a]1st reduction peak in CV of 3 mM solution in 0.03 M Bu_4NClO_4/DMF at a Pt cathode at 0.1 V/s. In THF, clear reduction peaks could not be observed.

Scheme 4. Presumed Reaction Mechanism of Electroreductive Coupling of Coumarins with Benzophenones



Scheme 5. Electroreduction of 1a in the Presence of TMSCl



Desilylation of Adducts 3a-l with 1 M HCl aq/dioxane and 1 M HCl/MeOH.

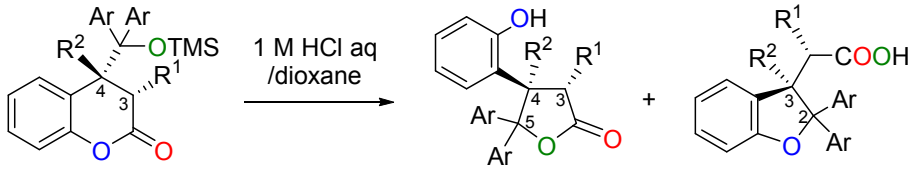
The adducts **3a-j** were stirred in 1 M HCl aq and dioxane (1:1) at 25 ºC until almost all of **3a-j** were consumed (Table 3). From **3a-e**, 4-(2-hydroxyphenyl)-5,5-diaryl-γ-butyrolactones **6a-e** were obtained after stirring for 5-12 h in good to high yields (runs 1, 3, 5, 7, and 9), although a considerable amount of **3d** (23%) remained even after prolonged reaction time of 96 h (run 7). In

the case of **3f**, 2-(2,3-dihydrobenzofuran-3-yl)acetic acid derivative **7f** was formed as the major product with a small amount of γ-butyrolactone **5f** after stirring for 3 h (run 11) and as the sole product after 24 h in 81% yield (run 12). From 3-methyl substituted 3,4-*cis*-adducts ***cis*-3g-j** (R^1 = Me, R^2 = H), 3,4-*trans*-γ-butyrolactones ***trans*-6g-j** were obtained as the sole products in high yields (runs 13 and 15-17). The stereostructures of ***trans*-6g,h,j** were confirmed by X-ray crystallography. On the contrary, 4-methyl substituted adducts **3k,l** (R^1 = H, R^2 = Me) were completely inert under the same conditions at 25 ºC. Next, the mixtures of **3a-e** in 1 M HCl aq and dioxane (1:1) were refluxed until almost all of initially formed **6a-e** were disappeared. In lieu of **6a-e**, 2-(2,2-diaryl-2,3-dihydrobenzofuran-3-yl)acetic acids **7a-e** were obtained as the sole products in moderate to good yields (runs 2, 4, 6, 8, and 10). However, the transformation of the 3-methyl substituted γ-butyrolactones ***trans*-6g-j** to **7g-j** (R^1 = Me, R^2 = H) was very slow even under the reflux conditions. As an example, ***trans*-6g** was diminished to less than 10% after reflux for 144 h to give **7g** in 42% yield as a single stereoisomer (run 14). The stereoconfiguration of the obtained **7g** was assumed to be *threo* as described below. In contrast, the 4-methyl substituted **3k,l** (R^1 = H, R^2 = Me) were readily transformed to 3-methyl substituted **7k,l** after reflux for 24 h (runs 18 and 19).

Second, the adducts **3a-l** were treated with 1 M HCl in MeOH and the results are summarized in Table 4. In the reactions of **3a,b,e-h**, methyl esters of **7a,b,e-h** (**8a,b,e-h**) were effectively produced through γ-butyrolactones **6** at 25 ºC (runs 1,3,7-9, and 11). From other adducts **3c,d,i,k,l**, the corresponding methyl esters **8c,d,i,k,l** were obtained under the same conditions but at reflux temperature (runs 5,6,12,16, and 17). Although **8j** (52%) was given from ***cis*-3j**, a considerable amount of ***trans*-6j** (45%) was remained even after reflux for 108 h (run 14). From ***cis*-3g-j** (R^1 = Me, R^2 = H), methyl esters **8g-j** were obtained as single stereoisomers (runs 9-14). Since the stereoconfiguration of **8h** could be determined to be *threo* by X-ray crystallography, those of **8g,i,j** were assumed to be *threo*. The esterification of **7g** obtained from run 14 in Table 3 certainly afforded the methyl ester ***threo*-8g**.

The presumed reaction mechanism of the transformation of **3a** (***cis*-3g**) to **6a** (***trans*-6g**) and **7a** (***threo*-7g**) in 1 M HCl aq/dioxane is depicted in Scheme 6. It is assured that acid catalyzed desilylation of **3a** (***cis*-3g**) generates **9a** (***cis*-9g**), although **9a** (***cis*-9g**) could not be detected. Transformation of **9a** (***cis*-9g**) to **6a** (***trans*-6g**) rapidly proceeds through successive acid catalyzed processes as follows: ring closure of protonated **9a** (**F**: R^1 = H) to **G**, proton migration from **G** to **H**, six-membered ring opening of **H** to **I**, and finally deprotonation of **I** produce **6a**. Similarly, 3,4-*cis*-δ-lactone ***cis*-9g** (R^1 = Me) is transformed to stereochemically retained 3,4-*trans*-γ-butyrolactone ***trans*-6g**. Under reflux conditions, **6a** is further converted to **7a** via ring opening of protonated **6a** (**J)** to carbocation **K**, intramolecular nucleophilic substitution of the phenoxy group in **K**, and deprotonation of the resultant **L**. In the transformation of ***trans*-6g** to ***threo*-7g**, the stereoconfiguration is retained. In 1 M HCl/MeOH, the acid catalyzed transformation of **3a** and ***cis*-3g** to **6a** and ***trans*-6g** proceeds rapidly in the same way. As shown in Scheme 7, methanolysis of **6a** takes place rapidly to give methyl ester **M**. Successive acid catalyzed dehydration of **M** to carbocation **N**, ring closure of **N** to **O**, and finally deprotonation of **O** afford **8a**. From ***trans*-6g** (R^1 = Me), ***threo*-8g** is formed with complete retention of the stereochemistry.

Table 3. Desilylation of 3a-l with 1 M HCl aq/dioxane



3a-f $R^1 = R^2 = H$
***cis*-3g-j** R^1 = Me; $R^2 = H$
3k,l $R^1 = H$; R^2 = Me

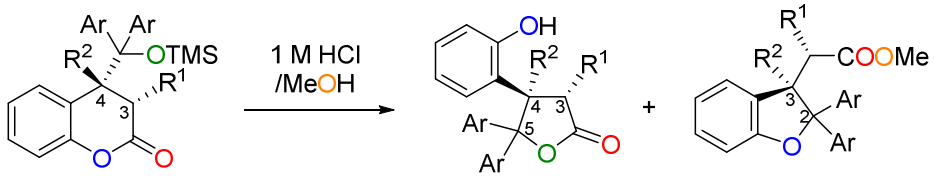
6a-f
***trans*-6g-j**

7a-f
***threo*-7g**
7k.l

run	**3**	temp.	time	**6**	% yield[a]	**7**	% yield[a]
1	**3a**	25 ºC	6 h	**6a**	85		
2	**3a**	reflux	24 h			**7a**	83
3	**3b**	25 ºC	12 h	**6b**	87		
4	**3b**	reflux	24 h			**7b**	61
5	**3c**	25 ºC	5 h	**6c**	92		
6	**3c**	reflux	24 h			**7c**	69
7	**3d**	25 ºC	96 h	**6d**	68[b]		
8	**3d**	reflux	72 h			**7d**	73
9	**3e**	25 ºC	12 h	**6e**	83		
10	**3e**	reflux	7 h			**7e**	75
11	**3f**	25 ºC	3 h	**6f**	5	**7f**	77
12	**3f**	25 ºC	24 h			**7f**	81
13	***cis*-3g**	25 ºC	24 h	***trans*-6g**	92[c]		
14	***cis*-3g**	reflux	144 h	***trans*-6g**	8[c]	***threo*-7g**	42
15	***cis*-3h**	25 ºC	24 h	***trans*-6h**	98[c]		
16	***cis*-3i**	25 ºC	24 h	***trans*-6i**	99[c]		
17	***cis*-3j**	reflux	24 h	***trans*-6j**	90[c]		
18	**3k**	reflux	24 h			**7k**	98
19	**3l**	reflux	24 h			**7l**	72

[a]Isolated yields. [b]**3d** (23%) was recovered. [c]Obtained as *trans* only.

Table 4. Desilylation of 3a-l with 1 M HCl/MeOH



3a-f $R^1 = R^2 = H$
***cis*-3g-j** $R^1 = Me$; $R^2 = H$
3k,l $R^1 = H$; $R^2 = Me$

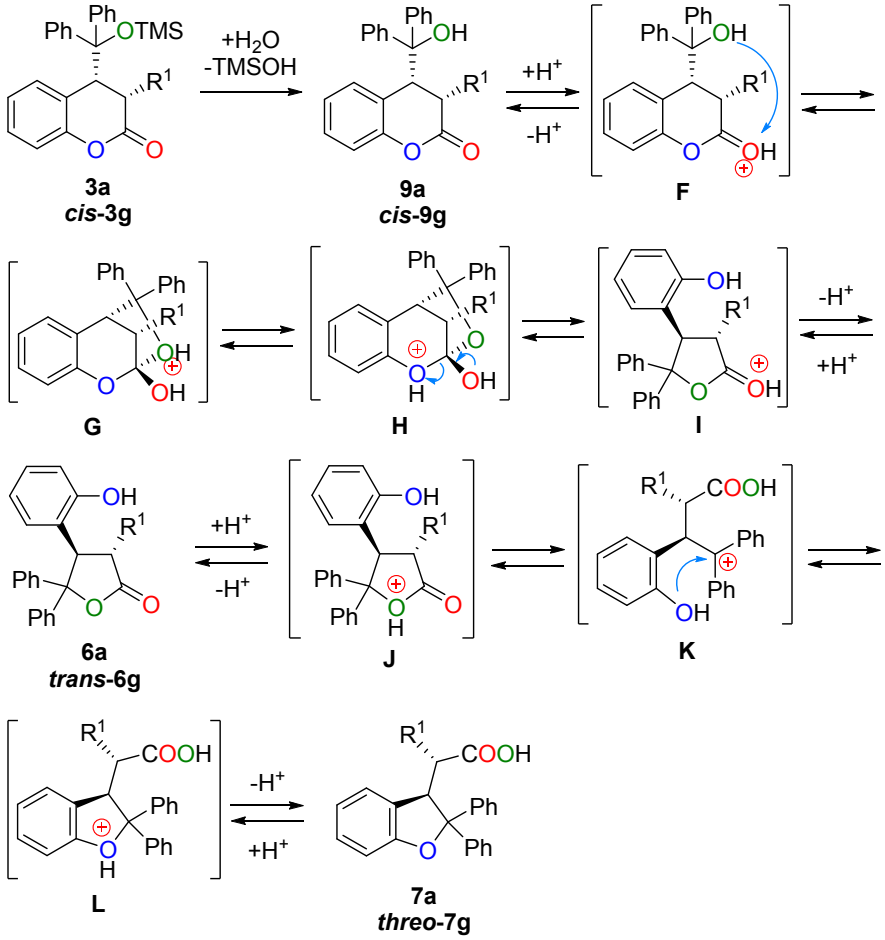
6c
***trans*-6j**
6k

8a-f
***threo*-8g-j**
8k,l

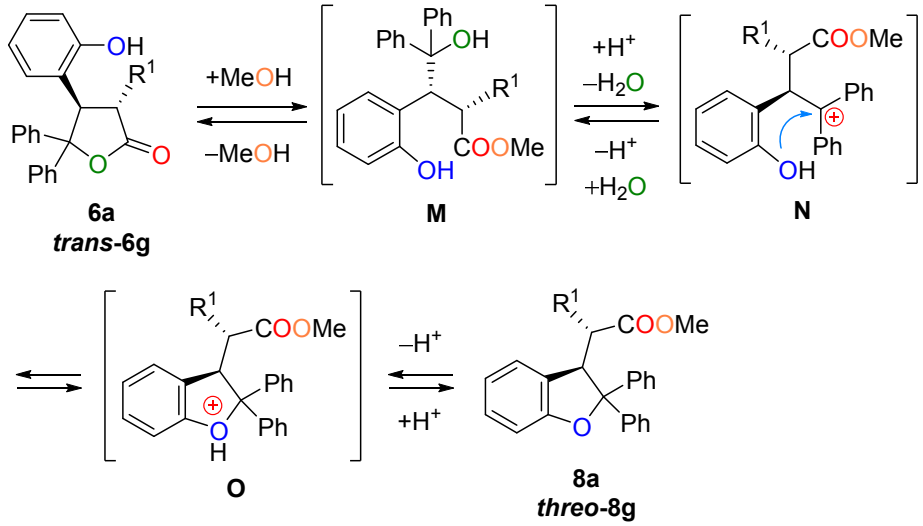
run	**3**	temp.	time	**6**	% yield[a]	**8**	% yield[a]
1	**3a**	25 ºC	12 h			**8a**	86
2	**3a**	reflux	2 h			**8a**	82
3	**3b**	25 ºC	12 h			**8b**	87
4	**3c**	25 ºC	2 h	**6c**	95		
5	**3c**	reflux	2 h			**8c**	73
6	**3d**	reflux	12 h			**8d**	95
7	**3e**	25 ºC	12 h			**8e**	90
8	**3f**	25 ºC	2 h			**8f**	84
9	***cis*-3g**	25 ºC	12 h			***threo*-8g**	96[b]
10	***cis*-3g**	reflux	2 h			***threo*-8g**	89[b]
11	***cis*-3h**	25 ºC	12 h			***threo*-8h**	92[b]
12	***cis*-3i**	reflux	6 h			***threo*-8i**	86[b]
13	***cis*-3j**	reflux	12 h	***trans*-6j**	85[c]	***threo*-8j**	12[b]
14	***cis*-3j**	reflux	108 h	***trans*-6j**	45[c]	***threo*-8j**	52[b]
15	**3k**	25 ºC	12 h	**6k**	48	**8k**	47
16	**3k**	reflux	2 h			**8k**	85
17	**3l**	reflux	2 h			**8l**	96

[a]Isolated yields. [b]Obtained as *threo* only. [c]Obtained as *trans* only.

Scheme 6. Presumed Reaction Mechanism of Acid Catalyzed Transformation of 3a (*cis*-3g) to 6a (*trans*-6g) and 7a (*threo*-7g)



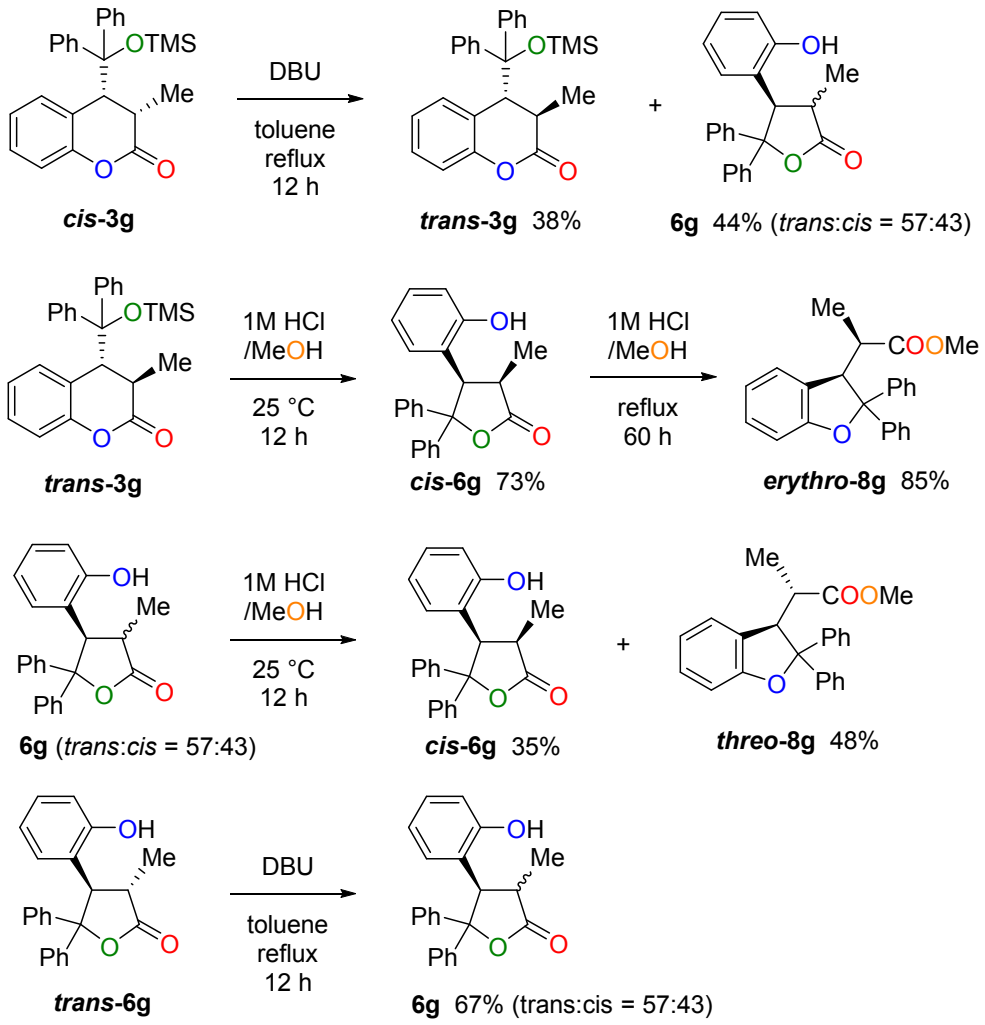
Scheme 7. Presumed Reaction Mechanism of Acid Catalyzed Transformation of 6a (*trans*-6g) to 8a (*threo*-8g) in 1 M HCl/MeOH



Isomerization of *cis*-3g and *trans*-6g to *trans*-3g and *cis*-6g

Since the isomerization of ***cis*-3g** by treatment with cat. DBU at 25 ºC did not proceed entirely, the reaction was carried out in refluxing toluene (Scheme 8). Although the desired ***trans*-3g** was given in 38% yield stereoselectively after 12 h, a significant amount of **6g** (44%) was also formed with a *trans*:*cis* ratio of 57:43. The obtained ***trans*-3g** was selectively transformed to ***cis*-6g** and ***erythro*-8g** by treatment with 1 M HCl in MeOH at 25 ºC and reflux temperature, respectively. This result shows that ***cis*-6g** is inert in 1 M HCl/MeOH at 25 ºC in contrast to ***trans*-6g**. Actually, when the diastereomeric mixture of **6g** (*trans*:*cis* = 57:43) was treated with 1 M HCl in MeOH at 25 ºC, ***threo*-8g** was selectively formed from ***trans*-6g** whereas ***cis*-6g** completely remained. On the other hand, the treatment of ***trans*-6g** with cat. DBU in refluxing toluene for 12 h gave an equilibrium mixture of **6g** (*trans*:*cis* = 57:43). This result suggests that ***trans*-6g** is slightly stable than ***cis*-6g** under the conditions. The DFT calculations of the both isomers of **6g** at the B3LYP/6-311+G(2d,p) level using the IEFPCM model in toluene at 383 K also showed that ***trans*-6g** is a little lower in energy than ***cis*-6g** (0.41 kcal/mol corresponding to 63:37 dr).

