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Phosphine-Catalyzed (4 + 1) Annulation of *o*-Hydroxyphenyl and *o*-Aminophenyl Ketones with Allylic Carbonates: Syntheses and Transformations of 3-Hydroxy-2,3-Disubstituted Dihydrobenzofurans and Indolines

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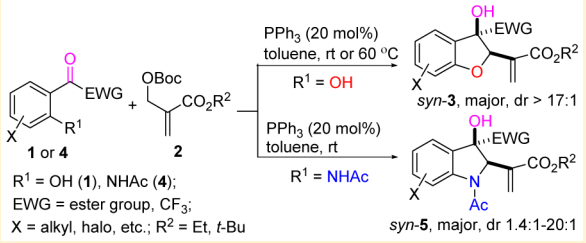
Supporting Information

ABSTRACT: A phosphine-catalyzed (4 + 1) annulation reaction of *o*-hydroxyphenyl and *o*-aminophenyl ketones with ester-modified allylic carbonates has been developed, providing a facile and efficient method to synthesize functionalized 2,3-disubstituted dihydrobenzofurans and indolines. Under mild conditions and in the catalysis of PPh_3 (20 mol %), the reactions of *o*-hydroxyphenyl or *o*-aminophenyl ketones readily furnish highly functionalized 3-hydroxy-2,3-disubstituted dihydrobenzofurans or 3-hydroxy-2,3-disubstituted indolines in 40−99% yields with generally high diastereoselectivity. To further expand the utility of this annulation reaction to the synthesis of functionalized benzofurans and indoles, the $CuSO_4$-promoted chemical transformations of the annulation products have also been studied.



INTRODUCTION

Both 2,3-disubstituted dihydrobenzofuran and indoline motifs represent common structural features embodied in a large number of bioactive natural products and pharmaceutically active molecules.[1] The structural diversity and biological importance have made these two families of heterocycles attractive to both synthetic organic chemists and medicinal chemists.[2] As specific members, 3-hydroxy-2,3-disubstituted dihydrobenzofuran and 3-hydroxy-2,3-disubstituted indoline substructures are found in many natural products possessing desired medicinal activities and pharmaceutical agents (Figure 1).[3] Added to this fact is that the presence of the hydroxyl functionality also further strengthens their versatility of 2,3-disubstituted dihydrobenzofurans and indolines in the syntheses of valuable benzofuran and indole derivatives.[4] Given their prevalence in biologically important molecules and versatility in organic synthesis, it is surprising that the development of efficient and general synthetic methods for such functionalized dihydrobenzofuran and indoline motifs from readily available materials has not attracted deserved attention from organic chemists until recently.[5] For example, Hu et al. developed a highly efficient and stereoselective synthesis of 3-hydroxy-2,3-multisubstituted indolines via a $Rh_2(OAc)_4$-catalyzed annulation reaction between diazo esters and 2-aminophenyl ketones.[5a] Through a cascade insertion−cyclization process of in situ generated arynes and α-amino ketones, Dai et al. realized another convergent synthetic method for 3-hydroxyl 2,3-disubstituted indolines.[5b] Based on hydroxyl-preinstalled substrates like 1-(2-(sulfonylamino)-phenyl)prop-2-yn-1-ols, a gold/silver-catalyzed intramolecular hydroamination strategy was unveiled by Chan et al., providing highly efficient and stereoselective access to 3-hydroxy-2-methyleneindolines.[4c,5c] On the other hand, for the assembly of the 3-hydroxy-2,3-disubstituted dihydrobenzofuran motif, however, there is no known and general method reported in the literature, except a couple of individual cases were revealed in the syntheses of complex molecules.[3b−d,6] Thus, developing new and efficient synthetic methods for both 3-hydroxy-2,3-disubstituted dihydrobenzofurans and indolines from readily available starting materials remains highly demanding.

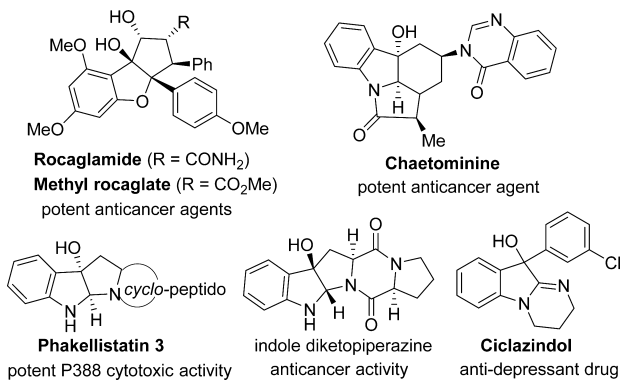


Figure 1. Representative bioactive molecules containing 3-hydroxy-2,3-disubstituted dihydrobenzofuran or indoline motifs.

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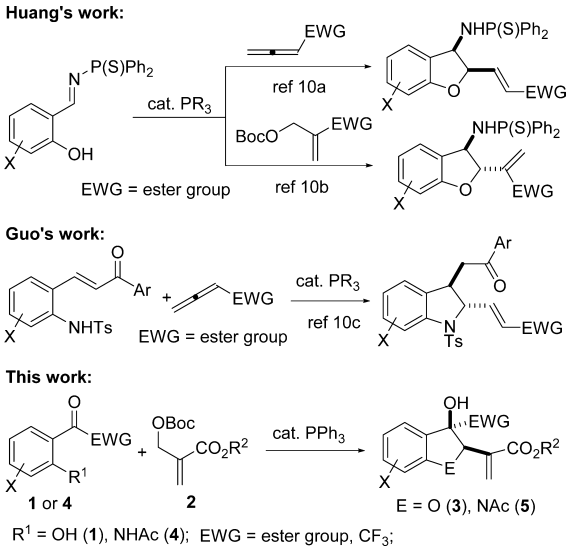
Over the past two decades, nucleophilic phosphine-catalyzed annulations have emerged as powerful tools for the syntheses of carbo- and heterocycles.[7] The majority of the annulation reactions are the so-called phosphine-catalyzed (3 + 2) and (4 + 1) annulations based on the prevailing substrates such as electron-deficient allenes, alkynes, and modified allylic carbonates (also called Morita−Baylis−Hillman carbonates), providing easy access to five-membered carbo- and heterocycles.[8,9] Recently, the phosphine catalysis protocol has also been validated in the assembly of dihydrobenzofuran and indoline motifs (Scheme 1).[10] Huang et al. first reported the phosphine-

Scheme 1. Syntheses of Dihydrobenzofurans and Indolines via Phosphine-Catalyzed (4 + 1) Annulations

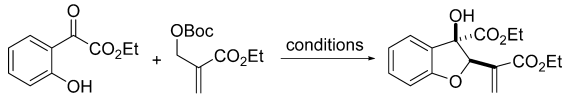


catalyzed (4 + 1) annulation reactions of salicyl *N*-thiophosphinyl imines with allenoates and allylic carbonates, respectively, leading to highly diastereoselective synthesis of 3-amino dihydrobenzofurans.[10a,b] Most recently, Guo et al. unveiled an effective and diastereoselective synthesis of 2,3-disubstituted indolines via the phosphine-catalyzed (4 + 1) annulation of 2-tosylaminochalcones with allenoates.[10c] In our continuous exploration on the reactivity of in situ generated allylic phosphorus ylides from tertiary phosphines and allylic carbonates or allenoates with carbonyl compounds,[11] we found that such formed allylic phosphorus ylides tend to undertake the phosphine stoichiometric Wittig olefinations with various aldehydes including salicylaldehydes,[12] although a couple of phosphine-catalyzed reactions have also been realized from aldehydes in our laboratory.[13] Under the same conditions, common ketones are usually inert in those olefinations.[12,14] Considering the reactivity bias of the allylic phosphorus ylides between aldehydes and ketones, recently we investigated the reactions of *o*-hydroxyphenyl and *o*-aminophenyl ketones with allylic carbonates under the mediation of tertiary phosphines in order to devise an organocatalytic phosphorus ylide-initiated synthesis of 3-hydroxy dihydrobenzofuran and 3-hydroxy indoline motifs.[5a] To our delight, under mild conditions, the reactions readily furnished the expected heterocycles, leading to a new and efficient synthetic method for 3-hydoxy-2,3-disubstituted dihydrobenzofurans and indolines (Scheme 1). Herein, we report the relevant results from such investigations.

RESULTS AND DISCUSSION

We commenced our study with the model reaction of ketone **1a** and allylic carbonate **2a** (Table 1). In the presence of PPh_3

Table 1. Survey on the Model Reaction Conditions[a]



1a 2a 3a

entry	solvent	catalyst	time (h)	yield[b] (%)	dr[c]
1	toluene	PPh_3	24	65[d]	>20:1
2	toluene	PPh_3	24	85	>20:1
3	toluene	PBu_3	72	complex	
4	toluene	$PPhMe_2$	72	complex	
5	toluene	$(p\text{-}ClC_6H_4)_3P$	24	80	15:1
6	toluene	$(p\text{-tolyl})_3P$	24	57	1.1:1
7	toluene	DABCO	72	none	
8	CH_2Cl_2	PPh_3	48	29	1:2
9	THF	PPh_3	48	26	1:5
10	CH_3CN	PPh_3	48	none	
11	toluene	PPh_3	10	91[e]	13:1

[a]Typical conditions: under a N_2 atmosphere and at room temperature, to a stirred solution of ketone **1a** (0.2 mmol) and catalyst (0.04 mmol) in a solvent (2.0 mL) was dropwise added **2a** (0.4 mmol) by means of a syringe. The resulting mixture was stirred at rt for specified hours. [b]Isolated yield as a diastereomeric mixture. [c]Referring to the ratio of *syn*-**3a** versus *anti*-**3a** and determined by ^1H NMR assay of the isolated product. [d]1.2 equiv of **2a** (0.24 mmol) was used. [e]The reaction was run at 60 °C.

(0.04 mmol, 20 mol %), the reaction of **1a** (0.2 mmol) and **2a** (0.24 mmol) in toluene (2.0 mL) was stirred at rt for 24 h, readily delivering the desired annulation product **3a** in 65% isolated yield and high diastereoselectivity (Table 1, entry 1). Adjusting the loading of **2a** to 2.0 equiv (0.4 mmol) resulted in a substantial yield increase while a high diastereoselectivity was retained (entry 2). More nucleophilic phosphines such as tributylphosphine and dimethylphenylphosphine proved to be ineligible for the annulation reaction since both of them only produced a complex mixture (entries 3 and 4). Other triarylphosphines like tris(*p*-chlorophenyl)phosphine and tris-(*p*-tolyl)phosphine were effective catalysts but afforded inferior yields and diastereoselectivity while compared to PPh_3 (entries 5 and 6). Nucleophilic Lewis base 1,4-diazabicyclo[2.2.2]octane (DABCO) was completely ineffective for the annulation reaction (entry 7). With PPh_3 chosen as the catalyst, other common solvents were surveyed. The reactions run in CH_2Cl_2 or THF only delivered the annulation product **3a** in low yields and poor diastereoselectivity (entries 8 and 9). Solvent acetonitrile was even detrimental to the reaction (entry 10). At an elevated temperature (60 °C), the PPh_3-catalyzed model reaction in toluene afforded a better yield (91%) of **3a** but a slightly lower diastereoselectivity while compared with the reaction run at rt (entries 2 and 11). Thus, the preferable conditions for the model reaction were established as follows: catalyst PPh_3 (20 mol %), solvent toluene, and at rt or 60 °C.

