Note

Highly Selective Synthesis of 2-tert-Butoxy-1-Arylethanones via Copper(I)-Catalyzed Oxidation/tert-Butoxylation of Aryl Olefins with TBHP

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Highly Selective Synthesis of 2-*tert*-Butoxy-1-Arylethanones *via* Copper(I)-Catalyzed Oxidation/*tert*-Butoxylation of Aryl Olefins with TBHP

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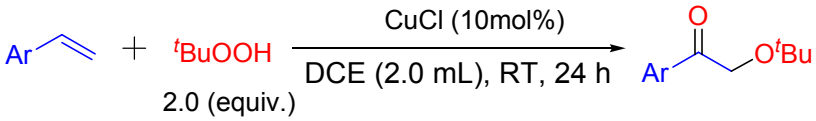
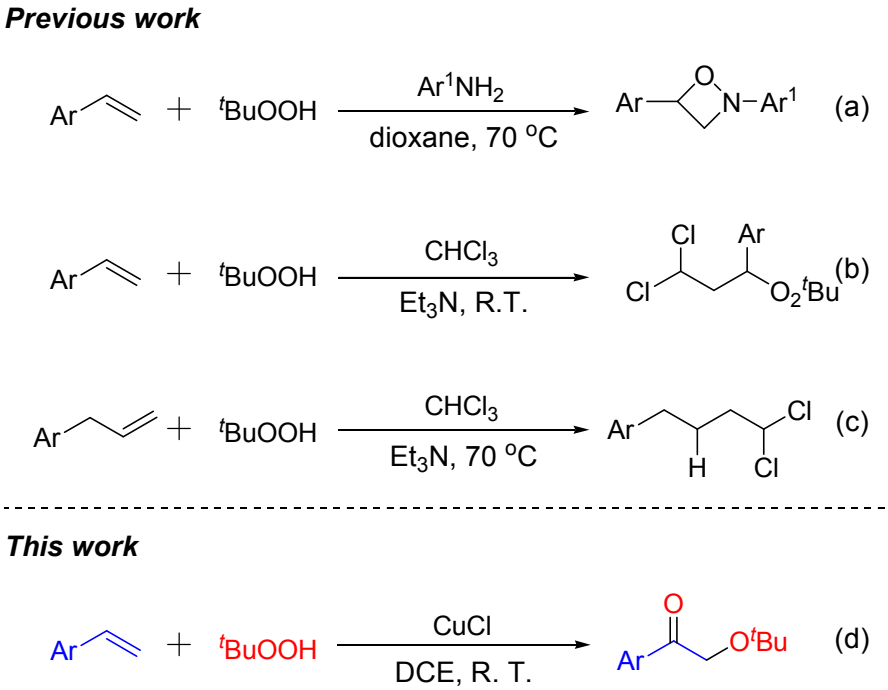


Abstract: A practical and environmentally friendly protocol for the selective oxidation of aryl olefins to arylethanone derivatives by using a Cu(I) catalyst and *tert*-butyl hydroperoxide (TBHP) has been developed. A series of 2-*tert*-butoxy-1-arylethanones were obtained in moderate to good yields under mild conditions with high selectivity. In this method, TBHP acts not only as an oxidant but also as the *tert*-butoxy and carbonyl oxygen sources. This enables one-step oxidation/*tert*-butoxylation. Various allyl peroxides were also synthesized from allyl substrates.

Alkenes are abundant organic molecules and represent a useful chemical feedstock. They are extensively used in organic synthesis because of their simplicity, low cost, ready availability, and unique reactivity profiles. Methods for their direct, selective functionalization are attractive as an important approach to assembling more complex molecular structures.[1] With the renaissance of radical chemistry, the radical three-component difunctionalization of alkenes is attracting increasing attention and has been intensively studied in recent years.[2-3]

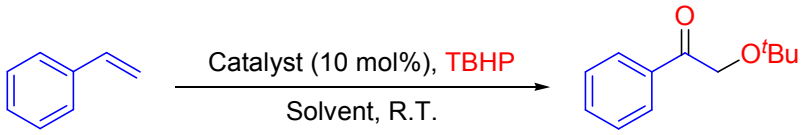
Scheme 1. Difuctionlization of Alkenes with TBHP.



Tert-butyl hydroperoxide (TBHP) is a commercially available, inexpensive, and versatile reagent, with roles such as an oxidant,[4] radical initiator,[5] and precursor of the *tert*-butoxy[6] and *tert*-butyl peroxide[7] radicals. For example, in 2012, Wang's group reported a novel and efficient TBHP/I_2-promoted oxidative coupling reaction of acetophenones with amines for the synthesis of α-ketoamides.[4f] Recently, Bao et al. developed the Cu-catalyzed radical acyl-cyanation of alkenes with aldehydes, by using TBHP as an initiator, to access various unsymmetrical β-cyano ketones with various functional groups.[5a] In 2019, Yang and co-workers reported a convenient Fe-catalyzed decarbonylative alkylation–peroxidation of alkenes with aliphatic aldehydes and TBHP to provide chain-elongated peroxides.[7c] Syntheses of aldehydes,[8] styrene epoxides,[9] and acidic compounds[10] through the selective oxidation of styrenes by peroxides in the presence of transition-metal catalysts have been well documented. However, to the best of our knowledge, relatively few studies have focused on the oxidation/*tert*-butoxylation of styrenes. Here, as a continuation of our work on

TBHP-mediated oxidative coupling reactions (Scheme 1a–c),[11] we report a highly efficient and general strategy for the preparation of various 2-*tert*-butoxy-1-arylethanones *via* Cu(I)-catalyzed oxidation/*tert*-butoxylation of alkenes with TBHP under mild conditions (Scheme 1d). Notably, the oxygen atom in the newly formed carbonyl moiety is derived from TBHP.

