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N-Heterocyclic Carbene-Mediated Oxidative Esterification of Aldehydes: Ester Formation and Mechanistic Studies

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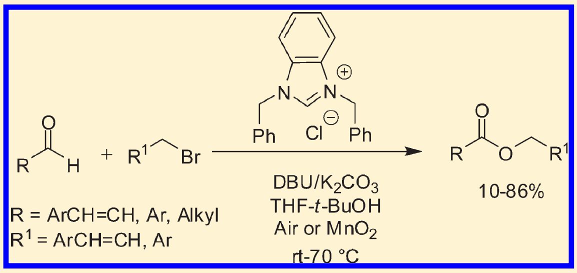
S Supporting Information

ABSTRACT: An unexpected N-heterocyclic carbene-catalyzed esterification of α,β-unsaturated aldehydes including aromatic aldehydes with reactive cinnamyl bromides in the presence of air oxygen or MnO_2 as an oxidant is described. In the presence of oxygen, halogenated and electron-deficient aldehydes react smoothly to furnish esters in good yields. Great efforts have been made on mechanistic studies to deduce a plausible mechanism, based on the experimental results and isotopic labeling experiment.



INTRODUCTION

Ester is the most commonly encountered functionality, prevalent in a wide range of organic compounds. In general, classical ester synthesis involves reaction of a stoichiometric amount of "activated carboxylates"[1] with appropriate nucleophiles. A plethora of protocols have been reported for ester synthesis, out of which oxidative esterification of aldehydes via oxidation of hemiacetals, acetals, and cyanohydrins has become more sought after.[2,3] Nowadays, N-heterocyclic carbene (NHC)-catalyzed one-pot esterification of aldehydes has become prominent.[4−6] Recently, Rovis and Bode groups developed an organocatalytic NHC-catalyzed transformation of α-halogenated aliphatic aldehydes to the corresponding esters via internal redox esterification.[4b−d] Later, the same strategy has been applied to other substrates such as α,β-unsaturated aldehydes,[4e−k] epoxy aldehydes,[4l] and formylcyclopropanes.[4m] During the past few years, NHC-mediated generation of the Breslow intermediate and its succeeding reaction with sp^2-carbon-centered electrophiles are being significantly explored.[7] However, comparable reaction of Breslow intermediate with sp^3-centered electrophiles is extremely rare.[8] By taking the above facts into consideration, we[9] envisioned the carbon−carbon bond formation reaction between cinnamaldehyde **1a** and cinnamyl bromide **2a** (Scheme 1). However, to our surprise, the above stated reaction furnished cinnamyl cinnamate **3a**. Recently, Gois and Deng groups reported aerobic oxidative esterification of aromatic aldehydes with boronic acids and benzyl bromides, respectively.[8a,10] Cinnamate and benzoate ester derivatives play a significant role in synthetic organic, pharmaceutical, and material chemistry.[11] Similarly, naturally occurring sintenin and its synthetic analogues represent cinnamyl cinnamate based derivatives,[12] which exhibit cytotoxic and glucosidase inhibitory activities. The above stated facts and the unexpected formation of cinnamyl cinnamate motivated us to develop a simple and efficient esterification reaction. Herein, we wish to report a NHC-catalyzed synthesis of cinnamyl cinnamate and cinnamyl benzoate derivatives from α,β-unsaturated aldehydes and aromatic aldehydes respectively.

RESULTS AND DISCUSSION

Initial investigations were carried out on the reaction of cinnamaldehyde **1a** (1.0 equiv) with cinnamyl bromide **2a** (1.2 equiv) catalyzed by easily accessible NHC catalysts **A**−**F** (0.2 equiv) and DBU (0.2 equiv) as a base under N_2 atmosphere in THF-*t*-BuOH (9:1) solvent mixture (Figure 1). After 48 h, benzimidazolium NHC catalyst **D1** gave cinnamyl cinnamate ester **3a** in 10% yield instead of desired C−C bond forming product **3a′**. When the same reaction was performed under atmospheric air, the yield of **3a** increased to 27%. From this initial observation, it was anticipated that the reaction walks off through an oxygen insertion type mechanism. This is quite similar to the previously reported results by Chen[13] and Deng.[8a]

Next, the reaction was examined with other catalysts (**A**−**F**) in the presence of air; catalysts **A1**, **A2**, **B**, and **C** showed very poor catalytic activity toward ester **3a** after 48 h (Table 1, entries 1−4). The catalysts **E** and **F** were completely inert toward ester **3a** formation (entries 6 and 7). By using the same catalyst (i.e., **D1**), the same set of reactions was screened with other bases such as K_2CO_3, NaH, NaOMe, and *t*-BuOK. However, there was no significant improvement observed in the yield of **3a** (entries 8−11). Initially, it was speculated that HBr generated from the reaction mixture might lower the yield of **3a**. Hence, additional organic/inorganic bases such as pyridine, 2,6-dimethylpyridine, K_2CO_3, Cs_2CO_3, and $NaHCO_3$ were added to the reaction. When bases such as pyridine, 2,6-dimethylpyridine, and DMAP were used as an additive, the desired ester **3a** was formed in poor yield along

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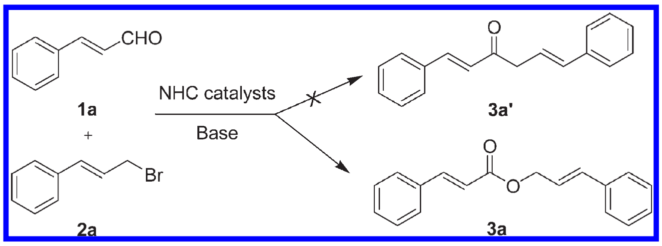
Scheme 1. Unexpected Formation of Cinnamyl Cinnamate



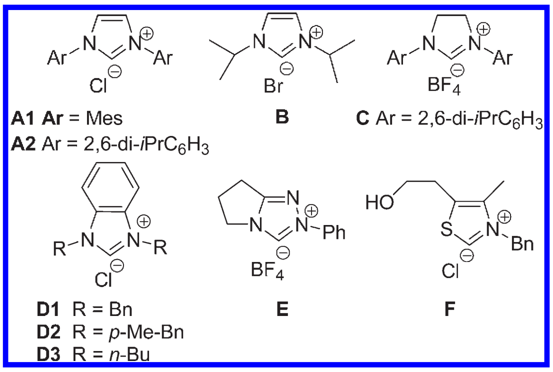


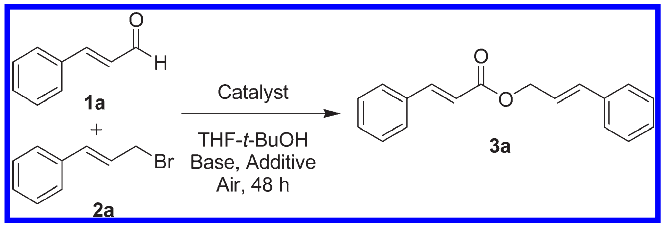
Figure 1. Evaluation of N-heterocyclic carbene precursors on the reaction.