With the preferred conditions in hand, the substrate scope of the annulation reaction was investigated (Table 2). With allylic carbonate **2a** employed as a representative reactant, a series of differently substituted 2-hydroxyphenyl ketones **1** were examined. Ketones **1** bearing electron-donating or electron-withdrawing groups were all effective, giving the annulation

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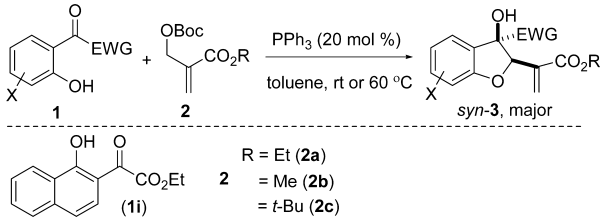
Table 2. Synthesis of Highly Functionalized Dihydrobenzofurans 3[a]



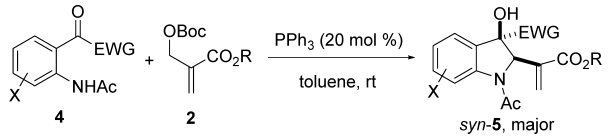
entry	X, EWG in **1**	**2**	time (h)	**3**, yield[b] (%)	dr[c]
1	H, CO_2Et (**1a**)	**2a**	24	**3a**, 85	>20:1
2	4-Cl, CO_2Et (**1b**)	**2a**	24	**3b**, 74	18:1
3	5-Me, CO_2Et (**1c**)	**2a**	24	**3c**, 63	>20:1
4	5-OMe, CO_2Et (**1d**)	**2a**	24	**3d**, 64	>20:1
5	3-Me, CO_2Et (**1e**)	**2a**	24	**3e**, 99	>20:1
6	5-*t*-Bu, CO_2Et (**1f**)	**2a**	24	**3f**, 68	>20:1
7	4-OMe, CO_2Et (**1g**)	**2a**	36	**3g**, 80	>20:1
8	4-Me, CO_2Et (**1h**)	**2a**	24	**3h**, 68	>20:1
9	**1i**	**2a**	48	**3i**, 80	>20:1
10	**1a**	**2b**	10	**3j**, 52	>20:1
11	**1a**	**2c**	4	**3k**, 95	>20:1
12	**1b**	**2c**	3	**3l**, 93	>20:1
13	**1c**	**2c**	3	**3m**, 97	>20:1
14	**1d**	**2c**	4	**3n**, 83	>20:1
15	**1e**	**2c**	3	**3o**, 98	>20:1
16	**1f**	**2c**	5	**3p**, 77	17:1
17	**1g**	**2c**	48	**3q**, 73	>20:1
18	**1h**	**2c**	3	**3r**, 74	>20:1
19	**1i**	**2c**	6	**3s**, 60	>20:1
20	H, CF_3 (**1j**)	**2c**	72	**3t**, 77	>20:1

[a]Typical conditions: under a N_2 atmosphere and at rt or 60 °C, to a stirred solution of ketone **1** (0.2 mmol) and PPh_3 (0.04 mmol) in toluene (2.0 mL) was dropwise added carbonate **2** (0.4 or 0.6 mmol) by means of a syringe. The resulting mixture was stirred at the same temperature until **1** was consumed (TLC monitored). For entries 1−10, the reactions were run at rt with **2** (0.4 mmol) used; for entries 11−20, the reactions were run at 60 °C with **2** (0.6 mmol) used. [b]Isolated yield based on **1**. [c]Determined by ^1H NMR assay of the isolated product and referring to *syn*-**3** versus *anti*-**3**.

products **3** in moderate to high yields and high diastereoselectivity (entries 1−8). The reaction of 4-methoxy-substituted ketone **1g** took a considerably longer time to complete (entry 7). 1-Hydroxy-2-naphthyl ketone **1i** also readily afforded the corresponding annulation product **3i** in 80% yield with high diastereoselectivity after an elongated time (entry 9). Methyl ester-modified allylic carbonate **2b** was also checked in the reaction with ketone **1a**, only delivering its annulation product **3j** in 52% yield (entry 10). Bulky *tert*-butyl ester-modified allylic carbonate **2c** proved to be superior in the annulation reaction. At an elevated temperature (60 °C), the annulation reactions of ketones **1a−i** with carbonate **2c** (3.0 equiv, 0.6 mmol) readily delivered the corresponding products **3k−s** in 60−98% yields with high diastereoselectivity (entries 11−19). The reactions completed within 6 h, except the reaction of 4-methoxy-substituted ketone **1g** took a much longer time again (entry 17). Trifluoromethyl ketone **1j** also proved to be effective in the annulation reaction with **2c**, producing **3t** in 77% yield and high diastereoselectivity after an elongated time (entry 20).

Under similar conditions, the scope of the (4 + 1) annulation reaction was further extended to *o*-aminophenyl ketones **4** that afforded highly functionalized indolines **5** (Table 3). In the

Table 3. Synthesis of Highly Functionalized Indolines 5[a]



entry	X, EWG in **4**	**2**	time (h)	**5**, yield[b] (%)	dr[c]
1	H, CO_2Et (**4a**)	**2a**	48	*syn*-**5a**, 40[d]	3:1
2	H, CO_2Et (**4a**)	**2c**	24	*syn*-**5b**, 70[d]	5:1
3	H, CO_2Me (**4b**)	**2c**	72	*syn*-**5c**, 42[d]	14:1
4	H, CO_2Pr-*i* (**4c**)	**2c**	48	*syn*-**5d**, 78[d]	6:1
5	H, CO_2Bu-*t* (**4d**)	**2c**	48	*syn*-**5e**, 82[d]	7:1
6	4-Br, CO_2Pr-*i* (**4e**)	**2c**	48	**5f**, 98	4:1
7	5-Br, CO_2Pr-*i* (**4f**)	**2c**	48	*syn*-**5g**, 90[d]	9:1
8	5-Me, CO_2Pr-*i* (**4g**)	**2c**	72	**5h**, 99	2.6:1
9	5-NO_2, CO_2Pr-*i* (**4h**)	**2c**	48	**5i**, 75	20:1
10	5-F, CO_2Pr-*i* (**4i**)	**2c**	48	**5j**, 84	2:1
11	5-Cl, CO_2Pr-*i* (**4j**)	**2c**	48	**5k**, 74	2:1
12	5-OMe, CO_2Pr-*i* (**4k**)	**2c**	48	**5l**, 99	1.4:1

[a]Typical conditions: under a N_2 atmosphere and at rt, to a stirred solution of ketone **4** (0.3 mmol) and PPh_3 (0.06 mmol) in toluene (3.0 mL) was dropwise added carbonate **2** (0.9 mmol) by means of a syringe. The resulting mixture was stirred at rt until **4** was consumed (TLC monitored). [b]Isolated yield based on **4**. [c]Determined by ^1H NMR assay of the crude product and referring to *syn*-**5** versus *anti*-**5**. [d]Pure minor product *anti*-**5** was not obtained.

presence of PPh_3 (20 mol %) and at rt, the reaction of *o*-aminophenyl ketones **4** (0.3 mmol) and allylic carbonates **2** (0.9 mmol) readily gave the corresponding annulation product **5** as a mixture of separable diastereomers after 24−72 h. The reaction of ketone **4a** bearing an ethyl ester group with allylic carbonate **2a** delivered the corresponding product **5a** in a moderate yield with a 3:1 diastereomer ratio (Table 3, entry 1). With bulky *tert*-butyl ester-modified allylic carbonate **2c** used instead of **2a**, the reaction delivered the annulation product **5b** in a better yield with an improved dr value (entry 2). With carbonate **2c** employed as a reactant, a series of differently substituted ketones **4** were further explored. Ketones **4b−d** bearing different ester groups were first examined (entries 3−5). Ketone **4b** with a methyl ester group smoothly gave its normal annulation product **5c** in modest yield but in good diastereoselectivity (entry 3). Ketones **4c** and **4d** both bearing bulky ester groups all delivered their annulation products **5d** and **5e** in good yields and moderate diastereoselectivity (entries 4 and 5). Other available ketones **4e−k** bearing electron-donating or electron-withdrawing substituents at the benzene ring all uneventfully afforded their normal annulation products **5** in good to excellent yields with varied diastereoselectivities (entries 6−12). Thus, the phosphine-catalyzed (4 + 1) annulation reaction of *o*-hydroxyphenyl and *o*-aminophenyl ketones (**1** and **4**) with modified allylic carbonates **2** constitutes a new and facile synthetic method for important 3-hydroxy-2,3-disubstituted dihydrobenzofurans and 3-hydroxy-2,3-disubstituted indolines.

On the basis of previous reports[9d,10,12b] and our results obtained in this study, a rationale about formation of the (4 + 1) annulation products **3** and **5** is depicted in Scheme 2 as exemplified by formation of **3a**. The reaction sequence is presumably initiated with in situ generation of allylic phosphorus ylide **A** from PPh_3 and carbonate **2a**.[15] Ylide **A** then undergoes a sterically favored γ-addition to ketone **1a**, generating intermediate **B**. Through a proton transfer and a

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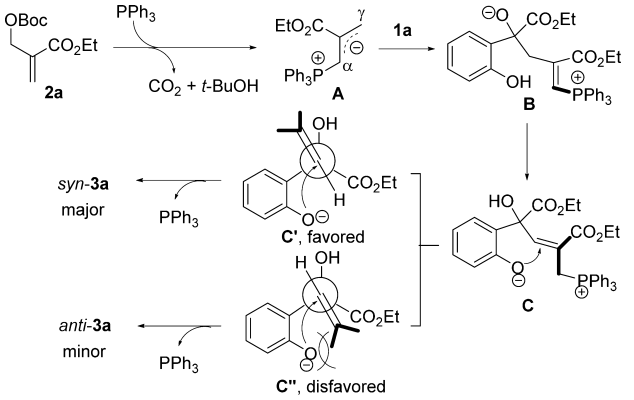
Scheme 2. Rationale for Formation of 3

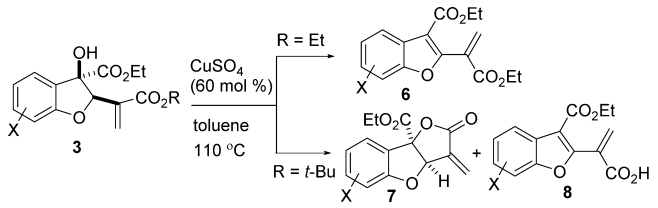


double-bond migration,[16] intermediate **B** converts to intermediate **C**, which finally engages in a ring closure via an oxo-Michael addition−elimination process (also called an intramolecular allylic substitution) to yield the annulation product like **3a** and regenerate the catalyst PPh_3. In the ring-closure step, intermediate **C** adopts a favored conformation **C′** to produce the major isomer *syn*-**3a**; alternatively, a disfavored conformation **C″** leads to the minor isomer *anti*-**3a** (Scheme 2). Formation of indolines **5** is supposed to be through the same sequence.

To further expand the utility of this annulation reaction to the synthesis of functionalized benzofurans and indoles, the $CuSO_4$-promoted transformations of the annulation products **3** and **5** were investigated. It is reported that silica-supported $CuSO_4$ (20%, w/w) is an effective promoter for the intramolecular dehydration of aliphatic alcohols to generate alkenes under mild conditions.[17] Under similar conditions, an intramolecular dehydration of 3-hydroxy dihydrobenzofurans **3** was first examined (Table 4). In the presence of silica-supported $CuSO_4$ (60 mol %) and heated at 110 °C for 2−5 h, a series of 3-hydroxy dihydrobenzofurans **3a−i**, prepared from ethyl ester-modified allylic carbonate **2a**, readily afforded the expected dehydration products benzofurans **6a−i** in moderate to excellent yields (Table 4, entries 1−9). In contrast, a series of 3-hydroxy dihydrobenzofurans **3k,l,n−r**, which were prepared from *tert*-butyl ester-modified allylic carbonate **2c**, failed to deliver any expected dehydration products while treated under the same conditions (entries 10−16). Compounds **3k** and **3l** both exclusively gave their corresponding tricyclic lactones **7a** and **7b** as a single diastereomer in 99% and 73% yields, respectively (entries 10 and 11). Presumably, the formation of lactones **7** is through an intramolecular trans-esterification process. Other 3-hydroxy dihydrobenzofurans **3n−r**, however, only furnished free carboxylic acids **8a−e** as a major product in modest to good yields (entries 12−16). In the case of **3o**, lactone **7c** was also collected as a minor product in 31% yield (entry 13).

