JOC The Journal of Organic Chemistry

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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-(Diarylmethyl)coumarins

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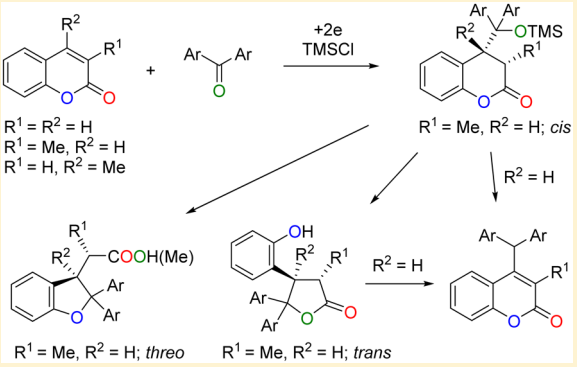
Supporting Information

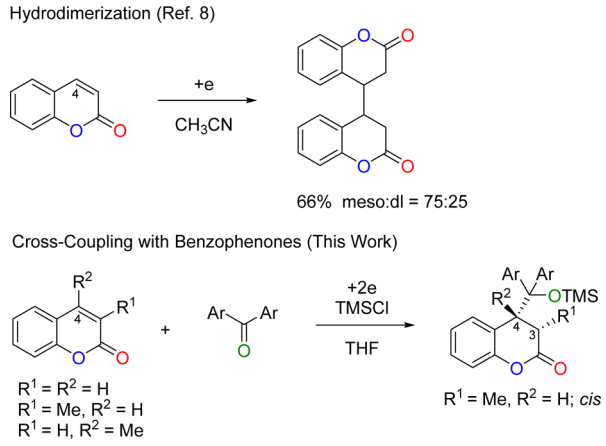
**ABSTRACT:** The electroreductive coupling of coumarins with benzophenones in the presence of TMSCl gave adducts reacted at the 4-position of coumarins as trimethylsilyl ethers. From 3-methylcoumarin, 3,4-*cis*-adducts were formed stereoselectively. The de-trimethylsilylation of the adducts with 1 M HCl aq or TBAF in THF at 25 °C 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 de-trimethylsilylation of the adducts with 1 M HCl in MeOH afforded 2-(2,2-diaryl-2,3-dihydrobenzofuran-3-yl)acetic acid methyl esters. The de-trimethylsiloxylation of the adducts or dehydration of the γ-butyrolactones brought about 4-(diarylmethyl)coumarins.




## INTRODUCTION

Recently, 3- and 4-substituted coumarin derivatives have been extensively investigated as pharmacologically active compounds, such as anticancer, anti-neurodegenerative, and antituberculous agents.[1] Therefore, the synthesis of 3- and 4-substituted coumarins attracts much attention from the synthetic chemists.[2,3] On the other hand, electroreduction is one of the useful methods 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 de-trimethylsilylation of the trimethylsilyl ethers and subsequent dehydration of the resultant alcohols. Contrary to our expectations, 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 °C (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 dehydrosilox-

**Scheme 1. Electroreductive Hydorodimerization and Cross-Coupling of Coumarins**



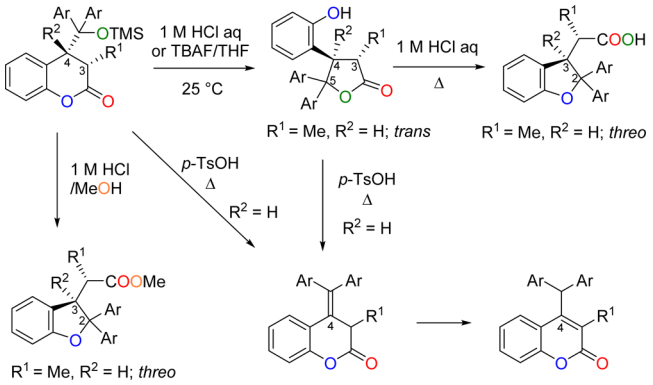

**Received:** August 22, 2016
**Published:** October 5, 2016





DOI: 10.1021/acs.joc.6b02056
J. Org. Chem. 2016, 81, 11043−11056

**Scheme 2. Transformation of Adducts**

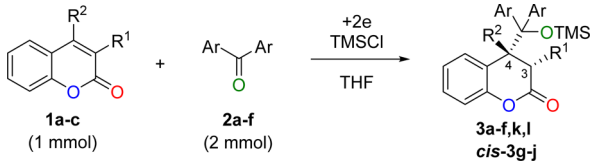



ylation of the adducts or dehydration of the γ-butyrolactones with cat. *p*-TsOH in refluxing toluene or xylene. Reaction mechanisms of the electroreductive coupling and the transformations of the adducts were also discussed.