Table 1. Optimization Studies [a]



1a **2a**

Entry	Catalyst	Solvent	Time /h	Yield[b] /%
1	CuCl	DMSO	12	26
2	CuCl	DMSO	24	45
3	CuI	DMSO	24	32
4	CuBr	DMSO	24	20
5	Cu_2O	DMSO	24	28
6	$CuBr_2$	DMSO	24	trace
7	$CuCl_2$	DMSO	24	trace
8	CuO	DMSO	24	trace
9	$Cu(OAc)_2$	DMSO	24	trace
10	CuCl	Hexane	24	25
11	CuCl	Dioxane	24	68
12	CuCl	DMF	24	trace
13	**CuCl**	**DCE**	**24**	**77**
14[c]	CuCl	DCE	24	36
15[d]	CuCl	DCE	24	77
16[e]	CuCl	DCE	24	77
17	-	DCE	36	trace
18[f]	CuCl	DCE	24	77
19[g]	CuCl	DCE	24	77

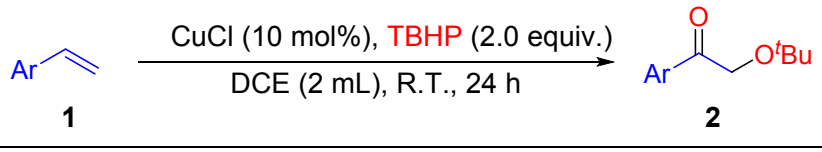
[a] Reaction conditions: **1a** (0.5 mmol), TBHP (2.0 equiv.), solvent (2.0 mL), catalyst (10 mol%). [b] GC yield. [c] TBHP: 1.0 equiv. [d] TBHP: 3.0 equiv. [e] CuCl: 50 mol%. [f] O_2 (balloon). [g] N_2 (balloon).

Initially, we selected styrene **1a** as a model substrate for optimization of the reaction conditions (Table 1). First, the reaction was performed in the presence of CuCl (10 mol%) in combination with TBHP (2.0 equiv) in DMSO at room temperature for 12 h. The desired product **2a** was obtained in 26% yield; most of the starting material was recovered (entry 1). Prolonging the reaction time to 24 h

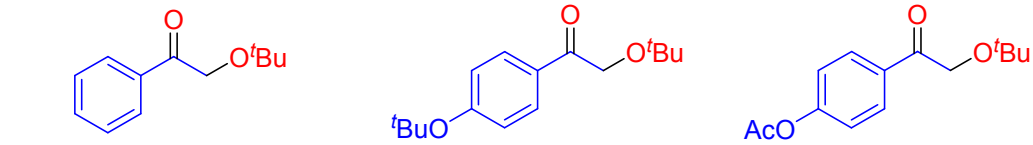
increased the yield of **2a** to 45% (entry 2). We next explored the use of various Cu salts for this transformation (entries 3–9). The results indicate that the type of metal catalyst significantly affects the reaction yield and CuCl is a better choice than other Cu salts. In the next optimization step, we examined the effects of the solvent by screening various reaction media, namely hexane, dioxane, DMF, and DCE. The results show that the conversion is sensitive to the solvent; DCE is the best solvent because the other solvents gave smaller yields of the expected product **2a** (entries 10–13). A lower yield was obtained when the TBHP loading was decreased to 1.0 equiv (entry 14). However, increasing the amount of TBHP or CuCl had no obvious effect on the outcome (entries 15 and 16). It is worth noting that in the absence of the CuCl catalyst only a trace amount of 2-*tert*-1-butoxyphenylethanone (**2a**) was formed and the starting material remained almost intact (entry 17). The yields of the desired product **2a** were the same under an O_2 or N_2 atmosphere (entries 18 and 19).

With the optimum conditions in hand (Table 1, entry 13), we then systematically studied the generality and limitations of this oxidation/*tert*-butoxylation reaction; the results are summarized in Table 2. Groups with different electronic properties at the *para* position of the aromatic ring were examined. All the reactions proceeded smoothly to give the desired products in moderate to good yields (**2b**–**k**). The reactivities of phenyl rings with strongly electron-withdrawing substituents (–CF_3, –NO_2) were higher than those of phenyl rings with electron-donating substituents. This suggests that electron-withdrawing groups enhance the reaction efficiency (**2j** and **2k**). Substrates with substituents at the *ortho* or *meta* positions were also compatible with this mild Cu-catalyzed protocol. The corresponding products were obtained in 60%–73% yields (**2l**–**p**).

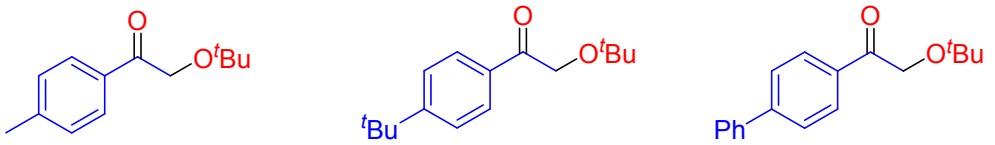
Table 2. Scope of the Substrates[a]



