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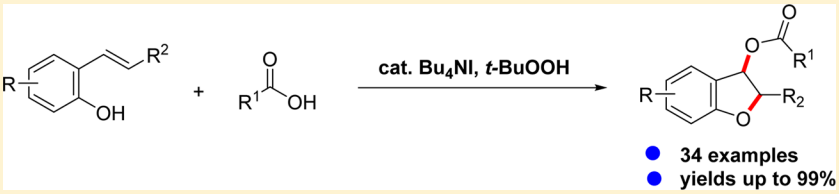
Metal-Free Coupling of 2-Vinylphenols and Carboxylic Acids: An Access to 3-Acyloxy-2,3-dihydrobenzofurans

Jijun Chen,[†] Ying Shao,*[,†,‡] Hao Zheng,[‡] Jiang Cheng,[‡] and Xiaobing Wan*[,†]

[†]Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, P. R. China

[‡]Jiangsu Key Laboratory of Advanced Catalytic Materials and Technology, Changzhou University, Changzhou 213164, P. R. China

Supporting Information



ABSTRACT: A new coupling reaction between 2-vinylphenols and carboxylic acids was developed to synthesize 3-acyloxy-2,3-dihydrobenzofurans using Bu_4NI as a catalyst and *t*-BuOOH as an oxidant. This simple and practical methodology is notable due to the ability to complete it under metal-free conditions, with easily available precursors, resulting in a product with high atom economy and high functional group tolerance. Upon the basis of experimental observations and literature, a plausible mechanism is proposed.

INTRODUCTION

2,3-Dihydrobenzofurans are unique structural motifs that can be found in nature, as well as pharmacological molecules.[1] Among the various 2,3-didydrobenzofurans, 3-substituted derivatives have drawn considerable interest due to exhibiting outstanding biologically active properties such as prostaglandin (PG) D2 receptor antagonists,[2] and γ-secretase inhibitors (GSIs).[3] The conventional approach toward synthesizing these compounds include hydrogenation of substituted benzofurans,[4] C−H bond insertion−cyclization,[5] and Michael addition.[6] Recently, much attention has been focused toward the direct difunctionalization of alkenes, which represent an atom economic protocol for the synthesis of 3-substituted-2,3-dihydrobenzofurans.[7] Fu[8a] and Brown[8b] elegantly generated the C(sp^3)−M complex through sequential carbometalation of arylboron reagents that bear a pendant olefin, then subsequently coupling the complex with halides (Scheme 1, path a). Apart from ionic methods, a radical process involving an intramolecular 5-*exo*-cyclization has also been explored to construct 3-substituted-2,3-dihydrobenzofurans, as demonstrated by several groups (Scheme 1, path b).[9] Despite these contributions, further successful development of simple and efficient strategies for the construction of 3-substituted-2,3-dihydrobenzofurans will be greatly valuable to the field.

The acyloxyl group is of great interest due to its importance in medicinal molecules[10] and possibility for further chemical modification. However, only few methods have been developed to introduce acyloxyl group into dihydrobenzofurans at the 3-position, including palladium-catalyzed acyloxyarylation of benzofurans[11] and acyl migratio−-cyclization of substituted bromoacetophenones.[12] Recently, oxidative coupling carboxylic acids with sp^3 or sp^2 C−H bond via iodine-catalysis have been reported in literature;[13] this has been successfully achieved in our lab.[13f,13l] Zhu[14] and Sudalai[15] also reported an iodine-catalyzed acyloxylation of alkenes. Herein, we report a simple and practical coupling reaction between 2-vinylphenols and carboxylic acids for the synthesis of 3-acyloxy-2,3-dihydrobenzofurans using Bu_4NI as a catalyst and *t*-BuOOH as an oxidant (Scheme 1, path c).

RESULTS AND DISCUSSION

The reaction of 2-vinylphenol **1a** with 4-*tert*-butyl benzoic acid **2a** was chosen as a model reaction to identify the reaction conditions for the synthesis of 3-acyloxy-2,3- dihydrobenzofurans. After extensive screening over a wide range, it was determined that the combination of Bu_4NI (10 mol %) and *t*-BuOOH (1.5 equiv, 70% aqueous solution) in 1,2-dichloroethane (DCE) at 60 °C for 6 h in air was the most effective configuration, producing the desired 2,3-dihydrobenzofuran-3-yl 4-(*tert*-butyl)benzoate **3a** in 99% yield (Table 1, entry 1). The choice of oxidant was crucial for this transformation; replacing *t*-BuOOH with other common oxidants, such as oxone, DDQ, benzoquinone, H_2O_2, and O_2, suppressed or decreased yield (Table 1, entries 2−6). No product **3a** was observed in the absence of Bu_4NI or *t*-BuOOH (Table 1, entries 7 and 8). Replacing Bu_4NI with Bu_4NCl, Bu_4NBr, and Bu_4NOH showed no positive activity (Table 1, entries 9−11). The use of other quaternary ammonium iodides, such as Me_4NI and Me_3BnNI resulted in lower yields (Table 1, entries 14 and

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Scheme 1. Difunctionalization of Alkenes for the Synthesis of 3-Substituted-2,3-Dihydrobenzofurans

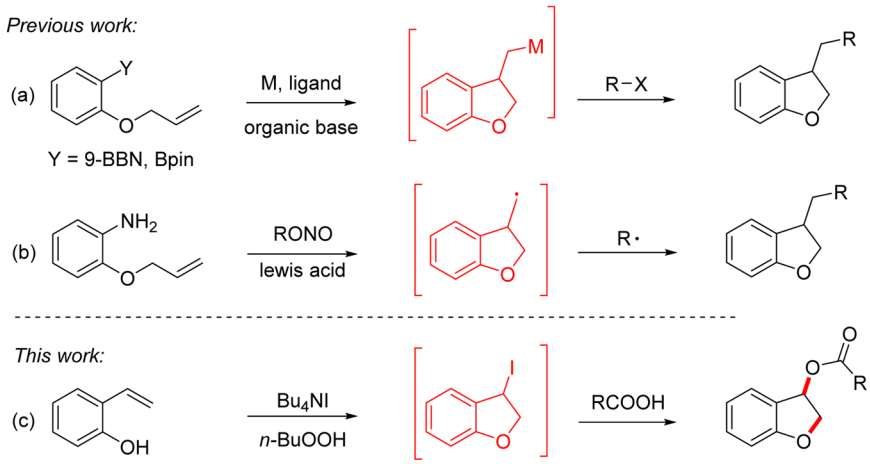
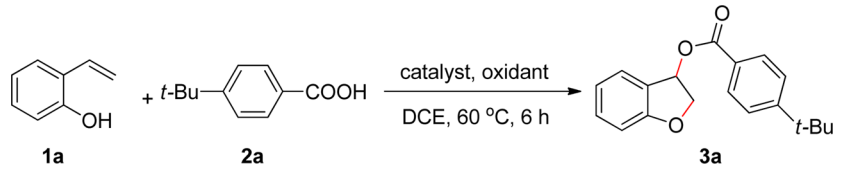


Table 1. Optimization of the Reaction Conditions[a]



1a **2a** **3a**

entry	catalyst	oxidant	yield (%)[b]
1	**Bu_4NI**	***t*-BuOOH**	**99**
2	Bu_4NI	oxone[c]	<5
3	Bu_4NI	DDQ[d]	<5
4	Bu_4NI	benzoquinone	<5
5	Bu_4NI	H_2O_2[e]	49
6	Bu_4NI	O_2[f]	<5
7	Bu_4NI	-	<5
8	-	*t*-BuOOH	<5
9	Bu_4NCI	*t*-BuOOH	<5
10	Bu_4NBr	*t*-BuOOH	<5
11	Bu_4NOH	*t*-BuOOH	<5
12	KI	*t*-BuOOH	<5
13	I_2	*t*-BuOOH	<5
14	Me_4NI	*t*-BuOOH	72
15	Me_3BnNI	*t*-BuOOH	34
16	CuI	*t*-BuOOH	<5
17	$PhI(OAc)_2$	*t*-BuOOH	<5
18	$NaIO_4$	*t*-BuOOH	<5
19	NIS	*t*-BuOOH	<5

[a]Reaction conditions: **1a** (0.7 mmol), **2a** (0.5 mmol), catalyst (10 mol %), oxidant (1.5 equiv), DCE (1.0 mL) under air, at 60 °C for 6 h. [b]Isolated yield. [c]Oxone, potassium peroxymonosulfate. [d]DDQ, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone. [e]H_2O_2 30% in water. [f]Under an oxygen atmosphere (1.0 atm).

