Advanced Synthesis & Catalysis

## Accepted Article

**Title:** PdCl2/CuCl2/Bi(OTf)3-promoted Construction of Sulfonyl Dibenzooxabicyclo[3.3.1]nonanes and Arylnaphthalenes via Intramolecular Annulation of Sulfonyl o-Allylarylchromanones

**Authors:** Nai-Chen Hsueh and Meng-Yang Chang



**To be cited as:** *Adv. Synth. Catal.* 10.1002/adsc.202001021

**Link to VoR:** https://doi.org/10.1002/adsc.202001021

10.1002/adsc.202001021

FULL PAPER

DOI: 10.1002/adsc.201((will be filled in by the editorial staff))

# $PdCl_2/CuCl_2/Bi(OTf)_3$-promoted Construction of Sulfonyl Dibenzooxabicyclo[3.3.1]nonanes and Arylnaphthalenes via Intramolecular Annulation of Sulfonyl *o*-Allylarylchromanones

Nai-Chen Hsueh[a] and Meng-Yang Chang*[a,b]

[a] Department of Medicinal and Applied Chemistry, Kaohsiung Medical University, Kaohsiung 807, Taiwan
Email: mychang@kmu.edu.tw
[b] Department of Medical Research, Kaohsiung Medical University Hospital, Kaohsiung 807, Taiwan

Received: ((will be filled in by the editorial staff))

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201######.((Please delete if not appropriate))

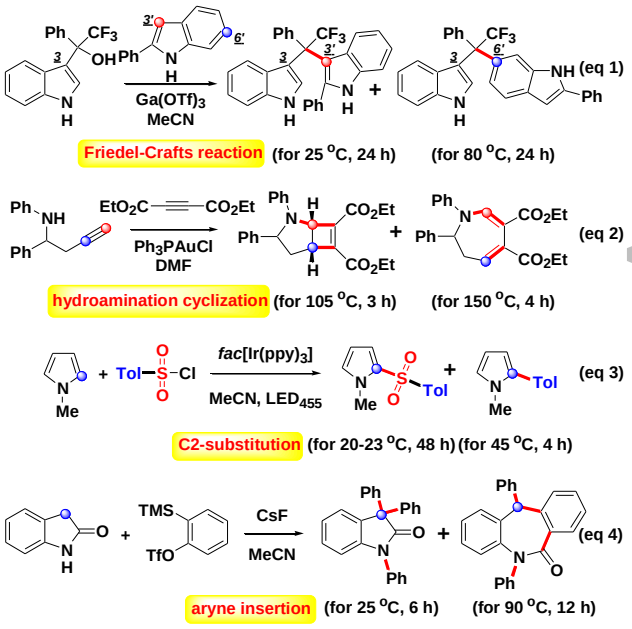
**Abstract.** $PdCl_2/CuCl_2/Bi(OTf)_3$-promoted intramolecular domino annulation of sulfonyl *o*-allylarylchromanones provides tetracyclic sulfonyl dibenzooxabicyclo[3.3.1]nonanes and bicyclic arylnaphthalenes with good to excellent yields in MeOH at room (25 °C) and refluxing (65 °C) temperature, respectively. The starting sulfonyl *o*-allylarylchromanones can be easily obtained from the intermolecular cyclocondensation of α-sulfonyl *o*-hydroxyacetophenones and *o*-allylbenzaldehydes. The uses of various catalysts and solvent systems are investigated herein for convenient transformation. A plausible mechanism is proposed and discussed. This protocol provides one-pot ring closure via carbon-carbon (C-C) bond formation.

**Keywords:** Domino reactions; Oxygen heterocycles; Polycycles; Carbocycles; Oxidation.

## Introduction

In general, the product distribution and tendency for chemoselectivity for organic reactions depends on the synthetic conditions. By switching one parameter, similar reaction conditions can lead to different results. Among these diverse kinds of reaction routes, a number of synthetic efforts have attempted to control one factor or variant to generate different products with approximate or distinct skeletons in recent reports. These adjusting factors included temperature,[1]-[14] catalyst,[15]-[21] additive (e.g. ligand,[22]-[25] base[26]-[27] and reagent[28]-[31]) and solvent.[32]-[35] On the basis of the abovementioned investigations, we found that controlling the temperature change is a simple, economical and direct protocol for affecting the formation of different products in comparison with other variables. Some representative examples are shown in Scheme 1. Rao *et al.* demonstrated that temperature can be used to control $Ga(OTf)_3$-catalyzed regioselective synthesis of unsymmetrical 3,3'- and 3,6'-bisindolylmethanes via the Friedel-Crafts reaction of 3-indolylmethanols with 2-aryl indoles (eq 1).[1] With the involvement of $Ph_3PAuCl$, the Li group reported that a higher temperature can trigger the ring-opening of pyrrolo-*b*-cyclobutenes to dihydro-1*H*-azepines (eq 2).[2]

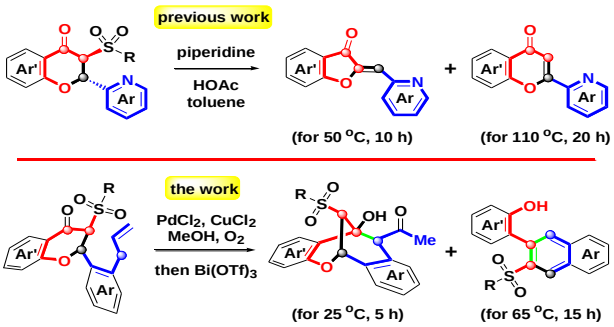
**Scheme 1**. Examples on temperature-controlled reactions



10.1002/adsc.202001021

With the use of *fac*[Ir(ppy)$_3$], Reiser and coworkers established that a slight temperature change (20-23 °C vs. 45 °C) can control two photocatalytic pathways (C2-sulfonylation and desulfonyative C2-arylation) to construct 2-sulfonylpyrroles and 2-arylpyrroles, respectively (eq 3).[3] Mehta *et al.* found that the refluxing temperature can force conversion from *in situ* generated *N*,3,3-triarylated oxindoles to dibenzo[*b*,*e*]azepinones during multiple aryne insertions into the oxindole process (eq 4).[4] Very recently, we have reported the temperature-controlled synthesis of azaaryl aurones and flavones via desulfonylative condensation of α-sulfonyl *o*-hydroxyacetophenones and 2-formyl azaarenes (Scheme 2).[5]

**Scheme 2**. Our temperature-controlled reactions

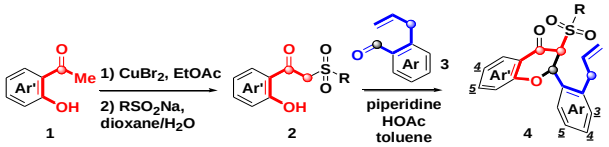



Based on the above literature search for temperature-controlled synthetic methods, and continuing our previous research into temperature-adjusted conversion from aurones to flavones, herein, we present a novel PdCl$_2$/CuCl$_2$/Bi(OTf)$_3$-promoted construction of tetracyclic sulfonyl dibenzooxabicyclo[3.3.1]nonanes and bicyclic arylnaphthalenes via an intramolecular domino Wacker-type annulation of sulfonyl *o*-allylarylchromanones under 25 °C/5 h and 65 °C/15 h conditions, respectively. Two frameworks can play a key role in organic fields. For the preparation of the dibenzooxabicyclo[3.3.1]nonane core system, there are many reports researching the family, such as Kagan's ether.[36]-[37] Recently, with the involvement of BF$_3$·OEt$_2$, we also reported on the synthesis of dibenzofused oxabicyclo[3.3.1]nonane via the intramolecular Friedel-Crafts-type stereocontrolled benzannulation.[38] On the other hand, recent syntheses for sulfonyl arylnaphthalenes have been explored with the chelation assistance of directing groups via ruthenium-catalyzed selective C-H sulfonylation.[39]-[40]

## Results and Discussion

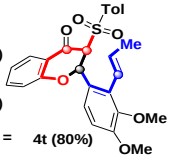
In Scheme 3, the starting sulfonyl 2-allylarylchromanones **4** were prepared via Knoevenagel condensation of sulfonyl *o*-hydroxyacetocephenones **2** and *o*-allylbenzaldehydes **3** with yields in the range of 74%-86% in the presence of piperidine and HOAc under boiling toluene conditions for 10 h. Skeleton **2** was easily prepared from a two-step synthetic route, including (1) CuBr$_2$-mediated α-bromination of *o*-hydroxyacetophenones **1** in refluxing EtOAc and (2) sequential nucleophilic substitution of the corresponding α-bromo-*o*-hydroxyacetophenones with RSO$_2$Na in a refluxing cosolvent of dioxane and H$_2$O.[5] Additionally, skeleton **3** was synthesized from commercially available *m*-hydroxybenzaldehyde via a three-step synthetic route (*O*-allylation, Claisen rearrangement, *O*-alkylation) according to our previous reports.[41]-[43]

**Scheme 3**. Synthesis of **4**




Ar' = Ph, Ar = 3,4-(MeO)$_2$C$_6$H$_2$
R =
4a, Tol (86%)
4b, Ph (83%)
4c, Me (80%)
4d, *n*Bu (78%)
4e, 4-FC$_6$H$_4$ (86%)
4f, 4-MeOC$_6$H$_4$ (84%)
4g, 3-MeC$_6$H$_4$ (78%)
4h, 4-EtC$_6$H$_4$ (79%)
4i, 4-*i*PrC$_6$H$_4$ (84%)
4j, 4-*t*BuC$_6$H$_4$ (80%)

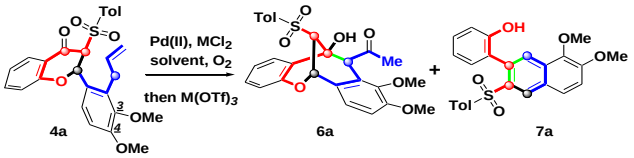
R = Tol, Ar = 3,4-(MeO)$_2$C$_6$H$_2$, Ar' =
4k, 4-FC$_6$H$_3$ (76%)
4l, 5-MeOC$_6$H$_3$ (78%)
R = Tol, Ar' = Ph, Ar =
4m, 3-MeO-4-*i*PrOC$_6$H$_2$ (83%)
4n, 3-MeO-4-*n*BuOC$_6$H$_2$ (82%)
4o, 3-MeOC$_6$H$_3$ (80%)
4p, 3,5-(MeO)$_2$C$_6$H$_2$ (74%)
4q, 3-*n*BuO-5-MeOC$_6$H$_2$ (76%)
4r, 3-BnO-5-MeOC$_6$H$_2$ (80%)
R = Tol, Ar' = 4-Br-naphthyl, Ar =
4s, 3,4-(MeO)$_2$C$_6$H$_2$ (76%)
R = Tol, Ar = 3,4-(MeO)$_2$C$_6$H$_2$, Ar' =
4u, 4-ClC$_6$H$_3$ (76%)
R = Tol, Ar = Ph, Ar' =
4v, Ph (78%)




To examine the Wacker-type aerobic oxidative annulation[44] of sulfonyl *o*-allylarylchromanones **4**, our study commenced with the treatment of model substrate **4a** (R = Tol, Ar' = Ph, Ar = 3,4-(MeO)$_2$Ph, 0.5 mmol) with a combination of PdCl$_2$ (10 mg, 5.6 mol%), CuCl$_2$ (94 mg, 1.4 equiv) and Bi(OTf)$_3$ (100 mg, 15.2 mol%) in MeOH (20 mL) at 25 °C for 5 h (Table 1, entry 1). Initially, with the use of PdCl$_2$/CuCl$_2$, the olefin moiety on **4a** can be converted into methyl ketone under oxygen atmosphere conditions at 25 °C (monitored by TLC). Without further purification, treatment of the reaction mixture with Bi(OTf)$_3$ produced **6a** with a dibenzooxabicyclo[3.3.1]nonane core as the sole product in 78% yield via intramolecular aldol reaction of *in situ* formed **5a** with a 1,7-diketone moiety. In the following step (entry 2), by extending the time from 5 h to 10 h, a similar yield for **6a** was obtained (76%). However, by elevating the temperature as reflux (65 °C), **7a** was yielded as the major product (62%) along with 26% of **6a** (entry 3) for 5 h. By controlling the temperature at 65 °C, extended time (10 h, 15 h, 20 h) can increase the yield of **7a** (75%, 84%, 80% entries 4-6). These results indicate that one can switch between the formation of **6a** (at 25 °C) and **7a** (at 65 °C) by

controlling the temperature: 25 °C/5 h and 65 °C/15 h. The variations for palladium(II) catalysts, metal(II) chloride salts and metal(III) triflates were examined next. With these ideas in mind, $Pd(OAc)_2$ and $Pd(TFA)_2$ were screened (entries 7-10). Compared with $PdCl_2$ (entries 1, 5), $Pd(OAc)_2$ and $Pd(TFA)_2$ provided lower yields in the formation of **6a** or **7a**. Subsequently, $PdCl_2$ and $MnCl_2$ could not initiate Wacker oxidation, and no reaction was observed (entry 11).

**Table 1**. Reaction conditions[a]




| entry | Pd(II)/$MCl_2$/M(OTf)$_3$ | temp | solvent | time | **6a**/**7a**, %[b] |
|---|---|---|---|---|---|
| 1 | $PdCl_2$/$CuCl_2$/Bi(OTf)$_3$ | 25 | MeOH | 5 | 78/—[c] |
| 2 | $PdCl_2$/$CuCl_2$/Bi(OTf)$_3$ | 25 | MeOH | 10 | 76/—[c] |
| 3 | $PdCl_2$/$CuCl_2$/Bi(OTf)$_3$ | 65 | MeOH | 5 | 26/62 |
| 4 | $PdCl_2$/$CuCl_2$/Bi(OTf)$_3$ | 65 | MeOH | 10 | 11/75 |
| 5 | $PdCl_2$/$CuCl_2$/Bi(OTf)$_3$ | 65 | MeOH | 15 | —[c]/84 |
| 6 | $PdCl_2$/$CuCl_2$/Bi(OTf)$_3$ | 65 | MeOH | 20 | —[c]/80 |
| 7 | $Pd(OAc)_2$/$CuCl_2$/Bi(OTf)$_3$ | 25 | MeOH | 5 | 60/—[c] |
| 8 | $Pd(OAc)_2$/$CuCl_2$/Bi(OTf)$_3$ | 65 | MeOH | 15 | —[c]/48 |
| 9 | $Pd(TFA)_2$/$CuCl_2$/Bi(OTf)$_3$ | 25 | MeOH | 5 | 66/—[c] |
| 10 | $Pd(TFA)_2$/$CuCl_2$/Bi(OTf)$_3$ | 65 | MeOH | 15 | —[c]/51 |
| 11 | $PdCl_2$/$MnCl_2$/Bi(OTf)$_3$ | 25 | MeOH | 5 | —[d] |
| 12 | $PdCl_2$/$HgCl_2$/Bi(OTf)$_3$ | 25 | MeOH | 5 | —[e] |
| 13 | $PdCl_2$/$CuCl_2$/In(OTf)$_3$ | 25 | MeOH | 5 | 65/12 |
| 14 | $PdCl_2$/$CuCl_2$/In(OTf)$_3$ | 65 | MeOH | 15 | 21/40 |
| 15 | $PdCl_2$/$CuCl_2$/Fe(OTf)$_3$ | 25 | MeOH | 5 | 67/8 |
| 16 | $PdCl_2$/$CuCl_2$/Fe(OTf)$_3$ | 65 | MeOH | 15 | 18/45 |
| 17 | $PdCl_2$/$CuCl_2$/Bi(OTf)$_3$ | 25 | EtOH | 5 | 70/—[c] |
| 18 | $PdCl_2$/$CuCl_2$/Bi(OTf)$_3$ | 65 | EtOH | 15 | —[c]/78 |
| 19 | $PdCl_2$/$CuCl_2$/Bi(OTf)$_3$ | 25 | THF | 5 | —[f] |
| 20 | $PdCl_2$/$CuCl_2$/Bi(OTf)$_3$ | 25 | $MeNO_2$ | 5 | —[f] |
| 21[g] | $PdCl_2$/$CuCl_2$/Bi(OTf)$_3$ | 25 | MeOH | 5 | 75/—[c] |
| 22[h] | $PdCl_2$/$CuCl_2$/Bi(OTf)$_3$ | 25 | MeOH | 5 | 18[f]/—[c] |

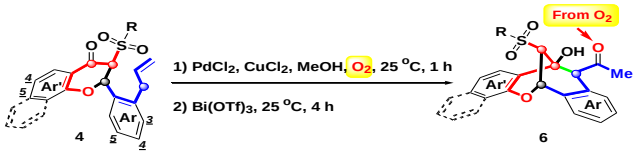
[a] The reactions were run on a 0.5 mmol scale with **4a**, palladium(II) catalyst (10 mg), metal(II) chloride (1.4 equiv), $O_2$ (bubbled), monitored by TLC plate; then, metal(III) triflate (100 mg), temp (°C), solvent (20 mL), time (h).
[b] Isolated yields.
[c] No detection.
[d] No reaction.
[e] Complex unknown products.
[f] **4a** (for entry 19, 73%; entry 20, 68%; entry 22, 49%) was recovered.
[g] 200 mg of Bi(OTf)$_3$.
[h] Dry air.