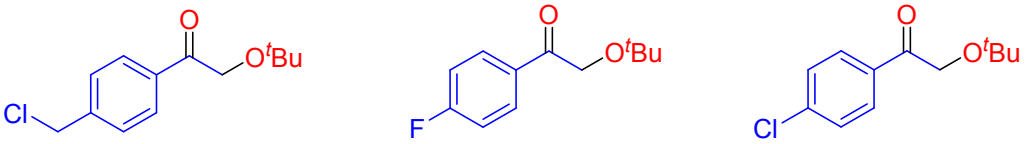
1 **2**



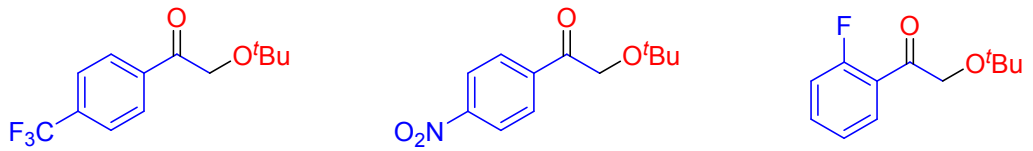
2a, 72% **2b**, 62% **2c**, 63%



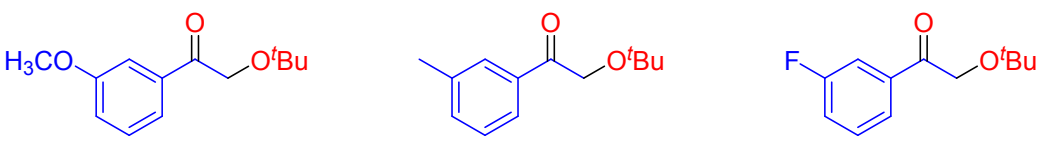
2d, 69% **2e**, 67% **2f**, 64%



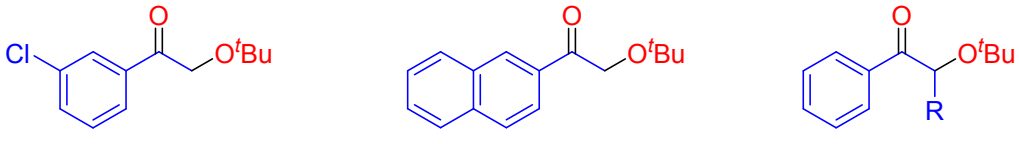
2g, 65% **2h**, 73% **2i**, 72%



2j, 85% **2k**, 82% **2l**, 70%



2m, 60% **2n**, 70% **2o**, 73%



2p, 69% **2q**, 63%

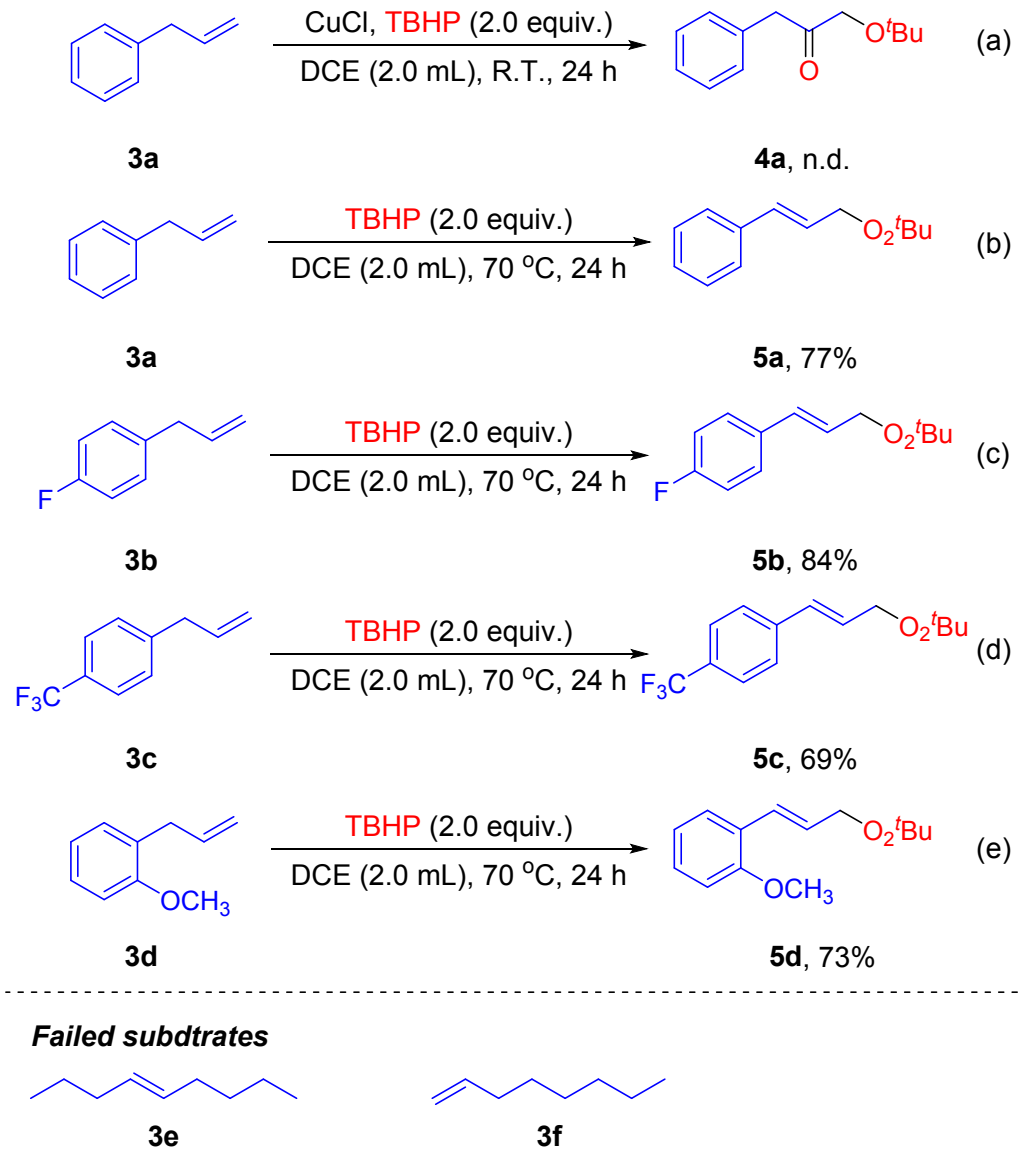
2r, R = CH_3, n.d.[c]
2s, R = *n*-Pr, n.d.[c]

2t, n.d.[c] **2u**, 89%

[a] Unless otherwise specified, all reactions were carried out on 1.0 mmol scale for 24 h. [b] Isolated yield.
[c] A complex system was obtained, and no desired product was detected.