with some other inseparable and undesired compounds (Table 1, entries 12−14). Other inorganic bases such as $NaHCO_3$ and Cs_2CO_3 provided the desired ester **3a** in 30 and 43%, respectively (entries 16 and 17). In addition, when the reaction was conducted with excess DBU (i.e., 1.5 equiv, for 30 min), most of the cinnamyl bromide was decomposed in the reaction mixture and only trace amount of ester **3a** was observed (from TLC). Noteworthy, among the additives tested, K_2CO_3 furnished ester **3a** in the best yield of 72% after 48 h (entry 15). Other benzimidazolium catalysts such as **D2** and **D3** were also investigated for this catalytic esterification (entries 18 and 19, 48 and 38% for **D2** and **D3**, respectively). It can be seen that, among the benzimidazolium NHC-carbene catalysts, catalyst **D1** was found to be the most suitable to perform the esterification.

Furthermore, we have also screened the leaving fitness of the cinnamyl halides. Among −Cl, −Br, −OAc, −OCO_2Et, and −OTs, bromo was found to be the best leaving group (Table 2, entries 1−5). In summary, the optimum condition for the NHC-catalyzed esterification involved a suspended solution of NHC catalysts **D1** (0.2 equiv), cinnamaldehyde (1.0 equiv), cinnamyl bromide (1.2 equiv), and K_2CO_3 (1.5 equiv) in THF-*t*-BuOH (9:1) with DBU (0.2 equiv) and ultimately furnished cinnamyl cinnamate **3a** in 72% after 48 h.

Encouraged by these results, next, we investigated the scope of this catalytic method for the synthesis of various cinnamyl cinnamate derivatives (Table 3). Under the optimal conditions, cinnamaldehyde scaffolds were varied as shown in Table 3. Electron-withdrawing substituents such as *p*-bromo, *o*-bromo, *o*-chloro, *p*-chloro, and *p*-nitro gave the corresponding cinnamyl cinnamate derivatives in good to excellent yields (Table 3, entries 2−6). Whereas cinnamaldehyde with an electron-donating substituent such as 2-$MeOC_6H_4$ produced the desired cinnamte in moderate yield at 70 °C after 48 h (Table 3, entry 9). 2-Furan cinnamaldehyde and aliphatic α,β-unsaturated aldehydes such as crotonaldehyde also responded well to this catalytic method, providing the cinnamates in 58 and 51% yields, respectively, under the same reaction conditions (Table 3, entries 7 and 8).

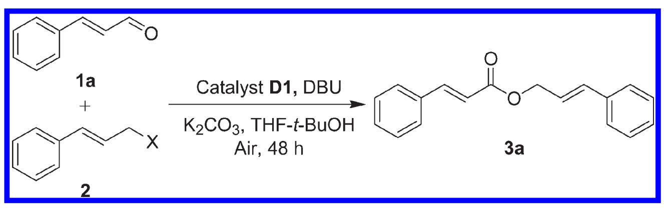
Table 1. Optimization of Reaction Conditions for the Ester Formation[a]



entry	catalyst	base	additive	yield (%)
1	**A1**	DBU	none	<5
2	**A2**	DBU	none	<5
3	**B**	DBU	none	trace
4	**C**	DBU	none	<5
5	**D1**	DBU	none	27
6	**E**	DBU	none	0
7	**F**	DBU	none	0
8	**D1**	K_2CO_3	none	0
9	**D1**	NaH	none	trace
10	**D1**	NaOMe	none	<5
11	**D1**	*t*-BuOK	none	8
12	**D1**	DBU	pyridine	34[b]
13	**D1**	DBU	2,6-lutidine	35[b]
14	**D1**	DBU	DMAP	23[b]
15	**D1**	DBU	K_2CO_3	72
16	**D1**	DBU	$NaHCO_3$	30
17	**D1**	DBU	Cs_2CO_3	43
18	**D2**	DBU	K_2CO_3	48
19	**D3**	DBU	K_2CO_3	38

[a] Reaction conditions: aldehyde **1a** (1 equiv), cinnamyl bromide **2a** (1.2 equiv), catalyst (0.2 equiv), and additive (1.5 equiv) were mixed together in 5 mL/mmol of THF, *t*-BuOH (5:1 ratio) in the presence of air and finally base DBU (0.2 equiv) was added, 25 °C, 48 h. [b] Desired ester **3a** was formed in poor yield along with some other inseparable and unidentified compounds.

Table 2. Optimization Studies To Investigate Effects of the Leaving Group on the Reaction[a]



entry	leaving group (X)	time (h)	yield (%)
1	Cl	48	63
2	Br	48	72
3	OTs	48	trace
4	OCO_2Et	48	0
5	OAc	48	0

[a] Reaction conditions are identical to that of Table 1.

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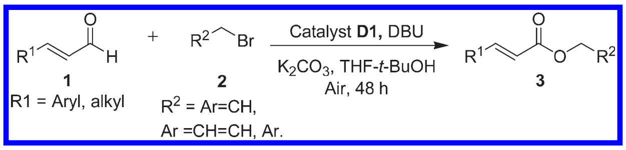
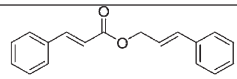
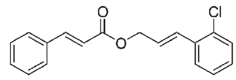
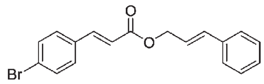
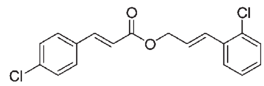
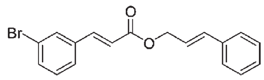
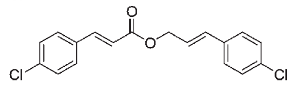
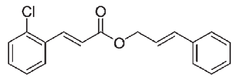
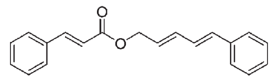
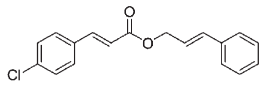
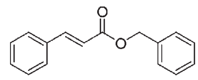
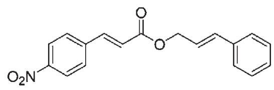
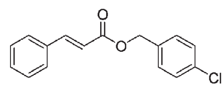
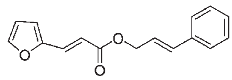
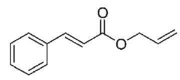
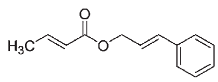
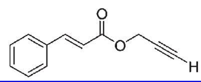
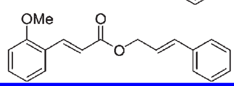
Table 3. Exploring the Substrate Scope of α,β-Unsaturated Aldehydes in the Synthesis of Cinnamyl Cinnamate Derivatives[a]