15). Interestingly, no **3a** was formed in the presence of catalytic KI, I_2, $PhI(OAc)_2$, $NaIO_4$, and NIS (Table 1, entries 12, 13, and 17–19). Notably, the addition of a metal catalyst, such as CuI, suppressed the transformation (Table 1, entry 16).

With the use of the optimized reaction conditions, a variety of substituted aryl carboxylic acids were tested to probe the versatility of the catalytic system (Scheme 2). Benzoic acids bearing either electron-donating groups or electron-withdrawing groups all produced corresponding 3-acyloxy-2,3-dihydrobenzofurans in moderate to excellent yields. Generally, benzoic acids bearing electron-withdrawing substituents produced corresponding products but with decreased yields (**3c**–**3e**, **3g**–**3i**). When 2,6-dimethylbenzoic acid was reacted with 2-vinylphenol, the steric effect was noticeable, and the reaction required higher amounts of catalyst and oxidant. Additionally, a high level of functional group tolerance was observed, such as halogen (**3c**–**3e**, **3k**), methoxyl (**3f**), sulfone (**3g**), cyano (**3h**), nitro (**3i**), keto (**3l**), and trifluoromethyl (**3n**). The exact structure of **3f** was unequivocally confirmed by single-crystal X-ray analysis (Figure S1 in Supporting Information).

To further investigate the potential of this methodology, other types of carboxylic acids were applied to this process. The

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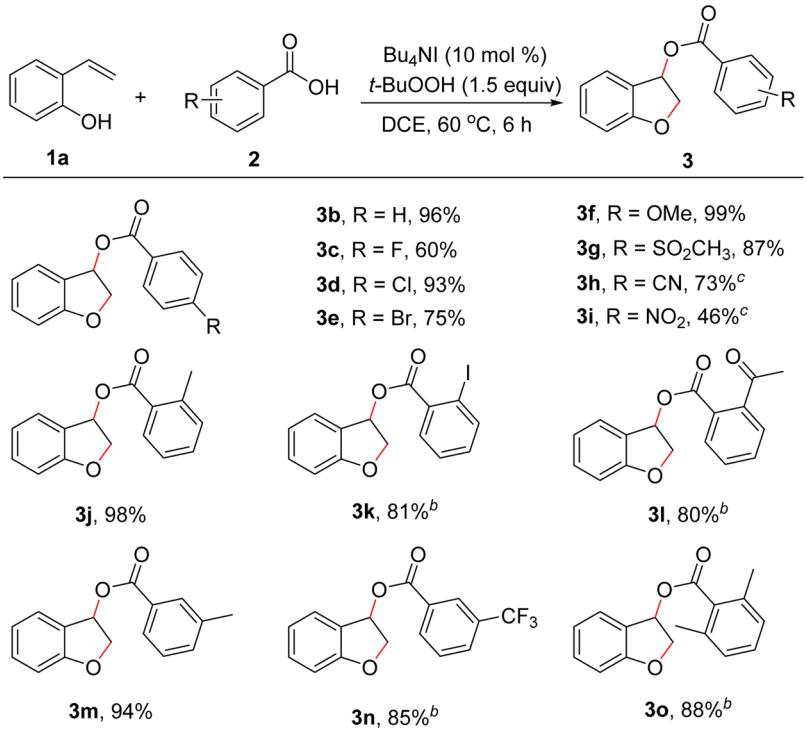
Scheme 2. Scope of Aryl Carboxylic Acids[a]



[a]**1a** (0.7 mmol), **2** (0.5 mmol), Bu_4NI (10 mol %), *t*-BuOOH (1.5 equiv), DCE (1.0 mL) under air, at 60 °C for 6 h. [b]Bu_4NI (20 mol %), *t*-BuOOH (3.0 equiv) was used. [c]Bu_4NI (50 mol %), *t*-BuOOH (3.0 equiv) was used.

results are summarized in Scheme 3. A series of aliphatic carboxylic were reacted with 2-vinylphenol **2a**, providing the corresponding products at excellent yields (**4c**−**4f**). Treatment with heteroaryl acids, including indazole and thiophene, also resulted in the production of 3-acyloxy-2,3-dihydrobenzofurans in moderate to excellent yields (**4i**−**4g**). Interestingly, when phenylglyoxylic acid was used as the reaction partner, it provided the 2,3-dihydrobenzofuran-3-yl benzoate **3b** in the yield of 86% via decarbonylation.[16]

Next, various 2-vinylphenols were examined for this transformation; they are presented in Scheme 4. Broad functionality tolerance was observed again, including bromo (**5a**), chloro (**5b**), nitro (**5d**), and methoxyl (**5e**). The use of substituents on terminal of 2-vinylphenols was also acceptable in the present system, resulting in products at excellent yields (**5g**−**5h**).

3-Iodo-2,3-dihydrobenzofuran was detected using LC−MS (Scheme 5a). Further investigation using control experiments were conducted to gain mechanistic insight into this reaction. When 2,2,6,6-tetra-methylpiperidine-*N*-oxyl (TEMPO), a well-known radical scavenger, was added to the reaction, product **3a** was isolated with a high yield of 97% (Scheme 5b), suggesting this 3-acyloxy-2,3- dihydrobenzofurans formation reaction is not a radical process. The in situ generation of hypoiodite results in the desired product **3a** at 52% yield (Scheme 5c). Interestingly, only trace amounts of **3a** were generated in the presence of KI (Table 1, entry 12). When the Bu_4NCl was added to the reaction as a phase transfer catalyst, product **3a** was isolated at 91% yield, suggesting that Bu_4N^+ was pivotal for this transformation (Scheme 5d).

On the basis of these observations and previous relevant studies, a plausible mechanism was proposed, as shown in Scheme 6. The active species, Bu_4NOI **A**, which is generated in situ from Bu_4NI in the presence of *t*-BuOOH,[13g,13i,17] reacts with 2-vinylphenol **1a** to give iodonium ion **B**.[18] Intramolecular cyclization of **B** generated the 3-iodo-2,3-dihydrobenzofuran **C**, which underwent nucleophilic substitution by carboxylic acid to release the desired 3-acyloxy-2,3-dihydrobenzofurans.