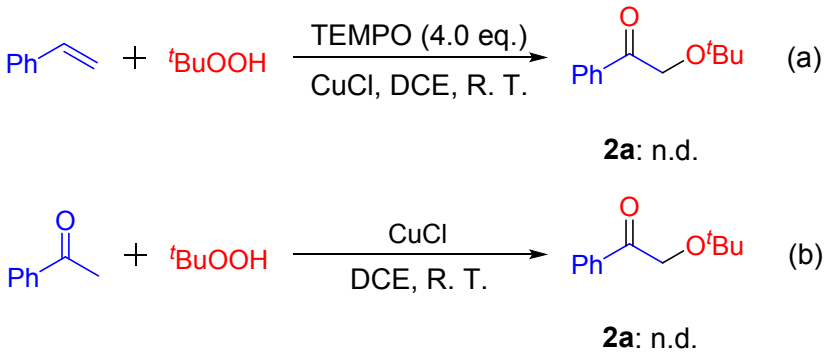
Notably, the position of the substituent did not affect the reaction productivities and yields (**2h**, **2l**, and **2o**). 2-Naphthyl-substituted **1q** was also tolerated in the present system, and the oxidation/*tert*-butoxylation product **2q** was obtained in reasonable yield. Disubstituted alkenes are not good candidates for this Cu-catalyzed reaction. **1r**–**1t** cound not provided the desired products under the optimum conditions, and complex reaction systems were formed. The phenyl ring in **1a** can be replaced by a heterocycle (thienyl, **1u**) to yield **2u**.

Scheme 2. Explore the Substrate Scope.



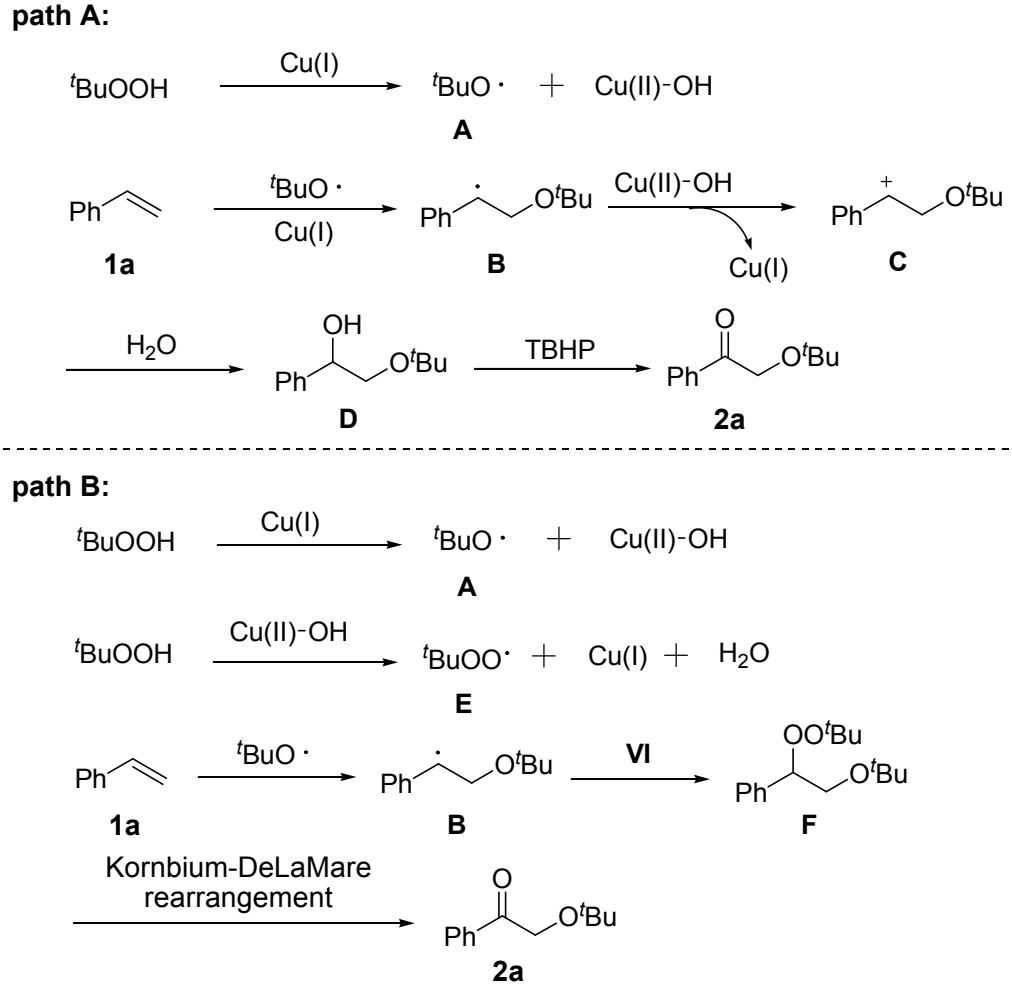
To further expand the substrate scope, we investigated the use of alkenes with a terminal alkyl group, *i.e.*, **3a**–**d**, as substrates for this oxidation/*tert*-butoxylation reaction under the standard conditions. These alkenes proved to be poor substrates for this transformation. When the reactions were performed at 70 °C, these substrates failed to provide the desired products, and the allyl peroxide products **5a**–**d** were obtained as the main products (Scheme 2b–e). Organic peroxides not only serve as key reactive intermediates in diverse organic synthetic reactions such as Kornblum–DeLaMare reactions[12] and epoxidations,[13-14] but also have important roles in cell damage, food safety, and as therapeutic drugs in medicinal chemistry. We investigated the need to use CuCl and found that its presence was unnecessary (Scheme 2). The reactions of other internal or terminal alkenes, *i.e.*, (*E*)-non-4-ene (**3e**) and oct-1-ene (**3f**)**,** were also examined under these conditions, but the reactions were sluggish and no major products were formed.

Scheme 3. Control Experiments.



