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N-Heterocyclic Carbene/Brønsted Base Cascade Catalysis: Base-Controlled Selective Synthesis of Multifunctional Benzofuran-3-ones or Flavone Derivatives from the Reaction of 3-(2-Formylphenoxy)propenoates with Imines

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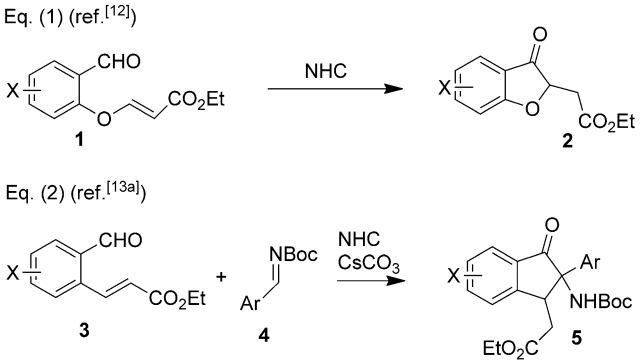
Abstract: The N-heterocyclic carbene/Brønsted base cascade catalysis in the reaction of 3-(2-formylphenoxy)propenoates with *N*-Boc-arylimines has been studied. Both multifunctional benzofuran-3-ones and benzopyran-4-ones (flavone derivatives) were selectively synthesized in good yields simply by regulating the loading of the base catalyst.

Keywords: benzofuran-3-ones; carbenes; domino reactions; flavones; 3-(2-formylphenoxy)propenoates; imines; organic catalysis

Introduction

Cascade catalysis[1] that incorporates multiple catalytic cycles in a single procedure is a powerful strategy for the rapid construction of complex molecular structures with avoidance of isolation and purification of intermediates. The development of novel catalytic systems in which one or several catalysts act sequentially to promote the multistep catalytic processes is of great importance and is attracting growing interest.[2] One of the challenges of cascade catalysis is to overcome the problems of compatibility of catalysts with reactants, intermediates and products. In this regard, the use of N-heterocyclic carbene (NHC) catalysts appears advantageous because they are compatible with acids,[3] bases,[4,5] oxidants[6] and transition metal-based catalysts.[7] For example, the cooperative catalysis of N-heterocyclic carbenes and Lewis or Brønsted acids in various reactions has been demonstrated to improve the reactivity and/or stereoselectivity of the reactions.[3] On the other hand, the cascade catalysis in the one-pot annulation reaction of α,β-unsaturated aldehydes with 1,3-diketones[4a] or β-keto sulfones,[4b,c] the annulation of aliphatic aldehydes with activated enones,[4d] and the Diels–Alder/benzoin reaction of 2,4-dienals with indenones,[4e] have been achieved by the combination of NHCs and secondary amines. In addition, some dual catalytic approaches using NHCs in concert with Brønsted or Lewis bases have been applied to the asymmetric acylation of secondary alcohols,[5a] the enantioselective annulation between α,β-unsaturated aldehydes and 2-(bromomethyl)-*ortho*-(*tert*-butyldimethylsilyl)phenol,[5b] the reaction of 2-(2-propynyloxy)benzaldehydes with aldehydes,[5c,d] and the dimerization of 2-(aroylvinyl)arylaldehydes.[5e] In these cascade catalytic reactions, bases are able to accelerate the reaction rate, to enhance the stereoselectivity, or to alter the reaction pathway. As evidenced by these advances, cooperative and cascade catalysis employing NHCs in concert with other catalysts has emerged as a very promising research area.

Both benzofuran-3-one derivatives,[8] especially 2,2-disubstituted benzofuran-3-ones, and benzopyran-4-ones (chromones and flavones)[9] are known to exhibit strong and a broad spectrum of biological activities, such as anticancer,[8a–c,9a–f] anti-inflammatory,[8d,9g,h] antioxidant,[9e–j] antipsychotic (Alzheimer's disease),[8e] antiviral,[8f,g] antibacterial and antifungal properties.[8h,i] Because of their potential applications in synthetic and medicinal chemistry, the interest in the synthesis of benzofuran-3-one, chromone and flavone derivatives remains undiminished.[10,11] It has been reported that, under the catalysis of NHCs, 3-(2-formylphenoxy)propenoates **1** undergo an intramolecular Stetter reaction to form benzofuran-3-one-2-acetates

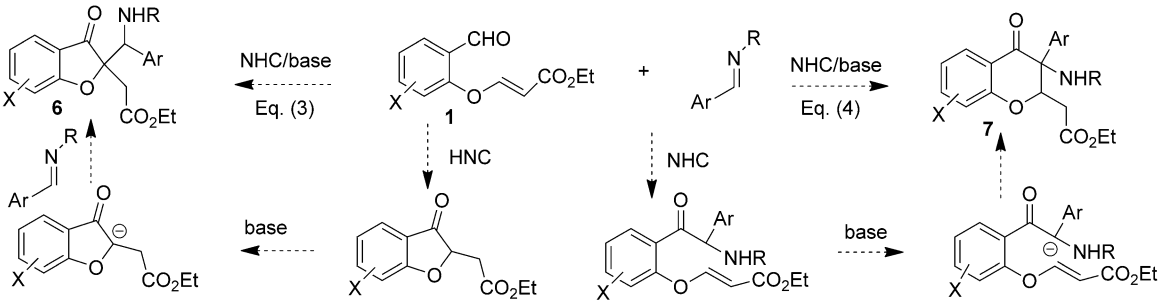


Scheme 1. The reported NHC-catalyzed intramolecular reaction of 3-(2-formylphenoxy)propenoates **1** and the intermolecular reaction of 3-(2-formylphenyl)propenoates **3** with *N*-Boc(aryl)imines **4**.

2 [Scheme 1, Eq. (1)].[12] Also, the NHC/base-catalyzed reaction of 3-(2-formylphenyl)propenoates **3** with *N*-Boc(aryl)imines **4** proceeded *via* a cascade intermolecular aza-bezoin reaction and intramolecular Michael addition to produce indanone derivatives **5** [Scheme 1, Eq. (2)].[13a] We envisioned that the NHC/Brønsted base cascade catalysis in the reaction between 3-(2-formylphenoxy)propenoates **1** and imines would either follow the cascade intramolecular Stetter reaction and intermolecular nucleophilic addition to produce multifunctionalized dihydrobenzofuran-3-ones **6** [Scheme 2, Eq. (3)], or proceed through an aza-bezoin/Michael cascade to provide 3-aminotetrahydrobenzopyran-4-one derivatives **7** [Scheme 2, Eq. (4)]. With the aim to develop highly efficient methods for the construction of multifunctional benzofuran-3-ones and benzopyran-4-ones utilizing an organocascade catalysis strategy, we undertook the current study on the NHC/Brønsted base-catalyzed reaction of 3-(2-formylphenoxy)propenoates **1** with *N*-Boc-(aryl)imines. Surprisingly, instead of the formation of 3-aminotetrahydrobenzopyran-4-ones **7** (R = Boc), both 2,2-disubstituted benzofuran-3-ones and 2-arylchromones (flavones) were obtained in good yields in a highly selective manner from the reaction of 3-(2-formylphenoxy)propenoates **1** with *N*-Boc(aryl)imines simply by controlling the amount of base catalyst. We report herein the details of our study.

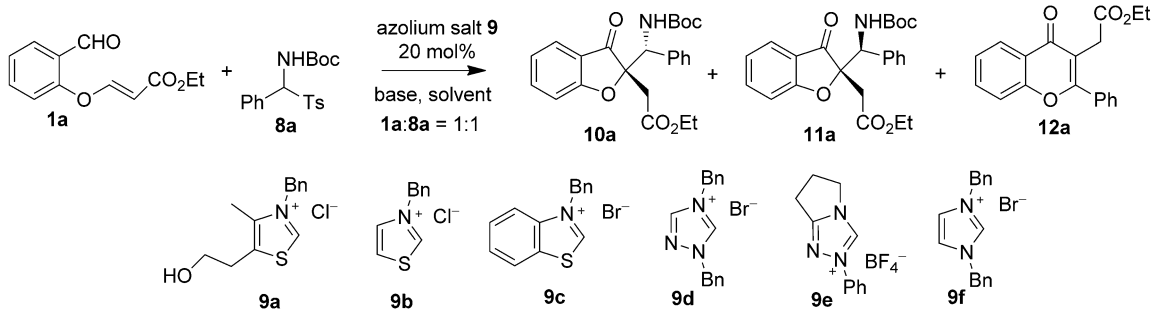
Results and Discussion

Since most imine compounds are not very stable, *tert*-butyl aryl(tosyl)methylcarbamates **8** are generally used as the surrogates of *N*-Boc(aryl)imines **4** in the NHC-catalyzed reactions due to their ready preparation, high stability and easy transformation into imines upon the treatment with a base.[13] We initiated our study by examining the reaction of 3-(2-formylphenoxy)propenoate **1a** with *tert*-butyl phenyl-(tosyl)methylcarbamate **8a** employing a variety of N-heterocyclic carbene catalysts **9′** (20 mol%). The NHC catalysts were generated *in situ* from the interaction of azolium salts **9** with Cs_2CO_3 (0.6 equiv.) in dichloromethane at ambient temperature. As indicated in Table 1, the reactions catalyzed by thiazole carbenes **9a′** and **9b′** afforded 2-[(*tert*-butoxycarbonylamino)(phenyl)methyl]benzofuran-3-one-2-acetate **10a** in 35–42% yields along with 5–8% yields of diastereomer **11a**. In stark contrast, benzthiazole, triazole and imidazole carbenes **9c′**–**9f′** were found to be inactive towards this reaction (Table 1, entries 1–6). Under the catalysis of NHC catalyst **9a′**, the reaction conditions were further optimized by varing the solvent, reaction temperature and base. It was found that the nature of the solvent strongly influenced the outcomes of the reaction. For example, in polar solvents including acetone, 1,4-dioxane and acetonitrile, the reactions of **1a** with **8a** produced diastereomeric benzofuran-3-ones **10a** and **11a** in 19–29% and 23–34% yields, respectively, with low diastereoselectivity (**10a**:**11a**: ~1:1 to 1:1.5) (Table 1, entries 7–9). However, the use of non-polar benzene as solvent led to the predominant formation of diastereomer **10a** in 53% yield along with a trace amount of **11a** (**10a**:**11a**: ~13:1) (Table 1, entry 11). The yield of product **10a** was improved to 80% when reaction temperature was elevated to the boiling point of benzene