CONCLUSIONS

In conclusion, we have successfully developed an efficient Bu_4NI-catalyzed coupling of 2-vinylphenols with carboxylic acids, producing the 3-acyloxy-2,3-dihydrobenzofuran derivatives in moderate to excellent yields. Considering the ease of synthesis of 2-vinylphenols and the low cost of Bu_4NI and *t*-BuOOH, this reaction represents a simple and practical access to introduce an acyloxyl group to 2,3-dihydrobenzofurans. This study is currently being expanded with efforts to develop an asymmetric version of the synthesis of 3-acyloxy-2,3-dihydrobenzofuran.

EXPERIMENTAL SECTION

General Information. All manipulations were carried out under air atmosphere. Column chromatography was generally performed on silica gel (300−400 mesh) and reactions were monitored by thin layer chromatography (TLC) using UV light to visualize the course of the reactions. The ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) data were recorded with $CDCl_3$ as solvent at room temperature. The chemical shifts (δ) are reported in parts per million (ppm) and coupling constants (J) in hertz (Hz). ^1H NMR spectra were recorded with tetramethylsilane (δ = 0.00 ppm) as internal reference; ^{13}C NMR spectra were recorded with $CDCl_3$ (δ = 77.00 ppm) as internal reference.

General Procedures for the Synthesis of 3a−3o, 4a−4j, 5a−5h. Carboxylic acids (0.5 mmol), 2-vinylphenols (0.7 mmol), tetrabutylammonium iodide (Bu_4NI) (10−50 mol %), *tert*-butyl hydroperoxide (*t*-BuOOH) (1.5 or 3.0 equiv, 70% aqueous solution)

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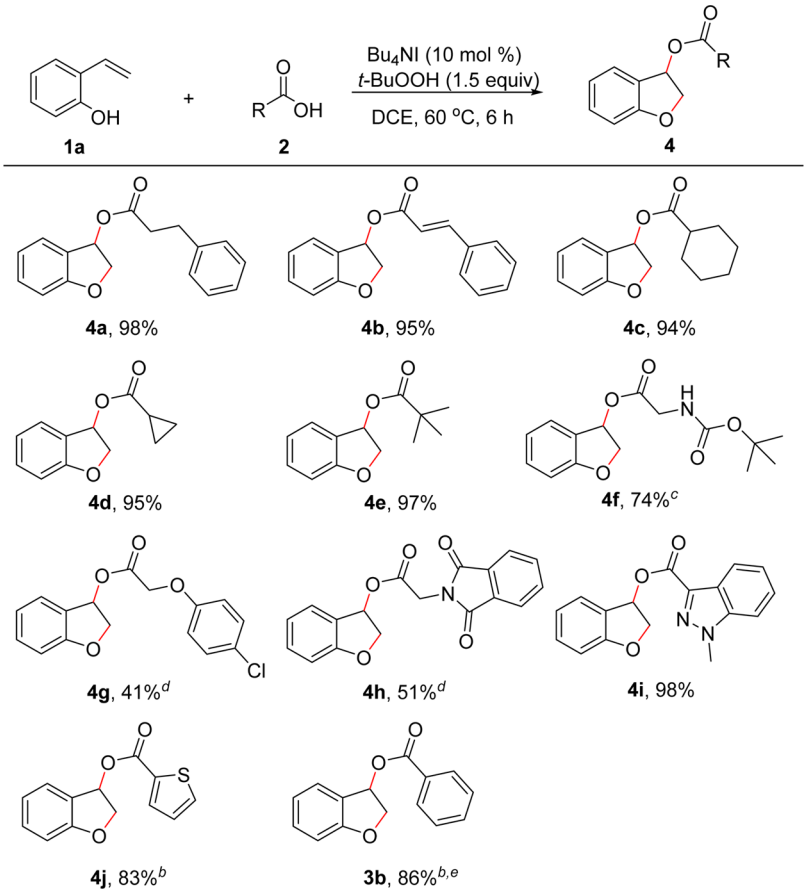
Scheme 3. Scope of Carboxylic Acids[a]



[a]**1a** (0.7 mmol), **2** (0.5 mmol), Bu_4NI (10 mol %), *t*-BuOOH (1.5 equiv), DCE (1.0 mL) under air, at 60 °C for 6 h. [b]Bu_4NI (20 mol %), *t*-BuOOH (3.0 equiv) was used. [c]Bu_4NI (30 mol %), *t*-BuOOH (3.0 equiv) was used. [d]Bu_4NI (50 mol %), *t*-BuOOH (3.0 equiv) was used. [e]Phenylglyoxylic acid was used.

and 1,2-dichloroethane (1.0 mL) were added to a test tube under air. The reaction mixture was stirred at 60 °C for 6 h. The reaction mixture was quenched with saturated Na_2SO_3 solution, extracted repeatedly with ethyl acetate, and dried over $MgSO_4$. Removal of the organic solvent followed by flash column chromatographic purification afforded products using petroleum and ethyl acetate.

*2,3-Dihydrobenzofuran-3-yl 4-(tert-Butyl)benzoate (**3a**).* Colorless oil, 99% yield (146 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.5 Hz, 2H), 7.51 (d, J = 7.4 Hz, 1H), 7.41 (d, J = 8.5 Hz, 2H), 7.31−7.27 (m, 1H), 6.95−6.90 (m, 2H), 6.48 (dd, J = 6.6, 2.4 Hz, 1H), 4.71 (dd, J = 11.4, 6.7 Hz, 1H), 4.63 (dd, J = 11.4, 2.5 Hz, 1H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 161.1, 156.8, 131.1, 129.6, 126.8, 125.2, 124.4, 120.9, 110.4, 76.0, 74.4, 35.0, 31.0; HRMS (ESI-TOF): Anal. Calcd for $C_{19}H_{20}O_3$ + Na^+, 319.1305; found, 319.1310. IR (neat, cm^{-1}): υ 2963, 1712, 1609, 1478, 1267, 1095, 751.

*2,3-Dihydrobenzofuran-3-yl Benzoate (**3b**).* White solid, 96% yield (115 mg), mp: 71−72 °C. ^{1}HNMR (400 MHz, $CDCl_3$) δ 8.01−7.99 (m, 2H), 7.53−7.48 (m, 2H), 7.39−7.35 (m, 2H), 7.31−7.27 (m, 1H), 6.95−6.91 (m, 2H), 6.47 (dd, J = 6.6, 2.5 Hz, 1H), 4.70 (dd, J = 11.4, 6.6 Hz, 1H), 4.63 (dd, J = 11.4, 2.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 161.1, 133.1, 131.2, 129.7, 129.6, 128.3, 126.8, 124.3, 121.0, 110.4, 76.0, 74.6; HRMS (ESI-TOF): Anal. Calcd for $C_{15}H_{12}O_3$ + Na^+, 263.0679; found, 263.0687. IR (neat, cm^{-1}): υ 2972, 1705, 1594, 1478, 1263, 1113, 709.

*2,3-Dihydrobenzofuran-3-yl 4-Fluorobenzoate (**3c**).* White solid, 60% yield (77 mg), mp: 55−57 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04−7.99 (m, 2H), 7.52 (d, J = 7.5 Hz, 1H), 7.32−7.28 (m, 1H), 7.08−7.03 (m, 2H), 6.96−6.91 (m, 2H), 6.47 (dd, J = 6.6, 2.4 Hz, 1H), 4.70 (dd, J = 11.5, 6.6 Hz, 1H), 4.63 (dd, J = 11.5, 2.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8 (d, J = 253.0 Hz), 165.3, 161.1, 132.3 (d, J = 9.3 Hz), 131.3, 126.8, 125.9 (d, J = 2.9 Hz), 124.2, 121.0, 115.5 (d, J = 21.9 Hz), 110.5, 76.0, 74.8; HRMS (ESI-TOF): Anal. Calcd for $C_{15}H_{11}FO_3$ + Na^+, 281.0584; found, 281.0590. IR (neat, cm^{-1}): υ 2962, 1703, 1600, 1479, 1271, 1103, 747.