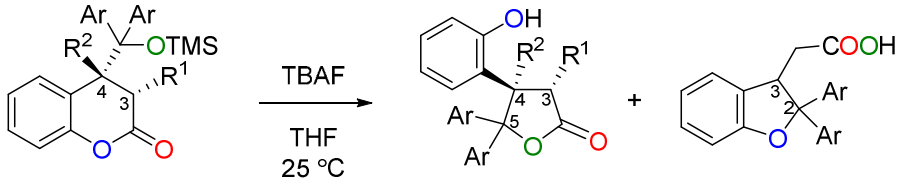
Scheme 8. Isomerization of *cis*-3g and *trans*-6g



Desilylation of Adducts 3a-l with TBAF/THF.

The adducts **3a-l** were treated with TBAF in THF at 25 ºC for 15 min (Table 5). Except for the reaction of **3f**, the γ-butyrolactones **6a-e** and **6g-l** were obtained in good to excellent yields (runs 1-5 and 8-13). The reaction of **3f** for 15 min afforded **7f** as the major product with a small amount of **6f** (run 6). After 3h, **7f** was obtained as the sole product in 60% yield (run 7). Similarly to the acid catalyzed desilylation described above, ***trans*-6g-j** were selectively formed from ***cis*-3g-j** (runs 8-11).

Table 5. Desilylation of 3a-l with TBAF/THF



3a-f $R^1 = R^2 = H$
***cis*-3g-j** R^1 = Me; R^2 = H
3k,l R^1 = H; R^2 = Me

6a-f
***trans*-6g-j**
6k,l

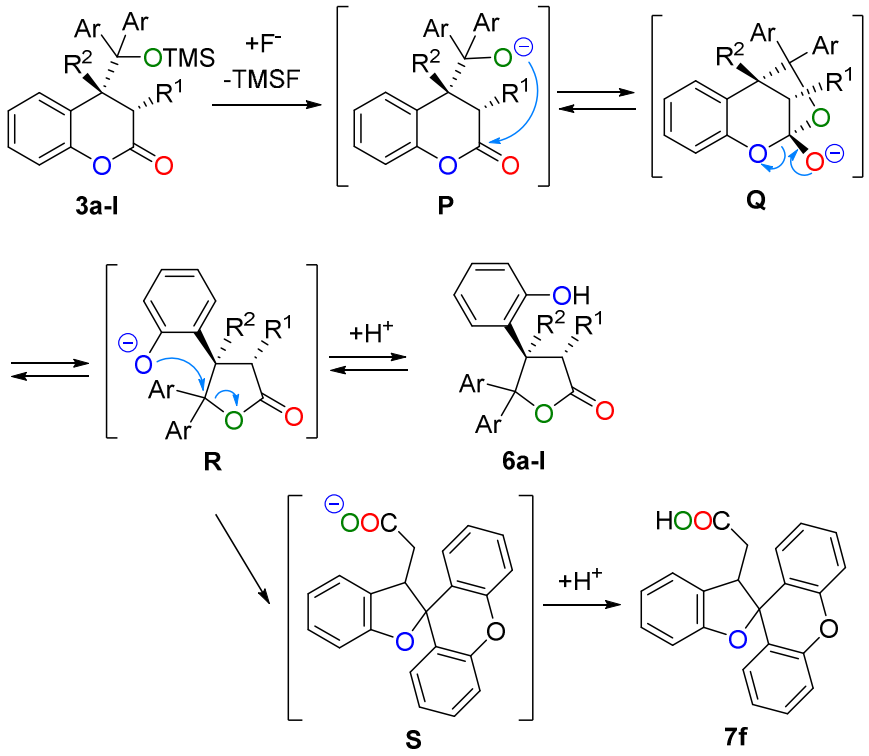
7f

run	**3**	time	**6**	% yield[a]	**7**	% yield[a]
1	**3a**	15 min	**6a**	95		
2	**3b**	15 min	**6b**	83		
3	**3c**	15 min	**6c**	98		
4	**3d**	15 min	**6d**	99		
5	**3e**	15 min	**6e**	82		
6	**3f**	15 min	**6f**	18	**7f**	58
7	**3f**	3 h			**7f**	60
8	***cis*-3g**	15 min	***trans*-6g**	86[b]		
9	***cis*-3h**	15 min	***trans*-6h**	97[b]		
10	***cis*-3i**	15 min	***trans*-6i**	74[b]		
11	***cis*-3j**	15 min	***trans*-6j**	84[b]		
12	**3k**	15 min	**6k**	81		
13	**3l**	15 min	**6l**	73		

[a]Isolated yields. [b]Obtained as *trans* only.

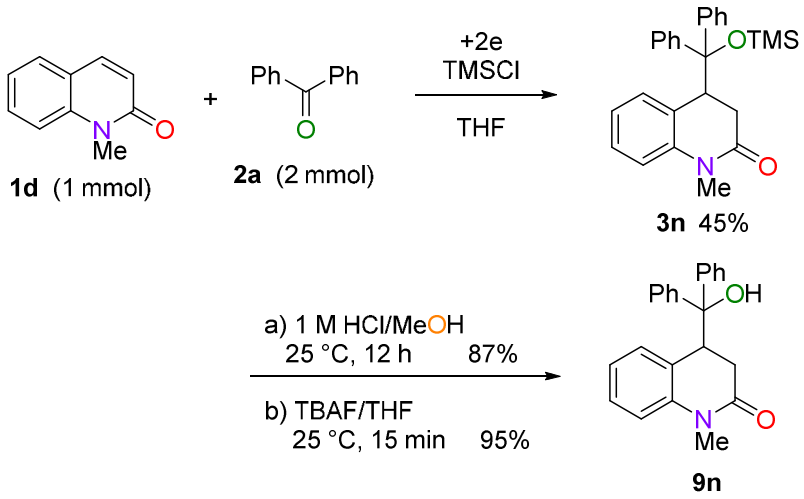
The presumed reaction mechanism of the transformation of **3a-l** to **6a-l** and **7f** is exhibited in Scheme 9. Treatment of **3a-l** with TBAF generates alkoxide anion **P**. Ring closure by intramolecular nucleophilic addition of **P** and subsequent ring opening of the six-membered ring in the resultant **Q** to **R** rapidly occur. While γ-butyrolactones **6a-l** are produced by protonation of the phenoxide anion in **R**, **7f** is formed by intramolecular nucleophilic substitution probably due to the electronic effect of the xanthone ring in **R** and subsequent protonation of the resultant carboxylate anion **S**.

Scheme 9. Presumed Reaction Mechanism of Transformation of 3a-l to 6a-l and 7f with TBAF



The rapid conversion from δ-lactones **3a-l** to γ-butyrolactones **6a-l** under both acidic and basic conditions described above did not proceed in the case of δ-lactam **3n** which was prepared by the electroreductive coupling of 1-methylquinolin-2(1H)-one (**1d**) with **2a** (Scheme 10). The treatment of **3n** with 1 M HCl in MeOH or TBAF in THF at 25 ºC gave desilylated δ-lactam **9n** in a high yield.

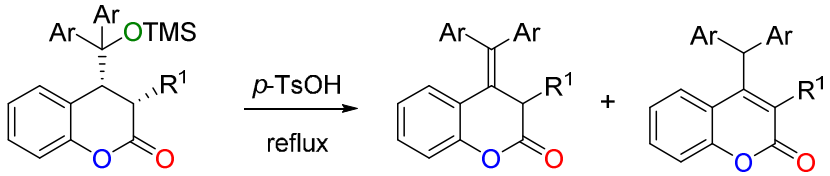
Scheme 10. Electroreductive Coupling of 1d with 2a and desilylation of adduct 3n



Detrimethylsiloxylation of 3a-j.

Detrimethylsiloxylation[7] of **3a-j** was carried out by reflux in xylene or toluene containing a catalytic amount of *p*-TsOH (Table 6). From **3a-f** (R^1 = H), 4-diarylmethylcoumarins **11a-f** were obtained as the sole products (runs 1-6). On the contrary, 4-(diarylmethylene)-3-methylchroman-2-ones **10g-i** were exclusively produced from ***cis*-3g-i** (R^1 = Me) (runs 7-9). From ***cis*-3j** (R^1 = Me), 4-diarylmethylcoumarin **11j** (59%) was obtained with **10j** (37%) after reflux in xylene for 24 h (run 10). However, the isomerization of **10j** to **11j** did not complete even after 96 h (run 11). Similarly, detrimethylsiloxylation of **3n** in toluene for 12 h gave 4-benzhydryl-1-methylquinolin-2(1H)-one (**11n**) in 85% yield (run 12). Isomerization of *exo*-alkenes **10g,h** to *endo*-alkenes **11g,h** could be readily effected by treatment with a catalytic amount of DBU in THF at 25 ºC (Scheme 11).

Table 6. Detrimethylsiloxylation of 3a-j



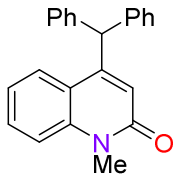
3a-f R^1 = H
***cis*-3g-j** R^1 = Me

10g-j

11a-f,j

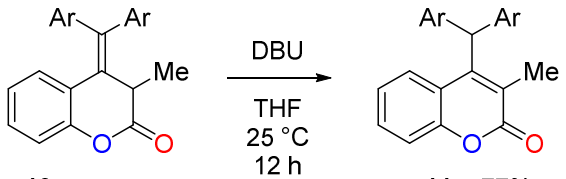
run	**3**	solvent	time	**10**	% yield[a]	**11**	% yield[a]
1	**3a**	xylene	24 h			**11a**	82[b]
2	**3b**	xylene	24 h			**11b**	80[c]
3	**3c**	xylene	48 h			**11c**	79
4	**3d**	toluene	12 h			**11d**	90
5	**3e**	xylene	24 h			**11e**	95
6	**3f**	toluene	24 h			**11f**	65
7	***cis*-3g**	xylene	24 h	**10g**	80		
8	***cis*-3h**	xylene	24 h	**10h**	85		
9	***cis*-3i**	xylene	24 h	**10i**	78		
10	***cis*-3j**	xylene	24 h	**10j**	59	**11j**	37
11	***cis*-3j**	xylene	96 h	**10j**	34	**11j**	63
12	**3n**	toluene	12 h			**11n**	85

[a]Isolated yields. [b]**7a** (8%) was formed as a by-product. [c]**7b** (16%) was formed as a by-product.



11n

Scheme 11. Isomerization of 10g,h to 11g,h

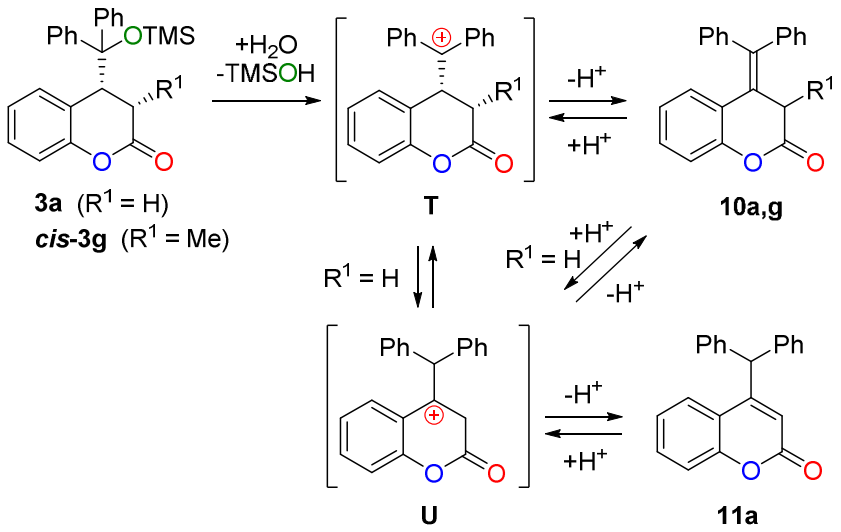


10g Ar = Ph
10h Ar = 4-FC_6H_4

11g 77%
11h 70%

The presumed reaction mechanism of transformation of **3a** and ***cis*-3g** to **11a** and **10g** was shown in Scheme 12. Acid catalyzed detrimethylsiloxylation of **3a** and ***cis*-3g** generates carbocation **T** and subsequent deprotonation of **T** affords **10a,g**. In the reaction of **3a** (R^1 = H), carbocation **U** is formed by hydride migration of **T** or protonation to **10a** and subsequently deprotonated to give **11a**. Consequently, **11a** is obtained as the sole product by the displacement of equilibrium. In contrast, the result of run 7 in Table 6 shows that the isomerization of **10g** (R^1 = Me) to **11g** does not proceed entirely under the conditions.

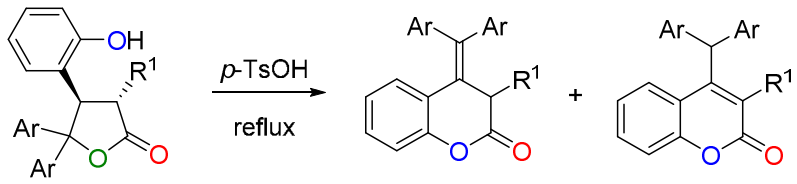
Scheme 12. Presumed Reaction Mechanism of Detrimethylsiloxylation of 3a,g to 10g and 11a



On the other hand, the γ-butyrolactones **6a-h** were also transformed to the 4-diarylmethylcoumarins **11a-h** under the same conditions as above (Table 7). From **6a-f** (R^1 = H), **11a-f** were obtained by reflux in toluene for 12 h (runs 1-6). It is noted that **11g,h** were formed together with **10g,h** from ***trans*-6g,h** (R^1 = Me) in refluxing xylene (runs 7 and 8). In addition, the (2,3-dihydrobenzofuran-3-yl)acetic acid **7a** was also transformed to **11a** by reflux in xylene for only 6 h (Scheme 13). From these results, the reaction mechanism of acid catalyzed transformation of **6a**, ***trans*-6g**, and **7a** to **10g** and **11a,g** can be proposed as shown in Scheme 14. Carbocation **K** is

formed by acid catalyzed ring opening of **6a**, ***trans*-6g**, and **7a** as shown in Scheme 6. Deprotonation of **K** and following lactonization of the resultant carboxylic acid **V** give **10a,g**. Alternatively, carbocation **W** is formed by hydride migration of **K** or protonation to **V** and then undergoes deprotonation to give carboxylic acid **X**. Finally, lactonization of **X** produces **11a,g**. In the reactions of **6a** and **7a** (R^1 = H), **10a** isomerizes to **11a** through **U** according to the mechanism shown in Scheme 12.

