JOC The Journal of Organic Chemistry

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J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.9b02455 • Publication Date (Web): 26 Nov 2019

Just Accepted

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Base Mediated One-pot Synthesis of Oxygen Based Heterocycles from 2-Hydroxyphenyl-substituted *para*-Quinone Methides

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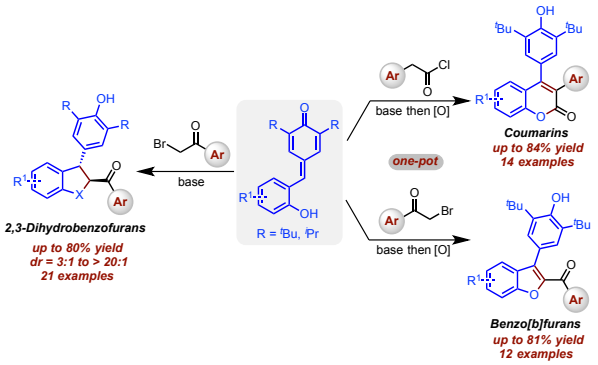


Abstract: A one-pot synthesis of oxygen-containing heterocycles has been achieved through alkylation/acylation of 2-hydroxyphenyl-substituted *para*-quinone methides followed by an intramolecular 1,6-conjugate addition/cyclization and oxidation sequence. This protocol provides access to a wide range of oxygen based heterocycles, such as 2,3-disubstituted benzo[*b*]furans, 2,3-dihydrobenzofurans and diaryl-substituted coumarin derivatives in moderate to good yields.

Introduction:

Oxygen based heterocycles such as 2,3-dihydrobenzofurans, benzo[*b*]furans and coumarins are privileged moieties found in various class of natural products and other biologically active unnatural molecules (Fig. 1).[1] For example, pterocarpan derivatives, a second largest group

of natural isoflavanoids, are found to display impressive antiproliferative activities in various human cancer cell lines.[2a] One of the dihydrobenzofuran derivatives, (+)-obtusafuran exhibits remarkable biological properties ranging from anti-carcinogenic to insect antifeedant activities.[2b] The naturally occurring 2,3-diaryl-substituted benzo[*b*]furan, amurensin H is being used in the treatment of allergic airway inflammation.[2c] Similarly, one of the resveratrol aneuploids, diptoindonesin G shows potent immunosuppressive activity.[2d] Warfarin, a well-known coumarin derivative, is being used as a drug for the treatment of thromboembolic diseases.[2e]

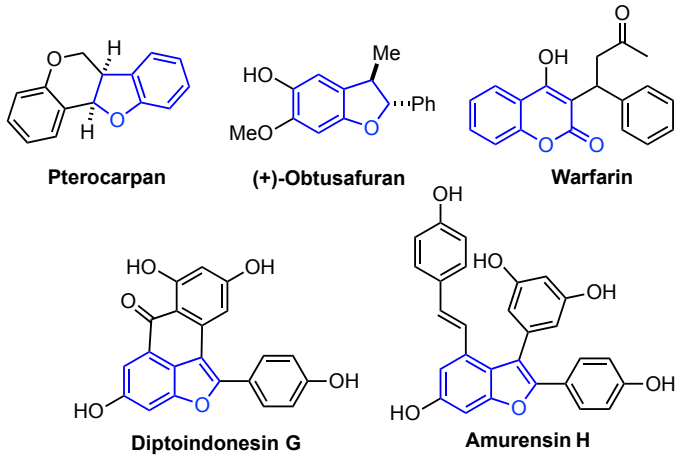


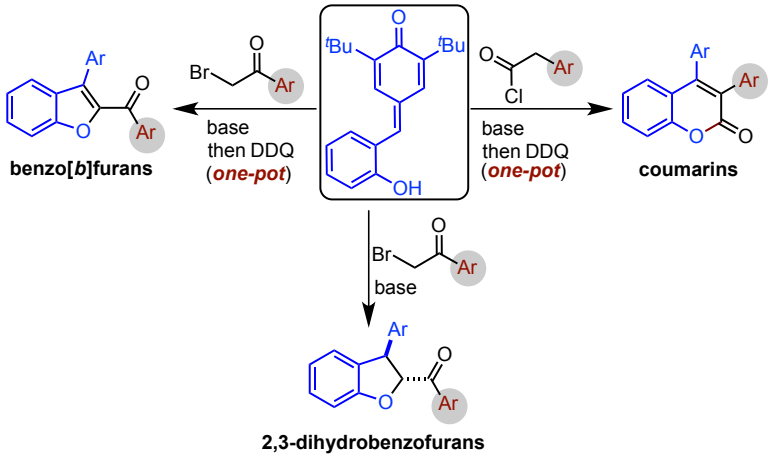
Figure 1. Oxygen-containing Biologically Significant Heterocycles

Owing to their wide range of pharmaceutical applications, the synthesis of oxygen-containing heterocycles[3] has gained interest over the last several years. In fact, the chemical syntheses of benzo[*b*]furan,[4a] 2,3-dihydrobenzofuran[4b] and coumarin[1b,4c] based natural products through various approaches have been reviewed recently. The major ways in which the substituted benzo[*b*]furan core could be constructed involve the metal catalyzed intramolecular *O*-arylation of enolates,[5] intramolecular annulation of 2-alkynyl phenols/anisoles under metal-catalyzed or metal-free conditions,[6,7] and metal-catalyzed oxidative annulation of phenols with unactivated internal alkynes/alkenes.[8] Similarly, the 2,3-dihydrobenzofuran core could be majorly accessed

either through a formal [4+1]-annulation of *o*-quinone methides[9] or by metal catalyzed intra- or intermolecular C–O/C–C bond forming reactions.[10] Apart from the traditional ways, such as Knoevenagal[11] and Pechmann[12] condensations, the coumarin derivatives could be obtained through many different synthetic strategies,[4c] including metal catalyzed intramolecular cyclization of alkynoates,[13] carbonylative annulation,[14] carbonylative cyclization of *o*-alkenylphenols,[15] etc.

Recently, the synthetic utility of 2-hydroxyphenyl-substituted *p*-quinone methides has been revealed in the preparation of many heterocycles[16] including 2,3-dihydrobenzofurans[17] and dihydrocoumarin derivatives.[18] In line with this, we have recently reported a one-pot protocol to access 2,3-diaryl-substituted benzo[*b*]furan derivatives through *N*-heterocyclic carbene (NHC) catalyzed 1,6-conjugate addition of aryl aldehydes to 2-hydroxyphenyl-substituted *p*-quinone methides followed by acid mediated dehydrative cyclization.[19] In continuation with our ongoing research in the area of *p*-QMs,[20] herein, we disclose an efficient one-pot method for the synthesis 2,3-dihydrobenzofurans through a base mediated *O*-alkylation of 2-hydroxyphenyl-substituted *p*-quinone methides with α-halo ketones followed by intramolecular 1,6-conjugate addition strategy (Scheme 1). This method was also elaborated for the synthesis of 2,3-disubstituted benzo[*b*]furan derivatives through the *in situ* oxidation of 2,3-dihydrobenzofurans. Similar protocol was also developed for the one-pot synthesis of 3,4-diaryl-substituted coumarin derivatives through *O*-acylation of 2-hydroxyphenyl-substituted *p*-quinone methides with arylacetyl halides followed by intramolecular 1,6-conjugate addition/oxidation strategy (Scheme 1). Although a few reports are available for the synthesis of 2,3-dihydrobenzofurans either through a formal [4+1]-annulation of 2-hydroxyphenyl-substituted *p*-QMs with sulfur ylides[17a-c] and allenoates[17d] or through the reaction of 2-hydroxyphenyl-substituted *p*-QMs with α-halo carbonyl compounds,[17e,f] the direct one-pot synthesis of 2,3-disubstituted benzo[*b*]furans and 3,4-diaryl-substituted coumarin

derivatives from 2-hydroxyphenyl-substituted *p*-QMs through *O*-alkylation followed by cyclization and oxidation strategy (Scheme 1) has not been reported yet. Therefore, we have decided to explore these transformations.

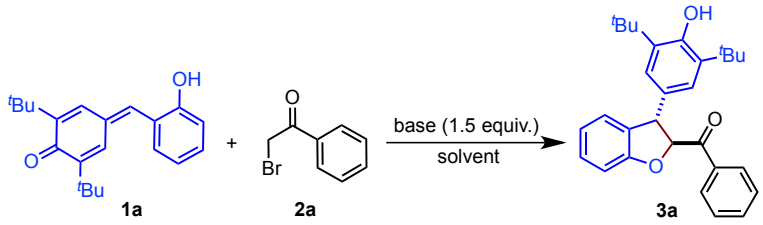


Scheme 1. One-pot Synthesis of 2,3-Dihydrobenzofurans, Benzo[*b*]furans and Coumarins

Results and Discussion:

Since the proposed strategy to synthesize benzo[*b*]furans involves 2,3-dihydrobenzofurans as intermediates, we thought of identifying the best conditions for the synthesis of 2,3-dihydrobenzofurans before exploring the one-pot synthesis of benzo[*b*]furans. In this regard, the optimization studies were initiated using a 2-hydroxyphenyl-substituted *p*-QM **1a** and 2-bromoacetophenone (phenacyl bromide) **2a** under various conditions (Table 1). Initially, the reaction between **1a** and **2a** was performed under basic conditions using 1.5 equivalents of K_2CO_3 in chlorinated solvents. However, the desired product **3a** was obtained only in trace quantities even after 24 h (entries 1 & 2). Interestingly, when the same reaction was performed in acetonitrile, the

Table 1. Optimization Studies[a]



entry	base	solvent	time [h]	*dr* (*trans*:*cis*)[e]	isolated yield of *trans*-**3a** [%]
1	K_2CO_3	CH_2Cl_2	24	-	trace
2	K_2CO_3	$CHCl_3$	24	-	trace
3	K_2CO_3	CH_3CN	12	6:1	67
4	K_2CO_3	Acetone	8	9:1	73
5	Cs_2CO_3	CH_3CN	1.5	9:1	73
6	**Cs_2CO_3**	**Acetone**	**1.5**	**10:1**	**80**
7	NEt_3	Acetone	24	3:1	40
8	DBU	Acetone	24	7:1	46
9[b]	Cs_2CO_3	Acetone	24	9:1	71
10[c]	Cs_2CO_3	Acetone	1	9:1	80
11[d]	Cs_2CO_3	Acetone	24	9:1	30

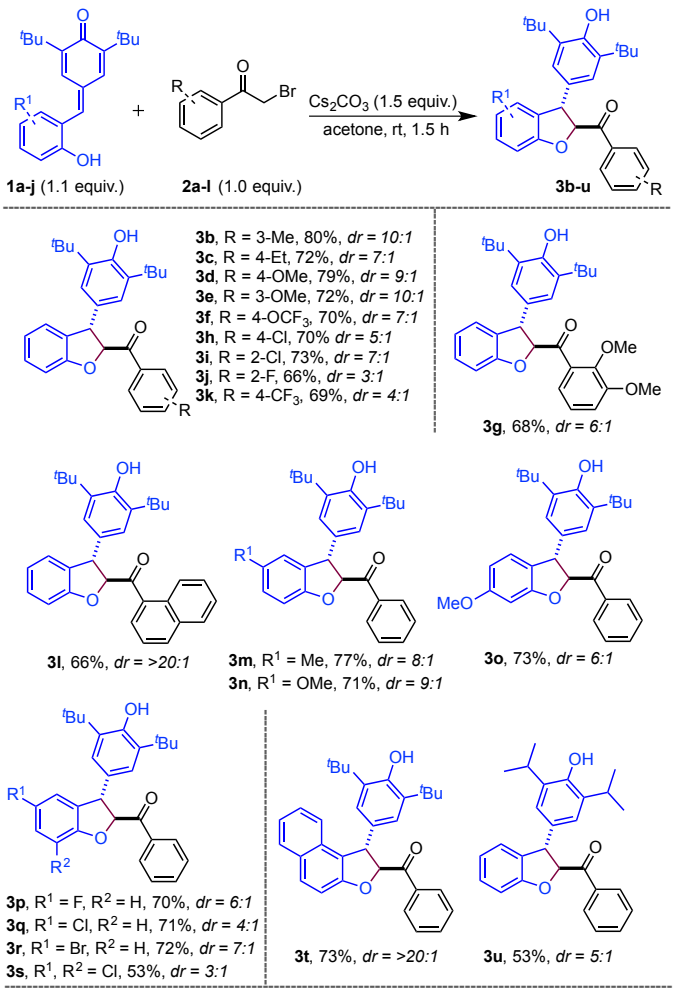
[a] All reactions were carried out with **1a** (0.097 mmol), **2a** (0.088 mmol) and 1.5 equivalent of base in 1.5 mL of solvent. [b] 1.0 equivalent of base was used. [c] 2.0 equivalent of base was used. [d] Reaction was carried at 0 °C and 1.5 equivalent of base was used. [e] The diastereomeric ratio (*dr*) was calculated based on the ^{1}H NMR analysis of crude reaction mixture. The structure and the relative stereochemistry of the product **3a** was assigned by comparing the ^{1}H NMR data with the previous reports.[17]