*2,3-Dihydrobenzofuran-3-yl 4-Chlorobenzoate (**3d**).* White solid, 93% yield (127 mg), mp: 117−119 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94−7.91 (m, 2H), 7.51 (d, J = 7.5 Hz, 1H), 7.36−7.33 (m, 2H), 7.32−7.28 (m, 1H), 6.96−6.91 (m, 2H), 6.47 (dd, J = 6.5, 2.4 Hz, 1H), 4.70 (dd, J = 11.5, 6.6 Hz, 1H), 4.63 (dd, J = 11.5, 2.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 161.1, 139.6, 131.3, 131.0, 128.6, 128.0, 126.8, 124.1, 121.0, 110.5, 75.9, 74.9; HRMS (ESI-TOF): Anal. Calcd for $C_{15}H_{11}{}^{35}ClO_3$ + Na^+, 297.0289; $C_{15}H_{11}{}^{37}ClO_3$ + Na^+, 299.0259; found, 297.0284, 299.0255. IR (neat, cm^{-1}): υ 2964, 1704, 1592, 1479, 1270, 1101, 746.

*2,3-Dihydrobenzofuran-3-yl 4-Bromobenzoate (**3e**).* White solid, 75% yield (119 mg), mp: 130−131 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.6 Hz, 2H), 7.53−7.51 (m, 3H), 7.33−7.28 (m, 1H), 6.96−6.91 (m, 2H), 6.47 (dd, J = 6.5, 2.3 Hz, 1H), 4.70 (dd, J = 11.5, 6.6 Hz, 1H), 4.63 (dd, J = 11.5, 2.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 161.1, 131.6, 131.4, 131.2, 128.5, 128.3, 126.8, 124.0, 121.0, 110.5, 75.9, 75.0; HRMS (ESI-TOF): Anal. Calcd for $C_{15}H_{11}{}^{79}BrO_3$ + Na^+, 340.9784; $C_{15}H_{11}{}^{81}BrO_3$ + Na^+, 342.9763; found, 340.9786, 342.9762. IR (neat, cm^{-1}): υ 2963, 1704, 1599, 1477, 1269, 1101, 747.

*2,3-Dihydrobenzofuran-3-yl 4-Methoxybenzoate (**3f**).* White solid, 99% yield (133 mg), mp: 111−113 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.9 Hz, 2H), 7.52 (d, J = 7.4 Hz, 1H), 7.31−7.27 (m, 1H), 6.95−6.90 (m, 2H), 6.86 (d, J = 8.9 Hz, 2H), 6.45 (dd, J = 6.6, 2.3 Hz, 1H), 4.70 (dd, J = 11.4, 6.7 Hz, 1H), 4.62 (dd, J = 11.4, 2.5

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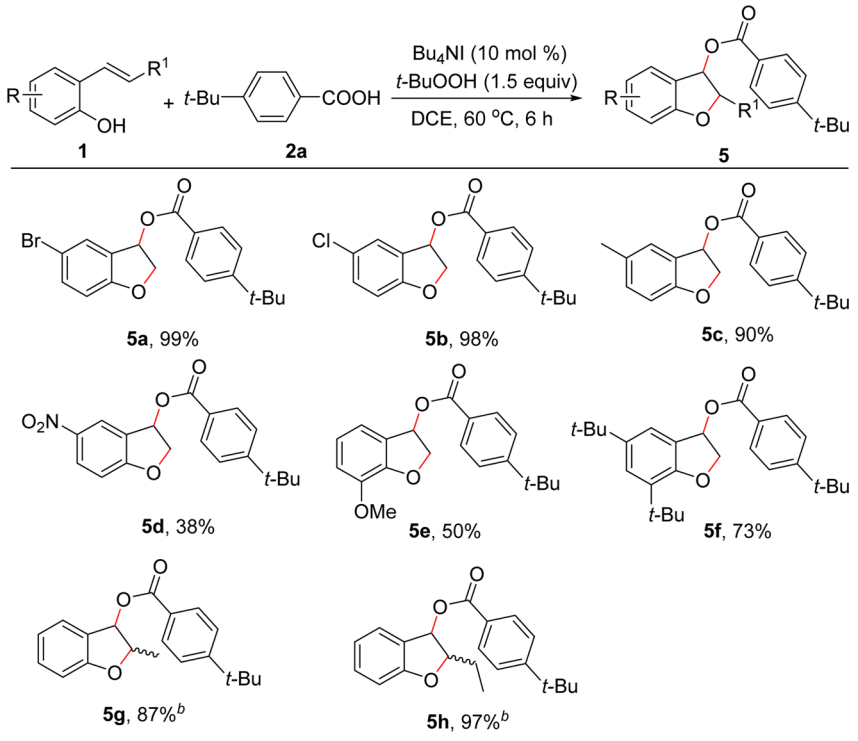
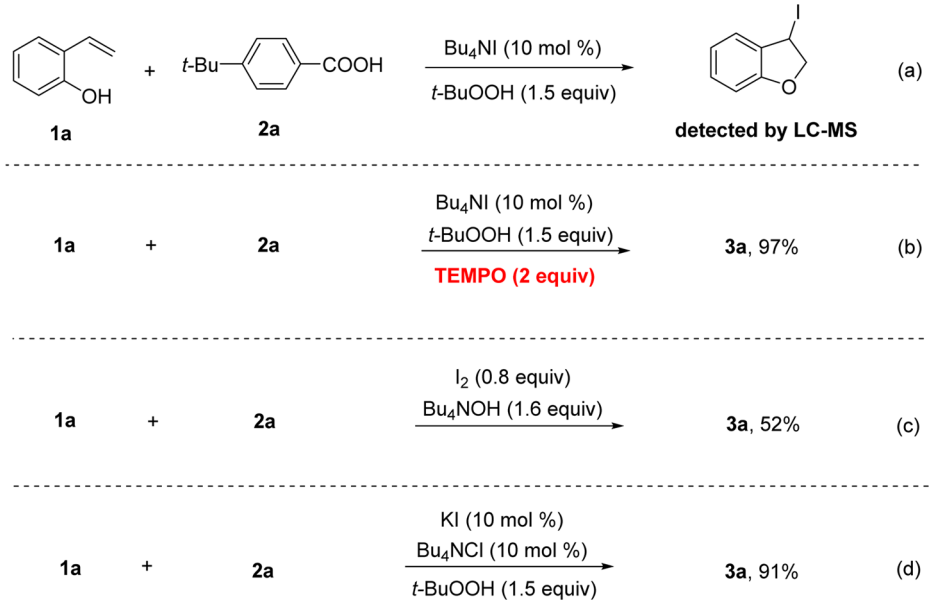
Scheme 4. Scope of 2-Vinylphenols[a]



[a]**1** (0.7 mmol), **2a** (0.5 mmol), Bu_4NI (10 mol %), *t*-BuOOH (1.5 equiv), DCE (1.0 mL) under air, at 60 °C for 6 h. [b]Bu_4NI (20 mol %), *t*-BuOOH (3.0 equiv) was used.