## 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

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



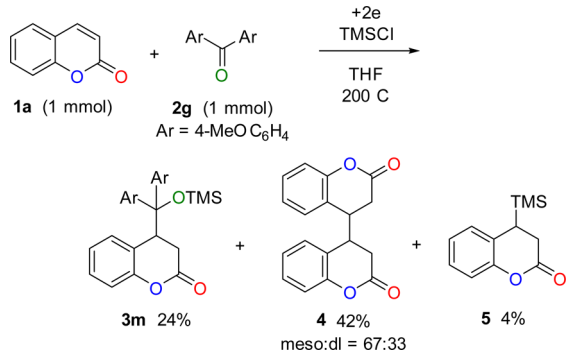

| run | 1 | $R^1$ | $R^2$ | 2 | $Ar_2C{=}O$ | 3 | % yield[b] |
|---|---|---|---|---|---|---|---|
| 1 | **1a** | H | H | **2a** | Ar = Ph | **3a** | 75 |
| 2 | **1a** | H | H | **2b** | Ar = 4-$FC_6H_4$ | **3b** | 73 |
| 3 | **1a** | H | H | **2c** | dibenzosuberone | **3c** | 86 |
| 4 | **1a** | H | 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.

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 the *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

**Scheme 3. Electroreduction of 1a and 2g**




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 a 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 two-electron transfer to **1a** followed by *O*-silylation with TMSCl and subsequent desilylation of the resultant ketene silyl acetal **E** during workup.

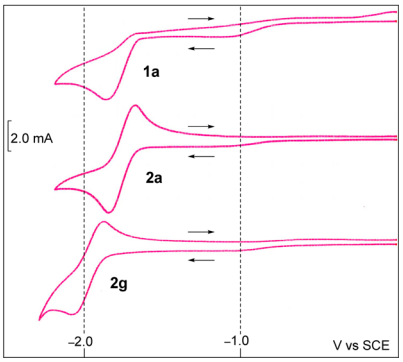
**Desilylation of Adducts 3a−l with 1 M HCl aq/Dioxane and 1 M HCl/MeOH.** The adducts **3a−j** were stirred in 1 M HCl aq and dioxane (1:1) at 25 °C until almost all of **3a−j** were consumed (Table 3). From **3a−e**, 4-(2-hydroxyphenyl)-5,5-diaryl-γ-butyrolactones **6a−e** were obtained after stirring 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 **6f** 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),


DOI: 10.1021/acs.joc.6b02056
J. Org. Chem. 2016, 81, 11043−11056

**Table 2. $E_p$ Values of 1a−c and 2a−g Derived from CV at 25 °C**

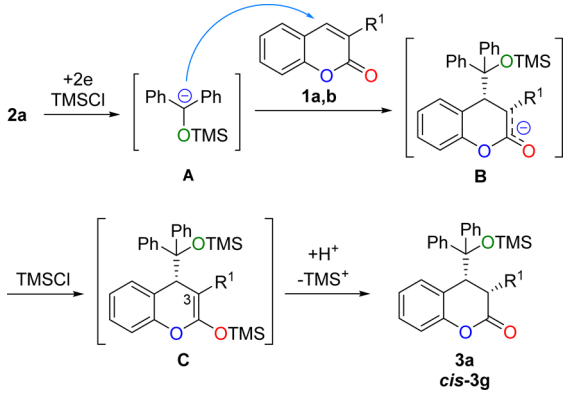
| compound | $E_p$ (V vs. SCE)[a] |
|---|---|
| **1a** | −1.88 |
| **1b** | −1.96 |
| **1c** | −1.94 |
| **2a** | −1.85 |
| **2b** | −1.85 |
| **2c** | −1.78 |
| **2d** | −1.79 |
| **2e** | −1.38 |
| **2f** | −1.76 |
| **2g** | −2.08 |

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




[a]First 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**

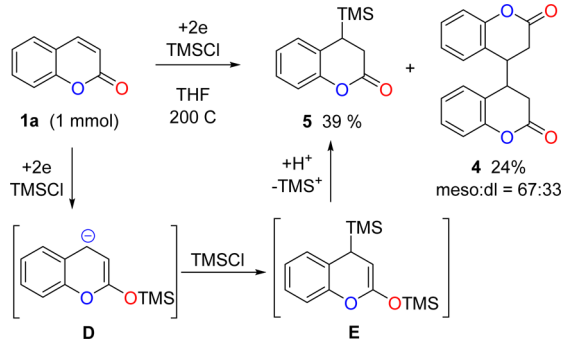
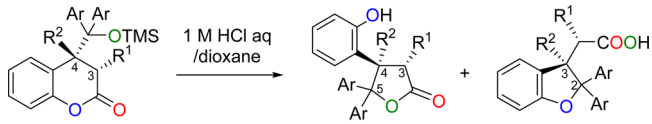



**Table 3. Desilylation of 3a−l with 1 M HCl aq/Dioxane**




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

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

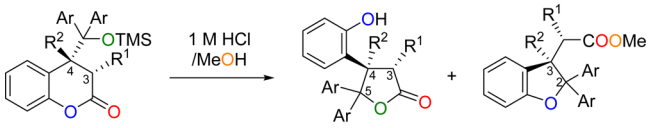
3,4-*trans*-γ-butyrolactones ***trans*-6g−j** were obtained as the sole products in high yields (runs 13 and 15−17). The stereostructures of ***trans*-6g,h,j** were confirmed by X-ray crystallography. On the contrary, 4-methyl-substituted adducts **3k,l** ($R^1$ = H, $R^2$ = Me) were completely inert under the same conditions at 25 °C. 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** 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 °C (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