Under the same conditions for dehydration, the isolated *syn*-isomers of 3-hydroxy indolines **5** were also examined (Scheme 3). Indoline *syn*-**5a** bearing ethyl ester groups kept intact after being treated for a prolonged time (24 h). A selection of 3-hydroxy indolines *syn*-**5d,f−h** bearing a *tert*-butyl ester group all produced tricyclic lactones **9** in 42−95% yields as an inseparable mixture of diastereomers with varied dr values of 1.2:1−7:1 after being treated for 2−6 h.[18] In cases of *syn*-**5f−h**, functionalized indoles **10a−c** bearing a carboxylic acid group were also collected as a minor product in 26, 16, and 29% yields, respectively (Scheme 3). On the basis of the above results, we assume that formation of the free carboxylic acids **8**

Table 4. $CuSO_4$-Promoted Transformations of 3-Hydroxy Dihydrobenzofurans 3[a]



entry	X, R in **3**	time (h)	**6**, yield[b] (%)	**7**, yield[b] (%)	**8**, yield[b] (%)
1	H, Et (**3a**)	4	**6a**, 94		
2	6-Cl, Et (**3b**)	5	**6b**, 65		
3	5-Me, Et (**3c**)	4	**6c**, 52		
4	5-OMe, Et (**3d**)	4	**6d**, 71		
5	7-Me, Et (**3e**)	4	**6e**, 99		
6	5-*t*-Bu, Et (**3f**)	3	**6f**, 98		
7	6-OMe, Et (**3g**)	2	**6g**, 99		
8	6-Me, Et (**3h**)	2	**6h**, 99		
9	benzo, Et (**3i**)	3	**6i**, 88		
10	H, *t*-Bu (**3k**)	6		**7a**, 99	
11	6-Cl, *t*-Bu (**3l**)	4		**7b**, 73	
12	5-OMe, *t*-Bu (**3n**)	4			**8a**, 40
13	7-Me, *t*-Bu (**3o**)	4		**7c**, 31	**8b**, 65
14	5-*t*-Bu, *t*-Bu (**3p**)	4			**8c**, 63
15	6-OMe, *t*-Bu (**3q**)	4			**8d**, 50
16	6-Me, *t*-Bu (**3r**)	4			**8e**, 87

[a]Typical conditions: a stirred suspension of 3-hydroxy dihydrobenzofuran **3** (0.15 mmol) and 20% silica-supported $CuSO_4$ (0.09 mmol, 60 mol %) in toluene (1.5 mL) was heated at 110 °C for the specified time. [b]Isolated yield based on **3**.

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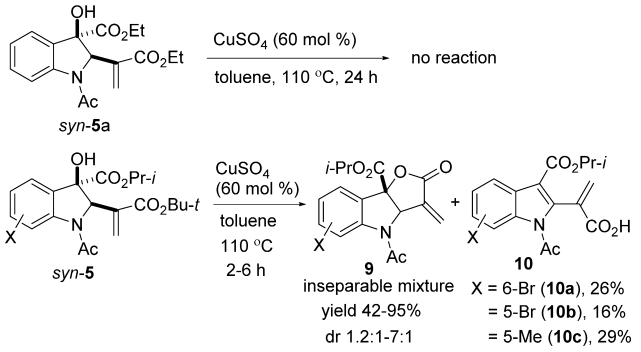
Scheme 3. $CuSO_4$-Promoted Transformations of 3-Hydroxy Indolines 5



and **10** is through a ring-opening elimination step from their corresponding tricyclic lactone precursors.

All new compounds (**3**, **5**−**8**, **10**) obtained in this study have been identified by NMR (^{1}H and ^{13}C) and HRMS. The structures of representative compounds **3k** and *anti*-**5j** have been further confirmed by X-ray single-crystal diffraction analysis.

■ CONCLUSION

In summary, we have successfully developed a phosphine-catalyzed (4 + 1) annulation reaction of *o*-hydroxyphenyl and *o*-aminophenyl ketones with modified allylic carbonates that constitutes a new and facile synthetic method for important 3-hydroxy-2,3-disubstituted dihydrobenzofuran and 3-hydroxy-2,3-disubstituted indoline motifs. Mechanistically, it represents an organocatalytic and phosphorus ylide-initiated synthetic strategy, which is definitely complementary to the transition-metal-catalyzed methodology in the syntheses of 3-hydroxy-2,3-disubstituted indolines.[5] It also represents the first general synthesis of 3-hydroxy-2,3-disubstituted dihydrobenzofurans with a good substrate scope and satisfactory yields. The $CuSO_4$-promoted chemical transformations have clearly demonstrated the potential of the annulation products to be easily converted to functionalized benzofurans and indoles. We accordingly anticipate that this annulation reaction will have a broad use in the syntheses of benzofuran and indole derivatives.

■ EXPERIMENT SECTION

Solvents were purified prior to use according to conventional procedures. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ with tetramethylsilane (TMS) as the internal standard. HRMS spectra were acquired in the ESI mode (positive ion) with the mass analyzer of TOF used. Column chromatography was performed on silica gel (200−300 mesh) using a mixture of petroleum ether/ethyl acetate as eluent. *o*-Hydroxyphenyl ketones **1** and *o*-aminophenyl ketones **4** were prepared according to the reported methods.[19] Silica-supported $CuSO_4$ was prepared according to a reported procedure.[17,20]

General Procedure for Synthesis of 3-Hydroxy Dihydrobenzofurans 3 (Table 2). Under a N_2 atmosphere and at rt or 60 °C, to a stirred solution of ketone **1** (0.2 mmol) and PPh_3 (0.04 mmol) in toluene (2.0 mL) was dropwise added carbonate **2** (0.4 or 0.6 mmol) by means of a syringe. The resulting mixture was stirred at the same temperature for specified hours until **1** was consumed, as monitored by TLC. The solvent was removed on a rotary evaporator under reduced pressure, and the residue was subjected to column chromatographic isolation on silica gel (gradient elution, petroleum ether (bp 60−90 °C)/ethyl acetate 15:1−5:1) to give product **3**. The diastereomeric ratio of *syn*-**3** versus *anti*-**3** was measured by integrating the intensity of the diagnostic methine proton signal (relative to that of *syn*-isomer, the signal of *anti*-isomer shifts about 0.3 ppm upfield).

*Ethyl 2-(3-Ethoxy-3-oxoprop-1-en-2-yl)-3-hydroxy-2,3-dihydrobenzofuran-3-carboxylate (**3a**).* Following the general procedure, *o*-hydroxyphenyl ketone **1a** (39 mg, 0.2 mmol) and allylic carbonate **2a** (92 mg, 0.4 mmol) were reacted at rt for 24 h to give product **3a** (52 mg, 85% yield, >20:1 dr) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34−7.25 (m, 1H), 7.19−7.15 (m, 1H), 7.00−6.90 (m, 2H), 6.48 (s, 1H), 6.14 (s, 1H), 5.82 (s, 1H), 4.45−4.18 (m, 4H), 3.98 (s, 1H), 1.35−1.23 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 165.4, 159.2, 134.8, 131.1, 127.9, 126.2, 123.8, 121.5, 110.5, 86.3, 81.3, 63.1, 61.0, 14.0; HRMS-ESI [M + Na]$^+$ Calcd for $C_{16}H_{18}NaO_6$ 329.0996, found 329.1000.

*Ethyl 6-Chloro-2-(3-ethoxy-3-oxoprop-1-en-2-yl)-3-hydroxy-2,3-dihydrobenzofuran-3-carboxylate (**3b**).* Following the general procedure, *o*-hydroxyphenyl ketone **1b** (46 mg, 0.2 mmol) and allylic carbonate **2a** (92 mg, 0.4 mmol) were reacted at rt for 24 h to give product **3b** (51 mg, 74% yield, 18:1 dr) as a slightly yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, J = 8.1 Hz, 1H), 6.97 (d, J = 1.8 Hz, 1H), 6.93 (dd, J = 8.1, 1.8 Hz, 1H), 6.50−6.46 (m, 1H), 6.10 (dd, J = 1.6, 1.1 Hz, 1H), 5.83 (t, J = 1.6 Hz, 1H), 4.40−4.20 (m, 4H), 4.00 (s, 1H), 1.35−1.25 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 165.3, 160.0, 136.6, 134.4, 126.7, 126.4, 124.6, 122.0, 111.3, 87.2, 80. 8, 63.3, 61.1, 14.0; HRMS-ESI [M + Na]$^+$ Calcd for $C_{16}H_{17}ClNaO_6$ 363.0606, found 363.0607.

*Ethyl 2-(3-Ethoxy-3-oxoprop-1-en-2-yl)-3-hydroxy-5-methyl-2,3-dihydrobenzofuran-3-carboxylate (**3c**).* Following the general procedure, *o*-hydroxyphenyl ketone **1c** (42 mg, 0.2 mmol) and allylic carbonate **2a** (92 mg, 0.4 mmol) were reacted at rt for 24 h to give product **3c** (41 mg, 63% yield, >20:1 dr) as a slightly yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, J = 8.2 Hz, 1H), 6.96 (s, 1H), 6.84 (d, J = 8.2 Hz, 1H), 6.46 (s, 1H), 6.12 (s, 1H), 5.80 (s, 1H), 4.45−4.20 (m, 4H), 3.93 (s, 1H), 2.28 (s, 3H), 1.30 (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 165.5, 157.2, 135.0, 131.7, 131.0, 127.7, 126.2, 124.0, 110.0, 86.4, 81.5, 63.0, 61.0, 20.7, 14.0; HRMS-ESI [M + Na]$^+$ Calcd for $C_{17}H_{20}NaO_6$ 343.1152, found 343.1157.

*Ethyl 2-(3-Ethoxy-3-oxoprop-1-en-2-yl)-3-hydroxy-5-methoxy-2,3-dihydrobenzofuran-3-carboxylate (**3d**).* Following the general procedure, *o*-hydroxyphenyl ketone **1d** (45 mg, 0.2 mmol) and allylic carbonate **2a** (92 mg, 0.4 mmol) were reacted at rt for 24 h to give product **3d** (43 mg, 64% yield, >20:1 dr) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89−6.84 (m, 2H), 6.69 (s, 1H), 6.47 (s, 1H), 6.13 (s, 1H), 5.81 (s, 1H), 4.44−4.29 (m, 2H), 4.23 (q, J = 7.0 Hz, 2H), 3.96 (s, 1H), 3.74 (s, 3H), 1.32−1.28 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 165.5, 154.8, 153.4, 134.9, 128.2, 126.3, 117.7, 110.9, 108.3, 86.6, 81.8, 63.1, 61.0, 56.0, 14.0; HRMS-ESI [M + Na]$^+$ Calcd for $C_{17}H_{20}NaO_7$ 359.1101, found 359.1106.

*Ethyl 2-(3-Ethoxy-3-oxoprop-1-en-2-yl)-3-hydroxy-7-methyl-2,3-dihydrobenzofuran-3-carboxylate (**3e**).* Following the general procedure, *o*-hydroxyphenyl ketone **1e** (42 mg, 0.2 mmol) and allylic carbonate **2a** (92 mg, 0.4 mmol) were reacted at rt for 24 h to give product **3e** (64 mg, 99% yield, >20:1 dr) as a slightly yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, J = 7.5 Hz, 1H), 6.99 (d, J = 7.5 Hz, 1H), 6.85 (t, J = 7.5 Hz, 1H), 6.48 (s, 1H), 6.15 (s, 1H), 5.81 (s, 1H), 4.45−4.27 (m, 2H), 4.26−4.20 (m, 2H), 3.92 (s, 1H), 2.30 (s, 3H), 1.35−1.25 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 165.5, 157.7, 135.0, 132.1, 127.2, 126.1, 121.5, 121.0, 120.8, 86.0, 81.8, 63.0, 61.0, 15.1, 14.1, 14.1; HRMS-ESI [M + Na]$^+$ Calcd for $C_{17}H_{20}NaO_6$ 343.1152, found 343.1158.