2,3-dihydrobenzofuran **3a** was obtained as a diastereomeric pair [*dr* = 6:1 (*trans*:*cis*)] and the pure *trans*-**3a** was isolated in 67% chemical yield (entry 3). It was found that the reaction worked well in acetone as the product *trans*-**3a** was obtained in 73% isolated yield (entry 4). When the reaction was carried out in acetonitrile, there was no change in the yield and diastereomeric ratio though the reaction time was reduced to 1.5 h (entry 5). Further optimization studies were carried out in acetone using other organic and inorganic bases. By using 1.5 equivalents of Cs_2CO_3 as a base, the 2,3-dihydrobenzofuran **3a** was obtained as a diastereomeric pair (*dr* = 10:1) and the pure *trans*-**3a** was isolated in the maximum of 80% yield within 1.5 h (entry 6). Organic bases, such as triethylamine and DBU were found to be less effective for this transformation (entries 7 & 8). The

yield of **3a** was relatively low (71%) when the reaction was carried out with 1 equivalent of Cs_2CO_3 (entry 9) and, there was no change in the yield and diastereoselectivity of **3a** when 2 equivalents of Cs_2CO_3 was used (entry 10). Since some decomposition was observed in most of the optimization experiments at room temperature, an experiment was conducted at lower temperature (0 ^oC) using 1.5 equivalents of Cs_2CO_3. However, in that case, although the reaction was found to be clean, the rate of the reaction was low and, the product **3a** was obtained only in 30% isolated yield after 24 h (entry 11).

After finding the optimal reactions conditions (entry 6, Table 1), the substrate scope was investigated by employing a wide range of 2-hydroxyphenyl-substituted *p*-QMs (**1a-j**) and bromomethyl aryl ketones (**2a-l**), and the results are summarized in Table 2. In general, most of the bromomethyl aryl ketones (**2b-l**) reacted with **1a** and provided the respective *trans*-2,3-dihydrobenzofuran derivatives (**3b-l**) in moderate to good isolated yields. For example, the reaction of **1a** with bromomethyl aryl ketones **2a-k** (containing alkyl-, alkoxy- and halo-substitution at aryl ring) provided the corresponding *trans*-2,3-dihydrobenzofuran derivatives **3a-k** in 66-80% isolated yields. In the case of bromomethyl 1-naphthyl ketone (**2l**), the product **3l** was obtained in 66% yield. In the cases of reaction between **2a** and 2-hydroxyphenyl-substituted *p*-QMs **1b-h** (derived from the respective alkyl-, halo- and alkoxy-substituted salicylaldehydes), the *trans*-2,3-dihydrobenzofuran derivatives **3m-s** were obtained in the rage of 53-77% chemical yields. In the case of 2-hydroxyphenyl-substituted *p*-QM **1i** (derived from 2-hydroxy-1-naphthaldehyde), the respective product *trans*-**3t** was obtained in 73% yield. When the *p*-QM **1j** (derived from 2,6-diisopropylphenol), the product **3u** was isolated as a diastereomeric mixture in 53% yield.

Table 2. Substrate scope for the synthesis of *trans*-2,3-dihydrobenzofurans[a]

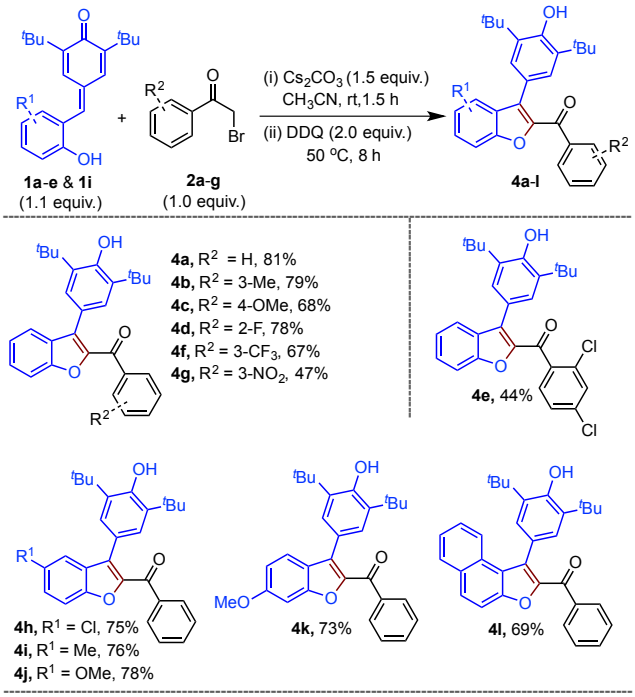


[a] All reactions were carried out in ~ 0.1 mmol scale of **1**(**a**-**j**) in 1.5 mL of acetone. Yields represented are isolated yields of the pure *trans*-isomer (major isomer). The diastereomeric ratios (*dr*) were calculated based on the ^{1}H NMR analysis of crude reaction mixtures.

To show the importance of this methodology, this concept was also elaborated to the one-pot synthesis of 2,3-disubstituted benzo[*b*]furans, directly from the 2-hydroxyphenyl-substituted *p*-QMs through the *in situ* dehydrogenative oxidation of 2,3-dihydrobenzofurans by DDQ, and the results are summarized in Table 3. It was found that the one-pot conversion of **1a** to the corresponding 2,3-disubstituted benzo[*b*]furan **4a** worked well using 2 equivalents of DDQ in acetonitrile and, in this case, **4a** was obtained in 81% yield. However, the same transformation in acetone provided the product **4a** only in 73% yield even after 24 h. Since acetonitrile was found

to be better solvent than acetone for this transformation, further elaboration of the substrate scope had been performed in acetonitrile. As shown in Table 3, most of the reactions between **1a** and various bromomethyl aryl ketones (**2b-g**) worked well, and the respective products **4b-g** were obtained in the range of 44-79% yields. In the cases of reaction between **2a** and 2-hydroxyphenyl-substituted *p*-QMs **1b-e**, the benzo[*b*]furan derivatives **4h-k** were obtained in the rage of 73-78% yields. In the case of 2-hydroxyphenyl-substituted *p*-QM **1i**, the respective product **4l** was obtained in 69% yield.

Table 3. Substrate scope for the synthesis of benzo[*b*]furans[a]

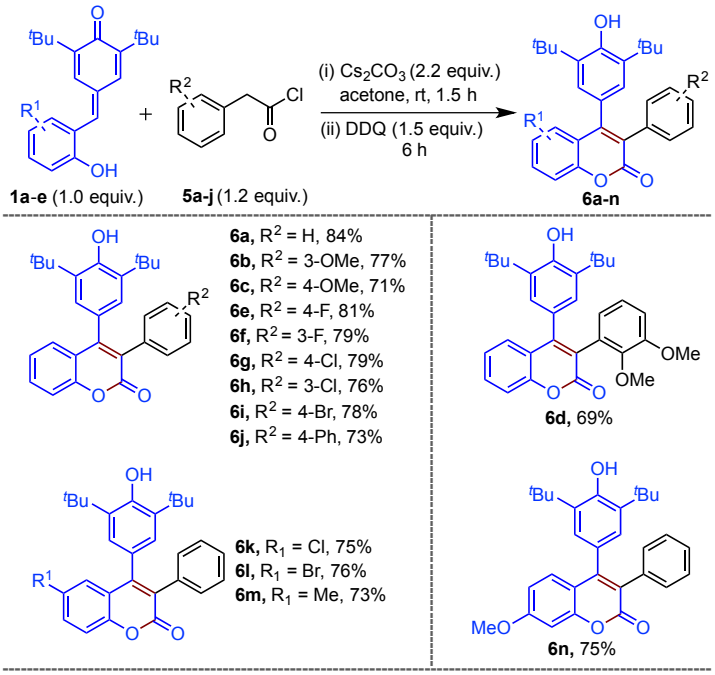


[a] All reactions were carried out in ~ 0.1 mmol scale of **1**(**a-e**) & **1i** in 1.5 mL of MeCN. Yields reported are isolated yields.

After exploring the application potential of this methodology in the synthesis of various 2,3-dihydrobenzofuran and benzo[*b*]furan derivatives, our attention was shifted to further elaborate this concept for the synthesis of other oxygen based heterocycles. We envisioned that it could be a possible to access 3,4-diaryl-substituted coumarin derivatives by treating 2-

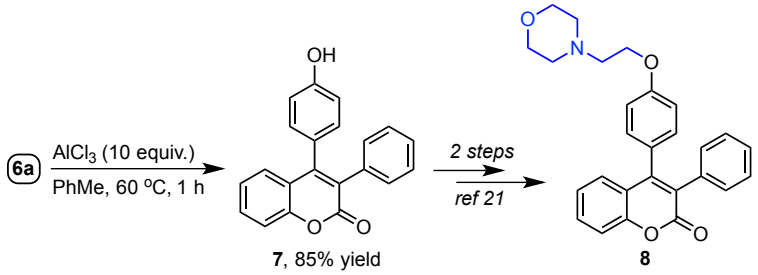
hydroxyphenyl-substituted *p*-QMs with arylacetyl halides followed by one-pot dehydrogenative oxidation with DDQ. In this regard, an initial experiment was carried out by treating **1a** with phenylacetyl chloride (**5a**) [1.2 equiv.] and Cs_2CO_3 (2.2 equiv.) in acetone for 1.5 h followed by addition of DDQ (1.5 equiv.). As expected, in that case, the desired coumarin derivative **6a** was obtained in 84% isolated yield (Table 4). Encouraged by this result, the scope and limitations of this transformation were examined using various 2-hydroxyphenyl-substituted *p*-QMs (**1a-e**) and arylacetyl halides (**5a-j**), and the results are summarized in Table 4. Most of the arylacetyl halides (**5b-j**) reacted smoothly with **1a** and the respective products, after oxidation with DDQ, gave the corresponding diaryl-substituted coumarin derivatives **6b-j** in the range of 69-79% isolated yields. In addition, other 2-hydroxyphenyl-substituted *p*-QMs (**1b-e**) also reacted with phenylacetyl chloride (**5a**) and provided the desired products **6k-n** in good yields (73-76%).

