有机化学 DOI: 10.6023/cjoc202307019 研究论文
Chinese Journal of Organic Chemistry ARTICLE

邻亚甲醌与硫叶立德反应合成 2,3-二取代苯并二氢呋喃化合物

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摘要 发展了一种简便有效的通过邻甲亚醌与硫叶立德反应合成苯并二氢呋喃化合物的方法. 在二氯甲烷中和二异丙基乙基胺存在下, 反应能够在室温下 1 h 内完成, 以良好至优秀的收率得到反式-2,3-二取代二氢苯并呋喃产物. 反应能够扩大到克级规模, 产物能够转化为潜在生物活性的苯并呋喃衍生物, 并推测了可能的反应机理,
关键词 苯并二氢呋喃; 邻亚甲醌; 硫叶立德; [4＋1]环加成; 碱催化

Synthesis of 2,3-Disubstituted Dihydrobenzofurans from *o*-Quinone Methides and Sulfur Ylides

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Abstract A facile and efficient approach to dihydrobenzofurans from sulfur ylides and *o*-quinone methides (*o*-QMs) was developed. In most cases, the reaction could be completed in the presence of *N*,*N*-diisopropylethylamine (DIPEA) in CH_2Cl_2 at room temperature within 1 h, providing *trans*-2,3-disubstitiuted dihydrobenzofurans in good to excellent yields. The reaction could expand to a scale of grams, and the products could be converted into the potentially bioactive benzofuran derivatives. The plausible mechanism is proposed.
Keywords dihydrobenzofuran; *o*-quinone methides; sulfur ylide; [4＋1] cycloaddition; base-catalysis

1 Introduction

2,3-Dihydrobenzofurans, as an important class of key structural units, are ubiquitous in numerous natural products, pharmaceuticals and bioactive molecules.[1] As shown in Figure 1, compound **I** is an anticancer agent,[2] **II** serves as an antibacterial agent,[3] natural product megapodiol **III** can be used as a potential antileukemic agent[4] and **IV** has good insecticidal properties.[5] Owing to their versatile biological activities and medicinal values, 2,3-dihydrobenzofuran framework attracted much attention from synthetic chemists. The new methods for the synthesis of 2,3-dihydrobenzofuran are emerging continuously. There are many common methods including hydrogenation of substituted benzofuran,[6] difunctionalization of alkenes,[7] C—H bond insertion-cyclization,[8] Michael addition,[9] cycloaddition,[10] and so on. Despite these impressive progresses, methods for the preparation of highly functionalized 2,3-dihydrobenzofurans with high efficiency and broad scope under mild conditions are highly desirable.

In recent years, sulfur ylides serve as a class of powerful

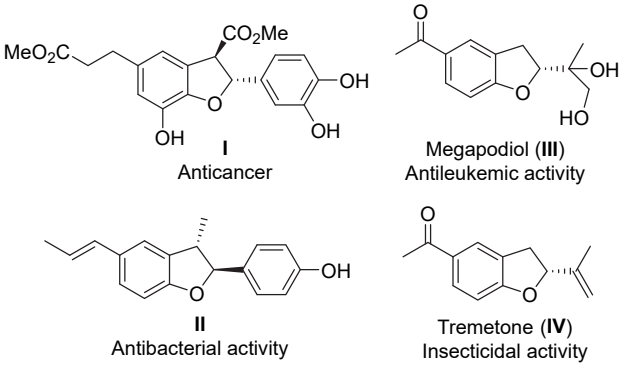

Figure 1 Selected bioactive dihydrobenzofuran compounds

synthon for the carbon-carbon bond and carbon-heteroatom bond formations.[11] The inherent zwitterionic properties and reactivity enable their participation in various chemical transformations, especially in the efficient construction of cyclic systems. Likewise, sulfur ylides were also utilized by many researchers for the construction of 2,3-dihydrobenzofuran framework,[12] demonstrating that

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Received July 19, 2023; revised August 28, 2023; published online September 21, 2023.
Project supported by the National Key Research and Development Program of China (No. 2017YFD0200301).
国家重点研发计划(No. 2017YFD0200301)资助项目.

[4＋1] cycloaddition is a very reliable strategy. Among most of the reported cycloaddition methods, the reaction of sulfur ylides with the precursor of *o*-quinone methides (*o*-QMs) has been well studied. However, due to the limited stability of *o*-QMs in some cases, few examples involving the straightforward utilization of *o*-QMs for the formation of 2,3-dihydrobenzofuran skeleton were reported.[13]

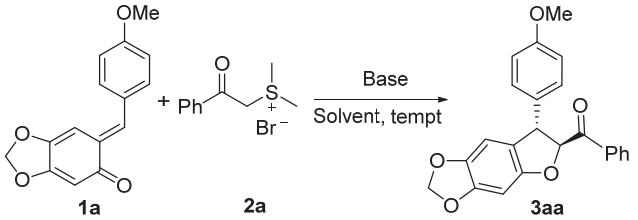
In our continuing effort to develop the concise and efficient methods for the construction of fused-heterocyclic framework,[14] we recently found that only if the *o*-QMs were successfully achieved, the subsequent reaction with sulfur ylide would rapidly produce the corresponding 2,3-dihydrobenzofuran compounds under mild conditions. The similar results have been reported by Zhou *et al*.[12d] however, in their work the *o*-QMs only serve as the reaction intermediates and indirectly employed. Herein we provide much more detailed and direct use of the *o*-QMs, which well complements to the previous reports in the construction of 2,3-dihydrobenzofuran frameworks.

2 Results and discussion

In the beginning, the reaction of *o*-QMs **1a** with sulfur ylide **2a** was selected to optimize the reaction conditions. *o*-QMs can be prepared from sesamol through a two-step reaction.[15] Base, solvents, temperature and reaction time were examined and the corresponding results were shown in Table 1. In the presence of K_2CO_3, different solvents were first investigated (Entries 1～8). The choice of solvents is quite important. In methanol no target product was found after 24 h. In most of the screened solvents, the reaction could be completed within 6～24 h. CH_2Cl_2 gave a much higher yield of dihydrobenzofuran **3aa** (91%, Entry 4) after 6 h. Subsequently, *t*-BuOK, K_2CO_3, Cs_2CO_3, Na_2CO_3, Et_3N and *N*,*N*-diisopropylethylamine (DIPEA) as bases were tested for the reaction (Entries 9～14). DIPEA proved to be a more effective base than the others (Entry 14), affording **3aa** in 97% yield within only 1 h. The reaction temperature also had a certain effect on the reaction. It was found that 25 ℃ was an appropriate temperature for the reaction, and a decrease and increase of the reaction temperature could not lead to an improvement in the yield of **3aa** (Entries 15 and 16). The ratio of *trans*/*cis* isomers of the product **3aa** was determined to be ＞19∶1 by comparing with the NMR data from literature.[12] Therefore the optimal conditions were identified as following: DIPEA (2 equiv.), CH_2Cl_2 as solvent at room temperature (Entry 14).