Scheme 5. Probe for Possible Mechanism



Hz, 1H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 163.5, 161.0, 131.7, 131.1, 126.8, 124.4, 121.9, 120.9, 113.5, 110.3, 76.0, 74.3, 55.3; HRMS (ESI-TOF): Anal. Calcd for $C_{16}H_{14}O_4 + Na^+$, 293.0784; found, 293.0798. IR (neat, cm^{-1}): υ 2961, 1696, 1602, 1480, 1271, 1096, 746.

2,3-Dihydrobenzofuran-3-yl 4-(Methylsulfonyl)benzoate (***3g***). White solid, 87% yield (138 mg), mp: 132−134 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20−8.18 (m, 2H), 7.99 (d, J = 8.5 Hz, 2H), 7.53 (d, J = 7.5 Hz, 1H), 7.34−7.30 (m, 1H), 6.98−6.92 (m, 2H), 6.53 (dd, J = 6.2, 2.5 Hz, 1H), 4.73 (dd, J = 11.6, 6.3 Hz, 1H), 4.68 (dd, J = 11.6, 2.6 Hz, 1H), 3.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 161.1, 144.3, 134.2, 131.5, 130.5, 127.3, 126.8, 123.7, 121.0, 110.5, 75.6, 75.5, 44.0; HRMS (ESI-TOF): Anal. Calcd for $C_{16}H_{14}O_5S + Na^+$, 341.0454; found, 341.0448. IR (neat, cm^{-1}): υ 2923, 1724, 1597, 1477, 1151, 752.

2,3-Dihydrobenzofuran-3-yl 4-Cyanobenzoate (***3h***). White solid, 73% yield (97 mg), mp: 91−92 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13−8.11 (m, 2H), 7.72−7.70 (m, 2H), 7.54−7.52 (m, 1H), 7.35−7.31 (m, 1H), 6.99−6.93 (m, 2H), 6.52 (dd, J = 6.4, 2.3 Hz, 1H), 4.73 (dd, J = 11.6, 6.4 Hz, 1H), 4.67 (dd, J = 11.6, 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 161.2, 133.4, 132.1, 131.6, 130.2, 126.8, 123.7, 121.1, 117.8, 116.6, 110.6, 75.7, 75.6; HRMS (ESI-TOF): Anal.

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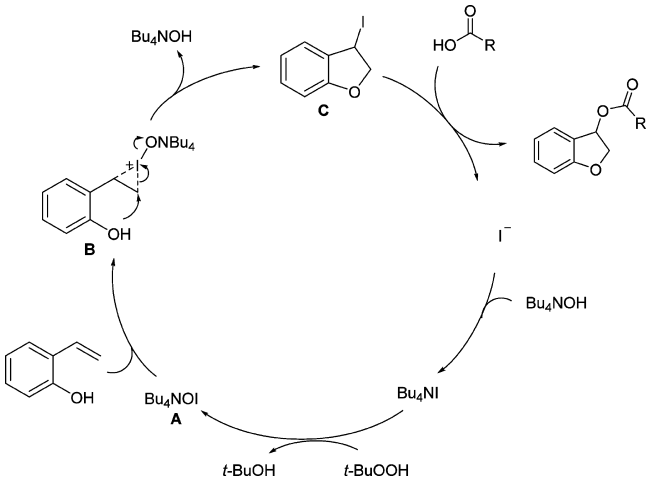
Scheme 6. Proposed Reaction Mechanism



Calcd for $C_{16}H_{11}NO_3$ + Na^+, 288.0631; found, 288.0627. IR (neat, cm^{-1}): υ 2919, 2233, 1720, 1597, 1477, 1267, 1100, 760.

*2,3-Dihydrobenzofuran-3-yl 4-Nitrobenzoate (**3i**).* White solid, 46% yield (65 mg), mp: 125−126 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27−8.25 (m, 2H), 8.20−8.18 (m, 2H), 7.54 (d, J = 7.5 Hz, 1H), 7.37−7.32 (m, 1H), 7.00−6.94 (m, 2H), 6.54 (dd, J = 6.3, 2.4 Hz, 1H), 4.74 (dd, J = 11.6, 6.3 Hz, 1H), 4.69 (dd, J = 11.6, 2.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 161.2, 150.6, 135.0, 131.7, 130.8, 126.9, 123.7, 123.5, 121.2, 110.6, 75.8, 75.7; HRMS (ESI-TOF): Anal. Calcd for $C_{15}H_{11}NO_5$ + Na^+, 308.0529; found, 308.0526. IR (neat, cm^{-1}): υ 2957, 1714, 1600, 1268, 1115, 769, 716.

*2,3-Dihydrobenzofuran-3-yl 2-methylbenzoate (**3j**).* Colorless oil, 98% yield (124 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87−7.84 (m, 1H), 7.53−7.51 (m, 1H), 7.36−7.32 (m, 1H), 7.30−7.26 (m, 1H), 7.20−7.14 (m, 2H), 6.95−6.90 (m, 2H), 6.45 (dd, J = 6.7, 2.5 Hz, 1H), 4.69 (dd, J = 11.4, 6.7 Hz, 1H), 4.61 (dd, J = 11.4, 2.6 Hz, 1H), 2.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 161.1, 140.4, 132.2, 131.6, 131.1, 130.7, 128.8, 126.7, 125.6, 124.4, 120.9, 110.4, 76.0, 74.4, 21.7; HRMS (ESI-TOF): Anal. Calcd for $C_{16}H_{14}O_3$ + Na^+, 277.0835; found, 277.0842. IR (neat, cm^{-1}): υ 2967, 1712, 1600, 1478, 1241, 1069, 735.

*2,3-Dihydrobenzofuran-3-yl 2-Iodobenzoate (**3k**).* Yellow oil, 81% yield (148 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95−87.93 (m, 1H), 7.74−7.71 (m, 1H), 7.57−7.55 (m, 1H), 7.33−7.28 (m, 2H), 7.11−7.07 (m, 1H), 6.97−6.91 (m, 2H), 6.51−6.49 (m, 1H), 4.70- 4.69 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 161.1, 141.2, 134.2, 132.8, 131.4, 131.0, 127.8, 126.9, 123.9, 121.0, 110.4, 94.1, 75.7, 75.4; HRMS (ESI-TOF): Anal. Calcd for $C_{15}H_{11}IO_3$ + Na^+, 388.9645; found, 388.9635. IR (neat, cm^{-1}): υ 2941, 1721, 1598, 1478, 1239, 1013, 737.

*2,3-Dihydrobenzofuran-3-yl 2-Acetylbenzoate (**3l**).* Colorless oil, 80% yield (113 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79−7.77 (m, 1H), 7.55−7.51 (m, 2H), 7.47−7.40 (m, 2H), 7.31−7.27 (m, 1H), 6.96−6.89 (m, 2H), 6.47−6.45 (m, 1H), 4.68−4.67 (m, 2H), 2.47 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.2, 166.8, 161.1, 142.2, 131.9, 131.3, 130.1, 129.6, 128.7, 126.8, 126.5, 123.7, 121.0, 110.4, 75.6, 75.4, 29.6; HRMS (ESI-TOF): Anal. Calcd for $C_{17}H_{14}O_4$ + Na^+, 305.0784; found, 305.0775. IR (neat, cm^{-1}): υ 2958, 1703, 1598, 1479, 1263, 1100, 753.