Table 4. Substrate scope for the synthesis of coumarin derivatives[a]



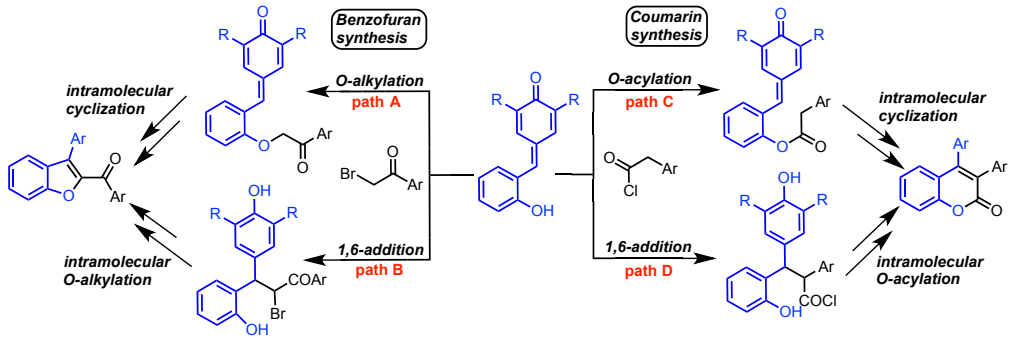
[a] All reactions were carried out in ~ 0.1 mmol scale of **1**(**a-e**) in 1.5 mL of acetone. Yields reported are isolated yields.

To show a practical application of this transformation, we thought of elaborating one of the coumarin derivatives to a biologically active 3,4-diaryl-substituted coumarin derivative **8**, which was found to act as an immunomodulating agent.[21] It has been reported that the coumarin derivative **8** could be easily accessed in a couple of steps from **7** through *O*-alkylation followed by amination with morpholine.[21] In fact, the coumarin derivative **7** could be prepared in one step from **6a** by removal of *t*-Bu groups. In this regard, the de-*tert*-butylation reaction of **6a** was carried out by treating it with excess of $AlCl_3$ (10 equiv.) in toluene at 60 °C, and the expected product **7** was obtained in 85% yield (Scheme 2).



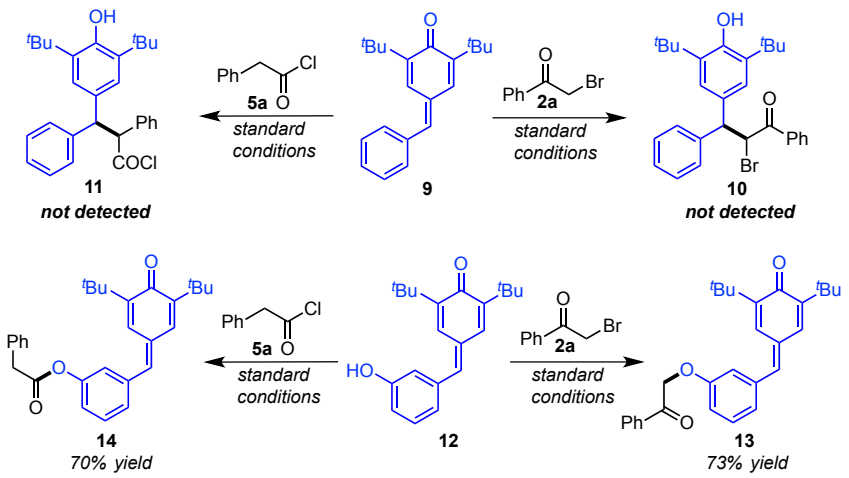
Scheme 2. Formal Synthesis of Immunomodulating Agent **8**

Later, we turned our attention to understand the mechanism of these transformations. There are two different pathways possible for both the transformations [benzofuran as well as coumarin formation] (Scheme 3); (i) *O*-alkylation followed by intramolecular cyclization (path A) or 1,6-conjugate addition followed by intramolecular *O*-alkylation (path B) in the case of 2,3-dihydrobenzofuran/benzo[*b*]furan formation and, (ii) *O*-acylation followed by intramolecular cyclization (path C) or 1,6-conjugate addition followed by intramolecular *O*-acylation (path D) in the case of coumarin formation.



Scheme 3. Possible Reaction Pathways

During the optimization studies, we thought of isolating the intermediate(s) in the reaction between 2-hydroxyphenyl-substituted *p*-QM (**1a**) and 2-bromoacetophenone (**2a**) [entry 6, Table 1]. However, we were not able to isolate any of the intermediates as we could not notice any other spot in the TLC except the starting materials (**1a** & **2a**) and the product (**3a**). Most probably, the transformation of the intermediate to the product **3a** could be spontaneous. In fact, the ^{1}H NMR analysis of the crude reaction mixture before completion of the reaction did not help much in identifying the intermediate(s). Therefore, to understand the actual reaction pathway(s), a few control experiments have been performed (Scheme 4). Initially, a couple of experiments had been carried out by treating phenyl-substituted *p*-QM **9** (instead of **1a**) with phenacyl bromide (**2a**) and phenylacetyl chloride (**5a**), individually under standard conditions. However, in both the cases, the corresponding 1,6-adducts **10** and **11** were not observed even after 24 h (Scheme 4). In fact, the starting material **9** was recovered unreacted in both the experiments.



Scheme 4. Control Experiments

In another set of experiments, 3-hydroxyphenyl-substituted *p*-QM **12**[23] (instead of **1a**) was treated with **2a** and **5a**, individually under the standard conditions (Scheme 4). Interestingly, in those cases, the corresponding *O*-alkylated product **13** and *O*-acylated product **14** were obtained in 73% and 70% yields, respectively within an hour. Moreover, the corresponding 1,6-adducts were not at all observed in both the cases. The above-mentioned control experiments clearly indicate that the reaction is proceeding through *O*-alkylation followed by intramolecular cyclization[17e] in the case of 2,3-dihydrobenzofuran/benzo[*b*]furan formation (path A, Scheme 3). Similarly, in the case of coumarin formation, one can conclude that the reaction is proceeding through *O*-acylation followed by intramolecular cyclization (path C, Scheme 3).

In summary, an effective one-pot protocol has been developed for the diastereoselective synthesis of *trans*-2,3-dihydrobenzofurans from 2-hydroxyaryl-substituted *p*-quinone methides through *O*-alkylation followed by 1,6-conjugate addition/cyclization strategy. This methodology has been elaborated for the one-pot synthesis of benzo[*b*]furans through the *in situ* dehydrogenative oxidation of the *trans*-2,3-dihydrobenzofuran intermediates. Similar methodology was also developed for the one-pot synthesis of 3,4-diaryl-substituted coumarin

derivatives through the reaction between 2-hydroxyaryl-substituted *p*-quinone methides and arylacetyl chlorides followed by oxidation. Under the optimal conditions, the above-mentioned oxygen-containing heterocycles could be accessed in moderate to good yields.

Experimental Section:

General Information. All reactions were carried out under an argon atmosphere in an oven dried round bottom flask. All the solvents were distilled before use and stored under argon atmosphere. Most of the reagents and starting materials were purchased from commercial sources and used as such. The substituted 2-bromoacetophenones were prepared according to the literature procedure.[22] All 2-hydroxyphenyl-subsituted *p*-quinone methides (**1a-j**)[16a] and 3-hydroxy phenyl-substituted *p*-quinone methide (**12**)[23] were prepared by following literature procedures. Melting points were recorded on SMP20 melting point apparatus and are uncorrected. ^{1}H, ^{13}C and ^{19}F spectra were recorded in $CDCl_3$ (400, 100 and 376 MHz respectively) on Bruker FT–NMR spectrometer. Chemical shift (δ) values are reported in parts per million relative to TMS or $CDCl_3$ (7.26 ppm for ^{1}H and 77.16 ppm for ^{13}C NMR) and the coupling constants (*J*) are reported in Hz. High resolution mass spectra were recorded on Waters Q–TOF Premier–HAB213 spectrometer. FT-IR spectra were recorded on a Perkin-Elmer FTIR spectrometer. Thin layer chromatography was performed on Merck silica gel 60 F_{254} TLC pellets and visualized by UV irradiation and $KMnO_4$ stain. Column chromatography was carried out through silica gel (100–200 mesh) using EtOAc/hexane as an eluent.

General procedure for the synthesis of 2,3-dihydrobenzofuran derivatives (3a-s):

Bromomethyl aryl ketone [**2a-l**] (0.1 mmol, 1.0 equiv.) was added to a mixture of 2-hydroxyphenyl-subsituted *p*-QM [**1a-j**] (0.11 mmol, 1.1 equiv.) and Cs_2CO_3 (0.15 mmol, 1.5

equiv.) in acetone (1.5 mL, 0.06 M) and, the resulting suspension was stirred at room temperature until the bromomethyl aryl ketone was completely consumed (based on TLC analysis). The reaction mixture was concentrated under reduced pressure and, the residue [a mixture of *cis*- and *trans*-2,3-dihydrobenzofurans along with some amounts of the starting material(s)] was then purified through a silica gel column using EtOAc/Hexane mixture as an eluent to get the *trans*-2,3-dihydrobenzofuran derivatives (**3a**-**u**).

trans-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)-2,3-dihydrobenzofuran-2-yl](phenyl)methanone ***(3a)***:[17b] The reaction was performed at 0.097 mmol scale of **1a**; white solid (31.0 mg, 80% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.93 (m, 2H), 7.60 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.8 Hz, 2H), 7.22 (t, J = 7.9 Hz, 1H), 7.06 (d, J = 7.4 Hz, 1H), 7.00 (d, J = 8.0 Hz, 1H), 6.96 (s, 2H), 6.91 (t, J = 7.4 Hz, 1H), 5.80 (d, J = 6.6 Hz, 1H), 5.20 (s, 1H), 4.86 (d, J = 6.6 Hz, 1H), 1.40 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 195.3, 159.3, 153.2, 136.3, 134.7, 133.8, 132.7, 129.5, 129.4, 128.8, 128.7, 125.6, 124.9, 121.6, 109.9, 90.9, 51.4, 34.5, 30.4; FT-IR (thin film, neat): 3636, 2959, 1694, 1261, 750 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{29}H_{31}O_3$ $[M–H]^–$: 427.2273; found : 427.2288.

trans-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)-2,3-dihydrobenzofuran-2-yl](m-tolyl)methanone ***(3b)***:[17c] The reaction was performed at 0.097 mmol scale of **1a**; white solid (31.6 mg, 80% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 7.7 Hz, 1H), 7.66 (s, 1H), 7.40 (d, J = 7.5 Hz, 1H), 7.33 (t, J = 7.6 Hz, 1H), 7.21 (t, J = 7.7 Hz, 1H), 7.04 (d, J = 7.4 Hz, 1H), 6.99 (d, J = 8.1 Hz, 1H), 6.95 (s, 2H), 6.90 (t, J = 7.4 Hz, 1H), 5.80 (d, J = 6.8 Hz, 1H), 5.18 (s, 1H), 4.81 (d, J = 6.8 Hz, 1H), 2.36 (s, 3H), 1.38 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 195.5, 159.4, 153.2, 138.5, 136.4, 134.8, 134.6, 132.6, 129.9, 129.5, 128.8, 128.6, 126.6, 125.5, 124.9, 121.5, 110.0, 90.9, 51.7, 34.5, 30.4, 21.5; FT-IR (thin film, neat): 3636, 2958, 1695, 1479, 1267, 759 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{30}H_{33}O_3$ $[M–H]^–$: 441.2430; found : 441.2448.

*trans-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)-2,3-dihydrobenzofuran-2-yl](4-ethylphenyl)-methanone (**3c**):* The reaction was performed at 0.097 mmol scale of **1a**; white solid (29 mg, 72% yield); m. p. = 151–153 ºC; R_f = 0.2 (5% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 7.4 Hz, 2H), 7.28 – 7.26 (m, 2H), 7.21 (t, J = 7.6 Hz, 1H), 7.05 (d, J = 7.5 Hz, 1H), 6.99 (d, J = 8.1 Hz, 1H), 6.95 (s, 2H), 6.90 (t, J = 7.5 Hz, 1H), 5.77 (d, J = 6.6 Hz, 1H), 5.18 (s, 1H), 4.84 (d, J = 6.6 Hz, 1H), 2.72 (q, J = 7.5 Hz, 2H) 1.38 (s, 18H), 1.27 (t, J = 7.5 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 195.0, 159.4, 153.1, 150.9, 136.3, 132.8, 132.4, 129.7, 129.5, 128.8, 128.3, 125.6, 124.9, 121.5, 109.9, 90.8, 51.5, 34.5, 30.4, 29.2, 15.3; FT-IR (thin film, neat): 3636, 2963, 1689, 1461, 1275, 750 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{31}H_{35}O_3$ $[M–H]^-$: 455.2586; found : 455.2599.