Several control experiments were conducted to clarify the reaction mechanism (Scheme 3). The reaction was completely inhibited by TEMPO (4.0 equiv), which suggests that a radical pathway is probably involved (Scheme 3a). When acetophenone was treated with TBHP under the standard conditions, **2a** was not detected (Scheme 3b).

Scheme 4. Possible Mechanism for Cu(I)-Catalyzed Oxidation/*tert*-Butoxylation Transformation.



Based on the these results and literature reports,[4-7,11] a possible mechanism for this Cu(I)-catalyzed oxidation/*tert*-butoxylation transformation, with **1a** as an example, is shown in Scheme 4. Initially, TBHP is reduced by low-valent Cu(I) to generate a *tert*-butoxy radical **A** and a Cu(II) complex.[14-15] Radical addition to styrene then produces benzyl radical **B**, which undergoes direct oxidation to **C** by Cu(II),[16] along with regeneration of Cu(I) for the next catalytic cycle. Next, species **C** is trapped by H_2O[17] to form species **D**, which is further oxidized by TBHP to give the final product **2a** (path a).[18] Another possible mechanism, namely path b, cannot be excluded. First, alkyloxy radical **A** and alkylperoxy radical **E** are generated *via* a series of steps. Benzyl radical **B** is then obtained *via* a radical addition process and is selectively trapped by the ^{t}BuOO· radical to afford the *tert*-butyl peroxide

intermediate **F**.[19] In the final step, **F** undergoes a Kornblum–DeLaMare rearrangement[12] to give the desired product **2a**.

In conclusion, we have developed an efficient and general method for the highly selective construction of 2-*tert*-1-butoxyarylethanone frameworks *via* a Cu(I)-catalyzed oxidation/*tert*-butoxylation reaction. This synthetic method has many advantages such as simple starting materials, green reaction conditions, and high selectivity, and is expected to provide a valuable alternative protocol in appropriate areas. In this method, TBHP acts not only as the oxidant but also as the *tert*-butoxy and carbonyl oxygen sources for this oxidation/*tert*-butoxylation transformation. Various allyl peroxides were also synthesized from allyl substrates. Further investigations into the difunctionalization of alkenes with TBHP are currently underway in our laboratory.

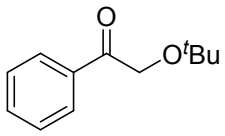
EXPERIMENTAL SECTION

General Information. All the reactions were carried out at room temperature for 24 h in a round-bottom flask equipped with a magnetic stir bar. Unless otherwise stated, all reagents and solvents were purchased from commercial suppliers and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz spectrometer in solutions of $CDCl_3$ using tetramethylsilane as the internal standard; δ values are given in ppm, and coupling constants (J) in Hz. Mass spectra were obtained from high resolution *ESI* mass spectrometer. HR-MS were obtained on a Q-TOF micro spectrometer.

Typical procedure for the synthesis of 2a: 2-*tert*-butoxy-1-phenylethanone (**2a**). A mixture of styrene (**1a**) (104 mg, 1.0 mmol), CuCl (9.8 mg, 0.1 mmol), TBHP (258 mg, 2.0 mmol, 70% in water), and 1,2-dichloroethane (DCE) (2.0 mL) was added successively in a round-bottom flask,

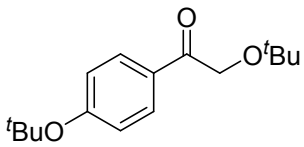
and the resulting solution was stirred for 24 h at room temperature. The mixture was purified by column chromatography on silica gel to afford product **2a** with PE/EA = 30:1 as the eluent.

2-*tert*-butoxy-1-phenylethanone (2a) [20]



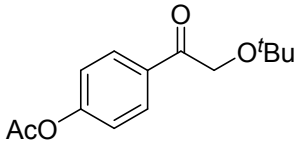
Yield: 72% (138 mg); a pale yellow oil liquids; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.97 (d, J = 8.4 Hz, 2H), 7.57 (t, J = 7.6 Hz, 1H), 7.46 (t, J = 7.2 Hz, 2H), 4.66 (s, 2H), 1.29 (s, 9H); ^{13}C NMR {1H} ($CDCl_3$, 100 Hz) δ 197.2, 135.4, 133.1, 128.5, 128.1, 74.6, 66.3, 27.4.

2-*tert*-butoxy-1-(4-*tert*-butoxyphenyl)ethanone (2b)



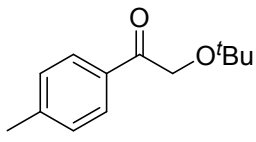
Yield: 62% (163 mg); a pale yellow oil liquids; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.93 (d, J = 7.6 Hz, 2H), 7.03 (d, J = 7.6 Hz, 2H), 4.61 (s, 2H), 1.42 (s, 9H), 1.28 (s, 9H); ^{13}C NMR {1H} ($CDCl_3$, 100 Hz) δ 196.4, 160.4, 129.9, 129.7, 122.2, 74.5, 66.2, 28.9, 27.4; HRMS (ESI): calcd for $C_{16}H_{24}NaO_3$: [M+Na$^+$] 287.1612, found 287.1619.

4-(2-*tert*-butoxyacetyl)phenyl acetate (2c)



Yield: 63% (157 mg); a pale yellow oil liquids; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 8.03 (d, J = 7.6 Hz, 2H), 7.20 (d, J = 7.6 Hz, 2H), 4.62 (s, 2H), 2.33 (s, 9H), 1.28 (s, 9H); ^{13}C NMR {1H} ($CDCl_3$, 100 Hz) δ 196.0, 168.8, 154.8, 133.0, 129.9, 121.7, 74.7, 66.4, 27.4, 21.1; HRMS (ESI): calcd for $C_{14}H_{18}NaO_4$: [M+Na$^+$] 273.1097, found 273.1099.