Table 7. Dehydration of 6a-h



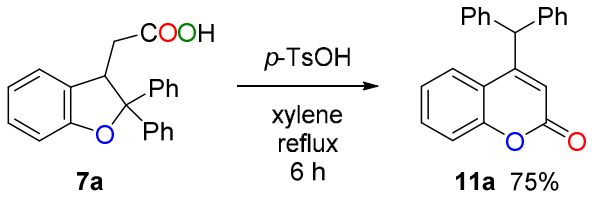
6a-f R^1 = H
***trans*-6g,h** R^1 = Me

10g,h **11a-h**

run	**6**	solvent	time	**10**	% yield[a]	**11**	% yield[a]
1	**6a**	toluene	12 h			**11a**	80
2	**6b**	toluene	12 h			**11b**	42[b]
3	**6c**	toluene	12 h			**11c**	73
4	**6d**	toluene	12 h			**11d**	63
5	**6e**	toluene	12 h			**11e**	76
6	**6f**	toluene	12 h			**11f**	99
7	***trans*-6g**	xylene	24 h	**10g**	46	**11g**	50
8	***trans*-6h**	xylene	12 h	**10h**	16	**11h**	47

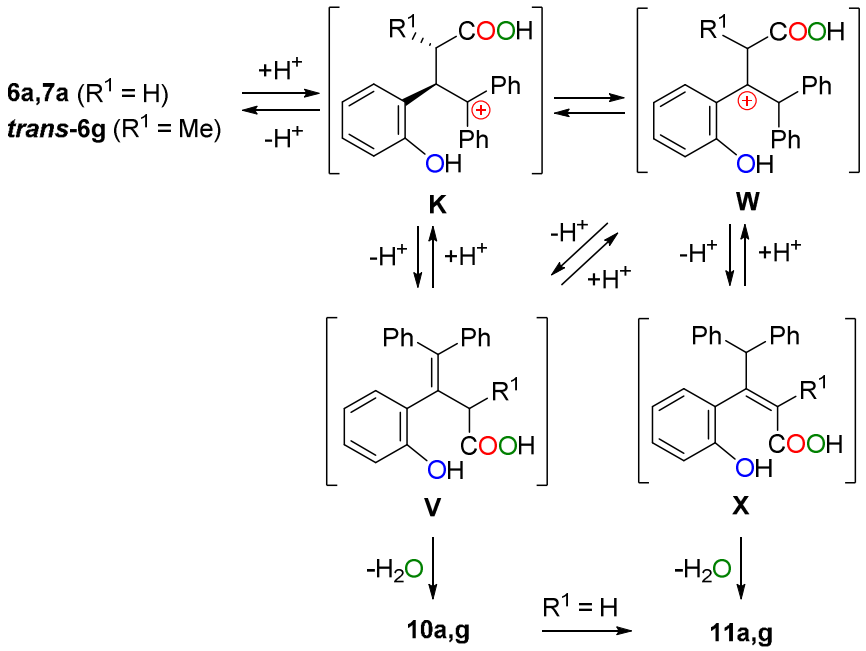
[a]Isolated yields. [b]**7b** (19%) was formed as a by-product.

Scheme 13. Dehydration of 7a to 11a



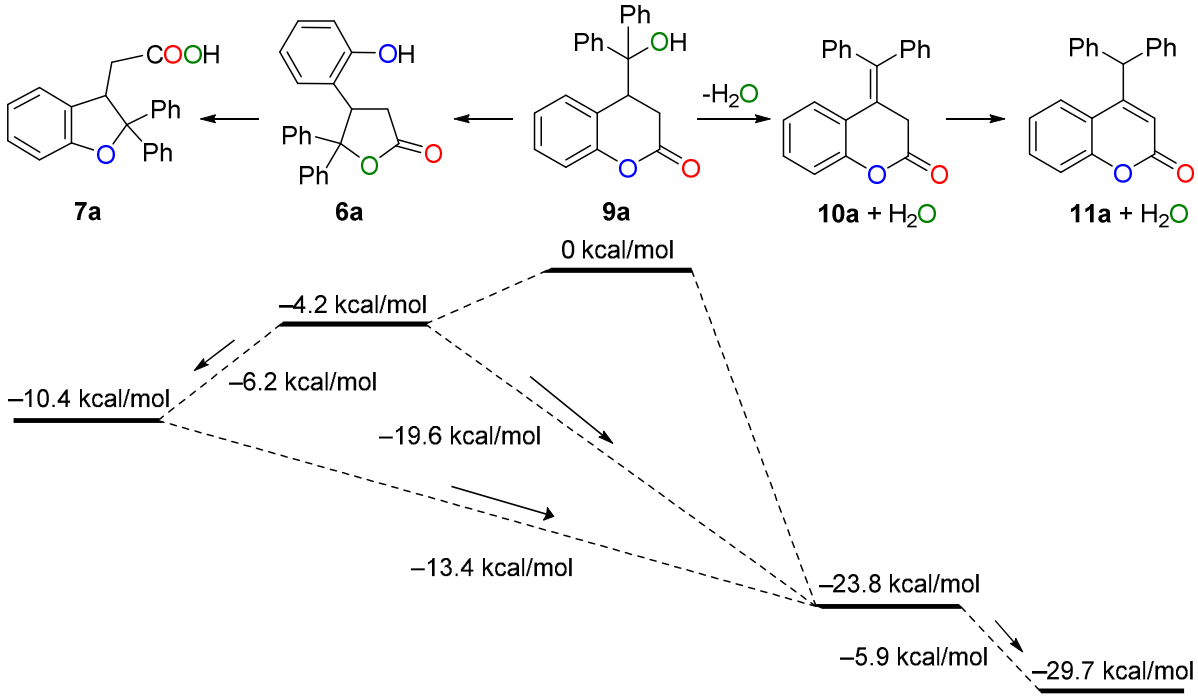
7a **11a** 75%

Scheme 14. Presumed Reaction Mechanism of Dehydration of 6a, *trans*-6g and 7a to 10g and 11a,g



These reaction mechanisms shown in Schemes 12 and 14 are supported by the DFT calculations of **6a-11a** at the B3LYP/6-311+G(2d,p) level in toluene at 383 K. The energy profile illustrated in Scheme 15 indicates that the energies of **9a**, **6a**, and **7a** decrease in this order. Dehydrated product **10a** is much more stable than **7a** (13.4 kcal/mol) and **6a** (19.6 kcal/mol). It is to be anticipated that *endo*-alkene **11a** is lower in energy (5.9 kcal/mol) than *exo*-alkene **10a**. Consequently, the product of the dehydration of **6a** and **7a** converges with **11a**.

Scheme 15. Energy Profile from 9a to 6a, 7a, 10a, and 11a Calculated by the B3LYP/6-311+G(2d,p)/IEFPCM(toluene) Method at 383K



CONCLUSION

The electroreductive intermolecular coupling of coumarins **1a-c** with benzophenones **2a-f** in the presence of TMSCl in THF gave the adducts reacted at the 4-position of **1a-c** as TMS ethers **3a-l**. From 3-methylcoumarin (**1b**), only 3,4-*cis*-adducts ***cis*-3g-j** were selectively obtained. The treatment of **3a-l** with 1 M HCl/dioxane aq or TBAF in THF at 25 ºC gave 4-(2-hydroxyphenyl)-5,5-diaryl-γ-butyrolactones **6a-l**. The desilylation of ***cis*-3g-j** under the both conditions selectively produced 3,4-*trans*-γ-butyrolactones ***trans*-6g-j**. At reflux temperature in 1 M HCl aq/dioxane, **6a-g,k,l** were further transformed to (2,2-diaryl-2,3-dihydrobenzofuran-3-yl)acetic acids **7a-g,k,l**. On the other hand, methyl esters of **7a-l** (**8a-l**) were formed from **3a-l** by treatment with 1 M HCl in MeOH. From ***cis*-3g-j**, *threo*-isomers of **8g-j** (***threo*-8g-j**) were selectively obtained with completely retaining the stereochemistry. Detrimethylsiloxylation of **3a-f** or dehydration of **6a-f** with refluxing cat.

p-TsOH/toluene or xylene afforded 4-diarylmethyl substituted coumarins **11a-f**. Although the detrimethylsiloxylation of ***cis*-3g,h** under the same conditions produced 4-diarylmethylene-3-methyl substituted coumarins **10g,h**, these *exo*-alkenes **10g,h** were readily isomerized to *endo*-alkenes **11g,h** by treatment with cat. DBU in THF at 25 ºC.

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 CaH_2.

Typical Procedure of Electroreductive Coupling. A 0.3 M solution of Bu_4NClO_4 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 X 5 cm^2), a platinum anode (2 X 1 cm^2), and a ceramic cylindrical diaphragm (1.5 cm diameter). A 0.3 M solution of Et_4NOTs in DMF (4 mL) was placed in the anodic chamber (inside the diaphragm). Coumarin (**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 (2 *F*/mol for **2a**) of electricity was passed at a constant current of 200 mA at 25 ºC 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, 10:1) to give **3a** (286 mg) in 71% yield.

4-(Diphenyl((trimethylsilyl)oxy)methyl)chroman-2-one (3a): colorless paste (301 mg, 75%); *Rf* 0.2 (hexanes-ethyl acetate, 10:1); IR (ATR) 1763 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ −0.16 (s, 9H), 2.27 (dd, 1H, *J* = 8.1, 17.2 Hz), 3.19 (d, 1H, *J* = 17.2 Hz), 4.07 (d, 1H, *J* = 8.1 Hz), 6.76-6.80 (m, 1H), 6.90-6.94 (m, 1H), 6.98-7.01 (m, 1H), 7.11-7.36 (m, 11H); ^{13}C NMR ($CDCl_3$) δ 1.5 (q), 31.0 (t), 45.3 (d), 84.0 (s), 116.2 (d), 120.9 (s), 122.7 (d), 127.31 (d), 127.34 (d), 127.8 (d), 128.4 (d), 128.6

(d), 128.7 (d), 131.3 (d), 140.8 (s), 141.1 (s), 152.5 (s), 167.2 (s); HRMS (ESI, ion trap) calcd for $C_{25}H_{27}O_3Si$ ($M + H^+$) 403.1729; found 403.1726.

4-(Bis(4-fluorophenyl)((trimethylsilyl)oxy)methyl)chroman-2-one (3b): colorless paste (320 mg, 73%); *Rf* 0.4 (hexanes-ethyl acetate, 5:1); IR (ATR) 1761 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.16 (s, 9H), 2.78 (dd, 1H, *J* = 8.0, 17.2 Hz), 3.15 (d, 1H, *J* = 17.2 Hz), 4.04 (d, 1H, *J* = 8.0 Hz), 6.78-6.81 (m, 1H), 6.93-7.04 (m, 6H), 7.06-7.11 (m, 2H), 7.19-7.28 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 1.5 (q), 30.9 (t), 45.4 (d), 83.1 (s), 114.3 (d, J_{CCF} = 21.6 Hz), 114.4 (d, J_{CCF} = 20.4 Hz), 116.4 (d), 120.5 (s), 123.0 (d), 128.8 (d), 130.4 (d, J_{CCCF} = 8.4 Hz), 130.6 (d, J_{CCCF} = 8.4 Hz), 131.2 (d), 136.4 (s), 136.8 (s), 152.4 (s), 162.19 (s, J_{CF} = 248.3 Hz), 162.23 (s, J_{CF} = 249.8 Hz), 167.1 (s); HRMS (ESI, ion trap) calcd for $C_{25}H_{25}F_2O_3Si$ ($M + H^+$) 439.1541; found 439.1538.

4-(5-((Trimethylsilyl)oxy)-10,11-dihydro-5H-dibenzo[a,d][7]annulen-5-yl)chroman-2-one (3c): colorless paste (369 mg, 86%); *Rf* 0.3 (hexanes-ethyl acetate, 10:1); IR (ATR) 1767 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.12 (s, 9H), 2.27 (dd, 1H, *J* = 9.6, 15.3 Hz), 2.51 (dd, 1H, *J* = 7.7, 17.0 Hz), 2.64 (dd, 1H, *J* = 9.6, 15.3 Hz), 2.87 (dd, 1H, *J* = 9.6, 15.3 Hz), 3.04-3.11 (m, 2H), 3.73 (d, 1H, *J* = 7.7 Hz), 6.34-6.40 (m, 1H), 6.74-6.80 (m, 1H), 6.96-7.01 (m, 1H), 7.02-7.11 (m, 2H), 7.14-7.20 (m, 2H), 7.22-7.32 (m, 2H), 7.42-7.47 (m, 1H), 7.78-7.84 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 1.8 (q), 30.3 (t), 35.5 (t), 36.1 (t), 51.2 (d), 86.6 (s), 116.3 (d), 121.7 (s), 122.8 (d), 125.2 (d), 125.4 (d), 127.7 (d), 127.8 (d), 128.5 (d), 129.6 (d), 129.9 (d), 130.7 (d), 131.4 (d), 131.8 (d), 139.2 (s), 140.68 (s), 140.73 (s), 141.2 (s), 152.5 (s), 167.8 (s); HRMS (ESI, ion trap) calcd for $C_{27}H_{29}O_3Si$ ($M + H^+$) 429.1886; found 429.1882.

4-(5-((Trimethylsilyl)oxy)-5H-dibenzo[a,d][7]annulen-5-yl)chroman-2-one (3d): white solid (380 mg, 89%); *Rf* 0.5 (hexanes-ethyl acetate, 5:1); mp 201-203 ºC; IR (ATR) 1759 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.30 (s, 9H), 2.11 (d, 1H, *J* = 16.5 Hz), 2.26 (dd, 1H, *J* = 7.5, 16.5 Hz), 3.83 (d, 1H, *J* = 7.5 Hz), 5.71-5.76 (m, 1H), 6.53-6.58 (m, 1H), 6.95-7.16 (m, 5H), 7.17-7.20 (m, 1H), 7.27-7.32 (m, 1H), 7.35-7.44 (m, 3H), 7,48-7.53 (m, 1H), 7.88-7.91 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 3.0 (q), 29.9 (t),

38.7 (d), 88.7 (s), 115.8 (d), 121.7 (s), 122.2 (d), 126.96 (d), 126.98 (d), 127.04 (d), 127.1 (d), 127.2 (d), 128.2 (d), 129.3 (d), 130.27 (d), 130.34 (d), 131.6 (d), 131.9 (d), 132.1 (s), 132.4 (s), 139.5 (s), 140.5 (s), 152.6 (s), 168.0 (s). Anal. Calcd for $C_{27}H_{26}O_3Si$: C, 76.02; H, 6.14. Found: C, 76.07; H, 6.13.

4-(9-((Trimethylsilyl)oxy)-9H-fluoren-9-yl)chroman-2-one (3e): colorless paste (320 mg, 80%); *Rf* 0.45 (hexanes-ethyl acetate, 5:1); IR (ATR) 1769 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.37 (s, 9H), 2.40 (d, 1H, *J* = 7.5 Hz), 2.50 (dd, 1H, *J* = 7.5, 16.8 Hz), 3.49 (d, 1H, *J* = 7.5 Hz), 6.80-6.85 (m, 1H), 6.98-7.02 (m, 1H), 7.10-7.17 (m, 2H), 7.25-7.30 (m, 2H), 7.32-7.42 (m, 4H), 7.60-7.66 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 0.9 (q), 29.8 (t), 45.9 (d), 85.0 (s), 116.2 (d), 119.96 (d), 120.00 (d), 121.1 (s), 122.8 (d), 124.1 (d), 125.2 (d), 127.1 (d), 127.3 (d), 128.7 (d), 129.1 (d), 129.6 (d), 132.0 (d), 139.6 (s), 139.7 (s), 144.8 (s), 146.6 (s), 152.2 (s), 166.7 (s); HRMS (ESI, ion trap) calcd for $C_{25}H_{24}O_3Si$ ($M + H^+$) 401.1573; found 401.1571.

4-(9-((Trimethylsilyl)oxy)-9H-xanthen-9-yl)chroman-2-one (3f): colorless paste (325 mg, 78%); *Rf* 0.3 (hexanes-ethyl acetate, 10:1); IR (ATR) 1767 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.16 (s, 9H), 2.52 (dd, 1H, *J* = 7.5, 16.6 Hz), 2.79 (d, 1H, *J* = 16.6 Hz), 3.18 (d, 1H, *J* = 7.5 Hz), 6.71-6.77 (m, 1H), 6.87-6.91 (m, 1H), 6.94-6.98 (m, 1H), 7.00-7.14 (m, 5H), 7.24-7.36 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 1.5 (q), 29.8 (t), 50.5 (d), 74.0 (s), 115.9 (d), 116.05 (d), 116.12 (d), 120.6 (s), 122.4 (d), 122.5 (d), 122.8 (d), 124.6 (s), 127.4 (d), 127.5 (d), 128.8 (d), 129.1 (d), 129.5 (d), 131.4 (d), 150.0 (s), 150.1 (s), 152.4 (s), 167.2 (s); HRMS (ESI, ion trap) calcd for $C_{25}H_{25}O_4Si$ ($M + H^+$) 417.1522; found 417.1519.