With the optimal conditions in hand, the scope and generality of substrates for this cycloaddition were then checked. The scope of sulfur ylides **2** was explored (Table 2). Sulfur ylides with all kinds of substituents (F, Cl, Br, CN, CF_3, CH_3 and OCH_3) on the benzene ring as R^2 were well tolerated in this reaction, resulting in good to excellent yields (**3ab**～**ak**). Even the strong electron-withdrawing groups 4-CF_3 and 3-NO_2 (**3ae** and **3ai**, 86% and 96% yields) or reactive groups 3-OMe and 2-OH (**3ag** and **3ak**, 87% and 92% yields) had hardly influence on the reactivities of the reaction. Moreover, when this procedure was applied to those sulfur ylides with other aryl groups, the same good yields were also afforded (78%～87% yields, Entries 11～13), though the reaction time required being prolonged to 6 or 8 h for heteroaryl substituted substrates **2m** and **2n** (Entries 12 and 13). It is noteworthy that the alkyl substituents at sulfur ylides were also compatible with the reaction (Entries 14～16), giving the products in high yields (80%～87%), indicating the steric hindrance has no obvious effect on the reaction.

Table 1 Optimization for the reaction conditions[a]

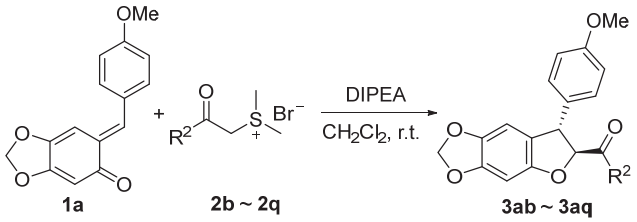


Entry	Solvent	Base	*T*/℃	Time/h	Yield[b]/%
1	CH_3CN	K_2CO_3	r.t.	6	75
2	THF	K_2CO_3	r.t.	6	85
3	$CHCl_3$	K_2CO_3	r.t.	6	86
4	CH_2Cl_2	K_2CO_3	r.t.	6	91
5	Dioxane	K_2CO_3	r.t.	12	68
6	Acetone	K_2CO_3	r.t.	16	73
7	Toluene	K_2CO_3	r.t.	24	85
8	CH_3OH	K_2CO_3	r.t.	24	—
9	CH_2Cl_2	Li_2CO_3	r.t.	6	93
10	CH_2Cl_2	Na_2CO_3	r.t.	6	89
11	CH_2Cl_2	Cs_2CO_3	r.t.	12	91
12	CH_2Cl_2	*t*-BuOK	r.t.	12	30
13	CH_2Cl_2	Et_3N	r.t.	1	85
14	CH_2Cl_2	DIEPA	r.t.	1	97
15	CH_2Cl_2	DIEPA	0	6	83
16	CH_2Cl_2	DIEPA	40	1	90

[a] Unless otherwise noted, the reactions were conducted with 0.10 mmol of **1a** (1.0 equiv.), 0.15 mmol of **2a** (1.5 equiv.) and 0.2 mmol of base (2.0 equiv.) in solvent (2.0 mL) at room temperature. [b] Isolated yields.

Next, the scope of *o*-QMs **1** was examined. As shown in Table 3, a series of relatively stable *o*-QMs were used for this cycloaddition.[16] The electronic properties of substituents on the aryl ring of **1b**～**1j** affected the yields to some extent. It appeared that those with electron-withdrawing substituents (Entries 4, 5 and 6; F, Cl and Br) displayed a much higher reactivities and provided relatively higher yields than those with electron-donating groups (Entries 2, 3, 7, 8). The electron-rich 2-thienyl ring has a negative effect on this reaction, giving only 24% yield of product **3ja** (Entry 9). In addition, when the substrate was changed to dimethoxy *o*-QMs **1a'**, the same excellent yield was also achieved (Scheme 1, 92%). In general, for substrates *o*-QMs **1b**～**1j** bearing electron-donating substituents, the reaction demonstrated much lower reactivities than those with electron-withdrawing groups.

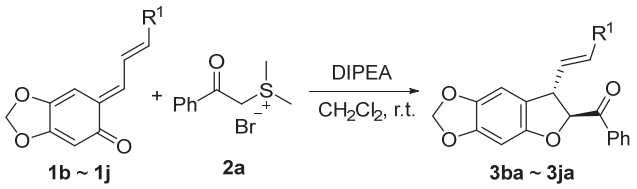
Table 2 Substrate scope for sulfur ylides[a]



Entry	R^2	Product	Time/h	Yield[b]/%	*dr*[c]
1	4-ClC_6H_4	**3ab**	1	88	>19∶1
2	4-BrC_6H_4	**3ac**	1	80	>19∶1
3	4-CNC_6H_4	**3ad**	1	89	>19∶1
4	4-$CF_3C_6H_4$	**3ae**	1	86	>19∶1
5	4-$CH_3C_6H_4$	**3af**	1	98	>19∶1
6	3-$MeOC_6H_4$	**3ag**	1	87	>19∶1
7	3-FC_6H_4	**3ah**	1	75	>19∶1
8	3-$O_2NC_6H_4$	**3ai**	1	96	>19∶1
9	2-FC_6H_4	**3aj**	1	81	>19∶1
10	2-HOC_6H_4	**3ak**	1	92	>19∶1
11	2-Naphthyl	**3al**	1	83	>19∶1
12	2-Furyl	**3am**	6	78	>19∶1
13	2-Thienyl	**3an**	8	87	>19∶1
14	Cyclopropyl	**3ao**	1	80	>19∶1
15	*t*-Bu	**3ap**	1	87	>19∶1
16	Adamantyl	**3aq**	1	81	>19∶1

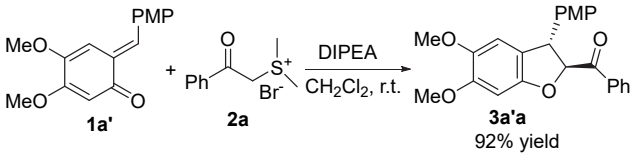
[a] Unless otherwise noted, the reactions were conducted with 0.10 mmol of **1**, 0.15 mmol of **2a** and 0.2 mmol of DIPEA in CH_2Cl_2 (2.0 mL) at r.t. [b] Isolated yields. [c] Determined by ^1H NMR spectra.

Table 3 Substrate scope for *o*-QMs[a]



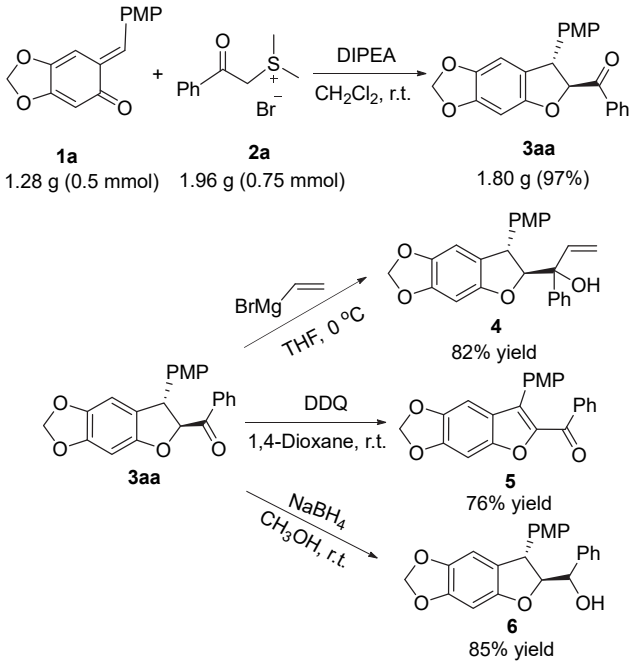
Entry	R^1	Product	Time/h	Yield[b]/%	*dr*[c]
1	Ph	**3ba**	1	55	>19∶1
2	4-$CH_3C_6H_4$	**3ca**	1	68	>19∶1
3	4-$MeOC_6H_4$	**3da**	12	67	>19∶1
4	4-FC_6H_4	**3ea**	1	85	>19∶1
5	4-ClC_6H_4	**3fa**	1	85	>19∶1
6	4-BrC_6H_4	**3ga**	1	83	>19∶1
7	3-MeC_6H_4	**3ha**	1	68	>19∶1
8	2-$MeOC_6H_4$	**3ia**	12	52	>19∶1
9	2-Thienyl	**3ja**	1	24	>19∶1

[a] Unless otherwise noted, the reactions were conducted with 0.10 mmol of **1a** (1.0 equiv.), 0.15 mmol of 2 (1.5 equiv.) and 0.2 mmol of DIPEA (2.0 equiv.) in CH_2Cl_2 (2.0 mL) at r.t. [b] Isolated yields. [c] Determined by ^1H NMR spectra.