Entry	Product 3		Yield (%)	Entry	Product 3		Yield (%)
1		**3a**	72	10		**3j**	61
2		**3b**	86	11		**3k**	76
3		**3c**	78	12		**3l**	81
4		**3d**	76	13		**3m**	68
5		**3e**	86	14[d]		**3n**	46(23)[e]
6		**3f**	56	15[d]		**3o**	48(21)[e]
7		**3g**	58	16[d]		**3p**	13(34)[e]
8		**3h**	51[b]	17[d]		**3q**	11(42)[e]
9		**3i**	53[c]				

[a] Reaction conditions: aldehyde **1** (1.0 equiv), alkyl bromide **2** (1.2 equiv), benzimidazolium catalyst **D1** (0.2 equiv), and K_2CO_3 (1.5 equiv) were mixed together in 5 mL/mmol of THF, *t*-BuOH (9:1 ratio) in the presence of air and finally DBU (0.2 equiv) was added, 25 °C, 48 h. [b] Aldehyde (1.5 equiv) was used. [c] Reaction was performed at 70 °C. [d] Alkyl bromide was used (1.5 equiv) after 72 h. [e] Yields in parentheses refer to the recovery of unreacted cinnamaldehyde.

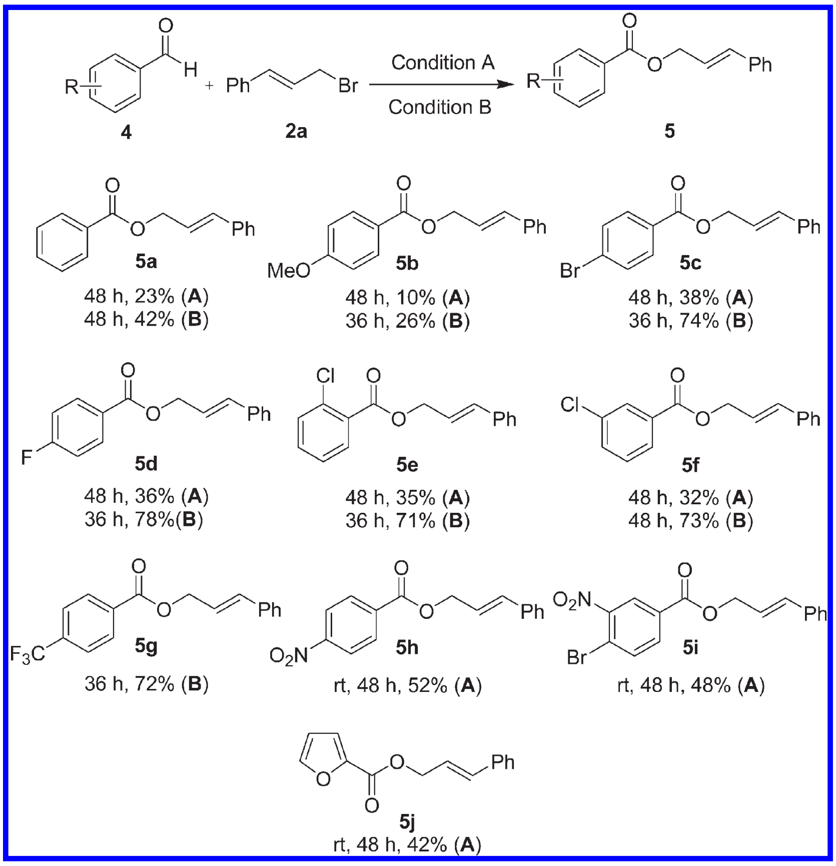
Next, we extended this catalytic protocol toward other cinnamyl bromide derivatives. 2-Chloro, 4-chlorocinnamyl bromide, and extended cinnamyl bromide derivative (i.e., (5-bromopenta-1,3-dienyl)benzene) smoothly underwent this catalytic reaction and gave the desired esters in good yields (entries 10−13). Simple benzyl bromide derivatives also produced benzyl cinnamate esters in moderate yields along with unreacted cinnamaldehyde after 72 h (entries 14 and 15). Next we utilized this protocol for the synthesis of cinnamate ester from simple allyl and propargyl bromides as alkylating reagents. Both allyl and propargyl bromides gave the esters in 13 and 11%, respectively (entries 16 and 17).

After successful development of aerobic oxidation of enals with reactive cinnamyl bromides, we extended this protocol to aromatic aldehydes. Initially, benzaldehyde was reacted with cinnamyl bromide under the optimized conditions, that is, in the presence of air. Trace amount of cinnamyl benzoate (**5a**) was obtained after 48 h at room temperature. However, when the reaction was carried out at 70 °C, the yield was slightly increased to 23%. The low yields could be attributed to the lower reactivity of the benzaldehyde. Employment of MnO_2 (5.0 equiv) as an oxidant resulted in cinnamyl benzoate in 42% yield at 70 °C, in the presence of additional water (1.5 equiv) after 48 h. Here the reaction proceeds mostly via acid formation and then simple conventional alkylation in the presence of base. Therefore, by using MnO_2 as an oxidant, we carried out the reaction on other aromatic aldehydes and conducted a comparative study with air oxygen versus MnO_2 as oxidants (Scheme 2). Electron-rich 4-methoxy benzaldehyde also delivered the desired ester but in low yield of 26%. On the contrary, when MnO_2 was used as an oxidant, reactive halogenated and electron-withdrawing constituents containing aromatic aldehydes (i.e., 4-BrC_6H_4CHO, 4-FC_6H_4CHO, 2-ClC_6H_4CHO, 3-ClC_6H_4CHO, and 4-$CF_3C_6H_4CHO$) underwent reaction smoothly with cinnamyl bromide to give esters **5c**−**5g** in excellent yields (Scheme 2). Electron-withdrawing substituent containing, for example, 4-$NO_2C_6H_4CHO$ and 4-bromo-3-nitrobenzaldehyde also readily gave the esters with cinnamyl bromides in good yields (Scheme 2; **5h** and **5i**) even at room temperature in the presence of air. Heteroaromatic aldehydes such as furfural also responded well for the ester **5j** with cinnamyl bromide at room temperature in the presence of air oxygen.