Scheme 2. The proposed NHC/Brønsted base-catalyzed cascade reactions between 3-(2-formylphenoxy)propenoates **1** and imines.

Table 1. Optimization of reaction conditions.

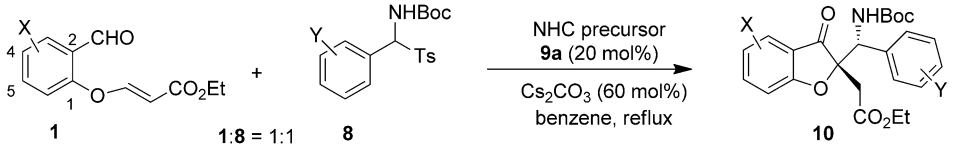


Entry	9	Base (equiv.)	Solvent	Temperature	Time [h]	Yield [%]		
						10a	**11a**	**12a**
1	**9a**	Cs_2CO_3 (0.6)	DCM	room temp.	16	42	8	–
2	**9b**	Cs_2CO_3 (0.6)	DCM	room temp.	12	35	5	–
3	**9c**	Cs_2CO_3 (0.6)	DCM	room temp.	18	–	–	–
4	**9d**	Cs_2CO_3 (0.6)	DCM	room temp.	13	trace	–	–
5	**9e**	Cs_2CO_3 (0.6)	DCM	room temp.	18	trace	–	–
6	**9f**	Cs_2CO_3 (0.6)	DCM	room temp.	15	–	–	–
7	**9a**	Cs_2CO_3 (0.6)	dioxane	room temp.	18	24	24	–
8	**9a**	Cs_2CO_3 (0.6)	acetonitrile	room temp.	12	19	23	–
9	**9a**	Cs_2CO_3 (0.6)	acetone	room temp.	12	29	34	–
10	**9a**	Cs_2CO_3 (0.6)	acetone	reflux	12	31	39	–
11	**9a**	Cs_2CO_3 (0.6)	benzene	room temp	18	53	4	–
12	**9a**	**Cs_2CO_3** (0.6)	**benzene**	**reflux**	**15**	**80**	**5**	–
13	**9a**	*t*-BuOK (0.6)	benzene	reflux	16	64	trace	–
14	**9a**	NaH (0.6)	benzene	reflux	16	75	5	–
15	**9a**	DBU (0.6)	benzene	reflux	18	64	6	–
16	**9a**	Cs_2CO_3 (0.8)	benzene	reflux	9	20	–	65
17	**9a**	**Cs_2CO_3 (1.2)**	**benzene**	**reflux**	**9**	–	–	**78**

(Table 1, entry 12). To further increase the efficiency and selectivity of the reaction, the bases were then screened in refluxing benzene. Disappointingly, the replacement of Cs_2CO_3 by *t*-BuOK, NaH, and DBU all led to slight decreases in the yield of product **10a** (Table 1, entries 13–15). Interestingly and unexpectedly, on varying the loading of Cs_2CO_3 to 0.8 equivalents, the formation of another product **12a** was observed (Table 1, entry 16). Gratifyingly, flavone **12a** was isolated as the sole product in 78% yield from the reaction utilizing1.2 equiv. of Cs_2CO_3 as a base catalyst in boiling benzene (Table 1, entry 17).

Under the optimized conditions for the selective formation of benzofuran-3-ones **10**, the substrate scope was surveyed by varying the 3-(2-formylphenoxy)propenoates **1** as well as the *tert*-butyl aryl(tosyl)methylcarbamates **8**. It was found that this protocol tolerated electron-donating and electron-withdrawn substituents on both reactants **1** and **8**. The nature of the substituents and the substitution pattern showed only a small influence on the outcomes of the reaction. For example, in boiling benzene, irrespective of the electronic features of the aryl groups of the aryl(tosyl)methylcarbamates **8**, all reactions of aldehyde **1a** with substrates **8a–8e** that contain a phenyl, *para*-anisyl, *para*-tolyl, *para*-bromophenyl and *para*-fluorophenyl groups proceeded smoothly to produce the corresponding benzofuran-3-ones **10a–10e** in good yields with high diastereoselectivity (65–83%, *dr* 9:1–>20:1) (Table 2, entries 1–5). In addition, the reactions of aldehyde **1a** with aryl(tosyl)methylcarbamates **8b**, **8f** and **8g** substituted by *ortho*-anisyl, *meta*-anisyl, and *para*-anisyl afforded products **10b**, **10f** and **10g**, respectively, in similar yields (74–83%) (Table 2, entries 2, 6, 7). It is also noteworthy that the variation of the electronic features and substitution patterns of the substituents on the benzaldehyde moiety of substrates **1** only marginally affected the efficiency and the diastereoselectivity of the reaction. For instance, the reaction of **8a** with aldehydes **1b–1h** that bear either an electron-donating or an electron-withdrawn group on different positions of the phenyl rings afforded products **10h–10l** in 75–88% yields with excellent diastereoselectivity (*dr* >20:1) (Table 2, entries 8–14). During the optimization of the reaction conditions, we found that polar solvents, like acetone, 1,4-dioxane and acetonitrile, were beneficial to the formation of the *cis*-configured diastereomer **11a**, and

Table 2. Selective synthesis of benzofuran-3-one derivatives **10** from the reaction of 3-(2-formylphenoxy)propenoates **1** with *tert*-butyl aryl(tosyl)methylcarbamates **8** catalyzed by a thiazole carbene and Cs_2CO_3 (0.6 equiv.) in refluxing benzene.



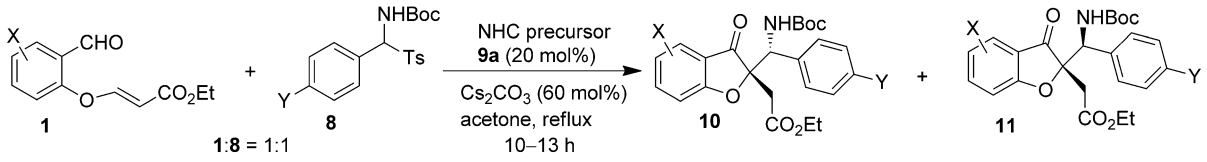
Entry	**1**	X	**8**	Y	Time [h]	**10**	Yield [%]	*dr*[a]
1	**1a**	H	**8a**	H	15	**10a**	80	13:1
2	**1a**	H	**8b**	4-OMe	15	**10b**	83	15:1
3	**1a**	H	**8c**	4-Me	15	**10c**	78	>20:1
4	**1a**	H	**8d**	4-Br	15	**10d**	65	9:1
5	**1a**	H	**8e**	4-F	15	**10e**	77	9:1
6	**1a**	H	**8f**	2-OMe	10	**10f**	84	>20:1
7	**1a**	H	**8g**	3-OMe	10	**10g**	74	>20:1
8	**1b**	4-OMe	**8a**	H	11	**10h**	86	>20:1
9	**1c**	6-OMe	**8a**	H	12	**10i**	86	>20:1
10	**1d**	4-Me	**8a**	H	12	**10j**	76	>20:1
11	**1e**	5-Me	**8a**	H	10	**10k**	75	>20:1
12	**1f**	6-Me	**8a**	H	10	**10l**	88	>20:1
13	**1g**	4-Br	**8a**	H	8	**10m**	77	>20:1
14	**1h**	5-Br	**8a**	H	11	**10n**	86	>20:1

[a] Diastereomeric ratios were determined by ^{1}H NMR on the crude products.

the highest yield of **11a** was obtained from the reaction in acetone (Table 1, entries 7–9). In order to isolate and identify the diastereomers **11**, the reactions of 3-(2-formylphenoxy)propenoates **1** with *tert*-butyl aryl(tosyl)methylcarbamates **8** were then carried out in refluxing acetone. From these reactions, the *cis*-diastereomers **11** were isolated in 31–39% yields, along with the *anti*-diastereomers **10** in 26–33% yields (Scheme 3).