Scheme 1 Reaction of dimethoxy *o*-QMs

To demonstrate the synthetic utility of this protocol, the present cycloaddition reaction could be expanded to the gram scale. As shown in Scheme 2, under the standard conditions, [4+1] addition occurred smoothly for 1 h at room temperature to deliver the desired product **3aa** in 97% yield (1.80 g). Furthermore, the products **3aa** were readily converted into potentially bioactive compounds. In tetrahydrofuran (THF), **3aa** reacted with vinyl magnesium bromide to afford the tertiary alcohol product **4**.[17] Dehydrogenation of **3aa** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in dioxane for 24 h at room temperature led to the benzofuran skeleton **5** possessing versatile biological activities.[12d] Reduction of **3aa** with $NaBH_4$ in CH_3OH afforded the product **6** in 85% yield.



Scheme 2 Gram-scale reaction and further transformations

The X-ray crystal diffraction analysis for compound **3ao** indicated that 2,3-disubstituents are located at the *trans*-position (Figure 2, CCDC 2267289).[18] A plausible mechanism for this cycloaddition was proposed. Sulfur ylides as nucleophiles attacked at the external carbon of *o*-QMs as Michael addition, affording the phenoxide **A**. Subsequently, the intermediate **A** underwent intramolecular nucleophilic attack and simultaneously lost one molecular dimethyl sulfide, providing the final product dihydrobenzofuran **3aa**. Actually, in this process a couple of enantiomers were achieved (Scheme 3).

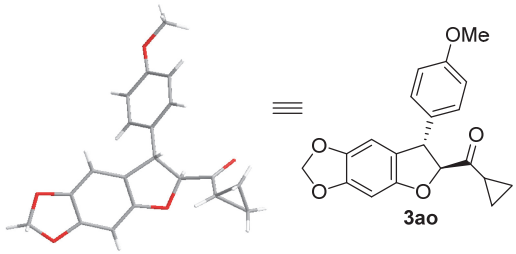
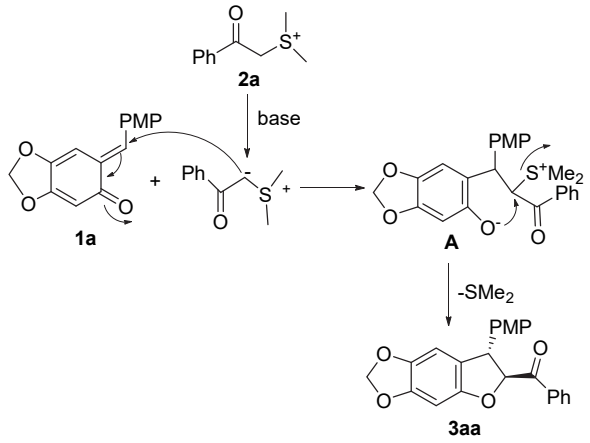


Figure 2 Structure of **3ao**



Scheme 3 Plausible reaction mechanism

3 Conclusions

In summary, a facile and efficient approach to dihydrobenzofurans through the reaction of sulfur ylides with *o*-quinone methides in the presence of DIPEA in CH_2Cl_2 was developed. In most cases the reaction could be completed at room temperature within 1 h, providing *trans*-2,3-disubstitiuted dihydrobenzofurans in good to excellent yields (up to 98% yield). The products could be conveniently converted to tertiary alcohol by Grignard reagents, secondary alcohol by reduction and benzofurans using DDQ as the oxidant. This work well complements the previous reports of Zhou and others,[12] providing an intensive and direct understanding for the reaction of *o*-QMs. Applications of this [4+1] cycloaddition reaction to other substrates and to the construction of biologically relevant compounds are ongoing in our laboratory.

4 Experimental section

4.1 General information

Unless otherwise stated, all solvents were purified and dried by standard procedures. The *o*-QMs were prepared according to the related literatures.[15-16] Sulfur ylides were synthesized based on the literature methods.[12a] NMR spectra were recorded on a Bruker Avance III HD 500 spectrometer using TMS as an internal standard (500 MHz for ^{1}H NMR, 125 MHz for ^{13}C NMR and 470 MHz for ^{19}F NMR). High-resolution mass spectrometry (HRMS) data were collected on a Bruker ultrafleXtreme MALDI TOF/TOF mass spectrometer.

4.2 General procedure for product **3**

To a Schlenk tube were added *o*-QMs **1** (0.1 mmol), sulfonium salt **2** (0.15 mmol) and DIPEA (0.2 mmol) in CH_2Cl_2 (2 mL), and the mixture was stirred at room temperature for 1 h (monitored by thin-layer chromatography). Then water (10 mL) was added, the organic layer was separated and the aqueous layer was extracted with dichloromethane (5 mL×3). The combined organic layer was dried by anhydrous sodium sulfate, and concentrated under vacuum. Then the residue was purified by column chromatography on silica gel (100～200 mesh) using petroleum-ethyl acetate (V∶V=3∶1～10∶1) as an eluent to afford the pure product **3**.

(7-(4-Methoxyphenyl)-6,7-dihydro-[1,3]dioxolo[4,5-*f*]-benzofuran-6-yl)(phenyl) methanone (**3aa**): 97% yield. White solid, m.p. 78～80 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.91 (dd, J=8.3, 1.4 Hz, 2H), 7.57 (d, J=8.6 Hz, 1H), 7.44 (t, J=7.8 Hz, 2H), 7.13 (d, J=8.6 Hz, 2H), 6.86 (d, J=8.7 Hz, 2H), 6.53 (s, 1H), 6.41 (s, 1H), 5.87 (d, J=10.7 Hz, 2H), 5.75 (d, J=6.2 Hz, 1H), 4.78 (d, J=6.2 Hz, 1H), 3.79 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 194.79, 158.91, 153.56, 147.94, 142.42, 134.33, 134.26, 133.70, 129.17, 128.98, 128.62, 120.38, 114.29, 104.90, 101.29, 93.16, 91.44, 55.23, 50.38; HRMS (ESI) calcd for $C_{23}H_{18}O_5Na$ $[M+Na]^+$ 397.1052, found 397.1050.

(4-Chlorophenyl)(7-(4-methoxyphenyl)-6,7-dihydro-[1,3]dioxolo[4,5-*f*]benzofuran-6-yl) methanone (**3ab**): 88% yield. Yellow solid, m.p. 36～38 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.87 (d, J=8.6 Hz, 2H), 7.42 (d, J=8.6 Hz, 2H), 7.14 (d, J=8.7 Hz, 2H), 6.87 (d, J=8.6 Hz, 2H), 6.52 (s, 1H), 6.41 (d, J=0.9 Hz, 1H), 5.89 (d, J=9.5 Hz, 2H), 5.67 (d, J=6.4 Hz, 1H), 4.80 (d, J=6.4 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 193.79, 159.00, 153.37, 148.01, 142.56, 140.26, 134.13, 132.69, 130.66, 129.03, 128.98, 120.29, 114.37, 104.93, 101.36, 93.17, 91.54, 55.27, 50.22; HRMS (ESI) calcd for $C_{23}H_{17}O_5NaCl$ $[M+Na]^+$ 431.0662, found 431.0660.