*Ethyl 5-tert-Butyl-2-(3-ethoxy-3-oxoprop-1-en-2-yl)-3-hydroxy-2,3-dihydrobenzofuran-3-carboxylate (**3f**).* Following the general procedure, *o*-hydroxyphenyl ketone **1f** (50 mg, 0.2 mmol) and allylic carbonate **2a** (92 mg, 0.4 mmol) were reacted at rt for 24 h to give product **3f** (49 mg, 68% yield, >20:1 dr) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 8.5 Hz, 1H), 7.16 (s, 1H), 6.88 (d, J = 8.5 Hz, 1H), 6.47 (s, 1H), 6.13 (s, 1H), 5.82 (s, 1H), 4.43−4.32 (m, 2H), 4.23 (q, J = 7.1 Hz, 2H), 3.93 (s, 1H), 1.38−1.19 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 165.5, 157.1, 144.8, 135.0, 128.3, 127.4, 126.2, 120.3, 109.7, 86.5, 81.6, 62.9, 61.0, 34.4, 31.6, 14.0;

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HRMS-ESI [M + Na]$^+$ Calcd for $C_{20}H_{30}NO_6$ 380.2068, found 380.2071.

*Ethyl 2-(3-Ethoxy-3-oxoprop-1-en-2-yl)-3-hydroxy-6-methoxy-2,3-dihydrobenzofuran-3-carboxylate (**3g**).* Following the general procedure, *o*-hydroxyphenyl ketone **1g** (45 mg, 0.2 mmol) and allylic carbonate **2a** (92 mg, 0.4 mmol) were reacted at rt for 36 h to give product **3g** (54 mg, 80% yield, >20:1 dr) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (d, J = 9.1 Hz, 1H), 6.52−6.48 (m, 2H), 6.46 (s, 1H), 6.11 (s, 1H), 5.84 (s, 1H), 4.42−4.28 (m, 2H), 4.26−4.19 (m, 2H), 3.79 (s, 3H), 1.29 (t, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 165.4, 162.6, 160.7, 135.0, 126.1, 124.2, 120.1, 108.2, 96.1, 87.2, 81.1, 63.0, 61.0, 55.5, 14.1, 14.0; HRMS-ESI [M + Na]$^+$ Calcd for $C_{17}H_{20}NaO_7$ 359.1101, found 359.1107.

*Ethyl 2-(3-Ethoxy-3-oxoprop-1-en-2-yl)-3-hydroxy-6-methyl-2,3-dihydrobenzofuran-3-carboxylate (**3h**).* Following the general procedure, *o*-hydroxyphenyl ketone **1h** (42 mg, 0.2 mmol) and allylic carbonate **2a** (92 mg, 0.4 mmol) were reacted at rt for 24 h to give product **3h** (44 mg, 68% yield, >20:1 dr) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07−7.02 (m, 1H), 6.80−6.72 (m, 2H), 6.46 (s, 1H), 6.12 (s, 1H), 5.81 (s, 1H), 4.44−4.28 (m, 2H), 4.26−4.19 (m, 2H), 3.91 (s, 1H), 2.34 (s, 3H), 1.35−1.24 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 165.4, 159.5, 141.7, 135.0, 126.1, 125.1, 123.4, 122.5, 111.0, 86.5, 81.2, 63.0, 61.0, 21.7, 14.0; HRMS-ESI [M + Na]$^+$ Calcd for $C_{17}H_{20}NaO_6$ 343.1152, found 343.1157.

*Ethyl 2-(3-Ethoxy-3-oxoprop-1-en-2-yl)-3-hydroxy-2,3-dihydronaphtho[1,2-b]furan-3-carboxylate (**3i**).* Following the general procedure, 1-hydroxy-2-naphthyl ketone **1i** (49 mg, 0.2 mmol) and allylic carbonate **2a** (92 mg, 0.4 mmol) were reacted at rt for 48 h to give product **3i** (57 mg, 80% yield, >20:1 dr) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15−8.07 (m, 1H), 7.86−7.79 (m, 1H), 7.57−7.47 (m, 2H), 7.46−7.41 (m, 1H), 7.23 (d, J = 8.8 Hz, 1H), 6.52 (s, 1H), 6.24 (s, 1H), 6.03 (s, 1H), 4.46−4.20 (m, 4H), 4.06 (s, 1H), 1.36−1.23 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 165.5, 155.7, 135.4, 134.9, 128.0, 127.1, 126.2, 125.8, 121.8, 121.7, 120.8, 120.7, 120.3, 87.1, 82.4, 63.1, 61.0, 14.1; HRMS-ESI [M + Na]$^+$ Calcd for $C_{20}H_{20}NaO_6$ 379.1152, found 379.1152.

*Ethyl 3-Hydroxy-2-(3-methoxy-3-oxoprop-1-en-2-yl)-2,3-dihydrobenzofuran-3-carboxylate (**3j**).* Following the general procedure, *o*-hydroxyphenyl ketone **1a** (39 mg, 0.2 mmol) and allylic carbonate **2b** (87 mg, 0.4 mmol) were reacted at rt for 10 h to give product **3j** (31 mg, 52% yield, >20:1 dr) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34−7.28 (m, 1H), 7.17 (d, J = 7.4 Hz, 1H), 7.00−6.91 (m, 2H), 6.49 (s, 1H), 6.17 (s, 1H), 5.81 (s, 1H), 4.45−4.30 (m, 2H), 3.97 (s, 1H), 3.77 (s, 3H), 1.30 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 165.8, 159.2, 134.4, 131.1, 127.9, 126.6, 123.8, 121.6, 110.5, 86.3, 81.3, 63.2, 51.9, 14.1; HRMS-ESI [M + Na]$^+$ Calcd for $C_{15}H_{16}NaO_6$ 315.0839, found 315.0845.

*Ethyl 2-(3-tert-Butoxy-3-oxoprop-1-en-2-yl)-3-hydroxy-2,3-dihydrobenzofuran-3-carboxylate (**3k**).* Following the general procedure, *o*-hydroxyphenyl ketone **1a** (39 mg, 0.2 mmol) and allylic carbonate **2c** (155 mg, 0.6 mmol) were reacted at 60 °C for 4 h to give product **3k** (64 mg, 95% yield, >20:1 dr) as a white solid; mp 79−80 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31−7.26 (m, 1H), 7.17 (d, J = 7.4 Hz, 1H), 6.97−6.91 (m, 2H), 6.34 (s, 1H), 6.01 (s, 1H), 5.81 (s, 1H), 4.41−4.28 (m, 2H), 3.97 (s, 1H), 1.49 (s, 9H), 1.27 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 164.8, 159.3, 136.4, 131.0, 127.8, 125.0, 123.9, 121.4, 110.4, 86.4, 81.5, 81.5, 63.0, 27.9, 14.0; HRMS-ESI [M + Na]$^+$ Calcd for $C_{18}H_{22}NaO_6$ 357.1309, found 357.1312.

*Ethyl 2-(3-tert-Butoxy-3-oxoprop-1-en-2-yl)-6-chloro-3-hydroxy-2,3-dihydrobenzofuran-3-carboxylate (**3l**).* Following the general procedure, *o*-hydroxyphenyl ketone **1b** (46 mg, 0.2 mmol) and allylic carbonate **2c** (155 mg, 0.6 mmol) were reacted at 60 °C for 3 h to give product **3l** (69 mg, 93% yield, >20:1 dr) as a slightly yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, J = 8.1 Hz, 1H), 6.96 (d, J = 1.8 Hz, 1H), 6.92 (dd, J = 8.1, 1.8 Hz, 1H), 6.34 (t, J = 1.2 Hz, 1H), 6.00−5.96 (m, 1H), 5.82 (t, J = 1.5 Hz, 1H), 4.41−4.29 (m, 2H), 3.99 (s, 1H), 1.48 (s, 9H), 1.28 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.1, 164.7, 160.1, 136.5, 136.0, 126.6, 125.1, 124.7, 121.8, 111.2, 87.3, 81.7, 80.9, 63.2, 28.0, 27.9, 14.0; HRMS-ESI [M + Na]$^+$ Calcd for $C_{18}H_{21}ClNaO_6$ 391.0919, found 391.0913.

*Ethyl 2-(3-tert-Butoxy-3-oxoprop-1-en-2-yl)-3-hydroxy-5-methyl-2,3-dihydrobenzofuran-3-carboxylate (**3m**).* Following the general procedure, *o*-hydroxyphenyl ketone **1c** (42 mg, 0.2 mmol) and allylic carbonate **2c** (155 mg, 0.6 mmol) were reacted at 60 °C for 3 h to give product **3m** (68 mg, 97% yield, >20:1 dr) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (dd, J = 8.2, 1.1 Hz, 1H), 6.96 (d, J = 1.1 Hz, 1H), 6.83 (d, J = 8.2 Hz, 1H), 6.33 (d, J = 1.2 Hz, 1H), 6.00 (t, J = 1.5 Hz, 1H), 5.79 (d, J = 1.5 Hz, 1H), 4.44−4.26 (m, 2H), 3.93 (s, 1H), 2.27 (s, 3H), 1.48 (s, 9H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 164.9, 157.3, 136.5, 131.7, 130.9, 127.6, 124.9, 124.0, 110.0, 86.5, 81.6, 81.5, 63.0, 27.9, 20.7, 14.0; HRMS-ESI [M + Na]$^+$ Calcd for $C_{19}H_{24}NaO_6$ 371.1465, found 371.1466.

*Ethyl 2-(3-tert-Butoxy-3-oxoprop-1-en-2-yl)-3-hydroxy-5-methoxy-2,3-dihydrobenzofuran-3-carboxylate (**3n**).* Following the general procedure, *o*-hydroxyphenyl ketone **1d** (45 mg, 0.2 mmol) and allylic carbonate **2c** (155 mg, 0.6 mmol) were reacted at 60 °C for 4 h to give product **3n** (61 mg, 83% yield, >20:1 dr) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 (d, J = 1.6 Hz, 2H), 6.69 (d, J = 1.6 Hz, 1H), 6.33 (t, J = 1.6 Hz, 1H), 6.01 (t, J = 1.6 Hz, 1H), 5.79 (t, J = 1.6 Hz, 1H), 4.43−4.27 (m, 2H), 3.97 (s, 1H), 3.73 (s, 3H), 1.49 (s, 9H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 164.9, 154.7, 153.5, 136.6, 128.1, 125.1, 117.7, 110.9, 108.4, 86.7, 81.9, 81.6, 63.1, 56.0, 27.9, 14.1; HRMS-ESI [M + Na]$^+$ Calcd for $C_{19}H_{24}NaO_7$ 387.1414, found 387.1413.

*Ethyl 2-(3-tert-Butoxy-3-oxoprop-1-en-2-yl)-3-hydroxy-7-methyl-2,3-dihydrobenzofuran-3-carboxylate (**3o**).* Following the general procedure, *o*-hydroxyphenyl ketone **1e** (42 mg, 0.2 mmol) and allylic carbonate **2c** (155 mg, 0.6 mmol) were reacted at 60 °C for 3 h to give product **3o** (68 mg, 98% yield, >20:1 dr) as a slightly yellow solid; mp 81−82 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, J = 7.4 Hz, 1H), 6.99 (d, J = 7.4 Hz, 1H), 6.84 (t, J = 7.4 Hz, 1H), 6.34 (t, J = 1.6 Hz, 1H), 6.02 (t, J = 1.6 Hz, 1H), 5.80 (t, J = 1.6 Hz, 1H), 4.36−4.31 (m, 2H), 3.92 (s, 1H), 2.29 (s, 3H), 1.48 (s, 9H), 1.28 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 164. 9, 157.8, 136.6, 132.0, 127.1, 124.9, 121.3, 121.1, 120.7, 86.1, 81.9, 81.5, 63.0, 27.9, 15.1, 14.0; HRMS-ESI [M + Na]$^+$ Calcd for $C_{19}H_{24}NaO_6$ 371.1465, found 371.1466.