(3*R,4*S**)-4-(Diphenyl((trimethylsilyl)oxy)methyl)-3-methylchroman-2-one (*cis*-3g)**: colorless paste (358 mg, 86%); *Rf* 0.3 (hexanes-ethyl acetate, 10:1); IR (ATR) 1763 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.14 (s, 9H), 1.25 (d, 3H, *J* = 6.9 Hz), 2.92-3.01 (m, 1H), 4.13 (d, 1H, *J* = 5.8 Hz), 6.75-6.87 (m, 3H), 6.98-7.04 (m, 2H), 7.13-7.21 (m, 3H), 7.24-7.28 (m, 1H), 7.33-7.38 (m, 3H), 7.44-7.50 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 1.7 (q), 14.7 (q), 38.0 (d), 51.4 (d), 84.8 (s), 116.1 (d), 122.5 (d), 124.6 (s),

126.7 (d), 127.3 (d), 127.6 (d), 128.3 (d), 128.4 (d), 128.7 (d), 130.8 (d), 140.3 (s), 142.0 (s), 152.1 (s), 170.6 (s); HRMS (ESI, ion trap) calcd for $C_{26}H_{29}O_3Si$ ($M + H^+$) 417.1886; found 417.1884.

(3*R,4*S**)-4-(Bis(4-fluorophenyl)((trimethylsilyl)oxy)methyl)-3-methylchroman-2-one (*cis*-3h)**: colorless paste (380 mg, 84%); *Rf* 0.25 (hexanes-ethyl acetate, 10:1); IR (ATR) 1763 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.15 (s, 9H), 1.25 (d, 3H, *J* = 7.3 Hz), 2.94-3.02 (m, 1H), 4.07 (d, 1H, *J* = 5.9 Hz), 6.75-6.80 (m, 1H), 6.83-6.89 (m, 4H), 6.93-6.99 (m, 2H), 7.02-7.08 (m, 2H), 7.18-7.23 (m, 2H), 7.38-7.44 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 1.8 (q), 15.0 (q), 38.1 (d), 51.7 (d), 84.2 (s), 113.9 (d, J_{CCF} = 20.4 Hz), 114.5 (d, J_{CCF} = 21.6 Hz), 116.6 (d), 122.9 (d), 124.4 (s), 130.4 (d, J_{CCCF} = 8.4 Hz), 130.6 (d, J_{CCCF} = 8.4 Hz), 130.8 (d), 136.1 (s), 137.8 (s), 152.3 (s), 162.3 (s, J_{CF} = 248.0 Hz), 162.4 (s, J_{CF} = 248.0 Hz); HRMS (ESI, ion trap) calcd for $C_{26}H_{27}F_2O_3Si$ ($M + H^+$) 453.1698; found 453.1694.

(3*R,4*S**)-3-Methyl-4-(5-((trimethylsilyl)oxy)-10,11-dihydro-5H-dibenzo[a,d][7]annulen-5-yl)chroman-2-one (*cis*-3i)**: colorless paste (230 mg, 52%); *Rf* 0.4 (hexanes-ethyl acetate, 10:1); IR (ATR) 1765 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.12 (s, 9H), 1.55 (d, 3H, *J* = 7.2 Hz), 2.29-2.37 (m, 1H), 2.70-2.77 (m, 1H), 2.83-2.96 (m, 2H), 4.04 (d, 1H, *J* = 5.9 Hz), 6.22 (brs, 1H), 6.68-6.77 (m, 2H), 6.89-6.93 (m, 1H), 6.95-7.00 (m, 1H), 7.09-7.34 (m, 5H), 7.79-7.83 (m, 1H), 7.93 (brs, 1H); ^{13}C NMR ($CDCl_3$) δ 1.8 (q), 14.7 (q), 34.8 (t), 36.2 (t), 38.7 (d), 57.0 (d), 87.7 (s), 116.7 (d), 122.9 (d), 125.2 (s), 125.6 (d), 125.7 (d), 127.8 (d), 128.3 (d), 128.6 (d), 129.6 (d), 129.7 (d), 130.0 (d), 131.4 (d), 132.5 (d), 140.8 (s), 141.1 (s), 152.5 (s), 170.7 (s); HRMS (ESI, ion trap) calcd for $C_{28}H_{31}O_3Si$ ($M + H^+$) 443.2042; found 443.2038.

(3*R,4*S**)-3-Methyl-4-(5-((trimethylsilyl)oxy)-5H-dibenzo[a,d][7]annulen-5-yl)chroman-2-one (*cis*-3j)**: white solid (378 mg, 86%); *Rf* 0.3 (hexanes-ethyl acetate, 10:1); mp 201-203 ºC; IR (ATR) 1767 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.37 (s, 9H), 0.44 (d, 3H, *J* = 7.5 Hz), 2.69-2.76 (m, 1H), 4.01 (d, 1H, *J* = 5.7 Hz), 5.73-5.76 (m, 1H), 6.47-6.50 (m, 1H), 6.92-6.95 (m, 1H), 7.02-7.06 (m, 1H), 7.08-7.10 (m, 2H), 7.11 (s, 2H), 7.22-7.27 (m, 1H), 7.34-7.43 (m, 3H), 7.44-7.48 (m, 1H), 7.86-7.89 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 3.4 (q), 12.3 (q), 37.3 (d), 43.0 (d), 88.1 (s), 116.0 (d), 121.9 (d),

125.8 (s), 126.5 (d), 126.7 (d), 127.0 (d), 127.27 (d), 127.34 (d), 127.6 (d), 128.4 (d), 128.8 (d), 129.7 (d), 130.2 (d), 132.2 (d), 132.3 (d), 132.6 (s), 133.3 (s), 140.5 (s), 141.7 (s), 152.3 (s), 171.9 (s). Anal. Calcd for $C_{28}H_{28}O_3Si$: C, 76.33; H, 6.41. Found: C, 76.41; H, 6.42.

4-(Diphenyl((trimethylsilyl)oxy)methyl)-4-methylchroman-2-one (3k): white solid (345 mg, 83%); *Rf* 0.3 (hexanes-ethyl acetate, 10:1); mp 173-175 ºC; IR (ATR) 1761, 1749 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.26 (s, 9H), 1.52 (s, 3H), 2.42 (d, 1H, *J* = 16.2 Hz), 3.10 (d, 1H, *J* = 16.2 Hz), 6.63-6.69 (m, 1H), 6.83-6.88 (m, 1H), 7.02-7.05 (m, 1H), 7.10-7.18 (m, 4H), 7.20-7.25 (m, 2H), 7.34-7.42 (m, 3H), 7.64-7.69 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 1.3 (q), 24.0 (q), 40.2 (t), 48.2 (s), 88.4 (s), 116.4 (d), 122.5 (d), 126.5 (d), 127.2 (d), 127.4 (d), 127.6 (d), 128.28 (s), 128.31 (d), 129.4 (d), 129.7 (d), 130.1 (d), 141.2 (s), 141.5 (s), 152.2 (s), 168.1 (s). Anal. Calcd for $C_{26}H_{28}O_3Si$: C, 74.96; H, 6.77. Found: C, 74.97; H, 6.75.

4-(Bis(4-fluorophenyl)((trimethylsilyl)oxy)methyl)-4-methylchroman-2-one (3l): white solid (280 mg, 62%); *Rf* 0.3 (hexanes-ethyl acetate, 10:1); mp 139-141 ºC; IR (ATR) 1757 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.25 (q, 9H), 1.47 (s, 3H), 2.42 (d, 1H, *J* = 16.0 Hz), 2.98 (d, 1H, *J* = 16.0 Hz), 6.67-6.72 (m, 1H), 6.81-6.87 (m, 2H), 6.89-6.94 (m, 1H), 7.03-7.15 (m, 5H), 7.24-7.29 (m, 1H), 7.60-7.67 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 1.2 (q), 23.8 (q), 40.1 (t), 48.3 (s), 87.7 (s), 113.4 (d, J_{CCF} = 21.6 Hz), 114.2 (d, J_{CCF} = 20.4 Hz), 116.6 (d), 122.7 (d), 127.9 (s), 128.7 (d), 129.3 (d), 131.5 (d, J_{CCCF} = 8.4 Hz), 131.8 (d, J_{CCCF} = 7.2 Hz), 136.9 (s, J_{CCCCF} = 3.6 Hz), 137.2 (s, J_{CCCCF} = 3.3 Hz), 152.2 (s), 161.9 (s, J_{CF} = 248.3 Hz), 162.0 (s, J_{CF} = 249.5 Hz), 167.9 (s). Anal. Calcd for $C_{26}H_{26}F_2O_3Si$: C, 69.00; H, 5.79. Found: C, 69.04; H, 5.80.

4-(Bis(4-methoxyphenyl)((trimethylsilyl)oxy)methyl)chroman-2-one (3m): colorless paste as a mixture with **2g** containing 129 mg of **3m** (28%). Although **3m** could not be purified, **6m** and **8m** were isolated after desilylation with 1 M HCl aq/dioxane and 1 M HCl/MeOH described below; *Rf* 0.6 (hexanes-ethyl acetate, 5:1); ^1H NMR ($CDCl_3$) δ −0.17 (s, 9H), 2.73 (dd, 1H, *J* = 8.0, 17.2 Hz), 3.16 (d, 1 H, *J* = 17.2 Hz), 3.812 (s, 3 H), 3.814 (s, 3H), 4.01 (d, 1 H, *J* = 8.0 Hz), 6.74-6.81 (m, 5 H), 6.92-6.96 (m, 1 H), 6.99-7.05 (m, 3H), 7.16-7.21 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 1.6 (q), 31.0 (t),

45.7 (d), 55.0 (q), 112.50 (d), 112.54 (d), 116.3 (d), 121.2 (s), 122.8 (d), 128.4 (d), 129.9 (d), 130.1 (d), 134.4 (d), 132.8 (s), 133.3 (s), 152.5 (s), 158.96 (s), 159.04 (s), 167.5 (s); HRMS (ESI, ion trap) calcd for $C_{27}H_{31}O_5Si$ ($M + H^+$) 463.1941; found 463.1939.

4-(Diphenyl((trimethylsilyl)oxy)methyl)-1-methyl-3,4-dihydroquinolin-2(1H)-one (3n): colorless paste (187 mg, 45%); *Rf* 0.6 (hexanes-ethyl acetate, 2:1); IR (ATR) 1672 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.24 (s, 9H), 2.54 (s, 3H), 2.78 (dd, 1H, *J* = 8.7, 17.7 Hz), 3.06 (d, 1H, *J* = 17.7 Hz), 4.06 (d, 1H, *J* = 8.7 Hz), 6.60-6.62 (m, 1H), 6.95-6.98 (m, 1H), 7.09-7.22 (m, 6H), 7.30-7.37 (6H); ^{13}C NMR ($CDCl_3$) δ 1.4 (q), 28.6 (q), 33.0 (t), 44.7 (d), 83.1 (s), 113.6 (d), 121.2 (d), 123.5 (s), 126.3 (d), 127.2 (d), 127.6 (d), 127.7 (d), 128.7 (d), 129.2 (d), 130.2 (d), 141.0 (s), 141.05 (s), 141.10 (s), 167.9 (s); HRMS (ESI, ion trap) calcd for $C_{26}H_{30}NO_2Si$ ($M + H^+$) 416.2046; found 416.2043.

4-(Trimethylsilyl)chroman-2-one (5): colorless paste (132 mg, 60%); *Rf* 0.35 (hexanes-ethyl acetate, 10:1); IR (ATR) 1761 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.04 (s, 9H), 2.46 (dd, 1H, *J* = 2.6, 7.5 Hz), 2.86 (dd, 1H, *J* = 2.6, 16.2 Hz), 2.91 (dd, 1H, *J* = 7.5, 16.2 Hz), 7.02-7.09 (m, 3H), 7.15-7.19 (m, 1H); ^{13}C NMR ($CDCl_3$) δ −3.4 (q), 26.2 (d), 30.3 (t), 117.0 (d), 124.1 (d), 125.7 (s), 126.5 (d), 127.4 (d), 150.9 (s), 168.9 (s); HRMS (ESI) calcd for $C_{12}H_{17}O_2Si$ ($M + H^+$) 221.0998; found 221.0997.

Typical Procedure of Desilylation of 3a-l with 1 M HCl aq and dioxane. To a solution of **3a** (101 mg, 0.25 mmol) in dioxane (5 mL) was added 1 M HCl aq (5 mL) at 25 ºC, and then the solution was stirred at this temperature for 6 h. The mixture was neutralized with sat. $NaHCO_3$ aq and extracted with ethyl acetate (10 mL X 3). After removal of the solvent *in vacuo*, the residue was purified by column chromatography on silica gel (hexanes-EtOAc, 3:1) to give **6a** (70 mg) in 85% yield.

Typical Procedure of Desilylation of 3a-l with TBAF in THF. To a solution of **3a** (101 mg, 0.25 mmol) in THF (5 mL) was added 1 M TBAF in THF (0.25 mL, 0.25 mmol) at 25 ˚C and the mixture was stirred for 15 min. After addition of AcOH (15 mg, 0.25 mmol), the solvent was removed *in vacuo*. The residue was purified by column chromatography on silica gel

(hexanes-EtOAc, 3:1) to give **6a** (78 mg) in 95% yield.

4-(2-Hydroxyphenyl)-5,5-diphenyldihydrofuran-2(3H)-one (6a): white solid (70 mg, 85%); *Rf* 0.4 (hexanes-ethyl acetate, 2:1); mp 176-178 ºC; IR (ATR) 3348, 1746 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.77 (dd, 1H, *J* = 2.0, 17.5 Hz), 2.98 (dd, 1H, *J* = 8.7, 17.5 Hz), 5.00 (brs, 1H), 5.02 (dd, 1H, *J* = 2.0, 8.7 Hz), 6.51-6.55 (m, 1H), 6.71-6.76 (m, 1H), 6.92-7.04 (m, 5H), 7.17-7.22 (m, 2H), 7.30-7.35 (m, 1H), 7.38-7.44 (m, 2H), 7.71-7.76 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 37.0 (t), 43.6 (d), 94.0 (s), 115.3 (d), 120.4 (d), 125.77 (d), 125.84 (d), 126.1 (s), 126.8 (d), 127.2 (d), 128.0 (d), 128.3 (d), 128.6 (d), 128.8 (d), 140.3 (s), 143.5 (s), 153.3 (s), 177.9 (s). Anal. Calcd for $C_{22}H_{18}O_3$: C, 79.98; H, 5.49. Found: C, 79.93; H, 5.50.

5,5-Bis(4-fluorophenyl)-4-(2-hydroxyphenyl)dihydrofuran-2(3H)-one (6b): colorless paste (80 mg, 87%); *Rf* 0.45 (hexanes-ethyl acetate, 2:1); IR (ATR) 3341, 1749 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.82 (dd, 1H, *J* = 2.2, 17.9 Hz), 2.98 (dd, 1H, *J* = 8.5, 17.9 Hz), 4.95 (dd, 1H, *J* = 2.2, 8.5 Hz), 5.81 (brs, 1H), 6.56-6.60 (m, 1H), 6.65-6.71 (m, 2H), 6.72-6.77 (m, 1H), 6.88-6.93 (m, 1H), 6.95-7.00 (m, 1H), 7.06-7.13 (m, 4H), 7.66-7.71 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 36.7 (t), 43.8 (d), 93.3 (s), 114.0 (d, J_{CCF} = 21.6 Hz), 115.3 (d), 115.6 (d, J_{CCF} = 21.6 Hz), 120.5 (d), 125.5 (s), 127.6 (d, J_{CCCF} = 8.4 Hz), 127.8 (d, J_{CCCF} = 8.4 Hz), 128.56 (d), 128.62 (d), 135.9 (s, J_{CCCCF} = 3.0 Hz), 139.0 (s, J_{CCCCF} = 3.0 Hz), 153.3 (s), 161.5 (s, J_{CF} = 247.1 Hz), 162.3 (s, J_{CF} = 247.7 Hz), 177.6 (s); HRMS (ESI, ion trap) calcd for $C_{22}H_{17}F_2O_3$ ($M + H^+$) 367.1146; found 367.1144.

3'-(2-Hydroxyphenyl)-3',4',10,11-tetrahydro-5'H-spiro[dibenzo[a,d][7]annulene-5,2'-furan]-5'-one (6c): white solid (82 mg, 92%); *Rf* 0.45 (hexanes-ethyl acetate, 2:1); mp 211-213 ºC; IR (ATR) 3310, 1744 cm^{-1}; ^1H NMR ($CDCl_3$, 60 °C) δ 2.57 (d, 1H, *J* = 17.2 Hz),), 2.64-2.74 (m, 1H), 2.90-3.03 (m, 2H), 3.32-3.43 (m, 1H), 3.77-3.87 (m, 1H), 4.70-4.80 (m, 1H), 6.10 (brs, 1H), 6.54-6.66 (m, 2H), 6.75-6.83 (m, 1H), 6.74-7.02 (m, 4H), 7.09-7.23 (m, 3H), 7.53-7.59 (m, 1H), 7.68-7.76 (m, 1H); ^{13}C NMR ($CDCl_3$, 60 °C) δ 32.3 (t), 32.5 (t), 36.9 (t), 47.2 (d), 93.1 (s), 115.7 (d), 120.4 (d), 123.9 (d), 125.6 (d), 125.8 (d), 126.3 (d), 126.4 (s), 127.6 (d), 128.2 (d), 128.3 (d),

129.1 (d), 129.9 (d), 131.7 (d), 136.7 (s), 137.4 (s), 138.0 (s), 141.1 (s), 153.0 (s), 178.2 (s). Anal. Calcd for $C_{24}H_{20}O_3$: C, 80.88; H, 5.66. Found: C, 80.80; H, 5.69.