(4-Bromophenyl)(7-(4-methoxyphenyl)-6,7-dihydro-[1,3]dioxolo[4,5-*f*]benzofuran-6-yl) methanone (**3ac**): 80% yield. Light yellow solid, m.p. 54～56 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.78 (d, J=8.6 Hz, 2H), 7.58 (d, J=8.6 Hz, 2H), 7.13 (d, J=8.7 Hz, 2H), 6.86 (d, J=8.7 Hz, 2H), 6.51 (s, 1H), 6.41 (d, J=0.9 Hz, 1H), 5.88 (d, J=9.5 Hz, 2H), 5.67 (d, J=6.4 Hz, 1H), 4.79 (d, J=6.4 Hz, 1H), 3.79 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 193.95, 158.95, 153.32, 147.97, 142.51, 134.07, 133.04, 131.92, 130.69, 129.02, 128.99, 120.24, 114.32, 104.89, 101.32, 93.13, 91.47, 55.23, 50.17; HRMS (ESI) calcd for $C_{23}H_{17}O_5NaBr$ $[M+Na]^+$ 475.0157, found 475.0156.

4-(7-(4-Methoxyphenyl)-6,7-dihydro-[1,3]dioxolo[4,5-*f*]-benzofuran-6-carbonyl) benzonitrile (**3ad**): 89% yield. Yellow solid, m.p. 42～44 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.04 (d, J=8.4 Hz, 2H), 7.76 (d, J=8.5 Hz, 2H), 7.14 (d, J=8.7 Hz, 2H), 6.88 (d, J=8.7 Hz, 2H), 6.50 (s, 1H), 6.43 (d, J=0.9 Hz, 1H), 5.90 (dd, J=10.6, 1.3 Hz, 2H), 5.66 (d, J=6.5 Hz, 1H), 4.85 (d, J=6.5 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 194.02, 159.11, 153.10, 148.13, 142.77, 137.57, 133.82, 132.41, 129.72, 129.03, 120.11, 117.79, 116.87, 114.45, 104.96, 101.46, 93.21, 91.77, 55.32, 49.98; HRMS (ESI) calcd for $C_{24}H_{17}NO_5Na$ $[M+Na]^+$ 422.1004, found 422.1002.

(7-(4-Methoxyphenyl)-6,7-dihydro-[1,3]dioxolo[4,5-*f*]-benzofuran-6-yl)(4-(trifluoromethyl)phenyl) methanone (**3ae**): 86% yield. Yellow solid, m.p. 58～60 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.04 (d, J=8.1 Hz, 2H), 7.71 (d, J=8.3 Hz, 2H), 7.14 (d, J=8.7 Hz, 2H), 6.87 (d, J=8.7 Hz, 2H), 6.51 (s, 1H), 6.42 (d, J=0.9 Hz, 1H), 5.89 (dd, J=

10.7, 1.4 Hz, 2H), 5.70 (d, J=6.5 Hz, 1H), 4.83 (d, J=6.4 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 194.24, 159.07, 153.26, 148.09, 142.68, 137.17, 134.97, 134.72, 133.98, 129.62, 129.01, 125.66, 125.62, 124.55, 122.39, 120.19, 114.41, 104.95, 101.41, 93.20, 91.74, 55.27, 50.12; ^{19}F NMR (471 MHz, $CDCl_3$) δ: −63.20; HRMS (ESI) calcd for $C_{24}H_{17}O_5NaF_3$ $[M+Na]^+$ 465.0926, found 465.0925.

(7-(4-Methoxyphenyl)-6,7-dihydro-[1,3]dioxolo[4,5-*f*]-benzofuran-6-yl)(*p*-tolyl) methanone (**3af**): 98% yield. Yellow solid, m.p. 58～60 ℃; ^{1}H NMR (500 MHz, $CHCl_3$) δ: 7.81 (d, J=8.3 Hz, 2H), 7.23 (d, J=8.4 Hz, 2H), 7.13 (d, J=8.7 Hz, 2H), 6.86 (d, J=8.7 Hz, 2H), 6.53 (s, 1H), 6.40 (d, J=0.9 Hz, 1H), 5.87 (dd, J=11.0, 1.4 Hz, 2H), 5.73 (d, J=6.2 Hz, 1H), 4.76 (d, J=6.2 Hz, 1H), 3.79 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (126 MHz, $CHCl_3$) δ: 194.36, 158.87, 153.63, 147.90, 144.69, 142.35, 134.43, 131.71, 129.32, 129.27, 128.98, 120.45, 114.26, 104.89, 101.26, 93.13, 91.36, 55.22, 50.44, 21.67; HRMS (ESI) calcd for $C_{24}H_{20}O_5Na$ $[M+Na]^+$ 411.1208, found 411.1204.

(3-Methoxyphenyl)(7-(4-methoxyphenyl)-6,7-dihydro-[1,3]dioxolo[4,5-*f*]benzofuran-6-yl) methanone (**3ag**): 87% yield. Canary yellow solid, m.p. 48～50 ℃; ^{1}H NMR (500 MHz, $CHCl_3$) δ: 7.45 (d, J=7.6 Hz, 2H), 7.33 (t, J=7.9 Hz, 1H), 7.13 (d, J=8.7 Hz, 3H), 6.86 (d, J=8.7 Hz, 2H), 6.54 (s, 1H), 6.40 (d, J=1.0 Hz, 1H), 5.87 (dd, J=10.1, 1.4 Hz, 2H), 5.74 (d, J=6.2 Hz, 1H), 4.74 (d, J=6.2 Hz, 1H), 3.78 (d, J=6.0 Hz, 6H); ^{13}C NMR (126 MHz, $CHCl_3$) δ: 194.61, 159.76, 158.91, 153.58, 147.94, 142.39, 135.48, 134.31, 129.58, 128.96, 121.74, 120.53, 120.31, 114.27, 112.96, 104.86, 101.28, 93.15, 91.43, 55.27, 55.22, 50.59; HRMS (ESI) calcd for $C_{24}H_{20}O_6Na$ $[M+Na]^+$ 427.1158, found 427.1156.

(3-Fluorophenyl)(7-(4-methoxyphenyl)-6,7-dihydro-[1,3]dioxolo[4,5-*f*]benzofuran-6-yl) methanone (**3ah**): 75% yield. White solid, m.p. 56～58 ℃; ^{1}H NMR (500 MHz, $CHCl_3$) δ: 7.69 (d, J=7.8 Hz, 1H), 7.66～7.62 (m, 1H), 7.42 (td, J=8.0, 5.5 Hz, 1H), 7.31～7.26 (m, 1H), 7.13 (d, J=8.7 Hz, 2H), 6.87 (d, J=8.7 Hz, 2H), 6.52 (s, 1H), 6.41 (d, J=0.9 Hz, 1H), 5.88 (dd, J=10.8, 1.4 Hz, 2H), 5.67 (d, J=6.4 Hz, 1H), 4.81 (d, J=6.4 Hz, 1H), 3.79 (s, 3H); ^{13}C NMR (126 MHz, $CHCl_3$) δ: 194.77, 194.73, 162.41, 160.38, 158.76, 153.53, 147.91, 142.38, 135.04, 134.97, 134.72, 131.13, 131.11, 128.61, 124.64, 124.61, 123.68, 123.57, 120.36, 116.55, 116.37, 114.11, 104.87, 101.26, 93.50, 93.45, 93.15, 55.18, 50.13; ^{19}F NMR (471 MHz, $CHCl_3$) δ: −108.57; HRMS (ESI) calcd for $C_{23}H_{17}O_5NaF$ $[M+Na]^+$ 415.0958, found 415.0959.