*2,3-Dihydrobenzofuran-3-yl 3-Methylbenzoate (**3m**).* White solid, 94% yield (119 mg), mp: 95−96 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.5 Hz, 2H), 7.52 (d, J = 7.4 Hz, 1H), 7.33−7.25 (m, 3H), 6.96−6.91 (m, 2H), 6.48 (dd, J = 6.6, 2.4 Hz, 1H), 4.70 (dd, J = 11.4, 6.6 Hz, 1H), 4.63 (dd, J = 11.4, 2.5 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 161.1, 138.1, 133.9, 131.2, 130.2, 129.5, 128.2, 126.9, 126.8, 124.4, 121.0, 110.4, 76.0, 74.6, 21.1; HRMS (ESI-TOF): Anal. Calcd for $C_{16}H_{14}O_3$ + Na^+, 277.0835; found, 277.0840. IR (neat, cm^{-1}): υ 2956, 1715, 1595, 1475, 1270, 1190, 945, 743.

*2,3-Dihydrobenzofuran-3-yl 3-(Trifluoromethyl)benzoate (**3n**).* White solid, 85% yield (131 mg), mp: 56−57 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 8.20 (d, J = 7.9 Hz, 1H), 7.79 (d, J = 7.8 Hz, 1H), 7.53−7.51 (m, 2H), 7.34−7.30 (m, 1H), 6.98−6.93 (m, 2H), 6.53 (dd, J = 6.3, 2.6 Hz, 1H), 4.75−4.66 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 161.2, 132.9, 131.5, 131.2, 130.9, 130.6, 129.73, 129.69, 129.66, 129.62, 129.0, 127.6, 126.9, 126.65, 126.61, 126.57, 126.53, 124.9, 124.0, 122.2, 121.1, 119.5, 110.6, 75.8, 75.4; HRMS (ESI-TOF): Anal. Calcd for $C_{16}H_{11}F_3O_3$ + Na^+, 331.0552; found, 331.0550. IR (neat, cm^{-1}): υ 2971, 1717, 1594, 1476, 1327, 1237, 1128, 753.

*2,3-Dihydrobenzofuran-3-yl 2,6-Dimethylbenzoate (**3o**).* White solid, 88% yield (118 mg), mp: 54−56 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55−7.53 (m, 1H), 7.31−7.26 (m, 1H), 7.16−7.12 (m, 1H), 6.98−6.89 (m, 4H), 6.53 (dd, J = 6.4, 2.3 Hz, 1H), 4.70 (dd, J = 11.4, 6.5 Hz, 1H), 4.63 (dd, J = 11.4, 2.4 Hz, 1H), 2.26 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.6, 161.1, 135.0, 132.9, 131.3, 129.5, 127.6, 126.7, 124.2, 121.0, 110.5, 75.7, 74.8, 19.6; HRMS (ESI-TOF): Anal. Calcd for $C_{17}H_{16}O_3$ + Na^+, 291.0992; found, 291.0988. IR (neat, cm^{-1}): υ 2971, 1713, 1597, 1478, 1263, 1113, 1055, 750.

*2,3-Dihydrobenzofuran-3-yl 3-Phenylpropanoate (**4a**).* Colorless oil, 98% yield (131 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.36 (m, 1H), 7.28−7.22 (m, 3H), 7.18−7.12 (m, 3H), 6.92−6.86 (m, 2H), 6.20 (dd, J = 6.7, 2.2 Hz, 1H), 4.53 (dd, J = 11.4, 6.7 Hz, 1H), 4.39 (dd, J = 11.4, 2.4 Hz, 1H), 2.91 (t, J = 7.7 Hz, 2H), 2.60 (t, J = 7.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 161.0, 140.0, 131.1, 128.4, 128.2, 126.6, 126.2, 124.2, 120.9, 110.3, 75.8, 74.1, 35.6, 30.7; HRMS (ESI-TOF): Anal. Calcd for $C_{17}H_{16}O_3$ + Na^+, 291.0992; found, 291.0987. IR (neat, cm^{-1}): υ 2972, 1714, 1597, 1478, 1263, 1055, 750.

*2,3-Dihydrobenzofuran-3-yl Cinnamate (**4b**).* White solid, 95% yield (126 mg), mp: 68−69 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 16.0 Hz, 1H), 7.51−7.45 (m, 3H), 7.34−7.26 (m, 4H), 6.96−6.90 (m, 2H), 6.42−6.36 (m, 2H), 4.64 (dd, J = 11.4, 6.6 Hz, 1H), 4.57 (dd, J = 11.4, 2.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 161.0, 145.5, 134.0, 131.2, 130.4, 128.8, 128.0, 126.7, 124.3, 120.9, 117.4, 110.4, 76.0, 74.1; HRMS (ESI-TOF): Anal. Calcd for $C_{17}H_{14}O_3$ + Na^+, 289.0835; found, 289.0832. IR (neat, cm^{-1}): υ 2959, 1699, 1629, 1476, 1163, 761.

*2,3-Dihydrobenzofuran-3-yl Cyclohexanecarboxylate (**4c**).* Colorless oil, 94% yield (116 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42−7.40 (m, 1H), 7.29−7.25 (m, 1H), 6.94−6.87 (m, 2H), 6.24 (dd, J = 6.8, 2.4 Hz, 1H), 4.61 (dd, J = 11.3, 6.8 Hz, 1H), 4.44 (dd, J = 11.3, 2.5 Hz, 1H), 2.32−2.24 (m, 1H), 1.90−1.84 (m, 2H), 1.77−1.70 (m, 2H), 1.62−1.58 (m, 1H), 1.47−1.37 (m, 2H), 1.30−1.17 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.8, 160.9, 131.0, 126.5, 124.5, 120.9, 110.3, 76.0, 73.7, 42.9, 28.8, 28.7, 25.6, 25.24, 25.21; HRMS (ESI-TOF): Anal. Calcd for $C_{15}H_{18}O_3$ + Na^+, 269.1148; found, 269.1147. IR (neat, cm^{-1}): υ 2931, 2855, 1726, 1599, 1163, 956, 751.

*2,3-Dihydrobenzofuran-3-yl Cyclopropanecarboxylate (**4d**).* Colorless oil, 95% yield (97 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44−7.42 (m, 1H), 7.30−7.26 (m, 1H), 6.95−6.88 (m, 2H), 6.24 (dd, J = 6.7, 2.4 Hz, 1H), 4.59 (dd, J = 11.3, 6.7 Hz, 1H), 4.49 (dd, J = 11.3, 2.5 Hz, 1H), 1.62−1.56 (m, 1H), 1.03−0.99 (m, 2H), 0.88−0.83 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.6, 161.0, 131.1, 126.6, 124.4, 120.9, 110.4, 76.0, 74.1, 12.8, 8.70, 8.69; HRMS (ESI-TOF): Anal. Calcd for $C_{12}H_{12}O_3$ + Na^+, 227.0679; found, 227.0686. IR (neat, cm^{-1}): υ 3016, 1720, 1599, 1479, 1394, 1162, 750.

*2,3-Dihydrobenzofuran-3-yl Pivalate (**4e**).* Colorless oil, 97% yield (107 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41−7.39 (m, 1H), 7.30−7.26 (m, 1H), 6.94−6.87 (m, 2H), 6.24 (dd, J = 6.9, 2.6 Hz, 1H), 4.63 (dd, J = 11.3, 7.0 Hz, 1H), 4.43 (dd, J = 11.3, 2.7 Hz, 1H), 1.18 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.4, 161.0, 131.1, 126.6, 124.6, 121.0, 110.4, 76.1, 74.0, 38.6, 27.0; HRMS (ESI-TOF): Anal. Calcd for $C_{13}H_{16}O_3$ + Na^+, 243.0992; found, 243.0990. IR (neat, cm^{-1}): υ 2972, 1723, 1600, 1467, 1278, 1141, 960, 751.