By changing the metal(II) salt from $MnCl_2$ to $HgCl_2$, a complex unknown mixture was detected (entry 12). Next, two Lewis acids: In(OTf)$_3$ and Fe(OTf)$_3$, were surveyed. Under the 25 °C/5 h conditions (entries 13, 15), two metal triflates provided **6a** as the major product (65% and 67%). Thus, the trend for metal triflates is Bi(OTf)$_3$ > In(OTf)$_3$ ≥ Fe(OTf)$_3$. Changing the conditions to 65 °C/15 h (entries 14, 16), major **7a** was obtained (40% and 45%). From the above results, the combination of $PdCl_2$, $CuCl_2$ and Bi(OTf)$_3$ gave optimal results for the one-pot construction of a benzocyclic ring system. Then, three reaction solvents (EtOH, THF, $MeNO_2$) were investigated. In entries 17 and 18, EtOH can provide **6a** and **7a** in 70% and 78% yields, respectively, under 25 °C/5 h or 65 °C/15 h conditions. Compared with MeOH (entries 1, 5, 78% and 84%), EtOH provided slightly lower yields. For THF and $MeNO_2$ (two nonalcoholic solvents), however, no Wacker-type oxidation was triggered for either solvent, and only **4a** was recovered in 73% and 68% yields (entries 19, 20). Based on these results, we understand that Wacker-type oxidation requires the involvement of alcoholic solvents (MeOH or EtOH). Wang *et al.* demonstarted that MeOH can be used to initiate a catalytic cycle.[45] By increasing the catalytic amount of Bi(OTf)$_3$, entry 21 shows that the yield of **6a** is maintained (75%). In entry 22, by displacing the molecular oxygen to dry air conditions, only 18% of **6a** is generated, along with the recovery of **4a** (49%). As a result, we conclude that the combination of $PdCl_2$/$CuCl_2$/Bi(OTf)$_3$ provides optimal conditions (25 °C/5 h; 65 °C/15 h) in the presence of an oxygen atmosphere for the preparation of **6a** and **7a**.

To study the scope and limitations of this approach, sulfonyl *o*-allylarylchromanones **4** were reacted with a combination of $PdCl_2$, $CuCl_2$ and Bi(OTf)$_3$ to afford diversified **6** in the presence of a molecular oxygen atmosphere under 25 °C and 5 h conditions, as shown in Table 2. Among entries 1-14, the one-pot domino formation of **6a**-**6n** shows that these substituents (Ar', R and Ar) do not obviously affect the yield changes (70%-83%). For the aryl substituents (Ar') of **4**, phenyl, 4-fluorophenyl, 4-chlorophenyl and 4-bromo-2-naphthyl groups were found to be appropriate. For sulfonyl substituents (R) of **4**, both aliphatic (Me and *n*Bu) and aromatic (Tol, Ph, 3-Me$C_6H_4$, 4-Et$C_6H_4$, 4-*i*Pr$C_6H_4$ and 4-*t*Bu$C_6H_4$) groups were well-tolerated. Different electron-donating oxygenated aryl groups (for Ar) on **4** were also suitable for generating the dibenzofused bridged structure **6**. Furthermore, the stereochemical tetracyclic core bridged structures of **6d** and **6j** with four contiguous stereocenters were determined by the single-crystal X-ray crystallography.[46]

10.1002/adsc.202001021

**Table 2**. Synthesis of **6**[a]

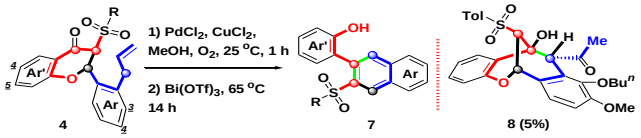



| entry | **4**, Ar' =, R =, Ar = | **6** (%)[b] |
|---|---|---|
| 1 | **4a**, Ph, Tol, 3,4-$(MeO)_2C_6H_2$ | **6a**, 78 |
| 2 | **4b**, Ph, Tol, 3,4-$(MeO)_2C_6H_2$ | **6b**, 70 |
| 3 | **4c**, Ph, Me, 3,4-$(MeO)_2C_6H_2$ | **6c**, 72 |
| 4 | **4d**, Ph, *n*Bu, 3,4-$(MeO)_2C_6H_2$ | **6d**, 76 |
| 5 | **4g**, Ph, 3-$MeC_6H_4$, 3,4-$(MeO)_2C_6H_2$ | **6e**, 80 |
| 6 | **4h**, Ph, 4-$EtC_6H_4$, 3,4-$(MeO)_2C_6H_2$ | **6f**, 74 |
| 7 | **4i**, Ph, 4-*i*$PrC_6H_4$, 3,4-$(MeO)_2C_6H_2$ | **6g**, 82 |
| 8 | **4j**, Ph, 4-*t*$BuC_6H_4$, 3,4-$(MeO)_2C_6H_2$ | **6h**, 76 |
| 9 | **4k**, 4-$FC_6H_3$, Tol, 3,4-$(MeO)_2C_6H_2$ | **6i**, 80 |
| 10 | **4o**, Ph, Tol, 3-$MeOC_6H_3$ | **6j**, 73 |
| 11 | **4p**, Ph, Tol, 3,5-$(MeO)_2C_6H_2$[c] | **6k**, 76 |
| 12 | **4q**, Ph, Tol, 3-*n*BuO-5-$MeOC_6H_2$[c] | **6l**, 83 |
| 13 | **4s**, 4-Br-2-naphthyl, Tol, 3,5-$(MeO)_2C_6H_2$ | **6m**, 80 |
| 14 | **4u**, 4-$ClC_6H_3$, Tol, 3,4-$(MeO)_2C_6H_2$ | **6n**, 78 |

[a] The reactions were run on a 0.5 mmol scale with **4**, $PdCl_2$ (10 mg, 5.6 mol%), $CuCl_2$ (94 mg, 1.4 equiv), $O_2$ (bubbled, 1 atm), MeOH (20 mL), 25 °C, 1 h; then $Bi(OTf)_3$ (100 mg, 15.2 mol %), 25 °C, 4 h.
[b] Isolated yields.
[c] **4p** (ratio = 8:1) and **4q** (ratio = 6:1) were obtained as a mixture of isomers (by $^1$H-NMR spectrum).

With these results in hand, the reaction conditions, 65 °C and 15 h, were investigated next for the generation of sulfonyl arylnaphthalenes, as shown in Table 3, entries 1-15. For the formation of **7a**-**7o**, Ar', R and Ar substituents on **4** can maintain the isolated yields in the range of 70%-88%. For the electronic nature of aryl substituents (Ar') of **4**, not only were electron-neutral (phenyl) groups suitable but so were electron-withdrawing (fluoro) and electron-donating (methoxy) groups. For the sulfonyl substituents (R) of **1**, aliphatic (methyl, *n*-butyl) and aromatic (alkylphenyl, fluorophenyl, methoxyphenyl) groups were well-tolerated. For the Ar substituent of **4**, arene with dioxygenated groups (3,4-$(MeO)_2C_6H_2$, 3-*i*PrO-4-$MeOC_6H_2$, 3-*n*BuO-4-$MeOC_6H_2$) could be applied. In particular, **8** with an *endo*-acetyl group can be isolated in trace amounts (5% yield). The stereochemical structure of **8** with four contiguous stereocenters was determined by single-crystal X-ray crystallography.[46] By use of the reflux temperature and extended time, the one-pot domino conversion from tetracyclic sulfonyl dibenzooxabicyclo[3.3.1]nonane to bicyclic sulfonyl arylnaphthalenes was achieved via a cascade procedure.

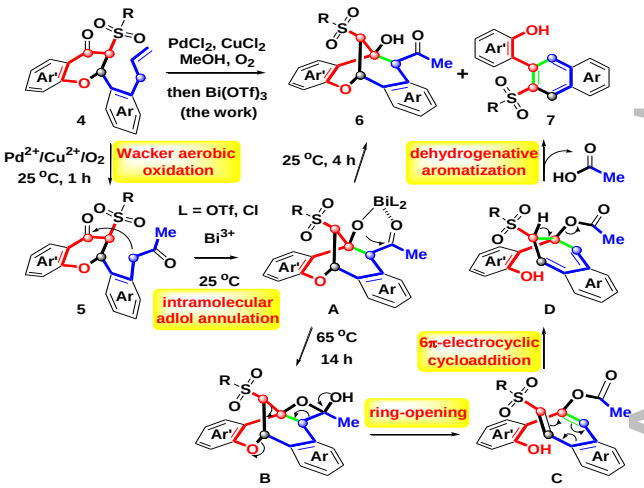
**Table 3**. Synthesis of **7**[a]




| entry | **4**, Ar' =, R =, Ar = | **7** (%)[b] |
|---|---|---|
| 1 | **4a**, Ph, Tol, 3,4-$(MeO)_2C_6H_2$ | **7a**, 84 |
| 2 | **4b**, Ph, Tol, 3,4-$(MeO)_2C_6H_2$ | **7b**, 85 |
| 3 | **4c**, Ph, Me, 3,4-$(MeO)_2C_6H_2$ | **7c**, 80 |
| 4 | **4d**, Ph, *n*Bu, 3,4-$(MeO)_2C_6H_2$ | **7d**, 83 |
| 5 | **4e**, Ph, 4-$FC_6H_4$, 3,4-$(MeO)_2C_6H_2$ | **7e**, 78 |
| 6 | **4f**, Ph, 4-$MeOC_6H_4$, 3,4-$(MeO)_2C_6H_2$ | **7f**, 88 |
| 7 | **4g**, Ph, 3-$MeC_6H_4$, 3,4-$(MeO)_2C_6H_2$ | **7g**, 83 |
| 8 | **4h**, Ph, 4-$EtC_6H_4$, 3,4-$(MeO)_2C_6H_2$ | **7h**, 74 |
| 9 | **4i**, Ph, 4-*i*$PrC_6H_4$, 3,4-$(MeO)_2C_6H_2$ | **7i**, 76 |
| 10 | **4j**, Ph, 4-*t*$BuC_6H_4$, 3,4-$(MeO)_2C_6H_2$ | **7j**, 78 |
| 11 | **4k**, 4-$FC_6H_3$, Tol, 3,4-$(MeO)_2C_6H_2$ | **7k**, 72 |
| 12 | **4l**, 5-$MeOC_6H_3$, Tol, 3,4-$(MeO)_2C_6H_2$ | **7l**, 83 |
| 13 | **4m**, Ph, Tol, 3-*i*PrO-4-$MeOC_6H_2$ | **7m**, 82 |
| 14 | **4n**, Ph, Tol, 3-*n*BuO-4-$MeOC_6H_2$ | **7n**, 79[c] |
| 15 | **4u**, 4-$ClC_6H_3$, Tol, 3,4-$(MeO)_2C_6H_2$ | **7o**, 70 |

[a] The reactions were run on a 0.5 mmol scale with **4**, $PdCl_2$ (10 mg, 5.6 mol%), $CuCl_2$ (94 mg, 1.4 equiv), $O_2$ (bubbled, 1 atm), MeOH (20 mL), 25 °C, 1 h; then $Bi(OTf)_3$ (100 mg, 15.2 mol %), 65 °C, 14 h.
[b] Isolated yields.
[c] 5% of **8** was isolated.

**Scheme 4**. Plausible reaction pathway

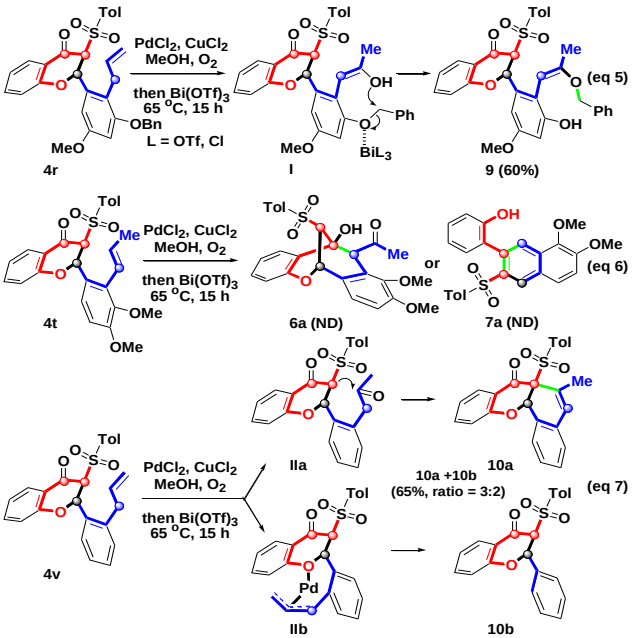



On the basis of our experimental results (Tables 2 and 3), a plausible reaction pathway for the formation of **6** and **7** is illustrated in Scheme 4. Initially, by the Dean-Stark distillation condition (a common combination of piperidine and HOAc), intermolecular Knoevenagel condensation of **2** with **3** formed **4**. Then, $PdCl_2$/$CuCl_2$-promoted Wacker oxidation of the terminal olefinic group on **4** generated **5** with a

10.1002/adsc.202001021

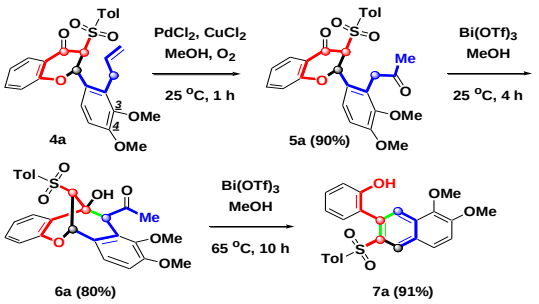
methylketone moiety in the presence of an oxygen atmosphere. Under the 25°C condition, $Bi(OTf)_3$ promoted intramolecular aldol annulation leading to **A** with a ring bismuth-cheated six-member bridged conformation. After extending the reaction time (4 h), **6** was generated via the hydrolysis of **A**. On the other hand, by elevating the reaction temperature (65 °C), the hydroxyl group of **A** can attack its carbonyl group to provide **B**. Furthermore, by releasing the ring-strain on the four-membered ring on **B**, a ring-opening of oxetane and sequential leaving of the phenol group yielded **C** with a divinylaryl structure. In the following 6π-electrocyclic cycloaddition, **D** with a dihydronaphthalene core skeleton was achieved. Finally, the construction of **7** was realized via the dehydrogenative aromatization of **D**. From the predicted process, we found that switching temperature and time organized a continuous sequence of intramolecular ring-opening and ring closure, such that the formation of **6** and **7** was provided selectively. To the best of our knowledge, no temperature- and time-dependent transformations from the bridged structure of **6** to fused naphthalene **7** have been reported previously.

**Scheme 5**. $PdCl_2/CuCl_2/Bi(OTf)_3$-promoted reaction of **4r**, **4t**, and **4v**




With the above experimental results, three sulfonyl *o*-allylarylchromanones **4r**, **4t** and **4v** were examined next (Scheme 5). In particular, when **4r** was chosen as the starting substrate with a C3-benzyloxy aryl group (for Ar), sole **9** having a moiety of benzyl enol ether was isolated in 60% yield under 65 °C and 15 h conditions via the benzyl migration process (for intermediate **I**, eq 5). The desired bridged or naphthalene skeleton was not detected via the $PdCl_2/CuCl_2/Bi(OTf)_3$-promoted process. On the other hand, by controlling **4r** with an internal olefin moiety as the starting material, no desired **6a** and **7a** was produced under 65 °C and 15 h conditions. Only **4t** was recovered in 72% yield (eq 6). On the basis of these experimental results, we understand that the terminal alkenyl group is an important substituent in decreasing the reactivity of the initial Wacker oxidation on **4**. In particular, after changing the Ar substituent from an electron-donating aromatic group to a phenyl group (Ar = Ph), $PdCl_2/CuCl_2/Bi(OTf)_3$-promoted reactions of **4v** produced the unseparated mixture of dihydrobenzo[*c*]xanthen-7-one **10a** and flavanone **10b** with a ratio of 3:2 (determinated by $^1$H-NMR spectrum) in 65% yield (eq 7). After accomplishing Wacker aerobic oxidation, the intramolecular aldol cyclocondensation of **IIa** provided **10a**. On the other way, minor amounts of **10b** could be isolated[47] via palladium-promoted direct deallylation of **IIb** having the plausible chelation between oxygen atom and $\eta^3$-allylpalladium. However, similar phenomenon on rhodium and iron-promoted deallylation of substituted allylarenes has been investigated by the Kakiuchi group[48a] and the Jiao group.[48b]-[48c] Compared with the electron-neutral phenyl group, these results indicate that the oxygenated Ar group can enrich electron density of the aromatic system such that *in situ* formed α-enolized carbon of methyl ketone on **5** is prepared to attack the carbonyl group of chromanone easily in the formation of **6**.