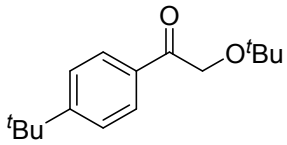
2-*tert*-butoxy-1-*p*-tolylethanone (2d)



Yield: 69% (142 mg); a pale yellow oil liquids; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.88 (d, J = 8.4 Hz,

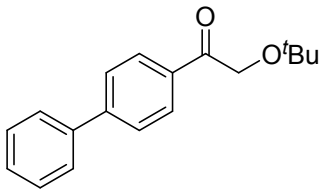
2H), 7.26 (d, J = 8.0 Hz, 2H), 4.66 (s, 2H), 2.42 (s, 3H), 1.29 (s, 9H); ^{13}C NMR {1H} ($CDCl_3$, 100 Hz) δ 196.8, 144.0, 132.9, 129.2, 128.2, 74.5, 66.2, 27.4; HRMS (ESI): calcd for $C_{13}H_{18}NaO_2$: [M+Na$^+$] 229.1199, found 229.1195.

2-*tert*-butoxy-1-(4-*tert*-butylphenyl)ethanone (2e)



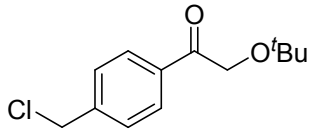
Yield: 67% (166 mg); a pale yellow oil liquids; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.92 (d, J = 8.8 Hz, 2H), 7.47 (d, J = 8.8 Hz, 2H), 4.65 (s, 2H), 1.35 (s, 9H), 1.29 (s, 9H); ^{13}C NMR {1H} ($CDCl_3$, 100 Hz) δ 196.7, 156.9, 132.8, 128.0, 125.4, 74.5, 66.2, 35.1, 31.0, 27.4; HRMS (ESI): calcd for $C_{16}H_{24}NaO_2$: [M+Na$^+$] 271.1668, found 271.1677.

2-*tert*-butoxy-1-(4-phenylphenyl)ethanone (2f)



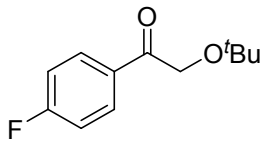
Yield: 64% (171 mg); a pale yellow oil liquids; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 8.06 (d, J = 8.4 Hz, 2H), 7.69 (d, J = 8.0 Hz, 2H), 7.63 (d, J = 8.4 Hz, 2H), 7.46 (d, J = 8.4 Hz, 2H), 7.40 (t, J = 8.4 Hz, 1H), 4.68 (s, 2H), 1.31 (s, 9H); ^{13}C NMR {1H} ($CDCl_3$, 100 Hz) δ 196.5, 154.1, 139.6, 134.3, 128.9, 128.8, 128.2, 127.2, 127.1, 74.9, 65.6, 27.5; HRMS (ESI): calcd for $C_{18}H_{20}NaO_2$: [M+Na$^+$] 291.1355, found 291.1368.

2-*tert*-butoxy-1-(4-(chloromethyl)phenyl)ethanone (2g)



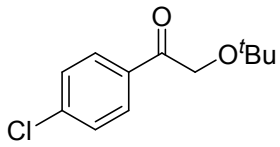
Yield: 65% (156 mg); a pale yellow oil liquids; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.98 (d, J = 8.4 Hz, 2H), 7.49 (d, J = 8.0 Hz, 2H), 4.63 (s, 2H), 4.62 (s, 2H), 1.29 (s, 9H); ^{13}C NMR {1H} ($CDCl_3$, 100 Hz) δ 196.8, 144.0, 132.9, 129.2, 128.2, 74.5, 66.2, 27.4; HRMS (ESI): calcd for $C_{13}H_{17}ClNaO_2$: [M+Na$^+$] 263.0809, found 263.0814.

2-*tert*-butoxy-1-(4-fluorophenyl)ethanone (2h)



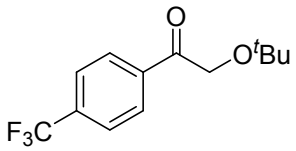
Yield: 73% (153 mg); a yellow oil liquids; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 8.04 (m, 2H), 7.13 (t, J = 8.4 Hz, 2H), 4.60 (s, 2H), 1.28 (s, 9H); ^{13}C NMR {1H} ($CDCl_3$, 100 Hz) δ 195.9, 165.8 (d, $^1J_{C\text{-}F}$ = 246.4 Hz), 131.8 (d, $^4J_{C\text{-}F}$ = 3.1 Hz), 131.0 (d, $^3J_{C\text{-}F}$ = 9.2 Hz), 115.6 (d, $^2J_{C\text{-}F}$ = 21.7 Hz), 74.7, 66.5, 27.4; HRMS (ESI): calcd for $C_{12}H_{15}FNaO_2$: [M+Na$^+$] 233.0948, found 233.0952.

2-*tert*-butoxy-1-(4-chlorophenyl)ethanone (2i) [21]



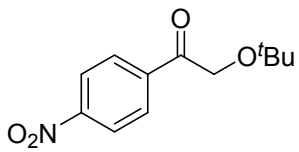
Yield: 72% (162 mg); a pale yellow oil liquids; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.94 (d, J = 8.8 Hz, 2H), 7.44 (d, J = 8.8 Hz, 2H), 4.59 (s, 2H), 1.28 (s, 9H); ^{13}C NMR {1H} ($CDCl_3$, 100 Hz) δ 196.3, 139.3, 133.3, 129.8, 128.8, 74.7, 66.5, 27.4.

2-*tert*-butoxy-1-(4-(trifluoromethyl)phenyl)ethanone (2j)



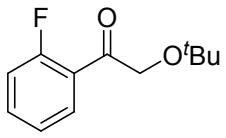
Yield: 85% (221 mg); a pale yellow oil liquids; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 8.10 (d, J = 7.6 Hz, 2H), 7.73 (d, J = 7.6 Hz, 2H), 4.63 (s, 2H), 1.28 (s, 9H); ^{13}C NMR {1H} ($CDCl_3$, 100 Hz) δ 196.7, 138.1, 128.7, 125.7, 125.5 (q, $^1J_{C\text{-}F}$ = 269.5 Hz), 124.8, 74.9, 66.7, 27.4; HRMS (ESI): calcd for $C_{13}H_{15}F_3NaO_2$: [M+Na$^+$] 283.0916, found 283.0924.