*Ethyl 2-(3-tert-Butoxy-3-oxoprop-1-en-2-yl)-5-tert-butyl-3-hydroxy-2,3-dihydrobenzofuran-3-carboxylate (**3p**).* Following the general procedure, *o*-hydroxyphenyl ketone **1f** (50 mg, 0.2 mmol) and allylic carbonate **2c** (155 mg, 0.6 mmol) were reacted at 60 °C for 5 h to give product **3p** (60 mg, 77% yield, 17:1 dr) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (dd, J = 8.6, 2.0 Hz, 1H), 7.16 (d, J = 2.0 Hz, 1H), 6.87 (d, J = 8.6 Hz, 1H), 6.34 (t, J = 1.6 Hz, 1H), 6.01 (t, J = 1.6 Hz, 1H), 5.80 (t, J = 1.6 Hz, 1H), 4.36 (q, J = 7.1 Hz, 2H), 3.93 (s, 1H), 1.49 (s, 9H), 1.33−1.25 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 164.9, 157.1, 144.7, 136.5, 128.2, 127.2, 125.0, 120.4, 109.7, 86.5, 81.8, 81.5, 62.9, 34.4, 31.6, 27.9, 14.0; HRMS-ESI [M + Na]$^+$ Calcd for $C_{22}H_{30}NaO_6$ 413.1935, found 413.1931.

*Ethyl 2-(3-tert-Butoxy-3-oxoprop-1-en-2-yl)-3-hydroxy-6-methoxy-2,3-dihydrobenzofuran-3-carboxylate (**3q**).* Following the general procedure, *o*-hydroxyphenyl ketone **1g** (45 mg, 0.2 mmol) and allylic carbonate **2c** (155 mg, 0.6 mmol) were reacted at 60 °C for 48 h to give product **3q** (53 mg, 73% yield, >20:1 dr) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (d, J = 8.8 Hz, 1H), 6.53−6.47 (m, 2H), 6.34 (t, J = 1.5 Hz, 1H), 5.99 (t, J = 1.5 Hz, 1H), 5.83 (t, J = 1.5 Hz, 1H), 4.39−4.29 (m, 2H), 3.85 (br s, 1H), 3.79 (s, 3H), 1.48 (s, 9H), 1.28 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 164.8, 162.5, 160.8, 136.5, 124.9, 124.3, 120.0, 108.1, 96.0, 87.3, 81.5, 81.2, 62.9, 55.5, 27.9, 14.0; HRMS-ESI [M + Na]$^+$ Calcd for $C_{19}H_{24}NaO_7$ 387.1414, found 387.1417.

*Ethyl 2-(3-tert-Butoxy-3-oxoprop-1-en-2-yl)-3-hydroxy-6-methyl-2,3-dihydrobenzofuran-3-carboxylate (**3r**).* Following the general procedure, *o*-hydroxyphenyl ketone **1h** (42 mg, 0.2 mmol) and allylic carbonate **2c** (155 mg, 0.6 mmol) were reacted at 60 °C for 3 h to give product **3r** (52 mg, 74% yield, >20:1 dr) as a white solid; mp 82−83 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (d, J = 7.6 Hz, 1H), 6.79−6.72 (m, 2H), 6.33 (t, J = 1.6 Hz, 1H), 6.00 (t, J = 1.6 Hz, 1H), 5.80 (t,

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J = 1.6 Hz, 1H), 4.45−4.25 (m, 2H), 3.91 (br s, 1H), 2.34 (s, 3H), 1.48 (s, 9H), 1.28 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 164.8, 159.6, 141.6, 136.5, 125.0, 124.9, 123.5, 122.4, 110.9, 86.6, 81.5, 81.3, 63.0, 27.9, 21.7, 14.0; HRMS-ESI $[M + Na]^+$ Calcd for $C_{19}H_{24}NaO_6$ 371.1465, found 371.1469.

*Ethyl 2-(3-tert-Butoxy-3-oxoprop-1-en-2-yl)-3-hydroxy-2,3-dihydronaphtho[1,2-b]furan-3-carboxylate (**3s**).* Following the general procedure, 1-hydroxy-2-naphthyl ketone **1i** (49 mg, 0.2 mmol) and allylic carbonate **2c** (155 mg, 0.6 mmol) were reacted at 60 °C for 6 h to give product **3s** (46 mg, 60% yield, >20:1 dr) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16−8.06 (m, 1H), 7.87−7.81 (m, 1H), 7.55−7.48 (m, 2H), 7.43 (d, J = 8.4 Hz, 1H), 7.23 (d, J = 8.4 Hz, 1H), 6.39 (s, 1H), 6.11 (s, 1H), 6.02 (s, 1H), 4.42−4.29 (m, 2H), 4.04 (s, 1H), 1.50 (s, 9H), 1.26 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 164.9, 155.8, 136.5, 135.4, 128.0, 127.1, 125.8, 125.1, 121.8, 121.6, 120.7, 120.7, 120.4, 87.2, 82.6, 81.6, 63.1, 27.9, 14.0; HRMS-ESI $[M + Na]^+$ Calcd for $C_{22}H_{28}NO_6$ 402.1911, found 402.1911.

*tert-Butyl 2-(3-Hydroxy-3-(trifluoromethyl)-2,3-dihydrobenzofuran-2-yl)acrylate (**3t**).* Following the general procedure, *o*-hydroxyphenyl ketone **1j** (38 mg, 0.2 mmol) and allylic carbonate **2c** (155 mg, 0.6 mmol) were reacted at 60 °C for 72 h to give product **3t** (51 mg, 77% yield, >20:1 dr) as a white solid; mp 97−98 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 7.6 Hz, 1H), 7.39−7.33 (m, 1H), 7.02 (t, J = 7.5 Hz, 1H), 6.90 (d, J = 8.1 Hz, 1H), 6.34 (s, 1H), 5.91 (s, 1H), 5.49 (s, 1H), 4.50 (s, 1H), 1.44 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 159.9, 136.4, 132.0, 129.3, 125.8, 124.6 (q, J = 283.5 Hz), 123.0, 121.8, 110.3, 84.9, 83.3, 82.5 (q, J = 30.4 Hz), 27.7; Anal. Calcd for $C_{16}H_{17}F_3O_4$: C 58.18, H 5.19; found C 57.88, H 4.86.

General Procedure for Synthesis of 3-Hydroxy Indolines 5 (Table 3). Under a N_2 atmosphere and at rt, to a stirred solution of ketone **4** (0.3 mmol) and PPh_3 (0.06 mmol) in toluene (3.0 mL) was dropwise added carbonate **2** (0.9 mmol) by means of a syringe. The resulting mixture was stirred at rt for specified hours until **4** was consumed, as monitored by TLC. The solvent was removed on a rotary evaporator under reduced pressure, and the residue was subjected to column chromatographic isolation on silica gel (gradient elution, petroleum ether (bp 60−90 °C)/ethyl acetate 10:1−3:1) to give product **5**. Isomer *syn*-**5** was collected as the early fraction and *anti*-**5** as the later one.

*(syn)-Ethyl 1-Acetyl-2-(3-ethoxy-3-oxoprop-1-en-2-yl)-3-hydroxyindoline-3-carboxylate (syn-**5a**).* Following the general procedure, *o*-aminophenyl ketone **4a** (71 mg, 0.3 mmol) and allylic carbonate **2a** (207 mg, 0.9 mmol) were reacted for 48 h to give major product *syn*-**5a** (42 mg, 40% yield) as a slightly yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29−8.21 (m, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.25−7.17 (m, 1H), 7.11 (t, J = 7.6 Hz, 1H), 6.41 (s, 1H), 5.66 (s, 1H), 5.54 (s, 1H), 4.39−4.14 (m, 4H), 4.05 (s, 1H), 2.17 (s, 3H), 1.32 (t, J = 7.0 Hz, 3H), 1.21 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 168.8, 166.2, 142.5, 136.2, 130.6, 125.5, 124.7, 123.7, 117.6, 80.8, 67.1, 63.2, 61.4, 23.7, 14.0, 13.9; HRMS-ESI $[M + H]^+$ Calcd for $C_{18}H_{22}NO_6$ 348.1442, found 348.1440.

*(syn)-Ethyl 1-Acetyl-2-(3-tert-butoxy-3-oxoprop-1-en-2-yl)-3-hydroxyindoline-3-carboxylate (syn-**5b**).* Following the general procedure, *o*-aminophenyl ketone **4a** (71 mg, 0.3 mmol) and allylic carbonate **2c** (233 mg, 0.9 mmol) were reacted for 24 h to give major product *syn*-**5b** (79 mg, 70% yield) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27−8.21 (m, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.25−7.18 (m, 1H), 7.15−7.05 (m, 1H), 6.31 (s, 1H), 5.57 (s, 1H), 5.50 (s, 1H), 4.37−4.28 (m, 1H), 4.24−4.13 (m, 1H), 4.00 (br s, 1H), 2.17 (s, 3H), 1.51 (s, 9H), 1.20 (t, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 168.8, 165.3, 142.4, 137.5, 130.5, 130.3, 124.6, 123.7, 117.6, 81.9, 80.8, 67.2, 63.0, 27.9, 23.6, 13.9; HRMS-ESI $[M + H]^+$ Calcd for $C_{20}H_{26}NO_6$ 376.1755, found 376.1754.

*(syn)-Methyl 1-Acetyl-2-(3-tert-butoxy-3-oxoprop-1-en-2-yl)-3-hydroxyindoline-3-carboxylate (syn-**5c**).* Following the general procedure, *o*-aminophenyl ketone **4b** (66 mg, 0.3 mmol) and allylic carbonate **2c** (233 mg, 0.9 mmol) were reacted for 72 h to give major product *syn*-**5c** (46 mg, 42% yield) as a slightly yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30−8.23 (m, 1H), 7.43−7.05 (m, 3H), 6.32 (s, 1H), 5.58 (s, 1H), 5.52 (s, 1H), 4.04 (br s, 1H), 3.80 (s, 3H), 2.17 (s, 3H), 1.51 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5, 168.9, 165.3, 142.4, 137.4, 130.6, 130.1, 124.7, 123.8, 117.6, 82.0, 80.8, 67.2, 54.0, 27.9, 23.7; HRMS-ESI $[M + H]^+$ Calcd for $C_{19}H_{24}NO_6$ 362.1598, found 362.1600.

*(syn)-Isopropyl 1-Acetyl-2-(3-tert-butoxy-3-oxoprop-1-en-2-yl)-3-hydroxyindoline-3-carboxylate (syn-**5d**).* Following the general procedure, *o*-aminophenyl ketone **4c** (75 mg, 0.3 mmol) and allylic carbonate **2c** (233 mg, 0.9 mmol) were reacted for 48 h to give major product *syn*-**5d** (91 mg, 78% yield) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25−8.19 (m, 1H), 7.34 (t, J = 7.6 Hz, 1H), 7.25−7.16 (m, 1H), 7.14−7.05 (m, 1H), 6.31 (s, 1H), 5.57 (s, 1H), 5.47 (s, 1H), 5.13−5.04 (m, 1H), 4.00 (br s, 1H), 2.16 (s, 3H), 1.51 (s, 9H), 1.26 (d, J = 5.5 Hz, 3H), 1.07 (d, J = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 168.7, 165.2, 142.3, 137.5, 130.4, 124.6, 124.5, 123.5, 117.5, 81.8, 80.9, 71.1, 67.1, 27.9, 23.5, 21.4, 21.1; HRMS-ESI $[M + H]^+$ Calcd for $C_{21}H_{28}NO_6$ 390.1911, found 390.1915.

*(syn)-tert-Butyl 1-Acetyl-2-(3-tert-butoxy-3-oxoprop-1-en-2-yl)-3-hydroxyindoline-3-carboxylate (syn-**5e**).* Following the general procedure, *o*-aminophenyl ketone **4d** (79 mg, 0.3 mmol) and allylic carbonate **2c** (233 mg, 0.9 mmol) were reacted for 48 h to give major product *syn*-**5e** (99 mg, 82% yield) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24−8.16 (m, 1H), 7.37−7.31 (m, 1H), 7.23−7.16 (m, 1H), 7.13−7.07 (m, 1H), 6.30 (s, 1H), 5.55 (s, 1H), 5.44 (s, 1H), 4.03 (br s, 1H), 2.17 (s, 3H), 1.52 (s, 9H), 1.38 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 168.5, 165.0, 142.2, 137.6, 130.9, 130.2, 124.5, 124.3, 123.3, 117.5, 84.0, 81.7, 81.0, 67.0, 27.9, 27.6, 23.5; HRMS-ESI $[M + H]^+$ Calcd for $C_{22}H_{30}NO_6$ 404.2068, found 404.2075.