*trans-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)-2,3-dihydrobenzofuran-2-yl](4-methoxyphenyl)-methanone (**3d**):*[17b] The reaction was performed at 0.097 mmol scale of **1a**; white solid (31.6 mg, 79% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.6 Hz, 2H), 7.20 (t, J = 7.7 Hz, 1H), 7.05 (d, J = 7.4 Hz, 1H), 6.98 – 6.96 (m, 3H), 6.92 – 6.88 (m, 3H), 5.74 (d, J = 6.8 Hz, 1H), 5.18 (s, 1H), 4.86 (d, J = 6.8 Hz, 1H), 3.87 (s, 3H), 1.38 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 193.8, 164.0, 159.3, 153.1, 136.3, 132.7, 131.8, 129.6, 128.7, 127.7, 125.6, 125.0, 121.5, 113.9, 109.9, 90.8, 55.6, 51.5, 34.5, 30.4; FT-IR (thin film, neat): 3636, 2959, 1674, 1456, 1262, 750 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{30}H_{33}O_4$ $[M–H]^-$: 457.2379; found : 457.2397.

*trans-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)-2,3-dihydrobenzofuran-2-yl](3-methoxyphenyl)-methanone (**3e**):*[17c] The reaction was performed at 0.097 mmol scale of **1n**; white solid (28.8 mg, 72% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 7.6 Hz, 1H), 7.38 (s, 1H), 7.35 (t, J = 8.0 Hz, 1H), 7.21 (t, J = 7.7 Hz, 1H), 7.13 (d, J = 8.1 Hz, 1H), 7.03 (d, J = 7.4 Hz, 1H), 7.00 (d, J = 8.1 Hz, 1H), 6.94 (s, 2H), 6.90 (t, J = 7.4 Hz, 1H), 5.79 (d, J = 6.7 Hz, 1H), 5.19 (s, 1H), 4.79 (d,

J = 6.7 Hz, 1H), 3.74 (s, 3H), 1.38 (s, 18H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 195.2, 159.8, 159.3, 153.2, 136.4, 135.9, 132.7, 129.7, 129.4, 128.8, 125.6, 124.9, 122.0, 121.6, 120.5, 113.4, 110.0, 90.9, 55.4, 51.8, 34.5, 30.3; FT-IR (thin film, neat): 3632, 2958, 1699, 1480, 1263, 750 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{30}H_{33}O_4$ $[M–H]^-$: 457.2379; found : 457.2399.

*trans-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)-2,3-dihydrobenzofuran-2-yl](4-(trifluoromethoxy)-phenyl)methanone (**3f**):* The reaction was performed at 0.097 mmol scale of **1a**; white solid (31.7 mg, 70% yield); m. p. = 127–129 ºC; R_f = 0.3 (5% EtOAc in hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.4 Hz, 2H), 7.21 (t, J = 7.7 Hz, 1H) 7.06 (d, J = 7.3 Hz, 1H), 6.98 – 6.96 (m, 3H), 6.91 (t, J = 7.4 Hz, 1H), 5.71 (d, J = 6.8 Hz, 1H), 5.20 (s, 1H), 4.90 (d, J = 6.8 Hz, 1H), 1.38 (s, 18H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 193.9, 159.0, 153.3, 153.1 (q, $J_{C\text{-}F}$ = 1.6 Hz), 136.5, 132.9, 132.4, 131.6, 129.3, 128.9, 125.7, 124.9, 121.8, 120.4, 120.39 (q, $J_{C\text{-}F}$ = 257.4 Hz), 110.0, 91.0, 51.1, 34.5, 30.4; $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ –57.54; FT-IR (thin film, neat): 3639, 2960, 1696, 1479, 1268, 750 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{30}H_{30}F_3O_4$ $[M–H]^-$: 511.2096; found : 511.2119.

*trans-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)-2,3-dihydrobenzofuran-2-yl](2,3-dimethoxyphenyl)-methanone (**3g**):* The reaction was performed at 0.097 mmol scale of **1a**; white solid (29.5 mg, 68% yield); m. p. = 153–155 ºC; R_f = 0.1 (5% EtOAc in hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, J = 7.6 Hz, 1H), 7.11 – 7.07 (m, 2H), 7.06 – 7.04 (m, 1H), 7.02 (d, J = 7.4 Hz, 1H), 6.94 (d, J = 8.1 Hz, 1H), 6.87 (t, J = 7.4 Hz, 1H), 6.80 (s, 2H), 5.77 (d, J = 6.5 Hz, 1H), 5.10 (s, 1H), 4.70 (d, J = 6.4 Hz, 1H), 3.85 (s, 3H), 3.68 (s, 3H), 1.33 (s, 18H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 200.0, 159.5, 152.9, 152.8, 148.0, 136.0, 133.1, 131.9, 129.2, 128.7, 125.6, 124.7, 124.1, 121.3, 121.2, 116.1, 109.9, 93.3, 61.5, 56.0, 51.6, 34.4, 30.3; FT-IR (thin film, neat): 3627, 2956,

1699, 1478, 1267, 750 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{31}H_{35}O_5$ $[M–H]^-$: 487.2484; found : 487.2502.

*trans-(4-chlorophenyl)[3-(3,5-di-tert-butyl-4-hydroxyphenyl)-2,3-dihydrobenzofuran-2-yl]-methanone (**3h**):*[17b] The reaction was performed at 0.097 mmol scale of **1a**; white solid (29.2 mg, 70% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 7.21 (t, J = 7.7 Hz, 1H), 7.06 (d, J = 7.4 Hz, 1H), 6.98 – 6.96 (m, 3H), 6.92 (t, J = 7.4 Hz, 1H), 5.71 (d, J = 6.9 Hz, 1H), 5.20 (s, 1H), 4.89 (d, J = 6.9 Hz, 1H), 1.39 (s, 18H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 194.3, 159.1, 153.2, 140.3, 136.5, 133.1, 132.4, 130.9, 129.4, 129.0, 128.8, 125.6, 124.9, 121.7, 110.0, 91.0, 51.2, 34.5, 30.4; FT-IR (thin film, neat): 3636, 2959, 1695, 1479, 1261, 750 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{29}H_{30}ClO_3$ $[M–H]^-$: 461.1883; found : 461.1904.

*trans-(2-chlorophenyl)[3-(3,5-di-tert-butyl-4-hydroxyphenyl)-2,3-dihydrobenzofuran-2-yl]-methanone (**3i**):* The reaction was performed at 0.097 mmol scale of **1a**; white solid (30.4 mg, 73% yield); m. p. = 133–135 ºC; R_f = 0.2 (5% EtOAc in hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 3H), 7.30 – 7.28 (m, 1H), 7.18 (t, J = 7.6 Hz, 1H), 7.05 (d, J = 7.4 Hz, 1H), 6.91 – 6.90 (m, 2H), 6.84 (s, 2H), 5.69 (d, J = 6.5 Hz, 1H), 5.13 (s, 1H), 4.82 (d, J = 6.7 Hz, 1H), 1.34 (s, 18H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 200.1, 159.1, 153.1, 137.1, 136.2, 132.5, 132.2, 131.7, 130.5, 129.6, 129.0, 128.9, 126.8, 125.7, 124.6, 121.7, 110.0, 92.9, 51.5, 34.4, 30.3; FT-IR (thin film, neat): 3633, 2958, 1716, 1478, 1232, 751 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{29}H_{30}ClO_3$ $[M–H]^-$: 461.1883; found : 461.1894.

*trans-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)-2,3-dihydrobenzofuran-2-yl](2-fluorophenyl)-methanone (**3j**):* The reaction was performed at 0.097 mmol scale of **1a**; white solid (25.8 mg, 66% yield); m. p. = 129–131 ºC; R_f = 0.2 (5% EtOAc in hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 (t, J = 7.4 Hz, 1H), 7.54 (q, J = 7.1, 1H), 7.26 – 7.23 (m, 1H), 7.18 (t, J = 7.7 Hz, 1H), 7.12 – 7.07

(m, 1H), 7.04 (d, J = 7.4 Hz. 1H), 6.94 (d, J = 8.1 Hz, 1H), 6.91 (s, 2H), 6.88 (d, J = 7.5 Hz, 1H), 5.73 (d, J = 6.1 Hz, 1H), 5.14 (s, 1H), 4.82 (d, J = 6.0 Hz, 1H), 1.37 (s, 18H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 195.5 (d, $J_{C\text{-}F}$ = 3.6 Hz), 161.4 (d, $J_{C\text{-}F}$ = 253.9 Hz), 159.2, 153.0, 136.1, 135.0 (d, $J_{C\text{-}F}$ = 8.9 Hz), 132.7, 131.3 (d, $J_{C\text{-}F}$ = 2.8 Hz), 129.3, 128.8, 125.6, 124.72, 124.68, 124.4 (d, $J_{C\text{-}F}$ = 13.5 Hz), 121.6, 116.6 (d, $J_{C\text{-}F}$ = 22.9 Hz), 109.9, 93.1 (d, $J_{C\text{-}F}$ = 5.8 Hz), 51.0, 34.5, 30.4; $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ –108.95; FT-IR (thin film, neat): 3637, 2958, 1694, 1480, 1233, 751 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{29}H_{30}FO_3$ $[M–H]^-$: 445.2179; found : 445.2189.

*trans-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)-2,3-dihydrobenzofuran-2-yl]{4-(trifluoromethyl)-phenyl}methanone (**3k**):*[17c] The reaction was performed at 0.097 mmol scale of **1a**; pale yellow solid (30.8 mg, 69% yield); m. p. = 110–114 ºC; ^1H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 8.0 Hz, 2H), 7.74 (d, J = 8.1 Hz, 2H), 7.24 (t, J = 7.8 Hz, 1H), 7.09 (d, J = 7.4 Hz, 1H), 6.99 – 6.93 (m, 4H), 5.76 (d, J = 6.9 Hz, 1H), 5.23 (s, 1H), 4.94 (d, J = 6.9 Hz, 1H), 1.41 (s, 18H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 194.7, 159.0, 153.3, 137.6, 136.6, 135.0 (q, $J_{C\text{-}F}$ = 32.5 Hz), 132.4, 129.9, 129.3, 128.9, 125.72 (q, $J_{C\text{-}F}$ = 3.7 Hz), 125.67, 124.9, 123.6 (q, $J_{C\text{-}F}$ = 271.2 Hz), 121.8, 110.0, 91.2, 51.1, 34.5, 30.4; $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ –63.20; FT-IR (thin film, neat): 3639, 2960, 1699, 1479, 1325, 750 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{30}H_{30}F_3O_3$ $[M–H]^-$: 495.2147; found : 495.2161.

*trans-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)-2,3-dihydrobenzofuran-2-yl](phenyl)methanone (**3l**):* The reaction was performed at 0.097 mmol scale of **1a**; white solid (27.9 mg, 66% yield); m. p. = 145–147 ºC; R_f = 0.2 (5% EtOAc in hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, J = 8.4 Hz, 1H), 8.00 (d, J = 8.2 Hz, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.75 (d, J = 7.2 Hz, 1H), 7.63 – 7.54 (m, 2H), 7.41 (t, J = 7.6 Hz, 1H), 7.22 (t, J = 7.6 Hz, 1H), 7.03 (d, J = 7.4 Hz, 1H), 7.00 (d, J = 8.0 Hz, 1H), 6.91 (t, J = 7.4 Hz, 1H), 6.76 (s, 2H), 5.88 (d, J = 7.0 Hz, 1H), 5.12 (s, 1H), 4.81 (d, J =

7.0 Hz, 1H), 1.30 (s, 18H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 199.2, 159.5, 153.0, 136.2, 134.0, 133.4, 133.1, 132.6, 130.9, 129.05, 129.01, 128.9, 128.7, 128.5, 126.8, 125.7 (2C), 124.7, 124.3, 121.6, 110.0, 92.4, 51.8, 34.4, 30.3; FT-IR (thin film, neat): 3627, 2958, 1683, 1479, 1261, 750 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{33}H_{33}CO_3$ $[M–H]^-$: 477.2430; found : 477.2450.