*2,3-Dihydrobenzofuran-3-yl (tert-Butoxycarbonyl)glycinate (**4f**).* Colorless oil, 74% yield (109 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 7.5 Hz, 1H), 7.31−7.27 (m, 1H), 6.95−6.88 (m, 2H), 6.30 (dd, J = 6.4, 2.0 Hz, 1H), 5.16 (s, 1H), 4.59 (dd, J = 11.5, 6.5 Hz, 1H), 4.52 (dd, J = 11.5, 2.3 Hz, 1H), 3.94−3.81 (m, 2H), 1.43 (s, 9H); ^{13}C

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NMR (100 MHz, $CDCl_3$) δ 170.2, 161.0, 155.6, 131.4, 126.7, 123.7, 121.0, 110.4, 79.9, 75.6, 75.0, 42.4, 28.2; HRMS (ESI-TOF): Anal. Calcd for $C_{15}H_{19}NO_5 + Na^+$, 316.1155; found, 316.1158. IR (neat, cm^{-1}): υ 3328, 2985, 2934, 1747, 1682, 1540, 1166, 955, 756.

*2,3-Dihydrobenzofuran-3-yl 2-(4-Chlorophenoxy)acetate (**4g**).* White solid, 41% yield (62 mg), mp: 79−80 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.45−7.43 (m, 1H), 7.34−7.29 (m, 1H), 7.23−7.20 (m, 2H), 6.96−6.90 (m, 2H), 6.81−6.77 (m, 2H), 6.37 (dd, J = 6.4, 2.1 Hz, 1H), 4.65−4.52 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 161.1, 156.2, 131.7, 129.5, 126.8, 123.7, 121.2, 116.0, 110.6, 75.5, 75.4, 65.4; HRMS (ESI-TOF): Anal. Calcd for $C_{16}H_{13}{}^{35}ClO_4 + Na^+$, 327.0395; $C_{16}H_{13}{}^{37}ClO_4 + Na^+$, 329.0365; found, 327.0399, 329.0373. IR (neat, cm^{-1}): υ 2916, 1750, 1600, 1480, 1172, 1079, 959, 826, 748.

*2,3-Dihydrobenzofuran-3-yl 2-(1,3-Dioxoisoindolin-2-yl)acetate (**4h**).* White solid, 51% yield (82 mg), mp: 108−109 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.88−7.85 (m, 2H), 7.76−7.73 (m, 2H), 7.43 (d, J = 7.5 Hz, 1H), 7.32−7.28 (m, 1H), 6.95−6.88 (m, 2H), 6.33 (dd, J = 6.2, 2.4 Hz, 1H), 4.62−4.53 (m, 2H), 4.43 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 167.1, 161.0, 134.2, 131.8, 131.5, 126.8, 123.4, 123.4, 121.1, 110.4, 75.7, 75.5, 38.8; HRMS (ESI-TOF): Anal. Calcd for $C_{18}H_{13}NO_5 + Na^+$, 346.0686; found, 346.0679. IR (neat, cm^{-1}): υ 2922, 1714, 1482, 1417, 1176, 949, 712.

*2,3-Dihydrobenzofuran-3-yl 1-Methyl-1H-indazole-3-carboxylate (**4i**).* White solid, 98% yield (144 mg), mp: 134−135 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.2 Hz, 1H), 7.61 (d, J = 7.4 Hz, 1H), 7.40−7.35 (m, 2H), 7.31−7.22 (m, 2H), 6.96−6.91 (m, 2H), 6.64−6.61 (m, 1H), 4.80−4.73 (m, 2H), 4.09 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1, 161.0, 140.7, 133.8, 131.1, 126.9, 126.6, 124.1, 123.2, 123.0, 121.8, 120.8, 110.3, 109.3, 75.7, 74.5, 36.1; HRMS (ESI-TOF): Anal. Calcd for $C_{17}H_{14}N2O_3 + Na^+$, 317.0897; found, 317.0891. IR (neat, cm^{-1}): υ 2974, 1704, 1598, 1474, 1208, 1111, 750.

*2,3-Dihydrobenzofuran-3-yl Thiophene-2-carboxylate (**4j**).* White solid, 83% yield (102 mg), mp: 64−65 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.78−7.76 (m, 1H), 7.53−7.52 (m, 2H), 7.32−7.28 (m, 1H), 7.06−7.04 (m, 1H), 6.96−6.91 (m, 2H), 6.45 (dd, J = 6.3, 2.7 Hz, 1H), 4.71−4.62 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9, 161.1, 133.8, 133.2, 132.9, 131.3, 127.7, 126.9, 124.1, 121.0, 110.4, 75.8, 74.9; HRMS (ESI-TOF): Anal. Calcd for $C_{13}H_{10}O_3S + Na^+$, 269.0243; found, 269.0232. IR (neat, cm^{-1}): υ 3106, 2977, 1698, 1595, 1464, 1414, 1254, 1092, 736.

*5-Bromo-2,3-dihydrobenzofuran-3-yl 4-(tert-Butyl)benzoate (**5a**).* White solid, 99% yield (185 mg), mp: 66−68 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.5 Hz, 2H), 7.63 (d, J = 2.1 Hz, 1H), 7.42 (d, J = 8.5 Hz, 2H), 7.38−7.35 (m, 1H), 6.78 (d, J = 8.6 Hz, 1H), 6.44 (dd, J = 6.8, 2.6 Hz, 1H), 4.73 (dd, J = 11.4, 6.8 Hz, 1H), 4.65 (dd, J = 11.4, 2.7 Hz, 1H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 160.2, 157.1, 133.9, 129.7, 129.6, 126.8, 126.5, 125.3, 112.6, 112.0, 76.5, 73.8, 35.0, 31.0; HRMS (ESI-TOF): Anal. Calcd for $C_{19}H_{19}{}^{79}BrO_3 + Na^+$, 397.0410; $C_{19}H_{19}{}^{81}BrO_3 + Na^+$, 399.0389; found, 397.0405, 399.0378. IR (neat, cm^{-1}): υ 2925, 1705, 1606, 1471, 1238, 1114, 809, 671.

*5-Chloro-2,3-dihydrobenzofuran-3-yl 4-(tert-Butyl)benzoate (**5b**).* Colorless oil, 98% yield (161 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 7.96−7.93 (m, 2H), 7.49 (d, J = 2.3 Hz, 1H), 7.43−7.40 (m, 2H), 7.24−7.21 (m, 1H), 6.82 (d, J = 8.6 Hz, 1H), 6.43 (dd, J = 6.8, 2.6 Hz, 1H), 4.74 (dd, J = 11.4, 6.8 Hz, 1H), 4.65 (dd, J = 11.4, 2.7 Hz, 1H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 159.7, 157.1, 131.1, 129.6, 126.8, 126.5, 126.2, 125.6, 125.3, 111.4, 76.5, 73.9, 35.0, 31.0; HRMS (ESI-TOF): Anal. Calcd for $C_{19}H_{19}{}^{35}ClO_3 + Na^+$, 353.0915; $C_{19}H_{19}{}^{37}ClO_3 + Na^+$, 355.0885; found, 353.0902, 355.0882. IR (neat, cm^{-1}): υ 2963, 1706, 1608, 1476, 1267, 1092, 707.