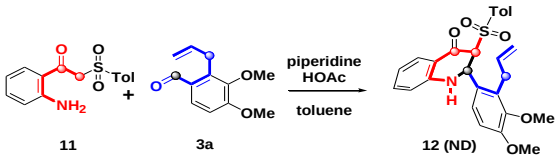
**Scheme 6**. Stepwise control experiments




To understand the reaction procedure, stepwise control experiments were examined, as shown in Scheme 6. Initially, $PdCl_2/CuCl_2$-promoted Wacker oxidation of **4a** produced **5a** in 90% yield at 25 °C for 1 h. **5a** can be a key intermediate to initiate the following reactions. With **5a** in hand, the formation of **6a** and **7a** was studied next. By using catalytic amounts of $Bi(OTf)_3$, **5a** was converted to **6a** in 80% yield under 25 °C/4 h conditions. Then, by extending the time, **7a** was produced in 91% yield under 65 °C/10 h conditions. Compared with the one-pot process from **4a** to **6a** (78%) or **7a** (84%), the stepwise route provided lower total yields for the formation of **6a** (72%) and **7a** (66%). The stepwise

pathway confirms that temperature and time can control the overall mechanism (see Scheme 4).

**Scheme 7**. Reaction of **11** and **3a**




11 3a 12 (ND)

To understand the liminations of the substrate scope, 1-(2-aminophenyl)ethanone **11** was chosen as a starting substrate to examine the abovementioned $PdCl_2/CuCl_2/Bi(OTf)_3$-promoted domino annulation, as shown in Scheme 7. However, Knoevenagel condensation of **11** with **3a** afforded unidentified and unknown mixture in the presence of piperidine and HOAc under refluxing toluene conditions. The desired **12** was not obtained such that the following conversions (for **6** and **7**) could not be examined. Compared with *o*-hydroxyacetocephenones **2**, **11** is an inappropriate substrate for domino annulation. Although the substrate scope is limited, the present route can provide a convenient transformation for generating sulfonyl dibenzooxabicyclo[3.3.1]nonanes and sulfonyl arylnaphthalenes.

## Conclusion

In summary, we have developed a temperature-controlled one-pot route for the synthesis of tetracyclic sulfonyl dibenzooxabicyclo[3.3.1]nonanes and bicyclic arylnaphthalenes via $PdCl_2/CuCl_2/Bi(OTf)_3$-promoted domino annulation of sulfonyl *o*-allylarylchromanones in MeOH at room (25 °C) or refluxing (65 °C) temperature. The one-pot process provides a series of cascade pathways for carbon-carbon (C-C) bond formation. The structures of the key bridged products were confirmed by X-ray crystallography. Further investigations regarding the synthetic application of temperature-controlled reactions will be conducted and published in due course.

## Experimental Section

**General.** All reagents and solvents were obtained from commercial sources and used without further purification. Reactions were routinely carried out under an atmosphere of dry air with magnetic stirring. The heating mantle is used to provide a stable heat source. Products in organic solvents were dried with anhydrous magnesium sulfate before concentration in vacuo. Melting points were determined with a SMP3 melting apparatus. $^1H$ and $^{13}C$ NMR spectra were recorded on a Varian INOVA-400 spectrometer operating at 400 and at 100 MHz, respectively. Chemical shifts (δ) are reported in parts per million (ppm) and the coupling constants (*J*) are given in Hertz. High resolution mass spectra (HRMS) were measured with a mass spectrometer Finnigan/Thermo Quest MAT 95XL. X-ray crystal structures were obtained with an Enraf-Nonius FR-590 diffractometer (CAD4, Kappa CCD).

The starting materials **2** and **3** were known compounds and the analytical data were consistent with those in the references.[41]-[43]

**A representative synthetic procedure of skeleton 4 is as follows:** Piperidine (70 mg, 0.8 mmol) was added to a solution of **2** (1.0 mmol) and **3** (1.1 mmol) and in toluene (10 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 10 min. Then, HOAc (40 mg, 0.7 mmol) was added to the reaction mixture. The reaction mixture was stirred at reflux (110 °C) for 10 h. The reaction mixture was cooled to 25 °C and the solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with $CH_2Cl_2$ (3 x 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc = 8/1~4/1) afforded **4**.

**2-(2-Allyl-3,4-dimethoxyphenyl)-3-(toluene-4-sulfonyl)chroman-4-one (4a).** Yield = 86% (411 mg); Colorless solid; mp = 145-147 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{27}H_{27}O_6S$ 479.1528, found 479.1523; $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.76 (dd, *J* = 1.6, 8.0 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.43 (dt, *J* = 2.0, 7.6 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 6.94 (dt, *J* = 0.8, 8.0 Hz, 1H), 6.81 (dt, *J* = 0.4, 8.0 Hz, 1H), 6.68 (s, 1H), 6.67 (d, *J* = 8.8 Hz, 1H), 6.56 (d, *J* = 8.8 Hz, 1H), 6.09-6.00 (m, 1H), 5.12 (dq, *J* = 1.6, 10.0 Hz, 1H), 5.03 (dq, *J* = 1.6, 16.8 Hz, 1H), 4.30 (d, *J* = 0.8 Hz, 1H), 3.79 (s, 3H), 3.75 (s, 3H), 3.74-3.68 (m, 1H), 3.63-3.57 (m, 1H), 2.38 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 182.7, 159.3, 153.2, 147.9, 145.6, 137.3, 136.3, 134.2, 132.0, 129.5 (2x), 129.3 (2x), 127.5, 126.7, 121.7, 121.4, 120.3, 118.2, 115.8, 109.9, 73.5, 72.6, 60.8, 55.5, 29.9, 21.6.

**2-(2-Allyl-3,4-dimethoxyphenyl)-3-benzenesulfonylchroman-4-one (4b).** Yield = 83% (385 mg); Colorless solid; mp = 168-170 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{26}H_{25}O_6S$ 465.1372, found 465.1378; $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.82-7.79 (m, 2H), 7.76 (dd, *J* = 1.6, 8.0 Hz, 1H), 7.58 (dt, *J* = 1.2, 7.6 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.44-7.40 (m, 1H), 6.94 (dt, *J* = 1.2, 8.4 Hz, 1H), 6.80 (dd, *J* = 0.4, 8.4 Hz, 1H), 6.70 (s, 1H), 6.67 (d, *J* = 8.8 Hz, 1H), 6.56 (d, *J* = 8.8 Hz, 1H), 6.10-6.00 (m, 1H), 5.12 (dq, *J* = 1.6, 10.0 Hz, 1H), 5.03 (dq, *J* = 1.6, 16.8 Hz, 1H), 4.34 (d, *J* = 0.8 Hz, 1H), 3.79 (s, 3H), 3.75 (s, 3H), 3.74-3.67 (m, 1H), 3.64-3.58 (m, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 182.5, 159.3, 153.2, 147.9, 137.5, 137.1, 136.3, 134.4, 132.0, 129.3 (2x), 128.9 (2x), 127.4, 126.7, 121.8, 121.5, 120.3, 118.2, 115.9, 109.9, 73.5, 72.6, 60.8, 55.5, 29.9.

**2-(2-Allyl-3,4-dimethoxyphenyl)-3-methanesulfonylchroman-4-one (4c).** Yield = 80% (322 mg); Colorless gum; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{23}O_6S$ 403.1215, found 403.1218; $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.88 (dd, *J* = 1.6, 8.0 Hz, 1H), 7.50 (dt, *J* = 2.0, 7.6 Hz, 1H), 7.00 (dt, *J* = 0.8, 8.0 Hz, 1H), 6.96 (d, *J* = 8.4 Hz, 1H), 6.72 (d, *J* = 8.8 Hz, 1H), 6.64 (s,

1H), 6.60 (d, *J* = 8.4 Hz, 1H), 6.09-5.99 (m, 1H), 5.11 (dq, *J* = 1.6, 10.0 Hz, 1H), 5.01 (dq, *J* = 1.6, 16.8 Hz, 1H), 4.28 (s, 1H), 3.78 (s, 3H), 3.75 (s, 3H), 3.70-3.59 (m, 2H), 3.05 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 183.4, 159.5, 153.1, 147.8, 137.9, 136.4, 132.1, 127.3, 126.8, 121.8, 121.7, 119.9, 118.5, 115.6, 109.8, 71.9, 70.2, 60.6, 55.4, 40.9, 29.9.

**2-(2-Allyl-3,4-dimethoxyphenyl)-3-(butane-1-sulfonyl)chroman-4-one (4d).** Yield = 78% (346 mg); Colorless solid; mp = 111-113 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{24}H_{29}O_6S$ 445.1685, found 445.1689; $^{1}H$ NMR (400 MHz, $CDCl_3$): δ 7.89 (dd, *J* = 1.6, 8.0 Hz, 1H), 7.53 (dt, *J* = 2.0, 7.6 Hz, 1H), 7.03 (dt, *J* = 0.8, 8.4 Hz, 1H), 6.99 (dd, *J* = 0.8, 8.4 Hz, 1H), 6.74 (d, *J* = 8.8 Hz, 1H), 6.66 (br d, *J* = 0.8 Hz, 1H), 6.62 (d, *J* = 8.8 Hz, 1H), 6.11-6.01 (m, 1H), 5.12 (dq, *J* = 1.6, 10.0 Hz, 1H), 5.02 (dq, *J* = 1.6, 16.8 Hz, 1H), 4.22 (d, *J* = 1.2 Hz, 1H), 3.80 (s, 3H), 3.79 (s, 3H), 3.71-3.59 (m, 2H), 3.27-3.15 (m, 2H), 1.89-1.82 (m, 2H), 1.52-1.43 (m, 2H), 0.95 (t, *J* = 7.6 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 184.0, 159.7, 153.2, 148.0, 138.0, 136.5, 132.2, 127.7, 126.9, 121.9, 121.7, 120.2, 118.6, 115.8, 109.9, 71.9, 68.6, 60.8, 55.5, 52.9, 30.0, 23.5, 21.6, 13.5.

**2-(2-Allyl-3,4-dimethoxyphenyl)-3-(4-fluorobenzenesulfonyl)chroman-4-one (4e).** Yield = 84% (405 mg); Colorless solid; mp = 132-134 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{26}H_{24}FO_6S$ 483.1278, found 483.1293; $^{1}H$ NMR (400 MHz, $CDCl_3$): δ 7.83-7.79 (m, 2H), 7.75 (dd, *J* = 1.6, 8.0 Hz, 1H), 7.44 (dt, *J* = 2.0, 7.6 Hz, 1H), 7.12-7.08 (m, 2H), 6.95 (dt, *J* = 1.2, 8.0 Hz, 1H), 6.80 (dd, *J* = 0.4, 8.4 Hz, 1H), 6.69 (s, 1H), 6.66 (d, *J* = 8.8 Hz, 1H), 6.57 (d, *J* = 8.8 Hz, 1H), 6.11-6.01 (m, 1H), 5.13 (dq, *J* = 1.6, 10.0 Hz, 1H), 5.03 (dq, *J* = 1.6, 16.8 Hz, 1H), 4.33 (d, *J* = 1.2 Hz, 1H), 3.79 (s, 3H), 3.76 (s, 3H), 3.74-3.67 (m, 1H), 3.64-3.58 (m, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 182.5, 166.2 (d, *J* = 256.3 Hz), 159.2, 153.3, 148.0, 137.6, 136.3, 133.1 (d, *J* = 3.1 Hz), 132.3 (d, *J* = 9.1 Hz, 2x), 132.0, 127.3, 126.7, 121.8, 121.6, 120.2, 118.2, 116.2 (d, *J* = 22.7 Hz, 2x), 115.9, 109.9, 73.6, 72.7, 60.8, 55.5, 30.0.

**2-(2-Allyl-3,4-dimethoxyphenyl)-3-(4-methoxybenzenesulfonyl)chroman-4-one (4f).** Yield = 84% (415 mg); Colorless solid; mp = 130-132 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{27}H_{27}O_7S$ 495.1478, found 495.1482; $^{1}H$ NMR (400 MHz, $CDCl_3$): δ 7.75 (dd, *J* = 1.6, 8.0 Hz, 1H), 7.69 (d, *J* = 8.8 Hz, 2H), 7.40 (dt, *J* = 1.6, 8.8 Hz, 1H), 6.92 (dt, *J* = 0.8, 8.0 Hz, 1H), 6.87 (d, *J* = 9.2 Hz, 2H), 6.79 (dd, *J* = 0.8, 8.4 Hz, 1H), 6.66 (s, 1H), 6.66 (d, *J* = 8.4 Hz, 1H), 6.55 (d, *J* = 8.8 Hz, 1H), 6.09-5.99 (m, 1H), 5.10 (dq, *J* = 1.6, 10.0 Hz, 1H), 5.02 (dq, *J* = 1.6, 17.2 Hz, 1H), 4.30 (d, *J* = 1.2 Hz, 1H), 3.80 (s, 3H), 3.77 (s, 3H), 3.73 (s, 3H), 3.72-3.66 (m, 1H), 3.62-3.58 (m, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 182.7, 164.2, 159.2, 153.1, 147.8, 137.3, 136.3, 131.9, 131.5 (2x), 128.3, 127.4, 126.6, 121.7, 121.3, 120.2, 118.1, 115.8, 114.0 (2x), 109.8, 73.6, 72.7, 60.7, 55.6, 55.4, 29.9.

**2-(2-Allyl-3,4-dimethoxyphenyl)-3-(toluene-3-sulfonyl)chroman-4-one (4g).** Yield = 78% (373 mg); Colorless solid; mp = 144-146 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{27}H_{27}O_6S$ 479.1528, found 479.1534; $^{1}H$ NMR (400 MHz, $CDCl_3$): δ 7.76 (dd, *J* = 1.6, 8.0 Hz, 1H), 7.62-7.59 (m, 2H), 7.42 (dt, *J* = 2.0, 8.8 Hz, 1H), 6.38-6.31 (m, 2H), 6.94 (dt, *J* = 1.2, 8.0 Hz, 1H), 6.80 (dd, *J* = 0.4, 8.4 Hz, 1H), 6.67 (s, 1H), 6.66 (d, *J* = 8.4 Hz, 1H), 6.56 (d, *J* = 8.8 Hz, 1H), 6.09-5.99 (m, 1H), 5.11 (dq, *J* = 1.6, 10.0 Hz, 1H), 5.02 (dq, *J* = 1.6, 17.2 Hz, 1H), 4.33 (d, *J* = 0.8 Hz, 1H), 3.79 (s, 3H), 3.75 (s, 3H), 3.74-3.67 (m, 1H), 3.62-3.56 (m, 1H), 2.34 (s, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 182.5, 159.3, 153.2, 147.9, 139.2, 137.4, 136.8, 136.3, 135.2, 132.0, 129.5, 128.8, 127.5, 126.6, 126.5, 121.7, 121.4, 120.3, 118.1, 115.8, 109.9, 73.5, 72.6, 60.8, 55.5, 29.9, 21.2.

**2-(2-Allyl-3,4-dimethoxyphenyl)-3-(4-ethylbenzenesulfonyl)chroman-4-one (4h).** Yield = 79% (389 mg); Colorless solid; mp = 133-135 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{28}H_{29}O_6S$ 493.1685, found 493.1691; $^{1}H$ NMR (400 MHz, $CDCl_3$): δ 7.75 (dd, *J* = 1.6, 8.0 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.40 (dt, *J* = 2.0, 9.2 Hz, 1H), 7.24 (d, *J* = 8.8 Hz, 2H), 6.93 (dt, *J* = 0.8, 8.0 Hz, 1H), 6.78 (dd, *J* = 0.8, 8.4 Hz, 1H), 6.67 (s, 1H), 6.66 (d, *J* = 8.8 Hz, 1H), 6.56 (d, *J* = 8.4 Hz, 1H), 6.09-5.99 (m, 1H), 5.12 (dq, *J* = 1.6, 10.0 Hz, 1H), 5.03 (dq, *J* = 1.6, 17.2 Hz, 1H), 4.31 (d, *J* = 1.2 Hz, 1H), 3.79 (s, 3H), 3.75 (s, 3H), 3.74-3.67 (m, 1H), 3.62-3.56 (m, 1H), 2.66 (q, *J* = 7.6 Hz, 2H), 1.20 (t, *J* = 7.6 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 192.7, 159.2, 153.2, 151.6, 147.9, 137.3, 136.3, 134.2, 132.0, 129.5 (2x), 128.3 (2x), 127.5, 126.7, 121.8, 121.4, 120.3, 118.1, 115.9, 109.9, 73.6, 72.7, 60.8, 55.5, 29.9, 28.9, 15.0. Single-crystal X-ray diagram: crystal of compound **4h** was grown by slow diffusion of EtOAc into a solution of compound **4h** in $CH_2Cl_2$ to yield colorless prisms. The compound crystallizes in the triclinic crystal system, space group P -1, *a* = 8.3132(9) Å, *b* = 8.4764(9) Å, *c* = 17.733(2) Å, *V* = 1209.3(2) $Å^3$, *Z* = 2, $d_{calcd}$ = 1.353 $g/cm^3$, *F*(000) = 520, 2*θ* range 1.180~26.411°, R indices (all data) R1 = 0.1052, wR2 = 0.2771.