2-*tert*-butoxy-1-(4-nitrophenyl)ethanone (2k)



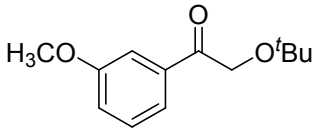
Yield: 82% (194 mg); an orange oil liquids; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 8.31 (d, J = 7.6 Hz, 2H), 8.16 (d, J = 7.6 Hz, 2H), 4.62 (s, 2H), 1.28 (s, 9H); ^{13}C NMR {1H} ($CDCl_3$, 100 Hz) δ 196.3, 150.2, 140.0, 129.6, 123.6, 75.2, 67.0, 27.4; HRMS (ESI): calcd for $C_{12}H_{15}NNaO_4$: [M+Na$^+$] 260.0893, found 260.0888.

2-*tert*-butoxy-1-(2-fluorophenyl)ethanone (2l)



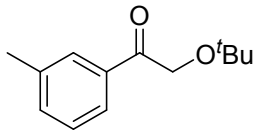
Yield: 70% (147 mg); a yellow oil liquids; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.94 (m, 1H), 7.52 (m, 1H), 7.26 (m, 1H), 7.14 (m, 1H), 4.62 (s, 2H), 1.28 (s, 9H); ^{13}C NMR {1H} ($CDCl_3$, 100 Hz) δ 195.7, 162.8 (d, $^{1}J_{C\text{-}F}$ = 256.0 Hz), 134.5 (d, $^{3}J_{C\text{-}F}$ = 8.8 Hz), 130.7 (d, $^{4}J_{C\text{-}F}$ = 3.5 Hz), 124.5 (d, $^{3}J_{C\text{-}F}$ = 3.1 Hz), 123.8 (d, $^{2}J_{C\text{-}F}$ = 21.8 Hz), 116.3 (d, $^{2}J_{C\text{-}F}$ = 23.6 Hz), 74.3, 69.2, 27.4; HRMS (ESI): calcd for $C_{12}H_{15}FNaO_2$: [M+Na$^+$] 233.0948, found 233.0955.

2-*tert*-butoxy-1-(3-methoxyphenyl)ethanone(2m)



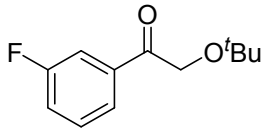
Yield: 60% (133 mg); a pale yellow oil liquids; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.54 (m, 2H), 7.37 (d, J = 7.6 Hz, 1H), 7.54 (m, 1H), 4.65 (s, 2H), 3.86 (s, 3H), 1.29 (s, 9H), 1.28 (s, 9H); ^{13}C NMR {1H} ($CDCl_3$, 100 Hz) δ 197.0, 159.6, 136.6, 129.5, 120.5, 119.6, 112.5, 74.6, 66.3, 55.4, 27.4; HRMS (ESI): calcd for $C_{13}H_{18}NaO_3$: [M+Na$^+$] 245.1148, found 245.1155.

2-*tert*-butoxy-1-m-tolylethanone (2n)



Yield: 70% (144 mg); a pale yellow oil liquids; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.79 (s, 1H), 7.77 (d, J = 8.4 Hz, 1H), 7.37 (m, 2H), 4.67 (s, 2H), 2.43 (s, 3H), 1.31 (s, 9H); ^{13}C NMR {1H} ($CDCl_3$, 100 Hz) δ 196.8, 138.3, 134.9, 133.9, 128.5, 128.4, 125.2, 74.5, 66.2, 27.4, 21.3; HRMS (ESI): calcd for $C_{13}H_{18}NaO_2$: [M+Na$^+$] 229.1199, found 229.1208.

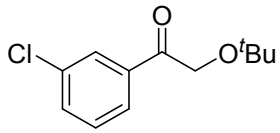
2-*tert*-butoxy-1-(3-fluorophenyl)ethanone (2o)



Yield: 73% (153 mg); a yellow oil liquids; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.77 (t, J = 8.0 Hz, 1H), 7.69 (m, 1H), 7.44 (m, 1H), 7.26 (m, 1H), 4.61 (s, 2H), 1.29 (s, 9H); ^{13}C NMR {1H} ($CDCl_3$, 100 Hz) δ 196.1, 162.6 (d, $^{1}J_{C\text{-}F}$ = 256.0 Hz), 137.3 (d, $^{3}J_{C\text{-}F}$ = 8.1 Hz), 130.1 (d, $^{3}J_{C\text{-}F}$ = 8.2 Hz), 123.9 (d,

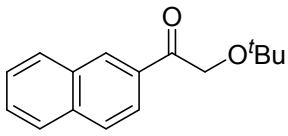
$^4J_{C\text{-}F}$ = 3.0 Hz), 120.1 (d, $^2J_{C\text{-}F}$ = 21.4 Hz), 115.1 (d, $^2J_{C\text{-}F}$ = 22.3 Hz), 74.7, 66.5, 27.4; HRMS (ESI): calcd for $C_{12}H_{15}FNaO_2$: [M+Na$^+$] 233.0948, found 233.0944.

2-*tert*-butoxy-1-(3-chlorophenyl)ethanone (2p)



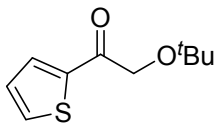
Yield: 69% (155 mg); a pale yellow oil liquids; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.96 (s, 1H), 7.87 (d, J = 8.4 Hz, 1H), 7.54 (d, J = 8.4 Hz, 1H), 7.41 (t, J = 8.4 Hz, 1H), 4.61 (s, 2H), 1.29 (s, 9H); ^{13}C NMR {1H} ($CDCl_3$, 100 Hz) δ 196.2, 136.9, 133.1, 129.8, 129.6, 128.4, 126.4, 74.5, 66.5, 27.4; HRMS (ESI): calcd for $C_{12}H_{15}ClNaO_2$: [M+Na$^+$] 249.0653, found 249.0655.