*5-Methyl-2,3-dihydrobenzofuran-3-yl 4-(tert-Butyl)benzoate (**5c**).* Colorless oil, 90% yield (140 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 7.97−7.94 (m, 2H), 7.42−7.39 (m, 2H), 7.32−7.31 (m, 1H), 7.10−7.07 (m, 1H), 6.80 (d, J = 8.2 Hz, 1H), 6.45 (dd, J = 6.7, 2.5 Hz, 1H), 4.69 (dd, J = 11.3, 6.7 Hz, 1H), 4.61 (dd, J = 11.3, 2.6 Hz, 1H), 2.29 (s, 3H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 159.0, 156.8, 131.7, 130.3, 129.6, 127.0, 126.9, 125.2, 124.4, 109.9, 76.1, 74.6, 35.0, 31.0, 20.6; HRMS (ESI-TOF): Anal. Calcd for $C_{20}H_{22}O_3 + Na^+$, 333.1461; found, 333.1458. IR (neat, cm^{-1}): υ 2963, 1708, 1608, 1493, 1266, 1113, 775, 707.

*5-Nitro-2,3-dihydrobenzofuran-3-yl 4-(tert-Butyl)benzoate (**5d**).* White solid, 38% yield (64 mg), mp: 153−155 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, J = 2.4 Hz, 1H), 8.28−8.26 (m, 1H), 7.96−7.94 (m, 2H), 7.46−7.44 (m, 2H), 6.99 (d, J = 9.0 Hz, 1H), 6.53 (dd, J = 6.9, 2.7 Hz, 1H), 4.93 (dd, J = 11.6, 7.0 Hz, 1H), 4.81 (dd, J = 11.6, 2.8 Hz, 1H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.02, 165.96, 157.5, 142.2, 129.7, 128.1, 126.1, 125.9, 125.4, 123.6, 110.6, 78.0, 72.8, 35.1, 31.0; HRMS (ESI-TOF): Anal. Calcd for $C_{19}H_{19}NO_5 + Na^+$, 364.1155; found, 364.1153. IR (neat, cm^{-1}): υ 2967, 1700, 1601, 1517, 1334, 1257, 945, 674.

*7-Methoxy-2,3-dihydrobenzofuran-3-yl 4-(tert-Butyl)benzoate (**5e**).* White solid, 50% yield (182 mg), mp: 109−110 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.96−7.94 (m, 2H), 7.43−7.41 (m, 2H), 7.15−7.10 (m, 1H), 6.93−6.88 (m, 2H), 6.52 (dd, J = 6.7, 2.5 Hz, 1H), 4.79 (dd, J = 11.4, 6.8 Hz, 1H), 4.70 (dd, J = 11.4, 2.6 Hz, 1H), 3.91 (s, 3H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 157.0, 149.9, 145.0, 129.6, 126.8, 125.6, 125.3, 121.7, 118.5, 113.4, 76.7, 74.9, 56.0, 35.0, 31.0; HRMS (ESI-TOF): Anal. Calcd for $C_{20}H_{22}O_4 + Na^+$, 349.1410; found, 349.1408. IR (neat, cm^{-1}): υ 2969, 1703, 1595, 1496, 1264, 940, 773.

*5,7-Di-tert-butyl-2,3-dihydrobenzofuran-3-yl 4-(tert-Butyl)-benzoate (**5f**).* Colorless oil, 73% yield (149 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.5 Hz, 2H), 7.38 (d, J = 1.7 Hz, 1H), 7.31 (d, J = 1.8 Hz, 1H), 6.47 (dd, J = 6.8, 2.3 Hz, 1H), 4.72 (dd, J = 11.3, 6.9 Hz, 1H), 4.61 (dd, J = 11.3, 2.5 Hz, 1H), 1.40 (s, 9H), 1.32 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 157.2, 156.8, 143.7, 133.0, 129.7, 127.1, 125.3, 125.1, 124.1, 120.8, 75.8, 75.0, 35.1, 34.5, 34.4, 31.7, 31.1, 29.4; HRMS (ESI-TOF): Anal. Calcd for $C_{27}H_{36}O_3 + Na^+$, 431.2557; found, 431.2545. IR (neat, cm^{-1}): υ 2957, 1716, 1610, 1483, 1267, 1098, 707.

*2-Methyl-2,3-dihydrobenzofuran-3-yl 4-(tert-Butyl)benzoate (**5g**).* Colorless oil, 87% yield (135 mg), dr = 6.7:1 (as an inseparable mixture). ^1H NMR (400 MHz, $CDCl_3$) δ 7.98−7.96 (m, 2H + 2H × 0.15), 7.48−7.40 (m, 3H + 3H × 0.15), 7.29−7.25 (m, 1H + 1H × 0.15), 6.92−6.88 (m, 2 + 2H × 0.15), 6.43 (d, J = 6.2 Hz, 1H), 6.13 (d, J = 2.2 Hz, 1H × 0.15), 4.89−4.82 (m, 1H + 1H × 0.15), 1.56 (d, J = 6.6 Hz, 3H), 1.50 (d, J = 6.7 Hz, 3H × 0.15), 1.33 (s, 9H × 0.15), 1.31 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 165.9, 160.6, 160.5, 157.1, 156.9, 131.2, 131.0, 129.63, 129.59, 127.2, 127.01, 126.96, 126.90, 125.7, 125.4, 125.31, 125.28, 120.9, 120.8, 110.5, 110.2, 84.3, 81.6, 80.3, 74.3, 41.6, 35.0, 31.0, 18.9, 13.9, 13.8; HRMS (ESI-TOF): Anal. Calcd for $C_{20}H_{22}O_3 + Na^+$, 333.1461; found, 333.1460. IR (neat, cm^{-1}): υ 2964, 1714, 1609, 1466, 1266, 1095, 752.

*2-Ethyl-2,3-dihydrobenzofuran-3-yl 4-(tert-Butyl)benzoate (**5h**).* Colorless oil, 97% yield (157 mg), dr = 10:1 (as an inseparable mixture). ^1H NMR (400 MHz, $CDCl_3$) δ 7.97−7.94 (m, 2H + 2H × 0.1), 7.50−7.48 (m, 1H + 1H × 0.1), 7.42 (d, J = 8.5 Hz, 2H + 2H × 0.1), 7.28−7.24 (m, 1H + 1H × 0.1), 6.91−6.87 (m, 2H + 2H × 0.1), 6.46 (d, J = 6.0 Hz, 1H), 6.24 (d, J = 2.5 Hz, 1H × 0.1), 4.60−4.55 (m, 1H + 1H × 0.1), 2.08−1.93 (m, 2H + 2H × 0.1), 1.33 (s, 9H × 0.1), 1.30 (s, 9H), 1.13 (t, J = 7.4 Hz, 3H), 1.07 (t, J = 7.2 Hz, 3H × 0.1); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 165.8, 160.7, 160.5, 156.8, 131.13, 130.98, 129.6, 127.05, 127.03, 125.9, 125.4, 125.30, 125.26, 120.8, 120.6, 110.3, 110.2, 89.0, 86.8, 78.7, 73.6, 35.0, 31.0, 26.3, 21.8, 21.7, 10.5, 9.4; HRMS (ESI-TOF): Anal. Calcd for $C_{21}H_{24}O_3 + Na^+$, 347.1618; found, 347.1621. IR (neat, cm^{-1}): υ 2965, 1714, 1609, 1466, 1266, 1090, 752.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01941.

Crystallographic data for compound **3f** (CIF)

Copies of ^1H NMR, ^{13}C NMR, and HRMS spectra for all products, and single-crystal X-ray data (PDF)

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AUTHOR INFORMATION

Corresponding Authors

*E-mail: shaoying810724@163.com

*E-mail: wanxb@suda.edu.cn

Notes

The authors declare no competing financial interest.

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