The generality for the selective synthesis of flavones **12** from 3-(2-formylphenoxy)propenoates **1** and *tert*-butyl aryl(tosyl)methylcarbamates **8** was then scrutinized by means of employing 1.2 equiv. of Cs_2CO_3 as a base catalyst. It was found that both electron-rich and electron-deficient phenyls are accommodated on the aldehydes **1** and aryl(tosyl)methylcarbamates **8**. All examined reactants **1** and **8**, which are substituted by either electron-donating or electron-withdrawn groups on different positions of the phenyl rings, underwent the reaction efficiently to form flavones **12** in good yields (63–86%) *via* benzofuran-3-ones **10** under the optimized reaction conditions (Table 3, entries 1–14).

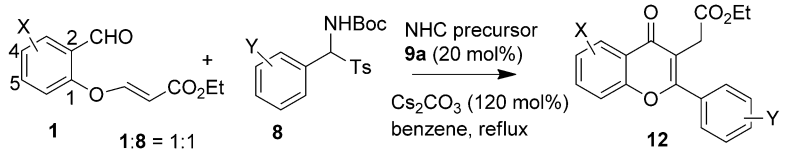
The structures of all products were elucidated on the basis of spectroscopic data. NMR spectra and mass data indicated that products **10** and **11** were isomeric compounds derived from the 1+1 addition reaction between aldehydes **1** and aryl(tosyl)methylcarbamates **8** with the loss of a *para*-toluenesulfinic acid molecule, while products **12** were the 1+1 combination of substrates **1** and **8** with the loss of both a *para*-toluenesulfinic acid and a *tert*-butyl carbamate molecule. The structures and stereochemistry of the products were finally determined by



X = Y = H: **10a**: 31% **11a**: 39%
X =H, Y = OMe: **10b**: 30% **11b**: 33%
X =H, Y = Me: **10c**: 33% **11c**: 39%
X =H, Y = Br: **10d**: 26% **11d**: 32%
X = 4-OMe, Y = H: **10h**: 31% **11h**: 31%
X = 4-Br, Y = H: **10m**: 28% **11m**: 35%

Scheme 3. The reaction of 3-(2-formylphenoxy)propenoates **1** with *tert*-butyl aryl(tosyl)methylcarbamates **8** catalyzed by a thiazole carbene and Cs_2CO_3 (0.6 equiv.) in refluxing acetone.

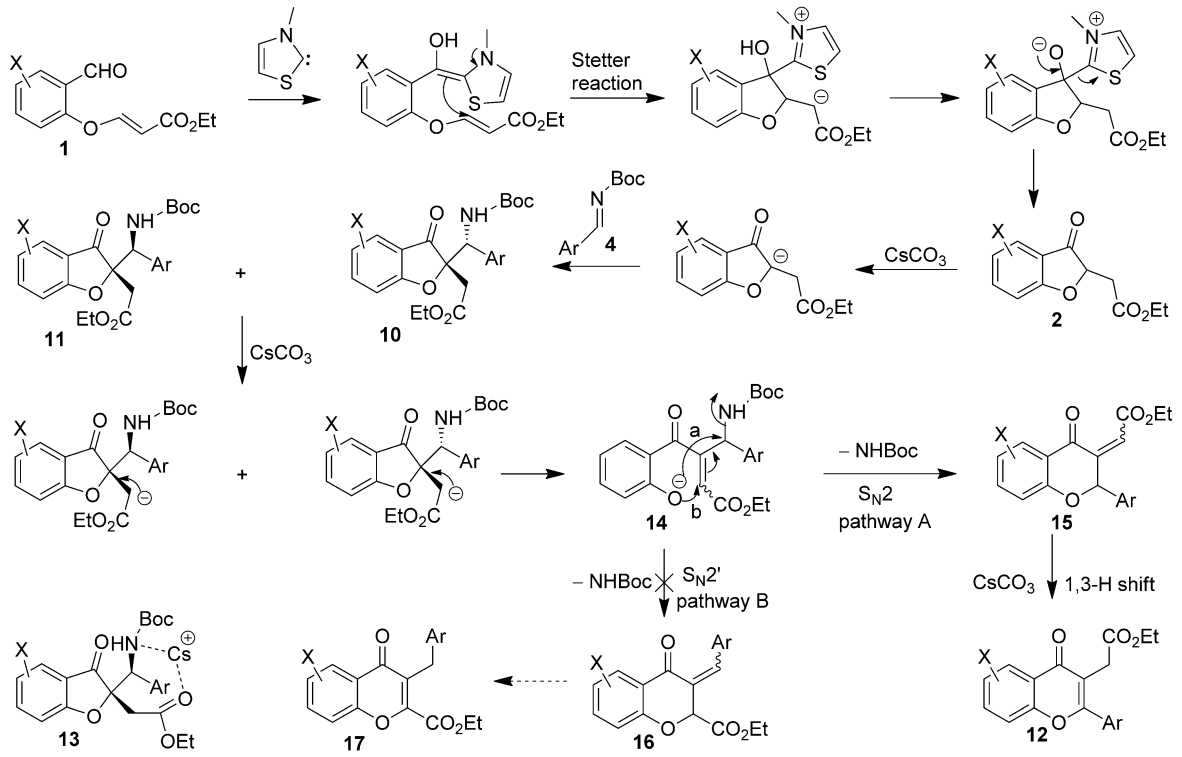
Table 3. Selective synthesis of flavones **12** from the reaction of 3-(2-formylphenoxy)propenoates **1** with *tert*-butyl aryl-(tosyl)methylcarbamates **8** catalyzed by a thiazole carbene and Cs_2CO_3 (1.2 equiv.) in refluxing benzene.



Entry	1	X	8	Y	Time [h]	12	Yield [%]
1	**1a**	H	**8a**	H	15	**12a**	67
2	**1a**	H	**8b**	4-OMe	7	**12b**	73
3	**1a**	H	**8c**	4-Me	24	**12c**	68
4	**1a**	H	**8d**	4-Br	8	**12d**	64
5	**1a**	H	**8e**	4-F	8	**12e**	78
6	**1a**	H	**8f**	2-OMe	24	**12f**	69
7	**1a**	H	**8g**	3-OMe	7	**12g**	78
8	**1b**	4-OMe	**8a**	H	8	**12h**	75
9	**1c**	6-OMe	**8a**	H	5	**12i**	86
10	**1d**	4-Me	**8a**	H	8	**12j**	63
11	**1e**	5-Me	**8a**	H	8	**12k**	69
12	**1f**	6-Me	**8a**	H	10	**12l**	64
13	**1g**	4-Br	**8a**	H	24	**12m**	84
14	**1h**	5-Br	**8a**	H	7	**12n**	80

single crystal X-ray diffraction analysis, which revealed unambiguously that the products **10b** and **12i** are ethyl (2*S**)-2-[(*R**)-(*tert*-butoxycarbonylamino)-(*para*-methoxyphenyl)methyl]benzofuran-3-one-2-acetate and ethyl 8-methoxy-2-phenylbenzopyran-4-one-3-acetate, respectively (see Figure 1 in the Supporting Information).[14]

The mechanisms for the formation of benzofuran-3-ones **10**, **11** and flavones **12** from 3-(2-formylphenoxy)propenoates **1** and aryl(tosyl)methylcarbamates **8** are proposed. As delineated in Scheme 4, 3-(2-formylphenoxy)propenoates **1** catalyzed by a thiazole carbene undergo an intramolecular Stetter reaction to form benzofuran-3-one-2-acetates **2**. A consecutive base-catalyzed nucleophilic addition of benzofuran-3-one-2-acetates **2** to *N*-Boc-(aryl)imines **4**, that are generated *in situ* from aryl(tosyl)methylcarbamates **8** by the treatment with Cs_2CO_3, produces 2-[(aryl)(*tert*-butoxycarbonylamino)methyl]benzofuran-3-one-2-acetates **10** and **11**. When benzene was used as reaction medium, the highly selective formation of *anti*-diastereomers **10** rather than the *cis* products **11** was most probably because the formation of an *anti*-substituted C–C bond could reduce the repulsion between the large *tert*-butoxycarbonylamino and acetate groups. In the polar solvent like acetone, the solubility of Cs_2CO_3 is higher than that in benzene, leading to the coordination of the cesium cation with the nitrogen atom of *tert*-butoxycarbonylamino and the oxygen atom of acetate group, which increased the stability of the transition state in the formation of *cis*-diastereomers **11** (see structure **13** in Scheme 4). Therefore, the formation of *cis*-diastereomers **11** became favorable in acetone. In the presence of Cs_2CO_3 base catalyst, deprotonation of 2-[(aryl)(*tert*-butoxycarbonylamino)methyl]benzofuran-3-one-2-acetates **10** and **11** initiates the ring-expansion of tetrahydrofuran leading to the formation of phenoxides **14**. The intramolecular nucleophilic substitution (S_N2) of phenoxides to the BocNH group converts **14** to benzopyran-4-ones **15** (see Scheme 4, pathway A). Finally, a base-promoted 1,3-H shift furnishes the isomerization of **15** to flavones **12**. Theoretically, the nucleophilic attack of phenoxides to the vinyl carbon of **14** accompanied by allylic rearrangement and elimination of BocNH- group (a S_N2' nucleophilic substitution) could yield the benzopyran-4-ones **16** (see Scheme 4, pathway B), which would undergo isomerization to give benzopyran-4-ones **17** in the presence of a base. However, neither regioisomers **16** nor **17** of flavones **12** were detected in these reactions. To validate the proposed cascade catalytic mechanism, pure benzofuran-3-one-2-acetate **2a** and *N*-Boc-(phenyl)-imine **4a**, that were prepared respectively from the NHC-catalyzed intramolecular reaction of 3-(2-formylphenoxy)propenoate **1a** and base-catalyzed elimination of *tert*-butyl phenyl(tosyl)methylcarbamate **8a**, were used as substrates in the Cs_2CO_3-catalyzed reaction in boiling benzene. Indeed, the desired product **10a** did result from this reaction. Furthermore, the base-mediated transformation of benzofuran-3-ones **10** and **11** to flavones **12** was also proved by converting **10a** and **11a** to **12a** under the catalysis of Cs_2CO_3.