3'-(2-Hydroxyphenyl)-3',4'-dihydro-5'H-spiro[dibenzo[a,d][7]annulene-5,2'-furan]-5'-one (6d): white solid (60 mg, 68%); *Rf* 0.45 (hexanes-ethyl acetate, 2:1); mp 244-245 ºC; IR (ATR) 3385, 1757 cm^{-1}; ^1H NMR ($CDCl_3$, 60 °C) δ 2.55 (d, 1H, *J* = 17.6 Hz), 2.76 (dd, 1H, *J* = 9.9, 17.6 Hz), 4.06-4.18 (m, 1H), 6.08 (brs, 1H), 6.47-6.55 (m, 1H), 6.57-6.66 (m, 1H), 6.77-6.86 (m, 1H), 6.86-6.93 (m, 1H), 5.95 (brs, 1H), 6.46-6.60 (m, 2H), 6.73-6.87 (m, 2H), 6.89-7.11 (m, 4H), 7.16-7.24 (m, 1H), 7.27-7.33 (m, 1H), 7.34-7.43 (m, 2H), 7.74-7.80 (m, 1H), 7.89-7.94 (m, 1H); ^{13}C NMR ($CDCl_3$, 60 °C) δ 35.3 (t), 48.7 (d), 91.5 (s), 115.8 (d), 119.7 (d), 123.3 (d), 124.2 (d), 126.7 (d), 127.0 (s), 127.4 (d), 128.2 (d), 128.3 (d), 128.4 (d), 128.8 (d), 129.6 (d), 130.0 (d), 132.1 (s), 132.2 (s), 133.9 (d), 137.0 (s), 141.2 (s), 153.4 (s), 178.1 (s). Anal. Calcd for $C_{24}H_{18}O_3$: C, 81.34; H, 5.12. Found: C, 81.27; H, 5.15.

3'-(2-Hydroxyphenyl)-3',4'-dihydro-5'H-spiro[fluorene-9,2'-furan]-5'-one (6e): white solid (68 mg, 83%); *Rf* 0.4 (hexanes-ethyl acetate, 2:1); mp 268-270 ºC; IR (ATR) 3420, 1751 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.44 (d, 2H, *J* = 8.6 Hz), 4.52 (t, 1H, *J* = 8.6 Hz), 6.57-6.69 (m, 2H), 6.83-6.89 (m, 1H), 6.91-6,98 (m, 1H), 7.00-7.06 (m, 1H), 7.06-7.11 (m, 1H), 7.23-7.30 (m, 1H), 7.33-7.38 (m, 1H), 7.38-7.45 (m, 1H), 7.49-7.55 (m, 1H), 7.56-7.61 (m, 1H), 7.62-7.68 (m, 1H), 8.93 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 34.7 (t), 43.4 (d), 93.6 (s), 115.0 (d), 118.4 (d), 119.6 (d), 119.7 (d), 123.1 (s), 123.5 (d), 125.4 (d), 126.9 (d), 127.8 (d), 128.0 (d), 128.2 (d), 129.3 (d), 129.5 (d), 139.2 (s), 139.9 (s), 141.9 (s), 145.5 (s), 155.3 (s), 176.7 (s). Anal. Calcd for $C_{22}H_{16}O_3$: C, 80.47; H, 4.91. Found: C, 80.44; H, 4.90.

3-(2-Hydroxyphenyl)-3,4-dihydro-5H-spiro[furan-2,9'-xanthen]-5-one (6f): white solid (15 mg, 18%); *Rf* 0.45 (hexanes-ethyl acetate, 2:1); mp 229-231 ºC; IR (ATR) 3310, 1748 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.06 (dd, 1H, *J* = 9.2, 17.8 Hz), 3.20 (dd, 1H, *J* = 9.2, 17.8 Hz), 4.20 (t, 1H, *J* = 9.2 Hz), 4.37 (brs, 1H), 6.42-6.45 (m, 1H), 6.48-6.51 (m, 1H), 6.56-6.60 (m, 1H), 6.91-6.99 (m, 2H), 7.02-7.07 (m, 1H), 7.11-7.15 (m, 1H), 7.19-7.24 (m, 1H), 7.25-7.29 (m, 1H), 7.32-7.40 (m, 2H),

7.64-7.67 (m, 1H); ^{13}C NMR ($CDCl_3$, DMSO-d_6) δ 33.3 (t), 50.1 (d), 83.2 (s), 114.6 (d), 115.6 (d), 115.9 (d), 118.2 (d), 120.6 (s), 121.1 (s), 122.3 (d), 123.2 (d), 123.8 (d), 124.9 (d), 125.0 (s), 127.8 (d), 127.9 (d), 128.6 (d), 128.7 (d), 150.0 (s), 150.3 (s), 155.0 (s), 176.6 (s). Anal. Calcd for $C_{22}H_{16}O_4$: C, 76.73; H, 4.68. Found: C, 76.68; H, 4.66.

(3*R,4*S**)-4-(2-Hydroxyphenyl)-3-methyl-5,5-diphenyldihydrofuran-2(3H)-one (*trans*-6g)**: white solid (79 mg, 92%); *Rf* 0.55 (hexanes-ethyl acetate, 2:1); mp 167-169 ºC; IR (ATR) 3537, 3401, 1740 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.15 (d, 3H, *J* = 7.3 Hz), 2.91-2.98 (m, 1H), 4.66 (d, 1H, *J* = 10.7 Hz), 5.13 (brs, 1H), 6.09-6.17 (m, 1H), 6.57-6.62 (m, 1H), 6.71-6.76 (m, 1H), 7.00-7.07 (m, 3H), 7.13-7.22 (m, 3H), 7.25-7.37 (m, 3H), 7.65-7.70 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 13.5 (q), 42.9 (d), 50.0 (d), 92.2 (d), 115.6 (d), 119.8 (d), 122.9 (s), 126.85 (d), 126.91 (d), 127.5 (d), 127.9 (d), 128.2 (d), 128.4 (d), 129.8 (d), 140.1 (s), 143.7 (s), 154.3 (s), 179.7 (s). Anal. Calcd for $C_{23}H_{20}O_3$: C, 80.21; H, 5.85. Found: C, 80.23; H, 5.88.

(3*R,4*S**)-5,5-Bis(4-fluorophenyl)-4-(2-hydroxyphenyl)-3-methyldihydrofuran-2(3H)-one (*trans*-6h)**: colorless paste (93 mg, 98%); *Rf* 0.55 (hexanes-ethyl acetate, 2:1); IR (ATR) 3345, 1749 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.16 (d, 3H, *J* = 7.5 Hz), 2.90-2.99 (m, 1H), 4.66 (d, 1H, *J* = 10.3 Hz), 5.83 (brs, 1H), 6.08-6.18 (m, 1H), 6.59-6.65 (m, 1H), 6.75-6.81 (m, 1H), 6.81-6.88 (m, 2H), 6.90-6.97 (m, 2H), 6.97-7.09 (m, 3H), 7.62-7.68 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 13.5 (q), 42.5 (d), 50.1 (d), 91.3 (s), 114.5 (d, J_{CCF} = 21.6 Hz), 115.1 (d, J_{CCF} = 21.6 Hz), 115.7 (d), 120.1 (d), 122.4 (s), 128.7 (d, J_{CCCF} = 9.0 Hz), 128.9 (d, J_{CCCF} = 7.8 Hz), 129.8 (d), 135.9 (s), 139.4 (s), 154.3 (s), 162.1 (s, J_{CF} = 248.0 Hz), 162.3 (s, J_{CF} = 247.7 Hz), 179.1 (s); HRMS (ESI, ion trap) calcd for $C_{23}H_{19}F_2O_3$ ($M + H^+$) 381.1302; found 381.1299.

(3'*R,4'*S**)-3'-(2-Hydroxyphenyl)-4'-methyl-3',4',10,11-tetrahydro-5'H-spiro[dibenzo[a,d][7]annulene-5,2'-furan]-5'-one (*trans*-6i)**: colorless paste (92 mg, 99%); *Rf* 0.55 (hexanes-ethyl acetate, 2:1); IR (ATR) 3331, 1740, 1705 cm^{-1}; ^{1}H NMR ($CDCl_3$, 60 °C) δ 1.11 (d, 3H, *J* = 7.5 Hz), 2.48-2.62 (m, 1H), 2.79-2.94 (m, 3H), 3.45-3.61 (m, 1H), 4.27-4.52 (m, 1H), 5.68 (brs, 1H),

6.54-6.66 (m, 3H), 6.78-6.83 (m, 1H), 6.91-6.95 (m, 1H), 7.00-7.13 (m, 3H), 7.15-7.24 (m, 2H), 7.67-7.77 (m, 2H); ^{13}C NMR ($CDCl_3$, 60 °C) δ 16.3 (q), 32.8 (t), 43.9 (d), 54.2 (d), 91.9 (s), 115.6 (d), 120.4 (d), 125.6 (d), 125.7 (d), 125.9 (d), 126.2 (s), 126.5 (d), 127.9 (d), 128.0 (d), 128.3 (d), 129.2 (s), 130.1 (d), 131.2 (d), 137.4 (s), 138.0 (s), 142.9 (s), 153.5 (s), 180.6 (s); HRMS (ESI, ion trap) calcd for $C_{25}H_{23}O_3$ ($M + H^+$) 371.1647; found 371.1645.

(3'*R,4'*S**)-3'-(2-Hydroxyphenyl)-4'-methyl-3',4'-dihydro-5'H-spiro[dibenzo[a,d][7]annulene-5,2'-furan]-5'-one (*trans*-6j)**: white solid (83 mg, 90%); *Rf* 0.2 (hexanes-ethyl acetate, 5:1); mp 243-245 ºC; IR (ATR) 3265, 1748, 1730 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.98 (d, 3H, *J* = 7.7 Hz), 2.87 (dq, 1H, *J* = 1.6, 7.7 Hz), 3.59 (d, 1H, *J* = 1.6 Hz), 5.94 (brs, 1H), 6.41-6.45 (m, 1H), 6.62-6.66 (m, 1H), 6.71 (d, 1H, *J* = 11.6 Hz), 6.86-6.93 (m, 2H), 7.00-7.06 (m, 1H), 7.06-7.12 (m, 2H), 7.20-7.25 (m, 1H), 7.29-7.33 (m, 1H), 7.38-7.42 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 18.3 (q), 42.5 (d), 57.4 (d), 90.2 (s), 115.5 (d), 118.8 (d), 123.2 (d), 123.9 (d), 126.5 (d), 127.2 (d), 127.4 (s), 127.8 (d), 128.0 (d), 128.6 (d), 128.8 (d), 129.3 (d), 129.7 (d), 131.7 (d), 131.9 (s), 134.8 (d), 137.1 (s), 142.4 (s), 153.4 (s), 182.6 (s). Anal. Calcd for $C_{25}H_{20}O_3$: C, 81.50; H, 5.47. Found: C, 81.53; H, 5.46.

4-(2-Hydroxyphenyl)-4-methyl-5,5-diphenyldihydrofuran-2(3H)-one (6k): white solid (70 mg, 81%); *Rf* 0.5 (hexanes-ethyl acetate, 2:1); mp 222-223 ºC; IR (ATR) 3352, 1736 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.47 (s, 3H), 2.72 (d, 1H, *J* = 17.8 Hz), 3.55 (d, 1H, *J* = 17.8 Hz), 5.69 (brs, 1H), 6.54-6.58 (m, 1H), 6.86-6.92 (m, 1H), 7.01-7.10 (m, 4H), 7.18-7.39 (m, 6H), 7.42-7.46 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 28.5 (q), 44.4 (t), 50.5 (s), 94.7 (s), 116.9 (d), 119.7 (d), 126.6 (d), 126.7 (d), 126.8 (d), 126.9 (d), 127.5 (d), 128.1 (d), 128.8 (d), 128.9 (d), 129.5 (s), 140.4 (s), 142.0 (s), 154.6 (s), 178.5 (s). Anal. Calcd for $C_{23}H_{20}O_3$: C, 80.21; H, 5.85. Found: C, 80.18; H, 5.86.

5,5-Bis(4-fluorophenyl)-4-(2-hydroxyphenyl)-4-methyldihydrofuran-2(3H)-one (6l): colorless paste (69 mg, 73%); *Rf* 0.55 (hexanes-ethyl acetate, 2:1); IR (ATR) 3302, 1748 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.43 (s, 3H), 2.72 (d, 1H, *J* = 17.8 Hz), 3.46 (d, 1H, *J* = 17.8 Hz), 6.59-6.73 (m, 4H), 6.83-6.89 (m, 1H), 6.97-7.16 (m, 5H), 7.29-7.38 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 28.4 (q), 44.3 (t),

50.5 (s), 94.0 (s), 113.6 (d, J_{CCF} = 21.0 Hz), 115.0 (d, J_{CCF} = 21.6 Hz), 116.8 (d), 119.9 (d), 128.4 (d, J_{CCCF} = 7.8 Hz), 128.60 (d), 128.61 (d, J_{CCCF} = 8.1 Hz), 129.0 (s), 129.2 (d), 136.3 (s, J_{CCCCF} = 3.3 Hz), 137.8 (s, J_{CCCCF} = 2.7 Hz), 154.5 (s), 161.5 (s, J_{CF} = 247.1 Hz), 162.0 (s, J_{CF} = 248.3 Hz), 178.1 (s); HRMS (ESI, ion trap) calcd for $C_{23}H_{19}F_2O_3$ ($M + H^+$) 381.1302; found 381.1300.

5,5-Bis(4-methoxyphenyl)-4-(2-hydroxyphenyl)dihydrofuran-2(3H)-one (6m): colorless paste (81 mg, 83%); *Rf* 0.3 (hexanes-ethyl acetate, 2:1); IR (ATR) 3348, 1746 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.79 (dd, 1H, *J* = 2.3, 17.6 Hz), 2.98 (dd, 1H, *J* = 8.6, 17.6 Hz), 3.64 (s, 3H), 3.81 (s, 3H), 4.94 (dd, 1H, *J* = 2.3, 8.6 Hz), 5.47 (brs, 1H), 6.51-6.57 (m, 3H), 6.72-6.76 (m, 1H), 6.89-6.93 (m, 3H), 6.94-6.99 (m, 1H), 7.00-7.05 (m, 2H), 7.59-7.63 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 37.0 (t), 43.6 (d), 55.0 (q), 55.2 (q), 93.8 (s), 112.4 (d), 113.8 (d), 115.2 (d), 120.5 (d), 126.1 (s), 127.2 (d), 127.3 (d), 128.3 (d), 128.7 (d), 132.9 (s), 135.7 (s), 153.2 (s), 158.0 (s), 159.0 (s), 177.8 (s); HRMS (ESI) calcd for $C_{24}H_{23}O_5$ ($M + H^+$) 391.1545; found 391.1542.

2-(2,2-Diphenyl-2,3-dihydrobenzofuran-3-yl)acetic acid (7a): white solid (71 mg, 83%); *Rf* 0.5 (hexanes-ethyl acetate, 1:2); mp 213-214 ºC; IR (ATR) 3200-2400 (br), 1734, 1693 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.24 (dd, 1H, *J* = 8.6, 16.8 Hz), 2.36 (dd, 1H, *J* = 6.2, 16.8 Hz), 4.62 (dd, 1H, *J* = 6.2, 8.6 Hz), 6.82-6.88 (m, 1H), 6.92-6.96 (m, 1H), 7.13-7.41 (m, 10H), 7.64-7.69 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 38.7 (t), 46.2 (d), 94.8 (s), 110.3 (d), 121.2 (d), 124.6 (d), 126.7 (d), 126.8 (d), 127.6 (d), 127.8 (d), 128.1 (d), 128.2 (d), 129.0 (d), 130.3 (s), 141.0 (s), 144.1 (s), 157.5 (s), 177.9 (s). Anal. Calcd for $C_{22}H_{18}O_3$: C, 79.98; H, 5.49. Found: C, 79.87; H, 5.54.