DOI: 10.1021/acs.joc.6b02056
J. Org. Chem. 2016, 81, 11043−11056

**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**

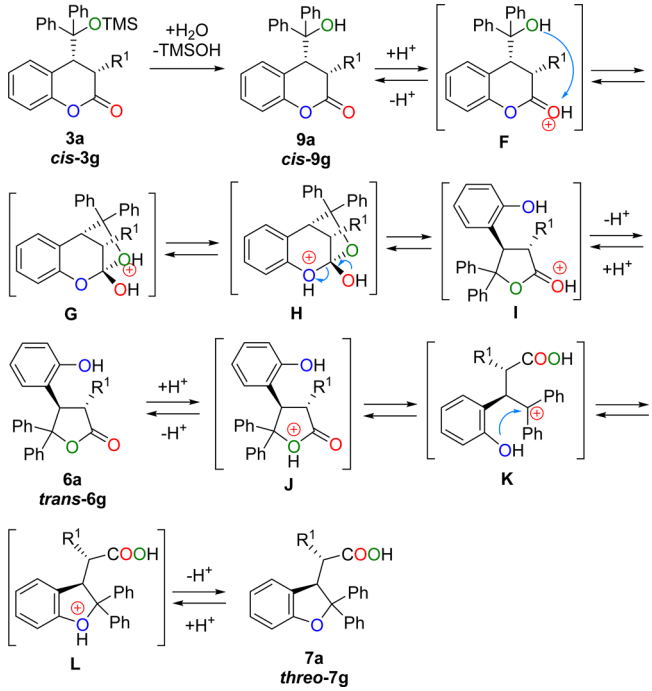
| run | 3 | temp (°C) | time (h) | 6 | % yield[a] | 8 | % yield[a] |
|---|---|---|---|---|---|---|---|
| 1 | **3a** | 25 | 12 | | | **8a** | 86 |
| 2 | **3a** | reflux | 2 | | | **8a** | 82 |
| 3 | **3b** | 25 | 12 | | | **8b** | 87 |
| 4 | **3c** | 25 | 2 | **6c** | 95 | | |
| 5 | **3c** | reflux |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

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

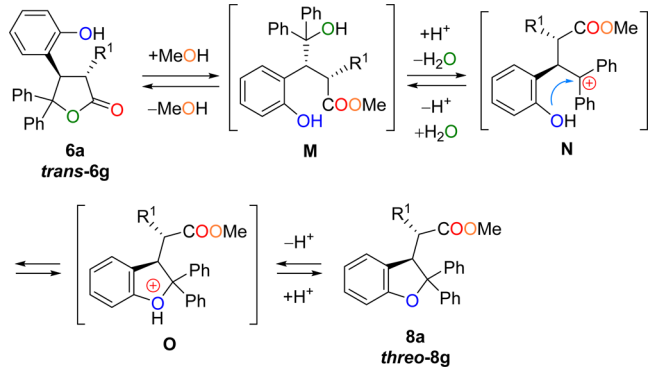
same conditions but at reflux temperature (runs 5, 6, 12, 16, and 17). Although **8j** (52%) was obtained from ***cis*-3j**, a considerable amount of ***trans*-6j** (45%) was remained even after reflux for 108 h (run 14). From ***cis*-3g–j** ($R^1$ = Me, $R^2$ = H), methyl esters **8g–j** were obtained 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 was found 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

**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**



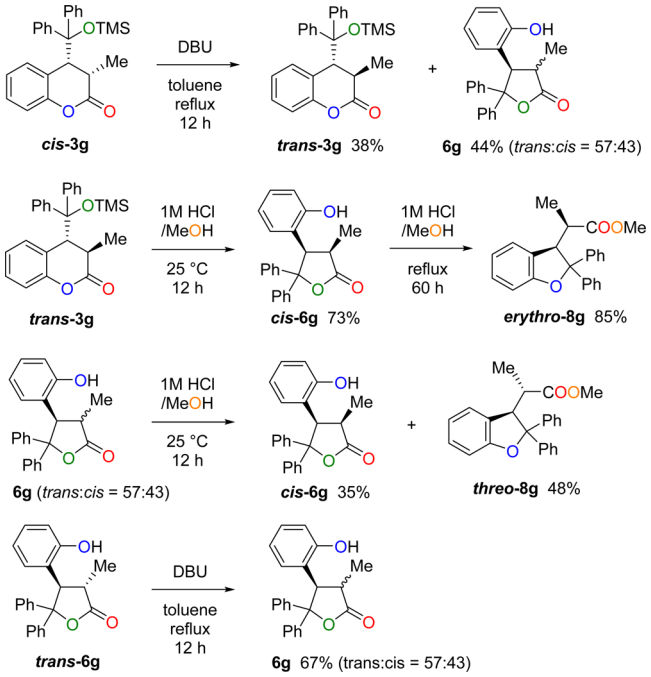

**8a**. From ***trans*-6g** ($R^1$ = Me), ***threo*-8g** is formed with complete retention of the stereochemistry.

**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 °C 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 °C and reflux temperature, respectively. This result shows that ***cis*-6g** is inert in 1 M HCl/MeOH at 25 °C 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 °C, ***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



DOI: 10.1021/acs.joc.6b02056
J. Org. Chem. 2016, 81, 11043–11056

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

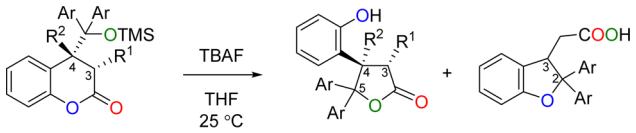



h gave an equilibrium mixture of **6g** (*trans*/*cis* = 57:43). This result suggests that ***trans*-6g** is slightly more stable than ***cis*-6g** under the conditions. The DFT calculations of both isomers of **6g** at the B3LYP/6-311+G(2d,p) level using the IEFPCM model in toluene at 383 K also showed that ***trans*-6g** is a little lower in energy than ***cis*-6g** (0.41 kcal/mol corresponding to 63:37 dr).