Scheme 4. Plausible reaction mechanism.

Conclusions

In summary, we have demonstrated a novel NHC/Brønsted base-catalyzed cascade reaction of 3-(2-formylphenoxy)propenoates with imines. Under the catalysis of a thiazole carbene (20 mol%) and Cs_2CO_3 (60 mol%) in refluxing benzene, the reaction of 3-(2-formylphenoxy)propenoates with *N*-Boc-(aryl)imines that were generated *in situ* from *tert*-butyl aryl(tosyl)methylcarbamates produced (2*S**)-2-[(*R**)-(aryl)(*tert*-butoxycarbonylamino)methyl]benzofuran-3-one-2-acetates in 65–88% yields with excellent diastereoselectivity. Upon increasing the loading of Cs_2CO_3 to 120 mol%, the same reaction afforded exclusively 2-arylbenzopyran-4-one-3-acetates (flavone derivatives) in 63–86% yields. This work has not only provided a simple and efficient strategy for the highly selective synthesis of 2,2-disubstituted benzofuran-3-ones and flavone derivatives from the same reactants simply by varying the loading of base catalyst, but has also demonstrated the unique application of NHC/Brønsted base cascade catalysis in organic synthesis.

Experimental Section

Commercially available chemical reagents were used without further purification. Anhydrous benzene was prepared by distillation over Na. Melting points are uncorrected. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) were recorded in the indicated solvents using a Bruker instrument. *J* values are reported in Hz. IR spectra were recorded using an AVATAR 360 FT-IR spectrometer. Mass spectra were recorded on a LCT Premier XE (ESI) or a micrOTOF-Q II (ESI) instrument. Column chromatography was performed using 200–300 mesh silica gel. The 3-(2-formylphenoxy)propenoates **1**,[15] *tert*-butyl aryl(tosyl)methylcarbamates **8**[16] and NHC precursor **9a**[17] were prepared according to literature methods.

General Procedure for the Selective Synthesis of (2*S**,1′*R**)-2-[(Aryl)(*tert*-butoxycarbonylamino)-methyl]benzofuran-3-one-2-acetates 10 from the NHC/Base-Catalyzed Reaction of 3-(2-Formylphenoxy)propenoates 1 with N-Boc-(aryl)imines

Under a nitrogen atmosphere, 3-(2-formylphenoxy)propenoates **1**[15] (0.5 mmol), *tert*-butyl aryl(tosyl)methylcarbamates **8**[16] (0.5 mmol), thiazolium salt **9a**[17] (0.1 mmol) and $CsCO_3$ (0.3 mmol) were mixed in dry benzene (15 mL). The resulting mixture was refluxed in benzene for 8–15 h until the reactants were consumed. The $CsCO_3$ was filtered and washed with dichloromethane (15×2 mL). The combined filtrate was concentrated under vacuum. The residue was chromatographyed on a silica gel column eluting with a mixture of petroleum ether and ethyl acetate (15:1–5:1) to give products **10** in 65–88% yields.

Ethyl (2*S,1′*R**)-2-[(*tert*-butoxycarbonylamino)-(phenyl)methyl]benzofuran-3-one-2-acetate (10a):** yield: 171 mg (80%); mp 113–114 °C; IR: ν = 3351, 1739, 1720,

1615 cm^{-1}; ^1H NMR (400 MHz, CD_3OD): $\delta = 7.63$ (t, $J = 8.2$ Hz, 1H), 7.57 (d, $J = 7.6$ Hz, 1H), 7.43 (dd, $J = 8.2$, 1.5 Hz, 2H), 7.24–7.32 (m, 3H), 7.13–7.19 (m, 2H), 7.08 (t, $J = 7.4$ Hz, 1H), 5.13 (d, $J = 10.0$ Hz, 1H), 3.78–3.89 (m, 2H), 3.12 (d, $J = 16.1$ Hz,1H), 2.60 (d, $J = 16.1$ Hz, 1H), 1.31 (s, 9H), 0.90 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, acetone-d_6): $\delta = 200.7$, 172.0, 167.7, 154.7, 137.6, 137.3, 128.6, 128.1, 128.0, 123.2, 123.0, 121.8, 113.2, 89.0, 78.7, 60.3, 60.0, 39.9, 27.5, 13.1; HR-MS (MALDI-TOF): $m/z = 464.1470$ $[M+K]^+$, calcd. for $C_{24}H_{27}NKO_6$: 464.1475.

Ethyl (2*S,1′*R**)-2-[(*tert*-butoxycarbonylamino)(*para*-methoxyphenyl)methyl]benzofuran-3-one-2-acetate (10b):** yield: 202 mg (83%); mp 122–123 °C; IR: $\nu = 3365$, 1731, 1694, 1612 cm^{-1}; ^1H NMR (400 MHz, acetone-d_6): $\delta = 7.49$ (t, $J = 7.6$ Hz, 1H), 7.41 (d, $J = 7.4$ Hz, 1H), 7.34 (d, $J = 8.2$ Hz, 2H), 6.95 (d, $J = 6.8$ Hz, 1H), 6.94 (t, $J = 6.4$ Hz, 1H), 6.73 (d, $J = 8.0$ Hz, 2H), 6.43 (d, $J = 9.3$ Hz, 1H), 4.99 (d, $J = 10.2$ Hz, 1H), 3.65–3.74 (m, 2H), 3.63 (s, 3H), 3.03 (d, $J = 16.2$ Hz, 1H), 2.53 (d, $J = 16.2$ Hz, 1H), 1.13 (s, 9H), 0.76 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, acetone-d_6): $\delta = 201.6$, 172.8, 168.6, 160.4, 155.5, 138.1, 130.6, 124.0, 123.9, 122.6, 114.3, 114.0, 90.2, 79.5, 61.1, 59.3, 55.5, 40.8, 28.4, 14.0; HR-MS (ESI-microTOF-QII): $m/z = 478.1851$ $[M+Na]^+$, calcd. for $C_{25}H_{29}NNaO_7$: 478.1836.

Ethyl (2*S,1′*R**)-2-[(*tert*-butoxycarbonylamino)(*para*-methylphenyl)methyl]benzofuran-3-one-2-acetate (10c):** yield: 174 mg (78%); mp 102–103 °C; IR: $\nu = 3383$, 1745, 1713, 1613 cm^{-1}; ^1H NMR (400 MHz, CD_3OD): $\delta = 7.64$ (t, $J = 7.5$ Hz, 1H), 7.57 (d, $J = 7.6$ Hz, 1H), 7.31 (d, $J = 8.0$ Hz, 2H), 7.07–7.16 (m, 5H), 5.07 (d, $J = 10.1$ Hz, 1H), 3.77–3.88 (m, 2H), 3.09 (d, $J = 16.1$ Hz,1H), 2.58 (d, $J = 16.1$ Hz, 1H), 2.30 (s, 3H), 1.30 (s, 9H), 0.90 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, acetone-d_6): $\delta = 200.7$, 172.0, 167.7, 154.6, 137.5, 137.2, 134.7, 128.7, 128.5, 123.2, 123.0, 121.7, 113.2, 89.1, 78.6, 60.2, 58.7, 39.9, 27.5, 20.2, 13.1; HR-MS (ESI-microTOF-QII): $m/z = 462.1881$ $[M+Na]^+$, calcd. for $C_{25}H_{29}NNaO_6$: 462.1887.

Ethyl (2*S,1′*R**)-2-[(*tert*-butoxycarbonylamino)(*para*-bromophenyl)methyl]benzofuran-3-one-2-acetate (10d):** yield: 183 mg (65%); mp 113–114 °C; IR: $\nu = 3360$, 1738, 1717, 1615 cm^{-1}; ^1H NMR (400 MHz, acetone-d_6): $\delta = 7.65$ (t, $J = 7.4$ Hz, 1H), 7.50–7.57 (m, 5H), 7.10 (t, $J = 7.2$ Hz, 1H), 7.09 (d, $J = 7.7$ Hz, 1H), 6.73 (d, $J = 9.9$ Hz, 1H), 5.19 (d, $J = 10.2$ Hz, 1H), 3.77–3.89 (m, 2H), 3.22 (d, $J = 16.3$ Hz,1H), 2.69 (d, $J = 16.3$ Hz, 1H), 1.28 (s, 9H), 0.91 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, acetone-d_6): $\delta = 200.4$, 171.9, 167.6, 154.7, 137.4, 137.1, 131.1, 130.7, 123.2, 122.8, 121.9, 121.6, 113.2, 88.7, 78.9, 60.3, 58.3, 39.8, 27.5, 13.1; HR-MS (ESI-microTOF-QII): $m/z = 526.0812$ $[M+Na]^+$, calcd. for $C_{24}H_{26}BrNNaO_6$: 526.0836.