2-(2,2-Bis(4-fluorophenyl)-2,3-dihydrobenzofuran-3-yl)acetic acid (7b): colorless paste (56 mg, 61%); *Rf* 0.1 (hexanes-ethyl acetate, 2:1); IR (ATR) 3200-2400 (br), 1705 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.27 (dd, 1H, *J* = 7.9, 16.9 Hz), 2.33 (dd, 1H, *J* = 6.9, 16.9 Hz), 4.55 (t, 1H, *J* = 7.3 Hz), 6.86-6.95 (m, 2H), 6.96-7.04 (m, 4H), 7.15-7.23 (m, 2H), 7.30-7.36 (m, 2H), 7.59-7.65 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 38.6 (t), 46.4 (d), 94.0 (s), 110.3 (d), 115.0 (d, J_{CCF} = 21.6 Hz), 115.1 (d, J_{CCF} = 21.3 Hz), 121.5 (d), 124.6 (d), 128.5 (d, J_{CCCF} = 8.4 Hz), 128.8 (d, J_{CCCF} = 7.8 Hz), 129.2 (d), 129.9 (s), 136.5

(s, J_{CCCCF} = 3.3 Hz), 139.7 (s, J_{CCCCF} = 3.0 Hz), 157.1 (s), 162.1 (s, J_{CF} = 248.3 Hz), 162.3 (s, J_{CF} = 247.1 Hz), 177.7 (s); HRMS (ESI, ion trap) calcd for $C_{22}H_{17}F_2O_3$ (M + H^+) 367.1146; found 367.1143.

2-(10',11'-Dihydro-3H-spiro[benzofuran-2,5'-dibenzo[a,d][7]annulen]-3-yl)acetic acid (7c): white solid (61 mg, 69%); *Rf* 0.15 (hexanes-ethyl acetate, 2:1); mp 261-263 ºC; IR (ATR) 3200-2400 (br), 1694 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.13 (dd, 1H, *J* = 11.6, 16.2 Hz), 2.43 (dd, 1H, *J* = 3.4, 16.2 Hz), 2.96-3.09 (m, 2H), 3.35-3.43 (m, 1H), 3.62-3.67 (m, 1H), 4.28 (dd, 1H, *J* = 3.4, 11.6 Hz), 6.81-6.87 (m, 1H), 7.01-7.07 (m, 1H), 7.07-7.10 (m, 1H), 7.11-7.18 (m, 4H), 7.19-7.28 (m, 3H), 7.53-7.57 (m, 1H), 7.91-7.95 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 32.3 (t), 33.8 (t), 39.7 (t), 50.7 (d), 94.1 (s), 109.8 (d), 121.3 (d), 125.2 (d), 125.3 (d), 126.1 (d), 126.4 (d), 127.0 (d), 127.8 (d), 128.0 (d), 129.2 (d), 129.6 (s), 130.3 (d), 131.2 (d), 137.1 (s), 137.6 (s), 138.3 (s), 142.8 (s), 157.3 (s), 177.5 (s). Anal. Calcd for $C_{24}H_{20}O_3$: C, 80.88; H, 5.66. Found: C, 80.78; H, 5.71.

2-(3H-Spiro[benzofuran-2,5'-dibenzo[a,d][7]annulen]-3-yl)acetic acid (7d): white solid (65 mg, 73%); *Rf* 0.2 (hexanes-ethyl acetate, 2:1); mp 238-240 ºC; IR (ATR) 3200-2400 (br), 1699 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.87 (dd, 1H, *J* = 12.1, 16.0 Hz), 2.01-2.07 (m, 1H), 3.99 (dd, 1H, *J* = 3.4, 12.1 Hz), 6.76-6.81 (m, 1H), 7.01-7.09 (m, 2H), 7.15-7.28 (m, 5H), 7.31-7.37 (m, 2H), 7.37-7.42 (m, 1H), 7.43-7.49 (m, 1H), 7.65-7.69 (m, 1H), 9.04-9.09 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 38.8 (t), 44.1 (d), 92.7 (s), 110.1 (d), 121.4 (d), 124.1 (d), 124.9 (d), 125.6 (d), 126.8 (d), 127.2 (d), 128.6 (d), 128.8 (d), 128.9 (d), 129.0 (d), 129.1 (d), 129.4 (s), 130.9 (d), 132.3 (s), 132.4 (d), 137.7 (s), 141.2 (s), 157.2 (s), 178.0 (s). Anal. Calcd for $C_{24}H_{18}O_3$: C, 81.34; H, 5.12. Found: C, 81.25; H, 5.16.

2-(3H-Spiro[benzofuran-2,9'-fluoren]-3-yl)acetic acid (7e): colorless paste (62 mg, 75%); *Rf* 0.3 (hexanes-ethyl acetate, 2:1); IR (ATR) 3200-2400 (br), 1713 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.24 (dd, 1H, *J* = 5.0, 17.0 Hz), 2.60 (dd, 1H, *J* = 9.3, 17.0 Hz), 4.45 (dd, 1H, *J* = 5.0, 9.3 Hz), 6.89-6.92 (m, 1H), 6.96-7.01 (m, 1H), 7.10-7.17 (m, 2H), 7.22-7.33 (m, 3H), 7.34-7.41 (m, 2H), 7.54-7.58 (m, 1H), 7.59-7.64 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 35.5 (t), 46.3 (d), 96.2 (s), 110.3 (d), 119.9 (d), 120.3 (d),

121.0 (d), 124.0 (d), 124.4 (d), 127.7 (d), 128.4 (d), 129.0 (d), 129.91 (d), 129.94 (d), 130.0 (d), 140.2 (s), 140.3 (s), 142.8 (s), 145.5 (s), 159.5 (s), 177.5 (s); HRMS (ESI, ion trap) calcd for $C_{22}H_{17}O_3$ ($M + H^+$) 329.1178; found 329.1175.

2-(3H-Spiro[benzofuran-2,9'-xanthen]-3-yl)acetic acid (7f): white solid (70 mg, 81%); *Rf* 0.3 (hexanes-ethyl acetate, 2:1); mp 232-233 ºC; IR (ATR) 3200-2400 (br), 1701 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.27 (dd, 1H, *J* = 7.6, 17.2 Hz), 2.41 (dd, 1H, *J* = 7.6, 17.2 Hz), 4.10 (t, 1H, *J* = 7.6 Hz), 6.99-7.04 (m, 2H), 7.06-7.11 (m, 1H), 7.12-7.20 (m, 4H), 7.30-7.38 (m, 4H), 7.52-7.56 (m, 1H); ^{13}C NMR ($CDCl_3$, DMSO-d_6) δ 36.2 (t), 53.5 (d), 84.0 (s), 108.0 (d), 115.7 (d), 116.1 (d), 120.5 (s), 121.1 (d), 122.7 (d), 123.3 (d), 124.3 (d), 125.46 (d), 125.50 (s), 126.3 (d), 127.7 (s), 128.6 (d), 128.7 (d), 129.2 (d), 149.0 (s), 149.4 (s), 158.8 (s), 172.8 (s). Anal. Calcd for $C_{22}H_{16}O_4$: C, 76.73; H, 4.68. Found: C, 76.62; H, 4.63.

(*R)-2-((*R**)-2,2-Diphenyl-2,3-dihydrobenzofuran-3-yl)propanoic acid (*threo*-7g)**: colorless paste (36 mg, 42%); *Rf* 0.15 (hexanes-ethyl acetate, 2:1); IR (ATR) 3200-2400 (br), 1697 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.82 (d, 3H, *J* = 7.2 Hz), 2.64-2.71 (m, 1H), 4.67 (d, 1H, *J* = 5.4 Hz), 6.82-6.88 (m, 1H), 6.93-6.97 (m, 1H), 7.14-7.33 (m, 8H), 7.49-7.56 (m, 2H), 7.64-7.69 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 12.8 (q), 40.8 (d), 51.1 (d), 94.9 (s), 110.3 (d), 120.8 (d), 126.0 (d), 126.4 (d), 127.3 (d), 127.4 (d), 127.56 (d), 127.60 (s), 128.0 (d), 128.1 (d), 129.0 (d), 140.5 (s), 145.1 (s), 158.1 (s), 181.8 (s); HRMS (ESI, ion trap) calcd for $C_{23}H_{21}O_3$ ($M + H^+$) 345.1491; found 345.1488.

2-(3-Methyl-2,2-diphenyl-2,3-dihydrobenzofuran-3-yl)acetic acid (7k): white solid (84 mg, 98%); *Rf* 0.35 (hexanes-ethyl acetate, 2:1); mp 224-226 ºC; IR (ATR) 3200-2400 (br), 1701 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.67 (s, 3H), 2.38 (d, 1H, *J* = 14.0 Hz), 2.47 (d, 1H, *J* = 14.0 Hz), 6.87-6.91 (m, 1H), 6.99-7.02 (m, 1H), 7.12-7.19 (m, 4H), 7.22-7.26 (m, 1H), 7.28-7.34 (m, 3H), 7.36-7.40 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 21.3 (q), 45.0 (t), 51.2 (s), 98.3 (s), 109.8 (d), 121.0 (d), 124.0 (d), 126.8 (d), 127.4 (d), 127.6 (d), 127.67 (d), 127.74 (d), 128.1 (d), 129.0 (d), 133.8 (s), 140.6 (s), 140.9 (s), 157.6 (s), 177.2 (s). Anal. Calcd for $C_{23}H_{20}O_3$: C, 80.21; H, 5.85. Found: C, 80.13; H, 5.88.

2-(2,2-Bis(4-fluorophenyl)-3-methyl-2,3-dihydrobenzofuran-3-yl)acetic acid (7l): white solid (68 mg, 72%); *Rf* 0.25 (hexanes-ethyl acetate, 2:1); mp 200-202 ºC; IR (ATR) 3200-2400 (br), 1709, 1697 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.36 (d, 1H, *J* = 14.3 Hz), 2.40 (d, 1H, *J* = 14.3 Hz), 6.83-6.93 (m, 3H), 6.97-7.00 (m, 1H), 7.05-7.11 (m, 2H), 7.13-7.16 (m, 1H), 7.22-7.27 (m, 3H), 7.58-7.63 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 21.3 (q), 44.9 (t), 51.2 (s), 97.7 (s), 109.9 (d), 114.7 (d, J_{CCF} = 20.4 Hz), 115.1 (d, J_{CCF} = 21.6 Hz), 121.3 (d), 124.0 (d), 128.5 (d, J_{CCCF} = 7.2 Hz), 129.3 (d), 129.4 (d, J_{CCCF} = 7.2 Hz), 133.6 (s), 136.4 (s, J_{CCCCF} = 3.3 Hz), 136.7 (s, J_{CCCCF} = 3.6 Hz), 157.2 (s), 162.0 (s, J_{CF} = 248.6 Hz), 162.1 (s, J_{CF} = 248.6 Hz), 176.9 (s). Anal. Calcd for $C_{23}H_{18}F_2O_3$: C, 72.62; H, 4.77. Found: C, 72.55; H, 4.81.

4-(Hydroxydiphenylmethyl)-1-methyl-3,4-dihydroquinolin-2(1H)-one (9n): white solid (81 mg, 95%); *Rf* 0.3 (hexanes-ethyl acetate, 2:1); mp 180-182 ºC; IR (ATR) 3422, 1636 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.35 (brs, 1H), 2.81 (dd, 1H, *J* = 7.5, 16.6 Hz), 2.97 (dd, 1H, *J* = 2.3, 16.6 Hz), 3.16 (s, 3H), 4.00 (dd, 1H, *J* = 2.3, 7.5 Hz), 6.58-6.62 (m, 1H), 6.71-6.76 (m, 1H), 6.89-6.94 (m, 1H), 7.17-7.28 (m, 7H), 7.30-7.35 (m, 2H), 7.40-7.44 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 29.2 (q), 33.4 (t), 44.2 (d), 81.2 (s), 114.5 (d), 121.7 (d), 123.5 (s), 126.4 (d), 126.5 (d), 126.9 (d), 127.2 (d), 127.8 (d), 127.9 (d), 128.1 (d), 130.9 (d), 141.6 (s), 143.8 (s), 144.7 (s), 169.1 (s). Anal. Calcd for $C_{23}H_{21}NO_2$: C, 80.44; H, 6.16; N, 4.08. Found: C, 80.49; H, 6.18, N, 4.02.

Typical Procedure of Desilylation of 3a-l with 1 M HCl/MeOH. To a solution of **3a** (101 mg, 0.25 mmol) in MeOH (5 mL) was added TMSCl (0.64 mL, 0.5 mmol) at 25 ºC, and then the solution was stirred at this temperature for 12 h. After removal of the solvent *in vacuo*, the residue was purified by column chromatography on silica gel (hexanes-EtOAc, 10:1) to give **8a** (74 mg) in 86% yield.

Methyl 2-(2,2-diphenyl-2,3-dihydrobenzofuran-3-yl)acetate (8a): colorless paste (74 mg, 86%); *Rf* 0.6 (hexanes-ethyl acetate, 5:1); IR (ATR) 1732 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.21 (dd, 1H, *J* = 7.5, 16.3 Hz), 2.31 (dd, 1H, *J* = 7.5, 16.3 Hz), 3.51 (s, 3H), 4.66 (t, 1H, *J* = 7.5 Hz), 6.82-6.86 (m, 1H), 6.92-6.95 (m, 1H), 7.12-7.17 (m, 2H), 7.20-7.39 (m, 8H), 7.67-7.71 (m, 2H); ^{13}C NMR ($CDCl_3$)

δ 38.7 (t), 46.6 (d), 51.5 (q), 94.8 (s), 110.0 (d), 121.0 (d), 124.5 (d), 126.7 (d), 126.9 (d), 127.3 (d), 127.6 (d), 127.9 (d), 128.1 (d), 128.8 (d), 130.4 (s), 140.9 (s), 144.2 (s), 157.5 (s), 172.2 (s); HRMS (ESI, ion trap) calcd for $C_{23}H_{21}O_3$ ($M + H^+$) 345.1491; found 345.1489.

Methyl 2-(2,2-bis(4-fluorophenyl)-2,3-dihydrobenzofuran-3-yl)acetate (8b): colorless paste (83 mg, 87%); *Rf* 0.6 (hexanes-ethyl acetate, 5:1); IR (ATR) 1730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.24 (dd, 1H, *J* = 7.5, 16.6 Hz), 2.28 (dd, 1H, *J* = 7.5, 16.6 Hz), 3.51 (s, 3H), 4.60 (t, 1H, *J* = 7.5 Hz), 6.85-6.89 (m, 1H), 6.90-6.94 (m. 1H), 6.95-7.05 (m, 4H), 7.13-7.20 (m, 2H), 7.29-7.34 (m, 2H), 7.64-7.69 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 38.6 (t), 46.9 (d), 51.6 (q), 94.0 (s), 110.1 (d), 114.8 (d, J_{CCF} = 21.6 Hz), 115.0 (d, J_{CCF} = 21.3 Hz), 121.4 (d), 124.6 (d), 128.6 (d, J_{CCCF} = 8.4 Hz), 128.9 (d, J_{CCCF} = 8.4 Hz), 129.0 (d), 130.0 (s), 136.6 (s), 139.9 (s), 157.2 (s), 162.0 (s, J_{CF} = 247.1 Hz), 162.2 (s, J_{CF} = 247.4 Hz), 172.1 (s); HRMS (ESI, ion trap) calcd for $C_{23}H_{19}F_2O_3$ ($M + H^+$) 381.1302; found 381.1299.

Methyl 2-(10',11'-dihydro-3H-spiro[benzofuran-2,5'-dibenzo[a,d][7]annulen]-3-yl)acetate (8c): colorless paste (68 mg, 73%); *Rf* 0.6 (hexanes-ethyl acetate, 5:1); IR (ATR) 1734 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.10 (dd, 1H, *J* = 11.3, 15.9 Hz), 2.37 (dd, 1H, *J* = 3.9, 15.9 Hz), 2.95-3.08 (m, 2H), 3.36-3.43 (m, 1H), 3.60 (s, 3H), 3.66-3.75 (m, 1H), 4.30 (dd, 1H, *J* = 3.9, 11.3 Hz), 6.81-6.85 (m, 1H), 6.99-7.07 (m, 2H), 7.10-7.27 (m, 7H), 7.53-7.57 (m, 1H), 7.90-7.95 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 32.2 (t), 33.8 (t), 39.8 (t), 51.0 (d), 51.6 (q), 94.1 (s), 109.7 (d), 121.2 (d), 125.1 (d), 125.3 (d), 126.0 (d), 126.3 (d), 127.0 (d), 127.7 (d), 127.9 (d), 129.0 (d), 129.8 (s), 130.3 (d), 131.1 (d), 137.2 (s), 137.6 (s), 138.4 (s), 142.9 (s), 157.3 (s), 172.1 (s); HRMS (ESI, ion trap) calcd for $C_{25}H_{23}O_3$ ($M + H^+$) 371.1647; found 371.1645.