■ MECHANISM STUDIES

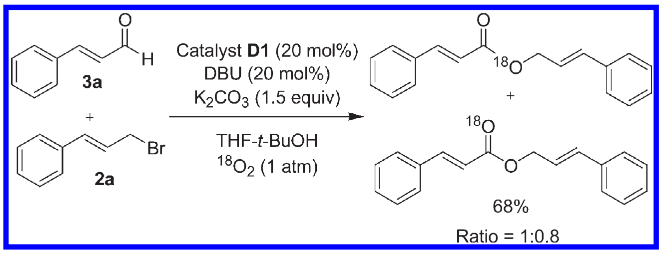
To investigate the possible reaction mechanism, we conducted several experiments. First, cinnamaldehyde was reacted with methanol (2.5 equiv) under the same catalytic conditions in the presence of an oxygen balloon (1 atm). However, no considerable amount of

Scheme 2. Synthesis of Esters from Aromatic Aldehydes[a]



[a] Condition A: catalyst **D1** (0.3 equiv), DBU (0.3 equiv), K_2CO_3 (1.5 equiv), 5 mL/mmol of THF, *t*-BuOH (9:1 ratio), air, 70 °C or rt. Condition B: catalyst **D1** (0.3 equiv), DBU (0.3 equiv), K_2CO_3 (1.5 equiv), MnO_2 (5 equiv), H_2O (1.5 equiv), 5 mL/mmol of THF, *t*-BuOH (9:1 ratio), 70 °C.

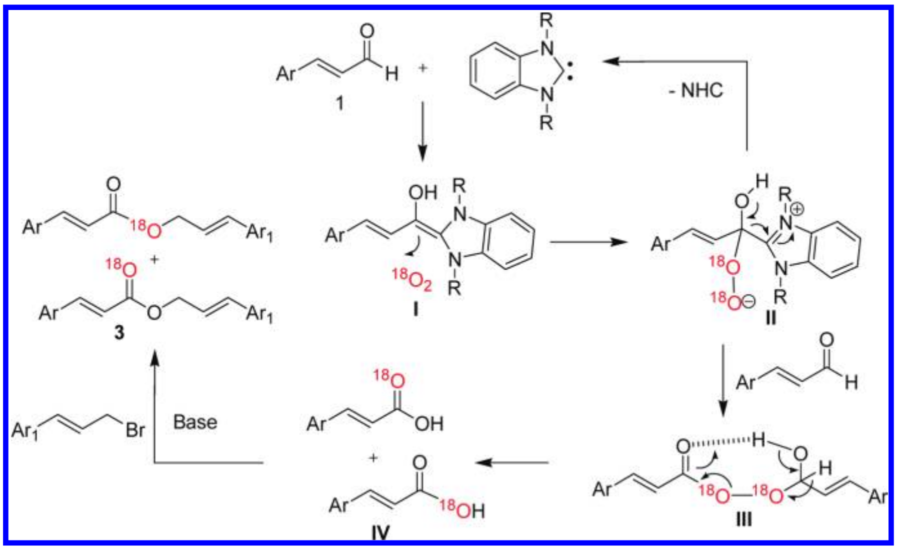
Scheme 3. Isotopic Labeling Experiment with $^{18}O_2$



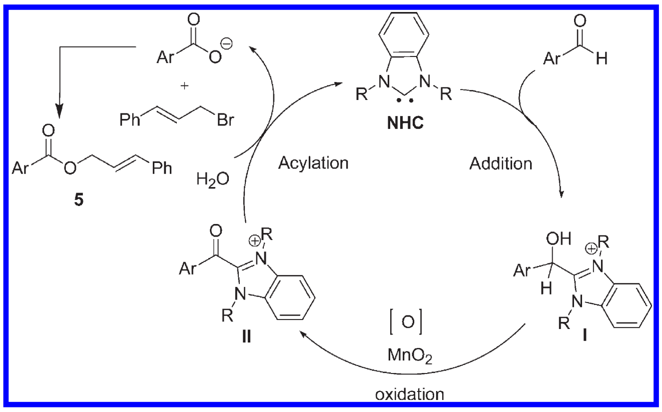
methyl ester was detected even after 48 h. This experiment clearly suggests that, for enals, active acyl imidazolium intermediate was not formed during the course of the reaction when oxygen was used as an oxidant. Second, when the same reaction was conducted in the presence of water, the yield of the ester **3a** was decreased to lower than 10%. Therefore, the concentration of water in the reaction mixture is the detrimental factor to obtain good yields of the ester. Further, to understand the mechanism clearly, an isotopic labeling experiment was conducted using $^{18}O_2$ (Scheme 3). It was observed that the reaction occurred smoothly in the presence of $^{18}O_2$ atmosphere to provide ester in 68% yield. The GC-MS[10,14] spectrum of the precursor ion at m/z at 266.1 exhibited an intensive characteristic fragment at m/z 131.0 and 133.0 with 1:0.8 ratio, which could be attributed to the fragments of $[266.1\text{-PhCH=CHCH}_2{}^{18}\text{OH}]^+$ and $[266.1\text{-PhCH=CHCH}_2{}^{16}\text{OH}]^+$. This isotopic labeling experiment clearly proves that dioxygen plays an important role in the transformation of esters from enals. On the basis of the isotope labeling experiment, an oxygen insertion type mechanism (Scheme 4) is proposed. As shown in Scheme 4, the Breslow intermediate **I** reacts with $^{18}O_2$ (dioxygen) to deliver the corresponding peroxide intermediate **II**. Subsequently, after the carbene liberation, peroxide intermediate **II** forms a corresponding deprotonated peracid intermediate (doubly ^{18}O-marked at the peracid moiety). It is well-known[15] that peracid reacts with another molecule of aldehyde to provide hydroxy peroxyl adduct **III**, which in turn generates 2 equiv of corresponding acids **IV**. At this juncture, the acid (carboxylate under the conditions) must bear exactly one labeled O atom. Alkylation with the allyl bromide leads to the ester **3** which bears the ^{18}O labeling both at the carbonyl O atom and also at the alcohol O atom (around 1:1 ratio), in good agreement with the isotopic labeling experiment.