(2-Fluorophenyl)(7-(4-methoxyphenyl)-6,7-dihydro-[1,3]dioxolo[4,5-*f*]benzofuran-6-yl) methanone (**3ai**): 96% yield. Yellow solid, m.p. 42～44 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.78 (s, 1H), 8.43 (dd, J=8.2, 1.2 Hz, 1H), 8.29 (d, J=7.8 Hz, 1H), 7.67 (t, J=8.0 Hz, 1H), 7.16 (d, J=8.7 Hz, 2H), 6.88 (d, J=8.7 Hz, 2H), 6.50 (s, 1H), 6.44 (d, J=0.9 Hz, 1H), 5.89 (dd, J=11.9, 1.4 Hz, 2H), 5.69 (d, J=6.6 Hz, 1H), 4.91 (d, J=6.6 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 193.20, 159.08, 153.01, 148.30, 148.06, 142.74, 135.76, 134.79, 133.64, 129.83, 129.06, 127.82, 124.28, 120.10, 114.42, 104.92, 101.42, 93.20, 91.79, 55.27, 49.85; HRMS (ESI) calcd for $C_{23}H_{17}NO_7Na$ $[M+Na]^+$ 442.0903, found 442.0901.

(2-Fluorophenyl)(7-(4-methoxyphenyl)-6,7-dihydro-[1,3]dioxolo[4,5-*f*]benzofuran-6-yl)methanone (**3aj**): 81% yield. White solid, m.p. 48～50 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.81 (td, J=7.4, 1.9 Hz, 1H), 7.60～7.48 (m, 1H), 7.23 (dd, J=7.6, 1.1 Hz, 1H), 7.15～7.03 (m, 3H), 6.83 (d, J=8.7 Hz, 2H), 6.51 (s, 1H), 6.41 (d, J=0.9 Hz, 1H), 5.89～5.83 (m, 2H), 5.69 (dd, J=5.2, 2.4 Hz, 1H), 4.70 (dd, J=5.4, 1.9 Hz, 1H), 3.78 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 193.70, 163.69, 158.99, 153.34, 147.99, 142.55, 136.39, 136.34, 134.05, 130.30, 130.24, 128.99, 125.01, 124.98, 120.84, 120.67, 120.24, 114.34, 104.90, 101.34, 93.16, 91.57, 55.24, 50.17; ^{19}F NMR (471 MHz, $CDCl_3$) δ: −111.27; HRMS (ESI) calcd for $C_{23}H_{17}O_5NaF$ $[M+Na]^+$ 415.0958, found 415.0956.

(2-Hydroxyphenyl)(7-(4-methoxyphenyl)-6,7-dihydro-[1,3]dioxolo[4,5-*f*]benzofuran-6-yl) methanone (**3ak**): 92% yield. White solid, m.p. 98～100 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 11.89 (s, 1H), 7.55 (dd, J=8.1, 1.7 Hz, 1H), 7.52～7.45 (m, 1H), 7.14 (d, J=8.7 Hz, 2H), 7.01 (dd, J=8.5, 1.2 Hz, 1H), 6.88 (d, J=8.7 Hz, 2H), 6.85～6.80 (m, 1H), 6.57 (s, 1H), 6.41 (d, J=0.8 Hz, 1H), 5.89 (dd, J=9.4, 1.4 Hz, 2H), 5.80 (d, J=5.9 Hz, 1H), 4.74 (d, J=5.8 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 200.10, 163.38, 159.10, 153.59, 148.15, 142.64, 137.03, 133.95, 130.30, 128.96, 120.15, 119.02, 118.74, 116.98, 114.44, 104.86, 101.40, 93.13, 90.33, 55.27, 51.12; HRMS (ESI) calcd for $C_{23}H_{18}O_6Na$ $[M+Na]^+$ 413.1001, found 413.0999.

(7-(4-Methoxyphenyl)-6,7-dihydro-[1,3]dioxolo[4,5-*f*]-benzofuran-6-yl)(naphthalen-2-yl) methanone (**3al**): 83% yield. Yellow solid, m.p. 51～53 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.32 (d, J=1.8 Hz, 1H), 8.01 (dd, J=8.6, 1.8 Hz, 1H), 7.90～7.83 (m, 2H), 7.83～7.78 (m, 1H), 7.62～7.56 (m, 1H), 7.55～7.49 (m, 1H), 7.15 (d, J=8.7 Hz, 2H), 6.87 (d, J=8.7 Hz, 2H), 6.56 (s, 1H), 6.42 (d, J=0.9 Hz, 1H), 5.94～5.84 (m, 3H), 4.82 (d, J=6.4 Hz, 1H), 3.79 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 194.69, 159.00, 153.68, 147.99, 142.45, 135.80, 134.40, 132.26, 131.51, 131.44, 129.66, 129.14, 128.84, 128.52, 127.75, 126.82, 124.37, 120.40, 114.34, 104.93, 101.31, 93.20, 91.63, 55.27, 50.74; HRMS (ESI) calcd for $C_{27}H_{20}O_5Na$ $[M+Na]^+$ 447.1208, found 447.1207.

Furan-2-yl(7-(4-methoxyphenyl)-6,7-dihydro-[1,3]dioxolo[4,5-*f*]benzofuran-6-yl) methanone (**3am**): 78% yield. White solid, m.p. 130～132 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.63 (d, J=1.6 Hz, 1H), 7.27 (d, J=3.6 Hz, 1H), 7.13 (d, J=8.7 Hz, 2H), 6.86 (d, J=8.7 Hz, 2H), 6.54 (s, 2H), 6.43 (d, J=0.8 Hz, 1H), 5.89 (dd, J=9.8, 1.4 Hz, 2H), 5.47 (d, J=6.3 Hz, 1H), 4.77 (d, J=6.3 Hz, 1H), 3.79 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 184.39, 158.90, 153.62, 150.32, 148.01, 147.51, 142.54, 134.26, 128.93, 120.32, 120.13, 114.23, 112.41, 104.99, 101.35, 93.10,

91.68, 55.23, 50.97; HRMS (ESI) calcd for $C_{21}H_{16}O_6Na$ $[M+Na]^+$ 387.0845, found 387.0841.

(7-(4-Methoxyphenyl)-6,7-dihydro-[1,3]dioxolo[4,5-*f*]-benzofuran-6-yl)(thiophen-2-yl) methanone (**3an**): 87% yield. Yellow solid, m.p.138～140 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.78 (dd, J=3.8, 1.2 Hz, 1H), 7.70 (dd, J=5.0, 1.2 Hz, 1H), 7.15 (d, J=8.7 Hz, 2H), 7.12 (dd, J=4.9, 3.8 Hz, 1H), 6.87 (d, J=8.7 Hz, 2H), 6.56 (s, 1H), 6.44 (d, J=0.9 Hz, 1H), 5.90 (dd, J=10.8, 1.4 Hz, 2H), 5.48 (d, J=6.4 Hz, 1H), 4.83 (d, J=6.5 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 189.06, 158.92, 153.48, 147.99, 142.57, 140.62, 135.05, 134.18, 134.04, 128.99, 128.18, 120.20, 114.27, 104.98, 101.35, 93.16, 92.68, 55.23, 51.27; HRMS (ESI) calcd for $C_{21}H_{16}O_5NaS$ $[M+Na]^+$ 403.0616, found 403.0614.