**2-(2-Allyl-3,4-dimethoxyphenyl)-3-(4-isopropylbenzenesulfonyl)chroman-4-one (4i).** Yield = 84% (425 mg); Colorless solid; mp = 152-154 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{29}H_{31}O_6S$ 507.1841, found 507.1846; $^{1}H$ NMR (400 MHz, $CDCl_3$): δ 7.75 (dd, *J* = 2.0, 8.0 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.38 (dt, *J* = 2.0, 9.2 Hz, 1H), 7.25 (d, *J* = 8.8 Hz, 2H), 6.91 (dt, *J* = 0.8, 8.0 Hz, 1H), 6.74 (dd, *J* = 0.8, 8.4 Hz, 1H), 6.67 (s, 1H), 6.66 (d, *J* = 8.4 Hz, 1H), 6.56 (d, *J* = 8.8 Hz, 1H), 6.07-5.99 (m, 1H), 5.12 (dq, *J* = 1.6, 10.0 Hz, 1H), 5.03 (dq, *J* = 1.6, 17.2 Hz, 1H), 4.32 (d, *J* = 1.2 Hz, 1H), 3.78 (s, 3H), 3.75 (s, 3H), 3.74-3.66 (m, 1H), 3.62-3.56 (m, 1H), 2.94-2.87 (m, 1H), 1.20 (d, *J* = 7.2 Hz, 6H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ 182.6, 159.2, 156.1, 153.2, 147.9, 137.3, 136.3, 134.3, 132.0, 129.6 (2x), 127.5, 126.9 (2x), 126.7, 121.8, 121.4, 120.3, 118.1, 115.9, 109.9, 73.8, 72.8, 60.8, 55.5, 34.2, 30.0, 23.5, 23.4.

**2-(2-Allyl-3,4-dimethoxyphenyl)-3-(4-t-butylbenzenesulfonyl)chroman-4-one (4j).** Yield = 80% (432 mg); Colorless gum; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{30}H_{33}O_6S$ 521.1998, found 521.2003; $^{1}H$

NMR (400 MHz, $CDCl_3$): δ 7.74 (dd, *J* = 2.0, 8.0 Hz, 1H), 7.71 (d, *J* = 8.8 Hz, 2H), 7.40 (d, *J* = 8.8 Hz, 2H), 7.35 (dt, *J* = 1.6, 8.4 Hz, 1H), 6.91 (dt, *J* = 0.8, 8.0 Hz, 1H), 6.73 (dd, *J* = 0.4, 8.4 Hz, 1H), 6.67 (d, *J* = 8.8 Hz, 1H), 6.66 (s, 1H), 6.55 (d, *J* = 8.8 Hz, 1H), 6.08-5.99 (m, 1H), 5.12 (dq, *J* = 1.6, 10.0 Hz, 1H), 5.03 (dq, *J* = 1.6, 17.2 Hz, 1H), 4.33 (d, *J* = 0.8 Hz, 1H), 3.78 (s, 3H), 3.75 (s, 3H), 3.74-3.66 (m, 1H), 3.62-3.55 (m, 1H), 1.27 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 182.6, 159.1, 158.4, 153.1, 147.9, 137.3, 136.3, 133.8, 132.0, 129.3 (2x), 127.4, 126.7, 125.8 (2x), 121.7, 121.3, 120.3, 118.1, 115.9, 109.8, 73.8, 72.7, 60.8, 55.5, 35.2, 30.9 (3x), 29.9.

**2-(2-Allyl-3,4-dimethoxyphenyl)-6-fluoro-3-(toluene-4-sulfonyl)chroman-4-one (4k).** Yield = 76% (377 mg); Colorless solid; mp = 126-128 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{27}H_{26}FO_6S$ 497.1434, found 497.1428; $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.4 Hz, 2H), 7.42 (dd, *J* = 3.2, 8.0 Hz, 1H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.16 (dt, *J* = 3.2, 7.6 Hz, 1H), 6.81 (dd, *J* = 4.0, 9.2 Hz, 1H), 6.69 (s, 1H), 6.62 (d, *J* = 8.8 Hz, 1H), 6.57 (d, *J* = 8.8 Hz, 1H), 6.09-5.99 (m, 1H), 5.11 (dq, *J* = 1.6, 10.0 Hz, 1H), 5.01 (dq, *J* = 1.6, 16.8 Hz, 1H), 4.31 (d, *J* = 0.8 Hz, 1H), 3.79 (s, 3H), 3.76 (s, 3H), 3.72-3.58 (m, 2H), 2.40 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 182.3, 157.1 (d, *J* = 241.1 Hz), 155.4, 153.3, 148.0, 145.8, 136.3, 134.1, 132.3, 129.6 (2x), 129.3 (2x), 127.1, 125.0 (d, *J* = 24.3 Hz), 121.8, 120.5 (d, *J* = 6.8 Hz), 120.1 (d, *J* = 6.8 Hz), 115.8, 111.5 (d, *J* = 23.5 Hz), 109.8, 73.6, 72.0, 60.8, 55.5, 30.0, 21.6. Single-crystal X-ray diagram: crystal of compound **4k** was grown by slow diffusion of EtOAc into a solution of compound **4k** in $CH_2Cl_2$ to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P 21/c, *a* = 16.703(5) Å, *b* = 16.441(5) Å, *c* = 8.656(3) Å, *V* = 2329.9(12) $Å^3$, *Z* = 4, $d_{calcd}$ = 1.416 g/$cm^3$, *F*(000) = 1040, 2$\theta$ range 1.755~26.599°, R indices (all data) R1 = 0.1068, wR2 = 0.2328.

**2-(2-Allyl-3,4-dimethoxyphenyl)-7-methoxy-3-(toluene-4-sulfonyl)chroman-4-one (4l).** Yield = 78% (396 mg); Colorless solid; mp = 173-175 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{28}H_{29}O_7S$ 509.1634, found 509.1639; $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.71 (d, *J* = 8.8 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 6.70 (d, *J* = 8.4 Hz, 1H), 6.66 (s, 1H), 6.58 (d, *J* = 8.8 Hz, 1H), 6.52 (dd, *J* = 2.4, 9.2 Hz, 1H), 6.27 (d, *J* = 2.4 Hz, 1H), 6.09-6.00 (m, 1H), 5.11 (dq, *J* = 1.6, 10.0 Hz, 1H), 5.02 (dq, *J* = 1.6, 17.2 Hz, 1H), 4.23 (d, *J* = 0.4 Hz, 1H), 3.79 (s, 6H), 3.76 (s, 3H), 3.75-3.56 (m, 2H), 2.40 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 180.8, 167.3, 161.6, 153.1, 147.8, 145.5, 136.4, 134.3, 132.0, 129.9, 129.5 (2x), 129.3 (2x), 128.6, 127.7, 121.8, 115.8, 114.4, 110.6, 109.9, 73.6, 72.3, 60.8, 55.7, 55.5, 29.9, 21.6.

**2-(2-Allyl-3-isopropoxy-4-methoxy-phenyl)-3-(toluene-4-sulfonyl)chroman-4-one (4m).** Yield = 83% (420 mg); Colorless solid; mp = 85-87 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{29}H_{31}O_6S$ 507.1841, found 507.1846; $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.75 (dd, *J* = 2.0, 8.0 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.41 (dt, *J* = 2.0, 8.8 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 2H), 6.92 (dt, *J* = 1.2, 8.0 Hz, 1H), 6.78 (dt, *J* = 0.8, 8.4 Hz, 1H), 6.72 (s, 1H), 6.62 (d, *J* = 8.8 Hz, 1H), 6.52 (d, *J* = 8.8 Hz, 1H), 6.05-5.95 (m, 1H), 5.11 (dq, *J* = 1.6, 10.0 Hz, 1H), 5.07 (dq, *J* = 1.6, 16.8 Hz, 1H), 4.54-4.48 (m, 1H), 4.29 (d, *J* = 0.8 Hz, 1H), 3.77-3.70 (m, 1H), 3.70 (s, 3H), 3.65-3.60 (m, 1H), 2.36 (s, 3H), 1.25 (d, *J* = 6.0 Hz, 3H), 1.23 (d, *J* = 6.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 182.7, 159.3, 153.1, 145.6, 145.5, 137.2, 136.0, 134.1, 132.3, 129.4 (2x), 129.3 (2x), 127.6, 126.6, 121.3, 121.1, 120.3, 118.1, 115.8, 109.6, 74.6, 73.5, 72.7, 55.3, 30.3, 22.6, 22.5, 21.5.

**2-(2-Allyl-3-*n*-butoxy-4-methoxyphenyl)-3-(toluene-4-sulfonyl)chroman-4-one (4n).** Yield = 82% (427 mg); Colorless gum; HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{30}H_{33}O_6S$ 521.1998, found 521.1993; $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.75 (dd, *J* = 1.6, 7.6 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.42 (dt, *J* = 1.6, 8.4 Hz, 1H), 7.23 (d, *J* = 8.4 Hz, 2H), 6.93 (dt, *J* = 0.8, 7.6 Hz, 1H), 6.80 (dt, *J* = 0.8, 8.4 Hz, 1H), 6.69 (s, 1H), 6.65 (d, *J* = 8.8 Hz, 1H), 6.54 (d, *J* = 8.8 Hz, 1H), 6.08-5.99 (m, 1H), 5.11 (dq, *J* = 1.6, 10.0 Hz, 1H), 5.04 (dq, *J* = 1.6, 16.8 Hz, 1H), 4.31 (d, *J* = 0.8 Hz, 1H), 3.92 (t, *J* = 6.4 Hz, 2H), 3.73-3.62 (m, 1H), 3.72 (s, 3H), 3.61-3.57 (m, 1H), 2.37 (s, 3H), 1.77-1.70 (m, 2H), 1.53-1.44 (m, 2H), 0.96 (t, *J* = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 182.6, 159.3, 153.2, 147.2, 145.5, 137.2, 136.3, 134.1, 132.0, 129.4 (2x), 129.2 (2x), 127.4, 126.6, 121.5, 121.3, 120.2, 118.1, 115.7, 109.7, 73.4, 72.8, 72.6, 55.4, 32.2, 29.9, 21.5, 19.0, 13.8.

**2-(2-Allyl-3-methoxyphenyl)-3-(toluene-4-sulfonyl)chroman-4-one (4o).** Yield = 80% (359 mg); Colorless solid; mp = 164-166 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{26}H_{25}O_5S$ 449.1423, found 449.1430; $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.75 (dd, *J* = 1.6, 8.0 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.46 (dt, *J* = 1.6, 8.8 Hz, 1H), 7.24 (d, *J* = 8.4 Hz, 2H), 6.99 (t, *J* = 8.0 Hz, 1H), 6.96 (dt, *J* = 1.2, 8.4 Hz, 1H), 6.86 (d, *J* = 0.8, 8.4 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 6.79 (s, 1H), 6.56 (d, *J* = 8.0 Hz, 1H), 6.07-5.97 (m, 1H), 5.10-5.02 (m, 2H), 4.32 (s, 1H), 3.79 (s, 3H), 3.69-3.54 (m, 2H), 2.38 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 182.3, 159.7, 158.1, 145.6, 137.4, 135.8, 134.1, 129.5 (3x), 129.3 (2x), 127.4, 126.7, 125.9, 121.4, 120.3, 118.0, 117.9, 115.5, 111.2, 73.7, 72.6, 55.7, 29.5, 21.6.

**2-(2-Allyl-3,5-dimethoxyphenyl)-3-(toluene-4-sulfonyl)chroman-4-one (4p).** Two isomers, ratio: 8:1; Yield = 74% (354 mg); Colorless solid; mp = 175-177 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{27}H_{27}O_6S$ 479.1528, found 479.1532; for major product: $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.75 (dd, *J* = 1.6, 7.6 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.47 (dt, *J* = 1.6, 8.4 Hz, 1H), 7.24 (d, *J* = 8.4 Hz, 2H), 6.97 (dt, *J* = 0.8, 7.6 Hz, 1H), 6.89 (dt, *J* = 0.8, 8.4 Hz, 1H), 6.77 (s, 1H), 6.36 (d, *J* = 2.4 Hz, 1H), 6.10 (d, *J* = 2.4 Hz, 1H), 6.04-5.94 (m, 1H), 5.07-4.98 (m, 2H), 4.30 (d, *J* = 0.8 Hz, 1H), 3.76 (s, 3H), 3.58-3.43 (m, 2H), 3.47 (s, 3H), 2.38 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 182.2, 159.8, 159.1, 158.9, 145.6, 137.4, 136.4, 136.3, 134.1, 129.5 (2x), 129.4, 129.3 (2x), 126.7, 121.5, 117.9, 117.7, 115.1, 102.6, 98.5, 73.8, 72.6, 55.7, 54.9, 29.0, 21.6.

**2-(2-Allyl-3-*n*-butoxy-5-methoxyphenyl)-3-(toluene-4-sulfonyl)chroman-4-one (4q).** Two isomers, ratio: 6:1; Yield = 76% (395 mg); Colorless solid; mp = 90-92 °C

(recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{30}H_{33}O_6S$ 521.1998, found 521.1996; for major product: $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.75 (dd, *J* = 1.6, 7.6 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.46 (dt, *J* = 1.6, 8.4 Hz, 1H), 7.24 (d, *J* = 8.4 Hz, 2H), 6.96 (dt, *J* = 0.8, 7.6 Hz, 1H), 6.87 (dt, *J* = 0.8, 8.4 Hz, 1H), 6.77 (s, 1H), 6.34 (d, *J* = 2.4 Hz, 1H), 6.08 (d, *J* = 2.4 Hz, 1H), 6.03-5.93 (m, 1H), 5.16-5.02 (m, 2H), 4.31 (d, *J* = 0.8 Hz, 1H), 3.89 (t, *J* = 6.0 Hz, 2H), 3.58-3.44 (m, 2H), 3.47 (s, 3H), 2.38 (s, 3H), 1.78-1.71 (m, 2H), 1.52-1.39 (m, 2H), 0.96 (t, *J* = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 182.2, 159.8, 158.8, 158.6, 145.6, 137.4, 136.3, 136.2, 134.1, 129.5 (2x), 129.4, 129.3 (2x), 126.7, 121.5, 120.4, 117.9, 115.1, 102.5, 99.1, 73.8, 72.6, 67.9, 54.9, 31.2, 29.2, 21.6, 19.3, 13.8.

**2-(2-Allyl-3-benzyloxy-5-methoxyphenyl)-3-(toluene-4-sulfonyl)chroman-4-one (4r).** Yield = 80% (443 mg); Colorless gum; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{33}H_{31}O_6S$ 555.1841, found 555.1846; $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.77 (dd, *J* = 1.6, 8.0 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.48 (dt, *J* = 1.6, 8.4 Hz, 1H), 7.41-7.30 (m, 5H), 7.25 (d, *J* = 8.4 Hz, 2H), 6.97 (dt, *J* = 0.8, 7.6 Hz, 1H), 6.91 (dt, *J* = 0.8, 8.4 Hz, 1H), 6.80 (s, 1H), 6.43 (d, *J* = 2.4 Hz, 1H), 6.13 (d, *J* = 2.4 Hz, 1H), 6.09-5.99 (m, 1H), 5.10-5.06 (m, 2H), 5.02 (s, 2H), 4.33 (d, *J* = 0.8 Hz, 1H), 3.64-3.51 (m, 2H), 3.46 (s, 3H), 2.39 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 182.2, 159.8, 158.7, 158.1, 145.6, 137.4, 136.7, 136.5, 136.2, 134.1, 129.5 (2x), 129.3 (2x), 128.5 (2x), 127.9, 127.0 (2x), 126.7, 121.5, 120.4, 118.0, 117.8, 115.3, 103.0, 99.7, 73.8, 72.6, 70.2, 54.9, 29.2, 21.6.