When MnO_2 was used as an oxidant, the reaction proceeds through a different pathway. As shown in Scheme 5, the catalytic cycle is initiated by generation of carbene, which undergoes nucleophilic addition to the aldehyde, forming a tetrahedral intermediate **I**. This is oxidized to acyl benzimidazolium intermediate **II** by MnO_2.[16] Next, this acyl imidazolium intermediate[17] was trapped by water to form acid[18] as an intermediate with regeneration of carbene **D**. In the presence of base, the carboxylic anion reacts with cinnamyl bromides to produce ester **5**.[19] In an

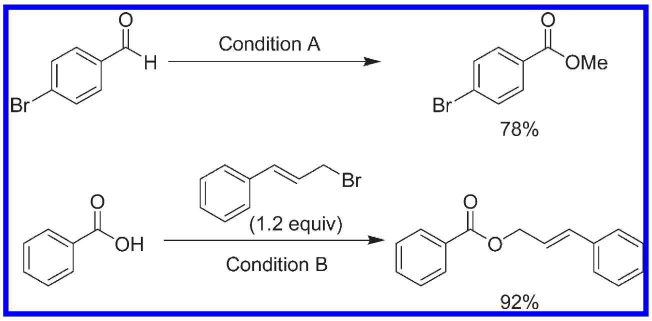
Scheme 4. Mechanism Illustrating the Insertion of Oxygen in the Reaction



Scheme 5. Esterification of Aromatic Aldehydes with MnO_2 as an Oxidant



Scheme 6. Experimental Reactions with 4-Bromobenzaldehyde and Benzoic Acid[a]



[a] Condition A: catalyst **D1** (0.3 equiv), DBU (0.3 equiv), THF-^{t}BuOH, MnO_2 (5 equiv), MeOH (2.5 equiv), 70 °C, 24 h. Condition B: catalyst **D1** (0.3 equiv), DBU (0.3 equiv), K_2CO_3 (1.5 equiv), THF-^{t}BuOH, 70 °C, 24 h.

attempt to support the above elucidated mechanism (Scheme 5), we conducted an experiment in the presence of methanol (2.5 equiv) with 4-bromobenzaldehyde under the same reaction conditions. Moreover, when MnO_2 was used as an oxidant, methyl 4-bromobenzoate was formed in 78% yield, which confirms the formation of an active acyl imidazolium intermediate during the course of the reaction (Scheme 6). Another parallel experiment was carried out with simple benzoic acid and cinnamyl bromide as an alkylating agent using the same optimized reaction condition where ester **5a** was obtained in 92% yield after 24 h (Scheme 6).

■ CONCLUSION

In conclusion, we presented a mild NHC-catalyzed unexpected transformation of cinnamyl cinnamate esters from cinnamaldehyde derivatives by employing simple air oxygen as an oxidant. This is an alternate method for the synthesis of esters from reactive alkyl halides and α,β-unsaturated or aromatic aldehydes. Electron-deficient aldehydes comparatively gave better yields than electron-rich aldehydes. A salient feature of this methodology is that the reaction proceeds without *cis*—*trans* isomerization of the α,β-olefinic linkage in the cinnamyl cinnamate ester derivatives. In the presence of MnO_2 as an oxidant, aromatic aldehydes provide esters in good yields.

■ EXPERIMENTAL SECTION

α,β-Unsaturated aldehydes **1a**, **1f**, **1h**, and **1i** and all aromatic aldehydes were purchased from suppliers and were used without any further purification. Other cinnamaldehyde derivatives were prepared from the standard literature procedures.[20] Cinnamyl bromide derivatives **2** were prepared from their corresponding alcohols and PBr_3 treatment.[21] All of the NHC catalysts were purchased from commercial suppliers, and catalysts **D1**, **D2**, and **D3** were prepared with standard literature procedure.[22]

General Procedure for Synthesis of Cinnamyl Cinnamate Derivatives 3. To a well-stirred suspended solution of NHC catalyst **D1** (50 mg, 0.15 mmol), cinnamaldehyde (100 mg, 0.76 mmol), cinnamyl bromide (180 mg, 0.91 mmol), and K_2CO_3 (160 mg, 1.14 mmol) in THF-*t*-BuOH (4 mL, 9:1 ratio) was added a catalytic amount of DBU (25 mg, 0.15 mmol) in the presence of air. Then the reaction mixture was allowed to stir at 25 °C. On completion, the reaction was diluted with EtOAc (5 mL) and filtered through a short plug of Celite. The combined organic layer was washed with brine and dried over Na_2SO_4. After removal of the solvents under reduced pressure, the crude reaction mixture was subjected to purification by flash column chromatography using EtOAc/hexanes as eluent to afford 144 mg of cinnamyl cinnamate **3a** in 72% yield.

Characterization of 3-Phenylacrylic acid-3-phenyl allyl ester[2e] (3a): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.78 (d, *J* = 16.0 Hz, 1H), 7.53−7.51 (m, 2H), 7.42−7.26 (m, 8H), 6.70 (d, *J* = 16.0 Hz, 1H), 6.48 (d, *J* = 16.0 Hz, 1H), 6.39−6.33 (m, 1H), 4.87 (dd, *J* = 6.4, 1.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.8, 145.1, 136.3, 134.3, 130.4, 128.9 (2C), 128.6 (2C), 128.15 (2C), 128.11 (3C), 126.7, 123.3, 117.9, 65.2; HRMS (EI) calcd for $C_{18}H_{16}O_2$ 265.1229 *m/z* (M + H)$^+$, found 265.1232 *m/z*.

3-(4-Bromophenyl)acrylic acid 3-phenyl allyl ester (3b): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.65 (d, *J* = 16.0 Hz, 1H), 7.52−7.49 (m, 2H), 7.41−7.24 (m, 7H), 6.70 (d, *J* = 16.0 Hz, 1H), 6.46 (d, *J* = 16.0 Hz, 1H), 6.38−6.31 (m, 1H), 4.86 (dd, *J* = 6.4, 1.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.5, 143.8, 136.3, 134.5, 133.4, 132.2 (2C), 129.6 (2C), 128.7 (2C), 128.2, 126.7 (2C), 124.7, 123.2, 118.7, 65.4; HRMS (EI) calcd for $C_{18}H_{15}O_2Br$ 365.0153 *m/z* (M + Na)$^+$, found 365.0149 *m/z*.

3-(3-Bromophenyl)acrylic acid 3-phenyl allyl ester (3c): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.66 (d, *J* = 4.1 Hz, 1H), 7.63 (d, *J* = 16.0 Hz, 1H), 7.51−7.48 (m, 1H), 7.43−7.34 (m, 3H), 7.33−7.30 (m, 2H), 7.32−7.23 (m, 2H), 6.70 (d, *J* = 16.0 Hz, 1H), 6.46 (d, *J* = 16.0 Hz, 1H), 6.38−6.31 (m, 1H), 4.87 (d, *J* = 6.9 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.4, 143.4, 136.5, 136.3, 134.5, 133.2, 130.9, 130.5, 128.7 (2C), 128.2, 126.7, 126.8 (2C), 123.2, 123.1, 119.5, 65.4; HRMS (EI) calcd for $C_{18}H_{15}O_2Br$ 365.0153 *m/z* (M + Na)$^+$, found 365.0150 *m/z*.