Cyclopropyl(7-(4-methoxyphenyl)-6,7-dihydro-[1,3]-dioxolo[4,5-*f*]benzofuran-6-yl) methanone (**3ao**): 80% yield. White solid, m.p. 88～90 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.13 (d, J=8.7 Hz, 2H), 6.86 (d, J=8.7 Hz, 2H), 6.54 (s, 1H), 6.43 (d, J=0.9 Hz, 1H), 5.92～5.88 (m, 2H), 5.00 (d, J=6.4 Hz, 1H), 4.62 (d, J=6.5 Hz, 1H), 3.79 (s, 3H), 2.25 (ddd, J=12.5, 7.8, 4.6 Hz, 1H), 1.13 (s, 2H), 1.04～0.93 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 208.58, 158.88, 153.69, 148.00, 142.48, 134.57, 128.83, 120.32, 114.27, 105.06, 101.36, 94.69, 93.15, 55.27, 51.18, 16.76, 12.19, 11.98; HRMS (ESI) calcd for $C_{20}H_{18}O_5Na$ $[M+Na]^+$ 361.1052, found 361.1048.

1-(7-(4-methoxyphenyl)-6,7-dihydro-[1,3]dioxolo[4,5-*f*]-benzofuran-6-yl)-2,2-dimethylpropan-1-one (**3ap**): 87% yield. White solid, m.p. 32～34 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.15～7.08 (m, 2H), 6.88～6.82 (m, 2H), 6.46 (s, 1H), 6.39 (d, J=1.0 Hz, 1H), 5.88 (dd, J=8.4, 1.4 Hz, 2H), 5.23 (d, J=6.6 Hz, 1H), 4.66 (d, J=6.6 Hz, 1H), 3.79 (s, 3H), 1.17 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 211.30, 158.82, 153.49, 142.33, 134.40, 128.93, 120.72, 114.21, 104.94, 101.28, 92.85, 90.59, 55.23, 50.87, 43.80, 26.00; HRMS (ESI) calcd for $C_{21}H_{22}O_5Na$ $[M+Na]^+$ 377.1365, found 377.1365.

Adamantan-1-yl(7-(4-methoxyphenyl)-6,7-dihydro-[1,3]-dioxolo[4,5-*f*]benzofuran-6-yl) methanone (**3aq**): 81% yield. White solid, m.p. 138～140 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.11 (d, J=8.7 Hz, 2H), 6.85 (d, J=8.6 Hz, 2H), 6.47 (s, 1H), 6.39 (d, J=0.9 Hz, 1H), 5.91～5.84 (m, 2H), 5.26 (d, J=6.5 Hz, 1H), 4.64 (d, J=6.4 Hz, 1H), 3.79 (s, 3H), 2.02 (s, 3H), 1.90～1.79 (m, 6H), 1.70 (dd, J=30.7, 11.6 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 209.96, 158.76, 153.55, 147.80, 142.25, 134.36, 128.87, 120.77, 114.19, 104.90, 101.24, 92.82, 89.52, 55.21, 50.39, 46.08, 37.52, 36.37, 27.67; HRMS (ESI) calcd for $C_{27}H_{28}O_5Na$ $[M+Na]^+$ 455.1834, found 455.1832.

(*E*)-Phenyl(7-styryl-6,7-dihydro-[1,3]dioxolo[4,5-*f*]ben-zofuran-6-yl) methanone (**3ba**): 55% yield. White solid, m.p. 110～112 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.06～7.98 (m, 2H), 7.60 (t, J=7.5 Hz, 1H), 7.47 (t, J=7.8 Hz, 2H), 7.37 (d, J=7.0 Hz, 2H), 7.31 (t, J=7.6 Hz, 2H), 7.25 (d, J=7.2 Hz, 1H), 6.58 (d, J=0.8 Hz, 1H), 6.56～6.47 (m, 2H), 6.33 (dd, J=15.6, 8.7 Hz, 1H), 5.89 (dd, J=9.7, 1.4 Hz, 2H), 5.72 (d, J=6.4 Hz, 1H), 4.42 (dd, J=8.8, 6.4 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 193.71, 152.43, 147.14, 141.35, 135.33, 133.27, 132.79, 131.53, 128.20, 127.76, 127.69, 127.61, 126.88, 125.43, 117.65, 103.96, 100.36, 92.40, 87.92, 48.36; HRMS (ESI) calcd for $C_{24}H_{18}O_4Na$ $[M+Na]^+$ 393.1103, found 393.1100.

(*E*)-(7-(4-Methylstyryl)-6,7-dihydro-[1,3]dioxolo[4,5-*f*]-benzofuran-6-yl)(phenyl) methanone (**3ca**): 68% yield. Yellow solid, m.p. 58～60 ℃; ^{1}H NMR (500 MHz, $CHCl_3$) δ: 8.08～7.95 (m, 2H), 7.60 (t, J=7.4 Hz, 1H), 7.48 (t, J=7.8 Hz, 2H), 7.27 (d, J=8.0 Hz, 2H), 7.13 (d, J=7.9 Hz, 2H), 6.58 (s, 1H), 6.53～6.42 (m, 2H), 6.28 (dd, J=15.7, 8.8 Hz, 1H), 5.90 (d, J=8.1 Hz, 2H), 5.72 (d, J=6.4 Hz, 1H), 4.39 (dd, J=8.8, 6.4 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 194.79, 153.44, 148.12, 142.34, 137.79, 134.28, 133.78, 133.56, 132.43, 129.32, 129.20, 128.70, 127.75, 126.35, 118.79, 104.99, 101.35, 93.39, 88.99, 49.48, 21.17; HRMS (ESI) calcd for $C_{25}H_{20}O_4Na$ $[M+Na]^+$ 407.1259, found 407.1259.

(*E*)-(7-(4-Methoxystyryl)-6,7-dihydro-[1,3]dioxolo[4,5-*f*]-benzofuran-6-yl)(phenyl) methanone (**3da**): 67% yield. Canary yellow solid, m.p. 96～98 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.02 (d, J=7.0 Hz, 2H), 7.60 (t, J=7.4 Hz, 1H), 7.48 (t, J=7.8 Hz, 2H), 7.30 (d, J=8.8 Hz, 2H), 6.85 (d, J=8.7 Hz, 2H), 6.58 (d, J=0.9 Hz, 1H), 6.51 (s, 1H), 6.45 (d, J=15.7 Hz, 1H), 6.19 (dd, J=15.6, 8.8 Hz, 1H), 5.89 (dd, J=9.6, 1.4 Hz, 2H), 5.70 (d, J=6.4 Hz, 1H), 4.39 (dd, J=8.8, 6.4 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 194.83, 159.44, 153.42, 148.09, 142.33, 134.32, 133.76, 131.99, 129.21, 129.13, 128.69, 127.64, 126.58, 118.92, 114.03, 104.99, 101.35, 93.38, 89.10, 55.28, 49.48; HRMS (ESI) calcd for $C_{25}H_{20}O_5Na$ $[M+Na]^+$ 423.1208, found 423.1205.