Methyl 2-(3H-spiro[benzofuran-2,5'-dibenzo[a,d][7]annulen]-3-yl)acetate (8d): colorless paste (87 mg, 95%); *Rf* 0.6 (hexanes-ethyl acetate, 5:1); IR (ATR) 1734 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.84 (dd, 1H, J = 11.4, 15.4 Hz), 1.99 (dd, 1H, J = 3.9, 15.4 Hz), 3.54 (s, 3H), 4.01 (dd, 1H, J = 3.9, 11.4 Hz), 6.76-6.81 (m, 1H), 6.94-6.99 (m, 1H), 7.03-7.09 (m, 1H), 7.14-7.26 (m, 5H), 7.29-7.40 (m,

3H), 7.42-7.47 (m, 1H), 7.65-7.69 (m, 1H), 8.04-8.08 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 38.9 (t), 44.5 (d), 51.4 (q), 92.7 (s), 110.0 (d), 121.3 (d), 124.1 (d), 124.9 (d), 125.6 (d), 126.7 (d), 127.1 (d), 128.5 (d), 128.7 (d), 128.9 (d), 129.1 (d), 129.7 (s), 131.0 (d), 132.3 (d), 132.4 (d), 137.8 (s), 141.3 (s), 157.2 (s), 172.0 (s); HRMS (ESI, ion trap) calcd for $C_{25}H_{21}O_3$ (M + H^+) 369.1491; found 369.1490.

Methyl 2-(3H-spiro[benzofuran-2,9'-fluoren]-3-yl)acetate (8e): colorless paste (77 mg, 90%); *Rf* 0.6 (hexanes-ethyl acetate, 5:1); IR (ATR) 1734 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.26 (dd, 1H, *J* = 5.8, 16.5 Hz), 2.62 (dd, 1H, *J* = 8.8, 16.5 Hz), 3.43 (s, 3H), 4.49 (dd, 1H, *J* = 5.8, 8.8 Hz), 6.89-6.92 (m, 1H), 6.95-7.00 (m, 1H), 7.11-7.16 (m, 2H), 7.20-7.26 (m, 2H), 7.28-7.32 (m, 1H), 7.34-7.42 (m, 2H), 7.54-7.58 (m, 1H), 7.60-7.64 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 35.6 (t), 46.5 (d), 51.5 (q), 96.2 (s), 110.2 (d), 119.8 (d), 120.2 (d), 120.9 (d), 123.9 (d), 124.2 (d), 124.4 (d), 127.5 (d), 128.3 (d), 128.8 (d), 129.76 (d), 129.80 (d), 130.1 (s), 140.1 (s), 140.2 (s), 142.7 (s), 145.8 (s), 159.4 (s), 171.6 (s); HRMS (ESI, ion trap) calcd for $C_{23}H_{19}O_3$ (M + H^+) 343.1334; found 343.1333.

Methyl 2-(3H-spiro[benzofuran-2,9'-xanthen]-3-yl)acetate (8f): colorless paste (75 mg, 84%); *Rf* 0.6 (hexanes-ethyl acetate, 5:1); IR (ATR) 1726 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.24 (dd, 1H, J = 7.5, 16.8 Hz), 2.41 (dd, 1H, J = 7.5, 16.8 Hz), 3.47 (s, 3H), 4.13 (t, 1H, J = 7.5 Hz), 6.96-7.01 (m, 2H), 7.06-7.10 (m, 2H), 7.12-7.16 (m, 1H), 7.17-7.21 (m, 2H), 7.28-7.37 (m, 4H), 7.51-7.54 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 36.9 (t), 51.0 (q), 54.0 (d), 84.4 (s), 108.8 (d), 116.3 (d), 116.5 (d), 120.7 (s), 121.5 (d), 123.2 (d), 123.8 (d), 124.5 (d), 125.7 (d), 126.1 (s), 126.9 (d), 127.7 (s), 129.17 (d), 129.20 (d), 129.7 (d), 149.3 (s), 150.2 (s), 159.4 (s), 171.4 (s); HRMS (ESI, ion trap) calcd for $C_{23}H_{19}O_4$ (M + H^+) 359.1283; found 359.1281.

Methyl (*R)-2-((*S**)-2,2-diphenyl-2,3-dihydrobenzofuran-3-yl)propanoate (*threo*-8g)**: colorless paste (86 mg, 96%); *Rf* 0.55 (hexanes-ethyl acetate, 5:1); IR (ATR) 1726 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.85 (d, 3H, *J* = 7.0 Hz), 2.57-2.64 (m, 1H), 3.46 (s, 3H), 4.61 (d, 1H, *J* = 6.9 Hz), 6.80-6.85 (m, 1H), 6.92-6.96 (m, 1H), 7.10-7.33 (m, 8H), 7.45-7.51 (m, 2H), 7.66-7.71 (m, 2H); ^{13}C NMR

($CDCl_3$) δ 13.8 (q), 40.9 (d), 51.5 (d), 51.7 (d), 95.1 (s), 110.2 (d), 120.6 (d), 126.2 (d), 126.4 (d), 127.2 (d), 127.4 (d), 127.78 (d), 127.81 (s), 128.0 (d), 128.8 (d), 140.4 (s), 145.1 (s), 158.1 (s), 176.0 (s); HRMS (ESI, ion trap) calcd for $C_{24}H_{23}O_3$ ($M + H^+$) 359.1647; found 359.1645.

Methyl (*R)-2-((*S**)-2,2-bis(4-fluorophenyl)-2,3-dihydrobenzofuran-3-yl)propanoate (*threo*-8h)**: white solid (91 mg, 92%); *Rf* 0.6 (hexanes-ethyl acetate, 5:1); mp 120-122 ºC; IR (ATR) 1719 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.92 (d, 3H, *J* = 7.3 Hz), 2.48-2.55 (m, 1H), 3.43 (s, 3H), 4.49 (d, 1H, *J* = 7.6 Hz), 6.83-6.88 (m, 1H), 6.91-7.02 (m, 5H), 7.12-7.19 (m, 2H), 7.37-7.44 (m, 2H), 7.62-7.67 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.5 (q), 41.0 (d), 51.8 (q), 51.9 (d), 94.5 (s). 110.3 (d), 114.6 (d, J_{CCF} = 21.6 Hz), 115.0 (d, J_{CCF} = 21.6 Hz), 120.9 (d), 126.5 (d), 127.6 (s), 128.3 (d, J_{CCCF} = 8.4 Hz), 129.0 (d), 129.6 (d, J_{CCCF} = 8.4 Hz), 136.0 (s, J_{CCCCF} = 3.3 Hz), 140.6 (s, J_{CCCCF} = 2.7 Hz), 162.0 (s, J_{CF} = 246.8 Hz), 162.1 (s, J_{CF} = 246.2 Hz), 176.1 (s); HRMS (ESI, ion trap) calcd for $C_{24}H_{21}F_2O_3$ ($M + H^+$) 395.1459; found 395.1456.

Methyl (*R)-2-((*S**)-10',11'-dihydro-3H-spiro[benzofuran-2,5'-dibenzo[a,d][7]annulen]-3-yl)propanoate (*threo*-8i)**: colorless paste (83 mg, 86%); *Rf* 0.6 (hexanes-ethyl acetate, 5:1); IR (ATR) 1732, 1724 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.55 (d, 3H, *J* = 6.9 Hz), 2.67-2.73 (m, 1H), 2.98-3.07 (m, 2H), 3.56-3.63 (m, 1H), 3.66 (s, 3H), 3.74-3.82 (m, 1H), 4.50 (d, 1H, *J* = 2.6 Hz), 6.83-6.88 (m, 1H), 6.92-7.02 (m, 2H), 7.06-7.28 (m, 7H), 7.45-7.50 (m, 1H), 7.98-8.03 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 11.3 (q), 32.0 (t), 33.0 (t), 40.8 (d), 51.9 (q), 54.7 (d), 94.2 (s), 109.4 (d), 121.1 (d), 125.3 (d), 125.8 (d), 125.9 (d), 126.2 (d), 126.5 (s), 126.8 (d), 127.4 (d), 128.0 (d), 129.0 (d), 130.7 (d), 131.1 (d), 137.0 (s), 137.3 (s), 138.1 (s), 142.9 (s), 158.2 (s), 175.4 (s); HRMS (ESI, ion trap) calcd for $C_{26}H_{25}O_3$ ($M + H^+$) 385.1804; found 385.1802.

Methyl (*R)-2-((*S**)-3H-spiro[benzofuran-2,5'-dibenzo[a,d][7]annulen]-3-yl)propanoate (*threo*-8j)**: colorless paste (50 mg, 52%); *Rf* 0.65 (hexanes-ethyl acetate, 5:1); IR (ATR) 1726 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.37 (d, 3H, J = 7.0 Hz), 2.28-2.33 (m, 1H), 3.66 (s, 3H), 4.17 (d, 1H, J = 2.3 Hz), 6.78-6.85 (m, 2H), 7.09-7.25 (m, 6H), 7.30-7.35 (m, 2H), 7.39-7.42 (m, 1H), 7.43-7.47 (m,

1H), 7.64-7.67 (m, 1H), 8.07-8.11 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 9.7 (q), 41.4 (d), 49.3 (d), 51.7 (q), 92.5 (s), 121.3 (d), 123.8 (d), 125.2 (d), 125.9 (d), 126.4 (s), 126.6 (d), 127.0 (d), 128.55 (d), 128.61 (d), 128.7 (d), 128.8 (d), 129.1 (d), 131.3 (d), 132.2 (s), 132.31 (d), 132.34 (s), 137.3 (s), 142.4 (s), 158.1 (s), 175.1 (s); HRMS (ESI, ion trap) calcd for $C_{26}H_{23}O_3$ ($M + H^+$) 383.1647; found 383.1645.

Methyl 2-(3-methyl-2,2-diphenyl-2,3-dihydrobenzofuran-3-yl)acetate (8k): colorless paste (76 mg, 85%); *Rf* 0.45 (hexanes-ethyl acetate, 10:1); IR (ATR) 1732 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.67 (s, 3H), 2.38 (d, 1H, J = 13.8 Hz), 2.44 (d, 1H, J = 13.8 Hz), 3.40 (s, 3H), 6.88-6.93 (m, 1H), 7.00-7.03 (m, 1H), 7.06-7.10 (m, 1H), 7.14-7.19 (m, 3H), 7.22-7.26 (m, 1H), 7.28-7.34 (m, 3H), 7.35-7.41 (m, 2H), 7.65-7.70 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.4 (q), 45.1 (t), 51.2 (d), 51.4 (q), 98.2 (s), 109.7 (d), 120.8 (d), 123.8 (d), 126.8 (d), 127.4 (d), 127.5 (d), 127.6 (d), 127.7 (d), 128.0 (d), 128.9 (d), 134.1 (s), 140.70 (s), 141.1 (s), 157.6 (s), 171.6 (s); HRMS (ESI, ion trap) calcd for $C_{24}H_{23}O_3$ ($M + H^+$) 359.1647; found 359.1645.

Methyl 2-(2,2-bis(4-fluorophenyl)-3-methyl-2,3-dihydrobenzofuran-3-yl)acetate (8l): colorless paste (95 mg, 96%); *Rf* 0.6 (hexanes-ethyl acetate, 5:1); IR (ATR) 1732 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.64 (s, 3H), 2.36 (s, 2H), 3.42 (s, 3H), 6.84-6.90 (m, 2H), 6.91-6.95 (m, 1H), 6.97-7.01 (m, 1H), 7.06-7.12 (m, 3H), 7.23-7.29 (m, 3H), 7.59-7.65 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 21.5 (q), 45.0 (t), 51.3 (q), 51.4 (s), 97.5 (s), 109.8 (d), 114.6 (d, J_{CCF} = 21.6 Hz), 115.0 (d, J_{CCF} = 20.4 Hz), 121.2 (d), 123.9 (d), 128.5 (d, J_{CCCF} = 8.4 Hz), 129.1 (d), 129.4 (d, J_{CCCF} = 7.2 Hz), 133.8 (s), 136.5 (s, J_{CCCCF} = 2.7 Hz), 136.8 (s, J_{CCCCF} = 3.6 Hz), 157.2 (s), 161.9 (s, J_{CF} = 247.1 Hz), 162.0 (s, J_{CF} = 247.1 Hz), 171.3 (s); HRMS (ESI, ion trap) calcd for $C_{24}H_{21}F_2O_3$ ($M + H^+$) 395.1459; found 395.1457.

Methyl 2-(2,2-bis(4-methoxyphenyl)-2,3-dihydrobenzofuran-3-yl)acetate (8m). Colorless paste (86 mg, 85%); *Rf* 0.4 (hexanes-ethyl acetate, 5:1); IR (ATR) 1732 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.21 (dd, 1H, J = 7.5, 16.5 Hz), 2.29 (dd, 1H, J = 7.5, 16.5 Hz), 3.51 (s, 3H), 3.75 (s, 3H), 3.77 (s, 3H), 4.58 (t. 1H, J = 7.5 Hz), 6.76-6.92 (m, 6H), 7.10-7.17 (m, 2H), 7.20-7.27 (m, 2H), 7.54-7.60 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 38.8 (t), 46.7 (d), 51.5 (q), 55.16 (q), 55.20 (q), 94.6 (s), 110.0 (d), 113.2

(d), 113.4 (d), 120.9 (d), 124.5 (d), 128.1 (d), 128.3 (d), 128.8 (d), 130.7 (s), 133.6 (s), 136.7 (s), 157.6 (s), 158.8 (s), 159.0 (s), 172.4 (s); HRMS (ESI, ion trap) calcd for $C_{25}H_{25}O_5$ ($M + H^+$) 405.1702; found 405.1700.

Isomerization of *cis*-3g with DBU. A solution of ***cis*-3g** (208 mg, 0.5 mmol) and DBU (10 mg) in toluene (10 mL) was refluxed under nitrogen atmosphere for 12 h. After removal of the solvent *in vacuo*, the residue was purified by column chromatography on silica gel (hexanes-EtOAc, 10:1 and 3:1) to give ***trans*-3g** (79 mg) in 38% yield and **6g** (76 mg) in 44% yield (*trans*:*cis* = 57:43).

(*3R*,4R)-4-(Diphenyl((trimethylsilyl)oxy)methyl)-3-methylchroman-2-one (*trans*-3g)**: colorless paste (79 mg, 38%); *Rf* 0.3 (hexanes-ethyl acetate, 10:1); IR (ATR) 1771 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.17 (s, 9H), 1.25 (d, 3H, *J* = 7.5 Hz), 3.28 (q, 1H, *J* = 7.5 Hz), 3.74 (s, 3H), 6.75-6.78 (m, 1H), 6.89-7.04 (m, 2H), 7.09-7.13 (m, 2H), 7.16-7.36 (m, 9H); ^{13}C NMR ($CDCl_3$) δ 1.7 (q), 17.9 (q), 36.3 (d), 53.8 (d), 84.4 (s), 116.0 (d), 119.5 (s), 123.0 (d), 127.5 (d), 127.7 (d), 127.95 (d), 127.98 (d), 128.6 (d), 128.7 (d), 128.8 (d), 132.6 (d), 141.3 (s), 141.5 (s), 152.0 (s), 170.8 (s); HRMS (ESI, ion trap) calcd for $C_{26}H_{29}O_3Si$ ($M + H^+$) 417.1886; found 417.1883.

(*3R*,4R)-4-(2-Hydroxyphenyl)-3-methyl-5,5-diphenyldihydrofuran-2(3H)-one (*cis*-6g)**: colorless paste (63 mg, 73%); *Rf* 0.55 (hexanes-ethyl acetate, 2:1); IR (ATR) 3356, 1748 cm^{-1}; ^1H NMR ($CDCl_3$, 60 °C) δ 0.97 (d, 3H, *J* = 6.9 Hz), 3.01-3.07 (m, 1H), 5.03-5.23 (m, 1H), 5.34 (brs, 1H), 6.57-6.68 (m, 2H), 6.84-6.96 (m, 3H), 6.98-7.04 (m, 2H), 7.22-7.27 (m, 1H), 7.29-7.39 (m, 4H), 7.69-7.74(m, 2H); ^{13}C NMR ($CDCl_3$, 60 °C) δ 10.4 (q), 39.8 (d), 46.4 (d), 91.2 (s), 115.4 (d), 120.9 (d), 123.1 (s), 125.1 (d), 125.5 (d), 126.6 (d), 127.67 (d), 127.73 (d), 128.8 (d), 141.6 (s), 144.5 (s), 153.9 (s), 179.2 (s); HRMS (ESI, ion trap) calcd for $C_{23}H_{20}O_3$ ($M + H^+$) 345.1491; found 345.1490.

Methyl (*R)-2-((*R**)-2,2-diphenyl-2,3-dihydrobenzofuran-3-yl)propanoate (*erythro*-8g)**: colorless paste (56 mg, 85%); *Rf* 0.55 (hexanes-ethyl acetate, 5:1); IR (ATR) 1732 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.81 (d, 3H, *J* = 7.2 Hz), 2.69-2.75 (m, 1H), 3.43 (s, 3H), 4.39 (d, 1H, *J* = 6.2 Hz), 6.79-6.85 (m, 1H), 6.91-6.96 (m, 1H), 7.08-7.32 (m, 8H), 7.44-7.51 (m, 2H), 7.60-7.67 (m, 2H); ^{13}C

NMR ($CDCl_3$) δ 14.4 (q), 42.8 (d), 51.4 (q), 53.1 (d), 84.6 (s), 110.1 (d), 120.8 (d), 124.9 (d), 126.5 (d), 127.4 (d), 127.50 (d), 127.54 (d), 127.7 (d), 128.1 (d), 128.9 (d), 129.3 (s), 140.6 (s), 145.3 (s), 157.9 (s), 174.7 (s); HRMS (ESI, ion trap) calcd for $C_{24}H_{22}O_3$ ($M + H^+$) 359.1647; found 359.1644.