3-(2-Chlorophenyl)acrylic acid 3-phenyl allyl ester (3d): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.13 (d, *J* = 16.4 Hz, 1H), 7.63−7.61 (m, 1H), 7.42−7.25 (m, 8H), 6.72 (d, *J* = 16.0 Hz, 1H), 6.47 (d, *J* = 16.0 Hz, 1H), 6.39−6.32 (m, 1H), 4.89 (d, *J* = 6.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.4, 141.1, 136.3, 135.1, 134.5, 132.8, 131.3, 130.3, 128.8 (2C), 128.2, 127.8, 127.2, 126.8 (2C), 123.3, 120.7, 65.5; HRMS (EI) calcd for $C_{18}H_{15}O_2Cl$ 321.0658 *m/z* (M + Na)$^+$, found 321.0654 *m/z*.

3-(4-Chlorophenyl)acrylic acid 3-phenyl allyl ester (3e): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.66 (d, *J* = 16.4 Hz, 1H), 7.46−7.26 (m, 9H), 6.70 (d, *J* = 16.0 Hz, 1H), 6.47 (d, *J* = 16.0 Hz, 1H), 6.38−6.31 (m, 1H), 4.86 (d, *J* = 6.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.5, 143.7, 136.3, 136.2, 134.4, 132.9, 129.35 (2C), 129.3 (2C), 128.7 (2C), 128.2, 126.7 (2C), 123.2, 118.6, 63.3; HRMS (EI) calcd for $C_{18}H_{15}O_2Cl$ 321.0658 *m/z* (M + Na)$^+$, found 321.0656 *m/z*.

3-(4-Nitrophenyl)acrylic acid 3-phenyl allyl ester (3f): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.25 (d, *J* = 8.7 Hz, 2H), 7.75 (d, *J* = 16.0 Hz, 1H), 7.68 (d, *J* = 9.1 Hz, 2H), 7.44−7.26 (m, 5H), 6.72 (d, *J* = 16.0 Hz, 1H), 6.60 (d, *J* = 16.0 Hz, 1H), 6.39−6.31 (m, 1H), 4.89 (dd, *J* = 6.4, 1.2 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.9, 148.6, 142.2, 140.5, 136.2, 134.8, 128.8 (4C), 128.3, 126.7 (2C), 124.3 (2C), 122.8, 122.3, 65.7; HRMS (EI) calcd for $C_{18}H_{15}O_4N$ 332.0899 *m/z* (M + Na)$^+$, found 332.0902 *m/z*.

3-Furan-2-yl acrylic acid 3-phenyl allyl acetate (3g): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.49−7.23 (m, 7H), 6.69 (d, *J* = 16.0 Hz, 1H), 6.60 (d, *J* = 3.2 Hz, 1H), 6.47−6.45 (m, 1H), 6.38−6.30 (m, 2H), 4.84 (dd, *J* = 6.4, 1.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.9, 151.0, 144.9, 136.4, 134.2, 131.5, 128.7 (2C), 128.1, 126.7 (2C), 123.4, 115.6, 115.0, 112.4, 65.2; HRMS (EI) calcd for $C_{16}H_{14}O_3$ 255.1021 *m/z* (M + H)$^+$, found 255.1029 *m/z*.

But-2-enoic acid 3-phenyl allyl ester[23] (3h): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40−7.20 (m, 5H), 7.07−6.97 (m, 1H), 6.65 (d, *J* = 16.0 Hz, 1H), 6.34−6.27 (m, 1H), 5.88 (dd, *J* = 16.0 Hz, 1.4 Hz, 1H), 4.78 (dd, *J* = 6.4, 1.4 Hz, 2H), 1.88 (d, *J* = 6.4, Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.4, 145.2, 136.4, 134.1, 128.7 (2C), 128.2, 126.7 (2C), 123.5, 122.6, 64.9, 18.1; HRMS (EI) calcd for $C_{13}H_{14}O_2$ 203.1072 *m/z* (M + H)$^+$, found 203.1072 *m/z*.

3-(2-Methoxyphenyl)acrylic acid 3-phenyl allyl ester (3i): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.04 (d, *J* = 16.0 Hz, 1H), 7.52−7.50 (m, 1H), 7.44−7.23 (m, 6H), 6.97−6.90 (m, 1H), 6.92 (d, *J* = 8.0 Hz, 1H), 6.72 (d, *J* = 16.0 Hz, 1H), 6.59 (d, *J* = 16.0 Hz, 1H), 6.40−6.35 (m, 1H), 4.87 (dd, *J* = 6.4, 1.2 Hz, 2H), 3.88 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 167.3, 158.4, 140.6, 136.3, 134.0, 131.6, 129.0, 128.6 (2C), 128.0, 126.7 (2C), 123.6, 123.4, 120.7, 118.4, 111.2, 65.0, 55.5; HRMS (EI) calcd for $C_{19}H_{18}O_3$ 295.1334 *m/z* (M + H)$^+$, found 295.1333 *m/z*.

3-Phenyl acrylic acid 3-(2-chlorophenyl)allyl ester (3j): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.77 (d, *J* = 16.0 Hz, 1H), 7.59−7.55 (m, 3H), 7.41−7.36 (m, 4H), 7.26−7.20 (m, 2H), 7.13 (d, *J* = 16.0 Hz, 1H), 6.51 (d, *J* = 16.0 Hz, 1H), 6.41−6.34 (m, 1H), 4.93 (d, *J* = 6.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.7, 145.2, 134.42, 134.4, 133.3, 130.4, 130.1, 129.8, 129.1, 128.9 (2C), 128.1 (2C), 127.0, 126.9, 126.2, 117.8, 65.0; HRMS (EI) calcd for $C_{18}H_{15}O_2Cl$ 321.0658 *m/z* (M + Na)$^+$, found 321.0655 *m/z*.

3-(4-Chlorophenyl)acrylic acid 3-(2-chlorophenyl)allyl ester (3k): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.68 (d, *J* = 16.0 Hz, 1H), 7.56−7.54 (m, 1H), 7.47−7.44 (m, 2H), 7.38−7.28 (m, 3H), 7.26−7.18 (m, 2H), 7.10 (d, *J* = 16.0 Hz, 1H), 6.46 (d, *J* = 16.0 Hz, 1H), 6.38−6.30 (m, 1H), 4.91 (dd, *J* = 6.4, 1.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.5, 143.8, 136.4, 134.5, 133.4, 132.9, 130.2, 129.8, 129.4 (2C), 129.3 (2C), 129.2, 127.1, 127.0, 126.1, 118.5, 65.1; HRMS (EI) calcd for $C_{18}H_{14}O_2Cl_2$ 355.0269 *m/z* (M + Na)$^+$, found 355.0273 *m/z*.