**Desilylation of Adducts 3a–l with TBAF/THF.** The adducts **3a–l** were treated with TBAF in THF at 25 °C 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 3 h, **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).

The presumed reaction mechanism of the transformation of **3a–l** to **6a–l** and **7f** is exhibited in Scheme 9. Treatment of

**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

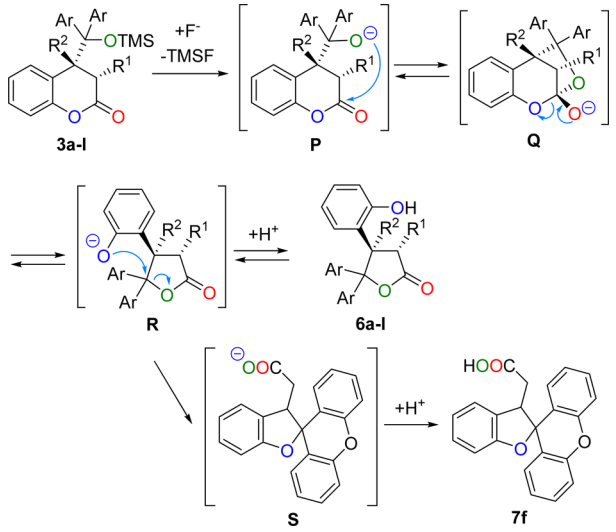
**6a-f**
***trans*-6g-j**
**6k,l**

**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.

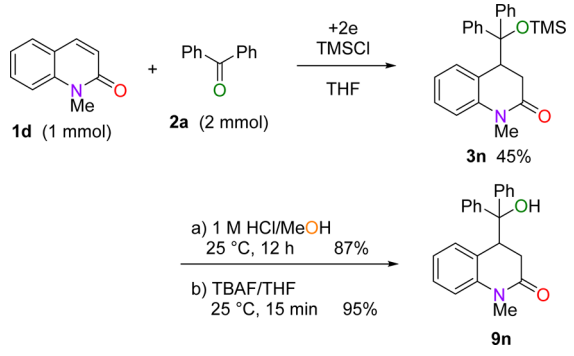
**Scheme 9. Presumed Reaction Mechanism of Transformation of 3a–l to 6a–l and 7f with TBAF**




**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**.

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(1*H*)-one (**1d**) with **2a** (Scheme 10). The treatment of **3n** with 1 M HCl in MeOH or TBAF in THF at 25 °C gave desilylated δ-lactam **9n** in a high yield.

**Scheme 10. Electroreductive Coupling of 1d with 2a and Desilylation of Adduct 3n**

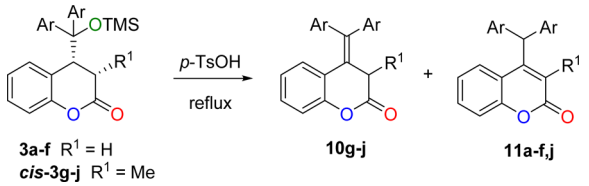





DOI: 10.1021/acs.joc.6b02056
J. Org. Chem. 2016, 81, 11043–11056

**De-trimethylsiloxylation of 3a–j.** De-trimethylsiloxylation[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**

**Table 6. De-trimethylsiloxylation of 3a–j**

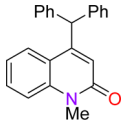



**3a-f** $R^1$ = H
***cis*-3g-j** $R^1$ = Me

**10g-j** **11a-f,j**

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

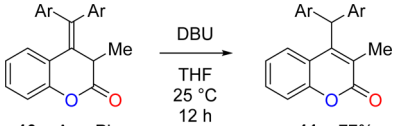
[a]Isolated yields. [b]**7a** (8%) was formed as a byproduct. [c]**7b** (16%) was formed as a byproduct.




**11n**

($R^1$ = H), 4-(diarylmethyl)coumarins **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-(diarylmethyl)coumarin **11j** (59%) was obtained with **10j** (37%) after reflux in xylene for 24 h (run 10). However, the isomerization of **10j** to **11j** was not complete even after 96 h (run 11). Similarly, de-trimethylsiloxylation of **3n** in toluene for 12 h gave 4-benzhydryl-1-methylquinolin-2(1*H*)-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 °C (Scheme 11).