2-*tert*-butoxy-1-(naphthalen-3-yl)ethanone (2q)



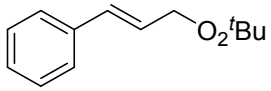
Yield: 63% (152 mg); an orange oil liquids; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 8.53 (s, 1H), 8.02 (d, J = 8.4 Hz, 1H), 7.98 (d, J = 8.0 Hz, 1H), 7.89 (t, J = 8.4 Hz, 2H), 7.58 (m, 2H), 4.78 (s, 2H), 1.33 (s, 9H); ^{13}C NMR {1H} ($CDCl_3$, 100 Hz) δ 197.1, 135.6, 132.7, 132.4, 129.8, 129.5, 128.4, 128.3, 127.8, 126.7, 123.9, 74.7, 66.5, 27.5; HRMS (ESI): calcd for $C_{16}H_{18}NaO_2$: [M+Na$^+$] 265.1199, found 265.1191.

2-*tert*-butoxy-1-(thiophen-2-yl)ethanone (2u)



Yield: 89% (176 mg); a pale yellow oil liquids; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.31 (dd, J = 1.2 Hz, J = 4.0 Hz, 1H), 7.65 (dd, J = 1.2 Hz, J = 4.0 Hz, 1H), 7.14 (dd, J = 4.0 Hz, J = 5.2 Hz, 1H), 4.45 (s, 2H), 1.30 (s, 9H); ^{13}C NMR {1H} ($CDCl_3$, 100 Hz) δ 191.1, 141.1, 133.9, 133.2, 127.7, 74.9, 67.4, 27.3; HRMS (ESI): calcd for $C_{10}H_{14}NaO_2S$: [M+Na$^+$] 221.0606, found 221.0612.

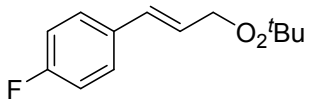
1-((E)-3-(*tert*-butylperoxy)prop-1-enyl)benzene (5a)



Yield: 77% (158 mg); a pale yellow oil liquids; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.31 (m, 5H), 6.07 (m,

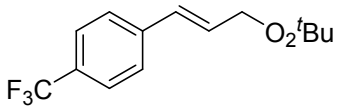
1H), 5.29 (m, 3H), 1.26 (s, 9H); ^{13}C NMR {1H} ($CDCl_3$, 100 Hz) δ 139.3, 136.8, 128.3, 127.9, 127.4, 86.8, 80.4, 26.5; HRMS (ESI): calcd for $C_{13}H_{18}NaO_2$: [M+Na$^+$] 229.1199, found 229.1192.

1-((E)-3-(*tert*-butylperoxy)prop-1-enyl)-4-fluorobenzene (5b)



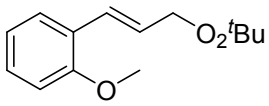
Yield: 84% (188 mg); a pale yellow oil liquids; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.37 (m, 2H), 6.99 (m, 2H), 6.58 (d,J = 16 Hz,1H), 6.23 (m, 1H), 4.57 (dd, J = 6.8 Hz, J = 1.2 Hz, 1H), 1.28 (s, 9H); ^{13}C NMR {1H} ($CDCl_3$, 100 Hz) δ 141.6 (d, $^1J_{C\text{-}F}$ = 247.0 Hz), 133.1, 132.7 (d, $^4J_{C\text{-}F}$ = 3.2 Hz), 128.1(d, $^3J_{C\text{-}F}$ = 8.1 Hz), 123.6, 115.5 (d, $^2J_{C\text{-}F}$ = 21.5 Hz), 80.4, 75.7, 26.3; HRMS (ESI): calcd for $C_{13}H_{17}FNaO_2$: [M+Na$^+$] 247.1105, found 247.1117.

1-((E)-3-(*tert*-butylperoxy)prop-1-enyl)-4-(trifluoromethyl)benzene (5c)



Yield: 69% (189 mg); a pale yellow oil liquids; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.57 (d,J = 8.0 Hz, 2H), 7.49 (d,J = 8.0 Hz, 2H),6.66 (d,J = 16 Hz, 1H), 6.44 (m, 1H), 4.61 (dd,J = 1.2 Hz, J = 6.4 Hz, 2H), 1.28 (s, 9H); ^{13}C NMR {1H} ($CDCl_3$, 100 Hz) δ 140.0, 132.4, 126.9, 126.7 (q, $^1J_{C\text{-}F}$ = 245.8 Hz), 125.5, 125.4, 125.3, 80.5, 75.3, 26.3; HRMS (ESI): calcd for $C_{14}H_{17}F_3NaO_2$: [M+Na$^+$] 297.1073, found 297.1061.

1-((E)-3-(*tert*-butylperoxy)prop-1-enyl)-2-methoxybenzene (5d)



Yield: 73% (172 mg); a pale yellow oil liquids; ^{1}H NMR ($CDCl_3$, 400 Hz) δ 7.47 (dd,J = 2.4 Hz, J = 7.6 Hz, 1H), 7.25 (m,1H), 6.94 (m,3H), 6.34 (m, 1H), 4.61 (dd,J = 1.2 Hz, J = 6.4 Hz, 2H), 3.81 (s, 3H), 1.29 (s, 9H); ^{13}C NMR {1H} ($CDCl_3$, 100 Hz) δ 156.8, 129.4, 128.9, 127.1, 125.4, 124.2, 120.6, 110.8, 80.3, 76.3, 55.4, 26.4; HRMS (ESI): calcd for $C_{14}H_{20}NaO_3$: [M+Na$^+$] 259.1305, found 259.1310.

Supporting Information Available: Copies of ^{1}H and ^{13}C NMR {1H} of all the new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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