*Isopropyl 1-Acetyl-6-bromo-2-(3-tert-butoxy-3-oxoprop-1-en-2-yl)-3-hydroxyindoline-3-carboxylate (**5f**).* Following the general procedure, *o*-aminophenyl ketone **4e** (99 mg, 0.3 mmol) and allylic carbonate **2c** (233 mg, 0.9 mmol) were reacted for 48 h to give major product *syn*-**5f** (110 mg, 78% yield) as a colorless oil and minor product *anti*-**5f** (28 mg, 20% yield) as a colorless oil. For *syn*-**5f**, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.23 (d, J = 7.5 Hz, 1H), 7.07 (d, J = 7.5 Hz, 1H), 6.32 (s, 1H), 5.55 (s, 1H), 5.46 (s, 1H), 5.15−5.05 (m, 1H), 4.05 (br s, 1H), 2.16 (s, 3H), 1.51 (s, 9H), 1.26 (d, J = 5.4 Hz, 3H), 1.10 (d, J = 5.7 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 168.7, 165.0, 143.4, 137.2, 129.5, 127.6, 124.7, 124.6, 124.2, 120.6, 82.0, 80.4, 71.4, 67.3, 27.9, 23.5, 21.4, 21.2; HRMS-ESI $[M + H]^+$ Calcd for $C_{21}H_{27}BrNO_6$ 468.1016, found 468.1018. For *anti*-**5f**, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 7.25 (d, J = 8.1, 1H), 6.92 (d, J = 8.1 Hz, 1H), 6.30 (s, 1H), 5.55 (s, 1H), 5.32 (s, 1H), 5.07−4.98 (m, 1H), 4.52 (s, 1H), 2.14 (s, 3H), 1.53 (s, 9H), 1.21 (d, J = 6.2 Hz, 3H), 1.15 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 169.2, 164.1, 144.5, 137.4, 127.6, 126.4, 125.3, 124.4, 120.6, 82.7, 82.3, 72.6, 71.8, 27.9, 23.6, 21.5, 21.0; HRMS-ESI $[M + H]^+$ Calcd for $C_{21}H_{27}BrNO_6$ 468.1016, found 468.1014.

*(syn)-Isopropyl 1-Acetyl-5-bromo-2-(3-tert-butoxy-3-oxoprop-1-en-2-yl)-3-hydroxyindoline-3-carboxylate (syn-**5g**).* Following the general procedure, *o*-aminophenyl ketone **4f** (99 mg, 0.3 mmol) and allylic carbonate **2c** (233 mg, 0.9 mmol) were reacted for 48 h to give major product *syn*-**5g** (127 mg, 90% yield) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16−8.09 (m, 1H), 7.50−7.41 (m, 1H), 7.33 (s, 1H), 6.32 (s, 1H), 5.54 (s, 1H), 5.45 (s, 1H), 5.13−5.06 (m, 1H), 4.10 (s, 1H), 2.15 (s, 3H), 1.51 (s, 9H), 1.27 (d, J = 5.0 Hz, 3H), 1.11 (d, J = 5.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 168.6, 165.0, 141.5, 137.1, 133.3, 132.5, 126.7, 124.6, 119.0, 116.8, 81.9, 80.4, 71.5, 67.3, 27.9, 23.4, 21.4, 21.2; HRMS-ESI $[M + H]^+$ Calcd for $C_{21}H_{27}BrNO_6$ 468.1016, found 468.1024.

*Isopropyl 1-Acetyl-2-(3-tert-butoxy-3-oxoprop-1-en-2-yl)-3-hydroxy-5-methylindoline-3-carboxylate (**5h**).* Following the general procedure, *o*-aminophenyl ketone **4g** (79 mg, 0.3 mmol) and allylic carbonate **2c** (233 mg, 0.9 mmol) were reacted for 72 h to give major product *syn*-**5h** (87 mg, 72% yield) as a colorless oil and minor product *anti*-**5h** (33 mg, 27% yield) as a colorless oil. For *syn*-**5h**, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 8.1 Hz, 1H), 7.14 (d, J = 8.1 Hz, 1H), 7.01 (s, 1H), 6.30 (s, 1H), 5.56 (s, 1H), 5.44 (s, 1H), 5.14−5.06 (m, 1H), 3.98 (s, 1H), 2.29 (s, 3H), 2.14 (s, 3H), 1.51 (s, 9H),

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1.27 (d, J = 6.2 Hz, 3H), 1.09 (d, J = 6.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 168.3, 165.3, 140.1, 137.5, 134.5, 131.0, 130.4, 124.5, 123.8, 117.3, 81.8, 80.8, 71.1, 67.3, 27.9, 23.4, 21.5, 21.2, 20.9; HRMS-ESI $[M + H]^+$ Calcd for $C_{22}H_{30}NO_6$ 404.2068, found 404.2074. For *anti*-**5h**, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23−8.15 (m, 1H), 7.22−7.17 (m, 1H), 6.86 (s, 1H), 6.28 (s, 1H), 5.56 (s, 1H), 5.29 (s, 1H), 5.05−4.95 (m, 1H), 4.46 (br s, 1H), 2.31 (s, 3H), 2.12 (s, 3H), 1.53 (s, 9H), 1.23 (d, J = 5.8 Hz, 3H), 1.16 (d, J = 5.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 168.8, 164.4, 141.2, 137.7, 134.2, 131.1, 130.8, 126.2, 124.3, 117.3, 82.7, 82.4, 72.4, 71.4, 27.9, 23.5, 21.4, 21.0; HRMS-ESI $[M + H]^+$ Calcd for $C_{22}H_{30}NO_6$ 404.2068, found 404.2070.

*Isopropyl 1-Acetyl-2-(3-tert-butoxy-3-oxoprop-1-en-2-yl)-3-hydroxy-5-nitroindoline-3-carboxylate (**5i**).* Following the general procedure, *o*-aminophenyl ketone **4h** (88 mg, 0.3 mmol) and allylic carbonate **2c** (233 mg, 0.9 mmol) were reacted for 48 h to give major product **5i** (98 mg, 75% yield, 20:1 dr) as a yellow solid; mp 123−124 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42−8.24 (m, 3H), 5.57 (s, 1H), 5.22−5.12 (m, 1H), 4.42 (s, 1H), 3.77 (s, 1H), 3.22−3.14 (m, 1H), 2.44 (s, 3H), 1.53 (s, 9H), 1.33 (t, J = 7.7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 169.0, 167.2, 148.3, 144.1, 128.7, 127.3, 126.9, 124.3, 121.1, 1169, 90.6, 83.0, 70.8, 69.7, 54.1, 27.8, 24.2, 21.5, 21.4; HRMS-ESI $[M + H]^+$ Calcd for $C_{21}H_{27}N_2O_8$ 435.1762, found 435.1762.

*Isopropyl 1-Acetyl-2-(3-tert-butoxy-3-oxoprop-1-en-2-yl)-5-fluoro-3-hydroxyindoline-3-carboxylate (**5j**).* Following the general procedure, *o*-aminophenyl ketone **4i** (80 mg, 0.3 mmol) and allylic carbonate **2c** (233 mg, 0.9 mmol) were reacted for 48 h to give major product *syn*-**5j** (69 mg, 56% yield) as a colorless oil and minor product *anti*-**5j** (34 mg, 28% yield) as a white solid. For *syn*-**5j**, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24−8.18 (m, 1H), 7.09−7.00 (m, 1H), 6.94−6.89 (m, 1H), 6.33 (s, 1H), 5.56 (s, 1H), 5.47 (s, 1H), 5.15−5.05 (m, 1H), 4.11 (br s, 1H), 2.15 (s, 3H), 1.52 (s, 9H), 1.27 (d, J = 6.2 Hz, 3H), 1.10 (d, J = 6.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 168.4, 165.1, 159.6 (d, J = 244.4 Hz), 138.5, 137.2, 132.3 (d, J = 8.0 Hz), 124.6, 118.7 (d, J = 7.4 Hz), 117.0 (d, J = 23.1 Hz), 110.7 (d, J = 24.7 Hz), 81.9, 80.5, 71.4, 67.5, 27.9, 23.3, 21.4, 21.2; HRMS-ESI $[M + H]^+$ Calcd for $C_{21}H_{27}FNO_6$ 408.1817, found 408.1820. For *anti*-**5j**, mp 116−117 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35−8.23 (m, 1H), 7.15−7.05 (m, 1H), 6.85−6.75 (m, 1H), 6.30 (s, 1H), 5.56 (s, 1H), 5.33 (s, 1H), 5.09−5.00 (m, 1H), 4.59 (br s, 1H), 2.12 (s, 3H), 1.53 (s, 9H), 1.23 (d, J = 6.2 Hz, 3H), 1.17 (d, J = 6.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 168.9, 164.2, 159.4 (d, J = 243.8 Hz), 139.6, 137.5, 132.3, 126.3, 118.6, 117.2 (d, J = 23.0 Hz), 111.1 (d, J = 25.8 Hz), 82.6, 82.4, 72.5, 71.8, 27.9, 23.4, 21.5, 21.1; HRMS-ESI $[M + H]^+$ Calcd for $C_{21}H_{27}FNO_6$ 408.1817, found 408.1822.

*Isopropyl 1-Acetyl-2-(3-tert-butoxy-3-oxoprop-1-en-2-yl)-5-chloro-3-hydroxyindoline-3-carboxylate (**5k**).* Following the general procedure, *o*-aminophenyl ketone **4j** (85 mg, 0.3 mmol) and allylic carbonate **2c** (233 mg, 0.9 mmol) were reacted for 48 h to give major product *syn*-**5k** (63 mg, 49% yield) as a colorless oil and minor product *anti*-**5k** (32 mg, 25% yield) as a white solid. For *syn*-**5k**, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 8.6 Hz, 1H), 7.31 (d, J = 8.6 Hz, 1H), 7.18 (s, 1H), 6.32 (s, 1H), 5.55 (s, 1H), 5.45 (s, 1H), 5.16−5.06 (m, 1H), 4.08 (s, 1H), 2.15 (s, 3H), 1.51 (s, 9H), 1.27 (d, J = 6.2 Hz, 3H), 1.11 (d, J = 6.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 168.6, 165.1, 141.0, 137.1, 132.2, 130.4, 129.5, 124.7, 123.8, 118.6, 82.0, 80.4, 71.5, 67.4, 27.9, 23.4, 21.4, 21.2; HRMS-ESI $[M + H]^+$ Calcd for $C_{21}H_{27}ClNO_6$ 424.1521, found 424.1520. For *anti*-**5k**, mp 138−139 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30−8.21 (m, 1H), 7.39−7.31 (m, 1H), 7.03 (s, 1H), 6.30 (s, 1H), 5.54 (s, 1H), 5.33 (s, 1H), 5.10−5.00 (m, 1H), 4.55 (s, 1H), 2.14 (s, 3H), 1.53 (s, 9H), 1.24 (d, J = 6.2 Hz, 3H), 1.17 (d, J = 6.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 169.1, 164.2, 142.1, 137.5, 132.4, 130.5, 129.3, 126.4, 124.3, 118.6, 82.7, 82.3, 72.5, 71.9, 27.9, 23.5, 21.5, 21.1; HRMS-ESI $[M + H]^+$ Calcd for $C_{21}H_{27}ClNO_6$ 424.1521, found 424.1523.