**2-(2-Allyl-3,4-dimethoxyphenyl)-6-bromo-3-(toluene-4-sulfonyl)-2,3-dihydrobenzo[*h*]chromen-4-one (4s).** Yield = 76% (461 mg); Colorless solid; mp = 163-165 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{31}H_{28}BrO_6S$ 607.0790, found 607.0796; $^1H$ NMR (400 MHz, $CDCl_3$): δ 8.24 (d, *J* = 8.4 Hz, 1H), 8.13 (d, *J* = 8.4 Hz, 1H), 8.02 (s, 1H), 7.23 (dt, *J* = 1.2, 8.0 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.56 (dt, *J* = 0.8, 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 1H), 6.97 (s, 1H), 6.67 (d, *J* = 8.8 Hz, 1H), 6.53 (d, *J* = 8.4 Hz, 1H), 6.17-6.07 (m, 1H), 5.20 (dq, *J* = 1.6, 10.4 Hz, 1H), 5.11 (dq, *J* = 1.6, 17.2 Hz, 1H), 4.39 (s, 1H), 3.84-3.69 (m, 2H), 3.79 (s, 3H), 3.73 (s, 3H), 2.22 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 180.9, 157.1, 153.4, 147.9, 145.8, 136.3, 135.9, 133.7, 131.9, 131.4, 129.5 (2x), 129.2 (2x), 127.4, 127.1, 126.8, 125.7, 124.4, 124.3, 121.7, 116.1, 115.4, 115.1, 110.0, 74.5, 72.2, 60.8, 55.5, 29.9, 21.4.

**2-(3,4-Dimethoxy-2-propenylphenyl)-3-methanesulfonylchroman-4-one (4t).** Yield = 80% (322 mg); Colorless solid; mp = 129-131 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{23}O_6S$ 403.1215, found 402.1143; $^1H$ NMR (400 MHz, $CDCl_3$ + $d_8$-THF): δ 7.89 (dd, *J* = 1.6, 8.0 Hz, 1H), 7.56 (dt, *J* = 2.0, 7.6 Hz, 1H), 7.06-7.02 (m, 2H), 6.75 (d, *J* = 8.8 Hz, 1H), 6.69 (s, 1H), 6.59 (d, *J* = 8.8 Hz, 1H), 6.46 (dq, *J* = 1.6, 16.0 Hz, 1H), 6.23 (dq, *J* = 6.4, 16.0 Hz, 1H), 4.29 (s, 1H), 3.77 (s, 3H), 3.71 (s, 3H), 3.06 (s, 3H), 1.99 (dd, *J* = 1.6, 6.4 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$ + $d_8$-THF): δ 183.5, 159.8, 153.2, 147.4, 138.1, 134.2, 132.1, 127.0, 126.5, 122.6, 121.82, 121.77, 120.0, 118.5, 110.0, 72.5, 70.0, 60.1, 55.6, 41.2, 19.4. Single-crystal X-ray diagram: crystal of compound **4t** was grown by slow diffusion of EtOAc into a solution of compound **4t** in $CH_2Cl_2$ to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P 21/c, *a* = 11.5161(16) Å, *b* = 8.2608(12) Å, *c* = 22.300(3) Å, *V* = 2121.4(5) $Å^3$, *Z* = 4, $d_{calcd}$ = 1.260 g/$cm^3$, *F*(000) = 848, 2$\theta$ range 1.768~26.518°, R indices (all data) R1 = 0.0560, wR2 = 0.0908.

**2-(2-Allyl-3,4-dimethoxyphenyl)-6-chloro-3-(toluene-4-sulfonyl)chroman-4-one (4u).** Yield = 76% (389 mg); Colorless gum; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{27}H_{26}ClO_6S$ 513.1139, found 513.1145; $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 2.8 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.38 (dd, *J* = 2.8, 8.8 Hz, 1H), 7.29 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 1H), 6.70 (s, 1H), 6.62 (d, *J* = 8.4 Hz, 1H), 6.57 (d, *J* = 8.8 Hz, 1H), 6.08-5.97 (m, 1H), 5.11 (dq, *J* = 1.6, 10.0 Hz, 1H), 5.01 (dq, *J* = 1.6, 16.8 Hz, 1H), 4.30 (d, *J* = 0.4 Hz, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 3.72-3.58 (m, 2H), 2.41 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 182.0, 157.7, 153.4, 148.0, 145.9, 137.1, 136.3, 134.1, 132.2, 129.7 (2x), 129.3 (2x), 127.0, 127.0, 125.9, 121.7, 121.0, 120.1, 115.9, 109.9, 73.6, 72.1, 60.8, 55.5, 30.0, 21.7.

**2-(2-Allylphenyl)-3-(toluene-4-sulfonyl)chroman-4-one (4v).** Yield = 78% (326 mg); Colorless gum; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{25}H_{23}O_4S$ 419.1317, found 419.1314; $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.77 (dd, *J* = 1.6, 8.0 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.44 (dt, *J* = 1.6, 8.8 Hz, 1H), 7.25-7.22 (m, 4H), 7.03-6.94 (m, 3H), 6.85 (dd, *J* = 0.8, 8.4 Hz, 1H), 6.82 (s, 1H), 6.10-6.00 (m, 1H), 5.18 (dq, *J* = 1.6, 10.0 Hz, 1H), 5.10 (dq, *J* = 1.6, 16.8 Hz, 1H), 4.33 (d, *J* = 1.2 Hz, 1H), 3.67-3.56 (m, 2H), 2.38 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 182.3, 159.4, 145.6, 137.6, 137.4, 136.3, 134.3, 134.0, 131.2, 129.5 (2x), 129.3 (2x), 129.1, 126.7, 126.5, 125.6, 121.5, 120.3, 118.0, 116.8, 73.5, 72.4, 36.3, 21.6.

**2-[3,4-Dimethoxy-2-(2-oxopropyl)phenyl]-3-(toluene-4-sulfonyl)chroman-4-one (5a).** $PdCl_2$ (10 mg, 5.6 mol%) and $CuCl_2$ (94 mg, 0.7 mmol) were added to a solution of **4a** (239 mg, 0.5 mmol) in MeOH (20 mL) at 25 °C. Molecular oxygen was slowly bubbled into the reaction mixture for 5 min, and stirring occurred at 25 °C for 1 h. The solvent of the reaction mixture was concentrated, and the resulting residue was extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product. Purification on silica gel (hexanes/EtOAc = 10/1~6/1) afforded **5a**. Yield = 90% (222 mg); Colorless solid; mp = 176-178 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{27}H_{27}O_7S$ 495.1478, found 495.1483; $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.76 (dd, *J* = 1.6, 8.0 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.42 (dt, *J* = 2.0, 8.4 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 2H), 6.94 (dt, *J* = 1.2, 8.0 Hz, 1H), 6.72 (dd, *J* = 0.4, 8.4 Hz, 1H), 6.68 (d, *J* = 8.4 Hz, 1H), 6.60 (d, *J* = 8.8 Hz, 1H), 6.52 (s, 1H), 4.38 (d, *J* = 0.8 Hz, 1H), 4.09 (s, 2H), 3.75 (s, 3H), 3.74 (s, 3H), 2.40 (s, 3H), 2.39 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 205.6, 182.6, 158.7, 153.0, 148.1, 145.6, 137.4, 134.2, 129.6 (2x), 129.3 (2x), 128.5, 127.6, 126.7, 121.7, 121.6, 120.3, 118.3, 110.5, 73.5, 71.8, 60.4, 55.5, 41.3, 30.1, 21.6.

**A representative synthetic procedure of compounds 6a-6n is as follows:** $PdCl_2$ (10 mg, 5.6 mol%) and $CuCl_2$ (94 mg, 0.7 mmol) were added to a solution of **4a-4d**, **4g-4k**, **4o-4q**, **4s**, **4u** (0.5 mmol) in MeOH (20 mL) at 25 °C. Molecular oxygen was slowly bubbled into the reaction mixture for 5 min, and stirring occurred at 25 °C for 1 h. The reaction was monitored by TLC plate until the strating materials were consumed. Then, $Bi(OTf)_3$ (100 mg, 15.2 mol%) was added to the reaction mixture at 25 °C. The reaction mixture was stirred at 25 °C for 4 h. The solvent of the reaction mixture was concentrated, and the resulting residue was extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product. Purification on silica gel (hexanes/EtOAc = 30/1~3/1) afforded **6a-6n**.

**1-(12-Hydroxy-9,10-dimethoxy-13-tosyl-11,12-dihydro-6*H*-6,12-methanodibenzo[*b,f*]oxocin-11-yl)ethan-1-one (6a).** Yield = 78% (193 mg); Colorless gum; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{27}H_{27}O_7S$ 495.1478, found 495.1483; $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.66-7.64 (m, 3H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 1H), 6.70-6.89 (m, 2H), 6.83 (d, *J* = 8.4 Hz, 1H), 6.25 (dd, *J* = 1.6, 8.0 Hz, 1H), 5.72 (d, *J* = 2.4 Hz, 1H), 4.70 (d, *J* = 2.4 Hz, 1H), 4.66 (br s, 1H), 4.52 (s, 1H), 3.77 (s, 3H), 3.69 (s, 3H), 2.58 (s, 3H), 2.35 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 209.1, 152.5, 149.9, 145.4, 144.9, 135.7, 129.3, 129.01 (2x), 128.95 (2x), 128.9, 127.4, 126.7, 125.20, 125.15, 121.7, 116.4, 112.6, 73.1, 70.4, 62.5, 61.0, 59.6, 55.7, 34.1, 21.5.

**1-(12-Hydroxy-9,10-dimethoxy-13-phenylsulfonyl-11,12-dihydro-6*H*-6,12-methanodibenzo[*b,f*]oxocin-11-yl)ethan-1-one (6b).** Yield = 70% (168 mg); Colorless gum; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{26}H_{25}O_7S$ 481.1321, found 481.1325; $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.80-7.77 (m, 2H), 7.66-7.64 (m, 1H), 7.50-7.46 (m, 1H), 7.37-7.33 (m, 2H), 7.12 (d, *J* = 8.4 Hz, 1H), 6.94-6.89 (m, 2H), 6.83 (d, *J* = 8.8 Hz, 1H), 6.26-6.24 (m, 1H), 5.76 (d, *J* = 2.0 Hz, 1H), 4.75 (d, *J* = 2.4 Hz, 1H), 4.52 (s, 1H), 3.76 (s, 3H), 3.68 (s, 3H), 2.58 (s, 3H), 1.80 (br s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 209.1, 152.5, 149.9, 145.3, 138.7, 133.8, 129.6, 128.9 (2x), 128.8 (2x), 128.4, 127.2, 126.5, 125.2, 125.1, 121.7, 116.4, 112.5, 73.1, 70.3, 62.5, 61.0, 59.6, 55.6, 34.0.

**1-(12-Hydroxy-9,10-dimethoxy-13-methylsulfonyl-11,12-dihydro-6*H*-6,12-methanodibenzo[*b,f*]oxocin-11-yl)ethan-1-one (6c).** Yield = 72% (150 mg); Colorless solid; mp = 210-212 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{23}O_7S$ 419.1165, found 419.1170; $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.67 (dd, *J* = 1.6, 7.6 Hz, 1H), 7.21 (d, *J* = 8.4 Hz, 1H), 7.14 (dt, *J* = 1.6, 8.0 Hz, 1H), 7.00 (dt, *J* = 1.2, 8.0 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 6.71 (dd, *J* = 0.8, 8.0 Hz, 1H), 5.92 (d, *J* = 2.4 Hz, 1H), 4.60 (d, *J* = 2.4 Hz, 1H), 4.57 (s, 1H), 3.97 (s, 1H), 3.80 (s, 3H), 3.72 (s, 3H), 2.93 (d, *J* = 0.4 Hz, 3H), 2.62 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 209.5, 152.6, 150.7, 145.3, 130.1, 129.2, 127.1, 126.8, 125.5, 125.0, 122.2, 117.0, 112.6, 72.7, 70.6, 62.0, 59.7, 59.6, 55.7, 44.2, 34.1.

**1-(13-*n*-Butylsulfonyl-12-hydroxy-9,10-dimethoxy-11,12-dihydro-6*H*-6,12-methanodibenzo[*b,f*]oxocin-11-yl)ethan-1-one (6d).** Yield = 76% (175 mg); Colorless solid; mp = 172-174 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{24}H_{29}O_7S$ 461.1634, found 461.1642; $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.64 (dd, *J* = 2.0, 8.0 Hz, 1H), 7.21 (d, *J* = 8.4 Hz, 1H), 7.12 (dt, *J* = 1.6, 8.4 Hz, 1H), 6.97 (dt, *J* = 1.6, 8.4 Hz, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 6.72 (dd, *J* = 0.8, 8.4 Hz, 1H), 5.89 (d, *J* = 2.4 Hz, 1H), 4.63 (d, *J* = 2.4 Hz, 1H), 4.56 (br s, 1H), 3.86 (s, 1H), 3.77 (s, 3H), 3.72 (s, 3H), 3.04 (t, *J* = 8.0 Hz, 2H), 2.63 (s, 3H), 1.85-1.71 (m, 2H), 1.44-1.35 (m, 2H), 0.90 (t, *J* = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 209.6, 152.5, 150.8, 145.2, 129.8, 129.3, 127.3, 127.0, 125.5, 124.6, 121.9, 116.9, 112.6, 72.6, 70.7, 61.8, 59.6, 57.4, 56.4, 55.6, 34.0, 23.3, 21.5, 13.4. Single-crystal X-ray diagram: crystal of compound **6d** was grown by slow diffusion of EtOAc into a solution of compound **6d** in $CH_2Cl_2$ to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P 21/c, *a* = 16.547(11) Å, *b* = 16.693(11) Å, *c* = 8.092(4) Å, *V* = 2209(2) Å$^3$, *Z* = 4, $d_{calcd}$ = 1.385 g/cm$^3$, *F*(000) = 976, 2$\theta$ range 1.245~26.881°, R indices (all data) R1 = 0.1967, wR2 = 0.3853.

**1-(12-Hydroxy-9,10-dimethoxy-13-(*m*-tolylsulfonyl)-11,12-dihydro-6*H*-6,12-methanodibenzo[*b,f*]oxocin-11-yl)ethan-1-one (6e).** Yield = 80% (198 mg); Colorless gum; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{27}H_{27}O_7S$ 495.1478, found 495.1475; $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.68-7.61 (m, 2H), 7.54 (d, *J* = 1.6 Hz, 1H), 7.30-7.24 (m, 2H), 7.12 (d, *J* = 8.4 Hz, 1H), 6.96-6.89 (m, 2H), 6.83 (d, *J* = 8.4 Hz, 1H), 6.28-6.25 (m, 1H), 5.73 (d, *J* = 2.0 Hz, 1H), 4.72 (d, *J* = 2.4 Hz, 1H), 4.69 (s, 1H), 4.52 (s, 1H), 3.77 (s, 3H), 3.69 (s, 3H), 2.59 (s, 3H), 2.30 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 209.1, 152.6, 150.0, 145.4, 138.8, 138.6, 134.6, 129.6, 129.3, 128.9, 128.3, 127.4, 126.6, 126.2, 125.2, 125.1, 121.7, 116.4, 112.6, 73.1, 70.3, 62.5, 61.0, 59.7, 55.7, 34.1, 21.2.

**1-(13-(4-Ethylphenylsulfonyl)-12-hydroxy-9,10-dimethoxy-11,12-dihydro-6*H*-6,12-methanodibenzo[*b,f*]oxocin-11-yl)ethan-1-one (6f).** Yield = 74% (188 mg); Colorless gum; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{28}H_{29}O_7S$ 509.1634, found 509.1638; $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.68-7.63 (m, 3H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 1H), 6.93-6.88 (m, 2H), 6.83 (d, *J* = 8.4 Hz, 1H), 6.22-6.18 (m, 1H), 5.74 (d, *J* = 2.0 Hz, 1H), 4.76 (s, 1H), 4.69 (d, *J* = 2.4 Hz, 1H), 4.52 (s, 1H), 3.77 (s, 3H), 3.69 (s, 3H), 2.63 (q, *J* = 7.6 Hz, 1H), 2.59 (s, 3H), 1.58 (s, 1H), 1.20 (t, *J* = 7.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 209.0, 152.4, 150.8, 149.7, 145.2, 135.5, 129.3, 129.0 (2x), 127.7 (2x), 127.33, 127.28, 126.4, 125.02, 125.01, 121.4, 116.1, 112.4, 73.0, 70.1, 62.4, 60.8, 59.5, 55.5, 33.9, 28.7, 14.8.