Detrimethylsiloxylation of 3. A solution of **3a** (101 mg, 0.25 mmol) and *p*-TsOH (10 mg) in xylene (10 mL) was refluxed using Dean-Stark apparatus under nitrogen atmosphere for 24 h. After the solvent was removed *in vacuo*, the residue was purified by column chromatography on silica gel (hexanes-EtOAc, 5:1 and 1:2) to give **11a** (64 mg, 82%) and **7a** (6 mg, 8%).

4-Benzhydryl-2H-chromen-2-one (11a): white solid (64 mg, 82%); *Rf* 0.4 (hexanes-ethyl acetate, 5:1); mp 187-189 ºC; IR (ATR) 1707 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.77 (s, 1H), 5.94 (s, 1H), 7.12-7.17 (m, 5H), 7.25-7.37 (m, 7H), 7.45-7.49 (m, 1H), 7.51-7.55 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 52.8 (d), 117.1 (d), 117.2 (d), 118.9 (s), 124.1 (d), 125.4 (d), 127.4 (d), 128.9 (d), 129.1 (d), 131.4 (d), 139.8 (s), 153.6 (s), 157.2 (s), 160.9 (s). Anal. Calcd for $C_{22}H_{16}O_2$: C, 84.59; H, 5.16. Found: C, 84.55; H, 5.18.

4-(Bis(4-fluorophenyl)methyl)-2H-chromen-2-one (11b): colorless paste (70 mg, 80%); *Rf* 0.25 (hexanes-ethyl acetate, 5:1); IR (ATR) 1721 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.75 (s, 1H), 5.89 (s, 1H), 7.01-7.07 (m, 4H), 7.07-7.12 (m, 4H), 7.14-7.18 (m, 1H), 7.33-7.38 (m, 1H), 7.45-7.51 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 51.1 (d), 115.9 (d, J_{CCF} = 21.6 Hz), 117.1 (d), 117.3 (d), 118.6 (s), 124.2 (d), 125.2 (d), 130.6 (d, J_{CCCF} = 8.4 Hz), 131.7 (d), 135.4 (s, J_{CCCCF} = 3.3 Hz), 153.6 (s), 156.8 (s), 160.7 (s), 161.9 (s, J_{CF} = 247.2 Hz); HRMS (ESI, ion trap) calcd for $C_{22}H_{15}F_2O_2$ ($M + H^+$) 349.1040; found 349.1038.

4-(10,11-Dihydro-5H-dibenzo[a,d][7]annulen-5-yl)-2H-chromen-2-one (11c): white solid (69 mg, 79%); *Rf* 0.3 (hexanes-ethyl acetate, 5:1); mp 212-214 ºC; IR (ATR) 1713 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.74-2.83 (m, 2H), 3.36-3.45 (m, 2H), 5.38 (s, 1H), 6.05 (d, 1H, *J* = 1.7 Hz), 7.09-7.15 (m, 3H), 7.20-7.24 (m, 4H), 7.31-7.34 (m, 1H), 7.37-7.41 (m, 2H), 7.42-7.46 (m, 2H), 7.84-7.87 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 31.4 (t), 56.8 (d), 117.3 (d), 117.6 (d), 118.9 (s), 123.9 (d), 126.0 (d), 126.8 (d),

128.0 (d), 130.7 (d), 131.1 (d), 131.3 (d), 137.5 (s), 139.5 (s), 153.7 (s), 156.8 (s), 161.0 (s). Anal. Calcd for $C_{24}H_{18}O_2$: C, 85.18; H, 5.36. Found: C, 85.16; H, 5.36.

4-(5H-Dibenzo[a,d][7]annulen-5-yl)-2H-chromen-2-one (11d): white solid (76 mg, 90%); *Rf* 0.65 (hexanes-ethyl acetate, 2:1); mp 215-217 ºC; IR (ATR) 1699 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.85 (s, 1H), 5.78 (s, 1H), 6.91 (s, 2H), 7.01-7.06 (m, 1H), 7.22-7.26 (m, 1H), 7.30-7.39 (m, 5H), 7.43-7.50 (m, 2H), 7.57-7.62 (m, 2H), 7.64-7.68 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 55.7 (d), 116.1 (d), 117.2 (d), 119.0 (s), 123.5 (d), 125.7 (d), 127.3 (d), 129.3 (d), 129.78 (d), 129.81 (d), 130.6 (d), 130.9 (d), 134.7 (s), 136.5 (s), 150.6 (s), 153.6 (s), 160.8 (s). Anal. Calcd for $C_{24}H_{16}O_2$: C, 85.69; H, 4.79. Found: C, 85.68; H, 4.80.

4-(9H-Fluoren-9-yl)-2H-chromen-2-one (11e): colorless paste (74 mg, 95%); *Rf* 0.45 (hexanes-ethyl acetate, 10:1); IR (ATR) 1717 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.03 (s, 0.45H), 5.56 (s, 0.55H), 5.76 (s, 0.55H), 6.15 (d, 0.45H, J = 8.3 Hz), 6.60-6.66 (m, 0.45H), 6.85 (s, 0.45H), 7.23-7.31 (m, 3H), 7.33-7.38 (m, 2H), 7.42-7.55 (m, 3H), 7.66-7.69 (m, 0.55H), 7.81-7.86 (m, 1.1H), 7.89-7.94 (m, 0.9H), 8.21-8.26 (m, 0.55H); ^{13}C NMR ($CDCl_3$) δ 47.6 (d), 54.4 (d), 112.8 (d), 117.0 (d), 117.1 (s), 117.6 (d), 118.5 (d), 119.7 (s), 120.3 (d), 120.6 (d), 123.8 (d), 124.39 (d), 124.44 (d), 124.7 (d), 124.8 (d), 125.5 (d), 127.6 (d), 127.7 (d), 128.18 (d), 128.22 (d), 131.2 (d), 132.1 (d), 140.4 (s), 141.2 (s), 143.8 (s), 144.2 (s), 153.8 (s), 154.0 (s), 154.3 (s), 156.1 (s), 160.5 (s), 160.7 (s); HRMS (ESI) calcd for $C_{22}H_{15}O_2$ ($M + H^+$) 311.1072; found 311.1069.

4-(9H-Xanthen-9-yl)-2H-chromen-2-one (11f): white solid (53 mg, 65%); *Rf* 0.3 (hexanes-ethyl acetate, 5:1); mp 246-248 ºC; IR (ATR) 1721 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.63 (s, 1H), 6.46 (s, 1H), 6.95-7.00 (m, 2H), 7.04-7.12 (m, 3H), 7.17-7.20 (m, 2H), 7.25-7.30 (m, 2H), 7.32-7.36 (m, 1H), 7.41-7.46 (m, 1H), 7.55-7.61 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 41.5 (d), 117.1 (d), 117.3 (d), 117.4 (s), 117.5 (d), 120.2 (s), 123.5 (d), 124.1 (d), 125.6 (d), 128.4 (d), 129.1 (d), 131.5 (d), 150.3 (s), 154.5 (s), 156.5 (s), 160.6 (s). Anal. Calcd for $C_{22}H_{14}O_3$: C, 80.97; H, 4.32. Found: C, 81.01; H, 4.33.

4-(Diphenylmethylene)-3-methylchroman-2-one (10g): white solid (65 mg, 80%); *Rf* 0.55

(hexanes-ethyl acetate, 5:1); mp 161-163 ºC; IR (ATR) 1765 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.38 (d, 3H, *J* = 7.3 Hz), 3.76 (q, 1H, *J* = 7.3 Hz), 6.75-6.81 (m, 2H), 7.03-7.09 (m, 3H), 7.13-7.24 (m, 6H), 7.30-7.39 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 18.5 (q), 41.0 (d), 116.6 (d), 121.9 (s), 123.7 (d), 127.6 (d), 127.8 (s), 128.0 (d), 128.3 (d), 128.5 (d), 128.9 (d), 129.1 (d), 130.5 (d), 130.6 (d), 141.1 (s), 141.3 (s), 142.9 (s), 150.8 (s), 170.3 (s). Anal. Calcd for $C_{23}H_{18}O_2$: C, 84.64; H, 5.56. Found: C, 84.59; H, 5.57.

4-Benzhydryl-3-methyl-2H-chromen-2-one (11g): white solid (41 mg, 50%); *Rf* 0.25 (hexanes-ethyl acetate, 10:1); mp 176-178 ºC; IR (ATR) 1701 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.06 (s, 3H), 6.12 (s, 1H), 7.01-7.06 (m, 1H), 7.15-7.19 (m, 4H), 7.25-7.35 (m, 7H), 7.36-7.41 (m, 1H), 7.45-7.49 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 14.8 (q), 51.2 (d), 117.0 (d), 119.9 (s), 123.7 (d), 125.2 (s), 126.4 (d), 127.1 (d), 128.8 (d), 130.1 (d), 139.8 (s), 150.2 (s), 152.4 (s), 162.5 (s). Anal. Calcd for $C_{23}H_{18}O_2$: C, 84.64; H, 5.56. Found: C, 84.63; H, 5.56.

4-(Bis(4-fluorophenyl)methylene)-3-methylchroman-2-one (10h): white solid (77 mg, 85%); *Rf* 0.55 (hexanes-ethyl acetate, 5:1); mp 179-181 ºC; IR (ATR) 1771 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.37 (d, 3H, *J* = 7.3 Hz), 3.72 (q, 1H, *J* = 7.3 Hz), 6.74-6.77 (m, 1H), 6.80-6.84 (m, 1H), 6.87-6.93 (m, 2H), 6.98-7.03 (m, 2H), 7.04-7.15 (m, 5H), 7.18-7.22 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 18.2 (q), 41.0 (d), 115.4 (d, J_{CCF} = 21.6 Hz), 115.6 (d, J_{CCF} = 22.2 Hz), 116.7 (d), 121.5 (s), 123.8 (d), 128.4 (s), 129.1 (d), 130.2 (d), 130.8 (d, J_{CCCF} = 7.8 Hz), 132.3 (d, J_{CCCF} = 8.4 Hz), 136.8 (s, J_{CCCCF} = 3.6 Hz), 137.0 (s, J_{CCCCF} = 3.6 Hz), 140.4 (s), 150.7 (s), 162.1 (s, J_{CF} = 248.3 Hz), 162.4 (s, J_{CF} = 248.3 Hz), 169.7 (s). Anal. Calcd for $C_{23}H_{16}F_2O_2$: C, 76.23; H, 4.45. Found: C, 76.31; H, 4.48.

4-(Bis(4-fluorophenyl)methyl)-3-methyl-2H-chromen-2-one (11h): colorless paste (43 mg, 47%); *Rf* 0.45 (hexanes-ethyl acetate, 5:1); IR (ATR) 1701 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.05 (s, 3H), 6.05 (s, 1H), 6.99-7.08 (m, 5H), 7.09-7.15 (m, 4H), 7.32-7.36 (m, 1H), 7.37-7.43 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.8 (q), 49.8 (d), 115.9 (d, J_{CCF} = 21.6 Hz), 117.2 (d), 119.5 (s), 123.8 (d), 125.2 (s), 126.0 (d), 130.3 (d, J_{CCCF} = 8.4 Hz), 130.4 (d), 135.4 (s, J_{CCCCF} = 3.6 Hz), 149.6 (s), 152.4 (s), 161.8

(s, J_{CF} = 247.1 Hz), 162.3 (s); HRMS (ESI, ion trap) calcd for $C_{23}H_{17}F_2O_2$ ($M + H^+$) 363.1197; found 363.1195.

4-(10,11-Dihydro-5H-dibenzo[a,d][7]annulen-5-ylidene)-3-methylchroman-2-one (10i): white solid (69 mg, 78%); *Rf* 0.6 (hexanes-ethyl acetate, 5:1); mp 193-194 ºC; IR (ATR) 1759 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.06 (d, 3H, *J* = 7.3 Hz), 2.85-2.93 (m, 1H), 2.95-3.04 (m, 1H), 3.44-3.52 (m, 2H), 4.06 (q, 1H, *J* = 7.3 Hz), 6.70-6.73 (m, 1H), 6.76-6.80 (m, 1H), 6.85-6.89 (m, 1H), 6.90-6.95 (m, 1H), 7.07-7.10 (m, 1H), 7.12-7.26 (m, 7H); ^{13}C NMR ($CDCl_3$) δ 16.7 (q), 31.5 (t), 32.8 (t), 39.3 (d), 116.7 (d), 120.9 (s), 123.5 (d), 126.2 (d), 126.5 (s), 126.6 (d), 126.8 (d), 127.8 (d), 127.9 (d), 128.91 (d), 128.94 (d), 129.0 (d), 130.0 (d), 130.3 (d), 137.5 (s), 138.2 (s), 138.6 (s), 140.0 (s), 141.8 (s), 151.1 (s), 170.6 (s). Anal. Calcd for $C_{25}H_{20}O_2$: C, 85.20; H, 5.72. Found: C, 85.14; H, 5.69.

4-(5H-Dibenzo[a,d][7]annulen-5-ylidene)-3-methylchroman-2-one (10j): white solid (52 mg, 59%); *Rf* 0.4 (hexanes-ethyl acetate, 10:1); mp 215-216 ºC; IR (ATR) 1773 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.93 (d, 3H, *J* = 7.5 Hz), 3.96 (q, 1H, *J* = 7.5 Hz), 6.17-6.20 (m, 1H), 6.67-6.71 (m, 1H), 7.00-7.08 (m, 4H), 7.12-7.16 (m, 1H), 7.18-7.22 (m, 1H), 7.29-7.36 (m, 3H), 7.39-7.48 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 17.4 (q), 38.7 (d), 116.5 (d), 120.8 (s), 123.5 (d), 127.0 (d), 127.2 (d), 127.4 (d), 127.5 (d), 127.7 (s), 128.4 (d), 128.5 (d), 128.90 (d), 128.94 (d), 129.1 (d), 129.5 (d), 130.9 (d), 131.0 (d), 134.7 (s), 134.8 (s), 136.2 (s), 137.9 (s), 139.8 (s), 151.0 (s), 170.7 (s). Anal. Calcd for $C_{25}H_{18}O_2$: C, 85.69; H, 5.18. Found: C, 85.63; H, 5.21.

4-(5H-Dibenzo[a,d][7]annulen-5-yl)-3-methyl-2H-chromen-2-one (11j): white solid (55 mg, 63%); *Rf* 0.3 (hexanes-ethyl acetate, 10:1); mp 203-205 ºC; IR (ATR) 1705 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.18 (s, 3H), 5.78 (s, 1H), 7.02 (s, 2H), 7.05-7.18 (m, 5H), 7.21-7.26 (m, 2H), 7.33-7.36 (m, 2H), 7.41-7.49 (m, 2H), 7.61-7.64 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 16.0 (q), 47.4 (d), 117.1 (d), 120.3 (s), 123.0 (d), 126.0 (s), 126.9 (d), 127.0 (d), 128.5 (d), 129.4 (d), 129.7 (d), 130.4 (d), 132.5 (d), 136.1 (s), 137.3 (s), 148.4 (s), 152.1 (s), 162.4 (s). Anal. Calcd for $C_{25}H_{18}O_2$: C, 85.69; H, 5.18. Found: C, 85.69; H, 5.19.

4-Benzhydryl-1-methylquinolin-2(1H)-one (11n): white solid (69 mg, 85%); *Rf* 0.4 (hexanes-ethyl acetate, 2:1); mp 209-211 ºC; IR (ATR) 1641 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.73 (s, 3H), 5.90 (s, 1H), 6.26 (s, 1H), 7.09-7.16 (m, 5H), 7.22-7.33 (m, 6H), 7.37-7.41 (m, 1H), 7.49-7.53 (m, 1H), 7.68-7.72 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 29.3 (q), 52.7 (d), 114.5 (d), 120.4 (s), 122.0 (d), 123.0 (d), 125.8 (d), 126.9 (d), 128.6 (d), 129.3 (d), 130.2 (d), 139.9 (s), 141.0 (s), 151.6 (s), 162.1 (s). Anal. Calcd for $C_{23}H_{19}NO$: C, 84.89; H, 5.89; N, 4.30. Found: C, 84.86; H, 5.60, N, 4.33.

ASSOCIATED CONTENT

Supporting Information

A PDF file of ^{1}H and ^{13}C NMR spectra of products, X-ray crystallographic data (ortep) of **3d, *cis*-3j 3k, 3l, 6a, *trans*-6g, *trans*-6h, *trans*-6j, 6k, 7c, 7d, 7l, *threo*-8h, 9n, 10h, 10i, 11a, 11c, 11d, 11f, 11g, and 11j**, DFT calculation data, and CV data (PDF). X-ray crystallographic CIF data for **3d, *cis*-3j 3k, 3l, 6a, *trans*-6g, *trans*-6h, *trans*-6j, 6k, 7c, 7d, 7l, *threo*-8h, 9n, 10h, 10i, 11a, 11c, 11d, 11f, 11g, and 11j**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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