Ethyl (2*S,1′*R**)-2-[(*tert*-butoxycarbonylamino)(*para*-fluorophenyl)methyl]benzofuran-3-one-2-acetate (10e):** yield: 189 mg (77%); mp 112–113 °C; IR: $\nu = 3355$, 1740, 1720, 1615 cm^{-1}; ^1H NMR (400 MHz, CD_3OD): $\delta = 7.65$ (t, $J = 8.3$ Hz, 1H), 7.57 (d, $J = 7.6$ Hz, 1H), 7.46 (d, $J = 8.7$ Hz, 1H), 7.45 (d, $J = 8.6$ Hz, 1H), 7.20 (d, $J = 9.8$ Hz, 1H), 7.14 (d, $J = 8.4$ Hz, 1H), 7.45 (t, $J = 7.4$ Hz, 1H), 6.99–7.03 (m, 2H), 5.14 (d, $J = 10.0$ Hz, 1H), 3.81–3.88 (m, 2H), 3.14 (d, $J = 16.1$ Hz,1H), 2.63 (d, $J = 16.1$ Hz, 1H), 1.32 (s, 9H), 0.91 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, acetone-d_6): $\delta =$ 200.6, 171.9, 167.7, 162.4 (d, $J = 243$ Hz), 154.7, 137.4, 133.8, 130.6 (d, $J = 8$ Hz), 123.2, 122.9, 121.8, 114.8 (d, $J = 21$ Hz), 113.2, 88.8, 78.8, 60.3, 58.2, 39.8, 27.5, 13.1; HR-MS (ESI-microTOF-QII): $m/z = 466.1630$ $[M+Na]^+$, calcd. for $C_{24}H_{26}FNNaO_6$: 466.1636.

Ethyl (2*S,1′*R**)-2-[(*tert*-butoxycarbonylamino)(*ortho*-methoxyphenyl)methyl]benzofuran-3-one-2-acetate (10f):** yield: 195 mg (84%); mp 135–136 °C; IR: $\nu = 3454$, 1731, 1713, 1609 cm^{-1}; ^1H NMR (400 MHz, CD_3OD): $\delta = 7.38$–7.43 (m, 2H), 7.24 (d, $J = 7.2$ Hz, 1H), 7.06 (t, $J = 7.5$ Hz, 1H), 6.86–6.90 (m, 2H), 6.70–6.80 (m, 2H), 5.49 (d, $J = 7.6$ Hz, 1H), 3.64 (s, 3H), 3.54–3.60 (m, 2H), 2.94 (d, $J = 16.4$ Hz,1H), 2.32 (d, $J = 15.9$ Hz, 1H), 1.07 (s, 9H), 0.65 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, acetone-d_6): $\delta = 201.0$, 172.6, 168.8, 157.9, 155.5, 137.8, 130.4, 130.1, 126.9, 124.2, 124.0, 122.5, 121.5, 114.0, 111.8, 90.4, 79.4, 61.1, 56.0, 39.9, 30.6, 28.4, 14.0; HR-MS (ESI-microTOF-QII): $m/z = 478.1855$ $[M+Na]^+$, calcd. for $C_{25}H_{29}NNaO_7$: 478.1836.

Ethyl (2*S,1′*R**)-2-[(*tert*-butoxycarbonylamino)(*meta*-methoxyphenyl)methyl]benzofuran-3-one-2-acetate (10g):** yield: 168 mg (74%); mp 109–110 °C; IR: $\nu = 3443$, 1747, 1723, 1606 cm^{-1}; ^1H NMR (400 MHz, CD_3OD): $\delta = 7.56$ (t, $J = 7.5$ Hz, 1H), 7.49 (d, $J = 7.6$ Hz, 1H), 7.13 (t, $J = 7.9$ Hz, 1H), 7.08 (d, $J = 8.4$ Hz, 1H), 7.01 (t, $J = 7.4$ Hz, 1H), 6.94 (s, 1H), 6.91 (d, $J = 7.6$ Hz, 1H), 6.75 (d, $J = 8.0$ Hz, 1H), 5.02 (d, $J = 10.4$ Hz, 1H), 3.73–3.81 (m, 2H), 3.71 (s, 3H), 3.03 (d, $J = 16.1$ Hz, 1H), 2.54 (d, $J = 16.1$ Hz, 1H), 1.23 (s, 9H), 0.82 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, acetone-d_6): $\delta = 200.6$, 172.0, 167.7, 159.7, 154.7, 139.2, 137.2, 129.1, 123.2, 123.0, 121.7, 120.8, 114.2, 113.6, 113.2, 89.1, 78.6, 60.3, 59.0, 54.7, 39.9, 27.5, 13.1; HR-MS (ESI-microTOF-QII): $m/z = 478.1839$ $[M+Na]^+$, calcd. for $C_{25}H_{29}NNaO_7$: 478.1836.

Ethyl (2*S,1′*R**)-2-[(*tert*-butoxycarbonylamino)-(phenyl)methyl]-5-methoxybenzofuran-3-one-2-acetate (10h):** yield: 197 mg (86%); mp 138–139 °C; IR: $\nu = 3448$, 3368, 1736, 1721, 1709 cm^{-1}; ^1H NMR (500 MHz, CD_3OD): $\delta = 7.32$ (d, $J = 6.6$ Hz, 2H), 7.18–7.21 (m, 3H), 7.14 (dd, $J = 9.0$, 2.7 Hz, 1H), 7.07 (d, $J = 9.9$ Hz, 1H), 6.96 (d, $J = 9.0$ Hz, 1H), 6.92 (d, $J = 9.0$ Hz, 1H), 5.00 (d, $J = 9.9$ Hz, 1H), 3.70–3.78 (m, 2H), 3.68 (s, 3H), 2.99 (d, $J = 16.0$ Hz,1H), 2.47 (d, $J = 16.0$ Hz, 1H), 1.22 (s, 9H), 0.82 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, acetone-d_6): $\delta = 201.7$, 168.6, 168.0, 155.9, 155.6, 138.6, 129.4, 128.9, 128.8, 127.3, 123.8, 114.9, 104.7, 90,4, 79.6, 61.1, 59,9, 56.3, 40.9, 28.4, 14.0; HR-MS (ESI-microTOF-QII): $m/z = 478.1840$ $[M+Na]^+$, calcd. for $C_{25}H_{29}NNaO_7$: 478.1836.

Ethyl (2*S,1′*R**)-2-[(*tert*-butoxycarbonylamino)-(phenyl)methyl]-7-methoxybenzofuran-3-one-2-acetate (10i):** yield: 201 mg (86%); mp 142–143 °C; IR: $\nu = 3455$, 1742, 1713 cm^{-1}; ^1H NMR (400 MHz, CD_3OD): $\delta = 7.32$ (d, $J = 6.7$ Hz, 2H), 7.14–7.20 (m, 3H), 7.11 (d, $J = 7.9$ Hz, 1H), 7.07 (d, $J = 10.6$ Hz, 1H), 7.01 (d, $J = 7.6$ Hz, 1H), 6.70 (t, $J = 7.8$ Hz, 1H), 5.02 (d, $J = 9.8$ Hz, 1H), 3.84 (s, 3H), 3.70–3.79 (m, 2H), 3.05 (d, $J = 16.2$ Hz,1H), 2.56 (d, $J = 16.2$ Hz, 1H), 1.22 (s, 9H), 0.81 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, acetone-d_6): $\delta = 201.7$, 168.6, 162.9, 155.6, 147.3, 138.3, 129.3, 128.9, 128.8, 125.1, 123.2, 120.0, 115.2, 90.0, 79.6, 61.2, 59.8, 56.7, 40.7, 28.4, 14.0; HR-MS (ESI-microTOF-QII): $m/z = 478.1835$ $[M+Na]^+$, calcd. for $C_{25}H_{29}NNaO_7$: 478.1836.

Ethyl (2*S,1′*R**)-2-[(*tert*-butoxycarbonylamino)-(phenyl)methyl]-5-methylbenzofuran-3-one-2-acetate (10j):** yield: 172 mg (76%); mp 114–115 °C; IR: v = 3416, 1737, 1718, 1698 cm^{-1}; ^1H NMR (400 MHz, CD_3OD): $\delta = 7.47$ (d,

J=8.4 Hz, 1H), 7.42 (d, J=6.8 Hz, 2H), 7.36 (s, 1H), 7.24–7.32 (m, 3H), 7.04 (d, J=8.4 Hz, 1H), 5.09 (d, J=6.2 Hz, 1H), 3.78–3.89 (m, 2H), 3.09 (d, J=16.0 Hz,1H), 2.58 (d, J=16.0 Hz, 1H), 2.33 (s, 3H), 1.31 (s, 9H), 0.92 (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, acetone-d_6): δ=200.7, 170.4, 167.7, 154.7, 138.4, 137.7, 131.3, 128.6, 128.1, 127.9, 122.8, 122.6, 112.8, 89.1, 78.7, 60.3, 58.9, 40.0, 27.6, 19.6, 13.2; HR-MS (ESI-microTOF-QII): m/z=462.1885 [M+Na]$^+$, calcd. for $C_{25}H_{29}NNaO_6$: 462.1887.