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

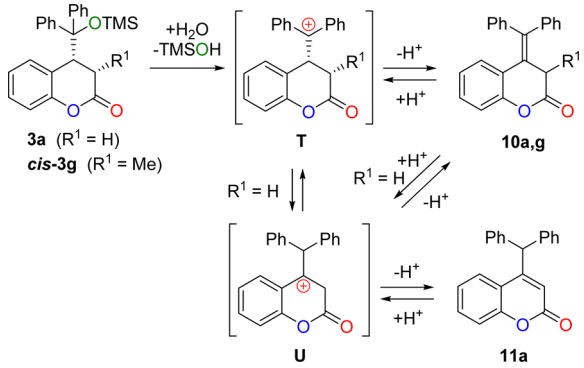



**10g** Ar = Ph
**10h** Ar = 4-$FC_6H_4$

**11g** 77%
**11h** 70%

The presumed reaction mechanism of transformation of **3a** and ***cis*-3g** to **11a** and **10g** is shown in Scheme 12. Acid-catalyzed de-trimethylsiloxylation 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

**Scheme 12. Presumed Reaction Mechanism of De-trimethylsiloxylation of 3a,g to 10g and 11a**




**3a** ($R^1$ = H)
***cis*-3g** ($R^1$ = Me)

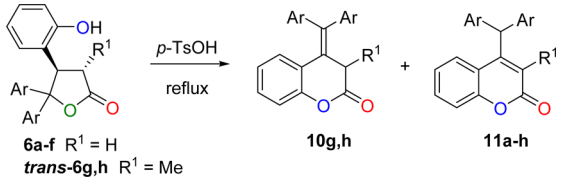
**T** **10a,g**

**U** **11a**

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.

On the other hand, the γ-butyrolactones **6a–h** were also transformed to the 4-(diarylmethyl)coumarins **11a–h** under the same conditions as above (Table 7). From **6a–f** ($R^1$ = H),

**Table 7. Dehydration of 6a–h**




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

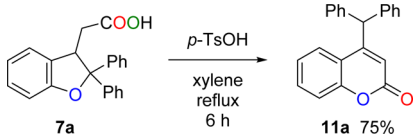
**10g,h** **11a-h**

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

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

**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

**Scheme 13. Dehydration of 7a to 11a**



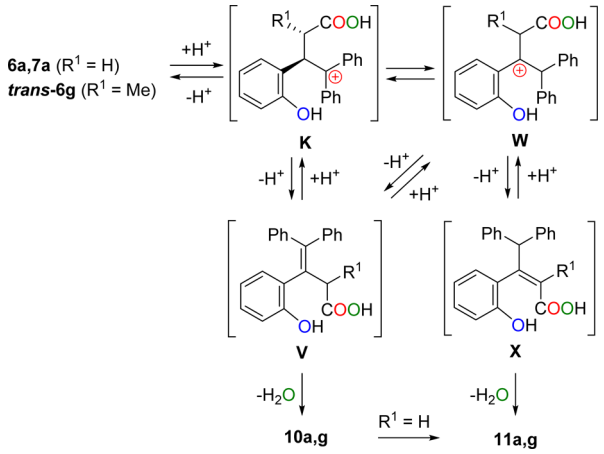

**7a** **11a** 75%

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



DOI: 10.1021/acs.joc.6b02056
J. Org. Chem. 2016, 81, 11043–11056

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




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.

The 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**.

## CONCLUSION

The electroreductive intermolecular coupling of coumarins **1a**−**c** with benzophenones **2a**−**f** in the presence of TMSCl in THF gave adducts that 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 °C gave 4-(2-hydroxyphenyl)-5,5-diaryl-γ-butyrolactones **6a**−**l**. The desilylation of ***cis*-3g**−**j** under 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. De-trimethylsiloxylation 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 de-trimethylsiloxylation 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 °C.

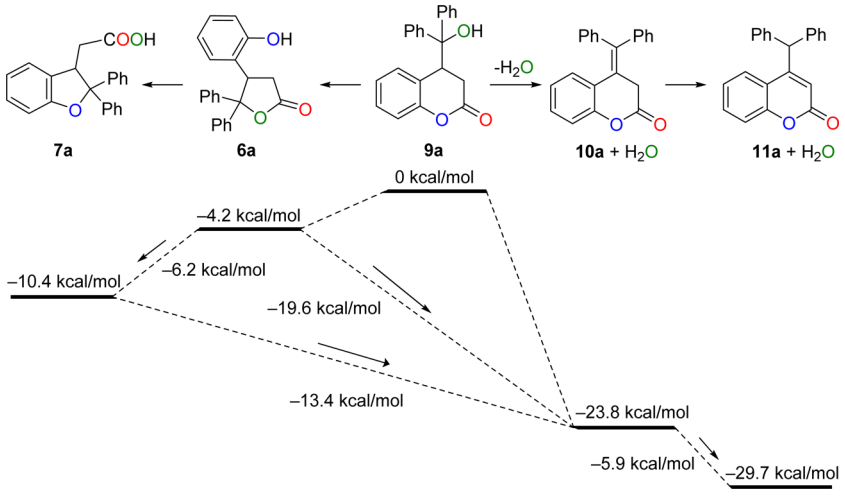
## EXPERIMENTAL SECTION

**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 × 5 $cm^2$), a platinum anode (2 × 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 °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, 10:1) to give **3a** (286 mg) in 71% yield.