**1-(12-Hydroxy-13-(4-isopropylphenylsulfonyl)-9,10-dimethoxy-11,12-dihydro-6*H*-6,12-methanodibenzo[*b,f*]oxocin-11-yl)ethan-1-one (6g).** Yield = 82% (428 mg); Colorless solid; mp = 141-143 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{29}H_{31}O_7S$ 523.1791, found 523.1796; $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.67-7.63 (m, 3H), 7.14 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 1H), 6.91-6.86 (m, 2H), 6.83 (d, *J* = 8.4 Hz, 1H), 6.16-6.14 (m, 1H), 5.76 (d, *J* = 2.0 Hz, 1H), 4.85 (s, 1H), 4.69 (d, *J* = 2.4

Hz, 1H), 4.52 (s, 1H), 3.77 (s, 3H), 3.69 (s, 3H), 2.91-2.84 (m, 1H), 2.59 (s, 3H), 1.20 (dt, *J* = 0.8, 7.2 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 209.1, 155.4, 152.5, 149.8, 145.4, 135.6, 129.5, 129.3 (2x), 127.5, 127.4, 126.5, 126.4 (2x), 125.24, 125.15, 121.6, 116.2, 112.6, 73.1, 70.1, 62.6, 61.0, 59.7, 55.7, 34.2, 34.1, 23.5, 23.4.

**1-(13-(4-*t*-Butylphenylsulfonyl)-12-hydroxy-9,10-dimethoxy-11,12-dihydro-6*H*-6,12-methanodibenzo[*b,f*]oxocin-11-yl)ethan-1-one (6h).** Yield = 76% (204 mg); Colorless gum; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{30}H_{33}O_7S$ 537.1947, found 537.1952; $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.8 Hz, 2H), 7.64 (dd, *J* = 1.6, 8.4 Hz, 1H), 7.30 (d, *J* = 8.8 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 1H), 6.91-6.82 (m, 3H), 6.25 (dd, *J* = 1.6, 8.0 Hz, 1H), 5.77 (d, *J* = 2.4 Hz, 1H), 4.89 (br s, 1H), 4.69 (d, *J* = 2.0 Hz, 1H), 4.52 (s, 1H), 3.77 (s, 3H), 3.69 (s, 3H), 2.60 (s, 3H), 1.27 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 209.2, 157.7, 152.5, 149.7, 145.4, 135.1, 129.5, 129.0 (2x), 128.8, 127.5, 126.5, 125.3, 125.2 (2x), 125.2, 121.5, 116.2, 112.6, 73.1, 70.1, 62.6, 60.9, 59.7, 55.7, 35.1, 34.1, 30.9 (3x).

**1-(2-Fluoro-12-hydroxy-9,10-dimethoxy-13-tosyl-11,12-dihydro-6*H*-6,12-methanodibenzo[*b,f*]oxocin-11-yl)ethan-1-one (6i).** Yield = 80% (205 mg); Colorless gum; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{27}H_{26}FO_7S$ 513.1383, found 513.1376; $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.4 Hz, 2H), 7.36 (dd, *J* = 3.2, 9.2 Hz, 1H), 7.16 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.8 Hz, 1H), 6.84 (d, *J* = 8.4 Hz, 1H), 6.65 (dt, *J* = 3.2, 8.4 Hz, 1H), 6.21 (dd, *J* = 4.8, 9.2 Hz, 1H), 5.71 (d, *J* = 2.4 Hz, 1H), 4.78 (s, 1H), 4.69 (d, *J* = 2.0 Hz, 1H), 4.48 (s, 1H), 3.78 (s, 3H), 3.71 (s, 3H), 2.57 (s, 3H), 2.36 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 208.8, 157.8 (d, *J* = 229.0 Hz), 152.6, 145.9, 145.4, 145.2, 135.5, 129.1 (2x), 129.0 (2x), 128.6, 127.7, 127.1, 125.2, 117.6 (d, *J* = 7.5 Hz), 116.4 (d, *J* = 23.5 Hz), 112.7, 111.4 (d, *J* = 24.2 Hz), 73.2, 62.3, 60.5, 59.7, 55.7, 34.1, 29.7, 21.6.

**1-(12-Hydroxy-10-methoxy-13-tosyl-11,12-dihydro-6*H*-6,12-methanodibenzo[*b,f*]oxocin-11-yl)ethan-1-one (6j).** Yield = 73% (169 mg); Colorless solid; mp = 243-245 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{26}H_{25}O_6S$ 465.1372, found 465.1378; $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.67-7.64 (m, 3H), 7.21 (t, *J* = 8.0 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 7.2 Hz, 1H), 6.95-6.90 (m, 2H), 6.69 (dd, *J* = 0.8, 8.4 Hz, 1H), 6.26-6.24 (m, 1H), 5.76 (d, *J* = 2.4 Hz, 1H), 4.76 (d, *J* = 2.0 Hz, 1H), 4.69 (s, 1H), 4.49 (s, 1H), 3.69 (s, 3H), 2.56 (s, 3H), 2.35 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 209.3, 156.3, 149.9, 144.9, 135.5, 135.3, 129.2, 129.00 (2x), 128.99 (2x), 128.9, 126.8, 125.2, 123.6, 121.7, 121.6, 116.3, 110.5, 73.3, 70.4, 62.0, 60.8, 55.2, 34.1, 21.5. Single-crystal X-ray diagram: crystal of compound **6j** was grown by slow diffusion of EtOAc into a solution of compound **6j** in $CH_2Cl_2$ to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P 21/n, *a* = 12.4337(9) Å, *b* = 9.0715(6) Å, *c* = 20.5612(15) Å, *V* = 2220.2(3) Å$^3$, *Z* = 4, $d_{calcd}$ = 1.390 g/cm$^3$, *F*(000) = 976, 2$\theta$ range 1.725~26.499°, R indices (all data) R1 = 0.0546, wR2 = 0.0977.

**1-(12-Hydroxy-8,10-dimethoxy-13-tosyl-11,12-dihydro-6*H*-6,12-methanodibenzo[*b,f*]oxocin-11-yl)ethan-1-one (6k).** Yield = 76% (188 mg); Colorless solid; mp = 218-220 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{27}H_{27}O_7S$ 495.1478, found 495.1485; $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.66-7.64 (m, 3H), 7.13 (dd, *J* = 0.4, 8.4 Hz, 2H), 6.95-6.91 (m, 2H), 6.49 (d, *J* = 2.4 Hz, 1H), 6.28-6.25 (m, 2H), 5.70 (d, *J* = 2.4 Hz, 1H), 4.74 (d, *J* = 2.4 Hz, 1H), 4.65 (s, 1H), 4.39 (s, 1H), 3.76 (s, 3H), 3.66 (s, 3H), 2.53 (s, 3H), 2.35 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 209.8, 160.3, 157.3, 149.9, 144.9, 135.7, 135.6, 129.2, 129.01 (2x), 128.99 (2x), 126.8, 125.2, 121.6, 116.4, 116.2, 104.4, 99.5, 73.6, 70.4, 61.5, 60.9, 55.4, 55.3, 34.0, 21.6.

**1-(10-*n*-Butoxy-12-hydroxy-8-methoxy-13-tosyl-11,12-dihydro-6*H*-6,12-methanodibenzo[*b,f*]oxocin-11-yl)ethan-1-one (6l).** Yield = 83% (223 mg); Colorless solid; mp = 162-164 °C (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{30}H_{33}O_7S$ 537.1947, found 537.1952; $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.68-7.63 (m, 3H), 7.13 (dd, *J* = 0.8, 8.4 Hz, 2H), 6.97-6.92 (m, 2H), 6.48 (d, *J* = 2.4 Hz, 1H), 6.28-6.26 (m, 2H), 5.70 (d, *J* = 2.0 Hz, 1H), 4.71 (d, *J* = 2.4 Hz, 1H), 4.66 (s, 1H), 4.38 (s, 1H), 3.87-3.80 (m, 1H), 3.77 (s, 3H), 3.73-3.68 (m, 1H), 2.55 (s, 3H), 2.35 (s, 3H), 1.74-1.65 (m, 2H), 1.46-1.33 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 209.7, 160.2, 156.8, 150.0, 144.9, 135.62, 135.57, 129.2, 129.0 (2x), 128.9 (2x), 126.9, 125.2, 121.6, 116.24, 116.20, 104.2, 100.0, 73.6, 70.4, 67.9, 61.7, 60.9, 55.4, 34.1, 30.9, 21.5, 19.1, 13.8.

**1-(5-Bromo-7-hydroxy-9,10-dimethoxy-15-tosyl-8,13-dihydro-7*H*-7,13-methanobenzo[*f*]naphtho[1,2-*b*]oxocin-8-yl)ethan-1-one (6m).** Yield = 80% (249 mg); Colorless gum; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{31}H_{28}BrO_7S$ 623.0739, found 623.0745; $^1H$ NMR (400 MHz, $CDCl_3$): δ 8.01 (s, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.73 (dd, *J* = 0.8, 8.4 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.46 (dt, *J* = 1.6, 8.0 Hz, 1H), 7.33 (dt, *J* = 1.2, 8.4 Hz, 1H), 7.19 (d, *J* = 8.4 Hz, 1H), 6.84 (d, *J* = 8.8 Hz, 1H), 6.79 (d, *J* = 8.0 Hz, 2H), 6.01 (d, *J* = 2.0 Hz, 1H), 5.09 (s, 1H), 4.76 (d, *J* = 2.4 Hz, 1H), 4.59 (s, 1H), 3.74 (s, 3H), 3.70 (s, 3H), 2.63 (s, 3H), 1.91 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 208.9, 152.7, 145.5, 145.0 (2x), 144.9, 134.8, 132.2, 129.1 (2x), 128.6 (2x), 127.8, 127.2, 126.5, 125.8, 125.7, 125.20, 125.15, 122.7, 120.3, 114.4, 112.6, 73.7, 69.9, 61.9, 60.7, 59.7, 55.7, 34.1, 21.1.

**1-(2-Chloro-12-hydroxy-9,10-dimethoxy-13-tosyl-11,12-dihydro-6*H*-6,12-methanodibenzo[*b,f*]oxocin-11-yl)ethan-1-one (6n).** Yield = 78% (206 mg); Colorless gum; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{27}H_{26}ClO_7S$ 529.1088, found 529.1093; $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 2.4 Hz, 1H), 7.17 (d, *J* = 8.8 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 1H), 6.90 (dd, *J* = 2.4, 8.8 Hz, 1H), 6.83 (d, *J* = 8.8 Hz, 1H), 6.23 (d, *J* = 8.8 Hz, 1H), 5.71 (d, *J* = 2.4 Hz, 1H), 4.74 (s, 1H), 4.69 (d, *J* = 2.0 Hz, 1H), 4.48 (s, 1H), 3.78 (s, 3H), 3.71 (s, 3H), 2.58 (s, 3H), 2.36 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 208.8, 152.6, 148.6, 145.2, 135.4, 129.7, 129.3, 129.1 (2x), 128.9 (2x), 128.5, 128.2, 126.9, 126.5, 125.14, 125.05, 117.9, 112.7, 73.3, 70.2, 62.2, 60.4, 59.7, 55.7, 34.1, 21.6.

**A representative synthetic procedure of compounds 7a-7o and 8 is as follows:** $PdCl_2$ (10 mg, 5.6 mol%) and

$CuCl_2$ (94 mg, 0.7 mmol) were added to a solution of **4a-4n**, **4u** (0.5 mmol) in MeOH (20 mL) at 25 °C. Molecular oxygen was slowly bubbled into the reaction mixture for 5 min, and stirring occurred at 25 °C for 1 h. The reaction was monitored by TLC plate until the starting materials were consumed. Then, $Bi(OTf)_3$ (100 mg, 15.2 mol%) was added to the reaction mixture at 25 °C. The reaction mixture was stirred at reflux (65 °C) for 14 h. The solvent of the reaction mixture was concentrated, and the resulting residue was extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product. Purification on silica gel (hexanes/EtOAc = 15/1~3/1) afforded **7a-7o** and **8**.

**2-[7,8-Dimethoxy-3-(toluene-4-sulfonyl)naphthalen-2-yl]phenol (7a).** Yield = 84% (183 mg); Colorless gum; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{25}H_{23}O_5S$ 435.1266, found 435.1269; $^1H$ NMR (400 MHz, $CDCl_3$): δ 8.94 (s, 1H), 7.94 (s, 1H), 7.87 (d, *J* = 9.2 Hz, 1H), 7.47 (d, *J* = 9.2 Hz, 1H), 7.27 (dt, *J* = 2.0, 7.6 Hz, 1H), 7.15 (d, *J* = 8.4 Hz, 2H), 7.00 (d, *J* = 8.4 Hz, 2H), 6.95 (dd, *J* = 0.8, 8.0 Hz, 1H), 6.71 (dt, *J* = 1.2, 7.6 Hz, 1H), 6.53 (dd, *J* = 1.6, 7.6 Hz, 1H), 5.44 (br s, 1H), 4.04 (s, 3H), 3.92 (s, 3H), 2.33 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 153.7, 151.3, 143.7, 136.8, 135.7, 131.7, 130.9, 130.6, 130.2, 129.7, 129.1 (2x), 128.9, 127.8 (2x), 127.6, 127.2, 126.6, 125.9, 120.5, 118.0, 116.6, 61.2, 56.6, 21.5.

**2-(3-Benzenesulfonyl-7,8-dimethoxynaphthalen-2-yl)phenol (7b).** Yield = 85% (179 mg); Colorless gum; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{24}H_{21}O_5S$ 421.1110, found 421.1113; $^1H$ NMR (400 MHz, $CDCl_3$): δ 8.95 (s, 1H), 7.94 (s, 1H), 7.86 (d, *J* = 8.8 Hz, 1H), 7.46 (d, *J* = 8.8 Hz, 1H), 7.40 (dt, *J* = 2.0, 7.6 Hz, 1H), 7.29-7.18 (m, 5H), 6.91 (dd, *J* = 0.8, 8.0 Hz, 1H), 6.70 (dt, *J* = 0.8, 8.0 Hz, 1H), 6.54 (dd, *J* = 0.8, 7.6 Hz, 1H), 5.47 (br s, 1H), 4.03 (s, 3H), 3.91 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 153.7, 151.3, 142.5, 139.8, 135.3, 132.7, 132.2, 131.7, 130.8, 130.7, 130.1, 129.7, 128.4 (2x), 128.2, 127.6 (2x), 126.5, 125.9, 120.3, 117.6, 116.5, 61.1, 56.6.

**2-(3-Methanesulfonyl-7,8-dimethoxynaphthalen-2-yl)phenol (7c).** Yield = 80% (143 mg); Colorless gum; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{19}H_{19}O_5S$ 359.0953, found 359.0957; $^1H$ NMR (400 MHz, $CDCl_3$): δ 8.71 (s, 1H), 8.07 (s, 1H), 7.82 (d, *J* = 8.8 Hz, 1H), 7.46 (d, *J* = 8.8 Hz, 1H), 7.40 (dt, *J* = 2.0, 7.6 Hz, 1H), 7.27 (dd, *J* = 2.0, 7.6 Hz, 1H), 7.10 (dd, *J* = 0.8, 8.0 Hz, 1H), 7.07 (dt, *J* = 0.8, 8.0 Hz, 1H), 5.69 (br s, 1H), 4.05 (s, 3H), 3.96 (s, 3H), 2.82 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 153.7, 151.4, 142.6, 135.0, 131.9, 131.7, 130.9, 130.7, 130.6, 127.9, 127.1, 126.6, 126.0, 121.1, 118.8, 116.6, 61.3, 56.6, 43.0.

**2-[3-(*n*-Butane-1-sulfonyl)-7,8-dimethoxynaphthalen-2-yl]phenol (7d).** Yield = 83% (166 mg); Colorless gum; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{22}H_{25}O_5S$ 401.1423, found 401.1426; $^1H$ NMR (400 MHz, $CDCl_3$): δ 8.68 (s, 1H), 8.07 (s, 1H), 7.83 (d, *J* = 9.2 Hz, 1H), 7.47 (d, *J* = 8.8 Hz, 1H), 7.41 (dt, *J* = 1.6, 7.6 Hz, 1H), 7.22 (dd, *J* = 1.6, 7.6 Hz, 1H), 7.13 (dd, *J* = 0.8, 8.4 Hz, 1H), 7.07 (dd, *J* = 1.2, 7.6 Hz, 1H), 5.89 (br s, 1H), 4.05 (s, 3H), 3.97 (s, 3H), 2.89-2.82 (m, 1H), 2.79-2.82 (m, 1H), 1.65-1.53 (m, 1H), 1.45-1.35 (m, 1H), 1.33-1.19 (m, 2H), 0.77 (t, *J* = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 153.9, 151.4, 142.6, 133.2, 132.2, 131.6, 131.4, 130.9, 130.6, 128.5, 127.2, 126.7, 125.9, 121.2, 119.4, 116.6, 61.3, 56.7, 53.8, 24.5, 21.3, 13.3.