*trans-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)-5-methyl-2,3-dihydrobenzofuran-2-yl](phenyl)-methanone (**3m**):*[17b] The reaction was performed at 0.092 mmol scale of **1b**; white solid (29.1 mg, 77% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 7.8 Hz, 2H), 7.59 (t, J = 7.6 Hz, 1H), 7.44 (t, J = 7.4 Hz, 2H), 7.00 (d, J = 8.2 Hz, 1H), 6.96 (s, 2H), 6.88 – 6.86 (m, 2H), 5.77 (d, J = 6.4 Hz, 1H), 5.19 (s, 1H), 4.80 (d, J = 6.4 Hz, 1H), 2.25 (s, 3H), 1.40 (s, 18H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 195.4, 157.3, 153.1, 136.3, 134.7, 133.7, 132.9, 130.9, 129.44, 129.40, 129.3, 128.7, 126.0, 124.9, 109.4, 91.1, 51.5, 34.5, 30.4, 20.9; FT-IR (thin film, neat): 3636, 2958, 1699, 1489, 1275, 750 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{30}H_{33}O_3$ $[M–H]^-$: 441.2430; found : 441.2444.

*trans-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)-5-methoxy-2,3-dihydrobenzofuran-2-yl](phenyl)-methanone (**3n**):*[17b] The reaction was performed at 0.088 mmol scale of **1c**; white solid (26.2 mg, 71% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J= 7.8 Hz, 2H), 7.59 (t, J= 7.4 Hz, 1H), 7.44 (t, J = 7.5 Hz, 2H), 6.98 (s, 2H), 6.89 (d, J= 8.7 Hz, 1H), 6.76 (d, J= 8.8 Hz, 1H), 6.62 (s, 1H), 5.76 (d, J= 6.6 Hz, 1H), 5.20 (s, 1H), 4.85 (d, J = 6.6 Hz, 1H), 3.71 (s, 3H), 1.40 (s, 18H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 195.4, 154.9, 153.4, 153.2, 136.4, 134.7, 133.8, 132.4, 130.3, 129.4, 128.7, 124.9, 114.4, 111.1, 110.0, 91.2, 56.2, 51.7, 34.5, 30.4; FT-IR (thin film, neat): 3627, 2957, 1695, 1486, 1234, 750 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{30}H_{33}O_4$ $[M–H]^-$: 457.2379; found : 457.2398.

*trans-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)-6-methoxy-2,3-dihydrobenzofuran-2-yl](phenyl)-methanone (**3o**):*[17b] The reaction was performed at 0.088 mmol scale of **1d**; white solid (26.9 mg,

73% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 7.7 Hz, 2H), 7.60 (t, J = 7.5 Hz, 1H), 7.45 (t, J = 7.4 Hz, 2H), 6.94 – 6.91 (m, 3H), 6.59 (s, 1H), 6.46 (d, J = 8.2 Hz, 1H), 5.79 (d, J = 6.2 Hz, 1H), 5.18 (s, 1H), 4.75 (d, J = 6.2 Hz, 1H), 3.81 (s, 3H), 1.39 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 195.4, 160.9, 160.7, 153.1, 136.3, 134.6, 133.8, 133.0, 129.4, 128.7, 125.7, 124.8, 121.3, 107.7, 96.2, 91.8, 55.6, 51.0, 34.5, 30.4; FT-IR (thin film, neat): 3632, 2958, 1699, 1503, 1275, 750 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{30}H_{33}O_4$ $[M–H]^–$: 457.2379; found : 457.2397.

*trans-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)-5-fluoro-2,3-dihydrobenzofuran-2-yl](phenyl)-methanone (**3p**)*:[17b] The reaction was performed at 0.091 mmol scale of **1e**; white solid (25.1 mg, 70% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 7.9 Hz, 2H), 7.60 (t, J = 7.2 Hz, 1H), 7.45 (t, J = 7.5 Hz, 2H), 6.94 (s, 2H), 6.89 (d, J = 6.3 Hz, 2H), 6.75 (d, J = 7.8 Hz, 1H), 5.81 (d, J = 6.6 Hz, 1H), 5.21 (s, 1H), 4.84 (d, J = 6.5 Hz, 1H), 1.39 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 195.0, 158.2 (d, $J_{C\text{-}F}$ = 236.5 Hz), 155.2 (d, $J_{C\text{-}F}$ = 1.3 Hz), 153.3, 136.5, 134.5, 133.9, 132.0, 131.0 (d, $J_{C\text{-}F}$ = 8.5 Hz), 129.5, 128.8, 124.8, 115.2 (d, $J_{C\text{-}F}$ = 24.3 Hz), 112.5 (d, $J_{C\text{-}F}$ = 24.7 Hz), 110.2 (d, $J_{C\text{-}F}$ = 8.4 Hz), 91.4, 51.4, 34.5, 30.4; ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ –123.14; FT-IR (thin film, neat): 3636, 2959, 1699, 1483, 1233, 751 cm^{-1}; HRMS (ESI): *m/z* calcd for $C29H_{30}FO_3$ $[M–H]^–$: 445.2179; found : 445.2201.

*trans-[5-chloro-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-2,3-dihydrobenzofuran-2-yl](phenyl)-methanone (**3q**)*:[17b] The reaction was performed at 0.087 mmol scale of **1f**; white solid (26.4 mg, 71% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.0 Hz, 2H), 7.61 (t, J = 7.2 Hz, 1H), 7.45 (t, J = 7.5 Hz, 2H), 7.16 (d, J = 8.6 Hz, 1H), 7.01 (s, 1H), 6.94 (s, 2H), 6.91 (d, J = 8.6 Hz, 1H), 5.83 (d, J = 6.4 Hz, 1H), 5.22 (s, 1H), 4.81 (d, J = 6.4 Hz, 1H), 1.40 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 194.7, 157.9, 153.4, 136.6, 134.4, 134.0, 132.0, 131.6, 129.4, 128.81, 128.78,

126.3, 125.6, 124.8, 111.0, 91.4, 51.3, 34.5, 30.4; FT-IR (thin film, neat): 3633, 2959, 1699, 1475, 1261, 749 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{29}H_{30}ClO_3$ $[M–H]^-$: 461.1883; found : 461.1902.

*trans-[5-bromo-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-2,3-dihydrobenzofuran-2-yl](phenyl)-methanone (**3r**):*[17b] The reaction was performed at 0.077 mmol scale of **1g**; white solid (25.7 mg, 72% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 7.6 Hz, 2H), 7.60 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 7.30 (d, J = 8.5 Hz, 1H), 7.15 (s, 1H), 6.94 (s, 2H), 6.87 (d, J = 8.5 Hz, 1H), 5.82 (d, J = 6.4 Hz, 1H), 5.23 (s, 1H), 4.81 (d, J = 6.4 Hz, 1H), 1.40 (s, 18H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 194.6, 158.4, 153.4, 136.6, 134.4, 134.0, 132.1, 132.0, 131.7, 129.4, 128.8, 128.5, 124.8, 113.4, 111.6, 91.3, 51.2, 34.5, 30.4; FT-IR (thin film, neat): 3633, 2958, 1699, 1471, 1262, 749 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{29}H_{30}BrO_3$ $[M–H]^-$: 505.1378; found : 505.1397.

*trans-[5,7-dichloro-3-(3,5-di-tert-butyl-4-hydroxyphenyl)-2,3-dihydrobenzofuran-2-yl](phenyl)methanone (**3s**) :* The reaction was performed at 0.079 mmol scale of **1h**; pale yellow gummy solid (21.0 mg, 53% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.93 (m, 2H), 7.63 – 7.59 (m, 1H), 7.48 – 7.44 (m, 2H), 7.22 (dd, J = 2.0, 0.7 Hz, 1H), 6.93 (s, 2H), 6.92 (dd, J = 2.0, 1.1 Hz, 1H), 5.88 (d, J = 6.8 Hz, 1H), 5.24 (s, 1H), 4.91 (d, J = 6.8 Hz, 1H), 1.40 (s, 18H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 193.9, 154.1, 153.6, 136.7, 134.3, 134.1, 132.8, 131.2, 129.5, 128.9 (2C), 126.7, 124.8, 124.1, 116.0, 91.5, 51.9, 34.5, 30.3; FT-IR (thin film, neat): 3638, 2959, 1699, 1456, 1238, 735 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{29}H_{29}Cl_2O_3$ $[M–H]^-$: 495.1494; found : 495.1475.

*trans-[3-(3,5-di-tert-butyl-4-hydroxyphenyl)-2,3-dihydronaphtho[2,3-b]furan-2-yl](phenyl)-methanone (**3t**):* The reaction was performed at 0.083 mmol scale of **1i**; pale yellow solid (26.3 mg, 73% yield); m. p. = 171–173 ºC; R_f = 0.2 (5% EtOAc in hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 7.8 Hz, 2H), 7.81 – 7.77 (m, 2H), 7.63 (t, J = 7.4 Hz, 1H), 7.49 (t, J = 7.4 Hz, 2H),

7.32 (d, J = 8.2 Hz, 2H), 7.29 – 7.23 (m, 2H), 7.00 (s, 2H), 5.94 (d, J = 5.1 Hz, 1H), 5.16 – 5.14 (m, 2H), 1.36 (s, 18H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 195.2, 157.2, 153.1, 136.4, 134.4, 133.9, 132.8, 130.6, 130.4, 130.2, 129.5, 128.8 (2C), 126.6, 124.6, 123.2, 123.1, 120.2, 112.2, 91.9, 51.2, 34.5, 30.4; FT-IR (thin film, neat): 3627, 2958, 1699, 1435, 1233, 750 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{33}H_{33}O_3$ $[M–H]^-$: 477.2430; found : 477.2451.

*(3-(4-hydroxy-3,5-diisopropylphenyl)-2,3-dihydrobenzofuran-2-yl)(phenyl)methanone (**3u**):* The reaction was performed at 0.11 mmol scale of **1j** and the product **3u** was obtained as an inseparable diastereomeric mixture; pale yellow gummy solid (22.6 mg, 53% yield); R_f = 0.1 (5% EtOAc in hexane); ^1H NMR (400 MHz, $CDCl_3$) [*major isomer*] δ 7.95 (t, J = 7.6 Hz, 4H), 7.63 – 7.58 (m, 2H), 7.51 – 7.43 (m, 4H), 7.25 – 7.21 (m, 1H), 7.04 – 6.99 (m, 2H), 6.93 (s, 2H), 5.79 (d, J = 6.8 Hz, 1H), 5.09 (s, 1H), 4.91 (d, J = 6.8 Hz, 1H), 3.33 – 3.23 (m, 2H), 1.20 (d, J = 6.6 Hz, 6H), 1.12 (d, J = 6.8 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) [*diastereomers*] δ 195.1, 193.9, 159.3, 152.5, 142.3, 138.6, 134.7, 134.6, 133.9, 129.4, 129.2, 129.0, 128.8, 128.0, 125.5, 124.2, 121.7, 110.1, 90.7, 51.3, 26.8, 24.2, 24.1; FT-IR (thin film, neat): 3505, 2961, 1694, 1471, 1226, 750 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{27}H_{27}O_3$ $[M–H]^-$: 399.1960; found : 399.1942.