*4-(Diphenyl((trimethylsilyl)oxy)methyl)chroman-2-one (**3a**):* colorless paste (301 mg, 75%); $R_f$ 0.2 (hexanes−ethyl acetate, 10:1); IR (ATR) 1763 $cm^{-1}$; $^1H$ 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

**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 383 K**






DOI: 10.1021/acs.joc.6b02056
J. Org. Chem. 2016, 81, 11043−11056

(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%); $R_f$ 0.4 (hexanes−ethyl acetate, 5:1); IR (ATR) 1761 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ −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 ($CDCl_3$) $\delta$ 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%); $R_f$ 0.3 (hexanes−ethyl acetate, 10:1); IR (ATR) 1767 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ −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 ($CDCl_3$) $\delta$ 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%); $R_f$ 0.5 (hexanes−ethyl acetate, 5:1); mp 201−203 °C; IR (ATR) 1759 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 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 ($CDCl_3$) $\delta$ 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%); $R_f$ 0.45 (hexanes−ethyl acetate, 5:1); IR (ATR) 1769 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ −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 ($CDCl_3$) $\delta$ 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%); $R_f$ 0.3 (hexanes−ethyl acetate, 10:1); IR (ATR) 1767 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ −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 ($CDCl_3$) $\delta$ 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.

*(3R*,4S*)-4-(Diphenyl((trimethylsilyl)oxy)methyl)-3-methylchroman-2-one* (**cis-3g**): colorless paste (358 mg, 86%); $R_f$ 0.3 (hexanes−ethyl acetate, 10:1); IR (ATR) 1763 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ −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 ($CDCl_3$) $\delta$ 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.

*(3R*,4S*)-4-(Bis(4-fluorophenyl)((trimethylsilyl)oxy)methyl)-3-methylchroman-2-one* (**cis-3h**): colorless paste (380 mg, 84%); $R_f$ 0.25 (hexanes−ethyl acetate, 10:1); IR (ATR) 1763 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ −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 ($CDCl_3$) $\delta$ 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.

*(3R*,4S*)-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%); $R_f$ 0.4 (hexanes−ethyl acetate, 10:1); IR (ATR) 1765 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ −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 ($CDCl_3$) $\delta$ 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.

*(3R*,4S*)-3-Methyl-4-(5-((trimethylsilyl)oxy)-5H-dibenzo[a,d][7]-annulen-5-yl)chroman-2-one* (**cis-3j**): white solid (378 mg, 86%); $R_f$ 0.3 (hexanes−ethyl acetate, 10:1); mp 201−203 °C; IR (ATR) 1767 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 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 ($CDCl_3$) $\delta$ 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%); $R_f$ 0.3 (hexanes−ethyl acetate, 10:1); mp 173−175 °C; IR (ATR) 1761, 1749 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ −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 ($CDCl_3$) $\delta$ 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%); $R_f$ 0.3 (hexanes−ethyl acetate, 10:1); mp 139−141 °C; IR (ATR) 1757 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ −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 ($CDCl_3$) $\delta$ 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; $R_f$ 0.6 (hexanes−ethyl acetate, 5:1); $^1H$ NMR ($CDCl_3$) $\delta$ −0.17 (s, 9H), 2.73 (dd, 1H, $J$ = 8.0, 17.2 Hz), 3.16 (d, 1


DOI: 10.1021/acs.joc.6b02056
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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 ($CDCl_3$) $\delta$ 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%); $R_f$ 0.6 (hexanes−ethyl acetate, 2:1); IR (ATR) 1672 $cm^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ −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 ($CDCl_3$) $\delta$ 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%); $R_f$ 0.35 (hexanes−ethyl acetate, 10:1); IR (ATR) 1761 $cm^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 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 ($CDCl_3$) $\delta$ −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 for 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 °C, and then the solution was stirred at this temperature for 6 h. The mixture was neutralized with satd $NaHCO_3$ 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, 3:1) to give **6a** (70 mg) in 85% yield.

**Typical Procedure for 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%); $R_f$ 0.4 (hexanes−ethyl acetate, 2:1); mp 176−178 °C; IR (ATR) 3348, 1746 $cm^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 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 ($CDCl_3$) $\delta$ 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%); $R_f$ 0.45 (hexanes−ethyl acetate, 2:1); IR (ATR) 3341, 1749 $cm^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 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 ($CDCl_3$) $\delta$ 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%); $R_f$ 0.45 (hexanes−ethyl acetate, 2:1); mp 211−213 °C; IR (ATR) 3310, 1744 $cm^{-1}$; $^1$H NMR ($CDCl_3$, 60 °C) $\delta$ 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) $\delta$ 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%); $R_f$ 0.45 (hexanes−ethyl acetate, 2:1); mp 244−245 °C; IR (ATR) 3385, 1757 $cm^{-1}$; $^1$H NMR ($CDCl_3$, 60 °C) $\delta$ 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) $\delta$ 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%); $R_f$ 0.4 (hexanes−ethyl acetate, 2:1); mp 268−270 °C; IR (ATR) 3420, 1751 $cm^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 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 ($CDCl_3$) $\delta$ 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%); $R_f$ 0.45 (hexanes−ethyl acetate, 2:1); mp 229−231 °C; IR (ATR) 3310, 1748 $cm^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 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-$d_6$) $\delta$ 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.