3-(4-Chlorophenyl)acrylic acid 3-(4-chlorophenyl)allyl ester (3l): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.67 (d, *J* = 16.0 Hz, 1H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.36−7.23 (m, 6H), 6.65 (d, *J* = 16.0 Hz, 1H), 6.44 (d, *J* = 16.0 Hz, 1H), 6.36−6.28 (m, 1H), 4.86 (dd, *J* = 6.4, 1.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.5, 143.9, 136.4, 134.8, 133.9, 133.1, 132.9, 129.4 (2C), 129.3 (2C), 128.9 (2C), 127.9 (2C), 123.4, 118.5, 65.1; HRMS (EI) calcd for $C_{18}H_{14}O_2Cl_2$ 355.0269 *m/z* (M + Na)$^+$, found 355.0271 *m/z*.

3-Phenyl acrylic acid 5-phenylpenta-2,4-dienyl ester (3m): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.73 (d, *J* = 16.0 Hz, 1H), 7.55−7.52 (m, 2H), 7.43−7.20 (m, 8H), 6.83−6.77 (m, 1H), 6.61 (d, *J* = 16.0 Hz, 1H), 6.54−6.47 (m, 2H), 6.00−5.91 (m, 1H), 4.80 (d, *J* = 6.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.8, 145.2, 137.0, 134.7, 134.5, 133.9, 130.4, 129.0 (2C), 128.7 (2C), 128.2 (2C), 127.9, 127.8, 127.1, 126.6 (2C), 118.0, 65.0; HRMS (EI) calcd for $C_{20}H_{18}O_2$ 313.1204 *m/z* (M + Na)$^+$, found 313.1215 *m/z*.

3-Phenyl acrylic acid benzyl ester[2e] (3n): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.72 (d, *J* = 16.0 Hz, 1H), 7.51−7.50 (m, 2H), 7.45−7.31 (m, 8H), 6.48 (d, *J* = 16.0 Hz, 1H), 5.24 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.9, 145.3, 136.1, 134.4, 130.4, 129.0 (2C), 128.7 (2C), 128.4, 128.3 (2C), 128.2 (2C), 118.0, 66.4; HRMS (EI) calcd for $C_{16}H_{14}O_2$ 261.0891 *m/z* (M + Na)$^+$, found 261.0904 *m/z*.

3-Phenyl acrylic acid 4-chlorobenzyl ester[24] (3o): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.72 (d, *J* = 16.0 Hz, 1H), 7.53−7.50 (m, 2H), 7.41−7.32 (m, 7H), 6.47 (d, *J* = 16.0 Hz, 1H), 5.21 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.8, 145.5, 134.7, 134.4, 134.3, 130.6, 129.8 (2C), 129.0 (2C), 128.9 (2C), 128.2 (2C), 117.7, 65.6.

3-Phenyl acrylic acid allyl ester[2e] (3p): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.73 (d, *J* = 16.0 Hz, 1H), 7.55−7.52 (m, 2H), 7.40−7.38 (m, 3H), 6.48 (d, *J* = 16.0 Hz, 1H), 6.08−5.96 (m, 1H), 5.38 (dd, *J* = 16.0, 1.4 Hz, 1H), 5.28 (dd, *J* = 16.0, 1.4 Hz, 1H), 4.72 (dd, *J* = 6.0, 1.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.7, 145.2, 134.5, 132.4, 130.5, 129.0 (2C), 128.2 (2C), 118.4, 118.0, 65.4; HRMS (EI) calcd for $C_{12}H_{12}O_2$ 189.0916 *m/z* (M + H)$^+$, found 189.0909 *m/z*.

3-Phenyl acrylic acid 3-phenyl-2-ynyl ester (3q): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.74 (d, *J* = 16.0 Hz, 1H), 7.55−7.52 (m, 2H), 7.42−7.37 (m, 3H), 6.47 (d, J = 16.0 Hz, 1H), 4.82 (d, J = 2.3 Hz, 2H), 2.51 (t, J = 2.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.3, 146.2, 134.3, 130.8, 129.1 (2C), 128.4 (2C), 117.2, 78.0, 75.1, 52.2; HRMS (EI) calcd for $C_{12}H_{10}O_2$ 209.0578 m/z $(M + Na)^+$, found 209.0584 m/z.

General Procedure for Synthesis of Cinnamyl Benzoate Derivatives Using MnO_2 as an Oxidant (5). To a well-stirred suspended solution of NHC-carbene catalyst **D1** (54 mg, 0.16 mmol), 4-bromobenzaldehyde (100 mg, 0.54 mmol), cinnamyl bromide (130 mg, 0.65 mmol), K_2CO_3 (120 mg, 0.81 mmol), and MnO_2 (240 mg, 2.7 mmol) in THF-*t*-BuOH (4 mL, 9:1 ratio) was added a catalytic amount of DBU (24 mg, 0.16 mmol). After a few minutes, water (15 μL, 0.81 mmol) was added in the reaction mixture and stirred for 36 h at 70 °C. After completion of the reaction, the reaction mixture was diluted with EtOAc (5 mL) and filtered through a short plug of Celite. After removal of the solvents under reduced pressure, the crude reaction mixture was subjected to purification by flash column chromatography using EtOAc/hexanes as eluent to afford 126 mg of cinnamyl benzoate **5c** in 74% yield.

Benzoic acid 3-phenyl allyl ester[25] (5a): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.08 (d, J = 7.76, 2H), 7.56−7.52 (m, 1H), 7.44−7.39 (m, 4H), 7.33−7.23 (m, 3H), 6.72 (d, J = 16.0 Hz, 1H), 6.43−6.36 (m, 1H), 4.97 (d, J = 6.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.5, 136.4, 134.4, 133.2, 130.4, 129.8 (2C), 128.8 (2C), 128.5 (2C), 128.2, 126.8 (2C), 123.4, 65.7; HRMS (EI) calcd for $C_{16}H_{14}O_2$ 261.0891 m/z $(M + Na)^+$, found 261.0875 m/z.