(*E*)-(7-(4-Fluorostyryl)-6,7-dihydro-[1,3]dioxolo[4,5-*f*]-benzofuran-6-yl)(phenyl) methanone (**3ea**): 85% yield. White solid, m.p. 36～38 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.02 (dd, J=8.4, 1.4 Hz, 2H), 7.61 (d, J=14.9 Hz, 1H), 7.49 (t, J=7.8 Hz, 2H), 7.34 (dd, J=8.6, 5.4 Hz, 2H), 7.01 (t, J=8.7 Hz, 2H), 6.58 (d, J=0.9 Hz, 1H), 6.54 – 6.42 (m, 2H), 6.25 (dd, J=15.7, 8.7 Hz, 1H), 5.90 (dd, J=9.8, 1.4 Hz, 2H), 5.70 (d, J=6.5 Hz, 1H), 4.43 (dd, J=8.7, 6.4 Hz, 1H); ^{13}C NMR (126 MHz, CDCl3) δ: 194.70, 163.43, 161.46, 153.41, 148.18, 142.39, 134.31, 133.83, 131.38, 129.23, 128.71, 128.00, 127.94, 118.60, 115.63, 115.46, 104.93, 101.40, 93.45, 88.96, 49.20; ^{19}F NMR (471 MHz, $CDCl_3$) δ: −113.81; HRMS (ESI) calcd for $C_{24}H_{17}O_4NaF$ $[M+Na]^+$ 411.1009, found 411.1007.

(*E*)-(7-(4-Chlorostyryl)-6,7-dihydro-[1,3]dioxolo[4,5-*f*]-benzofuran-6-yl)(phenyl) methanone (**3fa**): 85% yield. Yellow solid, m.p. 40～42 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.02 (d, J=7.1 Hz, 2H), 7.61 (t, J=7.4 Hz, 1H), 7.49 (t, J=7.8 Hz, 2H), 7.32～7.27 (m, 4H), 6.58 (d, J=0.9 Hz, 1H), 6.53～6.41 (m, 2H), 6.31 (dd, J=15.7, 8.7 Hz, 1H), 5.91 (dd, J=9.6, 1.4 Hz, 2H), 5.69 (d, J=6.5 Hz, 1H), 4.45 (dd, J=8.7, 6.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 194.67, 153.43, 148.25, 142.45, 134.89, 134.36, 133.85, 133.56, 131.37, 129.49, 129.26, 128.80, 128.73,

127.65, 118.49, 104.94, 101.43, 93.49, 88.95, 49.14; HRMS (ESI) calcd for $C_{24}H_{17}O_4NaCl$ [M + Na]$^+$ 471.0208, found 471.0208.

(*E*)-(7-(4-Bromostyryl)-6,7-dihydro-[1,3]dioxolo[4,5-*f*]-benzofuran-6-yl)(phenyl) methanone (**3ga**): 83% yield. White solid, m.p. 42～44 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.01 (dd, J=8.4, 1.4 Hz, 2H), 7.60 (t, J=7.4 Hz, 1H), 7.47 (t, J=7.8 Hz, 2H), 7.42 (d, J=8.4 Hz, 2H), 7.22 (d, J=8.5 Hz, 2H), 6.56 (d, J=0.9 Hz, 1H), 6.52～6.39 (m, 2H), 6.32 (dd, J=15.7, 8.6 Hz, 1H), 5.89 (dd, J=10.1, 1.4 Hz, 2H), 5.69 (d, J=6.4 Hz, 1H), 4.44 (dd, J=8.6, 6.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 194.56, 153.35, 148.17, 142.36, 135.25, 133.79, 131.67, 131.32, 129.56, 129.19, 128.66, 127.90, 121.60, 118.37, 104.87, 101.36, 93.40, 88.78, 49.06; HRMS (ESI) calcd for $C_{24}H_{17}O_4NaCl$ [M+Na]$^+$ 404.8460, found 404.8461.

(*E*)-(7-(3-Methylstyryl)-6,7-dihydro-[1,3]dioxolo[4,5-*f*]-benzofuran-6-yl)(phenyl) methanone (**3ha**): 68% yield. White solid, m.p. 86～88 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.10～7.92 (m, 2H), 7.61 (t, J=7.4 Hz, 1H), 7.49 (t, J=7.8 Hz, 2H), 7.24～7.15 (m, 3H), 7.08 (d, J=7.4 Hz, 1H), 6.61～6.54 (m, 1H), 6.54～6.46 (m, 2H), 6.33 (dd, J=15.6, 8.8 Hz, 1H), 5.90 (dd, J=9.0, 1.4 Hz, 2H), 5.72 (d, J=6.3 Hz, 1H), 4.41 (dd, J=8.8, 6.3 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 194.76, 153.47, 148.16, 142.37, 138.23, 136.30, 134.28, 133.81, 132.61, 129.21, 128.73, 128.69, 128.60, 128.54, 127.13, 123.65, 118.72, 105.00, 101.38, 93.42, 88.97, 49.46, 21.35; HRMS (ESI) calcd for $C_{25}H_{20}O_4Na$ [M+Na]$^+$ 407.1259, found 407.1256.

(*E*)-(7-(2-Methoxystyryl)-6,7-dihydro-[1,3]dioxolo[4,5-*f*]-benzofuran-6-yl)(phenyl) methanone (**3ia**): 52% yield. Light yellow solid, m.p. 126～128 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.06～8.01 (m, 2H), 7.61 (t, J=7.4 Hz, 1H), 7.49 (t, J=7.8 Hz, 2H), 7.43 (dd, J=7.6, 1.7 Hz, 1H), 7.26～7.22 (m, 1H), 6.93 (td, J=7.5, 1.1 Hz, 1H), 6.90～6.83 (m, 2H), 6.60 (d, J=0.9 Hz, 1H), 6.52 (s, 1H), 6.37 (dd, J=15.8, 8.9 Hz, 1H), 5.90 (dd, J=9.2, 1.3 Hz, 2H), 5.75 (d, J=6.2 Hz, 1H), 4.41 (dd, J=8.9, 6.2 Hz, 1H), 3.84 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 194.82, 156.85, 153.46, 148.09, 142.32, 134.26, 133.71, 129.42, 129.24, 128.91, 128.69, 127.55, 127.03, 125.35, 120.61, 119.03, 110.89, 105.08, 101.34, 93.35, 89.07, 55.38, 50.13; HRMS (ESI) calcd for $C_{25}H_{20}O_5Na$ [M+Na]$^+$ 423.1208, found 423.1206.

(*E*)-Phenyl(7-(2-(thiophen-3-yl)vinyl)-6,7-dihydro-[1,3]-dioxolo[4,5-f]benzofuran-6-yl) methanone (**3ja**): 24% yield. Yellow solid, m.p. 128～130 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.06～8.00 (m, 2H), 7.61 (t, J=7.4 Hz, 1H), 7.49 (t, J=7.8 Hz, 2H), 7.18～7.15 (m, 1H), 6.98～6.95 (m, 2H), 6.67～6.58 (m, 2H), 6.50 (s, 1H), 6.17 (dd, J=15.5, 8.7 Hz, 1H), 5.91 (dd, J=10.6, 1.4 Hz, 2H), 5.70 (d, J=6.4 Hz, 1H), 4.41 (dd, J=8.7, 6.4 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 194.65, 153.44, 148.20, 142.39, 141.37, 134.31, 133.83, 129.25, 128.74, 128.29, 127.41, 126.17, 125.74, 124.52, 118.47, 104.99, 101.40, 93.45, 88.91, 49.04; HRMS (ESI) calcd for $C_{22}H_{16}O_4NaS$ [M+Na]$^+$ 399.0667, found 399.0665.