Ethyl (2*S,1′*R**)-2-[(*tert*-butoxycarbonylamino)-(phenyl)methyl]-6-methylbenzofuran-3-one-2-acetate (10k):** yield: 167 mg (75%); mp 102–103 °C; IR: ν=3333, 1738, 1719 cm^{-1}; ^{1}H NMR (400 MHz, acetone-d_6): δ=7.39 (d, J=7.3 Hz, 2H), 7.28 (d, J=7.8 Hz, 1H), 7.09–7.19 (m, 3H), 6.77 (d, J=7.5 Hz, 1H), 6.78 (s, 1H), 6.45 (d, J=9.4 Hz, 1H), 5.03 (d, J=10.2 Hz, 1H), 3.64–3.76 (m, 2H), 3.02 (d, J=16.1 Hz, 1H), 2.54 (d, J=16.2 Hz, 1H), 2.26 (s, 3H), 1.15 (s, 9H), 0.79 (t, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, acetone-d_6): δ=200.7, 173.3, 168.6, 155.6, 150.0, 138.6, 129.4, 128.9, 128.8, 124.1, 123.8, 121.5, 114.0, 90.0, 79.6, 61.1, 59.8, 40.7, 28.4, 22.3, 14.0; HR-MS (ESI-TOF): m/z=462.1894 [M+Na]$^+$, calcd. for $C_{25}H_{29}NNaO_6$: 462.1893.

Ethyl (2*S,1′*R**)-2-[(*tert*-butoxycarbonylamino)-(phenyl)methyl]-7-methylbenzofuran-3-one-2-acetate (10l)** yield: 195 mg (88%); mp 111–112 °C; IR: ν=3388, 3371, 1739, 1722, 1704 cm^{-1}; ^{1}H NMR (400 MHz, CD_3OD): δ=7.23 (d, J=6.9 Hz, 3H), 7.18 (d, J=7.6 Hz, 1H), 7.05–7.11 (m, 4H), 6.78 (t, J=7.5 Hz, 1H), 4.93 (d, J=10.0 Hz, 1H), 3.61–3.70 (m, 2H), 2.98 (d, J=16.0 Hz, 1H), 2.50 (d, J=15.9 Hz, 1H), 2.14 (s, 3H), 1.15 (s, 9H), 0.70 (t, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, acetone-d_6): δ=201.8, 171.5, 168.6, 155.6, 138.5, 129.3, 129.0, 128.83, 128.77, 124.0, 123.1, 122.6, 121.3, 89.6, 79.6, 61.1, 59.8, 40.8, 28.4, 14.3, 13.9; HR-MS (ESI-TOF): m/z=462.1894 [M+Na]$^+$, calcd. for $C_{25}H_{29}NNaO_6$: 462.1893.

Ethyl (2*S,1′*R**)-5-bromo-2-[(*tert*-butoxycarbonylamino)-(phenyl)methyl]benzofuran-3-one-2-acetate (10m):** yield: 202 mg (77%); mp 160–161 °C; IR: ν=3427, 1731, 1717, 1707 cm^{-1}; ^{1}H NMR (500 MHz, CD_3OD): δ=7.63 (dd, J=8.8, 2.0 Hz, 1H), 7.59 (s, 1H), 7.32 (d, J=6.5 Hz, 2H), 7.18–7.22 (m, 3H), 7.00 (d, J=8.7 Hz, 1H), 4.99 (s, 1H), 3.70–3.82 (m, 2H), 3.05 (d, J=16.5 Hz,1H), 2.49 (d, J=16.5 Hz, 1H), 1.28 (s, 9H), 0.85 (t, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, acetone-d_6): δ=200.3, 171.7, 168.6, 155.6, 140.4, 138.3, 129.5, 129.1, 129.0, 126.3, 125.9, 116.3, 114.5, 91.2, 79.7, 61.4, 59.9, 40.8, 28.4, 14.0; HR-MS (ESI-microTOF-QII): m/z=526.0825 [M+Na]$^+$, calcd. for $C_{24}H_{26}BrNNaO_6$: 526.0836.

Ethyl (2*S,1′*R**)-6-bromo-2-[(*tert*-butoxycarbonylamino)-(phenyl)methyl]benzofuran-3-one-2-acetate (10n):** yield: 222 mg (84%); mp 70–71 °C; IR: ν=3425, 1736, 1715, 1604 cm^{-1}; ^{1}H NMR (500 MHz, CD_3OD): δ=7.38 (d, J=8.1 Hz, 1H), 7.32 (d, J=6.2 Hz, 2H), 7.32 (s, 1H), 7.19–7.22 (m, 3H), 7.16 (d, J=8.0 Hz, 1H), 4.99 (s, 1H), 3.73–3.79 (m, 2H), 3.03 (d, J=16.5 Hz, 1H), 2.46 (d, J=16.5 Hz, 1H), 1.20 (s, 9H), 0.84 (t, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, CD_3OD): δ=202.0, 173.7, 169.6, 157.0, 138.2, 133.1, 129.7, 129.5, 129.4, 126.7, 125.5, 123.3, 118.0, 91.8, 80.9, 62.1, 60.4, 40.9, 28.6, 14.0; HR-MS (ESI-TOF): m/z=526.0845 [M+Na]$^+$, calcd. for $C_{24}H_{26}BrNNaO_6$: 526.0836.

Preparation of (2*R**,1′*R**)-2-[(Aryl)(*tert*-butoxycarbonylamino)methyl]benzofuran-3-one-2-Acetates 11 from the NHC/Base-Catalyzed Reaction of 3-(2-Formylphenoxy)propenoates 1 with N-Boc-(aryl)imines in Acetone

Under a nitrogen atmosphere, 3-(2-formylphenoxy)propenoates **1** (0.5 mmol), *tert*-butyl aryl(tosyl)methylcarbamates **8** (0.5 mmol), thiazolium salt **9a** (0.1 mmol) and $CsCO_3$ (0.3 mmol) were mixed in acetone (15 mL). The resulting mixture was refluxed in acetone for 10–13 h. The $CsCO_3$ was filtered and washed with dichloromethane (15×2 mL). The combined filtrate was concentrated under vacuum. The residue was chromatographyed on a silica gel column eluting with a mixture of petroleum ether and ethyl acetate (15:1–5:1) to give *cis*-diastereomers **11**; yield: 31–39% along with products **10**; yield:26–33% .

Ethyl (2*R,1′*R**)-2-[(*tert*-butoxycarbonylamino)-(phenyl)methyl]benzofuran-3-one-2-acetate (11a):** yield: 83 mg (39%); mp 116–117 °C; IR: ν=3296, 1741, 1723, 1670 cm^{-1}; ^{1}H NMR (500 MHz, acetone-d_6): δ=7.53 (t, J=7.9 Hz, 1H), 7.30 (d, J=7.6 Hz, 3H), 7.06–7.11 (m, 4H), 7.02 (d, J=8.4 Hz, 1H), 6.92 (t, J=7.4 Hz, 1H), 5.05 (d, J=10.2 Hz, 1H), 3.82–3.92 (m, 2H), 3.24 (s, 2H), 1.43 (s, 9H), 0.92 (t, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, acetone-d_6): δ=200.8, 172,7, 168.8, 156.4, 138.0, 137.2, 129.4, 128.6, 124.1, 123.8, 122.4, 113.3, 91.4, 79.7, 61.1, 59.6, 39.7, 28.5, 14.0; HR-MS (MALDI-TOF): m/z=464.1478 [M+K]$^+$, calcd. for $C_{24}H_{27}NKO_6$: 464.1475.

Ethyl (2*R,1′*R**)-2-[(*tert*-butoxycarbonylamino)(*para*-methoxyphenyl)methyl]benzofuran-3-one-2-acetate (11b):** yield: 75 mg (33%); mp 152–153 °C; IR: ν=3295, 1740, 1715, 1612 cm^{-1}; ^{1}H NMR (400 MHz, acetone-d_6): δ=7.41 (t, J=7.3 Hz, 1H), 7.17 (d, J=7.6 Hz, 1H), 7.06 (d, J=8.6 Hz, 2H), 6.88 (d, J=8.4 Hz, 1H), 6.84 (brs, 1H), 6.78 (t, J=7.4 Hz, 1H), 6.50 (d, J=8.7 Hz, 2H), 4.85 (d, J=10.2 Hz, 1H), 3.63–3.78 (m, 2H), 3.50 (s, 3H), 3.07 (s, 2H), 1.28 (s, 9H), 0.76 (t, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, acetone-d_6): δ=200.8, 172.7, 168.8, 160.1, 156.3, 138.0, 130.6, 129.2, 124.1, 123.8, 122.4, 114.0, 91.6, 79.7, 61.1, 59.0, 55.4, 39.7, 28.5, 14.0; HR-MS (ESI-TOF): m/z=478.1837 [M+Na]$^+$, calcd. for $C_{25}H_{29}NNaO_7$: 478.1842.