General procedure for the synthesis of Benzofuran derivatives (4a-l)

Bromomethyl aryl ketone [**2a-g**] (1.0 equiv.) was added to the suspension of 2-hydroxyphenyl-subsituted *p*-QM [**1a-e** & **1i**] (1.1 equiv.) and Cs_2CO_3 (1.5 equiv.) in acetonitrile (0.06 M) and the resulting suspension was stirred at room temperature. After the reaction was complete (based on TLC analysis), DDQ (2.0 equiv.) was added and the reaction mixture was stirred at 50 ^oC until the former reaction product was completely consumed (based on TLC analysis). The residue was filtered through a pad of celite and the filtrate was then concentrated under reduced pressure. The

residue was purified through a silica gel column, using EtOAc/Hexane mixture as an eluent, to get the pure product (**4a-l**).

*[3-(3,5-di-tert-butyl-4-hydroxyphenyl)benzofuran-2-yl](phenyl)methanone (**4a**):*[17b] The reaction was performed at 0.097 mmol scale of **1a**; white solid (31.2 mg, 81% yield); ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.75 (d, J = 7.9 Hz, 1H), 7.67 (t, J = 7.7 Hz, 3H), 7.55 – 7.51 (m, 1H), 7.39 -7.34 (m, 2H) 7.20 – 7.17 (m, 4H), 5.25 (s, 1H), 1.35 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 186.7, 155.0, 154.1, 146.8, 137.4, 136.1, 132.4, 130.8, 129.9, 128.3 (2C), 127.9, 127.3, 123.9, 122.8, 121.9, 112.6, 34.4, 30.3; FT-IR (thin film, neat): 3631, 2958, 1649, 1448, 1161, 728 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{29}H_{31}O_3$ $[M+H]^-$: 427.2273; found : 427.2257.

*[3-(3,5-di-tert-butyl-4-hydroxyphenyl)benzofuran-2-yl](m-tolyl)methanone (**4b**):* The reaction was performed at 0.097 mmol scale of **1a**; white solid (31 mg, 79% yield); m. p. = 180–182 ºC; R_f = 0.6 (5% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.75 (d, J = 7.9 Hz, 1H), 7.67 (d, J = 8.4 Hz, 1H), 7.54 – 7.51 (m, 2H), 7.42 (s, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.16 (d, J = 7.6 Hz, 1H), 7.14 (s, 2H), 7.09 (t, J = 7.6 Hz, 1H), 5.25 (s, 1H), 2.16 (s, 3H), 1.34 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 186.9, 155.1, 154.1, 146.8, 137.5, 137.3, 136.0, 133.2, 130.7, 130.6, 128.31, 128.28, 127.9, 127.2, 127.0, 123.8, 122.8, 122.1, 112.6, 34.3, 30.2, 21.2; FT-IR (thin film, neat): 3627, 2958, 1645, 1436, 1238, 1144, 744 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{30}H_{33}O_3$ $[M+H]^+$: 441.2430; found : 441.2415.

*[3-(3,5-di-tert-butyl-4-hydroxyphenyl)benzofuran-2-yl](4-methoxyphenyl)methanone (**4c**):* The reaction was performed at 0.097 mmol scale of **1a**; white solid (27.1 mg, 68% yield); m. p. = 182–184 ºC; R_f = 0.4 (5% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.75 (d, J = 7.9 Hz, 1H), 7.70 – 7.65 (m, 3H), 7.51 (t, J = 7.8 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.17 (s, 2H), 6.66 (d, J = 8.6 Hz, 2H), 5.26 (s, 1H), 3.76 (s, 3H), 1.36 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 185.3,

163.1, 154.9, 154.0, 147.1, 136.1, 132.3, 130.0, 129.8, 128.3, 128.0, 127.3, 123.8, 122.6, 122.1, 113.1, 112.5, 55.4, 34.4, 30.3; FT-IR (thin film, neat): 3627, 2958, 1639, 1435, 1258, 1160, 750 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{30}H_{33}O_4$ $[M+H]^+$: 457.2379; found : 457.2399.

[3-(3,5-di-tert-butyl-4-hydroxyphenyl)benzofuran-2-yl](2-fluorophenyl)methanone ***(4d)****:* The reaction was performed at 0.097 mmol scale of **1a**; white solid (30.3 mg, 78% yield); m. p. = 166–168 ºC; R_f = 0.6 (5% EtOAc in hexane); ^1H NMR (400 MHz, $CDCl_3$), δ 7.68 – 7.63 (m, 2H), 7.55 – 7.46 (m, 2H), 7.33 (t, J = 7.5 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.17 (s, 2H), 7.02 (t, J = 7.5 Hz, 1H), 6.79 (t, J = 9.1 Hz, 1H), 5.26 (s, 1H), 1.37 (s, 18H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 182.9, 160.1 (d, $J_{C\text{-}F}$ = 252.0 Hz), 155.1, 154.1, 147.1, 135.7, 133.2 (d, $J_{C\text{-}F}$ = 8.4 Hz), 132.2 (d, $J_{C\text{-}F}$ = 0.9 Hz), 130.8 (d, $J_{C\text{-}F}$ = 2.4 Hz), 128.9, 128.8, 127.4 (d, $J_{C\text{-}F}$ = 13.8 Hz), 127.1, 123.94 (d, $J_{C\text{-}F}$ = 3.6 Hz), 123.90, 123.1, 121.4, 115.9 (d, $J_{C\text{-}F}$ = 21.6 Hz), 112.6, 34.3, 30.3; $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ –111.80; FT-IR (thin film, neat): 3632, 2959, 1652, 1454, 1153, 750 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{29}H_{30}FO_3$ $[M+H]^+$: 445.2165; found : 445.2179.

[3-(3,5-di-tert-butyl-4-hydroxyphenyl)benzofuran-2-yl](2,4-dichlorophenyl)methanone ***(4e)****:* The reaction was performed at 0.097 mmol scale of **1a**; white solid (19.5 mg, 44% yield); m. p. = 167–169 ºC; R_f = 0.6 (5% EtOAc in hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.60 (m, 2H), 7.54 (t, J = 7.3 Hz, 1H), 7.33 (t, J = 7.4 Hz, 1H), 7.21 (d, J = 8.2 Hz, 1H), 7.18 (s, 1H), 7.10 (s, 2H), 7.01 (d, J = 8.2 Hz, 1H), 5.30 (s, 1H), 1.40 (s, 18H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 183.7, 155.3, 154.3, 146.6, 136.7, 136.5, 135.8, 133.3, 132.9, 131.0, 129.8, 129.3, 129.0, 126.73, 126.71, 124.1, 123.3, 121.2, 112.7, 34.4, 30.3; FT-IR (thin film, neat): 3632, 2959, 1652, 1434, 1238, 1144, 967 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{29}H_{29}Cl_2O_3$ $[M+H]^+$: 495.1494; found : 495.1516.

[3-(3,5-di-tert-butyl-4-hydroxyphenyl)benzofuran-2-yl](3-(trifluoromethyl)phenyl)methanone ***(4f)****:* The reaction was performed at 0.097 mmol scale of **1a**; white solid (28.5 mg, 67% yield); m.

p. = 155–157 ºC; R_f = 0.7 (5% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.78 – 7.73 (m, 3H), 7.67 (d, J = 8.4 Hz, 1H), 7.56 (t, J = 7.4 Hz, 1H), 7.45 (d, J = 8.0 Hz, 2H), 7.38 (t, J = 7.6 Hz, 1H), 7.15 (s, 2H), 5.29 (s, 1H), 1.35 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 185.4, 155.2, 154.5, 146.4, 140.6 (q, $J_{C\text{-}F}$ = 0.9 Hz), 136.3, 133.6, 133.3, 132.1, 130.0 (2C), 128.9, 128.2, 127.2, 124.8 (q, $J_{C\text{-}F}$ = 3.6 Hz), 124.1, 123.6 (q, $J_{C\text{-}F}$ = 270.9 Hz), 123.0, 121.6, 112.7, 34.4, 30.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ –63.17; FT-IR (thin film, neat): 3632, 2959, 1651, 1436, 1168, 762 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{30}H_{30}F_3O_3$ $[M+H]^+$: 495.2147; found : 495.2125.

[3-(3,5-di-tert-butyl-4-hydroxyphenyl)benzofuran-2-yl](3-nitrophenyl)methanone ***(4g)****:* The reaction was performed at 0.097 mmol scale of **1a**; pale yellow solid (19.1 mg, 47% yield); m. p. = 189–191 ºC; R_f = 0.4 (5% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 8.20 (d, J = 8.0 Hz, 1H), 8.13 (d, J = 7.6 Hz, 1H), 7.74 (d, J = 8.2 Hz, 1H), 7.69 (d, J = 8.4 Hz, 1H) 7.58 (t, J = 7.5 Hz, 1H), 7.50 (t, J = 7.9 Hz, 1H), 7.39 (t, J = 7.5 Hz, 1H), 7.12 (s, 2H), 5.29 (s, 1H), 1.32 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 184.0, 155.4, 154.4, 147.3, 145.9, 138.8, 136.4, 135.0, 132.6, 129.3, 129.2, 128.2, 127.3, 126.5, 125.4, 124.3, 123.1, 121.4, 112.7, 34.3, 30.1; FT-IR (thin film, neat): 3626, 2959, 1652, 1435, 1275, 750 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{29}H_{30}NO_5$ $[M+H]^+$: 472.2124; found : 472.2144.

[5-chloro-3-(3,5-di-tert-butyl-4-hydroxyphenyl)benzofuran-2-yl](phenyl)methanone ***(4h)****:* The reaction was performed at 0.087 mmol scale of **1f**; pale yellow gummy solid (27.8 mg, 75% yield); R_f = 0.5 (5% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.66 (m, 3H), 7.59 (d, J = 8.8 Hz, 1H), 7.47 (d, J = 8.8 Hz, 1H), 7.38 (t, J = 7.4 Hz, 1H), 7.19 (t, J = 7.5 Hz, 2H), 7.12 (s, 2H), 5.28 (s, 1H), 1.35 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 186.4, 154.3, 153.3, 147.8, 137.1, 136.3, 132.6, 130.0, 129.9, 129.7, 129.6, 128.6, 127.9, 127.1, 122.2, 121.3, 113.7, 34.4,

30.3; FT-IR (thin film, neat): 3632, 2958, 1645, 1430, 1160, 733 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{29}H_{30}ClO_3$ $[M+H]^+$: 461.1883; found : 461.1868.

[3-(3,5-di-tert-butyl-4-hydroxyphenyl)-5-methylbenzofuran-2-yl](phenyl)methanone ***(4i)****:* The reaction was performed at 0.092 mmol scale of **1b**; white solid (28.6 mg, 76% yield); m. p. = 142–144 ºC; R_f = 0.5 (5% EtOAc in hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 7.7 Hz, 2H), 7.54 (d, J = 8.5 Hz, 1H), 7.51 (s, 1H), 7.38 – 7.33 (m, 2H), 7.19 (d, J = 7.5 Hz, 2H), 7.15 (s, 2H), 5.25 (s, 1H), 2.47 (s, 3H), 1.35 (s, 18H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 186.6, 154.1, 153.5, 147.0, 137.5, 136.0, 133.5, 132.3, 130.6, 129.92, 129.88, 128.4, 127.8, 127.2, 122.2, 122.1, 112.1, 34.3, 30.3, 21.6; FT-IR (thin film, neat): 3627, 2958, 1645, 1431, 1239, 749 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{30}H_{33}O_3$ $[M+H]^+$: 441.2430; found : 441.2408.