(5,6-Dimethoxy-3-(4-methoxyphenyl)-2,3-dihydroben-zofuran-2-yl)(phenyl) methanone (**3a'a**): 92% yield, m.p. 58～60 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.93 (d, J=7.1 Hz, 2H), 7.58 (t, J=7.4 Hz, 1H), 7.45 (t, J=7.9 Hz, 2H), 7.13 (d, J=8.7 Hz, 2H), 6.87 (d, J=8.7 Hz, 2H), 6.63 (s, 1H), 6.52 (d, J=0.9 Hz, 1H), 5.74 (d, J=6.2 Hz, 1H), 4.84 (d, J=6.1 Hz, 1H), 3.87 (s, 3H), 3.80 (s, 3H), 3.72 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 194.95, 158.89, 153.19, 149.94, 144.31, 134.46, 134.34, 133.66, 129.18, 129.04, 128.60, 119.03, 114.27, 108.48, 94.94, 91.32, 56.59, 56.01, 55.23, 50.68; HRMS (ESI) calcd for $C_{24}H_{22}O_5Na$ [M+Na]$^+$ 413.1365, found 413.1363.

4.3 Synthesis procedure of compound **4**

Under N_2 atmosphere, to a Schlenk tube were added **3aa** (74.8 mg, 0.2 mmol) and THF (5.0 mL). After cooling to 0 ℃, vinyl magnesium bromide (0.4 mL, 1.0 mol/L in THF) was slowly added by syringe and the mixture was stirred at room temperature for another 1 h. A solution of saturated NH_4Cl (10 mL) was added, and the aqueous phase was extracted with EtOAc (10 mL×3). The combined organic layer was dried by anhydrous Na_2SO_4, and concentrated under vacuum. Then the residue was purified by column chromatography on silica gel (100～200 mesh) using petroleum-ethyl acetate (V∶V=5∶1) as an eluent to afford 1-(7-(4-methoxyphenyl)-6,7-dihydro-[1,3]dioxolo[4,5-*f*]benzofuran-6-yl)-1-phenylprop-2-en-1-ol (**4**), 66 mg, 82% yield. Canary oil liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.37～7.33 (m, 2H), 7.27 (s, 1H), 7.25 (s, 2H), 6.59 (d, J=8.7 Hz, 2H), 6.47 (s, 1H), 6.41 (d, J=8.7 Hz, 2H), 6.33 (dd, J=17.3, 10.8 Hz, 1H), 6.26 (s, 1H), 5.89～5.85 (m, 2H), 5.44 (d, J=16.3 Hz, 1H), 5.29 (d, J=10.7 Hz, 1H), 5.00 (d, J=7.1 Hz, 1H), 4.36 (d, J=7.0 Hz, 1H), 3.72 (s, 3H), 2.42 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 158.07, 153.84, 147.49, 142.07, 141.50, 140.35, 136.04, 129.02, 128.24, 127.38, 126.02, 122.53, 114.64, 113.57, 105.08, 101.18, 96.33, 92.56, 55.16, 48.46, 29.68; HRMS (ESI) calcd for $C_{25}H_{22}O_5Na$ [M+Na]$^+$ 425.1365, found 425.1368.

4.4 Synthesis procedure of compound **5**

To a solution of **3aa** (37.4 mg, 0.1 mmol) in 1,4-dioxane (5.0 mL) was added DDQ (90.8 mg, 0.4 mmol). The mixture was stirred at room temperature for 24 h. Upon completion, H_2O (10 mL) was added, and the aqueous solution was extracted with EtOAc (10 mL×3). The combined organic layer was washed with brine (5.0 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. Then the residue was purified by column chromatography on silica gel (100～200 mesh) using petroleum-ethyl acetate (V∶V=5∶1) as an eluent to afford (7-(4-methoxyphenyl)-[1,3]dioxolo[4,5-f]benzofu-ran-6-yl)(phenyl) methanone (**5**), 28.3 mg, 76% yield. Light yellow solid, m.p. 118～120 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.86～7.79 (m, 2H), 7.45 (t, J=7.4 Hz, 1H), 7.38 (d, J=8.8 Hz, 2H), 7.33 (t, J=7.8 Hz, 2H), 7.05 (s, 1H), 6.98 (s, 1H), 6.88 (d, J=8.7 Hz, 2H), 6.04 (s, 2H),

3.82 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 184.75, 159.61, 150.82, 149.80, 145.92, 137.64, 132.15, 131.12, 130.52, 129.66, 127.93, 123.16, 121.92, 113.81, 101.93, 99.58, 93.59, 55.26; HRMS (ESI) calcd for $C_{23}H_{16}O_5Na$ $[M+Na]^+$ 395.0895, found 395.0899.

4.5 Synthesis procedure of compound **6**

To a round-bottom flask were added **3aa** (37.4 mg, 0.1 mmol) and methanol (5.0 mL), followed by addition of $NaBH_4$ (18.9 mg, 0.5 mmol) at 0 ℃. After the reaction mixture was stirred for another 2 h at room temperature, H_2O (10 mL) was added. The aqueous solution was extracted with CH_2Cl_2 (10 mL×3). The organic layer was combined, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using petroleum-ethyl acetate (V∶V=10∶1) as an eluent to afford (7-(4-methoxyphenyl)-6,7-dihydro-[1,3]dioxolo[4,5-*f*]benzofuran-6-yl)(phenyl) methanol (**6**), 32.0 mg, 85% yield. Light oil liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.40～7.35 (m, 2H), 7.34～7.30 (m, 2H), 7.29～7.25 (m, 1H), 6.65 (s, 4H), 6.44 (s, 1H), 6.35 (s, 1H), 5.90～5.83 (m, 2H), 5.11 (t, J=3.7 Hz, 1H), 4.79 (dd, J=6.6, 4.3 Hz, 1H), 4.49 (d, J=6.8 Hz, 1H), 3.72 (s, 3H), 2.46～2.33 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ: 158.18, 153.98, 147.55, 141.95, 138.66, 135.66, 128.85, 128.39, 127.86, 126.39, 121.83, 113.76, 105.24, 101.16, 95.14, 92.60, 74.04, 55.14, 47.63; HRMS (ESI) calcd for $C_{23}H_{20}O_5Na$ $[M+Na]^+$ 399.1208, found 399.1207.

4.6 Procedure for the gram-scale experiment of **3aa**

To a 25 mL reaction flask were added *o*-QMs **1a** (1.28 g, 0.5 mmol), sulfonium salt **2a** (1.96 g, 0.75 mmol) and DIPEA (1.0 mmol) in CH_2Cl_2 (10 mL), and the mixture was stirred at room temperature for 1 h. Then water (20 mL) was added, the organic layer was separated and the aqueous layer was extracted with dichloromethane (10 mL×3). The combined organic layer was dried by anhydrous sodium sulfate, and concentrated under vacuum. Then the residue was purified by column chromatography on silica gel (100～200 mesh) using petroleum-ethyl acetate (V∶V=3∶1) as an eluent to afford the product **3aa** (1.80 g, 97% yield).

Supporting Information ^{1}H NMR and ^{13}C NMR spectra of products. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn.

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[18] For more X-ray crystal structure information of **3ao** (CCDC 2267289) see Supporting Information. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

(Zhao, C.)