**2-[3-(4-Fluorobenzenesulfonyl)-7,8-dimethoxynaphthalen-2-yl]phenol (7e).** Yield = 78% (171 mg); Colorless gum; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{24}H_{20}FO_5S$ 439.1016, found 439.1018; $^1H$ NMR (400 MHz, $CDCl_3$): δ 8.95 (s, 1H), 7.96 (s, 1H), 7.88 (d, *J* = 9.2 Hz, 1H), 7.48 (d, *J* = 9.2 Hz, 1H), 7.30-7.26 (m, 3H), 6.95 (dd, *J* = 1.2, 8.0 Hz, 1H), 6.90-6.86 (m, 2H), 6.77 (dd, *J* = 0.8, 7.6 Hz, 1H), 6.60 (dd, *J* = 1.6, 7.6 Hz, 1H), 5.32 (br s, 1H), 4.04 (s, 3H), 3.93 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 165.1 (d, *J* = 254.0 Hz), 153.7, 151.4, 142.6, 135.9 (d, *J* = 3.8 Hz), 135.3, 131.9, 131.8, 131.0, 130.8, 130.6 (d, *J* = 9.1 Hz, 2x), 129.9, 127.12, 127.05, 126.7, 126.0, 120.5, 117.8, 116.7, 115.8 (d, *J* = 21.9 Hz, 2x), 61.2, 56.6.

**2-[7,8-Dimethoxy-3-(4-methoxybenzenesulfonyl)naphthalen-2-yl]phenol (7f).** Yield = 88% (198 mg); Colorless gum; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{25}H_{23}O_6S$ 451.1215, found 451.1223; $^1H$ NMR (400 MHz, $CDCl_3$): δ 8.93 (s, 1H), 7.94 (s, 1H), 7.87 (d, *J* = 9.2 Hz, 1H), 7.46 (d, *J* = 8.8 Hz, 1H), 7.28 (dt, *J* = 2.0, 7.6 Hz, 1H), 7.18 (d, *J* = 8.8 Hz, 2H), 6.98 (dd, *J* = 1.2, 8.0 Hz, 1H), 6.77 (dt, *J* = 1.2, 7.6 Hz, 1H), 6.67 (d, *J* = 8.8 Hz, 2H), 6.58 (dd, *J* = 1.6, 7.6 Hz, 1H), 5.48 (br s, 1H), 4.04 (s, 3H), 3.92 (s, 3H), 3.79 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 163.0, 153.8, 151.3, 142.6, 136.0, 132.2, 131.8, 131.2, 130.8, 130.4, 130.0 (2x), 129.8, 127.7, 127.2, 126.6, 125.9, 120.5, 118.1 116.5, 113.8 (2x), 61.2, 56.6, 55.6.

**2-[7,8-Dimethoxy-3-(toluene-3-sulfonyl)naphthalen-2-yl]phenol (7g).** Yield = 83% (180 mg); Colorless gum; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{25}H_{23}O_5S$ 435.1266, found 435.1270; $^1H$ NMR (400 MHz, $CDCl_3$): δ 8.95 (s, 1H), 7.94 (s, 1H), 7.88 (d, *J* = 8.8 Hz, 1H), 7.47 (d, *J* = 8.8 Hz, 1H), 7.27 (dt, *J* = 2.0, 7.6 Hz, 1H), 7.22-7.20 (m, 1H), 7.14-7.11 (m, 2H), 7.01 (br s, 1H), 6.96 (dd, *J* = 0.8, 8.0 Hz, 1H), 6.72 (dt, *J* = 1.2, 7.6 Hz, 1H), 6.55 (dd, *J* = 1.6, 7.6 Hz, 1H), 5.44 (br s, 1H), 4.04 (s, 3H), 3.92 (s, 3H), 2.19 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 153.8, 151.3, 142.6, 139.5, 138.6, 135.7, 133.6, 132.2, 131.8, 130.9, 130.6, 129.7, 128.4, 128.3, 127.3, 127.2, 126.6, 125.9, 124.9, 120.4, 117.8, 116.6, 61.2, 56.6, 21.0.

**2-[3-(4-Ethylbenzenesulfonyl)-7,8-dimethoxynaphthalen-2-yl]phenol (7h).** Yield = 74% (166 mg); Colorless gum; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{26}H_{25}O_5S$ 449.1423, found 449.1426; $^1H$ NMR (400 MHz, $CDCl_3$): δ 8.95 (s, 1H), 7.94 (s, 1H), 7.88 (d, *J* = 9.2 Hz, 1H), 7.47 (d, *J* = 9.2 Hz, 1H), 7.26 (dt, *J* = 2.0, 7.6 Hz, 1H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.02 (d, *J* = 8.4 Hz, 2H), 6.96 (dd, *J* = 0.8, 8.0 Hz, 1H), 6.68 (dt, *J* = 0.8, 7.6 Hz, 1H), 6.50 (dd, *J* = 1.6, 7.6 Hz, 1H), 5.44 (br s, 1H), 4.04 (s, 3H), 3.92 (s, 3H), 2.62 (q, *J* = 7.6 Hz, 2H), 1.19 (t, *J* = 7.6 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 153.7, 151.3, 149.9, 142.6, 136.9, 135.8, 132.2, 131.7, 130.9, 130.5, 129.7, 128.0 (2x), 127.9 (2x), 127.6, 127.2, 126.6, 125.9, 120.5, 118.1, 116.6, 62.2, 56.6, 28.8, 15.3.

**2-[3-(4-Isopropylbenzenesulfonyl)-7,8-dimethoxynaphthalen-2-yl]phenol (7i).** Yield = 76%

(176 mg); Colorless gum; HRMS (ESI-TOF) *m/z*: [M + H]$^+$ calcd for $C_{27}H_{27}O_5S$ 463.1579, found 463.1586; $^1$H NMR (400 MHz, $CDCl_3$): δ 8.95 (s, 1H), 7.93 (s, 1H), 7.87 (d, *J* = 9.2 Hz, 1H), 7.47 (d, *J* = 9.2 Hz, 1H), 7.26 (dt, *J* = 2.0, 7.6 Hz, 1H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 2H), 6.95 (dd, *J* = 0.8, 8.0 Hz, 1H), 6.67 (dt, *J* = 0.8, 7.6 Hz, 1H), 6.49 (dd, *J* = 1.6, 7.6 Hz, 1H), 5.45 (br s, 1H), 4.04 (s, 3H), 3.92 (s, 3H), 2.91-2.84 (m, 1H), 1.203 (d, *J* = 6.8 Hz, 3H), 1.200 (d, *J* = 6.8 Hz, 3H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$): δ 154.4, 153.7, 151.3, 142.6, 137.0, 135.8, 132.2, 131.6, 130.9, 130.5, 129.7, 127.8 (2x), 127.6, 127.1, 126.62 (2x), 126.58, 125.9, 120.5, 118.1, 116.6, 61.2, 56.6, 34.1, 23.62, 23.55.

**2-[3-(4-*t*-Butylbenzenesulfonyl)-7,8-dimethoxynaphthalen-2-yl]phenol (7j).** Yield = 78% (186 mg); Colorless solid; mp = 158-160 ºC (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: [M + H]$^+$ calcd for $C_{28}H_{29}O_5S$ 477.1736, found 477.1742; $^1$H NMR (400 MHz, $CDCl_3$): δ 8.95 (s, 1H), 7.93 (s, 1H), 7.88 (d, *J* = 8.8 Hz, 1H), 7.47 (d, *J* = 9.2 Hz, 1H), 7.24 (dt, *J* = 2.0, 7.6 Hz, 1H), 7.19 (br s, 4H), 6.95 (dd, *J* = 1.2, 8.0 Hz, 1H), 6.65 (dt, *J* = 0.8, 7.6 Hz, 1H), 6.47 (dd, *J* = 1.6, 7.6 Hz, 1H), 5.44 (br s, 1H), 4.04 (s, 3H), 3.91 (s, 3H), 1.27 (s, 9H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$): δ 156.6, 153.7, 151.3, 142.6, 136.5, 135.8, 132.2, 131.6, 130.9, 130.4, 129.6, 127.6, 127.5 (2x), 127.1, 126.6, 126.0, 125.5 (2x), 120.5, 118.1, 116.5, 61.2, 56.6, 35.0, 31.0 (3x).

**2-[7,8-Dimethoxy-3-(toluene-4-sulfonyl)naphthalen-2-yl]-4-fluorophenol (7k).** Yield = 72% (163 mg); Colorless gum; HRMS (ESI-TOF) *m/z*: [M + H]$^+$ calcd for $C_{25}H_{22}FO_5S$ 453.1172, found 453.1180; $^1$H NMR (400 MHz, $CDCl_3$): δ 8.92 (s, 1H), 7.91 (s, 1H), 7.88 (d, *J* = 9.2 Hz, 1H), 7.48 (d, *J* = 8.8 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 2.0 Hz, 1H), 6.96 (d, *J* = 8.4 Hz, 1H), 6.04 (dt, *J* = 1.6, 8.8 Hz, 1H), 5.59 (s, 1H), 4.04 (s, 3H), 3.93 (s, 3H), 2.36 (s, 3H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$): δ 156.8 (d, *J* = 238.0 Hz), 151.4, 149.9, 144.2, 142.6, 136.6, 135.3, 130.8, 130.5, 130.2, 129.2 (2x), 129.0 (d, *J* = 3.1 Hz), 127.7 (2x), 127.1, 126.3, 126.0, 119.8 (d, *J* = 8.3 Hz), 117.6 (d, *J* = 22.7 Hz), 116.7, 116.1 (d, *J* = 22.7 Hz), 61.2, 56.6, 21.5.

**2-[7,8-Dimethoxy-3-(toluene-4-sulfonyl)naphthalen-2-yl]-3-methoxyphenol (7l).** Yield = 83% (193 mg); Colorless solid; mp = 124-126 ºC (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: [M + H]$^+$ calcd for $C_{26}H_{25}O_6S$ 465.1372, found 465.1379; $^1$H NMR (400 MHz, $CDCl_3$): δ 8.92 (s, 1H), 7.92 (s, 1H), 7.86 (d, *J* = 8.8 Hz, 1H), 7.45 (d, *J* = 8.8 Hz, 1H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.53 (d, *J* = 2.4 Hz, 1H), 6.44 (d, *J* = 8.4 Hz, 1H), 6.31 (dd, *J* = 2.4, 8.8 Hz, 1H), 5.48 (s, 1H), 4.04 (s, 3H), 3.92 (s, 3H), 3.84 (s, 3H), 2.34 (s, 3H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$): δ 161.1, 154.8, 151.3, 143.7, 142.5, 136.9, 136.1, 132.2, 132.1, 130.9, 130.6, 129.1 (2x), 127.8 (2x), 127.2, 127.1, 125.9, 119.8, 116.5, 106.9, 102.9, 61.2, 56.6, 55.4, 21.5.

**2-[8-Isopropoxy-7-methoxy-3-(toluene-4-sulfonyl)naphthalen-2-yl]phenol (7m).** Yield = 82% (189 mg); Colorless solid; mp = 162-164 ºC (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: [M + H]$^+$ calcd for $C_{27}H_{27}O_5S$ 463.1579, found 463.1586; $^1$H NMR (400 MHz, $CDCl_3$): δ 8.93 (s, 1H), 7.96 (s, 1H), 7.85 (d, *J* = 9.2 Hz, 1H), 7.46 (d, *J* = 9.2 Hz, 1H), 7.25 (dt, *J* = 1.6, 8.0 Hz, 1H), 7.15 (d, *J* = 8.8 Hz, 2H), 7.00 (d, *J* = 8.4 Hz, 2H), 6.95 (dd, *J* = 0.8, 8.4 Hz, 1H), 6.71 (dt, *J* = 1.2, 7.6 Hz, 1H), 6.54 (dd, *J* = 1.6, 7.6 Hz, 1H), 5.30 (br s, 1H), 4.67-4.61 (m, 1H), 4.01 (s, 3H), 2.33 (s, 3H), 1.26 (d, *J* = 6.0 Hz, 3H), 1.25 (d, *J* = 6.0 Hz, 3H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$): δ 153.8, 151.5, 143.6, 140.7, 137.0, 135.7, 132.2, 131.8, 131.7, 130.6, 129.7, 129.1 (2x), 127.8 (2x), 127.5, 127.4, 127.2, 125.5, 120.4, 117.8, 116.6, 75.6, 56.6, 22.6 (2x), 21.5.

**2-[8-*n*-Butoxy-7-methoxy-3-(toluene-4-sulfonyl)naphthalen-2-yl]phenol (7n).** Yield = 79% (188 mg); Colorless gum; HRMS (ESI-TOF) *m/z*: [M + H]$^+$ calcd for $C_{28}H_{29}O_5S$ 477.1736, found 477.1745; $^1$H NMR (400 MHz, $CDCl_3$): δ 8.94 (s, 1H), 7.93 (s, 1H), 7.86 (d, *J* = 9.2 Hz, 1H), 7.46 (d, *J* = 9.2 Hz, 1H), 7.26 (dt, *J* = 2.0, 7.6 Hz, 1H), 7.15 (d, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 8.4 Hz, 2H), 6.95 (dd, *J* = 0.8, 8.0 Hz, 1H), 6.71 (dt, *J* = 1.2, 7.6 Hz, 1H), 6.53 (dd, *J* = 1.6, 7.6 Hz, 1H), 5.40 (br s, 1H), 4.06 (t, *J* = 6.8 Hz, 2H), 4.02 (s, 3H), 2.33 (s, 3H), 1.78-1.70 (m, 2H), 1.48-1.35 (m, 2H), 0.90 (t, *J* = 7.2 Hz, 3H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$): δ 153.7, 151.3, 143.6, 142.0, 137.1, 136.9, 135.7, 131.7, 130.6, 130.2, 129.7, 129.4, 129.1 (2x), 128.9, 127.8 (2x), 126.8, 125.7, 120.4, 117.9, 116.7, 73.6, 56.7, 32.2, 21.5, 19.0, 13.7.

**1-(10-*n*-Butoxy-12-hydroxy-9-methoxy-13-tosyl-11,12-dihydro-6*H*-6,12-methanodibenzo[*b*,*f*]oxocin-11-yl)ethan-1-one (8).** Rotamer; Yield = 5% (13 mg); Colorless solid; mp = 183-185 ºC (recrystallized from hexanes and EtOAc); HRMS (ESI-TOF) *m/z*: [M + H]$^+$ calcd for $C_{30}H_{33}O_7S$ 537.1947, found 537.1954; $^1$H NMR (400 MHz, $CDCl_3$): δ 7.60 (br s, 2H), 7.22 (dd, *J* = 1.6, 8.0 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.92 (br s, 2H), 6.80 (dt, *J* = 1.6, 8.4 Hz, 1H), 6.38 (br s, 1H), 5.80 (br s, 1H), 4.90 (br s, 1H), 4.65 (s, 1H), 4.48 (s, 1H), 4.00 (br s, 1H), 3.79 (t, *J* = 7.6 Hz, 2H), 3.78 (s, 3H), 2.33 (s, 3H), 1.62-1.57 (m, 2H), 1.38-1.31 (m, 2H), 1.10 (s, 3H), 0.91 (t, *J* = 7.2 Hz, 3H). Single-crystal X-ray diagram: crystal of compound **8** was grown by slow diffusion of EtOAc into a solution of compound **8** in $CH_2Cl_2$ to yield colorless prisms. The compound crystallizes in the monoclinic crystal system, space group P $2_1$/c, *a* = 16.6327(7) Å, *b* = 14.6990(7) Å, *c* = 10.4191(5) Å, *V* = 2540.6(2) Å$^3$, *Z* = 4, $d_{calcd}$ = 1.403 g/cm$^3$, *F*(000) = 1136, 2$\theta$ range 1.851~26.413º, R indices (all data) R1 = 0.418, wR2 = 0.0912.