Ethyl (2*R,1′*R**)-2-[(*tert*-butoxycarbonylamino)(*para*-methylphenyl)methyl]benzofuran-3-one-2-acetate (11c):** yield: 86 mg (39%); mp 125–126 °C; IR: ν=3305, 1742, 1722, 1692 cm^{-1}; ^{1}H NMR (400 MHz, acetone-d_6): δ=7.39 (t, J=7.4 Hz, 1H), 7.17 (d, J=7.6 Hz, 1H), 7.02 (d, J=8.0 Hz, 2H), 6.88 (d, J=8.4 Hz, 1H), 6.86 (brs, 1H), 6.78 (t, J=7.5 Hz, 1H), 6.76 (d, J=7.9 Hz, 2H), 4.86 (d, J=10.2 Hz, 1H), 3.65–3.77 (m, 2H), 3.07 (s, 2H), 1.99 (s, 3H), 1.28 (s, 9H), 0.76 (t, J=7.1 Hz, 3H); ^{13}C NMR (100 MHz, acetone-d_6): δ=200.7, 172.7, 168.8, 156.3, 138.0, 137.9, 134.3, 129.3, 129.2, 124.2, 123.8, 122.3, 113.3, 91.4, 79.7, 61.1, 59.3, 39.7, 28.5, 20.9, 14.0; HR-MS (ESI-TOF): m/z=462.1888 [M+Na]$^+$, calcd. for $C_{25}H_{29}NNaO_6$: 462.1893.

Ethyl (2*R,1′*R**)-2-[(*tert*-butoxycarbonylamino)(*para*-bromophenyl)methyl]benzofuran-3-one-2-acetate (11d):** yield: 81 mg (32%); mp 113–114 °C; IR: ν=3285, 1742, 1721, 1689 cm^{-1}; ^{1}H NMR (400 MHz, acetone-d_6): δ=7.42 (t, J=7.7 Hz, 1H), 7.20 (d, J=7.2 Hz, 1H), 7.10–7.16 (m, 4H), 7.06 (d, J=8.7 Hz, 1H), 6.82 (t, J=7.2 Hz, 1H), 4.89 (d, J=9.9 Hz, 1H), 3.65–3.82 (m, 2H), 3.10 (s, 2H), 1.28 (s,

9H), 0.78 (t, $J=7.1$ Hz, 3H); ^{13}C NMR (100 MHz, acetone-d_6): $\delta=199.7$, 171.7, 167.8, 155.4, 137.4, 135.8, 130.8, 130.6, 123.3, 122.7, 121.7, 121.3, 112.5, 90.2, 79.0, 60.3, 58.2, 38.7, 27.6, 13.1; HR-MS (MALDI-TOF): $m/z=542.0587$ $[M+K]^+$, calcd. for $C_{24}H_{26}BrKNO_6$: 542.0581.

Ethyl (2*R,1′*R**)-2-[(*tert*-butoxycarbonylamino)-(phenyl)methyl]-5-methoxybenzofuran-3-one-2-acetate (11h):** yield: 71 mg (31%); mp 127–128 °C; IR: $\nu=3355$, 1739, 1713 cm^{-1}; ^{1}H NMR (400 MHz, acetone-d_6): $\delta=7.14$ (d, $J=6.5$ Hz, 2H), 6.90–6.99 (m, 5H), 6.80 (d, $J=9.0$ Hz, 1H), 6.59 (d, $J=2.3$ Hz, 1H), 4.88 (d, $J=10.1$ Hz, 1H), 3.67–3.80 (m, 2H), 3.56 (s, 3H), 3.06 (s, 2H), 1.28 (s, 9H), 0.80 (t, $J=7.1$ Hz, 3H); ^{13}C NMR (100 MHz, acetone-d_6): $\delta=200.8$, 168.8, 167.8, 156.3, 155.6, 137.3, 129.4, 128.6, 128.5, 127.1, 123.8, 114.2, 104.9, 92,0, 79.7, 61.1, 59,7, 56.1, 39.8, 28.5, 14.1; HR-MS (ESI-TOF): $m/z=478.1845$ $[M+Na]^+$, calcd. for $C_{25}H_{29}NNaO_7$: 478.1842.

Ethyl (2*R,1′*R**)-5-bromo-2-[(*tert*-butoxycarbonylamino)-(phenyl)methyl]benzofuran-3-one-2-acetate (11m):** yield: 88 mg (35%); mp 147–148 °C; IR: $\nu=3434$, 1736, 1721, 1702, 1608 cm^{-1}; ^{1}H NMR (400 MHz, acetone-d_6): $\delta=7.50$ (dd, $J=8.8$, 1.9 Hz, 1H), 7.28 (d, $J=1.8$ Hz, 1H), 7.15 (d, $J=5.9$ Hz, 2H), 6.97–6.98 (m, 4H), 6.88 (d, $J=8.7$ Hz, 1H), 4.91 (d, $J=10.0$ Hz, 1H), 3.70–3.82 (m, 2H), 3.13 (s, 2H), 1.27 (s, 9H), 0.84 (t, $J=7.1$ Hz, 3H); ^{13}C NMR (100 MHz, acetone-d_6): $\delta=199.6$, 171.5, 168.9, 156.4, 153.0, 140.4, 136.9, 129.4, 128.7, 126.4, 125.7, 115.5, 114.3, 92.5, 79.9, 61.4, 59.7, 39.7, 28.5, 14.1; HR-MS (ESI-TOF): $m/z=504.1017$ $[M+H]^+$, calcd. for $C_{24}H_{27}BrNO_6$: 504.1022.

General Procedure for the Selective Synthesis of 2-Arylbenzopyran-4-one-3-acetates 12 from the NHC/Base-Catalyzed Reaction of 3-(2-Formylphenoxy)-propenoates 1 with *N*-Boc(aryl)imines

Under a nitrogen atmosphere, 3-(2-formylphenoxy)propenoates **1** (0.5 mmol), *tert*-butyl aryl(tosyl)methylcarbamates **8** (0.5 mmol), thiazolium salt **9a** (0.1 mmol) and $CsCO_3$ (0.6 mmol) were mixed in dry benzene (15 mL). The resulting mixture was refluxed in benzene for 5–24 h until the reactants and intermediate products **10** were all consumed. The $CsCO_3$ was filtered and washed with dichloromethane (15×2 mL). The combined filtrate was concentrated under vacuum. The residue was chromatographyed on a silica gel column eluting with a mixture of petroleum ether and ethyl acetate (12:1–7:1) to give products **12**; yield: 65–88%.

Ethyl 2-phenylbenzopyran-4-one-3-acetate (12a): yield: 103 mg (67%); mp 102–103 °C [lit.[18] mp 102–102.5 °C].

Ethyl 2-(*para*-methoxyphenyl)benzopyran-4-one-3-acetate (12b): yield: 124 mg (73%); mp 123–124 °C [lit.[18] mp 124–125 °C].

Ethyl 2-(*para*-methylphenyl)benzopyran-4-one-3-acetate (12c): yield: 110 mg (68%); mp 109–110 °C; IR: $\nu=1731$, 1641 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=8.24$ (d, $J=7.7$ Hz, 1H), 7.67 (t, $J=7.6$ Hz, 1H), 7.55 (d, $J=7.8$ Hz, 2H), 7.47 (d, $J=8.4$ Hz, 1H), 7.40 (t, $J=7.5$ Hz, 1H), 7.32 (d, $J=7.8$ Hz, 2H), 4.19 (q, $J=7.1$ Hz, 2H), 3.56 (s, 2H), 2.44 (s, 3H), 1.27 (t, $J=7.1$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=177.9$, 171.3, 163.5, 156.3, 141.0, 133.6, 130.0, 129.4, 128.6, 125.9, 124.9, 122.7, 117.9, 115.8, 60.9, 32.2, 21.5, 14.2; HR-MS (ESI-TOF): $m/z=323.1292$ $[M+H]^+$, calcd. for $C_{20}H_{19}O_4$: 323.1283.

Ethyl 2-(*para*-bromophenyl)benzopyran-4-one-3-acetate (12d): yield: 123 mg (64%); mp 114–115 °C; IR: $\nu=1729$, 1629 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=8.24$ (dd, $J=7.8$, 0.8 Hz, 1H), 7.70 (dd, $J=8.4$, 1.3 Hz, 1H), 7.66 (d, $J=8.4$ Hz, 2H), 7.55 (d, $J=8.4$ Hz, 2H), 7.47 (d, $J=8.4$ Hz, 1H), 7.42 (t, $J=7.5$ Hz, 1H), 4.20 (q, $J=7.1$ Hz, 2H), 3.52 (s, 2H), 1.28 (t, $J=7.1$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=177.7$, 171.2, 162.2, 156.2, 133.9, 132.1, 131.7, 130.3, 126.0, 125.3, 125.2, 122.7, 118.0, 116.3, 61.2, 32.1, 14.2; HR-MS (ESI-TOF): $m/z=387.0233$ $[M+H]^+$, calcd. for $C_{19}H_{16}BrO_4$: 387.0232.