*Isopropyl 1-Acetyl-2-(3-tert-butoxy-3-oxoprop-1-en-2-yl)-3-hydroxy-5-methoxyindoline-3-carboxylate (**5l**).* Following the general procedure, *o*-aminophenyl ketone **4k** (84 mg, 0.3 mmol) and allylic carbonate **2c** (233 mg, 0.9 mmol) were reacted for 48 h to give major product *syn*-**5l** (73 mg, 58% yield) as a colorless oil and minor product *anti*-**5l** (52 mg, 41% yield) as a colorless oil. For *syn*-**5l**, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 8.8 Hz, 1H), 6.88 (dd, J = 8.8, 2.2 Hz, 1H), 6.75 (d, J = 2.2 Hz, 1H), 6.31 (s, 1H), 5.57 (s, 1H), 5.45 (s, 1H), 5.15−5.05 (m, 1H), 3.76 (s, 3H), 2.14 (s, 3H), 1.52 (s, 9H), 1.27 (d, J = 6.2 Hz, 3H), 1.09 (d, J = 6.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 168.0, 165.2, 156.9, 137.4, 136.0, 131.6, 124.5, 118.5, 116.1, 108.3, 81.8, 80.8, 71.2, 67.3, 55.6, 27.9, 23.2, 21.4, 21.2; HRMS-ESI $[M + H]^+$ Calcd for $C_{22}H_{30}NO_7$ 420.2017, found 420.2017. For *anti*-**5l**, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 8.8 Hz, 1H), 6.93 (d, J = 8.8 Hz, 1H), 6.59 (s, 1H), 6.29 (s, 1H), 5.57 (s, 1H), 5.29 (s, 1H), 5.10−5.00 (m, 1H), 4.40 (br s, 1H), 3.76 (s, 3H), 2.10 (s, 3H), 1.53 (s, 9H), 1.23 (d, J = 6.0 Hz, 3H), 1.16 (d, J = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 168.5, 164.3, 156.7, 137.7, 137.2, 131.9, 126.3, 118.4, 116.1, 109.0, 82.7, 82.5, 72.4, 71.5, 55.6, 27.9, 23.3, 21.5, 21.0; HRMS-ESI $[M + H]^+$ Calcd for $C_{22}H_{30}NO_7$ 420.2017, found 420.2014.

General Procedure for $CuSO_4$-Promoted Transformations of Compounds 3 or 5 (Table 4 and Scheme 3). A stirred suspension of 3-hydroxy dihydrobenzofurans **3** or 3-hydroxy indolines *syn*-**5** (0.15 mmol) and 20% silica-supported $CuSO_4$ (0.09 mmol) in toluene (1.5 mL) was heated at 110 °C for specified hours until **3** or **5** was consumed, as monitored by TLC. The reaction mixture was cooled to rt, and ether (10 mL) was added into it with stirring. After the silica-supported $CuSO_4$ was filtered off, the filtrate was concentrated on a rotary evaporator under reduced pressure, and the residue was subjected to column chromatographic isolation on silica gel (gradient elution, petroleum ether (bp 60−90 °C)/ethyl acetate 15:1−2:1) to give products (**6**, **7**, **8**, **9**, **10**).

*Ethyl 2-(3-Ethoxy-3-oxoprop-1-en-2-yl)benzofuran-3-carboxylate (**6a**).* Following the general procedure, 3-hydroxy dihydrobenzofuran **3a** (46 mg, 0.15 mmol) was treated for 4 h to give product **6a** (41 mg, 94% yield) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05−8.01 (m, 1H), 7.53−7.48 (m, 1H), 7.39−7.32 (m, 2H), 6.65 (d, J = 0.8 Hz, 1H), 6.29 (d, J = 0.8 Hz, 1H), 4.36 (q, J = 7.1 Hz, 2H), 4.27 (q, J = 7.1 Hz, 2H), 1.39 (t, J = 7.1 Hz, 3H), 1.28 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 163.4, 156.2, 153.9, 132.8, 131.0, 126.0, 125.6, 124.1, 122.3, 111.4, 111.3, 61.4, 60.7, 14.2, 14.0; HRMS-ESI $[M + H]^+$ Calcd for $C_{16}H_{17}O_5$ 289.1071, found 289.1071.

*Ethyl 6-Chloro-2-(3-ethoxy-3-oxoprop-1-en-2-yl)benzofuran-3-carboxylate (**6b**).* Following the general procedure, 3-hydroxy dihydrobenzofuran **3b** (51 mg, 0.15 mmol) was treated for 5 h to give product **6b** (32 mg, 65% yield) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.4 Hz, 1H), 7.52 (d, J = 1.6 Hz, 1H), 7.33 (dd, J = 8.4, 1.6 Hz, 1H), 6.67 (s, 1H), 6.30 (s, 1H), 4.36 (q, J = 7.1 Hz, 2H), 4.27 (q, J = 7.1 Hz, 2H), 1.39 (t, J = 7.1 Hz, 3H), 1.28 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 163.0, 156.8, 153.9, 132.5, 131.5, 131.5, 125.0, 124.8, 123.0, 111.8, 111.3, 61.6, 60.9, 14.2, 14.0; HRMS-ESI $[M + H]^+$ Calcd for $C_{16}H_{16}ClO_5$ 323.0681, found 323.0684.

*Ethyl 2-(3-Ethoxy-3-oxoprop-1-en-2-yl)-5-methylbenzofuran-3-carboxylate (**6c**).* Following the general procedure, 3-hydroxy dihydrobenzofuran **3c** (48 mg, 0.15 mmol) was treated for 4 h to give product **6c** (24 mg, 52% yield) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.38 (d, J = 8.4 Hz, 1H), 7.18 (d, J = 8.4 Hz, 1H), 6.63 (s, 1H), 6.27 (s, 1H), 4.36 (q, J = 7.1 Hz, 2H), 4.26 (q, J = 7.1 Hz, 2H), 2.48 (s, 3H), 1.39 (t, J = 7.1 Hz, 3H), 1.27 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 163.6, 156.3, 152.4, 133.8, 133.0, 130.9, 126.9, 126.2, 122.0, 111.2, 110.8, 76.7, 61.4, 60.7, 21.5, 14.3, 14.1; HRMS-ESI $[M + H]^+$ Calcd for $C_{17}H_{19}O_5$ 303.1227, found 303.1225.

*Ethyl 2-(3-Ethoxy-3-oxoprop-1-en-2-yl)-5-methoxybenzofuran-3-carboxylate (**6d**).* Following the general procedure, 3-hydroxy dihydrobenzofuran **3d** (51 mg, 0.15 mmol) was treated for 4 h to give product **6d** (34 mg, 71% yield) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 2.7 Hz, 1H), 7.39 (d, J = 9.0 Hz, 1H), 6.97 (dd, J = 9.0, 2.7 Hz, 1H), 6.63 (s, 1H), 6.26 (s, 1H), 4.35 (q, J = 7.1 Hz, 2H), 4.27 (q, J = 7.1 Hz, 2H), 3.88 (s, 3H), 1.38 (t, J = 7.1 Hz, 3H), 1.28 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 163.5, 156.9, 156.8, 148.9, 133.0, 130.9, 126.8, 114.8, 111.9, 111.4,

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104.1, 61.5, 60.7, 55.8, 14.2, 14.0; HRMS-ESI [M + H]$^+$ Calcd for $C_{17}H_{19}O_6$ 319.1176, found 319.1182.

*Ethyl 2-(3-Ethoxy-3-oxoprop-1-en-2-yl)-7-methylbenzofuran-3-carboxylate (**6e**).* Following the general procedure, 3-hydroxy dihydrobenzofuran **3e** (48 mg, 0.15 mmol) was treated for 4 h to give product **6e** (45 mg, 99% yield) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 7.8 Hz, 1H), 7.24 (t, J = 7.8 Hz, 1H), 7.17 (d, J = 7.8 Hz, 1H), 6.65 (d, J = 0.8 Hz, 1H), 6.29 (d, J = 0.8 Hz, 1H), 4.35 (q, J = 7.1 Hz, 2H), 4.27 (q, J = 7.1 Hz, 2H), 2.53 (s, 3H), 1.39 (t, J = 7.1 Hz, 3H), 1.28 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 163.6, 156.0, 153.0, 133.0, 130.9, 126.5, 125.6, 124.2, 121.6, 119.7, 111.6, 61.4, 60.7, 14.9, 14.2, 14.1; HRMS-ESI [M + H]$^+$ Calcd for $C_{17}H_{19}O_5$ 303.1227, found 303.1233.

*Ethyl 5-(tert-Butyl)-2-(3-ethoxy-3-oxoprop-1-en-2-yl)benzofuran-3-carboxylate (**6f**).* Following the general procedure, 3-hydroxy dihydrobenzofuran **3f** (54 mg, 0.15 mmol) was treated for 3 h to give product **6f** (51 mg, 98% yield) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.46−7.41 (m, 2H), 6.63 (s, 1H), 6.26 (s, 1H), 4.36 (q, J = 7.1 Hz, 2H), 4.26 (q, J = 7.1 Hz, 2H), 1.45−1.35 (m, 12H), 1.27 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 163.6, 156.3, 152.2, 147.4, 133.0, 130.8, 125.8, 123.6, 118.4, 111.4, 110.6, 61.4, 60.6, 34.9, 31.7, 14.2, 14.1; HRMS-ESI [M + H]$^+$ Calcd for $C_{20}H_{25}O_5$ 345.1697, found 345.1704.

*Ethyl 2-(3-Ethoxy-3-oxoprop-1-en-2-yl)-6-methoxybenzofuran-3-carboxylate (**6g**).* Following the general procedure, 3-hydroxy dihydrobenzofuran **3g** (51 mg, 0.15 mmol) was treated for 2 h to give product **6g** (47 mg, 99% yield) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.7 Hz, 1H), 7.01 (d, J = 1.5 Hz, 1H), 6.97 (dd, J = 8.7, 1.5 Hz, 1H), 6.59 (s, 1H), 6.25 (s, 1H), 4.34 (q, J = 7.1 Hz, 2H), 4.27 (q, J = 7.1 Hz, 2H), 3.86 (s, 3H), 1.38 (t, J = 7.1 Hz, 3H), 1.28 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 163.4, 158.8, 155.2, 154.9, 132.9, 130.3, 122.5, 119.4, 113.3, 111.3, 95.5, 76.7, 61.4, 60.7, 55.7, 14.2, 14.0; HRMS-ESI [M + H]$^+$ Calcd for $C_{17}H_{19}O_6$ 319.1176, found 319.1181.

*Ethyl 2-(3-Ethoxy-3-oxoprop-1-en-2-yl)-6-methylbenzofuran-3-carboxylate (**6h**).* Following the general procedure, 3-hydroxy dihydrobenzofuran **3h** (48 mg, 0.15 mmol) was treated for 2 h to give product **6h** (45 mg, 99% yield) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.0 Hz, 1H), 7.30 (s, 1H), 7.16 (d, J = 8.0 Hz, 1H), 6.61 (s, 1H), 6.26 (s, 1H), 4.35 (q, J = 7.1 Hz, 2H), 4.26 (q, J = 7.1 Hz, 2H), 2.48 (s, 3H), 1.38 (t, J = 7.1 Hz, 3H), 1.27 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 163.5, 155.6, 154.3, 136.0, 133.0, 130.7, 125.6, 123.6, 121.8, 111.4, 111.3, 61.4, 60.7, 21.7, 14.2, 14.0; HRMS-ESI [M + H]$^+$ Calcd for $C_{17}H_{19}O_5$ 303.1227, found 303.1235.

*Ethyl 2-(3-Ethoxy-3-oxoprop-1-en-2-yl)naphtho[1,2-b]furan-3-carboxylate (**6i**).* Following the general procedure, 3-hydroxy dihydrobenzofuran **3i** (54 mg, 0.15 mmol) was treated for 3 h to give product **6i** (45 mg, 88% yield) as a slightly yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, J = 8.1 Hz, 1H), 8.07 (d, J = 8.7 Hz, 1H), 7.94 (d, J = 8.1 Hz, 1H), 7.75 (d, J = 8.7 Hz, 1H), 7.60 (t, J = 7.5 Hz, 1H), 7.53 (t, J = 7.5 Hz, 1H), 6.68 (s, 1H), 6.37 (s, 1H), 4.39 (q, J = 7.1 Hz, 2H), 4.29 (q, J = 7.1 Hz, 2H), 1.42 (t, J = 7.1 Hz, 3H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 163.6, 155.3, 149.8, 133.0, 132.0, 130.8, 128.4, 126.7, 125.9, 124.9, 122.2, 120.9, 120.0, 120.0, 112.6, 61.5, 60.9, 14.3, 14.1; HRMS-ESI [M + H]$^+$ Calcd for $C_{20}H_{19}O_5$ 339.1227, found 339.1233.