**4-Chloro-2-[7,8-dimethoxy-3-(toluene-4-sulfonyl)naphthalen-2-yl]phenol (7o).** Yield = 70% (164 mg); Colorless gum; HRMS (ESI-TOF) *m/z*: [M + H]$^+$ calcd for $C_{25}H_{22}ClO_5S$ 469.0877, found 469.0883; $^1$H NMR (400 MHz, $CDCl_3$): δ 8.93 (s, 1H), 7.91 (s, 1H), 7.88 (d, *J* = 9.2 Hz, 1H), 7.48 (d, *J* = 9.2 Hz, 1H), 7.20 (dt, *J* = 2.8, 8.8 Hz 1H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 1H), 6.18 (d, *J* = 2.4 Hz, 1H), 5.62 (br s, 1H), 4.05 (s, 3H), 3.94 (s, 3H), 2.38 (s, 3H); $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$): δ 152.7, 151.4, 144.3, 142.7, 136.5, 135.4, 130.81, 130.77, 130.4, 129.5, 129.4, 129.3 (2x), 129.0, 127.6 (2x), 127.2, 126.5, 126.0, 125.7, 120.0, 116.8, 61.3, 56.6, 21.5.

**2-[2-(2-Benzyloxypropenyl)-3-hydroxy-5-methoxyphenyl]-3-(toluene-4-sulfonyl)chroman-4-one (9).** $PdCl_2$ (10 mg, 5.6 mol%) and $CuCl_2$ (94 mg, 0.7

mmol) were added to a solution of **4r** (277 mg, 0.5 mmol) in MeOH (20 mL) at 25 °C. Molecular oxygen was slowly bubbled into the reaction mixture for 5 min, and stirring occurred at 25 °C for 1 h. The reaction was monitored by TLC plate until **4r** was consumed. Then, $Bi(OTf)_3$ (100 mg, 15.2 mol%) was added to the reaction mixture at 25 °C. The reaction mixture was stirred at 25 °C for 4 h. The solvent of the reaction mixture was concentrated, and the resulting residue was extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product. Purification on silica gel (hexanes/EtOAc = 30/1~3/1) afforded **9**. Yield = 60% (171 mg); Colorless gum; HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{33}H_{31}O_7S$ 571.1791, found 571.1799; $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.75-7.72 (m, 3H), 7.47-7.43 (m, 1H), 7.27-7.11 (m, 8H), 6.97-6.91 (m, 2H), 6.80 (s, 1H), 6.49 (d, *J* = 0.8 Hz, 1H), 6.42 (s, 1H), 4.43 (d, *J* = 0.8 Hz, 1H), 4.11 (s, 2H), 3.52 (s, 3H), 2.47 (d, *J* = 0.8 Hz, 3H), 2.39 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 182.0, 159.4, 155.9, 154.5, 153.9, 145.7, 140.3, 137.3, 134.2, 129.6 (2x), 129.4 (2x), 128.6 (2x), 128.1 (2x), 127.0, 125.8, 125.0, 121.7, 120.5, 120.4, 117.9, 113.5, 104.7, 100.5, 75.0, 72.3, 56.3, 29.9, 21.6, 14.2.

**6-Methyl-6a-(toluene-4-sulfonyl)-6a,12a-dihydrobenzo[c]xanthen-7-one (10a) and 2-Phenyl-3-(toluene-4-sulfonyl)chroman-4-one (10b).** $PdCl_2$ (10 mg, 5.6 mol%) and $CuCl_2$ (94 mg, 0.7 mmol) were added to a solution of **4v** (209 mg, 0.5 mmol) in MeOH (20 mL) at 25 °C. Molecular oxygen was slowly bubbled into the reaction mixture for 5 min, and stirring occurred at 25 °C for 1 h. The reaction was monitored by TLC plate until **4v** was consumed. Then, $Bi(OTf)_3$ (100 mg, 15.2 mol%) was added to the reaction mixture at 25 °C. The reaction mixture was stirred at 25 °C for 14 h. The solvent of the reaction mixture was concentrated, and the resulting residue was extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product. Purification on silica gel (hexanes/EtOAc = 10/1~5/1) afforded a unseparated mixture of compounds **10a** and **10b** (ratio = 3:2). Yield = 65% (135 mg); Colorless gum; For compound **10a**: $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.97 (dd, *J* = 2.0, 8.0 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.46 (dt, *J* = 1.6, 8.4 Hz, 1H), 7.34-7.20 (m, 6H), 7.16 (d, *J* = 8.4 Hz, 2H), 6.74 (q, *J* = 1.2 Hz, 1H), 5.97 (s, 1H), 2.35 (s, 3H), 1.77 (d, *J* = 1.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 185.2, 161.4, 145.2, 136.6, 132.0, 131.0 (2x), 129.8, 128.8 (2x), 128.6, 128.5, 128.0, 126.6, 124.6, 122.3, 117.8, 123.2, 122.2, 120.9, 117.8, 77.9, 77.5, 21.6, 21.2. For compound **10b**: $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.72-7.70 (m, 3H), 7.46 (dt, *J* = 1.6, 8.4 Hz, 1H), 7.27-7.19 (m, 7H), 6.95 (dd, *J* = 0.8, 7.6 Hz, 1H), 6.91 (dd, *J* = 0.8, 8.4 Hz, 1H), 6.57 (s, 1H), 4.39 (d, *J* = 1.6 Hz, 1H), 2.38 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 182.0, 159.0, 145.7, 137.3, 136.2, 134.2, 129.5 (2x), 129.4 (2x), 129.0 (2x), 128.7, 126.9, 126.0 (2x), 121.7, 120.8, 118.2, 76.2, 73.0, 21.6. Compound **10b** is a known compound and the analytical data are consistent with those in the literature.[47]

**1-(2-Aminophenyl)-2-(toluene-4-sulfonyl)ethanone (11).** $CuBr_2$ (450 mg, 2.0 mmol) was added to a solution of commercial available substituted *o*-nitroacetocephenone (165 mg, 1.0 mmol) in EtOAc (30 mL) at 25 °C. The reaction mixture was stirred at reflux for 10 h. Then, the reaction mixture was cooled to 25 °C, filtered, neutralized with saturated $NaHCO_{3(aq)}$ (30 mL), and extracted with EtOAc (3 x 30 mL). The combined organic layers were washed with brine, dried, filtered, and evaporated to afford crude product under reduced pressure. Without further purification, sodium toluenesulfinate (374 mg, 2.1 mmol) was added to the crude α-bromo *o*-nitroacetocephenone in a cosolvent of dioxane and water (20 mL, v/v = 1/1) at 25 °C. The reaction mixture was stirred at reflux for 3 h. The reaction mixture was cooled to 25 °C and extracted with $CH_2Cl_2$ (3 x 30 mL). The combined organic layers were washed with brine, dried, filtered, and evaporated to afford crude product under reduced pressure. Without further purification, Pd/C (10%, 30 mg) was added to a solution of the resulting α-sulfonyl *o*-nitroacetocephenone in EtOH (20 mL) at 25 °C in a non-reactant borosilicate glass vessel under the shaker hydrogenation apparatus. Hydrogen gas was installed to the reaction mixture at 25 °C. The pressure was increased to 2 atmospheres. The reaction mixture was stirred at 25 °C for 20 h. The pressure was decreased to 1 atmosphere and the solvent was concentrated. The residue was diluted with water (10 mL) and the mixture was extracted with $CH_2Cl_2$ (3 x 20 mL). The combined organic layers were washed with brine, dried, filtered and evaporated to afford crude product under reduced pressure. Purification on silica gel (hexanes/EtOAc = 8/1~1/1) afforded **11**. Yield of three step = 51% (147 mg); Colorless solid; mp = 133-135 °C (recrystallized from hexanes and EtOAc); HRMS (ESI, $M^+$+1) calcd for $C_{15}H_{16}NO_3S$ 290.0851, found 290.0856; $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.70 (br s, 2H), 7.54 (d, *J* = 9.2 Hz, 1H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.8 Hz, 1H), 7.30 (dd, *J* = 6.4, 8.8 Hz, 1H), 7.25 (d, *J* = 8.8 Hz, 2H), 7.02 (dd, *J* = 6.4, 8.8 Hz, 1H), 4.92 (s, 2H), 2.40 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 157.2, 155.3, 145.7, 134.5, 131.1, 130.0 (2x), 128.3 (2x), 125.2, 119.3, 118.1, 115.2, 57.5, 21.7.

## Acknowledgements

The authors would like to thank the Ministry of Science and Technology of the Republic of China (Taiwan) for financial support (MOST 109-2113-M-037-014-MY3).

## References

[1] Y. Ling, D. An, Y. Zhou, W. Rao, *Org. Lett.* **2019**, *21*, 3396-3401.
[2] X. Li, S. Wang, S. Li, K. Li, X. Mo, L. Liu, W. Chang J. Li, *J. Org. Chem.* **2019**, *84*, 1288-1298.
[3] S. K. Pagire, A. Hossain, O. Reiser, *Org. Lett.* **2018**, *20*, 648-651.
[4] R. Samineni, C. R. C. Bandi, P. Srihari, G. Mehta, *Org. Lett.* **2016**, *18*, 6184-6187.
[5] M.-Y. Chang, H.-Y. Chen, Y.-L. Tsai, *J. Org. Chem.* **2019**, *84*, 326-337.
[6] J. Wang, C. Deng, Q. Zhang, Y. Chai, *Org. Lett*. **2019**, *21*, 1103-1107.
[7] T.-T. Kao, B.-K. Peng, M.-C. Liang, C.-J. Lee, I.-C. Chen, K.-S. Shia, Y.-K. Wu, *J. Org. Chem.* **2018**, *83*, 14688-14697.

[8] L. A. Jouanno, V. Tognetti, L. Joubert, C. Sabot, P.-Y. Renard, *Org. Lett.* **2013**, *15*, 2530-2533.
[9] P. V. Ramachandran, P. B. Chanda, *Org. Lett.* **2012**, *14*, 4346-4349.
[10] T.-S. Jiang, R.-Y. Tang, X.-G. Zhang, X.-H. Li, J.-H. Li, *J. Org. Chem.* **2009**, *74*, 8834-8837.
[11] J. Hu, Q. Zhang, H. Yuan, Q. Liu, *J. Org. Chem.* **2008**, *73*, 2442-2445.
[12] C. Yang, A. Nakamura, G. Fukuhara, Y. Origane, T. Mori, T. Wada, Y. Inoue, *J. Org. Chem.* **2006**, *71*, 3126-3136.
[13] J. M. Hernández-Torres, J. Achkar, A. Wei, *J. Org. Chem.* **2004**, *69*, 7206-7211.
[14] O. Arjona, R. F. de la Pradilla, J. Plumet, A. Viso1, *J. Org. Chem.* **1992**, *57*, 772-774.
[15] L. Zhang, H. Yuan, W. Lin, Y. Cheng, P. Li, W. Li, *Org. Lett.* **2018**, *20*, 4970-4974.
[16] X. Fu, H. Y. Bai, G.-D. Zhu, Y. Huang, S.-Y. Zhang, *Org. Lett.* **2018**, *20*, 3469-3472.
[17] S. M. Maddox, A. N. Dinh, F. Armenta, J. Um, J. L. Gustafson, *Org. Lett.* **2016**, *18*, 5476-5479.
[18] W.-H. Rao, X.-S. Yin, B.-F. Shi, *Org. Lett.* **2015**, *17*, 3758-3761.
[19] S. Lee, S. Mah, S. Hong, *Org. Lett.* **2015**, *17*, 3864-3867.
[20] L. Zhang, Z. Li, R. Fan, *Org. Lett.* **2013**, *15*, 2482-2485.
[21] K. R. Fandrick, J. Ogikubo, D. R. Fandrick, N. D. Patel, J. Saha, H. Lee, S. Ma, N. Grinberg, C. A. Busacca, C. H. Senanayake, *Org. Lett.* **2013**, *15*, 1214-1217.
[22] B. Yu, K.-F. Yang, X.-F. Bai, J. Cao, Z.-J. Zheng, Y. M. Cui, Z. Xu, L. Li, L.-W. Xu, *Org. Lett.* **2018**, *20*, 2551-2554.
[23] Y. Ogiwara, Y. Sakurai, H. Hattori, N. Sakai, *Org. Lett.* **2018**, *20*, 4204-4208.
[24] S. Zhang, Y. Yamamoto, M. Bao, *J. Org. Chem.* **2018**, *83*, 13981-13990.
[25] Y. Hua, H. H. Nguyen, W. R. Scaggs, J. Jeon, *Org. Lett.* **2013**, *15*, 3412-3415.
[26] K. H. Oh, S. M. Kim, S. Y. Park, J. K. Park, *Org. Lett.* **2016**, *18*, 2204-2207.
[27] M. F. Z. J. Amaral, A. A. Baumgartner, R. Vessecchi, G. C. Clososki, *Org. Lett.* **2015**, *17*, 238-241.
[28] S. E. Soliman, C. S. Bennett, *Org. Lett.* **2018**, *20*, 3413-3417.
[29] M. Fàbregas, A. Gómez-Palomino, M. Pellicena, D. F. Reina, P. Romea, F. Urpí, M. Font-Bardia, *Org. Lett.* **2014**, *16*, 6220-6223.
[30] T. Okitsu, K. Sato, A. Wada, *Org. Lett.* **2010**, *12*, 3506-3509.
[31] F. F. Fleming, Y. Wei, W. Liu, Z. Zhang, *Org. Lett.* **2007**, *9*, 2733-2736.
[32] J. Jia, A. Yu, S. Ma, Y. Zhang, K. Li, X. Meng, *Org. Lett.* **2017**, *19*, 6084-6087.
[33] M.Miao, Y. Luo, H. Xu, Z. Chen, J. Xu, H. Ren, *Org. Lett.* **2016**, *18*, 4292-4295.
[34] Y. Su, H. Zhou, J. Chen, J. Xu, X. Wu, A. Lin, H. Yao, *Org. Lett.* **2014**, *16*, 4884-4887.
[35] L. Hintermann, R. Masuo, K. Suzuki, *Org. Lett.* **2008**, *10*, 4859-4862.
[36] J. Kagan, D. A. Agdeppa, A. I. Jr. Chang, S.-A. Chen, M. A. Harmata, B. Melnick, G. Patel, C. Poorker, S. P. Singh, *J. Org. Chem.* **1981**, *46*, 2916-2920.
[37] M. Harmata, T. Murray, *J. Org. Chem.* **1989**, *54*, 3761-3733.
[38] M.-Y. Chang, H.-Y. Chen, Y.-L. Tsai, *J. Org. Chem.* **2019**, *84*, 443-449, and references cited therein.
[39] G. Li, B. Zhu, X. Ma, C. Jia, X. Lv, J. Wang, F. Zhao, Y. Lv, S. Yang, *Org. Lett.* **2017**, *19*, 5166-5169.
[40] P. Bai, S. Sun, Z. Li, H. Qiao, X. Su, F. Yang, Y. Wu, Y. Wu, *J. Org. Chem.* **2017**, *82*, 12119-12127, and references cited therein.
[41] M.-Y. Chang, H.-Y. Chen, Y.-L. Tsai, *Synthesis* **2019**, *51*, 2553-2563.
[42] M.-Y. Chang, Y.-T. Hsiao, K.-H. Lai, *J. Org. Chem.* **2018**, *83*, 14110-14119.
[43] N.-C. Hsueh, H.-Y. Chen, M.-Y. Chang, *J. Org. Chem.* **2017**, *82*, 13324-13332.
[44] P.-Y. Chen, K. S. Huang, C.-C. Tsai, T.-P. Wang, E.-C. Wang, *Org. Lett.* **2012**, *14*, 4930-4933.
[45] S. M. Sigman, E. W. Werner, *Acc. Chem. Res.* **2012**, *45*, 874-884.
[46] CCDC 1938641 (**4h**), 1938642 (**4k**), 1938643 (**4t**), 1938644 (**6d**), 1938645 (**6j**) and 1938646 (**8**) contain the supplementary crystallographic data for this paper. This data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: 44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).
[47] M.-Y. Chang, Y.-L. Tsai, Y.-L. Chang *J. Org. Chem.* **2020**, *85*, 1033-1043.
[48] Transition metal-promoted direct deallylation of allylbenzene, see: a) S. Onodera, S. Ishikawa, T. Kochi, F. Kakiuchi, *J. Am. Chem. Soc.* **2018**, *140*, 9788-9792; b) J. Liu, X. Wen, C. Qin, X. Li, X. Luo, A. Sun, B. Zhu, S. Song, N. Jiao, *Angew. Chem., Int. Ed.* **2017**, *56*, 11940-11944; c) C. Qin, W. Zhou, F. Chen, Y. Ou, N. Jiao, *Angew. Chem., Int. Ed.* **2011**, *50*, 12595-12599.

10.1002/adsc.202001021

FULL PAPER

# $PdCl_2$/$CuCl_2$/$Bi(OTf)_3$-promoted Construction of Sulfonyl Dibenzooxabicyclo[3.3.1]nonanes and Arylnaphthalenes via Intramolecular Annulation of Sulfonyl *o*-Allylarylchromanones

*Adv. Synth. Catal.* **Year**, *Volume*, Page – Page

Nai-Chen Hsueh and Meng-Yang Chang*