Ethyl 2-(*para*-fluorophenyl)benzopyran-4-one-3-acetate (12e): yield: 127 mg (78%); mp 135–136 °C; IR: $\nu=1713$, 1643 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=8.17$ (dd, $J=7.9$, 1.1 Hz, 1H), 7.59–7.64 (m, 3H), 7.40 (d, $J=8.4$ Hz, 1H), 7.35 (t, $J=7.7$ Hz, 1H), 7.14 (t, $J=8.6$ Hz, 2H), 4.13 (q, $J=7.1$ Hz, 2H), 3.46 (s, 2H), 1.21 (t, $J=7.1$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=177.7$, 171.2, 164.0 (d, $J=250$ Hz), 162.3, 156.2, 133.8, 130.9 (d, $J=9$ Hz), 128.9, 126.0, 125.1, 122.6, 117.9, 115.9 (d, $J=22$ Hz), 115.8, 61.1, 32.1, 14.2; HR-MS (ESI-TOF): $m/z=327.1022$ $[M+H]^+$, calcd. for $C_{19}H_{16}O_4F$: 327.1033.

Ethyl 2-(*ortho*-methoxyphenyl)benzopyran-4-one-3-acetate (12f): yield: 116 mg (69%); mp 113–114 °C; IR: $\nu=1730$, 1636 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=8.26$ (dd, $J=7.9$, 1.4 Hz, 1H), 7.65 (td, $J=8.6$, 1.5 Hz, 1H), 7.50 (td, $J=7.6$, 1.6 Hz, 1H), 7.47 (d, $J=7.6$ Hz, 1H), 7.44 (d, $J=8.6$ Hz, 1H), 7.40 (t, $J=7.3$ Hz, 1H), 7.08 (t, $J=7.5$ Hz, 1H), 7.03 (d, $J=8.4$ Hz, 1H), 4.10 (q, $J=7.1$ Hz, 2H), 3.82 (s, 3H), 3.39 (s, 2H), 1.21 (t, $J=7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=177.6$, 170.9, 161.3, 156.8, 156.6, 133.5, 132.1, 130.6, 126.0, 124.8, 123.0, 121.7, 120.7, 118.1, 117.8, 111.4, 60.7, 55.6, 31.9, 14.2; HR-MS (ESI-TOF): $m/z=339.1240$ $[M+H]^+$, calcd. for $C_{20}H_{19}O_5$: 339.1232.

Ethyl 2-(*meta*-methoxyphenyl)benzopyran-4-one-3-acetate (12g): yield: 132 mg (78%); mp 84–85 °C; IR: $\nu=1720$, 1646, 1625 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=8.24$ (d, $J=7.9$ Hz, 1H), 7.68 (t, $J=7.8$ Hz, 1H), 7.48 (d, $J=8.4$ Hz, 1H), 7.40–7.45 (m, 2H), 7.23 (d, $J=7.6$ Hz, 1H), 7.21 (s, 1H), 7.07 (d, $J=8.2$ Hz, 1H), 4.19 (q, $J=7.1$ Hz, 2H), 3.82 (s, 3H), 3.56 (s, 2H), 1.27 (t, $J=7.1$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=177.9$, 171.3, 163.2, 159.7, 156.3, 134.0, 133.7, 129.9, 126.0, 125.1, 122.7, 121.0, 118.0, 116.6, 116.1, 114.0, 61.0, 55.4, 32.2, 14.2; HR-MS (ESI-TOF): $m/z=339.1240$ $[M+H]^+$, calcd. for $C_{20}H_{19}O_5$: 339.1232.

Ethyl 6-methoxy-2-phenylbenzopyran-4-one-3-acetate (12h): yield: 126 mg (75%); mp 135–136 °C; IR: $\nu=1726$, 1630, 1612 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.57$–7.59 (m, 2H), 7.54 (d, $J=2.6$ Hz, 1H), 7.42–7.46 (m, 3H), 7.35 (d, $J=9.1$ Hz, 1H), 7.20 (dd, $J=9.7$, 2.7 Hz, 1H), 4.12 (q, $J=7.1$ Hz, 2H), 3.83 (s, 3H), 3.49 (s, 2H), 1.21 (t, $J=7.1$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=177.7$, 171.3, 163.1, 156.9, 151.2, 132.9, 130.6, 128.7, 123.9, 123.2, 119.4, 115.3, 104.9, 61.0, 55.9, 32.3, 14.2; HR-MS (ESI-TOF): $m/z=339.1218$ $[M+H]^+$, calcd. for $C_{20}H_{19}O_5$: 339.1232.

Ethyl 8-methoxy-2-phenylbenzopyran-4-one-3-acetate (12i): yield: 148 mg (88%); mp 153–154 °C; IR: $\nu=1725$, 1638 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.80$ (d, $J=7.8$ Hz, 1H), 7.68–7.69 (m, 2H), 7.52 (brs, 3H), 7.33 (d, $J=7.9$ Hz, 1H), 7.18 (d, $J=7.8$ Hz, 1H), 4.19 (q, $J=7.0$ Hz, 2H), 3.97 (s, 3H), 3.57 (s, 2H), 1.28 (t, $J=7.0$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=177.8$, 171.2, 163.0, 148.9,

146.8, 132.8, 130.6, 128.8, 128.7, 124.7, 123.7, 116.8, 116.0, 114.3, 61.0, 56.3, 32.2, 14.-2; HR-MS (ESI-TOF): m/z = 339.1228 $[M+H]^+$, calcd. for $C_{20}H_{19}O_5$: 339.1232.

Ethyl 6-methyl-2-phenylbenzopyran-4-one-3-acetate (12j): yield: 107 mg (63%); mp 105–106 °C; IR: ν = 1723, 1634, 1621 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.02 (s, 1H), 7.64–7.66 (m, 2H), 7.51–7.53 (m, 3H), 7.49 (dd, J = 8.4, 2.0 Hz, 1H), 7.37 (d, J = 8.6 Hz, 1H), 4.18 (q, J = 7.2 Hz, 2H), 3.55 (s, 2H), 2.47 (s, 3H), 1.27 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.9, 171.3, 163.2, 154.6, 135.0, 133.0, 130.6, 128.7, 128.68, 125.3, 122.4, 117.8, 115.9, 61.0, 32.2, 21.0, 14.2; HR-MS (TOF-ESI): m/z = 345.1093 $[M+Na]^+$, calcd. for $C_{20}H_{18}O_4Na$: 345.1103.

Ethyl 7-methyl-2-phenylbenzopyran-4-one-3-acetate (12k): yield: 111 mg (69%); mp 97–98 °C [lit.[18] mp 98–100 °C].

Ethyl 8-methyl-2-phenylbenzopyran-4-one-3-acetate (12l): yield: 103 mg (64%); mp 95–96 °C; IR: ν = 1719, 1633 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.08 (d, J = 7.4 Hz, 1H), 7.67–7.70 (m, 2H), 7.51–7.55 (m, 4H), 7.30 (t, J = 7.6 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 3.58 (s, 2H), 2.5 (s, 3H), 1.27 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.3, 171.3, 162.9, 154.8, 134.5, 133.0, 130.6, 128.72, 128.7, 127.4, 124.6, 123.5, 122.5, 115.8, 61.0, 32.2, 15.6, 14.2; HR-MS (ESI-TOF): m/z = 345.1108 $[M+Na]^+$, calcd. for $C_{20}H_{18}O_4Na$: 345.1103.

Ethyl 6-bromo-2-phenylbenzopyran-4-one-3-acetate (12m): yield: 163 mg (84%); mp 132–133 °C; IR: ν = 1721, 1640, 1619 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.36 (d, J = 2.4 Hz, 1H), 7.76 (dd, J = 8.9, 2.5 Hz, 1H), 7.63–7.65 (m, 2H), 7.52–7.55 (m, 3H), 7.38 (d, J = 8.9 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 3.54 (s, 2H), 1.27 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.6, 171.0, 163.5, 155.0, 136.7, 132.5, 130.9, 128.8, 128.7, 128.6, 124.0, 120.0, 118.4, 116.3, 61.1, 32.2, 14.2; HR-MS (ESI-TOF): m/z = 409.0060 $[M+Na]^+$, calcd. for $C_{19}H_{15}BrO_4Na$: 409.0051.

Ethyl 7-bromo-2-phenylbenzopyran-4-one-3-acetate (12n): yield: 155 mg (80%); mp 100–101 °C; IR: ν = 1726, 1642, 1625, 1603 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.10 (d, J = 8.5 Hz, 1H), 7.69 (d, J = 1.4 Hz, 1H), 7.73 (dd, J = 7.7, 1.4 Hz, 2H), 7.51–7.54 (m, 4H), 4.19 (q, J = 7.2 Hz, 2H), 3.54 (s, 2H), 1.27 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.2, 171.1, 163.3, 156.3, 132.4, 130.9, 128.8, 128.7, 128.6, 128.0, 127.4, 121.6, 121.1, 116.4, 61.1, 32.1, 14.2; HR-MS (MALDI-TOF): m/z = 424.9778 $[M+K]^+$, calcd. for $C_{19}H_{15}BrKO_4$: 424.9791.

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