*Ethyl 3-Methylene-2-oxo-2,3,3a,8b-tetrahydrofuro[3,2-b]benzofuran-8b-carboxylate (**7a**).* Following the general procedure, 3-hydroxy dihydrobenzofuran **3k** (50 mg, 0.15 mmol) was treated for 6 h to give product **7a** (39 mg, 99% yield) as a white solid; mp 94−95 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 7.8 Hz, 1H), 7.38 (t, J = 7.8 Hz, 1H), 7.03 (t, J = 7.8 Hz, 1H), 6.90 (d, J = 7.8 Hz, 1H), 6.68 (s, 1H), 6.32 (s, 1H), 5.86 (s, 1H), 4.43−4.28 (m, 2H), 1.35 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 166.9, 160.9, 133.4, 132.9, 131.4, 126.3, 122.3, 122.1, 111.0, 89.3, 82.8, 63.1, 14.1; HRMS-ESI [M + H]$^+$ Calcd for $C_{14}H_{13}O_5$ 261.0757, found 261.0762.

*Ethyl 6-Chloro-3-methylene-2-oxo-2,3,3a,8b-tetrahydrofuro[3,2-b]benzofuran-8b-carboxylate (**7b**).* Following the general procedure, 3-hydroxy dihydrobenzofuran **3l** (55 mg, 0.15 mmol) was treated for 4 h to give product **7b** (32 mg, 73% yield) as a white solid; mp 94−95 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 8.2 Hz, 1H), 7.02 (dd, J = 8.2, 1.6 Hz, 1H), 6.92 (d, J = 1.6 Hz, 1H), 6.70 (d, J = 1.5 Hz, 1H), 6.34 (d, J = 1.5 Hz, 1H), 5.90 (s, 1H), 4.41−4.28 (m, 2H), 1.35 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 166.4, 161.5, 138.7, 132.7, 132.0, 127.0, 122.6, 121.0, 111.7, 88.5, 83.6, 63.3, 14.0; HRMS-ESI [M + H]$^+$ Calcd for $C_{14}H_{12}ClO_5$ 295.0368, found 295.0373.

*Ethyl 5-Methyl-3-methylene-2-oxo-2,3,3a,8b-tetrahydrofuro[3,2-b]benzofuran-8b-carboxylate (**7c**).* Following the general procedure, 3-hydroxy dihydrobenzofuran **3o** (52 mg, 0.15 mmol) was treated for 4 h to give minor product **7c** (13 mg, 31% yield) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 7.6 Hz, 1H), 7.19 (d, J = 7.6 Hz, 1H), 6.93 (t, J = 7.6 Hz, 1H), 6.68 (d, J = 1.5 Hz, 1H), 6.34 (d, J = 1.5 Hz, 1H), 5.85 (s, 1H), 4.42−4.27 (m, 2H), 2.23 (s, 3H), 1.35 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 167.0, 159.4, 133.8, 133.5, 131.4, 123.4, 122.0, 121.5, 121.4, 89.9, 82.5, 63.0, 15.0, 14.1; HRMS-ESI [M + H]$^+$ Calcd for $C_{15}H_{15}O_5$ 275.0914, found 275.0919.

*2-(3-(Ethoxycarbonyl)-5-methoxybenzofuran-2-yl)acrylic Acid (**8a**).* Following the general procedure, 3-hydroxy dihydrobenzofuran **3n** (55 mg, 0.15 mmol) was treated for 4 h to give product **8a** (18 mg, 40% yield) as a white solid; mp 97−98 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.88 (br s, 1H), 7.50 (d, J = 2.6 Hz, 1H), 7.39 (d, J = 9.0 Hz, 1H), 6.97 (dd, J = 9.0, 2.6 Hz, 1H), 6.76 (s, 1H), 6.39 (s, 1H), 4.37 (q, J = 7.1 Hz, 2H), 3.88 (s, 3H), 1.39 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 163.4, 157.0, 155.8, 149.0, 132.9, 132.2, 126.7, 115.1, 111.9, 111.8, 104.1, 60.8, 55.9, 14.1; HRMS-ESI [M + H]$^+$ Calcd for $C_{15}H_{15}O_6$ 291.0863, found 291.0868.

*2-(3-(Ethoxycarbonyl)-7-methylbenzofuran-2-yl)acrylic Acid (**8b**).* Following the general procedure, 3-hydroxy dihydrobenzofuran **3o** (52 mg, 0.15 mmol) was treated for 4 h to give major product **8b** (27 mg, 65% yield) as a slightly yellow solid; mp 111−112 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.85 (br s, 1H), 7.85 (d, J = 7.5 Hz, 1H), 7.23−7.12 (m, 2H), 6.79 (s, 1H), 6.42 (s, 1H), 4.38 (q, J = 7.1 Hz, 2H), 2.54 (s, 3H), 1.40 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 163.5, 155.1, 153.2, 133.0, 132.2, 126.6, 125.5, 124.3, 121.6, 119.8, 112.0, 60.8, 14.9, 14.2; HRMS-ESI [M + H]$^+$ Calcd for $C_{15}H_{15}O_5$ 275.0914, found 275.0917.

*2-(5-(tert-Butyl)-3-(ethoxycarbonyl)benzofuran-2-yl)acrylic Acid (**8c**).* Following the general procedure, 3-hydroxy dihydrobenzofuran **3p** (59 mg, 0.15 mmol) was treated for 4 h to give product **8c** (30 mg, 63% yield) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.53 (br s, 1H), 8.06 (s, 1H), 7.48−7.40 (m, 2H), 6.76 (s, 1H), 6.39 (s, 1H), 4.38 (q, J = 7.1 Hz, 2H), 1.42−1.38 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 163.6, 155.4, 152.3, 147.5, 132.8, 132.2, 125.6, 123.8, 118.4, 111.8, 110.6, 60.8, 34.9, 31.7, 14.1; HRMS-ESI [M + H]$^+$ Calcd for $C_{18}H_{21}O_5$ 317.1384, found 317.1385.

*2-(3-(Ethoxycarbonyl)-6-methoxybenzofuran-2-yl)acrylic Acid (**8d**).* Following the general procedure, 3-hydroxy dihydrobenzofuran **3q** (55 mg, 0.15 mmol) was treated for 4 h to give product **8d** (22 mg, 50% yield) as a yellow solid; mp 95−96 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.57 (br s, 1H), 7.88 (d, J = 8.7 Hz, 1H), 7.02 (d, J = 1.9 Hz, 1H), 6.97 (dd, J = 8.7, 1.9 Hz, 1H), 6.73 (s, 1H), 6.38 (s, 1H), 4.36 (q, J = 7.1 Hz, 2H), 3.87 (s, 3H), 1.39 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 163.5, 159.0, 155.1, 154.3, 132.4, 132.0, 122.6, 119.3, 113.5, 111.8, 95.5, 60.8, 55.7, 14.2; HRMS-ESI [M + H]$^+$ Calcd for $C_{15}H_{15}O_6$ 291.0863, found 291.0865.

*2-(3-(Ethoxycarbonyl)-6-methylbenzofuran-2-yl)acrylic Acid (**8e**).* Following the general procedure, 3-hydroxy dihydrobenzofuran **3r** (52 mg, 0.15 mmol) was treated for 4 h to give product **8e** (36 mg, 87% yield) as a white solid; mp 122−123 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.16 (br s, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.31 (s, 1H), 7.17 (d, J = 8.0 Hz, 1H), 6.75 (s, 1H), 6.39 (s, 1H), 4.37 (q, J = 7.0 Hz, 2H), 2.49 (s, 3H), 1.39 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 163.5, 154.7, 154.4, 136.2, 132.7, 132.1, 125.7, 123.5, 121.8, 111.7, 111.4, 60.8, 21.7, 14.2; HRMS-ESI [M + H]$^+$ Calcd for $C_{15}H_{15}O_5$ 275.0914, found 275.0917.

*2-(1-Acetyl-6-bromo-3-(isopropoxycarbonyl)-1H-indol-2-yl)-acrylic Acid (**10a**).* Following the general procedure, 3-hydroxy

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indoline *syn*-**5f** (70 mg, 0.15 mmol) was treated for 6 h to give minor product **10a** (15 mg, 26% yield) as a yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 8.05 (d, J = 8.4 Hz, 1H), 7.49 (d, J = 8.4 Hz, 1H), 6.85 (s, 1H), 6.01 (s, 1H), 5.29−5.20 (m, 1H), 2.63 (s, 3H), 1.35 (d, J = 6.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 169.1, 163.1, 138.7, 136.3, 133.9, 133.2, 127.9, 125.7, 123.2, 119.7, 118.1, 113.9, 68.7, 27.7, 21.9; HRMS-ESI $[M + NH_4]^+$ Calcd for $C_{17}H_{20}BrN_2O_5$ 411.0550, found 411.0547.

*2-(1-Acetyl-5-bromo-3-(isopropoxycarbonyl)-1H-indol-2-yl)-acrylic Acid (**10b**).* Following the general procedure, 3-hydroxy indoline *syn*-**5g** (70 mg, 0.15 mmol) was treated for 6 h to give minor product **10b** (10 mg, 16% yield) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.95 (d, J = 8.8 Hz, 1H), 7.50 (d, J = 8.8 Hz, 1H), 6.85 (s, 1H), 6.00 (s, 1H), 5.28−5.22 (m, 1H), 2.63 (s, 3H), 1.36 (d, J = 5.7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 169.2, 163.1, 139.3, 134.4, 133.9, 133.1, 128.8, 128.6, 124.8, 118.0, 116.4, 113.3, 68.8, 27.6, 21.8; HRMS-ESI $[M + NH_4]^+$ Calcd for $C_{17}H_{20}BrN_2O_5$ 411.0550, found 411.0548.

*2-(1-Acetyl-3-(isopropoxycarbonyl)-5-methyl-1H-indol-2-yl)-acrylic Acid (**10c**).* Following the general procedure, 3-hydroxy indoline *syn*-**5h** (60 mg, 0.15 mmol) was treated for 6 h to give minor product **10c** (14 mg, 29% yield) as a slightly yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.87 (d, J = 8.2 Hz, 1H), 7.21 (d, J = 8.2 Hz, 1H), 6.78 (s, 1H), 5.94 (s, 1H), 5.28−5.21 (m, 1H), 2.65 (s, 3H), 2.48 (s, 3H), 1.35 (d, J = 6.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 169.7, 163.6, 138.5, 134.4, 134.1, 133.7, 132.1, 127.3, 127.1, 121.9, 114.4, 113.9, 68.4, 29.7, 27.6, 21.8, 21.4; HRMS-ESI $[M + H]^+$ Calcd for $C_{18}H_{20}NO_5$ 330.1336, found 330.1343.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00596.

Copies of NMR (^{1}H, ^{13}C) spectra of new compounds **3**, **5**−**8**, and **10** (PDF)

X-ray crystallographic data for compound **3k** (CIF)

X-ray crystallographic data for compound *anti*-**5j** (CIF)

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Notes

The authors declare no competing financial interest.

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(20) A typical procedure for preparation of silica-supported $CuSO_4$ dehydration agent: To a solution of $CuSO_4(H_2O)_5$ (23.5 g) in water (80 mL) was added silica gel (60 g, 200−300 mesh) with stirring. The resulting mixture was vibrated by means of an ultrasonic vibrator until no gas bubbles emerged, and then was kept still for 2 h. Water was evaporated under reduced pressure to give the $CuSO_4$-absorbed silica gel, which was transferred into a crucible and baked at 200 °C for 3 h in a muffle furnace to give silica-supported $CuSO_4$ (20%, w/w) dehydration agent. The agent was cooled to rt and stored in a desiccator.

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