[3-(3,5-di-tert-butyl-4-hydroxyphenyl)-6-methoxybenzofuran-2-yl](phenyl)methanone ***(4j)****:* The reaction was performed at 0.088 mmol scale of **1d**; white solid (28.6 mg, 78% yield); m. p. = 181–183 ºC; R_f = 0.4 (5% EtOAc in hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 7.8 Hz, 2H), 7.59 (d, J = 8.7 Hz, 1H), 7.34 (t, J = 7.3 Hz, 1H), 7.18 – 7.13 (m, 5H), 6.98 (d, J = 8.7 Hz, 1H), 5.25 (s, 1H), 3.91 (s, 3H), 1.34 (s, 18H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 186.1, 161.3, 156.5, 154.1, 146.5, 137.8, 136.0, 132.1, 131.6, 129.8, 127.8, 127.2, 123.3, 122.1, 121.7, 114.3, 95.6, 55.9, 34.3, 30.3; FT-IR (thin film, neat): 3627, 2959, 1634, 1267, 1156, 750 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{30}H_{33}O_4$ $[M+H]^+$: 457.2379; found : 457.2361.

[3-(3,5-di-tert-butyl-4-hydroxyphenyl)-5-methoxybenzofuran-2-yl](phenyl)methanone ***(4k)****:* The reaction was performed at 0.088 mmol scale of **1c**; pale yellow gummy solid (26.8 mg, 73% yield); R_f = 0.3 (5% EtOAc in hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 7.7 Hz, 2H), 7.56 – 7.54 (m, 1H), 7.37 (t, J = 7.3 Hz, 1H), 7.21 – 7.18 (m, 4H), 7.15 – 7.13 (m, 2H), 5.26 (s, 1H), 3.84 (s, 3H), 1.36 (s, 18H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 186.5, 156.7, 154.1, 150.2, 147.6,

137.5, 136.1, 132.4, 130.7, 129.9, 128.7, 127.9, 127.2, 122.0, 118.4, 113.3, 103.5, 56.0, 34.4, 30.3; FT-IR (thin film, neat): 3627, 2957, 1645, 1481, 1275, 750 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{30}H_{33}O_4$ $[M+H]^+$: 457.2379; found : 457.2365.

[3-(3,5-di-tert-butyl-4-hydroxyphenyl)naphtho[2,3-b]furan-2-yl](phenyl)methanone ***(4l)****:* The reaction was performed at 0.083 mmol scale of **1i**; yellow gummy solid (24.8 mg, 69% yield); R_f = 0.2 (5% EtOAc in hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.93 (m, 3H), 7.79 (d, J = 9.0 Hz, 1H), 7.60 (d, J = 7.9 Hz, 2H), 7.48 (t, J = 7.2 Hz, 1H), 7.39 – 7.31 (m, 2H), 7.16 – 7.13 (m, 4H), 5.24 (s, 1H), 1.35 (s, 18H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 186.4, 154.0, 153.7, 147.7, 137.8, 135.9, 132.7, 131.9, 131.2, 130.5, 129.51, 129.46, 129.3, 127.71, 127.68, 126.8, 125.2, 123.4, 122.9, 121.8, 113.1, 34.4, 30.4; FT-IR (thin film, neat): 3618, 2924, 1644, 1433, 1233, 709 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{33}H_{33}O_3$ $[M+H]^+$: 477.2430; found : 477.2412.

General procedure for the synthesis of coumarin derivatives

Arylacetyl halide [**5a-j**] (1.2 equiv.) was added to a mixture of 2-hydroxyphenyl-subsituted *p*-QM [**1a-e**] (1.0 equiv.) and Cs_2CO_3 (2.2 equiv.) in acetone (0.06 M) and, the resulting suspension was stirred at room temperature for 1.5 h. Then DDQ (1.5 equiv.) was added to the reaction mixture and the resultant mixture was stirred at room temperature for additional 6 h. The reaction mixture was filtered through a pad celite and the filtrate was concentrated under reduced pressure. The crude was purified through a silica gel column using EtOAc/Hexane mixture as an eluent to get the pure coumarin derivative (**6a-n**).

4-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-phenyl-2H-chromen-2-one ***(6a)****:* The reaction was performed at 0.097 mmol scale of **1a**; white solid (34.6 mg, 84% yield); m. p. = 197–199 ºC; R_f = 0.3 (10% EtOAc in hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.52 (m, 2H), 7.44 (d, J = 8.3 Hz, 1H), 7.26 – 7.22 (m, 1H), 7.20 – 7.14 (m, 3H), 7.05 (d, J = 7.6 Hz, 2H), 6.87 (s, 2H), 5.28 (s,

1H), 1.29 (s, 18H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 161.6, 154.0, 153.6, 152.8, 135.8, 134.9, 131.3, 130.7, 128.2, 127.8, 127.3, 127.2, 126.6, 125.0, 124.1, 120.7, 117.0, 34.3, 30.3; FT-IR (thin film, neat): 3633, 2957, 1717, 1451, 763 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{29}H_{31}O_3$ $[M+H]^+$: 427.2273; found : 427.2260.

*4-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-(3-methoxyphenyl)-2H-chromen-2-one (**6b**):* The reaction was performed at 0.097 mmol scale of **1a**; white solid (34 mg, 77% yield); m. p. = 197–199 ºC; R_f = 0.2 (10% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.53 (m, 2H), 7.43 (d, *J* = 8.5 Hz, 1H), 7.26 – 7.22 (m, 1H), 7.15 (t, *J* = 7.9 Hz, 1H), 6.89 (s, 2H), 6.82 (d, *J* = 7.5 Hz, 1H), 6.72 (d, *J* = 8.3 Hz, 1H), 6.42 (s, 1H), 5.30 (s, 1H), 3.52 (s, 3H), 1.29 (s, 18H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 161.5, 159.1, 154.0, 153.6, 152.7, 136.0, 135.9, 131.4, 128.9, 128.1, 127.1, 126.4, 125.1, 124.1, 123.3, 120.6, 117.0, 115.4, 114.3, 55.1, 34.4, 30.2; FT-IR (thin film, neat): 3625, 2957, 1716, 1601, 758 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{30}H_{33}O_4$ $[M+H]^+$: 457.2379; found : 457.2360.

*4-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-(4-methoxyphenyl)-2H-chromen-2-one (**6c**):* The reaction was performed at 0.097 mmol scale of **1a**; white solid (31.3 mg, 71% yield); m. p. = 224–226 ºC; R_f = 0.2 (10% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.51 (m, 2H), 7.42 (d, *J* = 8.5 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 2H), 6.87 (s, 2H), 6.72 (d, *J* = 8.4 Hz, 2H), 5.28 (s, 1H), 3.74 (s, 3H), 1.30 (s, 18H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 158.8, 153.9, 153.7, 153.5, 152.3, 135.8, 131.9, 131.2, 128.1, 127.2, 127.1, 126.2, 125.2, 124.1, 116.9, 113.4, 110.9, 55.4, 34.4, 30.3; FT-IR (thin film, neat): 3604, 2923, 1717, 1608, 763 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{30}H_{33}O_4$ $[M+H]^+$: 457.2379; found : 457.2374.

4-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-(3,4-dimethoxyphenyl)-2H-chromen-2-one ***(6d)****:* The reaction was performed at 0.097 mmol scale of **1a**; white solid (32.4 mg, 69% yield); m. p. = 256–258 ºC; R_f = 0.2 (20% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.51 (m, 2H), 7.43 (d, J = 8.5 Hz, 1H), 7.26 – 7.22 (m, 1H), 6.90 – 6.88 (m, 3H), 6.79 (d, J = 8.3 Hz, 1H), 6.33 (s, 1H), 5.32 (s, 1H), 3.83 (s, 3H), 3.50 (s, 3H), 1.30 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.7, 153.9, 153.4, 152.1, 148.3, 148.2, 136.0, 131.2, 128.0, 127.2, 127.1, 126.0, 125.4, 124.1, 123.6, 120.6, 116.9, 114.2, 110.6, 56.1, 55.6, 34.4, 30.3; FT-IR (thin film, neat): 3632, 2957, 1716, 1603, 1251, 764 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{31}H_{35}O_5$ $[M+H]^+$: 487.2484; found : 487.2466.

4-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-(4-fluorophenyl)-2H-chromen-2-one ***(6e)****:* The reaction was performed at 0.097 mmol scale of **1a**; white solid (34.8 mg, 81% yield); m. p. = 204–206 ºC; R_f = 0.3 (10% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.50 (m, 2H), 7.43 (d, J = 8.2 Hz, 1H), 7.26 – 7.22 (m, 1H), 7.05 – 7.02 (m, 2H), 6.90 – 6.86 (m, 4H), 5.32 (s, 1H), 1.30 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.0 (d, $J_{C\text{-}F}$ = 245.6 Hz), 161.6, 154.1, 153.5, 153.1, 136.0, 132.5 (d, $J_{C\text{-}F}$ = 8.0 Hz), 131.5, 130.9 (d, $J_{C\text{-}F}$ = 3.5 Hz), 128.2, 127.1, 125.5, 124.8, 124.2, 120.5, 117.0, 114.8 (d, $J_{C\text{-}F}$ = 21.5 Hz), 34.4, 30.3; ^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ –114.7; FT-IR (thin film, neat): 3611, 2960, 1713, 1450, 803 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{29}H_{30}FO_3$ $[M+H]^+$: 445.2179; found : 445.2163.

4-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-(3-fluorophenyl)-2H-chromen-2-one ***(6f)****:* The reaction was performed at 0.097 mmol scale of **1a**; white solid (33.9 mg, 79% yield); m. p. = 229–231 ºC; R_f = 0.3 (10% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.52 (m, 2H), 7.44 (d, J = 8.2 Hz, 1H), 7.28 – 7.24 (m, 1H), 7.20 – 7.14 (m, 1H), 6.90 – 6.86 (m, 2H), 6. 88 (s, 2H), 6.77 – 6.74 (m, 1H), 5.33 (s, 1H), 1.31 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.4 (d, $J_{C\text{-}F}$ = 244.1 Hz), 161.2, 154.2, 153.6, 153.5, 137.1(d, $J_{C\text{-}F}$ = 8.3 Hz), 136.0, 131.7, 129.2 (d, $J_{C\text{-}F}$ = 8.2

Hz), 128.3, 127.0, 126.6 (d, $J_{C\text{-}F}$ = 2.9 Hz), 125.3 (d, $J_{C\text{-}F}$ = 7.6 Hz), 124.6, 124.3, 120.4, 117.8 (d, $J_{C\text{-}F}$ = 22.3 Hz), 117.0, 114.2 (d, $J_{C\text{-}F}$ = 20.8 Hz), 34.4, 30.2; $^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ –114.3; FT-IR (thin film, neat): 3632, 2959, 1716, 1484, 758 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{29}H_{30}FO_3$ $[M+H]^+$: 445.2179; found : 445.2165.

*3-(4-chlorophenyl)-4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2H-chromen-2-one (**6g**):* The reaction was performed at 0.097 mmol scale of **1a**; white solid (35.2 mg, 79% yield); m. p. = 207–209 ºC; R_f = 0.3 (10% EtOAc in hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, J = 14.2, 8.1 Hz, 2H), 7.44 (d, J = 8.2 Hz, 1H), 7.27 – 7.23 (m, 1H), 7.17 (d, J = 8.1 Hz, 2H), 7.00 (d, J = 8.1 Hz, 2H), 6.85 (s, 2H), 5.34 (s, 1H), 1.31 (s, 18H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.4, 154.2, 153.6, 153.3, 136.0, 133.5, 133.3, 132.1, 131.6, 128.2, 127.9, 127.1, 125.3, 124.7, 124.3, 120.4, 117.0, 34.4, 30.2; FT-IR (thin film, neat): 3611, 2957, 1713, 1602, 758 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{29}H_{30}ClO_3$ $[M+H]^+$: 461.1883; found : 461.1858.