4-Methoxybenzoic acid 3-phenyl allyl ester[26] (5b): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.04 (d, J = 9.1 Hz, 2H), 7.42−7.40 (m, 2H), 7.32 (t, J = 7.6 Hz, 2H), 7.27−7.23 (m, 1H), 6.91 (d, J = 9.1 Hz, 2H), 6.72 (d, J = 15.6 Hz, 1H), 6.44−6.36 (m, 1H), 4.95 (dd, J = 6.4, 1.4 Hz, 2H), 3.84 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 166.3, 163.6, 136.4, 134.2, 131.8 (2C), 128.8 (2C), 128.2, 126.8 (2C), 123.7, 122.8, 113.8 (2C), 65.4, 55.6.

4-Bromobenzoic acid 3-phenyl allyl ester (5c): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.92 (d, J = 8.7 Hz, 2H), 7.56 (d, J = 8.7 Hz, 2H), 7.42−7.26 (m, 5H), 6.72 (d, J = 16.0 Hz, 1H), 6.41−6.34 (m, 1H), 4.95 (dd, J = 6.6, 1.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.8, 136.25, 134.7, 131.9 (2C), 131.35 (2C), 129.25, 128.8 (2C), 128.35, 128.3, 126.8 (2C), 123.1, 66.0.

4-Fluorobenzoic acid 3-phenyl allyl ester (5d): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.12−8.05 (m, 2H), 7.44−7.24 (m, 5H), 7.13−7.05 (m, 2H), 6.73 (d, J = 16.0 Hz, 1H), 6.43−6.35 (m, 1H), 4.96 (dd, J = 6.8, 1.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.9 (d, J_{C-F} = 252.8 Hz), 165.6, 136.3, 134.7, 132.4 (d, J_{C-F} = 9.5 Hz), 128.8 (2C), 128.3, 126.8 (2C), 126.6 (d, J_{C-F} = 2.9 Hz), 123.3, 115.7 (d, J_{C-F} = 21.9 Hz), 65.9; HRMS (EI) calcd for $C_{16}H_{13}O_2F$ 279.0797 m/z $(M + Na)^+$, found 279.0787 m/z.

2-Chlorobenzoic acid 3-phenyl allyl ester (5e): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.84 (dd, J = 7.8, 1.8 Hz, 1H), 7.43−7.22 (m, 8H), 6.73 (d, J = 16.0 Hz, 1H), 6.41−6.34 (m, 1H), 4.97 (dd, J = 6.8, 1.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.5, 136.2, 134.8, 133.9, 132.7, 131.6, 131.2, 130.1, 128.7 (2C), 128.3, 126.8 (2C), 126.7, 122.8, 66.2; HRMS (EI) calcd for $C_{16}H_{13}O_2Cl$ 295.0502 m/z $(M + Na)^+$, found 295.0508 m/z.

3-Chlorobenzoic acid 3-phenyl allyl ester (5f): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.05 (m, 1H), 7.97−7.94 (m, 1H), 7.54−7.51 (m, 1H), 7.42−7.22 (m, 6H), 6.74 (d, J = 16.0 Hz, 1H), 6.43−6.35 (m, 1H), 4.98 (dd, J = 6.8, 1.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.4, 136.3, 134.9, 134.7, 133.2, 132.1, 129.93, 129.91, 128.8 (2C), 128.4, 128.0, 126.9 (2C), 123.0, 66.1; HRMS (EI) calcd for $C_{16}H_{13}O_2Cl$ 295.0502 m/z $(M + Na)^+$, found 295.0514 m/z.

4-Trifluoromethylbenzoic acid 3-phenyl allyl ester (5g): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.2 (d, J = 8.0 Hz, 2H), 7.8 (d, J = 8.0 Hz, 2H), 7.36−7.24 (m, 5H), 6.74 (d, J = 16.0 Hz, 1H), 6.43−6.35 (m, 1H), 4.98 (dd, J = 6.4, 1.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.4, 152.8, 136.3, 134.8, 131.8 (2C), 128.85 (2C), 128.82 (d, J_{C-F} = 5.8 Hz), 120.4, 126.8 (2C), 123.1, 120.5 (d, J_{C-F} = 257.6 Hz), 120.47 (2C), 66.0; HRMS (EI) calcd for $C_{17}H_{13}O_2F_3$ 329.0765 m/z $(M + Na)^+$, found 329.0767 m/z.

4-Nitrobenzoic acid 3-phenyl allyl ester[27] (5h): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.30−8.20 (m, 4H), 7.45−7.39 (m, 2H), 7.38−7.25 (m, 3H), 6.75 (d, J = 16.0 Hz, 1H), 6.43−6.36 (m, 1H), 5.02 (dd, J = 1.4, 6.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 164.6, 150.6, 136.0, 135.6, 135.3, 130.9 (2C), 128.8 (2C), 128.5, 126.8 (2C), 123.6 (2C), 122.4, 66.6; HRMS (EI) calcd for $C_{16}H_{13}NO_4$ 306.0742 m/z $(M + Na)^+$, found 306.0749 m/z.

4-Bromo-3-nitrobenzoic acid 3-phenyl allyl ester (5i): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.48 (d, J = 1.8 Hz, 1H), 8.08 (dd, J = 1.8, 8.2 Hz, 1H), 7.82 (d, J = 8.6 Hz, 1H), 7.42−7.40 (m, 2H), 7.36−7.25 (m, 3H), 6.75 (d, J = 16.0 Hz, 1H), 6.41−6.34 (m, 1H), 5.08 (dd, J = 1.4, 6.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 163.8, 150.0, 136.0, 135.7, 135.6, 133.7, 131.0, 128.8 (2C), 128.6, 126.9 (2C), 126.6, 122.3, 119.8, 66.8; HRMS (EI) calcd for $C_{16}H_{12}NO_4Br$ 383.9847 m/z $(M + Na)^+$, found 383.9860 m/z.

Furan-2-carboxylic acid 3-phenyl allyl ester[28] (5j): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.57 (s, 1H), 7.41−7.38 (m, 2H), 7.35−7.21 (m, 4H), 6.72 (d, J = 15.6 Hz, 1H), 6.50−6.48 (m, 1H), 6.40−6.32 (m, 1H), 4.95 (dd, J = 1.4, 6.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.6, 146.5, 144.7, 136.2, 134.9, 128.7 (2C), 128.3, 126.8 (2C), 122.9, 118.3, 112.0, 65.6; HRMS (EI) calcd for $C_{14}H_{12}O_3$ 251.0684 m/z $(M + Na)^+$, found 251.0694 m/z.

ASSOCIATED CONTENT

Supporting Information. Copies of spectral data of compounds **3a**−**3q** and **5a**−**5j**. This material is available free of charge via the Internet at http://pubs.acs.org.

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