*(3R*,4S*)-4-(2-Hydroxyphenyl)-3-methyl-5,5-diphenyldihydrofuran-2(3H)-one (**trans-6g**):* white solid (79 mg, 92%); $R_f$ 0.55 (hexanes−ethyl acetate, 2:1); mp 167−169 °C; IR (ATR) 3537, 3401, 1740 $cm^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 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 ($CDCl_3$) $\delta$ 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.

*(3R*,4S*)-5,5-Bis(4-fluorophenyl)-4-(2-hydroxyphenyl)-3-methyldihydrofuran-2(3H)-one (**trans-6h**):* colorless paste (93 mg, 98%); $R_f$ 0.55 (hexanes−ethyl acetate, 2:1); IR (ATR) 3345, 1749 $cm^{-1}$; $^1$H NMR ($CDCl_3$) $\delta$ 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 ($CDCl_3$) $\delta$ 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


DOI: 10.1021/acs.joc.6b02056
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(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%); $R_f$ 0.55 (hexanes−ethyl acetate, 2:1); IR (ATR) 3331, 1740, 1705 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 60 °C) $\delta$ 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) $\delta$ 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%); $R_f$ 0.2 (hexanes−ethyl acetate, 5:1); mp 243−245 °C; IR (ATR) 3265, 1748, 1730 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 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 ($CDCl_3$) $\delta$ 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%); $R_f$ 0.5 (hexanes−ethyl acetate, 2:1); mp 222−223 °C; IR (ATR) 3352, 1736 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 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 ($CDCl_3$) $\delta$ 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%); $R_f$ 0.55 (hexanes−ethyl acetate, 2:1); IR (ATR) 3302, 1748 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 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 ($CDCl_3$) $\delta$ 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%); $R_f$ 0.3 (hexanes−ethyl acetate, 2:1); IR (ATR) 3348, 1746 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 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 ($CDCl_3$) $\delta$ 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%); $R_f$ 0.5 (hexanes−ethyl acetate, 1:2); mp 213-214 °C; IR (ATR) 3200−2400 (br), 1734, 1693 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 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 ($CDCl_3$) $\delta$ 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%); $R_f$ 0.1 (hexanes−ethyl acetate, 2:1); IR (ATR) 3200−2400 (br), 1705 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 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 ($CDCl_3$) $\delta$ 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%); $R_f$ 0.15 (hexanes−ethyl acetate, 2:1); mp 261−263 °C; IR (ATR) 3200−2400 (br), 1694 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 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 ($CDCl_3$) $\delta$ 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%); $R_f$ 0.2 (hexanes−ethyl acetate, 2:1); mp 238−240 °C; IR (ATR) 3200−2400 (br), 1699 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 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 ($CDCl_3$) $\delta$ 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%); $R_f$ 0.3 (hexanes−ethyl acetate, 2:1); IR (ATR) 3200−2400 (br), 1713 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 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 ($CDCl_3$) $\delta$ 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%); $R_f$ 0.3 (hexanes−ethyl acetate, 2:1); mp 232−233 °C; IR (ATR) 3200−2400 (br), 1701 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 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-$d_6$) $\delta$ 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%); $R_f$ 0.15 (hexanes−ethyl acetate, 2:1); IR (ATR) 3200−2400 (br), 1697 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 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 ($CDCl_3$) $\delta$ 12.8 (q), 40.8 (d), 51.1 (d), 94.9 (s), 110.3 (d), 120.8 (d), 126.0 (d),



DOI: 10.1021/acs.joc.6b02056
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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%); $R_f$ 0.35 (hexanes−ethyl acetate, 2:1); mp 224−226 °C; IR (ATR) 3200−2400 (br), 1701 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 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 ($CDCl_3$) $\delta$ 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%); $R_f$ 0.25 (hexanes−ethyl acetate, 2:1); mp 200−202 °C; IR (ATR) 3200−2400 (br), 1709, 1697 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 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 ($CDCl_3$) $\delta$ 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%); $R_f$ 0.3 (hexanes−ethyl acetate, 2:1); mp 180−182 °C; IR (ATR) 3422, 1636 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 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 ($CDCl_3$) $\delta$ 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 °C, 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%); $R_f$ 0.6 (hexanes−ethyl acetate, 5:1); IR (ATR) 1732 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 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 ($CDCl_3$) $\delta$ 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%); $R_f$ 0.6 (hexanes−ethyl acetate, 5:1); IR (ATR) 1730 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 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 ($CDCl_3$) $\delta$ 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%); $R_f$ 0.6 (hexanes−ethyl acetate, 5:1); IR (ATR) 1734 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 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 ($CDCl_3$) $\delta$ 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%); $R_f$ 0.6 (hexanes−ethyl acetate, 5:1); IR (ATR) 1734 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 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 ($CDCl_3$) $\delta$ 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%); $R_f$ 0.6 (hexanes−ethyl acetate, 5:1); IR (ATR) 1734 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 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 ($CDCl_3$) $\delta$ 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%); $R_f$ 0.6 (hexanes−ethyl acetate, 5:1); IR (ATR) 1726 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 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 ($CDCl_3$) $\delta$ 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%); $R_f$ 0.55 (hexanes−ethyl acetate, 5:1); IR (ATR) 1726 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 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 ($CDCl_3$) $\delta$ 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%); $R_f$ 0.6 (hexanes−ethyl acetate, 5:1); mp 120−122 °C; IR (ATR) 1719 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 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 ($CDCl_3$) $\delta$ 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.