*3-(3-chlorophenyl)-4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2H-chromen-2-one (**6h**):* The reaction was performed at 0.097 mmol scale of **1a**; white solid (33.9 mg, 76% yield); m. p. = 259–261 ºC; R_f = 0.3 (10% EtOAc in hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.53 (m, 2H), 7.44 (d, J = 8.2 Hz, 1H), 7.28 – 7.24 (m, 1H), 7.18 – 7.13 (m, 2H), 7.08 – 7.04 (m, 1H), 6.94 (s, 1H), 6.86 (s, 2H), 5.34 (s, 1H), 1.31 (s, 18H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 161.2, 154.3, 153.7, 153.6, 136.7, 136.1, 133.6, 131.8, 131.0, 129.0, 128.9, 128.3, 127.4, 127.0, 125.2, 124.6, 124.3, 120.4, 117.0, 34.4, 30.2; FT-IR (thin film, neat): 3637, 2960, 1717, 1438, 759 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{29}H_{30}ClO_3$ $[M+H]^+$: 461.1883; found : 461.1900.

*3-(4-bromophenyl)-4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2H-chromen-2-one (**6i**):* The reaction was performed at 0.097 mmol scale of **1a**; white solid (38.1 mg, 78% yield); m. p. = 271–273 ºC;

R_f = 0.3 (10% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.52 (m, 2H), 7.44 (d, J = 8.2 Hz, 1H), 7.32 (d, J = 8.1 Hz, 2H), 7.27 – 7.23 (m, 1H), 6.93 (d, J = 8.1 Hz, 2H), 6.84 (s, 2H), 5.33 (s, 1H), 1.31 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.3, 154.2, 153.6, 153.2, 136.0, 134.0, 132.4, 131.7, 130.9, 128.2, 127.2, 125.3, 124.7, 124.3, 121.6, 120.4, 117.0, 34.4, 30.3; FT-IR (thin film, neat): 3608, 2957, 1723, 1438, 758 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{29}H_{30}BrO_3$ $[M+H]^+$: 505.1378; found : 505.1362.

3-([1,1'-biphenyl]-4-yl)-4-(3,5-di-tert-butyl-4-hydroxyphenyl)-2H-chromen-2-one ***(6j)****:* The reaction was performed at 0.097 mmol scale of **1a**; white solid (35.5 mg, 73% yield); m. p. = 239–241 ºC; R_f = 0.3 (10% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.54 (m, 2H), 7.50 (d, J = 7.8 Hz, 2H), 7.47 – 7.40 (m, 5H), 7.35 – 7.31 (m, 1H), 7.28 – 7.24 (m, 1H), 7.13 (d, J = 7.9 Hz, 2H), 6.91 (s, 2H), 5.30 (s, 1H), 1.29 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.7, 154.1, 153.6, 152.8, 141.2, 140.3, 135.9, 134.01, 133.99, 131.4, 131.1, 128.8, 128.2, 127.3, 127.2, 126.6, 126.1, 124.9, 124.2, 120.6, 117.0, 34.4, 30.3; FT-IR (thin film, neat): 3625, 2958, 1716, 1486, 765 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{35}H_{35}O_3$ $[M+H]^+$: 503.2586; found : 503.2599.

6-chloro-4-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-phenyl-2H-chromen-2-one ***(6k)****:* The reaction was performed at 0.087 mmol scale of **1f**; white solid (30.1 mg, 75% yield); m. p. = 228–230 ºC; R_f = 0.3 (10% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 2.0 Hz, 1H), 7.49 (dd, J = 8.8, 2.0 Hz, 1H), 7.37 (d, J = 8.7 Hz, 1H), 7.21 – 7.18 (m, 3H), 7.05 – 7.03 (m, 2H), 6.84 (s, 2H), 5.32 (s, 1H), 1.29 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.1, 154.2, 151.9, 151.6, 136.0, 134.5, 131.3, 130.6, 129.5, 128.7, 127.9, 127.5, 127.4, 127.2, 124.3, 121.9, 118.4, 34.4, 30.2; FT-IR (thin film, neat): 3606, 2965, 1732, 1439, 759 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{29}H_{30}ClO_3$ $[M+H]^+$: 461.1883; found : 461.1863.

*6-bromo-4-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-phenyl-2H-chromen-2-one (**6l**):* The reaction was performed at 0.077 mmol scale of **1g**; white solid (29.6 mg, 76% yield); m. p. = 246–248 ºC; R_f = 0.3 (10% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.62 (d, J = 8.8 Hz, 1H), 7.31 (d, J = 8.7 Hz ,1H), 7.22 – 7.18 (m, 3H), 7.05 – 7.03 (m, 2H), 6.84 (s, 2H), 5.32 (s, 1H), 1.29 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.1, 154.3, 152.4, 151.5, 136.0, 134.5, 134.1, 130.62, 130.58, 127.9, 127.6, 127.4, 127.2, 124.2, 122.3, 118.7, 116.9, 34.4, 30.2; FT-IR (thin film, neat): 3606, 2968, 1732, 1439, 759 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{29}H_{30}BrO_3$ $[M+H]^+$: 505.1378; found : 505.1361.

*4-(3,5-di-tert-butyl-4-hydroxyphenyl)-6-methyl-3-phenyl-2H-chromen-2-one (**6m**):* The reaction was performed at 0.092 mmol scale of **1b**; white solid (29.7 mg, 73% yield); m. p. = 217–219 ºC; R_f = 0.3 (10% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.31 (m, 3H), 7.18 – 7.15 (m, 3H), 7.04 (d, J = 7.3 Hz, 2H), 6.86 (s, 2H), 5.28 (s, 1H), 2.35 (s, 3H), 1.29 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 161.9, 153.9, 152.7, 151.7, 135.7, 135.1, 133.7, 132.3, 130.7, 127.9, 127.8, 127.3, 127.2, 126.5, 125.1, 120.3, 116.7, 34.4, 30.3, 21.2; FT-IR (thin film, neat): 3611, 2962, 1717, 1440, 764 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{30}H_{33}O_3$ $[M+H]^+$: 441.2430; found : 441.2413.

*4-(3,5-di-tert-butyl-4-hydroxyphenyl)-7-methoxy-3-phenyl-2H-chromen-2-one (**6n**):* The reaction was performed at 0.088 mmol scale of **1d**; white solid (30.2 mg, 75% yield); m. p. = 195–197 ºC; R_f = 0.2 (10% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 9.0 Hz, 1H), 7.18 – 7.13 (m, 3H), 7.03 (d, J = 7.3 Hz, 2H), 6.93 (d, J = 1.6 Hz, 1H), 6.84 (s, 2H), 6.82 – 6.80 (m, 1H), 5.26 (s, 1H), 3.90 (s, 3H), 1.28 (s, 18H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.5, 155.3, 153.9, 153.0, 150.4, 135.7, 135.1, 130.8, 129.2, 127.8, 127.2, 127.1, 125.3, 123.4, 114.1, 112.3, 100.8,

55.9, 34.3, 30.3; FT-IR (thin film, neat): 3631, 2958, 1708, 1438, 764 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{30}H_{33}O_4$ $[M+H]^+$: 457.2379; found : 457.2393.

Procedure for de-tert-butylation of 6a

$AlCl_3$ (109 mg, 0.82 mmol, 10 equiv.) was added to a solution of **6a** (35 mg, 0.082 mmol, 1 equiv.) in dry toluene (2 mL) under argon atmosphere. The resulting reaction mixture was stirred at 60 ^oC for 1 h and then quenched with 5 mL of cold ice water. It was extracted with EtOAc (3 x 10 mL) and the combined organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was then purified through a silica gel column using EtOAc/Hexane mixture as an eluent to get the pure product **7**[21] (21.9 mg, 85%); ^1H NMR (400 MHz, DMSO-d_6) δ 9.67 (s, 1H), 7.63 (t, J = 7.8 Hz, 1H), 7.49 (d, J = 8.2 Hz, 1H), 7.29 (t, J = 7.8 Hz, 1H), 7.22 – 7.17 (m, 4H), 7.13 (d, J = 7.3 Hz, 2H), 6.97 (d, J = 8.2 Hz, 2H), 6.70 (d, J = 8.2 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 160.4, 157.3, 152.6, 151.4, 134.6, 131.7, 130.7, 130.6, 127.6, 127.5, 127.2, 126.4, 124.5, 124.4, 120.5, 116.4, 115.1; FT-IR (thin film, neat): 3218, 2923, 1674, 1441, 1295, 765 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{21}H_{15}O_3$ $[M+H]^+$: 315.1021; found : 315.1010.

Procedure for synthesis of 13

2-Bromoacetophenone [**2a**] (17.5 mg, 0.088 mmol, 1.0 equiv.) was added to a mixture of 3-hydroxyphenyl-subsituted *p*-QM [**12**][23] (30 mg, 0.097 mmol, 1.1 equiv.) and Cs_2CO_3 (43 mg, 0.132 mmol, 1.5 equiv.) in acetone (1.5 mL) and, the resulting suspension was stirred at room temperature until the 2-bromoacetophenone was completely consumed (based on TLC analysis). The reaction mixture was concentrated under reduced pressure and, the residue was then purified through a silica gel column using EtOAc/Hexane mixture as an eluent to get the pure compound **13**. Yellow gummy solid (30.3 mg, 73% yield); R_f = 0.2 (10% EtOAc in hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.99 (m, 2H), 7.63 (t, J = 7.4 Hz, 1H), 7.53 – 7.49 (m, 3H), 7.39 – 7.34 (m,

1H), 7.13 (s, 1H), 7.09 (d, J = 7.5 Hz, 1H), 7.00 – 6.97 (m, 3H), 5.34 (s, 2H), 1.32 (s, 9H), 1.27 (s, 9H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 194.1, 186.7, 158.4, 149.6, 148.0, 142.1, 137.4, 135.2, 134.4, 134.2, 132.4, 130.1, 129.0, 128.2, 127.8, 123.9, 116.3, 115.9, 70.9, 35.6, 35.1, 29.7, 29.6; FT-IR (thin film, neat): 2957, 1705, 1438, 1614, 1557, 754 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{29}H_{33}O_3$ $[M+H]^+$: 429.2430; found : 429.2439.

Procedure for synthesis of 14

Phenyl acetylchloride [**5a**] (25.5 µL, 0.193 mmol, 1.2 equiv.) was added to a mixture of 3-hydroxyphenyl-subsituted *p*-QM [**12**][23] (50.0 mg, 0.161 mmol, 1.0 equiv.) and Cs_2CO_3 (115.4 mg, 0.354 mmol, 2.2 equiv.) in acetone (2.0 mL) and, the resulting suspension was stirred at room temperature until the phenyl acetylchloride was completely consumed (based on TLC analysis). The reaction mixture was concentrated under reduced pressure and, the residue was then purified through a silica gel column using EtOAc/Hexane mixture as an eluent to get the pure compound **14**. Yellow gummy solid (40.0 mg, 70% yield); R_f = 0.2 (10% EtOAc in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 2.3 Hz, 1H), 7.44 – 7.41 (m, 1H), 7.40 – 7.36 (m, 4H), 7.34 – 7.32 (m, 1H), 7.31 – 7.29 (m, 1H), 7.14 – 7.09 (m, 3H), 6.98 (d, J = 2.3 Hz, 1H), 3.88 (s, 2H), 1.33 (s, 9H), 1.28 (s, 9H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 186.7, 170.0, 151.0, 149.8, 148.2, 140.9, 137.4, 135.0, 133.4, 132.7, 129.9, 129.3(2C), 128.9, 127.9, 127.6, 123.4, 122.1, 41.6, 35.6, 35.2, 29.64, 29.62; FT-IR (thin film, neat): 2957, 1760, 1614, 1362, 754 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{29}H_{33}O_3$ $[M+H]^+$: 429.2430; found : 429.2432.

Supporting Information

^{1}H, ^{13}C and ^{19}F spectra of all new compounds

Notes

The authors declare no competing financial interest.

Acknowledgements

The authors gratefully acknowledge IISER Mohali for the financial support and infrastructure. GS, SK and AC thank IISER Mohali for a research fellowship. The NMR and HRMS facilities at IISER Mohali are gratefully acknowledged.

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