DOI: 10.1021/acs.joc.6b02056
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*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%); $R_f$ 0.6 (hexanes−ethyl acetate, 5:1); IR (ATR) 1732, 1724 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 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 ($CDCl_3$) $\delta$ 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%); $R_f$ 0.65 (hexanes−ethyl acetate, 5:1); IR (ATR) 1726 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 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 ($CDCl_3$) $\delta$ 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%); $R_f$ 0.45 (hexanes−ethyl acetate, 10:1); IR (ATR) 1732 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 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 ($CDCl_3$) $\delta$ 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%); $R_f$ 0.6 (hexanes−ethyl acetate, 5:1); IR (ATR) 1732 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 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 ($CDCl_3$) $\delta$ 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, JCF = 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%); $R_f$ 0.4 (hexanes−ethyl acetate, 5:1); IR (ATR) 1732 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 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 ($CDCl_3$) $\delta$ 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%); $R_f$ 0.3 (hexanes−ethyl acetate, 10:1); IR (ATR) 1771 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ −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 ($CDCl_3$) $\delta$ 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%); $R_f$ 0.55 (hexanes−ethyl acetate, 2:1); IR (ATR) 3356, 1748 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 60 °C) $\delta$ 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) $\delta$ 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%); $R_f$ 0.55 (hexanes−ethyl acetate, 5:1); IR (ATR) 1732 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 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 ($CDCl_3$) $\delta$ 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.

**De-trimethylsiloxylation 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%); $R_f$ 0.4 (hexanes−ethyl acetate, 5:1); mp 187−189 °C; IR (ATR) 1707 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 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 ($CDCl_3$) $\delta$ 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%); $R_f$ 0.25 (hexanes−ethyl acetate, 5:1); IR (ATR) 1721 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 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 ($CDCl_3$) $\delta$ 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%); $R_f$ 0.3 (hexanes−ethyl acetate, 5:1); mp 212−214 °C; IR (ATR) 1713 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 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 ($CDCl_3$) $\delta$ 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%); $R_f$ 0.65 (hexanes−ethyl acetate, 2:1); mp 215−217 °C; IR (ATR) 1699 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 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 ($CDCl_3$) $\delta$ 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.



DOI: 10.1021/acs.joc.6b02056
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*4-(9H-Fluoren-9-yl)-2H-chromen-2-one (**11e**):* colorless paste (74 mg, 95%); $R_f$ 0.45 (hexanes−ethyl acetate, 10:1); IR (ATR) 1717 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 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 ($CDCl_3$) $\delta$ 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%); $R_f$ 0.3 (hexanes−ethyl acetate, 5:1); mp 246−248 °C; IR (ATR) 1721 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 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 ($CDCl_3$) $\delta$ 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%); $R_f$ 0.55 (hexanes−ethyl acetate, 5:1); mp 161−163 °C; IR (ATR) 1765 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 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 ($CDCl_3$) $\delta$ 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%); $R_f$ 0.25 (hexanes−ethyl acetate, 10:1); mp 176−178 °C; IR (ATR) 1701 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 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 ($CDCl_3$) $\delta$ 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%); $R_f$ 0.55 (hexanes−ethyl acetate, 5:1); mp 179−181 °C; IR (ATR) 1771 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 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 ($CDCl_3$) $\delta$ 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%); $R_f$ 0.45 (hexanes−ethyl acetate, 5:1); IR (ATR) 1701 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 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 ($CDCl_3$) $\delta$ 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%); $R_f$ 0.6 (hexanes−ethyl acetate, 5:1); mp 193−194 °C; IR (ATR) 1759 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 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 ($CDCl_3$) $\delta$ 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%); $R_f$ 0.4 (hexanes−ethyl acetate, 10:1); mp 215−216 °C; IR (ATR) 1773 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 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 ($CDCl_3$) $\delta$ 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%); $R_f$ 0.3 (hexanes−ethyl acetate, 10:1); mp 203−205 °C; IR (ATR) 1705 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 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 ($CDCl_3$) $\delta$ 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%); $R_f$ 0.4 (hexanes−ethyl acetate, 2:1); mp 209−211 °C; IR (ATR) 1641 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 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 ($CDCl_3$) $\delta$ 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

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02056.

$^1H$ and $^{13}C$ NMR spectra of products, X-ray crystallographic data (ORTEP) of **3d**, ***cis*-3j**, **3k,l**, **6a**, ***trans*-6g**, ***trans*-6h**, ***trans*-6j,k**, **7c,d,l**, ***threo*-8h**, **9n**, **10h,i**, and **11a,c,d,f,g,j**, DFT calculation data, and CV data (PDF)

X-ray crystallographic CIF data for **3d**, ***cis*-3j**, **3k,l**, **6a**, ***trans*-6g**, ***trans*-6h**, ***trans*-6j,k**, **7c,d,l**, ***threo*-8h**, **9n**, **10h,i**, **11a,c,d,f,g,j** (ZIP)

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### Notes

The authors declare no competing financial interest.

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